Oligosaccharide Analogues of Polysaccharides

Part 19[1])

Synthesis of 2-(Naphthalen-1-yl)ethyl Cellooligoglycosides and [(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[cellooligoglycosides]

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Glucosyl, cellobiosyl, cellotriosyl, cellotetraosyl, and cellooctaosyl residues were attached to naphthalene-1,8-diethanol (**3**) with the goal of preparing mimics of cellulose I. Among the templates that were considered, 1,8-diethynylnaphthalene (**1**) led to unstable products, and glycosidation of naphthalene-1,8-dimethanol (**2**) gave orthoesters that could not be rearranged to glycosides (*Scheme 1*). The conformation of **3** in the crystal and of its dimethyl ether **14** in solution was studied by X-ray analysis and force-field calculation (*Figs. 1–3*). Rotation around the Ar–CH_2 and CH_2–CH_2 bonds of **14** is only weakly hindered and the O···O distance of crystalline **3** (6.01 Å) corresponds to the mean distance of the parallel chains of cellulose I_β. The acetylated glycosyl bromides **18** and **19** were prepared by a new convergent synthesis (*Scheme 2*). Glycosylation of **3** by the glycosyl bromides **15**–**19** under established conditions of the *Koenigs-Knorr* reaction proved problematic, particularly on account of an acetyl transfer blocking one of the hydroxyethyl groups. Basic zinc carbonate, however, promoted glycosylation of **12** and **3** by the glycosyl bromides **15**–**19** and did not lead to transacetylation (*Scheme 3*). The mono- to tetrasaccharides **32**–**35** and **42**–**45** were isolated in yields of 56–82%, and the octasaccharides **36** and **46** in 32 and 16%, respectively. The mono- and disaccharides **32**, **33**, **42**, and **43** were deacetylated with NaOMe in MeOH. Aqueous NaOH was used for the tri-, tetra-, and octasaccharides **34**–**36** and **44**–**46**, as their partially deacetylated derivatives proved insoluble in MeOH. The fully deprotected saccharides **37**–**41** and **47**–**50** were isolated in over 90%, while the yield of the dioctaoside **51** was lower on account of its poor water solubility.

Introduction. – There are at least four polymorphs of cellulose, *viz.* cellulose I–IV [2] of which cellulose I, the native forms, and cellulose II, the mercerized (regenerated) form are most frequently encountered. Cellulose II is the most stable polymorph. Cellulose I exists as two allomorphs, cellulose I_α and cellulose I_β. Cellulose I_β is more stable than cellulose I_α and obtained by hydrothermal annealing of cellulose I_α [3].

There is a single cellulose chain in the unit cell (triclinic) of cellulose I_α [4]. The conformation of the chain and the H-bond network have not been elucidated. The crystal structures of cellulose I_β and cellulose II have been discussed in detail [5–8]. Crystals of cellulose I_β and cellulose II are monoclinic with two independent chains in their unit cell. The chains are parallel in cellulose I_β and antiparallel in cellulose II. As the crystal-structure determination of cellulose I_β and cellulose II is based only on limited X-ray diffraction data of polycrystalline samples (a few tens of reflections) combined with computer modelling, efforts have been directed at the analysis of crystalline cellooligomers as closely related models. The higher resolution of the single-crystal analysis of cellooligomers should give precise data which may even allow

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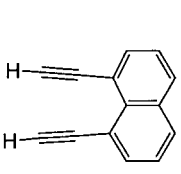
location of the OH groups and determination of the H-bond network. The X-ray diffraction patterns [9][10], solid-state CP/MAS ^{13}C-NMR [11], and IR spectra [12][13] of cellooligomers (degree of polymerization (*DP*) ≥ 4) are indeed quite similar to those of cellulose II. Thus, beyond a given *DP*, the central glucosyl residues of cellotetraose and higher cellooligomers should possess conformations and crystal packing similar or identical to cellulose II. Indeed, the unit cell, the packing, and the conformation of the chains (except the orientation around the C(5)–C(6) bonds) of a single crystal of cellotetraose hemihydrate [14–16] are closely related to those of cellulose II.

However, there is no model compound for the metastable cellulose I_β. Conceivably, the required parallel orientation of the cellulose or cellooligosaccharide chains may be enforced by attaching the chains to a common template. A suitable template should be sufficiently rigid to keep the attached chains close together and to allow or dictate similar distances between the chains as they are found in cellulose I_β. Apart from this, the template should affect the conformation of neither the chains nor the H-bonds. To the best of our knowledge, no investigations of H-bond interactions between linked oligosaccharide chains have been published other than for disaccharides[2]).

We have already prepared 1,2-bis[(β-D-glucopyranosyl)ethynyl]benzenes [20] and studied the interaction of the glucopyranosyl)ethynyl moieties under conditions of the *Bergman-Sondheimer-Masamune* rearrangement. However, as expected from the angle of 60° between the *ortho*-substituents and the rigidity of the ethynyl group that hinder a significant interaction between the chains, there was no clear indication of an interaction between the two glucopyranosyl moieties. In contrast to 1,2-disubstituted benzenes, 1,8-disubstituted naphthalenes should allow a parallel orientation of their substituents. A comparison of 1,8-disubstituted naphthalenes carrying cellooligosaccharide chains with 1-substituted naphthalenes should allow to detect interactions between the cellooligosaccharide strands in solution and in the solid state.

In this paper, we describe the evaluation of the template and the synthesis of the mono- and distranded cellooligosaccharides. The following papers will be dedicated to analytic and spectroscopic investigations of these template-bound cellooligosaccharides.

Results and Discussion. – 1. *Evaluation of the Templates.* The (naphthalene-1,8-diyl)-linked dialkyne **1**, dimethanol **2** [21], diethanol **3** [22], and dipropanol **4** [23] were selected as candidates for a template. The corresponding bis(oligosaccharides) ('distranded saccharides') should be accessible by cross-coupling between a 1,8-dihalogenonaphthalene and 1-*C*-ethynyl(oligo)glucosides [20] or by glycosylation of **2**–**4**.



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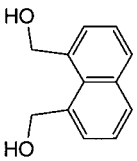

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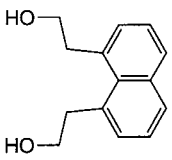

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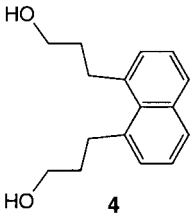

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[2]) Lactosyl moieties have been attached to glycerol [17] and *Tris* (= 2-amino-2-(hydroxymethyl)propane-1,3-diol) [18] and cellobiosyl moieties to threitols [19].

According to force-field calculations[3]), the four templates possess a similar C(1)···C(8) distance of 2.48–2.54 Å. The distance between the acetylenic H-atom of **1** (3.41 Å) and the maximal O···O distance for **2** (5.73 Å), however, are distinctly smaller than the mean distance of *ca.* 6.0 Å between neighbouring chains in different sheets of cellulose I_β [25], while the maximal O···O distances for **3** (7.65 Å) and **4** (10.5 Å) are larger. Thus, **3** and **4** may be appropriate templates, while **1** and **2** are not suitable, as they should lead to severe destabilizing steric interactions between the first glucopyranosyl residues.

Cross-coupling of the diiodide **6** [26] with the octynitol **5** [27] gave 39% of the dialkyne **7**, besides 5% of the corresponding monoalkynylated monoiodide (*Scheme 1*)[4]). However, in view of the low stability of **7** (it decomposed at 23° within a few days), we quickly abandoned this type of compounds.

AgOTf-Promoted glycosidation of **2** with the peracetylated glucopyranosyl or cellobiosyl bromides in $ClCH_2CH_2Cl$ or in THF failed, as did glycosidation by the corresponding thioglycosides (*N*-iodosuccinimide and TfOH in CH_2Cl_2). Glycosidation of **2** with the trichloroacetimidates **8** [28] and **9** [29][30] in the presence of $BF_3 \cdot OEt_2$ in THF gave the C_2-symmetric orthoesters **10** (87%) and **11** (88%), respectively. These orthoesters proved stable at 23° for several days and could be stored at −20° for several months without decomposition. Attempts to rearrange **10** and **11** to the corresponding diglycosides by treatment with $HgBr_2$ or Me_3SiOTf [31][32] were accompanied by hydrolysis and led only to 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose and $2^I,2^{II},3^I,3^{II},4^{II},6^I,6^{II}$-hepta-*O*-acetyl-D-cellobiose [33]. The *peri*-substituent has a strong influence on the glycosidation. Whereas the $ZnCO_3$-catalysed glycosidation of naphthalene-1-methanol by the cellobiosyl bromide **16** (*Scheme 2*) gave up to 56% of the β-cellobioside, the analogous $ZnCO_3$- or $Hg(CN)_2$-catalyzed glycosidation of 8-[(allyloxy)methyl]naphthalene-1-methanol gave mixtures of the orthoester (up to 74%) and the β-glycoside (up to 35%) [34].

The orthoester moiety of **10** and **11** is revealed by characteristic ^{1}H- and ^{13}C-NMR resonances; *i.e.*, a *s* at 1.83 ppm for the $MeCO_3$ group, a *s* at 121.86 or 121.68 ppm for the quaternary C, and a *d* at 97.26 or 96.80 ppm for $C(1^I)$, resp. (the Roman-numeral superscripts refer to the monosaccharide units with respect to the naphthalene units). $C(1^{II})$ of **11** resonating at 101.83 ppm indicates the β-D-configuration. The $H-C(1^I)$ *d* at 5.63 and 5.54 ppm is clearly shifted downfield relative to the H–C(1) signals of β-D-glucopyranosides (compare with the $H-C(1^{II})$ *d* of **11** at 4.68 ppm). The skew-boat conformation ($^3S_5$) of the pyranose unit containing the orthoester moiety is deduced from the small values of $J(1^I,2^I)$, $J(2^I,3^I)$, and $J(3^I,4^I)$ (5.2–5.3, 2.8, and 1.6–2.8 Hz, resp.) and from a long-range coupling between $H-C(2^I)$ and $H-C(4^I)$ (*ca.* 1 Hz [35–37]). A NOE (2.2%) between $MeCO_3$ and $H-C(5^I)$ of **10** reveals the (*S*)-configuration for the orthoester center. The similarity of the ^{1}H- and ^{13}C-NMR spectra of **10** and **11** suggests the same configuration for **11**, in keeping with the expected *exo* attack of **2** on the intermediate dioxolenium ion.

To characterize the conformational behaviour of the ethanediyl moiety of glycosides derived from **3**, the monoether **13** [38][39] and the diether **14** were prepared, analysed by NMR spectroscopy, and modelled by force-field calculations. These ethers are easily obtained by methylation of the alcohols **12** and **3** (*Scheme 1*).

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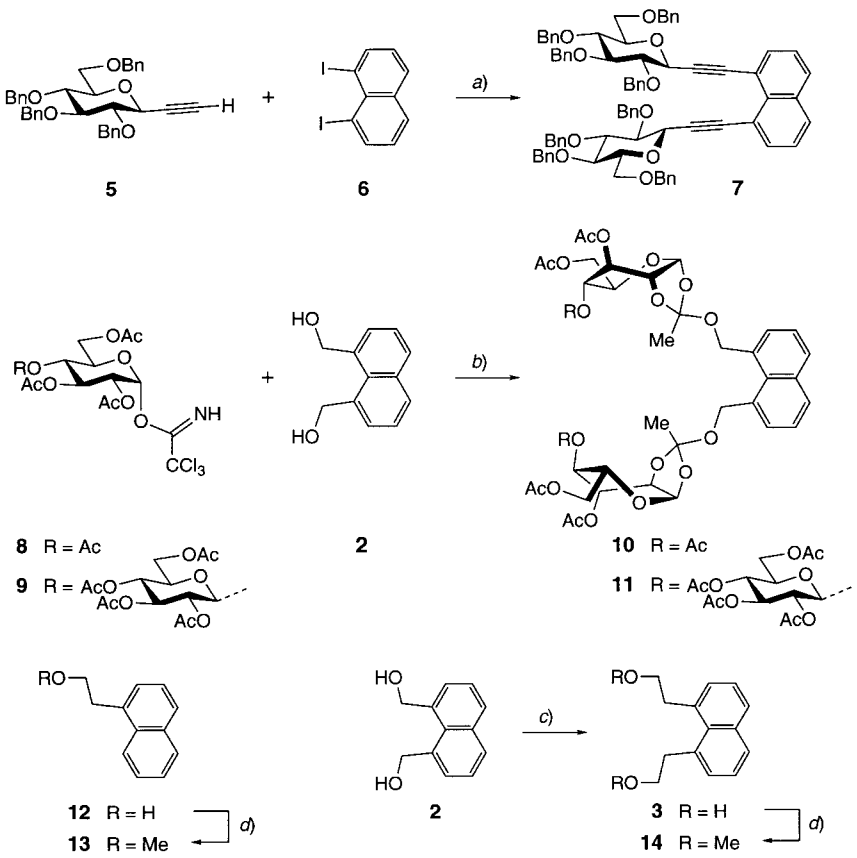
[3]) Macromodel V. 6.0, MM3* force field, gas phase [24].

[4]) Several attempts to reproduce this reaction failed.

Scheme 1



a) 2 equiv. of **5**, **6**, $[Pd(PPh_3)_4]$, CuI, piperidine; 39%. *b*) 2 equiv. of **8** or **9**, **2**, $BF_3 \cdot OEt_2$; **10** (87%) or **11** (88%). *c*) PBr_3, pyridine, Et_2O; Ph_3P, DMF; $NaNH_2$, NH_3/Et_2O, then $CH_2O \rightarrow$ 70% of 1,8-divinylnaphthalene [40]; $NaBH_4$, 2-methylbut-2-ene, $BF_3 \cdot OEt_2$, THF, then 20% aq. NaOH and 30% H_2O_2 soln.; 81% from 1,8-divinylnaphthalene. *d*) **12** or **3**, NaH, MeI, DMF; **13** (90%) or **14** (92%).

The naphthalene-1,8-diethanol **3** is accessible by transforming **2** into 1,8-divinylnaphthalene [40] followed by hydroboration and oxidative workup [22].

Rather large $\Delta\delta$ values are observed for the corresponding ^{1}H-NMR signals of the $MeOCH_2CH_2$ groups of the mono- and disubstituted naphthalenes **13** and **14** (MeO: $\Delta\delta$ 0.08 (MeO), 0.17 (CH_2O), 0.07 ppm ($ArCH_2$)), as well as for their ^{13}C-NMR signals ($\Delta\delta$ 1.7 (MeO), 1.3 (CH_2O), 3.9 ppm ($ArCH_2$)). These differences evidence the influence of the substituent in *peri*-position and hint at a different conformational preference of these naphthalenes. The vicinal coupling constants $J(CH_2,CH_2)$ (7.2 Hz) indicate a more or less free rotation around the CH_2-CH_2 bonds. The isochronicity of the benzylic H-atoms in both **13** and **14** may indicate the absence of strong hindrance of the rotation around the $CH_2-C(Ar)$ bonds.

The conformational preference of **13** and **14** was further investigated by force-field calculations[3]). Rotation around the $CH_2-C(Ar)$ bond of the monosubstituted

naphthalene **13** led to energy minima for the three conformers **13A**, **13B**, and **13C** (*Fig. 1*). Conformer **13B** is *ca.* 2 kcal/mol less stable than the enantiomers **13A** and **13C**. The conformers **13F** and **13G** obtained from **13A** by a rotation of 60° around the $CH_2-C(Ar)$ bond do not correspond to energy minima. The former is near the transition state between **13B** and **13C** ($\Delta G^{\neq}$ *ca.* 2.7 kcal/mol) and the latter is half-way between **13C** and the transition state **13H** ($\Delta G^{\neq}$ *ca.* 7.9 kcal/mol). Thus, the conversion of conformer **13A** to **13C** *via* **13B** is associated with a small energy barrier. Rotation around the CH_2-CH_2 bond of conformer **13A** leads to two additional minima, **13D** and **13E**, higher in energy than **13A** ($\Delta E < 1$ kcal/mol). The energy barriers between these conformers are smaller than 2 kcal/mol. Thus, force-field calculation suggests a more or less free rotation around both the $CH_2-C(Ar)$ and the CH_2-CH_2 bond of **13**.

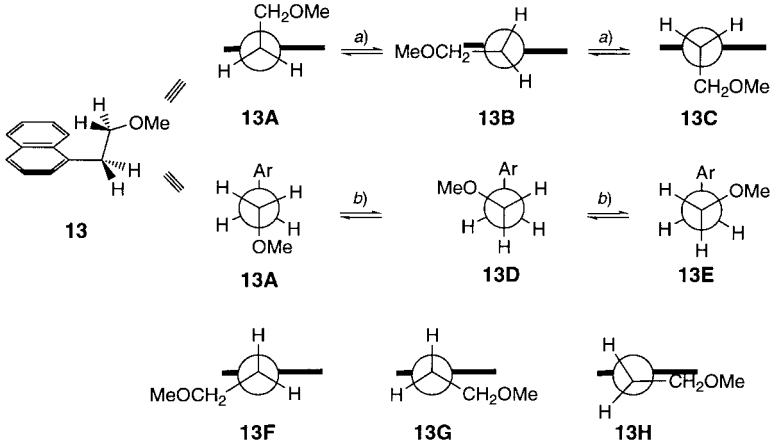


Fig. 1. *MM3* Calculation for* **13**: *minima obtained* a) *by rotation around the* $CH_2-C(Ar)$ *bond and* b) *by rotation around the* CH_2-CH_2 *bond*

A combination of the three conformers **13A**, **13C**, and **13B** for **13** leads to nine conformers of the disubstituted naphthalene **14** (*Fig. 2,A*). Conformers **14CC**, **14BC**, and **14CB** are identical to **14AA**, **14AB**, and **14BA**, respectively. The conformers **14CA** and **14AC** are enantiomers, as are **14BA** and **14AB**. Thus, only the four conformers **14AA**, **14AB**, **14AC**, and **14BB** (*Fig. 2,B*) have to be analysed more closely. Force-field calculation[3]) shows that these four conformers correspond to energy minima. The global minimum is found for **14AC**, in which the two CH_2-CH_2 bonds are perpendicular and on opposite sides of the naphthalene ring. Conformer **14AA** is destabilized by 2.2 kcal/mol due to unfavourable steric and electronic interactions between the two CH_2OMe moieties, as reflected by a smaller dihedral angle $C(2)-C(1)-CH_2-CH_2$ ($-70°$). Conformer **14AB** is similar in energy to **14AA**, whereas conformer **14BB** is disfavoured by 4.5 kcal/mol. The highest energy barrier (4.5 kcal/mol) is observed for the conversion of **14AC** into **14AB**. The conversions of **14AB** to **14AA** ($\Delta G^{\neq} = 0.8$ kcal/mol) and to **14BB** ($\Delta G^{\neq} = 2.7$ kcal/mol) are much easier. The barriers for rotation around the $CH_2-C(Ar)$ bond are higher in **14** than in the monosubstituted naphthalene **13**. Nevertheless, they indicate a relatively easy conversion of **14AA** *via*

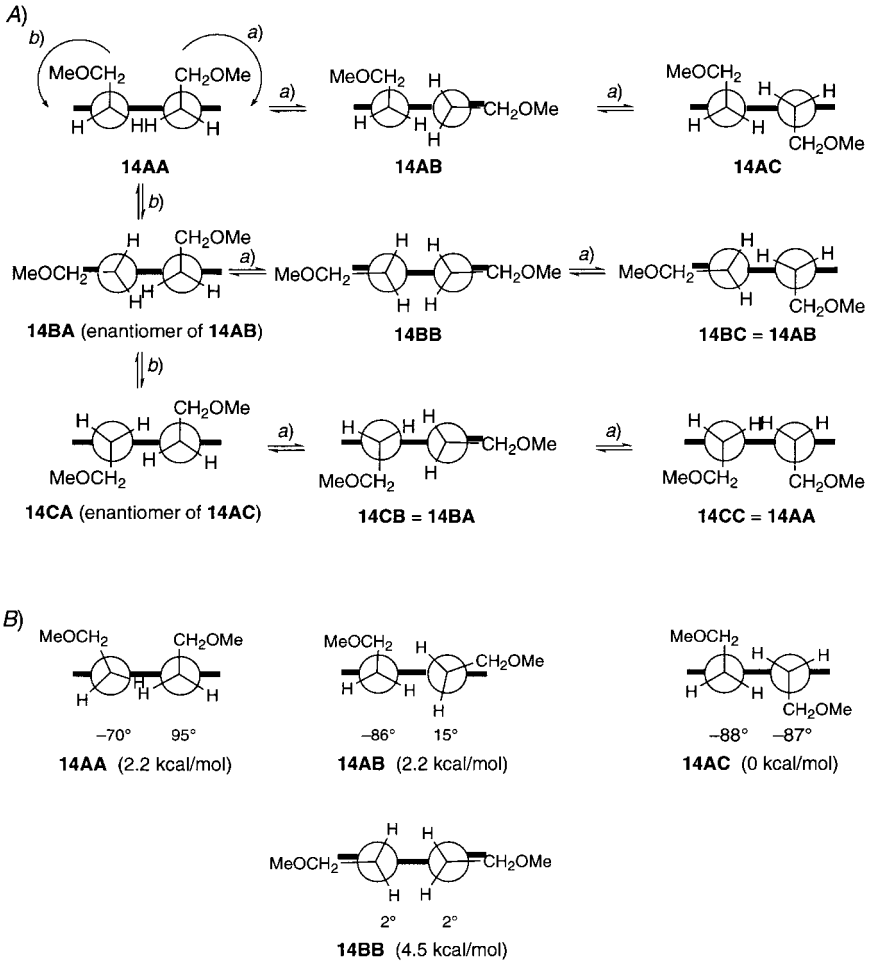


Fig. 2. A) *Stable conformers of* **14** *as deduced by a combination of the stable conformers of* **13**; a) *rotation around the right* $CH_2-C(Ar)$ *bond and* b) *rotation around the left* $CH_2-C(Ar)$ *bond*. B) *MM3* Calculation for* **14AA**, **14AB**, **14AC**, *and* **14BB**. ΔE Values in parentheses and the dihedral angles $C(2)-C(1)-CH_2-CH_2$ and $C(7)-C(8)-CH_2-CH_2$ below the *Newman* projections.

14AB to **14AC**. The distance between the two O-atoms of **14** varies in the range of 4.2 to 6.5 Å.

