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-$NO_2C_6H_4$ 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 'acetylenocelluloses' [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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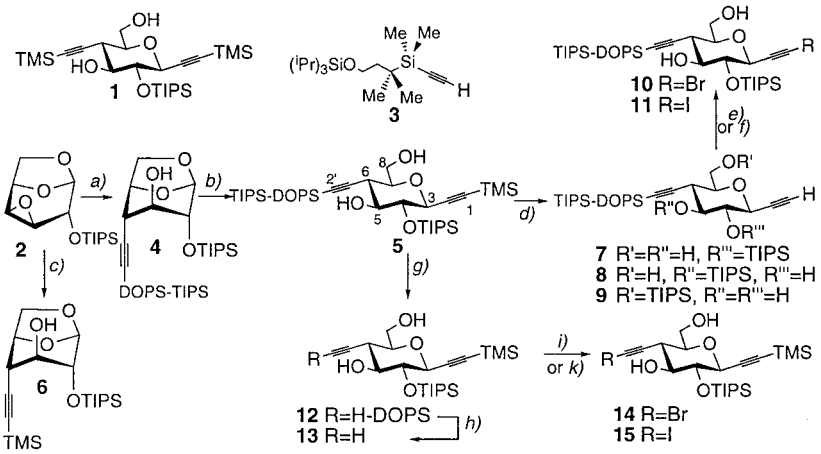
sequential alkynylating opening of the oxirane and dioxolane rings of the intermediate epoxide **2** with (trimethylsilyl) acetylene [1]. For the analogous introduction of the DOPS-protected[2]) alkyne **3** [5], we treated the epoxide **2** with the acetylide derived from **3**, BuLi, and $AlMe_3$ (*Scheme 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 persue this reaction.

Scheme 1



$TMS = Me_3Si$, $TIPS = (^iPr)_3Si$, $DOPS = OCH_2CH_2C(Me)_2Si(Me)_2$

a) TIPS-DOPS–C≡CH (**3**), BuLi, $AlMe_3$; 87%. *b*) 3 equiv. of $Me_3SiC{\equiv}CH$, 3 equiv. of BuLi, 3 equiv. of $AlCl_3$, toluene; 72%. *c*) $Me_3SiC{\equiv}CH$, BuLi, $AlMe_3$; 80%. *d*) 0.25M MeONa, MeOH; 94%. *e*) NBS, $AgOCOCF_3$, acetone; 97% from **7**. *f*) NIS, $AgOCOCF_3$, 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 MeOH[3]) 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 $AgOCOCF_3$ [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

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[2]) DOPS = (1,1-*d*imethyl-3-*oxyp*ropyl)dimethyl*s*ilyl.

[3]) If MeOH contained traces of carbonate, the secondary $(i\text{-Pr})_3Si$ (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 $(CH_3)_3Si$ groups appear at 0.17 and the *s*'s of the $(CH_3)_2Si$ groups at 0.10 ppm; the *q*'s of the $(CH_3)_3Si$ groups resonate at −0.30 to −0.57 and those of the $(CH_3)_2Si$ 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 H−C≡C unit is evidenced by a *d* at 2.2 ppm (H−C(2′)) or at 2.5 ppm (H−C(1)) with $J(H,H) \approx 2.2$ Hz and a ^{13}C *d* at 80–81 ppm.

The ^{1}H-NMR spectra of **5**, **7**, **12**, and **13** in $CDCl_3$ and (D_6)DMSO show well-resolved OH signals (*Table 1*). There are relevant differences for the HO−C(5) and to some extent also for the HO−C(8) signals. For the spectra of **5**, **7**, **12**, and **13** in $CDCl_3$, the *J*(HO−C(5),H−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 O−C(5) of the neighbouring unit, HO−C(5) of **5**, **7**, **12**, and **13** may form an intramolecular H-bond to O−C(4), as confirmed by the IR band at *ca.* 3600 cm^{-1} [15][5]. In keeping with this, the *J*(OH,H) coupling for HO−C(5) increases to *ca.* 8 Hz in the spectra of (D_6)DMSO. This is rationalized by a H-bond to DMSO and by the restricted rotation of the C(5)−OH group, due to the interaction with the bulky C(4)−OTIPS substituent. Indeed, $J(HO-C(5), H-C(5)) \approx 5.8$ Hz for HO−C(5) of the fully deprotected dialkyne corresponding to **12** [4] is as expected for a freely rotating OH group [19].

Table 1. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of monomers* **5**, **7**, **12**, *and* **13** *in $CDCl_3$ and (D_6)DMSO Solution at 22°*

	In $CDCl_3$				In (D_6)DMSO			
	5	**7**	**12**	**13**	**5**	**7**	**12**	**13**
HO−C(5)	2.35	2.34	3.03	2.51	5.00	5.00	5.04	5.15
HO−C(8)	2.08	2.00	2.40	2.21	4.74	4.73	4.73	4.74
J(HO−C(5),H−C(5))	2.8	2.8	2.8	2.9	8.4	7.8	8.1	8.1
J(HO−C(8),H−C(8))	7.6	7.4	br.	7.4	5.0	5.2	5.0	5.6
J(HO−C(8′),H−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 HO−C(5) and HO−C(8), respectively, presumably due to an intramolecular H-bond from the DOPS moiety of **12** to either HO−C(5) or HO−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 HO−C(5) and HO−C(8) to higher fields[6]. 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 ($[Pd_2(dba)_3]$ (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

