

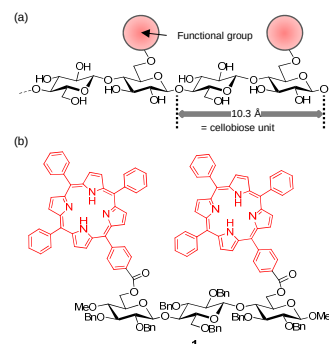
# Chiroptical properties of alternately functionalized cellotriose bearing two porphyrin groups

Keita Sakakibara,<sup>\*ab</sup> Fumiaki Nakatsubo,<sup>c</sup> Alfred D. French<sup>d</sup> and Thomas Rosenau<sup>\*a</sup>

Right-handedness derived from bisporphyrins attached to a cellotriose backbone at O-6 and O''-6 positions is revealed for the first time. This cellotriose is proposed as a model of alternately functionalized cellulose, which have promising properties for applications in optoelectronics and molecular receptors owing to the chirality and rigid backbone effects.

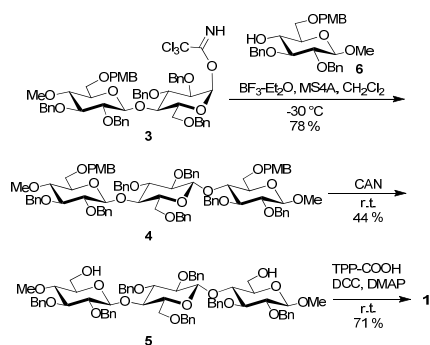
Cellulose, which certainly needs no further introduction as green and renewable bioresource, combines good physical properties, such as strength and elasticity, and favourable chemical behaviour, such as chemical and thermal stress resistance, in its different material appearances.<sup>1</sup> Its derivatives with photoactive properties have become increasingly important.<sup>2</sup> At present, regioselective cellulose functionalization and subsequent self-assembling procedures are a reliable approach to producing cellulosic functional nanomaterials. For example, we have reported an efficient artificial photosynthetic system of thin films of 6-O-porphyrinated-2,3-di-O-acylcelluloses and revealed that the attached chromophores as photoelectroactive actuators are spaced at a fixed distance, which is set by the inherent cellulose structure acting as a molecular scaffold, leading to efficient cellulose-based photovoltaics.<sup>3</sup> For obtaining advanced cellulosic materials, the following points should be considered and utilized: 1) inherent linearity, rigidity and regularity of the cellulose backbone, inducing equal distances between regioselective substituents, 2) its helicity, possibly inducing supramolecular structures, and 3) the necessity of a precise control of topology and substituent pattern. In their crystal structures cellulose polymorphs are helices with two-fold screw axes, but due to the geometry of the chiral D-glucose building block, cellulose molecules adopt left-handed helical architectures in solution.<sup>4</sup> A tendency towards left-handed helices is also observed when geometries from related small molecules are imposed on cellulose chains.<sup>5</sup> Thus, chromophores attached to cellulose chains, either covalently or in non-bonded complexes,<sup>6</sup> would be helical as well.<sup>6</sup> Some of such cellulose derivatives have been applied in practical chiral packing materials for HPLC,<sup>7</sup> though details of the formation of chiral helices at all levels are currently far from being sufficiently exploited.

The intriguing potential of alternately functionalized celluloses lies in equally spaced functional groups at the repeating distance of 10.3 Å along its axis (Fig. 1a), resulting in promising properties for chiroptical and chiral molecular receptor applications. Reports on such functionalizations are scarce, but Isogai and coworkers have recently reported on the synthesis of an alternating glucose/glucuronic acid co-polysaccharide prepared through TEMPO-oxidation of native celluloses.<sup>8</sup>



**Fig.1** (a) Alternately functionalized cellulose and (b) chemical structure of cellotriose derivative **1**.

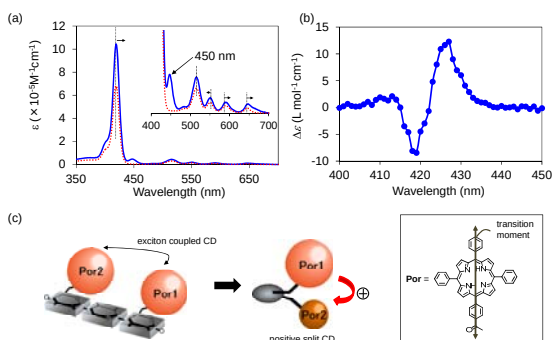
In this report we communicate the synthesis of alternately functionalized cellotriose (**1**) with  $\pi$ -electron functionality, porphyrins, which is a suitable model to study the fundamental properties of alternately functionalized cellulose. The compound **1** contains two porphyrins at O-6 and O''-6 positions, two methyl (Me) groups at the glycosidic end and at O-4'', and seven benzyl (Bn) groups at the remaining hydroxyl positions (Fig. 1b). For the otherwise deprotected model compounds, the two methyl groups at the proximal reducing end (methyl glycoside) and the terminal 4-O are required to avoid making hydrogen bonds that would not be found in cellulose, by allowing only lateral interactions and suppressing H-bonds from the terminal 4-OH and the glycosidic OH.<sup>9</sup> The resulting debenzylated cellotriose, with these two methyl groups representing truncated cellulose chains, thus can be seen as a structural section of a cellulose molecule. Porphyrins were chosen since the exciton-coupled circular dichroic (CD) method<sup>10</sup> as well as host-guest complexation with fullerene (C<sub>60</sub>)<sup>11</sup> are well established. Herein, we demonstrate that the compound **1** exhibits intramolecular electron coupling as compared to the corresponding monomer **2** (chemical structure is shown in the ESI<sup>†</sup>) and right-handedness arising from porphyrin-porphyrin couplet between the two points of attachments, which has not been reported so far. Furthermore, the placement of the substituents on the first and third residues provides an optimum receptor function for C<sub>60</sub>, inducing an electronic interaction in the  $\pi$ -space environment between the two chromophores.



**Scheme 1** Synthesis of cellotriose derivative **1**.

The synthetic details of the path towards compound **1** are given in the ESI.<sup>†</sup> As depicted in Scheme 1, the cellotriose structure was produced by a glycosidation coupling of a novel cellobiosyl donor activated by a trichloroacetimidoyl group at C-1 position (donor; **3**) and a known glucose-based receptor with a free 4-OH group (acceptor; **6**) under Schmidt conditions (summarized in Table S1). The reaction proceeded in a satisfying way, yielding 78% of  $\beta$ -configured cellotriose **4**, when 0.2 eq. of  $\text{BF}_3/\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  were employed. Key intermediate **5** was prepared through the liberation of primary hydroxyl groups at C-6 and C-6'' by CAN oxidation in a 44% yield. The coupling of **5** with porphyrin carboxylic acid (TPP-COOH) gave the desired compound **1** in a 71% yield.

Target **1** was comprehensively analytically characterized. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, recorded in  $\text{CDCl}_3$ , are shown in Fig. S1. The doublets at 4.29, 4.54, and 4.67 ppm of the  $^1\text{H}$  NMR spectrum with their  $^3J_{\text{H,H}}$  coupling constants of approx. 8 Hz are assigned to the characteristic protons at C-1, C-1', and C-1'', respectively, indicative of  $\beta$ -configuration throughout. Another characteristic of the  $^1\text{H}$  NMR is that three Bn aromatic protons are shifted upfield ( $\Delta\delta = \text{ca. } 0.5 \text{ ppm}$ ), arising from extensive aromatic ring-current shielding. This suggests that pronounced  $\pi$ - $\pi$  stacking interactions between the two porphyrin moieties are formed even though the porphyrins can rotate freely in solution, presumably due to the straightness and stiffness of the bulkily substituted (benzylated) cellotriose chain. The carbon signals corresponding to two porphyrin carbonyls and to the carbons of porphyrinated (C-6 and 6'') and benzylated (C-6') glucose units prove the alternating substitution pattern.

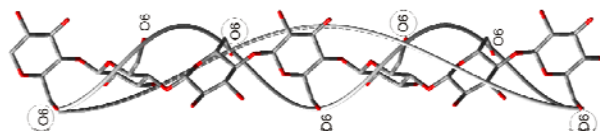


**Fig. 2** (a) UV/VIS and (b) CD spectra of **1** in  $\text{CHCl}_3$  (blue) and that of the corresponding glucose derivative **2** in  $\text{CHCl}_3$  (red);  $c = 2.5 \mu\text{M}$  (UV/VIS) and  $5.0 \mu\text{M}$  (CD).  $\Delta\epsilon$  is quoted per chromophoric unit. (c) Proposed right-handed helicity of the bisporphyrins on the basis of CD spectrum.

Fig. 2a shows the UV/VIS absorption spectra of **1** and **2** in

$\text{CHCl}_3$ . The compound **1** has typical intense Soret ( $\lambda_{\text{max}} = 419 \text{ nm}$ ) and satellite five Q bands (between 490 and 700 nm) were evident, which are due to  $\pi$ - $\pi^*$  transitions of the conjugated macrocycles. The Soret band shows a reduced molar absorption coefficient slightly blue-shifted by ca. 2 nm as compared to the corresponding monomer **2** ( $\lambda_{\text{max}} = 421 \text{ nm}$ ) owing to the interaction of neighboring porphyrin molecules. This is also observed in the Q-band regions. It should be noted that the spectrum of **1** shows a new shoulder band at 450 nm. A similar observation was reported by Qiu and coworkers<sup>12</sup> and Redl and coworkers.<sup>4f</sup> They described that a J-type aggregate structure leads to such a shoulder band. On the other hand, the  $\text{CHCl}_3$  solution of **1** was diluted ( $2.5 \mu\text{M}$ ) and appeared clear without any turbid substance. It seems appropriate, therefore, that this band at 450 nm would be due to the intramolecular electron coupling between the two porphyrin moieties, which is likely the result of the conformational restriction because of the nature of the rigid oligosaccharide backbone.

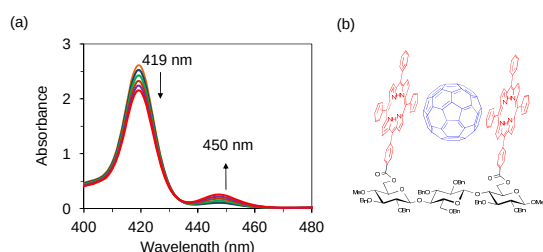
The CD spectrum for **1** dissolved in  $\text{CHCl}_3$  ( $5 \mu\text{M}$ ) is shown in Fig. 2b. In spite of the fact that the porphyrin chromophores are not attached directly to the chiral carbons of the anhydroglucopyranose units, a positive bisignate CD curve with a maximum molar circular dichroism ( $\Delta\epsilon$ ) of  $12.3 \text{ L mol}^{-1} \text{ cm}^{-1}$  per chromophoric unit at 427 nm was observed, corresponding to the right-handed helical arrangement of the chromophores. This exciton splitting observed in the CD spectrum could be explained by some extent of the conformational rigidity as well as enough distance ( $10.3 \text{ \AA}$ ) between adjacent porphyrins of **1**, since the porphyrin moieties are not free to assume many orientations even in solution. It should be emphasized that the positive cotton effect (Fig. 2c) has never been observed so far in the reports of cellulose derivatives that give rise to CD bands exhibiting exciton splitting. For example, Harkness and Gray reported that the CD spectrum of 6-O- $\alpha$ -(1-naphthylmethyl)-2,3-di-O-pentylcellulose in cyclohexane exhibits a weak negative CD band at 228 nm.<sup>4b</sup> Similarly, Redl and coworkers reported the electron coupling between the porphyrin moieties attached to the methylcellulose chains at the C-6 position, observing the negative Cotton effect with a maximum  $\Delta\epsilon$  of ca.  $200 \text{ L mol}^{-1} \text{ cm}^{-1}$  per chromophoric unit at about 420 nm.<sup>4f</sup> Since this value is much larger than the  $\Delta\epsilon$  of **1**, it can be safely concluded that the exciton-coupled CD of alternately functionalized celluloses has not been recognized so far because of the weak intensity, and the right-handedness derived from alternately substituted porphyrins on the cellotriose backbone is revealed for the first time.



**Fig. 3** Schematic drawing of a cellulose helix that is left-handed, with exactly three anhydroglucopyranose (AHG) residues per turn of the helix. Two turns are shown, so that the first, fourth and seventh AHG residue all have the same orientation. Each O6 is labeled, and every other O6 has a circle around it to represent a porphyrin substituent. Also shown are two "helical threads" that connect the O6 atoms.<sup>5</sup> (A similar thread could connect any particular type of atom, as long as the molecule is a helix.) One of the threads connects all of the O6 atoms, and it is left-handed. The other helix only connects the circled O6 atoms, and it is right-handed. Since the CD measurements detects only the chromophoric porphyrin

rings at every second AHG unit, a right-handed helix is reported, even though the helical thread through all of the O6 (in every AHG unit) is left-handed.

Analogous to cellulose, the backbone of the cellotriose segment would take a left-handed twist, which was confirmed by QM minimizations of **1**. The values of the interglycosidic torsion angles  $\phi$  and  $\psi$  were within the observed range for crystal structures.<sup>5</sup> At the same time, the porphyrin groups, as demonstrated herein, have a right-handed helical character, which puts the question how a left-handed cellulose helix can give rise to a right-handed chromophore helix? The reason for the opposite handedness is the placement of the porphyrins on every second anhydroglucopyranose unit. Consider a 3-fold cellulose helix with perfect 3-fold screw-axis symmetry (Fig. 3): a left-handed helix is generated when the glucose residues are rotated  $-120^\circ$  and advanced 5 Å along the helix axis. The porphyrin residues are rotated  $-240^\circ$  since they are on every second residue only. At the same time, by the rules of helix definition, one would define this helix by rotating instead  $+120^\circ$ , giving a right-handed helix of chromophores (Fig. 3). These theoretical considerations explain and confirm the above experimental observations.



**Fig. 4** (a) UV/VIS absorption changes of **1** ( $c = 2.5 \mu\text{M}$ ) upon addition of  $\text{C}_{60}$  (1,2,3,4, and 5 eq.) in  $\text{CHCl}_3$ . The absorbance of fullerene had been subtracted from the spectra. (b) Schematic representation of the  $\text{C}_{60}$  assembly with **1**.

To demonstrate the receptor ability of **1**, supramolecular complexes formed between the porphyrin tweezers host and fullerene ( $\text{C}_{60}$ ) was conducted. Fig. 4a presents the UV/Vis spectra of **1** in  $\text{CHCl}_3$  in the presence of incremental amount of  $\text{C}_{60}$ , exhibiting a substantial decrease of the Soret band as well as an increase of a band at 450 nm. Since the van der Waals diameter of  $\text{C}_{60}$  is about 1 nm,<sup>13</sup>  $\pi$ - $\pi$  stacking (sandwich formation) between the bisporphyrins in **1** and fullerene is likely (Fig. 4b). While these results are preliminary, they do show that alternately functionalized celluloses are expected to become a novel type of synthetic molecular receptors owing to their inherent scaffolding properties.

