Supplementary Information

Backbone Modified Amphiphilic Cyclic Di- and Tetrasaccharides

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General methods

Solvents were dried and distilled according to literature procedures. Chemicals were purchased from commercial sources and were used without further purification. Silica gel (100–200 and 230-400 mesh) was used for column chromatography and TLC analysis was performed on commercial plates coated with silica gel 60 F_{254}. Visualization of the spots on TLC plates was achieved by UV radiation or spraying 5% sulfuric acid in ethanol. High resolution mass spectra were obtained from Q-TOF instrument by electrospray ionization (ESI). ^{1}H and ^{13}C NMR spectral analyses were performed on a spectrometer operating at 400 MHz, and 100 MHz, respectively. Chemical shifts are reported with respect to tetramethylsilane (TMS) or the solvent peak for ^{1}H NMR spectrum and the central line (77.0 ppm) of $CDCl_3$ for ^{13}C NMR spectrum. Coupling constants (*J*) are reported in Hz. Standard abbreviations s, d, t, dd, br s, m and app. refer to singlet, doublet, triplet, doublet of doublet, broad singlet, multiplet and apparent. For disaccharide derivatives **3**-**7**, H-1 denotes anomeric proton of the reducing end sugar moiety and H-1' denotes anomeric proton of non-reducing end sugar moiety and H-7 denotes the protons of hydoxymethyl (-CH_2O-) moiety.

Synthesis

***p*-Methoxybenzyl 2,3,6-tri-*O*-benzyl-4-*C*-hydroxymethyl-(2,3,6-tri-*O*-benzyl-4-*C*-acetoxymethyl-α-D-glucopyanosyl) β-D-glucopyranoside (3)**

TMSOTf (7 μL, 0.03 mmol, 0.2 molar equiv.) in Et_2O (1 mL) was added to a mixture of **1**[1] (0.10 g, 0.17 mmol) and **2**[1] (0.166 g, 0.25 mmol) and molecular sieves (4Å) (1 g) in Et_2O (15 mL), stirred for 30 min. at room temperature, quenched with Et_3N (0.2 mL), solvents removed *in vacuo* and the resulting crude product purified (hexane/EtOAc = 7.5:1) to afford **3** (0.122 g, 66 %), as a gum. R_f = 0.42 (hexane/EtOAc = 3:0.5); $[\alpha]_D$ 2.0 (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.25 (band,

32 H, aromatic), 6.84 (d, 2 H, *J* = 8.8, aromatic), 4.97 (d, 1 H, *J* = 11.6, Ph*CH*$_2$), 4.91-4.87 (band, 3 H, Ph*CH*$_2$), 4.80 (d, 1 H, *J* = 3.6, H-1'), 4.70 (d, 1 H, *J* = 11.6, Ph*CH*$_2$), 4.65-4.55 (band, 7 H, Ph*CH*$_2$), 4.48 (d, 1 H, *J* = 7.8, H-1), 4.47 (d, 1 H, *J* = 11.6, Ph*CH*$_2$), 4.46 (d, 1 H, *J* = 11.6, Ph*CH*$_2$), 4.23 (dd, 1 H, *J* = 2.4, 11.6, H_a-7), 3.96 (dd, 1 H, *J* = 2.4, 11.6 Hz, H_b-7), 3.86-3.84 (m, 2 H, H-3', H-3), 3.78 (s, 3 H, OMe), 3.88-3.76 (m, 2 H, $H_{a,b}$-7'), 3.73-3.69 (m, 2 H, H-5', H-5), 3.64 (dd, 1 H, *J* = 5.4, 10.8, H_a-6'), 3.60 (dd, 1 H, *J* = 5.4, 10.8, H_b-6'), 3.55 (dd, 1 H, *J* = 3.6, 9.6, H-2'), 3.51 (dd, 1 H, *J* = 8.0, 7.8, H-2), 3.48-3.46 (m, 2 H, $H_{a,b}$-6), 2.03-2.00 (m, 1 H, H-4), 1.99-1.95 (m, 1 H, H-4'), 1.81 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5 (C=O), 159.3 (aromatic), 138.7-137.8 (aromatic), 129.7-127.5 (aromatic), 113.8 (aromatic), 102.4 (C-1), 97.7 (C-1'), 91.8 (C-2'), 83.6 (C-2), 81.4(C-3'), 78.3 (Ph*C*H$_2$), 75.3 (Ph*C*H$_2$), 75.0 (Ph*C*H$_2$), 74.7 (Ph*C*H$_2$), 73.9 (Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 73.3 (C-3), 72.7 (C-5), 70.4 (C-3'), 69.9 (C-5'), 69.5 (C-6), 68.4 (C'-6), 63.8 (C-7'), 60.1 (C-7), 55.2 (OMe), 43.8 (C-4), 41.9 (C-4'), 20.5 (COMe); HRMS *m/z*: $[M+Na]^+$ calcd. for: $C_{66}H_{72}O_{13}Na$ = 1095.4872; found 1099.4871.

