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for

A Model for Cell-Surface Exposed Carbohydrate Moieties Suitable for Structural Studies by NMR

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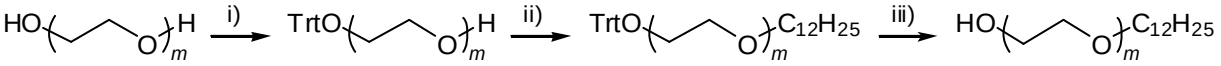
Experimental details for compounds 2, 3, 4-1, 4-2, 4-3, 5-1, 5-2, 6-1, 6-2, 7-1, 7-2, 7-3, 7-4, 7-5, 12-2, 12-3, 13-2, 14-2, 15-1, 15-2, 15-3, 15-4, 15-5, 15-6, 16-2, 16-3, 17-2, 18-2, 19-1, 19-2, 19-3, 19-4, 19-5, 20, 21, 22 and 23:



m = 3: **20**
m = 6: **21**

m = 3: **22**
m = 6: **23**

m = 3: **2**
m = 6: **3**

Scheme S1. The synthetic route to the linker moieties. Reagents used are i) TrtCl, DMAP, pyr; ii) $C_{12}H_{25}Br$, NaH, TBAI, THF; iii) AcOH/MeOH.

3,6,9-Trioxahenicosanol (2)[1,2]: Compound **22** (7.45 g, 13.3 mmol) was dissolved in 150 mL methanol/acetic acid (2:1 *v/v*) and the solution was refluxed for 16h. After cooling to RT the reaction mixture was concentrated under reduced pressure and co-evaporated with to-luene. The residue was purified by flash column chromatography (silica gel, toluene/ethyl acetate 3:1 → 1:1) to afford compound **2** (3.86 g, 12.1 mmol, 91%).

3,6,9,12,15-Hexaoxatriacontanol (3)[2]: Compound **23** (14.3 g, 20.6 mmol) was dissolved in 300 mL methanol/acetic acid (2:1 *v/v*) and the solution was refluxed for 16h. After cooling to RT the reaction mixture was concentrated under reduced pressure and co-evaporated with toluene. The residue was purified by flash column chromatography (silica gel, toluene/ace-tone 2:1 → 1:1 → 1:2) to afford compound **3** (8.7 g, 19.3 mmol, 94%).

Synthesis of methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (4-1)[3]: Compound **4-1** was prepared from methanol (20 mL, 494 µmol) and the mannosyl donor **1** (3.64 g, 5.71 mmol) according to GP I. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 8:1 → 5:1) to afford **4-1** (2.54 g, 5.01 mmol, 88%) as a pale, colorless oil.

Synthesis of methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (4-2)[4,5]: Compound **4-1** (1.78 g, 3.51 mmol) was deprotected according to GP II to afford **8-1** (1.53 g, 3.29 mmol, 94%).

Compound **4-2** was prepared from **8-1** (1.53 g, 3.29 mmol) and the mannosyl donor **1** (2.73 g, 4.29 mmol) according to GP I. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 → 3:1) to afford **4-2** (2.83 g, 3.01 mmol, 91%) as a pale, colorless oil.

Synthesis of methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (4-3)[6]: Compound **4-2** (1.80 g, 1.92 mmol) was deprotected according to GP II to afford **8-2** (1.59 g, 1.77 mmol, 92%).

Compound **4-3** was prepared from **8-2** (1.59 g, 1.77 mmol) and the mannosyl donor **1** (1.47 g, 2.31 mmol) according to GP I. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 8:1 → 3:1) to afford **4-3** (1.84 g, 1.34 mmol, 76%) as pale, colorless oil in sufficient purity for further conversions. For analytical data a small portion was purified by MPLC (silica gel, petroleum ether/ethyl acetate 4:1).

Synthesis of Dodecyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (5-1): Compound **5-1** was prepared from dodecanol (1.10 g, 5.90 mmol) and the mannosyl donor **1** (4.45 g, 6.99 mmol) according to GP I. The residue was purified by flash column chroma-tography (silica gel, petroleum ether/ethyl acetate 10:1) to afford **5-1** (3.41 g, 5.16 mmol, 87%) as a pale, colorless oil. TLC: R_f = 0.60 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D^{20}$ = +19.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (pseudo t, 3H, C*H*$_3$), 1.20-1.32 (m, 18H, 9C*H*$_2$), 1.55 (pseudo quint, 2H, C*H*$_2$), 2.15 (s, 3H, COC*H*$_3$), 3.37-3.42 (m, 1H, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.63-3.72 (m, 2H, *H*-6, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.78-3.83 (m, 2H, *H*-5, *H*-6´), 3.88 (dd, 1H, *H*-4), 3.99 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 9.3 Hz, 1H, *H*-3), 4.46-4.73 (m, 4H, 2PhC*H*$_2$), 4.83 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, *H*-1), 4.86 (d, 2H, 1PhC*H*$_2$), 5.36 (dd, $^3J_{1,2}$ = 1.8 Hz, $^3J_{2,3}$ = 3.4 Hz, 1H, *H*-2), 7.15-7.37 (m, 15H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.11 (1C, *C*H$_3$), 21.15 (1C, COC*H*$_3$), 22.68-31.97 (10C, 10*C*H$_2$), 68.01 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 68.89 (2C, *C*-2, *C*-6), 71.28 (1C, *C*-5), 71.78-73.41 (2C, 2*C*H$_2$Ph), 74.39 (1C, *C*-4), 75.20 (1C, 1*C*H$_2$Ph), 78.30 (1C, *C*-3), 97.71 (1C, *C*-1), 127.54-138.36 (18C, *Ph*), 170.55 (1C, *C*OCH$_3$), ppm; elemental analysis is calcd. (%) for $C_{41}H_{56}O_7$ (660.9): C: 74.51, H: 8.54; found: C: 74.20, H: 8.33; $C_{41}H_{56}O_7$ (660.9); MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 683.4, found: 683.8; [*M*+K]$^+$ calcd.: 699.4, found: 699.8.

Synthesis of Dodecyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (5-2): Compound **5-1** (3.40 g, 5.14 mmol) was de-protected according to GP II to afford **9-1** (3.01 g, 4.86 mmol, 96%).

Compound **5-2** was prepared from **9-1** (780 mg, 1.26 mmol) and the mannosyl donor **1** (1.04 g, 1.63 mmol) according to GP I. The residue was purified by flash column chroma-tography (silica gel, petroleum ether/ethyl acetate 8:1 → 5:1) to afford **5-2** (1.08 g, 988 µmol, 78%) as a pale, colorless oil. TLC: R_f = 0.78 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{20}$ = +18.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (pseudo t, 3H, C*H*$_3$), 1.20-1.32 (m, 18H, 9C*H*$_2$), 1.50 (pseudo quint, 2H, 1C*H*$_2$), 2.13 (s, 3H, COC*H*$_3$), 3.25-3.30 (m, 1H, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.57-3.62 (m, 1H, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.69-3.81 (m, 5H, *H*-5a or *H*-5b, *H*-6a, *H*-6a´, *H*-6b, *H*-6´b), 3.82-3.87 (m, 2H, *H*-4a, *H*-4b), 3.91-3.94 (dd, $^3J_{2a,3a}$ = 3.0 Hz, $^3J_{3a,4a}$ = 9.6 Hz, 1H, *H*-3a), 3.96-4.01 (m, 3H, *H*-2a, *H*-3b, *H*-5a or *H*-5b), 4.39-4.70 (m, 10H, 5PhC*H*$_2$), 4.84-4.88 (m, 3H, *H*-1a, 1PhC*H*$_2$), 5.10 (d, 1H, *H*-1b), 5.55 (dd, $^3J_{1b,2b}$ = 1.9 Hz, $^3J_{2b,3b}$ = 3.3 Hz, 1H, *H*-2b), 7.15-7.37 (m, 30H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.11 (1C, *C*H$_3$), 21.12 (1C, COC*H*$_3$), 22.67-31.91 (10C, 10*C*H$_2$), 67.72 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 68.72 (1C, *C*-2b), 69.03 (1C, *C*-6a or *C*-

6b), 69.28 (1C, *C*-6a or *C*-6b), 71.73 (1C, *C*-5a or *C*-5b), 71.75 (1C, *C*-5a or *C*-5b), 71.88-73.35 (4C, 4*C*H_2Ph), 74.35 (1C, *C*-4a or *C*-4b), 74.68 (1C, *C*-4a or *C*-4b), 74.94 (1C, *C*-2a), 75.01-75.15 (2C, 2*C*H_2Ph), 78.13 (1C, *C*-3b), 79.77 (1C, *C*-3a), 98.61 (1C, *C*-1a), 99.52 (1C, *C*-1b), 127.34-138.53 (36C, *Ph*), 170.93 (1C, *C*OCH_3) ppm; ; elemental analysis is calcd. (%) for $C_{68}H_{84}O_{12}$ (1093.4): C: 74.70, H: 7.74; found: C: 74.66, H: 8.02; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1115.6, found: 1115.3; [*M*+K]$^+$ calcd.: 1131.7, found: 1131.4.

Synthesis of 3,6,9-Trioxahenicosanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (6-1): Compound **6-1** was prepared from the glycol **2** (1.00 g, 3.14 mmol) and the mannosyl donor **1** (2.39 g, 3.75 mmol) according to GP I. The residue was purified by flash co-lumn chromatography (silica gel, toluene/acetone 20:1 → 10:1) to afford **6-1** (2.34 g, 2.95 mmol, 94%) as a pale, colorless oil. TLC: R_f = 0.58 (toluene/acetone 5:1) $[\alpha]_D^{20}$ = +6.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (pseudo t, 3H, C*H*$_3$), 1.21-1.34 (m, 18H, 9C*H*$_2$), 1.56 (pseudo quint, 2H, C*H*$_2$), 2.14 (s, 3H, COC*H*$_3$), 3.42 (pseudo t, 2H, OC*H*$_2$ $C_{11}H_{23}$), 3.54-3.57 (m, 2H, 1OC*H*$_2$), 3.60-3.65 (m, 9H, 9/2OC*H*$_2$), 3.70 (dd, $^3J_{5,6}$ = 1.3 Hz, $^2J_{6,6'}$ = 10.3 Hz, 1H, *H*-6), 3.77-3.84 (m, 3H, *H*-5, *H*-6´, 1/2OC*H*$_2$), 3.89 (dd, 1H, *H*-4), 3.99 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 9.3 Hz, 1H, *H*-3), 4.46-4.60 (m, 6H, 3PhC*H*$_2$), 4.88 (d, $^3J_{1,2}$ = 1.8 Hz, 1H, *H*-1), 5.41 (dd, $^3J_{1,2}$ = 1.8 Hz, $^3J_{2,3}$ = 3.3 Hz, 1H, *H*-2), 7.14-7.36 (m, 15H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.11 (1C, *C*H_3), 21.12 (1C, CO*C*H_3), 22.67-31.90 (10C, 10*C*H_2), 66.86 (1C, 1O*C*H_2), 68.68 (1C, *C*-2), 68.84 (1C, *C*-6),70.01-70.67 (5C, 5O*C*H_2), 71.35 (1C, *C*-5), 71.53 (1C, O*C*$H_2C_{11}H_{23}$), 71.79-73.43 (2C, 2*C*H_2Ph), 74.29 (1C, *C*-4), 75.16 (1C, 1*C*H_2Ph), 78.19 (1C, *C*-3), 97.87 (1C, *C*-1), 127.56-138.38 (18C, *Ph*), 170.41 (1C, *C*OCH_3), ppm; $C_{47}H_{68}O_{10}$ (793.0); MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 815.5, found: 815.5; [*M*+K]$^+$ calcd.: 831.5, found: 831.5.

