Oligosaccharide Analogues of Polysaccharides

Part 24[1])

Synthesis of Cyclodextrin Analogues Containing a Substituted Buta-1,3-diyne or a 1,2,3-Triazole Unit and Analysis of Intramolecular Hydrogen Bonds

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The α- and γ-CD analogues **6** and **18**, which possess a hexa-2,5-diyne-1,6-dioxy unit, were synthesised by intramolecular coupling of the bis-*O*-propargylated maltohexaoside **4**, or the analogous maltooctaoside **16**, followed by deprotection. The dialkynylated linear oligosaccharides were obtained by glycosidation of propargyl alcohol with the thioglycosides **1** and **13**, reductive cleavage of the benzylidene acetal, and propargylation of the terminal HO–C(4) group, respectively. The β-CD analogues **23** and **25**, which possess a penta-1,3-diyn-1-yl-5-oxy unit, were similarly obtained by intramolecular oxidative coupling of **20** and **21**, respectively. The linear dialkynylated oligosaccharides **20** and **21** were obtained by two consecutive glycosylations, first with the maltohexaosyl-*S*-glycoside **1** as donor, and then by glycosylation of the resulting propargyl maltohexoside with the *C*(4)-ethynylated donor **19**. The proximity of the terminal units of maltooligosaccharides allowed a facile intramolecular cycloaddition of the azido alkyne **29** to the isomeric triazoles **30** and **31**, which were deprotected to **32** and **33**, respectively. Analysis of the intramolecular H-bonds in **6**, **23**, **25**, **32**, and **33** showed that insertion of a noncarbohydrate link interrupts a single flip-flop H-bond.

Introduction. – The enzymatic degradation of starch leads to linear and cyclic oligosaccharides (dextrins or amyloses, and cyclodextrins, resp.) [2]. Cyclodextrins (CDs, cycloamyloses) are the major cyclic oligosaccharides obtained upon this degradation. Their formation has been correlated with the helical structure of starch and the proximity of glucosyl units separated by approximately one turn. Similarly, the preferred conformation of amyloses of appropriate length results in the proximity of the terminal glucosyl units and should favour the interaction of substituents attached to them. Indeed, intramolecular glycosylations used in the total synthesis of CDs proceeded remarkably well [3]. With the goal of obtaining novel CD analogues, we have synthesised amyloses carrying a terminal ethynyl group at C(1^{I}) and at C(4^{VIII}). They were prepared by glycosidic attachment of (ethynyl)glucosyl units to amyloses obtained by an efficient acetolysis of cyclodextrins [4]. As expected, the resulting dialkynes cyclise readily under the conditions of the *Hay* coupling, even if the newly introduced (ethynyl)glucosyl moieties are attached *via* β-D-glucosidic bonds. The resulting CD analogues possess a buta-1,3-diyne-1,4-diyl moiety and differ markedly in the shape of their cavities. Their synthesis, however, is fairly long, albeit well worked out, and proceed with good yields. It also lengthens the original amylose by two glucosyl units. For these reasons, we wished to replace one or both ethynylated glucosyl units by propargyl (= prop-2-yn-1-yl) moieties. This should shorten the synthesis, and restrict or

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prevent lengthening of the amylose precursor. Extensive studies on the intramolecular homo- and heterocoupling of *C*-ethynylated saccharides [1][5–7] argued well for the cyclisation of such propargyl glycosides, as did the independent studies of the homocoupling of such glucosides by *Roy et al.* [8]. We also intended to demonstrate the versatility of the butadiyne moiety by transforming it into a thiophene unit. To take further advantage of the proximity of terminal substituents of maltodextrins and to illustrate its consequences for the preparation of CD analogues, we considered to examine an intramolecular 1,3-dipolar cycloaddition. We also intended to analyse the intramolecular H-bonds of the new CD analogues, and to compare them to those of CDs.

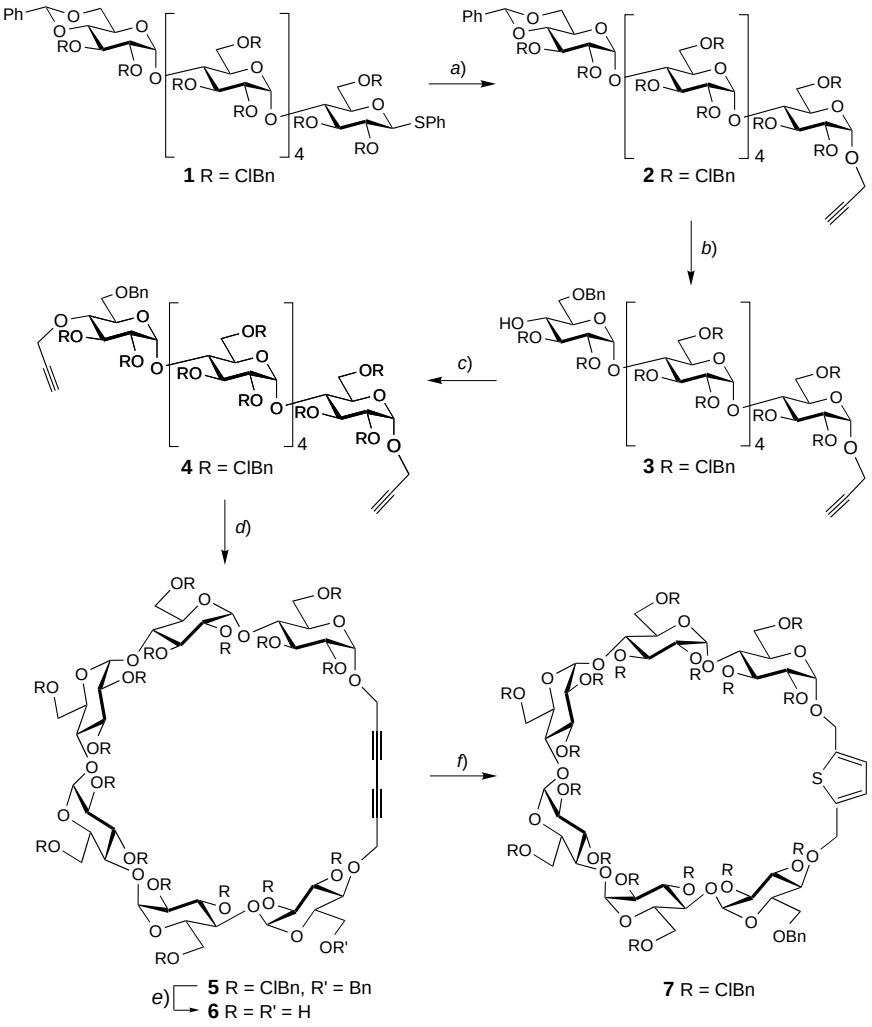
Results and Discussion. – The 4-chlorobenzylated maltohexaosyl *S*-glycoside **1** is available from α-CD in six steps and in an overall yield of 55% on a 50-g scale [4]. It reacted with propargyl alcohol under standard glucosylation conditions (*N*-iodosuccinimide (NIS), trifluoromethanesulfonic acid (TfOH), Et_2O) [4] to yield 92% of the α-hexaoside **2** (*Scheme 1*). The 1,3-dioxane ring of **2** was cleaved with Et_3SiH in the presence of $BF_3 \cdot Et_2O$ [9], providing the alcohol **3** in 82% yield. Alkylation of **3** with propargyl bromide gave the dialkyne **4** (88% yield), which cyclized under the conditions of the *Eglinton* reaction at 60° [6][10] to the α-CD analogue **5** (83%). Treatment of **5** with $FeCl_3$ in CH_2Cl_2 (cf. [5][11]) resulted in the completely deprotected **6** (52%). The buta-1,3-diyne derivative **5** was converted in 70% yield into the thiophene derivative **7** by heating with $Na_2S \cdot 9\ H_2O$ in 2-methoxyethanol [12].

Similarly as described for the acetolysis of α-CD [13], treatment of the fully acetylated γ-CD **8** under our improved conditions [4] cleaved one glycosidic bond, yielding 80% of the acetylated anomeric maltooctaoses **9** (*Scheme 2*). This mixture (α/β 10:1) was converted to the (phenylthio)-β-octaoside **10** (79%) according to *Hanessian*'s method [14]. Deacetylation of **10** yielded 98% of the *S*-glycoside **11**. Its benzylidene acetal **12** was best prepared with α,α-dibromotoluene in pyridine according to the method of *Garegg* and *Swahn* [15], and isolated by chromatography as a 1:1 adduct with Et_3N. It was chlorobenzylated to **13** (81% from **11**). This fully protected thioglycoside was transformed into the α-D-glycoside **14** (92%) by treatment with propargyl alcohol under standard conditions, followed by cleavage of the 1,3-dioxane ring with ($Et_3SiH/BF_3 \cdot Et_2O$). The resulting alcohol **15** (71%) was alkylated with propargyl bromide to the dialkyne **16** (91%), which was cyclised with $Cu(OAc)_2$ in pyridine at 60°. The buta-1,3-diyne derivative **17** was isolated in 78% by chromatography and deprotected similarly as described for **5** to provide the γ-CD analogue **18** in 48% yield.

The last cyclisations based upon the oxidative coupling of a dialkyne were performed with the anomeric heptaosides **20** and **21** (*Scheme 3*). They were obtained by glycosylation of the propargyl maltohexaoside **3** with the ethynylated thioglycoside **19** [4] under standard conditions in 82% yield (**20**/**21** 45:55), and isolated by flash chromatography. Upon treatment with excess $Cu(OAc)_2$ in dilute solution (0.41 mM) in pyridine, **20** cyclised to **22** (78%), and **21** to **24** (73%). Deprotection of **22** and **24** with $FeCl_3$ in CH_2Cl_2 yielded the β-CD analogues **23** and **25** in 80 and 77%, respectively.

The α-D-configuration of unit I of **2** and **14** is evidenced by the *d* for H–C(1^I) at 5.13 and 5.12 ppm ($J = 3.0$ and 3.6 Hz), and the *d* for C(1^I) at 94.5 and 94.7 ppm, respectively. The propargyl moiety of **2** and **14** is evidenced by the alkynyl H-atom, resonating as a *t* at 2.48 ppm ($J = 2.1$ and 2.4 Hz, resp.), two ^{13}C alkynyl *s* [16]

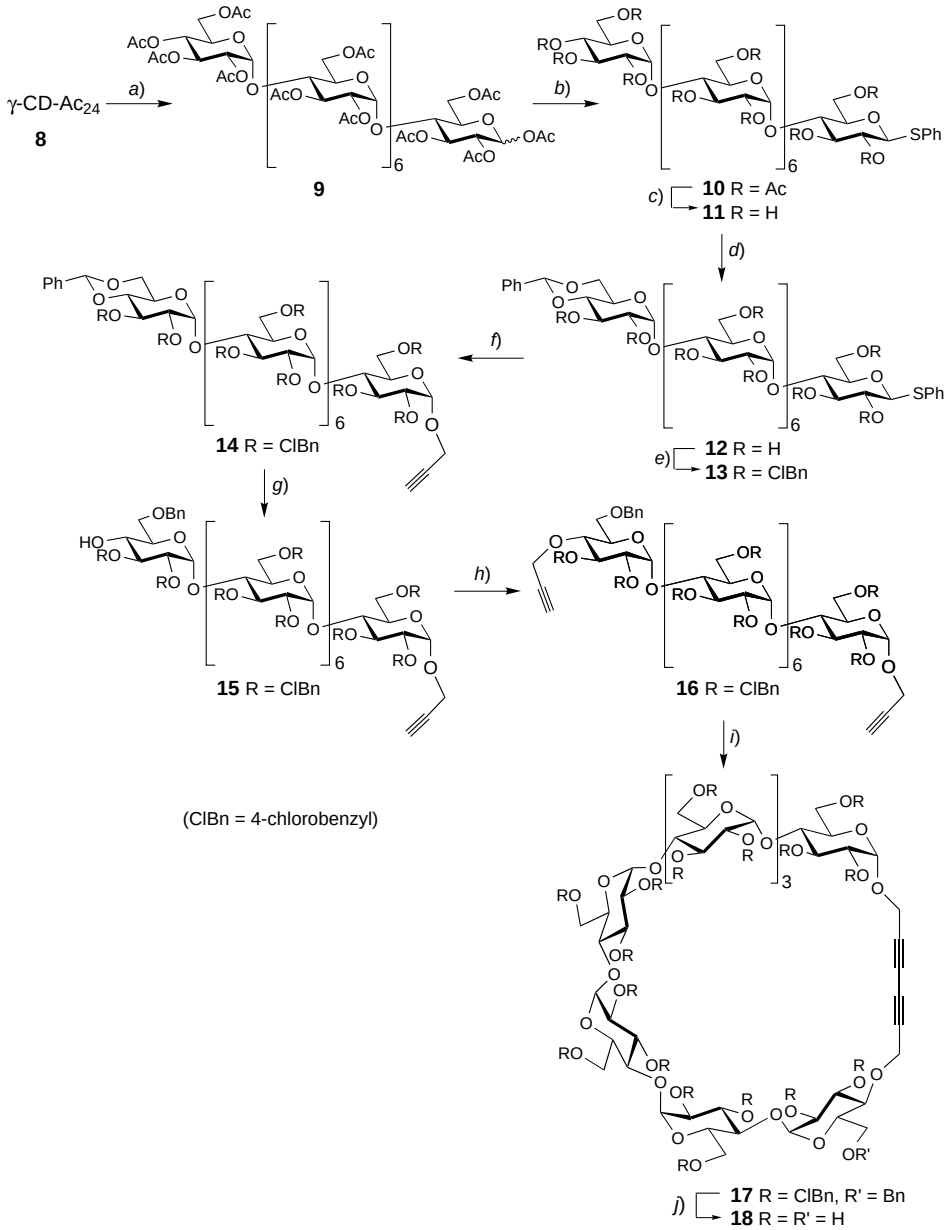
Scheme 1



a) $HOCH_2C{\equiv}CH$, NIS, TfOH, 3-Å molecular sieves, Et_2O, $-60°$; 92%. *b*) Et_3SiH, $BF_3 \cdot Et_2O$, CH_2Cl_2; 82%. *c*) $BrCH_2C{\equiv}CH$, NaH, DMF; 88%. *d*) $Cu(OAc)_2$, pyridine, 60°; 83%. *e*) $FeCl_3$, CH_2Cl_2; 52%. *f*) $Na_2S \cdot 9\,H_2O$, $MeOCH_2CH_2OH$; 70%.

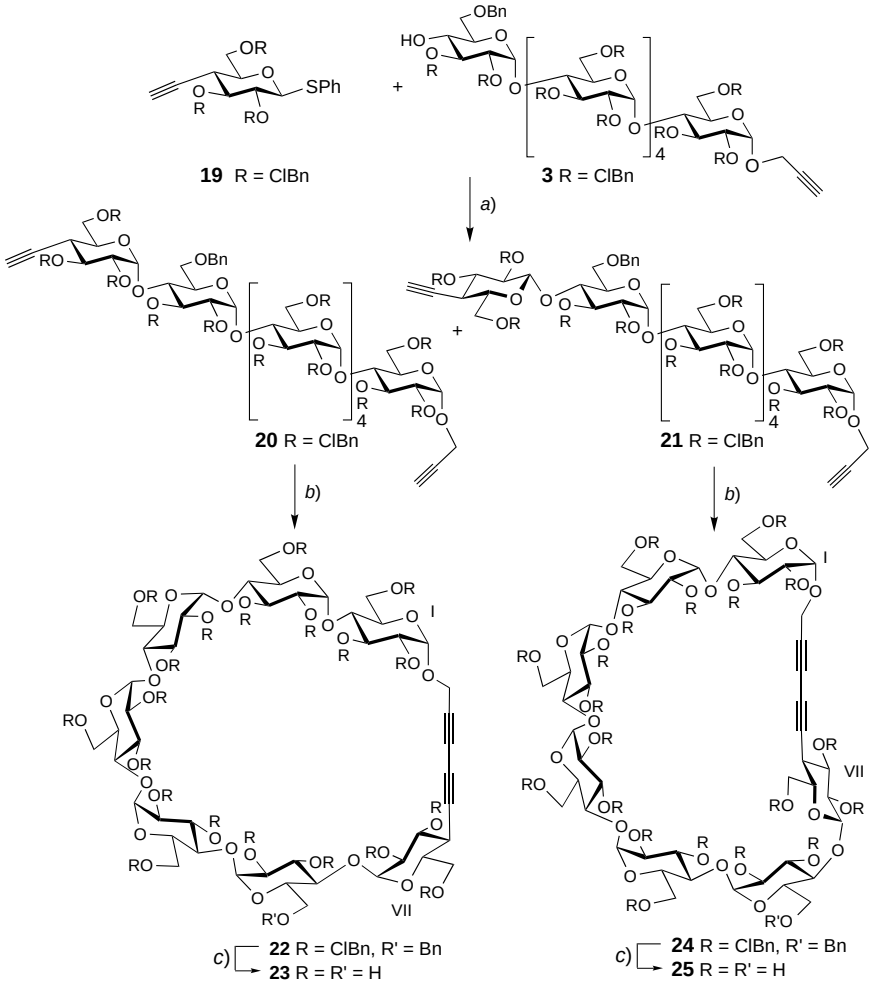
(78.9 and 75.3 ppm for **2**; 78.7 and 75.1 ppm for **14**), and a ^{13}C *t* (54.7 and 54.8 ppm). The regioselectivity of the dioxane ring opening, leading to **3** and **15**, is evidenced by the C(4)O*H d* at 2.67 ppm, while *J*(4,OH) of 2.3 Hz is typical of an intramolecular H-bond to the neighbouring O–C(3) [17][18]. The second propargyl group in **4** and **16** is evidenced by an additional *t* at 2.41 ppm ($J = 2.4$ Hz) for the alkynyl H-atom, and a *dd* at 4.15 ppm ($J = 2.4$ and 15.8 Hz), corresponding to 1 H of the propargylic CH_2 group, the other one being hidden; the corresponding ^{13}C-signals are *s*'s at 79.8 and 74.5 ppm and a *t* at 60 ppm (same value for **4** and **16**). The cyclisation of **4** to **5** and of **16** to **17** is evidenced by the disappearence of the acetylenic H-signals and typical ^{13}C resonances of a buta-1,3-diyne-1,4-diyl moiety. The ring closure is accompanied by a downfield shift of 1.5–

Scheme 2



a) 70% aq. $HClO_4$, Ac_2O; α-**9**/β-**9** 10:1 (80%). *b*) ZnI_2, Me_3SiSPh, CH_2Cl_2; 79%. *c*) 1M NaOMe in MeOH; 98%. *d*) $PhCHBr_2$, pyridine. *e*) NaH, 4-Cl-$C_6H_4CH_2Cl$, Bu_4NI, DMF; 81% from **11**. *f*) $HOCH_2C{\equiv}CH$, NIS, TfOH, 3-Å molecular sieves, Et_2O, $-60°$; 92%. *g*) Et_3SiH, $BF_3 \cdot Et_2O$, CH_2Cl_2; 71%. *h*) $BrCH_2C{\equiv}CH$, NaH, DMF; 91%. *i*) $Cu(OAc)_2$, pyridine, 60°; 78%. *j*) $FeCl_3$, CH_2Cl_2; 48%.

Scheme 3



a) NIS, TfOH, 3-Å molecular sieves, toluene, $-60°$; **20** (37%) and **21** (82%). *b*) $Cu(OAc)_2$, pyridine, 60°; **22** (78%); **24** (73%). *c*) $FeCl_3$, CH_2Cl_2; **23** (80%); **25** (77%).

3 ppm for CH_2 and of 0.33–0.44 ppm for H–C(1^{I}) of **5** and **17**. One also observes an upfield shift of $\geq$0.34 ppm for H–C(1^{II-VI}), and >0.3 ppm for H–C(4^{VI}) of **5**, and one of $\geq$0.13 ppm for H–C($1^{II-VIII}$) of **17**. The geminal coupling constants of the C≡CCH_2 groups of **5** are 16.5 and 15.2 Hz, and hint at a different arrangement of the propargylic CH_2 group and the lone pairs of the geminal O-atoms (*cf.* [19]). The anomeric H–C(1^{II-VI}) of **6** in D_2O resonate at 5.24–5.06 ppm, slightly upfield from the anomeric H–C($1^{II-VIII}$) of **18** (5.30–5.11 ppm), whereas H–C(1^{I}) of **6** and **18** resonate nearly at the same position (4.94 *vs.* 4.92 ppm). The two C≡CCH_2 groups of **6** show different geminal coupling constants (J = 16.0 *vs.* 17.0 Hz); $\Delta J \approx 1$ Hz is similar to that observed for **5**, and in agreement with a similar ring conformation of the protected and the deprotected

hexasaccharides. Only one of the corresponding geminal coupling constants of **18** could be assigned (16.9 Hz), and the spectrum of **17** was not amenable to a similar analysis. In the ^{13}C-NMR spectra, 4*s* at 78.6, 77.8, 72.7, and 71.9, and at 78.5, 78.4, 72.8, and 72.39 ppm reveal the buta-1,3-diyne-1,4-diyl moieties of **6** and **18**, respectively.