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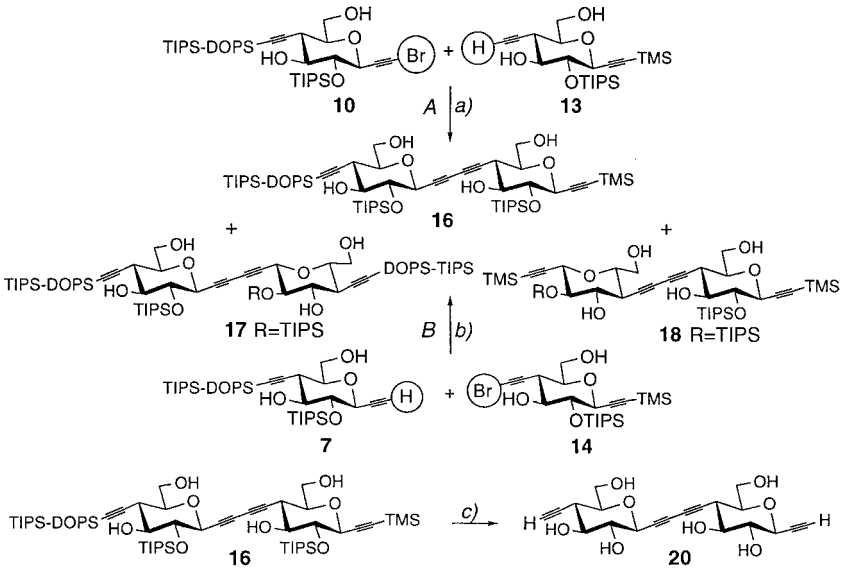
5) H-Bonds between OH and acetylene groups are known [16–18]; they are rather weak.

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



TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$

a) [$Pd_2(dba)_3$], CuI, LiI, PMP, DMSO: **16** (71%), **17** (3%), **18** (< 1%), or [$Pd_2(dba)_3$], CuI, P(fur)$_3$, Et_3N, DMSO: **16** (79%), **17** (2%), **18** (< 1%). *b*) [$Pd_2(dba)_3$], CuI, LiI, PMP, DMSO: **16** (61%), **17** (4%), **18** (9%); or [$Pd_2(dba)_3$], CuI, P(fur)$_3$, Et_3N, DMSO: **16** (64%), **17** (3%), **18** (12%). *c*) $Bu_4NF \cdot 3\,H_2O$, 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*.

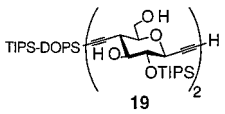
In agreement with the results of *Cadiot* and *Chodkiewicz* [21], we performed the reaction at 22°. *Brandsma et al.* suggested to proceed at the slightly elevated temperature resulting from slow addition of the bromoalkyne [22]. As we observed no heat evolution during the coupling of acetylenosaccharides, 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 Et_3N (*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**	*t* [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_3N	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_3N	55	12	<1	20
		10	$[Pd(PPh_3)_4]$, CuI, DMSO	Et_3N	49	8	<1	10
		11	$[Pd(PPh_3)_4]$, CuI, benzene	Et_3N	52	9	<1	10
	Coupling of **11** *and* **13**	*12*	$[Pd_2(dba)_3]$, CuI, DMSO	$P(fur)_3$, Et_3N	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_3N	64	3	12	10
	Coupling of **7** *and* **15**	*15*	$[Pd_2(dba)_3]$, CuI, DMSO	$P(fur)_3$, Et_3N	61	3	12	10

[a]) +11% of **19**. [b]) 16 equiv. of pyrrolidine; +2% of **19**.



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decreased the yield of **16** and the selectivity. Using $[Pd(PPh_3)_4]$ instead of $[Pd_2(dba)_3]$ 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 conditons (3 equiv. of Et_3N) [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 Pd^0) 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 $AgNO_2$/KCN in MeOH.

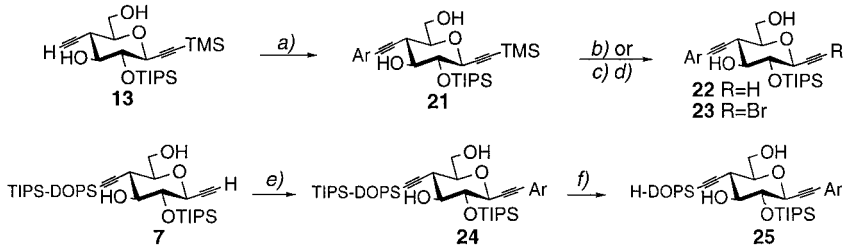
To check whether bromo- or iodoalkynes are to be preferred in the cross-coupling, we prepared the iodoalkynes **11** and **15** (*Scheme 1*). Surprisingly, coupling **11** to **13** (*Table 2*, *Entry 12*) slightly improved the selectivity in favour of the heterodimer **16**, while coupling of iodoalkyne **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 $[Pd_2(dba)_3]$, CuI, $P(fur)_3$, and Et_3N in DMSO, yielding 81% of the dimer **16**.

The dimer **16** was deprotected with $Bu_4NF \cdot 3\ H_2O$ 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-$NO_2C_6H_4$) groups to the unprotected acetylene moiety of the monomers **7** and **13** [27][28]. Coupling **13** and 1-iodo-4-nitrobenzene (4-$NO_2C_6H_4I$) in the presence of $[Pd(PPh_3)_4]$ and CuI in Et_3N/DMSO yielded 98% of the arylated monomer **21** (*Scheme 3*); similarly, coupling **7** with 4-$NO_2C_6H_4I$ led in 88% to **24**.

Scheme 3



Ar = 4-$NO_2C_6H_4$, TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$

a) 4-$NO_2C_6H_4I$, $[Pd(PPh_3)_4]$, 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**.

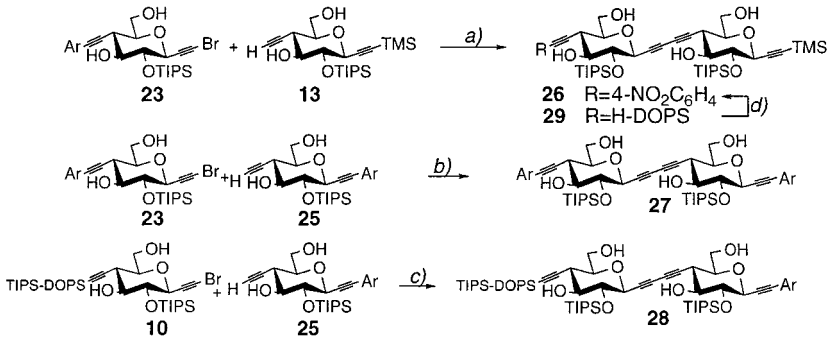
In the ^{1}H-NMR spectrum, H–C(3) and H–C(6) of the C(1) and C(2′) 4-nitrophenylated products, respectively, are deshielded by 0.2–0.3 ppm (*Table 3*, see *Exper. Part*). The chemical shift of the ring C-atoms of arylated compounds are very similar to those of the non-arylated ones; the ^{13}C-NMR signals 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-$NO_2C_6H_4$ substituent lowered the yields of the *Cadiot-Chodkiewicz* coupling ($[Pd_2(dba)_3]$, 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 $P(fur)_3$ 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

