A Simple glycosylation of allyl glycosides

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General Procedures. Glycosylation reactions were performed in Schlenk (Kjeldahl shape) flasks under a positive pressure of argon. The glycosylation partners were dried by azeotropic removal of water with toluene prior to initiation of the glycosylation reactions. Organic solutions were concentrated by rotary evaporation at ca. 12 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm).

Materials. Tetrahydrofuran, toluene, acetonitrile were distilled from appropriate drying reagents under a nitrogen atmosphere at 760 torr. Other chemicals were obtained from commercial vendors and used without further purification.

Instrumentation. Infrared (IR) data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C NMR) spectra were recorded on a 300 MHz and a 400 MHz NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl_3 : δ 7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration.

Spectroscopic Data

Disaccharide **11β**. Rf 0.37 (benzene/ethyl acetate 19:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.20 (m, 15 H), 5.90 (m, 1 H), 5.32 (dq, J = 17.2, 1.6 Hz, 1 H), 5.22 (ddt, J = 10.3, 1.7, 1.2 Hz, 1 H), 5.02 (s, 1 H), 4.91 (d, J = 7.7 Hz, 1 H), 4.88 (AB, J = 11.1 Hz, 1 H), 4.90-4.80 (AB, J = 11.0 Hz, 2 H), 4.71 (AB, J = 11.7 Hz, 1 H), 4.69 (AB, J = 11.1 Hz, 1 H), 4.63 (AB, J = 11.7 Hz, 1 H), 4.28-4.20 (m, 1 H), 4.19 (ABMX₂, J = 12.8, 5.3, 1.4 Hz, 1 H), 4.13 (dd, J = 5.6, 0.6 Hz, 1 H), 4.00 (ABMX₂, J = 12.8, 6.2, 1.3 Hz, 1 H), 3.98-3.91 (m, 1 H), 3.70-3.57 (m, 4 H), 3.34-3.27 (m, 1 H), 3.25-3.15 (m, 1 H), 1.51 (s, 3 H), 1.34 (s, 3 H), 1.27 (d, J = 5.7 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 138.6, 138.2, 133.6, 128.4, 128.3, 128.3, 128.1, 127.9, 127.8, 127.5, 117.8, 109.2, 101.9, 96.09, 8.85, 82.0, 78.2, 78.0, 77.9, 76.0, 75.6, 74.8, 73.2, 68.0, 64.2, 63.77, 27.8, 26.3, 17.6; FTIR (neat) cm^{-1} 3030, 2983, 2904, 1496, 1455, 1372, 1086; HRMS (ESI) m/z : Calcd for $\text{C}_{38}\text{H}_{46}\text{O}_9\text{Na}$ ($M+\text{Na}$) 669.3040, found 669.3029.

Disaccharide **11α**. Rf 0.30 (benzene/ethyl acetate 19:1); ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.20 (m, 15 H), 5.90 (m, 1 H), 5.30 (dq, J = 17.2, 1.6 Hz, 1 H), 5.21 (ddt, J = 10.3, 1.6, 1.2 Hz, 1 H), 5.01 (s, 1 H), 4.90 (s, 2 H), 3.88 (d, J = 3.7 Hz, 1 H), 4.81 (AB, J = 11.7 Hz, 1 H), 4.73 (AB, J = 11.6 Hz, 1 H), 4.69 (AB, J = 11.6 Hz, 1 H), 4.65 (AB, J = 11.6 Hz, 1 H), 4.22-4.11 (m, 3 H), 4.01-3.86 (m, 3 H), 3.86-3.75 (m, 1 H), 3.62-3.54 (m, 2 H), 3.46 (dd, J = 9.7, 3.7 Hz, 1 H), 3.37 (dd, J = 10.1, 7.4 Hz, 1 H), 1.49 (s, 3 H), 1.34 (s, 3 H), 1.31 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.8, 138.3, 138.0, 133.6, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.5, 117.8, 109.0, 98.0, 95.9, 81.4, 80.4, 79.7, 78.4, 76.1, 75.6, 74.3, 73.4, 67.8, 65.0, 60.4, 27.8, 26.5, 17.4; FTIR (neat) cm^{-1} 2904, 1496, 1369, 1086, 1027; HRMS (ESI) m/z : Calcd for $\text{C}_{38}\text{H}_{46}\text{O}_9\text{Na}$ ($M+\text{Na}$) 669.3040, found 669.3049.

