Supporting Information

Radical Halogenation-Mediated Latent-Active Glycosylations of Allyl Glycosides

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Table of Content

1.	Experimental details and characterization data of new compounds	S3
2.	¹ H NMR spectrum of 2	S14
3.	¹³ C NMR spectrum of 2	S14
4.	¹ H NMR spectrum of 20	S15
5.	¹³ C NMR spectrum of 20	S15
6.	¹ H NMR spectrum of 21	S16
7.	¹³ C NMR spectrum of 21	S16
8.	¹ H NMR spectrum of 22	S17
9.	¹³ C NMR spectrum of 22	S17
10.	¹ H NMR spectrum of 27	S18
11	¹³ C NMR spectrum of 27	S18
12.	¹ H NMR spectrum of 30	S19
13.	¹³ C NMR spectrum of 30	S19
14.	¹ H NMR spectrum of 31	S20

15.	¹³ C NMR spectrum of 31	S20
16.	¹ H NMR spectrum of 32	S21
17.	¹³ C NMR spectrum of 32	S21
18.	¹ H NMR spectrum of 33	S22
19.	¹³ C NMR spectrum of 33	S22
20.	¹ H NMR spectrum of 34	S23
21.	¹³ C NMR spectrum of 34	S23
22.	¹ H NMR spectrum of 35	S24
23.	¹³ C NMR spectrum of 35	S24
24.	¹ H NMR spectrum of 36	S25
25.	¹³ C NMR spectrum of 36	S25
26.	¹ H NMR spectrum of 37	S26
27.	¹³ C NMR spectrum of 37	S26
28.	¹ H NMR spectrum of 39	S27
29.	¹³ C NMR spectrum of 39	S27
30.	¹ H NMR spectrum of 40	S28
31.	¹³ C NMR spectrum of 40	S28
32.	¹ H NMR spectrum of 41	S29
33.	¹³ C NMR spectrum of 41	S29

34. GC-MS spectrum of the glycosylation reaction mixture showing the prese S30 acrolein (m/z 66, along with succinimide (m/z 99)).

Synthesis and Characterization:

General methods: Chemicals were purchased from commercial sources and used without further purification. *N*-Bromosuccinimide (NBS) was recrystallized in water. Solvents were dried and distilled according to literature procedures. Analytical TLC was performed on commercial Merck plates coated with silica gel 60 F_{254} . Silica gel (100-200 mesh) was used for column chromatography. Compound detection was performed either by exposure to UV light (253 nm) or by soaking in a solution of 10% H₂SO₄ in ethanol, followed by heating. ¹H and ¹³C NMR spectral analyses were performed on 400 and 100 MHz spectrometers, respectively. Chemical shifts in ¹H NMR spectra are expressed in ppm (δ) relative to the signal of Me₄Si. The following abbreviations are used to explain the multiplicities: s, singlet; app. s, apparent singlet; d, doublet; app. d, apparent doublet; t, triplet; app. t, apparent triplet; q, quartet; m, multiplet; br, broad. Coupling constant (*J*) are given in Hertz (Hz). Commercial molecular sieves were dried at 300 °C under high vacuum. High resolution mass spectrometeric analysis was performed on an electrospray ionization mass spectrometer.

Preparation of donors: Donors 1, 4, 7-9, were synthesized by a two-step procedure: (i) allylation of free sugars with allyl alcohol/AcCl under reflux to secure anomeric *O*-allyl glycosides and (ii) protection of remaining free hydroxyl groups with either Ac_2O or Bz_2O to afford the required glycosyl donors.

Characterization of the following compounds match with that reported in literature: 1, 7-9,¹ 3,² 4, 5, 12 and 24,³ 6 and 23,⁴ 11,⁵ 13 and 29,⁶ 14,⁷ 15,⁸ 16,⁹ 17,¹⁰ 18 and 38,¹¹ 19,¹² 25 and 26,¹³ 28,¹⁴ and methyl 2,3,4-*tri*-O-acetyl- β -L-fucoside.¹⁵

General procedure for glycosylation: A solution of allyl glycoside (1 molar equiv.) in CCl₄ (minimum volume to solubilize the glycosyl donor) was added to a suspension of *N*-bromosuccinimide (NBS) (0.9 molar equiv.), MS 4Å (twice the amount of glycosyl donor by weight) in CCl₄ (30 mL/mmol of glycosyl donor) and the reaction mixture protected from exposure to light. The suspension was degassed under Ar atmosphere for ~5 min., azo-bis-isobutyronitrile (AIBN) (cat.) was added, degassed again for ~5 min., refluxed for 30 min., cooled and the solvent removed *in vacuo* at room temperature without exposure of the reaction mixture (~5 mL), the suspension cooled to -40 °C, trifluoromethanesulfonic acid (TfOH) (0.1 molar equiv.) was

added and stirred for ~10 min. A solution of glycosyl or aglycosyl acceptor (0.70 molar equiv.) in CH_2Cl_2 (minimum volume to solubilize the acceptor) was added, reaction mixture stirred and allowed slowly to rise to 0 °C by ~2 h. The reaction mixture was neutralized with Et_3N (~1 mL), filtered through celite, washed with CHCl₃, combined filtrate washed with saturated aq. Na₂S₂O₃ solution, aq. NaHCO₃ solution and brine, dried (Na₂SO₄), concentrated *in vacuo* and purified by column chromatography (SiO₂) (eluent: hexanes/EtOAc or PhMe/EtOAc linear gradient) to afford the required glycoside product.

