

Comparative Studies on Lectin-Carbohydrate Interaction in Low and High Density Homo-and Heteroglycoclusters

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Supporting Information

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General Methods

Radical addition reactions: A solution of the tri-*O*-allylated pentaerythritol derivative **1**¹ and 1-thiosugar (**2** or **3**)^{2,3} (1.5 eq per mol of allyl group) in degassed MeOH (~7.5 mL per 0.1 g of 1-thiosugar) was irradiated at 250 nm under Ar for 1 h. The reaction mixture was then concentrated and the residue was purified by column chromatography using 1:1 EtOAc-petroleum ether as eluent.

Conventional Zemplen deacetylation: The acetylated compound was dissolved in dry MeOH (~2 mL per 100 mg of compound) and NaMeO 1 M (0.1 eq per mol of acetate) was added. The solution was stirred at room temperature for 30 min, then neutralised using Amberlite IR-120 (H⁺) ion exchange resin, filtered, concentrated and freeze-dried.

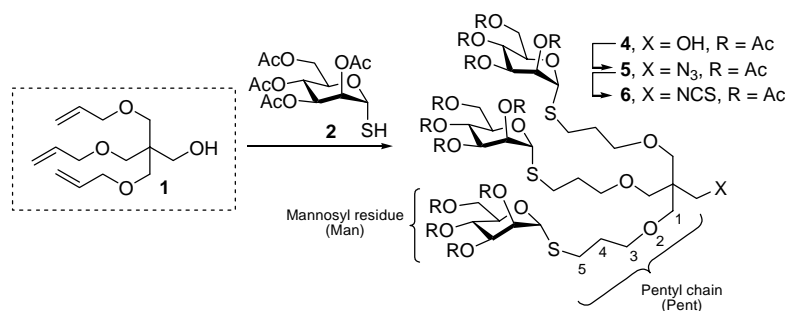
Azide displacement procedure: To a solution of a pentaerythritol derivative in dry CH₂Cl₂ (~7 mL per mmol of erythritol derivative) at -25 °C, pyridine (3 eq per mol of hydroxyl group) and Tf₂O (1.5 eq per mol of hydroxyl group) were added under N₂. The solution was stirred for 30 min at -25 °C, then washed with cold aqueous saturated NaHCO₃, dried (MgSO₄) and concentrated to give the corresponding triflate ester, which was used in the next step without further purification. The residue was dissolved in DMF (10 mL per mmol of triflate ester) and NaN₃ (3 eq per mol of triflate ester) was added. The mixture was stirred at room temperature for 2 h, concentrated, the resulting residue was dissolved in CH₂Cl₂ (10 mL), washed with H₂O (2 × 10 mL), dried (MgSO₄), concentrated and purified by column chromatography (1:1 petroleum ether-EtOAc).

Isothiocyanation procedure: To a solution of azide (450 mg, 0.45 mmol) in dioxane (~15 mL per mmol of azide), triphenylphosphine (1.1 eq per mol of azide) and CS₂ (10 eq per mol of azide) were added. The reaction mixture was stirred at room temperature under Ar for 16 h, then concentrated and the residue was purified by column chromatography using 1:1 petroleum ether-EtOAc as eluent.

Amine-isothiocyanate coupling reaction procedure: To a mixture of **24** in pyridine (~10 mL per mmol of **24**), Et₃N was added (1.1 eq) and stirred at room temperature until it was completely dissolved. A solution of isothiocyanate glycodendron⁴ (1.1 eq) in pyridine (~10 mL per mmol of isothiocyanate) was then added and the resulting solution

was stirred at room temperature for 48 h. CH_2Cl_2 was added (5 mL) and the organic phase was washed with cold H_2O (5 mL) and H_2SO_4 2 N, dried (MgSO_4), filtered and concentrated. The residue was purified by column chromatography, using EtOAc \rightarrow 45:5:3 EtOAc-EtOH- H_2O as eluent, to give the corresponding hemiacetylated adduct.

Preparation of the isothiocyanate-armed triantennated homoglycodendrons **6** and **9**.

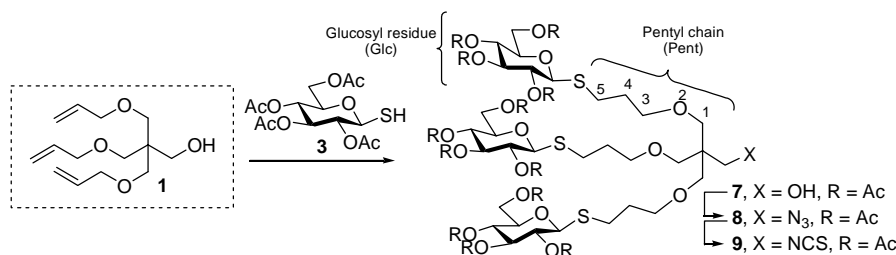


2,2,2-Tris[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethanol (4**).** Compound **4** was obtained from **1** (0.32 g, 1.3 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio- α -D-mannopyranose **2** (2.12 g, 5.85 mmol) by UV-irradiation following the radical addition procedure above described in the general methods. Yield: 1.23 g (70%); $R_f = 0.32$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = +84.6$ (c 1.0 in CH_2Cl_2); $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 5.32$ (dd, 3 H, $J_{2,3} = 3.1$ Hz, $J_{1,2} = 1.5$ Hz, H-2_{Man}), 5.30 (t, 3 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4_{Man}), 5.25 (dd, 3 H, H-3_{Man}), 5.24 (d, 3 H, H-1_{Man}), 4.36 (ddd, 3 H, $J_{5,6a} = 5.4$ Hz, $J_{5,6b} = 1.8$ Hz, H-5_{Man}), 4.30 (dd, 3 H, $J_{6a,6b} = 11.7$ Hz, H-6a), 4.07 (dd, 3 H, H-6b_{Man}), 3.63 (s, 2 H, CH_2OH), 3.46 (t, 6 H, $^3J_{\text{H,H}} = 6.4$ Hz, H-3_{Pent}), 3.39 (s, 6 H, H-1_{Pent}), 2.69, 2.66 (2 dt, 6 H, $^2J_{\text{H,H}} = 13.3$ Hz, $^3J_{\text{H,H}} = 6.4$ Hz, H-5_{Pent}), 2.15, 2.07, 2.04, 1.97 (4 s, 36 H, MeCO), 1.87 (m, 6 H, H-4_{Pent}); $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3): $\delta = 170.5, 170.0, 169.7, 169.6$ (CO), 82.6 (C-1_{Man}), 71.1 (C-2_{Man}, C-1_{Pent}), 69.6 (C-3_{Pent}), 69.4 (C-3_{Man}), 69.0 (C-5_{Man}), 66.3 (C-4_{Man}), 65.0 (CH_2OH), 62.3 (C-6_{Man}), 44.9 (C_q), 29.6 (C-4_{Pent}), 28.2 (C-5_{Pent}), 20.6-20.5 (MeCO); FABMS: m/z 1371 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{56}\text{H}_{84}\text{O}_{31}\text{S}_3$: C 49.84, H 6.28. Found: C 49.99, H 5.92.

2,2,2-Tris[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl azide (5**).** Compound **5** was obtained by reaction of **4** (0.49 g, 0.36 mmol) by the azide displacement procedure above described in the general methods. Yield: 0.42 g (86%); $R_f = 0.40$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = +83.2$ (c 0.7 in CH_2Cl_2); IR (KBr): $\nu_{\text{max}} = 2104$ cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.33$ (dd, 3 H, $J_{2,3} = 3.3$ Hz, $J_{1,2} = 1.5$ Hz, H-2_{Man}), 5.30 (t, 3 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.24 (bs, 3 H, H-1_{Man}), 5.23 (dd, 3 H, H-3_{Man}), 4.36 (ddd, 3 H, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 2.2$ Hz, H-5_{Man}), 4.29 (dd, 3 H, $J_{6a,6b} = 12.1$ Hz, H-6a_{Man}), 4.08 (dd, 3 H, H-6b_{Man}), 3.45 (t, 6 H, $^3J_{\text{H,H}} = 5.9$ Hz, H-3_{Pent}), 3.30 (s, 8 H, CH_2N_3 , H-1_{Pent}), 2.70, 2.65 (2 dt, 6 H, $^2J_{\text{H,H}} = 13.2$ Hz, $^3J_{\text{H,H}} = 6.3$ Hz, H-5_{Pent}), 2.15-1.97 (4 s, 36 H, MeCO), 1.87 (m, 6 H, H-4_{Pent}); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3): $\delta = 170.4, 169.8, 169.6, 169.5$ (CO), 82.6 (C-1_{Man}), 71.1 (C-2_{Man}), 69.6 (C-1_{Pent}), 69.4 (C-3_{Pent}, C-3_{Man}), 68.9 (C-5_{Man}), 66.3 (C-4_{Man}), 62.4 (C-6_{Man}), 51.9 (CH_2N_3), 45.3 (C_q), 29.5 (C-4_{Pent}), 27.3 (C-5_{Pent}), 20.8, 20.6, 20.5, 20.4 (MeCO); FABMS m/z 1396 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{56}\text{H}_{83}\text{O}_{30}\text{N}_3\text{S}_3$: C, 48.93, H, 6.09, N, 3.06; Found: C, 48.63, H, 5.74, N, 2.92.

2,2,2-Tris[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl isothiocyanate (6**).** Compound **6** was obtained by isothiocyanation of azide **5** (0.15 g, 0.11 mmol) with TPP (32 mg, 0.12 mmol) and CS_2 (0.1 mL, 1.1 mmol) following the procedure above described in the general methods. Yield: 0.13 g (85%); $R_f = 0.23$ (1:1 EtOAc-hexane); $[\alpha]_D = +61.9$ (c 0.4 in CH_2Cl_2); IR (KBr): $\nu_{\text{max}} = 2105$ cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.33$ (dd, 3

H, $J_{2,3} = 3.3$ Hz, $J_{1,2} = 1.5$ Hz, H-2_{Man}), 5.31 (t, 3 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4_{Man}), 5.25 (bs, 3 H, H-1_{Man}), 5.24 (dd, 3 H, H-3_{Man}), 4.37 (ddd, 3 H, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 2.3$ Hz, H-5_{Man}), 4.32 (dd, 3 H, $J_{6a,6b} = 12.2$ Hz, H-6a_{Man}), 4.09 (dd, 3 H, H-6b_{Man}), 3.55 (s, 2 H, CH₂NCS), 3.48 (t, 6 H, $^3J_{H,H} = 5.9$ Hz, H-3_{Pent}), 3.35 (s, 6 H, H-1_{Pent}), 2.71, 2.65 (2 dt, 6 H, $^2J_{H,H} = 13.2$ Hz, $^3J_{H,H} = 6.3$ Hz, H-5_{Pent}), 2.16-1.98 (4 s, 36 H, MeCO), 1.88 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): $\delta = 170.9, 170.4, 169.8, 169.6$ (CO), 131.0 (NCS), 82.6 (C-1_{Man}), 71.4 (C-2_{Man}), 69.7 (C-3_{Pent}), 69.6 (C-1_{Pent}), 69.4 (C-3_{Man}), 69.0 (C-5_{Man}), 66.3 (C-4_{Man}), 62.3 (C-6_{Man}), 45.8, 45.3 (CH₂NCS, C_q), 29.4 (C-4_{Pent}), 28.2 (C-5_{Pent}), 20.8, 20.6, 20.5, 20.4 (MeCO); FABMS: m/z 1412 [M + Na]⁺. Anal. Calcd. for C₅₇H₈₃NO₃₀S₄: C 49.23, H 6.02, N 1.01. Found: C 48.99, H 5.96, N 1.03.



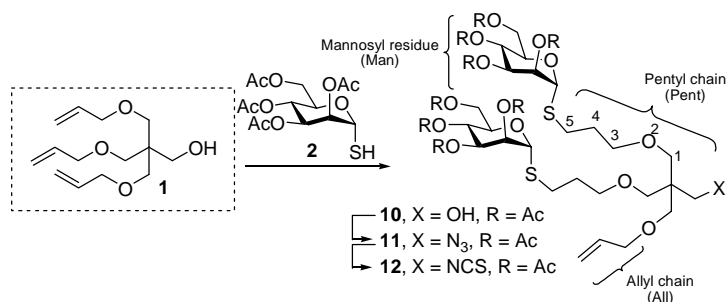
2,2,2-Tris[5-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]ethanol (7). Compound **7** was obtained from **1** (0.32 g, 1.3 mmol) and 2,3,4,6-tetra-O-acetyl-1-thio- β -D-glucopyranose **3** (2.12 g, 5.85 mmol) by UV-irradiation following the radical addition procedure above described in the general methods. Yield: 1.51 g (86%); $R_f = 0.24$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = -22.8$ (c 0.8 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): $\delta = 5.18$ (t, 3 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3_{Glc}), 5.04 (t, 3 H, $J_{4,5} = 9.4$ Hz, H-4_{Glc}), 4.98 (t, 3 H, $J_{1,2} = 9.4$ Hz, H-2_{Glc}), 4.46 (d, 3 H, H-1_{Glc}), 4.21 (dd, 3 H, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 4.8$ Hz, H-6a_{Glc}), 4.09 (dd, 3 H, $J_{5,6b} = 1.7$ Hz, H-6b_{Glc}), 3.68 (ddd, 3 H, H-5_{Glc}), 3.61 (s, 2 H, CH₂OH), 3.42 (t, 6 H, $^3J_{H,H} = 5.8$ Hz, H-3_{Pent}), 3.36 (s, 6 H, H-1_{Pent}), 2.71, 2.67 (2 dt, 6 H, $^2J_{H,H} = 12.8$ Hz, $^3J_{H,H} = 6.0$ Hz, H-5_{Pent}), 2.04-1.99 (4 s, 36 H, MeCO), 1.81 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): $\delta = 170.6, 170.2, 169.5, 169.4$ (CO), 83.7 (C-1_{Glc}), 75.8 (C-5_{Glc}), 73.8 (C-3_{Glc}), 71.2 (C-1_{Pent}), 69.8 (C-2_{Glc}), 69.6 (C-3_{Pent}), 68.2 (C-4_{Glc}), 65.4 (CH₂OH), 62.1 (C-6_{Glc}), 44.9 (C_q), 29.8 (C-4_{Pent}), 27.0 (C-5_{Pent}), 20.8, 20.6 (MeCO); FABMS: m/z 1371 [M + Na]⁺. Anal. Calcd. for C₅₆H₈₄O₃₁S₃: C 49.84, H 6.28. Found: C 49.75, H 6.17.

2,2,2-Tris[5-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]ethyl azide (8). Compound **8** was obtained by reaction of **7** (0.62 g, 0.50 mmol) by the azide displacement procedure above described in the general methods. Yield: 0.58g (85%); $R_f = 0.38$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = -25.0$ (c 1.0 in CH₂Cl₂); IR (KBr): $\nu_{max} = 2103$ cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 5.19$ (t, 3 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3_{Glc}), 5.04 (t, 3 H, $J_{4,5} = 9.4$ Hz, H-4_{Glc}), 4.99 (t, 3 H, $J_{1,2} = 9.4$ Hz, H-2_{Glc}), 4.47 (d, 3 H, H-1_{Glc}), 4.20 (dd, 3 H, $J_{6a,6b} = 12.3$ Hz, $J_{5,6a} = 4.8$ Hz, H-6a_{Glc}), 4.09 (dd, 3 H, $J_{5,6b} = 2.1$ Hz, H-6b_{Glc}), 3.67 (ddd, 3 H, H-5_{Glc}), 3.42 (t, 6 H, $^3J_{H,H} = 6.0$ Hz, H-3_{Pent}), 3.27 (s, 6 H, H-1_{Pent}), 3.26 (s, 2 H, CH₂N₃), 2.72, 2.67 (2 dt, 6 H, $^2J_{H,H} = 12.8$ Hz, $^3J_{H,H} = 7.3$ Hz, H-5_{Pent}), 2.04-2.00 (4 s, 36 H, MeCO), 1.82 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): $\delta = 170.6, 170.1, 169.4, 169.3$ (CO), 83.8 (C-1_{Glc}), 75.8 (C-5_{Glc}), 73.9 (C-3_{Glc}), 69.9 (C-2_{Glc}), 69.6 (C-3_{Pent}, C-1_{Pent}), 68.3 (C-4_{Glc}), 62.1 (C-6_{Glc}), 52.0 (CH₂N₃), 45.4 (C_q), 29.8 (C-4_{Pent}), 27.1 (C-5_{Pent}), 20.7, 20.6, 20.5 (MeCO); FABMS m/z 1396 [M + Na]⁺. Anal. Calcd. for C₅₆H₈₃O₃₀N₃S₃: C 48.93, H 6.09, N 3.06. Found: C 48.78, H 6.05, N 2.83.

2,2,2-Tris[5-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]ethyl isothiocyanate (9). Compound **9** was obtained by isothiocyanation of azide **8** (0.32 g, 0.23 mmol) with TPP (67.1 mg, 0.26 mmol) and CS₂ (0.15 mL, 2.33 mmol) following the procedure above described in the general methods. Yield: 0.26 g (80%); $R_f = 0.50$ (2:1

EtOAc-hexane); $[\alpha]_D = -25.9$ (*c* 1.0 in CH_2Cl_2); IR: $\nu_{\text{max}} = 2104 \text{ cm}^{-1}$; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.19$ (t, 3 H, $J_{2,3} = J_{3,4} = 9.4 \text{ Hz}$, H-3_{Glc}), 5.05 (t, 3 H, $J_{4,5} = 9.4 \text{ Hz}$, H-4_{Glc}), 4.99 (t, 3 H, $J_{1,2} = 9.4 \text{ Hz}$, H-2_{Glc}), 4.48 (d, 3 H, H-1_{Glc}), 4.21 (dd, 3 H, $J_{6a,6b} = 12.3 \text{ Hz}$, $J_{5,6a} = 4.8 \text{ Hz}$, H-6a_{Glc}), 4.11 (dd, 3 H, $J_{5,6b} = 2.2 \text{ Hz}$, H-6b_{Glc}), 3.69 (ddd, 3 H, H-5_{Glc}), 3.54 (s, 2 H, CH_2NCS), 3.44 (t, 6 H, $^3J_{\text{H,H}} = 6.3 \text{ Hz}$, H-3_{Pent}), 3.32 (s, 6 H, H-1_{Pent}), 2.73, 2.69 (2 dt, 6 H, $^2J_{\text{H,H}} = 12.6 \text{ Hz}$, $^3J_{\text{H,H}} = 5.6 \text{ Hz}$, H-5_{Pent}), 2.04-2.00 (4 s, 36 H, MeCO), 1.83 (m, 6 H, H-4_{Pent}); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3): $\delta = 170.6, 170.1, 169.4, 169.3$ (CO), 134.0 (NCS), 83.9 (C-1_{Glc}), 75.9 (C-5_{Glc}), 73.9 (C-3_{Glc}), 70.0 (C-2_{Glc}), 69.9 (C-3_{Pent}), 69.8 (C-1_{Pent}), 68.3 (C-4_{Glc}), 62.1 (C-6_{Glc}), 45.9 (CH_2NCS), 45.7 (C_q), 29.8 (C-4_{Pent}), 27.0 (C-5_{Pent}), 20.7, 20.6, 20.5 (MeCO); FABMS: m/z 1412 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{57}\text{H}_{88}\text{NO}_{30}\text{S}_4$: C 49.23, H 6.02, N 1.01. Found: C 49.24, H 5.81, N 1.02.

Preparation of the isothiocyanate-armed divalent ligand 12.



2-(2-Oxapent-4-enyl)-2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethanol (10).

Compound **10** was obtained from **1**⁷ (0.2 g, 0.78 mmol) and 1-thiosugar **2** (0.85 g, 2.34 mmol) by UV-irradiation following the radical addition procedure above described in the general methods. Yield: 0.55 g (72%); $R_f = 0.50$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = +20.2$ (*c* 0.8 in CH_2Cl_2); $^1\text{H RMN}$ (500 MHz, CDCl_3): $\delta = 5.85$ (ddt, 1 H, $^3J_{\text{H,H}} = 15.9 \text{ Hz}$, $^3J_{\text{H,H}} = 10.5 \text{ Hz}$, $^3J_{\text{H,H}} = 5.5 \text{ Hz}$, $\text{OCH}_2\text{CH}=\text{}$), 5.32 (dd, 2 H, $J_{2,3} = 3.3 \text{ Hz}$, $J_{1,2} = 1.5 \text{ Hz}$, H-2_{Man}), 5.27 (t, 2 H, $J_{3,4} = J_{4,5} = 9.8 \text{ Hz}$, H-4_{Man}), 5.25 (sa, 2 H, H-1_{Man}), 5.24 (dd, 2 H, H-3_{Man}), 5.22 (dd, 1 H, $^2J_{\text{H,H}} = 1.7 \text{ Hz}$, =CH_a), 5.15 (dq, 1 H, $^4J_{\text{H,H}} = 1.7 \text{ Hz}$, =CH_b), 4.36 (ddd, 2 H, $J_{5,6a} = 5.2 \text{ Hz}$, $J_{5,6b} = 2.3 \text{ Hz}$, H-5_{Man}), 4.29 (dd, 2 H, $J_{6a,6b} = 12.1 \text{ Hz}$, H-6a_{Man}), 4.08 (dd, 2 H, H-6b_{Man}), 3.94 (dt, 2 H, $\text{OCH}_2\text{CH}=\text{}$), 3.66 (s, 2 H, CH_2OH), 3.47 (t, 4 H, $^3J_{\text{H,H}} = 6.0 \text{ Hz}$, H-3_{Pent}), 3.43 (s, 2 H, CH_2OAll), 3.42 (s, 4 H, H-1_{Pent}), 2.70, 2.67 (2 dt, 4 H, $^3J_{\text{H,H}} = 11.0 \text{ Hz}$, $^2J_{\text{H,H}} = 6.4 \text{ Hz}$, H-5_{Pent}), 2.04, 1.97, 2.15, 2.08 (4 s, 24 H, MeCO), 1.87 (m, 4 H, H-4_{Pent}); $^{13}\text{C RMN}$ (75.5 MHz, CDCl_3): $\delta = 170.4, 169.8, 169.6, 169.5$ (CO), 134.5 ($\text{CH}_2\text{CH}=\text{}$), 116.6 (=CH₂), 82.5 (C-1_{Man}), 72.2 ($\text{CH}_2\text{CH}=\text{}$), 71.0 (C-2_{Man}), 70.9 (C-1_{Pent}), 70.6 (CH_2OAll), 69.4 (C-3_{Pent}), 69.3 (C-3_{Man}), 68.9 (C-5_{Man}), 66.1 (C-4_{Man}), 65.5 (CH_2OH), 62.2 (C-6_{Man}), 44.7 (C_q), 29.3 (C-4_{Pent}), 28.1 (C-5_{Pent}), 20.7-20.4 (MeCO); FABMS: m/z 1007 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{42}\text{H}_{64}\text{O}_{22}\text{S}_2$: C 51.20, H 6.55. Found: C 50.95, H 6.23.

2-(2-Oxapent-4-enyl)-2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl- β -D-mannopyranosylthio)-2-oxapentyl]ethyl azide (11).

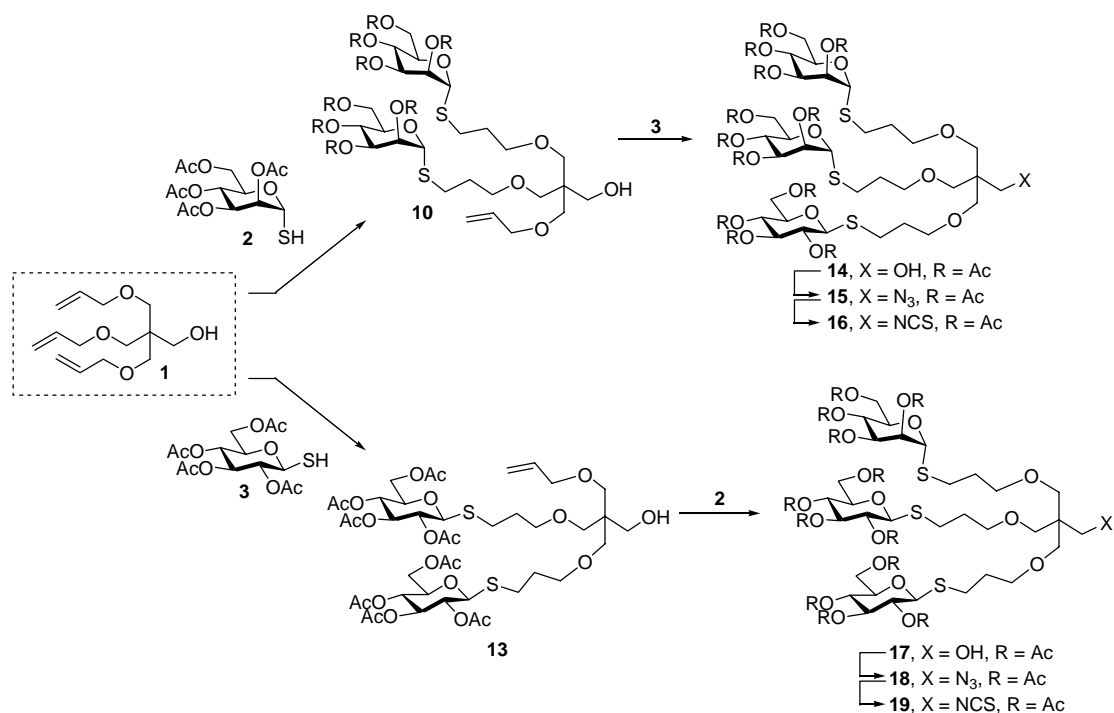
Compound **11** was obtained by reaction of **10** (544 mg, 0.55 mmol) by the azide displacement procedure above described in the general methods. Yield: 453.4 mg (80%); $R_f = 0.67$ (1:2 petroleum ether-EtOAc); $[\alpha]_D = +55.0$ (*c* 1.0 in CH_2Cl_2); IR (KBr): $\nu_{\text{max}} = 2103 \text{ cm}^{-1}$; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.85$ (ddt, 1 H, $^3J_{\text{H,H}} = 17.2 \text{ Hz}$, $^3J_{\text{H,H}} = 10.5 \text{ Hz}$, $^3J_{\text{H,H}} = 5.5 \text{ Hz}$, $\text{OCH}_2\text{CH}=\text{}$), 5.33 (dd, 2 H, $J_{2,3} = 3.5 \text{ Hz}$, $J_{1,2} = 1.5 \text{ Hz}$, H-2_{Man}), 5.29 (t, 2 H, H-4_{Man}), 5.25 (dd, 2 H, $J_{3,4} = 9.9 \text{ Hz}$, H-3_{Man}), 5.24 (d, 2 H, H-1_{Man}), 5.24 (bd, 1H, =CH_a), 5.15 (bd, 1 H, =CH_b), 4.37 (ddd, 2 H, $J_{4,5} = 9.5 \text{ Hz}$, H-5_{Man}), 4.30 (dd, 2 H, $J_{5,6a} = 5.3 \text{ Hz}$, H-6a_{Man}), 4.07 (dd, 2 H, $J_{6a,6b} = 12.2 \text{ Hz}$, $J_{5,6b} = 2.3 \text{ Hz}$, H-6b_{Man}), 3.93 (dt, 2 H, $^4J_{\text{H,H}} = 1.4 \text{ Hz}$, $\text{OCH}_2\text{CH}=\text{}$), 3.46 (t, 4 H, $^3J_{\text{H,H}} = 6.0 \text{ Hz}$, H-3_{Pent}), 3.33 (s, 6 H, H-1_{Pent}, CH_2OAll), 3.32 (s, 2 H, CH_2N_3), 2.67, 2.65 (2 dt, 4 H, $^2J_{\text{H,H}} = 13.4 \text{ Hz}$, $^3J_{\text{H,H}} = 7.3 \text{ Hz}$, H-5_{Pent}), 2.15, 2.08, 2.03, 1.98 (4 s, 24 H,

MeCO), 1.87 (m, 4 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.5-169.6 (CO), 134.8 (CH₂CH=), 116.6 (=CH₂), 82.7 (C-1_{Man}), 72.3 (CH₂CH=), 71.2 (C-2_{Man}), 69.6 (CH₂OAll, C-1_{Pent}), 69.4 (C-3_{Pent}), 69.3 (C-3_{Man}), 69.0 (C-5_{Man}), 66.3 (C-4_{Man}), 62.4 (C-6_{Man}), 52.0 (CH₂N₃), 45.4 (C_q), 29.5 (C-4_{Pent}), 28.3 (C-5_{Pent}), 20.9-20.6 (MeCO); FABMS: *m/z* 1032 [M + Na]⁺. Anal. Calcd. for C₄₂H₆₃N₃O₂₁S₂: C 49.94, H 6.29, N 4.16. Found: C 49.88, H 5.95, N 4.14.

