Supporting Information: Experimental Part

Synthesis and Stereoselective Glycosylation of D- and L-*glycero*- β -D-*manno*-Heptopyranoses

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General

Unless otherwise stated ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution. Optical rotations were recorded in CHCl_3 solution, unless otherwise stated. All solvents were dried and distilled by standard protocols. All reactions were conducted under a blanket of dry

nitrogen. All organic extracts were dried over sodium sulfate and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)- α -D-thiomannopyranoside (2).

A solution of compound **1**¹ (3.17 g, 5.56 mmol) in CH₂Cl₂ (30 mL) was treated dropwise with DIBAL-H (19 mL, 27.8 mmol, 1.5 M solution in toluene) at -78 °C, then slowly warmed up to 0 °C over a period of 5h. The reaction mixture was then poured into a saturated solution of K-Na-tartrate tetrahydrate and stirred vigorously for 2h and extracted with CH₂Cl₂. The organic layer was washed with saturated NH₄Cl solution and brine, dried and concentrated. Chromatographic purification (20% ethyl acetate in hexane) afforded **2** (2.87 g, 90%). $[\alpha]_D^{27} +85.4$ (*c* 1.5); ¹H NMR (500 MHz) δ : 7.46-7.29 (m, 17H), 6.93-6.92 (d, *J* = 8.5 Hz, 2H), 5.58 (s, 1H), 4.95-4.93 (d, *J* = 11.5 Hz, 1H), 4.74-4.66 (m, 5H), 4.18-4.16 (m, 1H), 4.12-4.09 (t, *J* = 9.5 Hz, 1H), 4.06 (s, 1H), 3.96-3.94 (dd, *J* = 2.5, 9.0 Hz, 1H), 3.87 (bs, 2H), 3.83 (s, 3H); ¹³C NMR (100 MHz) δ : 159.4, 138.2, 137.9, 134.1, 131.9, 130.6, 129.9, 129.2, 128.53, 128.51, 128.0, 127.9, 127.86, 127.82, 127.7, 113.9, 86.1, 80.2, 76.5, 75.1, 74.6, 73.4, 72.4, 72.3, 62.2, 55.3. Anal. Calcd for C₃₄H₃₆O₆S: C, 71.30; H, 6.34. Found: C, 70.85; H, 6.34.

Phenyl 2,3-di-*O*-benzyl-6,7-dideoxy-4-*O*-(*p*-methoxybenzyl)- α -D-thiohept-6-enopyranoside (3) and Phenyl 2,3-di-*O*-benzyl-4,6,7-trideoxy- α -D-thiohept-4,6-dienopyranoside (4).

To a solution of oxalyl chloride (667 μ L, 7.35 mmol) in CH₂Cl₂ (4 mL) was added a solution of DMSO (1.22 mL, 17.15 mmol) in CH₂Cl₂ (6 mL) at -65 °C and after 15 min. a solution of **2** (2.81 g, 4.90 mmol) in CH₂Cl₂ (20 mL) was added to the above solution *via* cannula. At -50 °C after 1h, Et₃N (2.73 mL, 19.60 mmol) was added to the above solution and the reaction mixture was allowed to warm up to room temperature over a period of 4h before it was

quenched with water and extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried and concentrated to give the crude aldehyde which was taken forward without purification. To a suspension of methyl triphenylphosphonium bromide (2.10 g, 5.88 mmol) in THF (10 mL) at -40 °C was added ⁿBuLi (2.35 mL, 5.88 mmol, 2.5 solution in hexane) and after 30 min. a solution of the above aldehyde in THF (20 mL) was added *via* cannula to that solution and the mixture was stirred at the same temperature for 1h. The reaction mixture was then warmed up to room temperature over a period of 4h before it was quenched with a saturated solution of NH₄Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried and concentrated. Chromatographic purification (5% ethyl acetate in hexane) afforded **3** (1.81 g, 65%) and **4** (0.30 g, 14%). **3** : $[\alpha]_D^{27} +77.4$ (*c* 1.0); ¹H NMR (500 MHz) δ : 7.40-7.24 (m, 17H), 6.87-6.85 (d, *J* = 8.5 Hz, 2H), 6.07-5.99 (m, 1H), 5.53 (s, 1H), 5.46-5.43 (d, *J* = 17.0 Hz, 1H), 5.31-5.29 (d, *J* = 10.5 Hz, 1H), 4.80-4.78 (d, *J* = 10.0 Hz, 1H), 4.75-4.72 (d, *J* = 12.5 Hz, 1H), 4.69-4.66 (d, *J* = 11.5 Hz, 1H), 4.63-4.61 (d, *J* = 11.5 Hz, 1H), 4.59-4.57 (d, *J* = 10.5 Hz, 1H), 4.54-4.51 (t, d, *J* = 8.5 Hz, 1H), 3.99 (s, 1H), 3.87-3.84 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.81-3.78 (m, 5H); ¹³C NMR (125 MHz) δ : 159.2, 138.3, 137.9, 134.9, 134.5, 131.5, 130.6, 129.8, 129.0, 128.41, 128.4, 127.9, 127.8, 127.7, 127.4, 118.3, 113.7, 85.8, 79.8, 78.5, 76.6, 74.9, 73.8, 72.4, 72.1, 55.3; ESI-HRMS Calcd for C₃₅H₃₆O₅SNa [M + Na]⁺ : 591.2181. Found 591.2170. **4** : $[\alpha]_D^{27} +161.4$ (*c* 1.0); ¹H NMR (400 MHz) δ : 7.55-7.53 (m, 2H), 7.38-7.31 (m, 13H), 6.13-6.06 (dd, *J* = 11.0, 17.0 Hz, 1H), 5.67-5.66 (d, *J* = 5.6 Hz, 1H), 5.59-5.55 (d, *J* = 17.6 Hz, 1H), 5.17-5.15 (d, *J* = 10.8 Hz, 1H), 5.04-5.03 (d, *J* = 3.6 Hz, 1H), 4.73-4.67 (t, *J* = 12.8 Hz, 2H), 4.61 (s, 2H), 4.27-4.21 (m, 1H), 3.87-3.84 (t, *J* = 4.8 Hz, 1H); ¹³C NMR (100 MHz) δ : 149.9, 138.3, 137.7, 133.1, 132.7, 132.4, 131.1, 130.9, 128.9, 128.8, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 115.7, 101.5, 83.7, 72.9,

71.9, 70.9, 68.7, 68.2; ESI-HRMS Calcd for C₂₇H₂₆O₃SNa [M + Na]⁺ : 453.1500. Found 453.1514.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-D-*glycero*- α -D-thio-*manno*-heptopyranoside (5) and Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-L-*glycero*- α -D-thio-*manno*-heptopyranoside (6).

