Supporting Information

for

TMSBr-mediated solvent- and work-up-free synthesis

of α-2-deoxyglycosides from glycals

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Experimental section

General experimental. All reactions were conducted in flame-dried glassware under nitrogen atmosphere. Acetonitrile, dichloromethane, N,N-dimethylformamide (DMF), were purified and dried through activated alumina under argon atmosphere. All reagents obtained from commercial sources were utilized without purification unless otherwise specified. Flash column chromatography was carried out as recommended with silica gel 60 (230–400 mesh, E. Merk). Thin layer chromatography (TLC) was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of Ce(NH4)2(NO3)6, (NH4)6Mo7O24 and H2SO4 in water and subsequent heating on a hot plate. Optical rotations were measured on a JASCO P-2000 polarimeter. 1H and 13C NMR spectra were recorded with Bruker AV400 and AVIII400 MHz instruments. Chemical shifts are in ppm from trimethylsilane (TMS), generated from the CDCl3 lock signal at δ 7.24. Multiplicities are reported by the following abbreviations: s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, br = broad; J = coupling constant values in Hertz. Mass spectra were analyzed by a Waters Premier XE mass spectrometer with ESI mode.
General procedures for preparation of 3,4,6-tri-O-acetyl-D-glycals. To a solution of O-acetyl-β-D-glycopyranose (10.0 g, 1.0 equiv) in CH₂Cl₂ (100 mL) was added 33% HBr/AcOH (1.2 equiv) at 0 °C. The reaction solution was gradually warm up to room temperature and stirred for 2 hours under nitrogen atmosphere. Then the reaction mixture was quenched by NaHCO₃ and then transferred to a separation funnel. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (50 mL × 2). The organic layers were combined and washed with brine (100 mL × 2), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The volatiles were removed in vacuo for 1 h. Then the crude compound dissolved in a solution of H₂O (30 mL) and AcOH (60 mL) was slowly added activated Zn powder (1.0 equiv) at −15 °C. The reaction solution was stirred violently for 2 hours at 0 °C. The solution was filtered and then extracted with EtOAc (50 mL × 2) via a separation funnel. The combined organic layer was washed with NaHCO₃ (50 mL × 2) and brine (50 mL × 2), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel and then the volatiles were removed in vacuo to obtain the product as colorless oil.

1,2-Dideoxy-3,4,6-tri-O-acetyl-D-arabino-1-hexenopyranose (1).¹ colorless oil, [α]²θD -17.9 (c 1.05, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.44 (d, J = 6.4 Hz, 1 H, H-1), 5.32-5.30 (m, 1 H, H-3), 5.19 (t, J = 6.0 Hz, 1 H, H-4), 4.81 (dd, J = 6.0, 3.2 Hz, 1 H, H-2), 4.37 (dd, J = 11.6, 5.6 Hz, 1 H, H-6), 4.25-4.20 (m, 1 H, H-5), 4.17 (dd, J = 7.6, 2.8 Hz, 1 H, H-6), 2.08, 2.05, 2.02 (s, 9 H, 3 OAc) ppm; ¹³C NMR: δ 170.7-169.7 (C=O), 145.8 (C-1), 99.2 (C-2), 74.2 (C-5), 67.6 (C-3), 67.5 (C-4), 61.6 (C-2), 21.1-20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C₁₂H₁₆O₇Na [M + Na]⁺ requires 295.0794, found 295.0787.

1,2-Dideoxy-3,4,6-tri-O-benzyl-D-arabino-1-hexenopyranose (3). To a solution of tri-O-acetyl glucal 1 (10.0 g, 0.038 mol) in MeOH (100 mL) was slowly added sodium methoxide (0.594 g, 0.011 mol). After stirring for 4 hours at room temperature under ambient atmosphere, the reaction mixture was quenched via sequential addition of amberlite IR (120 H⁺) acid resin. The solution was filtered and then concentrated under reduced pressure. The residue was dried in vacuo overnight. Then the crude product was dissolved in dried DMF. Benzyl bromide (16.0 mL, 0.135 mol) and NaH (60%, 5.40 g, 0.135 mol) was slowly added at 0 °C. The reaction solution was gradually warmed up to room temperature and stirred for 6 hours under nitrogen atmosphere. H₂O (30 mL) was added to quench the reaction. The solution was transferred to a separation funnel. The organic layer was separated, and the
aqueous layer was extracted with EtOAc (50 mL × 2). The combined organic layers were washed with brine (100 mL × 2), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (EtOAc/Hexane= 0/1 to 1/2) and then the volatiles were removed in vacuo to obtain the product as a white solid. [α]^{28}_D -16.8 (c 1.10, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 7.32-7.23 (m, 15 H, -ArH), 6.42 (dd, J = 6.0, 1.2 Hz, 1 H, H-1), 4.87 (dd, J = 6.0, 1.2 Hz, 1 H, H-2), 4.83 (d, J = 11.2 Hz, 1 H, PhCH), 4.65-4.59 (m, 2 H, PhCH), 4.57-4.53 (m, 3 H, PhCH), 4.21-4.20 (m, 1 H, H-3), 4.08-4.04 (m, 1 H, H-5), 3.85 (dd, J = 8.8, 6.4 Hz, 1 H, H-4), 3.78 (dd, J = 9.6, 5.2 Hz, 1 H, H-6) ppm; \(^{13}\)C NMR: δ 144.9 (C-1), 138.6-138.2 (Ph), 128.5-127.8 (Ph), 100.1 (C-2), 77.0 (C-5), 75.9 (C-3), 74.6 (C-4), 73.9 (CH2), 73.7 (CH2), 70.6 (CH2), 68.7 (CH2) ppm; HRMS (ESI, m/z) calcd for C\(_{27}\)H\(_{28}\)O\(_4\)Na [M + Na]^+ requires 439.1882, found 439.1882.

1,2-Dideoxy-3,4,6-tri-O-acetyl-D-lyxo-1-hexopyranose (4). Colorless oil, [α]^{28}_D -2.55 (c 0.32, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 6.42 (d, J = 6.4 Hz, 1 H, H-1), 5.51 (br, 1 H, H-3), 5.39-5.38 (m, 1 H, H-4), 4.70-4.68 (m, 1 H, H-2), 4.30-4.27 (m, 1 H, H-5), 4.25-4.15 (m, 2 H, H-6), 2.08, 2.04, 1.98 (s, 9 H, 3-OAc) ppm; \(^{13}\)C NMR: δ 170.7 (C=O), 170.4 (C=O), 170.3 (C=O), 145.6 (C-1), 99.0 (C-2), 72.98, 64.1, 64.0, 62.1, 20.9-20.8 (3 OAc) ppm; HRMS (ESI, m/z) calcd for C\(_{27}\)H\(_{28}\)O\(_4\)Na [M + Na]^+ requires 295.0794, found 295.0786.

1,2,6-Trideoxy-3,4-di-O-benzyl-D-arabino-1-hexopyranose (5). Colorless oil, [α]^{28}_D -61.4 (c 0.65, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 6.41 (d, J = 6.0 Hz, 1 H, H-1), 5.33-5.30 (m, 1 H, H-3), 5.01 (dd, J = 8.0, 2.0 Hz, 1 H, H-4), 4.76 (dd, J = 6.0, 2.8 Hz, 1 H, H-2), 4.12-4.08 (m, 1 H, H-5), 2.06, 2.02 (s, 6 H, 2 OAc), 1.29 (d, J = 6.8 Hz, 3 H, Me) ppm; \(^{13}\)C NMR: δ 170.8 (C=O), 170.0 (C=O), 146.2 (C-1), 99.0 (C-2), 72.7 (C-5), 72.1 (C-3), 68.5 (C-4), 21.2 (OAc), 21.0 (OAc), 16.7 (Me) ppm; HRMS (APCI, m/z) calcd for C\(_{10}\)H\(_{14}\)O\(_5\)Na [M + Na]^+ requires 237.0739, found 237.0733.

1,2,6-Trideoxy-3,4-di-O-acetyl-D-lyxo-1-hexopyranose (6). Colorless oil, [α]^{28}_D -8.53 (c 0.85, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 6.45 (dd, J = 6.4, 1.6 Hz, 1 H, H-1), 5.56-5.55 (m, 1 H, H-3), 5.27-5.26 (m, 1 H, H-4), 4.62 (dd, J = 8.0, 2.0 Hz, 1 H, H-2), 4.20 (q, J = 6.4 Hz, 1 H, H-5), 2.14, 2.0 (s, 6 H, 2 OAc), 1.26 (d, J = 6.5 Hz, 3 H, Me) ppm; \(^{13}\)C NMR: δ 170.7 (C=O), 170.4 (C=O), 146.1 (C-1), 98.2 (C-2), 71.5 (C-3), 66.2 (C-4), 65.0 (C-5), 20.9 (OAc), 20.7 (OAc), 16.5 (Me) ppm; HRMS (APCI, m/z) calcd for C\(_{16}\)H\(_{18}\)O\(_5\)Na [M + Na]^+ requires 237.0739, found 237.0739.
General procedures for preparation of $p$-tolyl 2-deoxy-1-thio-D-glycopyranosides. Glycal (100.0 mg, 1.0 equiv) and $p$-toluenethiol (1.20 equiv) were mixed in a dried round bottomed flask. After the reagents became homogeneous, bromotrimethylsilane (TMSBr, 1.0 equiv) was slowly added. After stirring 3 to 4 hours at room temperature under ambient atmosphere, the reaction mixture was directly purified by flash column chromatography on silica gel and then volatiles were removed in vacuo to afford expected products. The products and yields are shown in Table 1.

$p$-Tolyl 3,4,6-tri-O-acetyl-2-deoxy-1-thio-D-glycopyranoside (2). Colorless oil, $[\alpha]^2_230\text{D} 127.57 (c 0.68, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J$ = 8.4 Hz, 2 H, Ph-β), 7.34 (d, $J$ = 8.0 Hz, 2 H, Ph-α), 7.10 (d, $J$ = 8.8Hz, 2 H, Ph), 5.58 (d, $J$ = 5.6 Hz, 1 H, H-1α), 5.31-5.26 (m, 1 H, H-3α), 4.98 (t, $J$ = 9.6 Hz, 1 H, H-4α), 4.92 (t, $J$ = 9.6 Hz, 1 H, H-4β), 4.71 (dd, $J$ = 11.6, 2.0 Hz, 1 H, H-1β), 4.54-4.50 (t, $J$ = 9.6 Hz, 1 H, H-5α), 4.27 (dd, $J$ = 12.4, 5.6 Hz, 1 H, H-6α), 4.22 (dd, $J$ = 12.0, 5.2 Hz, 1 H, H-6β), 4.12 (dd, $J$ = 12.0, 2.4 Hz, 1 H, H-6β), 3.62-2.58(m, 1 H, H-5β), 2.42 (dd, $J$ = 12.8, 4.8 Hz, 1 H, H-2eq.), 2.33 (s, 3 H, Me-β), 2.30 (s, 3 H, Me-α), 2.20 (ddd, $J$ = 18.0, 12.0, 6.0 Hz, α-H-2ax.), 2.06-1.99 (s, 9 H, 3 OAc), 1.80 (q, 1 H, β-H-2 ax.) ppm; $^{13}$C NMR: $\delta$ 170.8-170.0 (C=O), 138.5 (C), 138.0 (C), 130.3-129.0 (Ph), 83.7 (α, C-1), 82.4 (β, C-1), 76.1 (β, C-5), 72.0 (β, C-3), 69.9 (α, C-5), 69.5 (α, C-3), 69.1 (β, C-4), 68.9 (α, C-4), 62.9 (β, C-6), 62.6 (α, C-6), 36.5 (β, C-2), 35.6 (α, C-2), 21.3-20.9 (Me) ppm; HRMS (APCI, m/z) calcd for C$_{19}$H$_{22}$O$_3$NaS [M + Na]$^+$ requires 419.1140, found 419.1135.