Procedure for the synthesis of allyl 2,3,4,6-*tetra-O*-benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,4-tri-O-benzoyl-a-D-mannopyranoside (31): A solution of glycosyl donor 7 (1.0 g, 1.57 mmol) in CCl₄ (minimum volume to solubilize the glycosyl donor) was added to a suspension of *N*-bromosuccinimide (NBS) (0.18 g, 1.41 mmol), MS 4Å (twice the amount of glycosyl donor by weight) in CCl₄ (100 mL) and the reaction mixture protected from exposure to light. The suspension was degassed under Ar atmosphere for ~15 min., AIBN (cat.) was added, degassed again for ~15 min., refluxed for 45 min., cooled and the solvent removed in vacuo at room temperature without exposure of the reaction mixture to light or moisture. Freshly distilled CH₂Cl₂ (~50 mL) was added to the reaction mixture, the suspension cooled to -40 °C, TfOH (13.8 µL, 0.157 mmol) was added and stirred for ~15 min. A solution of glycosyl acceptor 14 (0.76 g, 1.43 mmol) in CH₂Cl₂ (minimum volume to solubilize the acceptor) was added, reaction mixture stirred and allowed to rise to 0 °C by ~3 h. The reaction mixture was neutralized with Et₃N, filtered through celite, washed with CHCl₃, combined filtrate washed with saturated aq. Na₂S₂O₃ solution, aq. NaHCO₃ solution and brine, dried (Na₂SO₄), concentrated *in vacuo* and purified by column chromatography (SiO₂) (hexanes/EtOAc linear gradient) to afford the glycoside product 31, in 80 % yield.

1-Methoxy prop-2-enyl 2,3,4,6-*tetra-O*-acetyl-*a*-D-glucopyranoside (2): A solution of allyl*tetra-O*-acetyl-*a*-D-glucopyranoside (1) (0.250 g, 0.64 mmol) in CCl₄ (5 mL) was added to a suspension of NBS (0.140 g, 0.77 mmol), molecular sieves 4Å (0.50 g) in CCl₄ (30 mL) and the reaction mixture was protected from exposure to light. The suspension was degassed under Ar atmosphere for ~3 min., AIBN (10 mg) was added, degassed again for ~5 min. and refluxed for 30 min. The reaction mixture was cooled to 0 °C, added with either AgClO₄ (0.16 g, 0.77 mmol) or AgCO₃ (0.21 g, 0.77 mmol), MeOH (2 mL), stirred at room temperature for ~1 h, neutralized with Et₃N (~1 mL), filtered through celite, washed with CHCl₃, combined filtrate washed with saturated aq. Na₂S₂O₃ solution, aq. NaHCO₃ solution, brine, dried (Na₂SO₄), concentrated *in vacuo* and purified by column chromatography (SiO₂) (hexanes/EtOAc = 3:1), to afford **2**, as a foamy solid (0.24 g, 90%) and as an enantiomeric mixture (55%:45%). R_f = 0.2 (hexanes/EtOAc = 3:1); ¹H NMR (400 MHz, CDCl₃): δ 5.91-5.81 (m, 1.68 H), 5.55 - 5.51 (m, 1.61 H), 5.49 (broad, 0.91 H), 5.44 - 5.43 (m, 0.95 H), 5.39 - 5.38 (m, 1.84 H), 5.35 - 5.27 (m, 2.25 H), 5.10 - 5.05 (m, 3.18 H), 4.97 - 4.89 (m, 3.17 H), 4.26 - 4.18 (m, 3.34 H), 4.08 - 4.05 (m, 3.10 H), 3.44 (s, 3.00 H), 3.31 (s, 2.74 H), 2.08 - 2.02 (24.40 H) ;¹³C NMR (100 MHz, CDCl₃): δ 170.5, 170.4, 170.0, 169.8, 169.7, 169.5, 169.4, 134.1, 133.7, 119.2, 118.7, 103.6, 101.3, 100.3, 92.2, 91.5, 70.4, 70.3, 70.0, 69.9, 68.4, 68.3, 67.7, 67.6, 61.8, 61.7, 55.0, 52.3, 20.5, 50.4; HRMS (ESI) *m/z*: C₁₈H₂₆O₁₁ calcd. for [M+Na]⁺ 441.1373, found [M+Na]⁺ 441.1372.

