

Supporting Information
for

Amine-linked diglycosides: Synthesis facilitated by the enhanced reactivity of allylic electrophiles, and glycosidase inhibition assays

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Experimental section; copies of ¹H and ¹³C NMR spectra for new compounds

1. Experimental section
2. Copies of ¹H and ¹³C NMR spectra for new compounds

1. Experimental section

General procedures

Proton nuclear magnetic resonance (¹H) spectra were recorded on Bruker Avance II 500 (500 MHz), Bruker Avance II 400 (400 MHz) or Varian Mercury 400 (400 MHz) spectrometers; multiplicities are quoted as singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), apparent triplet (at), doublet of apparent triplets (dat), quartet (q), and multiplet (m). Carbon nuclear magnetic resonance (¹³C) spectra were recorded on Bruker Avance II 500 (125 MHz), Bruker Avance II 400 (100 MHz) or Varian Mercury 400 (100 MHz) spectrometers. ¹H and ¹³C spectra and ¹³C multiplicities were assigned using COSY, HSQC, DEPT experiments. All chemical shifts are quoted on the δ-scale in parts per million (ppm). Residual

solvent signals or TMS were used as an internal reference. Low- and high-resolution (HRMS) electrospray (ESI) mass spectra were recorded using a Bruker Microtof instrument. Infra-red spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using the thin film method on NaCl plates. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1 dm; concentrations are given in g/100mL. Thin layer chromatography (TLC) was carried out on Merck Kieselgel sheets, pre-coated with 60F₂₅₄ silica. Plates were visualised with UV light and developed using 10% sulfuric acid, or an ammonium molybdate (10% w/v) and cerium(IV) sulfate (2% w/v) solution in 10% sulfuric acid. Flash column chromatography was carried out on silica gel (35–70 μ m, Grace). The palladium catalyst was from Strem and used as supplied. Dichloromethane was distilled from calcium hydride. THF was dried using a solvent purifier by VAC. DMF and acetonitrile were bought anhydrous and used as supplied. Reactions performed under an atmosphere of nitrogen or argon were maintained by an inflated balloon.

Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-*threo*-hex-2-enopyranoside (4)

Galactal **3** (879 mg, 3.23 mmol) was dissolved in acetonitrile (30 mL) under Ar. EtOH (0.37 mL, 6.5 mmol) was added, and the reaction mixture was cooled in an ice-bath. Phosphomolybdic acid (62 mg, 0.032 mmol) was added slowly. The ice-bath was removed and the reaction mixture was stirred at RT for 2 h. After this time, TLC (Pentane–EtOAc, 2:1) indicated the formation of one major (R_f 0.8) and two minor (R_f 0.7, 0.5) products and the consumption of starting material (R_f 0.7). The reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with NaHCO₃ (sat. aq. 2 \times 50 mL), H₂O (50 mL) and brine (50 mL). Each aqueous phase was extracted with CH₂Cl₂ (25 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated to dryness to give a brown oil (863 mg). The crude product was purified by column chromatography (Pentane–EtOAc, 6:1 \rightarrow 4:1) to give the Ferrier product **4** (529 mg, 63%) as an oil, (α : β , 8:1); ¹H NMR: (selected for α anomer) δ = 1.25 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 2.07, 2.08 (2 \times s, 6 H, 2 \times C(O)CH₃), 3.59, 3.84 (dq, J_{gem} 9.6 Hz, J 7.2 Hz, 2 H, OCH₂CH₃), 4.22–4.24 (m, 2 H, 6'-H, 6-H), 4.37 (m, 1 H, 5-H), 5.02 (dd, $J_{3,4}$ 5.2 Hz, $J_{4,5}$ 2.4 Hz, 1 H, 4-H), 5.08 (d, $J_{1,2}$ 2.8 Hz, 1 H, 1-H), 6.03 (dd, $J_{2,3}$ 10.0 Hz, $J_{1,2}$ 2.8 Hz, 1 H, 2-H), 6.11 (ddd, $J_{2,3}$ 10.0, $J_{3,4}$ 5.2 Hz, J 0.8 Hz, 1 H, 3-H); as well as ethyl 2-deoxy-3,4,6-tri-*O*-acetyl- α -D-*lyxo*-hexopyranoside (169 mg, 16%); δ = 1.22 (t, J 7.2 Hz, 3 H, OCH₂CH₃), 1.86, 2.10 (2 \times m, 2 H, 2'-H, 2-H), 1.98, 2.05, 2.13 (3 \times s, 9 H, 3 \times COCH₃), 3.48, 3.69 (2 \times dq, J_{gem} 9.6 Hz, J 7.2 Hz, 2 H, OCH₂CH₃), 4.08–4.09 (2H, m, 6'-H, 6-H), 4.15 (m, 1 H, 5-H), 5.02 (d, $J_{1,2}$ 3.6 Hz, 1 H, 1-H), 5.28–5.33 (m, 2 H, 3-H, 4-H);

and ethyl 2-deoxy-3,4,6-tri-*O*-acetyl- β -D-*lyxo*-hexopyranoside (42 mg, 4%); δ = 1.25 (t, J 7.2 Hz, 3 H, OCH₂CH₃), 1.94–1.98 (m, 2 H, 2'-H, 2-H), 2.00, 2.04, 2.13 (3 \times s, 9 H, 3 \times COCH₃), 3.79 (dt, J 6.8 Hz, J 1.2 Hz, 1 H, 5-H), 3.48, 3.69 (2 \times dq, J_{gem} 9.6 Hz, J 7.2 Hz, 2 H, OCH₂CH₃), 4.09–4.20 (2H, m, 6'-H, 6-H), 4.57 (m, 1 H, 1-H), 5.00 (m, 1 H, 3-H), 5.27 (m, 1 H, 4-H).

Ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy- α -D-*threo*-hex-2-enopyranoside (2)

Compound **4** (470 mg, 1.82 mmol) was dissolved in MeOH (12 mL). Na (132 mg, 5.46 mmol) was added to MeOH (10 mL), and the resulting solution was added dropwise to the carbohydrate solution. The reaction mixture was stirred for 14 h, after which time TLC (EtOAc) indicated the complete consumption of starting material (R_f 0.9) and the formation of a major product (R_f 0.4). The reaction mixture was neutralized by the addition of NH₄Cl (292 mg, 5.46 mmol) and concentrated to dryness. The crude product was purified by column chromatography (EtOAc) to give the diol (277 mg, 87%) as a white solid; ¹H NMR (CD₃OD): δ = 1.22 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 3.71–3.77 (m, 2 H, 6'-H, 6-H), 3.79 (dd, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.4 Hz, 1 H, 4-H), 3.55, 3.89 (2 \times dq, J_{gem} = 9.6 Hz, J = 7.2 Hz, 2 H, OCH₂CH₃), 3.98 (ddd, J = 7.2 Hz, J = 5.2 Hz, $J_{4,5}$ = 2.4 Hz, 1 H, 5-H), 5.03 (d, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H), 5.88 (dd, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 2.8 Hz, 1 H, 2-H), 6.08 (ddd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 5.6 Hz, J = 0.4 Hz, 1 H, 3-H).

The diol (267 mg, 1.53 mmol) was dissolved in DMF (10 mL). Imidazole (209 mg, 3.07 mmol) was added and the reaction mixture was cooled to 0 °C in an ice-bath. TBDMSCl (254 mg, 1.68 mmol) was added and the reaction mixture was slowly warmed to RT. After 25 h, TLC (Pentane–EtOAc, 4:1) showed the almost complete consumption of starting material (R_f ~ 0) and the formation of a major product (R_f 0.4). The reaction was quenched by addition of H₂O (50 mL) and transferred to a separatory funnel. The aqueous phase was extracted with Et₂O (3 \times 50 mL), and the combined organic phases were dried (Na₂SO₄), filtered and concentrated to dryness to give a colourless oil (1.17 g). The crude product was purified by column chromatography (Pentane–EtOAc, 4:1) to give the silyl ether **2** (302 mg, 68%) as a colourless oil; ¹H NMR: δ = 0.09, 0.09 (2 \times s, 6 H, Si(CH₃)₂), 0.91 (s, 9 H, SiC(CH₃)₃), 1.23 (t, J = 6.8 Hz, 3 H, OCH₂CH₃), 3.54 (dq, J_{gem} = 9.6 Hz, J = 6.8 Hz, 1 H, OCHH'CH₃), 3.82–3.91 (m, 4 H, 5-H, 6-H, 6'-H, OCHH'CH₃), 4.08 (dt, J = 6.4 Hz, J = 2.4 Hz, 1 H, 4-H), 5.03 (d, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H), 5.91 (dd, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 2.8 Hz, 1 H, 2-H), 6.16 (ddd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 4.4 Hz, J = 0.8 Hz, 1 H, 3-H); ¹³C NMR: δ = –5.25, –5.29 (2 \times q, 2 \times SiCH₃), 15.4 (q, OCH₂CH₃), 18.4 (s, C(CH₃)₃), 25.9 (q, C(CH₃)₃), 62.1 (d, C-5), 63.0 (t, C-6), 63.7 (t, OCH₂CH₃), 70.7 (d, C-4), 94.2 (d, C-1), 128.8 (d, C-2), 129.4 (d, C-3).