The result of the calculations was corroborated by the crystal structure of the diethanol **3**[5]), which strongly resembles conformer **14AC** (*Fig. 3*). The experimental values of -95.2 and $-96.5°$ for the dihedral angles $C(2)-C(1)-CH_2-CH_2$ and $C(7)-C(8)-CH_2-CH_2$ are similar to the calculated ones (-88 and $-87°$). One side

[5]) A crystal of **3** was prepared by slow evaporation of a CH_2Cl_2 solution. The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-101541. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44(1223)336033; e-mail:deposit@ccdc.cam.ac.uk).

chain adopts a *zig-zag* conformation (169.9° for the dihedral angle C(8)–CH_2–CH_2–O), and the other one possesses a sickle conformation (67.3° for the dihedral angle C(1)–CH_2–CH_2–O). This may be the consequence of the intermolecular H-bond between the OH groups of the two conformationally different side chains with the OH group of the sickle chain as the H-donor. The longer distance between the two benzylic C-atoms (3.01 Å) than between C(1) and C(8) (2.57 Å) is due to steric repulsion between the two substituents in *peri*-position and has already been observed in 1,8-dimethylnaphthalene (2.93 *vs.* 2.54 Å [41]). The O···O distance of crystalline **3** is 6.01 Å and corresponds exactly to the mean distance of the parallel chains in cellulose I_β. This finding in conjunction with the force-field calculations suggests that **3** is a suitable template, and that attaching two cellooligosaccharide chains to it may lead to a model of cellulose I_β.

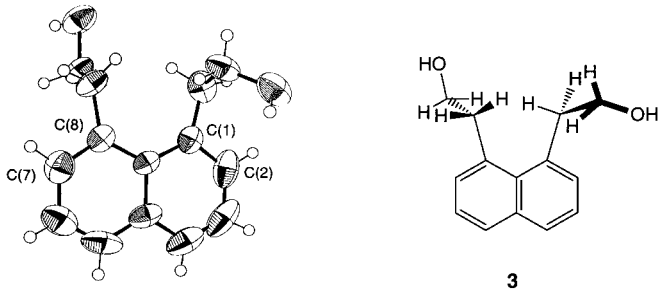


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Fig. 3. *X-Ray crystal structure of the diethanol* **3**

Preliminary experiments showed that a *Koenigs-Knorr* reaction between the cellobiosyl bromide **16** and **3** yields the desired distranded glycoside. Thus, similar reactions should afford distranded cellooligosaccharides of different chain length.

2. *Synthesis of the Glycosides.* – To study the influence of the chain length on the intramolecular interstrand association, we planned to attach glucosyl, cellobiosyl, cellotriosyl, cellotetraosyl, and cellooctaosyl chains to the di- and the monosubstituted naphthalenes **3** and **12**, respectively, using the *Koenigs-Knorr* reaction of the acetylated glycosyl bromides **15**–**19** (*Scheme 2*)[6]). The bromides **15**–**18** have been prepared in high yield from acetylated cellooligosaccharides. Penta-*O*-acetylglucose and octa-*O*-acetylcellobiose are commercially available; the higher cellooligosaccharides were obtained by degradation of cellulose [42][43]. As we required relatively large amounts of material, we looked for a convergent synthesis of multigram quantities of the tetramer **18** and the octamer **19**. Fully acetylated cellotetraose and cellooctaose have been prepared by a linear synthesis from allyl $2^{I},2^{II},3^{I},3^{II},6^{I},6^{II}$-hexa-*O*-benzyl-$4^{II}$-*O*-(4-methoxybenzyl)-$\beta$-cellobioside [44–46] and by a convergent synthesis from allyl 4^{II}-*O*-acetyl-$3^{I},3^{II}$-di-*O*-benzyl-$2^{I},2^{II},6^{I},6^{II}$-tetra-*O*-pivaloyl-$\beta$-cellobioside [47][48]. We opted for a synthesis from acetylated glycosyl bromides as donors and benzylated glycosyl acceptors. The acceptors are readily prepared from allyl glycosides by benzylidenation, benzylation, and regioselective reduction of the benzylidene acetal [49][50].

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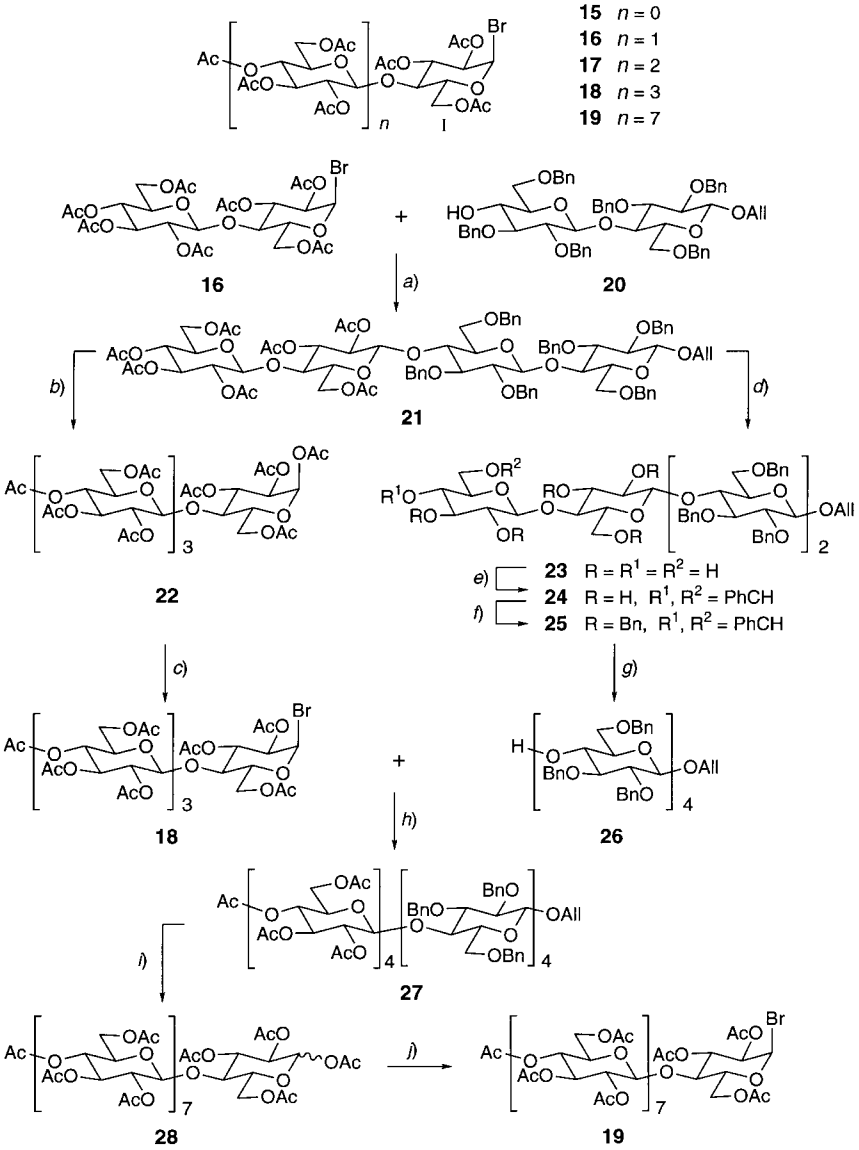
[6]) We thank Dr. *J. A. Hyatt*, *Eastman Research Laboratories*, Kingsport, TN 37662, USA, for a generous gift of cellooligosaccharides.

Scheme 2



a) **20**, 1.3 equiv. of **16**, AgOTf, 1,2-dichloroethane, −30°; 89%. *b*) [Ir(MePh$_2$P)$_2$(C$_8$H$_{12}$)]PF$_6$, THF; HgCl$_2$, HgO, acetone/H$_2$O 10 : 1; BF$_3$ · OEt$_2$, Ac$_2$O; 65–80%. *c*) 4.1M HBr in AcOH, AcOH/CH$_2$Cl$_2$; 76%. *d*) NaOMe, MeOH; 99%. *e*) ZnCl$_2$, PhCHO; 84%. *f*) NaH, BnBr, DMF; 93%. *g*) NaBH$_3$CN, 1M HCl in Et$_2$O; 92%. *h*) **26**, 1.3 equiv. of **18**, AgOTf, −30°; 76%. *i*) [Ir(MePh$_2$P)$_2$(C$_8$H$_{12}$)]PF$_6$, THF; HgCl$_2$, HgO, acetone/H$_2$O 10 : 1; 30% Pd/C, 6 bar of H$_2$, AcOEt/MeOH/H$_2$O 5 : 5 : 1; Ac$_2$O, pyridine; 87%. *j*) 4.1M HBr in AcOH, AcOH/CH$_2$Cl$_2$; 93%.

Glycosidation of the allyl cellobioside **20** [49][50] with acetylated cellobiosyl bromide **16** in the presence of AgOTf in 1,2-dichloroethane gave 89% of the tetrasaccharide **21**. Deallylation of **21** followed by acetolytic debenzylation yielded 65–80% of tetradeca-*O*-acetyl-α-cellotetraose **22** [42][43][51][52]. When the reaction was performed on a larger scale (29.3 g of **20**), we observed partial glycoside cleavage, leading to 5% of undeca-*O*-acetyl-α-cellotriose [42][43][51][52] (5%), 6% of octa-*O*-acetyl-α-cellobiose, and 4% of penta-*O*-acetyl-α-D-glucopyranose. The undeca-*O*-acetyl-α-cellotriose was used for the preparation of **17** [42][43]. Bromination of the peracetylated cellotetraose **22** yielded 76% of the bromide **18** [42][43]. The glycosyl acceptor **26** was prepared in four steps and an overall yield of 71% from the heptaacetate **21** by deacetylation to **23**, benzylidenation to **24**, and benzylation to **25**, followed by reductive cleavage of the dioxane ring. Glycosidation of the cellotetraoside **26** with the cellotetraosyl bromide **18** gave the cellooctaoside **27** in 76% yield. Deallylation of **27** followed by hydrogenolytic debenzylation and acetylation yielded 87% of a 1:1 mixture of the anomeric acetates **28** [48][52], which were transformed in high yield into the bromide **19**.

The cellotetraoside **21** is characterized by a MALDI-MS $[M+Na]^+$ peak at *m/z* 1563. Its ^{13}C-NMR spectrum shows two groups of signals characteristic of the Ac- and Bn-protected glucopyranosyl units. Seven *s*'s at 170.84–168.99 ppm are assigned to C=O groups and six *s*'s at 139.71–138.00 ppm to C(1) of the Bn groups. The anomeric C-atom of the Bn-protected units resonate at lower fields (102.88–102.44 ppm) than those of the Ac-protected units (101.03–99.73 ppm). Together with the $J(1,2)$ values of *ca.* 8.0 Hz, their chemical shift evidences the β-D-configuration of all anomeric centers. Similar observations were made for the octaoside **27**. It is further characterized by a MALDI-MS $[M+Na]^+$ peak at *m/z* 3004.

The monobenzylated naphthalene derivative **29** was chosen as model for the glycosidation (*Scheme 3*). It was prepared in 79% yield by treating the diethanol **3** with an equimolar amount of BnBr. Glycosidation of **29** with acetylated cellobiosyl bromide **16** under the conditions that were used for the preparation of the cellotetraoside **21** and the octaoside **27**, but at 0° instead of −30°, gave only 19% of the desired cellobioside **30**, besides 15% of the acetate **31** resulting from transesterification. The yield of **30** remained low (15–30%) when the glycosidation was promoted by either AgOTf or $HgBr_2$ in CH_2Cl_2, toluene, benzene, or Et_2O. Ag_2CO_3 and Ag_2O at room temperature led to a very slow reaction[7]), and large amounts of the starting materials **16** and **29** were recovered. Promoting the reaction of **16** and **29** by $CdCO_3$ in boiling toluene for 24 h gave **30** in a promising yield of 44%, besides *ca.* 5% of the acetate **31**. However, these conditions were not satisfactory for the glycosidation of the diol **3**. The main product was a mixture of monoglycosides, obtained by (intramolecular?) migration of an Ac group to one of the hydroxyethyl substituents. Basic zinc carbonate ($[ZnCO_3]_2[Zn(OH)_2]_3$) was then investigated as Zn is in the same periodic group as Cd. Under otherwise identical condition, replacement of $CdCO_3$ by basic zinc carbonate in the glycosidation of **29** by **16** improved the yield of **30** to 71%. To the best of our knowledge, basic zinc carbonate has not yet been reported as a glycosidation promoter, although $ZnCO_3$ has been examined as a weak promoter [53], and some zinc salts have been shown to accelerate glycosidation [54][55].

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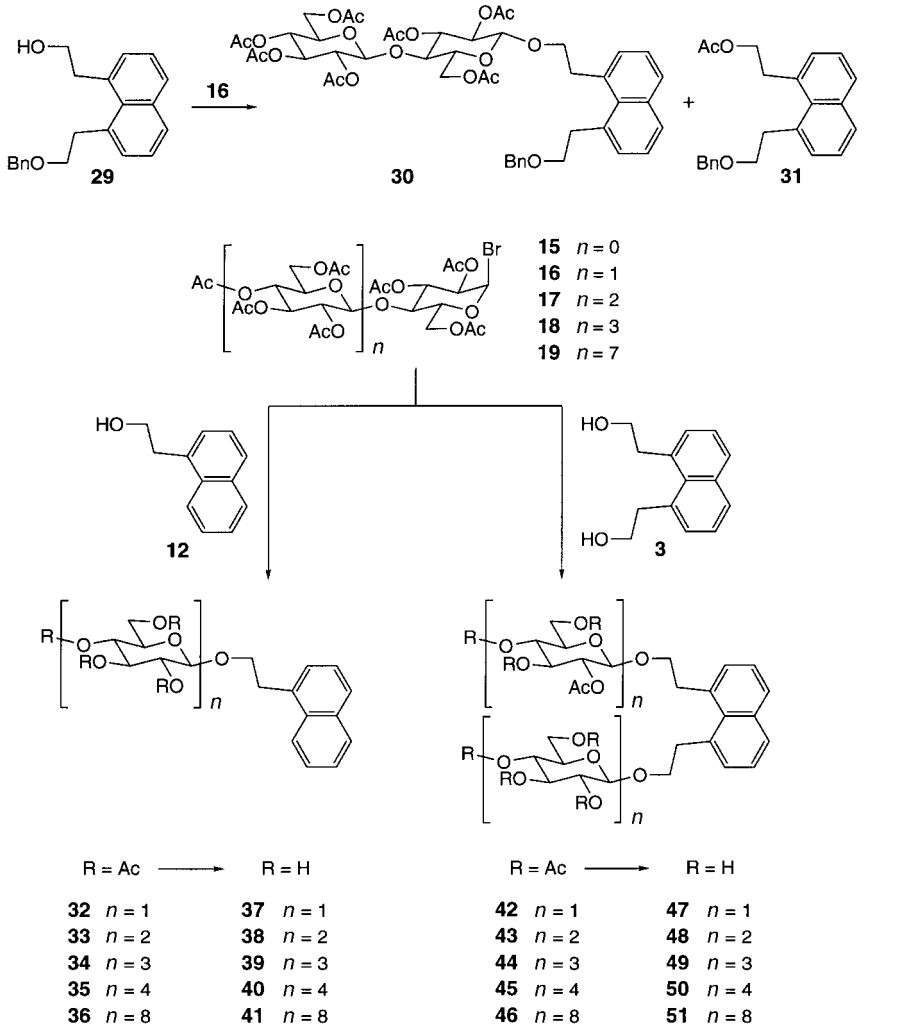
[7]) Ag_2CO_3 in Et_2O/benzene 1:1 led to *ca.* 20% conversion after 3 days at 23°, as estimated by TLC, while Ag_2O in Et_2O did not affect the starting material.

Scheme 3



The diethanol **3** did not react with acetylated cellobiosyl bromide **16** in the presence of basic zinc carbonate and powdered 3-Å molecular sieves in toluene at 23°, but afforded 74% of the expected diglycoside **43** at 110° (*Scheme 3*, *Table*). Similarly, the monoethanol **12** was transformed into the cellobioside **33** (82%). Both toluene and 1,2-dichloroethane were used as solvents in the reaction of **3** and **12** with the glucosyl bromide **15** with little difference in the yields of **32** and **42**, respectively. In the preparation of the bis(cellotetraoside) **45**, addition of 1,2-dichloroethane increased the solubility of the tetraosyl bromide **18**, improving the yield from 32 to 56% and shortening the reaction time from 24 h to 10 h as compared to the reaction in toluene only. The presence of molecular sieves hardly influenced the yield of this reaction. For the octaosides **36** and **46**, the presence of 1,2-dichloroethane again enhanced the

solubility of the glycosyl donors, but could not prevent a decrease of the yields to 32 and 16%, respectively. This indicates the limits of the scope of this glycosidation. While a weak excess of the glycosyl donor (1.2–1.4 equiv.) proved ideal in the glycosylation of the monoethanol **12**, a somewhat larger excess (2.7–4 equiv.) was required for the glycosylation of the diethanol **3**. Initially, we used 2 equiv. of basic zinc carbonate per OH of the donor. This amount could be lowered to 0.5 equiv. without significantly affecting the yield. At 110°, the glycosidations were complete within *ca.* 5 to 8 h. Prolonged reaction times did not lead to larger amounts of side products.

Table. *Glycosylation of the Monoethanol* **12** *and the Diethanol* **3** *in the Presence of 3-Å Molecular Sieves at 110° for 5–20 h*

Acceptor	Donor [equiv.]	Basic zinc carbonate [equiv.]	Solvent	Product (yield)
12	**15** (1.4)	2	toluene	**32** (70%)
12	**16** (1.4)	0.75	toluene	**33** (82%)
12	**17** (1.2)	1.2	$(CH_2Cl)_2$	**34** (67%)
12	**18** (1.3)	0.5	toluene	**35** (73%
12	**19** (0.9)	0.6	toluene/$(CH_2Cl)_2$ 6 : 5	**36** (32%)
3	**15** (3)	2	$(CH_2Cl)_2$	**42** (77%)
3	**16** (4)	1.8	toluene	**43** (74%)
3	**17** (2.7)	1.3	$(CH_2Cl)_2$	**44** (59%)
3	**18** (3.6)	2	toluene/$(CH_2Cl)_2$ 10 : 1	**45** (56%)
3	**19** (3.2)	1.6	toluene/$(CH_2Cl)_2$ 4 : 1	**46** (16%)

The mono- to tetraosides **32**–**35**, **42**, and **43** were purified by flash chromatography and the octaoside **36** by preparative HPLC. Chromatographic separation of **44**–**46** from the corresponding hemiacetals obtained by hydrolysis of the glycosyl bromides was difficult. In these cases, the crude product was acetylated with Ac_2O/pyridine to facilitate the isolation of the glycosides. Flash chromatography and preparative HPLC yielded pure **44**–**46**.

Deacetylation of the mono- and disaccharides **32**, **33**, **42**, and **43** with 1–2.85 equiv. of NaOMe in MeOH gave the deprotected glycosides **37**, **38**, **47**, and **48**, respectively, in excellent yields (> 93%). The poor solubility in MeOH of partially deprotected intermediates derived from the higher cellooligosaccharides **34**–**36** and **44**–**46** prevented a complete deprotection. The cellooligosaccharides **34**–**36**, **44**, and **45** were completely deprotected in the presence of 1–5.7 equiv. of NaOH in H_2O. The poor solubility of the partially deprotected intermediates derived from the dioctaoside **46** in H_2O required larger amounts of base (54 equiv. of NaOH were used), and yielded only 65% of **51**. The alcohols **37**–**40** and **47**–**50** were isolated and purified by reversed-phase HPLC. The octaosides **41** and **51** proved insoluble in H_2O, and were not purified any further. The saccharides **37**–**41** and **47**–**51** are colourless crystalline solids. As expected, their melting points increase with increasing molecular weight, **39** and **40** melting with decomposition at 249–255 and 290°, respectively, and **41**, **49**, and **50** at > 300°. With the exception of the octaosides, the R_f values of the single-stranded glycosides are smaller than the R_f values of the corresponding double-stranded glycosides.

$J(1,2) = 7.6–8.1$ Hz in the ^{1}H-NMR and the *d* for C(1) at 100.4–100.9 ppm of the acetates and at 102.1–102.7 ppm of the alcohols in the ^{13}C-NMR spectra of **32**–**51**

evidence the β-D-configuration of the glycosidic centers. A detailed discussion of the NMR spectra of **32**–**51** is the topic of a forthcoming paper [56].

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Experimental Part

General. See [20]. Basic zinc carbonate ($[ZnCO_3]_2[Zn(OH)_2]_3$; powder from *Fluka*) and *Lewis* acids such as AgOTf, $CdCO_3$, $HgCl_2$, $Hg(CN)_2$, $BF_3 \cdot OEt_2$ were used directly without further purification. HPLC: *Knauer Spherisorb SW* (5 µm, 250 × 20 mm), hexane/CH_2Cl_2/AcOEt or hexane/AcOEt; reversed phase: *Merck Lichrosorb RP-18* (7 µm, 250 × 25 mm), MeOH/H_2O *ca.* 1 : 1; *CN* phase: *Macherey-Nagel Nucleosil 5CN* (5 µm, 250 × 21 mm); detection by UV at 254 nm. NMR Spectra: *Varian-XL 300* (^{1}H, 300 MHz; ^{13}C, 75 MHz) or *Bruker-AMX 400* or *500*; chemical shifts in ppm, coupling constants *J* in Hz; in ambiguous cases, ^{1}H-assignments by selective homonuclear decoupling experiments and 2D experiments; locants with Roman-numeral superscripts refer to monosaccharide units, I being assigned to the unit(s) next to the naphthalene moiety. MS: *VG-Tribrid* (CI (NH_3) at 15 eV) or *VG-ZAB2-SEQ* spectrometer (FAB, bombardement with 35-keV Cs-atoms), or *Bruker-Reflex-TM* (MALDI) apparatus at 20–21.5 kV; for MALDI-MS, the sample was dissolved in DMSO or toluene and mixed with the same volume of 0.1M α-cyano-4-hydroxycinnamic acid in CF_3COOH/H_2O/MeCN 0.1 : 33.3 : 66.6 (DMSO) or in MeCN/EtOH/H_2O 50 : 45 : 5 (toluene).

Naphthalene-1,8-dimethanol (**2**). Prepared according to [21] from naphthalene-1,8-dicarboxylic acid anhydride in 66% yield. White needles. R_f (CH_2Cl_2/MeOH 9 : 1) 0.65. M.p. 156° ([21]: 160–161°). ^{1}H-NMR (300 MHz, (D_8)THF): 7.77 (*dd*, *J* = 1.3, 8.2, H–C(4)); 7.59 (br. *d*, *J* = 7.1, H–C(2)); 7.37 (*dd*, *J* = 7.1, 8.2, H–C(3)); 5.18 (*d*, *J* = 5.9, CH_2); 4.40 (*t*, *J* = 5.9, OH).