2-(2-Oxapent-4-enyl)-2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl

isothiocyanate (12). Compound **12** was obtained by isothiocyanation of azide **11** (450 mg, 0.45 mmol) with triphenylphosphine (129.5 mg, 0.49 mmol) and CS₂ (0.27 mL, 4.5 mmol) following the procedure above described in the general methods. Yield: 283 mg (61%); *R_f* = 0.29 (1:1 petroleum ether-EtOAc); [α]_D = +20.5 (*c* 0.3 in CH₂Cl₂); IR: ν_{\max} = 2205, 2101 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.84 (ddt, 1 H, ³*J*_{H,H} = 17.3 Hz, ³*J*_{H,H} = 10.5 Hz, ³*J*_{H,H} = 5.0 Hz, OCH₂CH=), 5.32 (dd, 2 H, *J*_{2,3} = 3.3 Hz, *J*_{1,2} = 1.6 Hz, H-2_{Man}), 5.30 (t, 2 H, *J*_{3,4} = *J*_{4,5} = 10.0 Hz, H-4_{Man}), 5.24 (d, 2 H, H-1_{Man}), 5.23 (dd, 2 H, H-3_{Man}), 5.22 (dq, 1 H, ⁴*J*_{H,H} = ²*J*_{H,H} = 1.7 Hz, =CH_a), 5.16 (dq, 1 H, ⁴*J*_{H,H} = 1.7 Hz, =CH_b), 4.36 (ddd, 2 H, *J*_{5,6a} = 5.2 Hz, *J*_{5,6b} = 2.3 Hz, H-5_{Man}), 4.30 (dd, 2 H, *J*_{6a,6b} = 12.2 Hz, H-6a_{Man}), 4.07 (dd, 2 H, H-6b_{Man}), 3.93 (dt, 2 H, OCH₂CH=), 3.56 (s, 2 H, CH₂NCS), 3.47 (t, 4 H, ³*J*_{H,H} = 5.9 Hz, H-3_{Pent}), 3.36 (s, 6 H, H-1_{Pent}, CH₂OAll), 2.70, 2.66 (2 dt, 4 H, ²*J*_{H,H} = 13.3 Hz, ³*J*_{H,H} = 6.9 Hz, H-5_{Pent}), 2.15, 2.08, 2.03, 1.97 (4 s, 24 H, MeCO), 1.99 (m, 4 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.4-169.6 (CO), 134.5 (CH₂CH=), 132.0 (NCS), 116.8 (=CH₂), 82.7 (C-1_{Man}), 72.3 (CH₂CH=), 71.1 (C-2_{Man}), 69.5 (CH₂OAll, C-1_{Pent}), 69.4 (C-3_{Pent}), 69.3 (C-3_{Man}), 68.9 (C-5_{Man}), 66.3 (C-4_{Man}), 62.4 (C-6_{Man}), 45.6 (C_q, CH₂NCS), 28.2 (C-4_{Pent}), 27.0 (C-5_{Pent}), 20.8-20.5 (MeCO); FABMS: *m/z* 1098 [M + Na]⁺. Anal. Calcd. for C₄₃H₆₃NO₂₁S₃: C 50.33, H 6.19, N 1.36. Found: C 50.27, H 5.98, N 1.31.

Preparation of the isothiocyanate-armed triantennated α -Mannose- β -Glucose heteroglycodendrons **16** and **19**.



2-[5-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]-2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethanol (14**).** Compound **14** was obtained from **10** (0.16 g, 0.25 mmol) and 1-

thio-sugar **2** (0.28 g, 0.75 mmol) by UV-irradiation following the radical addition procedure above described in the general methods. The compound was purified by column chromatography using 1:3 petroleum ether-EtOAc as eluent. Yield 0.23 g (68%); $R_f = 0.21$ (1:2 petroleum ether-EtOAc), $[\alpha]_D = +29.4$ (c 0.6 in CH_2Cl_2); $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.32$ (dd, 2 H, $J_{2,3} = 3.4$ Hz, $J_{1,2} = 1.5$ Hz, H-2_{Man}), 5.30 (t, 2 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4_{Man}), 5.24 (bs, 2 H, H-1_{Man}), 5.23 (dd, 2 H, H-3_{Man}), 5.21 (t, 1 H, H-3_{Glc}), 5.03 (t, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4_{Glc}), 4.98 (t, 1 H, $J_{1,2} = J_{2,3} = 10.1$ Hz, H-2_{Glc}), 4.46 (d, 1 H, H-1_{Glc}), 4.32 (ddd, 2 H, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 2.4$ Hz, H-5_{Man}), 4.26 (dd, 2 H, $J_{6a,6b} = 12.4$ Hz, H-6a_{Man}), 4.20 (dd, 1 H, $J_{6a,6b} = 12.2$ Hz, $J_{5,6a} = 4.6$ Hz, H-6a_{Glc}), 4.08 (dd, 1 H, $J_{5,6b} = 2.2$ Hz, H-6b_{Glc}), 4.04 (dd, 2 H, H-6b_{Man}), 3.69 (ddd, 1 H, H-5_{Glc}), 3.60 (s, 2 H, CH_2OH), 3.46, 3.45 (2 t, 6 H, $^3J_{\text{H,H}} = 5.9$ Hz, H-3_{Pent}), 3.36 (s, 6 H, H-1_{Pent}), 2.67, 2.63 (2 dt, 6 H, $^2J_{\text{H,H}} = 13.3$ Hz, $^3J_{\text{H,H}} = 6.9$ Hz, H-5_{Pent}), 2.05-1.93 (8 s, 36 H, MeCO), 1.83 (m, 6 H, H-4_{Pent}); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3): $\delta = 171.4$ -169.1 (CO), 83.6 (C-1_{Glc}), 82.6 (C-1_{Man}), 75.7 (C-5_{Glc}), 73.8 (C-3_{Glc}), 71.1 (C-2_{Man}), 69.9 (C-1_{Pent}), 69.8 (C-2_{Glc}), 69.5 (C-3_{Pent}), 69.4 (C-3_{Man}), 68.9 (C-5_{Man}), 68.3 (C-4_{Glc}), 67.9 (C-4_{Man}), 65.2 (CH_2OH), 62.3 (C-6_{Man}), 62.0 (C-6_{Glc}), 44.9 (C_q), 29.3 (C-4_{Pent}), 28.1 (C-5_{Pent}), 20.8-20.5 (MeCO); FABMS: m/z 1371 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{56}\text{H}_{84}\text{O}_{31}\text{S}_3$: C 49.84, H 6.28. Found: C 49.67, H 6.09.

2-[5-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]-2,2-bis[5-(2,3,4,6-tetra-O-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl azide (15**).** Compound **15** was obtained by reaction of **14** (0.44 g, 0.33 mmol) by the azide displacement procedure above described in the general methods. Yield: 0.36 g (79%); $R_f = 0.37$ (2:1 EtOAc-petroleum ether), $[\alpha]_D = +45.3$ (c 1.0 in CH_2Cl_2); IR (KBr): $\nu_{\text{max}} = 2103$ cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.33$ (dd, 2 H, $J_{2,3} = 3.3$ Hz, $J_{1,2} = 1.5$ Hz, H-2_{Man}), 5.31 (t, 2 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4_{Man}), 5.25 (bs, 2 H, H-1_{Man}), 5.24 (dd, 2 H, H-3_{Man}), 5.22 (t, 1 H, $J_{3,4} = J_{2,3} = 9.9$ Hz, H-3_{Glc}), 5.07 (t, 1 H, $J_{4,5} = 9.4$ Hz, H-4_{Glc}), 5.02 (t, 1 H, $J_{1,2} = 10.1$ Hz, H-2_{Glc}), 4.49 (d, 1 H, H-1_{Glc}), 4.37 (ddd, 2 H, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 2.3$ Hz, H-5_{Man}), 4.31 (dd, 2 H, $J_{6a,6b} = 12.2$ Hz, H-6a_{Man}), 4.23 (dd, 1 H, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 4.9$ Hz, H-6a_{Glc}), 4.12 (dd, 1 H, $J_{5,6b} = 2.2$ Hz, H-6b_{Glc}), 4.08 (dd, 2 H, H-6b_{Man}), 3.71 (ddd, 1 H, H-5_{Glc}), 3.46, 3.45 (2 t, 6 H, $^3J_{\text{H,H}} = 5.9$ Hz, H-3_{Pent}), 3.30 (s, 8 H, CH_2N_3 , H-1_{Pent}), 2.70, 2.66 (2 dt, 6 H, $^2J_{\text{H,H}} = 13.3$ Hz, $^3J_{\text{H,H}} = 6.9$ Hz, H-5_{Pent}), 2.16-1.98 (8 s, 36 H, MeCO), 1.86 (m, 6 H, H-4_{Pent}); $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3): $\delta = 170.3$ -169.1 (CO), 83.6 (C-1_{Glc}), 82.5 (C-1_{Man}), 75.6 (C-5_{Glc}), 73.7 (C-3_{Glc}), 71.0 (C-2_{Man}), 69.7 (C-2_{Glc}), 69.4 (C-3_{Pent}), 69.3 (C-3_{Man}), 69.3 (C-1_{Pent}), 68.8 (C-5_{Man}), 68.2 (C-4_{Glc}), 66.1 (C-4_{Man}), 62.2 (C-6_{Man}), 62.0 (C-6_{Glc}), 51.8 (CH_2N_3), 45.2 (C_q), 29.3 (C-4_{Pent}), 28.0 (C-5_{Pent}), 20.7-20.4 (MeCO); FABMS: m/z 1396 $[\text{M} + \text{Na}]^+$. Anal. Calcd. for $\text{C}_{56}\text{H}_{83}\text{O}_{30}\text{N}_3\text{S}_3$: C 48.93, H 6.09, N 3.06. Found: C 48.94, H 6.02, N 3.10.

2-[5-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]-2,2-bis[5-(2,3,4,6-tetra-O-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl isothiocyanate (16**).** Compound **16** was obtained by isothiocyanation of azide **15** (131 mg, 0.095 mmol) with TPP (28 mg, 0.10 mmol) and CS_2 (60 μL , 0.95 mmol) following the procedure above described in the general methods. Yield: 95 mg (72%); $R_f = 0.50$ (2:1 EtOAc-hexane); $[\alpha]_D = +40.8$ (c 1.0 in CH_2Cl_2); IR (KBr): $\nu_{\text{max}} = 2104$ cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.31$ (dd, 2 H, $J_{2,3} = 3.5$ Hz, $J_{1,2} = 1.6$ Hz, H-2_{Man}), 5.29 (t, 2 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4_{Man}), 5.24 (bs, 2 H, H-1_{Man}), 5.22 (dd, 2 H, H-3_{Man}), 5.20 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3_{Glc}), 5.05 (t, 1 H, $J_{4,5} = 9.9$ Hz, H-4_{Glc}), 5.00 (dd, 1 H, $J_{1,2} = 10.1$ Hz, H-2_{Glc}), 4.48 (d, 1 H, H-1_{Glc}), 4.35 (ddd, 2 H, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 2.3$ Hz, H-5_{Man}), 4.29 (dd, 2 H, $J_{6a,6b} = 12.3$ Hz, H-6a_{Man}), 4.21 (dd, 1 H, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 4.9$ Hz, H-6a_{Glc}), 4.10 (dd, 1 H, $J_{5,6b} = 2.3$ Hz, H-6b_{Glc}), 4.07 (dd, 2 H, H-6b_{Man}), 3.70 (ddd, 1 H, H-5_{Glc}), 3.53 (s, 2 H, CH_2NCS), 3.46, 3.45 (2 t, 6 H, $^3J_{\text{H,H}} = 5.9$ Hz, H-3_{Pent}), 3.33 (s, 6 H, H-1_{Pent}), 2.69, 2.65 (2 dt, 6 H, $^2J_{\text{H,H}} = 13.3$ Hz, $^3J_{\text{H,H}} = 7.0$ Hz, H-5_{Pent}), 2.14-1.96 (8 s, 36 H, MeCO), 1.86 (m, 6 H, H-4_{Pent}); $^{13}\text{C RMN}$ (125.7 MHz, CDCl_3): $\delta = 170.4$ -169.2 (CO), 130.4 (NCS), 83.7 (C-1_{Glc}), 82.6 (C-1_{Man}), 75.8 (C-5_{Glc}), 73.8 (C-3_{Glc}), 71.1 (C-2_{Man}), 69.8 (C-2_{Glc}), 69.6 (C-3_{Pent}), 69.5 (C-1_{Pent}), 69.4 (C-3_{Man}), 69.0 (C-5_{Man}), 68.3 (C-4_{Glc}), 66.2 (C-4_{Man}), 62.3 (C-6_{Man}),

62.1 (C-6_{Glc}), 45.8 (CH₂NCS), 45.6 (C_q), 29.4 (C-4_{Pent}), 28.2 (C-5_{Pent}), 20.9-20.5 (MeCO); FABMS: *m/z* 1412 [M + Na]⁺. Anal. Calcd. for C₅₇H₈₃NO₃₀S₄: C 49.23, H 6.01, N 1.00. Found: C 49.09, H 6.05, N 0.90.

2-(2-Oxapent-4-enyl)-2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)-2-oxapentyl] ethanol (13). A solution of **11** (0.20 g, 0.78 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose **3** (0.85 g, 2.34 mmol) in degassed MeOH (15 mL), was irradiated at 250 nm under Ar for 6 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography using 2:3 petroleum ether-EtOAc as eluent. Yield: 0.58 g (76%); *R_f* = 0.26 (2:3 petroleum ether-EtOAc); [α]_D = -26.6 (*c* 0.8 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 5.83 (ddt, 1 H, ³*J*_{H,H} = 17.2 Hz, ³*J*_{H,H} = 10.5 Hz, ³*J*_{H,H} = 5.1 Hz, OCH₂CH=), 5.21 (dd, 1 H, ²*J*_{H,H} = 1.1 Hz, =CH_a), 5.16 (t, 2 H, *J*_{2,3} = *J*_{3,4} = 9.5 Hz, H-3_{Glc}), 5.13 (dd, 1 H, =CH_b), 5.04 (t, 2 H, *J*_{4,5} = 9.5 Hz, H-4_{Glc}), 4.98 (t, 2 H, *J*_{1,2} = 9.5 Hz, H-2_{Glc}), 4.45 (d, 2 H, H-1_{Glc}), 4.20 (dd, 2 H, *J*_{6a,6b} = 12.4 Hz, *J*_{5,6a} = 4.9 Hz, H-6a_{Glc}), 4.08 (dd, 2 H, *J*_{5,6b} = 2.0 Hz, H-6b_{Glc}), 3.91 (d, 2 H, OCH₂CH=), 3.68 (ddd, 2 H, H-5_{Glc}), 3.63 (s, 2 H, CH₂OH), 3.43 (t, 4 H, ³*J*_{H,H} = 5.9 Hz, H-3_{Pent}), 3.39 (s, 2 H, CH₂OAll), 3.37 (s, 4 H, H-1_{Pent}), 2.73, 2.66 (2 dt, 4 H, ²*J*_{H,H} = 13.1 Hz, ³*J*_{H,H} = 7.3 Hz, H-5_{Pent}), 2.04-1.99 (4 s, 24 H, MeCO), 1.81 (m, 4 H, m, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.7, 170.2, 169.5, 169.4 (CO), 134.7 (OCH₂CH=), 116.8 (=CH₂), 83.8 (C-1), 75.8 (C-5), 73.8 (C-3), 72.4 (OCH₂CH=), 71.2, 70.7 (C-1_{Pent}), 69.8 (C-2), 69.6 (C-3_{Pent}), 68.2 (C-4), 65.7 (CH₂OH), 62.1 (C-6), 44.8 (C_q), 29.8 (C-4_{Pent}), 27.0 (C-5_{Pent}), 20.8, 20.6 (MeCO); FABMS: *m/z* 1007 [M + Na]⁺. Anal. Calcd. for C₄₂H₆₄O₂₂S₂: C 51.20, H 6.55. Found: C 51.03, H 6.33.

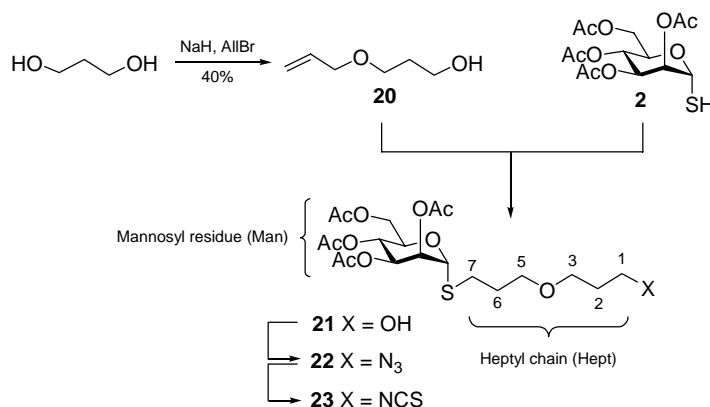
2,2-Bis[5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)-2-oxapentyl]-2-[5-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosylthio)-2-oxapentyl]ethanol (17). A solution of **13** (0.53 g, 0.54 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranose **2** (0.29 g, 0.81 mmol) in degassed MeOH (35 mL) was irradiated at 250 nm under Ar for 6 h. The solvent was removed by distillation and the residue was purified by column chromatography with 1:3 petroleum ether-EtOAc. Yield: 0.55 g (76%); *R_f* = 0.22 (1:1 petroleum ether-EtOAc); [α]_D = +15.5 (*c* 1.0 in CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃): δ = 5.30 (dd, 1 H, *J*_{2,3} = 3.2 Hz, *J*_{1,2} = 1.5 Hz, H-2_{Man}), 5.28 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 10.0 Hz, H-4_{Man}), 5.22 (d, 1 H, H-1_{Man}), 5.21 (dd, 1 H, H-3_{Man}), 5.19 (t, 2 H, *J*_{3,4} = *J*_{2,3} = 10.0 Hz, H-3_{Glc}), 5.04 (t, 2 H, *J*_{4,5} = 10.0 Hz, H-4_{Glc}), 4.47 (d, 2 H, *J*_{1,2} = 10.0 Hz, H-1_{Glc}), 4.99 (t, 2 H, H-2_{Glc}), 4.33 (ddd, 1 H, *J*_{5,6a} = 5.1 Hz, *J*_{5,6b} = 2.1 Hz, H-5_{Man}), 4.27 (dd, 1 H, *J*_{6a,6b} = 12.2 Hz, H-6a_{Man}), 4.20 (dd, 2 H, *J*_{6a,6b} = 12.4 Hz, *J*_{5,6a} = 4.8 Hz, H-6a_{Glc}), 4.08 (dd, 2 H, *J*_{5,6b} = 2.3 Hz, H-6b_{Glc}), 4.06 (dd, 1 H, H-6b_{Man}), 3.69 (ddd, 2 H, H-5_{Glc}), 3.61 (s, 2 H, CH₂OH), 3.44, 3.43 (2 t, 6 H, ³*J*_{H,H} = 5.8 Hz, H-3_{Pent}), 3.37 (s, 6 H, H-1_{Pent}), 2.72, 2.68 (2 dt, 6 H, ²*J*_{H,H} = 12.8 Hz, ³*J*_{H,H} = 5.8 Hz, H-5_{Pent}), 2.06-1.95 (8 s, 36 H, MeCO), 1.85 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 171.0-169.3 (CO), 83.7 (C-1_{Glc}), 82.6 (C-1_{Man}), 75.7 (C-5_{Glc}), 73.8 (C-3_{Glc}), 71.2 (C-2_{Man}), 71.1 (C-1_{Pent}), 69.8 (C-2_{Glc}), 69.6 (C-3_{Pent}), 69.3 (C-3_{Man}), 68.9 (C-5_{Man}), 68.2 (C-4_{Glc}), 66.2 (C-4_{Man}), 65.2 (CH₂OH), 62.3 (C-6_{Man}), 62.0 (C-6_{Glc}), 44.9 (C_q), 29.7 (C-4_{Pent}), 26.9 (C-5_{Pent}), 20.9-20.5 (MeCO); FABMS: *m/z* 1371 [M + Na]⁺. Anal. Calcd. for C₅₆H₈₄O₃₁S₃: C 49.84, H 6.27. Found: C 49.67, H 6.09.

2,2-Bis[5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)-2-oxapentyl]-2-[5-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosylthio)-2-oxapentyl]ethyl azide (18). Compound **18** was obtained by reaction of **17** (0.48 g, 0.36 mmol) by the azide displacement procedure above described in the general methods. Yield: 0.37 g (75%); *R_f* = 0.39 (1:2 petroleum ether-EtOAc); [α]_D = +8.2 (*c* 1.0 in CH₂Cl₂); IR (KBr): ν_{max} = 2104 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.30 (bs, 1 H, *J*_{2,3} = 4.4 Hz, H-2_{Man}), 5.28 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 9.8 Hz, H-4_{Man}), 5.21 (m, 2 H, H-1_{Man}, H-3_{Man}), 5.19 (t, 2 H, *J*_{2,3} = *J*_{3,4} = 9.9 Hz, H-3_{Glc}), 5.05 (t, 2 H, *J*_{4,5} = 9.9 Hz, H-4_{Glc}), 4.99 (t, 2 H, *J*_{1,2} = 10.1 Hz, H-2_{Glc}), 4.47 (d, 2 H, H-1_{Glc}), 4.31 (ddd, 1 H, *J*_{5,6a} = 5.2 Hz, *J*_{5,6b} = 2.2 Hz, H-5_{Man}), 4.28 (dd, 1 H, *J*_{6a,6b} = 12.2 Hz, H-6a_{Man}), 4.21 (dd, 2 H, *J*_{6a,6b} = 12.4 Hz, *J*_{5,6a} = 4.9 Hz, H-6a_{Glc}), 4.10 (dd, 2 H, *J*_{5,6b} = 2.3 Hz, H-6b_{Glc}), 4.06 (dd, 1 H, H-6b_{Man}),

3.69 (ddd, 2 H, H-5_{Glc}), 3.44, 3.43 (2 t, 6 H, ³J_{H,H} = 5.8 Hz, H-3_{Pent}), 3.29 (s, 6 H, H-1_{Pent}), 3.28 (s, 2 H, CH₂N₃), 2.73, 2.69 (2 dt, 6 H, ²J_{H,H} = 13.1 Hz, ³J_{H,H} = 7.4 Hz, H-5_{Pent}), 2.10-1.96 (8 s, 36 H, MeCO), 1.83 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.5-169.2 (CO), 83.8 (C-1_{Glc}), 82.6 (C-1_{Man}), 75.8 (C-5_{Glc}), 73.8 (C-3_{Glc}), 71.1 (C-2_{Man}), 69.8 (C-2_{Glc}), 69.5 (C-3_{Pent}), 69.4 (C-3_{Man}), 69.3 (C-1_{Pent}), 69.0 (C-5_{Man}), 68.3 (C-4_{Glc}), 66.2 (C-4_{Man}), 62.3 (C-6_{Man}), 62.1 (C-6_{Glc}), 51.9 (CH₂N₃), 45.4 (C_q), 29.9 (C-4_{Pent}), 27.0 (C-5_{Pent}), 20.6-20.5 (MeCO); FABMS: *m/z* 1396 [M + Na]⁺. Anal. Calcd. for C₅₆H₈₃O₃₀N₃S₃: C 48.93, H 6.09, N 3.06. Found: C 48.92, H 6.05, N 2.95.

2,2-Bis[5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)-2-oxapentyl]-2-[5-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosylthio)-2-oxapentyl]ethyl isothiocyanate (19): Compound **19** was obtained by isothiocyanation of azide **18** (0.25 g, 0.18 mmol) with TPP (52 mg, 0.20 mmol) and CS₂ (0.11 mL, 1.80 mmol) following the procedure above described in the general methods. Yield: 0.20 g (80%); *R_f* = 0.16 (1:1 EtOAc-hexane); [α]_D = + 9.7 (*c* 1.0 in CH₂Cl₂); IR (KBr): ν_{max} = 2104 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.30 (dd, 1 H, *J*_{2,3} = 3.3 Hz, *J*_{1,2} = 1.4 Hz, H-2_{Man}), 5.28 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 9.5 Hz, H-4_{Man}), 5.21 (m, 2 H, H-1_{Man}, H-3_{Man}), 5.19 (t, 2 H, *J*_{2,3} = *J*_{3,4} = 9.8 Hz, H-3_{Glc}), 5.05 (t, 2 H, *J*_{4,5} = 10.0 Hz, H-4_{Glc}), 4.99 (t, 2 H, H-2_{Glc}), 4.47 (d, 2 H, *J*_{1,2} = 10.1 Hz, H-1_{Glc}), 4.35 (ddd, 1 H, *J*_{5,6a} = 5.4 Hz, *J*_{5,6b} = 2.2 Hz, H-5_{Man}), 4.28 (dd, 1 H, *J*_{6a,6b} = 12.1 Hz, H-6a_{Man}), 4.20 (dd, 2 H, *J*_{6a,6b} = 12.5 Hz, *J*_{5,6a} = 4.8 Hz, H-6a_{Glc}), 4.10 (dd, 2 H, *J*_{5,6b} = 2.4 Hz, H-6b_{Glc}), 4.06 (1 H, dd, H-6b_{Man}), 3.69 (2 H, ddd, H-5_{Glc}), 3.53 (s, 2 H, CH₂NCS), 3.44, 3.43 (2 t, 6 H, ³J_{H,H} = 6.0 Hz, H-3_{Pent}), 3.31 (s, 6 H, H-1_{Pent}), 2.73, 2.70 (2 dt, 6 H, ²J_{H,H} = 12.9 Hz, ³J_{H,H} = 8.6 Hz, H-5_{Pent}), 2.14-1.96 (8 s, 36 H, MeCO), 1.83 (m, 6 H, H-4_{Pent}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.6-169.3 (CO), 130.7 (NCS), 83.8 (C-1_{Glc}), 82.7 (C-1_{Man}), 75.8 (C-5_{Glc}), 73.9 (C-3_{Glc}), 71.2 (C-2_{Man}), 69.9 (C-2_{Glc}), 69.8 (C-3_{Pent}), 69.6 (C-1_{Pent}), 69.4 (C-3_{Man}), 69.0 (C-5_{Man}), 68.3 (C-4_{Glc}), 66.3 (C-4_{Man}), 62.4 (C-6_{Man}), 62.1 (C-6_{Glc}), 45.9 (CH₂NCS), 45.7 (C_q), 29.8 (C-4_{Pent}), 27.1 (C-5_{Pent}), 20.9-20.6 (MeCO); FABMS: *m/z* 1411 [M + Na]⁺. Anal. Calcd. for C₅₇H₈₃NO₃₀S₄: C 49.23, H 6.01, N 1.00. Found: C 49.12, H 5.85, N 1.00.

Preparation of the isothiocyanate-armed monovalent ligand **23**.



