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NMR spectra of phthalimide precursors and final allylated products

\textbf{General Methods}. Melting points were determined with a hot-plate apparatus. Optical rotations were measured with a Perkin-Elmer Polarimeter PE-241 at the sodium line at ambient temperature in CHCl$_3$. IR spectra were recorded with a Perkin Elmer 1600/FTIR instrument in CCl$_4$. NMR

\textsuperscript{[1]} Numbers ending in S refer to products only cited in the Supporting Information.
Spectra were recorded with a Bruker AMX 400 spectrometer at 400 MHz for $^1$H and 100.6 MHz for $^{13}$C in CDCl$_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were recorded with a Waters LCT Premier XE spectrometer by using electrospray ionization (ESI+) or with a Micromass AutoSpec by using electron impact (EI) at 70 eV or fast atom bombardment (FAB), as state in each case. Elemental analyses were performed with a Leco TrueSpec Micro instrument. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF$_{254}$ were used with a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under nitrogen. TLC analysis was conducted with a spray of 0.5% vanillin in H$_2$SO$_4$/EtOH (4:1) and heating until the development of color.

**General procedure for phthalimide precursors**

DEAD (0.4 mL, 2.5 mmol) was added dropwise to a stirred solution of the alcohol (1 mmol), N-hydroxyphthalimide (0.4 g, 2.5 mmol) and PPh$_3$ (0.6 g, 2.5 mmol) in dry THF (10 mL) and the resulting solution was stirred at 0 °C until all the starting material was consumed. Then the solvent was removed and the crude was quenched with water and extracted with Et$_2$O. The combined extracts were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Column chromatography of the residue (hexanes–EtOAc) gave the corresponding phthalimide.
2-Propynyl 2,3,4,6-Tetra-\(\text{O}-\)acetyl-\(\alpha\)-D-mannopyranoside (1S). To a solution of 1,2,3,4,6-penta-\(\text{O}-\)acetyl-D-mannopyranose (11.4 g, 29.2 mmol) at 0 °C in dry CH\(_2\)Cl\(_2\) (114 mL) were dropwise added BF\(_3\)+Et\(_3\)O (6.8 mL, 1.9 mmol) and freshly distilled propargyl alcohol (6.8 mL, 116.8 mmol) and the reaction was stirred at rt for 48 h. Then it was poured into NaHCO\(_3\) saturated solution and extracted with CH\(_2\)Cl\(_2\). The combined organic extracts were dried over Na\(_2\)SO\(_4\) and evaporated. Column chromatography of the residue (hexanes–EtOAc, 75:25) gave 1S (8.9 g, 23.05 mmol, 79%) as a white solid. M. p. 103–104 °C (n-hexane/EtOAc). [\(\alpha\)]\(_D\) = +70.6 (\(c = 0.32\), in CHCl\(_3\)). \(^1\)H NMR: \(\delta = 1.98\) (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 2.15 (s, 3H), 2.47 (dd, \(J = 2.4, 2.4\), 1H), 4.01 (ddd, \(J = 9.5, 5.1, 2.4\) Hz, 1H), 4.10 (dd, \(J = 12.2, 2.4\), 1H), 4.26 (s, 1H), 4.27 (s, 1H), 4.28 (dd, \(J = 12.0, 5.2\) Hz, 1H), 5.02 (d, \(J = 1.6\) Hz, 1H), 5.26 (dd, \(J = 3.3, 1.8\) Hz, 1H), 5.28 (dd, \(J = 9.6, 9.6\) Hz, 1H), 5.33 (dd, \(J = 9.9, 3.3\) Hz, 1H) ppm. \(^13\)C NMR: \(\delta = 20.6\) (2 \(\times\) CH\(_3\)), 20.7 (CH\(_3\)), 20.8 (CH\(_3\)), 54.9 (CH\(_2\)), 62.3 (CH\(_2\)), 66.0 (CH), 68.9 (2 \(\times\) CH), 69.3 (CH), 75.5 (CH), 77.9 (C), 96.2 (CH), 169.7 (C), 169.8 (C), 169.9 (C), 170.6 (C) ppm. IR (CCl\(_4\)): \(\nu = 3274, 2959, 1750\) cm\(^{-1}\). MS (70 eV, EI): \(m/z\) (%) = 331 (7 [M – C\(_3\)H\(_3\)O]+), 243 (25 [M – C\(_6\)H\(_5\)O\(_4\)]\(^{+}\)), 157 (100). HRMS (EI): \(m/z\): calcd for C\(_{14}\)H\(_{19}\)O\(_9\) 331.1029 [M – C\(_3\)H\(_3\)O]+; found 331.1000. C\(_{17}\)H\(_{22}\)O\(_{10}\) (386.35): C 52.85, H 5.74; found: C 52.82, H 5.73.

Allyl 2,3,4,6-Tetra-\(\text{O}-\)acetyl-\(\alpha\)-D-mannopyranoside (2S). To a solution of alkyne 1S (740 mg, 1.92 mmol) in MeOH (17 mL) were added Pd/CaCO\(_3\) (37 mg) and quinoline (370 \(\mu\)L) and the mixture was hydrogenated at rt. After 2 h the reaction was filtered over celite and evaporated. Then it was poured into a 10% HCl aqueous solution and extracted with CH\(_2\)Cl\(_2\). The combined organic extracts were dried over Na\(_2\)SO\(_4\) and evaporated. Column chromatography of the residue (hexanes–EtOAc, 8:2) gave 2S (626 mg, 1.61 mmol, 84%) together with a small amount of propyl 2,3,4,6-tetra-\(\text{O}-\)acetyl-\(\alpha\)-D-mannopyranoside 3S (70 mg, 0.18 mmol, 9%) as colourless oils. Compound 2S: [\(\alpha\)]\(_D\) = +50.4 (\(c = 0.26\), in CHCl\(_3\)). \(^1\)H NMR: \(\delta = 1.99\) (s, 3H), 2.04 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 4.01 (ddd, \(J = 9.8, 5.3, 2.4\) Hz, 1H), 4.03 (ddddd, \(J = 13.0, 5.3, 1.6, 1.6\) Hz, 1H), 4.10 (dd, \(J = \)
12.4, 2.6 Hz, 1H), 4.19 (dddd, $J = 13.0, 5.3, 1.6, 1.6$ Hz, 1H), 4.28 (dd, $J = 12.2, 5.3$ Hz, 1H), 4.87 (d, $J = 1.8$ Hz, 1H), 5.24 (dddd, $J = 10.6, 1.1, 1.1, 1.1$ Hz, 1H), 5.26 (dd, $J = 3.4, 1.8$ Hz, 1H), 5.29 (dd, $J = 10.0, 10.0$ Hz, 1H), 5.31 (dddd, $J = 17.2, 1.6, 1.6, 1.6$ Hz, 1H), 5.37 (dd, $J = 10.0, 3.4$ Hz, 1H), 5.89 (dddd, $J = 17.5, 10.4, 6.4, 5.3$ Hz, 1H) ppm. $^{13}$C NMR: $\delta = 20.6$ ($2 \times \text{CH}_3$), 20.7 (CH$_3$), 20.8 (CH$_3$), 62.4 (CH$_2$), 66.2 (CH), 68.5 (CH), 68.6 (CH$_2$), 69.0 (CH), 69.6 (CH), 96.6 (CH), 118.4 (CH$_2$), 132.9 (CH), 169.7 (C), 169.8 (C), 170.0 (C), 170.6 (C) ppm. IR (CCl$_4$): $\tilde{\nu} = 2959, 1749, 1645$ cm$^{-1}$. MS (70 eV, EI): $m/z$ (%) = 331 (8) [M – C$_3$H$_5$O]$^+$, 157 (100). HRMS (EI): $m/z$: calcd for C$_{14}$H$_{19}$O$_9$ 331.1029 [M – C$_3$H$_5$O]$^+$; found 331.1069. C$_{17}$H$_{24}$O$_{10}$ (388.37): C 52.57, H 6.23; found: C 52.50, H 6.30.

2-Hydroxyethyl 2,3,4,6-Tetra-O-acetyl-$\alpha$-D-mannopyranoside (4S). A solution of 2S (120 mg, 0.31 mmol) in dry CH$_2$Cl$_2$/MeOH (1:1) (15 mL) was cooled to −78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was heated to 0 °C. Afterwards, NaBH$_4$ (35 mg, 0.93 mmol) was slowly added and the solution stirred for 30 min at room temperature. The reaction mixture was then stirred with an excess of solid NH$_4$Cl, filtered and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 1:1) gave 4S (100 mg, 0.25 mmol, 82%) as a colourless oil. $[\alpha]_D = +45.6$ ($c = 0.67$, in CHCl$_3$). $^1$H NMR: $\delta = 2.00$ (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.16 (s, 3H), 3.68 (m, 1H), 3.75–3.82 (m, 3H), 4.07 (ddd, $J = 9.9, 5.7, 2.4$ Hz, 1H), 4.13 (dd, $J = 12.1, 2.4$ Hz, 1H), 4.26 (dd, $J = 12.1, 5.7$ Hz, 1H), 4.87 (d, $J = 1.4$ Hz, 1H), 5.28 (dd, $J = 9.9, 9.9$ Hz, 1H), 5.28 (dd, $J = 3.0$, 1.8 Hz, 1H), 5.35 (dd, $J = 10.1$, 3.4 Hz, 1H) ppm. 1H from OH is missing. $^{13}$C NMR: $\delta = 20.6$ ($3 \times \text{CH}_3$), 20.7 (CH$_3$), 61.4 (CH$_2$), 62.5 (CH$_2$), 66.1 (CH), 68.6 (CH), 69.0 (CH), 69.4 (CH), 70.2 (CH$_2$), 97.8 (CH), 169.6 (C), 169.9 (C), 170.0 (C), 170.6 (C) ppm. IR (CCl$_4$): $\tilde{\nu} = 3478, 2938, 1747$ cm$^{-1}$. MS (70 eV, EI): $m/z$ (%) = 362 (<1) [M + H – CH$_3$O]$^+$, 331 (11) [M – C$_3$H$_5$O$_2$]$^+$, 73 (100). HRMS (EI): $m/z$: calcd for C$_{15}$H$_{22}$O$_{10}$ 362.1213 [M + H – CH$_3$O]$^+$; found 362.1194. C$_{16}$H$_{24}$O$_{11}$ (392.35): C 48.98, H 6.17; found: C 48.99, H 6.28.
2-O-Phthalimidoethyl 2,3,4,6-Tetra-O-acetyl-α-D-mannopyranoside (5). Phthalimide 5 prepared from alcohol 4S under the standard conditions, was obtained as an amorphous solid in 76% yield. \([\alpha]_D^0 = +26.6 \ (c = 0.96, \text{CHCl}_3)\). \(^1\text{H}\) NMR: 1.91 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 2.11 (s, 3H), 3.86 (ddd, \(J = 12.2, 4.0, 4.0 \text{ Hz, 1H}\)), 4.01 (m, 1H), 4.10 (dd, \(J = 12.0, 2.2 \text{ Hz, 1H}\)), 4.16 (m, 1H), 4.27 (dd, \(J = 11.9, 4.8 \text{ Hz, 1H}\)), 4.37 (dd, \(J = 4.4, 4.4 \text{ Hz, 2H}\)), 4.88 (d, \(J = 1.6 \text{ Hz, 1H}\)), 5.18 (dd, \(J = 2.9, 1.6 \text{ Hz, 1H}\)), 5.24 (dd, \(J = 5.8, 2.2 \text{ Hz, 2H}\)), 7.70–7.72 (m, 2H), 7.80–7.82 (m, 2H) ppm. \(^{13}\text{C}\) NMR: \(\delta = 20.5 \ (\text{CH}_3), 20.6 \ (2 \times \text{CH}_3), 20.7 \ (\text{CH}_3), 62.3 \ (\text{CH}_2), 65.9 \ (\text{CH}), 66.5 \ (\text{CH}_2), 68.6 \ (\text{CH}), 68.9 \ (\text{CH}), 69.3 \ (\text{CH}), 76.8 \ (\text{CH}_2), 98.1 \ (\text{CH}), 123.6 \ (2 \times \text{CH}), 128.7 \ (2 \times \text{C}), 134.5 \ (2 \times \text{CH}), 163.3 \ (2 \times \text{C}), 169.5 \ (\text{C}), 169.7 \ (\text{C}), 169.8 \ (\text{C}), 170.6 \ (\text{C}) \ ppm$. IR (CCl\textsubscript{4}): \(\nu = 3028, 1792, 1737, 1227 \text{ cm}^{-1}\). MS (ESI\textsuperscript{+}): \(m/z\) (%) = 560 (100) [M + Na]\textsuperscript{+}. HRMS (ESI\textsuperscript{+}): \(m/z\): calcd for C\textsubscript{24}H\textsubscript{27}N\textsubscript{3}O\textsubscript{13} 560.1380 [M + Na]\textsuperscript{+}; found 560.1376. C\textsubscript{24}H\textsubscript{27}N\textsubscript{3}O\textsubscript{13} (537.47): C 53.63, H 5.06, N 2.61; found: C 53.58, H 5.14, N 2.91.