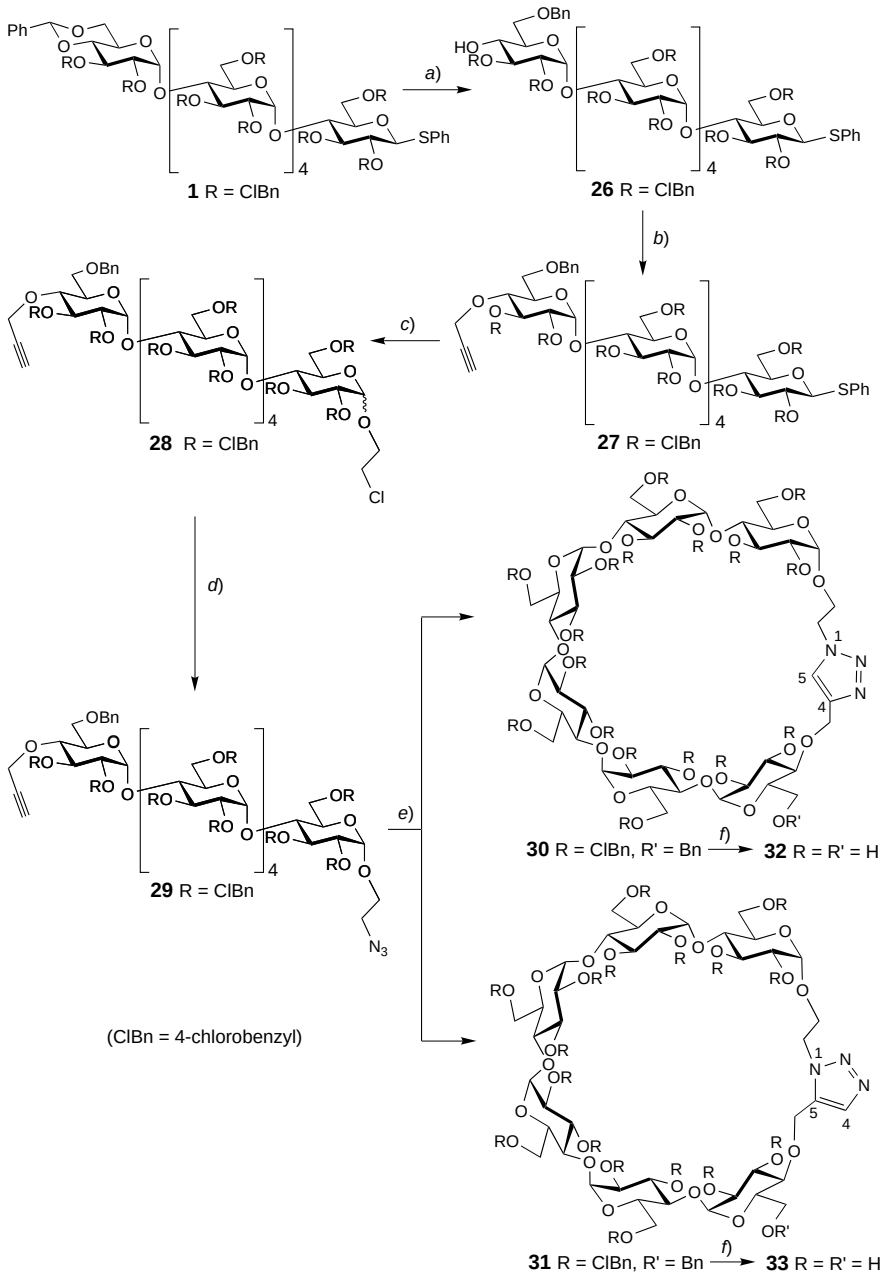
The ^{1}H-NMR spectra of **20** and **21** show signals for the acetylenic H-atom of the propargyl group as a *t* at 2.48 ppm ($J = 2.4$ Hz), while the ethynyl groups give rise to a *d* at 2.16 ($J = 2.2$ Hz) and 2.17 ppm ($J = 2.3$ Hz), respectively. The β-D-configuration of **21** is evidenced by $J(1^{VII},2^{VII}) \approx 8.6$ Hz, and by the C(1^{VII}) *d* at 102.3 ppm, whereas C(1^{VII}) of **20** resonates at a similar position as C(1^{I-VI}) (97.5–96.4 ppm). The cyclisation of **20** and of **21** is accompanied by the disappearance of the acetylenic H-signals. The ^{13}C-NMR spectra of the products do not reveal all signals of the buta-1,3-diyne unit, only three are visible for **22** (77.75, 70.83, 67.84 ppm), and only two for **24** (70.01, 67.99 ppm). Both ring closures lead to an upfield shift for H–C(1^{II-VII}) (≥ 0.24 ppm), and, opposite to that observed upon cyclisation of **4** and of **16**, also to an upfield shift for H–C(1^{I}) ($\Delta\delta = 0.38$ ppm). As expected, deprotection of **22** to **23**, and of **24** to **25** did not affect the anomeric configuration. H–C(1^{VII}) of **23** resonates together with H–C(1^{II-VI}) at 5.25–5.09 ppm (H–C(1^{I}) at 4.93 ppm), while H–C(1^{VII}) of **25** is hidden by the HDO signal (4.83 to 4.72 ppm); the six α-anomeric H–C(1) resonate between 5.24 and 5.11 ppm. The β-anomeric C(1^{VII}) of **23** resonates at 100 ppm, whereas the α-anomeric C(1) of **23** and **25** resonate at 102.2–104.2 ppm.

Thus, the oxidative dimerisation of the dialkynes **4**, **16**, **20**, and **21** proceeded well, as expected. To show that ring closure is not restricted to this type of reaction, we decided to transform the maltohexaose **1** into an azido alkyne, and to examine its intramolecular 1,3-dipolar cycloaddition [20]. Reductive opening of the dioxane ring of the hexasaccharide **1** yielded the desired secondary alcohol **26** (74%; *Scheme 4*)). Alkylation with propargyl bromide gave the propargyl ether **27** (87%), and glycosidation of **27** with 2-chloroethylalcohol yielded 95% of **28** as a mixture of anomers (α/β 9:1), which were separated by flash chromatography. Nucleophilic substitution of α-**28** with NaN_3 in DMF led to the azido alkyne **29**. This compound is stable at room temperature. The desired intramolecular 1,3-dipolar cycloaddition took place at 110° and gave the 1,4- and 1,5-substituted 1,2,3-triazoles **30** (24%) and **31** (31%), respectively, after chromatography. Deprotection of **30** and **31** with $FeCl_3$ in CH_2Cl_2 yielded the α-CD analogues **32** and **33** in 68 and 66% yield, respectively.

The spectral data of **26** are readily interpreted by comparison with those of **1** and **3**; similarly, those of **27** were compared to those of **1** and **4**. H–C(1^{I}) of α-**28** resonates as a *d* at 4.87 ppm ($J = 3.6$ Hz), downfield from the H–C(1^{I}) *d* of β-**28** at 4.48 ppm ($J = 7.9$ Hz). The configuration of **28** is corroborated by the chemical shifts of C(1^{I}) (α-**28**: 96.76, β-**28**: 103.59 ppm). The CH_2 of the chloroethyl group of α/β-**28** appear as *t*'s at 68.5–68.7 and 42.9 ppm. Azidation leads to a downfield shift of 7.8 ppm of the *t* at 42.9 ppm. The intramolecular 1,3-dipolar cycloaddition of **29** to **30** and **31** is evidenced by the replacement of the acetylenic H-signal by a triazole H-signal at 7.41 ppm for **30** and at 7.30–6.86 ppm for **31**. The 1,4-substitution of **30** and the 1,5-substitution of **31** are revealed by the characteristic chemical shifts of the triazole C(4) and C(5), respectively (**30**: *d* at 127.8, *s* at 145.5 ppm [21][22]; **31** *d* at 134.2, *s* hidden by ClBn *s* at 133.9–132.9 ppm [21–24]). The ^{13}C-NMR spectra of **30** and **31** show a *t* for C=CCH_2O (**30**: 66.6 ppm, **31**: 61.2 ppm) and two *t* for OCH_2CH_2N (**30**: 66.1 and 49.4 ppm; **31**: 68.3 and 47.3 ppm). The cycloaddition of **29** to **30** and **31** is accompanied by an upfield shift for H–C(1^{I}) (**30**: 0.06 ppm, **31**: 0.11 ppm) and for H–C(1^{II-VI}) (≥ 0.28 ppm).

Before analysing the intramolecular H-bonds of **6**, **23**, **25**, **32**, and **33**, we have examined the intramolecular H-bonds of CDs. Intramolecular H-bonding in CDs has been specified by crystal-structure analysis and ^{1}H-NMR spectroscopy. Crystal-structure analysis has revealed H-bonds between C(3)O–H$\cdots$OC(2′) and C(2′)O–H$\cdots$OC(3) for α-CD [25–29], flip-flop H-bonds between C(3)OH and C(2′)OH for β-CD [30], and four C(2′)O–H$\cdots$OC(3) and three C(3)O–H$\cdots$OC(2′) for γ-CD [31]. ^{1}H-NMR Spectroscopy of CDs in (D_6)DMSO has been the major

Scheme 4



a) Et_3SiH, $BF_3 \cdot Et_2O$, CH_2Cl_2; 74%. *b*) $BrCH_2C{\equiv}CH$, NaH, DMF; 87%. *c*) $ClCH_2CH_2OH$, NIS, TfOH, 3-Å molecular sieves, Et_2O, $-60°$; α-**28** (85%) and β-**28** (10%). *d*) α-**28**, NaN_3, DMF; 91%. *e*) DMF, 110°; **30** (24%) and **31** (31%). *f*) $FeCl_3$, CH_2Cl_2; **32** (68%); **33** (66%).

method for characterizing intramolecular H-bonds in solution. Slow exchange of OH protons in this solvent leads to well-separated OH signals and allows an accurate determination of the J(H,OH) values. Weak intramolecular H-bonds are readily broken in favour of H-bonds to DMSO. Intramolecular H-bonds between C(3)OH and C(2′)OH of CDs can involve C(3)OH or C(2′)OH as H-bond donors (C(3)O–H$\cdots$OC(2′) or (C(2′)O–H$\cdots$OC(3)), or be of an intermediate type where the two H-bonded species are in equilibrium (flip-flop H-bonds). *Casù* and *Reggiani* [32] were the first to postulate intramolecular H-bonds between HO–C(2′) and HO–C(3) on the basis of a downfield shift for both OH groups. *St-Jacques et al.* [33] observed a smaller $\Delta\delta/\Delta T$ for HO–C(3) than for HO–C(2′), and concluded that HO–C(3) acts (exclusively) as H-donor to O–C(2′) of α- and β-CD. *Christofides et al.* [34] also found that HO–C(3) acts as H-donor, based on SIMPLE ^{1}H-NMR experiments. *Onda* et *al.* [35] have reported increasing $|\Delta\delta(\mathrm{OH})/\Delta T|$ values for α-, β-, and γ-CD, but did not analyse the δ(OH) values. They deduced an increasing importance of flip-flop H-bonds, concluding that HO–C(3) in α- and β-CDs acts mainly as H-bond donor, whereas H-bonds in γ-CD are mainly of the flip-flop type (*Table 1*). *Bernet* and *Vasella* [17][18] have assigned the intramolecular and intermolecular H-bonds of mono- and oligosaccharides in (D_6)DMSO on the basis of an interpretation of combined δ(OH), J(H,OH), and $\Delta\delta$(OH)/ΔT values. The involvement of an OH group as H-donor in an intramolecular H-bond is revealed by an upfield shift, as compared to the shift calculated for a fully solvated OH group. A downfield shift for two OH groups may indicate a flip-flop H-bond between them. According to this analysis, a solution of maltose in DMSO is characterized by a *ca.* 2:1 equilibrium of the O(3)–H$\cdots$O(2′) and O(2′)–H$\cdots$O(3) H-bonded species [17].

Table 1. *Chemical Shifts* [ppm], *Vicinal Coupling Constants* [Hz], *and* $\Delta\delta/\Delta$T *Values* [ppb/K] *for the OH Groups of CDs in (*D_6*)DMSO at 35°* (exper. data from [35])

	HO–C(2)			HO–C(3)			HO–C(6)	
	δ(OH)	J(H,OH))	$\Delta\delta/\Delta$T	δ(OH)	J(H,OH))	$\Delta\delta/\Delta$T	δ(OH)	$\Delta\delta/\Delta$T
α-CD	5.32	7.0	−4.36	5.26	2.8	−2.67	4.28	−5.21
β-CD	5.52	6.7	−5.42	5.48	2.5	−4.16	4.26	−5.66
γ-CD	5.53	7.0	−5.59	5.57	2.5	−4.64	4.32	−5.59
Calc. for α-, β-, γ-CD [a])	5.10			5.10			4.48	
α-DMCD [b])	–	–		4.45	*ca.* 0	−1.61	–	–
β-DMCD [b])	–	–		4.70	*ca.* 0	−1.67	–	–
Calc. for α- and β-DMCD [a])				5.45				

[a]) Value for a completely solvated OH group. Calculated from the δ(OH) values for β-glucopyranose and an increment of +0.25 ppm for replacing a vicinal OH by OR and +0.1 ppm for replacing another OH by an OR group, and a correction for temperature (assuming $\Delta\delta/\Delta$T = −6 ppb/K) [17]. [b]) DMCD: Per-2,6-di-*O*-methyl-α- and β-CD.

The interpretation of the data of *Onda et al.* [35] on the basis of the rules of *Bernet* and *Vasella* [17][18] leads to the following result: $\Delta\delta$(OH)/ΔT for HO–C(3) of −1.6 ppb/K for α/β-DMCD (per-2,6-di-*O*-methyl-CD; *Table 1*) indicates that HO–C(3) is involved in a completely persistent intramolecular H-bond. J(3,OH) of

ca. 0 Hz corresponds to a H–C(3)–O–H dihedral angle of *ca.* 90°. This coupling and the upfield shift ($\Delta\delta^{e/c} = 0.75 - 1.0$ ppm)[2]) confirm that HO–C(3) acts exclusively as a H-donor in the inter-residue C(3)O–H···O(2′) H-bond. α-, β-, and γ-CD show a larger J(3,OH) (2.5–2.8 Hz) than α- and β- DMCDs, and a stronger temperature dependence for HO–C(3) (α-CD: −2.7, β-CD: −4.2, γ-CD: −4.64 ppb/K). These values evidence a partially persistent C(3)O–H···OC(2) H-bond and are in keeping with a flip-flop H-bond. The temperature dependence for HO–C(2) of these CDs is larger than for HO–C(3) (−4.4 to −5.6 ppkb/K) and indicates that HO–C(2) acts preferentially as H-acceptor. The flip-flop H-bonds of α-, β- and γ-CDs are confirmed by a downfield shift for both HO–C(2) and HO–C(3) ($\Delta\delta^{e/c} = 0.16 - 0.22$ ppm for α-CD, 0.38–0.47 ppm for β-CD, and 0.43–0.47 ppm for γ-CD). The similar extent of the downfield shifts for HO–C(2) and HO–C(3) (α-CD: $\Delta\Delta\delta^{e/c} = 0.06$, β-CD: $\Delta\Delta\delta^{e/c} = 0.04$, γ-CD: $\Delta\Delta\delta^{e/c} = -0.04$ ppm)[3]) is in keeping with a nearly 1:1 ratio of the C(3)O–H···OC(2′) and C(2′)O–H···OC(3) H-bonded species. The δ(OH) values of α-CD agree with those of α/β-maltose and amylose [17][33]. This analysis does not, however, rationalise the stronger downfield shift of HO–C(2) and HO–C(3) of β- and γ-CD, and their stronger temperature dependence.

DFQCOSY.GRASP and TOCSY spectra allowed the unambiguous assignment of the HO–C(2) and HO–C(3) signals of the terminal glucopyranosyl units of **6**, **23**, **25**, **32**, and **33**, except for HO–C(3^{I}) of **32** and **33**, and HO–C(2^{VI}) of **33** (*Table 2*). HO–C(2) and HO–C(3) of the central units[4]) of **6**, **23, 25**, **32**, and **33** were distinguished on the basis of their coupling (J(2,OH) = 6.4–7.3 Hz and J(3,OH) = 2.5–3.4 Hz), but could not be assigned to the individual central units. HO–C(2) and HO–C(3) of the central units resonate at 5.48–5.78 ppm, and thus at a similar position as HO–C(2) and HO–C(3) of β- and γ-CD (5.48–5.57 ppm), but clearly downfield from HO–C(2) and HO–C(3) of α-CD (5.26–5.32 ppm). This reveals a *ca.* 1:1 equilibrium of flip-flop H-bonded species. Thus, in this respect, the hexaosides **6**, **32**, and **33** are analogues of β-CD rather than of α-CD. The downfield shift for HO–C(3^{I}) of **6**, **23**, and **25** (5.57–5.60 ppm), for HO–C(2^{VI}) of **6** and **32**, and for HO–C(2^{VII}) of **23** (5.61–5.70 ppm) indicate that these OH groups are involved in inter-residue flip-flop H-bonds. HO–C(2^{I}) of **6**, **23**, **25**, **32**, and **33** resonates at higher fields (**6**, **23**, **25**, and **32**: 5.0–5.04 ppm, **33**: 4.80 ppm) and at a similar position as HO–C(2) of methyl α-maltoside (4.90 ppm [36]), evidencing a weakly persistent intra-residue H-bond to O–C(1^{I}) as it is typical for α-D-glucopyranosides (*cf.* [17]). HO–C(3^{VI}) (terminal unit) of **6**, **32**, and **33** shows a distinctly larger J(H,OH) value (5.6–5.7 Hz) than HO–C(3) of the central units, indicating that HO–C(3^{VI}) is more or less completely solvated. The near absence of a flip-flop H-bond is indicated by an upfield shift ($\Delta\delta^{e/c} \approx$ 0.35 ppm relative to δ(HO–C(3) of the central units); indeed, the chemical shift of HO–C(3^{VI}) (5.21–5.23 ppm) is not very different from the calculated value of 5.10 ppm for a completely solvated equatorial OH group. In spite of the downfield shift (5.48–5.50 ppm) and the larger J(H,OH) values (6.4–6.5 Hz) the HO–C(3^{VII}) groups

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[2]) $\Delta\delta^{e/c}$ represents the difference between the experimental and the calculated chemical shift values, $\Delta\Delta\delta^{e/c}$ the difference between $\Delta\delta^{e/c}$ for the specified signals.

[3]) Compare to $\Delta\Delta\delta^{e/c} = 0.11$ ppm for a 2:1 ratio of these species of α- and β-maltose [17].

[4]) All units, except the terminal ones.

(terminal unit) of **23** and **25** are also fully solvated. They are vicinal to a *trans* equatorial butadiynyl group, and this is, indeed (*cf.* [37]), accompanied by a downfield shift ($\Delta\delta(OH) \approx 0.3$ ppm) and by an increase of $J(H,OH)$ ($\Delta J \approx 0.8$ Hz). The heptaoside **25** is the only CD analogue of this series containing a β-D-glucopyranosyl unit (unit VII). A typical cellobiosyl unit possesses a strong inter-residue HO–C(3)···O–C(5′) H-bond and is characterized by a small $J(H,OH)$ value of ≤ 2.0 Hz [17][38] and a strong upfield shift (4.78 ppm for HO–C(3) of methyl β-cellobioside [17]). In contrast to this, $J(3^{VI},OH)$ of *ca.* 4.0 Hz and $\delta(HO-C(3^{VI})) = 4.98$ ppm evidence a weekly persistent inter-residue H-bond, similarly as observed in 4-*O*-β-D-glucopyranosyl-D-xylopyranosides [17][39], indicating at least some ring tension in **25**. As expected, all HO–C(6) of **6**, **23**, **25**, **32**, and **33** are completely solvated.

Table 2. *Chemical Shifts* [ppm] *and Vicinal Coupling Constants* [Hz] *for the OH Groups of the CD Analogues* **6**, **23**, **25**, **32**, *and* **33** *in* (D_6)*DMSO at 25°*

Compounds		HO–C(2)		HO–C(3)		HO–C(6)	
		δ(OH)	J(H,OH))	δ(OH)	J(H,OH))	δ(OH)	J(H,OH))
Unit I	**6**	5.01	6.8	5.57	3.0	[a])	
	23	5.04	6.4	5.59	3.0	[a])	
	25	5.01	6.5	5.60	2.5	[a])	
	32	5.00	6.1	[a])		[a])	
	33	4.80	6.3	[a])		[a])	
Units II–V [b])	**6**	5.56–5.76	6.6–6.9	5.58–5.62	2.9–3.4	4.45–4.50	
	23	5.60–5.75	6.0–6.6	5.67–5.78	2.6–3.1	4.48–4.55	5.5–6.0
	25 [c])	5.50–5.68	6.7	5.62–5.73	2.7	4.47–4.56	5.5–5.9
	32	5.52–5.72	6.6–7.3	5.57–5.73	2.5–2.8	4.43–4.55	5.2–5.6
	33	5.61–5.71	6.4–6.6	5.48–5.74	2.6–3.0	4.41–4.51	5.1–5.7
Unit VII [d])	**6**	5.61	6.9	5.22	5.6	4.70	6.0
	23	5.70	6.8	5.50	6.4	4.77	5.8
	25	5.55	3.9	5.48	6.5	4.65	5.6
	32	5.70	6.8	5.21	5.7	4.63	5.9
	33	[a])		5.23	5.7	[a])	

[a]) Not assigned (included in the signals for units II–V). [b]) Unit II–VI of **23** and **25**. [c]) $\delta(HO-C(3^{VI})) = 4.98$ ppm, $J(3^{VI},OH) \approx 4.0$ Hz. [d]) Unit VI of **6**, **32**, and **33**.