(1-Thioethyl -2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-methyl-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-4-*C*-hydroxymethyl-α-D-glucopyranoside (4)

Triflouroacetic acid (0.04 mL, 0.40 mmol) was added to a solution of **3** (0.22 g, 0.20 mmol) in aq. CH_2Cl_2 (10 mL) at 0 °C, stirred for 2 h at room temperature. The reaction mixture was diluted with water (50 mL), washed with aq. $NaHCO_3$ (5 %, 2 x 50 mL), extracted with CH_2Cl_2 (3 x 50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified (SiO_2) (hexane/EtOAc = 2:1) to afford lactal intermediate (0.14 g, 72 %), as a colorless gum. Acetic anhydride (0.02 mL, 0.22 mmol) was added to a solution of lactal intermediate (0.14 g, 0.14 mmol) in pyridine (3 mL) at 0 °C and stirred for 12 h at room temperature. The reaction mixture was diluted with water (50 mL), extracted with $CHCl_3$ (3 x 50 mL), washed with aq. HCl (2 N), aq. $NaHCO_3$ (5 %, 2 x 50 mL), dried

(Na_2SO_4), filtered, concentrated *in vacuo* and purified (SiO_2) (hexane/EtOAc = 4:1) to afford the diacetate intermediate (0.13 g, 92 %), as a gum. A solution of EtSH (0.08 mL, 1.3 mmol) in CH_2Cl_2 (2 mL) was added drop-wise to a mixture of diacetate intermediate (0.135 g, 0.13 mmol) and $BF_3{\cdot}Et_2O$ (19 μL, 0.13 mmol) in CH_2Cl_2 (5 mL) was stirred at 0 °C under N_2 atmosphere, for 30 min. at 0 °C. The reaction mixture was then quenched with Et_3N (0.2 mL), extracted with ether, washed with aq. $NaHCO_3$ solution (5%, 2x25 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was subjected to *O*-deacetylation, using NaOMe (cat.) and MeOH (20 mL), for 4 h at room temperature, quenched with resin (H^+, IR 15), filtered and filtrate concentrated *in vacuo*. Purification (SiO_2) (hexane/EtOAc = 2:1) afforded monomer **4** (0.11 g, 85 %, α/β = 1:1.7), as a colorless gum. R_f = 0.33 (hexane/EtOAc = 2:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.25 (band, 37.5 H, aromatic), 5.49 (d, 1 H, *J* = 5.6, H_β-1), 4.94 (band, 1 H, PhC*H*$_2$), 4.90-4.87 (band, 3 H, PhC*H*$_2$), 4.78 (d, 1 H, *J* = 3.6, H_α-1'), 4.70 (d, 2 H, *J* = 10.8, PhC*H*$_2$), 4.67-4.62 (band, 4.5 H, PhC*H*$_2$), 4.60 (band, 1.5 H, PhC*H*$_2$), 4.58-4.53 (band, 4.5 H, PhC*H*$_2$), 4.50 (app. s, 1 H, H_α-1), 4.64-4.40 (band, 3.5 H, PhC*H*$_2$), 4.37 (d, 1 H, *J* = 10.6, PhC*H*$_2$), 3.94-3.85 (band, 4.5 H, H_β-2, H_β-3, H_β-5), 3.77-3.62 (band, 10.5 H, H-3', H_α-5, H-5', H_α-$6_{a,b}$, $H_{a,b}$ -6', H_β-7_a, H_α-7_a, H_a -7'), 3.58-3.52 (band, 5 H, H_α-3, H-2', H_β-$6_{a,b}$), 3.48-3.42 (band, 4.5 H, H_α-2, H_b -7', H_α -7_b, H_β-7_b), 2.81-2.72 (m, 3 H, -SC*H*$_2$-), 2.62-2.49 (m, 2 H, -SC*H*$_2$-), 2.05-1.98 (m. 2.5 H, H_β-4, H-4'), 1.87-1.80 (m, 1 H, H_α-4), 1.34 (t, 4.5 H, *J* = 7.2, -SCH_2CH_3), 1.20 (t, 4.5 H, *J* = 7.2, -SCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4-137.7 (aromatic), 128.5-127.4 (aromatic), 97.8 (C_α-1'), 85.0 (C_α-1), 82.9 (C_β-1), 81.5 (C-2'), 81.4 (C_β-2), 80.8 (C_α-2), 80.1 (C_α-3), 75.7 (Ph*C*H$_2$), 75.3 (Ph*C*H$_2$), 75.2 (C'-3), 75.0 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 73.6 (C_β-3), Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 71.9 (Ph*C*H$_2$), 70.6 (C_α-5), 70.3 (C_β-5), 70.0 (C-5'), 69.3 (C-6'), 68.8 (C_α-6), 68.7 (C_β-6), 63.5 (C-7'), 59.4 (C_β-7), 59.1 (C_α-7), 45.7 (C-4'), 44.1 (C_β-4), 43.3 (C_α-4), 24.8 (-

