# 167. Oligosaccharide Analogues of Polysaccharides

Part 9

## Synthesis and Thermolysis of Acetylenosaccharide-Derived 1,2-Dialkynylbenzenes

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Thermolysis of the 1,2-bis(glucosylalkynyl)benzenes **6** and **16** was studied to evaluate the effects of intramolecular H-bonding on the activation energy of the *Bergman-Masamune-Sondheimer* cycloaromatization, and to evaluate the use of the cycloaromatization for the synthesis of di-glycosylated naphthalenes. The dialkynes were prepared by cross-coupling of the *O*-benzylated or *O*-silylated glucosylalkynes **1** and **4** (*Scheme 1*). Thiolysis of the known **1**, or acetolysis of **1**, followed by deacetylation (→ **2** → **3**) and silylation gave **4**. Cross-coupling of **1** or **4** with iodo- or 1,2-diiodobenzene depended upon the nature of the added amine and on the protecting group, and led to the mono- and dialkynylbenzenes **5** and **6**, or **12**, **13**, and **15**, respectively. The benzyl ethers **5** and **6** gave poor yields upon acetolysis catalyzed by $BF_3 \cdot OEt_2$, while $Ac_2O/CoCl_2 \cdot 6\ H_2O$ transformed **6** in good yields into the regioselectively debenzylated **10**. Desilylation of **7** and **13** gave the alcohols **8** and **14**, respectively. Thermolysis of **6** in PhCl gave **22** and **23**, independently of the presence or absence of 1,4-cyclohexadiene; **23** was formed from **22** (*Scheme 2*). Acetolysis of **22** gave the hexaacetate **24** that was completely debenzylated by thiolysis, yielding the diol **26** and *trans*-stilbene, evidencing the nature and position of the bridge between the glucosyl moieties (*Scheme 3*). Thiolysis of **22** yielded the unprotected 2,3-diglucosylnaphthalene **28**, a new type of *C*-glycosides. Depending upon conditions, hydrogenation of **22** led to **29** (after acetylation), **30**, or **32**. NMR and particularly NOE data evidence the *threo*-configuration of the bridge. The structure of **23** was confirmed by hydrolysis to the diol **34** and diphenylacetaldehyde, and by correlation of **23** with **22** *via* the common product **31**. Formation of **22** is rationalized by a *Bergman* cyclization to a diradical, followed by regioselective abstraction of a H-atom from the BnO–C(2) group, and diastereoselective combination of the doubly benzylic diradical (*Scheme 4*). While thermolysis of **3** in EtOH sets in around 140°, **16** did not react at 160° and decomposed at 180–220°. No evidence for intramolecular H-bonds of **16**, as compared to **14**, were found.

**Introduction.** – We have described an approach to study inter- and intramolecular H-bonds of celluloses, based on a comparison of cello-oligosaccharides to analogues where the glycosidic O-atom is replaced by butadiynediyl moieties [1–3]. Attaching cello-oligosaccharides and their analogues in a parallel or antiparallel orientation to a scaffold should enhance the interaction between individual saccharide chains, and contribute to define and rationalize the differences between cellulose I and II [4–6]. Benzene is among the simplest scaffolds to which *C*-alkynylated saccharides can be attached, but the bond angle of 60° may disfavor the interaction of the glycosyl units in *ortho*-disubstituted benzene derivatives.

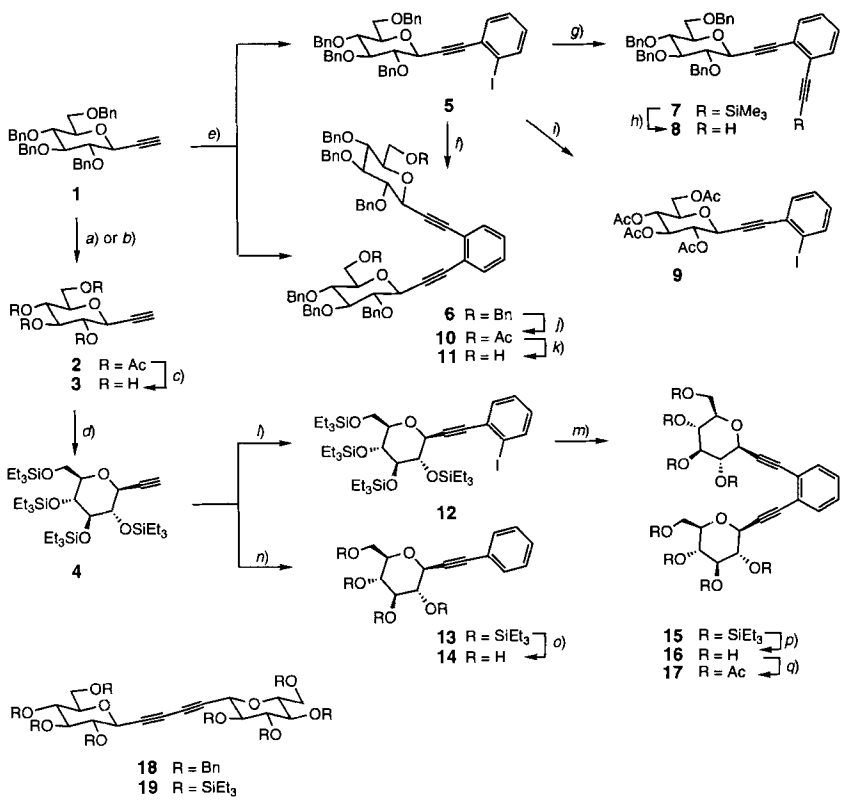
We wondered if the *Bergman-Masamune-Sondheimer* rearrangement [7–11] of protected and unprotected 1,2-bis(2′-glycosylalkynyl)benzenes will lead to 2,3-diglycosylated naphthalenes and provide reactivity-based information on the interresidue H-

[1]) Taken in part from the Diploma Thesis *A. E.*, ETHZ, 1994.

bonds, *i.e.*, if such H-bonds exist, and if they lower the energy of the transition state of the *Bergman* rearrangement. We describe the attachment of ethynylated deoxyglucoses in the *ortho*-position of benzene and the cycloaromatization of benzyl-protected and unprotected diglucosylated 1,2-diethynylbenzenes.

**Results and Discussion.** – *Synthesis of the 1,2-Dialkynylbenzenes: Cross-Coupling of Acetylenosaccharides with Aryl Iodides.* We used the benzyl-protected alkyne **1** and the triethylsilylated analogue **4** in the well-precedented Pd/Cu catalyzed reaction of *o*-dihaloarenes with alkynes [12–15] to synthesize the required 1,2-dialkynylbenzenes and to ensure their facile deprotection. The alkyne **1** is available in an overall yield of 65% from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose [16]. Thiolytic debenzylation of **1** yielded 91% of **3** (*Scheme 1*). Silylation of **3** gave 83% of **4**. This thiolysis proceeded in higher yields

*Scheme 1*




*a*) $BF_3 \cdot OEt_2$, $Ac_2O$; 84% of **2**. *b*) $BF_3 \cdot OEt_2$, EtSH; 91% of **3**. *c*) NaOMe, MeOH; 90%. *d*) $Et_3SiOTf$, pyridine; 83%. *e*) 2 equiv. of **1**, 1 equiv. of *o*-$PhI_2$, $[Pd(PPh_3)_4]$, CuI, piperidine, 80°; 84% of **6** (69% of **6** and 15% of **5** from 1 equiv. of **1** and 1.5 equiv. of *o*-$PhI_2$). *f*) 1 equiv. of **1**, 1 equiv. of **5**, $[Pd(PPh_3)_4]$, CuI, piperidine, 80°; 83%. *g*) 1 equiv. of **5** and 4 equiv. of $Me_3Si-C{\equiv}CH$, $[Pd(PPh_3)_4]$, CuI, piperidine, 80°; 84%. *h*) $Bu_4NF \cdot 3\,H_2O$, THF; 97%. *i*) As *a*); 6%. *j*) $Zn(OTf)_2$, $Ac_2O$; 22%; *or* $CoCl_2 \cdot 6\,H_2O$, $Ac_2O$; 81%. *k*) As *c*); 82%. *l*) 1 equiv. of **4**, 7 equiv. of *o*-$PhI_2$, $[Pd(PPh_3)_4]$, CuI, $Et_3N$, 50°; 95%. *m*) 1 equiv. of **12**, 1.02 equiv. of **4**, $[Pd(PPh_3)_4]$, CuI, $Et_3N$, 50°; 92%. *n*) 1 equiv. of **4**, 3 equiv. of PhI, $[Pd(PPh_3)_4]$, CuI, $Et_3N$, 50°; 89%. *o*) 0.1M HCl, reflux; 80%. *p*) As *o*); 93%. *q*) $Ac_2O$, pyridine; 84%.

than acetolysis of **1** to **2** followed by deacetylation (75% overall). The small vicinal coupling constants (3.8–5.0 Hz) of the ring H-atoms of **4** are best accounted for by an equilibrium mixture of the $^4C_1$ to $^3S_1$ conformers, reflecting the steric interactions of the $Et_3SiO$ groups.

The $[Pd(PPh_3)_4]$ [17] and CuI [18] [19] catalyzed arylation of the alkynes **1** and **4** by PhI or 1,2-diiodobenzene (*o*-$PhI_2$) depended strongly on the nature of the added amine [20] (*Scheme 1*). Coupling of **1** with 1.5 equiv. of *o*-$PhI_2$ proceeded best in piperidine, yielding 15% of the mono- and 69% of the dialkynylated benzenes **5** and **6**, respectively, while coupling in $Et_3N$ yielded 45% of **5**, 15% of **6**, and 8% of the dimer **18**, coupling in $PrNH_2$ 38% of **5** and 9% of **6**, and coupling in *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) only 24% of **5** and 8% of **6**, besides 18% of the known **18** [16].

The coupling also depended on the nature of the protecting groups. Under otherwise identical conditions, coupling of **4** with 1.5 equiv. of *o*-$PhI_2$ in $Et_3N$ gave the best results, yielding the mono- and dialkynylated benzenes **12** (35%) and **15** (34%), respectively, besides the diyne **19** (9%). A further improvement resulted from slow addition of **4**, reducing the extent of its dimerization. Optimized conditions led in 95% yield from **4** to **12**, in 90% from **12** to **15**, and in almost 90% from **4** and iodobenzene to **13**. Remarkably, coupling of 2 equiv. of **1** with *o*-$PhI_2$ gave exclusively **6** (84%), while coupling of 2 equiv. of **4** with *o*-$PhI_2$ under different, but also optimized conditions provided the monoalkynylated **12** (45%) and the dialkynylated **15** (37%). Coupling of the monoalkynylated iodobenzene **5** with **1** or with (trimethylsilyl)acetylene gave the dialkynes **6** (83%) and **7** (84%), respectively.

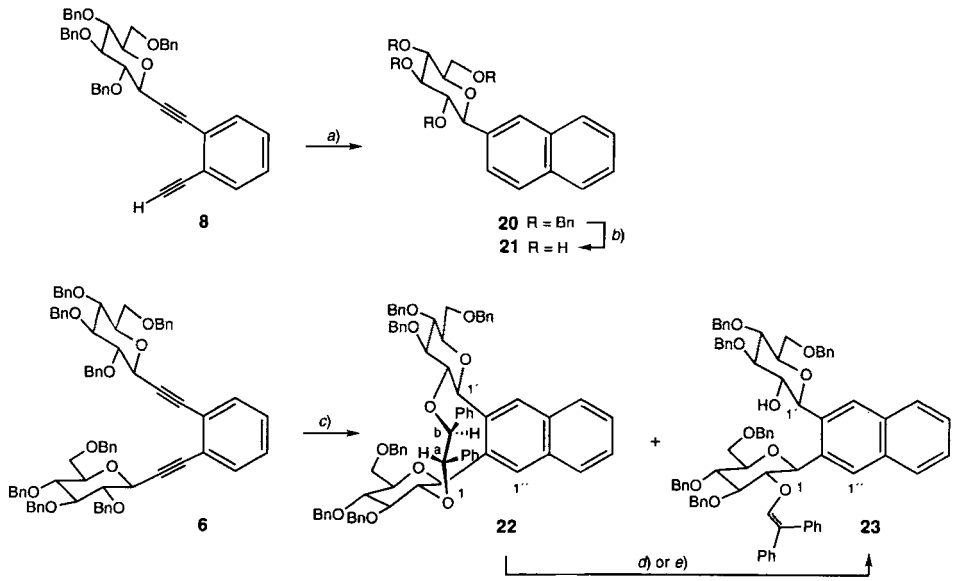
Acetolysis [16] of the benzyl ether **1** in the presence of $BF_3 \cdot OEt_2$ or of $FeCl_3$ led to **2** in 86–90% yield, while the $BF_3 \cdot OEt_2$-promoted acetolysis of the phenylacetylene **5** yielded only 6% of **9**. Similarly, treatment of **6** with $Ac_2O$ and $BF_3 \cdot OEt_2$ or $Me_3SiOTf$ (Tf = trifluoromethanesulfonyl) led to a complex mixture, while changing the catalyst to $Zn(OTf)_2$ or $CoCl_2 \cdot 6\ H_2O$ yielded 22 and 82%, respectively, of the regioselectively debenzylated acetate **10** that was deacetylated to **11**.

Desilylation of the $Me_3Si$-protected alkyne **7** with $Bu_4NF \cdot 3\ H_2O$ yielded 97% of **8**, and cleavage of the triethylsilyl ethers **13** and **15** with dilute HCl in boiling $MeOH/H_2O$ [16] gave the alcohols **14** (80%) and **16** (93%), respectively. The latter was acetylated to **17**.

The $^{13}$C-NMR spectra of the monoalkynylated **5** and **12** show the signals of the *I*-substituted C(2) of the Ph template as *s* at 100.65–100.80 ppm. The *s* of the alkynyl-substituted Ph C(1) of **12** is found at 129.25 ppm, while the one of **5** is hidden by benzyl resonances; 2 *s* at 90.01–92.35 and 86.82–87.28 ppm are assigned to C≡*C*–Ar and *C*≡C–Ar. The corresponding signals of the disubstituted compounds **6**, **7**, and **15** appear at 90.61–92.37 and 83.79–84.57 ppm, and the 2 *s* of their Ph moiety at 126.08–125.14 ppm. The phenylenediynes **6**–**8** and **15**–**17** are characterized by UV maxima at 240, 244, and 278 nm.

Bergman *Cyclization of the 1,2-Dialkynylbenzenes: Synthesis of 2,3-Diglucosylated Naphthalenes*. Thermolysis of the mono-glucosylated dialkyne **8** at 185° in PhCl and in the presence of cyclohexa-1,4-diene gave the 2-(β-D-glucosyl)-substituted naphthalene **20** in 39% yield (*Scheme 2*). Debenzylation yielded 89% of **21**. Thermolysis of the diglucosylated **6** required higher temperatures. Independently of the presence or absence of cyclohexa-1,4-diene, **6** was transformed at 230° into **22** (47–55%) and **23** (6–17%). Prolonging the reaction time increased the amount of **23**, suggesting that it is formed *via* **22**. Thermolysis of **22** under the same conditions, indeed, provided 17% of **23**.

*Scheme 2*




*a*) Cyclohexa-1,4-diene, PhCl, 185°; 39%. *b*) $BF_3 \cdot OEt_2$, EtSH; 89%. *c*) Cyclohexa-1,4-diene, PhCl, 230°; **22** (55%), **23** (6%), and **6** (2%). *d*) As *c*); **23** (17%) and **22** (65%). *e*) PhCl, 230°; **23** (18%) and **22** (80%).

Elemental analysis and the signals for $[M + Na]^+$ at $m/z$ 1170 in the MALDI-MS suggest that **22** and **23** are isomers $C_{78}H_{74}O_{10}$ differing from the expected *Bergman* product by the loss of $H_2$. Both, **22** and **23**, are naphthalenes, as evidenced in their $^1$H-NMR spectra by 2 *s* for 2 H at 8.28/7.98 and 8.07/7.92 ppm (*Table 1*, *Exper. Part*) and the characteristic signals for a 1,2-phenylene moiety at 7.98–7.52 and 7.83–7.44 ppm, respectively (*Exper. Part*). In keeping with the formation of naphthalenes, the *s*'s at 90.61 and 84.49 ppm for the acetylene groups of **6** are no longer present. The primary product **22** was thoroughly investigated by 2D-NMR spectroscopy (DQF-COSY, TOCSY, and HSCQ). The 2D-NMR spectra clearly show that the two missing $PhCH_2$ groups are replaced by a 1,2-diphenylethylene moiety, but they give no information about its position and its absolute configuration. This information was gleamed from a thorough analysis, including 2D-NMR spectroscopy, of the secondary product **23** of the thermolysis.

