Electronic Supplementary Material (ESI) for Chemical Communications

Probing Carbohydrate-Carbohydrate Interactions By Photoswitchable Supramolecular Glycoclusters.

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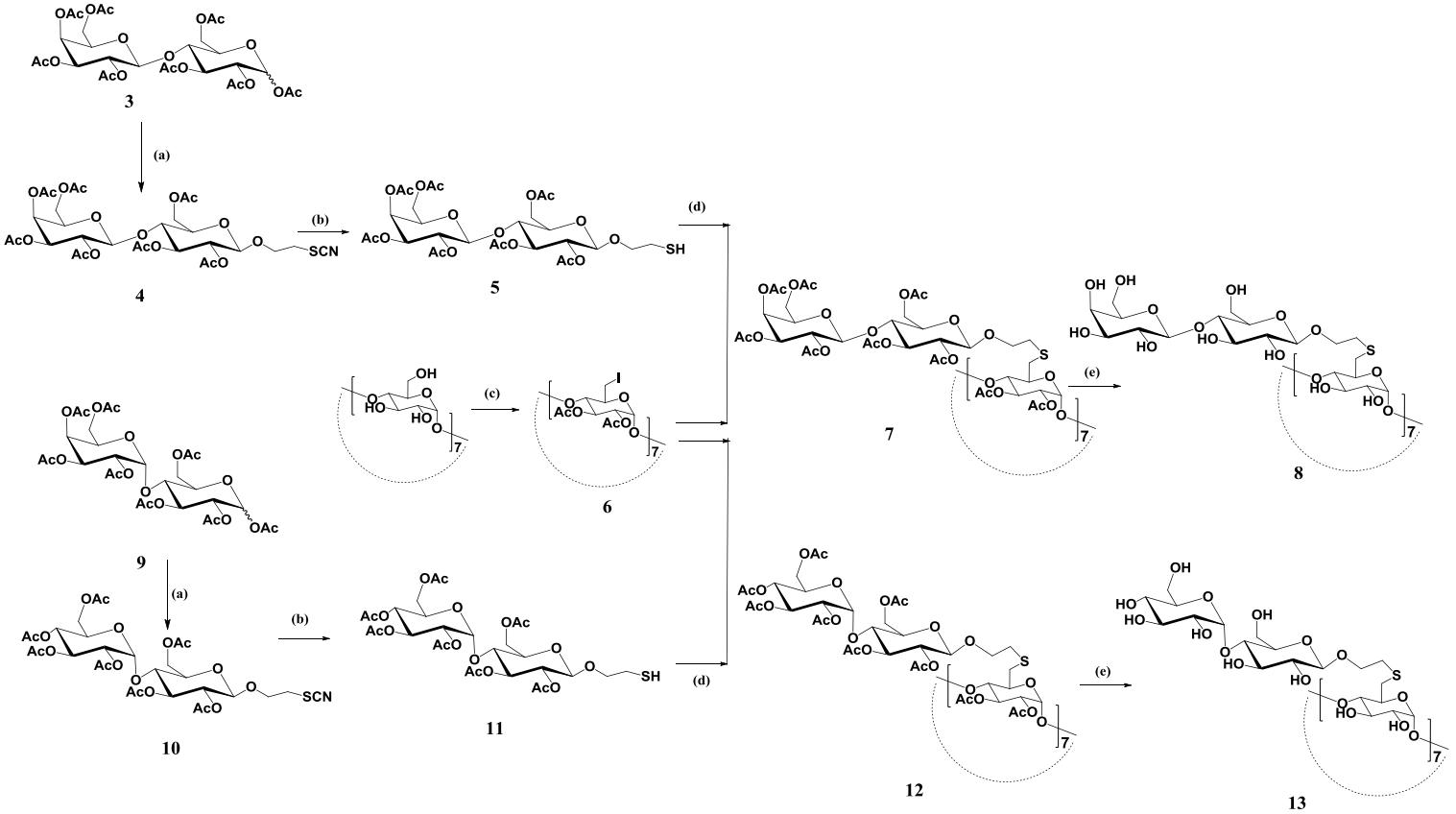
1. General Information

All chemicals were reagent grade and used as supplied except where noted. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25 mm). Compounds were visualized by UV irradiation or dipping the plate in CAM solution followed by heating. Column chromatography was carried out using force flow of the indicated solvent on Fluka Kieselgel 60 (230–400 mesh). ^{1}H and ^{13}C

NMR spectra were recorded on Jeol 400 MHz using residual solvents signals as an internal reference ($CDCl_3$ δH, 7.26 ppm, δc 77.3 ppm and CD_3OH δH 3.31 ppm, δc 49.0 ppm). The chemical shifts (δ) are reported in *ppm* and coupling constants (*J*) in Hz. IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. Uv-visible measurements were perform with a Evolution 300 UV-visible spectrophotometer (Thermo Fisher Scientific, USA). Circular dichroism measurements were performed with J-815 CD spectropolarimeter (Jasco, USA). Each CD profile is an average of five independent scans of the same sample collected at a scan speed of 30 nm min^{-1}.

2. **Synthesis of compound 8 and 13.**



Scheme S1: Synthesis of comp **8** and **13**: (a) Bromoethanol/$BF_3.Et_2O$; KSCN/DMF; (b) Zn/AcOH; (c) I_2,PhP_3; Ac_2O/Py; (d) **6**, Cs_2CO_3, DMF; (e) NaOMe, MeOH

General Procedure A : Synthesis of Bromoethanol-sugar derivatives

Per-acetylated sugar (1.0 eq) was dissolved in DCM (10 mL). Then $BF_3.Et_2O$ (6.0 eq) and bromoethanol (6.0 eq) were added at 0^oC for 1 hr and the reaction mixture was allowed to stir at room temperature for 12 h. Completion of reaction was monitored by TLC. After completion, the reaction mixture was neutralized with triethyl amine, followed by extraction with ethaylacetate : water (1:1) mixture. Organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was further purified on silica gel column chromatography using EtOAc/Pet-ether to get pure bromoethanol sugar derivatives.

General Procedure B: Synthesis of thiocyanate substituted sugar

Per-acetylated bromoethanol-sugar derivative (1.0 eq) was dissolved in DMF (10 mL). Then potassium thiocyanate (6.0 eq) was added and stirred at 80^oC for 12 h. The reaction mixture was diluted with 100 ml ethyl acetate and washed several times with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was further purified on silica gel column chromatography using EtOAc/Pet-ether to get pure **4** or **10**.

General Procedure C: Synthesis of thio substituted sugar.

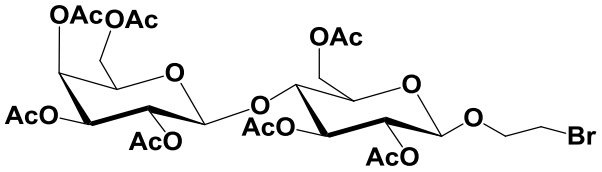
Peracetylated thiocynate-sugar derivative (1.0 eq) was dissolved in glacial acetic acid (30 mL). Then Zn dust (3.0 eq) was added and refluxed at 70^oC for 4 h. The compound was filtered to remove zinc dust. The organic layer was quenched with water (50 mL). Then product was extracted with EtOAc (3 X 50 mL) and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure to give crude product, which was further purified by silica gel column chromatography using EtOAc/Pet-ether to get pure **5** or **11**.

General Procedure D: Synthesis of sugar substituted β-cyclodextrin.

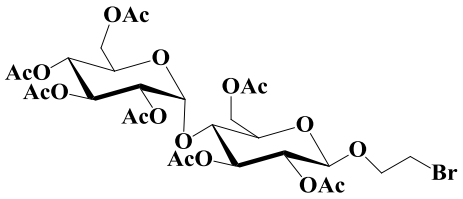
The per-acetylated thio-sugar (1.0 eq) in DMF (10 mL) was added to per-acetylated 6'-Iodo- β-cyclodextrin (0.07 equiv) and Cs_2CO_3 (1.0 equiv) and stirred at room temperature for 72 h. The reaction mixture was diluted with 100 ml ethyl acetate and washed several times with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was further purified on silica gel column chromatography using DCM/MeOH to get pure **7** or **12.**

General Procedure E: Deacetylation of Per-glycosylated β-cyclodextrin derivatives.

The sugar-substituted *β*-cyclodextrin (1.0 equiv) was dissolved in methanol (10 mL). Then sodium methoxide (20 eq) was added and stirred for 2 h at RT. The mixture was neutralized with amberlite–IR120H$^+$ resin, filtered and concentrated *in vacuo* to afford the final compound (**8** or **13**).

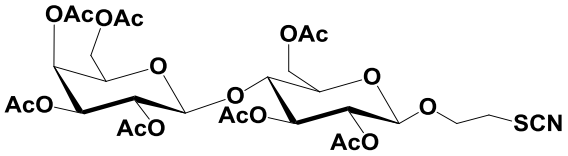


2- Bromoethoxy (2,3,4,6-tetra-*O*-acetyl-D- galactopyranoside *β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside): General procedure **A** using 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)1"*2",3",4",6"-penta-*O*-acetyl-D-glucopyranoside (1.93g, 2.84 mmol) $BF_3.Et_2O$ (1.2 ml, 17 mmol) bromoethanol (2.1 ml,17 mmole) and purified by flash column using petroleum ether : ethylacetate (40:60) to yield (0.55g, 47%) R_f = 0.5 (pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (d, 1H, *J* = 3.2 Hz); 5.20 (t, 1H, *J* = 9.2 Hz); 5.08 (dt, 1H, *J* = 10.4, 7.2 Hz); 4.98-4.87 (m, 2H); 4.56 – 4.42 (m, 2H), 4.10 (dtd, 5H, *J* = 7.6, 11.6, 15.2 Hz); 3.85 (t, 1H, *J* = 6.8Hz); 3.86 (t, 1H, *J* = 6.8 Hz); 3.84-3.73 (m, 1H); 3.61 (ddd, 1H, *J* = 2.0, 4.8 Hz); 3.46- 3.39 (m, 2H); 2.13, 2.10, 2.04, 2.03, 1.95 (s, 3H 3H 6H 6H 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ 170.2, 170.1, 169.8, 169.1,, 101.1, 100.8, 77.4, 76.2, 72.8, 72.6, 71.4, 71.0, 70.7, 69.8, 69.1, 66.6, 61.8, 60.9, 29.9, 20.9.20.8. HRMS m/z calc'd for $C_{28}H_{39}BrNaO_{18}$ $(M+Na)^+$: 765.1217; found:765.1216.

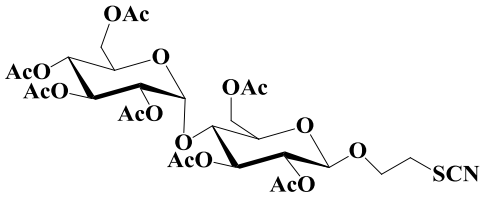


2- Bromoethoxy (2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside): General procedure **A** using 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)1"*2",3",4",6"-penta-*O*-acetyl-D-glucopyranoside (0.94g, 1.38 mmol) $BF_3.Et_2O$ (0.58 ml,8.31 mmol) bromoethanol (1.02 ml,8.31 mmole) and purified by flash column using petroleum ether : ethylacetate (40:60) to yield (0.53g, 46%) R_f = 0.5 (Pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (d, 1H, *J* = 4 Hz); 5.33 (t, 1H, *J* = 5.6 Hz); 5.24 (t, 1H, *J* = 9.6 Hz); 5.04 (t, 1H, *J* = 10 Hz); 4.86-4.78 (m, 3H); 4.58 (d, 1H, *J* = 8 Hz); 4.53-4.45 (m, 1H); 4.23 (td, 2H, *J* = 4.0, 12.8 Hz); 4.05-3.96 (m, 2H);

3.97-3.90 (m, 1H); 3.87-3.77 (m, 1H); 3.67 (td, 1H, *J* = 2.8, 5.6 Hz); 3.45-3.41 (m, 2H); 2.14, 2.09, 2.03, 2.01, 1.94 (s 3H, 3H, 6H, 3H, 6H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 169.7, 169.1, 101.1, 100.7, 76.1, 72.9, 72.6, 71.4, 70.7, 69.9, 69.4, 67.4, 66.6, 61.7, 60.8, 33.7, 29.7, 20.9, 20.7. HRMS m/z calc'd for $C_{28}H_{39}BrNaO_{18}$ $(M+Na)^+$: 765.1217; found:765.1212

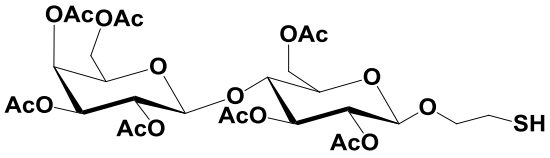


2- Thiocynoethoxy (2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside) 4: General procedure **B** using 2-bromoethoxy (2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside) (0.43g, 0.59 mmol) in DMF (10 ml) potassium thiocyanate (0.23g,2.37 mmol) and purified by flash column using Petroleum ether : ethylacetate (35:65) to yield (0.35g, 74%) R_f = 0.45 Pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.32 (d, 1H, *J* = 3.2 Hz); 5.18 (t, 1H, *J*= 9.2 Hz); 5.09 (t, 1H, *J* = 8.4 Hz); 4.95-4.87 (m, 2H); 4.54-4.44 (m, 2H); 4.13-4.03 (m, 6H); 3.84 (t, 2H, *J* = 7.2 Hz); 3.61-3.55 (m, 1H); 3.18-3.06 (m, 2H); 2.13, 2.11, 2.04, 2.02, 1.94 (s, 3H, 3H, 6H, 6H, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ 170.4, 170.2, 169.7, 169.1, 111.7, 101.1, 100.7, 76.1, 72.9, 72.6, 71.3, 71.0, 70.7, 69.1, 67.4, 66.6, 61.7, 60.8, 33.7, 20.9, 20.9, 20.7, 20.8, 20.6. HRMS m/z calc'd for $C_{29}H_{39}NNaSO_{18}$ $(M+Na)^+$: 765.1785; found:765.1785.

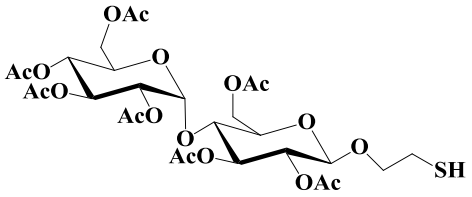


2- Thiocynoethoxy (2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-gluco pyranoside) 10: General procedure **B** using 2-bromoethoxy (2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-gluco pyranoside) (0.27g, 0.37 mmol) in DMF (10 ml) potassium thiocyanate (0.14g,1.48 mmol) and purified by flash column using petroleum ether : ethylacetate (35:65) to yield

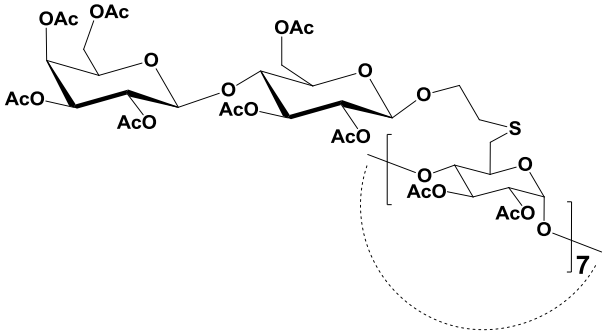
(0.22g, 89%) R_f = 0.45 (pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40 (d, 1H, *J* = 4.0 Hz); 5.34 (t, 1H, *J* = 9.2 Hz); 5.25 (t, 1H, *J* = 9.6 Hz); 5.04 (t, 1H, *J* = 10 Hz); 4.86-4.81 (m, 2H); 4.59 (d, 1H, *J* = 8.0 Hz); 4.53 (dd, 1H, *J* = 2.8, 12.0 Hz); 4.29-4.20 (m, 2H); 4.20-4.13 (m, 1H), 4.16 (t, 1H, *J* = 4.8 Hz); 4.07-3.97 (m, 1H); 3.94 (dt, 1H, *J* = 4.0, 10.0 Hz); 3.85-3.79 (m, 1H); 3. 68 (dt, 1H, *J* = 4.4, 9.6 Hz), 3.18-3.05 (m, 2H); 2.14, 2.09, 2.03, 2.01, 1.99, 1.98 (s, 3H, 3H, 6H, 3H, 3H, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.2, 170.1, 169.7, 100.4, 95.6, 75.1, 72.4, 71.9, 70.1, 69.4, 68.6, 68.0, 67.5, 62.5, 61.5, 33.7, 20.9, 20.6. HRMS m/z calc'd for $C_{29}H_{39}NNaSO_{18}$ $(M+Na)^+$: 765.1785; found:765.1787.



2-Thioethoxy (2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside) 5: General procedure **C** using 2-thiocyanoethoxy (2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside) (0.20g, 0.27 mmol) in glacial acetic acid (30 ml) zinc dust (0.072 g, 1.08 mmol) and purified by flash column using Petroleum ether : ethylacetate (30:70) to yield (0.16g, 84%) R_f = 0.30 (Pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40 (d, 1H, *J* = 3.2 Hz); 5.26 (t, 1H, *J*= 9.2 Hz); 5.16 (t, 1H, *J* = 8.4 Hz); 5.01 (dt, 1H, *J* = 3.2, 9.2 Hz); 4.96(t, 1H, *J* = 9.2 Hz); 4.56 (dd, 3H, *J* = 3.2, 9.2 Hz); 4.23-4.11 (m, 4H); 4.04-3.99 (m, 1H); 3.93 (t, 1H, *J* = 7.2 Hz); 3.85 (t, 1H, *J* = 9.2 Hz); 3.69-3.62 (m, 2H); 2.80-2.66 (m, 2H); 2.13, 2.11, 2.04, 2.02, 1.94 (s, 3H, 3H, 6H, 6H, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ 170.4, 170.2, 169.7, 169.1, 111.7, 101.1, 100.7, 76.1, 75.8, 72.9, 72.6, 71.3, 71.0, 70.7, 69.1, 67.4, 66.6, 61.7, 60.8, 33.7, 21.1, 20.9, 20.8, 20.1. HRMS m/z calc'd for $C_{28}H_{40}SNaO_{18}$ $(M+Na)^+$: 719.1832; found:719.1833.

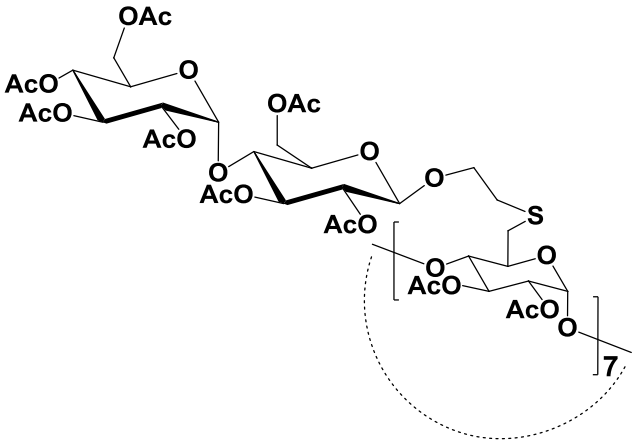


2-Thioethoxy (2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-gluco pyranoside) 11: General procedure **C** using 2-thiocyanoethoxy (2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-gluco pyranoside) (0.25g, 0.35 mmol) in acetic acid (30 ml) zinc dust (0.09 g,1.40 mmol) and purified by flash column using petroleum ether : ethylacetate (30:70) to yield (0.21g, 91%) R_f = 0.30 (pet ether:EtOAc (1:1)) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 (d, 1H, *J* = 4 Hz); 5.33 (t, 1H, *J* = 9.6 Hz); 5.23 (t, 1H, *J* = 9.6 Hz); 5.02 (t, 1H, *J* = 9.6 Hz); 4.88-4.77 (m, 2H); 4.55 (d, 1H, *J* = 7.6 Hz); 4.51-4.41 (m, 1H); 4.22 (ddd, 3H, *J* = 12.3, 9.1, 4.0 Hz), 4.05-3.91 (m, 4H), 3.75-3.64 (m, 2H); 2.78-2.64 (m, 2H); 2.15, 2.12, 2.08, 2.07, 2.06, 2.04, 2.03 (s, 3H, 3H, 3H, 3H, 3H, 3H, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.5, 169.8, 169.5, 100.6, 95.7, 77.3, 77.1, 75.3, 72.6, 72.1, 69.3, 69.4, 69.1, 68.6, 68.2, 62.5, 61.2, 31.5, 30.6, 20.1, 20.0. HRMS m/z calc'd for $C_{28}H_{40}SNaO_{18}$ $(M+Na)^+$: 719.1832; found:719.1837.

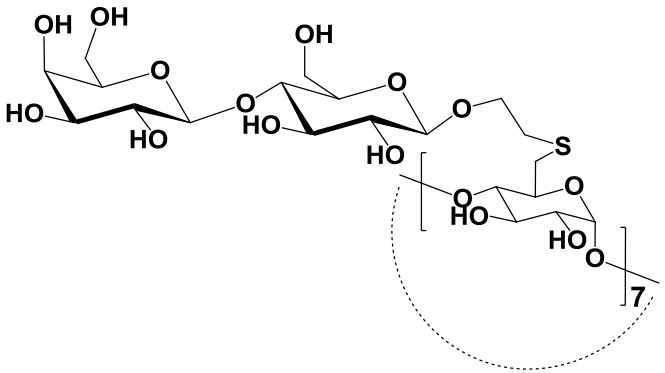


Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] 7: General procedure **D** using 2-(thioethoxy-{2,3,4,6-tetra-*O*-acetyl-D-galapyranoside *β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside} (0.39g, 0.54 mmol) per-acetylated hepta-6'-Iodo-*β*-cyclodextrin (0.1g, 0.04 mmol), Cs_2CO_3 (0.18g, 0.56 mmol) and purified by flash chromatography to yield Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (0.09g, 39%). R_f = 0.45 (CH_2Cl_2/MeOH, 93:7); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.35-5.31 (brs, 7 H); 5.18 (t, 7H, *J* = 12 Hz); 5.23 (t, 14 H, *J* = 12 Hz); 4.98-4.91 (m, 7 H); 4.85 (t, 7H, *J* = 8 Hz); 4.80- 4.69 (m, 7 H); 4.49 (dd, 28H, *J* = 12 Hz); 4.19 - 4.09 (m, 14 H); 4.06 (t, 14 H *J* = 8 Hz); 3.97-3.86(m, 14 H); 3.84-3.77 (m, 7H); 3.68-3.55 (brs, 14 H); 3.16-2.91 (brs, 21 H); 2.86-2.69 (m, 14 H); 2.11 (s,

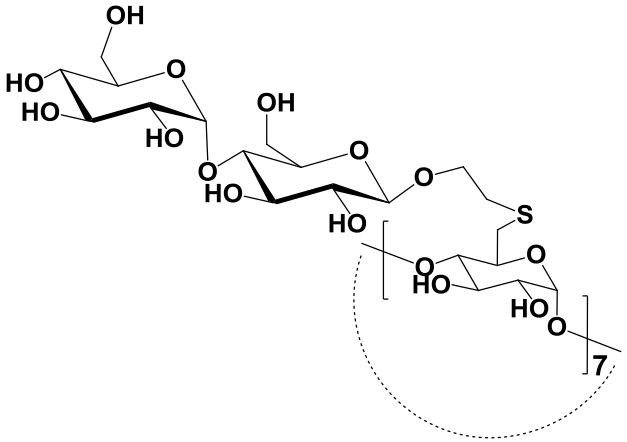
26 H); 2.03 (s, 135 H); 1.94 (s, 28H).[13]C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.1, 169.8, 101.1, 71.0, 70.6, 69.1, 66.6, 60.6, 29.7, 21.0, 20.9, 20.7, 20.6. ESI-MS (*m/z*); calcd. for $C_{266}H_{364}S_7O_{168}Na$ 6492.79; found:3246.39 $[M+Na/2]^+$.



Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] 12: General procedure D using 2-(thioethoxy-{2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside *β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside} (0.4 g, 0.55 mmol), per-acetylated hepta-6'-Iodo-*β*-cyclodextrin (0.1g, 0.04), Cs_2CO_3 (0.18 g, 0.55 mmol) and purified by flash chromatography to yield Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (0.12 g, 46%). R_f = 0.45 (CH_2Cl_2/MeOH, 93:7); [1]H NMR (400 MHz, $CDCl_3$): δ 5.4 (d, 7H, *J* = 4 Hz); 5.34 (t, 7H, *J* = 8 Hz); 5.28-5.18 (m, 14H); 5.05 (t, 14H, *J* = 12 Hz); 4.85 (dd, 7H, *J* = 4.0, 4.0 Hz); 4.79(t, 14H, *J* = 8 Hz); 4.57 (d, 7H, *J* = 8 Hz); 4.50 (d, 7H, *J* = 12Hz); 4.23 (t, 14H, *J* =12 Hz); 4.13-3.99 (m, 28H); 3.98-3.91(m, 14H); 3.75-3.67 (m, 7H); 3.65-3.58 (m, 7H); 3.03-2.93(m, 14H); 2.89-2.67 (m, 14H); 2.14, 2.08, 2.06, 2.02, 2.01, 1.99, 1.98 (s, 24H, 28H, 18H, 48H, 34H, 16H, 21H). [13]C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.6, 170.5, 170.2, 170.0, 169.6, 169.5, 100.3, 95.6, 75.3, 72.7, 72.2, 72.0, 70.0, 69.3, 68.4, 68.0, 62.7, 61.4, 21.0, 20.9, 20.7, 20.6 ESI-MS (*m/z*); calcd. for $C_{266}H_{364}S_7O_{168}Na$ 6492.79; found:3246.41 $[M+Na/2]^+$.

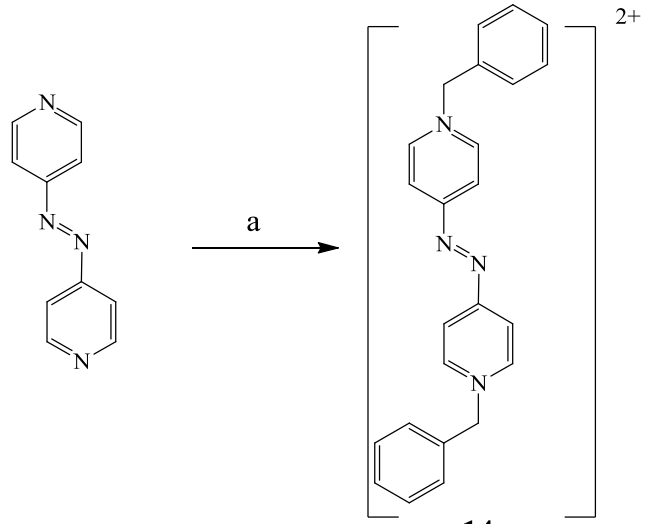


Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] 8: General procedure E using Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (0.1g, 0.015 mmol) and sodium methoxide (50 mg, 0.9 mmol) and purified by washing with amberlite-H+ resin to yield Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (30 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27-5.499 (m, 7H); 4.50 (d, 7H, *J*= 7.6 Hz); 4.45 (d, 7H, *J*= 8.0 Hz); 4.15-4.01 (m, 7H); 4.01-3.81 (m, 49H); 3.81-3.69 (m, 21H); 3.69-3.45 (m, 56H); 3.39-3.29 (m, 7H); 3.06-2.85 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.9, 102.1, 78.3, 72.7, 72.5,71.9, 70.9,69.0, 68.5, 61.0, 60.1. Cold sprayESI-MS (*m/z*); calcd. for $C_{140}H_{239}S_7O_{106}Na^{2+}$ 1932.56; found:1932.533 $[M+Na/2]^+$.



Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] 13: General procedure E using Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucoctopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (0.1g, 0.015 mmol) and sodium methoxide (50 mg, 0.9 mmol) and purified by washing with amberlite-H+ resin to yield Hepta-*α-(1-4)*[2',3'-O-acetyl-6'-{2-ethoxy-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside*β(1-4)*2",3",4",6"-tetra-*O*-acetyl-D-glucopyranoside)}] (30 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (s, 7H); 5.12 (d, 7H, J = 13.4 Hz); 4.50 (d, 7H, J = 7.8 Hz); 4.01-3.89 (m, 14H); 3.84-3.68 (m, 34H); 3.67-3.37 (m, 58H); 3.28 (t, 14H, J = 7.8 Hz); 3.20 (dt, 21H, J = 7.8 Hz); 2.98-2.71 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.2, 99.8, 77.0, 76.8, 76.1, 74.6, 71.7, 69.2, 68.9, 60.7, 60.5. cold spray ESI-MS (*m/z*); calcd. for $C_{140}H_{239}S_7O_{106}Na^{2+}$ 1932.56; found:1932.536 $[M+Na/2]^{+}$.

3. Synthesis of azo derivative



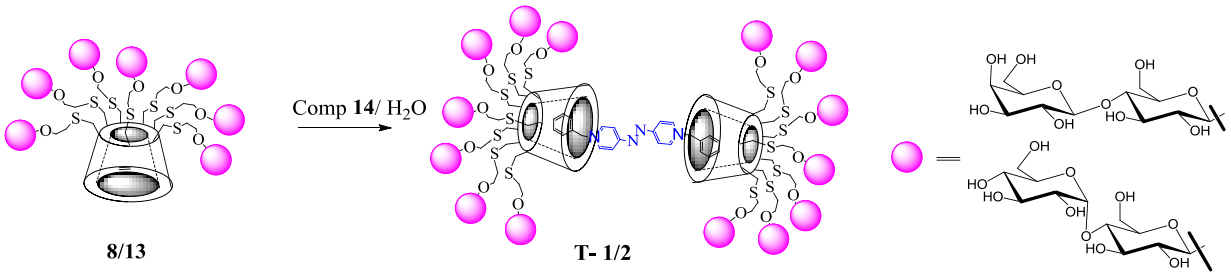
14

Scheme S2. Synthesis of azo –derivative: (a) Benzylbromide, acetonitril, 80^{O}C.

4,4'-bis(benzyl) azo-pyridine 14. 4, 4'-azopyridine (100 mg, 0.53 mmol) and benzyl bromide (0.14 ml, 1.16 mmol) was dissolved in acetonitril (10 mL) and refluxed at 80^{O}C for 24 h. Then cooled to 0^{O}C and brown precipitate was separated by filtration, yielded 4,4'-bis(benzyl) azo-pyridine (59 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (d, 4H, J = 6.8 Hz); 8.88 (d, 4H, J = 6.8 Hz); 7.5 (d, 4H, J = 7.2 Hz); 7.47 (d, 4H, J = 4.4 Hz); 7.13-7.09 (m, 2H); 5.9 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 151.2, 131.5, 129.8, 129.0, 128.8, 120.8, 65.4; HR-MS (*m/z*); calcd. for $C_{24}H_{22}N_4$ 367.1844; found:367.1842.

4. Synthesis of host-guest complexes

Compound **8** or **13** (20 mg, 5.17 μM) was mixed with azo-pyridine derivative **14** (1 mg, 2.71 μM) in 1mL of water or deuterated water and sonicated for 10 mins to afford **T-1** or **2** respectively. The host-guest complexation was characterized by ^{1}H-NOESY NMR studies.



Scheme S3. Synthesis of host-guest complexes

^{1}H-NOESY spectra

The formation of host-guest complexes was characterized by ^{1}H-NOESY NMR spectroscopy. NOESY spectra of **T-1** and **2** displayed the clear NOE cross peaks between cyclodextrin and phenyl group. However, it was difficult to identify **H3** and **H5** of **6** *and* ***6***'. Instead, our attention was drawn on to the protons of phenyl moiety as we observed a strong NOE interaction with protons from the **6** and **6'** region. It was observed that proton **Ha, Hb and Hc** of phenyl showed a strong overhauser effect with *β*-CD protons and a weak interaction with proton **Hd**. indicating the *β*-CD inner core is encapsulating the phenyl group of **8** (Fig **S4**). Finally, no NOE effect with azo-pyridine proton indicates the phenyl moiety is just holding the two *β*-CD at the peripheral region. Finally, above results correlates to our previous and Dan Grustein et al work.[2]

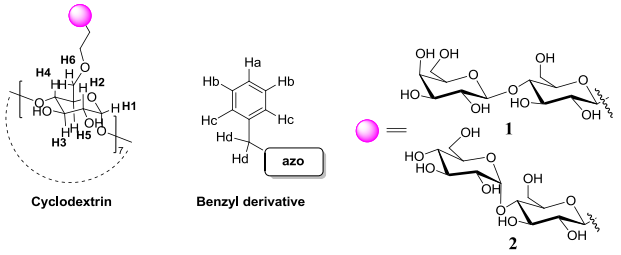


Figure 1. Proton designation of the relevant molecule moiety involved in host-guest complex.

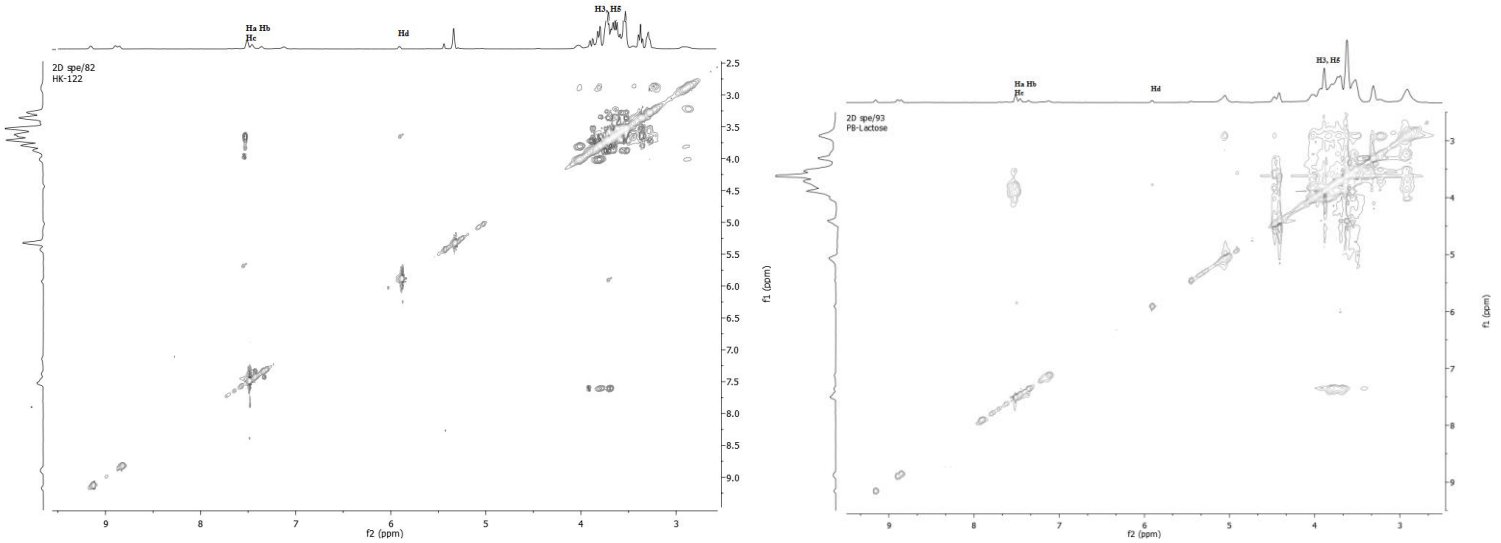


Figure S2. ^{1}H-NOESY spectra of **T-1** and **T-2** respectively.

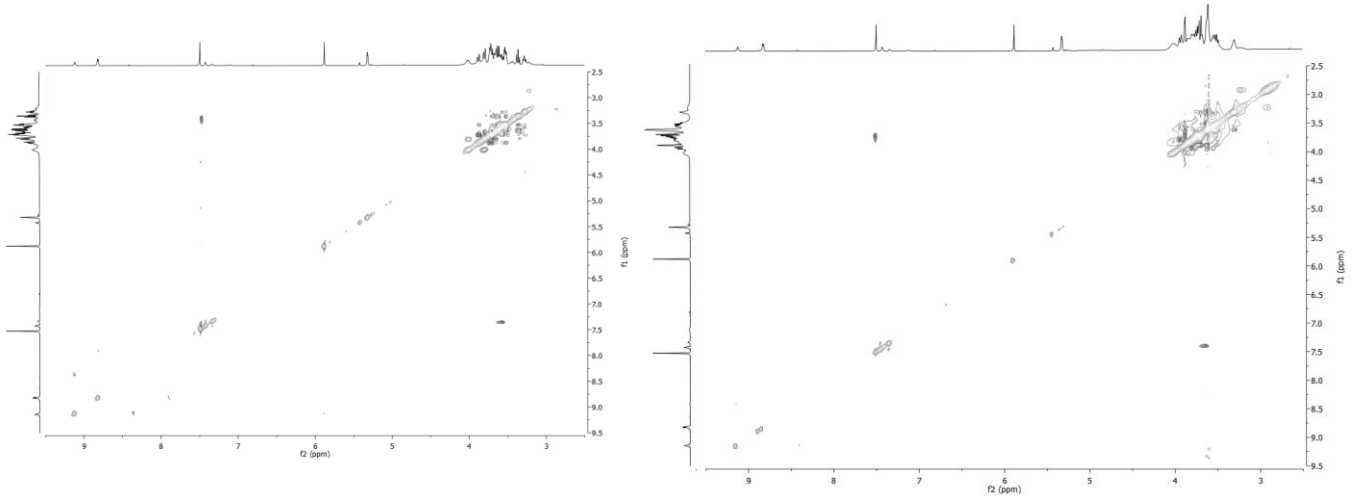
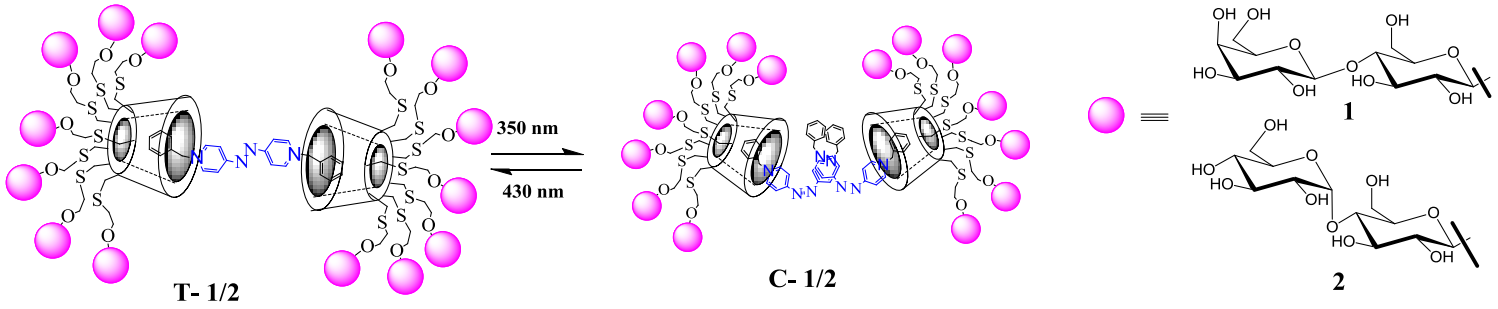


Figure S2'. ^{1}H-NOESY spectra of **C-1** and **C-2** respectively

5. Cis-trans isomerization



is

Scheme S4. Synthesis of Cis-trans complexes

Cis/trans isomerization was carried out by photochemical reaction.

Trans-to- Cis : 120-W Xe lamp with a cutoff fiter of ~350 nm for 1 hr,

Cis–to-Trans : 120-W visible lamp with a cutoff filter of -430 nm for 1 hr

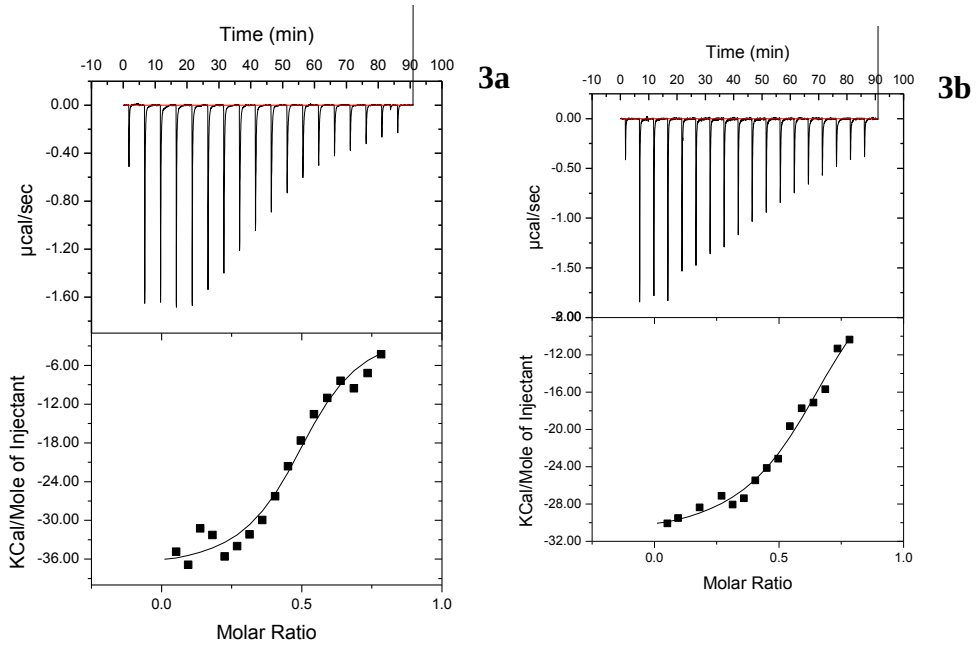


Figure S3. ITC titration curves of **14/8** (a) and **15/8** (b) respectively.

Complex	**n**	**Binding constant (M^{-1})**	**ΔH (Kcal/mol) X 10^4**	**ΔS (cal/mol/deg)**
14/8	0.505	6.04 ± 1.49 X **10^3**	-3.77 ± 0.13	-100
15/8	0.967	3.86 ± 0.71 X **10^3**	-3.17 ± 0.74	-80.7

Table S1. ITC profiles of **14/8** and **15/8** respectively .

6. ITC measurements.

The thermodynamic studies of carbohydrate-carbohydrate interaction was estimated by using isothermal titration calorimeter (ITC 200, USA). Trans/cis cyclodextrin analogs stock solution (0.03 or 0.05 mmol) was kept in the titration cell and was titrated by metal ions (Na^+, K^+ and Ca^{2+} individually 20 mmol). Each experiment consisted of 18 injections with a successive time gap of 100 s between two injections. For proper mixing of the solutions the stirring speed was maintained at 1000 rotations/min. Cell temperature was kept fixed at 298 K and nearly three successive titrations were averaged out to give the ITC curves.

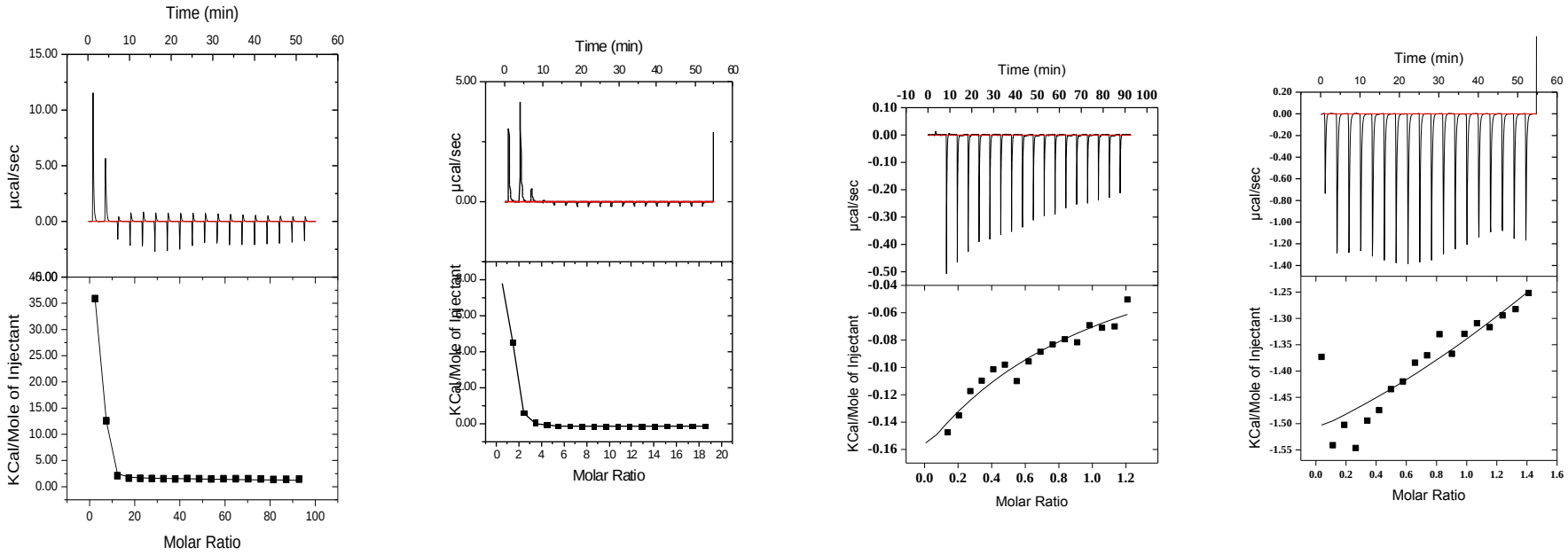


Figure S4. ITC profile for the interaction of **T-1** with Ca(II) ions: (a) Conc of **8** = 0.03 mM in water and $CaCl_2$ solution = 1 mM in water; (b) 10 mM. (c) 20 mM and (d) 50 mM.

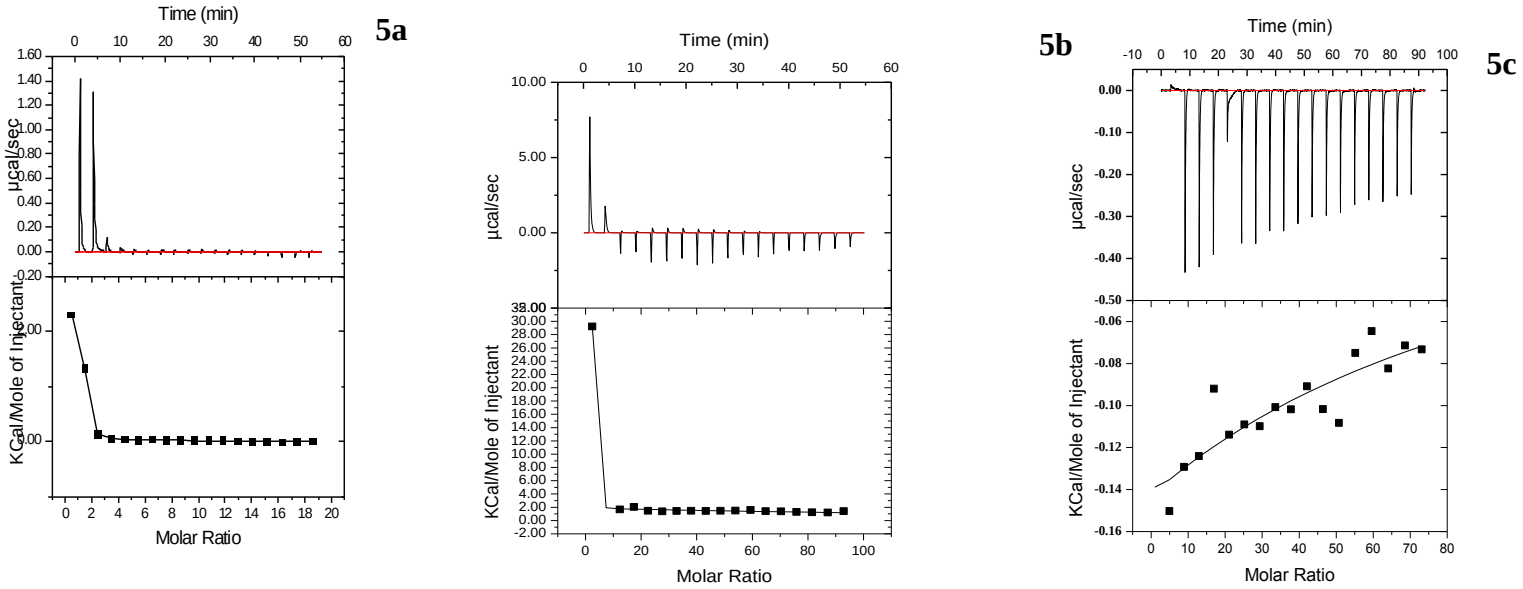


Figure S5. ITC profile for the interaction of lactose-β-CD **8** with Na(I), K(I) and Ca(II) ions: (a) Conc of **8** = 0.03 mM in water and NaCl solution = 20 mM in water; (b) Conc of **8** = 0.03 mM in water and KCL solution = 20 mM in water. (c) Conc of **8** = 0.03 mM in water and $CaCl_2$ solution = 20 mM in water.

