Supporting information

for

2-*O*-Propargyl Ethers: Readily-Cleavable, Minimally-Intrusive

Protecting Groups for β -Mannosyl Donors

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Table of Contents

Compound	Expt	Spectra
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -allyl-3- <i>O</i> - <i>p</i> -methoxybenzyl-1-thio- α -D-mannopyranoside (8).	S-3	S-20 S-21
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -allyl-1-thio- α -D-mannopyranoside (9).	S-3	S-22 S-23
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -allyl-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl-1-thio- α -D-mannopyranoside (10).	S-4	S-24 S-25
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>p</i> -methoxybenzyl-1-thio- α -D-mannopyranoside (11).	S-5	S-26 S-27
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl) -1-thio- α -D-mannopyranoside (12).	S-5	S-28 S-29
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl-1-thio- α -D-mannopyranoside (13).	S-6	S-30 S-31
3 β -Cholestanyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- α -D-mannopyranoside (15a).	S-7	S-32 S-33
3 β -Cholestanyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranoside (15b).	S-8	S-34 S-35
3 β -Cholestanyl 4,6- <i>O</i> -benzylidene-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranoside (16).	S-16	S-36 S-37
Methyl-4- <i>O</i> -[4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)-2,3- <i>O</i> -isopropylidene- α -L-rhamanopyranoside (18 b).	S-8	S-38 S-39
Methyl-4- <i>O</i> -[4,6- <i>O</i> -benzylidene-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)-2,3- <i>O</i> -isopropylidene- α -L-rhamanopyranoside (19).	S-17	S-40 S-41
Methyl-2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -[4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- α -D-mannopyranosyl](1 $\rightarrow$ 4)- α -D-glucopyranoside (21a).	S-9	S-42 S-43

Methyl-2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -[4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (21β).	S-10	S-44 S-45
Methyl-2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -(4,6- <i>O</i> -benzylidene-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (22).	S-17	S-46 S-47
Methyl-2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -(4,6- <i>O</i> -benzylidene-2- <i>O</i> -allyl-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23α).	S-10	S-48 S-49
Methyl-2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -(4,6- <i>O</i> -benzylidene-2- <i>O</i> -allyl-3- <i>O</i> - <i>tert</i> -butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23β).	S-11	S-50 S-51
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> - <i>p</i> -methoxybenzyl- β -D-mannopyranoside (24).	S-11	S-52 S-53
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranoside (25).	S-12	S-54 S-55
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2,3-di- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene- α -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (27α).	S-13	S-56 S-57
Phenyl 4,6- <i>O</i> -Benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2,3-di- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene- β -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (27β).	S-14	S-58 S-59
Methyl 2,3-di- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- α -D-mannopyranoside (28α).	S-14	S-60 S-61
Methyl 2,3-di- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- α -D-mannopyranoside (28β).	S-15	S-62 S-63
Methyl 2,3-di- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene- β -D-mannopyranoside (29).	S-18	S-64 S-65

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (8).

To a stirred solution of phenyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (1.68 g, 3.5 mmol) in dry dimethylformamide (10 mL), was added NaH 60% in oil (0.23 g, 7.5 mmol) followed by allyl bromide (0.46 mL, 5.2 mmol) at 0 °C. The stirring was continued overnight before the reaction mixture was quenched with methanol, diluted with CH₂Cl₂ (25 mL) and washed with sat. NaHCO₃. The organic layer was separated and dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (hexane:ethyl acetate 5:1) to give **8** (1.75 g, 96%); $[\alpha]_D^{25} + 148$ (c, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 3.82 (s, 3H), 3.89 (t, *J* = 10.0 Hz, 1H), 3.94-3.97 (m, 2H), 4.18-4.31 (m, 5H), 3.88 (d, *J* = 11.8 Hz, 1H), 4.81 (d, *J* = 11.8 Hz, 1H), 5.21 (ddd, *J* = 1.5, 2.5, 10.0 Hz, 1H), 5.31 (ddd, *J* = 1.5, 3.0, 17.0 Hz, 1H), 5.54 (s, 1H), 5.65 (s, 1H), 5.89-5.96 (m, 1H), 6.9 (d, *J* = 8.6 Hz, 1H), 7.3-7.45 (m, 10H), 7.5-7.56 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ : 55.3, 65.4, 68.5, 72.6, 72.8, 75.7, 78.1, 79.0, 87.3, 101.5, 113.8, 117.9, 126.1, 127.6, 128.2, 128.8, 129.1, 129.4, 130.4, 131.5, 133.8, 134.5, 137.6, 159.2. Anal. Calcd for C₃₀H₃₂O₆S: C, 69.21; H, 6.20. Found: C, 68.98; H, 6.22.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio- α -D-mannopyranoside (9).

To stirred solution of **8** (1.75 g, 3.36 mmol) in CH₂Cl₂ (10 mL) and water (0.5 mL) was added DDQ (1.53 g, 6.72 mmol) at room temp. After 3 h, sat. NaHCO₃ was added, and the mixture was extracted with CH₂Cl₂. The extract was washed several times with sat NaHCO₃, and dried over Na₂SO₄. Evaporation of the solvent in vacuo gave an oil, which

was chromatographed on a flash silica gel column (hexane:ethyl acetate, 4:1) to give colorless oil of **9** (1.25 g, 93%). $[\alpha]_D^{27} +155$ (*c*, 2.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 2.5 (bs, 1H), 3.85 (t, *J* = 10.2 Hz, 1H), 3.9 (t, *J* = 9.6 Hz, 1H), 4.02 (dd, *J* = 1.1, 3.6 Hz, 1H), 4.1-4.15 (m, 2H), 4.21-4.25 (m, 2H), 4.29-4.34 (m, 1H), 5.25 (ddd, *J* = 1.3, 2.5, 10.0 Hz, 1H), 5.33 (ddd, *J* = 1.5, 3.0, 17.0 Hz, 1H), 5.59 (s, 1H), 5.62 (s, 1H), 5.9-5.98 (m, 1H), 7.33-7.53 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ : 64.6, 68.5, 68.9, 72.1, 79.6, 79.7, 86.2, 102.2, 118.5, 126.3, 127.4, 128.3, 129.2, 131.6, 133.7, 133.8, 137.2. ESIHRMS Calcd for C₂₂H₃₂O₅S[M+Na]⁺: 423.1242. Found 423.1237.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (10**).**

