Supporting Information

Identification of 3,6-Di-O-acetyl-1,2,4-O-orthoacetyl-α-D-glucopyranose as a Direct Evidence for the 4–O-Acyl Group Participation in Glycosylation

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General Remarks for the Synthesis

All solvents were purchased from commercial sources and were used as received unless otherwise stated. Crushed 4Å molecular sieves were activated through flame-drying immediately prior to use. Optical rotations were measured at room temperature with a Perkin–Elmer 241 MC polarimeter. ${}^1$H and ${}^{13}$C NMR spectra were recorded on a Bruker Avance 400 instrument at 400 and 100 MHz, respectively, in CDCl$_3$. TMS was used as the internal standard and all $J$ values are given in hertz. High-resolution mass spectra (ESI) were recorded with APEXIII 7.0 TESLA FTMS.

Flash column chromatography was performed on silica gel H (10-40 μ). Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with ethanol/ sulfuric acid (10%, v/v).

Preparation of Glycosyl ortho-Hexynylbenzoates

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl ortho-hexynylbenzoate (1).

To a solution of penta-O-acetyl-β-D-glucopyranose (8.0 g, 20.5 mmol) in CH$_2$Cl$_2$ (50 mL), 33% HBr/HOAc (10.6 mL, 61.5 mmol) was added slowly at 0 °C. The temperature was allowed to warm up to rt. After 21 h, the mixture was poured into a freshly prepared cold solution of sodium hydroxide. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous Na$_2$SO$_4$, and then concentrated. The crude product was stirred with ortho-hexynylbenzoic acid (5.4 g, 26.7 mmol), BnNEt$_3$Cl (1.3 g, 4.1 mmol), and K$_2$CO$_3$ (14.2 g, 102.5 mmol) in a mixed solvent of dichloromethane and distilled water (120 mL, 1:1) for 24 h at rt. The resulting mixture was diluted with brine. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 7:1 to 5:1) to give 1 (9.8 g, 90% for two steps) as a white solid: $[\alpha]_D^{25} = -27.1$ (c 2.8, CHCl$_3$); $^1$H NMR (75 MHz, CDCl$_3$) δ 7.95 (d, $J = 8.1$ Hz), 7.58–7.24 (m, 2 H), 7.33 (t, $J = 7.5$ Hz, 1 H), 5.97 (d, $J = 6.6$ Hz, 1 H), 5.40-5.28 (m, 2 H), 5.26-5.14 (m, 2 H), 4.34 (dd, $J = 3.9$, 12.6 Hz, 1 H), 4.13 (d, $J = 12.6$ Hz, 1 H), 3.94 (d, $J = 9.6$ Hz, 1 H), 2.51 (t, $J = 6.6$ Hz, 2 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.00 (s, 3 H), 1.73–1.42 (m, 4 H), 0.96 (t, $J = 7.2$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.5, 169.9, 169.3, 169.2, 163.2, 134.6, 132.5, 130.7, 129.0, 127.2, 125.8, 97.3, 92.0, 78.9, 72.7, 72.6, 70.1, 67.8, 61.4, 30.5, 21.9, 20.5, 20.43, 20.39, 19.4, 13.5; HRMS (MALDI) m/z calcd C$_{27}$H$_{32}$O$_{11}$Na [M+Na]$^+$ 555.1837, found 555.1843.

2,3,4,6-Tetra-O-acetyl-D-galactopyranosyl ortho-hexynylbenzoate (S1).
A solution of galactose pentacetate (4.00 g, 10.14 mmol) and \(\text{BnNH}_{2}\) (1.66 mL, 15.22 mmol) in THF (20 mL) was stirred at rt for 14 h. After addition of 8.0 mL of 1 N HCl, the reaction mixture was stirred for one more hour. The reaction mixture was diluted with 1 N HCl (100 mL) and extracted with \(\text{CH}_2\text{Cl}_2\). The combined extracts were dried over anhydrous \(\text{Na}_2\text{SO}_4\) and concentrated. The residue was purified by chromatography on silica gel (hexane-ethyl acetate, 3:2) to give 2,3,4,6-tetra-O-acetyl-D-galactopyranose (3.30 g) as a colorless syrup.