![Chemical Structures](image)

**Allyl 2,3,4,6-Tetra-O-methyl-α-D-mannopyranoside (5S).** The allyl derivative 2S (1.3 g, 3.35 mmol) was dissolved in KOH-MeOH 2.5% (18.4 mL) and stirred at rt for 2 h. Dowex resin (50 × 8) was added to neutral pH and the mixture was filtered and evaporated. To a suspension of NaH (643 mg, 26.8 mmol) in dry DMF (30 mL) a solution of the crude alcohol (3.35 mmol) in dry THF (30 mL) was added dropwise at 0 °C. After 15 min, MeI (2.1 mL, 33.5 mmol) was slowly added and the mixture was stirred at rt for 1.5 h. The reaction was then poured into water, extracted with CH\textsubscript{2}Cl\textsubscript{2} and concentrated to dryness. Column chromatography of the residue (hexanes–EtOAc, 7:3) gave 5S (740 mg, 2.68 mmol, 80%) as a colourless oil. \([\alpha]_D^0 = +70.0 \ (c = 0.24, \text{in CHCl}_3)\). \(^1\text{H}\) NMR: \(\delta = 3.37 \ (s, 3H), 3.41 \ (dd, \ J = 9.1, 9.1 \text{ Hz, 1H}), 3.44 \ (s, 3H), 3.46 \ (s, 3H), 3.49 \ (s, 3H), 3.50 \ (dd, \ J = 9.3, 3.3 \text{ Hz, 1H}), 3.54–3.59 \ (m, 4H), 3.94 \ (dd, \ J = 12.9, 6.2 \text{ Hz, 1H}), 4.16 \ (dd, \ J = 12.9, 5.0 \text{ Hz, 1H}), 4.91 \ (d, \ J = 1.8 \text{ Hz, 1H}), 5.16 \ (dd, \ J = 10.0, 0 \text{ Hz, 1H}), 5.25 \ (dd, \ J = 17.3, 1.5 \text{ Hz, 1H}), 5.86 \ (ddddd, \ J = 16.8, 10.2, 5.6, 5.6 \text{ Hz, 1H}) \ ppm$. \(^{13}\text{C}\) NMR: \(\delta = 57.6 \ (\text{CH}_3), 58.8 \ (\text{CH}_3), 59.1 \ (\text{CH}_3), 60.5 \ (\text{CH}_3), 67.9 \ (\text{CH}_2), 71.3 \ (\text{CH}), 71.6 \ (\text{CH}_2), 76.4 \ (\text{CH}), 77.1 \ (\text{CH}), 81.2 \ (\text{CH}), 96.0 \ (\text{CH}), 117.3 \ (\text{CH}_2), 133.7 \ (\text{CH}) \ ppm$. IR (CCl\textsubscript{4}): \(\nu = 2912, 2828, 1630 \text{ cm}^{-1}\). MS (70 eV, EI): \(m/z\) (%) = 231 (<1) [M – C\textsubscript{2}H\textsubscript{5}O]\textsuperscript{+}, 101 (100). HRMS (EI): \(m/z\): calcd for C\textsubscript{11}H\textsubscript{15}O\textsubscript{5} 231.1232 [M – C\textsubscript{2}H\textsubscript{5}O]\textsuperscript{+}; found 231.1260. C\textsubscript{13}H\textsubscript{24}O\textsubscript{6}(276.33): C 56.51, H 8.75; found: C 56.53, H 8.74.
2-Hydroxyethyl 2,3,4,6-Tetra-O-methyl-α-D-mannopyranoside (6S). A solution of the olefin 5S (1.35 g, 4.89 mmol) in dry CH₂Cl₂/MeOH (1:1) (150 mL) was cooled to −78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was heated to 0 °C. Afterwards, NaBH₄ (1.1 g, 29.1 mmol) was slowly added and the solution stirred for 30 min at room temperature. The reaction mixture was then stirred with an excess of solid NH₄Cl, filtered and concentrated in vacuo. Column chromatography of the residue (EtOAc) gave 6S (1.23 mg, 4.39 mmol, 90%) as a colourless oil. [α]D = +43.2 (c = 0.80, in CHCl₃). ¹H NMR: (500 MHz) δ = 3.39 (m, 1H), 3.40 (s, 3H), 3.49 (s, 3H), 3.50 (s, 3H), 3.51 (s, 3H), 3.51–3.63 (m, 4H), 3.67–3.78 (m, 5H), 4.92 (d, J = 2.3 Hz, 1H) ppm, 1H from OH group is missing. ¹³C NMR: δ = 58.1 (CH₃), 59.3 (CH₃), 59.5 (CH₃), 60.9 (CH₃), 62.2 (CH₂), 70.9 (CH₂), 71.8 (CH), 72.2 (CH₂), 76.9 (CH), 77.5 (CH), 81.4 (CH), 97.9 (CH) ppm. IR (CCl₄): ν = 3500, 2930, 1455, 1112 cm⁻¹. MS (70 eV, EI): m/z (%) = 263 (7) [M – OH]⁺, 219 (11) [M – C₂H₅O₂]⁺, 88 (100). HRMS (EI): m/z: calcd for C₁₀H₁₀O₅ 219.1232 [M – C₂H₅O₂]⁺; found 219.1222. C₁₂H₂₃O₇ (280.31): C 51.42, H 8.63; found: C 51.19, H 8.97.

2-O-Phthalimidoethyl 2,3,4,6-Tetra-O-methyl-α-D-mannopyranoside (3). Phthalimide 3 prepared from alcohol 6S under the standard conditions, was obtained as a white solid in 77% yield. M. p. 103.4–104.9 °C (n-hexane-EtOAc). [α]D = +26.3 (c = 0.19, in CHCl₃). ¹H NMR: δ = 3.21 (s, 3H), 3.27–3.31 (m, 2H), 3.28 (s, 3H), 3.37 (s, 3H), 3.37 (m, 1H), 3.39 (s, 3H), 3.46–3.52 (m, 3H), 3.77 (m, 1H), 3.89 (ddd, J = 12.5, 4.2, 3.2 Hz, 1H), 4.29–4.32 (m, 2H), 4.88 (d, J = 1.9 Hz, 1H), 7.67–7.69 (m, 2H), 7.75–7.77 (m, 2H) ppm. ¹³C NMR: δ = 57.2 (CH₃), 58.6 (CH₃), 58.9 (CH₃), 60.2 (CH₃), 65.6 (CH₂), 71.2 (CH), 71.4 (CH₂), 76.0 (CH), 76.4 (CH₂), 76.5 (CH), 80.7 (CH), 97.0 (CH), 123.3 (2 × CH), 128.7 (2 × C), 134.3 (2 × CH), 163.0 (2 × C) ppm. IR (CCl₄): ν = 2930, 1794, 1740 cm⁻¹. MS (ESI⁺): m/z (%) = 448 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C₂₀H₂₇NNaO₉: 448.1584 [M + Na]⁺; found 448.1582. C₂₀H₂₇NO₉ (425.43): calcd. C 56.46, H 6.40, N 3.29; found C 56.24, H, 6.29, N, 2.98.
3-Hydroxypropyl 2,3,4,6-Tetra-O-methyl-α-D-mannopyranoside (7S).\(^1\)\(^2\) To a solution of 5S (740 mg, 2.68 mmol) in dry THF (40 mL) at 0 °C was added dropwise a 1 M solution of BH\(_3\)•THF complex (13.4 mL, 13.4 mmol) and stirred at rt for 3 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (42 mL). The oxidation was carried out by slow dropwise addition of 30% H\(_2\)O\(_2\) (42 mL). After stirring for an additional 0.75 h, the reaction mixture was poured into water and extracted with CH\(_2\)Cl\(_2\). The combined extracts were washed with brine, dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Column chromatography of the residue (hexanes–EtOAc, 35:65) gave alcohol 7S (568 mg, 1.93 mmol, 72%) as a colourless solid. [α]\(_D\) = +55.5 (c = 0.31, in CHCl\(_3\)).\(^3\)\(^1\)H NMR: \(\delta = 1.81\) (m, 2H), 2.18 (s br, 1H), 3.36 (dd, \(J = 9.2, 9.2\) Hz, 1H), 3.38 (s, 3H), 3.43 (s, 3H), 3.45 (m, 1H), 3.47 (s, 3H), 3.49 (s, 3H), 3.51–3.60 (m, 5H), 3.70–3.73 (m, 2H), 3.86 (ddd, \(J = 9.7, 6.2, 6.2\) Hz, 1H), 4.87 (d, \(J = 1.8\) Hz, 1H) ppm. \(^13\)C NMR: \(\delta = 32.1\) (CH\(_2\)), 57.7 (CH\(_3\)), 58.9 (CH\(_3\)), 59.2 (CH\(_3\)), 60.0 (CH\(_2\)), 60.5 (CH\(_3\)), 64.9 (CH\(_2\)), 71.4 (CH), 71.8 (CH\(_2\)), 76.5 (CH), 77.2 (CH), 81.2 (CH), 96.9 (CH) ppm. IR (CCl\(_4\)): \(\nu = 3461, 2926, 2829, 1455\) cm\(^{-1}\). MS (70 eV, EI): \(m/z\) (%): 294 (1%) [M]\(^{+}\), 219 (2) [M – C\(_3\)H\(_7\)O\(_2\)]\(^{+}\), 88 (100). HRMS (EI): \(m/z\) (%): calcd for C\(_{10}\)H\(_9\)O\(_5\): 219.1232 [M – C\(_3\)H\(_7\)O\(_2\)]\(^{+}\); found 219.1223. C\(_{13}\)H\(_{26}\)O\(_7\) (294.34): calcd. C 53.05, H 8.90; found C 53.08, H, 8.72.

