

Oligosaccharide Analogues of Polysaccharides

Part 16

Cross-Coupling of Partially Protected Dialkynyl Monosaccharides

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The dependency of the cross-coupling of orthogonally *C*-protected dialkynyl monosaccharides on the nature of the coupling partners has been studied. The required dialkyne **5** was synthesized from levoglucosan in six steps and 39% overall yield and transformed into **7**, **10**, **12**, **13**, and **14** by orthogonal *C*-deprotection and bromination (*Scheme 1*). Optimization of the conditions of their cross-coupling to **16** showed that yields were higher for the coupling of the propargylic bromoalkyne **10** than for the homopropargylic bromoalkyne **14** (*Scheme 2*). Deprotection of **16** gave the nano-crystalline dimer **20**. To obtain more highly crystalline products, the monomers **7** and **13** were coupled with 1-iodo-4-nitrobenzene to the arylated monomers **21** and **24** (*Scheme 3*). The 4-NO₂C₆H₄ substituent lowered the yield of the dimerizations to the mono- and diarylated dimers **26–28** (*Scheme 4*) but had no effect on crystallinity.

Introduction. – The binomial synthesis of oligomeric *O*-benzyl-protected ‘acetyl-enocelluloses’ [1], requiring selective *C*-deprotection, *C*-bromination, and cross-coupling, proceeded in excellent yields up to an octamer [2], while the yield of the hexadecamer dropped to 6% [3], presumably due to problems of solubility. This raises questions about the number and kind of OH-protecting groups that are required to provide soluble oligomers and about their influence on the individual steps of the binomial cycle and especially on cross-coupling. Exploratory experiments of Alzeer [4] indicated that the results of the cross-coupling may also depend upon the position of the halo substituent.

We wished to evaluate the influence on the cross-coupling of the nature and position of the halide substituent of the haloalkynes and of *C*-aryl groups that might favour the tendency of the products to crystallize. To investigate these aspects, we required an orthogonally *C*-protected dialkynylated monomer that allows the regioselective introduction of Br and I substituents and of OH-protecting groups.

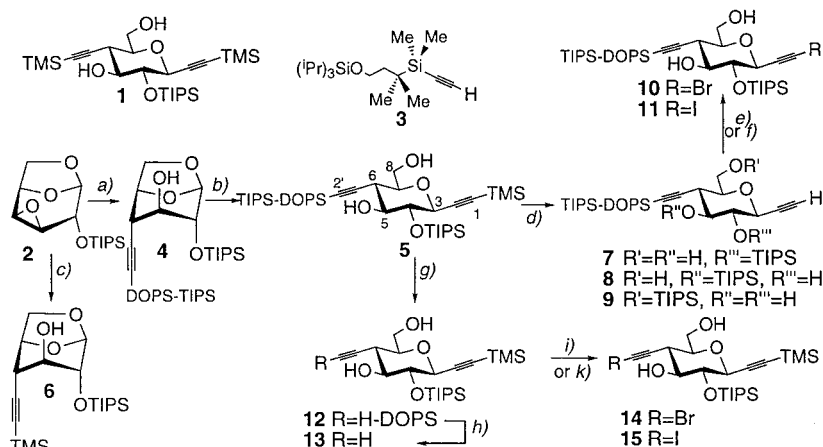
We report a short preparation of such an orthogonally *C*-protected, mono-*O*-silylated dialkyne **5**, its regioselective *C*-desilylation and *C*-halogenation, the cross-coupling of the resulting monomers, the coupling of the mono-*C*-desilylated monomers and dimers to 1-iodo-4-nitrobenzene, and the effect of the 4-nitrophenyl group on the cross-coupling.

Results and Discussion. – The bis-*C*-trimethylsilylated monomer **1** has been prepared in six steps and with an overall yield of 34% from levoglucosan by a

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sequential alkynylation opening of the oxirane and dioxolane rings of the intermediate epoxide **2** with (trimethylsilyl) acetylene [1]. For the analogous introduction of the DOPS-protected²⁾ alkyne **3** [5], we treated the epoxide **2** with the acetylide derived from **3**, BuLi, and AlMe₃ (Scheme 1). This yielded 87% of **4** that was readily transformed into **5** (63% from **2** on a scale of 15–20 g) [6]. The acetal **6** [1], however, that reacts well with excess TMS-acetylide, proved inert to **3**. As the orthogonal deprotection of **5** proceeded well, we did not pursue this reaction.

Scheme 1



a) TIPS-DOPS-C≡CH (**3**), BuLi, AlMe₃; 87%. b) 3 equiv. of Me₃SiC≡CH, 3 equiv. of BuLi, 3 equiv. of AlCl₃, toluene; 72%. c) Me₃SiC≡CH, BuLi, AlMe₃; 80%. d) 0.25M MeONa, MeOH; 94%. e) NBS, AgOCOCF₃, acetone; 97% from **7**. f) NIS, AgOCOCF₃, acetone; 94% from **7**. g) 0.01N HCl, EtOH, 45°; 97%. h) BuLi, THF, -78°; 97%; or DMSO, 60°; >98%. i) as e); 75%. k) as f); 73%.

Selective desilylation of **5** with MeONa in MeOH³⁾ gave **7** (97%; Scheme 1). Since bromoalkynes have led to a higher ratio of hetero- to homocoupling products than iodoalkynes [12], we brominated **7** with *N*-bromosuccinimide (NBS) in the presence of AgOCOCF₃ [2][13] to give 97% of the bromoalkyne **10**. It is remarkable that bromodesilylation [13] of the propargylic alkynyl group (*i.e.*, the alkynyl group at C(3)) of **5** with excess NBS was not complete after 65 h, while the analogous bromodesilylation of a homopropargylic alkynyl group (*i.e.*, the alkynyl group at C(6)) has been successful [2], reflecting the higher nucleophilicity of homopropargylic alkynyl ethers [8]⁴⁾. To remove the DOPS group of **5**, we had to selectively cleave the primary TIPS ether. This was readily achieved with dilute HCl, and the resulting H-DOPS-protected

²⁾ DOPS = (1,1-dimethyl-3-oxypropyl)dimethylsilyl.

³⁾ If MeOH contained traces of carbonate, the secondary (i-Pr)₃Si (TIPS) group migrated to O-C(5) and O-C(8) to give **8** and **9**, respectively, in varying yields. Such silyl migrations in the presence of either base [7] [8] or acid [9–11] are well precedented.

⁴⁾ Presumably, bromodesilylation occurs *via* a silver acetylide [2].

12 (97%) was transformed into **13** with catalytic amounts of BuLi at -78° (97%). The H-DOPS group was also removed by heating **12** in DMSO for 6 h at 60° (>98%). The bromoalkyne **14** was obtained in high yields by bromination of either **12** or **13**.

In the NMR spectra, the *s*'s of the $(\text{CH}_3)_3\text{Si}$ groups appear at 0.17 and the *s*'s of the $(\text{CH}_3)_2\text{Si}$ groups at 0.10 ppm; the *q*'s of the $(\text{CH}_3)_3\text{Si}$ groups resonate at -0.30 to -0.57 and those of the $(\text{CH}_3)_2\text{Si}$ groups at -4.00 to -4.43 ppm. The CH_2 groups of the DOPS moiety appear as broad *t*'s at 3.77 and 1.59 ppm. The $\text{H}-\text{C}\equiv\text{C}$ unit is evidenced by a *d* at 2.2 ppm ($\text{H}-\text{C}(2')$) or at 2.5 ppm ($\text{H}-\text{C}(1)$) with $J(\text{H},\text{H}) \approx 2.2$ Hz and a ^{13}C *d* at 80–81 ppm.

The ^1H -NMR spectra of **5**, **7**, **12**, and **13** in CDCl_3 and $(\text{D}_6)\text{DMSO}$ show well-resolved OH signals (Table 1). There are relevant differences for the $\text{HO}-\text{C}(5)$ and to some extent also for the $\text{HO}-\text{C}(8)$ signals. For the spectra of **5**, **7**, **12**, and **13** in CDCl_3 , the $J(\text{HO}-\text{C}(5), \text{H}-\text{C}(5))$ value of *ca.* 2.6–2.9 Hz is similar to the corresponding value for cellobiose [14]. However, while the *J* in cellobiose reflects the intramolecular H-bond to $\text{O}-\text{C}(5)$ of the neighbouring unit, $\text{HO}-\text{C}(5)$ of **5**, **7**, **12**, and **13** may form an intramolecular H-bond to $\text{O}-\text{C}(4)$, as confirmed by the IR band at *ca.* 3600 cm^{-1} [15]⁵. In keeping with this, the $J(\text{OH},\text{H})$ coupling for $\text{HO}-\text{C}(5)$ increases to *ca.* 8 Hz in the spectra of $(\text{D}_6)\text{DMSO}$. This is rationalized by a H-bond to DMSO and by the restricted rotation of the $\text{C}(5)-\text{OH}$ group, due to the interaction with the bulky $\text{C}(4)-\text{OTIPS}$ substituent. Indeed, $J(\text{HO}-\text{C}(5), \text{H}-\text{C}(5)) \approx 5.8$ Hz for $\text{HO}-\text{C}(5)$ of the fully deprotected dialkyne corresponding to **12** [4] is as expected for a freely rotating OH group [19].

Table 1. Selected ^1H -NMR Chemical Shifts [ppm] and Coupling Constants [Hz] of monomers **5**, **7**, **12**, and **13** in CDCl_3 and $(\text{D}_6)\text{DMSO}$ Solution at 22°

	In CDCl_3				In $(\text{D}_6)\text{DMSO}$			
	5	7	12	13	5	7	12	13
$\text{HO}-\text{C}(5)$	2.35	2.34	3.03	2.51	5.00	5.00	5.04	5.15
$\text{HO}-\text{C}(8)$	2.08	2.00	2.40	2.21	4.74	4.73	4.73	4.74
$J(\text{HO}-\text{C}(5), \text{H}-\text{C}(5))$	2.8	2.8	2.8	2.9	8.4	7.8	8.1	8.1
$J(\text{HO}-\text{C}(8), \text{H}-\text{C}(8))$	7.6	7.4	br.	7.4	5.0	5.2	5.0	5.6
$J(\text{HO}-\text{C}(8'), \text{H}-\text{C}(8'))$	6.0	6.0	br.	6.0	5.0	5.2	5.0	5.6

The transformation of **5** into **12** is reflected by a downfield shift of 0.7 and 0.3 ppm for $\text{HO}-\text{C}(5)$ and $\text{HO}-\text{C}(8)$, respectively, presumably due to an intramolecular H-bond from the DOPS moiety of **12** to either $\text{HO}-\text{C}(5)$ or $\text{HO}-\text{C}(8)$ as confirmed by an IR band at 3438 cm^{-1} . Removal of the H-DOPS group of **12** to **13** again shifted the signals of $\text{HO}-\text{C}(5)$ and $\text{HO}-\text{C}(8)$ to higher fields⁶). MM3* Calculations (Macromodel V.6.0) confirmed these observations and showed that H-bond distances are within the expected range.

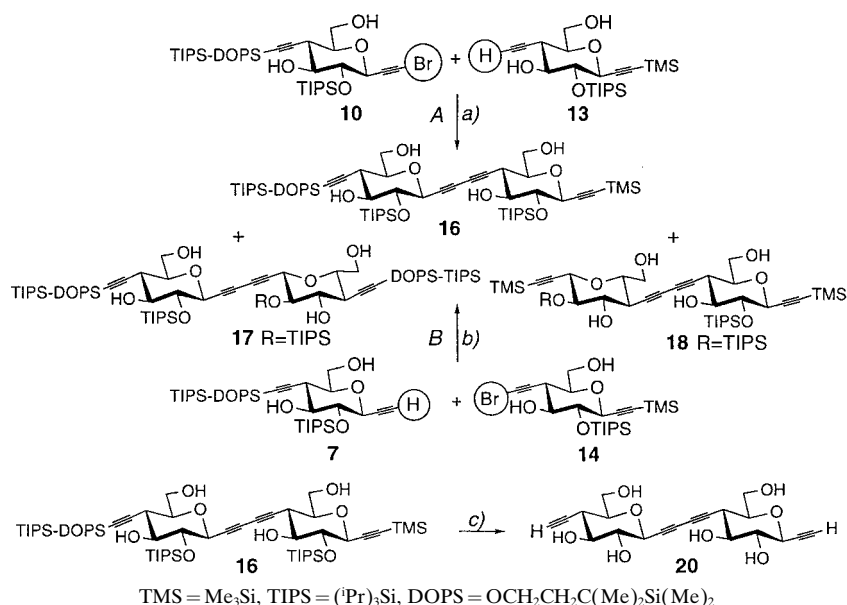
Chemical-shift values of **5** and **7–15** are summarized in Tables 3 and 4 (see *Exper. Part*).

To evaluate the influence of the position of the halo substituent on the cross-coupling, we compared the propargylic bromoalkynyl ether **10** and the homopropargylic bromoalkynyl ether **14**, coupling the former with the alkyne **13** and the latter with **7** (Scheme 2). Coupling **10** with **13** under the optimized conditions resulting from a study of simple alkynes ($[\text{Pd}_2(\text{dba})_3]$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one), CuI, LiI, and 1,2,2,6,6-pentamethylpiperidine (PMP) in DMSO [12]) gave 71% of the heterodimer **16**, besides 3% of the homodimer **17** and <1% of

⁵) H-Bonds between OH and acetylene groups are known [16–18]; they are rather weak.

⁶) The formation of 2,2,3,3-tetramethyl-1-oxasilacyclopentane was characterized by the appearance of two small *t* at 3.75 and 1.57 ppm [20]; it was removed under high vacuum concomitantly with DMSO.

Scheme 2



a) [Pd₂(dba)₃], CuI, LiI, PMP, DMSO: **16** (71%), **17** (3%), **18** (< 1%), or [Pd₂(dba)₃], CuI, P(fur)₃, Et₃N, DMSO: **16** (79%), **17** (2%), **18** (< 1%). b) [Pd₂(dba)₃], CuI, LiI, PMP, DMSO: **16** (61%), **17** (4%), **18** (9%); or [Pd₂(dba)₃], CuI, P(fur)₃, Et₃N, DMSO: **16** (64%), **17** (3%), **18** (12%). c) Bu₄NF · 3 H₂O, THF, 0°; 92%.

the homodimer **18** (Coupling A, Scheme 2). Coupling of the bromoalkyne **14** with the alkyne **7**, however, yielded 61% of **16**, 4% of **17** and 9% of **18** (Coupling B). It is clearly advantageous to use a propargylic bromoalkynyl ether in the cross-coupling.

However, as compared to previous results [2][12], we considered the cross-coupling yields insufficient. The results of an optimization are summarized in Table 2.

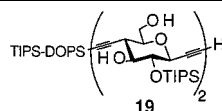
In agreement with the results of Cadiot and Chodkiewicz [21], we performed the reaction at 22°. Brandsma *et al.* suggested to proceed at the slightly elevated temperature resulting from slow addition of the bromoalkyne [22]. As we observed no heat evolution during the coupling of acetylenosaccharides, we performed the reaction of **10** and **13** at 50° (Table 2; Coupling A, Entry 2). This led to a faster reaction but decreased the yield of **16** and gave slightly higher amounts of the homodimer **17**. The results were not affected by the rate of addition of the bromoalkyne.