Synthesis of 3,6,9-Trioxahenicosanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (6-2): Compound **6-1** (2.18 g, 2.75 mmol) was deprotected according to GP II to afford **10-1** (2.00 g, 2.66 mmol, 97%).

Compound **6-2** was prepared from **10-1** (1.16 g, 1.54 mmol) and the mannosyl donor **1** (1.18 g, 1.85 mmol) according to GP I. The residue was purified by flash column chromatog-raphy (silica gel, toluene/acetone 20:1 → 10:1) to afford **6-2** (1.14 g, 930 µmol, 60%) as a pale, colorless oil. TLC: R_f = 0.68 (toluene/acetone 5:1) $[\alpha]_D^{20}$ = +14.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90 (pseudo t, 3H, C*H*$_3$), 1.23-1.36 (m, 18H, 9C*H*$_2$), 1.58 (pseudo quint, 2H,

1C*H*$_2$), 2.13 (s, 3H, COC*H*$_3$), 3.44 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.48-3.52 (m, 1H, 1/2OC*H*$_2$); 3.54-3.64 (m, 10H, 5OCH$_2$) 3.70-3.82 (m, *H*-5a or *H*-5b, *H*-6a, *H*-6b, *H*-6´a, *H*-6´b, 1/2OC*H*$_2$), 3.84-3.89 (m, 2H, *H*-4a, *H*-4b), 3.92-4.01 (m, 3H, *H*-3a, *H*-3b, *H*-5a or *H*-5b), 4.07 (dd, 1H, *H*-2a), 4.40-4.88 (m, 12H, 6PhC*H*$_2$), 4.92 (d, $^3J_{1a,2a}$ = 1.3 Hz, 1H, *H*-1a), 5.11 (d, $^3J_{1b,2b}$ = 1.8 Hz, 1H, *H*-1b), 5.56 (dd, $^3J_{1b,2b}$ = 1.8 Hz, $^3J_{2b,3b}$ = 2.7 Hz, 1H, *H*-2b), 7.16-7.38 (m, 30H, *Ph*) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 14.08 (1C, *C*H$_3$), 21.09 (1C, CO*C*H$_3$), 22.64-31.87 (10C, 10*C*H$_2$), 66.63 (1C, 1O*C*H$_2$), 68.67 (1C, *C*-2b), 68.97 (1C, *C*-6a or *C*-6b), 69.21 (1C, *C*-6a or *C*-6b), 70.00-70.60 (5C, 5O*C*H$_2$), 71.50 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 71.78 (2C, *C*-5a, *C*-5b), 71.85-73.36 (4C, 4*C*H$_2$Ph), 74.29 (1C, *C*-4a or *C*-4b), 74.57 (1C, *C*-4a or *C*-4b), 74.75 (1C, *C*-2a), 75.00-75.09 (2C, 2*C*H$_2$Ph), 78.09 (1C, *C*-3b), 79.62 (1C, *C*-3a), 98.72 (1C, *C*-1a), 99.52 (1C, *C*-1b), 127.33-138.45 (36C, *Ph*), 170.04 (1C, *C*OCH$_3$) ppm; elemental analysis is calcd. (%) for C$_{74}$H$_{96}$O$_{15}$ (1225.6): C: 72.52, H: 7.90; found: C: 72.11, H: 7.88; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1247.7, found: 1247.2; [*M*+K]$^+$ calcd.: 1263.7, found: 1263.2.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-a**-D-mannopyranoside (7-1)**: Compound **7-1** was prepared from the glycol **3** (1.43 g, 3.17 mmol) and the mannosyl donor **1** (2.46 g, 3.86 mmol) according to GP I. The residue was purified by flash column chromatography (silica gel, toluene/acetone 5:1 → 3:1) to afford **7-1** (2.56 g, 2.77 mmol, 87%) as a pale, colorless oil. TLC: R$_f$ = 0.25 (toluene/acetone 5:1); [α]$_D^{20}$ = +13.1 (c = 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 0.88 (pseudo t, 3H, C*H*$_3$), 1.21-1.34 (m, 18H, 9C*H*$_2$), 1.57 (pseudo quint, 2H, C*H*$_2$), 2.14 (s, 3H, COC*H*$_3$), 3.44 (pseudo t, 2H, C$_{11}$H$_{23}$OC*H*$_2$), 3.55-3.65 (m, 23H, 23/2OC*H*$_2$), 3.70 (d, $^3J_{5,6}$ = 3.7 Hz, $^2J_{6,6'}$ = 10.1 Hz, 1H, *H*-6), 3.76-3.84 (m, 3H, *H*-5, *H*-6´, 1/2OC*H*$_2$), 3.89 (dd, 1H, *H*-4), 3.99 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 9.3 Hz, 1H, *H*-3), 4.46-4.86 (3d, 6H, 3PhC*H*$_2$), 4.88 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, *H*-1), 5.41 (dd, $^3J_{1,2}$ = 1.8 Hz, $^3J_{2,3}$ = 3.4 Hz, 1H, *H*-2), 7.14-7.36 (m, 15H, *Ph*) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 14.11 (1C, *C*H$_3$), 21.11 (1C, CO*C*H$_3$), 22.68-31.90 (10C, 10*C*H$_2$), 66.84 (1C, 1O*C*H$_2$), 68.67 (1C, *C*-2),68.84 (1C, *C*-6) 70.01-70.64 (11C, 11O*C*H$_2$), 71.36 (1C, *C*-5), 71.54(1C, O*C*H$_2$C$_{11}$H$_{23}$) 71.78-73.43 (2C, 2*C*H$_2$Ph), 74.29 (1C, *C*-4), 75.16 (1C, 1*C*H$_2$Ph), 78.19 (1C, *C*-3), 97.87 (1C, *C*-1), 127.55-138.37 (18C, 3CH$_2$*Ph*), 170.40 (1C, *C*OCH$_3$), ppm; elemental analysis is calcd. (%) for C$_{53}$H$_{80}$O$_{13}$ (925.2): C: 68.80, H: 8.72; found: C: 68.59, H: 8.76; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 947.6, found: 947.7; [*M*+K]$^+$ calcd.: 963.6, found: 963.7.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (7-2): Compound **7-1** (2.24 g, 2.42 mmol) was deprotected according to GP II to afford **11-1** (1.92 g, 2.17 mmol, 90%).

Compound **7-2** was prepared from **11-1** (1.60 g, 1.81 mmol) and the mannosyl donor **1** (1.51 g, 2.37 mmol) according to GP I. The residue was purified by flash column chromatog-raphy (silica gel, toluene/acetone 8:1) to afford **7-2** (1.66 g, 1.22 mmol, 67%) as a pale, col-orless oil in sufficient purity for further conversions. For analytical data a small portion was purified by MPLC (silica gel, toluene/acetone 8:1). TLC: R_f = 0.32 (toluene/acetone 5:1); $[\alpha]_D^{20}$ = +13.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (pseudo t, 3H, C*H*$_3$), 1.20-1.34 (m, 18H, 9C*H*$_2$), 1.57 (pseudo quint, 2H, 1C*H*$_2$), 2.12 (s, 3H, COC*H*$_3$), 3.42-3.50 (m, 3H, 1/2OC*H*$_2$, OC*H*$_2$C$_{11}$H$_{23}$), 3.53-3.81 (m, 28H, *H*-5a or *H*-5b, *H*-6a, *H*-6b, *H*-6´a, *H*-6´b, 23/2OC*H*$_2$), 3.82-3.87 (m, 2H, *H*-4a, *H*-4b), 3.91-3.99 (m, 3H, *H*-3a, *H*-3b, *H*-5a or *H*-5b), 4.05 (dd, 1H, *H*-2a), 4.37-4.86 (m, 12H, 6PhC*H*$_2$), 4.89 (d, $^3J_{1a,2a}$ = 1.3 Hz, 1H, *H*-1a), 5.09 (d, 1H, *H*-1b), 5.54 (dd, $^3J_{1b,2b}$ = 1.8 Hz, $^3J_{2b,3b}$ = 2.7 Hz, 1H, *H*-2b), 7.13-7.36 (m, 30H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.10 (1C, *C*H$_3$), 21.12 (1C, CO*C*H$_3$), 22.66-31.88 (10C, 10*C*H$_2$), 66.60 (1C, 1O*C*H$_2$), 68.64 (1C, *C*-2b), 68.92 (1C, *C*-6a or *C*-6b), 69.17(1C, *C*-6a or *C*-6b), 69.00-70.58 (11C, 11O*C*H$_2$), 71.52 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 71.75 (2C, *C*-5, *C*-5b), 71.85-73.36 (4C, 4*C*H$_2$Ph), 74.25 (1C, *C*-4a or *C*-4b), 74.54 (1C, *C*-4a or *C*-4b), 74.68 (1C, *C*-2a), 75.02-75.12 (2C, 2*C*H$_2$Ph), 78.09 (1C, *C*-3b), 79.60 (1C, *C*-3a), 98.71 (1C, *C*-1a), 99.52 (1C, *C*-1b), 127.32-138.42 (36C, *Ph*), 170.08 (1C, *C*OCH$_3$) ppm; $C_{80}H_{108}O_{18}$ (1356.7); MALDI-MS (pos. mode, CHCA): $[M+Na]^+$ calcd.: 1379.8, found: 1379.6; $[M+K]^+$ calcd.: 1395.8, found: 1395.2.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (7-3): Compound **7-2** (1.35 g, 995 µmol) was deprotected according to GP II to afford **11-2** (1.18 g, 897 mmol, 90%).

Compound **7-3** was prepared from **11-2** (1.07 g, 813 µmol) and the mannosyl donor **1** (622 mg, 977 µmol) according to GP I. The residue was purified by flash column chromatography (silica gel, toluene/acetone 10:1 → 5:1) to afford **7-3** (1.09 g, 609 µmol, 75%) as pale, color-less oil in sufficient purity for further conversions. For analytical data a small portion was pu-rified by MPLC (silica gel, toluene/acetone 8:1). TLC: R_f = 0.41 (toluene/acetone 5:1); $[\alpha]_D^{20}$ =

+17.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (pseudo t, 3H, C*H*$_3$), 1.21-1.35 (m, 18H, 9C*H*$_2$), 1.58 (pseudo quint, 2H, 1C*H*$_2$), 2.14 (s, 3H, COC*H*$_3$), 3.43-3.47 (m, 3H, OC*H*$_2$C$_{11}$H$_{23}$, 1/2OC*H*$_2$), 3.51-3.84 (m, 32H, *H*-4a, *H*-4b, *H*-5a, *H*-6a, *H*-6b, *H*-6c, *H*-6´a, *H*-6´b, *H*-6´c, 23/2OC*H*$_2$), 3.86-3.96 (m, 5H, *H*-3a, *H*-3b, *H*-4c, *H*-5b, *H*-5c), 4.00 (dd, $^3J_{2c,3c}$ = 3.3 Hz, $^3J_{3c,4c}$ = 9.3 Hz, 1H, *H*-3c), 4.03 (dd, 1H, *H*-2a), 4.10 (dd, 1H, *H*-2b), 4.30-4.86 (m, 18H, 9PhC*H*$_2$), 4.94 (d, $^3J_{1a,2a}$ = 1.8 Hz, 1H, *H*-1a), 5.05 (d, $^3J_{1c,2c}$ = 1.8 Hz, 1H, *H*-1c), 5.20 (d, $^3J_{1b,2b}$ = 1.8 Hz, 1H, *H*-1b), 5.54 (dd, $^3J_{1c,2c}$ = 1.8 Hz, $^3J_{2c,3c}$ = 3.3 Hz, 1H, *H*-2c), 7.13-7.36 (m, 45H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.10 (1C, *C*H$_3$), 21.13 (1C, COC*H*$_3$), 22.66-31.88 (10C, 10*C*H$_2$), 66.65(1C, 1O*C*H$_2$), 68.69 (1C, *C*-2c), 68.72-69.45 (3C, *C*-6a, *C*-6b, *C*-6c),70.01-70.58 (11C, 11O*C*H$_2$), 71.52 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 71.78-72.16 (6C, *C*-5a, *C*-5b, *C*-5c, 3*C*H$_2$Ph), 73.22-73.32 (3C, 3*C*H$_2$Ph), 74.19 (1C, *C*-4c), 74.67 (1C, *C*-4b), 74.79 (1C, *C*-4a), 74.86-75.08 (5C, *C*-2a, *C*-2b, 3*C*H$_2$Ph), 78.09 (1C, *C*-3e), 79.27 (1C, *C*-3b), 79.44 (1C, *C*-3a), 98.83 (1C, *C*-1a), 99.36 (1C, *C*-1c), 100.57 (1C, *C*-1b), 127.34-138.54 (54C, *Ph*), 170.09 (1C, *C*OCH$_3$) ppm; C$_{107}$H$_{136}$O$_{23}$ (1790.2); MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd: 1813.2, found: 1812.8; [*M*+K]$^+$ calcd: 1829.3, found: 1828.6.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (7-4): Compound **7-3** (795 mg, 444 μmol) was deprotected according to GP II to afford **11-3** (712 mg, 407 μmol, 92%).

