Efficient Installation of β -Mannosides Using a Dehydrative Coupling Strategy

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Experimental Section

General procedures:

All chemicals used were reagent grade and used as supplied. TiF_2O was purified by drying over P_2O_5 for 4 hours followed by distillation. All reactions were performed in oven-dried glassware under an inert argon atmosphere unless noted otherwise. Reagent grade dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether and toluene were passed through activated neutral alumina column prior to use. Reagent grade *N,N*-dimethylformamide (DMF) and methanol (MeOH) were dried over activated molecular sieves prior to use. Pyridine, triethylamine and acetonitrile were distilled over CaH_2 prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25mm). Compounds were visualized by UV irradiation or dipping the plate in a cerium sulfate-ammonium molybdate solution. Flash column chromatography was carried out using forced flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh). ^1H and ^{13}C and NMR spectra were recorded on a Varian Mercury 300 (300 MHz and 75 MHz respectively), spectrometer in CDCl_3 with chemical shifts referenced to internal standards CDCl_3 (7.26 ppm ^1H , 77.0 ppm ^{13}C). High-resolution mass spectral (HRMS) analyses were performed by the MS-service at the Laboratorium für Organische Chemie at ETH Zürich. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Optical rotations were measured at room temperature using a Perkin Elmer 241 polarimeter.

Allyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (2): Allyl-4,6-*O*-benzylidene- α -D-mannoside (**1**) (10.0 g, 32 mmol) was dissolved in DMF (150 mL) and cooled to 0°C. Benzyl bromide (9.6 mL, 81 mmol) was added, followed by NaH (3.0 g, 75 mmol) in portions and a catalytic amount of TBAI. The reaction mixture was allowed to warm to room temperature overnight, after which TLC analysis showed complete consumption of the starting material. The reaction was quenched by the addition of MeOH (1.0 mL) at 0°C. After concentration of the mixture to a smaller volume, it was taken up in

diethyl ether and washed with water. The water layer was extracted twice with diethyl ether, after which the combined organic layers were washed with saturated aqueous NaCl, dried (MgSO_4) and concentrated. Purification by flash silica gel chromatography (0% to 20% EtOAc in hexanes) yielded **2** as a colourless oil (11.1 g, 22.7 mmol, 71%). R_f 0.75 (hexanes/EtOAc 3:1); $^1\text{H-NMR}$, δ : 3.83-4.07 (m, 6H), 4.15-4.21 (m, 1H), 4.28-4.34 (m, 2H), 4.70 (d, $J = 12.3$ Hz, 1H), 4.77 (d, $J = 12.3$ Hz, 1H), 4.85-4.90 (m, 3H), 5.20-5.29 (m, 2H), 5.69 (s, 1H), 5.88 (m, 1H), 7.33-7.57 (m, 15H); $^{13}\text{C-NMR}$, δ : 64.3, 68.0, 68.9, 73.2, 73.7, 76.4, 76.5, 79.2, 98.5, 101.4, 117.5, 126.0, 127.4, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.7, 129.2, 133.4, 137.6, 138.0, 138.6; $[\alpha]_D +41.8$ ($c = 1.0$); IR, ν : 3005, 2921, 1451.4, 1368.2, 1096.3, 1046.4 cm^{-1} ; HR-MS m/z : 511.2084 (calculated for $\text{C}_{30}\text{H}_{32}\text{O}_6\text{Na}$: 511.2097).

Allyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (3): Allyl-4,6-*O*-benzylidene- α -D-mannoside (**1**) (3.00 g, 9.7 mmol) was dissolved in DMF (50 mL) and cooled to 0°C . *p*-Methoxybenzyl chloride (2.8 mL, 20.4 mmol) was added, followed by NaH (814 mg, 20.4 mmol) in two portions. The reaction mixture was stirred and allowed to warm to room temperature overnight, after which TLC analysis showed complete consumption of the starting material. The reaction was quenched by the addition of MeOH (1.0 mL) at 0°C . After concentration of the mixture to a smaller volume, it was taken up in diethyl ether and washed with water. The water layer was extracted twice with diethyl ether, after which the combined organic layers were washed with saturated aqueous NaCl, dried (MgSO_4) and concentrated. Purification by flash silica gel chromatography (0% to 20% EtOAc in hexanes) yielded **3** as a slightly yellow oil (3.34 g, 6.1 mmol, 61%). R_f 0.60 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : 3.81-4.05 (m, 11H), 4.18 (m, 1H), 4.27 (m, 2H), 4.62 (d, $J = 11.7$ Hz, 1H), 4.69 (d, $J = 11.7$ Hz, 1H), 4.78 (d, $J = 11.7$ Hz, 2H), 4.82 (s, 1H), 5.23 (m, 2H), 5.67 (s, 1H), 5.88 (m, 1H), 6.89 (m, 4H), 7.29-7.57 (m, 9H); $^{13}\text{C-NMR}$, δ : 55.3, 64.3, 67.9, 68.8, 72.8, 73.2, 75.9, 76.1, 79.1, 98.6, 101.4, 113.6, 113.7, 117.4, 126.0, 128.1, 128.3, 128.7, 129.1, 129.7, 130.1, 130.7, 133.5, 137.7, 159.0, 159.2; $[\alpha]_D +32.2$ ($c = 1.0$); IR, ν : 3007, 1612, 1513, 1097, 1036 cm^{-1} ; HR-MS m/z : 571.2291 (calculated for $\text{C}_{32}\text{H}_{36}\text{O}_8\text{Na}$: 571.2308).

Allyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (4): To a suspension of allyl-4,6-*O*-benzylidene- α -D-mannose (6.02 g, 19.6 moles) in toluene (130 mL) was added Bu_2SnO (4.91 g, 19.6 mmoles). The mixture was heated to reflux for 3 h and cooled to room temperature. Tetrabutylammonium bromide

(Bu₄NBr, 6.72 g, 21.0 mmol), and cesium fluoride (CsF, 3.05 g, 20.1 mmol) and PMBCl (2.80 mL, 20.6 mmol) were added respectively. The mixture was stirred for 48 h and then heated to reflux for 1 h, after which it was cooled to room temperature and washed with saturated aqueous NaHCO₃ (70 mL). The water layer was then extracted with EtOAc (3 x 70 mL). The organic layers were combined and washed with water, brine, dried over MgSO₄ and filtered. The resulting organic solution was concentrated *in vacuo* to afford a yellow-brown oil (8.9 g), that was purified by flash chromatography. A pale yellow, viscous oil was obtained (8.73 g, 98 %). ¹H-NMR, δ : 2.66 (s, 1H), 3.81 (s, 3H), 3.85-4.18 (m, 8H), 4.65 (d, 1H, *J* = 11.4 Hz), 4.79 (d, 1H, *J* = 11.4 Hz), 4.92 (s, 1H), 5.20-5.32 (m, 2H), 5.62 (s, 1H), 5.84-5.97 (m, 1H), 6.78 (m, 2H), 7.26-7.52 (m, 9H). To a solution of allyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannoside (1.25 g, 2.9 mmol) in DMF (15 mL) were added TBSCl (656 mg, 4.35 mmol) and imidazole (5.92 g, 8.7 mmol). The reaction mixture was stirred at 60°C overnight, after which it was cooled to room temperature, diluted with diethyl ether and washed with water, aqueous 1N HCl, saturated aqueous NaHCO₃ and dried with MgSO₄. The solvents were evaporated under reduced pressure and the crude oil was purified by flash silica gel chromatography (0% to 20% EtOAc in hexanes) to give **4a** as a colorless oil (1.40 g, 2.54 mmol, 88%). *R_f* 0.80 (hexanes/EtOAc 2:1); ¹H-NMR, δ : 0.085 (s, 3H), 0.11 (s, 3H), 0.932 (s, 9H), 3.80 (s, 3H), 3.81-3.91 (m, 3H), 3.97 (m, 1H), 4.08-4.28 (m, 4H), 4.67-4.78 (m, 3H), 5.21-5.33 (m, 2H), 5.66 (s, 1H), 5.87-5.92 (m, 1H), 6.87 (m, 2H), 7.29-7.52 (m, 7H); ¹³C-NMR, δ : -5.11, -4.42, 18.2, 25.8, 55.1, 64.4, 67.8, 68.9, 71.3, 72.6, 75.4, 79.2, 100.7, 101.4, 113.5, 117.4, 126.0, 127.5, 128.0, 128.7, 129.3, 130.8, 133.6, 137.7, 158.9; [α]_D +9.4 (*c* = 1.0); IR, ν : 2923, 1512, 1097 cm⁻¹; HR-MS *m/z*: 565.2582 (calculated for C₃₀H₄₂O₇SiNa: 565.2598).

Allyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (5**):** Allyl-4,6-*O*-benzylidene- α -D-mannoside **1** (3.08 g, 10.0 mmol) was dissolved in DCM/DMF (20 mL, 10:1 v/v) and cooled to -20°C. Triethyl amine (1.53 mL, 11.0 mmol) and TBSOTf (2.53 mL, 11.0 mmol) were subsequently added and the mixture was stirred for 1.5 h, after which it was quenched with saturated aqueous NaHCO₃. The layers were separated and the water layer was extracted twice with DCM. The combined organic layers were washed with brine, dried (MgSO₄) and concentrated. The crude product was purified by flash silica gel chromatography (0% to 15% EtOAc in hexanes). *R_f* 0.60 (hexanes/EtOAc 2:1); ¹H-NMR, δ : 0.074 (s, 3H), 0.12 (s, 3H), 0.89 (s, 3H), 2.86 (s, 1H), 3.80-3.91 (m, 4H), 4.00 (m, 1H), 4.12

(m, 1H), 4.25 (m, 2H), 4.96 (d, $J = 1.5$ Hz, 1H), 4.28 (m, 2H), 5.56 (s, 1H), 5.91 (m, 1H), 7.35-7.50 (m, 5H). Allyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- α -D-mannoside (2.9 g, 6.86 mmol) was dissolved in DMF (50 mL) and cooled to 0°C. Benzyl bromide (2.44 mL, 20.6 mmol) was added, followed by NaH (329 mg, 8.23 mmol) in two portions and a catalytic amount of TBAI. The reaction mixture was allowed to warm to room temperature overnight, after which TLC analysis showed complete consumption of the starting material. The reaction was quenched by the addition of MeOH (1.0 mL) at 0°C. After concentration of the mixture to a smaller volume, it was taken up in diethyl ether and washed with water. The water layer was extracted twice with diethyl ether, after which the combined organic layers were washed with saturated aqueous NaCl, dried (MgSO₄) and concentrated. Purification by flash silica gel chromatography (0% to 7.5% EtOAc in hexanes) yielded **5** as a slightly yellow oil (3.34 g, 6.1 mmol, 61%). R_f 0.60 (hexanes/EtOAc 3:1); ¹H-NMR, δ : 0.048 (s, 3H), 0.10 (s, 3H), 0.902 (s, 9H), 3.71 (dd, $J = 1.5, 3.3$ Hz, 1H), 3.81 (m, 2H), 3.95 (m, 1H), 4.03 (t, $J = 9.3$ Hz, 1H), 4.12-4.24 (m, 3H), 4.69 (d, $J = 12.3$ Hz, 1H), 4.82 (d, $J = 1.8$ Hz, 1H), 4.94 (d, $J = 12.3$ Hz, 1H), 5.16-5.27 (m, 2H), 5.58 (s, 1H), 5.85 (m, 1H), 7.29-7.51 (m, 10H); ¹³C-NMR, δ : -4.53, -4.15, 18.6, 26.1, 64.6, 68.1, 69.0, 70.9, 74.6, 79.4, 79.5, 99.2, 102.1, 117.7, 126.5, 127.9, 128.1, 128.3, 128.6, 129.0, 133.8, 137.9, 138.7; $[\alpha]_D^{+25.0}$ ($c = 1.0$); IR, ν : 2933, 2851, 1456, 1256, 1096 cm⁻¹; HR-MS m/z : 535.2477 (calculated for C₂₉H₄₀O₆SiNa: 535.2492).