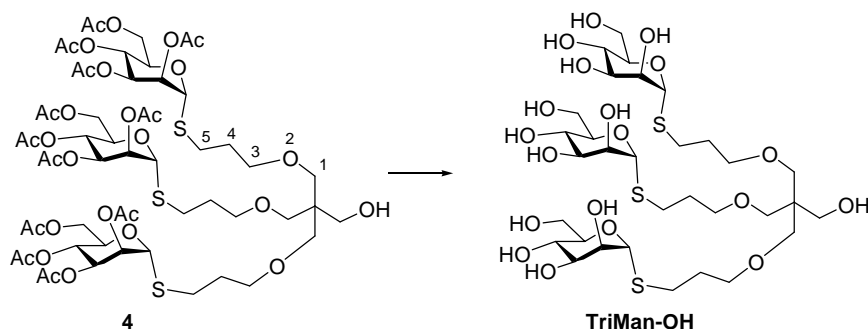
7-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosylthio)-4-oxaheptanol (21). A solution of 4-oxahept-6-en-1-ol **20**⁵ (1.19 g, 3.28 mmol), 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranose **2** (0.46 g, 3.94 mmol), and AIBN (129 mg, 0.79 mmol) in dry dioxane (12 mL), under Ar, was stirred at 75 °C for 45 min. Cyclohexene (2.6 mL) was then added, the solvents were removed under reduced pressure and the residue was purified by column chromatography using 1:1 → 1:2 petroleum ether-EtOAc as eluent. Yield: 1.12 g (71%); *R_f* = 0.26 (1:1 petroleum ether-EtOAc); [α]_D = + 55.7 (*c* 1.0 in CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 5.31 (dd, 1 H, *J*_{2,3} = 3.3 Hz, *J*_{1,2} = 1.6 Hz, H-2), 5.29 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 9.9 Hz, H-4), 5.25 (bs, 1 H, H-1), 5.24 (dd, 1 H, H-3), 4.35 (ddd, 1 H, *J*_{5,6a} = 5.3 Hz, *J*_{5,6b} = 2.4 Hz H-5), 4.29 (dd, 1 H, *J*_{6a,6b} = 12.2 Hz, H-6a), 4.08 (dd, 1 H, H-6b), 3.73 (t, 2 H, ³J_{H,H} = 5.9 Hz, CH₂OH), 3.58 (t, 2 H, ³J_{H,H} = 5.9 Hz, H-3_{Hept}), 3.50 (t, 2 H, ³J_{H,H} = 5.9 Hz, H-5_{Hept}), 2.71, 2.67 (2 dt, 2 H, ²J_{H,H} = 13.4 Hz, ³J_{H,H} = 6.9 Hz,

H-7_{Hept}), 2.15, 2.08, 2.03, 1.97 (4 s, 12 H, MeCO), 1.88 (m, 2 H, H-6_{Hept}), 1.80 (q, 2 H, H-2_{Hept}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.6, 170.0, 169.8, 169.7 (CO), 82.6 (C-1), 71.1 (C-2), 69.7 (C-3_{Hept}), 69.4 (C-3), 69.0 (C-5), 68.9 (C-5_{Hept}), 66.2 (C-4), 62.3 (C-6), 61.5 (CH₂OH), 32.0 (C-2_{Hept}), 29.4 (C-6_{Hept}), 28.1 (C-7_{Hept}), 20.9, 20.7, 20.6, 20.5 (MeCO); FABMS: *m/z* 503 [M + Na]⁺, 481 [M + H]⁺. Anal. Calcd. for C₂₀H₃₂O₁₁S: C 49.99, H 6.71. Found: C 49.93, H 6.80.

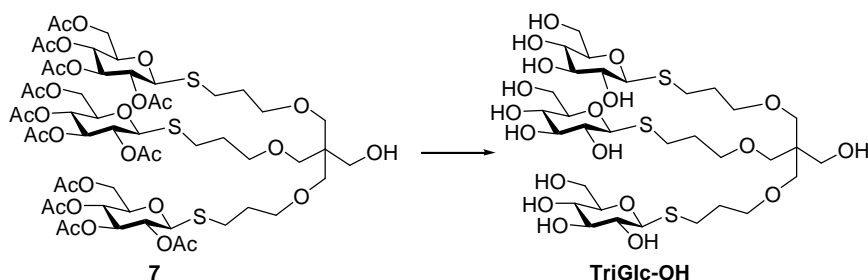
7-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosylthio)-4-oxaheptyl azide (22). To a solution of **21** (100 mg, 0.21 mmol) in dry CH₂Cl₂ (2 mL), tosyl chloride (60.1 mg, 0.32 mmol) and DMAP (38.6 mg, 0.32 mmol) were added. The reaction mixture was stirred at room temperature for 24 h, diluted with CH₂Cl₂ (5 mL) and washed with H₂O (7 mL). The organic layer was separated, dried (MgSO₄), evaporated, and the residue was purified by column chromatography (1:1 petroleum ether-EtOAc). A mixture of tosyl derivative (108 mg, 0.17 mmol) and NaN₃ (33 mg, 0.51 mmol) in dry DMF (3.5 mL) was vigorously stirred at 80 °C for 4 h. The reaction mixture was concentrated and the resulting residue was dissolved in CH₂Cl₂ (5 mL), washed with H₂O (2 × 5 mL), dried (MgSO₄) and purified by column chromatography (1:1 petroleum ether-EtOAc). Yield: 78 mg (74%); *R_f* = 0.51 (1:1 petroleum ether-EtOAc); [α]_D = + 78.3 (*c* 1.0 in CH₂Cl₂); IR (KBr): ν_{max} = 2109 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.32 (dd, 1 H, *J*_{2,3} = 3.3 Hz, *J*_{1,2} = 1.6 Hz, H-2), 5.29 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 9.9 Hz, H-4), 5.25 (bs, 1 H, H-1), 5.24 (dd, 1 H, H-3), 4.36 (ddd, 1 H, *J*_{5,6a} = 5.3 Hz, *J*_{5,6b} = 2.2 Hz, H-5), 4.30 (dd, 1 H, *J*_{6a,6b} = 12.2 Hz, H-6a), 4.07 (dd, 1 H, H-6b), 3.48 (t, 2 H, ³*J*_{H,H} = 6.0 Hz, H-5_{Hept}), 3.47 (t, 2 H, ³*J*_{H,H} = 6.3 Hz, H-3_{Hept}), 3.36 (t, 2 H, ³*J*_{H,H} = 6.6 Hz, CH₂N₃), 2.71, 2.68 (2 dt, 2 H, ²*J*_{H,H} = 13.3 Hz, ³*J*_{H,H} = 7.1 Hz, H-7_{Hept}), 2.15, 2.08, 2.03, 1.98 (4 s, 12 H, MeCO), 1.88 (m, 2 H, H-6_{Hept}), 1.81 (q, 2 H, H-2_{Hept}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.4, 169.8, 169.6, 169.5 (CO), 82.6 (C-1), 71.0 (C-2), 69.3 (C-3), 68.9 (C-5), 68.8 (C-5_{Hept}), 67.3 (C-3_{Hept}), 66.2 (C-4), 62.3 (C-6), 48.3 (CH₂N₃), 29.4 (C-6_{Hept}), 29.0 (C-2_{Hept}), 28.1 (C-7_{Hept}), 20.8-20.5 (MeCO); FABMS: *m/z* 528 [M + Na]⁺. Anal. Calcd. for C₂₀H₃₁N₃O₁₀S: C 47.52, H 6.18, N 8.31. Found: C 47.47, H 6.03, N 8.22.

7-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosylthio)-4-oxaheptyl isothiocyanate (23). Compound **23** was obtained by isothiocyanation of azide **22** (157 mg, 0.31 mmol) in dioxane (6.5 mL), triphenylphosphine (89 mg, 0.34 mmol) and CS₂ (0.19 mL, 3.1 mmol) following the procedure above described in the general methods. Yield: 119 mg (67%); *R_f* = 0.56 (1:1 EtOAc-hexane); [α]_D = + 75.9 (*c* 1.0 in CH₂Cl₂); IR (KBr): ν_{max} = 2089 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.29 (dd, 1 H, *J*_{2,3} = 3.5 Hz, *J*_{1,2} = 1.5 Hz, H-2_{Man}), 5.27 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 10.0 Hz, H-4_{Man}), 5.23 (bs, 1 H, H-1_{Man}), 5.22 (dd, 1 H, H-3_{Man}), 4.34 (dd, 1 H, *J*_{5,6a} = 5.0 Hz, *J*_{5,6b} = 2.5 Hz, H-5_{Man}), 4.27 (dd, 1 H, *J*_{6a,6b} = 12.0 Hz, H-6a_{Man}), 4.06 (dd, 1 H, H-6b_{Man}), 3.60 (t, 2 H, ³*J*_{H,H} = 6.5 Hz, CH₂NCS), 3.49 (t, 2 H, ³*J*_{H,H} = 6.0 Hz, H-3_{Hept}), 3.48 (t, 2 H, ³*J*_{H,H} = 6.0 Hz, H-5_{Hept}), 2.69, 2.66 (2 dt, 2 H, ²*J*_{H,H} = 13.5 Hz, ³*J*_{H,H} = 7.0 Hz, H-7_{Hept}), 2.12, 2.06, 2.01, 1.96 (4 s, 12 H, MeCO), 1.89 (q, 2 H, H-2_{Hept}), 1.86 (m, 2 H, H-6_{Hept}); ¹³C NMR (125.7 MHz, CDCl₃): δ = 170.4, 169.9, 169.7, 169.6 (CO), 130.2 (NCS), 82.6 (C-1_{Man}), 71.1 (C-2_{Man}), 69.3 (C-3_{Man}), 69.0 (C-5_{Hept}), 68.9 (C-5_{Man}), 66.7 (C-3_{Hept}), 66.2 (C-4_{Man}), 62.3 (C-6_{Man}), 42.0 (CH₂NCS), 30.0 (C-2_{Hept}), 29.4 (C-6_{Hept}), 28.2 (C-7_{Hept}), 20.8-20.5 (MeCO); FABMS: *m/z* 544 [M + Na]⁺. Anal. Calcd. for C₂₁H₃₁NO₁₀S₂: C 48.36, H 5.99, N 2.69. Found: C 48.46, H 6.24, N 2.71.

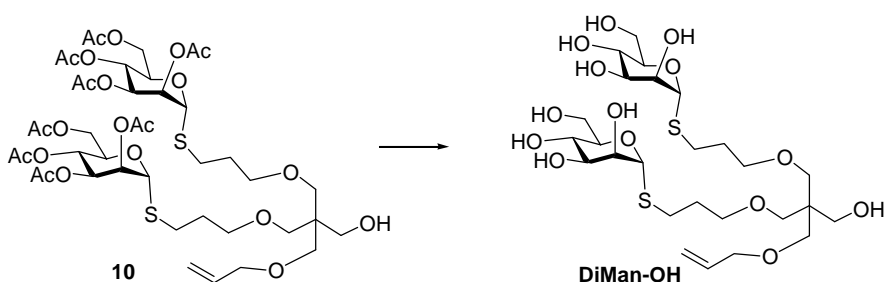
Preparation of pentaerythritol glycoclusters



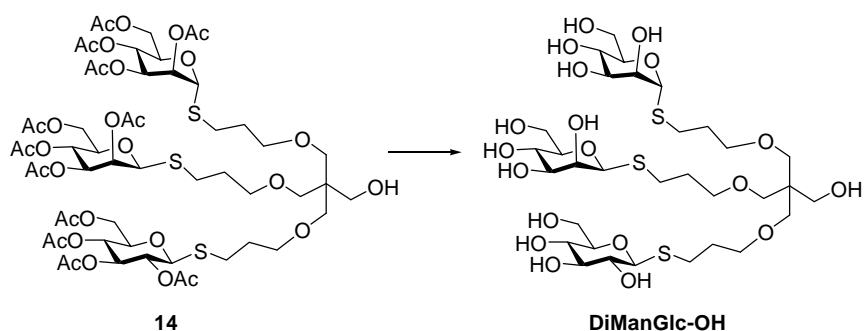
2,2,2-Tris-[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethanol (TriMan-OH). Conventional Zemplen deacetylation of **4** (190 mg, 0.14 μ mol) gave **TriMan-OH**. Yield: 123 mg (100%); $R_f = 0.26$ (4:1:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +159.6$ (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O): $\delta = 5.16$ (bs, 3 H, H-1_{Man}), 3.92 (dd, 3 H, $J_{2,3} = 3.2$ Hz, $J_{1,2} = 1.0$ Hz, H-2_{Man}), 3.85 (ddd, 3 H, $J_{4,5} = 9.8$ Hz, $J_{5,6b} = 5.9$ Hz, $J_{5,6a} = 2.1$ Hz, H-5_{Man}), 3.73 (dd, 3 H, $J_{6a,6b} = 12.3$ Hz, H-6a_{Man}), 3.64 (dd, 3 H, H-6b_{Man}), 3.63 (dd, 3 H, $J_{3,4} = 9.8$ Hz, H-3_{Man}), 3.53 (t, 3 H, H-4_{Man}), 3.50 (s, 2 H, CH₂OH), 3.47 (t, 6 H, $^3J_{H,H} = 5.9$ Hz, H-3_{Pent}), 3.32 (m, 6 H, H-1_{Pent}), 2.62, 2.60 (2 dt, 6 H, $^2J_{H,H} = 14.0$ Hz, $^3J_{H,H} = 5.9$ Hz, H-5_{Pent}), 1.78 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O): $\delta = 84.9$ (C-1_{Man}), 73.2 (C-5_{Man}), 71.9 (C-2_{Man}), 71.2 (C-3_{Man}), 70.1 (C-3_{Pent}), 69.9 (C-1_{Pent}), 67.1 (C-4_{Man}), 63.1 (CH₂OH), 60.9 (C-6_{Man}), 44.9 (C_q), 28.6 (C-4_{Pent}), 27.7 (C-5_{Pent}). FABMS m/z 867 [M + Na]⁺. Anal. Calcd. for C₃₂H₆₀O₁₉S₃: C 45.48, H 7.16, S 11.38; Found: C 45.59, H 7.44, S 11.05.



2,2,2-Tris-[5-(β -D-glucopyranosylthio)-2-oxapentyl]ethanol (TriGlc-OH). Conventional Zemplen deacetylation of **7** (103 mg, 76 μ mol) gave **TriGlc-OH**. Yield: 62 mg, 98%; $R_f = 0.47$ (6:3:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = -32.0$ (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O): $\delta = 4.45$ (d, 3 H, $J_{1,2} = 9.9$ Hz, H-1_{Glc}), 3.81 (dd, 3 H, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 2.0$ Hz, H-6a_{Glc}), 3.63 (dd, 3 H, $J_{5,6b} = 5.5$ Hz, H-6b_{Glc}), 3.52 (t, 6 H, $^3J_{H,H} = 6.2$ Hz, H-3_{Pent}), 3.49 (s, 2 H, CH₂OH), 3.41 (t, 3 H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3_{Glc}), 3.39 (s, 6 H, H-1_{Pent}), 3.37 (ddd, 3 H, $J_{4,5} = 9.3$ Hz, H-5_{Glc}), 3.33 (t, 3 H, H-4_{Glc}), 3.24 (t, 3 H, H-2_{Glc}), 2.68, 2.65 (2 dt, 6 H, $^2J_{H,H} = 13.4$ Hz, $^3J_{H,H} = 7.3$ Hz, H-5_{Pent}), 1.85 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O): $\delta = 85.7$ (C-1_{Glc}), 80.1 (C-5_{Glc}), 77.4 (C-3_{Glc}), 72.5 (C-2_{Glc}), 69.8 (C-3_{Pent}), 69.7 (C-4_{Glc}), 69.5 (C-1_{Pent}), 61.6 (CH₂OH), 61.1 (C-6_{Glc}), 45.2 (C_q), 29.4 (C-4_{Pent}), 27.0 (C-5_{Pent}). FABMS m/z 867 [M + Na]⁺. Anal. Calcd. for C₃₂H₆₀O₁₉S₃: C 45.58, H 7.16, S 11.38; Found: C 45.19, H 6.91, S 11.05.

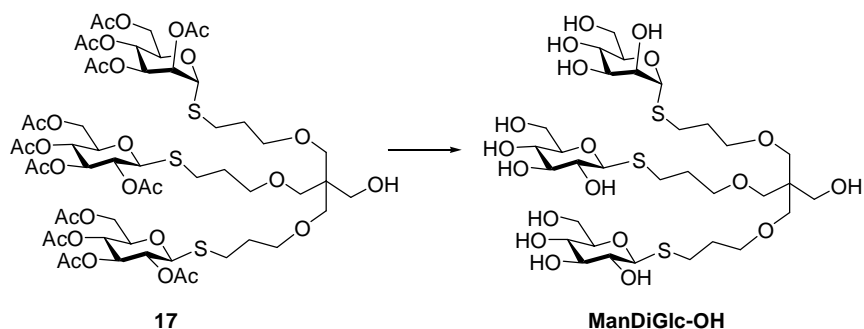


2-[2-Oxapent-4-enyl]-2,2-bis-[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethanol (DiMan-OH). Conventional Zemplen deacetylation of **10** (141 mg, 0.14 μ mol) gave **DiMan-OH**. Yield: 87 mg (96%); $R_f = 0.22$ (10:1:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +134.7$ (*c* 0.95, H₂O). ¹H NMR (500 MHz, D₂O): $\delta = 5.79$ (ddt, 1 H, ³ $J_{H,H} = 17.5$ Hz, ² $J_{H,H} = 12.0$ Hz, ³ $J_{H,H} = 6.0$ Hz, CH₂CH=), 5.17 (dd, 1 H, ² $J_{H,H} = 0.5$ Hz, =CH₂a), 5.11 (s, 2 H, H-1_{Man}), 5.10 (dd, 1 H, =CH₂b), 3.89 (bd, 2 H, $J_{2,3} = 2.3$ Hz, H-2_{Man}), 3.88 (bd, 2 H, CH₂CH=), 3.83 (ddd, 2 H, $J_{4,5} = 8.6$ Hz, $J_{5,6b} = 5.7$ Hz, $J_{5,6a} = 2.0$ Hz, H-5_{Man}), 3.71 (dd, 2 H, $J_{6a,6b} = 12.3$ Hz, H-6a_{Man}), 3.62 (m, 4 H, H-3_{Man}, H-6b_{Man}), 3.52 (t, 2 H, H-4_{Man}), 3.44 (t, 4 H, ³ $J_{H,H} = 5.9$ Hz, H-3_{Pent}), 3.42 (s, 2 H, CH₂OH), 3.31 (s, 2 H, CH₂OAll), 3.29 (s, 4 H, H-1_{Pent}), 2.60, 2.58 (2 dt, 4 H, ² $J_{H,H} = 13.5$ Hz, ³ $J_{H,H} = 7.0$ Hz, H-5_{Pent}), 1.80 (m, 4 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O): $\delta = 134.1$ (=CH), 117.8 (=CH₂), 84.9 (C-1_{Man}), 73.1 (C-5_{Man}), 72.4 (CH₂CH=), 71.8 (C-2_{Man}), 71.1 (C-3_{Man}), 69.9 (C-3_{PentMan}), 69.1 (C-3_{PentMan}), 68.9 (CH₂OAll), 67.0 (C-4_{Man}), 61.3 (CH₂OH), 60.8 (C-6_{Man}), 44.9 (C_q), 28.5 (C-4_{PentMan}), 27.6 (C-5_{PentMan}). FABMS *m/z* 671 [M + Na]⁺. Anal. Calcd. for C₂₆H₄₈O₁₄S₂: C 48.13, H 7.46; Found: C 48.24, H 7.31.



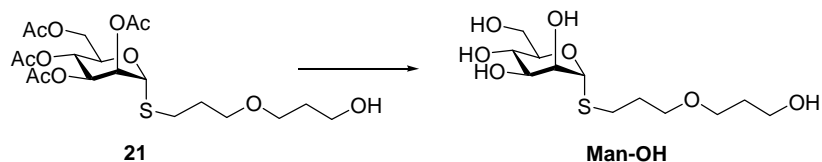
2-[5-(β -D-Glucopyranosylthio)-2-oxapentyl]-2,2-bis-[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethanol

(DiManGlc-OH). Conventional Zemplen deacetylation of **14** (150 mg, 0.11 μ mol) gave **DiManGlc-OH**. Yield: 99 mg (100%); $R_f = 0.53$ (6:3:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +88.1$ (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O): $\delta = 5.14$ (s, 2 H, H-1_{Man}), 4.36 (d, 1 H, $J_{1,2} = 10.0$ Hz, H-1_{Glc}), 3.90 (m, 2 H, H-2_{Man}), 3.84 (ddd, 2 H, $J_{4,5} = 9.3$ Hz, $J_{5,6b} = 6.1$ Hz, $J_{5,6a} = 1.8$ Hz, H-5_{Man}), 3.73 (dd, 1 H, $J_{6a,6b} = 12.3$ Hz, H-6a_{Glc}), 3.71 (d, 2 H, $J_{6a,6b} = 11.0$ Hz, H-6a_{Man}), 3.62 (m, 4 H, H-6b_{Man}, H-3_{Man}), 3.55 (dd, 1 H, $J_{5,6b} = 4.9$ Hz, H-6b_{Glc}), 3.52 (t, 2 H, $J_{3,4} = 9.7$ Hz, H-4_{Man}), 3.44 (m 6 H, H-3_{Pent}), 3.41 (s, 2 H, CH₂OH), 3.32 (t, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3_{Glc}), 3.30 (s, 2 H, H-1_{PentGlc}), 3.29 (m, 4 H, H-1_{PentMan}), 3.28 (m, 1 H, H-5_{Glc}), 3.24 (t, 1 H, $J_{4,5} = 9.4$ Hz, H-4_{Glc}), 3.16 (t, 1 H, H-2_{Glc}), 2.60, 2.58 (2 dt, 6 H, ² $J_{H,H} = 13.5$ Hz, ³ $J_{H,H} = 6.5$ Hz, H-5_{Pent}), 1.78 (s, 4 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O): $\delta = 85.5$ (C-1_{Glc}), 84.9 (C-1_{Man}), 79.8 (C-5_{Glc}), 77.2 (C-3_{Glc}), 73.1 (C-5_{Man}), 72.2 (C-2_{Glc}), 71.8 (C-2_{Man}), 71.1 (C-3_{Man}), 70.0 (C-3_{Pent}), 69.5 (C-4_{Glc}), 69.3 (C-1_{Pent}), 67.0 (C-4_{Man}), 61.4 (CH₂OH), 60.9 (C-6_{Glc}), 60.8 (C-6_{Man}), 45.1 (C_q), 29.1 (C-4_{PentGlc}), 28.5 (C-4_{PentMan}), 27.6 (C-5_{PentMan}), 26.7 (C-5_{PentGlc}). FABMS *m/z* 867 [M + Na]⁺. Anal. Calcd. for C₃₂H₆₀O₁₉S₃: C 45.48, H 7.16; Found: C 45.24, H 7.04.



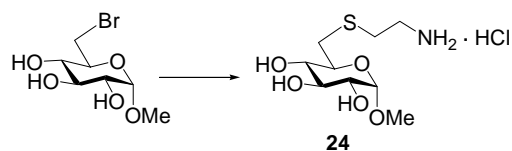
2,2-Bis-[5-(β -D-glucopyranosylthio)-2-oxapentyl]-2-[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethanol

(**ManDiGlc-OH**). Conventional Zemplen deacetylation of **17** (150 mg, 0.11 μ mol) gave **ManDiGlc-OH**. Yield: 99 mg (100%); $R_f = 0.50$ (6:3:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +33.0$ (c 1.0, H₂O). ¹H NMR (500 MHz, D₂O): $\delta = 5.12$ (bs, 1 H, H-1_{Man}), 4.40 (d, 2 H, $J_{1,2} = 10.1$ Hz, H-1_{Glc}), 3.93 (bd, 1 H, $J_{2,3} = 3.2$ Hz, H-2_{Man}), 3.86 (m, 1 H, H-5_{Man}), 3.78 (d, 2 H, $J_{6a,6b} = 11.5$ Hz, H-6a_{Glc}), 3.77 (bd, 1 H, $J_{6a,6b} = 11.6$ Hz, H-6a_{Man}), 3.59 (dd, 2 H, $J_{5,6b} = 5.1$ Hz, H-6b_{Glc}), 3.58 (m, 2 H, H-6b_{Man}, H-3_{Man}), 3.54 (t, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4_{Man}), 3.49 (s, 2 H, CH₂OH), 3.48 (m, 6 H, H-3_{Pent}), 3.37 (t, 2 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3_{Glc}), 3.32 (m, 2 H, H-5_{Glc}), 3.31 (m, 6 H, H-1_{Pent}), 3.28 (t, 2 H, $J_{4,5} = 9.0$ Hz, H-4_{Glc}), 3.18 (t, 2 H, H-2_{Glc}), 2.73, 2.66 (2 dt, 6 H, $^2J_{H,H} = 13.2$ Hz, $^3J_{H,H} = 6.8$ Hz, H-5_{Pent}), 1.80 (s, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O): $\delta = 85.5$ (C-1_{Glc}), 84.9 (C-1_{Man}), 79.8 (C-5_{Glc}), 77.2 (C-3_{Glc}), 73.2 (C-5_{Man}), 72.3 (C-2_{Glc}), 71.8 (C-2_{Man}), 71.1 (C-3_{Man}), 69.9 (C-3_{Pent}), 69.5 (C-4_{Glc}), 69.3 (C-1_{Pent}), 67.0 (C-4_{Man}), 61.5 (CH₂OH), 60.9 (C-6_{Glc}), 60.8 (C-6_{Man}), 45.0 (C_q), 29.2 (C-4_{PentGlc}), 28.5 (C-4_{PentMan}), 27.6 (C-5_{PentMan}), 26.8 (C-5_{PentGlc}). FABMS m/z 867 [M + Na]⁺. Anal. Calcd. for C₃₂H₆₀O₁₉S₃: C 45.48, H 7.16; Found: C 45.24, H 6.94.



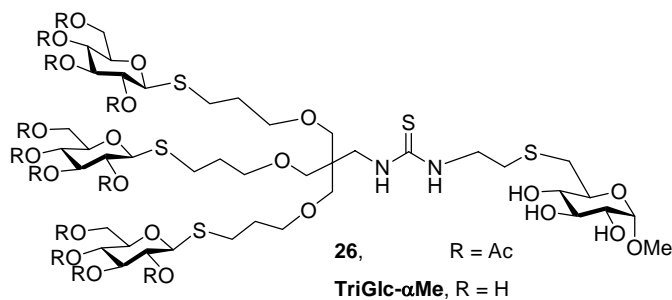
7-(α -D-Mannopyranosylthio)-4-oxaheptanol (**Man-OH**). Conventional Zemplen deacetylation of **21** (88 mg, 0.18 μ mol) followed by column chromatography purification, using 45:5:3 EtOAc-EtOH-H₂O as eluent, gave **Man-OH**. Yield: 52 mg (93%); $R_f = 0.16$ (45:5:3 EtOAc-MeOH-H₂O); $[\alpha]_D = +126.8$ (c 1.1, H₂O). ¹H NMR (300 MHz, D₂O): $\delta = 5.25$ (d, 2 H, $J_{1,2} = 1.5$ Hz, H-1_{Man}), 4.00 (dd, 1 H, $J_{2,3} = 3.3$ Hz, H-2_{Man}), 3.95 (ddd, 1 H, $J_{4,5} = 9.6$ Hz, $J_{5,6b} = 6.0$ Hz, $J_{5,6a} = 2.4$ Hz, H-5_{Man}), 3.84 (dd, 1 H, $J_{6a,6b} = 12.3$ Hz, H-6a_{Man}), 3.73 (dd, 1 H, H-6b_{Man}), 3.72 (dd, 1 H, $J_{3,4} = 8.0$ Hz, H-3_{Man}), 3.66 (t, 1 H, H-4_{Man}), 3.62 (t, 2 H, $^3J_{H,H} = 6.6$ Hz, H-5_{Hept}), 3.57 (t, 2 H, $^3J_{H,H} = 6.3$ Hz, H-1_{Hept}), 3.55 (t, 2 H, $^3J_{H,H} = 6.6$ Hz, H-3_{Hept}), 2.70, 2.68 (2 dt, 2 H, $^2J_{H,H} = 13.5$ Hz, $^3J_{H,H} = 7.2$ Hz, H-7_{Hept}), 1.87 (m, 2 H, H-6_{Hept}), 1.77 (m, 2 H, H-6_{Hept}). ¹³C NMR (75.5 MHz, D₂O): $\delta = 84.9$ (C-1_{Man}), 73.1 (C-5_{Man}), 71.8 (C-2_{Man}), 71.0 (C-3_{Man}), 68.9 (C-5_{Hept}), 67.4 (C-3_{Hept}), 67.1 (C-4_{Man}), 60.8 (CH₂OH), 58.7 (C-6_{Man}), 31.2 (C-6_{Hept}), 28.6 (C-2_{Hept}), 27.4 (C-7_{Hept}). FABMS m/z 335 [M + Na]⁺. Anal. Calcd. for C₁₂H₂₄O₇S: C 46.14, H 7.74; Found: C 45.95, H 7.68.

Preparation of methyl 6-(2-aminoethylthio)- α -D-glucopyranoside conjugates.



Methyl 6-(2-aminoethylthio)- α -D-glucopyranoside hydrochloride (24): To a solution of 2-aminoethanethiol hydrochloride (264 mg, 2.3 mmol, 2 eq) in freshly distilled DMF (3 mL), under Ar atmosphere, dry Et₃N (647 μ L, 4.64 mmol, 4 eq) was added using a syringe.^{4,6} To the resulting pale violet suspension, a solution of methyl 6-bromo-6-deoxy- α -D-glucopyranoside (0.3 g, 1.16 mmol) in DMF (1 mL) was added dropwise under Ar, and the reaction mixture was stirred for 24 h at room temperature. Solvents were eliminated under reduced pressure and the residue was purified by column chromatography using 10:1:1 MeCN-H₂O-NH₄OH as eluent. The white solid obtained was dissolved in H₂O (5 mL) and the solution was adjusted to pH 4 using diluted HCl and freeze-dried to give **24**. Yield: 300 mg (89%); $R_f = 0.14$ (10:1:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +48.1$ (c 1.0, H₂O). ¹H NMR (500 MHz, D₂O): $\delta =$

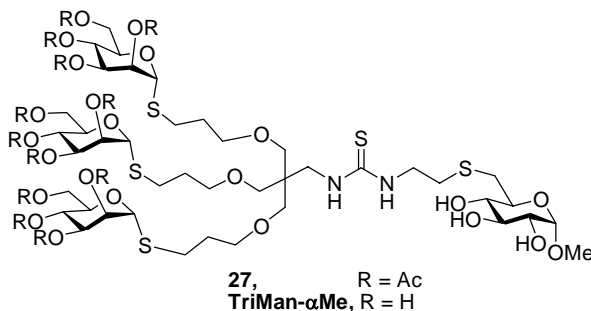
4.78 (d, 1 H, $J_{1,2} = 3.6$ Hz, H-1), 3.73 (ddd, 1 H, $J_{4,5} = 10.1$ Hz, $J_{5,6b} = 7.9$ Hz, $J_{5,6a} = 2.6$ Hz, H-5), 3.60 (dd, 1 H, $J_{2,3} = 9.8$ Hz, $J_{3,4} = 8.8$ Hz, H-3), 3.55 (dd, 1 H, H-2), 3.40 (s, 3 H, OMe), 3.35 (dd, 1 H, H-4), 3.23 (t, 2 H, $^3J_{H,H} = 6.6$ Hz, $\text{CH}_2\text{N}_{\text{Cyst}}$), 3.03 (dd, 1 H, $J_{6a,6b} = 14.1$ Hz, H-6a), 2.91 (t, 2 H, $\text{CH}_2\text{S}_{\text{Cyst}}$), 2.78 (dd, 1 H, H-6b). ^{13}C NMR (125.7 MHz, D_2O): $\delta = 100.7$ (C-1), 74.5 (C-3), 73.8 (C-4), 72.8 (C-2), 72.2 (C-5), 56.7 (OMe), 40.0 ($\text{CH}_2\text{N}_{\text{Cyst}}$), 34.0 (C-6), 30.8 ($\text{CH}_2\text{S}_{\text{Cyst}}$). FABMS: m/z 254 [$\text{M} - \text{Cl}$] $^+$. Anal. Calcd. for $\text{C}_9\text{H}_{20}\text{ClNO}_5\text{S}$: C 37.30, H 6.96, N 4.83. Found: C 37.07, H 6.76, N 4.76.



Methyl 6-[2-[3-[2,2,2-tris[5-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (26): Compound **26** was obtained by coupling reaction of **24** (25 mg, 86 μmol) and **9** (132 mg, 95 μmol , 1.1 eq) following the procedure above described in the general methods. Yield: 40 mg (30%); $R_f = 0.50$ (45:5:3 AcOEt-EtOH-H $_2$ O); $[\alpha]_D = -6.3$ (c 1.0, MeOH). ^1H NMR (500 MHz, CD_3OD): $\delta = 5.27$ (t, 3 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3 $_{\text{Glc}}$), 5.02 (t, 3 H, $J_{4,5} = 9.4$ Hz, H-4 $_{\text{Glc}}$), 4.94 (t, 3 H, $J_{1,2} = 9.4$ Hz, H-2 $_{\text{Glc}}$), 4.74 (d, 3 H, H-1 $_{\text{Glc}}$), 4.65 (d, 1 H, $J_{1,2} = 3.7$ Hz, H-1), 4.24 (dd, 3 H, $J_{6a,6b} = 12.4$ Hz, $J_{5,6a} = 5.0$ Hz, H-6a $_{\text{Glc}}$), 4.12 (dd, 3 H, $J_{5,6b} = 2.3$ Hz, H-6b $_{\text{Glc}}$), 3.90 (ddd, 3 H, H-5 $_{\text{Glc}}$), 3.70 (m, 2 H, $\text{CH}_2\text{N}_{\text{Cyst}}$), 3.64 (ddd, 1 H, $J_{4,5} = 9.1$ Hz, $J_{5,6b} = 8.0$ Hz, $J_{5,6a} = 2.1$ Hz, H-5), 3.56 (t, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3), 3.51 (t, 6 H, $^3J_{H,H} = 5.5$ Hz, H-3 $_{\text{Pent}}$), 3.42 (s, 3 H, OMe), 3.40 (s, 8 H, $\text{CH}_2\text{N}_{\text{Branch}}$, H-1 $_{\text{Pent}}$), 3.39 (dd, 1 H, H-2), 3.23 (t, 1 H, H-4), 3.02 (dd, 1 H, $J_{6a,6b} = 13.9$ Hz, H-6a), 2.84 (t, 2 H, $^3J_{H,H} = 6.0$ Hz, $\text{CH}_2\text{S}_{\text{Cyst}}$), 2.81, 2.76 (2 dt, 6 H, $^2J_{H,H} = 13.7$ Hz, $^3J_{H,H} = 5.5$ Hz, H-5 $_{\text{Pent}}$), 2.70 (dd, 1 H, H-6b), 2.06, 2.02, 1.99, 1.96 (4 s, 36 H, MeCO), 1.88 (m, 6 H, H-4 $_{\text{Pent}}$). ^{13}C NMR (125.7 MHz, CD_3OD): $\delta = 186.0$ (CS), 170.9, 170.2, 169.9, 169.7 (CO), 101.1 (C-1), 84.9 (C-1 $_{\text{Glc}}$), 76.8 (C-5 $_{\text{Glc}}$), 75.3 (C-3 $_{\text{Glc}}$), 75.1 (C-3), 74.6 (C-4), 73.6 (C-2, C-5), 72.0 (C-1 $_{\text{Pent}}$), 71.5 (C-2 $_{\text{Glc}}$), 70.9 (C-3 $_{\text{Pent}}$), 69.9 (C-4 $_{\text{Glc}}$), 63.5 (C-6 $_{\text{Glc}}$), 55.7 (OMe), 45.6 (C $_q$, $\text{CH}_2\text{N}_{\text{Branch}}$, $\text{CH}_2\text{N}_{\text{Cyst}}$), 34.7 (C-6), 33.3 ($\text{CH}_2\text{S}_{\text{Cyst}}$), 31.2 (C-4 $_{\text{Pent}}$), 28.4 (C-5 $_{\text{Pent}}$), 20.9-20.6 (MeCO). FABMS: m/z 1666 [$\text{M} + \text{Na}$] $^+$, 1644 [$\text{M} + \text{H}$] $^+$. Anal. Calcd. for $\text{C}_{66}\text{H}_{102}\text{N}_2\text{O}_{35}\text{S}_5$: C 48.22, H 6.25, N 1.70. Found: C 48.27, H 6.18, N 1.66.

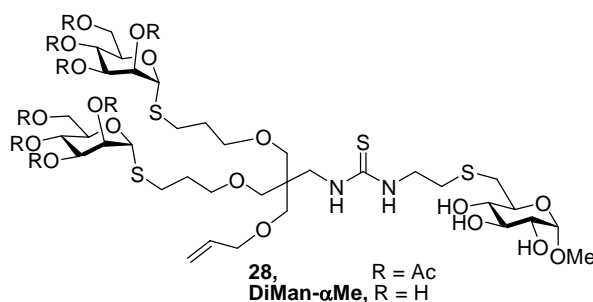
Methyl 6-[2-[3-[2,2,2-tris[5-(β -D-glucopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (TriGlc- α Me): Conventional Zemplen deacetylation of **26** (31 mg, 19 μmol) gave the fully unprotected conjugate **TriGlc- α Me**. Yield: 21 mg (100%); $R_f = 0.50$ (6:3:1 MeCN-H $_2$ O-NH $_4$ OH); $[\alpha]_D = -12.3$ (c 1.0, H $_2$ O). ^1H NMR (500 MHz, 333 K, D_2O): $\delta = 5.07$ (d, 1 H, $J_{1,2} = 4.0$ Hz, H-1), 4.80 (d, 3 H, $J_{1,2} = 10.0$ Hz, H-1 $_{\text{Glc}}$), 4.17 (dd, 3 H, $J_{6a,6b} = 12.5$ Hz, $J_{5,6a} = 2.0$ Hz, H-6a $_{\text{Glc}}$), 4.02 (ddd, 1 H, $J_{4,5} = 9.0$ Hz, $J_{5,6b} = 8.0$ Hz, $J_{5,6a} = 2.0$ Hz, H-5), 4.01 (dd, 3 H, $J_{5,6b} = 5.5$ Hz, H-6b $_{\text{Glc}}$), 4.00 (2 H, m, $\text{CH}_2\text{N}_{\text{Cyst}}$), 3.93 (t, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 3.88 (t, 6 H, $^3J_{H,H} = 6.0$ Hz, H-3 $_{\text{Pent}}$), 3.86 (dd, 1 H, H-2), 3.79 (t, 3 H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3 $_{\text{Glc}}$), 3.75 (ddd, 3 H, $J_{4,5} = 9.3$ Hz, H-5 $_{\text{Glc}}$), 3.74 (m, 8 H, H-1 $_{\text{Pent}}$, $\text{CH}_2\text{N}_{\text{Branch}}$), 3.73 (t, 3 H, H-4 $_{\text{Glc}}$), 3.65 (m, 3 H, OMe), 3.64 (dd, 1 H, H-4), 3.62 (t, 3 H, H-2 $_{\text{Glc}}$), 3.38 (dd, 1 H, $J_{6a,6b} = 14.0$ Hz, H-6a), 3.18 (t, 2 H, $^3J_{H,H} = 3.5$ Hz, $\text{CH}_2\text{S}_{\text{Cyst}}$), 3.14, 3.09 (2 dt, 6 H, $^2J_{H,H} = 13.2$ Hz, $^3J_{H,H} = 6.0$ Hz, H-5 $_{\text{Pent}}$), 3.08 (dd, 1 H, H-6b), 2.22 (m, 6 H, H-4 $_{\text{Pent}}$). ^{13}C NMR (125.7 MHz, 333 K, D_2O): $\delta = 180.6$ (CS), 99.7 (C-1), 86.0 (C-1 $_{\text{Glc}}$), 80.4 (C-5 $_{\text{Glc}}$), 77.9 (C-3 $_{\text{Glc}}$), 73.6 (C-3), 73.2 (C-4), 72.9 (C-2 $_{\text{Glc}}$), 71.9 (C-2), 71.5 (C-5), 71.0 (C-1 $_{\text{Pent}}$), 70.6 (C-3 $_{\text{Pent}}$), 70.2 (C-4 $_{\text{Glc}}$), 61.6 (C-6 $_{\text{Glc}}$), 55.7 (OMe), 44.7 (C $_q$), 44.1 ($\text{CH}_2\text{N}_{\text{Branch}}$,

CH₂N_{Cyst}), 33.7 (C-6), 32.1 (CH₂S_{Cyst}), 29.9 (C-4_{Pent}), 27.3 (C-5_{Pent}). FABMS: *m/z* 1161 [M + Na]⁺. Anal. Calcd. for C₄₂H₇₈N₂O₂₃S₅: C 44.27, H 6.90, N 2.46. Found: C. 44.16, H 6.79, N 2.37.



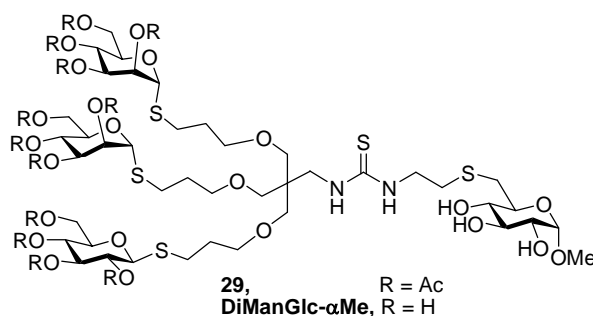
Methyl 6-[2-[3-[2,2,2-tris[5-(2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (27): Compound **27** was obtained by coupling reaction of **24** (20 mg, 69 μ mol) and **6** (106 mg, 76 μ mol, 1.1 eq) following the procedure above described in the general methods. Yield: 50 mg (44%); *R_f* = 0.50 (45:5:3 AcOEt-EtOH-H₂O); [α]_D = + 70.5 (*c* 1.0, MeOH). ¹H NMR (500 MHz, CD₃OD, 313 K): δ = 5.34 (bd, 3 H, *J*_{1,2} = 1.5 Hz, H-1_{Man}), 5.31 (dd, 3 H, *J*_{2,3} = 3.3 Hz, H-2_{Man}), 5.25 (t, 3 H, *J*_{3,4} = *J*_{4,5} = 10.0 Hz, H-4_{Man}), 5.18 (dd, 3 H, H-3_{Man}), 4.64 (d, 1 H, *J*_{1,2} = 3.8 Hz, H-1), 4.37 (ddd, 3 H, *J*_{5,6a} = 5.2 Hz, *J*_{5,6b} = 2.4 Hz, H-5_{Man}), 4.26 (dd, 3 H, *J*_{6a,6b} = 12.3 Hz, H-6a_{Man}), 4.11 (dd, 3 H, H-6b_{Man}), 3.68 (m, 2 H, CH₂N_{Cyst}), 3.97 (td, 1 H, *J*_{4,5} = *J*_{5,6b} = 8.9 Hz, *J*_{5,6a} = 2.2 Hz, H-5), 3.56 (t, 1 H, *J*_{2,3} = *J*_{3,4} = 9.2 Hz, H-3), 3.53 (t, 6 H, ³*J*_{H,H} = 5.9 Hz, H-3_{Pent}), 3.41 (s, 3 H, OMe), 3.40 (s, 8 H, CH₂N_{Branch}, H-1_{Pent}), 3.38 (dd, 1 H, H-2), 3.21 (t, 1 H, H-4), 3.01 (dd, 1 H, *J*_{6a,6b} = 13.9 Hz, H-6a), 2.83 (t, 2 H, ³*J*_{H,H} = 6.3 Hz, CH₂S_{Cyst}), 2.84, 2.80 (2 dt, 6 H, ²*J*_{H,H} = 14.1 Hz, ³*J*_{H,H} = 7.1 Hz, H-5_{Pent}), 2.70 (dd, 1 H, H-6b), 2.12-1.94 (4 s, 36 H, MeCO), 1.92 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, CD₃OD, 313 K): δ = 184.5 (CS), 172.3-171.5 (CO), 101.2 (C-1), 84.0 (C-1_{Man}), 75.1 (C-3), 74.6 (C-4), 73.7 (C-2), 73.6 (C-5), 72.4 (C-2_{Man}), 72.1 (C-1_{Pent}), 71.1 (C-3_{Man}), 70.8 (C-3_{Pent}), 70.5 (C-5_{Man}), 67.7 (C-4_{Man}), 63.7 (C-6_{Man}), 55.7 (OMe), 45.6 (C_q), 45.5 (CH₂N_{Branch}, CH₂N_{Cyst}), 34.8 (C-6), 33.3 (CH₂S_{Cyst}), 30.7 (C-4_{Pent}), 29.4 (C-5_{Pent}), 20.8-20.5 (MeCO). FABMS: *m/z* 1665 [M + Na]⁺. Anal. Calcd. for C₆₆H₁₀₂N₂O₃₅S₅: C 48.22, H 6.25, N 1.70. Found: C 48.05, H 6.27, N 1.61.

Methyl 6-[2-[3-[2,2,2-tris[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (TriMan- α Me): Conventional Zemplen deacetylation of **27** (30 mg, 18.2 μ mol) gave the fully unprotected conjugate **TriMan- α Me**. Yield: 19 mg (100%); *R_f* = 0.40 (6:3:1 MeCN-H₂O-NH₄OH), [α]_D = + 126.0 (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O, 343 K): δ = 5.69 (d, 3 H, *J*_{1,2} = 1.5 Hz, H-1_{Man}), 5.17 (d, 1 H, *J*_{1,2} = 3.5 Hz, H-1), 4.44 (dd, 3 H, *J*_{2,3} = 3.5 Hz, H-2_{Man}), 4.33 (ddd, 3 H, *J*_{4,5} = 9.5 Hz, *J*_{5,6b} = 5.5 Hz, *J*_{5,6a} = 2.0 Hz, H-5_{Man}), 4.24 (dd, 3 H, *J*_{6a,6b} = 12.5 Hz, H-6a_{Man}), 4.19 (dd, 3 H, H-6b_{Man}), 4.17 (dd, 3 H, *J*_{3,4} = 9.5 Hz, H-3_{Man}), 4.12 (ddd, 1 H, *J*_{4,5} = 10.0 Hz, *J*_{5,6b} = 8.0 Hz, *J*_{5,6a} = 2.5 Hz, H-5), 4.11 (t, 3 H, H-4_{Man}), 4.07 (m, 2 H, CH₂N_{Cyst}), 4.03 (t, 1 H, *J*_{2,3} = *J*_{3,4} = 10.0 Hz, H-3), 3.98 (t, 6 H, ³*J*_{H,H} = 6.5 Hz, H-3_{Pent}), 3.96 (dd, 1 H, H-2), 3.84 (m, 11 H, H-1_{Pent}, CH₂N_{Branch}, OMe), 3.74 (t, 1 H, H-4), 3.48 (dd, 3 H, *J*_{6a,6b} = 14.0 Hz, H-6a), 3.28 (t, 2 H, ³*J*_{H,H} = 6.5 Hz, CH₂S_{Cyst}), 3.16, 3.14 (2 dt, 6 H, ²*J*_{H,H} = 13.0 Hz, ³*J*_{H,H} = 6.5 Hz, H-5_{Pent}), 3.12 (dd, 3 H, H-6b), 2.32 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O, 343 K): δ = 180.9 (CS), 99.9 (C-1), 85.7 (C-1_{Man}), 74.0 (C-5_{Man}), 73.8 (C-3), 73.3 (C-4), 72.6 (C-2_{Man}), 72.1 (C-2), 71.9 (C-3_{Man}), 71.8 (C-5), 71.2 (C-1_{Pent}), 70.7 (C-3_{Pent}), 67.8 (C-4_{Man}), 61.6 (C-6_{Man}), 55.8 (OMe), 44.8 (C_q), 44.3 (CH₂N_{Branch}, CH₂N_{Cyst}), 33.9 (C-6), 32.3 (CH₂S_{Cyst}), 29.5 (C-4_{Pent}), 28.5 (C-5_{Pent}). FABMS: *m/z* 1161 [M + Na]⁺. Anal. Calcd. for C₄₂H₇₈N₂O₂₃S₅: C 44.27, H 6.90, N 2.46. Found: C 43.96, H 6.74, N 2.20.



Methyl 6-[2-[3-[2-(2-oxapent-4-enyl)-2,2-bis[5-(2,3,4,6-tetra-O-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (28): Compound **28** was obtained by coupling reaction of **24** (31 mg, 107 μ mol, 1.1 eq) and **12** (100 mg, 97 μ mol) following the procedure above described in the general methods. Yield: 95.2 mg (77%); $R_f = 0.57$ (45:5:3 AcOEt-EtOH-H₂O); $R_f = 0.42$ (10:1:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +72.6$ (c 1.0, MeOH). ¹H NMR (500 MHz, CD₃OD, 313 K): $\delta = 5.90$ (ddt, 1 H, ³ $J_{H,H} = 17.0$ Hz, ³ $J_{H,H} = 10.5$ Hz, ³ $J_{H,H} = 5.0$ Hz, OCH₂CH=), 5.33 (d, 2 H, $J_{1,2} = 1.5$ Hz, H-1_{Man}), 5.31 (dd, 2 H, $J_{2,3} = 3.0$ Hz, H-2_{Man}), 5.26 (dc, 1 H, ⁴ $J_{H,H} = 2J_{H,H} = 1.5$ Hz, =CH_a), 5.25 (t, 2 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4_{Man}), 5.18 (dd, 2 H, H-3_{Man}), 5.15 (dc, 1 H, ⁴ $J_{H,H} = 1.5$ Hz, =CH_b), 4.63 (d, 1 H, $J_{1,2} = 3.5$ Hz, H-1), 4.37 (ddd, 2 H, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 2.0$ Hz, H-5_{Man}), 4.25 (dd, 2 H, $J_{6a,6b} = 12.5$ Hz, H-6_{aMan}), 4.10 (dd, 2 H, H-6_{bMan}), 3.96 (dt, 2 H, OCH₂CH=), 3.68 (bs, 2 H, CH₂N_{Cyst}), 3.64 (ddd, 1 H, $J_{4,5} = 9.0$ Hz, $J_{5,6b} = 8.0$ Hz, $J_{5,6a} = 2.5$ Hz, H-5), 3.56 (t, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 3.52 (t, 4 H, ³ $J_{H,H} = 5.5$ Hz, H-3_{Pent}), 3.40 (m, 11 H, H-1_{Pent}, CH₂N_{Branch}, CH₂N_{Cyst}, CH₂OAll, OMe), 3.38 (d, 1 H, H-2), 3.21 (t, 1 H, H-4), 3.00 (dd, 1 H, $J_{6a,6b} = 14.0$ Hz, H-6a), 2.82 (t, 2 H, ³ $J_{H,H} = 7.0$ Hz, CH₂S_{Cyst}), 2.78, 2.75 (2 dt, 4 H, ² $J_{H,H} = 12.5$ Hz, ³ $J_{H,H} = 7.0$ Hz, H-5_{Pent}), 2.68 (dd, 2 H, H-6b), 2.12-1.98 (4 s, 36 H, MeCO), 1.99 (m, 4 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, CD₃OD, 313 K): $\delta = 182.4$ (CS), 172.3-171.5 (CO), 136.2 (CH₂CH=), 117.3 (=CH₂), 101.2 (C-1), 84.0 (C-1_{Man}), 75.1 (C-3), 74.6 (C-4), 73.7 (C-2), 73.6 (C-5), 73.5 (OCH₂CH=), 72.4 (C-2_{Man}), 69.3 (C-1_{Pent}), 71.2 (C-3_{Man}), 70.8 (C-3_{Pent}), 70.5 (C-5_{Man}), 67.7 (C-4_{Man}), 63.7 (C-6_{Man}), 55.7 (OMe), 45.6 (C_q, CH₂N_{Branch}, CH₂N_{Cyst}), 34.8 (C-6), 33.3 (CH₂S_{Cyst}), 30.7 (C-4_{Pent}), 29.4 (C-5_{Pent}), 20.8-20.5 (MeCO). FABMS: m/z 1300 [M + Na]⁺. Anal. Calcd. for C₅₂H₈₂N₂O₂₆S₄: C 48.81, H 6.96, N 2.19. Found: C 48.69, H 6.39, N 2.01.

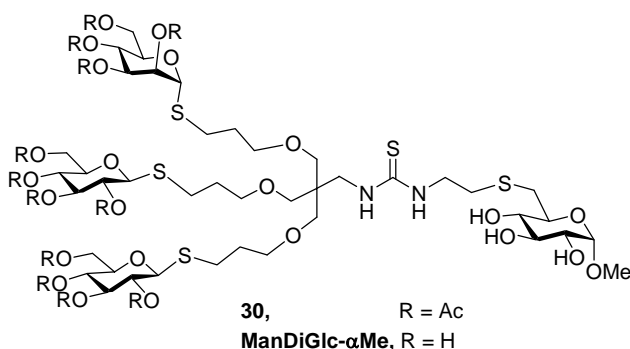
Methyl 6-[2-[3-[2-(2-oxapent-4-enyl)-2,2-bis[5-(β -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (DiMan- α Me). Conventional Zemplen deacetylation of **28** (25 mg, 19.5 μ mol) gave **DiMan- α Me**. Yield: 18 mg (100%); $R_f = 0.72$ (6:3:1 MeCN-H₂O-NH₄OH); $[\alpha]_D = +92.1$ (c 0.7, H₂O). ¹H NMR (500 MHz, D₂O, 313 K): $\delta = 6.02$ (ddt, 1 H, ³ $J_{H,H} = 17.0$ Hz, ³ $J_{H,H} = 10.5$ Hz, ³ $J_{H,H} = 6.0$ Hz, OCH₂CH=), 5.40 (dc, 1 H, ² $J_{H,H} = 4J_{H,H} = 1.7$ Hz, CH_a), 5.35 (d, 2 H, H-1_{Man}), 5.32 (dc, 1 H, ⁴ $J_{H,H} = 1.7$ Hz, =CH_b), 4.84 (d, 1 H, $J_{1,2} = 4.0$ Hz, H-1), 4.10 (dd, 2 H, $J_{2,3} = 3.5$ Hz, H-2_{Man}), 4.08 (dt, 2 H, OCH₂CH=), 4.02 (ddd, 2 H, $J_{4,5} = 10.0$ Hz, $J_{5,6b} = 6.0$ Hz, $J_{5,6a} = 2.5$ Hz, H-5_{Man}), 3.92 (dd, 2 H, $J_{6a,6b} = 12.0$ Hz, H-6_{aMan}), 3.85 (dd, 2 H, H-6_{bMan}), 3.83 (dd, 2 H, $J_{3,4} = 10.0$ Hz, H-3_{Man}), 3.80 (ddd, 1 H, $J_{4,5} = 9.0$ Hz, $J_{5,6b} = 8.5$ Hz, $J_{5,6a} = 2.5$ Hz, H-5), 3.76 (bs, 2 H, CH₂N_{Cyst}), 3.75 (t, 2 H, H-4_{Man}), 3.69 (t, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 3.65 (t, 4 H, t, ³ $J_{H,H} = 6.0$ Hz, H-3_{Pent}), 3.63 (dd, 1 H, H-2), 3.52 (m, 8 H, H-1_{Pent}, CH₂N_{Branch}, CH₂OAll), 3.50 (s, 3 H, OMe), 3.39 (t, 1 H, H-4), 3.15 (dd, 1 H, $J_{6a,6b} = 14.0$ Hz, H-6a), 2.94 (t, 2 H, ³ $J_{H,H} = 6.5$ Hz, CH₂S_{Cyst}), 2.83, 2.81 (2 dt, 4 H, ² $J_{H,H} = 13.0$ Hz, ³ $J_{H,H} = 6.5$ Hz, H-5_{Pent}), 2.84 (dd, 1 H, H-6b), 1.99 (m, 4 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O, 313 K): $\delta = 182.5$ (CS), 134.5 (CH₂CH=), 118.1 (=CH₂), 99.4 (C-1), 85.7 (C-1_{Man}), 73.5 (C-5_{Man}), 73.3 (C-3), 73.8 (C-4), 72.6 (CH₂CH=), 72.1 (C-2_{Man}), 71.6 (C-2), 71.5 (C-3_{Man}), 71.2 (C-5), 70.6 (C-1_{Pent}, CH₂OAll), 70.3 (C-3_{Pent}), 67.3 (C-4_{Man}), 61.1 (C-6_{Man}), 55.4 (OMe), 44.4 (C_q, CH₂N_{Cyst}, CH₂N_{Branch}), 33.3 (C-6), 31.8 (CH₂S_{Cyst}), 28.9 (C-4_{Pent}), 28.0 (C-5_{Pent}). FABMS: m/z 865 [M + Na]⁺. Anal. Calcd. for C₃₆H₆₆N₂O₁₈S₄: C 45.84, H 7.05, N 2.97. Found: C 45.72, H 6.83, N 2.86.



Methyl 6-[2-[3-[2-[5-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylthio)-2-oxapentyl]-[2,2-bis[5-(2,3,4,6-tetra-O-acetyl- α -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (29): Compound **29** was obtained by coupling reaction of **24** (26.5 mg, 90 μ mol) and **16** (140 mg, 100 μ mol, 1.1 eq) following the procedure above described in the general methods. Yield: 90 mg (61%); R_f = 0.56 (45:5:3 AcOEt-EtOH-H₂O); $[\alpha]_D^{25}$ = + 95.1 (*c* 1.0, MeOH). ¹H NMR (500 MHz, CD₃OD): δ = 5.36 (d, 2 H, $J_{1,2}$ = 1.0 Hz, H-1_{Man}), 5.32 (dd, 2 H, $J_{2,3}$ = 3.0 Hz, H-2_{Man}), 5.27 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, H-3_{Glc}), 5.25 (t, 2 H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4_{Man}), 5.18 (dd, 2 H, H-3_{Man}), 5.01 (t, 1 H, $J_{4,5}$ = 10.0 Hz, H-4_{Glc}), 4.94 (t, 1 H, $J_{1,2}$ = 10.0 Hz, H-2_{Glc}), 4.73 (d, 1 H, H-1_{Glc}), 4.64 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.37 (ddd, 2 H, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 2.0 Hz, H-5_{Man}), 4.27 (dd, 2 H, $J_{6a,6b}$ = 12.0 Hz, H-6a_{Man}), 4.23 (dd, 1 H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.0 Hz, H-6a_{Glc}), 4.12 (dd, 1 H, $J_{5,6b}$ = 2.0 Hz, H-6_{Glc}), 4.10 (dd, 2 H, H-6b_{Man}), 3.90 (ddd, 1 H, H-5_{Glc}), 3.69 (m, 2 H, CH₂N_{Cyst}), 3.64 (bt, 1 H, $J_{4,5}$ = 8.5 Hz, $J_{5,6b}$ = 8.5 Hz, $J_{5,6a}$ = 2.0 Hz, H-5), 3.56 (1 H, t, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, H-3), 3.52, 3.51 (2 t, 6 H, ³ $J_{H,H}$ = 5.0 Hz, H-3_{Pent}), 3.42 (s, 3 H, OMe), 3.41 (s, 8 H, CH₂N_{Branch}, H-1_{Pent}), 3.38 (1 H, dd, H-2), 3.21 (t, 1 H, H-4), 3.01 (dd, 1 H, $J_{6a,6b}$ = 14.0 Hz, H-6a), 2.83 (t, 2 H, ³ $J_{H,H}$ = 7.0 Hz, CH₂S_{Cyst}), 2.79 (2 dt, 2 H, ² $J_{H,H}$ = 14.0 Hz, ³ $J_{H,H}$ = 7.0 Hz, H-5_{PentGlc}), 2.75 (m, 4 H, H-5_{PentMan}), 2.69 (dd, 1 H, H-6b), 2.14-1.91 (s, 36 H, MeCO), 1.90 (m, 8 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, CD₃OD): δ = 183.0 (CS), 172.3-171.1 (CO), 101.1 (C-1), 84.8 (C-1_{Glc}), 83.9 (C-1_{Man}), 76.7 (C-5_{Glc}), 75.3 (C-3_{Glc}), 75.1 (C-3), 74.6 (C-4), 73.6 (C-2, C-5), 72.3 (C-2_{Man}), 72.0 (C-1_{Pent}), 71.5 (C-2_{Glc}), 71.1 (C-3_{Man}), 70.9 (C-3_{PentGlc}), 70.7 (C-3_{PentMan}), 70.4 (C-5_{Man}), 69.9 (C-4_{Glc}), 67.5 (C-4_{Man}), 63.7 (C-6_{Man}), 63.4 (C-6_{Glc}), 55.2 (OMe), 45.6 (C_q, CH₂N_{Branch}, CH₂N_{Cyst}), 34.7 (C-6), 33.3 (CH₂S_{Cyst}), 31.2 (C-4_{PentGlc}), 30.7 (C-4_{PentMan}), 29.4 (C-5_{PentMan}), 28.3 (C-5_{PentGlc}), 20.9-20.6 (MeCO). FABMS: *m/z* 1665 [M + Na]⁺, 1643 [M]⁺. Anal. Calcd. for C₆₆H₁₀₂N₂O₃₅S₅: C 48.22, H 6.25, N 1.70. Found: C 47.97, H 6.19, N 1.70.

Methyl 6-deoxy-6-[2-[3-[2-[5-(β -D-glucopyranosylthio)-2-oxapentyl]-[2,2-bis[5-(α -D-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]- α -D-glucopyranoside (DiManGlc- α Me): Conventional Zemplen deacetylation of **29** (26.2 mg, 16 μ mol) gave **DiManGlc- α Me**. Yield: 18 mg (100%); $[\alpha]_D^{25}$ = + 83.0 (*c* 1.2, H₂O). ¹H NMR (500 MHz, 343 K, D₂O): δ = 5.65 (d, 2 H, $J_{1,2}$ = 1.5 Hz, H-1_{Man}), 5.14 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.86 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1_{Glc}), 4.41 (dd, 2 H, $J_{2,3}$ = 3.3 Hz, H-2_{Man}), 4.30 (ddd, 2 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6b}$ = 5.4 Hz, $J_{5,6a}$ = 2.2 Hz, H-5_{Man}), 4.24 (dd, 1 H, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.0 Hz, H-6a_{Glc}), 4.21 (dd, 2 H, $J_{6a,6b}$ = 12.4 Hz, H-6a_{Man}), 4.16 (dd, 2 H, H-6b_{Man}), 4.13 (dd, 2 H, $J_{3,4}$ = 9.5 Hz, H-3_{Man}), 4.08 (td, 1 H, $J_{4,5}$ = $J_{5,6b}$ = 8.5 Hz, $J_{5,6a}$ = 2.5 Hz, H-5), 4.07 (t, 2 H, H-4_{Man}), 4.08 (dd, 1 H, $J_{5,6b}$ = 4.0 Hz, H-6b_{Glc}), 4.04 (m, 2 H, CH₂N_{Cyst}), 4.03 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 3.95 (m, 6 H, H-3_{Pent}), 3.94 (s, 3 H, OMe), 3.92 (dd, 1 H, H-2), 3.86 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 8.4 Hz, H-3_{Glc}), 3.80 (m, 10 H, H-4_{Glc}, H-5_{Glc}, CH₂N_{Branch}, H-1_{Pent}), 3.70 (t, 1 H, H-4), 3.69 (t, 1 H, H-2_{Glc}), 3.45 (dd, 1 H, $J_{6a,6b}$ = 13.5 Hz, H-6a), 3.25 (t, 2 H, ³ $J_{H,H}$ = 6.6 Hz, CH₂S_{Cyst}), 3.15 (dd, 1 H, H-6b), 3.14, 3.10 (2 dt, 6 H, ² $J_{H,H}$ = 12.5 Hz, ³ $J_{H,H}$ = 7.0 Hz, H-5_{Pent}), 2.30 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O, 343 K): δ = 180.8 (CS), 99.9 (C-1), 86.1 (C-1_{Glc}), 85.6 (C-1_{Man}), 80.9 (C-5_{Glc}), 78.0 (C-3_{Glc}), 73.9 (C-5_{Man}), 73.7 (C-3), 73.3 (C-4), 72.9 (C-2_{Glc}), 72.5 (C-2_{Man}), 72.0 (C-2), 71.9 (C-3_{Man}), 71.7 (C-5), 71.1 (C-1_{Pent}), 70.7 (C-3_{PentGlc}), 70.6, (C-3_{PentMan}), 70.3 (C-4_{Glc}), 67.8 (C-4_{Man}), 61.7 (C-6_{Glc}), 61.6

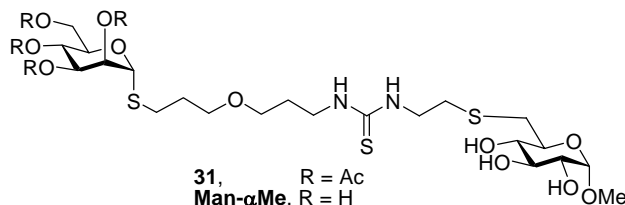
(C-6_{Man}), 46.7 (CH₂N_{Branch}, CH₂N_{Cyst}), 44.8 (C_q), 33.8 (C-6), 32.2 (CH₂S_{Cyst}), 30.0 (C-4_{PentGlc}), 29.4 (C-4_{PentMan}), 28.4 (C-5_{PentMan}), 27.4 (C-5_{PentGlc}). FABMS: *m/z* 1161 [M + Na]⁺. Anal. Calcd. for C₄₂H₇₈N₂O₂₃S₅: C 44.27, H 6.90, N 2.46. Found: C 43.94, H 6.81, N 2.17.



Methyl 6-[2-[3-[2,2-bis[5-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)-2-oxapentyl]-2-[5-(2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]-α-*D*-glucopyranoside (30): Compound **30** was obtained by coupling reaction of **24** (17 mg, 59 μmol) and **19** (90 mg, 65 μmol, 1.1 eq) following the procedure above described in the general methods. Yield: 33 mg (34%); *R_f* = 0.55 (10:1:1 MeCN-H₂O-NH₄OH); [α]_D = + 21.9 (*c* 1.0, H₂O). ¹H NMR (500 MHz, CD₃OD, 313 K): δ = 5.36 (d, 1 H, *J*_{1,2} = 1.5 Hz, H-1_{Man}), 5.32 (dd, 1 H, *J*_{2,3} = 3.4 Hz, H-2_{Man}), 5.26 (t, 2 H, *J*_{2,3} = *J*_{3,4} = 9.3 Hz, H-3_{Glc}), 5.25 (t, 1 H, *J*_{3,4} = *J*_{4,5} = 10.0 Hz, H-4_{Man}), 5.19 (dd, 1 H, H-3_{Man}), 5.01 (t, 2 H, *J*_{4,5} = 10.0 Hz, H-4_{Glc}), 4.93 (t, 2 H, *J*_{1,2} = 10.1 Hz, H-2_{Glc}), 4.76 (d, 2 H, H-1_{Glc}), 4.64 (d, 1 H, *J*_{1,2} = 3.7 Hz, H-1), 4.37 (ddd, 1 H, *J*_{5,6a} = 5.1 Hz, *J*_{5,6b} = 2.5 Hz, H-5_{Man}), 4.24 (dd, 1 H, *J*_{6a,6b} = 12.2 Hz, H-6a_{Man}), 4.23 (dd, 2 H, *J*_{6a,6b} = 12.3 Hz, *J*_{5,6a} = 4.9 Hz, H-6a_{Glc}), 4.13 (dd, 2 H, *J*_{5,6b} = 2.5 Hz, H-6b_{Glc}), 4.12 (dd, 1 H, H-6b_{Man}), 3.88 (ddd, 2 H, H-5_{Glc}), 3.69 (m, 2 H, CH₂N_{Cyst}), 3.64 (ddd, 1 H, *J*_{4,5} = 9.5 Hz, *J*_{5,6b} = 8.0 Hz, *J*_{5,6a} = 2.0 Hz, H-5), 3.56 (t, 1 H, *J*_{2,3} = *J*_{3,4} = 9.4 Hz, H-3), 3.51, 3.50 (2 t, 6 H, ³*J*_{H,H} = 5.9 Hz, H-3_{Pent}), 3.42 (s, 3 H, OMe), 3.40 (8 H, s, CH₂N_{Branch}, H-1_{Pent}), 3.39 (1 H, dd, H-2), 3.22 (1 H, t, H-4), 3.02 (1 H, dd, *J*_{6a,6b} = 14.0 Hz, H-6a), 2.84 (t, 2 H, ³*J*_{H,H} = 6.6 Hz, CH₂S_{Cyst}), 2.82, 2.74 (2 dt, 6 H, ²*J*_{H,H} = 13.1 Hz, ³*J*_{H,H} = 6.7 Hz, H-5_{Pent}), 2.70 (dd, 1 H, H-6b), 2.06-1.95 (s, 36 H, MeCO), 1.88 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, CD₃OD, 313 K): δ = 183.0 (CS), 171.3-171.1 (CO), 101.2 (C-1), 84.9 (C-1_{Glc}), 83.9 (C-1_{Man}), 76.8 (C-5_{Glc}), 75.4 (C-3_{Glc}), 75.2 (C-3), 74.6 (C-4), 73.7 (C-2), 73.6 (C-5), 72.4 (C-2_{Man}), 72.1 (C-1_{Pent}), 71.7 (C-2_{Glc}), 71.2 (C-3_{Man}), 71.0 (C-3_{PentGlc}), 70.9 (C-3_{PentMan}), 70.5 (C-5_{Man}), 70.0 (C-4_{Glc}), 67.7 (C-4_{Man}), 63.8 (C-6_{Man}), 63.5 (C-6_{Glc}), 55.7 (OMe), 45.7 (C_q), 45.6 (CH₂N_{Branch}, CH₂N_{Cyst}), 34.8 (C-6), 33.4 (CH₂S_{Cyst}), 31.2 (C-4_{PentGlc}), 30.8 (C-4_{PentMan}), 29.4 (C-5_{PentMan}), 28.3 (C-5_{PentGlc}), 20.8-20.5 (MeCO). FABMS: *m/z* 1161 [M + Na]⁺. Anal. Calcd. for C₆₆H₁₀₂N₂O₃₅S₅: C 48.22, H 6.25, N 1.70. Found: C 48.01, H 6.20, N 1.57.

Methyl 6-[2-[3-[2,2-bis[5-(β-*D*-glucopyranosylthio)-2-oxapentyl]-2-[5-(α-*D*-mannopyranosylthio)-2-oxapentyl]ethyl]thioureido]ethylthio]-α-*D*-glucopyranoside (ManDiGlc-αMe): Conventional Zemplen deacetylation of **30** (30 mg, 18.2 μmol) gave **ManDiGlc-αMe**. Yield: 21 mg (100%); *R_f* = 0.35 (6:3:1 MeCN-H₂O-NH₄OH); [α]_D = + 1.0 (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O, 333 K): δ = 5.59 (bs, 1 H, H-1_{Man}), 5.07 (d, 1 H, *J*_{1,2} = 3.5 Hz, H-1), 4.79 (d, 2 H, *J*_{1,2} = 9.5 Hz, H-1_{Glc}), 4.34 (bd, 1 H, *J*_{2,3} = 3.5 Hz, H-2_{Man}), 4.24 (ddd, 1 H, *J*_{4,5} = 9.5 Hz, *J*_{5,6b} = 5.5 Hz, *J*_{5,6a} = 2.0 Hz, H-5_{Man}), 4.17 (dd, 2 H, *J*_{6a,6b} = 12.0 Hz, *J*_{5,6a} = 2.0 Hz, H-6a_{Glc}), 4.13 (dd, 1 H, *J*_{6a,6b} = 11.5 Hz, H-6a_{Man}), 4.10 (dd, 1 H, H-6b_{Man}), 4.07 (dd, 1 H, *J*_{3,4} = 9.5 Hz, H-3_{Man}), 4.02 (ddd, 1 H, *J*_{4,5} = 9.0 Hz, *J*_{5,6b} = 7.0 Hz, *J*_{5,6a} = 2.5 Hz, H-5), 4.00 (dd, 2 H, *J*_{5,6b} = 3.5 Hz, H-6b_{Glc}), 3.99 (t, 1 H, H-4_{Man}), 3.98 (m, 2 H, CH₂N_{Cyst}), 3.93 (t, 1 H, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H-3), 3.88 (m, 6 H, H-3_{Pent}), 3.85 (dd, 1 H, H-2), 3.78 (t, 2 H, *J*_{2,3} = *J*_{3,4} = 9.2 Hz, H-3_{Glc}), 3.75 (m, 8 H, H-1_{Pent}, CH₂N_{Branch}), 3.74 (s, 3 H, OMe), 3.72 (m, 4 H, H-4_{Glc}, H-5_{Glc}), 3.63 (t, 1 H, H-4), 3.62 (t,

2 H, H-2_{Glc}), 3.38 (dd, 1 H, $J_{6a,6b}$ = 13.0 Hz, H-6a), 3.18 (t, 2 H, $^3J_{H,H}$ = 6.5 Hz, CH₂S_{Cyst}), 3.14, 3.09 (2 dt, 6 H, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 6.5 Hz, H-5_{Pent}), 3.07 (dd, 1 H, H-6b), 1.83 (m, 6 H, H-4_{Pent}). ¹³C NMR (125.7 MHz, D₂O, 333 K): δ = 181.0 (CS), 99.7 (C-1), 86.0 (C-1_{Glc}), 85.5 (C-1_{Man}), 80.4 (C-5_{Glc}), 77.9 (C-3_{Glc}), 73.8 (C-5_{Man}), 73.6 (C-3), 73.2 (C-4), 72.9 (C-2_{Glc}), 72.4 (C-2_{Man}), 71.9 (C-2), 71.8 (C-3_{Man}), 71.6 (C-5), 71.0 (C-1_{Pent}), 70.6 (C-3_{Pent}), 70.2 (C-4_{Glc}), 67.6 (C-4_{Man}), 61.6 (C-6_{Glc}), 61.4 (C-6_{Man}), 55.7 (OMe), 44.7 (C_q), 44.2 (CH₂N_{Branch}, CH₂N_{Cyst}), 33.7 (C-6), 32.1 (CH₂S_{Cyst}), 29.9 (C-4_{PentGlc}), 29.3 (C-4_{PentMan}), 28.3 (C-5_{PentMan}), 27.3 (C-5_{PentGlc}). FABMS: m/z 1161 [M + Na]⁺. Anal. Calcd. for C₄₂H₇₈N₂O₂₃S₅: C 44.27, H 6.90, N 2.46. Found: C 44.19, H 6.60, N 2.26.



Methyl 6-[2-[3-[7-(2,3,4,6-tetra-O-acetyl- α -D-mannopyranosylthio)-4-oxaheptyl]thioureido]-ethylthio]- α -D-glucopyranoside (31): Compound **31** was obtained by coupling reaction of **24** (18.4 mg, 63.5 μ mol, 1.1 eq) and **23** (30.1 mg, 57.7 μ mol) following the procedure above described in the general methods. Yield: 32.7 mg (73%); R_f = 0.41 (45:5:3 AcOEt-EtOH-H₂O); $[\alpha]_D$ = + 89.0 (*c* 1.0, MeOH). ¹H NMR (500 MHz, CD₃OD): δ = 5.36 (d, 1 H, $J_{1,2}$ = 1.5 Hz, H-1_{Man}), 5.32 (dd, 1 H, $J_{2,3}$ = 3.0 Hz, H-2_{Man}), 5.25 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4_{Man}), 5.22 (dd, 1 H, H-3_{Man}), 4.65 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.37 (ddd, 1 H, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 2.0 Hz, H-5_{Man}), 4.27 (dd, 1 H, $J_{6a,6b}$ = 12.0 Hz, H-6a_{Man}), 4.11 (dd, 1 H, H-6b_{Man}), 3.68 (m, 2 H, CH₂N_{Cyst}), 3.64 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 8.0 Hz, $J_{5,6a}$ = 2.5 Hz, H-5), 3.57 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10.0 Hz, H-5), 3.54 (t, 2 H, $^3J_{H,H}$ = 6.0 Hz, H-5_{Hept}), 3.50 (t, 2 H, $^3J_{H,H}$ = 6.0 Hz, H-3_{Hept}), 3.48 (m, 2 H, H-1_{Hept}), 3.42 (s, 3 H, OMe), 3.39 (dd, 1 H, H-2), 3.22 (t, 1 H, H-4), 3.01 (dd, 1 H, $J_{6a,6b}$ = 14.0 Hz, H-6a), 2.82 (t, 2 H, $^3J_{H,H}$ = 6.5 Hz, CH₂S_{Cyst}), 2.78, 2.76 (2 dt, 2 H, $^2J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.0 Hz, H-7_{Hept}), 2.69 (dd, 1 H, H-6b), 2.14, 2.06, 2.05, 2.00 (4 s, 12 H, MeCO), 1.91 (m, 2 H, H-6_{Hept}), 1.82 (m, 2 H, H-2_{Hept}). ¹³C NMR (125.7 MHz, CDCl₃): δ = 182.1 (CS), 172.0-171.5 (CO), 101.1 (C-1), 83.8 (C-1_{Man}), 75.0 (C-3), 74.6 (C-4), 73.6 (C-2), 73.5 (C-5), 72.3 (C-2_{Man}), 71.1 (C-3_{Man}), 70.4 (C-5_{Man}), 70.1 (C-5_{Hept}), 69.7 (C-3_{Hept}), 67.5 (C-4_{Man}), 63.7 (C-6_{Man}), 55.6 (OMe), 45.0 (CH₂N_{Cyst}), 42.5 (C-1_{Hept}), 34.6 (C-6), 33.3 (CH₂S_{Cyst}), 30.8 (C-6_{Hept}), 30.5 (C-2_{Hept}), 29.2 (C-7_{Hept}), 20.8-20.0 (MeCO). FABMS: m/z 797 [M + Na]⁺. Anal. Calcd. for C₃₀H₅₀N₂O₁₅S₃: C 46.50, H 6.50, N 3.62. Found: C 46.53, H 6.47, N 3.52.

Methyl 6-[2-[3-[7-(α -D-mannopyranosylthio)-4-oxaheptyl]thioureido]ethylthio]- α -D-glucopyranoside (Man- α Me). Conventional Zemplen deacetylation of **31** (29.6 mg, 38.2 μ mol) gave **Man- α Me**. Yield: 23 mg (100%); R_f = 0.67 (6:3:1 MeCN-H₂O-NH₄OH); $[\alpha]_D$ = + 113.5 (*c* 1.0, H₂O). ¹H NMR (500 MHz, D₂O, 313 K): δ = 5.35 (d, 1 H, $J_{1,2}$ = 1.5 Hz H-1_{Man}), 4.84 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1), 4.11 (dd, 1 H, $J_{2,3}$ = 3.2 Hz, H-2_{Man}), 4.03 (ddd, 1 H, $J_{4,5}$ = 9.4 Hz, $J_{5,6b}$ = 5.8 Hz, $J_{5,6a}$ = 2.1 Hz, H-5_{Man}), 3.92 (dd, 1 H, $J_{6a,6b}$ = 12.3 Hz, H-6a_{Man}), 3.85 (dd, 1 H, H-6b_{Man}), 3.84 (dd, 1 H, $J_{3,4}$ = 9.6 Hz, H-3_{Man}), 3.80 (ddd, 1 H, $J_{4,5}$ = 9.9 Hz, $J_{5,6b}$ = 8.0 Hz, $J_{5,6a}$ = 2.3 Hz, H-5), 3.75 (m, 2 H, CH₂N_{Cyst}), 3.74 (t, 1 H, H-4_{Man}), 3.69 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, H-3), 3.66 (t, 2 H, $^3J_{H,H}$ = 6.5 Hz, H-5_{Hept}), 3.64 (dd, 1 H, H-2), 3.63 (t, 2 H, $^3J_{H,H}$ = 6.3 Hz, H-3_{Hept}), 3.53 (m, 2 H, H-1_{Hept}), 3.41 (s, 3 H, OMe), 3.40 (t, 1 H, H-4), 3.15 (dd, 1 H, $J_{6a,6b}$ = 14.0 Hz, H-6a), 2.94 (t, 2 H, $^3J_{H,H}$ = 6.7 Hz, CH₂S_{Cyst}), 2.84 (dd, 1 H, H-6b), 2.82, 2.77 (2 dt, 2 H, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 6.2 Hz, H-7_{Hept}), 2.32 (m, 2 H, H-6_{Hept}), 1.92 (m, 2 H, H-2_{Hept}). ¹³C NMR (125.7 MHz, D₂O, 313 K): δ = 179.5 (CS), 99.4 (C-1), 85.1 (C-1_{Man}), 73.5 (C-5_{Man}), 73.2 (C-3), 72.8 (C-4), 72.1 (C-2_{Man}), 71.5 (C-2), 71.4 (C-3_{Man}), 71.1 (C-5), 69.2 (C-5_{Hept}), 68.2 (C-3_{Hept}), 67.3 (C-4_{Man}), 61.1 (C-6_{Man}), 55.4 (OMe), 43.6 (CH₂N_{Cyst}), 41.2 (C-1_{Hept}),

33.2 (C-6), 31.7 (CH₂S_{Cyst}), 28.9 (C-6_{Hept}), 28.3 (C-2_{Hept}), 27.8 (C-7_{Hept}). FABMS: m/z 629 [M + Na]⁺. Anal. Calcd. for C₂₂H₄₂N₂O₁₁S₃: C 43.55, H 6.98, N 4.62. Found: C 43.50, H 6.86, N, 4.50.

^1H and ^{13}C NMR Spectra for New Compounds.

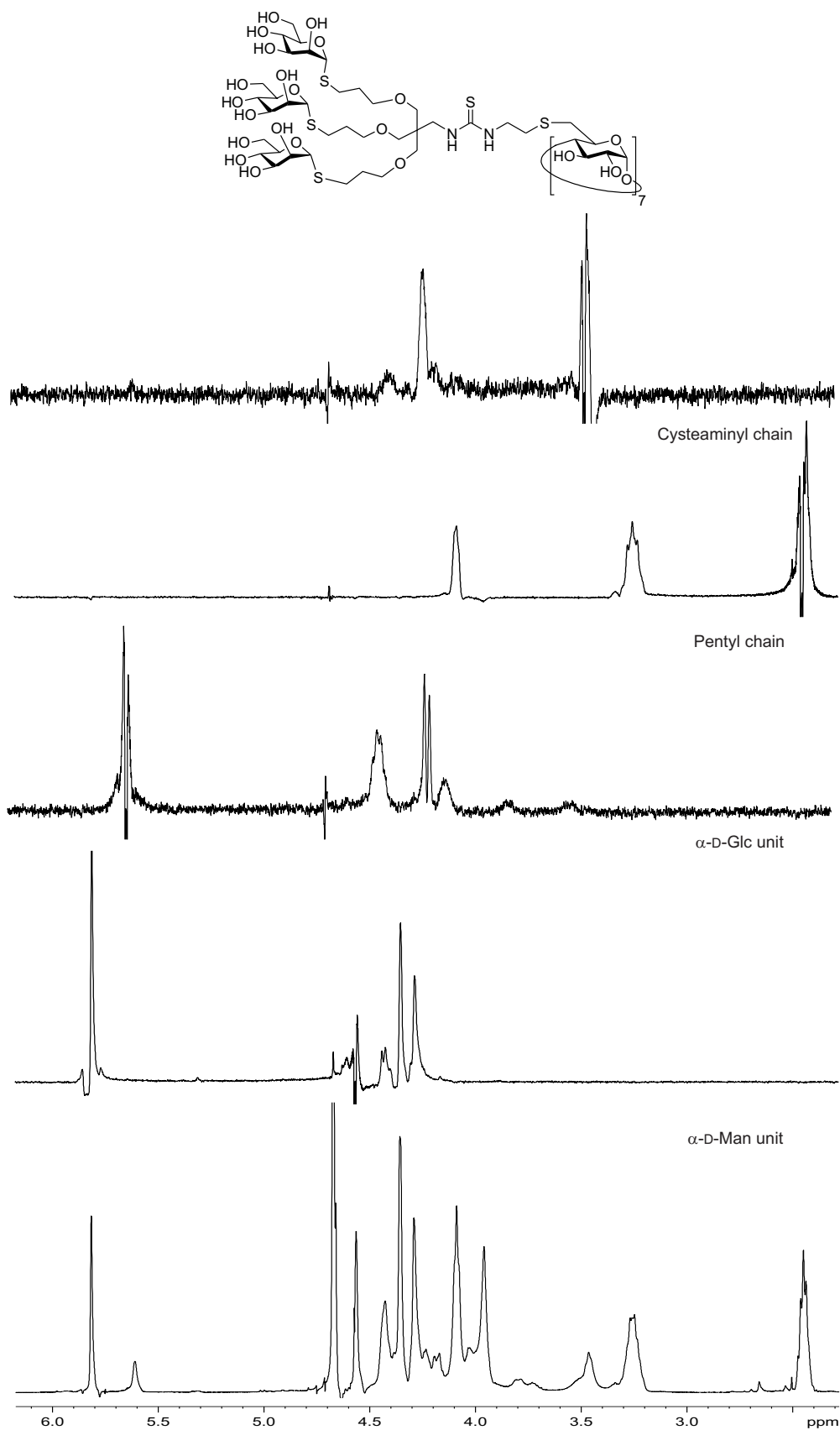


Figure 1. ^1H NMR and 1D TOCSY (500 MHz, D₂O, 353 K) spectra of compound TriMan- β CD.