Naphthalene-1,8-diethanol (**3**). Prepared according to [22]. A suspension of $NaBH_4$ (2.9 g, 76 mmol) and 2-methylbut-2-ene (21.4 ml, 202 mmol) in THF (150 ml) was treated with $BF_3 \cdot OEt_2$ (12.8 ml, 100 mmol) at 0°, stirred at r.t. for 1.5 h, cooled to 0°, treated with 1,8-divinylnaphthalene (5.662 g, 31.4 mmol; prepared from **2** *via* 1,8-bis(bromomethyl)naphthalene [40]), and stirred at 0° for 2 h and at r.t. overnight. The soln. was cooled to 0°, treated with 20% aq. NaOH soln. (120 ml) and 30% H_2O_2 soln. (120 ml), and kept at 35° for 1 h. Workup (Et_2O), FC (hexane/acetone 7 : 3 → 1 : 1), and recrystallization in benzene gave **3** (5.56 g, 81%). White needles. R_f (hexane/AcOEt 2 : 8) 0.15. M.p. 112°. IR (CH_2Cl_2): 3610*m*, 3404*m* (br.), 3054*m*, 2952*m*, 2884*m*, 1936*w*, 1598*w*, 1579*w*, 1479*w*, 1446*w*, 1421*w*, 1377*m*, 1345*w*, 1272*s*, 1170*s*, 1266*m*, 1035*s*, 824*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79–7.42 (*m*, 2 arom. H); 7.38–7.34 (*m*, 1 arom. H); 3.92 (br. *q*, *J* ≈ 7.5, addn. of D_2O → *t*, *J* = 7.2, $ArCH_2CH_2$); 3.49 (*t*, *J* = 7.2, $ArCH_2$); 1.72 (br. *s*, exchange with D_2O, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 136.11 (*s*, C(4a)); 134.11 (*s*, C(1)); 131.49 (*s*, C(8a)); 130.71, 129.32 (2*d*, C(2), C(4)); 125.09 (*d*, C(3)); 64.46 (*t*, $ArCH_2CH_2$); 40.14 (*t*, $ArCH_2$). CI-MS: 217 (25, $[M+1]^+$), 199 (100, $[M-OH]^+$).

X-Ray Crystal-Structure Analysis of **3** (CCDC-101541). Crystals were obtained from CH_2Cl_2 by slow evaporation. $C_{14}H_{16}O_2$ (216.27); monoclinic *Ia*; *a* = 7.525(3) Å, *b* = 22.580(6) Å, *c* = 7.530(4) Å; β = 111.18(4)°, *V* = 1193.0 Å^3; D_x = 1.204 Mg/m^3; *Z* = 4. Intensities were measured in the ω-scan mode on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, MoK_α, λ 0.71073 Å) at 293 K, Θ range 1.8–24.93°. Of the 1310 total collected reflections, 1157 unique reflections were observed. *R* = 0.0362, R_w = 0.0926. The structure was refined with the full-matrix least-squares on F^2 method.

Coupling of **5** *with* **6**. A suspension of **5** [27] (55 mg, 0.1 mmol), **6** [26] (19 mg, 0.05 mmol), $[Pd(PPh_3)_4]$ (2 mg), and CuI (1 mg) in piperidine (2 ml) was stirred at r.t. for 30 h. After evaporation, the residue was dissolved in AcOEt and worked up. FC (hexane/AcOEt 15 : 1 → 10 : 1) and HPLC (hexane/CH_2Cl_2/AcOEt 35 : 10 : 3) gave 3,7-anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-1-*C*-(8-iodonaphthalen-1-yl)-D-*glycero*-D-gulo-*oct-1-ynitol* (4 mg, 5%), **7** (24 mg, 39%), and two other unidentified fractions (12.6 and 11.5 mg). Compound **7** decomposed at r.t. within several days.

3,7-Anhydro-4,5,6,8-tetra-O-*benzyl-1,2-dideoxy-1*-C-*(8-iodonaphthalen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol:* Solid. R_f (hexane/CH_2Cl_2/AcOEt 7 : 2 : 1) 0.44. M.p. 88–89°. $[\alpha]_D^{25} = -11.3$ (*c* = 0.37, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3065*w*, 3007*m*, 2914*w*, 2869*w*, 1951*w*, 1878*w*, 1811*w*, 1603*w*, 1496*w*, 1454*m*, 1363*m*, 1292*w*, 1130*m*, 1092*s*, 1065*s*, 1028*m*, 997*w*, 951*w*, 866*w*. ^{1}H-NMR (300 MHz, C_6D_6): 8.07 (*dd*, *J* = 1.2, 7.3), 7.70 (*dd*, *J* = 1.3, 7.2), 6.85 (*dd*, *J* = 7.3, 8.2), 6.52 (*dd*, *J* = 7.6, 7.9) (4 arom. H); 7.41–6.99 (*m*, 22 arom. H); 5.26 (*d*, *J* = 11.0), 4.98 (*d*, *J* = 11.2), 4.92 (*d*, *J* = 11.2), 4.91 (*d*, *J* = 11.4), 4.87 (*d*, *J* = 11.3), 4.67 (*d*, *J* = 11.2), 4.58 (*d*, *J* = 12.0) (7 PhC*H*); 4.45 (*d*, *J* = 9.6, H–C(3^1)); 4.43 (*d*, *J* = 12.2, PhC*H*); 3.98 (*t*, *J* = 9.2, H–C(6^1)); 3.91 (*t*, *J* = 9.5, H–C(5^1)); 3.76

(*dd*, J = 3.5, 11.2, H–C(8^{I})); 3.70 (br. *d*, J = 11.5, H′–C(8^{I})); 3.69 (*t*, $J \approx$ 9.0, H–C(4^{I})); 3.39 (*ddd*, J = 1.8, 3.8, 9.8, H–C(7^{I})). ^{13}C-NMR (75 MHz, $CDCl_3$): 142.61 (*d*, C(7)); 138.62 (*s*); 138.15 (2*s*); 138.02 (*s*); 136.60 (*d*, C(2)); 134.84, 132.23 (2*s*, C(4a), C(8a)); 130.94, 130.15 (2*d*, C(4), C(5)); 128.48–127.40 (several *d*); 127.17, 125.38 (2*d*, C(3), C(6)); 121.90 (*s*, C(1)); 97.98 (*s*, C(8)); 93.02 (*s*, C(2^{I})); 86.28 (*d*, C(5^{I})); 85.47 (*s*, C(1^{I})); 81.88 (*d*, C(4^{I})); 79.26 (*d*, C(6^{I})); 77.82 (*d*, C(7^{I})); 75.85, 75.54, 75.20, 73.67 (4*t*, 4 Ph*C*H$_2$); 71.34 (*d*, C(3^{I})); 68.87 (*t*, C(8^{I})). CI-MS: 818 (1, $[M+NH_4]^+$), 800 (0.2, M^+), 709 (1), 674 (1), 583 (1), 408 (1), 181 (8), 91 (100).

*1,1′-(Naphthalene-1,8-diyl)bis[3,7-anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-*D*-glycero-*D*-gulo-oct-1-ynitol]* (**7**): Solid. R_f (hexane/CH_2Cl_2/AcOEt 7:2:1) 0.38. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.84 (*dd*, J = 1.0, 7.2), 7.80 (*dd*, J = 1.1, 7.2), 7.43 (*dd*, J = 7.4, 8.0) (3 arom. H); 7.34–7.08 (*m*, 20 arom. H); 5.22 (*d*, J = 10.9), 4.93 (*d*, J = 11.0), 4.85 (*d*, J = 10.9), 4.83 (*d*, J = 9.7), 4.80 (*d*, J = 10.9), 4.65 (*d*, J = 9.8), 4.53 (*d*, J = 10.1), 4.49 (*d*, J = 10.8) (8 PhC*H*); 4.54 (*d*, $J \approx$ 9.0, H–C(3^{I})); 3.93 (*t*, J = 9.1 with virtual coupling, H–C(4^{I})); 3.74–3.63 (*m*, H–C(5^{I}), H–C(6^{I}), 2 H–C(8^{I})); 3.54–3.47 (*m*, H–C(7^{I})). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.66, 138.30, 138.20, 138.07 (4*s*); 135.52 (*d*, C(2)); 133.95, 131.89 (2*s*, C(4a), C(8a)); 130.10 (*d*, C(4)); 128.50–127.54 (several *d*); 125.51 (*d*, C(3)); 121.03 (*s*, C(1)); 93.83 (*s*, C(2^{I})); 86.37 (*d*, C(5^{I})); 86.00 (*s*, C(1^{I})); 82.17 (*d*, C(4^{I})); 78.94 (*d*, C(6^{I})); 78.20 (*d*, C(7^{I})); 75.78, 75.42, 75.05, 73.33 (4*t*, 4 Ph*C*H$_2$); 70.74 (*d*, C(3^{I})); 68.96 (*t*, C(8^{I})). FAB-MS: 1222 (0.2), 1221 (0.1), 1220 (0.1, M^+), 1113 (0.2, $[M-Bn]^+$), 181 (23), 91 (100).

*Bis[3,4,6-tri-*O*-acetyl-α-*D*-glucopyranose] (*S,S*)-1,2:1′,2′-{[(Naphthalene-1,8-diyl)bis(methylene)] Diorthoacetate}* (**10**). A suspension of **2** (196 mg, 1.04 mmol), **8** [28] (1.031 g, 2.09 mmol), and 3-Å molecular sieves (1.5 g) in THF (30 ml) was stirred at r.t. for 1 h, cooled to −60°, treated with $BF_3 \cdot OEt_2$ (0.2 ml, 1.6 mmol), kept at −30° for 2 h, and treated with Et_3N (0.3 ml). The mixture was filtered through *Celite* and the residue washed with AcOEt. The combined org. layers were washed with brine. Workup and FC (hexane/AcOEt 1:1) gave **10** (779 mg, 87%). Solid. R_f (hexane/AcOEt 1:1) 0.23. M.p. 69–71°. $[\alpha]_D^{25} = +13.1$ (c = 0.93, $CHCl_3$). IR ($CHCl_3$): 2957*w*, 1746*s*, 1389*m*, 1370*m*, 1291*w*, 1226*s*, 1144*m*, 1102*m*, 1043*s*, 978*m*, 925*m*, 816*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.84 (*dd*, J = 1.2, 8.4), 7.59 (*dd*, J = 1.4, 6.9), 7.44 (*dd*, J = 7.2, 8.1) (3 arom. H); 5.63 (*d*, J = 5.3, H–C(1^{I})); 5.20 (*t*, J = 2.8, irrad. at 1.83 → NOE of 0.8%, H–C(3^{I})); 5.15 (*d*, J = 11.5), 5.09 (*d*, J = 11.5, irrad. at 1.83 → NOE of 1.3%, ArC*H*$_2$); 4.90 (*ddd*, J = 0.8, 2.8, 9.3, H–C(4^{I})); 4.24 (*ddd*, J = 0.7, 2.8, 5.3, H–C(2^{I})); 4.22–4.19 (*m*, 2 H–C(6^{I})); 3.96 (*ddd*, J = 3.4, 4.7, 9.6, irrad. at 1.83 → NOE of 2.2%, H–C(5^{I})); 2.10, 2.09, 2.07 (3*s*, 3 Ac); 1.83 (*s*, $MeCO_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.05, 170.01, 169.46 (3*s*, 3 C=O); 135.78 (*s*, C(4a)); 133.32 (*s*, C(1)); 131.20 (*s*, C(8a)); 131.07, 130.75 (2*d*, C(2), C(4)); 125.49 (*d*, C(3)); 121.86 (*s*, O_3C); 97.26 (*d*, C(1^{I})); 73.51 (*d*, C(2^{I})); 70.26 (*d*, C(3^{I})); 68.28 (*d*, C(4^{I})); 67.20 (*d*, C(5^{I})); 66.37 (*t*, ArC*H*$_2$); 63.14 (*t*, C(6^{I})); 21.69, 20.86 (2*q*, 2 Me); 20.80 (*q*, 2 Me). CI-MS: 866 (0.3, $[M+NH_4]^+$), 331 (84), 169 (100). Anal. calc. for $C_{40}H_{48}O_{20}$ (848.81): C 56.68, H 5.70; found: C 56.56, H 5.79.

*Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-α-*D*-glucopyranose] (*S,S*)-1,2:1′,2′-{[(Naphthalene-1,8-diyl)bis(methylene)] Diorthoacetate}* (**11**). A suspension of **2** (130 mg, 0.69 mmol), **9** [29][30] (1.078 g, 1.38 mmol), and 3-Å molecular sieves (500 mg) in THF (15 ml) was stirred at r.t. for 1 h, cooled to −78°, treated with $BF_3 \cdot OEt_2$ (69 µl, 0.55 mmol), slowly warmed to −20°, kept for 4 h, and treated with Et_3N (0.05 ml). Workup, as for **10**, and FC (hexane/AcOEt 3:7) gave **11** (870 mg, 88%). Solid. R_f (hexane/AcOEt 3:7) 0.48. $[\alpha]_D^{25} = -10.8$ (c = 0.68, $CHCl_3$). M.p. 98°. IR (CH_2Cl_2): 3056*w*, 2945*w*, 1757*s*, 1602*w*, 1422*w*, 1370*m*, 1229*s*, 1169*m*, 1120*m*, 1040*s*, 907*w*, 816*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.83 (*dd*, J = 1.3, 8.3), 7.60 (*dd*, J = 1.3, 7.1), 7.44 (*dd*, J = 7.1, 8.1) (3 arom. H); 5.54 (*d*, J = 5.2, irrad. at 4.20 → *s*, H–C(1^{I})); 5.53 (*dd*, J = 1.6, 2.8, H–C(3^{I})); 5.20 (*t*, J = 9.4, H–C(3^{II})); 5.16 (*d*, J = 12.7, ArC*H*); 5.13 (*t*, J = 9.6, irrad. at 3.77 → *d*, J = 9.5, H–C(4^{II})); 5.11 (*d*, J = 12.3, ArC*H*); 5.01 (*dd*, J = 8.2, 9.4, irrad. at 4.68 → *d*, J = 9.4, H–C(2^{II})); 4.68 (*d*, J = 8.1, H–C(1^{II})); 4.28 (*dd*, J = 4.6, 12.3, irrad. at 3.77 → *d*, J = 12.3, H–C(6^{II})); 4.25 (*dd*, J = 2.2, 12.1, irrad. at 3.85 → *d*, J = 12.1, H–C(6^{I})); 4.21 (*ddd*, J = 1.1, 2.8, 5.2, H–C(2^{I})); 4.15 (*dd*, J = 2.5, 12.2, irrad. at 3.77 → *d*, J = 12.1, H′–C(6^{II})); 4.10 (*dd*, J = 6.0, 12.0, irrad. at 3.85 → *d*, J = 12.1, H′–C(6^{I})); 3.85 (*ddd*, J = 2.2, 5.5, 9.5, irrad. at 3.63 → change of signal, H–C(5^{I})); 3.77 (*ddd*, J = 2.7, 4.4, 9.9, H–C(5^{II})); 3.63 (br. *d*, J = 9.5, H–C(4^{I})); 2.11, 2.09, 2.05, 2.04, 2.02, 2.00 (6*s*, 6 Ac); 1.83 (*s*, Me). ^{13}C-NMR (125 MHz, $CDCl_3$; assignment based on ^{1}H,^{13}C-COSY): 170.47 (*s*, 2 C=O); 170.09, 169.22, 169.19, 168.93 (4*s*, 4 C=O); 135.36 (*s*, C(4a)); 133.11 (*s*, C(1)); 130.89 (*s*, C(8a)); 130.69, 130.25 (2*d*, C(2), C(4)); 125.07 (*d*, C(3)); 121.68 (*s*, O_3C); 101.83 (*d*, C(1^{II})); 96.80 (*d*, C(1^{I})); 77.42 (*d*, C(4^{I})); 72.80 (*d*, C(3^{II})); 72.66 (*d*, C(2^{I})); 71.87 (*d*, C(5^{II})); 71.22 (*d*, C(2^{II})); 69.59 (*d*, C(3^{I})); 68.04 (*d*, C(4^{II})); 66.98 (*d*, C(5^{I})); 66.22 (*t*, ArC*H*$_2$); 63.27 (*t*, C(6^{I})); 61.73 (*t*, C(6^{II})); 21.05 (*q*, Me); 20.66 (*q*, 2 Me); 20.57 (*q*, Me); 20.42 (*q*, 2 Me); 20.37 (*q*, *Me*CO_3). MALDI-MS: 1147 ($[M+Na]^+$). Anal. calc. for $C_{64}H_{80}O_{36}$ (1425.30): C 53.93, H 5.66; found: C 53.86, H 5.81.

1-(2-Methoxyethyl)naphthalene [38][39] (**13**). At 0°, a soln. of naphthalene-1-ethanol (**12**; *Aldrich*; 52 mg, 0.25 mmol) in DMF (2.5 ml) was treated with NaH (55–65% in oil, 29 mg) and MeI (0.04 ml, 0.65 mmol), allowed to warm to r.t., and stirred for 12 h. After evaporation under high vacuum and workup, FC (hexane/

AcOEt 11:1) gave **13** (53 mg, 90%). Oil. R_f (hexane/AcOEt 11:1) 0.43. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.06 (br. *d*, *J* = 8.2), 7.86 (br. *d*, *J* = 7.1), 7.75 (br. *dd*, *J* = 2.2, 7.0) (3 arom. H); 7.56–7.36 (*m*, 4 arom. H); 3.74 (*t*, *J* = 7.2, OCH_2); 3.40 (*s*, MeO); 3.38 (*t*, *J* = 7.2, Ar*CH*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): 134.37 (*s*, C(1)); 133.92 (*s*, C(4a)); 131.70 (*s*, C(8a)); 128.40, 126.82, 126.66, 126.37 (4*d*, C(2), C(3), C(4), C(5)); 125.51, 125.13 (2*d*, C(6), C(7)); 123.23 (*d*, C(8)); 72.59 (*t*, OCH_2); 59.96 (*q*, MeO); 32.82 (*t*, Ar*CH*$_2$).

1,8-Bis(2-methoxyethyl)naphthalene (**14**). As described for **13**, with **3** (61 mg, 0.5 mmol), NaH (55–65% in oil, 29 mg), and MeI (0.04 ml, 0.65 mmol): **14** (62 mg, 92%). Oil. R_f (hexane/AcOEt 11:1) 0.15. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.73–7.68 (*m*, 1 arom. H); 7.34–7.31 (*m*, 2 arom. H); 3.57 (*t*, *J* = 7.2, OCH_2); 3.45 (*t*, *J* = 7.0, Ar*CH*$_2$); 3.32 (*s*, MeO). ^{13}C-NMR (50 MHz, $CDCl_3$): 135.52 (*s*, C(4a)); 134.25 (*s*, C(1)); 131.08 (*s*, C(8a)); 129.93, 128.62 (2*d*, C(2), C(4)); 124.53 (*d*, C(3)); 73.90 (*t*, OCH_2); 58.28 (*q*, MeO); 36.76 (*t*, Ar*CH*$_2$).

Allyl 2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**21**). At −60°, a suspension of **20** [49][50] (4.61 g, 5.0 mmol), AgOTf (2.57 g, 10.0 mmol), and 3-Å molecular sieves (7.5 g) in 1,2-dichloroethane (100 ml) was treated dropwise with a soln. of **16** [43] (4.54 g, 6.5 mmol) in 1,2-dichloroethane (70 ml) within 0.5 h, kept at −30° for 3 h, treated with Et_3N (1.7 ml, 12 mmol), and stirred for 10 min. The mixture was filtered through *Celite*, and the residue washed thoroughly with CH_2Cl_2. The combined org. layers were washed (aq. NH_4Cl soln. and H_2O) and dried ($MgSO_4$). FC (hexane/AcOEt 6:4) gave **21** (6.84 g, 89%). Solid. R_f (hexane/AcOEt 1:1) 0.52. M.p. 68.9°. $[\alpha]_D^{25} = -11.7$ (*c* = 0.85, $CHCl_3$). IR ($CHCl_3$): 3088*w*, 3085*w*, 3035*w*, 3007*w*, 2872*w*, 1951*w*, 1755*s*, 1496*w*, 1453*m*, 1366*m*, 1230*s*, 1201*s*, 1157*m*, 1062*s*, 908*w*, 804*w*, 711*m*, 677*w*, 598*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.36–7.13 (*m*, 30 arom. H); 5.94 (*dddd*, *J* = 17.3, 10.5, 6.5, 5.5, CH_2=*CH*); 5.32 (*dq*, *J* = 17.3, 1.7), 5.19 (*dq*, *J* = 10.5, 1.3) (*CH*$_2$=CH); 5.09 (*t*, *J* ≈ 9.1, H–C(3^{III})); 5.07 (*d*, *J* = 11.6, PhC*H*); 5.04 (*t*, *J* = 9.3, H–C(3^{IV})); 4.98 (*d*, *J* = 11.5, PhC*H*); 4.94 (*t*, *J* ≈ 9.3, H–C(4^{IV})); 4.91 (*dd*, *J* = 8.0, 9.1, H–C(2^{IV})); 4.87 (*d*, *J* = 10.9, PhC*H*); 4.80 (*dd*, *J* = 8.1, 9.6, H–C(2^{III})); 4.72 (*d*, *J* = 11.7), 4.68 (*d*, *J* = 10.9), 4.66 (*d*, *J* = 11.0), 4.65 (*d*, *J* = 11.6) (4 PhC*H*); 4.64 (*d*, *J* = 12.0, 2 PhC*H*); 4.56 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 8.0, H–C(1^{II})); 4.50 (*d*, *J* = 12.0, PhC*H*); 4.41–4.37 (*m*, 1 allyl. H); 4.40 (*d*, *J* = 7.8), 4.39 (*d*, *J* = 8.0), 4.38 (*d*, *J* = 7.7) (H–C(1^{I}), H–C(1^{III}), H–C(1^{IV})); 4.37 (*d*, *J* = 12.4, PhC*H*); 4.35 (*dd*, *J* = 4.1, 12.5, H–C(6^{III})); 4.24 (*d*, *J* = 12.1, PhC*H*); 4.21 (*dd*, *J* = 2.0, 12.0, H–C(6^{IV})); 4.13–4.09 (*m*, 1 allyl. H); 4.00 (*dd*, *J* = 2.2, 12.3, H′–C(6^{III})); 3.95 (*dd*, *J* = 9.3, 9.7, H–C(4^{II})); 3.90 (*dd*, *J* = 9.0, 9.7, H–C(4^{I})); 3.89 (*dd*, *J* = 4.0, 12.0, H′–C(6^{IV})); 3.79 (*dd*, *J* = 4.0, 10.9, H–C(6^{I})); 3.68 (*dd*, *J* = 2.1, 11.0, H′–C(6^{I})); 3.67 (*t*, *J* = 9.5, H–C(4^{III})); 3.61–3.52 (*m*, H–C(5^{III}), 2 H–C(6^{II})); 3.55 (*t*, *J* = 9.0, H–C(3^{I})); 3.43 (*dd*, *J* = 7.8, 9.1, H–C(2^{I})); 3.36 (*t*, *J* = 9.0, H–C(3^{II})); 3.30 (*ddd*, *J* = 2.0, 4.0, 10.0, H–C(5^{I})); 3.27 (*dd*, *J* = 7.9, 9.1, H–C(2^{II})); 3.08 (*ddd*, *J* = 1.8, 4.3, 10.0, H–C(5^{IV})); 3.02 (*ddd*, *J* = 1.6, 3.0, 9.8, H–C(5^{II})); 2.07, 2.01, 1.99, 1.98, 1.97, 1.92, 1.89 (7*s*, 7 Ac). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.49, 170.25, 170.20, 169.73, 169.42, 169.31, 168.99 (7*s*, 7 C=O); 139.41, 139.39, 138.54, 138.44, 138.22, 138.00 (6*s*); 134.14 (*d*, CH_2=*C*H); 128.55–127.03 (several *d*); 117.17 (*t*, *C*H$_2$=CH); 102.65 (*d*, C(1^{II})); 102.44 (*d*, C(1^{I})); 100.83 (*d*, C(1^{IV})); 99.73 (*d*, C(1^{III})); 82.95 (*d*, C(3^{I}), C(3^{II})); 81.93 (*d*, C(2^{II})); 81.71 (*d*, C(2^{I})); 76.95, 76.91 (2*d*, C(4^{I}), C(4^{II})); 76.22 (*d*, C(4^{III})); 74.97 (*t*, 3 PhC*H*$_2$); 74.88 (*d*, C(5^{I})); 74.74 (*t*, PhC*H*$_2$); 74.63 (*d*, C(5^{II})); 73.35, 73.19 (2*t*, 2 PhC*H*$_2$); 72.97 (*d*, C(5^{III})); 72.90 (*d*, C(3^{IV})); 72.33 (*d*, C(3^{III})); 72.09 (*d*, C(2^{III})); 71.91 (*d*, C(2^{IV})); 71.50 (*d*, C(5^{IV})); 70.23 (*t*, 1 allyl. C); 68.14 (*t*, C(6^{I})); 67.81 (*d*, C(4^{IV})); 67.69 (*t*, C(6^{II})); 61.86 (*t*, C(6^{III})); 61.54 (*t*, C(6^{IV}); 20.69, 20.66, 20.65 (3*q*, 3 Me); 20.54 (*q*, 3 Me); 18.44 (*q*, Me). MALDI-MS: 1563 ([*M* + Na]$^+$). Anal. calc. for $C_{83}H_{96}O_{28}$ (1541.65): C 64.67, H 6.28; found: C 64.85, H 6.55.