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannopyranose (6**):** Allyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (**2**, 1.7 g, 3.5 mmol) was dissolved in DMF (50 mL) and heated to 60°C. KO^{*t*}Bu (398 mg, 7.0 mmol) was added, upon which the reaction mixture turned dark brown. After 3 h, TLC analysis showed complete consumption of the starting material and the formation of a higher running spot. The mixture was cooled to room temperature and diluted with diethyl ether, washed subsequently with water, 1N aqueous HCl, and water, dried (MgSO₄) and concentrated to yield 1.8 g of the crude enol ether. The latter product was taken up in a mixture of THF and water (25 mL, 4:1 v/v) and treated with iodine (2.22 g, 8.75 mmol). The reaction was quenched after 2 h by the addition of saturated aqueous Na₂S₂O₃. After separation of the layers the water layer was extracted with EtOAc and the combined organic layers were washed with saturated aqueous NaCl, dried (MgSO₄) and concentrated. The crude lactol was purified by flash silica gel chromatography (0% to 40% EtOAc in hexanes) to yield **6** as a slightly yellow oil (1.31 g, 2.9 mmol, 83%). R_f 0.40 (hexanes/EtOAc 2:1); Major anomer (α): ¹H-NMR, δ : 3.90 (bs, 1H), 3.96 (t, $J = 10.2$ Hz,

1H), 4.12-4.16 (m, 2H), 4.32-4.41 (m, 2H), 4.75 (d, $J = 12.3$ Hz, 1H), 4.76 (d, $J = 12.3$ Hz, 1H), 4.85 (d, $J = 12.3$ Hz, 1H), 4.91 (d, $J = 12.3$ Hz, 1H), 5.16 (bd, $J = 3.3$ Hz, 1H), 5.75 (s, 1H), 7.38-7.68 (m, 15H); ^{13}C -NMR, δ : 63.2, 68.6, 72.7, 73.2, 75.6, 76.4, 78.9, 93.4, 101.2, 125.7, 125.8, 127.2, 127.4, 127.7, 127.9, 127.97, 128.05, 128.1, 128.2, 128.6, 137.2, 137.7, 138.2; IR, ν : 3394, 3005, 1451, 1379, 1025 cm^{-1} ; HR-MS m/z : 471.1770 (calculated for $\text{C}_{27}\text{H}_{28}\text{O}_6\text{Na}$: 471.1784).

4,6-*O*-Benzylidene-2,3-di-*O*-*p*-methoxybenzyl- α/β -D-mannopyranose (7): Deallylation of Allyl-4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**3**, 1.17 g, 2.13 mmol) was effected as described for the deprotection of allyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside **2**, to give **7** (890 mg, 1.59 mmol, 69%) as a yellowish oil. R_f 0.45 (hexanes/EtOAc 1:1); Major anomer (α): ^1H -NMR, δ : 3.79 (m, 8H), 4.00-4.04 (m, 2H), 4.11-4.27 (m, 2H), 4.58-4.77 (m, 4H), 5.09 (s, 1H), 5.65 (s, 1H), 6.86-6.90 (m, 4H), 7.26-7.57 (m 9H); ^{13}C -NMR, δ : 55.1, 63.9, 68.7, 72.5, 72.9, 75.4, 76.0, 79.0, 93.8, 101.2, 113.4, 113.5, 125.8, 127.9, 128.9, 129.5, 130.0, 130.4, 137.4, 158.7, 158.9; IR, ν : 3394, 3005, 1605, 1512, 1461, 1092, 1036 cm^{-1} ; HR-MS m/z : 531.1979 (calculated for $\text{C}_{29}\text{H}_{32}\text{O}_8\text{Na}$: 531.1995).

4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α/β -D-mannopyranose (8): Allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**4**, 590 mg, 1.09 mmol) was dissolved in EtOAc (7 mL), before 90% AcOH in water (20 mL), NaOAc (538 mg, 6.54 mmol) and PdCl_2 (290 mg, 1.63 mmol) were added. The heterogeneous reaction mixture was stirred vigorously overnight, filtered over Celite, which was washed with EtOAc. The mixture was washed with water, and then neutralized by washing with saturated aqueous $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$. The water layer was extracted twice with DCM, after which the combined organic layers were dried over MgSO_4 and concentrated. The crude product was purified by flash silica gel chromatography (0% to 17.5% EtOAc in hexanes) to yield **8** as a colorless oil (1.31 g, 2.9 mmol, 83%). R_f 0.60 (hexanes/EtOAc 2:1); Major anomer (α): ^1H -NMR, δ : 0.082 (s, 3H), 0.11 (s, 3H), 0.93 (s, 9H), 3.42 (d, $J = 3.0$ Hz, 1H), 3.80 (s, 3H), 3.81 (m, 1H), 3.91 (dd, $J = 3.0, 9.6$ Hz, 1H), 3.98-4.08 (m, 2H), 4.11-4.18 (m, 2H), 4.23 (dd, $J = 4.5, 9.9$ Hz, 1H), 4.65 (d, $J = 11.4$ Hz, 1H), 4.75 (d, $J = 11.4$ Hz, 1H), 5.03 (s, 1H), 5.64 (s, 1H), 6.87 (m, 2H), 7.28-7.55 (m, 7); ^{13}C -NMR, δ : -4.82, -4.14, 18.4, 26.0, 55.3, 64.5, 69.1, 71.5, 72.6, 74.9, 79.3, 96.4, 101.5, 113.5,

126.1, 128.0, 128.7, 129.3, 130.7, 137.7, 158.8.; IR, ν : 3394, 2861, 1507, 1466, 1025 cm^{-1} ; HR-MS m/z : 525.2271 (calculated for $\text{C}_{27}\text{H}_{38}\text{O}_7\text{SiNa}$: 525.2285).

