Synthesis of the Trisaccharide Repeating Unit of the Atypical *O*-Antigen Polysaccharide from Danish *Helicobacter pylori* Strains Employing the 2'-Carboxybenzyl Glycoside Method

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Supporting Information

General Methods. All reactions were conducted under a positive pressure of dry argon with dry, freshly distilled solvents unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane and acetonitrile were distilled from calcium hydride and DMF was distilled from barium oxide. Ethyl acetate and toluene were distilled and petroleum ether was used in the boiling range of 35–65 °C. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. NMR spectra were recorded on a 250 or 500 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS).

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (7). A solution of methyl 4,6-*O*-benzylidene- α -D-mannopyranoside (**6**)¹ (250 mg, 0.86 mmol), PMBCl (116 μ L, 0.86 mmol), and NaH (60%, 0.35 mmol, 0.88 mmol) in DMF (5 mL) was stirred at 0 °C for 1 h. The reaction mixture was quenched with NH₄Cl (5 mL) and extracted with EtOAc (2 $\times$ 9 mL). The combined organic layer was washed with saturated aqueous NH₄Cl (3 $\times$ 9mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 2:1, v/v) to afford the compound **7** (149 mg, 0.37 mmol, 43%); colorless oil, *R*_f = 0.39 (n-hexane/EtOAc, 2:1, v/v); ¹H NMR (250 MHz, CDCl₃) δ 3.34

(s, 3 H, OCH₃), 3.78 (s, 3 H, OCH₃), 3.78~3.80 (m, 3 H), 3.83~3.91 (m, 1 H), 3.95~3.96 (m, 1 H), 4.00~4.11 (m, 1 H), 4.22~4.26 (m, 1 H), 4.65 (dd, *J* = 11.5, 18.2 Hz, 2 H), 4.70 (brs, 1 H, H-1), 5.52 (s, 1 H, PhCHO₂), 6.84~6.90 (m, 2 H), 7.22~7.38 (m, 5 H), 7.46~7.50 (m, 2 H); ¹³C NMR (63 MHz, CDCl₃) δ 55.4, 63.9, 66.9, 67.7, 68.9, 69.7, 73.4, 78.1, 79.7, 98.3 (C-1), 102.2, 114.1, 122.2, 126.4, 127.9, 128.8, 129.8, 130.9(2), 132.6, 134.1, 137.5.

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl- α -D-arabino-hexopyranosid-3-ulose (8).

A solution of compound **7** (630 mg, 1.57 mmol) and PDC (2.95g, 7.84 mmol, 5 equiv.) in CH₂Cl₂ (7 mL) in the presence of 4A molecular sieves was stirred for 3 h at room temperature. The reaction mixture was poured into the diethyl ether (6 mL), filtered through celite and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1, v/v) to afford the compound **8** (478 mg, 1.19 mmol, 76%); colorless oil, *R_f* = 0.50 (n-hexane/EtOAc, 2:1, v/v); ¹H NMR (250 MHz, CDCl₃) δ 3.37 (s, 3 H, OCH₃), 3.81 (s, 3 H, OCH₃), 3.85 (d, *J* = 1.32 Hz, 1 H), 3.95~4.03 (m, 1 H), 4.05~4.16 (m, 1 H), 4.35~4.40 (m, 1 H), 4.41 and 4.60 (ABq, *J* = 11.5 Hz, 2 H, PhCH₂O), 4.86 (d, *J* = 9.32 Hz, 1 H), 4.95 (d, *J* = 1.06 Hz, 1 H, H-1), 5.60 (s, 1 H, PhCHO₂), 6.87~6.92 (m, 2 H), 7.23~7.53 (m, 7 H); ¹³C NMR (63 MHz, CDCl₃) δ 55.2, 55.4, 66.5, 69.5, 72.1, 81.2, 82.3, 102.3 (C-1), 103.4, 114.1(2), 126.5(3), 128.3, 128.4, 129.5, 130.2(2), 136.7, 159.9, 198.5

Methyl 3,3'-Anhydro-4,6-*O*-benzylidene-3-*C*-hydroxymethyl-2-*O*-*p*-methoxybenzyl- α -D-manno-hexopyranoside (9).

To a solution of trimethylsulphonium iodide (52 mg, 0.25mmol, 1.3eq) in THF (1.5mL) at –78 °C was added n-BuLi (222 μ L, 0.23 mmol, 1.2eq). The reaction mixture was stirred at –78 °C for further 35 min and allowed to warm to 0 °C and then compound **8** (78 mg, 0.19 mmol) in THF (5 mL) at –78 °C was added to the reaction mixture. After stirring for further 2.5 h at –78 °C, the reaction mixture was allowed to warm to room temperature, quenched with H₂O (5 ml) by stirring for 30 min, and extracted with EtOAc (3 $\times$ 7 mL). The combined organic layer was washed with brine (2 $\times$ 5 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-

hexane/EtOAc, 2:1, v/v) to afford the compound **9** (52 mg, 0.125 mmol, 66 %); colorless oil, R_f = 0.40 (n-hexane/EtOAc, 2:1, v/v); ^1H NMR (250 MHz, CDCl_3) δ 2.69 (d, J = 5.13 Hz, 1 H) 3.18 (d, J = 5.13 Hz, 1 H), 3.29 (d, J = 1.35 Hz, 1 H), 3.36 (s, 3 H), 3.80 (s, 3 H), 3.91~3.92 (m, 1 H), 3.94~3.96 (m, 1 H), 4.29 (dd, J = 2.8, 8.0 Hz, 1 H), 4.38~4.41 (m, 1 H), 4.63 and 4.85 (ABq, J = 11.7 Hz, 2 H, PhCH_2O), 4.72 (d, J = 1.3, 1 H, H-1), 5.59 (s, 1 H, PhCHO_2), 6.85~6.91 (m, 2 H), 7.28~7.46 (m, 7 H); ^{13}C NMR (63 MHz, CDCl_3) δ 46.9, 55.1, 55.4, 58.6, 65.0, 69.2, 72.2, 73.4, 79.7, 101.7 (C-1), 101.8, 113.9, 126.4(2), 128.3(2), 129.2, 129.8(2), 129.9(2), 137.3, 159.5.

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Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl-3'-*C*-methyl- α -D-manno-hexopyranoside (10**).** A solution of compound **9** (20 mg, 0.048 mmol), LAH (13 mg, 0.342 mmol, 7eq) in THF (4mL) was stirred at -78°C for 3.5 h and allowed to warm to room temperature and the reaction was quenched with MeOH (3 mL). After concentration of the solution to one third volume, the product solution was partitioned between methylene chloride and water. The organic layer was washed water, dried, and concentrated. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1, v/v) to afford the compound **10** (18 mg, 0.043 mmol, 91 %); colorless oil, R_f = 0.30 (n-hexane/EtOAc, 2:1, v/v); IR (CHCl_3 film) 3503, 2945, 2361, 1618, 1408, 1255, 1101 cm^{-1} ; $[\alpha]_D^{20}$ -50.7 (c, 0.14, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.45 (s, 3 H), 3.37 (s, 3 H, OCH_3), 3.41 (brs, 1 H), 3.81 (s, 3 H), 4.25 (d, J = 5.0 Hz, 1 H), 4.55 and 4.67 (ABq, J = 11.0 Hz, 2H, PhCH_2O), 4.75 (brs, 1 H, H-1), 5.54 (s, 1 H, PhCHO_2), 6.90 (d, J = 8.0 Hz, 2 H), 7.26~7.33 (m, 5 H), 7.47 (brs, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 18.6, 55.4(2), 62.5, 69.3, 70.8, 73.9, 82.2, 83.0, 99.8 (C-1), 102.2, 114.2, 126.5(2), 128.3(3), 129.1, 129.3, 129.9(3), 137.7. Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_7$: C, 66.33; H, 6.78. Found: C, 66.32; H, 6.82.

12

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (12**).** A solution of 2'-(benzyloxycarbonyl)benzyl 4,6-*O*-benzylidene- α -D-mannopyranoside (**11**)² (2.0 g, 4.06 mmol) and Bu_2SnO (1.31 g, 5.26 mmol, 1.3eq) in MeOH (10 mL) was refluxed for 1 h. After removal of the solvent in vacuo, the residue was dissolved

in DMF (10 mL) and then *p*-methoxybenzyl chloride (0.66 mL, 4.87 mmol, 1.2eq) and Bu₄NI (0.75 g, 2.03 mmol, 0.5eq) were added to the reaction mixture. After stirring at 60 °C for 1.5 h, the reaction mixture was diluted with EtOAc (50 mL) and quenched with saturated aqueous NH₄Cl (7 mL). The combined organic layer was washed with saturated aqueous NH₄Cl (2 × 50 mL) and brine (50 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1, v/v) to afford the compound **12** (2.06 g, 3.36 mmol, 83%); colorless oil, *R*_f = 0.20 (n-hexane/EtOAc, 2:1, v/v); IR (CHCl₃ film) 2918, 3478, 1721, 1609, 1511, 1450, 1378 cm⁻¹; [α]_D²⁰ +54.7 (c, 0.29, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.73 (s, 3 H, OCH₃), 3.80~3.87 (m, 2 H), 3.94~3.95 (m, 1 H), 4.03 (brs, 1 H), 4.11 (t, *J* = 4.53 Hz, 1 H), 4.22~4.23 (m, 1 H), 4.63 and 4.78 (ABq, *J* = 11.3 Hz, 2 H, PhCH₂O), 4.92 and 5.11 (ABq, *J* = 13.9 Hz, 2 H, PhCH₂O), 4.94 (brs, 1 H, H-1), 5.30 (s, 2 H, PhCH₂O), 5.59 (s, 1 H, PhCHO₂), 6.84 (d, *J* = 8.05 Hz, 2 H), 7.27~7.54 (m, 15 H), 7.99 (d, *J* = 7.57 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 55.2, 63.8, 66.8, 67.5, 68.9, 70.0, 72.4, 75.5, 78.9, 99.9 (C-1), 101.6, 113.9(2), 126.1(2), 127.4, 128.0, 128.2, 128.3(2), 128.7, 128.9, 129.6(2), 130.2, 130.8, 132.5, 135.9, 137.7, 139.5, 159.4, 166.7; Anal. Calcd for C₃₆H₃₆O₉: C, 70.57; H, 5.92. Found: C, 70.54; H, 5.78.