3-O-Phthalimidopropyl 2,3,4,6-Tetra-O-methyl-α-D-mannopyranoside (10).\(^2\) Phthalimide 10 prepared from alcohol 7S under the standard conditions, was obtained as a colourless oil in 83% yield. [α]\(_D\) = +31.9 (c = 0.18, in CHCl\(_3\)).\(^1\)H NMR: \(\delta = 1.97–2.11\) (m, 2H), 3.38 (s, 3H), 3.43 (dd, \(J = 9.2, 9.2\) Hz, 1H), 3.48 (m, 1H), 3.48 (s, 6H), 3.50 (s, 3H), 3.55–3.59 (m, 4H), 3.66 (ddd, \(J = 9.9, 7.3, 5.3\) Hz, 1H), 3.89 (ddd, \(J = 11.8, 9.9, 5.7\) Hz, 1H), 4.26–4.30 (m, 2H), 4.95 (d, \(J = 1.7\) Hz, 1H), 7.73 (m, 2H), 7.82 (m, 2H) ppm. \(^13\)C NMR: \(\delta = 28.4\) (CH\(_2\)), 57.6 (CH\(_3\)), 58.8 (CH\(_3\)), 59.2 (CH\(_3\)), 60.5 (CH\(_3\)), 63.8 (CH\(_2\)), 71.3 (CH\(_2\)), 71.6 (CH), 75.3 (CH\(_2\)), 76.4 (CH), 77.1 (CH), 81.2 (CH), 97.1 (CH), 123.5 (2 × CH), 128.9 (2 × C), 134.4 (2 × CH), 163.5 (2 × C) ppm. IR (CCl\(_4\)): \(\nu = 2925,\)

2828, 1789, 1735 cm$^{-1}$. MS (FAB$^+$): $m/z$ (%) = 462 (26) [M + Na]$^+$, 279 (100). HRMS (FAB$^+$): $m/z$: calcd for C$_{21}$H$_{29}$N$^+$Na$_2$O$_9$: 462.1740 [M + Na]$^+$; found 462.1745. C$_{21}$H$_{29}$NO$_9$ (439.46): calcd. C 57.39, H 6.65, N 3.19; found C 57.58, H, 6.79, N, 3.03.

**Allyl 2,3,4,6-Tetra-O-methyl-α-D-glucopyranoside (8S) and Allyl 2,3,4,6-Tetra-O-methyl-β-D-glucopyranoside (9S).** To a solution of D-glucose (4.2 g, 21.2 mmol) in freshly distilled allyl alcohol (25 mL, 365.9 mmol), CSA (25 mg, 0.11 mmol) was added and the reaction was stirred at 90 °C overnight. Then it was evaporated and the residue was used without any further purification. The resulting crude dissolved in dry DMF (76 mL) was dropwise added to a solution of NaH (3.7 g, 152.6 mmol) and DMF (70 mL) at 0 °C. Then, MeI (10 mL, 161.1 mmol) was dropwise added and the reaction was stirred at rt for 6 h. The mixture was poured into NH$_4$Cl saturated aqueous solution and extracted with Et$_2$O. The combined extracts were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Column chromatography of the residue (hexanes–EtOAc, 85:15) gave 8S (1.04 g, 3.78 mmol, 19%) and 9S (2.23 g, 8.09 mmol, 38%) as colourless oils. Compound 8S: [α]$_D$ = +63.7 (c = 0.27, in CHCl$_3$). $^1$H NMR: $\delta$ = 3.16 (dd, $J$ = 9.5, 3.7 Hz, 1H), 3.37 (s, 3H), 3.39–3.41 (m, 2H), 3.43 (s, 3H), 3.48 (m, 1H), 3.49 (s, 3H), 3.52 (dd, $J$ = 6.1, 3.4 Hz, 1H), 3.58 (s, 3H), 3.69 (m, 1H), 3.99 (m, 1H), 4.11 (m, 1H), 4.93 (d, $J$ = 3.5 Hz, 1H), 5.16 (d, $J$ = 10.0 Hz, 1H), 5.16 (d, $J$ = 17.2 Hz, 1H), 5.87 (m, 1H) ppm. $^{13}$C NMR: $\delta$ = 58.6 (CH$_3$), 59.1 (CH$_3$), 60.3 (CH$_3$), 60.7 (CH$_3$), 67.9 (CH$_2$), 70.0 (CH), 71.0 (CH$_2$), 79.4 (CH), 81.6 (CH), 83.3 (CH), 95.0 (CH), 117.9 (CH$_2$), 133.6 (CH) ppm. IR (CCl$_4$): $\nu$ = 2930, 1455, 1104 cm$^{-1}$. MS (70 eV, EI): $m/z$ (%) = 276 (1) [M]$^+$, 219 (93) [M – C$_3$H$_2$O]$^+$, 101 (100). HRMS (EI): $m/z$: calcd for C$_{13}$H$_{24}$O$_6$: 276.1573 [M]$^+$; found 276.1572. C$_{13}$H$_{24}$O$_6$ (276.33): calcd. C 56.51, H 8.75; found C 56.31, H 8.67. Compound 9S: [α]$_D$ = –29.4 (c = 0.67, in CHCl$_3$). $^1$H NMR: $\delta$ = 3.01 (dd, $J$ = 7.7, 7.7 Hz, 1H), 3.14 (dd, $J$ = 8.0, 8.0 Hz, 1H), 3.26 (m, 1H), 3.40 (s, 3H), 3.52 (s, 3H), 3.53–3.67 (m, 3H), 3.58 (s, 3H), 3.62 (s, 3H), 4.08 (dd, $J$ = 13.2, 5.8 Hz, 1H), 4.26 (d, $J$ = 7.7 Hz, 1H), 4.37 (dd, $J$ = 13.0, 5.0 Hz, 1H), 5.17 (dd, $J$ = 10.3, 0 Hz, 1H), 5.30 (dd, $J$ = 17.2, 0 Hz, 1H), 5.92 (m, 1H) ppm. $^{13}$C NMR: $\delta$ = 59.6 (CH$_3$), 60.6 (CH$_3$), 60.7 (CH$_3$), 61.0 (CH$_3$), 70.2 (CH$_2$), 71.6 (CH$_2$), 74.9 (CH), 79.7 (CH), 84.1 (CH), 86.8 (CH), 102.7 (CH), 117.2 (CH$_2$), 135.2 (CH) ppm. IR (CCl$_4$): $\nu$ = 2933, 1450, 1098 cm$^{-1}$. MS (70 eV, EI): $m/z$ (%) = 260 (15) [M – H – CH$_3$]$^+$, 103 (100). HRMS (EI): $m/z$: calcd for C$_{12}$H$_{20}$O$_6$: 260.1260; found 260.1270. C$_{13}$H$_{24}$O$_6$ (276.33): calcd. C 56.51, H 8.75; found C 56.29, H 8.73.
2-Hydroxyethyl 2,3,4,6-Tetra-O-methyl-α-D-glucopyranoside (10S). A solution of the olefin 8S (700 mg, 2.5 mmol) in dry CH₂Cl₂/MeOH (1:1) (100 mL) was cooled to −78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was heated to 0 °C. Afterwards, NaBH₄ (575 mg, 15.2 mmol) was slowly added and the solution stirred for 30 min at room temperature. The reaction mixture was then stirred with an excess of solid NH₄Cl, filtered and concentrated in vacuo. Column chromatography of the residue (EtOAc) gave 10S (615 mg, 0.45 mmol, 88%) as a colourless oil. [α]D +108.8 (c = 0.17, in CHCl₃). ¹H NMR: δ= 2.44 (br s, 1H), 3.14 (dd, J = 10.0, 8.7 Hz, 1H), 3.20 (dd, J = 9.8, 3.7 Hz, 1H), 3.39 (s, 3H), 3.44 (dd, J = 8.2, 8.2 Hz, 1H), 3.50 (s, 3H), 3.52 (s, 3H), 3.55 (dd, J = 2.7, 2.7 Hz, 1H), 3.65–3.79 (m, 5H), 4.94 (d, J = 3.7 Hz, 1H) ppm. ¹³C NMR: δ= 59.1 (CH₃), 59.2 (CH₃), 60.4 (CH₃), 60.8 (CH₃), 61.8 (CH₂), 70.3 (CH₂), 71.2 (CH₂), 79.6 (CH), 81.8 (CH), 83.4 (CH), 97.4 (CH) ppm. IR (CCl₄): ν = 3490, 2931, 1453, 1100 cm⁻¹. MS (70 eV, EI): m/z (%) = 248 (1) [M – CH₃OH]⁺, 101 (100). HRMS (EI): m/z: calcd for C₁₁H₂₀O₆ 248.1260 [M – CH₃OH]⁺; found 248.1272. C₁₁H₂₀O₆ (280.31): C 51.42, H 8.63; found C 51.33, H 8.63.