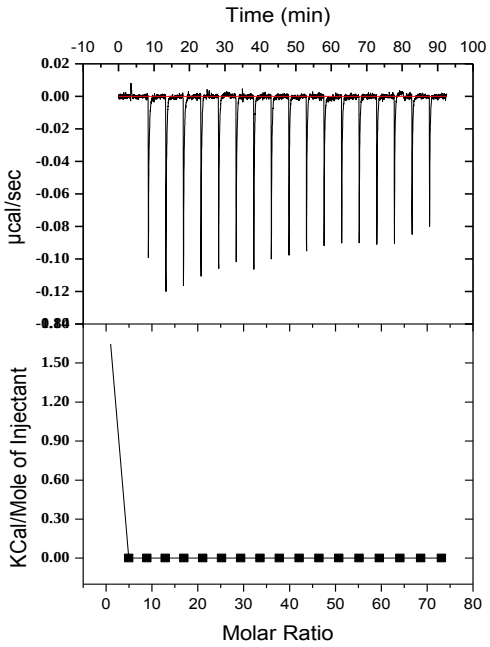


Figure S6. ITC profile for the interaction of maltose -β-CD **13** and Ca(II) ions: (a) Conc of **13** = 0.03 mM in water and $CaCl_2$ solution = 20 mM in water.

Metal	n	Binding constant (M^{-1})	ΔH (Kcal/mol) X 10^6	ΔS (cal/mol/deg)	N	R
$CaCl_2$ + 8	0.28	57.9 ± 4.7	-1.73 ± 0.02	-5.80 x 10^3	4	140.8
$CaCl_2$+ 13	-	NB	-	-		

Table S2. Binding parameter of **8** and **13.** NB = no binding

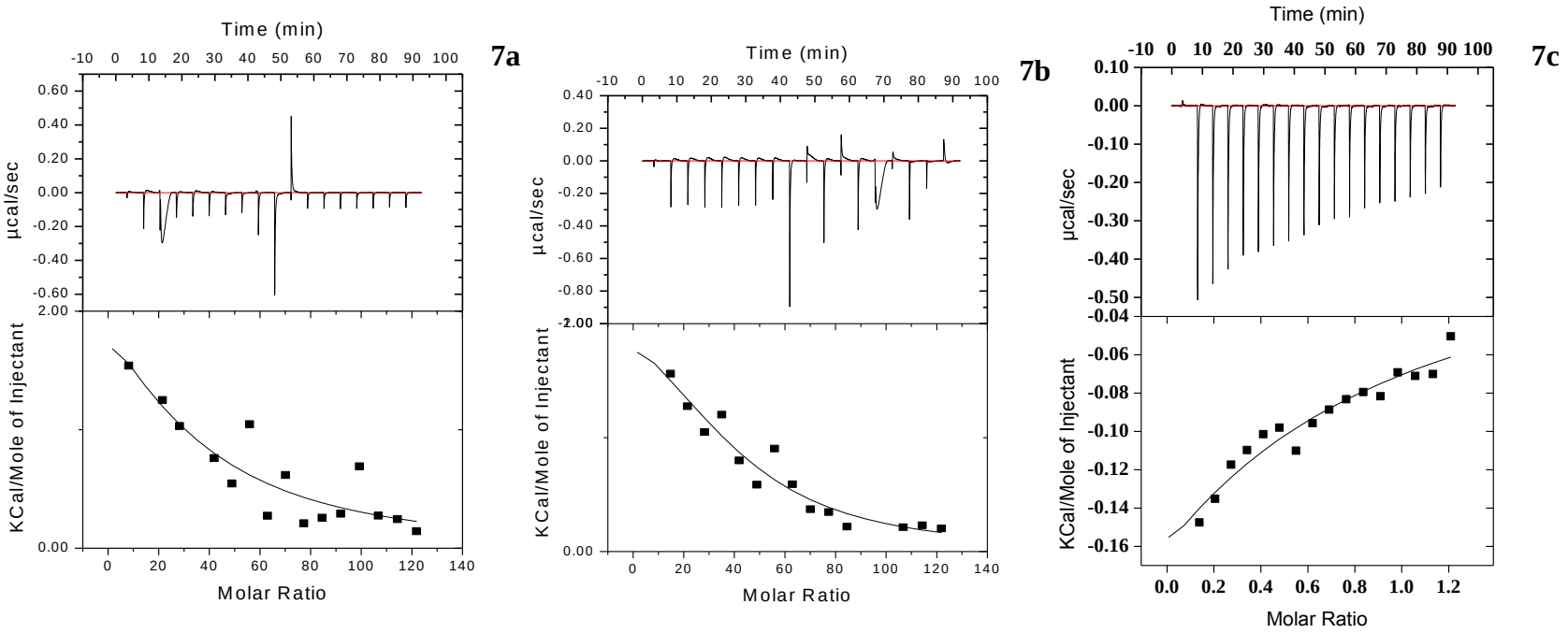


Figure S7. ITC profile for the interaction of **T-1** and Metal ions (Na(I), K(I), Ca(II) ions): (a) Conc of **T-1** = 0.05 mM in water and NaCl = 20 mM in water (b) Conc of **T-1** = 0.05 mM in water and KCl = 20 mM in water; (c) Conc of **T-1** = 0.05 mM in water and $CaCl_2$ = 20 mM in water

Metal	n	Binding constant (M^{-1})	ΔH (Kcal/mol)	ΔS (cal/mol/deg)	N	R
NaCl	-	NB	-	-		
KCl	-	NB	-	-		
$CaCl_2$	0.047	115 ± 23.0	-3.43 ± 0.81	-1.15 x 10^4	21	48.3

Table S3. Binding parameter of **T-1.** NB = no binding

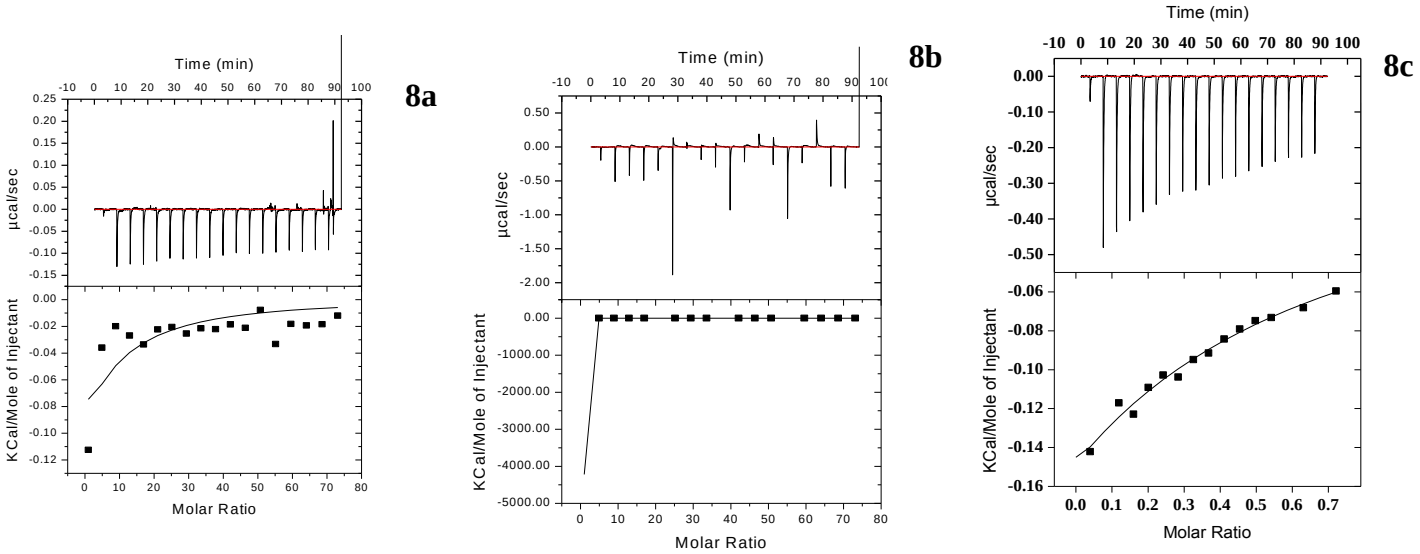


Figure S8. ITC profile for the interaction of **T-2** and Metal ions (Na(I), K(I), Ca(II) ions): (a) Conc of **T-2** = 0.03 mM in water and NaCl = 20 mM in water (b) Conc of **T-2** = 0.05 mM in water and KCl = 20 mM in water; (c) Conc of **T-2** = 0.03 mM in water and $CaCl_2$ = 20 mM in water

Metals	**n**	**Binding constant (M^{-1})**	**ΔH (Kcal/mol)**	**ΔS (cal/mol/deg)**	**N**	**R**
NaCl	-	NB	-	-		
KCl	-	NB	-	-		
$CaCl_2$	0.0051	104 ± 11.4	-2.18 ± 1.79	-7.32 x 10^3	196	37.5

Table S4. Binding parameter of **T-2.** NB = no binding

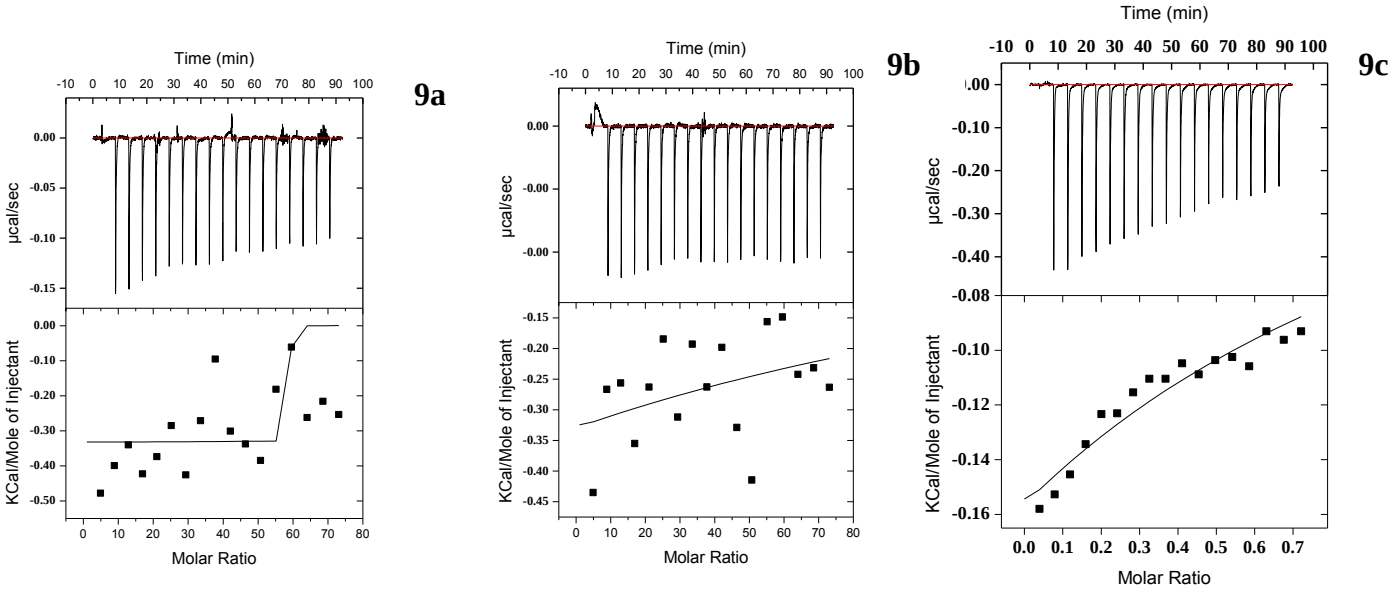


Figure S9. ITC profile for the interaction of **C-1** and Metal ions (Na(I), K(I), Ca(II) ions): (a) Conc of **C-1** = 0.05 mM in water and NaCl = 20 mM in water (b) Conc of **C-1** = 0.05 mM in water and KCl = 20 mM in water; (c) Conc of **C-1** = 0.05 mM in water and $CaCl_2$ = 20 mM in water

Metals	**N**	**Binding constant (M^{-1})**	**ΔH (Kcal/mol)**	**ΔS (cal/mol/deg)**	**N**	**R**
NaCl	-	NB	-	-		
KCl	-	NB	-	-		
$CaCl_2$	0.043	276 ± 39.7	-3.71 ± 0.2	-1.24 x 10^4	23	11.98

Table S5. Binding parameter of **C-1.** NB = no binding

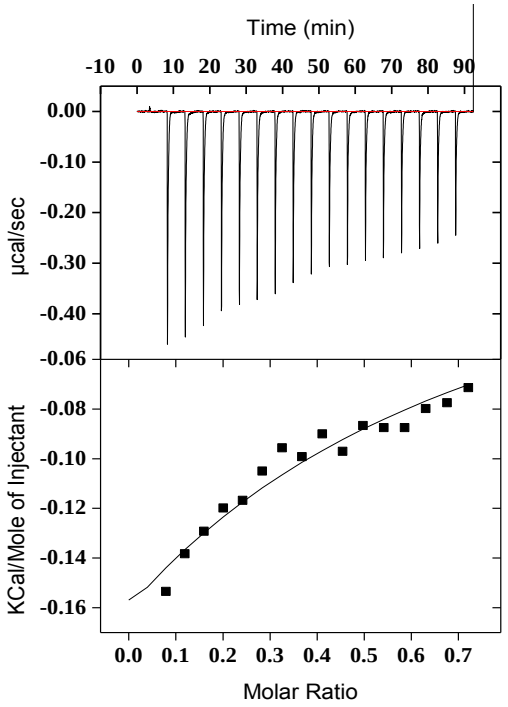


Figure S10. ITC profile for the interaction of **C-1** and Ca(II) ions: (a) Conc of **C-2** = 0.03 mM in water and $CaCl_2$ = 20 mM in water

Metal	n	Binding constant (M^{-1})	ΔH (Kcal/mol)	ΔS (cal/mol/deg)	N	R
$CaCl_2$	0.0052	205 ± 87.3	-7.13 ± 0.04	-2.39 x 10^4	192	33.28

Table S6. Binding parameter of **C-2.**

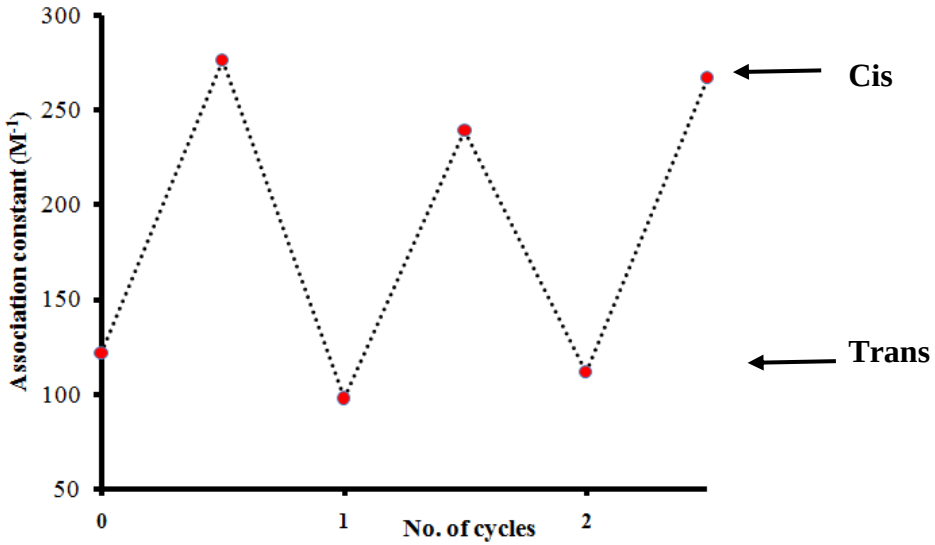


Figure S11. Representative CCIs association constant of the **Trans/cis** samples prepared by photo-irradiation with a cut-off filter of ~350 and ~430 nm respectively.

7. Atomic Force Microscopy (AFM) Measurement.

Topology of the micelles were investigated in the dry state with a AFM-JPK instrument with nanowizard-II setup.

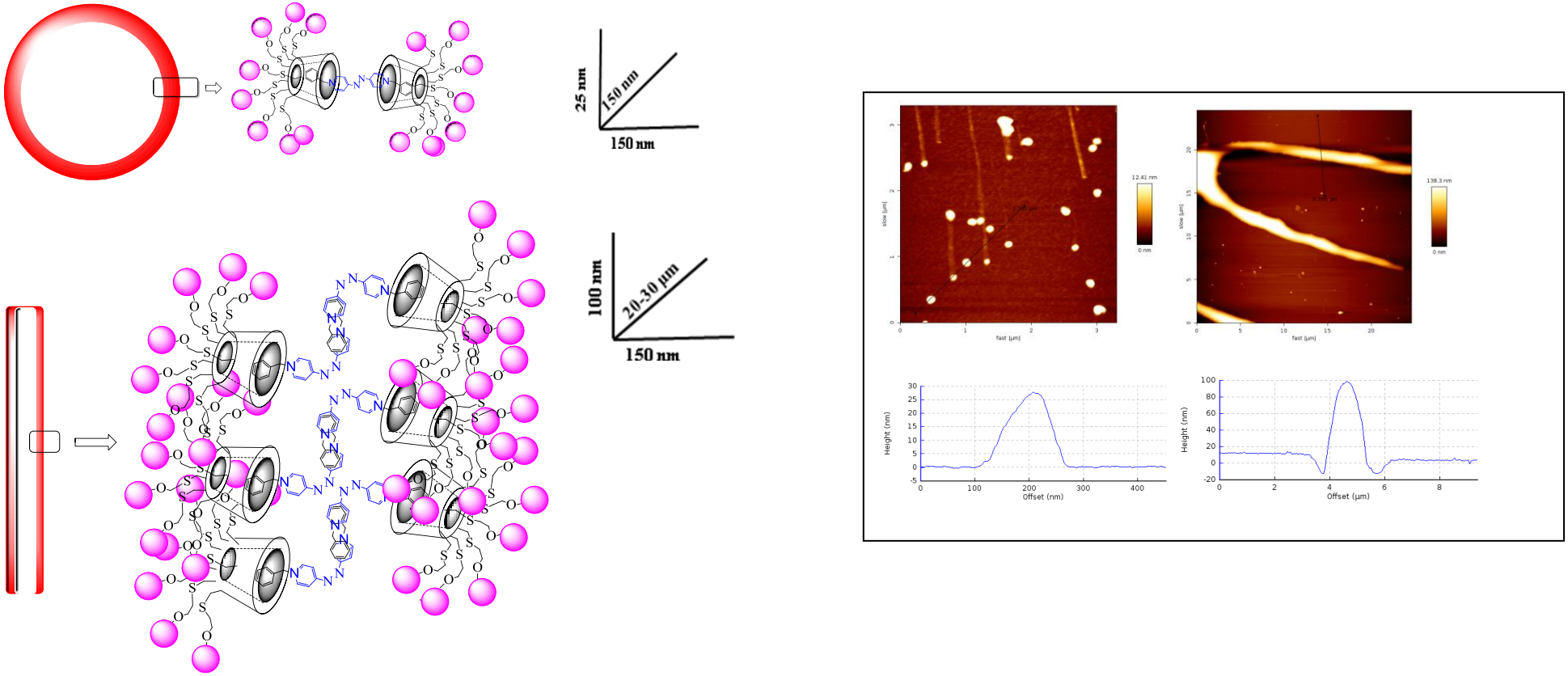


Figure S12. (a) schematic representation of supramolecular self assembly of **T-1** and **C-1**; (b) AFM images

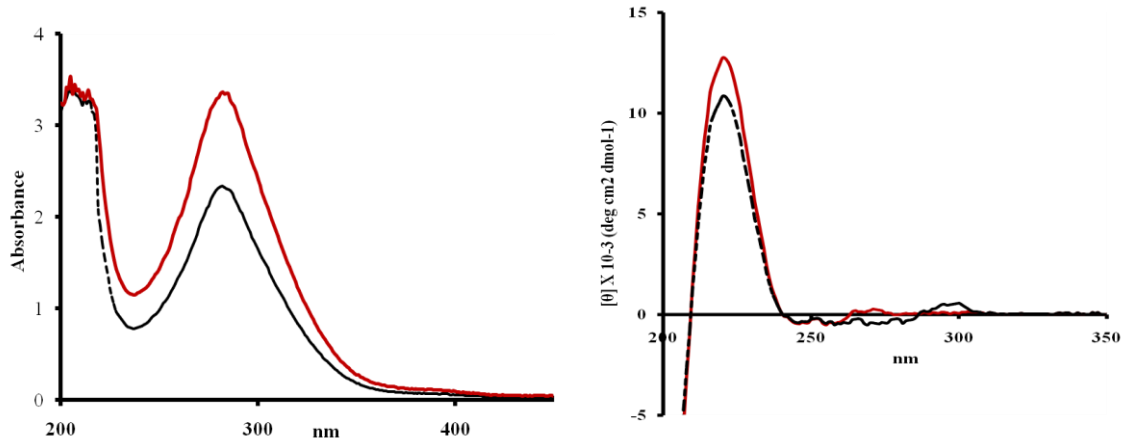
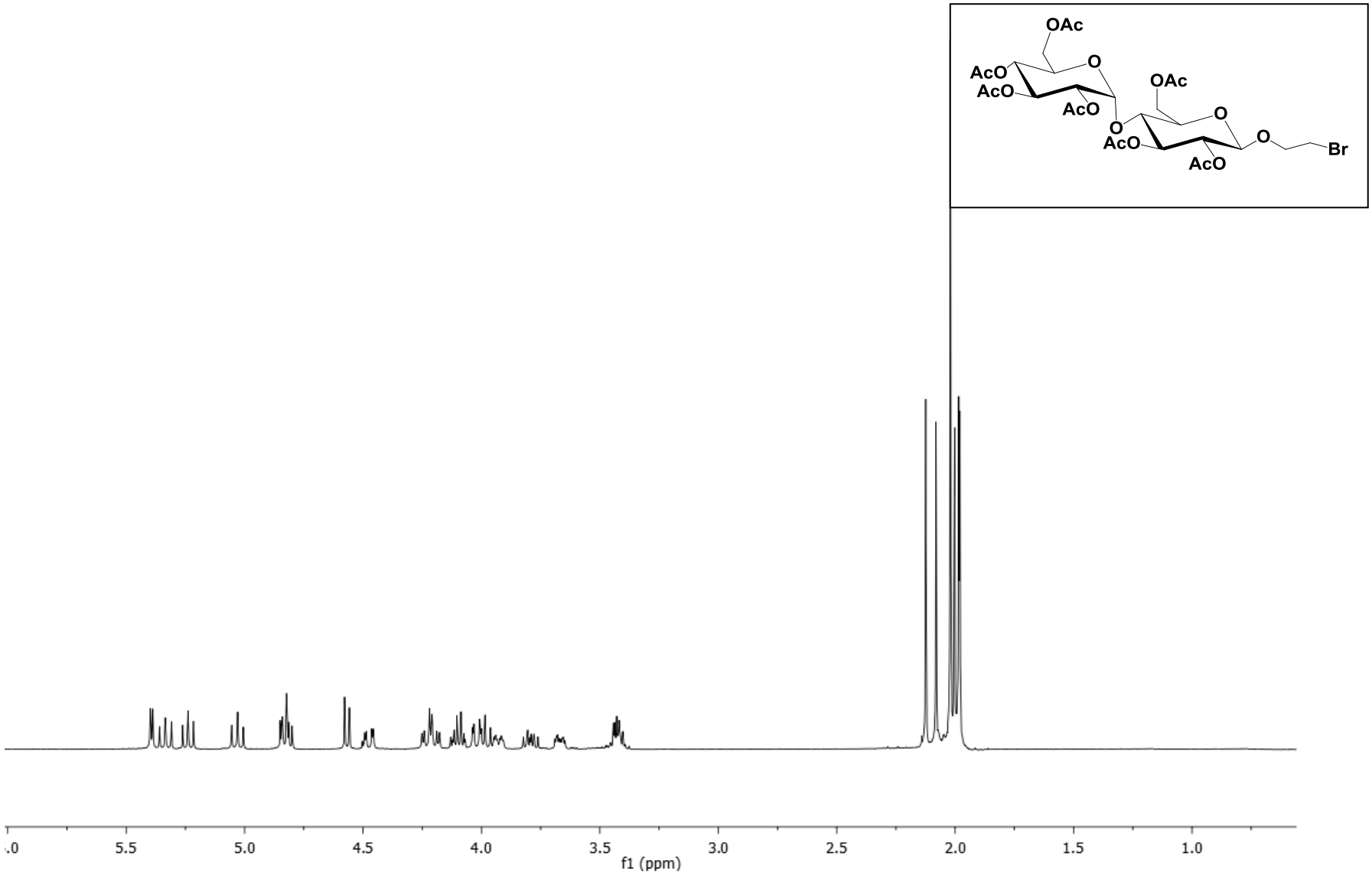


Figure S13. (a) UV-visible spectra of (T-1 —; C-1 ---) in water (50 μM) (b) CD spectra of (T-1 —; C-1 ---) in water (50 μM).

