

Supporting Information

Comparative Study of the Binding of Concanavalin A to Monolayers Containing a Thiolated Mannoside on Flat Gold and on Nanoporous Gold.

Binod Pandey^{1,2}, Yih Horng Tan^{1,2}, Kohki Fujikawa¹, Alexei V. Demchenko¹ and Keith J. Stine^{1,2,*}

¹Department of Chemistry and Biochemistry, University of Missouri – Saint Louis, Saint Louis, MO 63121, USA

²Center for Nanoscience, University of Missouri – Saint Louis, Saint Louis, MO 63121, USA

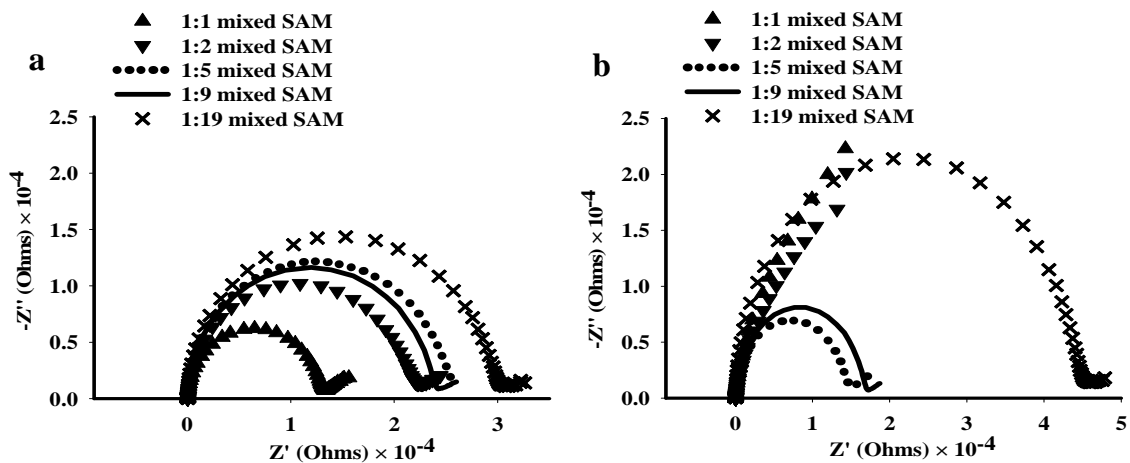


Figure S1. Representative Nyquist plots for different ratio mixed SAMs of OCT and thiolated α -mannoside on gold wire (a), and on NPG (b). EIS measurements were done in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ from 0.1 Hz to 0.1 MHz

Synthesis of 8-mercaptooctyl α -D-mannopyranoside

General. Column chromatography was performed on silica gel 60 (70 - 230 mesh), reactions were monitored by TLC on Kieselgel 60 F₂₅₄. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at < 40 °C. CH₂Cl₂, ClCH₂CH₂Cl, and CH₃CN were distilled from CaH₂ directly prior to application. Molecular sieves (3 Å or 4 Å), used for reactions, were crushed and activated *in vacuo* at 390°C during 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. AgOTf was co-evaporated with toluene and was dried *in vacuo* during 2-3 h prior to application. Optical rotations were measured using 'Jasco P-1020' polarimeter. ¹H-n.m.r. spectra were recorded in CDCl₃ at 300 MHz (Bruker Avance), ¹³C-NMR spectra were recorded in CDCl₃ at 75 MHz (Bruker Avance). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

8-Bromooctyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (1). To a stirring solution of 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose (4.0 g, 10.3 mmol), 8-bromooctanol (2.6 mL, 12.3 mmol) and molecular sieves 4 Å (1 g) in dichloromethane (100 mL) BF₃·OEt₂ (9.5 mL, 77.3 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 48 hours. The resulting mixture was neutralized by addition of Et₃N (20 mL) at 0 °C. The solids were filtered off, washed successively with dichloromethane, and the combined filtrate (~200 mL) was washed with sat. aq. NaHCO₃ (100 mL) and water (3 x 100 mL). The organic layer was separated, dried with MgSO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate / hexane, 1/4, v/v isocratic elution) to give the title compound as a colorless foam (2.5 g, 45%). Analytical data for