To a stirred solution of **9** (0.8 g, 1.9 mmol) and imidazole (0.28 g, 3.9 mmol) in dry dimethylformamide (10 mL) was added *tert*-butyldimethylsilyl chloride (0.46 g, 2.9 mmol) at room temperature and the mixture was stirred for 12 h. The solvent was evaporated off and the residue was dissolved in CH₂Cl₂ (15 mL) and washed with sat. NaHCO₃. The organic layer was separated and dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silicagel (hexane:ethyl acetate; 8:1) to yield **10** as a colorless oil (0.93 g, 92%) $[\alpha]_D^{25} +118.5$ (*c*, 2.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.114 and 0.16 (2s, 6H), 0.94 (s, 9H), 3.89-3.91 (m, 2H), 4.09 (t, *J* = 9.5 Hz, 1H), 4.19 (dd, *J* = 3.2, 9.8 Hz, 1H), 4.2-4.25 (m, 2H), 4.28-4.33 (m, 2H), 5.23 (dd, *J* = 1.4, 9.4 Hz, 1H), 4.1-4.15 (m, 2H), 4.21-4.25 (m, 2H), 4.29-4.34 (m, 1H), 5.23 (ddd, *J* = 1.0, 2.5, 10.0 Hz, 1H), 5.33 (ddd, *J* = 1.5, 3.5, 17.5 Hz, 1H), 5.57 (s, 1H), 5.61 (s, 1H), 5.9-5.98 (m, 1H), 7.33-

7.53 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3) δ : -4.7, -4.3, 18.4, 25.8, 65.5, 68.5, 70.6, 73.1, 79.1, 80.2, 87.6, 101.9, 117.9, 126.2, 127.5, 128.0, 128.8, 129.1, 131.3, 134.2, 134.7, 137.8. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_5\text{SSi}$: C, 65.33; H, 7.44. Found: C, 65.13; H, 7.37.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (11).

To a stirred solution of phenyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (2.5 g, 5.5 mmol) in dry dimethylformamide (15 mL) at 0 °C was added NaH 60% in oil (0.33 g, 8.3 mmol) and stirred for 15 min. Propargyl bromide (0.93 mL, 8.3 mmol) was added dropwise to the above reaction mixture and continued stirring for 3 h. The reaction mixture was quenched by addition of methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. NaHCO_3 . The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 8:1) to give **11** (2.46 g, 85%), $[\alpha]^{24.5}_{\text{D}} + 155.8$ (*c*, 2.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 2.4 (t, $J = 2.4$ Hz, 1H), 3.82 (s, 3H), 3.87 (t, $J = 11.0$ Hz, 1H), 3.98 (dd, $J = 3.0, 10.0$ Hz, 1H), 4.19-4.24 (m, 3H), 4.26-4.31 (m, 1H), 4.4 (dd, $J = 0.5, 2.0$ Hz, 2H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.81 (d, $J = 12.0$ Hz, 1H), 5.61 (d, $J = 1.5$ Hz, 1H), 5.63 (s, 1H), 6.9 (d, $J = 8.6$ Hz, 2H), 7.3-7.45 (m, 10H), 7.5-7.56 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ : 55.3, 58.8, 65.4, 68.5, 72.9, 75.2, 75.7, 77.6, 79.0, 79.4, 87.4, 101.5, 113.8, 126.1, 127.6, 128.2, 128.8, 129.1, 129.2, 129.4, 130.2, 131.6, 133.7, 134.5, 137.5, 159.3 ESIHRMS Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 541.1661. Found 541.1658.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-1-thio- α -D-mannopyranoside (12).

To stirred solution of **11** (0.47 g, 0.91 mmol) in CH₂Cl₂ (8 mL) and water (0.4 mL) was added DDQ (0.3 g, 1.3 mmol) at room temp. After 3 h, sat. NaHCO₃ was added, and the mixture was extracted with CH₂Cl₂. The extract was washed several times with sat NaHCO₃, and dried over Na₂SO₄. Evaporation of the solvent in vacuo gave an oil, which was chromatographed on a flash silica gel column (hexane:ethyl acetate; 4:1) to give **12** (0.34 g, 93%) as a white solid MP 128 °C [α]_D²⁷ + 119 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 2.49 (t, *J* = 2.4 Hz, 1H), 2.5 (bs, 1H), 3.84 (t, *J* = 10.2 Hz, 1H), 3.9 (t, *J* = 9.6 Hz, 1H), 4.16 (dd, *J* = 3.6, 10.0 Hz, 1H), 4.21-4.24 (m, 2H), 4.27-4.32 (m, 1H), 4.34 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.42 (dd, *J* = 2.4, 16.1 Hz, 1H), 5.59 (s, 1H), 5.68 (s, 1H), 7.32-7.53 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ : 58.6, 64.7, 68.4, 68.9, 75.7, 78.9, 79.3, 79.4, 86.4, 102.2, 126.3, 127.7, 128.3, 129.2, 131.7, 133.8, 137.2. ESIHRMS Calcd for C₂₂H₂₂O₅S [M+Na]⁺: 421.1086. Found 421.1095.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (13**).**

To a stirred solution of **12** (0.68 g, 1.7 mmol) and imidazole (0.23 g, 3.4 mmol) in dry dimethylformamide (10 mL) was added *tert*-butyldimethylsilyl chloride (0.39 g, 2.5 mmol) at room temperature and mixture was stirred for 12 h. The solvent was evaporated off and the residue was dissolved in CH₂Cl₂ (15 mL) and washed with sat. NaHCO₃. The organic layer was separated and dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 9:1) to yield **13** as a colorless oil (0.79 g, 92%) [α]_D²⁴ + 143 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.10 and 0.16 (2s,