The $^1$H- and $^{13}$C-NMR spectra of **22** – and also of **23** – show two different sets of signals for $\beta$-D-glucopyranosyl moieties (*Tables 1* and *2*, *Exper. Part*). The large vicinal coupling constants $J(1,2)$, $J(2,3)$, $J(3,4)$, and $J(4,5)$ (9–9.9 Hz) evidence the $^4C_1$ conformation. However, **22** has only six $PhCH_2$ groups. An isolated CH–CH moiety is indicated by two *d*'s at 4.92 and 3.38 ppm ($J$ = 7.5 Hz) and two *d*'s at 85.23 and 87.34 ppm. In addition, two Ph groups resonate at relatively high field. Characteristic signals for $H_o$, $H_m$, and $H_p$ of one Ph group are observed at 6.37, 6.77, and 6.80 ppm, and also for $H_m$ and $H_p$ of the other Ph group at 6.46 and 6.71 ppm, but not for $H_o$ which appear as a broad *s* at 6.5–6.3 ppm, indicating hindered rotation around the C–Ph bond. The secondary product **23** is an unsaturated monoalcohol, as evidenced by the IR spectrum (OH band at 3576 and C=C band at 1632 $cm^{-1}$) and by its transformation into the monoacetate **33** (see below). The NMR spectra of **23** show signals of a naphthalene-2,3-diyl group, two different $\beta$-D-glucopyranosyl moieties, and six $PhCH_2$ group. In addition, a *s* at 6.28 ppm and signals between 6.56 and 7.2 ppm for two Ph groups, a $^{13}$C *d* at 145.68, and a *s* at 119.09 ppm evidence

a 2,2-diphenylethenyloxy moiety [21] [22]. The OH group resonates at 2.20 ppm. Exchange by $D_2O$ led to a change of the H–C(2′) signal at *ca.* 3.66 ppm. The position of the diphenylethenyl group was evidenced by a NOE of 9% for H–C(2) at 4.29 ppm upon irradiation of the olefinic H at 6.28 ppm. Thus, **22** must be bridged by the 1,2-diphenylethylene group between O(2) and O(2′) and possesses a ten-membered ring.

The structural assignment was corroborated by chemical transformations of **22** and **23** (*Scheme 3*). The $BF_3 \cdot OEt_2$ or $Me_3SiOTf$-catalyzed acetolysis of **22** afforded 87% of a hexaacetate **24**, still containing the 1,2-diphenylethylenedioxy bridge. Deacetylation gave the hexol **25**. Treatment of **24** with $BF_3 \cdot OEt_2$ and EtSH gave **26** (58%), possessing two secondary OH and six AcO groups, besides some isomers derived from acetyl migration, as evidenced by the conversion, upon acetylation, of **26** and of these by-products to the octaacetate **27**. *trans*-Stilbene was isolated in 81% yield as the second main product of this thiolysis. Double elimination of the 1,2-diphenylethylene bridge should yield diphenylacetylene which must be reduced *in situ* by EtSH. Finally, $BF_3 \cdot OEt_2$-promoted thiolytic debenzylation of **22** yielded 89% of the completely deprotected 2,3-diglucosylated naphthalene **28**, representing a new type of *C*-glycosides.

Pd-Catalyzed hydrogenation of **22**, followed by acetylation, led to the partially hydrogenated hexaacetate **29** (84%), still containing the diphenylethylene bridge. Harsher conditions (10 bar of $H_2$) led to hydrogenolysis also of the diphenylethylenedioxy group, transforming **29** in 89% yield into the dihydroxy-hexaacetate **30**, the tetrahydro analogue of **26**. The partial hydrogenation of the naphthalene ring appears to be favored by the OH groups of the glucosyl moieties, hydrogenation of the hexaacetate **24** only proceeding under a pressure of 10 bar of $H_2$ to yield 80% of the tetrahydronaphthalene **29**. In agreement with this observation, hydrogenolysis of **22** went only to completion under still harsher conditions (10 bar of $H_2$, large amounts of catalyst, addition of AcOH), yielding 97% of the fully deprotected tetrahydronaphthalene **32**. Acetylation of **30** and of **32** gave **31** in high yields.

The secondary thermolysis product **23** was transformed to its monoacetate **33** (90%). Treatment of **23** with $CF_3COOH$ followed by aqueous workup afforded the symmetric diol **34** (77%) and diphenylacetaldehyde (50%), as expected from the hydrolysis of the 2,2-diphenylethenyloxy group. Hydrogenation of **23**, followed by acetylation, gave the heptaacetylated 2,2-diphenylethyl ether **35** (67%), again a tetrahydronaphthalene, which was cleaved by $AlCl_3$ to yield **36** (86%). Acetylation of **36** yielded the octaacetate **31** which had already been obtained from **22** *via* **29** and **30**.

Not only the $^1H$- and $^{13}C$-NMR spectra of the derivatives **33**, **35**, and **36**, differently substituted at O–C(2) and O–C(2′) show signals for two different $\beta$-D-glucopyranosyl residues (*Tables 1* and *2*), but also the spectra of the bridged derivatives **24**, **25**, and **29**; their differences are even more pronounced. Characteristic for the bridged compounds are the deshielding of H–C(1′)[2]) ($\Delta\delta$ 0.7–1.15 ppm for H–C(1′)/H–C(1)), H–C(2) ($\Delta\delta$ 2.03–2.64 ppm for H–C(2)/H–C(2′)), and H–C(a) ($\Delta\delta$ 1.33–1.71 ppm for H–C(a)/H–C(b)), independently of the nature of the protecting groups. The other glucose ring H-atoms show small $\Delta\delta$ values ( < 0.3 ppm). This is also observed for the glucose ring H-atoms of **23**, **33**, **35**, and **36** (with the exception of H–C(2)/H–C(2′)). The derivatives **26**–**28**, **30**–**32**, and **34** are $C_2$ symmetric and give rise to only one set of signals. The $^1H$-NMR spectra of **26** and **30** show OH signals at 2.54–2.51 and at 2.50 ppm, respectively, and their IR spectra are characterized by broad OH bands at 3688–3467 $cm^{-1}$. H–C(2) of **26** and **30** resonates at 3.93 and 3.72 ppm, respectively, upfield from H–C(2) of the fully acetylated analogues **27** (5.21 ppm) and **31** (5.06 ppm). The H–C(1) signals, however, are hardly affected by the acetylation of **26** and **30**. The $Ph_2CHCH_2$ moiety of **35** is evidenced by an $AB_2$ coupling system at 3.95, 3.57, and 2.97 ppm.

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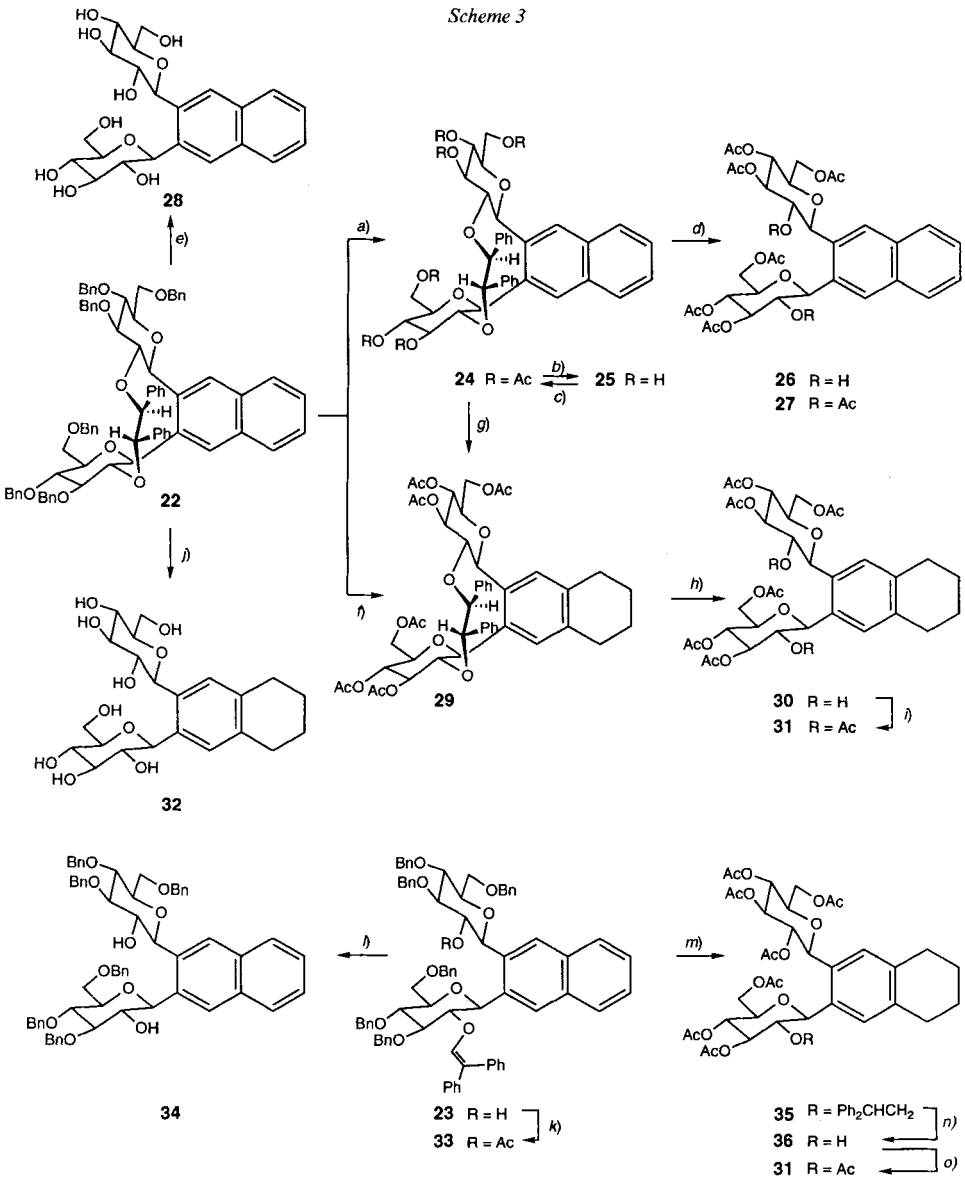
[2]) The saccharide unit whose H–C(1) points towards the other saccharide unit has primed locants. The bridge is labeled with 'a' (bound to the sugar unit with unprimed locants) and 'b'.

*Scheme 3*




*a*) $BF_3 \cdot OEt_2$, $Ac_2O$; 83%. *b*) NaOMe, MeOH; 94%. *c*) $Ac_2O$, pyridine; 93%. *d*) $BF_3 \cdot OEt_2$, EtSH; 58%. *e*) As *d*); 89%. *f*) 1) 30% Pd/C, 1 bar of $H_2$, MeOH/AcOEt. 2) As *c*); 84%. *g*) 30% Pd/C, 10 bar of $H_2$, MeOH/AcOEt; 80%. *h*) As *g*); 89%. *i*) As *c*); 99%. *j*) 30% Pd/C, 10 bar of $H_2$, AcOEt/AcOH; 97%. *k*) As *c*); 90%. *l*) $CF_3COOH$, $CH_2Cl_2$; 76%. *m*) 1) As *g*). 2) As *c*); 67%. *n*) $AlCl_3$, $CH_2Cl_2$; 86%. *o*) As *c*); 94%.

The formation of the 1,2-diphenylethylene bridge can lead to four products, two *threo*- ((a*R*,b*R*) and (a*S*,b*S*)) and two *erythro*-diastereoisomers ((a*R*,b*S*) and (a*S*,b*R*)). Force-field calculation (Macromodel V. 4.5, MM3* force field, gas phase [23]) of the four

diastereoisomers of the hexaacetate **24** shows in each case that the 10-membered ring adopts a saddle-like conformation and that ring inversion is strongly hindered. This does not lead to additional diastereoisomers, but does not allow to distinguish between *threo*- and *erythro*-configurated isomers. The conformation in the diphenylethylene moiety depends strongly upon the configuration of the bridge. A pseudoequatorial orientation of the Ph groups minimizes steric interactions between the Ph and the naphthalene groups. H–C(a) and H–C(b) of both *erythro*-isomers are synclinal; the calculated [24] $J$(a,b) is $\leq$ 3 Hz. The observed $J$(a,b) = 7.5–7.9 Hz for **22**, **24**, **25**, and **29** is only in agreement with a *threo*-configurated bridge, as in (*S*,*S*)-**24** (*Fig.*, *b*; (a*S*,b*S*)-configuration) and (*R*,*R*)-**24** (*Fig.*, *c*; (a*R*,b*R*)-configuration); the calculated $J$(a,b) is 8.0 Hz for (*S*,*S*)-**24** and 8.9 Hz for (*R*,*R*)-**24**. The fragment C(2)–O–C(a)–C(b)–O adopts opposite envelope conformations in (*S*,*S*)-**24** and in (*R*,*R*)-**24** (*Fig.*, *d* and *e*, resp.). The isomer (*S*,*S*)-**24** is 34.3 kJ/mol (8.2 kcal/mol) more stable than (*R*,*R*)-**24**. Two thirds of this energy difference are due to the different ring strains of the 10-membered rings, as shown by calculations of simplified analogues (Ph, AcO, and $AcOCH_2$ groups replaced by H), where $\Delta E$ favors the isomer with the ring system of (*S*,*S*)-**24** by 21.2 kJ/mol (5.1 kcal/mol).

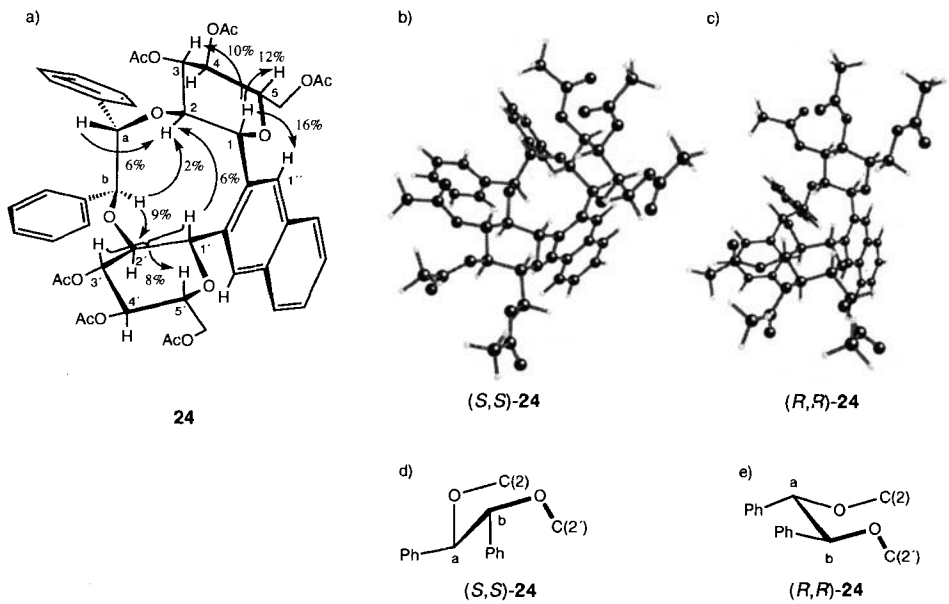



Figure. a) *Conformation of* **24** *as established by NOE's*; b) c) *calculated conformations of the (*a*S*,b*S*)- *and (*a*R*,b*R*)-configurated* threo-*hexaacetates (*S,S*)- *and (*R,R*)-***24***; d) e) conformation of the 1,2-diphenylethylene-dioxy bridge of (*S,S*)- and (*R,R*)-***24****, respectively*

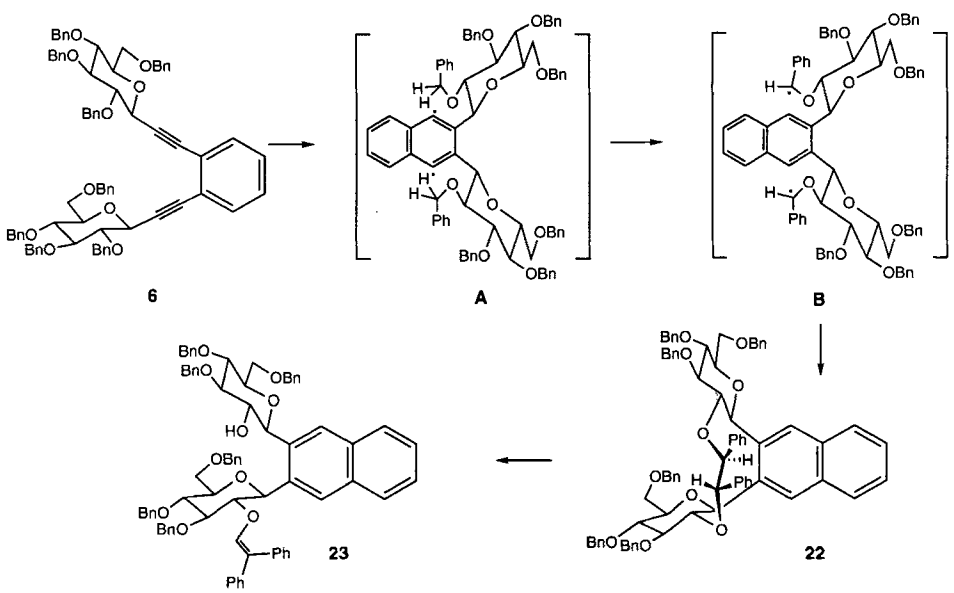
NOE's were measured for the hexaacetate **24** to avoid disturbing $PhCH_2$ signals (*Fig.*, *a*, and *Exper. Part*). Irradiation of H–C(1) at 4.69 ppm led to strong enhancements of the signals for H–C(1″) (16%) at 7.95 ppm, H–C(3) (10%) at 5.33 ppm, and H–C(5) (12%) at *ca.* 3.92 ppm, whereas irradiation of H–C(1′) and H–C(3′) at 5.40 ppm (located on the same side of the ring) led to medium enhancements of the signals of H–C(5′) at *ca.* 3.87 ppm (8%) and H–C(2) (6%) at 5.70 ppm. These measurements show unambiguously that H–C(1″) of the naphthalene moiety and H–C(1) of the glucopyranosyl residue possessing the strongly deshielded H–C(2) are in

close neighborhood. Irradiation of H–C(b) at 3.30 ppm caused NOE's for H–C(2′) (9%) at 3.68 ppm and H–C(2) (2%), and irradiation of H–C(a) at 4.63 ppm led to a NOE for H–C(2) (6%). This clearly fits for (*S,S*)-**24**, where H···H distances (H(b)···H(2′) 2.44 Å, H(b)···H(2) 3.08 Å, H(a)···H(2) 2.54 Å) agree well with the observed NOE's, but not for (*R,R*)-**24** (H(a)···H(2′) 3.08 Å, H(a)···H(2) 2.94 Å, H(b)···H(2) 3.02 Å). The deshielding of H–C(2) is readily rationalized by its close neighborhood to O(2′) (2.14 Å). One of the six Ac groups of **24** resonates as high field (1.65 ppm). It is shielded by a Ph group. That it must be AcO–C(3′) is confirmed by a weak NOE for H–C(3′) at 5.39 ppm ( < 0.5%) observed upon irradiation at 1.65 ppm. A NOE of 2% is also observed for the *t* at 6.90 ppm of $H_m$ of this Ph group. This *t* is broad, and on the same Ph ring (2D-$^1$H-NMR) as $H_o$ that give rise to an exceptionally broad signal, showing that rotation of this Ph group, sandwiched between AcO–C(3′) and the other Ph group is severely hindered.

