# 15. Oligosaccharide Analogues of Polysaccharides

Part 2

## Regioselective Deprotection of Monosaccharide-Derived Monomers and Dimers

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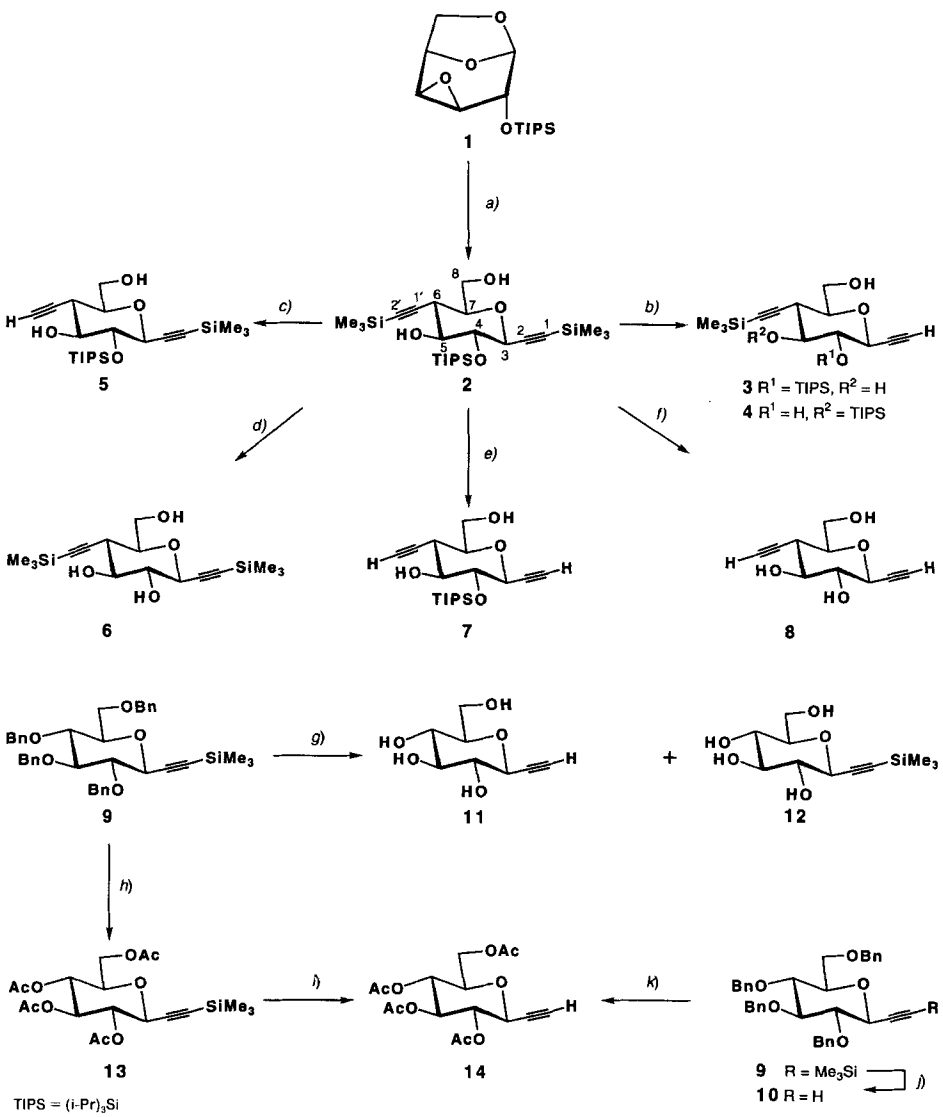
The $Me_3Si$–C(1) bond of the bis-(trimethylsilyl)ethynylated anhydroalditol **2** is selectively cleaved with BuLi to yield **3**/**4**, while $AgNO_2$/KCN in MeOH cleaves the $Me_3Si$–C(2′) bond, leading to **5** (*Scheme 1*). Both $Me_3Si$ groups are removed with NaOH in MeOH (→ **7**), the $(i\text{-}Pr)_3Si$ group is selectively cleaved with HCl in aq. MeOH (→ **6**); all silyl substituents are removed with $Bu_4NF$ (→ **8**). Acetolysis transformed **9** into **13**, which was desilylated to **14**, while thiolysis of **9** led to a mixture **11**/**12**. The tetraacetate **14** has also been obtained from **9** *via* **10**. Oxidative dimerisation of either **3** or **5**, or of a mixture **3**/**5** yields only the homodimers **15** and **16** (*Scheme 2*); treatment of **16** with $AgNO_2$/KCN yielded **17**, deprotection proceeding much more slowly than the cleavage of the $Me_3Si$–C(2′) group of **2**. The iodoalkyne **20**, required for the cross-coupling with **5** according to *Cadiot-Chodkiewicz*, was prepared by deprotection of **3**/**4** to **18**, methoxymethylation (→ **19**), and iodination. Cross-coupling yielded mostly **21**, besides the homodimer **22**. Similarly, cross-coupling of **20** and **23** (obtained from **5**) led to **24** and **22**. The structure of **24** was established by X-ray analysis (*Fig.*), showing a C(6)–C(5′) distance of 5.2 Å. The conditions for deprotecting **2** were applied to **21**, and led to **25** ($AgNO_2$/KCN), **26** (aq. NaOH), **27** ($Bu_4NF$), and **29** (HCl/MeOH; *Scheme 3*). Attempted deprotection of the propargylic-ether moiety with BuLi, however, failed. The dimer **27** was further deprotected to **28**. Acetolytic ($Ac_2O$/$Me_3SiOTf$) debenzylation of the dimer **30**, obtained from **10**, gave **31** (83%) which was deacetylated to **32** (*Scheme 4*). Cross-coupling of **5** and the bromoalkyne **33**, obtained from **10**, yielded **34**; again, acetolysis proceeded well, leading to **35**. The cellobiose derivative **38** was prepared from the lactone **36** *via* **37**. The glycosidic linkage of **38** proved resistant to the conditions of acetolysis, leading to **39**. Acetolysis of the benzylated thiophene **40** (from **30** with $Na_2S$) yielded the octaacetate **41**, but proceeded in substantially lower yields (50%).

**Introduction.** – The plan for a binomial synthesis of large butadiynediyl-linked saccharides, analogues of polysaccharides in which the interglycosidic O-atom is substituted at regular intervals by a butadiynediyl unit, has been detailed in [1]. The binomial synthesis requires a regioselective deprotection of either one of the terminal silyl-protected ethynyl moieties of monomers and oligomers, and a cross-coupling of the two resulting alkynes. We have described the synthesis of the protected 1,4-dideoxy-1,4-diethynyl-β-D-glucopyranose **2** from the intermediate **1** and the preparation of analogous *O*-benzyl-protected monomers. We now report on the regioselective, reagent-controlled deprotection of the monomers, the dimerisation of partially deprotected monomers, the deprotection of the silylated ethynyl groups of the dimers, and the selective *O*-debenzylation of monomers and of dimers derived from monoethynyl-*C*-glycosides.

**Results and Discussion.** – We first investigated the selective deprotection of the silylated ethynyl groups of the bis[(trimethylsilyl)ethynyl] derivative **2** (*Scheme 1*). Methods for the deprotection of silylated alkynes include treatment with alkali-metal

*Scheme 1*




*a*) $Me_3SiCCLi$, $Et_2AlCl$, toluene; 81%. *b*) BuLi, THF; **3** (70%), **4** (20%). *c*) $AgNO_2$, KCN, MeOH, $H_2O$; 96%. *d*) 0.1N HCl, MeOH; 87%. *e*) 0.5N NaOH, MeOH; 95%. *f*) $Bu_4NF \cdot 3\ H_2O$, THF; 82%. *g*) EtSH, $BF_3 \cdot OEt_2$; **11** (53%), **12** (37%). *h*) $Me_3SiOTf$, $Ac_2O$; 85%. *i*) $Bu_4NF \cdot 3\ H_2O$, THF; 94%. *j*) $Bu_4NF \cdot 3\ H_2O$; 96%. *k*) $Me_3SiOTf$, $Ac_2O$; 80%.

hydroxides or carbonates in MeOH, silver salts and cyanides, MeLi/LiBr, and fluorides in protic solvents [2]. Removal of a single $Me_3Si$ group from **2** with tetrabutylammonium fluoride ($Bu_4NF$) at different temperatures was not selective, and attempts to regioselectively deprotect **2** by treatment with aqueous NaOH or LiOH solution failed under a

variety of conditions. The controlled deprotection of either one of two $Me_3Si$-protected ethynyl groups has, to the best of our knowledge, not been described, but regioselective desilylation of one of two symmetrical and conjugated $Me_3SiC{\equiv}C$ groups has been reported by *Holmes et al.* [3], using the MeLi/LiBr complex at room temperature. A regioselective deprotection of a $Me_3Si$-protected ethynyl substituent has also been reported by *Myers et al.* [4], using a reagent prepared from $NaHB(OMe)_3$ and $H_2O$. For the regioselective deprotection of either one of the two $Me_3SiC{\equiv}C$ groups of **2**, we relied on the higher degree of electrophilicity of the C(1) silylethynyl group, which is part of a propargyl-ether moiety; conversely, the C(4) silylethynyl group ought to be more nucleophilic.

While $NaHB(OMe)_3/H_2O$ proved inadequate for the selective deprotection of **2**, treatment of **2** with BuLi cleaved the C(1) $Me_3SiC{\equiv}C$ group to give 70% of **3**, together with 20% of **4**, resulting from migration of the $(i\text{-}Pr)_3Si$ (TIPS) group. Conversely, treatment of **2** with $AgNO_2$ in aqueous MeOH, followed by aqueous KCN solution [5] gave exclusively **5** (96%) [1]; the C(1) $Me_3SiC{\equiv}C$ group was not affected under these conditions. The $(i\text{-}Pr)_3SiO$ group was removed by hydrolysis with HCl in MeOH [6] to give **6** in 87% yield without cleaving the $Me_3Si$ groups, whereas both $Me_3Si$ groups were removed with aq. NaOH in MeOH yielding **7** (95%) without affecting the $(i\text{-}Pr)_3SiO$ substituent. All silyl groups were removed, when **2** was treated with $Bu_4NF$ in THF, yielding 82% of **8**.

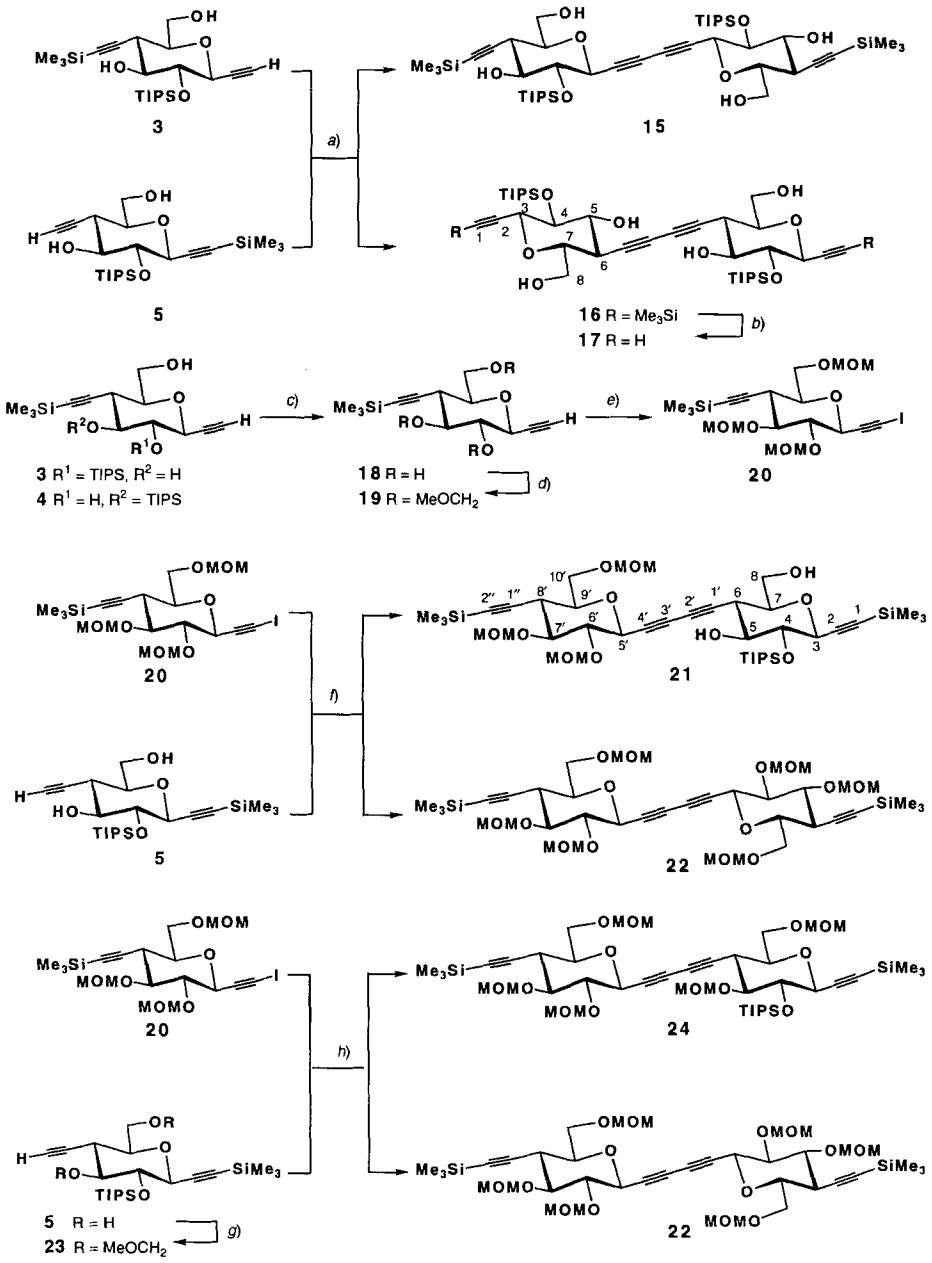
The compatibility of $Me_3SiC{\equiv}C$ and of $CH{\equiv}C$ groups with the conditions for the deprotection of benzyl ethers was evaluated by debenzylating the alkynes **9** and **10**. Thiolysis catalysed by $BF_3{\cdot}OEt_2$ had been used to cleave acetylenic benzyl ethers [7], but did not prove sufficiently selective, transforming **9** mostly into the fully deprotected **11** (57%), while yielding only 37% of the desired **12**. Attempted debenzylation of **9** with $Ca/NH_3$ [8] gave a complex mixture. During the synthesis of the monomers [1], however, we had noticed that acetylation by $Ac_2O$ in the presence of $Me_3SiOTf$ at 0° was accompanied by debenzylation. Treatment of **9** with $Ac_2O/Me_3SiOTf$ at 10–15° yielded 85% of the tetraacetate **13**; similar conditions transformed the desilylated analogue **10** into the tetraacetate **14** (80%). These procedures offer a satisfactory solution for the regioselective deprotection of ethynylated saccharides, but may not be suitable for dimers and oligomers containing the butadiyne moiety.

To evaluate the propensity of the monomeric alkynes towards oxidative heterodimerisation, we subjected a mixture of **3** and **5** to the conditions of oxidative coupling, but only obtained the homodimers **15** (44%) and **16** (40%; *Scheme 2*) which were also prepared by oxidative dimerisation of the individual monomers. Cleavage of the $Me_3Si$ groups of **16** with $AgNO_2/KCN$ yielded **17**, but proceeded about two to three times more slowly than cleavage of the $Me_3Si{-}C(2')$ group of **2**; we observed a stronger difference of reactivity between the two $Me_3Si$ groups of **2**, under similar conditions.

As the conditions of oxidative dimerisation did not lead to cross-coupling, we turned to the method of *Cadiot-Chodkiewicz* [9], which had been successfully used for the synthesis of carbohydrate-derived diynes by *Tronchet* and *Bonenfant* [10] [11]. Considering that OH groups might influence the regioselective *C*-desilylation by BuLi, we examined the heterodimerisation both of partially and of fully protected monomers.

