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Supplementary Material for:

Nodulation Factors: A Strategy for Convergent Assembly of a
Late-Stage Key intermediate Illustrated by the Total Synthesis of
NodRf-III (C18:1) (MeFuc)

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General Methods. All reactions were conducted under an inert argon atmosphere. THF was distilled from sodium benzophenone ketyl. Dichloromethane and acetonitrile were distilled from calcium hydride. Absolute ethanol was stored over 4Å molecular sieves. Solutions of compounds in organic solvents were dried over sodium sulfate prior to rotary evaporation. TLC plates were Kieselgel 60 F254 (Merck Art. 5554). Carbohydrate compounds were visualized on the TLC plate by charring with H₂SO₄/EtOH/H₂O (1:10:10). Flash column chromatography was done with silica gel 60 (230-400 mesh, Merck). Optical rotations were determined at the sodium D line with a Perkin-Elmer 241 polarimeter. Mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 3k resolution for low resolution fast atom bombardment (FAB) spectra. FAB mass spectra were conducted using a m-nitrobenzyl alcohol matrix with xenon as the fast atom. Accurate mass measurements were made using FAB at 10k resolution. ¹H and ¹³C NMR spectra were recorded on a Varian XL-300, Inova-400 or GE QE-300 spectrometer. Abbreviations for NMR data are as follows: s= singlet, bs= broad singlet, d= doublet, bd= broad doublet, m= multiplet, dd= doublet of doublets, t= triplet, bt= broad triplet. Coupling constants are reported in Hertz and chemical shifts are in ppm on the delta scale. ¹H and ¹³C chemical shifts are reported relative to internal tetramethylsilane (0.00 ppm).

4,5-Dibromopentanyl (3,4-Di-O-acetyl-6-O-benzyl-2-deoxy-2-tetrachlorophthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13a). To **4** (0.673 g, 0.924 mmol) and **6** (0.476 g, 0.711 mmol) (both dried by azeotroping together with toluene) in CH₂Cl₂ (6.6 mL) was added *N*-iodosuccinimide (0.291 g, 1.294 mmol) and triethylsilyl triflate (83.6 μL, 0.370 mmol). After stirring for 16 min at -20 °C the glycosyl donor had been consumed and the reaction was quenched with 10% aq Na₂S₂O₃ (4 mL) and of sat aq NaHCO₃ (4 mL) solution. The mixture was stirred for an additional 5 min before separating the layers and extracting the aqueous phase

with CH₂Cl₂ (3×15 mL). The concentrated CH₂Cl₂ solution was purified *via* flash chromatography eluting with 25:75 EtOAc / petroleum ether affording **13a** as a white foam (0.643 g, 71%); ¹H NMR (300 MHz, CDCl₃) δ 7.71-7.85 (m, 4H), 7.09-7.36 (m, 10H), 5.76 (t, *J*=9.6 Hz, 1H), 5.61 (dd, *J*=0.9, 10.2 Hz, 1H), 5.51 (d, *J*=8.3 Hz, 1H), 5.19-5.29 (m, 2H), 4.34-4.53 (m, 4H), 4.09-4.23 (m, 3H), 3.88-3.90 (m, 1H), 3.72-3.85 (m, 1H), 3.28-3.64 (m, 9H), 1.89 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H), 1.51-2.05 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 170.33, 169.62, 168.98, 167.74, 167.32, 163.51, 162.21, 140.01, 137.56, 137.22, 134.01, 131.31, 131.14, 129.35, 128.09, 127.95, 127.67, 127.47, 127.22, 126.71, 126.31, 123.30, 97.82, 97.75, 96.81, 74.56, 74.27, 73.16, 72.99, 72.57, 71.54, 70.63, 68.91, 68.27, 68.02, 67.73, 55.69, 54.81, 52.11, 35.92, 32.51, 32.46, 26.71, 26.65, 20.40, 20.35, 20.23.