6H), 0.92 (s, 9H), 2.4 (t, $J = 2.3$ Hz, 1H), 3.86 (t, $J = 10.2$ Hz, 1H), 4.0 (t, $J = 9.5$ Hz, 1H), 4.16 (dd, $J = 1.4, 3.1$ Hz, 1H), 4.18-4.23 (m, 2H), 4.26-4.31 (m, 1H), 4.48 (d, $J = 2.4$, 2H), 5.59 (s, 1H), 5.63 (s, 1H), 7.31-7.38 (m, 6H), 7.48-7.52 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ : -4.8, -4.5, 18.4, 25.8, 59.2, 65.5, 68.5, 70.8, 75.2, 79.2, 79.8, 87.7, 101.9, 126.2, 127.6, 128.0, 128.9, 129.2, 131.4, 133.9, 137.5. ESIHRMS Calcd for $\text{C}_{28}\text{H}_{36}\text{O}_5\text{SSi}$ $[\text{M}+\text{Na}]^+$: 535.1951. Found 535.1947.

General procedure for the coupling of mannosyl donors with acceptors using BSP/TTBP/Tf₂O system.

To a stirred solution of donor (0.12g, 1 eq) BSP (1.1 eq), TTBP (1.5 eq), and 4 Å molecular sieves in CH_2Cl_2 (0.05 M in substrate), at -60°C under an Ar atmosphere, was added Tf_2O (1.2 eq). After 30 min. of stirring at -60°C , a solution of the glycosyl acceptor (2 eq) in CH_2Cl_2 (0.02 M in acceptor) was added slowly. The reaction mixture was stirred for further 2 h. at -60°C , and allowed to reach room temperature. The reaction mixture was diluted with dichloromethane (10 mL) and molecular sieves were filtered off and washed with saturated NaHCO_3 . The organic layer was separated and dried and concentrated. Purification by flash column chromatography on silica gel (hexane /ethyl acetate) afforded the corresponding alpha/beta mannopyranosides.

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (15a). $[\alpha]_{\text{D}}^{24} + 75.1$ (c , 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 0.04 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.84-1.59 (m, 39H), 1.64-1.67 (m, 1H), 1.70-1.74 (m, 1H), 1.78-1.86 (m, 2H), 1.94-1.98 (m, 1H), 2.4 (t, $J =$

2.4 Hz, 1H), 3.48-3.58 (m, 1H), 3.79-3.86 (m, 3H), 3.9 (t, $J = 9.0$ Hz, 1H), 4.17 (dd, $J = 3.5, 10.0$ Hz, 1H), 4.2 (dd, $J = 3.0, 8.5$ Hz, 1H), 4.45 (dd, $J = 2.5, 16.5$ Hz, 1H) 4.48 (dd, $J = 2.5, 16.5$ Hz, 1H), 5.0 (d, $J = 1.5$ Hz, 1H), 5.5 (s, 1H) 7.33-7.37 (m, 3H), 7.47-7.49 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ : -4.9, -4.4, 12.0, 12.3, 14.1, 18.3, 18.7, 21.2, 22.5, 22.8, 23.8, 24.2, 25.8, 27.5, 28.0, 28.2, 28.7, 31.6, 32.0, 35.5, 35.6, 35.8, 35.9, 36.1, 36.8, 39.5, 40.0, 42.6, 44.9, 54.3, 56.2, 56.4, 56.5, 59.5, 64.0, 68.8, 70.5, 74.5, 76.5, 78.9, 79.5, 80.0, 98.0, 101.8, 125.0, 126.1, 128.0, 128.7, 128.9, 137.6. ESIHRMS Calcd for $\text{C}_{49}\text{H}_{78}\text{O}_6\text{Si}$ $[\text{M}+\text{Na}]^+$: 813.5466. Found 813.5469.

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (15 β). $[\alpha]_{\text{D}}^{24}$ - 28.8 (c , 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 0.05 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.86-1.7 (m, 36H), 1.78-1.8 (m, 1H), 1.86-1.9 (m, 1H), 1.93-1.98 (m, 1H), 2.39 (t, $J = 2.5$ Hz, 1H), 3.28-3.32 (m, 1H), 3.62-3.68 (m, 1H) 3.48-3.58 (m, 1H), 3.8-3.9 (m, 4H), 4.28 (dd, $J = 4.8, 10.4$ Hz, 1H), 4.55 (dd, $J = 2.3, 16.1$ Hz, 1H) 4.6 (dd, $J = 2.3, 16.1$ Hz, 1H), 4.68 (s, 1H), 5.52 (s, 1H) 7.32-7.37 (m, 3H), 7.45-7.48 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ : -4.9, -4.4, 12.0, 12.3, 18.5, 18.7, 21.2, 22.5, 22.8, 23.8, 24.2, 25.9, 28.0, 28.3, 28.9, 29.2, 32.1, 34.2, 35.5, 35.6, 35.8, 36.2, 36.9, 39.5, 40.0, 42.6, 44.6, 54.3, 56.2, 56.5, 60.0, 67.6, 68.6, 72.7, 74.5, 78.0, 78.6, 78.7, 99.3, 101.8, 126.1, 128.0, 128.8, 137.5. ESIHRMS Calcd for $\text{C}_{49}\text{H}_{78}\text{O}_6\text{Si}$ $[\text{M}+\text{Na}]^+$: 813.5466. Found 813.5478.

Methyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)-2,3-*O*-isopropylidene- α -L-rhamanopyranoside (18 β).