S*C*$H_2$$CH_3$), 23.8 (-S*C*$H_2$$CH_3$), 15.2 (-SC$H_2$*C*$H_3$), 14.8 (-SCH2*C*$H_3$); ESI-MS *m/z*: $[M+Na]^+$ calcd. for: $C_{58}H_{66}O_{10}SNa$ = 977.4274; found 977.4545.

Cyclo[(1→4)-2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-methyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-4-*C*-methylenyl-α-D-glucopyranoside (5) and cyclo[(1→4)-2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-methyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-methyl-α-D-glucopyranosyl]dioside (**6**)

Experiment using 3 mM concentration: Monomer **4** (0.10 g, 0.10 mmol) was dissolved in benzene (3 mL) and freeze-dried and this freeze-drying with benzene was repeated four times. A solution of *N*-iodosuccinimide (0.029 g, 0.13 mmol) was added to the freeze-dried monomer **4** (3 mM) in CH_2Cl_2 (35 mL), cooled to 0 °C. AgOTf (5 mg, 0.002 mmol) and molecular sieves (4Å) (1 g) were added to reaction mixture under N_2 atmosphere. After 12 h, the reaction was quenched with Et_3N (~200 μL), diluted with CH_2Cl_2 (100 mL), filtered through celite pad, washed with $Na_2S_2O_3$ (5 %, 2 x 50 mL), H_2O (2 x 50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude reaction mixture was purified (SiO_2) (hexane/EtOAc liner gradient) to afford **5** (0.010 g, 10 %) and **6** (0.06 g, 64 %), all as colorless gums.

Experiment using 20 mM concentration: Monomer **4** (0.07 g, 0.07 mmol) was dissolved in benzene (3 mL) and freeze-dried and this freeze-drying with benzene was repeated four times. A solution of *N*-iodosuccinimide (0.02 g, 0.09 mmol) and molecular sieves (4Å) (1 g) were added to the freeze-dried monomer **4** (20 mM) in CH_2Cl_2 (3.8 mL), cooled to 0 °C. TMSOTf (3 μL, 0.001 mmol, 0.02 equiv.) was added to the reaction mixture and stirred at room temperature under N_2 atmosphere. After 12 h, the reaction was quenched with Et_3N (200 μL), diluted with CH_2Cl_2 (100 mL), filtered through celite pad, washed with $Na_2S_2O_3$ (5 %, 2 x 50 mL), H_2O (2 x 50 mL), dried (Na_2SO_4) and concentrated. The

crude reaction mixture was purified (SiO_2) (hexane/EtOAc liner gradient) to afford **5** (0.007 g, 11 %) and **6** (0.040 g, 61 %), as colorless foamy solids.

5: R_f = 0.41 (hexane/EtOAc = 10:1); $[\alpha]_D^{24}$ +20.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.25 (band, 30 H, aromatic), 4.92 (d, 2 H, *J* = 2.0, H-1), 4.64-4.48 (band, 12 H, PhC*H*$_2$-), 4.10 (app. t, 2 H, *J* = 6.8, H-5), 4.04 (app. d, 2 H, *J* = 9.2, H-6$_a$), 3.93 (app. d, 2 H, *J* = 9.2, H-6$_b$), 3.78-3.75 (band, 4 H, H-2, H-3), 3.74-3.66 (band, 4 H, C*H*$_2$-O), 2.27 (br, 2 H, H-4); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 137.7, 137.6, 127.9, 127.8, 127.7, 127.6 (aromatic), 90.7 (C-1), 81.0 (C-2), 80.2 (C-3), 73.5 (Ph*C*H$_2$-), 71.9 (C-5), 71.0 (Ph*C*H$_2$-), 70.5 (Ph*C*H$_2$-), 69.5 (*C*H$_2$O-), 57.7 (C-6), 34.8 (C-4); ESI-MS *m/z*: $[M+Na]^+$ calcd. for: $C_{56}H_{60}O_{10}Na$ = 915.4084; found 915.4088.

