Oligosaccharide Analogues of Polysaccharides

Part 22[1])

Synthesis of Cyclodextrin Analogues Containing a Buta-1,3-diyne-1,4-diyl or a Butane-1,4-diyl Unit

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Dedicated to *Edgar Heilbronner* on the occasion of his 80th birthday

The peracetylated hexaamylose (maltohexaose) **18** was obtained by an improved acetolysis of cyclomaltohexaose (α-cyclodextrin, α-CD, **16**), and transformed into the benzyl- and 4-chlorobenzyl-protected thioglycosides **22** and **23**, respectively (*Scheme 2*). Sequential chain elongation of **22** and **23** by glycosidation of the *C*-ethynylated glucosides **9** and **11** gave the α-anomeric heptaglycosides **24** and **26**, respectively, and their anomers **25** and **27** (*Scheme 3*). These were transformed into the glycosyl acceptors **28**, **30**, and **31**. Glycosidation of **28** and **30** by **13** and **15**, respectively, led to the benzyl-protected octasaccharides **32** ($\alpha\alpha_5\alpha$) and **33** ($\beta\alpha_5\alpha$), and to the chlorobenzylated analogues **34** ($\alpha\alpha_5\alpha$) and **35** ($\beta\alpha_5\alpha$), while glycosidation of **31** led to the 4-chlorobenzyl-protected analogues **36** ($\alpha\alpha_5\beta$) and **37** ($\beta\alpha_5\beta$) (*Scheme 4*). *Hay* coupling of *O*-Bn- and *O*-Ac-protected linear octaoses **32** ($\alpha\alpha_5\alpha$) and **33** ($\beta\alpha_5\alpha$) led to the cyclooctaamylose (γ-cyclodextrin) analogues **38** and **43**, respectively (*Scheme 5*). Similarly, the 4-chlorobenzyl-protected analogues **34** and **35** gave **39** and **44**, and the anomeric linear precursors **36** and **37** provided the cyclootaamylose analogues **48** and **50**, respectively (*Scheme 6*). The influence of the constitution and configuration of the linear precursors on the rate and yield of the cyclisation was relatively weak. Deprotection and hydrogenation of **38** and **43** yielded the γ-CD analogues **42** ($\alpha\alpha_5\alpha$) and **47** ($\beta\alpha_5\alpha$), where one glycosidic O-atom is replaced by a butanediyl group, while $FeCl_3$-promoted dechlorobenzylation of **39** and **44** did not affect the butadiyne moiety and afforded the acetyleno γ-CD's **40** ($\alpha\alpha_5\alpha$) and **45** ($\beta\alpha_5\alpha$), respectively. Similarly, deprotection of **48** and **50** afforded the acetyleno γ-CD analogues **49** ($\alpha\alpha_5\beta$) and **51** ($\beta\alpha_5\beta$), respectively, which contain one butanediyl moiety instead of a glycosidic O-atom. MM3* Force-field calculations evidence the strong influence of the configuration and constitution of the new γ-CD analogues on the shape of the cavity.

Introduction and Plan. – Cyclodextrins (CDs, cycloamyloses) have commanded interest as catalysts [2][3], drug delivery systems [3–5], ligands [6], constituents of chiral separation media [7] and monolayers [8], and, particularly, as host molecules forming inclusion complexes [5][6][9]. The size and shape of the cavity of CDs plays an essential role in the formation of these inclusion complexes, with hydrophobic interactions, H-bonding, *Van der Waals* forces, and the reduction of conformational strain contributing to their stability [10–13]. There is strong interest in modifying the size and shape of the cavity, either by single or multiple substitution [14], capping [15], and changing the configuration [16], or by combining structural elements of CDs with noncarbohydrate moieties, as in the glycophanes [17], glyco-crown ethers [18], and cyclic acetylenosaccharides [19–21]. The known cyclic acetylenosaccharides result from

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combinations of glucose-1,4-diyl and buta-1,3-diyne-1,4-diyl residues [19][20], or from a ternary combination of glucose-1,4-diyl, buta-1,3-diyne-1,4-diyl, and 2,2′-dipyridinyl moieties [21]. In these acetylenosaccharides, all glycosidic O-atoms are replaced by buta-1,3-diyne-1,4-diyl groups. Thus, they cover an extreme point in the process of a progressive formal replacement of the glycosidic O-atom by buta-1,3-diyne-1,4-diyl moieties. We intended to synthesise CD analogues in which only one of the α-(1 → 4)-*O*-glycosidic linkages is replaced by a buta-1,3-diyne-1,4-diyl unit. Its incorporation will interrupt the cyclic H-bond network [22] of the related CD and diminish its rigidity that should be diminished further by reduction of the butadiyne to a butane-1,4-diyl moiety.

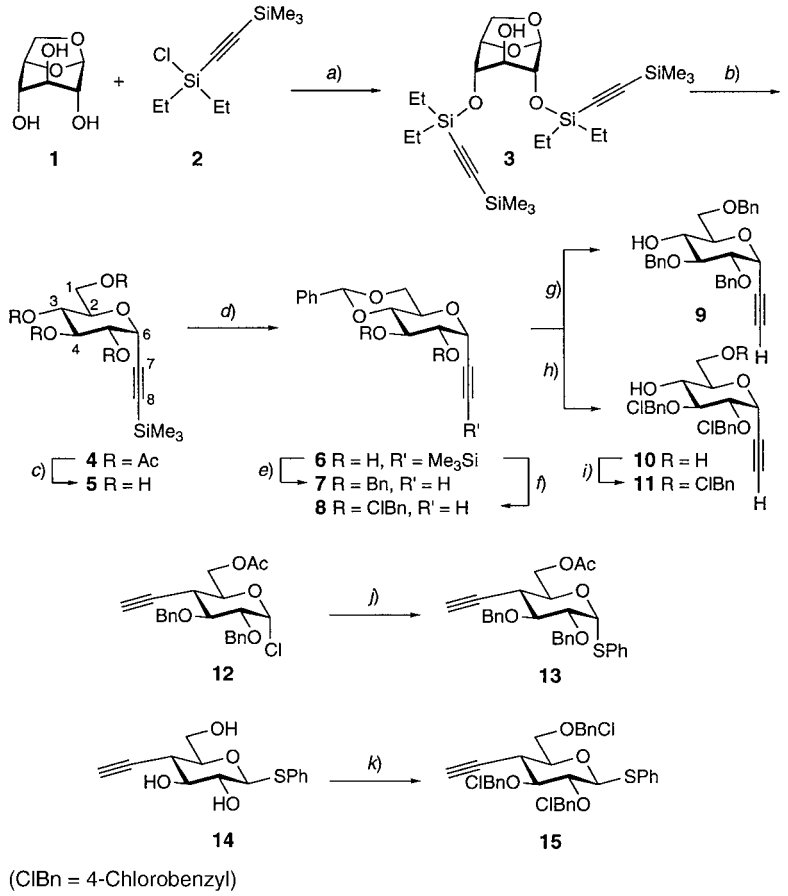
We planned to prepare a γ-CD analogue by *Hay* coupling of a linear 1,ω-diethynylated maltooctaose. The maltooctaose should be available by double glycosylation, first with a protected maltohexaose as glycosyl donor and then by glycosylation of the resulting maltoheptaose using a *C*(4)-ethynylated glucosyl donor. Maltohexaose should be derived from cyclomaltohexaose (α-CD) by known acetolytic ring cleavage [23], while the glucosyl donor and acceptor carrying an ethynyl group either at C(4) or at C(1) should be available from anhydroglucose **1** following established routes [19][24][25]. We intended to use *O*-Bn substituents as permanent protecting groups and to compare the resulting benzyl ethers to their 4-chlorobenzyl analogues that might crystallize more readily and be cleaved under milder conditions [26][27].

Results and Discussion. – The glucosyl acceptors **9** and **11** were prepared similarly to the known 1,4-diethynylated analogues [24][28], *i.e.*, by intramolecular invertive ring opening of an appropriate (ethynyl)silyl ether of 1,6-anhydroglucose (**1**) (*Scheme 1*). It proved advantageous to transform **1** into the bis-silyl ether **3**, using the chloro(ethynyl)silane **2**. The bis-silyl ether **3** was obtained in 82% yield and treated first with *in situ* generated $BuAlCl_2 \cdot LiCl$ and lutidine in toluene and then with 0.1M HCl in MeOH to remove any remaining SiO groups. The resulting crude *C*(1)-alkynylated tetraol **5** was purified *via* the acetate **4**, isolated in 50–55% yield, and benzylidenated. The resulting benzylidene acetal **6** was benzylated to **7** (97%), and 4-chlorobenzylated to **8** (86%). Reductive opening of the dioxane ring of **7** yielded the desired monomer **9** (84%), while **8** was debenzylidenated to **10** with I_2 in MeOH [29] (71%). The diol **10** was treated with $(Bu_3Sn)_2O$ [30] and 4-chlorobenzylated at O–C(6) to give **11** (75%).

Taking previous glycosidations with ethynylated glycosyl donors into account [28], we prepared the thioglycosides **13** and **15** as glucosyl donors; the former from the known glucosyl chloride **12** [24] under conditions of phase-transfer catalysis [31], and the latter by chlorobenzylation of the known thioglycoside **14** [25]. The different protecting groups of **13** were chosen to facilitate the separation of isomers at the octasaccharide stage; a combination of protecting groups had proven advantageous in the synthesis of linear acetylenosaccharides [32].

For the synthesis of maltohexaose, we acetolytically cleaved per-*O*-acetylated α-CD **17** [33], similarly as described by *Sakairi et al.* [23], but with Ac_2O and 70% $HClO_4$ at 0° (*Scheme 2*). This modified procedure yielded 95% of the fully acetylated hexamaltosaccharide **18** ($\alpha/\beta > 9:1$) after recrystallisation in EtOH, as compared to a yield of 41–52%, resulting from a cleavage with Ac_2O and H_2SO_4 at 50–60° [23]. The

Scheme 1

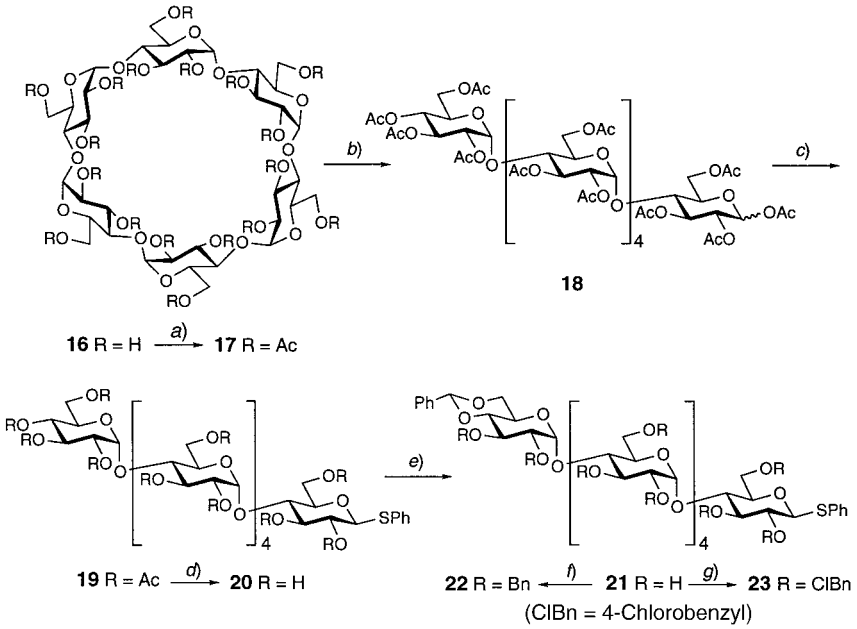


a) 2,6-Dimethylpyridine, $Cl(CH_2)_2Cl$; 82%. *b*) $AlCl_3$, BuLi, 2,6-dimethylpyridine, toluene, 85 → 100°; 0.1M HCl/MeOH; Ac_2O, pyridine; 53%. *c*) 0.1M HCl/EtOH; 96%. *d*) α,α-Dimethoxytoluene, $TsOH \cdot H_2O$; 84%. *e*) BnBr, NaH, DMF; 97%. *f*) 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, NaH, DMF; 86%. *g*) $NaBH_3CN$, 1M HCl in Et_2O, 3-Å molecular sieves, THF; 84%. *h*) 1% I_2/MeOH, reflux; 71%. *i*) 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, $(Bu_3Sn)_2O$, toluene; 75%. *j*) PhSH, Bu_4NSH, AcOEt; 50%. *k*) 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, NaH, DMF; 90%.

hexasaccharide **18** was converted to the phenyl thioglycoside **19** (85%) according to *Hanessian*'s method [34]. Deacetylation of **19** yielded 94% of the hexasaccharide **20**. The $4^{VI},6^{VI}$-*O*-benzylidene acetal **21** was best prepared with α,α-dibromotoluene in pyridine according to the method of *Garegg* and *Swahn* [35]; the acetal exchange method of *Evans* proved less satisfactory [36] (see also [23]). Partially purified **21** was, on the one hand, benzylated to the hexasaccharide thioglycoside **22** (78% from **20**) and, on the other hand, 4-chlorobenzylated to **23** (78% from **20**).

The Bn-protected acceptor **9** was glycosylated with the benzylated hexasaccharide donor **22** under standard conditions (NIS, TfOH, Et_2O) to yield 86% of the anomeric

Scheme 2



a) Ac_2O/pyridine; (quant.). *b*) 70% aq. $HClO_4$, Ac_2O, $0 \rightarrow 23°$; 95%. *c*) ZnI_2, Me_3SiSPh, CH_2Cl_2; 85%. *d*) 1M NaOMe in MeOH; 94%. *e*) α,α, Dibromotoluene, pyridine. *f*) NaH, BnBr, Et_4NI, imidazole, DMF; 78% from **20**. *g*) 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, NaH, DMF; 80% from **20**.

heptasaccharides **24** ($\alpha_5\alpha$)[2]) and **25** ($\alpha_5\beta$) in a ratio of 3:1 (*Scheme 3*). Similarly, the chlorobenzyl-protected acceptor **11** was glycosylated with the chlorobenzylated donor **23** to yield 95% of the anomeric heptasaccharides **26** ($\alpha_5\alpha$) and **27** ($\alpha_5\beta$) in a ratio of 5:4. The mixtures **24**/**25** and **26**/**27** were readily separated by flash chromatography. Cleavage of the dioxane ring of the fully α-D-configured benzylated **24** with $Me_3N \cdot BH_3$ and $AlCl_3$ in THF [37] yielded 75% of the alcohol **28**. Similarly to the monomeric benzylidene acetal **8**, the major $\alpha_5\alpha$-configured heptasaccharide **26** was debenzylidenated to afford 60% of the diol **29** that was regioselectively 4-chlorobenzylated *via* a tin alkoxide to yield 67% of **30**. The dioxane ring of the minor, 4-chlorobenzylated $\alpha_5\beta$-heptasaccharide **27** was reductively cleaved with Et_3SiH and $BF_3 \cdot OEt_2$ [38] to yield 76% of the alcohol **31**.

Glycosidation of the Bn-protected heptasaccharide **28** with **13** under standard conditions yielded 68% of the anomeric octasaccharides **32** ($\alpha\alpha_5\alpha$), and **33** ($\beta\alpha_5\alpha$) in a ratio of 5:2 (*Scheme 4*). These anomers were separated by flash chromatography, and their structure was determined by ^{1}H- and ^{13}C-NMR spectroscopy. Similarly, the 4-chlorobenzylated heptasaccharide **30** and the donor **15** afforded the anomeric octasaccharides **34** ($\alpha\alpha_5\alpha$) and **35** ($\beta\alpha_5\alpha$) that were isolated in 48 and 36% yield, respectively, after a tedious separation.

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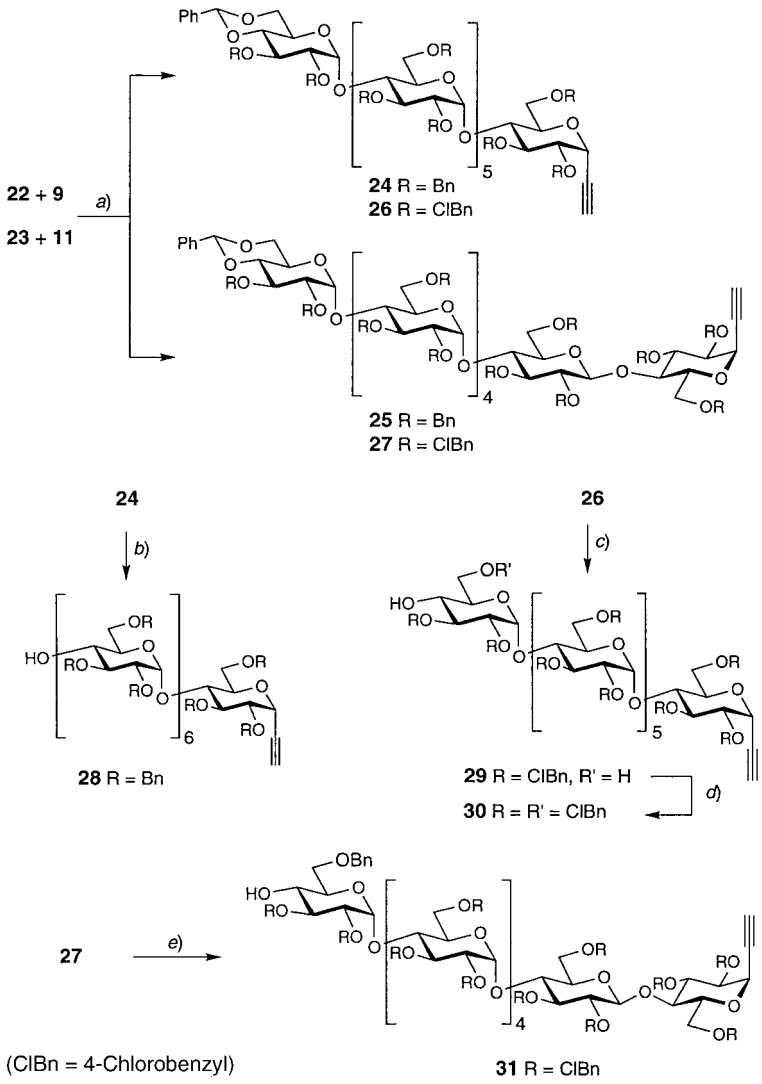
[2]) To readily identify the glycosides, we specify the configuration of the new glycosidic centers relative to the conserved ones of the hexamaltoside moiety.

Scheme 3

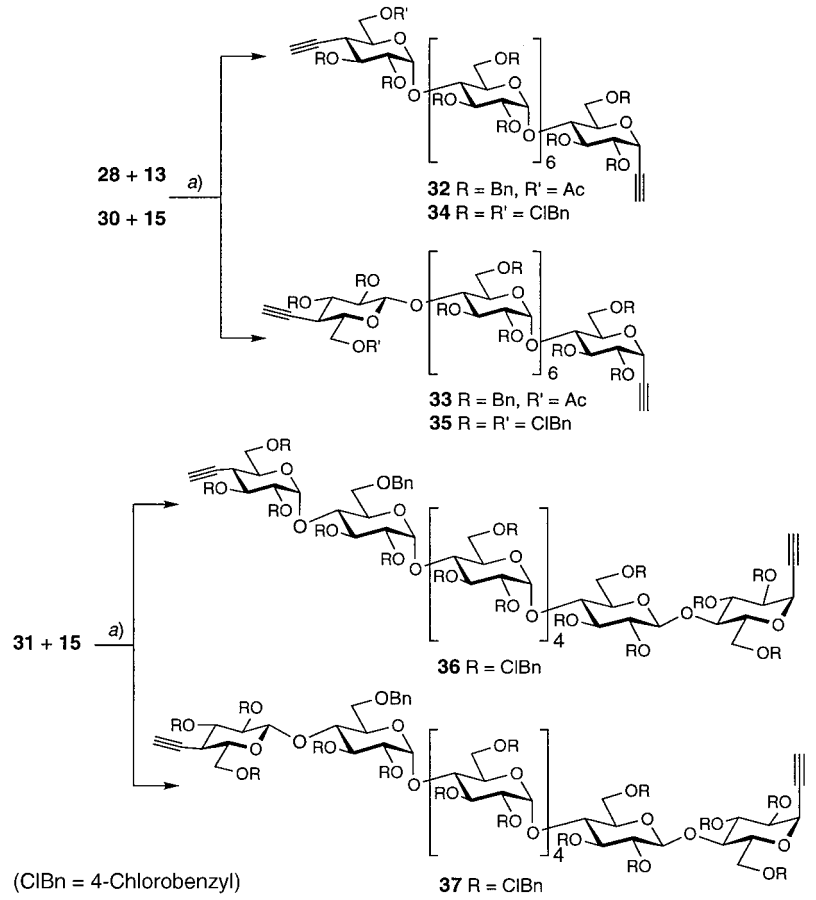


a) NIS (*N*-Iodosuccinimide), TfOH (trifluoromethanesulfonic acid), 3-Å molecular sieves, Et_2O, $-60°$; **24**/**25** 3:1 (86%); **26**/**27** 5:4 (95%). *b*) $Me_3N \cdot BH_3$, $AlCl_3$, 3-Å molecular sieves, THF; 75%. *c*) 1% I_2/MeOH, reflux; 60%. *d*) 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, $(Bu_3Sn)_2O$, toluene, 90°, 67%. *e*) $BF_3 \cdot OEt_2$, Et_3SiH, CH_2Cl_2; 76%.

Finally, glycosidation of the $\alpha_5\beta$-configured heptasaccharide **31** with **15** yielded 86% of the anomeric octasaccharides **36** ($\alpha\alpha_5\beta$) and **37** ($\beta\alpha_5\beta$) in a ratio of 5:4.

In the ^{1}H-NMR spectrum of **24**, the six anomeric H-atoms resonate at 5.68, 5.66, 5.64, 5.62, 5.60, and 5.54 ppm as *d*'s with coupling constants in the range of 3.5 Hz. The ^{1}H-NMR spectrum of **26** shows four *d* (5.52 (1 H), 5.51 (1 H), 5.48 (3 H), and 5.44 (1 H) ppm) for the six anomeric H-atoms, while the ^{1}H-NMR spectra of **25** and **27** only exhibit signals of five α-anomeric H-atoms. The H–C(1) signal of the β-D-linked moiety is

Scheme 4



a) NIS, TfOH, 3-Å molecular sieves, toluene, $-60°$; **32**/**33** 5:2 (68%); **34**/**35** 5:4 (84%); **36**/**37** 1:1 (86%).

hidden. The α-anomeric C(1^{III-VI}) of **25** and **27** resonate at 97.46, 96.74, 96.42, 96.22, and 96.12, and at 97.82, 96.86, 96.62 (2 C), and 96.44 ppm, respectively, and the β-anomeric C(1^{II}) at 102.15 and 102.20 ppm, respectively. The acetylenic H-atom gives rise to a *d* ($J = 2.3$ Hz) at 2.64 and 2.57 ppm for **24** and **25**, and at 2.68 and 2.64 for **27** and **26**, respectively. The ^{1}H-NMR spectrum of **29** shows a *d* at 2.39 ppm ($J = 2.3$ Hz) for HO–C(4^{VII}) and a *t* at 1.8 ppm ($J = 6.5$ Hz) for HO–C(6^{VII}), whereas the ^{1}H-NMR spectrum of **30** displays only a *d* at 2.55 ppm ($J = 2.4$ Hz) for HO–C(4^{VII}). The ^{1}H-NMR spectra of **32** and **33** show a signal at 2.18 ppm ($J = 2.3$ Hz), corresponding to a second acetylenic H-atom. Signals of H_α–C($1^{II-VIII}$) are visible in the spectrum of **32** and signals of H_α–C($1^{III-VIII}$) in the spectrum of **33**. The ^{13}C-NMR spectrum of **33** confirms the anomeric configuration showing a *d* at 102.27 ppm for C(2^{VII}). The ^{1}H-NMR spectrum of **34** shows a new *d* at 2.17 ppm ($J = 2.3$ Hz) corresponding to an acetylenic H-atom, confirming the incorporation of an alkynylated moiety. Five other diagnostic signals at 5.57 (*d*, $J = 3.5$), 5.55 (*m*, 3 H), 5.50 (*d*, $J = 3.5$), 5.48 (*d*, $J = 3.7$), and 5.46 (*d*, $J = 3.5$) ppm correspond to the seven equatorial anomeric H-atoms of the α-(1 → 4)-*O*-glycosidic linkages. For **35**, the β-D-configuration of C(1^{VIII}) is revealed by the characteristic *d* of H–C(1^{VIII}) at 4.22 ppm ($J = 8.0$ Hz), whereas the α-D-configured centers give rise to five *d* (5.66 (1 H), 5.52 (2 H), 5.48 (1 H), 5.48 (1 H), and 5.43 (1 H) ppm) with coupling constants of *ca*. 3.5 Hz for the six equatorial anomeric H–C(1^{II-VII}). In addition, the ^{13}C-NMR spectrum of **35** shows the signal for the β anomeric C(1^{VIII}) at 102.32 ppm.