Compound **7-4** was prepared from **11-3** (564 mg, 323 μmol) and the mannosyl donor **1** (250 mg, 392 μmol) according to GP I. The residue was purified by flash column chromatography (silica gel, toluene/acetone 10:1 → 8:1) to afford **7-4** (552 mg, 248 μmol, 77%) as pale colorless oil in sufficient purity for further conversions. For analytical data a small portion was purified by MPLC (silica gel, toluene/acetone 8:1). TLC: R_f = 0.48 (toluene/acetone 5:1); $[\alpha]_D^{20}$ = +15.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (pseudo t, 3H, C*H*$_3$), 1.20-1.36 (m, 18H, 9C*H*$_2$), 1.58 (pseudo quint, 2H, 1C*H*$_2$), 2.14 (s, 3H, COC*H*$_3$), 3.41-3.80 (m, 38H, *H*-4a, *H*-4b, *H*-4c, *H*-5a, *H*-6a, *H*-6b, *H*-6c, *H*-6d, *H*-6´a, *H*-6´b, *H*-6´c, *H*-6´d, 12OC*H*$_2$, OC*H*$_2$C$_{11}$H$_{23}$), 3.83-3.98 (m, 7H, *H*-3a, *H*-3b, *H*-3c, *H*-4d, *H*-5b, *H*-5c, *H*-5d), 4.00-4.04 (m, 2H, *H*-2a, *H*-3d), 4.08-4.18 (m, 3H, *H*-2b, *H*-2c, 1/2PhC*H*$_2$), 4.31-4.88 (m, 23H, 23/2PhC*H*$_2$), 4.96 (d, 1H, *H*-1a), 5.05 (d, 1H, *H*-1d), 5.18 (d, 1H, *H*-1c), 5.23 (d, 1H, *H*-1b), 5.57 (dd, $^3J_{1d,2d}$ = 1.8

Hz, $^{3}J_{2d,3d}$ = 3.0 Hz, 1H, *H*-2d), 7.03-7.35 (m, 60H, *Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.11 (1C, *C*H_3), 21.15 (1C, CO*C*H_3), 22.66-31.88 (10C, 10*C*H_2), 66.62 (1C, 1O*C*H_2), 68.57-69.50 (5C, *C*-2d, *C*-6a, *C*-6b, *C*-6c, *C*-6d), 69.99-70.56 (11C, 11O*C*H_2), 71.51 (1C, O*C*$H_2C_{11}H_{23}$), 71.60-72.18 (8C, *C*-5a, *C*-5b, *C*-5c, *C*-5d, 4*C*H_2Ph), 73.19-73.29 (4C, 4*C*H_2Ph), 74.18 (1C, *C*-4d), 74.58-75.14 (8C, *C*-2c, *C*-4a, *C*-4b, *C*-4c, 4*C*H_2Ph), 75.42 (1C, *C*-2b), 75.50 (1C, *C*-2a), 78.23 (1C, *C*-3d), 79.21 (2C, *C*-3a, *C*-3b), 79.31 (1C, *C*-3c), 98.79 (1C, *C*-1a), 99.33 (1C, *C*-1d), 100.68 (1C, *C*-1c), 101.09 (1C, *C*-1b), 127.28-138.55 (72C, *Ph*), 170.08 (1C, *C*OCH_3) ppm; elemental analysis is calcd. (%) for $C_{134}H_{164}O_{28}$ (2222.7): C: 72.41, H: 7.44; found: C: 72.43, H: 7.42; MALDI-MS (pos. mode, CHCA): $[M+Na]^+$ calcd.: 2245.7, found: 2245.4; $[M+K]^+$ calcd.: 2261.8, found: 2261.2.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (7-5): Compound **7-4** (307 mg, 138 μmol) was deprotected according to GP II to afford **11-4** (259 mg, 119 μmol, 86%).

Compound **7-5** was prepared from **11-4** (259 mg, 119 μmol) and the mannosyl donor **1** (100 mg, 157 mmol) according to GP I. The residue was purified by flash column chromatogra-phy (silica gel, toluene/acetone 10:1 → 8:1) to afford **7-5** (235 mg, 89 μmol, 75%) as pale, colorless oil in sufficient purity for further conversions. For analytical data a small portion was purified by MPLC (silica gel, toluene/acetone 8:1). TLC: R_f = 0.47 (toluene/acetone 5:1); $[\alpha]_D^{20}$ = +15.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (pseudo t, 3H, C*H*$_3$), 1.21-1.35 (m, 18H, 9C*H*$_2$), 1.58 (pseudo quint, 2H, 1C*H*$_2$), 2.13 (s, 3H, COC*H*$_3$), 3.40-3.98 (m, 50H, *H*-3a, *H*-3b, *H*-3c, *H*-3d, *H*-4a, *H*-4b, *H*-4c, *H*-4d, *H*-4e, *H*-5a, *H*-5b, *H*-5c, *H*-5d, *H*-5e, *H*-6a, *H*-6b, *H*-6c, *H*-6d, *H*-6e, *H*-6´a, *H*-6´b, *H*-6´c, *H*-6´d, *H*-6´e, 12OC*H*$_2$, O*C*$H_2C_{11}H_{23}$), 3.99-4.03 (m, 2H, *H*-2a, *H*-3e), 4.07-4.22 (m, 6H, *H*-2b, *H*-2c, *H*-2d, 3/2PhC*H*$_2$), 4.33-4.90 (m, 27H, 27/2PhC*H*$_2$), 4.98 (d, $^{3}J_{1a,2a}$ = 1.7 Hz, 1H, *H*-1a), 5.04 (d, $^{3}J_{1e,2e}$ = 1.8 Hz, 1H, *H*-1e), 5.16 (d, $^{3}J_{1d,2d}$ = 1.7 Hz, 1H, *H*-1d), 5.23 (d, $^{3}J_{1,2}$ = 1.6 Hz, 1H, *H*-1b or *H*-1c), 5.24 (d, $^{3}J_{1,2}$ = 1.5 Hz, 1H, *H*-1b or *H*-1c), 5.56 (dd, $^{3}J_{1e,2e}$ = 1.8 Hz, $^{3}J_{2e,3e}$ = 3.2 Hz, 1H, *H*-2e), 6.96-7.36 (m, H, 75*Ph*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.11 (1C, *C*H_3), 21.15 (1C, CO*C*H_3), 22.67-31.90 (10C, 10*C*H_2), 66.65 (1C, 1O*C*H_2), 68.63-69.61 (6C, *C*-2e, *C*-6a, *C*-6b, *C*-6c, *C*-6d, *C*-6e), 70.02-70.60 (11C, 11O*C*H_2), 71.53 (1C, O*C*$H_2C_{11}H_{23}$), 71.63-72.28 (10C, *C*-5a, *C*-5b, *C*-5c,

C-5d, *C*-5e, 5CH_2Ph), 73.21-73.32 (5C, 5CH_2Ph), 74.24 (1C, *C*-4e), 74.70-75.15 (10C, *C*-2d, *C*-4a, *C*-4b, *C*-4c, *C*-4d, 5CH_2Ph), 75.56 (1C, *C*-2b or *C*-2c), 75.79 (1C, *C*-2a), 76.18 (1C, *C*-2b or *C*-2c), 78.18 (1C, *C*-3e), 79.00-79.26 (3C, *C*-3a, *C*-3b, *C*-3c), 79.42 (1C, 3*C*-d), 98.84 (1C, *C*-1a), 99.38 (1C, *C*-1e), 100.73 (1C, *C*-1d), 101.30 (1C, *C*-1b or *C*-1c), 101.33 (1C, *C*-1b or *C*-1c), 127.27-138.63 (90C, *Ph*), 170.05 (1C, *C*OCH_3) ppm; elemental analysis is calcd. (%) for $C_{161}H_{192}O_{33}$ (2655.2): C: 72.83, H: 7.29; found: C: 72.30, H: 7.53; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 2678.2, found: 2677.4; [*M*+K]$^+$ calcd.: 2694.3, found: 2694.4.

Synthesis of methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (12-2)[7]: Compound **12-2** was prepared from **4-2** (1.06 g, 1.13 mmol) according to GP III. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 → 1:1) to afford **12-2** (449 mg, 690 µmol, 61%) as a foam.

Synthesis of methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (12-3): Compound **12-3** was prepared from **4-3** (380 mg, 277 µmol) according to GP III. The resi-due was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 1:1 → 1:2), followed by MPLC (silica gel, toluene/acetone 5:2) to afford **12-3** (116 mg, 124 µmol, 45%) as a foam. TLC: R_f = 0.41 (toluene/acetone 2:1); $[\alpha]_D^{20}$ = +23.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.98-2.13 (10s, 30 H, 10COCH_3), 3.39 (s, 3H, OCH_3), 3.89 (ddd, $^3J_{4a,5a}$ = 9.6 Hz, $^3J_{5a,6a}$ = 4.5 Hz, $^3J_{5a,6'a}$ = 2.4 Hz, 1H, *H*-5a), 4.01 (dd, 1 H, *H*-2a), 4.05-4.24 (m, 9H, *H*-2b, *H*-5b, *H*-5c, *H*-6a, *H*-6´a, *H*-6b, *H*-6´b, *H*-6c, *H*-6´c), 4.84 (d, $^3J_{1a,2a}$ = 2.0 Hz, 1 H, *H*-1a), 4.92 (d, $^3J_{1c,2c}$ = 1.8 Hz, 1 H, *H*-1c), 5.08 (d, $^3J_{1b,2b}$ = 2.0 Hz, 1H, *H*-1b), 5.22-5.33 (m, 6H, *H*-2c, *H*-3a, *H*-3b, *H*-4a, *H*-4b, *H*-4c), 5.37 (dd, $^3J_{2c,3c}$ = 3.4 Hz, $^3J_{3c,4c}$ = 10.0 Hz, 1H, *H*-3c) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.57-20.78 (10C, 10CO*C*H_3), 55.19 (1C, O*C*H_3), 62.09-62.54 (3C, *C*-6a, *C*-6b, *C*-6c), 66.16-66.26 (3C, *C*-4a, *C*-4b, *C*-4c), 68.34 (1C, *C*-3c), 68.44 (1C, *C*-5a), 69.21 (1C, *C*-5b or *C*-5c), 69.42 (1C, *C*-5b or *C*-5c), 69.51-70.37 (3C, *C*-2c, *C*-3a, *C*-3b), 76.56 (1C, *C*-2a), 77.36 (1C, *C*-2b), 99.18 (1C, *C*-1a), 99.33 (1C, *C*-1c), 99.75 (1C, *C*-1b), 169.33-170.81 (10C, 10*C*OCH_3) ppm; $C_{39}H_{54}O_{26}$ (938.8); MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 961.3, found: 962.1; [*M*+K]$^+$ calcd.: 977.3, found: 978.1.