1^I,2^I,2^{II},2^{III},2^{IV},3^I,3^{II},3^{III},3^{IV},4^{IV},6^I,6^{II},6^{III},6^{IV}-Tetradeca-O-*acetyl-α-cellotetraose* [42][43][51][52]. (**22**). At r.t., a soln. of **21** (3.08 g, 2 mmol) in THF (30 ml) was treated with a soln. of reduced (H_2) bis(methyldiphenylphosphine)(cycloocta-1,5-diene)iridium(I) hexafluorophosphate (52 mg, 0.06 mmol) in THF (8 ml) and stirred for 2 h. After evaporation, the residue was dissolved in acetone/H_2O 10:1 (40 ml), treated with $HgCl_2$ (600 mg, 2.21 mmol) and HgO (320 mg, 1.48 mmol), and stirred for 10 h. After evaporation, the residue was dissolved in CH_2Cl_2, washed with sat. aq. KI soln. and H_2O, dried ($MgSO_4$), and evaporated. The crude deallylated product (3.10 g) was dissolved in Ac_2O (40 ml), stirred at r.t. for 1 h, cooled to 0°, slowly treated with $BF_3 \cdot OEt_2$ (4.5 ml), allowed to warm to r.t., and kept for 24 h. Workup, FC (hexane/AcOEt 1:1 → 1:2), and crystallization (hexane/AcOEt) gave **22** (1.72 g, 69%). White solid. R_f (hexane/AcOEt 3:7) 0.32. M.p. 232–234° ([51]: 230–234°). ^{1}H- and ^{13}C-NMR: see [52].

2^I,2^{II},2^{III},2^{IV},3^I,3^{II},3^{III},3^{IV},4^{IV},6^I,6^{II},6^{III},6^{IV}-Trideca-O-*acetyl-α-cellotetraosyl Bromide* [42][43] (**18**). At 0°, 4.1M HBr in AcOH (4.5 ml) was added to a soln. of **22** (4.43 g, 3.53 mmol) in AcOH/CH_2Cl_2 6:5 (22 ml). The resulting soln. was allowed to warm to r.t., stirred for 6 h, cooled to 0°, and neutralized with aq. $NaHCO_3$ soln. Workup and crystallization from hexane/AcOEt gave **18** (3.43 g, 76%). Solid. M.p. 176–178° (dec.; [42]: 182–183° (dec.)). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.50 (*d*, *J* = 4.1, H–C(1^{I})); 5.48 (*t*, *J* ≈ 9.7, H–C(3^{I})); 5.09 (*t*, *J* = 9.3), 5.08 (*t*, *J* = 9.0), 5.06 (*t*, *J* = 9.0) (H–C(3^{II-IV})); 5.02 (*t*, *J* = 9.1, H–C(4^{IV})); 4.87 (*dd*, *J* = 8.0, 8.7), 4.82

(*dd*, *J* = 7.8, 9.2), 4.80 (*dd*, *J* = 7.8, 9.3) (H–C($2^{II–IV}$)); 4.71 (*dd*, *J* = 4.0, 10.0, H–C(2^{I})); 4.48 (*d*, *J* = 7.8), 4.44 (*d*, *J* = 7.6), 4.42 (*d*, *J* = 7.7) (H–C($1^{II–IV}$)); 4.49 (*dd*, *J* = 3.2, 12.0), 4.38 (br. *d*, *J* = 12.7, 2 H), 4.33 (*dd*, *J* = 4.3, 12.7) (H–C($6^{I–IV}$)); 4.06 (*dd*, *J* = 5.4, 12.9), 4.00 (*dd*, *J* = 1.6, 12.5), 4.20–4.10 (*m*, 3 H) (H–C(5^{I}), H′–C($6^{I–IV}$)); 3.78 (*t*, *J* = 9.5), 3.74 (*t*, *J* = 9.0), 3.73 (*t*, *J* = 9.2) (H–C($4^{I–III}$)); 3.65–3.50 (*m*, H–C($5^{II–IV}$)); 2.12, 2.11, 2.10 (3*s*, 3 Ac); 2.06 (*s*, 2 Ac); 2.03, 2.00 (2*s*, 2 Ac); 1.99 (*s*, 2 Ac); 1.97, 1.96, 1.95, 1.94 (4*s*, 4 Ac). MALDI-MS: 1298 ($[M+Na]^+$).

*Allyl β-*D*-Glucopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**23**). A soln. of **21** (4.00 g, 2.6 mmol) in MeOH (40 ml) was treated at 0° with 5.78M NaOMe (0.32 ml, 1.85 mmol), warmed to r.t. and stirred for 2 h. Neutralization with *Amberlite IR-120* (H^+ form), filtration, and evaporation gave **23** (3.22 g, 99%). Solid. R_f (CH_2Cl_2/MeOH 8 : 2) 0.44. M.p. 80°. $[\alpha]_D^{25} = +10.5$ (*c* = 0.64, $CHCl_3$). IR (CH_2Cl_2): 3407*s* (br.), 3088*w*, 3032*m*, 2876*s*, 1954*w*, 1869*w*, 1812*w*, 1646*w*, 1605*w*, 1496*m*, 1454*s*, 1398*m*, 1361*s*, 1310*m*, 1203*m*, 1155*s*, 1077*s* (br.), 933*w*, 821*w*. ^{1}H-NMR (500 MHz, $CDCl_3$ + *ca.* 1% CD_3OD): 7.30–7.04 (*m*, 30 arom. H); 5.94 (*dddd*, *J* = 17.3, 10.5, 6.5, 5.5, CH_2=C*H*); 5.32 (*dq*, *J* = 17.2, 1.6), 5.19 (*dq*, *J* = 10.5, 1.4) (CH_2=CH); 5.00 (*d*, *J* = 11.7), 4.90 (*d*, *J* = 11.4), 4.87 (*d*, *J* = 10.9), 4.77 (*d*, *J* = 11.3), 4.72 (*d*, *J* = 11.3), 4.71 (*d*, *J* = 11.7), 4.67 (*d*, *J* = 10.9), 4.64 (*d*, *J* = 11.4), 4.55 (*d*, *J* = 12.1), 4.43 (*d*, *J* = 12.1) (10 PhC*H*); 4.40–4.36 (*m*, 2 PhC*H*, 1 allyl. H); 4.47 (*d*, *J* = 7.6, H–C(1^{II}), H–C(1^{III})); 4.40 (*d*, *J* = 7.6, H–C(1^{I})); 4.35 (*d*, *J* = 7.8, H–C(1^{IV})); 4.12 (*ddt*, *J* = 13.0, 6.0, 1.3, 1 allyl. H); 3.96 (*t*, *J* = 9.3, H–C(4^{II})); 3.90 (*t*, *J* = 9.3, H–C(4^{I})); 3.80–3.57 (*m*, H–C($6^{I–IV}$), H′–C($6^{I, III, IV}$)); 3.56–3.23 (*m*, H–C($2^{III, IV}$), H–C($3^{III, IV}$), H–C($4^{III, IV}$), H–C($5^{I, III, IV}$), H′–C(6^{II})); 3.54 (*t*, *J* = 9.0, H–C(3^{I})); 3.42 (*dd*, *J* = 8.0, 9.0, H–C(2^{I})); 3.34 (*t*, *J* = 9.0, H–C(3^{II})); 3.24 (*dd*, *J* = 8.0, 9.0, H–C(2^{II})); 3.06 (br. *d*, *J* ≈ 9.0, H–C(5^{II})). ^{13}C-NMR (125 MHz, $CDCl_3$ + *ca.* 1% CD_3OD): 139.19, 138.73, 138.51, 138.28, 138.15, 137.97 (6*s*); 134.15 (*d*, CH_2=*C*H); 128.39–127.19 (several *d*); 117.20 (*t*, *C*H_2=CH); 102.66 (*d*, C(1^{III}), C(1^{IV})); 102.43 (*d*, C(1^{II})); 102.38 (*d*, C(1^{I})); 83.27 (*d*, C(3^{II})); 82.72 (*d*, C(3^{I})); 82.26 (*d*, C(2^{II})); 81.76 (*d*, C(2^{I})); 77.83 (*d*, C(4^{III})); 77.00 (*d*, C(4^{I})); 76.63 (*d*, C(4^{II})); 76.04 (*d*, C(3^{IV})); 75.15 (*t*, Ph*C*H_2); 75.05 (*d*, C(5^{I})); 75.02 (*t*, 2 Ph*C*H_2); 75.00 (*d*, C(5^{III}), C(5^{IV})); 74.89 (*d*, C(3^{III})); 74.81 (*d*, C(5^{II})); 73.93 (*d*, C(2^{III})); 73.30 (*t*, Ph*C*H_2); 73.26 (*t*, 2 Ph*C*H_2); 72.42 (*d*, C(2^{IV})); 70.25 (*t*, 1 allyl. C); 69.06 (*d*, C(4^{IV})); 68.33 (*t*, C(6^{II})); 68.08 (*t*, C(6^{I})); 60.89 (*t*, C(6^{III}), C(6^{IV})). MALDI-MS: 1269 ($[M+Na]^+$). Anal. calc. for $C_{69}H_{82}O_{21}$ (1247.39): C 66.44, H 6.63; found: C 66.49, H 6.47.

*Allyl 4,6-*O*-Benzylidene-β-*D*-glucopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**24**). A suspension of **23** (3.150 g, 2.53 mmol) in PhCHO (20 ml) was treated at 0° with freshly fused $ZnCl_2$ (530 mg, 3.90 mmol), warmed to r.t., stirred for 5 h, and treated with sat. aq. $NaHCO_3$ soln. (5 ml). After evaporation under high vacuum, the residue was dissolved in AcOEt. Workup and FC (hexane/CH_2Cl_2/acetone 5 : 2 : 3) gave **24** (2.835 g, 84%). Solid. R_f (CH_2Cl_2/MeOH 19 : 1) 0.31. M.p. 172°. $[\alpha]_D^{25} = +7.9$ (*c* = 0.33, $CHCl_3$). IR ($CHCl_3$): 3581*m*, 3477*m* (br.), 3088*w*, 3066*w*, 3032*w*, 2874*m*, 1954*w*, 1881*w*, 1814*w*, 1605*w*, 1494*m*, 1453*m*, 1428*w*, 1361*m*, 1313*m*, 1203*m*, 1070*s* (br.), 1028*s*, 917*m*, 820*w*. ^{1}H-NMR (500 MHz, $CDCl_3$ + *ca.* 1% D_2O): 7.46–7.16 (*m*, 35 arom. H); 5.95 (*dddd*, *J* = 17.3, 10.5, 6.5, 5.5, CH_2=C*H*); 5.50 (*s*, PhC*H*); 5.32 (*dq*, *J* = 17.2, 1.6), 5.19 (*dq*, *J* = 10.5, 1.3) (CH_2=CH); 5.01 (*d*, *J* = 11.6), 4.89 (*d*, *J* = 11.6), 4.88 (*d*, *J* = 10.9), 4.85 (*d*, *J* = 11.5), 4.74 (*d*, *J* = 11.3), 4.73 (*d*, *J* = 11.6), 4.70 (*d*, *J* = 11.3), 4.69 (*d*, *J* = 11.3), 4.58 (*d*, *J* = 12.1) (9 PhC*H*); 4.52 (*d*, *J* = 7.8, H–C(1^{III})); 4.50 (*d*, *J* = 7.9, H–C(1^{IV})); 4.46 (*d*, *J* = 7.8, H–C(1^{II})); 4.45 (*d*, *J* = 12.1), 4.44 (*d*, *J* = 12.0) (2 PhC*H*); 4.41 (*d*, *J* = 7.7, H–C(1^{I})); 4.38 (*d*, *J* = 12.1, PhC*H*); 4.41–4.37 (*m*, 1 allyl. H); 4.31 (*dd*, *J* = 4.5, 10.4, H_{eq}–C(6^{IV})); 4.15 (*ddt*, *J* = 13.0, 6.0, 1.4, 1 allyl. H); 4.01 (*t*, *J* = 9.2, H–C(4^{II})); 3.95 (*t*, *J* = 9.4, H–C(4^{I})); 3.81 (*dd*, *J* = 5.0, 11.0, H–C(6^{I})); 3.75 (*t*, *J* ≈ 9.0, H–C(4^{IV})); 3.76–3.72 (*m*, 2 H–C(6^{III}), H–C(6^{II})); 3.69 (*dd*, *J* = 1.6, 11.0, H′–C(6^{I})); 3.63 (*dd*, *J* = 2.3, 11.4, H′–C(6^{II})); 3.56 (*t*, *J* = 9.0, H–C(3^{I})); 3.52 (*t*, *J* = 9.0, H–C(3^{IV})); 3.48 (*t*, *J* = 9.0, H–C(4^{III})); 3.53–3.47 (*m*, H–C(2^{IV}), H–C(5^{IV}), H_{ax}–C(6^{IV})); 3.45 (*dd*, *J* = 7.8, 9.1, H–C(2^{I})); 3.44 (*t*, *J* = 9.0, H–C(3^{III})); 3.35 (*dd*, *J* = 7.9, 9.1, H–C(2^{III})); 3.34 (*t*, *J* = 9.1, H–C(3^{II})); 3.32 (*ddd*, *J* = 1.7, 5.3, 10.0, H–C(5^{I})); 3.30 (br. *t*, *J* ≈ 9.0, H–C(2^{II})); 3.21 (*td*, *J* = 2.8, 9.7, H–C(5^{II})); 3.01 (*td*, *J* = 3.4, 9.0, H–C(5^{III})). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.22, 139.08, 138.53, 138.23, 138.20, 137.68, 136.70 (7*s*); 134.13 (*d*, CH_2=*C*H); 129.38–126.26 (several *d*); 117.21 (*t*, *C*H_2=CH); 103.90 (*d*, C(1^{IV})); 102.70 (*d*, C(1^{III})); 102.65 (*d*, C(1^{II})); 102.45 (*d*, C(1^{I})); 101.97 (*d*, Ph*C*H); 83.46 (*d*, C(3^{II})); 82.79 (*d*, C(3^{I})); 82.32 (*d*, C(2^{II})); 81.74 (*d*, C(2^{I})); 80.77 (*d*, C(4^{III})); 80.04 (*d*, C(4^{IV})); 77.40 (*d*, C(4^{II})); 76.50 (*d*, C(4^{I})); 75.04 (*t*, 2 Ph*C*H_2); 74.99 (*t*, 2 Ph*C*H_2); 74.85 (*d*, C(5^{I})); 74.50 (*d*, C(5^{III})); 74.36 (*d*, C(2^{IV})); 74.29 (*d*, C(5^{II})); 74.22 (*d*, C(3^{III})); 74.05 (*d*, C(2^{III})); 73.34 (*t*, Ph*C*H_2); 73.21 (*t*, *d*, Ph*C*H_2, C(3^{IV})); 70.24 (*t*, 1 allyl. C); 68.41 (*t*, C(6^{II})); 68.19 (*t*, C(6^{IV})); 68.13 (*t*, C(6^{I})); 66.67 (*d*, C(5^{IV})); 61.84 (*t*, C(6^{III})). MALDI-MS: 1357 ($[M+Na]^+$). Anal. calc. for $C_{76}H_{86}O_{21}$ (1335.50): C 68.35, H 6.49; found: C 68.16, H 6.48.

Allyl 2,3-Di-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**25**). At 0°, NaH (925 mg, 55–65% in oil; washed with dry Et_2O) was added to a soln. of **24** (2.835 g, 2.12 mmol) in dry DMF (30 ml). The resulting suspension was stirred for 1 h, treated with BnBr (1.9 ml, 15.9 mmol), and stirred for 4 h, cooled to −30°, treated with MeOH (10 ml), warmed to r.t., and stirred for 0.5 h. After evaporation under high vacuum ($T < 40°$), the residue was diluted with Et_2O. Workup and FC (hexane/AcOEt 8:2) gave **25** (3.54 g, 93%). Solid. R_f (hexane/AcOEt 7:3) 0.57. M.p. 46°. $[\alpha]_D^{25} = +6.1$ ($c = 0.90$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3066*w*, 3015*m*, 2872*m*, 1951*w*, 1810*w*, 1605*w*, 1497*w*, 1454*m*, 1397*w*, 1361*m*, 1310*w*, 1248*w*, 1089*s*, 1072*s*, 1228*m*, 1001*m*, 914*w*, 832*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.47–7.08 (*m*, 60 arom. H); 5.94 (*dddd*, $J = 17.2, 10.5, 6.5, 5.5$, $CH_2{=}CH$); 5.45 (*s*, PhC*H*); 5.32 (*dq*, $J = 17.2, 1.7$), 5.18 (*dq*, $J = 10.5, 1.3$) ($CH_2{=}CH$); 5.12 (*d*, $J = 11.5$), 5.08 (*d*, $J = 11.6$), 4.90 (*d*, $J = 10.7$), 4.87 (*d*, $J = 10.9$), 4.86 (*d*, $J = 11.4$), 4.74 (*d*, $J = 11.2$) (6 PhC*H*); 4.72 (*d*, $J = 11.1$, 2 PhC*H*); 4.71 (*d*, $J = 12.3$, 2 PhC*H*); 4.70 (*d*, $J = 11.4$, 3 PhC*H*); 4.69 (*d*, $J = 10.6$), 4.68 (*d*, $J = 11.0$), 4.65 (*d*, $J = 12.4$), 4.56 (*d*, $J = 12.1$) (4 PhC*H*); 4.49 (*d*, $J = 7.8$), 4.46 (*d*, $J = 7.7$, 2 H), 4.40 (*d*, $J = 7.8$) (H−C($1^{I–IV}$)); 4.39 (*d*, $J = 12.0$, 2 PhC*H*); 4.35 (*d*, $J = 12.1$, PhC*H*); 4.41–4.37 (*m*, 1 allyl. H); 4.27 (*d*, $J = 12.1$), 4.20 (*d*, $J = 12.1$) (2 PhC*H*); 4.14 (*dd*, $J = 5.0, 10.6$, H_{eq}−C(6^{IV})); 4.11 (*ddt*, $J = 13.0, 6.0, 1.4$, 1 allyl. H); 4.01 (*dd*, $J = 9.1, 9.7$), 3.99 (*dd*, $J = 9.1, 9.7$), 3.96 (*t*, $J = 9.3$) (H−C($4^{I–III}$)); 3.82 (*dd*, $J = 4.2, 11.0$, H−C(6^{I})); 3.74 (*dd*, $J = 3.7, 11.0$, H−C(6^{II})), 3.69 (*dd*, $J = 3.8, 11.4$, H−C(6^{III})); 3.67 (*dd*, $J = 2.0, 11.5$), 3.64 (*dd*, $J = 2.0, 11.5$), 3.62 (*dd*, $J = 1.5, 10.8$) (H′−C($6^{I–III}$)); 3.56 (*t*, $J = 9.0$), 3.55 (*t*, $J = 9.0$, H−C(3^{I}), H−C(4^{IV})); 3.51 (*t*, $J = 10.1$, H_{ax}−C(6^{IV})); 3.43 (*t*, $J = 9.0$, H−C(3^{II}), H−C(3^{III})); 3.41 (*t*, $J = 9.0$, H−C(3^{IV})); 3.36–3.29 (*m*, H−C($2^{I–IV}$), H−C(5^{I})); 3.15 (*ddd*, $J = 1.5, 3.4, 10.0$), 3.12 (*ddd*, $J = 1.7, 3.6, 10.0$) (H−C($5^{II, III}$)); 3.07 (*td*, $J \approx 9.5, 5.0$, H−C(5^{IV})). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.39, 139.38, 139.09, 138.62, 138.58, 138.53 (6*s*); 138.48 (2*s*); 138.39, 138.28, 138.21, 137.43 (4*s*); 134.16 (*d*, $CH_2{=}CH$); 128.93–126.04 (several *d*); 117.13 (*t*, $CH_2{=}CH$); 102.71 (*d*), 102.66 (*d*), 102.53 (2*d*, C($1^{I–IV}$)); 101.08 (*d*, PhCH); 83.32, 83.05, 82.95, 82.46 (4*d*, C($3^{I–IV}$)); 82.05 (2*d*), 81.71 (*d*), 81.69 (*d*) (C($2^{I–IV}$)); 81.03 (*d*, C(4^{IV})); 77.05, 76.85, 76.67 (3*d*, C($4^{I–III}$)); 75.41, 75.33, 75.17 (3*t*, 3 PhCH_2); 75.10, 75.07, 75.03 (3*d*, C($5^{I–III}$)); 74.97, 74.95 (2*t*, 2 PhCH_2); 73.16 (*t*, 2 PhCH_2); 72.94 (*t*, 2 PhCH_2); 72.90 (*t*, 2 PhCH_2); 70.21 (*t*, 1 allyl. C); 68.76, 68.19, 68.08, 67.96 (4*t*, C($6^{I–IV}$)); 65.69 (*d*, C(5^{IV})). MALDI-MS: 1807 ([M + Na]$^+$). Anal. calc. for $C_{111}H_{116}O_{21}$ (1786.12): C 74.64, H 6.55; found: C 74.70, H 6.66.