To a solution of **3** (1.45 g, 2.55 mmol) in acetone:water (9:1, 20 mL) at 0 °C were added NMNO (0.60 g, 5.10 mmol) and OsO₄ (1.63 mL, 0.13 mmol, 2.5 w% solution in 2-methyl-2-propanol). The reaction mixture was then stirred at room temperature for 4h before it was quenched with a saturated solution of NaHSO₃. After stirring for additional 15 min. the reaction mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried and concentrated. Chromatographic purification (44% ethyl acetate in hexane) afforded **5** (0.94 g, 61%) and **6** (0.31 g, 20%). **5** : [α]_D²⁴ +96.8 (*c* 1.0); ¹H NMR (500 MHz) δ : 7.43-7.22 (m, 17H), 6.88-6.86 (d, *J* = 8.5 Hz, 2H), 5.47 (s, 1H), 4.98-4.96 (d, *J* = 10.5 Hz, 1H), 4.68-4.60 (m, 5H), 4.20-4.17 (dd, *J* = 5.5, 9.5 Hz, 1H), 4.08-4.05 (t, *J* = 9.5 Hz, 1H), 3.99 (s, 1H), 3.93-3.89 (m, 2H), 3.81 (s, 3H), 3.62-3.57 (m, 2H), 3.17 (bs, 1H), 2.08 (bs, 1H); ¹³C NMR (125 MHz) δ : 159.5, 137.8, 137.7, 133.4, 132.2, 129.9, 129.7, 129.2, 128.6, 128.5, 127.9, 127.8, 113.9, 85.9, 80.3, 76.4, 76.0, 74.8, 72.6, 72.5, 72.3, 71.9, 63.1, 55.3; ESI-HRMS Calcd for C₃₅H₃₈O₇SNa [M + Na]⁺ : 625.2236. Found 625.2239. **6** : [α]_D²⁷ +68.0 (*c* 0.8); ¹H NMR (400 MHz) δ : 7.38-7.24 (m 17H), 6.88-6.85 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 4.91-4.88 (d, *J* = 10.4 Hz, 1H), 4.70-4.61 (m, 5H), 4.22-4.17 (t, *J* = 9.2 Hz, 1H), 4.03-4.00 (d, *J* = 10.0 Hz, 1H), 3.97 (s, 2H), 3.89-3.86 (dd, *J* = 2.8, 9.2 Hz, 1H), 3.80 (s, 3H), 3.56-3.51 (m, 2H), 2.36 (bs, 1H), 1.83 (bs, 1H); ¹³C NMR (100 MHz) δ : 159.3, 138.1, 137.8, 133.2, 131.8, 130.4, 129.8, 129.3, 128.5, 127.95, 127.9, 127.8, 113.9, 85.8, 79.9, 76.0, 75.1, 74.1, 73.8,

72.5, 72.3, 69.2, 64.9, 55.3; ESI-HRMS Calcd for C₃₅H₃₈O₇SNa [M + Na]⁺ : 625.2236. Found 625.2224.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-*glycero-α*-D-thio-*manno*-heptopyranoside (8).

A solution of **5** (0.49 g, 0.82 mmol) and imidazole (0.14 g, 2.05 mmol) in CH₂Cl₂ (10 mL) at 0 °C was treated with TBDPSCl (231 μL, 0.90 mmol) and stirred at 0-10 °C for 2h. The reaction mixture was then diluted with CH₂Cl₂ and washed with a saturated solution of NH₄Cl. The organic layer was dried and concentrated to give the crude silyl ether **7** which was taken forward without purification. A solution of **7**, PPh₃ (0.43 g, 1.64 mmol) and *p*-nitrobenzoic acid (0.27 g, 1.64 mmol) in THF (10 mL) was treated with DIAD (323 μL, 1.64 mmol) at room temperature and stirred for 5h. The reaction mixture was then concentrated and chromatographic purification (8% ethyl acetate in hexane) afforded **8** (0.75 g, 92%). [α]_D²³ +47.9 (c 0.6); ¹H NMR (500 MHz) δ: 8.12-8.10 (d, *J* = 9.0 Hz, 2H), 8.03-8.02 (d, *J* = 8.5 Hz, 2H), 7.66-7.62 (dd, d, *J* = 8.0, 12.0 Hz, 4H), 7.46-7.33 (m, 20H), 7.16-7.08 (m, 3H), 6.88-6.87 (d, *J* = 8.5 Hz, 2H), 5.86-5.83 (t, *J* = 6.0 Hz, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 4.83-4.81 (d, *J* = 10.0 Hz, 1H), 4.74-4.69 (m, 5H), 4.48-4.46 (d, *J* = 10.0 Hz, 1H), 4.42-4.40 (d, *J* = 9.5 Hz, 1H), 4.08 (t, *J* = 2.5 Hz, 1H), 4.01-3.98 (dd, *J* = 2.5, 9.5 Hz, 1H), 3.96-3.91 (m, 2H), 3.81 (s, 3H), 0.97 (s, 9H); ¹³C NMR (125 MHz) δ: 164.1, 159.3, 137.9, 137.7, 135.6, 135.5, 133.4, 133.2, 131.8, 130.9, 130.3, 130.2, 129.7, 128.6, 128.5, 127.9, 127.8, 127.7, 127.6, 127.5, 123.4, 113.9, 85.7, 80.7, 76.4, 74.9, 73.5, 72.8, 72.4, 72.1, 70.7, 62.2, 55.3, 26.7, 19.1; ESI-HRMS Calcd for C₅₈H₅₉O₁₀SSiNK [M + K]⁺ : 1028.3266. Found 1028.3297.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-*glycero-α*-D-thio-*manno*-heptopyranoside (9).