Synthesis of Dodecyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (13-2): Compound **13-2** was prepared from **5-2** (630 mg, 576 µmol) according to GP III. The residue was purified by flash column chromatography (silica gel,

toluene/acetone 5:1 → 3:1) to afford **13-2** (413 mg, 513 µmol, 89%) as a pale, colorless oil. TLC: R_f = 0.54 (toluene/acetone 3:1); $[\alpha]_D^{20}$ = +24.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87 (pseudo t, 3H, C*H*$_3$), 1.19-1.37 (m, 18H, 9C*H*$_2$), 1.58 (pseudo quint, 2H, 1C*H*$_2$), 2.00-2.14 (7s, 21H, 7COC*H*$_3$), 3.39-3.44 (m, 1H, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.64-3.69 (m, 1H, 1/2OC*H*$_2$C$_{11}$H$_{23}$), 3.90 (ddd, $^3J_{4a,5a}$ = 9.3 Hz, $^3J_{5a,6a}$ = 4.2 Hz, $^3J_{5a,6'a}$ = 2.3 Hz, 1H, *H*-5a), 4.01 (dd, 1H, *H*-2a), 4.08-4.24 (m, 5H, *H*-5b, *H*-6a, *H*-6´a, *H*-6b, *H*-6´b), 4.90-4.92 (2d, 2H, *H*-1a, *H*-1b), 5.24-5.34 (m, 4H, *H*-2b, *H*-3a, *H*-4a, *H*-4b), 5.40 (dd, $^3J_{2b,3b}$ = 3.4 Hz, $^3J_{3b,4b}$ = 10.0 Hz, 1H, *H*-3b) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.10 (1C, *C*H$_3$), 20.66-20.87 (7C, 7CO*C*H$_3$), 22.66-31.88 (10C, 10*C*H$_2$), 62.19 (1C, *C*-6a), 62.52 (1C, *C*-6b), 66.23 (1C, *C*-4a), 66.34 (1C, *C*-4b), 68.35 (1C, *C*-5a or *C*-3b), 68.42 (1C, *C*-5a or *C*-3b), 68.53 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 69.07 (1C, *C*-5b), 69.75 (1C, *C*-2b), 70.34 (1C, *C*-3a), 77.18 (1C, *C*-2a), 98.22 (1C, *C*-1a or *C*-1b), 99.13 (1C, *C*-1a or *C*-1b), 169.42-170.88 (7C, 7*C*OCH$_3$) ppm; $C_{38}H_{60}O_{18}$ (804.9); MALDI-MS (pos. mode, CHCA): $[M+Na]^+$ calcd.: 827.4, found: 827.3; $[M+K]^+$ calcd.: 843.4, found: 843.3.

Synthesis of 3,6,9-Trioxahenicosanyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (14-2): Compound **14-2** was prepared from **6-2** (1.45 g, 1.18 mmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/acetone 5:1 → 3:1) to afford 770 mg of a mixture en-riched in 14-2. A portion (240 mg) was subjected to further purification by MPLC (silica gel, toluene/acetone 5:1) to afford **14-2** (132 mg, 141 µmol, 38%) as a foam. TLC: R_f = 0.47 (toluene/acetone 3:1); $[\alpha]_D^{20}$ = +38.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.86 (pseudo t, 3H, C*H*$_3$), 1.19-1.33 (m, 18H, 9C*H*$_2$), 1.55 (pseudo quint, 2H, 1C*H*$_2$), 1.99-2.14 (7s, 21H, 7COC*H*$_3$), 3.42 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.54-3.57 (m, 2H, OC*H*$_2$), 3.60-3.66 (m, 9H, 9/2OC*H*$_2$), 3.79-3.82 (m, 1H, 1/2OC*H*$_2$), 3.98 (ddd, $^3J_{4a,5a}$ = 9.4 Hz, $^3J_{5a,6a}$ = 3.7 Hz, $^3J_{5a,6'a}$ = 2.5 Hz, 1H, *H*-5a), 4.04 (dd, 1H, *H*-2a), 4.07-4.12 (m, 2H, *H*-6a, *H*-6b), 4.15 (ddd, $^3J_{4b,5b}$ = 10.0 Hz, $^3J_{5b,6b}$ = 5.4 Hz, $^3J_{5b,6'b}$ = 2.1 Hz, 1H, *H*-5b), 4.19-4.23 (m, 2H, *H*-6´a, *H*-6´b), 4.91 (d, $^3J_{1b,2b}$ = 1.3 Hz, 1H, *H*-1b), 4.96 (d, $^3J_{1a,2a}$ = 1.3 Hz, 1H, *H*-1a), 5.24-5.35 (m, 4H, *H*-2b, *H*-3a, *H*-4a, *H*-4b), 5.39 (dd, $^3J_{2b,3b}$ = 3.4 Hz, $^3J_{3b,4b}$ = 10.0 Hz, 1H, *H*-3b) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.07 (1C, *C*H$_3$), 20.62-20.84 (7C, 7CO*C*H$_3$), 22.63-31.85 (10C, 10*C*H$_2$), 62.02 (1C, *C*-6a or *C*-6b), 62.45 (1C, *C*-6a or *C*-6b), 66.09 (1C, *C*-4a), 66.32 (1C, *C*-4b), 67.36(1C, 1O*C*H$_2$), 68.32 (1C, *C*-3b), 68.39 (1C, *C*-5a), 69.06 (1C, *C*-5b), 69.72 (1C, *C*-2b), 69.92-69.97 (2C, 2O*C*H$_2$), 70.22 (1C, *C*-3a), 70.54-70.66 (3C, 3O*C*H$_2$), 71.50 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 77.04 (1C, *C*-2a), 98.30 (1C, *C*-1a), 99.12 (1C, *C*-1b), 169.32-170.86 (7C, 7*C*OCH$_3$) ppm; $C_{44}H_{72}O_{21}$

(937.0); elemental analysis is calcd. (%) for $C_{44}H_{72}O_{21}$ (937.0): C: 56.40, H: 7.74; found: C: 56.44, H: 7.58; MALDI-MS (pos. mode, CHCA): $[M+Na]^+$ calcd.: 959.5, found: 959.0; $[M+K]^+$ calcd.: 975.5, found: 975.0.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2,3,4,6-tetra-*O*-acetyl-α-D-manno-pyranoside (15-1): Compound **15-1** was prepared from **7-1** (380 mg, 411 µmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/ace-tone 5:2) to afford **15-1** (196 mg, 251 µmol, 61%) as a pale, colourless oil. TLC: R_f = 0.55 (toluene/acetone 3:2); $[\alpha]_D^{20}$ = +21.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87 (pseudo t, 3H, C*H*$_3$), 1.20-1.33 (m, 18H, 9C*H*$_2$), 1.56 (pseudo quint, 2H, 1C*H*$_2$), 1.97-2.14 (4s, 12H, 4COC*H*$_3$), 3.44 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.55-3.57 (m, 2H, 1OC*H*$_2$), 3.61-3.68 (m, 21H, 21/2OC*H*$_2$), 3.77-3.82 (m, 1H, 1/2OC*H*$_2$), 4.03-4.10 (m, 2H, *H*-5, *H*-6), 4.28 (dd, $^3J_{5,6'}$ = 4.9 Hz, $^2J_{6,6'}$ = 12.2 Hz, 1H, *H*-6´), 4.86 (d, $^3J_{1,2}$ = 1.7 Hz, 1H, *H*-1), 5.25 (dd, $^3J_{1,2}$ = 1.7 Hz, $^3J_{2,3}$ = 3.5 Hz, 1H, *H*-2), 5.27 (dd, 1H, *H*-4), 5.34 (dd, $^3J_{2,3}$ = 3.5 Hz, $^3J_{3,4}$ = 10.0 Hz, 1H, *H*-3) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.08 (1C, *C*H$_3$), 20.65-20.86 (4C, 4CO*C*H$_3$), 22.64-31.87 (10C, 10*C*H$_2$), 62.37 (1C, *C*-6), 66.11 (1C, *C*-4), 67.34 (1C, 1O*C*H$_2$), 68.35 (1C, *C*-5), 69.05 (1C, *C*-3), 69.53 (1C, *C*-2), 69.94-70.67 (11C, 11O*C*H$_2$), 71.51 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 97.68 (1C, *C*-1), 169.68-170.62 (4C, 4*C*OCH$_3$) ppm; elemental analysis is calcd. (%) for $C_{88}H_{68}O_{16}$ (780.9): C: 58.44, H: 8.78; found: C: 58.25, H: 9.34; MALDI-MS MALDI-MS (pos. mode, CHCA): $[M+Na]^+$ calcd.: 803.5, found: 803.3; $[M+K]^+$ calcd.: 819.5, found: 819.2.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopy-ranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (15-2): Compound **15-2** was pre-pared from **7-2** (817 mg, 602 µmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/acetone 5:2 → 2:1) followed by MPLC (silica gel, toluene/acetone 5:2) to afford **15-2** (226 mg, 211 µmol, 35%) as a pale, colorless oil. TLC: R_f = 0.51 (toluene/acetone 3:2); $[\alpha]_D^{20}$ = +19.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.83 (pseudo t, 3H, C*H*$_3$), 1.16-1.30 (m, 18H, 9C*H*$_2$), 1.53 (pseudo quint, 2H, 1C*H*$_2$), 1.97-2.11 (7s, 21H, 7COC*H*$_3$), 3.40 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.52-3.54 (m, 2H, OC*H*$_2$), 3.58-3.64 (m, 21H, 21/2OC*H*$_2$), 3.75-3.81 (m, 1H, 1/2OC*H*$_2$), 3.95 (ddd, 1H, *H*-5a), 4.02 (dd, 1H, *H*-2a), 4.05-4.14 (m, 3H, *H*-5b, *H*-6a, *H*-6b), 4.17-4.21 (m, 2H, *H*-6´a, *H*-6´b), 4.88 (d, 1H, *H*-1b), 4.94 (d, 1H, *H*-1a), 5.21-5.33 (m, 4H, *H*-2b, *H*-3a, *H*-4a, *H*-4b), 5.37 (dd, $^3J_{2b,3b}$ = 3.3 Hz, $^3J_{3b,4b}$ = 10.0 Hz, 1H, *H*-3b) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.01 (1C, *C*H$_3$), 20.56-20.77 (7C,