2-O-Phthalimidoethyl 2,3,4,6-Tetra-O-methyl-α-D-glucopyranoside (14). Phthalimide 14 prepared from alcohol 10S was obtained in 75% yield as a colourless oil. [α]D +70.0 (c = 0.16, in CHCl₃). ¹H NMR: δ= 3.12–3.17 (m, 2H), 3.34 (m, 1H), 3.36 (s, 3H), 3.42 (s, 3H), 3.45 (s, 3H), 3.49 (s, 3H), 3.53–3.56 (m, 2H), 3.67 (dd, J = 10.3, 2.1 Hz, 1H), 3.89 (m, 1H), 3.97 (m, 1H), 4.34–4.44 (m, 2H), 5.00 (d, J = 3.4 Hz, 1H), 7.68–7.73 (m, 2H), 7.77–7.81 (m, 2H) ppm. ¹³C NMR: δ= 58.7 (CH₃), 59.1 (CH₃), 60.2 (CH₃), 60.6 (CH₃), 65.5 (CH₂), 70.1 (CH), 71.0 (CH₂), 76.8 (CH₂), 79.2 (CH), 81.5 (CH), 82.9 (CH), 96.5 (CH), 123.4 (2 × CH), 129.0 (2 × C), 134.2 (2 × CH), 163.3 (2 × C) ppm. IR (CCl₄): ν = 2930, 1794, 1740, 1102 cm⁻¹. MS (ESI⁺): m/z: calcd for C₂₀H₂₇N₂NaO₇: 448.1584 [M + Na]⁺; found 448.1592. C₂₀H₂₇N₂O₇ (425.43): calcd. C 56.46, H 6.40, N 3.29; found C 56.40, H 6.30, N 3.32.
2-Hydroxyethyl 2,3,4,6-Tetra-O-methyl-β-D-glucopyranoside (11S). A solution of the olefin 9S (676 mg, 2.4 mmol) in dry CH₂Cl₂/MeOH (1:1) (100 mL) was cooled to −78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was heated to 0 °C. Afterwards, NaBH₄ (575 mg, 15.2 mmol) was slowly added and the solution stirred for 30 min at room temperature. The reaction mixture was then stirred with an excess of solid NH₄Cl, filtered and concentrated in vacuo. Column chromatography of the residue (EtOAc) gave 11S (490 mg, 1.75 mmol, 73%) as a colourless oil. [α]D −4.6 (c = 0.37, in CHCl₃). ¹H NMR: δ = 3.00 (br s, 1H), 3.03 (dd, J = 7.7, 7.7 Hz, 1H), 3.10 (dd, J = 9.5, 9.5 Hz, 1H), 3.17 (dd, J = 9.0, 9.0 Hz, 1H), 3.34 (dd, J = 9.8, 5.8, 2.1 Hz, 1H), 3.39 (s, 3H), 3.52 (s, 3H), 3.53 (dd, J = 10.6, 6.1 Hz, 1H), 3.59 (s, 3H), 3.62 (s, 3H), 3.63 (m, 1H), 3.68 (dd, J = 12.2, 5.0, 2.4 Hz, 1H), 3.75 (dd, J = 12.4, 6.6, 2.4 Hz, 1H), 3.82 (dd, J = J = 11.7, 6.6, 2.4 Hz, 1H), 3.93 (dd, J = 11.6, 5.3, 2.4 Hz, 1H), 4.26 (d, J = 7.7 Hz, 1H) ppm. ¹³C NMR: δ = 59.6 (CH₃), 60.7 (CH₃), 60.9 (CH₃), 61.1 (CH₃), 62.9 (CH₂), 71.8 (CH₂), 74.0 (CH₂), 74.6 (CH), 80.0 (CH), 84.0 (CH), 86.8 (CH), 104.3 (CH) ppm. IR (CCl₄): ν = 3507, 2934, 1088 cm⁻¹. MS (70 eV, EI): m/z (%) = 279 (7) [M − H]⁺, 101 (100). HRMS (EI): m/z: calcd for C₁₂H₂₃O₇ 279.1444 [M − H]⁺; found 279.1436. C₁₂H₂₄O₇ (280.31): C 51.42, H 8.63; found C 51.35, H 8.69.

2-O-Phthalimidoethyl 2,3,4,6-Tetra-O-methyl-β-D-glucopyranoside (17). Phthalimide 17 prepared from alcohol 11S, was obtained as a colourless oil in 84% yield. [α]D −17.4 (c = 0.50, in CHCl₃). ¹H NMR: δ = 2.93 (dd, J = 8.4, 8.4 Hz, 1H), 3.11 (dd, J = 9.3, 9.3 Hz, 1H), 3.16 (dd, J = 8.7, 8.7 Hz, 1H), 3.28 (m, 1H), 3.40 (s, 3H), 3.50 (s, 3H), 3.52 (s, 3H), 3.55 (dd, J = 10.6, 4.5 Hz, 1H), 3.60 (s, 3H), 3.61 (m, 1H), 3.95 (dd, J = 12.2, 7.2, 3.7 Hz, 1H), 4.17 (m, 1H), 4.33 (d, J = 7.7 Hz, 1H), 4.39–4.44 (m, 2H), 7.76–7.84 (m, 4H) ppm. ¹³C NMR: δ = 59.6 (CH₃), 60.6 (CH₃), 60.7 (CH₃), 61.0 (CH₃), 67.5 (CH₂), 71.6 (CH₂), 74.8 (CH), 77.4 (CH₂), 79.6 (CH), 83.9 (CH), 86.5 (CH), 103.7 (CH), 123.8 (2 × CH), 129.3 (2 × C), 134.8 (2 × CH), 163.8 (2 × C) ppm. IR (CCl₄): ν = 2933, 1794, 1740, 1105 cm⁻¹. MS (70 eV, EI): m/z (%) = 426 (5) [M + H]⁺, 425 (3) [M⁺], 101
Methyl 2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-O-methyl-6-O-phthalimido-α-D-galactopyranoside (21). Following the general procedure, the alcohol 12S gave after column chromatography (hexanes–EtOAc, 80:20) the phthalimide 21 (84%) as an amorphous solid: [α]D = +17.5 (c = 0.24, in CHCl3). 1H NMR: (500 MHz) δ = 1.15 (d, J = 6.3 Hz, 3H), 1.97 (s, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 3.44 (s, 3H), 3.48 (s, 3H), 3.52 (s, 3H), 3.59 (dd, J = 10.1, 2.7 Hz, 1H), 3.66 (dd, J = 10.1, 3.5 Hz, 1H), 3.95 (dddd, J = 9.9, 6.3, 6.3, 6.3 Hz, 1H), 4.13 (dddd, J = 6.1, 6.1, 0 Hz, 1H), 4.33 (dd, J = 11.1, 5.9 Hz, 1H), 4.36 (dd, J = 11.1, 6.2 Hz, 1H), 4.40 (dd, J = 1.1, 0 Hz, 1H), 4.87 (d, J = 3.5 Hz, 1H), 5.05 (dd, J = 9.9, 9.9 Hz, 1H), 5.07 (d, J = 1.5 Hz, 1H), 5.29 (d, J = 10.1, 3.3 Hz, 1H), 5.50 (dd, J = 3.0, 2.1 Hz, 1H), 7.74–7.78 (m, 2H), 7.82–7.86 (m, 2H) ppm. 13C NMR: (100.6 MHz): δ = 17.3 (CH3), 20.7 (CH3), 20.8 (CH3), 20.9 (CH3), 55.8 (CH3), 58.6 (CH3), 59.3 (CH3), 67.3 (CH), 67.6 (CH), 69.1 (CH), 69.9 (CH), 70.8 (CH), 75.0 (CH), 77.4 (CH2), 77.6 (CH), 79.6 (CH), 98.4 (CH), 99.3 (CH), 123.6 (2 × CH), 128.8 (2 × C), 134.6 (2 × CH), 163.5 (2 × C), 169.8 (C), 169.9 (C), 170.0 (C) ppm. IR (film): ν = 2939, 2835, 1791, 1735, 1372, 1225 cm⁻¹. MS (FAB): m/z (%) = 663 (3) [M + Na + H]+, 662 (9) [M + Na]+, 55 (100). HRMS (FAB): m/z: calcd for C29H38NNaO15 663.2139 [M + Na + H]+; found 663.2166. C29H37NO15 (639.60): C 54.46, H 5.83, N 2.19; found C 54.10, H 5.78, N 2.58.

Methyl 2,3,4-Tri-O-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-O-methyl-6-O-phthalimido-α-D-galactopyranoside (18). Following the general procedure, the precursor 13S gave after column chromatography (hexanes–EtOAc, 1:1) phthalimide 18 (82%) as a white foam: [α]D = +17.5 (c = 0.12, in CHCl3). 1H NMR: δ = 1.21 (d, J = 6.1 Hz, 3H), 3.08 (dd, J = 9.4, 9.4 Hz, 1H), 3.42 (dd, J =

9.3, 3.2 Hz, 1H), 3.45 (s, 3H), 3.47 (s, 3H), 3.48 (s, 3H), 3.50 (s, 3H), 3.51 (s, 6H), 3.54 (m, 1H), 3.56 (dd, \( J = 9.3, 2.9 \) Hz, 1H), 3.61 (dd, \( J = 10.1, 2.6 \) Hz, 1H), 3.71 (dd, \( J = 3.4, 2.1 \) Hz, 1H), 4.15 (ddd, \( J = 5.6, 5.6, 0 \) Hz, 1H), 4.31 (m, 1H), 4.33 (d, \( J = 5.6 \) Hz, 2H), 4.90 (d, \( J = 3.2 \) Hz, 1H), 5.15 (d, \( J = 1.9 \) Hz, 1H), 7.73–7.77 (m, 2H), 7.81–7.85 (m, 2H) ppm. \(^{13}\)C NMR: \( \delta = 17.6 \) (CH(3)), 55.7 (CH(3)), 57.6 (CH(3)), 58.5 (2 × CH(3)), 58.7 (CH(3)), 60.7 (CH(3)), 68.2 (CH), 68.8 (CH), 74.0 (CH), 77.4 (CH), 77.7 (CH), 78.3 (CH(2)), 80.0 (CH), 80.6 (CH), 81.8 (CH), 98.0 (CH), 98.5 (CH), 123.6 (2 × CH), 128.9 (2 × C), 134.5 (2 × CH), 163.4 (2 × C) ppm. IR \( \nu = 2931, 1793, 1106 \) cm\(^{-1} \). MS (70 eV, EI): \( m/z \) (%) = 554 (4) [M – H]\(^+\), 492 (100). HRMS (EI): \( m/z \): calcd for \( C_{26}H_{35}NO_{12} \): 554.2238 [M – H]\(^+\); found 554.2216. \( C_{26}H_{37}NO_{12} \) (555.57): C 56.21, H 6.71, N 2.52; found C 56.40, H 6.98, N 2.40.