$p$-Tolyl 3,4,6-tri-O-benzyl-2-deoxy-1-thio-D-glycopyranoside (7). Colorless oil, $[\alpha]^2_2$ 117.70 (c 0.85, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J$ = 8.0 Hz, 2 H, Ph-β), 7.40-7.20 (m, 13 H, Ph), 7.03 (d, $J$ = 7.6 Hz, 2 H, Ph-α), 5.60 (d, $J$ = 5.6 Hz, 1 H, H-1α), 4.90 (d, $J$ = 10.8 Hz, 1 H, PhCH-α), 4.88 (d, $J$ = 10.8 Hz, 1 H, PhCH-β), 4.68 (t, $J$ = 2.4 Hz, 1 H, Ph-β), 4.66-4.65 (m, 2 H, PhCH and H-1β), 4.62-4.51 (m, 3 H, Ph), 4.32-4.29 (m, 1 H, H-5α), 3.98-3.93 (m, 2 H, H-3α and H-5β), 3.81 (dd, $J$ = 10.8, 4.0 Hz, 1 H, H-6α), 3.72 (dd, $J$ = 10.8, 4.8 Hz, 1 H, H-6β), 3.69-3.59 (m, 3 H, H-6, H-4α, and H-3β), 3.49-3.45 (m, 1 H, H-4β), 2.45-2.42 (m, 1 H, H-2eq), 2.29 (s, 3 H, Me), 2.10 (ddd, 1 H, H-2ax), 1.88 (t, 1 H, β-H-2ax) ppm. $^{13}$C NMR: $\delta$ 138.4-137.2 (Ph), 137.6-137.2 (Ph), 129.9-129.6 (Ph), 128.4-127.4 (Ph), 84.3 (α, C-1), 82.3 (β, C-1), 80.7 (β, C-5), 79.3 (β, C-3), 77.9 (α, C-5), 77.3 (α, C-3), 77.2 (α, C-4), 74.9 (PhCH2), 73.3 (PhCH2), 71.8 (PhCH2), 71.6 (β, C-4), 69.5 (β, C-6), 68.9 (α, C-6), 36.9 (β, C-2), 36.1 (α, C-2), 21.1 (Me) ppm. HRMS (APCI, m/z) calcd for C$_{33}$H$_{36}$O$_4$NaS [M + Na]$^+$ requires 563.2232, found 563.2228.
**p-Toly 3,4,6-tri-O-acetyl-2-deoxy-1-thio-D-galacopyranoside** (8). Colorless oil, \([\alpha]^2_b\) -110.56 (c 0.74, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.38 (d, \(J=8.0\) Hz, 2 H, Ph-β), 7.32 (d, \(J=8.0\) Hz, 2 H, Ph-α), 7.12-7.08 (m, 4 H, Ph), 5.28-5.21 (m, 1 H, H-3α), 4.98-4.91 (m, 1 H, H-3β), 4.75 (t, \(J=9.2\) Hz, 1 H, H-4a), 4.72-4.67 (m, 2 H, H-4β and H-1β), 4.39-4.32 (m, 1 H, H-5α), 3.50-3.47 (m, 1 H, H-5β), 2.42 (m, 1 H, H-2eq.), 2.39 (s, 3 H, PhMe-β), 2.32 (s, 3 H, PhMe-α), 1.99-2.11 (m, 1 H, α-H-2ax.), 2.03-1.99 (s, 6 H, 2 OAc), 1.77 (q, \(J=12.4\) Hz, 1 H, β-H-2ax.), 1.23 (d, \(J=6.4\) Hz, 1 H, Me-β), 1.14 (d, \(J=6.4\) Hz, 1 H, Me-α) ppm. \(^{13}\)C NMR: \(\delta\) 170.3-170.0 (C=O), 138.1 (Ph), 137.5 (Ph), 133.0 (Ph), 131.9 (Ph), 130.57 (Ph), 129.7 (Ph), 129.6 (Ph), 128.8 (Ph), 83.3 (α, C-1), 81.7 (β, C-1), 74.8 (α, C-4), 74.2 (β, C-4), 73.8 (β, C-5), 71.7 (β, C-3), 69.3 (α, C-3), 66.6 (α, C-5), 36.5 (β, C-2), 35.7 (α, C-2), 21.1-20.7 (PhMe and OAc), 17.8-17.3 (Me) ppm. HRMS (APCI, m/z) calcd for C₁₃H₂₂O₅NaS [M + Na]⁺ requires 361.1086, found 361.1082.

**p-Toly 3,4-di-O-acetyl-2-deoxy-1-thio-D-rhamnopyranoside** (10). Colorless oil, \([\alpha]^2_b\) -110.56 (c 0.74, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.38 (d, \(J=8.0\) Hz, 2 H, Ph-β), 7.32 (d, \(J=8.0\) Hz, 2 H, Ph-α), 7.12-7.08 (m, 4 H, Ph), 5.50 (d, \(J=5.6\) Hz, 1 H, H-1α), 5.28-5.21 (m, 1 H, H-3α), 4.98-4.91 (m, 1 H, H-3β), 4.75 (t, \(J=9.2\) Hz, 1 H, H-4a), 4.72-4.67 (m, 2 H, H-4β and H-1β), 4.39-4.32 (m, 1 H, H-5α), 3.50-3.47 (m, 1 H, H-5β), 2.42 (m, 1 H, H-2eq.), 2.39 (s, 3 H, PhMe-β), 2.32 (s, 3 H, PhMe-α), 1.99-2.11 (m, 1 H, α-H-2ax.), 2.03-1.99 (s, 6 H, 2 OAc), 1.77 (q, \(J=12.4\) Hz, 1 H, β-H-2ax.), 1.23 (d, \(J=6.4\) Hz, 1 H, Me-β), 1.14 (d, \(J=6.4\) Hz, 1 H, Me-α) ppm. \(^{13}\)C NMR: \(\delta\) 170.3-170.0 (C=O), 138.1 (Ph), 137.5 (Ph), 133.0 (Ph), 131.9 (Ph), 130.57 (Ph), 129.7 (Ph), 129.6 (Ph), 128.8 (Ph), 83.3 (α, C-1), 81.7 (β, C-1), 74.8 (α, C-4), 74.2 (β, C-4), 73.8 (β, C-5), 71.7 (β, C-3), 69.3 (α, C-3), 66.6 (α, C-5), 36.5 (β, C-2), 35.7 (α, C-2), 21.1-20.7 (PhMe and OAc), 17.8-17.3 (Me) ppm. HRMS (APCI, m/z) calcd for C₁₃H₂₂O₅NaS [M + Na]⁺ requires 361.1086, found 361.1082.
**p-Tolyl 3,4-di-O-acetyl-2-deoxy-1-thio-D-fucopyranoside (11).** White soild, \([\alpha]^{28}_D\) -181.14 (c 0.81, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 7.41 (d, \(J=8.4\) Hz, 2 H, Ph-β), 7.32 (d, \(J=8.4\) Hz, 2 H, Ph-α), 7.11-7.08 (m, 2 H, Ph), 5.64 (d, \(J=6.0\) Hz, 1 H, H-1α), 5.28-5.23 (m, 1 H, H-3α), 5.21 (br, 1 H, H-4α), 5.10 (d, \(J=5.2\) Hz, 1 H, H-1β), 5.0-4.95 (m, 1 H, H-3β), 4.75-4.72 (m, 1 H, H-4β), 4.54 (q, \(J=6.4\) Hz, 1 H, H-5α), 3.67 (q, \(J=6.4\) Hz, 1 H, H-5β), 2.41 (ddd, \(J=25.6, 12.8, 6.0\) Hz, 1 H, H-2eq.), 2.32 (s, 3 H, PhMe-β), 2.30 (s, 3 H, PhMe-α), 2.13, 1.97 (s, 6 H, 2 OAc), 2.02-2.0 (m, 1 H, α-H-2ax), 1.29-1.24 (m, 1 H, β-H-2ax), 1.20 (d, \(J=6.4\) Hz, 1 H, Me-β), 1.12 (d, \(J=6.4\) Hz, 1 H, Me-α) ppm. \(^{13}\)C NMR: δ 170.8-170.1 (C=O), 37.9 (C), 137.5 (C), 132.5-129.7 (Ph), 84.2 (α, C-1), 82.8 (β, C-1), 73.3 (β, C-4), 70.1 (β, C-3), 69.9 (α, C-4), 68.7 (β, C-5), 67.4 (α, C-3), 65.8 (α, C-5), 31.5 (β, C-2), 30.6 (α, C-2), 21.2-20.8 (OAc), 17.1 (β, Me), 16.6 (α, Me) ppm. HRMS (ESI, m/z) calcd for C₁₇H₂₂O₅NaS [M + Na]⁺ requires 361.1086, found 361.1085.

**General procedure for preparation of 2-deoxy-D-glycopyranosides.** Glycals (50.0 mg, 1.0 equiv), acceptors (12–24, 2.0 equiv), and triphenylphosphine oxide (TPPO, 1.0 equiv) were mixed in a flame dried flask. After the reagents became homogeneous, TMSBr (1.0 equiv) was slowly added at room temperature under ambient atmosphere. After stirring for 1 to 2 hours, the mixture was directly purified by flash column chromatography on silica gel and then volatiles were removed in vacuo to afford expected products. The products and yields are shown in Tables 2–4.

**Benzyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (25).** Colorless oil, \([\alpha]^{28}_D\) 80.56 (c 0.52, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 5 H, Ph), 5.35-5.30 (m, 1 H, H-3), 5.02-4.97 (m, 2 H, H-4 and H-1), 4.66 (d, \(J=12.0\) Hz, 1 H, PhCH), 4.49 (d, \(J=12.0\) Hz, 1 H, PhCH), 4.27 (dd, \(J=12.4, 4.4\) Hz, 1 H, H-6), 4.01-3.96 (m, 2 H, H-6 and H-5), 2.26 (dd, \(J=13.2, 5.6\) Hz, 1 H, H-2eq), 2.08, 2.01, 1.98 (s, 9 H, 3 OAc), 1.82 (ddd, \(J=24.8, 12.0, 3.6\) Hz, 1 H, H-2ax) ppm; \(^{13}\)C NMR: δ 170.9 (C=O), 170.4 (C=O), 170.1 (C=O), 137.3 (Ph), 128.7 (Ph), 128.2 (Ph), 96.4 (α, C-1), 69.7 (α, C-5), 69.5 (PhCH2), 69.4 (α, C-3), 68.3 (α, C-4), 62.6 (α, C-6), 35.2 (α, C-2), 21.1-20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C₁₉H₂₄O₈Na [M + Na]⁺ requires 403.1369, found 403.1387.

**Methyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (26).** Colorless oil, \([\alpha]^{28}_D\) 111.41 (c 0.61, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 5.24 (m, 1 H, H-3), 4.95 (t, \(J=9.6\) Hz, 1 H, H-4), 4.79 (d, \(J=3.2\) Hz, 1 H, H-1), 4.25 (dd, \(J=12.4, 4.4\) Hz, 1 H, H-6), 4.02 (dd, \(J=12.4, 2.4\) Hz, 1 H, H-6), 3.89 (m, 1 H, H-5), 3.30 (s, 3 H, OCH₃), 2.19 (ddd, \(J=12.8, 7.6, 0.8\) Hz, 1 H, H-2eq), 2.04, 1.99, 1.96 (3s, 9 H, 3-OAc), 1.78
(dd, $J=24.8, 12.4, 3.6$ Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 170.9 (C=O), 170.3 (C=O), 170.1 (C=O), 98.2 (α, C-1), 69.6 (α, C-5), 69.3 (α, C-3), 67.9 (α, C-4), 62.6 (α, C-6), 55.0 (α, OCH3), 35.1 (α, C-2), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C13H20O8Na [M + Na]$^+$ requires 327.1056, found 327.1055.

** Allyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (27).** Colorless oil, [α]$^{28}_{D}$ 88.13 (c 0.58, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.86 (m, 1H, -CH=CH), 5.32-4.93 (m, 5H, H-3, H-4, -C=CH2, H-1), 4.25 (dd, $J=12.4, 4.8$ Hz, 1H, H-6a), 4.12-4.07 (m, 1H, -O-CH3), 4.02 (dd, $J=12.4, 2.0$ Hz, 1H, H-6b), 3.96-3.90 (m, 2H, -OCH3, H-5), 2.21 (dd, $J=12.4, 2.0$ Hz, 1H, H-2eq), 2.03, 1.99, 1.97 (3s, 9H, 3-COCH3), 1.78 (dd, $J=15.6, 12.8$, 4.0 Hz, 1H, H-2ax) ppm; $^{13}$C NMR: δ 170.9 (C=O), 170.3 (C=O), 170.1 (C=O), 133.8 (-C=CH2), 117.9 (=-CH2), 98.6 (C-1), 70.1 (C-5), 69.6 (C-3), 68.3 (-O-CH2-), 68.1 (C-4), 62.6 (C-6), 55.0 (OCH3), 34.1 (C-2), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C15H22O8Na [M + Na]$^+$ requires 353.1212, found 353.1226.

** Isopropyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (28).** Colorless oil, [α]$^{28}_{D}$ 94.13 (c 0.50, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.31 (m, 1H, H-3), 5.03 (d, $J=3.2$ Hz, 1 H, H-1), 4.95 (t, $J=10$ Hz, 1 H, H-4), 4.26 (dd, $J=12.4, 4.8$ Hz, 1 H, H-6), 4.04-3.98 (m, 2 H, H-5 and H-6), 3.83 (Sept., $J=6.0$ Hz, 1 H, O-CH-Me2), 2.14 (dd, $J=13.2, 5.8$ Hz, 1 H, H-2eq), 2.05, 2.02, 1.98 (3s, 9 H, 3-OAc), 1.79 (ddd, $J=24.4, 12.4, 4.0$ Hz, 1 H, H-2ax), 1.19 (d, $J=6.0$ Hz, 3 H, CH3), 1.12 (d, $J=6.4$ Hz, 3 H, CH3) ppm; $^{13}$C NMR: δ 170.9 (C=O), 170.4 (C=O), 170.1 (C=O), 98.2 (α, C-1), 70.5 (α, C-4), 69.9 (α, O-CH-Me2), 69.4 (α, C-3), 68.0 (α, C-5), 62.7 (α, C-6), 35.8 (α, C-2), 23.3 (CH3), 22.0 (CH3), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C15H24O8Na [M + Na]$^+$ requires 355.1369, found 355.1365.

** tert-Butyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (29).** Colorless oil, [α]$^{28}_{D}$ 82.68 (c 0.60, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.34 (m, 1 H, H-3), 5.22 (d, $J=3.2$ Hz, 1 H, H-1), 4.95 (t, $J=9.6$ Hz, 1 H, H-4), 4.27 (dd, $J=12.4, 4.4$ Hz, 1 H, H-6), 4.13 (m, 1 H, H-5), 3.97 (dd, $J=12.0, 2.4$ Hz, 1 H, H-6), 2.07-1.97 (m, 10 H, H-2eq, 3 OAc), 1.80 (ddd, $J=24.4, 12.0, 3.6$ Hz, 1H, H-2ax), 1.20 (S, 9H, tBu) ppm; $^{13}$C NMR: δ 170.9 (C=O), 170.4 (C=O), 170.2 (C=O), 91.7(C-1), 75.5 (C-(CH3)3), 70.2 (C-5), 69.6 (C-3), 67.7 (C-4), 62.9 (C-6), 36.8 (C-2), 28.7 (-CH3), 21.2-20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C16H26O8Na [M + Na]$^+$ requires 369.1525, found 369.1522.
5-Azido-1-pentyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (30). Colorless oil, $[\alpha]_{D}^{28} = 81.94$ (c 0.64, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.29 (m, 1 H, H-3), 5.04 (d, $J = 3.2$ Hz, 1 H, H-1), 4.90 (t, $J = 10.0$ Hz, 1 H, H-4), 4.21 (d, $J = 2.8$ Hz, 1 H, H-1), 4.25 (dd, $J = 12.4$, 4.8 Hz, 1 H, H-6), 4.02 (dd, $J = 12.4$, 2.4 Hz, 1 H, H-6), 3.90 (m, 1 H, H-5), 3.62-3.60 (m, 1 H), 3.36-3.33 (m, 1 H), 3.25 (t, $J = 6.4$ Hz, 2 H, -O-CH$_2$-), 2.18 (dd, $J = 12.8$, 5.2 Hz, 1 H, H-2eq), 2.04, 2.00, 1.97 (3 OAc), 1.78 (ddd, $J = 24.8$, 12.8, 3.6 Hz, 1H, H-2ax), 1.63-1.43 (m, 4 H), 1.45-0.40 (m, 2 H) ppm; $^{13}$C NMR: $\delta$170.9-170.1 (C = O), 97.1 (α, C-1), 69.7 (α, C-4), 69.5 (α, C-3), 68.0 (α, C-5), 67.6 (α, -O-CH$_2$-), 62.7 (α, C-6), 51.5 (-CH$_2$-N3), 35.2 (α, C-2), 29.2 (CH2), 28.8 (CH2), 23.7 (CH2), 21.06-20.89 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{15}$H$_{33}$N$_3$O$_8$Na $[M + Na]^+$ requires 424.1696, found 424.1705.

Cyclohexyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (31). Colorless oil, $[\alpha]_{D}^{28} = 86.58$ (c 0.71, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.28 (m, 1 H, H-3), 4.94 (t, $J = 10.0$ Hz, 1 H, H-4), 4.89 (d, $J = 2.8$ Hz, 1 H, H-1), 4.21 (dd, $J = 12.8$, 5.6 Hz, 1 H, H-6), 4.20 (dd, $J = 12.4$, 2.4 Hz, 1 H, H-6), 4.05-4.0 (m, 2 H, H-6 and H-5), 3.48 (m, 1H, -O-CH(CH$_2$)$_2$), 2.12 (dd, $J = 12.4$, 4.8 Hz, 1 H, H-2eq), 2.02, 1.97, 1.94 (3 OAc), 1.83-1.47 (m, 11 H, H-2ax, -Cy) ppm; $^{13}$C NMR: $\delta$ 170.8 (C = O), 170.4 (C = O), 170.1 (C = O), 95.1 (α, C-1), 75.6 (α, -O-CH(CH$_2$)$_2$), 71.0 (α, C-4), 69.5 (α, C-3), 68.0 (α, C-5), 62.8 (α, C-6), 35.8 (α, C-2), 33.6 (CH2), 32.3 (CH2), 25.7 (CH2), 24.2 (CH2), 24.0 (CH2), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{16}$H$_{28}$O$_9$Na $[M + Na]^+$ requires 395.1682, found 395.1689.

2-Adamantyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (32). Colorless oil, $[\alpha]_{D}^{28} = 82.66$ (c 0.82, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.37-5.31 (m, 1 H, H-3), 5.16 (d, $J = 3.2$ Hz, 1 H, H-1), 4.93 (t, $J = 9.6$ Hz, 1 H, H-4), 4.24 (dd, $J = 12.4$, 4.8 Hz, 1 H, H-6), 4.02-4.0 (m, $J = 9.2$ Hz, 2 H, H-6 and H-5), 3.68 (m, 1 H), 2.21 (dd, $J = 12.8$, 5.6 Hz, 1 H, H-2eq), 2.04, 1.99, 1.97, (3 OAc), 2.03-1.41 (m, 13 H, H-2ax and adamantanyl) ppm; $^{13}$C NMR: $\delta$ 170.8 (C = O), 170.4 (C = O), 170.1 (C = O), 95.6 (α, C-1), 79.8 (-O-CH-), 70.0 (α, C-4), 69.5 (α, C-3), 68.8 (α, C-5), 62.9 (α, C-6), 37.6-27.5 (adamantanyl), 35.8 (α, C-2), 23.3 (-CH$_3$), 22.0 (-CH$_3$), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{22}$H$_{32}$O$_9$Na $[M + Na]^+$ requires 447.1995, found 447.1991.

O-[3,4,6-Tri-O-acetyl-2-deoxy-D-glucopyranosyl]-N-carbobenzyloxy-L-serine methyl ester (33). Colorless oil, $[\alpha]_{D}^{28} = 66.17$ (c 1.05, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.30 (m, 5 H, Ph), 5.69 (d, $J = 8.0$ Hz, 1 H, NH), 5.23-5.16 (m, 1 H, H-3), 5.12 (s, 2 H, PhCH2), 4.93 (d, $J = 10.0$ Hz, 1 H, H-4), 4.89 (d, $J = 3.2$ Hz, 1 H, H-1), 4.53-4.51 (m, 1 H), 4.23 (dd, $J = 12.4$, 4.8 Hz, 1 H, H-6), 4.01 (dd, $J = 12.4$, 2.0
Hz, 1 H, H-6), 3.91-3.86 (m, 3 H), 3.76 (s, 3 H, OMe), 2.17 (dd, J = 12.4, 5.6 Hz, 1 H, H-2eq), 2.05, 2.02, 1.98 (s, 9 H, 3 OAc), 1.78 (ddd, J = 24.8, 12.0, 4.0 Hz, 1H, H-2ax) ppm; $^{13}$C NMR: δ 170.9-170.1 (C=O), 156.1 (C=O), 136.3 (Ph), 128.8-128.4 (Ph), 97.9 (α, C-1), 69.4 (α, C-4), 69.0 (α, C-3), 68.6 (α, C-5), 68.6 (CH2), 67.4 (CH2), 62.4 (α, C-6), 54.5 (CH), 52.9 (OMe), 35.0 (α, C-2), 21.1-20.9 (OAc) ppm; HRMS (ESI, $m/z$) calcd for C$_{24}$H$_{31}$NO$_{12}$Na [M + Na]$^+$ requires 548.1744, found 548.1745.

**O-[3,4,6-Tri-O-acetyl-2-deoxy-D-glucopyranosyl]-N-carbobenzyloxy-L-threonine methyl ester (34).** Colorless oil, [α]$^{28}_{D}$ 35.68 (c 0.54, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.29 (m, 5 H, Ph), 5.46 (d, J=9.6 Hz, 1 H, NH), 5.21-5.14 (m, 1 H, H-3), 5.11 (s, 2 H, PhCH2), 5.08 (d, J=3.2 Hz, 1 H, H-1), 4.92-4.88 (m, 2 H), 4.36 (d, J=9.6 Hz, 1 H), 4.29 (d, J=8.4 Hz, 1 H), 4.22 (dd, J=12.0, 8.4 Hz, 1 H, H-6), 4.0 (dd, J=12.8, 1.6 Hz, 1 H, H-6), 3.97-3.94 (m, 1 H, H-5), 3.70 (s, 3 H, OMe), 2.06-1.95 (m, 10 H, H-2eq and 3 OAc), 1.73 (ddd, J = 24.4, 12.0, 3.2 Hz, 1H, H-2ax), 1.25 (d, J=6.4 Hz, 3 H, Me). $^{13}$C NMR: δ 171.08 (C = O), 170.77 (C = O), 170.25 (C = O), 169.95 (C = O), 156.73 (C = O), 136.31 (Ph), 128.67-128.18 (Ph), 98.6 (α, C-1), 97.1 (CH), 76.40 (CH), 69.61 (α, C-4), 69.09 (α, C-3), 68.79 (α, C-5), 67.40 (CH2), 62.57 (α, C-6), 58.81 (CH), 52.62 (Ome), 35.34 (α, C-2), 21.01-20.79 (OAc), 18.40 (Me). HRMS (ESI, $m/z$) calcd for C$_{25}$H$_{33}$NO$_{12}$Na [M + Na]$^+$ requires 562.1900, found 562.1908.