Methyl 2,3,4,6-*tetra-O*-benzoyl-β-D-galactopyranosyl-(1→2)-3,4,6-*tri-O*-benzyl-α-D-mannopyranoside (20): Reaction of glycosyl donor 7 (0.150 g, 0.24 mmol) and glycosyl acceptor 11 (0.100 g, 0.22 mmol) was followed as given in the general procedure to afford 20, as a foamy solid. Yield = 82%; R_f = 0.5 (hexanes/EtOAc = 3:1); $[\alpha]_D^{24}$ = +12.78 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.65-7.14 (m, 27H), 6.00 (d, *J* = 3.4 Hz, 1H), 5.88 (dd, *J* = 8.2, 10.4 Hz, 1H), 5.59 (dd, *J* = 3.4, 10.4 Hz, 1H), 4.98 (d, *J* = 8.2 Hz, 1H), 4.81-4.78 (m, 2H), 4.71 (d, *J* = 1.2 Hz, 1H), 4.66-4.61 (m, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.46-4.40 (m, 2H), 4.32-4.22 (m, 4H), 3.91-3.88 (m, 1H), 3.70-3.63 (m, 2H), 3.57 (d, *J* = 10.4 Hz, 1H), 3.32 (dd, *J* = 5.2, 10.4 Hz, 1H), 3.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 165.7, 165.6, 165.0, 138.6, 138.5, 138.4, 133.6, 133.3, 133.2, 132.9, 130.1, 129.8, 129.7, 129.1, 128.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.5, 127.3, 100.7, 98.3, 78.3, 77.2, 74.9, 74.8, 74.7, 73.1, 71.9, 71.8, 71.7, 71.3, 69.9, 69.8, 68.2, 62.2, 54.8; HRMS (ESI) *m*/*z*: C₆₂H₅₈O₁₅ calcd. for [M+Na]⁺ 1065.3673, found [M+Na]⁺ 1065.3679.

Methyl 2,3,4,6-*tetra-O*-benzoyl- β -D-glucopyranosyl- $(1\rightarrow 2)$ -3,4,6-*tri-O*-benzyl- α -D-manno-

pyranoside (21): Reaction of glycosyl donor **4** (0.150 g, 0.24 mmol) and glycosyl acceptor **11** (0.100 g, 0.22 mmol) was followed as given in the general procedure to afford **21**, as a foamy solid. Yield = 79%; R_f = 0.25 (hexanes/EtOAc = 3:1); $[\alpha]_D^{22}$ = -3.20 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.99-7.84 (m, 8H), 7.49-7.13 (m, 27H), 5.95 (app. t, *J* = 9.6 Hz, 1H), 5.76-

5.66 (m, 2H), 5.05 (d, J = 8.0 Hz, 1H), 4.81-4.77 (m, 2H), 4.69-4.66 (m, 2H), 4.54-4.51 (m, 2H), 4.39 (d, J = 11.2 Hz, 1H), 4.28-4.17 (m, 4H), 3.89-3.87 (m, 1H), 3.66-3.65 (m, 2H), 3.55 (app. d, J = 10.4 Hz, 1H), 3.30 (dd, J = 5.6, 10.4 Hz, 1H), 3.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 165.7, 165.1, 164.8, 138.4, 138.2, 138.1, 133.3, 133.1, 133.0, 132.9, 129.7, 129.6, 129.4, 129.3, 128.6, 128.3, 128.2, 128.0, 127.4, 127.3, 127.2, 100.1, 98.0, 77.8, 77.3, 76.7, 74.4, 72.9, 72.8, 72.3, 71.8, 71.7, 71.0, 69.7, 69.6, 63.2, 54.6; HRMS (ESI) *m/z*: C₆₂H₅₈O₁₅ calcd. for [M+Na]⁺ 1065.3673, found [M+Na]⁺ 1065.3671.

Methyl 2,3,4,6-*tetra*-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-*tri*-*O*-benzyl-α-D-mannopyranoside (22): Reaction of glycosyl donor 9 (0.150 g, 0.24 mmol) and glycosyl acceptor 11 (0.10 g, 0.22 mmol) was followed as given in the general procedure to afford 22, as a foamy solid. Yield = 85%; R_f = 0.2 (hexanes/EtOAc = 3:1); $[α]_D^{22} = -30.49$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.59-7.08 (m, 27H), 6.10 (app. t, *J* = 10.0 Hz, 1H), 6.02-5.97 (m, 2H), 5.30 (app. s, 1H), 4.91 (app. d *J* = 12.0 Hz, 2H), 4.76-4.59 (m, 7H), 4.49 (dd, *J* = 4.8, 12.0 Hz, 1H), 4.11-3.96 (m, 3H), 3.83-3.78 (m, 3H), 3.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 165.4, 165.2, 164.9, 138.3, 138.2, 138.0, 133.9, 133.3, 132.9, 129.8, 129.7, 129.6, 129.3, 129.1, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.4, 99.5, 99.4, 79.6, 76.1, 75.1, 74.6, 73.2, 72.3, 71.5, 70.1, 69.9, 69.2, 69.0, 66.9, 62.9, 54.6; HRMS (ESI) *m/z*: C₆₂H₅₈O₁₅ calcd. for [M+Na]⁺ 1065.3673, found [M+Na]⁺ 1065.3671.