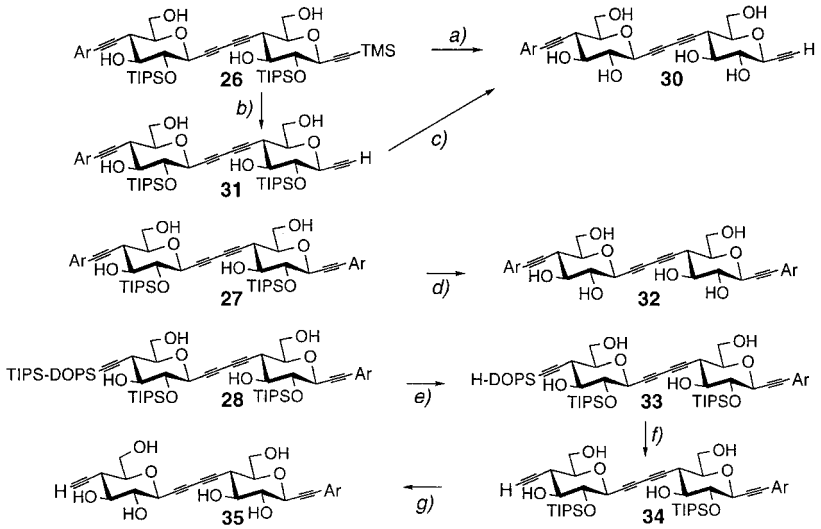


Ar = 4-$NO_2C_6H_4$, TMS = Me_3Si, TIPS = ($^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$

a) [$Pd_2(dba)_3$], CuI, LiI, PMP, DMSO: **26** (62%); or [$Pd_2(dba)_3$], CuI, P(fur)$_3$, Et_3N, DMSO: **26** (65%). *b*) as *a*); 46%. *c*) as *a*); 40%. *d*) 4-$NO_2C_6H_4I$, [$Pd(PPh_3)_4$], CuI, Et_3N, DMSO; 94%.

Complete desilylation ($Bu_4NF \cdot 3\,H_2O$) 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



Ar = 4-$NO_2C_6H_4$, TMS = Me_3Si, TIPS = ($^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$

a) $Bu_4NF \cdot 3\,H_2O$, THF, 0°; 29%. *b*) MeONa, MeOH, *c*) 0.3N HCl/MeOH, 55°; 92%. *d*) as *c*); 97%. *e*) 0.01N HCl, EtOH. *f*) Et_3N, MeOH. *g*) as *c*); 75% from **33**.

(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 Et_3N 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/H_2O) or indole-3-acetic acid (IAA, 0.05M in THF).

[3-(Ethynyldimethylsilyl)-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 CH_2Cl_2 (100 ml) was treated dropwise with (i-Pr)$_3$SiOTf (TIPSOTf; 10.5 ml, 39.1 mmol), stirred for 2 h, and treated with H_2O (40 ml). Usual workup (CH_2Cl_2, H_2O, 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 ($CHCl_3$): 2960*s*, 2944*s*, 2892*m*, 2866*s*, 1464*m*, 1410*w*, 1384*w*, 1365*w*, 1252*s* (br.), 1093*m*, 1069*m*, 1014*w*, 997*w*, 919*w*, 882*m*, 846*s*, 840*s*, 825*s*, 818*s* (br.). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.81 (*t*, *J* = 7.8, 2H–C(3)); 1.63 (*t*, *J* = 7.8, 2H–C(2)); 1.10–1.03 (*m*, (Me$_2$CH)$_3$Si); 0.98 (*s*, Me$_2$C); 0.16 (*s*, Me$_3$Si); 0.12 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 115.11, 112.22 (2*s*, C≡C); 60.58 (*t*, C(3)); 42.20 (*t*, C(2)); 23.61 (*q*, *Me*$_2$C); 18.69 (*s*, Me$_2$*C*); 18.26 (*q*, 3 *Me*$_2$CH); 12.22 (*d*, 3 Me$_2$*C*H); 0.05 (*q*, Me$_3$Si); –4.07 (*q*, Me$_2$Si). 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, Me$_3$Si$^+$), 59 (23). Anal. calc. for $C_{21}H_{46}OSi_3$ (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. Destillation (0.4 mbar, 54°) gave **3** (11.76 g, 98%). Transparent oil. R_f (hexane) 0.27. IR ($CHCl_3$): 3287*m*, 2944*s*, 2891*s*, 2866*s*, 2727*w*, 1464*s*, 1412*w*, 1384*m*, 1365*w*, 1255*s* (br.), 1162*w*, 1094*s*, 1070*s*, 1014*m*, 997*m*, 966*w*, 936*w*, 919*w*, 883*s*, 841*s*, 824*s* (br.), 571*w*, 508*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 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*, (Me$_2$CH)$_3$Si); 1.00 (*s*, Me$_2$C); 0.16 (*s*, Me$_2$Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 94.37 (*d*, H*C*≡C); 88.79 (*s*, HC≡*C*); 60.53 (*t*, C(3)); 42.02 (*t*, C(2)); 23.54 (*q*, *Me*$_2$C); 18.61 (*s*, Me$_2$*C*); 18.24 (*q*, 3 *Me*$_2$CH); 12.18 (*d*, 3 Me$_2$*C*H); –4.18 (*q*, Me$_2$Si). 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 Me$_3$Al (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. NH_4Cl soln. (5 ml). Filtration over *Celite*, usual workup (AcOEt, H_2O), and FC (AcOEt/hexane 1:15) gave **4** (15.3 g, 71%). Transparent syrup. R_f (toluene/AcOEt 15:1) 0.13. $[\alpha]_D^{25} = -53.05$ (c = 1.9, $CHCl_3$). IR ($CHCl_3$): 3424*m* (br.), 3007*s*, 2945*s*, 2867*s*, 2839*m*, 2177*w*, 1603*w*, 1464*m*, 1384*w*, 1334*w*, 1248*w*, 1101*m*, 1016*s*, 919*w*, 883*m*, 868*w*, 838*w*, 658*w* (br.). ^{1}H-NMR (500 MHz, $CDCl_3$): 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), CH_2CH_2OSi); 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, CH_2CH_2OSi); 1.13–1.06 (*m*, 2 (Me$_2$CH)$_3$Si); 0.97 (*s*, Me$_2$C); 0.10 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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*, CH_2CH_2OSi); 41.66 (*t*, CH_2CH_2OSi); 38.35 (*d*, C(4)); 23.41 (*q*, *Me*$_2$C); 18.63 (*s*, Me$_2$*C*); 18.07 (*q*, 3 *Me*$_2$CH); 18.03 (*q*, 3 *Me*$_2$CH); 12.20 (*d*, 3 Me$_2$*C*H); 12.02 (*d*, 3 Me$_2$*C*H); –4.15 (*q*, Me$_2$Si). CI-MS:

645 (2, $[M+NH_4]^+$), 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 $C_{33}H_{66}O_5Si_3$ (627.14): C 63.20, H 10.61; found: C 63.11, H 10.51.

3,7-Anhydro-1,2,6-trideoxy-6-C-{{dimethyl{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}silyl}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 ($CHCl_3$): 3595*w*, 3427*w*, 3008*m*, 2945*s*, 2892*s*, 2867*s*, 2174*w*, 1522*w*, 1464*m*, 1384*w*, 1365*w*, 1349*w*, 1290*w*, 1252*m* (br.), 1143*m*, 1101*s*, 1071*m*, 1048*m*, 1014*m*, 991*m*, 919*w*, 883*s*, 845*s*, 824*s* (br.), 604*w*, 571*w*, 532*w*, 524*w*, 506*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.95 (*d*, $J = 9.3$, H–C(3)); 3.93 (*ddd*, $J = 12.0, 7.6, 2.7$, H–C(8)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.73 (*dt*, $J \approx 12.0, 6.1$, H′–C(8)); 3.63 (*dd*, $J = 9.3, 8.3$, H–C(4)); 3.49 (*ddd*, $J \approx 10.3, 8.3, 2.8$, H–C(5)); 3.43 (*ddd*, $J \approx 10.3, 6.1, 2.7$, H–C(7)); 2.54 (*t*, $J = 10.3$, H–C(6)); 2.35 (*d*, $J = 2.8$, HO–C(5)); 2.08 (*dd*, $J \approx 7.6, 6.0$, HO–C(8)); 1.60 (*t*, $J = 7.7$, CH_2CH_2OSi); 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}H-NMR (300 MHz, (D_6)DMSO): 5.00 (*d*, $J = 8.4$, HO–C(5)); 4.74 (*t*, $J = 5.0$, HO–C(8)); 3.87 (*d*, $J = 9.0$, H–C(3)); 3.72 (*t*, $J = 7.7$, CH_2CH_2O-Si); 3.70–3.64 (*m*, H–C(8)); 3.44 (*dt*, $J = 11.8, 5.6$, H′–C(8)); 3.37–3.17 (*m*, H–C(4), H–C(5), H–C(7)); 2.47–2.43 (*m*, H–C(6)); 1.51 (*t*, $J = 7.8$, CH_2CH_2OSi); 1.21–1.02 (*m*, ($Me_2CH)_3Si$); 0.91 (*s*, Me_2C); 0.09 (*s*, Me_3Si); 0.04 (*s*, Me_2Si). ^{13}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 (2*q*); 18.52 (*s*); 18.36 (6*q*); 18.08 (6*q*); 13.09 (3*d*); 12.01 (3*d*); −0.37 (3*q*); −4.12 (2*q*). 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 $C_{38}H_{76}O_5Si_4$ (725.36): C 62.92, H 10.56; found: C 62.77, H 10.47.