Methyl 6-Deoxy-2,3,4-tri-O-methyl-\( \alpha \)-D-talopyranosyl-(1→4)-2,3-di-O-methyl-6-\( \alpha \)-phthalimido-\( \alpha \)-D-glucopyranoside (25). Following the general procedure, precursor \( 14S^{[4]} \) gave after column chromatography (Et\(_2\)O–EtOAc, 9:1) phthalimide \( 25 \) (45%) as a white foam: [\( \alpha \)]\(_D\) = +89.6 (c = 0.43, in CHCl\(_3\)). \(^1\)H NMR: \( \delta = 1.19 \) (d, \( J = 6.5 \) Hz, 3H), 3.25 (dd, \( J = 9.5, 3.5 \) Hz, 1H), 3.35 (m, 1H), 3.42 (dd, \( J = 3.5, 3.5 \) Hz, 1H), 3.45 (s, 3H), 3.46 (m, 1H), 3.46 (s, 3H), 3.48 (s, 3H), 3.49 (s, 3H), 3.52 (s, 3H), 3.53 (dd, \( J = 9.5, 9.5 \) Hz, 1H), 3.57 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.60 (s, 3H), 3.89 (ddddd, \( J = 6.5, 6.5, 6.5, 1.5 \) Hz, 1H), 3.93 (dddd, \( J = 9.0, 7.0, 2.0 \) Hz, 1H), 4.36 (dd, \( J = 11.5, 6.5 \) Hz, 1H), 4.42 (dd, \( J = 11.0, 2.0 \) Hz, 1H), 4.80 (d, \( J = 3.5 \) Hz, 1H), 5.26 (d, \( J = 1.5 \) Hz, 1H), 7.72–7.76 (m, 2H), 7.80–7.83 (m, 2H) ppm. \(^{13}\)C NMR: \( \delta = 16.5 \) (CH(3)), 55.6 (CH(3)), 56.6 (CH(3)), 58.7 (CH(3)), 59.1 (CH(3)), 60.9 (CH(3)), 61.4 (CH(3)), 67.7 (CH), 69.1 (CH), 76.9 (CH), 77.2 (CH), 77.3 (CH), 77.8 (CH(2)), 78.0 (CH), 81.9 (CH), 82.8 (CH), 97.2 (CH), 99.7 (CH), 123.5 (2 × CH), 128.8 (2 × C), 134.5 (2 × CH), 163.2 (2 × C) ppm. IR \( \nu = 1789, 1734 \) cm\(^{-1} \). MS (ESI\(^+\)): \( m/z \) (%) = 578 (100) [M\(^+\) + Na]. HRMS (ESI\(^+\)): \( m/z \): calcd for \( C_{26}H_{37}N\text{NaO}_{12} \): 578.2213; found 578.2230. \( C_{26}H_{37}N\text{NaO}_{12} \) (555.57): C 56.21, H 6.71, N 2.52; found C 56.02, H 6.92, N 2.35.
Methyl 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-O-acetyl-6-O-phthalimido-β-D-glucopyranoside (27). Following the general procedure, precursor 15S\(^{[4]}\) gave after column chromatography (hexanes–Et\(_2\)O, 3:7) the phthalimide 27 (76%) as a white foam: \([\alpha]_D^\text{\circ}=+76.6 \, (c = 0.32, \text{ in CHCl}_3)\). \(^1\)H NMR: \(\delta = 1.98 \, (s, 3H), 1.99 \, (s, 3H), 2.00 \, (s, 3H), 2.03 \, (s, 3H), 2.03 \, (s, 3H), 2.08 \, (s, 3H), 3.19 \, (s, 3H), 3.82 \, (ddd, \(J = 9.8, 4.5, 1.6 \, \text{Hz}, 1H), 4.03–4.09 \, (m, 2H), 4.28 \, (dd, \(J = 12.7, 4.5 \, \text{Hz}, 1H), 4.39 \, (dd, \(J = 7.9, 4.5 \, \text{Hz}, 1H), 4.42 \, (d, \(J = 9.0 \, \text{Hz}, 1H), 4.46 \, (dd, \(J = 13.0, 4.8 \, \text{Hz}, 1H), 4.58 \, (dd, \(J = 13.0, 1.6 \, \text{Hz}, 1H), 4.80 \, (dd, \(J = 9.3, 7.7 \, \text{Hz}, 1H), 4.87 \, (dd, \(J = 10.6, 4.0 \, \text{Hz}, 1H), 5.03 \, (dd, \(J = 9.8, 9.8 \, \text{Hz}, 1H), 5.24 \, (dd, \(J = 9.0, 9.0 \, \text{Hz}, 1H), 5.35 \, (dd, \(J = 10.6, 9.8 \, \text{Hz}, 1H), 5.45 \, (d, \(J = 4.0 \, \text{Hz}, 1H), 7.71–7.75 \, (m, 2H), 7.79–7.83 \, (m, 2H) \, \text{ppm}. \(^{13}\)C NMR: \(\delta = 20.5 \, (\text{CH}_3), 20.56 \, (2 \times \text{CH}_3), 20.62 \, (2 \times \text{CH}_3), 20.9 \, (\text{CH}_3), 56.3 \, (\text{CH}_3), 61.9 \, (\text{CH}_2), 68.1 \, (\text{CH}), 68.5 \, (\text{CH}), 69.5 \, (\text{CH}), 70.1 \, (\text{CH}), 71.7 \, (\text{CH}), 71.8 \, (\text{CH}), 73.8 \, (\text{CH}), 75.2 \, (\text{CH}), 75.4 \, (\text{CH}_2), 95.5 \, (\text{CH}), 101.0 \, (\text{CH}), 123.5 \, (2 \times \text{CH}), 128.8 \, (2 \times \text{C}), 134.5 \, (2 \times \text{CH}), 163.1 \, (2 \times \text{C}), 169.5 \, (\text{C}), 169.6 \, (\text{C}), 169.9 \, (\text{C}), 170.2 \, (\text{C}), 170.4 \, (\text{C}), 170.6 \, (\text{C}) \, \text{ppm}. \) IR: \(\nu = 1746 \, \text{cm}^{-1}. \) MS (70 eV, EI): \(m/z \, (\%) = 722 \, (<1) \, [\text{M} \rightarrow \text{CH}_3\text{O}]^+, 169 \, (100). \) HRMS (EI): \(m/z\): calcd for C\(_{32}\)H\(_{38}\)N\(_2\)O\(_{18}\): 722.1932 [M – CH\(_3\)O]\(^+\); found 722.1902. C\(_{33}\)H\(_{39}\)NO\(_{19}\)(753.66): C 52.59, H 5.22, N 1.86; found C 52.70, H 5.24, N 1.99.

\[\begin{align*}
&\text{Methyl 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-O-methyl-6-O-phthalimido-β-D-glucopyranoside (29). Following the general procedure, precursor 16S\(^{[3]}\) gave after column chromatography (benzene–EtOAc, 6:4) the phthalimide 29 (82%) as a syrup: \([\alpha]_D^\text{\circ}=+88.0 \, (c = 2.60, \text{ in CHCl}_3)\). \(^1\)H NMR: (500 MHz) \(\delta = 2.98 \, (dd, \(J = 8.7, 8.7 \, \text{Hz}, 1H), 3.15 \, (dd, \(J = 9.8, 3.7 \, \text{Hz}, 1H), 3.19 \, (dd, \(J = 9.7, 9.7 \, \text{Hz}, 1H), 3.31 \, (s, 3H), 3.34 \, (s, 3H), 3.37 \, (dd, \(J = 9.0, 9.0 \, \text{Hz}, 1H), 3.37 \, (dd, \(J = 9.0, 9.0 \, \text{Hz}, 1H), 3.50 \, (s, 3H), 3.51 \, (s, 3H), 3.51 \, (s, 3H), 3.54 \, (m, 4H), 3.55 \, (s, 3H), 3.59 \, (s, 3H), 3.71 \, (dd, \(J = 9.0, 9.0 \, \text{Hz}, 1H), 3.76 \, (dd, \(J = 10.0, 6.5 \, \text{Hz}, 1H), 4.14 \, (d, \(J = 7.7 \, \text{Hz}, 1H), 4.30 \, (dd, \(J = 12.5, 6.3 \, \text{Hz}, 1H), 4.51 \, (d, \(J = 12.5 \, \text{Hz}, 1H), 5.49 \, (d, \(J = 3.9 \, \text{Hz}, 1H), 7.7–7.73 \, (m, 2H), 7.77–7.81 \, (m, 2H) \, \text{ppm}. \(^{13}\)C NMR: (125.7 MHz) \(\delta = 56.7 \, (\text{CH}_3), 59.1 \, (\text{CH}_3), 59.4 \, (\text{CH}_3), 59.7 \, (\text{CH}_3), 60.1 \, (\text{CH}_3), 60.3 \, (\text{CH}_3), 60.7 \, (\text{CH}_3), 70.7 \, (\text{CH}_2), 71.0 \, (\text{CH}), 73.5 \, (\text{CH}), 73.6 \, (\text{CH}), 76.8 \, (\text{CH}_2), 79.1 \, (\text{CH}), 81.5 \, (\text{CH}), 83.0 \, (\text{CH}), 83.5 \, (\text{CH}), 85.7 \, (\text{CH}), 97.1 \, (\text{CH}), 103.8 \, (\text{CH}), 123.3 \, (2 \times \text{CH}), 128.9 \, (2 \times \text{C}), 134.3 \, (2 \times \text{CH}), 163.3 \, (2 \times \text{C}) \, \text{ppm}. IR (film): \(\nu = 1734 \, \text{cm}^{-1}. \) MS (70 eV, EI): \(m/z \, (\%) = 586 \, (<1) \, [\text{M} + \text{H}]^+, 410 \, (6). \) HRMS (EI): \(m/z\): calcd for C\(_{27}\)H\(_{40}\)NO\(_{13}\): 586.2499 [M + H]\(^+\); found 586.2490. C\(_{27}\)H\(_{39}\)NO\(_{13}\)(585.60): C 55.38, H 6.71, N 2.39; found C 55.46, H 6.67, N 2.30.\]
Methyl 2,3,4-Tri-O-acetyl-α-D-lyxopyranosyl-(1→4)-2,3-di-O-methyl-α-D-glucopyranoside (19S). To a solution of 2,3,4-tri-O-acetyl-1-O-2,2,2-trichloroethanimidoyl-α-D-lyxopyranose (17S)\(^5\) (664 mg, 1.58 mmol) and methyl 6-O-tert-butylidiphenyl)silyl-2,3-di-O-methyl-α-D-glucopyranoside (18S)\(^6\) (331 mg, 0.72 mmol) in dry CH\(_2\)Cl\(_2\) (14.5 mL) containing molecular sieves 3Å (241 mg) was added, at 0 °C, TMSOTf (6.5 μL, 0.036 mmol) and the mixture was stirred at room temperature for 1.5 h. Then the reaction mixture was poured into a saturated solution of NaHCO\(_3\) and extracted with CH\(_2\)Cl\(_2\). The organic layers were washed with brine, dried over Na\(_2\)SO\(_4\) anhydrous and concentrated under reduced pressure. To the residue in dry THF (18 mL) was added dropwise a 1M solution of Bu\(_4\)NF/THF (2.88 mL, 2.88 mmol) and the mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes–EtOAc, 1:1) to give the alcohol 19S (264 mg, 0.52 mmol, 73%) as a colourless oil: [α]\(_D\) = +160.0 (c = 0.03, in CHCl\(_3\)). \(^1\)H NMR: \(\delta = 2.01\) (s, 3H), 2.03 (s, 6H), 2.37 (br s, 1H), 3.15 (dd, \(J = 9.1, 3.3\) Hz, 1H), 3.37 (s, 3H), 3.45 (s, 3H), 3.49–3.57 (m, 4H), 3.55 (s, 3H), 3.69–3.83 (m, 2H), 3.88 (dd, \(J = 11.8, 4.1\) Hz, 1H), 4.77 (d, \(J = 3.4\) Hz, 1H), 5.00 (m, 1H), 5.11 (br s, 2H), 5.27 (d, \(J = 5.3\) Hz, 1H) ppm. \(^13\)C NMR: \(\delta = 20.5\) (CH\(_3\)), 20.6 (CH\(_3\)), 20.7 (CH\(_3\)), 55.1 (CH\(_3\)), 58.8 (CH\(_3\)), 61.0 (CH\(_3\)), 61.7 (2 × CH\(_2\)), 67.3 (CH), 68.2 (CH), 69.2 (CH), 69.9 (CH), 75.6 (CH), 82.2 (CH), 83.0 (CH), 97.3 (CH), 99.0 (CH), 169.5 (C), 169.6 (C), 169.8 (C) ppm. IR (CCl\(_4\)): \(\nu = 3530, 2933, 1753, 1123\) cm\(^{-1}\). MS (ESI\(^+\)): \(mlz\) (%): 503 (100) [M + Na]\(^+\). HRMS (ESI\(^+\)): \(mlz\): calcd for C\(_{20}\)H\(_{32}\)NaO\(_{13}\): 503.1741 [M + Na]\(^+\); found 503.1741. C\(_{20}\)H\(_{32}\)O\(_{13}\) (480.46): calcd. C 50.00, H 6.71; found C 50.13, H 7.01.