Methyl 2,3,4-*tri-O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl-(1→6)-2,3,4*tri-O*-benzyl-α-D-glucopyranoside (27): Reaction of glycosyl donor 10 (0.10 g, 0.13 mmol) and acceptor 5 (0.050 g, 0.11 mmol) was followed as given in the general procedure to afford 27, as a foamy solid; Yield = 65%; R_f = 0.5 (hexanes/EtOAc = 3:1); $[α]_D^{22} = -9.58$ (*c* 2.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): 8.06 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 4H), 7.64 (d, *J* = 8 Hz, 2H), 7.55-7.46 (m, 4H), 7.40-7.14 (m, 26H), 7.10-7.06 (m, 2H), 6.07 (app t, *J* = 10.0 Hz, 1H), 5.75 (dd, *J* = 3.2, 10.0 Hz, 1H), 5.67 (br, 1H), 5.11 (br, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 2H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.05 (dd, *J* = 2.4, 9.6 Hz, 1H), 3.98 (ap t, *J* = 9.2 Hz, 1H), 3.85 (dd, *J* = 4.4, 10.4 Hz, 1H), 3.79 (dd, *J* = 4.8, 9.6 Hz, 1H), 3.73-3.66 (m, 3H), 3.57 (dd, *J* = 3.6, 9.6 Hz, 1H), 3.51 (app t, = 9.2 Hz, 1H), 3.39 (s, 3H), 1.21 (s, 9H).¹³C NMR (100 MHz, CDCl₃): δ 165.5, 165.4, 165.2, 138.7, 138.2, 138.1, 135.7, 135.5, 133.3, 133.1, 133.0, 132.9, 129.9, 129.7, 129.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.6, 127.5, 97.9, 97.8, 82.1, 80.2, 77.7, 77.2, 75.7, 74.9, 73.5, 71.4, 70.6, 70.5, 69.9, 66.5, 66.3, 62.4, 55.2, 29.6, 26.6, 19.2. HRMS (ESI) *m/z*: C₇₁H₇₂O₁₄Si calcd for [M+Na]⁺ 1199.4589, found [M+Na]⁺ 1199.4586.

Allyl 2,3,4,6-*tetra-O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-*tri-O*-benzoyl-α-D-mannopyranoside (30): Reaction of glycosyl donor 4 (0.132 g, 0.21 mmol) and glycosyl acceptor 14 (0.10 g, 0.18 mmol) was followed as given in the general procedure to afford 30, as a foamy solid. Yield = 79%; $R_f = 0.3$ (hexanes/EtOAc= 3:1); $[\alpha]_D^{22} = -28.44$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.09-7.77 (m, 14H), 7.58-7.12 (m, 21H), 5.95 (app. t, *J* = 9.8 Hz, 1H), 5.87 (dd, *J* = 3.2, 9.8 Hz, 1H), 5.79-5.60 (m, 5H), 5.26 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.18-5.15 (m, 1H), 5.01 (d, *J* = 7.6 Hz, 1H), 4.84 (s, 1H), 4.63 (dd, *J* = 2.8, 12.0 Hz, 1H), 4.46 (dd, *J* = 4.8, 12.0 Hz, 1H), 4.34 (app. t, *J* = 8.8 Hz, 1H), 4.22-4.17 (m, 2H), 4.06-4.02 (m, 1H), 3.9-3.88 (m, 1H), 3.72-3.67 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 165.7, 165.5, 165.3, 165.1, 165.0, 133.4, 133.3, 133.1, 133.0, 132.9, 132.8, 132.7, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 117.7, 101.7, 96.0, 72.7, 72.1, 71.7, 70.4, 69.8, 69.7, 69.5, 67.9, 67.2, 62.9; HRMS (ESI) *m/z*: C₆₄H₅₄O₁₈ calcd. for [M+Na]⁺ 1133.3208.

Allyl 2,3,4,6-*tetra-O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-*tri-O*-benzoyl-α-D-mannopyranoside (31): Reaction of glycosyl donor 7 (0.132 g, 0.21 mmol) and glycosyl acceptor 14 (0.10 g, 0.18 mmol) was followed as given in the general procedure to afford 31, as a foamy solid. Yield = 90%; $R_f = 0.3$ (hexanes/EtOAc = 3:1); $[\alpha]_D^{22} = -2.87$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, J = 8.0 Hz, 4H), 8.00 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 4H), 7.64-7.22 (m, 21H), 5.99 (d, J = 4.0 Hz, 1H), 5.88-5.82 (m, 2H), 5.81-5.71 (m, 1H), 5.67 (app. t, J = 10.4 Hz, 1H), 5.62 (dd, J = 7.6, 10.4 Hz, 1H), 5.60-5.59 (m, 1H), 5.26 (dd, J = 1.2, 17.6 Hz, 1H), 5.19-5.16 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.77 (m, 1H), 4.61 (dd, J = 6.4, 11.0 Hz, 1H), 4.42-4.30 (m, 3H), 4.24-4.21 (m, 1H),4.03 (dd, J = 5.2, 12.8 Hz, 1H), 3.86 (dd, J = 8.4, 11.0 Hz, 1H), 3.62 (dd, J = 5.6, 12.8, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 165.7, 165.5, 165.4, 165.3, 133.5, 132.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.6, 128.5, 128.4, 128.2, 117.7, 102.3, 96.2, 77.2, 71.6, 71.3, 70.5, 70.0, 69.89, 69.8, 69.7, 68.0, 67.9, 67.4, 61.7; HRMS (ESI) *m/z*: C₆₄H₅₄O₁₈ calcd. for [M+Na]⁺ 1133.3208, found [M+Na]⁺ 1133.3208.