LiI, expected to reduce homo-coupling [12], had a negligible influence on the selectivity of the reaction (Entry 3). Use of P(fur)₃ [12][23][24] increased the yield of **16** from 71 to 75% (Entry 4); again, higher temperatures were not favourable (Entry 5). Replacing the bulky PMP by Et₃N (Entry 6) shortened the reaction time and improved the selectivity, in contradistinction to the results with simple alkynes [12]. Coupling in pyrrolidine (Entry 7) [25][26] induced partial desilylation of **16**; 11% of **19** and 43% of **16** being isolated after 10 h. This desilylation was almost completely suppressed in DMSO/pyrrolidine 5:1 (Entry 8), but these conditions showed no advantage over those specified in Entry 6. Coupling in benzene (Entry 9)

Table 2. Cross-Coupling of Alkynyl-Monomers at 22° (unless stated otherwise)

	Entry	Conditions		16	17	18	<i>t</i> [h]
Coupling A: Coupling of 10 and 13	1	[Pd ₂ (dba) ₃], CuI, DMSO	LiI, PMP	71	3	<1	30
	2		LiI, PMP, 50°	64	8	<1	24
	3		PMP	68	5	<1	30
	4		P(fur) ₃ , PMP	75	2	<1	30
	5		P(fur) ₃ , PMP, 50°	72	6	<1	15
	6		P(fur) ₃ , Et ₃ N	79	2	<1	10
	7	[Pd ₂ (dba) ₃], CuI, pyrrolidine		43 ^{a)}	8	<1	10
	8	[Pd ₂ (dba) ₃], CuI, DMSO	pyrrolidine ^{b)}	75	3	<1	12
	9	[Pd ₂ (dba) ₃], CuI, benzene	Et ₃ N	55	12	<1	20
	10	[Pd(PPh ₃) ₄], CuI, DMSO	Et ₃ N	49	8	<1	10
	11	[Pd(PPh ₃) ₄], CuI, benzene	Et ₃ N	52	9	<1	10
Coupling of 11 and 13	12	[Pd ₂ (dba) ₃], CuI, DMSO	P(fur) ₃ , Et ₃ N	81	3	<1	10
Coupling B: Coupling of 7 and 14	13	[Pd ₂ (dba) ₃], CuI, DMSO	LiI, PMP	61	4	9	30
	14		P(fur) ₃ , Et ₃ N	64	3	12	10
Coupling of 7 and 15	15	[Pd ₂ (dba) ₃], CuI, DMSO	P(fur) ₃ , Et ₃ N	61	3	12	10

^{a)} +11% of **19**. ^{b)} 16 equiv. of pyrrolidine; +2% of **19**.



decreased the yield of **16** and the selectivity. Using [Pd(PPh₃)₄] instead of [Pd₂(dba)₃] in either DMSO (Entry 10) or benzene (Entry 11) lowered the yields and the ratio **16/17**.

Since it is known that the H-DOPS group is removed *in situ* under cross-coupling conditions (3 equiv. of Et₃N) [2], we also tested the coupling of **10** with the H-DOPS-protected alkyne **12** under the conditions specified in Entry 6. Neither yield nor selectivity were affected.

The conditions described in Entry 6 were then applied to the alternative coupling of **7** to **14** (Coupling B, Entry 14). The yield of heterodimer **16** slightly increased, relative to those described in Entry 13, and so did the amount of the homodimer **18**.

The alkynylation of the (alkynyl)(bromo)palladium complex (formed by oxidative addition of the haloalkyne to Pd⁰) to give a bis(alkynyl)palladium(II) complex requires the deprotonation of the terminal alkyne [12]. This deprotonation depends upon the increased acidity resulting from coordination of the alkyne with Pd and Cu species. The homopropargylic moiety, being more nucleophilic, will coordinate more readily in keeping with the regioselective desilylation of homopropargylic C-silyl derivatives with AgNO₂/KCN in MeOH.

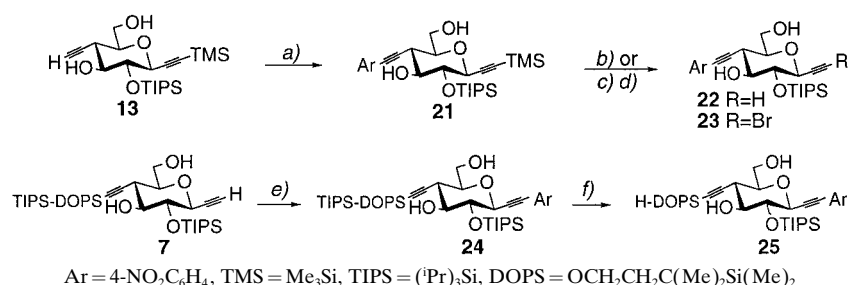
To check whether bromo- or iodoalkynes are to be preferred in the cross-coupling, we prepared the iodoalkynes **11** and **15** (Scheme 1). Surprisingly, coupling **11** to **13** (Table 2, Entry 12) slightly improved the selectivity in favour of the heterodimer **16**, while coupling of iodoalkyne **15** to **7** (Entry 15) led to a decreased selectivity. The difference between the alternative Couplings A and B is thus even more pronounced for the more highly reactive iodoalkynes.

In conclusion, the best results were obtained by coupling a propargylic iodoalkynyl ether and a homopropargylic H-DOPS-protected alkynyl ether in the presence of $[\text{Pd}_2(\text{dba})_3]$, CuI, $\text{P}(\text{fur})_3$, and Et_3N in DMSO, yielding 81% of the dimer **16**.

The dimer **16** was deprotected with $\text{Bu}_4\text{NF} \cdot 3 \text{H}_2\text{O}$ to give 92% of dimer **20** (Scheme 2). Crystallization of **20** from hot MeOH yielded a nano-crystalline material that refracted polarized light. At ca. 170° , the material started to soften, but it was difficult to determine a melting region. Differential scanning calorimetry (DSC) showed a narrow melting peak at 174° . The crystals, however, were not suitable for X-ray diffraction.

To obtain more readily crystallizable derivatives, we coupled *p*-nitrophenyl ($4\text{-NO}_2\text{C}_6\text{H}_4$) groups to the unprotected acetylene moiety of the monomers **7** and **13** [27][28]. Coupling **13** and 1-iodo-4-nitrobenzene ($4\text{-NO}_2\text{C}_6\text{H}_4\text{I}$) in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ and CuI in $\text{Et}_3\text{N}/\text{DMSO}$ yielded 98% of the arylated monomer **21** (Scheme 3); similarly, coupling **7** with $4\text{-NO}_2\text{C}_6\text{H}_4\text{I}$ led in 88% to **24**.

Scheme 3



a) $4\text{-NO}_2\text{C}_6\text{H}_4\text{I}$, $[\text{Pd}(\text{PPh}_3)_4]$, CuI, Et_3N , DMSO; 98%. b) NBS, AgOCOCF_3 , acetone; **23** (76%). c) MeONa, MeOH; **22** (79%). d) NBS, AgOCOCF_3 , acetone; **23** (97%). e) as a); 88%. f) 0.01N HCl, EtOH; 90%.

The brominating desilylation of **21**, using excess NBS and AgOCOCF_3 , proceeded slowly, providing 76% of **23** that was purified by HPLC. C-Desilylation of **21** to **22** (NaOMe/MeOH), followed by bromination gave **23** in about the same yield, but the product was much more readily purified. O-Desilylation of **24** at the TIPS-DOPS group yielded 90% of the H-DOPS-protected alkyne **25**.

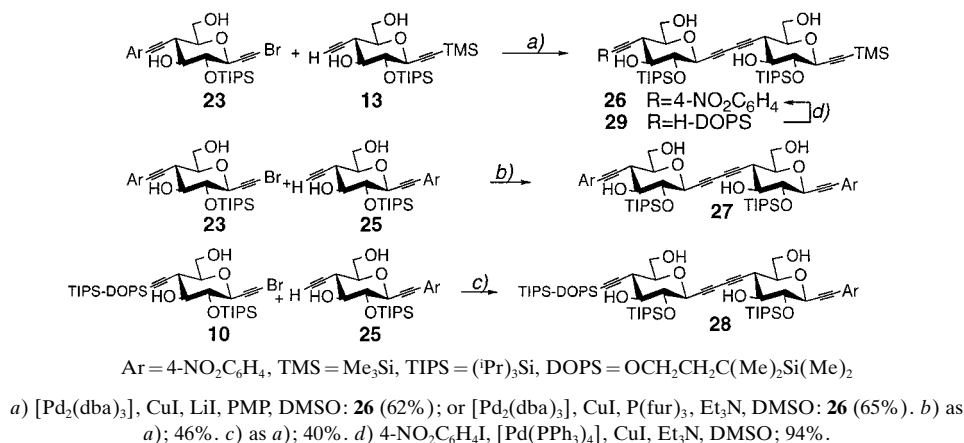
In the ^1H -NMR spectrum, H-C(3) and H-C(6) of the C(1) and C(2') 4-nitrophenylated products, respectively, are deshielded by 0.2–0.3 ppm (Table 3, see Exper. Part). The chemical shift of the ring C-atoms of arylated compounds are very similar to those of the non-arylated ones; the ^{13}C -NMR signals of the arylated ethyne C-atom, however, are shifted upfield by 7 to 12 ppm (Tables 4 and 5, see Exper. Part). The signals of the terminal or brominated ethyne moiety remained nearly unaffected.

The $4\text{-NO}_2\text{C}_6\text{H}_4$ substituent lowered the yields of the *Cadiot-Chodkiewicz* coupling ($[\text{Pd}_2(\text{dba})_3]$, CuI, LiI, and PMP in DMSO) of the arylated monomers **23** and **25** to the non-arylated monomers **10** and **13**, respectively (Scheme 4). The best yield of an arylated dimer resulted from coupling **23** to **13**; the monoarylated dimer **26** was obtained in 62%. Use of $\text{P}(\text{fur})_3$ and Et_3N (instead of LiI and PMP) led only to slightly better yields of **26**. High yields (94%) of **26**, however, resulted from coupling of **29**⁷⁾ to

7) Obtained by treatment of **16** with dilute acid.

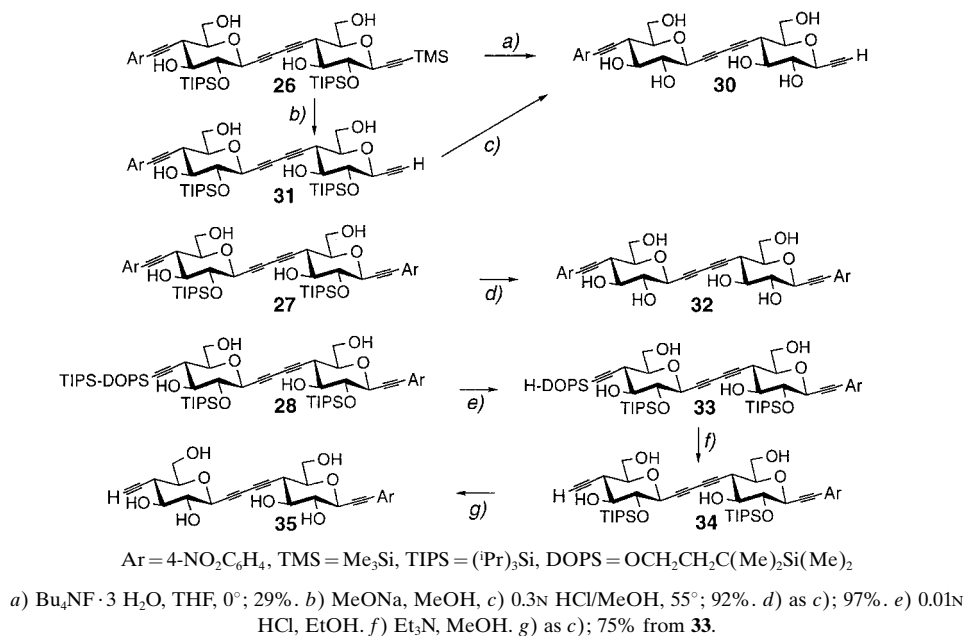
1-iodo-4-nitrobenzene. Coupling of the arylated **23** to the arylated **25** lead to **27** in only 46% yield; this decreased yield is due to the 4-nitrophenyl substituent attached at C(1), as evidenced by the coupling of **10** and **25**, yielding only 40% of **28**.

Scheme 4



Complete desilylation (Bu₄NF · 3 H₂O) of the dimer **26** to **30** proceeded in only 29% yield (Scheme 5), while C-desilylation of **26** (NaOMe/MeOH), followed by O-desilylation (0.3N HCl, 55°) yielded 92% of **30**. O-Desilylation of the diarylated **27**

Scheme 5



(0.3N HCl/MeOH, 55°) yielded 97% of **32**. Selective *O*-desilylation at the protected primary hydroxy group of **28** to **33** followed by treatment with Et₃N in MeOH gave **34** that was fully deprotected (0.3N HCl at 55°) to **35** (75%).

The deprotected arylated dimers are white to beige powders that refract polarized light. However, no crystals suitable for X-ray diffraction could be obtained.

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Experimental Part

General. See [1]. The molecular ions of the oligomers with molecular weight >1000 were detected by MALDI-TOF mass spectrometry with either α -cyano-4-hydroxycinnamic acid (CCA, 0.05–0.1M in MeCN/EtOH/H₂O) or indole-3-acetic acid (IAA, 0.05M in THF).

[3-(Ethinyl(dimethylsilyl)-3-methylbutoxy)triisopropylsilane (**3**). At 0°, a soln. of 3-[dimethyl[(trimethylsilyl)ethynyl]silyl]-3-methylbutan-1-ol [2] (7.29 g, 30.0 mmol) and 2,6-dimethylpyridine (8.7 ml, 75.0 mmol) in dry CH₂Cl₂ (100 ml) was treated dropwise with (i-Pr)₃SiOTf (TIPSOTf; 10.5 ml, 39.1 mmol), stirred for 2 h, and treated with H₂O (40 ml). Usual workup (CH₂Cl₂, H₂O, sat. NaCl) and FC (hexane) gave 1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethyl[(trimethylsilyl)ethynyl]silane (10.68 g, 96%). Transparent oil. *R*_f (hexane) 0.28. IR (CHCl₃): 2960s, 2944s, 2892m, 2866s, 1464m, 1410w, 1384w, 1365w, 1252s (br.), 1093m, 1069m, 1014w, 997w, 919w, 882m, 846s, 840s, 825s, 818s (br.). ¹H-NMR (300 MHz, CDCl₃): 3.81 (t, *J* = 7.8, 2H–C(3)); 1.63 (t, *J* = 7.8, 2H–C(2)); 1.10–1.03 (m, (Me₂CH)₃Si); 0.98 (s, Me₂C); 0.16 (s, Me₃Si); 0.12 (s, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 115.11, 112.22 (2s, C≡C); 60.58 (t, C(3)); 42.20 (t, C(2)); 23.61 (q, Me₂C); 18.69 (s, Me₂C); 18.26 (q, 3 Me₂CH); 12.22 (d, 3 Me₂CH); 0.05 (q, Me₃Si); –4.07 (q, Me₂Si). EI-MS: 398 (<1, *M*⁺), 359(7), 356(13), 355(40), 287(14), 286(34), 285(100), 244(15), 243(59), 215(54), 203(10), 202(15), 201(65), 157(16, TIPS⁺), 155(38), 145(7, DOPS⁺), 133(12), 73 (57, Me₃Si⁺), 59 (23). Anal. calc. for C₂₁H₄₆OSi₃ (398.85): C 63.24, H 11.62; found: C 63.12, H 11.49.