Methyl 6-amino-2,3,4-tri-*O*-benzyl-6-deoxy-6-*N*-(2-nitrobenzenesulfonyl)- α -D-mannopyranoside (9)

Amine **8** (985 mg, 2.13 mmol) was dissolved in CH₂Cl₂ (30 mL) at RT under N₂, and Et₃N (443 μ L, 3.19 mmol), NsCl (567 mg, 2.55 mmol), and DMAP (26 mg, 0.21 mmol) were added. After 15 min, TLC (toluene–EtOAc, 1:1) showed the complete consumption of starting material (*R*_f 0.1) and the formation of a single product (*R*_f 0.9). The mixture was concentrated in vacuo, and the crude product was purified by column chromatography (pentane–EtOAc, 5:1 \rightarrow 1:1) to give nosylamide **9** (1.22 g, 88%) as an orange oil; IR (film): 3366 (N–H), 1540 (N–O), 1363 cm^{–1}; ¹H NMR (500 MHz, CDCl₃): δ = 3.16–3.22 (m, 4 H, 6-H, OCH₃), 3.47 (ddd, *J*_{5,6'} = 2.7 Hz, *J*_{NH,6'} = 7.0 Hz, *J*_{6,6'} = 9.8 Hz, 1 H, 6'-H), 3.63 (m, 1 H, 5-H), 3.74–3.79 (m, 2 H, 2-H, 4-H), 3.84 (dd, *J*_{2,3} = 2.8 Hz, *J*_{3,4} = 9.3 Hz, 1 H, 3-H), 4.55 (br s, 1 H, 1-H), 4.59 (s, 2 H, PhCH₂), 4.62, 4.93 (2 \times d, *J* = 11.1 Hz, 2 H, PhCH₂), 4.64, 4.72 (2 \times d, *J* = 12.3 Hz, 2 H, PhCH₂), 5.69 (at, *J* = 5.9 Hz, 1 H, NH), 7.25–8.05 (m, 19 H, Ar-H); ¹³C NMR (125 MHz, CDCl₃): δ = 44.9 (t, C-6), 55.1 (q, OCH₃), 70.5 (d, C-5), 72.3, 73.1, 74.6, 75.2, 75.3 (3 \times t, 2 \times d, 3 \times PhCH₂, C-2, C-4), 80.1 (d, C-3), 99.4 (d, C-1), 125.4, 127.7, 127.8, 127.9, 128.0, 128.0, 128.4, 128.6, 128.6, 131.2, 132.7, 133.5 (12 \times d, Ar-CH), 134.0, 138.2, 138.4, 138.4, 148.2 (5 \times s, Ar-C); MS (ESI⁺): *m/z* (%) 687 (7) [M + K⁺], 671 (100) [M + Na⁺]; HRMS–ESI *m/z* [M + Na⁺] calcd for C₃₄H₃₆N₂O₉SNa: 671.2034; found: 671.2024.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-*threo*-hex-2-enopyranosid-4-yl)-2-nitrobenzenesulfonamide (10)**

Allylic alcohol **1** (50 mg, 0.17 mmol) and nosylamide **6** (113 mg, 0.17 mmol) were dissolved in THF (3 mL) and cooled to 0 °C under N₂. PPh₃ (92 mg, 0.35 mmol) was added, and after 10 min, DIAD (67 μ L, 0.35 mmol). After 30 min, a white precipitate appeared. The reaction mixture was allowed to warm to RT slowly in the ice-bath. After 12 h, TLC (pentane–EtOAc, 3:1) showed the formation of a product (*R*_f 0.3) and the complete consumption of the alcohol (*R*_f 0.5) and sulfonamide (*R*_f 0.1) starting materials. At this time, the reaction mixture was a colourless solution. CH₂Cl₂ (ca 3 mL) was added, and the solution was concentrated in vacuo. The residue was purified by flash column chromatography (twice: pentane–EtOAc, 3:1, followed by CH₂Cl₂–Et₂O, 9:1), to give the pseudodisaccharide **10** (145 mg, 91%) as a colourless oil; [α]_D²² –22.4 (*c* 1.0, CHCl₃); IR (film): 1545 (NO₂), 1370 (SO₂) cm^{–1}; ¹H NMR (500 MHz, CDCl₃): δ = 0.06 (s, 6 H, Si(CH₃)₂), 0.90 (s, 9 H, C(CH₃)₃), 1.20 (t, *J* = 7.0 Hz, 3 H, OCH₂CH₃), 3.06 (at, *J* = 9.2 Hz, 1 H, 4-H^{II}), 3.12 (s, 3 H, OCH₃), 3.42–3.47 (m, 2 H, 2-H^{II}, OCHH'CH₃), 3.58 (dd, *J*_{5,6} = 9.7 Hz, *J*_{6,6'} = 15.4 Hz, 1 H, 6-H^{II}), 3.73–3.78 (m, 2 H, 6-H^I, 5-H^{II}), 3.83–3.94 (m, 4 H, 3-H^{II}, 6'-H^{II}, 6'-H^I, OCHH'CH₃), 4.15

(m, 1 H, 5-H^I), 4.28 (m, 1 H, 4-H^I), 4.45 (d, $J_{1,2} = 3.5$ Hz, 1 H, 1-H^{II}), 4.58, 4.94 (2 × d, $J = 10.9$ Hz, 2 H, PhCH₂), 4.64, 4.76 (2 × d, $J = 12.1$ Hz, 2 H, PhCH₂), 4.79–4.81 (m, 2 H, 1-H^I, PhCHH'), 4.98 (d, $J = 10.8$ Hz, 1 H, PhCHH'), 5.86 (s, 2 H, 2-H^I, 3-H^I), 7.31–7.38 (m, 15 H, 3 × Ph-H), 7.54–7.67 (m, 3H, Ns-H), 8.08 (m, 1 H, Ns-H); ¹³C NMR (125 MHz, CDCl₃): $\delta = -5.2, -5.2$ (2 × q, Si(CH₃)₂), 15.1 (q, OCH₂CH₃), 18.3 (s, SiC(CH₃)₃), 25.9 (q, SiC(CH₃)₃), 47.9 (t, C-6^{II}), 50.9 (d, C-4^I), 55.7 (q, OCH₃), 63.1, 63.2 (2 × t, C-6^I, OCH₂CH₃), 69.1 (d, C-5^{II}), 71.9 (d, C-5^I), 73.2, 75.4, 75.7 (3 × t, 3 × PhCH₂), 80.0 (d, C-2^{II}), 80.4 (d, C-4^{II}), 81.9 (d, C-3^{II}), 93.5 (d, C-1^I), 97.9 (d, C-1^{II}), 124.0 (d, Ns-CH), 127.0, 130.5 (2 × d, C-2^I, C-3^I), 127.7, 127.9, 127.9, 128.0, 128.0, 128.2, 128.4, 128.5, 128.5 (9 × d, Ar-CH), 131.8, 132.4, 133.6 (3 × d, Ns-CH), 134.6, 148.0 (2 × s, Ns-C), 138.2, 138.7 (2 × s, Ph-C); MS (ESI⁺): m/z (%) 941 (100) [M + Na⁺]; HRMS–ESI m/z [M + Na⁺] calcd for C₄₈H₆₂O₁₂N₂SSiNa: 941.3685; found: 941.3706.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-threo-hex-2-enopyranosid-4-yl)-trifluoromethanesulfonamide (11)**

Allylic alcohol **1** (50 mg, 0.17 mmol) and triflamide **7** (103 mg, 0.17 mmol) were dissolved in THF (3 mL) and cooled to 0 °C under N₂. PPh₃ (92 mg, 0.35 mmol) was added, and after 10 min, DIAD (68 μ L, 0.35 mmol). Within 2 min, the yellow colour had disappeared. After 5 min, a white precipitate had appeared. The reaction mixture was removed from the ice-bath after 10 min and stirred at RT. After 2 h at RT, TLC (pentane–EtOAc, 5:1) showed the formation of a product (R_f 0.4) and the presence of the remaining alcohol (R_f 0.2) and sulfonamide (R_f 0.1) starting materials. At this time, the mixture still had the appearance of a white suspension. After 24 h, TLC showed the complete conversion of both of the starting materials into product; the reaction mixture was a colourless solution. CH₂Cl₂ (ca 3 mL) was added, and the solution was concentrated in vacuo. The residue was purified by flash column chromatography (pentane–EtOAc, 9:1) to give the pseudodisaccharide **11** (132 mg, 88%) as a colourless oil; $[\alpha]_D^{22} -47.8$ (c 1.0, CHCl₃); IR (film): 1395 (SO₂) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 0.06$ (s, 6 H, Si(CH₃)₂), 0.89 (s, 9 H, C(CH₃)₃), 1.18 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 3.04 (at, $J = 9.3$ Hz, 1 H, 4-H^{II}), 3.37–3.45 (m, 2 H, 6-H^{II}, OCHH'CH₃), 3.51 (s, 3 H, OCH₃), 3.51 (m (obs), 1 H, 2-H^{II}), 3.60 (d, $J_{6,6'} = 14.7$ Hz, 1 H, 6'-H^{II}), 3.76 (dd, $J_{5,6} = 7.7$ Hz, $J_{6,6'} = 11.2$ Hz, 1 H, 6-H^I), 3.82 (m, 1 H, OCHH'CH₃), 3.96 (dd, $J_{5,6'} = 3.3$ Hz, $J_{6,6'} = 11.3$ Hz, 1 H, 6'-H^I), 4.01 (at, $J = 9.3$ Hz, 1 H, 3-H^{II}), 4.04 (m, 1 H, 5-H^I), 4.10 (at, $J = 9.4$ Hz, 1 H, 5-H^{II}), 4.17 (m, 1 H, 4-H^I), 4.46, 4.94 (2 × d, $J = 11.0$ Hz, 2 H, PhCH₂), 4.65–4.69 (m, 1-H^I, 1-H^{II}, 3 H, PhCHH'), 4.78 (d, $J = 12.2$ Hz, 1 H, PhCHH'), 4.82, 5.02 (2 × d, $J = 10.8$ Hz, 2 H, PhCH₂), 5.70 (dd, $J_{3,4} = 5.5$ Hz, $J_{2,3} = 10.0$ Hz, 1 H, 3-H^I), 5.79 (dd, $J_{1,2} = 1.9$ Hz, 1 H, 2-H^I),

7.27–7.38 (m, 15 H, Ar-H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = -5.2, -5.2$ ($2 \times \text{q}$, $\text{Si}(\text{CH}_3)_2$), 15.2 (q, OCH_2CH_3), 18.2 (s, $\text{SiC}(\text{CH}_3)_3$), 25.9 (q, $\text{SiC}(\text{CH}_3)_3$), 48.7 (t, C-6^{II}), 53.0 (d, C-4^I), 57.1 (q, OCH_3), 62.7 (t, C-6^I), 63.5 (t, OCH_2CH_3), 69.3 (d, C-5^{II}), 71.1 (d, C-5^I), 73.3, 75.3, 75.8 ($3 \times \text{t}$, $3 \times \text{PhCH}_2$), 79.9 (br d, C-4^{II}), 80.1 (d, C-2^{II}), 82.0 (d, C-3^{II}), 93.4 (d, C-1^I), 98.6 (d, C-1^{II}), 120.3 (q, $J_{\text{C,F}}$ 324 Hz, CF_3), 124.2 (v br d, C-3^I), 127.8, 128.0, 128.1, 128.1, 128.4, 128.5, 128.5, 128.6 ($8 \times \text{d}$, Ar-CH), 133.7 (v br d, C-2^I), 138.1, 138.3, 138.7 ($3 \times \text{s}$, $3 \times \text{Ar-C}$); MS (ESI^+): m/z (%) 888 (100) [$\text{M} + \text{Na}^+$]; HRMS–ESI m/z [$\text{M} + \text{Na}^+$] calcd for $\text{C}_{43}\text{H}_{58}\text{O}_{10}\text{F}_3\text{NSSiNa}$: 888.3395; found: 888.3448.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-mannopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-threo-hex-2-enopyranosid-4-yl)-2-nitrobenzenesulfonamide (12)**