Pent-4-enyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-β-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13b). To **13a** (0.506 g, 0.398 mmol) in methyl ethyl ketone (18 mL) was added NaI (0.894g, 5.964 mmol). The reaction stirred 13 h at 80 °C and was then concentrated *in vacuo*. The syrup was dissolved in EtOAc (20 mL) and washed with 10% aq Na₂S₂O₃ (15 mL) back extracting the aqueous phase with EtOAc (2×15 mL). The concentrated EtOAc solution was purified *via* flash chromatography eluting with 40:60 EtOAc / petroleum ether affording **13b** as a white foam (0.442 g, 93%); ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.85 (m, 4H), 7.10-7.34 (m, 10H), 5.78 (dd, *J*=1.7, 10.6 Hz, 1H), 5.50-5.66 (m, 3H), 5.18-5.30 (m, 2H), 4.66-4.76 (m, 2H), 4.36-4.56 (m, 4H), 4.08-4.24 (m, 3H), 3.37-3.78 (m, 8H), 1.90 (s, 3H), 1.85 (s, 6H), 1.81-1.92 (m, 2H), 1.40-1.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.45, 169.74, 169.09, 167.79, 167.65, 163.64, 162.32, 140.11, 137.72, 137.47, 137.32, 134.08, 131.33 (bd), 129.46, 128.18, 128.01, 127.77, 127.55, 127.27, 126.83, 126.44, 123.28, 114.55, 97.85, 96.94, 74.74, 74.35, 73.27, 73.04, 72.65, 71.71, 70.77, 69.06, 68.71, 68.16, 67.78, 55.79, 54.98, 29.62, 28.28, 20.49, 20.41, 20.30.

Benzyl (3,4-Di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (15). To **14** (887.0 mg, 1.95 mmol) and **7** (958.1, 1.95 mmol) (both dried by azeotroping together with toluene) in Et₂O : CH₂Cl₂ (5:1, 17 mL) was added *N*-iodosuccinimide (677 mg, 3.01 mmol) and triethylsilyl triflate (146 μL, 0.645 mmol). After stirring for 25 minutes at room temperature, the glycosyl donor had been consumed and the reaction was quenched with 10% aq Na₂S₂O₃ (5 mL) and satd aq NaHCO₃ (5 mL). The mixture was diluted with CHCl₃ (150 mL) and washed with brine (2 × 50 mL). The aqueous layers were back extracted with CHCl₃ (3 × 50 mL). The concentrated CHCl₃ solution was purified *via* flash chromatography eluting with 65:35→45:55 petroleum ether/ ethyl acetate to

afford **15** as a white foam (1.0373 g, 1.21 mmol) and recovered **7** (259.5 mg, 0.53 mmol). The total yield of **15** was 85% based on recovered alcohol **7**. ^1H NMR (300 MHz, CDCl_3) δ 8.06 (d, $J = 7.1$ Hz, 2H), 7.89 (d, $J = 7.1$ Hz, 2H), 7.49 - 7.86 (m, 8H), 7.30 - 7.35 (m, 3H), 6.92 - 7.11 (m, 9H), 5.66 - 5.71 (m, 2H), 5.22 (d, $J = 3.7$ Hz, 1H), 5.16 - 5.19 (m, 1H), 4.78 (dt, $J = 2.4$ Hz, 12.5 Hz, 2H), 4.52 (t, $J = 13.3$ Hz, 2H), 4.43 - 4.46 (m, 1 H), 4.25 (dd, $J = 1.0$ Hz, 3.5 Hz, 2H), 3.89 - 4.14 (m, 4H), 3.70 - 3.75 (m, 1H), 3.51 (s, 3H), 2.75 (m, 1H), 1.23 (d, $J = 6.57$, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.92, 165.87, 165.50, 138.34, 137.11, 133.70, 133.32, 133.00, 131.67, 130.01, 129.81, 129.75, 129.65, 128.58, 128.29, 128.20, 128.10, 127.93, 127.59, 127.34, 123.27, 97.92, 97.28, 78.41, 76.34, 74.25, 73.69, 73.41, 72.19, 71.07, 70.64, 68.73, 65.25, 59.55, 55.55, 16.13.