6: R_f = 0.31 (hexane/EtOAc = 10:1); $[\alpha]_D^{24}$ +1.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.30 (band, 60 H, aromatic), 5.04 (app. s, 4 H, H-1), 4.67-4.44 (band, 24 H, PhC*H*$_2$-), 4.32 (app. t, 4 H, *J* = 6.4, H-3), 4.02 (dd, 4 H, *J* = 2.8, 8.8, C*H*$_2$-O), 3.94 (app. d, 4 H, *J* = 8.8, C*H*$_2$-O), 3.85 (br, 4 H, H-2), 3.81-3.79 (br, 4 H, H-5), 3.77 (dd, 4 H, *J* = 7.2, 9.6, H-6$_a$), 3.71 (dd, 4 H, *J* = 5.6, 9.6, H-6$_b$), 2.36 (br, 4 H, H-4); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.6, 138.2, 138.1, 128.9, 128.8, 128.7, 128.4 128.3, 128.2, 128.1, 128.0 (aromatic), 91.2 (C-1), 81.9 (C-2), 81.5 (C-5), 74.4 (C-3), 73.7 (Ph*C*H$_2$-), 72.8 (C-6), 71.6 (Ph*C*H$_2$-), 71.1 (Ph*C*H$_2$-), 68.5 (-*C*H$_2$O-), 32.5 (C-4). MALDI-TOF MS *m/z*: calcd. for: $C_{112}H_{120}O_{20}Na$ = 1807.6890; found 1807.6888.

Cyclo[(1→4)-4-deoxy-4-*C*-methyl-α-D-glucopyranosyl-(1→4)-4-deoxy-4-*C*-methyl-α-D-glucopyranosyl]dioside (7)

A solution of protected derivative **6** (0.1 g, 0.05 mmol) in MeOH and EtOAc (1:1, 20 mL) was hydrogenolyzed over Pd/C (10 %, 0.05 g) under positive pressure of H_2 gas for 24 h at room temperature, filtered through celite and evaporated *in vacuo*, to afford **7** (0.036 g, 91 %), as a foamy

solid. R_f = 0.41 ($CHCl_3$/MeOH = 3:1); $[\alpha]_D$ 72.3 (*c* 1, H_2O); ^1H NMR (D_2O, 400 MHz): δ 4.89 (app. s, 4 H, H-1), 4.22-4.19 (m, 4 H, H-3), 4.03-3.96 (m, 12 H, $H_{a,b}$-7, H-5), 3.89-3.84 (m, 8 H, H-2, H_a-6), 3.72 (dd, 4 H, *J* = 3.6, 12.0, H_b-6), 2.23 (br, 4 H, H-4); ^{13}C NMR (D_2O, 100 MHz): δ 92.3 (C-1), 75.7 (C-2), 75.3 (C-3), 73.9 (C-5), 68.1 (C-7), 63.6 (C-6), 34.9 (C-4); ESI-MS *m/z*: $[M+Na]^+$ calcd. for: $C_{28}H_{48}O_{20}Na$ = 727.2637; found 727.2617.

Solubilization studies

Pyrene: Pyrene was purified by recrystallizing in ethanol. A solution of **7** in EtOH (0.9 mM, 0.7 mM, 0.5 mM and 0.2 mM) was added with pyrene (1 mg) and stirred for 1 h at 25 °C, concentrated *in vacuo* and Millipore water was added to maintain above concentrations and the solution was stirred for 24 h at 45 °C. The solution was filtered (0.2 μm filter), the absorption and emission spectra of the filtrate were recorded. The stoichiometry of pyrene in **7** was identified from ^1H NMR analysis of the samples ($CDCl_3$), obtained after evaporation and drying of the filtrate.

Adamantane-1-carboxylic acid: A solution of **7** (5 mg) and adamantane-1-carboxylic acid (0.5 mg) in D_2O (600 μL) was stirred at 30 °C for 12 h. The solution was filtered (0.2 μm filter) and ^1H NMR spectrum of the filtrate was recorded.