Allylic alcohol **1** (153 mg, 0.527 mmol) and nosylamide **9** (401 mg, 0.619 mmol) were dissolved in THF (11 mL), and the reaction was cooled to 0 °C under nitrogen. PPh_3 (276 mg, 1.05 mmol) was added. After 10 min, DIAD (207 μL , 1.05 mmol) was added. After 30 min, the reaction mixture was allowed to reach RT. After 18 h, TLC (toluene–EtOAc, 5:1) showed only a little starting material remaining (**1** R_f 0.3, **9** R_f 0.7) and the formation of a single product (R_f 0.8). The mixture was concentrated in vacuo, and the crude product was purified by repeated column chromatography (pentane–EtOAc, 4:1) to give the pseudodisaccharide **12** (368 mg, 76%) as an oil; $[\alpha]_{\text{D}}^{25} -12.3$ (c 1.0, CHCl_3); IR (film): 1545 (N–O), 1370 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): $\delta = 0.01$ (s, 6 H, $\text{Si}(\text{CH}_3)_2$), 0.86 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.19 (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3), 3.07 (s, 3 H, OCH_3), 3.42, 3.85 ($2 \times \text{m}$, 2 H, OCH_2CH_3), 3.49 (at, $J = 8.5$ Hz, 1 H, 4-H^{II} or 5-H^{II}), 3.68 (m, 1 H, 2-H^{II}), 3.71–3.77 (m, 5 H, 4-H^{II} or 5-H^{II}, and 6'-H^I, 6'-H^I, 3-H^{II}, 6-H^{II}), 3.91 (m, 1 H, 6'-H^{II}), 4.15 (m, 1 H, 5-H^I), 4.28 (at, $J = 4.0$ Hz, 1 H, 4-H^I), 4.54–4.62 (m, 5 H, 1-H^{II}, PhCH_2 , $2 \times \text{PhCHH}'$), 4.69 (d, $J = 12.4$ Hz, 1 H, PhCHH'), 4.81 (d, $J_{1,2} = 2.6$ Hz, 1 H, 1-H^I), 4.92 (d, $J = 10.9$ Hz, 1 H, PhCHH'), 5.85 (dd, $J_{1,2} = 1.8$ Hz, $J_{2,3} = 10.0$ Hz, 1 H, 2-H^I), 5.93 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 5.4$ Hz, 1 H, 3-H^I), 7.26–7.38 (m, 15 H, Ar-H), 7.51 (at, $J = 7.8$ Hz, 1 H, Ar-H), 7.58 (d, $J = 7.8$ Hz, 1 H, Ar-H), 7.64 (at, $J = 7.8$ Hz, 1 H, Ar-H), 8.07 (d, $J = 7.8$ Hz, 1 H, Ar-H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = -5.2$ (q, $\text{Si}(\text{CH}_3)_2$), 15.2 (q, OCH_2CH_3), 18.4 (s, $\text{SiC}(\text{CH}_3)_3$), 26.0 (q, $\text{SiC}(\text{CH}_3)_3$), 48.4 (t, C-6^{II}), 50.9 (d, C-4^I), 55.1 (q, OCH_3), 63.1, 63.3 ($2 \times \text{t}$, C-6^I, OCH_2CH_3), 70.3, 77.3, 79.9 ($3 \times \text{d}$, C-3^{II}, C-4^{II}, C-5^{II}), 71.9 (d, C-5^I), 72.0, 72.6, 75.2 ($3 \times \text{t}$, $3 \times \text{PhCH}_2$), 75.0 (d, C-2^{II}), 93.6 (d, C-1^I), 98.6 (d, C-1^{II}), 124.0, 127.6, 127.7, 127.7, 127.7, 127.8, 128.2, 128.4, 128.4, 131.7, 132.5, 133.5 ($12 \times \text{d}$, Ar-CH), 127.4 (d, C-3^I), 130.2 (d, C-2^I), 134.6, 138.5, 138.6, 138.6, 148.1 ($5 \times \text{s}$, $5 \times \text{Ar-C}$); MS (ESI^+): m/z (%) 957 (5) [$\text{M} + \text{K}^+$], 941 (100) [$\text{M} + \text{Na}^+$]; HRMS–ESI m/z [$\text{M} + \text{Na}^+$] calcd for $\text{C}_{48}\text{H}_{62}\text{N}_2\text{O}_{12}\text{SSiNa}$: 941.3685; found: 941.3715.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-erythro-hex-2-enopyranosid-4-yl)-2-nitrobenzenesulfonamide (**13**)**

Allylic alcohol **2** (56 mg, 0.19 mmol) and nosylamide **6** (125 mg, 0.193 mmol) were dissolved in THF (3.6 mL), and the reaction mixture was cooled to 0 °C under nitrogen. PPh₃ (101 mg, 0.386 mmol) was added. After 10 min, DIAD (76 μ L, 0.39 mmol) was added, and within 10 min, the reaction mixture turned from a clear, pale yellow solution to a white slurry. After 30 min, the reaction mixture was allowed to reach RT. After 3 h, TLC (toluene–EtOAc, 5:1) showed the presence of a little remaining starting material (**2** *R*_f 0.3, **6** *R*_f 0.5), along with product formation (*R*_f 0.8). PPh₃ (50 mg, 0.19 mmol) was added to the pale yellow reaction mixture. After 10 min, DIAD (38 μ L, 0.19 mmol) was added, and again a white slurry was seen within 10 min. The reaction was allowed to reach RT and after 16 h, TLC showed that all starting material had been consumed and a single product had been formed. The reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography (toluene–EtOAc, 9:1) to give pseudodisaccharide **13** (147 mg, 91%) as a pale yellow oil; $[\alpha]_D^{25}$ +31.4 (*c* 1.0, CHCl₃); IR (film): 1546 (N–O), 1372 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ = 0.04, 0.07 (2 \times s, 6 H, Si(CH₃)₂), 0.90 (s, 9 H, C(CH₃)₃), 1.48 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃), 3.02 (dd, *J*_{5,6} = 10.1 Hz, *J*_{6,6'} = 15.5 Hz, 1 H, 6-H^{II}), 3.12 (at, *J* = 9.5 Hz, 1 H, 4-H^{II}), 3.44–3.53 (m, 5 H, 2-H^{II}, OCH₃, OCHH'CH₃), 3.57 (d, *J*_{6,6'} = 15.5 Hz, 1 H, 6-H^{IIb}), 3.66 (dd, *J*_{5,6} = 7.2 Hz, *J*_{6,6'} = 11.2 Hz, 1 H, 6-H^I), 3.83 (dq, *J* = 7.1 Hz, *J*_{gem} = 9.6 Hz, 1 H, OCHH'CH₃), 3.97 (dd, *J*_{5,6'} = 1.4 Hz, *J*_{6,6'} = 11.2 Hz, 1 H, 6-H^{Ib}), 4.08 (at, *J* = 9.2 Hz, 1 H, 3-H^{II}), 4.19 (m, 1 H, 5-H^I), 4.25 (atd, *J* = 10.0 Hz, *J*_{5,6'} = 1.3 Hz, 1 H, 5-H^{II}), 4.42 (m, 1 H, 4-H^I), 4.51, 4.97 (2 \times d, *J* = 11.5 Hz, 2 H, PhCH₂), 4.57 (d, *J*_{1,2} = 3.4 Hz, 1 H, 1-H^{II}), 4.67, 4.78 (2 \times d, *J* = 12.2 Hz, 2 H, PhCH₂), 4.80, 5.00 (2 \times d, *J* = 11.0 Hz, 2 H, PhCH₂), 4.92 (d, *J*_{1,2} = 2.6 Hz, 1 H, 1-H^I), 5.41 (d, *J*_{2,3} = 10.2 Hz, 1 H, 3-H^I), 5.83 (dat, *J* = 2.7 Hz, *J*_{2,3} = 10.2 Hz, 1 H, 2-H^I), 7.14 (m, 1 H, Ar-H), 7.24–7.37 (m, 15 H, Ar-H), 7.54–7.61 (m, 2 H, Ar-H), 7.85 (m, 1 H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = –5.2, –5.1 (2 \times q, Si(CH₃)₂) 15.4 (q, OCH₂CH₃), 18.4 (s, SiC(CH₃)₃), 26.1 (q, SiC(CH₃)₃), 47.9 (t, C-6^{II}), 54.1 (d, C-4^I), 55.6 (q, OCH₃), 63.2 (t, C-6^I), 63.3 (t, OCH₂CH₃), 69.1 (d, C-5^I), 69.7 (d, C-5^{II}), 73.3, 74.5, 75.7 (3 \times t, 3 \times PhCH₂), 79.8 (d, C-2^{II}), 80.5 (d, C-4^{II}), 81.7 (d, C-3^{II}), 93.0 (d, C-1^I), 97.9 (d, C-1^{II}), 124.2, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 131.9, 132.6, 133.7 (11 \times d, Ar-CH), 129.6 (d, C-3^I), 130.2 (d, C-2^I) 131.4, 138.2, 138.4, 138.8, 148.1 (5 \times s, 5 \times Ar-C); MS (ESI⁺): *m/z* (%) 957 (5) [M + K⁺], 941 (100) [M + Na⁺]; HRMS–ESI *m/z* [M + Na⁺] calcd for C₄₈H₆₂N₂O₁₂SSiNa: 941.3685; found: 941.3722.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-erythro-hex-2-enopyranosid-4-yl)-trifluoromethanesulfonamide (**14**)**