**6-O-[3,4,6-Tri-O-acetyl-2-deoxy-D-glucopyranosyl]-1,2,3,4-di-O-isopropylidene-D-galactopyranose (35).** Colorless oil, [α]$^{28}_{D}$ 10.91 (c 0.76, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.47 (d, J=4.8 Hz, 1 H, H-1'), 5.27 (ddd, J=20.8, 10.8, 5.6 Hz, 1 H, H-3), 4.99-4.93 (m, 2 H, H-1 and H-4), 4.59 (d, J=8.0 Hz, 1 H, H-6), 4.30-4.27 (m, 2 H, H-2' and H-3'), 4.21 (d, J=8.0 Hz, 1 H, H-6), 4.01-3.96 (m, 2 H, H-5' and H-4'), 3.91 (t, J=6.0 Hz, 1 H, H-5), 3.71 (dd, J=10.4 and 6.4 Hz, 1 H, H-6'), 3.62 (dd, J=10.0 and 6.8 Hz, 1 H, H-6'), 2.23 (dd, J=12.8 and 5.2 Hz, 1 H, H-2eq), 2.04, 1.99, 1.96 (s, 9 H, 3 OAc), 1.77 (ddd, J=24.0, 12.0, 3.6 Hz, 1 H, H-2ax), 1.51, 1.39, 1.31 (s, 12 H, 4 Me) ppm; $^{13}$C NMR: δ 170.7-169.7 (C=O), 109.4 (C), 108.6 (C), 97.1 (α, C-1'), 96.3 (α, C-1), 72.9 (CH), 70.6 (CH), 69.3 (CH), 69.2 (CH), 67.9 (CH), 66.3 (α, C-6'), 66.2 (CH), 62.3 (α, C-6), 35.0 (α, C-2), 26.1-24.4 (Me), 20.9-20.8 (OAc) ppm; HRMS (ESI, $m/z$) calcd for C$_{24}$H$_{36}$O$_{13}$Na [M + Na]$^+$ requires 555.2054, found 555.2068.

**Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-Dglucopyranosyl)-α-D-glucopyranoside (36).** Colorless oil, [α]$^{28}_{D}$ 64.71 (c 0.84, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.25 (m, 15 H, -Ar-H), 5.31-5.20 (m, 1 H, H-3), 4.99-4.95 (m, 4
H, H-1, H-4, and 2PhCH), 4.80-4.76 (m, 2 H, 2PhCH), 4.67 (d, J=12.0 Hz, 1 H, PhCH), 4.61-4.57 (m, 2 H, 2PhCH), 4.12 (dd, J=11.6, 4.0 Hz, 1 H, H-6), 4.0 (d, J=9.2 Hz, 1 H, H-3), 3.93-3.86 (m, 2 H, H-5 and H-6), 3.79-3.73 (m, 2 H, H-5 and H-6), 3.60-3.46 (m, 3 H, H-2, H-6, and H-5), 3.34 (s, 3 H, OMe), 2.25 (dd, 1 H, H-2eq), 2.01, 2.0, 1.99 (3s, 9 H, 3 OAc), 1.76 (ddd, J = 15.6, 12.0, 4.0 Hz, 1H, H-2ax) ppm; $^{13}$C NMR: δ 170.8-169.8 (C=O), 138.8-138.3 (Ph), 128.6-127.5 (Ph), 98.1(α, C-1), 97.4 (α, C-1), 82.3 (CH), 80.3 (CH), 78.0 (CH), 75.86 (CH2), 75.0 (CH2), 73.5 (CH2), 69.9 (CH), 69.4 (CH), 69.2 (CH), 68.06 (CH), 66.3 (α, C-6), 62.3 (α, C-6), 55.1 (OMe), 35.0 (α, C-2), 21.1-20.8 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{40}$H$_{48}$O$_{13}$Na [M + Na]$^+$ requires 759.2993, found 759.2972.

Methyl 2,3,6-tri-O-benzyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-gluco.pyranoside (37). Colorless oil, [α]$^{28}_D$ 60.74 (c 1.10, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31-7.23 (m, 15 H, -ArH), 5.40 (d, J=2.8 Hz, 1 H, H-1), 5.22-5.16 (m, 1 H, H-3), 5.02 (d, J=11.2 Hz, 1 H, PhCH), 4.88 (t, J=9.6 Hz, 1 H, H-4), 4.71 (d, J=12.0 Hz, 1 H, PhCH), 4.65-4.59 (m, 4 H, 4PhCH), 4.51 (d, J=12.0 Hz, 1 H, PhCH), 4.11 (dd, J=12.0, 4.0 Hz, 1 H, H-6), 3.92 (t, J=9.2 Hz, 1 H, H-3), 3.90-3.86 (m, 1 H), 3.78-3.74 (m, 2 H), 3.67-3.62 (m, 3 H), 3.50 (dd, J=9.6, 3.6 Hz, 1 H, H-6), 3.39 (s, 3 H), 2.03-1.68 (m, 10 H, H-2eq and 3 OAc), 1.60 (m, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 170.8 (C=O), 170.3 (C=O), 169.9 (C=O), 138.8 (Ph), 138.3 (Ph), 138.2 (Ph), 128.6-127.7 (Ph), 98.8 (α, C-1), 98.0 (α, C-1), 82.0 (CH), 80.4 (CH), 76.6 (CH), 75.5 (CH2), 73.6 (CH2), 73.4 (CH2), 69.9 (CH), 69.5 (α, C-6), 60.9 (CH), 68.9 (CH), 62.4 (α, C-6), 55.5 (OMe), 35.4 (α, C-2), 21.1-20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{46}$H$_{54}$O$_{17}$Na [M + Na]$^+$ requires 759.2993, found 759.3027.

Benzy1 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (38). Colorless oil, [α]$^{28}_D$ 54.99 (c 0.59, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.17 (m, 20 H, -ArH), 5.67 (d, J=3.2 Hz, 1 H, H-1), 4.90 (d, J=10.8 Hz, 1 H, PhCH), 4.69-4.62 (m, 4 H, PhCH), 4.54 (d, J=11.6 Hz, 1 H, PhCH), 4.44 (d, J=11.6 Hz, 1 H, PhCH), 4.05 (m, 1 H, H-3), 3.85-3.77 (m, 2 H, H-5 and H-6), 3.68-3.62 (m, 2 H, H-6 and H-4), 2.34 (dd, J=12.8, 5.6 Hz, 1 H, H-2eq), 1.76 (ddd, J=24.4, 12.4, 3.6 Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 138.9-137.9 (Ph), 128.5-127.9 (Ph), 97.0 (α, C-1), 78.6 (α, C-4), 78.4 (α, C-3), 75.2 (PhCH2), 73.7 (PhCH2), 72.0 (PhCH2), 71.3 (α, C-5), 69.2 (α,C-6), 69.1 (PhCH2), 35.7 (α, C-2) ppm; HRMS (ESI, m/z) calcd for C$_{34}$H$_{36}$O$_5$Na [M + Na]$^+$ requires 547.2460, found 547.2483.
Methyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (39). Colorless oil, $[\alpha]_D^{28}$ 62.98 (c 0.65, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.19 (m, 15 H, -ArH), 4.91 (d, $J$= 10.8 Hz, 1 H, PhCH), 4.86 (d, $J$= 2.8 Hz, 1 H, H-1), 4.70-4.52 (m, 5 H, PhCH), 4.01-3.95 (m, 1 H, H-3), 3.80-3.68 (m, 4 H, H-6, H-4, and H-5), 3.32 (s, 3 H), 2.29 (dd, $J$= 13.2, 5.2 Hz, 1 H, H-2eq), 1.72 (ddd, $J$= 24.4, 12.8, 3.6 Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 138.9-138.4 (Ph), 128.5-127.7 (Ph), 98.7 (α, C-1), 79.6 (α, C-4), 78.5 (α, C-3), 75.1 (PhCH2), 73.7 (PhCH2), 71.9 (PhCH2), 70.9 (α, C-5), 69.3 (α,C-6), 54.8 (OMe), 35.6 (α, C-2) ppm; HRMS (ESI, m/z) calcd for C$_{28}$H$_{32}$O$_3$Na [M + Na]$^+$ requires 471.2147, found 471.2169.

Allyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (40). Colorless oil, $[\alpha]_D^{28}$ 61.49 (c 0.58, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.17 (m, 15 H, -ArH), 5.87-5.83 (m, 1 H, H-3), 5.28 (dd, $J$= 17.2, 1.2 Hz, 1 H, CH=CH), 5.16 (dd, $J$= 10.4, 1.2 Hz, 1 H, CH=CH), 5.01 (d, $J$= 2.4 Hz, 1 H, H-1), 4.91 (d, $J$= 10.8 Hz, 1 H, PhCH), 4.69-4.62 (m, 3 H, PhCH), 4.55-4.51 (m, 2 H, PhCH), 4.16-4.14 (m, 2 H, -O-CH2-), 4.05-4.01 (m, 1 H, H-3), 3.95 (dd, $J$= 13.2, 6.4 Hz, 1 H, H-6), 3.81-3.61 (m, 3 H, H-4, H-5, and H-6), 2.31 (dd, $J$= 12.4, 4.8 Hz, 1 H, H-2eq), 1.75 (ddd, $J$= 24.8, 12.8, 4.0 Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 139.0-138.4 (Ph), 128.5-128.7 (Ph), 134.4 (CH=H), 117.2 (=CH2), 96.9 (α, C-1), 79.7 (α, C-4), 78.6 (α, C-3), 75.6 (PhCH2), 74.0 (PhCH2), 72.0 (PhCH2), 71.1 (α, C-5), 69.1 (α,C-6), 67.9 (-O-CH2-), 35.8 (α, C-2) ppm; HRMS (ESI, m/z) calcd for C$_{30}$H$_{34}$O$_3$Na [M + Na]$^+$ requires 497.2304, found 497.2321.

Isoproropyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (41). Colorless oil, $[\alpha]_D^{28}$ 60.39 (c 0.65, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.17 (m, 15 H, -ArH), 5.09 (d, $J$= 3.2 Hz, 1 H, H-1), 4.90 (d, $J$= 10.8 Hz, 1 H, PhCH), 4.69-4.61 (m, 3 H, PhCH), 4.54-4.50 (m, 2 H, PhCH), 4.05-3.91 (m, 1 H, H-3), 3.88 (sept, $J$= 6.4 Hz, 1 H, CH(Me)2), 3.86-3.79 (m, 2 H, H-5 and H-6), 3.68-3.61 (m, 2 H, H-6 and H-4), 2.25 (dd, $J$= 12.4, 4.8 Hz, 1 H, H-2eq), 1.75 (ddd, $J$= 24.8, 12.8, 4.0 Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 139.1-138.5 (Ph), 128.5-127.7 (Ph), 95.3 (α, C-1), 78.8 (α, C-4), 78.5 (α, C-3), 75.2 (PhCH2), 73.7 (PhCH2), 71.9 (PhCH2), 71.5 (α, C-5), 69.3 (α, C-6), 68.4 (α, -CH(Me)2), 36.2 (α, C-2), 23.5 (Me), 21.5 (Me) ppm; HRMS (ESI, m/z) calcd for C$_{30}$H$_{36}$O$_4$Na [M + Na]$^+$ requires 499.2460, found 499.2463.

tert-Butyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (42). Colorless oil, $[\alpha]_D^{28}$ 48.64 (c 0.53, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.17 (m, 15 H, -ArH), 5.27 (d, $J$= 2.4 Hz, 1 H, H-1), 4.88 (d, $J$= 10.8 Hz, 1 H, PhCH), 4.69-4.61 (m, 3 H, PhCH), 4.52-4.62 (m, 2 H, PhCH), 4.06-4.01 (m, 1 H, H-3), 3.95 (dt, $J$= 6.8, 2.8 Hz, 1 H,
H-5), 3.80 (dd, J = 10.4, 3.6 Hz, 1 H, H-6), 3.65-3.60 (m, 2 H, H-4, and H-6), 2.10 (dd, J = 12.4, 4.8 Hz, 1 H, H-2eq), 1.72 (ddd, J = 24.8, 12.8, 4.0 Hz, 1 H, H-2ax) ppm; $^{13}$C NMR: δ 139.2-138.0 (Ph), 128.5-127.6 (Ph), 92.2 (α, C-1), 80.2 (CH(Me)3), 78.9 (α, C-4), 78.1 (α, C-3), 75.1 (PhCH2), 73.8 (PhCH2), 71.9 (PhCH2), 70.6 (PhCH2), 69.2 (α-C-6), 37.3 (α, C-2), 29.9 (Me) ppm; HRMS (ESI, $m/z$) calcd for C$_{31}$H$_{38}$O$_{5}$Na [M + Na]$^+$ requires 513.2617, found 513.2620.