Allyl 2,3,6-Tri-O-*benzyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**26**). At 0°, 1M HCl in Et_2O (*ca.* 70 ml) was added dropwise to a suspension of **25** (3.58 g, 2.00 mmol), $NaBH_3CN$ (504 mg, 6.00 mmol), and 3-Å molecular sieves (1 g) in THF (50 ml). After complete conversion (TLC), the mixture was neutralized at 0° with solid Na_2CO_3 and filtered through a *Celite* column (AcOEt). The combined org. layers were washed with brine. Workup and FC (hexane/AcOEt 8:2) gave **26** (3.19 g, 92%). Oil. R_f (hexane/AcOEt 7:3) 0.46. $[\alpha]_D^{25} = +8.2$ ($c = 0.71$, $CHCl_3$). IR (CH_2Cl_2): 3596*w*, 3501*w*, 3090*w*, 3058*m*, 2868*m*, 1954*w*, 1875*w*, 1817*w*, 1605*w*, 1490*w*, 1448*m*, 1401*w*, 1359*m*, 1311*w*, 1206*w*, 1116*s*, 1090*s*, 1064*s*, 1027*m*, 990*w*, 916*w*, 826*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.05 (*m*, 60 arom. H); 5.94 (*dddd*, $J = 17.2, 10.5, 6.5, 5.5$, $CH_2{=}CH$); 5.32 (*dq*, $J = 17.3, 1.6$), 5.18 (*dq*, $J = 10.4, 1.3$) ($CH_2{=}CH$); 5.12 (*d*, $J = 11.6$), 5.08 (*d*, $J = 11.6$), 4.94 (*d*, $J = 11.0$), 4.87 (*d*, $J = 10.8$), 4.82 (*d*, $J = 11.3$), 4.76 (*d*, $J = 11.3$), 4.75 (*d*, $J = 11.1$), 4.73 (*d*, $J = 11.0$), 4.72 (*d*, $J = 11.0$) (9 PhC*H*); 4.70 (*d*, $J = 11.9$, 3 PhC*H*); 4.69 (*d*, $J = 11.6$), 4.67 (*d*, $J = 11.1$), 4.664 (*d*, $J = 11.2$), 4.660 (*d*, $J = 11.7$), 4.56 (*d*, $J = 12.1$) (5 PhC*H*); 4.46 (*d*, $J = 7.8$), 4.45 (*d*, $J = 7.6$), 4.40 (*d*, $J = 7.8$), 4.39 (*d*, $J = 7.7$) (H−C($1^{I–IV}$)); 4.42 (*d*, $J = 11.0$), 4.41 (*d*, $J = 12.0$), 4.38 (*d*, $J = 12.7$), 4.36 (*m*, $J = 11.9$), 4.35 (*d*, $J = 12.5$) (5 PhC*H*); 4.45–4.36 (*d*, 1 allyl. H); 4.25 (*d*, $J = 12.1$), 4.24 (*d*, $J = 12.1$) (2 PhC*H*); 4.11 (*ddt*, $J = 13.0, 6.0, 1.4$, 1 allyl. H); 4.00 (*t*, $J = 9.3$), 3.97 (*t*, $J = 9.3$), 3.96 (*t*, $J = 9.4$) (H−C($4^{I–III}$)); 3.82 (*dd*, $J = 4.2, 10.9$, H−C(6^{I})); 3.73 (*dd*, $J = 3.5, 11.0$, H−C(6^{II})); 3.70–3.58 (*m*, H′−C(6^{I}), H′−C(6^{II}), 2 H−C(6^{III})); 3.56 (br. *t*, $J = 9.0$, H−C(3^{I}), H−C(4^{IV})); 3.51 (*dd*, $J = 5.0, 10.1$, H−C(6^{IV})); 3.47 (*dd*, $J = 5.6, 10.1$, H′−C(6^{IV})); 3.43 (*t*, $J = 8.9$, H−C(3^{II}), H−C(3^{III})); 3.36 (*t*, $J = 9.0$, H−C(3^{IV})); 3.34–3.26 (*m*, H−C($2^{I–IV}$), H−C(5^{I})); 3.27 (*dt*, $J = 10.0, 5.3$, H−C(5^{IV})); 3.15–3.10 (*m*, H−C($5^{II, III}$)); 2.83 (*d*, $J = 1.8$, OH). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.42, 139.39, 139.24, 138.75, 138.62, 138.58, 138.50, 138.46, 138.41, 138.32, 138.29, 137.86 (12*s*); 134.16 (*d*, $CH_2{=}CH$); 128.40–127.02 (several *d*); 117.12 (*t*, $CH_2{=}CH$); 102.66, 102.55, 102.53, 102.36 (4*d*, C($1^{I–IV}$)); 84.25, 83.35, 83.09, 82.95 (4*d*, C($3^{I–IV}$)); 82.05 (2*d*), 82.01 (*d*), 81.69 (*d*) (C($2^{I–IV}$)); 77.05, 76.89, 76.44 (3*d*, C($4^{I–III}$)); 75.26, 75.13, 75.08 (3*t*, 3 PhCH_2); 75.06 (*d*), 75.04 (2*d*) (C($5^{I–III}$)); 75.02, 74.97, 74.91 (3*t*, 3 PhCH_2); 73.58 (*t*, 2 PhCH_2); 73.48 (*d*, C(4^{IV})); 73.16 (*t*, 2 PhCH_2); 73.00 (*t*, PhCH_2); 72.97 (*d*, C(5^{IV})); 72.89 (*t*, PhCH_2); 71.17 (*t*, C(6^{IV})); 70.21 (*t*, 1 allyl. C); 68.19 (*t*), 68.08 (2*t*) (C($6^{I–III}$)). MALDI-MS: 1809 ([M + Na]$^+$). Anal. calc. for $C_{111}H_{118}O_{21}$ (1788.14): C 74.56, H 6.65; found: C 74.36, H 6.51.

Allyl 2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*benzyl-*

*β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**27**). A suspension of **26** (2.967 g, 1.66 mmol), AgOTf (2.5 g, 3.32 mmol) and 3-Å molecular sieves in 1,2-dichloroethane (25 ml) was stirred for 1 h, cooled to −40°, treated dropwise with a soln. of **18** (2.78 g, 2.15 mmol) in 1,2-dichloroethane (30 ml) within 0.5 h, kept at −25 to −30° for 6 h, and neutralized with Et_3N (2.8 ml). After filtration through *Celite*, the filtrate was washed with aq. NH_4Cl soln. and H_2O and dried. FC (hexane/AcOEt 1:1) gave **27** (3.78 g, 76%). White solid. R_f (hexane/AcOEt 1:1) 0.22. M.p. 101°. $[\alpha]_D^{25} = -6.5$, ($c = 0.86$, $CHCl_3$). IR ($CHCl_3$): 3018*w*, 2871*w*, 1756*s*, 1496*w*, 1454*w*, 1366*m*, 1235*s*, 1156*w*, 1055*s*, 907*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.09 (*m*, 60 arom. H); 5.96 (br. *ddt*, $J \approx$ 16.5, 10.6, 5.6, CH_2=C*H*); 5.34 (*dq*, $J = 17.5, 1.6$), 5.10 (*dq*, $J = 10.3, 1.2$) (CH_2=CH); 5.17–2.95 (*m*, 82 H); 2.16, 2.14, 2.10, 2.05, 2.02, 2.019 (6*s*, 6 Ac); 2.010 (*s*, 2 Ac); 1.99, 1.97, 1.96, 1.92, 1.90 (5*s*, 5 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.84, 170.60 (2*s*, 2 C=O); 170.55 (*s*, 2 C=O); 170.51 (*s*, C=O); 170.08 (*s*, 2 C=O); 170.05 (*s*, C=O); 169.67 (*s*, 2 C=O); 169.64, 169.54, 169.45 (3*s*, 3 C=O); 139.71 (2*s*); 139.66 (2*s*); 138.89, 138.85 (2*s*); 138.71 (2*s*); 138.69 (*s*); 138.56 (2*s*); 138.35 (*s*); 134.44 (*d*, CH_2=*C*H); 128.76–127.27 (several *d*); 117.39 (*t*, *C*H_2=CH); 102.88 (*d*), 102.75 (2*d*), 102.62 (*d*) (C(1^{I-IV})); 101.03, 100.92, 100.77, 99.93 (4*d*, C(1^{V-VIII})); 83.56, 83.40, 83.12, 82.96 (4*d*, C(3^{I-IV})); 82.22 (2*d*), 82.02 (*d*), 81.86 (*d*, C(2^{I-IV})); 77.20, 77.17, 77.07, 76.86, 76.47, 76.31, 76.26 (7*d*, C(4^{I-VII})); 75.26, 75.19, 75.10, 74.74 (4*d*, C(5^{I-IV})); 73.04 (*d*), 72.95 (*d*), 72.82 (2*d*) (C(5^{V-VIII})); 72.76 (*d*), 72.48 (*d*), 72.20 (3*d*), 71.91 (2*d*), 71.73 (*d*) (C(3^{V-VIII}), C(2^{V-VIII})); 67.88 (*d*, C(4^{VIII})); 75.23 (*t*, 3 Ph*C*H_2); 75.30 (*t*, 3 Ph*C*H_2); 75.03, 74.90, 73.46 (3*t*, 3 Ph*C*H_2); 73.32 (*t*, 2 Ph*C*H_2); 73.03 (*t*, Ph*C*H_2); 70.36 (*t*, 1 allyl. C); 68.24, 68.21, 67.93, 67.88 (4*t*, C(6^{I-IV})); 62.22 (2*t*), 61.91 (*t*), 61.64 (*t*) (C(6^{V-VIII})); 20.85 (*q*, 3 Me), 20.73 (*q*, 4 Me), 20.60 (*q*, 6 Me). MALDI-MS: 3004 ($[M + Na]^+$). Anal. calc. for $C_{161}H_{184}O_{54}$ (2983.19): C 64.82, H 6.22; found: C 64.80, H 6.32.

*1^I,2^I,2^{II},2^{III},2^{IV},2^V,2^{VI},2^{VII},2^{VIII},3^I,3^{II},3^{III},3^{IV},3^V,3^{VI},3^{VII},3^{VIII},4^{VIII},6^I,6^{II},6^{III},6^{IV},6^V,6^{VI},6^{VII},6^{VIII}-Hexacosa-*O*-acetyl-α/β-cellooctaose* [52][48] (**28**). A soln. of bis(methyldiphenylphosphine)(cycloocta-1,5-diene)iridium(I) hexafluorophosphate in THF (5 ml) was degassed and stirred under H_2 for 0.5 h (red → orange soln.), flushed with Ar, and transferred to a stirred soln. of **27** (3.653 g, 1.22 mmol) in THF (15 ml). The mixture was stirred for 2 h and evaporated, the residue dissolved in acetone/H_2O 10:1 (20 ml), and the soln. treated with $HgCl_2$ (365 mg, 1.35 mmol) and HgO (198 mg, 0.92 mmol), stirred for 12 h, and evaporated. The residue was dissolved in CH_2Cl_2 and the soln. washed with sat. aq. KI and aq. NaSCN soln. and evaporated. FC (hexane/AcOEt 1:1) gave the deallylated product (3.40 g, 94%; R_f (hexane/AcOEt 4:6) 0.40). MALDI-MS: 2962 ($[M + Na - 1]^+$), 2963 ($[M + Na]^+$), 2964 ($[M + Na + 1]^+$), 2965 ($[M + Na + 2]^+$)).

A suspension of the deallylated product (3.086 g, 1.05 mmol) in AcOEt/MeOH/H_2O 5:5:1 (55 ml) was stirred in the presence of 30% Pd/C (500 mg) at 6 bar of H_2 and r.t. for 3 days. After filtration through *Celite*, the filter cake was washed with pyridine. The combined filtrate and washings were evaporated and co-evaporated with pyridine. The residue was dissolved in pyridine/Ac_2O 2:1 (15 ml) and the soln. stirred for 12 h. Evaporation, coevaporation with toluene, and FC (hexane/AcOEt 1:1 → 1:4) gave **28** (α-D/β-D 1:1; 2.19 g, 87%). White solid. M.p. 128–255° (dec.; [52]: 258–262° for α-D-anomer). R_f (hexane/AcOEt 1:4) 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.19 (*d*, $J = 3.6$, 0.5 H), 5.60 (*d*, $J = 8.1$, 0.5 H, H–C(1^1)). ^{1}H- and ^{13}C-NMR of α-D-anomer: see [52].

*2^I,2^{II},2^{III},2^{IV},2^V,2^{VI},2^{VII},2^{VIII},3^I,3^{II},3^{III},3^{IV},3^V,3^{VI},3^{VII},3^{VIII},4^{VIII},6^I,6^{II},6^{III},6^{IV},6^V,6^{VI},6^{VII},6^{VIII}-Pentacosa-*O*-acetyl-α-cellooctaosyl Bromide* (**19**). As described for **18**, with **28** (α-D/β-D 1:1; 2.19 g, 0.91 mmol) and 4.1M HBr in AcOH (1.2 ml): **19** (2.06 g, 93%). Solid. M.p. 146°. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.54 (*d*, $J = 4.1$, H–C(1^1)). MALDI-MS: 2451 ($[M + Na]^+$).

8-[2-(Benzyloxy)ethyl]naphthalene-1-ethanol (**29**). At 0°, a soln. of **3** (430 mg, 2.0 mmol) in DMF (20 ml) was treated with NaH (55–65% in oil, 100 mg), stirred for 0.5 h, treated with BnBr (238 µl, 2.0 mmol), allowed to warm to r.t., and stirred for 12 h. After evaporation under high vacuum, workup (Et_2O) and FC (hexane/AcOEt 7:3 → 1:1) gave **29** (485 mg, 79%). Oil. R_f (hexane/AcOEt 9:1) 0.48. IR (CH_2Cl_2): 3611*m*, 3431*m* (br.), 3055*m*, 2951*m*, 2864*m*, 1936*w*, 1877*w*, 1810*w*, 1733*w*, 1597*w*, 1580*w*, 1507*w*, 1495*m*, 1453*m*, 1376*m*, 1361*m*, 1204*w*, 1169*w*, 1094*s*, 1037*s*, 911*w*, 815*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.79–7.74 (*m*, 2 arom. H); 7.39–7.28 (*m*, 9 arom. H); 4.53 (*s*, PhCH_2); 3.89 (br. *t*, $J = 7.1$, addn. of D_2O → *t*, HOCH_2); 3.73 (*t*, $J = 7.5$, BnOCH_2); 3.51 (*t*, $J = 7.9$), 3.44 (*t*, $J = 7.5$, 2 ArCH_2); 1.61 (*t*, $J = 1.6$, exchange with D_2O, OH).

Cellobiosylation of **29**. *a*) At −60°, a suspension of **29** (15 mg, 0.05 mmol), AgOTf (30 mg, 0.10 mmol), and 3-Å molecular sieves (50 mg) in CH_2Cl_2/benzene 1:1 (2 ml) was treated with a soln. of **16** (35 mg, 0.05 mmol) in CH_2Cl_2 (2 ml), slowly warmed to 0° during 2 h, and treated with Et_3N (0.2 ml). Filtration through *Celite*, workup, and FC (hexane/AcOEt 6:4 → 1:1) gave **30** (18 mg, 19%) and **31** (7 mg, 15%).

b) A suspension of **29** (8 mg, 0.026 mmol), **16** (18 mg, 0.025 mmol), and $CdCO_3$ (13 mg, 0.075 mmol) in toluene (2 ml) was refluxed for 24 h. Filtration and FC (hexane/AcOEt 1:1) gave **30** (10 mg, 44%), 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-D-glucopyranose (6 mg, 36%), and **31** (*ca.* 1 mg).

2-{8-[2-(Benzyloxy)ethyl]naphthalen-1-yl}ethyl 2,3,4,6-Tetra-O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri*-O*-acetyl-β-*D*-glucopyranoside* (**30**): Solid. R_f (hexane/AcOEt 1:1) 0.30. M.p. 65.5°. $[\alpha]_D^{25} = -19.3$ ($c = 0.45$, $CHCl_3$). IR ($CHCl_3$): 3019*w*, 2956*w*, 2866*w*, 1755*s*, 1455*m*, 1430*m*, 1367*s*, 1240*s*, 1203*s*, 1167*m*, 1055*s*, 906*m*, 827*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.74–7.71 (*m*, 2 arom. H); 7.36–7.23 (*m*, 9 arom. H); 5.13 (*t*, $J = 9.1$), 5.11 (*t*, $J = 9.2$), 5.05 (*t*, $J = 9.4$) (H–C(3^I), H–C(3^{II}), H–C(4^{II})); 4.90 (*dd*, $J = 7.8, 9.7$), 4.89 (*dd*, $J = 7.8, 9.7$) (H–C(2^I), H–C(2^{II})); 4.49 (*s*, PhCH_2); 4.47 (*d*, $J = 8.0$, H–C(1^{II})); 4.46 (*dd*, $J = 1.5, 12.0$, H–C(6^{II})); 4.42 (*d*, $J = 7.8$, H–C(1^I)); 4.35 (*dd*, $J = 4.4, 12.1$, H–C(6^I)); 4.15–4.03 (*m*, $ArCH_2CH$); 4.04 (*dd*, $J = 5.0, 12.0$, H′–C(6^{II})); 4.02 (*dd*, $J = 1.9, 12.4$, H′–C(6^I)); 3.74 (*t*, $J = 9.3$, H–C(4^I)); 3.72–3.62 (*m*, $ArCH_2CH$, $ArCH_2CH_2$, H–C(5^{II})); 3.52 (*ddd*, $J = 2.2, 5.2, 10.0$, H–C(5^I)); 3.49–3.41 (*m*, 2 $ArCH_2$); 2.08, 2.07, 2.01, 2.00, 1.99, 1.97, 1.62 (7*s*, 7 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72, 170.57, 170.45, 170.00, 169.77, 169.52, 169.27 (7*s*, 7 C=O); 138.35, 135.97, 134.63, 134.29, 131.46 (5*s*); 130.78, 130.70, 129.27, 129.18 (4*d*); 128.51 (2*d*); 127.75 (3*d*), 125.11, 125.02 (2*d*); 100.85 (*d*, C(1^{II})); 100.40 (*d*, C(1^I)); 76.50 (*d*, C(4^I)); 73.05 (*t*, PhCH_2); 72.96 (*d*, C(3^{II})); 72.60 (*d*, C(5^I)); 72.52 (*d*, C(3^I)); 71.94 (*d*, C(5^{II})); 71.76 (*t*, $ArCH_2CH_2$); 71.60 (*d*, (2^I)); 71.42 (*d*, C(2^{II})); 71.05 (*t*, $ArCH_2CH_2$); 67.78 (*d*, C(4^{II})); 61.89 (*t*, C(6^I)); 61.52 (*t*, C(6^{II})); 37.41 (*t*, $ArCH_2$); 36.69 (*t*, $ArCH_2$); 20.78, 20.57 (2*q*, 2 Me); 20.46 (*q*, 5 Me). FAB-MS: 925 (22, $[M+1]^+$), 924 (12, M^+), 619 (100), 331 (61). Anal. calc. for $C_{47}H_{56}O_{19}$ (924.95): C 61.03, H 6.10; found: C 60.89, H 6.16.

2-{8-[2-(Benzyloxy)ethyl]naphthalen-1-yl}ethyl Acetate (**31**): Oil. IR ($CHCl_3$): 3054*m*, 3034*w*, 2960*m*, 2929*m*, 2900*m*, 2860*m*, 1936*w*, 1876*w*, 1735*s*, 1599*w*, 1582*w*, 1495*w*, 1453*m*, 1385*m*, 1364*m*, 1276*m*, 1270*m*, 1266*m*, 1250*s*, 1240*s*, 1095*s*, 1039*s*, 812*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.78–7.73 (*m*, 2 arom. H); 7.40–7.29 (*m*, 9 arom. H); 4.52 (*s*, PhCH_2); 4.31 (*t*, $J = 7.5$, AcOCH_2); 3.71 (*t*, $J = 7.5$, BnOCH_2); 3.53 (*t*, $J \approx 7.8$, $ArCH_2$); 3.51 (*t*, $J \approx 7.8$, $ArCH_2$); 2.03 (*s*, Ac). CI-MS: 366 (32, $[M+NH_4]^+$), 348 (5, M^+), 289 (100, $[M-AcO]^+$), 288 (63, $[M-AcOH]^+$), 271 (39), 167 (68), 91 (50).

2-(Naphthalen-1-yl)ethyl 2,3,4,6-Tetra-O*-acetyl-β-*D*-glucopyranoside* (**32**). A suspension of **12** (344 mg, 2.0 mmol), **15** (1.15 g, 2.8 mmol), basic zinc carbonate (2.196 g, 4.0 mmol), and 3-Å molecular sieves (500 mg) in dry toluene (80 ml) was kept for 7 h at 110°. Filtration, evaporation, and FC (hexane/AcOEt 4:1 → 7:3) gave **32** (702 mg, 70%). Solid. R_f (hexane/AcOEt 7:3) 0.26. M.p. 103°. $[\alpha]_D^{25} = -17.7$ ($c = 0.65$, $CHCl_3$). IR ($CHCl_3$): 3012*w*, 2958*w*, 2882*w*, 1755*s*, 1427*w*, 1367*m*, 1231*s*, 1171*m*, 1040*s*, 909*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignment based on homonuclear decoupling experiments): 8.00 (br. *d*, $J = 7.8$), 7.85 (*dd*, $J = 1.8, 7.5$), 7.72 (br. *d*, $J = 7.8$), 7.52 (br. *t*, $J = 7.3$), 7.48 (br. *t*, $J = 6.8$), 7.39 (*t*, $J = 7.5$), 7.34 (br. *d*, $J = 6.3$) (7 arom. H); 5.16 (*t*, $J = 9.2$, H–C(3^I)); 5.08 (*t*, $J = 9.3$, H–C(4^I)); 5.00 (*dd*, $J = 8.1, 9.0$, H–C(2^I)); 4.49 (*d*, $J = 7.8$, H–C(1^I)); 4.26 (*dd*, $J = 4.7, 12.5$, H–C(6^I)); 4.29–4.22 (*m*, $ArCH_2CH$); 4.12 (*dd*, $J = 2.2, 12.2$, H′–C(6^I)); 3.80 (*td*, $J \approx 7.4, 9.4$, $ArCH_2CH$); 3.66 (*ddd*, $J = 2.2, 4.6, 9.3$, H–C(5^I)); 3.45–3.28 (*AB* of *ABMX*, $ArCH_2$); 2.07, 2.01, 1.98, 1.83 (4*s*, 4 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.90, 170.48, 169.60, 169.43 (4*s*, 4 C=O); 134.35 (*s*, C(1)); 133.92 (*s*, C(4a)); 132.07 (*s*, C(8a)); 128.92, 127.28, 127.17, 126.15 (4*d*, C(2), C(3), C(4), C(5)); 125.66, 125.58 (2*d*, C(6), C(7)); 123.63 (*d*, C(8)); 100.90 (*d*, C(1^I)); 72.80 (*d*, C(3^I)); 71.82 (*d*, C(5^I)); 71.11 (*d*, C(2^I)); 70.14 (*t*, $ArCH_2CH_2$); 68.36 (*d*, C(4^I)); 61.92 (*t*, C(6^I)); 32.88 (*t*, $ArCH_2$); 20.65 (*q*, Me); 20.51 (*q*, 2 Me); 20.41 (*q*, Me). CI-MS: 520 (100, $[M+NH_4]^+$), 502 (14, M^+), 331 (29), 156 (27), 155 (70), 154 (78), 141 (20). Anal. calc. for $C_{26}H_{30}O_{10}$ (502.52): C 62.14, H 6.02; found: C 62.16, H 5.93.

