A Practical Synthesis of Benzyl α- and Allyl β-D-Glucopyranosides Regioselectively Substituted with $(CH_2)_3OH$ Groups: Stereocontrolled β-Galactosidation by Cation π-Interaction

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

Abstract: In a simple and efficient two-step reaction, the 2,3- and 4,6-di-*O*-hydroxypropyl regioselectively-functionalized glucose derivatives, **5**, **12** and **13** were synthesized by reaction of the allyl 4,6-*O*-benzylidene-β-D-glucopyranoside **(1)**, allyl 2,3-di-*O*-benzyl-β-D-glucopyranoside **(6)** and benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside **(7)** with 2-(3-bromopropoxy)tetrahydro-2*H*-pyran (BPTHP), followed by removal of the tetrahydropyranyl groups using pyridinium *p*-toluenesulfonate (PPTS). Reaction of **1** with 2-(3-bromopropoxy)tetrahydro-2*H*-pyran led to a mixture of three reaction products **2–4**. The major product **2** separated by column chromatography, was treated with PPTS to give allyl 4,6-*O*-benzylidene-2,3-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside **(5)**. In contrast to **3** and **4**, the regioisomers **10** and **11** could be separated and isolated in high yield. Compound **15** was synthesized by selective protection of the *O*-6 position with *tert*-butyldiphenylsilyl chloride and functionalization with BPTHP. Subsequent deprotection using TBAF led to **11**. The highly β-stereoselective galactosylation of **12** with 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl difluorophosphate **16** led to the allyl 2,3-di-*O*-benzyl-4,6-di-*O*-[3-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-oxypropyl)]-β-D-glucopyranoside **(17)**.

Key words: carbohydrates, spacer groups, glucopyranosides

Specific interactions of carbohydrate ligands and lectin receptors have recently received much attention,[1] because they represent a key step in many biological recognition processes.[1] As a direct consequence of these properties, considerable attention has been focused on the development of carbohydrate-centered multivalent glycomimetics, such as glycoclusters and glycodendrimers[2] or spacer-modified oligosaccharides[3] in many different forms with species whose molecular structures are comparable, in their sites and shapes, to biomolecules. These have recently been shown to serve as high affinity ligands in many carbohydrate-protein interactions due to the "multivalency effect",[4] their spacing and flexibility[1,5] playing a central role in such interactions.

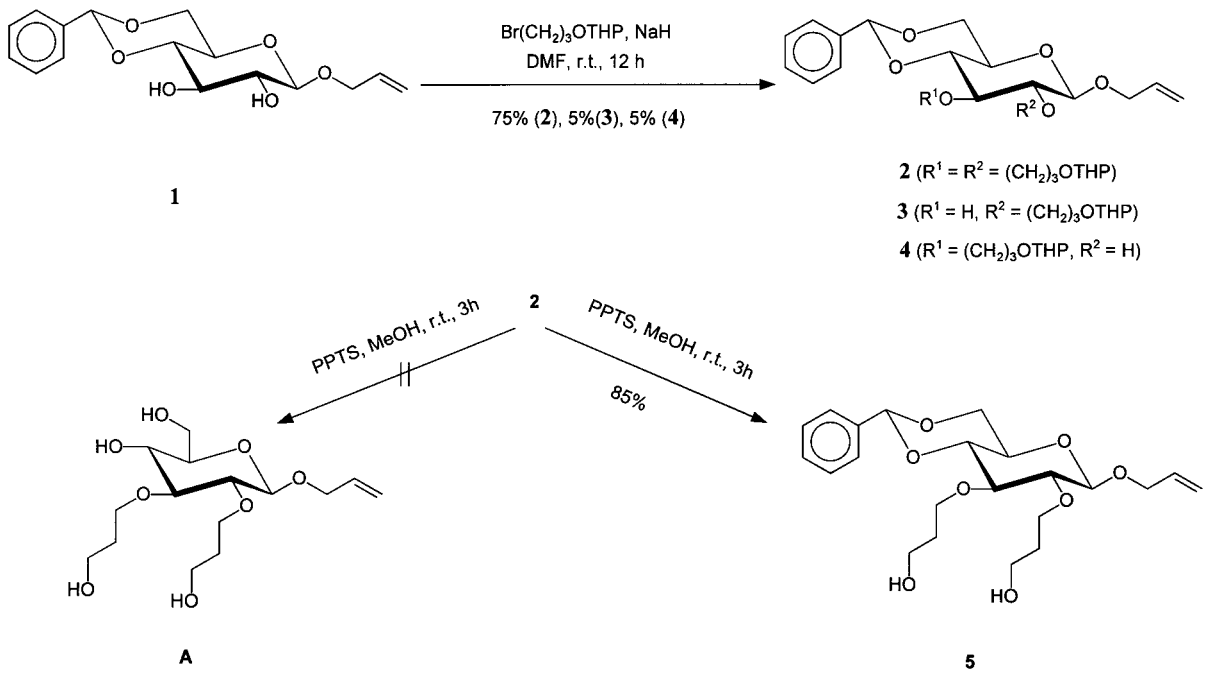
The chemistry of spacer-modified monosaccharides or multiantennary oligosaccharides from *O*-protected and *O*-unprotected sugars has been employed in many cases and is well described.[2g,3,6] However, the synthesis of (1→4)–(1→6)-linked di- or multiantennary oligosaccharides in which the glucose backbone involves multiple *O*-attachment of the sugar moiety through $(CH_2)_3O$-spacers[7] and allyl- or aminoalkyl groups located at the anomeric center, has not yet been investigated. This is due to the lack of efficient methods for the preparation of glycosyl acceptors bearing $HO(CH_2)_3O$-groups and allyl- or aminopropyl groups, the latter bonded stereoselectively to the anomeric center and acting as spacer groups for the binding to the solid phase.

In general, there are many strategies for the substitution of glucose with $(CH_2)_nOH$ groups; for example: allylation with allyl chloride under the conditions of inverse phase transfer catalysis[3f,8] and subsequent hydroboration with bis[3-methylbut-2-yl]borane,[3f,9] treatment of glucose with allyl alcohol and $BF_3.OEt_2$ and ozonolysis,[3f,10a,b] reaction of glucose derivatives with alkyl dichlorides and subsequent basic hydrolysis to hydroxy compounds[6a] or the fluorination of 1,2-*O*-ethanediyl-β-D-glucopyranoside with HF and subsequent basic solvolysis with sodium methanolate.[6b] However, our attempt to use these strategies for the preparation of allyl 4,6-di-*O*-benzylidene-2,3-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside **(5)** or allyl 2,3-di-*O*-benzyl-4,6-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside **(12)** failed, because the conversion of the allyl groups of the perallylated glucoside derivative[3f] into 3-hydroxypropyl spacers by the methods mentioned above could not be performed regioselectively.

We report here the substitution of anomerically pure allyl 4,6-*O*-benzylidene-β-D-glucopyranoside **(1)**,[11] allyl 2,3-di-*O*-benzyl-β-D-glucopyranoside **(6)**[12] and benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside **(7)**[13,14] with $(CH_2)_3OH$ groups, using 2-(3-bromopropoxy)tetrahydro-*2H*-pyran (BPTHP).[15] In order to investigate spacer-modified oligosaccharides as affinity ligands in the isolation of tumor cell lectins via affinity chromatography, the synthesis of a prototype **17** has been described.

It is known that glycosyl donors having phosphorous containing groups at the anomeric center allow the glycosylation of glycosyl acceptors under mild conditions without the use of strong Lewis acids.[16] In the present case we describe an efficient method for the highly β-stereoselective galactosylation of **12** using 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl difluorophosphate **(16)** as galactosyl donor.

According to Scheme 1, compound **2** was prepared from **1**[11] using an excess of BPTHP[15] in DMF in the presence of



Scheme 1

sodium hydride at room temperature. TLC investigation of the reaction solution exhibited a mixture of three reaction products **2–4** (Scheme 1) with different degrees of substitution. HPLC measurements revealed the derivative **2** as the major product in the mixture mentioned above. The allyl β-D-glucopyranoside derivative **2** was separated in high yield by silica gel column chromatography (Table 1), whereas the compounds **3** and **4** could only be isolated as a mixture.