Thus, the introduction of a noncarbohydrate link in CDs interrupts a single flip-flop H-bond only. The C(2)OH group vicinal to the link should be a better HO donor than the C(2)OH groups of the central units.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche*, Basel, for generous support and Mrs. *B. Brandenberg* for measuring the 500-MHz spectra.

Experimental Part

General. See [4].

Prop-2-yn-1-yl 2,3-Bis-O-*(4-chlorobenzyl)-4,6*-O-*benzylidene-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranoside* (**2**). Under Ar, a suspension of **1** [4] (25 g, 7.6 mmol), propargyl alcohol (1.3 ml, 22.8 mmol), and 3-Å molecular sieves (25 g) in dry Et_2O (1000 ml) was stirred at $-60°$ for 1 h, treated with NIS (3.07 g, 13.7 mmol) and TfOH (538 µl, 6.08 mmol), and stirred for 20 h at $-60°$. The suspension was filtered over *Celite*, washed with 10% aq. $Na_2S_2O_3$

soln. (500 ml), sat. aq. $NaHCO_3$ soln. (2 × 500 ml), H_2O (2 × 500 ml), and brine (500 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 60:1 → 30:1) gave **2** (22.6 g, 92%). White foam. R_f (toluene/AcOEt 18:2) 0.65. M.p. 58–60°. $[\alpha]_D^{25} = +60.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2928*m*, 2868*m*, 1600*m*, 1492*m*, 1457*m*, 1408*m*, 1361*m*, 1156*s*, 1090*s*, 1036*s*, 1016*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.38 (*m*, 4 arom. H); 7.28–6.84 (*m*, 69 arom. H); 5.53 (*s*, PhC*H*); 5.53–5.51 (*m*, 2 H), 5.48 (*d*, $J = 3.3$, 3 H) (H–C($1^{II–VI}$)); 5.13 (*d*, $J = 3.6$, H–C(1^I)); 4.91 (*d*, $J = 12.3$), 4.84 (*d*, $J = 11.4$), 4.76 (*d*, $J = 12.0$) (3 ArC*H*); 4.72–4.53 (*m*, 12 ArC*H*); 4.50–4.30 (*m*, 19 ArC*H*, $OCH_2C{\equiv}C$); 4.09–3.77 (*m*, 20 H); 3.70–3.56 (*m*, 8 H); 3.45–3.41 (*m,* 8 H); 2.48 (*t*, $J = 2.1$, C≡CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.61–136.18 (several *s*); 134.13–133.24 (several *s*); 129.71–126.17 (several *d*); 101.45 (*d*, PhC*H*); 98.04, 96.89, 96.68 (br., 3 C) (3*d*, C($1^{II–VI}$)); 94.75 (*d*, C(1^I)); 82.47 (*d*, C(4^{VI})); 81.78, 81.63, 81.55 (2 C), 81.42 (4*d*, C($3^{I–V}$)); 79.76 (4 C), 79.56, 78.88 (3*d*, C($2^{I–VI}$)); 78.79 (*d*, C(3^{VI})); 78.91 (*s*, *C*≡CH); 75.31 (*s*, C≡*C*H); 74.32–72.14 (several *t*); 73.91, 73.86, 73.70, 73.15, 73.02 (5*d*, C($4^{I–V}$)); 71.05 (2 C), 70.99, 70.86, 70.57 (4*d*, C($5^{I–V}$)); 68.93 (br. *t*, C($6^{I–VI}$)); 63.52 (*d*, C(5^{VI})); 54.80 (*t*, C≡C*C*H_2)). HR-MALDI: 3257.55 ($C_{165}H_{153}Cl_{17}NaO_{31}$, $[M + Na]^+$; calc. 3257.55). Anal. calc. for $C_{165}H_{153}Cl_{17}O_{31}$ (3234.70): C 61.27, H 4.77; found: C 61.35, H 4.89.

*Prop-2-yn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**3**). Under Ar, a soln. of **2** (22 g, 6.8 mmol) in dry CH_2Cl_2 (1000 ml) was stirred at −40° for 10 min, treated with Et_3SiH (21.6 ml, 136 mmol) and $BF_3 \cdot Et_2O$ (8.5 ml, 68 mmol), and stirred for 1 h at −60° and for 24 h at −10°. The soln. was washed with sat. aq. $NaHCO_3$ soln. (400 ml), H_2O (400 ml), and brine (400 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50:1 → 5:1) gave **3** (18.1 g, 82%). White foam. R_f (toluene/AcOEt 18:2) 0.39. M.p. 53–55°. $[\alpha]_D^{25} = +66.5$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2924*m*, 2868*m*, 1600*m*, 1492*m*, 1408*m*, 1361*m*, 1155*s*, 1091*s*, 1039*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.31–6.84 (*m*, 73 arom. H); 5.52 (*d*, $J = 3.6$), 5.49 (*d*, $J = 3.7$), 5.48–5.46 (*m*, 3 H) (H–C($1^{II–VI}$)); 5.12 (*d*, $J = 3.6$, H–C(1^I)); 4.91 (*d*, $J = 12.0$), 4.75 (*d*, $J = 12.0$) (2 ArC*H*); 4.70–4.63 (*m*, 7 ArC*H*); 4.62 (*d*, $J \approx 11.9$), 4.61 (*d*, $J = 12.0$, 2 H), 4.58 (*d*, $J \approx 12.0$), 4.55 (*d*, $J = 11.9$), 4.47 (*d*, $J \approx 12.0$), 4.46 (*d*, $J = 11.4$, 2 H), 4.45 (*d*, $J = 10.6$, 2 H) (10 ArC*H*); 4.38–4.29 (*m*, 17 ArC*H*, OC*H*C≡CH); 4.28 (*dd*, $J = 2.4$, 15.8, OC*H*C≡CH); 4.01–3.84 (*m,* H–C($3^{I–V}$), H–C($4^{I–V}$), 2 H–C(5), 1 H–C(6)); 3.82–3.73 (*m,* 3 H–C(5)); 3.73–3.64 (*m,* H–C(3^{VI}), H–C(5^{VI}), 4 H–C(6), 1 H′–C(6)); 3.64 (*dt*, $J = 2.3$, 9.2, H–C(4^{VI})); 3.58 (*dd*, $J = 3.7$, 9.3, H–C(2^{VI})); 3.53 (*dd*, $J = 3.7$, 9.7, H–C(6^{VI})); 3.49–3.41 (*m*, H–C($2^{II–V}$), 4 H′–C(6), H′–C(6^{VI})); 3.37 (*dd*, $J = 3.6$, 9.7, H–C(2^I)); 2.67 (*d*, $J = 2.3$, *H*O–C(4^{VI})); 2.47 (*t*, $J = 2.4$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.47–135.90 (several *s*); 133.86–132.76 (several *s*); 130.89–125.29 (several *d*); 97.18, 96.70, 96.48 (2 C), 96.44 (4*d*, C($1^{II–VI}$)); 94.56 (*d*, C(1^I)); 81.49, 81.45, 81.37, 81.35, 81.24, 81.21 (6*d*, C($3^{I–VI}$)); 79.59 (2 C), 79.55, 79.51, 79.39 (4*d*, C($2^{II–VI}$)); 78.87 (*d*, C(2^I)); 78.72 (*s*, *C*≡CH); 75.15 (*s*, C≡*C*H); 74.35–71.98 (several *t*); 73.70, 73.63, 73.61, 73.22, 73.08 (5*d*, C($4^{I–V}$)); 72.44 (*d*, C(4^{VI})); 70.93 (br., 3 C), 70.83, 70.41, 70.38 (4*d*, C($5^{I–VI}$)); 70.14 (*t*, C(6^{VI})); 68.94, 68.84 (br., 4 C) (2*t*, C($6^{I–V}$)); 54.66 (*t*, C≡C*C*H_2)). HR-MALDI: 3259.51 ($C_{165}H_{154}Cl_{17}NaO_{31}$, $[M + Na]^+$; calc. 3259.72). Anal. calc. for $C_{165}H_{154}Cl_{17}O_{31}$ (3235.71): C 61.25, H 4.80; found: C 61.09, H 4.93.

*Prop-2-yn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-4-*O*-(prop-2-yn-1-yl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**4**). Under Ar, a soln. of **3** (4 g, 1.23 mmol) in DMF (100 ml) was cooled to 0°, treated with NaH (55% in oil, 594 mg, 12.36 mmol), stirred for 15 min, treated with propargyl bromide (464 µl, 6.18 mmol), stirred at 0° for 1 h and at 23° for 10 h, treated dropwise with MeOH (5 ml), and diluted with H_2O (50 ml) and Et_2O (100 ml). The org. phase was separated, and the aq. phase was extracted with Et_2O (3 × 100 ml). The combined org. layers were washed with brine (100 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 50:1 → 20:1) gave **4** (3.5 g, 88%). White foam. R_f (toluene/AcOEt 18:2) 0.45. M.p. 44–45°. $[\alpha]_D^{25} = +68.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 2926*m*, 2868*m*, 1600*w*, 1492*m*, 1360*m*, 1298*m*, 1156*s*, 1090*s*, 1036*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.30–6.84 (*m*, 73 arom. H); 5.52 (*d*, $J = 3.6$), 5.48–5.46 (*m*, 3 H), 5.45 (*d*, $J = 3.6$) (H–C($1^{II–VI}$)); 5.12 (*d*, $J = 3.6$, H–C(1^I)); 4.90 (*d*, $J = 12.0$), 4.75 (*d*, $J = 12.0$), 4.71 (*d*, $J = 11.2$) (3 ArC*H*); 4.70–4.63 (*m*, 10 ArC*H*); 4.54 (*d*, $J = 11.9$), 4.48 (*d*, $J = 12.0$), 4.47 (*d*, $J = 12.0$), 4.46 (*d*, $J = 10.9$), 4.44 (*d*, $J = 12.5$), 4.41 (*d*, $J = 12.4$) (6 ArC*H*); 4.38–4.29 (*m*, 17 ArC*H*, OC*H*C≡CH); 4.28 (*dd*, $J = 2.4$, 15.8, OC*H*C≡CH); 4.15 (*dd*, $J = 2.4$, 15.8, OC*H*C≡C); 4.01–3.78 (*m,* 17 H); 3.76–3.64 (*m,* 6 H); 3.58 (*dd*, $J = 3.7$, 9.3, H–C(2)); 3.50 (*dd*, $J = 3.4$, 9.0, H–C(2)); 3.49–3.40 (*m,* 3 H–C(2), 7 H–C(6)); 3.35 (*dd*, $J = 3.6$, 9.8, H–C(2)); 2.47 (*t*, $J = 2.4$, C≡CH); 2.41 (*t*, $J = 2.4$, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.69–135.90 (several *s*); 133.86–130.89 (several *s*); 129.59–127.31 (several *d*); 97.33, 96.69, 96.48 (2 C), 96.44 (4*d*, C($1^{II–VI}$)); 94.55 (*d*, C(1^I)); 81.59, 81.45, 81.38 (3 C), 81.24 (4*d*, C($3^{I–VI}$)); 79.81 (*s*, *C*≡CH); 79.58 (2 C), 79.54, 79.48, 79.39, 79.33 (5*d*, C($2^{I–VI}$)); 78.72 (*s*, *C*≡CH); 77.54 (*d*, C(4^{VI})); 75.15 (*s*, C≡*C*H); 74.53 (*s*, C≡*C*H); 74.51–71.98 (several *t*); 73.76

(3 C), 73.58, 73.12 (3*d*, C(4^{I-V})); 71.02, 70.96, 70.89, 70.87, 70.83, 70.41 (6*d*, C(5^{I-VI})); 69.00, 68.94, 68.83 (br., 3 C), 68.28 (4*t*, C(6^{I-VI})); 60.03 (*t*, C≡C*C*H$_2$C(4^{IV})); 54.66 (*t*, C≡CCH$_2$C(1^{I})). HR-MALDI: 3297.52 ($C_{168}H_{157}Cl_{17}NaO_{31}$, $[M+Na]^+$; calc. 3297.76).

*6-Hydroxyhexa-2,4-diyn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 6 : 4^{VI}-Anhydride* (**5**). A soln. of $Cu(OAc)_2$ (110 mg, 0.611 mmol) in pyridine (110 ml) was treated at 60° under Ar with a soln. of **4** (200 mg, 0.061 mmol) in pyridine (12 ml) within 3 h, stirred for 1 h, and evaporated. A soln. of the residue in AcOEt (80 ml) was washed with an aq. soln. of Na_4TMEDA (367 µl, 2.44 mmol), H_2O (40 ml), and brine (40 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40 : 1 → 20 : 1) gave **5** (166 mg, 83%). White foam. R_f (toluene/AcOEt 18 : 2) 0.41. M.p. 55–58°. $[\alpha]_D^{25} = +16.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2925*m*, 2868*m*, 1600*m*, 1492*s*, 1456*m*, 1407*m*, 1359*m*, 1137*s*, 1090*s*, 1039*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.28–6.89 (*m*, 73 arom. H); 5.24 (*d*, $J = 3.4$), 5.23 (*d*, $J = 3.2$), 5.15 (*d*, $J = 3.5$), 5.10 (*d*, $J = 3.3$), 5.02 (*d*, $J = 3.2$) (H–C(1^{II-VI})); 4.91 (*d*, $J \approx 11.3$), 4.89 (*d*, $J \approx 11.0$), 4.86 (*d*, $J = 10.9$), 4.85 (*d*, $J = 11.5$), 4.80 (*d*, $J = 11.6$), 4.77 (*d*, $J = 11.7$), 4.71 (*d*, $J = 11.0$) (7 ArC*H*); 4.68 (*d*, $J = 3.7$, H–C(1^{I})); 4.66 (*d*, $J = 11.0$), 4.62 (*d*, $J = 12.4$), 4.60 (*d*, $J \approx 12.0$), 4.58 (*d*, $J = 11.7$), 4.53 (*d*, $J \approx 13.3$), 4.50 (*d*, $J = 12.3$, 2 H), 4.49 (*d*, $J \approx 12.3$), 4.46 (*d*, $J \approx 12.7$), 4.45 (*d*, $J = 10.9$), 4.41 (*d*, $J \approx 11.4$) (11 ArC*H*); 4.40–4.24 (*m*, 18 ArC*H*, 2 OC*H*C≡C); 4.23 (*d*, $J = 16.5$, OCHC≡C); 4.05 (*d*, $J = 15.2$, OCHC≡C); 3.98 (br. *dd*, $J \approx 2.0$, 9.7, H–C(5)); 3.91–3.71 (*m*, H–C(3^{I-VI}), H–C(4^{I-V}), 3 H–C(5), H–C(6^{I-VI})); 3.65–3.63 (*m*, H–C(5)); 3.62 (br. *d*, $J = 11.2$, H′–C(6)); 3.55–3.48 (*m*, 1 H–C(5), 4 H′–C(6)); 3.46 (*dd*, $J \approx 3.6$, 10.5, H–C(2)); 3.39–3.35 (*m*, 4 H–C(2), H′–C(6)); 3.31 (*t*, $J = 9.0$, H–C(4^{VI})); 3.29 (*dd*, $J = 3.2$, 10.0, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.48–136.07 (several *s*); 133.93–132.47 (several *s*); 130.89–127.53 (several *d*); 99.16, 98.63, 98.60, 98.30, 98.13, 97.71 (6*d*, C(1^{I-VI})); 81.26, 81.16, 80.83, 80.80, 80.70 (2 C) (5*d*, C(3^{I-VI})); 79.70, 79.58, 79.42, 79.32, 79.29 (2 C) (5*d*, C(2^{I-VI})); 79.23, 79.02, 78.54, 78.03, 77.42, 77.15 (6*d*, C(4^{I-VI})); 75.57, 75.53 (2*s*, *C*≡C–C≡*C*); 74.72–72.17 (several *t*); 71.55 (2 C), 71.52, 71.12, 70.86, 70.81 (5*d*, C(5^{I-VI})); 70.16, 69.84 (2*s*, C≡*C*–*C*≡C); 69.50, 69.42, 69.04, 68.95, 68.63, 68.20 (6*t*, C(6^{I-VI})); 60.72 (*t*, C≡C*C*H$_2$C(4^{VI})); 57.63 (*t*, C≡C*C*H$_2$C(1^{I})). MALDI-MS: 3295,8 ($[M+Na]^+$). Anal. calc. for $C_{168}H_{155}O_{31}Cl_{17}$ (3272.75): C 61.66, H 4.77; found: C 61.75, H 4.88.

*6-Hydroxyhexa-2,4-diyn-1-yl [α-*D*-Glucopyranosyl-(1 → 4)]$_5$-α-*D*-glucopyranoside 6 : 4^{VI}-Anhydride* (**6**). A soln. of **5** (49 mg, 14.9 µmol) in CH_2Cl_2 (5 ml) was treated with $FeCl_3$ (43.7 mg, 0.269 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (0.5 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) gave **6** (8.2 mg, 52%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) 0.21. ^{1}H-NMR (500 MHz, D_2O): 5.24 (*d*, $J = 4.1$), 5.23 (*d*, $J = 4.1$), 5.095 (*d*, $J = 3.6$), 5.09 (*d*, $J = 3.8$), 5.06 (*d*, $J = 3.6$) (H–C(1^{II-VI})); 4.94 (*d*, $J = 4.0$, H–C(1^{I})); 4.55, 4.45 (AB, $J = 16.0$, C≡CCH$_2$); 4.53, 4.38 (AB, $J = 16.9$, C≡CCH$_2$); 3.98 (*dd*, $J = 9.0$, 9.9, 1 H); 3.94 (*dd*, $J = 8.9$, 10.0, 1 H); 3.93–3.76 (*m*, 21 H); 3.74 (*dd*, $J = 4.7$, 11.6, H–C(6)); 3.66–3.58 (*m*, 9 H); 3.57 (*dd*, $J = 3.5$, 10.0, H–C(2)); 3.55 (*dd*, $J = 3.6$, 9.9, H–C(2)); 3.33 (*t*, $J = 9.2$, H–C(4^{VI})). ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY and a TOCSY spectrum): 5.76 (*d*, $J = 6.8$, HO–C(2)); 5.72 (*d*, $J = 3.4$), 5.715 (*d*, $J = 2.9$) (2 HO–C(3)); 5.71 (*d*, $J = 6.9$), 5.66 (*d*, $J = 6.8$) (2 HO–C(2)); 5.63 (*d*, $J = 3.0$, HO–C(3)); 5.61 (*d*, $J = 6.9$, HO–C(2^{VI})); 5.58 (*d*, $J = 3.0$, HO–C(3)); 5.57 (*d*, $J = 3.0$, HO–C(3^{I})); 5.56 (*d*, $J = 6.6$, HO–C(2)); 5.22 (*d*, $J = 5.6$, HO–C(3^{VI})); 5.01 (*d*, $J = 6.4$, HO–C(2^{I})); 4.98 (*d*, $J = 3.8$), 4.95 (*d*, $J = 3.8$), 4.87 (*d*, $J = 3.7$), 4.84 (*d*, $J = 3.7$) (H–C(1^{II-V})); 4.83 (*d*, $J = 3.7$, H–C(1^{VI})); 4.70 (*t*, $J = 6.0$, HO–C(6^{VI})); 4.68 (*d*, $J = 3.6$, H–C(1^{I})); 4.61, 4.32 (AB, $J = 16.0$, C≡CCH$_2$); 4.50–4.45 (*m*, HO–C(6^{I-V})); 4.36 (br. *s*, C≡CCH$_2$); 3.63–3.54 (*m*, 20 H); 3.52–3.36 (*m*, 6 H); 3.35–3.27 (*m*, 7 H); 3.25 (*ddd*, $J = 3.6$, 6.4, 10.3, H–C(2^{I})); 3.20 (*ddd*, $J = 3.7$, 6.9, 9.5, H–C(2^{VI})); 3.12 (*t*, $J = 9.2$, H–C(4^{VI})). ^{13}C-NMR (125 MHz, D_2O): 104.32, 104.16, 103.74, 103.70, 103.50, 102.89 (6*d*, C(1^{I-VI})); 83.35, 83.20, 82.86, 81.82, 81.60, 80.59 (6*d*, C(4^{I-VI})); 78.66, 77.81 (2*s*, *C*≡C–C≡*C*); 75.85, 75.74 (3 C), 75.58, 75.49, 74.83, 74.70, 74.58 (3 C), 74.47, 74.43, 74.19, 74.12, 74.04, 74.66, 73.60 (14*d*, C(2^{I-VI}), C(3^{I-VI}), C(5^{I-VI})); 72.67, 71.89 (2*s*, C≡*C*–*C*≡C); 65.19 (*t*, C≡C*C*H$_2$C(4^{VI})); 63.13, 63.04, 62.94 (2 C), 62.85, 62.76 (5*t*, C(6^{I-VI})); 60.56 (*t*, C≡C*C*H$_2$C(1^{I})). HR-MALDI : 1087.333 ($C_{42}H_{64}O_{31}Na$, $[M+Na]^+$; calc. 1087.333).