$[\alpha]_D^{24}$ - 60 (*c*, 10, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.05 and 0.1 (2s, 6H), 0.8 (s, 9H), 1.32 (d, *J* = 5.9 Hz, 3H), 1.36 (s, 3H), 1.52 (s, 3H), 2.39 (t, *J* = 2.4 Hz, 1H), 3.27-3.32 (m, 1H), 3.37 (s, 1H), 3.62-3.70 (m, 2H), 3.87-3.95 (m, 4H), 4.1 (d, *J* = 5.6 Hz, 1H), 4.2-4.26 (m, 2H), 4.5 (d, *J* = 2.4 Hz, 2H), 4.87 (s, 1H), 5.0 (s, 1H), 5.53 (s, 1H), 7.26-7.36 (m, 3H), 7.45-7.48 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ :-4.8, -4.4, 17.6, 18.4, 25.8, 26.5, 27.8, 54.8, 60.0, 64.1, 67.6, 68.6, 72.7, 74.5, 76.1, 77.5, 78.3, 78.34, 78.9, 80.2, 97.8, 99.4, 101.8, 109.3, 126.1, 128.0, 128.8, 137.5. Anal. Calcd for C₃₂H₄₈O₁₀Si: C, 61.91; H, 7.79. Found: C, 61.64; H, 7.56.

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl](1 $\rightarrow$ 4)- α -D-glucopyranoside (21a).

$[\alpha]_D^{24}$ + 32.7 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.01 and 0.07 (2s, 6H), 0.8 (s, 9H), 2.19 (t, *J* = 2.4 Hz, 1H), 3.4 (s, 3H), 3.57 (dd, *J* = 3.6, 9.4 Hz, 1H), 3.72 (d, *J* = 3.0 Hz, 2H), 3.76-3.78 (m, 4H), 3.87 (t, *J* = 9.4 Hz, 1H), 3.94 (m, 2H), 4.05 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.07 (t, *J* = 3.5 Hz, 1H), 4.12 (dd, *J* = 3.0, 10.0 Hz, 1H), 4.23 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 5.12 (d, *J* = 11.4 Hz, 1H), 5.33 (d, *J* = 1.7 Hz, 1H), 5.5 (s, 1H), 7.26-7.36 (m, 18H), 7.45-7.47 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ :-4.9, -4.4, 18.3, 25.8, 55.4, 59.2, 65.2, 68.6, 68.9, 69.5, 70.5, 73.2, 73.6, 74.7, 75.1, 76.9, 78.9, 80.0, 81.7, 97.5, 101.7, 101.8, 126.2, 126.9, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.8, 137.6, 137.8, 137.9, 138.7. ESIHRMS Calcd for C₅₀H₆₂O₁₁Si [M+Na]⁺: 889.3959. Found 889.3979.

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-tert-butyl-*dimethylsilyl*- β -D-mannopyranosyl] (1 $\rightarrow$ 4)- α -D-glucopyranoside (21 β).

$[\alpha]^{24}_{\text{D}} - 15.6$ (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.01 and 0.06 (2s, 6H), 0.8 (s, 9H), 2.3 (t, *J* = 2.5 Hz, 1H), 3.0-3.04 (m, 1H), 3.39 (s, 3H), 3.53 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.56 (d, *J* = 10.0 Hz, 1H), 3.66 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.68 (dd, *J* = 1.3, 10.5 Hz, 1H), 3.7-3.82 (m, 4H), 3.9 (t, *J* = 9.4 Hz, 1H), 3.95 (t, *J* = 9.4 Hz, 1H), 4.0 (dd, *J* = 5.0, 11.0 Hz, 1H), 4.47 (d, *J* = 12.5 Hz, 1H), 4.50 (dd, *J* = 3.0, 15.5 Hz, 1H), 4.54 (s, 1H), 4.55 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.61 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 5.4 (s, 1H), 7.26-7.38 (m, 18H), 7.41-7.46 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ : -4.8, -4.4, 18.3, 25.8, 55.3, 60.0, 67.3, 68.5, 68.7, 69.7, 72.7, 73.5, 73.6, 74.7, 75.2, 77.4, 78.48, 78.5, 79.2, 80.3, 98.3, 101.3, 101.8, 126.2, 127.3, 127.7, 127.8, 128.0, 128.1, 128.4, 128.5, 128.8, 137.5, 137.8, 138.3, 139.4. ESIHRMS Calcd for C₅₀H₆₂O₁₁Si $[M+Na]^+$: 889.3959. Found 889.395

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-tert-butyl-*dimethylsilyl*- β -D-mannopyranosyl) (1 $\rightarrow$ 4)- α -D-glucopyranoside (23 α).

$[\alpha]^{24}_{\text{D}} + 32.8$ (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.03 and 0.07 (2s, 6H), 0.8 (s, 9H), 3.4 (s, 3H), 3.52-3.54 (m, 1H), 3.58 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.66 (ddt, *J* = 1.5, 6.0, 12.5 Hz, 1H), 3.7-3.8 (m, 5H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.92 (dd, *J* = 9.0, 10.0 Hz, 1H), 3.94-3.98 (m, 2H), 4.09 (dd, *J* = 3.0, 9.7 Hz, 2H), 4.53 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 9.5 Hz, 1H), 4.64 (s, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 5.0 (ddd, *J* = 2.0, 3.5, 12.0 Hz, 1H), 5.05 (ddd, *J* = 2.0, 3.5, 17.0 Hz,

1H), 5.17 (d, $J = 12.0$ Hz, 1H), 5.24 (d, $J = 1.5$ Hz, 1H), 5.5 (s, 1H), 5.65-5.72 (m, 1H), 7.19-7.47 (m, 20H) ^{13}C NMR (125 MHz, CDCl_3) δ : -4.8, -4.4, 18.3, 25.8, 55.4, 65.2, 68.6, 69.0, 69.6, 70.3, 73.1, 73.3, 73.7, 75.0, 79.0, 80.0, 80.2, 81.7, 97.7, 101.7, 102.1, 116.6, 126.2, 126.7, 127.4, 127.6, 127.7, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.7, 135.0, 137.7, 137.8, 137.9, 138.7. ESIHRMS Calcd for $\text{C}_{50}\text{H}_{64}\text{O}_{11}\text{Si}$ $[\text{M}+\text{Na}]^+$: 891.4116. Found 891.4106.

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-tert-

butyldimethylsilyl- β -D-mannopyranosyl) (1 $\rightarrow$ 4)- α -D-glucopyranoside (23 β).