2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- α/β -D-mannopyranose (9):

Deallylation of Allyl-4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (**5**, 2.44 g, 4.80 mmol) was effected as described for the deprotection of allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside **4**, to give **9** (2.10 g, 4.45 mmol, 93%) as a colorless oil. R_f 0.40 (hexanes/EtOAc 2:1); Major anomer (α): ^1H -NMR, δ : 0.11 (s, 3H), 0.17 (s, 3H), 0.97 (s, 9H), 3.63 (d, J = 3.3 Hz, 1H), 3.73 (m, 1H), 3.87 (m, 1H), 3.99-4.12 (m, 2H), 4.22-4.31 (m, 2H), 4.72 (d, J = 12.0 Hz, 1H), 4.96 (d, J = 12.0 Hz, 1H), 5.12 (s, 1H), 5.62 (s, 1H), 7.32-7.56 (m, 10H); ^{13}C -NMR, δ : -4.71, -4.35, 18.4, 25.9, 64.2, 68.7, 70.0, 74.2, 79.2, 79.3, 94.3, 101.8, 126.0, 127.5, 127.7, 127.8, 128.0, 128.1, 137.4, 138.1; IR, ν : 3364, 2933, 1379, 1092 cm^{-1} ; HR-MS m/z : 495.2167 (calculated for $\text{C}_{26}\text{H}_{36}\text{O}_6\text{SiNa}$: 495.2179).

General procedure for dehydrative glycosylations:

A mixture of the glycosylating agent (1.5 equiv to nucleophile), Ph_2SO (2.0 equiv to glycosylating agent) and TTBP (3.0 equiv to glycosylating agent) in DCM (0.04 M in glycosylating agent) were stirred over flame dried molecular sieves for 30 min, after which the reaction mixture was cooled to -60°C . Ti_2O (1.0 equiv to glycosylating agent) was added and the mixture was first brought to -40°C and then slowly warmed to -20°C over a period of approximately 1.5 h. After the reaction was cooled to -25°C a solution of the acceptor (0.2 M) in DCM was added dropwise. The resulting mixture was warmed very slowly to room temperature (typically overnight), after which the reaction was quenched by the addition of Et_3N (10 equiv to glycosylating agent) and concentrated *in vacuo*. The crude product was purified by flash silica gel chromatography (EtOAc in hexanes or EtOAc in toluene).

Preparation of acceptor glycosides:

Allyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**10**) was prepared as reported in the synthesis of Allyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**4**).

Ethyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (15) was prepared analogous to Allyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (10). Spectral data were in full accord with those reported previously.²

Methyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*- α -L-rhamnopyranoside (17) was prepared as described previously.³

***n*-Pentenyl 3-*O*-Acetyl-6-*O*-benzyl-4-*O*-2-benzylloxycarbonylamino-2-deoxy- β -D-glucopyranoside (19)** was prepared as described previously.⁴

Allyl 4,6-*O*-benzylidene-2-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (11): Using the general procedure, **11** was prepared on a 0.208 mmol (nucleophile) scale. Yield: 81%. R_f 0.55 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : 3.27 (m, 1H), 3.56 (dd, $J = 3.3, 9.9$ Hz, 1H), 3.73 (m, 4H), 3.77-3.97 (m, 5H), 4.04-4.26 (m, 5H), 4.56-4.70 (m, 5H), 4.82 (d, $J = 1.5$ Hz, 1H), 4.93 (d, $J = 12.3$ Hz, 1H), 5.02 (d, $J = 12.3$ Hz, 1H), 5.20 (m, 2H), 5.48 (s, 1H), 5.57 (s, 1H), 5.83 (m, 1H), 6.79 (m, 2H), 7.20-7.62 (m, 22H); $^{13}\text{C-NMR}$, δ : 55.2, 64.2, 67.7, 68.0, 68.4, 68.8, 70.9, 72.1, 73.7, 74.5, 74.8, 75.8, 77.5, 78.4, 78.5, 97.3, 100.6, 101.3, 101.5, 113.4, 117.7, 125.9, 126.0, 127.4, 128.1, 128.2, 128.5, 128.8, 129.1, 130.8, 131.0, 133.3, 137.5, 138.3, 138.5, 158.9; $[\alpha]_D +32.6$ ($c = 2.0$); IR, ν : 3007, 2869, 1612, 1513, 1090 cm^{-1} ; HR-MS m/z : 881.3492 (calculated for $\text{C}_{51}\text{H}_{54}\text{O}_{12}\text{Na}$: 881.3513).

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (12): Using the general procedure, **12** was prepared on a 0.222 mmol (nucleophile) scale. Yield: 70%. R_f 0.70 (hexanes/EtOAc 1:1); $^1\text{H-NMR}$, δ : 3.31 (m, 1H), 3.55 (dd, $J = 3.3, 9.9$ Hz, 1H), 3.74-3.81 (m, 11H), 3.84-4.00 (m, 4H), 4.07-4.30 (m, 5H), 4.52-4.74 (m, 5H), 4.87 (s, 1H), 4.89 (d, $J = 11.7$ Hz, 1H), 4.97 (d, $J = 11.7$ Hz, 1H), 5.25 (m, 2H), 5.52 (s, 1H), 5.60 (s, 1H), 5.87 (m, 1H), 6.84 (m, 6H), 7.19-7.52 (m, 16H); $^{13}\text{C-NMR}$, δ : 55.1, 64.1, 67.6, 68.0, 68.4, 68.7, 70.8, 71.7, 73.6, 73.9, 74.6, 75.1, 78.3, 78.5, 97.3, 100.5, 101.1, 101.3, 113.3, 113.4, 113.5, 117.6, 125.9, 126.0, 128.0, 128.7, 128.9, 129.1, 130.1, 130.2, 130.4, 130.8, 133.2, 137.4, 137.5, 158.8, 158.9; $[\alpha]_D +29.6$ ($c = 1.0$); IR, ν : 2995, 1610, 1508, 1088, 1030 cm^{-1} ; HR-MS m/z : 941.3701 (calculated for $\text{C}_{53}\text{H}_{58}\text{O}_{14}\text{Na}$: 941.3725).