8. **NMR data**

140113-05-PB-Mal



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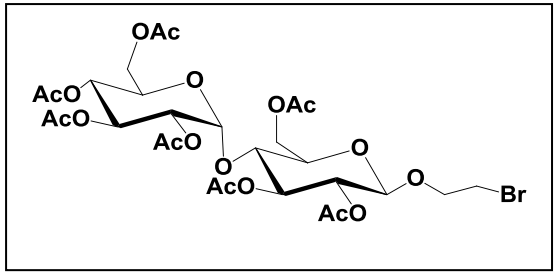
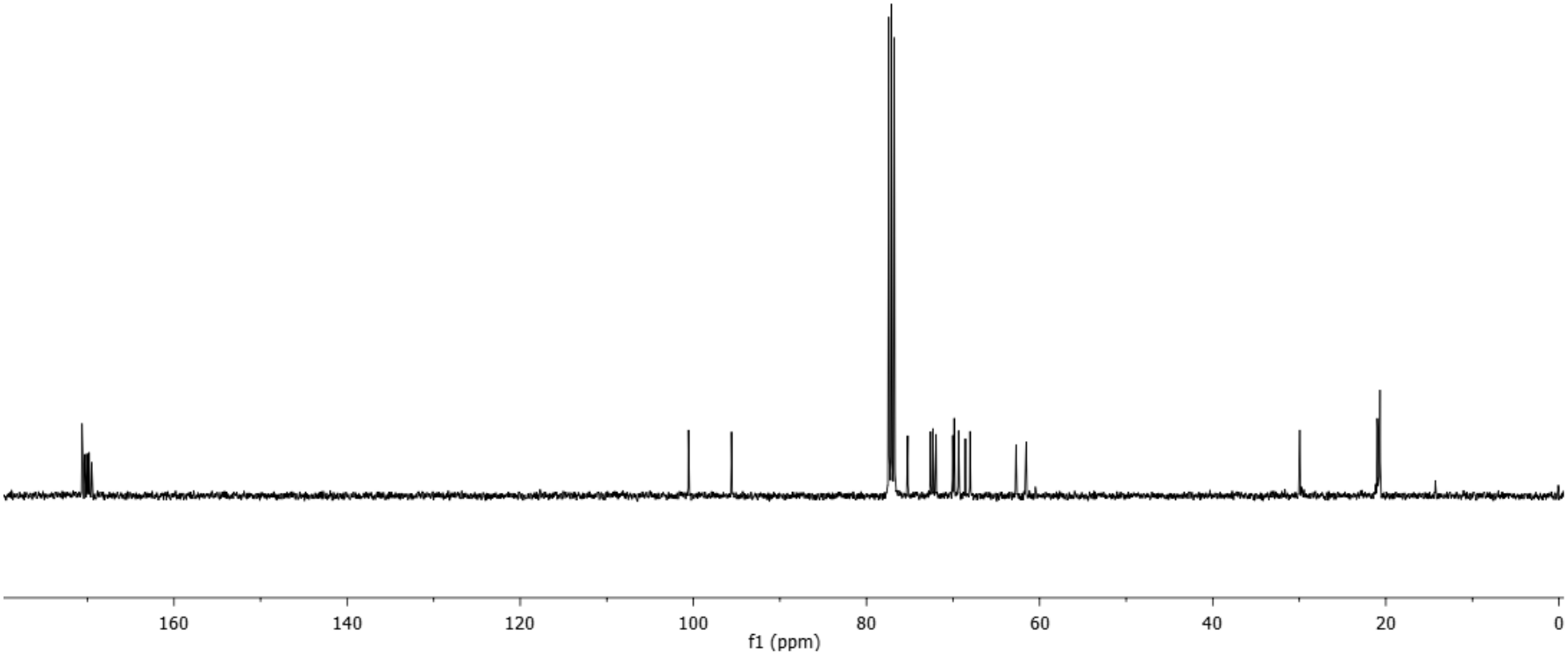
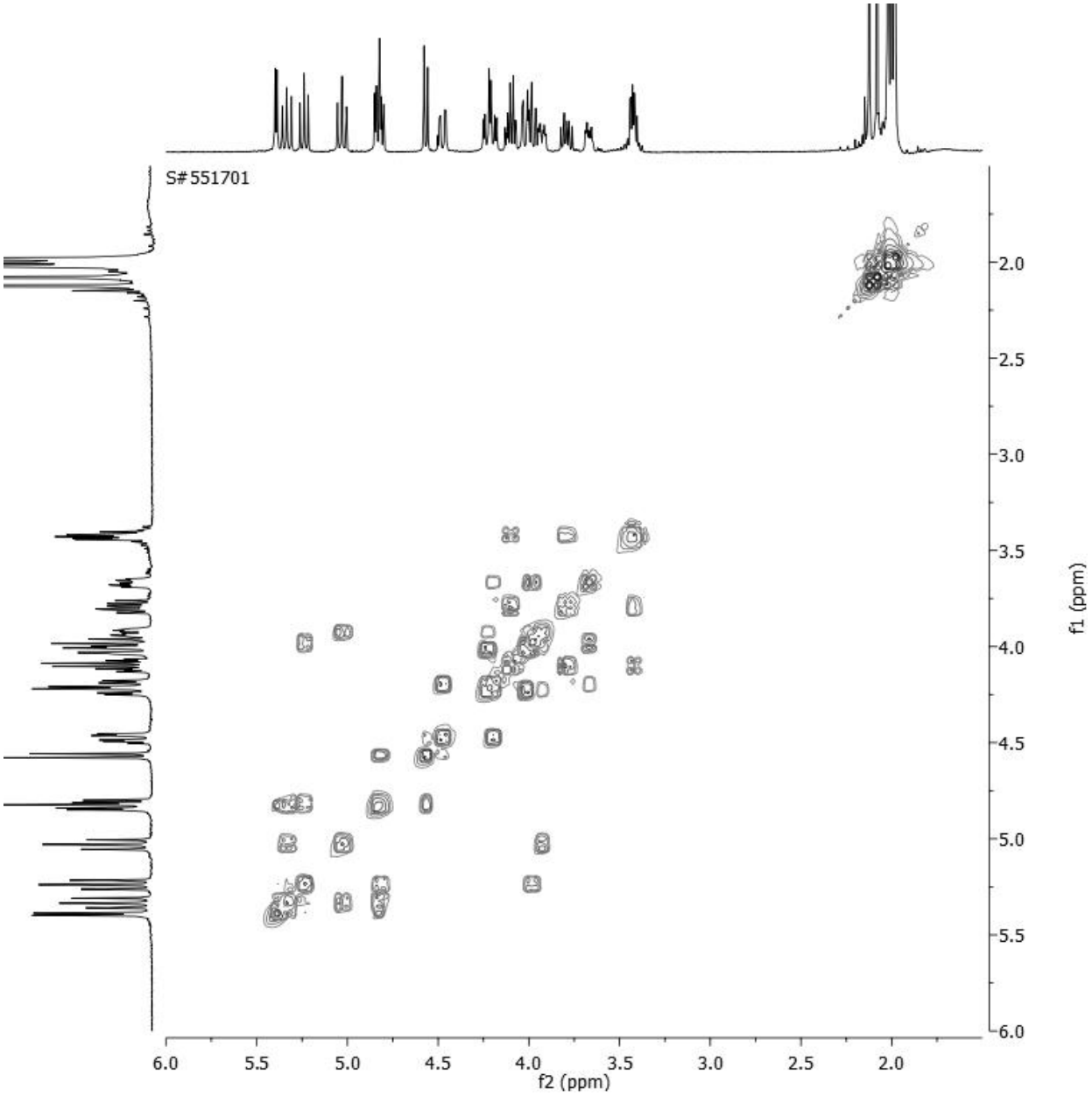
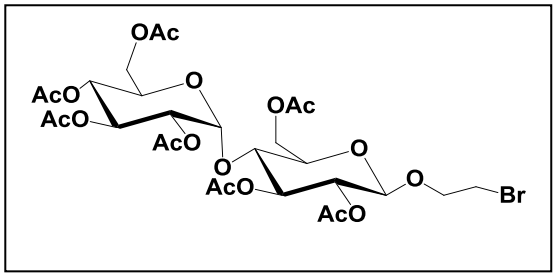
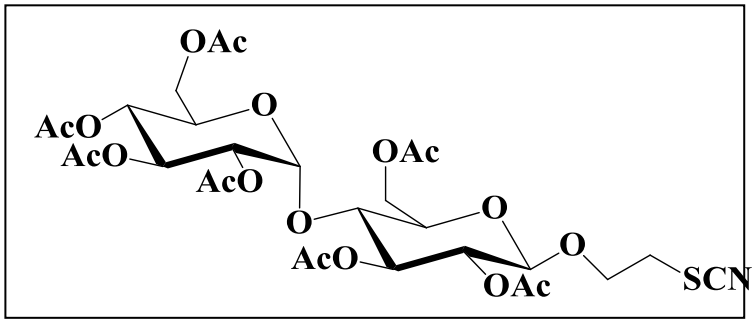


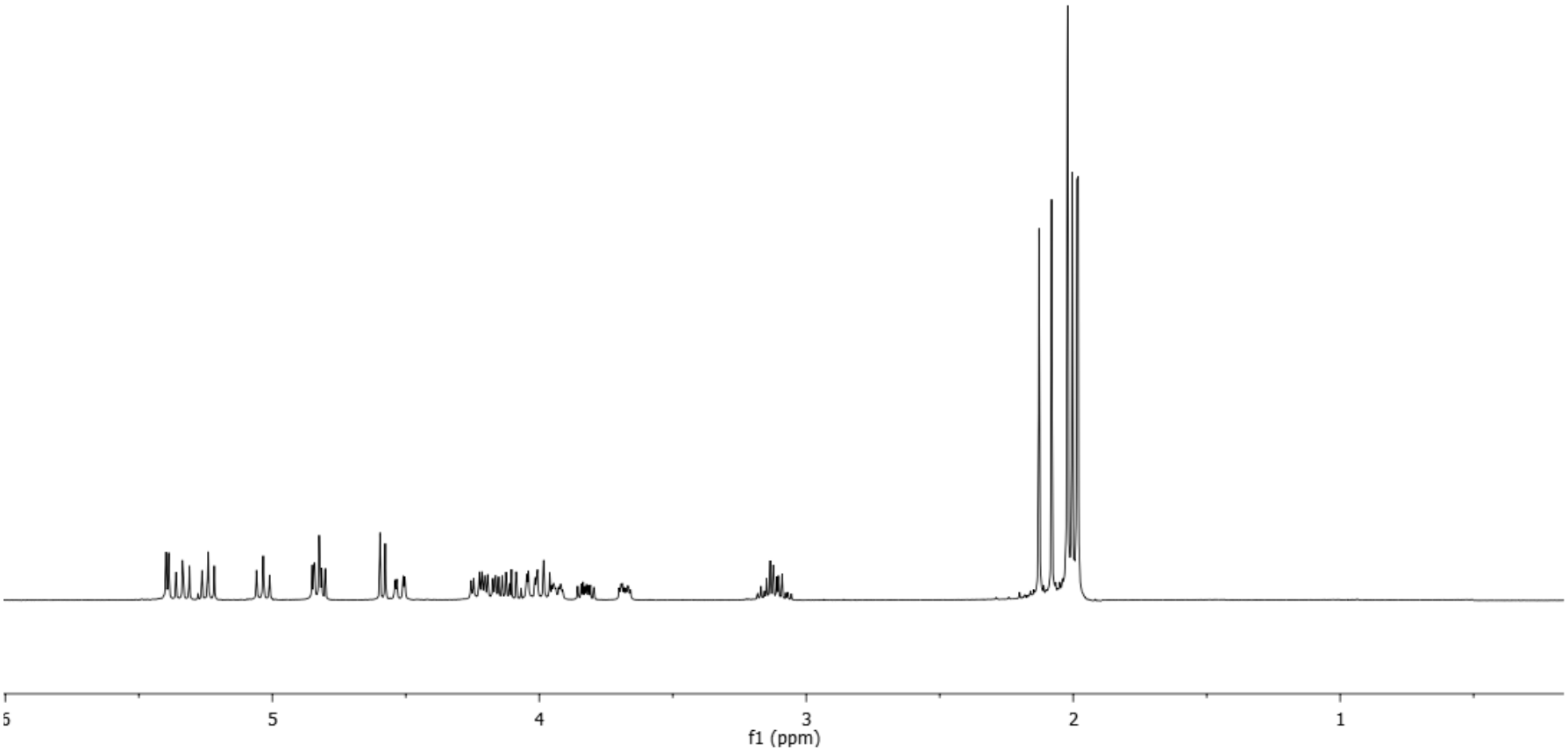






160113-18-PB-SCN





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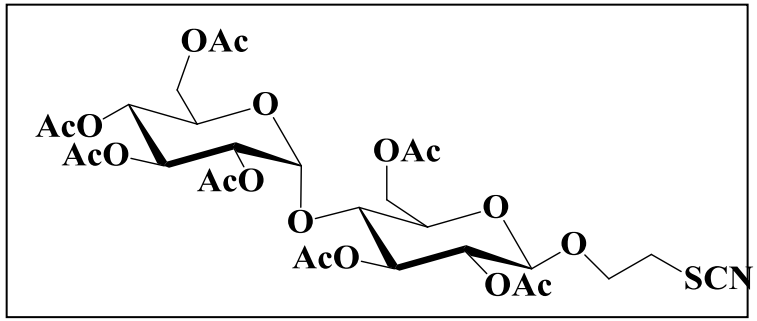
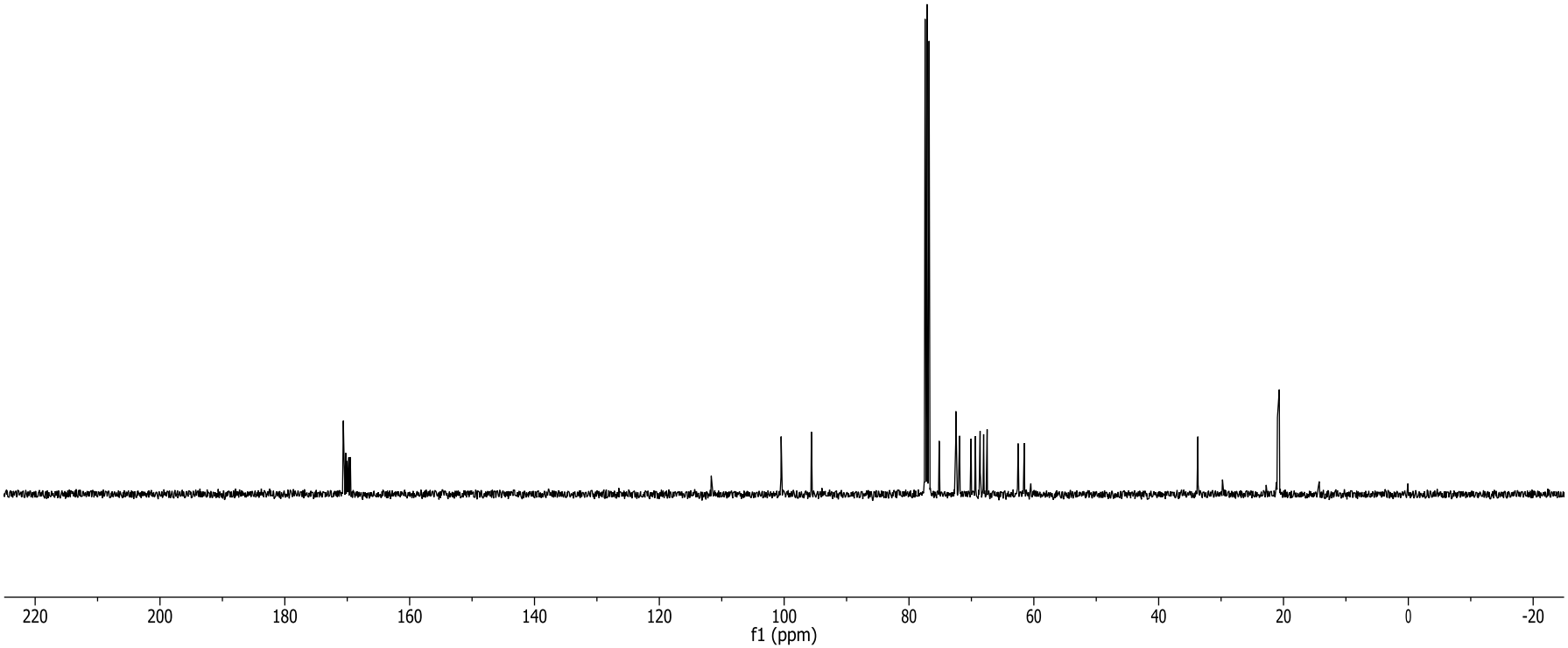
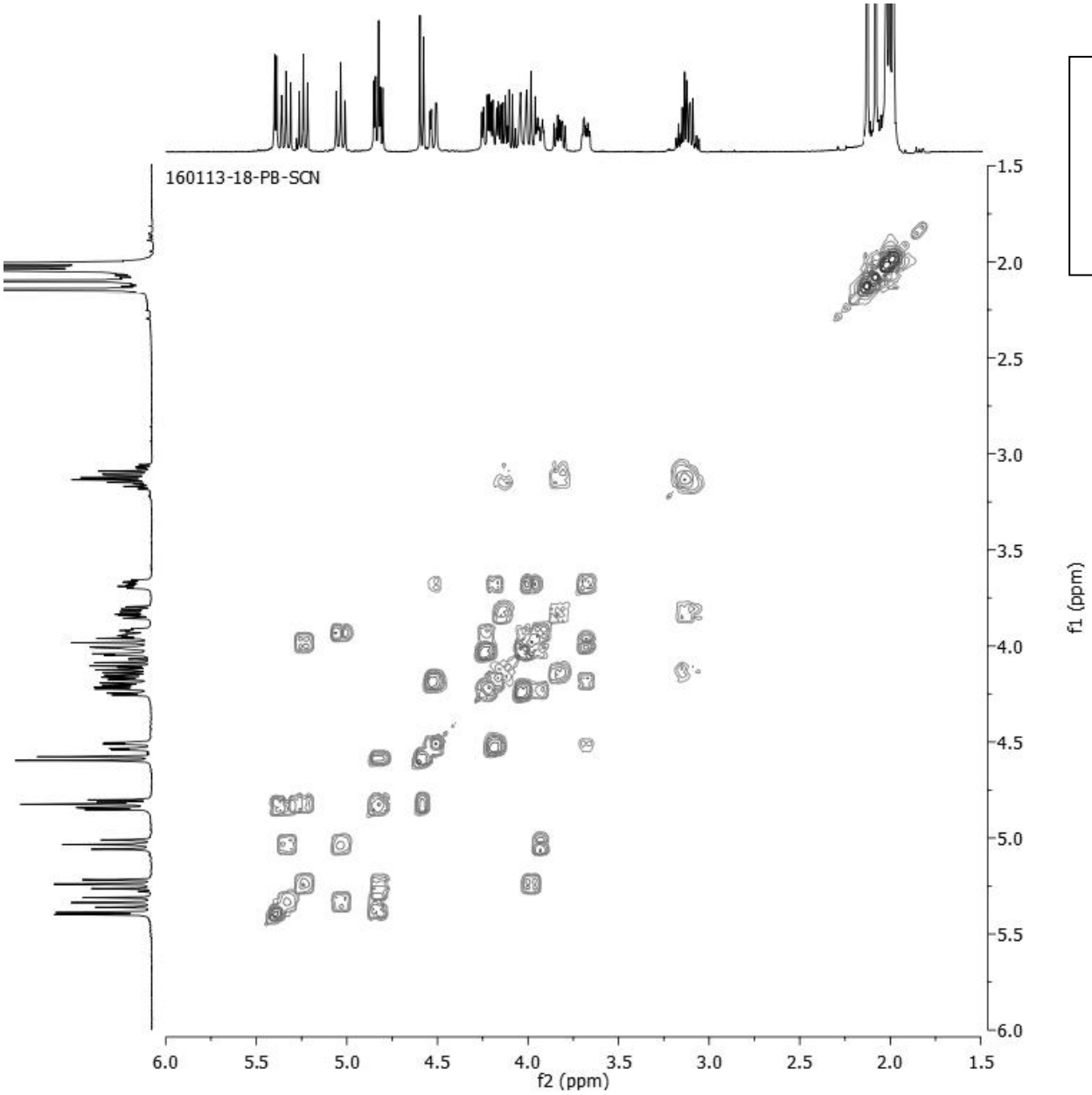
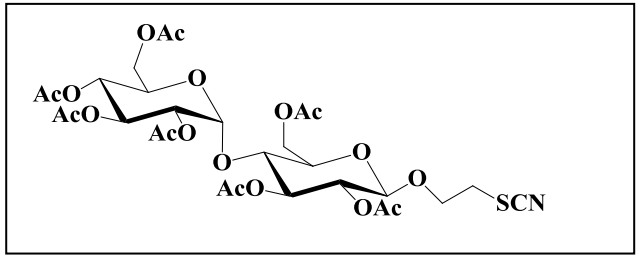
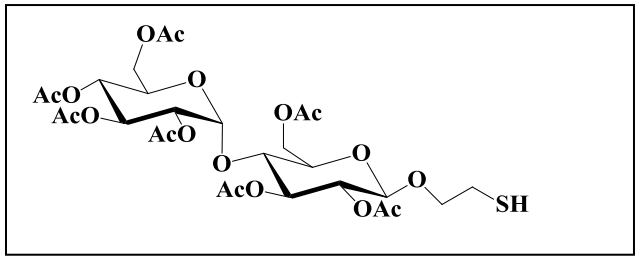