*(5-Hydroxymethylthiophen-2-yl)methyl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 1″ : 4^{VI}-Anhydride* (**7**). $Na_2S \cdot 9\,H_2O$ (58.6 mg, 0.244 mmol) was added to a soln. of **5** (100 mg, 30.5 µmol) in 2-methoxyethanol (2 ml). The mixture was heated under reflux for 5 min, cooled to 23°, diluted with AcOEt (0.5 ml) and hexane (0.8 ml), and stirred for a further 30 min. The mixture was filtered through *Celite*. Evaporation and FC (toluene/AcOEt 50 : 1 → 20 : 1) gave **7** (71 mg, 70%). White foam. R_f (toluene/AcOEt 18 : 2) 0.40. M.p. 52–54°. $[\alpha]_D^{25} = +33.3$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2929*m*, 2867*m*, 1599*m*, 1492*s*, 1478*m*, 1359*m*, 1261*m*, 1091*s*, 1039*s*, 1016*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–6.86 (*m*, 74 arom. H); 6.62 (*d*, $J = 3.6$,

C=CH); 5.21 (d, J = 3.6), 5.15 (d, $J \approx$ 3.0), 5.14 (d, $J \approx$ 3.6), 5.10 (d, J = 3.3), 5.05 (d, J = 3.3) (H–C($1^{II–VI}$)); 4.92 (d, J = 11.4), 4.90 (d, J = 11.4, 2 H), 4.87 (d, J = 10.5, 2 H), 4.84 (d, J = 11.7), 4.78 (d, $J \approx$ 11.7) (7 ArC*H*); 4.75 (d, J = 3.3, H–C(1^{I})); 4.73 (d, J = 12.0), 4.69 (d, J = 11.1), 4.64 (d, J = 12.0) (3 ArC*H*); 4.60–4.48 (m, 8 ArC*H*); 4.45–4.26 (m, 18 ArC*H*, $CH_2OC(4^{VI})$, $CH_2OC(1^{I})$); 3.94–3.72 (m, 22 H); 3.61–3.45 (m, 8 H); 3.44–3.34 (m, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.73, 140.42 (2s, C(2) and C(5) of thienyl); 137.87–137.56 (several s); 136.98–136.25 (several s); 133.98–133.13 (several s); 129.31–127.77 (several d); 126.48, 125.86 (2d, C(3) and C(4) of thienyl); 99.16, 98.78, 98.53, 98.47, 98.24 (5d, C($1^{II–VI}$)); 97.40 (d, C(1^{I})); 81.77, 81.24, 81.01 (2 C), 80.91, 80.70 (5d, C($3^{I–VI}$)); 80.12, 79.68 (br., 3 C), 79.59, 79.43 (4d, C($2^{I–VI}$)); 79.10, 79.00, 78.47, 78.26, 78.03, 77. 92 (6d, C($4^{I–VI}$)); 74.98–72.39 (several t); 71.76, 71.63, 71.51 (2 C), 71.34, 70.51 (5d, C($5^{I–VI}$)); 69.91, 69.65 (br., 2 C), 69.25, 69.19, 69.15 (5t, C($6^{I–VI}$)); 68.50 (t, $CH_2OC(4^{VI})$); 65.95 (t, $CH_2OC(1^{I})$). HR-MALDI: 3329.49 ($C_{168}H_{157}Cl_{17}NaO_{31}S$, $[M+Na]^+$; calc: 3329.75). Anal. calc. for $C_{168}H_{157}Cl_{17}O_{31}S$ (3306.83): C 61.02, H 4.79; found: C 61.04, H 4.91.

Hexacosa-O-*acetylmaltooctaose* (**9**). Under N_2 and with vigorous stirring, **8** (7.5 g, 3.77 mmol) was dissolved in Ac_2O (350 ml) at 23°. The soln. was cooled to 0°, treated with 70% $HClO_4$ (4 ml), stirred for 20 h, and warmed to 23°. After 2 h at 23°, when TLC showed complete disappearance of **8**, the soln. was cooled to 0° and neutralized by the addition of a 10% aq. $NaHCO_3$ soln. (160 ml). The mixture was concentrated to 1/4 of its original volume. The remaining soln. was diluted with AcOEt (200 ml) and washed with H_2O (200 ml). The aq. phase was extracted with AcOEt (3 × 100 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. Recrystallisation from EtOH gave **9** (7.26 g, 80%). Off-white solid. R_f (hexane/AcOEt 1:5) 0.37. M.p. 136–138°. $[\alpha]_D^{25} = +137.5$ (c = 1.00, $CHCl_3$). IR ($CHCl_3$): 2961m, 1750m, 1431m, 1372s, 1034s. ^{1}H-NMR (500 MHz, $CDCl_3$, α-**9**/β-**9** 10:1, assignment based on a DFQCOSY spectrum) of α-**9**: 6.24 (d, J = 3.7, H–C(1^{I})); 5.51 (dd, J = 10.0, 8.9, H–C(3^{I})); 5.44–5.37 (m, 7 H), 5.31–5.28 (m, 6 H) (H–C($1^{II–VIII}$), 6 H–C(3)); 5.35 (dd, J = 9.0, 10.3, 1 H–C(3)); 5.07 (t, J = 9.9, H–C(4^{VIII})); 4.95 (dd, J = 3.7, 10.4, H–C(2^{I})); 4.86 (dd, J = 4.0, 10.5, H–C(2)), 4.75 (dd, J = 4.0, 10.4, 2 H), 4.73 (dd, J = 4.0, 10.2, 2 H), 4.71 (dd, J = 4.1, 10.2, 2 H) (H–C($2^{II–VIII}$)); 4.55–4.48 (m, 7 H–C(6)); 4.31 (dd, J = 3.2, 12.3, 1 H–C(6′)); 4.29–4.11 (m, 1 H–C(6), 7 H–C(6′)); 4.04 (t, J = 8.8, H–C(4^{I})); 4.06–3.89 (m, H–C($4^{II–VII}$), H–C($5^{I–VIII}$)); 2.23 (s, 3 H), 2.208 (br. s, 9 H), 2.205 (s, 3 H), 2.192 (s, 3 H), 2.189 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.029 (s, 6 H), 2.022 (s, 12 H), 2.006 (s, 6 H), 2.002 (s, 3 H), 1.999 (s, 3 H), 1.987 (s, 3 H), 1.986 (s, 3 H), 1.983 (s, 3 H), 1.981 (s, 3 H), 1.980 (s, 3 H) (26 AcO); data of β-**9**: 5.74 (d, J = 8.0, H–C(1^{I})). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.73–168.79 (several s, 26 C=O); 95.88, 95.75, 95.71, 95.69, 95.64 (3 C) (5d, C($1^{II–VIII}$)); 88.87 (d, C(1^{I})); 73.28, 73.22 (2 C), 73.14, 73.10, 72.33, 72.26, 71.74 (2 C), 71.69, 71.66, 71.60, 70.57, 70.54 (2 C), 70.48, 70.42 (2 C), 70.37, 70.21, 70.05, 69.80, 69.36, 69.16, 69.01, 68.95 (3 C), 68.93 (2 C), 68.45, 67.94 (25d, C($2^{I–VIII}$), C($3^{I–VIII}$), C($4^{I–VIII}$), C($5^{I–VIII}$)); 62.49, 62.41, 62.33 (3 C), 62.16, 61.88, 61.36 (6t, C($6^{I–VIII}$)); 21.14–20.44 (several q, 26 Me). MALDI-MS: 2429 ($[M+Na]^+$).

Phenyl 2,3,4,6-Tetra-O-*acetyl*-α-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*]$_5$-(1 → 4)-*2,3,6-tri*-O-*acetyl*-*1-thio*-β-D-*glucopyranoside* (**10**). Under N_2, a soln. of **9** (8.8 g, 3.65 mmol) in dry CH_2Cl_2 (90 ml) was treated with ZnI_2 (4.7 g, 14.62 mmol) and [(trimethylsilyl)thio]benzene (2.75 ml, 14.62 mmol) and stirred at 23° for 48 h. The mixture was filtered over *Celite*. The filtrate was washed with 1M HCl (50 ml), sat. aq. $NaHCO_3$ soln. (2 × 80 ml), H_2O (2 × 80 ml), and brine (80 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 2:3 → 0:1) gave **10** (7.1 g, 79%). White foam. R_f (hexane/AcOEt 1:5) 0.51. M.p. 124–127°. $[\alpha]_D^{25} = +120.6$ (c = 1.00, $CHCl_3$). IR ($CHCl_3$): 2962m, 1753m, 1430m, 1370s, 1032s. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a DFQCOSY and a HSQC.GRASP spectrum): 7.53–7.45 (m, 2 arom. H); 7.40–7.28 (m, 3 arom. H); 5.41 (d, J = 4.0, H–C(1)); 5.40–5.36 (m, H–C($3^{II–VII}$)); 5.35 (t, J = 9.4, H–C(3^{VIII})); 5.30 (d, J = 4.4, H–C(1)); 5.295 (d, J = 4.1, 3 H–C(1)); 5.290 (d, $J \approx$ 4.2, H–C(1)); 5.28 (d, J = 8.9, H–C(3^{I})); 5.27 (d, J = 4.1), 5.25 (d, J = 4.0) (2 H–C(1)); 5.07 (t, J = 9.9, H–C(4^{VIII})); 4.86 (dd, J = 4.0, 10.5, H–C(2^{VIII})); 4.79–4.69 (m, H–C($2^{I–VII}$), H–C(1^{I})); 4.57 (dd, J = 3.1, 12.1, H–C(6^{I})); 4.54–4.48 (m, 6 H–C(6)); 4.35 (dd, J = 4.1, 12.2, H′–C(6^{I})); 4.30–4.24 (m, 1 H–C(6), 4 H′–C(6)); 4.21 (dd, J = 2.7, 12.3), 4.17 (dd, J = 2.3, 10.2), 4.06 (dd, J = 2.3, 12.4) (3 H′–C(6)); 4.01–3.39 (m, H–C($4^{I–VII}$), H–C($5^{II–VIII}$)); 3.74 (td, $J \approx$ 3.6, 9.6, H–C(5^{I})); 2.206 (s, 3 H), 2.204 (s, 3 H), 2.19 (s, 3 H), 2.18 (s, 3 H), 2.16 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.029 (s, 6 H), 2.025 (s, 6 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 2.006 (s, 3 H), 2.001 (s, 3 H), 1.99 (s, 3 H), 1.984 (s, 3 H), 1.983 (s, 3 H), 1.982 (s, 3 H), 1.979 (s, 3 H), 1.977 (s, 3 H), 1.966 (s, 3 H) (25 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on HSQC.GRASP spectrum): 170.74–169.47 (several s, 25 C=O); 133.61 (2d), 131.06 (s), 128.90 (2d), 128.48 (d) (PhS); 95.74 (2 C), 95.68 (2 C), 95.65 (3 C) (3d, C($1^{II–VIII}$)); 84.86 (d, C(1^{I})); 76.45 (d, C(3^{I})); 76.16 (d, C(5^{I})); 73.45, 73.43, 73.23 (3 C), 73.13, 72.37 (5d, C($4^{I–VII}$)); 71.78 (3 C), 71.74, 71.71, 71.66, 71.62 (5d, C($3^{II–VIII}$)); 70.74, 70.53, 70.47 (2 C), 70.44 (2 C), 70.38, 70.07 (6d, C($2^{I–VIII}$)); 69.38, 69.04, 69.01, 68.97 (3 C), 68.47 (5d, C($5^{II–VIII}$)); 67.96 (d, C(4^{VIII}); 62.47, 62.40 (2 C),

62.36 (3 C), 62.19, 61.39 (6*t*, C(6$^{I–VIII}$)); 21.05–20.55 (several *q*, 24 Me). MALDI-MS: 2501 ([*M* + K]$^+$), 2484 ([*M* + Na]$^+$). Anal. calc. for $C_{104}H_{136}O_{65}S$ (2458.25): C 50.81, H 5.58; found: C 50.80, H 5.66.

*Phenyl α-*D*-Glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-1-thio-β-*D*-glucopyranoside* (**11**). A soln. of **10** (3.3 g, 1.34 mmol) in MeOH/H_2O 1:1 (120 ml), was treated with 1M NaOMe in MeOH (6.6 ml), stirred for 20 h at 23°, treated with *Amberlite IR-120* (H^+ form), and filtered. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **11** (1.85 g, 98%). R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.30. White foam. M.p. 214–218°. $[\alpha]_D^{25} = +125.8$ ($c = 1.00$, MeOH). ^{1}H-NMR (500 MHz, CD_3OD): 7.57–7.55 (2 arom. H); 7.33–7.45 (*m*, 3 arom. H); 5.198 (*d*, $J \approx 4.2$), 5.190 (*d*, $J \approx 3.0$), 5.18 (*d*, $J \approx 4.1$), 5.17 (*d*, $J \approx 4.0$), 5.16 (*d*, $J \approx 3.3$), 5.15 (*d*, $J \approx 3.4$, 2 H) (H–C(1$^{II–VIII}$)); 4.64 (*d*, $J = 9.8$, H–C(1^I)); 3.90–3.75 (*m*, 27 H); 3.67 (*t*, $J = 8.9$, 3 H); 3.62 (*t*, $J = 9.3$, 1 H); 3.55 (*t*, $J = 9.0$, 1 H); 3.51–3.48 (*m*, 13 H); 3.450 (*ddd*, $J = 2.7$, 4.6, 9.6, H–C(5^I); 3.445 (*dd*, $J = 3.8$, 9.7, H–C(2)); 3.27 (*dd*, $J = 8.9$, 9.7, H–C(2^I)). ^{13}C-NMR (125 MHz, CD_3OD): 135.07 (*s*), 132.96 (2*d*), 130.00 (2*d*), 128.52 (*d*) (PhS); 102.89 (2 C), 102.73, 102.70, 102.65, 102.49 (2 C) (5*d*, C(1$^{II–VIII}$)); 89.37 (*d*, C(1^I)); 81.45, 81.40, 81.30 (2 C), 81.00, 80.65, 80.61 (6*d*, C(4$^{I–VII}$)); 79.42 (*d*, C(5^I)); 75.12, 75.00, 74.81, 74.30, 73.91, 73.84, 73.49, 73.38 (8*d*, C(2$^{I–VIII}$), C(3$^{I–VIII}$), C(5$^{II–VIII}$)); 71.55 (*d*, C(4^{VIII})); 64.36, 62.80, 62.45, 62.29 (4*d*, C(6$^{I–VIII}$)). MALDI-MS: 1448 ([*M* + K]$^+$), 1432 ([*M* + Na]$^+$). Anal. calc. for $C_{54}H_{86}O_{40}S \cdot 5\,H_2O$ (1432.86): C 43.31, H 6.46; found: C 43.53, H 6.52.

*Phenyl 4,6-*O*-Benzylidene-α-*D*-glucopyranosyl-[(1 → 4)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-1-thio-β-*D*-glucopyranoside* (**12**). A soln. of **11** (1.66 g, 1.18 mmol) in pyridine (20 ml) was treated with $PhCHBr_2$ (1.95 ml, 11.8 mmol), warmed from 25 to 95° over a period of 7 h, and stirred at 95° for 72 h. The mixture was filtered, and the residue was washed with pyridine (10 ml). The combined filtrate and washing was evaporated. FC (CH_2Cl_2/MeOH/H_2O 75:50:12; residue adsorbed on silica gel pretreated with Et_3N) gave **12** (1.32 g, containing 1 equiv. of Et_3N). Compound **12** was used immediately without further purification. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.78. ^{1}H-NMR (300 MHz, CD_3OD): 7.58–7.45 (*m*, 4 arom. H); 7.35–7.26 (*m*, 6 arom. H); 5.56 (*s*, PhC*H*); 5.20 (*d*, $J = 3.9$), 5.17 (*d*, $J = 3.6$, 6 H) (H–C(1$^{II–VIII}$)); 4.63 (*d*, $J = 9.6$, H–C(1^I)); 4.22 (*dd*, $J = 4.2$, 9.6, H_{eq}–C(6^{VIII})); 3.92–3.69 (*m*, 29 H); 3.66–3.40 (*m*, 17 H); 3.26 (*dd*, $J \approx 8.7$, 9.7, H–C(2^I)). ^{13}C-NMR (75 MHz, D_2O): 139.22 (*s*); 135.05 (*s*); 134.65 (2*d*); 132.90 (*d*); 132.35 (2*d*); 131.73 (2*d*); 131.14 (*d*); 129.27 (2*d*); 104.70, 103.57, 102.69 (br., 5 C) (3*d*, C(1$^{II–VIII}$)); 90.11 (*d*, C(1^I)); 83.07, 81.32, 80.50, 79.96 (br., 5 C) (4*d*, C(4$^{I–VIII}$); 79.62 (*d*, C(5^I)); 76.18 (br.), 75.22, 74.45 (br.), 74.09 (br.) (4*d*, C(2$^{I–VIII}$), C(3$^{I–VIII}$), C(5$^{II–VII}$)); 72.98 (*t*, C(6^{VIII})); 66.23 (*d*, C(5^{VIII})); 63.25 (br. *t*, C(6$^{I–VII}$)). MALDI-MS: 1518 ([*M* + Na]$^+$).

*Phenyl 4,6-*O*-Benzylidene-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-1-thio-β-*D*-glucopyranoside* (**13**). A soln. of **12** (1.2 g, 0.8 mmol) in DMF (350 ml) was cooled to 0°, treated with NaH (55% in oil, 3.5 g), stirred for 30 min, treated with 4-ClBnCl (11.9 g, 73.89 mmol) and Bu_4NI (10.2 g, 27.7 mmol), stirred at 0° for 1 h and at 23° for 12 h. The soln. was cooled to 0°, treated dropwise with MeOH (5 ml), and diluted with H_2O (50 ml) and Et_2O (50 ml). The org. and aq. phases were separated, and the aq. phases were extracted with Et_2O (2 × 50 ml). The combined org. layers were washed with brine (50 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 60:1 → 30:1) gave **13** (2.81 g, 81% from **11**). White foam. R_f (toluene/AcOEt 18:2) 0.52. M.p. 59–61°. $[\alpha]_D^{25} = +52.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 2923*m*, 1599*m*, 1491*m*, 1404*m*, 1361*m*, 1152*s*, 1090*s*, 1037*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.55 (*dd*, $J = 1.5$, 8.0, 2 arom. H); 7.43 (*dd*, $J = 1.9$, 5.6, 2 arom. H); 7.39 (*dd*, $J = 1.8$, 5.0, 2 arom. H); 7.28–6.84 (*m*, 96 arom. H); 5.53 (*s*, PhC*H*); 5.54–5.52 (*m*, 3 H), 5.51 (*d*, $J = 3.8$), 5.47 (*d*, $J = 3.6$), 5.45 (*d*, $J = 3.5$), 5.41 (*d*, $J = 3.5$) (H–C(1$^{II–VIII}$)); 4.83 (*d*, $J = 11.5$, 2 H), 4.80 (*d*, $J = 11.6$), 4.77 (*d*, $J \approx 12.0$), 4.72 (*d*, $J \approx 12.3$, 2 H), 4.70 (*d*, $J \approx 12.5$, 2 H) (8 ArC*H*); 4.67 (*d*, $J = 9.8$, H–C(1^I)); 4.66 (*d*, $J \approx 11.0$), 4.64 (*d*, $J = 12.6$, 2 H), 4.61 (*d*, $J = 11.6$, 2 H), 4.57 (*d*, $J = 12.4$, 3 H), 4.52 (*d*, $J = 11.0$, 2 H), 4.51 (*d*, $J = 12.0$, 2 H), 4.48 (*d*, $J = 12.1$, 2 H), 4.47 (*d*, $J = 12.1$), 4.46 (*d*, $J = 12.5$), 4.41 (*d*, $J = 12.2$, 2 H) (18 ArC*H*); 4.35–4.28 (*m*, 20 ArC*H*); 4.05 (*dd*, $J = 4.7$, 10.2, H_{eq}–C(6^{VIII})); 4.02–3.95 (*m*, 7 H); 3.94–3.84 (*m*, 10 H); 3.81–3.75 (*m*, 8 H); 3.73–3.65 (*m*, 6 H); 4.61 (*t*, $J = 10.6$, H_{ax}–C(6^{VIII})); 3.59 (*t*, $J = 9.4$, 1 H); 3.56–3.53 (*ddd*, $J \approx 2.5$, 4.6, 9.8, H–C(5^I)); 3.51 (br. *t*, $J = 9.5$, 1 H); 3.46–3.40 (*m*, 12 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.22–135.87 (several *s*); 133.77–133.05 (several *s*); 131.98–125.91 (several *d*); 101.24 (*d*, PhCH); 97.82, 96.93, 96.67, 96.60, 96.43, 96.36, 96.32 (7*d*, C(1$^{II–VIII}$)); 87.36 (*d*, C(1^I)); 86.35 (*d*, C(2^I)); 82.29 (*d*, C(4^{VIII})); 81.61, 81.37 (br., 3 C), 81.21 (2 C) (3*d*, C(3$^{II–VII}$)); 80.81 (*d*, C(3^I)); 79.55 (br., 3 C), 79.45 (br., 2 C), 79.32, 78.74 (4*d*, C(2$^{II–VIII}$)); 78.97 (*d*, C(5^I)); 78.61 (*d*, C(3^{VIII})); 74.45–72.27 (several *t*); 74.45, 73.93, 73.43, 72.79 (br., 4 C) (4*d*, C(4$^{I–VII}$)); 70.92 (br., 5 C), 70.69 (2*d*, C(5$^{II–VII}$)); 69.08 (*t*), 68.97 (*t*), 68.85–68.70 (br. *t*, 6 C) C(6$^{I–VIII}$)); 63.37 (*d*, C(5^{VIII})). MALDI-MS: 4380 ([*M* + Na]$^+$). Anal. calc. for $C_{222}H_{205}Cl_{23}O_{40}S$ (4360.52): C 61.15, H 4.74, Cl 18.70; found: C 61.08, H 4.94, Cl 18.90.