Benzyl (3,4-Di-O-acetyl-6-O-benzyl-2-deoxy-2-tetrachlorophthalimido- β -D-glucopyranosyl)-(1 \rightarrow 4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 4)-[(3,4-Di-O-benzoyl-2-O-methyl- α -L-fucopyranosyl)-(1 \rightarrow 6)]-3-O-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (3a**). To **13b** (0.413 g, 0.37 mmol) and **15** (0.245 g, 0.29 mmol) (both dried by azeotroping together with toluene) in CH_2Cl_2 (2.9 mL) at 0 °C was added *N*-iodosuccinimide (0.110 g, 0.48 mmol) and triethethylsilyl triflate (30 μL , 0.13 mmol). After stirring for 22 min at 0 °C, the reaction was quenched with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) and satd aq NaHCO_3 (2 mL). The mixture was diluted with CH_2Cl_2 (15 mL) before separating the layers. The aqueous phase was extracted with CH_2Cl_2 (3 \times 10 mL). The concentrated residue was purified via flash chromatography eluting with 2:3 ethyl acetate / petroleum ether to give **3a** as a white amorphous powder (0.349 g, 65%); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.3$ Hz, 2H), 7.90 - 7.92 (bs, 2H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.71 - 7.81 (m, 3H), 7.58 - 7.66 (m, 2H), 7.46 - 7.54 (m, 3H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.20 - 7.32 (m, 6H), 7.12 - 7.19 (m, 3H), 6.96 - 7.04 (m, 5H), 6.93 (d, $J = 6.7$ Hz, 2H), 6.77 (d, $J = 6.7$ Hz, 2H), 6.61 - 6.70 (m, 4H), 5.80 (dt, $J = 1.6$ Hz, 8.6 Hz, 1H), 5.58 - 5.66 (m, 4H), 5.49 (d, $J = 8.3$ Hz, 1H), 5.27 (d, $J = 3.5$ Hz, 1H), 5.17 (t, 9.4 Hz, 1H), 4.94 (d, $J = 8.6$ Hz, 1H), 4.67 (d, $J = 12.4$ Hz, 1H), 4.59 (d, $J = 12.9$ Hz, 1H), 4.32 - 4.47 (m, 7H), 4.11 - 4.24 (m, 5H), 4.03 - 4.08 (m, 1H), 3.91 (dd, $J = 6.5$ Hz, 3.5 Hz, 2H), 3.85 (d, $J = 11.0$ Hz, 1H), 3.78 (d, $J = 12.1$ Hz, 1H), 3.72 (d, $J = 9.6$ Hz, 1H), 3.41 - 3.60 (m, 8H), 3.32 (bd, $J = 7.8$ Hz, 1H), 1.89 (s, 3H), 1.80 (s, 6H), 1.14 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.55, 169.77, 169.27, 168.26, 167.63, 165.87, 165.31, 140.06, 138.27, 137.92, 137.46, 137.02, 134.49, 134.25, 133.17, 132.81, 131.59, 131.41, 129.98, 129.87, 129.77, 129.65, 129.42, 128.49, 128.26, 128.08, 128.04, 127.91, 127.65, 127.63, 127.55, 127.45, 127.34, 127.21, 126.94, 126.76, 126.71, 126.63, 126.33, 123.74, 123.41, 97.76, 96.79, 96.54, 96.28, 76.48, 76.12, 75.52, 75.28, 74.28, 74.18, 73.52, 73.40, 73.25, 72.65, 72.59, 72.37, 70.77, 70.64, 69.95,**

69.33, 68.49, 67.50, 64.74, 64.58, 59.44, 55.94, 55.84, 55.63, 20.63, 20.53, 20.41, 15.98; MS (FAB) m/z 1883.34 (M⁺).

