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Synthesis of Biologically Potent α1→2 Linked Disaccharide Derivatives via Regioselective One-pot Protection-glycosylation

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General Procedures. Dichloromethane, tetrahydrofuran, acetonitrile, and toluene were purified and dried through activated alumina under argon atmosphere.[1] Anhydrous *N,N*-dimethylfomamide and pyridine were purchased from Aldrich company. Flash column chromatography[2] was carried out as recommended with Silica Gel 60 (230-400 mesh, E. Merk). 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 $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, as well as H_2SO_4 in water and subsequent heating on a hot plate. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-370 polarimeter at ~25 ^oC. ^1H and ^{13}C NMR spectra were recorded with Bruker AC300 and AMX400 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CDCl_3$ lock signal at δ 7.26. Mass spectra were obtained with a VG 70-250S mass spectrometer in the EI and FAB modes. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were measured with a Perkin-Elmer 2400CHN instrument.

Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-trimethylsilyl-α-D-glucopyranoside (8). To a mixture of methyl α-D-glucopyranoside **7** (200 mg, 1.03 mmol) and α,α-dimethoxytoluene

(0.19 mL, 1.24 mmol) in acetonitrile (4 mL) was added 10-camphorsulfonic acid (12 mg, 52 μmol) under nitrogen atmosphere. The reaction was stirred at room temperature and monitored by TLC. After total consumption of the starting material **7**, freshly dried 4Å molecular sieves (500 mg) were added to trap methanol. After 30 min, triethylamine (1.43 mL, 10.3 mmol) and chlorotrimethylsilane (0.52 mL, 4.1 mmol) were sequentially added, and the resulting solution was kept stirring overnight. The mixture was evaporated *in vacuo*, and the residue was diluted with hexane followed by filtration. The filtrate was evaporated to get a solid, which was recrystallized in 95% ethanol to afford **8** (325 mg, 74 %) as colorless crystallines. The physical data is identical with the literature report.[3]

General Procedure for the Regioselective 3-*O*-Benzylation and 3-*O*-Allylation. A mixture of the trimethylsilyl ether (1.0 eq), freshly dried 3Å molecular sieves (1 mg per 1 mg trimethylsilyl ether), aldehyde (1.2 eq), triethylsilane (1.2 eq), and dichloromethane (8.5 mL per 1 mmol trimethylsilyl ether) was stirred at room temperature for 30 min under nitrogen atmosphere. The mixture was cooled down to –78 or –86 ^{o}C, trimethylsilyl trifluoromethanesulfonate (0.1 eq) was slowly added, and the reaction was monitored by TLC. After the starting material was totally consumed, a 1M solution of tetra-*n*-butylammonium fluoride (2.0 eq) in tetrahydrofuran was added, and the reaction mixture was gradually warmed up to room temperature. After stirring for 1.5 h, the resulting solution was filtered through celite, and the filtrate was evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the desired product. The yields are illustrated in Table 1 and 2, respectively.

Compounds 9, 10, 15, 19, 23, and 27. Comparison of our data of compounds **9**,[4] **10**,[5] **15**,[6] **19**,[7] **23**,[8] and **27**[9] with the literature report revealed identity with respect to ^{1}H or ^{13}C spectra.

Methyl 4,6-*O*-Benzylidene-3-*O*-(3,4-dimethoxybenzyl)-α-D-glucopyranoside (11).