A solution of the above lactol (3.23 g, 9.3 mmol) and \(\text{ortho}\)-hexynylbenzoic acid (2.24 g, 11.1 mmol) in dry \(\text{CH}_2\text{Cl}_2\) (15 mL) was added DMAP (1.68 g, 13.8 mmol) and DCC (2.84 g, 13.8 mmol). After being stirred at rt for 3 h, the mixture was diluted with \(\text{CH}_2\text{Cl}_2\), washed with saturated \(\text{NaHCO}_3\) and brine. The organic layer was dried over anhydrous \(\text{Na}_2\text{SO}_4\) and then concentrated. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 5:1) to provide \(\text{S1} (4.76 \text{ g}, 90\% \text{ for two steps; } \alpha/\beta = 1:1.2)\) as a white solid. A small portion of the \(\alpha/\beta\)-anomer was separated for characterization. The \(\alpha\)-anomer: \([\alpha]_{D}^{25} = 94.9\) (c 0.9, \(\text{CHCl}_3\)); \(^1\text{H} \text{NMR (400 MHz, } \text{CDCl}_3) \delta 7.94 (d, J = 8.4 \text{ Hz, 1 H}), 7.55 (d, J = 7.2 \text{ Hz, 1 H}), 7.47 (t, J = 7.4 \text{ Hz, 1 H}), 7.35 (t, J = 7.6 \text{ Hz, 1 H}), 6.66 (d, J = 2.8 \text{ Hz, 1 H}), 5.55 (br s, 1 H), 5.48-5.40 (m, 2 H), 4.53 (t, J = 6.8 \text{ Hz, 1 H}), 4.17 (dd, J = 7.0, 11.4 Hz, 1 H), 4.07 (dd, J = 6.4, 11.2 Hz, 1 H), 2.49 (m, 2 H), 2.16 (s, 3 H), 2.00 (s, 3 H), 1.992 (s, 3 H), 1.988 (s, 3 H), 1.61 (m, 2 H), 1.49 (m, 2 H), 0.94 (t, J = 7.2 \text{ Hz, 3 H}); \(^1\text{C} \text{NMR (100 MHz, CDCl}_3) \delta 170.2, 170.1, 170.0, 169.9, 164.1, 135.1, 132.3, 130.7, 129.9, 127.3, 125.1, 96.9, 90.5, 79.7, 69.1, 67.7, 67.3, 66.6, 61.1, 30.6, 22.0, 20.6, 20.5, 19.4, 13.6; \text{HRMS (ESI) m/z} \text{ calcld } \text{C}_{27}\text{H}_{32}\text{O}_{11}\text{Na} [\text{M+Na}]^+ 555.1837, \text{found } 555.1837.

The \(\beta\)-anomer: \([\alpha]_{D}^{25} = -9.6\) (c 0.9, \(\text{CHCl}_3\)); \(^1\text{H} \text{NMR (400 MHz, } \text{CDCl}_3) \delta 7.97 (dd, J = 1.2, 7.6 \text{ Hz, 1 H}), 7.53 (dd, J = 1.2, 7.6 \text{ Hz, 1 H}), 7.47 (dt, J = 1.2, 7.6 \text{ Hz, 1 H}), 7.32 (dt, J = 1.2, 7.6 \text{ Hz, 1 H}), 5.94 (d, J = 8.0 \text{ Hz, 1 H}), 5.53-5.47 (m, 2 H), 5.15 (dd, J = 3.2, 10.4 \text{ Hz, 1 H}), 4.19-4.11 (m, 3 H), 2.51 (t, J = 7.0 \text{ Hz, 2 H}), 2.18 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.99 (s, 3 H), 1.63 (m, 2 H), 1.51 (m, 2 H), 0.95 (t, J = 7.4 \text{ Hz, 3 H}); \(^1\text{C} \text{NMR (100 MHz, CDCl}_3) \delta 170.6, 170.1, 170.0, 169.8, 169.6, 163.1, 134.5, 132.3, 130.4, 129.7, 127.0, 125.7, 97.2, 90.7, 78.7, 73.2, 70.7, 68.4, 65.6, 62.1, 30.6, 22.0, 20.74, 20.68, 20.65, 20.52, 19.4, 13.6; \text{HRMS (ESI) m/z} \text{ calcld } \text{C}_{27}\text{H}_{32}\text{O}_{11}\text{Na} [\text{M+Na}]^+ 555.1837, \text{found } 555.1837.