This reaction was conducted in one gram scale of the glycosyl donor 7 by following the general glycosylation protocol and product **31** was obtained in 80% isolated yield.

Allyl 2,3,4,6-*tetra*-O-benzoyl-a-D-mannopyranosyl-(1 \rightarrow 6)-2,3,4-*tri*-O-benzoyl-a-D-mannopyranoside (32): Reaction of glycosyl donor 9 (0.132 g, 0.21 mmol) and acceptor 14 (0.10 g, 0.18 mmol) was followed as given in the general procedure to afford 32, as a foamy solid. Yield = 86 %; R_f = 0.34 (hexanes/EtOAc = 3:1); $[\alpha]_D^{24} = -196.18$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 8.0 Hz, 2H), 8.07-8.04 (m, 8H), 7.91-7.90 (m, 4H), 7.59-7.27 (m, 21H), 6.21-6.02 (m, 5H), 5.87-5.84 (app. d, *J* = 4 Hz, 2H), 5.54 (d, *J* = 8.0 Hz, 1H), 5.38 (d, *J* = 6.0 Hz, 1H), 5.23 (app. d, *J* = 8.0 Hz, 2H), 4.57 (d, *J* = 8.0 Hz, 1H), 4.50-4.48 (m, 3H), 4.37 (dd, *J* = 4.0, 12.0 Hz, 1H), 4.30 (dd, *J* = 8.0, 12.0 Hz, 1H), 4.20 (dd, *J* = 8.0, 12.0 Hz, 1H), 3.87-3.84 (app. d, *J* = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 165.7, 165.6, 165.5, 165.3, 165.2, 133.5, 133.2, 130.0, 129.9, 129.8, 129.7, 129.3, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 118.6, 97.8, 96.9, 70.6,70.3, 70.1, 69.7, 68.9, 67.0, 66.7, 62.6; HRMS (ESI) *m/z*: C₆₄H₅₄O₁₈ calcd. for [M+Na]⁺ 1133.3208, found [M+Na]⁺ 1133.3214.

Allyl 2,3,4,6-*tetra-O*-benzoyl- β -D-galactopyranosyl- $(1 \rightarrow 6)$ -2,3,4-*tri-O*-benzyl- α -D-manno-

pyranoside (33): Reaction of glycosyl donor **7** (0.142 g, 0.22 mmol) and glycosyl acceptor **15** (0.10 g, 0.20 mmol) was followed as given in the general procedure to afford **33**, as a foamy solid. Yield = 85%; R_f = 0.25 (hexanes/EtOAc = 3:1); [α]_D²² = +23.16 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.0 Hz, 4H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.36-7.20 (m, 27H), 5.90-5.77 (m, 2H), 5.54 (d, *J* = 4.0 Hz, 1H), 5.44 (app. s, 1H),5.38 (app. s, 1H), 5.20 (app. dd, *J* = 4.0, 16.0 Hz, 1H), 5.13-5.11 (m, 1H), 4.93-4.88 (m, 2H), 4.85 (app.dd, *J* = 4.0, 8.0 Hz, 1H), 4.73-4.60 (m, 7H), 4.15 (dd, *J* = 4.0, 12.0 Hz, 1H), 4.09 (app. t, *J* = 12.0 Hz, 1H), 4.02-3.94 (m, 4H), 3.85 (m, 1H), 3.78 (dd, *J* = 4.0, 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 165.8, 165.7, 165.3, 138.5, 138.4, 138.0, 133.7, 133.3, 133.2, 133.1, 132.9, 130.1, 130.0, 129.8, 129.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 117.2, 105.7,

97.4, 81.9, 81.1, 80.4, 77.5, 77.2, 75.2, 74.9, 74.8, 73.1, 72.3, 71.7, 70.3, 67.9, 67.0, 64.4; HRMS (ESI) *m/z*: C₆₄H₆₀O₁₅ calcd. for [M+Na]⁺ 1091.3830, found [M+Na]⁺ 1091.3838.