$[\alpha]^{28}_{D}$ = +55.3 (*c*=0.50, in $CHCl_3$); m.p 150-151 ^{o}C; IR ($CHCl_3$): ν = 3414, 2971, 2869, 1466, 1370, 994, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H, PhH), 7.38-7.35 (m, 3H, PhH), 6.90 (d, *J* = 2.0 Hz, 1H, 3,4-diOMePhH), 6.87 (dd, *J* = 8.4, 2.0 Hz, 1H, 3,4-diOMePhH), 6.78 (d, *J* = 8.4 Hz, 1H, 3,4-diOMePhH), 5.55 (s, 1H, PhCH), 4.85 (d, *J* = 11.2 Hz, 1H, 3,4-diOMePhCH_2), 4.78 (d, *J* = 4.0 Hz, 1H, H-1), 4.72 (d, *J* = 11.2 Hz, 1H, 3,4-diOMePhCH_2), 4.27 (dd, *J* = 9.6, 4.0 Hz, 1H, H-6_{eq}), 3.84 (s, 3H, OCH_3), 3.81 (dt, *J* = 9.6, 4.4 Hz, 1H, H-5), 3.78 (t, *J* = 9.6 Hz, 1H, H-3), 3.74 (t, *J* = 9.6 Hz, 1H, H-6_{ax}), 3.71 (s, 3H, OCH_3), 3.70 (ddd, *J* = 9.6, 8.0, 4.0 Hz, 1H, H-2), 3.43 (s, 3H, OCH_3), 2.22 (d, *J* = 8.0 Hz, 1H, OH-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.00 (C), 148.69 (C), 137.39 (C), 130.96 (C), 129.03 (CH), 128.26 (CH), 126.08 (CH), 120.63 (CH), 111.50 (CH), 110.89 (CH), 101.42 (CH), 99.90 (CH), 81.85 (CH), 78.39 (CH), 74.67 (CH_2), 72.53 (CH), 69.03 (CH_2), 62.59 (CH), 55.87 (CH_3), 55.67 (CH_3), 55.41 (CH_3); HRMS (FAB, M^+) calcd for $C_{23}H_{28}O_8$ 432.1784, found 432.1790. Anal. Calcd for $C_{23}H_{28}O_8$: C, 63.88; H, 6.53. Found: C, 63.58; H, 6.41.

Methyl 4,6-*O*-Benzylidene-3-*O*-(4-chlorobenzyl)-α-D-glucopyranoside (12). $[\alpha]^{26}_{D}$ = +79.0 (*c*=1.0, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H, PhH), 7.38-7.35 (m, 3H, PhH), 7.29-7.23 (m, 4H, 4-ClPhH), 5.33 (s, 1H, PhCH*)*, 4.87 (d, *J* = 12.0 Hz, 1H, 4-Cl$PhCH_2$), 4.79 (d, *J* = 3.6 Hz, 1H, H-1), 4.75 (d, *J* = 12.0 Hz, 1H, 4-Cl$PhCH_2$), 4.27 (dd, *J* = 9.6, 4.2 Hz, 1H, H-6_{eq}), 3.80 (dt, *J* = 9.6, 4.2 Hz, 1H, H-5), 3.76 (t, *J* = 9.6 Hz, 1H, H-6_{ax}), 3.73 (t, *J* = 9.6 Hz, 1H, H-3), 3.70 (ddd, *J* = 9.6, 8.4, 3.6 Hz, 1H, H-2), 3.60 (t, *J* = 9.6 Hz, 1H, H-4), 3.43 (s, 3H, OCH_3), 2.22 (d, *J* = 8.4 Hz, 1H, OH-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.27 (C), 137.00 (C), 133.37 (C), 129.25 (CH), 129.02 (CH), 128.46 (CH), 128.25 (CH), 127.97 (CH), 101.37 (CH), 99.87 (CH), 81.75 (CH), 78.99 (CH), 73.86 (CH_2), 72.48 (CH), 68.98 (CH_2), 62.54 (CH), 55.41 (CH_3); HRMS (FAB, MH^+) calcd for $C_{21}H_{24}ClO_6$ 407.1262, found 407.1257.