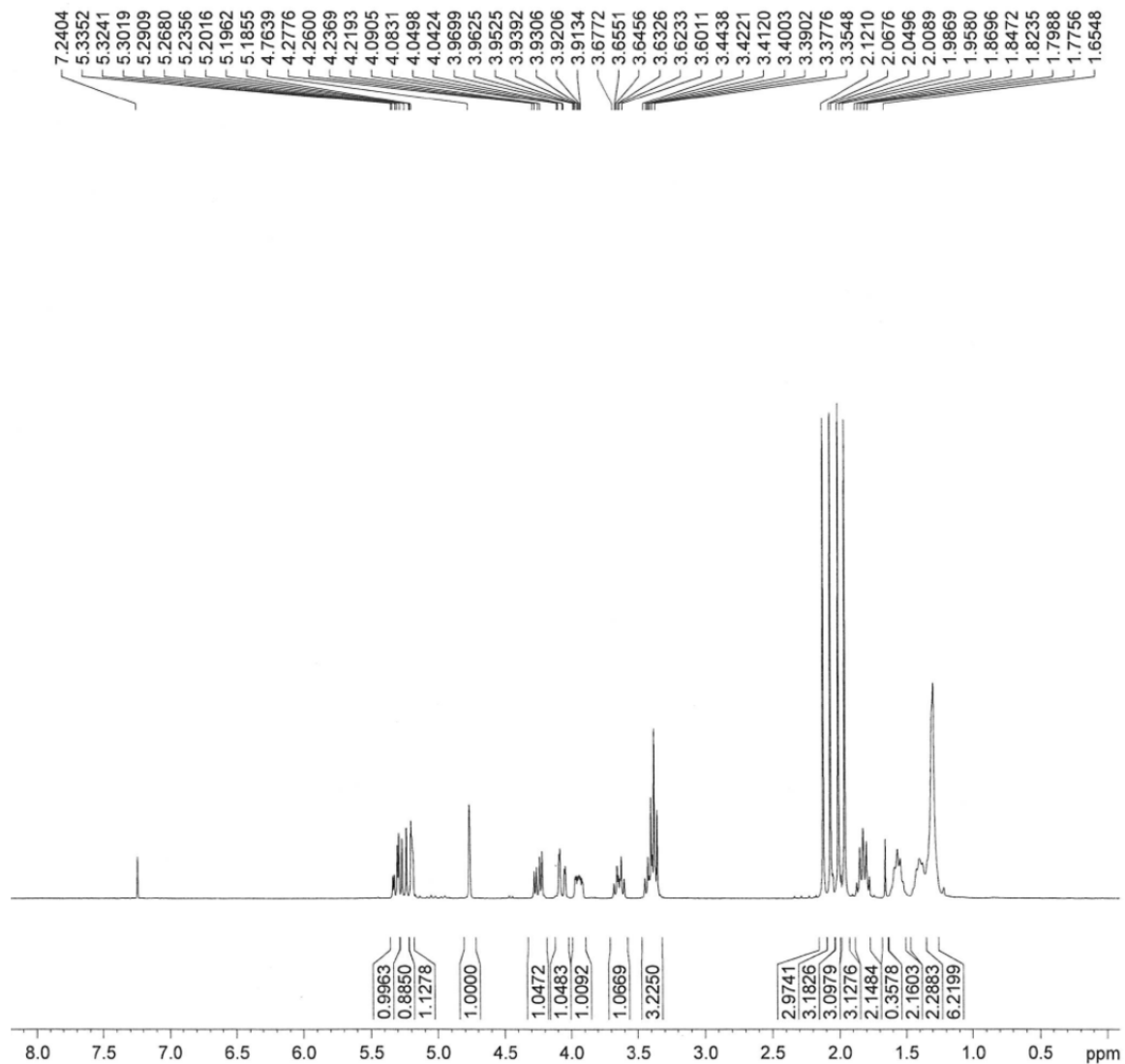
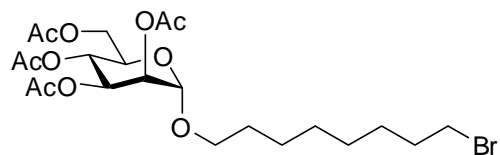
1: $R_f = 0.65$ (ethyl acetate / hexane, 1/2, v/v); $[\alpha]_D^{24} +3.5$ (c 0.7, CHCl_3); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ , 1.29-1.87 (m, 12 H, $-\text{CH}_2- \times 6$), 1.96 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.12 (s, 3 H, Ac), 3.35-3.44 (m, 3 H, CH_2Br , $-\text{OCH}_2^{\text{a}}$ -), 3.60-3.68 (m, 1 H, $-\text{OCH}_2^{\text{b}}$ -), 3.91-3.97 (m, 1 H, H-5), 4.06 (dd, 1 H, $J_{5,6a} = 2.2$ Hz, $J_{6a,6b} = 12.2$ Hz, H-6a), 4.24 (dd, 1 H, H-6b), 4.76 (d, 1 H, H-1), 5.18-5.20 (m, 1 H, H-2), 5.27 (t, 1 H, $J_{3,4} = J_{4,5} = 9.0$ Hz, H-4), 5.32 (dd, 1 H, $J_{2,3} = 3.0$ Hz, H-3) ppm; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ , 20.9, 21.0, 21.1, 26.2, 28.3, 28.8, 29.3, 29.4, 32.9, 34.2, 62.7, 66.4, 68.6, 68.7, 69.3, 69.9, 97.7, 169.9, 170.1, 170.3, 170.9 ppm; HR-FAB MS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{35}\text{BrO}_{10}\text{Na}^+$ 561.1311, found 561.1310.