Disaccharide 15α. ¹ R_f 0.47 (benzene/ethyl acetate 9:1); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.20 (m, 15 H), 5.53 (d, J = 5.1 Hz, 1 H), 4.92 (AB, J = 10.9 Hz, 1 H), 4.89 (d, J = 3.7 Hz, 1 H), 4.86 (AB, J = 10.9 Hz, 1 H), 4.75-4.68 (m, 3 H), 4.65-4.58 (m, 2 H), 4.37 (dd, J = 7.9, 1.8 Hz, 1 H), 4.32 (dd, J = 5.0, 2.4 Hz, 1 H), 4.04 (td, J = 6.1, 0.5 Hz, 1 H), 3.90 (t, J = 8.7 Hz, 1 H), 3.77 (ABX, J = 10.2, 6.0 Hz, 1 H), 3.71 (ABX, J = 10.2, 7.8 Hz, 1 H), 3.65-3.50 (m, 3 H), 3.46 (dd, J = 9.5, 3.6 Hz, 1 H), 1.55 (s, 3 H), 1.45 (s, 3 H), 1.33 (s, 3 H), 1.31 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 138.6, 138.6, 128.6, 128.5, 128.2, 128.0, 128.0, 127.9, 127.7, 109.4, 108.8, 97.4, 96.5, 81.5, 79.8, 78.3, 75.9, 73.7, 72.8, 71.0, 70.9, 70.8, 66.5, 66.0, 60.3, 29.9, 26.3, 25.2, 24.8; FTIR (neat) cm⁻¹ 2932, 1379, 1072; HRMS (ESI) *m/z*: Calcd for C₃₈H₄₆O₁₀Na (M+Na) 685.2989, found 685.2975.

Disaccharide 15β. ¹ R_f 0.37 (benzene/ethyl acetate 9:1); ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.20 (m, 15 H), 5.58 (d, J = 5.0 Hz, 1 H), 4.89 (AB, J = 11.1 Hz, 1 H), 4.88 (AB, J = 11.0 Hz, 1 H), 4.82 (AB, J = 11.0 Hz, 1 H), 4.72 (AB, J = 11.6 Hz, 1 H), 4.70 (AB, J = 11.1 Hz, 1 H), 4.61 (AB, J = 11.8 Hz, 1 H), 4.59 (dd, J = 7.9, 2.4 Hz, 1 H), 4.40 (d, J = 7.6 Hz, 1 H), 4.32 (dd, J = 5.0, 2.4 Hz, 1 H), 4.22 (dd, J = 7.9, 1.7 Hz, 1 H), 4.08-4.02 (m, 2 H), 3.90 (ABX, J = 11.7, 5.0 Hz, 1 H), 3.77 (dd, J = 12.0, 8.6 Hz, 1 H), 3.62-3.53 (m, 2 H), 3.38 (t, J = 7.7 Hz, 1 H), 3.19 (dd, J = 10.8, 9.2 Hz, 1 H), 1.49 (s, 3 H), 1.45 (s, 3 H), 1.32 (s, 3 H), 1.31 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 138.7, 138.6, 138.1, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.5, 109.4, 108.5, 104.9, 96.3, 83.6, 81.4, 77.7, 75.6, 74.5, 73.4, 71.3, 70.7, 70.4, 69.4, 67.1, 63.9; FTIR (neat) cm⁻¹ 3062, 3031, 2986, 2903, 1719, 1455, 1379, 1256, 1212, 1172, 1073; HRMS (ESI) *m/z*: Calcd for C₃₈H₄₆O₁₀Na (M+Na) 685.2989, found 685.2992.