13

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl-α-*D*-mannopyranoside (13**).** A solution of compound **12** (2.14 g, 3.49 mmol), imidazole (0.594 g, 8.72 mmol, 2.5 equiv.), and TBSCl (0.631 g, 4.19 mmol, 1.2 equiv.) in DMF (4 mL) was stirred at room temperature for 5 h. The reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL), extracted with CH₂Cl₂ (2 × 8 mL). The combined organic layer was washed with saturated aqueous NH₄Cl (2 × 8 mL) and brine (2 × 8 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 9:1, v/v) to afford the compound **13** (2.10 g, 2.89 mmol, 83 %); yellow oil, *R*_f = 0.38 (n-hexane/EtOAc, 9:1, v/v); IR (CHCl₃ film) 2918, 2851, 2357, 1722, 1515, 1455, 1248, 1128 cm⁻¹; [α]_D²⁰ +20.9 (c 1.44, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.12 (s, 3 H, SiCH₃), 0.17 (s, 3 H, SiCH₃), 0.98 (s, 9 H), 3.83 (s, 3 H, OCH₃), 3.87~3.90 (m, 2 H), 3.98~4.0 (m, 1 H), 4.17 (brs, 1 H), 4.23 (t, *J* = 8.77 Hz, 1 H), 4.29 (d, *J* = 5.1 Hz, 1 H), 4.72 and 4.84 (ABq, *J* = 11.5 Hz, 2 H, PhCH₂O), 4.87 (brs, 1 H, H-1), 5.01 and 5.18 (ABq, *J* = 14.2 Hz, 2 H, PhCH₂O), 5.36 (s, 2 H, PhCH₂O), 5.69 (s, 1 H), 6.91 (d, *J* = 8.3 Hz, 2 H), 7.36~7.59 (m, 15 H), 8.07 (d, *J* = 7.7 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ -5.0, -

4.3, 18.3, 25.9(3), 55.2, 64.8, 66.8, 67.5, 69.1, 71.5, 72.7, 75.4, 79.3, 101.5(2) (C-1, PhCHO₂), 113.6, 126.2(3), 127.4, 127.8, 128.2(3), 128.3(3), 128.7, 128.8, 129.6(2), 130.8, 130.9, 132.5(2), 136.0, 138.0, 139.9, 159.2, 166.7; Anal. Calcd for C₄₂H₅₀O₉Si: C, 69.39; H, 6.93. Found: C, 69.44; H, 6.82.

14

2'-(Benzyloxycarbonyl)benzyl 4,6-O-Benzylidene-2-O-tert-butyltrimethylsilyl- α -D-mannopyranoside (14). To a solution of compound **13** (1.14 g, 1.57 mmol) in CH₂Cl₂/H₂O (19 mL, 18:1, v/v) was added DDQ (0.463 g, 2.04 mmol, 1.3eq). After stirring at 0 °C for 40 min, the reaction mixture was quenched with NaHCO₃ (5 mL) and extracted with CH₂Cl₂ (2 $\times$ 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (2 $\times$ 9 mL) and brine (2 $\times$ 7mL), dried (MgSO₄), and concentrated in vacuo. The residue was dissolved in ether (5 mL) and the ether solution was vigorously stirred with saturated aqueous NaHSO₃ (5 mL) for 2 h. After the organic layer was dried and concentrated, the residue was purified by silica gel flash column chromatography (n-hexane/EtOAc/CH₂Cl₂, 9:1:1, v/v) to afford the compound **14** (0.838 g, 1.38 mmol, 88%); colorless oil, *R*_f = 0.49 (n-hexane/EtOAc/CH₂Cl₂, 9:1:1, v/v); IR (CHCl₃ film) 3493, 2930, 2853, 1721, 1271, 1132, 1086, 1030 cm⁻¹; [α]_D²⁰ +18.7 (c 2.58, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.19 (s, 3 H), 0.24 (s, 3 H), 1.05 (s, 9 H), 3.86~3.90 (m, 1 H), 3.95~3.98 (m, 2 H), 4.18 (s, 2 H), 4.32 (d, *J* = 8.5 Hz, 1 H), 4.95 (brs, 1 H, H-1), 5.07 and 5.24 (ABq, *J* = 13.9 Hz, 2 H), 5.42 (s, 2 H), 5.64 (s, 1 H), 7.41~7.72 (m, 13 H), 8.11 (d, *J* = 7.7 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ -4.9, -4.7, 18.1, 25.8(3), 63.9, 66.7, 67.4, 68.7, 68.8, 72.4, 79.4, 100.7 (C-1), 102.0, 126.3(2), 127.3, 127.7, 128.2(3), 128.3(2), 128.6(3), 129.0, 130.7, 132.4, 135.8, 137.4, 139.6, 166.5; Anal. Calcd for C₃₄H₄₂O₈Si: C, 67.30; H, 6.98. Found: C, 67.37; H, 6.80.

15

2'-(Benzyloxycarbonyl)benzyl 4,6-O-Benzylidene-2-O-tert-butyltrimethylsilyl- α -D-arabino-hexopyranoside-3-ulose (15). A solution of compound **14** (69 mg, 0.114mmol) and Dess-Martin periodinane (72 mg, 0.170mmol, 1.5eq) in CH₂Cl₂ (4 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered through celite and concentrated in vacuo. The

residue was purified by silica gel flash column chromatography (CH₂Cl₂/ petroleum ether, 9:1, v/v) to afford the compound **15** (64 mg, 1.06 mmol, 93%); colorless oil, *R_f* = 0.50 (CH₂Cl₂/ petroleum ether, 9:1, v/v); IR (CHCl₃ film) 2930, 2858, 1752, 1711, 1260, 1127, 1029 cm⁻¹; [α]_D²⁰ +32.7 (*c*, 6.09, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.09 (s, 3 H), 0.11 (s, 3 H), 0.92 (s, 9 H), 3.95 (t, *J* = 10.2 Hz, 1 H), 4.11~4.16 (m, 1 H), 4.18 (brs, 1 H), 4.31~4.34 (m, 1 H), 4.89 (d, *J* = 9.7 Hz, 1 H), 5.06 (brs, 1H, H-1), 4.99 and 5.16 (ABq, *J* = 14.1, 2 H), 5.32 (s, 2 H), 5.60 (s, 1 H), 7.32~7.58 (m, 13 H), 8.01 (d, *J* = 7.7 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ -5.0, -4.8, 18.1, 25.7(3), 66.8(2), 67.7, 69.5, 77.5, 80.6, 102.1, 103.6, 126.5(2), 127.5, 127.7, 127.8, 128.3(4), 128.7(2), 129.3(3), 130.8, 132.7, 135.9, 136.7, 139.2, 166.5, 198.2. Anal. Calcd for C₃₄H₄₀O₈Si: C, 67.52; H, 6.67. Found: C, 67.53; H, 6.52.

16

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-3-methylene-α-D-arabino-hexopyranoside (16). A solution of methyltriphenyl phosphonium bromide (84 mg, 0.235mmol, 1.3eq) and n-BuLi (1.6 M, 142 μL, 0.227 mmol, 1.25eq) in THF (3 mL) was stirred at -78 °C for 30 min. Compound **15** (110 mg, 0.182 mmol) in THF (4 mL) was added dropwise to the above solution at 0 °C and then the reaction mixture was stirred for 5.5 h. The reaction mixture was quenched with H₂O (5 ml), extracted with EtOAc (3×7 mL) and the combined organic layer was washed with brine (2×5 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc, 10:1, v/v) to afford the compound **16** (101 mg, 0.168 mmol, 92 %); colorless oil, *R_f* = 0.40 (petroleum ether/EtOAc, 10:1, v/v); IR (CHCl₃ film) 3457, 2930, 1721, 1260, 1137, 1066 cm⁻¹; [α]_D²⁰ +47.5 (*c*, 1.34, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.90 (s, 9 H), 3.80~3.90 (m, 2H), 4.19~4.22 (m, 1 H), 4.29 (brs, 1 H), 4.45 (d, *J* = 8.5 Hz, 1 H), 4.81 (brs, 1H, H-1), 4.99 and 5.13 (ABq, *J* = 14.6 Hz, 2 H), 5.12 (brs, 1 H), 5.26 (brs, 1 H), 5.33 (brs, 2 H), 5.67 (s, 1 H), 7.25~7.64 (m, 13 H), 7.99 (d, *J* = 7.8 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ -4.8, -4.4, 18.3, 25.9(3), 66.9, 67.0, 67.2, 69.6, 75.4, 77.0(2), 101.6, 101.8, 109.6, 126.4(3), 127.3, 127.6, 128.1, 128.4(3), 128.8(2), 129.1, 130.8, 132.6, 136.0, 137.8, 140.3, 142.3, 166.8. Anal. Calcd for C₃₅H₄₂O₇Si: C, 69.74; H, 7.02. Found: C, 69.76; H, 7.08.

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2'-(Benzyloxycarbonyl)benzyl 4,6-O-Benzylidene-3-deoxy-3-methylene- α -D-arabino-hexopyranoside (17). A solution of compound **16** (31 mg, 0.051 mmol) and Bu₄NF (1.0M, 0.102 μ L, 0.102 mmol, 2eq) in THF (3 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 3:1, v/v) to afford the compound **17** (24 mg, 0.049 mmol, 95 %); colorless oil, R_f = 0.20 (n-hexane/EtOAc, 3:1, v/v); IR (CHCl₃ film) 3452, 1711, 1255, 1132, 1055 cm⁻¹; $[\alpha]_D^{20}$ +80.4 (c, 1.85, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.84~3.86 (m, 1 H), 4.21~4.22 (m, 1 H), 4.29 (s, 1H), 4.49 (brs, 1 H), 4.91 (brs, 1 H, H-1), 4.98 and 5.12 (ABq, J = 14.2 Hz, 2 H), 5.13 (brs, 1 H), 5.31 (brs, 1 H), 5.32 (brs, 2 H), 5.64 (s, 1 H), 7.33~7.60 (m, 13 H), 7.98 (d, J = 7.5 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 66.6, 66.9, 67.4, 69.4, 74.6, 76.6, 100.7, 101.8, 111.1, 126.3(3), 127.4, 127.9, 128.7(4), 129.1(2), 129.7(2), 130.8, 132.6, 135.9, 137.7, 139.8, 141.6, 166.9. Anal. Calcd for C₂₉H₂₈O₇: C, 71.30; H, 5.78. Found: C, 71.21; H, 5.90.