3-*O*-[2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-1,2:5,6-di-*O*-

isopropylidene- α -D-glucofuranose (14): Using the general procedure, **14** was prepared on a 0.125 mmol (acceptor glycoside) scale. Yield: 95%. Spectral data were in full accord with those reported previously.¹

Ethyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (16): Using the general procedure, **16** was prepared on a 0.157 mmol (nucleophile) scale. Yield: 66%. R_f 0.80 (toluene/EtOAc 3:1); $^1\text{H-NMR}$, δ : 1.30 (t, $J = 7.2$ Hz, 3H), 2.64 (m, 2H), 3.31 (m, 1H), 3.57 (dd, $J = 3.3, 9.9$ Hz, 1H), 3.74-3.81 (m, 11H), 3.88-3.95 (m, 3H), 4.11 (t, $J = 9.0$ Hz, 1H), 4.19-4.30 (m, 3H), 4.33 (m, 1H), 4.53-4.71 (m, 5H), 4.89 (d, $J = 11.7$ Hz, 1H), 4.97 (d, $J = 11.7$ Hz, 1H), 5.31 (s, 1H), 5.51 (s, 1H), 5.60 (s, 1H), 6.84 (m, 6H), 7.19-7.52 (m, 16H); $^{13}\text{C-NMR}$, δ : 15.2, 25.8, 55.4, 64.9, 68.0, 68.8, 68.9, 71.1, 72.1, 74.2, 74.3, 75.6, 76.1, 76.7, 77.3, 78.7, 79.0, 82.8, 100.0, 101.6, 101.9, 113.8, 113.9, 126.3, 126.4, 128.4, 129.1, 129.4, 129.6, 130.5, 130.6, 130.8, 137.7, 137.8, 159.3; $[\alpha]_D -14.5$ ($c = 1.0$); IR, ν : 3008, 1612, 1513, 1092 cm^{-1} ; HR-MS m/z : 945.3473 (calculated for $\text{C}_{52}\text{H}_{58}\text{O}_{13}\text{SNa}$: 945.3496).

Methyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannopyranosyl]- α -L-rhamnopyranoside (18): Using the general procedure, **18** was prepared on a 0.168 mmol (nucleophile) scale. Yield: 90% (β/α 3.5:1). Anomers were partly separated. β -anomer: R_f 0.50 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : 1.36 (d, $J = 6.0$ Hz, 3H), 2.12 (s, 3H), 3.26 (m, 1H), 3.31 (m, 1H), 3.37 (s, 3H), 3.48 (t, $J = 9.6$ Hz, 1H), 3.68 (d, $J = 3.0$ Hz, 1H), 3.75 (dd, $J = 6.3, 10.2$ Hz, 1H), 3.88 (t, $J = 10.2$ Hz, 1H), 4.06 (dd, $J = 3.3, 9.6$ Hz, 1H), 4.16 (t, $J = 9.6$ Hz, 1H), 4.29-4.39 (m, 2H), 4.47 (d, $J = 12.3$ Hz, 1H), 4.65 (m, 3H), 4.70 (s, 1H), 4.86 (d, $J = 12.3$ Hz, 1H), 4.93 (d, $J = 12.3$ Hz, 1H), 5.13 (m, 1H), 5.59 (s, 1H), 7.12-7.68 (m, 20H); $^{13}\text{C-NMR}$, δ : 18.3, 21.3, 55.2, 67.7, 67.8, 68.8, 72.8, 73.4, 74.3, 75.3, 75.8, 77.8, 78.7, 81.6, 98.3, 101.6, 103.7, 126.0, 126.3, 127.0, 127.1, 127.6, 127.77, 127.81, 127.9, 128.0, 128.2, 128.3, 128.6, 128.7, 129.0, 129.6, 131.3, 137.8, 138.6, 138.7, 138.9, 170.4; $[\alpha]_D -20.7$ ($c = 1.0$); IR, ν : 2933, 1743, 1451, 1369, 1082 cm^{-1} ; HR-MS m/z : 763.3076 (calculated for $\text{C}_{43}\text{H}_{48}\text{O}_{11}\text{Na}$: 763.3695). The α -anomer was obtained in a mixture with Ph_2SO . α -anomer: R_f 0.52 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : 1.32 (d, $J = 6.0$ Hz, 3H), 2.09 (s, 3H),

3.27 (m, 1H), 3.28 (s, 3H), 3.61 (m, 1H), 3.73 (dd, $J = 6.3, 9.6$ Hz, 1H), 3.79 (d, $J = 9.9$ Hz, 1H), 3.92 (dd, $J = 3.3, 10.2$ Hz, 1H), 3.98 (m, 1H), 4.10-4.21 (m, 2H), 4.25 (t, $J = 9.6$ Hz, 1H), 4.37 (d, $J = 10.2$ Hz, 1H), 4.58 (m, 2H), 4.68 (m, 3H), 4.82 (d, $J = 12.3$ Hz, 1H), 5.15 (s, 1H), 5.14 (m, 1H), 5.61 (s, 1H), 7.04-7.48 (m, 20H).

***n*-Pentenyl 3-*O*-Acetyl-6-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannopyranosyl]-2-benzyloxycarbonylamino-2-deoxy- β -D-glucopyranoside (20):** Using the general procedure, **20** was prepared on a 0.198 mmol (nucleophile) scale. Yield: 80% (β/α 2.5:1). β -anomer: R_f 0.60 (toluene/EtOAc 3:1); $^1\text{H-NMR}$, δ : 1.68 (m, 2H), 1.97 (s, 3H), 2.09 (m, 2H), 3.16 (m, 1H), 3.38-3.55 (m, 4H), 3.65 (m, 3H), 3.80 (t, $J = 10.2$ Hz, 1H), 3.91 (m, 2H), 4.09 (t, $J = 9.3$ Hz, 1H), 4.27 (dd, $J = 4.5, 10.2$ Hz, 1H), 4.41 (m, 2H), 4.55-4.80 (m, 5H), 4.99 (m, 2H), 5.12 (m, 3H), 5.57 (s, 1H), 5.78 (m, 1H), 7.26-7.52 (m, 25H); $^{13}\text{C-NMR}$, δ : 20.9, 28.6, 29.9, 56.0, 66.8, 67.3, 68.3, 68.6, 69.0, 72.3, 72.6, 73.5, 74.6, 75.9, 76.4, 77.9, 78.6, 101.3, 101.6, 101.8, 115.0, 126.0, 126.7, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.9, 136.4, 137.5, 137.7, 138.0, 138.5, 138.6, 156.0, 170.7; $[\alpha]_D -23.5$ ($c = 1.0$); IR, ν : 3008, 2878, 1736, 1090 cm^{-1} ; HR-MS m/z : 966.4016 (calculated for $\text{C}_{43}\text{H}_{48}\text{O}_{11}\text{Na}$: 966.4041). The α -anomer was obtained in a mixture with Ph_2SO . α -anomer: R_f 0.65 (toluene/EtOAc 3:1); $^1\text{H-NMR}$, δ : 1.66 (m, 2H), 1.79 (s, 3H), 2.09 (m, 2H), 3.46 (m, 2H), 3.61 (m, 1H), 3.73 (m, 3H), 3.80-3.92 (m, 4H), 4.14 (m, 1H), 4.25 (t, $J = 8.7$ Hz, 1H), 4.42 (bs, 1H), 4.55-4.68 (m, 4H), 4.80 (m, 2H), 4.95-5.14 (m, 5H), 5.62 (s, 1H), 5.77 (m, 1H), 7.25-7.67 (m, 25H).