Disaccharide 18β. ² R_f 0.30 (petroleum ether/ethyl acetate 7:1); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.10 (m, 20 H), 5.94 (m, 1 H), 5.33 (dq, J = 17.2, 1.6 Hz, 1 H), 5.24 (ddt, J = 10.4, 1.6, 1.2 Hz, 1 H), 5.03 (s, 1 H), 4.97-4.91 (m, 3 H), 4.83 (AB, J = 10.9 Hz, 1 H), 4.79 (AB, J = 11.0 Hz, 1 H), 4.71 (AB, J = 11.1 Hz, 1 H), 4.62 (AB, J = 12.3 Hz, 1 H), 4.59 (AB, J = 11.0 Hz, 1 H), 4.55 (AB, J = 12.3 Hz, 1 H), 4.24 (m, 1 H), 4.21 (ABMX₂, J = 12.8, 5.3, 1.3 Hz, 1 H), 4.14 (d, J = 5.6 Hz, 1 H), 4.02 (ABMX₂, J = 12.8, 6.2, 1.3 Hz, 1 H), 3.75-3.62 (m, 6 H), 3.44-3.38 (m, 2 H), 1.47 (s, 3 H), 1.34 (d, J = 5.9 Hz, 3 H), 1.33 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 138.7, 138.6, 138.2, 133.6, 128.3, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 117.8, 109.2, 101.6, 96.1, 84.8, 82.4, 78.3, 78.2, 77.8, 76.0, 74.8, 74.7, 73.4, 68.6, 68.0, 64.4, 27.8, 26.3, 17.7; FTIR (neat) cm⁻¹ 3063, 3030, 2984, 2907, 1496, 1370, 1077; HRMS (ESI) *m/z*: Calcd for C₄₆H₅₄O₁₀Na (M+Na) 789.3615, found 789.3644.

¹ Known compounds, see Chen, Q.; Kong, F. *Carbohydr. Res.* **1995**, 272, 149.

² Known compounds, see: Mulard, L. A.; Costachel, C.; Sansonetti, P. J. *J. Carbohydr. Chem.* **2000**, 19, 849.

Disaccharide 18α. ² Rf 0.20 (petroleum ether/ethyl acetate 7:1); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.20 (m, 18 H), 7.20-7.10 (m, 2 H), 5.88 (m, 1 H), 5.29 (dq, J = 17.2, 1.5 Hz, 1 H), 5.21 (dq, J = 10.3, 1.2 Hz, 1 H), 4.98 (s, 1 H), 4.97 (AB, J = 10.9 Hz, 1 H), 4.96 (d, J = 3.7 Hz, 1 H), 4.88 (AB, J = 10.9 Hz, 1 H), 4.83 (AB, J = 11.0 Hz, 1 H), 4.79 (AB, J = 11.6 Hz, 1 H), 4.71 (AB, J = 11.6 Hz, 1 H), 4.62 (AB, J = 12.1 Hz, 1 H), 4.52 (AB, J = 10.9 Hz, 1 H), 4.49 (AB, J = 12.1 Hz, 1 H), 4.16-4.06 (m, 4 H), 4.01-2.92 (m, 2 H), 3.83-3.76 (m, 3 H), 3.63 (dd, J = 10.5, 2.0 Hz, 1 H), 3.60 (dd, J = 9.8, 3.6 Hz, 1 H), 3.33 (dd, J = 10.2, 7.0 Hz, 1 H), 1.42 (s, 3 H), 1.30 (d, J = 6.3 Hz, 3 H), 1.24 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 138.3, 138.0, 137.8, 133.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 117.8, 108.9, 98.3, 95.9, 82.2, 80.8, 79.7, 77.8, 76.0, 75.6, 75.1, 74.3, 73.5, 70.2, 67.9, 67.8, 64.9, 29.7, 28.1, 26.3, 17.4; FTIR (neat) cm⁻¹ 3063, 3031, 2984, 2929, 1454, 1366, 1086; HRMS (ESI) *m/z*: Calcd for C₄₆H₅₄O₁₀Na (M+Na) 789.3615, found 789.3639.

Disaccharide 19β. Rf 0.50 (hexanes/ethyl acetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.15 (m, 30 H), 5.90 (m, 1 H), 5.29 (d, J = 17.2 Hz, 1 H), 5.21 (d, J = 10.4 Hz, 1 H), 5.05-4.81 (m, 6 H), 4.69-4.50 (m, 6 H), 4.39-4.31 (m, 2 H), 4.11 (ABX, J = 13.0, 5.1 Hz, 1 H), 3.94 (ABX, J = 13.0, 7.0 Hz), 3.78-3.38 (m, 11 H); ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 139.0, 138.9, 138.8, 138.5, 138.2, 133.9, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 118.6, 102.7, 95.2, 85.1, 83.5, 81.3, 78.4, 77.8, 76.0, 75.3, 75.2, 75.0, 73.6, 73.6, 60.3; FTIR (neat) cm⁻¹ 3031, 2867, 1496, 1453, 1092; HRMS (ESI) *m/z*: Calcd for C₅₆H₆₀O₁₀Na (M+Na) 915.4084, found 915.4053.