L-Tyrosine: A solution of **7** (5 mg) and L-tyrosine (0.5 mg) in $CDCl_3$ (600 μL) was stirred at 30 °C for 12 h. The solution was filtered (0.2 μm filter) and ^1H NMR spectrum of the filtrate was recorded.

Acid-catalyzed hydrolysis

Acid catalyzed hydrolysis of **7** (4 mg) and α-cyclodextrin (4 mg) were performed in DCl/D_2O (2 N) (600 μL), in an NMR tube maintained at 60±1 ^oC in a thermostated water bath. ^1H NMR spectrum was recorded periodically by monitoring the peak intensities of anomeric proton of α-cyclodextrin and H-4 proton resulting from hydrolysis of **7**. ^1H NMR peak intensity profiles as a function of time were recorded till complete hydrolysis.

Instrumentation

UV-Vis absorption spectra were recorded using 1 cm-path quartz cell. Fluorescence spectra were recorded at room temperature on a spectrofluorimeter with a slit width of 5 nm, using 1 cm-path quartz cell and a Xenon lamp at the excitation source. Emission spectra were recorded, keeping excitation wavelength at 385 nm. Excitation spectrum was recorded at 385 nm emission wavelength.

Molecular modeling

The optimization of the glycosidic bond expanded cyclic tetrasaccharide **7**, was performed using density functional theory (DFT). The calculations were performed using the Gaussian03 suites of quantum chemical programs.[2] The hybrid Becke 3−Lee−Yang−Parr (B3LYP) exchange correlation functional was employed to predict the minimum energy molecular geometries of the compounds. Geometries were fully optimized in the gas phase at the B3LYP level of theory by using the 6-311+G* basis set. Frequency calculations were performed on each optimized structure using the same basis set to ensure that it was a minimum on the potential energy surface. The lowest energy conformer from ab initio calculations was used to find out bond lengths.

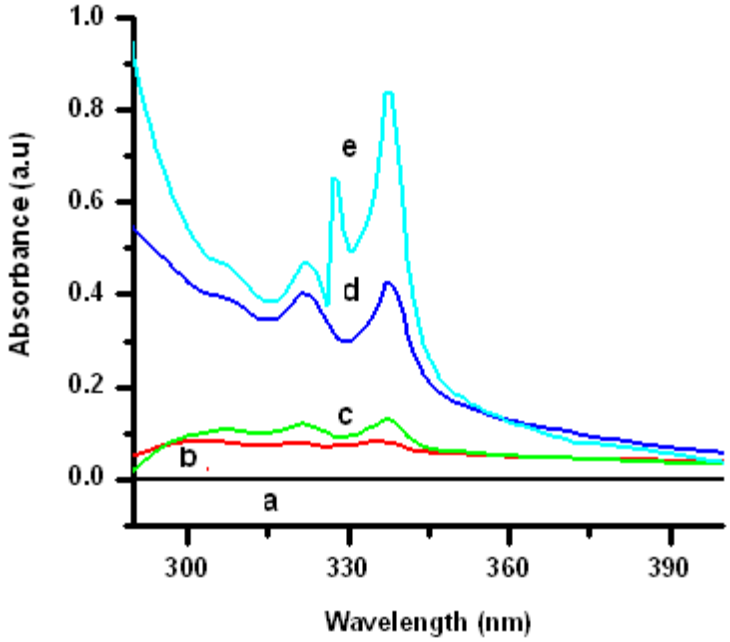


Figure 1. Absorption spectra of pyrene: (a) in H_2O; in varying concentration of **7**: (b) 0.2 mM; (c) 0.5 mM; (d) 0.7 mM and (e) 0.9 mM.