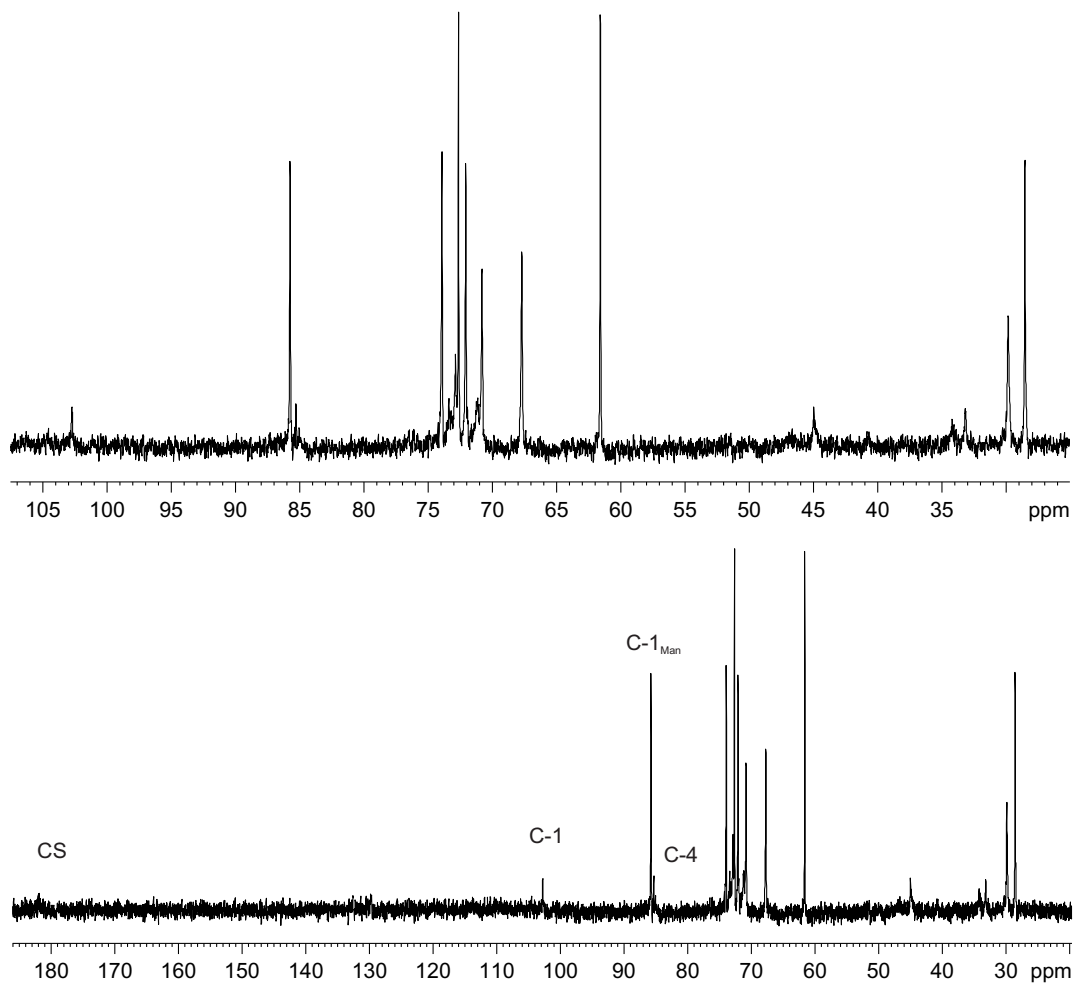
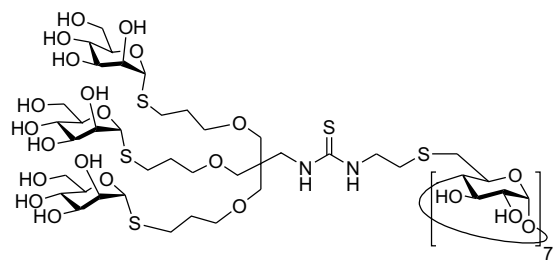


Figure 2. ^{13}C NMR (125.7 MHz, D_2O , 343 K) spectrum of compound **TriMan- β CD**.

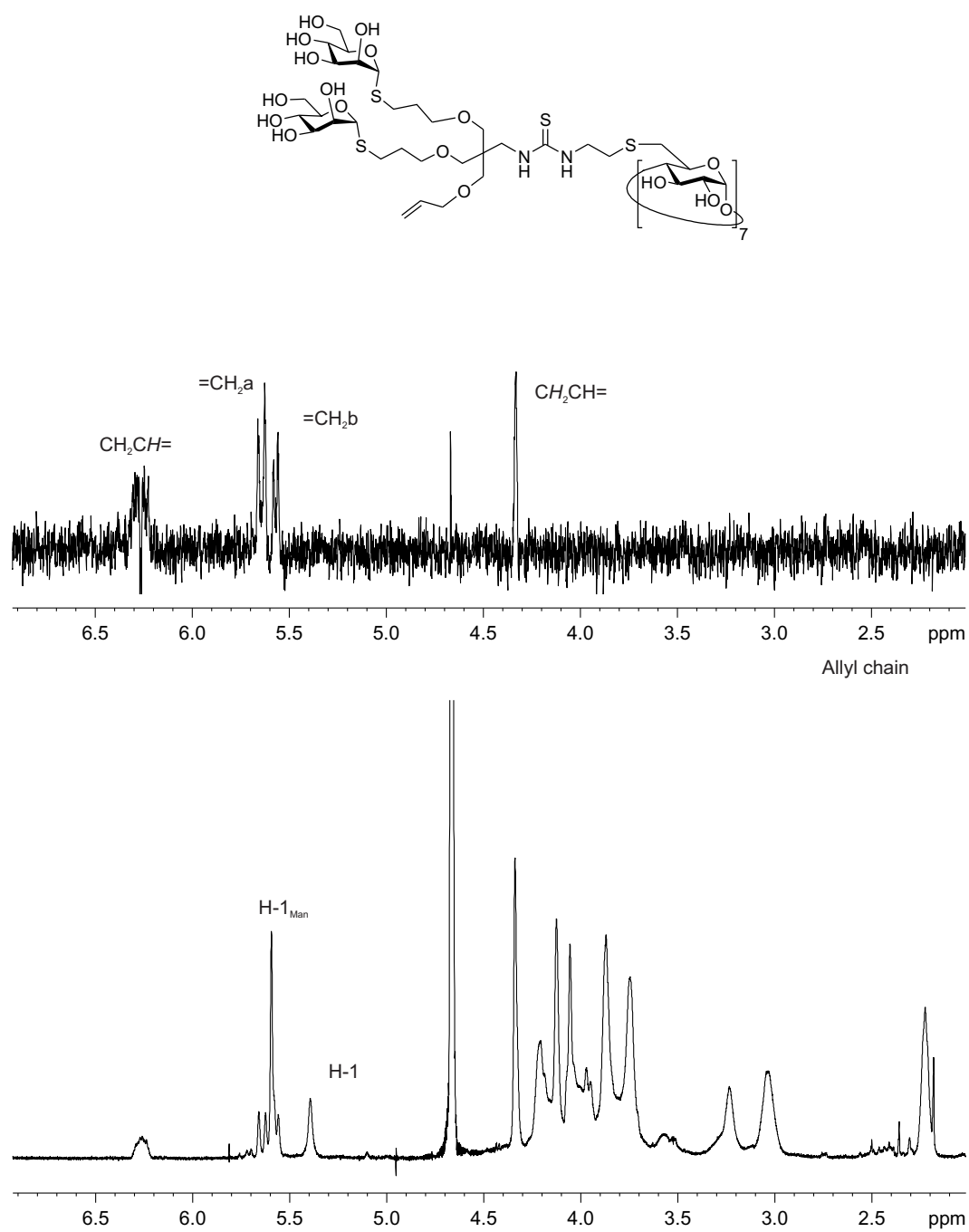


Figure 3. ¹H NMR and 1D TOCSY (500 MHz, D₂O, 333 K) spectra of compound **DiMan-βCD**.

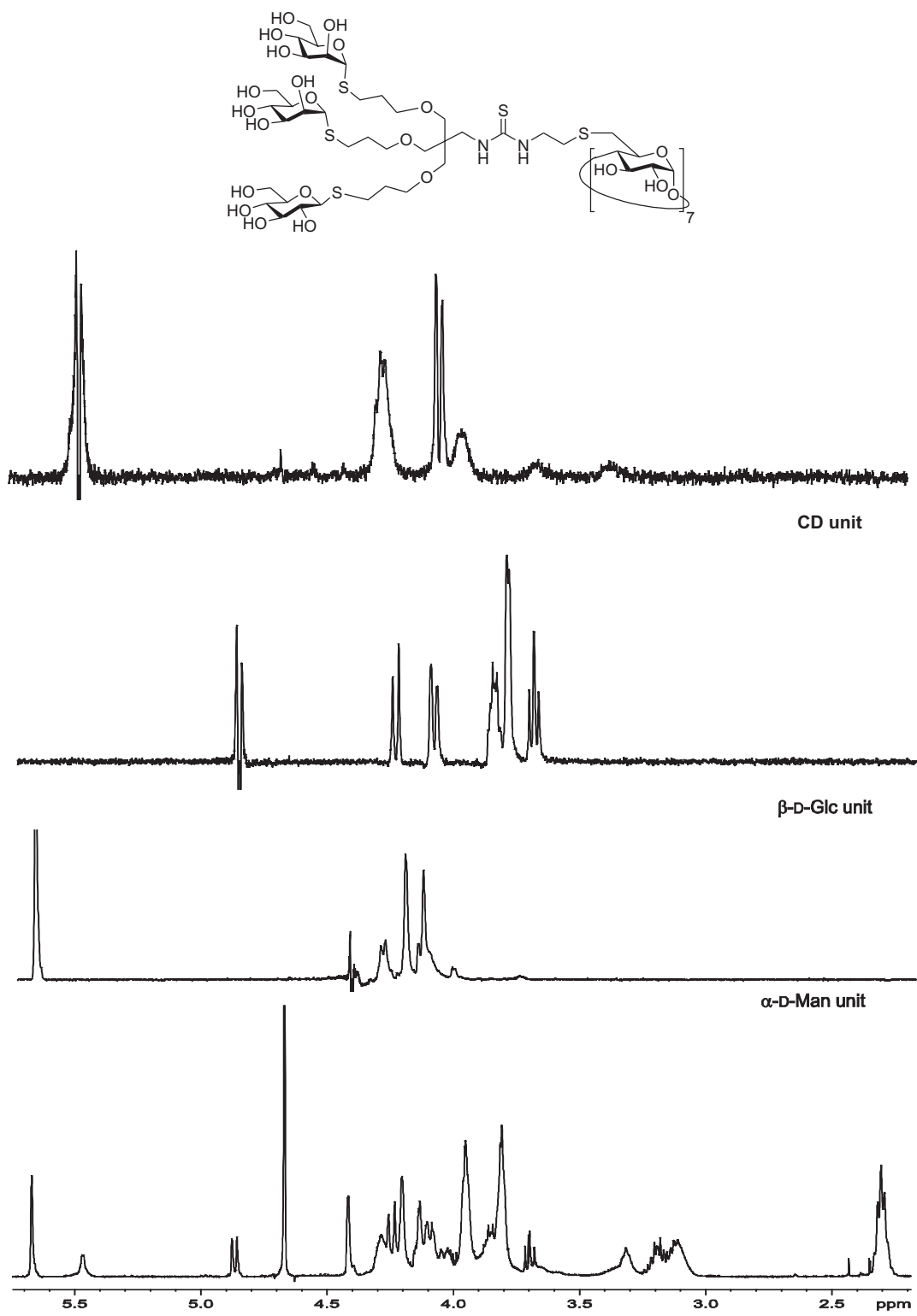


Figure 4. ¹H NMR and 1D TOCSY (500 MHz, D₂O, 353 K) spectra of compound DiManGlc-βCD.

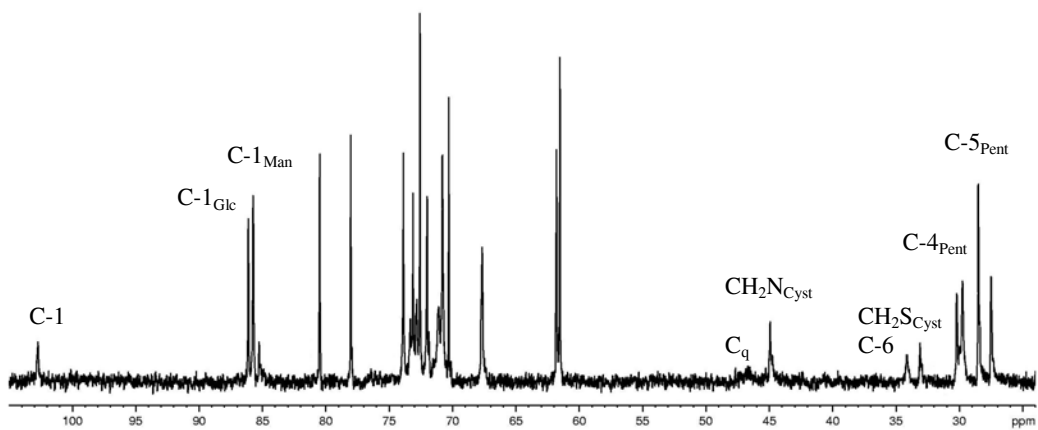
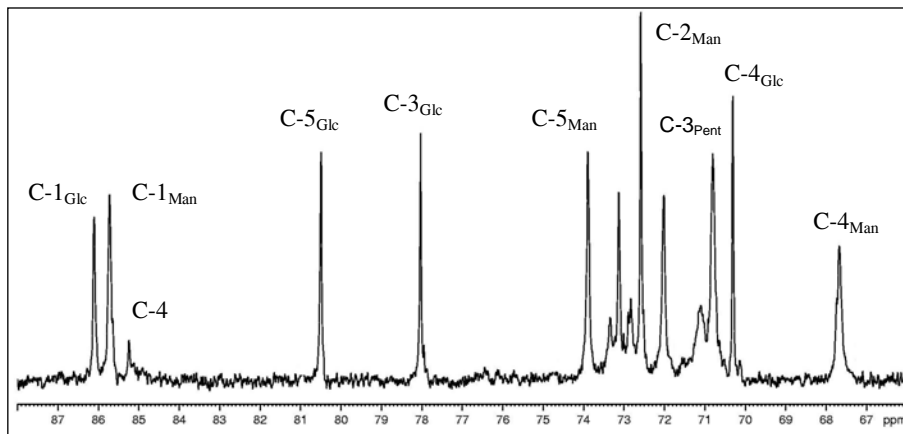
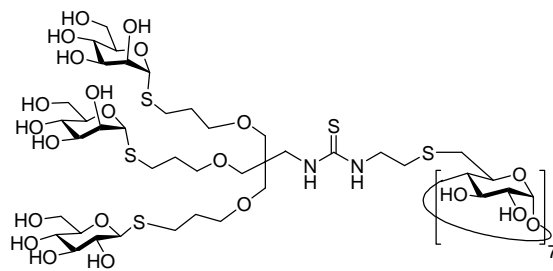


Figure 5. ^{13}C NMR (125.7 MHz, D_2O , 353 K) spectrum of compound DiManGlc- β CD.

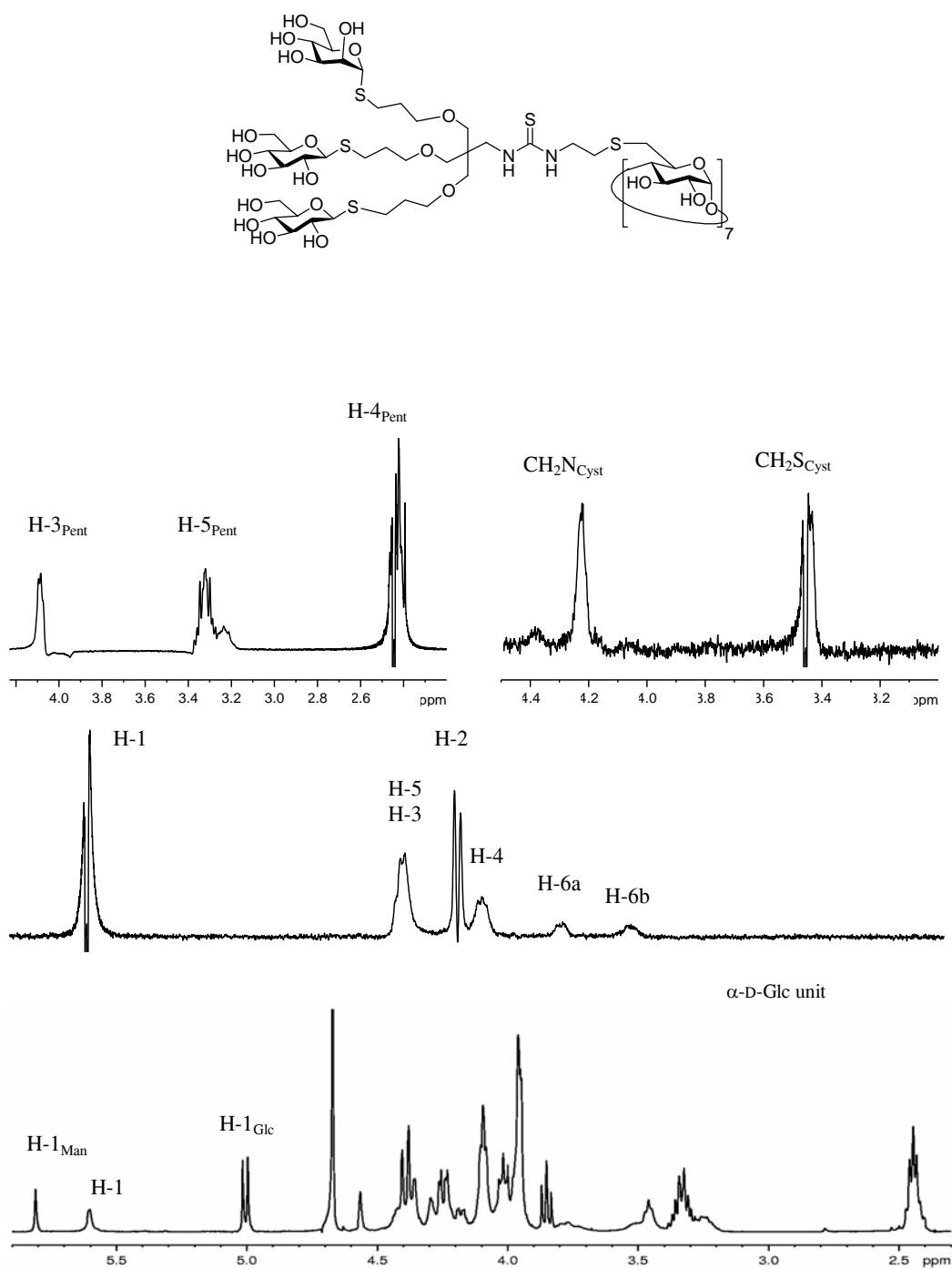


Figure 6. ¹H NMR and 1D TOCSY (500 MHz, D₂O, 353 K) spectra of compound **ManDiGlc-βCD**.

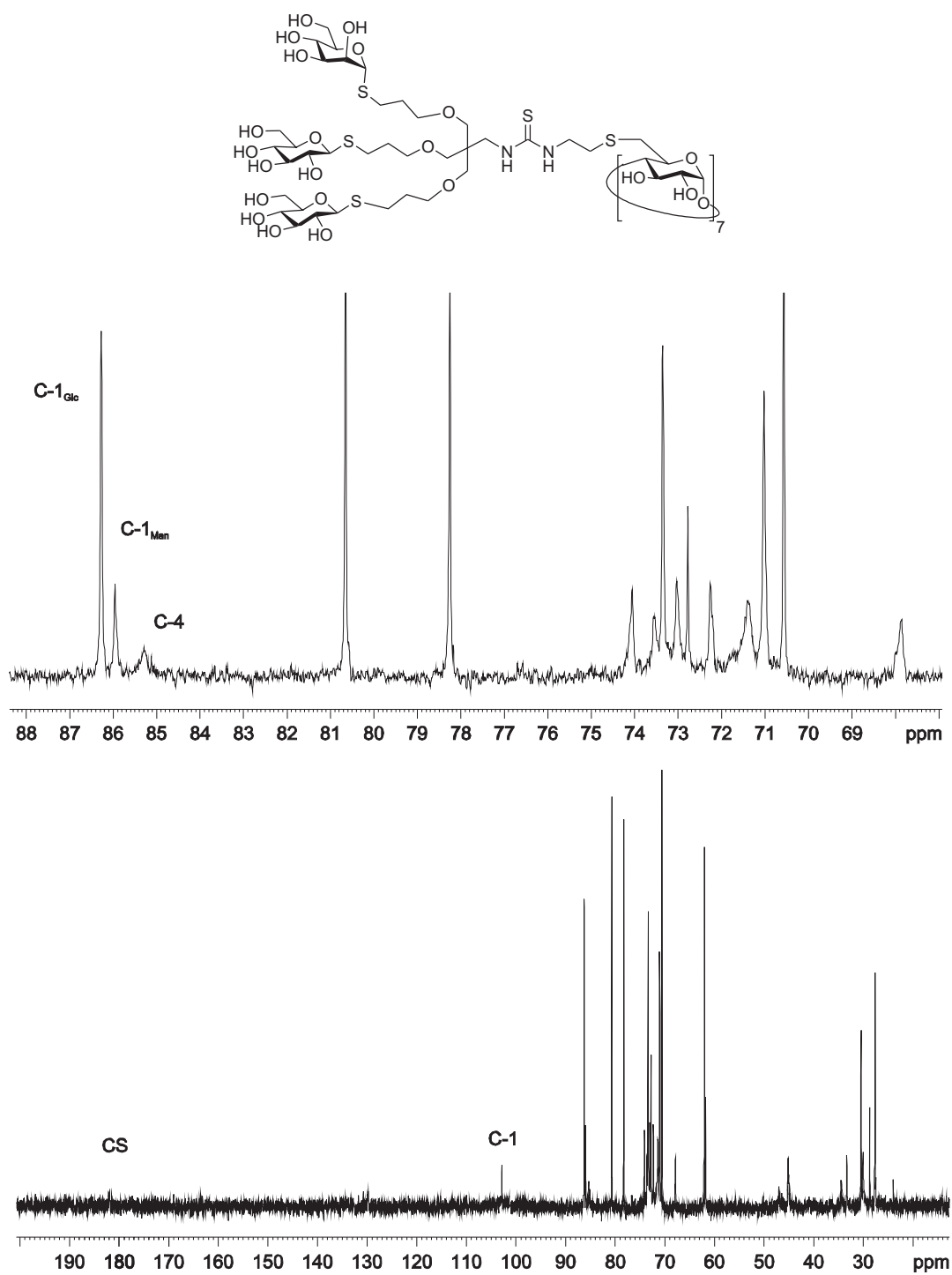


Figure 7. ^{13}C NMR (125.7 MHz, D_2O , 353 K) spectrum of compound **ManDiGlc-βCD**.

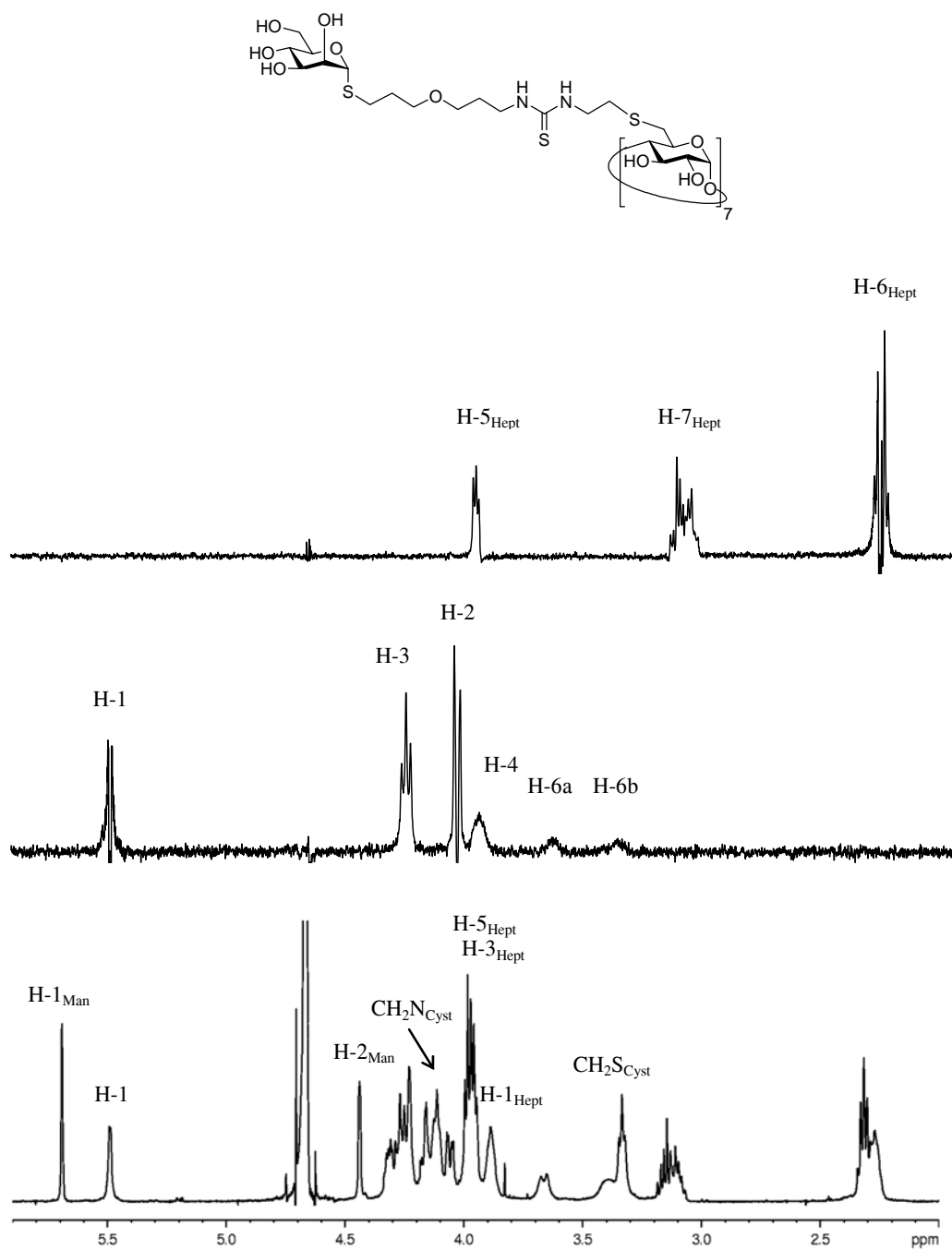


Figure 8. ¹H NMR and 1D TOCSY (500 MHz, D₂O, 343 K) spectra of compound **Man-βCD**.