The mixture of regioisomeric silyl ethers **3** and **4**, obtained by partial *C*-desilylation with BuLi, was transformed *via* the triol **18** (*Scheme 2*) into the tris-methoxymethylated

*Scheme 2*

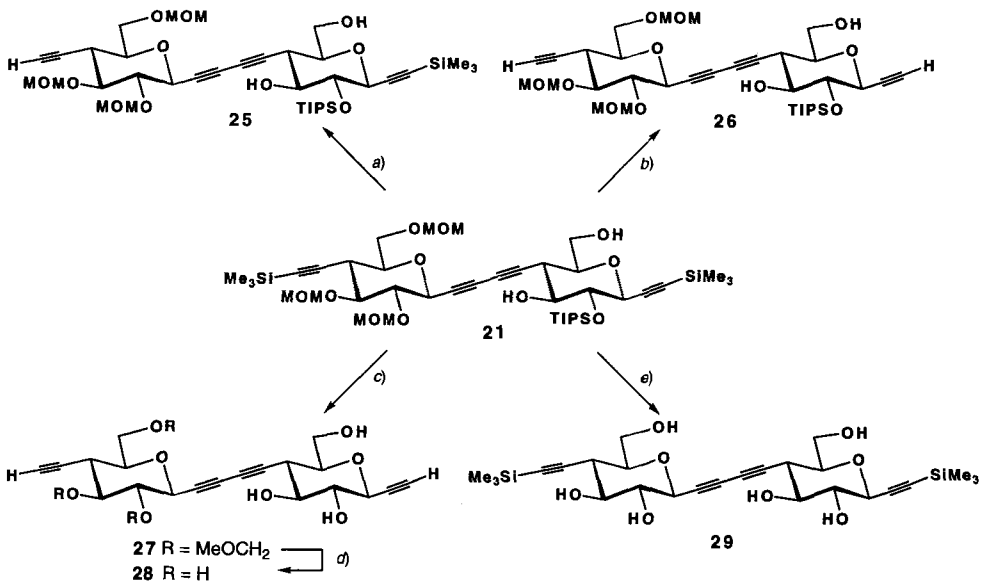



*a*) CuI, py; **15** (44%), **16** (40%). *b*) $AgNO_2$, KCN, MeOH, $H_2O$; 95%. *c*) 0.1N HCl, MeOH; 81%. *d*) $CH_2(OMe)_2$, $P_2O_5$; 95%. *e*) Morpholine, $I_2$, toluene; 93%. *f*) CuI, $[Pd(PPh_3)_4]$, $Et_3N$; **21** (64%), **22** (20%). *g*) $CH_2(OMe)_2$, $P_2O_5$, $CH_2Cl_2$; 95%. *h*) CuI, $[Pd(PPh_3)_4]$, py; **24** (56%), **22** (21%).

dialkynyl derivative **19**. Iodination of the unprotected alkynyl group with $I_2$ and morpholine [12] proceeded much more smoothly than bromination and gave the iodoacetylene **20** in an overall yield of 69% from **2**. CuI/[Pd($PPh_3$)$_4$]-Promoted coupling of **20** and **5** in the presence of $Et_3N$ gave 64% of the partially protected heterodimer **21** and 20% of the homodimer **22**. These conditions, however, failed to couple the iodoalkyne **20** and the bis-methoxymethyl derivative **23** derived from **5**, and coupling only proceeded when $Et_3N$ was replaced by pyridine, to afford 56% of the heterodimer **24** and 21% of the homodimer **22**, which were more easily separated from each other than **21** and **22**.

The conditions for the selective *C*-monodesilylation of **2** suceeded only partially with the dimer **21** (*Scheme 3*). While treatment with $AgNO_2$/KCN yielded 69% of the regioselectivity monodesilylated **25**, BuLi led to a rapid polymerisation that could not be avoided under a range of conditions, reflecting the greater sensitivity of the butadiyne moiety to BuLi. The OH groups of **21** are not responsible for the unsuccessful deprotection with BuLi, as similar treatment of **24** also resulted in polymerisation. Both $Me_3Si$ groups of **21** were cleaved with aqueous NaOH in MeOH, and **26** was isolated in 93%

*Scheme 3*

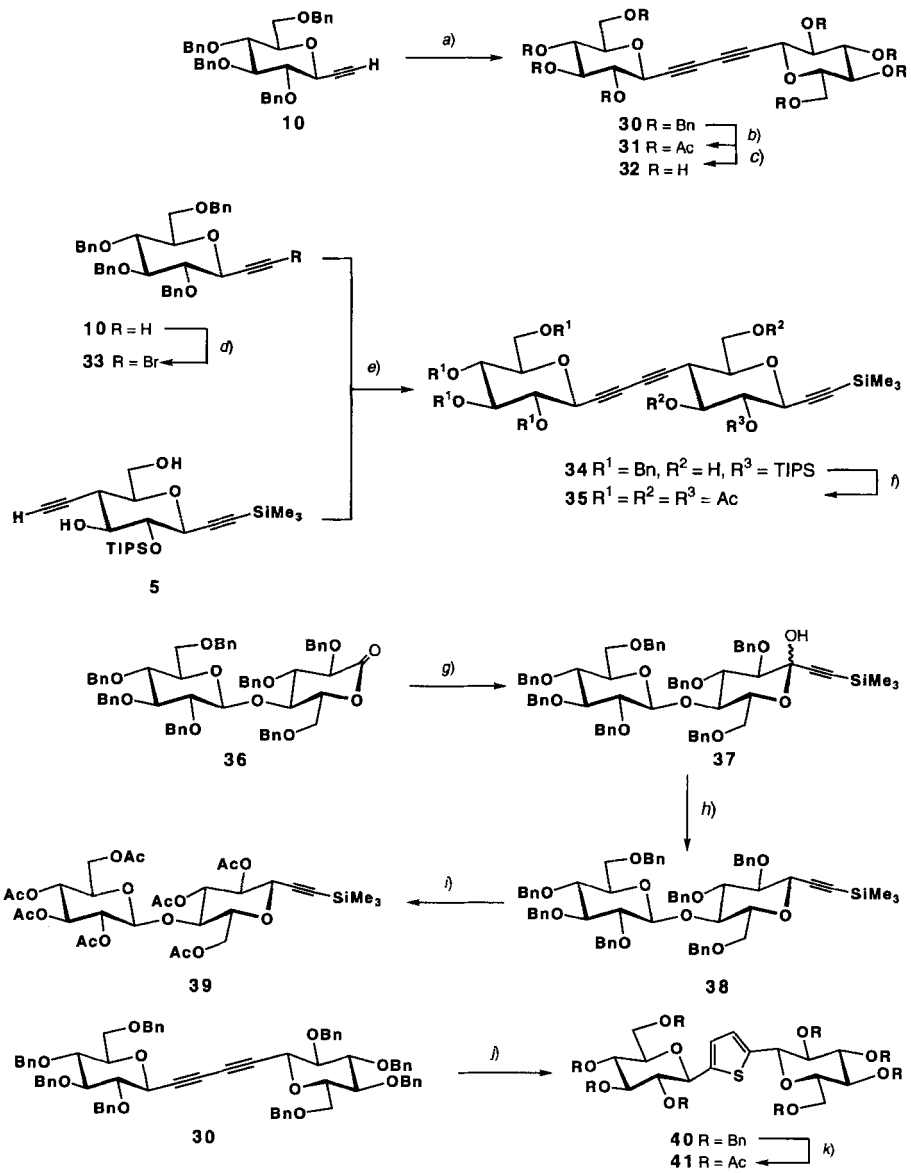



*a*) $AgNO_2$, KCN, MeOH, $H_2O$; 69%. *b*) NaOH, MeOH; 93%. *c*) $Bu_4NF \cdot 3\,H_2O$, THF; 91%. *d*) HCl, MeOH; 95%. *e*) HCl, MeOH; 94%.

yield. Treatment with $Bu_4NF$ in THF removed all silyl groups, yielding 91% of **27**, which was transformed by HCl in MeOH to the fully deprotected dimer **28** (95%). Conversely, the *O*-deprotected **29** was obtained in 94% yield by hydrolysis of **21** with HCl in MeOH.

The compatibility of the conditions for the acetolytic debenzylation of the monomers with the butadiynediyl moiety and with a glycosidic bond was studied with the homodimer **30** (*Scheme 4*), the (trimethylsilyl)ethynylated cellobiose derivative **38**, and the

*Scheme 4*




*a*) CuI, py; 99%.
*b*) $Me_3SiOTf$, $Ac_2O$; 83%.
*c*) NaOMe, MeOH; 95%.
*d*) $CBr_4$, $PPh_3$, $CH_2Cl_2$; 95%.
*e*) CuI, $[Pd(PPh_3)_4]$, $Et_3N$; 71%.
*f*) $Me_3SiOTf$, $Ac_2O$; 89%.
*g*) $Me_3SiCCLi$, THF; 98%.
*h*) $Et_3SiH$, $BF_3 \cdot OEt_2$, $CH_2Cl_2$, MeCN; 75%.
*i*) $Me_3SiOTf$, $Ac_2O$; 81%.
*j*) $Na_2S \cdot 9\,H_2O$, $MeO(CH_2)_2OH$; 71%.
*k*) $Me_3SiOTf$, $Ac_2O$; 50%.

*O*-benzyl- and *O*-silyl-protected heterodimer **35**; we also explored the compatibility of a thiophene to these conditions, by examining the acetolysis of **40**.

The homodimer **30** was obtained by oxidative coupling of the tetrabenzylated **10**. Treatment of **30** with $Ac_2O$ and $Me_3SiOTf$ yielded the octaacetate **31** (83%), which was deacetylated to the alcohol **32** (95%); the butadiyne moiety was not affected by these conditions. The heterodimer **34**, prepared in 71% yield from **5** and the bromoalkyne **33**, resulting from **10** upon exposure to $PPh_3/CBr_4$ [13], was similarly transformed into the heptaacetate **35** (89%).

The benzylated cellobionolactone **36** [14] was ethynylated by a standard procedure [14] to yield 73% of **38** *via* the anomeric hemiacetals **37**. Acetolytic debenzylation again proceeded smoothly to the cellobiose derivative **39** (81%).

The thiophene **40** was of interest in view of the preparation of saccharide analogues where the interglycosidic O-atom is replaced by a spacer leading to a relative orientation of the glycosyl moieties differing from the one realized in butadiynediyl-linked saccharides. There is precedent for the preparation of such thiophenes [15], and **40** was readily available in 71% yield by exposing **30** to $Na_2S \cdot 9\,H_2O$ [16] in 2-methoxyethanol. Transfer hydrogenation [17] of **40** led only to partial debenzylation, even after prolonged reaction periods, whereas acetolysis resulted in the formation of the acetate **41** in a yield of 50%; it appears that the reactivity of the thiophene ring marks the limits of the scope of these acetolysis conditions.

The generation of CH≡C unit during *C*-monodesilylation is evidenced by the loss of one $Me_3Si$ group and the appearance of a typical H–C≡C signal in the IR (3340–3300 $cm^{-1}$), $^1$H-NMR (*d* with small *J* typical for alkynes [18]), and $^{13}$C-NMR spectra (disappearance of a *s* at 92–89 ppm and appearance of a *d* at 82–80 ppm). These signals are assigned to either H–C(1) or H–C(2′), based on the chemical shift of their coupling partner H–C(3) or H–C(6), which resonate at 4.11–3.88 or at 2.59–2.49 ppm, respectively. These assignments are corroborated by the $^{13}$C-NMR signal of H–C≡C; typically, the ethynyl group at C(3), being part of a propargyl-ether moiety, resonates at lower fields (82.60–80.80 ppm) than the ethynyl group at C(6) (82.20–79.9 ppm).

The position of the $(i\text{-}Pr)_3Si$ group in **3**, **4**, and **7** is deduced from the position of the secondary OH group, as evidenced by the coupling with either H–C(4) or H–C(5), which are, in their turn, assigned from their coupling with H–C(3), or H–C(6). The coupling constants are small, but clearly evidenced by exchange with $D_2O$.

Upon iodination, C(1) is shifted upfield by *ca.* 75 ppm in the $^{13}$C-NMR spectrum; thus the *s* of C(1) of **20** is found at 4.64 ppm.

The assignment of the individual $^{13}$C-NMR signals of the butadiynediyl moiety of homodimers is based on the rule [19] according to which the signals of the terminal C-atoms are found at lower field than those of the central C-atoms. The heterodimers give rise to four signals of the butadiynediyl moiety which have similarly been assigned to the terminal or central C-atoms; individual signals are readily assigned from a comparison with the two homodimers derived from the constitutional units of the heterodimers.

The structure of **24** has been established by X-ray analysis[1]) (*Fig.*). The C–C and C≡C bond lengths are within the normal values for single and triple bonds.

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[1]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, Cambridge University, University Chemical Laboratory, Cambridge CB2 1EW, England.

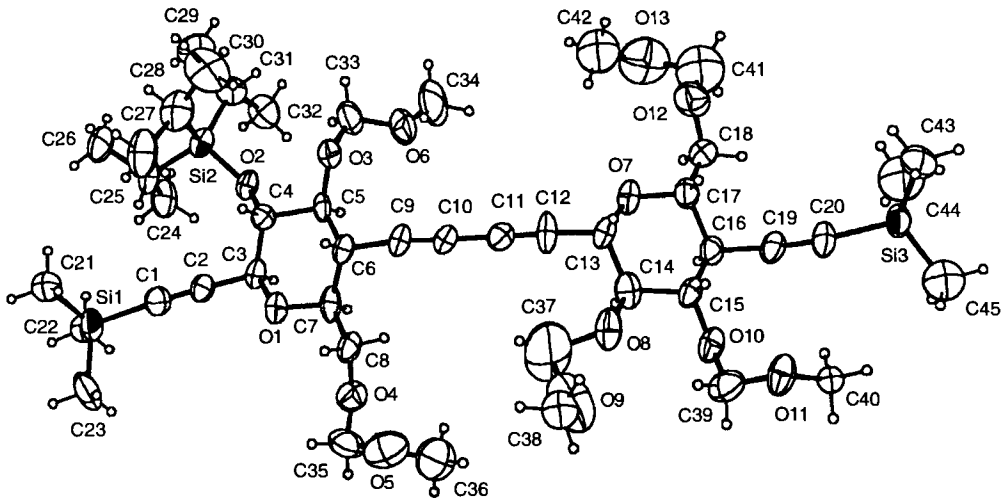


Fig. *X-Ray structure of the heterodimer* **24**. Arbitrary numbering.

The butadiyne moiety is nearly linear; the bond angles C(9)–C(10)–C(11) and C(10)–C(11)–C(12) are 175.3 and 177.7°, respectively. The distance between C(6) and C(13) is 5.22 Å, and the torsion angle O(7)–C(13)–C(6)–C(7) is −35.4°.

The thiophene **41** possesses a $C_2$ axis of symmetry, as evidenced by the $^1$H- and $^{13}$C-NMR spectra (*s* at 6.87 ppm, *s* and *d* at 139.22 and 125.42 ppm, resp., for the thiophene moiety). It is characterised by an IR absorption at 1730 cm$^{-1}$.