Methyl 2,3,4-Tri-O-acetyl-α-D-lyxopyranosyl-(1→4)-2,3-di-O-methyl-6-O-phtalimido-α-D-glucopyranoside (19S). Following the general procedure, precursor 19S gave after column

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chromatography (Et₂O) the phthalimide 32 as a colourless oil (91%): [α]D = +77.1 (c = 0.27, in CHCl₃). ¹H NMR: δ = 2.01 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 3.23 (dd, J = 9.5, 3.4 Hz, 1H), 3.43 (s, 3H), 3.48 (s, 3H), 3.56 (dd, J = 9.0, 9.0 Hz, 1H), 3.59 (s, 3H), 3.67 (dd, J = 11.7, 7.9 Hz, 1H), 3.78–3.90 (m, 3H), 4.40 (dd, J = 11.4, 4.8 Hz, 1H), 4.48 (dd, J = 11.4, 1.6 Hz, 1H), 4.76 (d, J = 3.4 Hz, 1H), 5.06 (ddd, J = 8.2, 8.2, 4.8 Hz, 1H), 5.15 (d, J = 3.7 Hz, 1H), 5.20 (dd, J = 3.6, 3.6 Hz, 1H), 5.29 (dd, J = 8.3, 3.3 Hz, 1H), 7.71–7.81 (m, 4H) ppm. ¹³C NMR: δ = 20.6 (CH₃), 20.7 (2 × CH₃), 55.6 (CH₃), 58.8 (CH₃), 61.0 (CH₃), 61.2 (CH₂), 67.2 (CH), 68.4 (CH), 69.1 (CH), 69.4 (CH), 76.7 (CH₂), 76.7 (CH), 81.8 (CH), 82.7 (CH), 97.4 (CH), 99.4 (CH), 123.4 (2 × CH), 128.9 (2 × C), 134.4 (2 × CH), 163.1 (2 × C), 169.6 (C), 169.7 (C), 169.9 (C) ppm. IR (CCl₄): ν = 2979, 1746, 1223 cm⁻¹. MS (ESI⁺): m/z (%) = 648 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C₂₈H₃₅NNaO₁₅: 648.1904 [M + Na]⁺; found 648.1904. C₂₈H₃₅NO₁₅ (625.57): calcd. C 53.76, H 5.64, N 2.24; found C 53.69, H 5.77, N 2.33.

Methyl 2,3,5-Tri-O-acetyl-α-D-arabinofuranosyl-(1→4)-6-O-tert-butylidiphenyl silyl-2,3-di-O-methyl-α-D-glucopyranoside (22S). To a solution of trichloroacetimidate 20S[^1] (425 mg, 0.98 mmol) and methyl 6-O-tert-butylidiphenylsilyl-2,3-di-O-methyl-α-D-glucopyranoside (21S)[^6] (101 mg, 0.22 mmol) in dry CH₂Cl₂ (6 mL) containing molecular sieves 3Å (425 mg) was added dropwise and at 0 °C, a 0.1M solution of TMSOTf/CH₂Cl₂ (55 µL, 5.5 µmol) and the mixture was stirred at that temperature for 1.5 h. Then the reaction mixture was poured into a saturated solution of NaHCO₃ and extracted with CH₂Cl₂. The organic layers were washed with brine, dried over Na₂SO₄ anhydrous and concentrated under reduced pressure. The residue was purified in column chromatography (hexanes–EtOAc, 7:3) to give the disaccharide 22S (160 mg, 0.22 mmol, 99%) as a colourless oil: [α]D = +83.6 (c = 0.42, in CHCl₃). ¹H NMR: δ = 1.05 (s, 9H), 1.96 (s, 3H), 1.97 (s, 3H), 2.07 (s, 3H), 3.19 (dd, J = 9.5, 3.7 Hz, 1H), 3.43 (s, 3H), 3.52 (s, 3H), 3.54–3.59 (m, 2H), 3.55 (s, 3H), 3.68 (m, 1H), 3.79 (dd, J = 11.1, 6.1 Hz, 1H), 3.83 (m, 1H), 3.86 (dd, J = 11.1, 2.1 Hz, 1H), 3.96 (dd, J = 11.9, 5.0 Hz, 1H), 4.07 (dd, J = 11.9, 4.0 Hz, 1H), 4.84 (d, J = 3.7 Hz, 1H), 4.92 (dd, J = 4.8, 1.6, 0.5 Hz, 1H), 5.07 (dd, J = 1.6, 0.5 Hz, 1H), 5.45 (s, 1H), 7.33–7.42 (m, 6H), 7.68–7.70 (m, 4H) ppm. ¹³C NMR: δ = 19.2 (C), 20.59 (CH₃), 20.62 (CH₃), 20.7 (CH₃), 26.7 (3 × CH₃), 54.8

Methyl 2,3,5-Tri-O-acetyl-α-D-arabinofuranosyl-(1→4)-2,3-di-O-methyl-α-D-glucopyranoside (23S). To a solution of disaccharide 22S (224 mg, 0.31 mmol) in dry THF (9 mL) was added dropwise a 1M solution of Bu₄NF/THF (0.77 mL, 0.77 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes–EtOAc, 3:7) to give the alcohol 23S (97.2 mg, 0.20 mmol, 65%) as a colourless oil: [α]D = +102.8 (c = 0.14, in CHCl₃). ¹H NMR: δ = 2.10 (s, 3H), 2.11 (s, 3H), 2.11 (s, 3H), 2.30 (br s, 1H), 3.21 (dd, J = 9.1, 3.5 Hz, 1H), 3.42 (s, 3H), 3.51 (s, 3H), 3.57 (s, 3H), 3.57–3.67 (m, 3H), 3.74–3.81 (m, 2H), 4.19 (dd, J = 11.4, 6.3 Hz, 1H), 4.31 (ddd, J = 6.1, 4.5, 4.5 Hz, 1H), 4.37 (dd, J = 11.4, 3.8 Hz, 1H), 4.82 (d, J = 3.5 Hz, 1H), 5.01 (dd, J = 4.6, 1.8 Hz, 1H), 5.17 (dd, J = 2.0, 0.8 Hz, 1H), 5.49 (s, 1H) ppm. ¹³C NMR: δ = 20.6 (CH₃), 20.6 (CH₃), 20.7 (CH₃), 55.2 (CH₃), 59.0 (CH₃), 61.0 (CH₃), 61.7 (CH₂), 63.4 (CH₂), 70.0 (CH), 74.2 (CH), 77.6 (CH), 80.7 (CH), 81.1 (CH), 82.2 (CH), 83.2 (CH), 97.6 (CH), 107.0 (CH), 169.3 (C), 169.9 (C), 170.6 (C) ppm. IR (CCl₄): ν = 3450, 2966, 1750, 1228 cm⁻¹. MS (ESI⁺): m/z (%) = 503 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C₂₀H₃₂NaO₁₃ 503.1741 [M + Na]⁺; found 503.1743. C₂₀H₃₂O₁₃ (480.46): C 50.00, H 6.71; found C 50.22, H 6.78.
Methyl 2,3,5-Tri-O-acetyl-α-D-arabinofuranosyl-(1→4)-2,3-di-O-methyl-6-O-phthalimido-α-D-glucopyranoside (35). Following the general procedure, precursor 23S gave after column chromatography (hexanes-EtOAc, 1:1) the phthalimide 35 as an amorphous white solid (76%): [α]D = +64.0 (c = 0.30, in CHCl₃). ¹H NMR: δ= 2.05 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 3.25 (dd, J = 9.5, 3.4 Hz, 1H), 3.47 (s, 3H), 3.51 (s, 3H), 3.57 (s, 3H), 3.62 (dd, J = 9.5, 8.7 Hz, 1H), 3.78 (dd, J = 10.1, 8.7 Hz, 1H), 3.93 (ddd, J = 10.1, 5.6, 1.6 Hz, 1H), 4.17 (m, 1H), 4.31–4.36 (m, 2H), 4.40 (dd, J = 11.1, 5.6 Hz, 1H), 4.46 (dd, J = 11.1, 1.9 Hz, 1H), 4.80 (d, J = 3.4 Hz, 1H), 5.00 (ddd, J = 4.8, 1.9, 0.8 Hz, 1H), 5.17 (dd, J = 1.9, 0.8 Hz, 1H), 5.52 (s, 1H), 7.73–7.77 (m, 2H), 7.81–7.85 (m, 2H) ppm. ¹³C NMR: δ= 20.6 (3 × CH₃), 55.6 (CH₃), 58.9 (CH₃), 60.8 (CH₃), 63.3 (CH₂), 68.9 (CH), 73.9 (CH), 77.0 (CH), 77.1 (CH₂), 81.0 (2 × CH), 81.7 (CH), 83.0 (CH), 97.4 (CH), 106.6 (CH), 123.4 (2 × CH), 128.9 (2 × C), 134.4 (2 × CH), 163.1 (2 × C), 169.3 (C), 170.1 (C), 170.5 (C) ppm. IR (CCl₄): ν = 2929, 2847, 1792, 1732, 1369, 1224 cm⁻¹. MS (ESI⁺): m/z (%) = 648 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calc for C₆H₃₅N+NaO₁₅: 648.1904 [M + Na]⁺; found 648.1896. C₂₈H₃₅N₅O₁₅ (625.58): C 53.76, H 5.64, N 2.24; found C 53.59, H 5.47, N 2.58.