At 22°, a soln. of 1,1-Dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethyl[(trimethylsilyl)ethynyl]silane (14.58 g, 36.6 mmol) in dry, freshly distilled MeOH (240 ml) was treated with freshly prepared MeONa (0.25M in MeOH, 30 ml) and stirred for 3 h. After addition of *Amberlite IR-120*, the mixture was filtered and the filtrate was evaporated under reduced pressure. Distillation (0.4 mbar, 54°) gave **3** (11.76 g, 98%). Transparent oil. *R*_f (hexane) 0.27. IR (CHCl₃): 3287m, 2944s, 2891s, 2866s, 2727w, 1464s, 1412w, 1384m, 1365w, 1255s (br.), 1162w, 1094s, 1070s, 1014m, 997m, 966w, 936w, 919w, 883s, 841s, 824s (br.), 571w, 508w. ¹H-NMR (300 MHz, CDCl₃): 3.82 (t, *J* ≈ 7.8, 2H–C(3)); 2.37 (s, HC≡C); 1.64 (t, *J* ≈ 7.8, 2H–C(2)); 1.07–1.03 (m, (Me₂CH)₃Si); 1.00 (s, Me₂C); 0.16 (s, Me₂Si). ¹³C-NMR (50 MHz, CDCl₃): 94.37 (d, HC≡C); 88.79 (s, HC≡C); 60.53 (t, C(3)); 42.02 (t, C(2)); 23.54 (q, Me₂C); 18.61 (s, Me₂C); 18.24 (q, 3 Me₂CH); 12.18 (d, 3 Me₂CH); –4.18 (q, Me₂Si). CI-MS: 327 (27, [*M*+1]⁺), 302(13), 301(50), 293(67), 231(24), 215(28), 214(20), 213(82), 185(44), 157(47, TIPS⁺), 145(28, DOPS⁺), 142(45), 49(100).

1,6-Anhydro-4-deoxy-4-C-{dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl}-2-O-(triisopropylsilyl)-β-D-glucopyranose (**4**). At –15°, a soln. of **3** (16.9 g, 51.7 mmol) in dry toluene (30 ml) was treated dropwise with BuLi (21 ml, 2.3M in hexane, 51.7 mmol), warmed to 20°, stirred for 30 min, cooled to –15°, treated dropwise with a soln. of Me₃Al (26 ml, 2M in toluene, 51.7 mmol), and stirred at 20° for 60 min (→ white precipitate). The suspension was heated to 75° and treated with a soln. of **2** [1] (10.4 g, 34.5 mmol) in toluene (30 ml) *via* a double-ended needle. After 2 h at 75°, the mixture was cooled to 0° and slowly treated with a sat. NH₄Cl soln. (5 ml). Filtration over *Celite*, usual workup (AcOEt, H₂O), and FC (AcOEt/hexane 1:15) gave **4** (15.3 g, 71%). Transparent syrup. *R*_f (toluene/AcOEt 15:1) 0.13. [α]_D²⁵ = –53.05 (*c* = 1.9, CHCl₃). IR (CHCl₃): 3424m (br.), 3007s, 2945s, 2867s, 2839m, 2177w, 1603w, 1464m, 1384w, 1334w, 1248w, 1101m, 1016s, 919w, 883m, 868w, 838w, 658w (br.). ¹H-NMR (500 MHz, CDCl₃): 5.40 (br. s, H–C(1)); 4.61 (br. d, *J* = 4.8, H–C(5)); 3.94 (d, *J* = 7.3, H_{endo}–C(6)); 3.81–3.78 (m, H–C(3), CH₂CH₂OSi); 3.67 (dd, *J* = 7.3, 4.8, H_{exo}–C(6)); 3.61 (dd, *J* = 3.0, 1.4, H–C(2)); 2.65 (dd, *J* = 3.9, 1.7, H–C(4)); 2.35 (d, *J* = 6.7, HO–C(3)); 1.62 (t, *J* = 7.3, CH₂CH₂OSi); 1.13–1.06 (m, 2 (Me₂CH)₃Si); 0.97 (s, Me₂C); 0.10 (s, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 106.11 (s, C(1')); 103.40 (d, C(1)); 84.84 (s, C(2')); 75.47 (d, C(5)); 73.42 (d, C(2)); 73.33 (d, C(3)); 68.16 (t, C(6)); 60.28 (t, CH₂CH₂OSi); 41.66 (t, CH₂CH₂OSi); 38.35 (d, C(4)); 23.41 (q, Me₂C); 18.63 (s, Me₂C); 18.07 (q, 3 Me₂CH); 18.03 (q, 3 Me₂CH); 12.20 (d, 3 Me₂CH); 12.02 (d, 3 Me₂CH); –4.15 (q, Me₂Si). CI-MS:

645 (2, $[M + \text{NH}_4]^+$), 628 (4, $[M + 1]^+$), 627 (49, M^+), 453 (16), 409 (16), 303 (16), 302 (46), 301 (100, TIPS-DOPS⁺), 248 (16), 233 (26), 205 (18), 157 (7, TIPS⁺), 145 (5, DOPS⁺), 132 (16). Anal. calc. for $\text{C}_{33}\text{H}_{66}\text{O}_5\text{Si}_3$ (627.14): C 63.20, H 10.61; found: C 63.11, H 10.51.

3,7-Anhydro-1,2,6-trideoxy-6-C- $\{[\text{dimethyl}[1,1\text{-dimethyl-3-}[(\text{triisopropylsilyl})\text{oxy}]\text{propyl}]\text{silyl}\}\text{ethynyl}\}$ -4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (5). At -15° , a soln. of (trimethylsilyl)-acetylene (7.5 ml, 55.2 mmol) in dry toluene (50 ml) was treated dropwise with BuLi (23.5 ml, 2.3M in hexane, 55.2 mmol), stirred for 30 min at 21° , diluted with THF (2 ml) and added to a -15° cold, mechanically stirred suspension of AlCl_3 (7.27 g, 55.2 mmol) in dry toluene (40 ml) *via* a double-ended needle. Upon stirring at 21° for 45 min, a white precipitate was formed. The mixture was heated to 90° (bath temp.) and treated dropwise with a soln. of **4** (11.39 g, 18.2 mmol) in dry toluene (80 ml) leading to dissolution of the precipitate. After stirring for 18 h at 90° , the soln. was cooled to 0° and treated with a sat. NH_4Cl soln. (10 ml). Usual workup (AcOEt, H_2O) and FC (AcOEt/hexane 1 : 15) gave **5** (9.77 g, 74%). White solid. R_f (toluene/hexane 15 : 1) 0.22. M.p. 82° . $[\alpha]_D^{25} = -23.2$ ($c = 1.2$, CHCl_3). IR (CHCl_3): 3595w, 3427w, 3008m, 2945s, 2892s, 2867s, 2174w, 1522w, 1464m, 1384w, 1365w, 1349w, 1290w, 1252m (br.), 1143m, 1101s, 1071m, 1048m, 1014m, 991m, 919w, 883s, 845s, 824s (br.), 604w, 571w, 532w, 524w, 506w. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 3.95 (*d*, $J = 9.3$, $\text{H}-\text{C}(3)$); 3.93 (*ddd*, $J = 12.0$, 7.6, 2.7, $\text{H}-\text{C}(8)$); 3.77 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.73 (*dt*, $J \approx 12.0$, 6.1, $\text{H}'-\text{C}(8)$); 3.63 (*dd*, $J = 9.3$, 8.3, $\text{H}-\text{C}(4)$); 3.49 (*ddd*, $J \approx 10.3$, 8.3, 2.8, $\text{H}-\text{C}(5)$); 3.43 (*ddd*, $J \approx 10.3$, 6.1, 2.7, $\text{H}-\text{C}(7)$); 2.54 (*t*, $J = 10.3$, $\text{H}-\text{C}(6)$); 2.35 (*d*, $J = 2.8$, $\text{HO}-\text{C}(5)$); 2.08 (*dd*, $J \approx 7.6$, 6.0, $\text{HO}-\text{C}(8)$); 1.60 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.24–1.06 (*m*, 2 (Me_2CH)₃Si); 0.96 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). $^1\text{H-NMR}$ (300 MHz, $(\text{D}_6)\text{DMSO}$): 5.00 (*dd*, $J = 8.4$, $\text{HO}-\text{C}(5)$); 4.74 (*t*, $J = 5.0$, $\text{HO}-\text{C}(8)$); 3.87 (*d*, $J = 9.0$, $\text{H}-\text{C}(3)$); 3.72 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{O-Si}$); 3.70–3.64 (*m*, $\text{H}-\text{C}(8)$); 3.44 (*dt*, $J = 11.8$, 5.6, $\text{H}'-\text{C}(8)$); 3.37–3.17 (*m*, $\text{H}-\text{C}(4)$, $\text{H}-\text{C}(5)$, $\text{H}-\text{C}(7)$); 2.47–2.43 (*m*, $\text{H}-\text{C}(6)$); 1.51 (*t*, $J = 7.8$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.21–1.02 (*m*, (Me_2CH)₃Si); 0.91 (*s*, Me_2C); 0.09 (*s*, Me_3Si); 0.04 (*s*, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 102.58 (*s*); 102.34 (*s*); 91.10 (*s*); 88.28 (*s*); 78.91 (*d*); 76.89 (*d*); 75.05 (*d*); 71.97 (*d*); 63.70 (*t*); 60.16 (*t*); 41.64 (*t*); 39.12 (*d*); 23.38 (*2q*); 18.52 (*s*); 18.36 (*6q*); 18.08 (*6q*); 13.09 (*3d*); 12.01 (*3d*); -4.12 (*2q*). MS: 726 (2, $[M + 1]^+$), 725 (4, M^+), 507 (6), 303 (14), 302 (40), 301 (100, TIPS-DOPS⁺), 297 (12), 231 (13), 205 (18), 157 (6, TIPS⁺), 145 (2, DOPS⁺), 73 (10, Me_3Si^+). Anal. calc. for $\text{C}_{38}\text{H}_{76}\text{O}_5\text{Si}_4$ (725.36): C 62.92, H 10.56; found: C 62.77, H 10.47.

3,7-Anhydro-1,2,6-trideoxy-6-C- $\{[\text{dimethyl}[1,1\text{-dimethyl-3-}[(\text{triisopropylsilyl})\text{oxy}]\text{propyl}]\text{silyl}\}\text{ethynyl}\}$ -4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (7). At 22° , a soln. of **5** (2.73 g, 3.77 mmol) in dry, freshly distilled MeOH (100 ml) was treated with freshly prepared MeONa (0.25M in MeOH, 5 ml) and stirred for 3.5 h. After addition of *Amberlite IR-120*, the mixture was filtered and the filtrate evaporated under reduced pressure to give **7** (2.31 g, 94%). Transparent syrup. R_f (AcOEt/hexane 3 : 17) 0.24. $[\alpha]_D^{25} = -24.6$ ($c = 0.54$, CHCl_3). IR (CHCl_3): 3592w, 3429w (br.), 3306w, 3008w, 2945s, 2892m, 2867s, 2171w, 1602w, 1464m, 1384w, 1366w, 1256w (br.), 1144m, 1097s, 1047m, 1014w, 963w, 932w, 883w, 840w, 823m (br.), 652w, 603w, 540w. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 3.95 (*dd*, $J = 9.3$, 2.2, $\text{H}-\text{C}(3)$); 3.93 (*ddd*, $J = 12.0$, 7.4, 2.6, $\text{H}-\text{C}(8)$); 3.77 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.72 (*dt*, $J = 12.0$, 6.0, $\text{H}'-\text{C}(8)$); 3.66 (*dd*, $J = 9.3$, 8.3, $\text{H}-\text{C}(4)$); 3.51 (*ddd*, $J = 10.3$, 8.3, 2.8, $\text{H}-\text{C}(5)$); 3.45 (*ddd*, $J = 10.3$, 6.0, 2.6, $\text{H}-\text{C}(7)$); 2.56 (*t*, $J = 10.3$, $\text{H}-\text{C}(6)$); 2.47 (*d*, $J = 2.2$, $\text{H}-\text{C}(1)$); 2.39 (*d*, $J = 2.8$, $\text{HO}-\text{C}(5)$); 2.00 (*dd*, $J = 7.4$, 6.1, $\text{HO}-\text{C}(8)$); 1.60 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.23–1.05 (*m*, 2 (Me_2CH)₃Si); 0.97 (*s*, Me_2C); 0.12 (*s*, Me_2Si). $^1\text{H-NMR}$ (300 MHz, $(\text{D}_6)\text{DMSO}$): 5.00 (*d*, $J = 7.8$, $\text{HO}-\text{C}(5)$); 4.73 (*t*, $J = 5.2$, $\text{HO}-\text{C}(8)$); 3.84 (*dd*, $J = 9.0$, 2.2, $\text{H}-\text{C}(3)$); 3.73 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.70–3.64 (*m*, $\text{H}-\text{C}(8)$); 3.44 (*dt*, $J = 11.8$, 5.6, $\text{H}'-\text{C}(8)$); 3.37 (*d*, $J = 2.2$, $\text{H}-\text{C}(1)$); 3.34–3.17 (*m*, $\text{H}-\text{C}(4)$, $\text{H}-\text{C}(5)$, $\text{H}-\text{C}(7)$); 2.47–2.43 (*m*, $\text{H}-\text{C}(6)$); 1.51 (*t*, $J = 7.8$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.21–1.02 (*m*, (Me_2CH)₃Si); 0.90 (*s*, Me_2C); 0.04 (*s*, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 102.44 (*s*); 88.43 (*s*); 81.04 (*d*); 79.02 (*d*); 76.78 (*d*); 75.02 (*d*); 74.54 (*s*); 71.38 (*d*); 63.89 (*t*); 60.14 (*t*); 41.83 (*t*); 39.14 (*d*); 23.34 (*2q*); 18.52 (*s*); 18.36 (*6q*); 18.08 (*6q*); 13.02 (*3d*); 12.01 (*3d*); -4.12 (*2q*). CI-MS: 654 (13, $[M + 1]^+$), 653 (24, M^+), 609 (10), 435 (9), 305 (18), 303 (13), 302 (37), 301 (100, TIPS-DOPS⁺), 248 (11), 231 (14), 205 (12), 157 (5, TIPS⁺), 145 (3, DOPS⁺), 111 (6). Anal. calc. for $\text{C}_{35}\text{H}_{68}\text{O}_5\text{Si}_3$ (653.18): C 64.36, H 10.49; found: C 64.35, H 10.43.

Isomerization of 7: Mixture of **7**, **3,7-Anhydro-1,2,6-trideoxy-6-C- $\{[\text{dimethyl}[1,1\text{-dimethyl-3-}[(\text{triisopropylsilyl})\text{oxy}]\text{propyl}]\text{silyl}\}\text{ethynyl}\}$ -5-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (8), and **3,7-Anhydro-1,2,6-trideoxy-6-C- $\{[\text{dimethyl}[1,1\text{-dimethyl-3-}[(\text{triisopropylsilyl})\text{oxy}]\text{propyl}]\text{silyl}\}\text{ethynyl}\}$ -8-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (9).** In the presence of traces of carbonate, **7** as well as the two isomers **8** and **9** have been isolated in varying yields.**

Data of 8: R_f (AcOEt/hexane 3 : 17) 0.08. $[\alpha]_D^{25} = -23.9$ ($c = 0.49$, CHCl_3). IR (CHCl_3): 3598m, 3306m, 2945s, 2892s, 2172m, 2122w, 1711w, 1464s, 1384m, 1365m, 1298w, 1252s (br.), 1141s, 1085s, 1014s, 997s, 919w, 883s, 818s, 582s, 509w. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 3.97 (*dd*, $J = 9.7$, 2.2, $\text{H}-\text{C}(3)$); 3.96 (*ddd*, $J = 12.0$, 7.3, 2.6, $\text{H}-\text{C}(8)$); 3.78 (*dd*, $J = 10.3$, 8.3, $\text{H}-\text{C}(5)$); 3.77 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.75 (*dt*, $J \approx 12.0$, 6.0, $\text{H}'-\text{C}(8)$); 3.47

(*ddd*, $J \approx 10.5$, 5.8, 2.6, H–C(7)); 3.40 (*ddd*, $J = 9.7$, 8.3, 3.1, H–C(4)); 2.60 (*t*, $J = 10.3$, H–C(6)); 2.57 (*d*, $J = 2.2$, H–C(1)); 2.31 (*d*, $J = 2.8$, HO–C(4)); 2.03 (*dd*, $J = 7.3$, 6.3, HO–C(8)); 1.60 (*t*, $J = 7.7$, CH₂CH₂OSi); 1.23–1.05 (*m*, 2 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.10 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 104.25 (*s*); 87.67 (*s*); 80.09 (*d*); 79.97 (*d*); 76.61 (*d*); 75.24 (*d*); 74.82 (*s*); 70.55 (*d*); 63.69 (*t*); 60.10 (*t*); 41.40 (*t*); 39.68 (*d*); 23.26 (*2q*); 18.53 (*s*); 18.43 (*6q*), 18.08 (*6q*); 13.06 (*3d*); 12.00 (*3d*); –4.32 (*q*); –4.40 (*q*). CI-MS: 654 (13, [*M* + 1]⁺), 653 (24, *M*⁺), 609 (10), 435 (9), 305 (18), 303 (13), 302 (37), 301 (100, TIPS-DOPS⁺), 248 (11), 231 (14), 205 (12), 157 (5, TIPS⁺), 145 (3, DOPS⁺), 111 (6). Anal. calc. for C₃₅H₆₈O₅Si₃ (653.18): C 64.36, H 10.49; found: C 64.41, H 10.39.

Data of 9: R_f (AcOEt/hexane 3:17) 0.22. [α]_D²⁵ = –23.1 (*c* = 0.47, CHCl₃). IR (CHCl₃): 3608*m*, 3306*m*, 3008*m*, 2945*s*, 2892*s*, 2867*s*, 2172*w*, 1734*m*, 1464*m*, 1386*w*, 1365*w*, 1260*s* (br.), 1133*s*, 1090*s*, 1014*s*, 883*s*, 818*s*, 653*w*. ¹H-NMR (300 MHz, CDCl₃): 4.50 (*dd*, $J = 12.1$, 1.8, H–C(8)); 4.21 (*dd*, $J = 12.1$, 6.0, H'–C(8)); 3.94 (*dd*, $J = 9.7$, 2.2, H–C(3)); 3.773 (*ddd*, $J \approx 10.1$, 8.4, 2.1, H–C(5)); 3.767 (*t*, $J \approx 7.6$, CH₂CH₂OSi); 3.60 (*ddd*, $J = 10.6$, 6.0, 1.8, H–C(7)); 3.42 (*ddd*, $J \approx 9.6$, 8.4, 3.2, H–C(4)); 2.60 (*t*, $J = 10.5$, H–C(6)); 2.57 (*d*, $J = 2.1$, HO–C(5)); 2.56 (*d*, $J = 2.2$, H–C(1)); 2.33 (*d*, $J = 2.8$, HO–C(4)); 1.58 (*t*, $J \approx 7.5$, CH₂CH₂OSi); 1.25–1.05 (*m*, 2 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.09 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 103.80 (*s*); 88.07 (*s*); 79.93 (*d*); 77.65 (*d*); 76.59 (*d*); 75.06 (*d*); 74.94 (*s*); 70.68 (*d*); 64.88 (*t*); 60.06 (*t*); 41.24 (*t*); 39.93 (*d*); 23.16 (*2q*); 18.52 (*s*); 18.39 (*6q*); 18.09 (*6q*); 13.05 (*3d*); 12.00 (*3d*); –4.38 (*q*); –4.43 (*q*). CI-MS: 654 (6, [*M* + 1]⁺), 653 (17, *M*⁺), 652 (35), 651 (66), 447 (11), 451 (20), 347 (17), 303 (11), 302 (27), 301 (100, TIPS-DOPS⁺), 248 (29), 247 (27), 231 (27), 157 (11, TIPS⁺), 145 (7, DOPS⁺), 117 (16), 75 (10). Anal. calc. for C₃₅H₆₈O₅Si₃ (653.18): C 64.36, H 10.49; found: C 64.40, H 10.41.

3,7-Anhydro-1-C-bromo-1,2,6-trideoxy-6-C-[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl]-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (10). A soln. of **7** (5.98 g, 9.07 mmol) and NBS (1.70 g, 9.53 mmol) in dry acetone (300 ml) was treated with AgOCOCF₃ (60.1 mg, 0.27 mmol) and stirred in the dark (Al foil) at 21° for 1 h. After completion, the mixture was worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 3:47) gave **10** (6.47 g, 97%). Transparent syrup. R_f (AcOEt/hexane 1:4) 0.59. [α]_D²⁵ = –27.6 (*c* = 0.5, CHCl₃). IR (CHCl₃): 3604*m*, 3008*m*, 2945*s*, 2892*m*, 2867*s*, 2172*w*, 1605*w*, 1464*m*, 1384*w*, 1366*w*, 1253*m*, 1002*s*, 1047*m*, 997*m*, 932*w*, 883*m*, 840*m*, 824*m* (br.), 654*m*, 602*w*, 504*w*. ¹H-NMR (500 MHz, CDCl₃): 3.97 (*d*, $J = 9.3$, H–C(3)); 3.93 (*ddd*, $J = 12.0$, 7.4, 2.6, H–C(8)); 3.78 (*t*, $J \approx 7.7$, CH₂CH₂OSi); 3.72 (*dt*, $J = 12.0$, 6.0, H'–C(8)); 3.64 (*dd*, $J = 9.3$, 8.4, H–C(4)); 3.50 (*ddd*, $J \approx 10.4$, 8.4, 2.8, H–C(5)); 3.44 (*ddd*, $J = 10.3$, 5.9, 2.6, H–C(7)); 2.55 (*t*, $J = 10.3$, H–C(6)); 2.35 (*d*, $J = 2.8$, HO–C(5)); 1.99 (*dd*, $J = 7.4$, 6.1, HO–C(8)); 1.60 (*t*, $J \approx 7.7$, CH₂CH₂OSi); 1.26–1.04 (*m*, 2 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.11 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 102.40 (*s*); 88.42 (*s*); 78.99 (*d*); 76.89 (*s*); 76.70 (*d*); 75.16 (*d*); 72.26 (*d*); 63.63 (*t*); 60.15 (*t*); 47.21 (*s*); 41.64 (*t*); 39.07 (*d*); 23.35 (*2q*); 18.37 (*s*); 18.26–18.21 (*6q*); 18.09 (*6q*); 12.94 (*3d*); 12.01 (*3d*); –4.12 (*2q*). CI-MS: 734 (2), 733 (5), 732 (2, [*M* + 1]⁺), 731 (4, *M*⁺), 303 (14), 302 (35), 301 (100, TIPS-DOPS⁺), 231 (11), 205 (20), 174 (6), 157 (7, TIPS⁺), 148 (6), 145 (4, DOPS⁺). Anal. calc. for C₃₅H₆₇BrO₅Si₃ (732.07): C 57.42, H 9.22; found: C 57.45, H 9.26.

3,7-Anhydro-1,2,6-trideoxy-6-C-[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl]-1-C-iodo-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (11). A soln. of **7** (2.1 g, 3.22 mmol) and NIS (0.798 g, 3.55 mmol) in dry acetone (110 ml) was treated with AgOCOCF₃ (36.0 mg, 0.161 mmol) and stirred in the dark (Al foil) at 21° for 1 h. After completion, the mixture was worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 1:9) gave **11** (2.35 g, 94%). White foam. R_f (AcOEt/hexane 1:3) 0.48. M.p. 101.5–102.5°. [α]_D²⁵ = –21.8 (*c* = 0.6, CHCl₃). IR (CHCl₃): 3593*w*, 2945*s*, 2892*s*, 2867*s*, 2172*w*, 1602*w*, 1464*m*, 1384*w*, 1365*w*, 1291*w*, 1261*s*, 1142*m*, 1099*s*, 1014*s*, 919*w*, 883*m*, 818*m*, 601*w*, 524*w*, 508*w*. ¹H-NMR (500 MHz, CDCl₃): 4.08 (*d*, $J = 9.3$, H–C(3)); 3.94 (*m*, H–C(8)); 3.77 (*t*, $J = 7.7$, CH₂CH₂OSi); 3.72 (*td*, $J = 12.0$, 6.0, H'–C(8)); 3.64 (*dd*, $J = 9.3$, 8.4, H–C(4)); 3.50 (*ddd*, $J \approx 10.4$, 8.4, 2.7, H–C(5)); 3.43 (*ddd*, $J = 10.4$, 6.0, 2.7, H–C(7)); 2.56 (*t*, $J \approx 10.4$, H–C(6)); 2.36 (*d*, $J = 2.7$, HO–C(5)); 2.01 (br. *t*, $J \approx 6.5$, HO–C(8)); 1.60 (*t*, $J = 7.7$, CH₂CH₂OSi); 1.28–1.06 (*m*, 2 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.11 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 102.42 (*s*); 91.37 (*s*); 88.38 (*s*); 78.98 (*d*); 76.73 (*d*); 75.34 (*d*); 72.79 (*d*); 63.63 (*t*); 60.15 (*t*); 41.64 (*t*); 39.04 (*d*); 23.37 (*2q*); 18.52 (*s*); 18.31 (*6q*); 18.09 (*6q*); 13.02 (*3d*); 12.01 (*3d*); 5.00 (*s*); 1.04 (*s*); –4.12 (*2q*). CI-MS: 779 (1, *M*⁺), 735 (1), 653 (3), 453 (3), 303 (10), 302 (25), 301 (100, TIPS-DOPS⁺), 231 (15), 205 (22), 173 (6), 157 (8, TIPS⁺), 145 (3, DOPS⁺), 131 (10), 103 (7), 49 (12). Anal. calc. for C₃₅H₆₇IO₅Si₃ (779.07): C 53.96, H 8.67, I 16.29; found: C 53.93, H 8.45, I 16.06.

3,7-Anhydro-1,2,6-trideoxy-6-C-[[3-hydroxy-1,1-dimethylpropyl]dimethylsilyl]ethynyl]-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (12). A soln. of **5** (109.8 mg, 0.151 mmol) in EtOH (2.5 ml) was treated with 0.1*N* HCl (0.3 ml) and stirred at 50° for 5.5 h. After evaporation, FC (AcOEt/hexane 3:17 → 1:3) gave **12** (83.6 mg, 97%). White foam. R_f (AcOEt/hexane 1:3) 0.17. M.p. 129–130°. [α]_D²⁵ = –29.8

($c = 1.72$, CHCl_3). IR (CHCl_3): 3597w, 3438w (br.), 3008m, 2946s, 2892s, 2866s, 2174m, 1602w, 1464m, 1386m, 1364m, 1349m, 1291m, 1252s, 1144s, 1102s, 1071s, 991s, 918w, 884s, 845s, 822m, 655w. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.95 ($d, J = 9.2$, $\text{H-C}(3)$); 3.96–3.92 ($m, \text{H-C}(8)$); 3.77 ($t, J = 7.2$, CH_2OH); 3.78–3.68 ($m, \text{H'-C}(8)$); 3.61 ($dd, J = 9.3, 8.4$, $\text{H-C}(4)$); 3.55–3.50 ($m, \text{H-C}(5)$); 3.43 ($ddd, J = 10.3, 6.2, 2.8$, $\text{H-C}(7)$); 3.03 ($d, J = 2.8$, $\text{HO-C}(5)$); 2.53 ($t, J = 10.3$, $\text{H-C}(6)$); 2.40 (br. s, $\text{HO-C}(8)$); 1.83 (br. s, $\text{CH}_2\text{CH}_2\text{OH}$); 1.60 ($t, J = 7.2$, $\text{CH}_2\text{CH}_2\text{OH}$); 1.19–1.08 ($m, (\text{Me}_2\text{CH})_3\text{Si}$); 0.95 (s, Me_2C); 0.16 (s, Me_3Si); 0.11 (s, Me_2Si). $^1\text{H-NMR}$ (300 MHz, $(\text{D}_6)\text{DMSO}$): 5.04 ($d, J = 8.1$, $\text{HO-C}(5)$); 4.73 ($t, J = 5.0$, $\text{HO-C}(8)$); 4.26 ($t, J = 5.0$, $\text{CH}_2\text{CH}_2\text{OH}$); 3.92 ($d, J = 9.3$, $\text{H-C}(3)$); 3.74–3.61 ($m, \text{H-C}(8)$); 3.49–3.43 ($m, \text{H'-C}(8)$, $\text{CH}_2\text{CH}_2\text{OH}$); 3.36–3.18 ($m, \text{H-C}(4), \text{H-C}(5), \text{H-C}(7)$); 2.51–2.48 ($m, \text{H-C}(6)$); 1.42 ($t, J = 7.8$, $\text{CH}_2\text{CH}_2\text{OH}$); 1.21–1.02 ($m, (\text{Me}_2\text{CH})_3\text{Si}$); 0.89 (s, Me_2C); 0.09 (s, Me_3Si); 0.04 (s, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 103.40 (s); 102.40 (s); 91.06 (s); 87.99 (s); 79.02 (d); 76.81 (d); 75.03 (d); 71.97 (d); 63.65 (t); 59.93 (t); 42.83 (t); 39.06 (d); 23.94 (2q); 18.87 (s); 18.23 (6q); 12.90 (3d); –0.56 (3q); –4.17 (2q). CI-MS: 569 (1, M^+), 444 (10), 443 (25), 442 (71), 425 (53), 322 (20), 321 (69), 255 (18), 233 (15), 148 (25), 146 (26), 145 (100, DOPS^+), 144 (11), 129 (67), 103 (25), 75 (97), 73 (37), 48 (14). Anal. calc. for $\text{C}_{29}\text{H}_{56}\text{O}_5\text{Si}_3$ (569.02): C 61.21, H 9.92; found: C 61.25, H 10.43.

3,7-Anhydro-1,2,6-trideoxy-6-C-ethynyl-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (13). As described in [1]; crystallization from Et_2O /hexane instead of FC. Data: see [1]. $^1\text{H-NMR}$ (300 MHz, $(\text{D}_6)\text{DMSO}$): 5.15 ($d, J = 8.1$, $\text{HO-C}(5)$); 4.74 ($t, J = 5.6$, $\text{HO-C}(8)$); 3.92 ($d, J = 9.3$, $\text{H-C}(3)$); 3.63 ($ddd, J = 11.4, 5.0, 0.8$, $\text{H-C}(8)$); 3.45 ($dt, J = 11.5, 5.3$, $\text{H'-C}(8)$); 3.36–3.18 ($m, \text{H-C}(4), \text{H-C}(5), \text{H-C}(7)$); 2.96 ($d, J = 2.2$, $\text{H-C}(2')$); 2.37 ($td, J = 10.3, 2.5$, $\text{H-C}(6)$); 1.21–1.02 ($m, (\text{Me}_2\text{CH})_3\text{Si}$); 0.09 (s, Me_3Si).