Thermolysis of **6** follows the established mechanism of the *Bergman* rearrangement, leading to the naphthalene diradical **A** (*Scheme 4*). Such radicals abstract hydrogen relatively slowly [25], and **A** is sufficiently long lived to adopt a conformation allowing the regioselective intramolecular H-abstraction from the BnO group at C(2) (→ **B**) [26]. External H-donors such as cyclohexa-1,4-diene or γ-terpinene do not compete with this abstraction, not even when cyclohexa-1,4-diene is the solvent. A disrotatory movement of the glucosyl residues around the C(2″)–C(1) and C(3″)–C(1′) bonds is necessary before the two PhCH radicals can recombine to give **22**. The formation of a single isomer may be rationalized by assuming that the larger ring strain, calculated for (*R,R*)-**24**, is partially effective in the transition state, resulting in a lower barrier leading to (*S,S*)-**24**. Since the H-abstraction in **A** is hardly stereoselective, isomerization of the dibenzyl diradical must be faster than the radical recombination.

The enol ether **23** is formally derived from a pinacol-type rearrangement, either induced by protonation (non-silanized glassware was used) or by a homolytic cleavage of the C–O bond, [1,2]-phenyl shift, and H-abstraction.

Scheme 4. *Proposed Mechanism for the Formation of* **22** *and* **23**



Intramolecular H-bonds may shorten the bonding distance between the alkynyl groups in **16** as compared to **6**, and lower the activation energy for the cycloaromatization [27]. Not unexpectedly, however, **16** proved only soluble in polar solvents. Macromodel calculations (MM3* force field, gas phase) show that a H-bond between HO–C(2) and O–C(2′) is feasible, but that it should be weak, and may hardly influence the distance between the alkynyl groups. Indeed, no significant difference was observed between the $\Delta\delta/\Delta T$ [28] [29] values of the OH signals for the monoacetylene **14** and the diacetylene **16**, nor for the mono- and diglucosylated naphthalenes **21** and **28**, all of them ranging between 5 and 6 ppb/K ((D$_6$)DMSO, 15 mM, T 300→400 K). Hence, there are at best very weak intramolecular H-bonds.

Thermolysis of **6** in EtOH for 24 h yielded **22** and a number of unidentified by-products, the yield of **22** being 33% at 180°, 6% at 160°, and 1% at 140°, besides 45, 80, and 93% of starting material, respectively. Thermolysis of **16** in EtOH and in the presence of cyclohexa-1,4-diene, however, did not proceed at 160°, and led to decomposition between 180 and 220°. The hypothetical cycloaromatization of **16** appears to require a higher temperature than the one of **6**; presumably, solvation of **16** and a less efficient H-abstraction of the intermediate diradical being important factors. Independently of this finding, the cycloaromatization of appropriately substituted diglycosylated 1,2-diethynylbenzenes constitutes a new method for the preparation of unusually modified 2,3-diglycosylnaphthalenes and a new example of the tandem cycloaromatization-functionalization reactions [15] [30] [31].

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

## Experimental Part

*General.* Unless indicated otherwise, reactions were run under Ar. Standard workup means the mixture was diluted with $CH_2Cl_2$ or AcOEt, and the org. layer washed with brine, dried ($Na_2SO_4$), and evaporated. For coupling reactions, the soln. of aromatic iodides and alkynes were degassed by the freeze-thaw method. For hydrogenations, the air of the reaction system containing the starting material and the catalyst (Pd/C) was exchanged with $N_2$ and then with $H_2$, prior to the addition of the solvent and subsequent degassing. Qual. TLC: 0.25-mm precoated silica-gel plates (*Merck*, silica gel *60* $F_{25}$); detection by spraying the plates with 'mostain' (400 ml of 10% $H_2SO_4$ soln., 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$) or vanillin in 5% aq. $H_2SO_4$ soln. followed by heating at *ca.* 200°. Flash chromatography: silica gel *Merck 60* (0.04–0.063 mm). M.p.: uncorrected. Optical rotations: 1-dm cell at 25°. IR Spectra: 4% solns. $^1$H- and $^{13}$C-NMR Spectra: chemical shifts $\delta$ in ppm rel. to $SiMe_4$ as internal standard; $^1$H assignments based on selective homonuclear decoupling experiments or $^1$H,$^1$H COSY.

*4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D*-glycero-*D*-gulo-octitol* (**2**). At r.t., a soln. of **1** (1.084 g, 1.978 mmol) in $Ac_2O$ (30 ml) was treated with $BF_3\cdot OEt_2$ (2.38 ml, 18.9 mmol) for 2.5 h, cooled to 0°, and then neutralized with aq. $NaHCO_3$ soln. Workup and FC (hexane/AcOEt 7:3) gave **2** (591 mg, 84%). Oil. $R_f$ (toluene/AcOEt 7:3) 0.30. $[\alpha]_D^{25} = +4.8$ ($c = 0.31$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3000*m*, 2800*m*, 2136*w*, 1756*s*, 1540*w*, 1350*m*, 1200*s*, 1020*m*, 1060*m*, 900*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 5.38 (*t*, $J = 9.6$, H–C(4)); 5.23 (*t*, $J = 9.2$, H–C(5)); 5.21 (*t*, $J = 9.5$, H–C(6)); 4.17 (*dd*, $J = 4.6$, 12.4, H–C(8)); 3.96 (*dd*, $J = 2.1$, 12.4, H′–C(8)); 3.82 (*dd*, $J = 2.2$, 9.9, H–C(3)); 3.04 (*dt*, $J = 2.1$, 4.6, 9.9, H–C(7)); 1.91 (*d*, $J = 2.2$, H–C(1)); 1.71 (*s*, Ac); 1.67 (*s*, Ac); 1.64 (*s*, Ac); 1.62 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.71 (*s*, C=O); 170.26 (*s*, C=O); 169.34 (*s*, C=O); 169.23 (*s*, C=O); 77.60 (*d*, C(1)); 76.03 (*s*, C(2)); 75.57 (*d*, C(7)); 73.48 (*d*, C(5)); 70.95 (*d*, C(4)); 68.50 (*d*, C(3)); 67.99 (*d*, C(6)); 61.99 (*t*, C(8)); 20.76 (*q*, Me); 20.62 (*q*, 3 Me). CI-MS: 374 (100, $[M + NH_4]^+$), 297 (34). Anal. calc. for $C_{16}H_{20}O_9$ (356.33): C 53.93, H 5.66; found: C 53.87, H 5.73.

*Deacetylation of* **2** *to* **3**. A soln. of **2** (356 mg, 1 mmol) in 10 ml of MeOH was treated with 5.78M NaOMe in MeOH (0.01 ml, 0.05 mmol) at r.t. for 3 h, neutralized with *Amberlite IR-120* ($H^+$ form), and filtered. Evaporation of the filtrate gave **3** (170 mg, 90%).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy*-D-glycero-D-gulo-*octitol* (**3**). A mixture of **1** (721 mg, 1.30 mmol), EtSH (15 ml), and $BF_3 \cdot OEt_2$ (5.0 ml, 41.6 mmol) was stirred at r.t. for 10 h and evaporated. FC ($Et_2O$/MeOH 9:1) gave **3** (223 mg, 91%) [16]. Oil. $R_f$ (toluene/MeOH 6:4) 0.25. $[\alpha]_D^{25} = +25.2$ ($c = 1.21$, MeOH). $^1$H-NMR (300 MHz, $CD_3OD$): 3.91 (*dd*, $J = 2.1, 9.2$, H–C(3)); 3.85 (*dd*, $J = 1.8, 12.3$, H–C(8)); 3.63 (*dd*, $J = 5.1, 12.0$, H′–C(8)); 3.28–3.19 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); 2.87 (*d*, $J = 2.1$, H–C(1)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 81.88 (*d*, C(5)); 78.97 (*d*, C(7)); 75.78 (*s*, C(2)); 75.26 (*d*, C(6)); 71.95 (*d*, C(4), C(1)); 71.39 (*d*, C(3)); 62.86 (*t*, C(8)). CI-MS: 206 (100, $[M + NH_4]^+$), 69 (100).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-4,5,6,8-tetrakis*-O-*(triethylsilyl)*-D-glycero-D-gulo-*octitol* (**4**). At r.t., a soln. of **3** (614 mg, 3.26 mmol) in pyridine (10 ml) was treated dropwise with a soln. of triethylsilyl trifluoromethanesulfonate ($Et_3SiOTf$) (3.71 ml, 19.5 mmol), kept at 60° for 2 h, and evaporated. Dissolution of the residue in $CH_2Cl_2$ (50 ml), workup, and FC (hexane/toluene 8:2) afforded **4** (1.752 g, 83%). Oil. $R_f$ (hexane/toluene 7:3) 0.27. $[\alpha]_D^{25} = +8.4$ ($c = 1.25$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 3007*w*, 2957*s*, 2912*s*, 2877*s*, 2735*w*, 1458*m*, 1436*w*, 1415*w*, 1099*s*, 1006*s*, 974*w*, 868*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 4.42 (*dd*, $J = 2.2, 8.2$, H–C(3)); 4.04 (*dd*, $J = 3.8, 5.0$, H–C(6)); 4.02 (*dd*, $J = 8.2, 3.8$, H–C(4)); 3.90–3.85 (*m*, H–C(5), 2 H–C(8)); 3.67 (*q*, $J = 4.9$, H–C(7)); 2.03 (*d*, $J = 2.2$, H–C(1)); 0.88–0.61 (*m*, 4 ($MeCH_2$)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 83.18 (*d*, C(1)); 82.43 (*d*, C(5)); 77.89 (*d*, C(4)); 77.21 (*d*, C(6)); 73.91 (*s*, C(2)); 70.09 (*d*, C(7)); 68.24 (*d*, C(3)); 63.42 (*t*, C(8)); 6.94 (*q*, ($MeCH_2$)$_3$Si); 6.87 (*q*, ($MeCH_2$)$_3$Si); 6.73 (*q*, 2 ($MeCH_2$)$_3$Si); 5.29 (*t*, ($MeCH_2$)$_3$Si); 4.94 (*t*, ($MeCH_2$)$_3$Si); 4.82 (*t*, ($MeCH_2$)$_3$Si); 4.37 (*t*, ($MeCH_2$)$_3$Si). EI-MS: 644 (2, $M^+$). Anal. calc. for $C_{32}H_{68}O_5Si_4$ (645.23): C 59.57, H 10.62; found: C 59.81, H 10.48.

*Coupling of* **1** *with 1,2-Diiodobenzene*. At r.t., a suspension of **1** (50 mg, 0.091 mmol) [16], 1,2-diiodobenzene (18 µl, 0.14 mmol), $[Pd(PPh_3)_4]$ (2 mg), and CuI (1 mg) in piperidine (1 ml) was stirred at 80° for 12 h and evaporated. Workup and FC (hexane/AcOEt 9:1) gave **5** (16 mg, 15%) and **6** (47 mg, 69%). The former was recrystallized in hexane/AcOEt 5:1.

*Data of 3,7-Anhydro-4,5,6,8-tetra*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1*-C-*(2-iodophenyl)*-D-glycero-D-gulo-*octitol* (**5**): Solid. M.p. 97°. $R_f$ (toluene/AcOEt 9:0.5) 0.47. $[\alpha]_D^{25} = -8.3$ ($c = 0.69$, $CHCl_3$). UV ($CHCl_3$): 253 (16000). IR ($CHCl_3$): 3089*w*, 3066*w*, 3007*m*, 2961*m*, 2910*m*, 2868*m*, 1952*w*, 1808*w*, 1603*w*, 1555*w*, 1496*m*, 1454*m*, 1431*w*, 1399*w*, 1360*w*, 1294*w*, 1261*s*, 1094*s*, 1067*s*, 1037*s*, 1017*s*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.49 (*dd*, $J = 1.1, 8.0$, H–C(3′)); 7.47 (*dd*, $J = 1.0, 7.0$, H–C(6′)); 7.44–7.04 (*m*, 20 arom. H); 6.69 (*dt*, $J = 7.6, 1.1$, H–C(5′)); 6.36 (*dt*, $J = 7.7, 1.7$, H–C(4′)); 5.28 (*d*, $J = 10.9$, PhC*H*); 4.93 (*d*, $J = 11.2$, PhC*H*); 4.91 (*d*, $J = 10.9$, PhC*H*); 4.88 (*d*, $J = 11.5$, PhC*H*); 4.83 (*d*, $J = 11.2$, PhC*H*); 4.63 (*d*, $J = 11.2$, PhC*H*); 4.51 (*d*, $J = 12.1$, PhC*H*); 4.39 (*d*, $J = 12.1$, PhC*H*); 4.30 (*d*, $J = 9.6$, H–C(3)); 3.84 (*t*, $J = 9.6$, H–C(6)); 3.84 (*t*, $J = 9.0$, H–C(4)); 3.70–3.68 (*m*, 2 H–C(8)); 3.60 (*t*, $J = 9.0$, H–C(5)); 3.31 (*ddd*, $J = 2.3, 3.3, 9.8$, H–C(7)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.80 (2*s*); 138.53 (*s*); 138.03 (*s*); 133.41 (*d*, C(3′)); 129.85 (*d*, C(6′)); 128.97–127.68 (several *d*); 128.96 (*s*, C(1′)); 100.65 (*s*, C(2′)); 90.01 (*s*, C(2)); 87.20 (*s*, C(1)); 86.20 (*d*, C(5)); 82.26 (*d*, C(4)); 79.26 (*d*, C(6)); 77.73 (*d*, C(7)); 75.77 (*t*, PhC*H*$_2$); 75.62 (*t*, PhC*H*$_2$); 75.16 (*t*, PhC*H*$_2$); 73.60 (*t*, PhC*H*$_2$); 70.47 (*d*, C(3)); 68.78 (*t*, C(8)). CI-MS: 768 (8, $[M + NH_4]^+$), 91 (100). Anal. calc. for $C_{42}H_{38}IO_5$ (749.66): C 67.29, H 5.11; found: C 67.04, H 5.33.

*Data of 1,1′-(1,2-Phenylene)bis[3,7-anhydro-4,5,6,8-tetra*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy*-D-glycero-D-gulo-*octitol]* (**6**): Yellow oil. $R_f$ (toluene/AcOEt 9:0.5) 0.38. $[\alpha]_D^{25} = -2.4$ ($c = 0.64$, $CHCl_3$). UV ($CHCl_3$): 240 (19200), 249 (13700), 263 (16800). IR ($CHCl_3$): 3089*w*, 3066*w*, 3007*m*, 2910*m*, 2868*m*, 2218*w*, 1951*w*, 1876*w*, 1812*w*, 1604*w*, 1496*m*, 1484*w*, 1454*m*, 1398*w* 1361*m*, 1296*w*, 1132*m*, 1093*s*, 1066*s*, 1028*m*, 1000*w*, 912*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.78 (*d*, $J = 5.8$, H–C(3′)); 7.50–7.02 (*m*, 40 arom. H); 6.70 (*dd*, $J = 3.3, 5.7$, H–C(4′)); 5.44 (*d*, $J = 11.2$, PhC*H*); 5.05 (*d*, $J = 11.2$, PhC*H*); 4.94 (*d*, $J = 11.2$, PhC*H*); 4.89 (*d*, $J = 11.4$, PhC*H*); 4.79 (*d*, $J = 11.1$, PhC*H*); 4.54 (*d*, $J = 11.2$, PhC*H*); 4.50 (*d*, $J = 11.2$, PhC*H*); 4.41 (*d*, $J = 12.4$, PhC*H*); 4.29 (*d*, $J = 9.6$, H–C(3)); 4.00 (*t*, $J = 9.3$, H–C(6)); 3.82 (*t*, $J = 9.3$, H–C(4)); 3.72–3.64 (*m*, 2 H–C(8)); 3.58 (*t*, $J = 9.0$, H–C(5)); 3.37 (*dt*, $J = 9.9, 2.7$, H–C(7)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.66 (*s*); 138.36 (*s*); 138.15 (2*s*); 132.68–127.68 (several *d*); 125.19 (*s*, C(1′)); 90.61 (*s*, C(2)); 86.16 (*d*, C(5)); 84.49 (*s*, C(1)); 82.71 (*d*, C(4)); 79.17 (*d*, C(6)); 78.00 (*d*, C(7)); 75.89 (*t*, PhC*H*$_2$); 75.66 (*t*, PhC*H*$_2$); 75.12 (*t*, PhC*H*$_2$); 73.53 (*t*, PhC*H*$_2$); 70.51 (*d*, C(3)); 69.03 (*t*, C(8)). FAB-MS: 1171 (70, $[M + 1]^+$), 1170 (50, $M^+$). Anal. calc. for $C_{78}H_{74}O_{10}$ (1171.44): C 79.97, H 6.37; found: C 79.90, H 6.35.