8-(Acetylthio)octyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (2). To a solution of compound **1** (2.5 g, 4.65 mmol) in DMF (23 mL) was added potassium thioacetate (636 mg, 5.58 mmol) at room temperature and the resulting mixture was stirred at 50 °C for 5 hours. The reaction mixture was extracted with ethyl acetate (100 mL) and washed with sat. aq. NaHCO_3 (100 mL) and ice-cold H_2O (3 x 100 mL). The organic layer was separated, dried with MgSO_4 , and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate / hexane, 1/3, v/v isocratic elution) to give the title compound as a colorless foam (2.0 g, 80%). Analytical data for **2:** $R_f = 0.55$ (ethyl acetate / hexane, 1/2, v/v); $[\alpha]_D^{24} +42.5$ (c 1.0, CHCl_3); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ , 1.25-1.68 (m, 12 H, $-\text{CH}_2- \times 6$), 2.08 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 2.15 (s, 3 H, Ac), 2.29 (s, 3 H, Ac), 2.84 (t, 2 H, $-\text{CH}_2\text{-SAc}$), 2.86-3.45 (m, 1 H, $-\text{OCH}_2-$), 3.60-3.68 (m, 1 H, $-\text{OCH}_2-$), 3.92-4.06 (m, 1 H, H-5), 4.24 (dd, 1 H, $J_{6,6'} = 12.2$ Hz, $J_{6,5} = 2.3$ Hz H-6), 4.28 (dd, 1 H, H-6'), 4.77 (d, 1 H, $J_{1,2} = 1.4$ Hz, H-1), 5.19-5.21 (m, 1 H, H-2), 5.24 (t, 1 H, H-4), 5.33 (dd, 1 H, $J_{2,3} = 3.4$ Hz, $J_{3,4} = 9.9$ Hz, H-3) ppm; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ , 20.8, 20.9, 21.1, 26.1, 28.9, 29.1, 29.2, 29.3, 29.4, 29.6, 30.8, 62.6, 66.4, 68.5, 68.6,

69.3, 69.8, 97.7, 169.9, 170.0, 170.2, 170.8, 196.2 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{24}H_{38}O_{11}SNa^+$ 557.2033, found 557.2041.