Methyl 4,6-*O*-Benzylidene-3-*O*-[(2-naphthyl)methyl]-α-D-glucopyranoside (13). $[\alpha]^{27}_{D}$ = +69.9 (*c*=1.0, in $CHCl_3$); IR ($CHCl_3$): ν = 3422, 2927, 2871, 1450, 1367, 1077, 994, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.71 (m, 4H, 2-NapH), 7.49-7.48 (m, 3H, 2-NapH), 7.45-7.40 (m, 2H, PhH), 7.38-7.36 (m, 3H, PhH), 5.57 (s, 1H, PhCH), 5.09 (d, *J* = 11.9 Hz, 1H, 2-NapCH_2), 4.95 (d, *J* = 11.9 Hz, 1H, 2-NapCH_2), 4.80 (d, *J* = 4.0 Hz, 1H, H-1), 4.28 (dd, *J* = 9.6, 4.4 Hz, 1H, H-6_{eq}), 3.85 (t, *J* = 9.2 Hz, 1H, H-3), 3.81-3.72 (m, 3H, H-5, H-6_{ax}, H-2), 3.66 (t, *J* = 9.2 Hz, 1H, H-4), 3.43 (s, 3H, OCH_3), 2.28 (d, *J* = 8.2 Hz, 1H, OH-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.35 (C), 135.90 (C), 133.25 (C), 132.97 (C), 128.95 (CH), 128.22 (CH), 128.07 (CH), 127.90 (CH), 127.61 (CH), 126.66 (CH), 126.06 (CH), 126.00 (CH), 125.93 (CH), 125.77 (CH), 101.34 (CH), 99.88 (CH), 81.85 (CH), 78.73 (CH), 74.70 (CH_2), 72.51 (CH), 68.98 (CH_2), 62.54 (CH), 55.33 (CH_3); HRMS (FAB, MH^+) calcd for $C_{25}H_{27}O_6$ 423.1808, found 423.1812.

Methyl 4,6-*O*-Benzylidene-3-*O*-(E-2-butenyl)-α-D-glucopyranoside (14). $[\alpha]^{25}_{D}$ = +108.3 (*c*=0.24, in $CHCl_3$); m.p 142-143 °C; IR ($CHCl_3$): ν = 3426, 2922, 2866, 1448, 1364, 1075, 991, 744, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H, PhH), 7.37-7.33 (m, 3H, PhH), 5.75-5.66 (m, 1H, $CH_3C\mathit{H}$=$CHCH_2$), 5.64-5.55 (m, 1H, CH_3CH=$C\mathit{H}CH_2$), 5.52 (s, 1H, PhCH), 4.79 (d, *J* = 3.6 Hz, 1H, H-1), 4.32 (dd, *J* = 11.6, 6.0 Hz, 1H, CH_3CH=$CHC\mathit{H_2}$), 4.26 (dd, *J* = 9.6, 4.0 Hz, 1H, H-6_{eq}), 4.17 (dd, *J* = 11.6, 6.0 Hz, 1H, CH_3CH=$CHC\mathit{H_2}$), 3.80 (dt, *J* = 9.6, 4.0 Hz, 1H, H-5), 3.75-3.61 (m, 3H, H-4, H-6_{ax}, H-2), 3.54 (t, *J* = 9.0 Hz, 1H, H-3), 3.44 (s, 3H, OCH_3), 2.30 (d, *J* = 6.8 Hz, 1H, OH-2), 1.17 (d, *J* = 6.1 Hz, 3H, $C\mathit{H_3}CH$=$CHCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.40 (C), 129.98 (CH), 128.92 (CH), 128.21 (CH), 127.73 (CH), 126.01 (CH), 101.24 (CH), 99.86 (CH), 81.95 (CH), 78.18 (CH), 73.65 (CH_2), 72.26 (CH), 69.01 (CH_2), 62.65 (CH), 55.40 (CH_3), 17.78 (CH_3); HRMS (FAB, MH^+) calcd for $C_{18}H_{25}O_6$ 337.1652, found 337.1641.