Allyl 2,3,4,6-*tetra-O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-*tri-O*-benzyl-α-D-manno-

pyranoside (34): Reaction of glycosyl donor **9** (0.142 g, 0.22 mmol) and glycosyl acceptor **16** (0.10 g, 0.20 mmol) was followed as given in the general procedure to afford **34**, as a foamy solid. Yield = 86%; R_f = 0.5 (hexanes/EtOAc =3:1); $[\alpha]_D^{22}$ = -20.66 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H), 7.93 (d, *J* = 8 Hz, 2H), 7.85 (d, *J* = 8 Hz, 2H), 7.61-7.08 (m, 27H), 6.09 (app. t, *J*= 10.0 Hz, 1H), 5.99-5.93 (m, 2H), 5.89-5.79 (m, 1H), 5.28 (br, 1H), 5.23 (dd, *J* = 1.2, 17.6 Hz, 1H), 5.16 (dd, *J* = 1.2, 10.4 Hz, 1H), 5.04 (d, *J* = 4.0 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.76-4.57 (m, 7H), 4.46 (dd, *J* = 4.4, 12.4 Hz, 1H), 4.18-3.98 (m, 4H), 3.92-3.76 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 165.5, 165.3, 165.0, 138.3, 138.2, 138.1, 133.6, 133.3, 133.0, 129.8, 129.7, 129.4, 129.2, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.5, 127.4, 117.4, 99.4, 97.9, 79.6, 77.2, 76.3, 75.3, 74.8, 73.2, 72.5, 71.8, 70.3, 70.0, 69.3, 69.1, 67.9, 66.9, 62.9; HRMS (ESI) *m/z*: C₆₄H₆₀O₁₅ calcd. for [M+Na]⁺ 1091.3830, found [M+Na]⁺ 1091.3832.

Allyl 2,3,4,6-*tetra-O*-benzoyl- α -D-mannopyranosyl- $(1\rightarrow 3)$ -2-*O*-benzoyl-4,6-*O*-benzylidine- α -D-galactopyranoside (35): Reaction of glycosyl donor 9 (0.110 g, 0.17 mmol) and glycosyl acceptor 17 (0.050 g, 0.12 mmol) was followed as given in the general procedure to afford 35, as a foamy solid. Yield = 81%; R_f = 0.2 (hexanes/EtOAc = 4:1); $[\alpha]_D^{22} = +42.25$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.58-7.23 (m, 20H), 6.13-6.03 (m, 2H), 5.78 (app. t, *J* = 3.2 Hz, 1H), 5.76 (app. t, *J* = 4.0 Hz, 1H), 5.67-5.66 (m, 1H), 5.56 (s, 1H), 5.42 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.34-5.28 (m, 3H), 4.69-4.65 (m, 2H), 4.50-4.33 (m, 4H), 4.24-4.13 (m, 3H), 3.98 (app. s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 165.9, 165.3, 165.2, 165.1, 137.6, 133.5, 133.4, 133.3, 133.2, 129.8, 129.7, 129.6, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 126.0, 118.8, 100.78, 95.7, 95.5, 74.2, 71.6, 70.6, 70.2, 69.8, 69.2, 68.8, 66.3, 62.4, 62.3; HRMS (ESI) *m/z*: C₅₇H₅₀O₁₆ calcd. for [M+Na]⁺ 1013.2997, found [M+Na]⁺ 1013.2999. Allyl 2,3,4,6-*tetra*-O-benzoyl-β-D-galactopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidine-*α*-D-galactopyranoside (36): Reaction of glycosyl donor 7 (0.110 g, 0.17 mmol) and glycosyl acceptor 17 (0.050 g, 0.12 mmol) was followed as given in the general procedure to afford 36, as a foamy solid. Yield = 86%; R_f = 0.2 (hexanes/EtOAc = 4:1); $[\alpha]_D^{22}$ = -128.03 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 7.4 Hz, 2H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.63-6.89 (m, 22H), 6.07-5.99 (m, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 5.80 (dd, *J* = 8, 10.4 Hz, 1H), 5.54-5.51 (m, 2H), 5.85 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.47 (s, 1H), 5.40 (d, *J* = 3.6 Hz, 1H), 5.24 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.12 (d, *J* = 8.0 Hz, 1H), 4.60-4.55 (m, 2H), 4.48 (dd, *J* = 3.6, 10.8 Hz, 1H), 4.45-4.28 (m, 4H), 4.29-4.19 (m, 1H), 4.06 (dd, *J* = 1.2, 12.4 Hz, 1H), 3.89 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 165.6, 165.5, 165.4, 137.7, 133.9, 133.5, 133.2, 132.9, 132.6, 129.9, 129.7, 129.7, 129.6, 129.2, 129.0, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 125.9, 117.2, 102.3, 100.5, 98.5, 74.8, 74.1, 71.8, 71.1, 70.5, 69.7, 69.2, 68.9, 67.9, 62.2, 61.8; HRMS (ESI) *m*/*z*: C₅₇H₅₀O₁₆ calcd. for [M+Na]⁺ 1013.2997, found [M+Na]⁺ 1013.2994.