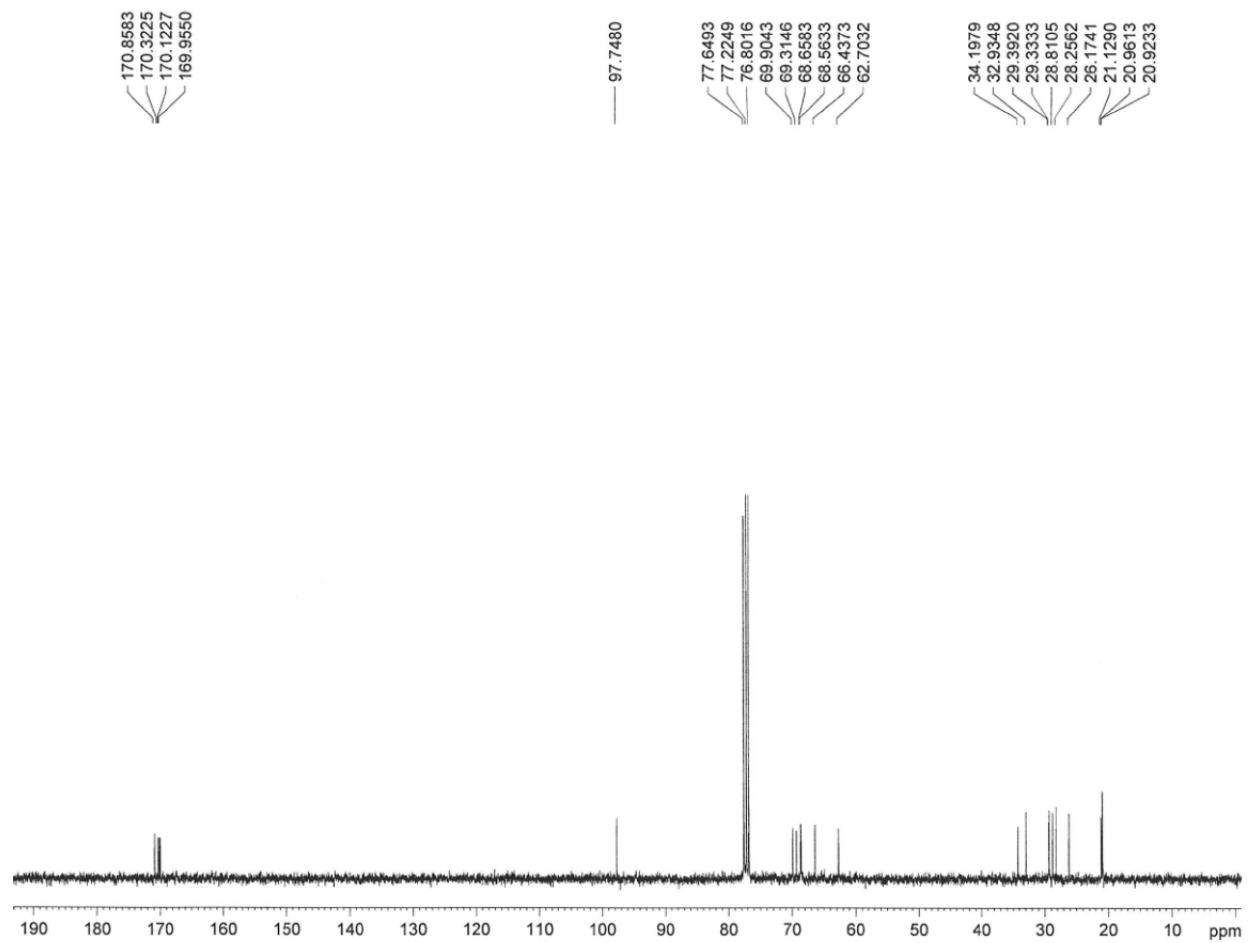
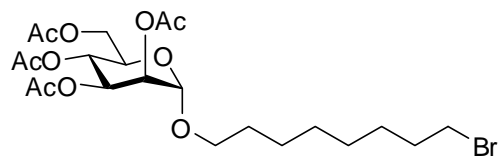
8-Mercaptooctyl α -D-mannopyranoside (3). To a solution of **2** (777 mg, 1.45 mmol) in MeOH/THF (14 mL, 1/1, v/v) NaOMe (29 mg, 0.15 mmol) was added and the reaction mixture was stirred at room temperature for 3 hours. The resulting mixture was neutralized with Dowex (H^+). The resin was filtered off, rinsed successively with MeOH, and the combined filtrate (~100 mL) was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (dichloromethane / methanol, 10/1 isocratic elution) to give the title compound as a colorless foam (400 mg, 85%). Analytical data for **3**: $R_f = 0.25$ (dichloromethane / methanol, 10/1, v / v); $[\alpha]_D^{24} -12.3$ (c 0.8, MeOH); 1H -NMR (300 MHz, $CD_3OD/CDCl_3$): δ , 1.24-1.53 (m, 12 H, $-CH_2-$ \times 6), 2.37-2.57 (m, 2 H, $-CH_2SH$), 3.23-3.86 (m, 8 H, $-OCH_2-$, H-2, H-3, H-4, H-5, H-6, H-6'), 4.66 (d, 1 H, H-1) ppm; ^{13}C -NMR (75 MHz, $CDCl_3$): δ , 24.4, 24.5, 26.0, 28.3, 28.8, 29.0, 29.3, 61.3, 66.8, 67.7, 70.8, 71.4, 72.2, 99.9; HR-FAB MS $[M + Na]^+$ calcd for $C_{14}H_{28}O_6SNa^+$ 347.1504, found 347.1515.