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## Experimental Part

*General.* Solvents were distilled before use: THF from Na and benzophenone; $CH_2Cl_2$ and MeCN from $CaH_2$. Reactions were run under Ar. Usual workup: The mixture was diluted with AcOEt and washed with brine, the org. layer dried ($MgSO_4$), filtered, and evaporated. Qual. TLC: 0.25 mm precoated silica-gel plates (*Merck*, silica-gel *60* $F_{25}$); detection by spraying the plates with mostain (400 ml of 10% $H_2SO_4$ soln., 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$) followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve. IR Spectra: 3% soln. in $CHCl_3$. $^1$H- and $^{13}$C-NMR Spectra: unless otherwise stated, at 300 and 75 MHz, resp., chemical shifts $\delta$ in ppm rel. to $SiMe_4$ as internal standard; in ambiguous cases, $^1$H-assignments by selective homonuclear decoupling experiments, $^{13}$C-assignments by $^1$H,$^{13}$C-HOMDQC spectra ($^1$H, 300 MHz). Mass spectra: CI ($NH_3$) at 70 eV.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**3**) *and 3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-5-*O*-(triisopropylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**4**). At −78°, 2.5M BuLi in hexane (0.69 ml, 1.74 mmol) was added dropwise to a soln. of **2** (433 mg, 0.87 mmol) in THF (50 ml). The mixture was warmed to r.t., stirred for 48 h, cooled to 0°, and treated with a sat. aq. $NH_4Cl$ soln. (5 ml). Extraction with AcOEt, washing with $H_2O$, drying ($MgSO_4$), evaporation, and FC (AcOEt/hexane 1:20) of the residue gave **3** (259 mg, 70%) and **4** (74 mg, 20%) as oils.

*Data of* **3**: $R_f$ (AcOEt/toluene 1:15) 0.57. $[\alpha]_D^{25} = -25.7$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 3300*w*, 2940*m*, 2860*w*, 2160*w*, 1730*w*, 1630*w*, 1510*w*, 1450*w*, 1390*w*, 1370*w*, 1350*w*, 1330*w*, 1290*w*, 1250*w*, 1140*m*, 1100*m*, 1070*m*, 1015*w*, 950*w*, 880*m*, 845*s*, 800*w*, 680*m*, 640*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.95 (*dd*, $J = 9.2, 2.1$, H–C(3)); 3.91 (br. *d*, $J = 11.9$, H–C(8)); 3.70 (br. *dd*, $J = 11.9, 6.0$, H′–C(8)); 3.65 (*dd*, $J = 9.1, 8.3$, H–C(4)); 3.50 (*t*, $J = 10.6, 9.4$, H–C(5)); 3.45 (*ddd*, $J = 10.3, 6.1, 2.7$, H–C(7)); 2.52 (*t*, $J = 10.3$, H–C(6)); 2.50 (br. *s*, OH–C(5)); 2.46 (*d*, $J = 2.2$, H–C(1)); 2.29 (br. *s*, OH–C(8)); 1.26–1.07 (*m*, (i-Pr)$_3$Si); 0.145 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 101.15 (*s*); 89.83 (*s*); 80.78 (*d*); 78.74 (*d*); 76.31 (*d*); 74.74 (*s*); 74.28 (*d*); 71.06 (*d*); 63.33 (*t*); 38.87 (*d*); 18.07 (6*q*); 12.74 (3*d*); −0.32 (3*q*). MS: 424 (100, $[M + NH_4]^+$). Anal. calc. for $C_{22}H_{40}O_4Si_2$ (424.73): C 62.21, H 9.49; found: C 62.47, H 9.31.

*Data of* **4**: $R_f$ (AcOEt/hexane 1:3) 0.57. $[\alpha]_D^{25} = -103.6$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3598*w*, 3305*w*, 3007*w*, 2945*m*, 2867*m*, 2173*w*, 1463*m*, 1391*w*, 1297*w*, 1252*m*, 1142*m*, 1082*m*, 1015*w*, 996*m*, 883*m*, 846*s*, 645*w*, 519*w*, 502*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.98 (*dd*, $J = 9.6, 2.1$, H–C(3)); 3.96 (*dd*, $J = 11.9, 2.5$, H–C(8)); 3.77 (*dd*, $J = 9.8, 8.4$, H–C(5)); 3.74 (*dd*, $J = 11.9, 5.7$, H′–C(8)); 3.46 (*ddd*, $J = 10.4, 5.8, 2.7$, H–C(7)); 3.39 (*t*, $J \approx 9.0$, H–C(4)); 2.57 (*d*, $J = 2.2$, H–C(1)); 2.56 (*t*, $J = 10.3$, H–C(6)); 2.37 (br. *s*, OH–C(4)); 2.04 (br. *s*, OH–C(8)); 1.12–1.02 (*m*, (i-Pr)$_3$Si); 0.12 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.68 (*s*); 89.18 (*s*); 80.72 (*d*); 79.54 (*d*); 76.37 (*d*); 74.95 (*s*); 74.48 (*d*); 70.52 (*d*); 63.46 (*t*); 39.35 (*d*); 18.00 (6*q*); 12.73 (3*d*); −0.57 (3*q*). EI-MS: 425 ($[M + 1]^+$). Anal. calc. for $C_{22}H_{40}O_4Si_2$ (424.73): C 62.21, H 9.49; found: C 61.97, H 9.26.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**5**) [1]. At 24°, a soln. of $AgNO_2$ (8.97 g, 57 mmol) in MeOH/$H_2O$ 25:8 (33 ml) was added dropwise to a soln. of **2** (9.7 g, 19 mmol) in MeOH (100 ml). After 3 h, the white mixture was cooled to 0°, treated with sat. aq. KCN soln. (15 ml), *carefully neutralised* with 2M HCl (*ca.* 30 ml), washed with $H_2O$, dried ($MgSO_4$), and evaporated: **5** (7.9 g, 96%) as a white solid.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**6**). A soln. of **2** (100 mg, 0.2 mmol) in dry MeOH (3 ml) was treated with 0.1N HCl (5 ml), heated under reflux for 48 h, neutralised with sat. aq. $NaHCO_3$ soln. (0.5 ml), diluted with AcOEt, washed with $H_2O$, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:2) gave **6** (59 mg, 87%). White solid. $R_f$ (AcOEt/hexane 1:1) 0.59. M.p. 137°. $[\alpha]_D^{25} = +1.8$ ($c = 0.55$, $CHCl_3$). IR ($CHCl_3$): 3594*m*, 3007*w*, 2959*s*, 2872*m*, 2858*m*, 2172*w*, 1458*w*, 1376*w*, 1298*w*, 1252*s*, 1082*m*, 1044*m*, 1022*w*, 978*m*, 853*s*, 844*s*, 639*w*, 613*w*, 575*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.98 (*d*, $J = 9.3$, H–C(3)); 3.92 (*ddd*, $J = 12.1, 7.4, 2.5$, H–C(8)); 3.72 (*dt*, $J = 12.1, 6.7$, H′–C(8)); 3.58 (*ddd*, $J = 9.9, 9.1, 2.7$, H–C(5)); 3.45 (*ddd*, $J = 10.1, 6.3, 2.6$, H–C(7)); 3.42 (*td*, $J = 9.5, 2.9$, H–C(4)); 3.01 (br. *d*, $J \approx 2.8$, exchange with $D_2O$, OH–C(5)); 2.90 (br. *d*, $J \approx 3.1$, exchange with $D_2O$, OH–C(4)); 2.56 (*t*, $J = 10.2$, H–C(6)); 2.25 (*t*, $J = 6.7$, exchange with $D_2O$, OH–C(8)); 0.15 (*s*, $Me_3Si$); 0.05 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 101.34 (*s*); 100.79 (*s*); 92.47 (*s*); 90.12 (*s*); 79.34 (*d*); 75.40 (*d*); 74.04 (*d*); 71.10 (*d*); 63.50 (*t*); 38.57 (*d*); −0.19 (3*q*); −0.17 (3*q*). EI-MS: 340 ($M^+$). Anal. calc. for $C_{16}H_{28}O_4Si_2$ (340.57): C 56.43, H 8.29; found: C 56.70, H 8.11.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**7**). A soln. of **2** (100 mg, 0.2 mmol) in MeOH (3 ml) was treated with 0.5N NaOH in MeOH (0.3 ml), stirred at 25° for 6 h, neutralised with 1N HCl (0.15 ml), diluted with AcOEt, washed with $H_2O$, and dried ($MgSO_4$). Evaporation gave **7** (65 mg, 92%). White solid. $R_f$ (AcOEt/hexane 1:4) 0.12. M.p. 116°. $[\alpha]_D^{25} = +54.5$ ($c = 0.55$, $CHCl_3$). IR ($CHCl_3$): 3593*w*, 3306*m*, 3051*w*, 2928*s*, 2871*s*, 2359*w*, 2130*w*, 1371*m*, 1559*w*, 1466*s*, 1376*m*, 1265*m*, 1252*m*, 1144*m*, 1099*m*, 1068*m*, 1016*w*, 998*m*, 962*w*, 884*m*, 649*m*, 609*w*, 576*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.98 (*dd*, $J = 9.2, 2.2$, H–C(3)); 3.95 (*ddd*, $J = 12.3, 6.8, 2.6$, H–C(8)); 3.75 (*dt*, $J = 12.1, 6.3$, H′–C(8)); 3.66 (*t*, $J = 9.3$, H–C(4)); 3.56 (*ddd*, $J = 10.4, 9.5, 3.1$, H–C(5)); 3.50 (*ddd*, $J = 10.2, 5.8, 2.4$, H–C(7)); 2.59 (*td*, $J = 10.4, 2.3$, H–C(6)); 2.50 (*d*, $J = 2.1$, H–C(1)); 2.48 (*d*, $J = 2.9$, exchange with $D_2O$, OH–C(5)); 2.24 (*d*, $J = 2.3$, H–C(2′)); 2.03 (*t*, $J = 6.5$, exchange with $D_2O$, OH–C(8)); 1.30–1.01 (*m*, (i-Pr)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 80.93 (*d*); 79.96 (*d*); 78.94 (*d*); 76.61 (*d*); 75.11 (*d*); 74.69 (*s*); 73.02 (*s*); 71.34 (*d*); 63.41 (*t*); 37.54 (*d*); 18.34 (6*q*); 12.99 (3*d*). MS: 370 (100, $[M + NH_4]^+$). Anal. calc. for $C_{19}H_{32}O_4Si$ (352.55): C 64.73, H 9.15; found: C 64.79, H 8.92.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-*D*-glycero-*D*-gulo-octitol* (**8**). At 0°, a soln. of $Bu_4NF \cdot 3\,H_2O$ (95.4 mg, 0.30 mmol) in THF (2 ml) was added dropwise to a soln. of **2** (100 mg, 0.20 mmol) in THF (3 ml). The soln. was stirred for 6 h, treated with $H_2O$ (1 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 2:1) gave **8** (32 mg, 82%). Oil. $R_f$ (AcOEt/hexane 9:1) 0.33. $[\alpha]_D^{25} = +28.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3647*w*, 3593*m*, 3395*s*, 3007*w*, 2960*m*, 2926*m*, 2856*m*, 2127*w*, 1731*w*, 1457*w*, 1399*w*, 1298*m*, 1261*s*, 1090*s*, 1053*s*, 1021*s*, 958*m*, 877*w*, 822*m*, 649*s*, 578*w*. $^1$H-NMR (300 MHz, $CD_3COCD_3$): 4.62 (br. *s*, OH–C(4), OH–C(5)); 3.95 (*dd*, $J = 9.6, 2.2$, H–C(3)); 3.82 (br. *d*, $J \approx 12.4$, addn. of $D_2O \rightarrow$ *dd*, $J = 12.1, 2.0$, H–C(8)); 3.70 (br. *s*, OH–C(8)); 3.67 (br. *dd*, $J \approx 9.8, 4.7$, addn. of $D_2O \rightarrow$ *dd*, $J = 12.1, 5.4$, H′–C(8)); 3.49 (*dd*, $J = 10.4, 8.7$, H–C(5)); 3.43 (*ddd*, $J = 10.2, 5.8, 1.8$, H–C(7)); 3.28

(*dd*, $J$ = 9.6, 8.6, H–C(4)); 2.93 (*d*, $J$ = 2.2, H–C(1)); 2.57 (*d*, $J$ = 2.4, H–C(2')); 2.49 (*td*, $J$ = 10.4, 2.4, H–C(6)). $^{13}$C-NMR (75 MHz, $CD_3COCD_3$): 82.64 (*d*); 82.28 (*d*); 80.91 (*d*); 76.71 (*d*); 75.47 (*d*); 75.05 (*s*); 73.00 (*s*); 71.54 (*d*); 63.57 (*t*); 38.27 (*d*). EI-MS: 196 ($M^+$).

*3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**10**). At 0°, a soln. of $Bu_4NF \cdot 3\,H_2O$ (170 mg, 0.53 mmol) in THF (1 ml) was added dropwise to a soln. of **9** (1.11 g, 1.79 mmol) in THF (7 ml). The soln. was stirred for 1 min, treated with $H_2O$ (1 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **10** (0.92 g, 94%). White solid. $R_f$ (AcOEt/hexane 3.5:10) 0.37. M.p. 58°. $[\alpha]_D^{25} = +17.4$ ($c$ = 1.6, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 3060*w*, 3000*w*, 2920*w*, 2880*w*, 2120*w*, 1900*w*, 1810*w*, 1600*w*, 1500*w*, 1450*m*, 1360*w*, 1290*w*, 1270*w*, 1150*m*, 1100*s*, 1070*s*, 1000*w*, 910*w*, 700*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.33–7.16 (*m*, 20 arom. H); 5.10 (*d*, $J$ = 10.9, PhC*H*); 5.01 (*d*, $J$ = 11.6, PhC*H*); 4.97 (*d*, $J$ = 11.5, PhC*H*); 4.90 (*d*, $J$ = 11.4, PhC*H*); 4.87 (*d*, $J$ = 10.8, PhC*H*); 4.72 (*d*, $J$ = 11.2, PhC*H*); 4.60 (*d*, $J$ = 12.1, PhC*H*); 4.48 (*d*, $J$ = 12.0, PhC*H*); 4.07 (*dd*, $J$ = 9.6, 2.1, H–C(3)); 3.88 (*t*, $J$ = 9.4, H–C(6)); 3.74 (*m*, H–C(4), 2 H–C(8)); 3.59 (*t*, $J$ = 9.0, H–C(5)); 3.30 (*ddd*, $J$ = 9.7, 3.4, 2.1, H–C(7)); 2.15 (*d*, $J$ = 2.1, H–C(1)). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.38 (*s*); 137.92 (2*s*); 137.83 (*s*); 128.14–127.54 (several *d*); 85.89 (*d*); 81.97 (*d*); 80.93 (*d*); 79.09 (*d*); 77.52 (*d*); 75.58 (*t*); 75.35 (*t*); 74.96 (*t*); 74.28 (*t*); 73.43 (*s*); 69.52 (*d*); 68.69 (*t*). MS: 566 (100, $[M + NH_4]^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**11**) *and 3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**12**). A soln. of **9** (70 mg, 0.11 mmol) in EtSH (1 ml) was treated with $BF_3 \cdot OEt_2$ (0.43 ml, 3.52 mmol), kept at r.t. for 24 h, neutralised (*Dowex 2* × *8*, $Cl^-$ form), and filtered. Evaporation and FC ($CH_2Cl_2$/MeOH 10:1) of the residue gave **11** (12 mg, 57%) as an oil and **12** (10 mg, 37%) as a white solid.

*Data of* **11**: $R_f$ ($CH_2Cl_2$/MeOH 5:1) 0.36. $[\alpha]_D^{25} = +21.3$ ($c$ = 0.4, MeOH). IR (KBr): 3387*m* (br.), 2920*m*, 2125*w*, 1645*s*, 1416*w*, 1304*w*, 1082*m*, 958*w*, 884*w*, 637*w*, 585*w*, 520*w*. $^1$H-NMR (300 MHz, $CD_3OD$): 3.91 (*dd*, $J$ = 9.2, 2.0, H–C(3)); 3.85 (*dd*, $J$ = 12.3, 1.9, H–C(8)); 3.61 (*dd*, $J$ = 12.1, 5.3, H'–C(8)); 3.30–3.25 (*m*, 4 H); 2.87 (*d*, $J$ = 2.1, H–C(1)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 82.60 (*d*); 81.97 (*d*); 79.11 (*d*); 75.46 (*s*); 75.34 (*d*); 72.03 (*d*); 71.43 (*d*); 61.00 (*t*). MS: 204 (100, $[M + NH_4]^+$).