Treatment of **2** with PPTS (acidic catalyst) in methanol at room temperature did not yield the expected allyl 2,3-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside **A**, instead the 4,6-benzylidene-protected derivative **5** was obtained in high yield via chemoselective removal of the terminal THP-groups which was purified by column chromatography (Table 1).

Similarly, the known derivatives **6**[12] and **7**[13,14] were converted by reaction with BPTHP[15] under the conditions described above into compounds **8–11** (Scheme 2). The products **12** and **13** were obtained by acid-catalyzed (PPTS[15]) removal of the THP-groups in **8** and **9**. After column chromatography purification, either the β- or the α-form of the glucopyranosides **8–13** were obtained exclusively in good yields (Table 1). In contrast to **3** and **4** (Scheme 1), the regioisomers **10** and **11** (Scheme 2) could be separated by silica gel column chromatography in high yield (Table 1). The marked difference in the polarity generated by unsymmetrically substituted *O*-4 and *O*-6 positions with $(CH_2)_3$OTHP groups permits the efficient separation of both regioisomers **10** and **11**.

The *O*-6 selective silylation of the known 4,6-*O*-unprotected derivative **7**[13,14] with *tert*-butyldiphenylsilyl chloride (TBDS)[17a,b,d] in the presence of imidazole leads to **14**. By *O*-4 alkylation of **14** with BPTHP in the presence of NaH and subsequent *O*-6 desilylation with $(Bu)_4N^+F^-$, the regioisomer **11** (via **15**, Scheme 3) is formed exclusively.

The structures of spacer-modified glucopyranosides **5**, **12** and **13** could be unequivocally confirmed by means of NMR spectroscopy and MS spectrometry. According to ^{1}H and ^{13}C NMR evidence, compounds **5**, **12** and **13** show doublets in the range of δ = 4.2–4.8 for the anomeric proton. The coupling constants ($^3J_{HH} \approx 8$ Hz) confirmed the β-configuration. By 2D-COLOC investigations, cross peaks ($^3J_{CH}$) between the protons of the spacer groups (in the case of **10** to the 6-C and in the case of **11** to the 4-C atom of the glucose backbone) could be observed. Thus, a specific assignment of the molecular structure via the connectivity of the spacer groups to the glucose backbone was now possible. In most cases, the protons of the propyl groups of the diols mentioned above are strongly coupled and are diastereotopic, leading to a general spin system [ABCDEF]. For the assignment of all protons, CH-correlation or HMQC spectra were used, because overlapping multiplets did not allow a simple assignment from routine 1D NMR spectra. Compounds **5, 12** and **13** are not only attractive building blocks in the synthesis of asymmetric diantennary or tetraantennary oligosaccharides, but also

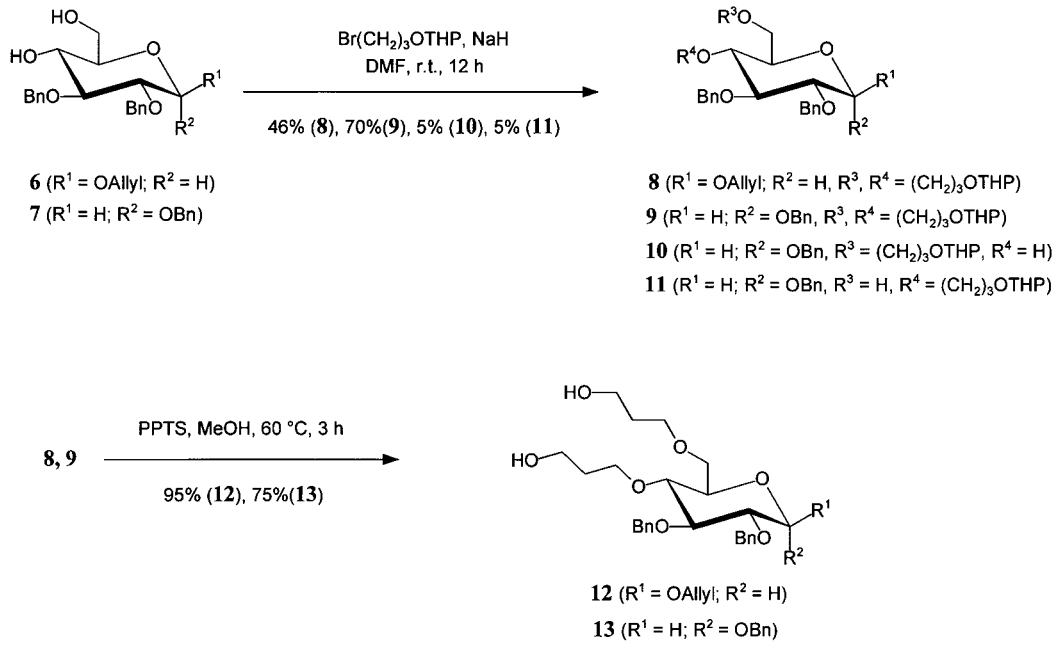
Table 1 Experimental Data for the Preparation of **2–5**, **9–13**

Starting Materials:[a] g (mmol)	Product(s)	Yield g (%)	R_f-values (solvents)[b]
1: 0.5 (1.5), BPTHP: 1.0 (4.6), NaH: 0.2 (9.3)	**2, 3** and **4**	**2**: 0.7 (75) **3**: 0.05 (5) **4**: 0.05 (5)	**2**: 0.4 (Et_2O/PE, 2:1) **3**: 0.3 (Et_2O/PE, 2:1) **4**: 0.3 (Et_2O/PE, 2:1)
6: 6.0 (15.0), BPTHP: 10.0 (45.0), NaH: 2.2 (90.0)	**8**	4.7 (46)	0.6 (Et_2O/PE, 2:1)
7: 0.5 (1.1), BPTHP: 0.7 (3.3), NaH: 0.2 (9.3)	**9, 10** and **11**	**9**: 0.6 (70) **10**: 0.04 (5) **11**: 0.04 (5)	**9**: 0.5 (Et_2O/PE, 2:1) **10**: 0.4 (Et_2O/PE, 2:1) **11**: 0.3 (Et_2O/PE, 2:1)
2: 0.3 (0.5), PPTS: 0.4 (1.4)	**5**	0.2 (85)	0.1 (Et_2O)
8: 3.4 (5.0), PPTS: 4.0 (15.7)	**12**	2.4 (95)	0.9 (EtOH)
9: 2.0 (2.7), PPTS: 2.1 (8.2)	**13**	1.1 (75)	0.2 (Et_2O)

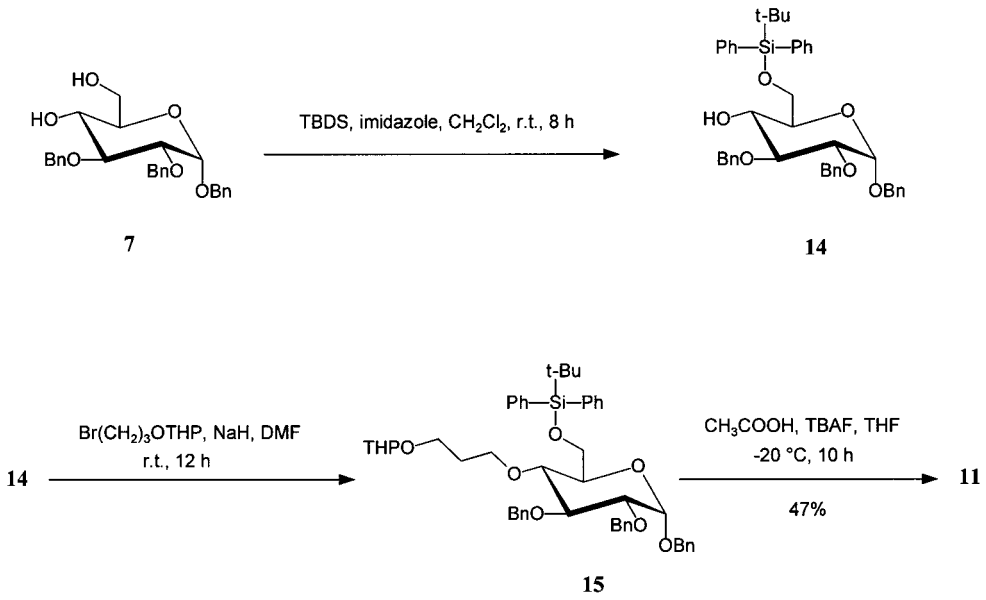
[a] cf. Schemes 1 and 2. BPTHP = 2-(3-bromopropoxy) tetrahydro-2*H*-pyran. PPTS: pyridinium *p*-toluenesulfonate.
[b] PE = petroleum ether.