*Coupling of* **5** *with* **1**. A suspension of **1** (16 mg, 0.028 mmol), **5** (21 mg, 0.028 mmol), $[Pd(PPh_3)_4]$ (2 mg), and CuI (1 mg) in piperidine (0.8 ml) was stirred at 85° for 3 h and evaporated. Workup and FC (hexane/AcOEt 9:1) gave **6** (32 mg, 83%).

*3,7-Anhydro-4,5,6,8-tetra*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1*-C-*{2-[(trimethylsilyl)ethynyl]-phenyl}*-D-glycero-D-gulo-*octitol* (**7**). A suspension of **5** (173 mg, 0.21 mmol), ethynyltrimethylsilane (0.11 ml, 0.8 mmol), $[Pd(PPh_3)_4]$ (5 mg), and CuI (3 mg) in piperidine (2 ml) was stirred at 80° for 3 h and evaporated. Workup and FC (hexane/AcOEt 20:1) gave **7** (141 mg, 84%). Oil. $R_f$ (hexane/$CH_2Cl_2$/AcOEt 7:2:1) 0.59. $[\alpha]_D^{25} = -12.1$ ($c = 0.67$, $CHCl_3$). UV ($CHCl_3$): 280 (14500), 265 (15800), 242 (22500). IR ($CHCl_3$): 3090*w*, 3066*w*,

3003*w*, 2957*m*, 2909*m*, 2868*m*, 2158*m*, 1952*w*, 1702*w*, 1603*w*, 1496*m*, 1478*m*, 1454*m*, 1398*w*, 1360*m*, 1296*m*, 1261*w*, 1251*m*, 1093*s*, 1066*s*, 1028*s*, 1001*m*, 911*m*, 865*s*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.45–6.68 (*m*, 24 arom. H); 5.26 (*d*, *J* = 10.9, PhC*H*); 4.96 (*d*, *J* = 11.2, PhC*H*); 4.91 (*d*, *J* = 10.9, PhC*H*); 4.88 (*d*, *J* = 11.5, PhC*H*); 4.83 (*d*, *J* = 11.3, PhC*H*); 4.63 (*d*, *J* = 11.2, PhC*H*); 4.51 (*d*, *J* = 12.3, PhC*H*); 4.37 (*d*, *J* = 9.6, H–C(3)); 4.36 (*d*, *J* = 11.1, PhC*H*); 3.87 (*t*, *J* = 9.3, H–C(6)); 3.86 (*t*, *J* = 9.4, H–C(4)); 3.77–3.67 (*m*, 2 H–C(8)); 3.62 (*t*, *J* = 9.0, H–C(5)); 3.33 (*ddd*, *J* = 2.0, 3.3, 9.5, H–C(7)); 0.31 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.65 (*s*); 138.13 (2*s*); 138.04 (*s*); 132.33 (*d*); 128.42–127.65 (several *d*); 126.08 (*s*, C(2′)); 125.14 (*s*, C(1′)); 103.39 (*s*, $Me_3SiC{\equiv}C$); 98.89 (*s*, $Me_3SiC{\equiv}C$); 90.20 (*s*, C(2)); 86.14 (*d*, C(5)); 84.57 (*s*, C(1)); 82.58 (*d*, C(4)); 79.17 (*d*, C(6)); 77.75 (*d*, C(7)); 75.71 (*t*, PhC$H_2$); 75.62 (*t*, PhC$H_2$); 75.13 (*t*, PhC$H_2$); 73.54 (*t*, PhC$H_2$); 70.59 (*d*, C(3)); 68.91 (*t*, C(8)); 0.07 (*q*, $Me_3Si$). CI-MS: 738 (58, $[M + NH_4]^+$), 721 (2, $[M + 1]^+$), 91 (100). Anal. calc. for $C_{47}H_{38}O_5Si$ (720.98): C 78.30, H 6.71; found: C 78.34, H 6.74.

*3,7-Anhydro-4,5,6,8-tetra*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1*-C-*(2-ethynylphenyl)*-D-glycero-D-gulo-*octitol* (**8**). At 0°, a soln. of **7** (173 mg, 0.24 mmol) in THF (40 ml) was treated with a soln. of $Bu_4NF_3 \cdot 3\ H_2O$ (47 mg, 0.15 mmol) in THF (5 ml), kept for 5 min, and evaporated. Workup and FC (hexane/AcOEt 10:1) gave **8** (152 mg, 97%). Oil. $R_f$ (hexane/AcOEt 95:15) 0.41. $[\alpha]_D^{25} = +4.8$ (*c* = 0.50, $CHCl_3$). IR ($CHCl_3$): 3308*w*, 3089*w*, 3066*m*, 3007*m*, 2911*m*, 2868*m*, 2235*w*, 1952*w*, 1869*w*, 1810*w*, 1603*w*, 1558*w*, 1497*m*, 1480*m*, 1454*m*, 1295*m*, 1131*m*, 1092*s*, 1066*s*, 1028*m*, 912*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.44–6.68 (*m*, 24 arom. H); 5.32 (*d*, *J* = 10.9, PhC*H*); 4.94 (*d*, *J* = 11.5, PhC*H*); 4.88 (*d*, *J* = 11.0, PhC*H*); 4.87 (*d*, *J* = 11.9, PhC*H*); 4.82 (*d*, *J* = 11.3, PhC*H*); 4.62 (*d*, *J* = 11.4, PhC*H*); 4.50 (*d*, *J* = 12.1, PhC*H*); 4.38 (*d*, *J* = 12.1, PhC*H*); 4.32 (*d*, *J* = 9.5, H–C(3)); 3.83 (*t*, *J* = 9.3, H–C(6), H–C(4)); 3.71–3.68 (*m*, 2 H–C(8)); 3.60 (*t*, *J* = 9.0, H–C(5)); 3.31 (*dt*, *J* = 9.2, 2.2, H–C(7)); 2.86 (*s*, HC≡C). $^{13}$C-NMR (75 MHz, $C_6D_6$): 139.57 (*s*); 139.33 (*s*); 139.19 (*s*); 139.03 (*s*); 132.99 (*d*); 132.83 (*d*); 128.95–127.42 (several *d*); 126.03 (*s*, C(2′)); 125.27 (*s*, C(1′)); 91.82 (*s*, C(2)); 86.57 (*d*, C(5)); 84.51 (*s*, C(1)); 83.11 (*d*, C(4)); 82.24 (*d*, HC≡C); 82.03 (*s*, HC≡C); 79.82 (*d*, C(6)); 78.19 (*d*, C(7)); 75.64 (*t*, PhC$H_2$); 75.61 (*t*, PhC$H_2$); 75.06 (*t*, PhC$H_2$); 73.76 (*t*, PhC$H_2$); 71.09 (*d*, C(3)); 69.43 (*t*, C(8)). CI-MS: 666 (2, $[M + NH_4]^+$), 91 (100).

*4,5,6,8-Tetra*-O-*acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1*-C-*(2-iodophenyl)*-D-glycero-D-gulo-*octitol* (**9**). At 0°, a soln. of **5** (210 mg, 0.28 mmol) in $Ac_2O$ (5 ml) was treated with $BF_3 \cdot OEt_2$ (0.4 ml, 3.2 mmol), kept at r.t. for 12 h, cooled to 0°, and then neutralized with aq. $NaHCO_3$ soln. Workup and FC (hexane/AcOEt 1:1) gave **9** (10 mg, 6%). Oil. $R_f$ (hexane/AcOEt 7:3) 0.15. $[\alpha]_D^{25} = -5.6$ (*c* = 0.32, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2959*w*, 2872*w*, 1852*w*, 1834*w*, 1755*s*, 1479*w*, 1467*w*, 1432*w*, 1371*m*, 1248*s*, 1099*m*, 1045*s*, 908*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.82 (*dd*, *J* = 1.0, 8.0, H–C(6′)); 7.46 (*dd*, *J* = 1.6, 7.8, H–C(3′)); 7.30 (*td*, *J* = 7.5, 1.1, H–C(5′)); 7.03 (*td*, *J* = 7.6, 1.7, H–C(4′)); 5.30 (*t*, *J* = 9.3, H–C(4)); 5.24 (*t*, *J* = 9.0, H–C(5)); 5.15 (*t*, *J* = 9.3, H–C(6)); 4.52 (*d*, *J* = 9.5, H–C(3)); 4.29 (*dd*, *J* = 4.7, 12.5, H–C(8)); 4.17 (*dd*, *J* = 2.2, 12.6, H′–C(8)); 3.76 (*ddd*, *J* = 2.2, 4.5, 9.7, H–C(7)); 2.11 (*s*, Ac); 2.09 (*s*, Ac); 2.04 (*s*, Ac); 2.03 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): 171.48 (*s*, C=O); 170.76 (*s*, C=O); 170.34 (*s*, C=O); 169.37 (*s*, C=O); 138.73 (*s*, C(1′)); 133.45 (*d*); 130.24 (2*d*); 127.83 (*d*); 100.46 (*s*, C(2′)); 86.35 (*s*, C(2)); 77.22 (*s*, C(1)); 76.03 (*d*, C(7)); 73.78 (*d*, C(5)); 71.11 (*d*, C(6)); 69.31 (*d*, C(4)); 68.08 (*d*, C(3)); 62.07 (*t*, C(8)); 21.01 (*q*, Me); 20.80 (*q*, Me); 20.66 (*q*, Me); 20.46 (*q*, Me). CI-MS: 576 (100, $[M + NH_4]^+$).

*1,1′-(1,2-Phenylene)bis[8*-O-*acetyl-3,7-anhydro-4,5,6-tri*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy*-D-glycero-D-gulo-*octitol]* (**10**). *a*) A mixture of **6** (60 mg, 0.051 mmol) and $Zn(OTf)_2$ (180 mg) in $Ac_2O$ (3 ml) was stirred at r.t. for 48 h. Workup and HPLC (*Si-60*, hexane/AcOEt 8:2) gave **10** (12 mg, 22%).

*b*) A soln. of **6** (70 mg, 0.060 mmol) in $Ac_2O$ (5 ml) was treated with $CoCl_2 \cdot 6\ H_2O$ (136 mg), stirred for 3 days at 30°, and evaporated. The residue was dissolved in acetone (14 ml), treated with $Ce(NH_4)_2(NO_3)_4$ (28 mg), stirred for 0.5 h, and evaporated. Workup and FC (hexane/AcOEt 8:2) gave **10** (53 mg, 81%). Oil. $R_f$ (toluene/AcOEt 9:0.8) 0.20. $[\alpha]_D^{25} = +2.3$ (*c* = 0.66, $CHCl_3$). UV ($CHCl_3$): 276 (13000), 263 (15500), 241 (17600). IR ($CHCl_3$): 3090*w*, 3066*w*, 3007*m*, 2912*w*, 2869*w*, 1737*s*, 1497*m*, 1484*w*, 1454*m*, 1363*m*, 1296*m*, 1248*s* (br.), 1154*m*, 1097*s*, 1065*s*, 1038*m*, 1028*s*, 909*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.50–7.28 (*m*, 34 arom. H); 5.20 (*d*, *J* = 10.4, PhC*H*); 4.98 (*d*, *J* = 11.0, PhC*H*); 4.86 (*d*, *J* = 11.9, 2 PhC*H*); 4.84 (*d*, *J* = 10.9, PhC*H*); 4.48 (*d*, *J* = 10.6, PhC*H*); 4.35 (*dd*, *J* = 1.7, 12.1, H–C(8)); 4.22 (*dd*, *J* = 4.3, 12.7, H′–C(8)); 4.21 (*d*, *J* = 9.5, H–C(3)); 3.79 (*t*, *J* = 9.1, H–C(6)); 3.67 (*t*, *J* ≈ 8.7, H–C(5)); 3.56 (*t*, *J* = 9.6, H–C(4)); 3.51–3.48 (*m*, H–C(7)); 2.01 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.77 (*s*, C=O); 138.34 (*s*); 138.10 (*s*); 137.73 (*s*); 132.62 (*d*); 128.50–127.80 (several *d*); 125.00 (*s*, C(1′)); 90.25 (*s*, C(2)); 85.99 (*d*, C(4)); 84.58 (*s*, C(1)); 82.67 (*d*, C(5)); 77.69 (*d*, C(6)); 77.14 (*d*, C(7)); 75.92 (*t*, PhC$H_2$); 75.64 (*t*, PhC$H_2$); 75.15 (*t*, PhC$H_2$); 70.35 (*d*, C(3)); 63.62 (*t*, C(8)); 20.91 (*q*, Me). FAB-MS: 1075 (43, $[M + 1]^+$), 91 (100). Anal. calc. for $C_{68}H_{66}O_{12}$ (1075.26): C 75.96, H 6.19; found: C 75.84, H 6.07.

*1,1′-(1,2-Phenylene)bis[3,7-anhydro-4,5,6-tri*-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy*-D-glycero-D-gulo-*octitol]* (**11**). A soln. of **10** (25 mg, 0.023 mmol) in 0.1M NaOMe (5 ml) was stirred at r.t. for 1 h, neutralized with 1M HCl, and evaporated. The residue was dissolved in AcOEt (50 ml), washed with $H_2O$, and evaporated to give **11** (19 mg, 82%). Oil. $R_f$ (hexane/AcOEt) 0.22. $[\alpha]_D^{25} = -62.2$ (*c* = 0.69, $CHCl_3$). IR ($CHCl_3$): 3692*m*, 3474*m*, 2914*m*, 2878*m*, 2237*w*, 1497*m*, 1482*m*, 1454*m*, 1399*w*, 1360*m*, 1296*m*, 1250*s* (br.), 1089*s*, 1028*s*, 910*m*, 885*w*. $^1$H-NMR

(300 MHz, $CDCl_3$): 7.47–7.26 (*m*, 34 arom. H); 5.15 (*d*, *J* = 11.0, PhC*H*); 4.98 (*d*, *J* = 11.0, PhC*H*); 4.91 (*d*, *J* = 11.1, PhC*H*); 4.90 (*d*, *J* = 10.9, PhC*H*); 4.88 (*d*, *J* = 10.9, PhC*H*); 4.68 (*d*, *J* = 11.0, PhC*H*); 4.33 (*d*, *J* = 9.0, H–C(3)); 3.86 (*dd*, *J* = 2.1, 12.3, H–C(8)); 3.76 (*t*, *J* = 9.0, H–C(6)); 3.74–3.70 (*m*, H′–C(8)); 3.69 (*t*, *J* = 9.0, H–C(5)); 3.64 (*t*, *J* = 9.1, H–C(4)); 3.41–3.38 (*m*, H–C(7)); 2.65 (br. *s*, OH). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.45 (*s*); 138.06 (2*s*); 131.89 (*d*); 128.50–127.70 (several *d*); 125.15 (*s*, C(1′)); 90.67 (*s*, C(2)); 85.84 (*d*, C(5)); 84.49 (*s*, C(1)); 82.58 (*d*, C(4)); 79.67 (*d*, C(6)); 77.50 (*d*, C(7)); 75.87 (*t*, PhC$H_2$); 75.71 (*t*, PhC$H_2$); 75.16 (*t*, PhC$H_2$); 70.40 (*d*, C(3)); 61.66 (*t*, C(8)). FAB-MS: 991 (4, $[M + 1]^+$), 90 (100).

*Coupling of* **4** *with 1,2-Diiodobenzene. a*) A soln. of **4** (825 mg, 1.28 mmol) in $Et_3N$ (10 ml) was slowly added to a suspension of 1,2-diiodobenzene (1.05 ml, 8.0 mmol), $[Pd(PPh_3)_4]$ (36 mg), and CuI (30 mg) in $Et_3N$ (30 m) within 3 h at 50°. The suspension was stirred for 5 h at 50° and evaporated. FC (hexane/toluene 9:1) gave crude **12** (1055 mg, 95%). A sample of **12** was purified for analysis. A soln. of **4** (775 mg, 1.20 mmol) in $Et_3N$ was added dropwise to a suspension of the remaining **12** (1000 mg, 1.18 mmol), $[Pd(PPh)_4]$ (36 mg), and CuI (25 mg) in $Et_3N$ (30 ml) at 50° till **12** was consumed ($^1$H-NMR). Normal workup and FC (hexane/toluene 8:2) gave **15** (1478 mg, 92%).

*b*) At 50°, a soln. of **4** (64 mg, 0.10 mmol) in $Et_3N$ (1.5 ml) was slowly added to a suspension of 1,2-diiodobenzene (6.5 µl, 0.05 mmol), $[Pd(PPh_3)_4]$ (3 mg), and CuI (3 mg) in $Et_3N$ (2 ml). The suspension was stirred for 5 h at 50°, filtered, and evaporated. The ratio of the residue **12**/**15** (1.2:1) was determined by the intergration of the $^1$H-NMR signals (300 MHz, $CDCl_3$) of H–C(3) at 4.56 (**12**) and 4.49 ppm (**15**). FC (hexane/toluene 8:2) gave **12** (38 mg, 45%) and **15** (24 mg, 37%).

*c*) A suspension of **4** (64 mg, 0.10 mmol), 1,2-diiodobenzene (8 µl, 0.075 mmol), $[Pd(PPh_3)_4]$ (3 mg), and CuI (3 mg) in $Et_3N$ (3 ml) was stirred for 5 h at 50°, filtered, and evaporated. FC (hexane/toluene 8:2) gave **12** (29 mg, 35%), **15** (22 mg, 34%), and **19** (6 mg, 9%).

