98. Oligosaccharide Analogues of Polysaccharides

Part 4

Synthesis of a Monosaccharide-Derived Octamer

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Dedicated to *Albert Eschenmoser* on the occasion of his 70th birthday

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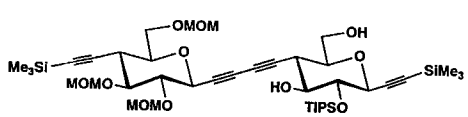
NaSMe in toluene leads to regioselective de-*C*-silylation of the bis[(trimethylsilyl)ethynyl]saccharide **2**, but to decomposition of butadiynes such as **1** or **12**. We have, therefore, combined the known reagent-controlled, regioselective desilylation of **2** and of **12** ($AgNO_2$/KCN) with a substrate-controlled regioselective de-*C*-silylation, based on *C*-silyl groups of different size. This combination was studied with the fully protected **3** which was mono-desilylated to **4** or to **5** (*Scheme 1*). Triethylsilylation of **5** (→ **6**) was followed by removal of the Me_3Si group (→ **7**), introduction of a (*t*-Bu)Me_2Si group (→ **8**) and removal of the Et_3Si group yielded **9**; these high-yielding transformations proceed with a high degree of selectivity. Iodination of **4** gave **10**. The latter was coupled with **5** to the homodimer **11** and the heterodimer **12**, which was desilylated to **13**. The second building block for the tetramer was obtained by coupling **14** (from **7**) with **5**, leading to **15** and **16**. Removal of the Me_3Si group (→ **17**) and iodination led to **18** which was coupled with **13** to the homotetramer **20** and the heterotetramer **19** (*Scheme 2*). Deprotection of **19** gave **21**, which was, on the one hand, iodinated to **22**, and, on the other hand, protected by the (*t*-Bu)Me_2Si group (→ **23**). Removal of the Et_3Si group (→ **24**) and coupling afforded the homooctamer **26** and the heterooctamer **25**. Yields of iodination, silylation, and desilylation were consistently high, while heterocoupling proceeded in only 50–55%. Cleavage of the (i-Pr)$_3$SiC and $MeOCH_2O$ groups of **11** (→ **27**), **15** (→ **28**), **20** (→ **29**) and **26** (→ **30**) proceeded in high yields (*Scheme 3*). Complete deprotection in two steps of the heterocoupling products **16** (→ **31** → **32**), **19** (→ **33** → **34**), and **25** (→ **35** → **36**) gave the unprotected dimer **32**, tetramer **34**, and octamer **36** in high yields (*Scheme 4*). Only the dimer **32** is soluble in H_2O; the ^{1}H-NMR spectra of **32**, **34**, and **36** in (D_6)DMSO (relatively low concentration) show no signs of association.

Introduction. – Our projected synthesis of polysaccharide analogues requires an orthogonal deprotection of the ethynyl substituents of dimers such as **1**, and of the corresponding higher oligomers [1]. The reagent-controlled orthogonal deprotection of the (trimethylsilyl)ethynyl ($Me_3SiC\equiv C$) groups is, however, restricted to monomers of the type **2** (*Scheme 1*) [2]. Dimers such as **1** possess a butadiynediyl group which does not tolerate BuLi in THF, conditions used for the desilylation of the propargylic ether moiety of **2** [2].

Parallel to synthesizing monomers which allow a substrate-controlled orthogonal deprotection [3], we have looked for alternative methods suitable for the reagent-con-



1 MOM = $MeOCH_2$, TIPS = (i-Pr)$_3$Si

trolled regioselective deprotection of the *C*-silylated propargylic ether moiety of dimers. We have also examined the synthesis of oligosaccharide analogues based on the regioselective deprotection of the $Me_3SiC{\equiv}C$ group attached at C(8′) of **1** to study the feasibility of the regioselective de-*C*-silylation, the *Cadiot-Chodkiewiecz* cross coupling, and the complete deprotection of the oligomers; this should provide us with the first probes of oligomer analogues and allow to assess their stability.

Results and Discussion. – Looking for alternatives to BuLi for desilylation, we have fully protected the monomer **2**[1]) and subjected the resulting **3** to a range of bases under a variety of conditions. Although NaSMe in toluene transformed **3** into the monodeprotected **4** (50%, besides 32% of starting material; *Scheme 1*), it led to decomposition of **1**. Similar results were obtained with $NaS(CH_2)_3SNa$, while NaSPh did not lead to desilylation of **4**, not even at 100°. Soft nucleophiles in the presence of *Lewis* acids, such as $EtSH/BF_3{\cdot}OEt_2$ [6] removed the $MeOCH_2$ (MOM) group of **4** without affecting the $Me_3SiC{\equiv}C$ group.

Considering these results, we have combined the reagent-controlled regioselective desilylation of **1** with a substrate-controlled regioselective deprotection of alkynyl moieties carrying silyl groups of different size. *Eaborn* and *Walton* [7] have shown that the rates of cleavage of alkynyl-silanes by aqueous methanolic alkali depends on the nature of the silyl group, the less bulky silyl group of bis(silylalkynes) being selectively removed [8] [9]. Thus, $Me_3SiC{\equiv}CPh$ is cleaved 280 times faster than $Et_3SiC{\equiv}CPh$, and *ca.* 1350 times faster than $(i\text{-}Pr)_3SiC{\equiv}CPh$. The combination of a reagent-controlled regioselective deprotection of bis [(trimethylsilyl)ethynyl]-substituted monomers and dimers [2], followed by the introduction of a Et_3Si group and a substrate-controlled regiocomplementary deprotection should lead to the building blocks for a tetramer; similarly, the use of a further, still bulkier trialkylsilyl group should give access to an octamer.

Selective removal of the Me_3Si group at C(1) of **3** with $AgNO_2/NaCN$ [2] [4] led to **5** (81%) which was silylated with Et_3SiCl and BuLi to yield 98% of the differentially protected dialkyne **6** [10] [11]. Removal of the Me_3Si group of **6** with 0.1N NaOH in MeOH proceeded smoothly to the Et_3Si-protected alkyne **7** (99%) [12]. The same product was obtained in 90% yield by treating **6** with $AgNO_2/NaCN$ at 40°; the $Et_3SiC{\equiv}C$ group was not affected under either condition. To show that the Et_3Si and the $(t\text{-}Bu)Me_2Si$ (TBDMS) groups can be similarly differentiated, we silylated **7** with $(t\text{-}Bu)Me_2SiOTf$ in the presence of $(Me_3Si)_2NK$ [13] in THF [14] and obtained 98% of **8**, which proved stable to NaOH in MeOH at concentrations between 0.1 and 2M, even when boiled under reflux. NaOMe in MeOH, however, cleaved the Et_3Si group of **8** to yield 80% of **9** [7].

To prepare the building blocks **13** and **18** for the synthesis of a tetramer, we iodinated the alkynes **4** and **7** with I_2 and morpholine. The reaction proceeded smoothly and gave the iodoalkynes **10** and **14** in 98 and 93% yield, respectively [15] [16]. Coupling of **10** and **5** promoted by CuI and $PdCl_2(PhCN)_2$ in the presence of $(i\text{-}Pr)_2NH$ [17] [18] gave the heterodimer **12** (53%) and the homodimer **11** (31%)[2]) derived from the iodoalkyne **10**. Similarly, **14** and **4** yielded 63% of the heterodimer **16** and 15% of the homodimer **15**.

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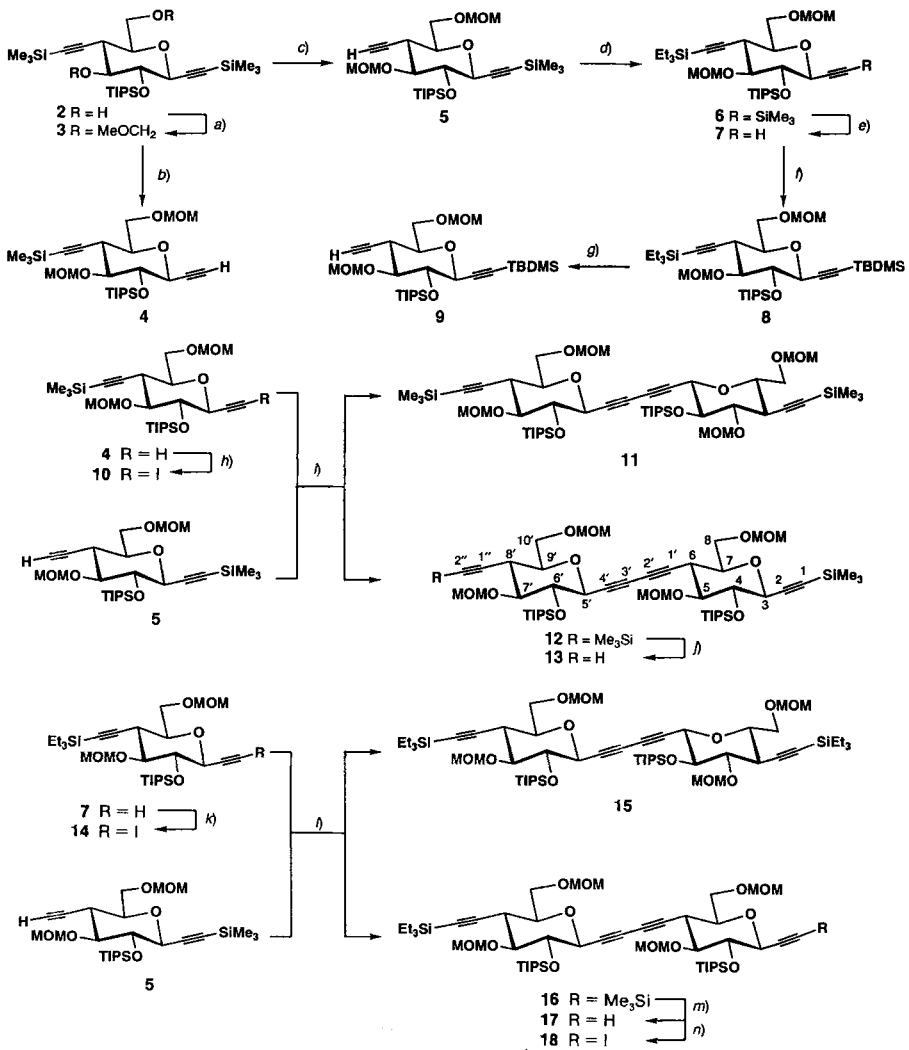
[1]) Treatment of **2** with BuLi caused partial migration of the $(i\text{-}Pr)_3Si$ group from OC(2) to OC(3) [2] [4] [5].

[2]) The formulae **15–17**, **22**, **30–32**, and **40–41** (Schemes 2 and 4) in [2] should be corrected, replacing the L- by a D-glucosylidene moiety. Similarly, the *gluco*-moiety in formula **75** (Scheme 6) in [3] should be D, and not L.

Scheme 1



MOM = $MeOCH_2$, TIPS = $(i\text{-Pr})_3Si$, TBDMS = $(t\text{-Bu})Me_2Si$

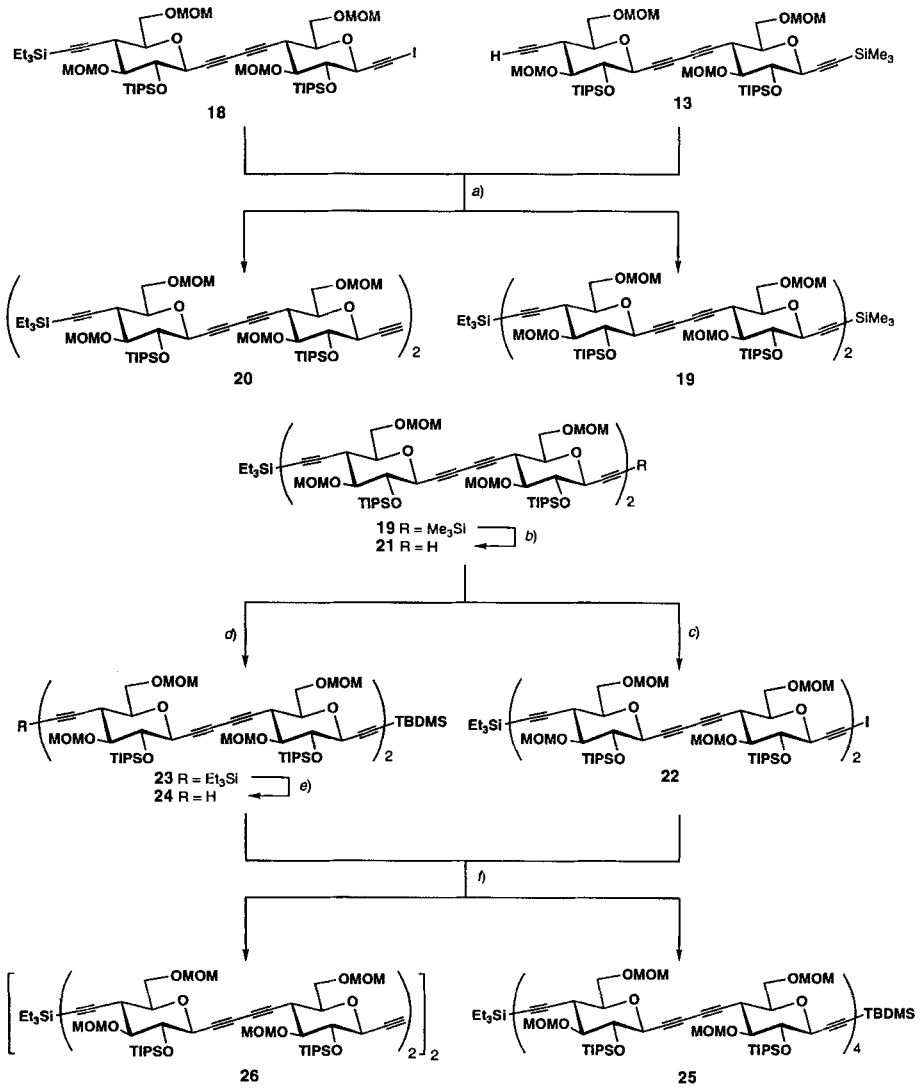
a) $CH_2(OMe)_2$, P_2O_5, 20°; 94%. *b*) NaSMe, toluene, 80°; **4** (50%), **3** (32%). *c*) $AgNO_2$, KCN, MeOH, H_2O, 24°; 81%. *d*) Et_3SiCl, BuLi, THF, −78°; 98%. *e*) NaOH, MeOH, 25°; 99%. *f*) $(t\text{-Bu})Me_2SiOTf$, $(Me_3Si)_2NK$, THF, −78°; 98%. *g*) NaOMe, MeOH, 50°; 80%. *h*) Morpholine, I_2, toluene, 45°; 98%. *i*) CuI, $[PdCl_2(PhCN)_2]$, $P(fur)_3$, $(i\text{-Pr})_2NH$, DMSO, 50°; **11** (31%), **12** (53%). *j*) As *c*); **12** (10%), **13** (70%). *k*) As *h*); 93%. *l*) As *i*); **16** (63%), **15** (15%). *m*) As *e*); 99%. *n*) As *h*); 95%.

Deprotection of **12** with $AgNO_2$/KCN yielded 70% of the selectively monodesilylated **13**, while NaSMe led to a complex mixture, showing that the sensitivity of **1** is not due to the presence of free OH groups, similarly as it has been shown for the treatment of related compounds with BuLi. The Me_3SiC moiety of **16** was cleaved with aqueous NaOH in

MeOH and the Et_3Si-protected **17** was isolated in 99% yield. Iodination of **17** proceeded smoothly and afforded **18** in high yields.

Coupling of **13** and the iodoalkyne **18** led to the heterotetramer **19** and the homotetramer **20** (*Scheme 2*) in yields of 50 and 30%, respectively. The Me_3SiC group of **19** was cleaved under the same conditions as the one of **16**, yielding 99% of the tetramer **21**. *C*-Silylation of **21** with 2 equiv. each of (*t*-Bu)Me_2SiOTf and $(Me_3Si)_2NK$ in THF yielded

Scheme 2



a) CuI, $[PdCl_2(PhCN)_2]$, $P(fur)_3$, $(i\text{-}Pr)_2NH$, DMSO, 50°; **19** (50%), **20** (30%). *b*) NaOH, MeOH, 48°; 99%. *c*) Morpholine, I_2, toluene, 45°; 99%. *d*) (*t*-Bu)Me_2SiOTf, $(Me_3Si)_2NK$, THF, −78°; 98%. *e*) *t*-BuOK, MeOH, 40°; **24** (65%), **23** (14%). *f*) CuI, $[Pd(PPh_3)_3]$, Et_3N, 50°; **25** (51%), **26** (21%).

only 50% of the tetramer **23**, but the yield was increased to 98%[3]), when 5 equiv. each of silylating reagent and base were used. The Et_3Si group of **23** was selectively removed with *t*-BuOK in MeOH, leading to 65% of **24**.