Methyl 2,3,5-Tri-O-methyl-α-D-arabinofuranosyl-(1→4)-6-O-tert-butylidiphenylsilyl-2,3-di-O-methyl-α-D-glucopyranoside (25S). To a solution of compound 24S (450 mg, 0.63 mmol) in MeOH (30 mL) was added K₂CO₃ (258 mg, 1.88 mmol) and the mixture was stirred at room temperature for 2 h, then neutralized with Dowex (50 × 8) H⁺ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue in dry DMF (7.5 mL) was added NaH, 55% dispersion in mineral oil, (164 mg, 3.76 mmol) and the mixture was stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (293 μL, 4.70 mmol) was added and stirring continued at this temperature for 3 h. Excess reagent was destroyed by addition of MeOH and the mixture was concentrated under high vacuum. Column chromatography (hexanes–EtOAc, 7:3) of the residue afforded 25S (278 mg, 0.44 mmol, 70%) as a colourless oil: [α]D =
+98.2 (c = 0.51, in CHCl₃). ¹H NMR: δ = 1.05 (s, 9H), 3.18 (dd, J = 10.6, 4.2 Hz, 1H), 3.20 (dd, J = 9.5, 3.7 Hz, 1H), 3.23 (s, 3H), 3.25 (dd, J = 10.6, 4.5 Hz, 1H), 3.30 (s, 3H), 3.40 (s, 3H), 3.44 (s, 3H), 3.45 (dd, J = 9.3, 9.3 Hz, 1H), 3.51 (s, 3H), 3.54 (dd, J = 6.1, 2.6 Hz, 1H), 3.57 (dd, J = 9.2, 9.2 Hz, 1H), 3.57 (s, 3H), 3.67 (dd, J = 2.6, 0.8 Hz, 1H), 3.68–3.74 (m, 2H), 3.78 (dd, J = 10.9, 7.2 Hz, 1H), 3.96 (dd, J = 10.9, 1.6 Hz, 1H), 4.84 (d, J = 3.7 Hz, 1H), 5.33 (s, 1H), 7.33–7.42 (m, 6H), 7.68–7.73 (m, 4H) ppm. ¹³C NMR: δ = 19.3 (C), 26.8 (3 × CH₃), 54.7 (CH₃), 57.5 (CH₃), 57.8 (CH₃), 58.6 (CH₃), 59.1 (CH₃), 60.8 (CH₃), 63.7 (CH₂), 71.2 (CH), 71.9 (CH₂), 74.7 (CH), 80.9 (CH), 82.5 (CH), 83.5 (CH), 85.5 (CH), 90.0 (CH), 96.7 (CH), 106.5 (CH), 127.5 (4 × CH), 129.4 (CH), 129.5 (CH), 133.8 (C), 133.9 (C), 135.68 (2 × CH), 135.71 (2 × CH) ppm. IR (CCl₄): ν = 2931, 2827, 1363, 1112 cm⁻¹. MS (ESI⁺): m/z (%) = 657 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C₃₃H₅₀NaO₁₀Si: 657.3071 [M + Na]⁺; found 657.3062. C₃₃H₅₀O₁₀Si (638.83): C 62.43, H 7.94; found C 62.34, H 7.96.

**Methyl 2,3,5-Tri-α-D-arabinofuranosyl-(1→4)-2,3-di-O-methyl-α-D-glucopyranoside (26S).** To a solution of compound 25S (280 mg, 0.44 mmol) in dry THF (11.4 mL) was added a 1M solution of TBAF/THF (1.11 mL, 1.10 mmol) and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (EtOAc) to give the alcohol 26S (174 mg, 0.44 mmol, 99%) as a colourless oil: [α]D = +160.8 (c = 0.37, in CHCl₃). ¹H NMR: δ = 3.23 (dd, J = 9.3, 3.7 Hz, 1H), 3.39 (s, 3H), 3.39 (s, 3H), 3.39 (s, 3H), 3.43 (s, 3H), 3.49 (s, 3H), 3.49 (dd, J = 10.6, 5.8 Hz, 1H), 3.53 (dd, J = 10.6, 4.8 Hz, 1H), 3.54–3.59 (m, 2H), 3.57 (dd, J = 9.3, 9.3 Hz, 1H), 3.58 (s, 3H), 3.65 (dd, J = 9.8, 9.1 Hz, 1H), 3.72 (br d, J = 12.7 Hz, 1H), 3.75 (dd, J = 2.9, 1.3 Hz, 1H), 3.84 (br d, J = 12.2 Hz, 1H), 4.12 (ddd, J = 6.1, 6.1, 4.5 Hz, 1H), 4.82 (d, J = 3.7 Hz, 1H), 5.41 (s, 1H) ppm. 1H from OH is missing. ¹³C NMR: δ = 55.1 (CH₃), 57.6 (CH₃), 58.0 (CH₃), 58.7 (CH₃), 59.3 (CH₃), 60.9 (CH₃), 61.7 (CH₂), 70.4 (CH), 72.6 (CH₂), 74.8 (CH), 81.3 (CH), 82.4 (CH), 83.1 (CH), 85.7 (CH), 89.6 (CH), 97.4 (CH), 107.2 (CH) ppm. IR (CCl₄): ν = 3468, 2926, 2830, 1459, 1096, 1051 cm⁻¹. MS (ESI⁺): m/z (%) = 419 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C_{17}H_{32}NaO_{10}: 419.1893 [M + Na]⁺; found 419.1886. C_{17}H_{32}O_{10} (396.43): C 51.51, H 8.14; found C 51.44, H 8.29.
Methyl 2,3,5-Tri-O-methyl-α-D-arabinofuranosyl-(1→4)-2,3-di-O-methyl-6-O-phthalimido-α-D-glucopyranoside (38). Following the general procedure, precursor 26S gave after column chromatography (hexanes-Et2O, 3:7) phthalimide 38 as a colourless oil (90%): [α]D = +108.4 (c = 0.69, in CHCl3). 1H NMR: δ = 3.24 (dd, J = 9.5, 3.4 Hz, 1H), 3.24 (s, 3H), 3.31 (s, 3H), 3.41 (s, 3H), 3.41 (dd, J = 10.9, 5.6 Hz, 1H), 3.45 (dd, J = 10.6, 4.5 Hz, 1H), 3.49 (s, 3H), 3.50 (s, 3H), 3.51 (dd, J = 5.8, 2.1 Hz, 1H), 3.58 (s, 3H), 3.59 (dd, J = 9.5, 9.5 Hz, 1H), 3.61 (dd, J = 10.3, 8.8 Hz, 1H), 3.72 (dd, J = 2.4, 0.8 Hz, 1H), 3.98 (m, 1H), 4.08 (ddd, J = 5.8, 5.8, 4.5 Hz, 1H), 4.38 (dd, J = 11.4, 6.9 Hz, 1H), 4.53 (dd, J = 11.4, 1.6 Hz, 1H), 4.82 (d, J = 3.2 Hz, 1H), 5.36 (s, 1H), 7.71–7.74 (m, 2H), 7.80–7.84 (m, 2H) ppm. 13C NMR: δ = 55.6 (CH3), 57.5 (CH3), 57.8 (CH3), 58.7 (CH3), 59.1 (CH3), 60.8 (CH3), 69.2 (CH), 72.6 (CH2), 74.9 (CH), 77.9 (CH2), 81.1 (CH), 82.0 (CH), 82.9 (CH), 85.8 (CH), 89.7 (CH), 97.3 (CH), 106.9 (CH), 123.4 (2 × CH), 129.1 (2 × C), 134.2 (2 × CH), 163.2 (2 × C) ppm. IR (CCl4): ν = 2933, 2829, 1791, 1733, 1374, 1107 cm⁻¹. MS (ESI⁺): m/z (%) = 564 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C25H35NNaO12 564.2057 [M + Na]⁺; found 564.2053. C25H35NO12 (541.54): C 55.45, H 6.51, N 2.59; found C 55.20, H 6.48, N 2.87.

Methyl 2,3,5,6-Tetra-O-acetyl-β-D-mannofuranosyl-(1→4)-6-O-tert-butyl diphenylsilyl-2,3-di-O-methyl-α-D-glucopyranoside (29S). To a solution of pent-4-enyl 2,3,5,6-tetra-O-acetyl-α-D-mannofuranoside (27S)[8] (1.77 g, 4.25 mmol) and methyl 6-O-tert-butylidiphenylsilyl-2,3-di-O-methyl-α-D-glucopyranoside (28S)[6] (1.90 g, 4.25 mmol) in dry CH2Cl2 (6 mL) were added N-iodosuccinimide (1.24 g, 5.51 mmol) and, at 0 °C, TMSOTf (230 µL, 1.27 mmol) and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was poured into a saturated solution of NaHCO3 and extracted with CH2Cl2. The organic layers were washed with brine, dried over Na2SO4 anhydrous and concentrated under reduced pressure. The residue was purified column

chromatography (hexanes–EtOAc, 8:2) to give the disaccharide 29S (2.02 g, 2.55 mmol, 60%) as an amorphous solid: [α]D = +89.6 (c = 0.24, in CHCl3). 1H NMR: δ = 1.03 (s, 9H), 1.83 (s, 3H), 1.90 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 3.15 (dd, J = 9.7, 3.6 Hz, 1H), 3.33 (dd, J = 10.1, 8.7 Hz, 1H), 3.46 (s, 3H), 3.48–3.55 (m, 2H), 3.49 (s, 3H), 3.51 (s, 3H), 3.60 (dd, J = 8.6, 4.4 Hz, 1H), 3.67 (m, 1H), 3.75 (dd, J = 10.9, 6.9 Hz, 1H), 3.84 (dd, J = 11.1, 1.6 Hz, 1H), 4.30 (dd, J = 12.0, 2.5 Hz, 1H), 4.83 (d, J = 3.4 Hz, 1H), 5.00 (dd, J = 4.9, 3.3 Hz, 1H), 5.09 (dd, J = 6.5, 2.0 Hz, 1H), 5.29 (dd, J = 4.6, 4.6 Hz, 1H), 5.40 (d, J = 3.4 Hz, 1H), 7.35–7.44 (m, 6H), 7.67–7.71 (m, 4H) ppm. 13C NMR: δ = 19.1 (C), 20.2 (2 × CH3), 20.5 (CH3), 20.6 (CH3), 26.6 (3 × CH3), 54.9 (CH3), 58.8 (CH3), 60.9 (CH3), 62.7 (CH2), 63.7 (CH2), 68.1 (CH), 70.6 (CH), 71.4 (CH), 75.7 (CH), 75.9 (2 × CH), 82.1 (CH), 83.2 (CH), 96.9 (CH), 105.6 (CH), 127.7 (4 × CH), 129.6 (2 × CH), 133.4 (2 × C), 135.5 (2 × CH), 135.7 (2 × CH), 169.2 (C), 169.4 (2 × C), 170.3 (C) ppm. IR (CCl4): ν = 2933, 1755, 1229 cm⁻¹. MS (ESI⁺): m/z (%) = 813 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calc for C39H54NaO15Si, 813.3130 [M + Na]⁺; found 813.3109. C39H54O15Si (790.92): C 59.22, H 6.88; found C 59.36, H 6.86.