Allyl 2,3,4,6-*tetra-O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidine-*a*-D-galactopyranoside (37): Reaction of glycosyl donor 4 (0.110 g, 0.17 mmol) and glycosyl acceptor 17(0.050 g, 0.12 mmol) was followed as given in the general procedure to afford 37, as a foamy solid. Yield = 75%; $R_f = 0.2$ (hexanes/EtOAc = 4:1); $[\alpha]_D^{24} = +290.36$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.53-6.89 (m, 22H), 5.94-5.86 (m, 1H), 5.84 (app. t, J = 9.6 Hz, 1H), 5.69 (app. t, J = 9.6 Hz, 1H), 5.55-5.46 (m, 3H), 5.34 (d, J = 3.6 Hz, 1H), 5.30 (dd, J = 1.6, 17.2 Hz, 1H), 5.13-5.11 (m, 2H), 4.71 (dd, J = 2.8, 12 Hz, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.45-4.38 (m, 2H), 4.30-4.26 (app. d, J = 12.0 Hz, 1H), 4.22-4.15 (m, 2H), 4.12-4.03 (m, 2H), 3.85 (br, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 165.7, 165.6, 165.1, 164.8, 137.7, 133.7, 133.4, 133.1, 132.9, 132.6, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 125.9, 117.4, 102.3, 100.4, 98.5, 77.2, 75.2, 74.1, 72.9, 72.1, 71.8, 70.4, 69.4, 69.1, 62.6, 62.1; HRMS (ESI) m/z: C₅₇H₅₀O₁₆ calcd. for [M+Na]⁺ 1013.2997, found [M+Na]⁺ 1013.2997.

2,3,4,6-*tetra-O*-benzoyl- β -D-galactopyranosyl- $(1 \rightarrow 6)$ -2,3,4-*tri-O*-benzoyl- α -D-manno-Allvl pyranosyl- $(1 \rightarrow 6)$ -2.3.4-*tri-O*-benzoyl- α -D-mannopyranoside (39): Reaction of glycosyl donor **31** (0.075 g, 0.07 mmol) and glycosyl acceptor **14** (0.025 g, 0.05 mmol) was followed as given in the general procedure to afford **39**, as a foamy solid. Yield = 75%; $R_f = 0.25$ (hexanes/EtOAc = 3:1); $[\alpha]_{D}^{25} = +1.32$ (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.19-7.76 (m, 20H), 7.61-7.19 (m, 30H), 6.09-6.03 (m, 2H), 5.96 (d, J = 3.2 Hz, 1H), 5.92-5.85 (m, 2H), 5.82-5.75 (m, 2H), 5.66-5.57 (m, 2H), 5.50 (dd, J = 1.2, 16.8 Hz, 1H), 5.36-5.34 (app. d, J = 12 Hz, 1H), 5.12(d, J = 4.0 Hz, 1H), 5.01-4.92 (m, 1H), 4.84 (d, J = 7.6 Hz, 1H), 4.71 (app. d, J = 4.0 Hz)1H), 4.56 (dd, J = 8.0, 12.0 Hz, 1H), 4.40 (dd, J = 4.0, 12.0 Hz, 1H), 4.33-4.15 (m, 5H), 4.02 (dd, J = 4.0, 12.0 Hz, 1H), 3.85 (dd, J = 8.0, 12.0 Hz, 1H), 3.69 (dd, J = 4.0, 12.0 Hz, 1H), 3.25(dd, J = 4.0, 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 165.7, 165.6, 165.5, 165.3, 165.2, 165.1, 133.5, 133.4, 133.2, 133.06, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 114.0, 102.4, 97.3, 96.8, 77.2, 71.7, 71.3, 70.5, 70.2, 69.8, 69.7, 69.6, 69.5, 68.8, 68.0, 67.3, 66.9, 66.3, 61.7; HRMS (ESI) m/z: C₉₁H₇₆O₂₆ calcd for [M+Na]⁺ 1607.4523, found [M+Na]⁺ 1607.4515.