*Data of 3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(2-iodophenyl)-4,5,6,8-tetrakis-*O*-(triethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**12**): Oil. $R_f$ (hexane/toluene 7:3) 0.44. $[\alpha]_D^{25} = +5.4$ (*c* = 0.50, $CHCl_3$). IR ($CHCl_3$): 3007*w*, 2957*s*, 2912*m*, 2876*m*, 1465*m*, 1430*w*, 1414*w*, 1261*w*, 1099*s*, 1016*m*, 976*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.52 (*dd*, *J* = 8.0, 1.1, H–C(3′)); 7.34 (*dd*, *J* = 7.8, 1.6, H–C(6′)); 6.75 (*dt*, *J* = 7.6, 1.2, H–C(5′)); 6.37 (*dt*, *J* = 7.6, 1.7, H–C(4′)); 4.78 (*d*, *J* = 8.0, H–C(3)); 4.26 (*ddd*, *J* = 0.7, 3.5, 7.9, H–C(4)); 4.14 (*dt*, *J* = 4.7, 0.7, H–C(6)); 4.00–3.96 (*m*, H–C(5), 2 H–C(8)); 3.79 (*q*, *J* = 4.7, H–C(7)); 1.14–1.04 (*m*, 4 (*Me*$CH_2$)$_3$Si); 0.92–0.63 (*m*, 4 (Me$CH_2$)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.76 (*d*); 133.15 (*d*); 129.45 (*d*); 129.25 (*s*, C(1′)); 127.60 (*d*); 100.80 (*s*, C(2′)); 92.35 (*s*, C(2)); 87.28 (*s*, C(1)); 82.21 (*d*, C(5)); 78.07 (*d*, C(4)); 77.45 (*d*, C(6)); 70.33 (*d*, C(7)); 69.38 (*d*, C(3)); 63.54 (*t*, C(8)); 7.03 (*q*, 2 (*Me*$CH_2$)$_3$Si); 6.93 (*q*, (*Me*$CH_2$)$_3$Si); 6.81 (*q*, (*Me*$CH_2$)$_3$)Si); 5.37 (*t*, (Me$CH_2$)$_3$Si); 5.04 (*t*, (Me$CH_2$)$_3$Si); 4.90 (*t*, (Me$CH_2$)$_3$Si); 4.46 (*t*, (Me$CH_2$)$_3$Si). FAB-MS: 847 (14, $M^+$). Anal. calc. for $C_{38}H_{71}IO_5Si_4$ (847.23): C 53.87, H 8.45, I 14.98; found: C 53.74, H 8.29, I 14.80.

*Data of 1,1′-(1,2-Phenylene)bis[3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-4,5,6,8-tetrakis-*O*-(triethylsilyl)-*D*-glycero-*D*-gulo-octitol]* (**15**): Oil. $R_f$ (hexane/toluene 7:3) 0.36. $[\alpha]_D^{25} = +34.9$ (*c* = 0.74, $CHCl_3$). UV ($CHCl_3$): 277 (15 500), 264 (17 200), 240 (21 500). IR ($CHCl_3$): 2956*s*, 2911*s*, 2876*s*, 2734*w*, 1592*w*, 1484*w*, 1458*m*, 1414*m*, 1379*w*, 1365*w*, 1327*w*, 1248*w*, 1098*s*, 1007*s*, 975*m*, 857*w*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.41 (*dd*, *J* = 3.3, 5.8, H–C(3′)); 6.78 (*dd*, *J* = 3.3, 5.8, H–C(4′)); 4.76 (*d*, *J* = 8.3, H–C(3)); 4.23 (*dd*, *J* = 3.0, 8.2, H–C(4), irrad. at 4.76→*d*, *J* = 3.0, irrad. at 3.95→*d*, *J* = 8.0); 4.17 (*t*, *J* = 5.0, H–C(6), irrad. at 3.80→*d*); 4.02–3.88 (*m*, H–C(5), 2 H–C(8)); 3.80 (*q*, *J* = 4.7, H–C(7), irrad. at 3.95→*d*); 1.18–1.02 (*m*, 4 (*Me*$CH_2$)$_3$Si); 0.98–0.68 (*m*, 4 (Me$CH_2$)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 133.00 (*d*), 127.75 (*d*); 125.35 (*s*, C(1′)); 92.37 (*s*, C(2)); 84.13 (*s*, C(1)); 82.15 (*d*, C(5)); 78.37 (*d*, C(4)); 77.37 (*d*, C(6)); 70.35 (*d*, C(7)); 69.30 (*d*, C(3)); 63.44 (*t*, C(8)); 6.98 (*q*, (*Me*$CH_2$)$_3$Si); 6.91 (*q*, (*Me*$CH_2$)$_3$Si); 6.74 (*q*, (*Me*$CH_2$)$_3$Si); 5.35 (*q*, (*Me*$CH_2$)$_3$Si); 5.20 (*t*, (Me$CH_2$)$_3$Si); 5.03 (*t*, (Me$CH_2$)$_3$Si); 4.88 (*t*, (Me$CH_2$)$_3$Si); 4.44 (*t*, (Me$CH_2$)$_3$Si). FAB-MS: 1364 (80, $M^+$). Anal. calc. for $C_{70}H_{138}O_{10}Si_8$ (1364.54): C 61.62, H 10.19; found: C 61.80, H 10.27.

*Data of 1,1′-(Buta-1,3-diyne-1,4-diyl)bis[(1*S*)-1,5-anhydro-2,3,4,6-tetrakis-*O*-(triethylsilyl)-*D*-glucitol]* (**19**): Oil. $R_f$ (hexane/toluene 7:3) 0.30. $[\alpha]_D^{25} = +1.6$ (*c* = 0.44, $CHCl_3$). IR ($CHCl_3$): 2959*s*, 2928*s*, 2857*s*, 1600*w*, 1463*m*, 1458*m*, 1291*s*, 1129*m*, 1074*m*, 1039*w*, 960*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.34 (*d*, *J* = 8.1, H–C(1)); 3.82 (*dd*, *J* = 3.0, 5.0, H–C(4)); 3.75 (*dd*, *J* = 3.0, 8.0, H–C(2)); 3.73–3.67 (*m*, H–C(3), 2 H–C(6)); 3.63 (*dd*, *J* = 5.0, 3.0, H–C(5)); 1.05–0.85 (*m*, 4 (*Me*$CH_2$)$_3$Si); 0.70–0.50 (*m*, 4 (Me$CH_2$)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 82.61 (*d*, C(3)); 78.16 (*d*, C(2)); 77.60 (*s*, *C*≡CC(1)); 77.17 (*d*, C(4)); 76.80 (*s*, C≡*C*C(1)); 70.47 (*d*, C(5)); 69.50 (*d*, C(1)); 63.75 (*t*, C(6)); 7.09 (*q*, (*Me*$CH_2$)$_3$Si); 7.03 (*q*, (*Me*$CH_2$)$_3$Si); 6.88 (*q*, (*Me*$CH_2$)$_3$Si); 6.10 (*q*, (*Me*$CH_2$)$_3$Si); 5.14 (*t*, (Me$CH_2$)$_3$Si); 5.05 (*t*, (Me$CH_2$)$_3$Si); 5.01 (*t*, (Me$CH_2$)$_3$Si); 4.58 (*t*, (Me$CH_2$)$_3$Si). FAB-MS: 1288 (36, $M^+$), 1287 (25, $[M - 1]^+$), 547 (100).

*1,1′-(1,2-Phenylene)bis[3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D*-glycero-*D*-gulo-octitol]* (**16**). A soln. of **15** (1042 mg, 0.765 mmol) in 0.1M HCl in MeOH (20 ml) was refluxed for 4 h and evaporated. The residue was dissolved in MeOH and neutralized with *Amberlite IRA 68* ($OH^-$ form) resin. Filtration, evaporation, and FC

($CH_2Cl_2$/MeOH 8:2) gave **16** (320 mg, 93%). Solid. M.p. 181°. $R_f$ (toluene/MeOH 6:4) 0.22. $[\alpha]_D^{25} = +15.5$ ($c = 0.90$, MeOH). UV (MeOH): 273 (12000), 259 (13200). IR (KBr): 3550*s*, 3355*s* (br.), 2909*m*, 2237*w*, 1636*w*, 1483*m*, 1458*m*, 1445*m*, 1420*m*, 1383*m*, 1359*m*, 1304*m*, 1228*w*, 1086*s*, 1047*s*, 1012*s*, 993*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 7.47 (*dd*, $J = 3.4, 5.8$, H–C(3′)); 7.32 (*dd*, $J = 3.4, 5.8$, H–C(4′)); 4.21 (*d*, $J = 9.4$, H–C(3)); 3.89 (*dd*, $J = 1.7, 12.0$, H–C(8)); 3.70 (*dd*, $J = 5.1, 12.2$, H′–C(8)); 3.47 (*t*, $J = 9.1$, H–C(4)); 3.38–3.34 (*m*, H–C(5), H–C(6)); 3.32–3.29 (*m*, H–C(7)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 132.00 (*d*); 129.46 (*d*); 126.55 (*s*, C(1′)); 91.61 (*s*, C(2)); 84.96 (*s*, C(1)); 82.22 (*d*, C(4)); 79.25 (*d*, C(7)); 75.42 (*d*, C(6)); 72.72 (*d*, C(5)); 71.48 (*d*, C(3)); 62.83 (*t*, C(8)). CI-MS: 451 (11, $M^+$).

*1,1′-(1,2-Phenylene)bis[4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D*-glycero-*D*-gulo-octitol]* (**17**). A mixture of **16** (54 mg, 0.119 mmol), $Ac_2O$ (1.0 ml), and pyridine (1.0 ml) was stirred for 8 h at r.t. and then evaporated. Normal workup and FC (hexane/AcOEt 1:1) gave **17** (79 mg, 84%). Solid. M.p. 75°. $R_f$ (hexane/AcOEt 1:1) 0.19. $[\alpha]_D^{25} = -21.4$ ($c = 0.56$, $CHCl_3$). UV ($CHCl_3$): 274 (13000), 259 (13800). IR ($CHCl_3$): 3038*w*, 2956*w*, 2858*w*, 2241*w*, 1755*s*, 1627*w*, 1486*w*, 1430*m*, 1368*s*, 1304*m*, 1248*s* (br.), 1100*m*, 1064*s*, 1039*s*, 979*w*, 954*w*, 907*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.42 (*dd*, $J = 3.3, 5.7$, H–C(3′)); 7.28 (*dd*, $J = 3.4, 5.8$, H–C(4′)); 5.29 (*t*, $J = 9.3, 7.3$, H–C(4)); 5.24 (*t*, $J = 7.4, 9.1$, H–C(5)); 5.16 (*t*, $J = 9.6$, H–C(6)); 4.53 (*d*, $J = 9.5$, H–C(3)); 4.30 (*dd*, $J = 4.6, 12.5$, H–C(8)); 4.19 (*dd*, $J = 2.0, 12.5$, H′–C(8)); 3.79 (*ddd*, $J = 2.2, 4.5, 9.8$, H–C(7)); 2.11 (*s*, Ac); 2.05 (*s*, Ac); 2.04 (*s*, Ac); 2.03 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.71 (*s*, C=O); 170.39 (*s*, C=O); 169.39 (*s*, C=O); 169.26 (*s*, C=O); 132.86 (*d*); 128.86 (*d*); 124.37 (*s*, C(1′)); 86.83 (*s*, C(2)); 85.02 (*s*, C(1)); 75.95 (*d*, C(7)); 73.72 (*d*, C(5)); 71.24 (*d*, C(4)); 69.27 (*d*, C(3)); 68.14 (*d*, C(6)); 62.03 (*t*, C(8)); 20.80 (*q*, Me); 20.69 (*q*, 2 Me); 20.62 (*q*, Me). MALDI-MS: 809 ($[M + Na]^+$). Anal. calc. for $C_{38}H_{42}O_{18}$ (786.74): C 58.01, H 5.38; found: C 57.92, H 5.58.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-phenyl-4,5,6,8-tetrakis-*O*-(triethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**13**). At 50°, a soln. of **4** (255 mg, 0.39 mmol) in $Et_3N$ (4 ml) was added dropwise to a suspension of $[Pd(PPh_3)_4]$ (20 mg, 0.017 mmol), CuI (10 mg, 0.052 mmol), and iodobenzene (0.15 ml, 1.3 mmol) in $Et_3N$ (3 ml). The resulting suspension was kept for 3 h at 50° and evaporated and the residue triturated with hexane. Filtration, evaporation, and FC (hexane/toluene 8:2) gave **13** (255 mg, 89%). Oil. $R_f$ (hexane/toluene 7:3) 0.37. $[\alpha]_D^{25} = +4.0$ ($c = 0.82$, $CHCl_3$). IR ($CHCl_3$): 2957*s*, 2942*s*, 2877*s*, 2231*w*, 1598*w*, 1491*m*, 1458*m*, 1414*m*, 1379*w*, 1366*w*, 1327*w*, 1098*s*, 1006*s*, 975*m*, 855*m*. $^1$H-NMR (300 MHz, $C_6D_6$): 7.51–7.48 (*m*, 2 arom. H); 7.00–6.92 (*m*, 3 arom. H); 4.71 (*d*, $J = 8.5$, H–C(3)); 4.18 (*dd*, $J = 3.7, 8.4$, H–C(4)); 4.12 (*t*, $J = 4.7$, H–C(6)); 3.99–3.92 (*m*, H–C(5), 2 H–C(8)); 3.77 (*q*, $J = 4.7$, H–C(7)); 1.20–0.64 (*m*, 4 ($MeCH_2$)$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 131.74 (2*d*); 128.24 (2*d*); 128.16 (*d*); 122.95 (*s*); 88.71 (*s*, C(2)); 85.60 (*s*, C(1)); 82.49 (*d*, C(5)); 78.22 (*d*, C(4)); 77.55 (*d*, C(6)); 70.22 (*d*, C(7)); 68.93 (*d*, C(3)); 63.46 (*t*, C(8)); 7.01 (*q*, ($MeCH_2$)$_3$Si); 6.97 (*q*, ($MeCH_2$)$_3$Si); 6.92 (*q*, ($MeCH_2$)$_3$Si); 6.76 (*q*, ($MeCH_2$)$_3$Si); 5.32 (*t*, ($MeCH_2$)$_3$Si); 4.98 (*t*, ($MeCH_2$)$_3$Si); 4.86 (*t*, ($MeCH_2$)$_3$Si); 4.41 (*t*, ($MeCH_2$)$_3$Si). CI-MS: 738 (6, $[M + NH_4]^+$), 720 ($M^+$), 301 (100). Anal. calc. for $C_{38}H_{72}O_5Si_4$ (721.33): C 63.27, H 10.06; found: C 63.24, H 10.00.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-phenyl-*D*-glycero-*D*-gulo-octitol* (**14**). As described for **16**, with **13** (200 mg, 0.27 mmol) and 0.1M HCl in MeOH (20 ml) for 2 h. FC ($CH_2Cl_2$/MeOH 8:2) gave **14** (59 mg, 80%). Solid. M.p. 119°. $R_f$ ($CH_2Cl_2$/MeOH 8:2) 0.68. $[\alpha]_D^{25} = +3.4$ ($c = 0.33$, MeOH). IR (KBr): 3395*s* (br.), 2925*m*, 2855*m*, 2223*w*, 1634*w*, 1491*w*, 1456*w*, 1363*w*, 1308*w*, 1082*m*, 1009*w*, 990*m*, 970*m*, 886*w*. $^1$H-NMR (300 MHz, $CD_3OD$): 7.45–7.29 (*m*, 5 arom. H); 4.16 (*d*, $J = 9.0$, H–C(3)); 3.87 (br. *d*, $J \approx 12.2$, H–C(8)); 3.67 (br. *d*, $J \approx 11.9$, H′–C(8)); 3.43–3.29 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 132.80 (2*d*); 129.72 (2*d*); 129.51 (*d*); 123.99 (*s*); 87.49 (*s*, C(2)); 86.44 (*s*, C(1)); 82.14 (*d*, C(4)); 79.28 (*d*, C(7)); 75.52 (*d*, C(6)); 72.68 (*d*, C(5)); 71.53 (*d*, C(3)); 62.96 (*t*, C(8)). CI-MS: 282 (100, $[M + NH_4]^+$), 265 (5, $[M + 1]^+$), 193 (92).