Methyl 3-*O*-Benzyl-4,6-*O*-isopropylidene-α-D-glucopyranoside (17). $[\alpha]^{25}_{D}$ = +95.5

(c=0.55, in $CHCl_3$); IR ($CHCl_3$): ν = 3467, 2986, 2913, 1450, 1264, 1056, 847 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H, PhH), 4.87 (d, 1H, J = 11.5 Hz, $PhCH_2$), 4.74 (d, 1H, J = 2.7 Hz, H-1), 4.73 (d, 1H, J = 11.5 Hz, $PhCH_2$), 3.87-3.83 (m, 1H, H-6_{eq}), 3.75-3.70 (m, 1H, J = 10 Hz, H-5), 3.66-3.62 (m, 4H, H-2, H-3, H-4, H-6_{ax}), 3.40 (s, 3H, OCH_3), 2.29 (s, 1H, 2-OH), 1.46 (s, 3H, CH_3), 1.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8 (C), 128.29 (CH), 127.81 (CH), 127.56 (CH), 99.82 (CH), 99.31 (C), 79.18 (CH), 74.64 (CH), 74.46 (CH_2), 72.27 (CH), 63.44 (CH), 62.52 (CH_2), 55.26 (CH_3), 29.18 (CH_3), 9.10 (CH_3). Anal. Calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.70; H, 7.49.

4-Methylphenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (21). $[\alpha]^{29}_D$ = -87.8 (c=1.0, in $CHCl_3$); m.p 165-166 °C; IR ($CHCl_3$): ν = 3014, 1523, 1426, 1219, 1043, 923, 765, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 4H, ArH), 7.39-7.26 (m, 8H, ArH), 7.12 (d, J = 8.0 Hz, 2H, 4-MePhH), 5.55 (s, 1H, PhCH), 4.93 (d, J = 11.6 Hz, 1H, $PhCH_2$), 4.78 (d, J = 11.6 Hz, 1H, $PhCH_2$), 4.55 (d, J = 9.7 Hz, 1H, H-1), 4.37 (dd, J = 10.5, 5.0 Hz, 1H, H-6_{eq}), 3.77 (t, J = 10.5 Hz, 1H, H-6_{ax}), 3.67 (t, J = 8.8 Hz, 1H, H-4), 3.62 (t, J = 8.8 Hz, 1H, H-3), 3.51-3.45 (m, 2H, H-2, H-5), 2.57 (d, J = 0.9 Hz, 1H, OH-2), 2.34 (s, 3H, $SPhCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.70 (C), 138.19 (C), 137.19 (C), 133.78 (CH), 129.79 (CH), 128.97 (CH), 128.42 (CH), 128.22 (CH), 128.07 (CH), 127.83 (CH), 127.22 (C), 125.98 (CH), 101.21 (CH), 88.56 (CH), 81.60 (CH), 81.10 (CH), 74.77 (CH_2), 72.12 (CH), 70.69 (CH), 68.60 (CH_2), 21.14 (CH_3).

6^A,6^B,6^C,6^D,6^E,6^F,6^G-Hepta-*O*-benzyl-β-cyclodextrin (25). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.20 (m, 5H, ArH), 6.60 (s, 1H, OH), 5.21 (s, 1H, OH), 4.97 (d, J = 3.2 Hz, 1H, H-1), 4.56 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.37 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.03 (t, J = 9.2 Hz, 1H, H-3), 3.86 (m, 1H, H-5), 3.76 (dd, J = 9.2, 3.2 Hz, 1H, H-2), 3.71 (dd, J = 10.0, 4.4 Hz, 1H, H-6a), 3.58 (t, J = 10.0 Hz, 1H, H-6b), 3.56 (t, J = 9.2 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.09 (C), 128.33 (CH), 127.60 (CH×2), 102.08 (CH), 82.52 (CH),

73.87 (CH), 73.33 (CH_2), 73.25 (CH), 71.13 (CH), 68.65 (CH_2); MS (MALDI, M^++Na) calcd for $C_{91}H_{112}NaO_{35}$ 1788 found 1788.