2,3,4,6-Tetra-O-acetyl-D-mannopyranosyl \text{ortho}\-hexynylenzoate (S2)
D-Mannopyranose pentacetate was synthesized as reported.\textsuperscript{51} Compound S2 was prepared following a procedure similar to that for the preparation of S1. Thus, silica gel chromatography gave S2 (4.83 g, 78% for three steps; \(\alpha/\beta=1.0:3\)) as a white solid. A small portion of the \(\alpha/\beta\)-anomer was separated for characterization. The \(\alpha\)-anomer: \([\alpha]_{D}^{25} = 57.1 \ (c 1.2, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.92 \ (d, \ J = 8.0 \text{ Hz, } 1 \text{ H}), 7.54 \ (d, \ J = 8.4 \text{ Hz, } 1 \text{ H}), 7.47 \ (t, \ J = 7.4 \text{ Hz, } 1 \text{ H}), 7.34 \ (t, \ J = 7.4 \text{ Hz, } 1 \text{ H}), 6.34 \ (d, \ J = 1.2 \text{ Hz, } 1 \text{ H}), 5.50 \ (dd, \ J = 3.4, 10.2 \text{ Hz}, 1 \text{ H}), 5.40 \ (m,2 \text{ H}), 4.31 \ (dd, \ J = 4.4, 12.4 \text{ Hz}, 1 \text{ H}), 4.24-4.20 \ (m, 1 \text{ H}), 4.12-4.08 \ (m, 1 \text{ H}), 2.49 \ (m, 2 \text{ H}), 2.07 \ (s, 3 \text{ H}), 2.03 \ (s, 3 \text{ H}), 2.01 \ (s, 3 \text{ H}), 1.99 \ (s, 3 \text{ H}), 1.60 \ (m, 2 \text{ H}), 1.47 \ (m, 2 \text{ H}), 0.93 \ (t, \ J = 7.2 \text{ Hz, } 3 \text{ H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.5, 169.7, 169.6, 169.4, 163.4, 135.0, 132.4, 130.7, 129.7, 127.3, 125.1, 97.0, 91.4, 79.5, 70.9, 68.8, 68.5, 65.6, 61.9, 30.6, 22.0, 20.7, 20.6, 20.55, 20.52, 19.4, 13.6; HRMS (ESI) \(m/z\) calcd C\(_{27}\)H\(_{32}\)O\(_{11}\)Na [M+Na]\(^+\) 555.1837, found 555.1837. The \(\beta\)-anomer: \([\alpha]_{D}^{25} = -27.4 \ (c 1.1, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.94 \ (dd, \ J = 1.2, 7.6 \text{ Hz}), 7.57-7.47 \ (m, 2 \text{ H}), 7.37 \ (dt, \ J = 1.2, 7.6 \text{ Hz, } 1 \text{ H}), 3.36 \ (d, \ J = 1.2 \text{ Hz}, 1 \text{ H}), 5.52 \ (dd, \ J = 3.6, 10.4 \text{ Hz, } 1 \text{ H}), 5.44-5.39 \ (m, 2 \text{ H}), 4.33 \ (dd, \ J = 4.8, 12.4 \text{ Hz, } 1 \text{ H}), 4.26-4.22 \ (m, 1 \text{ H}), 4.12 \ (dd, \ J = 2.4, 12.4 \text{ Hz, } 1 \text{ H}), 2.51 \ (t, \ J = 7.6 \text{ Hz, } 2 \text{ H}), 2.21 \ (s, 3 \text{ H}), 2.05 \ (s, 3 \text{ H}), 2.09 \ (s, 3 \text{ H}), 2.05 \ (s, 3 \text{ H}), 2.01 \ (s, 3 \text{ H}), 1.63 \ (m, 2 \text{ H}), 1.50 \ (m, 2 \text{ H}), 0.95 \ (t, \ J = 7.2 \text{ Hz, } 3 \text{ H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.3, 170.1, 169.9, 169.5, 163.2, 134.6, 132.5, 130.8, 129.1, 127.2, 125.9, 97.4, 92.5, 78.9, 71.7, 70.8, 67.8, 66.8, 60.9, 30.6, 22.0, 20.6, 20.5, 19.5, 13.6; HRMS (ESI) \(m/z\) calcd C\(_{27}\)H\(_{32}\)O\(_{11}\)Na [M+Na]\(^+\) 555.1837, found 555.1837. The 2-O-(Acetyl-d3)-3,4,6-tri-O-acetyl-D-glucopyranosyl ortho-hexynylbenzoate (9).