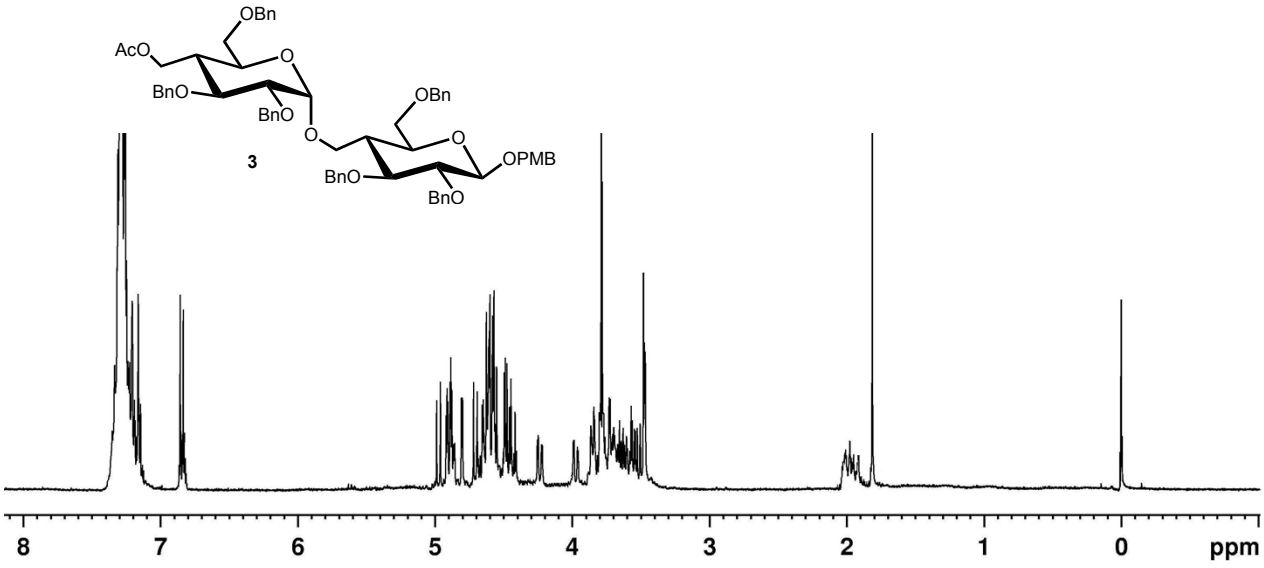


Figure 2. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

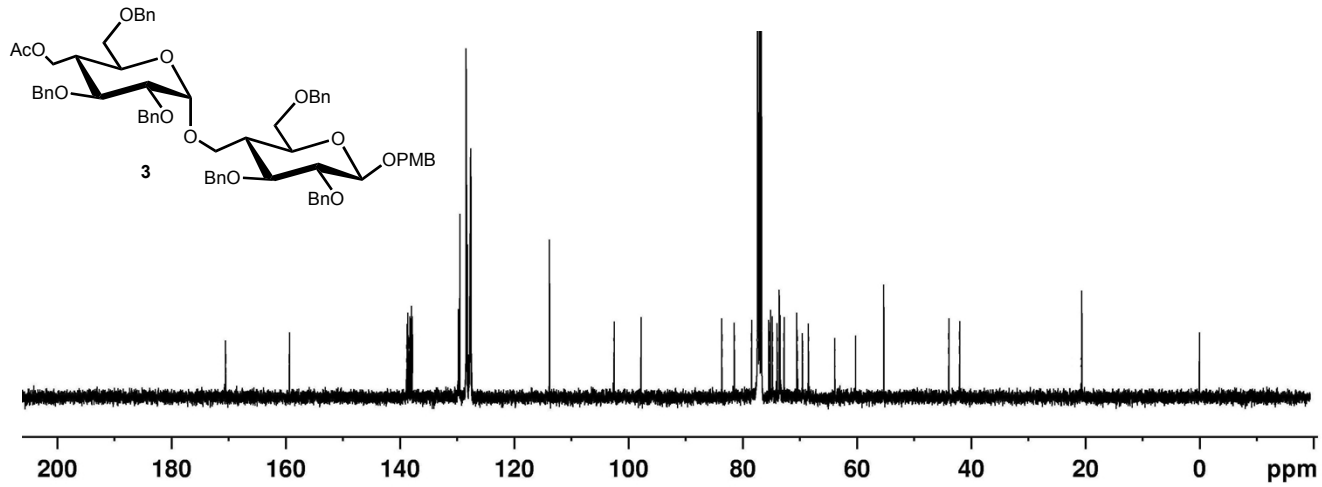


Figure 3. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