8-Bromooctyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (1)



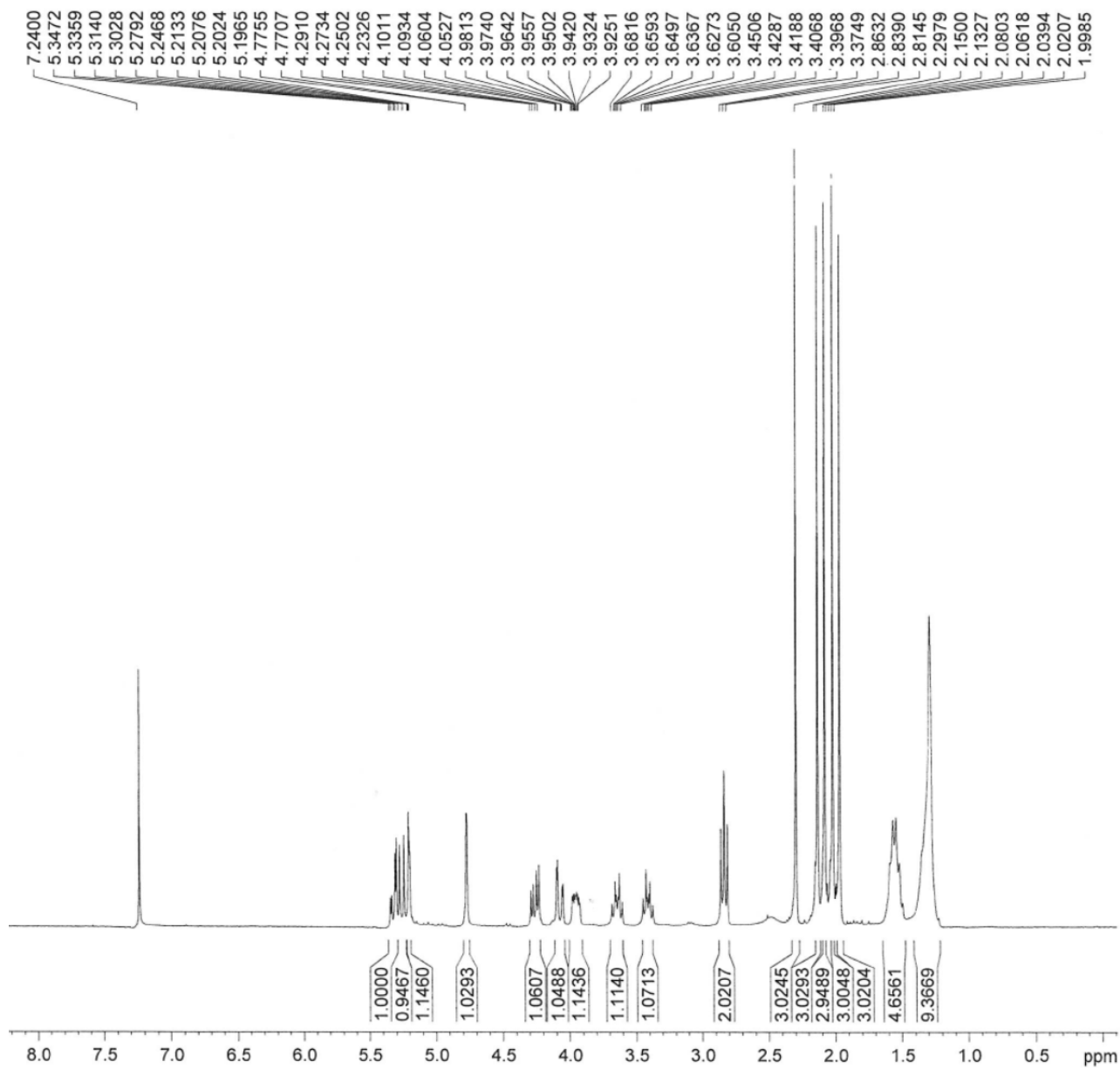
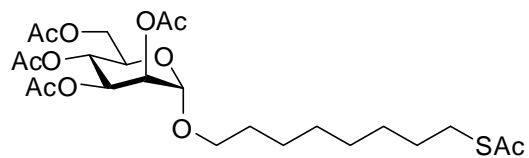
$^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3)