Allyl 2,3,4,6-*tetra-O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-*tri-O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-*tri-O*-benzoyl-α-D-mannopyranoside (40): Reaction of glycosyl donor 32 (0.191 g, 0.30 mmol) and glycosyl acceptor 14 (0.10 g, 0.22 mmol) was followed as given in the general procedure to afford 40, as a foamy solid. Yield = 76%; R_f = 0.23 (hexanes/EtOAc = 3:1); $[\alpha]_D^{23} = -91.54$ (*c* 1.0, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 8.22-8.12 (m, 4H), 8.06-7.86 (m, 16H), 7.59-7.32 (m, 28H), 7.28-7.20 (m, 2H), 6.25 (app. t, *J* = 10.4 Hz, 1H), 6.10-6.03 (m, 3H), 6.01-5.91 (m, 3H), 5.80 (dd, *J* = 1.8, 3.2 Hz, 1H), 5.58 (dd, *J* = 1.8, 3.2 Hz, 1H),5.44 (dd, *J* = 4.0, 16.0 Hz, 1H), 5.27 (dd, *J* = 1.2, 10.4 Hz, 1H), 5.20 (dd, *J* = 1.6, 5.2 Hz, 2H), 5.01-4.91 (m, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.55 (dd, *J* = 4.0, 10.4 Hz, 1H), 4.48-4.39 (m, 2H), 4.34-4.21 (m, 5H), 3.94 (dd, *J* = 6.0, 10.4 Hz, 1H), 3.83 (dd, *J* = 2.0, 10.2 Hz, 1H), 3.42 (dd, *J* = 2.0, 10.2 Hz, 1H); ¹³C NMR (CDCl₃ 100 MHz): δ 166.0, 165.8, 165.6, 165.5, 165.4, 165.2, 165.1, 139.3, 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 118.4, 98.0, 97.4, 96.9, 77.2, 70.6, 70.5, 70.3, 70.2, 70.1, 70.0, 69.6, 69.4, 68.8, 66.8, 66.7, 66.5, 66.4, 65.9, 62.4; HRMS (ESI) *m/z*: C₉₁H₇₆O₂₆ calcd. for [M+Na]⁺1607.4523, found [M+Na]⁺1607.4838. **Pentenyl 2,3,4-***tri***-O**-acetyl-β-L-fucoside: Reaction of glycosyl donor allyl 2,3,4-*tri*-O-acetyl-α-L-fucoside (0.050 g, 0.15 mmol) and *n*-pentanol (32 μL, 0.3 mmol) was followed as given in the general procedure to afford pentenyl 2,3,4-*tri*-O-acetyl-β-L-fucoside, as an foamy solid. Yield = 32%; $R_f = 0.45$ (hexanes/EtOAc = 3:1); $[\alpha]_D^{24} = -9.28$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 5.16-5.18 (m, 2H), 5.02 (dd, *J* = 3.2, 10.4 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 3.93-3.87 (m, 1H) 3.78 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.4-3.5 (m, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.55-1.61 (m, 2H), 1.25-1.32 (m, 4H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.91 (t, *J* = 4.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 170.7, 170.3, 169.4, 101.12, 71.4, 70.3, 70.0, 69.0, 29.0, 27.9, 22.3, 20.7, 20.6, 16.0, 13.9; HRMS (ESI) *m/z*: C₁₇H₂₈O₈ calcd for [M+Na]⁺ 383.1682, found [M+Na]⁺ 383.1682.

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Figure S1. ¹H NMR spectrum of 2 (400 MHz, CDCl₃).



Figure S2. ¹³C NMR spectrum of 2 (100 MHz, CDCl₃).



Figure S3. ¹H NMR spectrum of 20 (400 MHz, CDCl₃).



Figure S4. ¹³C NMR spectrum of 20 (100 MHz, CDCl₃).



Figure S5. ¹H NMR spectrum of 21 (400 MHz, CDCl₃).



Figure S6. ¹³C NMR spectrum of **21** (100 MHz, CDCl₃).



Figure S7. ¹H NMR spectrum of 22 (400 MHz, CDCl₃).



Figure S8. ¹³C NMR spectrum of 22 (100 MHz, CDCl₃).



Figure S9. ¹H NMR spectrum of 27 (100 MHz, CDCl₃).



Figure S10. ¹³C NMR spectrum of 27 (100 MHz, CDCl₃).



Figure S11. ¹H NMR spectrum of 30 (400 MHz, CDCl₃).



Figure S12. ¹³C NMR spectrum of **30** (100 MHz, CDCl₃).



Figure S13. ¹H NMR spectrum of 31 (400 MHz, CDCl₃).



Figure S14. ¹³C NMR spectrum of **31** (100 MHz, CDCl₃).



Figure S15. ¹H NMR spectrum of 32 (400 MHz, CDCl₃).



Figure S16. ¹³C NMR spectrum of **32** (100 MHz, CDCl₃).



Figure S17. ¹H NMR spectrum of 33 (400 MHz, CDCl₃).



Figure S18. ¹³C NMR spectrum of 33 (100 MHz, CDCl₃).



Figure S19. ¹H NMR spectrum of 34 (400 MHz, CDCl₃).



Figure S20. ¹³C NMR spectrum of 34 (100 MHz, CDCl₃).



Figure S21. ¹H NMR spectrum of 35 (400 MHz, CDCl₃).



Figure S22. ¹³C NMR spectrum of 35 (100 MHz, CDCl₃).



Figure S23. ¹H NMR spectrum of 36 (400 MHz, CDCl₃).



Figure S24. ¹³C NMR spectrum of 36 (100 MHz, CDCl₃).



Figure S25. ¹H NMR spectrum of 37 (400 MHz, CDCl₃).



Figure S26. ¹³C NMR spectrum of 37 (100 MHz, CDCl₃).



Figure S27. ¹H NMR spectrum of **39** (400 MHz, CDCl₃).



Figure S28. ¹³C NMR spectrum of **39** (100 MHz, CDCl₃).



Figure S29. ¹H NMR spectrum of 40 (400 MHz, CDCl₃).



Figure S30. ¹³C NMR spectrum of 40 (100 MHz, CDCl₃).



Figure S31. ¹H NMR spectrum of pentenyl 2,3,4-*tri*-O-acetyl-β-L-fucoside (39) (400 MHz, CDCl₃).



Figure S32. ¹³C NMR spectrum of pentenyl 2,3,4-*tri*-O-acetyl-β-L-fucoside (39) (100 MHz, CDCl₃).



Figure S33. GC-MS spectrum of the glycosylation reaction mixture showing the presence of acrolein (m/z 56, along with succinimide (m/z 99)).