A solution of **8** (1.29 g, 1.30 mmol) in MeOH:CH₂Cl₂ (20:1, 21 mL) was treated with K₂CO₃ (0.20 g, 1.43 mmol) and stirred at room temperature for 3h. The reaction mixture was then concentrated, dissolved in ethyl acetate and washed with water and brine, dried and concentrated. Chromatographic purification (14% ethyl acetate in hexane) afforded **9** (1.04 g, 95%). $[\alpha]_D^{23} +48.7$ (*c* 1.1); ¹H NMR (500 MHz) δ : 7.64-7.61 (m, 4H), 7.43-7.26 (m, 19H), 7.14-7.07 (m, 4H), 6.89-6.87 (d, *J* = 8.5 Hz, 2H), 5.56 (d, *J* = 2.0 Hz, 1H), 4.94-4.91 (d, *J* = 10.8 Hz, 1H), 4.76-4.73 (d, *J* = 12.5 Hz, 1H), 4.70-4.65 (m, 3H), 4.63-4.60 (d, *J* = 12.0 Hz, 1H), 4.27-4.23 (t, *J* = 10.0 Hz, 1H), 4.16-4.13 (d, *J* = 10.0 Hz, 1H), 4.10-4.06 (t, *J* = 7.2 Hz, 1H), 3.99 (m, 1H), 3.89-3.86 (dd, *J* = 3.0, 9.6 Hz, 1H), 3.82 (s, 3H), 3.68-3.64 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.56-3.52 (dd, *J* = 6.4, 9.6 Hz, 1H), 1.03 (s, 9H); ¹³C NMR (100 MHz) δ : 159.2, 138.3, 137.9, 135.6, 135.5, 134.0, 133.6, 133.3, 131.5, 130.9, 129.7, 129.6, 129.5, 128.9, 128.4, 127.9, 127.7, 127.6, 127.3, 113.8, 85.9, 80.4, 76.1, 75.0, 74.2, 72.2, 71.5, 69.6, 64.7, 55.3, 26.8, 19.2; ESI-HRMS Calcd for C₅₁H₅₆O₇SSiNa [M + Na]⁺ : 863.3414. Found 863.3394.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-glycero- α -D-thio-manno-heptopyranoside (10**).**

A solution of **5** (0.25 g, 0.41 mmol) and imidazole (0.07 g, 1.03 mmol) in CH₂Cl₂ (5 mL) at 0 °C was treated with TBDPSCl (115 μ L, 0.45 mmol) and stirred at 0-10 °C for 2h. The reaction mixture was then diluted with CH₂Cl₂ and washed with a saturated solution of NH₄Cl. The organic layer was dried and concentrated to give the crude silyl ether **7** which was taken forward without purification. A solution of **7** in CH₂Cl₂:water (9:1, 10 mL) was treated with DDQ (0.10 g, 0.45 mmol) at room temperature and stirred for 1h. The reaction mixture was then diluted with CH₂Cl₂ and washed with a saturated solution of NaHCO₃, water and brine.

The organic layer was dried and concentrated. Chromatographic purification (8% ethyl acetate in hexane) afforded **10** (0.29 g, 84%). $[\alpha]_D^{24} +69.9$ (*c* 0.6); ^1H NMR (500 MHz) δ : 7.69-7.68 (m, 2H), 7.51-7.49 (d, *J* = 8.5 Hz, 2H), 7.41-7.26 (m, 20H), 7.16-7.09 (m, 3H), 6.95-6.94 (d, *J* = 8.5 Hz, 2H), 5.74 (s, 1H), 5.53 (s, 1H), 4.88-4.86 (d, *J* = 12.0 Hz, 1H), 4.75 (s, 2H), 4.68-4.66 (d, *J* = 12.5 Hz, 1H), 4.38-4.34 (t, *J* = 10.0 Hz, 1H), 4.27-4.23 (t, *J* = 9.5 Hz, 1H), 4.07-4.05 (m, 2H), 3.98-3.96 (dd, *J* = 2.0, 10.0 Hz, 1H), 3.87 (m, 5H), 0.99 (s, 9H); ^{13}C NMR (125 MHz) δ : 159.8, 138.5, 137.8, 135.9, 135.7, 134.1, 133.8, 133.5, 131.2, 130.4, 129.9, 129.4, 128.4, 128.3, 128.1, 127.9, 127.64, 127.6, 127.5, 127.4, 127.3, 113.4, 100.9, 86.9, 78.1, 79.5, 77.9, 76.6, 73.2, 73.0, 65.6, 62.9, 55.3, 26.8, 19.3; ESI-HRMS Calcd for $\text{C}_{51}\text{H}_{55}\text{O}_7\text{SSi}$ $[\text{M} + \text{H}]^+$: 839.3438. Found 839.3433.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-thio-manno-heptopyranoside (11**) and Phenyl 2,3-di-*O*-benzyl-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-thio-manno-heptopyranoside (**12**).**

A solution of **6** (0.29 g, 0.48 mmol) and imidazole (0.08 g, 1.20 mmol) in CH_2Cl_2 (5 mL) at 0 $^\circ\text{C}$ was treated with TBDPSCl (135 μL , 0.53 mmol) and stirred at 0-10 $^\circ\text{C}$ for 2h. The reaction mixture was then diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl . The organic layer was dried and concentrated to give crude silyl ether **9** which was taken forward without purification. A solution of **9** in CH_2Cl_2 :water (9:1, 10 mL) was treated with DDQ (0.12 g, 0.53 mmol) at room temperature and stirred for 2h. The reaction mixture was then diluted with CH_2Cl_2 and washed with a saturated solution of NaHCO_3 , water and brine. The organic layer was dried and concentrated to obtain a crude mixture of **11** and **12**. A solution of the above crude mixture and CSA (0.01 g, 0.02 mmol) in CH_2Cl_2 (5 mL) was treated with *p*-methoxybenzylidene dimethyl acetal (165 μL , 0.96 mmol) and refluxed for 12h. The reaction

mixture was then cooled down to room temperature, washed with a saturated solution of NaHCO_3 , water and brine. The organic layer was dried and concentrated and the residue was dissolved in $\text{MeOH}:\text{CH}_2\text{Cl}_2$ (10:1, 11 mL). To this solution hydrazine (1 mL) was added and the mixture was stirred at room temperature for 4h. The reaction mixture was then concentrated and dissolved in CH_2Cl_2 , washed with water and brine, dried and concentrated. Chromatographic purification (5% ethyl acetate in hexane) afforded **11** (0.32 g, 80%). **11**: $[\alpha]_D^{23} +48.4$ (*c* 2.9); ^1H NMR (400 MHz) δ : 7.73-7.71 (d, *J* = 8.5 Hz, 4H), 7.46-7.26 (m, 23H), 6.95-6.93 (d, *J* = 8.5 Hz, 2H), 5.93 (s, 1H), 5.52 (d, *J* = 1.5 Hz, 1H), 4.83-4.79 (d, *J* = 12.5 Hz, 1H), 4.69-4.62 (m, 3H), 4.57-4.47 (m, 2H), 4.42-4.32 (m, 2H), 4.12-4.09 (dd, *J* = 3.0, 11.0 Hz, 1H), 4.01 (m, 1H), 3.90-3.86 (m, 4H), 1.08 (s, 9H); ^{13}C NMR (100 MHz) δ : 159.8, 138.5, 137.9, 135.8, 135.7, 134.0, 133.4, 133.3, 131.7, 130.6, 129.7, 129.1, 128.4, 128.3, 127.9, 127.7, 127.63, 127.61, 127.58, 127.5, 113.5, 95.4, 86.9, 78.0, 76.8, 75.3, 74.2, 73.0, 72.6, 67.1, 60.2, 55.3, 26.9, 19.2; ESI-HRMS Calcd for $\text{C}_{51}\text{H}_{54}\text{O}_7\text{SSiNa}$ $[\text{M} + \text{Na}]^+$: 861.3258. Found 861.3259. **12**: $[\alpha]_D^{23} +11.1$ (*c* 0.8); ^1H NMR (500 MHz) δ : 7.65-7.62 (m, 4H), 7.43-7.26 (m, 19H), 7.15-7.09 (m, 2H), 5.59 (d, *J* = 1.5 Hz, 1H), 4.71-4.69 (d, *J* = 12.5 Hz, 1H), 4.59-4.55 (dd, *J* = 4.0, 12.0 Hz, 2H), 4.51-4.49 (d, *J* = 11.5 Hz, 1H), 4.37-4.33 (t, *J* = 9.5 Hz, 1H), 4.15-4.12 (m, 2H), 4.01 (m, 1H), 3.71-3.67 (m, 2H), 3.60-3.57 (dd, *J* = 6.0, 10.0 Hz, 1H), 2.62 (d, *J* = 2.0 Hz, 1H), 2.39 (d, *J* = 6.0 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (125 MHz) δ : 137.8, 137.7, 135.6, 135.5, 134.0, 133.9, 133.4, 133.2, 131.4, 129.7, 129.6, 128.9, 128.6, 128.4, 127.9, 127.8, 127.7, 127.4, 85.9, 79.9, 75.3, 72.1, 71.9, 71.8, 69.8, 66.2, 64.6, 26.8, 19.2; ESI-HRMS Calcd for $\text{C}_{43}\text{H}_{48}\text{O}_6\text{SSiNa}$ $[\text{M} + \text{Na}]^+$: 743.2839. Found 743.2849.