Allylic alcohol **2** (70 mg, 0.24 mmol) and triflamide **7** (143 mg, 0.241 mmol) were dissolved in THF (4.3 mL), and the reaction was cooled to 0 °C under nitrogen. PPh₃ (126 mg, 0.482 mmol) was added to the mixture. After 10 min, DIAD (95 μ L, 0.48 mmol) was added, and the reaction mixture turned from a clear, pale yellow solution to a white slurry within 10 min. After 30 min, the reaction mixture was allowed to reach RT. After 16 h, TLC (toluene–EtOAc, 5:1) showed the presence of remaining starting material (**2** R_f 0.4, **7** R_f 0.4), and product formation (R_f 0.8). PPh₃ (68 mg, 0.24 mmol) was added, and the pale yellow mixture was cooled to 0 °C. After 10 min, DIAD (47 μ L, 0.24 mmol) was added, and again a white slurry was seen within 10 min. The reaction was allowed to reach RT. After a further 4 h, TLC showed that all starting material had been consumed and a single product had been formed. The reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography (pentane–EtOAc, 6:1) to give pseudodisaccharide **14** (189 mg, 91%) as a pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 0.04, 0.06 (2 \times s, 6 H, Si(CH₃)₂), 0.89 (s, 9 H, C(CH₃)₃), 1.16 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 2.91 (m, 1 H, 6-H^{II}), 3.08 (at, J = 9.3 Hz, 1 H, 4-H^{II}), 3.42–3.53 (m, 5 H, 2-H^{II}, OCH₂CH₃, OCH₃), 3.63–3.72 (m, 2 H, 6-H^I, 6'-H^{II}), 3.80 (dq, J = 7.1 Hz, J_{gem} = 9.6 Hz, 1 H, OCH₂CH₃), 3.91 (d, $J_{6,6'}$ = 11.0 Hz, 1 H, 6'-H^I), 4.04 (at, J = 9.2 Hz, 1 H, 3-H^{II}), 4.08 (m, 1 H, 5-H^{II}), 4.16 (m, 1 H, 5-H^I), 4.35 (m, 1 H, 4-H^I), 4.55, 4.89 (2 \times d, J = 11.6 Hz, 2 H, PhCH₂), 4.61 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H^{II}), 4.67, 4.78 (2 \times d, J = 12.1 Hz, 2 H, PhCH₂), 4.80, 4.99 (2 \times d, J = 10.9 Hz, 2 H, PhCH₂), 4.92 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H^I), 5.55, 5.93 (2 \times m, 2 H, 2-H^I, 3-H^I), 7.25–7.34 (m, 15 H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = –5.2, –5.1 (2 \times q, Si(CH₃)₂), 15.4 (q, OCH₂CH₃), 18.4 (s, C(CH₃)₃), 26.0 (q, C(CH₃)₃), 49.2 (t, C-6^{II}), 55.5 (d, C-4^I), 55.7 (q, OCH₃), 62.9 (t, C-6^I), 63.6 (t, OCH₂CH₃), 68.6 (d, C-5^I), 69.5 (d, C-5^{II}), 73.3, 74.6, 75.9 (3 \times t, 3 \times PhCH₂), 79.8, 80.0 (2 \times d, C-2^{II}, C-4^{II}), 81.7 (d, C-3^{II}), 93.0 (d, C-1^I), 98.1 (d, C-1^{II}), 127.8, 127.9, 128.1, 128.1, 128.2, 128.4, 128.4, 128.5, 128.6, 128.6, 131.5 (11 \times d, C-2^I, C-3^I, Ar-C), 138.0, 138.1, 138.7 (3 \times s, 3 \times Ar-C); MS (ESI⁺): m/z (%) 904 (5) [M + K⁺], 888 (100) [M + Na⁺]; HRMS–ESI m/z [M + Na⁺] calcd for C₄₃H₅₈NO₁₀F₃SSiNa: 888.3395; found: 888.3414.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-mannopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-erythro-hex-2-enopyranosid-4-yl)-2-nitrobenzenesulfonamide (15)**

Allylic alcohol **2** (101 mg, 0.348 mmol) and nosylamide **9** (248 mg, 0.383 mmol) were dissolved in THF (7 mL), and the reaction was cooled to 0 °C under nitrogen. PPh₃ (182 mg, 0.696 mmol) was added. After 10 min, DIAD (136 μ L, 0.696 mmol) was added. After 30 min, the reaction mixture was allowed to reach RT. After 18 h, TLC (toluene–EtOAc, 6:1) showed only a little starting material (**2** *R*_f 0.3, **9** *R*_f 0.7) remaining and the formation of a single product (*R*_f 0.75). The reaction mixture was concentrated in vacuo, and the crude product was purified by repeated column chromatography (pentane–EtOAc, 4:1) to give the pseudodisaccharide **15** (227 mg, 71%) as an oil; $[\alpha]_D^{25} +46.1$ (*c* 1.0, CHCl₃); IR (film): 1546 (N–O), 1372 cm^{–1}; ¹H NMR (500 MHz, CDCl₃): δ = 0.08, 0.11 (2 \times s, 6 H, Si(CH₃)₂), 0.94 (s, 9 H, C(CH₃)₃), 1.19 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃), 3.22 (dd, *J*_{5,6} = 10.2 Hz, *J*_{6,6'} = 15.3 Hz, 1 H, 6-H^{II}), 3.39 (s, 3 H, OCH₃), 3.51, 3.88 (2 \times dq, *J* = 7.1 Hz, *J*_{gem} = 9.4 Hz, 2 H, OCH₂CH₃), 3.61–3.68 (m, 2 H, 4-H^{II}, 6'-H^{II}), 3.74 (dd, *J*_{5,6} = 7.0 Hz, *J*_{6,6'} = 11.2 Hz, 1 H, 6-H^I), 3.78 (m, 1 H, 2-H^{II}), 3.97 (dd, *J*_{2,3} = 3.0 Hz, *J*_{3,4} = 9.3 Hz, 1 H, 3-H^{II}), 4.06 (d, *J*_{6,6'} = 11.0 Hz, 1 H, 6'-H^I), 4.24 (at, *J* = 9.8 Hz, 1 H, 5-H^{II}), 4.32 (at, *J* = 8.2 Hz, 1 H, 5-H^I), 4.49 (d, *J*_{4,5} = 9.8 Hz, 1 H, 4-H^I), 4.55, 5.05 (2 \times d, *J* = 11.5 Hz, 2 H, PhCH₂), 4.59 (m, 2 H, PhCH₂), 4.69–4.71 (m, 3 H, 1-H^{II}, PhCH₂), 4.95 (m, 1 H, 1-H^I), 5.42 (d, *J*_{2,3} = 10.2 Hz, 1 H, 2-H^I or 3-H^I), 5.86 (dat, *J* = 2.6 Hz, *J*_{2,3} = 10.2 Hz, 1 H, 2-H^I or 3-H^I), 7.11 (m, 1 H, Ar-H), 7.26–7.37 (m, 15 H, Ar-H), 7.54–7.60 (m, 2 H, Ar-H), 7.86 (m, 1 H, Ar-H); ¹³C NMR (125 MHz, CDCl₃): δ = –5.1, –5.0 (2 \times q, Si(CH₃)₂), 15.3 (q, OCH₂CH₃), 18.4 (s, SiC(CH₃)₃), 26.1 (q, SiC(CH₃)₃), 47.9 (t, C-6^{II}), 54.2 (d, C-4^I), 55.0 (q, OCH₃), 63.3, 63.4 (2 \times t, C-6^I, OCH₂CH₃), 69.1 (d, C-5^I), 70.7 (d, C-5^{II}), 72.0, 72.5, 74.7 (3 \times t, 3 \times PhCH₂), 74.5 (d, C-2^{II}), 77.2 (d, C-4^{II}), 80.1 (d, C-3^{II}), 93.0 (d, C-1^I), 98.6 (d, C-1^{II}), 124.1, 127.5, 127.6, 127.7, 127.7, 127.8, 127.9, 128.4, 128.5, 129.5, 130.2, 131.3, 132.4, 133.6 (14 \times d, C-2^I, C-3^I, Ar-CH), 131.9, 138.4, 138.4, 138.9, 148.1 (5 \times s, 5 \times Ar-C); MS (ESI⁺): *m/z* (%) 957 (2) [M + K⁺], 941 (100) [M + Na⁺]; HRMS–ESI *m/z* [M + Na⁺] calcd for C₄₈H₆₂N₂O₁₂SSiNa: 941.3685; found: 941.3708.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-4-deoxy- α -D-mannopyranosid-4-yl)-2-nitrobenzenesulfonamide (16)**

Alkene **13** (154 mg, 0.167 mmol) was dissolved in acetone/H₂O [4:1] (1.2 mL) at RT. AcOH (10 μ L, 0.18 mmol), then K₂OsO₄·2H₂O (2 mg, 5 μ mol) and then NMO (50% aq., 223 μ L, 0.951 mmol) were added. The reaction mixture slowly changed colour from yellow to black. TLC (toluene–EtOAc, 4:3) showed a slow but steady conversion of the starting material (*R*_f 0.9) to a

single product (R_f 0.3). After 72 h, the reaction was quenched by NaHSO_3 (satd. aq., 0.5 mL) and the mixture was left to stir for 30 min. Brine (5 mL) was added, and the mixture was extracted with EtOAc (3×10 mL). The organic phase was dried (MgSO_4), filtered and concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 5:1 \rightarrow 4:3) to give diol **16** (140 mg, 88%) as a slightly yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 0.01, 0.02 (2 \times s, 6 H, $\text{Si}(\text{CH}_3)_2$), 0.86 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.11 (t, J = 6.8 Hz, 3 H, OCH_2CH_3), 3.09–3.14 (m, 2 H, 4- H^{II} , 6- H^{II}), 3.41–3.52 (m, 6 H, 6- H^{I} , 2- H^{II} , $\text{OCHH}'\text{CH}_3$, OCH_3), 3.63–3.73 (m, 2 H, 6'- H^{II} , $\text{OCHH}'\text{CH}_3$), 3.80–3.93 (m, 5 H, 2- H^{I} , 3- H^{I} , 4- H^{I} , 5- H^{I} , 6'- H^{I}), 4.10 (at, J = 8.4 Hz, 1 H, 3- H^{II}), 4.26 (m, 1 H, 5- H^{II}), 4.54 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1- H^{II}), 4.57 (d, J = 11.5 Hz, 1 H, PhCHH'), 4.66 (d, J = 12.1 Hz, 1 H, PhCHH'), 4.76–4.81 (m, 3 H, 1- H^{I} , PhCHH' , PhCHH'), 4.99–5.04 (m, 2 H, 2 \times PhCHH'), 7.13–7.80 (m, 19 H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3): δ = -5.2, -5.0 (2 \times q, $\text{Si}(\text{CH}_3)_2$), 15.0 (q, OCH_2CH_3), 18.3 (s, $\text{SiC}(\text{CH}_3)_3$), 26.0 (q, $\text{SiC}(\text{CH}_3)_3$), 49.9 (t, C-6 $^{\text{II}}$), 56.2 (q, OCH_3), 57.3 (d, C-4 $^{\text{I}}$), 62.8 (t, OCH_2CH_3), 63.5 (t, C-6 $^{\text{I}}$), 66.4, 70.9, 71.6 (3 \times d, C-2 $^{\text{I}}$, C-3 $^{\text{I}}$, C-5 $^{\text{I}}$), 70.1 (d, C-5 $^{\text{II}}$), 73.4, 74.5, 75.8 (3 \times t, 3 \times PhCH_2), 80.1 (d, C-2 $^{\text{II}}$), 80.5 (d, C-4 $^{\text{II}}$), 81.5 (d, C-3 $^{\text{II}}$), 98.3 (d, C-1 $^{\text{II}}$), 98.5 (d, C-1 $^{\text{I}}$), 123.8, 127.6, 127.8, 128.1, 128.2, 128.6, 128.6, 131.4, 133.6 (9 \times d, Ar-CH), 131.9, 138.2, 138.4, 138.6, 147.8 (5 \times s, Ar-C); MS (ESI^+): m/z (%) 1927 (7) [$2\text{M} + \text{Na}^+$], 975 (100) [$\text{M} + \text{Na}^+$]; HRMS–ESI m/z [$\text{M} + \text{Na}^+$] calcd for $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_{14}\text{SSiNa}$: 975.3740; found: 975.3734.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-mannopyranosid-6-yl)-*N*-(ethyl 6-*O*-(tert-butyl)dimethylsilyl)-4-deoxy- α -D-mannopyranosid-4-yl)-2-nitrobenzenesulfonamide (**17**)**