Disaccharide 19α. Rf 0.43 (hexanes/ethyl acetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.10 (m, 30 H), 5.91 (m, 1 H), 5.70 (d, J = 3.6 Hz, 1 H), 5.34 (dq, J = 17.3, 1.4 Hz, 1 H), 5.21 (dq, J = 10.4, 1.0 Hz, 1 H), 4.97 (AB, J = 10.9 Hz, 1 H), 4.85-4.80 (m, 2 H), 4.77 (AB, J = 11.1 Hz, 1 H), 4.63 (AB, J = 12.0 Hz, 1 H), 4.60-4.50 (m, 6 H), 4.39 (AB, J = 11.1 Hz, 1 H), 4.30-4.21 (m, 3 H), 4.15 (m, 1 H), 4.02-3.92 (m, 2 H), 3.75 (m, 1 H), 3.68-3.61 (m, 2 H), 3.58-3.51 (m, 3 H), 3.41 (ABX, J = 10.7, 1.6 Hz, 1 H), 3.37 (ABX, J = 10.7, 2.7 Hz, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 139.1, 138.4, 138.4, 138.3, 138.0, 134.1, 128.8, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.1, 118.1, 97.0, 95.3, 82.3, 79.9, 79.6, 78.2, 78.1, 75.7, 74.9, 73.5, 73.0, 72.6, 72.3, 69.9, 68.3, 59.5; FTIR (neat) cm⁻¹ 3062, 3030, 2869, 1453, 1362, 1074; HRMS (ESI) *m/z*: Calcd for C₅₆H₆₀O₁₀Na (M+Na) 915.4084, found 915.4119.

Disaccharide 20β. Rf 0.23 (benzene/ethyl acetate 19:1); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.15 (m, 35 H), 5.87 (m, 1 H), 5.25 (dq, J = 17.2, 1.4 Hz, 1 H), 5.17 (dq, J = 10.3, 1.1 Hz, 1 H), 4.98 (AB, J = 10.9 Hz, 2 H), 4.90 (AB, J = 10.9 Hz, 1 H), 4.83-4.73 (m, 6 H), 4.70 (AB, J = 11.1 Hz, 1 H), 4.64 (AB, J = 12.1 Hz, 1 H), 4.59 (AB, J = 12.2 Hz, 1 H), 4.57-4.48 (m, 3 H), 4.35 (d, J = 7.8 Hz, 1 H), 4.18 (dd, J = 10.8, 1.8 Hz, 1 H), 4.13 (ABMX₂, J = 13.0, 5.0, 1.3 Hz, 1 H), 4.02 (t, J = 9.3 Hz, 1 H), 3.97 (ABMX₂, J = 13.0, 5.2, 1.3 Hz, 1 H), 3.87 (m, 1 H), 3.74-3.48 (m, 8 H), 3.44 (m, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.7, 138.5, 138.5, 138.4, 138.3, 138.2, 133.8, 128.6, 128.6, 128.5, 128.5,

128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 118.5, 103.9, 95.6, 85.0, 82.2, 82.1, 79.9, 78.1, 75.9, 75.9, 75.2, 75.1, 73.6, 73.4, 70.2, 69.2, 68.6, 68.2; FTIR (neat) cm^{-1} 3031, 2910, 1497, 1454, 1358, 1070; HRMS (ESI) m/z : Calcd for $\text{C}_{64}\text{H}_{68}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}$) 1035.4659, found 1035.4690.