General procedure for glycosidic bond formation.

A stirred solution of substrate, BSP (1.1 equiv.), TTBP (2.0 equiv.) and 3 Å sieves in CH₂Cl₂ (0.03 M in substrate) was kept at -60 °C for 15 min. Then Tf₂O (1.2 equiv.) was added and after 5 min. acceptor (1.5 equiv.) in CH₂Cl₂ (2.0 M) was added. Stirring was continued at -60 °C for 1h and then the reaction mixture was warmed up to room temperature over a period of 3h before it was filtered, washed with a saturated solution of NaHCO₃, and brine, dried and concentrated. Chromatographic purification (ethyl acetate in toluene) afforded the coupled products.

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero-*β*-*D*-manno-heptopyranosyl]-*α*-*D*-glucopyranoside (17).

Coupling of **10** with **13** following the general procedure afforded **17** in 81% yield. $[\alpha]^{24}_{\text{D}} -3.2$ (*c* 1.7); ¹H NMR (500 MHz) δ : 7.71 (m, 2H), 7.46-7.26 (m, 27H), 7.23-7.12 (m, 8H), 6.94-6.92 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 1H), 5.11-5.09 (d, *J* = 102.5 Hz, 1H), 4.90-4.88 (d, *J* = 12.0 Hz, 1H), 4.84 (s, 2H), 4.77-4.70 (m, 2H), 4.66 (s, 1H), 4.59-4.56 (dd, *J* = 2.0, 12.5 Hz, 2H), 4.36-4.33 (d, *J* = 12.0 Hz, 1H), 4.31 (s, 1H), 4.09-4.05 (t, *J* = 10.0 Hz, 1H), 3.90-3.85 (m, 4H), 3.83-3.79 (t, *J* = 9.0 Hz, 1H), 3.72-3.64 (m, 5H), 3.51 (s, 2H), 3.47-3.42 (m, 5H), 3.35-3.33 (dd, *J* = 2.0, 9.5 Hz, 1H), 3.16-3.12 (t, *J* = 9.0 Hz, 1H), 1.04 (s, 9H); ¹³C NMR (125 MHz) δ : 159.8, 139.8, 138.8, 138.7, 138.5, 137.4, 135.7, 133.8, 133.7, 130.6, 129.5, 129.4, 129.1, 128.5, 128.4, 128.36, 128.3, 128.24, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.58, 127.54, 127.52, 127.5, 127.3, 126.9, 113.3, 101.1 (¹*J*_{CH} = 155.9 Hz), 100.8 (¹*J*_{CH} = 161.1 Hz), 98.5 (¹*J*_{CH} = 164.0 Hz), 80.1, 79.3, 78.9, 78.6, 77.7, 77.6, 75.1, 75.0, 73.8, 73.6, 72.5, 69.6, 68.3, 67.3, 62.6, 55.3, 29.7, 26.9, 19.4; ESI-HRMS Calcd for C₇₃H₈₁O₁₃Si [*M* + *H*]⁺ : 1193.5446. Found 1193.5461.

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (18 β**) and Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-manno-heptopyranosyl]- α -D-glucopyranoside (**18 α**).**

Coupling of **11** with **13** following the general procedure afforded **18 β** and **α** in 86% yield in 8:1 ratio. **18 β** : $[\alpha]_D^{23}$ -2.0 (*c* 0.3); ^1H NMR (400 MHz) δ : 7.70-7.68 (d, *J* = 7.6 Hz, 2H), 7.62-7.60 (d, *J* = 7.6 Hz, 2H), 7.38-7.15 (m, 33H), 6.93-6.91 (d, *J* = 8.4 Hz, 2H), 5.90 (s, 1H), 4.94-4.91 (d, *J* = 12.8 Hz, 1H), 4.83-4.80 (d, *J* = 12.0 Hz, 1H), 4.76-4.71 (m, 4H), 4.62-4.53 (m, 4H), 4.46 (s, 1H), 4.39-4.34 (t, *J* = 10.0 Hz, 1H), 4.30-4.27 (d, *J* = 12.0 Hz, 1H), 4.19-4.13 (m, 2H), 3.95-3.87 (m, 3H), 3.85 (s, 3H), 3.63-3.61 (m, 2H), 3.55-3.49 (m, 1H), 3.43-3.42 (m, 1H), 3.41-3.35 (m, 5H), 3.26-3.23 (dd, *J* = 2.4, 9.6 Hz, 1H), 1.03 (s, 9H); ^{13}C NMR (100 MHz) δ : 159.7, 139.2, 138.7, 138.6, 138.2, 137.7, 135.9, 135.7, 133.2, 133.1, 130.8, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.4, 127.3, 127.1, 113.4, 102.6 ($^1J_{\text{CH}}$ = 155.2 Hz), 98.2 ($^1J_{\text{CH}}$ = 170.2 Hz), 95.2 ($^1J_{\text{CH}}$ = 163.7 Hz), 79.6, 79.4, 78.8, 74.9, 74.7, 74.4, 73.8, 73.6, 73.5, 72.6, 69.5, 69.3, 68.5, 60.1, 55.3, 55.2, 26.9, 19.1; ESI-HRMS Calcd for $\text{C}_{73}\text{H}_{80}\text{O}_{13}\text{SiNa}$ $[\text{M} + \text{Na}]^+$: 1215.5266. Found 1215.5269. **18 α** : $[\alpha]_D^{23}$ +11.5 (*c* 2.2); ^1H NMR (400 MHz) δ : 7.68-7.65 (d, *J* = 6.8 Hz, 4H), 7.43-7.12 (m, 31H), 7.06-7.04 (d, *J* = 7.2 Hz, 2H), 6.93-6.91 (d, *J* = 8.4 Hz, 2H), 5.87 (s, 1H), 5.26 (d, *J* = 2.0 Hz, 1H), 5.11-5.08 (d, *J* = 11.2 Hz, 1H), 4.79-4.77 (d, *J* = 12.0 Hz, 1H), 4.72-4.69 (d, *J* = 12.0 Hz, 1H), 4.65-4.55 (m, 6H), 4.52-4.49 (d, *J* = 12.0 Hz, 1H), 4.39-4.28 (m, 4H), 4.17-4.10 (m, 2H), 4.07-4.04 (dd, *J* = 2.0, 10.8 Hz, 1H), 3.85-3.79 (m, 5H), 3.73-3.71 (m, 4H), 3.58-3.55 (dd, *J* = 3.6, 9.2 Hz, 1H), 3.41 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz) δ : 159.7, 138.8, 138.7, 138.5, 137.9, 137.8, 135.7, 135.6, 133.4, 133.2, 130.7, 129.6, 128.5, 128.4, 128.3, 128.2,

128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.1, 126.9, 113.4, 101.1 ($^1J_{\text{CH}} = 170.8$ Hz), 97.8 ($^1J_{\text{CH}} = 166.9$ Hz), 95.2 ($^1J_{\text{CH}} = 162.8$ Hz), 81.5, 79.9, 77.7, 76.8, 75.5, 75.1, 74.1, 73.6, 73.2, 72.9, 72.7, 69.6, 68.9, 66.7, 59.7, 55.34, 55.32, 26.8, 19.2; ESI-HRMS Calcd for $\text{C}_{73}\text{H}_{80}\text{O}_{13}\text{SiNa}$ $[\text{M} + \text{Na}]^+$: 1215.5266. Found 1215.5272.

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -*L*-rhamnopyranoside (19).

Coupling of **10** with **14** following the general procedure afforded **19** in 88% yield. $[\alpha]_{\text{D}}^{24} - 24.3$ (c 0.9); ^1H NMR (500 MHz) δ : 7.71-7.69 (d, $J = 6.5$ Hz, 2H), 7.46-7.45 (d, $J = 8.5$ Hz, 2H), 7.40-7.26 (m, 18H), 6.92-6.91 (d, $J = 9.0$ Hz, 2H), 5.69 (s, 1H), 4.93-4.90 (d, $J = 12.5$ Hz, 1H), 4.88 (s, 1H), 4.84-4.81 (d, $J = 12.0$ Hz, 1H), 4.83 (s, 1H), 4.72-4.69 (d, $J = 12.5$ Hz, 1H), 4.62-4.59 (d, $J = 12.5$ Hz, 1H), 4.24-4.20 (t, $J = 9.5$ Hz, 1H), 4.13-4.11 (m, 1H), 4.07-4.03 (m, 3H), 3.98 (d, $J = 2.0$ Hz, 1H), 3.89-3.85 (m, 4H), 3.64-3.61 (m, 2H), 3.46-3.42 (m, 4H), 3.21-3.18 (t, $J = 9.0$ Hz, 1H), 1.33-1.32 (d, $J = 5.5$ Hz, 3H), 1.26 (s, 3H), 1.22 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (125 MHz) δ : 159.8, 138.7, 138.5, 135.7, 135.5, 133.7, 133.2, 130.4, 129.6, 129.5, 128.4, 128.3, 128.1, 127.6, 127.5, 127.45, 127.4, 113.3, 109.3, 101.3 ($^1J_{\text{CH}} = 158.6$ Hz), 100.8 ($^1J_{\text{CH}} = 160.8$ Hz), 97.9 ($^1J_{\text{CH}} = 166.5$ Hz), 80.2, 79.6, 78.4, 78.3, 76.8, 76.4, 75.9, 74.9, 72.3, 68.2, 64.1, 63.3, 55.3, 54.9, 29.7, 27.9, 26.8, 26.2, 19.3, 17.8; ESI-HRMS Calcd for $\text{C}_{55}\text{H}_{67}\text{O}_{12}\text{Si}$ $[\text{M} + \text{H}]^+$: 947.4402. Found 947.4427.

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- β -*D*-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -*L*-rhamnopyranoside (20).

Coupling of **11** with **14** following the general procedure afforded **20** in 85% yield. $[\alpha]_{\text{D}}^{27} - 56.5$ (c 0.5); ^1H NMR (400 MHz) δ : 7.70-7.68 (m, 2H), 7.42-7.23 (m, 20H), 6.92-6.89 (d, $J = 8.4$ Hz, 2H), 5.90 (s, 1H), 4.89-4.87 (d, $J = 6.8$ Hz, 2H), 4.84-4.81 (d, $J = 12.4$ Hz, 1H), 4.73-

4.70 (d, $J = 12.0$ Hz, 1H), 4.65-4.61 (d, $J = 12.8$ Hz, 1H), 4.56-4.53 (d, $J = 12.8$ Hz, 1H), 4.43-4.42 (m, 1H), 4.35-4.24 (m, 2H), 4.12-4.06 (m, 3H), 3.90 (s, 1H), 3.84 (s, 3H), 3.62-3.60 (m, 2H), 3.55-3.47 (m, 2H), 3.39 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.23-1.22 (d, $J = 6.0$ Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz) δ : 159.7, 138.8, 138.5, 135.5, 133.4, 133.1, 130.6, 129.7, 128.3, 127.99, 127.98, 127.7, 127.6, 127.4, 127.3, 127.2, 113.4, 109.4, 100.9 ($^1J_{\text{CH}} = 157.6$ Hz), 97.9 ($^1J_{\text{CH}} = 166.6$ Hz), 95.0 ($^1J_{\text{CH}} = 163.5$ Hz), 78.6, 78.4, 77.7, 76.1, 76.0, 75.7, 74.4, 73.8, 71.9, 69.0, 64.3, 59.6, 55.3, 54.9, 27.9, 26.8, 26.4, 19.2, 17.5; ESI-HRMS Calcd for $\text{C}_{55}\text{H}_{67}\text{O}_{12}\text{Si}$ $[\text{M} + \text{H}]^+$: 947.4402. Found 947.4411.