3,7-Anhydro-1,2,6-trideoxy-6-C-(bromoethynyl)-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (14). A soln. of **13** (322.4 mg, 0.759 mmol) and NBS (141.9 mg, 0.797 mmol) in dry acetone (40 ml) was treated with AgOCOCF_3 (8.4 mg, 0.0380 mmol) and stirred in the dark (Al foil) at 21° for 6 h. After completion, the mixture was worked up normally (Et_2O , H_2O). FC (AcOEt /hexane 1:9) gave **14** (0.29 g, 75%). White foam. R_f (AcOEt /hexane 1:2) 0.58. M.p. 65° . $[\alpha]_D^{25} = -33.3$ ($c = 0.5$, CHCl_3). IR (CHCl_3): 3579m, 2990s, 2945m, 2864w, 2172w, 1588m, 1490m, 1462m, 1351s (br.), 1139m, 1117m, 978s, 901w, 887m, 862m, 840s (br.), 643s (br.), 601m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.97 ($d, J = 9.1$, $\text{H-C}(3)$); 3.96–3.93 ($m, \text{H-C}(8)$); 3.73 ($dt, J = 12.0, 6.0$, $\text{H'-C}(8)$); 3.63 ($dd, J \approx 9.0, 8.3$, $\text{H-C}(4)$); 3.54 ($ddd, J = 10.3, 8.3, 3.0$, $\text{H-C}(5)$); 3.46 ($ddd, J = 10.3, 5.7, 2.5$, $\text{H-C}(7)$); 2.59 ($t, J = 10.3$, $\text{H-C}(6)$); 2.44 ($d, J = 3.0$, $\text{HO-C}(5)$); 2.05 ($dd, J = 7.4, 6.2$, $\text{HO-C}(8)$); 1.27–1.09 ($m, (\text{Me}_2\text{CH})_3\text{Si}$); 0.18 (s, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 101.82 (s); 91.02 (s); 78.44 (d); 76.47 (d); 75.83 (s); 74.91 (d); 71.01 (d); 63.17 (t); 43.36 (s); 38.33 (d); 18.06 (6q); 12.77 (3d); –0.68 (3q). CI-MS: 523 (34), 521 (32, $[M + \text{NH}_4]^+$), 505 (10), 503 (9, M^+), 442 (25), 426 (17), 401 (33), 399 (32), 321 (40), 148 (89), 157 (24, TIPS^+), 131 (87), 103 (61), 73 (100, Me_3Si^+). Anal. calc. for $\text{C}_{22}\text{H}_{39}\text{BrO}_4\text{Si}_2$ (503.62): C 52.47, H 7.81; found: C 52.55, H 7.69.

3,7-Anhydro-1,2,6-trideoxy-6-C-(iodoethynyl)-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (15). A soln. of **13** (126.9 mg, 0.299 mmol) and NIS (73.9 mg, 0.329 mmol) in dry acetone (3 ml) was treated with AgOCOCF_3 (3.3 mg, 0.0149 mmol) and stirred in the dark (Al foil) at 21° for 3 h. After completion, the mixture was worked up normally (Et_2O , H_2O). FC (AcOEt /hexane 1:9) gave **15** (120.2 mg, 73%). White foam. R_f (AcOEt /hexane 1:2) 0.57. $[\alpha]_D^{25} = -32.8$ ($c = 0.5$, CHCl_3). IR (CHCl_3): 3601s, 3008s, 2946s, 2867s, 2399m, 2180m, 1602m, 1520w, 1464m, 1391m, 1366m, 1349m, 1291m, 1265m, 1252s, 1144s, 1104s, 1072s, 1047s, 1017m, 991m, 931w, 884s, 846s, 653m, 638w. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.95 ($d, J = 9.0$, $\text{H-C}(3)$); 3.93 ($ddd, J = 11.8, 7.2, 2.5$, $\text{H-C}(8)$); 3.72 ($td, J = 11.8, 5.9$, $\text{H'-C}(8)$); 3.61 ($dd, J = 9.0, 8.4$, $\text{H-C}(4)$); 3.53 ($ddd, J = 10.3, 8.1, 3.1$, $\text{H-C}(5)$); 3.45 ($ddd, J = 10.3, 5.9, 2.8$, $\text{H-C}(7)$); 2.70 ($t, J = 10.3$, $\text{H-C}(6)$); 2.49 ($d, J = 2.8$, $\text{HO-C}(5)$); 2.12 (br. t, $J \approx 6.7, 6.2$, $\text{HO-C}(8)$); 1.25–1.10 ($m, (\text{Me}_2\text{CH})_3\text{Si}$); 0.16 (s, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 102.16 (s); 91.34 (s); 90.16 (s); 78.91 (d); 76.91 (d); 75.19 (d); 71.91 (d); 63.46 (t); 39.55 (d); 18.23 (6q); 14.01 (s); 12.92 (3d); –0.55 (3q). CI-MS: 568 (15, $[M + \text{NH}_4]^+$), 551 (9, $[M + 1]^+$), 447 (29), 444 (9), 443 (12), 442 (37), 425 (35), 321 (74), 297 (45), 255 (57), 157 (23, TIPS^+), 131 (96), 103 (60), 73 (100).

Coupling of 10 with 13. A soln. of **10** (3.45 g, 4.71 mmol), **13** (2.00 g, 4.71 mmol), $[\text{Pd}_2(\text{dba})_3]$ (129.3 mg, 0.14 mmol), CuI (26.9 mg, 0.14 mmol), and $\text{P}(\text{fur})_3$ (54.7 mg, 0.236 mmol) in DMSO (70 ml) in a flame-dried Schlenk flask was degassed for 15 min, treated with dry Et_3N (2.0 ml, 14.13 mmol), and stirred in the dark for 10 h. After completion, the mixture was poured onto ice/ H_2O , neutralized with 1N HCl and worked up normally (Et_2O , H_2O). FC (AcOEt /hexane 1:10 $\rightarrow$ 3:17) gave **17** (116.7 mg, 2%), **16** (4.00 g, 79%), and **18** (31.1 mg, <1%) as white foams.

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

	H–C(1)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(7)	H–C(8)	H'–C(8)	H–C(2')	HO–C(4)	HO–C(5)	HO–C(8)
5	–	3.95	3.63	3.49	2.54	3.43	3.93	3.73	–	–	2.35	2.08
7	2.48	3.95	3.66	3.52	2.56	3.46	3.93	3.72	–	–	2.34	2.00
8	2.57	3.97	3.40	3.78	2.60	3.47	3.96	3.75	–	2.31	–	2.03
9	2.56	3.94	3.42	3.77	2.60	3.60	4.50	4.21	–	2.33	2.57	–
10	–	3.97	3.64	3.50	2.55	3.44	3.93	3.72	–	2.35	1.99	–
11	–	4.08	3.64	3.50	2.56	3.43	3.94	3.72	–	–	2.36	2.01
12	–	3.95	3.61	3.53	2.53	3.43	3.94	3.75	–	–	3.03	2.40
13	–	3.97	3.64	3.54	2.66	3.47	3.95	3.75	2.24	–	2.51	2.21
14	–	3.97	3.63	3.54	2.59	3.46	3.94	3.72	–	–	2.44	2.05
15	–	3.95	3.61	3.53	2.70	3.45	3.93	3.72	–	–	2.49	2.12
21	–	4.03	3.70	3.65	2.85	3.57	4.00	3.81	–	–	2.53	2.13
22	2.53	4.05	3.74	3.67	2.88	3.60	3.99	3.81	–	–	2.53	2.11
23	–	4.05	3.72	3.64	2.86	3.59	4.00	3.80	–	–	2.55	2.09
24	–	4.22	3.76	3.56	2.62	3.53	3.98	3.80	–	–	2.40	2.05
25	–	4.21	3.75	3.60	2.62	3.54	4.00	3.80	–	–	3.18	2.40

Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]-silyl]ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diyntol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (**16**): R_f (AcOEt/hexane 1:4) 0.26. M.p. 85–86°. $[\alpha]_D^{25} = -38.1$ ($c=0.7$, CHCl_3). IR (CHCl_3): 3594w, 2962s, 2867s, 2254w, 2173w, 1602w, 1464m, 1384w, 1365w, 1328w, 1291w, 1261s, 1141m, 1098s, 1015s, 909m, 883m, 845m, 818s, 596w, 576w, 536w, 512w, 504w. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 3.99 (*dd*, $J=9.3$, 0.6, H–C(5')); 3.95 (*d*, $J=9.3$, H–C(3)); 3.94–3.87 (*m*, H–C(8), H–C(10')); 3.77 (*t*, $J=7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.73–3.67 (*m*, H'–C(8), H'–C(10')); 3.613 (*dd*, $J \approx 9.2$, 8.4, H–C(6')); 3.612 (*dd*, $J=9.2$, 8.3, H–C(4)); 3.55–3.47 (*m*, H–C(5), H–C(7')); 3.45–3.41 (*m*, H–C(7), H–C(9')); 2.65 (*t*, $J=10.3$, H–C(6)); 2.54 (*t*, $J=10.3$, H–C(8')); 2.43 (*d*, $J=3.4$, HO–C(5)); 2.40 (*d*, $J=2.8$, HO–C(7')); 2.13–2.09 (*m*, HO–C(8), HO–C(10')); 1.59 (*t*, $J=7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.26–1.04 (*m*, 3 (Me_2CH) $_3\text{Si}$); 0.95 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 102.31 (*s*); 102.00 (*s*); 91.39 (*s*); 88.49 (*s*); 79.13 (*d*); 78.69 (*d*); 76.79 (*d*); 76.64 (*s*); 75.11 (*d*); 75.07 (*d*); 75.05 (*s*); 71.98 (*d*); 71.83 (*d*); 70.56 (*s*); 68.44 (*s*); 63.59 (*t*); 63.34 (*t*); 60.14 (*t*); 41.61 (*t*); 39.07 (*d*); 38.30 (*d*); 23.36 (*2q*); 18.51 (*s*); 18.34–18.08 (several *q*); 13.02 (*3d*); 12.94 (*3d*); 12.00 (*3d*); –0.39 (*3q*); –4.13 (*2q*). MALDI-TOF-MS: 1098 ($[M + \text{Na}]^+$). Anal. calc. for $\text{C}_{57}\text{H}_{106}\text{O}_9\text{Si}_5$ (1075.89): C 63.63, H 9.93; found: C 63.72, H 9.73.

Data of 2,6'-11,15-Dianhydro-3,7,8,9,10,14-hexadeoxy-3,14-bis[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl]-5,12-bis-O-(triisopropylsilyl)-D-erythro-L-galacto-L-gulo-hexadeca-7,9-diyntol (**17**): R_f (AcOEt/hexane 1:4) 0.24. M.p. 117–117.5°. $[\alpha]_D^{25} = -20.6$ ($c=0.55$, CHCl_3). IR (CHCl_3): 3594w, 3008m, 2961s, 2945s, 2892m, 2867s, 2400w, 2171w, 1730w, 1601w, 1524w, 1464m, 1288m, 1261s (br.), 1143m, 1096s, 1014s, 883m, 818s (br.), 602w, 577w, 539w. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 4.02 (*d*, $J=9.2$, H–C(6)); 3.96–3.89 (*m*, H–C(1)); 3.77 (*t*, $J=7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.70 (*dt*, $J=11.8$, 6.0, H'–C(1)); 3.63 (*dd*, $J=9.1$, 8.3, H–C(5)); 3.49 (*ddd*, $J=10.5$, 8.3, 2.8, H–C(4)); 3.44 (*ddd*, $J=10.3$, 6.0, 2.7, H–C(2)); 2.54 (*t*, $J=10.3$, H–C(3)); 2.34 (*d*, $J=2.7$, HO–C(4)); 1.98 (*t*, $J=6.7$, HO–C(1)); 1.60 (*t*, $J=7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.26–1.05 (*m*, 2 (Me_2CH) $_3\text{Si}$); 0.96 (*s*, Me_2C); 0.12 (*s*, Me_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 102.32 (*s*); 88.49 (*s*); 79.10 (*d*); 76.97 (*s*); 76.82 (*d*); 74.85 (*d*); 71.96 (*d*); 70.22 (*s*); 63.55 (*t*); 60.14 (*t*); 41.60 (*t*); 39.05 (*d*); 23.33 (*2q*); 18.52 (*s*); 18.33–18.08 (several *q*); 12.93 (*3d*); 12.02 (*3d*); –4.13 (*2q*). MALDI-TOF-MS: 1327 ($[M + \text{Na}]^+$). Anal. calc. for $\text{C}_{70}\text{H}_{134}\text{O}_{10}\text{Si}_6$ (1304.34): C 64.46, H 10.35; found: C 64.58, H 10.22.

Data of 6,6'-(Buta-1,3-diene-1,4-diyl)bis[3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol] (**18**). R_f (AcOEt/hexane 1:2) 0.48. M.p. 251–253°. $[\alpha]_D^{25} = -50.2$ ($c=0.85$, CHCl_3). IR (CHCl_3): 3596m, 3008m, 2962s, 2946s, 2867s, 2179w, 1763w, 1722m, 1602w, 1463m, 1290m, 1261s, 1252s (br.), 1142s, 1101s, 1068s, 1016s, 998s, 919w, 883s, 847s, 818s (br.), 595w, 574w, 522w. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.95 (*d*, $J=9.0$, H–C(3)); 3.93 (*dd*, $J=12.1$, 2.5, H–C(8)); 3.72 (*dd*, $J=12.1$, 5.5, H'–C(8)); 3.61 (*dd*, $J=9.0$, 8.3, H–C(4)); 3.53 (*dd*, $J=10.0$, 8.3, H–C(5)); 3.44 (*ddd*, $J=10.0$, 5.5, 2.5, H–C(7)); 2.65 (*t*, $J=10.0$, H–C(6)); 2.34 (*m*, HO–C(5), HO–C(8)); 1.15–1.05 (*m*, (Me_2CH) $_3\text{Si}$); 0.17 (*s*, Me_2Si). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 101.98 (*s*); 91.44 (*s*); 78.71 (*d*); 76.17 (*d*); 75.18 (*d*); 74.56 (*s*); 71.94 (*d*); 68.71 (*s*); 63.42 (*t*);

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

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(1')	C(2')
5	91.10	102.34	71.97	75.05	76.89	39.12	78.91	63.70	102.58	88.28
7	81.04	74.54	71.38	75.02	76.78	39.14	79.02	63.89	102.44	88.43
8	80.09	74.82	70.55	75.24	76.61	39.68	79.97	63.69	104.25	87.67
9	79.93	74.94	70.68	75.06	76.59	39.93	77.65	64.88	103.80	88.07
10	47.21	76.89	72.26	75.16	76.70	39.07	78.99	63.64	102.40	88.42
11	5.00	91.37	72.79	75.34	76.73	39.04	78.18	63.63	102.42	88.38
12	91.06	102.40	71.97	75.03	76.81	39.06	79.02	63.65	103.40	87.99
13	89.93	101.15	71.06	74.74	76.31	38.82	78.74	63.33	74.27	80.78
14	91.02	101.82	71.64	74.91	76.47	38.33	78.44	63.17	75.83	43.36
15	91.34	102.16	71.91	75.19	76.91	39.55	78.91	63.46	90.16	14.01
21	91.54	101.93	71.93	75.38	76.83	38.19	78.83	63.56	90.79	83.03
22	80.70	74.90	71.35	75.32	76.67	38.31	78.97	63.54	90.62	83.03
23	47.67	77.14	72.23	75.47	76.54	38.16	78.92	63.51	90.57	83.03
24	83.67	91.90	71.92	75.04	76.79	39.19	79.11	63.65	102.24	88.63
25	83.88	92.00	72.01	75.09	76.75	39.32	79.30	63.69	103.18	88.31

38.10 (*d*); 18.35 (*6q*); 13.05 (*3d*); -0.40 (*3q*). MALDI-TOF-MS: 870 ($[M + \text{Na}]^+$). Anal. calc. for $\text{C}_{44}\text{H}_{78}\text{O}_8\text{Si}_4$ (847.44): C 62.36, H 9.28; found: C 62.46, H 9.30.