*Prop-2-yn-1-yl 4,6-*O*-Benzylidene-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**14**). Under

Ar, a suspension of **13** (450 mg, 0.11 mmol), propargyl alcohol (20 µl, 0.33 mmol), and 3-Å molecular sieves (500 mg) in dry Et_2O (23 ml) was stirred at $-60°$ for 1 h, treated with NIS (46 mg, 0.20 mmol) and TfOH (8 µl, 0.09 mmol), and stirred for 20 h at $-60°$. The suspension was filtered over *Celite*, washed with 10% aq. $Na_2S_2O_3$ soln. (10 ml), sat. aq. $NaHCO_3$ soln. (2 × 10 ml), H_2O (2 × 10 ml), and brine (20 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50:1 → 30:1) gave **14** (451 mg, 93%). White foam. R_f (toluene/AcOEt 18:2) 0.65. $[\alpha]_D^{25} = +60.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2928*m*, 2868*m*, 1600*m*, 1492*m*, 1464*m*, 1361*m*, 1156*s*, 1090*s*, 1036*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–6.84 (*m*, 97 arom. H); 5.53 (*s*, PhC*H*); 5.54–5.52 (*m*, 3 H), 5.51 (*d*, *J* = 3.8), 5.49 (*d*, *J* = 3.5), 5.49–5.47 (*m*, 2 H) (H–C($1^{II–VIII}$)); 5.12 (*d*, *J* = 3.6, H–C(1^{I})); 4.91 (*d*, *J* = 12.1), 4.83 (*d*, *J* = 11.6), 4.76 (*d*, *J* = 12.0), 4.71 (*d*, *J* = 11.3, 3 H), 4.68 (*d*, *J* ≈ 12.1), 4.67 (*d*, *J* = 11.5), 4.63 (*d*, *J* = 11.2, 2 H), 4.61 (*d*, *J* = 11.7, 2 H), 4.60 (*d*, *J* = 11.8, 2 H), 4.59 (*d*, *J* = 12.5, 2 H), 4.54 (*d*, *J* = 12.1, 3 H), 4.46 (*d*, *J* = 12.0), 4.45 (*d*, *J* = 10.5, 2 H), 4.41 (*d*, *J* = 12.2) (23 ArC*H*); 4.38–4.29 (*m*, 25 ArC*H*, OCH_2C≡CH); 4.06 (*dd*, *J* = 4.7, 10.3, H_{eq}–C(6^{VIII})); 4.05–3.95 (*m*, 7 H); 3.94–3.84 (*m*, 10 H); 3.83–3.75 (*m*, 7 H); 3.72–3.63 (*m*, 8 H); 3.61 (*t*, *J* ≈ 10.5, H_{ax}–C(6^{VIII})); 3.58 (*t*, *J* = 9.4, 1 H); 3.47–3.37 (*m*, 13 H); 2.48 (*t*, *J* = 2.4, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.30–135.87 (several *s*); 133.87–132.90 (several *s*); 131.04–125.91 (several *d*); 101.23 (*d*, PhCH); 97.82 (2 C), 96.68 (2 C), 96.39 (2 C), 96.31 (4*d*, C($1^{II–VIII}$)); 94.54 (*d*, C(1^{I})); 82.29 (*d*, C(4^{VIII})); 81.61, 81.46, 81.38 (br., 4 C), 81.27 (4*d*, C($3^{I–VII}$)); 79.57 (br., 4 C), 79.46, 79.43, 79.32, 78.73 (5*d*, C($2^{I–VIII}$)); 78.70 (*s*, *C*≡CH); 78.61 (*d*, C(3^{VIII})); 75.15 (*s*, C≡*C*H); 74.17–71.98 (several *t*); 73.64, 73.50, 73.44, 72.79 (br., 4 C) (4*d*, C($4^{I–VII}$)); 70.91 (2 C), 70.87 (2 C), 70.81, 70.69, 70.40 (5*d*, C($5^{I–VII}$)); 68.92, 68.83 (br., 4 C), 68.79, 68.72 (2 C) (4*t*, C($6^{I–VIII}$)); 63.37 (*d*, C(5^{VIII})); 54.66 (*t*, C≡C*C*H_2). MALDI-MS: 4345 ($[M+K]^+$). Anal. calc. for $C_{219}H_{203}Cl_{23}O_{41}$ (4306.40): C 61.08, H 4.75, Cl 18.93; found: C 60.79, H 4.84, Cl 19.07.

*Prop-2-yn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**15**). Under Ar, a soln. of **14** (540 mg, 0.125 mmol) in dry CH_2Cl_2 (25 ml) was stirred at $-40°$ for 10 min, treated with Et_3SiH (199 µl, 1.25 mmol) and $BF_3 \cdot Et_2O$ (79 µl, 0.62 mmol), and stirred for 1 h at $-40°$ and for 6 h at $-10°$. The soln. was washed with sat. aq. $NaHCO_3$ soln. (20 ml), H_2O (20 ml), and brine (20 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 5:1) gave **15** (382 mg, 71%). White foam. R_f (toluene/AcOEt 18:2) 0.55. $[\alpha]_D^{25} = +61.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 2926*m*, 2868*m*, 1722*w*, 1599*m*, 1492*s*, 1404*m*, 1360*m*, 1260*w*, 1151*s*, 1091*s*, 1039*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.84–6.86 (*m*, 97 arom. H); 5.56 (*d*, *J* = 3.3), 5.55 (*d*, *J* ≈ 3.0), 5.54 (*d*, *J* = 3.4), 5.51 (*d*, *J* = 3.9), 5.505 (*d*, *J* ≈ 4.0), 5.50 (*d*, *J* = 3.7, 2 H) (H–C($1^{II–VIII}$)); 5.14 (*d*, *J* = 3.6, H–C(1^{I})); 4.93 (*d*, *J* = 12.1), 4.78 (*d*, *J* = 12.0), 4.75–4.56 (*m*, 17 H) (19 ArC*H*); 4.49 (*d*, *J* = 12.0), 4.46 (*d*, *J* = 12.2, 2 H), 4.44 (*d*, *J* = 12.2, 2 H) (5 ArC*H*); 4.39–4.28 (*m*, 24 ArC*H*, OCH_2C≡CH); 4.04–3.86 (*m*, H–C($3^{I–VII}$), H–C($4^{I–VII}$), 2 H–C(5), H–C(6)); 3.84–3.79 (*m*, 5 H–C(5)); 3.75–3.64 (*m*, 6 H–C(6), H′–C(6), H–C(5^{VIII}), H–C(4^{VIII}), H–C(3^{VIII})); 3.61 (*dd*, *J* = 3.6, 9.3, H–C(2^{VIII})); 3.54 (*dd*, *J* = 3.7, 9.7, H–C(6^{VIII})); 3.49–3.40 (*m*, H–C($2^{II–VII}$), H′–C(6^{VIII}), 6 H′–C(6)); 3.38 (*dd*, *J* = 3.6, 9.7, H–C(2^{I})); 2.68 (br. *s*, HO–C(4^{VIII})); 2.50 (*t*, *J* = 2.3, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.47–135.44 (several *s*); 133.87–132.97 (several *s*); 129.44–127.32 (several *d*); 97.19, 96.69, 96.42, 96.40, 96.39 (2 C), 96.31 (6*d*, C($1^{II–VIII}$)); 94.56 (*d*, C(1^{I})); 81.49, 81.46 (2 C); 81.37 (br., 3 C), 81.26, 81.21 (5*d*, C($3^{I–VIII}$)); 79.59 (br., 3 C), 79.48 (2 C), 79.44, 79.33 (5*d*, C($2^{II–VIII}$)); 78.87 (*d*, C(2^{I})); 78.71 (*s*, *C*≡CH); 75.15 (*s*, C≡*C*H); 74.35–71.98 (several *t*); 73.52, 73.21, 73.14, 72.70 (2 C), 72.68 (2 C) (5*d*, C($4^{I–VII}$)); 72.38 (*d*, C(4^{VIII})); 70.93 (br., 3 C), 70.89 (2 C), 70.83, 70.41, 70.37 (5*d*, C($5^{I–VIII}$)); 70.14 (*t*, C(6^{VIII})); 68.94, 68.84 (br., 4 C), 68.80 (2 C) (3*t*, C($6^{I–VII}$)); 54.67 (*t*, C≡C*C*H_2)). MALDI-MS: 4331 ($[M+Na]^+$).

*Prop-2-yn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-4-*O*-(prop-2-yn-1-yl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**16**). Under Ar, a soln. of **15** (0.1 g, 0.023 mmol) in DMF (4 ml) was cooled to 0°, treated with NaH (0.011 g, 0.232 mmol), stirred for 15 min, treated with propargyl bromide (9 µl, 0.116 mmol), stirred at 0° for 1 h and at 23° for 10 h, treated dropwise with MeOH (1 ml), and diluted with H_2O (10 ml) and Et_2O (20 ml). The org. phase was separated, and the aq. phase was extracted with Et_2O (3 × 20 ml). The combined org. layers were washed with brine (50 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 40:1 → 20:1) gave **16** (92 mg, 91%). White foam. R_f (toluene/AcOEt 18:2) 0.51. M.p. 50–52°. $[\alpha]_D^{25} = +59.5$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2928*m*, 2865*m*, 1600*w*, 1492*m*, 1360*m*, 1266*m*, 1152*s*, 1091*s*, 1020*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.32–6.84 (*m*, 97 arom. H); 5.528 (*d*, *J* = 3.3, 2 H), 5.535 (*d*, *J* ≈ 3.0), 5.49 (*d*, *J* = 3.6), 5.47 (*d*, *J* = 3.5, 2 H), 5.45 (*d*, *J* = 3.6) (H–C($1^{II–VIII}$)); 5.12 (*d*, *J* = 3.6, H–C(1^{I})); 4.91 (*d*, *J* = 12.1), 4.76 (*d*, *J* = 12.0) (2 ArC*H*); 4.73–4.53 (*m*, 16 ArC*H*); 4.49–4.41 (*m*, 4 ArC*H*); 4.39–4.28 (*m*, 26 ArC*H*, 2 OC*H*C≡CH); 4.27 (*dd*, *J* = 2.4, *ca.* 15, OC*H*C≡CH); 4.15 (*dd*, *J* = 2.4, 15.2, OC*H*C≡CH); 4.03–3.76 (*m*, 23 H); 3.71–3.64 (*m*, 8 H); 3.54 (*dd*, *J* = 3.6, 9.3, H–C(2)); 3.50–3.39 (*m*, 15 H); 3.35 (*dd*, *J* = 3.6, 9.9, H–C(2)); 2.47 (*t*, *J* = 2.4, C≡CH); 2.41 (*t*, *J* = 2.4,

C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.70–135.86 (several *s*); 133.88–132.93 (several *s*); 129.60–127.31 (several *d*); 97.35, 96.68, 96.44, 96.42, 96.40 (2 C), 96.32 (6*d*, C($1^{II–VIII}$)); 94.56 (*d*, C(1^{I})); 81.60, 81.47, 81.37 (br., 5 C), 81.27 (4*d*, C($3^{I–VIII}$)); 79.82 (*s*, *C*≡CH); 79.59 (br., 3 C), 79.47 (br., 3 C), 79.34 (2 C) (3*d*, C($2^{I–VIII}$)); 78.72 (*s*, *C*≡CH); 77.55 (*d*, C(4^{VIII})); 75.15 (*s*, C≡*C*H); 74.54 (*s*, C≡*C*H); 74.51–71.98 (several *t*); 73.78, 73.71, 73.64, 73.52, 72.86, 72.82 (2 C) (6*d*, C($4^{I–VII}$)); 71.03, 70.98, 70.88 (4 C), 70.83, 70.42 (5*d*, C($5^{I–VIII}$)); 69.00, 68.95, 68.85 (2 C), 68.81 (2 C), 68.80, 68.28 (6*t*, C($6^{I–VIII}$)); 60.03 (*t*, *C*H_2OC(4^{IV})); 54.67 (*t*, *C*H_2OC(1^{I})). MALDI-MS: 4368 ([*M* + Na]$^+$). Anal. calc. for $C_{222}H_{207}Cl_{23}O_{41}$(4346.46): C 61.35, H 4.80; found: C 61.33, H 4.98.

*6-Hydroxyhexa-2,4-diyn-1-yl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_6$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 6 : 4^{VIII}-Anhydride* (**17**). A soln. of $Cu(OAc)_2$ (41 mg, 0.216 mmol) in pyridine (45 ml) was treated at 60° under Ar with a soln. of **16** (95 mg, 0.021 mmol) in pyridine (5 ml) within 3 h, stirred for 1 h, and evaporated. A soln. of the residue in AcOEt (40 ml) was washed with an aq. soln. of Na_4(TMEDA) (129 µl, 0.86 mmol), H_2O (20 ml), and brine (20 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40 : 1 → 20 : 1) gave **17** (74 mg, 78%). White foam. R_f (toluene/AcOEt 18 : 2) 0.45. $[\alpha]_D^{25} = +35.5$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2926*m*, 2867*m*, 1600*w*, 1492*m*, 1358*m*, 1091*s*, 1042*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30–6.87 (*m*, 97 arom. H); 5.41 (*d*, *J* = 3.3), 5.29 (*d*, *J* = 3.6), 5.25 (*d*, *J* = 3.9), 5.25–5.18 (*m*, 4 H) (H–C($1^{II–VIII}$)); 4.89 (*d*, *J* = 3.0, H–C(1^{I})); 4.85–4.58 (*m*, 13 ArC*H*); 4.55–4.20 (*m*, 35 ArC*H*, OCH_2C≡C, OCHC≡C); 4.16 (*d*, *J* = 15.9, OCHC≡C); 4.00–3.94 (*m*, 2 H); 3.91–3.70 (*m*, 28 H); 3.62 (br. *d*, *J* = 9.6, 1 H); 3.54–3.42 (*m*, 8 H); 3.41–3.37 (*m*, 8 H); 3.31 (*dd*, *J* = 3.3, 9.9, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.59–135.89 (several *s*); 133.91–132.88 (several *s*); 131.03–127.31 (several *d*); 98.39, 97.82 (2 C), 97.77, 97.66, 97.61, 96.49, 96.07 (7*d*, C($1^{I–VIII}$)); 81.55, 81.39, 81.30, 80.94, 80.72, (2 C), 80.64, 80.50 (7*d*, C($3^{I–VIII}$)); 80.40, 79.86, 79.54, 79.41 (br., 3 C), 79.24, 79.18 (6*d*, C($2^{I–VIII}$)); 78.15, 77.69, 77.54, 77.23, 76.91, 76.57, 76.17 (7*d*, C($4^{I–VII}$)); 73.94 (*d*, C(4^{VIII})); 76.01, 75.33 (2*s*, *C*≡C–C≡*C*); 74.57–72.31 (several *t*); 71.71, 71.58, 71.57, 71.33, 71.28, 71.14, 70.86, 70.67 (8*d*, C($5^{I–VIII}$)); 71.14, 70.32 (2*s*, C≡*C*–*C*≡C); 69.22, 69.06, 68.97 (br., 3 C), 68.87, 68.67, 68.26 (6*t*, C($6^{I–VIII}$)); 60.75 (*t*, *C*H_2OC(4^{VIII})); 56.13 (*t*, *C*H_2OC(1^{I})). HR-MALDI: 4368.67 ($C_{222}H_{205}Cl_{23}NaO_{41}$, [*M* + Na]$^+$; calc: 4368.46). Anal. calc. for $C_{222}H_{205}Cl_{23}O_{41}$ (4344.45): C 61.38, H 4.76; found: C 61.27, H 4.86.

*6-Hydroxyhexa-2,4-diyn-1-yl [α-*D*-Glucopyranosyl-(1 → 4)]$_7$-α-*D*-glucopyranoside 6 : 4^{VIII}-Anhydride* (**18**). A soln. of **17** (35 mg, 7.99 µmol) in CH_2Cl_2 (3.5 ml) was treated with $FeCl_3$ (31.1 mg, 0.19 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (0.5 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) gave **18** (5.3 mg, 48%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) 0.10. ^{1}H-NMR (500 MHz, D_2O): 5.30 (*d*, *J* = 4.4), 5.29 (*d*, *J* = 4.4), 5.27 (*d*, *J* = 4.1), 5.26 (*d*, *J* = 4.0), 5.18 (*d*, *J* = 3.8, 2 H), 5.11 (*d*, *J* = 3.8) (H–C($1^{II–VIII}$)); 4.92 (*d*, *J* = 3.8, H–C(1^{I})); 4.45 (br. *s*, C≡CCH_2); 4.43, 4.33 (AB, *J* = 16.9, C≡CCH_2); 3.94–3.84 (*m*, 8 H); 3.83–3.67 (*m*, 22 H); 3.65–3.55 (*m*, 17 H); 3.33 (*t*, *J* = 9.4, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, D_2O): 103.33, 102.87, 102.65, 102.33, 102.01, 101.82, 101.62, 101.20 (8*d*, C($1^{I–VIII}$)); 81.90, 81.27, 80.76, 80.62, 79.57, 79.54, 79.42 (2 C) (7*d*, C($4^{I–VIII}$)); 78.56, 78.41 (2*s*, *C*≡C–C≡*C*); 75.99, 75.94 (2 C), 75.79, 75.70, 75.61, 75.55, 75.43, 75.38, 75.21, 74.63, 74.56, 74.52, 74.49, 74.45, 74.19, 74.14, 74.00 (2 C), 73.85, 73.67 (2 C), 73.54, 73.29 (21*d*, C($2^{I–VIII}$), C($3^{I–VIII}$), C($5^{I–VIII}$)); 72.85, 72.39 (2*s*, C≡*C*–*C*≡C); 67.82 (*t*, C≡C*C*H_2C(4^{VI})); 63.10, 63.08 (2 C), 63.01 (2 C), 62.93, 62.74, 62.75 (6*t*, C($6^{I–VIII}$)); 59.75 (*t*, C≡C*C*H_2C(1^{I})). HR-MALDI : 1411.438 ($C_{54}H_{84}O_{41}Na$, [*M* + Na]$^+$; calc: 1411.438).

Glycosylation of **19** *with* **1**. Under Ar, a suspension of **1** (4.0 g, 1.23 mmol), **19** [4] (1.7 g, 2.47 mmol), and 3-Å molecular sieves (4 g) in dry toluene (150 ml) was stirred at −60° for 1 h, treated with NIS (500 mg, 2.22 mmol) and TfOH (55 µl, 0.62 mmol), and stirred for 4 h. The suspension was filtered over *Celite*, diluted with Et_2O (100 ml), washed with 10% aq. $Na_2S_2O_3$ soln. (100 ml), sat. aq. $NaHCO_3$ soln. (2 × 100 ml), H_2O (2 × 100 ml), and brine (100 ml), dried ($MgSO_4$), and evaporated. FC (silica H, toluene/AcOEt 50 : 1 → 20 : 1) gave **20** (1.75 g, 37%) and **21** (2.09 g, 45%).

*Prop-2-yn-1-yl 2,3,6-Tris-*O*-(4-chlorobenzyl)-4-deoxy-4-*C*-ethynyl-α-*D*-glucopyranosyl-(1 → 4)-6-*O*-benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside* (**20**). White foam. R_f (toluene/AcOEt 18 : 2) 0.60. $[\alpha]_D^{25} = +66.3$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 2925*m*, 2867*m*, 1599*m*, 1492*s*, 1408*m*, 1360*m*, 1152*m*, 1090*s*, 1036*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.27–6.84 (*m*, 85 arom. H); 5.57 (*d*, *J* = 3.5), 5.53 (*d*, *J* = 3.6, 2 H), 5.49 (*d*, *J* = 3.6), 5.48 (*d*, *J* = 3.5), 5.46 (*d*, *J* = 3.6) (H–C($1^{II–VII}$)); 5.12 (*d*, *J* = 3.6, H–C(1^{I})); 4.91 (*d*, *J* = 12.0), 4.84 (*d*, *J* = 10.9), 4.76 (*d*, *J* = 12.0), 4.71 (*d*, *J* = 12.0, 2 H), 4.70 (*d*, *J* = 11.9, 2 H), 4.64 (*d*, *J* ≈ 11.8, 2 H), 4.63 (*d*, *J* = 11.1), 4.62 (*d*, *J* ≈ 11.3, 2 H), 4.59 (*d*, *J* = 12.0, 2 H), 4.55 (*d*, *J* = 11.9, 2 H) (16 ArC*H*); 4.48–4.38 (*m*, 7 ArC*H*); 4.36–4.26 (*m*, 19 ArC*H*, OCH_2C≡CH); 4.03–3.77 (*m*, 21 H); 3.74–3.64 (*m*, 6 H); 3.59 (*dd*, *J* = 3.6, 9.4, H–C(2)); 3.51–3.39 (*m*, 5 H–C(2), 7 H–C(6)); 3.32 (*dd*, *J* = 3.5, 9.6, H–C(2^{I})); 2.84 (*dt*, *J* = 2.2, 10.6, H–C(4^{VII})); 2.48 (*t*, *J* = 2.4, CH_2C≡C*H*); 2.16 (*d*, *J* = 2.2, C≡C*H*). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.89–135.85

(several *s*); 133.85–132.95 (several *s*); 129.44–127.27 (several *d*); 97.53, 96.71, 96.48, 96.40 (3 C) (4*d*, C(1^{II-VII})); 94.53 (*d*, C(1^{I})); 81.54, 81.45 (2 C), 81.41, 81.36, 81.29, 81.26 (6*d*, C(3^{I-VII})); 79.56 (2 C), 79.50, 79.45, 79.35, 79.26, 79.18 (6*d*, C(2^{I-VII})); 78.70 (*s*, *C*≡CH); 75.15 (*s*, C≡*C*H); 74.60–71.97 (several *t*); 73.89 (2 C), 73.51, 73.00, 72.87 (2 C) (4*d*, C(4^{I-VI})); 70.97 (3 C), 70.90, 70.85, 70.80 (4*d*, C(5^{I-VI})); 70.39 (*d*, C(5^{VII})); 69.28 (*d*, C(6^{VII})); 68.8 (br. *t*, C(6^{I-VI})); 54.65 (*t*, C≡C*C*H_2); 36.51 (*d*, C(4^{VII})). MALDI-MS: 3803.7 ([*M* + Na]$^+$). Anal. calc. for $C_{194}H_{180}O_{35}Cl_{20}$ (3780.59): C 61.63, H 4.80; found: C 61.50, H 4.93.

Prop-2-yn-1-yl 2,3,6-Tris-O-*(4-chlorobenzyl)-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranoside* (**21**). R_f (toluene/AcOEt 18:2) 0.58. M.p. 57–59°. $[\alpha]_D^{25} = +64.5$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2913*m*, 2868*m*, 1599*m*, 1492*s*, 1408*w*, 1361*m*, 1153*m*, 1090*s*, 1036*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.36–6.84 (*m*, 85 arom. H); 5.65 (*d*, *J* = 3.8), 5.52 (*d*, *J* = 3.6), 5.48 (*d*, *J* = 3.3), 5.47 (*d*, *J* = 3.4), 5.45 (*d*, *J* = 3.9) (H–C(1^{II-VI})); 5.12 (*d*, *J* = 3.6, H–C(1^{I})); 4.96 (*d*, *J* = 11.3), 4.91 (*d*, *J* = 12.0), 4.83 (*d*, *J* = 11.0), 4.76 (*d*, *J* = 12.0), 4.70 (*d*, *J* ≈ 12.5), 4.69 (*d*, *J* = 11.9), 4.67 (*d*, *J* = 12.3, 2 H) (8 ArC*H*); 4.64–4.41 (*m*, 15 ArC*H*); 4.39–4.25 (*m*, 17 ArC*H*, H–C(1^{VII}), OCH_2C≡CH); 4.16 (*d*, *J* = 12.1), 4.14 (*d*, *J* = 12.1) (2 ArC*H*); 4.03–3.84 (*m*, H–C(3^{I-V}), H–C(4^{I-VI}), 3 H–C(5), H–C(6^{I})); 3.81–3.70 (*m*, H–C(3^{VI}), 2 H–C(5), H–C(6^{VI})); 3.69–3.64 (*m*, H–C(5^{VII}), H–C(6^{II-V}), H′–(6^{I}), H–C(6^{VII})); 3.59 (*dd*, *J* = 3.9, 9.3, H–C(2)); 3.50–3.35 (*m*, 4 H–C(2), H–C(2^{VI}), H′–C(6^{II-VI})); 3.31–3.26 (*m*, H–C(3^{VII}), H–C(5^{VI}), H′–C(6^{VII})); 3.09 (*t*, *J* ≈ 8.6, H–C(2^{VII})); 2.63 (*dt*, *J* = 2.3, 10.5, H–C(4^{VII})); 2.47 (*t*, *J* = 2.4, CH_2C≡C*H*); 2.17 (*d*, *J* = 2.3, C≡CH). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.60–135.87 (several *s*); 133.86–132.93 (several *s*); 129.59–127.27 (several *d*); 102.29 (*d*, C(1^{VII})); 97.20, 96.64, 96.42 (2 C), 96.34 (4*d*, C(1^{II-VI})); 94.56 (*d*, C(1^{I})); 82.34 (*d*, C(3^{VII})); 82.17 (*d*, C(2^{VII})); 81.55, 81.45, 81.37, 81.27, 81.24 (5*d*, C(3^{I-V})); 81.19 (*s*, *C*≡CH); 80.38 (*d*, C(3^{VI})); 79.71, 79.59 (br., 3 C), 79.41 (3*d*, C(2^{I-V})); 78.71 (*s*, CH_2*C*≡CH); 78.47 (*d*, C(2^{VI})); 76.19 (*d*, C(4^{VI})); 75.15 (*s*, CH_2C≡*C*H); 74.95 (*d*, C(5^{VI})); 73.71, 73.64, 73.50, 72.90, 72.41 (5*d*, C(4^{I-V})); 74.74–71.97 (several *t*); 71.20, 71.10, 70.87 (2 C), 70.82, 70.42 (5*d*, C(5^{I-V}), C(5^{VII})); 70.02 (*d*, C(6^{VI})); 68.94 (2 C), 68.84 (2 C), 68.71 (3*t*, C(6^{I-V})); 67.44 (*t*, C(6^{VII})); 54.66 (*t*, C≡C*C*H_2); 36.91 (*d*, C(4^{VII})); signal of C≡*C*H hidden by other signals. MALDI-MS: 3803 ([*M* + Na]$^+$). Anal. calc. for $C_{194}H_{180}O_{35}Cl_{20}$ (3780.59): C 61.63, H 4.80; found: C 61.72, H 4.92.

Penta-2,4-diyn-1-yl 2,3,6-Tris-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranoside 5:4^{VII}-Anhydride* (**22**). A soln. of $Cu(OAc)_2$ (43 mg, 0.23 mmol) in pyridine (50 ml) was treated at 60° under Ar with an soln. of **20** (90 mg, 0.023 mmol) in pyridine (6 ml) within 3 h, stirred for 1 h, and evaporated. A soln. of the residue in AcOEt (40 ml) was washed with an aq. soln. of Na_4TMEDA (143 µl, 0.96 mmol), H_2O (20 ml), and brine (20 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 20:1) gave **22** (69 mg, 78%). White foam. R_f (toluene/AcOEt 18:2) 0.41. M.p. 62–65°. $[\alpha]_D^{25} = +37.6$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2924*m*, 2869*m*, 1600*m*, 1492*s*, 1461*m*, 1407*m*, 1359*m*, 1138*s*, 1091*s*, 1040*s*, 1017*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.32–6.86 (*m*, 85 arom. H); 5.35 (*d*, *J* = 3.4), 5.23 (*d*, *J* = 3.5, 2 H), 5.18 (*d*, *J* = 3.6), 5.14 (*d*, *J* = 3.4), 5.08 (*d*, *J* = 3.5) (H–C(1^{II-VII})); 4.97 (*d*, *J* = 11.3), 4.89 (*d*, *J* = 11.7), 4.88 (*d*, *J* = 11.5), 4.87 (*d*, *J* = 11.0), 4.85 (*d*, *J* = 11.5), 4.81 (*d*, *J* = 11.0), 4.79 (*d*, *J* = 11.9), 4.77 (*d*, *J* = 11.5), 4.72 (*d*, *J* = 11.9) (9 ArC*H*); 4.70 (*d*, *J* = 3.7, H–C(1^{I})); 4.65 (*d*, *J* = 11.7, 2 H), 4.58 (*d*, *J* = 11.8), 4.53 (*d*, *J* = 12.2, 2 H), 4.52 (*d*, *J* = 11.0), 4.49 (*d*, *J* = 12.2, 2 H), 4.47 (*d*, *J* = 11.0) (9 ArC*H*); 4.43–4.29 (*m*, 23 ArC*H*, OC*H*C≡C); 4.26 (*d*, *J* = 12.3, ArC*H*); 4.23 (*d*, *J* ≈ 3.4, OC*H*C≡C); 3.94 (*t*, *J* = 9.0, H–C(3)); 3.93–3.74 (*m*, 6 H–C(3), H–C(4^{I-VI}), H–C(5^{I-VII}), 6 H–C(6)); 3.56 (br. *d*, *J* = 9.9, H–C(6)); 3.52–3.44 (*m*, 1 H–C(2), 5 H′–C(6)); 3.41–3.34 (*m*, 5 H–C(2), 2 H′–C(6)); 3.29 (*dd*, *J* = 3.4, 9.6, H–C(2)); 2.86 (*t*, *J* = 10.6, H–C(4^{VII})). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.32–135.88 (several *s*); 133.90–132.90 (several *s*); 129.51–127.31 (several *d*); 98.79, 98.54, 98.14 (2 C), 97.87 (2 C) (4*d*, C(1^{II-VII})); 97.24 (*d*, C(1^{I})); 81.03, 81.83 (2 C), 80.75 (2 C), 80.66 (4*d*, C(3^{I-VI})); 79.51, 79.39 (2 C), 79.29, 79.24, 79.19, 78.98 (6*d*, C(2^{I-VII})); 79.15 (*d*, C(3^{VII})); 78.52, 78.09 (2 C), 77.45, 77.25 (4*d*, C(4^{I-V})); 77.75 (*s*, *C*≡C–C≡C); 76.58 (*d*, C(4^{VI})); 74.80–72.21 (several *t*); 71.59, 71.44 (2 C), 71.19 (2 C), 70.74, 70.68 (5*d*, C(5^{I-VII})); 70.83, 67.84 (2*s*, C≡*C*–*C*≡C); 69.25, 69.18, 69.10, 68.98 (2 C), 68.95, 68.62 (6*t*, C(6^{I-VII})); 56.73 (*t*, C≡C*C*H_2); 37.38 (*d*, C(4^{VII})); signal for C≡C–C≡*C* hidden by other signals. HR-MALDI-MS: 3801.53 ($C_{194}H_{178}Cl_{20}NaO_{35}$, [*M* + Na]$^+$; calc: 3801.57). Anal. calc. for $C_{194}H_{178}Cl_{20}O_{35}$ (3778.57): C 61.67, H 4.75; found: C 61.66, H 4.81.

Penta-2,4-diyn-1-yl [α-D-*Glucopyranosyl-(1 → 4)]$_6$-α*-D-*glucopyranoside 5:4^{VII}-Anhydride* (**23**). A soln. of **22** (32 mg, 8.46 µmol) in CH_2Cl_2 (3 ml) was treated with $FeCl_3$ (28.8 mg, 0.178 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (0.5 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/

H_2O 75:50:12) gave **23** (8.1 mg, 80%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.15. ^{1}H-NMR (500 MHz, D_2O): 5.25 (*d*, *J* = 4.1), 5.24 (*d*, *J* = 4.1), 5.21 (*d*, *J* = 3.8), 5.14 (*d*, *J* = 4.0), 5.10 (*d*, *J* = 4.1), 5.09 (*d*, *J* = 4.1) (H–C($1^{II–VII}$)); 4.93 (*d*, *J* = 3.9, H–C(1^I)); 4.42 (br. *s*, C≡CCH_2); 3.97 (*ddd*, *J* ≈ 2.3, 4.6, 10.0, H–C(5)); 3.96–3.90 (*m*, 6 H); 3.89–3.77 (*m*, 20 H); 3.65–3.56 (*m*, 13 H); 3.53 (*dd*, *J* = 3.7, 9.7, H–C(2)); 2.70 (*t*, *J* = 10.5, H–C(4^{VII})). ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY and a TOCSY spectrum): 5.79 (*d*, *J* ≈ 6.0, HO–C(2^{VII})); 5.78 (*d*, *J* = 3.1, HO–C(3)); 5.75 (*d*, *J* = 6.0), 5.745 (*d*, *J* ≈ 6.0) (2 HO–C(2)); 5.74 (*d*, *J* = 2.6), 5.72 (*d*, *J* = 2.9, 2 H) (3 HO–C(3)); 5.67 (*d*, *J* = 2.7, HO–C(3)); 5.64 (*d*, *J* = 6.3), 5.63 (*d*, *J* = 6.6), 5.60 (*d*, *J* = 6.2) (3 HO–C(2)); 5.59 (*d*, *J* = 3.0, HO–C(3^I)); 5.50 (*d*, *J* = 6.4, HO–C(3^{VII})); 5.04 (*d*, *J* = 6.4, HO–C(2^I)); 4.98 (*d*, *J* = 3.5, H–C(1^{VII})); 4.94 (*d*, *J* = 4.2), 4.93 (*d*, *J* = 4.4), 4.92 (*d*, *J* = 4.1), 4.90 (*d*, *J* = 3.8), 4.87 (*d*, *J* = 3.7) (H–C($1^{II–VI}$)); 4.77 (*t*, *J* = 5.8, HO–C(6^{VII})); 4.67 (*d*, *J* = 3.6, H–C(1^I)); 4.55 (*t*, *J* = 5.7), 4.53 (*t*, *J* = 5.5), 4.51 (*t*, *J* = 5.7), 4.50 (*t*, *J* ≈ 5.5, 2 H), 4.48 (*t*, *J* ≈ 6.0) (HO–C($6^{I–VI}$)); 4.36, 4.22 (AB, *J* = 16.0, C≡CCH_2); 3.69 (br. *ddd*, *J* ≈ 1.5, 6.5, 11.5, H–C(5^{VII})); 3.63–3.47 (*m*, 19 H); 3.42–3.28 (*m*, 19 H); 3.28–3.25 (*m*, H–C(2^I)); 3.19 (br. *ddd*, *J* ≈ 3.5, 6.5, 9.5, H–C(2^{VII})); 2.55 (br. *t*, *J* = 10.3, H–C(4^{VII})). ^{13}C-NMR (125 MHz, D_2O): 104.19, 103.92, 103.70, 103.50, 103.43, 103.18, 102.16 (7*d*, C($1^{I–VII}$)); 82.74, 82.30, 82.25, 82.00, 81.62, 81.04 (6*d*, C($4^{I–VI}$)); 79.07, 76.03 (2*s*, *C*≡C–C≡*C*); 75.90, 75.80, 75.67 (2 C), 75.55, 75.41, 75.31, 75.13, 74.78, 74.66, 74.61, 74.43, 74.39, 74.35, 74.20, 74.10, 73.94, 73.75, 73.52, 73.42, 73.05 (20*d*, C($2^{I–VII}$), C($3^{I–VII}$), C($5^{I–VII}$)); 72.45, 70.37 (2*s*, C≡*C*–*C*≡C); 64.41 (*t*, C(6^{VII})); 63.05, 62.95, 62.89 (2 C), 62.81, 62.76 (5*t*, C($6^{I–VI}$)); 60.02 (*t*, C≡C*C*H_2); 40.14 (*d*, C(4^{VII})). HR-MALDI: 1219.375 ($C_{47}H_{72}NaO_{35}$, $[M+Na]^+$; calc. 1219.375).

*Penta-2,4-diyn-1-yl 2,3,6-Tris-*O*-(4-chlorobenzyl)-β-*D*-*glucopyranosyl-(1 → 4)-6-*O*-benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 5:4^{VII}-Anhydride* (**24**). A soln. of $Cu(OAc)_2$ (58 mg, 0.32 mmol) in pyridine (68 ml) was treated at 60° under Ar with a soln. of **21** (122 mg, 0.032 mmol) in pyridine (6 ml) within 3 h, stirred for 1 h, and evaporated. A soln. of the residue in AcOEt (40 ml) was washed with a aq. soln. of Na_4TMEDA (193 µl, 1.28 mmol), H_2O (20 ml), and brine (20 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 20:1) gave **24** (89 mg, 73%). White foam. R_f (toluene/AcOEt 18:2) 0.39. M.p. 66–68°. $[\alpha]_D^{25} = +20.9$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 2925*m*, 2869*m*, 1600*m*, 1492*s*, 1461*m*, 1407*m*, 1358*m*, 1136*s*, 1091*s*, 1041*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.33–6.83 (*m*, 85 arom. H); 5.41 (*d*, *J* = 3.7), 5.33 (*d*, *J* = 3.8), 5.26 (*d*, *J* = 3.3), 5.14 (*d*, *J* = 3.5), 5.10 (*d*, *J* = 3.5) (H–C($1^{II–VI}$)); 5.01 (*d*, *J* = 11.6), 4.83 (*d*, *J* = 11.8), 4.79 (*d*, *J* = 11.6), 4.78 (*d*, *J* ≈ 11.0), 4.74 (*d*, *J* ≈ 10.5, 2 H) (6 ArC*H*); 4.73 (*d*, *J* ≈ 3.3, H–C(1^I)); 4.68 (*d*, *J* = 11.5, 2 H), 4.67 (*d*, *J* = 11.0, 2 H) (4 ArC*H*); 4.60 (*d*, *J* = 7.1, H–C(1^{VII})); 4.58 (*d*, *J* = 11.9, 2 H), 4.54 (*d*, *J* = 12.2, 2 H), 4.50 (*d*, *J* = 11.6) (5 ArC*H*); 4.495 (*d*, *J* ≈ 15.8, OC*H*C≡C); 4.49 (*d*, *J* = 11.4), 4.48 (*d*, *J* = 12.4), 4.47 (*d*, *J* = 11.7), 4.46 (*d*, *J* = 10.9), 4.42 (*d*, *J* = 11.8), 4.39 (*d*, *J* = 11.6, 2 H), 4.38 (*d*, *J* = 12.4), 4.37 (*d*, *J* = 11.3, 3 H), 4.35 (*d*, *J* ≈ 12.0, 2 H) (13 ArC*H*); 4.33–4.21 (*m*, 14 ArC*H*, OC*H*C≡C); 4.13–4.11 (*m*, H–C(5^{VI})); 4.09 (*t*, *J* = 9.3, H–C(4)); 4.03–3.78 (*m*, 1 H–C(2), 4 H–C(3), 4 H–C(4), H–C(4^{VI}), 4 H–C(5), 5 H–C(6)); 3.74 (*t*, *J* = 9.2, H–C(3)); 3.70–3.61 (*m*, 1 H–C(5), 3 H–C(6)); 3.55–3.33 (*m*, 5 H–C(2), H–C(3^{VI}), H–C(3^{VII}), 4 H–C(6), H–C(6^{VII}), H′–C(6^{VII})); 3.29 (*td*, *J* = 10.6, H–C(5^{VII})); 3.18 (*t*, *J* = 7.3, H–C(2^{VII})); 2.64 (*t*, *J* = 10.4, H–C(4^{VII})). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.03–135.69 (several *s*); 133.94–132.86 (several *s*); 129.44–127.38 (several *d*); 99.03 (*d*, C(1^{VII})); 98.89 (*d*, C(1^I)); 98.58, 98.22, 97.85 (3 C) (3*d*, C($1^{II–VI}$)); 81.59 (*d*, C(2^{VII})); 81.38 (*d*, C(3^{VII})); 81.00, 80.96 (3 C), 80.79, 80.70 (4*d*, C($3^{I–VI}$)); 79.58 (2 C), 79.47, 79.20, 79.14, 79.01 (5*d*, C($2^{I–VI}$)); 78.48, 77.47, 77.14, 75.47, 74.85 (5*d*, C($4^{I–V}$)); 76.21 (*d*, C(4^{VI})); 73.56 (*d*, C(5^{VII})); 74.72–72.18 (several *t*); 71.49, 71.44, 71.41, 71.22, 71.19, 71.07 (6*d*, C($5^{I–VI}$)); 70.47 (*t*, C(6^{VII})); 69.41, 69.20, 69.13, 69.02, 68.87, 68.61 (6*t*, C($6^{I–VI}$)); 70.01, 67.99 (2*s*, C≡*C*–*C*≡C); 57.79 (*t*, C≡C*C*H_2); 37.47 (*d*, C(4^{VII})); signals for *C*≡C–C≡*C* hidden by other signals. HR-MALDI : 3801.57 ($C_{194}H_{178}Cl_{20}NaO_{35}$, $[M+Na]^+$; calc: 3801.57). Anal. calc. for $C_{194}H_{178}Cl_{20}O_{35}$ (3778.57): C 61.67, H 4.75; found: C 61.64, H 4.83.