Tertbutyldimethylsilyl (3,4-Di-O-acetyl-6-O-tertbutyldimethylsilyl-2-deoxy-2-tetrachlorophthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-tertbutyldimethylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-Di-O-benzoyl-2-O-methyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (3b). To **3a** (73.2 mg, 0.0388 mmol) in CH₂Cl₂ (2.6 mL) at 0 °C under strict anhydrous conditions was added FeCl₃ (100.6 mg, 0.62 mmol). The reaction was stirred at 0 °C for 2h 20 min before quenching with H₂O (1 mL). The mixture was diluted with CHCl₃ (25 mL) and extracted with brine (10 mL). The aqueous phase was extracted with CHCl₃ (2 × 10 mL) and the organic layers combined, filtered, and concentrated. The residue was flash chromatographed eluting with 45:55 CH₂Cl₂ / ethyl acetate to give the tetrol (48 mg, 81%) as a white solid. [MS (FAB) m/z 1523 (M⁺)] To the tetrol (196.4 mg, 0.129 mmol) in dimethylformamide (6 mL) at 0 °C was added imidazole (98.3 mg, 1.44 mmol). After 10 minutes, TBDMSCl (282.2 mg, 1.87 mmol) was added at 0 °C. The reaction was allowed to slowly come to room temperature and stirred 12 h before being quenched by addition of sat aq NaHCO₃. The excess dimethylformamide was concentrated *in vacuo*, and the residue was taken up in CHCl₃ (100 mL) and washed successively with sat aq NaHCO₃ (25 mL) and brine (25 mL). The aqueous layers were extracted with CHCl₃ (4 × 25 mL). The organic layers were combined, filtered, and concentrated. The residue was flash chromatographed eluting with 30:70 → 35:65 ethyl acetate / petroleum ether to afford **3b** (192.3 mg, 80%) as a white amorphous powder. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 6.9 Hz, 2H), 7.91 - 7.96 (m, 2H), 7.78 - 7.87 (m, 5H), 7.68 - 7.73 (m, 2H), 7.59 - 7.65 (m, 1 H), 7.46 - 7.53 (m, 3H), 7.28 - 7.35 (m, 3H), 5.72 - 5.77 (m, 1H), 5.61 - 5.67 (m, 1H), 5.55 (d, *J* = 3.4 Hz, 1H), 5.40 - 5.45 (m, 2H), 5.37 (d, *J* = 8.5 Hz, 1H), 5.35 (d, *J* = 8.2 Hz, 1H), 5.11 (t, *J* = 9.4 Hz, 1H), 4.91 (d, 3.4 Hz, 1H), 4.32 - 4.38 (m, 1H), 4.16 - 4.22 (m, 1H), 4.09 - 4.14 (m, 1H), 3.96 - 4.05 (m, 4H), 3.69 - 3.81 (m, 4H), 3.49 - 3.62 (m, 6H), 3.41 (s, 3H), 3.38 (m, 1H), 3.26 (dd, *J* = 6.2 Hz, 4.7 Hz, 1H), 1.99 (s, 3H), 1.94 (s, 3H), 1.84 (s, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 9H), 0.77 (m, 9H), 0.66 (m, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H), -0.04 (s, 3H), -0.08 (s, 3H), -0.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.57, 169.87, 169.16, 168.35, 167.80, 167.48, 167.09, 165.75, 165.31, 163.24, 162.44, 162.06, 140.62, 134.63, 134.42, 134.36, 134.13, 133.73, 133.14, 132.79, 131.81, 131.31, 131.17, 129.88, 129.72, 129.67, 129.49, 128.42, 128.17, 126.64, 123.91, 123.78, 123.45, 123.29, 122.75, 98.00, 97.00, 96.08, 93.17, 80.91, 75.99, 75.21, 74.42, 73.59, 73.57, 71.91, 71.04, 70.94, 70.15, 69.33, 69.20, 65.38, 64.27, 62.23, 61.48, 59.46,

57.95, 55.77, 54.86, 25.84, 25.69, 25.23, 20.75, 20.68, 20.40, 18.25, 18.01, 17.44, 16.03, -4.36, -5.54, -5.59, -5.62; MS (FAB) *m/e* 1865.1 (M).