To a solution of penta-O-acetyl-\(\beta\)-D-glucopyranose (80.0 g, 0.20 mmol) and PCl\(_5\) (47.2 g, 0.227 mol) in CH\(_2\)Cl\(_2\) (400 mL) was added BF\(_3\)·OEt\(_2\) (210 µL, 3.3 mmol). The mixture was stirred at rt overnight and then washed with water, saturated NaHCO\(_3\), and brine, respectively. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and concentration. The resulting pale yellow solid was dissolved in a mixed solvent of acetone (400 mL), DMF (16.0 mL), and water (36.9 mL). After being stirred at rt for 24 h, the solvent was removed by rotary evaporator. The residue was dissolved with CH\(_2\)Cl\(_2\) and washed with water and brine. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and then concentrated. The residue was crystallized from diethyl ether to give S3 (21.9 g, 31%) as a white solid.\textsuperscript{52} To a solution of S3 (3.48 g, 10.0 mmol) and acetic acid-d\(_4\) (0.85 mL, 15.0 mmol) in dry...
CH$_2$Cl$_2$ (50 mL) was added DMAP (1.46 g, 15.0 mmol), EDCI (2.48 g, 13.0 mmol), and DIPEA (2.2 mL, 13.0 mmol). After being stirred at rt for 3 h, the mixture was diluted with CH$_2$Cl$_2$. The mixture was washed with saturated NaHCO$_3$ and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$ and then concentrated. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 5:1) to provide S4 (3.93 g, 100%) as a white solid: [α]$^25_D$ = 93.5 (c 0.9, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 6.33 (d, $J$ = 4.0 Hz, 1 H), 5.47 (t, $J$ = 10 Hz, 1 H), 5.16-5.08 (m, 2 H), 4.26 (dd, $J$ = 4.4, 12.4 Hz, 1 H), 4.13-4.07 (m, 2 H), 2.18 (s, 3 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.5, 170.1, 169.6, 169.3, 168.7, 89.0, 69.7, 69.1, 67.8, 61.4, 20.8, 20.6, 20.55, 20.45; HRMS (ESI) m/z calcd C$_{16}$H$_{19}$D$_3$O$_{11}$Na [M+Na]$^+$ 416.1243, found 416.1253.

To a solution of the above S4 in DMF (15.0 mL) was added hydrazine monoacetate (1.11 g, 12.0 mmol). The mixture was stirred at 60 °C under Ar. The reaction was monitored by TLC. After S4 was completely consumed, the mixture was cooled to rt, which was then diluted with ethyl acetate. The resulting mixture was washed with 5% NaCl solution and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and then concentrated to provide the crude S5 as a pale yellow syrup, which was used in the next step without further purification.

Glucopyranosyl ortho-hexynylbenzoate 9 was prepared from S5 following a procedure similar to that for the preparation of S1. Thus, treatment of lactol S5 with DMAP, EDCI, and DIPEA, after silica gel chromatography gave 9 (2.06 g, 39% for two steps; α:β = 1:3) as a white solid. A small portion of the α/β-anomer was separated for characterization. 9α: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J$ = 8.0 Hz, 1 H), 7.58 (d, $J$ = 7.6 Hz, 1 H), 7.50 (t, $J$ = 7.6 Hz, 1 H) 7.38 (t, $J$ = 8.0 Hz, 1 H), 6.63 (d, $J$ = 3.6 Hz, 1 H), 5.61 (t, $J$ = 9.8 Hz, 1 H), 5.23-5.20 (m, 2 H), 4.34-4.29 (m, 2 H), 2.60-2.46 (m, 2 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.45 (m, 2 H), 0.96 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.5, 170.0, 169.7, 169.2, 163.9, 135.1, 132.3, 130.7, 129.7, 127.3, 125.2, 97.0, 89.8, 79.6, 70.2, 70.0, 69.3, 67.9, 59.3, 30.6, 22.0, 20.5, 20.4, 19.4, 13.5; HRMS (ESI) m/z calcd C$_{27}$H$_{29}$D$_3$O$_{11}$Na [M+Na]$^+$ 558.2025, found 558.2042.

9β: [α]$^25_D$ = -25.2 (c 1.6, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, $J$ = 8.0 Hz, 1 H), 7.53 (d, $J$ = 8.0 Hz, 1 H), 7.46 (t, $J$ = 7.2 Hz, 1 H), 7.32 (t, $J$ = 7.2 Hz, 1 H), 5.97 (d, $J$ = 7.6 Hz, 1 H), 5.33-5.31 (m, 2 H), 5.21-5.16 (m, 1 H), 4.33 (dd, $J$ = 4.4, 12.4Hz, 1 H), 4.13 (d, $J$ = 13.2 Hz, 1 H), 3.93 (qd, $J$ = 2.4, 10.0 Hz 1 H), 2.50 (t, $J$ = 7.6 Hz, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.05 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.46 (m, 2 H), 0.96 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.4, 169.9, 169.3, 169.2, 163.2, 134.6, 132.5, 130.7, 129.1, 127.2, 125.8, 97.3, 92.0, 78.9, 72.7, 72.7, 70.2, 67.8, 61.4, 30.6, 21.9, 20.5, 20.4, 19.4, 13.5; HRMS (ESI) m/z calcd C$_{27}$H$_{29}$D$_3$O$_{11}$Na [M+Na]$^+$ 558.2025, found 558.2041.