Alkene **15** (85 mg, 0.093 mmol) was dissolved in acetone/ H_2O [4:1] (1 mL). AcOH (5 μL , 0.09 mmol), then $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (7 mg, 19 μmol), and then NMO (43 mg, 0.37 mmol) were added. The reaction mixture slowly changed colour from yellow to black. TLC (toluene–EtOAc, 6:1) showed a slow but steady conversion of the starting material (R_f 0.7) to a single product (R_f 0.1). After 6 days, the reaction was quenched by NaHSO_3 (satd. aq., 0.5 mL), and the mixture was left to stir for 20 min. Brine (5 mL) was added, and the mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were dried (MgSO_4), filtered and concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 5:1 \rightarrow 1:1) to give diol **17** (65 mg, 73%) as an oil; ^1H NMR (500 MHz, CDCl_3): δ = 0.04, 0.06 (2 \times s, 6 H, $\text{Si}(\text{CH}_3)_2$), 0.89 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.12 (t, J = 7.0 Hz, 3 H, OCH_2CH_3), 2.23 (br s, 1 H, OH), 2.86 (d, J = 9.5 Hz, 1 H, OH), 3.26 (dd, $J_{5,6}$ = 9.9 Hz, $J_{6,6'}$ = 15.8 Hz, 1 H, 6- H^{II}), 3.35 (s, 3 H, OCH_3), 3.45 (dq, J = 7.1 Hz, J_{gem} = 9.7 Hz, 1 H, $\text{OCHH}'\text{CH}_3$), 3.59–3.69 (m, 2 H, 6- H^{I} , 4- H^{II}), 3.71–3.78 (m, 3 H, 2- H^{V} , 6'- H^{II} , $\text{OCHH}'\text{CH}_3$), 3.86–4.04 (m, 6 H, 2- H^{X} , 3- H^{I} , 4- H^{I} , 5- H^{I} , 6'- H^{I} , 3- H^{II}), 4.26 (at, J = 9.4 Hz, 1 H, 5- H^{II}), 4.58–4.72 (m, 6 H, 1- H^{V} , PhCHH' , 2 \times PhCH_2), 4.78 (s, 1 H, 1- H^{X}), 5.10 (d, J = 11.4 Hz, 1 H,

PhCHH'), 7.08–7.81 (m, 19 H, Ar-H); ^{13}C NMR (125 MHz, CDCl_3): δ = –5.1, –4.9 (2 \times q, $\text{Si}(\text{CH}_3)_2$), 14.9 (q, OCH_2CH_3), 18.4 (s, $\text{SiC}(\text{CH}_3)_3$), 26.0 (q, $\text{SiC}(\text{CH}_3)_3$), 47.1 (t, C-6^{II}), 55.5 (q, OCH_3), 57.5 (d, C-4^I), 62.7 (t, OCH_2CH_3), 63.7 (t, C-6^I), 66.4, 71.0, 71.6, 79.8 (4 \times d, C-2^x, C-3^I, C-5^I, C-3^{II}), 71.1 (d, C-5^{II}), 72.0, 72.7, 74.6 (3 \times t, 3 \times PhCH₂), 74.6 (d, C-2^y), 77.2 (d, 4-H^{II}), 98.5 (d, C-1^x), 98.8 (d, C-1^y), 123.6, 127.5, 127.6, 127.8, 127.8, 128.4, 128.5, 128.5, 129.2, 131.3, 132.1, 133.5 (12 \times d, Ar-CH), 131.8, 138.4, 138.9, 147.8 (4 \times s, Ar-C); MS (ESI⁺): m/z (%) 991 (2) [$\text{M} + \text{K}^+$], 975 (100) [$\text{M} + \text{Na}^+$]; HRMS–ESI m/z [$\text{M} + \text{Na}^+$] calcd for $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_{14}\text{SSiNa}$: 975.3740; found: 975.3770.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 2,3-di-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-4-deoxy- α -D-mannopyranosid-4-yl)-2-nitrobenzenesulfonamide (18)**

Diol **16** (65 mg, 0.068 mmol) was dissolved in Ac_2O /pyridine [1:1] (6 mL) at RT, and left to stir for 24 h. After this time, TLC (toluene–EtOAc, 5:1) showed the presence of a single product (R_f 0.5), and the reaction was concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 5:1) to give diacetate **18** (59 mg, 83%) as an oil; $[\alpha]_{\text{D}}^{25} +43.2$ (c 1.0, CHCl_3); IR (film): 1749 (C=O), 1548 (N–O), 1371 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.05, 0.07 (2 \times s, 6 H, $\text{Si}(\text{CH}_3)_2$), 0.90 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.14 (t, J = 7.0 Hz, 3 H, OCH_2CH_3), 1.20, 2.16 (2 \times s, 6 H, 2 \times $\text{C}(\text{O})\text{CH}_3$), 2.84 (dd, $J_{5,6} = 9.9$ Hz, $J_{6,6'} = 15.8$ Hz, 1 H, 6-H^{II}), 3.14 (dd, J = 8.9 Hz, J = 9.7 Hz, 1 H, 4-H^{II}), 3.45–3.49 (m, 5 H, 2-H^{II}, $\text{OCHH}'\text{CH}_3$, OCH_3), 3.67–3.79 (m, 3 H, 6-H^I, 6'-H^{II}, $\text{OCHH}'\text{CH}_3$), 4.02 (m, 1 H, 5-H^I), 4.05–4.14 (m, 2 H, 6'-H^I, 3-H^{II}), 4.20–4.27 (m, 2 H, 4-H^I, 5-H^{II}), 4.57, 4.96 (2 \times d, J = 11.2 Hz, 2 H, PhCH₂), 4.61 (d, $J_{1,2} = 3.3$ Hz, 1 H, 1-H^{II}), 4.65–4.68 (m, 2 H, 1-H^I, PhCHH'), 4.79 (d, J = 11.4 Hz, 1 H, PhCHH'), 4.82, 5.02 (2 \times d, J = 11.0 Hz, 2 H, PhCH₂), 5.18 (dd, $J_{1,2} = 1.8$ Hz, $J_{2,3} = 3.2$ Hz, 1 H, 2-H^I), 5.32 (dd, $J_{2,3} = 3.4$ Hz, $J_{3,4} = 11.0$ Hz, 1 H, 3-H^I), 7.17 (m, 1 H, Ar-H), 7.24–7.38 (m, 15 H, Ar-H), 7.49–7.60 (m, 2 H, Ar-H), 7.72 (m, 1 H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3): δ = –5.0, –4.9 (2 \times q, $\text{Si}(\text{CH}_3)_2$), 15.1 (q, OCH_2CH_3), 18.3 (s, $\text{SiC}(\text{CH}_3)_3$), 20.1, 21.1 (2 \times s, 2 \times $\text{C}(\text{O})\text{CH}_3$), 26.0 (q, $\text{SiC}(\text{CH}_3)_3$), 47.1 (t, C-6^{II}), 54.6 (d, C-4^I), 56.1 (q, OCH_3), 62.9 (t, OCH_2CH_3), 63.9 (t, C-6^I), 66.3 (d, C-3^I), 69.9, 70.1 (2 \times d, C-2^I, C-5^{II}), 71.7 (d, C-5^I), 73.4, 74.7, 75.6 (3 \times t, 3 \times PhCH₂), 80.1 (d, C-2^{II}), 81.2, 81.3 (2 \times d, C-3^{II}, C-4^{II}), 96.4 (d, C-1^I), 98.3 (d, C-1^{II}), 123.9, 127.7, 127.8, 127.9, 127.9, 128.1, 128.2, 128.4, 128.5, 128.5, 128.6, 129.2, 131.0, 131.9, 133.4 (15 \times d, Ar-CH), 132.4, 138.2, 138.5, 138.8, 148.2 (5 \times s, 5 \times Ar-C), 169.3, 170.5 (2 \times s, 2 \times C=O); MS (ESI⁺): m/z (%) 1075 (4) [$\text{M} + \text{K}^+$], 1059 (100) [$\text{M} + \text{Na}^+$]; HRMS–ESI m/z [$\text{M} + \text{Na}^+$] calcd for $\text{C}_{52}\text{H}_{68}\text{N}_2\text{O}_{16}\text{SSiNa}$: 1059.3951; found: 1059.3952.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 4-deoxy- α -D-mannopyranosid-4-yl)-2-nitrobenzenesulfonamide (**19**)**

From **13**: Alkene **13** (205 mg, 0.223 mmol) was dissolved in acetone/H₂O [4:1] (5 mL) at RT. AcOH (13 μ L, 0.22 mmol), then K₂OsO₄·2H₂O (8 mg, 22 μ mol), and then NMO (50% aq., 208 μ L, 0.892 mmol) were added. The reaction mixture slowly changed colour from yellow to black. TLC (toluene–EtOAc, 4:3) showed a slow but steady conversion of the starting material (*R*_f 0.9) to a single product (*R*_f 0.3). After 4 days, the reaction was quenched by NaHSO₃ (satd. aq., 2 mL), and the mixture was left to stir for 20 h, after which time TLC (toluene–EtOAc, 4:3) showed the complete conversion of the intermediate diol **16** (*R*_f 0.3) into a new product (*R*_f 0.1). NaHCO₃ (satd. aq., 5 mL) was added, and the mixture was extracted with EtOAc (3 \times 10 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 1:3) to give triol **19** (149 mg, 80%) as an oil.