3,7-Anhydro-1,2,6-trideoxy-6-C-{{dimethyl{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}silyl}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 ($CHCl_3$): 3592*w*, 3429*w* (br.), 3306*w*, 3008*w*, 2945*s*, 2892*m*, 2867*s*, 2171*w*, 1602*w*, 1464*m*, 1384*w*, 1366*w*, 1256*w* (br.), 1144*m*, 1097*s*, 1047*m*, 1014*w*, 963*w*, 932*w*, 883*w*, 840*w*, 823*m* (br.), 652*w*, 603*w*, 540*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.95 (*dd*, $J = 9.3, 2.2$, H–C(3)); 3.93 (*ddd*, $J = 12.0, 7.4, 2.6$, H–C(8)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.72 (*dt*, $J = 12.0, 6.0$, H′–C(8)); 3.66 (*dd*, $J = 9.3, 8.3$, H–C(4)); 3.51 (*ddd*, $J = 10.3, 8.3, 2.8$, H–C(5)); 3.45 (*ddd*, $J = 10.3, 6.0, 2.6$, H–C(7)); 2.56 (*t*, $J = 10.3$, H–C(6)); 2.47 (*d*, $J = 2.2$, H–C(1)); 2.39 (*d*, $J = 2.8$, HO–C(5)); 2.00 (*dd*, $J = 7.4, 6.1$, HO–C(8)); 1.60 (*t*, $J = 7.7$, CH_2CH_2OSi); 1.23–1.05 (*m*, 2 ($Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.12 (*s*, Me_2Si). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.00 (*d*, $J = 7.8$, HO–C(5)); 4.73 (*t*, $J = 5.2$, HO–C(8)); 3.84 (*dd*, $J = 9.0, 2.2$, H–C(3)); 3.73 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.70–3.64 (*m*, H–C(8)); 3.44 (*dt*, $J = 11.8, 5.6$, H′–C(8)); 3.37 (*d*, $J = 2.2$, H–C(1)); 3.34–3.17 (*m*, H–C(4), H–C(5), H–C(7)); 2.47–2.43 (*m*, H–C(6)); 1.51 (*t*, $J = 7.8$, CH_2CH_2OSi); 1.21–1.02 (*m*, ($Me_2CH)_3Si$); 0.90 (*s*, Me_2C); 0.04 (*s*, Me_2Si). ^{13}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 (2*q*); 18.52 (*s*); 18.36 (6*q*); 18.08 (6*q*); 13.02 (3*d*); 12.01 (3*d*); −4.12 (2*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 $C_{35}H_{68}O_5Si_3$ (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-{{dimethyl{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}silyl}ethynyl}-5-O-(triisopropylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**8**), *and 3,7-Anhydro-1,2,6-trideoxy-6-C-{{dimethyl{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}silyl}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 ($CHCl_3$): 3598*m*, 3306*m*, 2945*s*, 2892*s*, 2172*m*, 2122*w*, 1711*w*, 1464*s*, 1384*m*, 1365*m*, 1298*w*, 1252*s* (br.), 1141*s*, 1085*s*, 1014*s*, 997*s*, 919*w*, 883*s*, 818*s*, 582*s*, 509*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.97 (*dd*, $J = 9.7, 2.2$, H–C(3)); 3.96 (*ddd*, $J = 12.0, 7.3, 2.6$, H–C(8)); 3.78 (*dd*, $J = 10.3, 8.3$, H–C(5)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.75 (*dt*, $J \approx 12.0, 6.0$, H′–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*, $J = 7.7$, CH_2CH$_2$OSi); 1.23–1.05 (*m*, 2 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.10 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 (2*q*); 18.53 (*s*); 18.43 (6*q*), 18.08 (6*q*); 13.06 (3*d*); 12.00 (3*d*); –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 $C_{35}H_{68}O_5Si_3$ (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. $[\alpha]_D^{25} = -23.1$ ($c = 0.47$, $CHCl_3$). IR ($CHCl_3$): 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*. ^{1}H-NMR (300 MHz, $CDCl_3$): 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*, $J \approx 7.6$, CH$_2$CH_2OSi); 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*, $J \approx 7.5$, CH_2CH$_2$OSi); 1.25–1.05 (*m*, 2 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.09 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 (2*q*); 18.52 (*s*); 18.39 (6*q*); 18.09 (6*q*); 13.05 (3*d*); 12.00 (3*d*); –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 $C_{35}H_{68}O_5Si_3$ (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 $AgOCOCF_3$ (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 (Et_2O, H_2O). FC (AcOEt/hexane 3:47) gave **10** (6.47 g, 97%). Transparent syrup. R_f (AcOEt/hexane 1:4) 0.59. $[\alpha]_D^{25} = -27.6$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 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*. ^{1}H-NMR (500 MHz, $CDCl_3$): 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*, $J \approx 7.7$, CH$_2$CH_2OSi); 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, CH_2CH$_2$OSi); 1.26–1.04 (*m*, 2 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.11 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 (2*q*); 18.37 (*s*); 18.26–18.21 (6*q*); 18.09 (6*q*); 12.94 (3*d*); 12.01 (3*d*); –4.12 (2*q*). 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 $C_{35}H_{67}BrO_5Si_3$ (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 $AgOCOCF_3$ (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 (Et_2O, H_2O). 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°. $[\alpha]_D^{25} = -21.8$ ($c = 0.6$, $CHCl_3$). IR ($CHCl_3$): 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*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.08 (*d*, $J = 9.3$, H–C(3)); 3.94 (*m*, H–C(8)); 3.77 (*t*, $J = 7.7$, CH$_2$CH_2OSi); 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*, $J = 7.7$, CH_2CH$_2$OSi); 1.28–1.06 (*m*, 2 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.11 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 (2*q*); 18.52 (*s*); 18.31 (6*q*); 18.09 (6*q*); 13.02 (3*d*); 12.01 (3*d*); 5.00 (*s*); 1.04 (*s*); –4.12 (2*q*). 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 $C_{35}H_{67}IO_5Si_3$ (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 0.1N 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°. $[\alpha]_D^{25} = -29.8$