Disaccharide 20α. Rf 0.27 (methylenechloride/diethyl ether 60:1); ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.10 (m, 35 H), 5.91 (m, 1 H), 5.31 (d, $J = 17.2$ Hz, 1 H), 5.17 (d, $J = 10.2$ Hz, 1 H), 4.99-4.90 (m, 4 H), 4.84-4.75 (m, 4 H), 4.69-4.61 (m, 4 H), 4.58 (AB, $J = 12.2$ Hz, 1 H), 4.57 (AB, $J = 12.1$ Hz, 1 H), 4.46-4.39 (m, 2 H), 4.19-4.13 (m, 1 H), 4.03-3.93 (m, 3 H), 3.88-3.77 (m, 3 H), 3.70 (AB, $J = 11.3$ Hz, 1 H), 3.67-5.99 (m, 3 H), 3.58-3.51 (m, 2 H), 3.45 (dd, $J = 9.4, 3.6$ Hz, 1 H); FTIR (neat) cm^{-1} 3063, 3031, 2921, 1454, 1360, 1073; HRMS (ESI) m/z : Calcd for $\text{C}_{64}\text{H}_{68}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}$) 1035.4659, found 1035.4694.

Trisaccharide 21ββ. Rf 0.33 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.15 (m, 25 H), 5.90 (m, 1 H), 4.98 (AB, $J = 11.4$ Hz, 1 H), 4.93-4.86 (AB, $J = 11.0$ Hz, 2 H), 4.91 (d, $J = 7.6$ Hz, 1 H), 4.88 (d, $J = 7.4$ Hz, 1 H), 4.80 (d, $J = 12.2$ Hz, 2 H), 4.73-4.68 (m, 2 H), 4.66 (AB, $J = 12.1$ Hz, 1 H), 4.61 (AB, $J = 11.7$ Hz, 1 H), 4.51 (AB, $J = 10.1$ Hz, 1 H), 4.20-4.13 (m, 2 H), 4.10 (AB, $J = 5.6$ Hz, 1 H), 4.02-3.87 (m, 4 H), 3.65-3.56 (m, 3 H), 3.54-3.48 (m, 2 H), 3.36 (t, $J = 7.6$ Hz, 1 H), 3.26 (dd, $J = 8.7, 7.6$ Hz, 1 H), 3.22 (dd, $J = 11.5, 10.0$ Hz, 1 H), 3.04 (t, $J = 10.4$ Hz, 1 H), 1.48 (s, 3 H), 1.32 (s, 3 H), 1.25 (d, $J = 5.5$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 138.9, 138.7, 138.5, 138.4, 133.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 118.0, 109.5, 103.4, 101.8, 96.3, 84.1, 82.8, 79.8, 78.4, 78.2, 76.2, 75.9, 75.5, 75.2, 74.8, 73.5, 73.3, 68.2, 64.4, 64.1, 63.9, 28.0, 26.5, 17.8; FTIR (neat) cm^{-1} 3030, 2982, 2929, 1496, 1452, 1074; HRMS (ESI) m/z : Calcd for $\text{C}_{57}\text{H}_{66}\text{O}_{13}\text{Na}$ ($\text{M}+\text{Na}$) 981.4401, found 981.4420.

Trisaccharide 21αβ. Rf 0.27 (petroleum ether/diethyl ether 4:1); ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.15 (m, 25 H), 5.91 (m, 1 H), 5.56 (d, $J = 3.6$ Hz, 1 H), 5.33 (d, $J = 17.2$ Hz, 1 H), 5.21 (d, $J = 10.4$ Hz, 1 H), 5.01 (s, 1 H), 4.97 (d, $J = 7.8$ Hz, 1 H), 4.92 (s, 2 H), 4.88 (AB, $J = 10.5$ Hz, 1 H), 4.72 (AB, $J = 10.5$ Hz, 1 H), 4.66-4.55 (m, 4 H), 4.52 (AB, $J = 11.8$ Hz, 1 H), 4.22-4.17 (m, 2 H), 4.11 (d, $J = 5.7$ Hz, 1 H), 4.02-3.89 (m, 5 H), 3.78 (m, 1 H), 3.69-3.62 (m, 2 H), 3.51 (m, 1 H), 3.46-3.37 (m, 3 H), 3.2 (m, 1 H), 1.51 (s, 3 H), 1.35 (s, 3 H), 1.25 (d, $J = 5.2$ Hz, 3 H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.1, 138.8, 138.4, 138.3, 138.3, 133.9, 129.0, 128.6, 128.5, 128.5, 128.4, 128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.3, 118.0, 109.5, 102.1, 96.7, 96.3, 81.4, 80.1, 79.8, 79.4, 78.7, 78.3, 78.0, 76.2, 75.9, 75.0, 73.2, 73.0, 72.4, 68.2, 64.5, 63.2, 60.3, 29.9, 28.0, 26.6, 17.9; FTIR (neat) cm^{-1} 3031, 2983, 2908, 1454, 1371, 1085; HRMS (ESI) m/z : Calcd for $\text{C}_{57}\text{H}_{66}\text{O}_{13}\text{Na}$ ($\text{M}+\text{Na}$) 981.4401, found 981.4433.