$[\alpha]_{\text{D}}^{24}$ - 22.2 (c , 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 0.005 and 0.05 (2s, 6H), 0.8 (s, 9H), 3.0-3.04 (m, 1H), 3.4 (s, 3H), 3.49 (d, $J = 2.5$ Hz, 1H), 3.42-3.55 (m, 3H), 3.66 (dd, $J = 1.5, 10.5$ Hz, 1H), 3.7-3.76 (m, 2H), 3.82 (t, $J = 9.5$ Hz, 1H), 3.89 (t, $J = 9.0$ Hz, 1H), 3.97 (t, $J = 9.5$ Hz, 1H), 4.05 (dd, $J = 5.0, 10.0$ Hz, 1H), 4.27 (d, $J = 6.0$ Hz, 2H), 4.45 (d, $J = 12.5$ Hz, 1H), 4.49 (s, 1H), 4.62 (d, $J = 3.5$ Hz, 1H), 4.65 (d, $J = 12.5$ Hz, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.77 (d, $J = 10.5$ Hz, 1H), 4.82 (d, $J = 12.5$ Hz, 1H), 5.08-5.12 (m, 2H), 5.25 (ddd, $J = 1.5, 3.5, 17.5$ Hz, 1H), 5.46 (s, 1H), 5.92-5.97 (m, 1H), 7.26-7.36 (m, 20H) ^{13}C NMR (125 MHz, CDCl_3) δ : -4.8, -4.4, 18.3, 25.8, 55.4, 67.3, 68.6, 68.63, 69.7, 72.7, 73.6, 73.7, 74.9, 75.3, 76.9, 78.7, 79.0, 79.8, 80.3, 98.4, 101.1, 101.7, 116.6, 126.2, 127.3, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 128.8, 135.7, 137.6, 137.7, 138.4, 139.4. ESIHRMS Calcd for $\text{C}_{50}\text{H}_{64}\text{O}_{11}\text{Si}$ $[\text{M}+\text{Na}]^+$: 891.4116. Found 891.4123.

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl- β -D-mannopyranoside (24). To a stirred solution of donor **11** (277 mg, 0.53 mmol), BSP (134 mg 0.64 mmol), TTBP (199 mg, 0.8 mmol), and 4 Å molecular sieves in CH_2Cl_2 (6 mL),

at -60 °C under an Ar atmosphere, was added Tf₂O (117.3 μL 0.69 mmol). After 30 min. of stirring at -60 °C, dry methanol (64 μL 1.59 mmol) was added. The reaction mixture was stirred for further 2 h. at -60 °C, and allowed to reach room temperature. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and molecular sieves were filtered off and washed with saturated NaHCO₃. The organic layer was separated, dried and concentrated. The crude was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 8:1) to give **24** (186 mg, 79%) as colorless oil. $[\alpha]^{24.5}_{\text{D}}$ - 38.5 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 2.4 (t, *J* = 2.4 Hz, 1H), 3.0-3.3 (m, 1H), 3.53 (s, 3H), 3.6 (dd, *J* = 3.2, 10.0 Hz, 1H), 3.8 (s, 3H), 3.9 (t, *J* = 10.3 Hz, 1H), 4.1 (t, *J* = 9.6 Hz, 1H), 4.3 (dd, *J* = 4.9, 10.5, 1H), 4.4 (s, 1H), 4.5 (dd, *J* = 2.4, 16.1 1H), 4.6 (dd, *J* = 2.4, 16.1 1H), 4.73 (d, *J* = 12.0 1H), 4.76 (d, *J* = 12.0 1H), 5.6 (s, 1H), 6.84-6.87 (m, 2H), 7.26-7.4 (m, 5H), 7.48-7.5 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 57.4, 59.9, 67.5, 68.6, 72.1, 74.8, 75.1, 78.4, 80.2, 101.4, 102.9, 113.7, 126.0, 128.2, 128.8, 129.5, 130.2, 137.5, 159.2. ESIHRMS Calcd for C₂₅H₂₈O₇ [M+Na]⁺: 463.1733. Found 463.1729.

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (25). To stirred solution of **24** (108 mg, 0.25 mmol) in CH₂Cl₂ (5 mL) and water (0.2 mL) was added DDQ (167 mg, 0.74 mmol) at room temp. After 3 h, sat. NaHCO₃ was added, and the mixture was extracted with CH₂Cl₂. The extract was washed several times with sat NaHCO₃, and dried over Na₂SO₄ and concentrated on a rotary evaporator. The crude was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 4:1) to give **25** (93 mg, 95%) as white solid MP 126 °C; $[\alpha]^{27}_{\text{D}}$ - 119.9 (*c*, 1.0, CHCl₃); ¹H NMR (500

MHz, CDCl₃) δ : 2.5 (t, J = 2.4 Hz, 1H), 3.31-0-3.36 (m, 1H), 3.5 (s, 3H), 3.76-3.83 (m, 2H), 3.87 (t, J = 10.3 Hz, 1H), 4.0 (dd, J = 0.5, 3.2 Hz, 1H), 4.3 (dd, J = 4.9, 10.5 Hz, 1H), 4.46 (dd, J = 2.4, 16.1 1H), 4.48 (s, 1H), 4.6 (dd, J = 2.4, 16.1 1H), 5.5 (s, 1H), 7.26-7.38 (m, 3H), 7.48-7.5 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ : 57.5, 60.6, 67.0, 68.4, 70.3, 75.5, 77.2, 79.1, 79.7, 102.0, 103.0, 126.3, 128.2, 129.1, 137.2. ESIHRMS Calcd for C₁₇H₂₀O₆ [M+H]⁺: 321.1338. Found 321.1347.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl)-1-thio- α -D-mannopyranoside **27 α and the β -anomer **27 β** .**