Coupling of 14 with 7. As described for the coupling of **10** with **13**, with **14** (137.4 mg, 0.273 mmol), **7** (178.2 mg, 0.273 mmol), $[\text{Pd}_2(\text{dba})_3]$ (7.5 mg, 8.19 μmol), CuI (1.6 mg, 8.19 μmol), $\text{P}(\text{fur})_3$ (3.2 mg, 0.014 mmol), and dry Et_3N (114 μl , 0.819 mmol) in DMSO (2.7 ml; 10 h). FC (AcOEt/hexane 1:10 $\rightarrow$ 3:17) gave **17** (10.2 mg, 3%), **16** (188.6 mg, 64%), and **18** (27.4 mg, 12%) as white foams.

Coupling of 10 with 12. As described for the coupling of **10** with **13**, with **10** (1.05 g, 1.43 mmol), **12** (816.1 mg, 1.43 mmol), $[\text{Pd}_2(\text{dba})_3]$ (39.4 mg, 0.043 mmol), CuI (8.2 mg, 0.043 mmol), $\text{P}(\text{fur})_3$ (16.7 mg, 0.072 mmol), and dry Et_3N (0.6 ml, 4.30 mmol) in DMSO (14 ml; 10 h). FC (AcOEt/hexane 1:10 $\rightarrow$ 3:17) gave **17** (35.5 mg, 2%), **16** (1.22 g, 79%), and **18** (6.2 mg, <1%) as white foams.

Coupling of 11 with 13. As described for the coupling of **10** with **13**, with **11** (971.5 mg, 1.247 mmol), **13** (530.1 mg, 1.247 mmol), $[\text{Pd}_2(\text{dba})_3]$ (34.2 mg, 0.037 mmol), CuI (7.1 mg, 0.037 mmol), $\text{P}(\text{fur})_3$ (14.5 mg, 0.062 mmol), and dry Et_3N (0.52 ml, 3.74 mmol) in DMSO (12 ml; 10 h). FC (AcOEt/hexane 1:10 $\rightarrow$ 3:17) gave **17** (32.5 mg, 2%), **16** (1.09 g, 81%), and **18** (8.5 mg, <1%) as white foams.

Coupling of 15 with 7. As described for the coupling of **10** with **13**, with **15** (175.7 mg, 0.319 mmol), **7** (208.4 mg, 0.319 mmol), $[\text{Pd}_2(\text{dba})_3]$ (8.8 mg, 9.58 μmol), CuI (1.8 mg, 9.58 μmol), $\text{P}(\text{fur})_3$ (1.9 mg, 0.016 mmol), and dry Et_3N (67 μl , 0.479 mmol) in DMSO (3 ml; 10 h). FC (AcOEt/hexane 1:10 $\rightarrow$ 3:17) gave **17** (13.1 mg, 3%), **16** (208.9 mg, 61%), and **18** (32.8 mg, 12%) as white foams.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 $\rightarrow$ 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (19**).** Separated as byproduct upon coupling **10** and **13** in pyrrolidine instead of Et_3N (<11%).

Data of 19: R_f (AcOEt/hexane 1:4) 0.10. M.p. $75-77^\circ$. $[\alpha]_D^{25} = -50.4$ ($c = 0.6$, CHCl_3). IR (CHCl_3): 3597w, 3306w, 3008w, 2962s, 2867s, 2362w, 2254w, 2170w, 1602w, 1464m, 1392w, 1329w, 1261s (br.), 1097s, 1015s, 883m, 818s (br.), 602w, 577w, 509w. ^1H -NMR (500 MHz, CDCl_3): 4.00 (*dd*, $J = 9.3, 0.6$, $\text{H}-\text{C}(5')$); 3.97 (*d*, $J = 9.2, 2.1$, $\text{H}-\text{C}(3)$); 3.92 (*ddd*, $J \approx 12.1, 7.1, 2.6$, $\text{H}-\text{C}(8)$); 3.90 (*ddd*, $J \approx 12.1, 6.8, 2.4$, $\text{H}-\text{C}(10')$); 3.77 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 3.73–3.69 (*m*, $\text{H}'-\text{C}(8)$, $\text{H}'-\text{C}(10')$); 3.65 (*dd*, $J = 9.3, 8.3$, $\text{H}-\text{C}(6')$); 3.64 (*dd*, $J = 9.2, 8.4$, $\text{H}-\text{C}(4)$); 3.57–3.50 (*m*, $\text{H}-\text{C}(5)$); $\text{H}-\text{C}(7')$); 3.49–3.42 (*m*, $\text{H}-\text{C}(9')$, $\text{H}-\text{C}(7)$); 2.68 (*td*, $J = 10.3, 0.6$, $\text{H}-\text{C}(6)$); 2.54 (*t*, $J = 10.3$, $\text{H}-\text{C}(8')$); 2.49 (*d*, $J = 2.1$, $\text{H}-\text{C}(1)$); 2.37 (*d*, $J = 3.1$, $\text{HO}-\text{C}(5)$, $\text{HO}-\text{C}(7')$); 2.00 (*dd*, $J = 7.3, 6.3$, $\text{HO}-\text{C}(10')$); 1.96 (*t*, $J = 6.8$, $\text{HO}-\text{C}(8)$); 1.59 (*t*, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{OSi}$); 1.26–1.05 (*m*, 3 (Me_2CH) $_3\text{Si}$); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C -NMR (75 MHz, CDCl_3): 102.27 (*s*); 88.59 (*s*); 80.76 (*d*); 79.11 (*d*); 78.79 (*d*); 77.23 (*s*); 76.73 (*d*); 76.71 (*d*); 76.43 (*s*); 75.13 (*d*); 75.04 (*d*); 74.75 (*s*); 71.86 (*d*); 71.42 (*d*); 70.48 (*s*); 68.57 (*s*); 63.64 (*t*); 63.36 (*t*); 60.15 (*t*); 41.64 (*t*); 39.11 (*d*); 38.33 (*d*); 23.27 (*q*); 23.34 (*q*); 18.53 (*s*); 18.34–18.26 (*12q*); 18.08 (*6q*); 12.98 (*3d*); 12.96 (*3d*); 12.03 (*3d*); -4.12 (*q*); -4.14 (*q*). MALDI-TOF-MS: 1025 ($[M + \text{Na}]^+$). Anal. calc. for $\text{C}_{54}\text{H}_{98}\text{O}_9\text{Si}_4$ (1003.70): C 64.62, H 9.84; found: C 64.45, H 9.76.

3,7-Anhydro-1,2,6-trideoxy-6-C-[(4-nitrophenyl)ethynyl]-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (21). At 50°, a soln. of [Pd(PPh₃)₄] (30.1 mg, 0.026 mmol), CuI (15.6 mg, 0.082 mmol), and 1-iodo-4-nitrobenzene (900 mg, 3.62 mmol) in dry, degassed DMSO (24 ml) was treated dropwise with a soln. of **13** (512 mg, 1.21 mmol) in dry Et₃N (9 ml) and stirred overnight. Dilution with AcOEt (25 ml), neutralization with 2N aq. HCl (pH 7), normal workup (AcOEt, H₂O), and FC (AcOEt/hexane 1:4) gave **21** (0.650 g, 98%). Yellow powder. *R_f* (AcOEt/hexane 1:2) 0.49. M.p. 146–147°. [α]_D²⁵ = –41.7 (*c* = 0.50, CHCl₃). IR (CCl₄): 3598w, 2963m, 2946m, 2867m, 2226w, 2180w, 1726w, 1595m, 1522s, 1464w, 1346s, 1144m, 1108m, 1066m, 995w, 884m, 855s. ¹H-NMR (300 MHz, CDCl₃): 8.16 (*d*, *J* = 9.0), 7.56 (*d*, *J* = 9.0, 4 arom. H); 4.03 (*d*, *J* = 9.3, H–C(3)); 4.00 (*ddd*, *J* ≈ 12.0, 7.4, 2.6, H–C(8)); 3.81 (*dt*, *J* ≈ 11.9, 5.9, H'–C(8)); 3.70 (*dd*, *J* = 9.0, 8.2, H–C(4)); 3.65 (*td*, *J* = 8.2, 3.0, H–C(5)); 3.57 (*ddd*, *J* = 10.3, 5.6, 2.5, H–C(7)); 2.85 (*t*, *J* = 10.2, H–C(6)); 2.53 (*d*, *J* = 3.0, HO–C(5)); 2.13 (*dd*, *J* = 7.2, 6.4, HO–C(8)); 1.31–1.12 (*m*, (Me₂CH)₃Si); 0.19 (*s*, Me₃Si). ¹³C-NMR (75 MHz, CDCl₃): 147.14 (*s*); 132.60 (*2d*), 129.42 (*s*); 123.55 (*2d*); 101.93 (*s*); 91.54 (*s*); 90.79 (*s*); 83.03 (*s*); 78.83 (*d*); 76.83 (*d*); 75.38 (*d*); 71.93 (*d*); 63.56 (*t*); 38.19 (*d*); 18.32 (*6q*); 13.08 (*3d*); –0.42 (*3q*). CI-MS: 563 (100, [*M* + NH₄]⁺), 546 (22, [*M* + 1]⁺), 516 (69), 472 (51), 442 (74), 309 (54), 148 (37), 131 (41), 73 (37, Me₃Si⁺). Anal. calc. for C₂₈H₄₃NO₆Si₂ (545.82): C 61.61, H 7.94, N 2.57; found: C 61.44, H 7.99, N 2.53.

3,7-Anhydro-1,2,6-trideoxy-6-C-[(4-nitrophenyl)ethynyl]-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (22). At 22°, a soln. of **21** (299.7 mg, 0.5491 mmol) in MeOH (20 ml) was treated dropwise with a soln. of 0.25M MeONa in MeOH (0.5 ml) and stirred for 23 h. Addition of Amberlite IR-20, filtration, evaporation, and FC (AcOEt/hexane 1:3) gave **22** (204.6 mg, 79%). Yellow syrup. *R_f* (AcOEt/hexane 1:4) 0.12. [α]_D²⁵ = –37.4 (*c* = 0.43, CHCl₃). IR (CCl₄): 3606m, 3311m, 2945m, 2868m, 2225w, 1740w, 1596m, 1558w, 1525s, 1464w, 1344s, 1286w, 1244w, 1143m, 1124m, 1100m, 1069m, 962w, 883m, 856m, 669m, 641m. ¹H-NMR (300 MHz, CDCl₃): 8.18 (*d*, *J* = 8.9), 7.56 (*d*, *J* = 8.9, 4 arom. H); 4.05 (*dd*, *J* = 9.0, 2.1, H–C(3)); 4.00–3.97 (*m*, H–C(8)); 3.83–3.80 (*m*, H'–C(8)); 3.74 (*dd*, *J* = 9.0, 8.3, H–C(4)); 3.67 (*td*, *J* = 8.3, 3.1, H–C(5)); 3.60 (*ddd*, *J* = 10.4, 5.5, 2.5, H–C(7)); 2.88 (*t*, *J* = 10.3, H–C(6)); 2.53 (*d*, *J* = 2.1, H–C(1), HO–C(5)); 2.11 (*br. s.*, HO–C(8)); 1.30–1.12 (*m*, (Me₂CH)₃Si). ¹³C-NMR (75 MHz, CDCl₃): 147.16 (*s*); 132.60 (*2d*); 129.35 (*s*); 123.55 (*2d*); 90.62 (*s*); 83.03 (*s*); 80.70 (*d*); 78.97 (*d*); 76.67 (*d*); 75.32 (*d*); 74.90 (*s*); 71.35 (*d*); 63.54 (*t*); 38.21 (*d*); 18.33 (*6q*); 13.02 (*3d*). CI-MS: 491 (100, [*M* + NH₄]⁺), 474 (13, [*M* + 1]⁺), 444 (17), 282 (11), 237 (29), 148 (11). Anal. calc. for C₂₅H₃₅NO₆Si (473.64): C 63.40, H 7.45, N 2.96; found: C 63.22, H 7.29, N 2.88.

3,7-Anhydro-1-C-bromo-1,2,6-trideoxy-6-C-[(4-nitrophenyl)ethynyl]-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (23). A soln. of **21** (33 mg, 0.0604 mmol) and NBS (36.3 mg, 0.2039 mmol) in dry acetone (1.5 ml) was treated with AgOCOCF₃ (1.2 mg, 5.4 μmol) and stirred in the dark (Al foil) at 21° for 43 h. After completion, the mixture was normally worked up (Et₂O, H₂O). HPLC (Si 60; AcOEt/hexane 2:8, 10 ml/min; RID detection) gave **23** (25.3 mg, 76%). Yellow foam.

At 21°, a soln. of **22** (0.0275 g, 0.0468 mmol) and NBS (9.2 mg, 0.0514 mmol) in dry acetone (1.5 ml) was treated with AgOCOCF₃ (0.3 mg, 1.4 μmol) and stirred in the dark (Al foil) at 21° for 3 h. After completion, the mixture was worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 1:4) gave **23** (30.4 mg, 97%). Yellow foam. *R_f* (AcOEt/hexane 1:2) 0.37. M.p. 70–72°. [α]_D²⁵ = –43.4 (*c* = 0.23, CHCl₃). IR (CCl₄): 3606m, 2946m, 2868m, 2223w, 1734w, 1596m, 1525s, 1494w, 1464w, 1345s, 1287w, 1244w, 1142s, 1120s, 1068m, 1015w, 1000w, 920w, 883m, 856s, 686m. ¹H-NMR (300 MHz, CDCl₃): 8.18 (*d*, *J* = 8.9), 7.56 (*d*, *J* = 8.9, 4 arom. H); 4.05 (*d*, *J* = 8.9, H–C(3)); 4.00 (*ddd*, *J* = 11.8, 6.9, 2.0, H–C(8)); 3.80 (*dt*, *J* ≈ 12.0, 6.0, H'–C(8)); 3.72 (*dd*, *J* = 8.9, 8.3, H–C(4)); 3.64 (*ddd*, *J* = 10.3, 8.3, 3.1, H–C(5)); 3.59 (*ddd*, *J* = 10.4, 5.5, 2.4, H–C(7)); 2.86 (*t*, *J* = 10.1, H–C(6)); 2.55 (*br. s.*, HO–C(5)); 2.09 (*br. s.*, HO–C(8)); 1.30–1.11 (*m*, (Me₂CH)₃Si). ¹³C-NMR (75 MHz, CDCl₃): 147.17 (*s*); 132.60 (*2d*); 129.33 (*s*); 123.55 (*2d*); 90.57 (*s*); 83.03 (*s*); 78.92 (*d*); 77.14 (*s*); 76.58 (*d*); 75.47 (*d*); 72.23 (*d*); 63.51 (*t*); 47.67 (*s*); 38.16 (*d*); 18.21 (*6q*); 12.94 (*3d*). CI-MS: 570 (30, [*M* + NH₄]⁺), 569 (89), 568 (14), 552 (12, *M*⁺), 550 (5), 450 (13), 448 (12), 317 (17), 315 (17), 225 (11), 160 (10), 150 (11), 148 (40), 131 (19), 130 (12), 120 (15), 103 (12), 35 (31). Anal. calc. for C₂₅H₃₄BrNO₆Si (552.54): C 54.34, H 6.20, N 2.53; found: C 54.22, H 6.42, N 2.72.

3,7-Anhydro-1,2,6-trideoxy-6-C-[[dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]silyl]ethynyl]-1-C-(4-nitrophenyl)-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (24). Similarly as described for **21**, with **7** (95.5 mg, 0.146 mmol), 1-iodo-4-nitrobenzene (36.35 mg, 0.438 mmol), Et₃N (0.5 ml), [Pd(PPh₃)₄] (3.64 mg, 3.15 μmol), CuI (1.89 mg, 9.9 μmol), and DMSO (4 ml). FC (AcOEt/hexane 1:9) gave **24** (99.8 mg, 88%). Transparent syrup. *R_f* (AcOEt/hexane 1:4) 0.32. [α]_D²⁵ = –23.1 (*c* = 0.315, CHCl₃). IR (CCl₄): 3607m, 2944s, 2867s, 2170w, 1596m, 1525s, 1494w, 1464m, 1384w, 1345s, 1291w, 1253m, 1142s, 1092s, 1014m, 997m, 919w, 883s, 855s, 840m, 685s. ¹H-NMR (500 MHz, CDCl₃): 8.20 (*d*, *J* = 9.0), 7.57 (*d*, *J* = 9.0, 4 arom. H); 4.22 (*d*, *J* = 9.3, H–C(3)); 3.98 (*ddd*, *J* = 12.0, 7.2, 2.6, H–C(8)); 3.80–3.76 (*m*, H'–C(8), CH₂CH₂OSi); 3.76 (*dd*, *J* = 9.3, 8.3, H–C(4)); 3.56 (*ddd*, *J* = 10.3, 8.3, 2.8, H–C(5)); 3.53 (*ddd*, *J* = 10.3, 5.9, 2.6, H–C(7)); 2.62 (*t*, *J* = 10.3,

H–C(6)); 2.40 (*d*, *J* = 2.7, HO–C(5)); 2.05 (*t*, *J* ≈ 6.6, H–C(8)); 1.61 (*t*, *J* = 7.7, CH₂CH₂OSi); 1.21–1.06 (*m*, (Me₂CH)₃Si); 0.98 (*s*, Me₂C); 0.13 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 147.38 (*s*); 132.46 (2*d*); 129.10 (*s*); 123.61 (2*d*); 102.24 (*s*); 91.90 (*s*); 88.63 (*s*); 83.87 (*s*); 79.11 (*d*); 76.79 (*d*); 75.04 (*d*); 71.92 (*d*); 63.65 (*t*); 60.11 (*t*); 41.61 (*t*); 39.19 (*d*); 23.32 (2*q*); 18.50 (*s*); 18.24 (6*q*); 18.06 (6*q*); 12.94 (3*d*); 11.98 (3*d*); –4.14 (2*q*). CI-MS: 774 (12, *M*⁺), 665 (9), 431 (10), 429 (7), 156 (13), 145 (23). Anal. calc. for C₄₁H₇₁NO₇Si₃ (774.27): C 63.60, H 9.24, N 1.81; found: C 63.49, H 9.14, N 1.95.

3,7-Anhydro-1,2,6-trideoxy-6-C-[[3-hydroxy-1,1-dimethylpropyl]dimethylsilyl]ethynyl]-1-C-(4-nitrophenyl)-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (25). At 50°, a soln. of **24** (399.8 mg, 0.516 mmol) in EtOH (10 ml) was treated with 0.1N HCl (2 ml) and stirred for 3 h. After completion, the solvent was removed under reduced pressure. FC (AcOEt/hexane 1:4) gave **25** (287.3 mg, 90%). White solid. *R*_f (AcOEt/hexane 1:2) 0.20. [*α*]_D²⁵ = –35.5 (*c* = 0.36, CHCl₃). IR (CHCl₃): 3597*m*, 2963*s*, 2867*s*, 2359*w*, 2171*w*, 1596*m*, 1558*w*, 1540*w*, 1522*m*, 1494*w*, 1464*m*, 1411*m*, 1346*s*, 1262*s*, 1096*s*, 1014*s*, 882*m*, 856*s*, 818*s*, 603*w*. ¹H-NMR (300 MHz, CDCl₃): 8.19 (*d*, *J* = 9.0), 7.57 (*d*, *J* = 9.0, 4 arom. H); 4.23 (*d*, *J* = 9.2, H–C(3)); 4.01–3.95 (*m*, H–C(8)); 3.82–3.72 (*m*, H'–C(8)); 3.80 (*br. t*, *J* = 7.2, CH₂OH); 3.75 (*dd*, *J* = 9.2, 8.3, H–C(4)); 3.63–3.55 (*m*, H–C(5)); 3.54 (*ddd*, *J* = 10.2, 5.7, 2.4, H–C(7)); 3.18 (*d*, *J* = 3.2, HO–C(5)); 2.62 (*t*, *J* = 10.3, H–C(6)); 2.41–2.38 (*m*, HO–C(8)); 1.86–1.82 (*m*, CH₂CH₂OH); 1.62 (*t*, *J* = 7.2, CH₂CH₂OH); 1.19–1.07 (*m*, (Me₂CH)₃Si); 0.97 (*s*, Me₂C); 0.13 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 147.40 (*s*); 132.49 (2*d*); 129.14 (*s*); 123.64 (2*d*); 103.18 (*s*); 92.00 (*s*); 88.31 (*s*); 83.88 (*s*); 79.30 (*d*); 76.75 (*d*); 75.09 (*d*); 72.01 (*d*); 63.69 (*t*); 60.11 (*t*); 43.03 (*t*); 39.32 (*d*); 24.16 (2*q*); 18.52 (*s*); 18.29 (6*q*); 12.96 (3*d*); –3.95 (2*q*). CI-MS: 618 (1, [*M* + 1]⁺), 474 (5, [*M* – DOPS + 1]⁺), 444 (9), 370 (10), 306 (3), 162 (10), 146 (22, DOPS⁺), 145 (100), 129 (21), 75 (21), 74 (12). Anal. calc. for C₃₂H₅₁NO₇Si₂ (617.89): C 62.20, H 8.32, N 2.27; found: C 62.05, H 8.47, N 2.06.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(4-nitrophenyl)ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (26). At 22°, a soln. of **23** (83.4 mg, 0.151 mmol), **13** (64.13 mg, 0.151 mmol), [Pd₂(dba)₃] (4.12 mg, 0.0045 mmol), CuI (0.74 mg, 0.0039 mmol), and LiI (4.0 mg, 0.030 mmol) in DMSO (3.6 ml) in a flame-dried Schlenk flask was degassed for 15 min, treated with dry PMP (0.076 ml, 0.422 mmol), and stirred in the dark for 10 h. After completion, the mixture was poured onto ice/H₂O, neutralized with 1N HCl and worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 1:3) gave **26** (183.3 mg, 94%). White powder. *R*_f (AcOEt/hexane 1:2) 0.19. M.p. 138°. [*α*]_D²⁵ = –63.5 (*c* = 0.17, CHCl₃). IR (CCl₄): 3604*m*, 3497*w* (*br.*), 2946*s*, 2867*s*, 2256*w*, 2226*w*, 2185*w*, 1596*m*, 1525*s*, 1464*m*, 1345*s*, 1289*m*, 1252*m*, 1143*s*, 1120*s*, 1069*m*, 997*m*, 883*m*, 855*s*, 684*m*. ¹H-NMR (500 MHz, CDCl₃): 8.17 (*d*, *J* = 9.0), 7.55 (*d*, *J* = 9.0, 4 arom. H); 4.07 (*dd*, *J* = 9.0, 0.8, H–C(5')); 3.98 (*ddd*, *J* ≈ 12.2, 6.9, 2.4, H–C(10')); 3.96 (*d*, *J* = 9.3, H–C(3)); 3.91 (*ddd*, *J* = 12.0, 7.2, 2.5, H–C(8)); 3.79 (*dt*, *J* ≈ 12.0, 6.0, H'–C(10')); 3.71 (*dd*, *J* ≈ 9.8, 8.9, H–C(4)); 3.70 (*dt*, *J* ≈ 12.1, 5.9, H'–C(8)); 3.66 (*ddd*, *J* = 10.2, 8.4, 3.2, H–C(7)); 3.63 (*dd*, *J* = 9.2, 8.3, H–C(6')); 3.57 (*ddd*, *J* = 10.3, 5.4, 2.4, H–C(9')); 3.53 (*ddd*, *J* = 10.4, 8.3, 3.3, H–C(5)); 3.44 (*ddd*, *J* = 10.3, 5.7, 2.5, H–C(7)); 2.86 (*t*, *J* = 10.2, H–C(8')); 2.67 (*t*, *J* = 10.3, H–C(6)); 2.50 (*d*, *J* = 3.1, HO–C(7)); 2.37 (*d*, *J* = 3.3, HO–C(5)); 2.01 (*t*, *J* ≈ 6.7, HO–C(8), HO–C(10')); 1.27–1.10 (*m*, 2 (Me₂CH)₃Si); 0.17 (*s*, Me₂Si). ¹³C-NMR (125 MHz, CDCl₃): 147.27 (*s*); 132.64 (2*d*); 129.33 (*s*); 123.59 (2*d*); 101.94 (*s*); 91.49 (*s*); 90.48 (*s*); 83.14 (*s*); 79.06 (*d*); 78.67 (*d*); 76.93 (*s*); 76.85 (*d*); 76.68 (*d*); 75.47 (*d*); 75.13 (*d*); 74.63 (*s*); 72.01 (*d*); 71.86 (*d*); 70.88 (*s*); 68.33 (*s*); 63.53 (*t*); 63.36 (*t*); 38.25 (*d*); 38.23 (*d*); 18.34 (6*q*); 18.28–18.25 (6*q*); 13.04 (3*d*); 12.99 (3*d*); –0.40 (3*q*). MALDI-TOF-MS: 919 ([*M* + Na]⁺). Anal. calc. for C₄₇H₇₃NO₁₀Si₃ (896.35): C 62.98, H 8.21, N 1.56; found: C 62.74, H 7.96, N 1.40.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(4-nitrophenyl)ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-1-C-(4-nitrophenyl)-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (27). At 22°, a soln. of **25** (97.4 mg, 0.1576 mmol), **23** (87.1 mg, 0.1576 mmol), [Pd₂(dba)₃] (4.3 mg, 4.73 μmol), CuI (0.9 mg, 4.73 μmol), and LiI (4.2 mg, 0.032 mmol) in DMSO (2 ml) in a flame-dried Schlenk flask was degassed for 15 min, treated with dry PMP (86 μl, 0.473 mmol), and stirred in the dark for 14 h. After completion, the mixture was poured onto ice/H₂O, neutralized with 1N HCl and worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 1:3) gave **27** (68.5 mg, 46%). White solid. *R*_f (AcOEt/hexane 1:2) 0.21. M.p. 229–235°. [*α*]_D²⁵ = –48.4 (*c* = 0.31, CHCl₃). IR (CHCl₃): 3603*m*, 3444*w* (*br.*), 3008*m*, 2963*s*, 2868*s*, 2230*w*, 2226*w*, 1732*w*, 1596*m*, 1522*s*, 1493*w*, 1464*m*, 1346*s*, 1262*s*, 1094*s*, 1015*s*, 882*m*, 856*m*, 818*s*, 639*w*, 576*w*. ¹H-NMR (500 MHz, CDCl₃): 8.20 (*d*, *J* = 9.0), 8.18 (*d*, *J* = 9.0), 7.57 (*d*, *J* = 9.0), 7.56 (*d*, *J* = 9.0, 8 arom. H); 4.23 (*d*, *J* = 9.3, H–C(3)); 4.08 (*dd*, *J* = 9.1, 0.7, H–C(5')); 3.99 (*ddd*, *J* = 12.1, 7.0, 2.4, H–C(10')); 3.95 (*ddd*, *J* = 12.1, 6.8, 2.4, H–C(8)); 3.82–3.77 (*m*), 3.78–3.73 (*m*, H'–C(8), H'–C(10')); 3.76 (*dd*, *J* = 9.3, 8.3, H–C(4)); 3.72 (*dd*, *J* = 9.1, 8.4, H–C(6')); 3.66 (*dd*, *J* = 10.2, 8.3, 3.1, H–C(7)); 3.62 (*ddd*, *J* = 10.3, 8.3, 3.3, H–C(5)); 3.58 (*ddd*, *J* = 10.4, 5.4, 2.4, H–C(9')); 3.54 (*ddd*, *J* = 10.3, 5.4, 2.4, H–C(7)); 2.86 (*t*, *J* = 10.2, H–C(8')); 2.75 (*td*, *J* ≈ 10.3, 0.5, H–C(6)); 2.51 (*d*, *J* = 3.2, HO–C(7)); 2.41 (*d*, *J* = 3.3, HO–C(5)); 2.01