In conclusion, we have demonstrated for the first time the right-handedness of an alternately porphyrinated cellotriose. This finding provides an excellent argument in favor of the high application potential of alternately functionalized celluloses, and a good strategy for the preparation of corresponding model compounds.

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: General experimental procedures, synthesis, NMR spectra, supporting figures and table. See DOI: 10.1039/b000000x/
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## Electronic Supplementary Information (ESI) for

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#### bearing two porphyrin groups

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## 1. Experimental Section

**Materials.** Commercial chemicals were of the highest grade available and were used without further purification. Reagent-grade solvents were used for all extractions and workup procedures. Distilled water was used for all aqueous extractions and for all aqueous solutions. *n*-Hexane, diethyl ether, ethyl acetate, and petroleum ether used in chromatography were distilled before use. All reactions involving nonaqueous conditions were conducted in oven-dried (140 °C, overnight) or flame-dried glassware under an argon or nitrogen atmosphere. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates. Flash chromatography was performed using Baker silica gel (40µm particle size). The use of brine refers to saturated aqueous NaCl. Acetyl 2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (7), 2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranose (8), 2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl trichloroacetoimide (9) were synthesized according to standard oligosaccharide chemistry.

**Measurements.** Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Physical Chemistry at the University of Vienna. <sup>1</sup>H NMR spectra were recorded at 400.13 or 300.13 MHz for <sup>1</sup>H and at 150.86, 100.03 or 75.47 MHz for <sup>13</sup>C NMR in CDCl<sub>3</sub> as the solvent if not otherwise stated. Chemical shifts, relative to tetramethylsilane (TMS) as an internal standard, are given in δ values, and coupling constants in Hz. <sup>13</sup>C peaks were assigned by means of APT, HMQC, and HMBC spectra.

All products were purified to homogeneity by TLC/GCMS analysis. UV-vis spectra were recorded on a HITACHI U-3010 photometer in a quartz cuvette ( $d = 1\text{ cm}$ ) at  $20\text{ }^{\circ}\text{C}$ , CD spectra on a PiStar-180 U (Applied Photophysics, Leatherhead, UK) spectrometer equipped with a thermostatic cell holder.

**Allyl 2',3',4',6'-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-acetyl- $\beta$ -D-glucopyranoside**

**(10).** To a solution of compound **9** (12.2 g, 15.7 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  in the presence of molecular sieve ( $4\text{ \AA}$ , powder) was added allyl alcohol (5.3 mL, 18.5 mmol) at room temperature.  $\text{BF}_3\text{-Et}_2\text{O}$  (0.19 mL, 1.6 mmol) was added at  $-78\text{ }^{\circ}\text{C}$  and the solution was stirred for overnight at rt. The molecular sieve was filtered off, and the filtrate was concentrated, diluted with EtOAc, washed with saturated aqueous  $\text{NaHCO}_3$  solution, water, and brine, and dried over  $\text{Na}_2\text{SO}_4$ . The crude products was purified by flash column chromatography ( $\text{MeOH}/\text{CH}_2\text{Cl}_2$ ,  $v/v = 1:49$ ) to give a colorless solid (9.5 g, 97 %) which had spectra identical to that reported in the literature.<sup>1</sup>

**Allyl  $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranoside (11).** To a solution of compound **10** in a mixture solvent of  $\text{CH}_2\text{Cl}_2$  and MeOH ( $v/v = 1:1$ , 100 mL) was added NaOMe in MeOH (1 M, 1.53 mL) at  $0\text{ }^{\circ}\text{C}$ . The solution was stirred at room temperature overnight. The reaction mixture was neutralized with acidic ion-exchange resin DOWEX 50W X8. The resin was filtered off, and the filtrate was concentrated to give compound **11** (ca. 5 g, 100 % recovery yield) as a colorless solid which had spectra identical to that reported in the literature.<sup>2</sup> The solid was used for the subsequent step without further purification.

**Allyl 4',6'-O-*p*-methoxybenzylidene- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranoside (12).** The compound **11** (2.5 g, 7.7 mmol) was dissolved in DMF (50 mL), and *p*-anisaldehyde dimethyl acetal (1.6 mL, 9.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.29 g, 1.5 mmol) were added. The solution was swirled on a rotary evaporator under reduced pressure (4 kPa) at 40 °C for 4 hr. The reaction mixture was neutralized with NaHCO<sub>3</sub>. The reaction mixture was filtrated and concentrated. The residue was purified by flash column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/19 (v/v)) to give the compound **12** as a slightly yellowish solid (2.9 g, 84.7 %). The solid was used for the subsequent step without further purification.

**Allyl 2',3'-di-O-benzyl-4',6'-O-*p*-methoxybenzylidene- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- $\beta$ -D-glucopyranoside (13).** To a solution of acetal **12** (2.2 g, 5.0 mmol) in anhydrous THF (30 mL) and DMF (10 mL), 60 % NaH dispersed in mineral oil (2.0 g, 50 mmol) were added at 0 °C. After 30 min, benzyl bromide (3.7 mL, 30 mmol) and tetrabutylammonium iodide (0.093 g, 0.25 mmol) were added at 0 °C. The solution was refluxed for 5 hr. After addition of MeOH to decompose remaining NaH, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (toluene, then EtOAc/toluene) to give compound **13** as a colorless solid (1.1 g, 25.4 %): *R*<sub>f</sub> 0.82 (1:1 EtOAc/hexane, v/v); Found: C, 74.35; H, 6.45. Calc. for C<sub>58</sub>H<sub>62</sub>O<sub>12</sub>: C, 73.24; H, 6.57 %; <sup>1</sup>H-NMR (300.13 Hz, CDCl<sub>3</sub>, Me<sub>4</sub>Si,  $\delta$ ): 3.14 (1 H, t, *J* = 7.9 Hz, H-5'), 3.31 (1 H, dd, *J*<sub>5, 6a</sub> = 11.7, *J*<sub>5, 6b</sub>

= 2.2, H-5), 3.35 (1 H, t,  $J_{1,2}$  = 8.0 Hz, H-2'), 3.449 (1 H, t,  $J_{1,2}$  = 7.5 Hz, H-2), 3.455 (1 H, H-6'a), 3.53 (1 H, t,  $J_{2,3}$  = 8.6 Hz, H-3), 3.57-3.62 (2 H, H-3', H-4'), 3.66 (1 H, dd,  $J_{5,6a}$  = 1.5 Hz,  $J_{6a,6b}$  = 11.1 Hz, H-6a), 3.80-3.85 (1 H, dd,  $J_{5,6b}$  = 3.9 Hz, H-6b), 3.81 (3 H, s, OMe), 3.97 (1 H, t,  $J_{3,4}$  = 9.3 Hz, H-4), 4.12 (1 H, ddt,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 4.13-4.18 (1 H, m, H-6'b), 4.36 (1 H,  $\text{CH}_2\text{PhOMe}$ ), 4.37-4.42 (1 H, ddt,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 4.42 (1 H, d,  $J_{1',2'}$  = 8.4 Hz, H-1'), 4.53 (1 H, d,  $J_{1,2}$  = 7.8 Hz, H-1), 4.58 (1 H, d,  $\text{CH}_2\text{PhOMe}$ ), 4.69-4.92 (8 H, m,  $\text{CH}_2\text{Ph}$ ), 5.20 (1 H, ddt,  $J_{\alpha,\gamma(\text{long range})}$  = 1.4 Hz,  $J_{\gamma a,\gamma b(\text{geminal})}$  = 3.0 Hz,  $J_{\beta,\gamma a(\text{cis})}$  = 10.4 Hz,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.33 (1 H, ddt,  $J_{\alpha,\gamma(\text{long range})}$  = 1.6 Hz,  $J_{\gamma a,\gamma b(\text{geminal})}$  = 3.2 Hz,  $J_{\beta,\gamma a(\text{trans})}$  = 17.2 Hz,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.44 (1 H, s,  $\text{CHPhOMe}$ ), 5.95 (1 H, m,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.90 (d,  $J$  = 9.2 Hz,  $\text{PhOMe}$ ), 7.2-7.4 (27 H, Bn).  $^{13}\text{C}$ -NMR (75.47 Hz,  $\text{CDCl}_3$ ,  $\delta$ ): 55.28 (OMe), 65.80 (C-5'), 68.00 (C-6), 68.78 (C-6'), 70.25 ( $-\text{OCH}_2\text{CH}=\text{CH}_2$ ), 73.26, 74.93, 75.00 ( $3 \times \text{CH}_2\text{Ph}$ ), 75.09 (C-5), 75.40 ( $\text{CH}_2\text{Ph}$ ), 76.86 (C-4), 81.16 (C-3'), 81.70 (C-2), 82.74 (C-4'), 82.53 (C-2'), 82.91 (C-3), 101.08 ( $\text{CHPh}$ ), 102.68 (C-1), 102.79 (C-1'), 113.57 (Ph), 117.18 ( $-\text{OCH}_2\text{CH}=\text{CH}_2$ ), 127.35, 127.39, 127.57, 127.60, 127.66, 127.79, 127.81, 127.95, 128.11, 128.27, 128.36, 129.95 (Ph), 134.13 ( $-\text{OCH}_2\text{CH}=\text{CH}_2$ ), 138.19, 138.37, 138.56, 138.61, 139.06, 160.01 (Ph).

**Allyl 2',3'-di-O-benzyl-6'-O-p-methoxybenzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- $\beta$ -D-glucopyranoside (14).** A mixture of compound **13** (0.49 g, 1 mmol),  $\text{NaCNBH}_3$  (0.50 g, 8 mmol), and freshly activated 4Å molecular sieves (0.5 g) in dry DMF (5 mL) was stirred at room temperature under argon for 30 min. The  $\text{CF}_3\text{COOH}$  (0.77 mL, 10 mmol) was added dropwise at 0 °C. After stirring overnight at room temperature, the reaction mixture was quenched by addition of  $\text{NaHCO}_3$ .

The mixture was filtered, and diluted with EtOAc, washed with saturated aqueous NaHCO<sub>3</sub> solution, brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/toluene) to give compound **14** as a colorless oil (0.35 g, 71.4 %): *R*<sub>f</sub> 0.37 (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, v/v = 2:98); Found: C, 73.14; H, 6.54. Calc. for C<sub>58</sub>H<sub>64</sub>O<sub>12</sub>: C, 73.09; H, 6.77.; <sup>1</sup>H-NMR (300.13 Hz, CDCl<sub>3</sub>, Me<sub>4</sub>Si, δ): 2.93 (1 H, d, *J*<sub>4',OH</sub> = 1.8 Hz, 4'-OH), 3.24 (1 H, ddd, *J*<sub>5',6'</sub> = 3.6 Hz, *J*<sub>4',5'</sub> = 9.6 Hz, H-5'), 3.30 (1 H, t, *J*<sub>2',3'</sub> = 9.0 Hz, H-2'), 3.32 (1 H, t, *J*<sub>5,6</sub> = 4.5 Hz, H-5), 3.34 (1 H, dd, H-3'), 3.43-3.55 (4 H, m, H-2, H-6'a, H-3, H-6'b), 3.60 (1 H, t, *J*<sub>4',5'</sub> = 9.6 Hz, H-4') 3.69 (1 H, dd, *J*<sub>5,6a</sub> = 1.2 Hz, *J*<sub>6a,6b</sub> = 7.2 Hz, H-6a), 3.82-3.84 (dd, *J*<sub>5,6b</sub> = 3.9 Hz, H-6b), 3.78 (3 H, s, OMe), 3.97 (1 H, t, *J*<sub>3,4</sub> = 9.3 Hz, H-4), 4.12 (1 H, ddt, OCH<sub>2</sub>CH=CH<sub>2</sub>), 4.34 (1 H, CH<sub>2</sub>PhOMe), 4.37-4.42 (1 H, ddt, OCH<sub>2</sub>CH=CH<sub>2</sub>), 4.41 (1 H, d, *J*<sub>1,2</sub> = 7.8 Hz, H-1), 4.47 (1 H, d, *J*<sub>1',2'</sub> = 7.2 Hz, H-1'), 4.59 (1 H, d, CH<sub>2</sub>PhOMe), 4.68-4.95 (8 H, m, CH<sub>2</sub>Ph), 5.19 (1 H, ddt, *J*<sub>αa,γ(long range)</sub> = 1.2 Hz, *J*<sub>γa,γb(geminal)</sub> = 3.0 Hz, *J*<sub>β,γa(cis)</sub> = 10.5 Hz, OCH<sub>2</sub>CH=CH<sub>2</sub>), 5.33 (1 H, ddt, *J*<sub>αa,γ(long range)</sub> = 1.7 Hz, *J*<sub>γa,γb(geminal)</sub> = 3.3 Hz, *J*<sub>β,γa(trans)</sub> = 17.2 Hz, OCH<sub>2</sub>CH=CH<sub>2</sub>), 5.95 (1 H, m, OCH<sub>2</sub>CH=CH<sub>2</sub>), 6.84 (d, *J* = 8.6 Hz, PhOMe), 7.10-7.43 (27 H, Bn). <sup>13</sup>C-NMR (75.47 Hz, CDCl<sub>3</sub>, δ): 55.29 (OMe), 68.14 (C-6), 70.22 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 70.98 (C-6'), 72.94 (C-5'), 73.75 (C-4'), 74.92, 74.98 (2 × CH<sub>2</sub>Ph), 75.09 (C-5), 75.10, 75.26 (2 × CH<sub>2</sub>Ph), 76.61 (C-4), 81.72 (C-2), 82.07 (C-2'), 82.82 (C-3), 84.34 (C-3'), 102.35 (C-1'), 102.67 (C-1), 113.82 (Ph), 117.15 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 125.30, 127.63, 127.70, 127.75, 127.81, 127.85, 128.01, 128.09, 128.25, 128.27, 128.36, 128.39, 129.26 (Ph), 134.14 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 138.21, 138.48, 138.61, 138.78, 139.23 (Ph).