From **16**: Diol **16** (47 mg, 0.050 mmol) was dissolved in MeOH/HCl (1 M aq.) [10:1] (2 mL), and stirred at RT for 30 min, after which time TLC (toluene–EtOAc, 1:1) showed the complete conversion of the starting material (*R*_f 0.6) into a single product (*R*_f 0.2). The mixture was concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 2:5) to give triol **19** (31 mg, 74%) as an oil; [α]_D²⁵ +23.5 (*c* 1.0, CHCl₃); IR (film): 3435 (O–H), 1544 (N–O), 1371 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (t, *J* = 7.0 Hz, 3 H, OCH₂CH₃), 2.72 (br s, 1 H, OH), 2.86 (d, *J* = 7.6 Hz, 1 H, OH), 3.02–3.14 (m, 3 H, 4-H^{II}, 6-H^{II}, OH), 3.41 (s, 3 H, OCH₃), 3.45–3.52 (m, 2 H, 2-H^{II}, OCH₂CH₃), 3.62–3.73 (m, 3 H, 6-H^I, 6'-H^{II}, OCH₂CH₃), 3.80–3.87 (m, 4 H, 2-H^I, 3-H^I, 5-H^I, 6'-H^I), 4.01 (at, *J* = 10.2 Hz, 1 H, 4-H^I), 4.10 (at, *J* = 9.2 Hz, 1 H, 3-H^{II}), 4.28 (at, *J* = 9.7 Hz, 1 H, 5-H^{II}), 4.51 (d, *J*_{1,2} = 3.2 Hz, 1 H, 1-H^{II}), 4.57, 5.02 (2 \times d, *J* = 11.5 Hz, 2 H, PhCH₂), 4.66 (d, *J* = 12.1 Hz, 1 H, PhCH₂H'), 4.78–4.82 (m, 2 H, PhCH₂H', PhCH₂H'), 4.84 (s, 1 H, 1-H^I), 5.00 (d, *J* = 10.8 Hz, 1 H, PhCH₂H'), 7.13–7.83 (m, 19 H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 15.1 (q, OCH₂CH₃), 47.0 (t, C-6^{II}), 56.4 (q, OCH₃), 56.4 (d, C-4^I), 61.7 (t, C-6^I), 63.3 (t, OCH₂CH₃), 66.2, 70.1, 71.4 (3 \times d, C-2^I, C-3^I, C-5^I), 70.2 (d, C-5^{II}), 73.5, 74.6, 75.8 (3 \times t, 3 \times PhCH₂), 80.1 (d, C-2^{II}), 80.5 (d, C-4^{II}), 81.5 (d, C-3^{II}), 98.5 (d, C-1^{II}), 99.0 (d, 1-H^I), 123.9, 127.7, 127.8, 127.9, 128.1, 128.1, 128.3, 128.6, 128.6, 129.1, 131.4, 132.2, 133.8 (13 \times d, Ar-CH); 131.5, 139.2, 138.3, 138.6, 147.8 (5 \times s, Ar-CH); MS (ESI⁺): *m/z* (%) 877 (3) [M + K⁺], 861 (100) [M + Na⁺]; HRMS–ESI *m/z* [M + Na⁺] calcd for C₄₂H₅₀N₂O₁₄SNa: 861.2875; found: 861.2883.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-mannopyranosid-6-yl)-*N*-(ethyl 4-deoxy- α -D-mannopyranosid-4-yl)-2-nitrobenzenesulfonamide (**20**)**

Diol **17** (65 mg, 0.068 mmol) was dissolved in MeOH/HCl (1 M aq.) [10:1] (5 mL), and stirred at RT for 20 min, after which time TLC (toluene–EtOAc, 1:1) showed complete conversion of starting material (R_f 0.6) into a single product (R_f 0.2). The reaction was quenched by the addition of Et₃N (0.5 mL) and the mixture concentrated in vacuo. The crude product was purified by column chromatography (toluene–EtOAc, 1:3) to give triol **20** (49 mg, 86%) as an oil; IR (film): 3524 (O–H), 1544 (N–O), 1372 cm^{–1}; ¹H NMR (500 MHz, CDCl₃): δ = 1.15 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 2.78 (br s, 3 H, OH), 3.21 (dd, $J_{5,6}$ = 9.9 Hz, $J_{6,6'}$ = 15.8 Hz, 1 H, 6-H^{II}), 3.35 (s, 3 H, OCH₃), 3.50 (dq, J = 7.1 Hz, J_{gem} = 9.7 Hz, 1 H, OCHH'CH₃), 3.61 (at, J = 9.5 Hz, 1 H, 4-H^{II}), 3.69 (dq, J = 7.1 Hz, J_{gem} = 9.7 Hz, 1 H, OCHH'CH₃), 3.78–3.82 (m, 3 H, 2-H^x, 6-H^I, 6'-H^{II}), 3.88 (br s, 1 H, 2-H^y), 3.94–4.09 (m, 5 H, 3-H^I, 4-H^I, 5-H^I, 6'-H^I, 3-H^{II}), 4.29 (at, J = 9.3 Hz, 1 H, 5-H^{II}), 4.59–4.67 (m, 5 H, 1-H^x, 2 \times PhCHH', PhCH₂), 4.74 (d, J = 12.3 Hz, 1 H, PhCHH'), 4.88 (br s, 1 H, 1-H^y), 5.10 (d, J = 11.6 Hz, 1 H, PhCHH'), 7.11–7.85 (m, 19 H, Ar-H); ¹³C NMR (125 MHz, CDCl₃): δ = 15.1 (q, OCH₂CH₃), 47.2 (t, C-6^{II}), 55.8 (q, OCH₃), 56.6 (d, C-4^I), 61.9 (t, C-6^I), 63.2 (t, OCH₂CH₃), 66.1, 70.3, 79.8 (3 \times d, C-3^I, C-5^I, C-3^{II}), 71.2 (d, C-5^{II}), 71.4 (d, C-2^y), 72.1, 72.9, 74.7 (3 \times t, PhCH₂), 74.7 (d, C-2^x), 77.2 (d, C-4^{II}), 99.0 (d, C-1^y), 99.1 (d, C-1^x), 123.8, 127.6, 127.6, 127.8, 127.8, 127.8, 128.3, 128.5, 128.5, 129.1, 131.4, 132.0, 133.8 (13 \times d, Ar-CH), 131.3, 138.3, 138.8, 147.8 (4 \times s, Ar-C); MS (ESI⁺): m/z (%) 877 (2) [M + K⁺], 861 (100) [M + Na⁺]; HRMS–ESI m/z [M + Na⁺] calcd for C₄₂H₅₀N₂O₁₄Na: 861.2875; found: 861.2881.

***N*-(methyl 6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 4-deoxy- α -D-mannopyranosid-4-yl)-amine (**21**)**

NH₃ (ca. 20 mL) was condensed at –78 °C and Na (100 mg, 4.3 mmol) was added, giving the mixture a dark blue colour. A few drops of MeOH were added and the colouration remained. Triol **19** (145 mg, 0.173 mmol) was dissolved in THF (2 mL) and transferred to the reaction vessel, after which the mixture turned brown. Further Na (100 mg, 4.3 mmol) was added, and the dark blue colour returned. After 30 min, the reaction was quenched by the addition of NH₄Cl (s) (465 mg, 8.68 mmol). After a few min, the blue colour disappeared. The mixture was allowed to warm to RT for the ammonia to evaporate, and then concentrated in vacuo. The residue was dissolved in CHCl₃–MeOH, 1:1 and filtered to remove inorganic salts. The procedure was repeated, after which the crude product was concentrated in vacuo and purified by column chromatography (MeOH–CHCl₃–NH₄OH (25% aq.), 5:5:1) to give diglycoside **21** (52 mg, 78%) as an oil; ¹H NMR (500 MHz, D₂O): δ = 1.25 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 2.85 (at J = 10.3 Hz, 1 H, 4-H^I), 2.87

(dd, $J_{5,6} = 8.2$ Hz, $J_{6,6'} = 12.6$ Hz, 1 H, 6-H^{II}), 3.14 (dd, $J_{5,6'} = 2.7$ Hz, $J_{6,6'} = 12.5$ Hz, 1 H, 6'-H^{II}), 3.35 (at, $J = 9.4$ Hz, 1 H, 4-H^{II}), 3.47 (s, 3 H, OCH₃), 3.59–3.63 (m, 2 H, 2-H^{II}, OCH₂CH₃), 3.66–3.73 (m, 3 H, 3-H^I or 5-H^I and 3-H^{II}, 5-H^{II}), 3.78–3.83 (m, 2 H, 6-H^I, OCH₂CH₃), 3.87 (dd, $J = 3.4$ Hz, $J = 10.3$ Hz, 1 H, 3-H^I or 5-H^I), 3.90–3.94 (m, 2 H, 2-H^I, 6'-H^I), 4.84 (d, $J_{1,2} = 3.8$ Hz, 1 H, 1-H^{II}), 4.92 (d, $J_{1,2} = 1.6$ Hz, 1 H, 1-H^I); ¹³C NMR (125.1 MHz, D₂O): $\delta = 14.2$ (q, OCH₂CH₃), 49.1 (t, C-6^{II}), 55.5 (q, OCH₃), 56.0 (d, C-4^I), 61.9 (t, C-6^I), 63.6 (t, OCH₂CH₃), 69.1, 70.8, 72.2, 73.1 (4 × d, C-3^I, C-5^I, C-3^{II}, C-5^{II}), 69.7 (d, C-2^I), 71.4 (d, C-2^{II}), 71.9 (d, C-4^{II}), 99.5 (d, C-1^{II}), 99.7 (d, C-1^I); MS (ESI⁺): m/z (%) 789 (26) [2M + Na⁺], 406 (41) [M + Na⁺], 384 (100) [M + H⁺]; HRMS–ESI m/z [M + Na⁺] calcd for C₁₅H₂₉NO₁₀Na: 406.1684; found: 406.1672.