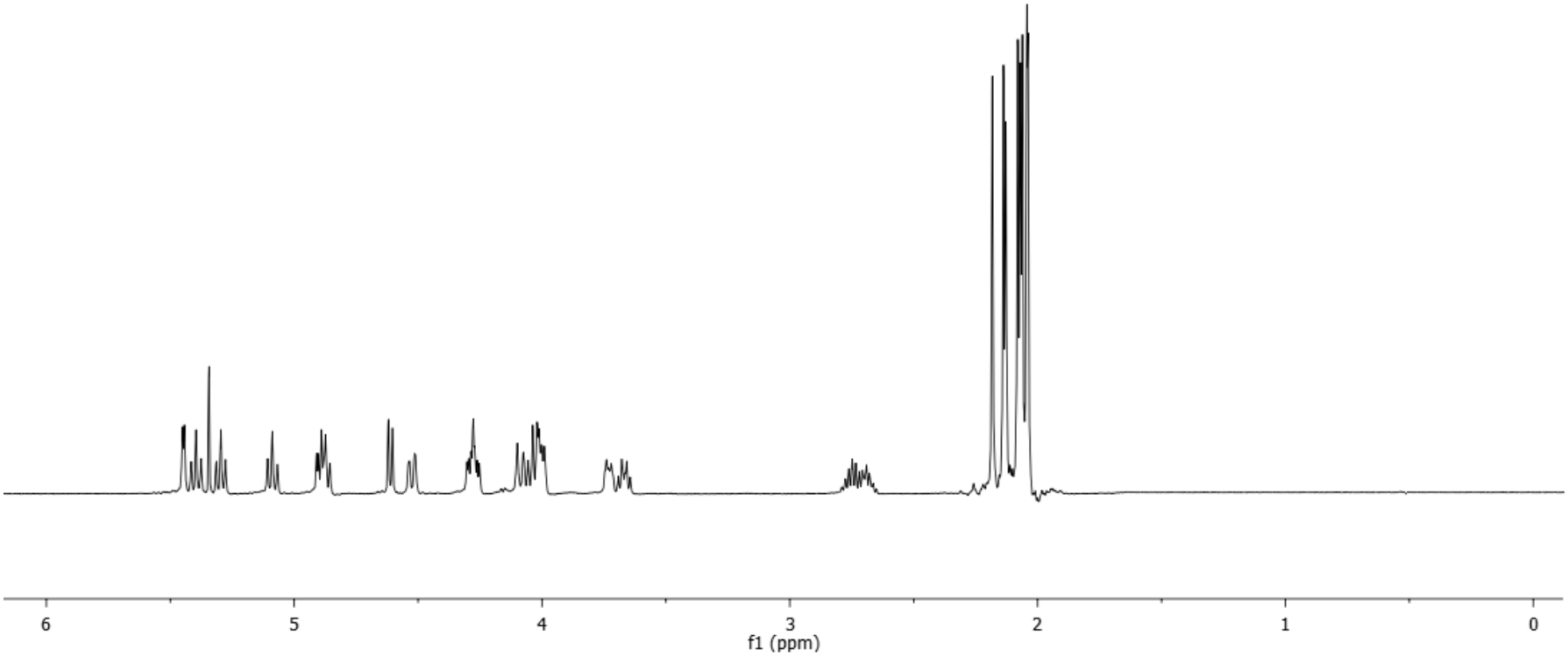


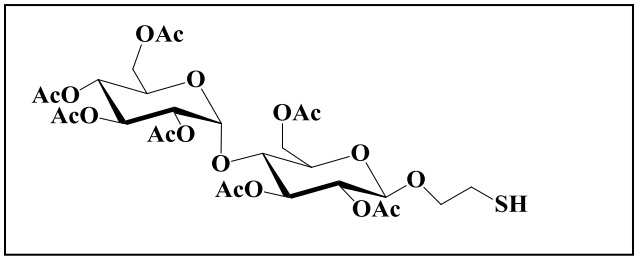


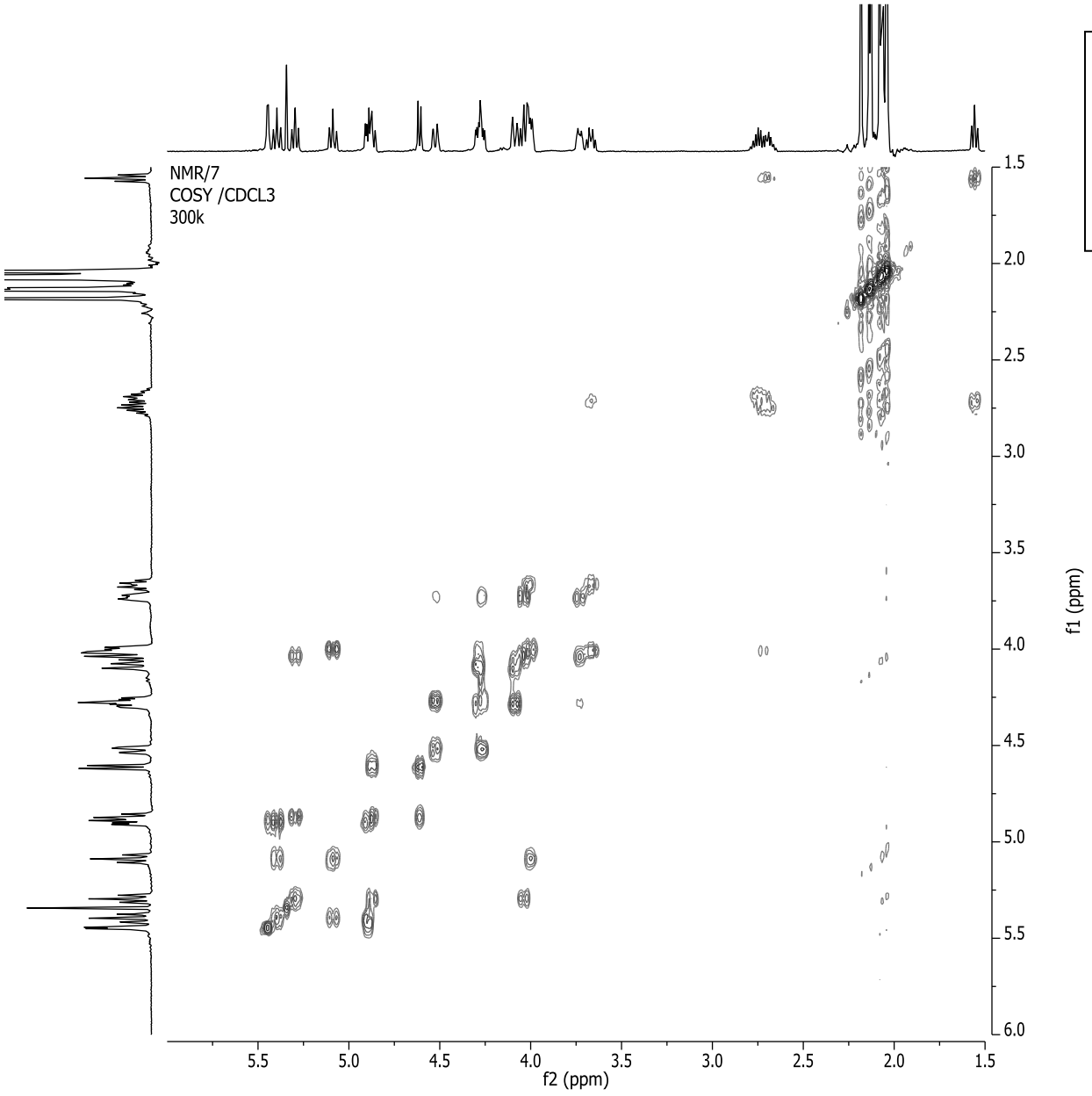


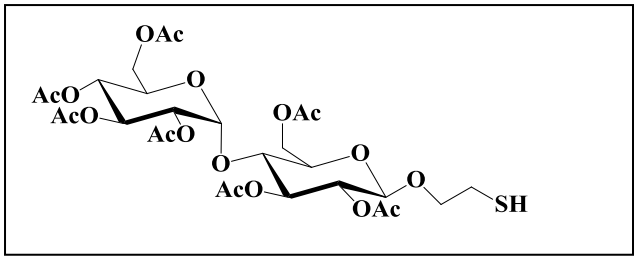
NMR/6
PB-SH
1H/CDCL3
300k 21/01/2013











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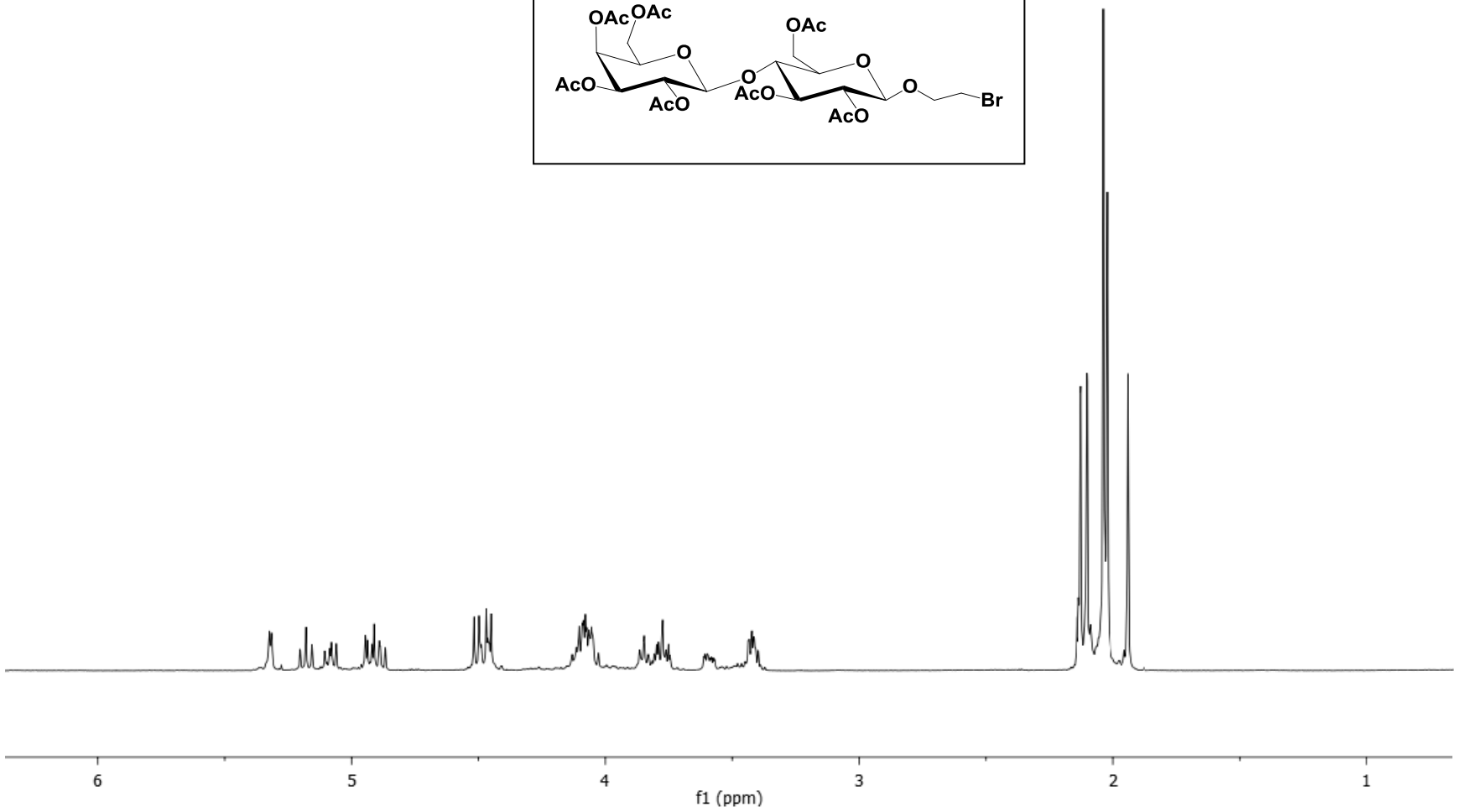
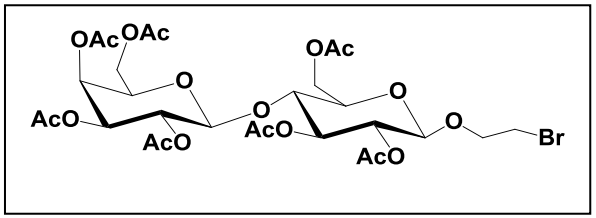
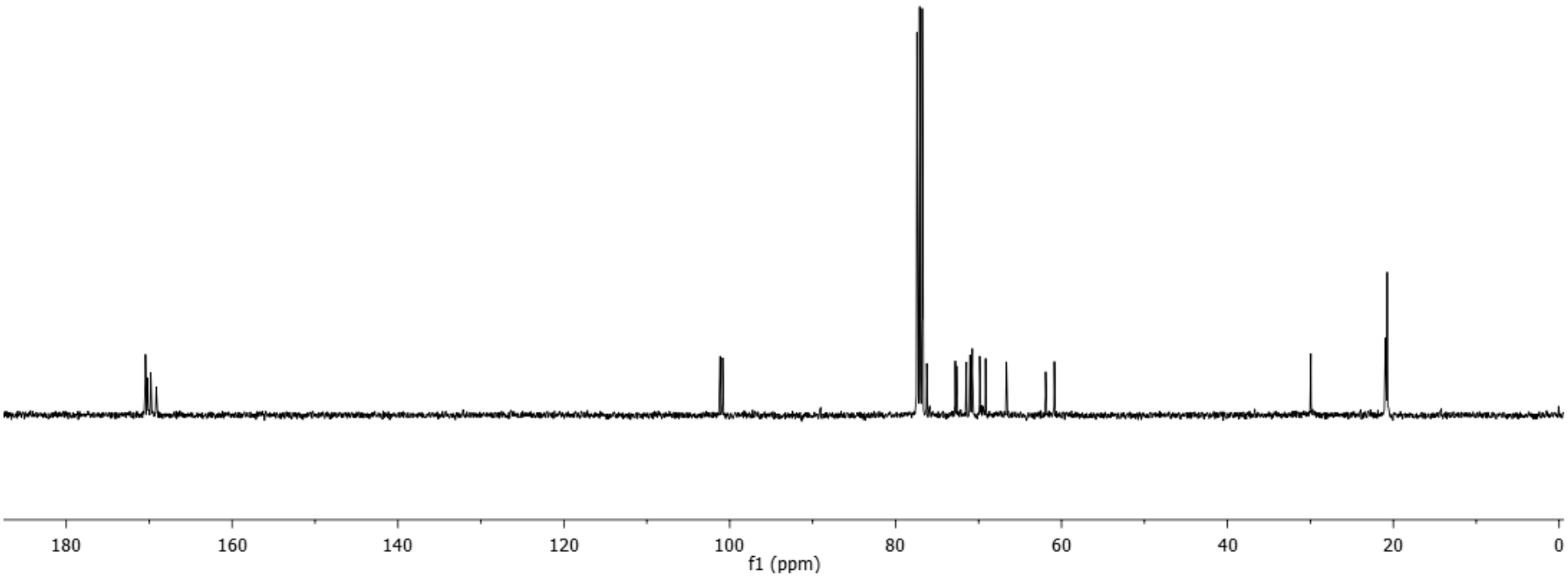
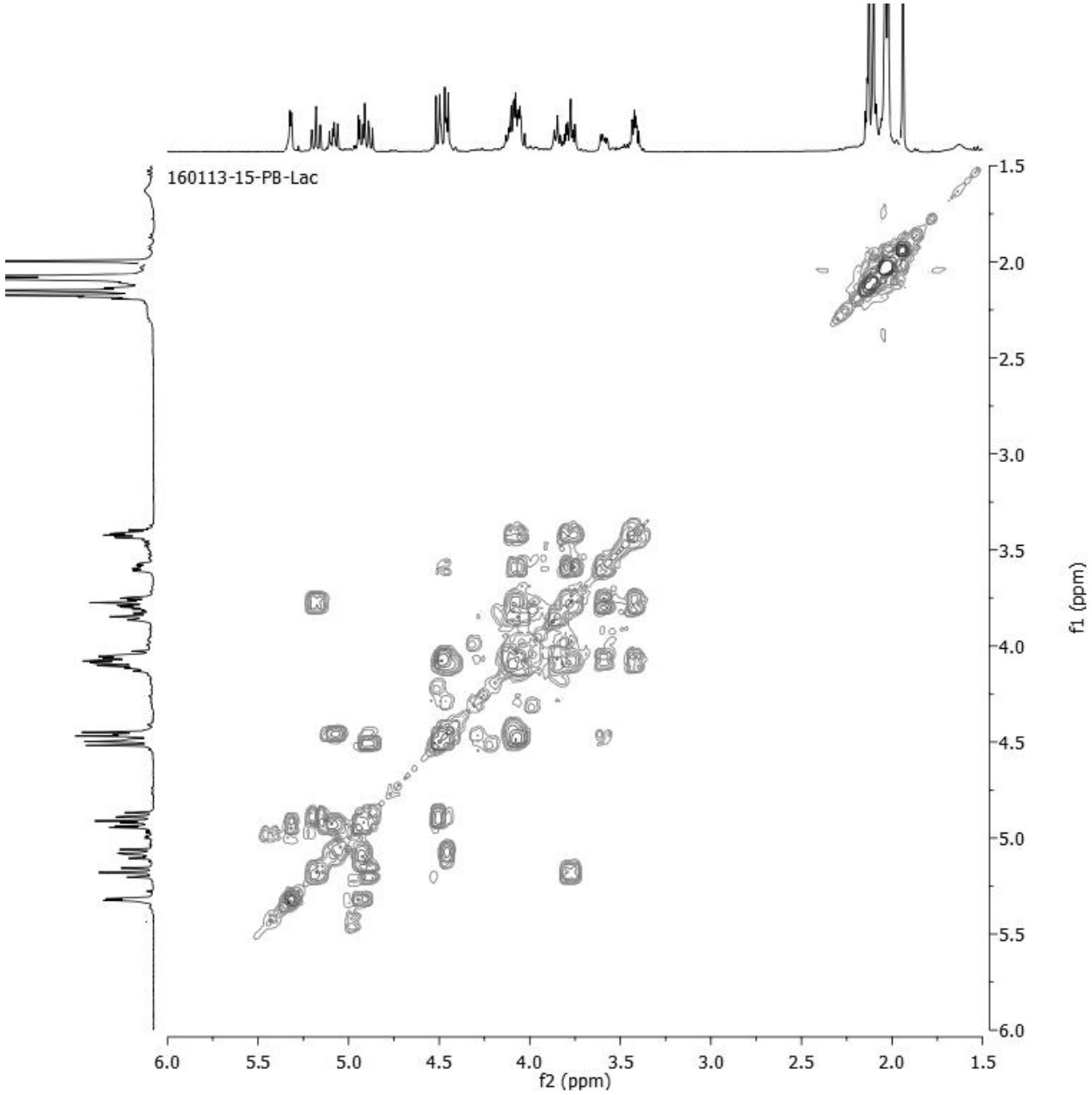
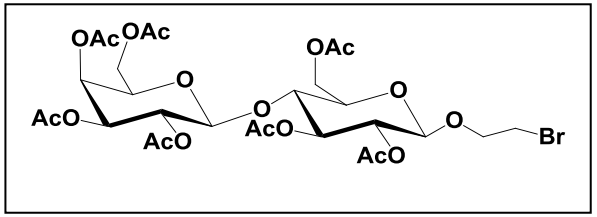


170113-24-PB-Lac

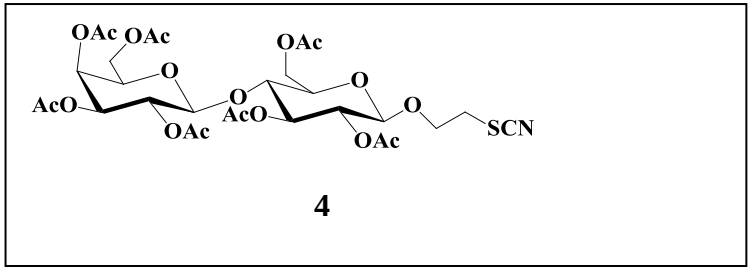








230113-08-PB-LScn



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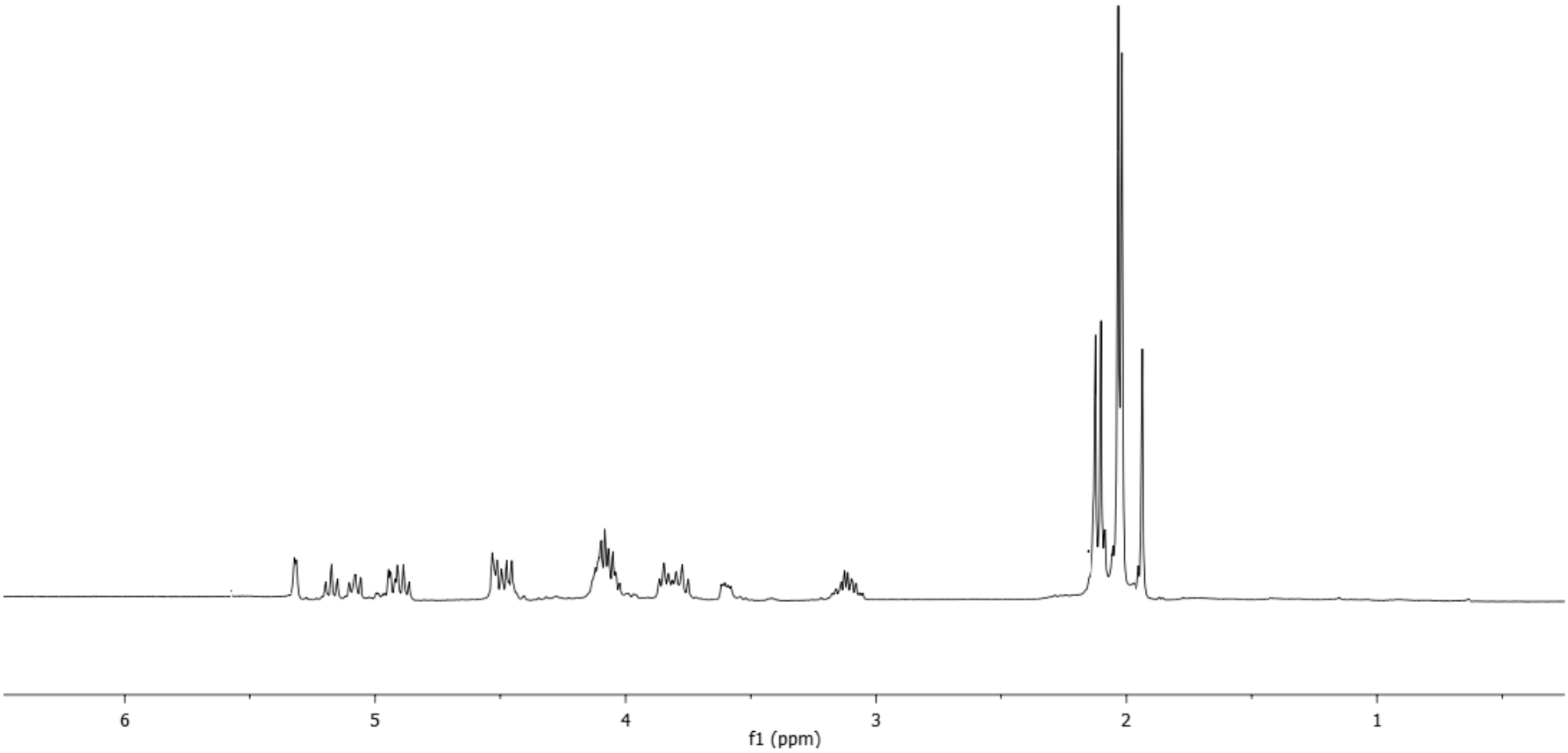

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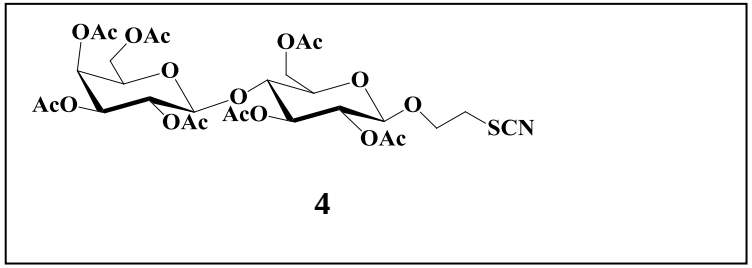