(*t*, *J* = 6.9, HO–C(10')); 1.96 (*t*, *J* = 6.6, HO–C(8)); 1.19–1.09 (*m*, 2 (Me₂CH)₃Si). ¹³C-NMR (75 MHz, CDCl₃): 147.92 (*s*); 147.67 (*s*); 133.11 (2*d*); 132.96 (2*d*); 129.77 (*s*); 129.38 (*s*); 124.11 (2*d*); 124.03 (2*d*); 91.88 (*s*); 90.88 (*s*); 84.49 (*s*); 83.47 (*s*); 79.52 (*d*); 79.28 (*d*); 76.95 (2*d*); 75.74 (*d*); 75.45 (*d*); 75.24 (*s*); 72.29 (*d*); 72.16 (*d*); 71.13 (*s*); 68.81 (*s*); 63.72 (*t*); 63.61 (*t*); 38.68 (*d*); 38.48 (*d*); 18.50 (12*q*); 13.18 (3*d*); 13.11 (3*d*); 1*s* missing. FAB-MS: 946 (63, [*M* + 1]⁺), 945 (100, *M*⁺), 901 (91), 841 (62), 696 (70), 652 (58), 613 (63). Anal. calc. for C₅₀H₆₈N₂O₁₂Si₂ (945.26): C 63.53, H 7.25, N 2.96; found: C 63.48, H 7.18, N 2.86.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(dimethyl[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl)silyl]ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-1-C-(4-nitrophenyl)-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (28). At 22°, a soln. of **25** (99.9 mg, 0.1617 mmol), **10** (118.4 mg, 0.1617 mmol), [Pd₂(dba)₃] (4.4 mg, 4.85 μmol), CuI (0.9 mg, 4.85 μmol), and LiI (4.3 mg, 0.323 mmol) in DMSO (2 ml) in a flame-dried Schlenk flask was degassed for 15 min, treated with dry PMP (88 μl, 0.485 mmol), and stirred in the dark for 14 h. After completion, the mixture was poured onto ice/H₂O, neutralized with 1*N* HCl and worked up normally (Et₂O, H₂O). FC (AcOEt/hexane 1 : 3) gave **28** (72.7 mg, 40%). White powder. *R*_f (AcOEt/hexane 1 : 3) 0.20. M.p. 87–88.5°. [*α*]_D²⁵ = –31.4 (*c* = 0.41, CHCl₃). IR (CHCl₃): 3599*w*, 2963*s*, 2867*m*, 2359*w*, 2168*w*, 1596*w*, 1522*m*, 1464*m*, 1412*m*, 1346*m*, 1262*s*, 1095*s*, 1015*s*, 856*m*, 818*s*, 600*w*, 508*w*. ¹H-NMR (500 MHz, CDCl₃): 8.20 (*d*, *J* = 9.0), 7.57 (*d*, *J* = 9.0, 4 arom. H); 4.23 (*d*, *J* = 9.3, H–C(3)); 4.00 (*dd*, *J* = 9.2, 0.7, H–C(5')); 3.94 (*ddd*, *J* = 12.1, 7.0, 2.5, H–C(8)); 3.92 (*ddd*, *J* = 12.2, 7.4, 2.5, H–C(10')); 3.77 (*t*, *J* = 7.7, CH₂CH₂OSi); 3.75 (*dd*, *J* = 9.3, 8.4, H–C(4)); 3.78–3.72 (*m*), 3.74–3.69 (*m*, H'–C(8), H'–C(10')); 3.65 (*dd*, *J* = 9.2, 8.4, H–C(6')); 3.61 (*ddd*, *J* = 10.3, 8.3, 3.3, H–C(5)); 3.53 (*ddd*, *J* = 10.3, 5.4, 2.4, H–C(7)); 3.51 (*ddd*, *J* = 10.6, 8.4, 2.8, H–C(7')); 3.45 (*ddd*, *J* = 10.3, 6.0, 2.5, H–C(9')); 2.73 (*td*, *J* ≈ 10.2, 0.5, H–C(6)); 2.55 (*t*, *J* = 10.3, H–C(8')); 2.39 (*d*, *J* = 3.3, HO–C(5)); 2.37 (*d*, *J* = 2.8, HO–C(7')); 1.97 (*dd*, *J* = 7.3, 6.2, HO–C(8)); 1.93 (*t*, *J* = 6.7, HO–C(10')); 1.60 (*t*, *J* = 7.7, CH₂CH₂OSi); 1.23–1.08 (*m*, 3 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.11 (*s*, Me₂Si). ¹³C-NMR (75 MHz, CDCl₃): 147.74 (*s*); 132.76 (2*d*); 129.23 (*s*); 123.91 (2*d*); 102.46 (*s*); 91.75 (*s*); 88.69 (*s*); 84.24 (*s*); 79.34 (*d*); 79.08 (*d*); 76.82 (2*d*); 76.47 (*s*); 75.41 (*s*); 75.21 (2*d*); 72.09 (*d*); 71.96 (*d*); 70.58 (*s*); 68.81 (*s*); 63.69 (*t*); 63.42 (*t*); 60.25 (*t*); 41.67 (*t*); 39.13 (*d*); 38.50 (*d*); 23.32 (2*q*); 18.54 (*s*); 18.30–18.10 (18*q*); 12.96 (3*d*); 12.93 (3*d*); 12.03 (3*d*); –4.16 (2*q*). MALDI-TOF-MS: 1148 ([*M* + Na]⁺). Anal. calc. for C₆₀H₁₀₁NO₁₁Si₄ (1124.74): C 64.07, H 9.05, N 1.25; found: C 64.15, H 9.02, N 1.25.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl]-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (29). A soln. of **16** (870.1 mg, 0.81 mmol) in EtOH (15 ml) was treated with 0.1*N* HCl (4.6 ml) and stirred at 50° for 3 h. The solvent was removed under reduced pressure. FC (AcOEt/hexane 1 : 2 → 1 : 1) gave **29** (677.8 mg, 91%). White foam. *R*_f (AcOEt/hexane 4 : 6) 0.27. M.p. 112–114°. [*α*]_D²⁵ = –44.4 (*c* = 0.6, CHCl₃). IR (CHCl₃): 3598*m*, 3424*w* (br.), 3007*m*, 2962*s*, 2946*s*, 2892*s*, 2867*s*, 2261*w*, 2173*m*, 1602*w*, 1464*m*, 1385*w*, 1366*m*, 1329*m*, 1291*m*, 1261*s* (sh), 1143*s*, 1100*s*, 1016*s*, 883*s*, 845*s*, 818*s*, 600*w*, 575*w*. ¹H-NMR (500 MHz, CDCl₃): 4.01 (*dd*, *J* = 9.3, 0.7, H–C(5')); 3.96 (*d*, *J* = 9.3, H–C(3)); 3.92–3.87 (*m*, H–C(8), H–C(10')); 3.78 (*td*, *J* = 7.0, 6.1, CH₂OH); 3.73–3.67 (*m*, H'–C(8), H'–C(10')); 3.63 (*dd*, *J* = 9.2, 8.1, H–C(6')); 3.62 (*dd*, *J* = 9.2, 8.0, H–C(4)); 3.54–3.50 (*m*, H–C(5), H–C(7')); 3.45 (*ddd*, *J* = 10.6, 5.8, 2.5, H–C(9')); 3.43 (*ddd*, *J* = 10.4, 5.7, 2.5, H–C(7)); 3.05 (*d*, *J* = 3.3, HO–C(7')); 2.65 (*t*, *J* = 10.3, H–C(6)); 2.55 (*t*, *J* = 10.3, H–C(8')); 2.39 (*d*, *J* = 3.3, HO–C(5)); 2.15–2.13 (*m*, HO–C(8)); 2.06 (*t*, *J* = 6.7, HO–C(10')); 2.04 (*d*, *J* = 6.2, CH₂OH); 1.61 (*t*, *J* = 7.0, CH₂CH₂OH); 1.26–1.04 (*m*, 2 (Me₂CH)₃Si); 0.96 (*s*, Me₂C); 0.17 (*s*, Me₂Si); 0.12 (*s*, Me₂Si). ¹³C-NMR (125 MHz, CDCl₃): 103.13 (*s*); 102.01 (*s*); 91.40 (*s*); 88.25 (*s*); 79.22 (*d*); 78.68 (*d*); 76.83 (*d*); 76.69 (*d*); 76.60 (*s*); 75.13 (*d*); 75.08 (*d*); 72.01 (*d*); 71.91 (*d*); 70.52 (*s*); 68.47 (*s*); 63.68 (*t*); 63.36 (*t*); 60.11 (*t*); 43.04 (*t*); 39.18 (*d*); 38.31 (*d*); 24.13 (2*q*); 19.07 (*s*); 18.35–18.27 (several *q*); 13.03 (3*d*); 12.95 (3*d*); –0.39 (3*q*); –3.97 (*q*); –4.00 (*q*); 1*s* missing. MALDI-TOF-MS: 942 ([*M* + Na]⁺). Anal. calc. for C₄₈H₈₆O₉Si₄ (919.55): C 62.70, H 9.43; found: C 62.52, H 9.19.

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(4-nitrophenyl)ethynyl]-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-D-glycero-D-gulo-oct-1-ynitol (30). At 22°, a soln. of **26** (17.7 mg, 0.01975 mmol) in dry MeOH (2 ml) was treated with freshly prepared 0.25*M* MeONa in MeOH (0.2 ml) and stirred for 8 h. After the addition of Amberlite IR-120, the mixture was filtered, and the filtrate was evaporated under reduced pressure to give **31**. Stirring of **31** in 0.3*N* HCl/MeOH at 55° during 36 h gave **30** (8.9 mg, 92%) as a beige powder.

At 0°, a soln. of **26** (21.3 mg, 0.0238 mmol) in THF (1.5 ml) was treated dropwise with a soln. of Bu₄NF · 3 H₂O (21.0 mg, 0.0665 mmol) in THF (1.5 ml) and stirred for 6 h. Normal workup (AcOEt, H₂O) and FC (AcOEt/hexane 9 : 1) gave **30** (3.4 mg, 29%). White powder. *R*_f (AcOEt/hexane 9 : 1) 0.09. M.p. 215° (dec.). IR (KBr): 3569*m* (br.), 3422*m* (br.), 2922*w*, 2259*w*, 2127*w*, 1629*w*, 1570*w*, 1534*w*, 1508*w*, 1458*w*, 1375*w*, 1250*w*,

Table 5. Selected ^{13}C -NMR (CDCl_3) Chemical-Shift Values [ppm] of Dimers

	16	19	26	27	28
C(1)	91.39	80.76	91.49	84.49	84.24
C(2)	102.00	77.23	101.94	91.88	91.75
C(3)	71.98	71.42	71.86	72.16	71.96
C(4)	75.07	75.04	75.13	75.74	75.21
C(5)	76.79	76.73	76.85	76.95	76.82
C(6)	38.50	38.33	38.23	38.48	38.50
C(7)	78.69	78.79	78.67	79.28	79.34
C(8)	63.34	63.36	63.36	63.61	63.42
C(1')	76.64	76.43	74.63	75.24	75.41
C(2')	68.44	68.57	68.33	68.81	68.81
C(3')	70.56	70.48	70.88	71.13	70.58
C(4')	75.05	74.75	76.93	^{a)}	76.47
C(5')	71.83	71.86	72.01	72.29	72.09
C(6')	75.11	75.13	75.47	75.45	75.21
C(7')	76.70	76.71	76.68	76.95	76.82
C(8')	39.07	39.11	38.25	38.68	39.13
C(9')	79.13	79.11	79.06	79.52	79.08
C(10')	63.59	63.64	63.53	63.72	63.69
C(1'')	102.31	102.27	90.48	90.88	102.46
C(2'')	88.49	88.59	83.14	83.47	88.69

^{a)} Hidden by other signals.

1182w, 1075m, 1051m, 990w, 961w, 883w, 641w, 579w, 529w, 437w. ^1H -NMR (300 MHz, CD_3OD): 8.20 (*d*, *J* = 8.7), 7.64 (*d*, *J* = 8.7, 4 arom. H); 4.07 (*d*, *J* = 9.7, H–C(5')); 3.93 (*dd*, *J* = 9.6, 2.2, H–C(3)); 3.94–3.64 (*m*, 2 H–C(8), 2 H–C(10')); 3.54–3.41 (*m*, H–C(5), H–C(7), H–C(9')); 3.31–3.25 (*m*, H–C(4)); 3.21 (*dd*, *J* = 9.5, 8.4, H–C(6')); 2.88 (*d*, *J* = 2.2, H–C(1)); 2.78 (*t*, *J* = 10.3, H–C(8')); 2.61 (*t*, *J* = 10.3, H–C(6')). ^{13}C -NMR (75 MHz, CD_3OD): 147.27 (*s*); 132.74 (2*d*); 129.31 (*s*); 123.59 (2*d*); 90.52 (*s*); 83.17 (*s*); 81.81 (*d*); 81.41 (*d*); 80.95 (*d*); 78.68 (*d*); 78.00 (*d*); 77.32 (*s*); 76.56 (*s*); 75.57 (*s*, *d*); 75.44 (*d*); 72.64 (2*d*); 71.13 (*s*); 68.81 (*s*); 63.69 (*t*); 63.42 (*t*); 38.25 (*d*); 38.23 (*d*).

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[(4-nitrophenyl)ethynyl]-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-1-C-(4-nitrophenyl)-D-glycero-D-gulo-oct-1-ynitol (**32**). At 55°, a soln. of **27** (26.2 mg, 0.0277 mmol) in 0.3N HCl/MeOH (2.5 ml) was stirred for 45 h. Evaporation and FC (AcOEt/hexane 9 : 1) gave **32** (16.8 mg, 97%). Beige powder. R_f (AcOEt/hexane 9 : 1) 0.08. M.p. 222° (dec.). IR (KBr): 3573*m* (br.), 3423*m* (br.), 2923w, 2261w, 2127w, 1629w, 1570w, 1560w, 1534w, 1508w, 1376w, 1251w, 1182*m*, 1075*m*, 1051*m*, 990w, 961w, 883*m*, 640w, 531w. ^1H -NMR (300 MHz, CD_3OD): 8.20 (*d*, *J* = 8.4), 7.65 (*d*, *J* = 8.6, 4 arom. H); 8.17 (*d*, *J* = 8.3), 7.62 (*d*, *J* = 8.4, 4 arom. H); 4.21 (*d*, *J* = 9.0, H–C(3)); 4.06 (*dd*, *J* = 9.0, 0.7, H–C(5')); 3.92–3.84 (*m*, H–C(8), H–C(10')); 3.76–3.62 (*m*, H'–C(8), H'–C(10')); 3.53–3.47 (*m*, H–C(5), H–C(7), H–C(7'), H–C(9')); 3.33–3.20 (*m*, H–C(4), H–C(6')); 2.77–2.54 (*m*, H–C(6), H–C(8')). ^{13}C -NMR (75 MHz, CD_3OD): 147.93 (*s*); 147.67 (*s*); 133.12 (2*d*); 132.98 (2*d*); 129.77 (*s*); 129.34 (*s*); 124.12 (2*d*); 124.01 (2*d*); 91.89 (*s*); 90.91 (*s*); 84.49 (*s*); 83.47 (*s*); 81.39 (*d*); 80.93 (*d*); 78.67 (*d*); 78.00 (*d*); 76.43 (*s*); 75.57 (*d*); 75.44 (*d*); 75.05 (*s*); 72.63 (*d*); 72.61 (*d*); 71.13 (*s*); 68.82 (*s*); 63.74 (2*t*); 38.69 (*d*); 38.48 (*d*).

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-ethynyl-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-1-C-(4-nitrophenyl)-D-glycero-D-gulo-oct-1-ynitol (**35**). At 50°, a soln. of **28** (13.0 mg, 0.0116 mmol) in EtOH (2 ml) was treated with 0.1N HCl (0.9 ml) and stirred for 12 h. After completion, the solvent was removed under reduced pressure and gave **33** (12.1 mg). At 22°, a soln. of **33** (12.1 mg raw) in MeOH (2 ml) was treated with Et_3N (0.1 ml) and stirred for 10 h. Evaporation and FC (AcOEt/hexane 4 : 7) gave **34** (7.2 mg). Refluxing a soln. of **34** (7.2 mg, 9.02 μmol) in 0.3N HCl/MeOH (5 ml) during 52 h, evaporation, washing with hexane and ice-cold H_2O gave **35** (4.3 mg, 75%). Beige powder. R_f (AcOEt/hexane 9 : 1) 0.07. M.p. 222° (dec.). IR (KBr): 3571*m* (br.), 3423*m*, 2923w, 2259w, 2127w, 1629w, 1570w, 1560w, 1534w, 1508w, 1376w, 1250w, 1182*m*, 1075*m*, 1051*m*, 990w, 961w, 883w, 641w, 579w, 529w. ^1H -NMR (300 MHz, CD_3OD): 8.17 (*d*, *J* = 8.3), 7.62 (*d*, *J* = 8.4, 4 arom. H); 4.23 (*d*, *J* = 9.7, H–C(3)); 4.02 (*d*, *J* = 9.7, H–C(5));

3.89–3.64 (*m*, 2 H–C(8), 2 H–C(10')); 3.53–3.43 (*m*, H–C(5), H–C(7), H–C(7'), H–C(9')); 3.31–3.22 (*m*, H–C(4), H–C(6')); 2.59 (*t*, $J \approx 10.3$, H–C(6)); 2.54 (*d*, $J = 2.2$, H–C(2'')); 2.46 (*td*, $J = 10.3$, 2.4, H–C(8')).
¹³C-NMR (75 MHz, CD₃OD): 147.75 (*s*); 132.76 (*2d*); 129.24 (*s*); 123.88 (*2d*); 102.46 (*s*); 91.75 (*s*); 84.22 (*s*); 81.41 (*d*); 80.93 (*2d*); 78.67 (*d*); 78.01 (*d*); 76.51 (*s*); 75.58 (*s*); 75.56 (*d*); 75.41 (*d*); 72.64 (*d*); 72.61 (*d*); 70.88 (*s*); 68.62 (*s*); 63.63 (*t*); 63.60 (*t*); 38.75 (*d*); 38.25 (*d*).

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