Upon treatment with excess $Cu(OAc)_2$ in dilute solution (4.6 μM in MeCN/pyridine 3:1 [39]), the octasaccharides **32**, **33**, **34**, **35**, **36**, and **37** cyclised smoothly to the 1,3-butadiynediyl-saccharides **38**, **43**, **39**, **44**, **48**, and **50**, respectively. The ($\alpha\alpha_5\alpha$)-octasaccharides **32** and **34** cyclised most rapidly, and the ($\alpha\alpha_5\beta$)-isomer **36** most slowly, although the time required to complete the reaction did not differ by much (3 *vs.* 5 h). Yields ranged from 40 to 60%. Cyclisation was readily ascertained by the disappearance of the acetylenic signals in the ^{1}H-NMR spectrum of the products. There was no obvious difference in the physicochemical properties of the Bn or 4-chlorobenzyl-protected intermediates and CD analogues. However, the easier removal of the 4-chlorobenzyl group by *Lewis* acids proved an advantage.

Hydrogenation of **38** and **43** in the presence of $Pd(OH)_2$ in 2-methoxyethanol removed the Bn groups and reduced the butadiyne moiety, leading to the monoacetates **41** (99%) and **46** (96%), respectively (*Scheme 5*). Their de-*O*-acetylation gave the desired butano-CDs **42** and **47** in high yields. The 4-chlorobenzylated butadiynes **39**, **44**, **48**, and **50** were deprotected with $FeCl_3$ in CH_2Cl_2, leading in 75–80% to the butadiynes **40**, **45**, **49**, and **51**, respectively (*Schemes 5* and *6*).

In (D_6)DMSO, HO–C(2) of α- and β-CD resonates as a *d* at 5.48 and 5.70 ppm with J(H,OH) ≈ 6.5 Hz and HO–C(3) as a *d* at 5.40 and 5.65 ppm with J(H,OH) ≈ 2.3 Hz, respectively. The coupling constants J(2,OH) and J(3,OH) are similar to those of maltobioses (J(2′,OH) = 6.2–6.3 Hz, J(3,OH) = 3.2 Hz [40]) and indicate a *ca.* 1:1 flip-flop equilibrium between the O(3)–H···O(2′)–H and the O(2′)–H···O(3)–H H-bonded species (see also [22]). In γ-CD, HO–C(2) and HO–C(3) appear at 5.73 ppm as a broad signal. The interruption of the H-bond network in the new CD analogues is visible in the ^{1}H-NMR spectra in (D_6)DMSO of the butano-CD's **42** ($\alpha\alpha_5\alpha$) and **47** ($\beta\alpha_5\alpha$). The 300-MHz ^{1}H-NMR spectrum of **42** shows a broad signal at 5.84–5.36 ppm integrating for 13–14 OH and an OH *d* at 4.71 ppm (J = 4.8 Hz). One or possibly two OH signals are hidden below the H–C(1) signals. The upfield shift of two OH signals suggests that HO–C(5^{I}) (at 4.71 ppm) and HO–C(3^{VIII}), both vicinal to a butane-1,4-diyl group, are more or less completely solvated, and that the inter-residue flip-flop H-bonds for the seven maltobiosyl units are maintained. The 500-MHz ^{1}H-NMR spectrum of **47** shows signals for 12 OH groups at 5.8–5.38 ppm and 4 OH *d*'s at higher field (at 5.06, 4.97, 4.925, and 4.78 ppm) with J(H,OH) of 4.7, *ca.* 2.5, 5.0, and 5.8 Hz, respectively. According to a ^{1}H,^{1}H-COSY spectrum, the signals at 5.06 and 4.78 ppm belong to HO–C(2^{VIII}), and HO–C(3^{VIII}). Signal overlapping prevents an unambiguous assignment of the other OH signals. The comparison with **42** suggests that the signal at 4.925 ppm belongs to HO–C(5^{I}). The small J(H,OH) value (*ca.* 2.5 Hz) of the signal at 4.97 ppm may reveal a completely persistent H-bond of HO–C(3^{VII}) to OC(5^{VIII}) as it is observed in cellobiosyl units (J(3,OH) ≈ 2 Hz [40]). The coupling constants of the other 3 OH groups resonating at higher field indicate more or less completely solvated OH groups. The 6 inter-residue flip-flop H-bonds of **47** are evidenced by the downfield shift for 12 OH at 5.8–5.38 ppm.

Possible ring conformations of the γ-CD analogues **40**, **42**, **45, 47**, **49**, and **51** were obtained by molecular modeling (Macromodel V. 7.0 with a modified MM3* force field, gas phase [41]). The conformer of γ-CD possessing O(2′)–H···O(3)–H interresidue H-bonds was used a starting structure. The O(2′)–H···O(3)–H interresidue H-bonds of the maltosyl units and the preset O(3)–H···O(5′) interresidue H-bond for the cellobiosyl unit were kept during the optimisation[3]). The minimal-energy conformations of **40**, **42, 45**, **47**, **49**, and **51** lack any strong ring strain but indicate significantly different shapes (*Fig*). The CD analogues **40** and **42** ($\alpha\alpha_5\alpha$) possess a cavity in the form of a flattened circle. The cavity of **47** ($\beta\alpha_5\alpha$) is slightly elliptical, the one of **45** ($\beta\alpha_5\alpha$)

[3]) For geometric reasons, no O(3)–H···O(5′) interresidue H-bonds are tolerated in the $\alpha\alpha_5\beta$-configured **49** and only one (set between the units 7 and 8) in the $\beta\alpha_5\beta$-configured **51**.

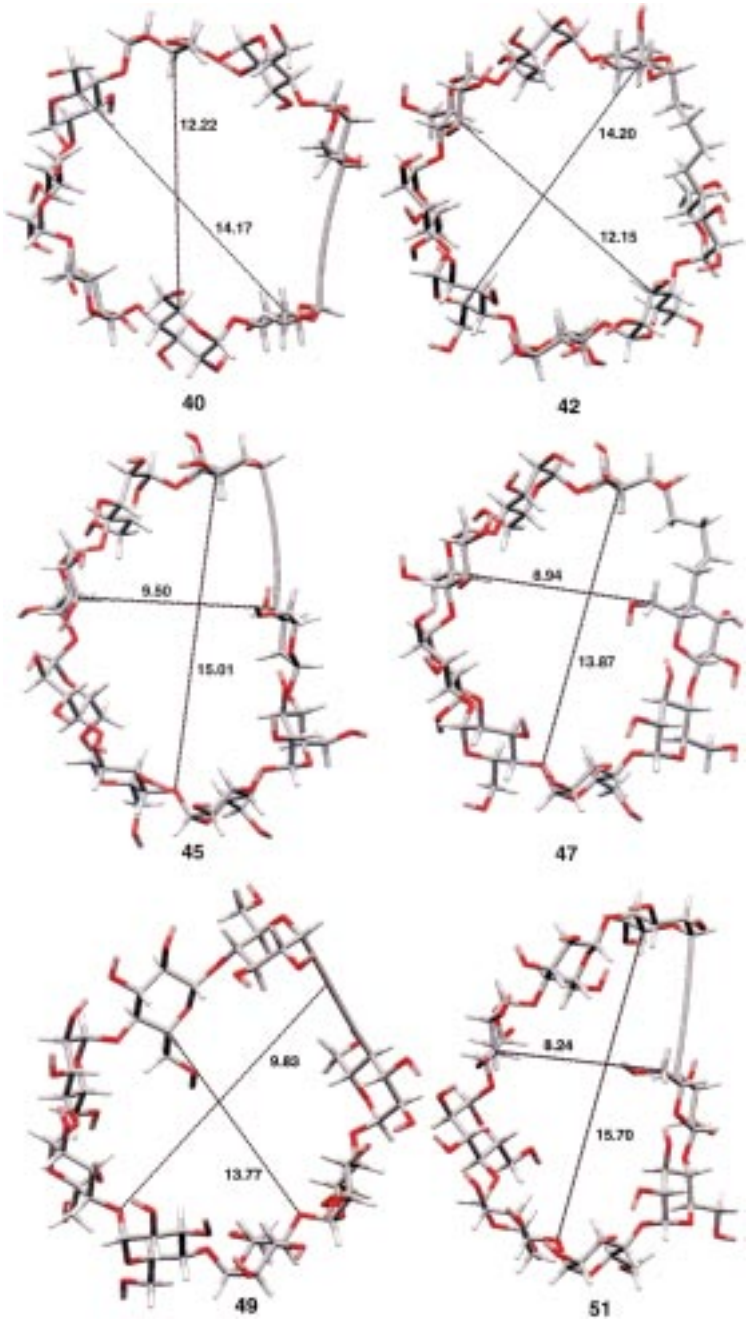
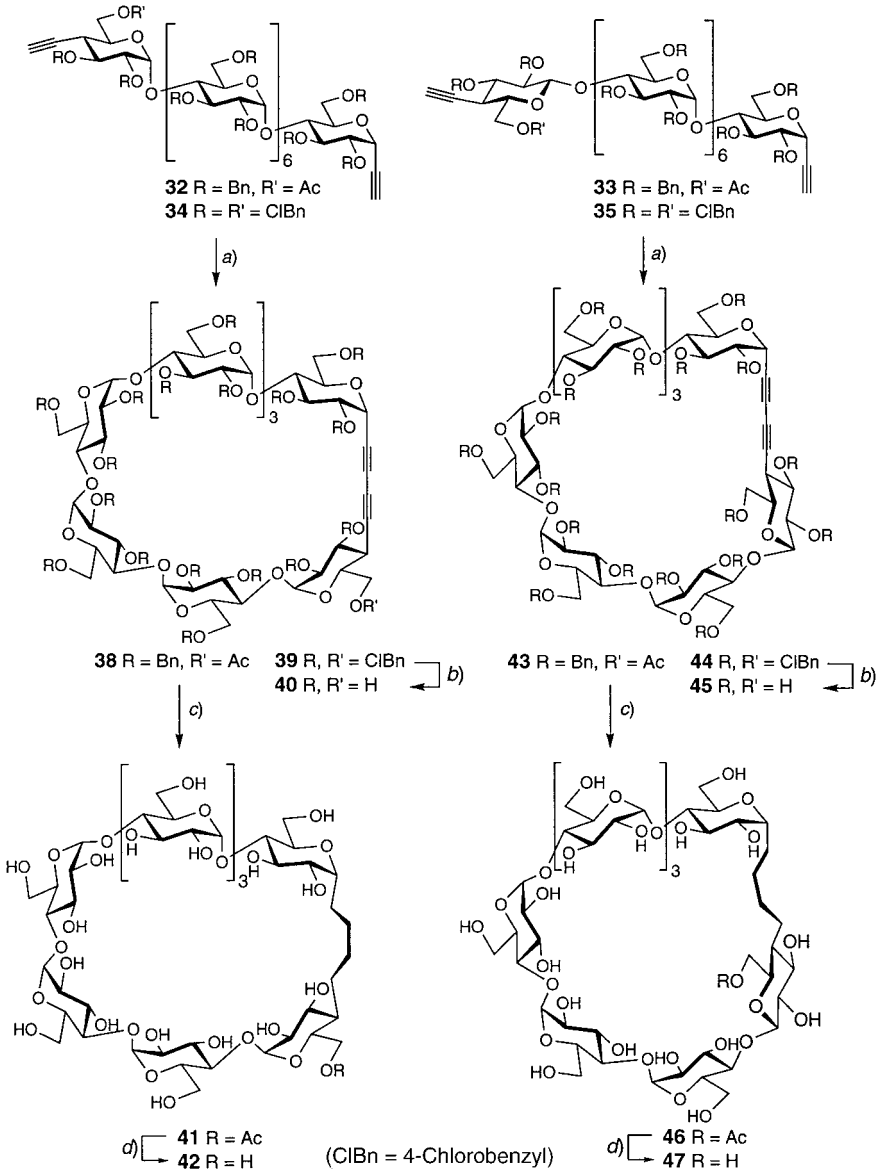


Figure. *MM3*-Calculated structures of the γ-CD-analogues* **40**, **42**, **45**, **47**, **49**, *and* **51**. Numbers in the formulae give the maximal and the minimal distances between heavy atoms [Å].

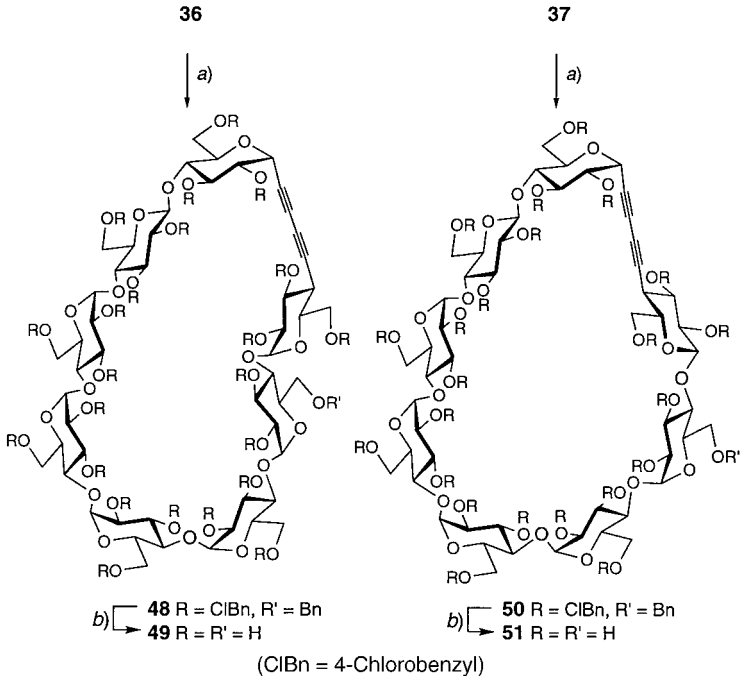
Scheme 5



a) $Cu(OAc)_2$, MeCN, pyridine, 80°; **38** (50%), **39** (60%), **43** (60%), **44** (56%). *b*) $FeCl_3$, CH_2Cl_2; **40** (73%), **45** (75%). *c*) H_2, $Pd(OH)_2$, $MeOCH_2CH_2OH$; **41** (quant.), **46** (89%). *d*) 1M NaOMe in MeOH; **42** (97%), **47** (quant.).

more strongly so, and the cavity of **49** ($\alpha\alpha_5\beta$) and **51** ($\beta\alpha_5\beta$) are clearly irregular, showing that both the position and the number of β-D-configured glycosidic centers have a strong impact on the shape of the cavity.

Scheme 6



a) $Cu(OAc)_2$, MeCN, pyridine, 80°; **48** (40%), **50** (45%). *b*) $FeCl_3$, CH_2Cl_2; **49** (78%), **51** (71%).

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Experimental Part

General. Solvents were distilled before use: Et_2O, THF, and toluene from Na and benzophenone, CH_2Cl_2 from P_2O_5, DMF from $CaSO_4$, pyridine from KOH, and MeOH from CaH_2. Trifluoromethanesulfonic acid (TfOH) was distilled prior to use. *N*-Iodosuccinimide (NIS) and $AlCl_3$ were sublimed prior to use. NaH (55–65% on free-flowing powder moistened with oil) was washed with hexane. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60* F_{254}). Flash chromatography (FC): silica gel *Fluka 60* (0.04–0.063 mm), silica H *Fluka* (5–40 μm). M.p.'s uncorrected. Optical rotations: 1-dm cell at 25°, 589 nm. FT-IR spectra: *ca*. 2% soln. in $CHCl_3$ (or in the indicated solvent). ^{1}H- and ^{13}C-NMR spectra: 300 or 500 MHz, and 75 or 125 MHz, respectively. The assignment of ^{13}C-NMR *multiplets* is based on DEPT spectra; due to the characteristic J(C,H) coupling, $C{\equiv}CH$ appears in the DEPT spectrum as a very weak positive signal, whereas $C{\equiv}CH$ gives no DEPT signal both these signal were assigned as *s*; see also [42]. MS: chemical ionisation (CI) with NH_3, fast-atom bombardment (FAB), or matrix-assisted laser-desorption ionisation mass spectrometry (MALDI-MS).

1,6-Anhydro-2,4-bis-O-*{diethyl[2-(trimethylsilyl)ethynyl]silyl}-β*-D-*glucopyranose* (**3**). A suspension of **1** (35.7 g, 0.22 mol) in 1,2-dichloroethane (380 ml) was treated with 2,6-lutidine (105 ml, 0.904 mol) at 23°, stirred for 1.5 h, treated dropwise with **2** (100 g, 0.458 mol) over a period of 2 h, and stirred at 23° for 30 min. The mixture was diluted with $CHCl_3$ (500 ml) and washed with H_2O (250 ml). The aq. layer was extracted twice with $CHCl_3$ (2 × 250 ml). The combined org. fractions were washed with brine (100 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 20:1 → 10:1) gave **3** (103 g, 82%). White solid. R_f (hexane/AcOEt 3:1) 0.68. M.p. 45–46°. IR ($CHCl_3$): 3540*w* (br.), 2962*s*, 2900*m*, 2878*m*, *ca*. 2100*w*, 1459*m*, 1411*m*, 1108*s* (br.), 1076*s* (br.), 1008*m*, 972*m*, 896*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.36 (br. *s*, H–C(1)); 4.52 (br. *d*, J = 5.1, H–C(5)); 3.91

(d, J = 7.3, H_{endo}–C(6)); 3.75–3.60 (m, H–C(2), H–C(3), H–C(4), H_{exo}–C(6)); 2.45 (d, J = 5.0, HO–C(3)); 1.08–1.00 (m, 2 ($MeCH_2$)$_2$Si); 0.78–0.62 (m, 2 (MeCH_2)$_2$Si); 0.18 (s, 2 Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 116.72, 116.59, 109.26, 109.17 (4s, 2 SiC≡CSi); 103.33 (d, C(1)); 77.98 (2d); 75.27 (2d); 66.73 (t, C(6)); 6.47 (q, 2 ($MeCH_2$)$_2$Si); 6.31 (t, 2 (MeCH_2)$_2$Si); −0.25 (q, 2 Me_3Si). CI-MS: 544 (100, $[M+NH_4]^+$).

1,3,4,5-Tetra-O-*acetyl-2,6-anhydro-7,8-dideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**4**). Under Ar, a suspension of freshly sublimed $AlCl_3$ (91.0 g, 0.684 mol) in toluene (1500 ml) was cooled to 0°, treated with 1.6M BuLi (428 ml, 0.684 mol), warmed to 23°, stirred for 30 min, heated to 80°, treated with a soln. of **3** (80.0 g, 0.152 mol) and 2,6-lutidine (35.5 ml, 0.304 mol) in toluene (800 ml) over a period of 15 min, stirred at 85° for 3.5 h and at 100° for 1 h, and allowed to cool to 23°. After evaporation, the residue was dissolved in 0.1M HCl in MeOH (1500 ml) and stirred for 10 h at 40°. The soln. was evaporated and co-evaporated twice with toluene. The residue was dissolved in pyridine (2080 ml), treated with Ac_2O (1300 ml), and stirred at 23° for 3 h. After evaporation, the residue was dissolved in AcOEt (500 ml) and washed with H_2O (500 ml). The aq. layer was extracted with AcOEt (2 × 250 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 10:1 → 5:1) gave **4** (34.6 g, 53%). White solid. R_f (hexane/AcOEt 1:1) 0.50. M.p. 113–114°. $[\alpha]_D^{25}$ = +151.1 (c = 0.51, $CHCl_3$). IR ($CHCl_3$): 2962w, 2901w, 1751s, 1602w, 1430w, 1368m, 1068m, 1039m, 984w, 847m. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.48 (br. dd, J = 9.6, 10.0, H–C(4)); 5.03 (d, J = 5.8, H–C(6)); 5.03 (br. dd, J = 9.6, 10.0, H–C(3)); 4.90 (dd, J = 6.2, 10.0, H–C(5)); 4.36–4.18 (m, 2 H–C(1), H–C(2)); 2.10, 2.08, 2.05, 2.03 (4s, 4 AcO); 0.24 (s, Me_3Si), ^{13}C-NMR (75 MHz, $CDCl_3$): 170.93, 170.33, 170.14, 169.88 (4s, 4 C=O); 97.64, 97.10 (2s, C≡C); 71.10, 70.75, 69.80, 68.37 (4d, C(2), C(3), C(4), C(5)); 65.93 (d, C(6)); 61.96 (t, C(1)); 20.73 (q, 2 Me); 20.63 (q, 2 Me); −0.32 (q, Me_3Si). CI-MS: 446 (100, $[M+NH_4]^+$), 429 (42, $[M+1]^+$). Anal. calc. for $C_{19}H_{28}O_9Si$ (428.51): C 53.26, H 6.59; found: C 53.31, H 6.33.

2,6-Anhydro-7,8-dideoxy-8-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**5**). A soln. of **4** (33.5 g, 0.078 mol) in 0.1M HCl in EtOH (3000 ml) was stirred at 90° for 4 h. Evaporation and FC (CH_2Cl_2/MeOH 5:1) gave **5** (19.5 g, 96%). Off-white solid. R_f (CH_2Cl_2/MeOH 5:1) 0.23. M.p. 173–175°. IR (KBr): 3550–3290s, 2960m, 2905m, 2179w, 1386m, 1344m, 1252s, 1135m, 1108s, 1091s, 1057s, 1016s, 906m, 842s, 760m. ^{1}H-NMR (200 MHz, CD_3OD): 4.64 (d, J = 5.8, H–C(6)); 3.86–3.56 (m, 2 H–C(1), H–C(2), H–C(4)); 3.46 (dd, J = 5.8, 9.6, H–C(5)); 3.30 (br. t, J = 9.2, H–C(3)); 0.17 (s, Me_3Si). ^{13}C-NMR (75 MHz, CD_3OD): 102.33 (s, C≡CSi); 95.10 (s, C≡CSi); 76.97, 76.25, 72.36,71.81, (4d, C(2), C(3), C(4), C(5)); 70.42 (d, C(6)); 62.95 (t, C(1)); −0.07 (q, Me_3Si). CI-MS: 278 (100, $[M+NH_4]^+$), 260 (2, M^+). Anal. calc. for $C_{11}H_{20}O_5Si$ (260.36): C 50.75, H 7.74; found: C 50.71, H 7.36.

*2,6-Anhydro-(*R*)-1,3*-O-*benzylidene-7,8-dideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**6**). A soln. of **5** (9.56 g, 36.9 mmol) in MeCN (210 ml) was treated with α,α-dimethoxytoluene (7.00 ml, 47.9 mmol) and TsOH · H_2O (200 mg), stirred at 23° for 10 min and at 70° for 2 h (MeOH is distilled off). The soln. was allowed to cool to 23°, treated with Et_3N (3 ml), and evaporated. FC (toluene/AcOEt 1:0 → 2:1) gave **6** (11.2 g, 84%). White solid. R_f (toluene/AcOEt 2:1) 0.27. M.p. 128–129°. IR ($CHCl_3$): 3594m, 3386w (br.), 3066w, 3007m, 2962m, 2871m, 2169w, 1457m, 1378m, 1331m, 1294m, 1107s, 1073s, 1035s, 993s, 917s, 886s, 848s. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.54–7.50 (m, 2 arom. H); 7.41–7.36 (m, 3 arom. H); 5.53 (s, PhCH); 4.79 (d, J = 4.6, H–C(6)); 4.34 (dd, J = 4.7, 10.3, H_{eq}–C(1)); 4.03–3.89 (m, H–C(2), H–C(4)); 3.67–3.74 (m, H–C(5), H_{ax}–C(1)); 3.44 (br. t, $J \approx$ 9.3, H–C(3)); 2.98 (br. s, HO–C(4)); 2.44 (d, J = 7.2, HO–C(5)); 0.22 (s, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.21 (s); 129.55 (d); 128.63 (2d); 126.48 (2d); 102.07 (d, PhCH); 98.80 (s, C≡CSi); 96.89 (s, C≡CSi); 81.21 (d, C(3)); 72.69, 71.55 (2d, C(4), C(5)); 69.50 (d, C(2)); 69.05 (t, C(1)); 65.89 (d, C(6)); −0.15 (q, Me_3Si). CI-MS: 349 (100, $[M+1]^+$).

2,6-Anhydro-4,5-di-O-*benzyl-1,3*-O-*benzylidene-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**7**). Under Ar, a soln. of **6** (9.70 g, 27.8 mmol) in DMF (100 ml) was cooled to 0°, treated with NaH (1.40 g, 58.4 mmol), stirred for 15 min, treated with BnBr (7.94 ml, 69.5 mmol), stirred at 0° for 1 h, treated dropwise with MeOH (25 ml), and diluted with H_2O (100 ml) and $CHCl_3$ (100 ml). The org. and aq. phases were separated, and the aq. phase was extracted with $CHCl_3$ (2 × 150 ml). The combined org. layers were washed with brine (80 ml), dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 10:1 → 1:1) gave **7** (13.3 g, 97%). White foam. R_f (hexane/Et_2O 3:1) 0.32. M.p. 101–102°. $[\alpha]_D^{25}$ = +11.9 (c = 1.84, $CHCl_3$). IR ($CHCl_3$): 3305m, 3167w, 3007m, 2908m, 2869w, 2118w, 1602w, 1497w, 1454m, 1368m, 1339w, 1314w, 1280w, 1174w, 1092s, 1029m, 988m, 913w. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.55–7.26 (m, 15 arom. H); 5.60 (s, PhCH); 5.01–4.74 (m, 2 ArCH); 4.74 (dd, J = 2.1, 5.8, H–C(6)); 4.36 (dd, J = 4.8, 10.4, H_{eq}–C(1)); 4.16–4.04 (m, H–C(2)); 4.06 (br. t, $J \approx$ 9.6, H–C(4)); 3.78–3.58 (m, H–C(3), H–C(5)); 3.67 (br. t, $J \approx$ 10.0, H_{ax}–C(1)); 2.68 (d, J = 2.1, C≡CH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.87, 138.01, 137.57 (3s); 126.24–129.13 (several d); 101.41 (d, PhCH); 82.05 (d, C(3)); 79.58 (d); 78.56 (s, C≡CH); 78.18 (d); 77.61 (s, C≡CH); 75.48, 73.70 (2t, 2 ArCH$_2$); 69.04 (t, C(1)); 67.77 (d, C(2)); 66.15

(*d*, C(6)). CI-MS: 457 (21, $[M+1]^+$), 365 (13, $[M-\mathrm{Bn}]^+$), 91 (100). Anal. calc. for $C_{29}H_{28}O_5$ (456.54): C 76.30, H 6.18; found: C 76.18, H 6.18.

2,6-Anhydro-4,5-bis-O-*(4-chlorobenzyl)-1,3*-O-*benzylidene-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**8**). Under Ar, a soln. of **6** (11.2 g, 32.09 mmol) in DMF (120 ml) was cooled to 0°, treated with NaH (4.33 g, 90.35 mmol), stirred for 15 min, treated with 4-$ClC_6H_4CH_2Cl$ (17.32 g, 107.5 mmol) and Bu_4NI (39.7 g, 107.5 mmol), stirred at 0° for 3 h and at 23° for 2 h, treated dropwise with MeOH (30 ml), and diluted with H_2O (100 ml) and Et_2O (100 ml). The phases were separated, and the aq. phase was extracted with Et_2O (2 × 150 ml). The combined org. layers were washed with brine (100 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 40:1 → 10:1) gave **8** (14.39 g, 86%). White foam. R_f (toluene) 0.29. $[\alpha]_D^{25} = +22.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3303*m*, 2870*w*, 2103*w*, 1599*m*, 1492*m*, 1459*w*, 1368*m*, 1089*s*, 999*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.26 (*m*, 13 arom. H); 5.57 (*s*, PhC*H*); 4.90, 4.79 (2*d*, $J = 11.4$, ArC*H*); 4.76 (*dd*, $J = 2.4$, 6.0, H–C(6)); 4.71, 4.70 (2*d*, $J = 12.0$, ArC*H*); 4.35 (*dd*, $J = 4.5$, 10.2, H_{eq}–C(1)); 4.08 (*dt*, $J = 4.9$, 9.9, H–C(2)); 4.00 (*t*, $J = 9.1$, H–C(4)); 3.71 (*t*, $J = 10.1$, H_{ax}–C(1)); 3.63 (*dd*, $J = 6.0$, 9.0, H–C(5)); 3.58 (*t*, $J = 9.3$, H–C(3)); 2.66 (*d*, $J = 2.1$, C≡CH). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.56, 137.43 (2*s* of ClC_6H_4); 136.54 (*s* of Ph); 134.10, 133.66 (2*s* of ClC_6H_4); 129.52 (2*d*); 129.49 (2*d*); 129.34 (*d*); 128.99 (2*d*); 128.74 (2*d*); 128.58 (2*d*); 126.33 (2*d*); 101.60 (*d*, PhCH); 82.02 (*d*, C(3)); 79.53, 78.40 (2*d*, C(4), C(5)); 78.43 (*s*, *C*≡CH); 77.94 (*s*, C≡*C*H); 74.55, 72.78 (2*t*, 2 Ar*C*H_2); 69.03 (*t*, C(1)); 67.62 (*d*, C(2)); 66.22 (*d*, C(6)). HR-MALDI-MS: 547.103 ($C_{29}H_{25}Cl_2NaO_5$, $[M+\mathrm{Na}]^+$; calc. 547.105). Anal. calc. for $C_{29}H_{26}O_5Cl_2$ (525.43): C 66.29, H 4.99, Cl 13.49; found: C 66.22, H 5.18, Cl 13.51

2,6-Anhydro-1,4,5-tri-O-*benzyl-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**9**). Under Ar, a suspension of **7** (13.3 g, 27.0 mmol) and 3-Å molecular sieves (6.70 g) in THF (500 ml) was treated with $NaBH_3CN$ (6.80 g, 108 mmol), stirred at 23° for 15 min, treated with 1M HCl in Et_2O (120 ml, 119 mmol) over a period of 60 min, and stirred at 23° for 2 h. The suspension was filtered over *Celite* (washed with THF). Evaporation and FC (hexane/AcOEt 10:1 → 5:1) gave **9** (11.2 g, 84%). Transparent syrup. R_f (hexane/AcOEt 3:1) 0.40. $[\alpha]_D^{25} = +44.1$ ($c = 1.10$, $CHCl_3$). IR ($CHCl_3$): 3587*m*, 3305*m*, 3067*w*, 3008*m*, 2914*m*, 2672*m*, 2117*w*, 1603*w*, 1496*m*, 1454*m*, 1365*m*, 1262*m*, 1072*s*, 1028*s*, 911*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.40–7.26 (*m*, 15 arom. H); 5.03 (*d*, $J = 11.6$, PhC*H*); 4.81–4.73 (*m*, 3 PhC*H*); 4.78 (*dd*, $J = 2.1$, 5.8, H–C(6)); 4.63 (br. *d*, $J \approx 12.2$, PhC*H*); 4.55 (br. *d*, $J \approx 12.2$, PhC*H*); 4.04–3.95 (*td*, $J \approx 4.0$, 10.0, H–C(2)); 3.87–3.57 (*m*, 2 H–C(1), H–C(3), H–C(4), H–C(5)); 2.64 (*d*, $J \approx 2.3$, C≡CH); 2.50 (*d*, $J = 2.1$, HO–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.75, 137.92, 137.77 (3*s*); 128.62–127.80 (several *d*); 82.37, 78.34 (2*d*, C(4), C(5)); 78.43 (*s*, *C*≡CH); 77.73 (*s*, C≡*C*H); 75.42, 73.64 (2*t*, 2 Ar*C*H_2); 73.32 (*d*, C(2)); 72.94 (*t*, Ar*C*H_2); 70.65 (*d*, C(3)); 69.54 (*t*, C(1)); 66.62 (*d*, C(6)). CI-MS: 476 (100, $[M+\mathrm{NH_4}]^+$), 459 (4, $[M+\mathrm{H}]^+$), 458 (3, M^+), 367 $[M-\mathrm{Bn}]^+$). Anal. calc. for $C_{29}H_{30}O_5$ (458.55): C 75.96, H 6.59; found: C 75.83, H 6.42.

2,6-Anhydro-4,5-bis-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**10**). Under Ar, a soln. of **8** (160 mg, 0.30 mmol) in a soln. of 1% I_2 in MeOH (15 ml) was stirred under reflux for 15 min. After evaporation, the soln. of the residue in AcOEt (20 ml) was washed with sat. aq. $Na_2S_2O_3$ soln. (20 ml), H_2O (20 ml), and brine (30 ml), dried ($MgSO_4$), and evaporatead. FC (toluene/AcOEt 2:1) gave **10** (74 mg, 71%).White foam. R_f (toluene/AcOEt 2:1) 0.13. $[\alpha]_D^{25} = +79.5$ ($c = 0.95$, $CHCl_3$). IR ($CHCl_3$): 3603*m*, 3432*m*, 3304*m*, 2102*w*, 1600*m*, 1493*m*, 1456*m*, 1364*m*, 1089*s*, 1039*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.35–7.23 (*m*, 8 arom. H); 4.92 (*d*, $J = 11.6$, ArC*H*); 4.77 (*t*, $J = 2.0$, 5.8, H–C(6)); 4.75 (*d*, $J = 11.6$), 4.65 (*d*, $J = 11.8$), 4.60 (*d*, $J \approx 12.0$) (3 ArC*H*); 3.89–3.80 (*m*, 2 H–C(1), H–C(2)); 3.78 (*t*, $J = 9.2$, H–C(4)); 3.58 (*dt*, $J = 3.4$, 9.2, H–C(3)); 3.55 (*dd*, $J = 5.8$, 9.2, H–C(5)); 2.91 (*d*, $J = 3.4$, HO–C(3)); 2.66 (*d*, $J = 2.0$, C≡CH); 2.31 (br. *t*, $J \approx 5.2$, HO–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.27, 136.33, 134.16, 133.86 (4*s*); 129.48 (2*d*); 129.31 (2*d*); 128.97 (2*d*); 128.92 (2*d*); 82.39, 78.75 (2*d*, C(4), C(5)); 78.22 (*s*, *C*≡CH); 78.12 (*s*, C≡*C*H); 74.66 (*t*, Ar*C*H_2); 74.44 (*d*, C(2)); 72.13 (*t*, Ar*C*H_2); 70.13 (*d*, C(3)); 66.46 (*d*, C(6)); 62.33 (*t*, C(1)). FAB-MS: 435 (100, $[M-1]^+$), 338 (65), 311 (24, $[M-4\text{-}ClC_6H_4CH_2]^+$), 125 (98, 4-$ClC_6H_4CH_2^+$).

2,6-Anhydro-1,4,5-tris-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**11**). A mixture of **10** (640 mg, 1.46 mmol) and $(Bu_3Sn)_2O$ (440 µl, 1.09 mmol) in toluene (9 ml) was stirred under reflux with azeotropic removal of H_2O (*Dean-Stark* apparatus) for 4 h. After evaporation, the residual soln. was treated with 4-$ClC_6H_4CH_2Cl$ (470 mg, 2.92 mmol) and Bu_4NI (647 mg, 1.75 mmol), and stirred for 16 h at 90°. After evaporation *in vacuo*, the soln. of the residue in AcOEt (25 ml) was treated with aq. KF (10 ml) and stirred for 1 h. The org. layer was separated, dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 1:0 → 2:1) gave **11** (614 mg, 75%). White foam. R_f (toluene/AcOEt 2:1) 0.49. $[\alpha]_D^{25} = +49.6$ ($c = 0.95$, $CHCl_3$). IR ($CHCl_3$): 3603*m*, 3499*m*, 3304*m*, 2102*w*, 1600*m*, 1492*s*, 1455*w*, 1408*m*, 1363*m*, 1089*s*, 1074*s*, 1016*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.33–7.24 (*m*, 12 arom. H); 4.90 (*d*, $J = 12.0$, ArC*H*); 4.77 (*dd*, $J = 2.4$, 5.4, H–C(6)); 4.73 (*d*, $J = 11.7$), 4.65 (*d*, $J = 11.7$); 4.60 (*d*, $J = 11.4$), 4.56 (*d*, $J = 11.7$), 4.50 (*d*, $J = 12.0$) (5 ArC*H*); 3.96 (*td*, $J \approx 3.9$, 9.6, H–C(2)); 3.76 (*t*, $J = 9.0$, H–C(4)); 3.72 (*dd*, $J = 4.2$, 10.5, H–C(1)); 3.66 (*dd*, $J = 3.5$, 10.5, H′– C(1)); 3.60 (*dt*, $J = 2.4$, 9.3,

H–C(3)); 3.56 (*dd*, *J* = 5.7, 9.3, H–C(5)); 2.63 (*d*, *J* = 2.1, C≡CH); 2.48 (*d*, *J* = 3.0, HO–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.35, 136.59, 136.38, 134.15, 133.84, 133.76 (6*s*); 129.49 (2*d*); 129.33 (2*d*);129.27 (2*d*); 128.97 (2*d*); 128.93 (2*d*); 128.83 (2*d*); 82.43, 78.56 (2*d*, C(4), C(5)); 78.27 (*s*, *C*≡CH); 78.03 (*s*, C≡*C*H); 74.64 (*t*, 2 Ar*C*H$_2$); 73.35 (*d*, C(2)); 73.01, 72.14 (2*t*, 2 Ar*C*H$_2$); 70.87 (*d*, C(2)); 69.82 (*t*, C(1)); 66.54 (*d*, C(6)). FAB-MS: 561 (32, $[M+1]^+$), 435 (13, $[M-4\text{-}ClC_6H_4CH_2]^+$), 125 (98, 4-$ClC_6H_4CH_2^+$). Anal. calc. for $C_{29}H_{27}Cl_3O_5$ (561.89): C 61.99, H 4.84, Cl 18.93; found: C 62.19, H 4.83, Cl 19.11.

Phenyl-6-O-*Acetyl-2,3-di*-O-*benzyl-4-deoxy-4*-C-*ethynyl-1-thio-α*-D-*glucopyranoside* (**13**). A soln. of freshly prepared **12** [24] (17.70 g, 4.13 mmol) in AcOEt (500 ml) was treated with a soln. of PhSH (5.08 ml, 4.95 mmol) and Bu_4NSH (21.0 g, 62.0 mmol) in 1M Na_2CO_3 (500 ml) and stirred vigorously at 23° for 4 h. The mixture was diluted with AcOEt (500 ml) and aq. $NaHCO_3$ soln. (500 ml). The org. phase was washed with sat. $NaHCO_3$ soln. (2 × 400 ml), brine (400 ml), and dried ($MgSO_4$). Evaporation and FC (hexane/AcOEt 4:1 → 0:1) gave **13** (10.4 g, 50%). White solid. R_f (hexane/AcOEt 3:2) 0.41. M.p. 78–80°. $[\alpha]_D^{25} = +161.0$ (*c* = 1.00, CH_2Cl_2). IR (CH_2Cl_2): 3302*s*, 3033*m*, 1953*w* (br.), 1741*s*, 1605*m*, 1584*m*, 1496*m*, 1481*m*, 1454*m*, 1440*m*, 1386*m*, 1368*s*, 1237*s*, 1102*s* (br.), 1038*s*, 911*w*, 653*m*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a DQFCOSY spectrum): 7.24–7.49 (*m*, 15 arom. H); 5.64 (*d*, *J* = 5.3, H–C(1)); 4.93 (*d*, *J* = 10.5, ArC*H*); 4.91 (*d*, *J* = 10.5, ArC*H*); 4.76 (*d*, *J* = 11.8, ArC*H*); 4.70 (*d*, *J* = 11.8, ArC*H*); 4.52 (*ddd*, *J* = 3.2, 4.7, 10.8, H–C(5)); 4.34–4.32 (*m*, 2 H–C(6)); 3.87 (*t*, *J* ≈ 9.6, H–C(3)); 3.78 (*dd*, *J* = 5.4, 9.4, H–C(2)); 2.68 (*dt*, *J* = 2.3, 10.6, H–C(4)); 2.21 (*d*, *J* = 2.3, C≡CH); 1.99 (*s*, AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC spectrum): 170.62 (*s*, C=O); 138.27, 137.60, 133.84 (3*s*); 131.70–127.34 (several *d*); 87.03 (*d*, C(1)); 80.47 (*s*, *C*≡CH); 79.41 (*d*, C(2)); 79.29 (*d*, C(3)); 76.11, 72.54 (2*t*, 2 Ar*C*H$_2$); 72.44 (*s*, C≡*C*H); 69.57 (*d*, C(5)); 64.16 (*t*, C(6)); 37.00 (*d*, C(4)); 20.74 (*q*, Me). FAB-MS: 503 ($[M+1]^+$). Anal. calc. for $C_{30}H_{30}O_5S$ (502.63): C 71.69, H 6.02; found: C 71.74, H 6.11.

Phenyl 2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-1-thio-β*-D-*glucopyranoside* (**15**). Under Ar, a soln. of **14** [25] (2.5 g, 8.9 mmol) in DMF (40 ml) was cooled to 0°, treated with NaH (1.41 g, 29.4 mmol), stirred for 15 min, treated with 4-$ClC_6H_4CH_2Cl$ (5.0 g, 31.2 mmol) and Bu_4NI (9.88 g, 26.75 mmol), stirred at 0° for 3 h and at 23° for 3 h, treated dropwise with MeOH (5 ml), and diluted with H_2O (50 ml) and Et_2O (50 ml). The phases were separated, and the aq. phase was extracted with Et_2O (2 × 50 ml). The combined org. layers were washed with brine (50 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 7:1) gave **15** (5.55 g, 90%). White foam. R_f (hexane/AcOEt 10:4) 0.46. $[\alpha]_D^{25} = +21.0$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3305*m*, 2908*m*, 2868*m*, 1599*m*, 1491*m*, 1407*w*, 1276*w*, 1087*s*, 1017*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.56–7.53 (*m*, 2 arom. H); 7.36–7.24 (*m*, 15 arom. H); 4.99 (*d*, *J* = 10.8), 4.87 (*d*, *J* = 10.8), 4.79 (*d*, *J* = 11.2) (3 ArC*H*); 4.72 (*d*, *J* = 9.4, H–C(1)); 4.67 (*d*, *J* = 10.8), 4.58 (*d*, *J* = 12.2), 4.57 (*d*, *J* = 12.4) (3 ArC*H*); 3.94 (*dd*, *J* = 1.6, 10.8, H–C(6)); 3.76 (*dd*, *J* = 5.4, 10.8, H′–C(6)); 3.66 (*ddd*, *J* = 1.6, 5.4, 10.8, H–C(5)); 3.60 (*dd*, *J* = 8.8, 10.8, H–C(3)); 3.37 (*dd*, *J* = 8.8, 9.6, H–C(2)); 2.80 (*dt*, *J* = 2.4, 10.4, H–C(4)); 2.19 (*d*, *J* = 2.0, C≡CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.04, 136.85, 136.77 (3*s*); 133.90 (3*s*); 133.55 (*s*); 132.04 (2*d*); 129.59 (2*d*); 129.56 (2*d*); 129.25 (2*d*); 129.17 (2*d*); 128.85 (2*d*); 128.81 (2*d*); 128.73 (2*d*); 127.87 (*d*); 87.91 (*d*, C(1)); 84.43 (*d*, C(2)); 81.08 (*s*, *C*≡CH); 80.65 (*d*, C(3)); 79.01 (*d*, C(5)); 75.13, 74.83, 72.72 (3*t*, 3 Ar*C*H$_2$); 72.72 (*s*, C≡*C*H); 70.45 (*t*, C(6)); 37.18 (*d*, C(4)). HR-MALDI-MS: 629.09 ($C_{31}H_{31}Cl_3NaO_4S$, $[M+Na]^+$; calc. 628.99). Anal. calc. for $C_{31}H_{31}Cl_3O_4S$ (605.7): C 64.27, H 4.78; found: C 64.15, H 5.01.

Icosa-O-*acetylmaltohexaose* (**18**) [33]. Under N_2 and with vigorous stirring, **17** [33] (67.0 g, 0.038 mol) was dissolved in Ac_2O (2000 ml) at 23°. The soln. was cooled to 0° and treated with 70% $HClO_4$ (27.0 ml, 0.174 mol), stirred for 20 h, and warmed to 23°. After 2 h at 23°, when TLC showed complete disappearance of **17**, the soln. was cooled to 0° and neutralized by the addition of a 10% aq. $NaHCO_3$ soln. (1600 ml). The mixture was concentrated to 1/4 of its original volume (*ca*. 1000 ml) under reduced pressure. The remaining soln. was diluted with AcOEt (1000 ml) and washed with H_2O (1000 ml). The aq. phase was extracted with AcOEt (3 × 500 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. Recrystallisation from EtOH gave *α*-**18**/*β*-**18** > 9:1 (66.2 g, 95%). Off-white solid. R_f (hexane/AcOEt 1:3) 0.30. R_f (CH_2Cl_2/EtOH 35:1) 0.41. M.p. 79–80°. ^{1}H- and ^{13}C-NMR data are in agreement with the values in [12]. MALDI-MS: 1871 ($[M+K]^+$), 1854 ($[M+Na]^+$).

Phenyl 2,3,4,6-Tetra-O-*acetyl-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tri*-O-*acetyl-1-thio-β*-D-*glucopyranoside* (**19**) [23]. Under N_2, a soln. of *α*-**18**/*β*-**18** > 9:1 (58.0 g, 31.6 mmol) in dry CH_2Cl_2 (300 ml) was treated with ZnI_2 (46.2 g, 0.148 mol) and *S*-(trimethylsilyl)thiophenol (27.4 ml, 0.148 mol) and stirred at 23° for 48 h. The mixture was filtered over *Celite*. The filtrate was washed with 1M HCl (100 ml), sat. aq. $NaHCO_3$ soln. (2 × 80 ml), H_2O (2 × 80 ml), and brine (80 ml), dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 2:3 → 0:1) gave **19** (50.5 g, 85%). White foam. R_f (hexane/AcOEt 1:3) 0.44. ^{1}H- and ^{13}C-NMR data are in agreement with the values in [23]. MALDI-MS: 1922 ($[M+K]^+$), 1905 ($[M+Na]^+$).

*Phenyl α-*D*-Glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-1-thio-β-*D*-glucopyranoside* (**20**) [23]. A soln. of **19** (20.6 g, 10.9 mmol) in MeOH/H_2O 1:1 (800 ml) was treated with 1M NaOMe in MeOH (40 ml), stirred for 20 h at 23°, treated with *Amberlite IR-120* (H^+ form) and filtered. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **20** (11.2 g, 94%). R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.34. M.p. 180° (dec.). MALDI-MS: 1121 ($[M+K]^+$), 1106 ($[M+Na]^+$). ^{1}H- and ^{13}C-NMR data are in agreement with the values in [23].