5-Azido-1-pentyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (43). Colorless oil, [$\alpha$]$^{28}$D 52.13 (c 0.60, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.17 (m, 15 H, -ArH), 4.94 (d, J = 3.2 Hz, 1 H, H-1), 4.90 (d, J = 10.8 Hz, 1 H, PhCH), 4.70-4.61 (m, 3 H, PhCH), 5.40-5.10 (d, J = 11.2 Hz, 2 H, PhCH), 4.0 (m, 1 H, H-3), 3.80-3.73 (m, 2 H, H-6 and H-4), 3.62-3.58 (m, 3 H, H-6 and H-5), 3.37-3.35 (m, 1 H), 3.25 (t, J = 6.8 Hz, 2 H, -O-CH$_2$-), 2.28 (dd, J = 12.8, 4.8 Hz, 1 H, H-2eq), 1.72 (ddd, J = 24.8, 12.8, 2.4 Hz, 1 H, H-2ax), 1.64-1.56 (m, 5 H), 1.45-1.40 (m, 2 H) ppm; $^{13}$C NMR: δ 139.0-138.5 (Ph), 128.5-127.7 (Ph), 97.6 (α, C-1), 78.6 (α, C-4), 77.9 (α, C-3), 75.2 (PhCH2), 74.0 (PhCH2), 71.6 (PhCH2), 71.1 (α, C-5), 69.4 (-O-CH$_2$-), 67.2 (α, C-6), 51.5 (-CH$_2$-N3), 35.8 (α, C-2), 29.3 (CH2), 28.9 (CH2), 13.7 (CH2) ppm; HRMS (ESI, $m/z$) calcd for C$_{32}$H$_{39}$N$_3$O$_5$Na [M + Na]$^+$ requires 568.2787, found 568.2795.

Cyclohexyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (44). Colorless oil, [$\alpha$]$^{28}$D 63.57 (c 0.52, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.17 (m, 15 H, -ArH), 5.12 (d, J = 2.8 Hz, 1 H, H-1), 4.90 (d, J = 10.8 Hz, 1 H, PhCH), 4.70-4.64 (m, 3 H, PhCH), 4.52-4.49 (m, 2 H, PhCH), 4.03 (m, 1 H, H-3), 3.87-3.82 (m, 2 H, H-5), 3.79 (dd, J = 10.4, 4.0 Hz, 1 H, H-1), 3.68 (dd, J = 10.4, 2.4 Hz, 1 H, H-6), 3.61 (t, J = 9.2 Hz, 1 H, H-3), 3.56 (m, 1 H, Cy), 2.24 (dd, J = 12.8, 4.4 Hz, 1 H, H-2eq), 1.86-1.84 (m, 2 H, Cy), 1.77-1.70 (m, 3 H, Cy and H-2ax), 1.52 (m, 1 H, Cy), 1.32-1.19 (m, 3 H, Cy) ppm; $^{13}$C NMR: δ 139.1-138.5 (Ph), 128.5-127.7 (Ph), 95.3 (α, C-1), 78.8 (α, C-4), 78.1 (α, C-3), 75.4 (PhCH2), 74.6 (Cy), 72.0 (PhCH2), 71.0 (α, C-5), 69.1 (α, C-6), 36.3 (α, C-2), 33.6 (CH2), 31.7 (CH2), 24.5 (CH2), 24.3 (CH2), 24.2 (CH2). HRMS (ESI, $m/z$) calcd for C$_{33}$H$_{40}$O$_{5}$Na [M + Na]$^+$ requires 539.2773, found 539.2773.

2-Adamantyl 3,4,6-tri-O-benzyl-2-deoxy-D-glucopyranoside (45). Colorless oil, [$\alpha$]$^{28}$D 73.30 (c 0.61, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33-7.14 (m, 15 H, -ArH), 5.09 (d, J = 2.8 Hz, 1 H, H-1), 4.88 (d, J = 10.8 Hz, 1 H, PhCH), 4.69-4.62 (m, 3 H, PhCH), 4.50 (d, J = 10.4 Hz, 1 H, PhCH), 4.49 (d, J = 10.4 Hz, 1 H, PhCH), 4.07-4.02 (m, 1 H, H-3), 3.85 (dt, J = 8.0, 2.0 Hz, 1 H, H-5), 3.78 (dd, J = 10.4, 3.0 Hz, 1 H, H-6), 3.65 (dd, J = 10.4, 1.6 Hz, 1 H, H-6), 3.60 (d, J = 9.2 Hz, 1 H, H-4), 2.21
(dd, \( J = 12.8, 4.4 \) Hz, 1 H, H-2eq), 2.05-1.59 (m, 12 H, adamantanyl), 1.45 (d, \( J = 12.0 \) Hz, 2 H, adamantanyl) ppm; \(^{13}\)C NMR: \( \delta \) 139.0-138.5 (Ph), 128.5-127.7 (Ph), 95.5 (\( \alpha \), C-1), 79.0 (CH), 78.9 (CH), 78.0 (\( \alpha \), C-3), 75.2 (PhCH2), 73.6 (PhCH2), 72.0 (PhCH2), 71.2 (\( \alpha \), C-5), 69.4 (\( \alpha \), C-6), 37.6 (CH2), 36.9 (CH2), 36.6 (CH2), 36.5 (CH2), 33.7 (CH), 32.0 (CH2), 31.8 (CH), 27.7 (CH), 27.5 (CH) ppm; HRMS (ESI, \( m/z \)) calcd for \( C_{37}H_{44}O_7Na \) [M + Na]\(^{+} \) requires 591.3086, found 591.3094.

**O-[3,4,6-Tri-O-benzyl-2-deoxy-D-glucopyranosyl]-N-carbobenzyloxy-L-serine methyl ester (46).** Colorless oil, \([\alpha]^{28}_D\) 53.16 (c 1.32, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.23-7.14 (m, 20 H, -ArH), 5.73 (d, \( J = 6.4 \) Hz, 1 H, NH), 5.09 (t, d, \( J = 12.8 \) Hz, 2 H, CH2Ph), 4.88 (d, \( J = 2.8 \) Hz, 1 H, H-1), 4.84 (d, \( J = 10.8 \) Hz, 1 H, PhCH), 4.61 (s, 2 H, CH2Ph), 4.58 (d, \( J = 10.8 \) Hz, 1 H, PhCH), 4.48-4.42 (m, 3 H, PhCH), 4.92-3.82 (m, 3 H), 3.73 (s, 3 H, OMe), 3.71-3.66 (m, 2 H), 3.64-3.75 (m, 2 H), 2.22 (dd, \( J = 12.8, 4.4 \) Hz, 1 H, H-2eq), 1.68 (ddd, \( J = 24.8, 12.8, 2.4 \) Hz, 1 H, H-2ax) ppm; \(^{13}\)C NMR: \( \delta \) 170.8 (C=O), 156.2 (C=O), 138.8-138.3 (Ph), 136.4 (Ph), 128.7-127.8 (Ph), 98.7 (\( \alpha \), C-1), 78.3 (\( \alpha \), C-4), 78.0 (\( \alpha \), C-3), 75.1 (PhCH2), 76.3 (PhCH2), 72.1 (PhCH2), 71.6 (\( \alpha \), C-5), 68.9 (\( \alpha \), C-6), 68.5 (PhCH2), 67.3 (CH2), 54.6 (CH), 52.7 (OMe), 35.5 (\( \alpha \), C-2) ppm; HRMS (ESI, \( m/z \)) calcd for \( C_{39}H_{43}O_8Na \) [M + Na]\(^{+} \) requires 692.2836, found 692.2842.

**O-[3,4,6-Tri-O-benzyl-2-deoxy-D-glucopyranosyl]-N-carbobenzyloxy-L-threonine methyl ester (47).** Colorless oil, \([\alpha]^{28}_D\) 45.10 (c 0.60, CHCl\(_3\)); \([\alpha]^{28}_D\) 82.66 (c 0.82, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.37-7.14 (m, 30 H, -ArH), 5.36 (d, \( J = 9.6 \) Hz, 1 H, NH), 5.13 (s, 2 H, PHCH), 4.88-4.84 (m, 2 H), 4.62-4.60 (m, 3 H), 4.49-4.46 (m, 2 H), 4.33-4.30 (m, 2 H), 3.89-3.82 (m, 1 H, H-3), 3.78-3.75 (m, 2H), 3.73 (s, 3 H, OCH3), 3.63-3.61 (m, 2 H), 3.55 (t, \( J = 9.6 \) Hz, 1 H), 2.16 (dd, \( J = 12.8, 4.4 \) Hz, 1 H, H-2eq), 1.62 (ddd, \( J = 24.8, 12.8, 2.4 \) Hz, 1 H, H-2ax) ppm; \(^{13}\)C NMR: \( \delta \) 171.4 (C=O), 156.8 (C=O), 138.7-138.3 (Ph), 136.4 (Ph), 128.8-127.8 (Ph), 99.3 (\( \alpha \), C-1), 78.3 (\( \alpha \), C-4), 76.9 (\( \alpha \), C-3), 75.8 (CH), 75.2 (PhCH2), 73.7 (PhCH2), 72.0 (PhCH2), 71.7 (\( \alpha \), C-5), 69.1 (PHCH2), 67.5 (\( \alpha \), C-6), 59.0 (NCH), 52.6 (OMe), 35.9 (\( \alpha \), C-2), 29.9 (CH), 18.8 (Me) ppm; HRMS (ESI, \( m/z \)) calcd for \( C_{40}H_{45}O_9Na \) [M + Na]\(^{+} \) requires 706.2992, found 706.3023.