should be a suitable precursor for the preparation of neoglycoconjugates by solid-phase synthesis or for a solid-phase carbohydrate library.[17d] It is our aim to synthesize diantennary, β, β-selectively functionalized oligosaccharides from **12**.

We have already described the synthesis of allyl 2,3-di-*O*-benzyl-4,6-di-*O*-[3-(β-D-galactopyranosyloxypropyl)]-β-D-glucopyranoside **(17)**,[7a] using 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl trichloroacetimidate[19] as galactosyl donor and **12** as glucosyl acceptor.[7a] However, by this method a mixture of anomers of **17** was formed (β,β,β/



Scheme 2



Scheme 3

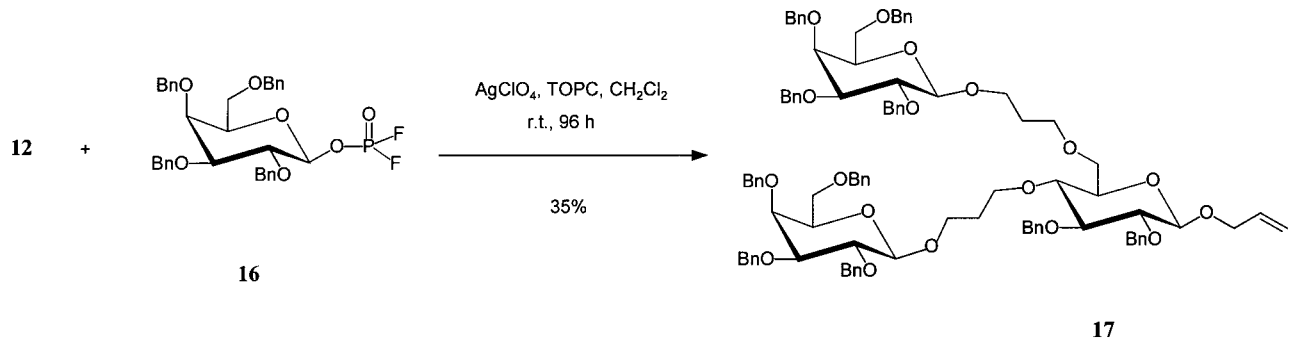
β,β,α/β,α,β), which could not be separated by column chromatography. Therefore, we have synthesized the new galactosyl donor **16** employing difluorophosphate[20] as anomeric leaving group by reaction of trimethylsilyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside[17c] with phosphorus oxyfluoride in the presence of phosphorus pentafluoride.

By using **16** as galactosyl donor, with $AgClO_4$ added to activate the leaving group and tetra-*O*-propylated cone-calix[4]arene[21] (TOPC) for its stabilizing effect by cation-π-interaction,[22] a β-stereoselective galactosylation of the anomerically pure compound **12** to **17** could be conducted successfully (Scheme 4). The crude product was purified by silica gel column chromatography leading exclusively to the β,β,β-isomer.

According to ^1H and ^{13}C NMR evidence, a stereospecific course of galactosylation was observed. Compound **17** display typical coupling constants ($^3J_{HH} \approx 8$ Hz) for the anomeric protons due to the exclusively β-configuration at all anomeric centers. The modification of allyl group functions by galactosylation reaction was not observed.

This highly efficient β-stereoselectivity may be explained by the complexation ability of TOPC through cation-π-interaction.[22] However, due to the intramolecular complexation-decomplexation equilibrium[22] in the cone-TOPC-$AgClO_4$ complex, Ag^+ is capable of activating the leaving group.

The results of the investigations of the TOPC-oxonium complex by computional studies and NMR spectroscopy indicate that the cationic guest is selectively included in the cone cavity and that the preorganization of the benzene rings is indispensable to the formation of the "cation-π- and π-π-interactions".[23]



Scheme 4

We assume that the reaction involves a β-nucleophilic attack on the anomeric center, probably due to two factors:1) the stabilization of the glycosyl cation by complexation at the α-face and 2) the π-π-interaction between *O*-2 benzyl group of the oxocarbenium cation and TOPC by the electron-rich faces of host aromatic rings.

In conclusion, the results presented here provide an efficient synthesis of the 2,3- or 4,6-di-*O*-hydroxypropyl-functionalized glucose derivatives **5**, **12** and **13**. These compounds represent potential precursors for the synthesis of multiantennary oligosaccharides as for example **17**. We have developed a new method for the β-stereoselective galactosylation bearing galactosyl difluorophosphate as galactosyl donor and TOPC as stabilizator for the oxocarbenium ion. The latter compound is intended to serve (via immobilization on solid phase and subsequent deprotection) as affinity ligand in the isolation of tumour cell lectins via affinity chromatography.

NMR spectra were recorded on a Bruker AC 400 spectrometer and on a Bruker DMX 600 spectrometer with inverse probe head. Chemical shifts (δ) are given in ppm downfield from TMS. Coupling constants are given in Hz. Many assignments were made with support of DEPT, $^1H^1H$-COSY, $^1H^{13}C$-COSY, HMQC, HMBC and TOCSY experiments. Mass spectra (ESI) were recorded using a Finnigan MAT TSQ 700 triple quadrupole mass spectrometer equipped with a NanoES ion source. Elemental analyses were conducted at the Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig. TLC was performed on silica gel 60 F_{254} coated foil (Merck). Preparative column chromatography was performed with silica gel 60 (63–200 μm, Merck).

Estherification of Glucosides 1, 6 and 7 with 2-(3-Bromopropoxy)tetrahydro-2*H*-pyran (BPTHP); General Procedure

Under N_2 atmosphere, compounds **1**[11], **6**[12] and **7**[13,14] (Table) were dissolved in anhyd DMF (60 mL). To these solutions, the corresponding amounts of NaH [freshly washed with anhyd hexane (20 mL), Table] were added. The suspensions were stirred at r.t. for 30 min. After cooling to 0 °C, BPTHP[15] was added within 2 min (Table). After stirring at r.t. for 12 h, EtOH (10 mL) and H_2O (20 mL) were added. The products were extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were separated and dried (Na_2SO_4). After filtration, the solvents were evaporated in vacuo. The residues were purified by silica gel column chromatography (eluent: Et_2O/hexane, 3:1, v/v), leading to the expected products **2, 8–11** in oily consistence (Table 1). Compounds **3** and **4** could only be isolated as a mixture of regioisomers.