*(1S)-1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-1-*C*-(naphthalen-2-yl)-*D*-glucitol* (**20**). A soln. of **8** (116 mg) in PhCl (3 ml) and cyclohexa-1,4-diene (3 ml) in a 20-ml glass tube was degassed. The tube was sealed under $N_2$ and then kept for 20 h at 185°. Evaporation and FC (hexane/AcOEt 15:1) gave **20** (46 mg, 39%). Solid. M.p. 117°. $R_f$ (hexane/AcOEt 95:15) 0.49. $[\alpha]_D^{25} = +5.7$ ($c = 0.54$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3065*w*, 3007*m*, 2905*w*, 2868*m*, 1951*w*, 1810*w*, 1717*w*, 1684*w*, 1653*w*, 1508*w*, 1496*m*, 1454*m*, 1397*w*, 1360*m*, 1128*m*, 1069*s*, 1028*m*, 1001*w*, 951*w*, 909*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.94–7.44 (*m*, 7 arom. H); 7.42–6.80 (*m*, 20 arom. H); 5.01 (*d*, $J = 11.1$, PhC*H*); 4.95 (*d*, $J = 11.0$, PhC*H*); 4.92 (*d*, $J = 10.8$, PhC*H*); 4.71 (*d*, $J = 12.3$, PhC*H*); 4.70 (*d*, $J = 10.7$, PhC*H*); 4.62 (*d*, $J = 12.2$, PhC*H*); 4.46 (*d*, $J = 9.6$, H–C(1)); 4.38 (*d*, $J = 10.2$, PhC*H*); 3.88 (*dd*, $J = 4.9, 12.5$, H–C(6)); 3.87 (2*t*, $J = 9.4$, H–C(3), H–C(4)); 3.86 (*dd*, $J = 2.2, 12.4$, H′–C(6)); 3.75 (*d*, $J = 10.5$, irrad. at 4.38→*s*, PhC*H*); 3.74–3.64 (*m*, H–C(5)); 3.63 (*t*, $J = 9.3$, irrad. at 4.46→*d*, $J = 9.7$, H–C(2)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.75 (*s*); 138.40 (*s*); 138.24 (*s*); 137.46 (*s*); 136.66 (*s*); 133.39 (*s*); 133.22 (*s*); 128.46–127.58 (several *d*); 127.08 (*d*); 126.11 (*d*); 126.02 (*d*); 125.21 (*d*); 86.85 (*d*, C(5)); 84.28 (*d*, C(3)); 81.82 (*d*, C(4)); 79.45 (*d*, C(2)); 78.41 (*d*, C(1)); 75.73 (*t*, PhC$H_2$); 75.19 (*t*, PhC$H_2$); 75.01 (*t*, PhC$H_2$); 73.49 (*t*, PhC$H_2$); 69.16 (*t*, C(6)). EI-MS: 650 (3, $M^+$), 559 (35, $[M - Bn]^+$), 91 (100). Anal. calc. for $C_{44}H_{42}O_5$ (650.81): C 81.20, H 6.50; found: C 81.09, H 6.67.

*(1S)-1,5-Anhydro-1-C-(naphthalen-2-yl)-D-glucitol* (**21**). A soln. of **20** (31 mg, 0.048 mmol) and $BF_3 \cdot OEt_2$ (0.05 ml) in EtSH (1 ml) was stirred for 12 h at r.t. and evaporated. The residue was stirred in $Ac_2O$ (0.5 ml) and pyridine (1 ml) for 12 h. Evaporation and FC (hexane/AcOEt 1:1) gave an acetylated derivative of **21**, which was converted to **21** (12 mg, 89%) by deacetylation with NaOMe in MeOH. Solid. M.p. 95°. $R_f$ ($CH_2Cl_2$/MeOH 9:1) 0.25. $[\alpha]_D^{25} = +28.4$ ($c = 0.50$, MeOH). IR (KBr): 3366*s* (br.), 2922*m*, 2844*m*, 1355*m*, 1311*w*, 1122*m*, 984*m*, 897*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 7.90 (br. *s*, H–C(1′)); 7.88–7.80 (*m*, H–C(4′), H–C(6′), H–C(7′)); 7.64 (*dd*, $J = 1.5, 8.4$, H–C(3′)); 7.55–7.49 (*m*, H–C(5′), H–C(8′)); 4.86 (*d*, $J = 9.0$, H–C(1)); 3.91 (*dd*, $J = 1.6, 11.6$, H–C(6)); 3.74 (*dd*, $J = 5.2, 11.8$, H′–C(6)); 3.55–3.43 (*m*, H–C(2), H–C(3), H–C(4), H–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 138.37 (*s*); 134.79 (*s*); 134.65 (*s*); 129.07 (*d*); 128.68 (2*d*); 128.21 (*d*); 127.00 (*d*); 126.95 (*d*); 126.74 (*d*); 83.80 (*d*, C(5)); 82.33 (*d*, C(3)); 79.91 (*d*, C(4)); 76.50 (*d*, C(2)); 72.01 (*d*, C(1)); 63.23 (*t*, C(6)). CI-MS: 308 (8, $[M + NH_4]^+$), 290 (23, $M^+$), 199 (42), 141 (100).

*2-O,2′-O-[(1S,2S)-1,2-Diphenylethylene]-1,1′-(naphthalene-2,3-diyl)bis[(1S)-1,5-anhydro-3,4,6-tri-O-benzyl-D-glucitol]* (**22**) *and (1S)-1,5-Anhydro-3,4,6-tri-O-benzyl-2-O-(2,2-diphenylethenyl)-1-C-[3-(3,4,6-tri-O-benzyl-β-D-glucopyranosyl)naphthalen-2-yl]-D-glucitol* (**23**). A soln. of **6** (869 mg, 0.74 mmol) in cyclohexa-1,4-diene (3.5 ml, 37 mmol) and chlorobenzene (50 ml) was cooled to −78° in a 200-ml autoclave, degassed (high-vacuum pump), and kept at 230° for 13 h. Evaporation and HPLC (*Si-60*, hexane/$CH_2Cl_2$/AcOEt 10:5:1) gave **22** (474 mg, 55%), **23** (67 mg, 6%), and **6** (13 mg, 1.5%).

*Data of* **22**: Solid. M.p. 83°. $R_f$ (hexane/$CH_2Cl_2$/AcOEt 70:20:6) 0.26. $[\alpha]_D^{25} = +8.3$ ($c = 0.84$, $CHCl_3$). UV (MeOH): 263 (3900), 229 (68500), 210 (65200). IR ($CHCl_3$): 3089*w*, 3065*w*, 3006*w*, 2960*w*, 2909*w*, 2869*w*, 1950*w*, 1809*w*, 1730*w*, 1603*w*, 1496*w*, 1454*m*, 1360*w*, 1261*m*, 1094*s*, 1066*s*, 1027*s*, 908*s*, 866*w*. $^1$H-NMR (500 MHz, $CDCl_3$; assignment by $^1$H,$^1$H-COSY, TOCSY): *Table 1*; additionally, 7.98–7.95, 7.89–7.87 (2*m*, H–C(5″), H–C(8″)); 7.59–7.52 (*m*, H–C(6″), H–C(7″)); 7.34–7.10 (*m*, 30 arom. H); 6.80 (*tt*, $J = 7.3, 1.4$, $H_p$); 6.77 (br. *t*, $J \approx 7.3$, 2 $H_m$); 6.71 (*tt*, $J = 8.0, 1.2$, $H'_p$); 6.46 (*dd*, $J = 8.2, 7.5$, 2 $H'_m$); 6.37 (*dd*, $J = 7.5, 1.5$, 2 $H_o$); 6.5–6.3 (br. *s*, only visible on intergration, 2 $H'_o$); 5.06 (*d*, $J = 11.7$, PhC*H*); 5.01 (*d*, $J = 10.7$, PhC*H*); 4.92 (*d*, $J = 11.7$, PhC*H*); 4.84 (*d*, $J = 11.2$, PhC*H*); 4.81 (*d*, $J = 11.1$, PhC*H*); 4.74 (*d*, $J = 10.8$, PhC*H*); 4.69 (*d*, $J = 10.7$, PhC*H*); 4.63 (*d*, $J = 12.2$, PhC*H*); 4.62 (*d*, $J = 12.1$ PhC*H*); 4.55 (*d*, $J = 10.7$, PhC*H*); 4.54 (*d*, $J = 12.2$, PhC*H*); 4.50 (*d*, $J = 12.2$, PhC*H*). $^{13}$C-NMR (125 MHz, $CDCl_3$; assignment by $^1$H,$^{13}$C-COSY): *Table 2*; additionally, 139.23 (2*s*); 138.81 (*s*); 138.64 (*s*); 138.52 (2*s*); 138.48 (*s*); 138.47 (*s*); 137.73 (*s*); 133.96 (*s*); 133.75 (*s*); 132.87 (*s*); 132.31 (*d*, C(1″)); 128.75 (*d*, C(4″)); 128.10–126.90 (several *d*); 126.81 (*d*); 126.75 (*d*); 75.64 (*t*, PhC$H_2$); 75.49 (*t*, PhC$H_2$); 75.08 (*t*, PhC$H_2$); 74.88 (*t*, PhC$H_2$); 73.33 (*t*, 2 PhC$H_2$). FAB-MS: 1171 (8, $[M + 1]^+$), 1170 (20, $M^+$), 91 (100). Anal. calc. for $C_{78}H_{74}O_{10}$ (1171.44): C 79.97, H 6.37; found: C 80.10, H 6.20.

*Data of* **23**: Solid. M.p. 53°. $R_f$ (hexane/AcOEt 8:2) 0.27. $[\alpha]_D^{25} = -14.8$ ($c = 0.65$, $CHCl_3$). IR ($CH_2Cl_2$): 3576*m*, 3015*w*, 2907*s*, 2869*s*, 1953*w*, 1880*w*, 1812*w*, 1632*m*, 1598*m*, 1496*s*, 1453*s*, 1361*s*, 1308*m*, 1203*s*, 1097*s*, 1027*s*, 930*m*, 889*m*, 808*m*. $^1$H-NMR (500 MHz, $CDCl_3$; assignment by $^1$H,$^1$H-COSY, TOCSY): *Table 1*; additionally, 7.81 (*dd*, $J = 2.2, 8.0$, H–C(5″)); 7.78 (*dd*, $J = 2.0, 7.8$, H–C(8″)); 7.48–7.43 (*m*, H–C(6″), H–C(7″)); 7.32–7.04 (*m*, 35 arom. H); 7.02 (*tt*, $J = 7.3, 1.2$, 1 H); 6.95 (*tt*, $J = 7.3, 1.3$, 2 H); 6.56 (*dd*, $J = 7.1, 1.3$, 1 H, irrad. at 6.28→NOE (9%)); 6.28 (*s*, HC=C); 4.90 (*d*, $J = 11.5$, PhC*H*); 4.87 (*d*, $J = 11.5$, PhC*H*); 4.84 (*d*, $J = 10.6$, PhC*H*); 4.83 (*d*, $J = 10.6$, 3 PhC*H*); 4.65 (*d*, $J = 10.9$, PhC*H*); 4.64 (*d*, $J = 10.9$, PhC*H*); 4.63 (*d*, $J = 12.2$, PhC*H*); 4.59 (*d*, $J = 12.2$, PhC*H*); 4.50 (*d*, $J = 12.2$, PhC*H*); 4.46 (*d*, $J = 12.2$, PhC*H*); 4.29 (*t*, $J = 9.0$, irrad. at 6.28→NOE (9%), H–C(2′)); 2.20 (*d*, $J = 3.4$, exchange with $D_2O$, OH). $^{13}$C-NMR (125 MHz, $CDCl_3$; assignment by $^1$H,$^{13}$C-COSY): *Table 2*; additionally, 145.62 (*d*, $Ph_2C$=*C*H); 140.08 (*s*); 138.85 (*s*); 138.52 (*s*); 138.39 (*s*); 138.27 (2*s*); 138.23 (*s*); 138.03 (*s*); 137.48 (*s*); 136.17 (*s*); 133.91 (*s*); 133.36 (*s*); 132.80 (*s*); 129.61 (*d*); 128.4–126.0 (several *d*); 119.03 (*s*, $Ph_2C$=C); 75.50 (*t*, PhC$H_2$); 75.19 (*t*, PhC$H_2$); 74.98 (*t*, PhC$H_2$); 74.79 (*t*, PhC$H_2$); 73.44 (*t*, PhC$H_2$); 73.42 (*t*, PhC$H_2$). FAB-MS: 1171 (90, $[M + 1]^+$), 91 (100). Anal. calc. for $C_{78}H_{74}O_{10}$ (1171.44): C 79.98, H 6.37; found: C 79.98, H 6.50.

*Thermolysis of* **22**. A soln. of **22** (25 mg) in chlorobenzene (1 ml) and cyclohexa-1,4-diene (0.1 ml) in a 10-ml glass tube was degassed. The tube was sealed under $N_2$ and kept at 230° for 16 h. FC (hexane/$CH_2Cl_2$/AcOEt 14:4:1) gave **23** (5 mg, 20%) and **22** (19 mg, 76%).

*2-O,2′-O-[(1S,2S)-1,2-Diphenylethylene]-1,1′-(naphthalene-2,3-diyl)bis[(1S)-3,4,6-tri-O-acetyl-1,5-anhydro-D-glucitol]* (**24**). At 0°, a soln. of **22** (120 mg, 0.10 mmol) in $Ac_2O$ (10 ml) was treated with $BF_3 \cdot OEt_2$ (0.15 ml, 1.2 mmol), stirred for 15 h, neutralized with aq. $NaHCO_3$ soln., diluted with AcOEt, washed ($H_2O$), dried ($Na_2SO_4$), and evaporated. FC (hexane/AcOEt 1:1) gave **24** (73 mg, 83%). Solid. M.p. 137°. $R_f$ (hexane/AcOEt 1:1) 0.29. $[\alpha]_D^{25} = -14.2$ ($c = 0.57$, $CHCl_3$). UV (MeOH): 271 (33000), 231 (99000). IR ($CHCl_3$): 3007*w*, 2961*w*, 1743*s*, 1603*w*, 1494*w*, 1455*w*, 1374*m*, 1248*s* (br.), 1095*m*, 1048*s*, 908*s*, 865*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 8.00–7.93 (*m*, H–C(5″), H–C(8″)); 7.65–7.52 (*m*, H–C(6″), H–C(7″)); 6.98–6.40 (*m*, 5 H, Ph); 6.84 (*tt*, $J = 1.0, 7.3$, $H_p$); 6.76 (*tt*, $J = 1.3, 7.2$, 2 $H_m$); 6.29 (*dd*, $J = 1.3, 7.0$, 2 $H_o$); 2.11 (*s*, Ac); 2.10 (*s*, Ac); 2.09 (*s*, Ac);

Table 1. *Selected $^1$H-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Diglucosylated Naphthalenes* **22**–**36**[2])

| | **22** | **24**[a]) | **25**[b]) | **29** | **23** | **33** | **35** | **36** |
|---|---|---|---|---|---|---|---|---|
| H–C(1) | 4.64 | 4.70 | 5.04 | 4.40 | 4.94 | 4.91 | 4.66 | 4.74 |
| H–C(2) | 5.82 | 5.70 | 6.47 | 5.53 | 4.29 | 4.01 | 3.38 | 3.75 |
| H–C(3) | 4.07 | 5.33–5.23 | 4.34 | 5.22 | 3.87 | 3.90 | 5.24 | 5.23 |
| H–C(4) | 3.79 | 5.33–5.23 | 4.44 | 5.19 | 3.92 | 3.95 | 5.23 | 5.35 |
| H–C(5) | 3.69 | 3.95–3.85 | 4.23–4.15 | 3.84–3.78 | 3.76–3.67 | 3.76–3.70 | 3.88–3.77 | 3.90–3.80 |
| H–C(6) | 3.86 | 4.33 | 4.54 | 4.30 | 3.70 | 3.73 | 4.27 | 4.27 |
| H–C(6) | 3.80 | 4.19 | 4.37 | 4.15 | 3.65 | 3.36 | 4.07 | 4.13 |
| H–C(1′) | 5.51 | 5.41 | 6.19 | 5.20 | 4.75 | 4.80 | 5.07 | 4.80 |
| H–C(2′) | 3.56 | 3.68 | 3.83 | 3.50 | 3.72 | 5.21 | 5.35 | 5.26 |
| H–C(3′) | 3.83 | 5.39 | 4.49 | 5.31 | 3.64 | 3.72 | 5.05 | 5.32 |
| H–C(4′) | 3.79 | 5.12 | 4.28 | 5.02 | 3.89 | 3.98 | 5.06 | 5.16 |
| H–C(5′) | 3.52 | 3.95–3.85 | 4.23–4.15 | 3.84–3.78 | 3.35 | 3.12–3.03 | 3.88–3.77 | 3.90–3.80 |
| H–C(6′) | 3.71 | 4.37 | 4.33 | 4.29 | 3.74 | 3.80 | 4.26 | 4.27 |
| H–C(6′) | 3.66 | 4.19 | 4.27 | 4.16 | 3.60 | 3.55 | 4.05 | 4.11 |
| H–C(a) | 4.925 | 4.63 | 5.56 | 4.60 | | | | |
| H–C(b) | 3.38 | 3.30 | 3.85 | 3.23 | | | | |
| H–C(1″) | 7.98 | 7.95 | 8.57 | 7.12 | 7.92 | 7.93 | [d]) | 7.16 |
| H–C(4″) | 8.28 | 8.28 | 8.07 | 7.39 | 8.07 | 8.12 | [d]) | 7.09 |
| *J*(1,2) | 9.9 | 9.8 | 10.0 | 9.5 | 9.5 | 9.6 | 9.6 | 10.0 |
| *J*(2,3) | 9.3 | 9.8 | 9.6 | 9.3 | 9.0 | 9.3 | 9.1 | 9.5 |
| *J*(3,4) | 9.3 | [d]) | 9.6 | 9.5 | 9.0 | 9.3 | 9.6 | 9.6 |
| *J*(4,5) | 9.3 | [d]) | 9.6 | 9.6 | 9.2 | 9.0 | 9.6 | 9.6 |
| *J*(5,6) | 2.0 | 2.0 | 2.1 | 2.7 | 1.8 | 2.9 | 2.0 | 2.1 |
| *J*(5,6) | 3.1 | 5.2 | 5.6 | 4.6 | 4.3 | 4.5 | 5.3 | 4.7 |
| *J*(6,6) | 11.1 | 12.2 | 12.0 | 12.2 | 11.7 | 11.0 | 12.8 | 12.0 |
| *J*(1′,2′) | 9.3 | 9.5 | 9.3 | 9.9 | 9.2 | 9.9 | 9.6 | 9.7 |
| *J*(2′,3′) | 9.0 | 9.3 | 9.0 | 9.3 | 9.0 | 9.5 | 9.6 | 9.2 |
| *J*(3′,4′) | 9.0 | 9.6 | 9.1 | 9.3 | 9.2 | 9.5 | 9.4 | 9.2 |
| *J*(4′,5′) | 9.3 | 10.0 | 9.1 | 9.6 | 9.8 | 9.0 | 9.7 | 9.2 |
| *J*(5′,6′) | 1.9 | 2.0 | 4.1 | 2.7 | 3.0 | [d]) | 2.0 | 2.5 |
| *J*(5′,6′) | 3.4 | 5.0 | 4.1 | 5.2 | 4.1 | [d]) | 5.1 | 4.7 |
| *J*(6′,6′) | 11.3 | 12.2 | 12.9 | 12.2 | 10.0 | 11.0 | 12.0 | 12.3 |
| *J*(a,b) | 7.5 | 7.9 | 7.6 | 7.8 | | | | |