7COCH$_3$), 22.56-31.78 (10C, 10*C*H$_2$), 61.95 (1C, *C*-6a or *C*-6b), 62.39 (1C, *C*-6a or *C*-6b), 66.01 (1C, *C*-4a), 66.25 (1C, *C*-4b), 67.29(1C, 1O*C*H$_2$), 68.26 (1C, *C*-3b), 68.33 (1C, *C*-5a), 69.00 (1C, *C*-5b), 69.64 (1C, *C*-2b), 69.85-69.91 (2C, 2O*C*H$_2$), 70.15 (1C, *C*-3a), 70.44-70.56 (9C, 9O*C*H$_2$), 71.41 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 76.97 (1C, *C*-2a), 98.23 (1C, *C*-1a), 99.04 (1C, *C*-1b), 169.27-170.79 (7C, 7*C*OCH$_3$) ppm; $C_{50}H_{84}O_{24}$ (1069.2); MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1091.5, found: 1090.9; [*M*+K]$^+$ calcd.: 1107.5, found: 1106.9.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2,3,4,6-tetra-*O*-acetyl-α-D-manno-pyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (15-3): Compound **15-3** was prepared from **7-3** (292 mg, 163 µmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/acetone 3:1) followed by MPLC (silica gel, toluene/acetone 3:1) to afford **15-3** (132 mg, 97 µmol, 60%) as a pale, colorless oil. TLC: R_f = 0.43 (toluene/acetone 3:2); $[\alpha]_D^{20}$ = +15.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.85 (pseudo t, 3H, C*H*$_3$), 1.17-1.31 (m, 18H, 9C*H*$_2$), 1.54 (pseudo quint, 2H, 1C*H*$_2$), 1.97-2.12 (10s, 30H, 10COC*H*$_3$), 3.41 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.53-3.56 (m, 2H, 1OC*H*$_2$), 3.59-3.65 (m, 21H, 21/2OC*H*$_2$), 3.77-3.83 (m, 1H, 1/2OC*H*$_2$), 3.97 (ddd, $^3J_{4a,5a}$ = 9.1 Hz, $^3J_{5a,6a}$ = 4.0 Hz, $^3J_{5a,6'a}$ = 2.4 Hz, 1H, *H*-5a), 4.02 (dd, 1H, *H*-2a), 4.05-4.23 (m, 9H, *H*-2b, *H*-5b, *H*-5c, *H*-6a, *H*-6b, *H*-6c, *H*-6´a, *H*-6´b, *H*-6´c), 4.92 (d, $^3J_{1c,2c}$ = 1.8 Hz, 1H, *H*-1c), 4.96 (d, $^3J_{1a,2a}$ = 1.8 Hz, 1H, *H*-1a), 5.08 (d, $^3J_{1b,2b}$ = 2.0 Hz, 1H, *H*-1b), 5.22-5.33 (m, 6H, *H*-2c, *H*-3a, *H*-3b, *H*-4a, *H*-4b, *H*-4c), 5.36 (dd, $^3J_{2c,3c}$ = 3.4 Hz, $^3J_{3c,4c}$ = 10.0 Hz, 1H, *H*-3c) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.03 (1C, *C*H$_3$), 20.56-20.77 (10C, 10COCH$_3$), 22.59-31.82 (10C, 10*C*H$_2$), 61.95-62.43(3C, *C*-6a, *C*-6b, *C*-6c), 66.08-66.20 (3C, *C*-4a, *C*-4b, *C*-4c), 67.33 (1C, 1O*C*H$_2$), 68.31 (1C, *C*-3c), 68.44 (1C, *C*-5a), 69.16 (1C, *C*-5c), 69.37 (1C, *C*-5b), 69.50 (1C, *C*-2c), 69.61 (1C, *C*-3a or *C*-3b), 69.88-69.95 (2C, 2O*C*H$_2$), 70.41 (1C, *C*-3a or *C*-3b), 70.47-70.57 (9C, 9O*C*H$_2$), 71.46 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 76.61 (1C, *C*-2a), 77.35 (1C, *C*-2b), 98.27 (1C, *C*-1a), 99.30 (1C, *C*-1c), 99.70 (1C, *C*-1b), 169.27-170.80 (10C, 10*C*OCH$_3$) ppm; elemental analysis is calcd. (%) for $C_{62}H_{100}O_{32}$ (1357.4): C: 54.86, H: 7.43; found: C: 55.04, H: 7.66; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1380.4, found: 1380.1; [*M*+K]$^+$ calcd.: 1396.5, found: 1396.1.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2,3,4,6-tetra-*O*-acetyl-α-D-manno-pyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (15-4): Compound **15-4**

was prepared from **7-4** (192 mg, 86 µmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/acetone 3:2) followed by MPLC (silica gel, toluene/acetone 3:2) to afford **15-4** (118 mg, 72 µmol, 83%) as a foam. TLC: R_f = 0.36 (toluene/acetone 3:2); $[\alpha]_D^{20}$ = +29.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.84 (pseudo t, 3H, C*H*$_3$), 1.17-1.31 (m, 18H, 9C*H*$_2$), 1.54 (pseudo quint, 2H, 1C*H*$_2$), 1.97-2.13 (13s, 39H, 13COC*H*$_3$), 3.41 (pseudo t, 2H, OC*H*$_2$C$_{11}$H$_{23}$), 3.53-3.55 (m, 2H, OC*H*$_2$), 3.59-3.65 (m, 21H, 21/2OC*H*$_2$), 3.77-3.82 (m, 1H, 1/2OC*H*$_2$), 3.97 (ddd, $^3J_{4a,5a}$ = 9.9 Hz, $^3J_{5a,6a}$ = 4.1 Hz, $^3J_{5a,6'a}$ = 2.5 Hz, 1H, *H*-5a), 4.00-4.23 (m, 14H, *H*-2a, *H*-2b, *H*-2c, *H*-5b, *H*-5c, *H*-5d, *H*-6a, *H*-6b, *H*-6c, *H*-6d, *H*-6´a, *H*-6´b, *H*-6´c, *H*-6´d), 4.94 (d, $^3J_{1d,2d}$ = 1.8 Hz, 1H, *H*-1d), 4.96 (d, $^3J_{1a,2a}$ = 1.9 Hz, 1H, *H*-1a), 5.05 (d, $^3J_{1,2}$ = 2.2 Hz, 1H, *H*-1b or *H*-1c), 5.11 (d, $^3J_{1,2}$ = 2.0 Hz, 1H, *H*-1b or *H*-1c), 5.22-5.35 (m, 8H, *H*-2d, *H*-3a, *H*-3b, *H*-3c, *H*-4a, *H*-4b, *H*-4c, *H*-4d), 5.36 (dd, $^3J_{2d,3d}$ = 3.4 Hz, $^3J_{3d,4d}$ = 10.0 Hz, 1H, *H*-3d) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.03 (1C, *C*H_3), 20.52-20.78 (13C, 13CO*C*H_3), 22.59-31.81 (10C, 10*C*H_2), 61.97-62.37 (4C, *C*-6a, *C*-6b, *C*-6c, *C*-6d), 65.99-66.38 (4C, *C*-4a, *C*-4b, *C*-4c, *C*-4d), 67.34 (1C, 1O*C*H_2), 68.27 (1C, *C*-3d), 68.39 (1C, *C*-5a), 69.13-69.39 (3C, *C*-5b, *C*-5c, *C*-5d), 69.49 (1C, *C*-2d), 69.59 (1C, *C*-3b or *C*-3c), 69.71 (1C, *C*-3b or *C*-3c), 69.88-69.94 (2C, 2O*C*H_2), 70.33 (1C, *C*-3a), 70.46-70.57 (9C, 9O*C*H_2), 71.45 (1C, O*C*H_2C$_{11}$H$_{23}$), 76.42-77.13 (3C, *C*-2a, *C*-2b, *C*-3c), 98.31 (1C, *C*-1a), 99.15 (1C, *C*-1d), 99.55 (1C, *C*-1b or *C*-1c), 99.73 (1C, *C*-1b or *C*-1c), 169.20-170.75 (13C, 13*C*OCH$_3$) ppm; elemental analysis is calcd. (%) for $C_{74}H_{116}O_{40}$ (1645.7): C: 54.01, H: 7.10; found: C: 53.95, H: 7.43; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1668.7, found: 1668.7; [*M*+K]$^+$ calcd.: 1684.8, found: 1684.3.

Synthesis of 3,6,9,12,15,18-Hexaoxatriacontanyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (15-5): Compound **15-5** was prepared from **7-5** (225 mg, 85 mmol) according to GP III. The residue was purified by flash column chromatography (silica gel, toluene/acetone 3:2) followed by MPLC (silica gel, toluene/acetone 3:2) to afford **15-5** (116 mg, 60 mmol, 71%) as a foam. TLC: R_f = 0.32 (toluene/acetone 3:2); $[\alpha]_D^{20}$ = +28.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.84 (pseudo t, 3H, C*H*$_3$), 1.16-1.31 (m, 18H, 9C*H*$_2$), 1.54 (pseudo quint, 2H, 1C*H*$_2$), 1.97-2.13 (16s, 48H, 16COC*H*$_3$), 3.41 (pseudo t, 2H,

OCH_2C$_{11}$H$_{23}$), 3.53-3.55 (m, 2H, OCH_2), 3.59-3.65 (m, 21H, 21/2OCH_2), 3.77-3.82 (m, 1H, 1/2OCH_2), 3.97 (ddd, $^3J_{4a,5a}$ = 9.8 Hz, $^3J_{5a,6a}$ = 3.9 Hz, $^3J_{5a,6´a}$ = 2.5 Hz, 1H, *H*-5a), 4.01-4.24 (18H, *H*-2a, *H*-2b, *H*-2c, *H*-2d, *H*-5b, *H*-5c, *H*-5d, *H*-5e, *H*-6a, *H*-6b, *H*-6c, *H*-6d, *H*-6e, *H*-6´a, *H*-6´b, *H*-6´c, *H*-6´d, *H*-6´e), 4.94 (d, 1H, *H*-1e), 4.96 (d, $^3J_{1a,2a}$ = 1.6 Hz, 1H, *H*-1a), 5.07 (d, $^3J_{1,2}$ = 2.0 Hz, 1H, *H*-1b or *H*-1c or *H*-1d), 5.09 (d, $^3J_{1,2}$ = 1.9 Hz, 1H, *H*-1b or *H*-1c or *H*-1d), 5.14 (d, $^3J_{1,2}$ = 1.4 Hz, 1H, *H*-1b or *H*-1c or *H*-1d), 5.19-5.35 (m, 10H, *H*-2e, *H*-3a, *H*-3b, *H*-3c, *H*-3d, *H*-4a, *H*-4b, *H*-4c, *H*-4d, *H*-4e), 5.37 (dd, $^3J_{2e,3e}$ = 3.2 Hz, $^3J_{3e,4e}$ = 10.0 Hz, 1H, *H*-3e) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.02 (1C, *C*H$_3$), 20.51-20.75 (16C, 16CO*C*H$_3$), 22.58-31.81 (10C, 10*C*H$_2$), 61.93-62.34 (5C, *C*-6a, *C*-6b, *C*-6c, *C*-6d, *C*-6e), 65.92-66.37 (5C, *C*-4, *C*-4b, *C*-4c, *C*-4d, *C*-4e), 67.33 (1C, 1O*C*H$_2$), 68.26 (1C, *C*-3e), 68.40 (1C, *C*-5a), 69.09-69.39 (4C, *C*-5b, *C*-5c, *C*-5d, *C*-5e), 69.50 (1C, *C*-2e), 69.57-69.73 (3C, *C*-3b, *C*-3c, *C*-3d), 69.64 (1C, *C*-2b), 69.87-69.94 (2C, 2O*C*H$_2$), 70.33 (1C, *C*-3a), 70.46-70.56 (9C, 9O*C*H$_2$), 71.45 (1C, O*C*H$_2$C$_{11}$H$_{23}$), 75.89-77.1 (3C, *C*-2a, *C*-2c, *C*-2d), 98.33 (1C, *C*-1a), 99.22 (1C, *C*-1e), 99.36 (1C, *C*-1b or *C*-1c or *C*-1d), 99.48 (1C, *C*-1b or *C*-1c or *C*-1d), 99.78 (1C, *C*-1b or *C*-1c or *C*-1d), 169.14-170.75 (16C, 16*C*OCH$_3$) ppm; elemental analysis is calcd. (%) for C$_{86}$H$_{132}$O$_{48}$ (1933.9): C: 53.41, H: 6.88; found: C: 53.64, H: 7.37; MALDI-MS (pos. mode, CHCA): [*M*+Na]$^+$ calcd.: 1956.3, found: 1956.1; [*M*+K]$^+$ calcd.: 1972.4, found: 1972.3.