Trisaccharide 21β. Rf 0.30 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.15 (m, 25 H), 5.89 (m, 1 H), 5.29 (dq, $J = 17.2, 1.54$ Hz, 1 H), 5.20 (dq, $J = 10.4, 1.1$ Hz, 1 H), 4.98 (s, 1 H), 4.95 (AB, $J = 11.4$ Hz, 1 H), 4.91 (d, $J = 7.7$ Hz, 1 H), 4.90 (s, 2 H), 4.86-4.80 (m, 3 H), 4.71 (AB, $J = 11.7$ Hz, 1 H), 4.68-4.58 (m, 3 H), 4.41 (AB, $J = 11.0$ Hz, 1 H), 4.22 (t, $J = 9.3$ Hz, 1 H), 4.17-4.09 (m, 3 H), 3.99-3.91 (m, 3 H), 3.74 (m, 1 H), 3.63 (m, 1 H), 3.59-3.52 (m, 2 H), 3.49-3.32 (m, 3 H), 3.30 (dd, $J = 10.0, 7.0$ Hz, 1 H), 3.14 (t, $J = 11.3$ Hz, 1 H), 1.46 (s, 3 H), 1.31 (s, 3 H), 1.24 (d, $J = 6.3$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 138.8, 138.4, 137.9, 133.8, 128.7, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 118.0, 109.1, 103.1, 97.6, 96.1, 84.2, 83.0, 81.4, 80.7, 78.5, 76.2, 76.2, 75.8, 75.3, 74.3, 3.3, 73.4, 68.0, 65.0, 63.9, 60.7, 28.0, 26.6, 17.8; FTIR (neat) cm^{-1} 3033, 2985, 2906, 1497, 1368, 1267, 1078; HRMS (ESI) m/z : Calcd for $\text{C}_{57}\text{H}_{66}\text{O}_{13}\text{Na}$ ($\text{M}+\text{Na}$) 981.4401, found 981.4430.

Disaccharide 22β. Rf 0.25 (benzene/ethyl acetate 19:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.20 (m, 12 H), 6.85 (d, $J = 8.5$ Hz, 2 H), 5.91 (m, 1 H), 5.34 (dq, $J = 17.2, 1.6$ Hz, 1 H), 5.22 (dq, $J = 10.4, 1.5$ Hz, 1 H), 5.01 (s, 1 H), 4.91 (d, $J = 7.6$ Hz, 1 H), 4.89 (AB, $J = 11.1$ Hz, 1 H), 4.80-4.75 (AB, $J = 10.6$ Hz, 2 H), 4.71 (AB, $J = 11.7$ Hz, 1 H), 4.69 (AB, $J = 11.1$ Hz, 1 H), 4.62 (AB, $J = 11.7$ Hz, 1 H), 4.24-4.15 (m, 2 H), 4.12 (AB, $J = 5.7$ Hz, 1 H), 4.01 (ABMX₂, $J = 12.7, 6.2, 1.3$ Hz, 1 H), 3.93 (m, 1 H), 3.80 (s, 3 H), 3.67-3.57 (m, 4 H), 3.29 (m, 1 H), 3.20 (m, 1 H), 1.51 (s, 3 H), 1.34 (s, 1 H), 1.26 (d, $J = 5.7$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.3, 138.9, 138.5, 138.9, 131.1, 129.8, 128.6, 128.5, 128.3, 128.0, 127.8, 118.0, 113.9, 109.5, 102.1, 96.3, 83.8, 82.2, 78.4, 78.2, 78.2, 76.2, 75.5, 75.0, 73.4, 68.2, 64.5, 64.0, 55.5, 28.0, 26.6, 17.8; FTIR (neat) cm^{-1} 2984, 2934, 1612, 1514, 1247, 1085; HRMS (ESI) m/z : Calcd for $\text{C}_{39}\text{H}_{48}\text{O}_{10}\text{Na}$ ($\text{M}+\text{Na}$) 699.3145, found 699.3168.