***N*-(methyl 6-deoxy- α -D-mannopyranosid-6-yl)-*N*-(ethyl 4-deoxy- α -D-mannopyranosid-4-yl)-amine (22)**

NH₃ (ca. 20 mL) was condensed at –78 °C, and Na (100 mg, 4.3 mmol) was added, giving the mixture a dark blue colour. Triol **20** (109 mg, 0.130 mmol) was dissolved in THF (2 mL) and transferred to the reaction vessel, after which the mixture turned brown. Further Na (100 mg, 4.3 mmol) was added, and the dark blue colour returned. After 30 min, the reaction was quenched by the addition of NH₄Cl (s) (465 mg, 8.68 mmol). After a few min, the blue colour disappeared. The mixture was allowed to warm to RT for the ammonia to evaporate, and then concentrated in vacuo. The residue was dissolved in CHCl₃–MeOH, 1:1 and filtered to remove inorganic salts. The procedure was repeated, after which the crude product was concentrated in vacuo and purified by column chromatography (MeOH–CHCl₃–NH₄OH (25%), 20:10:1) to give diglycoside **22** (27 mg, 53%) as an oil; ¹H NMR (400 MHz, D₂O): $\delta = 1.13$ (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 2.92–2.99 (m, 2 H, 4-H^I, 6-H^{II}), 3.19 (d, $J = 12.7$ Hz, 1 H, 6'-H^{II}), 3.37 (s, 3 H, OCH₃), 3.45–3.53 (m, 2 H, 4-H^{II}, OCH₂CH₃), 3.61 (m, 1 H, 5-H^{II}), 3.65–3.75 (m, 4 H, 5-H^I, 6-H^I, 3-H^{II}, OCH₂CH₃), 3.78 (m, 1 H, 6'-H^I), 3.82 (dd, $J_{1,2} = 1.7$ Hz, $J_{2,3} = 3.3$ Hz, 1 H, 2-H^I), 3.85 (dd, $J_{1,2} = 1.7$ Hz, $J_{2,3} = 3.4$ Hz, 1 H, 2-H^{II}), 3.88 (dd, $J_{2,3} = 3.1$ Hz, $J_{3,4} = 10.4$ Hz, 1 H, 3-H^I), 4.68 (d, $J_{1,2} = 1.7$ Hz, 1 H, 1-H^{II}), 4.81 (d, $J_{1,2} = 1.7$ Hz, 1 H, 1-H^I); ¹³C NMR (100 MHz, D₂O): $\delta = 14.0$ (q, OCH₂CH₃), 48.4 (t, C-6^{II}), 55.1 (q, OCH₃), 56.3 (d, C-4^I), 61.7 (t, C-6^I), 63.6 (t, OCH₂CH₃), 67.8 (d, C-3^I), 67.8 (d, C-4^{II}), 69.4 (d, C-2^I), 69.8 (d, C-2^{II}), 70.2, 70.3 (2 × d, C-5^I, C-3^{II}, C-5^{II}), 99.5 (d, C-1^I), 101.0 (d, C-1^{II}); MS (ESI⁺): m/z (%) 789 (6) [2M + Na⁺], 406 (100) [M + Na⁺], 384 (10) [M + H⁺]; HRMS–ESI m/z [M + Na⁺] calcd for C₁₅H₂₉NO₁₀Na: 406.1684; found: 406.1684.

Ethyl 4-*O*-trichloroacetimidoyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy- α -D-threo-hex-2-enopyranoside (23)

Allylic alcohol **2** (149 mg, 0.517 mmol) was dissolved in freshly distilled CH₂Cl₂ (10 mL) under Ar. Trichloroacetonitrile (0.13 mL, 1.29 mmol) and DBU (0.09 mL, 0.62 mmol) were added, and the reaction mixture was stirred for 1 h 35 min. After this time, TLC (pentane–EtOAc, 6:1) indicated the complete consumption of starting material (*R*_f 0.1) and the formation of a major product (*R*_f 0.9). The reaction mixture was concentrated to dryness to give a black oil (650 mg). The crude product was purified by column chromatography (toluene, 1% Et₃N) to give trichloroacetimidate **23** (223 mg, 99%) as a yellow oil; [α]_D²⁴ –81.0 (*c* 0.7, CHCl₃); IR (film): 1662 (C=O) cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ = 0.04, 0.06 (2 \times s, 6 H, Si(CH₃)₂), 0.88 (s, 9 H, SiC(CH₃)₃), 1.25 (t, *J* = 7.2 Hz, 3 H, OCH₂CH₃), 3.58 (dq, *J*_{gem} = 10.0 Hz, *J* = 7.2 Hz, 1 H, OCHH'CH₃), 3.81–3.93 (m, 3 H, 6-H, 6'-H, OCHH'CH₃), 4.26 (dat, *J* = 6.8 Hz, *J*_{4,5} = 2.4 Hz, 1 H, 5-H), 5.11 (d, *J*_{1,2} = 2.8 Hz, 1 H, 1-H), 5.17 (dd, *J*_{3,4} = 5.6 Hz, *J*_{4,5} = 2.4 Hz, 1 H, 4-H), 6.07 (dd, *J*_{2,3} = 10.0 Hz, *J*_{1,2} = 2.8 Hz, 1 H, 2-H), 6.31 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 5.2 Hz, 1 H, 3-H), 8.29 (s, 1 H, C(NH)CCl₃); ¹³C NMR (400 MHz, CDCl₃): δ = –5.25, –5.30 (2 \times q, Si(CH₃)₂), 15.4 (q, OCH₂CH₃), 18.3 (s, SiC(CH₃)₃), 25.9 (q, SiC(CH₃)₃), 61.9 (t, C-6), 63.9 (t, OCH₂CH₃), 67.5 (d, C-5), 70.1 (d, C-4), 91.6 (s, CCl₃), 93.9 (d, C-1), 124.4 (d, C-3), 131.7 (d, C-2), 162.1 (d, C=NH); MS (ESI⁺): *m/z* 454 (100) [M + H⁺]; HRMS–ESI *m/z* [M + H⁺] calcd for C₁₆H₂₈Cl₃NO₄Si: 454.0751; found: 454.0763.

***N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-threo-hex-4-enopyranosid-2-yl)-amine (24), *N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-threo-hex-2-enopyranosid-4-yl)-amine (25), and *N*-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy- α -D-glucopyranosid-6-yl)-*N*-(ethyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy- α -D-erythro-hex-2-enopyranosid-4-yl)-amine (26)**

Trichloroacetimidate **23** (95 mg, 0.219 mmol), amine **5** (305 mg, 0.659 mmol), TMPP (trimethylolpropane phosphite, 3.5 mg, 0.022 mmol) and Pd(dba)₂ (6.4 mg, 0.011 mmol) were added to a Schlenk tube (10 mL). The tube was put under vacuum and backfilled with argon. This process was repeated three times. Degassed MeCN (1.3 mL) and Et₃N (70 μ L, 0.678 mmol) were added, and the reaction mixture was stirred at RT. After 19 h, TLC (pentane–EtOAc, 2:1) indicated the complete consumption of trichloroacetimidate (*R*_f 0.9) and the formation of what appeared to be three products (*R*_f 0.7, 0.6, 0.3). The reaction mixture was evaporated to give a brown oil (423 mg). The crude product was purified by column chromatography (Pentane–EtOAc, 3:1) to give **24**

(71 mg, 44%), an inseparable mixture (19 mg), and a mixture of **25–27** (57 mg) which was separated by column chromatography (CH₂Cl₂–EtOAc, 7:1) to give **25** (24 mg, 15%), **26** (8 mg, 5%), and **27** (10 mg, 6%).

Data for **24**: $[\alpha]_D^{24} +55.9$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.04, 0.05 (2 × s, 6 H, Si(CH₃)₂), 0.88 (s, 9 H, C(CH₃)₃), 1.22 (t, *J* = 7.2 Hz, 3 H, OCH₂CH₃), 2.74 (dd, *J*_{6,6'} = 12.4 Hz, *J*_{5,6} = 6.0 Hz, 1 H, 6-H^{II}), 2.86 (m, 1 H, 2-H^I), 3.00 (dd, *J*_{6,6'} = 12.4 Hz, *J*_{5,6'} = 2.8 Hz, 1 H, 6'-H^{II}), 3.36 (s, 3 H, OCH₃), 3.46–3.62 (m, 4 H, 6-H^I, 2-H^{II}, 4-H^{II}, OCHH'CH₃), 3.69–3.72 (m, 2 H, 6'-H^I, 5-H^{II}), 3.81 (dq, *J*_{gem} = 9.6 Hz, *J* = 7.2 Hz, 1 H, OCHH'CH₃), 3.97 (at, *J* = 9.2 Hz, 1 H, 3-H^{II}), 4.13 (m, 1 H, 5-H^I), 4.53 (d, *J*_{1,2} = 3.6 Hz, 1 H, 1-H^{II}), 4.66, 4.79 (2 × d, *J* = 12.0 Hz, 2 H, PhCH₂), 4.62, 4.88 (2 × d, *J* = 11.2 Hz, 2 H, PhCH₂), 4.81, 4.97 (2 × d, *J* = 10.8 Hz, 2 H, PhCH₂), 4.86 (s, 1 H, 1-H^I), 5.81–5.89 (m, 2 H, 3-H^I, 4-H^I), 7.27–7.37 (m, 15 H, Ar-H); ¹³C NMR (400 MHz, CDCl₃): δ = –5.2, –5.2 (2 × q, Si(CH₃)₂), 15.3 (q, OCH₂CH₃), 18.5 (s, SiC(CH₃)₃), 26.0 (q, SiC(CH₃)₃), 47.1 (t, C-6^{II}), 54.4 (d, C-2^I), 55.3 (q, OCH₃), 63.7 (t, OCH₂CH₃), 65.6 (d, C-6^I), 69.1 (d, C-5^I), 70.6 (d, C-5^{II}), 73.5, 75.1, 75.8 (3 × t, 3 × PhCH₂), 79.1 (d, C-4^{II}), 79.1 (d, C-2^{II}), 82.2 (d, C-3^{II}), 98.0 (d, C-1^{II}), 98.9 (d, C-1^I), 125.7 (d, C-3^I), 128.3 (d, C-4^I), 127.7, 127.8, 128.0, 128.0, 128.1, 128.2, 128.5, 128.5, 128.6 (9 × d, Ar-CH), 138.4, 138.6, 139.0 (3 × s, 3 × Ar-C); MS (ESI⁺): *m/z* (%) 734 (100) [M + H⁺]; HRMS–ESI *m/z* [M + H⁺] calcd for C₄₂H₆₀NO₈Si: 734.4083; found: 734.4032.