Synthesis of methyl α**-D-mannopyranosyl-(1→2)-**α**-D-mannopyranoside (16-2)**[2]: Compound **16-2** (58 mg, 163 μmol) was prepared from **12-2** (110 mg, 169 μmol) according to GP II as a colorless lyophilizate.

Synthesis of methyl α**-D-mannopyranosyl-(1→2)-**α**-D-mannopyranosyl-(1→2)-**α**-D-man-nopyranoside (16-3)**[3]: Compound **16-3** (43 mg, 83 μmol) was prepared from **12-3** (81 mg, 86 μmol) according to GP II as a colorless lyophilizate.

Synthesis of 8-triphenylmethyloxy-3,6-dioxaoctanol (20)[8]: Triethylene glycol (11.2 g, 75.2 mmol), tritylchloride (20.9, 75.0 mmol) and DMAP (1.0 g, 8.2 mmol) were dissolved in dry pyridine (200 mL) and stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure to 1/3 of the original volume. Precipitated salts were removed by filtration over cellite. The filtrate was reduced and purified by flash column chromatography (silica gel, toluene/acetone 10:1 → 2:1) to afford compound **20** (15.3 g, 39.0 mmol, 52%) as a oil.

Synthesis of 17-triphenylmethoxy-3,6,9,12,15,-pentaoxaheptadecanol (21)[9]: Hexaethylene glycol (15.0 g, 53.1 mmol), tritylchloride (14.8 g, 53.1 mmol) and DMAP (650 mg, 5.32 mmol) were dissolved in dry pyridine (400 mL) and stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure to 1/3 of the original volume. Precipitated salts were removed by filtration over cellite. The filtrate was reduced and purified by flash column chromatography (silica gel, toluene/acetone 2:1 → 1:1 → 0:1) to afford compound **21** (13.1 g, 25.0 mmol, 47%) as a oil and not consumed hexaethylene glycol (5.5 g, 19.5 mmol, 37%).

1-Triphenylmethoxy-3,6,9-trioxahenicosan (22): Compound **20** (3.10 g, 7.90 mmol) and TBAI (200 mg, 0.54 mmol) were dissolved in dry THF (80 mL) and NaH (300 mg, 1.25 mol) is added in small portions. After the H_2 development had stopped dodecyl bromide (2.30 mL, 2.39 g, 9.60 mmol) was added. The reaction mixture is refluxed for 16 h. After cooling to RT the precipitated salts were removed by filtration. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, toluene/ethyl acetate 20:1 → 10:1) to afford compound **22** (3.52 g, 6.28 mmol, 79%) as a oil. TLC: R_f = 0.58 (toluene/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85-0.92 (m, 3H, C*H*$_3$), 1.20-1.39 (m, 18H, 9C*H*$_2$), 1.52-1.60 (m, 2H, 1C*H*$_2$), 3.20-3.28 (m, 2H, 1OC*H*$_2$), 3.40-3.48 (m, 2H, 1OC*H*$_2$), 3.52-3.75 (m, 10H, 5OC*H*$_2$), 7.18-7.49 (m, 15H, Ph) ppm; $C_{37}H_{52}O_4$ (560.8); MALDI-MS (pos. mode, DHB): $[M+Na]^+$ calcd.: 583.4, found: 583.5; $[M+K]^+$ calcd.: 599.5, found: 599.5.

1-Triphenylmethoxy-3,6,9,12,15,18-hexaoxatriacontan (23)[10]: Compound **21** (13.0 g, 24.8 mmol) and TBAI (900 mg, 2.44 mmol) were dissolved in dry THF (200 mL) and NaH (1.3 g (60%), 32.5 mmol) is added in small portions. After the H_2 development had stopped dodecyl bromide (7.70 mL, 8.01 g, 32.1 mmol) was added. The reaction mixture is refluxed for 16 h. After cooling to RT the precipitated salts were removed by filtration. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, toluene/acetone 2:1) to afford compound **23** (14.4 g, 20.8 mmol, 84%) as a oil .

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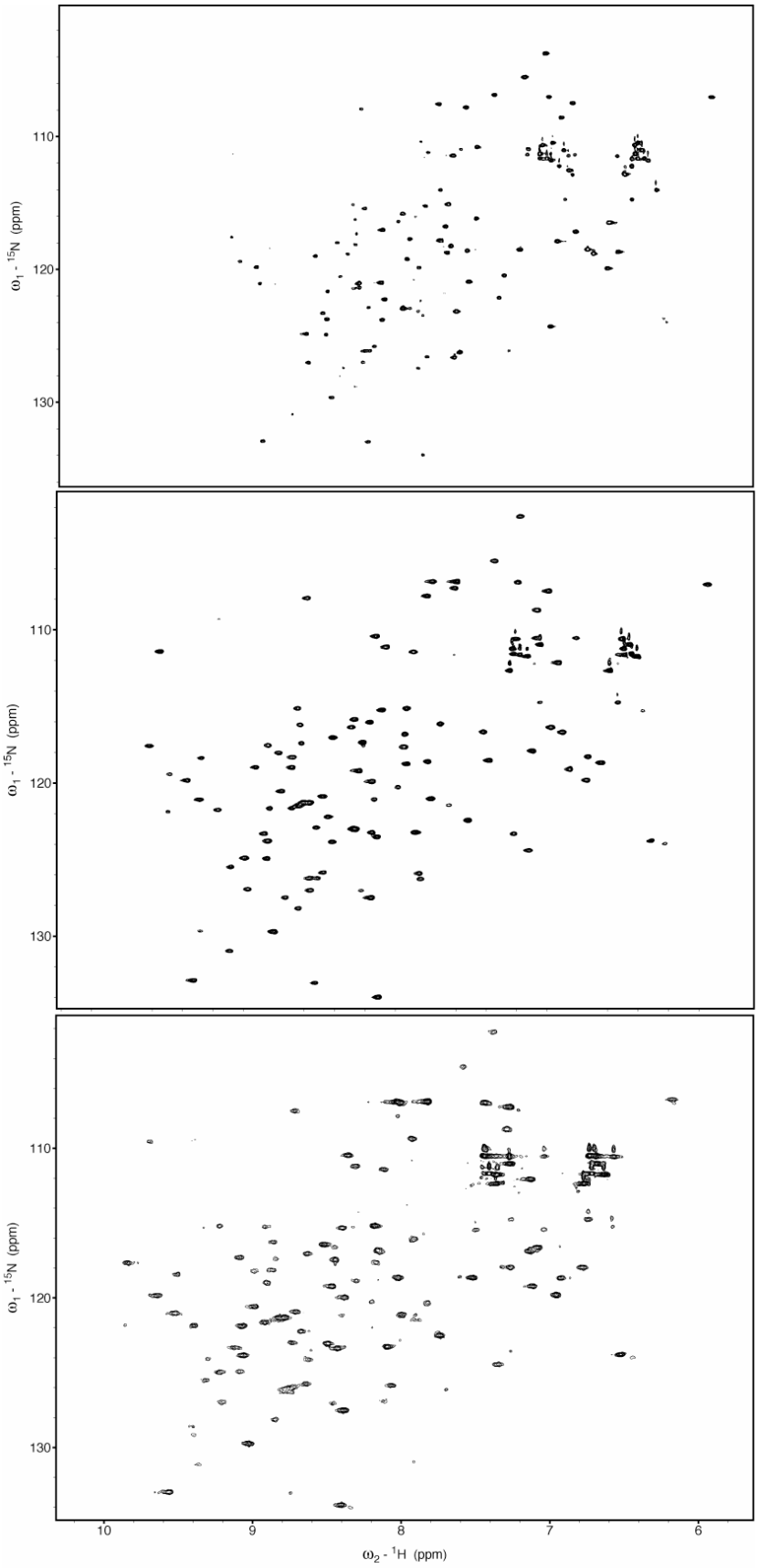

Figure S3: [^{15}N,^{1}H]-HSQC spectra of CVN/DPC in the absence of glycolipids (top), in the presence of **19-2** (middle) and **19-3** (bottom).

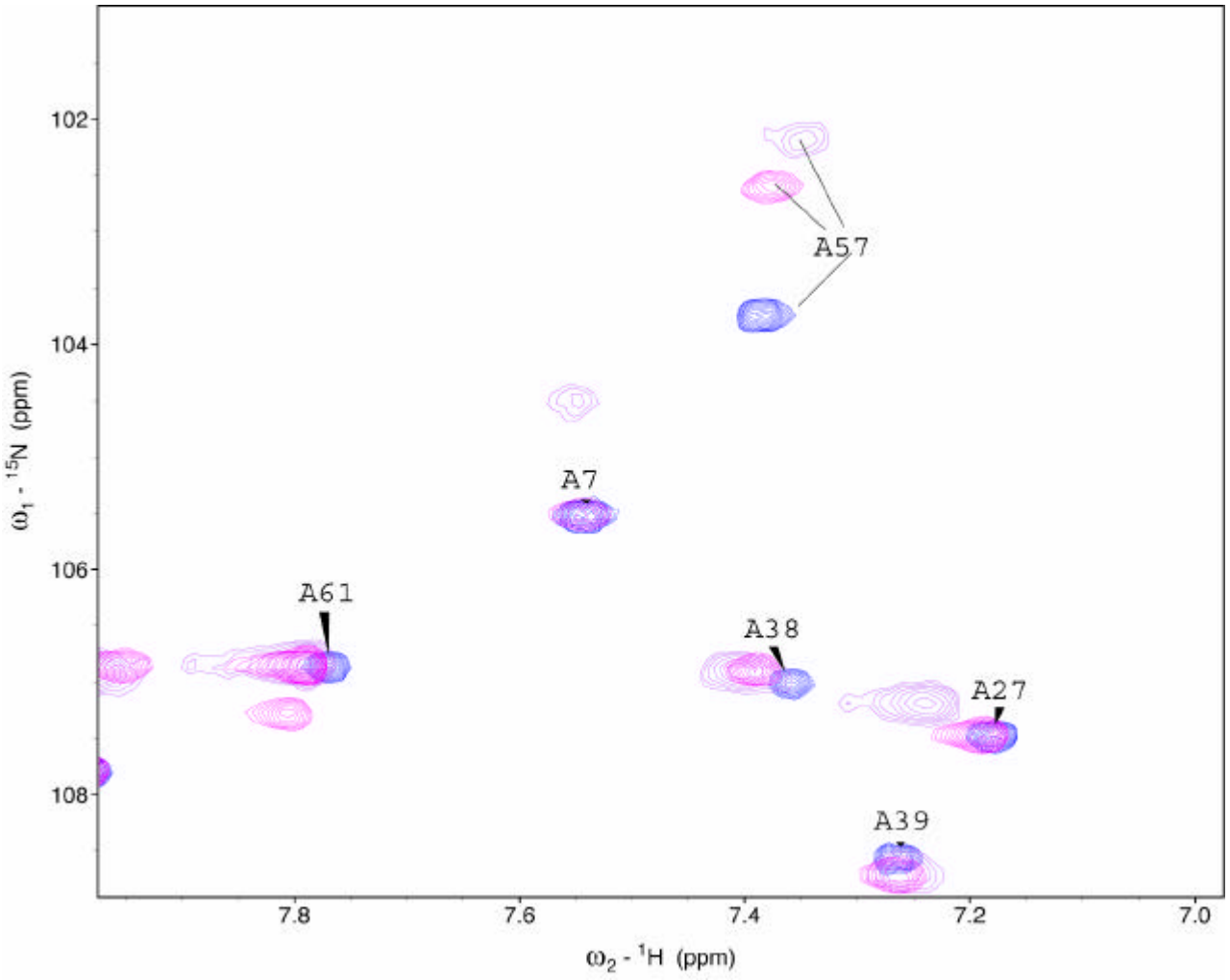

Figure S4: Overlay of [^{15}N,^{1}H]-HSQC spectra of CVN/DPC in the absence of glycolipids (blue contours), in the presence of **19-2** (magenta) and **19-3** (purple).