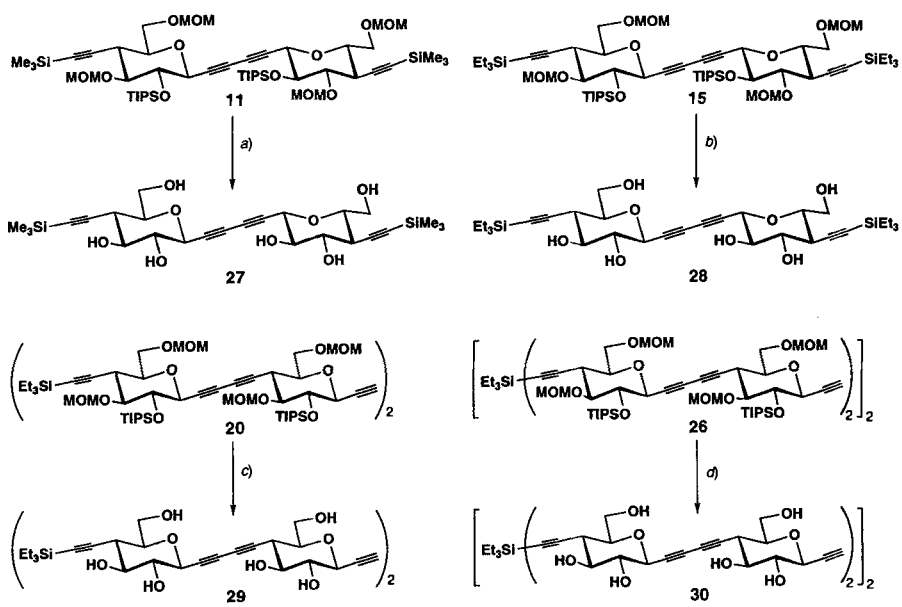
Coupling of **24** with the iodoalkyne **22** gave 51% of the heterooctamer **25** besides 21% of the homooctamer **26**, which again results from dimerization of the iodoalkyne.

Iodination of **21** to **22** with 10 equiv. of I_2 and 20 equiv. of morpholine – conditions which had led to a high yield of **10**, **14**, and **18** – led only to 70% conversion. Higher temperature and longer reaction times did not enhance the yield, but using 15 and 30 equiv. of I_2 and base, respectively, gave **22** in 99% yield.

To evaluate the stability of these acetylenosaccharides towards the conditions of deprotection, we studied the de-*O*-silylation and demethoxymethylation of the homo-oligosaccharides and then the sequential C- and O-desilylation and demethoxymethylation of the heterooligosaccharides.

Methanolic HCl in MeOH/THF led to parallel *O*-desilylation and demethoxymethylation of the homodimers **11** and **15** to give **27** and **28**, respectively, in high yields (*Scheme 3*).

Scheme 3



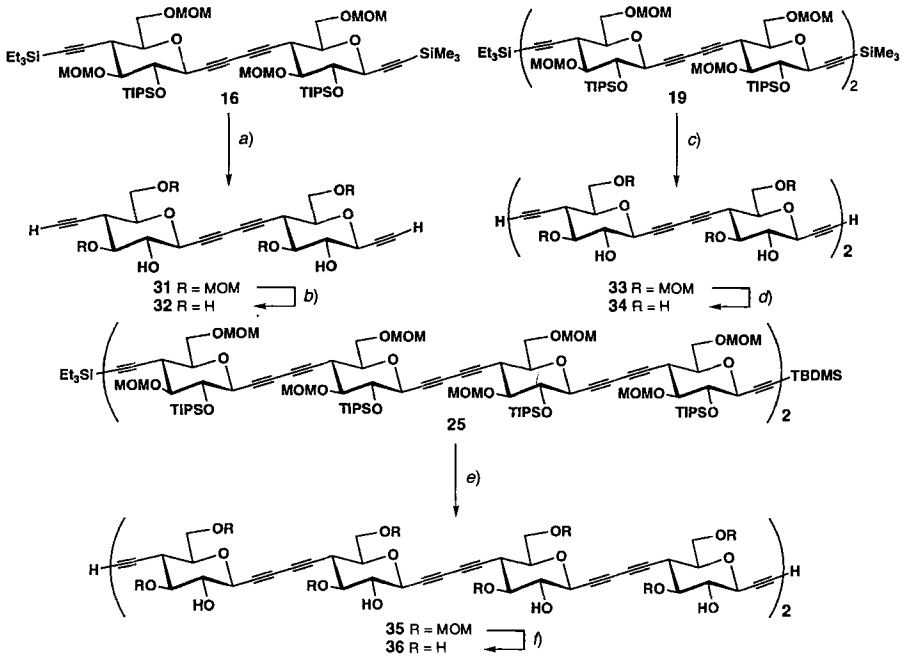
a) 0.3N HCl, MeOH/THF 1:1, reflux; 95%. *b*) As *a*); 98%. *c*) As *a*); 99%. *d*) As *a*); 82%.

3). Similarly, **20** and **26** were deprotected to **29** and **30**, respectively (*Scheme 3*). The $Me_3SiC{\equiv}C$ and $Et_3SiC{\equiv}C$ groups were stable under these conditions.

Treatment of the heterodimer **16** with Bu_4NF in THF removed all silyl groups and yielded 97% of **31**, which was completely deprotected by HCl/MeOH to afford **32** (95%). Similarly, the fully deprotected tetramer **34** and octamer **36** were obtained in 87 and 90%

[3]) The temperature should be kept at −78°; at −50°, the mixture turned brown and the product did not migrate on TLC, not even with MeOH as the mobile phase.

Scheme 4



a) $Bu_4NF \cdot 3\ H_2O$, THF, 0°; 97%. *b*) 0.3N HCl, MeOH/THF 1:1, reflux; 95%. *c*) As *a*); 93%. *d*) As *b*); 93%. *e*) As *a*); 96%. *f*) As *b*); 94%.

yield, respectively, by desilylation (→ **33** and **35**, resp.), and acidic hydrolysis of **19** and **25** (*Scheme 4*). The dimer **32** is soluble in H_2O or MeOH, whereas the tetramer **34** and the octamer **36** are hardly, if at all, soluble in these solvents[4]).

A priori, protection of the OH groups of **36**, bis-trimethylsilylation of the ethynyl groups and repetition of the combination of the regioselective deprotection with $AgNO_2$/KCN and the introduction/regioselective removal of the Et_3Si and (*t*-Bu)Me_2Si groups should give access to the next higher acetylenosaccharides. While the high yields of the deprotection, and the stability of the products augur well for such an undertaking, the large number of steps and the unsatisfactory yields of the cross coupling show that improvement of the methodology is required for a practicable synthesis of the higher oligomers.

MALDI-MS shows the molecular peaks of the protected and deprotected dimers to octamers at $[M + Na]^+$. Iodination shifts the H–C(3) signal downfield by *ca.* 0.1 ppm, and the C(1) signal upfield by *ca.* 75 ppm in the NMR spectra; the corresponding *d*'s of **10**, **14**, **18**, and **22** are found at 4.04, 4.07, 4.06, and 4.06 ppm, and the *s*'s at 5.81, 5.70, 6.00, and 6.30 ppm, respectively. The ^{13}C signals of the butadiynediyl moiety were assigned as described [2]. The interpretation of the ^1H-NMR spectra of the tetramer **21** is based on a 2D HOHAHA spectrum. The sharp *t* at 2.73 ppm (J = 10.2 Hz) is assigned to H–C(8_D)[5]), the broad *t*, at 2.81 ppm integrating for 2 H (J = 10.5 Hz) to H–C(8_B) and H–C(8_C), and the broad *t* at 2.83 ppm (J = 10.5 Hz) to H–C(6_A). The broadening of the H–C(8_B)

[4]) So far, only qualitative data have been obtained.

[5]) The sugar units of heterotetramers and heterooctamers are marked with A, B, C, *etc.*, starting from the extreme propargylic ether end and those of homooctamers similarly starting from the most central sugar unit.

and H–C(8_C) signals is due to a long-range coupling through the butadiynediyl fragment ($J \approx 0.5$ Hz). Similar relative shifts are observed for H–C(6) (2.83 ppm) and H–C(8) (2.73 ppm) of the dimer **17**. The same trend is seen for the H–C(3_A) and H–C(5_B), H–C(5_C), and H–C(5_D) signals of **21**. H–C(3_A) couples with the acetylenic H–C(1) and appears at 3.95 ppm as a *dd* ($J = 9.2$, 2.2 Hz). The broad *d*'s at 3.99 ppm integrating for 2 H ($J = 9.0$ Hz) are assigned to H–C(5_B) and H–C(5_C), whereas H–C(5_D) appears as a *d* ($J = 8.9$ Hz) at 4.00 ppm; again, a slight downfield shift of H–C(5_{B-D}) is observed in the dimer **17**. H–C(5') of **17** linked to the butadiynediyl group, appears at 4.00 ppm and H–C(3), linked to the terminal ethynyl group, appears at 3.93 ppm. The large coupling constants J(3,4) (9.2–8.9 Hz), J(4,5) (8.6–8.2 Hz), J(5,6) (10.1–9.8 Hz), and J(6,7) (10.5–10.2 Hz), indicate a $^4C_1$ conformation and the equatorial position of all substituents of the tetrahydropyran rings.

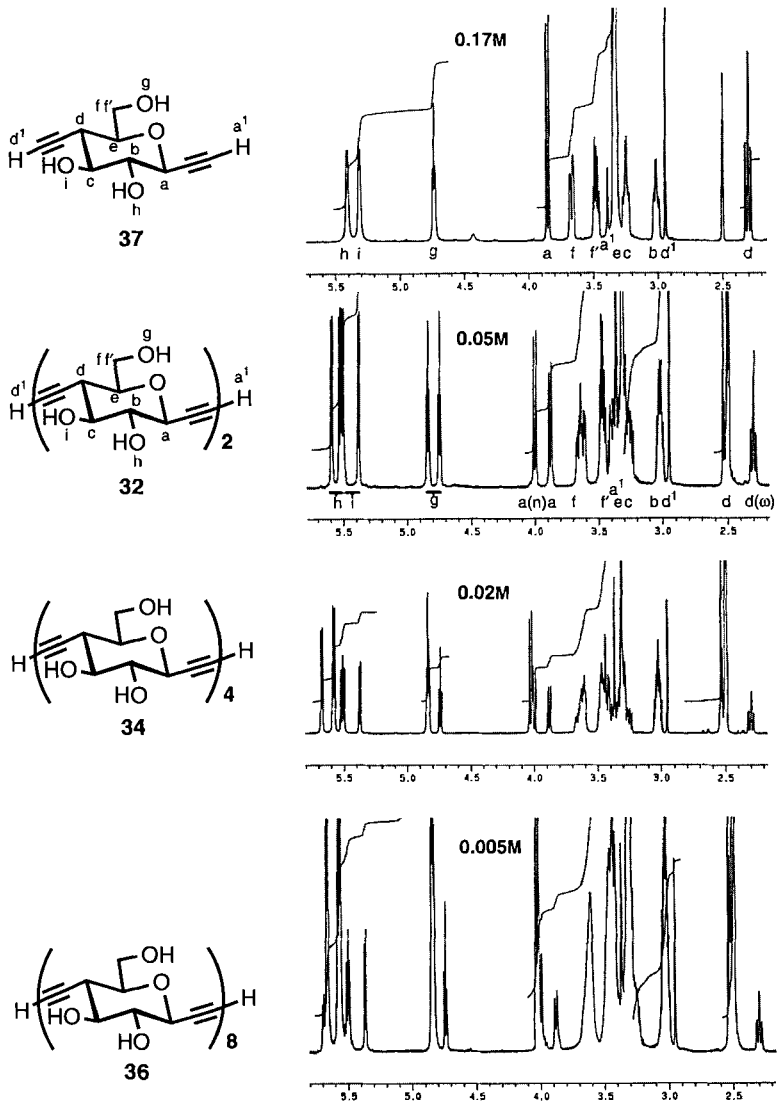


Figure. *500-MHz ^{1}H-NMR Spectra* ((D$_6$)DMSO) *of the dimer* **32**, *tetramer* **34**, *and octamer* **36**, *compared to the one of the monomer* **37**

The ^{13}C-NMR spectrum of the tetramer **21** shows two signals corresponding to C(6_A), C(8_B), C(8_C), and C(8_D): C(6_A), C(8_B), and C(8_C) appear at 37.36 ppm and C(8_D) at 37.91 ppm. Similarly, C(5_B), C(5_C), and C(5_D) appear at 72.26 ppm, and C(3_A) at 71.75 ppm. The ^{1}H and ^{13}C signals of the heterotetramers were assigned by comparison to those of **21**. The structure of heterooctamers is further evidenced by the ^{1}H- and ^{13}C-NMR spectra, which display similar patterns as those of the tetramer **23** with the difference of the integration. The signals of the H–C groups linked to the butadiynediyl moiety typically resonate at 2.80–2.73 ppm and integrate for eight H, in keeping with the presence of eight tetrahydropyranyl units. In the ^{1}H-NMR spectra ((D$_6$)DMSO) of the fully deprotected oligomers, the secondary OH groups appear as *d*'s (J = 7.0–5.6 Hz) and the primary ones as *t*'s (J = 5.8–5.4 Hz); they exchange with D_2O. The C–H groups linked to the alkyne or to the butadiynediyl groups show a large coupling constant ($J \approx 9.0$ Hz). H–C(1), being part of a propargylic ether moiety, resonates at higher field (3.37–3.35 ppm) than H–C≡C–C(8) (2.95–2.94 ppm). In the ^{1}H-NMR spectrum of **32**, H–C(8) and H–C(10′) resonate at 3.67–3.61 ppm (J(8,7) = J(10′,9′) = 1.8 Hz), whereas H′–C(8) and H′–C(10′) are found at 3.49–3.43 ppm (J(8,7) = J(10′,9′) = 5.6 Hz). If H_{pro}-*R* is more shielded, the rotamer population is *gg*/*gt* = 53:47, otherwise, *gg*/*tg* = 68:32.

A comparison of the ^{1}H-NMR spectra (*Fig.*) of the fully deprotected monomer to octamer, at the single concentrations, at which these spectra have been measured, shows no evidence for association of these compounds.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [2]. MALDI at 20–21.5 kV [19].

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**3**). At 20°, $CH_2(OMe)_2$ (150 ml), P_2O_5 (5 g), and *Celite* (5 g) were added to a soln. of **2** (8 g, 0.016 mol) in CH_2Cl_2 (10 ml). After stirring for 20 h, filtration through silica gel and evaporation gave **3** (8.8 g, 94%). Solid. R_f (AcOEt/hexane 1:9) 0.47. M.p. 71°. $[\alpha]_D^{25} = -255.7$ (c = 0.7, $CHCl_3$). IR ($CHCl_3$): 3007*w*, 2959*s*, 2929*s*, 2867*m*, 2175*w*, 1465*m*, 1408*w*, 1374*w*, 1290*w*, 1251*s*, 1151*s*, 1097*m*, 1065*m*, 1040*s*, 941*w*, 918*m*, 883*m*, 853*s*, 846*s*, 654*w*, 610*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.99 (*d*, J = 5.6, C*H*OMe); 4.76 (*d*, J = 5.9, C*H*OMe); 4.68 (*s*, CH_2OMe); 3.93 (*d*, J = 9.3, H–C(3)); 3.90 (*dd*, J = 11.4, 2.1, H–C(8)); 3.83 (*dd*, J = 11.3, 6.4, H′–C(8)); 3.73 (*dd*, J = 9.1, 8.3, H–C(4)); 3.52 (*ddd*, J = 10.4, 6.4, 2.1, H–C(7)); 3.42 (*dd*, J = 10.2, 8.2, H–C(5)); 3.47 (*s*, MeO); 3.39 (*s*, MeO); 2.57 (*t*, J = 10.3, H–C(6)); 1.30–1.03 (*m*, (i-Pr)$_3$Si); 0.14 (*s*, 2 Me$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.58 (*s*); 102.42 (*s*); 98.16 (*t*); 96.64 (*t*); 91.30 (*s*); 88.86 (*s*); 82.48 (*d*); 78.71 (*d*); 74.98 (*d*); 72.48 (*d*); 67.30 (*t*); 56.78 (*q*); 55.32 (*q*); 37.88 (*d*); 18.27 (6*q*); 13.84 (3*d*); –0.12 (3*q*); –0.43 (3*q*). CI-MS: 602 (100, $[M + NH_4]^+$). Anal. calc. for $C_{29}H_{56}O_6Si_3$ (585.02): C 59.54, H 9.41; found: C 59.73, H 9.64.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**4**). At 24°, a soln. of MeSNa (978 mg, 13.97 mmol) in toluene (5 ml) was added dropwise to a soln. of **3** (1.166 g, 1.99 mmol) in toluene (10 ml). After stirring the mixture at 80° for 12 h, it was cooled to 20° and filtered through cotton. The filtrate was washed with brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:24) gave **3** (376 mg, 32%) and **4** (511 mg, 50%). Oils. R_f (AcOEt/hexane 1:4) 0.57. $[\alpha]_D^{25} = -48.8$ (c = 0.5, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3007*m*, 2947*s*, 2897*s*, 2867*s*, 2174*w*, 1613*w*, 1465*m*, 1406*w*, 1391*w*, 1368*w*, 1349*w*, 1291*m*, 1251*s*, 1151*s*, 1097*s*, 1067*s*, 1040*s*, 1020*s*, 950*w*, 919*w*, 883*m*, 845*s*, 645*m*, 591*w*, 542*w*, 515*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.01 (*d*, J = 5.9, C*H*OMe); 4.77 (*d*, J = 5.8, C*H*OMe); 4.68 (*s*, CH_2OMe); 3.96 (*dd*, J = 9.2, 2.2, H–C(3)); 3.88 (*dd*, J = 11.4, 2.4, H–C(8)); 3.83 (*dd*, J = 11.6, 4.9, H′–C(8)); 3.75 (*dd*, J = 9.1, 8.1, H–C(4)); 3.56 (*ddd*, J = 10.5, 4.7, 2.5, H–C(7)); 3.53 (*dd*, J = 10.3, 8.0, H–C(5)); 3.47 (*s*, MeO); 3.39 (*s*, MeO); 2.76 (*t*, J = 10.3, H–C(6)); 2.45 (*d*, J = 2.2, H–C(1)); 1.30–1.05 (*m*, (i-Pr)$_3$Si); 0.15 (*s*, Me$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.50 (*s*); 98.08 (*t*); 96.66 (*t*); 88.97 (*s*); 82.21 (*d*); 81.09 (*d*); 78.74 (*d*); 74.99 (*s*); 74.98 (*d*); 71.80 (*d*); 67.63 (*t*); 56.78 (*q*); 55.33 (*q*); 37.84 (*d*); 18.25 (6*q*); 13.78 (3*d*); –0.14 (3*q*). CI-MS: 530 (100, $[M + NH_4]^+$). Anal. calc. for $C_{26}H_{48}O_6Si_2$ (512.44): C 60.89, H 9.43; found: C 61.15, H 9.27.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**5**) [2]. At 24°, a soln. of $AgNO_2$ (71 mg, 0.46 mmol) in MeOH/H_2O 3:1 (4 ml) was added dropwise to a soln. of **3** (120 mg, 0.23 mmol) in MeOH (2 ml). After 2 h, the white