Tertbutyldimethylsilyl (3,4-Di-O-acetyl-2-deoxy-2-((11Z)-octadecenamido)-6-O-tertbutyldimethylsilyl-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-tertbutyldimethylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-[(3,4-Di-O-benzoyl-2-O-methyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (3c). To **3b** (194.6 mg, 0.108 mmol) in 1.3 mL of 3:1 acetonitrile:tetrahydrofuran was added ethylenediamine (15.2 μL, 0.227 mmol) before heating to 60 °C. The reaction mixture was stirred for 10 h, allowed to cool to room temperature, concentrated and then filtered through a short column of silica gel with 10:90 methanol:CH₂Cl₂. The amine was then added to cis-11-octadecenoic acid (0.146 g, 0.517 mmol) pretreated with both triethylamine (0.144 mL, 1.03 mmol) for 15 min and then 2-chloro-N-methylpyridinium iodide (0.132 g, 0.517 mmol) for 15 min at 40 °C. The reaction stirred 2.5 h and was then concentrated *in vacuo*. To the residue was added acetic anhydride (0.256 mL, 2.71 mmol), triethylamine (45 μL, 0.325 mmol) and DMAP (40.0 mg, 0.325 mmol) in CH₂Cl₂ (1 mL) for 12 h. The reaction mixture was diluted with CH₂Cl₂ (15 mL) and washed with sat aq NaHCO₃ (8 mL) back extracting the aqueous portion with CH₂Cl₂ (4×15 mL). The reaction mixture was concentrated, and the residue was purified by flash chromatography eluting with 40:60 EtOAc / petroleum ether. Compound **3b** was recovered as a film (49 mg, 25%); ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J*=6.8 Hz, 2H), 7.78-7.87 (m, 5H), 7.62-7.75 (m, 5H), 7.44-7.54 (m, 3H), 7.26-7.32 (m, 3H), 5.54-5.76 (m, 5H), 5.46 (d, *J*=7.9 Hz, 1H), 5.32-5.37 (m, 2H), 5.29 (d, *J*=3.4 Hz, 1H), 5.14 (d, *J*=8.9 Hz, 1H), 5.07 (t, *J*=10.3 Hz, 1H), 4.98 (t, *J*=9.2 Hz, 1H), 4.69 (d, *J*=8.5 Hz, 1H), 4.48 (m, 1H), 4.18-4.27 (m, 2H), 4.02-4.10 (m, 2H), 3.85-3.96 (m, 3H), 3.63-3.75 (m, 5H), 3.57 (d, *J*=9.6 Hz, 2H), 3.47 (s, 3H), 3.36-3.42 (m, 1H), 1.97-2.05 (m, 6H), 1.96 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.87 (s, 3H), 1.20-1.37 (m, 22H), 1.17 (d, *J*=6.8 Hz, 3H), 0.97 (s, 9H), 0.83-0.09 (m, 12H), 0.66 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H), -0.01 (s, 3H), -0.02 (s, 3H), -0.03 (s, 3H), -0.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.27, 170.93, 170.29, 169.28, 168.11 (bs), 167.39, 167.27, 165.92, 165.18, 134.23, 134.08, 133.93, 133.23, 132.85, 131.69, 131.48, 131.37, 129.93, 129.79, 129.75, 128.53, 128.24, 123.67, 123.26 (bs), 100.23, 96.19, 95.68, 93.24, 77.20, 76.47, 75.09, 74.88, 74.38, 73.64, 72.96, 72.37, 72.31, 71.23, 70.28, 70.21, 69.19, 64.98, 64.51, 62.33, 61.41, 59.02, 57.22, 55.29, 54.54, 36.44, 31.77, 29.78, 29.72, 29.55, 29.39, 29.34, 29.29, 28.98, 28.88, 27.21, 26.09, 25.82, 25.24, 22.65, 21.05, 20.78, 20.67, 18.20, 17.48, 16.20, 14.12, -0.02, -4.35, -4.94, -5.27, -5.59, -5.62, -5.66; HRMS (FAB) calcd 1904.9088, found 1904.9178 (M+H)⁺.