8-Bromooctyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (1)



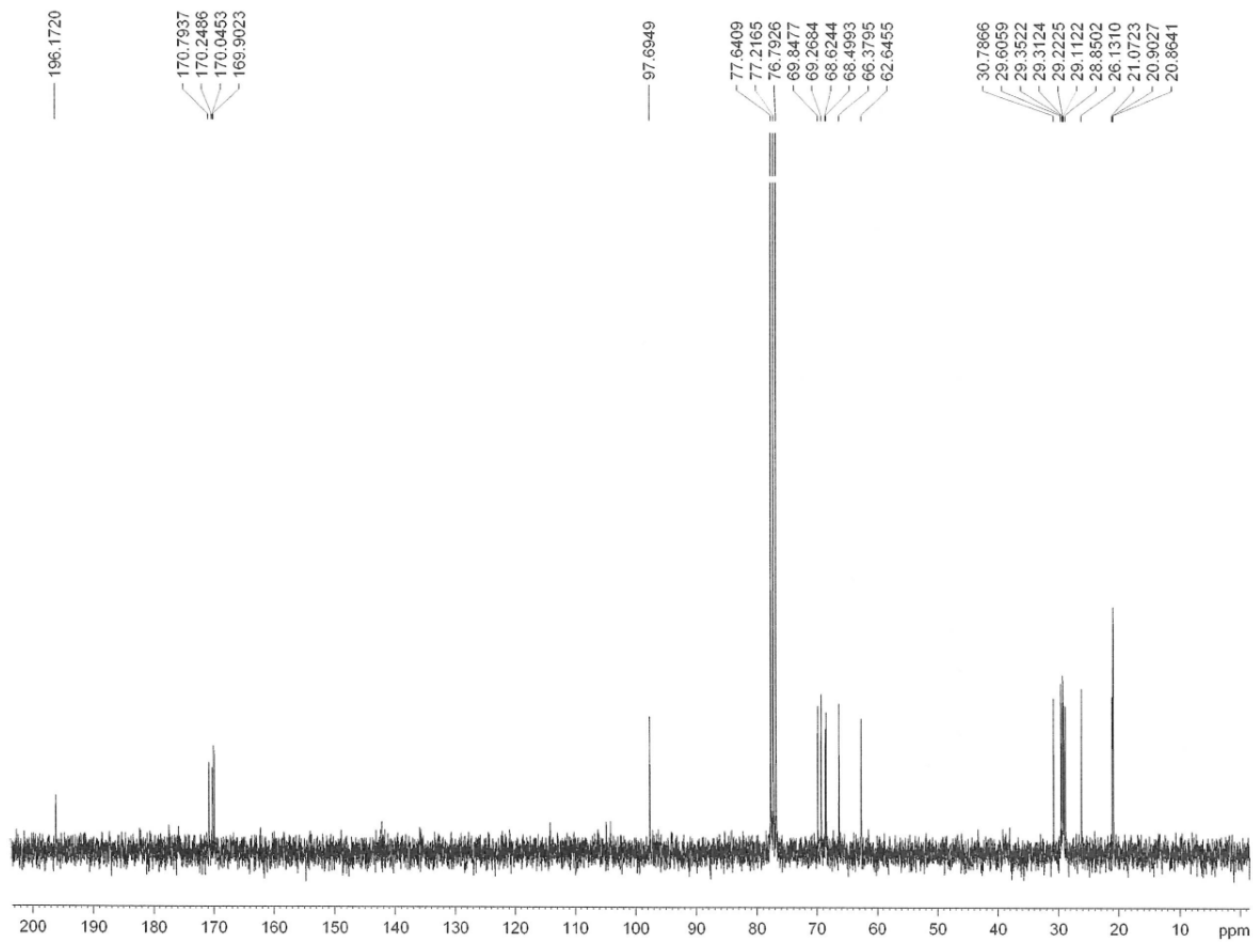
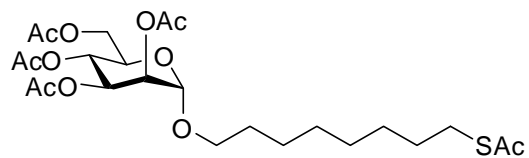
^{13}C -NMR spectrum (75 MHz, CDCl_3)