To a stirred solution of donor **26** (480 mg, 0.88 mmol), BSP (223 mg 1.06 mmol), TTBP (331 mg, 1.33 mmol), and 4 Å molecular sieves in CH₂Cl₂ (5 mL), at -60 °C under an Ar atmosphere, was added Tf₂O (195 μ L 1.15 mmol). After 30 min. the temperature was brought down to -78 °C, and then acceptor **12** (424 mg 1.06 mmol) in CH₂Cl₂ (3 mL), was slowly added. The reaction mixture was stirred for 2h. at -78 °C, and quenched by the addition of triethylphosphite (435 μ L, 2.7 mmol), and continued stirring for 1 h at -78 °C and allowed to reached room temperature. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and molecular sieves were filtered off and washed with saturated NaHCO₃. The organic layer was separated, dried and concentrated. The crude was purified by radial chromatography (hexane:ethyl acetate; 8:1) to give **27 α** and **27 β** in 5% and 83% yield respectively. **27 α** : [α]_D²⁴ + 76.4 (c , 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 2.4 (t, J = 2.4 Hz, 1H), 3.8 (t, J = 10.5 Hz, 1H), 3.92-3.96 (m, 2H), 3.99-3.-4.04 (m, 2H), 4.15 (t, J = 9.5 Hz, 1H), 4.2 (dd, J = 2.5, 16.1 Hz, 1H), 4.25-4.38 (m, 7H),

4.5 (d, $J = 12.4$ Hz, 1H), 4.62 (d, $J = 12.4$ Hz, 1H), 4.63 (d, $J = 12.2$ Hz, 1H), 4.7 (d, $J = 12.2$ Hz, 1H), 5.4 (d, $J = 1.2$ Hz, 1H), 5.57 (s, 1H), 5.59 (s, 1H), 5.67 (s, 1H), 7.15-7.52 (m, 25H); ^{13}C NMR (125 MHz, CDCl_3) δ : 58.3, 64.7, 65.1, 68.5, 68.8, 72.1, 72.7, 72.8, 75.3, 75.7, 78.5, 79.0, 79.2, 86.9, 99.6, 101.4, 101.9, 125.9, 126.1, 127.51, 127.57, 127.67, 127.85, 128.2, 128.4, 128.8, 129.2, 129.3, 131.6, 133.5, 137.3, 137.7, 138.5. ESIHRMS Calcd for $\text{C}_{49}\text{H}_{48}\text{O}_{10}\text{S}$ $[\text{M}+\text{Na}]^+$: 851.2866. Found 851.2874. **27 β** : $[\alpha]_{\text{D}}^{24} + 26.3$ (c, 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 2.23 (t, $J = 2.4$ Hz, 1H), 3.29-3.34 (m, 1H), 3.6 (dd, $J = 3.2, 9.7$ Hz, 1H), 3.86 (t, $J = 10.3$ Hz, 1H), 3.93 (t, $J = 10.3$ Hz, 1H), 4.0 (d, $J = 3.0$ Hz, 1H), 4.13 (t, $J = 9.7$ Hz, 1H), 4.25-4.40 (m, 8H), 4.65 (d, $J = 12.5$ Hz, 1H), 4.76 (d, $J = 12.5$ Hz, 1H), 4.84 (s, 1H), 4.86 (d, $J = 11.9$ Hz, 1H), 4.98 (d, $J = 11.8$ Hz, 1H), 5.58 (s, 1H), 5.62 (s, 1H), 5.64 (s, 1H), 7.24-7.49 (m, 25H); ^{13}C NMR (125 MHz, CDCl_3) δ : 57.5, 65.3, 67.8, 68.5, 68.6, 72.3, 73.4, 74.8, 75.6, 75.7, 76.5, 77.5, 77.6, 78.6, 79.0, 86.0, 98.9, 101.3, 101.9, 126.0, 126.2, 127.4, 127.6, 127.64, 127.8, 128.0, 128.1, 128.23, 128.25, 128.4, 128.8, 129.0, 129.2, 131.6, 133.6, 137.3, 137.6, 138.4, 138.7. ESIHRMS Calcd for $\text{C}_{49}\text{H}_{48}\text{O}_{10}\text{S}$ $[\text{M}+\text{Na}]^+$: 851.2866. Found 851.2875.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- α -D-mannopyranoside **28 α and the β -anomer **28 β** .** To a stirred solution of donor **27 β** (146 mg, 0.17 mmol), BSP (44 mg 0.21 mmol), TTBP (66 mg, 0.26 mmol), and 4 Å molecular sieves in CH_2Cl_2 (4 mL), at -60°C under an Ar atmosphere, was added TiF_4 (39 μL 0.23 mmol). After 30 min. of stirring at -60°C , acceptor **25** (67 mg, 0.21 mmol) in CH_2Cl_2 (3 mL), was added slowly. The reaction mixture was stirred for