Disaccharide 22α. Rf 0.17 (benzene/ethyl acetate 19:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.25 (m, 12 H), 6.85 (d, $J = 8.5$ Hz, 2 H), 5.90 (m, 1 H), 5.31 (dq, $J = 16.8, 1.5$ Hz, 1 H), 5.22 (dq, $J = 10.4, 0.86$ Hz, 1 H), 5.01 (s, 1 H), 4.88 (d, $J = 3.6$ Hz, 1 H), 4.82 (s, 2 H), 4.81 (AB, $J = 11.5$ Hz, 1 H), 4.77-4.66 (AB, $J = 11.7$ Hz, 2 H), 4.65 (AB, $J = 11.7$ Hz, 1 H), 4.20-4.12 (m, 3 H), 4.00-3.78 (m, 7 H), 3.61-3.51 (m, 2 H), 3.46 (dd, $J = 9.7, 3.7$ Hz, 1 H), 3.37 (dd, $J = 10.0, 7.5$ Hz, 1 H), 1.45 (s, 3 H), 1.30 (s, 3 H), 1.28 (d, $J = 6.3$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.3, 138.6, 138.3, 133.8, 131.2, 129.8, 128.6, 128.4, 128.1, 128.0, 118.0, 114.0, 109.2, 98.3, 96.2, 81.5, 80.6, 78.0, 78.7, 76.4, 75.6, 74.5, 73.6, 68.0, 65.3, 60.7, 55.5, 28.0, 26.7, 17.7; FTIR (neat) cm^{-1} 2905, 1513, 1457, 1246, 1086; HRMS (ESI) m/z : Calcd for $\text{C}_{39}\text{H}_{48}\text{O}_{10}\text{Na}$ ($\text{M}+\text{Na}$) 699.3145, found 699.3175.

Disaccharide 23β. Rf 0.23 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.20 (m, 10 H), 5.91 (m, 1 H), 5.32 (dq, $J = 17.2, 1.6$ Hz, 1 H), 5.22 (ddt, $J = 10.4, 1.6, 1.2$ Hz, 1 H), 5.02 (s, 1 H), 4.92 (AB, $J = 11.5$ Hz, 1 H), 4.90 (d, $J = 7.5$ Hz, 1 H), 4.74 (AB, $J = 11.9$ Hz, 1 H), 4.65 (AB, $J = 11.5$ Hz, 1 H), 4.63 (AB, $J = 11.9$ Hz, 1 H), 4.23-4.15 (m, 2 H), 4.13-4.10 (m, 1 H), 4.00 (ABMX₂, $J = 12.8, 6.2, 1.3$ Hz, 1 H), 3.94 (dd, $J = 11.6, 5.3$ Hz, 1 H), 3.73-3.60 (m, 3 H), 3.52 (m, 1 H), 3.21 (dd, $J = 11.6, 9.7$ Hz, 1 H), 3.17 (dd, $J = 9.1, 7.6$ Hz, 1 H), 2.56 (d, $J = 2.1$ Hz,

1 H), 1.50 (s, 3 H), 1.34 (s, 3 H), 1.27 (d, J = 5.7 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 138.4, 133.8, 128.7, 128.6, 128.3, 128.1, 128.0, 127.99, 127.98, 118.0, 109.5, 101.7, 96.3, 81.3, 78.4, 78.2, 76.9, 76.3, 75.8, 74.5, 73.1, 68.2, 64.4, 64.0, 28.0, 26.6, 17.8; FTIR (neat) cm^{-1} 3486, 3064, 3030, 2984, 2934, 1497, 1454, 1372, 1242, 1221, 1084, 1026; HRMS (ESI) m/z : Calcd for $\text{C}_{31}\text{H}_{40}\text{O}_9\text{Na}$ (M+Na) 579.2570, found 579.2580.