mixture was cooled to 0°, treated with a sat. aq. soln. of KCN (1 ml), *carefully neutralized* with 2N HCl (*ca.* 2 ml), washed with H_2O, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **5** (85 mg, 81%). Oil. R_f (AcOEt/hexane 1:1) 0.59.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-6-*C*-[2-(triethylsilyl)ethynyl]-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**6**). At −78°, 1.3M BuLi in hexane (0.43 ml, 0.56 mmol) was added dropwise to a soln. of **5** (192 mg, 0.37 mmol) in THF (4 ml). The soln. was stirred for 30 min, treated with Et_3SiCl (0.12 ml, 0.71 mmol), stirred for 5 min, neutralised with 0.1N HCl (0.5 ml), diluted with AcOEt, washed with H_2O, and dried ($MgSO_4$). Evaporation gave **6** (230 mg, 98%). Solid. R_f (AcOEt/hexane 1:14) 0.35. M.p. 65°. $[\alpha]_D^{25} = -172.2$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 2990*s*, 2950*s*, 2890*s*, 2160*w*, 1475*m*, 1425*w*, 1375*w*, 1350*w*, 1300*w*, 1275*s*, 1200*s*, 1175*s*, 1155*s*, 1065*m*, 1025*m*, 1005*m*, 875*m*, 665*m*, 615*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.00 (*d*, $J = 5.5$, C*H*OMe); 4.79 (*d*, $J = 5.5$, C*H*OMe); 4.68 (*s*, CH_2OMe); 3.95 (*d*, $J = 9.3$, H–C(3)); 3.90 (*dd*, $J = 11.1$, 1.9, H–C(8)); 3.83 (*dd*, $J = 11.0$, 5.0, H′–C(8)); 3.72 (*dd*, $J = 9.2$, 8.1, H–C(4)); 3.50 (*ddd*, $J = 10.5$, 5.0, 1.9, H–C(7)); 3.48 (*dd*, $J = 10.3$, 7.9, H–C(5)); 3.45 (*s*, MeO); 3.38 (*s*, MeO); 2.74 (*t*, $J = 10.4$, H–C(6)); 1.30–1.00 (*m*, (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.8$, (*Me*CH$_2$)$_3$Si); 0.60 (*q*, $J = 7.7$, (MeC*H*$_2$)$_3$Si); 0.15 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.70 (*s*); 102.46 (*s*); 98.11 (*t*); 96.70 (*t*); 91.24 (*s*); 86.50 (*s*); 82.65 (*d*); 78.83 (*d*); 74.77 (*d*); 72.43 (*d*); 67.73 (*t*); 56.75 (*q*); 55.32 (*q*); 37.01 (*d*); 18.29 (6*q*); 13.80 (3*d*); 7.42 (3*q*); 4.31 (3*t*); −0.42 (3*q*). CI-MS: 602 (100, $[M + NH_4]^+$). Anal. calc. for $C_{29}H_{56}O_6Si_3$ (585.02): C 59.54, H 9.41; found: C 59.73, H 9.64.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-6-*C*-[2-(triethylsilyl)ethynyl]-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (7). A soln. of **3** (1.1 g, 1.75 mmol) in MeOH (40 ml) was treated with 0.1N NaOH in MeOH (10 ml), stirred at 25° for 4 h, neutralised with 2N HCl (*ca.* 2 ml), diluted with AcOEt, washed with H_2O, and dried ($MgSO_4$). Evaporation gave 7 (963 mg, 99%). Oil. R_f (AcOEt/hexane 1:14) 0.23. $[\alpha]_D^{25} = -242.4$ ($c = 1.25$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3007*m*, 2959*s*, 2890*s*, 2869*s*, 2171*w*, 1602*w*, 1464*m*, 1414*w*, 1368*w*, 1291*w*, 1151*s*, 1097*s*, 1067*s*, 1040*s*, 1020*s*, 949*w*, 919*m*, 883*m*, 653*m*, 592*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.00 (*d*, $J = 5.5$, C*H*OMe); 4.80 (*d*, $J = 5.5$, C*H*OMe); 4.67 (*s*, CH_2OMe); 3.95 (*dd*, $J = 9.2$, 2.1, H–C(3)); 3.88 (*dd*, $J = 11.8$, 1.9, H–C(8)); 3.82 (*dd*, $J = 11.9$, 5.0, H′–C(8)); 3.78 (*dd*, $J = 9.1$, 8.2, H–C(4)); 3.54 (*ddd*, $J = 10.3$, 5.0, 1.9, H–C(7)); 3.51 (*dd*, $J = 10.2$, 8.2, H–C(5)); 3.46 (*s*, MeO); 3.38 (*s*, MeO); 2.76 (*t*, $J = 10.3$, H–C(6)); 2.45 (*d*, $J = 2.1$, H–C(1)); 1.30–1.00 (*m*, (i-Pr)$_3$Si); 1.00 (*t*, $J = 7.8$, (*Me*CH$_2$)$_3$Si); 0.60 (*q*, $J = 7.7$, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.61 (*s*); 98.04 (*t*); 96.72 (*t*); 86.59 (*s*); 82.38 (*d*); 81.11 (*d*); 78.86 (*d*); 74.96 (*d*); 74.75 (*s*); 71.74 (*d*); 67.76 (*t*); 56.73 (*q*); 55.32 (*q*); 37.97 (*d*); 18.28 (6*q*); 13.74 (3*d*); 7.42 (3*q*); 4.31 (3*t*). CI-MS: 572 (100, $[M + NH_4]^+$). Anal. calc. for $C_{29}H_{54}O_6Si_2$ (554.92): C 62.77, H 9.81; found: C 62.53, H 9.63.

*3,7-Anhydro-1-*C*-[(*tert*-butyl)dimethylsilyl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-6-*C*-[2-(triethylsilyl)ethynyl]-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**8**). At −78°, 0.4N $(Me_3Si)_2NK$ (0.43 ml, 0.21 mmol) in hexane was added dropwise to a soln. of 7 (80 mg, 0.14 mmol) in THF (2 ml). The soln. was stirred for 30 min, treated with (*t*-Bu)Me_2SiOTf (49 µl, 0.21 mmol), stirred for 4 h, neutralised with 0.1N HCl (0.1 ml), diluted with AcOEt, washed with H_2O, and dried ($MgSO_4$). Evaporation gave **8** (94 mg, 98%). Solid. R_f (AcOEt/hexane 1:14) 0.35. M.p. 78°. $[\alpha]_D^{25} = -33.7$ ($c = 0.45$, $CHCl_3$). IR ($CHCl_3$): 3006*w*, 2956*s*, 2867*s*, 2172*w*, 1463*m*, 1413*w*, 1390*w*, 1354*w*, 1290*w*, 1251*m*, 1151*s*, 1097*s*, 1069*s*, 1024*s*, 939*w*, 919*m*, 883*m*, 840*m*, 826*m*, 654*w*, 582*w*, 533*w*, 514*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.00 (*d*, $J = 5.5$, C*H*OMe); 4.79 (*d*, $J = 5.5$, C*H*OMe); 4.67 (*s*, CH_2OMe); 3.96 (*d*, $J = 9.0$, H–C(3)); 3.90 (*dd*, $J = 11.0$, 1.9, H–C(8)); 3.80 (*dd*, $J = 11.0$, 5.1, H′–C(8)); 3.72 (*dd*, $J = 9.1$, 7.9, H–C(4)); 3.57 (*ddd*, $J = 10.3$, 5.2, 1.9, H–C(7)); 3.50 (*dd*, $J = 10.1$, 8.0, H–C(5)); 3.45 (*s*, MeO); 3.38 (*s*, MeO); 2.72 (*t*, $J = 10.2$, H–C(6)); 1.30–1.05 (*m*, (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.8$, (*Me*CH$_2$)$_3$Si); 0.91 (*s*, *t*-Bu); 0.58 (*q*, $J = 7.7$, (MeC*H*$_2$)$_3$Si); 0.08 (*s*, MeSi); 0.07 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.89 (*s*); 103.53 (*s*); 97.97 (*t*); 96.58 (*t*); 89.36 (*s*); 86.37 (*s*); 82.57 (*d*); 78.68 (*d*); 74.68 (*d*); 72.46 (*d*); 67.68 (*t*); 56.69 (*q*); 55.21 (*q*); 37.96 (*d*); 26.07 (3*q*); 18.26 (6*q*); 16.51 (*s*); 13.76 (3*d*); 7.43 (3*q*); 4.33 (3*t*); −4.80 (*q*); −4.89 (*q*). CI-MS: 686 (100, $[M + NH_4]^+$). Anal. calc. for $C_{35}H_{68}O_6Si_3$ (669.18): C 62.82, H 10.24; found: C 62.84, H 10.11.

*3,7-Anhydro-1-*C*-[(*tert*-butyl)dimethylsilyl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**9**). A soln. of **8** (60 mg, 0.09 mmol) in MeOH (1 ml) was treated with 1N NaOMe in MeOH (0.1 ml), stirred at 50° for 12 h, neutralised with 1N HCl (*ca.* 0.2 ml), diluted with AcOEt, washed with H_2O, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **9** (40 mg, 80%). Oil. R_f (AcOEt/hexane 1:14) 0.20. $[\alpha]_D^{25} = -50.9$ ($c = 1.5$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3004*w*, 2947*s*, 2891*s*, 2866*s*, 2178*w*, 1464*m*, 1410*w*, 1390*w*, 1364*w*, 1348*w*, 1290*w*, 1251*m*, 1151*s*, 1098*s*, 1067*s*, 1024*s*, 939*w*, 918*m*, 883*m*, 840*m*, 826*m*, 653*m*, 590*w*, 538*w*, 520*w*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, $J = 6.2$, C*H*OMe); 4.75 (*d*, $J = 6.2$, C*H*OMe); 4.68 (*s*, CH_2OMe); 3.96 (*d*, $J = 9.0$, H–C(3)); 3.88 (*dd*, $J = 11.2$, 2.1, H–C(8)); 3.83 (*dd*, $J = 11.2$, 5.0, H′–C(8)); 3.75 (*dd*, $J = 9.1$, 7.9, H–C(4)); 3.56–3.52 (*m*, H–C(7)); 3.51 (*dd*, $J = 10.1$, 7.9, H–C(5)); 3.45 (*s*, MeO); 3.38 (*s*, MeO); 2.69 (*td*, $J = 10.1$, 2.3, H–C(6)); 2.17 (*d*, $J = 2.3$, H–C(2′)); 1.31–1.05 (*m*, (i-Pr)$_3$Si); 0.92 (*s*, *t*-Bu); 0.08 (*s*, MeSi); 0.07 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.39 (*s*); 98.01

(*t*); 96.49 (*t*); 89.53 (*s*); 82.94 (*d*); 81.56 (*d*); 78.40 (*d*); 74.87 (*d*); 72.46 (*s*); 72.15 (*d*); 67.41 (*t*); 56.58 (*q*); 55.23 (*q*); 36.66 (*d*); 26.06 (3*q*); 18.23 (6*q*); 16.51 (*s*); 13.79 (3*d*); −4.83 (*q*); −4.91 (*q*). CI-MS: 572 (100, $[M + NH_4]^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-iodo-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**10**). At 0°, a soln. of morpholine (18.86 ml, 216.6 mmol) in toluene (25 ml) was added dropwise to a soln. of I_2 (27.5 g, 108.3 mmol) in toluene (30 ml). The mixture was stirred at 45° for 45 min, treated with a soln. of **4** (3.7 g, 7.22 mmol) in toluene (30 ml), stirred for further 4 h at 45°, cooled to 20°, and filtered through cotton. The filtrate was treated with sat. aq. Na_2SO_3 soln. (10 ml), stirred for 30 min, washed with brine, and dried ($MgSO_4$). Evaporation gave **10** (4.54 g, 98%). Solid. R_f (AcOEt/hexane 1:9) 0.46. M.p. 85°. $[\alpha]_D^{25} = -215$ (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 3100*m*, 3040*s*, 2980*s*, 2960*s*, 2280*w*, 1650*w*, 1510*m*, 1440*w*, 1410*w*, 1390*w*, 1330*w*, 1300*m*, 1291*m*, 1200*s*, 1140*s*, 1110*s*, 1080*s*, 1060*s*, 990*s*, 965*m*, 925*m*, 880*s*, 850*m*, 690*w*, 660*w*, 625*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, *J* = 5.9, C*H*OMe); 4.76 (*d*, *J* = 5.9, C*H*OMe); 4.67 (*s*, CH_2OMe); 4.05 (*d*, *J* = 9.2, H–C(3)); 3.87 (*dd*, *J* = 10.9, 2.1, H–C(8)); 3.82 (*dd*, *J* = 11.0, 4.1, H′–C(8)); 3.75 (*dd*, *J* = 9.2, 8.3, H–C(4)); 3.53 (*ddd*, *J* = 10.4, 4.1, 2.1, H–C(7)); 3.50 (*dd*, *J* = 10.2, 8.4, H–C(5)); 3.47 (*s*, MeO); 3.39 (*s*, MeO); 2.75 (*t*, *J* = 10.3, H–C(6)); 1.17–1.00 (*m*, (i-Pr)$_3$Si); 0.15 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.36 (*s*); 98.18 (*t*); 96.67 (*t*); 91.31 (*s*); 89.00 (*s*); 82.19 (*d*); 78.73 (*d*); 75.32 (*d*); 73.25 (*d*); 67.49 (*t*); 56.81 (*q*); 55.35 (*q*); 37.82 (*d*); 18.20 (6*q*); 13.87 (3*d*); 5.81 (*s*); −0.13 (3*q*). CI-MS: 656 (100, $[M + NH_4]^+$). Anal. calc. for $C_{26}H_{47}IO_6Si$ (638.7): C 48.89, H 7.42; found: C 49.18, H 7.39.

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1S)-1,5-anhydro-4-deoxy-3,6-bis-*O*-(methoxymethyl)-2-*O*-(triisopropylsilyl)-4-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glucitol}* (**11**) *and 3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-8-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**12**). At 20°, CuI (29 mg, 0.157 mmol), $[PdCl_2(PhCN)_2]$ (58.4 mg, 0.157 mmol), tri(fur-2-yl)phosphine ((fur)$_3$P; 71 mg, 0.31 mmol), and (i-Pr)$_2$NH (2.23 ml, 15.78 mmol) were added to a soln. of **10** (3.582 g, 5.57 mmol) and **5** (2.60 g, 5.26 mmol) in DMSO (852.6 ml). The soln. was stirred for 4 h at 50°, neutralised with 2N HCl (*ca.* 3 ml), diluted with Et_2O, washed with H_2O, and dried ($MgSO_4$). Evaporation and FC (hexane/Et_2O 4:1) gave **12** (2.76 g, 53%) and **11** (1.77 g, 31%).

Data of **11**: Solid. R_f (AcOEt/hexane 1:5) 0.52. M.p. 115. $[\alpha]_D^{25} = -67.6$ (*c* = 0.25, $CHCl_3$). IR ($CHCl_3$): 2990*w*, 2946*m*, 2861*m*, 2174*w*, 1465*m*, 1366*w*, 1288*w*, 1251*w*, 1151*s*, 1096*m*, 1067*m*, 1040*s*, 1020*s*, 936*w*, 918*m*, 884*m*, 846*s*, 654*m*, 591*w*, 553*w*, 539*w*, 532*w*, 515*m*, 504*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, *J* = 5.9, C*H*OMe); 4.78 (*d*, *J* = 5.9, C*H*OMe); 4.67 (*s*, CH_2OMe); 4.03 (*d*, *J* = 8.7, H–C(1)); 3.85 (*dd*, *J* = 12.0, 1.9, H–C(6)); 3.78 (*dd*, *J* = 12.1, 4.9, H′–C(6)); 3.73 (*dd*, *J* = 8.6, 8.3, H–C(2)); 3.51 (*ddd*, *J* = 10.1, 4.8, 2.0, H–C(5)); 3.50 (*dd*, *J* = 9.9, 8.1, H–C(3)); 3.46 (*s*, MeO); 3.38 (*s*, MeO); 2.73 (*t*, *J* = 10.0, H–C(4)); 1.22–1.09 (*m*, (i-Pr)$_3$Si); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.43 (*s*); 97.96 (*t*); 96.68 (*t*); 88.97 (*s*); 82.05 (*d*); 78.65 (*d*); 77.12 (*s*); 74.68 (*d*); 72.35 (*d*); 70.73 (*s*); 67.65 (*t*); 56.72 (*q*); 55.28 (*q*); 37.68 (*d*); 18.24 (6*q*); 13.61 (3*d*); −0.13 (3*q*). FAB-MS: 991 ($[M - MeO]^+$). Anal. calc. for $C_{52}H_{94}O_{12}Si_4$ (1023.64): C 61.13, H 9.08; found: C 61.36, H 8.96.

Data of **12**: Solid. R_f (Et_2O/hexane 1:2) 0.38. M.p. 105°. $[\alpha]_D^{25} = -347.1$ (*c* = 0.35, $CHCl_3$). IR ($CHCl_3$): 3050*w*, 3007*m*, 2946*s*, 2892*m*, 2867*s*, 2259*w*, 2175*w*, 1604*w*, 1465*m*, 1367*w*, 1291*m*, 1264*m*, 1251*s*, 1151*s*, 1096*s*, 1066*s*, 1040*s*, 918*m*, 883*m*, 846*s*, 645*m*, 591*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, C*H*OMe); 4.89 (*d*, *J* = 6.1, C*H*OMe); 4.77 (*d*, *J* = 5.8, C*H*OMe); 4.72 (*d*, *J* = 6.1, C*H*OMe); 4.67 (*s*, CH_2OMe); 4.66 (*s*, CH_2OMe); 3.99 (*dd*, *J* = 9.1, 0.5, H–C(5′)); 3.90 (*d*, *J* = 9.3, H–C(3)); 3.85 (*dd*, *J* = 11.1, 2.0, H–C(10′)); 3.83 (*dd*, *J* = 11.5, 2.3, H–C(8)); 3.81 (*dd*, *J* = 11.1, 5.0, H′–C(10′)); 3.77 (*dd*, *J* = 11.4, 5.0, H′–C(8)); 3.73 (*dd*, *J* = 9.2, 8.2, H–C(4)); 3.71 (*dd*, *J* = 9.2, 8.5, H–C(6′)); 3.53 (*ddd*, *J* = 10.4, 4.9, 2.0, H–C(9′)); 3.51 (*dd*, *J* = 10.2, 8.1, H–C(5)); 3.49 (*ddd*, *J* = 10.3, 5.1, 2.4, H–C(7)); 3.47 (*dd*, *J* = 10.4, 8.7, H–C(7′)); 3.46 (*s*, MeO); 3.43 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 2.80 (br. *t*, *J* = 10.3, H–C(6)); 2.74 (*t*, *J* = 10.3, H–C(8′)); 1.11–1.09 (*m*, 2 (i-Pr)$_3$Si); 0.14 (*s*, 2 Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.32 (*s*); 102.13 (*s*); 98.09 (*t*); 97.95 (*t*); 97.66 (2*t*); 91.49 (*s*); 89.06 (*s*); 82.61 (*d*); 82.14 (*d*); 78.80 (*d*); 78.38 (*d*); 77.84 (*s*); 74.95 (*d*); 74.71 (*d*), 74.55 (*s*); 72.45 (*d*); 72.33 (*d*); 70.20 (*s*); 68.18 (*s*); 67.51 (*t*); 67.37 (*t*); 56.78 (*q*); 56.42 (*q*); 55.31 (2*q*); 37.80 (*d*); 37.47 (*d*); 18.21 (12*q*); 13.78 (3*d*); 13.71 (3*d*); −0.14 (3*q*); −0.44 (3*q*). FAB-MS: 991 ($[M - MeO]^+$).

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetrahydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**13**). As described for **5**, with $AgNO_2$ (3.80 g, 24.5 mmol), MeOH/H_2O 15:5 (20 ml), **12** (4.18 g, 4.09 mmol), MeOH (40 ml; after 2 h at 40°), sat. aq. NaCN soln. (2 ml), and 2N HCl (*ca.* 3 ml): **12** (400 mg, 10%) and **13** (1.78 g, 70%). Oil. R_f (AcOEt/hexane 1:4) 0.22. $[\alpha]_D^{25} = -74.6$ (*c* = 0.65, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3007*m*, 2946*s*, 2892*s*, 2867*s*, 2250*w*, 2180*w*, 1464*m*, 1367*m*, 1351*w*, 1291*m*, 1251*m*, 1151*s*, 1097*s*, 1066*s*, 1040*s*, 1023*s*, 938*m*, 918*m*, 883*s*, 846*s*, 645*m*, 609*w*, 519*w*, 534*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.96 (*d*, *J* = 6.1, C*H*OMe); 4.90 (*d*, *J* = 6.1, C*H*OMe); 4.83 (*d*, *J* = 6.2, C*H*OMe);

4.76 (*d*, *J* = 6.1, C*H*OMe); 4.67 (*s*, CH_2OMe); 4.66 (*s*, CH_2OMe); 4.00 (*dd*, *J* = 9.1, 0.5, H–C(5′)); 3.94 (*d*, *J* = 9.3, H–C(3)); 3.85 (*dd*, *J* = 11.2, 2.1, H–C(10′)); 3.83 (*dd*, *J* = 11.1, 4.8, H′–C(10′)); 3.82 (*dd*, *J* = 11.0, 2.1, H–C(8)); 3.76 (*dd*, *J* = 11.1, 4.5, H′–C(8)); 3.74 (*dd*, *J* = 9.2, 8.1, H–C(4)); 3.72 (*dd*, *J* = 9.2, 8.1, H–C(6′)); 3.54 (*ddd*, *J* = 10.4, 4.7, 2.1, H–C(9′)); 3.52 (*dd*, *J* = 10.2, 8.1, H–C(5)); 3.49 (*ddd*, *J* = 10.3, 4.6, 2.0, H–C(7)); 3.47 (*dd*, *J* = 10.2, 8.0, H–C(7′)); 3.44 (*s*, MeO); 3.43 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 2.81 (br. *t*, *J* = 10.3, H–C(6)); 2.71 (*td*, *J* = 10.3, 2.3, H–C(8′)); 2.19 (*d*, *J* = 2.4, H–C(2″)); 1.27–1.09 (*m*, 2 (i-Pr)$_3$Si); 0.14 (*s*, Me$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 102.13 (*s*); 98.03 (*t*); 97.91 (*t*); 96.63 (2*t*); 91.45 (*s*); 82.64 (2*d*); 81.19 (*d*); 78.62 (*d*); 78.34 (*d*); 77.87 (*s*); 74.90 (*s*); 74.69 (2*d*); 74.44 (*s*); 72.42 (*d*); 72.28 (*d*); 71.18 (*s*); 68.12 (*s*); 67.38 (2*t*); 56.58 (*q*); 56.36 (*q*); 55.25 (2*q*); 37.44 (*d*); 36.60 (*d*); 18.17 (6*q*); 13.73 (3*d*); 13.66 (3*d*); –0.48 (3*q*). FAB-MS: 919 ([*M* – MeOH]$^+$). Anal. calc. for $C_{49}H_{86}O_{12}Si_3$ (951.47): C 61.86, H 9.11; found: C 61.92, H 8.87.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-iodo-5,8-bis-*O*-(methoxymethyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**14**). As described for **10**, with morpholine (9.10 ml, 105 mmol) in toluene (10 ml), I_2 (12.38 g, 52.5 mmol) in toluene (10 ml), and **7** (1.94 g, 3.5 mmol) in toluene (20 ml): **14** (2.21 g, 93%). Solid. R_f (AcOEt/hexane 1:14) 0.24. M.p. 85°. $[\alpha]_D^{25} = -254$ (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 3007*w*, 2956*s*, 2890*s*, 2869*s*, 2171*w*, 1602*w*, 1464*m*, 1414*w*, 1363*w*, 1348*w*, 1291*w*, 1151*s*, 1096*s*, 1067*s*, 1023*s*, 949*w*, 940*w*, 919*m*, 884*m*, 654*w*, 606*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.99 (*d*, *J* = 5.5, C*H*OMe); 4.79 (*d*, *J* = 5.6, C*H*OMe); 4.67 (*s*, CH_2OMe); 4.07 (*d*, *J* = 9.3, H–C(3)); 3.90 (*dd*, *J* = 10.9, 1.8, H–C(8)); 3.83 (*dd*, *J* = 11.0, 4.9, H′–C(8)); 3.75 (*dd*, *J* = 9.2, 8.3, H–C(4)); 3.53 (*ddd*, *J* = 10.3, 4.9, 1.8, H–C(7)); 3.50 (*dd*, *J* = 10.2, 8.2, H–C(5)); 3.45 (*s*, MeO); 3.40 (*s*, MeO); 2.75 (*t*, *J* = 10.3, H–C(6)); 1.30–1.01 (*m*, (i-Pr)$_3$Si); 1.00 (*t*, *J* = 7.8, (*Me*CH$_2$)$_3$Si); 0.59 (*q*, *J* = 7.7, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.48 (*s*); 98.13 (*t*); 96.72 (*t*); 91.36 (*s*); 86.63 (*s*); 82.36 (*d*); 78.84 (*d*); 75.12 (*d*); 73.20 (*d*); 67.63 (*t*); 56.76 (*q*); 55.35 (*q*); 37.97 (*d*); 18.22 (6*q*); 13.83 (3*d*); 7.42 (3*q*); 5.70 (*s*); 4.31 (3*t*). CI-MS: 698 (100, [*M* + NH_4]$^+$).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-1,5-anhydro-4-deoxy-3,6-bis-*O*-(methoxymethyl)-4-*C*-[2-(triethylsilyl)ethynyl]-2-*O*-(triisopropylsilyl)-*D*-glucitol}* (**15**) *and 3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetrahydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**16**). As described for **11** and **12**, with CuI (15.1 mg, 0.078 mmol), [$PdCl_2$(PhCN)$_2$] (30.5 mg, 0.078 mmol), (fur)$_2$P (37.5 mg, 0.156 mmol), (i-Pr)$_2$NH (1.13 ml, 7.8 mmol), **14** (1.809 g, 2.6 mmol) **4** (1.36 g, 2.6 mmol), and DMSO (26 ml). Neutralisation with 2N HCl (*ca.* 1 ml). FC (AcOEt/hexane 1:24) gave **15** (441 mg, 15%) as an oil and **16** (1.9 g, 67%) as a white solid.

Data of **15**: R_f (AcOEt/hexane 1:5) 0.63. $[\alpha]_D^{25} = -58.3$ (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 2951*s*, 2869*s*, 2171*w*, 1464*m*, 1366*m*, 1344*m*, 1289*m*, 1150*s*, 1097*s*, 1017*s*, 949*m*, 917*m*, 884*m*, 839*w*, 653*m*, 583*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.00 (*d*, *J* = 5.6, C*H*OMe); 4.80 (*d*, *J* = 5.6, C*H*OMe); 4.66 (*s*, CH_2OMe); 4.04 (*d*, *J* = 8.8, H–C(1)); 3.88 (*dd*, *J* = 11.0, 2.0, H–C(6)); 3.77 (*dd*, *J* = 11.1, 5.1, H′–C(6)); 3.73 (*dd*, *J* = 8.8, 8.0, H–C(2)); 3.55 (*ddd*, *J* = 10,1, 5,0, 2.1, H–C(5)); 3.50 (*dd*, *J* = 9.9, 8.0, H–C(3)); 3.44 (*s*, MeO); 3.37 (*s*, MeO); 2.73 (*t*, *J* = 10.0, H–C(4)); 1.29–1.05 (*m*, (i-Pr)$_3$Si); 0.98 (*t*, *J* = 7.7 (*Me*CH$_2$)$_3$Si); 0.59 (*q*, *J* = 7.8, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.59 (*s*); 97.91 (*t*); 96.72 (*t*); 86.58 (*s*); 82.24 (*d*); 78.77 (*d*); 77.13 (*s*); 74.52 (*d*); 72.27 (*d*); 70.72 (*s*); 67.76 (*t*); 56.68 (*q*); 55.26 (*q*); 37.81 (*d*); 18.21 (6*q*); 13.56 (3*d*); 7.41 (3*q*); 4.30 (3*t*). FAB-MS: 1075 ([*M* – MeO]$^+$). Anal. calc. for $C_{58}H_{106}O_{12}Si_4$ (1107.81): C 62.88, H 9.64; found: C 62.74, H 9.66.

Data of **16**: R_f (AcOEt/hexane 1:5) 0.46. M.p. 111°. $[\alpha]_D^{25} = -68.3$ (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): 2948*s*, 2980*s*, 2868*s*, 2259*w*, 2172*w*, 1465*m*, 1413*w*, 1368*m*, 1350*m*, 1289*m*, 1251*m*, 1152*s*, 1097*s*, 1066*s*, 1040*s*, 1020*s*, 940*m*, 919*m*, 883*s*, 846*s*, 655*m*, 608*w*, 591*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.99 (*d*, *J* = 5.5, C*H*OMe); 4.90 (*d*, *J* = 6.1, C*H*OMe); 4.80 (*d*, *J* = 5.5, C*H*OMe); 4.72 (*d*, *J* = 6.0, C*H*OMe); 4.66 (*s*, 2 CH_2OMe); 4.01 (*dd*, *J* = 9.2, 0.5, H–C(5′)); 3.93 (*d*, *J* = 9.3, H–C(3)); 3.88 (*dd*, *J* = 11.1, 1.9, H–C(10′)); 3.82 (*dd*, *J* = 11.1, 2.1, H–C(8)); 3.80 (*dd*, *J* = 11.1, 4.9, H′–C(10′)); 3.76 (*dd*, *J* = 11.2, 4.7, H′–C(8)); 3.73 (*dd*, *J* = 9.3, 8.2, H–C(4)); 3.71 (*dd*, *J* = 9.2, 8.1, H–C(6′)); 3.53 (*ddd*, *J* = 10.5, 5.0, 1.8, H–C(9′)); 3.52–3.50 (*m*, H–C(7)); 3.49 (*dd*, *J* = 10.1, 8.1, H–C(5)); 3.47 (*dd*, *J* = 10.2, 8.0, H–C(7′)); 3.45 (*s*, MeO); 3.43 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 2.80 (br. *t*, *J* = 10.2, H–C(6)); 2.73 (*t*, *J* = 10.2, H–C(8′)); 1.27–1.05 (*m*, 2 (i-Pr)$_3$Si); 0.97 (*t*, *J* = 7.8, (*Me*CH$_2$)$_3$Si); 0.54 (*q*, *J* = 7.8, (MeCH_2)$_3$Si); 0.14 (*s*, Me$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.47 (*s*); 102.14 (*s*); 98.03 (*t*); 97.93 (*t*); 97.67 (2*t*); 91.45 (*s*); 86.67 (*s*); 82.61 (*d*); 82.31 (*d*); 78.91 (*d*); 78.38 (*d*); 77.79 (*s*); 74.71 (2*d*); 74.61 (*s*); 72.44 (*d*); 72.26 (*d*); 71.14 (*s*); 68.19 (*s*); 67.63 (*t*); 67.35 (*t*); 56.72 (*q*); 56.39 (*q*); 55.29 (2*q*); 37.92 (*d*); 37.46 (*d*); 18.21 (12*q*); 13.76 (3*d*); 13.65 (3*d*); 7.41 (3*q*); 4.30 (3*t*); –0.45 (3*q*). MALDI-MS: 1087 ([*M* + N]$^+$). Anal. calc. for $C_{55}H_{100}O_{12}Si_4$ (1065.73): C 61.99, H 9.46; found: C 62.18, H 9.44.

*3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**17**). As described for

7, with **16** (1.3 g, 1.22 mmol): **17** (1.2 g, 99%). Oil. R_f (AcOEt/toluene 1:15) 0.57. M.p. 84°. $[\alpha]_D^{25} = -74.8$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 2948*s*, 2890*s*, 2868*s*, 2259*w*, 2172*w*, 1465*m*, 1413*w*, 1368*m*, 1350*m*, 1289*m*, 1251*m*, 1152*s*, 1097*s*, 1066*s*, 1040*s*, 1020*s*, 940*m*, 919*m*, 883*s*, 846*s*, 655*m*, 608*w*, 591*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.99 (*d*, $J = 5.6$, C*H*OMe); 4.91 (*d*, $J = 6.1$, C*H*OMe); 4.80 (*d*, $J = 5.6$, C*H*OMe); 4.73 (*d*, $J = 6.1$, C*H*OMe); 4.66 (*s*, CH_2OMe); 4.65 (*s*, CH_2OMe); 4.00 (*dd*, $J = 8.9$, 0.5, H–C(5′)); 3.93 (*dd*, $J = 9.2$, 2.1, H–C(3)); 3.87 (*dd*, $J = 11.1$, 1.9, H–C(10′)); 3.80 (*dd*, $J = 11.3$, 2.3, H–C(8)); 3.79 (*dd*, $J = 11.0$, 5.3, H′–(10′)); 3.77 (*dd*, $J = 11.2$, 5.0, H′–C(8)); 3.74 (*d*, $J = 9.2$, 8.3, H–C(4)); 3.73 (*dd*, $J = 9.0$, 8.2, H–C(6′)); 3.53 (*ddd*, $J = 10.4$, 5.2, 2.0, H–C(9′)); 3.53–3.51 (*m*, H–C(7)); 3.50 (*dd*, $J = 10.1$, 8.4, H–C(5)); 3.49 (*dd*, $J = 9.6$, 8.1, H–C(7′)); 3.45 (*s*, MeO); 3.43 (*s*, MeO); 3.37 (*s*, 2 MeO); 2.83 (br. *t*, $J = 10.2$, H–C(6)); 2.73 (*t*, $J = 10.3$, H–C(8′)); 2.44 (*d*, $J = 2.1$, H–C(1)); 1.25–1.09 (*m*, 2 (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.9$, (*Me*CH$_2$)$_3$Si); 0.58 (*q*, $J = 7.8$, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.45 (*s*); 98.04 (*t*); 97.89 (*t*); 96.71 (2*t*); 86.71 (*s*); 82.35 (*d*); 80.84 (*d*); 78.93 (*d*); 78.39 (*d*); 77.66 (*s*); 75.07 (*s*); 74.75 (*s*); 74.68 (2*d*); 72.28 (*d*); 72.26 (*d*); 71.77 (*d*); 71.12 (*s*); 68.19 (*s*); 67.65 (*t*); 67.42 (*t*); 56.74 (*q*); 56.41 (*q*); 55.29 (2*q*); 37.94 (*d*); 37.41 (*d*); 18.23 (12*q*); 13.72 (3*d*); 13.64 (3*d*); 7.41 (3*q*); 4.30 (3*t*). FAB-MS: 961 ([*M* – MeO]$^+$). Anal. calc. for $C_{53}H_{92}O_{12}Si_3$ (993.55): C 62.86, H 9.33; found: C 63.11, H 9.21.

*3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-iodo-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**18**). As described for **10**, with morpholine (3.02 ml, 34.77 mmol) in toluene (10 ml) I_2 (4.39 g, 17.38 mmol) in toluene (15 ml), and **17** (1.15 g, 1.15 mmol) in toluene (15 ml). Workup with sat. aq. Na_2SO_3 soln. (5 ml): **18** (1.23 g, 95%). Oil. R_f (AcOEt/hexane 1:5) 0.40. $[\alpha]_D^{25} = -53.0$ ($c = 0.4$, $CHCl_3$). IR ($CHCl_3$): 3005*w*, 2948*s*, 2890*s*, 2868*s*, 2259*w*, 2171*w*, 1464*m*, 1414*w*, 1368*m*, 1290*m*, 1258*w*, 1151*s*, 1096*s*, 1067*s*, 1040*s*, 1020*s*, 919*m*, 883*m*, 655*m*, 608*w*, 593*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.99 (*d*, $J = 5.5$, C*H*OMe); 4.90 (*d*, $J = 6.1$, C*H*OMe); 4.80 (*d*, $J = 5.4$, C*H*OMe); 4.72 (*d*, $J = 6.1$, C*H*OMe); 4.66 (*s*, CH_2OMe); 4.65 (*s*, CH_2OMe); 4.06 (*d*, $J = 9.3$, H–C(3)); 4.01 (br. *d*, $J = 9.1$, H–C(5′)); 3.88 (*dd*, $J = 11.1$, 1.8, H–C(10′)); 3.81 (*dd*, $J = 11.2$, 2.3, H–C(8)); 3.80 (*dd*, $J = 11.2$, 5.2, H′–C(10′)); 3.77 (*dd*, $J = 11.3$, 4.5, H′–C(8)); 3.73 (*dd*, $J = 9.2$, 8.3, H–C(4)); 3.72 (*dd*, $J = 9.1$, 8.2, H–C(6′)); 3.52–3.50 (*ddd*, $J = 10.5$, 5.1, 1.7, H–C(9′)); 3.52 (*m*, H–C(7)); 3.49 (*dd*, $J = 10.3$, 8.2, H–C(5)); 3.47 (*dd*, $J = 10.5$, 8.3, H–C(7′)); 3.44 (*s*, MeO); 3.43 (*s*, MeO); 3.37 (*s*, MeO); 3.35 (*s*, MeO); 2.82 (br. *t*, $J = 10.3$, H–C(6)); 2.73 (br. *t*, $J = 10.4$, H–C(8′)); 1.27–1.09 (*m*, 2 (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.8$, (*Me*CH$_2$)$_3$Si); 0.57 (*q*, $J = 7.8$, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.45 (*s*); 98.00 (*t*); 97.86 (*t*); 96.68 (2*t*); 91.05 (*s*); 86.68 (*s*); 82.35 (2*d*); 78.91 (*d*); 78.36 (*d*); 77.66 (*s*); 75.09 (*s*); 74.68 (*d*); 74.67 (*d*); 73.39 (*d*); 72.43 (*d*); 71.26 (*s*); 68.44 (*s*); 67.81 (*t*); 67.48 (*t*); 56.89 (*q*); 56.60 (*q*); 55.48 (2*q*); 38.09 (*d*); 37.59 (*d*); 18.36 (12*q*); 13.96 (3*d*); 13.80 (3*d*); 7.58 (3*q*); 6.00 (*s*); 4.47 (3*t*). FAB-MS: 1117 (M^+).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**19**) *and 1,1′-{(Buta-1,3-diyne-1,4-diyl)bis[(1S)-1,5-anhydro-4-deoxy-3,6-bis-*O*-(methoxymethyl)-2-*O*-(triisopropylsilyl)-*D*-glucitol-1,4-diyl]}bis{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-gulo-decitol}* (**20**). As described for **11** and **12**, with CuI (6.6 mg, 0.034 mmol), $[PdCl_2(PhCN)_2]$ (13.3 mg, 0.034 mmol), (fur)$_2$P (16.3 mg, 0.069 mmol), (i-Pr)$_2$NH (0.49 ml, 3.48 mmol), **18** (1.29 g, 1.16 mmol), **13** (1.103 g, 1.16 mmol), and DMSO (26 ml). Workup with 2N HCl (*ca.* 1 ml). FC (AcOEt/hexane 1:24) gave **19** (1.12 g, 50%) as a white solid and **20** (562 mg, 30%) as an oil.

Data of **19**: R_f (AcOEt/hexane 1:4) 0.18. M.p. 122°. $[\alpha]_D^{25} = -64.9$ ($c = 0.65$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2946*s*, 2891*m*, 2868*m*, 2259*w*, 2172*w*, 1464*m*, 1373*m*, 1291*m*, 1251*m*, 1151*s*, 1097*s*, 1066*s*, 1042*s*, 1020*s*, 918*m*, 883*s*, 846*m*, 655*m*, 609*w*, 535*w*, 516*w*. ^{1}H-NMR (500 MHz, $CDCl_3$)[5]: 4.99 (*d*, $J = 5,5$, C*H*OMe); 4.90 (*d*, $J = 6.1$, C*H*OMe); 4.89 (*d*, $J = 5.6$, C*H*OMe); 4.88 (*d*, $J = 5.6$, C*H*OMe); 4.80 (*d*, $J = 5.6$, C*H*OMe); 4.72 (*d*, $J = 6.1$, C*H*OMe); 4.71 (*d*, $J = 6.0$, C*H*OMe); 4.70 (*d*, $J = 6.1$, C*H*OMe); 4.66 (*s*, 2 CH_2OMe); 4.64 (*s*, 2 CH_2OMe); 4.00 (br. *d*, $J \approx 9.2$, H–C(5_D)); 3.99 (br. *d*, $J \approx 9.2$, H–C(5_B), H–C(5_C)); 3.93 (*d*, $J = 9.2$, H–C(3_A)); 3.88 (*dd*, $J = 11.3$, 2.0, H–C(10_D)); 3.82 (*dd*, $J = 11.1$, 1.9, H–C(8_A)); 3.78 (*dd*, $J = 11.4$, 5.1, H′–C(10_D)); 3.77 (*dd*, $J = 11.2$, 2.2, H–C(10_B), H–C(10_C)); 3.75 (*dd*, $J = 11.3$, 4.6, H′–C(10_B), H′–C(10_C)); 3.74 (*dd*, $J = 11.0$, 4.6, H′–C(8_A)); 3.72 (br. *t*, $J \approx 8.6$, H–C(6_B), H–C(6_C), H–C(6_D)); 3.71 (*dd*, $J = 9.1$, 8.1, H–C(4_A)); 3.53 (*ddd*, $J = 10.4$, 5.0, 1.9, H–C(9_D)); 3.59 (br. *dd*, $J \approx 10.1$, 8.2, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.49–3.44 (*m*, H–C(7_A), H–C(9_B), H–C(9_C)); 3.44 (*s*, MeO); 3.426 (*s*, MeO); 3.425 (*s*, MeO); 3.423 (*s*, MeO); 3.375 (*s*, MeO); 3.370 (*s*,

MeO); 3.367 (*s*, MeO); 3.365 (*s*, MeO); 2.80 (br. *t*, J = 10,2, H–C(6_A), H–C(8_B), H–C(8_C)); 2.73 (*t*, J = 10.3, H–C(8_D)); 1.37–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.97 (*t*, J = 7.8, (*Me*CH$_2$)$_3$Si); 0.58 (*q*, J = 7.8, (MeC*H*$_2$)$_3$Si); 0.14 (*s*, Me$_3$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 104.43 (*s*); 102.14 (*s*); 98.03 (*t*); 97.90 (3*t*); 97.68 (4*t*); 91.49 (*s*); 86.71 (*s*); 82.62 (*d*); 82.43 (*d*); 82.29 (2*d*); 78.93 (*d*); 78.42 (2*d*); 78.36 (*d*); 77.95 (*s*); 77.63 (*s*); 77.45 (*s*); 74.73 (4*d*); 74.41 (*s*); 74.58 (*s*); 74.27 (*s*); 72.44 (*d*); 72.29 (3*d*); 71.25 (*s*); 71.17 (*s*); 71.06 (*s*); 68.33 (*s*); 68.20 (*s*); 68.09 (*s*); 67.43 (*t*); 67.29 (3*t*); 56.70 (*q*); 56.39 (*q*); 56.23 (3*q*); 55.31 (3*q*); 37.93 (*d*); 37.46 (*d*); 37.37 (2*d*); 18.19 (24*q*); 13.91 (6*d*); 13.76 (6*d*); 7.40 (3*q*); 4.30 (3*t*); –0.46 (3*q*). MALDI-MS: 1963 ([M + Na]$^+$). Anal. calc. for $C_{101}H_{176}O_{24}Si_6$ (1943.01): C 62.43, H 9.13; found: C 62.53, H 8.93.

Data of **20**: R_f (AcOEt/hexane 1:4) 0.27. $[\alpha]_D^{25} = -59.3$ (c = 0.9, CHCl$_3$). IR (CHCl$_3$): 2947*s*, 2891*m*, 2868*m*, 2259*w*, 2171*w*, 1464*m*, 1374*m*, 1290*m*, 1248*m*, 1151*s*, 1096*s*, 1042*s*, 1020*s*, 919*m*, 883*m*, 846*w*, 655*m*, 592*m*, 536*w*, 512*w*. ^{1}H-NMR (500 MHz, CDCl$_3$): 4.99 (*d*, J = 5.6, C*H*OMe); 4.89 (*d*, J = 6.1, C*H*OMe); 4.80 (*d*, J = 5.5, C*H*OMe); 4.72 (*d*, J = 6.2, C*H*OMe); 4.66 (*s*, CH$_2$OMe); 4.64 (*s*, CH$_2$OMe); 4.01 (*d*, J = 8.9, H–C(5)); 3.99 (*d*, J = 9.1, H–C(1′)); 3.88 (*dd*, J = 11.1, 1.8, H–C(10)); 3.79 (*dd*, J = 11.1, 5.2, H′–C(10)); 3.78 (*dd*, J = 11.2, 1.9, H–C(6′)); 3.74 (*dd*, J = 11.2, 5.1, H′–C(6′)); 3.73 (*dd*, J = 9.2, 8.0, H–C(2′)); 3.72 (*dd*, J = 9.0, 8.1, H–C(6)); 3.53 (*ddd*, J = 10.3, 5.1, 1.8, H–C(9)); 3.52–3.50 (*m*, H–C(5′)); 3.49 (*dd*, J = 10.1, 8.1, H–C(7)); 3.48 (*dd*, J = 10.0, 8.1, H–C(3′)); 3.44 (*s*, MeO); 3.42 (*s*, MeO); 3.37 (*s*, MeO); 3.36 (*s*, MeO); 2.80 (*t*, J = 10.1, H–C(4′)); 2.73 (*t*, J = 10.2, H–C(8)); 1.21–1.07 (*m*, 2 (i-Pr)$_3$Si); 0.97 (*t*, J = 7.9, (*Me*CH$_2$)$_3$Si); 0.58 (*q*, J = 7.8, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 104.49 (*s*); 98.01 (*t*); 97.93 (*t*); 97.77 (*t*); 96.65 (*t*); 86.67 (*s*); 82.30 (*d*); 82.21 (*d*); 78.91 (*d*); 78.30 (*d*); 77.58 (*s*); 77.05 (*s*); 76.84 (*s*); 74.72 (*d*); 74.45 (*d*); 72.25 (2*d*); 71.08 (*s*); 70.68 (*s*); 68.26 (*s*); 67.63 (*t*); 67.35 (*t*); 56.71 (*q*); 56.34 (*q*); 55.26 (2*q*); 37.92 (*d*); 37.25 (*d*); 18.20 (12*q*); 13.62 (3*d*); 13.52 (3*d*); 7.39 (3*q*); 4.29 (3*t*). MALDI-MS: 2005 ([M + Na]$^+$). Anal. calc. for $C_{104}H_{182}O_{24}Si_6$ (1985.09): C 62.93, H 9.24; found: C 62.98, H 8.94.

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**21**). As described for **7**, with **19** (475 mg, 0.24 mmol), MeOH (60 ml), and 0.2N NaOH in MeOH (3 ml; 48° for 3 h). Workup with 1N HCl (*ca.* 1 ml): **21** (452 mg, 99%). Oil. R_f (AcOEt/hexane 3:10) 0.29. $[\alpha]_D^{25} = -70.2$ (c = 0.4, CHCl$_3$). IR (CHCl$_3$): 3306*w*, 2947*s*, 2891*m*, 2868*s*, 2259*w*, 2171*w*, 1464*m*, 1371*m*, 1291*m*, 1259*m*, 1151*s*, 1097*s*, 1067*s*, 1040*s*, 1019*s*, 918*m*, 883*s*, 656*m*, 593*w*, 547*w*, 537*w*, 526*w*, 505*m*. ^{1}H-NMR (500 MHz, CDCl$_3$; assignments based on 2D HOHAHA)[5]: 4.99 (*d*, J = 5.6, C*H*OMe); 4.91 (*d*, J = 5.9, C*H*OMe); 4.89 (*d*, J = 5.9, 2 C*H*OMe); 4.80 (*d*, J = 5.6, C*H*OMe); 4.73 (*d*, J = 5.1, C*H*OMe); 4.72 (*d*, J = 6.1, C*H*OMe); 4.71 (*d*, J = 5.1, C*H*OMe); 4.67 (*s*, C*H*OMe); 4.66 (*s*, CH$_2$OMe); 4.65 (*s*, 2 CH$_2$OMe); 4.00 (br. *d*, $J \approx$ 9.2, H–C(5_D)); 3.99 (br. *d*, $J \approx$ 9.0, H–C(5_B), H–C(5_C)); 3.95 (*dd*, J = 9.3, 2.2, H–C(3_A)); 3.89 (*dd*, J = 11.2, 1.8, H–C(10_D)); 3.81 (*dd*, J = 11.4, 2.0, H–C(8_A)); 3.80 (*dd*, J = 11.1, 5.0, H′–C(10_D)); 3.79 (*dd*, J = 11.1, 1.9, H–C(10_B), H–C(10_C)); 3.76 (*dd*, J = 11.5, 4.5, H′–C(8_A)); 3.75 (*dd*, J = 12.2, 4.3, H′–C(10_B), H′–C(10_C)); 3.75 (*dd*, J = 9.2, 8.2, H–C(4_A)); 3.72 (br. *dd*, $J \approx$ 9.0, 8.6, H–C(6_B), H–C(6_C), H–C(6_D)); 3.53 (*ddd*, J = 10.6, 4.9, 1.8, H–C(9_D)); 3.52–4.49 (*m*, H–C(7_A)); 3.48 (br. *dd*, $J \approx$ 9.4, 8.8, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.44 (*s*, MeO); 3.46–4.43 (*m*, H–C(9_B), H–C(9_C)); 3.423 (*s*, MeO); 3.42 (*s*, MeO); 3.41 (*s*, MeO); 3.37 (*s*, 2 MeO); 3.36 (*s*, 2 MeO); 2.83 (br. *t*, J = 10.5, H–C(6_A)); 2.81 (*t*, J = 10.5, H–C(8_B), H–C(8_C)); 2.73 (*t*, J = 10.2, H–C(8_D)); 2.45 (*d*, J = 2.1, H–C(1_A)); 1.25–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.97 (*t*, J = 7.8, (*Me*CH$_2$)$_3$Si); 0.57 (*q*, J = 7.8, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 104.44 (*s*); 98.00 (2*t*); 97.87 (3*t*); 96.66 (3*t*); 86.67 (*s*); 82.28 (4*d*); 80.79 (*d*); 78.91 (*d*); 78.42 (2*d*); 78.54 (*d*); 77.80 (*s*); 77.61 (*s*); 77.50 (*s*); 75.09 (*s*); 74.70 (4*d*); 74.09 (*s*); 74.40 (*s*); 74.31 (*s*); 74.31 (*s*); 72.26 (3*d*); 71.75 (*d*); 71.21 (*s*); 71.15 (*s*); 71.04 (*s*); 68.31 (*s*); 68.20 (*s*); 68.12 (*s*); 67.60 (*t*); 67.37 (*t*); 67.26 (2*t*); 56.71 (*q*); 56.66 (*q*); 56.37 (*q*); 55.24 (*q*); 55.03 (2*q*); 54.97 (2*q*); 37.91 (*d*); 37.36 (3*d*); 18.18 (24*q*); 13.69 (6*d*); 13.61 (6*d*); 7.39 (3*q*); 4.24 (3*t*). MALDI-MS: 1891 ([M + Na]$^+$). Anal. calc. for $C_{98}H_{168}O_{24}Si_5$ (1870.82): C 62.92, H 9.03; found: C 63.07, H 9.07.

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl-}-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-iodo-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**22**). As described for **10**, with morpholine (0.18 ml, 2.08 mmol) in toluene (1 ml), I_2 (264 mg, 1.04 mmol) in toluene (2 ml), and **21** (130 mg, 0.069 mmol) in toluene (2 ml; 24 h at 45°). Workup with sat. aq. Na_2SO_3 soln. (1 ml): **22** (137 mg, 99%). Solid. R_f (AcOEt/

toluene 1:15) 0.58. M.p. 74°. $[\alpha]_D^{25} = -92.5$ ($c = 0.2$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2947*s*, 2891*s*, 2868*s*, 2259*w*, 2171*w*, 1464*m*, 1368*m*, 1291*m*, 1261*s*, 1151*s*, 1097*s*, 1066*s*, 1040*s*, 1020*s*, 918*m*, 883*m*, 818*m*, 591*w*, 532*w*, 515*w*. ^{1}H-NMR (500 MHz, $CDCl_3$)[5]: 4.99 (*d*, $J = 5.5$, C*H*OMe); 4.90 (*d*, $J = 6.2$, C*H*OMe); 4.89 (*d*, $J = 6.1$, C*H*OMe); 4.88 (*d*, $J = 6.2$, C*H*OMe); 4.80 (*d*, $J = 5.5$, C*H*OMe); 4.72 (*d*, $J = 6.1$, C*H*OMe); 4.71 (*d*, $J = 6.2$, 2 C*H*OMe); 4.66 (*s*, CH_2OMe); 4.65 (*s*, CH_2OMe); 4.64 (*s*, 2 CH_2OMe); 4.06 (br. *d*, $J \approx 9.3$, H–C(3_A)); 4.00 (br. *d*, $J \approx 9.1$, H–C(5_D)); 3.99 (*d*, $J = 9.1$, H–C(5_B), H–C(5_C)); 3.88 (*dd*, $J = 11.2$, 1.9, H–C(10_D)); 3.79 (*dd*, $J = 11.3$, 1.9, H–C(8_A)); 3.78 (*dd*, $J = 11.1$, 5.0, H′–C(10_D)); 3.77 (*dd*, $J = 11.3$, 2.0, H–C(10_B), H–C(10_C)); 3.75 (*dd*, $J = 9.0$, 8.0, H–C(4_A)); 3.74 (*dd*, $J = 11.3$, 5.0, H′–C(10_B), H′–C(10_C)); 3.73 (*dd*, $J = 11.2$, 4.9, H′–C(8_A)); 3.72 (br. *dd*, $J \approx 9.0$, 8.4, H–C(6_B), H–C(6_C), H–C(6_D)); 3.53 (*ddd*, $J = 10.3$, 4.9, 1.8, H–C(9_D)); 3.49 (br. *dd*, $J \approx 10.1$, 8.3, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.48–3.45 (*m*, H–C(7_A), H–C(9_B), H–C(9_C)); 3.44 (*s*, MeO); 3.426 (*s*, 2 MeO); 3.422 (*s*, MeO); 3.37 (*s*, 2 MeO); 3.366 (*s*, MeO); 3.364 (*s*, MeO); 2.84 (br. *t*, $J = 10.2$, H–C(6_A)); 2.80 (br. *t*, $J = 10.2$, H–C(8_B), H–C(8_C)); 2.73 (*t*, $J = 10.2$, H–C(8_D)); 1.25–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.8$, (*Me*-CH_2)$_3$Si); 0.58 (*q*, $J = 7.8$, (MeC*H*$_2$)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.43 (*s*); 98.00 (*t*); 97.90 (3*t*); 96.69 (4*t*); 91.05 (*s*); 86.04 (*s*); 82.29 (4*d*); 78.92 (*d*); 78.42 (*d*); 78.33 (2*d*); 77.61 (*s*); 77.45 (*s*); 77.23 (*s*); 75.08 (*d*); 74.70 (3*d*); 74.69 (*s*); 74.41 (*s*); 74.32 (*s*); 73.22 (*d*); 72.28 (3*d*); 71.22 (*s*); 71.18 (*s*); 71.06 (*s*); 68.33 (*s*); 68.21 (*s*); 68.17 (*s*); 67.63 (*t*); 67.29 (3*t*); 56.73 (*q*); 56.41 (3*q*); 55.29 (4*q*); 37.93 (*d*); 37.37 (3*d*); 18.18 (24*q*); 13.79 (6*d*); 13.62 (6*d*); 7.40 (3*q*); 6.30 (*s*); 4.30 (3*t*). MALDI-MS: 2019 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1-*C*-[(tert-butyl)dimethylsilyl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**23**). As described for **8**, with 0.4N $(Me_3Si)_2NK$ (1.34 ml, 0.67 mmol) in hexane, **21** (251 mg, 0.13 mmol), THF (10 ml), and immediately, (*t*-Bu)Me_2SiOTf (0.15 ml, 0.67 mmol). Workup with 1N HCl (*ca.* 0.5 ml): **23** (261 mg, 98%). Solid. R_f (AcOEt/hexane 3:10) 0.38. M.p. 79°. $[\alpha]_D^{25} = -28.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 2946*s*, 2890*m*, 2867*m*, 2259*w*, 2172*w*, 1464*m*, 1390*m*, 1366*w*, 1290*m*, 1259*m*, 1152*s*, 1097*s*, 1066*s*, 1028*s*, 938*w*, 918*m*, 883*m*, 838*m*, 639*m*, 579*w*, 533*w*, 516*w*, 404*w*. ^{1}H-NMR (500 MHz, $CDCl_3$)[5]: 4.99 (*d*, $J = 5.5$, C*H*OMe); 4.89 (*d*, $J = 6.1$, 3 C*H*OMe); 4.80 (*d*, $J = 5.5$, C*H*OMe); 4.72 (*d*, $J = 6.2$, C*H*OMe); 4.71 (*d*, $J = 6.2$, 2 C*H*OMe); 4.66 (*s*, 2 CH_2OMe); 4.65 (*s*, CH_2OMe); 4.64 (*s*, CH_2OMe); 4.00 (br. *d*, $J \approx 9.4$, H–C(5_D)); 3.98 (br. *d*, $J \approx 9.5$, H–C(5_B), H–C(5_C)); 3.94 (*d*, $J = 9.3$, H–C(3_A)); 3.88 (*dd*, $J = 11.2$, 1.9, H–C(10_D)); 3.80 (*dd*, $J = 11.7$, 1.9, H–C(8_A)); 3.79 (*dd*, $J = 11.1$, 4.9, H′–C(10_D)); 3.78 (*dd*, $J = 11.3$, 2.0, H–C(10_B), H–C(10_C)); 3.74 (*dd*, $J = 11.5$, 5.0, H′–C(8_A), H′–C(10_B), H′–C(10_C)); 3.74 (*dd*, $J = 9.1$, 8.2, H–C(4_A)); 3.72 (br. *t*, $J \approx 9.1$, H–C(6_B), H–C(6_C), H–C(6_D)); 3.53 (*ddd*, $J = 10.5$, 4.9, 1.9, H–C(9_D)); 3.50 (br. *dd*, $J \approx 9.9$, 8.2, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.50–3.45 (*m*, H–C(7_A), H–C(9_B), H–C(9_C)); 3.44 (*s*, MeO); 3.42 (*s*, 2 MeO); 3.369 (*s*, MeO); 3.366 (*s*, 2 MeO); 3.365 (*s*, 2 MeO); 2.80 (br. *t*, $J = 10.4$, H–C(8_B), H–C(8_C)); 2.78 (*t*, $J = 10.6$, H–C(6_A)); 2.73 (*t*, $J = 10.3$, H–C(8_D)); 1.28–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.97 (*t*, $J = 7.9$, (*Me*CH_2)$_3$Si); 0.91 (*s*, *t*-Bu); 0.58 (*q*, $J = 7.9$, (MeC*H*$_2$)$_3$Si); 0.07 (*s*, MeSi); 0.06 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.43 (*s*); 103.19 (*s*); 98.04 (*t*); 97.90 (*t*); 97.83 (*t*); 96.69 (*t*); 96.46 (*t*); 89.66 (*s*); 86.72 (*s*); 82.53 (*d*); 82.29 (3*d*); 78.93 (*d*); 78.45 (*d*); 78.19 (*d*); 78.10 (*d*); 77.64 (*s*); 77.22 (*s*); 77.03 (*s*); 74.75 (2*d*); 74.69 (2*d*); 74.40 (*s*); 74.25 (2*s*); 72.44 (*d*); 72.29 (3*d*); 71.29 (*s*); 71.18 (*s*); 71.08 (*s*); 68.32 (*s*); 68.20 (*s*); 68.03 (*s*); 67.64 (*t*); 67.29 (3*t*); 56.74 (*q*); 56.44 (*q*); 56.36 (2*q*); 55.29 (2*q*); 55.16 (2*q*); 37.93 (*d*); 37.38 (3*d*); 25.88 (3*q*); 18.20 (24*q*); 16.49 (*s*); 13.72 (6*d*); 13.64 (6*d*); 7.41 (3*q*); 4.30 (3*t*); −4.93 (*q*); −5.53 (*q*). MALDI-MS: 2079 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1-*C*-[(tert-butyl)dimethylsilyl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**24**). A soln. of **23** (68 mg, 0.034 mmol) in MeOH (2 ml) was treated with 2N *t*-BuOK in MeOH (1.5 ml), stirred at 40° for 5 h, neutralised with 1N HCl (*ca.* 3 ml), diluted with AcOEt, washed with H_2O, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:5) gave **23** (10 mg, 14%) and **24** (37 mg, 65%) as oils. R_f (AcOEt/hexane 2:5) 0.48. $[\alpha]_D^{25} = -42.4$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 3005*m*, 2946*s*, 2891*m*, 2867*s*, 2259*w*, 2176*w*, 1464*m*, 1366*m*, 1290*m*, 1258*m*, 1151*s*, 1113*s*, 1066*s*, 1040*s*, 919*m*, 883*m*, 839*m*, 825*m*, 654*m*, 591*w*, 537*w*, 511*w*. ^{1}H-NMR (500 MHz, $CDCl_3$)[5]: 4.96 (*d*, $J = 5.2$, C*H*OMe); 4.89 (*d*, $J = 6.2$, 3 C*H*OMe); 4.75 (*d*, $J = 6.2$, C*H*OMe); 4.71 (*d*, $J = 6.1$, C*H*OMe); 4.70 (*d*, $J = 6.2$, 2 C*H*OMe); 4.67 (*s*, CH_2OMe); 4.65 (*s*, 2 CH_2OMe); 4.64 (*s*, CH_2OMe); 4.00 (br. *d*, $J \approx 9.1$ H–C(5_D)); 3.97 (br. *d*, $J \approx 9.0$, H–C(5_B), H–C(5_C)); 3.94 (*d*, $J = 9.1$, H–C(3_A)); 3.86 (*dd*, $J = 11.3$, 2.2, H–C(10_D)); 3.82

(*dd*, J = 11.3, 4.8, H'–C(10$_D$)); 3.77 (*dd*, J = 11.5, 1.9, H–C(8$_A$)); 3.75 (*dd*, J = 9.1, 8.1, H–C(4$_A$)); 3.74 (*dd*, J = 11.5, 2.0, H–C(10$_B$), H–C(10$_C$)); 3.73 (*dd*, J = 11.7, 4.4, H'–C(8$_A$), H'–C(10$_B$), H'–C(10$_C$)); 3.72 (br. *dd*, $J \approx$ 9.0, 8.1, H–C(6$_B$), H–C(6$_C$), H–C(6$_D$)); 3.55 (*ddd*, J = 10.4, 4.7, 2.1, H–C(9$_D$)); 3.52 (*dd*, J = 10.1, 8.2, H–C(5$_A$)); 3.48 (br. *dd*, $J \approx$ 10.0, 8.0, H–C(7$_B$), H–C(7$_C$), H–C(7$_D$)); 3.47–3.43 (*m*, H–C(7$_A$), H–C(9$_B$), H–C(9$_C$)); 3.427 (*s*, MeO); 3.424 (*s*, 2 MeO); 3.423 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 3.36 (*s*, 2 MeO); 2.81 (br. *t*, J = 10.3, H–C(8$_B$), H–C(8$_C$)); 2.78 (*t*, J = 10.3, H–C(6$_A$)); 2.71 (*td*, J = 10.3, 2.3, H–C(8$_D$)); 2.19 (*d*, J = 2.4, H–C≡C–C(8$_D$)); 1.30–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.91 (*s*, *t*-Bu); 0.07 (*s*, MeSi); 0.06 (*s*, MeSi). ^{13}C-NMR (75 MHz, CDCl$_3$): 103.19 (*s*); 98.07 (*t*); 97.91 (2*t*); 97.87 (*t*); 96.68 (3*t*); 96.46 (*t*); 90.49 (*s*); 82.65 (*d*); 82.52 (*d*); 82.44 (*d*); 82.28 (*d*); 81.17 (*d*); 78.66 (2*d*); 78.44 (*d*); 78.19 (*d*); 77.82 (*s*); 77.46 (*s*); 77.45 (*s*); 74.91 (*s*); 74.71 (2*d*); 74.65 (2*d*); 74.59 (*s*); 74.38 (*s*); 74.25 (*s*); 72.43 (*d*); 72.37 (*d*); 72.30 (2*d*); 71.18 (*s*); 70.70 (*s*); 70.61 (*s*); 68.16 (*s*); 67.91 (*s*); 67.70 (*s*); 67.42 (2*t*); 67.26 (2*t*); 56.63 (*q*); 56.41 (*q*); 56.35 (*q*); 55.33 (2*q*); 55.29 (2*q*); 55.15 (*q*); 37.38 (3*d*); 36.62 (*d*); 26.03 (3*q*); 18.19 (24*q*); 16.56 (*s*); 13.69 (6*d*); 13.68 (6*d*); –4.87 (*q*); –4.93 (*q*). MALDI-MS: 1891 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-[2-(triethylsilyl)ethynyl]-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1-yl}-1-*C*-[(tert-butyl)dimethylsilyl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-octitol* (**25**) *and 1,1'-{(Buta-1,3-diyne-1,4-diyl)bis[(1S)-1,5-anhydro-4-deoxy-3,6-bis-*O*-(methoxymethyl)-2-*O*-(triisopropylsilyl)-D-glucitol-1,4-diyl]bis[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1,8-diyl]bis-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol-1,8-diyl]}bis{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-8-*C*-[2-(triethylsilyl)ethynyl]-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-decitol}* (**26**). At 20°, CuI (1.09 mg, 5.7 μmol) and [Pd(PPh$_3$)$_4$] (1.5 mg, 0.57 μmol) were added to a soln. of **22** (38.8 mg, 0.019 mmol) and **24** (36 mg, 0.019 mmol) in Et$_3$N (2 ml). After stirring for 9 h at 50°, the solvent was evaporated. The residue was dissolved in AcOEt, washed with brine, and dried (MgSO$_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **25** (36 mg, 51%) and **26** (15 mg, 21%) as oils.