Allyl

**2',3'-di-O-benzyl-6'-O-*p*-methoxybenzyl-4'-O-methyl-β-D-glucopyranosyl-**

**(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (15).** A solution of compound **14** (0.67 g, 0.70 mmol) in anhydrous THF (10 mL) was cooled down to 0 °C followed by addition of 60 % NaH dispersed in mineral oil (56 mg, 1.4 mmol). After 30 min, methyl iodide (66 μL, 0.11 mmol) was added at 0 °C. The resulting suspension was stirred until no starting material was found. After addition of MeOH to decompose remaining NaH, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (EtOAc/toluene, v/v = 1:9) to give compound **15** as a colorless solid (0.59 g, 86.2 %). *R*<sub>f</sub> 0.55 (EtOAc-hexane, v/v = 1:2); Found: C, 73.75; H, 5.88. Calc. for C<sub>59</sub>H<sub>66</sub>O<sub>12</sub>: C, 73.27; H, 6.88.; <sup>1</sup>H-NMR (300.13 Hz, CDCl<sub>3</sub>, Me<sub>4</sub>Si, δ): 3.18 (1 H, dd, *J*<sub>5',6'</sub> = 3.6 Hz, *J*<sub>4',5'</sub> = 9.6 Hz, H-5'), 3.30 (1 H, t, *J*<sub>2',3'</sub> = 8.7 Hz, H-2'), 3.31 (1 H, t, *J*<sub>5,6</sub> = 8.7 Hz, H-5), 3.33 (1 H, t, *J*<sub>4',5'</sub> = 8.1 Hz, H-4'), 3.42 (1 H, dd, *J*<sub>3',4'</sub> = 8.7 Hz, H-3'), 3.46 (3 H, s, 4'-OMe), 3.48 (1 H, t, *J*<sub>2,3</sub> = 9.0 Hz, H-2), 3.50 (1 H, dd, *J*<sub>5',6a'</sub> = 4.2 Hz, *J*<sub>6'a,6'b</sub> = 10.8 Hz, H-6'a), 3.57 (1 H, t, *J*<sub>3,4</sub> = 9.3 Hz, H-3), 3.64 (1 H, dd, *J*<sub>5',6b'</sub> = 1.2 Hz, *J*<sub>6'a,6'b</sub> = 11.1 Hz, H-6'b), 3.67 (1 H, dd, *J*<sub>5,6a</sub> = 1.5 Hz, *J*<sub>6a,6b</sub> = 11.1 Hz, H-6a), 3.76 (3 H, s, PhOMe), 3.80 (1 H, m, H-6b), 3.99 (1 H, t, *J*<sub>3,4</sub> = 9.0 Hz, H-4), 4.11 (1 H, ddt, OCH<sub>2</sub>CH=CH<sub>2</sub>), 4.35 (1 H, CH<sub>2</sub>PhOMe), 4.36-4.42 (1 H, ddt, OCH<sub>2</sub>CH=CH<sub>2</sub>), 4.41 (1 H, d, *J*<sub>1,2</sub> = 7.8 Hz, H-1), 4.47 (1 H, d, *J*<sub>1',2'</sub> = 6.3 Hz, H-1'), 4.58 (1 H, d, CH<sub>2</sub>PhOMe), 4.66-5.06 (8 H, m, CH<sub>2</sub>Ph), 5.18 (1 H, ddt, *J*<sub>αa,γ(long range)</sub> = 1.2 Hz, *J*<sub>γa,γb(geminal)</sub> = 3.0 Hz, *J*<sub>β,γa(cis)</sub> = 10.5 Hz, OCH<sub>2</sub>CH=CH<sub>2</sub>(cis)), 5.32 (1 H, ddt, *J*<sub>αa,γ(long range)</sub> = 1.7 Hz, *J*<sub>γa,γb(geminal)</sub> = 3.3 Hz, *J*<sub>β,γa(trans)</sub> = 17.2 Hz, OCH<sub>2</sub>CH=CH<sub>2</sub>(trans)), 5.94 (1 H, m, OCH<sub>2</sub>CH=CH<sub>2</sub>), 6.80 (d, *J* = 9.0 Hz, PhOMe), 7.15-7.36 (27 H, Ph). <sup>13</sup>C-NMR (75.47 Hz, CDCl<sub>3</sub>, δ): 55.25 (PhOMe), 60.58 (4'-OMe), 68.24 (C-6), 68.70 (C-6'), 70.22 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 72.93, 73.26, 74.89, 74.94 (4 × CH<sub>2</sub>Ph), 75.12 (C-5, C-5'), 75.52

(CH<sub>2</sub>Ph), 76.64 (C-4), 80.00 (C-4'), 81.75 (C-2), 82.57 (C-2'), 82.85 (C-3), 84.84 (C-3'), 102.35 (C-1'), 102.65 (C-1), 113.62 (Ph), 117.11 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 127.07, 127.50, 127.55, 127.70, 127.73, 127.82, 127.85, 128.00, 128.11, 128.22, 128.27, 128.32, 129.09, 130.68 (Ph), 134.17 (-OCH<sub>2</sub>CH=CH<sub>2</sub>), 138.25, 138.54, 138.61, 138.72, 139.41 (Ph).

**2',3'-Di-O-benzyl-6'-O-*p*-methoxybenzyl-4'-O-methyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranose (16).** (1,5-Cyclooctadiene)bis(methyldiphenyl-phosphine)iridium(I)

hexafluorophosphate (26 mg, 30 μmol) in anhydrous THF (5 mL) was activated with H<sub>2</sub>. To a solution of compound **15** (0.56 g, 0.61 mmol) in anhydrous THF (5 mL) was added to the activated iridium catalyst under argon at rt, then the solution was stirred for 5 min. Water (2 mL) and iodine (0.31 g, 1.2 mmol) were added and stirred for 30 min. The reaction mixture was diluted with EtOAc, washed with 5 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (EtOAc/toluene, v/v = 1:3) to give compound **16** as colorless syrup (0.46 g, 83.1 %). *R*<sub>f</sub> 0.17 (EtOAc-toluene, v/v = 1:2); Found: C, 72.72; H, 5.58. Calc. for C<sub>56</sub>H<sub>62</sub>O<sub>12</sub>: C, 72.55; H, 6.74.; <sup>1</sup>H-NMR (300.13 Hz, CDCl<sub>3</sub>, Me<sub>4</sub>Si, δ): 3.19 (1 H, dd, *J*<sub>5',6'</sub> = 2.7 Hz, *J*<sub>4',5'</sub> = 9.9 Hz, H-5'), 3.29 (1 H, t, *J*<sub>2',3'</sub> = 6.9 Hz, H-2'), 3.27-3.90 (m, ring proton), 3.47 (3 H, s, 4'-OMe), 3.77 (3 H, s, PhOMe), 3.98 (1 H, t, H-4), 4.37 (1 H, CH<sub>2</sub>PhOMe), 4.42 (1 H, d, *J*<sub>1',2'</sub> = 6.9 Hz, H-1'), 4.54-4.87 (8 H, m, CH<sub>2</sub>Ph), 5.07 (1 H, d, *J*<sub>1,2</sub> = 11.4 Hz, H-1β), 5.18 (1 H, t, *J*<sub>1,2</sub> = 3.6 Hz, H-1α), 6.81 (d, *J* = 8.4 Hz, PhOMe), 7.14-7.33 (27 H, Ph).

**2',3'-Di-O-benzyl-6'-O-*p*-methoxybenzyl-4'-O-methyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- $\alpha,\beta$ -D-glucopyranosyl trichloroacetoimidate (3).** To a solution of **16** (0.19 g, 0.21 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0 °C was added DBU (9.2  $\mu$ L, 62  $\mu$ mol) and trichloroacetonitrile (64  $\mu$ L, 0.62  $\mu$ mol). The solution was stirred at rt for 2 hr. The reaction mixture was directly purified by flash column chromatography (EtOAc/toluene, v/v = 1:19, containing 1 % of triethylamine, v/v) to give donor **3** as colorless syrup (0.19 g, 88.2 %). The donor was unstable when stored at rt for several days, so that it was used for the subsequent glycosidation step immediately after purification.

**Methyl 4,6-O-*p*-methoxybenzylidene- $\beta$ -D-glucopyranoside (18).** Methyl  $\beta$ -D-glucopyranoside (**17**, 10 g, 51.5 mmol) was dissolved in DMF (50 mL), and *p*-anisaldehyde dimethyl acetal (10.5 mL, 61.8 mmol) and *p*-toluenesulfonic acid monohydrate (1.96 g, 10.3 mmol) were added. The solution was swirled on a rotary evaporator under reduced pressure (4 kPa) at 40 °C for 4 hr, then at 70 °C for 1 hr to further push the reaction to completion. The reaction mixture was neutralized with NaHCO<sub>3</sub>. The reaction mixture was filtrated and concentrated. The residue was purified by flash column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, v/v = 1/19 to 1/9) to give compound **18** as a colorless solid (12.9 g, 80.0 %) which had spectra identical to that reported in the literature.<sup>3</sup>

**Methyl 4,6-O-*p*-methoxybenzylidene-2,3-di-O-benzyl- $\beta$ -D-glucopyranoside (19).** To a solution of acetal **18** (9.8 g, 31.5 mmol) in THF (100 mL), 60 % NaH dispersed in mineral oil (5.04 g, 126 mmol) were added at 0 °C. After 30 min, benzyl bromide (8.97 mL, 75.5 mmol) and tetrabutylammonium

iodide (0.58 g, 1.58 mmol) were added at 0 °C. The solution was stirred at rt overnight. After addition of MeOH to decompose remaining NaH, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (toluene, then EtOAc/toluene) to give compound **19** as a colorless solid (5.4 g, 34.5 %) which had spectra identical to that reported in the literature.<sup>3</sup>

**Methyl 2,3-di-O-benzyl-6-O-p-methoxybenzyl-β-D-glucopyranoside (6).** A mixture of compound **19** (0.49 g, 1 mmol), NaCNBH<sub>3</sub> (0.50 g, 8 mmol), and freshly activated 4Å molecular sieves (0.5 g) in dry DMF (5 mL) was stirred at room temperature under argon for 30 min. The CF<sub>3</sub>COOH (0.77 mL, 10 mmol) was added dropwise at 0 °C. After stirring overnight at room temperature, the reaction mixture was quenched by addition of NaHCO<sub>3</sub>. The mixture was filtered, and diluted with EtOAc, washed with saturated aqueous NaHCO<sub>3</sub> solution, brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/toluene) to give glucoside acceptor **6** as a colorless solid (0.35 g, 71.4 %) which had spectra identical to that reported in the literature.<sup>3</sup>

**Methyl 2'',3''-di-O-benzyl-6''-O-p-methoxybenzyl-4''-O-methyl-β-D-glucopyranosyl-(1→4)-2',3',6'-tri-O-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-p-methoxybenzyl-β-D-glucopyranoside (4).** To a solution of donor **3** (0.234 g, 0.218 mmol) and acceptor **6** (0.113 g, 0.229 mmol) with molecular sieves 4A (0.3 g) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added BF<sub>3</sub>-Et<sub>2</sub>O (5.4 μL, 0.044 mmol) at – 30 °C. The solution was stirred at – 30 °C for 6 hr. The reaction

mixture was neutralized with triethylamine at 0 °C, filtered molecular sieves, diluted with EtOAc, washed with saturated aqueous NaHCO<sub>3</sub> and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (EtOAc/toluene, v/v = 1:9 then 1:4) to give compound **4** with an unidentified carbohydrate derived from donor **11** as colorless syrup (0.224 g, 73.1 % calculated from donor **11**). *R*<sub>f</sub> 0.56 (EtOAc/toluene, v/v = 1:4); <sup>1</sup>H-NMR (300.13 Hz, CDCl<sub>3</sub>, Me<sub>4</sub>Si, δ): 4.25-4.86 (H-1, H-1', H-1'', CH<sub>2</sub>Ph), 5.09 (1 H, t, *J* = 11.3 Hz), 5.39 (1 H, d, *J* = 2.7 Hz), 5.57 (1 H, d, *J* = 2.7 Hz), 6.77 (2 H, d, *J* = 8.7 Hz, *PhOMe*), 6.80 (2 H, d, *J* = 8.6 Hz, *PhOMe*), 7.10-7.41 (39 H, Bn). <sup>13</sup>C-NMR (75.47 Hz, CDCl<sub>3</sub>, δ): 55.07, 55.20 (2 × *PhOMe*), 56.99 (1-*OMe*), 60.56 (4''-*OMe*), 67.81, 67.76, 68.08, 68.71 (C-6, C-6', C-6''), 72.56, 72.61, 72.90, 72.98, 73.32, 73.80, 74.80, 74.94, 75.09, 75.38, 75.47 (CH<sub>2</sub>Ph), 75.01, 75.25, 75.57 (C-5, C-5', C-5''), 78.41, 79.74, 79.98 (C-4, C-4', C-4''), 81.70, 82.05, 82.56, 83.40, 84.75, 82.85 (C-2, C-2', C-2'', C-3, C-3', C-3''), 102.41, 102.48 (C-1', C-1''), 104.62 (C-1), 104.27, 107.28, 113.55, 113.70, 126.75-128.47, 129.03, 129.79, 130.66, 130.23, 137.60-139.43, 158.96, 159.07 (Ph).

**Methyl 2'',3''-di-*O*-benzyl-4''-*O*-methyl-β-D-glucopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-glucopyranoside (5).** Compound **4** (0.0615 g, 0.044 mmol) was dissolved in dichloromethane-acetone-water (2 mL, v/v/v = 4:4:1). Ammonium cerium(IV) nitrate (CAN) (0.192 g, 0.35 mmol) was added and stirred at rt for 1 hr. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through celite and concentrated to dryness. The residue was purified by flash column chromatography (EtOAc/toluene, v/v = 1:4 to 1:2) to give compound **5** as colorless syrup

(0.022 g, 43.9%).  $R_f$  0.35 (EtOAc/hexane, v/v = 1:1);  $^1\text{H-NMR}$  (300.13 Hz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ,  $\delta$ ): 3.43 (3 H, 4''-OMe), 3.54 (3 H, s, 1-OMe), 4.23 (1 H, d,  $\text{CH}_2\text{Ph}$ ), 4.31 (1 H, d,  $J_{1,2} = 7.6$  Hz, H-1), 4.38 (1 H, d,  $\text{CH}_2\text{Ph}$ ), 4.38 (1 H, d,  $J_{1,2} = 8.0$  Hz, H-1' or H-1''), 4.57 (1 H, d,  $J_{1'',2''} = 7.9$  Hz, H-1' or H-1''), 4.65-4.83 (10 H, m,  $\text{CH}_2\text{Ph}$ ), 4.95, 5.09 (2 H,  $2 \times$  d,  $\text{CH}_2\text{Ph}$ ), 7.14-7.34 (35 H, Bn).  $^{13}\text{C-NMR}$  (75.47 Hz,  $\text{CDCl}_3$ ,  $\delta$ ): 57.27 (1-OMe), 60.61 (4''-OMe), 61.15, 61.79 (C-6, C-6''), 67.97 (C-6'), 73.10, 74.93, 74.97, 75.10, 75.57 ( $\text{CH}_2\text{Ph}$ ), 74.86, 75.06, 75.28 (C-5, C-5', C-5''), 77.15, 77.22 (C-4, C-4'), 80.04, 81.86, 81.98 (C-2, C-2', C-2''), 82.52, 82.61, 83.14 (C-3, C-3', C-3''), 84.54 (C-4''), 102.32, 102.88 (C-1', C-1''), 104.66 (C-1), 127.00, 127.11, 127.52, 127.56, 127.68, 127.84, 128.03, 128.36, 138.22, 138.34, 138.53, 138.62, 139.08, 139.34 (Ph).