4-O-(Acetyl-d$_3$)-2,3,6-tri-O-acetyl-D-glucopyranosyl ortho-hexynylbenzoate (10).
1,2,3,6-Tetra-O-acetyl-D-glucopyranose S6 was prepared from D-glucose following literature transformations (4 steps, 32% total yield).\textsuperscript{33-35} Compound 10 was prepared from S6 (3 steps, 62% total yield) following a procedure similar to that for S3\textasciitilde{}9. 10\(\alpha\): \([\alpha]\)\textsubscript{D}\textsuperscript{25} = 102.0 (c 1.4, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J = 8.0\) Hz, 1 H), 7.58 (d, \(J = 7.6\) Hz, 1 H), 7.50 (t, \(J = 7.6\) Hz, 1 H), 7.38 (t, \(J = 8.0\) Hz, 1 H), 6.61 (d, \(J = 3.9\) Hz, 1 H), 5.60 (t, \(J = 10.1\) Hz, 1 H), 5.24-5.17 (m, 2 H), 4.34-4.27 (m, 2 H), 4.11-4.06 (m, 2 H), 2.54-2.46 (m, 2 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.99 (s, 3 H), 1.65-1.60 (m, 2 H), 1.55-1.45 (m, 2 H), 0.94 (t, \(J = 7.4\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 170.0, 169.8, 169.3, 164.0, 135.2, 132.4, 130.7, 129.8, 127.3, 125.2, 97.1, 89.8, 79.7, 70.2, 70.0, 69.3, 67.9, 61.3, 30.7, 22.1, 20.6, 20.4, 19.8, 19.5, 13.6; HRMS (ESI) \(m/z\) calcd C\(_{27}\)H\(_{29}\)D\(_3\)O\(_{11}\)Na [M+Na]\(^+\) 558.2025, found 558.2042. 10\(\beta\): \([\alpha]\)\textsubscript{D}\textsuperscript{25} = -25.7 (c 2.2, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (d, \(J = 8.0\) Hz, 1 H), 7.51 (d, \(J = 8.0\) Hz, 1 H), 7.46 (t, \(J = 7.2\) Hz, 1 H), 7.32 (t, \(J = 7.2\) Hz, 1 H), 5.97 (d, \(J = 7.6\) Hz, 1 H), 5.33-5.31 (m, 2 H), 5.20-5.15 (m, 1 H), 4.33 (dd, \(J = 4.4, 12.4\) Hz, 1 H), 4.13 (dd, \(J = 2.1, 13.2\) Hz, 1 H), 3.93 (qd, \(J = 2.4, 10.0\) Hz 1 H), 2.49 (t, \(J = 7.6\) Hz, 2 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 1.98 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.46 (m, 2 H), 0.94 (t, \(J = 7.2\) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 170.1, 169.4, 169.3, 163.2, 134.7, 132.6, 130.8, 129.0, 127.3, 125.9, 97.4, 92.1, 79.0, 72.8, 72.7, 70.2, 67.8, 61.4, 30.6, 22.0, 20.6, 20.5, 19.5, 13.6; HRMS (ESI) \(m/z\) calcd C\(_{27}\)H\(_{29}\)D\(_3\)O\(_{11}\)Na [M+Na]\(^+\) 558.2025, found 558.2042.

**Glycosylation of 4-Pentenol with Peracetyl Glycosyl ortho-Hexynylbenzoates.**

**A Typical procedure.** To a mixture of a peracetyl glycosyl ortho-hexynylbenzoate (128 mg, 0.24 mmol), 4-penten-1-ol (20 \(\mu\)L, 0.20 mmol), and 4 Å MS (200 mg) in dry CH\(_2\)Cl\(_2\) (10 mL) was added a solution of PPh\(_3\)AuNTf\(_2\) in CH\(_2\)Cl\(_2\) (0.05 N, 0.4 mL). After being stirred at rt for 3 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated. The residue was subjected to silica gel column chromatography (petroleum ether-EtOAc) to provide the described products.

**With Peracetyl Glucopyranosyl ortho-Hexynylbenzoate 1.**
PPh3AuNTf2 (0.1 equiv), 4A MS, CH2Cl2, rt

\[ \text{13\%} \]

4\( \text{a/b} = 4.9:1 \)

The analytical data of compounds 4, 6, 7, 8 are in good agreement with those reported in the literatures. The yields are calculated based on the donor 1.