8-(Acetylthio)octyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (2)



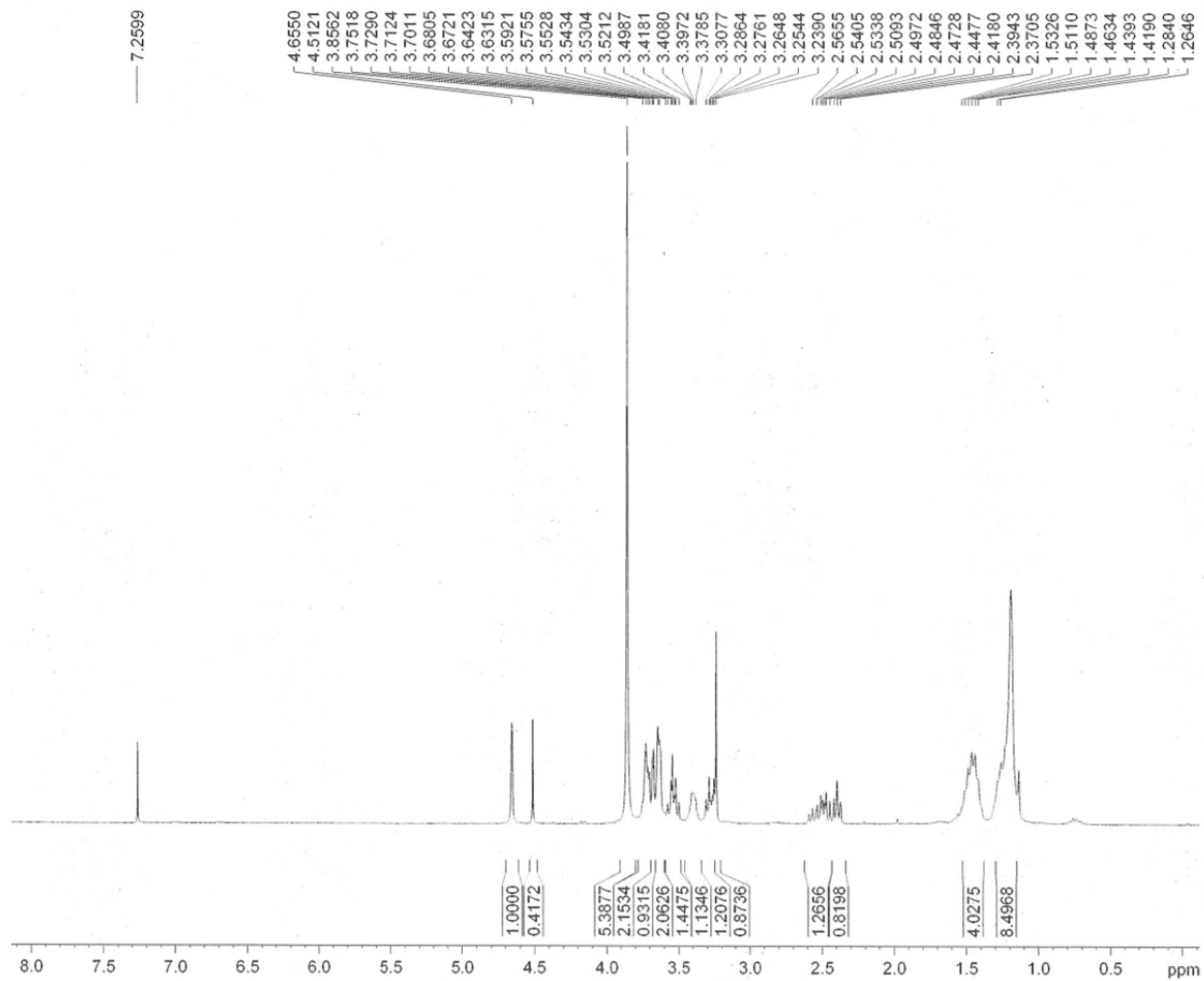
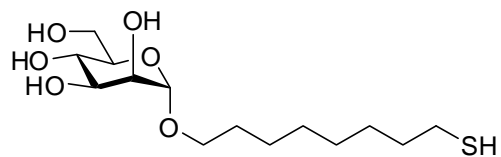
$^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3)