Regioselective Synthesis of Compound 11

A solution of **7**[13,14] (6.0 g, 15.0 mmol), imidazole (2.0 g, 30 mmol) and *tert*-butyldiphenylsilyl chloride (4.9 g, 18 mmol) in CH_2Cl_2 (20 mL) was stirred for 8 h at r.t. under N_2 atmosphere. Subsequently, H_2O (40 mL) were added and the two layers were separated. The organic layer was dried (Na_2SO_4). After filtration, the solvent was evaporated in vacuo and the oily residue was dissolved in anhyd DMF (10 mL). To this solution, the corresponding amount of NaH (0.7 g, 30 mmol, freshly washed with dry hexane (20 mL)) was added. The suspension was stirred at r.t. for 30 min. Subsequently, it was cooled to 0 °C and BPTHP[15] (4.5 g, 20 mmol) was added within 2 min. After stirring for 12 h, EtOH (10 mL) and H_2O (20 mL) were added to the reaction mixture. The product was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was separated and dried (Na_2SO_4). After filtration, the solvent was evaporated in vacuo. The residue was dissolved in anhyd THF (20 mL) and molecular sieves (4 Å) were added. After stirring for 30 min at r.t., AcOH (0.05 mL) and a solution of Bu_4NF in THF (1 mL, 1 M) was added at –20 °C. After stirring for 10 h at this temperature, the mixture was poured onto ice water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic solutions were dried and the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography (eluent: Et_2O/hexane, 2:1, v/v), leading to the expected product **11** with oily consistency; yield:4.2 g (47%).

Deprotection of 2, 8 and 9 with Pyridinium *p*-Toluenesulfonate (PPTS); General Procedure

In a three-necked round-bottom flask, fitted with a reflux-condenser, the starting compound (**2, 8** and **9**, respectively) and PPTS[15] (amounts, see Table) were dissolved in anhyd MeOH (40 mL). The solution was stirred for 3 h at 60 °C. Subsequently, satd aq $NaHCO_3$ solution (50 mL) was added. The reaction product was extracted with $CHCl_3$ (3 x 100 mL). The organic layer was separated and dried (Na_2SO_4). The solvent was evaporated in vacuo and the oily residue was purified by silica gel column chromatography (eluent: Et_2O). In this manner, all byproducts were removed from the column. The products **5, 12** and **13** were obtained by washing the silica gel with ethanol. Subsequently, the solvent was removed in vacuo. The oily reaction products remained in pure form (Table 1).

Allyl 4,6-*O*-Benzylidene-2,3-di-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-β-D-glucopyranoside (2)

^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.41–7.20 (m, 20 H, arom), 5.85 (m_c ≈ dddd, 4 H, OCH_aH_bCH = CH_cH_d), 5.45 (s, 4 H, C*H*Ph), 5.24 (m_c ≈ dddd, 4 H, OCH_aH_bCH = CH_cH_d), 5.13 (m_c ≈ dddd, 4 H, OCH_aH_bCH = CH_cH_d), 4.41 and 4.51 (m_c ≈ t, 8 H, 1-C_{THP}H), 4.36 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, 1-H_{gluc}), 4.29 (m_c ≈ dddd, 4 H, OCH_aH_bCH = CH_cH_d), 4.24 (m_c, 4 H, 6-$C_{gluc}H_aH_b$), 4.05 (m_c ≈ dddd, 4 H, OCH_aH_bCH = CH_cH_d), 3.77 (m_c, 8 H, 5-$C_{THP}H_aH_b$), 3.75 (m_c, 8 H, $THPOCH_aH_bCH_2CH_2O$), 3.74 (m_c, 16 H, $THPOCH_2CH_2CH_2O$), 3.68 (m_c, 4 H, 6-$C_{gluc}H_aH_b$), 3.47 (m_c ≈ t, 4 H, 4-H_{gluc}), 3.44 (m_c, 8 H, 5-$C_{THP}H_aH_b$), 3.38 (m_c ≈ t, 4 H, 3-H_{gluc}), 3.42 (m_c, 8 H, $THPOCH_aH_bCH_2CH_2O$), 3.27 (m_c ≈ ddd, 4 H, 5-H_{gluc}), 3.12 (m_c ≈ t, 4 H, 2-H_{gluc}), 1.81 (m_c ≈ quin, 8 H, $THPOCH_2CH_2CH_2O$), ≈ 1.75 (m_c, 8 H, 3-$C_{THP}H_aH_b$), ≈ 1.70 (m_c ≈ quin, 8 H, $THPOCH_2CH_2CH_2O$), ≈ 1.60 (m_c, 8 H, 2-$C_{THP}H_aH_b$), ≈ 1.50 (m_c, 8 H, 2-$C_{THP}H_aH_b$), 1.48 (m_c, 8 H, 4-$C_{THP}H_aH_b$), 1.44 (m_c, 8 H, 4-$C_{THP}H_aH_b$), ≈ 1.40 (m_c, 8 H, 3-$C_{THP}H_aH_b$).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 133.76 (4 C, OCH_2CH = CH_2), 128.79–125.90 (20 C, *C*H, arom), 117.36, 117.35 (4 C, OCH_2CH = CH_2), 103.04, 102.98 (4 C, 1-C_{gluc}), 101.10, 101.00 (4 C, *C*HPh), 98.75, 98.73, 98.68 (8 C, 1-C_{THP}), 82.37, 82.28 (4 C, 2-C_{gluc}), 81.36, 81.31 (4 C, 3-C_{gluc}), 81.29, 81.21 (4 C, 4-C_{gluc}), 70.54, 70.52 (4 C, OCH_2CH = CH_2), 70.46, 70.45, 70.43, 70.40, 70.24, 70.21 (8 C, $THPOCH_2$ CH_2CH_2O), 68.71 (4 C, 6-C_{gluc}), 65.98, 65.95 (4 C, 5-C_{gluc}), 64.50, 64.41 (8 C, $THPOCH_2CH_2CH_2O$), 62.14, 62.11, 62.01 (8 C, 5-C_{THP}), 30.65, 30.62 (8 C, 2-C_{THP}), 30.55, 30.69, 30.61 (8 C, $THPOCH_2CH_2CH_2O$), 25.46, 25.44 (8 C, 4-C_{THP}), 19.54, 19.48 (8 C, 3-C_{THP}).

MS (ESI): m/z = 614 ($M+Na^+$).

Anal. calcd for $C_{33}H_{50}O_{10}$ (606.8): C, 65.33; H 8.30. Found C, 65.79; H, 8.43.

Allyl 4,6-*O*-benzylidene-2-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-β-D-glucopyranoside **(3)** and allyl 4,6-benzylidene-3-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-β-D-glucopyranoside **(4)** could only be isolated as a mixture by column chromatography using Et_2O/hexane (2:1) as solvent. Characterization was done by mass spectrometry.

MS (ESI): m/z = 486 ($M+Na^+$).

Anal. calcd for $C_{25}H_{35}O_8$ (463.6): C, 64.78; H, 7.61. Found C, 64.79; H, 7.43.

Allyl 4,6-*O*-Benzylidene-2,3-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside (5)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.49–7.25 (m, 5 H, arom), 5.85 (m_c ≈ dddd, 1 H, $OCH_aH_bCH = CH_cH_d$), 5.53 (s, 1 H, CHPh), 5.30 (m_c ≈ dddd, 1 H, $OCH_aH_bCH = CH_cH_d$), 5.20 (m_c ≈ dddd, 1 H, $OCH_aH_bCH = CH_cH_d$), 4.42 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, 1-H_{gluc}), 4.18 (m_c, 1 H, 6-$C_{gluc}H_aH_b$), 3.80 (m_c, 1 H, 6-$C_{gluc}H_aH_b$), 3.70 (m_c, 4 H, $HOCH_2CH_2CH_2O$), 3.65 (m_c, 4 H, $HOCH_2CH_2CH_2O$), 3.49 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.35 (m_c ≈ t, 1 H, 3-H_{gluc}), 3.29 (m_c ≈ ddd, 1 H, 5-H_{gluc}), 3.09 (m_c ≈ t, 1 H, 2-H_{gluc}), 2.28 (s, 2 H, $HOCH_2CH_2CH_2O$), 1.82 (m_c ≈ quin, 2 H, $HOCH_2CH_2CH_2O$), 1.78 (m_c ≈ quin, 2 H, $HOCH_2CH_2CH_2O$).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 137.12 (1 C, quart, arom), 133.51 (1 C, $OCH_2CH = CH_2$), 129.14–126.00 (5 C, CH, arom), 117.80 (1 C, $OCH_2CH = CH_2$), 102.50 (1 C, 1-C_{gluc}), 101.31 (1 C, CHPh), 81.88 (1 C, 2-C_{gluc}), 81.69 (1 C, 3-C_{gluc}), 81.06 (1 C, 4-C_{gluc}), 71.88, 71.15 (2 C, $HOCH_2CH_2CH_2O$), 70.60 (1 C, $OCH_2CH = CH_2$), 68.50 (1 C, 6-C_{gluc}), 65.99 (1 C, 5-C_{gluc}), 61.14, 60.97 (2 C, $HOCH_2CH_2CH_2O$), 32.43, 32.34 (2 C, $HOCH_2CH_2CH_2O$).