Methyl 3,4-*O*-Isopropylidene-6-*O*-(4-methoxybenzyl)-α-D-galactopyranoside (28). IR ($CHCl_3$): ν = 3618, 3020, 2938, 1606, 1513, 1474, 1423, 1389, 1214, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 11.3 Hz, 2H, 4-OMePhH), 6.85 (d, *J* = 11.3 Hz, 2H, 4-OMePhH), 4.75 (d, *J* = 3.8 Hz, 1H, H-1), 4.56 (d, *J* = 11.6 Hz, 1H, 4-OMePhCH_2), 4.46 (d, *J* = 11.6 Hz, 1H, 4-OMePhCH_2), 4.20-4.12 (m, 3H, H-3, H-4, H-5), 3.80-3.76 (m, 1H, H-2), 3.78 (s, 3H, OCH_3), 3.72-3.64 (m, 2H, H-6a, H-6b), 3.44 (s, 3H, OCH_3), 2.30 (d, *J* = 6.7 Hz, 1H, OH-2), 1.50 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.18 (C), 130.35 (C), 129.20 (CH), 113.75 (CH), 109.51 (C), 98.42 (CH), 76.13 (CH), 73.30 (CH), 73.08 (CH_2), 69.57 (CH), 69.24 (CH_2), 67.32 (CH), 55.44 (CH_3), 55.26 (CH_3), 27.73 (CH_3), 25.93 (CH_3).

Methyl 3,4-*O*-Isopropylidene-6-*O*-(2-naphthylmethyl)-α-D-galactopyranoside (29). IR ($CHCl_3$): ν = 3612, 3019, 2973, 1525, 1477, 1425, 1217, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.78 (m, 4H, NapH), 7.47-7.43 (m, 3H, NapH), 4.80 (d, *J* = 12.3 Hz, 1H, NapCH_2), 4.77 (d, *J* = 3.8 Hz, 1H, H-1), 4.70 (d, *J* = 12.3 Hz, 1H, NapCH_2), 4.22-4.18 (m, 3H, H-3, H-4, H-5), 3.79-3.71 (m, 3H, H-2, H-6a, H-6b), 3.38 (s, 3H, OCH_3), 2.28 (s, 1H, OH-2), 1.47 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.74 (C), 128.12 (CH), 127.83 (CH), 127.68 (CH), 126.33 (CH), 126.08 (CH), 125.84 (CH), 125.66 (CH), 109.56 (C), 98.42 (CH), 76.12 (CH), 73.52 (CH_2), 73.31 (CH), 69.55 (CH_2), 67.37 (CH), 55.46 (CH_3), 27.72 (CH_3), 25.92 (CH_3); HRMS (FAB, M^+) calcd for $C_{21}H_{26}O_6$ 374.1729, found 374.1736.

Ethyl 6-*O*-Benzyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (31). $[\alpha]^{24}_D$ = -11.5 (*c*=1.65, in $CHCl_3$); IR ($CHCl_3$): ν = 3446, 2932, 1455, 1372, 1219, 1084, 871 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 5H, PhH), 4.62 (d, *J* = 12.0 Hz, 1H, PhCH_2), 4.53

(d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.23 (d, *J* = 10.2 Hz, 1H, H-1), 4.20 (dd, *J* = 5.4, 2.2 Hz, 1H, H-4), 4.03 (dd, *J* = 7.0, 5.4 Hz, 1H, H-3), 4.94 (dt, *J* = 6.0, 2.2 Hz, 1H, H-5), 3.76 (d, *J* = 6.0 Hz, 2H, H-6a, H-6b), 3.54 (ddd, *J* = 10.2, 7.0, 1.7 Hz, 1H, H-3), 2.77-2.68 (m, 2H, SCH_2CH_3), 2.35 (d, *J* = 1.7 Hz, 1H, OH-2), 1.49 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.30 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.13 (C), 128.32 (CH), 127.59 (CH×2), 110.08 (C), 85.49 (CH), 78.92 (CH), 75.92 (CH), 73.78 (CH), 73.52 (CH_2), 72.19 (CH), 69.49 (CH_2), 28.14 (CH_3), 26.26 (CH_3), 24.50 (CH_2), 15.34 (CH_3).