***n*-Pentenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannoside (22):** Using the general procedure, **22** was prepared on a 0.267 mmol (glycosylating agent scale, 0.33 equiv to nucleophile) scale. Yield: 81% (α/β 3:1). Anomers were not separated. R_f 0.65 (hexanes/EtOAc 3:1); $^1\text{H-NMR}$, δ : 1.68 (m, 0.6H), 1.78 (m, 2H), 2.06-2.22 (m, 2.6H), 3.30-3.39 (m, 3.3H), 3.47 (m, 1H), 3.61 (dd, $J = 3.3, 9.9$ Hz, 1H), 3.67 (m, 0.3H), 3.72-4.03 (m, 4.2H), 4.22-4.37 (m, 2.6H), 4.46 (s, 1H), 4.61 (d, $J = 12.6$ Hz, 1H), 4.67-4.74 (m, 1.6H), 4.79 (m, 0.6H), 4.84-4.93 (m, 1.6H), 4.99-5.01 (m, 3.3H), 5.65 (s, 1H), 5.68 (s, 0.3H), 5.65-5.96 (m, 1.3 H), 7.25-7.55 (m, 19.5H); $^{13}\text{C-NMR}$, δ : 28.3, 28.8, 29.6, 30.2, 64.1, 66.9, 67.2, 67.4, 68.5, 68.7, 68.8, 69.5, 72.3, 73.0, 73.5, 74.6, 75.6, 76.4, 77.9, 78.6, 79.1, 99.3, 101.3, 102.2, 114.9, 115.0, 126.0, 127.5, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 137.5, 137.8, 138.0,

138.2, 138.3; IR, ν : 3007, 2928, 1453, 1368, 1095 cm^{-1} ; HR-MS m/z : 539.2396 (calculated for $\text{C}_{32}\text{H}_{36}\text{O}_6\text{Na}$: 539.2410).

6-*O*-[2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (24): Using the general procedure, **24** was prepared on a 0.137-0.179 mmol (nucleophile) scale. The yield and selectivity depended on the reaction solvent and sulfoxide reagent: ($\text{Ph}_2\text{SO}/\text{Tf}_2\text{O}$, DCM, -50°C to room temperature: 89%, β/α 3:1; $\text{Ph}_2\text{SO}/\text{Tf}_2\text{O}$, toluene/DCM (5:1), -50°C to room temperature: 97%, β/α 3:2; $(\text{Tol})_2\text{SO}/\text{Tf}_2\text{O}$, DCM, -50°C to room temperature: 91%, β/α 3:1; BSP/ Tf_2O , DCM, -50°C to room temperature: 52%, β/α 3:2;. Spectral data were in full accord with those reported previously.¹

Allyl 4,6-*O*-benzylidene-2-*O*-[2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- α/β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (25): Using the general procedure, **25** was prepared on a 0.141-0.148 mmol (nucleophile) scale. The yield and selectivity depended on the reaction solvent and temperature: (DCM, -25°C to room temperature: 92%, β/α 3:2; toluene/DCM (5:1), -50°C to room temperature: 88%, β/α 3:2; DCM, -50°C to room temperature: 82%, β/α 2:3. Anomers were not separated. R_f 0.70 (hexanes/EtOAc 2:1); ^1H -NMR, δ : 0.061 (s, 2.1H), 0.11 (s, 5.1H), 0.15 (s, 3H), 0.93 (s, 6.3H), 0.94 (s, 9H), 3.33 (m, 0.7H), 3.73 (s, 3H), 3.79 (s, 2.1H), 3.79-3.90 (m, 8.8H), 4.00-4.32 (m, 15H), 4.42 (d, J = 11.7 Hz, 1H), 4.57-4.82 (m, 5.1H), 4.89 (s, 1H), 4.94 (s, 0.7H), 4.95 (d, J = 11.4 Hz, 0.7 H), 5.02 (d, J = 11.4 Hz, 0.7H), 5.23-5.35 (m, 4.4H), 5.51 (s, 0.7H), 5.56 (s, 0.7H), 5.60 (s, 1H), 5.65 (s, 1H), 5.88-5.93 (m, 1.7H), 6.80-6.85 (m, 3.4H), 7.26-7.56 (m, 20.4H); ^{13}C -NMR, δ : -4.85, -4.73, -4.38, 18.3, 18.4, 26.8, 25.9, 55.1, 55.2, 63.9, 64.2, 64.9, 67.8, 68.0, 68.1, 68.5, 68.7, 68.8, 68.9, 70.1, 71.0, 72.9, 73.2, 73.8, 74.4, 75.2, 75.7, 76.1, 78.5, 78.6, 79.0, 79.6, 79.7, 97.4, 99.2, 100.2, 101.2, 101.5, 101.7, 113.4, 113.7, 117.7, 126.00, 126.05, 126.11, 127.2, 127.4, 127.6, 128.0, 128.1, 128.4, 128.8, 128.9, 129.1, 129.4, 130.4, 130.9, 133.3, 137.5, 138.4, 138.8, 158.9, 159.2; IR, ν : 2930, 2858, 1513, 1088, 1036 cm^{-1} ; HR-MS m/z : 905.3886 (calculated for $\text{C}_{50}\text{H}_{62}\text{O}_{12}\text{SiNa}$: 905.3909).

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α/β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside

(26): Using the general procedure, **26** was prepared on a 0.198 mmol (nucleophile) scale. Yield: 79% (β/α 4:1). β -anomer: R_f 0.55 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : 0.16 (s, 3H), 0.21 (s, 3H), 0.95 (s, 9H), 3.72 (m, 1H), 3.50 (dd, $J = 2.7, 9.6$ Hz, 1H), 3.79 (s, 3H), 3.80 (m, 3H), 3.81 (s, 3H), 3.92-3.99 (m, 2H), 4.08-4.23 (m, 7H), 4.42 (s, 1H), 4.57 (d, $J = 11.4$ Hz, 1H), 4.66-4.73 (m, 3H), 4.83 (d, $J = 1.2$ Hz, 1H), 5.19-5.30 (m, 2H), 5.55 (s, 1H), 5.59 (s, 1H), 5.80-5.95 (m, 1H), 6.82-6.87 (m, 4H), 7.26-7.55 (m, 14H); $^{13}\text{C-NMR}$, δ : -4.2, -3.6, 18.5, 25.9, 55.0, 64.1, 67.8, 67.9, 68.5, 68.6, 70.2, 71.6, 71.8, 73.4, 75.3, 78.1, 78.6, 97.7, 100.6, 101.1, 101.3, 113.1, 113.3, 113.7, 117.6, 125.7, 127.8, 128.5, 128.7, 129.1, 130.2, 130.7, 133.3, 137.25, 137.32, 158.4, 158.7; $[\alpha]_D -18.6$ ($c = 0.5$); IR, ν : 2933, 1512, 1087 cm^{-1} ; HR-MS m/z : 935.3992 (calculated for $\text{C}_{51}\text{H}_{62}\text{O}_{13}\text{SiNa}$: 935.4014). α -anomer: R_f 0.60 (hexanes/EtOAc 2:1); $^1\text{H-NMR}$, δ : -0.049 (s, 3H), 0.032 (s, 3H), 0.87 (s, 9H), 3.78 (s, 3H), 3.79 (s, 3H), 3.78-3.89 (m, 6H), 3.96 (m, 3H), 4.11-4.24 (m, 5H), 4.59-5.80 (m, 5H), 4.91 (d, $J = 1.5$ Hz, 1H), 5.18-5.29 (m, 2H), 5.62 (s, 1H), 5.64 (s, 1H), 5.81-5.90 (m, 1H), 6.84 (m, 4H), 7.22-7.54 (m, 14H); $^{13}\text{C-NMR}$, δ : -5.0, -4.0, 18.2, 25.9, 55.2, 55.3, 64.0, 64.9, 67.9, 68.8, 68.9, 71.2, 72.7, 72.9, 75.0, 75.1, 79.3, 99.0, 101.3, 101.4, 103.9, 113.4, 113.5, 113.7, 117.6, 126.0, 128.1, 128.67, 128.73, 129.2, 129.3, 130.4, 130.8, 133.3, 137.51, 137.54, 158.8, 159.0; $[\alpha]_D +11.4$ ($c = 0.5$); IR, ν : 2933, 1512, 1133, 1082 cm^{-1} ; HR-MS m/z : 935.3992 (calculated for $\text{C}_{51}\text{H}_{62}\text{O}_{13}\text{SiNa}$: 935.4014).

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (27): A solution of 4,6-*O*-benzylidene-2-(9-fluorenylmethoxycarbonyl)-3-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl trichloroacetimidate (1.07 g, 1.41 mmol) and allyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (0.40 g, 0.94 mmoles) in dichloromethane (16 mL) at -40°C was dried over powdered molecular sieves. Subsequently a solution of TMSOTf (1.44 mL, 0.1 M, 0.14 mmoles) was added and the reaction was stirred for 30 mins before quenching with Et_3N (3 mL) at -40°C . DMF (15 mL) was added and the reaction was allowed to stir for 5 mins at -40°C before allowing the mixture to warm slowly to room temperature. The reaction mixture was filtered over celite and the resulting filtrate was concentrated *in vacuo*, to afford a yellow oil, which was subsequently dissolved in EtOAc. The organic solution was washed with 1 M HCl. The aqueous layer was then extracted with EtOAc (3x). The combined organic fractions were dried over MgSO_4 , filtered, concentrated *in vacuo* and purified by flash chromatography (0 to 35 % EtOAc in hexane). Compound **27** was obtained as a colourless oil

(0.45 g, 0.57 mmol, 60 %). R_f 0.33 (hexanes/EtOAc 1:1) $^1\text{H-NMR}$, δ : 2.65 (s, 1H), 4.26-3.79 (m, 20H), 4.84-4.60 (m, 5H), 5.32-5.15 (m, 3H), 5.62 (s, 2H), 5.84-5.91 (m, 1H), 6.89-6.83 (m, 4H), 7.53-7.25 (m, 14H); $^{13}\text{C-NMR}$, δ : 55.5, 64.1, 64.3, 68.2, 68.9, 69.0, 70.0, 73.0, 73.1, 75.3, 75.7, 79.1, 99.2, 101.7, 102.4, 114.00, 114.04, 117.9, 126.2, 126.3, 128.4, 128.4, 129.1, 129.2, 129.4, 129.8, 130.3, 130.5, 133.6, 137.7, 137.7, 159.4, 159.6; $[\alpha]_D - 139.0$ ($c = 0.1$); IR, ν : 30008, 1610, 1512, 1369 cm^{-1} ; HR-MS m/z : 821.3129 (calculated for $\text{C}_{45}\text{H}_{50}\text{O}_{13}\text{Na}$: 821.3149).

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2-*O*-{4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl}-3-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (28): Using the general procedure, **28** was prepared on a 0.251 mmol (nucleophile) scale. Yield: 64%. R_f 0.65 (hexanes/EtOAc 1:1); $^1\text{H-NMR}$, δ : 2.81-2.89 (m, 1H), 3.25 (dd, $J = 3.3, 9.9$ Hz, 1H), 3.53 (s, 3H), 3.70-3.82 (m, 13H), 3.96-4.14 (m, 8H), 4.17-4.27 (m, 5H), 4.48 (d, $J = 11.8$ Hz, 1H), 4.54 (d, $J = 10.8$ Hz, 1H), 4.61 (d, $J = 11.7$, 1H), 4.69-4.87 (m, 7H), 4.93 (d, $J = 12.0$ Hz, 1H), 5.12 (s, 1H), 5.24-5.34 (m, 2H), 5.47 (s, 1H), 5.56 (s, 1H), 5.66 (s, 1H), 5.86-5.98 (m, 1H), 6.74-6.88 (m, 8H), 7.19-7.68 (m, 23H); $^{13}\text{C-NMR}$, δ : 55.3, 55.4, 64.1, 65.0, 67.4, 68.3, 68.8, 69.0, 69.1, 71.3, 72.2, 73.3, 74.0, 74.3, 75.7, 76.0, 76.5, 76.6, 78.5, 79.0, 79.8, 99.3, 100.6, 101.0, 101.4, 101.7, 101.8, 113.7, 113.8, 113.9, 114.0, 114.1, 118.1, 125.0, 126.2, 126.3, 128.3, 128.4, 128.5, 128.9, 129.1, 129.2, 129.3, 129.5, 129.6, 130.3, 130.6, 131.0, 131.3, 133.6, 137.7, 137.8, 138.0, 159.2, 159.3, 159.4, 159.6; $[\alpha]_D - 46.8$ ($c = 1.0$); IR, ν : 2912, 1610, 1507, 1087, 1030 cm^{-1} ; HR-MS m/z : 1311.5110 (calculated for $\text{C}_{74}\text{H}_{80}\text{O}_{20}\text{Na}$: 1311.5141).

Allyl 3,4,6-tri-*O*-acetyl-2-*O*-[3,4,6-tri-*O*-acetyl-3-*O*-{2,3,4,6-tetra-*O*-acetyl- β -D-mannopyranosyl}- α -D-mannopyranosyl]- α -D-mannopyranoside (30): Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-3-*O*-{4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl}-2-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (**28**) (87 mg, 0.068 mmol) was dissolved in DCM (4.2 mL). 1,2-ethanedithiol (45 μL , 0.53 mmol) was added, followed by TFA (0.23 mL, 3.0 mmol). The mixture was allowed to stir for 5 mins at room temperature. The mixture was diluted with EtOAc and extracted with water (3x). The aqueous layer was collected and concentrated *in vacuo* to afford a white solid (30 mg, 82 %). The solid (30 mg, 0.05 mmol) was dissolved in pyridine (1.5 mL) and Ac_2O (1 mL) was added. The mixture was allowed to stir overnight

and the mixture was concentrated *in vacuo*. The resulting oil was purified by flash chromatography (0–80% EtOAc in toluene) to afford a colourless solid (34 mg, 64 %). R_f 0.20 (hexanes/EtOAc 1:4); $^1\text{H-NMR}$ (500 MHz), δ : 1.93 (s, 3H), 1.95 (s, 3H), 1.99 (s, 9H), 2.04 (m, 12H), 2.14 (s, 3H), 3.63–3.66 (m, 1H), 3.89–3.92 (m, 1H), 3.94–4.06 (m, 3H), 4.12 (m, 1H), 4.15 (m, 1H), 5.18 (d, $J = 4.9$ Hz, 1H), 4.20 (d, $J = 4.9$ Hz, 1H), 4.25 (m, 1H), 4.27 (d, $J = 2.9$ Hz, 1H), 4.73 (s, 1H), 4.86 (d, $J = 3.0$ Hz, 1H), 4.91 (d, $J = 2.3$ Hz, 1H), 5.01–5.10 (m, 3H), 5.15–5.23 (m, 4H), 5.26 (m, 1H), 5.27 (d, $J = 3.2$ Hz, 1H), 5.29 (d, $J = 3.2$ Hz, 1H), 5.41 (dd, $J = 0.8, 3.0$ Hz, 1H), 5.80–5.87 (m, 1H); $^{13}\text{C-NMR}$ (75 MHz), δ : 20.7, 20.80, 20.82, 20.85, 20.87, 20.90, 21.1, 62.2, 62.5, 62.6, 66.4, 66.8, 68.7, 68.87, 68.94, 69.7, 70.3, 70.6, 70.9, 72.3, 72.5, 75.8, 96.7, 97.6, 99.1, 118.3, 133.4, 169.5, 169.8, 170.1, 170.2, 170.6, 170.85, 170.88, 171.1; $[\alpha]_D -3.3$ ($c = 1.0$); IR (CHCl_3) ν : 3015.4, 1748.7, 1364.1, 1051.3 cm^{-1} ; HR-MS m/z : 987.2934 (calculated for $\text{C}_{41}\text{H}_{56}\text{O}_{26}\text{Na}$: 987.2958).

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Allyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (2):

Allyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (3):

Allyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (4):

Allyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (5):

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannopyranose (6):

4,6-*O*-Benzylidene-2,3-di-*O*-*p*-methoxybenzyl- α/β -D-mannopyranose (7):

4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α/β -D-mannopyranose (8):

2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- α/β -D-mannopyranose (9):

Allyl 4,6-*O*-benzylidene-2-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (11):

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (12):

Ethyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (16):

Methyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-α-L-rhamnopyranoside (18):

Methyl **2-*O*-acetyl-4-*O*-benzyl-3-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl]- α -L-rhamnopyranoside (18):**

n-Pentenyl 3-*O*-Acetyl-6-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-2-benzyloxycarbonylamino-2-deoxy- β -D-glucopyranoside (20):

n-Pentenyl 3-*O*-Acetyl-6-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl]-2-benzyloxycarbonylamino-2-deoxy- β -D-glucopyranoside (20):

***n*-Pentenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β -D-mannoside (22):**

Allyl 4,6-*O*-benzylidene-2-*O*-[2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- α / β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (25):

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- α -D-mannopyrannosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (26):

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (26):

Allyl **4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (27):**

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-3-*O*-{4,6-*O*-benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-mannopyranosyl}-2-*O*-*p*-methoxybenzyl- α -D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl- α -D-mannopyranoside (28):

Allyl 3,4,6-tri-*O*-acetyl-2-*O*-[3,4,6-tri-*O*-acetyl-3-*O*-{2,3,4,6-tetra-*O*-acetyl- β -D-mannopyranosyl}- α -D-mannopyranosyl]- α -D-mannopyranoside (30):