18

2''-(Benzyloxycarbonyl)benzyl 3,3'-Anhydro-4,6-O-benzylidene-3-C-hydroxymethyl- α -D-manno-hexopyranoside (18). A solution of compound **17** (23 mg, 0.047 mmol) and *m*-CPBA (16 mg, 0.093 mmol, 2eq) in the presence of NaHCO₃ (6 mg, 0.071 mmol, 1.5eq) in CH₂Cl₂ (4 mL) was stirred at 0 °C for 4 h. The reaction mixture was quenched with saturated aqueous NaHCO₃ (3 mL) extracted with CH₂Cl₂ (3 $\times$ 5 mL). The combined organic layer was washed with brine (2 $\times$ 4 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography n-hexane/EtOAc, 1:1, v/v) to afford the compound **18** (19 mg, 0.038 mmol, 80%); colorless oil, R_f = 0.54 (n-hexane/EtOAc, 1:1, v/v); IR (CHCl₃ film) 2925, 2858, 1731, 1378, 1260, 1137, 1096, 1040 cm⁻¹; $[\alpha]_D^{20}$ +35.4 (c, 1.05, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.85 (d, J = 4.9 Hz, 1 H), 3.31 (d, J = 4.9 Hz, 1 H), 3.58 (brs, 1 H), 3.87 (t, J = 10.0 Hz, 1 H), 3.98~4.06 (m, 1 H), 4.27 (dd, J = 4.2, 9.8 Hz, 1 H), 4.41 (d, J = 9.4 Hz, 1 H), 4.97 and 5.17 (ABq, J = 14.0, 2 H), 5.02 (brs, 1 H, H-1), 5.32 (s, 3 H), 5.54 (s, 1 H), 7.31~7.53 (m, 13 H), 8.00 (d, J = 7.5 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 49.6, 59.6, 64.7, 66.9, 67.6,

69.0, 72.8, 74.3, 100.8 (C-1), 101.6, 126.2(3), 127.5, 127.6, 128.2, 128.3(3), 128.4(2), 128.7, 129.0, 130.8, 132.5, 135.8, 137.1, 139.5, 166.7. Anal. Calcd for C₂₉H₂₈O₈: C, 69.04; H, 5.59. Found: C, 69.09; H, 5.61.

3

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3'-*C*-methyl- α -D-manno-hexopyranoside

(3). A solution of compound **18** (0.162 g, 0.32 mmol), NaI (121 mg, 0.81 mmol, 2.5equiv.), n-Bu₃SnH (216 μ L, 0.81 mmol, 2.5equiv.) and AIBN (3 mg, 0.018 mmol, 0.06equiv.) in 1,2-dimethoxyethane (6 mL) was stirred at 90 °C for 4 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography n-hexane/EtOAc, 1:1, v/v) to afford the compound **3** (133 mg, 0.26 mmol, 82 %); amorphous solid, R_f = 0.35 (n-hexane/EtOAc, 1:1, v/v); IR (CHCl₃ film) 3447, 2914, 1711, 1255, 1034, 1076 cm⁻¹; $[\alpha]_D^{20}$ +35.0 (c, 0.98, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.53 (s, 3 H, CH₃), 3.24 (d, J = 1.7 Hz, 1 H), 3.73 (brs, 1 H), 3.78~3.85 (m, 2 H), 3.89~3.95 (m, 1 H), 4.22~4.26 (m, 1 H), 5.02 (brs, 1H, H-1), 4.95 and 5.19 (ABq, J = 14.1 Hz, 2 H), 5.35 (s, 2 H), 5.56 (s, 1 H), 7.35~7.62 (m, 13 H), 8.02 (d, J = 7.8 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 19.7, 62.5, 66.9, 68.3, 69.1, 71.3, 75.1, 81.0, 100.5 (C-1), 102.2, 126.3(2), 127.4, 127.8, 128.2, 128.3(4), 128.4, 128.7(2), 129.2, 130.8, 132.5, 135.8, 137.4, 139.7, 166.7. Anal. Calcd for C₂₉H₃₀O₈: C, 68.76; H, 5.97. Found: C, 68.78; H, 6.07.

20

2'-(Benzyloxycarbonyl)benzyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranoside (20). To a stirred solution of 2,3,4,6-tetra-*O*-acetyl- α -L-rhamnosyl bromide (**19**)³ (3.2 g, 9.06 mmol) in acetonitrile (25 mL) at 0 °C was added mercury (II) bromide (3.92 g, 10.88 mmol, 1.2 equiv), mercury (II) cyanide (2.75 g, 10.89 mmol, 1.2 equiv), and benzyl 2-(hydroxymethyl)benzoate (2.42 g, 9.99 mmol, 1.1 equiv). After stirring at 0 °C for further 20 min, the reaction mixture was filtered and the filtrate was concentrated. The resulting oil was dissolved in CH₂Cl₂ (50 mL) and the solution was washed with saturated aqueous NaHCO₃ (2 $\times$ 50 mL) and brine (50 mL). The organic phase was dried (MgSO₄) and concentrated in vacuo and the residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 1:1, v/v) to afford the compound

20 (4.00 g, 7.77 mmol, 86%); colorless oil, $R_f = 0.52$ (n-hexane/EtOAc, 1:1, v/v); IR (CHCl₃ film) 2976, 2935, 1752, 1230, 1066 cm⁻¹; $[\alpha]_D^{20} +15.5$ (c, 2.84, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.21 (m, 3 H), 2.01 (s, 3 H, COCH₃), 2.06 (s, 3 H, COCH₃), 2.16 (s, 3 H, COCH₃), 3.89~3.95 (m, 1 H), 4.90 (brs, 1 H, H-1), 4.98 and 5.15 (ABq, $J = 14.4$ Hz, 2 H, PhCH₂O), 5.10 (t, $J = 9.6$ Hz, 1 H), 5.3 (s, 2 H, PhCH₂O), 5.37 (brs, 1 H), 5.41 (d, $J = 3.50$ Hz, 1 H), 7.3~7.7 (m, 8 H), 7.9~8.0 (m, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 17.5, 20.8, 20.9, 21.0, 66.7, 66.9, 67.7, 69.4, 69.9, 71.2, 97.4 (C-1), 127.4, 127.6, 128.0, 128.5, 128.4, 128.7, 130.8, 132.7, 136.0, 139.5, 166.6, 170.1(2), 170.2. Anal. Calcd for C₂₇H₃₀O₁₀: C, 63.03; H, 5.88. Found: C, 63.02; H, 5.85.

21

2'-(Benzyloxycarbonyl)benzyl α -L-Rhamnopyranoside (21). To a solution of compound **20** (5.54 g, 10.77 mmol) in MeOH (50 mL) was added NaOMe (87 mg, 1.61 mmol, 0.15 equiv.) at 0 °C. After stirring at room temperature for further 20 min, the reaction mixture was neutralized with DOWEX CCR-3 (H⁺ mode), filtered through celite and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (CH₂Cl₂/MeOH, 5:1, v/v) to afford the compound **21** (3.81 g, 9.81 mmol, 91%); solid, $R_f = 0.61$ (CH₂Cl₂/MeOH, 5:1, v/v); IR (CHCl₃ film) 3401, 2925, 1711, 1255, 1055 cm⁻¹; $[\alpha]_D^{20} +45.3$ (c, 1.03, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.27~1.29 (m, 3 H), 3.57~3.71 (m, 2 H), 3.89~4.04 (m, 2 H), 4.28~4.36 (m, 2 H), 4.71 (d, $J = 5.85$ Hz, 1 H), 4.88 (brs, 1 H, H-1), 4.89 and 5.04 (ABq, $J = 14.4$ Hz, 2 H, PhCH₂O), 5.28 (s, 2 H, PhCH₂O), 7.21~7.70 (m, 8 H), 7.91~7.94 (m, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 17.7, 66.9, 67.4, 69.8, 71.1, 72.0, 73.0, 99.7 (C-1), 122.2, 127.2, 128.3, 128.4, 128.7, 129.1, 130.7, 134.2, 135.8, 139.7, 166.8. Anal. Calcd for C₂₁H₂₄O₇: C, 64.94; H, 6.23. Found: C, 64.97; H, 6.24.

22

2'-(Benzyloxycarbonyl)benzyl 3-O-*p*-Methoxybenzyl- α -L-rhamnopyranoside (22). A solution of compound **21** (1.66 g, 4.28 mmol) and Bu₂SnO (1.44g, 5.78mmol, 1.3eq) in MeOH (10 mL) was refluxed for 1 h. The solvent was then removed by concentration in vacuo. The residue was dissolved in DMF (10 mL) and then *p*-methoxybenzyl chloride (0.87mL, 6.48mmol, 1.4eq) and Bu₄NI (0.79g, 2.14mmol, 0.5eq) were added to this solution. The reaction mixture

was stirred at 60 °C for 1.5 h, diluted with EtOAc (50 mL), and quenched with saturated aqueous NH₄Cl (7 mL). The combined organic layer was washed with saturated aqueous NH₄Cl (2 × 50 mL) and brine (50 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 1:2, v/v) to afford the compound **22** (1.81 g, 3.56 mmol, 83%); colorless oil, *R_f* = 0.55 (n-hexane/EtOAc, 1:2, v/v); IR (CHCl₃ film) 3452, 3012, 2914, 1716, 1250, 1050 cm⁻¹; [α]_D²⁰ -27.2 (*c*, 2.01, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.25~1.32 (m, 3 H), 3.55~3.65 (m, 1 H), 3.67~3.73 (m, 2 H), 3.77 (s, 3 H, OCH₃), 4.02 (brs, 1 H), 4.63 and 4.50 (ABq, *J* = 11.2 Hz, 2 H, PhCH₂O), 4.90 (brs, 1 H, H-1), 4.93 and 5.07 (ABq, *J* = 14.0, 2 H, PhCH₂O), 5.32 (s, 2 H, PhCH₂O), 6.88 (d, *J* = 8.6 Hz, 2 H), 7.25~7.54 (m, 10 H), 7.99 (d, *J* = 7.9 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 17.8, 55.3, 66.9, 67.3, 68.0, 68.2, 71.4, 71.6, 79.5, 99.2 (C-1), 114.2, 127.3, 127.8(2), 128.4(2), 128.7, 129.8(3), 130.8, 132.4, 135.9, 139.9, 159.7, 166.8. Anal. Calcd for C₂₉H₃₂O₈: C, 68.49; H, 6.34. Found: C, 68.50; H, 6.47.