($c = 1.72$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3438*w* (br.), 3008*m*, 2946*s*, 2892*s*, 2866*s*, 2174*m*, 1602*w*, 1464*m*, 1386*m*, 1364*m*, 1349*m*, 1291*m*, 1252*s*, 1144*s*, 1102*s*, 1071*s*, 991*s*, 918*w*, 884*s*, 845*s*, 822*m*, 655*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.95 (*d*, $J = 9.2$, H–C(3)); 3.96–3.92 (*m*, H–C(8)); 3.77 (*t*, $J = 7.2$, CH_2OH); 3.78–3.68 (*m*, H′–C(8)); 3.61 (*dd*, $J = 9.3$, 8.4, H–C(4)); 3.55–3.50 (*m*, H–C(5)); 3.43 (*ddd*, $J = 10.3$, 6.2, 2.8, H–C(7)); 3.03 (*d*, $J = 2.8$, HO–C(5)); 2.53 (*t*, $J = 10.3$, H–C(6)); 2.40 (br. *s*, HO–C(8)); 1.83 (br. *s*, CH_2CH_2OH); 1.60 (*t*, $J = 7.2$, CH_2CH_2OH); 1.19–1.08 (*m*, $(Me_2CH)_3Si$); 0.95 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.04 (*d*, $J = 8.1$, HO–C(5)); 4.73 (*t*, $J = 5.0$, HO–C(8)); 4.26 (*t*, $J = 5.0$, CH_2CH_2OH); 3.92 (*d*, $J = 9.3$, H–C(3)); 3.74–3.61 (*m*, H–C(8)); 3.49–3.43 (*m*, H′–C(8), CH_2CH_2OH); 3.36–3.18 (*m*, H–C(4), H–C(5), H–C(7)); 2.51–2.48 (*m*, H–C(6)); 1.42 (*t*, $J = 7.8$, CH_2CH_2OH); 1.21–1.02 (*m*, $(Me_2CH)_3Si$); 0.89 (*s*, Me_2C); 0.09 (*s*, Me_3Si); 0.04 (*s*, Me_2Si). ^{13}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 (2*q*); 18.87 (*s*); 18.23 (6*q*); 12.90 (3*d*); −0.56 (3*q*); −4.17 (2*q*). 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 $C_{29}H_{56}O_5Si_3$ (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}H-NMR (300 MHz, (D_6)DMSO): 5.15 (*d*, $J = 8.1$, HO–C(5)); 4.74 (*t*, $J = 5.6$, HO–C(8)); 3.92 (*d*, $J = 9.3$, H–C(3)); 3.63 (*ddd*, $J = 11.4$, 5.0, 0.8, H–C(8)); 3.45 (*dt*, $J = 11.5$, 5.3, H′–C(8)); 3.36–3.18 (*m*, H–C(4), H–C(5), H–C(7)); 2.96 (*d*, $J = 2.2$, H–C(2′)); 2.37 (*td*, $J = 10.3$, 2.5, H–C(6)); 1.21–1.02 (*m*, $(Me_2CH)_3Si$); 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 ($CHCl_3$): 3579*m*, 2990*s*, 2945*m*, 2864*w*, 2172*w*, 1588*m*, 1490*m*, 1462*m*, 1351*s* (br.), 1139*m*, 1117*m*, 978*s*, 901*w*, 887*m*, 862*m*, 840*s* (br.), 643*s* (br.), 601*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.97 (*d*, $J = 9.1$, H–C(3)); 3.96–3.93 (*m*, H–C(8)); 3.73 (*dt*, $J =$ 12.0, 6.0, H′–C(8)); 3.63 (*dd*, $J \approx 9.0$, 8.3, H–C(4)); 3.54 (*ddd*, $J = 10.3$, 8.3, 3.0, H–C(5)); 3.46 (*ddd*, $J = 10.3$, 5.7, 2.5, H–C(7)); 2.59 (*t*, $J = 10.3$, H–C(6)); 2.44 (*d*, $J = 3.0$, HO–C(5)); 2.05 (*dd*, $J = 7.4$, 6.2, HO–C(8)); 1.27–1.09 (*m*, $(Me_2CH)_3Si$); 0.18 (*s*, Me_3Si). ^{13}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 (6*q*); 12.77 (3*d*); −0.68 (3*q*). CI-MS: 523 (34), 521 (32, $[M + NH_4]^+$), 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 $C_{22}H_{39}BrO_4Si_2$ (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 ($CHCl_3$): 3601*s*, 3008*s*, 2946*s*, 2867*s*, 2399*m*, 2180*m*, 1602*m*, 1520*w*, 1464*m*, 1391*m*, 1366*m*, 1349*m*, 1291*m*, 1265*m*, 1252*s*, 1144*s*, 1104*s*, 1072*s*, 1047*s*, 1017*m*, 991*m*, 931*w*, 884*s*, 846*s*, 653*m*, 638*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.95 (*d*, $J = 9.0$, H–C(3)); 3.93 (*ddd*, $J = 11.8$, 7.2, 2.5, H–C(8)); 3.72 (*td*, $J = 11.8$, 5.9, H′–C(8)); 3.61 (*dd*, $J = 9.0$, 8.4, H–C(4)); 3.53 (*ddd*, $J = 10.3$, 8.1, 3.1, H–C(5)); 3.45 (*ddd*, $J = 10.3$, 5.9, 2.8, H–C(7)); 2.70 (*t*, $J = 10.3$, H–C(6)); 2.49 (*d*, $J = 2.8$, HO–C(5)); 2.12 (br. *t*, $J \approx 6.7$, 6.2, HO–C(8)); 1.25–1.10 (*m*, $(Me_2CH)_3Si$); 0.16 (*s*, Me_3Si). ^{13}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 (6*q*); 14.01 (*s*); 12.92 (3*d*); −0.55 (3*q*). CI-MS: 568 (15, $[M + NH_4]^+$), 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), $[Pd_2(dba)_3]$ (129.3 mg, 0.14 mmol), CuI (26.9 mg, 0.14 mmol), and $P(fur)_3$ (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 → 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}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-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* (**16**): R_f (AcOEt/hexane 1:4) 0.26. M.p. 85–86°. $[\alpha]_D^{25} = -38.1$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 3594*w*, 2962*s*, 2867*s*, 2254*w*, 2173*w*, 1602*w*, 1464*m*, 1384*w*, 1365*w*, 1328*w*, 1291*w*, 1261*s*, 1141*m*, 1098*s*, 1015*s*, 909*m*, 883*m*, 845*m*, 818*s*, 596*w*, 576*w*, 536*w*, 512*w*, 504*w*. ^{1}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*, $J = 7.7$, CH_2CH_2OSi); 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*, $J = 7.7$, CH_2CH_2OSi); 1.26–1.04 (*m*, 3 ($Me_2CH)_3Si$); 0.95 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}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*); 76.70 (*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 (2*q*); 18.51 (*s*); 18.34–18.08 (several *q*); 13.02 (3*d*); 12.94 (3*d*); 12.00 (3*d*); −0.39 (3*q*); −4.13 (2*q*). MALDI-TOF-MS: 1098 ($[M + Na]^+$). Anal. calc. for $C_{57}H_{106}O_9Si_5$ (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-diynitol* (**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 ($CHCl_3$): 3594*w*, 3008*m*, 2961*s*, 2945*s*, 2892*m*, 2867*s*, 2400*w*, 2171*w*, 1730*w*, 1601*w*, 1524*w*, 1464*m*, 1288*m*, 1261*s* (br.), 1143*m*, 1096*s*, 1014*s*, 883*m*, 818*s* (br.), 602*w*, 577*w*, 539*w*. ^{1}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*, $J = 7.7$, CH_2CH_2OSi); 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*, $J = 7.7$, CH_2CH_2OSi); 1.26–1.05 (*m*, 2 ($Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.12 (*s*, Me_2Si). ^{13}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 (2*q*); 18.52 (*s*); 18.33–18.08 (several *q*); 12.93 (3*d*); 12.02 (3*d*); −4.13 (2*q*). MALDI-TOF-MS: 1327 ($[M + Na]^+$). Anal. calc. for $C_{70}H_{134}O_{10}Si_6$ (1304.34): C 64.46, H 10.35; found: C 64.58, H 10.22.