further 2 h. at -60 °C, and allowed to reach room temperature. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and molecular sieves were filtered off and washed with saturated NaHCO₃. The organic layer was separated, dried and concentrated. The crude was purified by radial chromatography on silica gel (Hexane: Chloroform; 4:1) to give **28a** and **28b** in 13% and 67% yield, respectively. **28a**: [α]_D²⁴ - 58.3 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 1.6 (t, *J* = 2.3 Hz, 1H), 2.66 (t, *J* = 2.2 Hz, 1H), 3.27-3.32 (m, 1H), 3.36-3.41 (m, 1H), 3.56 (s, 3H), 3.57 (m, 1H), 3.8-3.93 (m, 4H), 3.96-4.09 (m, 4H), 4.14-4.20 (m, 5H), 4.28 (dd, *J* = 4.6, 10.2 Hz, 1H), 4.35 (dd, *J* = 4.9, 10.6 Hz, 1H), 4.45-4.58 (m, 4H), 4.63 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.73 (s, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.93 (d, *J* = 11.9 Hz, 1H), 5.3 (d, *J* = 1.4 Hz, 1H), 5.54 (s, 1H), 5.56 (s, 1H), 7.22-7.36 (m, 25H); ¹³C NMR (125 MHz, CDCl₃) δ : 57.7, 58.1, 60.0, 67.1, 67.6, 68.5, 68.8, 72.2, 73.1, 73.7, 74.1, 74.7, 75.0, 76.1, 76.3, 77.5, 77.7, 78.56, 78.6, 79.0, 80.4, 99.2, 99.7, 101.3, 101.7, 101.8, 103.3, 126.0, 126.1, 126.3, 127.3, 127.6, 127.7, 128.0, 128.1, 128.2, 128.29, 128.3, 128.8, 128.9, 129.2, 137.2, 137.5, 137.6, 138.4, 138.7. ESIHRMS Calcd for C₆₀H₆₂O₁₆ [M+Na]⁺: 1061.3936. Found 1061.3917. **28b**: [α]_D²⁴ - 151.3 (*c*, 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 1.9 (t, *J* = 2.3 Hz, 1H), 2.49 (t, *J* = 2.3 Hz, 1H), 3.36-3.40 (m, 3H), 3.54 (m, 1H), 3.56 (s, 3H), 3.87-4.12 (m, 9H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.26-4.93 (m, 3H), 4.36 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.47 (dd, *J* = 2.4, 16.5 Hz, 1H), 4.5 (s, 1H), 4.55 (dd, *J* = 2.3, 16.3 Hz, 1H), 4.65 (d, *J* = 12.7 Hz, 2H), 4.7 (d, *J* = 12.7 Hz, 2H), 4.8 (d, *J* = 11.9 Hz, 1H), 4.98 (s, 1H), 5.03 (d, *J* = 11.9 Hz, 1H) 5.07 (s, 1H), 5.55 (s, 1H), 5.60 (s, 1H), 7.26-7.46 (m, 25H); ¹³C NMR (125 MHz, CDCl₃) δ : 57.7, 59.3, 59.5, 67.5, 67.9, 67.95, 68.5, 71.9, 72.1, 72.3, 73.2, 73.7, 74.7, 74.8, 75.2, 76.2, 76.7, 78.5, 80.6, 97.4, 97.7, 101.3, 101.5, 101.7, 103.5, 125.99, 126.0, 126.2, 127.3,

127.6, 127.7, 128.0, 128.2, 128.3, 128.4, 128.8, 128.9, 128.95, 137.2, 137.5, 138.3, 138.8.

ESIHRMS Calcd for $C_{60}H_{62}O_{16}$ $[M+Na]^+$: 1061.3936. Found 1061.3939.

General procedure for deprotection of propargyl ethers

To a stirred solution of propargyl ether (1 mmol) in dry THF (5 mL) was added KO^tBu (1.1 mmol), stirring was continued at room temperature for 3-12 h until TLC indicated completion. The reaction mixture was diluted with CH_2Cl_2 (10 mL). The organic phase was separated, washed with water, dried (Na_2SO_4) and concentrated on a rotary evaporator to give the allenyl ethers in quantitative yields. A homogeneous solution of allenyl ethers (1 mmol) in acetone: water (4:1, 5 mL) was treated with OsO_4 (0.1 mmol) and *N*-methyl morpholine *N*-oxide (2 mmol) and the mixture was stirred for 3 h at room temperature. After completion of the reaction, acetone was removed under vacuum and the residue was dissolved in CH_2Cl_2 (10 mL) and washed with sat. $NaHSO_3$. The organic phase was separated, dried (Na_2SO_4), and concentrated on a rotary evaporator. The residues were purified by flash or radial chromatography on silica gel to yield **16**, **19**, **22** and **28** in 80-91%

3 β -Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (16). Following the general procedure compound **15 β** was isomerized to corresponding allene after stirring 3 h at room temperature. $[\alpha]_D^{27} - 18.9$ (*c*, 1.0, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ : 0.07 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.86-1.7 (m, 36H), 1.78-1.8 (m, 1H), 1.86-1.9 (m, 1H), 1.93-1.98 (m, 1H), 3.32-3.35 (m, 1H), 3.62-3.68 (m, 1H), 3.84-3.88 (m, 3H), 3.92 (d, *J* = 1.4 Hz, 1H), 4.31 (dd, *J* = 4.9, 10.5

Hz, 1H), 4.7 (s, 1H), 5.53 (s, 1H) 7.33-7.38 (m, 3H), 7.46-7.48 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: -5.0, -4.3, 12.06, 12.2, 18.1, 18.7, 21.2, 22.6, 22.3, 23.3, 24.2, 25.7, 25.8, 28.0, 28.2, 28.9, 29.1, 32.1, 34.1, 35.4, 35.6, 35.8, 36.2, 37.0, 39.5, 40.0, 42.6, 44.7, 54.4, 56.2, 56.5, 66.7, 68.6, 72.2, 72.6, 77.8, 78.6, 97.4, 97.9, 101.7, 126.0, 128.1, 128.8, 137.4. EIHMS Calcd for C₄₆H₇₆O₆Si [M]⁺: 751.5333. Found 751.5311.

Methyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (19).

Following the general procedure compound **18β** was isomerized to corresponding allene after stirring 3 h at room temperature [α]_D²⁴ - 68.8 (*c*, 10, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.07 and 0.1 (2s, 6H), 0.9 (s, 9H), 1.32 (d, *J* = 5.7 Hz, 3H), 1.36 (s, 3H), 1.54 (s, 3H), 2.6 (bs, 1H), 3.31-3.35 (m, 1H), 3.37 (s, 1H), 3.69-3.71 (m, 2H), 3.84-3.91 (m, 3H), 4.0 (d, *J* = 3.1 Hz, 1H), 4.1 (d, *J* = 5.5 Hz, 1H), 4.22-4.25 (m, 1H), 4.29 (dd, *J* = 4.9, 10.4 Hz, 1H), 4.86 (s, 1H), 5.1 (s, 1H), 5.5 (s, 1H), 7.34-7.38 (m, 3H), 7.48-7.49 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ: -5.0, -4.3, 17.5, 18.1, 25.7, 26.4, 27.8, 54.8, 63.9, 66.8, 68.6, 71.9, 72.0, 76.2, 77.9, 78.4, 78.9, 97.8, 98.7, 101.7, 109.4, 126.0, 128.1, 128.8, 137.4. ESIHMS Calcd for C₂₉H₄₆O₁₀Si[M+Na]⁺: 605.2758. Found 605.2759.