(1-Adamantanyl) 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-*glycero*- β -D-*manno*-heptopyranoside (21).

Coupling of **10** with **15** following the general procedure afforded **21** in 88% yield. $[\alpha]_{\text{D}}^{24} - 12.8$ (c 1.3); ^1H NMR (400 MHz) δ : 7.76-7.71 (dd, $J = 7.0, 14.8$ Hz, 2H), 7.52-7.25 (m, 20H), 6.95-6.92 (d, $J = 8.8$ Hz, 2H), 5.89 (s, 1H), 5.05-5.02 (d, $J = 12.4$ Hz, 1H), 4.97-4.94 (d, $J = 12.4$ Hz, 1H), 4.76 (s, 1H), 4.73-4.70 (d, $J = 12.4$ Hz, 1H), 4.60-4.57 (d, $J = 12.4$ Hz, 1H), 4.27-4.23 (t, $J = 9.6$ Hz, 1H), 4.04-3.93 (m, 3H), 3.86 (s, 3H), 3.80-3.79 (d, $J = 2.4$ Hz, 1H), 3.64-3.61 (dd, $J = 2.4, 9.6$ Hz, 1H), 3.46-3.41 (t, $J = 9.2$ Hz, 1H), 2.12 (bs, 2H), 1.88-1.76 (m, 6H), 1.65-1.56 (m, 7H), 1.04 (s, 9H); ^{13}C NMR (100 MHz) δ : 159.8, 138.6, 135.9, 135.5, 133.8, 133.2, 130.6, 129.5, 128.9, 128.3, 128.0, 127.6, 127.4, 113.3, 100.9 ($^1J_{\text{CH}} = 161.0$ Hz), 94.9 ($^1J_{\text{CH}} = 152.1$ Hz), 79.2, 78.9, 77.6, 76.8, 76.7, 75.2, 74.6, 72.4, 66.9, 62.7, 55.3, 42.4, 36.2, 30.6, 26.7, 19.3; ESI-HRMS Calcd for $\text{C}_{55}\text{H}_{65}\text{O}_8\text{Si}$ $[\text{M} + \text{H}]^+$: 881.4449. Found 881.4408.

***N*-Benzyloxycarbonyl-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-*glycero*- β -D-*manno*-heptopyranosyl]-L-threonine methyl ester (22).**

Coupling of **10** with **16** following the general procedure afforded **22** in 89% yield. $[\alpha]^{24}_{\text{D}} -9.3$ (c 2.0); ^1H NMR (500 MHz) δ : 7.77-7.73 (m, 2H), 7.48-7.21 (m, 25H), 6.94-6.93 (d, $J = 8.5$ Hz, 2H), 5.67 (s, 1H), 5.57-5.55 (d, $J = 8.5$ Hz, 1H), 5.17-5.13 (m, 2H), 4.88-4.86 (d, $J = 12.0$ Hz, 1H), 4.79-4.75 (m, 2H), 4.66-4.63 (d, $J = 12.5$ Hz, 1H), 4.47-4.44 (m, 2H), 4.41-4.39 (dd, $J = 2.5, 8.5$ Hz, 1H), 4.24-4.20 (t, $J = 9.5$ Hz, 1H), 4.02-3.95 (m, 2H), 3.86-3.77 (m, 4H), 3.68 (s, 3H), 3.64-3.61 (dd, $J = 2.0, 10.0$ Hz, 1H), 3.45-3.42 (t, $J = 9.0$ Hz, 1H), 1.19-1.18 (d, $J = 6.5$ Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz) δ : 170.5, 159.8, 156.6, 138.5, 138.4, 136.1, 135.8, 135.6, 133.5, 133.2, 130.3, 129.6, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 113.4, 100.9 ($^1J_{\text{CH}} = 161.1$ Hz), 98.4 ($^1J_{\text{CH}} = 154.3$ Hz), 79.2, 78.5, 77.5, 76.2, 74.5, 73.0, 72.6, 67.6, 67.2, 62.7, 58.8, 55.3, 52.6, 29.7, 26.7, 19.4, 15.8; ESI-HRMS Calcd for $\text{C}_{58}\text{H}_{65}\text{NO}_{12}\text{SiK}$ $[\text{M} + \text{K}]^+$: 1034.3913. Found 1034.3959.

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-D-*glycero*- β -D-*manno*-heptopyranosyl]- α -D-glucopyranoside (23**).**

A solution of **17** (0.23 g, 0.19 mmol) in THF (5 mL) was treated with TBAF (380 μL , 0.38 mmol, 1 M solution in THF) and stirred at room temperature for 2h. The reaction mixture was then diluted with ethyl acetate and washed with a saturated solution of NH_4Cl . The organic layer was dried and concentrated and the residue was dissolved in MeOH (4 mL). To this solution CSA (0.01 g, 0.02 mmol) was added, followed by heating to reflux for 3h. The reaction mixture was then concentrated and dissolved in ethyl acetate, washed with a saturated solution of NaHCO_3 and brine, dried and concentrated. Chromatographic purification (60% ethyl acetate in hexane) afforded **23** (0.13 g, 79%). $[\alpha]^{25}_{\text{D}} -32.2$ (c 0.9); ^1H NMR (400 MHz) δ : 7.37-7.21 (m, 25H), 4.99-4.96 (d, $J = 11.2$ Hz, 1H), 4.84-4.81 (d, $J = 12.0$ Hz, 2H), 4.75-4.72 (d, $J = 12.4$ Hz, 1H), 4.70-4.63 (m, 3H), 4.61-4.60 (d, $J = 3.6$ Hz,

1H), 4.48-4.45 (d, $J = 11.6$ Hz, 1H), 4.38-4.34 (dd, $J = 2.8, 12.0$ Hz, 2H), 4.28 (s, 1H), 3.98-3.94 (t, $J = 9.2$ Hz, 1H), 3.87-3.84 (m, 2H), 3.74-3.72 (m, 1H), 3.65-3.60 (dd, $J = 2.4, 18.4$ Hz, 1H), 3.56-3.41 (m, 7H), 3.17-3.13 (dd, $J = 2.4, 16.0$ Hz, 1H), 3.05-2.99 (m, 2H), 2.36-2.34 (t, $J = 6.0$ Hz, 1H), 1.71 (bs, 1H); ^{13}C NMR (100 MHz) δ : 139.0, 138.3, 137.8, 137.5, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 100.5 ($^1J_{\text{CH}} = 155.8$ Hz), 98.5 ($^1J_{\text{CH}} = 167.6$ Hz), 81.4, 80.2, 79.1, 77.0, 76.1, 75.5, 74.5, 74.1, 73.7, 73.7, 72.8, 71.4, 69.6, 69.2, 68.4, 63.2, 55.4; ESI-HRMS Calcd for $\text{C}_{49}\text{H}_{56}\text{O}_{12}\text{Na}$ $[\text{M} + \text{Na}]^+$: 859.3669. Found 859.3650.