**Methyl 2'',3''-di-O-benzyl-4''-O-methyl-6''-O-[p-(10,15,20-triphenyl-5-porphyrinyl)-benzoyl]- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2',3',6'-tri-O-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3-di-O-benzyl-6-O-[p-(10,15,20-triphenyl-5-porphyrinyl)-benzoyl]- $\beta$ -D-glucopyranoside (1).** To a solution of 5-(4'-carboxyphenyl)-10,15,20-triphenylporphin (0.027 g, 0.045 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (1 mL), 1,3-dicyclohexylcarbodiimide (DCC) (0.010 g, 0.050 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.0073 g, 0.059 mmol) were added at 0 °C and stirred for 15 min. The compound **5** (0.023 g, 0.020 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2 mL) was then added and stirred at rt overnight under light shielding. A second portion of the porphin (0.013 g, 0.020 mmol), DCC (0.0049 g, 0.0024 mmol), and DMAP (0.0037 g, 0.030 mmol) was added and stirred overnight. Solids were filtered off through celite, and the filtrate was evaporated. The residue was purified by flash column

chromatography (EtOAc-toluene, v/v = 1:19) to give target **1** as purple solid (0.034 g, 70.9 %):  $R_f$  0.84 (EtOAc-hexane, v/v = 1:1);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  419 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  104 490), 449 (45 200);  $^1\text{H-NMR}$  (400.13 Hz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ,  $\delta$ ): 3.55 (3 H, s, 4''-OMe), 3.59 (3 H, s, 1-OMe), 4.29 (1 H, d,  $J_{1,2} = 7.6$  Hz, H-1), 4.54 (1 H, d,  $J_{1',2'} = 8.0$  Hz, H-1'), 4.67 (1 H, d,  $J_{1'',2''} = 8.4$  Hz, H-1''), 4.40-4.87 (12 H, m,  $\text{CH}_2\text{Ph}$ ), 4.95, 5.09 (1 H,  $2 \times$  d,  $\text{CH}_2\text{Ph}$ ), 6.56 (1 H, ddt,  $J = 1.4$  Hz,  $J = 2.8$  Hz,  $J = 7.4$  Hz, Bn), 6.74 (2 H, ddt,  $J = 1.5$  Hz,  $J = 3.2$  Hz,  $J = 7.6$  Hz, Bn), 7.01 (2 H, dd,  $J = 1.2$  Hz,  $J = 8.2$  Hz, Bn), 7.04-7.07 (3 H, m, Bn), 7.11-7.28 (26 H, Bn), 7.38 (2 H, dd,  $J = 1.7$  Hz,  $J = 7.9$  Hz, Bn), 7.68-7.78 (18 H, m, 10,15,20-porphyrin-aromatic-*meta* and *para*-H), 8.15-8.23 (16 H, m, 10,15,20-porphyrin-aromatic-*ortho*-H, 5-porphyrin-aromatic-*meta*-H), 8.30, 8.35 (4 H,  $2 \times$  d,  $J = 8.4$  Hz, 5-porphyrin-aromatic-*ortho*-H), 8.71 (4 H, dd,  $J = 4.9$  Hz,  $J = 9.2$  Hz,  $\beta$ -H), 8.77-8.86 (12 H, m,  $\beta$ -H);  $^{13}\text{C-NMR}$  (100.03 Hz,  $\text{CDCl}_3$ ,  $\delta$ ): 57.09 (1-OMe), 60.94 (4''-OMe), 63.41, 63.89 (C-6, C-6''), 68.08 (C-6'), 73.12, 74.76, 74.96, 75.19, 75.67 ( $\text{CH}_2\text{Ph}$ ), 73.00, 73.36, 75.41 (C-5, C-5', C-5''), 77.25, 77.64 (C-4, C-4'), 80.13, 81.75, 82.27 (C-2, C-2', C-2''), 82.33, 82.45, 83.30 (C-3, C-3', C-3''), 84.72 (C-4''), 102.75 (C-1', C-1''), 104.52 (C-1), 118.45, 118.55, 120.35, 120.54, 126.72, 127.12, 127.22, 127.39, 127.56, 127.58, 127.70, 127.76, 127.87, 127.93, 127.99, 128.13, 128.17, 128.21, 128.36, 129.26, 129.42, 134.54, 137.87, 138.28, 138.39, 138.46, 139.03, 139.16 142.06, 147.09 (Ph), 166.08, 166.39 (C=O).

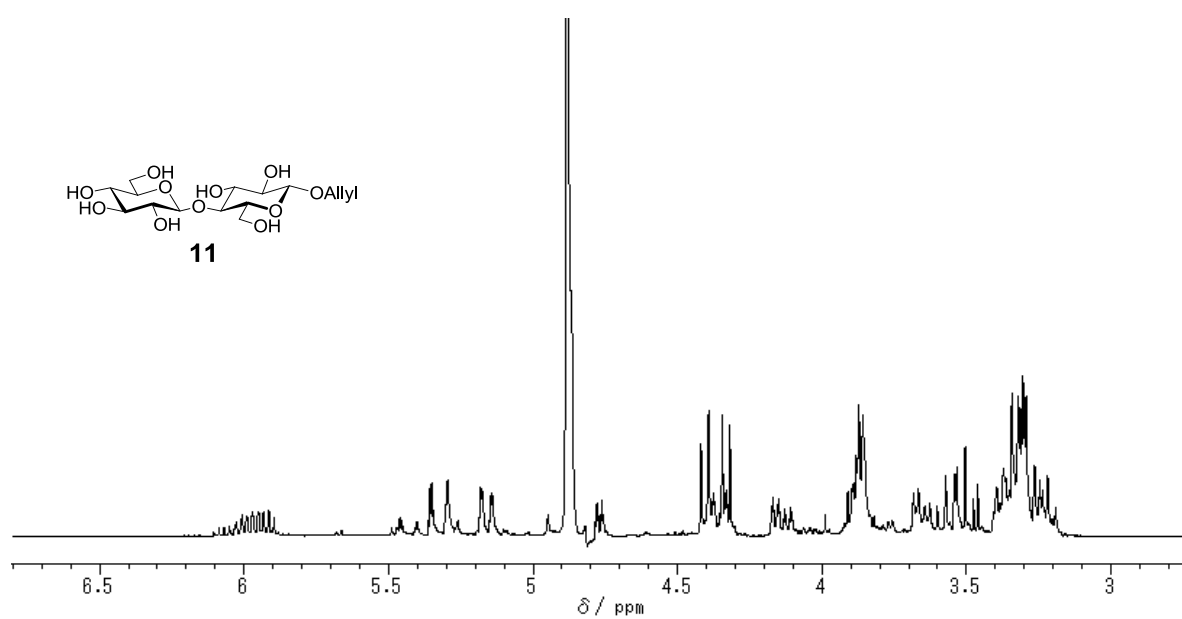
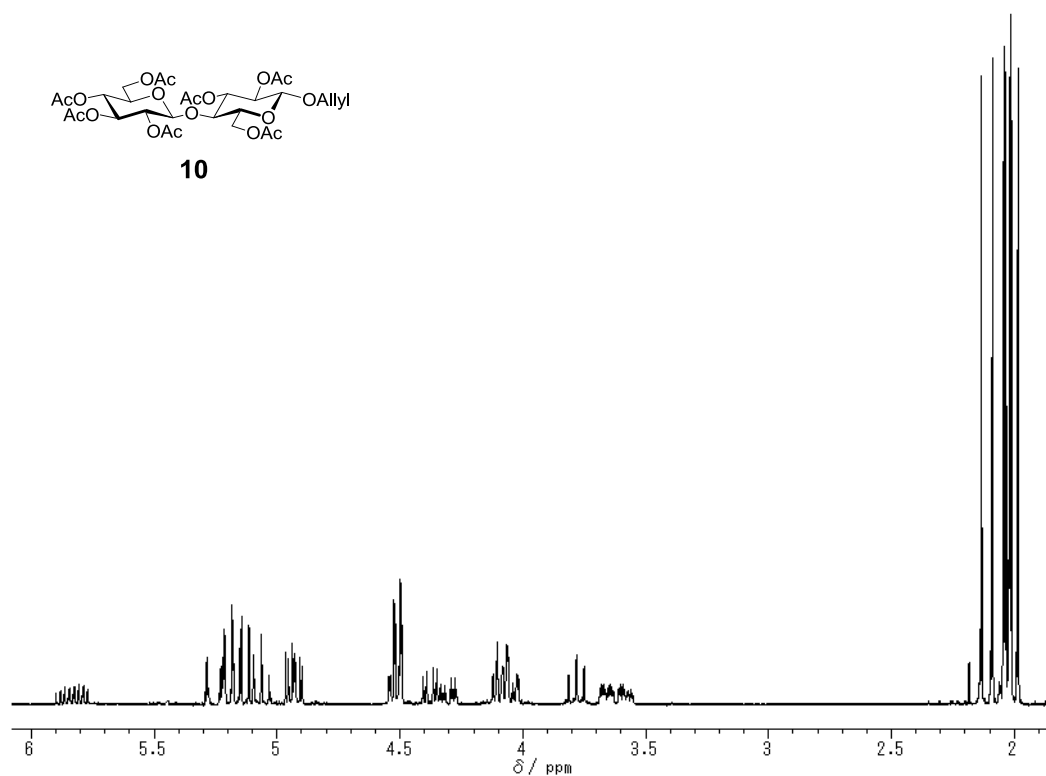
**Methyl 2,3-di-O-benzyl-6-O-*p*-methoxybenzyl-4-O-methyl- $\beta$ -D-glucopyranoside (20).** A solution of compound **6** (1.35 g, 2.7 mmol) in anhydrous THF (20 mL) was cooled down to 0 °C followed by addition of 60 % NaH dispersed in mineral oil (0.22 g, 5.5 mmol). After 30 min, methyl iodide (0.26 mL,

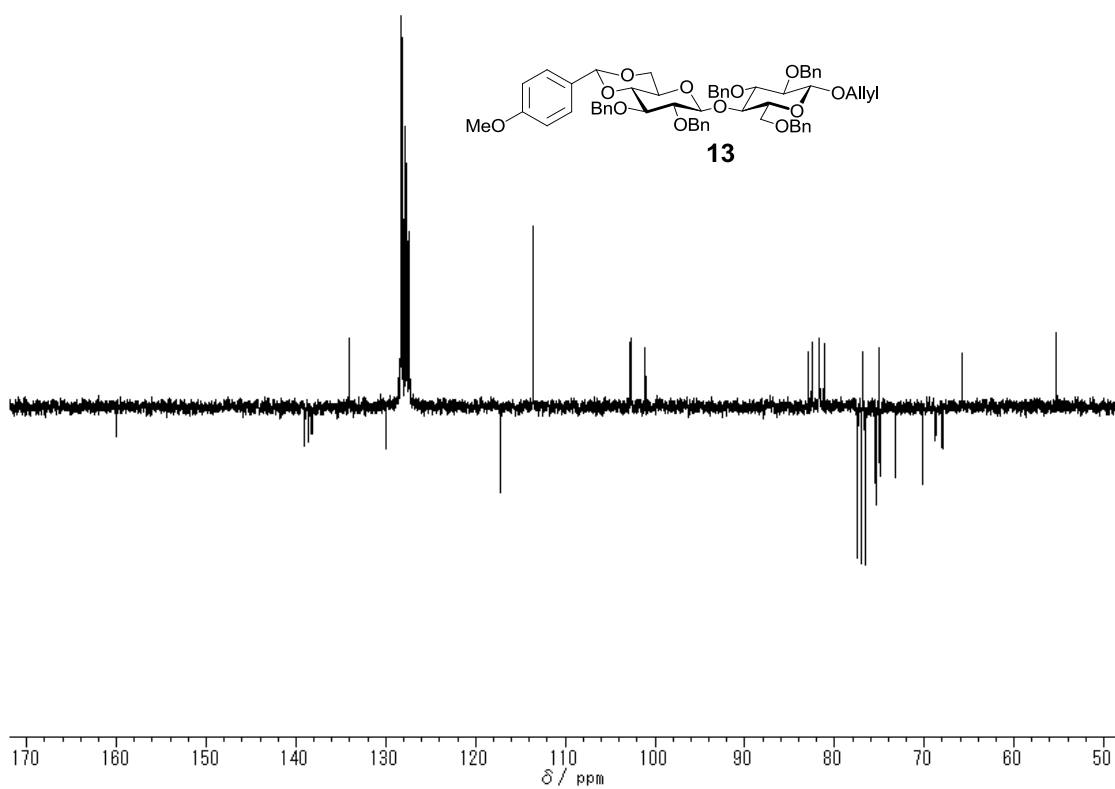
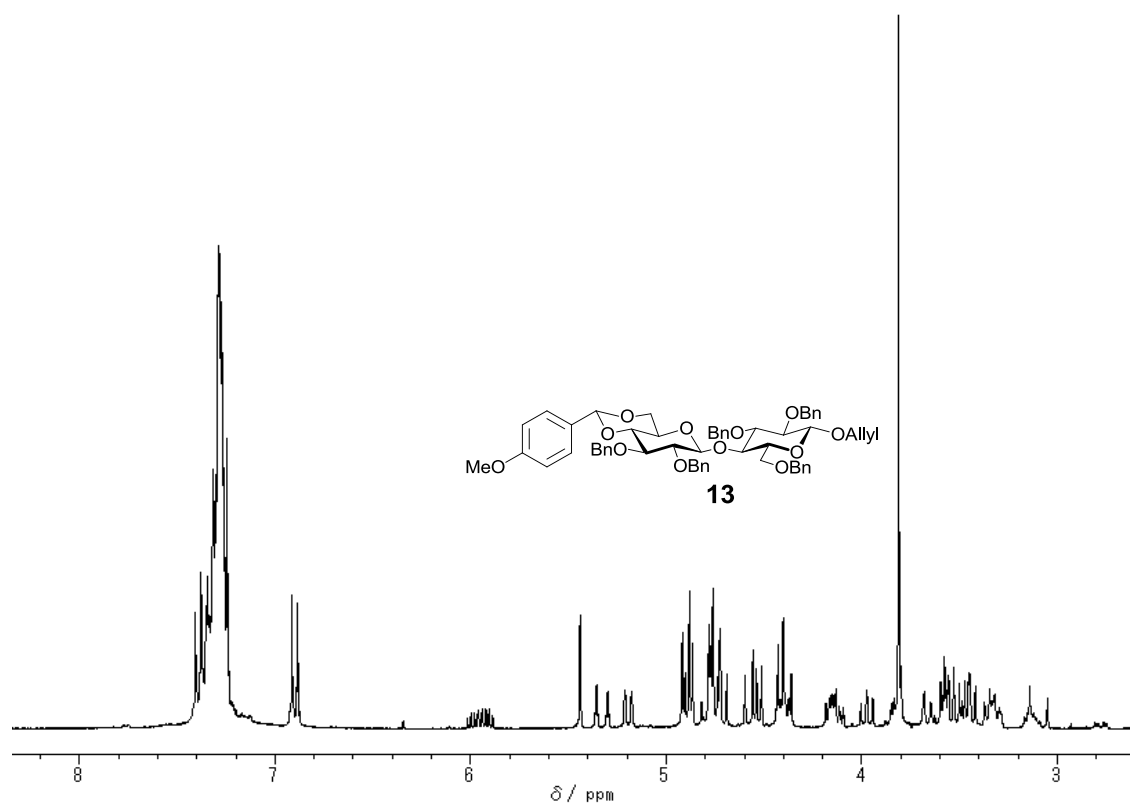
4.1 mmol) was added at 0 °C. The resulting suspension was stirred until no starting material was found. After addition of MeOH to decompose remaining NaH, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash column chromatography (EtOAc/toluene, v/v = 1:9) to give compound **20** as a colorless solid (1.4 g, 100 %) which had spectra identical to that reported in the literature.<sup>4</sup>