2-(Naphthalen-1-yl)ethyl 2,3,4,6-Tetra-O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri*-O*-acetyl-β-*D*-glucopyranoside* (**33**). A suspension of **12** (34 mg, 0.2 mmol), **16** (200 mg, 0.28 mmol), basic zinc carbonate (80 mg, 0.15 mmol), and 3-Å molecular sieves (80 mg) in dry toluene (13 ml) was stirred at 110° for 12 h. Filtration, evaporation, and FC (hexane/AcOEt 6:4) gave **33** (128 mg, 82%). Solid. R_f (hexane/AcOEt 1:1) 0.33. M.p. 176°. $[\alpha]_D^{25} = -20.7$ ($c = 0.56$, $CHCl_3$). IR ($CHCl_3$): 3026*m*, 2958*w*, 2879*w*, 1755*s*, 1598*w*, 1511*w*, 1429*w*, 1367*s*, 1239*s*, 1167*m*, 1130*m*, 1039*s*, 906*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98 (br. *d*, $J = 7.6$), 7.84 (*dd*, $J = 1.9, 7.2$), 7.72 (br. *d*, $J = 7.5$), 7.55–7.43 (*m*, 2 H), 7.38 (*t*, $J = 7.5$), 7.32 (br. *d*, $J = 7.0$) (7 arom. H); 5.13 (*t*, $J = 9.2$), 5.12 (*t*, $J = 9.3$, H–C(3^I), H–C(3^{II})); 5.04 (*t*, $J = 9.3$, H–C(4^{II})); 4.90 (*dd*, $J = 7.8, 9.0$), 4.89 (*dd*, $J = 7.8, 9.0$) (H–C(2^I), H–C(2^{II})); 4.49 (*d*, $J = 7.8$, H–C(1^I)); 4.48 (*d*, $J = 7.8$, H–C(1^{II})); 4.47 (*dd*, $J = 1.5, 12.0$, H–C(6^I)); 4.36 (*dd*, $J = 4.4, 12.5$, H–C(6^{II})); 4.07 (*dd*, $J = 5.0, 11.8$, H′–C(6^I)); 4.01 (*dd*, $J = 1.9, 12.5$, H′–C(6^{II})); 4.20 (*ddd*, $J = 6.0, 7.5, 9.5$, $ArCH_2CH$); 3.75 (*t*, $J = 9.4$, H–C(4^I)); 3.79 (*td*, $J \approx 7.5, 9.5$, $ArCH_2CH$); 3.64 (*ddd*, $J = 2.3, 4.1, 9.6$, H–C(5^{II})); 3.55 (*ddd*, $J = 1.9, 5.0, 9.5$, H–C(5^I)); 3.42–3.26 (*AB* of *ABMX*, $ArCH_2$); 2.09, 2.07, 2.01, 1.997, 1.995, 1.991, 1.96 (7*s*, 7 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.67, 170.49, 170.39, 169.96, 169.68, 169.47, 169.21 (7*s*, 7 C=O); 134.32 (*s*, C(1)); 133.88 (*s*, C(4a)); 132.05 (*s*, C(8a)); 128.88, 127.25, 127.08, 126.11 (4*d*, C(2), C(3), C(4), C(5)); 125.63, 125.53 (2*d*, C(6), C(7)); 123.57 (*d*, C(8)); 100.81 (*d*, C(1^{II})); 100.70

(*d*, C(1^{I})); 76.48 (*d*, C(4^{I})); 72.89 (*d*, C(3^{II})); 72.66 (*d*, C(5^{I})); 72.44 (*d*, C(3^{I})); 71.90 (*d*, C(5^{II})); 71.56 (*d*, C(2^{I})); 71.37 (*d*, C(2^{II})); 70.07 (*t*, ArCH$_2$*C*H$_2$); 67.71 (*d*, C(4^{II})); 61.86 (*t*, C(6^{I})); 61.47 (*t*, C(6^{II})); 32.86 (*t*, Ar*C*H$_2$); 20.75, 20.52 (2*q*, 2 Me); 20.41 (*q*, 5 Me). CI-MS: 809 (33), 808 (70, $[M+NH_4]^+$), 790 (6, M^+), 619 (7), 331 (42), 169 (43), 154 (100). Anal. calc. for $C_{38}H_{46}O_{18}$ (790.77): C 57.72, H 5.86; found: C 57.64, H 5.91.

2-(Naphthalen-1-yl)ethyl 2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranoside* (**34**). A suspension of **12** (52 mg, 0.30 mmol), **17** [43] (377 mg, 0.37 mmol), basic zinc carbonate (200 mg, 0.36 mmol), and 3-Å molecular sieves (150 mg) in dry 1,2-dichloroethane (15 ml) was stirred at 110° for 20 h. Filtration, evaporation, and FC (hexane/AcOEt 1 : 1) gave **34** (220 mg, 67%). Solid. R_f (hexane/AcOEt 4 : 6) 0.37. M.p. 201°. $[\alpha]_D^{25} = -24.0$ ($c = 0.93$, $CHCl_3$). IR ($CHCl_3$): 3015*w*, 2975*w*, 2866*w*, 1755*s*, 1368*m*, 1236*s*, 1165*w*, 1048*m*, 905*w*, 877*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98 (*dd*, *J* = 1.4, 7.8), 7.85 (*dd*, *J* = 1.8, 7.5), 7.73 (br. *d*, *J* = 8.1), 7.51 (*dt*, *J* = 1.8, 6.8), 7.47 (*dt*, *J* = 1.2, 6.8), 7.38 (*dd*, *J* = 7.2, 8.1), 7.32 (*dd*, *J* = 1.3, 6.9) (7 arom. H); 5.12 (*t*, *J* = 9.2), 5.11 (*t*, *J* = 9.3, 2H) (H−C(3^{I}), H−C(3^{II}), H−C(3^{III})); 5.04 (*t*, *J* = 9.3, H−C(4^{III})); 4.89 (*dd*, *J* = 7.8, 9.6), 4.88 (*dd*, *J* = 8.0, 9.6) (H−C(2^{I}), H−C(2^{III})); 4.83 (*dd*, *J* = 7.8, 9.3, H−C(2^{II})); 4.51 (*dd*, *J* = 2.2, 12.5, H−C(6^{I})); 4.46 (*d*, *J* = 7.9, H−C(1^{II}); H−C(1^{III})); 4.44 (*d*, *J* = 8.1, H−C(1^{I})); 4.39 (*dd*, *J* = 1.9, 12.2, H−C(6^{II})); 4.34 (*dd*, *J* = 4.4, 12.8, H−C(6^{III})); 4.20 (*ddd*, *J* = 5.9, 7.4, 9.6, ArCH$_2$C*H*); 4.10 (*dd*, *J* = 5.0, 11.8, H′−C(6^{II})); 4.06 (*dd*, *J* = 4.6, 12.2, H′−C(6^{I})); 4.03 (*dd*, *J* = 2.2, 12.4, H′−C(6^{III})); 3.79 (*td*, *J* ≈ 7.5, 9.6, ArCH$_2$C*H*); 3.75 (*dd*, *J* = 9.1, 9.6, H−C(4^{I})); 3.74 (*t*, *J* = 9.5, H−C(4^{II})); 3.62 (*ddd*, *J* = 2.2, 4.1, 9.7, H−C(5^{III})); 3.60–5.51 (*m*, H−C(5^{I}), H−C(5^{II})); 3.425–3.26 (*AB* of *ABMX*, ArC*H*$_2$); 2.14, 2.09, 2.08, 2.02, 2.01, 2.00, 1.98, 1.97, 1.95, 1.82 (10*s*, 10 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.70, 170.51 (2*s*, 2 C=O); 170.39 (*s*, 2 C=O); 169.96 (*s*, 2 C=O); 169.67 (*s*, C=O); 169.50 (*s*, 2 C=O); 169.28 (*s*, C=O); 134.38 (*s*, C(1)); 133.93 (*s*, C(4a)); 132.14 (*s*, C(8a)); 128.93, 127.30, 127.12, 126.17 (4*d*, C(2), C(3), C(4), C(5)); 125.66, 125.58 (2*d*, C(6), C(7)); 123.62 (*d*, C(8)); 100.86 (*d*, C(1^{III})); 100.60 (*d*, C(1^{II})); 100.52 (*d*, C(1^{I})); 76.52 (*d*, C(4^{I})); 76.18 (*d*, C(4^{II})); 72.92 (*d*, C(5^{I})); 72.74 (*d*, C(3^{II}), C(3^{III}), C(5^{II})); 72.44 (*d*, C(3^{I})); 72.05 (*d*, C(5^{III})); 71.81 (*d*, C(2^{II})); 71.60 (*d*, C(2^{I})); 71.54 (*d*, C(2^{III})); 70.09 (*t*, ArCH$_2$*C*H$_2$); 67.76 (*d*, C(4^{III})); 62.15 (*t*, C(6^{II})); 61.81 (*t*, C(6^{I})); 61.52 (*t*, C(6^{III})); 32.92 (*t*, Ar*C*H$_2$); 20.81, 20.67, 20.55 (3*q*, 3 Me); 20.46 (*q*, 7 Me). FAB-MS: 1101 (28, $[M+Na]^+$), 1079 (13, $[M+1]^+$), 1078 (19, M^+), 908 (13), 907 (30), 619 (100), 331 (39), 155 (73). Anal. calc. for $C_{50}H_{62}O_{26}$ (1079.02): C 55.66, H 5.79; found: C 55.35, H 5.83.

2-(Naphthalen-1-yl)ethyl 2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranoside* (**35**). A suspension of **12** (52 mg, 0.30 mmol), **18** (510 mg, 0.40 mmol), basic zinc carbonate (80 mg, 0.15 mmol), and 3-Å molecular sieves (70 mg) in dry toluene (10 ml) was stirred at 110° for 7 h. Filtration, evaporation, and FC (hexane/AcOEt 3 : 7) gave **35** (300 mg, 73%). Solid. R_f (hexane/AcOEt 3 : 7) 0.50. M.p. 216°. $[\alpha]_D^{25} = -23.0$ (c = 0.50, $CHCl_3$). IR ($CHCl_3$): 3028*w*, 2957*w*, 2874*w*, 1755*s*, 1429*w*, 1367*m*, 1232*s*, 1164*w*, 1129*w*, 1054*m*, 905*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.98 (*d*, *J* = 8.3), 7.84 (*dd*, *J* = 1.5, 7.9), 7.72 (*d*, *J* = 8.1), 7.51 (*dt*, *J* = 1.7, 6.9), 7.45 (*dt*, *J* = 1.3, 6.7), 7.38 (*dd*, *J* = 7.1, 8.1), 7.32 (br. *d*, *J* = 6.0) (7 arom. H); 5.11 (*t*, *J* = 9.3), 5.10 (*t*, *J* = 9.3), 5.092 (*t*, *J* = 9.2), 5.091 (*t*, *J* = 9.2), 5.04 (*t*, *J* = 9.6) (H−C(3$^{I–IV}$), H−C(4^{IV})); 4.89 (*dd*, *J* = 7.9, 9.2), 4.88 (*dd*, *J* = 7.9, 9.6), 4.816 (*dd*, *J* = 7.8, 9.4), 4.813 (*dd*, *J* = 7.9, 9.4) (H−C(2$^{I–IV}$)); 4.46 (*d*, *J* = 7.9), 4.45 (*d*, *J* = 7.8), 4.44 (*d*, *J* = 7.9), 4.43 (*d*, *J* = 7.9) (H−C(1$^{I–IV}$)); 4.49 (*dd*, *J* = 2.1, 12.1), 4.390 (*dd*, *J* = 2.0, 12.0), 4.389 (*dd*, *J* = 2.5, 12.4) (H−C(6$^{I–III}$)); 4.34 (*dd*, *J* = 4.4, 12.5, H−C(6^{IV})); 4.19 (*ddd*, *J* = 5.7, 7.6, 9.6, ArCH$_2$C*H*); 4.08 (*dd*, *J* = 5.0, 12.0, 2 H), 4.06 (*dd*, *J* = 5.1, 12.0) (H′−C(6$^{I–III}$)); 4.03 (*dd*, *J* = 2.2, 12.5, H′−C(6^{IV})); 3.79 (*td*, *J* = 7.5, 9.7, ArCH$_2$C*H*); 3.78 (*dd*, *J* = 8.7, 9.7), 3.73 (*dd*, *J* = 9.0, 9.5, 2 H) (H−C(4$^{I–III}$)); 3.62 (*ddd*, *J* = 2.3, 4.3, 9.9), 3.57 (*ddd*, *J* ≈ 2.0, 5.0, 9.5), 3.56 (*ddd*, *J* ≈ 2.0, 5.0, 9.5), 5.54 (*ddd*, *J* ≈ 2.0, 5.0, 9.5) (H−C(5$^{I–IV}$)); 3.38–3.28 (*AB* of *ABMX*, ArC*H*$_2$); 2.13, 2.12, 2.09, 2.03, 2.02 (5*s*, 5 Ac); 2.00 (*s*, 2 Ac); 1.99, 1.98, 1.97, 1.95, 1.94, 1.82 (6*s*, 6 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.57, 170.41, (2*s*, 2 C=O); 170.26 (*s*, 3 C=O); 169.86 (*s*, C=O); 169.81 (*s*, 2 C=O); 169.52, 169.40, 169.37, 169.32, 169.16 (5*s*, 5 C=O); 134.25 (*s*, C(1)); 133.80 (*s*, C(4a)); 131.97 (*s*, C(8a)); 128.80, 127.16, 127.00, 126.03 (4*d*, C(2), C(3), C(4), C(5)); 125.55, 125.47 (2*d*, C(6), C(7)); 123.51 (2*d*, C(8)); 100.75 (*d*, C(1^{IV})); 100.58, 100.49 (2*d*, C(1^{II}), C(1^{III})); 100.45 (*d*, C(1^{I})); 76.41 (*d*, C(4^{I})); 76.09, 75.99 (2*d*, C(4^{II}), C(4^{III})); 72.76 (*d*, C(5^{I})); 72.64 (*d*, C(3^{IV})); 72.58 (*d*, C(5^{II}), C(5^{III})); 72.52 (2*d*), 72.26 (*d*) (C(3$^{I–III}$)); 71.90 (*d*, C(5^{IV})); 71.75, 71.61 (2*d*, C(2^{II}), C(2^{III})); 71.43 (*d*, C(2^{I})); 71.35 (*d*, C(2^{IV})); 69.96 (*t*, ArCH$_2$*C*H$_2$); 67.58 (*d*, C(4^{IV})); 61.97 (*t*, C(6^{II}), C(6^{III})); 61.71 (*t*, C(6^{I})); 61.35 (*t*, C(6^{IV})); 32.77 (*t*, Ar*C*H$_2$); 20.68 (*q*, Me); 20.58 (*q*, 2 Me); 20.45 (*q*, 5 Me); 20.33 (*q*, 5 Me). FAB-MS: 1499 (26), 1389 (59), 1368 (50), 1367 (73, $[M+1]^+$), 1366 (100, M^+), 1195 (67), 907 (60), 619 (79), 155 (34), 154 (44). Anal. calc. for $C_{62}H_{78}O_{34}$ (1367.27): C 54.46, H 5.75; found: C 54.49, H 5.94.

2-(Naphthalen-1-yl)ethyl 2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,-3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-

D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranoside* (**36**). A suspension of **12** (35 mg, 0.22 mmol), **19** (500 mg, 0.20 mmol), basic zinc carbonate (80 mg, 0.14 mmol), and 3-Å molecular sieves (70 mg) in dry toluene/1,2-dichloroethane 6 : 5 (11 ml) was stirred at 110° for 5 h. Filtration, evaporation, and FC (hexane/AcOEt/MeOH 5 : 5 : 0.1) gave crude **36** (252 mg), and HPLC (hexane/AcOEt 2 : 8) pure **36** (161 mg, 32%). White solid. R_f (hexane/AcOEt/MeOH 5 : 5 : 1) 0.52. M.p. 263°. $[\alpha]_D^{25} = -20.9$ ($c = 0.74$, $CHCl_3$). IR ($CHCl_3$): 3035*w*, 2958*w*, 2873*w*, 1756*s*, 1429*w*, 1368*m*, 1232*s*, 1162*w*, 1053*m*, 904*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.95 (*dd*, $J = 1.3$, 8.0), 7.81 (*dd*, $J = 2.1$, 8.2), 7.69 (br. *d*, $J = 7.8$), 7.48 (*dt*, $J = 1.6$, 7.0), 7.44 (*dt*, $J = 1.9$, 7.0), 7.36 (*dd*, $J = 7.2$, 7.7), 7.30 (br. *d*, $J = 7.9$) (7 arom. H); 5.12–4.97 (*m*, H–C($3^{I–VIII}$), H–C(4^{VIII})); 4.90–4.72 (*m*, H–C($2^{I–VIII}$)); 4.49–4.28 (*m*, H–C($1^{I–VIII}$), H–C($6^{I–VIII}$)); 4.20–4.11 (*m*, $ArCH_2CH$); 4.10–3.98 (*m*, H′–C($6^{I–VIII}$)); 3.86–3.74 (*m*, $ArCH_2CH$); 3.79–3.64 (*m*, H–C($4^{I–VII}$)); 3.64–3.42 (*m*, H–C($5^{I–VIII}$)); 3.35–3.22 (*AB* of *ABMX*, $ArCH_2$); 2.10–1.91 (*m*, 25 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.61, 170.45 (2*s*, 2 C=O); 170.34 (*s*, 7 C=O); 169.85 (*s*, 7 C=O); 169.57 (*s*, C=O); 169.40 (*s*, 7 C=O); 169.20 (*s*, C=O); 134.29 (*s*, C(1)); 133.84 (*s*, C(4)), 132.03 (*s*, C(8a)); 128.82, 127.19, 127.03, 126.07 (4*d*, C(2), C(3), C(4), C(5)); 125.59, 125.49 (2*d*, C(6), C(7)); 123.55 (*d*, C(8)); 100.77 (*d*), 100.57 (*d*), 100.46 (6*d*) (C($1^{I–VIII}$)); 76.42 (*d*), 76.02 (6*d*) (C($4^{I–VII}$)); 72.81 (*d*), 72.72 (6*d*), 72.56 (*d*), 72.46 (6*d*), 72.31 (*d*), 71.94 (*d*) (C($3^{I–VIII}$), C($5^{I–VIII}$)); 71.76 (6*d*), 71.49 (*d*), 71.44 (*d*) (C($2^{I–VIII}$)); 70.00 (*t*, $ArCH_2CH_2$); 67.43 (*d*, C(4^{VIII})); 61.96 (*t*, C($6^{I–VIII}$)); 32.81 (*t*, $ArCH_2$); 20.61–20.37 (several *q*, 25 Me). MALDI-MS: 2559 ($[M + K]^+$), 2543 ($[M + Na]^+$), 2501 ($[M + Na - Ac]^+$). Anal. calc. for $C_{110}H_{142}O_{66}$ (2520.28): C 52.42, H 5.68; found: C 52.15, H 5.63.

2-(Naphthalen-1-yl)ethyl β-D-*Glucopyranoside* (**37**). A suspension of **32** (700 mg, 1.39 mmol) and 5.78M NaOMe (0.25 ml, 1.44 mmol) in MeOH (20 ml) was stirred at r.t. for 2 h. The homogeneous soln. was neutralized with *Amberlite 120* (H^+ form). Filtration (washing with MeOH) and evaporation gave **37** (448 mg, 96%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1 : 1). Solid. R_f (*RP-18*, MeOH/H_2O 1 : 1) 0.18. M.p. 122–124°. $[\alpha]_D^{25} = -25.2$ ($c = 0.70$, H_2O). IR (KBr): 3374*s* (br.), 3044*m*, 2945*m*, 2909*s*, 2876*s*, 1597*w*, 1508*w*, 1467*m*, 1450*m*, 1418*m*, 1403*m*, 1374*m*, 1362*m*, 1333*w*, 1342*w*, 1285*w*, 1265*m*, 1228*w*, 1196*w*, 1167*s*, 1131*s*, 1099*s*, 1071*s*, 1035*s*, 898*w*, 872*w*, 856*w*, 838*w*. ^{1}H-NMR (500 MHz, D_2O; assignment based on homonuclear decoupling experiments): 8.09 (*d*, $J = 8.5$), 7.90 (*dd*, $J = 1.2$, 7.9), 7.81–7.77 (*m*), 7.55 (*dt*, $J = 1.4$, 6.8), 7.51 (*dt*, $J = 1.1$, 6.8), 7.45–7.41 (*m*, 2 H) (7 arom. H); 4.37 (*d*, $J = 8.0$, H–C(1^I)); 4.14 (*dt*, $J = 7.2$, 10.2, $ArCH_2CH$); 3.94 (*dt*, $J = 7.3$, 10.2, $ArCH_2CH$); 3.80 (*dd*, $J = 1.8$, 12.2, H–C(6^I)); 3.66 (*dd*, $J = 5.4$, 12.3, H′–C(6^I)); 3.39 (*dd*, $J = 8.8$, 9.1, H–C(3^I)); 3.36 (*t*, $J \approx 7.3$, $ArCH_2$); 3.31 (*ddd*, $J = 2.2$, 5.5, 9.7, H–C(5^I)); 3.30 (*dd*, $J = 8.8$, 9.7, H–C(4^I)); 3.19 (*dd*, $J = 8.0$, 9.3, H–C(2^I)). ^{13}C-NMR (75 MHz, D_2O): 134.40 (*s*, C(1)); 133.72 (*s*, C(4a)); 131.74 (*s*, C(8a)); 128.95 (*d*); 127.33 (*d*); 126.53 (*d*); 126.08 (3*d*); 123.83 (*d*, C(8)); 102.49 (*d*, C(1^I)); 75.87 (*d*, C(3^I), C(5^I)); 73.20 (*d*, C(2^I)); 70.20 (*t*, $ArCH_2CH_2$); 69.60 (*d*, C(4^I)); 60.74 (*t*, C(6^I)); 32.38 (*t*, $ArCH_2$). ESI-MS: 691 (100, $[2M + Na]^+$), 357 (80, $[M + Na]^+$), 352 (70, $[M + NH_4]^+$).