Methyl 2,3,5,6-Tetra-O-methyl-α-D-mannofuranosyl-(1→4)-6-O-[tert-butyl (diphenyl)silyl]-2,3-di-O-methyl-α-D-glucopyranoside (30S). To a solution of compound 29S (654 mg, 0.83 mmol) in MeOH (27 mL) was added K2CO3 (457 mg, 3.31 mmol) and the mixture was stirred at room temperature for 3 h, then neutralized with Dowex (50 × 8) H⁺ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue in dry acetone (8.3 mL) were added Ag2O (1.53 g, 6.62 mmol) and methyl iodide (412 µL, 6.62 mmol) and the mixture was stirred at room temperature under nitrogen for 24 h. Then the reaction mixture was filtered through celite and concentrated under reduced pressure. Column chromatography (hexanes–EtOAc, 7:3) of the residue afforded the title compound 30S (368 mg, 0.54 mmol, 65%) as a colourless oil: [α]D = +78.7 (c = 0.24, in CHCl3). 1H NMR: δ = 1.03 (s, 9H), 2.99 (dd, J = 10.6, 6.1 Hz, 1H), 3.02 (s, 3H), 3.17 (dd, J = 9.6, 3.7 Hz, 1H), 3.27–3.39 (m, 3H), 3.33 (s, 3H), 3.42–3.58 (m, 3H), 3.44 (s, 3H), 3.46 (s, 3H), 3.47 (s, 3H), 3.50 (s, 3H), 3.55 (s, 3H), 3.66–3.73 (m, 3H), 3.89 (dd, J = 9.5, 0 Hz, 1H), 4.84 (d, J = 3.7 Hz, 1H), 5.30 (d, J = 4.0 Hz, 1H), 7.35–7.43 (m, 6H), 7.69–7.72 (m, 4H) ppm. 13C NMR: δ = 19.2 (C), 26.7 (3 × CH3), 54.9 (CH3), 57.9 (CH3), 58.5 (CH3), 58.7 (CH3), 58.8 (CH3), 59.9 (CH3), 60.8 (CH3), 64.0 (CH2), 71.8 (CH), 72.8 (CH2), 74.8 (CH), 77.2 (CH), 77.9 (CH), 79.8 (CH), 82.3
(CH), 83.4 (CH), 87.0 (CH), 96.9 (CH), 105.9 (CH), 127.6 (4 × CH), 129.5 (2 × CH), 133.6 (2 × C), 135.6 (2 × CH), 135.7 (2 × CH) ppm. IR (CCl₄): ν = 2931, 1107, 1064 cm⁻¹. MS (ESI⁺): m/z (%)

= 701 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcld for C₃₅H₅₄NaO₁₁Si, 701.3333 [M + Na]⁺; found 701.3334. C₃₅H₅₄O₁₁Si (678.88): C 61.92, H 8.02; found C 61.80, H 7.92.
Methyl 2,3,5,6-Tetra-\(O\)-methyl-\(\alpha\)-D-mannofuranosyl-(1→4)-2,3-di-\(O\)-methyl-\(\alpha\)-D-glucopyranoside (31S). To a solution of compound 30S (217 mg, 0.32 mmol) in dry THF (30 mL) was added a 1M solution of TBAF/THF (0.96 mL, 0.96 mmol) and the mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (EtOAc) to give the alcohol 31S (108 mg, 0.24 mmol, 77%) as a colourless oil: [\(\alpha\)]\(D\) = +103.6 (c = 0.11, in CHCl\(_3\)). \(^1\)H NMR: \(\delta\) = 2.99 (br s, 1H), 3.19 (dd, \(J\) = 9.5, 3.7 Hz, 1H), 3.35 (s, 3H), 3.37 (s, 3H), 3.38 (s, 3H), 3.44 (s, 3H), 3.46 (s, 3H), 3.48–3.58 (m, 4H), 3.50 (s, 3H), 3.55 (s, 3H), 3.62–3.65 (m, 3H), 3.70 (dd, \(J\) = 3.7 Hz, 1H), 3.81 (dd, \(J\) = 12.4, 2.9 Hz, 1H), 3.88 (dd, \(J\) = 3.4, 3.4 Hz, 1H), 4.10 (dd, \(J\) = 9.0, 3.2 Hz, 1H), 4.77 (d, \(J\) = 3.4 Hz, 1H), 5.41 (d, \(J\) = 4.0 Hz, 1H) ppm. \(^{13}\)C NMR: \(\delta\) = 54.9 (CH\(_3\)), 57.0 (CH\(_3\)), 58.6 (2 × CH\(_3\)), 59.2 (CH\(_3\)), 60.1 (CH\(_3\)), 60.7 (CH\(_3\)), 60.7 (CH\(_3\)), 69.7 (CH\(_2\)), 70.4 (CH), 74.5 (CH), 76.9 (CH), 77.8 (CH), 79.7 (CH), 82.1 (CH), 83.1 (CH), 87.2 (CH), 97.4 (CH), 107.0 (CH) ppm. IR (CCl\(_4\)): \(\nu\) = 3684, 3512, 2932, 1102 cm\(^{-1}\). MS (ESI\(^+\)): \(m/z\) (%) = 463 (100) [\(M + Na\)]\(^+\). HRMS (ESI\(^+\)): \(m/z\) calcd for C\(_{19}\)H\(_{36}\)NaO\(_{11}\), 463.2155 [\(M + Na\)]\(^+\); found 463.2153. C\(_{19}\)H\(_{36}\)O\(_{11}\) (440.48): C 51.81, H 8.24; found C 52.02, H 8.07.

Methyl 2,3,5,6-Tetra-\(O\)-methyl-\(\alpha\)-D-mannofuranosyl-(1→4)-2,3-di-\(O\)-methyl-6-\(O\)-phthalimido-\(\alpha\)-D-glucopyranoside (42). Following the general procedure, precursor 31S gave after column chromatography (Et\(_2\)O) phthalimide 42 as a white crystalline solid (90%): M. p. 117.2–117.9 °C (\(n\)-hexane-EtOAc). [\(\alpha\)]\(D\) = +127.1 (c = 0.27, in CHCl\(_3\)). \(^1\)H NMR: \(\delta\) = 3.16 (dd, \(J\) = 9.3, 3.4 Hz, 1H), 3.21 (s, 3H), 3.33 (s, 3H), 3.35 (m, 1H), 3.38 (s, 3H), 3.41 (s, 3H), 3.42 (s, 3H), 3.45 (s, 3H), 3.47–3.58 (m, 4H), 3.51 (s, 3H), 3.66 (dd, \(J\) = 4.1, 4.1 Hz, 1H), 3.83 (dd, \(J\) = 3.2, 3.2 Hz, 1H), 3.88 (ddd, \(J\) = 8.2, 8.2, 0 Hz, 1H), 3.97 (dd, \(J\) = 8.7, 3.2 Hz, 1H), 4.30 (dd, \(J\) = 11.7, 6.9 Hz, 1H), 4.39 (d, \(J\) = 3.4 Hz, 1H), 4.69 (d, \(J\) = 3.4 Hz, 1H), 5.33 (d, \(J\) = 4.0 Hz, 1H), 7.65–7.69 (m, 2H), 7.73–7.77 (m, 2H) ppm. \(^{13}\)C NMR: \(\delta\) = 55.4 (CH\(_3\)), 57.2 (CH\(_3\)), 58.5 (CH\(_3\)), 58.6 (CH\(_3\)), 59.0 (CH\(_3\)), 59.9 (CH\(_3\)), 60.5 (CH\(_3\)), 69.2 (CH), 70.7 (CH\(_2\)), 74.9 (CH), 76.9 (CH), 77.1 (CH\(_2\)), 77.6
(CH), 79.7 (CH), 81.5 (CH), 82.8 (CH), 87.4 (CH), 97.2 (CH), 106.6 (CH), 123.2 (2 × CH), 128.9 (2 × C), 134.2 (2 × CH), 163.1 (2 × C) ppm. IR (CCl₄): υ = 1932, 1790, 1738, 1102 cm⁻¹. MS (ESI⁺): m/z (%) = 608 (100) [M + Na]⁺. HRMS (ESI⁺): m/z: calcd for C₂₇H₃₉NNaO₁₃, 608.2319 [M + Na]⁺; found 608.2322. C₂₇H₃₉NNaO₁₃ (585.60): C 55.38, H 6.71, N 2.39; found C 55.56, H 6.43, N 2.44.
\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \]
$^13\text{C NMR (CDCl}_3, 100.6 \text{ MHz)}$
$^1$H NMR (CDCl$_3$, 500 MHz)
$\text{MeO} \quad \text{MeO} \quad \text{MeO} \quad \text{MeO}$

$\text{OH}$

$\text{OMe}$

$\text{OMe}$

$\text{OMe}$

$\text{OMe}$

$\text{OH}$

4

$^{13}\text{C NMR (CDCl}_3, 125.7 \text{ MHz)}$
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
10

$^1$H NMR (CDCl$_3$, 500 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
17

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 125.7 MHz)
NDE interaction between 1'-H with 5-H
1H NMR (CDCl$_3$, 400 MHz)
16

$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}H$ NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 125.7 MHz)
NOE interaction between 4'-H and 6'-Me
$^1$H NMR (CDCl$_3$, 400 MHz)
$\text{OMe}$

$\text{OMe}$

$\text{13C NMR (CDCl}_3$, 100.6 MHz$)$

$\text{20}$
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
NOE interaction between 4'-H and 6'-Me
$^{1}$$^{H}$NMR (CDCl$_3$, 400 MHz)
$\text{AllylO}$

$\text{AcO}$

$\text{OAc}$

$\text{OMe}$

$\text{C NMR (CDCl}_3\text{, 100.6 MHz)}$

$23$
$\text{OMe}$

$\text{OMe}$

$\text{OMe}$

$\text{AcO}$

$\text{AcO}$

$\text{AcO}$

$\text{AcO}$

$\text{24}$

$^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}$
$\text{C NMR (CDCl}_3, 100.6 \text{MHz)}$
$^1$H NMR (CDCl$_3$, 500 MHz)
$\text{δ} \text{ C NMR (CDCl}_3 \text{, 125.7 MHz)}$
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
27

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{17}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^1$H NMR (CDCl$_3$, 100.6 MHz)
NOE interaction between 5-H with 1- and 3-H for the major isomer 5R.
29

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
30

$^1$H NMR (CDCl$_3$, 400 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}H$ NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
1H NMR (CDCl₃, 400 MHz)
32

$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
23S

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)
\[ \text{13C NMR (CDCl}_3, 100.6 \text{ MHz)} \]
36

$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 125.7 MHz)
NOE Interactions between 6'-H and 2'-H
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 125.7 MHz)
NOE correlations between 6'-H and 3'-H
26S

$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (125 MHz, CDCl$_3$)
NOE correlations between 6'-H and 3'-H
$^{1}$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
NOE correlations between 5'-H and 1'-H
$^{1}H$ NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
'H NMR (CDCl₃, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100.6 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)
$\text{MeO} - O - O - \text{MeO} - O - \text{MeO}$

$\text{MeO} - O - \text{MeO}$

$\text{MeO} - O - \text{MeO}$

$\text{MeO} - O - \text{MeO}$

$\text{MeO} - O - \text{MeO}$

$\text{43}$

$^{13}\text{C NMR (CDCl}_3, 100.6\text{ MHz)}$
$^1$H NMR (CDCl$_3$, 400 MHz)
13C NMR (CDCl3, 100.6 MHz)