MS (ESI): m/z = 447 ($M+Na^+$).

Anal. calcd for $C_{22}H_{32}O_8$ (424.5): C, 62.25; H, 7.59. Found C, 62.88; H, 7.78.

Allyl 2,3-Di-*O*-benzyl-4,6-di-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-β-D-glucopyranoside (8)

^{1}H NMR (600.13 MHz, $CDCl_3$): δ = 7.34–7.20 (m, 40 H, arom), 5.87 (m_c ≈ dddd, 4 H, $OCH_2CH = CH_2$), 5.26 (m_c ≈ dddd, 4 H, $OCH_2CH = CH_aH_b$), 5.11 (m_c ≈ dddd, 4 H, $OCH_2CH = CH_aH_b$), 4.85 (AB, 4 H, CH_aH_bPh), 4.80 (AB, 4 H, CH_aH_bPh), 4.69 (AB, 4 H, CH_aH_bPh), 4.61 (AB, 4 H, CH_aH_bPh), 4.48 (m_c ≈ t, 4 H, 1-$C_{THP}H$), 4.46 (m_c ≈ t, 2 H, 1-$C_{THP}H$), 4.43 (m_c ≈ t, 2 H, 1-$C_{THP}H$), 4.34 (m_c ≈ dddd, 4 H, $OCH_aH_bCH = CH_2$), 4.33 (m_c, 8 H, 5-$C_{THP}H_aH_b$), 4.32 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, 1-H_{gluc}), 4.05 (m_c ≈ dddd, 4 H, $OCH_aH_bCH = CH_2$), 3.81 (m_c, 4 H, $THPOCH_2CH_2CH_aH_bO$), 3.56 (m_c, 4 H, $THPOCH_2CH_2CH_aH_bO$), ≈ 3.55 (m_c, 8 H, 6-$C_{gluc}H_2$), 3.45 (m_c ≈ t, 4 H, 3-H_{gluc}), 3.54 (m_c, 4 H, $THPOCH_2CH_2CH_aH_bO$), 3.49 (m_c, 4 H, $THPOCH_2CH_2CH_aH_bO$), 3.39 (m_c, 8 H, 5-$C_{THP}H_aH_b$), 3.37 (m_c, 8 H, $THPOCH_aH_bCH_2CH_2O$), 3.33 (m_c ≈ t, 4 H, 2-H_{gluc}), 3.25 (m_c, 8 H, 4-H_{gluc}, 5-H_{gluc}), 1.81 (m_c, 8 H, $THPOCH_2CH_2CH_2O$), 1.75 (m_c, 8 H, $THPOCH_2CH_2CH_2O$), ≈ 1.45 (m_c, 16 H, 3-$C_{THP}H_2$), 1.44 (m_c, 16 H, 4-$C_{THP}H_2$), 1.43 (m_c, 16 H, 2-$C_{THP}H_2$).

^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 138.71, 138.55 (8 C, quart, arom), 134.12 (4 C, $OCH_2CH = CH_2$), 128.82–127.55 (40 C, CH, arom), 117.36, 117.21 (4 C, $OCH_2CH = CH_2$), 102.64 (4 C, 1-C_{gluc}), 98.94, 98.90, 98.84 (8 C, 1-C_{THP}), 84.59, 84.51 (4 C, 3-C_{gluc}), 82.19 (4 C, 2-C_{gluc}), 78.27 (4 C, 4-C_{gluc}), 75.61, 75.54 (4 C, CH_2Ph), 75.06 (4 C, 5-C_{gluc}), 74.88, 74.71 (4 C, CH_2Ph), 69.86 (4 C, 6-C_{gluc}), 70.60–68.72 (8 C, $THPOCH_2CH_2CH_2O$), 64.56, 64.48, 64.41 (8 C, $THPOCH_2CH_2CH_2O$), 62.55–61.00 (8 C, 5-C_{THP}), 32.81–30.13 (16 C, $THPOCH_2CH_2CH_2O$, 2-C_{THP}), 25.48 (8 C, 4-C_{THP}), 19.64 (8 C, 3-C_{THP}).

MS (ESI): m/z = 707 ($M+Na^+$).

Anal. calcd for $C_{39}H_{56}O_{10}$ (684.9): C, 68.40; H, 8.24. Found C, 68.80; H, 8.42.

Benzyl 2,3-Di-*O*-benzyl-4,6-di-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-α-D-glucopyranoside (9)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.34–7.16 (m, 60 H, arom), 4.86 (m, AB, 4 H, CH_aH_bPh), 4.73 (m_c ≈ d, 4 H, 1-H_{gluc}), 4.72 (m, AB, 4 H, CH_aH_bPh), 4.58 (m, AB, 4 H, CH_aH_bPh), 4.55 (m, AB, 4 H, CH_aH_bPh), 4.48 (m, AB, 8 H, CH_aH_bPh), 4.45 (m_c ≈ t, 8 H, 1-$C_{THP}H$), ≈ 3.85 (m_c, 8 H, $THPOCH_2CH_2CH_aH_bO$), 3.84 (m_c ≈ t, 4 H, 3-H_{gluc}), 3.74 (m, 8 H, 5-$C_{THP}H_aH_b$), 3.72 (m_c, 8 H, $THPOCH_aH_bCH_2CH_2O$), 3.62 (m_c ≈ ddd, 4 H, 5-H_{gluc}), 3.56 (m_c, 8 H, 6-$C_{gluc}H_2$) ≈ 3.55 (m_c, 8 H, $THPOCH_2CH_2CH_aH_bO$), 3.39 (m_c ≈ t, 4 H, 2-H_{gluc}), 3.38 (m_c, 8 H, $THPOCH_aH_bCH_2CH_2O$), 3.37 (m, 8 H, 5-$C_{THP}H_aH_b$), 3.31 (m_c ≈ t, 4 H, 4-H_{gluc}), 1.82 (m_c ≈ quin., 8 H, $THPOCH_2CH_2CH_2O$), 1.76 (m_c ≈ quin., 8 H, $THPOCH_2CH_2CH_2O$), 1.69 (m, 8 H, 2-$C_{THP}H_aH_b$), ≈ 1.51 (m, 8 H, 3-$C_{THP}H_aH_b$), ≈ 1.48 (m, 8 H, 3-$C_{THP}H_aH_b$), 1.45 (m, 8 H, 4-$C_{THP}H_aH_b$), 1.41 (m, 8 H, 4-$C_{THP}H_aH_b$), ≈ 1.40 (m, 8 H, 2-$C_{THP}H_aH_b$).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 138.95, 138.24, 137.24 (12 C, quart, arom), 128.43–127.48 (60 C, CH, arom), 98.88, 98.85 (8 C, 1-C_{THP}), 95.47 (4 C, 1-C_{gluc}), 81.96 (4 C, 3-C_{gluc}), 79.75 (4 C, 2-C_{gluc}), 77.88 (4 C, 4-C_{gluc}), 75.61, 75.58 (4 C, CH_2Ph), 72.99 (4 C, CH_2Ph), 70.45 (4 C, 5-C_{gluc}), 69.99–68.66 (12 C, $THPOCH_2CH_2CH_2O$, 6-C_{gluc}), 68.94 (4 C, CH_2Ph), 64.55, 64.53, 64,46 (8 C, $THPOCH_2CH_2CH_2O$), 62.37, 62.32, 62.26, 62.22 (8 C, 5-C_{THP}), 30.75, 29.99 (8 C, $THPOCH_2CH_2CH_2O$), 25.46 (8 C, 4-C_{THP}), 30.70, 30.06 (8 C, 2-C_{THP}), 19.69, 19.65, 19.62,19.59 (8 C, 3-C_{THP}).

MS (ESI): m/z = 757 ($M+Na^+$).

Anal. calcd for $C_{43}H_{58}O_{10}$ (734.9): C, 70.28; H, 7.95. Found C, 70.19; H, 8.00.

Benzyl 2,3-Di-*O*-benzyl-6-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-α-D-glucopyranoside (10)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.34–7.17 (m, 30 H, arom), 4.94 (AB, 1 H, CH_aH_bPh), 4.92 (AB, 1 H, CH_aH_bPh), 4.76 (m_c ≈ d, 1 H, 1-H_{gluc}), 4.75 (m_c ≈ d, 1 H, 1-H_{gluc}), 4.71 (AB, 1 H, CH_aH_bPh), 4.68 (AB, 1 H, CH_aH_bPh), 4.59 (AB, 2 H, CH_aH_bPh), 4.56 (AB, 1 H, CH_aH_bPh), 4.55 (AB, 1 H, CH_aH_bPh), 4.50 (m_c ≈ t, 1 H, 1-$C_{THP}H$), 4.49 (AB, 2 H, CH_aH_bPh), 4.48 (AB, 1 H, CH_aH_bPh), 4.47 (AB, 1 H, CH_aH_bPh), 4.41 (m_c ≈ t, 1 H, 1-$C_{THP}H$), 3.83 (m_c, 1 H, $THPOCH_aH_bCH_2CH_2O$→6-C_{gluc}), 3.78 (m_c ≈ t, 2 H, 3-H_{gluc}), 3.76 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 3.74 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 3.72 (m_c, 1 H, $THPOCH_aH_bCH_2CH_2O$→6-C_{gluc}), 3.67 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.65 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.56 (m_c, 2 H, 6-$C_{gluc}H_aH_b$), 3.55 (m_c, 1 H, $THPOCH_2CH_2CH_aH_bO$→6-C_{gluc}), 3.54 (m_c ≈ ddd, 2 H, 5-H_{gluc}), 3.54 (m_c, 1 H, $THPOCH_2CH_2CH_aH_bO$→6-C_{gluc}), 3.52 (m_c, 2 H, 6-$C_{gluc}H_aH_b$), 3.46 (m_c, 1 H, $THPOCH_2CH_2CH_aH_bO$→6-C_{gluc}), 3.44 (m_c, 1 H, $THPOCH_2CH_2CH_aH_bO$→6-C_{gluc}), 3.43 (m_c ≈ t, 2 H, 2-H_{gluc}), 3.42 (m_c, 1 H, $THPOCH_aH_bCH_2CH_2O$→6-C_{gluc}), 3.39 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 3.36 (m_c, 1 H, $THPOCH_aH_bCH_2CH_2O$→6-C_{gluc}), 3.33 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 1.79 (m_c, 8 H, $THPOCH_2CH_2CH_2O$→6-C_{gluc}, 2-$C_{THP}H_2$), 1.71 (m_c, 2 H, 2-$C_{THP}H_aH_b$), 1.45 (m_c, 2 H, 4-$C_{THP}H_aH_b$), 1.42 (m_c, 2 H, 3-$C_{THP}H_aH_b$), 1.40 (m_c, 2 H, 4-$C_{THP}H_aH_b$).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 139.03–137.17 (6 C, quart, arom), 128.44–127.58 (30 C, CH, arom), 99.63, 98.76 (2 C, 1-C_{THP}), 95.64, 95.51 (2 C, 1-C_{gluc}), 81.69, 81.55 (2 C, 3-C_{gluc}), 79.57, 79.52 (2 C, 2-C_{gluc}), 75.52, 75.37 (2 C, CH_2Ph), 72.95, 72.78 (2 C, CH_2Ph), 70.91 (2 C, 5-C_{gluc}), 70.44, 70.05 (2 C, 4-C_{gluc}), 70.12, 69.86 (2 C, 6-C_{gluc}), 69.01 (2 C, CH_2Ph), 68.81, 68.25 (2 C, $THPOCH_2CH_2CH_2O$→6-C_{gluc}), 64.21, 64.11 (2 C, $THPOCH_2CH_2CH_2O$→ 6-C_{gluc}), 63.23, 62.33 (2 C, 5-C_{THP}), 30.88, 30.60, 29.75, 29.64 (4 C, 2-C_{THP}, $THPOCH_2CH_2CH_2O$→6-C_{gluc}), 25.38, 25.36 (2 C, 4-C_{THP}), 20.23, 19.57 (2 C, 3-C_{THP}).

MS (ESI): m/z = 614 ($M+Na^+$).

Anal. calcd for $C_{35}H_{43}O_8$ (591.7): C, 71.04; H, 7.32. Found C, 71.02; H, 7.84

Benzyl 2,3-Di-*O*-benzyl-4-*O*-[3-(tetrahydro-2*H*-pyranyl)oxypropyl]-α-D-glucopyranoside (11)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.34–7.17 (m, 30 H, arom), 4.86 (AB, 2 H, CH_aH_bPh), 4.73 (AB, 2 H, CH_aH_bPh), 4.60 (AB, 2 H, CH_aH_bPh), 4.56 (AB, 2 H, CH_aH_bPh), 4.51 (AB, 2 H, CH_aH_bPh), 4.49 (AB, 2 H, CH_aH_bPh), 4.48 (m_c ≈ d, 2 H, 1-H_{gluc}), 4.47 (m_c ≈ t, 2 H, 1-$C_{THP}H$), 3.89 (m_c, 1 H, $THPOCH_2CH_2CH_aH_bO$→4-C_{gluc}),

3.88 (m_c ≈ t, 2 H, 3-H_{gluc}), 3.86 (m_c, 1 H, THPOCH$_2$CH$_2$C*H*$_a$H$_b$O→4-C_{gluc}), 3.75 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 3.73 (m_c, 1 H, 5-$C_{THP}H_aH_b$), 3.72 (m_c, 2 H, THPOC*H*$_a$H$_b$CH$_2$CH$_2$O →4-C_{gluc}), 3.66 (m_c, 2 H, 6-$C_{gluc}H_aH_b$), 3.63 (m_c, 2 H, 6-$C_{gluc}H_aH_b$), 3.62 (m_c, 1 H, THPOCH$_2$CH$_2$CH$_a$*H*$_b$O→4-C_{gluc}), 3.61 (m_c, 1 H, THPOCH$_2$CH$_2$CH$_a$*H*$_b$O→4-C_{gluc}), 3.58 (m_c, 1 H, 5-H_{gluc}), 3.57 (m_c, 1 H, 5-H_{gluc}), 3.39 (m_c, 2 H, 5-$C_{THP}H_aH_b$), 3.38 (m_c, 2 H, THPOCH$_a$*H*$_b$CH$_2$CH$_2$O→4-C_{gluc}), 3.34 (m_c ≈ t, 2 H, 2-H_{gluc}), 3.30 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.27 (m_c ≈ t, 1 H, 4-H_{gluc}), 1.76 (m_c, 8 H, THPOCH$_2$C*H*$_2$CH$_2$O→ 4-C_{gluc}, 2-$C_{THP}H_2$), 1.45 (m_c, 4 H, 4-$C_{THP}H_2$), 1.43 (m_c, 4 H, 3-$C_{THP}H_2$).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 138.84–137.09 (6 C, quart, arom), 128.35–127.47 (30 C, *C*H, arom), 98.98, 98.91 (2 C, 1-C_{THP}), 95.52 (2 C, 1-C_{gluc}), 81.85, 81.71 (2 C, 3-C_{gluc}), 79.88 (2 C, 2-C_{gluc}), 78.11, 78.00 (2 C, 4-C_{gluc}), 75.53, 75.46 (2 C, *C*H$_2$Ph), 73.02, 73.00 (2 C, *C*H$_2$Ph), 71.18, 71.08 (2 C, 5-C_{gluc}), 70.07, 69.97 (2 C, THPOCH$_2$CH$_2$*C*H$_2$O→4-C_{gluc}), 69.13, 69.11 (2 C, *C*H$_2$Ph), 64.30, 64.21 (2 C, THPO*C*H$_2$CH$_2$CH$_2$O→4-C_{gluc}), 62.61, 62.31 (2 C, 5-C_{THP}), 61.86, 61.67 (2 C, 6-C_{gluc}), 30.70, 30.61, 30.52 (4 C, THPOCH$_2$*C*H$_2$CH$_2$O→4-C_{gluc}, C, 2-C_{THP}), 25.39, 25.36 (2 C, 4-C_{THP}), 19.76, 19.58 (2 C, 3-C_{THP}).

MS (ESI): m/z = 614 ($M+Na^+$).

Anal. calcd for $C_{35}H_{43}O_8$ (591.7): C, 71.04; H, 7.32. Found C, 71.13; H, 7.55.

Allyl 2,3-Di-*O*-benzyl-4,6-di-*O*-(3-hydroxypropyl)-β-D-glucopyranoside (12)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.18–7.24 (m, 10 H, arom), 5.87 (m_c ≈ dddd, 1 H, OCH$_a$H$_b$C*H* = CH$_c$H$_d$), 5.33 (m_c ≈ dddd, 1 H, OCH$_a$H$_b$CH = C*H*$_c$H$_d$), 5.19 (m_c ≈ dddd, 1 H, OCH$_a$H$_b$C*H* = CH$_c$*H*$_d$), 4.93 (m_c, 1H, CH$_a$*H*$_b$Ph), 4.89 (m_c, 1H, CH$_a$*H*$_b$Ph), 4.74 (m_c, 1H, C*H*$_a$H$_b$Ph), 4.68 (m_c, 1H, C*H*$_a$H$_b$Ph), 4.41 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 1-H_{gluc}), 3.71 (m_c, 1 H, HOC*H*$_a$H$_b$CH$_2$CH$_2$O),≈ 4.40 (m_c≈ dddd, 1 H, OCH$_a$H$_b$C*H* = CH$_c$H$_d$), ≈ 4.15 (m_c ≈ dddd, 1 H, OC*H*$_a$H$_b$C*H* = CH$_c$H$_d$), 3.95 (m_c, 1 H, 6-C*H*$_a$H$_b$), 3.75 (m_c ≈ t, 2 H, HOC*H*$_2$ CH$_2$CH$_2$O), 3.70 (m_c, 1 H, 6-CH$_a$*H*$_b$), 3.69 (m_c, 1 H, HOCH$_2$CH$_2$CH$_a$*H*$_b$O), 3.68 (m_c, 3 H, HOCH$_2$CH$_2$C*H*$_2$O, HOC*H*$_2$CH$_2$CH$_2$O), 3.66 (m_c, 1 H, HOCH$_2$CH$_2$C*H*$_a$H$_b$O), 3.52 (m_c ≈ t, 1 H, 3-H_{gluc}), 3.41 (m_c ≈ t, 1 H, 2-H_{gluc}), 3.35 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.33 (m_c ≈ ddd, 1 H, 5-H_{gluc}), 2.25 (s, 2 H, *H*OCH$_2$CH$_2$CH$_2$O), 1.82 (m_c ≈ quin, 2 H, HOCH$_2$C*H*$_2$CH$_2$O), 1.75 (m_c ≈ quin, 2 H, HOCH$_2$C*H*$_2$CH$_2$O).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 138.51, 138.33 (2 C, quart, arom), 133.88 (1 C, OCH$_2$*C*H = CH$_2$), 127.58–128.32 (10 C, *C*H, arom), 117.36 (1 C, OCH$_2$CH = *C*H$_2$), 102.57 (1 C, 1-C_{gluc}), 84.35 (1 C, 3-C_{gluc}), 82.12 (1 C, 2-C_{gluc}), 78.34 (1 C, 4-C_{gluc}), 75.49 (1 C, *C*H$_2$Ph), 74.82 (1 C, *C*H$_2$Ph), 74.55 (1 C, 5-C_{gluc}), 71.23 (1 C, 6-C_{gluc}), 70.28 (1 C, O*C*H$_2$CH = CH$_2$), 70.13 (1 C, HOCH$_2$CH$_2$*C*H$_2$O), 69.95 (1 C, HOCH$_2$CH$_2$*C*H$_2$O), 61.06 (1 C, HO*C*H$_2$CH$_2$CH$_2$O), 60.73 (1 C, HO*C*H$_2$CH$_2$CH$_2$O), 32.72 (1 C, HOCH$_2$*C*H$_2$CH$_2$O), 31.94 (1 C, HOCH$_2$*C*H$_2$CH$_2$O).

MS (ESI): m/z = 539 ($M+Na^+$).

Anal. calcd for $C_{29}H_{40}O_8$•0.5 MeOH (516.6•MeOH): C, 66.52; H, 7.95. Found C, 66.82; H, 7.90.

Benzyl 2,3-Di-*O*-benzyl-4,6-di-*O*-(3-hydroxypropyl)-α-D-glucopyranoside (13)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 15 H, arom), 4.97 (m_c, 1 H, 6-C*H*$_a$H$_b$), 4.82 (d, $^3J_{HH}$ = 3.9 Hz, 1 H, 1-H_{gluc}), 4.76 (m_c, 1 H, 6-CH$_a$*H*$_b$), 4.65 (AB, 2 H, C*H*$_2$Ph), 4.52 (AB, 2 H, C*H*$_2$Ph), 3.98–3.89 (m, 2 H), 3.77–3.57 (m, 8 H), 3.55 (dd, J_{HH} = 10.8 Hz, J_{HH} = 1.7 Hz, 1 H), 3.48 (dd, $^3J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 3.9 Hz, 1 H, 2-H_{gluc}), 3.39 (m, 1 H, 4-H_{gluc}), 2.62 (s, 2 H, O*H*), 1.92–1.69 (m_c, 4 H, HOCH$_2$C*H*$_2$CH$_2$O).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 138.8, 138.0, 137.1 (3 C, quart, arom), 128.4–127.5 (15 C, *C*H, arom), 95.5 (1 C, 1-C_{gluc}), 81.8 (1 C, 3-C_{gluc}), 79.9 (1 C, 2-C_{gluc}), 78.0 (1 C, 4-C_{gluc}), 75.5 (1 C, *C*H$_2$Ph), 72.9 (1 C, *C*H$_2$Ph), 71.1 (1 C, 5-C_{gluc}), 70.1 (1 C, *C*H$_2$Ph), 69.5 (2 C, HOCH$_2$CH$_2$*C*H$_2$O, 6-C_{gluc}), 69.1 (1 C, HOCH$_2$CH$_2$*C*H$_2$O), 60.7 (1 C, HO*C*H$_2$CH$_2$CH$_2$O), 60.6 (1 C, HO*C*H$_2$CH$_2$CH$_2$O), 32.8 (1 C, HOCH$_2$*C*H$_2$CH$_2$O), 31.9 (1 C, HOCH$_2$*C*H$_2$ CH$_2$O).

MS (ESI): m/z = 589 ($M+Na^+$).

Anal. calcd for $C_{33}H_{42}O_8$ (566.7): C, 69.94; H, 7.47. Found C, 69.43; H, 7.42.