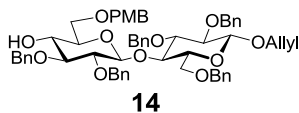
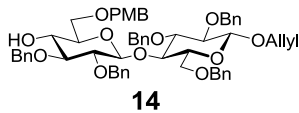
**Methyl 2,3-di-O-benzyl-4-O-methyl-β-D-glucopyranoside (21).** Compound **20** was reacted according to the synthesis of compound **5**. Final purification by chromatography (EtOAc/toluene, v/v = 1:9) gave **21** as a white solid which had spectra identical to the reported in the literature.<sup>4</sup>

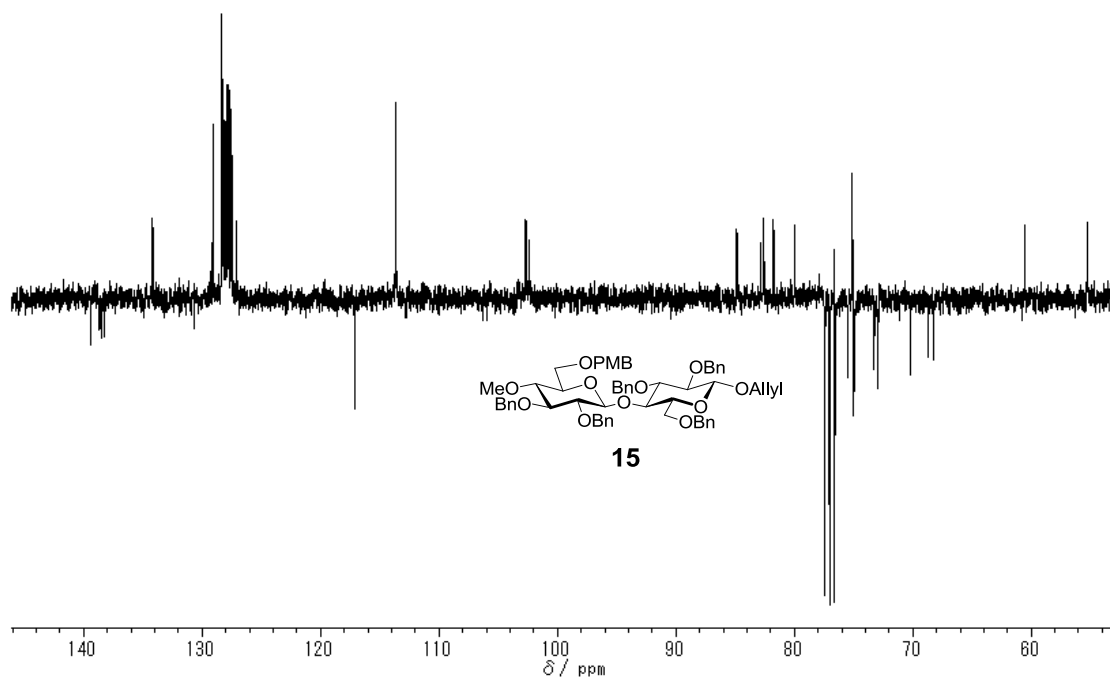
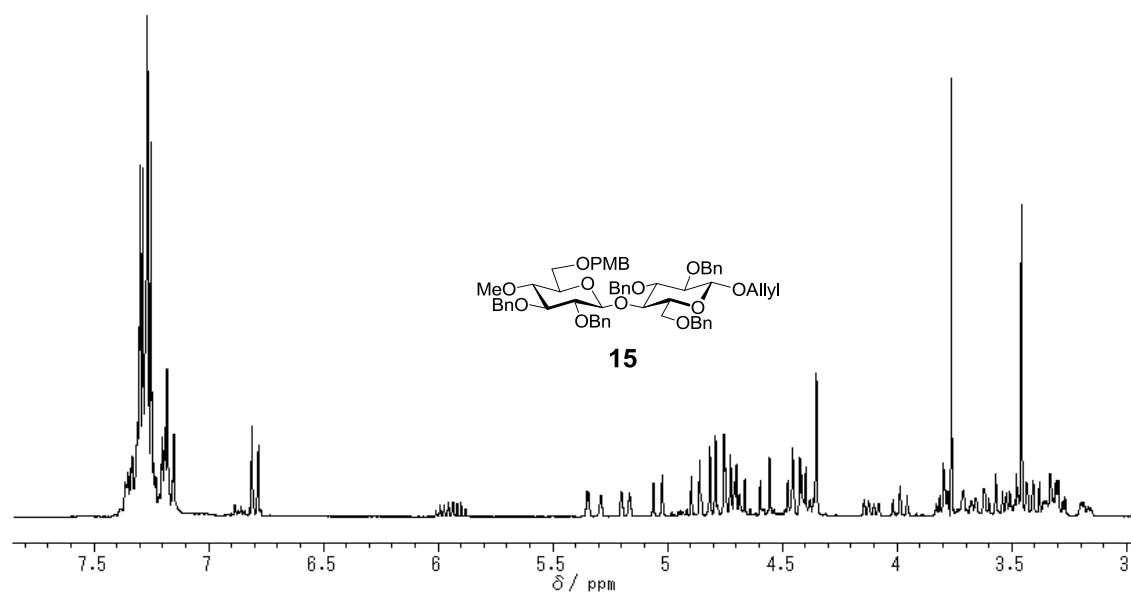
**Methyl 2,3-di-O-benzyl-4-O-methyl-6-O-[p-(10,15,20-triphenyl-5-porphyrinyl)-benzoyl]-β-D-glucopyranoside (2).** Compound **21** was reacted according to the synthesis of compound **1**. Final purification by chromatography (EtOAc/toluene, v/v = 1:19) gave **2** as a purple solid.

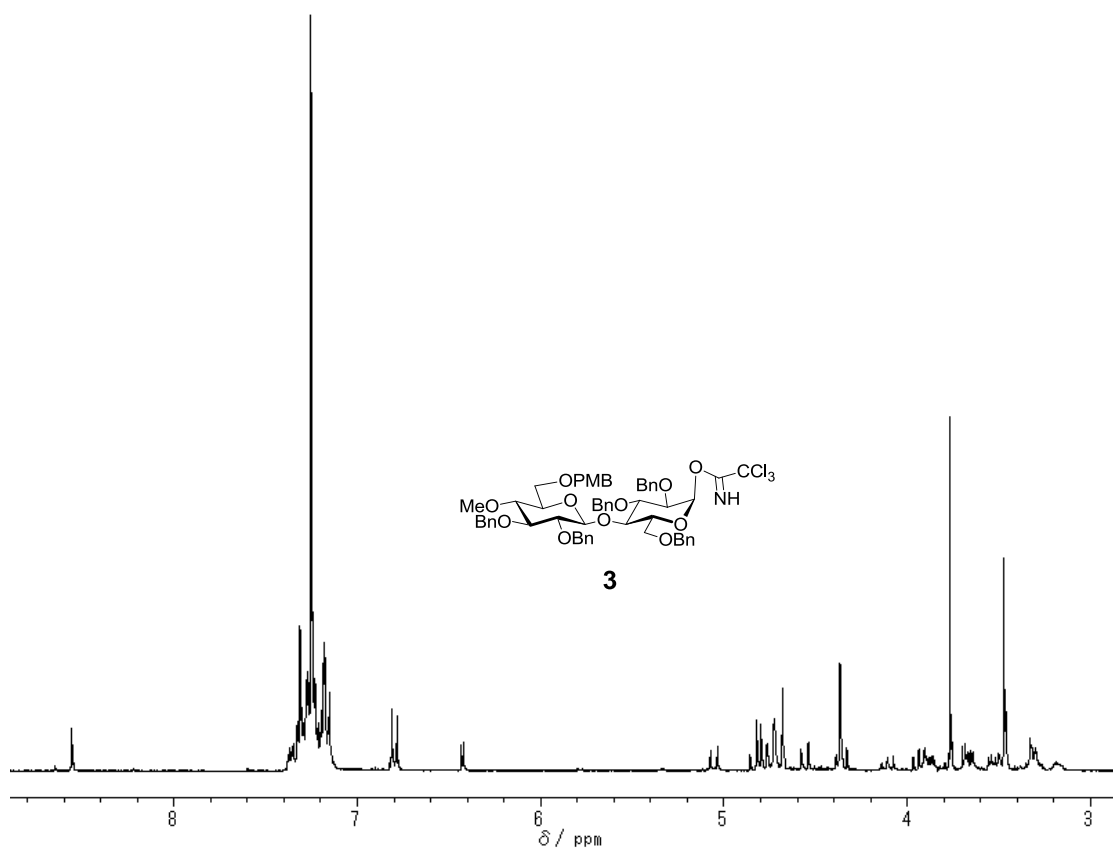
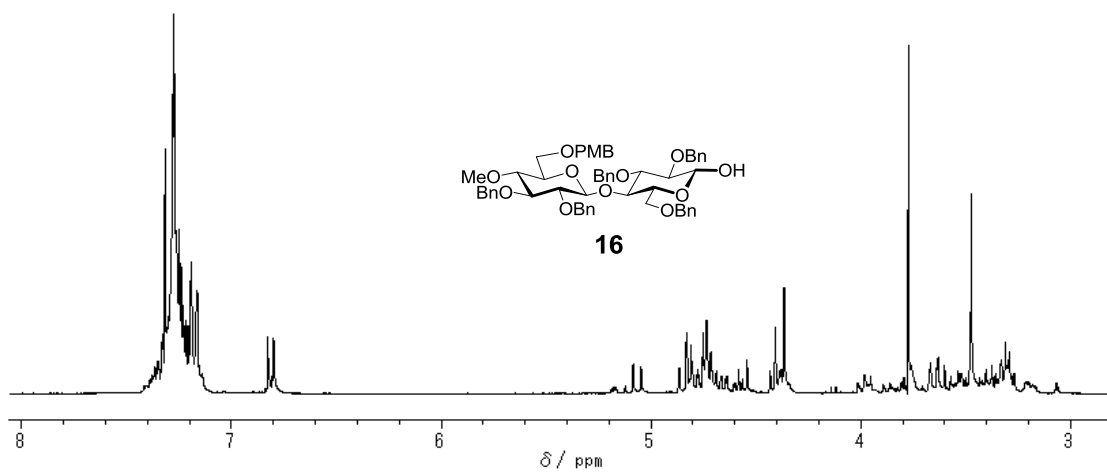
## 2. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