*Penta-2,4-diyn-1-yl β-*D*-Glucopyranosyl-(1 → 4)-[α-*D*-glucopyranosyl-(1 → 4)]$_5$-α-*D*-glucopyranoside 5:4^{VII}-Anhydride* (**25**). A soln. of **24** (40 mg, 10.5 µmol) in CH_2Cl_2 (4 ml) was treated with $FeCl_3$ (36.0 mg, 0.222 mmol) and stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75:50:12) gave **25** (9.7 mg, 77%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75:50:12) 0.14. ^{1}H-NMR (500 MHz, D_2O): 5.24 (*d*, *J* = 4.1), 5.21 (*d*, *J* = 4.0), 5.17 (*d*, *J* = 4.0), 5.15 (*d*, *J* = 4.0), 5.11 (*d*, *J* = 3.7) (H–C($1^{II–VI}$)); 4.96 (*d*, *J* = 3.9, H–C(1^I)); 4.59 (*dd*, *J* ≈ 0.5, 17.2), 4.31 (*d*, *J* = 17.3) (C≡CCH_2); 4.11 (*t*, *J* = 9.6, H–C(3^{VI})); 4.07 (*ddd*, *J* = 2.3, 5.1, 9.9, H–C(5^{VI})); 3.97–3.91 (*m*, 5 H); 3.90–3.79 (*m*, 19 H); 3.77–3.58 (*m*, 14 H); 3.25 (*dd*, *J* = 7.7, 9.1, H–C(2^{VII})); 2.67 (*t*, *J* = 10.2, H–C(4^{VII})); H–C(1^{VII}) hidden by HDO signal. ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY and a TOCSY spectrum): 5.73 (*d*, *J* = 2.7, HO–C(3)); 5.68–5.62 (*m*, 3 HO–C(2), 3 HO–C(3)); 5.61 (*d*, *J* = 6.7, HO–C(2)); 5.60 (*d*, *J* = 2.5, HO–C(3^I)); 5.55 (*d*, *J* = 3.9, HO–C(2^{VII})); 5.50 (*d*, *J* = 7.6, HO–C(2^{VI})); 5.48 (*d*, *J* = 6.5,

HO–C(3^{VII})); 5.01 (*d*, *J* = 6.5, HO–C(2^{I})); 4.98 (*d*, *J* ≈ 4.0, HO–C(3^{VI})); 4.97 (*d*, *J* ≈ 4.0), 4.965 (*d*, *J* ≈ 4.0), 4.96 (*d*, *J* ≈ 4.0), 4.94 (*d*, *J* = 4.0), 4.89 (*d*, *J* = 3.8) (H–C($1^{II–VI}$)); 4.67 (*d*, *J* = 3.5, H–C(1^{I})); 4.65 (*t*, *J* = 5.6, HO–C(6^{VII})); 4.57 (*d*, *J* ≈ 8.3, H–C(1^{VII})); 4.56 (*t*, *J* = 5.9), 4.54 (*t*, *J* = 5.5), 4.52 (*t*, *J* ≈ 5.8), 4.50 (*t*, *J* = 5.6), 4.475 (*t*, *J* = 5.8), 4.47 (*t*, *J* = 5.9) (HO–C($6^{I–VI}$)); 4.34, 4.22 (AB, *J* = 16.1, C≡CCH$_2$); 3.86 (*dt*, *J* = 4.0, 9.6, H–C(3^{VI})); 3.77 (br. *ddd*, *J* ≈ 1.5, 6.5, 10.0, H–C(5^{VI})); 3.63–3.45 (*m*, 19 H); 3.44–3.37 (*m*, 8 H); 3.35–3.27 (*m*, 10 H); 3.25 (*d*, *J* ≈ 3.5, 6.5, 9.6, H–C(2^{I})); 2.93 (*dt*, *J* = 3.9, 7.9, H–C(2^{VII})); 2.54 (*t*, *J* = 11.0, H–C(4^{VII})). ^{13}C-NMR (125 MHz, D$_2$O): 104.01, 103.87, 103.76, 103.53, 103.45, 103.34 (6*d*, C($1^{I–VI}$)); 99.98 (*d*, C(1^{VII})); 82.82, 82.41 (2 C), 81.85, 81.33, 78.03 (5*d*, C($4^{I–VI}$)); 79.33, 76.85 (2*s*, *C*≡C–C≡*C*); 77.23, 76.57, 76.44, 75.98, 75.84, 75.74, 75.68, 75.65, 75.60, 74.77, 74.67, 74.64, 74.59, 74.56, 74.49, 74.24, 74.06, 73.99, 73.83, 73.45, 70.69 (21*d*, C($2^{I–VII}$), C($3^{I–VII}$), C($5^{I–VII}$)); 72.15, 70.48 (2*s*, C≡*C*–*C*≡C); 64.63 (*t*, C(6^{VII})); 63.39, 63.13, 63.08, 62.97, 62.89, 62.78 (6*t*, C($6^{I–VI}$)); 60.87 (*t*, C≡C*C*H$_2$); 40.42 (*d*, C(4^{VII})). HR-MALDI: 1219.375 ($C_{47}H_{72}NaO_{35}$, $[M+Na]^+$; calc: 1219.375).

Phenyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-1-thio-β*-D-*glucopyranoside* (**26**). Under Ar, a soln. of **1** (4.00 g, 1.21 mmol) in dry CH_2Cl_2 (300 ml) was stirred at −40° for 10 min, treated with Et_3SiH (1.9 ml, 12.16 mmol) and $BF_3 \cdot Et_2O$ (760 µl, 6.05 mmol), and stirred for 1 h at −40° and for 6 h at −10°. The soln. was washed with sat. aq. $NaHCO_3$ soln. (100 ml), H_2O (100 ml), and brine (100 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 40:1 → 5:1) gave **26** (2.93 g, 74%). White foam. R_f (toluene/AcOEt 18:2) 0.48. M.p. 46–48°. $[\alpha]_D^{25} = +54.8$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3232*m*, 2874*m*, 1602*m*, 1493*s*, 1413*w*, 1355*m*, 1152*s*, 1086*s*, 1043*s*, 1006*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.55–7.53 (*m*, 2 arom. H); 7.32–6.85 (*m*, 76 arom. H); 5.51 (*d*, *J* = 3.6), 5.48 (*d*, *J* = 3.6), 5.47 (*d*, *J* = 3.6), 5.43 (*d*, *J* = 3.6), 5.40 (*d*, *J* = 3.6) (H–C($1^{II–VI}$)); 4.83 (*d*, *J* = 10.6), 4.78 (*d*, *J* = 12.1), 4.75 (*d*, *J* = 12.3) (3 ArC*H*); 4.71–4.64 (*m*, 5 ArC*H*, H–C(1^{I})); 4.64 (*d*, *J* = 11.6), 4.63 (*d*, *J* = 11.9), 4.62 (*d*, *J* = 12.1), 4.61 (*d*, *J* = 12.0), 4.58 (*d*, *J* = 12.3), 4.51 (*d*, *J* = 12.0), 4.49 (*d*, *J* ≈ 11.0), 4.47 (*d*, *J* ≈ 12.0), 4.44 (*d*, *J* = 12.0), 4.43 (*d*, *J* = 12.1) (10 ArC*H*); 4.38–4.29 (*m*, 18 ArC*H*); 3.99 (*t*, *J* = 9.0, 1 H); 3.98–3.77 (*m*, 14 H); 3.73–3.68 (*m*, 7 H); 3.65 (*dt*, *J* = 2.1, 9.6, H–C(4^{VI})); 3.55–3.40 (*m*, 12 H); 3.36 (*dd*, *J* = 3.5, 9.7, H–C(2)); 2.65 (*d*, *J* = 2.3, HO–C(4^{VI})). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.48–135.91 (several *s*); 133.76–133.00 (several *s*); 131.99–127.34 (several *d*); 97.18, 96.94, 96.70, 96.67, 96.47 (5*d*, C($1^{II–VI}$)); 87.37 (*d*, C(1^{I})); 86.34 (*d*, C(2^{I})); 81.47, 81.33, 81.32, 81.21, 81.19 (5*d*, C($3^{II–VI}$)); 80.83 (*d*, C(3^{I})); 79.56, 79.53, 79.51, 79.39 (4*d*, C($2^{II–V}$)); 79.00 (*d*, C(5^{I})); 78.88 (*d*, C(2^{VI})); 74.59, 74.12, 73.62, 73.25, 73.08 (5*d*, C($4^{I–V}$)); 72.38 (*d*, C(4^{VI})); 74.44–72.29 (several *t*); 70.97 (4 C) (*d*, C($5^{II–V}$)); 70.40 (*d*, C(5^{VI})); 70.17 (*t*, C(6^{VI})); 69.11, 69.01, 68.86 (2 C), 68.83 (4*t*, C($6^{I–V}$)). HR-MALDI : 3313.49 ($C_{168}H_{157}Cl_{17}NaO_{30}S$, $[M+Na]^+$; calc. 3313.49). Anal. calc. for $C_{168}H_{157}Cl_{17}O_{30}S$ (3290.83): C 61.32, H 4.81, Cl 18.31; found: C 61.47, H 5.07, Cl 18.28.

Phenyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-4*-O-*(prop-2-yn-1-yl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-1-thio-β*-D-*glucopyranoside* (**27**). Under Ar, a soln. of **26** (930 mg, 0.28 mmol) in DMF (30 ml) was cooled to 0°, treated with NaH (68 mg, 1.41 mmol), stirred for 15 min, treated with propargyl bromide (106 µl, 1.41 mmol), stirred at 0° for 1 h and at 23° for 10 h, treated dropwise with MeOH (2 ml), and diluted with H_2O (30 ml) and Et_2O (100 ml). The org. phase was separated, and the aq. phase was extracted with Et_2O (3 × 100 ml). The combined org. layers were washed with brine (100 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 50:1 → 20:1) gave **27** (813 mg, 87%). White foam. R_f (toluene/AcOEt 18:2) 0.62. M.p. 46–48°. $[\alpha]_D^{25} = +63.5$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3302*w*, 2924*m*, 2868*m*, 1600*m*, 1492*s*, 1461*m*, 1408*w*, 1360*m*, 1156*s*, 1090*s*, 1035*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.30–6.84 (*m*, 78 arom. H); 5.51 (*d*, *J* = 3.6), 5.47 (*d*, *J* = 3.6), 5.45 (*d*, *J* = 3.6), 5.43 (*d*, *J* = 3.5), 5.39 (*d*, *J* = 3.6) (H–C($1^{II–VI}$)); 4.83 (*d*, *J* = 10.7), 4.79 (*d*, *J* = 12.0), 4.75 (*d*, *J* = 12.0), 4.71 (*d*, *J* ≈ 11.1, 2 H), 4.69 (*d*, *J* ≈ 12.1, 2 H) (7 ArC*H*); 4.67 (*d*, *J* = 9.7, H–C(1^{I})); 4.65 (*d*, *J* = 11.8), 4.64–4.62 (*m*, 3 H), 4.61 (*d*, *J* = 12.2), 4.58 (*d*, *J* = 12.2), 4.51 (*d*, *J* = 12.2), 4.50 (*d*, *J* ≈ 11.0), 4.48 (*d*, *J* = 12.1), 4.47 (*d*, *J* = 11.9), 4.41 (*d*, *J* = 12.2), 4.37 (*d*, *J* = 11.9) (12 ArC*H*); 4.36–4.30 (*m*, 17 ArC*H*); 4.30 (*dd*, *J* = 2.4, 15.3, OC*H*C≡CH); 4.15 (*dd*, *J* = 2.4, 15.2, OC*H*C≡CH); 3.99 (*t*, *J* = 9.1, H–C(4)); 3.98–3.88 (*m*, H–C($3^{II–V}$), 4 H–C(4), 1 H–C(5), 1 H–C(6)); 3.86–3.83 (*m*, 1 H–C(5)); 3.82–3.73 (*m*, H–C(3^{VI}), 2 H–C(5), 1 H′–C(6)); 3.71–3.68 (*m*, H–C(2^{I}), 4 H–C(6)); 3.66–3.64 (*m*, 1 H–C(5)); 3.54–3.51 (*m*, H–C(5^{I})); 3.53–3.39 (*m*, 4 H–C(2), H–C(3^{I}), H–C(4^{VI}), H–C(6^{VI}), H′–C(6^{VI}), 4 H′–C(6)); 3.35 (*dd*, *J* = 3.6, 9.9, H–C(2)); 2.41 (*t*, *J* = 2.4, OCH$_2$C≡C*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HMQC spectrum): 137.71–135.91 (several *s*); 133.76–132.95 (several *s*); 131.99 (2*d*); 129.36–127.32 (several *d*); 97.33, 96.94, 96.67 (2 C), 96.46 (4*d*, C($1^{II–VI}$)); 87.37 (*d*, C(1^{I})); 86.34 (*d*, C(2^{I})); 81.59, 81.35, 80.32 (2 C), 81.18 (4*d*, C($3^{II–VI}$)); 80.83 (*d*, C(3^{I})); 79.82 (*s*, *C*≡CH); 79.55, 79.53, 79.48, 79.39, 79.35 (5*d*, C($2^{II–VI}$)); 78.99 (*d*, C(5^{I})); 78.22 (*d*, C(4^{VI})); 74.59, 78.14, 73.81, 73.59, 73.09 (5*d*, C($4^{I–V}$)); 74.51 (*s*, C≡*C*H); 74.51–72.29 (several *t*); 71.05,

70.97 (2 C), 71.92, 70.89 (4*d*, C($5^{II–VI}$)); 69.11, 69.00 (2 C), 68.85 (2 C) (3*t*, C($6^{I–V}$)); 68.32 (*t*, C(6^{VI})); 60.03 (*t*, C≡C*C*H2). Anal. calc. for $C_{171}H_{159}Cl_{17}O_{30}$ (3328.88): C 61.70, H 4.81; found: C 61.66, H 4.84.

2-Chloroethyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-4*-O-*(prop-2-yn-1-yl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α/β*-D-*glucopyranoside* (**28**). Under Ar, a suspension of **27** (755 mg, 0.226 mmol), 2-chloroethanol (18 µl, 0.271 mmol), and 3-Å molecular sieves (800 mg) in dry Et_2O (50 ml) was stirred at −60° for 1 h, treated with NIS (92 mg, 0.408 mmol) and TfOH (10 µl, 0.113 mmol), and stirred for 4 h at −60°. The suspension was filtered over *Celite*, washed with 10% aq. $Na_2S_2O_3$ soln. (40 ml), sat. aq. $NaHCO_3$ soln. (2 × 50 ml), H_2O (2 × 50 ml), and brine (50 ml), and dried ($MgSO_4$). Evaporation and FC (toluene/AcOEt 50 : 1 → 30 : 1) gave *α*-**28** (636 mg, 85%) and *β*-**28** (76 mg, 10%).

Data for *α*-**28**: White foam. R_f (toluene/AcOEt 18 : 2) 0.55. M.p. 48–49°. $[\alpha]_D^{25} = +63.3$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 2927*m*, 2867*m*, 1599*m*, 1492*s*, 1408*w*, 1360*m*, 1157*s*, 1080*s*, 1036*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.32–6.84 (*m*, 73 arom. H); 5.52 (*d*, *J* = 3.6), 5.475 (*d*, *J* = 3.5), 5.47 (*d*, *J* = 3.4), 5.46 (*d*, *J* = 3.6), 5.44 (*d*, *J* = 3.5) (H−C($1^{II–VI}$)); 4.90 (*d*, *J* = 12.0, ArC*H*); 4.87 (*d*, *J* = 3.6, H−C(1^{I})); 4.75 (*d*, *J* = 12.1), 4.72 (*d*, *J* = 12.1), 4.71 (*d*, *J* = 11.3), 4.70 (*d*, *J* = 11.8), 4.69 (*d*, *J* ≈ 12.0), 4.68 (*d*, *J* = 12.6) (6 ArC*H*); 4.64–4.57 (*m*, 7 ArC*H*); 4.48 (*d*, *J* = 12.0), 4.46 (*d*, *J* ≈ 11.0), 4.42 (*d*, *J* = 12.1), 4.41 (*d*, *J* = 12.2) (4 ArC*H*); 4.39–4.28 (*m*, 18 ArC*H*, OC*H*C≡CH); 4.15 (*dd*, *J* = 2.4, 15.2, OC*H*C≡CH); 4.02 (*t*, *J* = 8.5, H−C(3^{I})); 3.99–3.85 (*m*, H−C($3^{II–V}$), H−C($4^{I–V}$), H−C(5^{I}), 1 H−C(5), 2 H−C(6)); 3.80–3.76 (*m*, H−C(3^{VI}), 3 H−C(5), OCH_2CH_2Cl); 3.74–3.62 (*m*, H−C(5^{VI}), 3 H−C(6), 2 H′−C(6), OCH$_2$CH_2Cl); 3.56 (*dd*, *J* = 3.6, 9.3, H−C(2)); 3.51–3.39 (*m*, 4 H−C(2), H−C(4^{VI}), 1 H−C(6), 4 H′−C(6)); 3.35 (*dd*, *J* = 3.6, 9.9, H−C(2)); 2.41 (*t*, *J* = 2.4, OCH$_2$C≡C*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.66–135.88 (several *s*); 133.87–132.90 (several *s*); 129.31–127.32 (several *d*); 97.32, 96.70, 96.53, 96.49, 96.43 (5*d*, C($1^{II–VI}$)); 96.76 (*d*, C(1^{I})); 81.58, 81.37 (3 C), 80.24, 81.17 (4*d*, C($3^{I–VI}$)); 80.02 (*d*, C(2^{I})); 79.80 (*s*, *C*≡CH); 79.58, 79.52, 79.48, 79.37, 79.30 (5*d*, C($2^{II–VI}$)); 77.51 (*d*, C(4^{VI})); 74.53 (*s*, C≡*C*H); 74.51–72.23 (several *t*); 74.14, 73.76, 73.71, 73.59, 73.12 (5*d*, C($4^{I–V}$)); 70.99, 70.93, 70.87, 70.84, 70.79 (5*d*, C($5^{II–VI}$)); 70.19 (*d*, C(5^{I})); 68.96, 68.91 (2 C), 68.79 (2 C), 68.23 (4*t*, C($6^{I–VI}$)); 68.47 (*t*, O*C*H$_2$CH$_2$Cl); 60.02 (*t*, C≡C*C*H$_2$); 42.89 (*t*, OCH$_2$*C*H$_2$Cl). HR-MALDI: 3321.45 ($C_{167}H_{154}Cl_{18}NaO_{31}$, $[M + Na]^+$; calc: 3321.45). Anal. calc. for $C_{167}H_{154}Cl_{18}O_{31}$ (3295.18): C 60.87, H 4.71; found: C 60.75, H 4.93.

Data for *β*-**28**: White foam. R_f (toluene/AcOEt 18 : 2) 0.54. $[\alpha]_D^{25} = +58.8$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.36–6.88 (*m*, 73 arom. H); 5.54 (*d*, *J* = 3.6), 5.49 (*d*, *J* = 3.6), 5.48 (*d*, *J* = 3.7), 5.47 (*d*, *J* = 3.7), 5.46 (*d*, *J* = 3.6) (H−C($1^{II–VI}$)); 4.94 (*d*, *J* = 11.4), 4.83 (*d*, *J* = 12.1), 4.75 (*d*, *J* = 11.3), 4.72 (*d*, *J* ≈ 11.0), 4.71 (*d*, *J* ≈ 12.1), 4.69 (*d*, *J* ≈ 12.0, 2 H), 4.67 (*d*, *J* ≈ 12.0, 3 H), 4.64 (*d*, *J* ≈ 12.0, 2 H), 4.59 (*d*, *J* ≈ 12.0), 4.56 (*d*, *J* = 11.4), 4 51 (*d*, *J* = 12.2), 4.49 (*d*, *J* = 12.0) (16 ArC*H*); 4.48 (*d*, *J* = 7.9, H−C(1^{I})); 4.47 (*d*, *J* = 11.7), 4.42 (*d*, *J* = 12.3) (2 ArC*H*); 4.40–4.30 (*m*, 18 ArC*H*); 4.31 (*dd*, *J* = 2.4, 15.4, OC*H*C≡CH); 4.16 (*dd*, *J* = 2.3, 15.3, OC*H*C≡CH); 4.15 (*td*, *J* = 5.1, 11.2, OC*H*CH$_2$Cl); 4.00–3.77 (*m*, H−C($3^{II–VI}$), H−C($4^{I–V}$), H−C($5^{II–V}$), 1 H−C(6), OC*H*CH$_2$Cl); 3.74–3.67 (*m*, H−C(3^{I}), 4 H−C(6), 1 H′−C(6), OCH$_2$CH_2Cl); 3.66–3.67 (*m*, H−C(5^{VI})); 3.54–3.52 (*ddd*, *J* ≈ 1.5, 6.5, 10.7, H−C(5^{I})); 3.51–3.40 (*m*, 5 H−C(2), H−C(4^{VI}), 1 H−C(6), 5 H′−C(6)); 3.36 (*dd*, *J* = 3.6, 10.0, H−C(2)); 2.40 (*t*, *J* = 2.4, OCH$_2$C≡C*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.68–135.90 (several *s*); 133.57–132.91 (several *s*); 129.48–127.59 (several *d*); 103.59 (*d*, C(1^{I})); 97.30, 96.65, 96.54, 96.46 (2 C) (4*d*, C($1^{II–VI}$)); 84.20 (*d*, C(3^{I})); 81.56 (*d*, C(3^{VI})); 81.48 (*d*, C(2^{I})); 81.33 (3 C), 80.18 (2*d*, C($3^{II–V}$)); 79.79 (*s*, *C*≡CH); 79.51, 79.44 (2 C), 79.37, 79.32 (4*d*, C($2^{II–VI}$)); 77.53 (*d*, C(4^{VI})); 74.72 (*d*, C(5^{I})); *ca.* 74.5 (*s*, C≡*C*H); 74.48–72.45 (several *t*); 73.92, 73.79, 73.68, 73.56, 73.49 (5*d*, C($4^{I–V}$)); 71.01, 70.95, 70.85 (3 C) (3*d*, C($5^{II–VI}$)); 68.74 (*t*, O*C*H$_2$CH$_2$Cl); 68.94 (2 C), 68.82 (2 C), 68.28 (2 C) (3*t*, C($6^{I–VI}$)); 60.00 (*t*, C≡C*C*H$_2$); 42.88 (*t*, OCH$_2$*C*H$_2$Cl). HR-MALDI : 3321.55 ($C_{167}H_{154}Cl_{18}NaO_{31}$, $[M + Na]^+$; calc: 3321.45).