Allyl 2,3-Di-*O*-benzyl-4,6-di-*O*-[3-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl- oxypropyl)]-β-D-glucopyranoside (17)

A solution of **12** (0.1 g, 0.19 mmol) in CH_2Cl_2 (2 mL) was added to a mixture of the galactosyl donor **16**[20] (0.25 g, 0.40 mmol), $AgClO_4$ (1.24 g, 6 mmol, dried before use for 1 d at 160 °C/0.02 Torr), powdered molecular sieves 4 Å (0.4 g), TOPC[21] (0.23 g, 0.39 mmol) and CH_2Cl_2 (4 mL) at –10 °C. After stirring for 4 days at r.t. under N_2 (the progress of the reaction was monitored by TLC), the mixture was diluted with CH_2Cl_2 (50 mL), the precipitated silver salt was removed by filtration through Celite and washed with satd aq solution of $Na_2S_2O_3$ (20 mL) and then with H_2O (20 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: hexane/Et_2O/CH_2Cl_2, 3:1:0.2, v/v), leading to the expected product with oily consistency; yield:0.10 g (35%).

^{1}H NMR (600.13 MHz, CD_2Cl_2): δ = 7.94–7.04 (m, 50 H, arom), 6.02 (m_c ≈ dddd, 1 H, OCH$_2$C*H* = CH$_2$), 5.39 (m_c ≈ dddd, 1 H, OCH$_2$CH = C*H*$_a$H$_b$), 5.24 (m_c ≈ dddd, 1 H, OCH$_2$CH = CH$_a$*H*$_b$), 4.98 (m, AB, 2 H, CH$_a$*H*$_b$Ph), 4.97 (m, AB, 1 H, C*H*$_a$H$_b$Ph), 4.96 (m, AB, 1 H, C*H*$_a$H$_b$Ph), 4.91 (m, AB, 2 H, C*H*$_a$H$_b$Ph), 4.90 (m, AB, 2 H, C*H*$_a$H$_b$Ph), 4.81 (m, AB, 2 H, CH$_a$*H*$_b$Ph), 4.80 (m, AB, 1 H, CH$_a$*H*$_b$Ph), 4.76 (m, AB, 2 H, CH$_a$*H*$_b$Ph), 4.73 (m, AB, 1 H, CH$_a$*H*$_b$Ph), 4.62 (m, AB, 2 H, C*H*$_a$H$_b$Ph), 4.54 (m, AB, 2 H, C*H*$_a$H$_b$Ph), 4.49 (m, AB, 2 H, CH$_a$*H*$_b$Ph), 4.43 (m_c ≈ dddd, 1H, OC*H*$_a$H$_b$-CH = CH$_2$), 4.43 (d, $^3J_{HH}$ = 7.77 Hz, 1 H, 1-H_{gluc}), 4.41 (d, $^3J_{HH}$ = 7.74 Hz, 1 H, 1-$H_{gal\ 1}$), 4.35 (d, $^3J_{HH}$ = 7.64 Hz, 1 H, 1-$H_{gal\ 2}$), 4.16 (m_c ≈ dddd, 1 H, OCH$_a$*H*$_b$-CH = CH$_2$), 3.99 (m_c ≈ t, 1 H, 4-$H_{gal\ 1}$), 3.99 (m, 1 H, Gal^{2}C*H*$_a$H$_b$CH$_2$CH$_2$O→6-Gluc), 3.98 (m, 1 H, Gal^{1}C*H*$_a$H$_b$CH$_2$CH$_2$O→4-Gluc), 3.97 (m_c ≈ t, 1 H, 4-$H_{gal\ 2}$), 3.88 (m, 1 H, Gal^{1}CH$_2$ CH$_2$C*H*$_a$H$_b$O→4-Gluc), 3.73 (m_c ≈ t, 1 H, 2-$H_{gal\ 2}$), 3.70 (m,1H, Gal^{1}CH$_2$CH$_2$CH$_a$*H*$_b$O →4-Gluc), 3.69 (m, 1 H, Gal^{2}CH$_a$*H*$_b$CH$_2$CH$_2$O→6-Gluc), 3.68 (m,1 H, Gal^{2}CH$_2$CH$_2$C*H*$_a$H$_b$O→6-Gluc), 3.66 (m, 1 H, 6-$C_{gluc}H_aH_b$), 3.65 (m, 1 H, Gal^{2}CH$_2$CH$_2$CH$_a$*H*$_b$O →6-Gluc), 3.63 (m, 2 H, 6-$C_{gal\ 1,\ gal\ 2}H_aH_b$), 3.62 (m, 1 H, 6-C$^{Gluc}H_aH_b$), 3.61 ($m_c$, 2 H, 5-$H_{gal\ 1,\ 2}$), 3.59 (m, 1 H, Gal^{1}CH$_a$*H*$_b$CH$_2$CH$_2$O→4-Gluc),3.58 (m_c, 1 H, 3-$H_{gal\ 1}$), 3.57 (m, 2 H, 6-$C_{gal\ 1,\ gal\ 2}H_aH_b$), 3.55 ($m_c$, 1 H, 3-$H_{gal\ 2}$), 3.53 ($m_c$ ≈ t, 1 H, 3-H_{gluc}), 3.48 (m_c ≈ t, 1 H, 2-$H_{gal\ 1}$), 3.41 (m_c ≈ t, 1 H, 2-H_{gluc}), 3.38 (m_c ≈ t, 1 H, 4-H_{gluc}), 3.34 (m_c ≈ t, 1 H, 5-H_{gluc}), 1.96 (m_c ≈ quin, 1 H, Gal^{2}CH$_2$CH$_a$*H*$_b$CH$_2$O→6-Gluc), 1.93 (m_c ≈ quin, 1H, Gal^{2}CH$_2$C*H*$_a$H$_b$CH$_2$O→6-Gluc), 1.92 (m_c ≈ quin, 1 H, Gal^{1}CH$_2$ C*H*$_a$H$_b$CH$_2$ O→4-Gluc), 1.89 (m_c ≈ quin, 1 H, Gal^{1}CH$_2$CH$_a$*H*$_b$CH$_2$O→4-Gluc).

^{13}C NMR (150.92 MHz, CD_2Cl_2): δ = 139.97–139.07 (10 C, quart, arom), 135.13 (1 C, OCH$_2$*C*H = CH$_2$), 129.11–128.13 (50 C, *C*H, arom), 117.41 (1 C, OCH$_2$CH = *C*H$_2$), 104.75 (1 C, 1-$C_{gal\ 1}$), 104.69 (1 C, 1-$C_{gal\ 2}$), 103.40 (1 C, 1-C_{gluc}), 85.13 (1 C, 3-C_{gluc}), 82.98 (2 C, 3-$C_{gal\ 1,\ 2}$), 82.97 (1 C, 2-C_{gluc}), 80.35 (1 C, 2-$C_{gal\ 1}$), 80.32 (1 C, 2-$C_{gal\ 2}$), 78.92 (1 C, 4-C_{gluc}), 75.60 (1 C, 5-C_{gluc}), 75.59–74.14 (10 C, *C*H$_2$Ph), 74.95 (2 C, 4-$C_{gal\ 1,\ 2}$), 73.92 (2 C, 5-$C_{gal\ 1,\ 2}$), 70.74 (1 C, OC*H*$_2$CH = CH$_2$), 70.43 (1 C, 6-C_{gluc}),70.40 (1 C, Gal^{1}CH$_2$CH$_2$*C*H$_2$O→4-Gluc), 69.48 (1 C, Gal^{2}CH$_2$CH$_2$*C*H$_2$O→6-Gluc), 69.15 (2 C, 6-$C_{gal\ 1,\ 2}$), 67.75 (1 C, Gal^{2}CH$_2$CH$_2$CH$_2$O→6-Gluc), 67.67 (1 C, Gal^{1}CH$_2$CH$_2$ CH$_2$O→4-Gluc), 31.61 (1 C,

Gal[1]$CH_2CH_2CH_2O\rightarrow$4-Gluc), 31.06 (1 C, Gal[2]$CH_2CH_2CH_2O\rightarrow$6-Gluc).

MS (ESI): m/z = 1583 ($M+Na^+$).

Anal. calcd for $C_{97}H_{108}O_{18}.CH_2Cl_2$ (1561.9•CH_2Cl_2): C, 71.47; H, 6.73.646.85. Found C, 71.90; H, 6.94.

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