Methyl 4-*O*-[D-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (24).

A solution of **23** (0.11 g, 0.13 mmol) in MeOH (5 mL) was treated with 10% Pd/C (0.16 g) and shaken under H_2 (50 psi) for 26h. The reaction mixture was then filtered and washed with MeOH (3 X 10 mL) and concentrated to afford **24** (0.05 g, 94%). $[\alpha]_{\text{D}}^{24} +56.4$ (c 1.3, MeOH); ^1H NMR (400 MHz, D_2O) δ : 4.66 (s, 1H), 4.54 (s, 1H), 3.92-3.89 (m, 2H), 3.71-3.45 (m, 8H), 3.33-3.30 (dd, $J = 2.0, 10.0$ Hz, 1H), 3.26 (s, 3H), 3.19 (s, 2H); ^{13}C NMR (100 MHz, D_2O) δ : 99.9 ($^1J_{\text{CH}} = 159.7$ Hz), 98.9 ($^1J_{\text{CH}} = 169.2$ Hz), 77.9, 77.1, 72.9, 71.4, 71.1, 70.8, 70.3, 70.1, 67.0, 61.4, 59.9, 54.9; ESI-HRMS Calcd for $\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{Na}$ $[\text{M} + \text{Na}]^+$: 409.1322. Found 409.1317.

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-L-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (25).

A solution of **18 β** (0.25 g, 0.21 mmol) in THF (5 mL) was treated with TBAF (420 μL , 0.42 mmol, 1 M solution in THF) and stirred at room temperature for 3h. The reaction mixture was then diluted with ethyl acetate and washed with a saturated solution of NH_4Cl . The organic layer was dried and concentrated and the residue was dissolved in MeOH (4 mL). To this

solution CSA (0.01g, 0.02 mmol) was added, followed by heating to reflux for 1h. The reaction mixture was then concentrated and dissolved in ethyl acetate, washed with a saturated solution of NaHCO₃ and brine, dried and concentrated. Chromatographic purification (60% ethyl acetate in hexane) afforded **25** (0.13 g, 75%). $[\alpha]^{23}_{\text{D}} -33.3$ (*c* 0.6); ¹H NMR (400 MHz) δ : 7.42-7.23 (m, 25H), 4.97-4.94 (d, *J* = 10.0 Hz, 1H), 4.92-4.89 (d, *J* = 12.4 Hz, 1H), 4.88-4.85 (d, *J* = 11.6 Hz, 1H), 4.77-4.76 (d, *J* = 3.2 Hz, 1H), 4.74-4.73 (d, *J* = 2.4 Hz, 1H), 4.72-4.68 (dd, *J* = 6.0, 12.0 Hz, 2H), 4.63-4.61 (d, *J* = 4.4 Hz, 1H), 4.54-4.51 (d, *J* = 12.4 Hz, 1H), 4.43-4.39 (d, *J* = 11.4 Hz, 1H), 4.38-4.35 (d, *J* = 11.6 Hz, 1H), 4.25 (s, 1H), 4.14-4.09 (t, *J* = 9.6 Hz, 1H), 3.88-3.74 (m, 3H), 3.69-3.68 (d, *J* = 3.2 Hz, 1H), 3.64-3.60 (m, 4H), 3.55-3.52 (dd, *J* = 4.0, 9.2 Hz, 2H), 3.42 (s, 3H), 3.08-3.05 (dd, *J* = 2.8, 9.2 Hz, 1H), 2.91-2.88 (dd, *J* = 2.8, 10.0 Hz, 1H), 2.77 (bs, 1H), 2.21 (bs, 1H); ¹³C NMR (100 MHz) δ : 138.5, 138.4, 138.3, 137.9, 137.4, 128.7, 128.5, 128.4, 128.3, 128.2, 128.18, 128.11, 127.9, 127.8, 127.64, 127.61, 127.56, 100.8 (¹*J*_{CH} = 155.9 Hz), 98.7 (¹*J*_{CH} = 167.1 Hz), 81.6, 80.5, 79.2, 78.7, 76.1, 75.8, 74.6, 74.2, 73.9, 73.7, 71.4, 69.7, 68.5, 68.1, 66.5, 63.7, 55.5; ESI-HRMS Calcd for C₄₉H₅₆O₁₂Na [M + Na]⁺ : 859.3670. Found 859.3669.

Methyl 4-*O*-[L-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (26**).**

A solution of **25** (0.09 g, 0.11 mmol) in MeOH (5 mL) was treated with 10% Pd/C (0.14 g) and shaken under H₂ (50 psi) for 29h. The reaction mixture was then filtered and washed with MeOH (3 X 10 mL) and concentrated to afford **26** (0.04 g, 95%). $[\alpha]^{23}_{\text{D}} +56.7$ (*c* 2.4, MeOH); ¹H NMR (500 MHz, D₂O) δ : 4.68 (s, 1H), 4.61 (s, 1H), 3.91-3.88 (m, 2H), 3.73-3.67 (m, 2H), 3.64-3.60 (m, 3H), 3.54-3.48 (m, 3H), 3.29 (s, 2H), 3.26-3.22 (m, 4H); ¹³C NMR (125 MHz, D₂O) δ : 99.7 (¹*J*_{CH} = 159.0 Hz), 99.0 (¹*J*_{CH} = 169.3 Hz), 78.1, 74.9, 72.9, 71.0, 70.6, 70.2,

68.7, 65.8, 62.9, 60.0, 55.0, 48.9; ESI-HRMS Calcd for $C_{14}H_{26}O_{12}Na$ $[M + Na]^+$: 409.1322.

Found 409.1307.

Methyl 4-*O*-[2,3-di-*O*-benzyl-*D*-glycero- β -*D*-manno-heptopyranosyl]- α -L-rhamnopyranoside (27).