*Phenyl 4,6-*O*-Benzylidene-α-*D*-glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-1-thio-β-*D*-glucopyranoside* (**21**). A soln. of **20** (4.65 g, 4.29 mmol) in pyridine (150 ml) was treated with α,α-dibromotoluene (5.55 ml, 33.5 mmol), warmed from 25 to 95° over a period of 7 h, and stirred at 95° for 72 h. The mixture was filtered, and the residue was washed with pyridine (50 ml). The combined filtrate and washings were evaporated. FC (CH_2Cl_2/MeOH/H_2O 75:50:12; residue adsorbed on silica gel pre-treated with Et_3N) gave crude **21** and **20**. Compound **21** was used immediately as isolated. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.75. ^{1}H-NMR (300 MHz, CD_3OD): 7.60–7.42 (*m*, 4 arom. H); 7.40–7.21 (*m*, 6 arom. H); 5.57 (*s*, PhC*H*); 5.21–5.15 (*m*, H–C(1^{II-VI})); 4.60 (*d*, *J* = 10.0, H–C(1^I)); 4.22 (*dd*, *J* = 4.4, 9.6, H_{eq}–C(6^{VI})); 3.98–3.38 (*m*, 35 H). ^{13}C-NMR (75 MHz, CD_3OD): 139.42, 135.36 (2*s*); 133.20 (2*d*); 130.28 (2*d*); 130.22 (2*d*); 129.39 (2*d*); 128.75 (2*d*); 127.84 (2*d*); 103.70. 103.30, 102.86 (3 C) (3*d*, C(1^{II-VI})); 102.75 (PhCH); 89.55 (*d*, C(1^I)); 82.74, 81.83, 81.43 (2 C), 80.81 (2 C) (4*d*, C(4^{I-VI}); 79.62 (*d*, C(5^I)); 75.13 (4 C), 75.05 (2 C), 74.03 (3 C), 73.63 (2 C), 73.52 (4 C), 72.32 (6*d*, C(2^{I-VI}), C(3^{I-VI}), C(5^{II-V})); 70.00 (*t*, C(6^{VI})); 65.22 (C(5^{VI})); 62.53 (2 C), 62.38 (3 C) (2*t*, C(6^{I-V})). MALDI-MS: 1194 ($[M+Na]^+$).

*Phenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tri-*O*-benzyl-1-thio-β-*D*-glucopyranoside* (**22**) [23]. A soln. of **21** (5.03 g, 4.29 mmol) in DMF (80 ml) was cooled to 0°, treated with NaH (11.96 g), BnBr (25.51 ml, 214.55 mmol), Et_4NI (141 mg, 0.055 mmol), and imidazole (37.3 mg, 0.055 mmol), warmed to 23°, and stirred for 20 h. The mixture was cooled to 0° and treated dropwise with MeOH (50 ml) and H_2O (50 ml). The mixture was diluted with CH_2Cl_2 (200 ml). The org. layer was washed with sat. aq. $NaHCO_3$ soln. (2 × 80 ml), H_2O (2 × 80 ml), and brine (80 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 20:1) gave **22** (9.06 g, 78% from **20**). White solid. R_f (toluene/AcOEt 18:1) 0.55. ^{1}H- and ^{13}C-NMR data are in agreement with the values in [23]. MALDI-MS: 2744 ($[M+K]^+$), 2726 ($[M+Na]^+$).

*Phenyl 2,3-Bis-*O*-(4-chlorobenzyl)-4,6-*O*-benzylidene-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)]-2,3,6-tris-*O*-(4-chlorobenzyl)-1-thio-β-*D*-glucopyranoside* (**23**). A soln. of **21** (5.70 g, 4.86 mmol) in DMF (180 ml) was cooled to 0°, treated with NaH (17 g, 354 mmol), stirred for 30 min, treated with 4-$ClC_6H_4CH_2Cl$ (56 g, 350 mmol) and Bu_4NI (44 g, 121 mmol), stirred at 0° for 1 h and at 23° for 12 h. The soln. was cooled to 0°, treated dropwise with MeOH (20 ml), and diluted with H_2O (200 ml) and Et_2O (200 ml). The phases were separated, and the aq. phases were extracted with Et_2O (2 × 200 ml). The combined org. layers were washed with brine (200 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 60:1 → 30:1) gave **23** (13.5 g, 80% from **20**). White foam. R_f (toluene/AcOEt 40:1) 0.29. $[\alpha]_D^{25} = +55.1$ (*c* = 0.95, $CHCl_3$). IR ($CHCl_3$): 2927*m*, 2867*m*, 1600*w*, 1492*m*, 1362*m*, 1155*m*, 1090*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.55–7.52 (*m*, 2 arom. H); 7.48–7.43 (*m*, 2 arom. H); 7.41–7.36 (*m*, 2 arom. H); 7.30–6.81 (*m*, 72 arom. H); 5.53 (*s*, PhC*H*); 5.52 (*d*, *J* = 4.4), 5.51 (*d*, *J* = 4.1), 5.47 (*d*, *J* = 3.6), 5.43 (*d*, *J* = 3.6), 5.40 (*d*, *J* = 3.6) (H–C(1^{II-VI})); 4.840 (*d*, *J* = 11.8), 4.838 (*d*, *J* ≈ 11.5), 4.80 (*d*, *J* = 12.0), 4.76 (*d*, *J* = 12.0), 4.72 (*d*, *J* ≈ 12.0), 4.70 (*d*, *J* = 11.9) (6 ArC*H*); 4.68 (*d*, *J* ≈ 9.7, H–C(1^I)); 4.66 (*d*, *J* = 11.7), 4.64 (*d*, *J* = 11.0), 4.62 (*d*, *J* = 11.4), 4.59 (*d*, *J* ≈ 12.0), 4.58 (*d*, *J* = 11.7), 4.56 (*d*, *J* = 12.0), 4.53 (*d*, *J* = 12.1), 4.52 (*d*, *J* = 12.0), 4.49 (*d*, *J* = 11.0), 4.48 (*d*, *J* = 12.0), 4.44 (*d*, *J* = 11.3), 4.42 (*d*, *J* = 12.1), 4.39 (*d*, *J* = 11.2) (13 ArC*H*); 4.36–4.27 (*m*, 15 ArC*H*); 4.05 (*dd*, *J* = 4.6, 10.1, H_{eq}–C(6^{VI})); 4.02 (*t*, *J* = 9.6), 3.99 (*t*, *J* = 9.4), 3.97 (*t*, *J* = 9.5, 2 H) (4 H–C(4)); 3.93–3.86 (*m*, irrad. at 3.43 → change, H–C(3^{II-VI}), 1 H–C(4), 1 H–C(5), H–C(6^I)); 3.83–3.73 (*m*, 4 H–C(5), H′–C(6^I)); 3.72 (*t*, *J* = 8.8, H–C(3^I)); 3.70–3.67 (*m*, 4 H–C(6)); 3.61 (*t*, *J* = 10.2, H_{ax}–C(6^{VI})); 3.59 (*t*, *J* = 9.4, H–C(4^{VI})); 3.55 (*ddd*, *J* = 1.3, 3.8, 9.6, H–C(5^I)); 3.52 (*dd*, *J* = 8.8, 9.6, irrad. at 4.68 → change, H–C(2^I)); 3.50–3.39 (*m*, irrad. at 5.48 → change, H–C(2^{II-VI}), 4 H′–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.87–135.87 (several *s*); 133.77–133.04 (several *s*); 131.99–125.30 (several *d*); 101.25 (*d*, PhCH); 97.83 (*d*, C(1^{VI})); 96.95, 96.67 (2 C), 96.46 (3*d*, C(1^{II-V})); 87.37 (*d*, C(1^I)); 86.35 (*d*, C(3^I)); 82.30 (*d*, C(4^{VI})); 81.60, 81.36, 81.33, 81.20 (4*d*, C($^{III-V}$)); 80.82 (*d*, C(2^I)); 79.56 (2 C), 79.52, 79.38 (3*d*, C(2^{II-V})); 78.98 (*d*, C(5^I)); 78.76 (*d*, C(2^{VI})); 78.61 (*d*, C(3^{VI})); 74.45–72.30 (several *t*, 17 ArCH$_2$); 74.55, 74.18, 74.09, 73.52, 73.25 (5*d*, C(4^{I-V})); 70.92 (3 C), 70.72 (2*d*, C(5^{II-V})); 69.09 (*t*, C(6^I)); 68.98, 68.77, 68.72, 68.17 (4*t*, C(6^{II-V})); 68.85 (*t*, C(6^{VI})); 63.38 (*d*, C(5^{VI})). MALDI-MS: 3309.5 ($[M+Na]^+$). Anal. calc. for $C_{168}H_{155}Cl_{17}O_{30}S$ (3288.82): C 61.35, H 4.74, Cl 18.33; found: C 61.58, H 4.80, Cl 18.06.

Glycosylation of **9** *with* **22**. Under Ar. a suspension of **9** (1.02 g, 2.22 mmol), **22** (5.00 g, 1.85 mmol), and 3-Å molecular sieves (2.50 g) in dry Et_2O (100 ml) was stirred at $-60°$ for 1 h, treated with NIS (0.750 g, 3.33 mmol) and TfOH (82.0 µl, 0.925 mmol), and stirred for 48 h. The suspension was filtered over *Celite*, washed with 10% aq. $Na_2S_2O_3$ soln. (40 ml), sat. aq. $NaHCO_3$ soln. (2 × 30 ml), H_2O (2 × 30 ml), and brine (30 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 20:1) gave **24** (3.64 g, 64%) and **25** (1.21 g, 22%).

2,3-Di-O-*benzyl-4,6*-O-*benzylidene-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tri*-O-*benzyl-α*-D-*glucopyranosyl]$_5$-(1 → 3)-2,6-anhydro-1,4,5-tri*-O-*benzyl-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**24**). White foam. R_f (toluene/AcOEt 18:1) 0.48. M.p. 60–61°. $[\alpha]_D^{25} = +91.3$ ($c = 1.02$, CH_2Cl_2). IR (CH_2Cl_2): 3300*w*, 3032*m*, 2868*m*, 1605*w*, 1496*m*, 1420*m*, 1364*m*, 1208*m*, 1154*m*, 1093*s*, 1028*s*, 913*m*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.49 (*dd*, $J = 2.2$, 7.9, 2 arom. H); 7.40–7.00 (*m*, 103 arom. H); 5.68 (*d*, $J = 3.8$), 5.66 (*d*, $J = 3.6$), 5.64 (*d*, $J = 3.6$), 5.62 (*d*, $J = 3.6$), 5.60 (*d*, $J = 3.6$), 5.54 (*d*, $J = 3.5$) (H–C($1^{II–VII}$)); 5.52 (*s*, PhC*H*); 5.02–4.75 (*m*, 9 ArC*H*); 4.74 (*dd*, $J = 2.3$, 5.8, H–C(6^I)); 4.73–4.72 (*m*, 31 ArC*H*); 4.13–3.97 (*m*, H–C(3^I), H–C($3^{II–VII}$), H–C(4^I), H–C($4^{II–VI}$), H_{ax}–C(6^{VII})); 3.94–3.81 (*m*, H–C(2^I), H–C($5^{II–VII}$), H_{eq}–C(6^{VII})); 3.78–3.64 (*m*, H–C(5^I), 6 H–C(6)); 3.60–3.46 (*m*, H–C($2^{II–VII}$), H–C(4^{VII}), 6 H′–C(6)); 2.64 (*d*, $J = 2.3$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 139.01–137.65 (several *s*); 128.81–126.07 (several *d*); 101.14 (*d*, PhCH); 97.46, 96.70, 96.23 (2 C), 96.20 (4*d*, C($1^{II–VII}$)); 82.75 (*d*, C(4^I)); 82.35 (*d*, C(4^{VII})); 81.16, 81.85, 81.70, 81.67, 81.51 (5*d*, C($3^{II–VI}$)); 79.71, 79.57, 79.54, 79.44, 79.40 (5*d*, C($2^{II–VI}$)); 78.90 (*d*, C(2^{VII})); 78.74 (*d*, C(3^{VII})); 78.72 (*d*, C(5^I)); 78.63 (*s*, C≡CH); 77.81 (*s*, C≡CH); 75.34–72.39 (several *t*, 20 ArCH$_2$); 73.98, 73.86, 73.07, 72.70, 72.57, 72.10 (6*d*, C(3^I), C($4^{II–VI}$)); 70.85, 70.81 (2 C), 70.79, 70.75, 70.57 (5*d*, C(2^I), C($5^{II–VI}$)); 68.97, 68.69 (5 C), 68.12 (3*t*, C(1^I), C($6^{II–VII}$)); 66.38 (*d*, C(6^I)); 63.21 (*d*, C(5^{VII})). MALDI-MS: 3091 ($[M+K]^+$), 3074 ($[M+Na]^+$). Anal. calc. for $C_{191}H_{196}O_{35}$ (3051.66): C 75.18, H 6.47; found: C 74.94, H 6.51.

2,3-Di-O-*benzyl-4,6*-O-*benzylidene-α*-D-*glucopyranosyl]-[(1 → 4)-(2,3,6-tri*-O-benzyl-*α*-D-*glucopyranosyl]$_4$-(1 → 4)-(2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-(1 → 4)-2,6-anhydro-1,4,5-tri*-O-*benzyl-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**25**). White foam. R_f (toluene/AcOEt 18:1) 0.39. M.p. 57–60°. $[\alpha]_D^{25} = 78.9$ ($c = 1.00$, CH_2Cl_2). IR (CH_2Cl_2): 3300*w*, 3032*m*, 2869*m*, 1605*w*, 1496*m*, 1453*m*, 1419*m*, 1364*m*, 1208*m*, 1554*m*, 1092*s*, 1028*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.50 (*dd*, $J = 2.2$, 7.8, 2 arom. H); 7.39–7.35 (*m*, 4 arom. H); 7.39–7.00 (*d*, 99 arom. H); 5.68 (*t*, $J = 4.0$, 2 H), 5.62 (*t*, $J = 4.0$, 2 H), 5.53 (*d*, $J = 3.3$) (H–C($1^{III–VII}$)); 5.53 (*s*, PhC*H*); 5.07 (*d*, $J = 11.5$, ArC*H*); 4.91–4.55 (*m*, 20 ArC*H*); 4.51–4.36 (*m*, 18 ArC*H*, H–C(6^I), H–C(1^{II})); 4.29 (*d*, $J = 12.0$, ArC*H*); 4.17–3.96 (*m*, H–C(3^I), H–C($3^{III–VII}$), H–C(4^{II}), H–C($4^{III–VI}$), H_{ax}–C(6^{VII})); 3.94–3.79 (*m*, H–C(1^I), H–C(2^I), H–C(4^I), H–C($5^{III–VII}$)); 3.79–3.68 (*m*, 5 H–C(6), H_{eq}–C(6^{VII})); 3.59–3.44 (*m*, H′–C(1^I), H–C($2^{III–VII}$), H–C(3^{II}), H–C(4^{VII}), H–C(5^I), 5 H′–C(6)); 3.41 (*t*, $J = 8.0$, H–C(2^{II})); 3.30 (br. *ddd*, $J = 1.5$, 3.5, 9.6, H–C(5^{II})); 2.57 (*d*, $J = 2.3$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 139.39–137.66 (several *s*); 128.82–126.08 (several *d*);102.20 (*d*, C(1^{II})); 101.15 (*d*, PhCH); 97.46, 96.74, 96.42, 96.22, 96.12 (5*d*, C($1^{III–VII}$)); 84.74 (*d*, C(3^{II})); 82.56 (*d*, C(2^{II})); 82.36 (*d*, C(4^{VII})); 81.87, 81.67 (2 C), 81.58 (3*d*, C($3^{III–VI}$)); 81.16 (*d*, C(3^I)); 79.74, 79.57, 79.48, 79.33 (4*d*, C($2^{III–VI}$)); 78.90 (*d*, C(2^{VII})); 78.73 (2*d*, C(3^{VII}), C(5^I)); 78.68 (*s*, C≡CH); 77.85 (*s*, C≡CH); 76.04, 74.35 (2*d*, C(3^I), C(4^{II})); 75.02 (*d*, C(5^{II})); 73.81 (*d*, C(2^I)); 73.09, 72.85, 72.19, 72.09 (4*d*, C($4^{III–VI}$)); 75.30–72.56 (several *t*, 20 ArCH$_2$); 70.84 (3 C), 70.78, 70.58 (3*d*, C($5^{II–VI}$)); 69.10, 68.98, 68.69 (2 C), 68.61 (2 C) (4*t*, C($6^{II–VII}$)); 67.89 (*t*, C(1^I)); 66.81 (*d*, C(6^I)); 63.22 (*d*, C(5^{VII})). MALDI-MS: 3090 ($[M+K]^+$), 3074 ($[M+Na]^+$). Anal. calc. for $C_{191}H_{196}O_{35} \cdot 2\,H_2O$ (3087.70): C 74.30, H 6.53; found: C 74.34, H 6.83.

Glycosidation of **11** *with* **23**. Under Ar, a suspension of **11** (95 mg, 0.17 mmol), **23** (500 mg, 0.15 mmol), and 3-Å molecular sieves (500 mg) in dry Et_2O (20 ml) was stirred at $-60°$ for 1 h, treated with NIS (61 mg, 0.27 mmol) and TfOH (7 µl, 0.085 mmol) and stirred for 48 h. The suspension was filtered over *Celite*. The filtrate was washed with 10% aq. $Na_2S_2O_3$ soln. (10 ml), sat. aq. $NaHCO_3$ soln. (2 × 10 ml), H_2O (2 × 10 ml), and brine (10 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 20:1) gave **26** (316 mg, 55%) and **27** (229 mg, 40%).

2,3-Bis-O-*(4-chlorobenzyl)-4,6*-O-*benzylidene-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_5$-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**26**). White foam. R_f (toluene/AcOEt 18:1) 0.36. $[\alpha]_D^{25} = +57.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3304*w*, 2927*m*, 2867*m*, 1600*w*, 1492*m*, 1362*m*, 1155*m*, 1090*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.45–7.34 (*m*, 5 arom. H); 7.27–6.84 (*m*, 80 arom. H); 5.53 (*s*, PhC*H*); 5.53 (*d*, $J \approx 3.5$), 5.52 (*d*, $J = 3.7$), 5.51 (*d*, $J = 3.8$), 5.483 (*d*, $J = 3.5$), 5.473 (*d*, $J = 3.5$), 5.44 (*d*, $J = 3.5$) (H–C($1^{II–VII}$)); 4.89 (*d*, $J = 11.9$), 4.83 (*d*, $J = 11.7$) (2 ArC*H*); 4.79 (*dd*, $J = 2.4$, 5.7, H–C(6^I)); 4.77 (*d*, $J = 12.1$), 4.74 (*d*, $J = 11.6$), 4.71 (*d*, $J = 12.1$), 4.68 (*d*, $J = 12.0$) (4 ArC*H*); 4.67–4.56 (*m*, 10 ArC*H*); 4.55 (*d*, $J = 11.9$), 4.52 (*d*, $J = 11.9$),

4.465 (*d*, *J* = 11.9), 4.455 (*d*, *J* = 12.2), 4.435 (*d*, *J* = 12.1), 4.41 (*d*, *J* = 12.1) (6 ArC*H*); 4.40–4.29 (*m*, 18 ArC*H*); 4.06 (*dd*, *J* = 4.8, 10.3, H_{eq}–C(6^{VII})); 4.05–3.86 (*m*, H–C(1^{I}), H–C(2^{I}), H–C(3^{I}), H–C(4^{I}), H–C($3^{II–VII}$), H–C($4^{II–VI}$)); 3.81–3.75 (*m*, H–C($5^{II–VII}$)); 3.69–3.64 (*m*, H–C($6^{II–VI}$)); 3.63–3.58 (*m*, H–C(5^{I}), H′–C(1^{I}), H_{ax}–C(6^{VII})); 3.58 (*t*, *J* = 9.4, H–C(4^{VII})); 3.48–3.40 (*m*, H–C($2^{II–VII}$), H′–C($6^{II–VI}$)); 2.68 (*d*, *J* = 2.3, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.27–135.88 (several *s*); 133.95–133.00 (several *s*); 129.58–125.92 (several *d*); 101.26 (*d*, PhCH); 97.83 (*d*, C(1^{VII})); 96.66, 96.60, 96.45 (2 C), 96.42 (4*d*, C($1^{II–VI}$)); 82.47 (*d*, C(4^{I})); 82.31 (*d*, C(4^{VII})); 81.61, 81.40, 81.37 (2 C), 81.22 (4*d*, C($3^{II–VI}$)); 79.63, 79.58 (2 C), 79.48, 79.37 (4*d*, C($2^{II–VI}$)); 78.86 (*d*, C(5^{I})); 78.77 (*d*, C(2^{VII})); 78.62 (*d*, C(3^{VII})); 78.17 (br. *s*, C≡CH); 74.18–72.10 (several *t*, 20 ArCH$_2$); 74.07, 73.67, 73.62, 73.45, 73.16, 73.04 (6*d*, C(3^{I}), C($4^{II–VI}$)); 70.93 (2 C), 70.88 (2 C), 70.82, 70.72 (4*d*, C(2^{I}), C($5^{II–VI}$)); 68.98 (2 C); 68.85 (3 C), 68.76 (2 C) (3*t*, C(1^{I}), C($6^{II–VII}$)); 66.11 (*d*, C(6^{I})); 63.38 (*d*, C(5^{VII})). MALDI-MS: 3763.1 ([*M* + Na]$^+$). Anal. calc. for $C_{191}H_{176}Cl_{20}O_{35}$ (3740.52): C 61.33, H 4.74, Cl 18.96; found: C 61.52, H 4.95, Cl 19.24.