23

2'-(Benzyloxycarbonyl)benzyl 3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl-α-L-rhamnopyranoside (23**).** A solution of compound **22** (2.84 g, 5.58 mmol), pivaloyl chloride (1.17 mL, 13.9 mmol, 2.5equiv.), DMAP (136 mg, 1.11 mmol, 0.2equiv.), and Et₃N (3 mL) in CH₂Cl₂ (15 mL) was stirred at 0 °C for 2 h. The reaction mixture was quenched with NaHCO₃ (5 mL) and extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (2 × 30 mL) and brine (50 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 1:1, v/v) to afford the compound **23** (3.47 g, 5.13 mmol, 92 %); colorless oil, *R_f* = 0.55 (n-hexane/EtOAc, 1:1, v/v); IR (CHCl₃ film) 2976, 1731, 1255, 1143, 1066 cm⁻¹; [α]_D²⁰ -20.0 (*c*, 2.05, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.20 (s, 9 H), 1.24 (s, 9 H), 1.20~1.24 (m, 3 H), 3.79 (s, 3 H, OCH₃), 3.83~3.87 (m, 1 H), 3.89~3.94 (m, 1 H), 4.35 and 4.59 (ABq, *J* = 10.9 Hz, 2 H, PhCH₂O), 4.89 (brs, 1 H, H-1), 4.98 and 5.14 (ABq, *J* = 14.2 Hz, 2 H, PhCH₂O), 5.09 (t, *J* = 9.90 Hz, 1 H, H-4), 5.36 (s, 2H, PhCH₂O), 5.46 (m, 1 H, H-2), 6.85 (d, *J* = 8.6 Hz, 2 H), 7.18~7.60 (m, 10 H), 8.04 (d, *J* = 7.8 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 17.7, 27.2(6), 38.9, 39.1, 55.3, 66.9, 67.1, 67.6, 68.1, 70.9, 72.1, 74.9, 97.9 (C-1), 113.6, 127.5, 127.7, 128.3(3), 128.4, 128.7, 129.4, 129.9, 130.8, 132.6, 135.9, 139.7, 159.2, 166.7, 177.4, 177.8. Anal. Calcd for C₃₉H₄₈O₁₀: C, 69.21; H, 7.15. Found: C, 69.24; H, 7.34.

2'-Carboxybenzyl 3-O-*p*-Methoxybenzyl-2,4-di-O-pivaloyl- α -L-rhamnopyranoside (4**).**

Compound **23** (800 mg, 1.18 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 126 mg, 0.118 mmol, 0.1 equiv) and ammonium acetate (91 mg, 1.18 mmol, 1 equiv) in MeOH (3.5 mL) at room temperature for 1 h. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 1:1, v/v) to afford compound **4** (588 mg, 1.00 mmol, 85%); solid, R_f = 0.45 (n-hexane/EtOAc, 1:1, v/v); mp 55 - 57 °C; IR (CHCl₃ film) 2971, 1731, 1516, 1280, 1250, 1066, 1137 cm⁻¹; $[\alpha]_D^{20}$ -18.5 (c, 1.43, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.18 (s, 9 H), 1.23 (s, 9 H), 1.18~1.23 (m, 3 H), 3.78 (s, 3 H, OCH₃), 3.87~3.89 (m, 1 H), 3.94 (d, J = 8.02 Hz, 1 H), 4.38 and 4.59 (ABq, J = 10.9 Hz, 2 H, PhCH₂O), 4.94 (brs, 1 H, H-1), 5.00 and 5.19 (ABq, J = 14.5 Hz, 2 H, PhCH₂O), 5.10 (t, J = 9.8 Hz, 1 H, H-4), 5.47 (brs, 1 H, H-2), 6.84 (d, J = 8.3 Hz, 2 H), 7.19 (d, J = 8.2 Hz, 2 H), 7.41 (t, J = 3.7 Hz, 1 H), 7.63 (d, J = 3.6 Hz, 2 H), 8.12 (d, J = 7.7 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 17.6, 27.2(6), 38.8, 39.1, 55.3, 67.2, 67.7, 68.2, 70.9, 72.1, 74.8, 98.0 (C-1), 127.1, 127.4, 129.5(3), 129.9, 131.7, 133.4, 140.5, 159.2, 172.1, 177.4, 177.9. Anal. Calcd for C₃₂H₄₂O₁₀: C, 65.51; H, 7.22. Found: C, 65.48; H, 7.28.

2'-(Benzyloxycarbonyl)benzyl 4,6-O-Benzylidene-3-O-*p*-methoxybenzyl-2-O-pivaloyl- α -D-mannopyranoside (24**).** A solution of compound **12** (0.20 g, 0.33 mmol), pivaloyl chloride (53 μ L, 0.43 mmol, 1.3equiv.), DMAP (8 mg, 0.065 mmol, 0.2 equiv.), and Et₃N (1 mL) in CH₂Cl₂ (5mL) was stirred at 0 °C for 3.5 h. The reaction mixture was quenched with NaHCO₃ (5 mL) and extracted with CH₂Cl₂ (2 $\times$ 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (2 $\times$ 30 mL) and brine (50 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 6:1, v/v) to afford the compound **24** (0.205 g, 0.29 mmol, 89%); colorless oil, R_f = 0.35 (n-hexane/EtOAc, 6:1, v/v); ¹H NMR (500 MHz, CDCl₃) δ 1.25 (s, 9 H), 3.78 (s, 3 H, OCH₃), 3.82 (d, J = 10.1 Hz, 1 H), 3.86~3.91 (m, 1 H), 4.00 (t, J = 9.2 Hz, 1 H), 4.05~4.07 (m, 1 H), 4.21~4.24 (m, 1 H), 4.62 and 4.57 (ABq, J = 11.5 Hz, 2H, PhCH₂O), 4.89 (brs, 1H, H-1), 4.96

and 5.12 (ABq, $J = 14.1$ Hz, 2H, PhCH_2O), 5.33 (s, 2H, PhCH_2O), 5.45 (brs, 1H, H-2), 5.62 (s, 1H, PhCHO_2), 6.83 (d, $J = 8.34$ Hz, 2 H), 7.25~7.56 (m, 15 H), 8.01 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 27.4(3), 55.4, 64.3, 66.9, 67.8, 69.0, 69.4, 71.7, 73.8, 78.8, 99.0 (C-1), 101.8, 113.8, 126.3(2), 127.5, 127.8, 128.3(2), 128.4(2), 128.8, 129.0, 129.5(3), 130.4, 130.9, 132.7, 136.0, 137.7, 139.6, 159.3, 166.7, 177.8

25

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-3-O-*p*-methoxybenzyl-2-O-pivaloyl- α -D-mannopyranoside (25). To a solution of compound **24** (0.16 g, 0.23 mmol) in THF (5mL) was added BH_3/THF (2.30mL, 0.23mmol) and Bu_2BOTf (0.23mL, 0.023mmol). After stirring at 0 °C for 3 h, the reaction mixture was quenched with Et_3N (0.2mL) and stirred for further 1 h. The reaction mixture was diluted with MeOH (1 mL), and then concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 2:1, v/v) to afford the compound **25** (0.14 g, 0.20 mmol, 87%); colorless oil, $R_f = 0.33$ (n-hexane/EtOAc, 2:1, v/v); IR (CHCl_3 film) 3508, 2919, 1716, 1250, 1137, 1071 cm^{-1} ; $[\alpha]_D^{20} +24.9$ (c, 1.84, CHCl_3); ^1H NMR (250 MHz, CDCl_3) δ 1.23 (s, 9 H), 3.69~3.77 (m, 3 H), 3.80 (s, 3 H, OCH_3), 3.80~3.84 (m, 2 H), 4.04 (dd, $J = 3.1, 8.9$ Hz, 1H), 4.45 and 4.65 (ABq, $J = 10.6$ Hz, 2H, PhCH_2O), 4.62 and 4.89 (ABq, $J = 10.9$, 2H, PhCH_2O), 4.91 (brs, 1 H, H-1), 4.95 and 5.09 (ABq, $J = 14.1$ Hz, 2 H, PhCH_2O), 5.33 (s, 2H, PhCH_2O), 5.45 (dd, $J = 1.9, 3.0$ Hz, 1 H, H-2), 6.85 (d, $J = 6.8$ Hz, 2 H), 7.23~7.55 (m, 15 H), 8.01 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (63 MHz, CDCl_3) δ 27.3(3), 39.1, 55.4, 62.2, 66.9, 67.6, 68.1, 71.1, 72.1, 73.9, 75.3, 78.0, 97.9 (C-1), 113.7, 127.5, 127.4, 128.0, 128.1, 128.3(4), 128.4, 128.5, 128.8, 129.8, 130.3, 130.8, 132.7, 135.9, 138.3, 139.6, 159.3, 166.7, 177.7. Anal. Calcd for $\text{C}_{41}\text{H}_{46}\text{O}_{10}$: C, 70.47; H, 6.63. Found: C, 70.31; H, 6.69.

26

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-6-deoxy-3-O-*p*-methoxybenzyl-2-O-pivaloyl- α -D-mannopyranoside (26). A solution of the compound **25** (1.35 g, 1.93 mmol), PPh_3 (0.16g, 0.062mmol, 3eq), imidazole (0.04g, 0.62mmol, 3eq) and I_2 (0.11g, 0.41mmol, 2eq) in toluene (6 mL) was stirred at reflux for 2 h. The reaction mixture was quenched with

saturated aqueous NaHCO₃ (5 mL), and extracted with EtOAc (2 × 15 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (2 × 15 mL) and brine (2 × 10 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 3:1, v/v) to afford the compound **26** (1.386 g, 1.72 mmol, 89%); yellow oil, *R_f* = 0.50 (n-hexane/EtOAc, 3:1, v/v); IR (CHCl₃ film) 2971, 1726, 1522, 1255, 1132, 1070 cm⁻¹; [α]_D²⁰ +17.7 (c, 1.27, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.27 (s, 9 H), 3.37~3.42 (m, 1 H), 3.46 (d, *J* = 2.8 Hz, 2 H), 3.70 (t, *J* = 9.1 Hz, 1H), 3.78 (s, 3 H, OCH₃), 4.05 (dd, *J* = 3.0, 9.2 Hz, 1 H), 4.28 and 4.65 (ABq, *J* = 10.6 Hz, 2 H, PhCH₂O), 4.68 and 4.93 (ABq, *J* = 10.3 Hz, 2 H, PhCH₂O), 4.92 (brs, 1 H, H-1), 4.95 and 5.14 (ABq, *J* = 14.0 Hz, 2 H, PhCH₂O), 5.33 (s, 2 H, PhCH₂O), 5.44~5.46(m, 1 H, H-2), 6.84 (d, *J* = 8.5 Hz, 2 H), 7.24~7.54 (m, 15 H), 7.99 (d, *J* = 7.7 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 9.0, 27.4(3), 39.1, 55.3, 66.9, 67.9, 68.0, 70.2, 71.1, 75.6, 77.7, 78.0, 97.8, 113.8, 127.5, 127.8, 128.0, 128.3(2), 128.4(4), 128.6, 128.7, 129.9, 130.2, 130.8, 132.6, 135.9, 138.2, 139.4, 159.3, 166.7, 177.7. Anal. Calcd for C₄₁H₄₅O₉: C, 60.89; H, 5.61. Found: C, 60.92; H, 5.61.