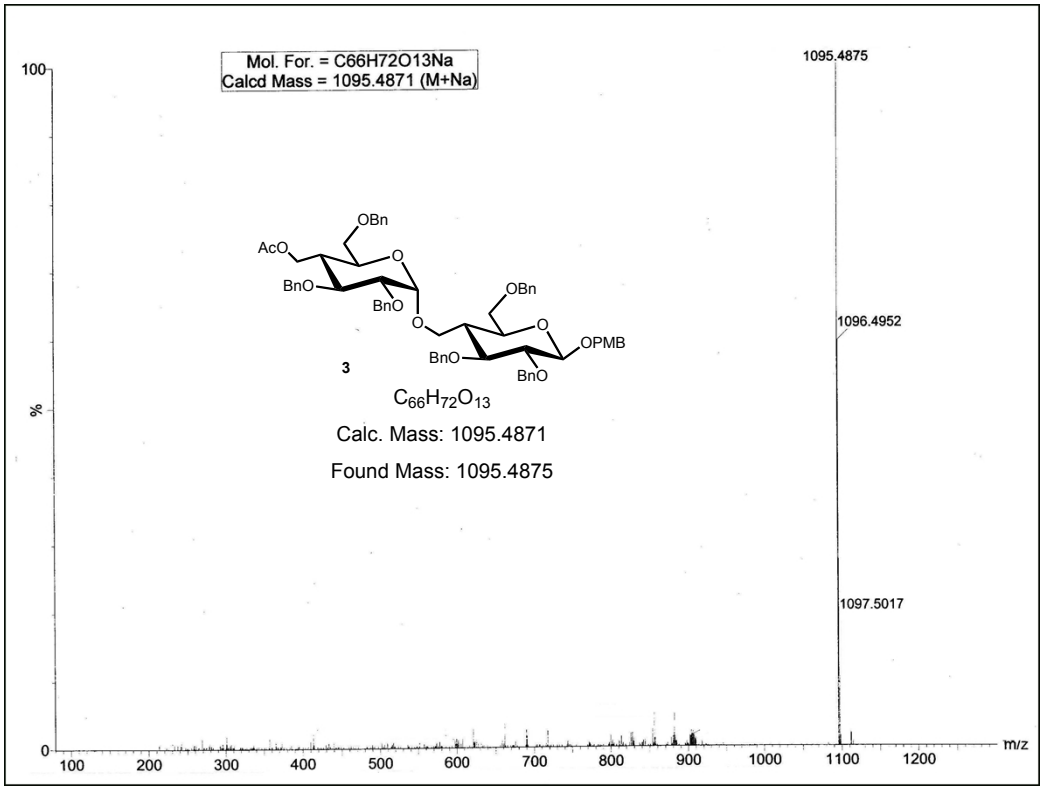


Figure 4. ESI mass spectrum of **3**.

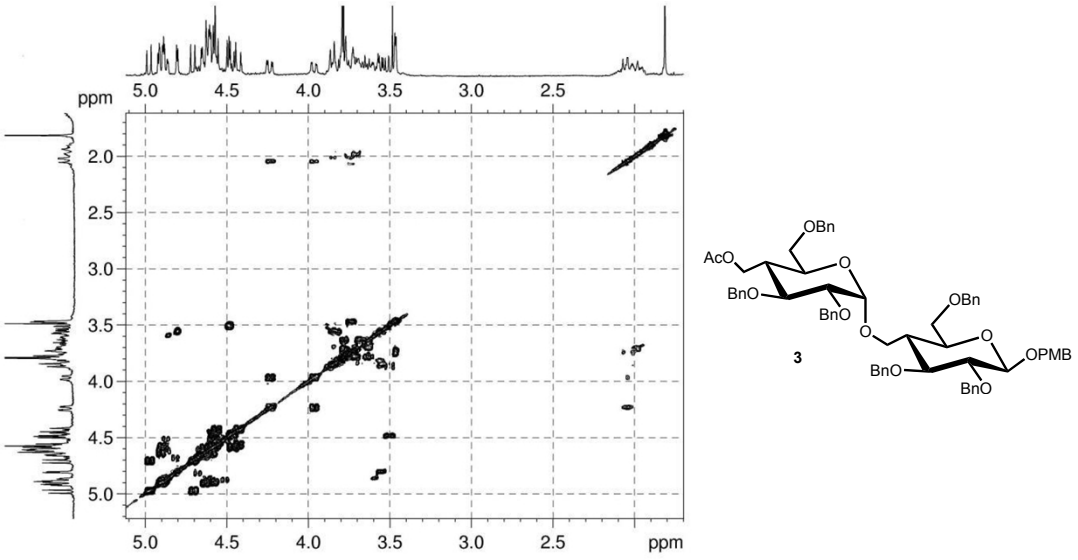


Figure 5. COSY spectrum of **3** (400 MHz, $CDCl_3$).