2,3-Bis-O-*(4-chlorobenzyl)-4,6-O-benzylidene-α*-D-*glucopyranosyl]-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl)-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**27**). White foam. R_f (toluene/AcOEt 18:1) 0.30. $[\alpha]_D^{25} = +50.1$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3303*w*, 2869*m*, 1600*w*, 1492*m*, 1465*m*, 1408*m*, 1361*m*, 1090*s*, 1036*s*. ^{1}H-NMR (500 MHZ, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.47–7.40 (*m*, 5 arom. H); 7.31–6.87 (*m*, 80 arom. H); 5.55 (*s*, PhC*H*), 5.55 (*d*, *J* ≈ 3.7), 5.53 (*d*, *J* = 3.7), 5.51 (br. *d*, *J* ≈ 2.9, 2 H), 5.41 (*d*, *J* = 3.5) (H–C($1^{III–VII}$)); 4.98 (*d*, *J* = 12.0), 4.85 (*d*, *J* = 11.7), 4.81 (*d*, *J* = 12.0), 4.76 (*d*, *J* ≈ 11.4) (4 ArC*H*); 4.76 (*dd*, *J* = 2.4, 5.8, H–C(6^{I})); 4.75–4.59 (*m*, 15 ArC*H*); 4.57 (*d*, *J* = 12.1), 4.54 (*d*, *J* = 11.6), 4.48 (*d*, *J* ≈ 12.0), 4.44 (*d*, *J* = 12.1) (4 ArC*H*); 4.41–4.29 (*m*, 18 ArC*H*); 4.04 (*d*, *J* = 7.7, H–C(1^{II})); 4.25 (*d*, *J* = 12.2, ArC*H*); 4.09 (*dd*, *J* = 4.6, 10.3, H_{eq}–C(6^{VII})); 4.40 (*t*, *J* = 9.5, H–C(4)); 4.02 (*t*, *J* = 9.4, 2 H–C(4)); 3.98–3.89 (*m*, H–C(3^{I}), H–C($3^{III-VII}$), 2 H–C(4), 1 H–C(5)); 3.87–3.78 (*m*, H–C(1^{I}), H–C(2^{I}), 3 H–C(5), H–C(5^{VII})); 3.77 (*t*, *J* = 9.1, H–C(4^{I})); 3.76–3.69 (*m*, H–C($6^{II–VI}$)); 3.64 (*t*, *J* = 10.3, H_{ax}–C(6^{VII})); 3.61 (*t*, *J* = 9.5, H–C(4^{VII})); 3.57 (br. *dd*, *J* ≈ 1.5, 10.5, H′–C(1^{I})); 3.54 (*dd*, *J* = 5.8, 9.3, H–C(5^{I})); 3.535 (br. *dd*, *J* ≈ 1.5, 11.0, H′–C(6^{II})); 3.49 (*t*, *J* = 8.9, H–C(3^{II})); 3.48–3.42 (*m*, H–C($2^{III–VII}$), H–C(3^{II}), H′–C($6^{III–VII}$)); 3.34 (*dd*, *J* = 8.0, 9.0, H–C(2^{II})); 3.29 (br. *ddd*, *J* ≈ 1.5, 3.5, 9.5, H–C(5^{II})); 2.64 (*d*, *J* = 2.3, C≡CH). ^{13}C-NMR (125 MHZ, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.87–135.89 (several *s*); 133.79–132.87 (several *s*); 129.51–125.30 (several *d*); 102.15 (*d*, C(1^{II})); 101.25 (*d*, PhCH); 97.82 (*d*, C(1^{VII})); 96.86, 96.62 (2 C), 96.44 (3*d*, C($1^{III–VI}$)); 84.67 (*d*, C(3^{II})); 82.33 (*d*, C(2^{II}), C(4^{VII})); 81.61, 81.37, 81.34, 81.24 (4*d*, C($3^{III–VI}$)); 81.01 (*d*, C(4^{I})); 79.56 (3 C), 79.38 (2*d*, C($2^{III–VI}$)); 78.77 (*d*, C(2^{VII})); 78.62 (*d*, C(3^{VII})); 78.15 (*d*, C(5^{I})); 78.15 (*s*, C≡*C*H); 77.76 (*s*, *C*≡CH); 75.91, 75.06 (2*d*, C(3^{I}), C(4^{II})); 74.97 (*d*, C(5^{II})); *ca.* 74.1 (*d*, C(2^{I})); 74.0–73.0 (4*d*, C($4^{III–VI}$)); 74.97–72.33 (several *t*, 20 ArCH$_2$); 70.94 (3 C), 70.71 (2*d*, C($5^{III–VI}$)); 69.05 (*t*, C(6^{II})); 68.85, 68.77 (2 C), 68.72 (2 C) (3*t*, C($6^{III–VII}$)); 67.90 (*t*, C(1^{I})); 66.43 (*d*, C(6^{I})); 63.38 (*d*, C(5^{VII})). MALDI-MS: 3763.6 ([*M* + Na]$^+$). Anal. calc. for $C_{191}H_{176}Cl_{20}O_{35}$ (3740.52): C 61.33, H 4.74; found: C 61.37, H 4.87.

[(1 → 4)-2,3,6-Tri-O-*benzyl-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-1,4,5-tri*-O-*benzyl-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**28**). A suspension of **24** (2.52 g, 0.826 mol), dried 3-Å molecular sieves (1.50 g), $Me_3N \cdot BH_3$ (1.20 g, 16.5 mmol), and $AlCl_3$ (2.20 g, 16.5 mmol) in THF (100 ml) was stirred at 23° for 48 h. The suspension was filtered over *Celite*, diluted with Et_2O (200 ml), washed with 5% aq. HCl soln. (100 ml), H_2O (2 × 80 ml), and brine (80 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 40:1 → 15:1) gave **28** (1.89 g, 75%). White foam. R_f (toluene/AcOEt 18:1) 0.16. M.p. 47–55°. $[\alpha]_D^{25} = +64.2$ (*c* = 1.00, CH_2Cl_2). IR (CH_2Cl_2): 3595*w*, 3300*w*, 3031*m*, 2926*m*, 2870*m*, 1954*w* (br.), 1733*w*, 1700*w*, 1605*m*, 1496*m*, 1453*m*, 1363*m*, 1215*m*, 1154*s*, 1095*s*, 1028*s*, 911*w*, 811*w*. ^{1}H-NMR (500 MHZ, $CDCl_3$, assignment based on a COSY spectrum): 7.41–7.01 (*m*, 105 arom. H); 5.68 (*d*, *J* = 3.5), 5.65 (*d*, *J* = 3.6), 5.64 (*d*, *J* = 3.6), 5.62 (*d*, *J* = 3.5), 5.60 (*d*, *J* = 3.8), 5.53 (*d*, *J* = 3.5) (H–C($1^{II–VII}$)); 5.00 (*d*, *J* = 11.5, ArC*H*); 4.95–4.75 (*m*, 8 ArC*H*); 4.74 (*dd*, *J* = 2.3, 5.8, H–C(6^{I})); 4.73–4.61 (*m*, 7 ArC*H*); 4.50–4.33 (*m*, 25 ArC*H*); 4.30 (*d*, *J* = 12.2, ArC*H*); 4.11–3.96 (*m*, H–C(3^{I}), H–C($3^{II–VI}$), H–C(4^{I}), H–C($4^{II–VI}$)); 3.95–3.82 (*m*, H–C(2^{I}), H–C($5^{II–VI}$), H–C(6)); 3.79–3.70 (*m*, 5 H–C(6), H–C(3^{VIII}), H–C(5^{VII})); 3.68–3.63 (*m*, H–C(4^{VII}), H–C(5^{I}), 1 H′–C(6)); 3.54–3.48 (*m*, H–C($2^{II–VI}$), H–C(6^{VII}), 5 H′–C(6)); 3.41 (2*dd*, *J* = 3.6, 9.8, H–C(2^{VII}), H–C(6^{VII})); 2.64 (*d*, *J* = 2.3, C≡CH); 2.52 (br. *s*, OH). ^{13}C-NMR (125 MHZ, $CDCl_3$, assignment based on a HMQC spectrum): 139.01–137.72 (several *s*); 128.46–126.47 (several *d*); 96.73, 96.70, 96.28, 96.23 (2 C), 96.19 (5*d*, C($1^{II–VII}$)); 82.75 (*d*, C(4^{I})); 81.80, 81.70, 81.67, 81.62, 81.50 (5*d*, C($3^{II–VI}$)); 81.39 (*d*, C(3^{VII})); 79.67, 79.57, 79.53, 79.43, 79.40 (5*d*, C($2^{II–VI}$)); 79.02 (*d*, C(2^{VII})); 78.75 (*d*, C(5^{I})); 78.63 (*s*, C≡CH); 77.81 (*s*, C≡*C*H); 75.20, 74.54 (2*t*, 2 ArCH); 73.98, 73.69, 73.07, 72.57, 72.45, 72.30 (6*d*, C(3^{I}), C($4^{II–VI}$)); 73.86–72.72 (several *t*, 19 ArCH$_2$); 71.61 (*d*, C(4^{VII})); 70.84 (4 C); 70.75 (2 C) (2*d*, C(2^{I}), C($5^{II–VI}$)); 70.36 (*d*, C(5^{VII})); 69.83 (*t*, C(6^{VII})); 68.80, 68.70 (5 C)

(2*t*, C(1^{I}), C(6$^{II–VI}$)); 66.38 (*d*, C(6^{I})). MALDI-MS: 3091 ([*M*+K]$^{+}$), 3074 ([*M*+Na]$^{+}$). Anal. calc. for $C_{191}H_{198}O_{35}\cdot 2\,H_2O$ (3089.71): C 74.25, H 6.60; found: C 74.00, H 6.50.

2,3-Bis-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_5$-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**29**). Under Ar, **26** (1.4 g, 0.37 mmol) in a soln. of 1% I_2 in MeOH (66 ml) was stirred under reflux for 5 h. After evaporation, the crude was diluted with AcOEt (200 ml). The org. phase was washed with a sat.aq. $Na_2S_2O_3$ soln. (150 ml), H_2O (150 ml), and brine (1500 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 25 : 1 → 4 : 1) gave **29** (800 mg, 60%). White foam. R_f (toluene/AcOEt 18 : 6) 0.31. $[\alpha]_D^{25} = +64.2$ ($c = 0.95$, $CHCl_3$). IR ($CHCl_3$): 3593*w*, 3303*w*, 2926*m*, 2869*m*, 1785*w*, 1600*m*, 1492*m*, 1463*m*, 1361*m*, 1261*m*, 1154*s*, 1090*s*, 1015*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.32 – 6.85 (*m*, 80 arom. H); 5.52 (*d*, *J* = 3.6, 2 H), 5.48 (*d*, *J* = 3.5), 5.47 (*d*, *J* = 3.3), 5.44 (*d*, *J* = 3.4), 5.43 (*d*, *J* = 3.5) (H–C(1$^{II–VII}$)); 4.90 (*d*, *J* = 12.0, ArC*H*); 4.79 (*dd*, *J* = 2.3, 5.8, H–C(6^{I})); 4.77 (*d*, *J* = 12.0), 4.75 (*d*, *J* = 12.5), 4.74 (*d*, *J* = 11.6), 4.72 (*d*, *J* = 11.8), 4.70 (*d*, *J* ≈ 11.0), 4.68 (*d*, *J* = 10.5, 2 H), 4.64 (*d*, *J* = 11.8), 4.63 (*d*, *J* ≈ 12.0, 2 H), 4.607 (*d*, *J* = 12.1), 4.599 (*d*, *J* ≈ 11.0), 4.591 (*d*, *J* = 11.7), 4.58 (*d*, *J* ≈ 12.3), 4.53 (*d*, *J* = 11.7), 4.47 (*d*, *J* = 12.2), 4.44 (*d*, *J* = 12.2) (17 ArC*H*); 4.42 – 4.28 (*m*, 22 ArC*H*); 4.04 – 3.99 (*m*, H–C(2^{I})); 3.98 – 3.87 (*m*, H–C(1^{I}), H–C(3^{I}), H–C(4^{I}), H–C(3$^{II–VI}$), H–C(4$^{II–VI}$), H–C(3^{VII})); 3.81 – 3.77 (*m*, 4 H–C(5)); 3.72 – 3.60 (*m*, H′–C(1^{I}), H–C(5^{I}), 2 H–C(5), H–C(6$^{II–VI}$), 2 H–C(6^{VII})); 3.53 (*dt*, *J* = 2.8, 8.9, H–C(4^{VII})); 3.47 – 3.41 (*m*, H–C(2$^{II–VI}$), H′–C(6$^{II–VI}$)); 3.32 (*dd*, *J* = 3.6, 9.7, H–C(2^{VII})); 2.67 (*d*, *J* = 2.3, C≡CH); 2.39 (*d*, *J* = 3.0, HO–C(4^{VII})); 1.81 (br. *t*, *J* = 6.5, HO–C(6^{VII})). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.26 – 135.89 (several *s*); 133.96 – 133.01 (several *s*); 129.61 – 127.33 (several *d*); 97.03 (2 C); 96.63, 96.58, 96.50, 96.43 (5*d*, C(1$^{II–VII}$)); 82.47 (*d*, C(4^{I})); 81.43 (2 C), 81.36 (2 C), 81.25 (2 C) (3*d*, C(3$^{II–VII}$)); 79.63, 79.59, 79.45 (2 C), 79.39, 79.24 (5*d*, C(2$^{II–VII}$)); 78.86 (*d*, C(5^{I})); 78.16 (br. *s*, C≡CH); 74.03, 73.62, 73.46, 73.17, 73.02 (2 C) (5*d*, C(3^{I}), C(4$^{II–VI}$)); 74.33 – 72.10 (several *t*, 20 ArCH_2); 71.84 (*d*, C(4^{VII})); 70.99 (2 C), 70.95 (2 C), 70.91 (2 C), 70.82 (4*d*, C(2^{I}), C(5$^{II–VII}$)); 68.97, 68.91, 68.86, 68.79 (2 C), 68.64 (5*t*, C(1^{I}), C(6$^{II–VI}$)); 66.11 (*d*, C(6^{I})); 62.49 (*t*, C(6^{VII})). MALDI-MS: 3675.4 ([*M*+Na]$^{+}$). Anal. calc. for $C_{184}H_{172}Cl_{20}O_{35}\cdot H_2O$ (3652.42): C 60.21, H 4.77, Cl 19.41; found: C 60.11, H 5.03, Cl 19.74.

[(1 → 4)-(2,3,6-Tris-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_5$-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**30**). A mixture of **29** (160 mg, 0.044 mmol) and $(Bu_3Sn)_2O$ (13 µl, 0.033 mmol) in toluene (5 ml) was stirred under reflux with azeotropic removal of H_2O for 4 h. Toluene (3 ml) was distilled off. The residual soln. was treated with 4-$ClC_6H_4CH_2Cl$ (14 mg, 0.087 mmol) and Bu_4NI (16 mg, 0.044 mmol), and was stirred for 16 h at 90°. After evaporation *in vacuo*, a soln. of the residue in AcOEt (10 ml) was stirred with aq. KF for 1 h. After separation, the org. layer was dried ($MgSO_4$) and evaporated. FC (toluene/AcOEt 25 : 1 → 9 : 2) gave **30** (110 mg, 67%). White foam. R_f (toluene/AcOEt 18 : 2) 0.35. $[\alpha]_D^{25} = 59.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3303*w*, 2925*m*, 2869*m*, 1600*m*, 1492*m*, 1361*m*, 1154*s*, 1090*s*, 1015*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.32 – 6.84 (*m*, 84 arom. H); 5.52 (*d*, *J* = 3.6, 2 H), 5.49 (*d*, *J* = 3.4), 5.48 (*d*, *J* = 3.6, 2 H), 5.44 (*d*, *J* = 3.6) (H–C(1$^{II–VII}$)); 4.90 (*d*, *J* = 11.8, ArC*H*); 4.79 (*dd*, *J* = 2.3, 5.7, H–C(6^{I})); 4.78 (*d*, *J* = 12.0), 4.74 (*d*, *J* = 10.8), 4.73 (*d*, *J* = 11.0), 4.72 (*d*, *J* = 12.0), 4.71 (*d*, *J* = 12.1), 4.69 (*d*, *J* = 12.4), 4.68 (*d*, *J* = 12.1), 4.67 (*d*, *J* = 11.7), 4.65 (*d*, *J* ≈ 12.0), 4.62 (*d*, *J* = 12.0, 2 H), 4.60 (*d*, *J* = 11.8), 4.59 (*d*, *J* = 12.0), 4.55 (*d*, *J* ≈ 12.0), 4.52 (*d*, *J* = 11.7), 4.50 (*d*, *J* = 12.5), 4.48 (*d*, *J* = 12.2), 4.47 (*d*, *J* = 12.2), 4.45 (*d*, *J* = 11.1), 4.44 (*d*, *J* = 12.3), 4.43 (*d*, *J* = 12.2) (21 ArC*H*); 4.40 – 4.27 (*m*, 21 ArC*H*); 4.05 – 4.02 (*m*, H–C(2^{I})); 4.00 – 3.85 (*m*, H–C(1^{I}), H–C(3^{I}), H–C(4^{I}), H–C(3$^{II–VII}$), H–C(4$^{II–VI}$)); 3.82 – 3.77 (*m*, H–C(5$^{II–VI}$)); 3.72 – 3.60 (*m*, H′–C(1^{I}), H–C(5^{I}), H–C(6$^{II–VI}$), H–C(5^{VII}), 2 H–C(6^{VII})); 3.49 (*dd*, *J* = 3.7, 9.9, H–C(2)); 3.48 – 3.39 (*m*, 4 H–C(2), H′–C(6$^{II–VI}$), H–C(4^{VII})); 3.37 (*dd*, *J* = 3.6, 9.6, H–C(2)); 2.67 (*d*, *J* = 2.3, C≡CH); 2.55 (*d*, *J* = 2.4, OH). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.31 – 135.42 (several *s*); 133.93 – 132.99 (several *s*); 131-23 – 125.28 (several *d*); 97.11, 96.62, 96.57 (2 C), 96.42 (2 C) (4*d*, C(1$^{II–VII}$)); 82.44 (*d*, C(4^{I})); 81.47, 81.33 (2 C); 81.22 (3 C) (3*d*, C(3$^{II–VII}$)); 79.56 (2 C), 79.46, 79.36, 78.93 (2 C) (4*d*, C(2$^{II–VII}$)); 78.84 (*d*, C(5^{I})); 78.14 (br. *s*, C≡CH); 74.03, 73.64, 73.59, 73.46, 73.10, 73.05 (6*d*, C(3^{I}), C(4$^{II–VI}$)); 74.36 – 72.07 (several *t*, 21 ArCH_2); 71.88 (*d*, C(4^{VII})); 70.92 (3 C), 70.87, 70.80, 70.44, 70.02 (4*d*, C(2^{I}), C(5$^{II–VII}$)); 70.01 (*t*, C(6^{VII})); 68.95, 68.84 (2 C), 68.77 (3 C) (3*t*, C(1^{I}), C(6$^{II–VI}$)); 66.09 (*d*, C(6^{I})). MALDI-MS: 3801.1 ([*M*+Na]$^{+}$), 3817.0 ([*M*+K]$^{+}$).

6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl)-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**31**). Under Ar, a soln. of **27** (2.5 g, 0.66 mmol) in dry CH_2Cl_2 (110 ml) was stirred at −40° for 10 min, treated with Et_3SiH (2.1 ml, 13.36 mmol), and $BF_3\cdot Et_2O$ (0.84 ml, 6.68 mmol), and stirred for 1 h at −40° and for 24 h at −10°. The soln. was washed with sat. aq. $NaHCO_3$ soln. (70 ml), H_2O (70 ml), and brine (70 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50 : 1 → 5 : 1) gave **31** (1.9 g, 76%). White foam. R_f (toluene/AcOEt 18 : 2) 0.35. $[\alpha]_D^{25} = +55.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3608*w*, 3304*w*, 2927*m*, 2869*m*, 1600*m*, 1492*m*, 1408*m*, 1361*m*, 1090*s*, 1039*s*, 1017*s*. ^{1}H-NMR

(500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.32–6.85 (*m*, 84 arom. H); 5.51 (*d*, *J* = 3.5), 5.48 (*d*, *J* = 3.4), 5.38 (*d*, *J* = 3.5) (H–C($1^{III-VII}$)); 4.96 (*d*, *J* = 12.0, ArC*H*); 4.75 (*d*, *J* = 10.9, ArC*H*), 4.74 (*dd*, *J* = 3.4, 5.8, H–C(6^{I})); 4.73 (*d*, *J* = 10.9, ArC*H*); 4.72–4.58 (*m*, 15 ArC*H*); 4.51 (*d*, *J* = 11.4), 4.44 (*d*, *J* = 12.0), 4.43 (*d*, *J* = 12.1) (3 ArC*H*); 4.38–4.30 (*m*, 20 ArC*H*, H–C(1^{II})); 4.23 (*d*, *J* = 12.1, ArC*H*); 4.00–3.86 (*m*, H–C(3^{I}), H–C($3^{III-VII}$), H–C(4^{II-VI}), 1 H–C(5)); 3.83–3.76 (*m*, H–C(1^{I}), H–C(2^{I}), 3 H–C(5)); 3.76–3.66 (*m*, H–C(4^{I}), H–C(5^{VII}), 6 H–C(6)); 3.64 (*t*, *J* = 9.4, H–C(4^{VII})); 3.56–3.48 (*m*, H′–C(1^{I}), H–C(5^{I}), 1 H–C(6), H–C(6^{II})); 3.47–3.41 (*m*, H–C(2^{III-VI}), H–C(3^{II}), 3 H–C(6), H′–C(6^{II})); 3.36 (*dd*, *J* = 3.5, 9.7, H–C(2^{VII})); 3.31 (*t*, *J* = 8.8, H–C(2^{II})); 3.20 (br. *ddd*, *J* ≈ 1.5, 3.5, 9.3, H–C(5^{VII})); 2.65 (br. *s*, *J* = 2.3, OH); 2.62 (*d*, *J* = 2.3, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.77–135.95 (several *s*); 133.79–132.87 (several *s*); 129.51–127.35 (several *d*); 102.15 (*d*, C(1^{II})); 97.18, 96.85, 96.64, 96.60, 96.45 (5*d*, C($1^{III-VII}$)); 84.67 (*d*, C(3^{II})); 82.34 (*d*, C(2^{II})); 81.49, 81.35 (2 C), 81.22 (2 C) (3*d*, C($3^{III-VII}$)); 81.00 (*d*, C(4^{I})); 79.56 (2 C), 79.50, 79.39 (3*d*, C(2^{III-VI})); 78.88 (*d*, C(2^{VII})); 78.14 (*s*, C≡*C*H); 78.07 (*d*, C(5^{I})); 77.77 (*s*, *C*≡CH); 75.90, 75.05 (2*d*, C(3^{I}), C(4^{II})); 74.97 (*d*, C(5^{II})); 73.77 (*d*, C(2^{I})); 73.65, 73.46, 73.25, 73.05 (4*d*, C(4^{III-VI})); 74.42–72.34 (several *t*, 21 Ar*C*H_2); 70.95 (4 C) (*d*, C(5^{III-VI})); 70.39 (*d*, C(5^{VII})); 70.15 (*t*, C(6^{II})); 69.06 (3 C), 68.82 (2 C) (2*t*, C($6^{III-VII}$)); 67.91 (*t*, C(1^{I})); 66.61 (*d*, C(6^{I})). MALDI-MS: 3766 ([*M* + Na]$^+$). Anal. calc. for $C_{191}H_{178}Cl_{20}O_{35}$ (3742.54): C 61.30, H 4.79; found: C 61.30, H 4.79.

Glycosidation of **13** *by* **28**. Under Ar, a suspension of **13** (243 mg, 0.48 mmol), **28** (590 mg, 0.19 mmol), and 3-Å molecular sieves (500 mg) in dry toluene (60 ml) was stirred at −45° for 1 h, treated with NIS (780 mg, 0.35 mmol) and TfOH (8.5 µl, 0.096 mmol) and stirred for 20 h. The suspension was filtered over *Celite*, diluted with Et_2O (100 ml), washed with 10% aq. NaS_2O_3 soln. (40 ml), sat. aq. $NaHCO_3$ soln. (2 × 30 ml), H_2O (2 × 30 ml), and brine (30 ml), dried ($MgSO_4$), and evaporated. FC (silica H, toluene/AcOEt 40:1 → 30:1) gave **32** (289 mg, 49%) and **33** (112 mg, 19%).