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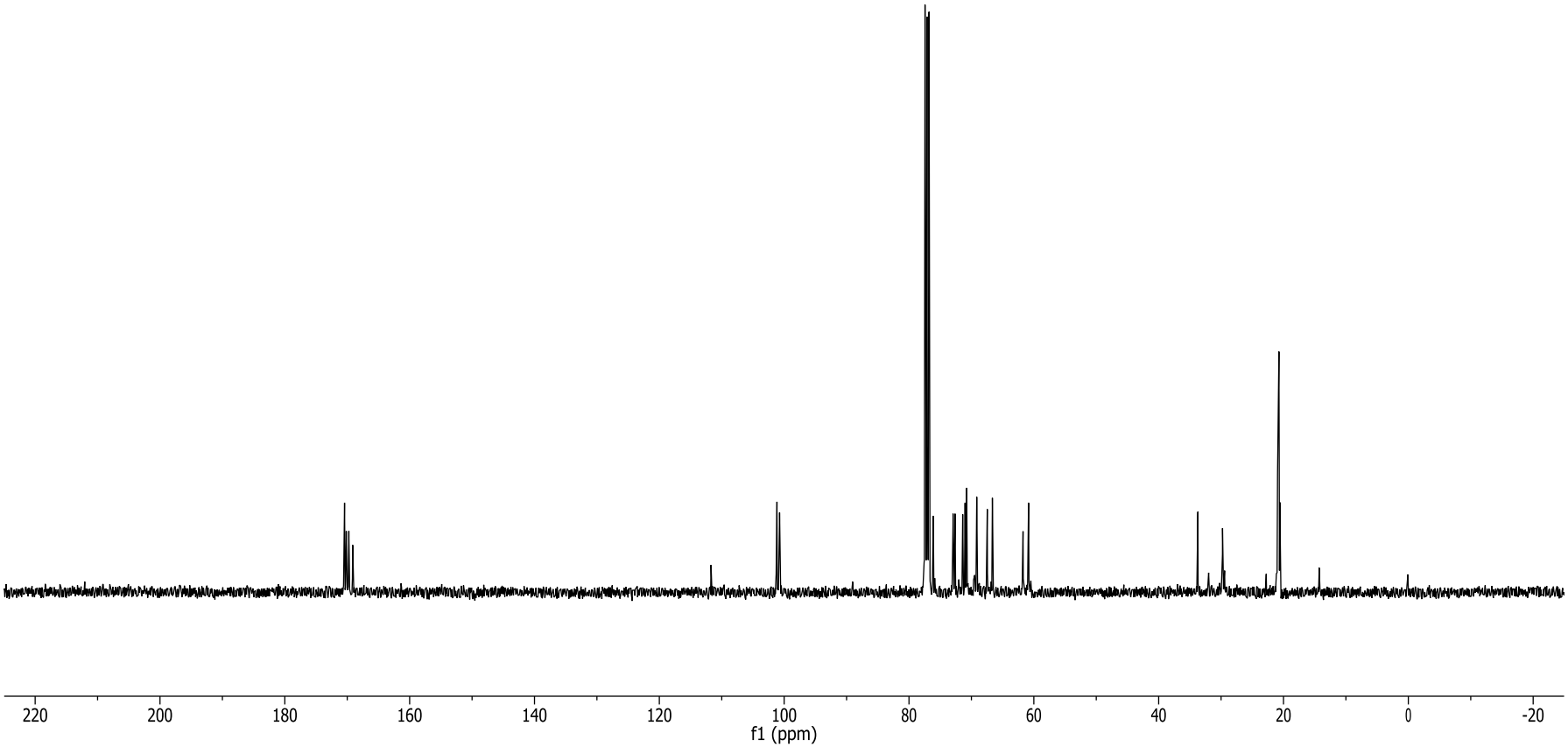
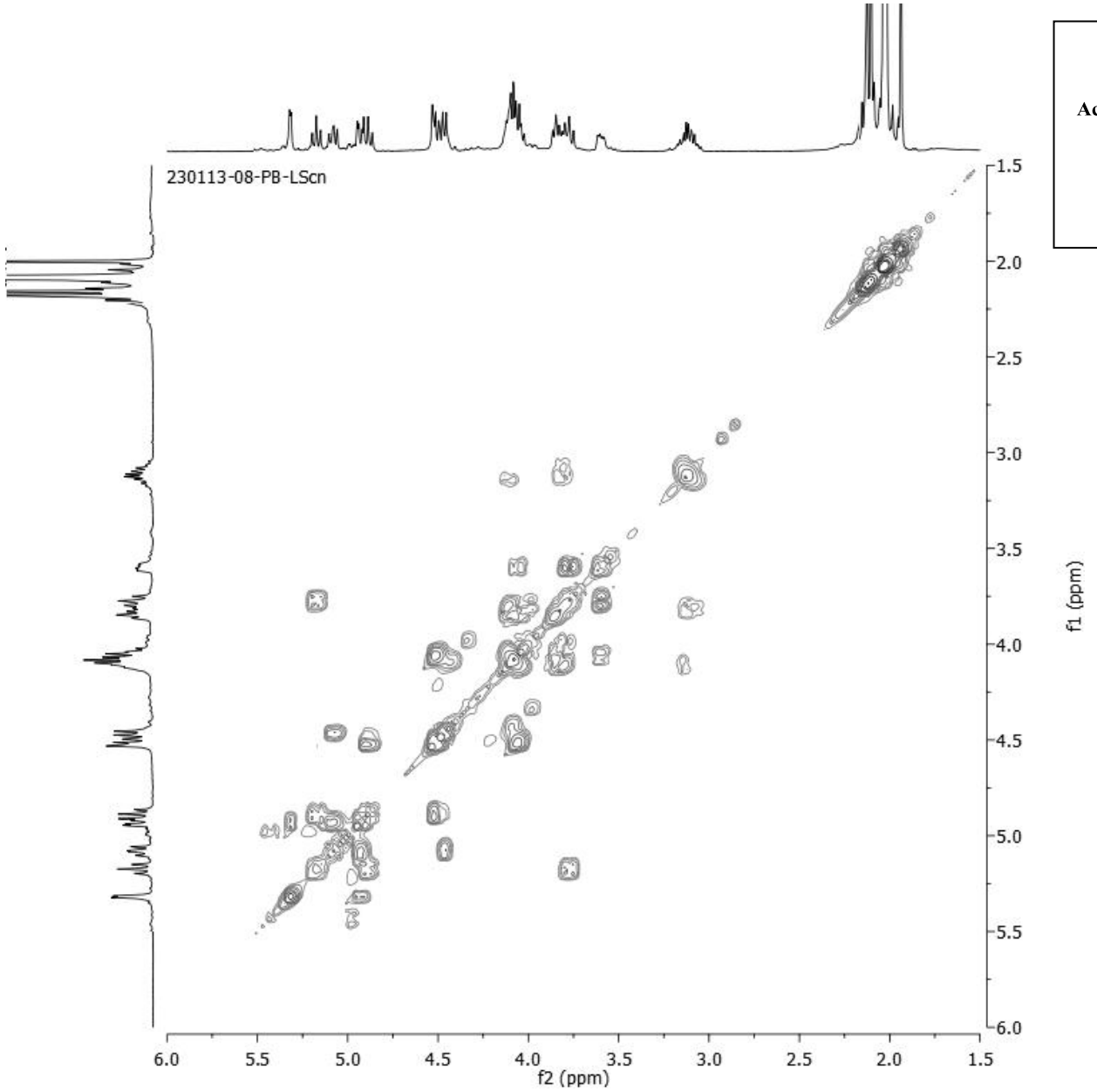
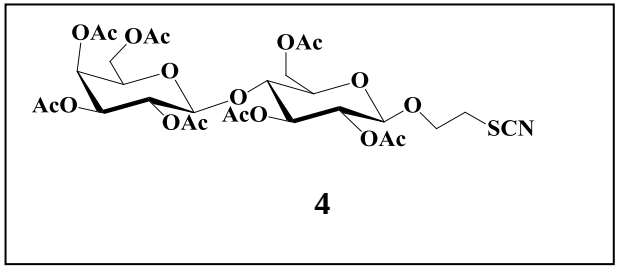
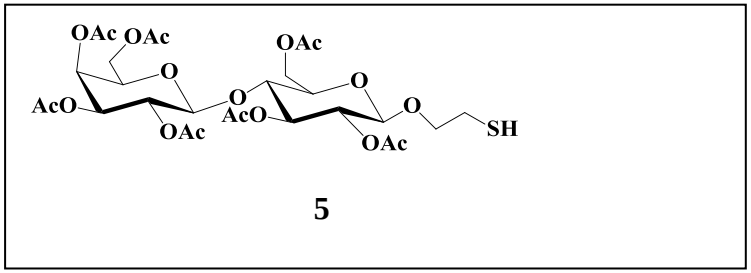






4

NMR/17
HK-122
CD3OH 300K



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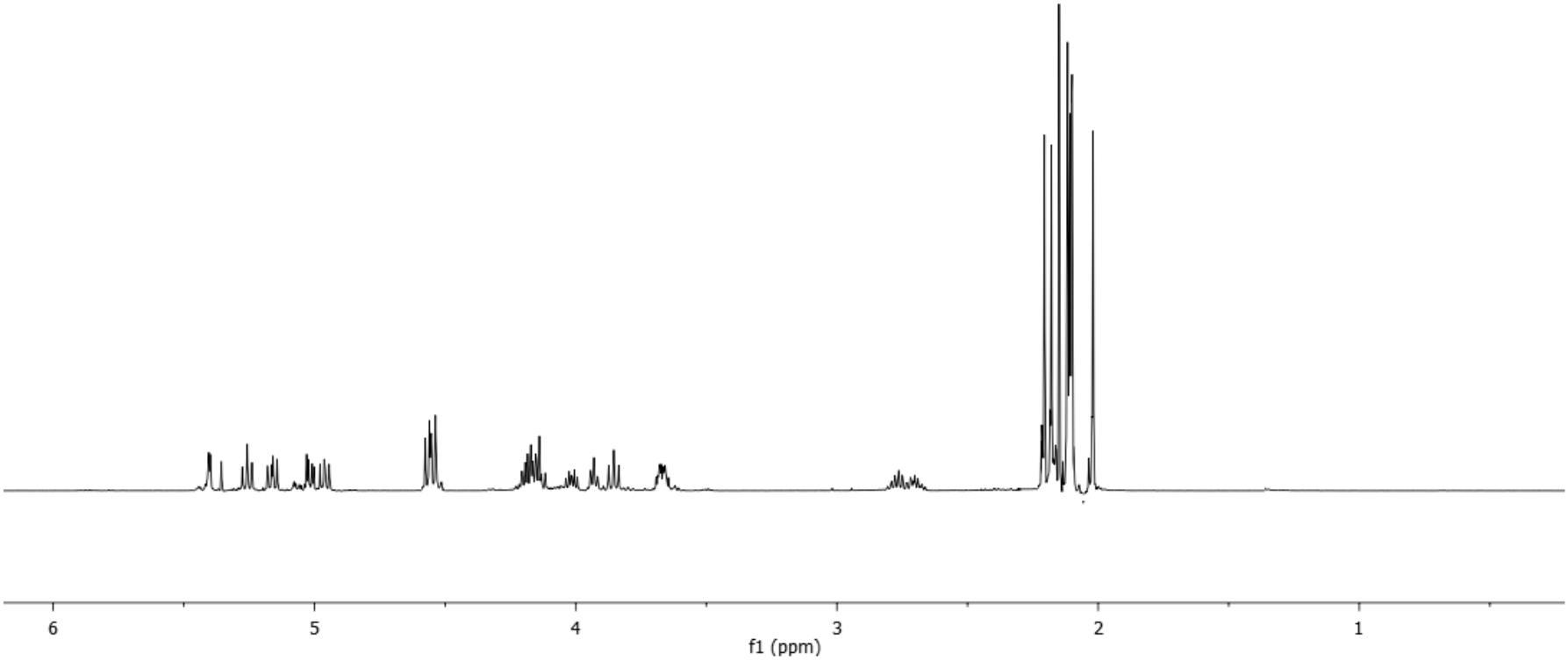

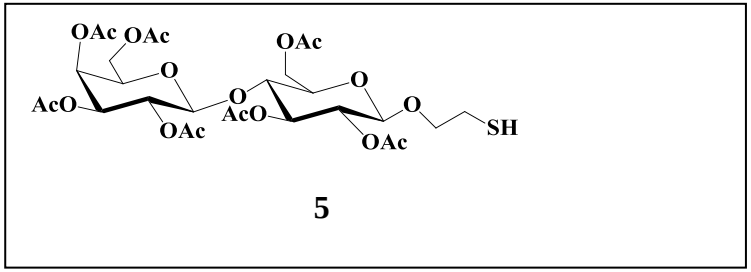

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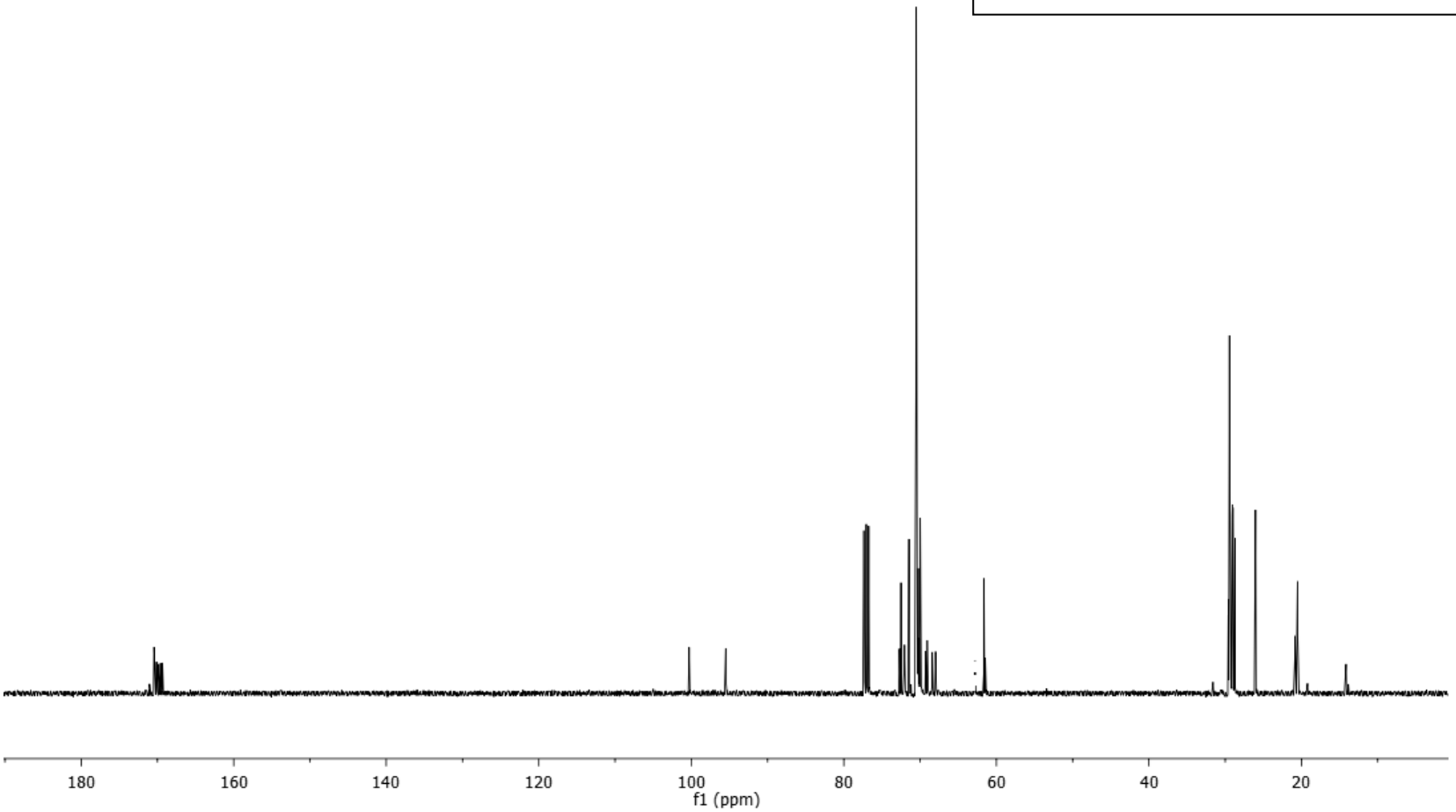

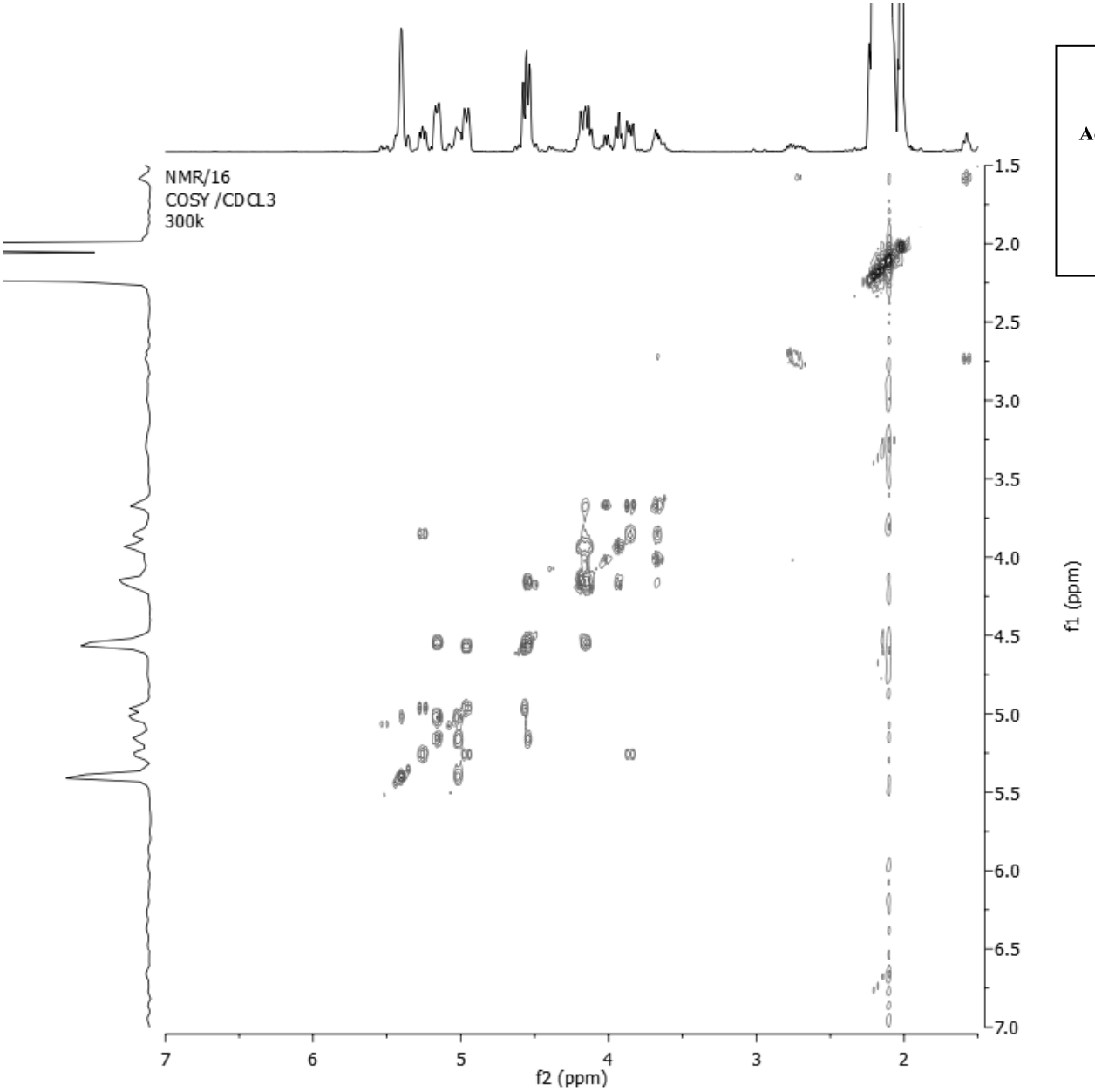

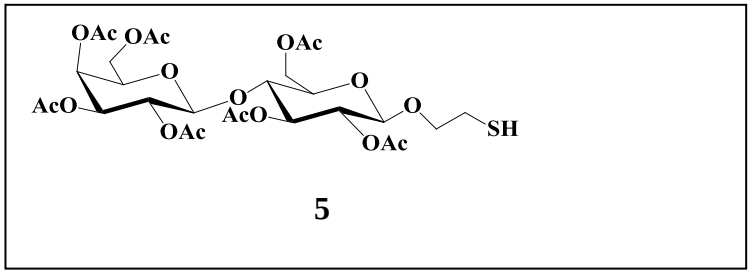

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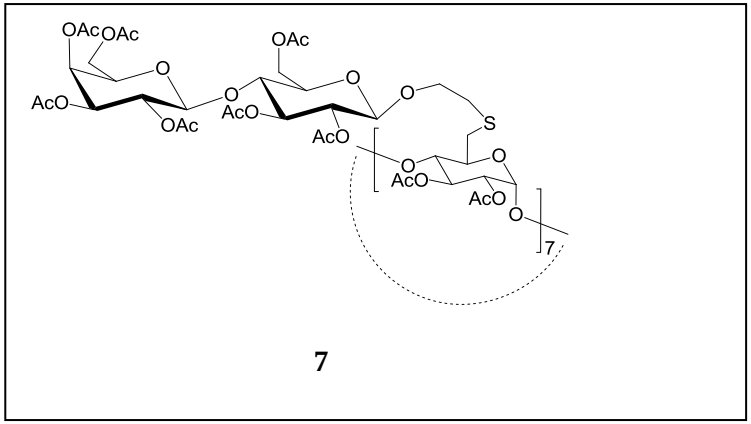
090412-10-HK-112



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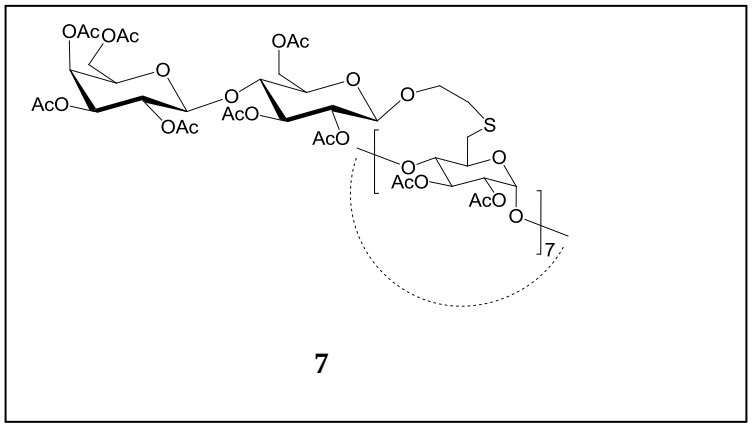
090412-10-HK-112