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl) (1→4)-α-D-glucopyranoside (22).

Following the general procedure compound **21β** was isomerized to corresponding allene after stirring 12 h at room temperature [α]_D²⁵ - 10.6 (*c*, 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ : 0.03 and 0.05 (2s, 6H), 0.8 (s, 9H), 2.6 (bs, 1H), 3.04-3.09 (m, 1H), 3.37, (s,

3H), 3.35 (dd, $J = 3.7, 9.5$ Hz, 1H), 3.57 (t, $J = 10.3$ Hz, 1H), 3.59 (dd, $J = 3.4, 9.3$ Hz, 1H), 3.64 (dd, $J = 1.2, 10.9$ Hz, 1H), 3.74 (t, $J = 9.3$ Hz, 1H), 3.76-3.79 (m, 3H), 3.97 (m, 2H), 4.09 (dd, $J = 4.9, 10.4$ Hz, 1H), 4.45 (d, $J = 12.1$ Hz, 1H), 4.59 (d, $J = 1.0$ Hz, 1H), 4.60 (d, $J = 11.8$ Hz, 1H), 4.65 (d, $J = 12.3$ Hz, 1H), 4.7 (d, $J = 12.1$ Hz, 1H), 4.80 (d, $J = 12.2$ Hz, 1H), 4.85 (d, $J = 10.6$ Hz, 1H), 5.0 (d, $J = 10.6$ Hz, 1H), 5.4 (s, 1H), 7.26-7.40 (m, 20H), ^{13}C NMR (125 MHz, CDCl_3) δ : -5.0, -4.3, 18.1, 25.7, 55.2, 66.6, 68.3, 68.6, 69.6, 71.7, 71.9, 73.6, 75.4, 78.5, 79.2, 80.4, 98.3, 100.5, 101.7, 126.1, 127.4, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 128.5, 128.9, 137.4, 137.7, 138.3, 139.3 ESIHRMS Calcd for $\text{C}_{47}\text{H}_{60}\text{O}_{11}\text{Si}$ $[\text{M}+\text{Na}]^+$: 851.3803. Found 851.3799.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranoside (29).

$[\alpha]_{\text{D}}^{24}$ - 106.7 (c , 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ : 2.6 (bs, 1H), 3.17-3.20 (m, 1H), 3.21 (bs, 1H), 3.40-3.44 (m, 2H), 3.55 (dd, $J = 3.0, 9.7$ Hz, 1H), 3.6 (s, 3H), 3.81 (t, $J = 10.3$ Hz, 1H), 3.86 (t, $J = 10.4$ Hz, 1H), 3.88 (t, $J = 10.3$ Hz, 1H), 3.97 (d, $J = 3.1$ Hz, 1H), 4.07-4.13 (m, 3H), 4.16-4.28 (m, 6H), 4.36 (dd, $J = 4.9, 10.6$ Hz, 1H), 4.51 (s, 1H), 4.62 (d, $J = 12.6$ Hz, 1H), 4.68 (d, $J = 13.2$ Hz, 2H), 4.8 (d, $J = 12.0$ Hz, 1H), 4.88 (s, 1H), 5.0 (d, $J = 12.0$ Hz, 1H), 5.47 (s, 1H), 5.53 (s, 1H), 5.57 (s, 1H), 7.20-7.49 (m, 25H); ^{13}C NMR (125 MHz, CDCl_3) δ : 57.3, 66.9, 67.2, 67.7, 67.9, 68.5, 68.57, 68.6, 69.1, 72.0, 74.0, 74.3, 74.7, 75.8, 76.7, 77.5, 78.4, 96.8, 98.4, 101.0, 101.4, 101.6, 101.9, 126.0, 126.1, 127.4, 127.5, 127.6, 128.1, 128.2, 128.3, 128.8, 128.9, 129.3, 136.9, 137.2,

137.6, 138.4, 138.7. ESIHRMS Calcd for $\text{C}_{60}\text{H}_{62}\text{O}_{16}$ $[\text{M}+\text{Na}]^+$: 985.3623. Found 985.3618.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-p-methoxybenzyl-1-thio- α -D-mannopyranoside (8).

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-p-methoxybenzyl-1-thio- α -D-mannopyranoside (8).

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio- α -D-mannopyranoside (9).

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio- α -D-mannopyranoside (9).

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (10).

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (10).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-p-methoxybenzyl-1-thio- α -D-mannopyranoside (11).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-p-methoxybenzyl-1-thio- α -D-mannopyranoside (11).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl) -1-thio- α -D-mannopyranoside (12)

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl) -1-thio- α -D-mannopyranoside (12)

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (13).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-mannopyranoside (13).

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D –mannopyranoside (15a).

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (15a).

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (15 β).

3 β -Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (15 β).

3 β -Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (16).

3 β -Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranoside (16).

Methyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3-*O*-isopropylidene- α -L-rhamanopyranoside (18 β).

Methyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3-*O*-isopropylidene- α -L-rhamanopyranoside (18 β).

Methyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3-*O*-isopropylidene- α -L-rhamanopyranoside (19).

Methyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-1 $\rightarrow$ 4)-2,3-*O*-isopropylidene- α -L-rhamanopyranoside (19).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl](1 $\rightarrow$ 4)- α -D-glucopyranoside (21a).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (21a).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (21 β).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (21 β).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (22).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (22).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23a).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23a).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23 β).

Methyl-2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23 β).

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (24).

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (24).

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranoside (25).

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranoside (25).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (**27a**).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (27a).

Phenyl 4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (27 β).

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl)-1-thio- α -D-mannopyranoside (27 β).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- α -D-mannopyranoside (28a).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- α -D-mannopyranoside (28a).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranoside (28 β).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)- β -D-mannopyranoside (28 β).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranoside (29).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-*O*-benzylidene- β -D-mannopyranoside (29).