Methyl 4,6-*O*-Benzilidene-3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galatopyranosyl)-α-D-glucopyranoside (34). $[\alpha]^{27}_D$ = +96.4 (*c*=1.0, in $CHCl_3$); IR ($CHCl_3$): ν = 2913, 2850, 1719, 1655, 1556, 1451,1365, 1052 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.47 (m, 2H, PhH), 7.40-7.24 (m, 26H, PhH), 7.18-7.12 (m, 2H, PhH), 5.53 (s, 1H, PhCH), 4.98 (d, *J* = 3.5 Hz, 1H, H-1'), 4.91 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.90 (d, *J* = 10.9 Hz, 1H, $PhCH_2$), 4.89 (d, *J* = 3.9 Hz, 1H, H-1), 4.84 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.81 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.30-4.28 (m, 3H, $PhCH_2$, H-5'), 4.28 (dd, *J* = 10.2, 3.1 Hz, 1H, $H\text{-}6_{eq}$), 4.10 (t, *J* = 9.6 Hz, 1H, H-3), 4.04 (dd, *J* = 10.1, 3.5 Hz, H-2'), 3.95 (dd, *J* = 10.1, 2.7 Hz, 1H, H-3'), 3.86 (dd, *J* = 9.6, 3.9 Hz, 1H, H-2), 3.84 (dt, *J* = 10.1, 4.7 Hz, 1H, H-5), 3.78 (d, *J* = 1.8 Hz, 1H, H-4'), 3.71 (t, *J* = 10.2 Hz, 1H, $H\text{-}6_{ax}$), 3.55 (t, *J* = 9.6 Hz, 1H, H-4), 3.49 (dd, *J* = 9.7, 6.4 Hz, 1H, H-6a'), 3.43 (s, 3H, OCH_3), 3.35 (dd, 1H, *J* = 9.7, 6.4 Hz, H-6b'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.88 (C), 138.84 (C), 138.70 (C), 138.69 (C), 138.41 (C), 137.41 (C), 128.86 (CH), 128.34 (CH), 128.25 (CH), 128.17 (CH), 128.07 (CH), 127.88 (CH), 127.56 (CH), 127.48 (CH), 127.44 (CH), 127.37 (CH), 125.99 (CH), 101.19 (CH), 97.38 (CH), 94.87 (CH), 82.38 (CH), 78.80 (CH), 77.20 (CH), 76.99 (CH), 75.97 (CH), 75.32 (CH_2), 75.03 (CH), 74.72 (CH_2), 73.98 (CH), 73.07 (CH_2), 72.90 (CH_2), 72.80 (CH_2), 69.00 (CH_2), 68.92 (CH), 68.86 (CH_2), 62.31 (CH), 55.35 (CH_3); HRMS (FAB, MH^+) calcd

for $C_{55}H_{57}O_{11}$ 893.3901, found 893.3908.