6-O-*Acetyl-2,3-di*-O-*benzyl-4-deoxy-4*-C-*ethynyl-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tri*-O-*benzyl-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-1,4,5-tri*-O-*benzyl-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**32**). White foam. R_f (toluene/AcOEt 17:1) 0.32. M.p. 52–55°. $[\alpha]_D^{25} = +86.4$ (*c* = 1.00, CH_2Cl_2). IR (CH_2Cl_2): 3301*m*, 2925*m*, 2870*m*, 1955*w* (br.), 1740*m*, 1605*m*, 1496*m*, 1454*m*, 1364*m*, 1237*m*, 1209*m*, 1154*s*, 1095*s*, 1028*s*, 913*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.46–7.01 (*m*, 115 arom. H); 5.66 (*d*, *J* = 3.5), 5.65 (*d*, *J* = 4.0), 5.65 (*d*, *J* = 3.4), 5.64 (*d*, *J* = 3.2, 2 H), 5.62 (*d*, *J* = 3.7), 5.53 (*d*, *J* = 3.5) (H–C($1^{II-VIII}$)); 5.06–4.68 (*m*, 19 ArC*H*); 4.67–4.47 (*m*, 27 ArC*H*, H–C(6^{I})); 4.22 (*dd*, *J* = 3.9, 12.1, H–C(6^{VIII})); 4.12–3.97 (*m*, 17 H); 3.95–3.82 (*m*, 8 H); 3.80–3.70 (*m*, 5 H); 3.69–3.61 (*m*, 3 H); 3.55–3.48 (*m*, 12 H); 3.31 (*dd*, *J* = 3.5, 9.5, H–C(2)); 2.67 (*dt* , *J* = 2.3, 10.7, H–C(4^{VIII})); 2.64 (*d*, *J* = 2.3, H–C(8^{I})); 2.18 (*d*, *J* = 2.3, C≡CH); 1.97 (*s*, AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 170.64 (*s*, C=O); 139.14–137.20 (several *s*); 128.47–126.44 (several *d*); 97.00 (2 C), 96.71, 96.42, 96.23, 96.17 (2 C) (5*d*, C($1^{II-VIII}$)); 82.75 (*d*, C(4^{I})); 81.69 (2 C), 81.62 (2 C), 81.51, 81.26 (4*d*, C(3^{II-VII})); 80.02 (*s*, *C*≡CH); 79.59, 79.54 (2 C), 79.50 (2 C), 79.42, 78.94, 78.76 (5*d*, C(5^{I}), C($2^{II-VIII}$)); 78.64 (*d*, C(8^{I})); 77.82 (*s*, C(7^{I})); 75.74, 75.45 (2*t*, 2 Ar*C*H_2); 73.99, 73.81, 73.08, 72.91 (2 C), 72.88 (2 C), 72.85 (6*d*, C($4^{II-VIII}$)); 73.76–72.01 (several *t*, 21 Ar*C*H_2); 72.04 (*s*, C≡*C*H); 70.84 (4 C), 70.76 (3 C) (2*d*, C(2^{I}), C(5^{II-VII})); 69.18 (C(5^{VIII})); 68.68 (7 C) (*t*, C(1^{I}), C(6^{II-VII})); 66.38 (*d*, C(6^{I})); 64.00 (*t*, C(6^{VIII})); 36.71 (*d*, C(4^{VIII})); 20.80 (*q*, Me). MALDI-MS: 3485 ([*M* + K]$^+$), 3466 ([*M* + Na]$^+$). Anal. calc. for $C_{215}H_{222}O_{40}$ (3446.09): C 74.94, H 6.49; found: C 74.91, H 6.62.

6-O-*Acetyl-2,3-di*-O-*benzyl-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tri*-O-*benzyl-α*-D-*glucopyranosyl]$_6$-(1 → 3)-1,4,5-tri*-O-*benzyl-2,6-anhydro-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**33**). R_f (toluene/AcOEt 17:1) 0.29. M.p. 54–56°. $[\alpha]_D^{25} = +84.2$ (*c* = 1.00, CH_2Cl_2). IR (CH_2Cl_2): 3301*m*, 3088*m*, 3031*m*, 2924*m*, 2870*m*, 1736*m*, 1605*m*, 1496*m*, 1454*m*, 1364*m*, 1209*m*, 1154*s*, 1094*s*, 1028*s*, 912*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.54–6.98 (*m*, 115 arom. H); 5.80 (*d*, *J* = 3.9), 5.66 (*d*, *J* = 3.7), 5.64 (*d*, *J* = 3.6), 5.62 (*d*, *J* = 3.6), 5.56 (*d*, *J* = 3.5), 5.53 (*d*, *J* = 3.5) (H–C(1^{II-VII})); 5.05–4.22 (*m*, 48 PhC*H*, C(6^{I}), C(1^{VIII})); 4.21–4.18 (*m*, H–C(6^{VIII})); 4.12–3.82 (*m*, 22 H); 3.80–3.59 (*m*, 9 H); 3.55–3.43 (*m*, 12 H); 3.30–3.19 (*m*, 2 H); 3.09 (*t*, *J* = 8.1, H–C(4)); 2.64 (*d*, *J* = 2.3, H–C(8^{I})); 2.53 (*dt*, *J* = 2.4, 10.5, H–C(4^{VIII})); 2.18 (*d*, *J* = 2.3, C≡CH), 1.86 (*s*, AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 170.83 (*s*, C=O); 139.51–137.73 (several *s*); 128.86–126.52 (several *d*); 102.27 (*d*, C(1^{VIII})); 96.99, 96.71, 96.23, 96.16 (2 C), 96.00 (5*d*, C(1^{II-VII})); 82.76 (*d*, C(4^{I})); 82.19, 81.93, 81.89, 81.68, 81.64 (2 C), 81.51 (6*d*, C($3^{II-VIII}$)); 80.42 (*d*, C≡*C*H); 79.96, 79.53 (2 C), 78.76, 78.16 (2 C), 77.82 (2 C) (5*d*, C(5^{I}), C($2^{II-VIII}$)); 78.64 (*s*, C(8^{I})); 77.83 (*d*, C(7^{I})); 75.73–72.23 (several *t*, 23 Ar*C*H_2); 73.91 (2 C), 73.84 (2 C), 73.22, 73.09 (2 C), 72.88 (5*d*, C(4^{I}), C($3^{II-VIII}$)); 71.17 (2 C), 70.82 (3 C), 70.65 (2 C) (3*d*, C(2^{I}), C(5^{II-VII})); 68.92 (2 C), 68.70 (3 C), 68.61 (2 C) (3*t*, C(1^{I}), C(6^{II-VII})); 67.60 (*d*, C(6^{I})); 66.39 (*d*, C(5^{VIII})); 64.29 (*t*, C(6^{VIII})); 36.89 (*d*, C(4^{VIII})); 20.68 (*q*, Me). MALDI-MS: 3485 ([*M* + K]$^+$), 3468 ([*M* + Na]$^+$). Anal. calc. for $C_{215}H_{222}O_{40}$ (3446.09): C 74.94, H 6.49; found: C 74.36, H 6.48.

Glycosidation of **15** *with* **30**. Under Ar, a suspension of **30** (470 mg, 0.125 mmol), **15** (174 mg, 0.25 mmol), and 3-Å molecular sieves (500 mg) in dry toluene (20 ml) was stirred at $-60°$ for 1 h, treated with NIS (51 mg, 0.22 mmol) and TfOH (5.5 µl, 0.06 mmol), and stirred for 20 h. The suspension was filtered over *Celite*. The filtrate was diluted with Et_2O (40 ml), washed with 10% aq. NaS_2O_3 soln. (40 ml), sat. aq. $NaHCO_3$ soln. (2 × 30 ml), H_2O (2 × 30 ml), and brine (30 ml), dried ($MgSO_4$), and evaporated. FC (silica H, toluene/AcOEt 60:1 → 30:1) gave **34** (260 mg, 48%) and **35** (190 mg, 36%).

2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**34**). White foam. R_f (toluene/AcOEt 9:1) 0.62. $[\alpha]_D^{25} = +64.7$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3304*w*, 2922*m*, 1599*m*, 1492*m*, 1404*m*, 1360*m*, 1150*s*, 1090*s*, 1037*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.31 – 6.86 (*m*, 96 arom. H); 5.57 (*d*, $J = 3.5$), 5.55 – 5.54 (*m*, 3 H), 5.50 (*d*, $J = 3.5$), 5.48 (*d*, $J = 3.7$), 5.46 (*d*, $J = 3.5$) (H–C($1^{II–VIII}$)); 4.90 (*d*, $J = 11.9$), 4.89 (*d*, $J = 12.4$), 4.87 (*d*, $J = 10.8$) (3 ArC*H*); 4.81 (*dd*, $J = 2.3$, 5.8, H–C(6^I)); 4.75 (*d*, $J = 11.9$, ArC*H*); 4.72 – 4.58 (*m*, 15 ArC*H*); 4.55 – 4.44 (*m*, 5 ArC*H*); 4.40 – 4.27 (*m*, 22 ArC*H*); 4.08 – 3.88 (*m*, 18 H); 3.86 – 3.78 (*m*, 8 H); 3.75 – 3.61 (*m*, 8 H); 3.56 (*dd*, $J = 3.6$, 9.3, H–C(2)); 3.49 – 3.37 (*m*, 13 H); 3.32 (*dd*, $J = 3.5$, 9.6, H–C(2)); 2.83 (*dt*, $J = 2.9$, 8.1, H–C(4^{VIII})); 2.69 (*d*, $J = 2.3$, H–C(8^I)); 2.17 (*d*, $J = 2.3$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.26 – 135.44 (several *s*); 133.95 – 133.01 (several *s*); 129.79 – 127.31 (several *d*); 97.58, 96.58 (2 C), 96.41 (2 C), 96.35, 96.31 (5*d*, C($1^{II–VIII}$)); 82.46 (*d*, C(4^I)); 81.54, 81.47, 81.38 (4 C), 81,22 (4*d*, C($3^{II–VIII}$)); 81.22 (*s*, *C*≡CH); 79.63 (2 C), 79.49 (3 C), 79.36, 79.16 (4*d*, C($2^{II–VIII}$)); 78.86 (*d*, C(5^I)); 78.16 (br. *s*, C(8^I), C(7^I)); 74.61 (*t*, ArCH); 74.03, 73.61 (2 C), 73.56 (2 C), 73.01, 72.87 (5*d*, C(3^I), C($4^{II–VII}$)); 72.77 – 72.23 (several *t*, 23 Ar*C*H_2); 72.09 (*s*, C≡*C*H); 70.99, 70.90 (6 C), 70.82 (3*d*, C(2^I), C($5^{II–VIII}$)); 69.33, 68.97 (3 C), 68.86 (3 C), 68.56 (4*t*, C(1^I), C($6^{II–VIII}$)); 66.11 (*d*, C(6^I)); 36.54 (*d*, C(4^{VIII})). MALDI-MS: 4346.2 ([M + Na]$^+$). Anal. calc. for $C_{220}H_{202}Cl_{24}O_{39}$ (4320.86): C 61.15, H 4.71; found: C 61.31, H 4.83.

2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-1,4,5-tris*-O-*(4-chlorobenzyl)-2,6-anhydro-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**35**). White foam. R_f (toluene/AcOEt 9:1) 0.58. $[\alpha]_D^{25} = +55.7$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3301*w*, 2925*m*, 2870*m*, 1599*m*, 1492*m*, 1360*m*, 1090*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.32 – 6.83 (*m*, 96 arom. H); 5.66 (*d*, $J = 3.9$), 5.52 (*d*, $J = 3.6$, 2 H), 5.48 (*d*, $J = 3.6$), 5.45 (*d*, $J = 3.5$), 5.43 (*d*, $J = 3.5$) (H–C($1^{II–VII}$)); 4.97 (*d*, $J = 11.4$), 4.90 (*d*, $J = 11.3$, 2 H) (3 ArC*H*); 4.79 (*dd*, $J = 2.3$, 5.8, H–C(6^I)); 4.78 (*d*, $J = 13.0$), 4.73 (*d*, $J = 12.0$), 4.72 (*d*, $J = 12.0$), 4.69 (*d*, $J = 12.1$), 4.65 (*d*, $J = 11.8$), 4.64 (*d*, $J = 12.1$), 4.63 (*d*, $J = 10.9$, 2 H), 4.60 (*d*, $J = 11.9$), 4.59 (*d*, $J = 12.5$, 2 H), 4.56 (*d*, $J = 12.4$, 2 H), 4.55 (*d*, $J = 11.3$), 4.53 (*d*, $J = 11.7$, 2 H), 4.50 (*d*, $J = 10.3$) (17 ArC*H*); 4.48 – 4.42 (*m*, 3 ArC*H*); 4.39 – 4.29 (*m*, 21 ArC*H*); 4.28 (*d*, $J = 12.5$, ArC*H*); 4.22 (*d*, $J = 8.0$, H–C(1^{VIII})); 4.18 (*d*, $J = 13.5$), 4.06 (*d*, $J = 12.2$), 4.02 (*d*, $J = 11.9$) (3 ArC*H*); 4.04 (*t*, $J \approx 9.0$, H–C(3^I)); 3.98 – 3.84 (*m*, H–C($3^{II–VI}$), H–C(4^I), H–C($4^{II–VII}$), H–C(2^I), H–C(1^I)); 3.80 – 3.73 (*m*, 5 H–C(5), H–C(3^{VII}), H–C(6^{VII})); 3.69 – 3.60 (*m*, H–C(5^I), 1 H–C(5), H′–C(1^I), 4 H–C(6), H–C(6^{VIII})); 3.48 – 3.35 (*m*, 4 H–C(2), H–C(2^{VII}), 6 H–C(6), H′–C(6^{VII})); 3.30 – 3.24 (*m*, H–C(2), H–C(5^{VIII}), H–C(6^{VIII})); 3.20 (*t*, $J = 8.7$, H–C(3^{VIII})); 3.10 (*t*, $J = 8.6$, H–C(2^{VIII})); 2.67 (*d*, $J = 2.3$, H–C(8^I)); 2.64 (*dt*, $J = 2.3$, 10.4, H–C(4^{VIII})); 2.18 (*d*, $J = 2.3$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC.GRASP spectrum): 137.45 – 135.85 (several *s*); 133.94 – 132.97 (several *s*); 129.82 – 125.29 (several *d*); 102.32 (*d*, C(1^{VIII})); 97.17, 96.58 (2 C), 96.43 (2 C), 96.35 (4*d*, C($1^{II–VII}$)); 82.77 (*d*, C(3^{VIII})); 82.46 (*d*, C(4^I)); 82.08 (*d*, C(2^{VIII})); 81.39 (*s*, *C*≡CH), 81.60, 81.37, 81.25, 81.22 (2 C) (4*d*, C($3^{II–VI}$)); 80.36 (*d*, C(3^{VII})); 79.74, 79.58 (2 C), 79.48, 79.39 (4*d*, C($2^{II–VI}$)); 78.85 (*d*, C(5^I)); 78.44 (*d*, C(2^{VII})); 78.15 (br. *s*, C≡CH); 76.19 (*d*, C(4^{VII})); 75.11 (*d*, C(5^{VIII})); 74.00, 73.54, 73.35, 73.16, 73.02 (2 C) (5*d*, C(3^I), C($4^{II–VI}$)); 75.01 – 72.00 (several *t*, 24 Ar*C*H_2); 72.09 (*s*, C≡*C*H); 71.21, 70.96 (2 C), 70.87 (2 C), 70.80 (2 C) (4*d*, C(2^I), C($5^{II–VII}$)); 70.06 (*t*, C(6^{VII})); 68.95 (3 C), 68.83 (2 C), 68.76 (3*t*, C(1^I), C($6^{II–VI}$)); 67.47 (*t*, C(6^{VIII})); 66.11 (*d*, C(6^I)); 36.95 (*d*, C(4^{VIII})). MALDI-MS: 4349 ([M + Na]$^+$). Anal. calc. for $C_{220}H_{202}Cl_{24}O_{39}$ (4320.86): C 61.15, H 4.71; found: C 61.38, H 4.90.

Glycosylation of **15** *with* **31**. Under Ar, a suspension of **31** (3.5 g, 0.93 mmol), **15** (1.3 g, 1.87 mmol), and 3-Å molecular sieves (4 g) in dry toluene (150 ml) was stirred at $-60°$ for 1 h, treated with NIS (379 mg, 0.168 mmol) and TfOH (41 µl, 0.46 mmol), and stirred for 2 h. The suspension was filtered over *Celite*. The filtrate was diluted with Et_2O (100 ml), washed with 10% aq. $Na_2S_2O_3$ soln. (100 ml), sat. aq. $NaHCO_3$ soln. (2 × 100 ml), H_2O (2 × 100 ml), and brine (100 ml), dried ($MgSO_4$), and evaporated. FC (silica H, toluene/AcOEt 60:1 → 30:1) gave **36** (1.65 g, 41%) and **37** (1.8 g, 45%).

2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-α*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-(2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 3)-2,6-anhydro-1,4,5-tris*-O-*(4-chlorobenzyl)-7,8-dideoxy*-D-

glycero-L-gulo-*oct-7-ynitol* (**36**). White foam. R_f (toluene/AcOEt 18:2) 0.44. $[\alpha]_D^{25} = +56.3$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 2927*m*, 2868*m*, 1599*m*, 1492*m*, 1408*m*, 1360*m*, 1090*s*, 1036*s*, 1015*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.32–6.85 (*m*, 97 arom. H); 5.56 (*d*, $J = 3.5$), 5.53 (*d*, $J = 3.2$), 5.52 (*d*, $J = 3.0$), 5.50 (*d*, $J = 3.5$), 5.46 (*d*, $J = 3.5$), 5.39 (*d*, $J = 3.5$) (H–C($1^{III–VIII}$)); 4.96 (*d*, $J =$ 12.0), 4.89 (*d*, $J = 10.8$), 4.76 (*d*, $J = 11.5$), 4.75 (*d*, $J = 11.5$) (4 ArC*H*); 4.74 (*dd*, $J = 2.2$, 6.0, H–C(6^I)); 4.71 (*d*, $J = 11.8$, ArC*H*), 4.69–4.55 (*m*, 15 ArC*H*), 4.52 (*d*, $J = 11.5$), 4.47 (*d*, $J = 12.4$), 4.45 (*d*, $J = 12.1$), 4.44 (*d*, $J = 11.7$) (4 ArC*H*); 4.42–4.29 (*m*, 23 ArC*H*, H–C(1^{II})), 4.24 (*d*, $J = 12.1$, ArC*H*); 4.01–3.79 (*m*, H–C(1^I), H–C(2^I), H–C(3^I), H–C($3^{III–VIII}$), H–C($4^{II–VII}$), H–C($5^{III–VIII}$)); 3.75 (*t*, $J = 9.2$, H–C(4^I)); 3.73–3.66 (*m*, H–C($6^{II–VIII}$)); 3.56–3.39 (*m*, H′–C(1^I), H–C(5^I), H–C(3^{II}), H–C($2^{III–VII}$), H′–C($6^{II–VIII}$)); 3.32 (*t*, $J = 9.5$, H–C(2^{II})); 3.31 (*dd*, $J = 3.6$, 9.6, H–C(2^{VIII})); 3.25 (*ddd*, $J = 1.5$, 3.5, 9.5, H–C(5^{II})); 2.83 (*dt*, $J = 2.1$, 10.6, H–C(4^{VIII})); 2.62 (*d*, $J = 2.2$, H–C(8^I)); 2.14 (*d*, $J = 2.2$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.93–135.91 (several *s*); 133.79–132.86 (several *s*); 129.50–127.29 (several *d*); 102.15 (*d*, C(1^{II})); 97.54, 96.82, 96.67, 96.50, 96.40, 96.33 (6*d*, C($1^{III–VIII}$)); 84.67 (*d*, C(3^{II})); 82.33 (*d*, C(2^{II})); 81.58 (*s*, *C*≡CH); 81.48, 81.40, 81.30 (2 C), 81.25 (4*d*, C($3^{III–VII}$)); 81.00 (*d*, C(4^I)); 79.58 (2 C), 79.51, 79.46, 79.40, 79.27 (5*d*, C($2^{III–VIII}$)); 79.20 (*d*, C(3^{VIII})); 78.07 (*d*, C(5^I)); 78.14 (*s*, C(8^I)); 77.76 (*s*, C(7^I)); 75.89, 74.98 (2*d*, C(3^I), C(4^{II})); 74.98 (*d*, C(5^{II})); 73.77 (*d*, C(2^I)); 73.62, 73.42, 73.00, 72.70, 72.80 (5*d*, C($4^{III–VII}$)); 74.74–72.30 (several *t*, 24 ArCH_2); 72.00 (*s*, C≡*C*H); 71.00 (2 C), 70.97, 70.93 (3 C) (3*d*, C($5^{III–VIII}$)); 69.35 (2 C), 69.05 (3 C), 68.92 (2 C) (3*t*, C($6^{II–VIII}$)); 67.91 (*t*, C(1^I)); 66.10 (*d*, C(6^I)); 36.54 (*d*, C(4^{VIII})). MALDI-MS: 4306 ($[M + Na]^+$). Anal. calc. for $C_{220}H_{203}Cl_{23}O_{39}$ (4286.41): C 61.55, H 4.77; found: C 61.41, H 4.84.

2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 3)-1,4,5-tris*-O-*(4-chlorobenzyl)-2,6-anhydro-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**37**). R_f (toluene/AcOEt 9:1) 0.43. $[\alpha]_D^{25} = 52.7$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 2925*m*, 2867*m*, 1599*m*, 1492*m*, 1361*m*, 1090*s*, 1035*s*, 1015*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.35–6.84 (*m*, 97 arom. H); 5.64 (*d*, $J = 3.8$), 5.56 (*d*, $J = 3.5$), 5.51 (*d*, $J = 3.6$), 5.49 (*d*, $J = 3.6$), 5.43 (*d*, $J = 3.5$) (H–C($1^{III–VII}$)); 4.96 (*d*, $J = 11.4$), 4.83 (*d*, $J = 11.0$), 4.77 (*d*, $J = 12.1$) (3 ArC*H*); 4.73 (*dd*, $J = 2.3$, 5.8, H–C(6^I)); 4.72–4.58 (*m*, 10 ArC*H*); 4.55–4.42 (*m*, 13 ArC*H*); 4.38–4.22 (*m*, 19 ArC*H*, H–C(1^{II}), H–C(1^{VIII})); 4.24 (*d*, $J = 12.7$), 4.16 (*d*, $J = 12.1$), 4.13 (*d*, $J = 12.1$) (3 ArC*H*); 4.20–3.78 (*m*, H–C(1^I), H–C(2^I), H–C(3^I), H–C($3^{III–VII}$), H–C($4^{II–VII}$), 4 H–C(5)); 3.76–3.62 (*m*, H–C(3^{VIII}), H–C(4^I), H–C(5^{VIII}), H–C($6^{II–VIII}$)); 3.56–3.33 (*m*, H′–C(1^I), H–C($2^{II–VII}$), H–C(3^{II}), H–C(5^I), H′–C($6^{II–VII}$)); 3.32–3.25 (*m*, H–C(2^{II}), H–C(5^{II}), H′–C(6^{VIII})); 3.09 (*t*, $J = 8.6$, H–C(2^{VIII})); 2.63 (*dt*, $J =$ 2.3, 10.3, H–C(4^{VIII})); 2.62 (*d*, $J = 2.2$, H–C(8^I)); 2.16 (*d*, $J = 2.3$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 137.93–135.91 (several *s*); 133.79–132.87 (several *s*); 129.50–127.29 (several *d*); 102.31, 102.15 (2*d*, C(1^{II}), C(1^{VIII})); 97.17, 96.82, 96.55, 96.52, 96.30 (5*d*, C($1^{III–VII}$)); 84.67 (*d*, C(3^{II})); 82.36 (*d*, C(2^{II})); 82.34 (*d*, C(3^{VII})); 81.18 (*d*, C(2^{VIII})); 81.56, 81.28, 81.24, 81.20 (4*d*, C($3^{III–VI}$)); 81.33 (*s*, C≡*C*H), 80.38 (*d*, C(3^{VIII})); 79.70, 79.58 (2 C), 79.42 (3*d*, C($2^{III–VI}$)); 78.48 (*d*, C(2^{VII})); 78.07 (*d*, C(5^I)); 78.15 (*s*, C(8^I)); 77.76 (*s*, C(7^I)); 76.19 (*d*, C(4^{VII})); 75.90, 75.02 (2*d*, C(3^I), C(4^{II})); 74.97 (*d*, C(5^{II})); 73.77 (*d*, C(2^I)); 73.50, 73.31, 72.75, 72.45 (4*d*, C($4^{III–VI}$)); 74.75–72.24 (several *t*, 24 ArCH_2); 72.01 (*s*, C≡*C*H); 71.21, 71.11, 70.93 (4 C), (3*d*, C($5^{III–VIII}$)); 70.03 (*t*, C(6^{VII})); 69.06 (2 C), 68.99, 68.82, 68.71 (4*t*, C($6^{II–VI}$)); 67.91 (*t*, C(1^I)); 67.47 (*t*, C(6^{VIII})); 66.61 (*d*, C(6^I)); 36.93 (*d*, C(4^{VIII})). HR-MALDI-MS: 4309.149 ($C_{220}H_{202}Cl_{23}NaO_{39}$), $[M + Na]^+$; calc: 4309.211). Anal. calc. for $C_{220}H_{203}Cl_{23}O_{39}$ (4286.41): C 61.65, H 4.77; found: C 61.75, H 4.88.