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-6-deoxy-3-O-*p*-methoxybenzyl-2-O-pivaloyl-α-D-rhamnnopyranoside (27). A solution of the compound **26** (90 mg, 0.11 mmol), n-Bu₃SnH (0.05 mL, 0.17 mmol, 1.5eq) and AIBN (2 mg, 0.01mmol, 0.1eq) in toluene (6 mL) was stirred at reflux for 2 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 5:1, v/v) to afford the compound **27** (67 mg, 0.098 mmol, 89%); colorless oil, *R_f* = 0.35 (n-hexane/EtOAc, 5:1, v/v); IR (CHCl₃ film) 2971, 2909, 1721, 1250, 1137, 1066 cm⁻¹; [α]_D²⁰ +17.0 (c, 2.57, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.23 (s, 9 H), 1.28 (d, *J* = 6.1 Hz, 3 H), 3.39 (t, *J* = 9.4 Hz, 1H), 3.75~3.81 (m, 1H), 3.78 (s, 3 H), 3.99 (dd, *J* = 3.2, 9.3 Hz, 1 H), 4.64 and 4.49 (ABq, *J* = 10.6 Hz, 2H, PhCH₂O), 4.60 and 4.88 (ABq, *J* = 10.5 Hz, 2 H, PhCH₂O), 4.84 (d, *J* = 1.6 Hz, 1 H, H-1), 4.95 and 5.12 (ABq, *J* = 14.3 Hz, 2 H, PhCH₂O), 5.33 (s, 2 H, PhCH₂O), 5.45 (dd, *J* = 1.9, 3.1 Hz, 1 H), 6.82~6.87 (m, 2 H), 7.23~7.55 (m, 15 H), 8.00 (d, *J* = 7.9 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 18.3, 27.3(3), 39.1, 55.3, 66.9, 67.4, 68.5, 68.6, 71.1, 75.4, 78.1, 80.0, 97.7 (C-1), 113.7, 127.3, 127.7, 128.0, 128.2, 128.3, 128.4(2), 128.4(3), 128.7, 129.8, 130.5, 130.8, 132.6, 136.0, 138.5, 139.9, 159.2, 166.7, 177.7. Anal. Calcd for C₄₁H₄₆O₉: C, 72.12; H, 6.79. Found: C, 72.08; H, 6.93.

5

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-2-O-pivaloyl- α -D-rhamnopyranoside (5). To a solution of compound **27** (510 mg, 0.75 mmol) in CH_2Cl_2 / H_2O (9.5 mL, 18:1, v/v) was added DDQ (0.22 g, 0.97 mmol, 1.3eq). After stirring at 0 °C for 40 min, the reaction mixture was quenched with NaHCO_3 (5 mL) and extracted with CH_2Cl_2 (2 $\times$ 30 mL). The combined organic layer was washed with saturated aqueous NaHCO_3 (2 $\times$ 9 mL) and brine (2 $\times$ 9 mL), dried (MgSO_4), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 4:1, v/v) to afford the compound **5** (397 mg, 0.71 mmol, 94%); colorless oil; R_f = 0.26 (n-hexane/EtOAc, 4:1, v/v); IR (CHCl_3 film) 3499, 2964, 1716, 1449, 1261, 1128, 1061 cm^{-1} ; $[\alpha]_D^{20}$ +30.3 (c, 2.59, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.24 (s, 9 H), 1.31 (d, J = 5.4 Hz, 3 H), 3.33 (t, J = 9.0 Hz, 1 H), 3.77 (m, 1 H), 4.18 (m, 1 H), 4.70 and 4.80 (ABq, J = 11.1, 2 H), 4.82 (brs, 1 H, H-1), 4.94 and 5.07 (ABq, J = 14.2, 2 H), 5.18 (brs, 1 H), 5.12 (brs, 2 H), 7.30~7.59 (m, 13 H), 7.97 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (63 MHz, CDCl_3) δ 18.2, 27.2(3), 39.1, 66.8, 67.5, 67.8, 70.6, 72.5, 75.1, 81.5, 97.4 (C-1), 127.3, 127.6, 128.0(2), 128.2(2), 128.3(2), 128.6(3), 128.7(3), 130.7, 132.5, 136.0, 139.9, 166.7, 178.2. Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{O}_8$: C, 70.44; H, 6.81. Found: C, 70.53; H, 6.67.

28

2'-(Benzyloxycarbonyl)benzyl (3-O-*p*-Methoxybenzyl-2,4-di-O-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-O-benzyl-2-O-pivaloyl- α -D-rhamnopyranoside (28). A solution of the donor **4** (50 mg, 0.085 mmol), acceptor **5** (67 mg, 0.119 mmol, 1.4 equiv.), and 2,6-di-*tert*-butyl-4-methylpyridine (52 mg, 0.253 mmol, 3 equiv.) in CH_2Cl_2 (5 mL) in the presence of 4A molecular sieves was stirred for 10 min at room temperature and cooled to -78 °C. After addition of TiF_4 (21 μL , 0.125 mmol, 1.5 equiv.), the reaction mixture was stirred at -78 °C for 1 h and allowed to warm over 1 h to 0 °C. The reaction mixture was quenched with saturated aqueous NaHCO_3 (5 mL), extract with CH_2Cl_2 (6 mL) washed with saturated aqueous NaHCO_3 (2 $\times$ 5 mL) and brine (2 $\times$ 5 mL), dried (MgSO_4), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane /EtOAc, 3:1, v/v) to afford compound **28** (75 mg, 0.075 mmol, 88%); colorless oil, R_f = 0.38 (n-hexane /EtOAc, 3:1, v/v);

IR (CHCl₃ film) 2971, 2925, 1737, 1260, 1143, 1096, 1737 cm⁻¹; [α]_D²⁰ +13.6 (c, 1.1, CHCl₃); ¹H NMR (250 MHz, CDCl₃) δ 1.09~1.11 (m, 12 H), 1.25 (s, 9 H), 1.28~1.32 (m, 12 H), 3.89 (t, J = 9.5 Hz, 1 H), 3.64 (s, 3 H), 3.78~3.83 (m, 2 H), 3.92~3.98 (m, 1 H), 4.24 (d, J = 3.1 Hz, 1 H), 4.29 and 4.55 (ABq, J = 11.5 Hz, 2 H), 4.48 and 4.68 (ABq, J = 10.9 Hz, 2 H), 4.84 (brs, 1 H), 4.96 and 5.07 (ABq, J = 13.3 Hz, 2 H), 5.06 (t, J = 10.3 Hz, 1 H), 5.27~5.30 (m, 1 H), 5.32 (s, 2 H), 5.37~5.38 (m, 1 H), 6.75 (d, J = 8.59 Hz, 2 H), 7.14~7.60 (m, 15 H), 7.99 (d, J = 7.8 Hz, 1 H); ¹³C NMR (63 MHz, CDCl₃) δ 17.7, 18.0, 27.2(3), 27.3(6), 38.8, 39.1, 55.2, 66.9(2), 67.2, 67.3(3), 68.0, 70.4, 71.9, 72.9, 74.0, 75.8, 79.9, 94.0, 97.5, 113.7, 127.3, 127.6, 127.9(3), 128.0(2), 128.3(2), 128.4(2), 128.6(2), 128.7, 129.6, 129.7(2), 130.8, 132.7, 136.0, 137.8, 139.8, 159.2, 166.7, 177.3(2), 177.4. Anal. Calcd for C₅₇H₇₂O₁₅: C, 68.66; H, 7.28. Found: C, 68.53; H, 7.38.

2'-Carboxybenzyl (3-O-*p*-Methoxybenzyl-2,4-di-O-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-O-benzyl-2-O-pivaloyl- α -D-rhamnopyranoside (2). Compound **28** (0.12 g, 0.12 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 13 mg, 0.012 mmol, 0.1 equiv) and ammonium acetate (9 mg, 0.117 mmol, 1 equiv) in MeOH (4 mL) at room temperature for 1 h. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane/EtOAc, 3:1, v/v) to afford compound **2** (103 mg, 0.11 mmol, 95%); colorless oil, R_f = 0.08 (n-hexane/EtOAc, 3:1, v/v); IR (CHCl₃ film) 3442, 2914, 1716, 1255, 1076, 1035 cm⁻¹; [α]_D²⁰ +6.99 (c, 0.80, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.11 (m, 12 H), 1.24 (s, 9 H), 1.32 (m, 12 H), 3.40 (t, J = 9.4 Hz, 1 H), 3.65 (s, 3 H), 3.78~3.85 (m, 2 H), 3.94~3.97 (m, 1 H), 4.25~4.27 (m, 1 H), 4.30 and 4.54 (ABq, J = 11.3 Hz, 2 H), 4.49 and 4.69 (ABq, J = 10.8 Hz, 2 H), 4.89 (brs, 1 H), 5.06 (t, J = 11.1 Hz, 1 H), 4.97 and 5.10 (ABq, J = 14.9 Hz, 2 H), 5.30 (brs, 1 H), 5.40 (s, 1 H), 6.75 (d, J = 8.1 Hz, 2 H), 7.14~7.61 (m, 10 H), 8.05 (d, J = 7.6 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 17.7, 18.1, 27.3(9), 38.9, 39.2, 55.2, 67.4(3), 67.8, 68.2, 70.4, 71.9, 73.0, 74.1, 75.8, 79.9, 94.1 (C -1, $J_{C,H1}$ = 171.1 Hz), 97.7, 101.6, 113.7, 127.2(2), 127.5, 127.9(2), 128.6(2), 129.7(2), 131.5, 133.4, 137.8, 140.3, 159.3, 171.2, 177.6(3); Anal. Calcd for C₅₀H₆₆O₁₅: C, 66.21; H, 7.33. Found: C, 66.37; H, 7.14.

1

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-manno-hexopyranoside (1). A solution of donor **2** (93 mg, 0.103 mmol), acceptor **3** (73 mg, 0.144 mmol, 1.4 equiv.), and 2,6-di-*tert*-butyl-4-methylpyridine (64 mg, 0.312 mmol, 3 equiv.) in CH₂Cl₂ (7 mL) in the presence of 4A molecular sieves was stirred for 10 min at room temperature and cooled to -78°C and then Tf₂O (26 μL , 0.155 mmol, 1.5 equiv.) was added to this solution. The reaction mixture was stirred at -78°C for 1 h and allowed to warm over 1 h to 0°C . The reaction mixture was quenched with saturated aqueous NaHCO₃ (5 mL), extract with CH₂Cl₂ (6 mL). Organic layer was washed with saturated aqueous NaHCO₃ (2 $\times$ 5 mL) and brine (2 $\times$ 5 mL), dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (n-hexane /EtOAc, 2:1, v/v) to afford α -trisaccharide **1** (90 mg, 0.071 mmol, 69%) and its β -anomer (14 mg, 0.011 mmol, 11%).

