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Synthesis of novel photolabile glycosides from methyl 4,6-*O*-(*o*-nitro)benzylidene-α-D-glycopyranosides

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ABSTRACT

Novel photolabile sugar derivatives bearing a 4- or 6-*O*-(*o*-nitro)benzyl group have been prepared from the corresponding methyl 4,6-*O*-(*o*-nitro)benzylidene α-D-glycopyranosides. Regioselective cleavage with $BF_3{\cdot}Et_2O/Et_3SiH$ led to the methyl 6-*O*-(*o*-nitro)benzyl *gluco*- and *manno*-α-D-glycopyranosides **3** and **6**. Inversion of configuration at 4-OH position of *gluco* and *manno* derivatives offered the otherwise inaccessible methyl 6-*O*-(*o*-nitro)benzyl *galacto*- and *talo*-α-D-glycopyranosides **4**, **5**, and **7**. Careful reaction with $PhBCl_2/Et_3SiH$ (3 equiv of reagents, 10 min at −78 °C) led to the desired methyl 4-*O*-(*o*-nitro)benzyl *gluco*- and *manno*-α-D-glycopyranosides **8** and **9** in very good yield. However, prolonged reaction with 6 equiv of $PhBCl_2/Et_3SiH$ transformed the methyl 4,6-*O*-(*o*-nitro)benzylidene α-D-glucopyranoside **11** into the reduced D-glucitol derivative **15**. Oxidative cleavage of 5,6-diol function of **15** gave the corresponding photolabile L-xylose **17**. The photolabile glucosides **3** and **8** have been further transformed into the photolabile α-*C*-allyl D-glucopyranosides **20** and **22**.

1. Introduction

Photolabile protecting groups have found wide applications in synthetic chemistry and bioorganic chemistry.[1] As protecting groups, their deprotection requires only light irradiation, no reagent is needed. The use of photolabile protecting groups in oligonucleotides and peptide chemistry has been well established. They have been successfully used in the photolithographic synthesis of DNA chips[2] and peptide arrays[3] for use in genomics and proteomics. Various caged proteins and nucleic acids have also been synthesized for in situ delivery of reactive compounds or for analysis of biological functions with respect to time and location[1c] Though the photolabile groups have been used as linker for the solid-phase synthesis of oligo- and polysaccharides,[4] only a few photoremovable sugar derivatives have been reported.[5] With the emergence of glycomics research,[6] photolabile protecting groups could also be employed for the light-directed synthesis of defined oligosaccharides, glycoconjugates or carbohydrate arrays for the biological investigation. Synthesis of various photolabile sugar building blocks is therefore necessary.

Amongst the photolabile groups, the *o*-nitrobenzyl group is the most popular. Deprotection of *o*-nitrobenzyl group is usually realized by photoirradiation at 350–365 nm where most common functional groups do not absorb in this region of spectrum.[5f,7] Very recently, *o*-nitrobenzyl photolabile protecting groups with red-shifted absorption have been reported.[8] Concerning photolabile sugars, *o*-nitrobenzylated glycosides have been prepared.[5] Iwamura and co-workers reported an efficient synthesis of 6-*O*-(*o*-nitro)-benzyl-D-*gluco*- and *manno*-pyranosides (compounds **1** and **2** in Fig. 1) by regioselective opening of the corresponding benzylidene derivatives and their photo-deprotection to the corresponding glycosides.[5f] However, the *galacto* derivative was not available with this methodology. Moreover, synthesis of 4-*O*-(*o*-nitro)benzyl glycosides has never been reported. We report herein the synthesis of 4- or 6-*O*-(*o*-nitro)benzyl-D-glycopyranosides orthogonally protected with benzyl or acetyl groups from the corresponding methyl 4,6-*O*-(*o*-nitro)benzylidene α-D-glycopyranosides (compounds **3**–**9** in Fig. 1).

2. Results and discussion

Synthesis of methyl 6-*O*-(*o*-nitro)benzyl-α-D-glycopyranosides **3**–**7** was attempted from (*o*-nitro)benzylidene derivatives as shown in Schemes 1 and 2. Methyl 4,6-*O*-(*o*-nitro)benzylidene-α-D-glucopyranoside **10**[9] was firstly protected as benzyl ether **11**. Reductive opening of *o*-nitrobenzylidene acetal with $BF_3{\cdot}Et_2O$ (6 equiv)/Et_3SiH (12 equiv)[5f] led to the 6-*O*-(*o*-nitro)benzyl-D-glucoside **3** in 52% yield (Scheme 1). The *galacto* derivative **4** was obtained by

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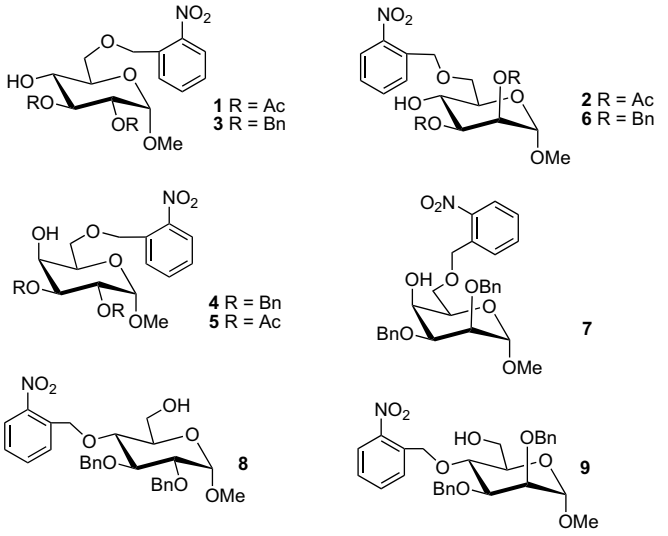
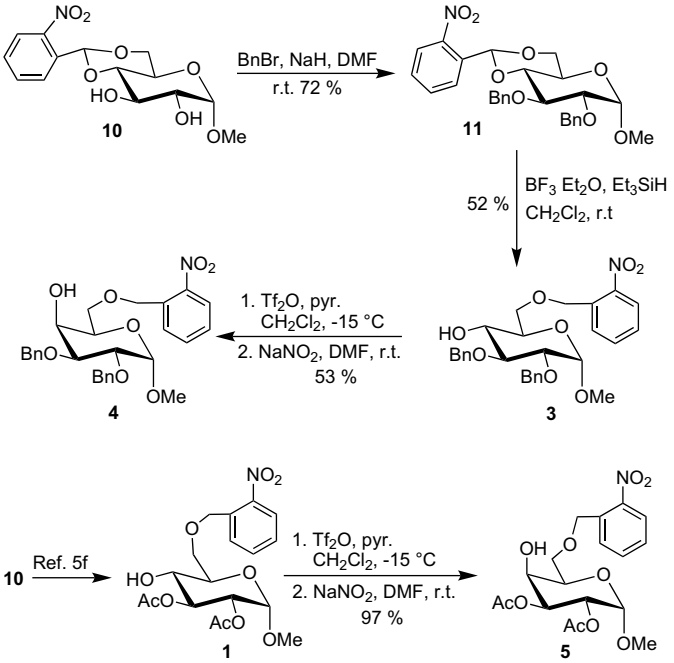


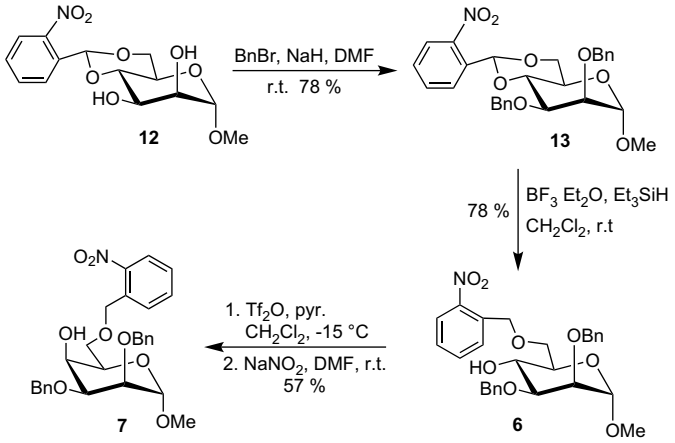
Figure 1. Structure of methyl 4- or 6-*O*-(*o*-nitro)benzyl-α-D-glycopyranosides.

inverting the configuration at C-4 position of the *gluco*-compound **3**, by activation of alcohol function with Tf_2O followed by treatment with $NaNO_2$.[10] Similarly, the acetyl protected glucoside **1** has been transformed into the galactoside **5** in 97% yield. The 6-*O*-(*o*-nitro)-benzyl-D-*manno*- and *talo*-pyranosides **6** and **7** were prepared from methyl 4,6-*O*-(*o*-nitro)benzylidene-α-D-mannopyranoside **12**.[9] Protection as benzyl ether followed by regioselective ring opening provided the 6-*O*-(*o*-nitro)benzyl-D-mannopyranoside **6**. Inversion of the configuration at C-4 gave the talopyranoside **7** in 57% yield (Scheme 2).

Reductive ring opening of benzylidene acetals can be realized with different reagents including $LiAlH_4/AlCl_3$, $NaBH_3CN/HCl$, $NaBH_3CN/TMSCl$, $NaBH_3CN/TFA$, $BH_3\cdot NMe_3/AlCl_3$, DIBAL-H or $PhBCl_2/Et_3SiH$ to give the monobenzyl ether of the corresponding diols.[11] In general, $LiAlH_4/AlCl_3$, DIBAL-H, $NaBH_3CN/TMSCl$, $BH_3\cdot NMe_3/AlCl_3/PhMe$[12] or $PhBCl_2/Et_3SiH$[13] give products with

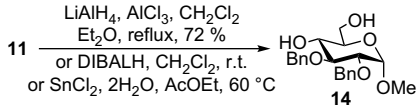


Scheme 1. Synthesis of *gluco* and *galacto* derivatives **3**, **4**, and **5**.



Scheme 2. Synthesis of *manno* and *talo* derivatives **6** and **7**.

unprotected 6-OH; while $NaBH_3CN/HCl$, $NaBH_3CN/TFA$ or $BH_3\cdot NMe_3/AlCl_3/THF$[12] produce a free 4-OH group. Treatment of the benzylidene **11** with $NaBH_3CN/TMSCl$ or $BH_3\cdot NMe_3/AlCl_3/THF$ did not induce any transformation. However, reaction with $LiAlH_4/AlCl_3$ led to the free diol **14**[14] in 72% yield (Scheme 3). Similar result has been obtained with DIBAL-H. This result may be explained by previous reduction of *o*-nitro group to amine by $LiAlH_4/AlCl_3$ or DIBAL-H, which might participate in the removal of the benzylidene acetal. To check this hypothesis, we then decided to reduce the *o*-nitrobenzylidene function with stannous chloride.[15] Once again, only the free diol **14** can be isolated.



Scheme 3. Reactivity of **11** with LAH, DIBALH or $SnCl_2$.

We then decided to study the reactivity of the 4,6-*O*-(*o*-nitro)-benzylidene acetal **11** with $PhBCl_2/Et_3SiH$.[13] Treatment of **11** with $PhBCl_2$ and Et_3SiH (6 equiv each) at −78 to −40 °C for 2 h opened regioselectively the benzylidene ring. However, the anomeric proton and carbon disappeared on ^1H and ^{13}C NMR spectra, with the appearance of a new CH_2 group. This new compound has been identified as the D-glucitol **15**, resulting from the reductive opening of both benzylidene and pyranoside rings (Fig. 2). The structure of **15** has been further confirmed by its acetylated product **16** (Scheme 4). Oxidative cleavage of **15** with $NaIO_4$ led to the corresponding L-xylose derivative **17**. After careful examination of the reaction conditions, we found that the opening of the benzylidene ring is faster than that of the pyranoside. The desired 4-*O*-(*o*-nitro)benzyl protected gluco-pyranoside **8** can be obtained using 3 equiv of reagents for 10 min at −78 °C in excellent yield. The *manno* derivative **9** can be prepared under similar conditions in good yield (Scheme 4).

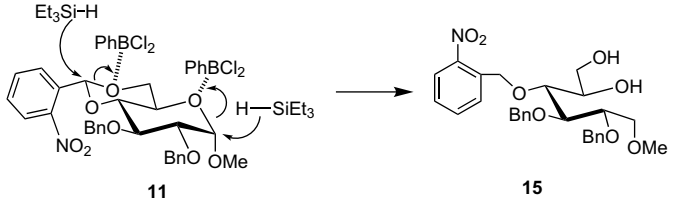
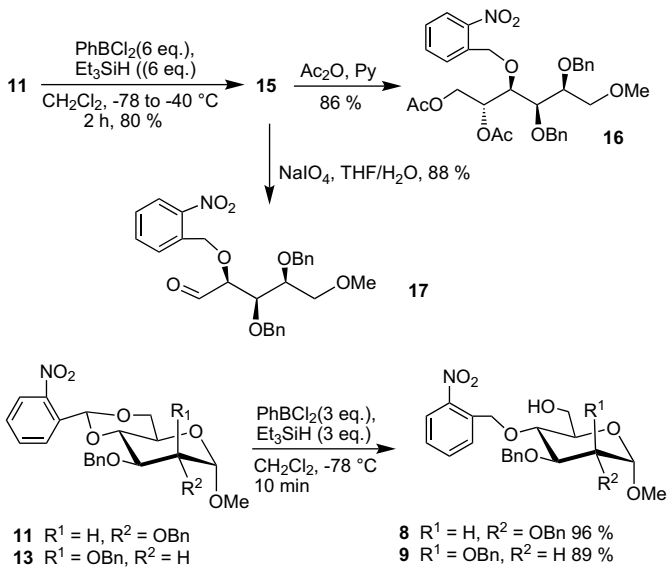
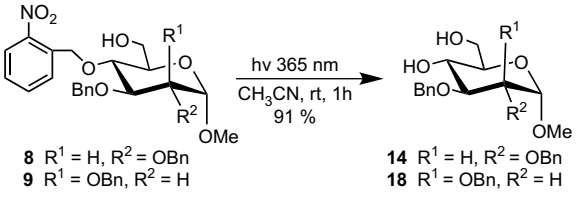


Figure 2. Proposed mechanism for the formation of **15**.



Scheme 4. Action of $PhBCl_2/Et_3SiH$ on 4,6-*O*-(*o*-nitro)benzylidene acetals **11** and **13**.

Photo-deprotection of 6-*O*-(*o*-nitro)benzyl-α-D-glycosides have already been realized by Iwamura and co-workers.[5f] Photolysis of 4-*O*-(*o*-nitro)benzyl-α-D-*gluco*- and *manno*-pyranosides **8** and **9** was studied in a CH_3CN soln. Both compounds can be fully deprotected to the free diols **14** and **18**[16] after 1 h irradiation at 365 nm in 91% yield (Scheme 5). These photolabile sugar derivatives should be useful as building blocks. As shown in Scheme 6, we have succeeded in the synthesis of the first photolabile α-*C*-allyl glucosides **20** and **22** from the methyl glucosides **3** and **8** under usual conditions[14,17] after acetylation of the 4- or 6-OH group.



Scheme 5. Photolysis of compounds **8** and **9**.

In conclusion, photolabile 6-*O*-(*o*-nitro)benzyl-D-*gluco*-, *galacto*-, *manno*-, and *talo*-pyranosides **3**–**7** have been successfully prepared from the corresponding *gluco*- and *manno*-4,6-*O*-(*o*-nitro)benzylidene derivatives. The key steps are regioselective ring opening of benzylidene acetals by $BF_3\cdot Et_2O/Et_3SiH$ to 6-*O*-(*o*-nitro)benzyl derivatives followed by inversion of the configuration at 4-OH position to 6-*O*-(*o*-nitro)benzyl-D-*galacto*- and *talo*- derivatives. Both acetyl and benzyl protected D-*galacto*- and *talo*- derivatives can be prepared in this way. Reductive opening of 4,6-*O*-(*o*-nitro)benzylidene acetals by $PhBCl_2/Et_3SiH$ led either to 4-*O*-(*o*-nitro)benzyl-D-*gluco*- and *manno*-pyranosides **8**, **9** or to the reduced D-glucitol **15**, depending on the reaction conditions. In the latter case, photolabile L-xylose **17** can be prepared by oxidative cleavage of 5,6-diol function of **15**. Furthermore, 4- or 6-*O*-(*o*-nitro)benzyl-D-glucosides have been successfully used as glycosyl donor for the stereoselective synthesis of α-*C*-allyl glucosides **20** and **22**. These novel photolabile sugars might find applications in the synthesis of diverse sugar derivatives and glycoconjugates.

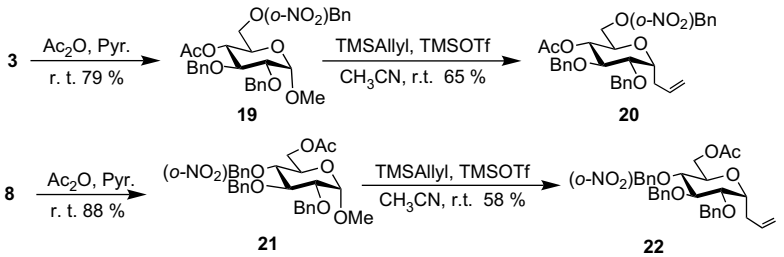
3. Experimental section

3.1. General

Solvents were purified by standard procedures. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 or Jeol 400 spectrometers in $CDCl_3$ solutions. Optical rotations were measured using a Perkin–Elmer 241 polarimeter at rt with a 10-cm 1-mL cell. Column chromatography was performed on E. Merck Silica Gel 60 (230–400 mesh). Analytical thin-layer chromatography was performed on E. Merck aluminum percolated plates of Silica Gel $60F_{254}$ with detection by UV and by spraying with 6 N H_2SO_4 and heating about 2 min at 300 °C. High resolution mass spectra (HRMS) were recorded on a MA1212 instrument using standard conditions (ESI, 70 eV). The UV light was supplied by a 200 W Hg–Xe high pressure lamp (Hamamatsu LC6). The light was passed successively through a 365 nm interference filter, only light of a wavelength of 365 nm was used. The output from the light guide is about 200 mW/cm^2 at the optimal distance (about 1.0 cm away from its end).

3.2. Synthesis of methyl 2,3-di-*O*-benzyl-4,6-*O*-(*o*-nitro)benzylidene-α-D-glucopyranoside 11

To a soln of 4,6-*O*-(*o*-nitro)benzylidene-α-D-glucopyranoside (**10**) (2.48 g, 7.6 mmol) in DMF (10 mL) was added NaH (60%, 790 mg, 19.76 mmol) at 0 °C. After stirring at 0 °C for 45 min, BnBr (2.17 mL, 19.76 mmol) was added to the reaction mixture. After 16 h, the reaction was quenched with MeOH (10 mL) and evaporated. The residue was dissolved in CH_2Cl_2, extracted with CH_2Cl_2 (3×20 mL) and the combined organic layer was washed with H_2O, dried over $MgSO_4$, and filtered. Evaporation of the solvent and purification by column chromatography (1:3 EtOAc–cyclohexane) afforded **11** as a yellow oil (2.76 g, 72%). TLC: R_f=0.67 (EtOAc–cyclohexane, 1:2); $[\alpha]_D$ −31.2 (*c* 0.98, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): δ 3.39 (s, 3H, OMe), 3.54 (dd, 1H, *J*=3.7, 9.5 Hz, H-2), 3.63 (t, 1H, *J*=9.2 Hz, H-4), 3.69–3.79 (m, 2H, H-6a, H-6b), 3.99 (t, 1H, *J*=9.2 Hz, H-3), 4.22 (m, 1H, H-5), 4.57 (d, 1H, *J*=3.7 Hz, H-1), 4.66 (d, 1H, ^2J=12 Hz, C*H*Ph), 4.74 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.84 (d, 2H, ^2J=12 Hz, 2×C*H*Ph), 6.17 (s, 1H, H-7), 7.27–7.42 (m, 10H, 2×Ph), 7.45 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.65 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.75 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 8.07 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 62.0, 69.2, 73.8, 75.1, 78.3, 79.1, 82.3, 97.1, 99.2, 124.2, 127.4, 127.5, 127.8, 128.0, 128.1, 128.2, 128.4,



Scheme 6. Synthesis of photolabile α-*C*-glycosides **20** and **22**.

129.6, 131.2, 132.7, 138.0, 138.6, 148.3. HRESIMS: calcd for $C_{28}H_{29}NO_8Na$: 530.1791; found: *m*/*z* 530.1798.

3.3. Synthesis of methyl 2,3-di-*O*-benzyl-6-*O*-(*o*-nitro)benzyl-α-D-glucopyranoside 3

To a soln of compound **11** (1.42 g, 2.8 mmol) in CH_2Cl_2 (20 mL) was added triethylsilane (5.32 mL, 33.6 mmol) and boron trifluoride etherate (2.02 mL, 16.8 mmol) at 0 °C under argon atmosphere. After the reaction mixture was stirred 16 h at rt, the reaction mixture was diluted with CH_2Cl_2 (20 mL). The solution was successively washed with aqueous $NaHCO_3$, H_2O, dried over anhydrous $MgSO_4$, filtered, evaporated under reduced pressure, and the residue was purified by column chromatography (1:1 EtOAc–cyclohexane) to afford **3** as a yellow oil (850 mg, 52%). TLC: R_f=0.51 (EtOAc–cyclohexane, 1:2); $[\alpha]_D$ +5.8 (*c* 0.28, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (d, 1H, *J*=2.2 Hz, 4-OH), 3.40 (s, 3H, OMe), 3.54 (dd, 1H, *J*=3.7, 9.5 Hz, H-2), 3.62 (m, 1H, H-5), 3.74–3.83 (m, 4H, H-3, H-4, H-6a, H-6b), 4.65 (d, 1H, *J*=3.7 Hz, H-1), 4.67 (d, 1H, ^2J=12.5 Hz, C*H*Ph), 4.73 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.78 (d, 1H, ^2J=12.1 Hz, C*H*Ph), 4.94 (m, 2H, 2×C*H*Ph), 5.04 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 7.27–7.42 (m, 10H, 2×Ph), 7.45 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.65 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.75 (d, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 8.07 (d, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 70.01, 70.04, 70.07, 70.14, 73.0, 75.4, 79.6, 81.3, 98.1, 124.5, 127.8–128.0, 128.4, 128.5, 128.6, 133.5, 134.9, 137.9, 138.6. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1963.

3.4. Synthesis of methyl 2,3-di-*O*-benzyl-6-*O*-(*o*-nitro)benzyl-α-D-galactopyranoside 4

To a soln of Tf_2O (27.4 μL, 0.16 mmol) and pyridine (25.4 μL) in CH_2Cl_2 (1 mL) was added a soln of compound **3** (52 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) at −15 °C under argon. After 2 h at −15 °C, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and extracted with CH_2Cl_2 (3×2 mL). The combined organic layer was washed successively with 5% HCl, saturated $NaHCO_3$, and H_2O, then dried over $MgSO_4$, filtered, and evaporated. The residue was dissolved in DMF (2 mL) and then $NaNO_2$ (73 mg, 1.05 mmol) was added. After 20 h stirring at rt, the reaction mixture was diluted with CH_2Cl_2 (5 mL), extracted with CH_2Cl_2 (3×5 mL), the combined organic layer was washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (1:4 EtOAc–cyclohexane) to afford **4** as a yellow oil (27.4 mg, 53%). TLC: R_f=0.47 (EtOAc–cyclohexane, 1:2); $[\alpha]_D$ +39.6 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 1H, 4-OH), 3.40 (s, 3H, OMe), 3.73–4.06 (m, 6H, H-2, H-3, H-4, H-5, H-6a, H-6b), 4.66 (d, 1H, *J*=3.3 Hz, H-1), 4.67 (d, 1H, ^2J=12 Hz, C*H*Ph), 4.72 (d, 1H, ^2J=11.7 Hz, C*H*Ph), 4.82 (d, 2H, ^2J=12.3 Hz, 2×C*H*Ph), 4.95 (s, 2H, CH_2Ph), 7.30–7.43 (m, 10H, 2×Ph), 7.45 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.65 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.75 (d, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 8.07 (d, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 67.9, 68.2, 69.9, 70.3, 72.8, 73.5, 75.6, 77.1, 98.5, 124.6, 127.7–127.9, 128.3, 128.4, 128.6, 133.5, 134.8, 138.0, 138.2. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1943.

3.5. Synthesis of methyl 2,3-di-*O*-acetyl-6-*O*-(*o*-nitro)benzyl-α-D-galactopyranoside 5

Compound **1** (53 mg, 0.13 mmol) was treated with Tf_2O and $NaNO_2$ as for the compound **3** to afford **5** as a yellow oil after purification by column chromatography (1:3 EtOAc–cyclohexane) (51.4 mg, 97%). TLC: R_f=0.34 (EtOAc–cyclohexane, 1:2); $[\alpha]_D$ +129.4 (*c* 0.26, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.61 (s, 1H, 4-OH), 3.42 (s, 3H, OMe), 3.85 (m, 2H, H-6a, H-6b), 4.08 (t, 1H, *J*=4.7 Hz, H-5), 4.25 (m, 1H, H-4), 4.97 (s, 2H, CH_2Ph), 5.01 (d, 1H, *J*=2.6 Hz, H-1), 5.29 (m, 2H, H-2, H-3), 7.45 (t, 1H, *J*=8.0 Hz, *o*-NO_2–Ph*H*), 7.65 (t, 1H, *J*=8.0 Hz, *o*-NO_2–Ph*H*), 7.75 (d, 1H, *J*=8.0 Hz, *o*-NO_2–Ph*H*), 8.07 (d, 1H, *J*=8.0 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 20.8, 55.3, 68.0, 68.2, 68.6, 70.1, 70.2, 70.5, 97.3, 124.7, 128.1, 128.5, 133.6, 134.3, 147.6, 169.9, 170.3. HRESIMS: calcd for $C_{18}H_{23}NO_{10}Na$: 436.1220; found: *m*/*z* 436.1225.

3.6. Synthesis of methyl 2,3-di-*O*-benzyl-4,6-*O*-(*o*-nitro)benzylidene-α-D-mannopyranoside 13

The methyl 4,6-*O*-(*o*-nitro)benzylidene-α-D-mannopyranoside (**12**) (190 mg, 0.58 mmol) was benzylated as for the compound **10** to afford **13** as a yellow oil after purification by column chromatography (1:3 EtOAc–cyclohexane) (229 mg, 78%). TLC: R_f=0.84 (EtOAc–cyclohexane, 2:3); $[\alpha]_D$ −10.3 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.31 (s, 3H, OMe), 3.73 (td, 1H, *J*=9.9, 4.2 Hz, H-5), 3.83 (dd, 1H, *J*=1.2, 3 Hz, H-2), 3.87–3.93 (m, 2H, H-6a, H-6b), 4.20 (dd, 1H, *J*=3.6, 10.2 Hz, H-3), 4.28 (t, 1H, *J*=9.9 Hz, H-4), 4.59 (d, 1H, ^2J=12 Hz, C*H*Ph), 4.68 (d, 1H, *J*=1.2 Hz, H-1), 4.72 (d, 1H, ^2J=9.3 Hz, C*H*Ph), 4.76 (d, 1H, ^2J=9.3 Hz, C*H*Ph), 4.83 (d, 1H, ^2J=12.3 Hz, C*H*Ph), 6.25 (s, 1H, H-7), 7.28–7.36 (m, 10H, 2×Ph), 7.50 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.62 (t, 1H, *J*=7.4 Hz, *o*-NO_2–Ph*H*), 7.87 (m, 2H, 2×*o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.8, 63.8, 69.0, 72.8, 73.6, 76.1, 76.2, 79.4, 97.3, 100.5, 124.2, 127.4–128.3, 129.5, 131.5, 132.5, 138.0, 138.6, 148.4. HRESIMS: calcd for $C_{28}H_{29}NO_8Na$: 530.1791; found: *m*/*z* 530.1794.

3.7. Synthesis of methyl 2,3-di-*O*-benzyl-6-*O*-(*o*-nitro)benzyl-α-D-mannopyranoside 6

Compound **13** (600 mg, 1.18 mmol) was treated with Et_3SiH and $BF_3{\cdot}Et_2O$ as for the compound **11** to afford **6** as a yellow oil after purification by column chromatography (1:4 EtOAc–cyclohexane) (468 mg, 78%). TLC: R_f=0.63 (EtOAc–cyclohexane, 2:3); $[\alpha]_D$ −10.7 (*c* 0.30, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.37 (s, 3H, OMe), 3.69–3.79 (m, 2H, H-3, H-5), 3.81 (dd, 1H, *J*=1.8, 3 Hz, H-2), 3.91 (m, 2H, H-6a, H-6b), 4.11 (t, 1H, *J*=9.6 Hz, H-4), 4.46 (d, 1H, ^2J=11.8 Hz, C*H*Ph), 4.59 (d, 1H, ^2J=11.7 Hz, C*H*Ph), 4.64 (d, 1H, ^2J=12.3 Hz, C*H*Ph), 4.70 (d, 1H, ^2J=12.3 Hz, C*H*Ph), 4.82 (d, 1H, *J*=1.8 Hz, H-1), 5.00 (2d, 2H, PhCH_2), 7.26–7.37 (m, 10H, 2×Ph), 7.40 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.58 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.86 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 8.06 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.8, 66.8, 69.9, 71.56, 71.63, 72.5, 73.6, 79.6, 99.0, 124.4, 127.6–127.8, 128.3, 128.5, 128.6, 133.6, 135.3, 137.9, 138.0. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1951.

3.8. Synthesis of methyl 2,3-di-*O*-benzyl-6-*O*-(*o*-nitro)benzyl-α-D-talopyranoside 7

Compound **6** (75 mg, 0.15 mmol) was treated with Tf_2O and $NaNO_2$ as for the compound **3** to afford **7** as a yellow oil after purification by column chromatography (1:2 EtOAc–cyclohexane) (43 mg, 57.3%). TLC: R_f=0.65 (EtOAc–cyclohexane, 2:3); $[\alpha]_D$ +37.8 (*c* 2.22, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 3H, OMe), 3.77 (m, 1H), 3.88 (m, 2H, H-6a, H-6b), 3.98–4.02 (m, 2H), 4.54 (d, 1H, ^2J=11.7 Hz, C*H*Ph), 4.56 (d, 1H, ^2J=12.1 Hz, C*H*Ph), 4.68 (d, 1H, ^2J=11.7 Hz, C*H*Ph), 4.69 (d, 1H, ^2J=12.1 Hz, C*H*Ph), 4.74 (d, 1H, *J*=1.8 Hz, H-1), 4.94 (d, 1H, ^2J=12.3 Hz, C*H*Ph), 5.04 (d, 1H, ^2J=12.3 Hz, C*H*Ph), 5.45 (t, 1H, *J*=9.9 Hz), 7.30–7.39 (m, 10H, 2×Ph), 7.42 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.55 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.86 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 8.07 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 68.8, 69.4, 69.8, 72.2, 72.9, 74.4, 77.1, 81.3, 98.9, 124.4, 127.6–128.4, 133.8, 134.9, 137.1, 137.7, 146.5. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1962.

3.9. Synthesis of methyl 2,3-di-*O*-benzyl-4-*O*-(*o*-nitro)benzyl-α-D-glucopyranoside 8

Molecular sieves 4 Å (1.0 g) were placed in a 10-mL flask and dried at 140 °C for 4 h under vacuum (ca. 0.1 mmHg). After cooling to rt, a soln of compound **11** (105 mg, 0.207 mmol) in CH_2Cl_2 (2 mL) was added to the flask under argon atmosphere. After stirring for 1 h at rt, the mixture was cooled to −78 °C, and then Et_3SiH (0.100 mL, 0.62 mmol) and a soln of dichlorophenylborane in CH_2Cl_2 (1.2 mL, 0.62 mmol) were added successively. After 10 min at −78 °C, TLC indicated a complete conversion of the starting material. Et_3N (0.5 mL) and MeOH (0.5 mL) were added successively, and the mixture was diluted with $CHCl_3$ (20 mL), washed with aqueous saturated $NaHCO_3$ (2×10 mL), water (10 mL), brine (2×10 mL), dried over $MgSO_4$, filtered, and then concentrated in vacuo. The crude product was purified by flash column chromatography (3:7 EtOAc–cyclohexane) to give **8** as a yellow solid (101 mg, 96%). TLC: R_f=0.18 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +22.3 (*c* 2.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 1H, OH), 3.38 (s, 3H, OMe), 3.51 (dd, 1H, *J*=3.7, 8.7 Hz, H-2), 3.60 (t, 1H, *J*=8.7 Hz, H-4), 3.69–3.72 (m, 2H, H-5,6a), 3.76–3.79 (m, 1H, H-6b), 4.00 (t, 1H, *J*=8.7 Hz, H-3), 4.58 (d, 1H, *J*=3.7 Hz, H-1), 4.64–4.66 (m, 2H, C*H*$_2$Ph), 4.76 (d, 1H, ^2J=11.0 Hz, C*H*Ph), 4.94 (d, 1H, ^2J=11.0 Hz, C*H*Ph), 4.98 (d, 1H, ^2J=14.6 Hz, C*H*Ph), 5.23 (d, 1H, ^2J=14.6 Hz, C*H*Ph), 7.19–7.34 (m, 10H, 2×Ph), 7.39 (t, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*), 7.56 (t, 1H, *J*=7.6 Hz, *o*-NO_2–Ph*H*), 7.69 (d, 1H, *J*=7.6 Hz, *o*-NO_2–Ph*H*), 8.01 (d, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 61.9, 70.7, 71.3, 73.5, 75.7, 77.9, 80.1, 81.9, 98.3, 124.7, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 128.6, 133.7, 135.2, 138.1, 138.5, 146.9. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1942.

3.10. Synthesis of methyl 2,3-di-*O*-benzyl-4-*O*-(*o*-nitro)benzyl-α-D-mannopyranoside 9

Compound **13** (109 mg, 0.215 mmol) was treated with Et_3SiH and $PhBCl_2$ as for the compound **11** to afford **9** as a yellow oil after purification by column chromatography (3:7 EtOAc–cyclohexane) (97 mg, 89%). TLC: R_f=0.17 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +32.4 (*c* 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 1H, OH), 3.32 (s, 3H, OMe), 3.63–3.68 (m, 1H), 3.75–3.79 (m, 2H), 3.82 (dd, 1H, *J*=2.3, 11.9 Hz), 3.88 (dd, 1H, *J*=2.8, 9.2 Hz), 4.02 (t, 1H, *J*=9.6 Hz, H-4), 4.45 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.55 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.67 (d, 1H, ^2J=12.4 Hz, C*H*Ph), 4.72 (d, 1H, *J*=1.8 Hz, H-1), 4.75 (d, 1H, ^2J=12.4 Hz, C*H*Ph), 5.04 (d, 1H, ^2J=14.6 Hz, C*H*Ph), 5.31 (d, 1H, ^2J=14.6 Hz, C*H*Ph), 7.21–7.33 (m, 10H, 2×Ph), 7.39 (t, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*), 7.56 (t, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.71 (d, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 8.01 (d, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.0, 62.5, 71.3, 71.8, 72.1, 73.0, 74.3, 75.3, 80.1, 99.4, 124.6, 127.5, 127.6, 127.8, 127.9, 128.4, 128.5, 129.0, 133.6, 135.4, 138.2, 147.1. HRESIMS: calcd for $C_{28}H_{31}NO_8Na$: 532.1947; found: *m*/*z* 532.1942.

3.11. Synthesis of 2,3-di-*O*-benzyl-1-*O*-methyl-4-*O*-(*o*-nitro)benzyl-D-glucitol 15

Molecular sieves 4 Å (2.0 g) were placed in a 10-mL flask and dried at 140 °C for 4 h under vacuum (ca. 0.1 mmHg). After cooling to rt, a soln of compound **11** (532 mg, 1.05 mmol) in CH_2Cl_2 (20 mL) was added to the flask under argon atmosphere. After stirring for 1 h at rt, the mixture was cooled to −78 °C, and then Et_3SiH (1.0 mL, 6.2 mmol) and a soln of dichlorophenylborane in CH_2Cl_2 (0.8 mL, 6.2 mmol) were added successively. After being stirred for 2 h at −78 to −40 °C, Et_3N (2 mL) and MeOH (2 mL) were added, and the mixture was diluted with $CHCl_3$ (50 mL), washed with aqueous saturated $NaHCO_3$ (2×25 mL), water (25 mL), brine (2×25 mL), dried over $MgSO_4$, filtered, and then concentrated in vacuum. The crude product was purified by flash column chromatography (2:8 EtOAc–cyclohexane) to give **15** as a yellow oil (430 mg, 80%). TLC: R_f=0.61 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +32.4 (*c* 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.36 (s, 3H, OMe), 3.61 (dd, 1H, *J*=5.5, 10.5 Hz, H-1a), 3.70–3.73 (m, 2H, H-1b, H-3), 3.80–3.83 (m, 1H, H-2), 4.14 (dd, 1H, *J*=2.3, 6.4 Hz, H-4), 4.23 (t, 1H, *J*=8.7 Hz, H-6a), 4.45 (dd, 1H, *J*=7.3, 8.7 Hz, H-6b), 4.57 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.60 (d, 1H, ^2J=11.5 Hz, C*H*Ph), 4.71 (d, 1H, ^2J=11.5 Hz, C*H*Ph), 4.76 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.78–4.81 (m, 1H, H-5), 5.08 (d, 1H, ^2J=15.2 Hz, C*H*Ph), 5.21 (d, 1H, ^2J=15.2 Hz, C*H*Ph), 7.27–7.43 (m, 10H, 2×Ph), 7.67 (m, 2H, 2×*o*-NO_2–Ph*H*), 7.73 (d, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.90 (d, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.3, 67.2, 71.7, 72.3, 73.0, 74.6, 77.9, 78.3, 79.6, 81.9, 124.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.5, 128.6, 128.7, 131.4, 133.6, 134.7, 135.5, 138.0, 138.2, 146.6. HRESIMS: calcd for $C_{28}H_{33}NO_8Na$: 534.2104; found: *m*/*z* 534.2098.

3.12. Synthesis of 5,6-di-*O*-acetyl-2,3-di-*O*-benzyl-1-*O*-methyl-4-*O*-(*o*-nitro)benzyl-D-glucitol 16

To a soln of compound **15** (29 mg, 0.057 mmol) in pyridine (2 mL) was added Ac_2O (0.8 mL) at rt. After 16 h, the reaction mixture was evaporated and residue was dissolved in CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. Evaporation of the solvent gave a crude product, which was purified by column chromatography (2:8 EtOAc–cyclohexane) to afford **16** (25 mg, 86%) as a yellow oil. TLC: R_f=0.3 (EtOAc–cyclohexane, 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 3H, OAc), 2.02 (s, 3H, OAc), 3.28 (s, 3H, OMe), 3.56 (dd, 1H, *J*=6.0, 10.1 Hz, H-1a), 3.62 (dd, 1H, *J*=4.1, 10.1 Hz, 1H, H-1b), 3.73 (dd, 1H, *J*=4.6, 6.4 Hz, 1H, H-3), 3.81–3.83 (m, 1H, H-2), 3.95 (dd, 1H, *J*=6.4, 3.7 Hz, 1H, H-4), 4.18 (dd, 1H, *J*=7.3, 11.9 Hz, H-6a), 4.49 (dd, 1H, *J*=2.7, 11.9 Hz, H-6b), 4.56 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.57 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.63 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.71 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 5.06 (d, 1H, ^2J=15.6 Hz, C*H*Ph), 5.11 (d, 1H, ^2J=15.6 Hz, C*H*Ph), 5.35–5.37 (m, 1H, H-5), 7.20–7.31 (m, 10H, 2×Ph), 7.41 (t, 1H, *J*=7.6 Hz, *o*-NO_2–Ph*H*), 7.59 (t, 1H, *J*=7.6 Hz, *o*-NO_2–Ph*H*), 7.78 (d, 1H, *J*=7.6 Hz, *o*-NO_2–Ph*H*), 8.05 (d, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 21.2, 59.2, 62.9, 71.3, 72.3, 72.5, 73.3, 74.8, 78.1, 79.2, 80.3, 124.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.5, 128.8, 133.8, 135.3, 138.1, 138.4, 146.9, 170.3, 170.9. HRESIMS: calcd for $C_{32}H_{37}NO_{10}Na$: 618.2315; found: *m*/*z* 618.2310.

3.13. Synthesis of 3,4-di-*O*-benzyl-2-*O*-(*o*-nitro)benzyl-L-xylose 17

To a soln of **15** (52 mg, 0.102 mmol) in THF (2 mL) and H_2O (1.0 mL) was added $NaIO_4$ (45 mg, 0.208 mmol) at rt. After 2 h, the reaction mixture was evaporated and residue was diluted with EtOAc (10 mL), washed with water (2×5 mL), brine (2×5 mL), dried over $MgSO_4$, filtered, and then concentrated in vacuum. The crude product was purified by flash column chromatography (2:8 EtOAc–cyclohexane) to afford 43 mg (88%) of aldehyde **17** as a yellow oil. TLC: R_f=0.73 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +21.8 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (s, 3H, OMe), 3.45 (dd, 1H, *J*=4.6, 9.2 Hz, H-5a), 3.53 (dd, 1H, *J*=5.5, 9.2 Hz, H-5b), 3.80–3.83 (m, 1H, H-4), 3.98–4.04 (m, 2H, H-2, H-3), 4.48 (d, 1H, ^2J=11.5 Hz, C*H*Ph), 4.51 (d, 1H, ^2J=11.5 Hz, C*H*Ph), 4.64 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.71 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.88 (d, 1H, ^2J=14.7 Hz, C*H*Ph), 5.09 (d, 1H, ^2J=14.7 Hz, C*H*Ph), 7.24–7.32 (m, 10H, 2×Ph), 7.44 (t, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.62 (t, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.78 (d, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 8.05 (d, 1H, *J*=8.3 Hz, *o*-NO_2–Ph*H*), 9.75 (s, 1H, H-1); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.2, 69.9, 71.4, 73.2, 74.3, 76.5,

78.9, 82.8, 124.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.7, 129.1, 133.9, 134.4, 137.6, 137.8, 147.3, 199.7. HRESIMS: calcd for $C_{27}H_{29}NO_7Na$: 502.1842; found: *m*/*z* 502.1836.

3.14. Photolysis of compounds 8 and 9

A soln of compound **8** (35 mg, 0.069 mmol) or **9** (42 mg, 0.082 mmol) in acetonitrile (1.0 mL) was irradiated by 365 nm UV-light (200 mW/cm^2) in quartz cell for 1 h. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (1:1 EtOAc–cyclohexane) to afford the corresponding free diols **14** or **18** in 91% yield.

3.15. Synthesis of methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-(*o*-nitro)benzyl-α-D-glucopyranoside 19

To a soln of compound **3** (390 mg, 0.77 mmol) in pyridine (8 mL) was added Ac_2O (1 mL) at rt. After 16 h, the reaction mixture was evaporated and residue was dissolved in CH_2Cl_2, washed with H_2O, extracted with CH_2Cl_2, dried over $MgSO_4$, and filtered. Evaporation of the solvent gave a crude product, which was purified by column chromatography (1:5 EtOAc–cyclohexane) to afford **19** (388 mg, 92%) as a yellow oil. TLC: R_f=0.53 (EtOAc–cyclohexane, 1:3); $[\alpha]_D$ +50.0 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 3H, OAc), 3.42 (s, 3H, OMe), 3.58–3.63 (m, 3H, H-2, H-6a, H-6b), 3.84–3.89 (m, 1H, H-5), 3.94 (t, 1H, *J*=9.5 Hz, H-3), 4.63 (d, 1H, *J*=3.8 Hz, H-1), 4.65 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.66 (d, 1H, ^2J=11.4 Hz, C*H*Ph), 4.79–4.96 (m, 4H, 2×CH_2Ph), 5.07 (dd, 1H, *J*=9.6, 9.2 Hz, H-4), 7.27–7.38 (m, 10H, 2×Ph), 7.41 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.54 (t, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 7.85 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*), 8.05 (d, 1H, *J*=8.1 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 55.3, 68.6, 69.8, 69.9, 70.2, 73.4, 75.3, 79.2, 79.6, 98.1, 124.4, 127.5, 127.8–128.4, 128.6, 133.7, 134.8, 137.9, 138.5, 146.9, 169.6. HRESIMS: calcd for $C_{30}H_{33}NO_9Na$: 574.2053; found: *m*/*z* 574.2039.

3.16. Synthesis of 3-(4′-*O*-acetyl-2′,3′-di-*O*-benzyl-6′-*O*-(*o*-nitro)benzyl-α-D-glucopyranosyl)-1-propene 20

To a soln of **19** (52 mg, 0.094 mmol) in CH_3CN (2 mL), were added allylTMS (0.08 mL, 0.5 mmol) and TMSOTF (0.1 mL, 0.5 mmol) at rt. After 72 h, the reaction mixture was diluted with CH_2Cl_2 (5 mL), extracted with CH_2Cl_2 (2×5 mL), washed with H_2O, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (1:3 EtOAc–cyclohexane) to afford **20** as a yellow oil (34 mg, 65%). TLC: R_f=0.59 (EtOAc–cyclohexane, 1:3); $[\alpha]_D$ +48.3 (*c* 1.21, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 3H, OAc), 2.52 (m, 2H, H-3), 3.63 (m, 2H, H-6′a, H-6′b), 3.70–3.85 (m, 3H), 4.07–4.13 (m, 1H), 4.57–4.70 (m, 3H), 4.81–4.88 (m, 3H), 5.00–5.17 (m, 3H), 5.76–5.85 (m, 1H, H-1), 7.28–7.34 (m, 10H, 2×Ph), 7.36 (t, 1H, *J*=6.6 Hz, *o*-NO_2–Ph*H*), 7.41 (t, 1H, *J*=6.6 Hz, *o*-NO_2–Ph*H*), 7.85 (d, 1H, *J*=6.6 Hz, *o*-NO_2–Ph*H*), 8.04 (d, 1H, *J*=6.6 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 30.3, 69.8, 70.2, 70.3, 70.4, 73.0, 73.1, 74.6, 78.2, 78.9, 117.1, 124.4, 127.6, 127.7–127.8, 128.3, 128.4, 128.7, 133.7, 134.3, 135.0, 137.9, 138.2, 146.8, 169.8. HRESIMS: calcd for $C_{32}H_{35}NO_8Na$: 584.2260; found: *m*/*z* 584.2265.

3.17. Synthesis of methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-(*o*-nitro)benzyl-α-D-glucopyranoside 21

Compound **8** (39 mg, 0.077 mmol) was acetylated as **3**. Purification by flash column chromatography (2:8 EtOAc–cyclohexane) afforded **21** (37 mg, 88%) as a yellow oil. TLC: R_f 0.41 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +34.3 (*c* 1.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H, OAc), 3.40 (s, 3H, OMe), 3.53–3.59 (m, 2H, H-2,4), 3.85–3.88 (m, 1H, H-5), 4.00 (t, 1H, *J*=9.2 Hz, H-3), 4.23 (dd, 1H, *J*=4.1, 11.9 Hz, H-6a), 4.29 (dd, 1H, *J*=1.8, 11.9 Hz, H-6b), 4.60 (d, 1H, *J*=3.2 Hz, H-1), 4.64 (d, 1H, ^2J=11.0 Hz, C*H*Ph), 4.65 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.78 (d, 1H, ^2J=11.9 Hz, C*H*Ph), 4.95 (d, 1H, ^2J=11.0 Hz, C*H*Ph), 4.96 (d, 1H, ^2J=14.7 Hz, C*H*Ph), 5.24 (d, 1H, ^2J=14.7 Hz, C*H*Ph), 7.17–7.34 (m, 10H, 2×Ph), 7.41 (t, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.58 (t, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 7.72 (d, 1H, *J*=7.8 Hz, *o*-NO_2–Ph*H*), 8.04 (d, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 55.5, 63.2, 68.5, 71.3, 73.5, 75.8, 78.1, 80.0, 81.8, 98.2, 124.7, 127.7, 127.9, 128.1, 128.2, 128.4, 128.6, 133.8, 135.1, 138.0, 138.4, 146.7, 170.8. HRESIMS: calcd for $C_{30}H_{33}NO_9Na$: 574.2053; found: *m*/*z* 574.2048.

3.18. Synthesis of 3-(6′-*O*-acetyl-2′,3′-di-*O*-benzyl-4′-*O*-(*o*-nitro)benzyl-α-D-glucopyranosyl)-1-propene 22

Compound **21** (42 mg, 0.076 mmol) was *C*-allylated as for the compound **19**. Purification by flash column chromatography (3:7 EtOAc–cyclohexane) afforded **22** (25 mg, 58%) as a yellow oil. TLC: R_f 0.62 (EtOAc–cyclohexane, 3:7); $[\alpha]_D$ +52.0 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H, OMe), 2.50 (m, 2H, H-3), 3.52 (t, 1H, *J*=8.7 Hz), 3.72–3.76 (m, 2H), 3.80 (t, 1H, *J*=8.7 Hz), 4.07–4.12 (m, 1H, H-1′), 4.16 (dd, 1H, *J*=5.0, 11.4 Hz, H-6′a), 4.25 (dd, 1H, *J*=1.8, 11.4 Hz, H-6′b), 4.59–4.69 (m, 3H, 3×C*H*Ph), 4.87–4.94 (m, 2H, 2×C*H*Ph), 5.08–5.16 (m, 2H, H-1), 5.25 (d, 1H, ^2J=14.7 Hz, C*H*Ph), 5.73–5.83 (m, 1H, H-2), 7.17–7.30 (m, 10H, 2×Ph), 7.41 (t, 1H, *J*=7.1 Hz, *o*-NO_2–Ph*H*), 7.59 (t, 1H, *J*=7.1 Hz, *o*-NO_2–Ph*H*), 7.72 (d, 1H, *J*=7.1 Hz, *o*-NO_2–Ph*H*), 8.04 (d, 1H, *J*=8.2 Hz, *o*-NO_2–Ph*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 29.9, 63.7, 69.8, 71.3, 73.7, 75.4, 77.4, 78.7, 80.1, 81.8, 117.1, 124.8, 127.8, 127.9, 128.0, 128.1, 128.5, 128.6, 138.1, 138.4, 146.7, 171.3. HRESIMS: calcd for $C_{32}H_{35}NO_8Na$: 584.2260; found: *m*/*z* 584.2255.

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