6-O-*Acetyl-2,3-di*-O-*benzyl-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*benzyl-α*-D-*glucopyranosyl]$_6$-(1 → 3)-1,4,5-tri*-O-*benzyl-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol* $10^I,4^{VIII}$-*Anhydride* (**38**). A soln. of **32** (215 mg, 0.0624 mmol) in pyridine (40 ml) and MeCN (120 ml) was heated to 85°, treated with $Cu(OAc)_2$ (57.0 mg, 3.12 mmol), refluxed for 3 h, and cooled to 23°. Evaporation and FC (silica H, toluene/AcOEt 40:1 → 30:1) gave 38 (107 mg, 50%). White foam. R_f (toluene/AcOEt 17:1) 0.28. M.p. 63–68°. $[\alpha]_D^{25} =$ +60.1 ($c = 1.00$, CH_2Cl_2). IR (CH_2Cl_2): 3031*m*, 2925*m*, 2870*m*, 1741*m*, 1605*m*, 1496*m*, 1454*m*, 1362*m*, 1237*m*, 1209*m*, 1095*s*, 1028*s*, 910*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.46–6.87 (*m*, 115 arom. H): 5.57 (*d*, $J = 3.8$), 5.47 (*d*, $J = 3.4$), 5.34 (*d*, $J = 3.7$), 5.30 (*d*, $J = 3.7$), 5.21 (*d*, $J = 3.6$), 5.19 (*d*, $J = 3.6$), 5.17 (*d*, $J = 3.4$) (H–C($1^{II–VIII}$)); 5.10 (*d*, $J = 11.1$, PhC*H*); 5.04 (*d*, $J = 11.0$, PhC*H*); 4.99 (*d*, $J = 10.8$, PhC*H*); 4.93–4.72 (*m*, 6 PhC*H*); 4.79 (*d*, $J = 10.6$, PhC*H*); 4.75 (*s*, 2 PhC*H*); 4.71–4.61 (*m*, 6 PhC*H*); 4.57 (*d*, $J = 10.8$, PhC*H*); 4.99–4.34 (*m*, 28 PhC*H*, H–C(6^I)); 4.18–4.10 (*m*, 2 H–C(6^{VIII})); 4.01–3.82 (*m*, 27 H); 3.81–3.71 (*m*, H–C(5), 2 H–C(6)); 3.67 (*dd*, $J = 6.0$, 9.1, H–C(5^I)); 3.58–3.41 (*m*, 13 H); 3.30 (*dd*, $J = 3.5$, 9.5, H–C(2)); 2.79 (*t*, $J = 10.6$, H–C(4^{VIII})); 1.97 (*s*, AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 170.96 (*s*, C=O); 139.30–137.66 (several *s*); 128.48–126.53 (several *d*); 98.26 (2 C), 98.21, 98.04, 97.86, 97.57, 97.42 (6*d*, C($1^{II–VIII}$)); 82.94 (*d*, C(4^I)); 81.17 (2 C), 81.06 (2 C), 80.93 (3 C) (3*d*, C($3^{II–VIII}$));

79.40 (2 C), 79.30, 79.17, 78.90, 78.85, 78.76, 78.48 (7*d*, C(5^{I}), C(2$^{II–VIII}$)); 78.27 (*s*, C(8^{I}), C(9^{I})); 77.51, 75.35 (2 C), 74.37 (2 C), 74.29 (2 C) (4*d*, C(3^{I}), C(4$^{II–VII}$)); 75.87, 68.28 (2*s*, C(7^{I}), C(10^{I})); 75.12–72.77 (several *t*, 23 ArCH_2); 71.65, 71.57, 71.51, 71.35, 71.27, 71.94 (6*d*, C(2^{I}), C(5$^{II–VIII}$)); 69.18, 69.00 (2 C), 68.93 (2 C), 68.80, 68.72 (5*t*, C(1^{I}), C(6$^{II–VII}$)); 67.32 (*d*, C(6^{I})); 64.18 (*t*, C(6^{VIII})); 37.69 (*d*, C(4^{VIII})); 20.79 (*q*, MeO). MALDI-MS: 3482 ([*M* + K]$^+$), 3466 ([*M* + Na]$^+$). Anal. calc. for $C_{215}H_{220}O_{40}$ (3444.12): C 74.98, H 6.44; found: C 74.65, H 6.73.

2,3,6-Tris-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-1,4,5-tris*-O-*(4-chlorobenzyl)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^{I},4^{VIII}-Anhydride* (**39**). A soln. of **39** (53 mg, 0.012 mmol) in pyridine (6.6 ml) and MeCN (20 ml) was heated to 85°, treated with $Cu(OAc)_2$ (11 mg, 0.062 mol), refluxed for 3 h, and cooled to 23°. Evaporation and FC (silica H, toluene/AcOEt 60:1 → 30:1) gave **39** (31.7 mg, 60%). White foam. R_f (toluene/AcOEt 18:2) 0.56. $[\alpha]_D^{25}$ = +62.0 (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 2924*m*, 2869*m*, 1599*m*, 1491*m*, 1404*m*, 1358*m*, 1138*s*, 1090*s*, 1041*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HMQC.GRASP spectrum): 7.28–6.79 (*m*, 96 arom. H); 5.51 (*d*, *J* = 3.8), 5.46 (*d*, *J* = 3.5), 5.30 (*d*, *J* = 3.7), 5.15 (*d*, *J* = 3.5), 5.14 (*d*, *J* ≈ 4.0), 5.12 (*d*, *J* ≈ 4.0), 5.07 (*d*, *J* = 3.5) (H–C(1$^{II–VIII}$)); 5.02 (*d*, *J* = 5.9, H–C(6^{I})); 4.96 (*d*, *J* = 11.5), 4.89 (*d*, *J* = 11.3), 4.86 (*d*, *J* = 10.9), 4.85 (*d*, *J* = 11.8), 4.80 (*d*, *J* = 11.5), 4.77 (*d*, *J* = 11.5), 4.73 (*d*, *J* = 12.4), 4.71 (*d*, *J* = 10.8, 2 H), 4.66 (*d*, *J* = 11.6, 2 H) (11 ArC*H*); 4.55–4.50 (*m*, 6 ArC*H*); 4.45–4.26 (*m*, 31 ArC*H*); 3.95–3.68 (*m*, H–C(4^{I}), H–C(3$^{II–VIII}$), H–C(3^{I}), H–C(4$^{II–VII}$), H–C(2^{I}), H–C(5$^{II–VIII}$), 2 H–C(1^{I}), 4 H–C(6)); 3.65 (*dd*, *J* = 5.6, 9.1, H–C(5^{I})); 3.56 (br. *d*, *J* = 10.2), 3.52 (br. *d*, *J* = 10.0), 3.49 (br. *d*, *J* = 10.5) (3 H–C(6)); 3.48–3.40 (*m*, H′–C(6$^{II–VIII}$)); 3.41 (*dd*, *J* ≈ 3.5, 9.1), 3.42 (*dd*, *J* ≈ 3.5, 9.1), 3.39 (*dd*, *J* ≈ 3.7, 8.8, 2 H), 3.34 (*dd*, *J* = 3.6, 9.1, 2 H), 3.33 (*dd*, *J* = 3.6, 9.1) (H–C(2$^{II–VIII}$)); 3.36 (br. *d*, *J* ≈ 11.8, H′–C(6^{VIII})); 2.95 (*t*, *J* = 10.6, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC.GRASP spectrum): 137.16–135.65 (several *s*); 134.13–132.48 (several *s*); 131.09–127.24 (several *d*); 98.33, 98.25, 98.19, 98.11, 98.06, 97.79, 97.41 (7*d*, C(1$^{II–VIII}$)); 82.91 (*d*, C(4^{I})); 81.01 (*d*, C(3^{VIII})); 80.72, 80.71 (3 C), 80.62, 80.61 (4*d*, C(3$^{II–VII}$)); 79.69, 79.51, 79.40, 79.34, 78.93, 78.92, 78.90 (7*d*, C(2$^{II–VIII}$)); 78.92 (*d*, C(5^{I})); 78.52, 78.25, 78.09, 77.90, 77.02 (5*d*, C(4$^{II–VI}$)); 77.89 (*s*, C(8^{I}), C(9^{I})); 74.84, 74.37 (2*d*, C(3^{I}), C(4^{VII})); 74.64–72.32 (several *t*, 24 ArCH_2); 73.42, 68.00 (2*s*, C(7^{I}), C(10^{I})); 71.76, 71.67, 71.56, 71.46, 71.32, 71.15, 70.59 (7*d*, C(2^{I}), C(5$^{II–VIII}$)); 69.28, 69.19, 69.09, 68.91 (2 C), 68.17 (3 C) (5*t*, C(1^{I}), C(6$^{II–VIII}$)); 67.06 (*d*, C(6^{I})); 37.49 (*d*, C(4^{VIII})). MALDI-MS: 4341 ([*M* + Na]$^+$).

α-D-*Glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^{I},4^{VIII}-Anhydride* (**40**). A soln. of **39** (111 mg, 0.026 mmol) in CH_2Cl_2 was treated with $FeCl_3$ (253 mg, 1.56 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75/50/12) gave **40** (25 mg, 73%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.15. $[\alpha]_D^{25}$ = +116.3 (*c* = 1.00, H_2O). ^{1}H-NMR (500 MHz, D_2O): 5.37 (br. *s*), 5.34 (*d*, *J* = 3.9), 5.24 (*d*, *J* = 4.0), 5.22 (*d*, *J* = 3.8), 5.17 (*d*, *J* = 3.3, 2 H), 4.91 (*d*, *J* = 3.6) (H–C(1$^{II–VIII}$)); 4.89 (*d*, *J* = 6.0, H–C(6^{I})); 4.14 (*t*, *J* = 8.1, 1 H); 3.97–3.72 (*m*, 29 H); 3.71–3.52 (*m*, 16 H); 3.39 (*t*, *J* = 9.4, 1 H); 2.71 (*t*, *J* = 10.5, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, D_2O): 103.90, 103.58, 103.47, 103.12, 102.74, 102.00, 101.93 (7*d*, C(1$^{II–VIII}$)); 82.43, 81.59, 81.16, 80.86, 80.79, 79.99, 79.69 (7*d*, C(3^{I}), C(4$^{II–VII}$)); 77.38–71.22 (several *d*, C(5^{I}), C(2$^{II–VIII}$), C(4^{I}), C(3$^{II–VIII}$), C(2^{I}), C(5$^{II–VIII}$), C(6^{I})); 79.76, 76.37 (2*s*, C(7^{I}), C(10^{I})); 71.61, 70.09 (2*s*, C(8^{I}), C(9^{I})); 64.42, 63.25, 63.12, 63.06 (2 C), 62.88, 62.84, 62.79 (7*t*, C(1^{I}), C(6$^{II–VIII}$)); 40.25 (*d*, C(4^{VIII})). HR-MALDI-MS: 1351.44 ($C_{52}H_{80}NaO_{39}$, [*M* + Na]$^+$; calc. 1351.42).

6-O-*Acetyl-α*-D-*glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*decitol 10^{I},4^{VIII}-Anhydride* (**41**). A suspension of **38** (120 mg, 0.0348 mmol) and 10% $Pd(OH)_2$/C (80 mg) in 2-methoxyethanol (10 ml) under H_2 (pressure 6 bar) was stirred at 23° for 48 h. The suspension was filtered over *Celite*, and the residue was washed with 2-methoxyethanol (2 ml), MeOH (2 ml), and H_2O (2 ml). After evaporation of the combined filtrate and washings, the residue was dissolved in H_2O (10 ml) and freeze-dried to give **41** (49.0 mg, 99%). White foam. M.p. 219° (dec.). ^{1}H-NMR (300 MHz, CD_3OD): 5.17 (*d*, *J* = 4.0, 2 H), 5.10 (*d*, *J* = 3.7), 5.09 (*d*, *J* = 4.0), 5.05 (*d*, *J* = 3.7, 2 H), 5.02 (*d*, *J* = 4.0) (H–C(1$^{II–VIII}$)); 4.31 (br. *d*, *J* = 11.8, 2 H–C(6)); 4.15–4.01 (*m*, H–C(4^{VIII})); 4.00–3.38 (*m*, 47 H); 2.08 (*s*, AcO); 1.77–1.24 (*m*, $(CH_2)_4$). ^{13}C-NMR (75 MHz, CD_3OD): 173.24 (*s*, C=O); 103.85 (6 C), 102.59 (2*d*, C(1$^{II–VIII}$)); 82.72 (2 C), 82.35 (3 C), 81.91 (2 C) (3*d*, C(3^{I}), C(4$^{II–VII}$)); 77.48, 76.14, 75.25 (5 C), 75.06 (5 C), 74.73 (3 C), 74.13 (3 C), 73.87 (3 C), 73.58 (2 C), 73.06 (9*d*, C(2^{I}), C(4^{I}), C(5^{I}), C(2$^{II–VIII}$), C(3$^{II–VIII}$), C(5$^{II–VIII}$)); 66.07 (*d*, C(6^{I})); 62.17 (7 C) (*t*, C(1^{I}), C(6$^{II–VII}$)); 59.18 (*t*, C(6^{VIII})); 43.75 (*d*, C(4^{VIII})); 25.47 (*t*, 2 CH_2); 25.22 (*t*, 2 CH_2); 20.84 (*q*, OC(O)CH_3). MALDI-MS: 1403 ([*M* + Na]$^+$).

α-D-*Glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*decitol 10^{I},4^{VIII}-Anhydride* (**42**). A soln. of **41** (49.0 mg, 0.0348 mmol) in MeOH/H_2O 1:1 (10 ml) was treated with 1M NaOMe in (1 ml) and stirred at 23° for 20 h. The soln. was treated with *Amberlite IR-120* (H^+

form) and filtered. Evaporation, dissolution in H_2O (10 ml), and lyophilisation gave **42** (46.0 mg, 97%). White powder. M.p. 240° (dec.). ^{1}H-NMR (500 MHz, D_2O): 5.38 (*d*, *J* = 3.8), 5.28 (*d*, *J* = 3.8), 5.27 (*d*, *J* = 4.0), 5.20 (*d*, *J* = 3.8, 2 H), 5.19 (*d*, *J* = 3.9), 5.16 (*d*, *J* = 3.9) (H–C($1^{II-VIII}$)); 3.96–3.76 (*m*, 31 H); 3.72 (*dd*, *J* = 2.1, 7.8, 2 H); 3.69 (*dd*, *J* = 2.1, 7.8, 1 H); 3.67–3.54 (*m*, 15 H); 3.53 (*dd*, *J* = 3.9, 9.4, 1 H); 1.68–1.55, 1.37–1.32 (2*m*, H–C(4^{VIII}), (CH_2)$_4$). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.80–5.38 (*m*, HO–C($2^{II-VIII}$), HO–C(4^I), HO–C(3^{II-VII})); 5.00 (*d*, *J* = 3.9), 4.96 (*d*, *J* = 3.6), 4.93 (*d*, *J* = 3.6) (3 H–C(1)); 4.92–4.88 (*m*, 4 H, H–C(1), HO–C(5^I)); 4.87 (*d*, *J* = 3.4, H–C(1)); 4.71 (*d*, *J* = 4.8, HO–C(3^{VIII})); 4.58–4.42 (*m*, 8 H, HO–C(1^I), HO–C($6^{II-VIII}$)); 3.68–3.46 (*m*, 27 H); 3.37–3.20 (*m*, 21 H); 1.59–1.36 (*m*, 6 H), 1.30–1.18 (*m*, 3 H) (H–C(4^{VIII}), (CH_2)$_4$). ^{13}C-NMR (125 MHz, D_2O): 103.81, 103.56, 103.52, 103.06, 103.01, 102.74, 102.47 (7*d*, C($1^{II-VIII}$)); 81.85, 81.80, 81.69, 81.12, 81.05, 80.79 (2 C) (6*d*, C(3^I), C(4^{II-VII})); 77.98 (*d*, C(6^I)); 76.24–72.13 (several *d*, C(5^I), C(4^I), C(2^I), C($2^{II-VIII}$), C($3^{II-VIII}$), C($5^{II-VIII}$)); 64.13, 63.45, 63.12, 63.03 (2 C), 62.88 (2 C), 62.80 (6*t*, C(1^I), C($6^{II-VIII}$)); 44.07 (*d*, C(4^{VIII})); 27.90, 27.76, 27.67, 26.16 (4*t*, 4 CH_2). MALDI-MS: 1360 ([*M* + Na]$^+$). Anal. calc. for $C_{52}H_{88}O_{39} \cdot 7\,H_2O$ (1462.35): C 42.68, H 7.02 found: C 42.76, H 6.75.

6-O-*Acetyl-2,3-di*-O-*benzyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*benzyl-α*-D-*glucopyranosyl]$_6$-(1 → 3)-1,4,5-tri*-O-*benzyl-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^I,4^{VIII}-Anhydride* (**43**). A soln. of **33** (99.2 mg, 0.0287 mmol) in pyridine (15 ml) and MeCN (45 ml) was heated to 85°, treated with $Cu(OAc)_2$ (26.1 mg, 0.144 mmol), refluxed for 3 h, and cooled to 23°. Evaporation and FC (silica H, toluene/AcOEt 40 : 1 → 30 : 1) gave **43** (59.3 mg, 60%). White foam. R_f (toluene/AcOEt 17 : 1) 0.37. M.p. 61–65°. $[\alpha]_D^{25}$ = +49.8 (*c* = 0.75, CH_2Cl_2). IR (CH_2Cl_2): 3030*m*, 2925*m*, 1741*m*, 1605*m*, 1496*m*, 1454*m*, 1362*m*, 1094*s*, 1028*s*, 826*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on COSY spectra): 7.46–7.00 (*m*, 115 arom. H); 5.56 (*d*, *J* = 3.6), 5.37 (*d*, *J* = 3.7), 5.35 (*d*, *J* = 3.8), 5.28 (*d*, *J* = 3.4), 5.24 (*t*, *J* ≈ 4.4, 2 H) (H–C(1^{II-VII})); 5.05 (*d*, *J* = 11.1, ArC*H*); 4.99 (*d*, *J* = 11.0, 2 ArC*H*); 4.93 (*d*, *J* = 11.1, ArC*H*); 4.87 (*d*, *J* = 10.8, ArC*H*); 4.86 (*d*, *J* = 10.6, 2 ArC*H*); 4.82–4.28 (*m*, 39 ArC*H*, H–C(6^I), H–C(1^{VIII})); 4.16 (*t*, *J* = 8.2, 1 H); 4.42–4.01 (*m*, 3 H); 4.00–3.87 (*m*, 23 H); 3.83–3.80 (*m*, 1 H); 3.52–3.41 (*m*, 16 H); 3.40–3.30 (*m*, 2 H); 3.21 (*t*, *J* = 7.0, H–C(4)); 2.74 (*t*, *J* = 10.3, H–C(4^{VIII})); 1.95 (*s*, AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 170.28 (*s*, C=O); 139.25–137.78 (several *s*); 128.44–126.54 (several *d*); 99.53 (*d*, C(1^{VIII})); 98.17, 98.06, 98.00, 97.63, 97.37, 96.83 (6*d*, C(1^{II-VII})); 82.54 (*d*, C(4^I)); 81.95 (*d*, C(2^{VIII})); 81.47, 81.39, 81.15 (2 C), 80.98 (2 C) (6*d*, C(3^{II-VII})); 80.93, 79.99 (2*s*, C(8^I), C(9^I)); 79.63, 79.50, 79.03, 78.83, 78.71, 78.19, 78.00 (7*d*, C(5^I), C(2^{II-VII})); 77.75 (*s*, C(7^I), C(10^I)); 75.44–72.90 (several *t*, 23 ArCH_2); 74.87 (4 C), 74.41 (2 C), 73.85 (2 C) (3*d*, C(4^I), C($3^{II-VIII}$)); 72.70, 72.93, 71.47, 71.43, 71.35, 71.18, 71.10, 70.93 (8*d*, C(2^I), C($5^{II-VIII}$)); 69.12 (2 C), 69.04, 68.85, 68.74 (2 C), 68.44 (5*t*, C(1^I), C(6^{II-VII})); 67.31 (*d*, C(6^I)); 64.57 (*t*, C(6^{VIII})); 37.22 (*d*, C(4^{VIII})); 20.86 (*q*, Me). MALDI-MS: 3483 ([*M* + K]$^+$), 3466 ([*M* + Na]$^+$). Anal. calc. for $C_{215}H_{220}O_{40}$ (3444.09): C 74.98, H 6.44; found: C 74.89, H 6.86.

2,3,6-Tris-O-*(-4-chlorobenzyl)-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl)]$_6$-*(1 → 3)-1,4,5-tris-O-*(4-chlorobenzyl)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^I,4^{VIII}-Anhydride* (**44**). A soln. of **35** (177 mg, 0.041 mmol) in pyridine (22 ml) and MeCN (66 ml) was heated to 85°, treated with $Cu(OAc)_2$ (60 mg, 0.33 mmol), refluxed for 3 h, and cooled to 23°. Evaporation and FC (silica H, toluene/AcOEt 60 : 1 → 30 : 1) gave **44** (105 mg, 56%). White foam. R_f (toluene/AcOEt 18 : 2) 0.53. $[\alpha]_D^{25}$ = +61.6 (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 2926*m*, 2868*m*, 1724*m*, 1599*m*, 1492*s*, 1408*m*, 1359*m*, 1261*m*, 1090*s*, 1039*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.91–6.80 (*m*, 96 arom. H); 5.31 (*d*, *J* = 3.4), 5.21 (*d*, *J* = 3.3), 5.20 (*d*, *J* = 3.0), 5.19 (*d*, *J* = 3.0, 2 H), 5.14 (*d*, *J* = 3.4) (H–C(1^{II-VII})); 4.97 (*d*, *J* = 11.7, ArC*H*); 4.89 (*d*, *J* = 6.0, H–C(6^I)); 4.77 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 11.6), 4.76 (*d*, *J* = 11.6), 4.72 (*d*, *J* = 11.3) (4 ArC*H*); 4.71 (*d*, *J* ≈ 7.5, H–C(1^{VIII})); 4.70 (*d*, *J* ≈ 11.0), 4.67 (*d*, *J* = 11.3), 4.63 (*d*, *J* = 11.3), 4.61 (*d*, *J* = 11.7), 4.58 (*d*, *J* ≈ 11.0, 3 H), 3.61 (*d*, *J* = 11.7), 4.58 (*d*, *J* = 11.0), 4.54 (*d*, *J* = 11.7), 4.51 (*d*, *J* = 11.4, 2 H), 4.46 (*d*, *J* = 11.8, 2 H), 4.43 (*d*, *J* = 13.1, 2 H), 4.40 (*d*, *J* = 13.2, 2 H) (20 ArC*H*); 4.37–4.28 (*m*, 23 ArC*H*); 4.03–3.97 (*m*, H–C(3^1), H–C(2^I), H–C(1^I), 2 ArC*H*); 3.93–3.73 (*m*, H–C(4^I), H–C(3^{II-VII}), H–C(4^{II-VII}), H–C(5^{II-VII}), 5 H–C(6)); 3.66–3.58 (*m*, H–C(5^I), H′–C(1^I), H–C(6)); 3.54–3.34 (*m*, H–C(2^{II-VII}), H–C(3^{VIII}), H′–C(6^{II-VII})); 3.32–3.24 (*m*, H–C(5^{VIII})); 3.16 (*t*, *J* = 7.3, H–C(2^{VIII})); 2.82 (*t*, *J* = 10.4, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.34–135.78 (several *s*); 134.01–132.99 (several *s*); 130.88–127.36 (several *d*); 99.55 (*d*, C(1^{VIII})); 98.47, 98.36, 98.15, 97.94, 97.85, 97.27 (6*d*, C(1^{II-VII})); 82.36 (*d*, C(4^I)); 81.58 (*d*, C(2^{VIII})); 81.42 (*d*, C(3^{VIII})); 80.87, 80.71 (2 C), 80.62 (2 C), 80.44 (4*d*, C(3^{II-VII})); 70.39 (3 C), 79.25 (3 C) (2*d*, C(2^{II-VII})); 78.77 (*d*, C(4^{VI})); 78.36 (*d*, C(5^I)); 77.74 (2*s*, C(7^I), C(10^I)); 78.10, 77.89, 77.59 (2 C), 75.51, 74.62 (5*d*, C(3^I), C(4^{II-VI})); 73.26, 68.18 (2*s*, C(8^I), C(9^I)); 74.62–72.23 (several *t*, 24 ArCH_2); 71.70 (2 C), 71.49, 71.40 (2 C), 71.15, 70.91 (5*d*, C(2^I), C(5^{II-VII})); 70.39, 69.30 (2 C), 69.04 (2 C), 68.95 (2 C), 68.28 (5*t*, C(1^I), C($6^{II-VIII}$)); 67.19 (*d*, C(6^I)); 37.20 (*d*, C(4^{VIII})). MALDI-MS: 4340 ([*M* + Na]$^+$). Anal. calc. for $C_{220}H_{200}Cl_{24}O_{39}$ (4318.84): C 61.18, H 4.67, Cl 19.70; found: C 61.34, H 4.93, Cl 19.54.