**6-O-[3,4,6-Tri-O-benzyl-2-deoxy-D-glucopyranosyl]-1,2,3,4-di-O-isopropylidene-D-galactopyranose (48).** Colorless oil, \([\alpha]^{28}_D\) 10.44 (c 0.92, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.34-7.24 (m, 15 H, -ArH), 5.50 (d, \( J = 5.2 \) Hz, 1 H, H-1'), 5.01 (d, \( J = 3.2 \) Hz, 1 H, H-1), 4.86 (d, \( J = 10.8 \) Hz, 1 H, PhCH), 4.66-4.47 (m, 7 H), 4.29 (dd, \( J = 2.4, 1.3 \) Hz, 1 H, H-2eq).
Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-2-deoxy-Dglucopyranosyl)-α-D-glucopyranoside (49). White solid, [α]D 25 59.04 (c 0.61, CHCl3); \(^1\)H NMR (400 MHz, CDCl3) δ 7.35-7.18 (m, 30 H, -ArH), 4.97 (d, J = 10.8 Hz, 1 H, PhCH), 4.85 (dd, J = 10.8, 2.0 Hz, 2 H, PhCH), 4.78 (d, J = 10.8 Hz, 2 H, PhCH), 4.64 (d, J = 11.2 Hz, 1 H, PhCH), 4.69-4.50 (m, 7 H, PhCH, H-1, and H-1'), 4.15 (dd, J = 9.6, 1.6 Hz, 1 H), 4.06 (dd, J = 10.4, 1.6 Hz, 1 H), 3.98 (t, J = 9.2 Hz, 1 H), 3.74-3.69 (m, 3 H, H-3), 3.56-3.50 (m, 4 H, H-2'), 3.42 (t, J = 9.6 Hz, 1 H), 3.34 (s, 3 H, OMe), 2.19 (dd, J = 12.8, 4.4 Hz, 1 H, H-2eq), 1.68 (ddd, J = 24.8, 12.8, 2.4 Hz, 1 H, H-2ax) ppm; \(^13\)C NMR: δ 139.1-138.4 (Ph), 128.7-127.7 (Ph), 108.7 (C), 97.5 (α, C-1'), 96.6 (α, C-1), 78.5 (α, C-4), 78.3 (α, C-3), 75.1 (PhCH2), 73.7 (PhCH2), 72.0 (PhCH2), 70.9 (CH), 70.7 (CH), 69.1 (α, C-6), 65.6 (CH), 66.0 (α, C-6'), 35.7 (α, C-2), 26.4 (Me), 26.3 (Me), 25.1 (Me), 25.0 (Me) ppm; HRMS (ESI, m/z) calcd for C\(_{39}\)H\(_{48}\)O\(_{10}\)Na [M + Na]\(^+\) requires 699.3145, found 699.3170.

Methyl 2,3,6-tri-O-benzyl-4-O-(3,4,6-tri-O-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (50). Colorless oil, [α]D 25 44.80 (c 0.54, CHCl3); \(^1\)H NMR (400 MHz, CDCl3) δ 7.33-7.15 (m, 15 H, -ArH), 5.42 (d, J = 2.8 Hz, 1 H, H-1), 5.02 (d, J = 11.2 Hz, 1 H, PhCH), 4.83 (d, J = 10.8 Hz, 1 H, PhCH), 4.72 (d, J = 11.6 Hz, 1 H, PhCH), 4.63-4.59 (m, 3 H, PhCH), 4.54-5.51 (m, 4 H, PhCH and H-1'), 4.47-4.2 (m, 2 H, PhCH), 4.35 (d, J = 12.4 Hz, 1 H, PhCH), 3.88-3.84 (m, 2 H), 3.70-3.62 (m, 5 H), 4.60-3.58 (m, 1 H), 3.53-3.50 (m, 2 H), 3.38 (s, 3 H, OMe), 2.06 (dd, J = 12.8, 4.4 Hz, 1 H, H-2eq), 1.55 (ddd, J = 24.8, 12.8, 2.4 Hz, 1 H, H-2ax) ppm; \(^13\)C NMR: δ 138.7-138.0 (Ph), 128.4-127.4 (Ph), 99.4(α, C-1'), 97.6 (α, C-1), 82.1 (CH), 80.1 (CH), 78.1 (CH), 77.1 (CH), 76.2 (CH), 75.4 (PhCH2), 74.8 (PhCH2), 73.5 (PhCH2), 73.2 (PhCH2), 71.8 (CH), 71.7 (PhCH2), 69.8 (CH), 69.5 (α, C-6), 68.75 (α, C-6), 55.2 (OMe), 35.8 (α, C-2) ppm; HRMS (ESI, m/z) calcd for C\(_{55}\)H\(_{60}\)O\(_{10}\)Na [M + Na]\(^+\) requires 903.4084, found 903.4074.
Benzyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (51). Colorless oil, \([\alpha]^{28}_D\) 109.56 (c 0.66, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.27 (m, 5 H, -ArH), 5.33-5.28 (m, 2 H, H-4 and H-3), 5.29 (d, \(J = 3.2\) Hz, 1 H, H-1), 4.67 (d, \(J = 12.4\) Hz, 1 H, PhCH), 4.17 (d, \(J = 12.4\) Hz, 1 H, PhCH), 4.19 (t, \(J = 6.8\) Hz, 1 H, H-5), 4.11-4.07 (m, 2 H, H-6), 2.11, 2.04, 1.97 (s, 9 H, 3 OAc), 2.09-2.04 (m, 1 H, H-2eq.), 1.91-1.88 (m, 1 H, H-2ax.) ppm; \(^13\)C NMR: \(\delta\) 170.7 (C=O), 128.7-127.8 (Ph), 98.7 (\(\alpha\), C-1), 71.3 (\(\alpha\), C-4), 70.8 (PhCH2), 68.7 (\(\alpha\), C-3), 66.5 (\(\alpha\), C-5), 62.1 (\(\alpha\), C-6), 32.2 (\(\alpha\), C-2), 21.1-20.9 (OAc) ppm; HRMS (ESI, \(m/z\)) calcd for C\(_{19}\)H\(_{24}\)O\(_8\)Na [M + Na]\(^+\) requires 403.1369, found 403.1365.

Methyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (52). Colorless oil, \([\alpha]^{28}_D\) 133.20 (c 0.55, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.31-5.23 (m, 2 H, H-4 and H-3), 4.89 (d, \(J = 2.8\) Hz, 1 H, H-1), 4.13-4.07 (m, 3 H, H-5 and H-6), 3.34 (s, 3 H, OMe), 2.10, 2.01, 1.96 (s, 9 H, 3 OAc), 2.02-1.95 (m, 1 H, H-2eq.), 1.86-1.80 (m, 1 H, H-2ax.) ppm; \(^13\)C NMR: \(\delta\) 170.7 (C=O), 137.4-137.1 (Ph), 128.7-127.7 (Ph), 98.7 (\(\alpha\), C-1), 66.9 (\(\alpha\), C-4), 66.8 (\(\alpha\), C-3), 66.4 (\(\alpha\), C-5), 62.7 (\(\alpha\), C-6), 30.3 (\(\alpha\), C-2), 21.0-20.8 (OAc) ppm; HRMS (ESI, \(m/z\)) calcd for C\(_{19}\)H\(_{24}\)O\(_8\)Na [M + Na]\(^+\) requires 327.1056, found 327.1059.

Allyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (53). Colorless oil, \([\alpha]^{28}_D\) 133.13 (c 0.51, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.87-5.83 (m, 1 H, -CH=), 5.30-5.23 (m, 4 H, =CH\(_2\), H-3 and H-4), 5.02 (d, \(J = 3.2\) Hz, 1 H, H-1), 4.15-4.05 (m, 4 H, H-5, H-6, and –O-CH\(_2\)-), 3.94 (dd, \(J = 12.0, 5.6\) Hz , 1 H, -O-CH\(_2\)-), 2.09, 2.01, 1.94 (s, 9 H, 3 OAc), 2.07-2.02 (m, 1 H, H-2eq.), 1.87-1.83 (m, 1 H, H-2ax.) ppm; \(^13\)C NMR: \(\delta\) 170.6-170.1 (C=O), 133.9 (-CH=), 117.6 (=CH\(_2\)), 98.7 (\(\alpha\), C-1), 68.4 (-O-CH\(_2\)-), 67.0 (\(\alpha\), C-4), 66.9 (\(\alpha\), C-3), 66.4 (\(\alpha\), C-5), 62.6 (\(\alpha\), C-6), 30.3 (\(\alpha\), C-2), 21.0-20.8 (OAc) ppm; HRMS (ESI, \(m/z\)) calcd for C\(_{19}\)H\(_{24}\)O\(_8\)Na [M + Na]\(^+\) requires 355.1212, found 355.1207.

Isopropyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (54). Colorless oil, \([\alpha]^{28}_D\) 129.86 (c 0.73, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.27-5.22 (m, 2 H, H-4 and H-3), 5.08 (d, \(J = 3.6\) Hz, 1 H, H-1), 4.16 (t, \(J = 6.8\) Hz, 1 H, H-5), 4.09-4.01 (m, 2 H, H-6), 3.82 (sept., \(J = 6.4\) Hz, 1 H, H-5), 2.10, 2.01, 1.92 (s, 9 H, 3 OAc), 2.08-2.03 (m, 1 H, H-2eq.), 1.77-1.73 (m, 1 H, H-2ax.), 1.19 (d, \(J = 6.0\) Hz, 3 H, Me), 1.13 (d, \(J = 6.0\) Hz, 3 H, Me) ppm; \(^13\)C NMR: \(\delta\) 170.6-170.2 (C=O), 95.8 (\(\alpha\), C-1), 69.72 (-O-C(Me)\(_2\)), 67.1 (\(\alpha\), C-4), 66.8 (\(\alpha\), C-3), 66.6 (\(\alpha\), C-5), 62.7 (\(\alpha\), C-6), 30.9 (\(\alpha\), C-2), 23.3(CH), 21.7 (2 Me), 21.0-20.84 (OAc) ppm; HRMS (ESI, \(m/z\)) calcd for C\(_{19}\)H\(_{24}\)O\(_8\)(Na) [M + Na]\(^+\) requires 355.1369, found 355.1373.
**tert-Butyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (55).** Colorless oil, [α]$^2_b$ 114.78 (c 0.69, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.32-5.27 (m, 3 H, H-3, H-4, and H-1), 4.30 (t, d, J = 6.8 Hz, 1 H, H-5), 5.07-3.99 (m, 2 H, H-6), 2.09, 2.02, 1.95 (s, 9 H, 3 OAc), 2.07-2.03 (m, 1 H, H-2eq.), 1.69-1.65 (m, 1 H, H-2ax.), 1.21 (s, 9 H, 3 Me) ppm; $^{13}$C NMR: δ 170.7-170.3 (C=O), 92.2 (α, C-1), 75.2 (α, C), 67.2 (α, C-4), 66.73 (α, C-3), 66.4 (α, C-5), 62.7 (α, C-6), 31.9 (α, C-2), 28.7 (α, C-2), 21.0-20.8 (OAc) ppm; HRMS (ESI, $m/z$) calcd for C$_{18}$H$_{20}$O$_8$Na [M + Na]$^+$ requires 369.1525, found 355.1524.

**5-Azido-1-pentyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (56).** Colorless oil, [α]$^2_b$ 82.04 (c 0.77, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.28-5.22 (m, 2 H, H-4 and H-3), 4.96 (d, J = 2.8 Hz, 1 H, H-1), 4.11-4.04 (m, 3 H, H-5 and H-6), 3.64-3.59 (m, 1 H, -OCH2-), 3.38-3.24 (m, 1 H, -OCH2-), 2.35 (t, J = 6.8 Hz, 1 H, -CH2-N3), 2.09, 2.03, 1.96 (s, 9 H, 3 OAc), 2.07-2.04 (m, 1 H, H-2eq.), 1.84-1.80 (m, 1 H, H-2ax.), 1.63-1.53 (m, 4 H, -CH2CH2CH2-), 1.46-1.39 (m, 2 H, -CH2CH2CH2-) ppm; $^{13}$C NMR: δ 170.5-170.1 (C=O), 128.6-128.1 (C=O), 97.6 (α, C-1), 68.0 (α, -O-CH2-), 66.8 (α, C-4), 66.8 (α, C-3), 66.7 (α, C-5), 62.6 (α, C-6), 51.4 (α, -CH2-N3), 30.4 (α, C-2), 29.1 (CH2), 28.7 (CH2), 23.62 (CH2), 20.9-20.8 (3 OAc) ppm; HRMS (ESI, $m/z$) calcd for C$_{17}$H$_{27}$N$_3$O$_8$Na [M + Na]$^+$ requires 424.1696, found 424.1699.

**Cyclohexyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (57).** Colorless oil, [α]$^2_b$ 121.02 (c 0.53, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.31-5.26 (m, 3 H, H-2, H-4 and H-3), 5.14 (d, J = 2.8 Hz, 1 H, H-1), 4.21 (t, J = 6.4 Hz, 1 H, H-5), 4.20-4.33 (m, 2 H, H-6), 3.54-3.51 (m, 1 H, -O-CH-), 2.11, 2.02, 1.96 (s, 9 H, 3 OAc), 2.09-2.03 (m, 1 H, H-2eq.), 1.85-1.77 (m, 3 H, H-2ax. and Cy), 1.73-1.65 (m, 2 H, Cy), 1.51 (m, 1 H, Cy), 1.46-1.19 (m, 5 H, Cy) ppm; $^{13}$C NMR: δ 170.6-170.2 (C=O), 95.7 (α, C-1), 75.6 (α, -O-CH-), 67.0 (α, C-4), 66.8 (α, C-3), 66.6 (α, C-5), 62.8 (α, C-6), 33.5 (CH2), 31.7 (CH2), 31.0 (α, C-2), 25.8 (CH2), 24.6 (CH2), 24.1 (CH2), 20.99-20.81 (OAc) ppm; HRMS (ESI, $m/z$) calcd for C$_{18}$H$_{28}$O$_8$Na [M + Na]$^+$ requires 395.1682, found 395.1687.

**2-Adamantyl 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (58).** Colorless oil, [α]$^2_b$ 114.81 (c 0.77, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.34-5.15 (m, 2 H, H-4 and H-3), 5.14 (d, J = 2.8 Hz, 1 H, H-1), 4.21 (t, J = 6.4 Hz, 1 H, H-5), 4.09-4.0 (m, 2 H, H-6), 3.70 (br, 1 H, -O-CH-), 2.10, 2.01, 1.90 (s, 9 H, 3 OAc), 2.08-1.96 (m, 1 H, H-2eq.), 1.86 (m, 1 H, H-2ax.), 1.84-1.60 (m, 12 H, adamantanyl), 1.45 (t, J = 12.4 Hz, 1 H, adamantanyl) ppm; $^{13}$C NMR: δ 170.6-170.3 (C=O), 95.8 (α, C-1), 79.9 (α,
O-[3,4,6-Tri-O-acetyl-2-deoxy-D-galactopyranosyl]-N-carbobenzyloxy-L-serine methyl ester (59). Colorless oily, $[\alpha]^{25}_{D}$ 87.46 (c 0.54, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.40-5.29 (m, 5 H, -ArH), 5.71 (d, J = 8.0 Hz, 1 H, NH), 5.28 (s, 1 H, H-4), 5.17 (dt, J = 12.4, 2.8 Hz, 1 H, H-3), 5.08 (s, 1 H, PhCH₂), 4.95 (d, J = 3.2 Hz, 1 H, H-1), 4.53-4.51 (m, 1 H, CH₂), 4.10-4.01 (m, 4 H, CH₂, C-5, and C-6), 3.89 (br, 2 H, CH and C-6), 3.75 (OMe), 2.09, 2.0, 1.95 (3 OAc), 2.07-2.03 (m, 1 H, H-2eq.), 1.80 (dd, J = 12.8, 5.2 Hz, 1 H, H-2ax.) ppm; ¹³C NMR: δ 170.7-170.2 (C=O), 156.1 (C=O), 136.4 (Ph), 128.7-128.3 (Ph), 98.4 (α, C-1), 68.6 (PhCH₂), 67.5 (α, C-4), 67.3 (CH₂), 66.7 (α, C-3), 66.1 (α, C-5), 62.6 (α, C-6), 54.5 (α, NCH), 52.9 (α, OMe), 30.1 (α, C-2), 21.0-20.8 (OAc) ppm; HRMS (ESI, m/z) calcd for C₂₄H₃₂O₈Na [M + Na]⁺ requires 447.1995, found 447.1981.

O-[3,4,6-Tri-O-acetyl-2-deoxy-D-galactopyranosyl]-N-carbobenzyloxy-L-threonine methyl ester (60). Colorless oil, $[\alpha]^{25}_{D}$ 65.42 (c 0.64, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.30 (m, 5 H, -ArH), 5.45 (d, J = 9.6 Hz, 1 H, NH), 5.28 (s, 1 H, H-4), 5.17-5.11 (m, 3 H, H-3 and PhCH₂), 4.96 (d, J = 3.2 Hz, 1 H, H-1), 4.38-4.30, 4.15 (t, J = 6.4 Hz, 1 H, H-5), 4.05-4.02 (m, 2 H, H-6), 3.72 (s, 3 H, OMe), 2.09, 2.01, 1.95 (s, 9 H, 3 OAc), 2.03-1.98 (m, 1 H, H-2eq.), 1.70-1.66 (m, 1 H, H-2ax.), 1.28 (d, J = 6.4 Hz, 3 H, Me) ppm; ¹³C NMR: δ 171.2, 179.5, 170.3, 170.2 (C=O), 156.7 (C=O), 128.7-127.8 (Ph), 99.2 (α, C-1), 98.4 (β, C-1), 81.7 (CH), 79.9 (CH), 77.6 (CH), 76.9 (α, CH), 75.6 (CH₂), 73.8 (CH₂), 73.0 (CH₂), 51.1 (CH), 70.2 (CH), 69.8 (CH₂), 67.4 (α, C-4), 67.4 (PHCH₂), 66.8 (α, C-3), 66.1 (α, C-5), 62.7 (α, C-6), 58.9 (α, NCH), 55.4 (β, OMe), 52.6 (α, OMe), 30.5 (α, C-2), 20.9-20.8 (OAc), 18.5 (Me) ppm; HRMS (ESI, m/z) calcd for C₂₅H₃₃NO₁₂Na [M + Na]⁺ requires 562.1900, found 562.1912.

6-O-[3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl]-1,2,3,4-di-O-isopropylidene-D-galactopyranose (61). Colorless oil, $[\alpha]^{25}_{D}$ 25.53 (c 0.84, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.46 (d, J = 5.2 Hz, 1 H, H-1’), 5.39 (br, 1 H, H-4), 5.29-5.25 (m, 1 H, H-3), 5.04 (d, J = 3.2 Hz, 1 H, H-1), 4.60 (dd, J = 8.4, 2.0 Hz, 1 H), 4.27-4.25 (m, 1 H), 4.19-4.16 (m, 2 H), 4.09-4.02 (m, 2 H), 3.90 (m, 1 H), 3.73-3.69 (m, 1 H), 3.63-3.60 (m, 1 H), 2.07, 1.99, 1.92 (s, 9 H, 3 OAc), 2.05-2.01 (m, 1 H, H-2eq.), 1.87-1.83 (m, 1 H, H-2ax.), 1.49 (s, 3 H, Me), 1.38 (s, 3 H, Me), 1.28 (s, 6 H, 2 Me)
MMethyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-
α-D-glucopyranoside (62). Colorless oil, [α]$_D^{28}$ 85.13 (c 0.64, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33-7.25 (m, 15 H, -ArH), 5.25-5.20 (m, 2 H, H-4 and H-3), 5.03 (d, $J$= 2.8 Hz, 1 H, H-1), 4.96 (t, $J$= 11.2 Hz, 2 H, PhCH), 4.80-4.75 (m, 2 H, PhCH), 4.66 (d, $J$ = 12.0 Hz, 2 H, PhCH), 4.60-4.57 (m, 2 H, PhCH and H-1’), 4.03-3.93 (m, 4 H), 3.77-3.74 (m, 2 H), 3.62-3.60 (m, 1 H), 3.51 (dd, $J$= 9.6, 3.6 Hz, 1 H), 3.43 (t, $J$ = 9.2 Hz, 1 H), 3.36 (s, 3 H, OMe), 2.09, 1.83, 1.88 (s, 9 H, 3 OAc), 2.07-2.04 (m, 1 H, H-2eq.), 1.88-1.84 (dd, $J$ = 12.8, 5.6 Hz, 1 H, H-2ax.) ppm; $^{13}$C NMR: δ 171.2-170.1 (C=O), 138.8-138.3 (Ph), 128.6-127.6 (Ph), 98.1 (α, C-1), 97.8 (α, C-1’), 82.3 (α, C-3’), 78.1 (α, C-2’), 77.6 (α, C-4’), 75.9 (PhCH2), 75.1 (PhCH2), 73.4 (PhCH2), 70.0 (CH), 66.9 (α, C-4), 66.8 (α, C-3), 66.3 (α, C-5), 66.3 (α, C-6’), 62.6 (α, C-6), 55.3 (OMe), 30.2 (α, C-2), 21.1-20.8 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{24}$H$_{36}$O$_{13}$Na [M + Na]$^+$ requires 555.2054, found 555.2048.

Methyl 2,3,6-tri-O-benzyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-
α-D-glucopyranoside (63). Colorless oil, [α]$_D^{28}$ 63.82 (c 0.75, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.23 (m, 15 H, -ArH), 5.46 (d, $J$= 2.8 Hz, 1 H, H-1), 5.18-5.13 (m, 2 H, H-4 and H-3), 5.03 (d, $J$= 11.2 Hz, 1 H, PhCH), 4.71 (d, $J$= 11.2 Hz, 1 H, PhCH), 4.64-4.58 (m, 4 H, H-1’ and PhCH), 4.52 (d, $J$= 12.4 Hz, 1 H, PhCH), 3.95 (t, $J$ = 6.4 Hz, 1 H, H-5), 3.95-3.87 (m, 3 H, C-6 and C-3’), 3.74 (m, 1 H), 3.66-3.64 (m, 3 H, C-5’ and C=6’), 3.50 (dd, $J$= 9.6, 3.2 Hz, 1 H, H-2’), 3.39 (s, 3 H, OMe), 2.10, 1.95 (s, 9 H, 3 OAc), 1.91-1.89 (m, 1 H, H-2eq.), 1.71-1.64 (m, 1 H, H-2ax.) ppm; $^{13}$C NMR: δ 170.4-170.1 (C=O), 138.8-138.2 (Ph), 128.6-127.7 (Ph), 99.4 (α, C-1’), 97.9 (α, C-1), 82.0 (α, C-3’), 80.4 (α, C-2’), 76.5 (α, C-4’), 75.5 (PhCH2), 73.4 (PhCH2), 69.8 (α, C-5’), 69.4 (α, C-6’), 67.5 (α, C-4), 66.7 (α, C-3), 66.1 (α, C-5), 62.5 (α, C-6), 55.4 (α, OMe), 30.6 (α, C-2), 21.0-20.83 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{40}$H$_{48}$O$_{13}$Na [M + Na]$^+$ requires 759.2993, found 759.2986.
**p-Tolyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (64).**

1,2,3,4,6-Penta-O-acetyl-D-glucopyranose S1 (10.0 g, 0.0267 mol) and p-thiocresol (4.0 g, 0.032 mol) was dissolved in CH₂Cl₂ (100mL) in a flame dried flask under nitrogen atmosphere. Boron trifluoride diethyl etherate (5.60 mL, 0.04mol) was slowly added at 0 °C. After stirring for 16 hours at room temperature, the reaction mixture was diluted with CH₂Cl₂ (100mL), washed with NaHCO₃ (100 mL × 2) and brine (100 mL), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (EtOAc/Hexane = 0/1 to 1/2) to obtain 2,3,4-tri-O-acetyl-1-thio-β-D-glucopyranoside S2.

To a solution of compound S2 in methanol (100 mL) was added sodium methoxide (432.0 mg, 0.008mol) at room temperature under ambient atmosphere. After stirring for 4 hours, amberlite IR (120 H⁺) acid resin was added portionwise until the solution was neutralized. The mixture was filtered, concentrated under reduced pressure, and then volatiles were removed *in vacuo* to afford tetroglycoside S3.

To a solution of tetroglucopyranoside S3 and benzaldehyde dimethyl acetal (6.10 g, 0.040 mol) in dried acetonitrile (100 mL) was added camphorsulfonic acid (0.620 g, 2.670 mmol) in a flame dried flask under nitrogen atmosphere. After stirring for 6 hours at room temperature, the reaction solution was diluted with ethyl acetate (100 mL), washed with NaHCO₃ (50 mL × 2) and brine (50 mL), dried over anhydrous MgSO₄, filtered, concentrated under reduced pressure, and then volatiles were removed *in vacuo* to obtain 4,6-O-benzylidine-D-glucopyranoside S4.

To a solution of 4,6-O-benzylidine-D-glucopyranoside S4 in dried DMF (80 mL) was added benzyl bromide (7.0 mL, 0.059 mol) in a flame dried flask under nitrogen atmosphere. Sodium hydride (60% dispersion in mineral oil, 2.560 g, 0.064 mol) was added portionwise and gradually in the reaction solution at 0 °C. After
stirring for 16 hours at room temperature, the mixture was diluted with ethyl acetate (100 mL), quenched by water (50 mL×2) and washed with brine (50 mL), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (EtOAc/ Hexane= 0/1 to 1/4) and then volatiles were removed in vacuo to acquire the benzyl glycoside S5 as a white solid.

Compound S5 was dissolved in dried CH₂Cl₂ (50 mL) in a flame dried flask under nitrogen atmosphere. Borane-tetrahydrofuran complex (1M in THF, 130 mL, 0.13 mol) and trimethyl silyl trifluoromethanesulfonate (2.30 mL, 0.013 mol) was added subsequently in the reaction solution at 0°C. After stirring for 6 hours at 0°C, the reaction mixture was quenched by NaHCO₃ (50 mL×3), washed with brine (50 mL), dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (EtOAc/ Hexane= 0/1 to 1/2) and then volatiles were removed in vacuo to acquire the product (64) as white solid. [α]²⁸ D 4.93 (c 0.58, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.27 (m, 17 H, Ph), 7.11 (d, J=8.0 Hz, 2 H, Ph), 4.93- 4.83 (m, 3 H, PhCH), 4.76 (d, J=10.4 Hz, 1 H, PhCH), 4.61 (d, J=12.4 Hz, 2 H, PhCH and H-1), 3.89-3.83 (m, 1 H, H-6), 3.71 (t, J=9.2 Hz, 1 H, H-3), 3.70-3.65 (m, 1 H, H-6), 3.55 (t, J=9.2 Hz, 1 H, H-4), 3.45 (t, J=9.2 Hz, 1 H, H-2), 3.38-3.33 (m, 1 H, H-5), 2.33 (s, 3 H, Me), 1.89 (t, J=6.8 Hz, 1 H, OH) ppm; ¹³C NMR: δ 138.3-137.8 (C), 132.5 (CH), 129.7 (CH), 129.4 (CH), 128.4-127.6 (CH), 87.7 (CH), 86.5 (CH), 81.0 (CH), 79.2 (CH), 77.6 (CH), 75.6 (CH2), 75.3 (CH2), 75.0 (CH2), 62.0 (CH2), 20.9 (CH3) ppm; HRMS (ESI, m/z) calcd for C₃₄H₅₆O₅NaS [M + Na]⁺ requires 579.2181, found 579.2183.

**p-Tolyl 2,3,4-tri-O-benzyl-6-(3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (65).** 3.4,6-Tri-O-acetethyl glucal 1 (55.0 mg, 0.20 mmol), p-tolyl-2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside 64 (170.0 mg, 0.30 mmol), and TPPO (56.0 mg, 0.20 mmol) were dissolved in minimal CH₂Cl₂ in a flame dried flask under ambient atmosphere. After stirring homogeneously for 2 hours at room temperature, the reaction mixture was directly purified by flash column chromatography on silica gel (EtOAc/ Hexane= 0/1 to 1/1) and then volatiles were removed in vacuo to acquire p-tolyl-2,3,4-tri-O-benzyl-6-(3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosyl)-1-thio-β-D-glucopyranoside 65 (96.8%, αβ=7/1) as a white solid. α-isomer (65a): White solid, [α]²⁸ D 48.33 (c 0.57, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.34 (m, 5 H, Ph), 7.28 (br, 12 H, Ph), 7.09 (d, J=7.6 Hz, 2 H, Ph), 5.24-5.23 (m, 1 H), 4.97-4.93 (m, 2 H), 4.89-4.85 (m, 2 H), 4.79-4.76 (d, J=10.4 Hz, 1 H), 4.60-4.63 (dd, J=20.0, 11.8 Hz, 1 H), 4.17 (d, J =8.8 Hz, 1 H), 3.93 (d, J=8.8 Hz, 2 H), 3.76-3.72 (m, 1 H), 3.68-3.63 (m, 2 H),
3.50-3.39 (m, 2 H), 2.28 (s, 3 H, Me), 2.25-2.22 (m, 1 H, H-2eq.), 2.01, 1.98, 1.92 (s, 9 H, 3 OAc), 1.72 (t, J = 10.0 Hz, 1 H, H-2ax.) ppm; 13C NMR: δ 170.9-170.0 (C=O), 138.5-137.89 (Ph), 132.5 (Ph), 130.1 (Ph), 28.6-127.8 (Ph), 97.6 (C-1), 88.0 (CH), 86.9 (CH), 81.1 (CH), 78.4 (CH), 78.0 (CH), 76.0 (CH2), 75.6 (CH2), 75.1 (CH2), 69.4 (CH), 69.3 (CH), 68.1 (CH2), 62.4 (CH2), 35.1 (CH2), 21.4-20.8 (OAc) ppm; HRMS (ESI, m/z) calcd for C46H52O12NaS [M + Na]+ requires 851.3077, found 851.3065. β-isomer (65β): White solid, [α]28°D 7.27 (c 0.59, CHCl₃); 1H NMR (400 MHz, CDCl₃) δ 7.78 (J = 8.0 Hz, 2 H, Ph), 7.38 (d, J = 6.8 Hz, 2 H, Ph), 7.33-7.23 (m, 13 H, Ph), 7.09 (d, J = 8.0 Hz, 2 H, Ph), 4.99-4.88 (m, 4 H), 4.82 (t, J = 10.0 Hz, 2 H), 4.72 (d, J = 10.4 Hz, 1 H), 3.63 (d, J = 10.4 Hz, 1 H), 4.58 (d, J = 9.2 Hz, 1 H), 4.46 (d, J = 8.4 Hz, 1 H), 4.24 (dd, J = 12.0, 4.8 Hz, 1 H), 4.08 (d, J = 11.6 Hz, 2 H), 3.69 (t, J = 8.8 Hz, 1 H), 3.60 (dd, J = 11.2, 6.8 Hz, 1 H), 3.51-3.47 (m, 2 H), 3.47-3.38 (m, 2 H), 2.31 (s, 3 H, Me), 2.16 (dd, J = 12.8, 2.4 Hz, 1 H, H-2eq.), 2.02 (br, 9 H, 3 OAc), 2.04-2.02 (m, 1 H, H-2ax.) ppm; 13C NMR: δ 171.0-170.0 (C=O), 138.5-138.1 (Ph), 132.3 (Ph), 129.9 (Ph), 128.6-127.8(Ph), 100.0 (CH), 88.0 (CH), 86.9 (CH), 81.1 (CH), 79.0 (CH), 78.2 (CH), 76.0 (CH2), 75.6 (CH2), 75.1 (CH2), 72.0 (CH), 70.7 (CH), 69.4 (CH), 68.6 (CH2), 62.6 (CH2), 36.3 (CH2), 21.2-20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C46H52O12NaS [M + Na]+ requires 851.3077, found 851.3065.

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranosyl)-D-glucopyranosyl)-α-D-glucopyranoside (66). A suspension of disaccharide 65a (50.0 mg, 0.060 mmol), activated molecular sieves (4 Å, 300 mg), and AgOTf (20.0 mg, 0.072 mmol) in dried CH2Cl2 (0.5 mL) was stirred at −78 °C under nitrogen atmosphere for 1 hour. p-Toluenesulfonyl chloride (10.0 μL, 0.072mmol) was added to the reaction mixture at −78 °C. Upon completion of the reaction, the reaction solution was quenched with Et3N and filtered through a short pad of Celite®. The filtrate was evaporated in vacuo to furnish the crude product. Crude was purified by flash column chromatography (EtOAc/ Hexane= 0/1 to 1/1) on silica gel and then volatiles were removed in vacuo to give desired products 66 (71%, αβ=1/2). α-isomer (66a): Colorless oil, [α]28°D 29.06 (c 0.97, CHCl₃); 1H NMR (400 MHz, CDCl₃) δ 7.33-7.25 (m, 26 H, Ph), 5.24-7.14 (m, 4 H, Ph), 5.29-5.22 (m, 1 H), 5.02 (d, J = 2.8 Hz, 1 H), 4.99 (s, 1 H), 4.96-4.89 (m, 5 H), 4.78-4.73 (m, 4 H), 4.68-4.60 (m, 4 H), 4.48 (d, J = 11.2 Hz, 1 H), 4.28 (d, J = 8.0 Hz, 1 H), 4.19 (dd, 1 H), 4.11 (d, J = 8.0 Hz, 1 H), 3.97 (t, J = 9.6 Hz, 1 H), 3.94 (dd, J = 2.0 Hz, 1 H), 3.88-3.85 (m, 1 H), 3.78-3.75 (m, 2 H), 3.68-3.43 (m,
$^{1}$H NMR: δ 7.33–7.22 (m, 30 H, -ArH), 5.28–5.21 (m, 1 H), 4.99–4.91 (m, 8 H), 4.81–4.72 (m, 4 H), 4.69 (s, 2 H), 4.64–4.55 (m, 4 H), 4.0 (dd, $J = 12.0$, 4.0 Hz, 1 H), 3.86 (dd, $J = 12.4$, 1.6 Hz, 1 H), 3.82–3.77 (m, 4 H), 3.69–3.66 (m, 3 H), 3.53–3.49 (m, 3 H), 3.43 (dd, $J = 9.6$, 3.6 Hz, 1 H), 3.36 (s, 3 H, OMe), 2.21 (dd, $J = 12.4$, 2.0 Hz, 1H, H-2eq), 2.01, 1.99, 1.98 (s, 9 H, 3 OAc), 1.75–1.69 (m 1H, H-2ax) ppm; $^{13}$C NMR: δ 170.9–170.0 (C=O), 139.0–138.4 (Ph), 128.6–127.4 (Ph), 98.2 (CH), 97.4 (CH), 97.2 (CH), 82.3 (CH), 81.9 (CH), 80.5 (CH), 80.4 (CH), 78.0 (CH), 77.8 (CH), 75.9 (CH2), 75.7 (CH2), 75.1 (CH2), 74.9 (CH2), 73.6 (CH2), 72.6 (CH2), 70.6 (CH), 70.1 (CH), 69.5 (CH), 69.2 (CH), 68.1 (CH), 66.2 (CH2), 66.1 (CH2), 62.3 (CH2), 55.4 (CH3), 35.0 (CH2), 21.1–20.9 (OAc) ppm; HRMS (ESI, m/z) calcd for C$_{67}$H$_{76}$O$_{18}$Na [M + Na]$^+$ requires 1191.4929, found 1191.4934.

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lg fucose-Ac to fucosyl

6

7 (ω:β=2:1)

ppm

ppm