α -Trisaccharide **1**: amorphous solid $R_f = 0.48$ (n-hexane /EtOAc, 2:1, v/v); IR (CHCl₃ film) 2978, 2938, 1729, 1522, 1261, 1141, 1035 cm⁻¹; $[\alpha]_D^{20} +10.8$ (c, 0.75, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.16 (s, 10 H), 1.24 (s, 9 H), 1.28 (s, 12 H), 1.31~1.33 (m, 5 H), 3.40 (t, $J = 9.4$ Hz, 1 H), 3.65 (s, 3H, OCH₃), 3.82~3.85 (m, 4 H), 3.89~3.92 (m, 1 H), 3.99~4.02 (m, 1 H), 4.12~4.16 (m, 1 H), 4.25 (d, $J = 4.95$ Hz, 1 H), 4.31 and 4.55 (ABq, $J = 11.5$ Hz, 2 H), 4.49 and 4.70 (ABq, $J = 10.7$ Hz, 2 H), 4.90 (brs, 1 H), 5.04 (brs, 1 H), 5.08 (t, $J = 9.8$ Hz, 1 H), 4.96 and 5.18 (ABq, $J = 14.1$, 2 H), 5.21 (s, 1 H), 5.30 (s, 1 H), 5.36 (s, 2 H), 5.54 (s, 1 H), 5.62 (s, 1 H), 6.76 (d, $J = 8.2$ Hz, 2 H), 7.16 (d, $J = 8.1$ Hz, 2 H), 7.15~7.73 (m, 18 H), 8.03 (d, $J = 7.6$ Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 16.5, 17.7, 18.1, 27.1(3), 27.2(3), 27.3(3), 29.8, 38.9, 39.0(2), 55.2, 62.4, 67.0, 67.4, 68.1, 68.5, 69.2, 69.8, 70.4, 71.9, 72.1, 74.0, 74.2, 76.0, 78.3, 79.7, 81.5, 93.1(C''-1, $J_{C1,H1} = 170.3$ Hz), 93.6(C'-1, $J_{C1,H1} = 170.8$ Hz), 100.6(C-1, $J_{C1,H1} = 165.4$ Hz), 101.7, 113.7, 125.9(2), 126.3, 127.5(2), 128.0, 128.2(3), 128.4(3), 128.7(3), 128.8(3), 128.9, 129.7(3), 130.9, 132.6, 134.1, 135.9, 137.6, 139.7, 159.3, 166.8, 177.4(3); Anal. Calcd for C₇₁H₈₈O₂₀: C, 67.60; H, 7.03. Found: C, 67.63; H, 7.09; MALDI-TOF: m/z calcd. for C₇₁H₈₈O₂₀ [M+K]⁺ 1299.5506, found 1299.5564.

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- β -D-rhamnopyranosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-manno-hexopyranoside

β -Anomer of **1**: amorphous solid, R_f = 0.50 (n-hexane /EtOAc, 2:1, v/v); IR (CHCl₃ film) 2981, 2930, 1742, 1255, 1143, 1076 cm⁻¹; $[\alpha]_D^{20}$ +8.8 (c, 0.75, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.13 (s, 12 H), 1.24 (s, 15 H), 1.30 (s, 9 H), 3.37 (t, J = 9.4 Hz, 1 H), 3.62 (s, 3 H), 3.72 (s, 1 H), 3.79~3.81 (m, 6 H), 3.96 (m, 1 H), 4.16~4.18 (m, 2 H), 4.28 and 4.54 (ABq, J = 11.3 Hz, 2 H), 4.48 and 4.70 (ABq, J = 10.8 Hz, 2 H), 4.96~4.98 (m, 2 H), 5.03~5.08 (m, 2 H), 4.93 and 5.14 (ABq, J = 14.2 Hz, 2 H), 5.30 (s, 1 H), 5.33 (s, 2 H), 5.39 (s, 1 H), 5.59 (s, 1 H), 6.75 (d, J = 8.2 Hz, 2 H), 7.14 (d, J = 8.1 Hz, 1 H), 7.26~7.58 (m, 20 H), 8.00 (d, J = 7.6 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 14.3, 17.8, 17.9, 19.7, 21.2, 27.3(9), 29.8, 39.1, 55.2, 60.5, 62.9, 66.9, 67.4(2), 68.2, 68.7, 69.1, 70.5, 71.5, 71.9, 72.9, 74.2, 75.8, 79.8, 81.6, 82.6, 94.5, 100.2, 100.4, 102.2, 113.7, 126.5(2), 127.5, 127.7(2), 128.0(3), 128.1(3), 128.4(3), 128.6(5), 128.8(2), 129.2(2), 129.7, 130.9, 132.7, 137.7, 139.8, 166.5, 177.3(3); MALDI-TOF: m/z calcd. for C₇₁H₈₈O₂₀ [M+K]⁺ 1299.5506, found 1299.5559.

References

1. Coxon, B. *Tetrahedron*, **1965**, *21*, 3481–3503.
2. Kim, K. S.; Kim, J. H.; Lee, Y. Joo; Lee, Y. Jun; Park, J., *J. Am. Chem. Soc.* **2001**, *123*, 8477–8481.
3. Singh, G.; Vankayalapati, H. *Tetrahedron: Asymmetry*, **2001**, *12*, 1727–1735.

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**7**)

Current Data Parameters

NAME	VAL	UNIT
EXPNO	33	
PROCNO	1	

F2 - Acquisition Parameters

Date_	Time
20020705	16:51

INSTRUM spect

PROBHD 5 mm Dual 13C/

PULPROG zg30

TD 32768

SOLVENT CDCl3

NS 16

DS 2

SWH 5175.963 Hz

FIDRES 0.157958 Hz

AQ 3.1654389 sec

RG 57

DE 96.600 usec

TE 300.0 K

D1 2.00000000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 10.30 usec

PL1 -4.00 dB

SFO1 250.1312506 MHz

F2 - Processing parameters

SI	32768
SF	250.1300056 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY <td>36.55 cm</td>	36.55 cm
F1P <td>11.000 ppm</td>	11.000 ppm
F1 <td>2751.43 Hz</td>	2751.43 Hz
F2P <td>-1.000 ppm</td>	-1.000 ppm
F2 <td>-250.13 Hz</td>	-250.13 Hz
PPMCH <td>0.60000 ppm/ci</td>	0.60000 ppm/ci
HZCM <td>150.07800 Hz/cm</td>	150.07800 Hz/cm

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl- α -D-*arabino*-hexopyranosid-3-ulose (**8**)

Current Data Parameters

NAME	VAL	UNIT
EXPNO	43	
PROCNO	3	

F2 - Acquisition Parameters

Date_	Time
20021022	1.20

INSTRUM spect

PROBHD 5 mm Dual 13C/

PULPROG zg30

TD 32768

SOLVENT CDCl3

NS 91

DS 2

SWH 5175.983 Hz

FIDRES 0.157958 Hz

AQ 3.1554399 sec

RG 114

DM 96.600 usec

DE 6.00 usec

TE 300.0 K

D1 2.00000000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 10.30 usec

PL1 -4.00 dB

SFO1 250.1312506 MHz

F2 - Processing parameters

SI	32768
SF	250.130033 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

10 NMR Plot Parameters

CX	20.00 cm
CY <td>32.01 cm</td>	32.01 cm
FIP <td>11.000 dpm</td>	11.000 dpm
F1 <td>2751.43 Hz</td>	2751.43 Hz
F2P <td>-1.000 dpm</td>	-1.000 dpm
F2 <td>-250.13 Hz</td>	-250.13 Hz
PPMCM <td>0.50000 dpm/cm</td>	0.50000 dpm/cm
HZCM <td>150.07800 Hz/cm</td>	150.07800 Hz/cm

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl- α -D-*arabino*-hexopyranosid-3-ulose (8)

Methyl 3,3'-Anhydro-4,6-*O*-benzylidene-3-*C*-hydroxymethyl-2-*O*-*p*-methoxybenzyl- α -D-*manno*-hexopyranoside (**9**)

Methyl 3,3'-Anhydro-4,6-*O*-benzylidene-3-*C*-hydroxymethyl-2-*O*-*p*-methoxybenzyl- α -D-*manno*-hexopyranoside (**9**)

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl-3'-*C*-methyl- α -D-manno-hexopyranoside

(10)

Current Data Parameters

NAME	EXPNO	PROCNO	PROCN
kyt	74	1	

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1
20021111	10.45	spec	5 mm Dual 13C/	zg30	32768	CDCl3	32	2	5175.983 Hz	0.157958 Hz	3.1554389 sec	724.1	96.600 usec	6.00 usec	300.0 K	2.00000000 sec

===== CHANNEL f1 =====

NUC1	P1	SFO1
¹ H	10.30 usec	250.1312506 MHz

F2 - Processing parameters

SF	WDW	SSB	LB	GB	PC
32768	EM	0	0.30 Hz	0	1.00

1D NMR Plot Parameters

CX	CY	F1P	F2P	PPMCM	HZCM
20.00 cm	10.93 cm	11.000 ppm	2751.43 Hz	-1.000 ppm	-250.13 Hz
				0.60000 ppm/Ci	150.07800 Hz/Ci

Methyl 4,6-*O*-Benzylidene-2-*O*-*p*-methoxybenzyl-3'-*C*-methyl- α -D-*manno*-hexopyranoside

(10)

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**12**)

Current Data Parameters

NAME	EXPNO	PROCNO	PROCNO
NAME	117	2	2

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DM	DE	TE	D1
20030312	16.06	5 mm DUL 13C-	zq	32768	CDCl3	16	0	10000.000 Hz	0.305176 Hz	1.6384500 sec	16	50.000 usec	6.00 usec	300.0 K	2.00000000 sec	

===== CHANNEL f1 =====

NUC1	P1	PL1	SFO1
1H	8.20 usec	-5.00 dB	500.1323550 MHz

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
16384	500.1300467 MHz	EM	0	2.00 Hz	0	1.00

1D NMR plot parameters

CX	F1P	F1	F2P	F2	PPMCM	HZCM
20.00 ppm	11.000 ppm	5501.43 Hz	-1.000 ppm	-500.13 Hz	0.60000 ppm/cf	300.07803 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**12**)

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**13**)

Current Data Parameters
NAME KYC
EXPNO 139
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030408
Time 16.34
INSTRUM spect
PROBHD 5 mm DUL 13C-
PULPROG zg
TO 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384500 sec
RG 16
DM 50.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.20 usec
PL1 -5.00 dB
SFO1 500.1323550 MHz

F2 - Processing parameters
SI 16384
SF 500.1300094 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCM 0.60000 ppm/c
HZCM 300.07800 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**13**)