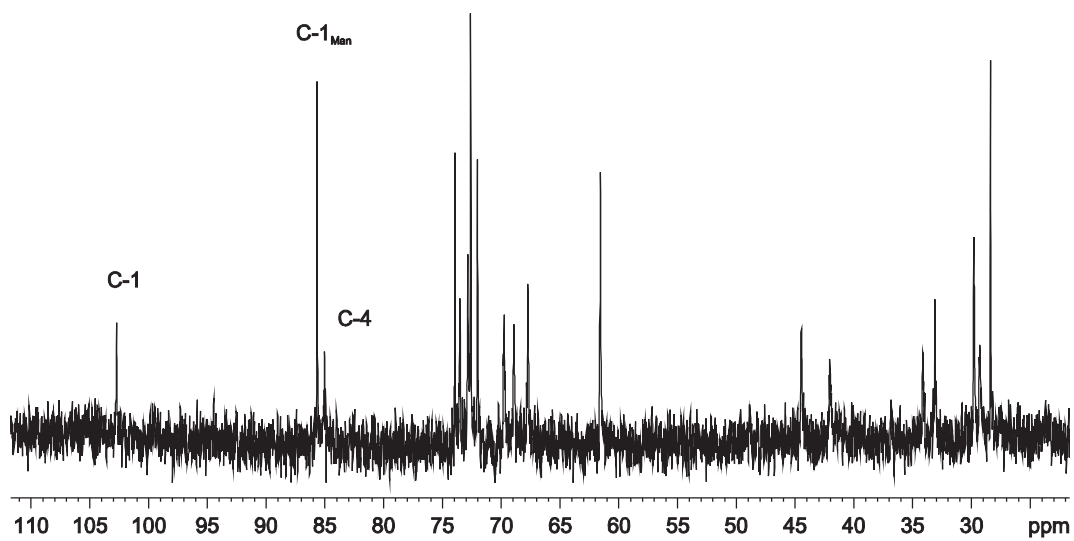
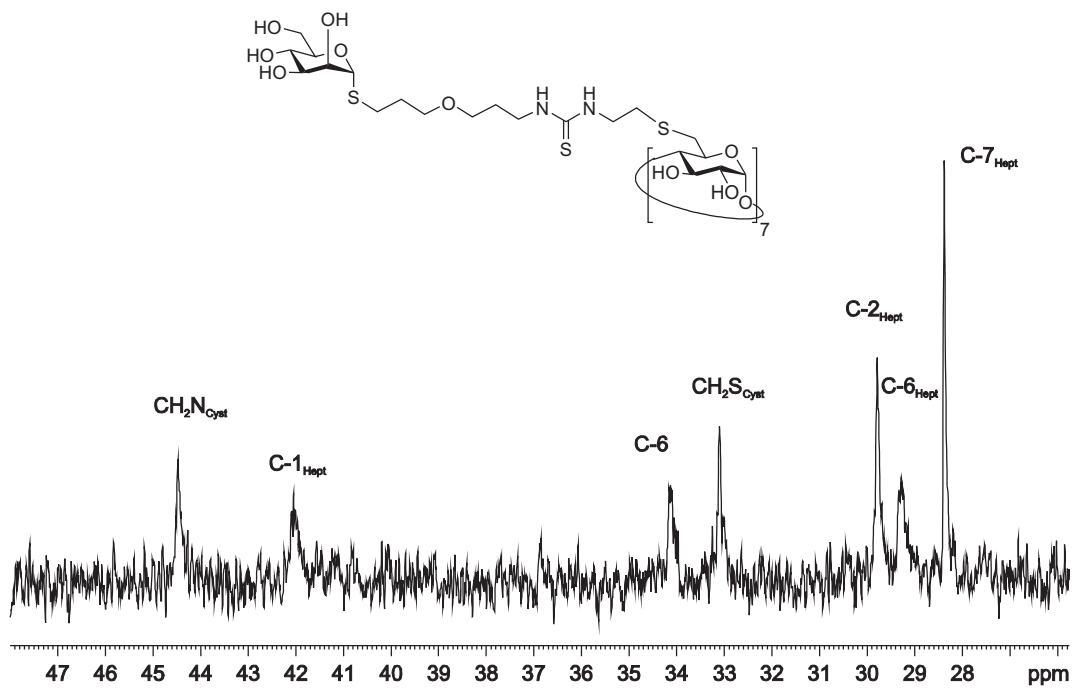


Figure 9. ¹³C NMR (125.7 MHz, D₂O, 343 K) spectrum of compound Man-β-CD.

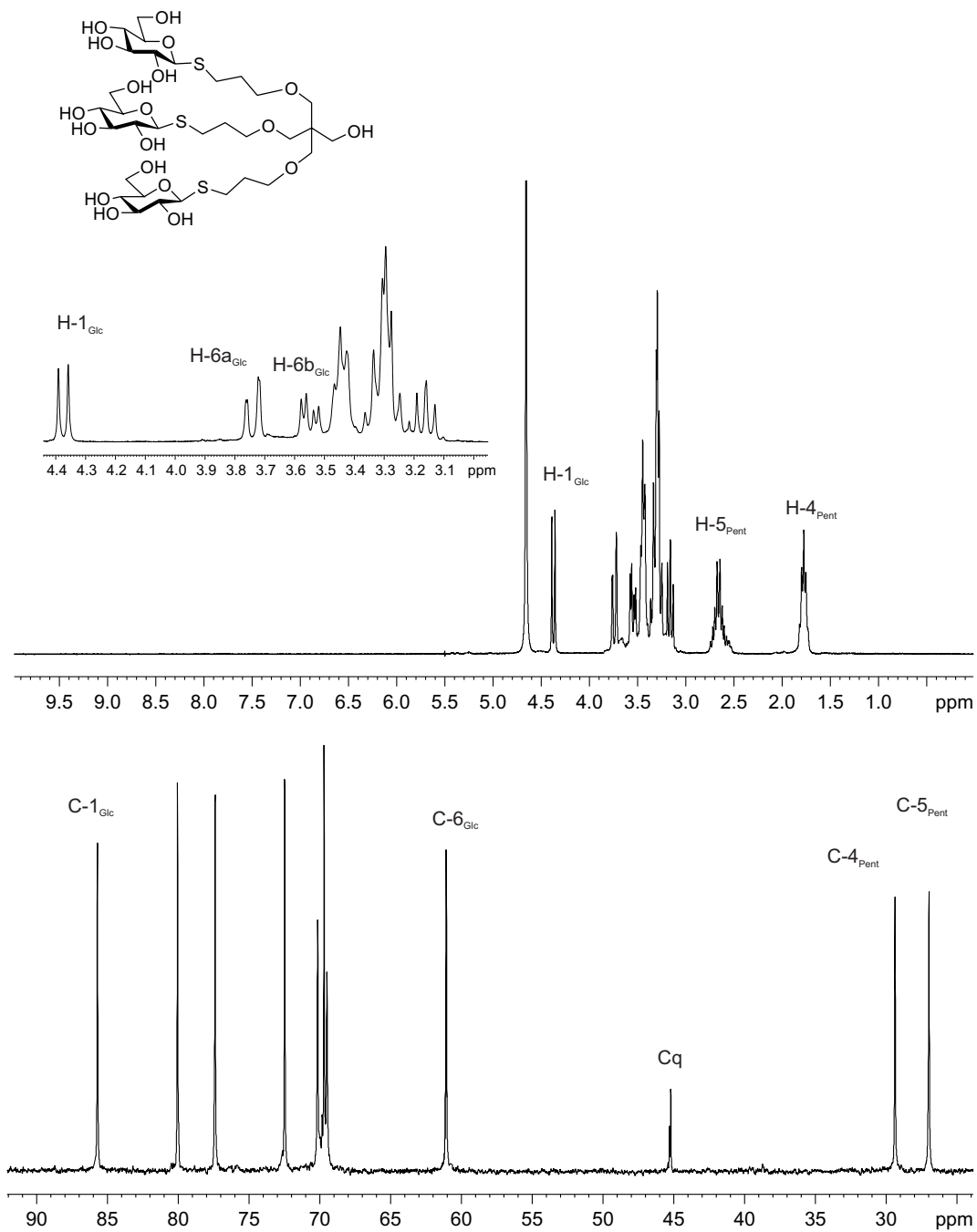


Figure 10. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O) spectra of compound TriGlc-OH.

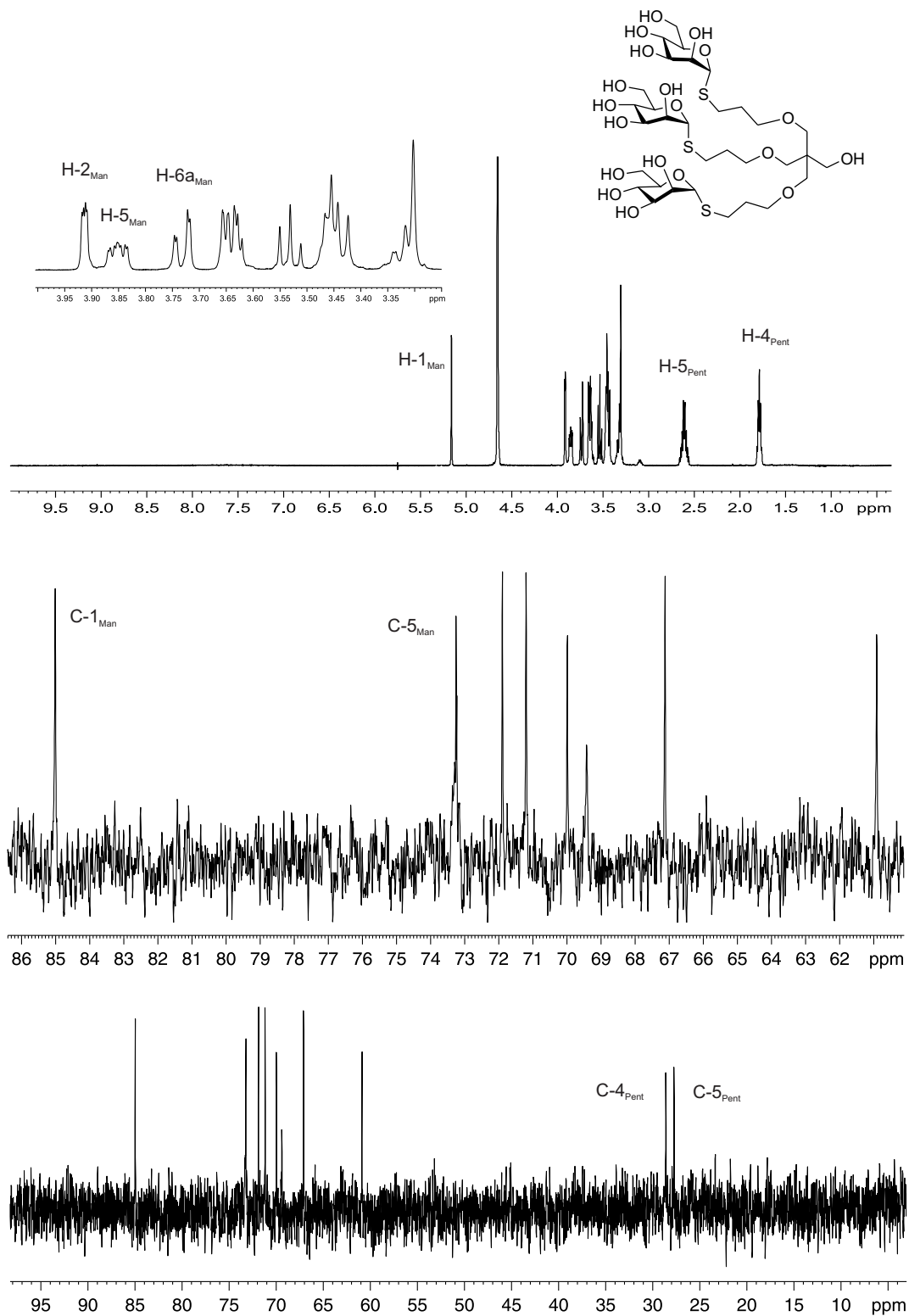


Figure 11. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O) spectra of compound **TriMan-OH**.

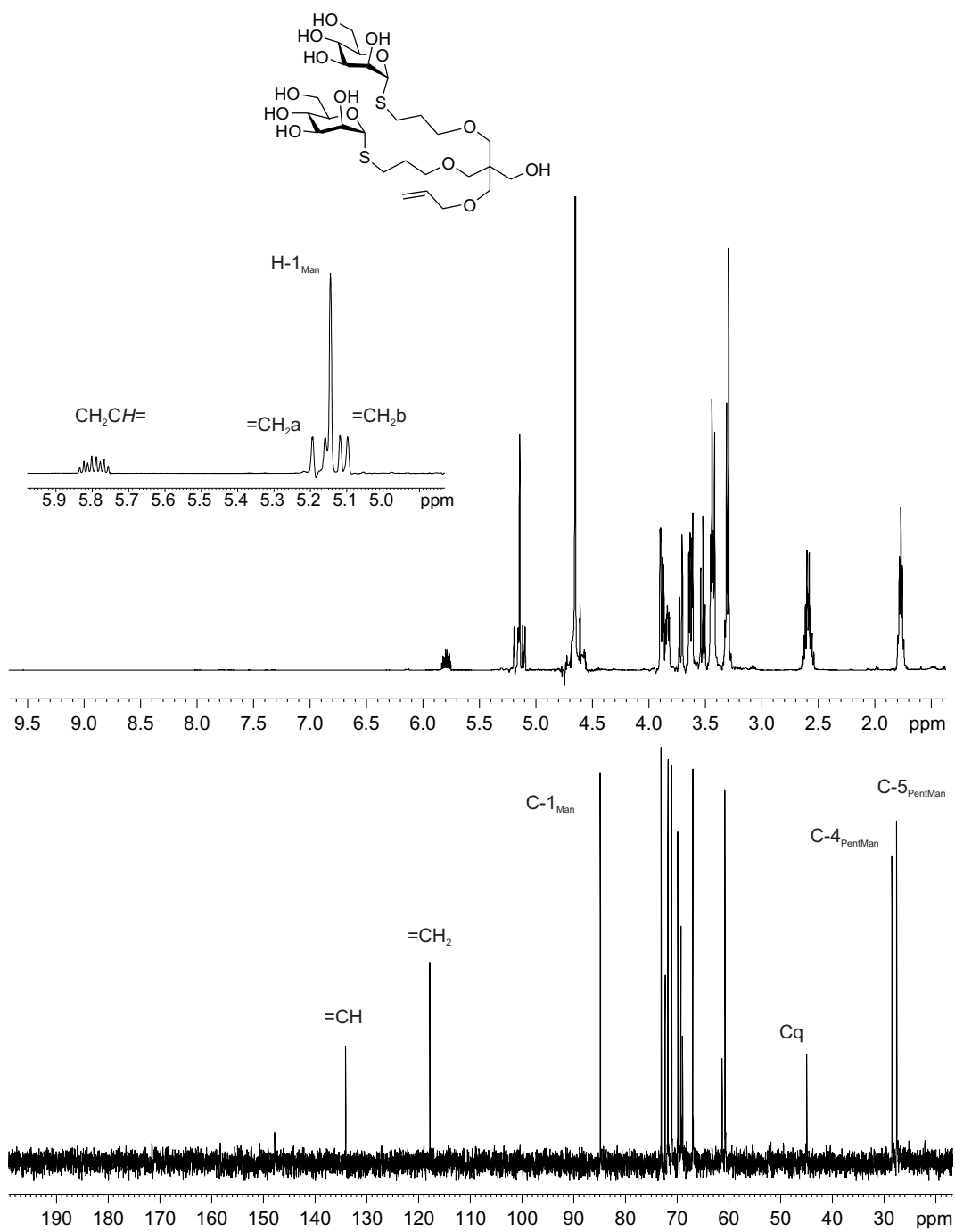


Figure 12. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O) spectra of compound **DiMan-OH**.

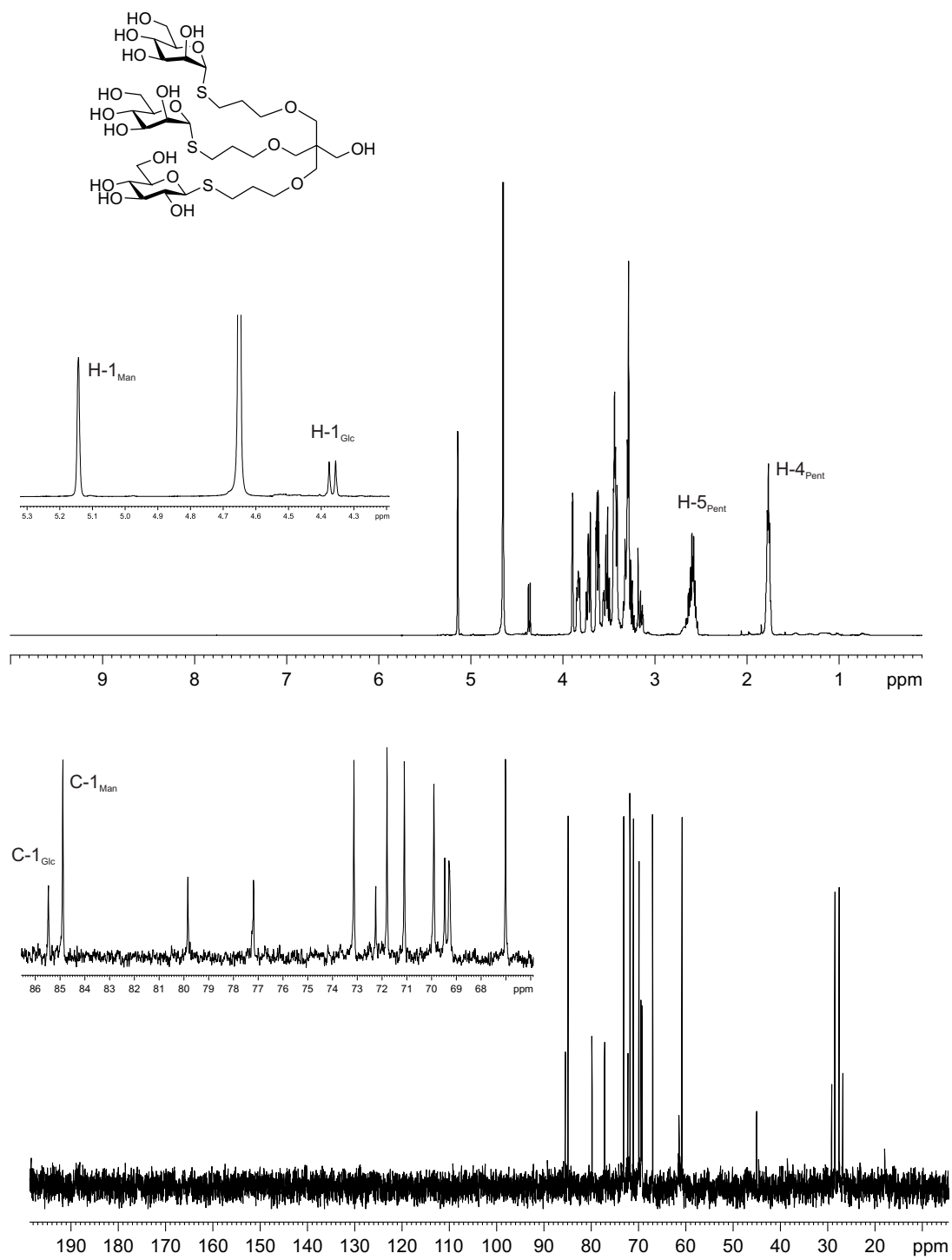


Figure 13. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O) spectra of compound **DiManGlc-OH**.

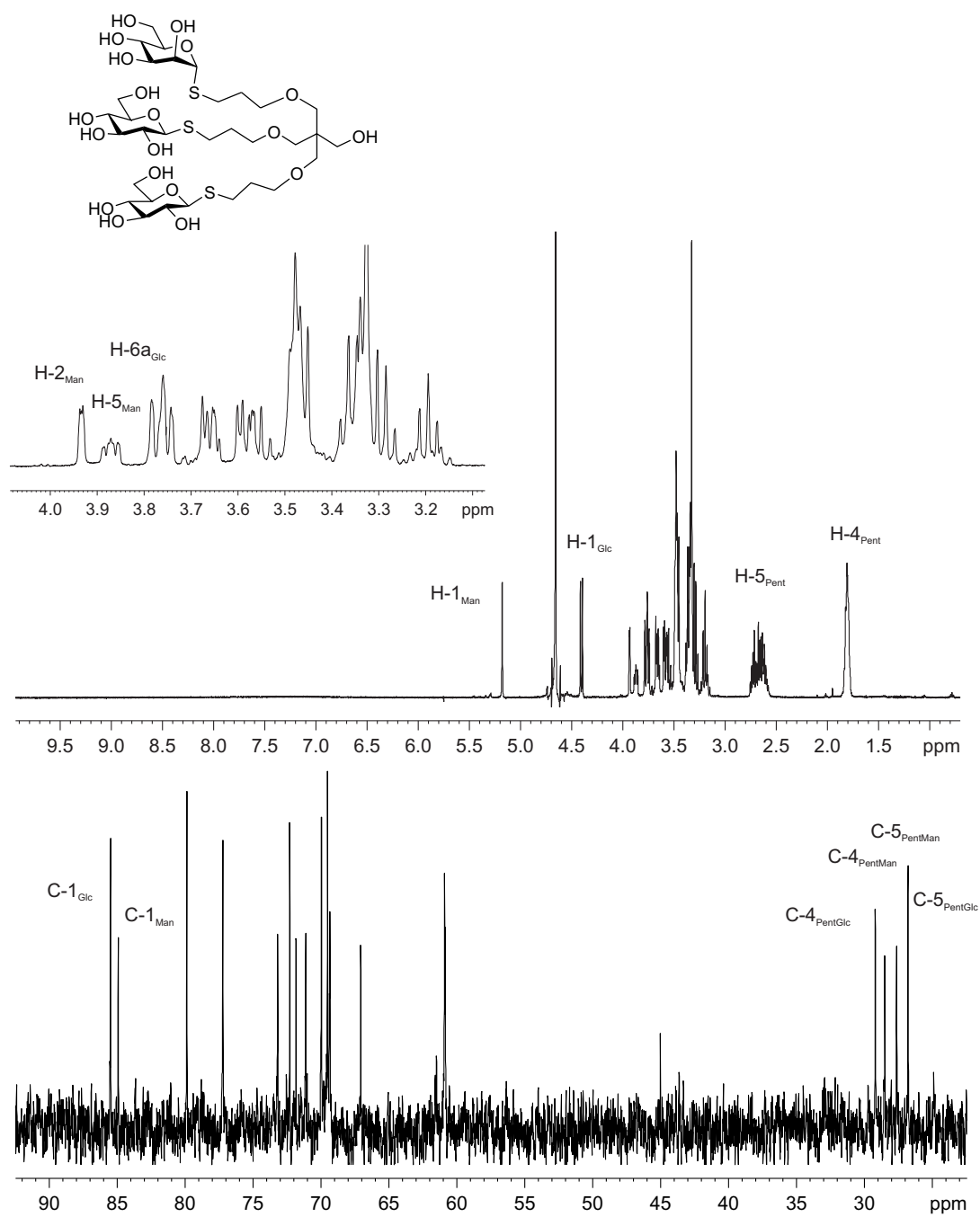


Figure 14. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O) spectra of compound **ManDiGlc-OH**.

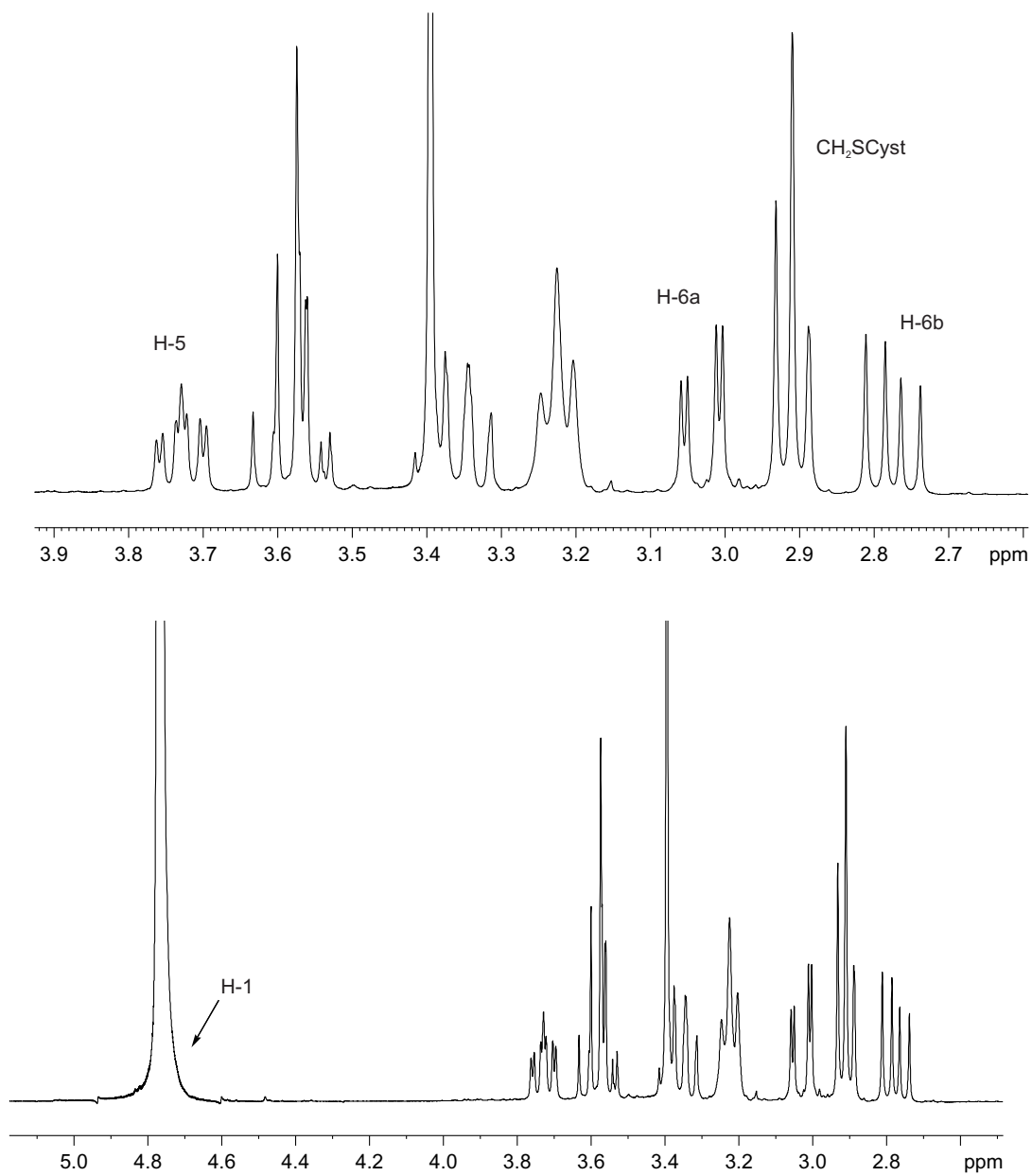
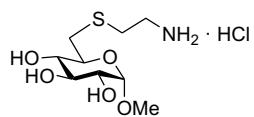


Figure 15. ¹H NMR (500 MHz, D₂O) spectrum of compound 24.