| | **26** | **27** | **28**[c]) | **34** | **30** | **31** | **32**[c]) |
|---|---|---|---|---|---|---|---|
| H–C(1) | 4.91 | 5.06 | 4.77 | 4.73 | 4.65 | 4.82 | 4.52 |
| H–C(2) | 3.93 | 5.21 | 3.83 | 4.02 | 3.72 | 5.06 | 3.63 |
| H–C(3) | 5.28 | 5.44 | 3.60 | 3.79 | 5.19 | 5.36 | 3.50 |
| H–C(4) | 5.18 | 5.29 | 3.41 | 3.82 | 5.11 | 5.22 | 3.37 |
| H–C(5) | 3.91 | 3.99 | 3.52 | 3.72–3.67 | 3.83 | 3.88 | 3.43 |
| H–C(6) | 4.28 | 4.32 | 3.90 | 3.72–3.67 | 4.23 | 4.26 | 3.86 |
| H–C(6) | 4.13 | 4.17 | 3.63 | 3.72–3.67 | 4.09 | 4.12 | 3.60 |
| H–C(1″) | 7.99 | 7.96 | 8.05 | 8.03 | 7.17 | 7.08 | 7.20 |
| *J*(1,2) | 9.6 | 9.9 | 9.6 | 9.6 | 9.6 | 9.9 | 9.4 |
| *J*(2,3) | 9.1 | 9.3 | 9.2 | 9.0 | 9.6 | 9.6 | 9.1 |
| *J*(3,4) | 9.6 | 9.3 | 8.7 | 9.0 | 9.3 | 9.6 | 8.7 |
| *J*(4,5) | 9.9 | 9.6 | 9.5 | 9.3 | 9.7 | 9.8 | 9.5 |
| *J*(5,6) | 2.1 | 2.3 | 1.6 | [d]) | 2.0 | 2.1 | 2.1 |
| *J*(5,6) | 5.0 | 5.6 | 6.6 | [d]) | 5.1 | 5.3 | 6.6 |
| *J*(6,6) | 12,4 | 12.3 | 11.7 | [d]) | 12.4 | 12.2 | 11.9 |

[a]) In $C_6D_6$. [b]) In ($D_5$)pyridine with 1% of $D_2O$. [c]) In $CD_3OD$. [d]) Not determined.

Table 2. *Selected* $^{13}C$*-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *of the Diglucosylated Naphthalenes* **22–36**

| | **22** | **24** | **25**[a]) | **29** | **23** | **33** | **35** | **36** |
|---|---|---|---|---|---|---|---|---|
| C(1) | 86.89 | 86.48 | 87.73 | 85.75 | 77.25 | 78.60 | 69.42 | 68.92 |
| C(2) | 79.01 | 77.49 | 78.72 | 77.39 | 86.34 | 85.83 | 82.47 | 72.81 |
| C(3) | 78.82 | 75.81 | 83.61 | 75.62 | 85.97 | 85.17 | 75.95 | 76.21 |
| C(4) | 88.27[b]) | 69.98 | 78.24 | 69.96 | 78.12 | 78.43 | 75.26 | 74.39 |
| C(5) | 80.70 | 77.37 | 80.90 | 77.30 | 76.74 | 77.53 | 77.22 | 77.23 |
| C(6) | 68.80 | 62.80 | 64.35 | 62.84 | 68.91[b]) | 68.86 | 63.05 | 62.29 |
| C(1′) | 77.44 | 77.20 | 71.61 | 77.17 | 78.32 | 75.97 | 68.77 | 68.46 |
| C(2′) | 83.10 | 82.06 | 85.07 | 80.99 | 79.38 | 79.77 | 74.46 | 74.31 |
| C(3′) | 78.46 | 69.42 | 73.04 | 69.40 | 86.86 | 85.78 | 75.90 | 76.50 |
| C(4′) | 85.44[b]) | 75.44 | 82.23 | 75.32 | 77.92 | 75.87 | 75.14 | 76.04 |
| C(5′) | 79.35 | 76.62 | 79.87 | 76.76 | 79.42 | 79.66 | 75.95 | 77.68 |
| C(6′) | 68.80 | 62.48 | 63.23 | 62.51 | 68.99[b]) | 69.39 | 62.88 | 62.88 |
| C(a) | 85.24 | 85.36 | 86.25 | 85.25 | | | | |
| C(b) | 87.42 | 88.61 | 88.77 | 88.27 | | | | |

| | **26** | **27** | **28** | **34** | **32**[a]) | **30** | **31** |
|---|---|---|---|---|---|---|---|
| C(1) | 68.72 | 68.86 | 72.34 | 75.61 | 72.53 | 68.67 | 68.78 |
| C(2) | 73.32 | 74.05 | 75.78 | 79.59 | 75.88 | 73.41 | 73.74 |
| C(3) | 76.77 | 75.90 | 80.13 | 87.09 | 80.27 | 76.60 | 75.66 |
| C(4) | 76.25 | 74.29 | 78.79 | 77.82 | 78.96 | 76.11 | 74.31 |
| C(5) | 78.33 | 76.35 | 82.72 | 78.08 | 82.67 | 77.93 | 76.22 |
| C(6) | 62.61 | 62.99 | 63.54 | 69.08 | 64.52 | 62.55 | 62.97 |

[a]) In $CD_3OD$. [b]) The assignment may be interchanged.

2.07 (*s*, Ac); 2.04 (*s*, Ac); 1.64 (*s*, Ac). $^{13}C$-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.79 (*s*, C=O); 170.63 (*s*, C=O); 170.41 (*s*, C=O); 170.02 (*s*, C=O); 169.96 (*s*, C=O); 169.84 (*s*, C=O); 137.96 (*s*); 137.90 (*s*); 136.63 (*s*); 133.62 (*s*); 132.85 (*s*); 132.73 (*s*); 132.20 (*d*); 128.69 (*d*); 127.90–126.80 (several *d*); 21.17 (*q*, Me); 20.95 (*q*, Me); 20.87 (*q*, Me); 20.79 (*q*, 2 Me); 20.71 (*q*, Me). CI-MS: 900 (100, $[M + NH_4]^+$). Anal. calc. for $C_{48}H_{50}O_{16}$ (882.92): C 65.30, H 5.71; found: C 65.28, H 5.95.

*2-O,2′-O-[(1S,2S)-1,2-Diphenylethylene]-1,1′-(naphthalene-2,3-diyl)bis[(1S)-1,5-anhydro-*D*-glucitol]* (**25**). A suspension of **24** (55 mg, 0.062 mmol) in MeOH (2 ml) was treated with a soln. of 5.78M NaOMe (0.03 ml) in MeOH, stirred for 0.5 h at r.t., neutralized with *Amberlite IR-120* ($H^+$ form), and filtered. Evaporation of the filtrate gave **25** (37 mg, 94%). Solid. M.p. 144°. $R_f$ ($CH_2Cl_2$/MeOH 9:1) 0.12. $[\alpha]_D^{25} = +20.7$ (*c* = 0.30, MeOH). UV (MeOH): 282 (62000), 271 (44000), 229 (850000). IR (KBr): 3394*s* (br.), 2917*m*, 2854*m*, 1699*w*, 1652*w*, 1455*w*, 1383*m*, 1069*s*, 1020*m*, 970*w*, 888*m*. $^1H$-NMR (500 MHz, ($D_5$)pyridine/$D_2O$ *ca.* 99:1): *Table 1*; additionally, 8.12, 7.87 (2*d*, *J* = 8.0, H–C(5″), H–C(8″)); 7.65, 7.58 (2*td*, *J* = 8.0, 1.1, H–C(6″), H–C(7″)); 7.02–6.80 (*m*, 5 H, Ph); 6.87 (*tt*, *J* = 1.3, 7.3, 1 $H_p$); 6.80 (br. *t*, *J* ≈ 7.5, 2 $H_m$); 6.70 (*dd*, *J* = 1.3, 7.0, 2 $H_o$). $^{13}C$-NMR (75 MHz, $CD_3OD$): *Table 2*; additionally, 140.70 (*s*); 139.73 (*s*); 135.71 (*s*); 134.98 (*s*); 134.25 (*s*); 133.47 (*d*); 129.68 (*d*); 129.29 (*s*); 128.72–127.89 (several *d*). CI-MS: 648 (5, $[M + NH_4]^+$), 630 (3, $M^+$), 180 (100).

*Transformation of* **25** *into* **24**. A mixture of **25** (40 mg), $Ac_2O$ (2 ml), and pyridine (4 ml) was stirred at r.t. for 12 h. Evaporation and FC (hexane/AcOEt 1:1) gave **24** (52 mg, 93%).

*1,1′-(Naphthalene-2,3-diyl)bis[(1S)-3,4,6-tri-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**26**) *and 1,1′-(Naphthalene-2,3-diyl)bis[(1S)-2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**27**). A soln. of **24** (30 mg, 0.034 mmol) in $CH_2Cl_2$ (1 ml) was treated with $BF_3 \cdot OEt_2$ (0.2 ml, 1.62 mmol) and EtSH (1 ml), stirred for 6 h at r.t., and evaporated. The residue was diluted with $CH_2Cl_2$ (50 ml) and the soln. washed with aq. $NaHCO_3$ soln. and $H_2O$ and evaporated. FC (hexane/AcOEt 1:1) gave **26** (14 mg, 58%), *Fraction A* (7 mg), and *Fraction B* (6 mg, $R_f$ (hexane/AcOEt 3:7) *ca.* 0.25). FC of *Fr. A* (hexane/$CH_2Cl_2$ 9:1) gave *trans*-stilbene (5 mg). *Fr. B* was acetylated in $Ac_2O$ (0.5 ml) and pyridine (1 ml) for 12 h. FC (hexane/AcOEt 1:1) gave **27** (4 mg).

*Data of* **26**: Solid. M.p. 119°. $R_f$ (hexane/AcOEt 3:7) 0.42. $[\alpha]_D^{25} = -14.5$ (*c* = 0.22, $CHCl_3$). IR ($CH_2Cl_2$): 3596*s*, 3055*m*, 2962*w*, 2928*w*, 1747*s*, 1420*w*, 1368*m*, 1234*s*, 1098*s*, 1032*s*, 895*w*, 866*w*, 807*s*. $^1H$-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 7.88 (*dd*, *J* = 3.1, 6.2, H–C(5′)); 7.54 (*dd*, *J* = 3.2, 6.3, H–C(6′)); 2.53 (br. *s*,

exchange with $D_2O$, OH); 2.11 (*s*, Ac); 2.09 (*s*, Ac); 2.07 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 171.18 (*s*, C=O); 170.75 (*s*, C=O); 169.88 (*s*, C=O); 133.77 (*s*); 133.09 (*s*); 127.96 (*d*); 127.32 (*d*); 127.05 (*d*); 20.91 (*q*, Me); 20.75 (*q*, 2 Me). CI-MS: 722 (3, $[M + NH_4]^+$), 43 (100). Anal. calc. for $C_{34}H_{40}O_{16}$ (704.68): C 57.95, H 5.72; found: C 58.00, H 5.75.

*Data of* **27**: Solid. M.p. 96°. $R_f$ (hexane/AcOEt 1:1) 0.27. IR ($CH_2Cl_2$): 3060*w*, 2958*w*, 1757*s*, 1603*w*, 1494*w*, 1431*w*, 1368*m*, 1276*m*, 1232*s*, 1100*m*, 1047*s*, 980*w*, 933*w*, 906*w*, 808*w*, 600*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 7.82 (*dd*, $J$ = 3.3, 6.4, H–C(5′)); 7.49 (*dd*, $J$ = 3.3, 6.3, H–C(6′)); 2.10 (*s*, Ac); 2.07 (*s*, Ac); 2.02 (*s*, Ac); 1.80 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.55 (*s*, C=O); 170.45 (*s*, C=O); 169.55 (*s*, C=O); 168.61 (*s*, C=O); 133.05 (*s*); 132.06 (*s*); 128.45 (*d*); 128.07 (*d*); 126.92 (*d*); 20.91 (*q*, 3 Me); 20.15 (*q*, Me). CI-MS: 806 (100, $[M + NH_4]^+$).

*1,1′-(Naphthalene-2,3-diyl)bis[(1*S*)-1,5-anhydro-*D*-glucitol]* (**28**). At 0°, a soln. of **22** (117 mg, 0.10 mmol) in EtSH (2 ml) was treated with $BF_3 \cdot OEt_2$ (0.2 ml, 1.62 mmol), stirred for 2 h at 0°, and evaporated. FC ($CH_2Cl_2$/MeOH 8:2) gave **28** (40 mg, 89%). Solid. M.p. 187–192°. $R_f$ ($CH_2Cl_2$/MeOH 7:3) 0.23. $[\alpha]_D^{25} = +14.0$ ($c$ = 0.53, MeOH). UV (MeOH): 270 (2000), 228 (87000). IR (KBr): 3380*s* (br.), 2915*m*, 2853*m*, 1641*m*, 1461*w*, 1357*m*, 1308*m*, 1085*s*, 987*m*, 901*w*, 867*w*. $^1$H-NMR (300 MHz, $CD_3OD$): *Table 1*; additionally, 7.87 (*dd*, $J$ = 3.2, 6.2, H–C(5′)); 7.47 (*dd*, $J$ = 3.2, 6.2, H–C(6′)). $^{13}$C-NMR (75 MHz, $CD_3OD$): *Table 2*; additionally, 137.29 (*s*); 134.33 (*s*); 128.94 (*d*); 128.08 (*d*); 127.37 (*d*). CI-MS: 470 (5, $[M + NH_4]^+$), 43 (100).

*2-O,2′-O-[(1*S*,2*S*)-1,2-Diphenylethylidene]-1,1′-(5,6,7,8-tetrahydronaphthalene-2,3-diyl)bis[(1*S*)-1,5-anhydro-3,4,6-tri-*O*-benzyl-*D*-glucitol]* (**29**). A suspension of **22** (47 mg) and 30% Pd/C (100 mg) in AcOEt/MeOH 1:1 (6 ml) was degassed and then stirred under 1 atm $H_2$ at r.t. for 20 h. The residue obtained by filtration and evaporation (28 mg, $R_f$ ($CH_2Cl_2$/MeOH 8:2) 057) was acetylated in pyridine/$Ac_2O$ (2:1, 3 ml; 5 h at r.t.). FC (hexane/AcOEt 1:1) gave **29** (30 mg, 84%). Solid. M.p. 124°. $R_f$ (hexane/AcOEt 1:1) 0.24. $[\alpha]_D^{25} = -12.6$ ($c$ = 0.095, MeOH). UV (MeOH): 233 (17000), 223 (12900), 211 (19500). IR ($CHCl_3$): 3028*w*, 3011*w*, 2929*w*, 2861*w*, 1746*s*, 1493*s*, 1455*w*, 1435*w*, 1366*m*, 1278*m*, 1236*s*, 1095*m*, 1053*s*, 921*w*, 873*w*, 811*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 6.97–6.42 (*m*, 10 arom. H); 2.90–2.85 (*m*, 2 H–C(5″), 2 H–C(8″)); 2.11 (*s*, Ac); 2.08 (*s*, Ac); 2.07 (*s*, Ac); 2.05 (*s*, Ac); 2.02 (*s*, Ac); 1.65 (*s*, Ac); 1.99–1.85 (*m*, 2 H–C(6″), 2 H–C(7″)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.77 (*s*, C=O); 170.63 (*s*, C=O); 170.36 (*s*, C=O); 170.02 (*s*, C=O); 169.92 (*s*, C=O); 169.81 (*s*, C=O); 139.09 (*s*); 138.34 (*s*); 138.20 (*s*); 137.79 (*s*); 135.31 (*s*); 133.74 (*d*); 132.03 (*s*); 129.09 (*d*); 127.69–126.84 (several *d*); 29.16 (*t*); 29.08 (*t*, C(5″), C(8″)); 23.21 (*t*, C(6″), C(7″)); 21.16 (*q*, Me); 20.93 (*q*, Me); 20.87 (*q*, Me); 20.77 (*q*, 2 Me); 20.69 (*q*, Me). CI-MS: 904 (64, $[M + NH_4]^+$), 180 (100). Anal. calc. for $C_{48}H_{54}O_{16}$ (886.95): C 65.00, H 6.14; found: C 64.93, H 6.34.

*Transformation of* **24** *into* **29**. A suspension of **24** (21 mg), 30% Pd/C (50 mg) in AcOEt/MeOH 1:1 (2 ml) was stirred at 10 bar of $H_2$ for 4 days. After filtration, evaporation and FC (hexane/AcOEt 1:1) gave **29** (17 mg, 80%) and traces of **30** ( < 1 mg).