Methyl 4,6-*O*-Benzylidene-3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-α-D-glucopyranoside (35). $[\alpha]^{27}_{D}$ = +55.7 (*c*=1.0, in $CHCl_3$); IR ($CHCl_3$): ν = 2914, 2855, 1607, 1452, 1371 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H, PhH), 7.40-7.24 (m, 23H, PhH), 7.18-7.12 (m, 2H, PhH), 7.10-7.08 (m, 1H, PhH), 7.03-7.00 (m, 2H, PhH), 5.51 (s, 1H, PhCH), 4.92 (d, *J* = 2.9 Hz, 1H, H-1'), 4.90 (d, *J* = 12.2 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 3.0 Hz, 1H, H-1), 4.72 (d, *J* = 10.6 Hz, 1H, $PhCH_2$), 4.68 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 9.2 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.51 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.35 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.27 (dd, *J* = 9.5, 4.4 Hz, 1H, $H\text{-}6_{eq}$), 4.07 (dd, *J* = 9.4, 3.2 Hz, 1H, H-5'), 4.05 (t, *J* = 9.4 Hz, 1H, H-4'), 3.98 (dd, *J* = 9.4, 2.9 Hz, 1H, H-3'), 3.90 (dd, *J* = 2.9, 1.8 Hz, 1H, H-2'), 3.86 (d, *J* = 2.3 Hz, 1H, H-2), 3.84 (t, *J* = 9.5 Hz, 1H, $H\text{-}6_{ax}$), 3.77 (dt, *J* = 9.5, 4.2 Hz, 1H, H-5), 3.69 (t, *J* = 9.5 Hz, 1H, H-4), 3.69 (dd, *J* = 9.4, 2.0 Hz, 1H, H-6a'), 3.58 (dd, 1H, *J* = 9.4, 0.9 Hz, H-6b'), 3.53 (t, *J* = 9.5 Hz, H-3), 3.32 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.88 (C), 138.85 (C), 138.45 (C), 138.37 (C), 137.96 (C), 137.35 (C), 128.86 (CH), 128.56 (CH), 128.34 (CH), 128.31 (CH), 128.26 (CH), 128.19 (CH), 128.15 (CH), 128.01 (CH), 127.83 (CH), 127.72 (CH),127.51 (CH), 127.30 (CH), 125.94 (CH), 101.16 (CH), 97.04 (CH), 94.84 (CH), 82.00 (CH), 80.08 (CH), 77.00 (CH), 75.63 (CH), 74.94 (CH_2), 74.83 (CH_2), 74.59 (CH), 73.11 (CH_2), 72.87 (CH_2), 72.30 (CH_2), 72.30 (CH), 71.43 (CH), 68.93 (CH_2), 68.80 (CH_2), 62.29 (CH_2), 55.23 (CH_3); HRMS (FAB, MH^+) calcd for $C_{55}H_{57}O_{11}$ 893.3901, found 893.3897.

Methyl 3,4-*O*-Isopropylidene-6-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-α-D-galactopyranoside (38). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.42-7.24 (m, 20H, PhH), 5.15 (d, *J* = 3.8 Hz, 1H, H-1'), 4.97 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.89 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 3.6 Hz, 1H, H-1), 4.76 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.72 (d, *J* =

11.8 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.35 (dd, *J* = 8.1, 5.4 Hz, 1H, H-3), 4.19 (dd, *J* = 5.4, 2.5 Hz, 1H, H-4), 4.14 (ddd, *J* = 7.4, 5.2, 2.5 Hz, 1H, H-5), 4.02 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2'), 4.00-3.95 (m, 2H, H-5', H-3'), 3.77 (dd, *J* = 10.1, 5.2 Hz, 1H, H-6a), 3.73 (dd, *J* = 10.1, 7.4 Hz, 1H, H-6b), 3.69 (dd, *J* = 8.1, 3.6 Hz, H-2), 3.66 (d, *J* = 2.3 Hz, 1H, H-4'), 3.37 (s, 3H, OCH_3), 1.50 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.08 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.19 (C), 138.81 (C), 138.60 (C), 138.27 (C), 128.86 (CH), 128.52 (CH), 128.35 (CH), 128.28 (CH), 128.15 (CH), 128.02 (CH), 127.88 (CH), 127.57 (CH), 127.38 (CH), 127.34 (CH), 109.15 (C), 99.48 (CH), 99.36 (CH), 82.43 (CH), 79.20 (CH), 78.10 (CH), 77.21 (CH), 76.02 (CH), 75.11 (CH), 74.75 (CH_2), 73.88 (CH), 73.48 (CH_2), 73.38 (CH_2), 72.13 (CH_2), 66.47 (CH), 55.35 (CH_3), 28.41 (CH_3), 26.51 (CH_3), 16.72 (CH_3).