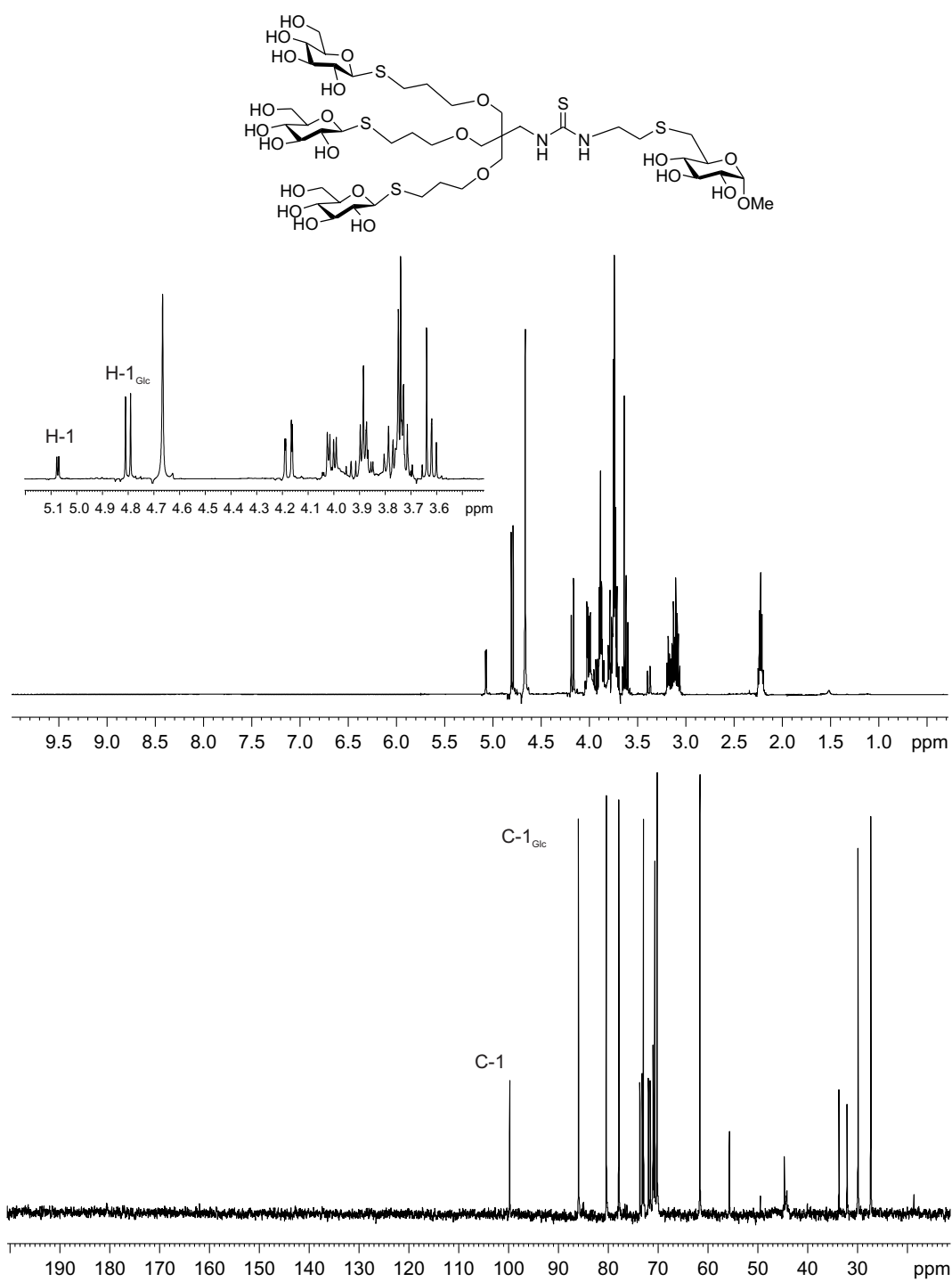


Figure 16. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O , 333 K) spectra of compound **TriGlc- α Me**.

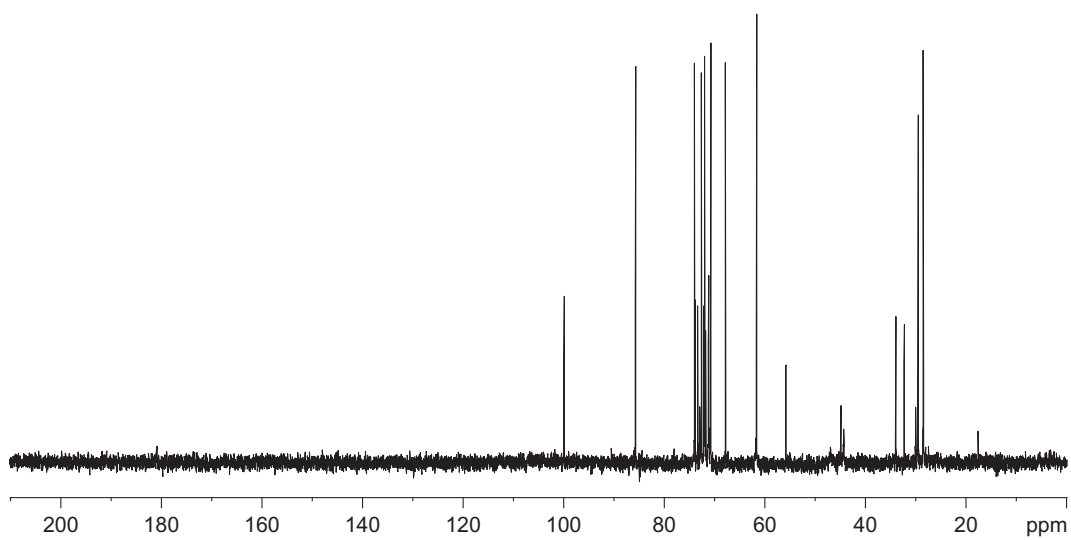
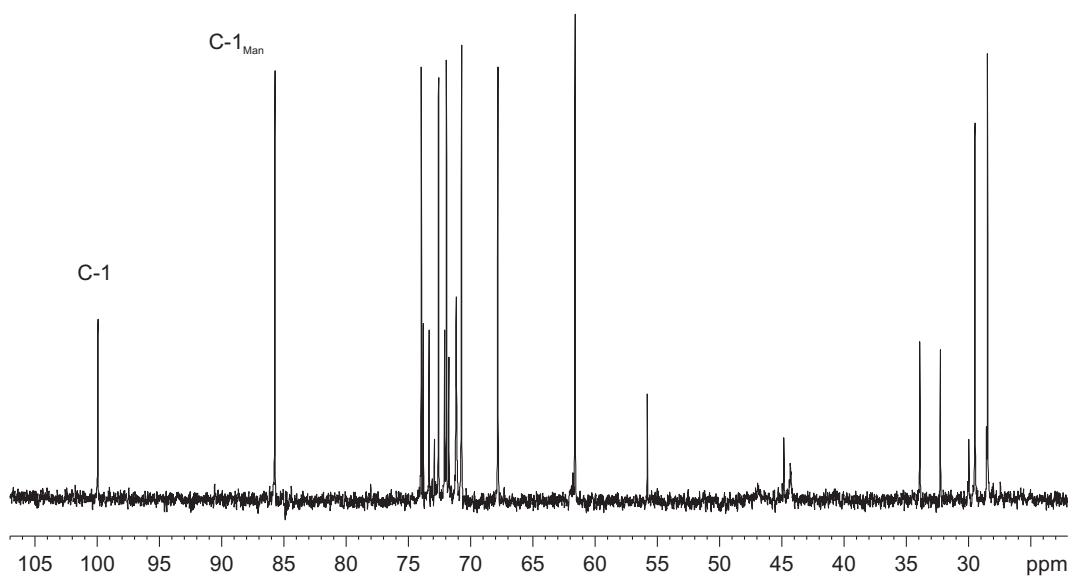
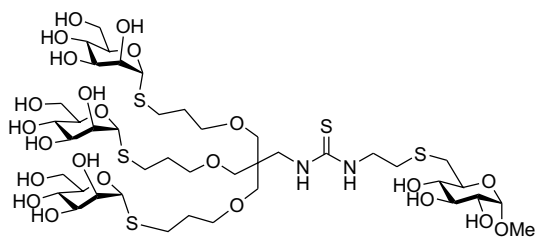


Figure 17. ^{13}C NMR (125.7 MHz, D_2O , 343 K) spectrum of compound **TriMan- α Me**.

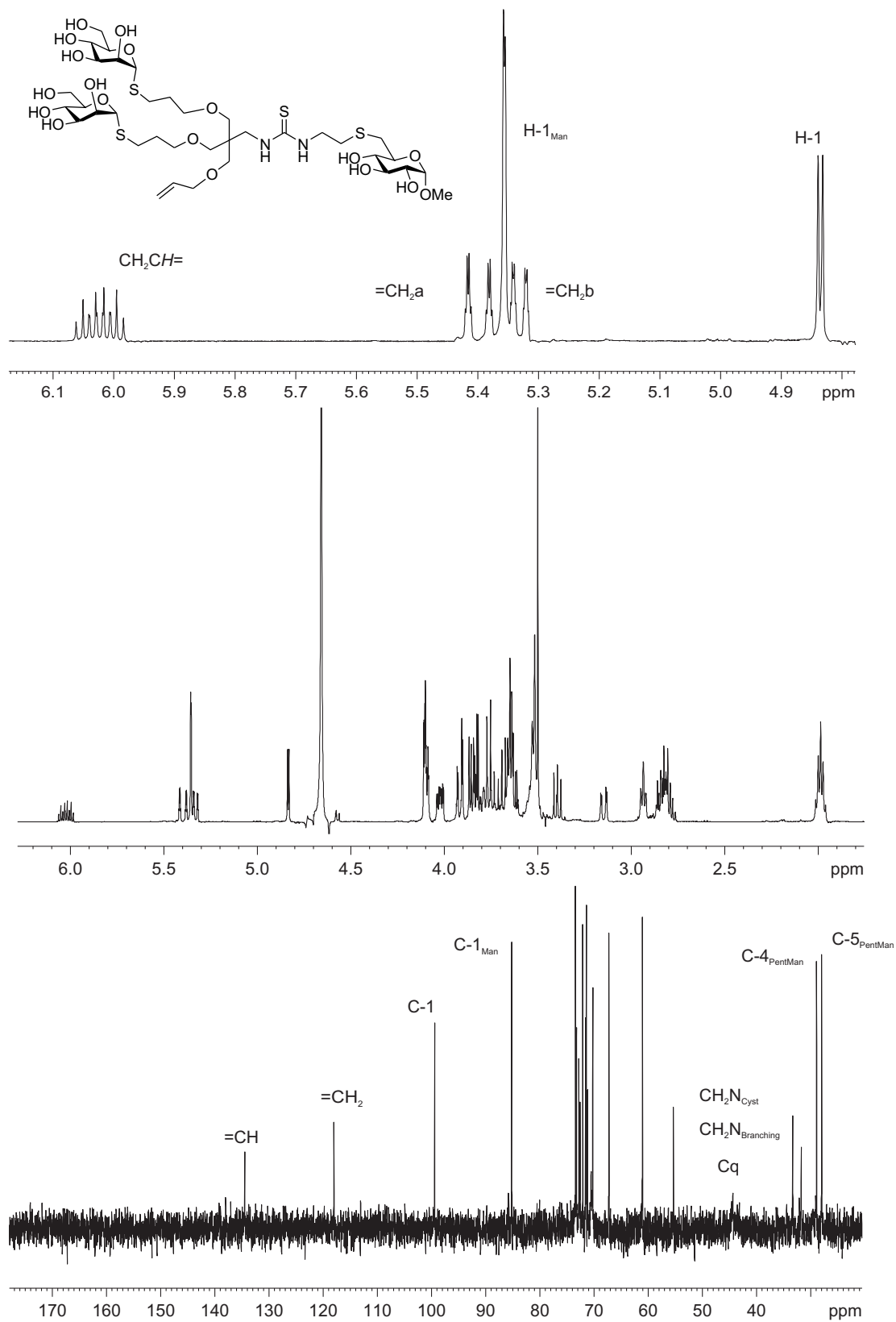


Figure 18. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O , 313 K) spectra of compound **DiMan- α -Me**.

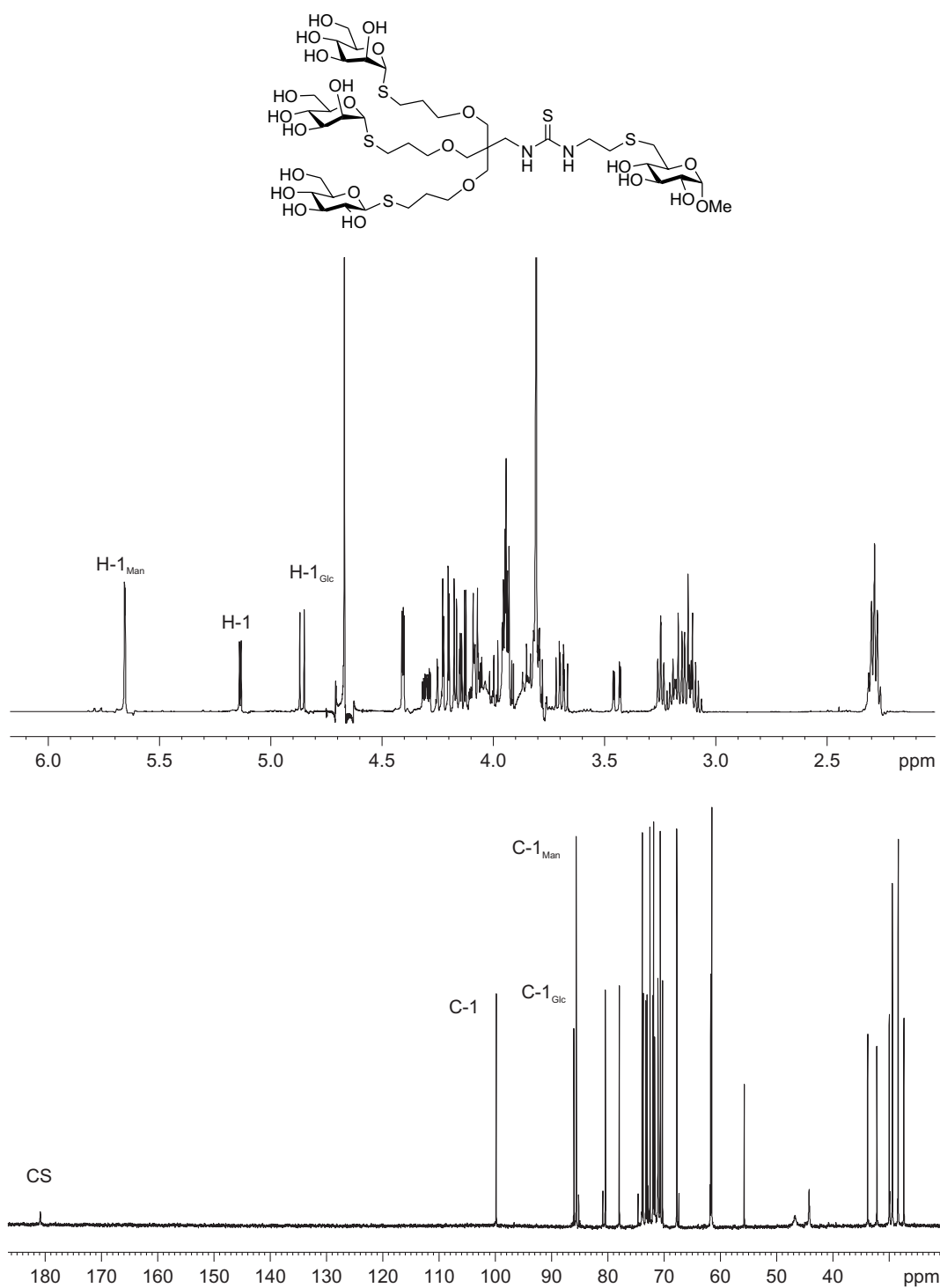


Figure 19. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D₂O, 343 K) spectra of compound DiManGlc- α Me.

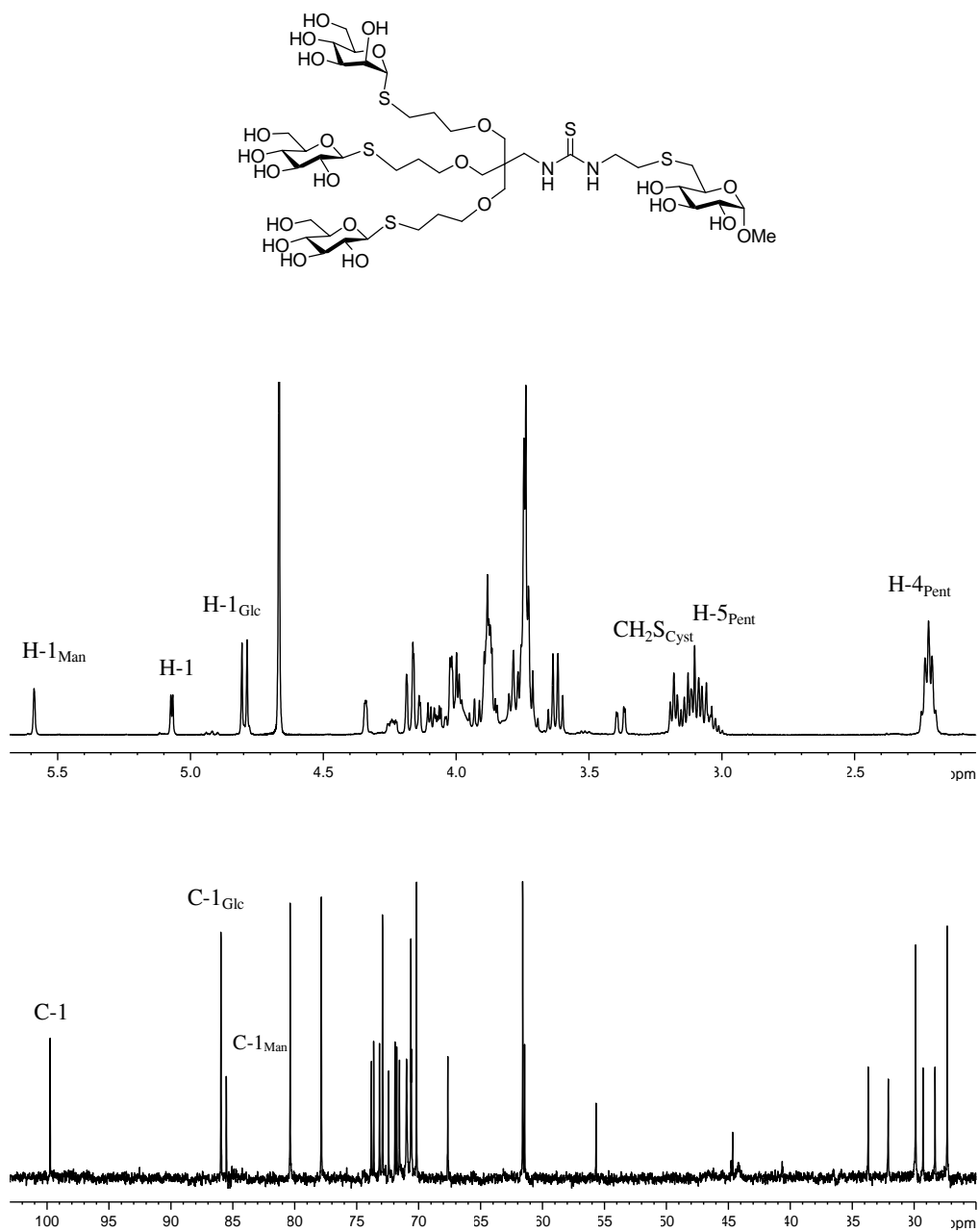


Figure 20. ^1H and ^{13}C NMR (500 and 125.7 MHz, respectively, D_2O , 333 K) spectra of compound **ManDiGlc- α Me**.

Surface Plasmon Resonance Sensorgrams (SPR). For interaction experiments, typically, a solution of carbohydrate containing material (15-30 μL) was flown across the sensor-chip for the association phase. Then, spontaneous dissociation was allowed to occur for another 3 min and subsequently the surface was regenerated, and stabilised for the next round of binding.

For calculation of the kinetics of the binding of the different compounds, samples were appropriately diluted in phosphate buffer, ranging from 0.5 mM to 4 mM for alcohol (Figure 21) and model glycodendrimers (Figure 22), and from 12.5 μM to 400 μM (figure 23) for βCD glycoclusters. Samples solutions at different concentrations were flown across the surfaces for 3 minutes, followed by a dissociation period of 6 minutes prior to regeneration.

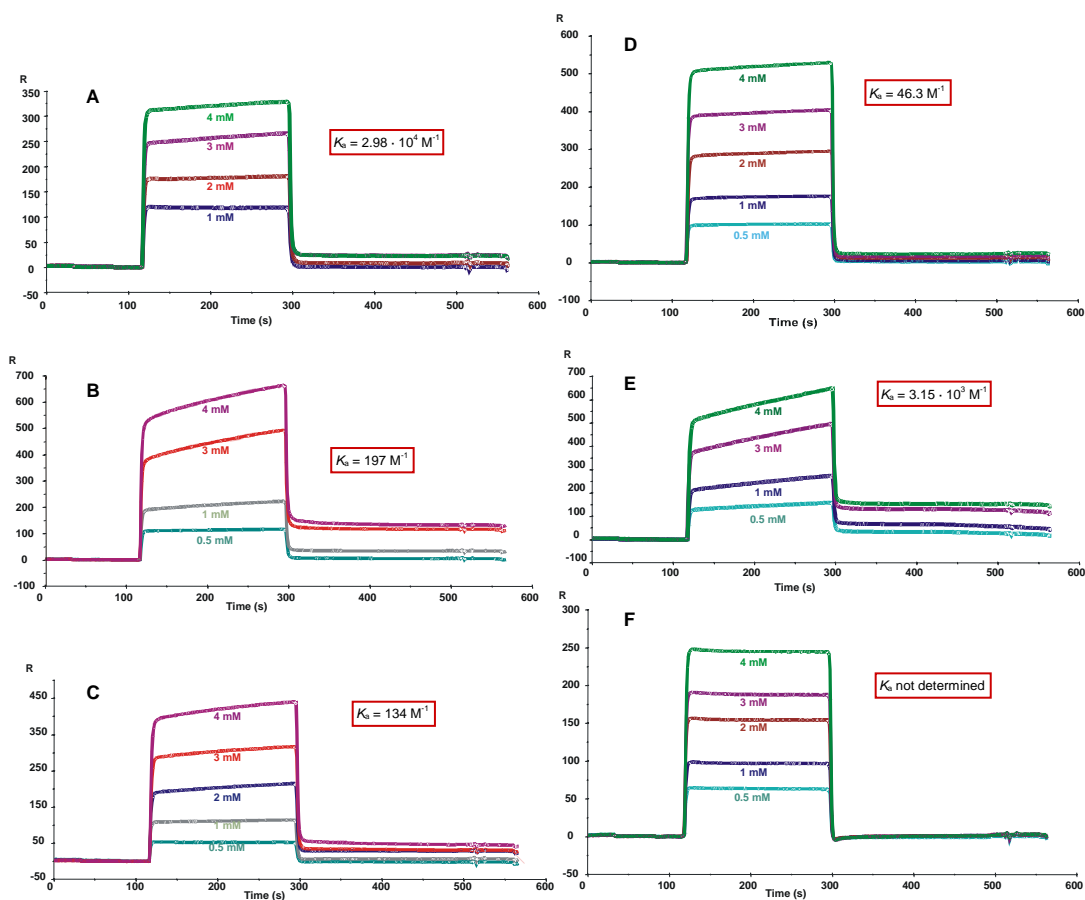


Figure 21. SPR-Sensorgrams of compounds **TriMan-OH** (A), **DiManGlc-OH** (B), **ManDiGlc-OH** (C), **TriGlc-OH** (D), **DiMan-OH** (E), and **Man-OH** (F) at 0.5, 1.0, 2.0, 3.0, and 4.0 mM in phosphate buffer.

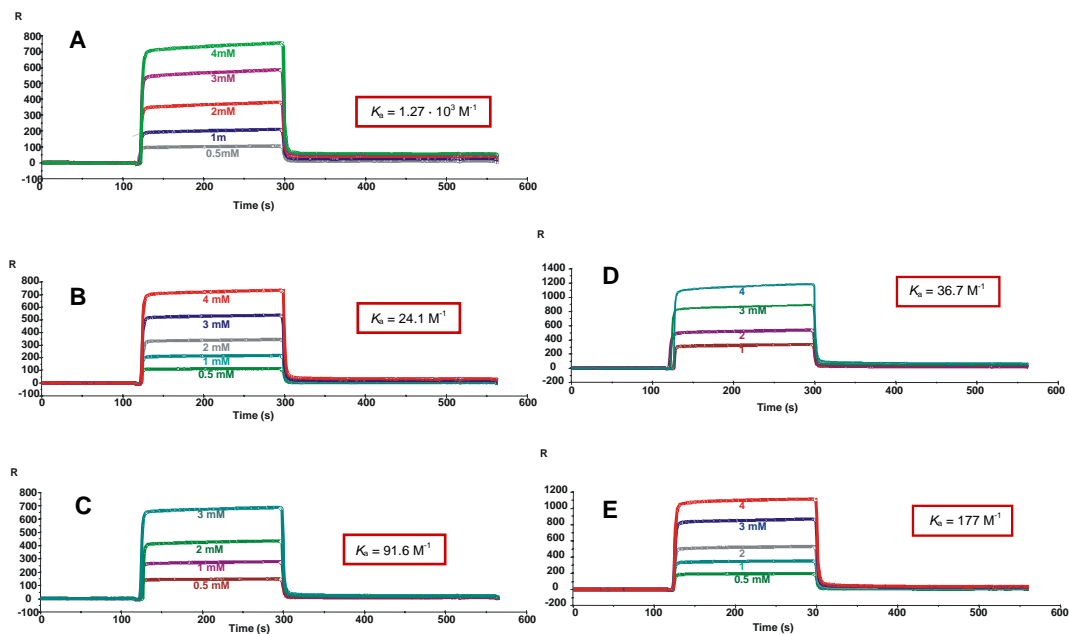


Figure 22. SPR-Sensorgrams of compounds **TriMan- α Me** (A), **DiManGlc- α Me** (B), **ManDiGlc- α Me** (C), **TriGlc- α Me** (D), and **DiMan- α Me** (E) at 0.5, 1.0, 2.0, 3.0, and 4.0 mM in phosphate buffer.

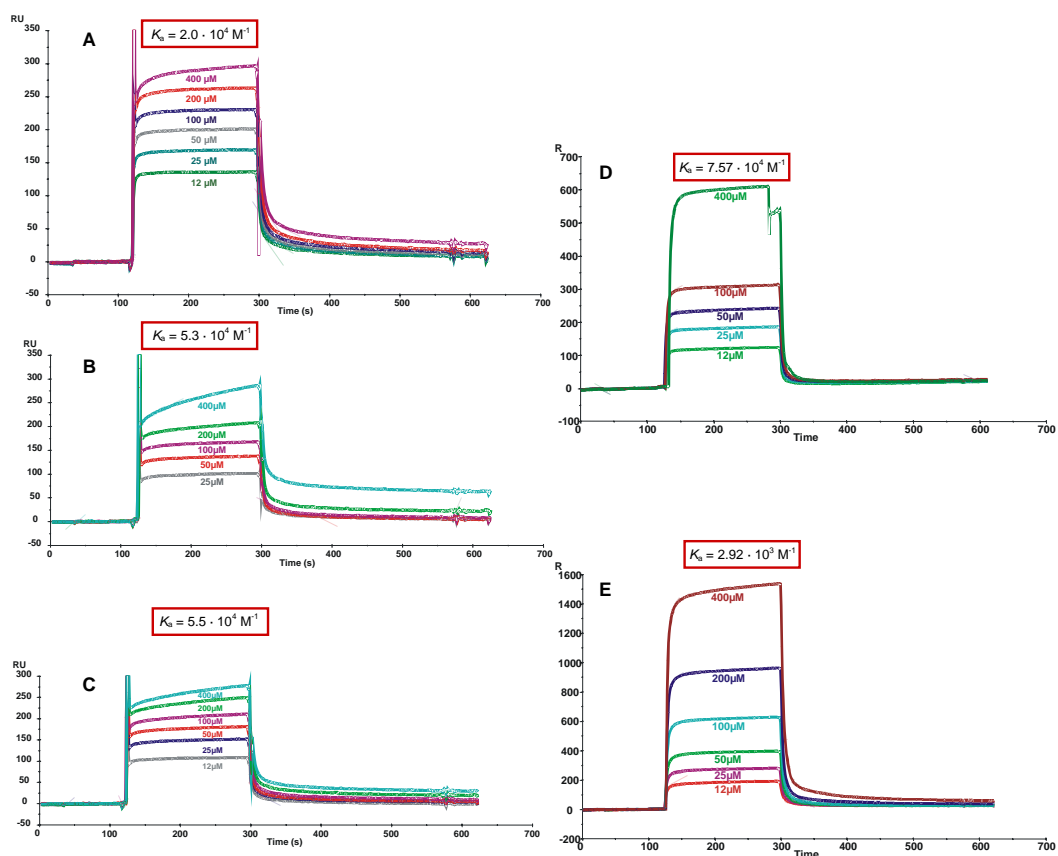


Figure 23. SPR-Sensorgrams of compounds **TriMan- β CD** (A), **DiManGlc- β CD** (B), **ManDiGlc- β CD** (C), **DiMan- β CD** (D), and **Man- β CD** (E) at 12.5, 25, 50, 100, 200, and 400 μM in phosphate buffer.

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