Tertbutyldimethylsilyl (2-deoxy-2-((11Z)-octadecenamido)-6-O-tertbutyldimethylsilyl-β-D-glucopyranosyl)-(1→4)-(6-O-tertbutyldimethylsilyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(2-O-methyl-α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-β-D-glucopyranoside (17). To **3c** (14.0 mg, 7.347 μmol) in EtOH (0.67 mL) and MeOH (0.33 mL) was added ethylenediamine (0.45 mL, 6.74 mmol). The reaction was stirred for 34 h at 90 °C and then concentrated *in vacuo*. The reaction mixture was filtered through a short column of silica gel with 12:88 MeOH / CH₂Cl₂. The residue was then treated with acetic anhydride (17 μL, 0.184 mmol) and NEt₃ (25 μL, 0.184 mmol) in CH₂Cl₂ for 45 min before the reaction mixture was concentrated *in vacuo*. To the residue was added NaOMe solution (0.25 mmol in 0.5 mL MeOH) in MeOH (1 mL). The reaction mixture was concentrated after 2 hrs and then purified by flash chromatography eluting with 12:88 MeOH / CH₂Cl₂. Compound **17** was recovered as a film (8.0 mg, 80%); ¹H NMR (400 MHz, 20% MeOD-d₄/80% CDCl₃) δ 5.19-5.27 (m, 2H), 4.73 (d, *J*=3.1 Hz, 1H), 4.44-4.50 (m, 1H), 4.33-4.41 (m, 1H), 4.3 (d, *J*=8.6 Hz, 1H), 3.92-4.0 (m, 1H), 3.15-3.90 (m, 33H), 2.05-2.12 (m, 1H), 1.86-1.92 (m, 4H), 1.85 (s, 3H), 1.84 (s, 3H), 1.12-1.25 (m, 22H), 1.10 (d, *J*=6.5 Hz, 3H), 0.78-0.82 (m, 12H), 0.77 (s, 9H), 0.73 (s, 9H), -0.08-(-0.02) (m, 15H), -0.13 (s, 3H); ¹³C NMR (100 MHz, 20% MeOD-d₄/80% CDCl₃) δ 175.67, 171.74 (bs), 129.71, 129.61, 101.49, 101.34, 95.54, 96.15, 79.67, 79.25, 78.62, 77.20, 76.29, 74.62, 72.96, 72.72, 72.36, 71.78, 70.53, 69.99, 65.96, 65.36, 63.26, 61.13, 59.86, 59.61, 57.32, 55.40, 54.65, 36.23, 31.55, 29.58, 29.47, 29.39, 29.25, 29.14, 28.75, 26.98, 25.64, 25.49, 25.34, 25.13, 22.63, 22.57, 22.42, 18.18, 17.76, 17.57, 15.75, 13.80, -0.34, -4.11, -4.61, -5.82, -6.10; HRMS (FAB) calcd 1352.8243, found 1352.8263 (M+H)⁺.

O- (2-deoxy-2-((11Z)-octadecenamido)-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-2-β-D-glucopyranosyl)-(1→4)-[(2-O-methyl-α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-D-glucopyranose (2). To **17** (2.5 mg, 1.8 μmol) in 300 μL THF:MeOH (3:1) was added glacial acetic acid (40 μL) and the mixture was cooled to 0 °C before dropwise addition of a 1M solution of TBAF (200 μL). The reaction was allowed to slowly come to room temperature and was stirred for 6 h before addition of an additional 100 μL of acetic acid. The mixture was concentrated and purified by C₁₈ chromatography eluting with H₂O → 3:1 H₂O / MeOH → 1:1 H₂O / MeOH → 1:3 H₂O / MeOH → MeOH. Lyophilization of the fractions containing the desired product gave compound **2** (1.5 mg, 83%) as a white powder and a monosilylated derivative of **2** (0.3 mg, 15%). R_f = 0.62 (2:1:1 n-BuOH: EtOH: H₂O); ¹H NMR (400 MHz, DMSO-d₆) δ 6.57 (bs, 1H), 5.32 (m, 2H), 5.10 (bs, 1H), 4.90 - 4.98 (m, 2H), 4.85 (bs, 1H), 4.78 (d, *J* = 5.81 Hz, 1H), 4.67 - 4.76 (m, 2H), 4.42 -

4.53 (m, 1H), 4.34 (d, $J = 8.2$ Hz, 2H), 3.57 - 3.8 (m, 6H), 3.26 - 3.49 (m, 10H), 2.97 - 3.19 (m, 6H), 1.95 - 2.07 (m, 4H), 1.82 (s, 3H), 1.80 (s, 3H), 1.40 - 1.54 (m, 4H), 1.21 - 1.3 (m, 24H), 1.52 (d, $J = 6.5$ Hz, 3H), 0.95 (s, 3H), 0.92 (t, $J = 7.5$ Hz, 2H), 0.81 - 0.87 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 172.11, 172.00, 168.99, 129.66, 129.60, 101.96, 101.53, 96.47, 90.53, 81.09, 80.62, 78.04, 76.93, 74.71, 73.99, 72.14, 71.80, 70.72, 66.37, 65.63, 65.03, 61.04, 60.09, 58.38, 57.49, 55.24, 53.65, 37.59, 35.75, 31.11, 29.15, 29.06, 29.02, 28.96, 28.66, 28.24, 27.57, 25.71, 25.65, 24.97, 23.04, 22.95, 22.06, 19.19, 16.33, 13.93, 13.47; HRMS (FAB) calcd 1010.5648, found 1010.5676 (M+H) $^+$.