β-D-*Glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl)]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^{I},4^{VIII}-Anhydride* (**45**). A soln. of **44** (100 mg, 0.023 mmol) in CH_2Cl_2 was treated with $FeCl_3$ (228 mg, 1.40 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **45** (26 mg, 75%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.16. $[\alpha]_D^{25} = +90.7$ ($c = 1.00$, H_2O). ^{1}H-NMR (300 MHz, D_2O): 5.36 (br. *s*); 5.32 (*d*, $J \approx 4.2$), 5.30 (*d*, $J \approx 4.8$), 5.27 (br. *s*), 5.22 (*d*, $J = 3.3$), 5.18 (*d*, $J = 3.3$) (H–C(1$^{II–VII}$)); 4.85 (*d*, $J = 5.7$, H–C(6^{I})); 4.46 (*d*, $J = 8.4$, H–C(1^{VIII})); 4.07 (*t*, $J \approx 9.0$, 1 H); 4.04–3.72 (*m*, 24 H); 3.69–3.53 (*m*, 20 H); 3.37 (*t*, $J = 9.0$, 1 H); 3.20 (*t*, $J = 8.4$, 1 H); 2.71 (*t*, $J = 10.2$, H–C(4^{VIII})). ^{13}C-NMR (75 MHz, D_2O): 104.07 (*d*, C(1^{VIII})); 103.55, 103.21, 102.69, 101.85, 101.33, 101.20 (6*d*, C(1$^{II–VII}$)); 81.35, 80.90, 80.31, 79.62, 79.44, 79.28, 79.09 (7 *d*, C(3^{I}), C(4$^{II–VII}$)); 78.16–71.33 (several *d*, C(2^{I}), C(3^{I}), C(5^{I}), C(6^{I}), C(2$^{II–VIII}$), C(3$^{II–VIII}$), C(5$^{II–VIII}$)); 79.97, 76.67 (2*s*, C(7^{I}), C(10^{I})); 72.53, 70.61 (2*s*, C(8^{I}), C(9^{I})); 64.81, 63.27, 63.45 (2 C), 63.31, 63.20 (3 C) (5*t*, C(1^{I}), C(6$^{II–VIII}$)); 40.59 (*d*, C(4^{VIII})). HR-MALDI-MS: 1351.44 ($C_{52}H_{80}NaO_{39}$, $[M + Na]^+$, calc: 1351.42).

6-O-*Acetyl-β*-D-*glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*decitol 10^{I},4^{VIII}-Anhydride* (**46**). A suspension of **37** (90.0 mg, 0.0261 mmol) and 10% $Pd(OH)_2$/C (70 mg) in 2-methoxymethanol (10 ml) was stirred at 23° under H_2 (6 bar) for 48 h. The suspension was filtered over *Celite* and the residue washed with 2-methoxyethanol (2 ml), MeOH (2 ml), and H_2O (2 ml). Evaporation, dissolution in H_2O (10 ml), and lyophilisation gave **46** (32.2 mg, 89%). White foam. M.p. 225° (dec.). ^{1}H-NMR (300 MHz, CD_3OD): 5.20 (*d*, $J = 4.0$), 5.17 (*d*, $J = 4.0$), 5.09 (*d*, $J = 3.7$), 5.07 (*d*, $J = 4.0$), 5.04 (*d*, $J = 3.7$), 5.02 (*d*, $J = 3.7$) (H–C(1$^{II–VII}$)); 4.40 (br. *t*, $J \approx 10.6$, 2 H); 4.02 (br. *dd*, $J = 7.8$, 11.8, 2 H); 3.98–3.12 (*m*, 46 H); 2.11 (*s*, AcO); 1.24–1.70 (*m*, $(CH_2)_4$). ^{13}C-NMR (75 MHz, CD_3OD): 173.20 (*s*, C=O); 104.50 (*d*, C(1^{VIII})); 104.00, 103.77 (2 C), 103.38, 103.10, 102.55 (5*d*, C(1$^{II–VII}$)); 82.90, 82.56 (2 C), 82.25 (2 C), 81.77, 81.59 (5*d*, C(3^{I}), C(4$^{II–VII}$)); 77.01, 76.77 (3 C), 76.12, 75.25 (5 C), 74.97 (2 C), 74.70 (4 C), 74.24 (2 C), 74.10 (2 C), 73.84 (2 C), 73.47, 73.19 (11*d*, C(2^{I}), C(4^{I}), C(5^{I}), C(2$^{II–VIII}$), C(3$^{II–VIII}$), C(5$^{II–VIII}$)); 66.02 (*d*, C(6^{I})); 63.18, 62.38 (2 C), 62.18 (4 C) (3*t*, C(1^{I}), C(6$^{II–VII}$)); 59.20 (*t*, C(6^{VIII})); 43.75 (*d*, C(4^{VIII})); 28.18 (br. *t*, 2 CH_2); 26.31, 25.71 (2*t*, 2 CH_2); 20.97 (*q*, Me). MALDI-MS: 1420 ($[M + K]^+$), 1404 ($[M + Na]^+$).

β-D-*Glucopyranosyl-[(1 → 4)-α*-D-*glucopyranosyl]$_6$-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*decitol 10^{I},4^{VIII}-Anhydride* (**47**). A soln. of **46** (32.2 mg, 0.0232 mmol) in MeOH/H_2O 1:1 (10 ml) was treated with 1M NaOMe in MeOH (1 ml) and stirred at 23° for 20 h. The soln. was treated with *Amberlite IR-120* (H^+ form) and filtered. Evaporation, dissolution in H_2O (10 ml), and lyophilisation gave **47** (31.2 mg, 99%). White powder. M.p. 221° (dec.). ^{1}H-NMR (500 MHz, D_2O, assignment based on a HMQC spectrum): 5.34 (*d*, $J = 4.2$), 5.30 (*d*, $J = 4.2$), 5.25 (*d*, $J = 3.7$), 5.22 (*d*, $J = 4.1$), 5.20 (*d*, $J = 3.8$), 5.16 (*d*, $J = 3.6$) (H–C(1$^{II–VII}$)); 4.52 (*d*, $J = 7.9$, H–C(1^{VIII})); 4.01–3.98 (*m*, H–C(6^{I})); 3.99 (*t*, $J = 9.0$, H–C(3)); 3.95–3.77 (*m*, 25 H); 3.74 (*dd*, $J = 5.7$, 13.2, 1 H); 3.72–3.71 (*m*, 2 H); 3.66–3.58 (*m*, 14 H); 3.55 (*t*, $J = 9.0$, H–C(4)); 3.49 (br. *t*, $J \approx 9.6$, H–C(5^{VIII})); 3.40 (*t*, $J = 10.0$, H–C(3^{VIII})); 3.22 (*dd*, $J = 8.0$, 9.1, H–C(2^{VIII})); 1.78–1.72 (*m*, 1 H, CH_2); 1.55–1.49 (*m*, 4 H, CH_2); 1.43–1.40 (*m*, 2 H, H–C(4^{VIII}), CH_2); 1.32–1.28 (*m*, 2 H, CH_2). ^{1}H-NMR (500 MHz, DMSO, assignment based on a COSY spectrum): 5.77–5.75 (*m*, 3 H, HO–C(2), HO–C(3)); 5.73 (*d*, $J = 6.8$, HO–C(2)); 5.68 (*d*, $J = 2.8$, HO–C(3)); 5.60 (*d*, $J = 7.3$, HO–C(2)); 5.58 (*d*, $J = 3.1$, HO–C(3)); 5.54 (*d*, $J = 8.2$, HO–C(2)); 5.53 (*d*, $J = 2.8$, HO–C(3)); 5.47 (*d*, $J = 7.1$, HO–C(2)); 5.46 (*d*, $J = 6.5$, HO–C(2)); 5.38 (*d*, $J = 2.7$, HO–C(3)); 5.06 (*d*, $J = 4.6$, HO–C(2^{VIII})); 5.03 (*d*, $J = 3.9$), 5.00 (*d*, $J = 3.9$), 4.96 (*d*, $J = 3.6$, 2 H), 4.94 (*d*, $J = 3.9$), 4.89 (*d*, $J = 3.5$) (H–C(1$^{II–VII}$)); 4.97 (*d*, $J \approx 2.6$, HO–C(3^{VII})); 4.92 (*d*, $J = 5.0$, HO–C(5^{I})); 4.78 (*d*, $J = 5.8$, HO–C(3^{VIII})); 4.77 (*t*, $J = 4.8$, HO–C(6^{VIII})); 4.57 (*t*, $J = 5.3$), 4.53–4.43 (*m*, 5 H), 4.40 (*t*, $J = 5.9$) (HO–C(6$^{II–VII}$), HO–C(1^{I})); 4.25 (*d*, $J = 7.4$, H–C(1^{VIII})); 3.61–3.45 (*m*, 27 H); 3.40–3.25 (*m*, 24 H); 3.20 (br. *t*, $J \approx 9.1$, H–C(5^{VIII})); 3.09–3.04 (*m*, H–C(3^{VIII})); 2.95–2.91 (*m*, H–C(2^{VIII})); 1.54–1.49 (*m*, 1 H, CH_2); 1.48–1.38 (*m*, 4 H, CH_2); 1.29–1.25 (*m*, 2H, H–C(4^{VIII}), CH_2); 1.18–1.09 (*m*, 2 H, CH_2). ^{13}C-NMR (125 MHz, D_2O, assignment based on a HMQC spectrum): 104.85 (*d*, C(1^{VIII})); 103.98, 103.27, 103.05, 102.95, 102.89, 102.72 (6*d*, C(1$^{II–VII}$)); 82.54, 82.49, 81.79, 81.26, 81.23, 81.17, 80.81 (7*d*, C(3^{I}), C(4$^{II–VII}$)); 79.96 (*d*, C(5^{VIII})); 78.09 (*d*, C(6^{I})); 77.65 (*d*, C(3^{VIII})); 77.48 (*d*, C(2^{VIII})); 76.66, 76.27, 76.07, 75.83, 75.67, 75.53, 75.29 (7*d*, C(4^{I}), C(3$^{II–VII}$)); 75.04, 74.89, 74.73, 74.56, 74.47 (3 C), 74.26, 74.15, 74.03 (3 C), 73.92, 73.85 (10*d*, C(5^{I}), C(2$^{II–VII}$), C(2^{I}), C(5$^{II–VII}$)); 63.46, 63.97, 63.27, 63.10, 63.05 (2 C), 62.88 (2 C) (6*t*, C(1^{I}), C(6$^{II–VIII}$)); 44.57 (*d*, C(4^{VIII})); 29.21, 28.97, 26.58, 26.51 (4*t*, 4 CH_2). MALDI-MS: 1360 ($[M + Na]^+$). Anal. calc. for $C_{52}H_{88}O_{39}$ (1327.24): C 42.68, H 7.02; found: C 42.83, H 6.70.

2,3,6-*Tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 3)-1,4,5-tris*-O-*(4-chlorobenzyl)-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol 10^{I},4^{VIII}-Anhydride* (**48**). A soln. of **36** (200 mg, 0.046 mmol) in pyridine (25 ml) and MeCN (75 ml) was heated to 85°, treated with $Cu(OAc)_2$ (42 mg, 0.23 mmol), refluxed for 5 h, and cooled to 23°. After

evaporation, a soln. of the residue in Et_2O (60 ml) was washed with an aq. soln. of (TMEDA)Na_4 (140 µl, 0.93 mmol), H_2O (50 ml), and brine (50 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50:1 → 20:1) gave **48** (80 mg, 40%). White foam. R_f (toluene/AcOEt 9:1) 0.55. $[\alpha]_D^{25} = +49.5$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2927*m*, 2869*m*, 1599*m*, 1492*s*, 1408*m*, 1359*m*, 1138*m*, 1090*s*, 1040*s*, 1016*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.30–6.87 (*m*, 97 arom. H); 5.49 (*d*, $J = 3.5$), 5.47 (*d*, $J = 3.7$), 5.39 (*d*, $J = 3.4$), 5.15 (*d*, $J = 3.5$), 5.12 (*t*, $J = 4.1$, 2 H) (H–C($1^{III–VIII}$)); 4.94 (*d*, $J = 11.2$), 4.93 (*d* = 11.5) (2 ArC*H*); 4.91 (*d*, $J = 6.5$, H–C(6^I)); 4.86 (*d*, $J = 11.2$), 4.85 (*d*, $J = 12.1$), 4.84 (*d*, $J = 11.5$), 4.78 (*d*, $J = 11.2$), 4.73 (*d*, $J \approx 11.0$), 4.72 (*d*, $J \approx 11.0$) (6 ArC*H*); 4.67–4.22 (*m*, 40 ArC*H*, H–C(1^{II})); 4.03 (*dt*, $J = 3.4$, 9.7, 1 H); 4.00–3.73 (*m*, 22 H); 3.70–3.53 (*m*, 9 H); 3.49–3.37 (*m*, 12 H); 3.31 (*t*, $J = 8.1$, H–C(2^{II})); 3.28 (*dd*, $J = 3.6$, 6.0, 1 H); 3.25 (*td*, $J = 3.2$, 9.6, H–C(5^{II})); 2.95 (*t*, $J = 10.5$, H–C(4^{VIII})). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.85–135.46 (several *s*); 134.12–133.01 (several *s*); 129.41–127.45 (several *d*); 101.48 (*d*, C(1^{II})); 98.69, 98.48, 98.30, 97.84, 96.77, 95.25 (6*d*, C($1^{III–VIII}$)); 84.94 (*d*, C(3^{II})); 82.24 (*d*, C(2^{II})); 81.59, 80.79 (2 C), 80.49 (2 C), 80.23, 79.80, 79.62, 79.34, 78.84, 78.73, 77.58 (2 C), 77.22 (3 C), 76.26, 76.21, 70.21, 75.54, 74.09, 73.75 (2 C) (17*d*, C(3^I), C(4^I), C(5^I), C($4^{II–VII}$), C($2^{II–VIII}$), C($3^{II–VIII}$)); 81.31, 77.97 (2*s*, C(7^I), C(10^I)); 74.70–72.06 (several *t*, 24 Ar*C*H_2); 71.93, 68.00 (2*s*, C(8^I), C(9^I)); 71.72 (4 C), 71.31, 70.81, 70.67, 70.19 (5*d*, C(2^I), C($5^{II–VIII}$)); 70.31, 69.59, 69.07 (3 C), 68.89 (2 C), 68.11 (5*t*, C(1^I), C($6^{II–VIII}$)); 66.56 (*d*, C(6^I)); 37.59 (*d*, C(4^{VIII})). MALDI-MS: 4306 ($[M + Na]^+$), 4324 ($[M + K]^+$).

*α-*D*-Glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_5$-(1 → 4)-β-*D*-glucopyranosyl-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol 10^I,4^{VIII}-Anhydride* (**49**). A soln. of **48** (95 mg, 0.022 mmol) in CH_2Cl_2 was treated with $FeCl_3$ (210 mg, 1.29 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **49** (23 mg, 78%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.13. ^{1}H-NMR (300 MHz, D_2O): 5.71 (*d*, $J = 3.6$), 5.42 (*d*, $J = 3.9$), 5.40 (*d*, $J \approx 4.2$), 5.34 (*d*, $J = 3.6$), 5.23 (*d*, $J = 3.9$), 5.20 (*d*, $J = 3.9$) (H–C($1^{III–VIII}$)); 4.92 (*d*, $J = 7.8$, H–C(1^{II})); 4.87 (*d*, $J = 6.3$, H–C(6^I)); 4.09 (*t*, $J = 9.6$, 1 H); 4.04–3.78 (*m*, 25 H); 3.74–3.53 (*m*, 20 H); 3.32 (*t*, $J = 9.0$, 1 H); 2.74 (*t*, $J = 10.2$, H–C(4^{VIII})). HR-MALDI-MS: 1351.44 ($C_{52}H_{80}NaO_{39}$, $[M + Na]^+$; calc: 1351.42).

*2,3,6-Tris-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 4)-6-*O*-benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 3)-1,4,5-tris-*O*-(4-chlorobenzyl)-2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol 10^I,4^{VIII}-Anhydride* (**50**). A soln. of **37** (320 mg, 0.07 mmol) in pyridine (39 ml) and MeCN (118 ml) was heated to 85°, treated with $Cu(OAc)_2$ (68 mg, 0.37 mmol), refluxed for 5 h, and cooled to 23°. After evaporation, a soln. of the residue in Et_2O (80 ml), was washed with an aq. soln. of (TMEDA)Na_4 (223 µl, 1.5 mmol), H_2O (50 ml), and brine (50 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50:1 → 20:1) gave **50** (146 mg, 45%). White foam. R_f (toluene/AcOEt 9:1) 0.70. $[\alpha]_D^{25} = 47.4$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2926*m*, 2869*m*, 1599*m*, 1492*s*, 1408*m*, 1359*m*, 1261*m*, 1090*s*, 1040*s*, 1016*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91–6.80 (*m*, 96 arom. H); 5.31 (*d*, $J = 3.4$), 5.21 (*d*, $J = 3.3$), 5.20 (*d*, $J = 3.0$), 5.19 (*d*, $J \approx 3.0$), 5.14 (*d*, $J = 3.4$) (H–C($1^{III–VII}$)); 4.97 (*d*, $J = 11.7$, ArC*H*); 4.89 (*d*, $J = 6.0$, H–C(6^I)); 4.77 (*d*, $J = 11.4$), 4.75 (*d*, $J = 11.6$, 2 H), 4.72 (*d*, $J = 11.3$), 4.70 (*d*, $J = 10.3$, 2 H), 4.67 (*d*, $J = 11.3$), 4.63 (*d*, $J = 11.3$), 4.61 (*d*, $J = 11.7$), 4.58 (*d*, $J \approx 11.0$, 3 H), 3.61 (*d*, $J = 11.7$), 4.58 (*d*, $J = 11.0$, 2 H), 4.54 (*d*, $J = 11.7$), 4.51 (*d*, $J = 11.4$, 2 H), 4.46 (*d*, $J = 11.8$, 2 H), 4.43 (*d*, $J = 13.1$, 2 H), 4.40 (*d*, $J = 13.2$, 2 H) (24 ArC*H*); 4.37–4.28 (*m*, 24 ArC*H*, H–C(1^{II}), H–C(1^{VIII})); 4.15 (*ddd*, $J = 2.0$, 3.5, 9.8, H–C(5)); 4.09 (*t*, $J = 8.9$, 1 H); 4.01–3.97 (*m*, 2 H); 4.93–3.81 (*m*, 16 H); 3.74 (*t*, $J = 8.6$, 1 H); 3.70–3.63 (*m*, 6 H); 3.60 (*dd*, $J = 4.0$, 10.7, 1 H); 3.54–3.32 (*m*, 16 H); 3.28 (*dd*, $J = 7.2$, 8.5, H–C(2)); 3.21 (*dd*, $J \approx 1.5$, 3.5, 9.5, H–C(5^{II})); 3.05 (*dd*, $J \approx 7.5$, 8.2, 1 H); 2.82 (*t*, $J = 10.4$, H–C(4^{VIII})). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.82–135.46 (several *s*); 134.98–132.90 (several *s*); 129.58–127.42 (several *d*); 100.39 (*d*, C(1^{II}), C(1^{VIII})); 98.61, 98.29, 97.81, 97.00, 96.50 (5*d*, C($1^{III–VII}$)); 84.43 (*d*, C(3^{II})); 82.49 (*d*, C(2^{II})); 81.99, 81.62, 81.30, 80.70, 80.65, 80.58, 80.17, 79.91, 79.56, 79.47, 79.36, 79.04, 78.69, 78.41 (2 C), 77.52, 77.24 (2 C), 75.98, 75.84, 74.45, 74.10, 73.76 (23*d*, C(3^I), C($4^{II–VII}$), C(5^I), C($2^{II–VIII}$), C(4^I), C($3^{II–VIII}$)); 77.90 (*s*, C(7^I), C(10^I)); 74.03–72.21 (several *t*, 24 Ar*C*H_2); 72.74, 71.73, 71.53, 71.45, 71.40, 71.18 (6*d*, C($5^{II–VII}$)); 70.40, 69.32 (2 C), 69.13 (3 C), 68.90, 68.65 (5*t*, C(1^I), C($6^{II–VIII}$)); 72.94, 68.44 (2*s*, C(8^I), C(9^I)); 66.57 (*d*, C(6^I)); 37.40 (*d*, C(4^{VIII})). MALDI-MS: 4305 ($[M + Na]^+$), 4324 ($[M + K]^+$).

*β-*D*-Glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_5$-(1 → 4)-β-*D*-glucopyranosyl-(1 → 3)-2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol 10^I,4^{VIII}-Anhydride* (**51**). A soln. of **50** (59 mg, 13.7 µmol) in CH_2Cl_2 was treated with $FeCl_3$ (134 mg, 0.826 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **51** (13 mg, 71%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.15. ^{1}H-NMR (500 MHz, D_2O): 5.47 (*d*, $J =$ 4.2), 5.30 (*d*, $J = 4.0$), 5.22 (*d*, $J = 4.0$), 5.15 (*d*, $J = 3.6$), 5.08 (*d*, $J = 3.6$) (H–C($1^{III–VII}$)); 4.88 (*d*, $J = 5.4$,

H–C(6^{I})); 4.79 (*d*, *J* = 7.7), 4.70 (*d*, *J* = 7.8) (H–C(1^{II}), H–C(1^{VIII})); 4.20 (*ddd*, *J* = 2.1, 5.1, 10.2, H–C(5)); 4.08 (*t*, *J* = 9.4, 1 H); 3.99 (*t*, *J* = 9.2, 1 H); 3.95–3.55 (*m*, 43 H); 3.40 (*t*, *J* = 9.5, 1 H); 2.72 (*t*, *J* = 10.4, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, D_2O): 104.12, 103.89 (*d*, C(1^{II}), C(1^{VIII})); 103.61, 102.90, 102.39, 102.01, 100.80 (5*d*, C(1$^{III–VII}$)); 83.24, 81.96, 81.92, 80.54, 80.47, 78.81, 78.36, 78.29, 77.54, 77.38, 77.33, 77.04, 76.56, 76.45, 76.26, 76.14, 75.98, 75.73, 75.56, 74.79, 74.49 (2 C), 74.39, 74.30, 74.20 (4 C), 74.07 (2 C), 73.82, 72.49, 71.06 (28*d*, C(3^{I}), C(4$^{II–VII}$), C(5^{I}), C(2$^{II–VIII}$), C(4^{I}), C(3$^{II–VIII}$), C(2^{I}), C(5$^{II–VIII}$), C(6^{I})); 64.60, 63.52, 63.21 (2 C), 63.12 (2 C), 63.00, 62.93 (6*t*, C(1^{I}), C(6$^{II–VIII}$)); 40.62 (*d*, C(4^{VIII})). HR-MALDI-MS: 1351.44 ($C_{52}H_{80}NaO_{39}$, $[M + Na]^+$; calc: 1351.42).

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