8-(Acetylthio)octyl 2,3,4,6-tetra-O-acetyl- α -D-mannopyranoside (2)



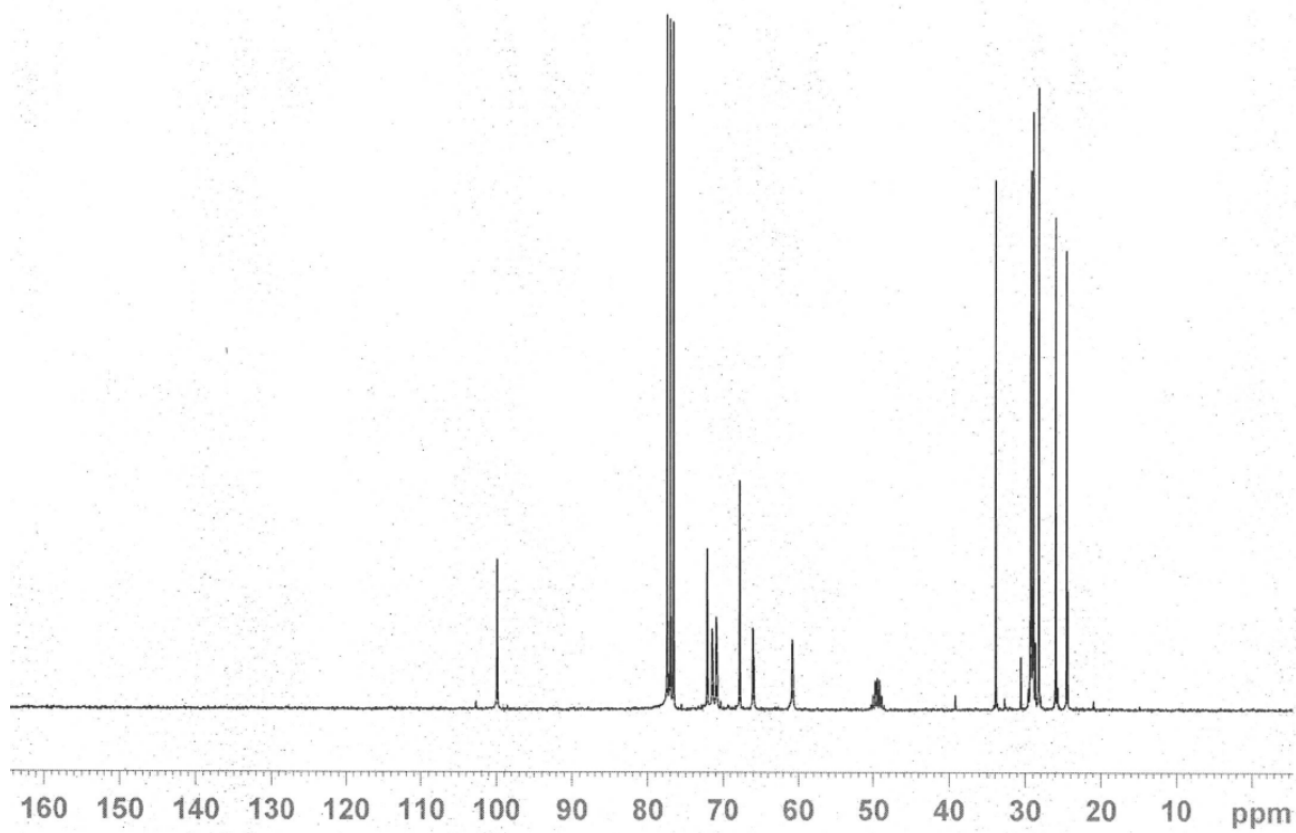
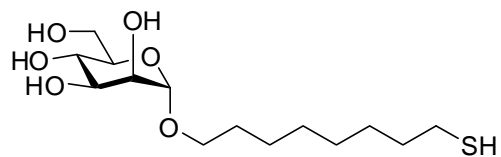
¹³C-NMR spectrum (75 MHz, CDCl₃)

8-Mercaptooctyl α -D-mannopyranoside (3)



$^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3)

8-Mercaptooctyl α -D-mannopyranoside (3)



^{13}C -NMR spectrum (75 MHz, CDCl_3)