Data of **25**: R_f (AcOEt/hexane 2:5) 0.54. M.p. 114°. $[\alpha]_D^{25}$ = –64.0 (*c* = 0.2, CHCl$_3$). IR (CHCl$_3$): 2946*m*, 2891*m*, 2867*m*, 2259*w*, 2172*w*, 1464*m*, 1367*m*, 1291*m*, 1151*s*, 1097*s*, 1066*s*, 1020*s*, 918*m*, 883*m*, 825*w*, 655*w*, 593*w*, 536*w*, 518*w*, 503*w*. ^{1}H-NMR (500 MHz, CDCl$_3$)[5]): 4.99 (*d*, J = 5.6, C*H*OMe); 4.89 (*d*, J = 6.0, 2 C*H*OMe); 4.88 (*d*, J = 6.2, 3 C*H*OMe); 4.80 (*d*, J = 6.6, C*H*OMe); 4.72 (*d*, J = 6.1, C*H*OMe); 4.71 (*d*, J = 6.2, 7 C*H*OMe); 4.66 (*s*, C*H*$_2$OMe); 4.65 (*s*, 2 C*H*$_2$OMe); 4.64 (*s*, 5 C*H*$_2$OMe); 4.00 (br. *d*, $J \approx$ 9.8, H–C(5$_H$)); 3.98 (br. *d*, $J \approx$ 9.4, H–C(5$_B$), H–C(5$_C$), H–C(5$_D$), H–C(5$_E$), H–C(5$_F$), H–C(5$_G$)); 3.94 (*d*, J = 9.0, H–C(3$_A$)); 3.86 ((*dd*, J = 11.3, 1.9, H–C(10$_H$)); 3.79 (*dd*, J = 11.1, 5.0, H'–C(10$_H$)); 3.77 (*dd*, J = 11.2, 1.9, H–C(8$_A$), H–C(10$_B$), H–C(10$_C$), H–C(10$_D$), H–C(10$_E$), H–C(10$_F$), H–C(10$_G$)); 3.73 (*dd*, J = 11.2, 4.9, H'–C(8$_A$), H'–C(10$_B$), H'–C(10$_C$), H'–C(10$_D$), H'–C(10$_E$), H'–C(10$_F$), H'–C(10$_G$)); 3.72 (br. *dd*, J = 9.2, 8.1, H–C(4$_A$), H–C(6$_B$), H–C(6$_C$), H–C(6$_D$), H–C(6$_E$), H–C(6$_F$), H–C(6$_G$), H–C(6$_H$)); 3.54–3.50 (*m*, H–C(7$_A$), H–C(9$_B$), H–C(9$_C$), H–C(9$_D$), H–C(9$_E$), H–C(9$_F$), H–C(9$_G$), H–C(9$_H$)); 3.49 (br. *dd*, $J \approx$ 10.1, 8.5, H–C(5$_A$), H–C(7$_B$), H–C(7$_C$), H–C(7$_D$), H–C(7$_E$), H–C(7$_F$), H–C(7$_G$), H–C(7$_H$)); 3.44 (*s*, 3 MeO); 3.425 (*s*, 3 MeO); 3.421 (*s*, 6 MeO); 3.42 (*s*, 4 MeO); 2.80 (br. *t*, J = 10.2, H–C(8$_B$), H–C(8$_C$), H–C(8$_D$), H–C(8$_E$), H–C(8$_F$), H–C(8$_G$)); 2.78 (*t*, J = 10.3, H–C(6$_A$)); 2.73 (*t*, J = 10.2, H–C(8$_H$)); 1.25–1.08 (*m*, 8 (i-Pr)$_3$Si); 0.96 (*t*, J = 7.8, (*Me*CH$_2$)$_3$Si); 0.91 (*s*, *t*-Bu); 0.58 (*q*, J = 7.8, (MeC*H*$_2$)$_3$Si); 0.07 (*s*, MeSi); 0.06 (*s*, MeSi). ^{13}C-NMR (75 MHz, CDCl$_3$): 104.43 (*s*); 103.33 (*s*); 97.91 (*t*); 97.83 (5*t*); 96.69 (5*t*); 96.57 (4*t*); 96.47 (*t*); 89.66 (*s*); 86.73 (*s*); 82.52 (*d*); 82.44 (*d*); 78.93 (6*d*); 78.84 (*d*); 78.42 (7*d*); 78.84 (*s*); 77.45 (6*s*); 74.71 (8*d*); 74.39 (7*s*); 72.29 (8*d*); 71.29 (*s*); 71.18 (3*s*); 71.07 (3*s*); 68.32 (2*s*); 68.22 (5*s*); 67.29 (8*t*); 56.74 (2*q*); 56.41 (6*q*); 55.50 (6*q*); 55.16 (2*q*); 37.92 (2*d*); 37.38 (6*d*); 26.04 (3*q*); 18.19 (48*q*); 16.50 (*s*); 13.64 (24*d*); 7.42 (3*q*); 4.30 (3*t*); –4.86 (*q*); –4.93 (*q*). MALDI-MS: 3757 ([*M* + Na]$^+$).

Data of **26**: R_f (AcOEt/hexane 2:5) 0.61. $[\alpha]_D^{25}$ = –60.3 (*c* = 1, CHCl$_3$). IR (CHCl$_3$): 2947*s*, 2891*m*, 2868*m*, 2260*w*, 2171*w*, 1602*w*, 1464*m*, 1378*w*, 1291*w*, 1258*w*, 1151*s*, 1097*m*, 1067*s*, 1040*s*, 1019*s*, 918*m*, 884*m*, 656*w*, 592*w*, 523*w*, 511*w*, 506*w*. ^{1}H-NMR (500 MHz, CDCl$_3$)[5]): 4.99 (*d*, J = 5.5, C*H*OMe); 4.89 (*d*, J = 5.9, C*H*OMe); 4.88

(*d*, J = 6.1, C*H*OMe); 4.87 (*d*, J = 5.5, C*H*OMe); 4.80 (*d*, J = 5.6, C*H*OMe); 4.72 (*d*, J = 6.1, C*H*OMe); 4.71 (*d*, J = 6.1, C*H*OMe); 4.70 (*d*, J = 6.1, C*H*OMe); 4.66 (*s*, CH_2OMe); 4.65 (*s*, CH_2OMe); 4.64 (*s*, 2 CH_2OMe); 4.01 (br. *d*, $J \approx 8.9$, H–C(1_A)); 4.00 (br. *d*, $J \approx 9.5$, H–C(5_D)); 3.99 (*d*, J = 9.6, H–C(5_B), H–C(5_C)); 3.88 (*dd*, J = 11.2, 2.0, H–C(10_D)); 3.77 (*dd*, J = 11.2, 5.0, H′–C(10_D)); 3.76 (*dd*, J = 11.3, 2.1, H–C(6_A), H–C(10_B), H–C(10_C)); 3.75 (*dd*, J = 11.5, 5.0, H′–C(6_A), H′–C(10_B), H′–C(10_C)); 3.72 (*dd*, J = 9.4, 8.3, H–C(6_D)); 3.71 (br. *dd*, $J \approx 9.2$, 8.2, H–C(2_A), H–C(6_B), H–C(6_C)); 3.54 (*ddd*, J = 10.2, 5.0, 2.0, H–C(9_D)); 3.48 (br. *dd*, $J \approx 10.1$, 8.1, H–C(3_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.47–3.45 (*m*, H–C(5_A), H–C(9_B), H–C(9_C)); 3.44 (*s*, MeO); 3.425 (*s*, 2 MeO); 3.421 (*s*, 2 MeO); 3.417 (*s*, 2 MeO); 3.412 (*s*, MeO); 2.80 (br. *t*, $J \approx 10.2$, H–C(4_A), H–C(8_B), H–C(8_C)); 2.73 (*t*, J = 10.3, H–C(8_D)); 1.21–1.08 (*m*, 4 (i-Pr)$_3$Si); 0.97 (*t*, J = 7.8, (*Me*CH_2)$_3$Si); 0.58 (*q*, J = 7.8, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.45 (*s*); 97.92 (2*t*); 96.69 (6*t*); 86.50 (*s*); 82.28 (4*d*); 78.92 (*d*); 78.44 (3*d*); 77.72 (*s*); 77.22 (2*s*); 76.80 (*s*); 74.75 (4*d*); 74.38 (3*s*); 72.29 (4*d*); 71.17 (2*s*); 71.07 (*s*); 68.22 (*s*); 68.13 (3*s*); 67.29 (4*t*); 56.73 (*q*); 56.42 (3*q*); 55.34 (4*q*); 37.93 (*d*); 37.36 (3*d*); 18.91 (24*q*); 13.63 (12*d*); 7.42 (3*q*); 4.30 (3*t*). MALDI-MS: 3757 ([M + Na]$^+$).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-1,5-anhydro-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glucitol}* (**27**). A soln. of **11** (45 mg, 0.04 mmol) in dry MeOH/THF 1:1 (2 ml) was treated with 0.3N HCl (2 ml), heated under reflux for 18 h, and neutralised (*Amberlite*, basic form). Evaporation and FC (AcOEt/hexane 1:2) gave **27** (22 mg, 95%). Solid. R_f (AcOEt/hexane 2:1) 0.2. M.p. 107°. $[\alpha]_D^{25} = -5.6$ (c = 0.25, MeOH). IR (KBr): 3500–3100*m* (br.), 2958*m*, 2925*m*, 2172*w*, 1637*w*, 1458*w*, 1411*w*, 1365*w*, 1300*w*, 1248*w*, 1079*m*, 842*m*, 638*w*, 576*w*, 529*w*. ^{1}H-NMR (300 MHz, CD_3OD): 4.01 (*d*, J = 9.5, H–C(1)); 3.85 (*dd*, J = 12.1, 1.9, H–C(6)); 3.68 (*dd*, J = 12.0, 5.5, H′–C(6)); 3.40 (*ddd*, J = 10.2, 5.4, 2.0, H–C(5)); 3.39 (*dd*, J = 10.2, 8.7, H–C(3)); 3.19 (*dd*, J = 9.5, 8.8, H–C(2)); 2.52 (*t*, J = 10.3, H–C(4)); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, CD_3OD): 104.67 (*s*); 91.03 (*s*); 81.54 (*d*); 77.00 (*s*); 76.93 (*d*); 75.43 (*d*); 72.54 (*d*); 70.20 (*s*); 63.79 (*t*); 39.82 (*d*); 0.02 (3*q*). FAB-MS: 535 ([M + 1]$^+$).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-1,5-anhydro-4-deoxy-4-*C*-[2-(triethylsilyl)ethynyl]-*D*-glucitol}* (**28**). As described for **27**, with **15** (40 mg, 0.036 mmol; reflux for 24 h): **28** (22 mg, 98%). Solid. R_f (AcOEt/hexane 2:1) 0.43. M.p. 102°. $[\alpha]_D^{25} = -6.4$ (c = 0.7, MeOH). IR (KBr): 3500 3100*m* (br.), 2955*m*, 2875*m*, 2171*w*, 1686*w*, 1458*w*, 1411*w*, 1364*w*, 1296*m*, 1248*w*, 1079*m*, 1017*m*, 883*w*, 638*w*, 579*w*, 530*w*. ^{1}H-NMR (300 MHz, CD_3OD): 4.03 (*d*, J = 9.6, H–C(1)); 3.85 (*dd*, J = 12.1, 1.8, H–C(6)); 3.65 (*dd*, J = 12.0, 5.5, H′–C(6)); 3.402 (*ddd*, J = 10.2, 5.6, 1.9, H–C(5)); 3.40 (*dd*, J = 10.4, 9.0, H–C(3)); 3.20 (*dd*, J = 9.6, 8.9, H–C(2)); 2.50 (*t*, J = 10.3, H–C(4)); 0.98 (*t*, J = 7.8, (*Me*CH_2)$_3$Si); 0.59 (*q*, J = 7.8, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, CD_3OD): 106.07 (*s*); 86.24 (*s*); 81.69 (*d*); 77.61 (*s*); 77.11 (*d*); 75.53 (*d*); 72.55 (*d*); 70.27 (*s*); 63.87 (*t*); 39.85 (*d*); 7.84 (3*q*); 5.36 (3*t*). FAB-MS: 641 ([M + Na]$^+$).

*1,1′-{(Buta-1,3-diyne-1,4-diyl)bis[(1*S*)-1,5-anhydro-4-deoxy-*D*-glucitol-1,4-diyl]}bis{5,9-anhydro-1,1,2,2,-3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-C-[2-(triethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-decitol}* (**29**). As described for **27**, with **20** (40 mg, 0.02 mmol; reflux for 24 h). FC (AcOEt/MeOH 10:1) gave **29** (20 mg, 99%). Solid. R_f (AcOEt/MeOH 5:1) 0.66. M.p. 220° (dec.). $[\alpha]_D^{25} = -11.0$ (c = 0.2, MeOH). IR (KBr): 3600–3000*m* (br.), 2955*m*, 2875*m*, 2260*w*, 2169*w*, 1685*w*, 1684*w*, 1637*w*, 1560*w*, 1542*w*, 1504*w*, 1458*w*, 1413*m*, 1299*m*, 1248*w*, 1077*m*, 884*w*, 846*w*, 637*w*, 577*w*, 526*w*. ^{1}H-NMR (300 MHz, CD_3OD): 4.05 (*d*, J = 9.2, H–C(1′)); 4.01 (*d*, J = 9.4, H–C(5)); 3.91 (br. *d*, J = 12.5, H–C(10)); 3.82 (br. *d*, J = 12.5, H–C(6′)); 3.69 (*dd*, J = 12.6, 5.1, H′–C(10)); 3.65 (*dd*, J = 12.6, 5.1, H′–C(6′)); 3.47–3.36 (*m*, H–C(3′), H–C(5′), H–C(7), H–C(9)); 3.21 (*dd*, J = 9.4, 9.0, H–C(6)); 3.19 (*dd*, J = 9.3, 9.0, H–C(2′)); 2.61 (*t*, J = 10.3, H–C(4′)); 2.50 (*t*, J = 10.3, H–C(8)); 0.97 (*t*, J = 7.8, (*Me*CH_2)$_3$Si); 0.56 (*q*, J = 7.8, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, CD_3OD): 106.09 (*s*); 86.24 (*s*); 81.61 (*d*); 81.04 (*d*); 78.51 (*s*); 77.25 (*s*); 77.09 (*d*); 76.58 (*d*); 75.61 (*d*); 75.51 (*s*); 75.31 (*d*); 72.58 (2*d*); 70.80 (*s*); 70.32 (*s*); 68.66 (*s*); 63.89 (*t*); 63.70 (*t*); 39.87 (*d*); 39.37 (*d*); 7.85 (3*q*); 5.36 (3*t*). MALDI-MS: 1029 ([M + Na]$^+$).

*1,1′-{(Buta-1,3-diyne-1,4-diyl)bis[(1*S*)-1,5-anhydro-4-deoxy-*D*-glucitol-1,4-diyl]bis(5,9-anhydro-1,1,2,2,3,3,-4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1,8-diyl)bis(5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1,8-diyl)}bis{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4-8-pentadeoxy-8-C-[2-(triethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-decitol}* (**30**). A soln. of **26** (14 mg, 3.7 µmol) in dry MeOH/THF 1:1 (2 ml) was treated with 0.3N HCl (1 ml) and heated under reflux for 24 h. Filtration gave **30** (5.5 mg, 82%). Solid. R_f (AcOEt/MeOH 10:3) 0.78. M.p. 200° (dec.). $[\alpha]_D^{25} = -3.0$ (c = 0.4, MeOH). IR (KBr): 3600–3100*m* (br.), 2924*m*, 2872*m*, 2810*m*, 2260*w*, 2169*w*, 1623*w*, 1457*w*, 1334*m*, 1298*w*, 1260*w*, 1078*m* (br.), 1067*m*, 1040*m*, 884*w*, 638*w*, 577*w*. ^{1}H-NMR (300 MHz, CD_3OD)[5]: 4.05 (br. *d*, $J \approx 9.2$, H–C(1_A)); 4.02 (br. *d*, $J \approx 9.4$, H–C(5_B), H–C(5_C), H–C(5_D)); 3.92 (br. *d*, J = 10.7, H–C(10_D)); 3.83 (br. *d*, J = 10.3, H–C(6_A), H–C(10_B), H–C(10_C)); 3.70–3.61 (*m*, H′–C(6_A), H′–C(10_B), H′–C(10_C), H′–C(10_D)); 3.45–3.43 (*m*, H–C(5_A), H–C(9_B), H–C(9_C), H–C(9_D)); 3.42 (br. *dd*, $J \approx 10.3$, 9.0, H–C(3_A), H–C(7_B), H–C(7_C), H–C(7_D)); 3.17 (br. *t*, $J \approx 9.3$, H–C(2_A), H–C(6_B), H–C(6_C), H–C(6_D)); 2.60 (br. *t*, $J \approx 10.1$, H–C(4_A), H–C(8_B), H–C(8_C)); 2.49 (*t*, J = 10.4,

H–C(8_D)); 0.98 (*t*, *J* = 7.8, (*Me*CH_2)$_3$Si); 0.58 (*q*, *J* = 7.8, (MeCH_2)$_3$Si). ^{13}C-NMR (75 MHz, CD_3OD): 106.06 (*s*); 85.05 (*s*); 80.99 (3*d*); 80.93 (*d*); 77.10 (2*s*); 76.90 (2*s*); 76.74 (*d*); 76.58 (3*d*); 75.59 (2*s*); 75.50 (*s*); 75.40 (3*d*); 73.31 (*d*); 72.62 (4*d*); 70.99 (2*s*); 70.83 (*s*); 70.80 (*s*); 68.62 (3*s*); 64.95 (3*t*); 63.70 (*t*); 39.86 (*d*); 39.37 (3*d*); 7.85 (3*q*); 5.36 (3*t*). FAB-MS: 1783 ([*M* + 1]$^+$).