Table S1. Proton and nitrogen chemical shifts of CVN and the triple mutant. Spectra were recorded at approx. 0.3 mM concentration of protein in 300mM DPC / 90% H_2O/10% ^2H_2O at 310 K and pH 6.5 in 50 mM sodium phosphate buffer. Chemical shifts are referenced via the proton chemical shift of the water resonance set to 4.63 at 310K. The ^{15}N chemical shift scale was calculated by multiplying the proton frequency of 0 ppm by 0.1013291444 to yield the ^{15}N frequency for 0 ppm.

Residue		^{15}N	$^{1}H^{N}$	Mutant		Residue				Mutant	
2	GLY	111.226	9.780			26	ASN	116.005	8.398	115.940	8.203
3	LYS(N)	119.342	9.716	120.941	8.573	27	GLY	107.434	7.211	107.762	7.562
4	PHE	121.607	9.056	120.571	9.055	28	GLY	107.756	8.013	107.633	7.875
5	SER	116.119	7.939	116.740	8.106	29	TYR	115.182	8.324	115.575	8.151
6	GLN	117.838	7.325	117.937	7.229	30	ASN	117.924	8.990	117.865	8.957
7	THR	105.475	7.567	103.989	7.535	31	THR	125.767	8.705	125.897	8.735
8	CYS	118.630	6.862	119.169	6.917	32	SER	122.830	8.751	122.460	8.770
9	TYR	119.774	9.597	119.774	9.604	33	SER	111.381	8.114	111.132	8.141
10	ASN	115.073	8.871	114.744	8.848	34	ILE	121.708	9.359	121.368	9.354
11	SER	115.047	8.146	115.057	8.170	35	ASP	126.096	8.776	126.385	8.779
12	ALA	124.808	9.220	124.816	9.230	36	LEU	126.970	9.201	126.865	9.205
13	ILE	119.805	8.361	119.753	8.375	37	ASN	117.270	8.841	117.353	8.854
14	GLN	127.377	8.377	127.375	8.368	38	SER	106.968	7.389	107.034	7.411
15	GLY	118.359	9.494	118.252	9.495	39	VAL	108.520	7.289	108.465	7.286
16	SER	120.494	8.968	120.478	8.966	40	ILE	119.873	6.942	119.863	7.005
17	VAL	123.106	8.084	123.129	8.091	41	GLU	126.522	8.313	125.315	8.324
18	LEU	132.936	8.755	132.897	8.749	42	ASN	120.740	8.410	120.447	8.439
19	THR	123.696	9.068	123.690	9.067	43	VAL	128.772	8.854	128.557	8.891
20	SER	116.985	8.641	117.038	8.669	44	ASP	127.983	8.966	127.847	8.982
21	THR	123.766	8.649	123.387	8.581	45	GLY	107.508	8.217	107.605	8.264
22	CYS	123.250	9.101	123.100	9.030	46	SER	112.832	7.210	112.383	7.252
23	GLU(I)	122.892	8.493	121.919	8.161	47	LEU	124.252	7.378	124.230	7.407
24	ARG	123.404	8.342	125.122	8.402	48	LYS	120.943	8.659	120.765	8.628
25	THR	118.943	9.147	118.109	8.937	49	TRP	122.209	8.624	122.494	8.647

Residue				Mutant	
50	GLN	126.586	8.101	126.840	8.097
51					
52	SER	112.190	6.763	112.970	6.855
53	ASN	110.714	9.408	110.990	9.483
54	PHE	118.194	8.126	118.194	8.128
55	ILE	118.764	7.053	118.743	7.052
56	GLU	118.450	7.096	118.317	7.092
57	THR	103.698	7.411	103.587	7.412
58	CYS	117.121	7.182	117.153	7.198
59	ARG	117.514	9.783	117.493	9.787
60	ASN	116.193	8.848	116.192	8.852
61	THR	106.818	7.799	106.877	7.807
62	GLN	118.790	8.909	118.881	8.913
63	LEU	122.884	8.433	120.787	7.963
64	ALA	132.872	9.542	132.685	9.542
65	GLY	110.330	8.356	110.345	8.357
66	SER	116.359	8.524	116.204	8.513
67	SER	111.138	8.301	110.967	8.274
68	GLU	120.881	7.990	121.925	8.010
69	LEU	126.079	8.739	124.389	8.714
70	ALA	129.616	9.030	129.645	9.041
71	ALA	119.170	8.458	119.047	8.462
72	GLU	117.778	8.205	117.660	8.216
73	CYS	121.068	9.455	121.005	9.471
74	LYS	122.309	8.358	122.182	8.357
75	THR	115.369	8.779	115.254	8.776
76	ARG	121.026	9.568	120.951	9.534
77	ALA	120.413	7.720	120.383	7.721
78	GLN	110.738	7.930	110.749	7.939
79	GLN	116.427	6.929	116.398	6.935
80	PHE	121.069	8.875	120.894	8.815
81	VAL	118.079	8.853	118.079	8.848
82	SER	117.668	8.439	117.633	8.447
83	THR	121.381	8.860	121.393	8.825
84	LYS	122.092	7.767	122.055	7.767
85	ILE	121.300	8.822	121.115	8.839
86	ASN	124.870	9.069	124.928	9.056
87	LEU	125.457	9.317	125.420	9.318
88	ASP	116.727	8.164	116.425	8.210
89	ASP	118.544	8.006	117.964	7.978
90	HIS	106.981	6.157	107.103	6.133
91	ILE	118.698	8.157	118.850	8.210
92	ALA	130.864	9.325	131.242	9.136
93	ASN(A)	115.759	8.486		
94	ILE	126.950	8.796		
95	ASP	127.364	8.941	130.009	9.416
96	GLY	107.886	8.805	102.867	8.582
97	THR	118.465	7.614	117.858	7.584
98	LEU	126.198	8.059	126.747	8.263
99	LYS	120.998	8.820	121.358	9.006
100	TYR	123.125	8.377	123.252	8.390
101	GLU	133.930	8.342	133.702	8.364

Table S2: Chemical shift changes of CV-N upon adding the lapidated mannobiose derivatives **17-2**, **18-2**, **19-2** to a solution of 0.2mM CV-N in 300mM DPC:

residue		**17-2**	**18-2**	**19-2**	residue		**17-2**	**18-2**	**19-2**
2	GLY	0.060	0.067	0.075	28	GLY	0.013	0.020	0.012
3	LYS	2.152	2.158	2.147	29	TYR	0.009	0.004	0.005
4	PHE	0.006	0.007	0.005	30	ASN	0.024	0.030	0.023
5	SER	0.007	0.003	0.012	31	THR	0.010	0.017	0.017
6	GLN	0.007	0.005	0.000	32	SER	0.006	0.010	0.006
7	THR	0.007	0.023	0.004	33	SER	0.001	0.004	0.002
8	CYS	0.014	0.017	0.010	34	ILE	0.028	0.029	0.020
9	TYR	0.005	0.005	0.003	35	ASP	0.030	0.038	0.037
10	ASN	0.006	0.015	0.016	36	LEU	0.012	0.045	0.035
11	SER	0.024	0.025	0.021	37	ASN	0.015	0.034	0.035
12	ALA	0.009	0.016	0.005	38	SER	0.057	0.067	0.054
13	ILE	0.017	0.021	0.022	39	VAL	0.022	0.073	0.050
14	GLN	0.020	0.024	0.021	40	ILE	0.026	0.062	0.047
15	GLY	0.019	0.026	0.021	41	GLU	0.245	0.241	0.235
16	SER	0.008	0.014	0.011	42	ASN	0.605	0.609	0.612
17	VAL	0.022	0.033	0.026	43	VAL	0.207	0.225	0.291
18	LEU	0.014	0.026	0.021	44	ASP	0.952	0.951	0.918
19	THR	0.010	0.008	0.006	45	GLY	0.391	0.397	0.389
20	SER	0.009	0.008	0.006	46	SER	0.368	0.355	0.338
21	THR	0.013	0.014	0.012	47	LEU	0.024	0.040	0.043
22	CYS	0.004	0.002	0.011	48	LYS	0.059	0.083	0.077
23	GLU				49	TRP	0.062	0.063	0.060
24	ARG				50	GLN	0.342	0.358	0.333
25	THR				51	PRO			
26	ASN	0.014	0.018	0.015	52	SER	0.260	0.265	0.263
27	GLY	0.009	0.013	0.004	53	ASN	0.019	0.554	0.032

residue		**17-2**	**18-2**	**19-2**	residue		**17-2**	**18-2**	**19-2**
54	PHE	0.875	0.867	0.903	78	GLN	0.781	1.214	1.579
55	ILE	0.162	0.155	0.137	79	GLN	0.184	0.219	0.281
56	GLU	0.153	0.147	0.173	80	PHE			
57	THR	0.634	0.594	0.512	81	VAL	0.059	0.082	0.110
58	CYS	0.168	0.181	0.233	82	SER	0.093	0.120	0.163
59	ARG	0.004	0.022	0.004	83	THR	0.070	0.076	0.101
60	ASN	0.010	0.026	0.020	84	LYS	0.129	0.133	0.127
61	THR	0.013	0.021	0.016	85	ILE	0.076	0.041	0.074
62	GLN	0.025	0.061	0.045	86	ASN	0.003	0.007	0.003
63	LEU	0.074	0.065	0.070	87	LEU	0.012	0.015	0.010
64	ALA	0.014	0.022	0.020	88	ASP	0.018	0.023	0.015
65	GLY	0.017	0.026	0.023	89	ASP	0.008	0.012	0.008
66	SER	0.014	0.025	0.019	90	HIS	0.025	0.020	0.012
67	SER	0.014	0.030	0.020	91	ILE	0.005	0.003	0.001
68	GLU	0.011	0.038	0.027	92	ALA	0.013	0.010	0.004
69	LEU	0.046	0.065	0.064	93	ASN	0.022	0.028	0.019
70	ALA	0.010	0.014	0.011	94	ILE	0.006	0.004	0.003
71	ALA	0.010	0.022	0.009	95	ASP	0.022	0.033	0.025
72	GLU	0.070	0.084	0.087	96	GLY	0.012	0.007	0.009
73	CYS	0.073	0.065	0.065	97	THR	0.003	0.005	0.004
74	LYS	0.499	0.513	0.462	98	LEU	0.010	0.013	0.007
75	THR	0.898	0.931	0.987	99	LYS	0.218	0.187	0.271
76	ARG	0.365	0.404	0.393	100	TYR	0.017	0.005	0.019
77	ALA	0.490	0.957	1.707	101	GLY			