2-(Naphthalen-1-yl)ethyl β-D-*Glucopyranosyl-(1 → 4)-β*-D-*glucopyranoside* (**38**). A soln. of **33** (197 mg, 0.25 mmol) and 0.067M NaOMe (0.4 ml, 0.027 mmol) in MeOH/THF 100 : 1 (10.1 ml) was stirred for 2 h. Workup as described for **37** gave **38** (120 mg, 97%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1 : 1). Solid. R_f (*RP-18*, MeOH/H_2O 1 : 1) 0.21. M.p. 186–189°. $[\alpha]_D^{25} = -21.6$ ($c = 0.50$, H_2O). IR ($CHCl_3$): 3416*s* (br.), 3056*w*, 2874*m*, 1636*w*, 1597*w*, 1374*m*, 1316*m*, 1263*m*, 1165*m*, 1031*s* (br.), 895*m*. ^{1}H-NMR (500 MHz, D_2O; assignment based on homonuclear decoupling experiments): 8.02 (*d*, $J = 8.5$), 7.80 (*d*, $J = 8.0$), 7.71–7.68 (*m*), 7.48 (*dd*, $J = 7.0$, 7.7), 7.43 (*dd*, $J = 7.1$, 7.7), 7.38–7.33 (*m*, 2 H) (7 arom. H); 4.41 (*d*, $J = 7.9$, H–C(1^{II})); 4.32 (*d*, $J = 7.9$, H–C(1^I)); 4.07 (br. *q*, $J \approx 8.0$, $ArCH_2CH$); 3.86 (br. *td*, $J \approx 7.2$, 9.5, $ArCH_2CH$); 3.84 (br. *d*, $J = 12.6$, H–C(6^I)); 3.81 (br. *d*, $J = 12.9$, H–C(6^{II})); 3.70 (*dd*, $J = 4.7$, 13.0, H′–C(6^I)); 3.66 (*dd*, $J = 5.6$, 12.6, H′–C(6^{II})); 3.51 (*t*, $J = 8.8$, H–C(4^I)); 3.49 (*t*, $J = 8.8$, H–C(3^I)); 3.43 (*t*, $J = 9.0$, H–C(3^{II})); 3.41–3.37 (*m*, $ArCH_2$); 3.36 (*t*, $J = 9.3$, H–C(4^{II})); 3.34–3.28 (*m*, H–(5^I), H–C(5^{II})); 3.24 (*dd*, $J = 8.1$, 8.7, H–C(2^{II})); 3.22 (*dd*, $J = 8.1$, 8.7, H–C(2^I)). ^{13}C-NMR (75 MHz, D_2O): 134.45 (*s*, C(1)); 133.74 (*s*, C(4a)); 131.73 (*s*, C(8a)); 128.95, 126.58, 126.38, 126.16 (4*d*, C(2), C(3), C(4), C(5)); 126.03 (*d*, C(6), C(7)); 123.83 (*d*, C(8)); 102.72 (*d*, C(1^{II})); 102.30 (*d*, C(1^I)); 78.70 (*d*, C(4^I)); 76.06 (*d*, C(5^{II})); 75.62 (*d*, C(3^{II})); 74.75 (*d*, C(5^I)); 74.40 (*d*, C(3^I)); 73.25 (*d*, C(2^{II})); 72.94 (*d*, C(2^I)); 70.24 (*t*, $ArCH_2CH_2$); 69.53 (*d*, C(4^{II})); 60.63 (*t*, C(6^{II})); 60.03 (*t*, C(6^I)); 32.38 (*t*, $ArCH_2$). ESI-MS: 1010 (100, $[2M + NH_4]^+$), 514 (90, $[M + NH_4]^+$).

2-(Naphthalen-1-yl)ethyl β-D-*Glucopyranosyl-(1 → 4)-β*-D-*glucopyranosyl-(1 → 4)-β*-D-*glucopyranoside* (**39**). A suspension of **34** (158 mg, 0.14 mmol) and 5.78M NaOMe (0.1 ml, 0.57 mmol) in H_2O (5 ml) was stirred at r.t. for 12 h. Workup as described for **37** gave **39** (94 mg, 97%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1 : 1). White solid. R_f (*RP-18*, MeOH/H_2O 1 : 1) 0.23. M.p. 249–255° (dec.). $[\alpha]_D^{25} = -19.6$ ($c = 0.32$, H_2O). IR (KBr): 3409*s* (br.), 2912*m*, 2866*m*, 1594*w*, 1508*w*, 1461*w*, 1421*m*, 1375*m*, 1328*m*, 1247*w*, 1161*s*, 1120*s*, 1097*s*, 1062*s*, 1028*s*, 901*w*. ^{1}H-NMR (500 MHz, D_2O): 8.12 (*d*, $J = 8.5$), 7.92 (*dd*, $J = 1.4$, 8.2), 7.83–7.79 (*m*), 7.57 (*ddd*, $J = 1.5$, 6.8, 8.5), 7.53 (*ddd*, $J = 1.3$, 6.9, 8.1), 7.47–7.43 (*m*, 2 H) (7 arom. H);

4.45 (*d*, *J* = 8.0), 4.44 (*d*, *J* = 7.9), 4.43 (*d*, *J* = 8.0) (H–C(1^{I}), H–C(1^{II}), H–C(1^{III})); 4.18 (*td*, *J* = 7.2, 10.2, $ArCH_2CH$); 3.99 (*td*, *J* = 7.3, 10.4, $ArCH_2CH$); 3.90 (*dd*, *J* = 2.1, 12.4), 3.86 (*dd*, *J* = 2.3, 12.4), 3.84 (*dd*, *J* = 2.2, 12.4) (H–C(6^{I}), H–C(6^{II}), H–C(6^{III})); 3.75 (*dd*, *J* = 4.9, 12.3), 3.71 (*dd*, *J* = 5.0, 12.3), 3.67 (*dd*, *J* = 5.8, 12.5) (H′–C(6^{I}), H′–C(6^{II}), H′–C(6^{III})); 3.60 (*t*, *J* = 9.0, H–C(4^{II})); 3.57 (*t*, *J* = 9.3, H–C(4^{I})); 3.55 (*t*, *J* = 8.8, H–C(3^{II})); 3.53 (*t*, *J* = 8.8, H–C(3^{I})); 3.56–3.52 (*m*, H–C(5^{II})); 3.47 (*ddd*, *J* = 2.2, 4.9, 9.4, H–C(5^{I})); 3.44 (*t*, *J* = 9.1, H–C(3^{III})); 3.42 (*ddd*, *J* = 2.2, 5.3, 9.5, H–C(5^{III})); 3.40 (*t*, *J* = 7.2, $ArCH_2$); 3.35 (*dd*, *J* = 9.1, 9.7, H–C(4^{III})); 3.28 (*dd*, *J* = 8.1, 9.2), 3.25 (*dd*, *J* = 8.0, 9.3), 3.23 (*dd*, *J* = 8.1, 9.2) (H–C(2^{I}), H–C(2^{II}), H–C(2^{III})). ^{13}C-NMR (75 MHz, D_2O): 134.60 (*s*, C(1)); 133.77 (*s*, C(4a)); 131.72 (*s*, C(8a)); 129.03, 127.48, 127.42, 126.66 (4*d*, C(2), C(3), C(4), C(5)); 126.28, 126.12 (*d*, C(6), C(7)); 123.89 (*d*, C(8)); 102.73, 102.49, 102.30 (3*d*, C(1^{I}), C(1^{II}), C(1^{III})); 78.61, 78.48 (2*d*, C(4^{I}), C(4^{II})); 76.06 (*d*, C(5^{III})); 75.58 (*d*, C(3^{III})); 74.90, 74.80 (2*d*, C(5^{I}), C(5^{II})); 74.35, 74.15 (2*d*, C(3^{I}), C(3^{II})); 73.24 (*d*, C(2^{III})); 73.03 (*d*, C(2^{I}), C(2^{II})); 70.29 (*t*, $ArCH_2CH_2$); 69.55 (*d*, C(4^{III})); 60.65 (*t*, C(6^{III})); 59.55 (*t*, C(6^{I}), C(6^{II})); 32.39 (*t*, $ArCH_2$). ESI-MS: 1339 (40, $[2M + Na]^+$), 1334 (20, $[2M + NH_4]^+$), 1317 (20, $[2M + 1]^+$), 681 (90, $[M + Na]^+$), 676 (100, $[M + NH_4]^+$), 658 (80, M^+).

*2-(Naphthalen-1-yl)ethyl β-*D*-Glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranoside* (**40**). A suspension of **35** (300 mg, 0.22 mmol) and 0.067M NaOMe (3 ml, 0.20 mmol) in H_2O (5 ml) was stirred at r.t. for 15 h. Workup as described for **37** gave **40** (182 mg, 100%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1:1). White solid. M.p. 290° (dec.). R_f (*RP-18*, MeOH/H_2O 1:1) 0.25. $[\alpha]_D^{25} = -14.0$ (*c* = 0.50, H_2O). IR (KBr): 3406*s* (br.), 2909*m*, 2862*m*, 1419*w*, 1379*m*, 1338*m*, 1309*m*, 1263*w*, 1234*w*, 1159*s*, 1119*s*, 1090*s*, 1067*s*, 1026*s*, 899*w*. ^{1}H-NMR (500 MHz, D_2O): 8.12 (*d*, *J* = 8.3), 7.92 (*d*, *J* = 8.0), 7.81–7.78 (*m*), 7.57 (*t*, *J* = 7.1), 7.52 (*t*, *J* = 7.0), 7.44 (*m*, 2 H) (7 arom. H); 4.46 (*d*, *J* = 7.6), 4.45 (*d*, *J* = 8.0), 4.44 (*d*, *J* = 8.0); 4.42 (*d*, *J* = 8.0) (H–C(1$^{I–IV}$)); 4.17 (*td*, *J* ≈ 7.3, 10.0, $ArCH_2CH$); 3.98 (*td*, *J* ≈ 7.1, 10.2, $ArCH_2CH$); 3.91 (br. *d*, *J* = 12.5, H–C(6^{II}), H–C(6^{III})); 3.85 (br. *d*, *J* = 12.5, H–C(6^{I}), H–C(6^{IV})); 3.75 (*dd*, *J* = 4.5, 12.3, 2 H), 3.71 (*dd*, *J* = 5.0, 12.5), 3.67 (*dd*, *J* = 5.8, 12.6) (H′–C(6$^{I–IV}$)); 3.64–3.52 (*m*, H–C(3$^{I–III}$), H–C(4$^{I–III}$), H–C(5$^{II, III}$)); 3.50–3.36 (*m*, H–C(5^{I}), H–C(5^{IV}), $ArCH_2$); 3.44 (*t*, *J* = 9.2, H–C(3^{IV})); 3.35 (*t*, *J* = 9.3, H–C(4^{IV})); 3.30 (*dd*, *J* = 8.0, 9.0), 3.28 (*dd*, *J* = 8.0, 9.0), 3.25 (*dd*, *J* = 7.9, 9.0), 3.23 (*dd*, *J* = 7.6, 8.7, H–C(2$^{I–IV}$)). ^{13}C-NMR (125 MHz, D_2O): 134.40 (*s*, C(1)); 133.58 (*s*, C(4a)); 131.53 (*s*, C(8a)); 128.83, 127.27, 127.21, 126.46 (4*d*, C(2), C(3), C(4), C(5)); 126.08, 125.93 (2*d*, C(6), C(7)); 123.69 (*d*, C(8)); 102.57 (*d*), 102.35 (2*d*), 102.16 (*d*) (C(1$^{I–IV}$)); 78.53, 78.41, 78.28 (3*d*, C(4$^{I–III}$)); 75.99 (*d*, C(5^{IV})); 75.50 (*d*, C(3^{IV})); 74.82 (2*d*), 74.74 (*d*) (C(5$^{I–III}$)); 74.27 (*d*), 74.05 (2*d*) (C(3$^{I–III}$)); 73.16 (*d*, C(2^{IV})); 72.93 (*d*, C(2$^{I–III}$)); 70.19 (*t*, $ArCH_2CH_2$); 69.47 (*d*, C(4^{IV})); 60.58 (*t*), 59.98 (*t*), 59.91 (2*t*) (C(6$^{I–IV}$)); 32.24 (*t*, $ArCH_2$). ESI-MS: 1658 (40, $[2M + NH_4]^+$), 1641 (20, $[2M + 1]^+$), 839 (40), 838 (90, $[M + NH_4]^+$), 822 (40), 821 (100, $[M + 1]^+$).

*2-(Naphthalen-1-yl)ethyl β-*D*-Glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-glucopyranoside* (**41**). A suspension of **36** (46 mg, 0.018 mmol) and 0.29M NaOMe (2 ml, 0.58 mmol) in MeOH (2 ml) was stirred for 3 h. After evaporation, the residue was suspended in H_2O (5 ml) and stirred at r.t. for 24 h. The suspension was neutralized with dil. aq. HCl. soln. and desalted (3×) by centrifugation of the aq. suspension. Lyophilization of the suspension afforded **41** (24 mg, 90%). Solid. M.p. > 300°. ^{1}H-NMR (500 MHz, (D_6)DMSO): see [56]. ^{13}C-NMR (75 MHz, (D_6)DMSO): see [56]. MALDI-MS: 1507 ($[M + K]^+$), 1491 ($[M + Na]^+$).

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside]* (**42**). A suspension of **3** (35 mg, 0.16 mmol), **15** (200 mg, 0.49 mmol), basic zinc carbonate (175 mg, 0.32 mmol), and 3-Å molecular sieves (100 mg) in dry 1,2-dichloroethane (10 ml) was refluxed for 20 h. Filtration, evaporation, and FC (hexane/AcOEt 6:4 → 1:1) gave **42** (110 mg, 77%). Solid. R_f (hexane/AcOEt 1:1) 0.21. M.p. 70°. $[\alpha]_D^{25} = -15.1$ (*c* = 0.33, $CHCl_3$). IR ($CHCl_3$): 3020*s*, 2957*w*, 2882*w*, 1755*s*, 1429*w*, 1367*m*, 1228*s*, 1170*w*, 1039*s*, 908*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.75–7.71 (*m*, 1 arom. H); 7.40–7.33 (*m*, 2 arom. H); 5.14 (*t*, *J* = 9.5, H–C(3^{I})); 5.06 (*t*, *J* = 9.4, H–C(4^{I})); 4.95 (*dd*, *J* = 8.1, 9.1, H–C(2^{I})); 4.44 (*d*, *J* = 7.8, H–C(1^{I})); 4.25 (*dd*, *J* = 4.7, 12.5, H–C(6^{I})); 4.17–4.10 (*m*, $ArCH_2CH$); 4.08 (*dd*, *J* = 2.1, 12.6, H′–C(6^{I})); 3.69 (br. *q*, *J* ≈ 8.0, $ArCH_2CH$); 3.64 (*ddd*, *J* = 2.4, 4.4, 9.6, H–C(5^{I})); 3.45 (*t*, *J* ≈ 6.8, $ArCH_2$); 2.06, 2.00, 1.97, 1.85 (4*s*, 4 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.87, 170.45, 169.59, 169.39 (4*s*, 4 C=O); 136.00 (*s*, C(4a)); 134.26 (*s*, C(1)); 131.36 (*s*, C(8a)); 130.84, 129.29 (2*d*, C(2), C(4)); 125.08 (*d*, C(3)); 100.69 (*d*, C(1^{I})); 72.80 (*d*, C(3^{I})); 71.79 (*d*, C(5^{I})); 71.05 (*d*, C(2^{I})); 70.98 (*t*, $ArCH_2CH_2$); 68.28 (*d*, C(4^{I})); 61.86 (*t*, C(6^{I})); 36.78 (*t*, $ArCH_2$); 20.65 (*q*, Me); 20.49 (*q*, 2 Me); 20.41 (*q*, Me). CI-MS: 895 (47), 894 (100, $[M + NH_4]^+$), 876 (6, M^+), 546 (10), 331 (71), 182 (12), 181 (20), 180 (16), 169 (53), 168 (13), 155 (22), 154 (20), 153 (16). Anal. calc. for $C_{42}H_{52}O_{20}$ (876.86): C 57.53, H 5.98; found: C 57.47, H 6.22.

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside]* (**43**). A suspension of **3** (7.0 mg, 0.032 mmol), **16** (90 mg, 0.128 mmol), basic zinc carbonate (32 mg, 0.058 mmol), and 3-Å molecular sieves (40 mg) in dry toluene (2 ml) was stirred at 110° for 17 h. Filtration, evaporation, and HPLC (hexane/CH_2Cl_2/AcOEt 2 : 3 : 5) gave **43** (35 mg, 74%). Solid. R_f (Et_2O/AcOEt 8 : 2) 0.39. M.p. 94° $[\alpha]_D^{25} = -19.5$ ($c = 0.48$, $CHCl_3$). IR ($CHCl_3$): 3015*m*, 2958*w*, 2873*w*, 1755*s*, 1429*w*, 1367*s*, 1236*s*, 1203*m*, 1166*m*, 1130*m*, 1055*s*, 906*w*, 828*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.74–7.70 (*m*, 1 arom. H); 7.46–7.30 (*m*, 2 arom. H); 5.15 (*t*, $J = 9.3$, H–C(3^I)); 5.11 (*dd*, $J = 9.0$, 9.7, H–C(3^{II})); 5.06 (*t*, $J = 9.5$, H–C(4^{II})); 4.90 (*dd*, $J = 8.1$, 9.1, H–C(2^I)); 4.87 (*dd*, $J = 8.1$, 9.7, H–C(2^{II})); 4.51 (*d*, $J = 8.1$, H–C(1^{II})); 4.48 (*dd*, $J = 1.5$, 12.0, H–C(6^I)); 4.41 (*d*, $J = 7.8$, H–C(1^I)); 4.38 (*dd*, $J = 4.0$, 12.4, H–C(6^{II})); 4.07 (*dd*, $J = 5.0$, 11.6, H′–C(6^I)); 4.03 (*dd*, $J = 2.2$, 12.5, H′–C(6^{II})); 4.12–4.06 (*m*, $ArCH_2CH$); 3.76 (*t*, $J = 9.5$, H–C(4^I)); 3.72–3.64 (*m*, $ArCH_2CH$); 3.65 (*ddd*, $J = 2.0$, 4.2, 9.5, H–C(5^{II})); 3.54 (*ddd*, $J = 1.5$, 4.9, 9.7, H–C(5^I)); 3.42 (*t*, $J \approx 7.0$, $ArCH_2$); 2.09, 2.07, 2.01, 2.00, 1.99, 1.97, 1.86 (7*s*, 7 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72, 170.52, 170.46, 170.02, 169.73, 169.54, 169.29 (7*s*, 7 C=O); 136.02 (*s*, C(4a)); 134.25 (*s*, C(1)); 131.39 (*s*, C(8a)); 130.81, 129.34 (2*d*, C(2), C(4)); 125.08 (*d*, C(3)); 100.83 (*d*, C(1^{II})); 100.55 (*d*, C(1^I)); 76.45 (*d*, C(4^I)); 72.97 (*d*, C(3^{II})); 72.74 (*d*, C(5^I)); 72.52 (*d*, C(3^I)); 71.94 (*d*, C(5^{II})); 71.61 (*d*, C(2^I)); 71.37 (*d*, C(2^{II})); 71.01 (*t*, $ArCH_2CH_2$); 67.81 (*d*, C(4^{II})); 61.92 (*t*, C(6^I)); 61.53 (*t*, C(6^{II})); 36.78 (*t*, $ArCH_2$); 20.80, 20.57 (2*q*, 2 Me); 20.46 (*q*, 5 Me). MALDI-MS: 1491 ($[M + K]^+$), 1475 ($[M + Na]^+$). Anal. calc. for $C_{66}H_{84}O_{36}$ (1453.37): C 54.54, H 5.83; found: C 54.27, H 6.08.

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside]* (**44**). A suspension of **3** (58 mg, 0.27 mmol), **17** (753 mg, 0.74 mmol), basic zinc carbonate (200 mg, 0.36 mmol), and 3-Å molecular sieves (150 mg) in 1,2-dichloroethane (20 ml) was kept for 20 h at 110°. Filtration, evaporation, acetylation in pyridine/Ac_2O 4 : 1 (2.5 ml) at r.t. for 12 h, evaporation, and FC (hexane/AcOEt 3 : 7) gave **44** (320 mg, 59%). Solid. R_f (hexane/AcOEt 2 : 8) 0.38. M.p. 211°. $[\alpha]_D^{25} = -22.6$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3015*w*, 1755*s*, 1429*w*, 1367*m*, 1228*s*, 1164*m*, 1054*m*, 906*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73–7.70 (*m*, 1 arom. H); 7.36–7.30 (*m*, 2 arom. H); 5.114 (*t*, $J = 9.3$), 5.110 (*t*, $J = 9.1$) (H–C(3^I), H–C(3^{II})); 5.08 (*t*, $J = 9.3$, H–C(3^{III})); 5.04 (*t*, $J = 9.5$, H–C(4^{III})); 4.89 (br. *t*, $J \approx 8.4$, H–C(2^{III})); 4.84 (*dd*, $J = 7.8$, 9.2), 4.82 (*dd*, $J = 7.9$, 9.3) (H–C(2^I), H–C(2^{II})); 4.47 (br. *d*, $J \approx 12.0$, H–C(6^I)); 4.46 (*d*, $J = 8.0$, H–C(1^{III}), H–C(1^{II})); 4.38 (*d*, $J = 8.1$, H–C(1^I)); 4.39 (br. *d*, $J \approx 12.0$, H–C(6^{II})); 4.34 (*dd*, $J = 4.4$, 12.7, H–C(6^{III})); 4.13–3.98 (*m*, H′–C(6^I), H′–C(6^{II}), H′–C(6^{III}), $ArCH_2CH$); 3.75 (*t*, $J = 9.3$, H–C(4^I)); 3.72 (*t*, $J = 9.3$, H–C(4^{II})); 3.68–3.48 (*m*, H–C(5^I), H–C(5^{II}), H–C(5^{III}), $ArCH_2CH$); 3.40 (br. *t*, $J \approx 6.9$, $ArCH_2$); 2.11, 2.08, 2.07, 2.02, 1.998, 1.995, 1.98, 1.97, 1.94, 1.84 (10*s*, 10 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.70, 170.48 (2*s*, 2 C=O); 170.40 (*s*, 2 C=O); 169.97 (*s*, 2 C=O); 169.65 (*s*, C=O); 169.51 (*s*, 2 C=O); 169.30 (*s*, C=O); 136.00 (*s*, C(4a)); 134.29 (*s*, C(1)); 131.37 (*s*, C(8a)); 130.79, 129.29 (2*d*, C(2), C(4)); 125.06 (*d*, C(3)); 100.86 (*d*, C(1^{III})); 100.60 (*d*, C(1^{II})); 100.49 (*d*, C(1^I)); 76.48 (*d*, C(4^I)); 76.19 (*d*, C(4^{II})); 72.92 (*d*, C(5^I)); 72.75 (*d*, C(5^{II}), C(3^{II}), C(3^{III})); 72.49 (*d*, C(3^I)); 72.03 (*d*, C(5^{III})); 71.79 (*d*, C(2^{II})); 71.60 (*d*, C(2^I)); 71.44 (*d*, C(2^{III})); 70.93 (*t*, $ArCH_2CH_2$); 67.75 (*d*, C(4^{III})); 62.15 (*t*, C(6^{II})); 61.81 (*t*, C(6^I)); 61.48 (*t*, C(6^{III})); 36.77 (*t*, $ArCH_2$); 20.80, 20.67, 20.57 (3*q*, 3 Me); 20.44 (*q*, 7 Me). MALDI-MS: 2052 ($[M + Na]^+$). Anal. calc. for $C_{90}H_{116}O_{52}$ (2029.88): C 53.25, H 5.76; found: C 53.20, H 5.83.