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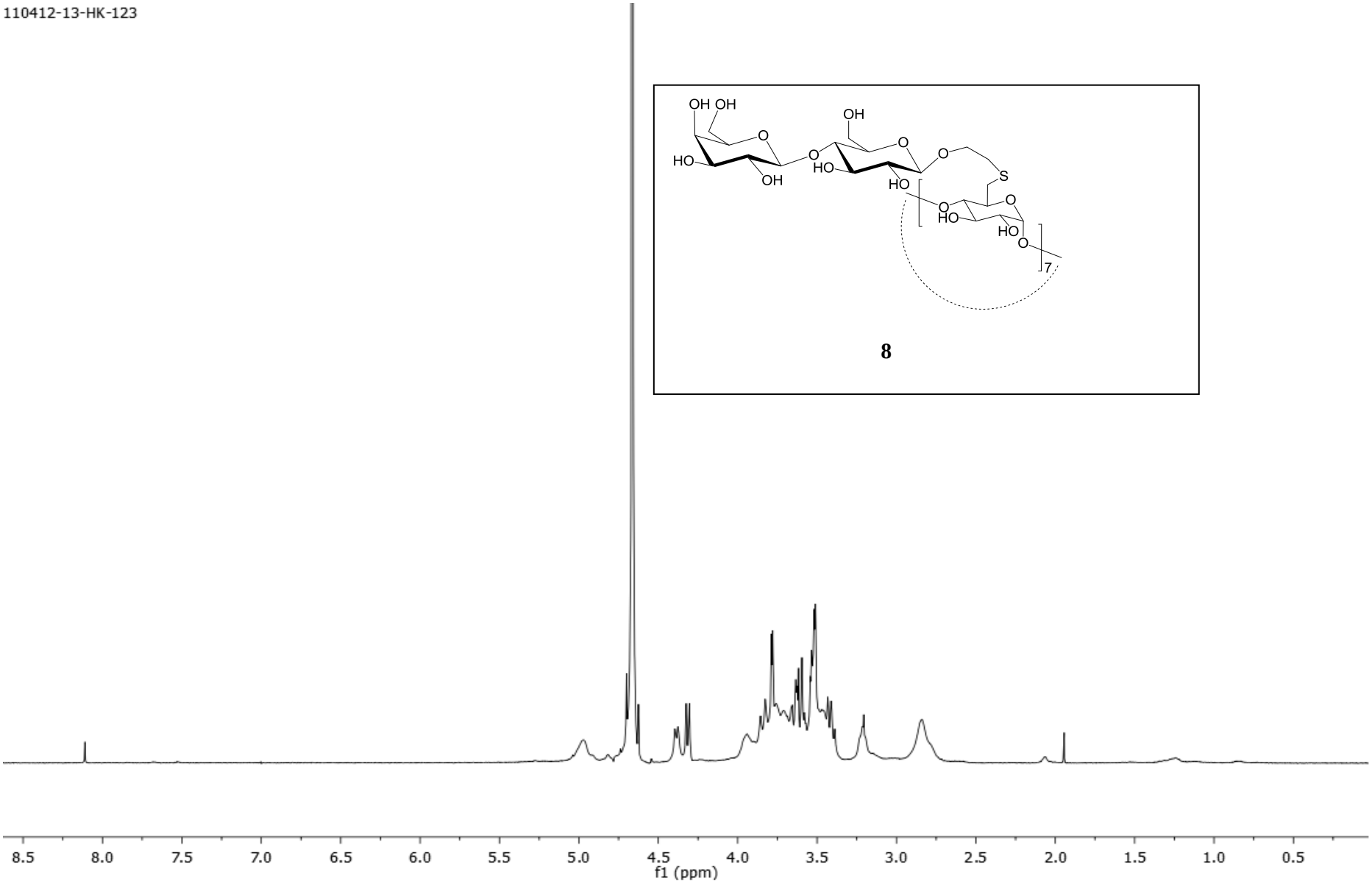
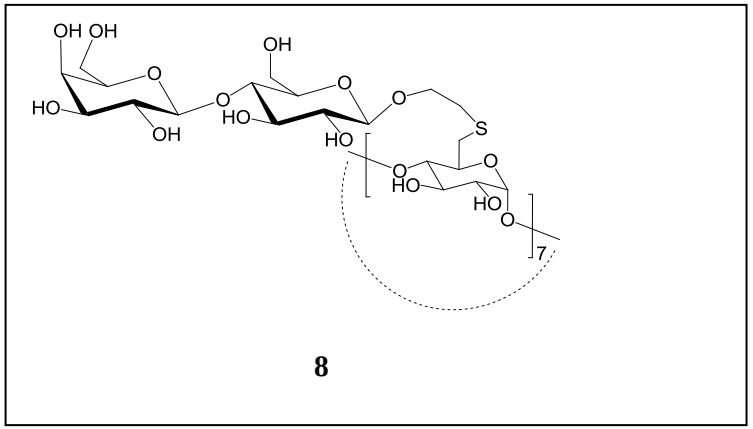


120412-18-HK-123



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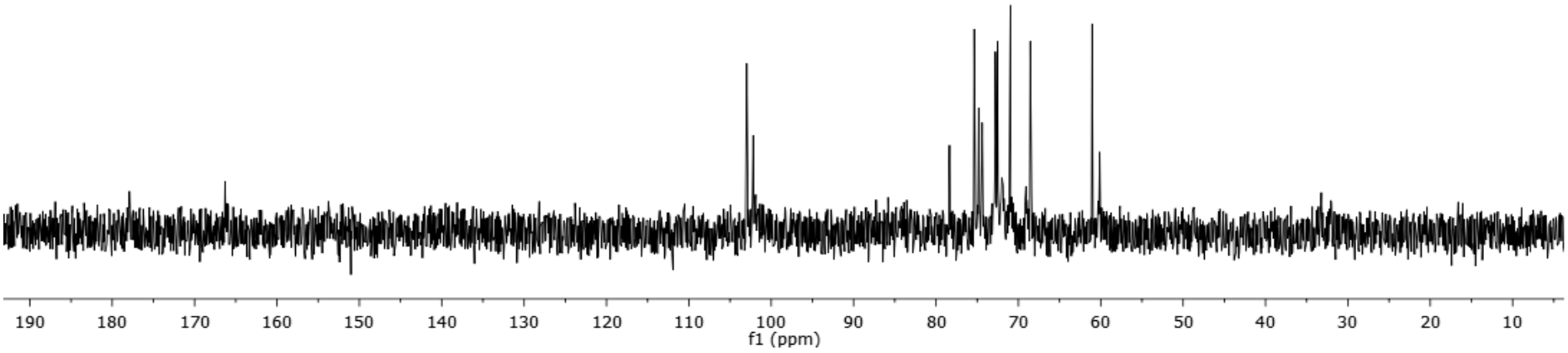
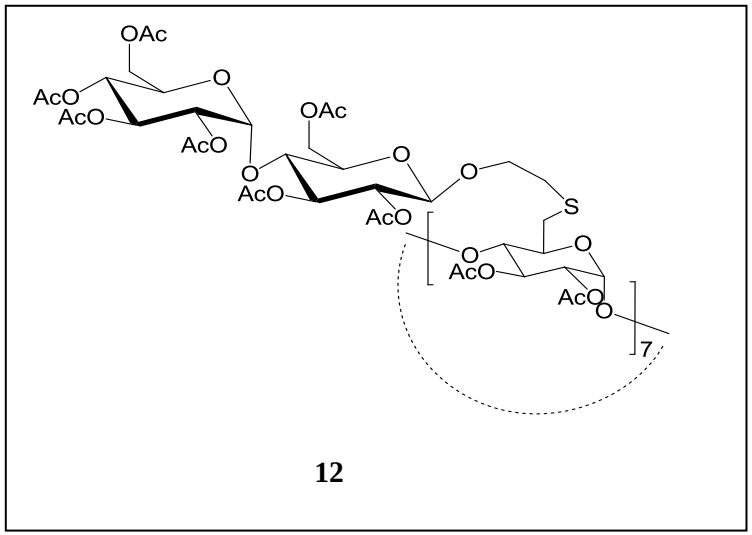


260312-18-HK-111



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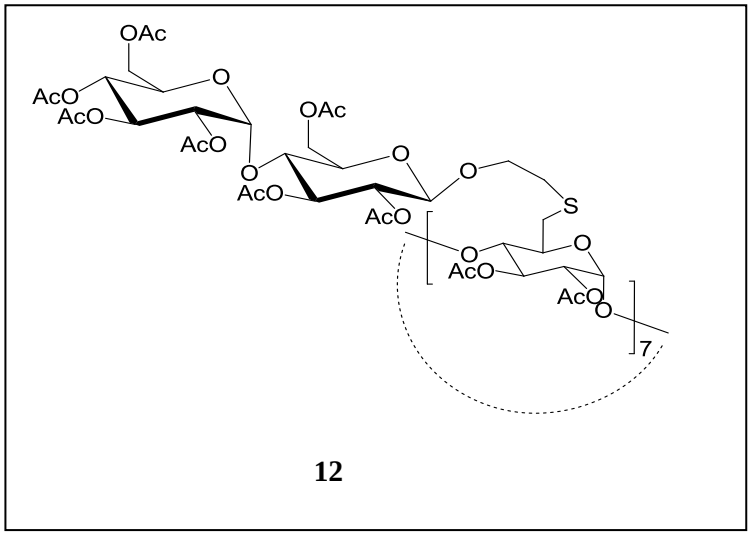

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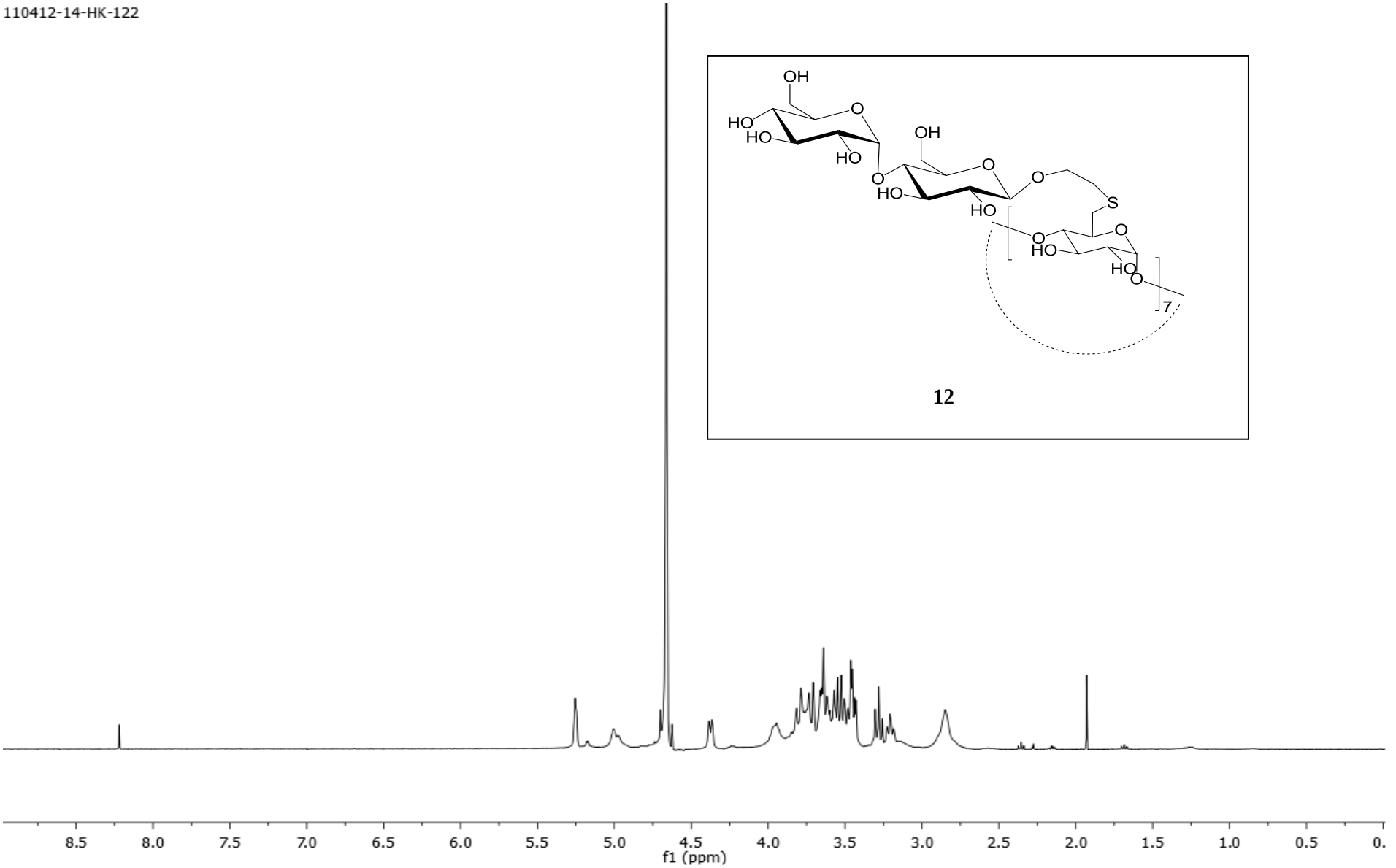
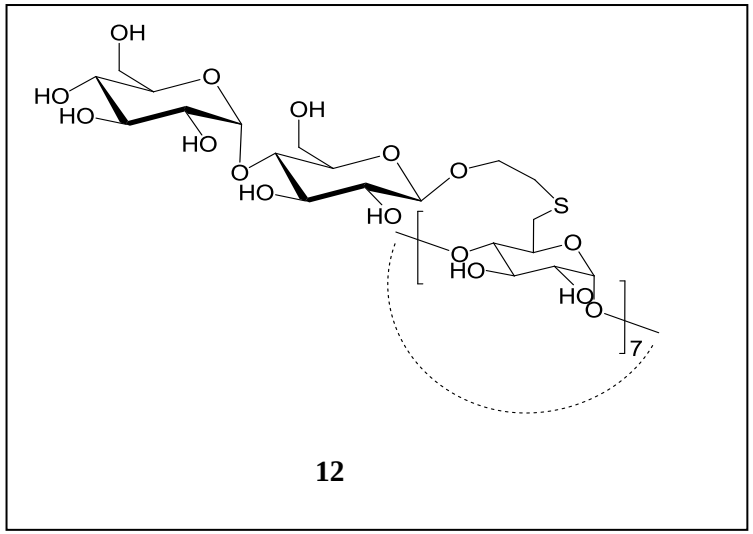


120412-17-HK-122



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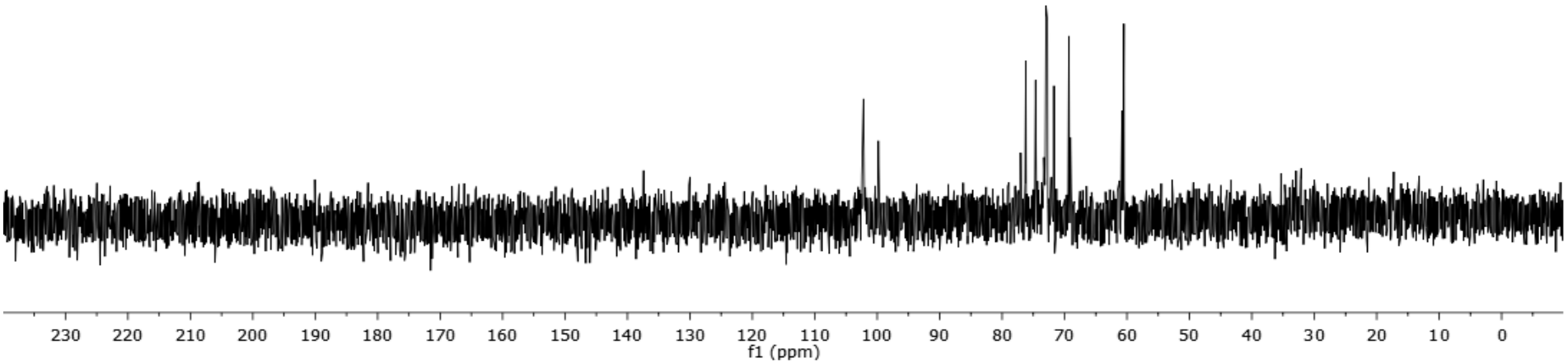