*1,1′-(5,6,7,8-Tetrahydronaphthalene-2,3-diyl)bis[(1*S*)-3,4,6-tri-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**30**). At r.t., a suspension of **29** (29 mg) and 30% Pd/C (60 mg) in AcOEt/MeOH 1:1 (4 ml) was degassed and stirred under 10 bar of $H_2$ for 3 days. Filtration, evaporation, and FC (hexane/AcOEt 1:1) gave **30** (18 mg, 89%). Solid. M.p. 199°. $R_f$ (AcOEt/hexane 7:3) 0.35. $[\alpha]_D^{25} = -0.4$ ($c$ = 0.73, $CHCl_3$). IR ($CHCl_3$): 3467*m* (br.), 2943*m*, 1747*s*, 1572*w*, 1507*w*, 1453*m*, 1435*m*, 1367*s*, 1208*s* (br.), 1101*s*, 1032*s* (br.), 956*w*, 927*w*, 869*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 2.50 (br. *s*, exchange with $D_2O$, HO–C(2′)); 2.09 (*s*, Ac); 2.07 (*s*, Ac); 2.06 (*s*, Ac); 1.87–1.79 (*m*, 2 H–C(6′)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.96 (*s*, C=O); 170.68 (*s*, C=O); 169.84 (*s*, C=O); 138.62 (*s*, C(9′)); 132.97 (*s*, C(2′)); 127.93 (*d*, C(1′)); 29.27 (*t*, C(5′)); 23.01 (*t*, C(6′)); 20.89 (*q*, Me); 20.70 (*q*, 2 Me). CI-MS: 726 (75, $[M + NH_4]^+$), 185 (100). Anal. calc. for $C_{34}H_{44}O_{16}$ (708.71): C 57.62, H 6.26; found: C 57.40, H 6.31.

*1,1′-(5,6,7,8-Tetrahydronaphthalene-2,3-diyl)bis[(1*S*)-2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-*D*-glucitol]* (**31**). A soln. of **30** (7.4 mg) in pyridine (1 ml) and $Ac_2O$ (0.5 ml) was stirred at r.t. for 12 h. Evaporation and FC (hexane/AcOEt 1:1) gave **31** (8.2 mg, 99%). Solid. M.p. 101°. $R_f$ (hexane/AcOEt 1:1) 0.25. $[\alpha]_D^{25} = -25.6$ ($c$ = 0.16, $CHCl_3$). IR ($CH_2Cl_2$): 3054*w*, 2941*w*, 1755*s*, 1605*w*, 1421*w*, 1231*s*, 1203*w*, 1100*m*, 1046*m*, 909*w*, 808*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 2.78–2.70 (*m*, 2 H–C(5′)); 2.08 (*s*, Ac); 2.05 (*s*, Ac); 2.00 (*s*, Ac); 1.84 (*s*, Ac); 1.80–1.74 (*m*, 2 H–C(6′)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.55 (*s*, C=O); 170.42 (*s*, C=O); 169.54 (*s*, C=O); 168.77 (*s*, C=O); 138.28 (*s*, C(9′)); 131.25 (*s*, C(2′)); 126.78 (*d*, C(1′)); 29.12 (*t*, C(5′)); 22.89 (*t*, C(6′)); 20.69 (*q*, 3 Me); 20.30 (*q*, Me). CI-MS: 810 (70, $[M + NH_4]^+$), 557 (100). Anal. calc. for $C_{38}H_{48}O_{18}$ (792.79): C 57.57, H 6.10; found: C 57.71, H 6.19.

*1,1′-(5,6,7,8-Tetrahydronaphthalene-2,3-diyl)bis[(1*S*)-1,5-anhydro-*D*-glucitol]* (**32**). At r.t., a suspension of **22** (45 mg) and 30% Pd/C (60 mg) in AcOEt/AcOH 1:2 (6 ml) was washed with $N_2$ and $H_2$, then stirred under 10 bar of $H_2$ for 3 days, and filtered. The filtrate was extracted with $H_2O$ and the aq. layer evaporated. FC

(AcOEt/EtOH 7:3) gave **32** (17 mg, 97%). Solid. M.p. 184°. $R_f$ ($CH_2Cl_2$/MeOH 1:1) 0.40. $[\alpha]_D^{25} = +22.7$ ($c = 0.11$, MeOH). IR (KBr): 3409*s* (br.), 2923*m*, 2853*m*, 1652*w*, 1634*w*, 1531*w*, 1321*w*, 1367*s*, 1086*m*, 988*w*. $^1$H-NMR (300 MHz, $CD_3OD$): *Table 1*; additionally, 2.80–2.70 (*m*, 2 H–C(5′)); 1.80–1.75 (*m*, 2 H–C(6′)). $^{13}$C-NMR (50 MHz, $CD_3OD$): *Table 2*; additionally, 138.28 (*s*, C(9′)); 136.67 (*s*, C(2′)); 129.42 (*d*, C(1′)); 30.37 (*t*, C(5′)); 24.61 (*t*, C(6′)). CI-MS: 474 ($[M + NH_4]^+$).

*Transformation of* **32** *to* **31**. A soln. of **32** (9 mg) in pyridine (1 ml) and $Ac_2O$ (0.5 ml) was stirred at r.t. for 12 h. Evaporation and FC (hexane/AcOEt 1:1) gave **31** (13 mg, 83%).

*(1*S*)-1-*C*-[3-(2-*O*-Acetyl-3,4,5-tri-*O*-benzyl-β-*D*-glucopyranosyl)naphthalen-2-yl]-1,5-anhydro-3,4,6-tri-O-benzyl-2-*O*-(2,2-diphenylethenyl)-*D*-glucitol* (**33**). A soln. of **23** (6 mg) and $Ac_2O$ (0.1 ml) in pyridine (1 ml) was stirred at r.t. for 12 h, evaporated, and co-evaporated with toluene. FC (hexane/AcOEt 9:1) gave **33** (6 mg, 90%). $R_f$ (hexane/AcOEt 8:2) 0.31. IR ($CH_2Cl_2$): 3088*w*, 3065*m*, 3032*m*, 2925*m*, 2869*m*, 1953*w*, 1880*w*, 1811*w*, 1744*s*, 1631*m*, 1598*m*, 1496*s*, 1453*s*, 1361*s*, 1307*m*, 1281*m*, 1228*s*, 1097*s* (br.), 1027*s*, 931*w*, 908*w*, 808*m*. $^1$H-NMR (500 MHz, $CDCl_3$): *Table 1*; additionally, 7.84 (*d*, $J = 7.1$), 7.76 (*d*, $J = 6.8$, H–C(5″), H–C(8″)); 7.48–7.44 (*m*, H–C(6″), H–C(7″)); 7.31–6.94 (*m*, 40 arom. H); 5.88 (*s*, HC=C); 4.92 (*d*, $J = 11.0$, PhC*H*); 4.85 (*d*, $J = 11.0$, PhC*H*); 4.83 (*d*, $J = 11.5$, PhC*H*); 4.82 (*d*, $J = 11.0$, PhC*H*); 4.79 (*d*, $J = 11.0$, PhC*H*); 4.68 (*d*, $J = 11.0$, PhC*H*); 4.66 (*d*, $J = 11.0$, PhC*H*); 4.63 (*d*, $J = 11.0$, PhC*H*); 4.61 (*d*, $J = 12.3$, PhC*H*); 4.60 (*d*, $J = 12.1$, PhC*H*); 4.50 (*d*, $J = 12.2$, PhC*H*); 4.43 (*d*, $J = 12.2$, PhC*H*). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 169.53 (*s*, C=O); 146.00 (*d*, $Ph_2C$=*C*H); 140.28 (*s*); 138.88 (3*s*); 138.57 (*s*); 138.50 (*s*); 138.40 (*s*); 138.34 (*s*); 137.86 (*s*); 134.73 (*s*); 134.66 (*s*); 133.33 (*s*); 129.99–126.49 (several *d*); 119.18 (*s*, $Ph_2C$=CH); 75.79 (*t*, Ph*C*$H_2$); 75.31 (*t*, 2 Ph*C*$H_2$); 75.02 (*t*, Ph*C*$H_2$); 73.69 (*t*, 2 Ph*C*$H_2$); 20.59 (*q*, Me). MALDI-MS: 1233 ($[M + Na]^+$).

*1,1′-(Naphthalene-2,3-diyl)bis[(1*S*)-1,5-anhydro-3,4,6-tri-*O*-benzyl-*D*-glucitol]* (**34**). A soln. of **23** (48 mg) in $CH_2Cl_2$ (5 ml) was treated with $CF_3COOH$ (1 ml) at r.t., stirred for 0.5 h, and evaporated. The residue was dissolved in $CH_2Cl_2$ (20 ml), washed with aq. $NaHCO_3$ soln. and $H_2O$, dried ($Na_2SO_4$), and evaporated. FC (hexane/AcOEt 9:1 to 7:3) gave **34** (31 mg, 76%) and diphenylacetaldehyde (**4** mg). Solid. M.p. 64°. $R_f$ (hexane/AcOEt 7:3) 0.45. $[\alpha]_D^{25} = +10.0$ ($c = 0.13$, $CHCl_3$). UV (MeOH): 229 (87000). IR ($CH_2Cl_2$): 3576*m*, 3446*w*, 3032*m*, 2908*s*, 2869*s*, 1954*w*, 1877*w*, 1812*w*, 1733*w*, 1603*w*, 1497*s*, 1453*s*, 1361*s*, 1306*m*, 1056*s* (br.), 908*m*, 885*m*, 820*w*. $^1$H-NMR (300 MHz, $CDCl_3$). *Table 1*; additionally, 7.84 (*dd*, $J = 3.3$, 6.2, H–C(5′)); 7.48 (*dd*, $J = 3.3$, 6.2, H–C(6′)); 7.42–7.23 (*m*, 30 arom. H); 4.96 (*d*, $J = 11.5$, PhC*H*); 4.93 (*d*, $J = 11.7$, PhC*H*); 4.92 (*d*, $J = 10.7$, PhC*H*); 4.65 (*d*, $J = 10.7$, PhC*H*); 4.63 (*d*, $J = 12.2$, PhC*H*); 4.53 (*d*, $J = 12.3$, PhC*H*); 2.60–2.30 (br. *s*, OH). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 138.78 (*s*); 138.23 (*s*); 138.05 (*s*); 134.80 (*s*); 133.12 (*s*); 128.52–126.48 (several *d*); 75.28 (*t*, Ph*C*$H_2$); 75.01 (*t*, Ph*C*$H_2$); 73.47 (*t*, Ph*C*$H_2$). FAB-MS: 993 ($M^+$), 91 (100). Anal. calc. for $C_{64}H_{64}O_{10}$ (993.20): C 77.48, H 6.49; found: C 77.42, H 6.67.

*(1*S*)-3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-*O*-(2,2-diphenylethyl)-1-*C*-[5,6,7,8-tetrahydro-3-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)naphthalen-2-yl]-*D*-glucitol* (**35**). A suspension of **23** (85 mg) and 30% Pd/C (160 mg) in AcOEt/MeOH 1:1 (4 ml) was kept under 10 bar of $H_2$ for 3 days, filtered, and evaporated. The residue (40 mg, $R_f$ ($CH_2Cl_2$/MeOH 8:2) 0.24) was dissolved in pyridine (2 ml) and $Ac_2O$ (1 ml) and stirred overnight. Evaporation and FC (hexane/AcOEt 1:1) gave **35** (50 mg, 67%). Solid. M.p. 147°. $R_f$ (hexane/AcOEt 1:1) 0.29. IR ($CHCl_3$): 3010*w*, 2961*w*, 1749*s*, 1601*w*, 1495*w*, 1451*w*, 1366*m*, 1260*s*, 1099*s*, 868*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 7.55–7.03 (*m*, 10 arom. H); 6.78 (*dd*, $J = 2.0$, 7.4, 2 $H_o$ of 1 Ph); 3.95 (*dd*, $J = 5.0$, 9.7, $Ph_2CHCH$, irrad. at 2.97→*d*); 3.57 (*t*, $J = 9.5$, $Ph_2CHCH$, irrad. at 2.97→*d*); 2.97 (*dd*, $J = 5.0$, 9.3, $Ph_2CH$); 2.81–2.69 (*m*, 2 H–C(5″), 2 H–C(8″)); 2.03 (*s*, 2 Ac); 2.06 (*s*, Ac); 1.99 (*s*, Ac); 1.90 (*s*, Ac); 1.81 (*s*, Ac); 1.58 (*s*, Ac); 1.80–1.71 (*m*, 2 H–C(6″), 2 H–C(7″)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.80 (*s*, C=O); 170.51 (*s*, C=O); 170.36 (*s*, C=O); 169.96 (*s*, C=O); 169.87 (*s*, C=O); 169.55 (*s*, C=O); 168.91 (*s*, C=O); 141.51 (*s*); 141.16 (*s*); 138.07 (*s*); 137.99 (*s*); 133.08 (*s*); 131.76 (*s*); 128.31 (*d*); 128.16 (*d*); 126.90 (*d*); 126.50 (*d*); 126.40 (*d*); 76.03 (*t*, $Ph_2CHCH_2$); 50.33 (*d*, $Ph_2CH$); 29.25, 29.18 (2*t*, C(5″), C(8″)); 23.01 (*t*, C(6″), C(7″)); 20.68 (*q*, 5 Me); 20.51 (*q*, Me); 20.22 (*q*, Me). CI-MS: 948 (100, $[M + NH_4]^+$), 331 (97), 181 (63). Anal. calc. for $C_{50}H_{58}O_{17}$ (931.00): C 64.51, H 6.28; found: C 64.34, H 6.46.

*(1*S*)-3,4,6-Tri-*O*-acetyl-1,5-anhydro-1-*C*-[5,6,7,8-tetrahydro-3-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-naphthalen-2-yl]-*D*-glucitol* (**36**). A suspension of **35** (43 mg, 0.046 mmol) and $AlCl_3$ (65 mg, 0.48 mmol) in $CH_2Cl_2$ (5 ml) was stirred for 0.5 h at r.t., cooled to 0°, and treated with aq. $NaHCO_3$ soln. Extraction with $CH_2Cl_2$ (10 times), evaporation of the org. layer, and FC (hexane/AcOEt 1:1) gave **36** (26 mg, 86%). Solid. M.p. 119°. $R_f$ (hexane/AcOEt 4:6) 0.38. $[\alpha]_D^{25} = -15.7$ ($c = 0.35$, $CHCl_3$). IR ($CH_2Cl_2$): 3598*w*, 3062*w*, 2942*w*, 1750*s*, 1606*w*, 1435*w*, 1348*m*, 1278*w*, 1231*s*, 1201*w*, 1103*w*, 1038*m*, 981*w*, 956*w*, 910*w*, 874*w*, 600*w*. $^1$H-NMR (300 MHz, $CDCl_3$): *Table 1*; additionally, 2.78–2.70 (*m*, 2 H–C(5″), 2 H–C(8″)); 2.48 (*d*, $J = 3.2$, exchange with $D_2O$, OH); 2.08 (*s*, 3 Ac); 2.06 (*s*, Ac); 2.05 (*s*, Ac); 2.02 (*s*, Ac); 1.83 (*s*, Ac); 1.81–1.74 (*m*, 2 H–C(6″), 2 H–C(7″)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 2*; additionally, 170.83 (*s*, C=O); 170.65 (*s*, C=O); 170.56 (*s*, C=O); 170.40 (*s*, C=O); 169.86 (*s*,

C=O); 169.49 (*s*, C=O); 169.10 (*s*, C=O); 138.80 (*s*); 138.16 (*s*); 133.16 (*s*); 131.39 (*s*); 127.75 (*d*); 127.62 (*d*); 29.45 (*t*, C(6″), C(7″)); 29.11 (*t*, C(5″), C(8″)); 22.94 (*q*, 2 Me); 20.99 (*q*, Me); 20.72 (*q*, 2 Me); 20.65 (*q*, Me); 20.46 (*q*, Me). CI-MS: 768 (58, $[M + NH_4]^+$), 43 (100). Anal. calc. for $C_{36}H_{46}O_{17}$ (750.75): C 57.60, H 6.18; found: C 57.59, H 6.28.

*Transformation of* **36** *into* **31**. A soln. of **36** (12 mg, 0.018 mmol) in pyridine (1 ml) and $Ac_2O$ (0.5 ml) was stirred for 5 h at r.t. Evaporation and FC (hexane/AcOEt 1:1) gave **31** (12 mg, 94%).

*Thermolysis of* **16** *and* **6**. Solns. of **16** (2 mg, 4.4 μmol) or **6** (5.2 mg, 4.4 μmol) in cyclohexa-1,4-diene/EtOH 1:10 (1 ml) were placed in 5-ml glass tubes and degassed at −78° (high-vacuum pump). The tubes were sealed under $N_2$ at r.t. and then placed in an oil bath at 140, 160, 180, or 200° for 24 h. After evaporation, the mixtures were analyzed by TLC and $^1$H-NMR. The thermolysis of **16** at 180 and 200° gave a complex mixture of unidentified products, whereas at 140 and 160°, no reaction occurred. The thermolysis of **6** gave mainly mixtures **6**/**22**. According to anal. HPLC (*Si-60*, hexane/$CH_2Cl_2$/AcOEt 7:2:0.4), the products obtained at 180, 160, and 140° contained 31, 6, and 1% of **22** and 45, 80, and 93% of **6**, respectively.

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