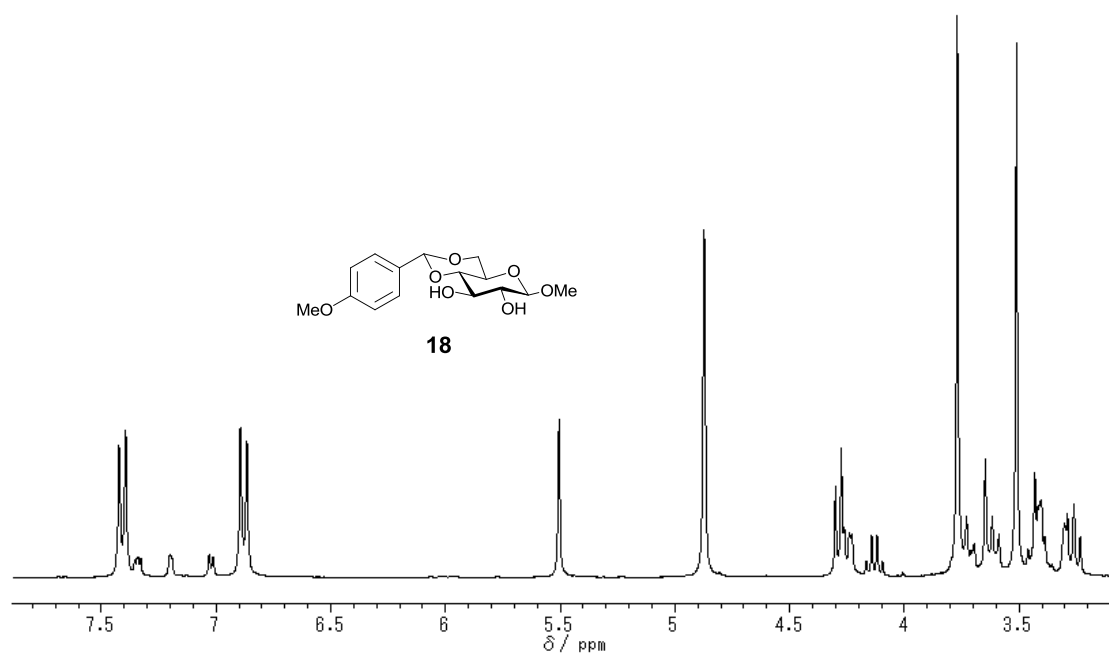


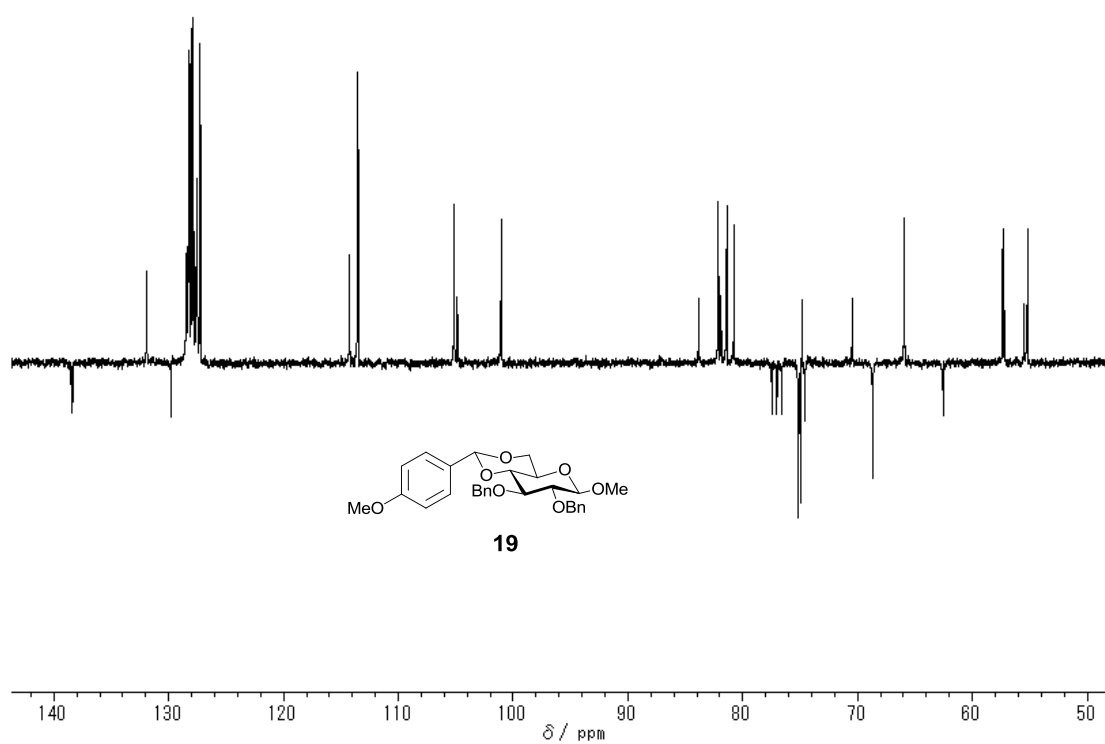
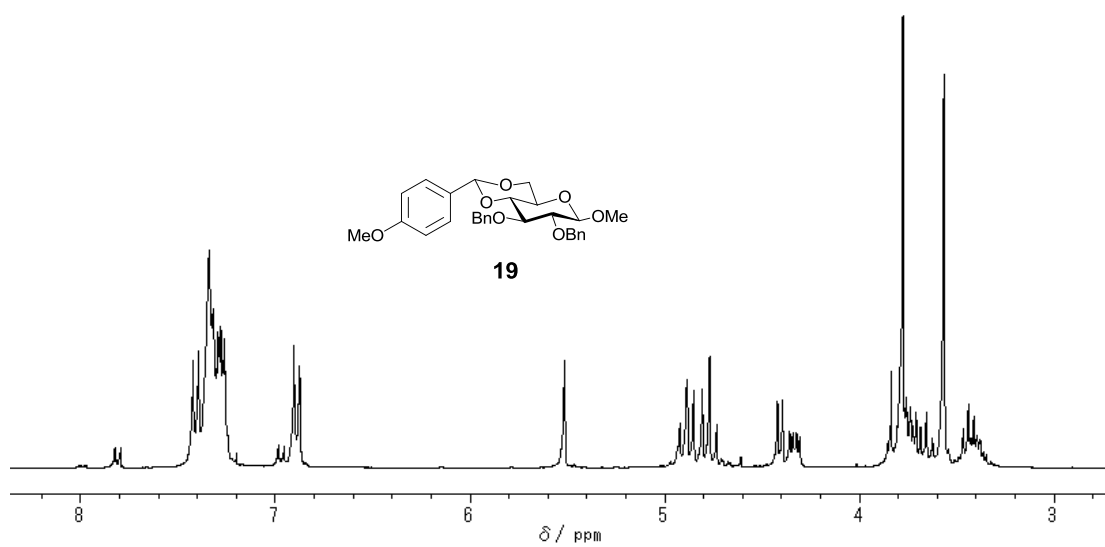


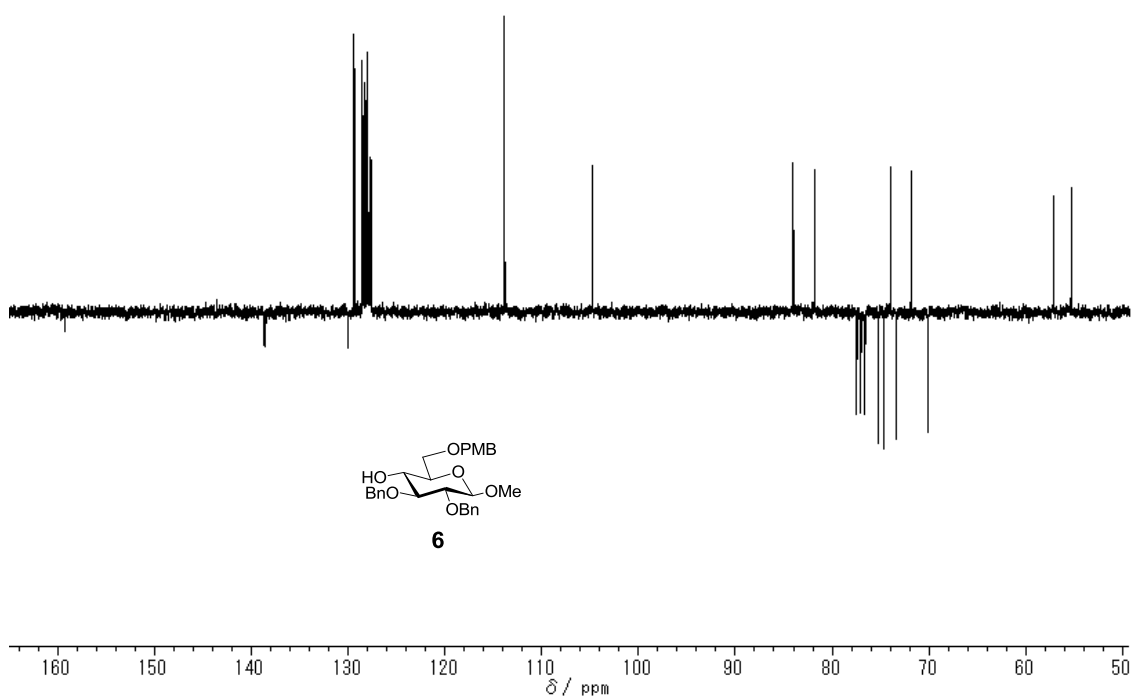
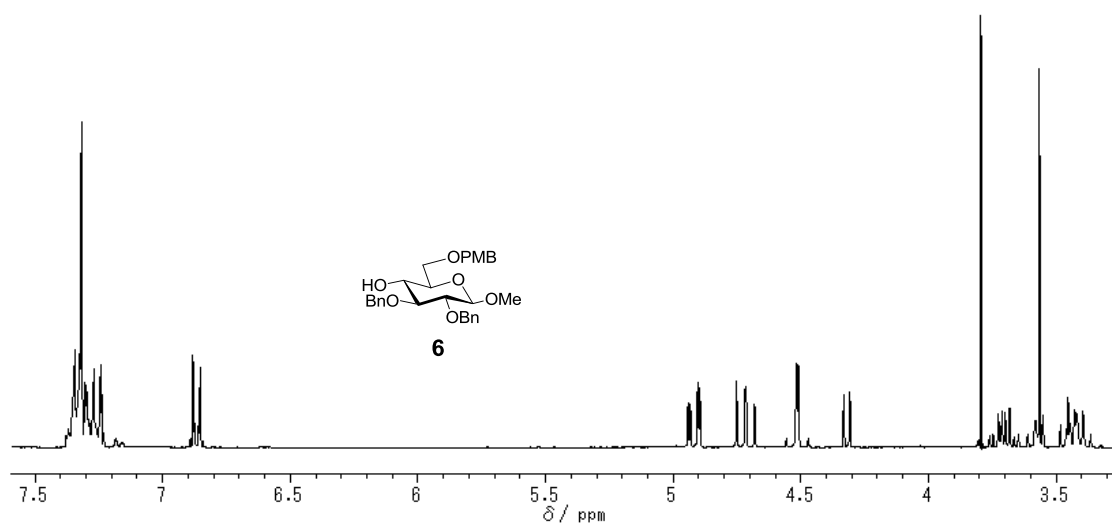


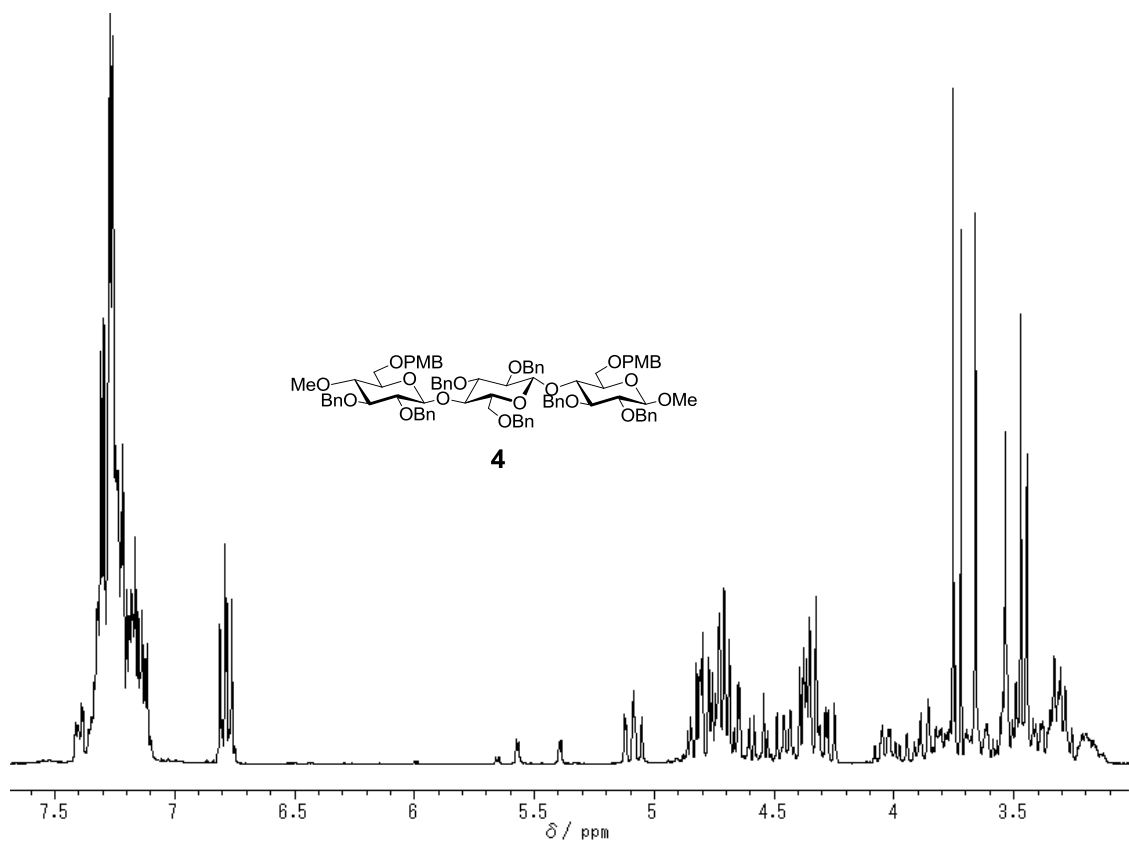


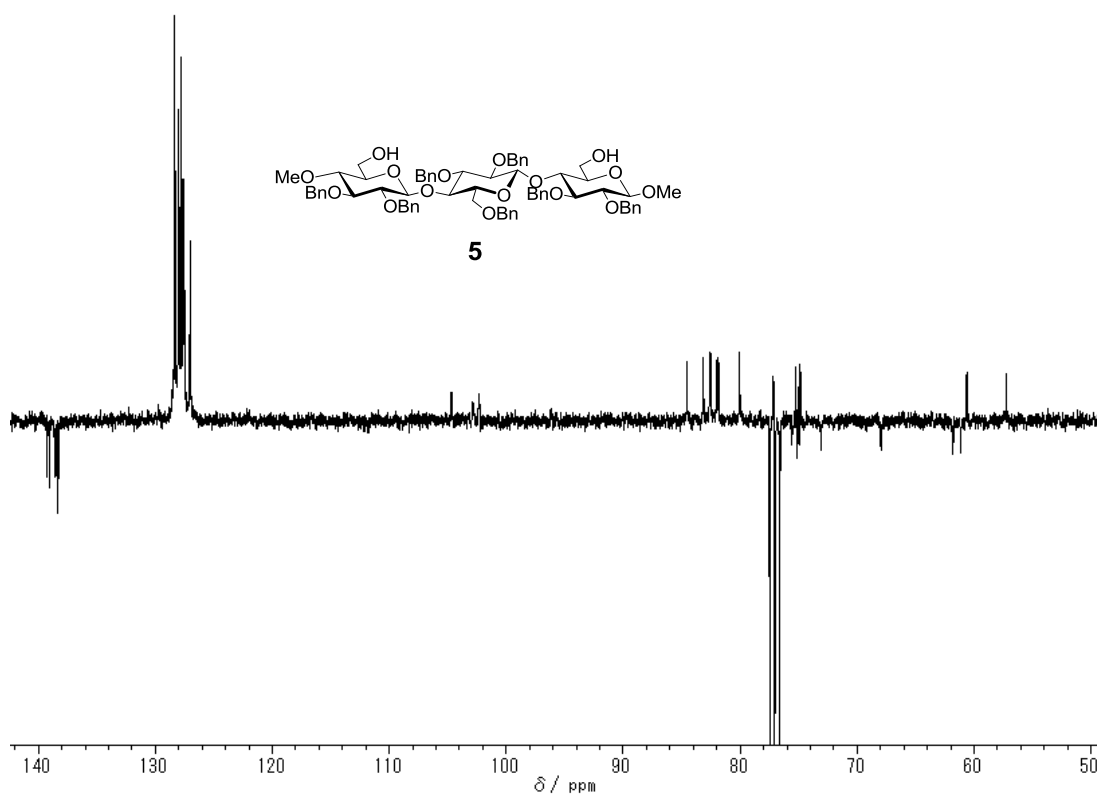
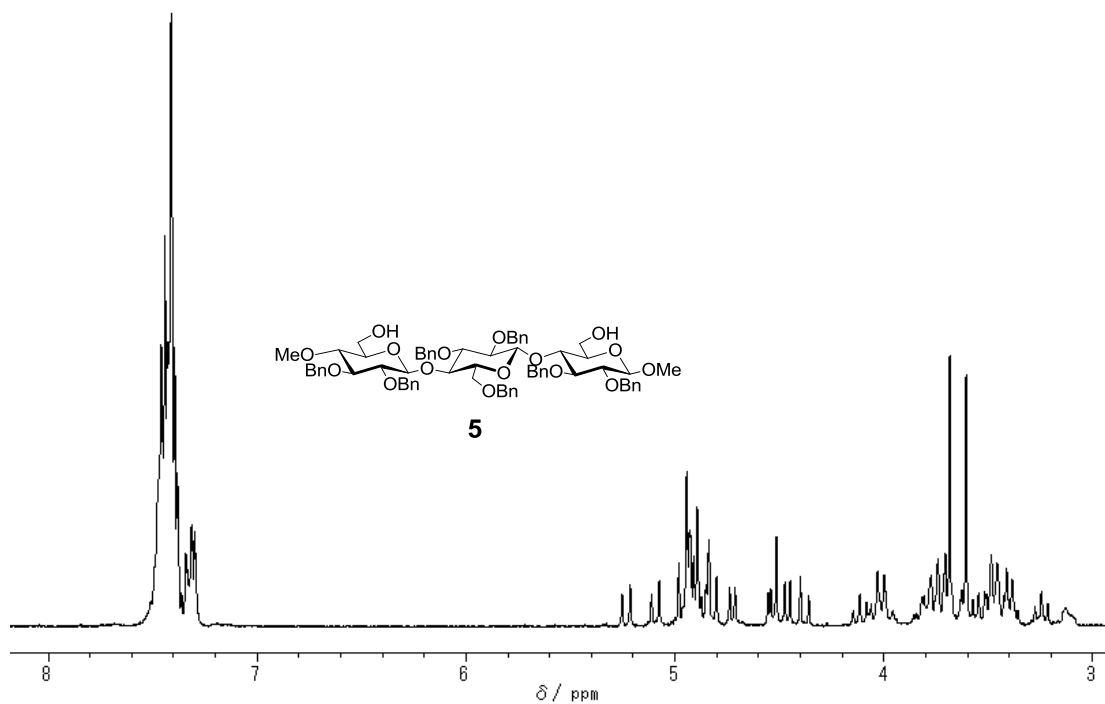