Current Data Parameters

NAME	KYC
EXPNO	139
PROCNO	1

F2 - Acquisition Parameters

Date_	20030408
Time	16.47
INSTRUM	spect
PROBHD	5 mm DUL 13C-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	194
DS	4
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651262 sec
RG	5792.6
DM	13.200 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec

===== CHANNEL f1 =====

NUC1	13C
P1	8.00 usec
PL1	4.00 dB
SFO1	125.7673644 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	-5.00 dB
PL12	17.00 dB
SFO2	500.1326076 MHz

F2 - Processing parameters

SI	32768
SF	125.7577874 MHz
WDW	EM
SSB	0
LB	10.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	25151.56 Hz
F2P	-15.000 ppm
F2	-1886.37 Hz
PPMCK	10.75000 ppm/cr
HZCM	1351.89624 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (**14**)

Current Data Parameters
NAME kvl
EXPNO 140
PROCNO 1
F2 - Acquisition Parameter
Date_ 20030410
Time 16.15
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 2
SWH 5175.983 Hz
FIDRES 0.157958 Hz
AQ 3.1554389 sec
RG 40.3
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 -4.00 dB
SF01 250.1312506 MHz
F2 - Processing parameters
S1 32768
SF 250.129965 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 26.20 cm
F1 11.000 ppm
F2 2751.43 Hz
F2P -1.000 ppm
PPMKM -250.13 Hz
PPKCM 0.60000 ppm
HZCM 150.07800 Hz/

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (**14**)

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-*arabino*-hexopyranosid-3-uloside (**15**)

Current Data Parameters

NAME	EXPNO	PROCNO
kyt	1112	1

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	P1	TD	SOLVENT	NS	DS	SWH	FIDRES
20030512	14.10	spect	5 mm DUL 13C-	14.10	32768	CDCl3	16	0	10000.000 Hz	0.305176 Hz

RG 16
 DW 50.000 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec

===== CHANNEL f1 =====

NUC1	P1	PL1	SFO1
¹ H	8.20 usec	-5.00 dB	500.1323550 MHz

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
16384	500.1300363 MHz	EM	0	2.00 Hz	0	1.00

10 NMR plot parameters

CX	F1P	F1	F2P	F2	PPMCM	HZCM
20.00 ppm	11.000 ppm	5501.43 Hz	-1.000 ppm	-500.13 Hz	0.60000 ppm/cm	300.07803 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-arabino-hexopyranosid-3-uloside (**15**)

Current Data Parameters

NAME	VALUE
EXPNO	1112
PROCNO	1

F2 - Acquisition Parameters

NAME	VALUE
Date_	20030512
Time	14.17
INSTRUM	spect
PROBHD	5 mm DUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	107
DS	4
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	4096
DM	13.200 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec

===== CHANNEL f1 =====

NAME	VALUE
NUC1	¹³ C
P1	8.00 usec
PL1	4.00 dB
SFO1	125.7673644 MHz

===== CHANNEL f2 =====

NAME	VALUE
CPDPRG2	waltz16
NUC2	¹ H
PCPD2	100.00 usec
PL2	-5.00 dB
PL12	17.00 dB
SFO2	500.1321091 MHz

F2 - Processing parameters

NAME	VALUE
SI	32768
SF	125.7577943 MHz
WDW	EM
SSB	0
LB	10.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

NAME	VALUE
CX	20.00 cm
F1P	210.000 ppm
F1	26409.13 Hz
F2P	-15.000 ppm
F2	-1886.37 Hz
PPMCM	11.25000 ppm/cm
HZCM	1414.77527 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-3-methylene- α -D-arabino-hexopyranoside (**16**)

Current Data Parameters
NAME kyt
EXPNO 149
PROCNO 2

F2 - Acquisition Parameters
Date_ 20030419
Time 13:53
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 5175.983 Hz
FIDRES 0.157958 Hz
AQ 3.1654389 sec
RG 203.2
DM 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 -4.00 dB
SF01 250.1312506 MHz

F2 - Processing parameters
SI 32768
SF 250.1300044 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 45.12 cm
F1P 11.000 ppm
F1 2751.43 Hz
F2P -250.13 Hz
F2 -1.000 ppm
PPMCM 0.60000 ppm/t
HZCM 150.07800 Hz/cr

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-3-methylene- α -D-*arabino*-hexopyranoside (**16**)

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-deoxy-3-methylene- α -D-arabino-hexopyranoside (17)

Current Data Parameters

NAME	VALUE
EXPNO	151
PROCNO	3

F2 - Acquisition Parameters

Date_	Time
20030424	16:48

INSTRUM spect

PROBHD 5 mm DUL 13C-

PULPROG zg

TD 32768

SOLVENT CDCl3

NS 35

DS 0

SWH 10000.000 Hz

FIDRES 0.305176 Hz

AQ 1.6384500 sec

RG 32

DM 50.000 usec

DE 6.00 usec

TE 300.0 K

D1 2.00000000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 8.20 usec

PL1 -5.00 dB

SFO1 500.1323550 MHz

F2 - Processing parameters

SI	SI
16384	500.1300277 MHz

WDW EM

SSB 0

LB 2.00 Hz

GB 0

PC 1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	5501.43 Hz
F2P	-1.000 ppm
F2	-500.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	300.07803 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-deoxy-3-methylene- α -D-arabino-hexopyranoside (17)

2''-(Benzyloxycarbonyl)benzyl 3,3'-Anhydro-4,6-O-benzylidene-3-C-hydroxymethyl- α -D-manno-hexopyranoside (**18**)

Current Data Parameters

NAME	EXPNO	PROCNO
182	1	1

F2 - Acquisition Parameters

Date_	Time
20030427	20.29

INSTRUM spect

PROBHD 5 mm Dual 13C/

PULPROG zg30

TD 32768

SOLVENT CDCl3

NS 32

DS 2

SWH 5175.983 Hz

FIDRES 0.157958 Hz

AQ 3.1654389 sec

RG 57

DM 96.600 us

DE 6.00 us

TE 300.0 K

D1 2.0000000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 10.30 us

PL1 -4.00 dB

SFO: 250.1312506 MHz

F2 - Processing parameters

SI	32768
SF	250.130097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	8.78 cm
F1P	11.000 ppr
F1	2751.43 Hz
F2P	-1.000 ppr
F2	-250.13 Hz
PPMDM	0.60000 ppr
HZCN	150.07800 Hz

2''-(Benzyloxycarbonyl)benzyl 3,3'-Anhydro-4,6-*O*-benzylidene-3-*C*-hydroxymethyl- α -D-*manno*-hexopyranoside (**18**)

2''-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3'-*C*-methyl- α -D-*manno*-hexopyranoside

(3)

Current Data Parameters

NAME	EXPNO	PROCNO	Ykt
20030916	2001	1	

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1
20030916	22.28	spect	5 mm Dual 13C/	zg30	32768	CDCl3	32	2	5175.583 Hz	0.157558 Hz	3.1654389 sec	161.3	96.600 usec	6.00 usec	300.0 K	2.00000000 sec

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
32768	250.1300000 MHz	EM	0	0.30 Hz	0	1.00

1D NMR plot parameters

CX	CY	F1P	F1	F2P	F2	PPHCM	HZCM
20.00 cm	12.78 cm	11.000 ppm	2751.43 Hz	-1.000 ppm	-250.13 Hz	0.60000 ppm/1	150.07800 Hz/c1

2''-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3'-*C*-methyl- α -D-*manno*-hexopyranoside

(3)

2'-(Benzyloxycarbonyl)benzyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranoside (**20**)

Current Data Parameters
 NAME kyt
 EXPNO 100
 PROCNO 5

F2 - Acquisition Parameters
 Date_ 20030211
 Time 23:59
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zg30
 TO 32768
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 5175.983 Hz
 FIDRES 0.157958 Hz
 AQ 3.1654389 sec
 RG 128
 DW 96.600 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.30 usec
 PL1 -4.00 dB
 SF01 250.1312506 MHz

F2 - Processing parameters
 SI 32768
 SF 250.1299985 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 21.58 cm
 F1P 11.000 ppm
 F1 2751.43 Hz
 F2P -1.000 ppm
 F2 -250.13 Hz
 PPMCM 0.60000 ppm/ci
 HZCM :50.07800 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranoside (**20**)

2'-(Benzyloxycarbonyl)benzyl α -L-Rhamnopyranoside (**21**)

Current Data Parameters

NAME	kyt
EXPNO	224
PROCNO	1

F2 - Acquisition Parameters

Date_	Time
20031127	23.23

INSTRUM spect

PROBHD 5 mm Dual 13C/

PULPROG zg30

TD 32768

SOLVENT CDCl₃

NS 16

DS 2

SWH 5175.983 Hz

FIDRES 0.157958 Hz

AQ 3.1654389 sec

RG 114

OK 96.600 usec

DE 6.00 usec

TE 300.0 K

D1 2.00000000 sec

===== CHANNEL f1 =====

NUC1 ¹H

P1 10.30 usec

PL1 -4.00 dB

SFO1 250.1312506 MHz

F2 - Processing parameters

SF	32768
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

10 NMR plot parameters

CX	20.00 cm
CV <td>-8.06 cm</td>	-8.06 cm
FJP <td>11.000 ppm</td>	11.000 ppm
F1 <td>2751.43 Hz</td>	2751.43 Hz
F2 <td>-1.000 ppm</td>	-1.000 ppm
F2 <td>-250.13 Hz</td>	-250.13 Hz
PPMCM <td>0.60000 ppm/cm</td>	0.60000 ppm/cm
HZCM <td>-150-07800 Hz/cm</td>	-150-07800 Hz/cm

2'-(Benzyloxycarbonyl)benzyl α-L-Rhamnopyranoside (21)

2'-(Benzyloxycarbonyl)benzyl 3-O-*p*-Methoxybenzyl- α -L-rhamnopyranoside (**22**)

2'-(Benzyloxycarbonyl)benzyl 3-O-*p*-Methoxybenzyl- α -L-rhamnopyranoside (**22**)

Current Data Parameters

NAME	kylc
EXPNO	108
PROCNO	1

F2 - Acquisition Parameters

Date_	20030220
Time	19.44
INSTRUM	spect
PROBHD	5 mm DUL 13C-
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	66
DS	4
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	6502
DN	13.200 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec

===== CHANNEL f1 =====

NUC1	¹³ C
P1	8.00 usec
PL1	4.00 dB
SFO1	125.7673544 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	¹ H
PCPD2	100.00 usec
PL2	-5.00 dB
PL12	17.00 dB
SFO2	500.1324572 MHz