*Data of* **12**: $R_f$ ($CH_2Cl_2$/MeOH 5:1) 0.48. M.p. 233.7°. $[\alpha]_D^{25} = +14.0$ ($c$ = 0.2, MeOH). IR (KBr): 3570*s*, 3400*w*, 2960*m*, 2950*m*, 2940*m*, 2900*m*, 2180*w*, 1740*w*, 1630*w*, 1560*w*, 1470*m*, 1420*m*, 1380*m*, 1360*m*, 1350*m*, 1330*m*, 1310*m*, 1250*s*, 1190*w*, 1120*s*, 1100*s*, 1080*s*, 1070*s*, 1030*s*, 1020*s*, 980*s*, 920*m*, 890*m*, 850*s*, 770*s*, 700*m*, 680*m*, 630*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 3.91 (*d*, $J$ = 9.2, H–C(3)); 3.86 (*dd*, $J$ = 12.2, 1.8, H–C(8)); 3.63 (*dd*, $J$ = 12.0, 5.1, H'–C(8)); 3.32–3.22 (*m*, 4 H); 0.15 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $D_2O$): 101.91 (*s*); 93.41 (*s*); 80.05 (*d*); 76.82 (*d*); 73.39 (*d*); 70.62 (*d*); 69.69 (*d*); 61.00 (*t*); –1.1 (3*q*). MS: 278 (100, $[M + NH_4]^+$).

*4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**13**). At –40°, a soln. of $Me_3SiOTf$ (0.11 ml, 0.64 mmol) in $Ac_2O$ (1 ml) was added dropwise to a soln. of **9** (50 mg, 0.08 mmol) in $Ac_2O$ (2 ml). The mixture was kept at 10–15° for 4 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (1 ml). Normal workup and FC (AcOEt/hexane 1:5) gave **13** (29 mg, 85%). White solid. $R_f$ (AcOEt/hexane 1:2) 0.24. M.p. 98.5° (AcOEt/hexane). $[\alpha]_D^{25} = +26.4$ ($c$ = 1.13, $CHCl_3$). IR ($CHCl_3$): 3000*w*, 2940*w*, 2160*w*, 1740*s*, 1350*m*, 1300*w*, 1230*s*, 1200*w*, 1100*w*, 1050*m*, 1020*m*, 960*w*, 940*w*, 910*w*, 830*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 5.57 (*t*, $J$ = 9.6, H–C(4)); 5.38 (*t*, $J$ = 9.2, H–C(5)); 5.30 (*t*, $J$ = 9.5, H–C(6)); 4.30 (*dd*, $J$ = 12.7, 4.7, H–C(8)); 4.06 (*dd*, $J$ = 12.5, 2.1, H'–C(8)); 4.03 (*d*, $J$ = 9.9, H–C(3)); 3.16 (*ddd*, $J$ = 9.8, 4.6, 2.2, H–C(7)); 1.78 (2 Ac); 1.75, 1.74 (2*s*, 2 Ac); 0.19 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 170.53 (*s*); 170.09 (*s*); 169 (*s*); 168.79 (*s*); 98.58 (*s*); 92.99 (*s*); 75.89 (*d*); 73.39 (*d*); 71.02 (*d*); 69.05 (*d*); 68.08 (*d*); 61.95 (*t*); 20.64 (*q*); 20.50 (*q*); 20.43 (2*q*); –0.59 (3*q*). MS: 446 (100, $[M + NH_4]^+$). Anal. calc. for $C_{19}H_{28}O_9Si$ (428.51): C 53.26, H 6.59; found: C 53.54, H 6.57.

*4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**14**). At –40°, a soln. of $Me_3SiOTf$ (0.5 ml, 2.9 mmol) in $Ac_2O$ (1 ml) was added dropwise to a soln. of **10** (200 mg, 0.36 mmol) in $Ac_2O$ (3 ml). The mixture was kept at 10–15° for 5 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (1 ml). Normal workup and FC (AcOEt/hexane 1:5) gave **14** (104 mg, 80%). White solid. $R_f$ (AcOEt/hexane 1:2) 0.24. M.p. 104° (AcOEt/hexane). $[\alpha]_D^{25} = +7.4$ ($c$ = 0.66, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 3020*w*, 2860*w*, 2120*w*, 1710*s*, 1430*w*, 1370*s*, 1300*w*, 1250*s*, 1200*w*, 1100*m*, 1070*s*, 1040*s*, 970*w*, 950*w*, 680*w*, 650*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 5.47 (*t*, $J$ = 9.7, H–C(4)); 5.22 (*t*, $J \approx 9.2$, H–C(5)); 5.17 (*t*, $J$ = 9.3, H–C(6)); 4.17 (*dd*, $J$ = 12.5, 4.6, H–C(8)); 3.95 (*dd*, $J$ = 12.4, 1.9, H'–C(8)); 3.82 (*dd*, $J$ = 10.0, 2.0, H–C(3)); 3.04 (*m*, H–C(7)); 1.93 (*d*, $J$ = 2.1, H–C(1)); 1.71, 1.66, 1.64, 1.62 (4*s*, 4 Ac). $^{13}$C-NMR (50 MHz, $CDCl_3$): 169.52 (*s*); 170.08 (*s*); 169.19 (*s*); 169.06 (*s*); 77.62 (*d*); 75.93 (*s*); 75.48 (*d*); 73.41 (*d*); 70.92 (*d*); 68.40 (*d*); 67.96 (*d*); 61.91 (*t*); 20.48 (4*q*). MS: 374 (100, $[M + NH_4]^+$). Anal. calc. for $C_{16}H_{20}O_9$ (356.32): C 53.93, H 5.66; found: C 54.18, H 5.41.

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis{(1S)-1,5-anhydro-4-deoxy-2-*O*-(triisopropylsilyl)-4-*C*-[2-(trimethylsilyl)-ethynyl]-*D*-glucitol}* (**15**) *and 6,6'-(Buta-1,3-diyne-1,4-diyl)bis{3,7-anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol}* (**16**). A soln. of **3** and **5** (34 mg, 0.08 mmol each) in pyridine (5 ml) was treated with CuCl (15.8 mg, 0.16 mmol), stirred under $O_2$ at 35° for 24 h, diluted with AcOEt (3 ml), and treated with sat. aq. $NH_4Cl$ soln. (2 ml). Normal workup and FC (AcOEt/hexane 1:4) gave **15** (30 mg, 44%) and **16** (27 mg, 40%) as white crystals.

*Data of* **15**: $R_f$ (AcOEt/hexane 1:3) 0.30. M.p. 116°. $[\alpha]_D^{25} = -36.6$ ($c = 0.70$, $CHCl_3$). IR ($CHCl_3$): 3592*m*, 2946*s*, 2867*s*, 2171*w*, 1949*w*, 1602*w*, 1463*m*, 1384*m*, 1365*m*, 1346*m*, 1073*s*, 1015*m*, 998*m*, 963*m*, 883*s*, 846*s*, 657*s*, 640*m*, 599*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.03 (*d*, $J = 9.2$, H–C(1)); 3.93 (*m*, addn. of $D_2O \rightarrow$ *dd*, $J = 12.2$, 2.6, H–C(6)); 3.73 (br. *dd*, addn. of $D_2O \rightarrow$ *dd*, $J = 12.1$, 5.9, H'–C(6)); 3.63 (*t*, $J = 8.8$, H–C(2)); 3.50 (*ddd*, $J = 10.3$, 8.9, 3.0, addn. of $D_2O \rightarrow$ *dd*, $J = 10.2$, 8.4, H–C(3)); 3.45 (*ddd*, $J = 10.2$, 5.9, 2.7, H–C(5)); 2.55 (*t*, $J = 10.3$, H–C(4)); 2.43 (*d*, $J = 2.8$, OH–C(3)); 2.04 (br. *t*, $J = 6.7$, OH–C(6)); 1.30–1.05 (*m*, (i-Pr)$_3$Si); 0.16 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 101.17 (*s*); 90.33 (*s*); 79.01 (*d*); 77.48 (*s*); 76.66 (*d*); 74.89 (*d*); 71.95 (*d*); 70.21 (*s*); 63.62 (*t*); 39.01 (*d*); 18.29 (6*q*); 12.92 (3*d*); –0.03 (3*q*). MS: 864 ($[M + NH_4]^+$). Anal. calc. for $C_{44}H_{78}O_8Si_4$ (847.44): C 62.36, H 9.28; found: C 62.59, H 9.06.

*Data of* **16**: $R_f$ (AcOEt/hexane 1:2) 0.50. M.p. 254°. $[\alpha]_D^{25} = -50.2$ ($c = 0.85$, $CHCl_3$). IR ($CHCl_3$): 3595*m*, 3007*m*, 2961*s*, 2867*s*, 2360*w*, 2341*w*, 2179*w*, 1731*w*, 1464*m*, 1365*m*, 1349*m*, 1329*m*, 1290*m*, 1252*s*, 1143*s*, 1102*s*, 1066*s*, 1018*m*, 994*s*, 919*w*, 883*s*, 846*s*, 657*m*, 638*m*, 596*w*, 572*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.96 (*d*, $J = 9.0$, H–C(3)); 3.91 (*m*, addn. of $D_2O \rightarrow$ *dd*, $J = 12.3$, 2.2, H–C(8)); 3.69 (*dt*, $J = 12.0$, 5.5, addn. of $D_2O \rightarrow$ *dd*, $J = 12.1$, 5.6, H'–C(8)); 3.61 (*t*, $J = 8.7$, H–C(4)); 3.53 (*ddd*, $J = 10.0$, 8.2, 2.9, addn. of $D_2O \rightarrow$ *dd*, $J = 10.1$, 8.2, H–C(5)); 3.44 (*ddd*, $J = 10.2$, 5.2, 2.2, H–C(7)); 2.61 (*t*, $J = 10.1$, H–C(6)); 2.50 (*d*, $J = 3.2$, exchange with $D_2O$, OH–C(5)); 2.10 (*t*, $J = 6.0$, exchange with $D_2O$, OH–C(8)); 1.28–1.04 (*m*, (i-Pr)$_3$Si); 0.18 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 101.98 (*s*); 91.41 (*s*); 78.71 (*d*); 76.70 (*d*); 75.17 (*d*); 74.56 (*s*); 71.95 (*d*); 68.71 (*s*); 63.41 (*t*); 36.10 (*d*); 18.34 (6*q*); 13.04 (3*d*); –0.39 (3*q*). EI-MS: 846 ($M^+$). Anal. calc. for $C_{44}H_{78}O_8Si_4$ (847.44): C 62.36, H 9.28; found: C 62.12, H 9.05.

*6,6'-(Buta-1,3-diyne-1,4-diyl)bis{3,7-anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol}* (**17**). At 24°, a soln. of $AgNO_2$ (14 mg, 0.09 mmol) in MeOH/$H_2O$ 2:1 (3 ml) was added dropwise to a soln. of **16** (30 mg, 0.036 mmol) in MeOH (2 ml). After 2.5 h, the white mixture was cooled to 0°, treated with sat. aq. NaCN soln. (0.5 ml), *carefully neutralised* with 2M HCl (*ca.* 1 ml), washed with $H_2O$, dried ($MgSO_4$), and evaporated: **17** (23 mg, 95%). White solid. $R_f$ (AcOEt/hexane 3:4) 0.33. M.p. 93°. $[\alpha]_D^{25} = -50.0$ ($c = 0.4$, $CHCl_3$). IR: 3595*m*, 3306*m*, 2946*s*, 2867*s*, 2131*w*, 1464*m*, 1366*w*, 1350*w*, 1328*w*, 1291*m*, 1262*m*, 1144*s*, 1122*s*, 1098*s*, 1067*s*, 1017*m*, 998*w*, 961*w*, 919*w*, 883*m*, 844*w*, 645*m*, 604*w*, 576*w*, 540*w*, 517*w*, 504*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.97 (*dd*, $J = 9.1$, 2.2, H–C(3)); 3.94 (*ddd*, $J = 11.9$, 5.9, 2.4, H–C(8)); 3.74 (*dt*, $J = 11.8$, 5.8, H'–C(8)); 3.65 (*dd*, $J = 9.0$, 8.7, H–C(4)); 3.55 (*ddd*, $J = 10.2$, 8.8, 3.0, H–C(5)); 3.48 (*ddd*, $J = 10.5$, 5.4, 2.3, H–C(7)); 2.68 (*t*, $J = 10.3$, H–C(6)); 2.49 (*d*, $J = 2.2$, H–C(1)); 2.48 (*d*, $J = 3.1$, OH–C(5)); 2.00 (*t*, $J = 6.3$, OH–C(8)); 1.30–1.05 (*m*, (i-Pr)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 80.72 (*d*); 78.81 (*d*); 76.88 (*d*); 75.14 (*d*); 74.81 (*s*); 74.46 (*s*); 71.36 (*d*); 68.76 (*s*); 63.41 (*t*); 38.09 (*d*); 18.32 (6*q*); 13.00 (3*d*). FAB-MS: 703 ($[M + 1]^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**18**). A soln. of **3** (222 mg, 0.52 mmol) in dry MeOH (10 ml) was treated with 0.1N HCl (5 ml), heated under reflux for 48 h, and neutralised with sat. aq. $NaHCO_3$ soln. (0.5 ml). Evaporation and FC gave **18** (126 mg, 90%). Oil. $R_f$ (AcOEt/hexane 1:1) 0.41. $[\alpha]_D^{25} = -5.5$ ($c = 1.4$, $CHCl_3$). IR: 3594*m*, 3442*w*, 3305*m*, 3042*w*, 3007*w*, 2962*w*, 2924*w*, 2171*w*, 2130*w*, 1731*w*, 1455*w*, 1403*w*, 1298*w*, 1252*s*, 1080*s*, 1051*m*, 1022*w*, 1003*w*, 986*w*, 956*w*, 846*s*, 645*m*, 604*w*, 576*w*, 529*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.08 (*dd*, $J = 9.4$, 2.1, H–C(3)); 3.92 (*ddd*, $J = 12.1$, 6.5, 2.4, H–C(8)); 3.75 (*dt*, $J = 11.9$, 5.6, H'–C(8)); 3.57 (*dd*, $J = 10.2$, 8.9, H–C(5)); 3.48 (*ddd*, $J = 10.2$, 5.4, 2.5, H–C(7)); 3.47 (*t*, $J = 9.2$, H–C(4)); 3.40 (br. *s*, OH); 3.20 (br. *s*, OH); 2.63 (*d*, $J = 2.2$, H–C(1)); 2.60 (*t*, $J = 10.3$, H–C(6)); 2.45 (*t*, $J = 6.5$, OH–C(8)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 101.24 (*s*); 90.82 (*s*); 79.93 (*d*); 79.43 (*d*); 75.52 (*s*); 75.17 (*d*); 73.86 (*d*); 70.39 (*d*); 63.43 (*t*); 38.53 (*d*); –0.18 (3*q*). EI-MS: 269 ($[M + 1]^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-4,5,8-tris-*O*-(methoxymethyl)-6-*C*-[2-(trimethylsilyl)-ethynyl]-*D*-glycero-*D*-gulo-octitol* (**19**). At 20°, $CH_2(OMe)_2$ (10 ml) and $P_2O_5$ (500 mg) were added to a soln. of **18** (270 mg, 1.0 mmol) in $CH_2Cl_2$ (10 ml). After stirring for 30 min, filtration through silica gel gave **19** (370 mg, 92%). Oil. $R_f$ (AcOEt/hexane 1:3) 0.29. $[\alpha]_D^{25} = -28.0$ ($c = 0.55$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3007*m*, 2958*m*, 2932*m*, 2898*m*, 2850*w*, 2827*w*, 2174*w*, 1442*w*, 1407*w*, 1369*w*, 1294*w*, 1252*s*, 1154*s*, 1095*s*, 1041*s*, 1019*s*, 985*m*, 920*m*, 846*s*, 645*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, $J = 6.5$, C*H*OMe); 4.90 (*d*, $J = 6.3$, C*H*OMe); 4.89 (*d*, $J = 6.4$, C*H*OMe); 4.86 (*d*, $J = 6.4$, C*H*OMe); 4.64 (*s*, $CH_2$OMe); 3.98 (*dd*, $J = 9.6$, 2.1, H–C(3)); 3.84 (*dd*, $J = 11.1$, 2.3, H–C(8)); 3.78 (*dd*, $J = 11.1$, 4.5, H'–C(8)); 3.64 (*dd*, $J = 10.3$, 9.0, H–C(5)); 3.50 (*t*, $J \approx 9.3$, H–C(4)); 3.47 (*ddd*, $J = 10.4$, 4.5, 2.3, H–C(7)); 3.47 (*s*, MeO); 3.43 (*s*, MeO); 3.36 (*s*, MeO); 2.74 (*t*, $J = 10.4$, H–C(6)); 2.49 (*d*,

$J$ = 2.2, H–C(1)); 0.12 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.86 (*s*); 97.98 (*t*); 97.8 (*t*); 96.59 (*t*); 89.39 (*s*); 80.46 (*d*); 79.90 (*d*); 78.83 (*d*); 78.54 (*d*); 74.67 (*s*); 69.95 (*d*); 67.36 (*t*); 56.89 (*q*); 56.70 (*q*); 55.24 (*q*); 38.06 (*d*); −0.20 (3*q*). MS: 399 ([$M$ − 1]$^+$). Anal. calc. for $C_{19}H_{32}O_7Si$ (400.54): C 56.97, H 8.05; found: C 57.15, H 7.78.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-iodo-4,5,8-tris-*O*-(methoxymethyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**20**). At 45°, a soln. of morpholine (2.67 ml, 30.75 mmol) in toluene (5 ml) was added dropwise to a soln. of $I_2$ (3.90 g, 15.37 mmol) in toluene (10 ml). The mixture was stirred at 45° for 30 min, treated with a soln. of **19** (615 mg, 1.53 mmol) in toluene (6 ml), stirred for further 4 h at 45°, cooled to 20°, and filtered through cotton. The filtrate was treated with sat. aq. $Na_2SO_3$ soln. (5 ml), stirred for 30 min, washed with brine, and dried ($MgSO_4$). Evaporation gave **20** (797 mg, 98%). Oil. $R_f$ (AcOEt/hexane 1:3) 0.42. $[\alpha]_D^{25} = -28.6$ ($c$ = 0.7, $CHCl_3$). IR ($CHCl_3$): 3042*w*, 3007*m*, 2958*m*, 2897*m*, 2850*w*, 2827*w*, 2174*w*, 1464*w*, 1442*w*, 1407*w*, 1369*w*, 1293*w*, 1252*m*, 1154*s*, 1116*s*, 1094*s*, 1021*s*, 940*m*, 919*m*, 846*s*, 616*w*, 535*w*, 514*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.95 (*d*, $J$ = 6.4, C*H*OMe); 4.89 (*d*, $J$ = 6.5, C*H*OMe); 4.87 (*d*, $J$ = 6.4, C*H*OMe); 4.85 (*d*, $J$ = 6.5, C*H*OMe); 4.66 (*s*, $CH_2$OMe); 4.11 (*d*, $J$ = 9.6, H–C(3)); 3.82 (*dd*, $J$ = 10.9, 2.3, H–C(8)); 3.81 (*dd*, $J$ = 11.1, 4.2, H′–C(8)); 3.63 (*dd*, $J$ = 10.5, 8.8, H–C(5)); 3.50 (*t*, $J \approx$ 9.2, H–C(4)); 3.49 (*ddd*, $J$ = 10.4, 4.2, 2.3, H–C(7)); 3.47 (*s*, MeO); 3.46 (*s*, MeO); 3.37 (*s*, MeO); 2.74 (*t*, $J$ = 10.5, H–C(6)); 0.13 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.47 (*s*); 97.75 (*t*); 97.50 (*t*); 96.31 (*t*); 90.42 (*s*); 89.19 (*s*); 79.72 (*d*); 78.42 (*d*); 78.33 (*d*); 71.07 (*d*); 66.98 (*t*); 56.58 (*q*); 56.41 (*q*); 55.01 (*q*); 37.74 (*d*); 4.64 (*s*); −0.48 (3*q*). EI-MS: 525 ([$M$ − 1]$^+$). Anal. calc. for $C_{19}H_{31}IO_7Si$ (526.44): C 43.35, H 5.94; found: C 43.49, H 5.74.

*3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-6,7,10-tris-*O*-(methoxymethyl)-8-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**21**) *and 1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-1,5-anhydro-4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glucitol}* (**22**). At 20°, CuI (2.4 mg, 1.3 μmol) and $[Pd(PPh_3)_4]$ (1.5 mg, 0.13 μmol) were added to a soln. of **20** (23 mg, 0.04 mmol) and **5** (20 mg, 0.04 mmol) in $Et_3N$ (5 ml). After stirring for 5 h at 50°, the solvent was evaporated, the residue dissolved in AcOEt, and the soln. washed with brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **21** (23 mg, 64%) and **22** (9 mg, 20%) as oils.

*Data of* **21**: $R_f$ (AcOEt/hexane 2:5) 0.33. $[\alpha]_D^{25} = -33.4$ ($c$ = 0.47, $CHCl_3$). IR ($CHCl_3$): 3595*m*, 3042*w*, 3007*m*, 2960*s*, 2260*w*, 2176*w*, 1720*w*, 1602*w*, 1464*m*, 1371*m*, 1326*m*, 1292*m*, 1252*s*, 1152*s*, 1099*s*, 846*s*, 657*m*, 596*w*, 575*w*, 534*w*, 518*w*, 502*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 4.98 (*d*, $J$ = 6.5, C*H*OMe); 4.88 (*d*, $J$ = 6.6, C*H*OMe); 4.87 (*d*, $J$ = 5.2, C*H*OMe); 4.85 (*d*, $J$ = 6.5, C*H*OMe); 4.66 (*s*, $CH_2$OMe); 4.03 (*dd*, $J$ = 9.1, 0.5, H–C(5′)); 3.94 (*d*, $J$ = 9.1, H–C(3)); 3.89 (*ddd*, $J$ = 12.2, 6.3, 2.5, H–C(8)); 3.82 (*dd*, $J$ = 11.2, 2.0, H–C(10′)); 3.78 (*dd*, $J$ = 11.2, 4.8, H′–C(10′)); 3.68 (*dt*, $J$ = 12.0, 6.0, H′–C(8)); 3.63 (*dd*, $J$ = 10.4, 8.8, H–C(7′)); 3.60 (*dd*, $J$ = 9.3, 8.4, H–C(4)); 3.52 (*ddd*, $J$ = 10.4, 8.3, 3.3, H–C(5)); 3.51 (*m*, H–C(9′)); 3.50 (*dd*, $J$ = 9.6, 9.0, H–C(6′)); 3.47 (*s*, MeO); 3.46 (*s*, MeO); 3.42 (*ddd*, $J$ = 10.3, 5.6, 2.5, H–C(7)); 3.38 (*s*, MeO); 2.72 (*t*, $J$ = 10.5, H–C(8′)); 2.64 (br. *t*, $J$ = 10.3, H–C(6)); 2.41 (*d*, $J$ = 3.3, OH–C(5)); 2.01 (*t*, $J$ = 6.3, OH–C(8)); 1.37–1.09 (*m*, (i-Pr)$_3$Si); 0.16 (*s*, $Me_3Si$); 0.14 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.77 (*s*); 102.05 (*s*); 98.03 (*t*); 97.83 (*t*); 97.66 (*t*); 91.37 (*s*); 89.54 (*s*); 80.03 (*d*); 78.98 (*d*); 78.64 (*d*); 78.33 (*d*); 76.73 (*d*); 75.18 (*d*); 74.59 (*s*); 74.30 (*s*); 72.00 (*d*); 70.52 (*d*); 70.45 (*s*); 68.72 (*s*); 67.36 (*t*); 63.38 (*t*); 56.71 (*q*); 56.66 (*q*); 55.28 (*q*); 38.28 (*d*); 38.09 (*d*); 18.31 (6*q*); 13.04 (3*d*); −0.22 (3*q*); −0.42 (3*q*). FAB-MS: 791 ([$M$ − MeOH]$^+$).

*Data of* **22**: $R_f$ (AcOEt/hexane 2:5) 0.28. $[\alpha]_D^{25} = -42.8$ ($c$ = 0.25, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2958*m*, 2899*m*, 2851*m*, 2827*w*, 2174*w*, 1464*w*, 1442*w*, 1374*m*, 1291*m*, 1251*s*, 1154*s*, 1094*s*, 1044*s*, 1018*s*, 919*m*, 846*s*, 634*w*, 608*w*, 536*w*, 513*w*, 502*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, $J$ = 6.5, C*H*OMe); 4.87 (*d*, $J$ = 6.4, C*H*OMe); 4.86 (*d*, $J$ = 6.5, C*H*OMe); 4.83 (*d*, $J$ = 6.4, C*H*OMe); 4.66 (*s*, $CH_2$OMe); 4.03 (*d*, $J$ = 9.6, H–C(1)); 3.82 (*dd*, $J$ = 11.3, 2.1, H–C(6)); 3.78 (*dd*, $J$ = 11.2, 4.5, H′–C(6)); 3.63 (*dd*, $J$ = 10.2, 8.8, H–C(3)); 3.48 (*t*, $J$ = 9.6, H–C(2)); 3.47 (*s*, MeO); 3.46 (*m*, H–C(5)); 3.45 (*s*, MeO); 3.37 (*s*, MeO); 2.73 (*t*, $J$ = 10.5, H–C(4)); 0.15 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.60 (*s*); 98.01 (*t*); 97.81 (*t*); 96.61 (*t*); 89.55 (*s*); 79.93 (*d*); 78.91 (*d*); 78.30 (*d*); 76.04 (*s*); 70.50 (*d*); 70.27 (*s*); 67.26 (*t*); 56.71 (*q*); 56.71 (*q*); 55.31 (*q*); 38.02 (*d*); −0.19 (3*q*). FAB-MS: 798 ($M^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**23**). At 20°, $CH_2(OMe)_2$ (5 ml) and $P_2O_5$ (160 mg) were added to a soln. of **5** (80 mg, 0.19 mmol) in $CH_2Cl_2$ (5 ml). After stirring for 30 min, filtration through silica gel gave **23** (91 mg, 95%). Oil. $R_f$ (AcOEt/hexane 1:9) 0.37. $[\alpha]_D^{25} = -51.3$ ($c$ = 0.7, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3005*s*, 2946*s*, 2892*m*, 2866*s*, 2180*w*, 1465*m*, 1407*w*, 1390*w*, 1367*w*, 1347*w*, 1290*m*, 1252*s*, 1151*s*, 1097*s*, 1066*s*, 1020*s*, 940*m*, 918*m*, 883*m*, 846*s*, 651*m*, 589*w*, 552*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, $J$ = 6.3, C*H*OMe); 4.74 (*d*, $J$ = 6.2, C*H*OMe); 4.08 (*s*, $CH_2$OMe); 3.94 (*d*, $J$ = 9.2, H–C(3)); 3.88 (*dd*, $J$ = 11.0, 2.5, H–C(8)); 3.83 (*dd*, $J$ = 11.0, 4.9, H′–C(8)); 3.73 (*dd*, $J$ = 9.2, 8.2, H–C(4)); 3.53 (*ddd*, $J$ = 10.5, 4.7, 2.5, H–C(7)); 3.50 (*dd*, $J$ = 10.3, 8.0, H–C(5)); 3.44 (*s*, MeO); 3.42 (*s*, MeO); 2.68 (*td*, $J$ = 10.5, 2.4, H–C(6)); 2.17 (*d*, $J$ = 2.4, H–C(2′)); 1.32–1.19 (*m*,

$(Me_2CH)_3Si$); 0.13 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.34 (*s*); 98.11 (*t*); 96.63 (*t*); 91.35 (*s*); 83.02 (*d*); 81.43 (*d*); 78.56 (*d*); 74.94 (*d*); 72.44 (*s*); 72.23 (*d*); 67.49 (*t*); 56.60 (*q*); 55.31 (*q*); 36.12 (*d*); 10.23 (6*q*); 13.82 (3*d*); −0.44 (3*q*). MS: 530 (100, $[M + NH_4]^+$). Anal. calc. for $C_{26}H_{48}O_6Si_2$ (512.83): C 60.89, H 9.43; found: C 60.43, H 9.53.

*3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-6,7,10-tris-*O*-(methoxymethyl)-8-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**24**). At 20°, CuI (9 mg, 0.05 mmol) and $[Pd(PPh_3)_4]$ (5.4 mg, 0.003 mmol) were added to a soln. of **23** (81 mg, 0.15 mmol) and **20** (83 mg, 0.15 mmol) in pyridine (5 ml). The mixture was stirred for 4 h at 40° and the solvent evaporated. The residue was dissolved in AcOEt and the soln. washed with brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **24** (81 mg, 56%), white solid, and **22** (28 mg, 21%) as an oil. **24**: $R_f$ (AcOEt/hexane 2:5) 0.55. $[\alpha]_D^{25} = -44.3$ (*c* = 0.47, $CHCl_3$). IR ($CHCl_3$): 2985*m*, 2961*m*, 2868*m*, 2259*w*, 2175*w*, 1465*m*, 1446*m*, 1374*s*, 1251*s*, 1153*s*, 1096*s*, 1044*s*, 1019*s*, 940*s*, 918*m*, 883*w*, 846*s*, 818*m*, 634*w*, 608*w*, 536*w*, 505*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 4.98 (*d*, *J* = 6.5, C*H*OMe); 4.90 (*d*, *J* = 6.4, C*H*OMe); 4.89 (*d*, *J* = 6.4, C*H*OMe); 4.86 (*d*, *J* = 7.4, C*H*OMe); 4.85 (*d*, *J* = 7.4, C*H*OMe); 4.70 (*d*, *J* = 6.3, C*H*OMe); 4.66 (*s*, $CH_2$OMe); 4.03 (*dd*, *J* = 9.3, 0.5, H–C(5′)); 3.92 (*d*, *J* = 9.3, H–C(3)); 3.84 (*dd*, *J* = 11.2, 2.1, H–C(8)); 3.80 (*dd*, *J* = 11.0, 2.2, H–C(10′)); 3.79 (*dd*, *J* = 11.2, 4.6, H′–C(8)); 3.77 (*dd*, *J* = 11.1, 4.5, H′–C(10′)); 3.72 (*dd*, *J* = 9.1, 8.1, H–C(4)); 3.63 (*dd*, *J* = 10.4, 8.7, H–C(7′)); 3.58 (*m*, H–C(7), H–C(9′)); 3.49 (*dd*, *J* = 9.4, 8.6, H–C(6′)); 3.48 (*dd*, *J* = 10.3, 8.1, H–C(5)); 3.47 (*s*, MeO); 3.45 (*s*, MeO); 3.43 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 2.80 (*t*, *J* = 10.4, H–C(8′)); 2.76 (br. *t*, *J* = 10.4, H–C(6)); 1.26–1.09 (*m*, (i-Pr)$_3$Si); 0.14 (*s*, 2 $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 102.72 (*s*); 102.11 (*s*); 98.11 (*t*); 97.96 (*t*); 97.82 (*t*); 96.64 (2*t*); 91.54 (*s*); 89.53 (*s*); 82.66 (*d*); 79.99 (*d*); 78.89 (*d*); 78.34 (*d*); 78.25 (*d*); 77.88 (*s*); 74.90 (*d*); 73.67 (*s*); 72.46 (*d*); 70.84 (*s*); 70.56 (*d*); 68.02 (*t*); 67.49 (*s*); 67.30 (*t*); 56.71 (*q*); 56.56 (*q*); 56.39 (*q*); 55.31 (2*q*); 38.05 (*d*); 37.50 (*d*); 18.23 (6*q*); 13.81 (3*d*); −0.19 (3*q*); −0.46 (3*q*). FAB-MS: 879 ($[M - MeOH]^+$). Anal. calc. for $C_{45}H_{78}O_{13}Si_3$ (911.36): C 59.31, H 8.63; found: C 59.49, H 8.48.

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-6,7,10-tris-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**25**). At 24°, a soln. of $AgNO_2$ (146 mg, 0.94 mmol) in MeOH/$H_2O$ 3:1 (4 ml) was added dropwise to a soln. of **21** (130 mg, 0.158 mmol) in MeOH (6 ml). After 3 h, the suspension was cooled to 0°, treated with sat. aq. NaCN soln. (15 ml), *carefully neutralised* with 2M HCl (*ca.* 30 ml), washed with $H_2O$, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 2:10) gave **25** (81 mg, 69%) as a white solid and **21** (20 mg, 15%). **25**: $R_f$ (AcOEt/hexane 3:5) 0.36. $[\alpha]_D^{25} = -17.5$ (*c* = 0.2, $CHCl_3$). IR ($CHCl_3$): 3596*m*, 3306*m*, 3007*m*, 2946*s*, 2895*s*, 2867*s*, 2828*m*, 2260*m*, 2179*w*, 1602*w*, 1463*m*, 1369*m*, 1326*w*, 1292*m*, 1251*s*, 1152*s*, 1102*s*, 1040*s*, 993*s*, 918*m*, 883*m*, 846*s*, 654*s*, 612*w*, 598*w*, 522*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 4.99 (*d*, *J* = 6.6, C*H*OMe); 4.91 (*d*, *J* = 6.6, C*H*OMe); 4.86 (*s*, $CH_2$OMe); 4.66 (*s*, $CH_2$OMe); 4.03 (*dd*, *J* = 9.1, 0.5, H–C(5′)); 3.99 (*d*, *J* = 9.3, H–C(3)); 3.90 (*ddd*, *J* = 12.1, 6.8, 2.2, H–C(8)); 3.86 (*dd*, *J* = 11.3, 2.0, H–C(10′)); 3.80 (*dd*, *J* = 11.2, 4.8, H′–C(10′)); 3.70 (*dt*, *J* ≈ 12.1, 6.0, H′–C(8)); 3.65 (*dd*, *J* = 10.4, 8.9, H–C(7′)); 3.61 (*dd*, *J* = 9.1, 8.3, H–C(4)); 3.54 (*ddd*, *J* = 10.4, 4.6, 1.9, H–C(9′)); 3.51 (*dd*, *J* = 9.2, 8.9, H–C(6′)); 3.51 (*ddd*, *J* = 10.4, 8.4, 3.3, H–C(5)); 3.47 (*s*, MeO); 3.46 (*s*, MeO); 3.42 (*ddd*, *J* = 10.3, 5.6, 2.5, H–C(7)); 3.38 (*s*, MeO); 2.72 (*td*, *J* = 10.5, 2.4, H–C(8′)); 2.65 (br. *t*, *J* = 10.3, H–C(6)); 2.45 (*d*, *J* = 3.3, OH–C(5)); 2.21 (*d*, *J* = 2.2, H–C(2″)); 2.07 (*t*, *J* = 6.8, OH–C(8)); 1.27–1.09 (*m*, (i-Pr)$_3$Si); 0.16 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 101.99 (*s*); 98.02 (*t*); 97.87 (*t*); 96.67 (*t*); 91.40 (*s*); 80.68 (*d*); 80.10 (*d*); 78.98 (*d*); 78.62 (*d*); 78.51 (*d*); 76.66 (*d*); 75.12 (*d*); 74.07 (*s*); 72.76 (2*s*); 71.95 (*d*); 70.52 (*s*); 70.46 (*d*); 68.49 (*s*); 67.24 (*t*); 63.37 (*t*); 56.72 (2*q*); 55.37 (*q*); 38.21 (*d*); 36.84 (*d*); 18.33 (6*q*); 13.04 (3*d*); −0.40 (3*q*). FAB-MS: 719 ($[M - MeOH]^+$). Anal. calc. for $C_{38}H_{62}O_{11}Si_2$ (751.07): C 60.77, H 8.32; found: C 60.82, H 8.19.

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-6,7,10-tris-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-octitol* (**26**). A soln. of **21** (33 mg, 0.044 mmol) in MeOH (2 ml) was treated with 0.5M NaOH in MeOH (0.1 ml), stirred at 25° for 6 h, neutralised with 1M HCl (0.05 ml), diluted with AcOEt, washed with $H_2O$, and dried ($MgSO_4$). Evaporation gave **26** (28 mg, 93%). Oil. $R_f$ (AcOEt/hexane 2:3) 0.28. $[\alpha]_D^{25} = -54.3$ (*c* = 0.35, $CHCl_3$). IR ($CHCl_3$): 3597*m*, 3306*s*, 3007*m*, 2946*s*, 2894*s*, 2867*s*, 2260*w*, 2131*w*, 1464*m*, 1370*m*, 1327*w*, 1292*m*, 1260*m*, 1152*s*, 1098*s*, 1040*s*, 919*s*, 883*s*, 649*s*, 603*w*, 575*w*, 546*w*, 537*w*, 514*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.94 (*d*, *J* = 6.6, C*H*OMe); 4.90 (*d*, *J* = 6.6, C*H*OMe); 4.86 (*s*, $CH_2$OMe); 4.66 (*s*, $CH_2$OMe); 4.04 (*dd*, *J* = 9.6, 0.5, H–C(5′)); 3.95 (*dd*, *J* = 9.1, 2.0, H–C(3)); 3.90 (*dd*, *J* = 12.2, 2.4, H–C(10′)); 3.85 (*dd*, *J* = 12.5, 4.3, H′–C(10′)); 3.79 (*ddd*, *J* = 11.5, 6.0, 2.1, H–C(8)); 3.68 (*dt*, *J* ≈ 11.6, 5.3, H′–C(8)); 3.65 (*dd*, *J* = 10.0, 8.6, H–C(7′)); 3.62 (*t*, *J* = 9.1, H–C(4)); 3.54 (*dd*, *J* = 10.3, 9.7, H–C(5)); 3.50 (*t*, *J* = 9.4, H–C(6′)); 3.49 (*m*, H–C(9′)); 3.47 (*s*, 2 MeO); 3.45 (*m*, H–C(7)); 3.51 (*s*, MeO); 2.72 (*td*, *J* = 10.5, 2.3, H–C(8′)); 2.68 (br. *t*, *J* = 10.3, H–C(6)); 2.51 (*s*,

OH–C(5)); 2.50 (*d*, $J = 2.2$, H–C(1)); 2.24 (br. *t*, $J = 6.0$, OH–C(8)); 2.20 (*d*, $J = 2.5$, H–C(2″)); 1.32–1.00 (*m*, (i-Pr)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 98.01 (*t*); 97.87 (*t*); 96.66 (*t*); 80.74 (*d*); 80.66 (*d*); 80.09 (*d*); 78.75 (*d*); 78.61 (*d*); 78.49 (*d*); 76.52 (*d*); 75.06 (*s*); 74.78 (*d*); 74.13 (*s*); 72.78 (*s*); 71.36 (*d*); 70.46 (*s*); 70.45 (*d*); 68.57 (*s*); 67.23 (*t*); 63.34 (*t*); 56.71 (2*q*); 55.39 (*q*); 38.23 (*d*); 36.83 (*d*); 18.34 (6*q*); 12.99 (3*d*). FAB-MS: 679 ($M^+$).

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-6,7,10-tris-*O*-(methoxymethyl)-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D*-glycero-*D*-gulo-octitol* (**27**). At 0°, a soln. of $Bu_4NF \cdot 3\ H_2O$ (21 mg, 0.05 mmol) in THF (0.5 ml) was added dropwise to a soln. of **21** (30 mg, 0.05 mmol) in THF (2 ml). The soln. was stirred at 25° for 4 h, treated with $H_2O$ (1 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 10:1) gave **27** (21 mg, 91%). Oil. $R_f$ (AcOEt) 0.52. $[\alpha]_D^{25} = -31.8$ ($c = 0.6$, $CHCl_3$). IR ($CHCl_3$): 3595*w*, 3435*w*, 3306*m*, 3007*m*, 2932*m*, 2899*m*, 2828*w*, 2260*w*, 2128*w*, 1519*w*, 1464*w*, 1443*w*, 1394*w*, 1374*m*, 1294*m*, 1248*s*, 1153*s*, 944*s*, 920*m*, 878*w*, 848*w*, 649*m*, 608*w*, 577*w*, 525*w*, 512*w*, 502*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.95 (*d*, $J = 6.6$, C*H*OMe); 4.92 (*d*, $J = 6.6$, C*H*OMe); 4.87 (*s*, $CH_2$OMe); 4.86 (*s*, $CH_2$OMe); 4.05 (*dd*, $J = 9.3$, 0.5, H–C(5′)); 4.02 (*dd*, $J = 9.6$, 2.2, H–C(3)); 3.92 (*ddd*, $J = 11.9$, 5.2, 2.2, H–C(8)); 3.87 (*dd*, $J = 11.5$, 2.6, H–C(10′)); 3.82 (*dd*, $J = 11.5$, 4.6, H′–C(10′)); 3.75 (*dt*, $J \approx 11.6$, 5.5, H′–C(8)); 3.61 (*dd*, $J = 10.0$, 9.0, H–C(7′)); 3.55 (*t*, $J = 9.2$, H–C(4)); 3.52 (*t*, $J = 9.6$, H–C(6′)); 3.51 (*m*, H–C(9′)); 3.50 (*m*, H–C(5)); 3.47 (*s*, 2 MeO); 3.46 (*m*, H–C(7)); 3.39 (*s*, MeO); 3.02 (*s*, OH–C(4)); 2.82 (*s*, OH–C(5)); 2.74 (*td*, $J = 10.1$, 2.2, H–C(8′)); 2.73 (br. *t*, $J = 10.3$, H–C(6)); 2.60 (*d*, $J = 2.1$, H–C(1)); 2.20 (*d*, $J = 2.3$, H–C(2″)); 2.13 (br. *t*, $J = 6.1$, OH–C(8)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 98.01 (*t*); 97.87 (*t*); 96.66 (*t*); 80.64 (*d*); 80.11 (*d*); 79.52 (*d*); 79.15 (*d*); 78.76 (*d*); 78.49 (*d*); 76.35 (*s*); 75.30 (*s*); 75.18 (*d*); 74.23 (*s*); 74.02 (*d*); 72.81 (*s*); 71.36 (*d*); 70.53 (*s*); 70.44 (2*d*); 68.68 (*s*); 67.22 (*t*); 63.23 (*t*); 56.73 (2*q*); 55.43 (*q*); 37.78 (*d*); 36.81 (*d*). FAB-MS: ($[M - 2\ MeOH]^+$).

*3,7-Anhydro-6-*C*-[5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D*-glycero-*D*-gulo-octitol* (**28**). A soln. of **21** (20 mg, 0.04 mmol) in dry MeOH (2 ml) was treated with 0.3N HCl (1 ml), heated under reflux for 18 h, and neutralised with a sat. aq. $NaHCO_3$ soln. (0.1 ml). Dilution with AcOEt and filtration through silica gel gave **28** (14 mg, 95%). White solid. $R_f$ (AcOEt/MeOH 15:1) 0.44. M.p. 225° (dec.). $[\alpha]_D^{25} = -15$ ($c = 0.4$, MeOH). IR (KBr): 3568*m* (br.), 3422*m* (br.), 2922*w*, 2259*w*, 2124*w*, 1629*w*, 1570*w*, 1560*w*, 1534*w*, 1508*w*, 1458*w*, 1375*w*, 1250*w*, 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, $CD_3OD$): 4.00 (*dd*, $J = 9.7$, 0.5, H–C(5′)); 3.93 (*dd*, $J = 9.6$, 2.1, H–C(3)); 3.85 (*dd*, $J = 12.1$, 2.1, H–C(10′)); 3.81 (*dd*, $J = 12.2$, 2.0, H–C(8)); 3.69 (*dd*, $J = 12.1$, 5.2, H′–C(10′)); 3.65 (*dd*, $J = 12.1$, 5.3, H′–C(8)); 3.44–3.40 (*m*, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.20 (*t*, $J = 9.6$, H–C(6′)); 3.19 (*t*, $J = 9.6$, H–C(4)); 2.87 (*d*, $J = 2.2$, H–C(1)); 2.61 (br. *t*, $J = 10.4$, H–C(6)); 2.50 (*d*, $J = 2.4$, H–C(2″)); 2.45 (*td*, $J = 10.3$, 2.4, H–C(8′)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 81.98 (*d*); 81.71 (*d*); 81.41 (*d*); 80.93 (*d*); 78.67 (*d*); 77.99 (*d*); 76.59 (*s*); 75.58 (*s*); 75.57 (*d*); 75.44 (*d*); 75.43 (*s*); 73.41 (*s*); 72.62 (2*d*); 70.80 (*s*); 68.60 (*s*); 63.76 (2*t*); 39.45 (*d*); 38.74 (*d*). FAB-MS: 389 ($[M - 1]^+$).

*3,7-Anhydro-6-*C*-{5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-[2-(trimethylsilyl)-ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**29**). A soln. of **21** (60 mg, 0.08 mmol) in dry MeOH/THF 2:1 (10 ml) was treated with 0.3N HCl (5 ml), heated under reflux for 48 h, and neutralised with sat. aq. $NaHCO_3$ soln. (0.2 ml). Dilution with AcOEt and filtration through silica gel gave **29** (40 mg, 94%). White solid. $R_f$ (AcOEt) 0.68. M.p. 240° (dec.). $[\alpha]_D^{25} = -31.3$ ($c = 0.45$, MeOH). IR (KBr): 3416*s* (br.), 2958*m*, 2899*m*, 2260*w*, 2173*w*, 1637*w*, 1560*w*, 1508*w*, 1410*w*, 1364*m*, 1300*m*, 1250*s*, 1181*w*, 1078*s*, 987*m*, 804*s*, 760*m*, 700*w*, 673*m*, 637*w*, 607*w*, 578*m*, 529*w*. $^1$H-NMR (300 MHz, $CD_3OD$): 4.00 (br. *d*, $J = 9.6$, H–C(5′)); 3.93 (*d*, $J = 9.7$, H–C(3)); 3.87 (*dd*, $J = 12.1$, 2.0, H–C(10′)); 3.82 (*dd*, $J = 12.3$, 1.9, H–C(8)); 3.67 (*dd*, $J = 12.3$, 5.2, H′–C(10′)); 3.65 (*dd*, $J = 12.2$, 5.2, H′–C(8)); 3.46–3.33 (*m*, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.18 (*t*, $J = 9.4$, H–C(6′)); 3.17 (*t*, $J = 8.8$, H–C(4)); 2.62 (br. *t*, $J = 10.3$, H–C(6)); 2.47 (*t*, $J = 10.2$, H–C(8′)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 104.71 (*s*); 103.74 (*s*); 91.08 (*s*); 89.05 (*s*); 81.50 (*d*); 81.00 (*d*); 78.67 (*s*); 76.92 (*d*); 76.85 (*d*); 76.73 (*s*); 75.54 (*d*); 75.45 (*d*); 72.65 (*d*); 72.54 (*d*); 70.82 (*s*); 68.60 (*s*); 63.81 (2*t*); 39.84 (*d*); 39.44 (*d*); 0.05 (3*q*); −0.16 (3*q*). FAB-MS: 557 ($[M + Na]^+$).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis[(1S)-1,5-anhydro-2,3,4,6-tetra-O-benzyl-D-glucitol]* (**30**). A soln. of **10** (861 mg, 1.57 mmol) in pyridine (25 ml) was treated with CuCl (155.5 mg, 1.57 mmol), stirred under $O_2$ at 35° for 3 h, diluted with AcOEt (20 ml), and treated with a sat. aq. $NH_4Cl$ soln. (20 ml). Normal workup gave **30** (825 mg, 96%). White crystals. $R_f$ (AcOEt/hexane 3:7) 0.52. M.p. 126° (AcOEt/hexane). $[\alpha]_D^{25} = -61.1$ ($c = 0.53$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3000*m*, 2920*m*, 2860*m*, 2160*w*, 1950*w*, 1880*w*, 1810*w*, 1130*w*, 1610*w*, 1540*w*, 1500*m*, 1455*s*, 1450*m*, 1290*m*, 1140*s*, 1065*s*, 1040*s*, 1000*m*, 910*w*, 820*w*, 700*s*. $^1$H-NMR (400 MHz, $C_6D_6$): 7.51–7.17 (*m*, 20 arom. H); 4.93 (*d*, $J = 10.9$, PhC*H*); 4.85 (*d*, $J = 11.9$, PhC*H*); 4.82 (*d*, $J = 12.0$, PhC*H*); 4.75 (*d*, $J = 11.4$, PhC*H*); 4.69 (*d*, $J = 10.9$, PhC*H*); 4.58 (*d*, $J = 11.3$, PhC*H*); 4.46 (*d*, $J = 12.1$, PhC*H*); 4.33 (*d*, $J = 12.2$, PhC*H*); 4.06 (*d*, $J = 9.5$, H–C(1)); 3.84 (*t*, $J = 9.4$, H–C(4)); 3.79–3.73 (*m*, 2 H–C(6)); 3.70 (*t*, $J = 9.3$, H–C(2)); 3.56 (*t*, $J = 9.0$,

H–C(3)); 3.27 (*ddd*, $J = 9.5, 5.2, 1.9$, H–C(5)). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.73 (*s*); 137.87 (2*s*); 137.49 (*s*); 128.35–127.38 (several *d*); 85.88 (*d*); 81.82 (*d*); 79.20 (*d*); 77.64 (*s*); 77.41 (*d*); 76.60 (*s*); 75.67 (*t*); 75.53 (*t*); 75.06 (*t*); 73.51 (*t*); 70.11 (*d*); 68.57 (*t*). MS: 1112 (100, $[M + NH_4]^+$). Anal. calc. for $C_{72}H_{70}O_{10}$ (1095.34): C 78.95, H 6.44; found: C 79.22, H 6.54.

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis[(1S)-2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**31**). At −40°, a soln. of $Me_3SiOTf$ (1.01 ml, 54.5 mmol) in $Ac_2O$ (10 ml) was added dropwise to a soln. of **30** (277 mg, 0.25 mmol) in $Ac_2O$ (20 ml). The mixture was kept at 10–15° for 15 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (5 ml). Normal workup gave **31** (129 mg, 72%). White solid. $R_f$ (AcOEt/hexane 6:5) 0.20. M.p. 234.3° (AcOEt/hexane). $[\alpha]_D^{25} = -29.4$ ($c = 0.675$, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2840*w*, 2760*w*, 2160*w*, 1740*s*, 1420*w*, 1350*m*, 1300*w*, 1250*s*, 1230*w*, 1200*w*, 1100*w*, 1050*m*, 1030*m*, 960*w*, 910*w*, 710*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 5.38 (*t*, $J = 9.6$, H–C(2)); 5.28 (*t*, $J = 9.4$, H–C(3)); 5.22 (*t*, $J = 9.4$, H–C(4)); 4.26 (*dd*, $J = 12.6, 4.8$, H–C(6)); 4.02 (*dd*, $J = 12.4, 2.1$, H'–C(6)); 3.84 (*d*, $J = 9.7$, H–C(1)); 3.10 (*ddd*, $J = 9.6, 4.5, 2.0$, H–C(5)); 1.86 (*s*, Ac); 1.76 (*s*, Ac); 1.74 (*s*, Ac); 1.71 (*s*, Ac). $^{13}$C-NMR (50 MHz, $CDCl_3$): 170.50 (*s*); 170.40 (*s*); 169.17 (*s*); 168.96 (*s*); 76.05 (*d*); 73.81 (*s*); 73.32 (*d*); 70.58 (*d*); 70.45 (*s*); 68.84 (*d*); 67.81 (*d*); 61.78 (*t*); 20.61 (*q*); 20.42 (3*q*). MS: 728 (100, $[M + NH_4]^+$). Anal. calc. for $C_{32}H_{38}O_{18}$ (710.63): C 54.09, H 5.39; found: C 54.04, H 5.62.

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis[(1S)-1,5-anhydro-*D*-glucitol]* (**32**). A soln. of **31** (85 mg, 0.12 mmol) in MeOH (7 ml) was treated with 0.23M NaOMe in MeOH (1.25 ml), stirred for 2 h at 0°, neutralised (*Dowex*, $H^+$-form), and filtered. Evaporation of the filtrate afforded **32** (42 mg, 95%). White solid. $R_f$ ($CH_2Cl_2$/MeOH 12:7) 0.47. M.p. > 300°. $[\alpha]_D^{25} = -4.7$ ($c = 1$, $H_2O$). IR (KBr): 3420*s*, 3320*s*, 2940*m*, 2900*m*, 2860*m*, 2160*w*, 1630*w*, 1560*w*, 1500*w*, 1470*w*, 1415*m*, 1385*m*, 1350*m*, 1300*w*, 1250*w*, 1230*w*, 1200*w*, 1140*m*, 1130*w*, 1110*s*, 1040*s*, 1015*m*, 1000*m*, 980*m*, 930*w*, 890*w*, 780*w*, 740*w*, 630*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 3.99 (*d*, $J = 9.0$, H–C(1)); 3.81 (br. *d*, $J = 12.3$, H–C(6)); 3.60 (*dd*, $J = 12.1, 3.4$, H'–C(6)); 3.56–3.22 (*m*, 4 H). $^{13}$C-NMR (50 MHz, $D_2O$): 80.27 (*d*); 76.76 (*d*); 76.16 (*s*); 73.16 (*d*); 70.67 (*d*); 70.07 (*s*); 69.57 (*d*); 60.98 (*t*). MS: 392 (100, $[M + NH_4]^+$). Anal. calc. for $C_{16}H_{22}O_{10}$ (374.34): C 51.34, H 5.92; found: C 51.42, H 6.14.

*3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1-*C*-bromo-1,1,2,2-tetradehydro-1,2-dideoxy-*D*-glycero-*D*-gulo-octitol* (**33**). At 20°, $PPh_3$ (413 mg, 1.57 mmol) was added to a soln. of **10** (144 mg, 0.26 mmol) and $CBr_4$ (261 mg, 0.78 mmol) in $CH_2Cl_2$ (4 ml). After stirring for 3 h, $Et_2O$ (2 ml) was added. Normal workup and FC (AcOEt/hexane 1:5) gave **33** (148 mg, 90%). Oil. $R_f$ (AcOEt/hexane 1:4) 0.54. $[\alpha]_D^{25} = -12.0$ ($c = 0.5$, $CHCl_3$). IR: 3080*w*, 3020*w*, 3000*w*, 2900*w*, 2860*w*, 2218*w*, 1495*w*, 1450*m*, 1400*w*, 1360*m*, 1290*w*, 1235*w*, 1155*m*, 1140*m*, 1090*s*, 1065*s*, 1030*s*, 1000*w*, 910*w*, 700*s*, 670*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.48–7.00 (*m*, 20 arom. H); 5.00 (*d*, $J = 10.9$, PhC*H*); 4.97 (*d*, $J = 11.1$, PhC*H*); 4.93 (*d*, $J = 10.9$, PhC*H*); 4.86 (*d*, $J = 11.4$, PhC*H*); 4.81 (*d*, $J = 10.8$, PhC*H*); 4.68 (*d*, $J = 11.2$, PhC*H*); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.42 (*d*, $J = 12.1$, PhC*H*); 4.02 (*d*, $J = 9.4$, H–C(3)); 3.84 (*t*, $J \approx 9.4$, H–C(6)); 3.76 (*dd*, $J = 10.9, 3.6$, H–C(8)); 3.73 (*dd*, $J = 11.0, 2.0$, H'–C(8)); 3.65 (*t*, $J = 9.3$, H–C(4)); 3.56 (*t*, $J = 9.0$, H–C(5)); 3.20 (*ddd*, $J = 9.9, 3.5, 2.0$, H–C(7)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.44 (*s*); 137.96 (2*s*); 137.75 (*s*); 128.42–127.73 (several *d*); 85.99 (*d*); 81.97 (*d*); 79.07 (*d*); 77.58 (*d*); 77.28 (*s*); 75.75 (*t*); 75.60 (*t*); 75.14 (*t*); 73.59 (*t*); 70.62 (*d*); 68.68 (*t*); 46.86 (*s*). MS: 644 (100, $[M + NH_4]^+$). Anal. calc. for $C_{36}H_{35}BrO_5$ (627.57): C 68.90, H 5.62; found: C 68.99, H 5.85.

*3,7-Anhydro-6-*C*-[5,9-anhydro-6,7,8,10-tetra-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-decitol-1-yl]-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**34**). At 20°, CuI (6.8 mg, 0.036 mmol) and $[Pd(PPh_3)_4]$ (4.15 mg, 0.0036 mmol) were added to a soln. of **5** (76.6 mg, 0.18 mmol) and **33** (170 mg, 0.27 mmol) in $Et_3N$ (5 ml). The soln. was stirred for 24 h and evaporated. The residue was dissolved in AcOEt and the soln. washed with brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **34** (124 mg, 71%). Oil. $R_f$ (AcOEt/hexane 1:4) 0.30. $[\alpha]_D^{25} = -57.5$ ($c = 0.8$, $CHCl_3$). IR: 3595*m*, 3089*w*, 3066*w*, 3042*w*, 3007*s*, 2945*s*, 2867*s*, 2259*m*, 2179*w*, 1391*m*, 1361*m*, 1329*m*, 1292*m*, 1252*s*, 1142*s*, 1094*s*, 1056*s*, 1028*s*, 997*s*, 912*w*, 883*m*, 846*s*, 657*m*, 597*w*, 572*w*. $^1$H-NMR (500 MHz, $C_6D_6$): 7.39–7.37 (*m*, 2 arom. H); 7.30–7.21 (*m*, 4 arom. H); 7.20–7.04 (*m*, 14 arom. H); 4.95 (*d*, $J = 11.0$, PhC*H*); 4.88 (*d*, $J = 11.3$, PhC*H*); 4.84 (*d*, $J = 11.3$, PhC*H*); 4.80 (*d*, $J = 11.3$, PhC*H*); 4.77 (*d*, $J = 11.0$, PhC*H*); 4.60 (*d*, $J = 11.3$, PhC*H*); 4.47 (*d*, $J = 12.1$, PhC*H*); 4.36 (*d*, $J = 12.1$, PhC*H*); 3.99 (*dd*, $J = 9.6, 0.7$, H–C(5′)); 3.73 (*d*, $J = 9.3$, H–C(3)); 3.71 (*t*, $J = 9.6, 9.2$, H–C(8′)); 3.66 (*t*, $J = 9.3$, H–C(4)); 3.65 (*dd*, $J = 11.3, 3.9$, H–C(10′)); 3.64 (*m*, H–C(8)); 3.61 (*dd*, $J = 11.1, 1.8$, H'–C(10′)); 3.60 (*t*, $J = 9.6, 9.2$, H–C(6′)); 3.48 (*t*, $J = 9.0$, H–C(7′)); 3.45 (*td*, $J = 12.4, 5.0$, H'–C(8)); 3.22 (*ddd*, $J = 10.4, 8.2, 3.9$, H–C(5)); 3.17 (*ddd*, $J = 9.8, 3.7, 1.9$, H–C(9′)); 2.96 (*ddd*, $J = 10.2, 5.0, 2.3$, H–C(7)); 2.53 (br. *t*, $J = 10.3$, H–C(6)); 1.88 (*d*, $J = 3.9$, OH–C(5)); 1.37 (*t*, $J = 6.3$, OH–C(8)); 1.34–1.21 (*m*, (i-Pr)$_3$Si); 0.15 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $C_6D_6$): 139.35 (*s*); 139.17 (*s*); 138.83 (*s*); 138.69 (*s*); 128.63–127.76 (several *d*); 103.67 (*s*); 90.79 (*s*); 86.41 (*d*); 82.44 (*d*); 79.79 (*d*); 78.99 (*d*); 77.95 (*d*); 77.64 (*s*); 76.64 (*d*); 76.04 (*s*); 75.75 (*d*); 75.62 (2*t*); 75.09 (*t*); 73.80 (*t*); 72.28 (*d*); 70.70 (*d*); 69.27 (*t*); 69.14 (*s*);

63.45 (*t*); 38.96 (*d*); 18.80 (6*q*); 13.49 (3*d*); −0.24 (3*q*). EI-MS: 970 ($M^+$). Anal. calc. for $C_{58}H_{74}O_8Si_2$ (971.39): C 71.72, H 7.68; found: C 71.94, H 7.76.

*4,5,8-Tri-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-[6,7,8,10-tetra-*O*-acetyl-5,9-anhydro-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-decitol-1-yl]-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**35**). At −40°, a soln. of $Me_3SiOTf$ (97 µl, 0.52 mmol) in $Ac_2O$ (2 ml) was added dropwise to a soln. of **34** (26 mg, 0.026 mmol) in $Ac_2O$ (2 ml). The mixture was kept at 4° for 48 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (2 ml). Normal workup gave **35** (18 mg, 89%). White solid. $R_f$ (AcOEt/hexane 2:3) 0.32. M.p. 222° (dec.; AcOEt/hexane). $[\alpha]_D^{25} = -9.0$ ($c = 0.1$, $CHCl_3$). IR ($CHCl_3$): 2986*m*, 2941*w*, 2264*w*, 2094*w*, 1731*s*, 1477*m*, 1465*w*, 1445*w*, 1374*s*, 1299*w*, 1251*s*, 1097*w*, 1046*s*, 929*w*, 848*w*, 818*w*, 632*w*, 608*w*, 564*w*, 511*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 5.32 (*t*, $J = 9.7$, H–C(6′)); 5.25–5.10 (*m*, H–C(4), H–C(5), H–C(7′)); 5.14 (*t*, $J = 9.8$, H–C(8′)); 4.23 (*dd*, $J = 12.4, 2.2$, H–C(8)); 4.15 (*dd*, $J = 12.4, 4.8$, H–C(10′)); 4.02 (*dd*, $J = 12.4, 5.4$, H′–C(8)); 3.95 (*dd*, $J = 12.7, 2.1$, H′–C(10′)); 3.86 (*d*, $J = 9.7$, H–C(5′)); 3.81 (*d*, $J = 9.9$, H–C(3)); 3.00 (*ddd*, $J = 10.6, 5.1, 2.2$, H–C(9′)); 2.89 (*ddd*, $J = 10.6, 5.1, 2.2$, H–C(7)); 2.60 (*t*, $J = 10.5$, H–C(6)); 1.80 (*s*, Ac); 1.78 (*s*, Ac); 1.76 (*s*, Ac); 1.65 (*s*, Ac); 1.64 (*s*, Ac); 1.62 (*s*, Ac); 1.53 (*s*, Ac); 0.29 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.55 (*s*); 170.30 (*s*); 170.15 (*s*); 169.95 (*s*); 169.29 (2*s*); 169.10 (*s*); 98.69 (*s*); 92.45 (*s*); 77.22 (*d*); 76.41 (*d*); 76.10 (*s*); 74.93 (*s*); 73.42 (*d*); 72.42 (*d*); 71.61 (*s*); 71.33 (*d*); 70.10 (*d*); 69.32 (*d*); 68.97 (*d*); 68.44 (*s*); 67.86 (*d*); 64.04 (*t*); 61.88 (*t*); 36.61 (*d*); 20.85 (2*q*); 20.76 (2*q*); 20.59 (3*q*); −0.47 (3*q*). EI-MS: 749 ($[M + 1]^+$).