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside]* (**45**). A suspension of **3** (70 mg, 0.32 mmol), **18** (1500 mg, 1.16 mmol), basic zinc carbonate (350 mg, 0.64 mmol), and 3-Å molecular sieves (300 mg) in dry toluene/1,2-dichloroethane 10 : 1 (55 ml) was kept for 10 h at 110°. Filtration, evaporation, acetylation in pyridine/Ac_2O 5 : 1 (6 ml) at r.t. for 12 h, evaporation, FC (hexane/AcOEt 4 : 6), and HPLC (hexane/AcOEt 1 : 4) gave **45** (478 mg, 56%). White solid. R_f (hexane/AcOEt 2 : 8) 0.42. M.p. 141°. $[\alpha]_D^{25} = -20.4$ ($c = 0.47$, $CHCl_3$). IR ($CHCl_3$): 3034*w*, 3007*w*, 2958*w*, 2876*w*, 1755*s*, 1429*w*, 1367*m*, 1239*s*, 1203*m*, 1163*m*, 1129*m*, 1055*s*, 952*w*, 905*w*, 833*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.74–7.70 (*m*, 1 arom. H); 7.34–7.30 (*m*, 2 arom. H); 5.12 (*t*, $J = 9.3$), 5.095 (*t*, $J = 9.1$), 5.094 (*t*, $J = 9.0$), 5.08 (*t*, $J = 9.3$) (H–C($3^{I–IV}$)); 5.05 (*t*, $J = 9.5$, H–C(4^{IV})); 4.89 (*dd*, $J = 8.0$, 9.3), 4.85 (*dd*, $J = 8.0$, 9.6), 4.82 (*dd*, $J = 7.9$, 9.3), 4.81 (*dd*, $J = 7.9$, 9.3) (H–C($2^{I–IV}$)); 4.47 (*d*, $J = 7.8$), 4.46 (*d*, $J = 7.8$), 4.44 (*d*, $J = 7.8$), 4.38 (*d*, $J = 7.9$) (H–C($1^{I–IV}$)); 4.46 (*dd*, $J \approx 2.2$, 12.0), 4.39 (*dd*, $J \approx 2.0$, 12.0), 4.37 (*dd*, $J \approx 2.5$, 12.0) (H–C($6^{I–III}$)); 4.35 (*dd*, $J = 4.3$, 12.4, H–C(6^{IV})); 4.08 (*dd*, $J = 5.0$, 12.0), 4.05 (*dd*, $J \approx 5.0$, 11.8), 4.04 (*dd*, $J = 5.4$, 11.9) (H′–C($6^{I–III}$)); 4.03 (*dd*, $J = 2.2$, 12.2, H′–C(6^{IV})); 4.07–4.04 (*m*, $ArCH_2CH$); 3.75 (*t*, $J = 9.3$), 3.73 (*t*, $J = 9.3$), 3.72 (*t*, $J = 9.4$) (H–C($4^{I–III}$)); 3.63 (*ddd*, $J = 2.4$, 4.1, 9.9, H–C(5^{IV})); 3.55 (*ddd*, $J = 2.0$, 4.8, 9.5), 3.54 (*ddd*, $J = 2.0$, 5.0, 9.7) (H–C(5^{II}), H–C(5^{III})); 3.51 (*ddd*, $J = 2.2$, 5.0, 10.0, H–C(5^I)); 3.68–3.63 (*m*, $ArCH_2CH$); 3.40 (br. *t*, $J \approx 7.0$, $ArCH_2$); 2.13, 2.12 (2*s*, 2 Ac); 2.08 (*s*, 2 Ac); 2.03, 2.02, 2.00, 1.998, 1.991,

1.97 (6*s*, 6 Ac); 1.94 (*s*, 2 Ac); 1.84 (*s*, Ac). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.49, 170.30, 170.21, 170.19, 170.18, 169.79 (6*s*, 6 C=O); 169.74 (*s*, 2 =O); 169.44, 169.34, 169.30, 169.26, 169.10 (5*s*, 5 C=O); 135.88 (*s*, C(4a)); 134.18 (*s*, C(1)); 131.26 (*s*, C(8a)); 130.68, 129.18 (2*d*, C(2), C(4)); 124.95 (*d*, C(3)); 100.81, 100.57, 100.52, 100.43 (4*d*, C(1^{I-IV})); 76.46, 76.22, 76.09 (3*d*, C(4^{I-III})); 72.90, 72.80, 72.75 (3*d*, C(5^{I-III})); 72.71, 72.68, 72.66, 72.45 (4*d*, C(3^{I-IV})); 72.05 (*d*, C(5^{IV})); 71.88, 71.77, 71.59, 71.41 (4*d*, C(2^{I-IV})); 70.91 (*t*, $ArCH_2CH_2$); 67.76 (*d*, C(4^{IV})); 62.10 (2*t*), 61.85 (*t*), 61.51 (*t*, C(6^{I-IV})); 36.83 (*t*, $ArCH_2$); 21.04, 20.87 (2*q*, 2 Me); 20.78 (*q*, 2 Me); 20.66, 20.58 (2*q*, 2 Me); 20.55 (*q*, 2 Me); 20.53 (*q*, 3 Me); 20.49, 20.48 (2*q*, 2 Me). MALDI-MS: 2645 ($[M+K]^+$), 2628 ($[M+Na]^+$). Anal. calc. for $C_{114}H_{148}O_{68}$ (2606.38): C 52.53, H 5.72; found: C 52.34, H 5.88.

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside]* (**46**). A suspension of **3** (42 mg, 0.194 mmol), **19** (1500 mg, 0.617 mmol), basic zinc carbonate (170 mg, 0.31 mmol), and 3-Å molecular sieves (150 mg) in dry toluene/1,2-dichloroethane 4 : 1 (25 ml) was kept for 24 h at 110°. Evaporation, acetylation in pyridine/Ac_2O 2 : 1 (15 ml) at r.t. for 10 h, evaporation, co-evaporation with toluene, and FC (hexane/AcOEt 3 : 7 → 0 : 1) gave crude **46** (450 mg). Two times HPLC (*CN*, hexane/AcOEt 3 : 7) gave **46** (156 mg, 16%). White solid. R_f (hexane/AcOEt/MeOH 5 : 5 : 1) 0.13. M.p. 180°. $[\alpha]_D^{25} = -12.6$ ($c = 0.83$, $CHCl_3$). IR ($CHCl_3$): 3013*w*, 2955*w*, 2877*w*, 1756*s*, 1429*w*, 1368*m*, 1228*s*, 1162*w*, 1053*m*, 907*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72–7.70 (*m*, 1 arom. H); 7.36–7.25 (*m*, 2 arom. H); 5.20–4.98 (*m*, H–C(3^{I-VIII}), H–C(4^{VIII})); 4.90–4.70 (*m*, H–C(2^{I-VIII})); 4.48–4.24 (*m*, H–C(1^{I-VIII}), H–C(6^{I-VIII})); 4.10–3.94 (*m*, H′–C(6^{I-VIII}), $ArCH_2CH$); 3.78–3.32 (*m*, H–C(4^{I-VII}), H–C(5^{I-VIII}), $ArCH_2CH$, $ArCH_2$); 2.09–1.90 (*m*, 25 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.59, 170.40 (2*s*, 2 C=O); 170.32 (*s*, 7 C=O); 169.85 (*s*, 7 C=O); 169.44 (*s*, C=O); 169.40 (*s*, 7 C=O); 169.18 (*s*, C=O); 135.91 (*s*, C(4a)); 134.21 (*s*, C(1)); 131.22 (*s*, C(8a)); 130.71, 129.19 (2*d*, C(2), C(4)); 124.97 (*d*, C(3)); 100.77 (*d*), 100.48 (7*d*) (C(1^{I-VIII})); 76.37 (*d*), 76.00 (6*d*) (C(4^{I-VII})); 72.72 (8*d*), 72.46 (7*d*), 71.94 (*d*) (C(3^{I-VIII}), C(5^{I-VIII})); 71.75 (7*d*), 71.49 (*d*) (C(2^{I-VIII})); 70.73 (*t*, $ArCH_2CH_2$); 67.64 (*d*, C(4^{VIII})); 61.94 (7*t*), 61.41 (*t*, C(6^{I-VIII})); 36.66 (*t*, $ArCH_2$); 20.87–20.28 (several *q*, 25 Me). MALDI-MS: 4935 ($[M+Na]^+$), 4893 ($[M-Ac+Na]^+$), 4876 ($[M-AcO+Na]^+$). Anal. calc. for $C_{210}H_{276}O_{132}$ (4912.38): C 51.35, H 5.66; found: C 50.78, H 5.42.

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis(β-*D*-glucopyranoside)* (**47**). As described for **37**, with **42** (477 mg, 0.54 mmol), 5.78M NaOMe (0.25 ml), and MeOH (25 ml), 2 h: **47** (273 mg, 93%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1 : 1). Solid. R_f (*RP-18*, MeOH/H_2O 1 : 1) 0.31. M.p. 184–187°. $[\alpha]_D^{25} = -29.8$ ($c = 0.50$, H_2O). IR (KBr): 3355*s* (br.), 2944*m*, 2888*m*, 1638*w*, 1600*w*, 1466*m*, 1427*m*, 1366*m*, 1249*m*, 1155*s*, 1076*s* (br.), 1035*s* (br.), 885*w*, 839*w*, 810*w*. ^{1}H-NMR (500 MHz, D_2O; assignment based on homonuclear decoupling experiments): 7.77 (*dd*, $J = 1.7$, 7.8), 7.39 (*dd*, $J = 1.5$, 7.0), 7.34 (*dd*, $J = 7.0$, 7.7) (3 arom. H); 4.27 (*d*, $J = 7.9$, H–C(1^I)); 4.00 (*td*, $J = 7.5$, 9.9, $ArCH_2CH$); 3.78 (*dd*, $J = 2.1$, 12.2, H–C(6^I)); 3.80–3.73 (*m*, $ArCH_2CH$); 3.61 (*dd*, $J = 5.3$, 11.8, H′–C(6^I)); 3.44 (*t*, $J \approx 7.5$, $ArCH_2$); 3.36 (*dd*, $J = 8.4$, 9.1, H–C(3^I)); 3.30 (*dd*, $J = 8.4$, 9.6, H–C(4^I)); 3.26 (*ddd*, $J = 2.0$, 5.4, 9.7, H–C(5^I)); 3.17 (*dd*, $J = 8.0$, 9.1, H–C(2^I)). ^{13}C-NMR (75 MHz, D_2O): 135.87 (*s*, C(4a)); 134.19 (*s*, C(1)); 131.06 (*s*, C(8a)); 130.94, 129.46 (2*d*, C(2), C(4)); 125.71 (*d*, C(3)); 102.40 (*d*, C(1^I)); 75.96 (*d*, C(5^I)); 75.83 (*d*, C(3^I)); 73.18 (*d*, C(2^I)); 71.19 (*t*, $ArCH_2CH_2$); 69.62 (*d*, C(4^I)); 60.72 (*t*, C(6^I)); 36.59 (*t*, $ArCH_2$). ESI-MS: 563 (100, $[M+Na]^+$), 558 (15, $[M+NH_4]^+$).

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[β-*D*-glucopyranosyl-(1 → 4)-β-*D*-glucopyranoside]* (**48**). A suspension of **43** (293 mg, 0.20 mmol) and 5.78M NaOMe (0.1 ml, 0.57 mmol) in MeOH (10 ml) was stirred for 1 h. After evaporation, the residue was suspended in H_2O (10 ml), stirred for 12 h, and neutralized with *Amberlite-IR 120* (H^+ form). Filtration and evaporation gave **48** (171 mg, 98%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1 : 1). Solid. R_f (*RP-18*, MeOH/H_2O 1 : 1) 0.36. M.p. 199–201°. $[\alpha]_D^{25} = -18.2$ ($c = 0.50$, H_2O). IR (KBr): 3405*s* (br.), 2881*m*, 1646*w* (br.), 1599*w*, 1581*w*, 1426*m* (br.), 1373*m*, 1256*m*, 1160*s*, 1024*s* (br.), 894*m*, 816*w*. ^{1}H-NMR (500 MHz, D_2O): 7.79 (br. *d*, $J = 8.0$), 7.42 (br. *d*, $J = 7.0$), 7.38 (*dd*, $J = 7.1$, 7.7) (3 arom. H); 4.42 (*d*, $J = 8.0$, H–C(1^{II})); 4.32 (*d*, $J = 7.9$, H–C(1^I)); 4.03 (*td*, $J \approx 7.5$, 9.8, $ArCH_2CH$); 3.85 (*dd*, $J = 2.2$, 12.5, H–C(6^I)); 3.83 (*dd*, $J = 2.1$, 12.4, H–C(6^{II})); 3.82–3.76 (*m*, $ArCH_2CH$); 3.70 (*dd*, $J = 4.9$, 12.3, H′–C(6^I)); 3.67 (*dd*, $J = 5.7$, 12.4, H′–C(6^{II})); 3.55 (*dd*, $J = 8.9$, 9.4, H–C(4^I)); 3.51 (*t*, $J = 8.9$, H–C(3^I)); 3.51–3.41 (*AB* of *ABMX*, $ArCH_2$); 3.44 (*t*, $J = 9.2$, H–C(3^{II})); 3.41 (*ddd*, $J = 2.3$, 5.7, 9.6, H–C(5^{II})); 3.35 (*dd*, $J = 9.1$, 9.7, H–C(4^{II})); 3.43–3.37 (*m*, H–C(5^I)); 3.24 (*dd*, $J = 8.1$, 9.2, H–C(2^{II})); 3.22 (*dd*, $J = 8.2$, 9.2, H–C(2^I)). ^{13}C-NMR (75 MHz, D_2O): 135.87 (*s*, C(4a)); 134.15 (*s*, C(1)); 131.08 (*s*, C(8a)); 131.08, 129.48 (2*d*, C(2), C(4)); 125.71 (*d*, C(3)); 102.70 (*d*, C(1^{II})); 102.22 (*d*, C(1^I)); 78.65 (*d*, C(4^I)); 76.07 (*d*, C(5^{II})); 75.60 (*d*, C(3^{II})); 74.78 (*d*, C(5^I)); 74.39 (*d*, C(3^I)); 73.24 (*d*, C(2^{II})); 72.94 (*d*, C(2^I)); 71.25

(*t*, $AcCH_2CH_2$); 69.52 (*d*, C(4^{II})); 60.61 (*t*, C(6^{II})); 60.01 (*t*, C(6^{I})); 36.58 (*t*, $ArCH_2$). ESI-MS: 1746 (10, $[2M+NH_4]^+$), 882 (100, $[M+NH_4]^+$), 865 (17, $[M+1]^+$).

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranoside]* (**49**). As described for **39**, with **44** (210 mg, 0.10 mmol) and 5.78M NaOMe (0.1 ml, 0.57 mmol) in H_2O (5 ml), 15 h: **49** (112 mg, 95%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1:1). White solid. R_f (*RP-18*, MeOH/H_2O 2:8) 0.38. M.p. >300° (dec.). $[\alpha]_D^{25} = -15.9$ ($c = 0.42$, H_2O). IR (KBr): 3409*s* (br.), 2889*s*, 1646*m* (br.), 1427*s*, 1375*s*, 1311*s*, 1259*s*, 1161*s*, 1045*s* (br.), 898*m*. ^{1}H-NMR (500 MHz, D_2O): 7.78 (br. *d*, $J = 7.3$, 1 arom. H); 7.49–7.36 (*m*, 2 arom. H); 4.44 (*d*, $J = 7.9$), 4.43 (*d*, $J = 7.9$), 4.30 (*d*, $J = 8.0$) (H–C(1^{I}), H–C(1^{II}), H–C(1^{III})); 4.02 (*td*, $J \approx 7.5$, 10.0, $ArCH_2CH$); 3.90 (*dd*, $J = 2.1$, 12.4, H–C(6^{II})); 3.85 (*dd*, $J = 2.2$, 12.4), 3.82 (br. *d*, $J \approx 12.0$) (H–C(6^{I}), H–C(6^{III})); 3.83–3.77 (*m*, $ArCH_2CH$); 3.75 (*dd*, $J = 4.9$, 12.4, H′–C(6^{II})); 3.70 (*dd*, $J = 5.0$, 12.3, H′–C(6^{I})); 3.67 (*dd*, $J = 5.8$, 12.3, H′–C(6^{III})); 3.60 (*t*, $J = 9.0$, H–C(4^{II})); 3.57 (*t*, $J = 9.1$, H–C(4^{I})); 3.55 (*t*, $J = 8.9$, H–C(3^{II})); 3.51 (*t*, $J = 8.9$, H–C(3^{I})); 3.56–3.52 (*m*, H–C(5^{II})); 3.51–3.41 (*AB* of *ABMX*, $ArCH_2$); 3.44 (*t*, $J = 9.1$, H–C(3^{III})); 3.43–3.38 (*m*, H–C(5^{I})); 3.42 (*ddd*, $J = 2.2$, 4.7, 9.8, H–C(5^{III})); 3.35 (*t*, $J \approx 9.3$, H–C(4^{III})); 3.29 (*dd*, $J = 8.1$, 9.7, H–C(2^{II})); 3.25 (*dd*, $J = 8.0$, 9.4), 3.22 (*dd*, $J = 8.0$, 9.0) (H–C(2^{I}), H–C(2^{III})). ^{13}C-NMR (75 MHz, D_2O): 135.85 (*s*, C(4a)); 134.15 (*s*, C(1)); 131.06 (*s*, C(8a)); 130.94, 129.46 (2*d*, C(2), C(4)); 125.70 (*d*, C(3)); 102.71, 102.47, 102.21 (3*d*, C(1^{I}), C(1^{II}), C(1^{III})); 78.50 (*d*, C(4^{I}), C(4^{II})); 76.07 (*d*, C(5^{III})); 75.57 (*d*, C(3^{III})); 74.89, 74.78 (2*d*, C(5^{I}), C(5^{II})); 74.34, 74.16 (2*d*, C(3^{I}), C(3^{II})); 73.22 (*d*, C(2^{III})); 73.09, 72.93 (2*d*, C(2^{I}), C(2^{II})); 71.22 (*t*, $ArCH_2CH_2$); 69.52 (*d*, C(4^{III})); 60.63 (*t*, C(6^{III})); 59.94 (*t*, C(6^{I}), C(6^{II})); 36.56 (*t*, $ArCH_2$). ESI-MS: 1212 (60), 1211 (100, $[M+Na]^+$).

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl) Bis[β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranoside]* (**50**). As described for **39**, with **45** (150 mg, 0.057 mmol), 0.067M NaOMe (1 ml, 0.067 mmol), and H_2O (5 ml, 15 h): **50** (78 mg, 90%) which was further purified by reversed-phase HPLC (MeOH/H_2O 1:1). White solid. R_f (*RP-18*, MeOH/H_2O 1:1) 0.40. M.p. >300°. $[\alpha]_D^{20} = -14.8$ ($c = 0.50$, H_2O). IR (KBr): 3417*s* (br.), 2910*s*, 1652*w*, 1428*s*, 1377*s*, 1312*s*, 1258*s*, 1161*s*, 1051*s*, 889*s*, 820*m*. ^{1}H-NMR (500 MHz, D_2O): 7.78 (br. *d*, $J = 7.5$, 1 arom. H); 7.41–7.35 (*m*, 2 arom. H); 4.46 (*d*, $J = 7.7$), 4.45 (*d*, $J = 7.8$), 4.44 (*d*, $J = 8.0$) (H–C(1^{II-IV})); 4.31 (*d*, $J = 8.0$, H–C(1^{I})); 4.01 (*td*, $J \approx 7.4$, 9.9, $ArCH_2CH$); 3.91 (*dd*, $J = 1.7$, 12.5, 2 H), 3.85 (*dd*, $J = 1.9$, 12.4), 3.83 (*dd*, $J = 1.8$, 12.1) (H–C(6^{I-IV})); 3.82–3.76 (*m*, $ArCH_2CH$); 3.76 (*dd*, $J = 4.5$, 12.4, 2 H), 3.71 (*dd*, $J = 4.8$, 12.4), 3.68 (*dd*, $J = 5.7$, 12.7) (H′–C(6^{I-IV})); 3.64–3.53 (*m*, H–C(3^{II-III}), H–C(4^{I-III}), H–C(5^{II-III})); 3.51 (*t*, $J = 8.9$, H–C(3^{I})); 3.45 (*t*, $J = 9.1$, H–C(3^{IV})); 3.49–3.38 (*m*, H–C(5^{I}), H–C(5^{IV}), $ArCH_2$); 3.35 (*dd*, $J = 9.2$, 9.6, H–C(4^{IV})); 3.30 (*dd*, $J = 8.0$, 9.0), 3.29 (*dd*, $J = 8.0$, 9.0), 3.25 (*dd*, $J = 8.1$, 9.3), 3.23 (*dd*, $J = 8.2$, 9.2) (H–C(2^{I-IV})). ^{13}C-NMR (125 MHz, D_2O): 135.66 (*s*, C(4a)); 133.97 (*s*, C(1)); 130.84 (*s*, C(8a)); 130.78, 129.26 (2*d*, C(2), C(4)); 125.52 (*d*, C(3)); 102.58 (*d*), 102.36 (2*d*), 102.09 (*d*) (C(1^{I-IV})); 78.48, 78.44, 78.32 (3*d*, C(4^{I-III})); 76.00 (*d*, C(5^{IV})); 75.51 (*d*, C(3^{IV})); 74.82 (2*d*), 74.29 (*d*) (C(5^{I-III})); 74.29 (*d*), 74.07 (2*d*) (C(3^{I-III})); 73.16 (*d*, C(2^{IV})); 72.94 (2*d*), 72.86 (*d*) (C(2^{I-III})); 71.14 (*t*, $ArCH_2CH_2$); 69.47 (*d*, C(4^{IV})); 60.60 (2*t*), 59.94 (2*t*) (C(6^{I-IV})); 36.53 (*t*, $ArCH_2$). ESI-MS: 1531 (64), 1530 (59, $[M+NH_4]^+$), 1513 (15, $[M+1]^+$), 774 (51).

*[(Naphthalene-1,8-diyl)di(ethane-2,1-diyl)] Bis[β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→4)-β-*D*-glucopyranoside]* (**51**). A suspension of **46** (156 mg, 0.043 mmol) and 5.78M NaOMe (0.4 ml, 2.31 mmol) in H_2O (8 ml) was stirred at r.t. for 12 h. The suspension was neutralized with aq. HCl soln. and desalted (4×) by centrifugation of the aq. suspension. The precipitate was collected and dried to give **51** (74 mg, 65%). ^{1}H-NMR (500 MHz, (D_6)DMSO): see [56]. ^{13}C-NMR (75 MHz, (D_6)DMSO): see [56]. MALDI-MS (20 mg of **51** and 30 mg of LiCl were dissolved in 1 ml of *N,N*-dimethylacetamide): 2817 ($[M+Li]^+$), 2526.

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