Data for **25**: $[\alpha]_D^{24} -35.0$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.02, 0.04 (2 × s, 6 H, Si(CH₃)₂), 0.86 (s, 9 H, SiC(CH₃)₃), 1.23 (t, *J* = 7.2 Hz, 3 H, OCH₂CH₃), 2.77 (dd, *J*_{6,6'} = 12.4 Hz, *J*_{5,6} = 4.4 Hz, 1 H, 6-H^{II}), 2.89 (dd, *J*_{3,4} = 5.2 Hz, *J*_{4,5} = 3.2 Hz, 1 H, 4-H^I), 3.06 (dd, *J*_{6,6'} = 12.4 Hz, *J*_{5,6'} = 2.8 Hz, 1 H, 6'-H^{II}), 3.34 (s, 3 H, OCH₃), 3.46 (m, 1 H, 2-H^{II}), 3.52, 3.90 (2 × m, 2 H, OCH₂CH₃), 3.64 (m, 1 H, 4-H^{II}), 3.69 (m, 1 H, 5-H^{II}), 3.81 (d, *J*_{5,6} = 6.4 Hz, 2 H, 6-H^I, 6'-H^I), 3.96 (at, *J* = 9.2 Hz, 1 H, 3-H^{II}), 4.05 (dat, *J*_{5,6} = 6.4 Hz, *J* = 2.8 Hz, 1 H, 5-H^I), 4.49 (d, *J*_{1,2} = 3.6 Hz, 1 H, 1-H^{II}), 4.64, 4.87 (2 × d, *J* = 10.8 Hz, 2 H, PhCH₂), 4.66, 4.80 (2 × d, *J* = 12.0 Hz, 2 H, PhCH₂), 4.81, 4.96 (2 × d, *J* = 10.8 Hz, 2 H, PhCH₂), 4.96 (m, 1 H, 1-H^I), 5.82 (dd, *J*_{2,3} = 10.0 Hz, *J*_{1,2} = 2.8 Hz, 1 H, 2-H^I), 6.19 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 5.2 Hz, 1 H, 3-H^I), 7.26–7.32 (m, 15 H, Ar-H); ¹³C NMR (400 MHz, CDCl₃): δ = –5.2, –5.3 (2 × q, Si(CH₃)₂), 15.4 (q, OCH₂CH₃), 18.4 (s, SiC(CH₃)₃), 25.9 (q, SiC(CH₃)₃), 46.8 (t, C-6^{II}), 50.4 (d, C-4^I), 55.2 (q, OCH₃), 63.3 (t, OCH₂CH₃), 63.5 (d, C-6^I), 70.7 (d, C-5^{II}), 71.9 (d, C-5^I), 73.6, 75.2, 75.9 (3 × t, 3 × CH₂Ph), 78.6 (d, C-4^{II}), 80.2 (d, C-2^{II}), 82.2 (d, C-3^{II}), 94.3 (d, C-1^I), 98.2 (d, C-1^{II}), 127.4 (d, C-2^I), 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 128.5, 128.6, (9 × d, Ar-CH), 131.0 (d, C-3^I), 138.4, 138.7, 139.0, (3 × s, 3 × Ar-C); MS (ESI⁺): *m/z* (%) 734 (100) [M + H⁺]; HRMS–ESI *m/z* [M + H⁺] calcd for C₄₂H₆₀NO₈Si: 734.4083; found: 734.4108.

Data for **26**: $[\alpha]_{\text{D}}^{24} +32.1$ (*c* 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.05 (s, 6 H, Si(CH₃)₂), 0.88 (s, 9 H, SiC(CH₃)₃), 1.22 (t, *J* = 7.2 Hz, 3 H, OCH₂CH₃), 2.74–2.81 (m, 2 H, 6-H^{II}, 6'-H^{II}), 3.03 (dat, *J*_{4,5} = 10.0 Hz, *J* = 1.6 Hz, 1 H, 4-H^I), 3.34 (s, 3 H, OCH₃), 3.36 (at, *J* = 9.2 Hz, 1 H, 4-H^{II}), 3.47 (dd, *J*_{2,3} = 9.6 Hz, *J*_{1,2} = 3.6 Hz, 1 H, 2-H^{II}), 3.49–3.56 (m, 1 H, OCHH'CH₃), 3.57–3.62 (m, 1 H, 5-H^I), 3.67–3.72 (m, 1 H, 5-H^{II}), 3.76 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{5,6} = 6.0 Hz, 1 H, 6-H), 3.82–3.94 (m, 2 H, 6'-H, OCHH'CH₃), 3.98 (t, *J* = 9.6 Hz, 1 H, 3-H^{II}), 4.51 (d, *J*_{1,2} = 3.6 Hz, 1 H, 1-H^{II}), 4.59, 4.88 (2 × d, *J* = 11.2 Hz, 2 H, PhCH₂), 4.66, 4.78 (2 × d, *J* = 12.0 Hz, 2 H, PhCH₂), 4.81 (d, *J* = 11.2 Hz, 1 H, PhCHH'), 4.96–4.99 (m, 2 H, 1-H, PhCHH'), 5.72 (dat, *J*_{2,3} = 10.0 Hz, *J* 2.4 Hz, 1 H, 2-H^I), 5.96 (br d, *J*_{2,3} = 10.0 Hz, 1 H, 3-H^I), 7.26–7.37 (m, 15 H, Ar-H); ¹³C NMR (400 MHz, CDCl₃): δ = -5.1, -5.1 (2 × q, Si(CH₃)₂), 15.5 (q, OCH₂CH₃), 18.6 (s, SiC(CH₃)₃), 26.1 (q, SiC(CH₃)₃), 47.2 (t, C-6^{II}), 52.7 (d, C-4^I), 55.2 (q, OCH₃), 63.6 (t, OCH₂CH₃), 64.4 (d, C-6^I), 70.7 (d, C-5^{II}), 71.7 (d, C-5^I), 73.5, 75.2, 75.9 (3 × t, 3 × PhCH₂), 79.6 (d, C-4^{II}), 80.3 (d, C-2^{II}), 82.2 (d, C-3^{II}), 94.1 (d, C-1^I), 97.9 (d, C-1^{II}), 125.8 (d, C-2^I), 127.7, 127.9, 128.0, 128.1, 128.1, 128.2, 128.5, 128.6, 128.6 (9 × d, Ar-CH), 132.1 (d, C-3^I), 138.3, 138.4, 138.9, (3 × s, 3 × Ar-C); MS (ESI⁺): *m/z* (%) 734 (100) [M + H⁺]; HRMS–ESI *m/z* [M + H⁺] calcd for C₄₂H₆₀NO₈Si: 734.4083; found: 734.4108.

Data for **27**: $[\alpha]_{\text{D}}^{24} -24.1$ (*c* 0.8, CHCl₃); IR (film): 1694 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 0.02, 0.04 (2 × s, 6 H, Si(CH₃)₂), 0.86 (s, 9 H, SiC(CH₃)₃), 1.23 (t, *J* = 6.8 Hz, 3 H, OCH₂CH₃), 3.28 (at, *J* = 9.2 Hz, 1 H, 4-H^{II}), 3.33 (s, 3 H, OCH₃), 3.38–3.46 (m, 3 H, 2-H^{II}, 6-H^{II}, 6'-H^{II}), 3.64 (m, 1 H, 5-H^{II}), 3.73–3.79 (m, 2 H, 6-H^I, 6'-H^I), 3.54, 3.88 (2 × m, 2 H, OCH₂CH₃), 3.98 (t, *J* = 9.2 Hz, 1 H, 3-H^{II}), 4.18 (m, 1 H, 5-H^I), 4.50 (d, *J*_{1,2} = 3.6 Hz, 1 H, 1-H^{II}), 4.59–4.66 (m, 2 H, PhCH₂), 4.78–4.86 (m, 3 H, PhCH₂, PhCHH'), 4.95 (dd, *J*_{3,4} = 5.2 Hz, *J*_{4,5} = 2.4 Hz, 1 H, 4-H^I), 4.98 (d, *J* = 10.8 Hz, 1 H, PhCHH'), 5.05 (m, 1 H, 1-H^I), 5.98 (dd, *J*_{2,3} = 10.0 Hz, *J*_{1,2} = 3.2 Hz, 1 H, 2-H^I), 6.15 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 5.2 Hz, 1 H, 3-H^I), 7.27–7.36 (m, 15 H, Ar-H); ¹³C NMR (400 MHz, CDCl₃): δ = -5.2, -5.3 (2 × q, Si(CH₃)₂), 15.3 (q, OCH₂CH₃), 18.3 (s, SiC(CH₃)₃), 25.9 (q, SiC(CH₃)₃), 41.7, 55.4 (q, OCH₃), 62.2, 63.5, 63.8, 69.3, 70.2, 73.6, 75.3, 75.9, 78.7, 80.0, 81.9, 91.9 (12 × d, t), 93.9 (d, C-1^I), 98.1 (d, C-1^{II}), 126.4 (d, C-2^I), 127.7, 128.0, 128.1, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7 (9 × d, Ar-CH), 130.4 (d, C-3^I), 138.0, 138.2, 138.8, (3 × s, 3 × Ar-C), 155.9, 163.4 (2 × s); MS (ESI⁺): *m/z* (%) 800 (100) [M + H⁺]; HRMS–ESI *m/z* [M + H⁺] calcd for C₄₂H₆₀NO₈Si: 800.3806; found: 800.3790.

Assays against glycosidases

The commercially available glycosidases tested were: α-L-Fucosidase (bovine kidney: EC 3.2.1.51), α-galactosidase (coffee beans: EC 3.2.1.22), β-galactosidase (*Escherichia coli* and

Aspergillus orizae: EC 3.2.1.23), α -glucosidase (yeast and rice: EC 3.2.1.20), amyloglucosidase (*Aspergillus niger*: EC 3.2.1.3), β -glucosidase (almonds: EC 3.2.1.21), α -mannosidase (jack beans: EC 3.2.1.24), β -mannosidase (snail: EC 3.2.1.25), β -xylosidase (*Aspergillus niger*: EC 3.2.1.37), β -*N*-acetylglucosaminidase (jack beans: EC 3.2.1.30). The experiments were performed essentially as previously described [1,2]. Briefly, 0.01–0.5 units/mL of enzyme and inhibitor were pre-incubated for 5 min at RT, and the reaction was started by addition of the substrate, buffered to the optimal pH of the enzyme. After 20 min of incubation at 37 °C, the reaction was stopped by addition of sodium borate buffer pH 9.8. The *p*-nitrophenolate formed was measured by visible absorption spectroscopy at 405 nm.

The assays against α -Glucosidase II were carried out as described previously [3].

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