1,2-O-(4-Penten-1-yl)-orthoacetyl-3,4,6-tri-O-acetyl-\( \alpha \)-D-glucopyranose (3): \( [\alpha]_{D}^{25} = 30.5 \) (c 1.6, CHCl3); \( ^1\)H NMR (400 MHz, CDCl3) \( \delta \) 5.79 (m, 1 H), 5.70 (d, \( J = 4.8 \) Hz, 1 H), 5.19 (t, \( J = 2.6 \) Hz, 1 H), 5.04-4.88 (m, 3 H), 4.32-4.30 (m, 1 H), 4.21-4.19 (m, 2 H), 3.96-3.92 (m, 1 H), 3.48 (t, \( J = 6.4 \) Hz, 2 H), 2.11 (s, 3 H), 2.093 (s, 3 H), 2.087 (s, 3 H), 1.71 (s, 3 H); \( ^{13} \)C NMR (100 MHz, CDCl3) \( \delta \) 170.6, 169.6, 169.1, 137.8, 121.2, 115.0, 96.8, 73.0, 70.1, 68.1, 66.9, 63.0, 62.8, 30.1, 28.7, 20.71 (2C), 20.67, 20.61; HRMS (ESI) \( m/z \) calcld C19H28O10Na [M+Na]+ 439.1575, found 439.1577.

1,2,4-Orthoacetyl-3,6-di-O-acetyl-\( \alpha \)-D-glucopyranose (5): \( [\alpha]_{D}^{25} = 27.9 \) (c 0.6, CHCl3); \( ^1\)H NMR (400 MHz, CDCl3) \( \delta \) 5.80 (d, \( J = 4.8 \) Hz, 1 H, H-1), 5.20 (d, \( J = 4.6 \) Hz, 1 H, H-3), 4.64 (t, \( J = 6.9 \) Hz, 1 H, H-5), 4.51 (m, 1 H, H-2), 4.31 (dd, \( J = 6.9, 11.3 \) Hz, 1 H, H-6), 4.21 (m, 2 H, H-4, H-6’), 2.13 (s, 3 H), 2.10 (s, 3 H), 1.66 (s, 3 H); \( ^{13} \)C NMR (100 MHz, CDCl3) \( \delta \) 169.5, 168.4, 118.3, 96.5 (C-1), 73.8 (C-5), 71.1 (C-2), 69.3 (C-3), 63.8 (C-4), 62.6 (C-6), 19.8, 19.7, 19.0; HRMS (ESI) \( m/z \) calcld C12H16O8Na [M+Na]+ 311.0735, found 311.0735.

With Peracetyl Galactopyranosyl \textit{ortho}-Hexynylbenzoate S1.

The analytical data of S8 was in good agreement with those reported in the literature.

1,2-O-(4-Penten-1-yl)-orthoacetyl-3,4,6-tri-O-acetyl-\( \alpha \)-D-galactopyranose (S7). A pair of the diastereoisomers were isolated and assigned by COSY, HMQC, and HMBC analysis. S7-I: \( ^1\)H NMR (400 MHz, CDCl3) \( \delta \) 5.82 (m, 1 H), 5.67 (d, \( J = 4.8 \) Hz, 1 H), 5.45 (m, 1 H), 5.42 (m, 1 H), 5.05 (dd, \( J = 4.8, 17 \) Hz, 1 H), 4.97 (d, \( J = 10.4 \) Hz, 1 H), 4.36 (t, \( J = 6.4 \) Hz, 1
H), 4.20 (dd, J = 5.6, 6.4 Hz, 1 H), 4.14 (m, 2 H), 3.59 (m, 2 H), 2.15 (m, 2 H), 2.12 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 1.71 (m, 2 H), 1.59 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ 170.5, 169.9 (2C), 138.0, 121.6, 114.9, 98.0, 73.2, 71.6, 69.0, 66.2, 63.0, 61.5, 30.1, 28.6, 23.0, 20.71, 20.69, 20.58; HRMS (ESI) m/z calcd C19H28O10Na [M+Na]+ 439.1578, found 439.1575. S7-11: 1H NMR (400 MHz, CDCl3) δ 5.80 (m, 2 H), 5.43 (t, J = 2.6 Hz, 1 H), 5.07 (m, 1 H), 5.03 (d, J = 18.0 Hz, 1 H), 4.97 (d, J = 10.0 Hz, 1 H), 4.31 (m, 2 H), 4.15 (m, 2 H), 3.51 (m, 2 H), 2.12 (m, 5 H), 2.073 (s, 3 H), 2.066 (s, 3 H), 1.69-1.62 (m, 5 H); 13C NMR (100 MHz, CDCl3) δ 170.4, 170.0, 169.7, 137.9, 121.0, 114.9, 97.4, 76.2, 71.3, 69.0, 65.9, 62.1, 61.3, 30.1, 28.6, 23.5, 20.61, 20.60, 20.8; HRMS (ESI) m/z calcd C19H28O10Na [M+Na]+ 439.1578, found 439.1575.