*Data of 6,6′-(Buta-1,3-diyne-1,4-diyl)bis{3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethyl-silyl-*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 ($CHCl_3$): 3596*m*, 3008*m*, 2962*s*, 2946*s*, 2867*s*, 2179*w*, 1763*w*, 1722*m*, 1602*w*, 1463*m*, 1290*m*, 1261*s*, 1252*s* (br.), 1142*s*, 1101*s*, 1068*s*, 1016*s*, 998*s*, 919*w*, 883*s*, 847*s*, 818*s* (br.), 595*w*, 574*w*, 522*w*. ^{1}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*, ($Me_2CH)_3Si$); 0.17 (*s*, Me_3Si). ^{13}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 (6*q*); 13.05 (3*d*); – 0.40 (3*q*). MALDI-TOF-MS: 870 ($[M+Na]^+$). Anal. calc. for $C_{44}H_{78}O_8Si_4$ (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), $[Pd_2(dba)_3]$ (7.5 mg, 8.19 μmol), CuI (1.6 mg, 8.19 μmol), $P(fur)_3$ (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 → 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), $[Pd_2(dba)_3]$ (39.4 mg, 0.043 mmol), CuI (8.2 mg, 0.043 mmol), $P(fur)_3$ (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 → 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), $[Pd_2(dba)_3]$ (34.2 mg, 0.037 mmol), CuI (7.1 mg, 0.037 mmol), $P(fur)_3$ (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 → 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), $[Pd_2(dba)_3]$ (8.8 mg, 9.58 μmol), CuI (1.8 mg, 9.58 μmol), $P(fur)_3$ (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 → 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 → 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°. $[\alpha]_D^{25} = -50.4$ ($c = 0.6$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3306*w*, 3008*w*, 2962*s*, 2867*s*, 2362*w*, 2254*w*, 2170*w*, 1602*w*, 1464*m*, 1392*w*, 1329*w*, 1261*s* (br.), 1097*s*, 1015*s*, 883*m*, 818*s* (br.), 602*w*, 577*w*, 509*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.00 (*dd*, $J = 9.3, 0.6$, H–C(5′)); 3.97 (*d*, $J = 9.2, 2.1$, H–C(3)); 3.92 (*ddd*, $J \approx 12.1, 7.1, 2.6$, H–C(8)); 3.90 (*ddd*, $J \approx 12.1, 6.8, 2.4$, H–C(10′)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.73–3.69 (*m*, H′–C(8), H′–C(10′)); 3.65 (*dd*, $J = 9.3, 8.3$, H–C(6′)); 3.64 (*dd*, $J = 9.2, 8.4$, H–C(4)); 3.57–3.50 (*m*, H–C(5)); H–C(7′)); 3.49–3.42 (*m*, H–C(9′), H–C(7)); 2.68 (*td*, $J = 10.3, 0.6$, H–C(6)); 2.54 (*t*, $J = 10.3$, H–C(8′)); 2.49 (*d*, $J = 2.1$, H–C(1)); 2.37 (*d*, $J = 3.1$, HO–C(5), HO–C(7′)); 2.00 (*dd*, $J = 7.3, 6.3$, HO–C(10′)); 1.96 (*t*, $J = 6.8$, HO–C(8)); 1.59 (*t*, $J = 7.7$, CH_2CH_2OSi); 1.26–1.05 (*m*, 3 $(Me_2CH)_3Si$); 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 (12*q*); 18.08 (6*q*); 12.98 (3*d*); 12.96 (3*d*); 12.03 (3*d*); – 4.12 (*q*); – 4.14 (*q*). MALDI-TOF-MS: 1025 ($[M+Na]^+$). Anal. calc. for $C_{54}H_{98}O_9Si_4$ (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 $[Pd(PPh_3)_4]$ (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 Et_3N (9 ml) and stirred overnight. Dilution with AcOEt (25 ml), neutralization with 2N aq. HCl (pH 7), normal workup (AcOEt, H_2O), 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°. $[\alpha]_D^{25} = -41.7$ ($c = 0.50$, $CHCl_3$). IR (CCl_4): 3598*w*, 2963*m*, 2946*m*, 2867*m*, 2226*w*, 2180*w*, 1726*w*, 1595*m*, 1522*s*, 1464*w*, 1346*s*, 1144*m*, 1108*m*, 1066*m*, 995*w*, 884*m*, 855*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 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*, $J \approx 12.0$, 7.4, 2.6, H–C(8)); 3.81 (*dt*, $J \approx 11.9$, 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*, $(Me_2CH)_3Si$); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.14 (*s*); 132.60 (2*d*), 129.42 (*s*); 123.55 (2*d*); 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 (6*q*); 13.08 (3*d*); –0.42 (3*q*). CI-MS: 563 (100, $[M + NH_4]^+$), 546 (22, $[M + 1]^+$), 516(69), 472(51), 442(74), 309(54), 148(37), 131(41), 73 (37, Me_3Si^+). Anal. calc. for $C_{28}H_{43}NO_6Si_2$ (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. $[\alpha]_D^{25} = -37.4$ ($c = 0.43$, $CHCl_3$). IR (CCl_4): 3606*m*, 3311*m*, 2945*m*, 2868*m*, 2225*w*, 1740*w*, 1596*m*, 1558*w*, 1525*s*, 1464*w*, 1344*s*, 1286*w*, 1244*w*, 1143*m*, 1124*m*, 1100*m*, 1069*m*, 962*w*, 883*m*, 856*m*, 669*m*, 641*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 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*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.16 (*s*); 132.60 (2*d*); 129.35 (*s*); 123.55 (2*d*); 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 (6*q*); 13.02 (3*d*). CI-MS: 491 (100, $[M + NH_4]^+$), 474 (13, $[M + 1]^+$), 444(17), 282(11), 237(29), 148(11). Anal. calc. for $C_{25}H_{35}NO_6Si$ (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 $AgOCOCF_3$ (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 (Et_2O, H_2O). 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 $AgOCOCF_3$ (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 (Et_2O, H_2O). 