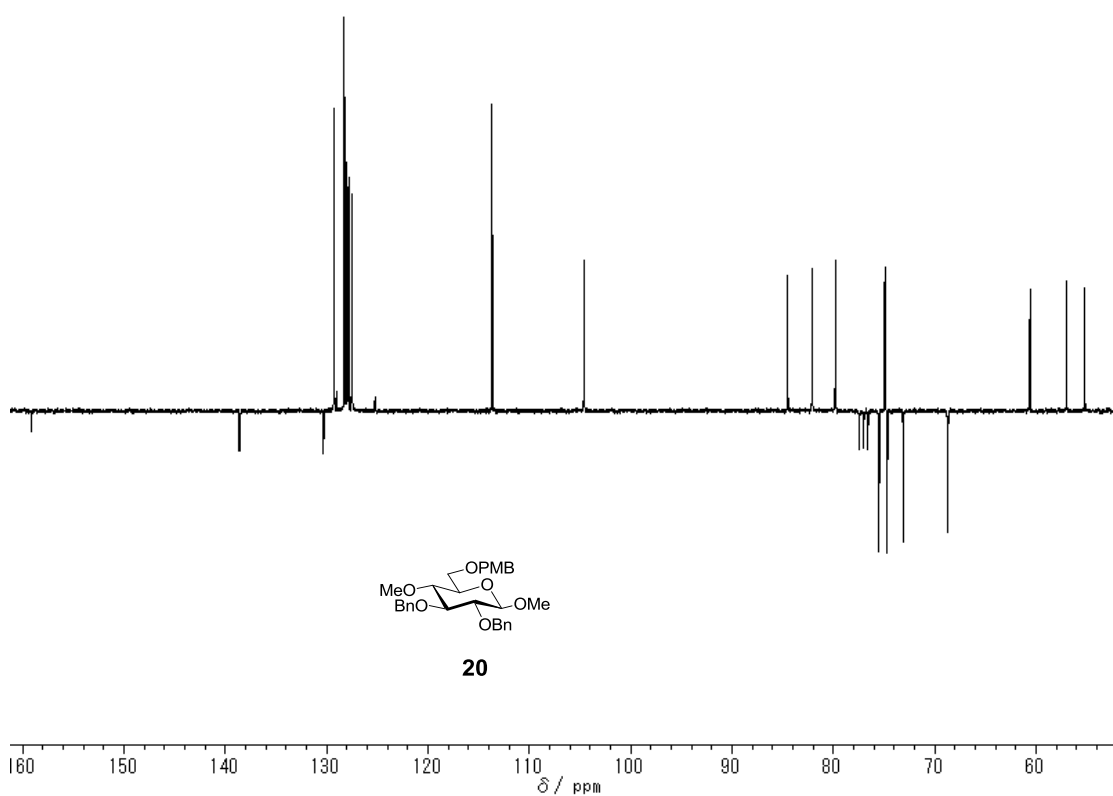
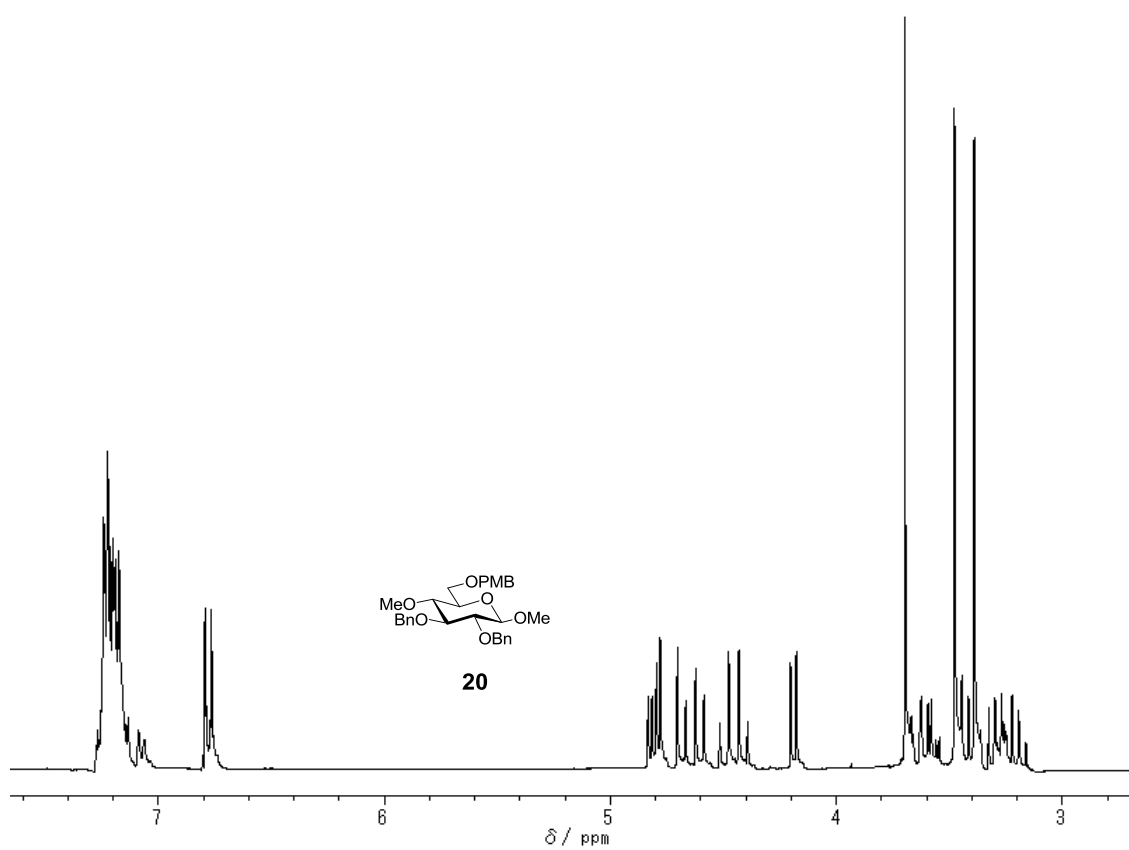


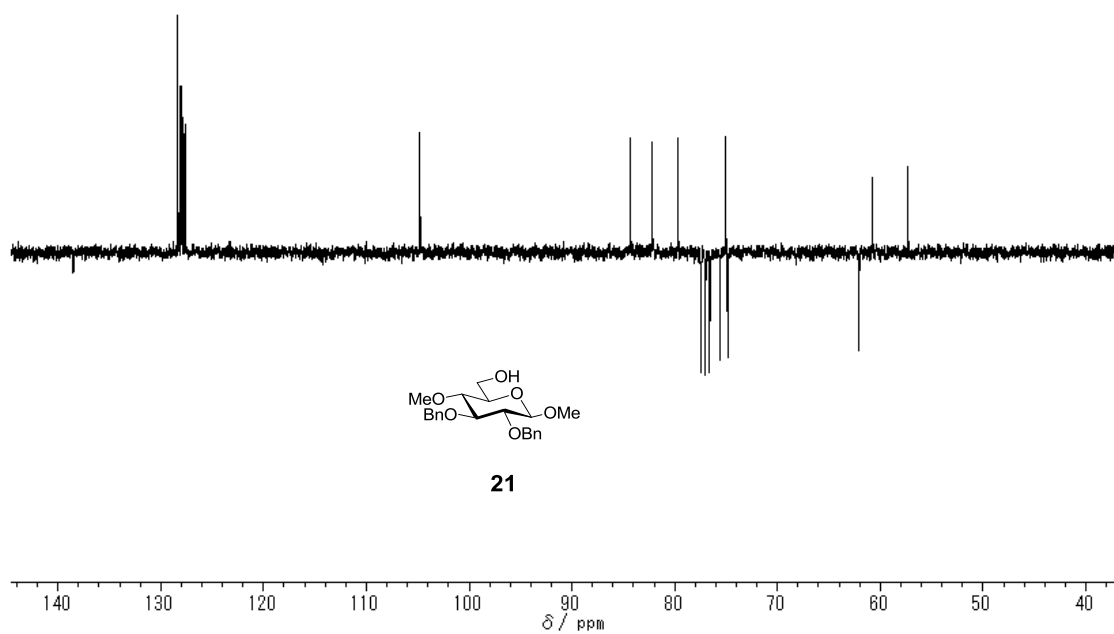
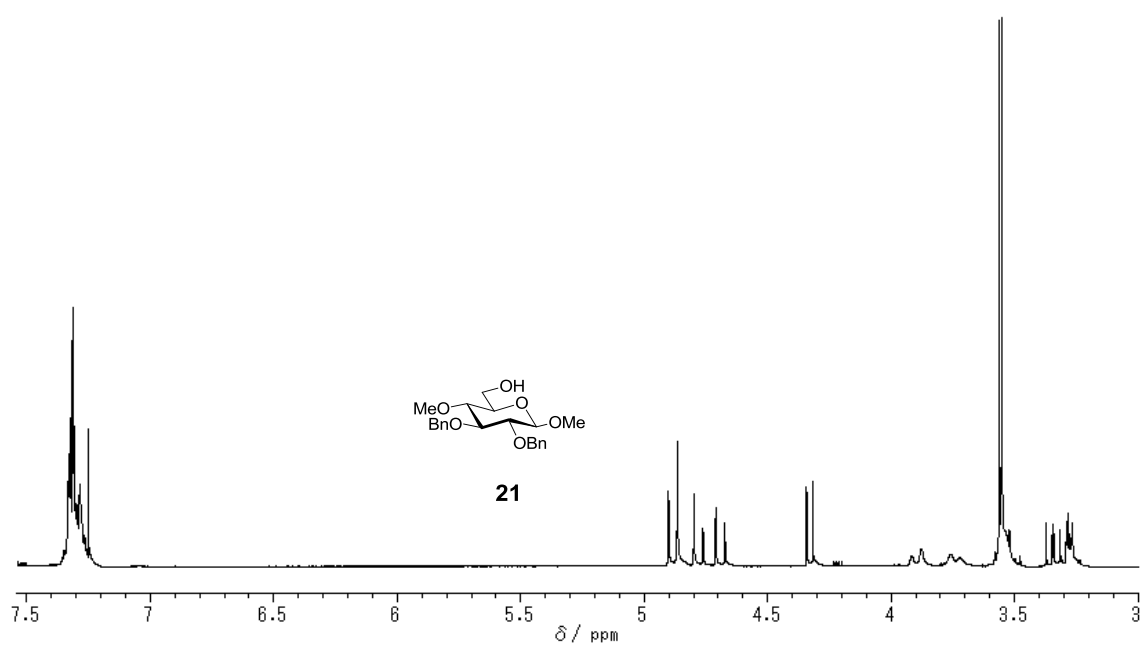