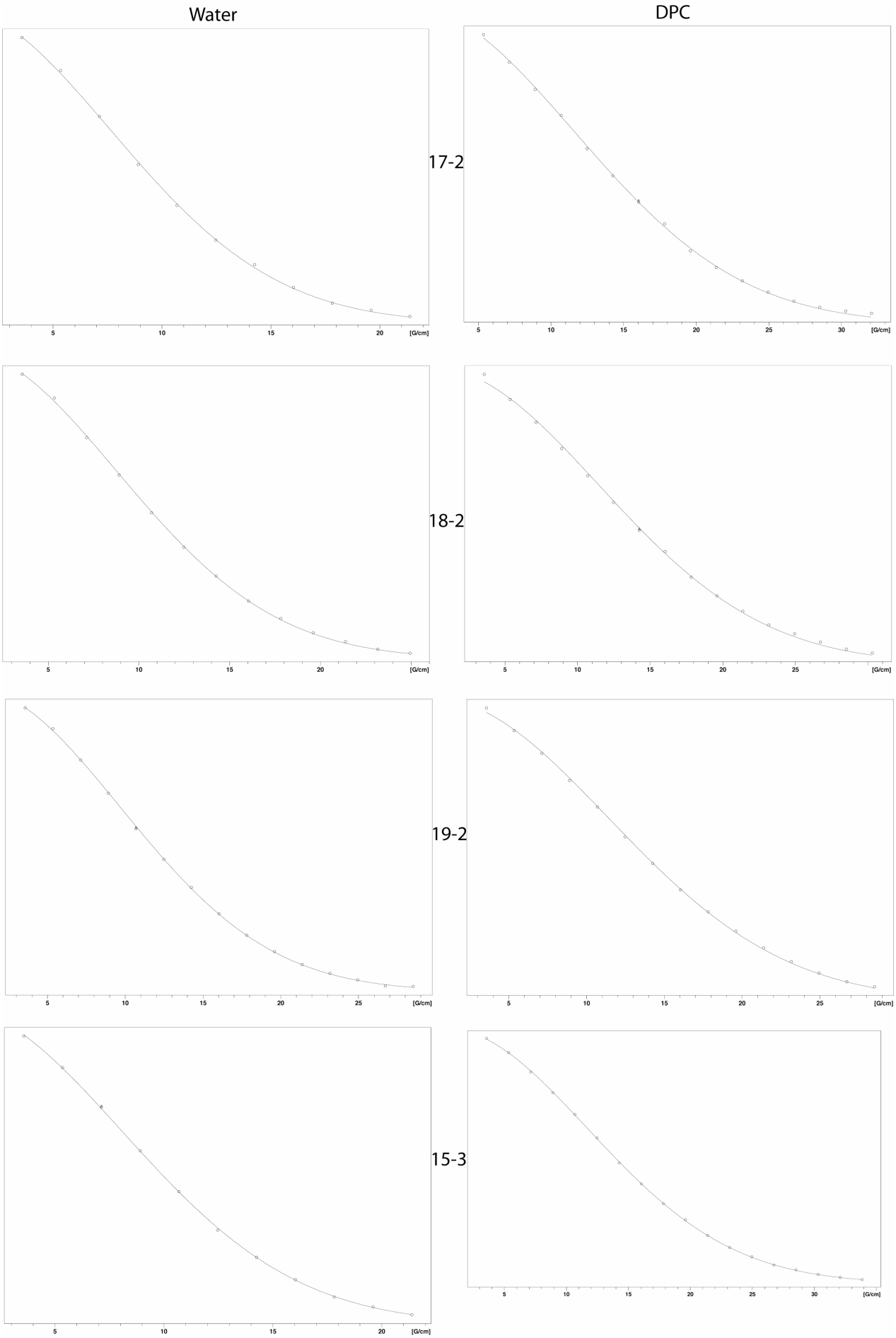

Figure S5: Selected curves from the diffusion measurements, 310K, D_2O

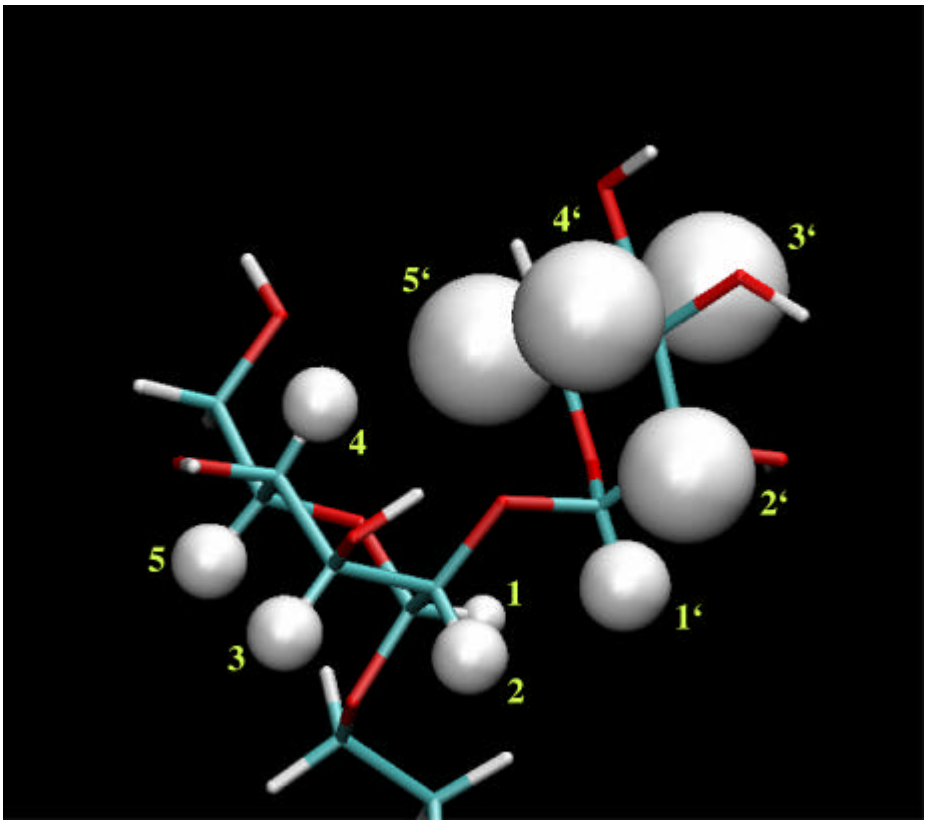

Figure S6: Model of the glycolipid **17-2**, in which the attenuation of carbohydrate proton signals due to the paramagnetic relaxation with the micelle-integrating spin label 5-doxylstearate has been encoded into the size of the atom radii (large radii correspond to little attenuation, small radii to large attenuation). The lipid anchor extends at the bottom of the figure and has been omitted for clarity. The bond angle about the glycosidic bond linking the two carbohydrate moieties has been adjusted to result in a configuration compatible with the SL data. However, there is flexibility about this bond, and the precision of the SL data is clearly not sufficient to define the carbohydrate conformation more precisely.

Table S5: Attenuations as extracted from i) the 1D proton spectrum, and ii) cross-peaks from a 80ms TOCSY spectrum

H Atom No.	**17-2**		**19-2**
1D data	Signal(SL)/ Signal(Ref)		
1	0.10	1	0.43
3	0.30	2	0.62
1’	0.22	1’	0.53
2’	0.51	2’	0.78
2D data			
1<->2	0.02		
2<->3	0.10		
3<->4	0.10		
3<->5	0.05		
1’<->2’	0.15		
2’<->3’	0.60		
3’<->4’	0.60		
4’<->5’	0.60		

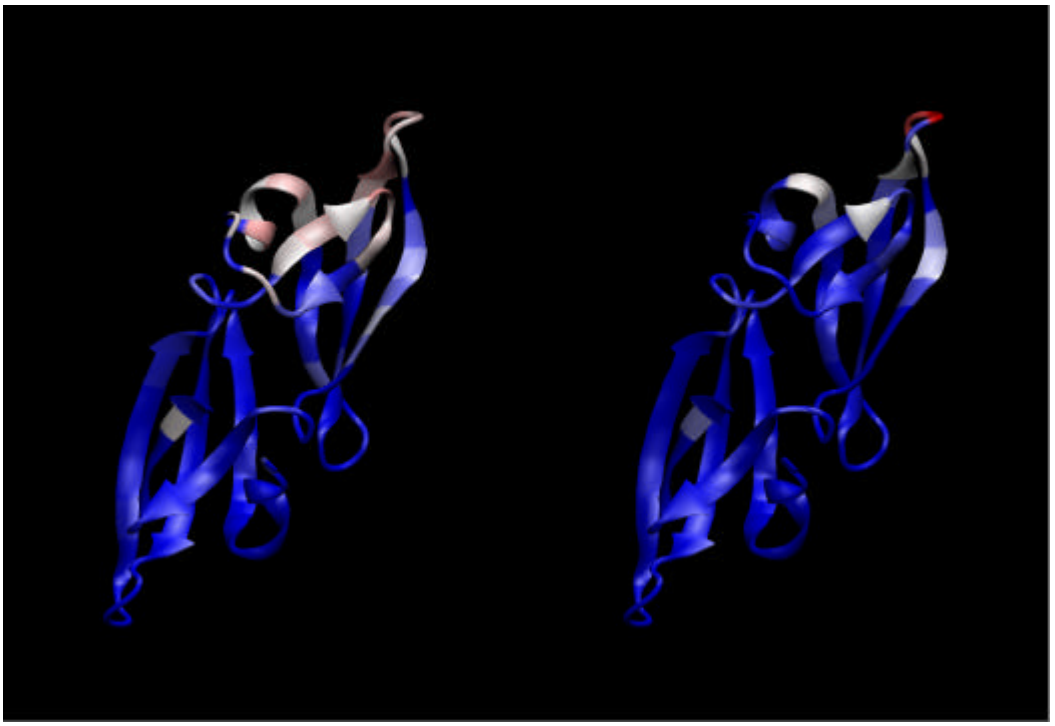

Figure S7: Chemical shift changes upon adding **17-2** to CV-N color-coded onto the structure (left), as well as *differences* of chemical shift changes induced by adding **17-2** or **19-2**.

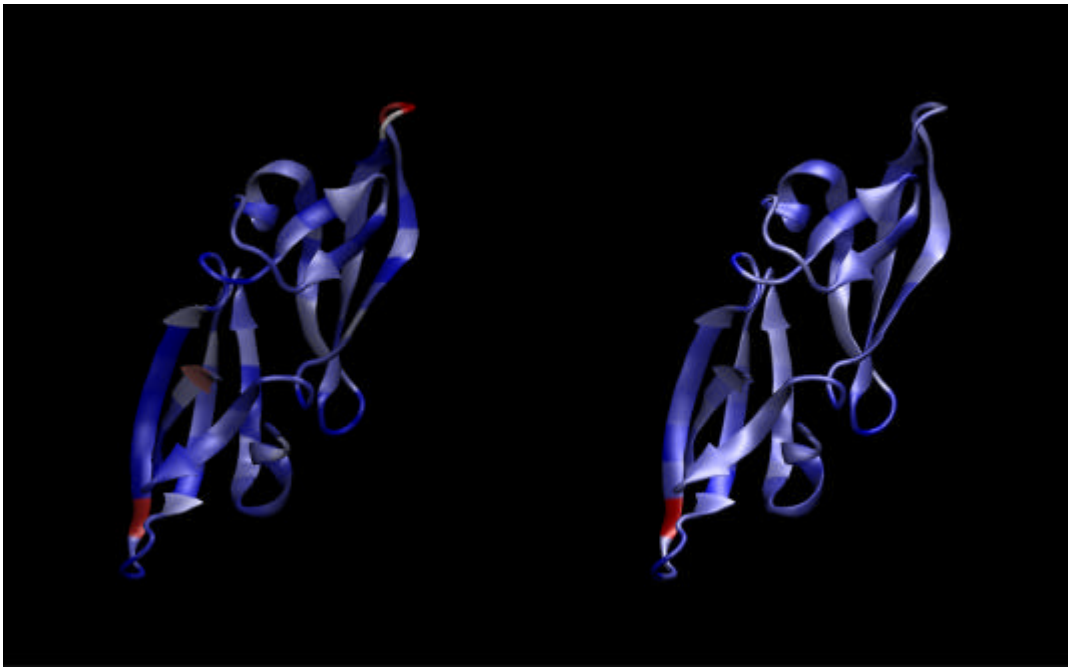

Figure S8: Attenuations of resonances of CV-N due to the presence of the spin label 5-doxylstearate upon adding **17-2** (left) or **19-2** (right) to CV-N color-coded onto the structure: