Supporting Information for
The 2,2-Dimethyl-2-(ortho-nitrophenyl)acetyl (DMNPA) Group: A
Novel Protecting Group In Carbohydrate Chemistry

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| S50                     | Table S1. Comparison of the \(^{13}\)C NMR data of the synthetic 54 with those reported in literature |
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**S53-S136** Copies of NMR spectra for all new compounds
General Comments:

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 5% H$_2$SO$_4$ (5% H$_2$SO$_4$ in ethanol) sprayed plates on a hot plate. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz). Optical rotations were measured at 20 °C with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (c) are given in g/100 mL. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

All solvents were processed under conventional way before using, and all reagents were purchased from Adamas and used without further purification.

DMNPAOH (I)

To a solution of (2-nitrophenyl)acetic acid (10 g, 55.2 mmol) in absolute MeOH (220 mL) was added SOCl$_2$ (30.3 mL, 426.8 mmol) dropwise at 0 °C under N$_2$ atmosphere. After the addition was completed, the reaction mixture was gradually warmed up to room temperature, and the stirring was continued for another 0.5 h. Evaporation in vacuo gave the methyl (2-nitrophenyl)acetate intermediate, which was used directly to the next step without further purification.
The above obtained (2-nitrophenyl)acetate intermediate was dissolved in dry DMF (100 mL), to which MeI (9.8 mL, 157.4 mmol) was added at room temperature. To the resultant solution a small portion of NaH (60% NaH in mineral oil) was slowly added at 0 °C until the mixture turned blue. Afterwards, the remaining portion NaH (total 6.15 g, 153.8 mmol) was added with stirring over 30 min while the reaction temperature was maintained at 0 to 4 °C. The resulting green solution was then gradually warmed up to room temperature and stirred for another 4 h, then water was added to dissolve the solid materials. The mixture was extracted with EtOAc for 3 times, the organic layers were combined and washed with water and brine successively, and then dried over anhydrous Na₂SO₄. Filtration and concentration under reduced pressure delivered the crude methyl 2,2-dimethyl-2-(ortho-nitrophenyl)acetate, which was used for the next step without further purification.

The above obtained methyl 2,2-dimethyl-2-(ortho-nitrophenyl)acetate was dissolved in MeOH (50 mL), to which 8N NaOH solution (in water) (50 mL) was added at room temperature. The resulting mixture was heated to reflux for 24 h, and was then cooled down to room temperature. 2N HCl was added to adjust the pH value of the reaction mixture to 3-4, and the resulting mixture was extracted with ethyl acetate for 3 times. The organic layers were combined, and the resulting solution was washed with water and brine successively, dried over anhydrous Na₂SO₄. Filtration was followed by concentration to afford crude 1, which was further purified by recrystallization from CH₂Cl₂/petroleum ether to provide pure 1 (9.2 g, 79% for 3
steps) as a white solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J = 8.0$ Hz, 1 H), 7.62 (d, $J = 4.0$ Hz, 2 H), 7.44-7.40 (m, 1 H), 1.70 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 181.8, 158.5, 138.9, 128.3, 128.1, 125.9, 46.5, 27.3; calcd for C$_{10}$H$_{11}$NO$_4$ [M+H]$^+$ 210.0760, found 210.0759.

**DMNPACl (2)**

![Reaction scheme for DMNPACl](image)

To a solution of DMNPAOH 1 (200 mg, 0.96 mmol) in dry CH$_2$Cl$_2$ (3 mL) was added oxalyl chloride (0.12 mL, 1.44 mmol) dropwise. The resultant solution was heated to reflux for 3 h. Evaporation under reduced pressure to give the crude product 2, which was then co-evaporated with toluene for two times and then used directly as acylating reagent without further purification.

**DMNPA (3)**

![Reaction scheme for DMNPA](image)

To a solution of 1 (1.0 g, 4.78 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added DCC (1.1 g, 5.34 mmol) at room temperature. The resulting solution was stirred at the same temperature for another 3 h, and then concentrated under reduced pressure. The crude product thus obtained was then purified with silica gel column chromatography (PE/EA = 4 : 1) to afford 3 (917 mg, 96%) as a light yellow solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (dd, $J = 1.2$, 8.4 Hz, 2 H), 7.56-7.52 (m, 2 H), 7.45 (dd, $J = 1.2$, 8.0 Hz, 2 H), 7.36-7.32 (m, 2 H), 1.58 (s, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.3, 147.6,
137.7, 133.7, 128.2, 128.0, 125.8, 47.4, 26.2; HRMS (ESI) calcd for C_{20}H_{21}N_{2}O_{7} [M+H]^{+} 401.1343, found 401.1342.

**Figure S1.** The ORTEP drawing of DMNPAA 3.\textsuperscript{[S1]}

**General procedure for the installation of DMNPA:**

To a solution of 4\textsuperscript{[S2]} (1.0 g, 1.97 mmol) and DMNPAA (948 mg, 2.37 mmol) in dry CH_{2}Cl_{2} (15 mL) was added TMSOTf (1.58 mL, 3.95 mmol) dropwise at \(-36^{\circ}\text{C}\) at the presence of 5A MS (550 mg) under N_{2} atmosphere. The resulting reaction mixture was stirred at the same temperature for another 40 min, at which time TLC showed the disappearance of all starting material. Et_{3}N (3.0 mL) was added to quench the reaction, the reaction mixture was then diluted with ethyl acetate. Washing with saturated aqueous NaHCO_{3}, brine successively and the organic phases was separated and combined, and was then dried over anhydrous Na_{2}SO_{4}. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to deliver the acylated product 5 (1.27 g, 96%).

**Methyl 2,3,4-tri-O-benzoyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-\alpha-D-glucopyranoside (5)**
Following the general procedure, 5 (63.4 mg, 91%) was obtained as a white foam:

\([\alpha]_D^{25} = +48.2 \ (c \ 1.0, \text{CHCl}_3)\); \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.99-7.95 \ (m, \ 3 \ H), 7.92 \ (dd, \ J = 1.2, 8.0 \ Hz, \ 2 \ H), 7.85 \ (dd, \ J = 1.2, 8.4 \ Hz, \ 2 \ H), 7.62-7.60 \ (m, \ 2 \ H), 7.52 \ (td, \ J = 1.2, 8.4 \ Hz, \ 2 \ H), 7.45-7.28 \ (m, \ 8 \ H), 6.11-6.05 \ (m, \ 1 \ H), 5.42 \ (t, \ J = 9.6 \ Hz, \ 1 \ H), 5.15-5.11 \ (m, \ 2 \ H), 4.35 \ (d, \ J = 9.6 \ Hz, \ 1 \ H), 4.24-4.18 \ (m, \ 2 \ H), 3.31 \ (s, \ 3 \ H), 1.70 \ (s, \ 3 \ H), 1.67 \ (s, \ 3 \ H); \(^{13}\text{C} \text{NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 175.0, 166.0, 165.9, 165.3, 148.7, 139.3, 133.5, 133.4, 133.2, 130.1, 130.0, 129.8, 129.4, 129.2, 129.1, 128.5 \ (2 \ C), 128.4, 128.2, 127.9, 125.9, 96.9, 72.1, 70.6, 69.5, 67.6, 63.5, 55.5, 46.6, 27.3, 27.2; \text{HRMS (ESI) calcd for C}_{38}\text{H}_{35}\text{NO}_{12}\text{Na} \ [M+Na]^+ \ 720.2051, \text{ found 720.2091.} \)

**Methyl 2,3,4-tri-O-benzyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-\(\alpha\)-D-glucopyranoside (21)**

Following the general procedure with 6\(^{[S3]}\) as the starting material, 21 (57 mg, 87%) was obtained as a light yellow syrup: \([\alpha]_D^{25} = +21.5 \ (c \ 1.0, \text{CHCl}_3)\); \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.90 \ (d, \ J = 8.0 \ Hz, \ 1 \ H), 7.58 \ (d, \ J = 4.0 \ Hz, \ 2 \ H), 7.39-7.24 \ (m, \ 16 \ H), 4.96 \ (d, \ J = 10.8 \ Hz, \ 1 \ H), 4.80-4.75 \ (m, \ 3 \ H), 4.66 \ (d, \ J = 12.0 \ Hz, \ 1 \ H), 4.55 \ (d, \ J = 3.6 \ Hz, \ 1 \ H), 4.47-4.42 \ (m, \ 2 \ H), 4.14 \ (dd, \ J = 6.0, 12.0 \ Hz, \ 1 \ H), 3.97 \ (t, \ J = 9.2 \ Hz, \ 1 \ H), 3.77-3.72 \ (m, \ 1 \ H), 3.44 \ (dd, \ J = 3.2, 9.6 \ Hz, \ 1 \ H), 3.29 \ (dd, \ J = 8.8, 10.4 \ Hz, \ 1 \ H), 2.25-2.18 \ (m, \ 2 \ H), 1.98 \ (s, \ 3 \ H), 1.26-1.20 \ (m, \ 2 \ H), 1.17 \ (s, \ 3 \ H), 1.14 \ (s, \ 3 \ H), 1.12 \ (s, \ 3 \ H); \(^{13}\text{C} \text{NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 175.0, 166.0, 165.9, 165.3, 148.7, 139.3, 133.5, 133.4, 133.2, 130.1, 130.0, 129.8, 129.4, 129.2, 129.1, 128.5 \ (2 \ C), 128.4, 128.2, 127.9, 125.9, 96.9, 72.1, 70.6, 69.5, 67.6, 63.5, 55.5, 46.6, 27.3, 27.2; \text{HRMS (ESI) calcd for C}_{38}\text{H}_{35}\text{NO}_{12}\text{Na} \ [M+Na]^+ \ 720.2051, \text{ found 720.2091.} \)
Hz, 1 H), 3.21 (s, 3 H), 1.67 (s, 3 H), 1.66 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
175.0, 148.6, 139.2, 138.6, 138.1, 137.9, 133.2, 128.4 (2 C), 128.0 (2 C), 127.9, 127.8, 127.7 (2 C), 125.6, 97.7, 81.9, 79.9, 78.1, 75.8, 75.1, 73.3, 68.6, 63.7, 54.9, 46.6, 27.2;
HRMS (ESI) calcd for C$_{38}$H$_{41}$NO$_9$Na [M+Na]$^+$ 678.2673, found 678.2669.

Methyl

2,3-di-$O$-acetyl-4-$O$-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-6-$O$-benzyl

$\alpha$-D-glucopyranoside (22)

Following the general procedure with $\mathbf{7}^{[S4]}$ as the starting material, 22 (54.8 mg, 98%)
was obtained as a light yellow solid: [$\alpha$]$_D^{25}$ = +59.4 ($c$ 1.06, CHCl$_3$); $^1$H NMR (400
MHz, CDCl$_3$) $\delta$ 7.94 (dd, $J = 1.2$, 8.0 Hz, 1 H), 7.63 (td, $J = 1.2$, 7.6 Hz, 1 H), 7.54
(dd, $J = 1.2$, 8.0 Hz, 1 H), 7.45-7.41 (m, 1 H), 7.37-7.25 (m, 5 H), 5.51 (t, $J = 9.6$ Hz,
1 H), 5.15 (t, $J = 10.0$ Hz, 1 H), 4.95 (d, $J = 3.6$ Hz, 1 H), 4.88 (dd, $J = 3.6$, 10.0 Hz, 1
H), 4.68 (d, $J = 12.0$ Hz, 1 H), 4.51 (d, $J = 12.0$ Hz, 1 H), 3.91-3.86 (m, 1 H), 3.64-3.55
(m, 2 H), 3.41 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 1.55 (s, 3 H), 1.53 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
174.3, 170.4, 170.3, 148.5, 138.5, 138.2, 133.6,
128.4, 128.3, 128.2, 128.0, 127.7, 126.0, 96.6, 73.6, 71.5, 69.8, 69.6, 69.0, 68.6, 55.5,
46.8, 27.1, 27.0, 21.1, 20.9; HRMS (ESI) calcd for C$_{28}$H$_{34}$NO$_{11}$ [M+H]$^+$ 560.2126,
found 560.2131.

Methyl

2,3-di-$O$-benzoyl-4-$O$-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-6-$O$-benzyl-$\alpha$-D-
glucopyranoside (23)

Following the general procedure with 8\textsuperscript{S5} as the starting material, 23 (65 mg, 95%) was obtained as a white foam: $[\alpha]_D^{25} = +152.9$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.2$ Hz, 4 H), 7.80 (dd, $J = 1.6$, 8.4 Hz, 1 H), 7.57-7.53 (m, 1 H), 7.50-7.46 (m, 2 H), 7.44-7.28 (m, 11 H), 5.97 (t, $J = 10.0$ Hz, 1 H), 5.45 (t, $J = 10.0$ Hz, 1 H), 5.20 (d, $J = 3.6$ Hz, 1 H), 5.15 (dd, $J = 3.6$, 10.0 Hz, 1 H), 4.75 (d, $J = 12.0$ Hz, 1 H), 4.58 (d, $J = 12.0$ Hz, 1 H), 4.04-4.00 (m, 1 H), 3.79 (dd, $J = 2.4$, 11.2 Hz, 1 H), 3.74 (dd, $J = 5.2$, 10.8 Hz, 1 H), 3.42 (s, 3 H), 1.46 (s, 3 H), 1.39 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.3, 165.9, 165.8, 148.5, 138.4, 138.3, 133.4 (2 C), 133.3, 130.0, 129.9, 129.5, 129.2, 128.4 (2 C), 127.9, 128.0, 127.6, 125.8, 96.8, 73.6, 72.5, 70.7, 69.4, 69.0, 68.6, 55.6, 46.7, 27.0, 26.7; HRMS (ESI) calcd for C$_{38}$H$_{38}$NO$_{11}$ [M+H]$^+$ 684.2439, found 684.2481.

Allyl

2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3,4-di-O-benzyl-α-L-rhamnopyranoside (24)

Following the general procedure with 9\textsuperscript{S6} as the starting material, 24 (50.6 mg, 88%) was obtained as a colorless syrup: $[\alpha]_D^{25} = +34.2$ (c 1.2, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.0$ Hz, 1 H), 7.61 (d, $J = 3.6$ Hz, 2 H), 7.45-7.41 (m, 1 H),
7.36-7.26 (m, 10 H), 5.93-5.84 (m, 1 H), 5.39 (t, \( J = 2.4 \) Hz, 1 H), 5.30-5.24 (m, 1 H), 5.20-5.17 (m, 1 H), 4.84 (d, \( J = 10.8 \) Hz, 1 H), 4.82 (d, \( J = 1.2 \) Hz, 1 H), 4.71 (d, \( J = 11.2 \) Hz, 1 H), 4.52 (d, \( J = 10.8 \) Hz, 1 H), 4.51 (d, \( J = 10.8 \) Hz, 1 H), 4.16-4.10 (m, 1 H), 4.00-3.94 (m, 2 H), 3.73-3.66 (m, 1 H), 3.09 (t, \( J = 9.2 \) Hz, 1 H), 1.69 (s, 3 H), 1.66 (s, 3 H), 1.16 (d, \( J = 6.0 \) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.7, 148.6, 139.4, 138.5, 138.4, 133.8, 133.3, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 126.0, 117.4, 96.7, 80.0, 78.2, 75.3, 71.4, 69.1, 68.3, 67.6, 46.9, 27.3, 27.0, 18.2; HRMS (ESI) calcd for C\(_{33}\)H\(_{38}\)NO\(_8\) [M+H]\(^+\) 576.2592, found 576.2597.

**Allyl**

2,3-O-isopropylidene-4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-\( \alpha \)-L-rhamnoside (25)

Following the general procedure with 10\(^{[S7]}\) as the starting material, 25 (40 mg, 91%) was obtained as a syrup: \([\alpha]_D^{25} = -76.1 \) (c 1.10, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.96 (d, \( J = 8.0 \) Hz, 1 H), 7.61 (d, \( J = 4.0 \) Hz, 2 H), 7.44-7.40 (m, 1 H), 5.94-5.84 (m, 1 H), 5.32-5.27 (m, 1 H), 5.23-5.19 (m, 1 H), 5.02 (s, 1 H), 4.85 (dd, \( J = 7.6, 10.0 \) Hz, 1 H), 4.18-4.13 (m, 1 H), 4.12-4.06 (m, 2 H), 4.02-3.96 (m, 1 H), 3.75-3.65 (m, 1 H), 1.70 (s, 3 H), 1.69 (s, 3 H), 1.54 (s, 3 H), 1.33 (s, 3 H), 1.25 (d, \( J = 6.4 \) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.9, 148.8, 139.1, 133.8, 133.3, 128.6, 128.0, 125.9, 118.0, 109.9, 96.4, 76.2, 76.0, 75.7, 68.4, 64.4, 47.2, 27.8, 27.4 (2 C), 27.3, 26.7, 17.4; HRMS (ESI) calcd for C\(_{22}\)H\(_{30}\)NO\(_8\) [M+H]\(^+\) 436.1965, found 436.1970.
Methyl 2,3-di-O-benzyl-4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-6-O-tert-butyldiphenylsilyl-α-D-glucopyranoside (26)

Following the general procedure with 11[S8] as the starting material, 26 (60.2 mg, 75%) was obtained as a white foam: \([\alpha]_D^{25} = +20.7 \ (c \ 1.0, \ CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67-7.62 (m, 5 H), 7.46-7.21 (m, 19 H), 4.88 (d, \(J = 11.6 \) Hz, 1 H), 4.86 (t, \(J = 8.8 \) Hz, 1 H), 4.67 (d, \(J = 12.0 \) Hz, 1 H), 4.61 (d, \(J = 3.6 \) Hz, 1 H), 4.56 (d, \(J = 12.0 \) Hz, 1 H), 4.50 (d, \(J = 11.6 \) Hz, 1 H), 3.86-3.71 (m, 4 H), 3.58 (dd, \(J = 3.6, 9.6 \) Hz, 1 H), 3.39 (s, 3 H), 1.41 (s, 3 H), 1.39 (s, 3 H), 1.01 (s, 9 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.3, 148.9, 138.8, 138.3, 138.0, 135.9, 135.8, 134.0, 133.7, 132.9, 129.6 (2 C), 128.6, 128.5, 128.3, 128.0, 127.9, 127.7, 127.6, 127.2, 127.0, 125.5, 97.6, 80.0, 79.2, 74.6, 73.3, 71.4, 70.8, 63.5, 55.3, 46.7, 26.9, 26.7, 19.4; HRMS (ESI) calcd for C\(_{47}\)H\(_{54}\)NO\(_9\)Si [M+H]\(^+\) 804.3562, found 804.3562.

1,2;3,4-Di-isopropylidene-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-galactopyranoside (27)

Following the general procedure with 12[S8] as the starting material, 27 (43.2 mg, 96%) was obtained as a white sol: \([\alpha]_D^{25} = -19.1 \ (c \ 1.02, \ CHCl_3)\); \(^1\)H NMR (400 MHz,
CDCl$_3$ $\delta$ 7.91 (dd, $J = 0.8$, 8.0 Hz, 1 H), 7.60-7.59 (m, 2 H), 7.42-7.38 (m, 1 H), 5.49 (d, $J = 5.2$ Hz, 1 H), 4.59 (dd, $J = 2.4$, 8.0 Hz, 1 H), 4.36 (dd, $J = 3.6$, 11.6 Hz, 1 H), 4.29 (dd, $J = 2.4$, 4.8 Hz, 1 H), 4.18-4.11 (m, 2 H), 4.00-3.96 (m, 1 H), 1.69 (s, 3 H), 1.68 (s, 3 H), 1.44 (s, 3 H), 1.42 (s, 3 H), 1.31 (s, 3 H), 1.30 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.2, 148.9, 139.4, 133.3, 128.3, 127.8, 125.7, 109.7, 108.8, 96.4, 71.2, 70.9, 70.6, 66.1, 64.1, 46.7, 27.5, 26.1, 26.0, 25.1, 24.5; HRMS (ESI) calcd for C$_{22}$H$_{30}$NO$_9$ [M+H]$^+$ 452.1915, found 452.1910.

**Methyl 2,3,6-tri-O-benzyl-4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-$\alpha$-D-glucopyranoside (28)**

![Diagram](image)

Following the general procedure with 13[S9] as the starting material, 28 (59 mg, 97%) was obtained as a light yellow solid: $[\alpha]_D^{25} = +50.9$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (dd, $J = 1.2$, 8.4 Hz, 1 H), 7.55 (td, $J = 1.2$, 8.0 Hz, 1 H), 7.48 (dd, $J = 1.6$, 8.0 Hz, 1 H), 7.40-7.36 (m, 3 H), 7.32-7.22 (m, 13 H), 5.04 (t, $J = 9.6$ Hz, 1 H), 4.97 (d, $J = 11.6$ Hz, 1 H), 4.68-4.62 (m, 3 H), 4.56-4.49 (m, 3 H), 3.92 (t, $J = 9.2$ Hz, 1 H), 3.83-3.78 (m, 1 H), 3.71 (dd, $J = 1.6$, 10.8 Hz, 1 H), 3.63-3.57 (m, 2 H), 3.39 (s, 3 H), 1.55 (s, 3 H), 1.52 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 148.8, 138.7, 138.6, 138.5, 137.9, 133.2, 128.5 (2 C), 128.3, 128.2 (2 C), 128.0 (2 C), 127.9, 127.4, 127.2, 127.0, 125.6, 97.7, 79.9, 78.9, 74.4, 73.5, 73.2, 71.3, 69.1, 69.0, 55.5, 55.4, 46.9, 27.2, 27.1; HRMS (ESI) calcd for C$_{38}$H$_{41}$NO$_9$Na [M+Na]$^+$ 678.2673, found 678.2668.
Methyl

2,3-di-O-benzyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (29)

Following the general procedure with 14[S10] as the starting material, 29 (45.2 mg, 80%) was obtained as a light yellow solid: \([\alpha]_D^{25} = +12.6 (c 0.96, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.84 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.50 (d, J = 4.0 \text{ Hz}, 2 \text{ H}), 7.32-7.17 (m, 11 \text{ H}), 4.88 (d, J = 11.6 \text{ Hz}, 1 \text{ H}), 4.68 (d, J = 12.0 \text{ Hz}, 1 \text{ H}), 4.67 (d, J = 11.2 \text{ Hz}, 1 \text{ H}), 4.57 (d, J = 12.4 \text{ Hz}, 1 \text{ H}), 4.48 (d, J = 3.2 \text{ Hz}, 1 \text{ H}), 4.24 (dd, J = 5.2, 12.0 \text{ Hz}, 1 \text{ H}), 4.18 (dd, J = 2.4, 12.0 \text{ Hz}, 1 \text{ H}), 3.69 (t, J = 9.2 \text{ Hz}, 1 \text{ H}), 3.62-3.57 (m, 1 \text{ H}), 3.35 (dd, J = 3.6, 9.6 \text{ Hz}, 1 \text{ H}), 3.27 (t, J = 9.6 \text{ Hz}, 1 \text{ H}), 3.14 (s, 3 \text{ H}), 1.580 (s, 3 \text{ H}), 1.576 (s, 3 \text{ H}); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 175.6, 148.6, 139.4, 138.4, 138.2, 133.4, 128.7, 128.6, 128.2 (2 \text{ C}), 128.1, 128.0, 127.9, 125.8, 98.1, 81.4, 79.7, 75.7, 73.3, 70.4, 69.4, 64.2, 55.1, 46.8, 27.5, 27.4; HRMS (ESI) calcd for C\(_{31}\)H\(_{36}\)NO\(_9\) [M+H]^+ 566.2384, found 566.2401.

\(p\)-Methoxyphenyl

2,3-di-O-benzoyl-4-O-(2,3,4-tri-O-benzoyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-β-D-galactopyranosyl)-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-β-D-glucopyranoside (30)
Except for the applied amount of DMNPAA (3.0 eq to 15) and TMSOTf (4.0 eq to 15), the general procedure was adopted to convert 15[S11] to 30 (114 mg, 93%) as a white foam: \([\alpha]_D^{25} = +13.6\) (c 1.0, CHCl\(_3\)); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (dd, \(J = 1.2, 8.4\) Hz, 2 H), 8.04 (dd, \(J = 1.6, 8.8\) Hz, 2 H), 7.99 (dd, \(J = 1.2, 8.0\) Hz, 2 H), 7.83 (dd, \(J = 1.2, 8.4\) Hz, 2 H), 7.75-7.65 (m, 8 H), 7.59-7.37 (m, 12 H), 7.30-7.26 (m, 1 H), 7.23 (t, \(J = 7.6\) Hz, 2 H), 7.07 (t, \(J = 7.6\) Hz, 2 H), 6.88 (d, \(J = 8.8\) Hz, 2 H), 6.72 (d, \(J = 9.2\) Hz, 2 H), 5.72 (t, \(J = 9.6\) Hz, 1 H), 5.62-5.53 (m, 3 H), 5.44 (dd, \(J = 3.6, 10.4\) Hz, 1 H), 5.02 (d, \(J = 8.0\) Hz, 1 H), 4.84 (d, \(J = 8.0\) Hz, 1 H), 4.61 (dd, \(J = 2.0, 12.4\) Hz, 1 H), 4.19 (dd, \(J = 3.2, 12.4\) Hz, 1 H), 4.06 (t, \(J = 9.6\) Hz, 1 H), 3.94 (t, \(J = 6.8\) Hz, 1 H), 3.72 (s, 3 H), 3.70-3.67 (m, 1 H), 3.57 (dd, \(J = 6.4\) Hz, 1 H), 3.41 (dd, \(J = 7.2, 11.6\) Hz, 1 H), 1.81 (s, 3 H), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.65 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.8 (2 C), 165.6, 165.4, 165.3, 165.2, 164.9, 155.9, 151.2, 148.9, 148.5, 139.2, 139.0, 133.8, 133.7, 133.4 (2 C), 133.2, 133.1, 130.1, 130.0, 129.9, 129.8 (2 C), 129.7, 129.4, 129.0 (2 C), 128.7, 128.6, 128.5, 128.4 (2 C), 128.3, 128.1, 126.2, 126.0, 119.6, 114.6, 101.3, 100.7, 75.2, 73.2, 72.4, 72.0, 71.7, 70.8, 69.8, 67.8, 61.9, 61.6, 55.7, 46.9, 46.5, 27.6 (2 C), 27.4 (2 C); HRMS (ESI) calcd for C\(_{74}H_{66}N_2O_{23}Na\) [M+Na]\(^+\) 1373.3948, found 1373.3974.

**Allyl**

2-\(O-(2,2\)-dimethyl-2-\((ortho\)-nitrophenyl)acetyl)-3,4,6-tri-\(O\)-acetyl-\(\beta\)-D-glucopyranoside (31)
Following the general procedure with 16[S12] as the starting material, 31 (51 mg, 95%) was obtained as a white foam: [α]D25 = +67.4 (c 1.10, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.99 (dd, J = 1.6, 8.0 Hz, 1 H), 7.63-7.55 (m, 2 H), 7.45-7.41 (m, 1 H), 5.91-5.81 (m, 1 H), 5.29-5.17 (m, 3 H), 5.13-5.04 (m, 2 H), 4.48 (d, J = 7.6 Hz, 1 H), 4.35-4.30 (m, 1 H), 4.26 (dd, J = 4.8, 12.4 Hz, 1 H), 4.15 (dd, J = 2.4, 12.4 Hz, 1 H), 4.09-4.03 (m, 1 H), 3.68-3.64 (m, 1 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.00 (s, 3 H), 1.64 (s, 3 H), 1.61 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ 173.8, 170.8 (2 C), 169.6, 148.3, 138.9, 133.5, 133.3, 128.3, 128.1, 126.0, 118.1, 100.0, 72.2, 71.8, 71.4, 70.2, 69.0, 62.1, 46.8, 27.2, 27.0, 21.0, 20.9, 20.8, 20.7; HRMS (ESI) calcd for C25H32NO12 [M+H]+ 538.1919, found 538.1922.

**p-Methoxyphenyl**

2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-allyl-4,6-O-benzylidene-β-D-g lucopyranoside (32)

Following the general procedure with 17[S13] as the starting material, 32 (120 mg, 90%) was obtained as a white solid: [α]D25 = +60.9 (c 0.8, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.88 (dd, J = 1.2, 7.6 Hz, 1 H), 7.56-7.35 (m, 8 H), 6.94 (d, J = 9.2 Hz, 2 H), 6.82 (d, J = 9.2 Hz, 2 H), 5.96-5.86 (m, 1 H), 5.56 (s, 1 H), 5.26-5.21 (m, 2 H), 5.14 (dq, J = 1.6, 10.4 Hz, 1 H), 5.03 (d, J = 7.6 Hz, 1 H), 4.39-4.33 (m, 2 H), 4.17-4.12 (m,
1 H), 3.89 (t, J = 9.6 Hz, 1 H), 3.82 (t, J = 10.4 Hz, 1 H), 3.77 (s, 3 H), 3.74 (t, J = 8.8 Hz, 1 H), 3.55-3.48 (m, 1 H), 1.67 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 155.4, 150.8, 148.9, 138.5, 137.3, 134.9, 133.0, 129.1, 128.7, 128.4, 128.0, 126.1, 125.6, 118.0, 117.1, 114.6, 101.4, 99.8, 81.4, 78.4, 73.4, 73.1, 68.9, 66.2, 55.8, 47.1, 27.2, 27.1; HRMS (ESI) calcd for C₃₃H₃₆NO₁₀ [M+H]⁺ 606.2334, found 606.2339.

**General procedure for the deprotection of DMNPA:**

To a suspension of 5 (1.0 g, 1.49 mmol) and Zn (976 mg, 14.9 mmol) in a mixed solvent of dioxane and H₂O (24 mL, v/v = 1 : 1) was added CuSO₄ (238 mg, 1.49 mmol) and HOAc (427 µL, 7.45 mmol) successively. The resulting mixture was stirred at ambient temperature for 30 minutes, at which time TLC showed that all starting material disappeared. Filtration to remove the solid was followed by dilution with ethyl acetate. The obtained mixture was washed successively with saturated NaHCO₃, brine, and then dried over Na₂SO₄. Filtration and concentration afforded the crude product which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to furnish 4 (692 mg, 92%).

**Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside (6)**

Following the general procedure of DMNPA deprotection, 21 (44 mg, 0.067 mmol) was converted to 6 (31 mg, 98%) efficiently.

**Methyl 2,3-di-O-acetyl-6-O-benzyl-α-D-glucopyranoside (7)**
Following the general deprotection procedure of DMNPA, 32 (36 mg, 0.064 mmol) was converted to 7 (22 mg, 93%) efficiently.

**Methyl 2,3-di-O-benzoyl-6-O-benzyl-α-D-glucopyranoside (8)**

Following the general deprotection procedure of DMNPA, 23 (33.7 mg, 0.05 mmol) was converted to 8 (21 mg, 88%) smoothly.

**Allyl 3,4-di-O-benzyl-α-L-rhamnopyranoside (9)**

Following the general deprotection procedure of DMNPA, 24 (33 mg, 0.057 mmol) was converted to 9 (21 mg, 96%) efficiently.

**Allyl 2,3-O-isopropylidene-α-L-rhamnopyranoside (10)**

Following the general deprotection procedure of DMNPA, 25 (22 mg, 0.05 mmol) was converted to 10 (11 mg, 95%) efficiently.

**Methyl 2,3-Di-O-benzyl-6-O-tert-butyldiphenylsilyl-α-D-glucopyranoside (11)**
Following the general deprotection procedure of DMNPA, 26 (40 mg, 0.05 mmol) was converted to 11 (25 mg, 83%) smoothly.

1,2;3,4-Di-isopropylidene-α-D-galactopyranoside (12)

Following the general deprotection procedure of DMNPA, 27 (24.8 mg, 0.055 mmol) was converted to 12 (13.6 mg, 98%) efficiently.

Methyl 2,3,6-tri-O-benzyl-α-D-glucopyranoside (13)

Following the standard deprotection procedure of DMNPA, 28 (53.4 mg, 0.08 mmol) was converted to 13 (33.8 mg, 90%) efficiently.

Methyl 2,3-di-O-benzyl-α-D-glucopyranoside (14)

Following the general deprotection procedure of DMNPA, 29 (36 mg, 0.063 mmol) was converted to 14 (21 mg, 91%) smoothly.

p-Methoxyphenyl

2,3-di-O-benzoyl-4-O-(2,3,4-tri-O-benzoyl-β-D-galactopyranosyl)-β-D-glucopyran
oside (15)

Except for the applied amounts of Zn (20.0 eq.), HOAc (10.0 eq.), and CuSO₄ (2.0 eq.), the general deprotection procedure was adopted to mediate the conversion of 30 (100 mg, 0.074 mmol) to 15 (70.3 mg, 98%).

Methyl 2,3-di-O-benzyl-4-O-chloroacetyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (33)

To a solution of 14 (196 mg, 0.345 mmol) in dry CH₂Cl₂ (4 mL) was added dry pyridine (0.48 mL, 5.9 mmol) and CCl₄ (0.35 mL, 0.44 mmol) dropwise via syringe at 0 °C. The reaction mixture was warmed up to room temperature and the stirring was continued for another 6 h. CH₂Cl₂ was added to dilute the reaction mixture, the resulting mixture was washed successively with 1N HCl, saturated NaHCO₃, and brine, and then dried over Na₂SO₄. Filtration and concentration gave a residue which was further purified by silica gel column chromatography (PE/EA = 6 : 1) to deliver 33 (170 mg, 77%) as a colorless syrup: [α]D²⁵ = 17.5 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.0 Hz, 1 H), 7.59 (d, J = 3.6 Hz, 2 H), 7.40-7.25 (m, 11 H), 4.88 (dd, J = 9.2, 10.8 Hz, 2 H), 4.80 (d, J = 12.0 Hz, 1 H), 4.65 (t, J = 12.0 Hz, 1 H), 4.55 (d, J = 3.2 Hz, 1 H), 4.18 (dd, J = 2.0, 12.0 Hz, 1 H), 4.02 (dd, J = 5.6, 12.0 Hz, 1 H).
Hz, 1 H), 3.91-3.79 (m, 3 H), 3.65 (d, J = 14.8 Hz, 1 H), 3.51 (dd, J = 3.6, 9.6 Hz, 1 H), 3.26 (s, 3 H), 1.66 (s, 3 H), 1.64 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.1, 166.2, 148.6, 139.4, 138.5, 138.0, 133.4, 128.7, 128.6, 128.3, 128.2, 127.9 (2 C), 125.8, 98.1, 79.8, 79.0, 75.5, 73.6, 71.5, 67.3, 63.3, 55.4, 46.6, 40.7, 27.4, 27.3;

HRMS (ESI) calcd for C$_{33}$H$_{36}$ClNO$_{10}$Na [M+Na]$^+$ 664.1920, found 664.1927.

Methyl 2,3-di-O-benzyl-4-O-levulinyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (34)

To a solution of 14 (30 mg, 0.053 mmol), LevOH (13 mg, 0.106 mmol), and DMAP (16 mg, 0.133 mmol) in dry CH$_2$Cl$_2$ (3.0 mL) was added DCC (27 mg, 0.133 mmol) at 0 °C under N$_2$ atmosphere. The resulting mixture was stirred at room temperature for 4 h, at which time TLC showed that all the starting material disappeared completely. CH$_2$Cl$_2$ was added to dilute the reaction mixture, the resultant mixture was washed with 1N NaOH, 1N HCl, saturated aqueous NaHCO$_3$, and brine successively, and was then dried over anhydrous Na$_2$SO$_4$. Filtration and concentration under reduced pressure yield a residue which was further purified by silica gel column chromatography (PE/EA = 2 : 1) to furnish 34 (34.5 mg, 98%) as a white solid: [α]$^D$_0 = 3.5 (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 8.0 Hz, 1 H), 7.59 (d, J = 3.6 Hz, 2 H), 7.40-7.36 (m, 1 H), 7.34-7.24 (m, 10 H), 4.85-4.80 (m, 2 H), 4.78 (d, J = 12.0 Hz, 1 H), 4.66 (t, J = 12.0 Hz, 1 H), 4.53 (d, J = 3.2 Hz, 1 H), 4.16 (dd, J = 9.6 Hz, 1 H), 3.91-3.79 (m, 3 H), 3.65 (d, J = 14.8 Hz, 1 H), 3.51 (dd, J = 3.6, 9.6 Hz, 1 H), 3.26 (s, 3 H), 1.66 (s, 3 H), 1.64 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.1, 166.2, 148.6, 139.4, 138.5, 138.0, 133.4, 128.7, 128.6, 128.3, 128.2, 127.9 (2 C), 125.8, 98.1, 79.8, 79.0, 75.5, 73.6, 71.5, 67.3, 63.3, 55.4, 46.6, 40.7, 27.4, 27.3;

HRMS (ESI) calcd for C$_{33}$H$_{36}$ClNO$_{10}$Na [M+Na]$^+$ 664.1920, found 664.1927.
2.0, 12.4 Hz, 1 H), 4.00 (dd, $J = 6.4, 12.0$ Hz, 1 H), 3.90 (t, $J = 9.2$ Hz, 1 H), 3.82-3.77 (m, 1 H), 3.48 (dd, $J = 3.6, 9.6$ Hz, 1 H), 3.22 (s, 3 H), 2.67 (t, $J = 6.8$ Hz, 2 H), 2.51-2.35 (m, 2 H), 2.14 (s, 3 H), 1.653 (s, 3 H), 1.646 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 175.0, 171.7, 148.7, 139.4, 138.6, 138.1, 133.3, 128.6, 128.5, 128.2 (2 C), 128.1, 127.8, 127.7, 125.8, 98.0, 79.6, 79.3, 75.5, 73.6, 70.4, 67.7, 63.6, 55.2, 46.6, 38.0, 29.9, 28.1, 27.4, 27.3; HRMS (ESI) calcd for C$_{36}$H$_{42}$NO$_{11}$ [M+H]$^+$ 664.2752, found 664.2756.

Methyl 2,3-di-O-benzyl-4-O-(2-azidomethylbenzoyl)-6-O-(2,2-dimethyl-2-(ortho-nitrophe nyl)acetyl)-$\alpha$-D-glucopyranoside (35)

To a solution of 14 (66 mg, 0.116 mmol), AZMBOH (41 mg, 0.232 mmol), and DMAP (36 mg, 0.29 mmol) in dry CH$_2$Cl$_2$ (3 mL) was added DCC (60 mg, 0.29 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 4 h, then was move to the refrigerator to precipitate the major urea byproduct. Rapid filtration was then conducted to remove the urea byproduct, and the white solid was washed thoroughly with cold ethyl acetate for three times. The filtrate was concentrated under reduced pressure to obtain the crude product which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to produce 35 (80 mg, 95%) as a white solid: $[\alpha]_{d}^{25} = -10.8$ (c 1.08, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (t, $J = 8.4$ Hz, 2 H), 7.61-7.52 (m, 4 H), 7.41-7.33 (m, 7 H), 7.13-7.10 (m, 5 H), 5.19 (t, $J = 9.6$ Hz, 1 H),
4.88 (d, J = 11.2 Hz, 1 H), 4.83 (d, J = 12.0 Hz, 1 H), 4.71 (s, 2 H), 4.70 (d, J = 12.0 Hz, 1 H), 4.61 (s, 1 H), 4.60 (d, J = 9.2 Hz, 1 H), 4.28 (dd, J = 2.0, 12.0 Hz, 1 H), 4.09-4.01 (m, 2 H), 4.00-3.96 (m, 1 H), 3.59 (dd, J = 3.6, 9.6 Hz, 1 H), 3.30 (s, 3 H), 1.67 (s, 3 H), 1.65 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 175.0, 165.0, 148.6, 139.4, 138.3, 138.2, 138.0, 133.4, 133.2, 131.2, 129.4, 128.7, 128.3, 128.2 (2 C), 128.1, 128.0, 127.8, 127.7, 125.8, 98.1, 79.7, 79.2, 75.6, 73.6, 70.5, 67.6, 63.6, 55.4, 53.1, 46.6, 27.3 (2 C); HRMS (ESI) calcd for C\(_{39}\)H\(_{40}\)N\(_4\)O\(_{10}\)Na \([M+Na]^+\) 747.2636, found 747.2643.

Methyl 2,3-di-O-benzyl-4-O-chloroacetyl-\(\alpha\)-D-glucopyranoside (18)

\[\begin{align*}
\text{DMNPA} & \xrightarrow{\text{ZnCuSO\(_4\), dioxane:H\(_2\)O}} \text{HOAc, rt. 88\%} \\
& \xrightarrow{\text{18}} \text{[18]} \\
\end{align*}\]

The general deprotection procedure of DMNPA was adopted to convert 33 (63 mg, 0.098 mmol) to 18 (39 mg, 88%) as a light yellow solid: \([\alpha]_D^{25} = 63.0\) (c 1.05, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.26 (m, 10 H), 4.97 (t, J = 10.0 Hz, 1 H), 4.93 (d, J = 11.2 Hz, 1 H), 4.83 (d, J = 12.0 Hz, 1 H), 4.67 (d, J = 3.6 Hz, 1 H), 4.64 (dd, J = 3.6, 14.8 Hz, 1 H), 4.00 (t, J = 9.2 Hz, 1 H), 3.81 (d, J = 14.8 Hz, 1 H), 3.70 (d, J = 14.4 Hz, 1 H), 3.69-3.62 (m, 2 H), 3.59 (dd, J = 3.6, 9.6 Hz, 1 H), 3.55 (d, J = 4.0, 12.8 Hz, 1 H), 3.39 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.3, 138.7, 137.9, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 98.3, 79.7, 78.8, 75.6, 73.7, 72.1, 69.3, 61.4, 55.6, 40.5; HRMS (ESI) calcd for C\(_{23}\)H\(_{27}\)ClO\(_7\)Na \([M+Na]^+\) 473.1337, found 473.1334.

Methyl 2,3-di-O-benzyl-4-O-levulinyl-\(\alpha\)-D-glucopyranoside (19)
The standard deprotection procedure of DMNPA was followed to convert 34 (120 mg, 0.18 mmol) to 19 (80.7 mg, 95%) as a white solid: \([\alpha]_D^{25} = 6.83\) (c 1.0, CHCl₃); \(^1^H\) NMR (400 MHz, CDCl₃) \(\delta\) 7.36-7.25 (m, 10 H), 4.92-4.87 (m, 2 H), 4.81 (d, \(J = 12.0\) Hz, 1 H), 4.71 (d, \(J = 11.6\) Hz, 1 H), 4.66 (d, \(J = 12.0\) Hz, 1 H), 4.61 (d, \(J = 3.6\) Hz, 1 H), 4.02 (t, \(J = 9.6\) Hz, 1 H), 3.66-3.55 (m, 4 H), 3.38 (s, 3 H), 2.81-2.73 (m, 1 H), 2.63-2.55 (m, 1 H), 2.54-2.47 (m, 1 H), 2.34-2.27 (m, 1 H), 2.15 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 206.5, 173.3, 138.9, 138.0, 128.6, 128.5, 128.3, 128.2, 127.9, 127.7, 98.4, 79.6, 79.0, 75.5, 73.7, 71.0, 69.7, 61.1, 55.5, 38.0, 29.8, 28.0; HRMS (ESI) calcd for C\(_{26}\)H\(_{33}\)O\(_8\) [M+H]\(^+\) 473.2169, found 473.2172.

Methyl 2,3-di-O-benzyl-4-O-(2-azidomethylbenzyl)-\(\alpha\)-D-glucopyranoside (20)

Except the reaction time (15 min) and the reagents amounts (reducing the reagents amounts by a half), the otherwise identical DMNPA deprotection procedure was adopted to convert 35 (16 mg, 0.022 mmol) to 20 (10 mg, 83%) as a colorless syrup: \([\alpha]_D^{25} = -7.8\) (c 1.1, CHCl₃); \(^1^H\) NMR (400 MHz, CDCl₃) \(\delta\) 7.88 (d, \(J = 7.6\) Hz, 1 H), 7.61 (td, \(J = 1.6, 7.6\) Hz, 1 H), 7.52 (d, \(J = 7.6\) Hz, 1 H), 7.39-7.30 (m, 6 H), 7.16-7.11 (m, 5 H), 5.19 (t, \(J = 9.6\) Hz, 1 H), 4.84 (d, \(J = 12.0\) Hz, 1 H), 4.81 (d, \(J = 14.8\) Hz, 1 H), 4.69-4.65 (m, 4 H), 4.16 (t, \(J = 9.2\) Hz, 1 H), 3.79-3.60 (m, 4 H), 3.42 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 166.5, 138.3, 138.2, 137.9, 133.4, 131.2, 129.8, 128.7, 128.7,
128.3 (2 C), 128.2, 127.9, 127.7 (2 C), 98.4, 79.8, 78.8, 75.5, 73.7, 71.0, 69.7, 61.3, 55.6, 53.2; HRMS (ESI) calcd for C_{29}H_{32}N_{3}O_{7} [M+H]^+ 534.2334, found 534.2339.

**Methyl 6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (36)**

To a solution of 5 (141 mg, 0.2 mmol) in a mixed solvent of THF and MeOH (18 mL, v/v = 1:2) was added K_{2}CO_{3} (85 mg, 0.6 mmol) at room temperature. The resultant suspension was stirred at the same temperature for 4 h, before resin (H\(^+\) form) was added to adjust the pH value of reaction to 7-8. Filtration to remove the resin, and the resin was thoroughly washed with MeOH. The filtrate was concentrated *in vacuo* to afford a residue, which was further purified by silica gel column chromatography (DCM/MeOH = 10:1) to deliver 36 (64 mg, 82%) as a white solid: \([\alpha]_{D}^{25} = +130.2\) (c 0.65, CH\(_{3}\)OH); \(^1\)H NMR (400 MHz, MeOH-d\(_4\)) \(\delta\) 7.88 (d, \(J = 8.0\) Hz, 1 H), 7.65 (d, \(J = 7.6\) Hz, 1 H), 7.60 (t, \(J = 7.6\) Hz, 1 H), 7.41 (dd, \(J = 7.2, 8.0\) Hz, 1 H), 4.73 (s, 3 H), 4.46 (d, \(J = 3.6\) Hz, 1 H), 4.32 (dd, \(J = 1.6, 11.6\) Hz, 1 H), 3.96 (dd, \(J = 6.8, 11.2\) Hz, 1 H), 3.52-3.47 (m, 1 H), 3.47 (t, \(J = 9.6\) Hz, 1 H), 3.22-3.19 (m, 2 H), 3.07 (s, 3 H), 3.04 (t, \(J = 9.2\) Hz, 1 H), 1.57 (s, 3 H), 1.56 (s, 3 H); \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 177.1, 150.0, 140.3, 134.6, 129.6, 129.1, 126.6, 101.0, 75.0, 73.4, 72.0, 70.9, 65.7, 55.3, 47.7, 27.7, 27.6; HRMS (ESI) calcd for C\(_{17}\)H\(_{23}\)NO\(_9\) [M+H]^+ 386.1445, found 386.1449.

**Methyl 4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-6-O-benzyl-α-D-glucopyranoside**
(37)—selective removal of acetyl groups in the presence of DMNPA

Except for the applied amounts of $K_2CO_3$ (2.0 eq.), similar procedure as that used for the synthesis 36 was adopted to convert 22 (26 mg, 0.046 mmol) to 37 (19 mg, 86%) as a white solid: $[\alpha]_D^{25} = +95.1$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (dd, $J = 1.2$, 8.0 Hz, 1 H), 7.66 (td, $J = 1.2$, 8.4 Hz, 1 H), 7.59 (dd, $J = 1.2$, 8.0 Hz, 1 H), 7.37-7.28 (m, 5 H), 4.97 (dd, $J = 9.2$, 10.0 Hz, 1 H), 4.85 (d, $J = 4.0$ Hz, 1 H), 4.66 (d, $J = 12.0$ Hz, 1 H), 4.54 (d, $J = 12.0$ Hz, 1 H), 3.88-3.84 (m, 2 H), 3.70 (dd, $J = 3.6$, 9.2 Hz, 1 H), 3.62 (dd, $J = 1.6$, 10.8 Hz, 1 H), 3.56 (dd, $J = 5.6$, 10.8 Hz, 1 H), 3.46 (s, 3 H), 1.62 (s, 3 H), 1.61 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.2, 148.5, 139.0, 138.1, 133.7, 128.4 (2 C), 128.1, 128.0, 127.7, 125.9, 99.0, 73.6, 73.0, 72.6, 72.4, 68.9 (2 C), 55.6, 47.1, 27.4, 27.3; HRMS (ESI) calcd for C$_{24}$H$_{29}$NO$_9$Na $[M+Na]^+$ 498.1734, found 498.1760.

Methyl 2,3-di-O-acetyl-4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (38)

To a solution of 22 (71 mg, 0.127 mmol) in EtOAc-H$_2$O (2.8 mL, v/v = 3 : 4) was added NaBrO$_3$ (57.6 mg, 0.381 mmol) and Na$_2$S$_2$O$_4$ (66 mg, 0.381 mmol) at 0 °C. After being stirred at room temperature for 4 h, the mixture was neutralized with
aqueous 10% Na$_2$S$_2$O$_3$ and diluted with EtOAc. The resulting mixture was washed with brine, and then dried over anhydrous Na$_2$SO$_4$. Filtration was followed by concentration in vacuo to give the crude product which was further purified by silica gel column chromatography (PE/EA = 1 : 1) to deliver 38 (50.6 mg, 85%) as a light yellow solid: $[\alpha]_D^{25} = 94.6$ (c 1.1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (dd, $J$ = 1.2, 8.0 Hz, 1 H), 7.67-7.57 (m, 2 H), 7.50-7.44 (m, 1 H), 5.59 (t, $J$ = 9.6 Hz, 1 H), 5.07 (t, $J$ = 9.6 Hz, 1 H), 4.98 (d, $J$ = 3.6 Hz, 1 H), 4.90 (dd, $J$ = 3.6, 10.0 Hz, 1 H), 3.75-3.72 (m, 3 H), 3.40 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.65 (s, 3 H), 1.62 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.6, 170.2 (2 C), 148.4, 138.4, 133.8, 128.3, 128.2, 126.0, 96.8, 71.4, 69.7, 69.6, 69.4, 61.0, 55.5, 46.9, 27.2, 27.0, 21.0, 20.8; HRMS (ESI) calcd for C$_{21}$H$_{28}$NO$_{11}$ [M+H]$^+$ 470.1656, found 470.1653.

4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-6-O-benzyl-\(\alpha\)-D-glucopyranoside (37)---selective removal of benzoyl groups in the presence of DMNPA

Except for the amounts of K$_2$CO$_3$ (2.0 eq.), similar procedure as that used for the synthesis of 36 from 5 was adopted to convert 23 to 37 (28 mg, 80%).

Methyl

2,3-di-O-benzyl-4-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-\(\alpha\)-D-glucopyranoside (39)
To a solution of 26 (40 mg, 0.05 mmol) in dry THF (1 mL) was added HOAc (11.4 µL, 0.2 mmol) and TBAF (26.1 mg, 0.1 mmol) successively at room temperature. The resulting mixture was stirred at the same temperature for another 12 h, and then ethyl acetate was added to dilute the reaction. The resulting solution was washed successively with saturated NaHCO₃, brine, and then dried over anhydrous Na₂SO₄. Filtration and evaporation under reduced pressure yielded the crude product which was further purified by silica gel column chromatography (PE/EA = 2 : 1) to deliver 39 (25 mg, 88%) as a white solid: [α]D²⁵ = 16.4 (c 1.15, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.0 Hz, 1 H), 7.61 (t, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.42 (t, J = 8.0 Hz, 1 H), 7.32-7.27 (m, 10 H), 4.91-4.55 (m, 6 H), 4.49 (d, J = 11.2 Hz, 1 H), 3.94 (td, J = 2.0, 9.6 Hz, 1 H), 3.84 (dd, J = 2.8, 13.6 Hz, 1 H), 3.70 (d, J = 13.6 Hz, 1 H), 3.61-3.57 (m, 2 H), 3.38 (s, 3 H), 1.59 (s, 3 H), 1.58 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 176.4, 148.6, 138.5 (2 C), 137.8, 133.5, 128.5, 128.3, 128.5, 128.2, 128.1 (2 C), 127.4, 127.2, 125.8, 98.0, 79.6, 78.6, 75.0, 73.3, 71.8, 69.8, 61.0, 55.5, 47.0, 27.4, 27.1; HRMS (ESI) calcd for C₃₁H₃₆NO₉ [M+H]⁺ 566.2384, found 566.2412.

2-O-(2,2-Dimethyl-2-(ortho-nitrophenyl)acetyl)-3,4,6-tri-O-acetyl-D-glucopyranose (40)

To a solution of 31 (200 mg, 37.2 mmol) in a mixed solvent of DCM and MeOH (20 mL, v/v = 1 : 1) was added PdCl₂ (26 mg, 14.8 mmol) at ambient temperature. The
black solution was stirred at the same temperature for another 3 h, before filtrating through a pad of Celite and silica gel to remove the black solid. After the black solid was thoroughly washed with ethyl acetate, the filtrate was condensed under reduced pressure. The obtained residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1.5 : 1) to afford 40 (174 mg, 94%) as a white foam in a α/β mixture (α/β = 5 : 1): [α]D25 = +53.1 (c 0.95, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.00 (dd, J = 1.2, 8.0 Hz, 1 H), 7.67-7.58 (m, 2.4 H), 7.48-7.43 (m, 1.2 H), 5.54 (t, J = 10.0 Hz, 1 H), 5.50 (d, J = 3.2 Hz, 1 H), 5.27 (t, J = 9.2 Hz, 0.2 H), 5.12-5.06 (m, 1.2 H), 4.96 (dd, J = 8.0, 10.0 Hz, 0.2 H), 4.89 (dd, J = 3.6, 10.0 Hz, 1 H), 4.70 (d, J = 8.4 Hz, 0.2 H), 4.27-4.22 (m, 2.2 H), 4.16-4.08 (m, 1.2 H), 3.74-3.70 (m, 0.2 H), 3.48 (brs, 1 H), 2.10 (s, 3 H), 2.09 (s, 0.6 H), 2.06 (s, 0.6 H), 2.02 (s, 3 H), 2.01 (s, 0.6 H), 2.01 (s, 3 H), 1.65 (d, J = 6.8 Hz, 7.2 H); 13C NMR (100 MHz, CDCl3) δ 176.0, 174.8, 171.0, 170.9, 170.5, 170.2, 169.8, 169.6, 148.2, 139.0, 138.6, 133.9, 133.8, 128.3, 128.2 (2 C), 126.0 (2 C), 95.9, 90.2, 74.0, 72.2, 71.9, 71.6, 69.6, 68.6, 68.4, 67.3, 62.1, 46.8, 46.6, 27.2 (2 C), 27.0, 20.9, 20.8 (3 C), 20.7; HRMS (ESI) calcd for C22H27NO12Na [M+Na]+ 520.1425, found 520.1425.

2-O-(2,2-Dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-allyl-4,6-O-benzylidene-D-glucopyranose (41)

![Chemical Structure](image)

To a suspension of 32 (200 mg, 0.33 mmol) and NaHCO3 (27.7 mg, 0.33 mmol) in a mixed solvent of CH3CN/H2O (7.8 mL, v/v =9 : 1) was added ceric ammonium nitrate (CAN) (905 mg, 1.65 mmol) at room temperature. Stirring was continued at the same
temperature until TLC indicated the disappearance of the raw material. Ethyl acetate was added to dilute the reaction mixture, and the resulting solution was washed successively with saturated aqueous Na$_2$S$_2$O$_3$, NaHCO$_3$, water, and brine, and then was dried over anhydrous Na$_2$SO$_4$. Filtration was followed by concentration gave a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4 : 1) to afford 41 (152 mg, 92%) as a light yellow foam in a mixture of $\alpha/\beta$ isomers: $[\alpha]_D^{25} = +12.8$ (c 0.65, CHCl$_3$); $^1$H NMR (400 MHz, acetone-D$_6$) $\delta$ 8.02 (dd, $J = 1.6$, 8.0 Hz, 1 H), 7.95 (dd, $J = 1.6$, 8.0 Hz, 0.15 H), 7.81-7.69 (m, 2.3 H), 7.57-7.47 (m, 3.45 H), 7.39-7.32 (m, 3.45 H), 5.97-5.95 (m, 1 H), 5.94-5.84 (m, 0.15 H), 5.80-5.71 (m, 1 H), 5.65 (s, 0.15 H), 5.64 (s, 1 H), 5.40 (t, $J = 4.0$ Hz, 1 H), 5.19-5.12 (m, 1.15 H), 5.05-4.99 (m, 1.15 H), 4.86 (t, $J = 8.4$ Hz, 0.15 H), 4.79 (dd, $J = 6.8$, 7.6 Hz, 0.15 H), 4.73 (dd, $J = 4.0$, 10.0 Hz, 1 H), 4.29-4.21 (m, 0.3 H), 4.17-3.97 (m, 4.45 H), 3.87 (t, $J = 9.6$ Hz, 1 H), 3.79 (t, $J = 10.0$ Hz, 0.15 H), 3.78 (t, $J = 10.4$ Hz, 1 H), 3.73 (d, $J = 7.6$ Hz, 0.15 H), 3.69 (t, $J = 9.6$ Hz, 1 H), 3.65 (t, $J = 8.8$ Hz, 0.15 H), 3.50-3.44 (m, 0.15 H), 1.70 (s, 3.45 H), 1.67 (s, 3.45 H); $^{13}$C NMR (100 MHz, acetone-D$_6$) $\delta$ 175.4, 174.6, 149.8, 149.4, 139.7, 139.2, 139.0, 138.9, 136.4 (2 C), 134.4, 133.9, 129.9, 129.4, 128.9 (2 C), 128.8, 127.0, 126.9, 126.4, 126.0, 116.2, 116.1, 101.9, 101.7, 96.7, 91.4, 82.8, 82.5, 79.1, 76.1, 75.7, 74.7, 74.6, 73.6, 73.5, 69.5, 69.2, 66.7, 63.0, 47.6, 47.1, 27.5, 27.4, 27.2, 27.1; HRMS (ESI) calcd for C$_{26}$H$_{30}$NO$_9$ [M+H]$^+$ 500.1915, found 500.1918.

**Methyl**

$2,3$-di-$O$-benzyl-$6$-$O$-(2,2-dimethyl-$2$-(ortho-nitrophenyl)acetyl)-$\alpha$-$D$-glucopyranos
A solution of 33 (40 mg, 0.063 mmol) and DBACO (105.3 mg, 0.945 mmol) in ethanol (12 mL) was stirred at 50 °C for 48 h. Concentration in vacuo and purification by silica gel column chromatography (PE/EA = 1 : 1) afforded 29 (32 mg, 91%) efficiently.

**Methyl**

2,3-di-O-benzyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside (29)---with compound 34 as the starting material

To a solution of 34 (40.6 mg, 0.061 mmol) in a mixed solvent of pyridine and HOAc (5 mL, v/v = 3 : 2) was added preformed NH₂NH₂-HOAc (42.1 µL, 0.61 mmol) at 0 °C. Then the reaction mixture was warmed up to room temperature, and the stirring was continued for another 5 h. Ethyl acetate was added to dilute the reaction, and the resulting solution was successively washed with 1N HCl, saturated aqueous NaHCO₃, and then dried over Na₂SO₄. Filtration was followed by concentration in vacuo to give a residue which was further purified by silica gel column chromatography (PE/EA = 4 : 1) to deliver 29 (30.7 mg, 89%).

**Methyl**

2,3-di-O-benzyl-6-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-α-D-glucopyranoside
side (29)---with compound 35 as the starting material

To a solution of 35 (20 mg, 0.028 mmol) in THF/H₂O (1 mL/0.1 mL) was added "Bu₃P (10% in hexane, 21 µL, 0.084 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h, before CH₂Cl₂ was added to dilute the reaction mixture. The resultant solution was washed with saturated aqueous NaHCO₃, water, and brine, and then was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3 : 1) to provide 29 (13.3 mg, 84%).

Allyl 3,4,6-tri-O-benzyl-2-O-(2-azidomethylbenzoyl)-β-D-galactopyranoside (S2)

To a vigorously stirred, cooled (ice bath) biphasic solution of S1[S14] (1.44 g, 3.46 mmol) in CH₂Cl₂ (46.8 mL), acetone (5.7 mL), and saturated aqueous NaHCO₃ (8.42 g in 46.8 mL H₂O), a solution of Oxone (12.9 g, 21.0 mmol) in H₂O was added dropwise over 15 min. The mixture was vigorously stirred at 0 °C for 30 min and then at room temperature for additional 2 h. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ for three times. The combined organic phase was washed successively with saturated aqueous Na₂SO₃, brine, and was then dried over anhydrous Na₂SO₄. Filtration was followed by concentration to give the epoxide intermediate, which was used without further purification to the next step.
The above obtained epoxide intermediate was dissolved in dry allyl alcohol (10 mL), and the solution was stirred at room temperature for 16 h. The volatile solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1.5 : 1) to provide the 2-OH free glycoside intermediate (1.44 g, 85%), which was directly used to the next step without detailed characterization.

The above obtained 2-OH free allyl galactoside intermediate (1.3 g, 2.65 mmol) was dissolved in dry CH$_2$Cl$_2$ (5 mL), to which DMAP (485 mg, 3.97 mmol) and DCC (2.18 g, 10.6 mmol) was added successively at room temperature under N$_2$ atmosphere. The reaction mixture was stirred at room temperature for 2 h, at which time TLC showed that all starting material disappeared. The reaction mixture was then moved to the refrigerator to let the urea byproduct precipitate from the solution. Quick filtration through a pad of Celite and thorough washing the white solid with cooled ethyl acetate removed the major urea byproduct. The filtrate was concentrated under reduced pressure and the resulting residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6 : 1) to afford **S19** (1.55 g, 90%) as a white solid: $[\alpha]_D^{25}$ = +18.9 (c 2.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J$ = 7.6 Hz, 1 H), 7.58-7.52 (m, 2 H), 7.39-7.15 (m, 16 H), 5.84-5.74 (m, 1 H), 5.66 (dd, $J$ = 8.0, 10.0 Hz, 1 H), 5.23 (dd, $J$ = 2.0, 17.2 Hz, 1 H), 5.10 (dd, $J$ = 1.6, 10.4 Hz, 1 H), 5.01 (d, $J$ = 11.6 Hz, 1 H), 4.79 (AB, 2 H), 4.69 (AB, 2 H), 4.56 (d, $J$ = 8.0 Hz, 1 H), 4.49 (d, $J$ = 12.0 Hz, 1 H), 4.49 (AB, 2 H), 4.36 (dd, $J$ = 5.2, 13.2 Hz, 1 H), 4.08-4.02 (m, 2 H), 3.70-3.60 (m, 4 H), $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5,
138.5, 138.0, 137.8, 137.4, 133.9, 132.6, 130.8, 129.3 (2 C), 128.6, 128.4 (2 C), 128.0 (2 C), 127.9, 127.8, 127.7 (2 C), 117.4, 100.3, 80.4, 74.6, 73.9, 73.7, 72.5, 72.2, 71.9, 69.6, 68.7, 52.9; HRMS (ESI) calcd for C$_{38}$H$_{39}$N$_3$O$_7$Na [M+Na]$^+$ 672.2680, found 672.2675.

2-O-(2-Azidomethylbenzoyl)-3,4,6-tri-O-benzyl-D-galactopyranosyl

**ortho-cyclopropylethynylbenzoate (42)**

To a solution of S2 (1.5 g, 2.33 mmol) in a mixed solvent of CH$_2$Cl$_2$ and MeOH (20 mL, v/v = 1 : 1) was added PdCl$_2$ (83 mg, 0.47 mmol) at room temperature. The resulting black mixture was stirred at the same temperature for 3 h before filtration through a pad of silica gel and Celite. The filtrate was concentrated under reduced pressure to give a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 4 : 1) to afford the hemiacetal intermediate (1.2 g, 85%).

The above obtained residue (1.2 g, 1.97 mmol) was dissolved in dry CH$_2$Cl$_2$ (3.0 mL), to which ABzOH (549 mg, 2.95 mmol), DIPEA (1.38 mL, 7.88 mmol), DMAP (457 mg, 3.74 mmol), and EDCI (906 mg, 4.73 mmol) were added successively at 0 °C under N$_2$ atmosphere. After the addition was completed, the reaction mixture was warmed up to room temperature gradually and the stirring was continued for another 3 h before ethyl acetate was added to dilute the reaction mixture. The resulting solution was washed with water, 1N HCl, aqueous NaHCO$_3$, and brine successively and then dried over anhydrous Na$_2$SO$_4$. Filtration was followed by concentration gave
a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10 : 1) to provide 42 (1.32 g, 73%) in a α/β mixture as a colorless foam. For 42α: [α]D25 = +43.2 (c 1.03, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.79 (dd, J = 4.4, 8.0 Hz, 2 H), 7.52-7.41 (m, 4 H), 7.38-7.22 (m, 17 H), 6.76 (d, J = 3.6 Hz, 1 H), 5.89 (dd, J = 4.0, 10.0 Hz, 1 H), 5.04 (d, J = 11.2 Hz, 1 H), 4.76-4.60 (m, 5 H), 4.49 (AB, 2 H), 4.36 (dd, J = 5.6, 8.4 Hz, 1 H), 4.29-4.24 (m, 2 H), 3.74 (t, J = 8.4 Hz, 1 H), 3.64 (dd, J = 5.2, 8.8 Hz, 1 H), 1.37-1.31 (m, 1 H), 0.79-0.72 (m, 4 H); 13C NMR (100 MHz, CDCl3) δ 165.7, 164.3, 138.5, 137.9 (2 C), 137.8, 134.9, 132.8, 132.2, 131.2, 130.9, 130.7, 129.1, 128.6, 128.5 (2 C), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8 (2 C), 127.6, 127.2, 125.1, 99.9, 91.5, 76.8, 75.1, 74.9, 73.8 (2 C), 72.5, 72.2, 70.2, 68.2, 53.0, 9.1 (2 C), 0.8; HRMS (ESI) calcd for C47H44N3O8 [M+H]+ 778.3122, found 778.3174. For 42β: [α]D25 = +39.3 (c 1.35, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.98 (d, J = 1.6, 8.0 Hz, 1 H), 7.80 (dd, J = 1.2, 7.6 Hz, 1 H), 7.54 (td, J = 1.6, 7.6 Hz, 1 H), 7.46 (dd, J = 1.2, 7.6 Hz, 1 H), 7.43-7.17 (m, 19 H), 5.98 (d, J = 8.4 Hz, 1 H), 5.91 (dd, J = 8.0, 10.0 Hz, 1 H), 5.03 (d, J = 11.2 Hz, 1 H), 4.72-4.60 (m, 4 H), 4.52 (d, J = 11.6 Hz, 1 H), 4.50 (AB, 2 H), 4.15 (d, J = 2.8 Hz, 1 H), 3.89 (dd, J = 5.6, 8.0 Hz, 1 H), 3.81 (dd, J = 2.8, 10.0 Hz, 1 H), 3.74 (dd, J = 8.0, 8.8 Hz, 1 H), 3.68 (dd, J = 5.2, 8.8 Hz, 1 H), 1.50-1.43 (m, 1 H), 0.87-0.79 (m, 4 H); 13C NMR (100 MHz, CDCl3) δ 165.3, 163.8, 138.4, 137.8, 137.6, 137.5, 134.4, 132.9, 132.5, 131.2, 131.0, 129.6, 129.3, 128.6, 128.5 (2 C), 128.4, 128.2, 128.0 (3 C), 127.8 (2 C), 127.1, 125.7, 100.4, 93.1, 80.1, 74.9, 74.6, 74.5, 73.7, 72.4, 72.0, 71.0, 67.9, 52.9, 9.0 (2 C), 0.8; HRMS (ESI) calcd for C47H44N3O8 [M+H]+ 778.3122, found 778.3168.
p-Methoxyphenyl 3,4-di-O-acetyl-α-D-xylopyranoside (S4)

Compound S3\[^{[S15]}\] (100 mg, 0.39 mmol) and \(\text{a}^6\text{Bu}_2\text{SnO} (107 mg, 0.43 \text{ mmol})\) were suspended in dry toluene (8 mL), and the mixture was heated to reflux for 5 h with azeotropic removal of water. The resulting solution was cooled to room temperature and AcCl (55 µL, 0.86 mmol) was added. After the mixture was stirred for 20 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2 : 1) to give S4 (101 mg, 76%) as a white solid: \([\alpha]_D^{25} = +151.1 \ (c \ 0.85, \text{CHCl}_3); \ ¹\text{H} \ NMR \ (400 \text{ MHz, CDCl}_3) \ \delta \ 6.99 \ (d, \ J = 9.2 \text{ Hz, 2 H}), \ 6.84 \ (d, \ J = 9.2 \text{ Hz, 2 H}), \ 5.56 \ (d, \ J = 3.2 \text{ Hz, 1 H}), \ 4.98-4.91 \ (m, \ 1 \text{ H}), \ 4.86 \ (dd, \ J = 3.6, \ 10.0 \text{ Hz, 1 H}), \ 4.31 \ (t, \ J = 9.6 \text{ Hz, 1 H}), \ 3.87 \ (dd, \ J = 6.0, \ 11.2 \text{ Hz, 1 H}), \ 3.77 \ (s, \ 3 \text{ H}), \ 3.72 \ (t, \ J = 10.8 \text{ Hz, 1 H}), \ 2.50 \ (brs, \ 1 \text{ H}), \ 2.15 \ (s, \ 3 \text{ H}), \ 2.12 \ (s, \ 3 \text{ H}); \ ¹³\text{C} \ NMR \ (100 \text{ MHz, CDCl}_3) \ \delta \ 171.0, \ 170.9, \ 155.4, \ 150.5, \ 118.1, \ 114.8, \ 95.6, \ 95.5, \ 73.4, \ 71.8, \ 69.4, \ 59.1, \ 55.8, \ 55.7, \ 21.0; \ \text{HRMS (ESI)} \ \text{calcd for C}_{17}\text{H}_{21}\text{O}_{10} [\text{M}+\text{HCOO}]^- \ 385.1129, \ \text{found} \ 385.1135.

\p-Methoxyphenyl

2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3,4-di-O-acetyl-α-D-xylopyranoside (S5)

The standard procedure for the DMNPA group installation was adopted to convert S4 (410 mg, 1.2 mmol) to S5 (603 mg, 95%) as a white foam: \([\alpha]_D^{25} = +106.9 \ (c \ 1.0,
$\text{CHCl}_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (dd, $J = 1.6, 8.4$ Hz, 1 H), 7.65-7.57 (m, 2 H), 7.46 (td, $J = 1.6, 8.4$ Hz, 1 H), 6.99 (d, $J = 8.8$ Hz, 2 H), 6.83 (d, $J = 9.2$ Hz, 2 H), 5.79 (t, $J = 9.6$ Hz, 1 H), 5.55 (d, $J = 3.6$ Hz, 1 H), 5.02-4.96 (m, 1 H), 4.91 (dd, $J = 9.2$, 10.0 Hz, 1 H), 3.86 (dd, $J = 6.0, 10.8$ Hz, 1 H), 3.76 (s, 3 H), 3.74 (t, $J = 10.8$ Hz, 1 H), 2.11 (s, 3 H), 2.10 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 170.6, 170.3, 155.4, 150.4, 148.2, 138.7, 133.6, 128.2, 128.1, 125.9, 117.9, 114.7, 95.2 (2 C), 70.9, 69.9, 69.1, 58.9, 55.7 (2 C), 46.9, 27.3, 27.2, 21.0 (2 C), 20.9 (2 C); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_{11}\text{Na}$ [M+Na]$^+$ 554.1632, found 554.1628

$p$-Methoxyphenyl

$2\text{-O-}(2,2\text{-dimethyl}\text{-2-(ortho-nitrophenyl)}\text{acytetyl})\text{-3-}\text{O-acytetyl-}\alpha\text{-D-xylopyranoside}$

(43)

To a solution of S5 (179.4 mg, 0.34 mmol) in a mixed solvent of CH$_2$Cl$_2$ and MeOH (8 mL, v/v = 1 : 1) was added AcCl (0.1 mL, 1.41 mmol) at room temperature. The resulting mixture was stirred at the same temperature for another 36 h before Et$_3$N was added to quench the reaction. The volatile solvent was removed under reduced pressure and the residue was passed through a silica gel column (petroleum ether/ethyl acetate = 2 : 1) to provide 43 (113 mg, 68%) as a white foam: $[\alpha]_D^{25} = +92.5$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (dd, $J = 1.6, 8.4$ Hz, 1 H), 7.65-7.56 (m, 2 H), 7.44 (td, $J = 1.6, 8.4$ Hz, 1 H), 6.89 (d, $J = 9.2$ Hz, 2 H), 6.80 (d, $J = 9.2$ Hz, 2 H), 5.57 (d, $J = 3.2$, 1 H), 5.39 (t, $J = 9.6$ Hz, 1 H), 4.97 (dd, $J = 3.2$, 10.0 Hz, 1 H), 3.89 (dd, $J = 4.0$, 10.8 Hz, 1 H), 3.81 (m, 1 H), 3.77 (s, 3 H), 3.72 (t, $J =$
10.8 Hz, 1 H), 2.55 (brs, 1 H), 2.12 (s, 3 H), 1.61 (s, 3 H), 1.59 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.9, 172.0, 155.3, 150.5, 148.3, 138.7, 133.7, 128.3, 128.1, 125.9, 117.9, 114.7, 95.4, 95.3, 73.6, 70.9, 69.3, 62.1, 55.8, 55.7, 46.5, 27.1, 26.8, 21.1, 21.0; HRMS (ESI) calcd for C$_{24}$H$_{27}$NO$_{10}$Na $\text{[M+Na]}^+$ 512.1527, found 512.1514.

$p$-Methoxyphenyl

2-O-(2-azidomethylbenzyl)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-acetyl-α-D-xylopyranoside (44)

To a solution of 42 (116 mg, 0.15 mmol) and 43 (49 mg, 0.1 mmol) in dry CH$_2$Cl$_2$ (3.0 mL) was added powered 5A MS at room temperature under N$_2$ atmosphere. The resulting suspension was stirred at room temperature for 10 min before Ph$_3$PAuNTf$_2$ (22 mg, 0.03 mmol) was added at the same temperature under N$_2$ atmosphere. The resulting mixture was then stirred at the same temperature for another 10 h. Filtration was followed by concentration in vacuo afforded the crude product, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3 : 1) to provide disaccharide 44 (92 mg, 85%) as a white foam: $[\alpha]_D^{25} = +143.8.8$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, $J = 1.2, 8.4$ Hz, 1 H), 7.82 (dd, $J = 1.2, 8.4$ Hz, 1 H), 7.62 (td, $J = 1.6, 8.0$ Hz, 1 H), 7.56-7.49 (m, 3 H), 7.40-7.26 (m, 12 H), 7.22-7.14 (m, 5 H), 6.78 (AB, 4 H), 5.51 (d, $J = 2.0, 9.2$ Hz, 1 H), 5.50 (d, $J = 3.6, 1$ H), 5.50 (dd, $J = 3.6, 12.4$ Hz, 1 H), 4.99 (d, $J = 11.6$ Hz, 1 H), 4.86 (dd, $J = 3.6,$
10.0 Hz, 1 H), 4.78 (AB, 2 H), 4.65 (d, J = 12.4 Hz, 1 H), 4.60 (d, J = 12.0 Hz, 1 H), 4.56 (d, J = 8.0 Hz, 1 H), 4.45 (s, 2 H), 4.44 (d, J = 12.4 Hz, 1 H), 4.01 (d, J = 2.8 Hz, 1 H), 3.95-3.89 (m, 1 H), 3.74 (s, 3 H), 3.65-3.57 (m, 6 H), 1.87 (s, 3 H), 1.56 (s, 3 H), 1.54 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.0, 169.8, 164.9, 155.2, 150.5, 148.4, 138.8, 138.6, 138.0, 137.9, 137.7, 133.6, 132.8, 130.8, 129.5, 128.7, 128.5, 128.4 (2 C), 128.3, 128.1 (2 C), 128.0 (2 C), 127.9, 127.7 (2 C), 125.9, 117.8, 114.6, 100.8, 95.2, 80.2, 75.0, 74.6, 74.0, 73.7, 72.6, 72.1, 71.8, 71.5, 69.9, 68.5, 60.1, 55.8, 53.0, 46.5, 27.1, 26.7, 20.9; HRMS (ESI) calcd for C$_{59}$H$_{60}$N$_4$O$_{16}$Na [M+Na]$^+$ 1103.3896, found 1103.3912.

$p$-Methoxyphenyl

3,4,6-tri-$O$-benzyl-$\beta$-$D$-galactopyranosyl-(1→4)-2-$O$-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-$O$-acetyl-$\alpha$-$D$-xylopyranoside (45)

Except for the phosphine reagent (Ph$_3$P instead of $^n$Bu$_3$P was used), reaction medium (MeOH instead of THF/H$_2$O), as well as the reaction temperature (40 °C instead of 0 °C to rt), similar procedure as that used for the synthesis of 29 from 35 was applied to convert 44 (212 mg, 0.196 mmol) to 45 (155 mg, 86%) as a white solid: $[\alpha]_D^{25} = +28.2$ (c 1.1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (dd, J = 1.2, 8.0 Hz, 1 H), 7.63 (td, J = 1.6, 8.4 Hz, 1 H), 7.57 (dd, J = 1.6, 8.8 Hz, 1 H), 7.42-7.38 (m, 1 H), 7.37-7.25 (m, 15 H), 5.56 (d, J = 3.6 Hz, 1 H), 5.55 (dd, J = 8.4, 9.6 Hz, 1 H), 4.92 (dd, J = 3.6, 10.0 Hz, 1 H), 4.90 (d, J = 11.6 Hz, 1 H), 4.72 (AB, 2 H), 4.57 (d, J =
11.6 Hz, 1 H), 4.49 (AB, 2 H), 4.26 (d, \( J \) = 7.6 Hz, 1 H), 4.00-3.94 (m, 1 H), 3.90 (d, \( J \) = 2.8 Hz, 1 H), 3.87 (dd, \( J \) = 7.6, 9.6 Hz, 1 H), 3.81-3.73 (m, 2 H), 3.76 (s, 3 H), 3.61-3.53 (m, 3 H), 3.38 (dd, \( J \) = 3.2, 10.0 Hz, 1 H), 1.97 (s, 3 H), 1.59 (s, 3 H), 1.57 (s, 3 H); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.9, 170.4, 155.2, 150.5, 148.3, 138.8 (2 C), 138.2, 137.9, 133.6, 128.6, 128.3 (2 C), 128.0, 127.9, 127.7, 127.6, 125.9, 117.9, 114.7, 102.0, 95.2, 82.0, 74.6, 73.9, 73.8, 73.7, 73.1, 72.6, 71.4, 71.0, 70.0, 68.6, 60.2, 55.8, 46.5, 27.1, 26.7, 21.0; HRMS (ESI) calcd for C\(_{51}\)H\(_{56}\)NO\(_{15}\) [M+H]\(^+\) 922.3644, found 922.3649.

2,3,4-Tri-O-benzoyl-\( \alpha \)-D-fucopyranosyl trichloroacetimidate (46)

To a solution of S6\(^{[S16]}\) (500 mg, 1.05 mmol) in dry CH\(_2\)Cl\(_2\) (2.0 mL) was added Cl\(_3\)CCN (526 \( \mu \)L, 5.25 mmol) and DBU (9 \( \mu \)L, 0.06 mmol) at room temperature under N\(_2\) atmosphere. The resulting mixture was stirred at the same temperature until TLC showed that all starting material disappeared. The solvent was removed under reduced pressure and the obtained residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8 : 1) to afford \( \alpha \)-46 (508 mg, 78%) exclusively as a white foam: \([\alpha]_D^{25} = +172.5 \) (c 1.0, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.61 (s, 1 H), 8.13 (dd, \( J \) = 1.2, 8.0 Hz, 2 H), 7.97 (dd, \( J \) = 1.6, 8.4 Hz, 2 H), 7.82 (dd, \( J \) = 1.6, 8.4 Hz, 2 H), 7.66-7.62 (m, 1 H), 7.53-7.48 (m, 3 H), 7.46 (tt, \( J \) = 1.2, 7.2 Hz, 1 H), 7.37 (t, \( J \) = 8.0 Hz, 4 H), 6.84 (d, \( J \) = 3.6 Hz, 1 H), 6.06 (dd, \( J \) = 3.6, 10.8 Hz, 1 H), 5.94 (dd, \( J \) = 3.6, 10.8 Hz, 1 H), 5.89 (dd, \( J \) = 1.2, 3.6 Hz, 1 H),
4.68-4.63 (m, 1 H), 1.34 (s, 3 H), 1.33 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 165.8 (2 C), 161.0, 133.7, 133.6, 133.4, 130.1, 130.0, 129.8, 129.3, 129.1, 128.9, 128.8, 128.5, 128.4, 94.3, 91.1, 71.5, 68.8, 68.2, 68.0, 16.3; HRMS (ESI) calcd for C$_{29}$H$_{23}$Cl$_3$NO$_8$ [M-H]$^-$ 618.0494, found 618.0484.

$p$-Methoxyphenyl 2,3,4-tri-O-benzoyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-acetyl-α-D-xylopyranoside (47)

To a solution of 45 (255 mg, 0.28 mmol) and donor 46 (257 mg, 0.42 mmol) in dry CH$_2$Cl$_2$ (10.0 mL) was added powdered 4A MS at room temperature under N$_2$ atmosphere. The suspension was stirred at room temperature for 10 min. Then the reaction mixture was chilled to 0 °C, to which TMSOTf (15 µL, 0.084 mmol) was added under N$_2$ atmosphere. After the addition was completed, the reaction mixture was gradually warmed up to room temperature and the stirring was continued for another 3 h. Filtration was followed by concentration in vacuo afforded the crude product, which was further purified by silica gel chromatography (petroleum ether/ethyl acetate = 3 : 1) to provide the trisaccharide 47 (378.8 mg, 98%) as a white foam: $[\alpha]_D^{25} = +142.5$ (c 1.20, CHCl$_3$), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, $J = 1.6$, 8.4 Hz, 2 H), 7.88 (td, $J = 1.6$, 8.4 Hz, 3 H), 7.79 (dd, $J = 1.2$, 8.4 Hz, 2 H), 7.67 (td, $J = 1.6$, 8.0 Hz, 1 H), 7.60 (dd, $J = 1.2$, 8.0 Hz, 1 H), 7.57 (tt, $J = 1.6$, 7.2 Hz, 1 H)},
7.45-7.13 (m, 24 H), 6.81 (d, J = 9.2 Hz, 2 H), 6.68 (d, J = 8.8 Hz, 2 H), 5.78 (dd, J = 8.0, 10.4 Hz, 1 H), 5.68 (d, J = 3.6 Hz, 1 H), 5.60 (t, J = 9.6 Hz, 1 H), 5.58 (d, J = 3.6 Hz, 1 H), 5.48 (dd, J = 3.2, 10.4 Hz, 1 H), 5.15 (d, J = 8.0 Hz, 1 H), 4.96 (d, J = 3.6, 10.0 Hz, 1 H), 4.50 (d, J = 12.0 Hz, 1 H), 4.44 (d, J = 12.4 Hz, 1 H), 4.40 (d, J = 7.2 Hz, 1 H), 4.38 (d, J = 10.4 Hz, 1 H), 4.34 (d, J = 11.2, 1 H), 4.34 (d, J = 13.2 Hz, 1 H), 4.22 (d, J = 12.0 Hz, 1 H), 4.17-4.03 (m, 3 H), 3.99 (dd, J = 7.6, 10.0 Hz, 1 H), 3.86-3.80 (m, 1 H), 3.71 (s, 3 H), 3.56 (d, J = 2.4 Hz, 1 H), 3.48 (dd, J = 2.4, 6.4 Hz, 1 H), 3.39 (d, J = 6.4, 7.2 Hz, 1 H), 3.36 (dd, J = 3.2, 10.0 Hz, 1 H), 2.02 (s, 3 H), 1.62 (s, 3 H), 1.60 (s, 3 H), 1.22 (d, J = 6.0 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 175.0, 170.2, 166.1, 165.8, 165.6, 155.2, 150.6, 148.4, 138.4, 138.2, 137.9, 133.6, 133.4, 133.2, 132.9, 130.1, 129.9 (2 C), 129.8, 129.4, 129.2, 128.6 (2 C), 128.5 (2 C), 128.3 (2 C), 128.2, 128.0, 127.9, 127.8 (3 C), 127.7, 127.4, 125.9, 117.8, 114.6, 101.8, 95.4, 81.3, 79.2, 74.7, 73.9, 73.6, 73.5, 73.4, 72.9, 72.6, 71.4, 71.3, 71.0, 70.7, 69.9, 68.6, 59.9, 55.7, 46.5, 27.1, 26.7, 21.1, 16.3; HRMS (ESI) calcd for C70H78NO24 [M+HCOO]− 1424.4908, found 1424.4953.

2,3,4-Tri-O-benzoyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-acetyl-D-xylopyranosyl ortho-cyclopropylethynylbenzoate (48)

To a solution of 47 (295 mg, 0.2 mmol) in a mixed solvent of CH3CN/buffer (pH = 7.0) was added CAN (1.1 g, 2.0 mmol) at 30 °C. The resulting mixture was stirred at
the same temperature for 10 min before aqueous saturated NaHCO₃ was added to quench the reaction. The mixture was extracted with ethyl acetate for three times, the organic layers were combined, washed with aqueous NaHCO₃ and brine successively, and then dried over anhydrous Na₂SO₄. Filtration was followed by concentration in vacuo afforded a residue, which was further purified by flash chromatography (petroleum ether/ethyl acetate = 1 : 1) to provide the hemiacetal intermediate (212 mg, 83%) used directly to next step without detailed characterization.

The above obtained hemiacetal intermediate (200 mg, 0.16 mmol) was then dissolved in dry CH₂Cl₂ (1.0 mL), to which ABzOH (58 mg, 0.3 mmol), DIPEA (110 µL, 0.63 mmol), DMAP (38 mg, 0.3 mmol), and EDCI (72 mg, 0.38 mmol) were added successively at room temperature under N₂ atmosphere. The resulting mixture was stirred at the same temperature for another 3 h, before ethyl acetate was added to dilute the reaction mixture. The resulting solution was washed successively with water, 1N HCl, aqueous saturated NaHCO₃, and brine and was then dried over anhydrous Na₂SO₄. Filtration and concentration in vacuo provided a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8 : 1) to provide 48 (207 mg, 66%, 2 steps) as a mixture of α/β isomers as a colorless foam. An aliquot of pure β-isomer was obtained for detailed characterization: 

$$\alpha = +12.5 \text{ (c 0.75, CHCl}_3)$$; $^1$H NMR (400 MHz, CDCl₃) δ 8.06-8.01 (m, 3 H), 7.89 (ddd, $J = 1.2$, 8.0, 9.6 Hz, 3 H), 7.79 (dd, $J = 1.2$, 8.4 Hz, 2 H), 7.59 (td, $J = 1.6$, 8.4 Hz, 1 H), 7.53 (dd, $J = 1.6$, 8.0 Hz, 1 H), 7.48-7.10 (m, 28 H), 5.91-5.90 (m, 1 H), 5.77 (dd, $J = 7.6$, 10.4 Hz, 1 H), 5.71 (d, $J = 4.0$ Hz, 1 H), 5.52 (dd, $J = 3.6$, 10.8 Hz,
1 H), 5.30-5.26 (m, 2 H), 5.23 (d, J = 8.0 Hz, 1 H), 4.59 (d, J = 11.6 Hz, 1 H), 4.54 (dd, J = 5.2, 12.0 Hz, 1 H), 4.42-4.32 (m, 5 H), 4.29 (d, J = 11.6 Hz, 1 H), 4.16-4.11 (m, 1 H), 4.07-4.01 (m, 2 H), 3.68-3.62 (m, 2 H), 3.53-3.46 (m, 2 H), 3.43-3.40 (m, 1 H), 3.37 (dd, J = 2.8, 9.6 Hz, 1 H), 2.06 (s, 3 H), 1.55 (m, 1 H), 1.51 (s, 3 H), 1.48 (s, 3 H), 1.37 (d, J = 6.4 Hz, 3 H), 0.90-0.85 (m, 4 H); 13C NMR (100 MHz, CDCl3) δ 174.2, 170.1, 166.2, 165.8, 165.5, 163.4, 148.3, 138.8, 138.6, 138.0, 137.8, 134.5, 133.5, 133.2, 133.0, 132.6, 131.3, 130.0, 129.9, 129.8 (2 C), 129.6, 129.3, 129.2, 128.8, 128.6, 128.3 (2 C), 128.2, 128.1, 127.9 (2 C), 127.8, 127.7, 127.6, 127.5, 127.2, 126.0, 103.3, 101.4, 100.6, 93.0, 82.0, 78.0, 75.8, 74.6, 74.2, 73.6, 73.5, 73.1, 72.7, 72.5, 71.2, 71.0, 70.5, 69.9, 68.5, 64.5, 46.6, 26.9, 21.2, 16.6, 9.1, 0.9; HRMS (ESI) calcd for C84H80NO24 [M+HCOO]- 1486.5046, found 1486.5115.

p-Methoxyphenyl

2,3,4-tri-O-benzoyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-O-(2,2-dimethyl-2-(ortho-nitrophenyl)acetyl)-3-O-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-O-benzyl-6-deoxy-α-D-glucopyranoside (50)

Similar procedure as that used for the synthesis of 44 was applied to conduct the condensation between 48 (176 mg, 0.12 mmol) and acceptor 49 [S17] (66 mg, 0.15 mmol) to provide tetrasaccharide 50 (197.8 mg, 95%) as a white foam: [α]D25 = +29.3 (c 0.5, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.07-8.03 (m, 3 H), 7.87 (dd, J = 1.2, 8.0 Hz, 2 H), 7.81 (dd, J = 1.2, 8.4 Hz, 2 H), 7.59 (dd, J = 1.6, 8.4 Hz, 1 H), 7.55 (dd,
$J = 1.6, 7.2$ Hz, $1$ H), $7.51 - 7.11$ (m, $33$ H), $7.07$ (dd, $J = 2.8, 7.6$ Hz, $2$ H), $6.88$ (d, $J = 9.2$ Hz, $2$ H), $6.79$ (d, $J = 9.2$ Hz, $2$ H), $5.79$ (dd, $J = 8.0, 10.4$ Hz, $1$ H), $5.58$ (d, $J = 3.2$ Hz, $1$ H), $5.42$ (dd, $J = 3.2, 10.4$ Hz, $1$ H), $5.36$ (d, $J = 3.2$ Hz, $1$ H), $5.32$ (d, $J = 7.6$ Hz, $1$ H), $5.23$ (t, $J = 8.8$ Hz, $1$ H), $5.10 - 5.04$ (m, $3$ H), $4.67$ (d, $J = 11.2$ Hz, $1$ H), $4.55 - 4.43$ (m, $5$ H), $4.38 - 4.31$ (m, $4$ H), $4.30$ (dd, $J = 5.2, 11.6$ Hz, $1$ H), $4.17$ (dd, $J = 12.0$ Hz, $1$ H), $3.99 - 3.92$ (m, $2$ H), $3.90 - 3.83$ (m, $1$ H), $3.77 - 3.70$ (m, $2$ H), $3.75$ (s, $3$ H), $3.54$ (d, $J = 2.4$ Hz, $1$ H), $3.48$ (d, $J = 6.4$ Hz, $2$ H), $3.38 - 3.27$ (m, $3$ H), $3.24$ (t, $J = 9.2$ Hz, $1$ H), $2.07$ (s, $3$ H), $1.75$ (s, $3$ H), $1.71$ (s, $3$ H), $1.20$ (d, $J = 6.0$ Hz, $3$ H), $1.14$ (d, $J = 6.4$ Hz, $3$ H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 170.6, 166.2, 165.8, 165.6, 155.1, 151.0, 148.7, 139.2, 139.0, 138.8, 138.3, 137.9, 137.8, 133.6, 133.2, 132.8, 130.0, 129.9, 129.8, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2 (2 C), 128.1, 127.9, 127.8, 127.7, 127.6 (2 C), 127.4, 126.1, 118.1, 114.7, 102.1, 101.8, 100.2, 95.3, 81.7, 81.3, 81.2, 79.2, 76.0, 75.4, 75.2, 74.0, 73.7, 73.5, 73.4, 73.1, 72.9, 72.6, 72.4 (2 C), 71.2, 71.1, 70.0, 68.5, 67.4, 63.7, 55.8, 47.1, 27.6, 27.2, 21.4, 18.1, 16.5; HRMS (ESI) calcd for C$_{99}$H$_{100}$NO$_{28}$ [M+HCOO]$^-$ 1751.6460, found 1751.6476.

$p$-Methoxyphenyl

2,3,4-tri-O-benzoyl-β-D-fucopyranosyl-(1$\rightarrow$2)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1$\rightarrow$4)-3-O-acetyl-β-D-xylopyranosyl-(1$\rightarrow$3)-2,4-di-O-benzyl-6-deoxy-α-D-gluco.pyranoside (51)
The standard deprotection procedure of the DMNP A group was applied to convert 50 (110 mg, 0.064 mmol) to 51 (95.8 mg, 98%) as a white solid: $[\alpha]_D^{25} = +34.4$ (c 0.85, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, J = 1.2, 8.0 Hz, 2 H), 7.87 (dd, J = 1.2, 8.0 Hz, 2 H), 7.80 (dd, J = 1.2, 8.0 Hz, 2 H), 7.56-7.47 (m, 3 H), 7.42-7.14 (m, 29 H), 7.10-7.07 (m, 2 H), 6.92 (d, J = 9.2 Hz, 2 H), 6.81 (d, J = 8.8 Hz, 2 H), 5.80 (dd, J = 8.0, 10.4 Hz, 1 H), 5.68 (d, J = 3.6 Hz, 1 H), 5.50 (dd, J = 3.6, 10.4 Hz, 1 H), 5.24 (d, J = 3.6 Hz, 1 H), 5.18 (d, J = 8.0 Hz, 1 H), 5.14 (t, J = 8.8 Hz, 1 H), 5.01 (d, J = 10.8 Hz, 1 H), 4.88 (d, J = 6.8 Hz, 1 H), 4.73 (AB, 2 H), 4.51-4.19 (m, 9 H), 4.22 (d, J = 12.0 Hz, 1 H), 4.07-3.83 (m, 4 H), 3.77 (s, 3 H), 3.68 (dd, J = 3.2, 9.6 Hz, 1 H), 3.59 (d, J = 2.4 Hz, 1 H), 3.56 (dd, J = 6.8, 8.8 Hz, 1 H), 3.48-3.44 (m, 2 H), 3.40-3.34 (m, 3 H), 3.17 (t, J = 9.2 Hz, 1 H), 2.06 (s, 3 H), 1.24 (d, J = 6.4 Hz, 3 H), 1.20 (d, J = 6.0 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.7, 166.1, 165.7, 165.6, 155.1, 150.8, 138.8, 138.4, 138.2, 137.9, 137.0, 133.4, 133.2, 132.9, 130.1, 129.9, 129.8, 129.4, 129.2, 128.8, 128.6, 128.5 (2 C), 128.3 (2 C), 128.2, 127.9 (2 C), 127.8 (2 C), 127.7, 127.5, 118.0, 114.7, 105.1, 102.1, 101.6, 95.3, 83.1, 81.4, 80.2, 79.5, 78.7, 75.1, 75.0, 74.8, 74.0, 73.5 (3 C), 73.1, 72.9, 72.8, 72.6, 71.2, 71.1, 70.0, 68.6, 67.5, 63.7, 55.8, 21.3, 18.0, 16.6; HRMS (ESI) calcd for C$_{88}$H$_{90}$O$_{23}$Na [M+Na]$^+$ 1537.5765, found 1537.5773.

p-Methoxyphenyl

2,3,4-tri-\(O\)-benzoyl-\(\beta\)-D-fucopyranosyl-(1\(\rightarrow\)2)-3,4,6-tri-\(O\)-benzyl-\(\beta\)-D-galactopyranosyl-(1\(\rightarrow\)4)-2-\(O\)-(2,3,4-tri-\(O\)-benzoyl-6-deoxy-\(\beta\)-D-glucopyranosyl)-3-\(O\)-acetyl-\(\beta\)-D-xylopyranosyl-(1\(\rightarrow\)3)-2,4-di-\(O\)-benzyl-6-deoxy-\(\alpha\)-D-glucopyranoside (53)
Similar procedure as that used for the synthesis of 47 was applied to conduct the coupling between 51 (100 mg, 0.066 mmol) and donor 52\(^{[S17]}\) (62 mg, 0.099 mmol) to provide pentasaccharide 53 (104 mg, 80%) as a colorless foam: \([\alpha]_D^{25} = +47.5 \text{ (c 0.9, CHCl}_3\text{)}\), \(^1\text{H NMR (400 MHz, CDCl}_3\text{)}\) \(\delta\) 8.09 (dd, \(J = 1.2, 8.0 \text{ Hz, 2 H})\), 7.98 (dd, \(J = 1.2, 8.0 \text{ Hz, 2 H})\), 7.89 (ddd, \(J = 1.2, 6.4, 8.0 \text{ Hz, 4 H})\), 7.83 (ddd, \(J = 1.2, 6.4, 8.0 \text{ Hz, 4 H})\), 7.68 (d, \(J = 9.2 \text{ Hz, 2 H})\), 6.84 (d, \(J = 9.2 \text{ Hz, 2 H})\), 5.88 (t, \(J = 9.6 \text{ Hz, 1 H})\), 5.77 (dd, \(J = 8.0, 10.4 \text{ Hz, 1 H})\), 5.74 (dd, \(J = 8.0, 10.4 \text{ Hz, 1 H})\), 5.59 (dd, \(J = 8.0, 8.8 \text{ Hz, 1 H})\), 5.54 (d, \(J = 3.6 \text{ Hz, 1 H})\), 5.44 (t, \(J = 9.6 \text{ Hz, 1 H})\), 5.39 (dd, \(J = 3.2, 10.8 \text{ Hz, 1 H})\), 5.30 (d, \(J = 3.6 \text{ Hz, 1 H})\), 5.26 (d, \(J = 7.6 \text{ Hz, 1 H})\), 5.14 (t, \(J = 9.6 \text{ Hz, 1 H})\), 5.08 (d, \(J = 7.6 \text{ Hz, 1 H})\), 5.08 (d, \(J = 11.2 \text{ Hz, 1 H})\), 5.03 (d, \(J = 8.0 \text{ Hz, 1 H})\), 4.93 (d, \(J = 10.8 \text{ Hz, 1 H})\), 4.68 (t, \(J = 11.2 \text{ Hz, 2 H})\), 4.50-4.47 (m, 2 H), 4.38-4.26 (m, 5 H), 4.19 (dd, \(J = 5.2, 11.6 \text{ Hz, 1 H})\), 4.10 (d, \(J = 12.0 \text{ Hz, 1 H})\), 3.94-3.79 (m, 7 H), 3.76 (s, 3 H), 3.45 (d, \(J = 2.4 \text{ Hz, 1 H})\), 3.42-3.34 (m, 2 H), 3.32-3.27 (m, 3 H), 3.18 (t, \(J = 9.2 \text{ Hz, 1 H})\), 1.94 (s, 3 H), 1.43 (d, \(J = 6.0 \text{ Hz, 3 H})\), 1.20 (d, \(J = 6.4 \text{ Hz, 3 H})\), 1.10 (d, \(J = 6.4 \text{ Hz, 3 H})\); \(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\) \(\delta\) 169.6, 166.2, 165.6, 165.2, 155.0, 151.1, 138.9, 138.7, 138.3, 138.2, 138.0, 133.5 (2 C), 133.4, 133.3, 133.1, 132.7, 130.1 (2 C), 130.0, 129.9, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4 (2 C), 128.3, 128.2 (2 C), 128.0, 127.9, 127.8, 127.7 (2 C), 127.6, 127.4, 118.3, 114.6, 101.8, 101.3, 101.2, 96.0, 81.9, 81.4, 80.8, 79.6, 78.2, 77.6, 75.1, 75.0, 74.3, 74.2, 73.7 (2 C), 73.4 (2 C), 73.3 (2 C),
72.8, 72.6, 71.2, 70.8, 69.8, 68.6, 67.0, 63.3, 55.7, 21.3, 18.2, 18.0, 16.6; HRMS (ESI) calcd for C_{115}H_{112}O_{30}Na [M+Na]^+ 1996.7164, found 1996.7165.

**p-Methoxyphenyl**

\[ \beta-D-fucopyranosyl-(1\rightarrow2)-\beta-D-galactopyranosyl-(1\rightarrow4)-2-O-(6-deoxy-\beta-D-glucopyranosyl)-\beta-D-xylopyranosyl-(1\rightarrow3)-6-deoxy-\alpha-D-glucopyranoside (54) \]

To a solution of 53 (45 mg, 0.022 mmol) in a mixed solvent of ethyl acetate and methanol (40 ml, v/v = 1 : 1) was added 10% Pd(OH)$_2$/C (25 mg) at room temperature. The reaction flask was evacuated under reduced pressure for 5 min, and was then refilled with H$_2$. After this process was repeated for 3 times, the reaction mixture was stirred at 30 °C for another 12 h under H$_2$ atmosphere. Filtration through a pad of Celite and silica gel and concentration under reduced pressure provided the debenzylated intermediate, which was used to the next step without further purification.

The above obtained debenzylated intermediate was dissolved in dry methanol (5 mL), to which the freshly prepared NaOMe (in methanol) was added until the pH value of the reaction was adjusted to 11. The resulting mixture was stirred at room temperature for 1 h, before resin (H$^+$) was added to neutralize the reaction mixture. Filtration and washing the resin thoroughly with methanol was followed by concentration under reduced pressure yielded a residue, which was further purified by LH-20 chromatography (H$_2$O/methanol = 1 : 1) to provide 54 (18.7 mg, 98% for 2 steps) as a
white solid: [α]D$^{25} = +19.1$ (c 0.5, MeOH); $^1$H NMR (400 MHz, D$_2$O) δ 5.50 (d, J = 3.2 Hz, 1 H), 4.72 (d, J = 7.6 Hz, 1 H), 4.71 (d, J = 8.0 Hz, 1 H), 4.60 (d, J = 6.4 Hz, 1 H), 4.58 (d, J = 6.4 Hz, 1 H), 4.16 (dd, J = 4.8, 11.2 Hz, 1 H), 3.95-3.26 (m, 24 H), 3.15 (t, J = 9.6 Hz, 1 H), 1.30 (d, J = 6.0 Hz, 3 H), 1.25 (d, J = 6.4 Hz, 3 H), 1.21 (d, J = 6.4 Hz, 3 H); $^{13}$C NMR (100 MHz, D$_2$O) δ 154.8, 149.9, 119.0, 115.2, 103.9, 103.7, 102.6, 100.6, 97.3, 83.8, 81.8, 80.0, 76.8, 75.2, 75.1, 74.7, 74.2, 74.0, 73.4, 72.6 (2 C), 72.3, 71.9, 71.3, 71.2, 70.5, 68.6, 68.5, 63.0, 61.0, 55.8, 16.6 (2 C), 15.7; HRMS (ESI) calcd for C$_{36}$H$_{56}$O$_{23}$Na [M+Na]$^+$ 879.3104, found 879.3109.

Table S1. Comparison of the $^{13}$C NMR data of the synthetic 54 with those reported in literature

<table>
<thead>
<tr>
<th>$^{13}$C NMR signal*</th>
<th>Synthetic 54</th>
<th>Reported data$^{[S17]}$</th>
<th>Δδ (ppm)</th>
</tr>
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<tr>
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<td>154.8</td>
<td>154.9</td>
<td>-0.1</td>
</tr>
<tr>
<td>2</td>
<td>149.9</td>
<td>150.0</td>
<td>-0.1</td>
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<tr>
<td>3</td>
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<td>119.1</td>
<td>-0.1</td>
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<tr>
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<td>115.2</td>
<td>0</td>
</tr>
<tr>
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<td>103.9</td>
<td>104.0</td>
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<tr>
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<td>103.8</td>
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<tr>
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<td>102.8</td>
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<td>-0.1</td>
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<td>11</td>
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<td>0</td>
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<tr>
<td>12</td>
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<td>80.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>13</td>
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<td>76.9</td>
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</tr>
<tr>
<td>14</td>
<td>75.2</td>
<td>75.3</td>
<td>-0.1</td>
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<tr>
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<td>-0.1</td>
</tr>
<tr>
<td>16</td>
<td>74.7</td>
<td>74.8</td>
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<tr>
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<tr>
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<tr>
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<tr>
<td>20</td>
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<tr>
<td>21</td>
<td>72.3</td>
<td>72.5</td>
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<tr>
<td>22</td>
<td>71.9</td>
<td>72.0</td>
<td>-0.1</td>
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</table>
The $^{13}$C signals are numbered from the biggest to the smallest.

**References:**

[S1] CCDC 1819242 (3) contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


6063-6067.


The provided image contains a spectrum analysis chart, which includes a graph and molecular structure. The spectrum is labeled with various chemical shifts in parts per million (ppm) and numerical values. The compound depicted is labeled as 1 (400 MHz, CDCl₃). The presence of a nitro group (NO₂) and a carboxylic acid (COOH) is noted in the molecular structure. The chart provides detailed chemical analysis data, which is typically used in organic chemistry to identify and characterize compounds.
1 (100 MHz, CDCl₃)
3 (400 MHz, CDCl₃)
$\text{3 (100 MHz, CDCl}_3\}$
$\text{ODMNPA}$

$\text{BzO}$

$\text{Me}$

$\text{5 (400 MHz, CDCl}_3\text{)}$
S58
$f_{1}$ (ppm)

$OH$

$CAO$

$BnO$

$BnO$

$OMe$

$^{18}_{}$ (400 MHz, CDCl$_3$)
$^1$H (ppm)

$-5.0E+08 -4.5E+08 -4.0E+08 -3.5E+08 -3.0E+08 -2.5E+08 -2.0E+08 -1.5E+08 -1.0E+08 -0.5E+08 0.0E+00 0.5E+08 1.0E+08 1.5E+08 2.0E+08 2.5E+08 3.0E+08 3.5E+08 4.0E+08 4.5E+08 5.0E+08

29.82 40.54 55.63 61.35 69.34 72.12 73.72 75.55 76.84 77.16 77.48 78.85 79.70

$^{18}$ (100 MHz, CDCl$_3$)

OH

CAO

BnO

BnO

OMe

S60
$^{19}$ (100 MHz, CDCl$_3$)
AZMBO
BnO
BnO
OMe

20 (100 MHz, CDCl₃)
21 (400 MHz, CDCl₃)
21 (100 MHz, CDCl₃)
22 (400 MHz, CDCl₃)
22 (100 MHz, CDCl₃)
\[ \text{DMNPAO} \]
\[ \text{OBn} \]
\[ \text{BzO} \]
\[ \text{BzO} \]
\[ \text{OMe} \]

23 (400 MHz, CDCl\textsubscript{3})
LH181010-2.2.1.1r

23 (100 MHz, CDCl₃)
24 (400 MHz, CDCl$_3$)
$24 \ (100 \text{ MHz, } \text{CDCl}_3)$
25 (400 MHz, CDCl₃)
The figure shows a 1H NMR spectrum of compound 26, determined at 400 MHz in CDCl₃. The spectrum displays characteristic peaks at various ppm values. The structure of compound 26 is also shown, with labels for functional groups such as O TBDPS, DMNPAO, BnO, and OMe, indicating the presence of these moieties in the molecule.
OTBDPS

26 (100 MHz, CDCl₃)
28 (100 MHz, CDCl₃)
29 (400 MHz, CDCl₃)
29 (100 MHz, CDCl₃)
31 (400 MHz, CDCl₃)
31 (100 MHz, CDCl₃)
$32$ (400 MHz, CDCl$_3$)
Ph

Allo

OMP

OMPNPA

32 (100 MHz, CDCl₃)
ODMNPA

CAO

BnO

BnO

OMe

33 (400 MHz, CDCl₃)
$34$ (400 MHz, CDCl$_3$)
**Diagram Description**

The diagram shows a 1H NMR spectrum of compound 34, labeled as ODMNPA. The spectrum is recorded at 100 MHz in CDCl₃. The peaks are indicated with their corresponding chemical shifts.

- **Chemical Structure**
  - The compound is labeled as ODMNPA.
  - The structure includes a LevO, BnO, and OMe groups.

- **Chemical Shifts**
  - The peaks are labeled with their chemical shifts in ppm.
  - Key peaks include 86.05, 79.61, 79.27, 77.48, 77.16, 77.16, 76.84, 75.49, 73.58, 70.35, 67.66, 63.57, 55.24, 46.62, 38.05, 29.91, 28.12, 27.37, 27.29.

**NMR Spectrum**

The spectrum displays various peaks, each representing different chemical environments within the compound. The scale on the x-axis indicates the chemical shift in ppm, with values ranging from 0 to 206.32 ppm, and the y-axis shows the intensity of the peaks.

- The x-axis is labeled as f1 (ppm), indicating the chemical shift in parts per million.
- The y-axis shows the intensity of the peaks.

**Notes**

- The spectrum is a crucial tool in organic chemistry for identifying and characterizing compounds.
- Understanding the chemical shifts helps in determining the molecular structure and the environment of the protons in the molecule.
S93

$\text{ODMNPA}$

$\text{AZMBO}$

$\text{BnO}$

$\text{BnO}$

$\text{OMe}$

$35$ (400 MHz, CDCl$_3$)
35 (100 MHz, CDCl₃)
Figure 36 (400 MHz, CD$_3$OD)

The figure shows a 1D NMR spectrum with peaks labeled in ppm. The chemical structure of ODMNPA is depicted above the spectrum.
36 (100 MHz, CD$_3$OD)
37 (400 MHz, CDCl₃)
$\text{DMNPAO}$

$\text{OBn}$

$\text{OMe}$

$\text{37}^{(100 \text{ MHz}, \text{CDCl}_3)}$
38 (400 MHz, CDCl₃)
38 (100 MHz, CDCl₃)
39 (400 MHz, CDCl₃)
39 (100 MHz, CDCl₃)
40 (400 MHz, CDCl₃)
40 (100 MHz, CDCl₃)
41 (400 MHz, Acetone-d$_6$)
Ph
O
O
OH
Allo
ODMNPA

41 (100 MHz, Acetone-d₆)
$42\alpha$ (400 MHz, CDCl$_3$)
42α (100 MHz, CDCl₃)
$^\beta 42$ (400 MHz, CDCl$_3$)
**43** (400 MHz, CDCl₃)
43 (100 MHz, CDCl₃)
44 (400 MHz, CDCl₃)
46 (400 MHz, CDCl₃)
46 (100 MHz, CDCl₃)
51 (400 MHz, CDCl₃)
53 (400 MHz, CDCl$_3$)
$S_2$ (100 MHz, CDCl$_3$)
S4 (400 MHz, CDCl₃)
S4 (100 MHz, CDCl₃)
$S_5$ (400 MHz, CDCl$_3$)
$\text{S5}$ (100 MHz, CDCl$_6$)