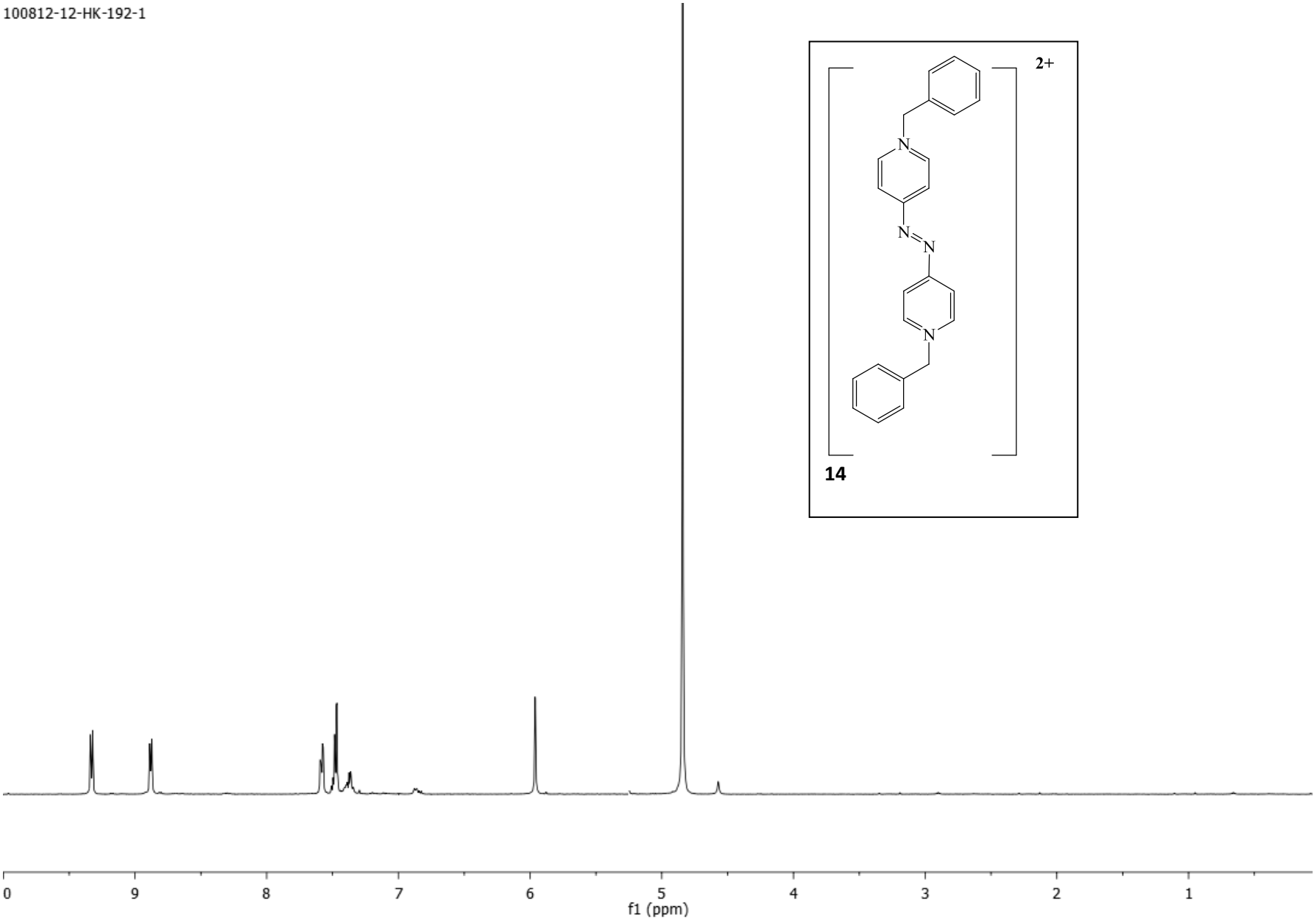

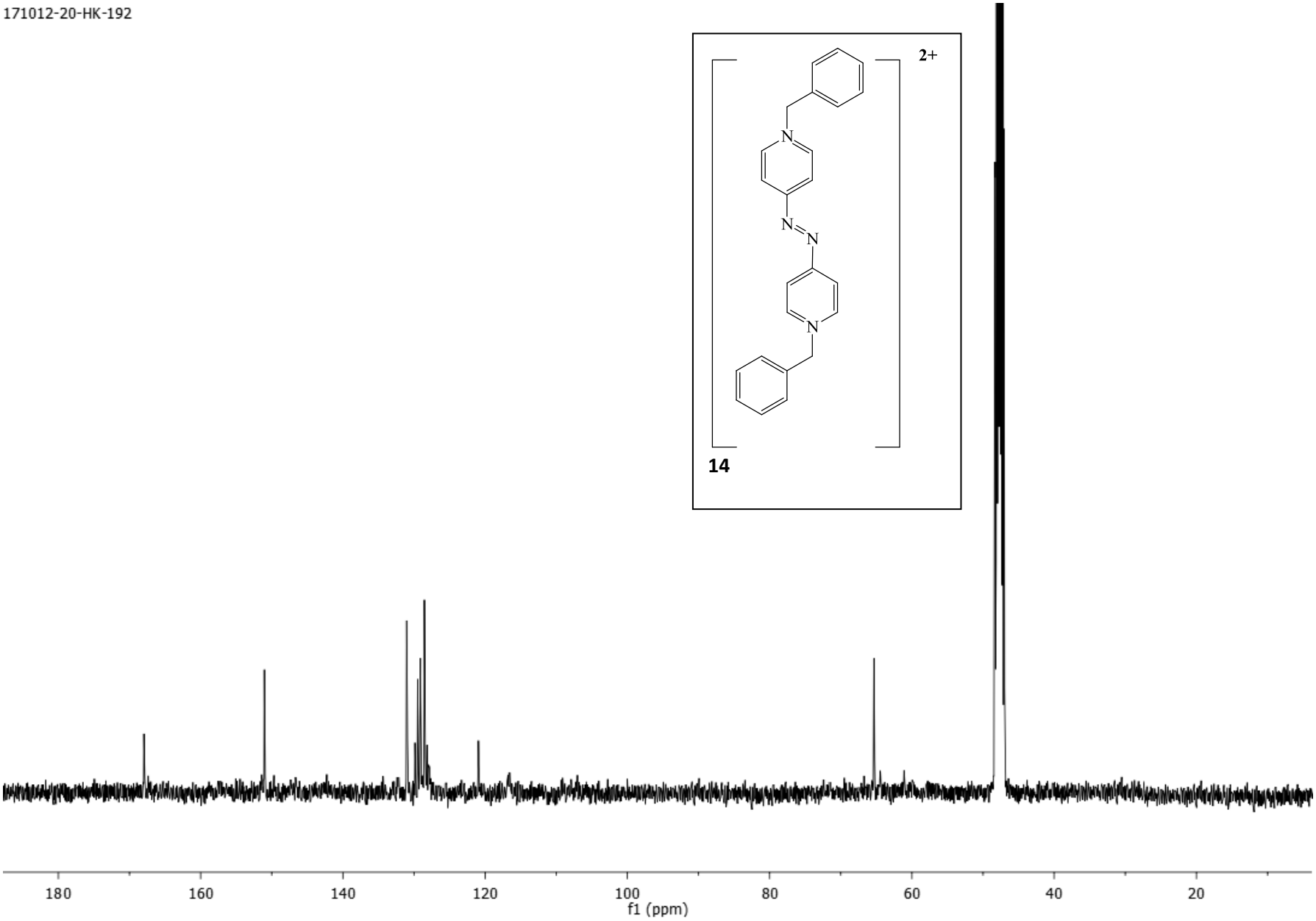

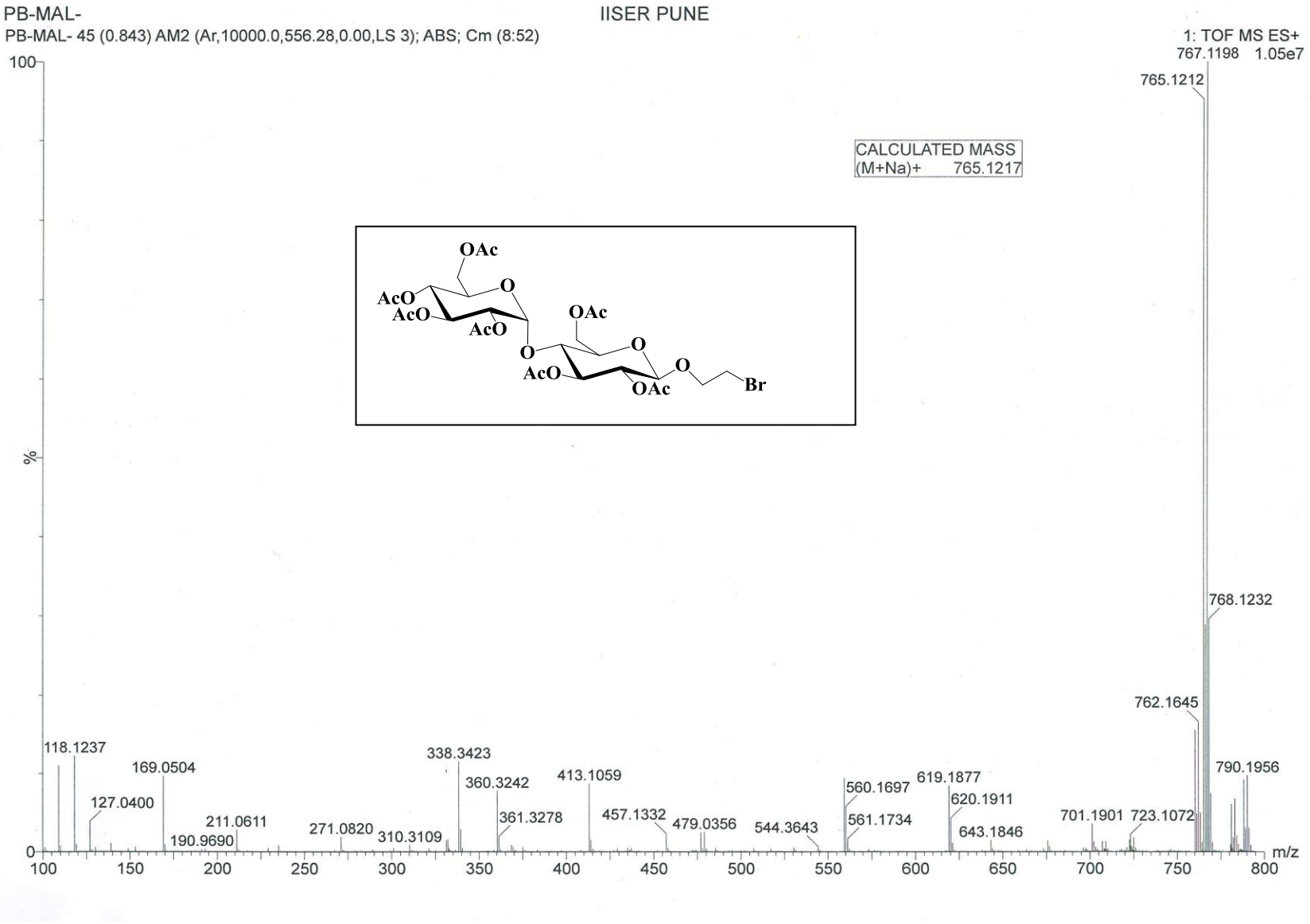

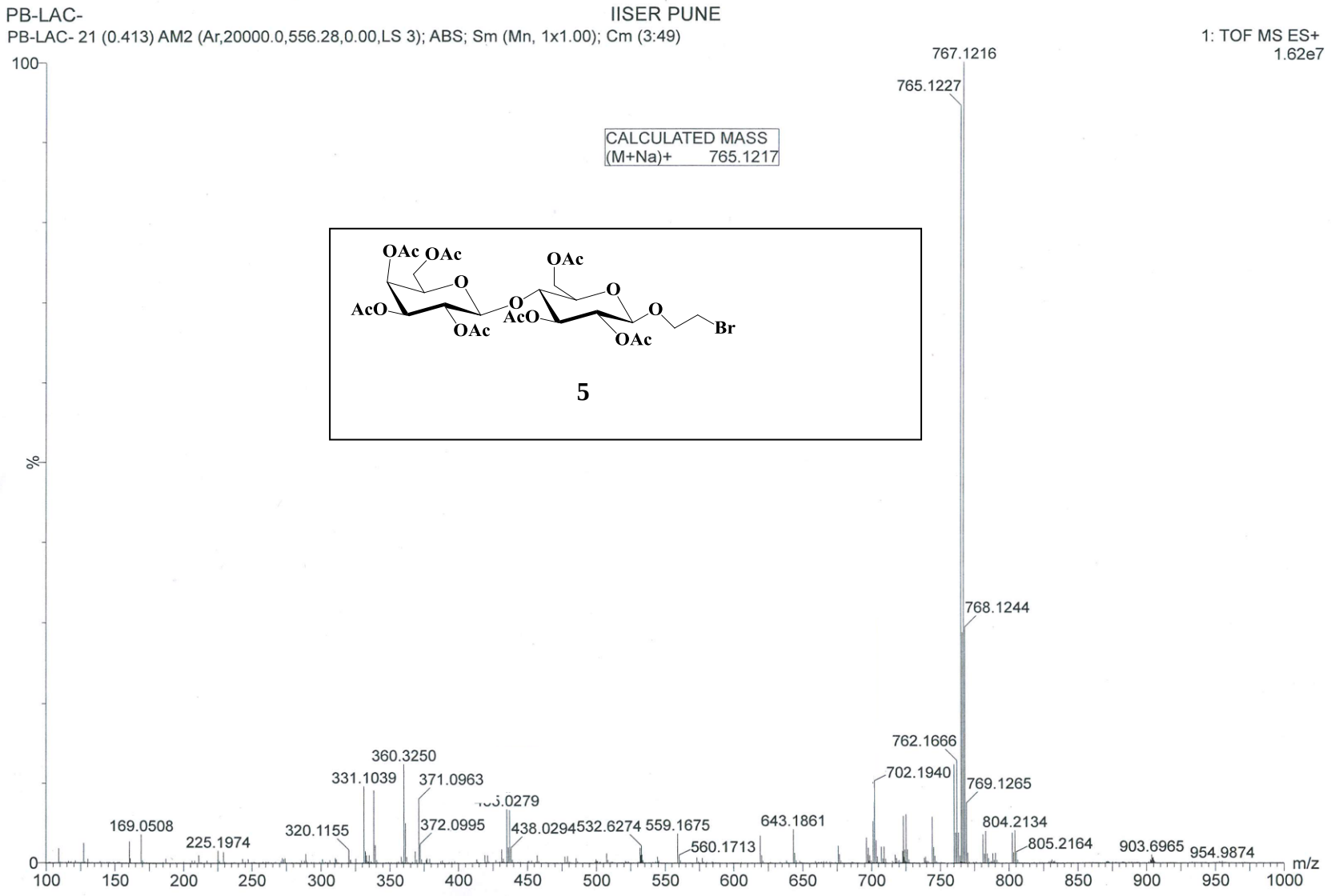

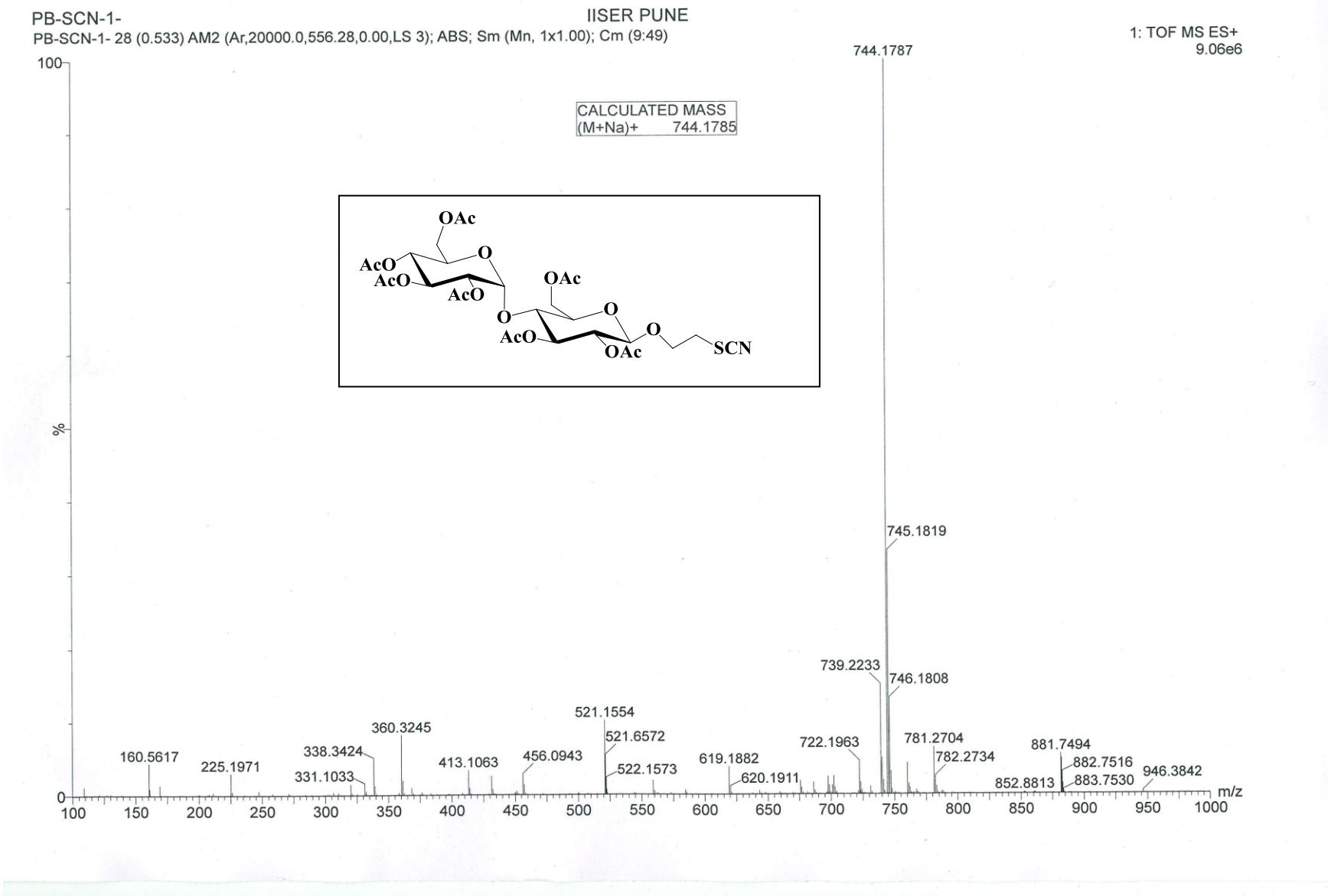

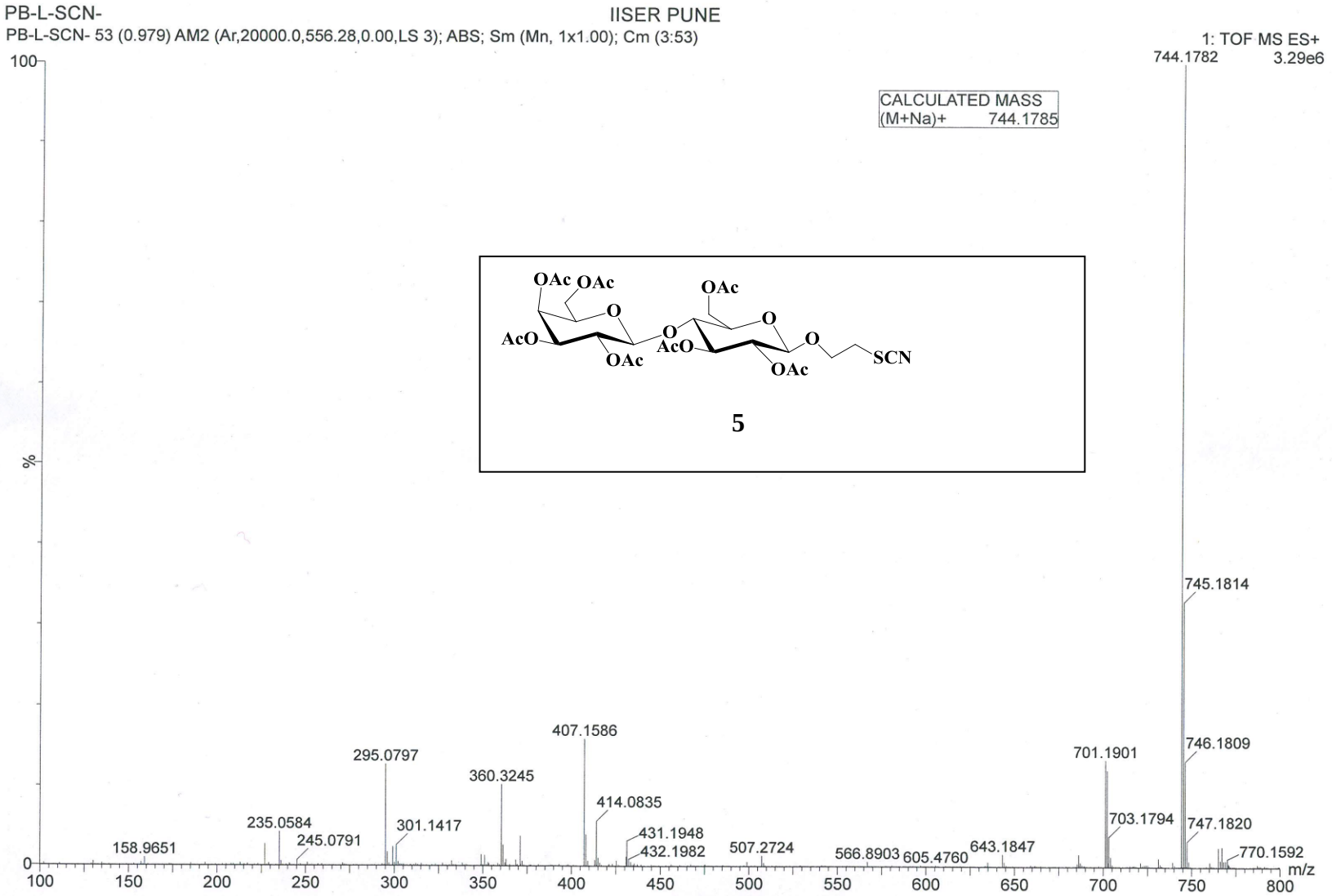

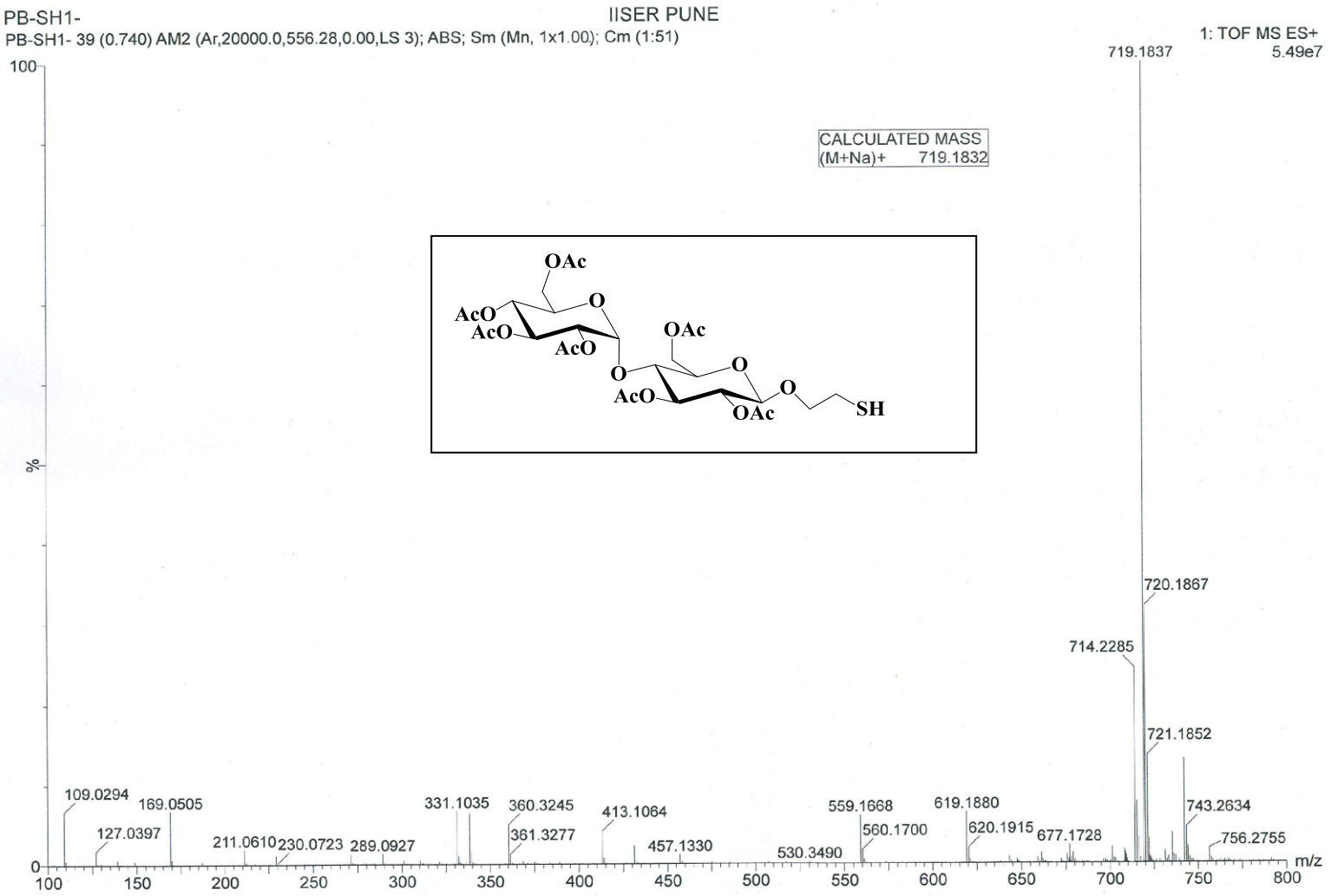

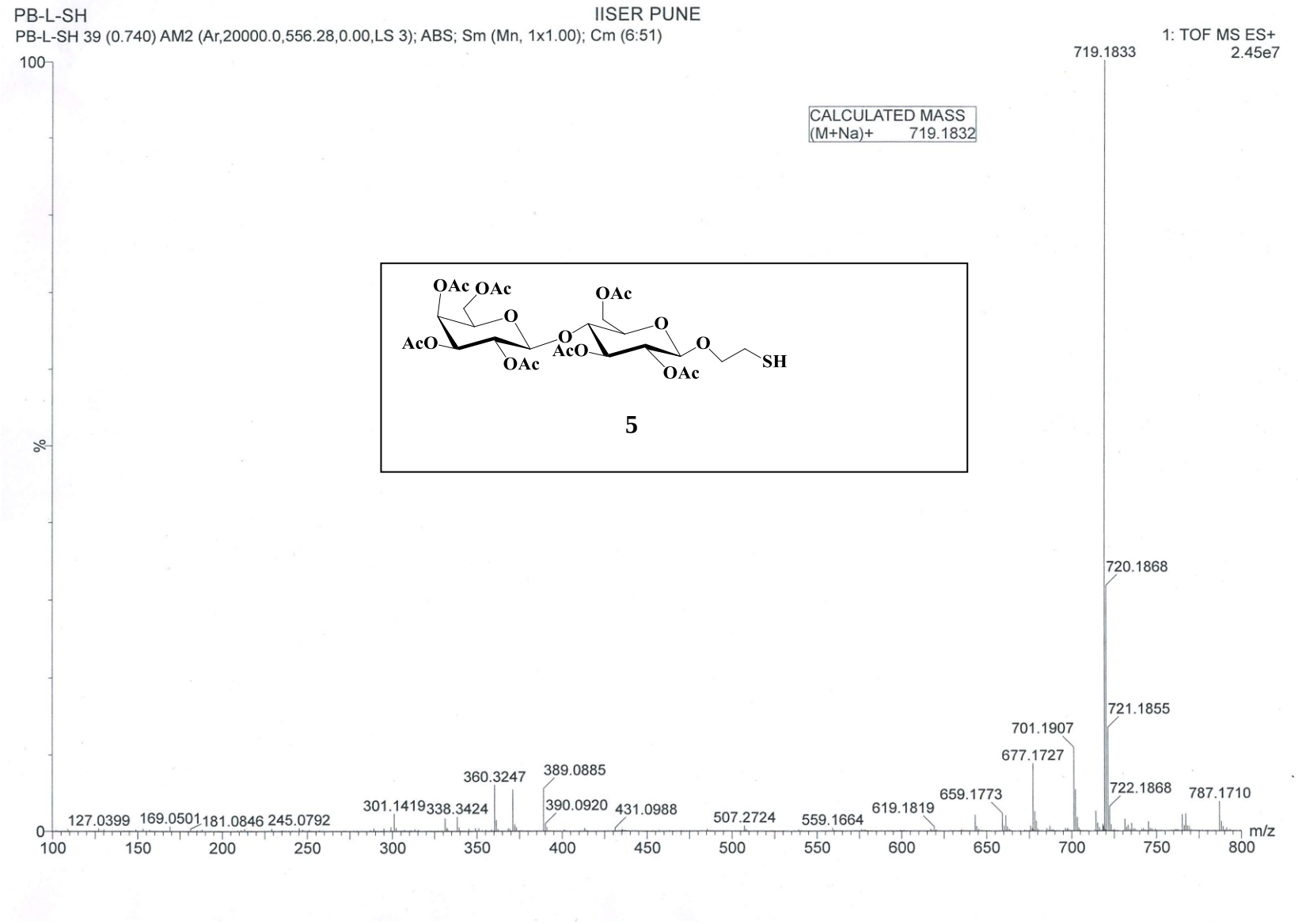

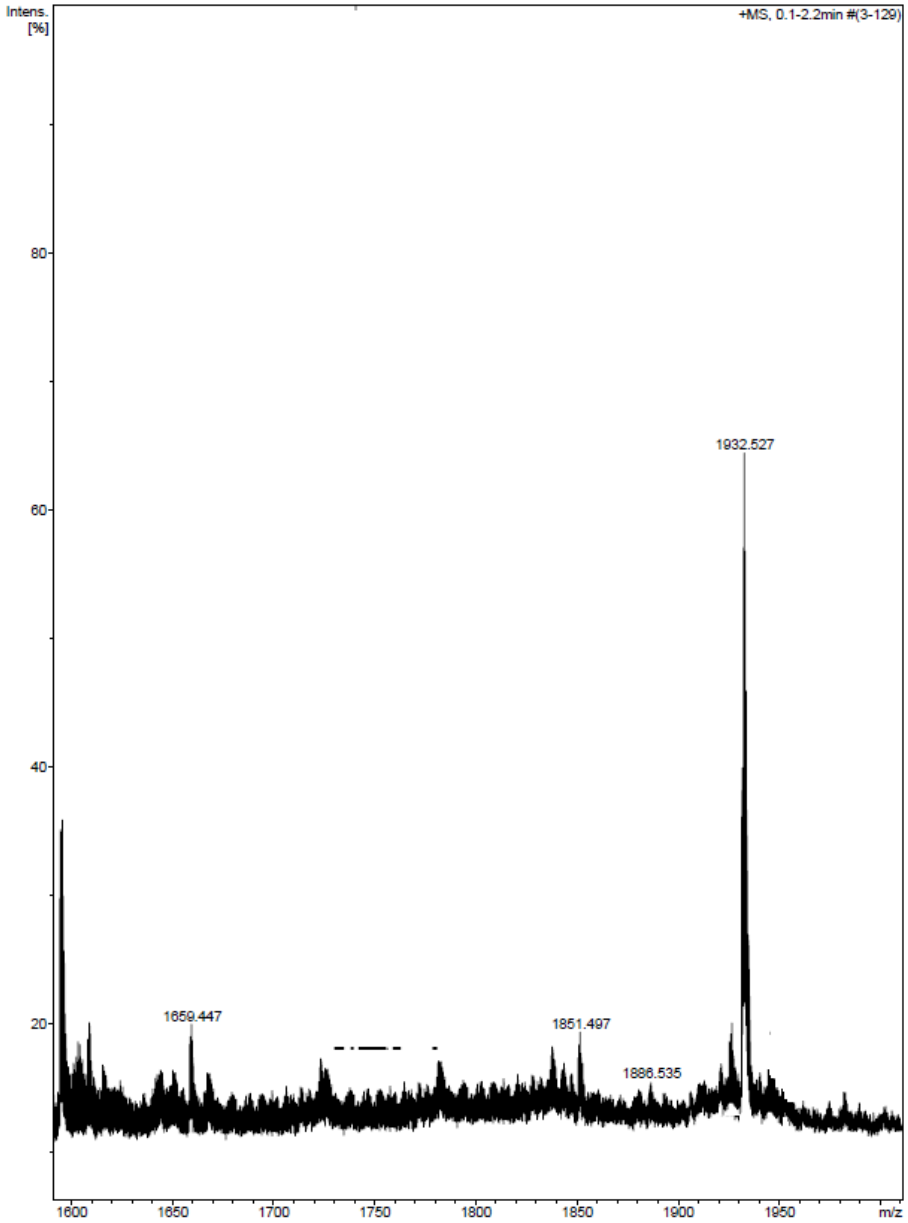

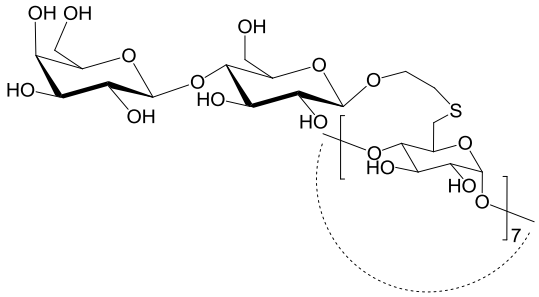

8

m/z (exp)	m/z (theo)	Sum formula
1932.533	1932.56	$C_{140}H_{239}O_{106}S_7Na^{2+}$