With Peracetyl Mannopyranosyl ortho-Hexynylbenzoate S2.

S8

With 4-0-(Acetyl-d3)-2,3,6-tri-O-acetyl-D-glucopyranosyl ortho-Hexynylbenzoate (10).

1,2,4-O-(Orthoacetyl-d3)-3,6-di-O-acetyl-α-D-glucopyranose (11): [α]D25 = 27.7 (c 0.5, CHCl3); 1H NMR (400 MHz, CDCl3) δ 5.80 (d, J = 4.8 Hz, 1 H, H-1), 5.20 (d, J = 4.6 Hz, 1 H, H-3), 4.64 (t, J = 6.9 Hz, 1 H, H-5), 4.51 (m, 1 H, H-2), 4.31 (dd, J = 6.9, 11.3 Hz, 1 H, H-6), 4.21 (m, 2 H, H-4, H-6'), 2.13 (s, 3 H), 2.00 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ 169.5, 168.4, 118.3, 96.4, 76.2, 71.2, 70.4, 65.4, 62.2, 61.7, 29.9, 28.5, 24.4, 20.57, 20.54, 20.51; HRMS (ESI) m/z calcd C12H13D3O8Na [M+Na]+ 314.0926, found 314.0930.

Reference

278, 43-57.


**1H NMR and 13C NMR Spectra of New Compounds**

1H NMR of 1 (CDCl3)

13C NMR of 1 (CDCl3)
$^1$H NMR of S1α (CDCl$_3$)

$^{13}$C NMR of S1α (CDCl$_3$)
$^1$H NMR of S1β (CDCl$_3$)

$^{13}$C NMR of S1β (CDCl$_3$)
$^1$H NMR of S2α (CDCl$_3$)

$^{13}$C NMR of S2α (CDCl$_3$)
$^1$H NMR of S2β (CDCl$_3$)

$^{13}$C NMR of S2β (CDCl$_3$)
$^1$H NMR of S4 (CDCl$_3$)

$^{13}$C NMR of S4 (CDCl$_3$)
$^1$H NMR of 9α (CDCl₃)

$^{13}$C NMR of 9α (CDCl₃)
$^1$H NMR of 9β (CDCl$_3$)

$^{13}$C NMR of 9β (CDCl$_3$)
$^1$H NMR of 10α (CDCl₃)

$^{13}$C NMR of 10α (CDCl₃)
$^1$H NMR of 10β (CDCl$_3$)

$^{13}$C NMR of 10β (CDCl$_3$)
$^1$H NMR of 3 (CDCl$_3$)

$^{13}$C NMR of 3 (CDCl$_3$)
COSY of 5 (CDCl₃)

HSQC of 5 (CDCl₃)
HMBC of 5 (CDCl₃)
$^1$H NMR of S7-I (CDCl$_3$)

$^{13}$C NMR of S7-I (CDCl$_3$)
$^1$H NMR of S9 (CDCl$_3$)

$^{13}$C NMR of S9 (CDCl$_3$)
H NMR of 11 (CDCl₃)

13C NMR of 11 (CDCl₃)