Methyl 3,4-*O*-Isopropylidene-6-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galacto-pyranosyl)-α-D-galactopyranoside (39). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.22 (m, 25H, PhH), 4.93 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 4.0 Hz, 1H, H-1'), 4.81 (d, *J* = 12.5 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 3.5 Hz, 1H, H-1), 4.72 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.65 (d, *J* = 12.5 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.40 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.36 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.32 (dd, *J* = 8.0, 5.0 Hz, 1H, H-3), 4.23 (dd, *J* = 8.5, 5.2 Hz, 1H, H-6a'), 4.17 (dd, *J* = 5.0, 2.5 Hz, 1H, H-4), 4.16 (ddd, *J* = 7.0, 5.2, 2.5 Hz, 1H, H-5), 4.08 (d, *J* = 2.5 Hz, 1H, H-4'), 4.07 (dd, *J* = 9.5, 2.5 Hz, H-3'), 4.02 (dd, *J* = 9.5, 4.0 Hz, 1H, H-2'), 3.78 (dd, *J* = 8.0, 3.5 Hz, H-2), 3.75 (dd, dd, *J* = 8.5, 5.2 Hz, 1H, H-6a), 3.72 (dd, *J* = 10.5, 7.0 Hz, 1H, H-6b), 3.60 (t, *J* = 8.5 Hz, 1H, H-6b'), 3.42 (dd, *J* = 8.5, 5.2 Hz, 1H, H-5'), 3.40 (s, 3H, OCH_3), 1.35 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.19 (C × 2), 138.89 (C), 138.27 (C), 138.04 (C), 128.34 (CH),

128.27 (CH), 128.22 (CH), 128.14 (CH), 128.12 (CH),127.87 (CH), 127.72 (CH), 127.66 (CH), 127.56 (CH), 127.48 (CH), 127.40 (CH), 127.34 (CH), 109.12 (C), 96.70 (CH), 95.34 (CH), 78.91 (CH), 77.20 (CH), 76.03 (CH), 74.91 (CH_2), 74.76 (CH), 77.61 (CH), 73.67 (CH), 73.48 (CH_2), 73.41 (CH_2), 73.08 (CH_2), 72.82 (CH_2), 69.61 (CH_2), 68.83 (CH), 68.60 (CH_2), 66.58 (CH), 55.37 (CH_3), 28.06 (CH_3), 26.39 (CH_3).

Methyl 3,4-*O*-Isopropylidene-6-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-galactopyranoside (**40**)**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.22 (m, 23H, PhH), 7.17-7.15 (m, 2H, PhH), 4.98 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 3.7 Hz, 1H, H-1'), 4.83 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.81 (d, *J* = 3.2 Hz, 1H, H-1), 4.81 (d, *J* = 11.3 Hz, 1H, $PhCH_2$), 4.75 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.65 (d, *J* = 12.2 Hz, 2H, $PhCH_2$), 4.58 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.49 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.42 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.30 (dd, *J* = 7.8, 5.4 Hz, 1H, H-3), 4.18-4.15 (m, 2H, H-6a, H-4), 4.09-4.05 (m, 2H, H-6b, H-5'), 3.79 (dd, *J* = 7.8, 3.2 Hz, 1H, H-2), 3.78-3.71 (m, 4H, H-4', H-3', H-5, H-6a'), 3.57 (dd, *J* = 8.6, 1.4 Hz, 1H, H-6b'), 3.56 (dd, *J* = 9.7 Hz, 1H, H-2'), 3.43 (s, 3H, OCH_3), 1.39 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.94 (C), 138.48 (C × 2), 138.24 (C), 137.93 (C), 129.65 (CH), 128.34 (CH), 128.30 (CH), 127.94 (CH), 127.86 (CH), 127.75 (CH), 127.56 (CH), 127.50 (CH), 109.07 (C), 96.70 (CH), 94.91 (CH), 81.80 (CH), 79.43 (CH), 77.55 (CH), 75.60 (CH_2), 74.49 (CH), 73.72 (CH), 73.61 (CH), 73.52 (CH_2), 73.45 (CH_2), 72.89 (CH_2), 70.04 (CH), 69.58 (CH_2), 68.16 (CH_2), 66.60 (CH), 55.30 (CH_3), 28.25 (CH_3), 26.29 (CH_3).

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