2-Azidoethyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-4*-O-*(prop-2-yn-1-yl)-α*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-α*-D-*glucopyranoside* (**29**). Under Ar, a soln. of **28** (250 mg, 7.58 µmol) in DMF (8 ml) was treated with NaN_3 (7.4 mg, 0.114 mmol), heated to 100°, and stirred for 1 h. The soln. was cooled to 23° and diluted with AcOEt (30 ml) and H_2O (20 ml). The org. and aq. phases were separated, and the aq. phases were extracted with AcOEt (2 × 30 ml). The combined org. layers were washed with brine (50 ml), dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 60 : 1 → 30 : 1) gave **29** (227 mg, 91%). White foam. R_f (toluene/AcOEt 18 : 2) 0.35. M.p. 43–45°. $[\alpha]_D^{25} = +61.9$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 2925*m*, 2868*m*, 2109*w*, 1599*m*, 1492*s*, 1408*w*, 1360*m*, 1156*s*, 1090*s*, 1036*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.32–6.85 (*m*, 73 arom. H); 5.53 (*d*, *J* = 3.6), 5.48 (*d*, *J* ≈ 3.0, 2 H), 5.46 (*d*, *J* = 3.7), 5.45 (*d*, *J* = 3.7) (H−C($1^{II–VI}$)); 4.89 (*d*, *J* = 12.0, ArC*H*); 4.84 (*d*, *J* = 3.5, H−C(1^{I})); 4.74 (*d*, *J* ≈ 12.3), 4.725 (*d*, *J* ≈ 12.0), 4.72 (*d*, *J* ≈ 11.3), 4.71 (*d*, *J* = 11.9), 4.69 (*d*, *J* ≈ 12.0), 4.68 (*d*, *J* = 11.7) (6 ArC*H*); 4.65–4.55 (*m*,

7 ArC*H*); 4.49 (*d*, *J* = 12.0), 4.47 (*d*, *J* ≈ 11.0), 4.44 (*d*, *J* = 11.9), 4.41 (*d*, *J* = 12.1) (4 ArC*H*); 4.39–4.30 (*m*, 18 ArC*H*); 4.31 (*dd*, *J* = 2.4, 15.2, OC*H*C≡CH); 4.16 (*dd*, *J* = 2.4, 15.2, OC*H*C≡CH); 4.04 (*t*, *J* = 8.9, H–C(3^{I})); 4.00–3.77 (*m*, H–C($3^{II–VI}$), H–C($4^{I–V}$), H–C($5^{I–V}$), 2 H–C(6)); 3.73–3.60 (*m*, H–C(5^{VI}), 3 H–C(6), 2 H′–C(6), OC*H*CH_2N_3); 3.56 (*ddd*, *J* = 3.2, 9.8, 19.7, OC*H*CH_2N_3); 3.55 (*dd*, *J* = 3.6, 9.4, H–C(2^{I})); 3.51–3.40 (*m*, 4 H–C(2), H–C(4^{VI}), 1 H–C(6), 4 H′–C(6), $OCH_2CH_2N_3$); 3.36 (*dd*, *J* = 3.6, 9.9, H–C(2)); 2.41 (*t*, *J* = 2.4, $OCH_2C{\equiv}CH$). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.69–135.91 (several *s*); 133.78–132.91 (several *s*); 129.15–127.30 (several *d*); 97.30, 96.84, 96.64, 96.51, 96.44 (2 C) (5*d*, C($1^{I–VI}$)); 81.58, 81.34 (3 C), 80.19, 81.13 (4*d*, C($3^{I–VI}$)); 80.00 (*d*, C(2^{I})); 79.80 (*s*, *C*≡CH); 79.56, 79.52, 79.47, 79.38, 79.34 (5*d*, C($2^{II–VI}$)); 77.54 (*d*, C(4^{VI})); 74.51 (*s*, C≡C*H*); 74.47–72.16 (several *t*); 74.25, 73.79, 73.72, 73.55, 73.06 (5*d*, C($4^{I–V}$)); 71.01, 70.95, 70.86 (2 C), 70.83 (5*d*, C($5^{II–VI}$)); 70.28 (*d*, C(5^{I})); 68.98 (4 C), 68.83 (2 C), 68.29 (3*t*, C($6^{I–VI}$), $OCH_2CH_2N_3$); 60.00 (*t*, C≡CCH_2); 50.65 (*t*, $OCH_2CH_2N_3$). Anal. calc. for $C_{167}H_{154}Cl_{17}N_3O_{31}$ (3301.75): C 60.75, H 4.70, N 1.27; found: C 60.75, H 4.90, N 1.32.

Thermolysis of **29**. Under Ar, a soln. of **29** (115 mg, 34.8 μmol) in DMF (35 ml) was heated to 110°, stirred for 4 days, and cooled to 23°. Evaporation and FC (toluene/AcOEt 50:1 → 5:1) gave **30** (28 mg, 24%) and **31** (36 mg, 31%).

*2-[4-(Hydroxymethyl)-1*H*-[1,2,3]triazol-1-yl]ethyl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 1″,4^{VI}-Anhydride* (**30**). White foam. R_f (toluene/AcOEt 18:2) 0.08. M.p. 57–59°. $[\alpha]_D^{25} = +32.0$ (*c* = 1.00, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.41 (*s*, C=CH); 7.35–6.85 (*m*, 73 arom. H); 5.20 (*d*, *J* = 3.4), 5.16 (*d*, *J* = 3.6), 5.07 (*d*, *J* = 3.5), 5.06 (*d*, *J* = 2.2, 2 H) (H–C($1^{II–VI}$)); 5.02 (*d*, *J* = 11.4), 4.94 (*d*, *J* = 11.4), 4.90 (*d*, *J* = 11.7), 4.90 (*d*, *J* = 12.2) (4 ArC*H*); 4.88 (*d*, *J* = 16.9, C=CCHO); 4.78 (*d*, *J* = 3.5, H–C(1^{I})); 4.77 (*d*, *J* = 10.7), 4.71 (*d*, *J* = 11.6) (2 ArC*H*); 4.68–4.64 (*m*, 2 ArC*H*, C=CCHO); 4.58 (*d*, *J* = 11.4), 4.54 (*d*, *J* ≈ 11.7, 2 H) (3 ArC*H*); 4.50–4.40 (*m*, 5 ArC*H*, OCH_2CH_2N); 4.39–4.28 (*m*, 20 ArC*H*); 3.95–3.75 (*m*, H–C($3^{I–VI}$), 5 H–C(4), H–C($5^{I–V}$), 4 H–C(6), 1 H′–C(6), OCH_2CH_2N); 3.68–3.67 (*m*, H–C(5^{VI})); 3.63 (*dd*, *J* = 4.4, 10.4, H–C(6)); 3.60 (*dd*, *J* ≈ 4.4, 10.4, H–C(6)); 3.58 (*t*, *J* = 9.5, H–C(4)); 3.54–3.46 (*m*, H–C(2^{I}), 5 H′–C(6)); 3.38 (*dd*, *J* = 3.0, 9.8), 3.37 (*dd*, *J* = 3.3, 9.8, 2 H), 3.36 (*dd*, *J* = 3.4, 9.6), 3.35 (*dd*, *J* = 3.3, 10.0) (H–C($2^{II–VI}$)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 145.46 (*s*, *C*=CH); 137.76–135.80 (several *s*); 134.01–132.89 (several *s*); 129.15–122.77 (several *d*); 122.77 (*d*, C=*C*H); 99.10, 98.72, 98.35, 98.18, 98.02 (5*d*, C($1^{II–VI}$)); 96.71 (*d*, C(1^{I})); 81.48, 80.83, 80.74 (2 C), 81.69 (2 C) (4*d*, C($3^{I–VI}$)); 79.64, 79.57, 79.53 (3*d*, 3 C(2)); 79.43, 79.30, 79.15 (2 C), 79.11, 79.05 (5*d*, 3 C(2), 3 C(4)); 78.47, 77.83 (2 C) (2*d*, 3 C(4)); 74.82–72.16 (several *t*); 71.60 (2 C), 71.54, 71.36, 71.33, 70.86 (5*d*, C($5^{I–VI}$)); 69.59, 69.45, 69.10, 69.01, 68.94 (2 C) (5*d*, C($6^{I–VI}$)); 66.59 (*t*, C=CCH_2O); 66.15 (*t*, OCH_2CH_2N); 49.38 (*t*, OCH_2CH_2N). HR-MALDI: 3328.50 ($C_{167}H_{155}Cl_{17}N_3NaO_{31}$, $[M + Na]^+$; calc: 3328.56). Anal. calc. for $C_{167}H_{155}Cl_{17}N_3O_{31}$ (3302.76): C 60.73, H 4.73, N 1.27; found: C 60.93, H 4.90, N 1.31.

*2-[5-(Hydroxymethyl)-1*H*-[1,2,3]triazol-1-yl]ethyl 6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranosyl]$_4$-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-α-*D*-glucopyranoside 1″,4^{VI}-Anhydride* (**31**). White foam. R_f (toluene/AcOEt 18:2) 0.08. $[\alpha]_D^{25} = +38.1$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 2926*m*, 2870*m*, 1898*w*, 1727*w*, 1599*m*, 1492*s*, 1408*m*, 1360*m*, 1090*s*, 1038*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 7.30–6.86 (*m*, 74 arom. H); 5.25 (*d*, *J* = 3.3), 5.11 (*d*, *J* = 3.7), 5.07 (*d*, *J* = 3.4) (3 H–C(1)); 5.04 (*d*, *J* ≈ 14.6, C=CCHO); 5.02 (*d*, *J* ≈ 3.7, H–C(1)); 5.01 (*d*, *J* ≈ 11.1, ArC*H*); 5.00 (*d*, *J* = 3.7, H–C(1)); 4.88 (br. *d*, *J* = 11.1, 2 H), 4.83 (*d*, *J* = 11.1), 4.82 (*d*, *J* = 11.6) (4 ArC*H*); 4.73 (*d*, *J* = 3.7, H–C(1^{I})); 4.69 (*d*, *J* = 12.4), 4.66 (*d*, *J* ≈ 12.0), 4.63 (*d*, *J* = 11.1) (3 ArC*H*); 4.61 (*d*, *J* = 14.3, C=CCHO); 4.60 (*d*, *J* ≈ 11.0), 4.59 (*d*, *J* ≈ 11.0), 4.58 (*d*, *J* = 11.1), 4.55 (*d*, *J* = 11.7) (4 ArC*H*); 4.41–4.22 (*m*, 24 ArC*H*, OCH_2CH_2); 3.99 (*dd*, *J* = 4.9, 11.0, H–C(6)); 3.98–3.70 (*m*, H–C($3^{I–VI}$), 5 H–C(4), H–C($5^{I–V}$), 2 H–C(6), 2 H′–C(6)); 3.71 (*dd*, *J* = 6.3, 10.9, H′–C(6)); 3.67–3.61 (*m*, H–C(5^{VI}), 1 H–C(6), 1 H′–C(6)); 3.57 (*dd*, *J* = 4.5, 10.1, 2 H–C(6)); 3.53 (*dd*, *J* = 6.1, 9.7, 2 H′–C(6)); 3.46 (*dd*, *J* = 3.2, 8.7, H–C(2)); 3.45 (*t*, *J* = 8.7, H–C(4)); 3.43–3.35 (*m*, H–C($2^{II–VI}$)); 3.08 (*d*, *J* = 2.9, OCH_2CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 137.43–137.00 (several *s*); 136.44–135.82 (several *s*); 134.21 (*d*, C=*C*H); 133.92–132.96 (several *s*); 129.13–125.52 (several *d*); 99.21, 99.04, 98.89, 98.83, 98.20 (5*d*, C($1^{II–VI}$)); 97.07 (*d*, C(1^{I})); 81.73, 80.97 (3 C), 80.62, 81.42 (2 C), 80.33 (2 C) (5*d*, C($3^{I–VI}$), 3 C(4)); 79.65, 79.53 (2 C), 79.35 (2 C), 78.84 (2 C) (4*d*, C($2^{I–VI}$), 1 C(4)); *ca.* 77.0, 76.24 (2*d*, 2 C(4)); 74.86–72.04 (several *t*); 71.68, 71.62, 71.41, 71.31, 70.87, 70.70 (6*d*, C($5^{I–VI}$)); 69.60, 69.50, 69.25, 69.06, 68.88, 67.25 (6*d*, C($6^{I–VI}$)); 68.28 (*t*, OCH_2CH_2N); 61.22 (*t*, C≡CCH_2O); 47.30 (*t*, OCH_2CH_2N). HR-MALDI: 3328.51 ($C_{167}H_{155}Cl_{17}N_3NaO_{31}$, $[M + Na]^+$; calc. 3328.56). Anal. calc. for $C_{167}H_{155}Cl_{17}N_3O_{31}$ (3302.76): C 60.73, H 4.73, N 1.27; found: C 60.67, H 4.90, N 1.23.

*2-[4-(Hydroxymethyl)-1*H*-[1,2,3]-triazol-1-yl]ethyl [(1 → 4)-α-*D*-Glucopyranosyl]$_5$-(1 → 4)-α-*D*-glucopyranoside 1″,4^{VI}-Anhydride* (**32**). A soln. of **30** (25 mg, 7.5 μmol) in CH_2Cl_2 (3 ml) was treated with $FeCl_3$ (22.7 mg, 0.14 mmol) stirred at 23° for 1.5 h. After the addition of H_2O (0.5 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) gave **32** (5.6 mg, 68%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) 0.12. ^{1}H-NMR (500 MHz, D_2O): 8.10 (*s*, C=CH); 5.25 (*d*, *J* = 4.0), 5.18 (*d*, *J* = 3.9), 5.13 (*d*, *J* = 3.8), 5.07 (*d*, *J* = 3.7), 5.05 (*d*, *J* = 3.6), 4.98 (*d*, *J* = 3.9) (H–C(1$^{I–VI}$)); 4.96, 4.81 (*AB*, *J* = 11.8, C=C–CH_2O); 4.68 (*t*, *J* ≈ 5.8, OCH_2CH$_2$N); 4.11–4.01 (*m*, OCH$_2$CH_2N); 3.97 (*dd*, *J* = 8.8, 9.9, 1 H); 3.94 (*dd*, *J* = 8.8, 9.9, 1 H); 3.93–3.79 (*m*, 18 H); 3.77 (*dd*, *J* = 4.1, 12.8, H–C(6)); 3.74 (*dd*, *J* = 4.1, 12.1), 3.69 (*dd*, *J* = 2.2, 12.3) (2 H–C(6)); 3.58–3.53 (*m*, 12 H); 3.51 (*t*, *J* = 9.4, 1 H). ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY and a TOCSY spectrum): 8.03 (*s*, C=CH); 5.73 (*d*, *J* ≈ 2.8, HO–C(3)); 5.72 (*d*, *J* = 6.6, HO–C(2)); 5.705 (*d*, *J* = 6.8, HO–C(2^{VI})); 5.70 (*d*, *J* = 2.5), 5.68 (*d*, *J* = 2.6) (2 HO–C(3)); 5.65 (*d*, *J* = 7.3), 5.60 (*d*, *J* = 7.4) (2 HO–C(2)); 5.57 (*d*, *J* = 2.9, 2 HO–C(3)); 5.52 (*d*, *J* = 7.3, HO–C(2)); 5.21 (*d*, *J* = 5.7, HO–C(3^{VI})); 5.00 (*d*, *J* = 6.1, HO–C(2^I)); 4.97, 4.60 (AB, *J* = 11.6, C=C–CH_2O); 4.94 (*d*, *J* = 3.7, H–C(1)); 4.89 (*d*, *J* = 3.7, H–C(1^{VI})); 4.87 (*d*, *J* = 3.5), 4.86 (*d*, *J* = 3.7), 4.84 (*d*, *J* = 3.6) (3 H–C(1)); 4.81 (*d*, *J* = 3.7, H–C(1^I)); 4.63 (*t*, *J* = 5.9, HO–C(6^{VI})); 4.55 (*t*, *J* ≈ 5.5, HO–C(6), OCH_2CH$_2$N); 4.53 (*t*, *J* = 5.5), 4.50 (*t*, *J* = 5.6), 4.44 (*t*, *J* = 5.6), 4.43 (*t*, *J* = 5.2) (4 HO–C(6)); 3.89–3.82 (*m*, OCH$_2$CH_2N); 3.67–3.57 (*m*, 14 H); 3.56–3.42 (*m*, 6 H); 3.40–3.23 (*m*, 16 H). ^{13}C-NMR (125 MHz, D_2O): 147.17 (*s*, *C*=CH); 127.78 (*d*, C=*C*H); 104.11, 104.04, 103.77, 103.47, 102.50 (5*d*, C(1$^{II–VI}$)); 100.77 (*d*, C(1^I)); 83.39, 83.01, 82.89, 81.62, 80.37, 80.29 (6*d*, C(4$^{I–VI}$)); 75.94, 75.75, 75.62, 75.57, 75.50, 75.32, 74.93, 74.62, 74.56 (4 C), 74.51, 74.25, 74.13 (2 C), 73.91, 73.13 (14 *d*, C(2$^{I–VI}$), C(3$^{I–VI}$), C(5$^{I–VI}$)); 69.28 (*t*, C=C*C*H$_2$O); 67.12 (*t*, O*C*H$_2$CH$_2$N); 63.14, 62.95 (4 C), 62.72 (3*t*, C(6$^{I–VI}$)); 52.48 (*t*, OCH$_2$*C*H$_2$N). HR-MALDI-MS: 1120.365 ($C_{41}H_{67}N_3NaO_{31}$, $[M + Na]^+$; calc: 1120.365).

*2-[5-(Hydroxymethyl)-1*H*-[1,2,3]-triazol-1-yl]ethyl [(1 → 4)-α-*D*-Glucopyranosyl]$_5$-(1 → 4)-α-*D*-glucopyranoside 1″,4^{VI}-Anhydride* (**33**). A soln. of **31** (45 mg, 13.6 μmol) in CH_2Cl_2 (5 ml) was treated with $FeCl_3$ (40.9 mg, 0.252 mmol) stirred at 23° for 1.5 h. After the addition of H_2O (1 ml), the soln. was stirred at 23° for 5 min. Evaporation and FC (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) gave **33** (9.8 mg, 66%). White foam. R_f (CH_2Cl_2/MeOH/H_2O 75 : 50 : 12) 0.13. ^{1}H-NMR (500 MHz, D_2O): 7.83 (*s*, C=CH); 5.29 (*d*, *J* = 3.7), 5.13 (*d*, *J* = 3.3), 5.12 (*d*, *J* = 3.5) (3 H–C(1)); 5.07, 4.94 (*AB*, *J* = 13.5, C=C–CH_2); 5.05 (*d*, *J* = 3.4), 5.04 (*d*, *J* = 3.0) (2 H–C(1)); 4.91 (*d*, *J* = 3.8, H–C(1^I)); 4.79 (*dt*, *J* = 4.4, 14.5), 4.64 (*dt*, *J* = 4.3, 14.7) (OCH_2CH$_2$N); 4.03–3.93 (*m*, 5 H); 3.91–3.80 (*m*, 12 H); 3.79–3.52 (*m*, 19 H); 3.48 (*t*, *J* = 9.6, 1 H); 2.92 (*dt*, *J* = 3.6, 9.6, H–C(5^I)). ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY and a TOCSY spectrum): 7.65 (*s*, C=CH); 5.74 (*d*, *J* = 2.6, HO–C(3)); 5.71 (*d*, *J* = 6.6, HO–C(2)); 5.68 (*d*, *J* ≈ 2.7, HO–C(3)); 5.66 (*d*, *J* ≈ 7.0), 5.65 (*d*, *J* = 6.5) (2 HO–C(2)); 5.64 (*d*, *J* ≈ 2.4, HO–C(3)); 5.615 (*d*, *J* = 6.4, HO–C(2)); 5.61 (*d*, *J* ≈ 2.2, HO–C(3)); 5.57 (*d*, *J* = 6.7, HO–C(2^{VI})); 5.48 (*d*, *J* = 3.0, HO–C(3)); 5.23 (*d*, *J* = 5.7, HO–C(3^{VI})); 5.03, 4.88 (*AB*, *J* = 13.0, C=C–CH_2O); 4.90 (*d*, *J* = 3.7, H–C(1^{VI})); 4.89 (*d*, *J* = 3.8), 4.84 (*d*, *J* = 3.6), 4.825 (*d*, *J* = 3.3), 4.82 (*d*, *J* = 3.3) (4 H–C(1)); 4.80 (*d*, *J* = 6.3, HO–C(2^I)); 4.73 (*d*, *J* = 3.7, H–C(1^I)); 4.68 (*td*, *J* = 5.4, 14.2, OC*H*CH$_2$N); 4.51 (*t*, *J* = 5.7, 2 HO–C(6)); 4.50 (*td*, *J* = 5.5, 13.9, OC*H*CH$_2$N); 4.45 (*t*, *J* = 5.7), 4.44 (*t*, *J* = 5.4), 4.43 (*t*, *J* = 5.1), 4.41 (*t*, *J* = 5.6) (4 HO–C(6)); 3.98 (*dt*, *J* = 5.5, 13.9, OCH$_2$CH_2N); 3.68–3.57 (*m*, 20 H); 3.52–3.50 (*m*, 2 H); 3.48–3.42 (*m*, 2 H); 3.41–3.16 (*m*, 12 H); 3.12 (*t*, *J* = 9.6, H–C(4^{VI})). HR-MALDI-MS: 1120.366 ($C_{41}H_{67}N_3NaO_{31}$, $[M + Na]^+$; calc. 1120.365).

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Received October 22, 2001