F2 - Processing parameters

SI	32768
SF	125.7577827 MHz
WDW	EM
SSB	0
LB	10.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
FJP	200.000 ppm
F1	25151.56 Hz
F2p	-10.000 ppm
F2	-1237.56 Hz
PPMCM	10.50000 ppm/c
HZCM	1320.45667 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranoside
(23)

2'-(Benzyloxycarbonyl)benzyl 3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranoside
(23)

2'-Carboxybenzyl 3-*O-p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranoside (**4**)

Current Data Parameters

NAME	EXPNO	PROCNO
kyt	188	1

F2 - Acquisition Parameters

Date_	Time
20030821	10.49

INSTRUM spect

PROBHD 5 mm Dual 13C/

PULPROG zg

TD 32768

SOLVENT CDCl3

NS 16

DS 0

SWH 7002.801 Hz

FIDRES 0.213709 Hz

AQ 2.3397565 sec

RG 11.3

DW 71.400 usec

DE 6.00 usec

TE 298.0 K

D1 2.00000000 sec

MCREST 0.00000000 sec

MCNRC 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 8.20 usec

PL1 -5.00 dB

SFO1 500.1323550 MHz

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
16384	500.1300115 MHz	EM	0	2.00 Hz	0	1.00

10 NMR plot parameters

CX	F1P	F2P	PPMCK	HZCM
20.00 cm	48.77 cm	11.000 ppm	5501.43 Hz	-1.000 ppm
			-500.13 Hz	
			0.50000 ppm/c	
			300.07800 Hz/cm	

2'-Carboxybenzyl 3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranoside (**4**)

Current Data Parameters
NAME kyc
EXPNO 188
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030821
Time 11.01
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg
TD 65536
SOLVENT Aceton
NS 160
DS 4
SWH 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8651384 sec
RG 4096
DM 13.200 usec
DE 5.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCHEST 0.00000000 sec
MCHK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 4.00 dB
SFO1 125.7673544 MHz

===== CHANNEL f2 =====
CQPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.00 dB
PL12 17.00 dB
SFO2 500.132630 MHz

F2 - Processing parameters
SI 32768
SF 125.757839 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

ID NMR plot parameters
CX 20.00 cm
CY 48.42 cm
F1P 210.000 ppm
F1 25609.13 Hz
F2P -1237.58 Hz
F2 11.00000 ppm/
PPMCH 1383.3357 Hz/Ci
HZ/M

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-*O*-*p*-methoxybenzyl-2-*O*-pivaloyl- α -D-mannopyranoside (**24**)

Current Data Parameters

NAME	EXPNO	PROCNO	PROCNO	DATE_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1
kyt	83	1	1	20021206	10.02	spec	5 mm DUL 13C-	zg	32768	CDCl3	32	0	10000.000 Hz	0.305176 Hz	1.6384500 sec	128	50.000 usec	6.00 usec	300.0 K	2.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 8.20 usec
PL1 -5.00 dB
SF01 500.1323550 MHz

F2 - Processing parameters
SI 16384
SF 500.1300167 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCH 0.60000 ppm/cr
HZCM 300.07800 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-Benzylidene-3-*O*-*p*-methoxybenzyl-2-*O*-pivaloyl- α -D-mannopyranoside (**24**)

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-3-O-*p*-methoxybenzyl-2-O-pivaloyl- α -D-mannopyranoside (**25**)

2'-(Benzyloxycarbonyl)benzyl 4-*O*-Benzyl-3-*O*-*p*-methoxybenzyl-2-*O*-pivaloyl- α -D-mannopyranoside (**25**)

2'-(Benzyloxycarbonyl)benzyl 4-*O*-Benzyl-6-deoxy-3-*O*-*p*-methoxybenzyl-6-iodo-2-*O*-pivaloyl- α -D-mannopyranoside (**26**)

2'-(Benzyloxycarbonyl)benzyl 4-*O*-Benzyl-6-deoxy-3-*O*-*p*-methoxybenzyl-6-iodo-2-*O*-pivaloyl- α -D-mannopyranoside (**26**)

2'-(Benzyloxycarbonyl)benzyl 4-*O*-Benzyl-6-deoxy-3-*O*-*p*-methoxybenzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (**27**)

2'-(Benzyloxycarbonyl)benzyl 4-*O*-Benzyl-6-deoxy-3-*O*-*p*-methoxybenzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (**27**)

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-2-O-pivaloyl- α -D-rhamnopyranoside (**5**)

Current Data Parameters

NAME	EXPNO	PROCNO	PROCPS
NAME	222	1	

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1	MCREST	MCRESK
20031211	21.04	5 mm Dual 13C/	5 mm Dual 13C/	zgpg30	32768	CDCl3	16	0	7002.801 Hz	0.213709 Hz	2.3357565 sec	16	71.400 usec	5.00 usec	298.0 K	2.00000000 sec	0.00000000 sec	0.01500000 sec

***** CHANNEL f1 *****

NUC1	P1	PL1	SFO1
1H	8.20 usec	-5.00 dB	500.1323550 MHz

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
16384	500.1300375 MHz	EM	0	2.00 Hz	0	1.00

10 NMR plot parameters

CX	CY	F1p	F1	F2p	F2	PPMCM	HZCM
20.00 cm	12.50 cm	11.000 ppm	5501.43 Hz	-1.000 ppm	-500.13 Hz	0.60000 ppm/ci	300.07803 Hz/cm

2'-(Benzyloxycarbonyl)benzyl 4-O-Benzyl-2-O-pivaloyl- α -D-rhamnopyranoside (**5**)

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (**28**)

Current Data Parameters

NAME	EXPNO	PROCNO
Kyt	189	1

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1
20030622	19:05	spect	5 mm Dual 13C/	zgpg30	32768	CDCl3	143	2	5175.983 Hz	0.157956 Hz	3.1654389 sec	143.7	96.600 usec	6.00 usec	300.0 K	2.00000000 sec

===== CHANNEL f1 =====

NUC1	P1	PL1	SFO1
¹ H	10.30 usec	-4.00 dB	250.1312506 MHz

F2 - Processing parameters

SF	WDW	SSB	LB	GB	PC
32768	EM	0	0.30 Hz	0	1.00

1D NMR plot parameters

CX	CY	F1P	F2P	PPMCM	HZCM
20.00 cm	27.53 cm	11.000 ppm	-1.000 ppm	-250.13 Hz	0.60000 ppm/c
		2751.43 Hz			150.07800 Hz/cm

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (**28**)

2'-Carboxybenzyl (3-*O-p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (2)

Current Data Parameters
NAME kyt
EXPNO 190
PROCNO 3

F2 - Acquisition Parameters
Date_ 20030915
Time 10.22
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7002.801 Hz
FIDRES 0.213709 Hz
AQ 2.3397565 sec
RG 50.8
DE 71.400 usec
TE 298.0 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCKRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.20 usec
PL1 -5.00 dB
SF01 500.1323550 MHz

F2 - Processing parameters
SI 16384
SF 500.1300132 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 25.91 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCK 0.50000 ppm/c
HZCK 300.07800 Hz/cm

2'-Carboxybenzyl (3-*O-p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnopyranoside (2)

Current Data Parameters

NAME	NAME	NAME
EXPNO	190	
PROCNO	3	

F2 - Acquisition Parameters

Date_	Time	INSTRUM
20030915	10.35	spect
PROBHD	5 mm TXI 13C Z	
PULPROG	zgpg30	
TD	65536	
SOLVENT	Aceton	
NS	697	
DS	4	
SWH	37878.789 Hz	
FIDRES	0.577984 Hz	
AQ	0.8651384 sec	
RG	4096	
DM	13.200 usec	
DE	6.00 usec	
TE	298.0 K	
D1	2.00000000 sec	
d11	0.03000000 sec	
MDRES	0.00000000 sec	
MDRKK	0.01500000 sec	

===== CHANNEL f1 =====

NUC1	13C
P1	8.00 usec
PL1	4.00 dB
SFO1	125.7673544 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	-5.00 dB
PL12	17.00 dB
SFO2	500.1323550 MHz

F2 - Processing parameters

SI	32768
SF	125.7677723 MHz
MDW	EM
SSB	0
LB	10.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CV	13.65 cm
F1P	200.000 ppm
F1	25151.55 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCK	10.50000 ppm/c
HZCM	1320.45667 Hz/cm

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-*manno*-hexopyranoside (**1**)

2'-(Benzyloxycarbonyl)benzyl (3-*O*-*p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- α -D-rhamnosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-*manno*-hexopyranoside (**1**)

Current Data Parameters
NAME kytc
EXPNO 193
PROCNO 2

F2 - Acquisition Parameters
Date_ 20030916
Time 19.57
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 65536
SOLVENT Aceton
NS 816
DS 0
SWH 50505.051 Hz
FIDRES 0.770646 Hz
AQ 0.648863 sec
RG 4096
DW 9.900 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 4.00 dB
SF01 125.7703168 MHz

F2 - Processing parameters
SI 32768
SF 125.757746 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

10 NMR plot parameters
CX 20.00 cm
CY 10.93 cm
F1P 200.000 ppm
F1 25151.55 Hz
F2P -10.000 ppm
F2 -1257.58 Hz
PNUC 10.50000 ppm/
HZCM 1320.45667 Hz/ci

2'-(Benzyloxycarbonyl)benzyl (3-*O-p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- β -D-rhamnopyranosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-*manno*-hexopyranoside (β anomer of **1**)

Current Data Parameters

NAME	EXPNO	PROCNO	PROCNO
NAME	192	3	

F2 - Acquisition Parameters

Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	RG	DM	DE	TE	D1	MCREST	MCNMR	
20030916	18.43	5 mm Dual 13C/	13C/	zg	32768	CDCl3	32	0	7002.801 Hz	0.213709 Hz	2.3397565 sec	57	71.400 use	6.00 use	298.0 K	2.00000000 sec	0.00000000 sec	0.01500000 sec

===== CHANNEL f1 =====

NUC1	P1	PL1	SFO1
1H	8.20 use	-5.00 dB	500.1323550 MHz

F2 - Processing parameters

SI	WDW	SSB	LB	GB	PC
16384	EM	0	2.00 Hz	0	1.00

1D NMR plot parameters

CX	CY	F1	F2	PPMCM	HZCM
20.00 cm	17.15 cm	11.000 ppi	5501.43 Hz	-500.13 Hz	0.60000 ppi

2'-(Benzyloxycarbonyl)benzyl (3-*O-p*-Methoxybenzyl-2,4-di-*O*-pivaloyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-(4-*O*-benzyl-2-*O*-pivaloyl- β -D-rhamnopyranosyl)-(1 $\rightarrow$ 2)-4,6-*O*-benzylidene-3-*C*-methyl- α -D-*manno*-hexopyranoside (β anomer of **1**)