*4,5,8-Tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-1-*C*-(trimethylsilyl)-*D*-gluco-oct-3-ulopyranose* (**37**). At −78°, BuLi (0.625 mmol) was added dropwise to a soln. of (trimethylsilyl)acetylene (86 µl, 0.625 mmol) in THF (2 ml). The soln. was kept at −78° for 30 min and then transferred by a syringe to a cooled soln. (−78°) of **36** (405 mg, 0.417 mmol) in THF (6 ml). The mixture was stirred for 30 min at −78°, treated with 2M HCl in MeOH (1 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine, and dried ($MgSO_4$). Evaporation afforded **37** (439 mg, 98%). Oil. IR ($CHCl_3$): 3560*w*, 3060*w*, 3000*w*, 2950*w*, 2940*w*, 2910*m*, 2870*m*, 2180*w*, 1950*w*, 1880*w*, 1810*w*, 1715*w*, 1610*w*, 1500*m*, 1455*m*, 1400*w*, 1360*m*, 1310*w*, 1290*w*, 1250*m*, 1170*m*, 1140*m*, 1120*s*, 1085*s*, 1070*s*, 1030*s*, 910*w*, 860*s*, 850*s*, 700*s*. MS: 1086 (100, $[M + NH_4]^+$). Anal. calc. for $C_{66}H_{72}O_{11}Si$ (1068): C 74.15, H 6.74; found: C 73.99, H 9.90.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**38**). At −40°, a soln. of $BF_3 \cdot Et_2O$ (5.34 ml, 42.8 mmol) and $Et_3SiH$ (6.8 ml, 42.8 mmol) in $MeCN/CH_2Cl_2$ 1:1 (20 ml) was added dropwise to a soln. of **37** (269 mg, 0.25 mmol) in $MeCN/CH_2Cl_2$ 1:1 (20 ml). The soln. was stirred for 6 h and treated with sat. aq. $NaHCO_3$ soln. (5 ml). Normal workup and FC (AcOEt/hexane 1:7) gave **38** (197 mg, 75%). Oil. $R_f$ (AcOEt/hexane 1.5:7) 0.48. $[\alpha]_D^{25} = -132.3$ ($c = 0.635$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3000*w*, 2960*w*, 2870*w*, 2180*w*, 1950*w*, 1810*w*, 1600*w*, 1500*w*, 1455*w*, 1400*w*, 1360*w*, 1290*w*, 1250*w*, 1150*w*, 1120*w*, 1090*s*, 1060*s*, 1030*m*, 910*w*, 850*m*, 700*s*. $^1$H-NMR (400 MHz, $C_6D_6$): 7.58–7.04 (*m*, 35 arom. H); 5.35 (*d*, $J = 11.6$, PhC*H*); 5.04 (*d*, $J = 10.8$, PhC*H*); 4.93 (*d*, $J = 11.4$, PhC*H*); 4.88 (*d*, $J = 10.8$, PhC*H*); 4.85–4.79 (*m*, 4 PhC*H*); 4.74 (*d*, $J = 7.8$, H–C(1′)); 4.69 (*d*, $J = 12.5$, PhC*H*); 4.56 (*d*, $J = 11.4$, PhC*H*); 4.49 (*d*, $J = 11.9$, PhC*H*); 4.39 (*d*, $J = 12.2$, PhC*H*); 4.35 (*t*, $J = 9.5$, H–C(4′)); 4.33 (*d*, $J = 12.5$, PhC*H*); 4.27 (*d*, $J = 11.9$, PhC*H*); 4.07 (*d*, $J = 9.6$, H–C(3)); 3.94 (*dd*, $J = 11.2, 3.1$, H–C(6′)); 3.74 (*t*, $J = 9.5, 9.1$, H–C(6)); 3.68 (*dd*, $J = 11.0, 1.7$, H′–C(6′)); 3.64 (*t*, $J = 9.3$, H–C(4)); 3.63 (*dd*, $J = 11.0, 1.1$, H–C(8)); 3.59 (*t*, $J = 9.1$, H–C(5)); 3.58 (*dd*, $J = 10.9, 4.2$, H′–C(8)); 3.52 (*t*, $J \approx 9.0$, H–C(3′)); 3.47 (*t*, $J \approx 8.6$, H–C(2′)); 3.35 (*ddd*, $J = 9.8, 4.1, 1.6$, H–C(7)); 3.10 (br. *d*, $J \approx 9.8$, H–C(5′)); 0.1 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 139.25 (*s*); 138.55 (*s*); 138.47 (*s*); 138.38 (*s*); 138.26 (*s*); 138.16 (*s*); 137.85 (*s*); 128.33–127.13 (several *d*); 102.54 (*s*); 102.25 (*d*); 93.78 (*s*); 84.87 (*d*); 84.06 (*d*); 82.76 (*d*); 81.6 (*d*); 79.28 (*d*); 78.0 (*d*); 76.10 (*d*); 75.58 (*t*); 75.54 (*t*); 75.12 (*t*); 75.03 (*t*); 74.96 (*t*); 74.75 (*d*); 73.26 (2*t*); 70.31 (*d*); 68.91 (*t*); 67.89 (*t*); −0.26 (3*q*). MS: 1070 (100, $[M + NH_4]^+$). Anal. calc. for $C_{66}H_{72}O_{10}Si$ (1053.37): C 75.28, H 6.89; found: C 75.16, H 7.01.

*4,5,8-Tri-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**39**). At −40°, a soln. of $Me_3SiOTf$ (0.186 ml, 1.02 mmol) in $Ac_2O$ (6 ml) was added dropwise to a soln. of **38** (54 mg, 0.051 mmol) in $Ac_2O$ (6 ml). The mixture was kept at 10–15° for 5 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (3 ml). Normal workup gave **39** (27 mg, 81%). White solid. $R_f$ (AcOEt/hexane 1:1) 0.32. M.p. 260° (AcOEt/hexane). $[\alpha]_D^{25} = -5.6$ ($c = 0.6$, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2960*w*, 2860*w*, 2190*w*, 1710*s*, 1460*w*, 1430*w*, 1370*w*, 1050*s*, 1310*w*, 1250*s*, 1200*w*, 1170*w*, 1050*s*, 990*w*, 910*w*, 850*m*. $^1$H-NMR (400 MHz, $C_6D_6$): 5.4 (*t*, $J = 9.8$, H–C(4)); 5.29 (*t*, $J = 9.4$, H–C(3′)); 5.27 (*t*, $J = 9.3$, H–C(5)); 5.16 (*t*, $J = 9.7$, H–C(4′)); 5.10 (*dd*, $J = 9.2, 7.9$, H–C(2′)); 4.41 (*dd*, $J = 11.9, 1.6$, H–C(8)); 4.34 (*dd*, $J = 12.4, 4.3$, H–C(6′)); 4.23 (*d*, $J = 7.8$, H–C(1′)); 4.01 (*dd*, $J = 11.9, 6.2$, H′–C(8)); 3.93 (*d*, $J = 9.9$, H–C(3)); 3.86 (*dd*, $J = 12.4, 2.1$, H′–C(6′)); 3.47 (*t*, $J = 9.4$, H–C(6)); 3.23 (*ddd*, $J = 10.0, 4.2, 2.2$, H–C(5′)); 3.02 (*ddd*, $J = 9.5, 6.0, 1.7$, H–C(7)); 1.89, 1.88, 1.83, 1.68, 1.67, 1.58 (6*s*, Ac); 0.05 (*s*, $Me_3Si$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 170.36 (*s*); 170.23 (*s*); 170.06 (*s*); 169.67 (*s*); 169.2 (*s*); 169.11 (*s*); 168.96 (*s*); 100.72 (*d*); 98.85 (*s*); 94.12 (*s*); 76.78 (*d*); 76.20

(*d*); 73.04 (*d*); 72.91 (*d*); 71.94 (*d*); 71.57 (*d*); 71.38 (*d*); 68.94 (*d*); 67.83 (*d*); 62.16 (*t*); 61.57 (*t*); 20.80–20.44 (several *q*); −0.55 (3*q*). MS: 734 (100, $[M + NH_4]^+$). Anal. calc. for $C_{31}H_{44}O_{17}Si$ (716.76): C 51.95, H 6.19; found: C 52.20, H 6.10.

*1,1'-(Thiophene-2,5-diyl)bis[(1*S*)-1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-*D*-glucitol]* (**40**). $Na_2S \cdot 9\,H_2O$ (702 mg, 2.92 mmol) was added to a soln. of **30** (400 mg, 0.36 mmol) in 2-methoxyethanol (8 ml). The mixture was heated under reflux for 1 min, cooled to r.t., diluted with AcOEt (3 ml) and hexane (5 ml), and stirred for a further 30 min. The mixture was filtered through *Celite*. Evaporation and FC (AcOEt/hexane 1:11) gave **40** (290 mg, 71%). White solid. $R_f$ (AcOEt/toluene 1:7) 0.34. M.p. 216.7°. $[\alpha]_D^{25} = -20.7$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3010*w*, 2920*w*, 2875*w*, 1950*w*, 1800*w*, 1650*w*, 1500*w*, 1460*w*, 1400*w*, 1365*w*, 1200*s*, 1070*s*, 1030*m*, 920*w*, 820*w*, 700*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.48–7.12 (*m*, 20 arom. H); 7.08 (*s*, 1 arom. H); 5.05 (*d*, $J = 11.4$, PhC*H*); 5.03 (*d*, $J = 11.3$, PhC*H*); 4.99 (*d*, $J = 11.4$, PhC*H*); 4.80 (*d*, $J = 12.3$, PhC*H*); 4.79 (*d*, $J = 11.2$, PhC*H*); 4.60 (*d*, $J = 11.3$, PhC*H*); 4.58 (*d*, $J = 11.2$, PhC*H*); 4.57 (*d*, $J = 12.2$, PhC*H*); 4.23 (*d*, $J = 10.9$, H–C(1)); 3.99 (*t*, $J = 9.3$, H–C(4)); 3.91–3.88 (*m*, H–C(2), 2 H–C(6)); 3.68 (*t*, $J = 9.1$, H–C(3)); 3.59 (br. *ddd*, $J \approx 9.7$, 3.5, 1.8, H–C(5)). $^{13}$C-NMR (50 MHz, $CDCl_3$): 142.17 (*s*); 138.55 (*s*); 138.29 (*s*); 138.08 (*s*); 137.68 (*s*); 128.21–127.45 (several *d*); 125.17 (*d*); 86.44 (*d*); 84.40 (*d*); 79.59 (*d*); 78.12 (*d*); 77.77 (*d*); 75.53 (*t*); 74.95 (*t*); 75.05 (*t*); 73.46 (*t*); 68.89 (*t*). MS: 1146 (100, $[M + NH_4]^+$). Anal. calc. for $C_{72}H_{72}O_{16}S$ (1129.42): S 2.84; found: S 3.07.

*1,1'-(Thiophene-2,5-diyl)bis[(1*S*)-2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**41**). At −40°, a soln. of $Me_3SiOTf$ (0.12 ml, 0.66 mmol) in $Ac_2O$ (2 ml) was added dropwise to a soln. of **40** (35 mg, 0.03 mmol) in $Ac_2O$ (6 ml). The soln. was kept at 20° for 20 h, cooled to 0°, and treated with sat. aq. $NaHCO_3$ soln. (3 ml). Normal workup and FC (AcOEt/hexane 2:3) gave **41** (14 mg, 60%). White solid. $R_f$ (AcOEt/toluene 1:7) 0.34. M.p. > 300°. $[\alpha]_D^{25} = -29.9$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2940*w*, 2860*w*, 1730*s*, 1410*w*, 1350*m*, 1225*s*, 1200*w*, 1100*w*, 1020*m*, 1015*m*, 960*w*, 910*w*, 730*w*, 640*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 6.87 (*s*, 1 arom. H); 5.51 (*t*, $J \approx 9.0$, H–C(2)); 5.44 (*t*, $J = 9.9$, H–C(3)); 5.41 (*t*, $J = 9.9$, H–C(4)); 4.37 (*dd*, $J = 12.4$, 4.9, H–C(6)); 4.27 (*d*, $J = 9.1$, H–C(1)); 4.11 (*dd*, $J = 12.3$, 1.9, H'–C(6)); 3.40 (*ddd*, $J = 9.1$, 5.0, 2.0, H–C(5)); 1.82, 1.80, 1.78, 1.77 (4*s*, Ac). $^{13}$C-NMR (50 MHz, $CDCl_3$): 170.48 (*s*); 170.06 (*s*); 169.28 (*s*); 168.80 (*s*); 139.22 (*s*); 125.42 (*d*); 76.06 (*d*); 75.76 (*d*); 73.90 (*d*); 72.53 (*d*); 68.28 (*d*); 62.08 (*t*); 20.58 (*q*); 20.44 (2*q*); 20.21 (*q*). MS: 762 (100, $[M + NH_4]^+$). Anal. calc. for $C_{32}H_{40}O_{18}S$ (744.74): C 51.60, H5.41; found: C 51.54, H 5.52.

## REFERENCES


[1] J. Alzeer, C. Cai, A. Vasella, *Helv. Chim. Acta* **1995,** *78,* 242.
[2] L.-E. Olsson, *Acta Pharm. Suec.* **1986,** *23,* 370.
[3] A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, *J. Chem. Soc., Chem. Commun.* **1979,** 840.
[4] A. G. Myers, P. M. Harrington, E. Y. Kuo, *J. Am. Chem. Soc.* **1991,** *113,* 694.
[5] H. M. Schmidt, J. F. Arenes, *Recl. Trav. Chim. Pays-Bas* **1967,** *86,* 1138.
[6] T. W. Greene, 'Protective Groups in Organic Synthesis', John Wiley & Sons, New York, 1981.
[7] K. Fuji, K. Ichikawa, M. Node, E. Fujita, *J. Org. Chem.* **1979,** *44,* 1661.
[8] J. R. Hwu, V. C. J. E. Schroeder, R. E. Barrans, K. P. Khoudary, N. Wang, J. M. Wetzel, *J. Org. Chem.* **1986,** *51,* 4731.
[9] P. Cadiot, W. Chodkiewicz, 'Chemistry of Acetylene', Marcel Dekker, New York, 1969, p. 597.
[10] J. M. J. Tronchet, A. Bonenfant, *Helv. Chim. Acta* **1977,** *60,* 892.
[11] J. M. J. Tronchet, A. P. Bonenfant, *Helv. Chim. Acta* **1981,** *64,* 1893.
[12] D. Michelot, *Synthesis* **1983,** 130.
[13] A. Wagner, M. P. Heitz, C. Mioskowski, *Tetrahedron Lett.* **1990,** *31,* 3141.
[14] J.-M. Lancelin, P. H. A. Zollo, P. Sinaÿ, *Tetrahedron Lett.* **1983,** *24,* 4833.
[15] J. M. J. Tronchet, F. Habashi, O. R. Martin, A. P. Bonenfant, B. Baehler, J.-B. Zumwald, *Helv. Chim. Acta* **1979,** *62,* 894.
[16] J. P. Beny, S. N. Dhawan, J. Kagan, S. Sundlass, *J. Org. Chem.* **1982,** *47,* 2201.
[17] A. M. Felix, E. P. Heimer, T. J. Lambros, C. Tzougraki, J. Meienhofer, *J. Org. Chem.* **1978,** *43,* 4191.
[18] E. Pretsch, W. Simon, J. Seibl, T. Clerc, 'Tables of Spectroscopy Data for Structure of Organic Compounds', Springer-Verlag, Berlin, 1989.
[19] F. Bohlmann, M. Brehm, *Org. Magn. Reson.* **1979,** *12,* 535.