A solution of **19** (0.17 g, 0.18 mmol) in THF (4 mL) was treated with TBAF (360 μ L, 0.36 mmol, 1 M solution in THF) and stirred at room temperature for 2h. The reaction mixture was then diluted with ethyl acetate and washed with a saturated solution of NH_4Cl . The organic layer was dried, concentrated and the residue was dissolved in MeOH (3 mL). To this solution CSA (0.005g, 0.02 mmol) was added, followed by heating to reflux for 3h. The reaction mixture was then concentrated and dissolved in ethyl acetate, washed with a saturated solution of $NaHCO_3$ and brine, dried and concentrated. Chromatographic purification (8% MeOH in CH_2Cl_2) afforded **27** (0.07 g, 72%). $[\alpha]^{25}_D -130.3$ (c 0.5); 1H NMR (500 MHz) δ : 7.39-7.37 (d, J = 8.0 Hz, 2H), 7.30-7.23 (m, 8H), 4.96 (s, 1H), 4.89-4.86 (d, J = 12.0 Hz, 1H), 4.68-4.66 (d, J = 11.5 Hz, 1H), 4.58 (s, 1H), 4.55 (s, 1H), 4.46-4.44 (d, J = 11.0 Hz, 1H), 4.36-4.34 (d, J = 12.0 Hz, 1H), 4.23-4.21 (m, 1H), 4.02-3.59 (m, 7H), 3.40-3.30 (m, 2H), 3.27 (s, 3H), 2.51 (bs, 1H), 1.32-1.31 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz) δ : 138.7, 137.9, 128.4, 128.2, 128.1, 127.8, 127.7, 127.5, 101.2 ($^1J_{CH}$ = 159.3 Hz), 100.8 ($^1J_{CH}$ = 167.9 Hz), 81.5, 77.5, 74.4, 73.7, 72.1, 71.4, 71.2, 70.2, 66.7, 62.2, 54.9, 17.9; ESI-HRMS Calcd for $C_{28}H_{38}O_{11}Na$ $[M + Na]^+$: 537.2312. Found 537.2332.

Methyl 4-*O*-[*D*-glycero- β -*D*-manno-heptopyranosyl]- α -L-rhamnopyranoside (28).

A solution of **27** (0.05 g, 0.09 mmol) in MeOH (5 mL) was treated with 10% Pd/C (0.08 g) and shaken under H_2 (50 psi) for 29h. The reaction mixture was then filtered and washed with MeOH (3 X 10 mL) and concentrated to afford **28** (0.03 g, 92%). $[\alpha]^{24}_D -42.6$ (c 1.4,

MeOH); ^1H NMR (500 MHz, D_2O) δ : 4.70 (s, 1H), 4.54 (s, 1H), 3.89 (s, 2H), 3.77 (s, 1H), 3.69-3.65 (m, 2H), 3.62-3.56 (m, 2H), 3.54-3.51 (m, 2H), 3.49-3.46 (m, 1H), 3.24-3.22 (bs, 4H), 1.20-1.19 (d, $J = 5.5$ Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ : 100.8 ($^1J_{\text{CH}} = 168.8$ Hz), 100.6 ($^1J_{\text{CH}} = 155.9$ Hz), 78.9, 75.8, 73.1, 72.3, 70.4, 70.2, 68.1, 67.0, 61.9, 54.7, 16.9; ESI-HRMS Calcd for $\text{C}_{14}\text{H}_{26}\text{O}_{11}\text{Na}$ $[\text{M} + \text{Na}]^+$: 393.1373. Found 393.1383.

References: 1. Crich, D.; Li, W.; Li, H. *J. Am. Chem. Soc.* **2004**, *126*, 15081.

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)- α -D-thiomannopyranoside (2)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)- α -D-thiomannopyranoside (2)

Phenyl 2,3-di-*O*-benzyl-6,7-dideoxy-4-*O*-(*p*-methoxybenzyl)- α -D-thiohept-6-enopyranoside (3)

Phenyl 2,3-di-*O*-benzyl-6,7-dideoxy-4-*O*-(*p*-methoxybenzyl)- α -D-thiohept-6-enopyranoside (3)

Phenyl 2,3-di-*O*-benzyl-4,6,7-trideoxy- α -D-thiohept-4,6-dienopyranoside (4)

Phenyl 2,3-di-*O*-benzyl-4,6,7-trideoxy- α -D-thiohept-4,6-dienopyranoside (4)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-D-glycero- α -D-thio-manno-heptopyranoside (5)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-D-glycero- α -D-thio-manno-heptopyranoside (5)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-L-glycero- α -D-thio-manno-heptopyranoside (6)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-L-glycero- α -D-thio-manno-heptopyranoside (6)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-manno-heptopyranoside (8)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-manno-heptopyranoside (8)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-manno-heptopyranoside (9)

Phenyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-*manno*-heptopyranoside (9)

**Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-glycero- α -D-thio-manno-heptopyranoside
(10)**

**Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-glycero- α -D-thio-manno-heptopyranoside
(10)**

**Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-manno-heptopyranoside
(11)**

**Phenyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-L-glycero- α -D-thio-manno-heptopyranoside
(11)**

Phenyl 2,3-di-*O*-benzyl-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-thio-manno-heptopyranoside (12)

Phenyl 2,3-di-*O*-benzyl-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-thio-manno-heptopyranoside (12)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]- α -*D*-glucopyranoside (17)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]- α -*D*-glucopyranoside (17)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (18 β)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (18 β)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-manno-heptopyranosyl]- α -D-glucopyranoside (18 α)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- α -D-manno-heptopyranosyl]- α -D-glucopyranoside (18 α)

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -*L*-rhamnopyranoside (19)

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -*L*-rhamnopyranoside (19)

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- β -D-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -L-rhamnapyranoside (20)

Methyl 4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*L*-glycero- β -*D*-manno-heptopyranosyl]-2,3-*O*-isopropylidene- α -*L*-rhamnopyranoside (20)

(1-Adamantanyl) 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-D-glycero- β -D-manno-heptopyranoside (21)

(1-Adamantanyl) 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranoside (21)

***N*-Benzyloxycarbonyl-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]-*L*-threonine methyl ester (22)**

***N*-Benzyloxycarbonyl-*O*-[2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)-7-*O*-(*t*-butyldiphenylsilyl)-*D*-glycero- β -*D*-manno-heptopyranosyl]-*L*-threonine methyl ester (22)**

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-D-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (23)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-D-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (23)

Methyl 4-*O*-[D-*glycero*- β -D-*manno*-heptopyranosyl]- α -D-glucopyranoside (24)

Methyl 4-*O*-[D-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (24)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-L-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (25)

Methyl 2,3,4-tri-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-L-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (25)

Methyl 4-*O*-[*L*-glycero- β -*D*-manno-heptopyranosyl]- α -*D*-glucopyranoside (26)

Methyl 4-*O*-[*L*-glycero- β -D-manno-heptopyranosyl]- α -D-glucopyranoside (26)

Methyl 4-*O*-[2,3-di-*O*-benzyl-D-glycero- β -D-manno-heptopyranosyl]- α -L-rhamnopyranoside (27)

Methyl 4-*O*-[2,3-di-*O*-benzyl-D-glycero- β -D-manno-heptopyranosyl]- α -L-rhamnopyranoside (27)

Methyl 4-*O*-[D-*glycero*- β -D-*manno*-heptopyranosyl]- α -L-rhamnopyranoside (28)

Methyl 4-*O*-[D-glycero- β -D-manno-heptopyranosyl]- α -L-rhamnopyranoside (28)