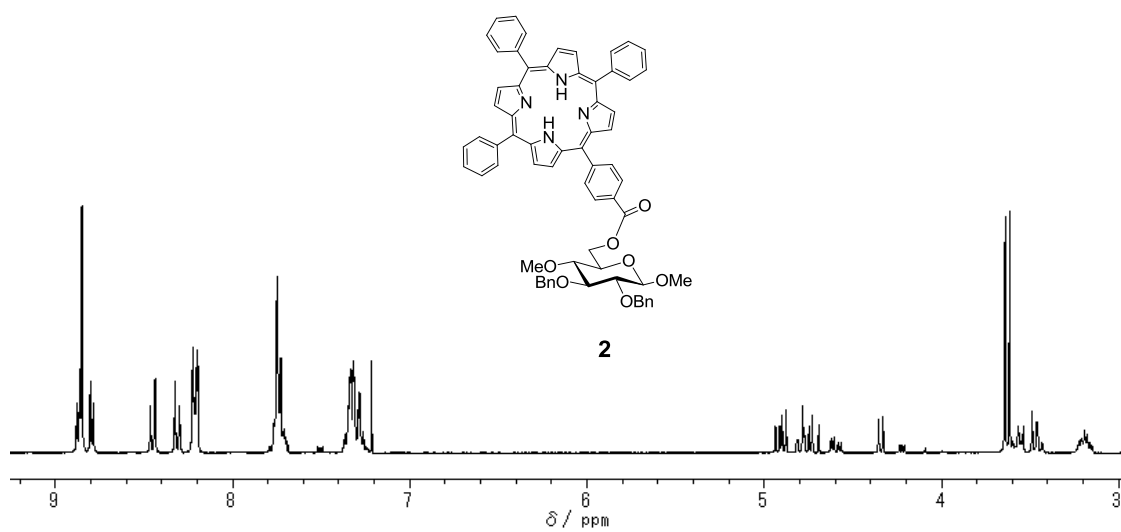




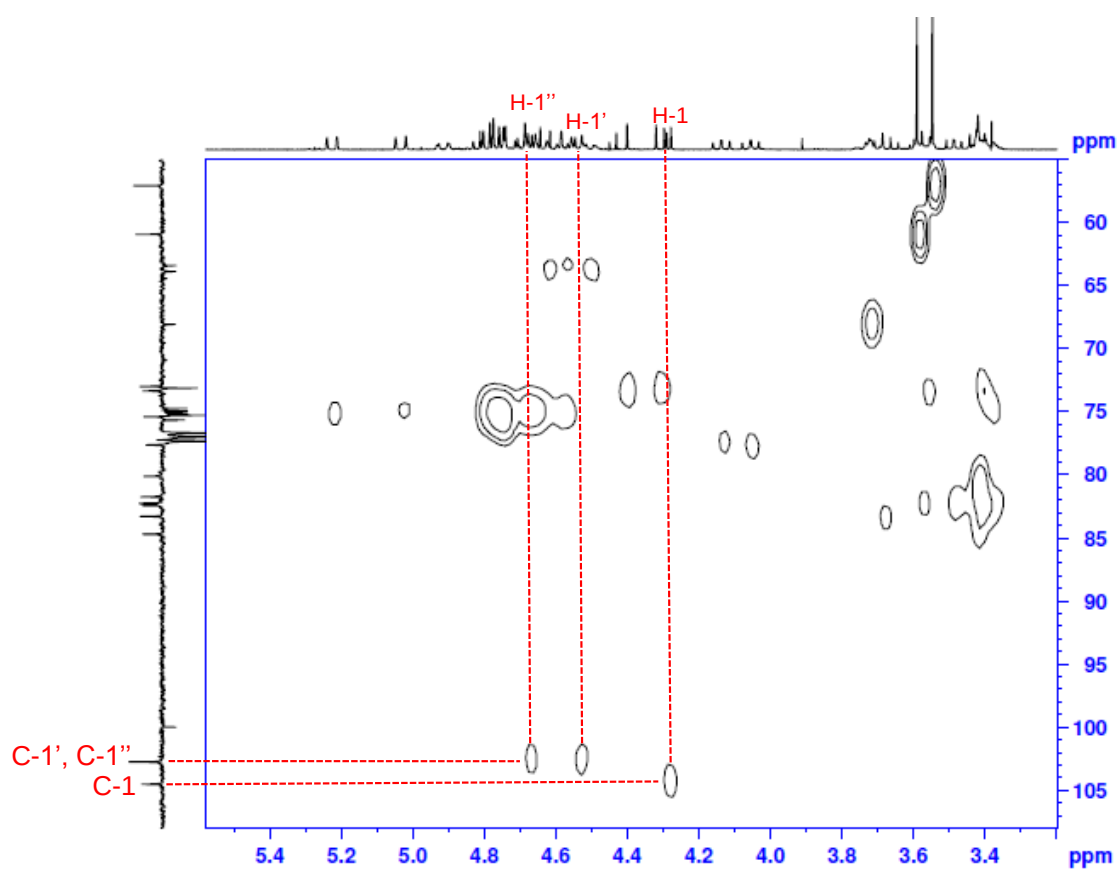






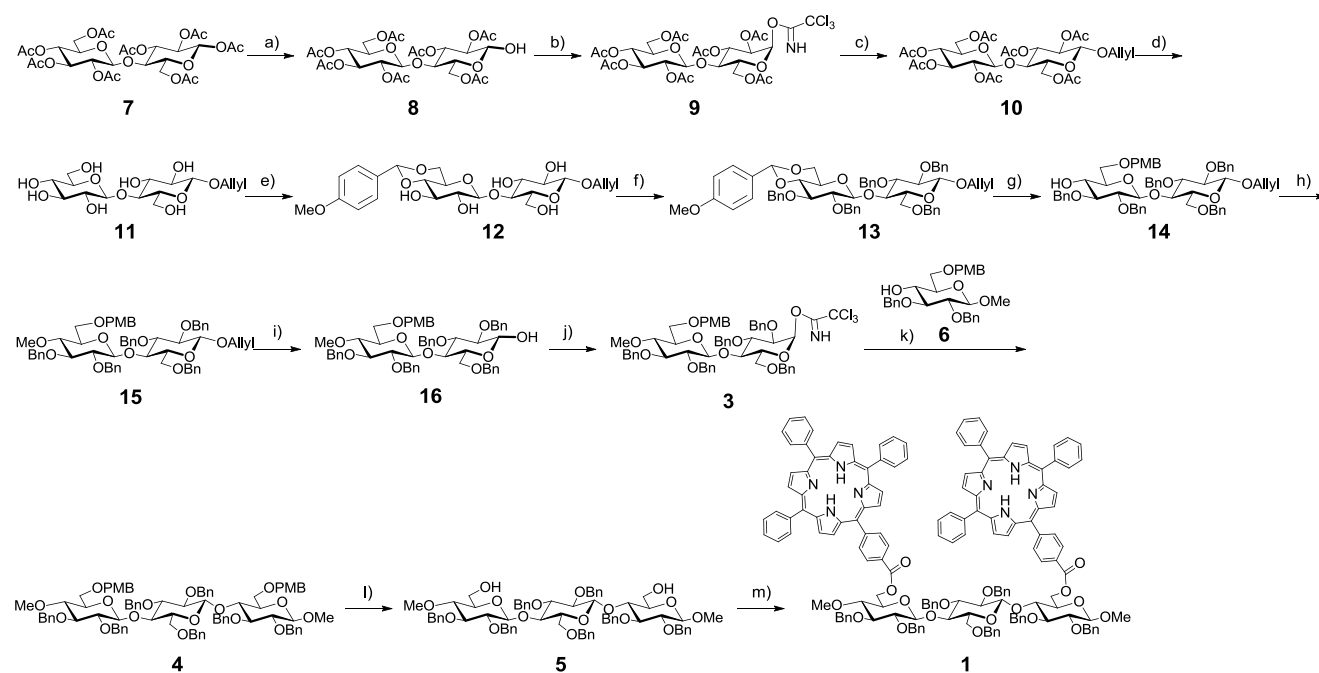


### 3. 2D [ $^1\text{H}$ , $^{13}\text{C}$ ] HSQC NMR spectrum of **1**



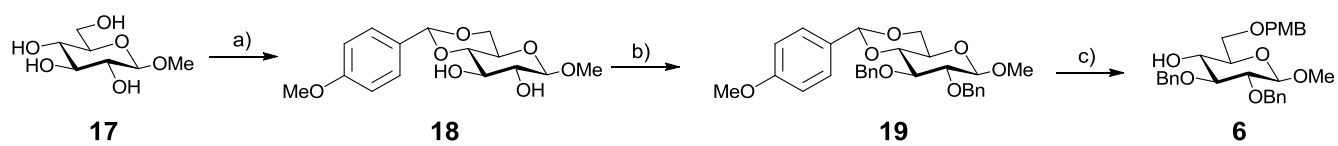
## 4. Supporting Figures

**Scheme S1.** Synthetic summary. Thirteen-step sequence leading to porphyrinated cellotrisose (**1**).



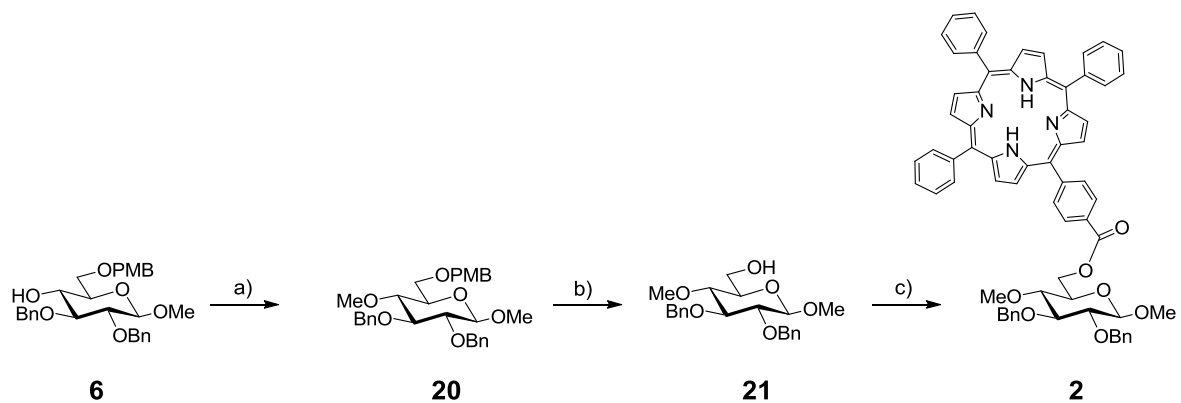
a)  $\text{H}_2\text{N-NH}_2$ , AcOH, DMF, rt, overnight, 81 %; b)  $\text{CCl}_3\text{CN}$ , DBU,  $\text{CH}_2\text{Cl}_2$ , rt, 3 h, quant.; c) AllylOH,  $\text{BF}_3\text{-Et}_2\text{O}$ , MS4A,  $\text{CH}_2\text{Cl}_2$ ,  $-78\text{ }^\circ\text{C}$ , rt, overnight, 97 %; d) NaOMe,  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  (1/1, v/v), rt, overnight, quant.; e)  $\text{PMB(OMe)}_2$ ,  $p\text{-TsOH-H}_2\text{O}$ , DMF,  $40\text{ }^\circ\text{C}$ , 4 hr, 85 %; f) BnBr, NaH,  $\text{Bu}_4\text{NI}$ , THF, reflux, 5 hr, 25 %; g)  $\text{CF}_3\text{COOH}$ , NaCNBH<sub>3</sub>, MS4A, DMF, rt, overnight, 71 %; h) MeI, NaH, THF, 2 hr, 86 %; i)  $\{\text{Ir(COD)[PCH}_3(\text{C}_6\text{H}_5)_2\}_2\}\text{PF}_6$ ,  $\text{H}_2$ , THF, 5 min, then  $\text{I}_2$ ,  $\text{H}_2\text{O}$ , 30 min, 83 %; j)  $\text{CCl}_3\text{CN}$ , DBU,  $\text{CH}_2\text{Cl}_2$ , rt, 3 h, 88 %; k) acceptor **15**,  $\text{BF}_3\text{-Et}_2\text{O}$ , MS4A,  $\text{CH}_2\text{Cl}_2$ ,  $-30\text{ }^\circ\text{C}$ , 6 hr, 73 % (calculated from donor **11**).; l) CAN,  $\text{CH}_2\text{Cl}_2\text{-(CH}_3)_2\text{CO-H}_2\text{O}$  (4:4:1, v/v/v), rt, 1 hr, 44 %; m) 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin, DCC, DMAP,  $\text{CH}_2\text{Cl}_2$ , rt, overnight, 71 %.

**Scheme S2.** Synthetic route for glucoside acceptor **6** from methyl  $\beta$ -D-glucoside.



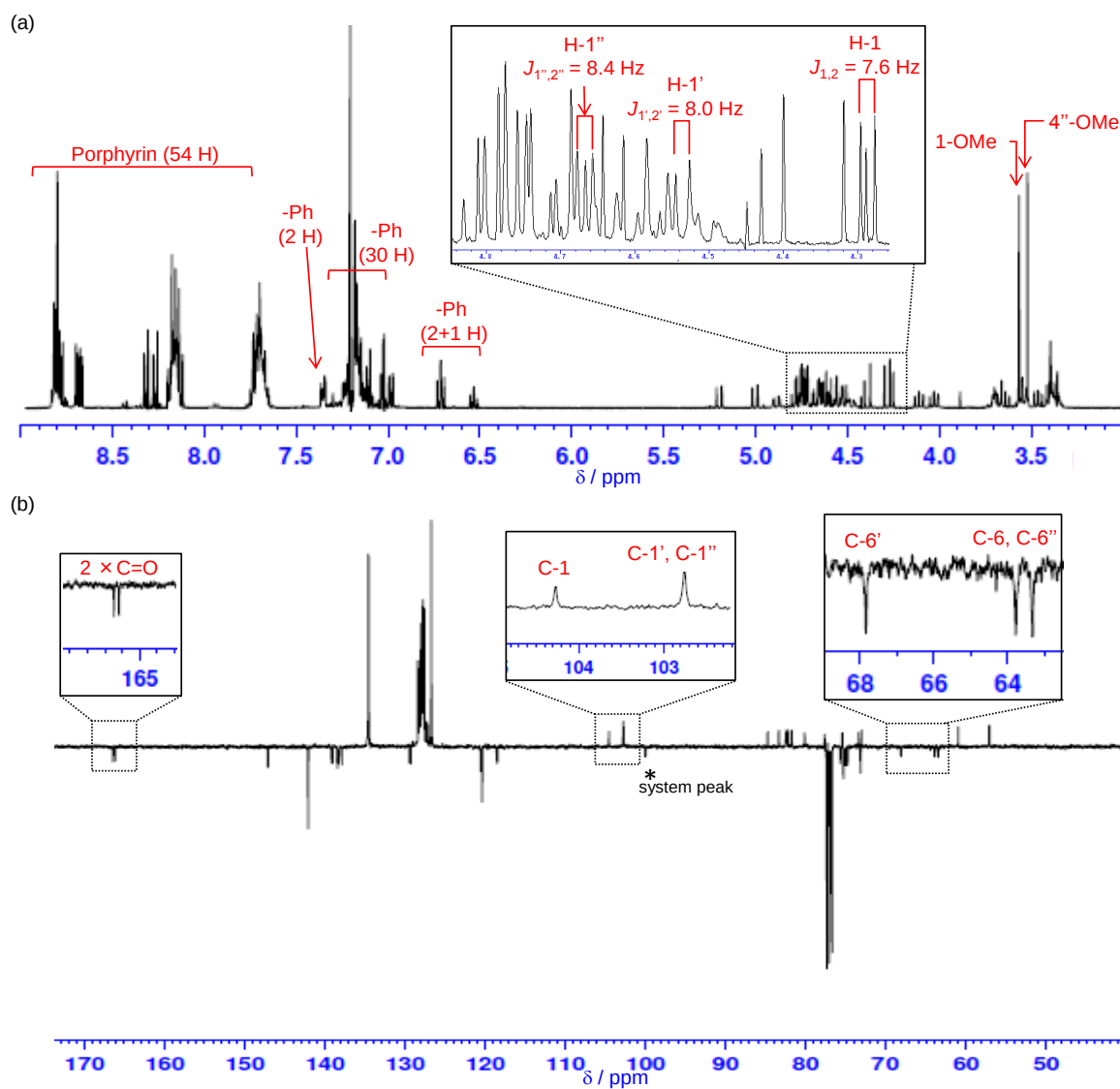
a) PMB(OMe)<sub>2</sub>, *p*-TsOH-H<sub>2</sub>O, DMF, 40 °C, 4 hr, 80 %.; b) BnBr, NaH, Bu<sub>4</sub>NI, THF, rt, overnight, 35 %.; c) CF<sub>3</sub>COOH, NaCNBH<sub>3</sub>, MS4A, DMF, rt, overnight, 71 %.

**Scheme S3.** Synthetic route for porphyrinated glucose derivative (**2**).



a) MeI, NaH, THF, rt.; b) CAN, CH<sub>2</sub>Cl<sub>2</sub>-(CH<sub>3</sub>)<sub>2</sub>CO-H<sub>2</sub>O (4:4:1, v/v/v), rt.; c)

5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, overnight.



**Figure S1.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of target **1** in  $\text{CDCl}_3$ .

**Table S1.** Glycosidation of donor **3** with acceptor **6** <sup>a</sup>.

| entry | catalyst                           | equiv. catalyst | temp (°C) | yield (%) | $\alpha/\beta$ ratio |
|-------|------------------------------------|-----------------|-----------|-----------|----------------------|
| 1     | BF <sub>3</sub> -Et <sub>2</sub> O | 0.05            | – 78      | 16.3      | —                    |
| 2     | TMSOTf                             | 0.05            | – 78      | 38.5      | 1:9.6                |
| 3     | TMSOTf                             | 0.2             | – 30      | 67.8      | 1:3.7                |
| 4     | BF <sub>3</sub> -Et <sub>2</sub> O | 0.2             | – 30      | 78.1      | mainly $\beta$       |

<sup>a</sup> reaction condition: feed ratio of donor **3** / acceptor **6** = 1 / 1.1; solvent: anhydrous CH<sub>2</sub>Cl<sub>2</sub>.

## 5. References

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2. F. A. W. Koeman, J. P. Kamerling and J. F. G. Vliegenthart, *Tetrahedron*, 1993, **49**, 5291-5304.
3. M. B. Carter, P. A. Petillo, L. Anderson and L. E. Lerner, *Carbohydr. Res.*, 1994, **258**, 299-306.
4. O. Kanie, T. Takeda and Y. Ogihara, *Carbohydr. Res.*, 1989, **190**, 53-64.