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-7,10-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-octitol* (**31**). At 0°, a soln. of $Bu_4NF \cdot 3\ H_2O$ (35 mg, 0.112 mmol) in THF (1 ml) was added dropwise to a soln. of **16** (30 mg, 0.03 mmol) in THF (1 ml). The soln. was stirred at 25° for 1 h, treated with H_2O (1 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine, and dried ($MgSO_4$). Evaporation gave **31** (15.6 mg, 97%). Solid. R_f (AcOEt/hexane 2:1) 0.37. M.p. 70°. $[\alpha]_D^{25} = -43.3$ (*c* = 0.55, $CHCl_3$). IR ($CHCl_3$): 3400–3350*w* (br.), 3307*m*, 3007*m*, 2940*m*, 2893*m*, 2829*w*, 2261*w*, 2130*w*, 1602*w*, 1463*w*, 1442*w*, 1371*w*, 1329*w*, 1295*w*, 1260*w*, 1148*s*, 1115*s*, 1098*s*, 1061*s*, 1040*s*, 1023*s*, 980*w*, 949*w*, 918*m*, 649*m*, 551*w*, 522*w*, 514*w*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.86 (*d*, *J* = 6.9, *CH*OMe); 4.83 (*d*, *J* = 6.3, *CH*OMe); 4.82 (*d*, *J* = 6.0, *CH*OMe); 4.80 (*d*, *J* = 7.1, *CH*OMe); 4.67 (*s*, CH_2OMe); 4.66 (*s*, CH_2OMe); 4.50 (br. *s*, HO–C(4), HO–C(6′)); 4.03 (br. *d*, *J* = 9.5, H–C(5′)); 3.96 (*dd*, *J* = 9.2, 2.1, H–C(3)); 3.84–3.78 (*m*, 2 H–C(10′), 2 H–C(8)); 3.57–3.33 (*m*, H–C(4), H–C(6′), H–C(9′), H–C(7′), H–C(5), H–C(7)); 3.49 (*s*, MeO); 3.48 (*s*, MeO); 3.39 (*s*, MeO); 3.38 (*s*, MeO); 2.85 (br. *t*, *J* = 10.3, H–C(6)); 2.76 (*td*, *J* = 10.2, 2.2, H–C(8′)); 2.55 (*d*, *J* = 2.1, H–C(1)); 2.17 (*d*, *J* = 2.2, H–C≡C–C(8′)). ^{13}C-NMR (75 MHz, $CDCl_3$): 98.60 (2*t*); 96.79 (2*t*); 86.35 (*d*); 85.95 (*d*); 80.34 (*d*); 80.01 (*d*); 78.73 (*d*); 78.40 (*d*); 76.32 (*s*); 74.60 (*s*); 73.57 (*s*); 72.79 (*d*); 72.61 (*s*); 72.36 (*d*); 71.33 (*d*); 70.78 (*d*); 70.53 (*s*); 67.97 (*s*); 67.43 (*t*); 67.31 (*t*); 56.39 (2*q*); 55.54 (2*q*); 36.80 (*d*); 35.97 (*d*). MALDI-MS: 591 ([*M* + Na + 2]$^+$).

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D*-glycero-*D*-gulo-octitol* (**32**) [2]. As described for **27**, with **31** (15 mg, 0.026 mmol), MeOH/THF 1:1 (2 ml), and 0.3N HCl (1 ml). Filtration gave **32** (10 mg, 97%). Solid.

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-7,10-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-octitol* (**33**). As described for **31**, with $Bu_4NF \cdot 3\ H_2O$ (45 mg, 0.14 mmol) in THF (2 ml) and **19** (70 mg, 0.035 mmol) in THF (2 ml). FC (AcOEt/hexane 2:1) gave **33** (39 mg, 95%). solid. R_f (AcOEt/hexane 3:1) 0.36. M.p. 174°. $[\alpha]_D^{25} = -42.3$ (*c* = 1.6, $CHCl_3$). IR ($CHCl_3$): 3400–3350*m* (br.), 3307*m*, 3007*m*, 2944*s*, 2893*m*, 2867*m*, 2259*w*, 1614*w*, 1463*m*, 1371*m*, 1329*m*, 1294*m*, 1248*w*, 1148*s*, 1136*s*, 1097*s*, 1041*s*, 980*w*, 950*w*, 910*m*, 884*w*, 842*w*, 649*m*, 541*w*, 522*w*, 513*w*, 502*w*. ^{1}H-NMR (300 MHz, $CDCl_3$)[5]: 4.86 (*d*, *J* = 6.9, *CH*OMe); 4.83 (*d*, *J* = 6.4, 2 *CH*OMe); 4.82 (*d*, *J* = 7.0, 2 *CH*OMe); 4.78 (*d*, *J* = 6.7, *CH*OMe); 4.77 (*d*, *J* = 7.1, *CH*OMe); 4.76 (*d*, *J* = 7.0, *CH*OMe); 4.66 (*s*, 2 CH_2OMe); 4.65 (*s*, 2 CH_2OMe); 4.50 (*d*, *J* = 3.6, 2 OH); 4.49 (*d*, *J* = 4.3, 2 OH); 4.02 (br. *d*, *J* ≈ 8.4, H–C(5_D)); 3.99 (br. *d*, *J* ≈ 8.7, H–C(5_B), H–C(5_C)); 3.39 (*dd*, *J* = 9.3, 2.1, H–C(3_A)); 3.83–3.73 (*m*, 2 H–C(8_A), H–C(10_B), H–C(10_C), H–C(10_D)); 3.83–3.73 (*m*, H–C(4_A), H–C(6_B), H–C(6_C), H–C(6_D), H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D), H–C(7_A), H–C(9_B), H–C(9_C), H–C(9_D)); 3.48 (*s*, MeO); 3.47 (*s*, 2 MeO); 3.38 (*s*, 2 MeO); 3.37 (*s*, 3 MeO); 2.86 (br. *t*, *J* = 10.3, H–C(6_A)); 2.86 (br. *t*, *J* = 10.3, H–C(8_B), H–C(8_C)); 2.73 (*td*, *J* = 10.3, 2.2, H–C(8_D)); 2.55 (*d*, *J* = 2.1, H–C(1_A)); 2.55 (*d*, *J* = 2.1, H–C≡C–C(8_D)). ^{13}C-NMR (75 MHz, $CDCl_3$): 98.45 (4*t*); 96.65 (4*t*); 86.16 (*d*); 85.88 (2*d*); 85.70 (*d*); 80.17 (*d*); 79.88 (*d*); 78.59 (*d*); 78.28 (3*d*); 76.63 (2*s*); 76.49 (*s*); 74.46 (*s*); 73.54 (*s*); 73.41 (*s*); 73.31 (*s*); 72.66 (*d*); 72.46 (3*d*); 72.24 (*s*); 71.16 (3*d*); 71.63 (*d*); 70.62 (*s*); 70.40 (*s*); 70.36 (*s*); 68.03 (2*s*); 67.92 (*s*); 67.20 (*t*); 67.18 (2*t*); 67.08 (*t*); 56.23 (4*q*); 55.40 (4*q*); 36.67 (*d*); 36.59 (2*d*); 36.83 (*d*). MALDI-MS: 1153 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-8-*C*-(5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D*-glycero-*D*-gulo-decitol-1-yl)-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D*-glycero-*D*-gulo-octitol* (**34**). A soln. of **33** (20 mg, 0.017 mmol) in dry MeOH/THF 1:1 (2 ml) was treated with 0.3N HCl (1 ml), and heated under reflux for 18 h. Filtration gave **34** (12.8 mg, 93%). Solid. R_f (AcOEt/MeOH 10:3) 0.24. M.p. 225° (dec.). $[\alpha]_D^{25} = -8.0$ (*c* = 0.3, DMSO). IR (KBr): 3400–3350*s* (br.), 3307*s*, 2919*m*, 2840*m*, 2258*w*, 2123*w*, 1636*w*, 1405*m*, 1369*m*, 1300*m*, 1100*s*, 1070*s*, 1050*s*, 1020*s*, 951*m*, 900*w*, 884*w*, 637*m*, 578*w*, 528*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO)[5]: 5.68 (*d*, *J* = 6.0, 2 OH); 5.59 (*d*, *J* = 5.8, OH); 5.58 (*d*, *J* = 6.2, 2 OH); 5.52 (*d*, *J* = 6.4, OH); 5.50 (*d*, *J* = 6.0, OH); 56.38 (*d*, *J* = 6.2, OH); 4.84 (*t*, *J* = 5.7, 3 OH); 4.74 (*t*, *J* = 5.8, OH); 4.02 (br. *d*, *J* ≈ 9.6, H–C(5_B), H–C(5_C)); 4.00 (br. *d*, *J* ≈ 9.7, H–C(5_D)); 3.88 (*dd*, *J* = 9.2, 2.1, H–C(3_A)); 3.67–3.59 (*m*, H–C(8_A), H–C(10_B), H–C(10_C), H–C(10_D)); 3.48–3.40 (*m*, H′–C(8_A), H′–C(10_B), H′–C(10_C), H′–C(10_D)); 3.39–3.22 (*m*, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D), H–C(7_A), H–C(9_B), H–C(9_C),

H–C(9_D)); 3.36 (*d*, *J* = 2.2, H–C(1_A)); 3.02 (*m*, H–C(4_A), H–C(6_B), H–C(6_C), H–C(6_D)); 2.95 (*d*, *J* = 2.2, H–C≡C–C(8_D)); 2.55–2.46 (*m*, H–C(6_A), H–C(8_B), H–C(8_C)); 2.31 (*td*, *J* = 10.3, 2.2, H–C(8_D)). ^{13}C-NMR (75 MHz, (D_6)DMSO): 82.45 (*d*); 81.77 (*d*); 79.47 (*d*); 79.40 (*s*); 79.23 (*s*); 79.12 (*s*); 78.98 (2*d*); 78.90 (*d*); 75.97 (*s*); 75.55 (*s*); 75.33 (*s*); 74.86 (*s*); 74.59 (*d*); 74.48 (3*d*); 73.74 (*s*); 73.68 (*d*); 73.62 (3*d*); 70.47 (3*d*); 70.14 (*d*); 69.36 (2*s*); 69.22 (*s*); 66.43 (*s*); 66.39 (*s*); 66.33 (*s*); 61.73 (4*t*); 37.78 (3*d*); 37.09 (*d*). MALDI-MS: 801 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl]-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-*D-gylcero-D-gulo-*octitol* (**35**). As described for **31**, with $Bu_4NF \cdot 3\,H_2O$ (13 mg, 0.04 mmol) in THF (1 ml) and **25** (20 mg, 5.3 µmol) in THF (1 ml; 0° for 5 min): **35** (11.5 mg, 96%). Solid. R_f (AcOEt) 0.75. M.p. 215°. $[\alpha]_D^{25} = -58.0$ (*c* = 0.45, $CHCl_3$). IR ($CHCl_3$): 3500–3100*m* (br.), 3307*m*, 3004*w*, 2936*m*, 2894*m*, 2829*w*, 2260*w*, 2172*w*, 1602*w*, 1463*m*, 1368*m*, 1329*m*, 1294*m*, 1261*m*, 1148*s*, 1135*s*, 1115*s*, 1097*s*, 1041*s*, 979*w*, 951*w*, 515*w*, 505*w*. ^{1}H-NMR (300 MHz, $CDCl_3$)[5]): 4.84 (*d*, *J* = 6.5, C*H*OMe); 4.893 (*d*, *J* = 6.6, 6 C*H*OMe); 4.82 (*d*, *J* = 6.8, 2 C*H*OMe); 4.80 (*d*, *J* = 6.7, C*H*OMe); 4.77 (*d*, *J* = 7.0, 6 C*H*OMe); 4.68 (*s*, 2 CH_2OMe); 4.66 (*s*, 6 CH_2OMe); 4.52 (br. *s*, HO–C(4_A), H–C(6_B), H–C(6_C), H–C(6_D), H–C(6_E), H–C(6_F), H–C(6_G), H–C(6_H)); 4.02 (br. *d*, *J* ≈ 9.1, H–C(5_H)); 3.96 (br. *d*, *J* ≈ 9.1, H–C(5_B), H–C(5_C), H–C(5_D), H–C(5_E), H–C(5_F), H–C(5_G)); 3.95 (*dd*, *J* = 9.3, 2.0, H–C(3_A)); 3.86–3.75 (*m*, 2 H–C(8_A), 2 H–C(10_B), 2 H–C(10_C), 2 H–C(10_D), 2 H–C(10_E), 2 H–C(10_F), 2 H–C(10_G), 2 H–C(10_H)); 3.55–3.32 (*m*, H–C(4_A), H–C(6_B), H–C(6_C), H–C(6_D), H–C(6_E), H–C(6_F), H–C(6_G), H–C(6_H), H–C(7_A), H–C(9_B), H–C(9_C), H–C(9_D), H–C(9_E), H–C(9_F), H–C(9_G), H–C(9_H), H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D), H–C(7_E), H–C(7_F), H–C(7_G), H–C(7_H)); 3.49 (*s*, 2 MeO); 3.47 (*s*, 4 MeO); 3.40 (*s*, MeO); 3.38 (*s*, 3 MeO); 3.37 (*s*, 6 MeO); 2.86 (br. *d*, *J* = 10.3, H–C(6_A)); 2.84 (*t*, *J* = 10.3, H–C(8_B), H–C(8_C), H–C(8_D), H–C(8_E), H–C(8_F), H–C(8_G)); 2.76 (*td*, *J* = 10.4, 2.2, H–C(8_H)); 2.55 (*d*, *J* = 2.1, H–C(1_A)); 2.18 (*d*, *J* = 2.2, H–C≡C–C(8_H)). ^{13}C-NMR (75 MHz, $CDCl_3$): 98.49 (8*t*); 96.66 (8*t*); 85.97 (7*d*); 85.82 (*d*); 80.17 (*d*); 79.88 (*d*); 78.60 (*d*); 78.30 (7*d*); 77.67 (*s*); 77.23 (5*s*); 76.43 (*s*); 73.55 (*s*); 73.41 (6*s*); 73.30 (*s*); 72.64 (*s*); 72.44 (8*d*); 71.16 (8*d*); 70.63 (*s*); 70.45 (*s*); 70.35 (5*s*); 68.10 (*s*); 68.04 (5*s*); 67.93 (*s*); 67.18 (8*t*); 56.24 (8*q*); 55.42 (8*q*); 36.59 (7*d*); 35.83 (*d*). MALDI-MS: 2281 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-8-*C*-(5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D-glycero-D-gulo-*decitol-1-yl)-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl]-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D-glycero-D-gulo-*octitol* (**36**). A soln. of **35** (10 mg, 4.4 µmol) in dry MeOH/THF 1:1 (2 ml) was treated with 0.3N HCl (3 ml) and heated under reflux for 10 h. Filtration gave **36** (6.4 mg, 94%). Solid. M.p. 220° (dec.). $[\alpha]_D^{25} = -4.8$ (*c* = 0.7, (D_6)DMSO). IR (KBr): 3500–3100*s* (br.), 2921*s*, 2850*s*, 2257*w*, 2123*w*, 1639*w*, 1436*m*, 1404*m*, 1368*m*, 1298*m*, 1048*m*, 1015*m*, 949*m*, 883*w*, 622*m*, 574*w*, 526*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO)[5]): 5.66 (*d*, *J* = 5.9, 6 OH); 5.58 (*d*, *J* = 5.7, OH); 5.57 (*d*, *J* = 6.0, 6 OH); 5.51 (*d*, *J* = 6.4, OH); 5.50 (*d*, *J* = 7.0, OH); 5.37 (*d*, *J* = 6.2, OH); 4.83 (*t*, *J* = 5.4, 7 OH); 4.75 (*t*, *J* = 5.8, OH); 4.02 (br. *d*, *J* ≈ 9.6, H–C(5_B), H–C(5_C), H–C(5_D), H–C(5_E), H–C(5_F), H–C(5_G)); 4.00 (br. *d*, *J* ≈ 9.5, H–C(5_H)); 3.88 (*dd*, *J* = 9.5, 2.0, H–C(3_A)); 3.68–3.55 (*m*, H–C(8_A), H–C(10_B), H–C(10_C), H–C(10_D), H–C(10_E), H–C(10_F), H–C(10_G), H–C(10_H)); 3.48–3.42 (*m*, H'–C(8_A), H'–C(10_B), H'–C(10_C), H'–C(10_D), H'–C(10_E), H'–C(10_F), H'–C(10_G), H'–C(10_H)); 3.39–3.22 (*m*, H–C(5_A), H–C(7_B), H–C(7_C), H–C(7_D), H–C(7_E), H–C(7_F), H–C(7_G), H–C(7_H), H–C(7_A), H–C(9_B), H–C(9_C), H–C(9_D), H–C(9_E), H–C(9_F), H–C(9_G), H–C(9_H)); 3.36 (*d*, *J* = 2.2, H–C(1_A)); 3.09–3.00 (*m*, H–C(4_A), H–C(6_B), H–C(6_C), H–C(6_D), H–C(6_E), H–C(6_F), H–C(6_G), H–C(6_H)); 2.95 (*d*, *J* = 2.2, H–C≡C–C(8_H)); 2.57–2.47 (*m*, H–C(6_A), H–C(8_B), H–C(8_C), H–C(8_D), H–C(8_E), H–C(8_F), H–C(8_G)); 2.30 (*td*, *J* = 10.4, 2.3, H–C(8_H)). ^{13}C-NMR (75 MHz, (D_6)DMSO): 82.75 (*d*); 82.07 (*d*); 79.78 (2*d*); 79.70 (2*s*); 79.52 (5*s*); 79.28 (6*d*); 75.85 (*s*); 75.79 (*s*); 75.63 (5*s*); 75.15 (2*d*); 74.80 (*s*); 74.79 (6*d*); 73.99 (*s*); 73.92 (8*d*); 70.77 (8*d*); 69.61 (7*s*); 66.67 (7*s*); 62.00 (8*t*); 37.61 (6*d*); 37.17 (2*d*). MALDI-MS: 1577 ([*M* + Na]$^+$).

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