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°. $[\alpha]_D^{25} = -43.4$ ($c = 0.23$, $CHCl_3$). IR (CCl_4): 3606*m*, 2946*m*, 2868*m*, 2223*w*, 1734*w*, 1596*m*, 1525*s*, 1494*w*, 1464*w*, 1345*s*, 1287*w*, 1244*w*, 1142*s*, 1120*s*, 1068*m*, 1015*w*, 1000*w*, 920*w*, 883*m*, 856*s*, 686*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 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*, $J \approx 12.0$, 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*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.17 (*s*); 132.60 (2*d*); 129.33 (*s*); 123.55 (2*d*); 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 (6*q*); 12.94 (3*d*). CI-MS: 570 (30, $[M + NH_4]^+$), 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 $C_{25}H_{34}BrNO_6Si$ (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), Et_3N (0.5 ml), $[Pd(PPh_3)_4]$ (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. $[\alpha]_D^{25} = -23.1$ ($c = 0.315$, $CHCl_3$). IR (CCl_4): 3607*m*, 2944*s*, 2867*s*, 2170*w*, 1596*m*, 1525*s*, 1494*w*, 1464*m*, 1384*w*, 1345*s*, 1291*w*, 1253*m*, 1142*s*, 1092*s*, 1014*m*, 997*m*, 919*w*, 883*s*, 855*s*, 840*m*, 685*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 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), CH_2CH_2OSi); 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, C*H*$_2$CH$_2$OSi); 1.21–1.06 (*m*, (Me$_2$CH)$_3$Si); 0.98 (*s*, Me$_2$C); 0.13 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 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 $C_{41}H_{71}NO_7Si_3$ (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. $[\alpha]_D^{25} = -35.5$ (*c* = 0.36, CHCl$_3$). IR (CHCl$_3$): 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*. ^{1}H-NMR (300 MHz, CDCl$_3$): 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, C*H*$_2$OH); 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*, CH$_2$CH$_2$OH); 1.62 (*t*, *J* = 7.2, C*H*$_2$CH$_2$OH); 1.19–1.07 (*m*, (Me$_2$CH)$_3$Si); 0.97 (*s*, Me$_2$C); 0.13 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 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, $[M-\text{DOPS}+1]^+$), 444(9), 370(10), 306(3), 162(10), 146 (22, DOPS$^+$), 145(100), 129(21), 75(21), 74(12). Anal. calc. for $C_{32}H_{51}NO_7Si_2$ (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), [Pd$_2$(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/H$_2$O, neutralized with 1N HCl and worked up normally (Et$_2$O, H$_2$O). FC (AcOEt/hexane 1:3) gave **26** (183.3 mg, 94%). White powder. R_f (AcOEt/hexane 1:2) 0.19. M.p. 138°. $[\alpha]_D^{25} = -63.5$ (*c* = 0.17, CHCl$_3$). IR (CCl$_4$): 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*. ^{1}H-NMR (500 MHz, CDCl$_3$): 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 (Me$_2$CH)$_3$Si); 0.17 (*s*, Me$_3$Si). ^{13}C-NMR (125 MHz, CDCl$_3$): 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 ($[M+\text{Na}]^+$). Anal. calc. for $C_{47}H_{73}NO_{10}Si_3$ (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), [Pd$_2$(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/H$_2$O, neutralized with 1N HCl and worked up normally (Et$_2$O, H$_2$O). 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°. $[\alpha]_D^{25} = -48.4$ (*c* = 0.31, CHCl$_3$). IR (CHCl$_3$): 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*. ^{1}H-NMR (500 MHz, CDCl$_3$): 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 (Me_2CH)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 $C_{50}H_{68}N_2O_{12}Si_2$ (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), $[Pd_2(dba)_3]$ (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/H_2O, neutralized with 1N HCl and worked up normally (Et_2O, H_2O). 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°. $[\alpha]_D^{25} = -31.4$ (c = 0.41, $CHCl_3$). IR ($CHCl_3$): 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*. ^{1}H-NMR (500 MHz, $CDCl_3$): 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, CH_2CH_2OSi); 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, $J \approx$ 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, CH_2CH_2OSi); 1.23–1.08 (m, 3 (Me_2CH)$_3$Si); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 $C_{60}H_{101}NO_{11}Si_4$ (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 0.1N 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°. $[\alpha]_D^{25} = -44.4$ (c = 0.6, $CHCl_3$). IR ($CHCl_3$): 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*. ^{1}H-NMR (500 MHz, $CDCl_3$): 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, CH_2OH); 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, CH_2OH); 1.61 (t, J = 7.0, CH_2CH_2OH); 1.26–1.04 (m, 2 (Me_2CH)$_3$Si); 0.96 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.12 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 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 $C_{48}H_{86}O_9Si_4$ (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 0.25M 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 0.3N 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 $Bu_4NF \cdot 3\ H_2O$ (21.0 mg, 0.0665 mmol) in THF (1.5 ml) and stirred for 6 h. Normal workup (AcOEt, H_2O) 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.

1182*w*, 1075*m*, 1051*m*, 990*w*, 961*w*, 883*w*, 641*w*, 579*w*, 529*w*, 437*w*. ^{1}H-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(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.), 2923*w*, 2261*w*, 2127*w*, 1629*w*, 1570*w*, 1560*w*, 1534*w*, 1508*w*, 1376*w*, 1251*w*, 1182*m*, 1075*m*, 1051*m*, 990*w*, 961*w*, 883*m*, 640*w*, 531*w*. ^{1}H-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*, 2923*w*, 2259*w*, 2127*w*, 1629*w*, 1570*w*, 1560*w*, 1534*w*, 1508*w*, 1376*w*, 1250*w*, 1182*m*, 1075*m*, 1051*m*, 990*w*, 961*w*, 883*w*, 641*w*, 579*w*, 529*w*. ^{1}H-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′)). ^{13}C-NMR (75 MHz, CD_3OD): 147.75 (*s*); 132.76 (2*d*); 129.24 (*s*); 123.88 (2*d*); 102.46 (*s*); 91.75 (*s*); 84.22 (*s*); 81.41 (*d*); 80.93 (2*d*); 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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