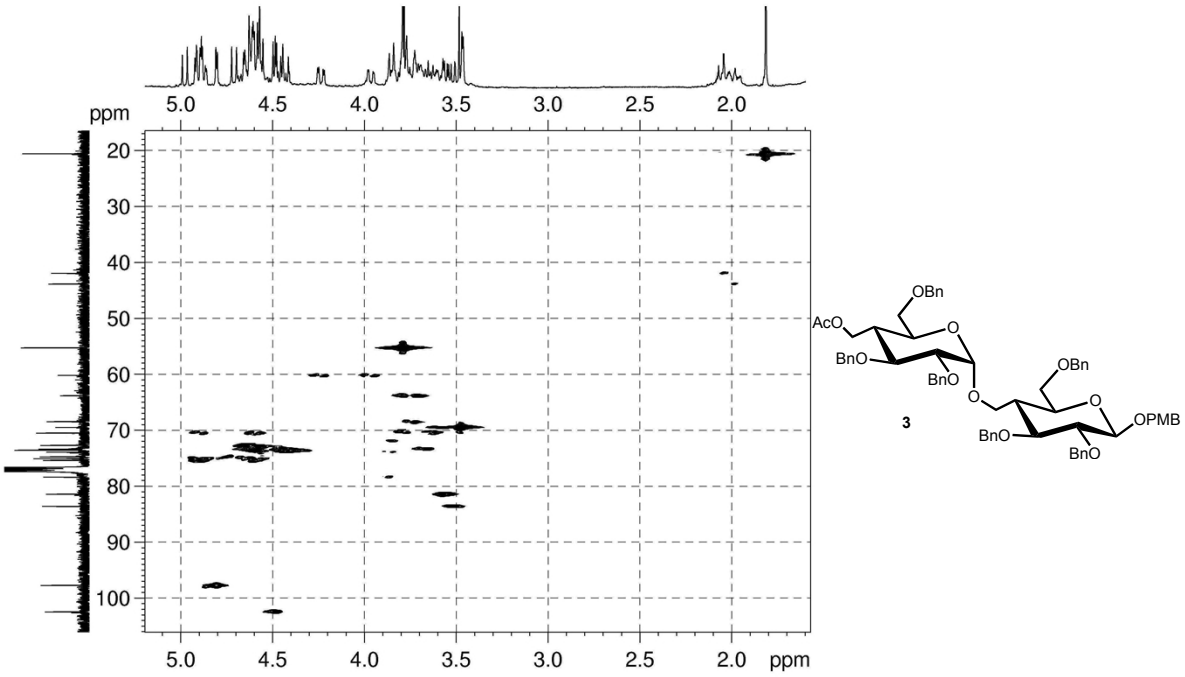


Figure 6. HSQC spectrum of **3** (100 MHz, $CDCl_3$).

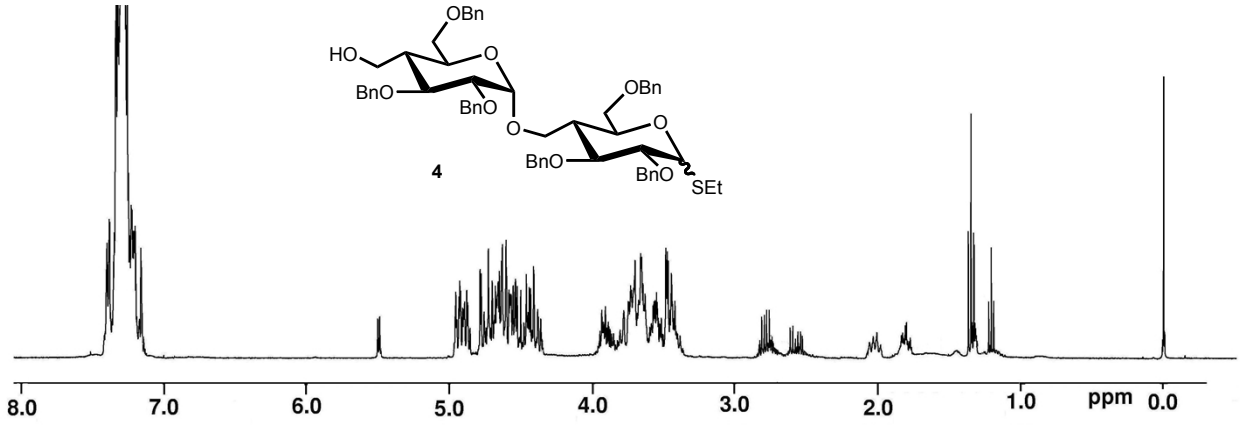


Figure 7. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

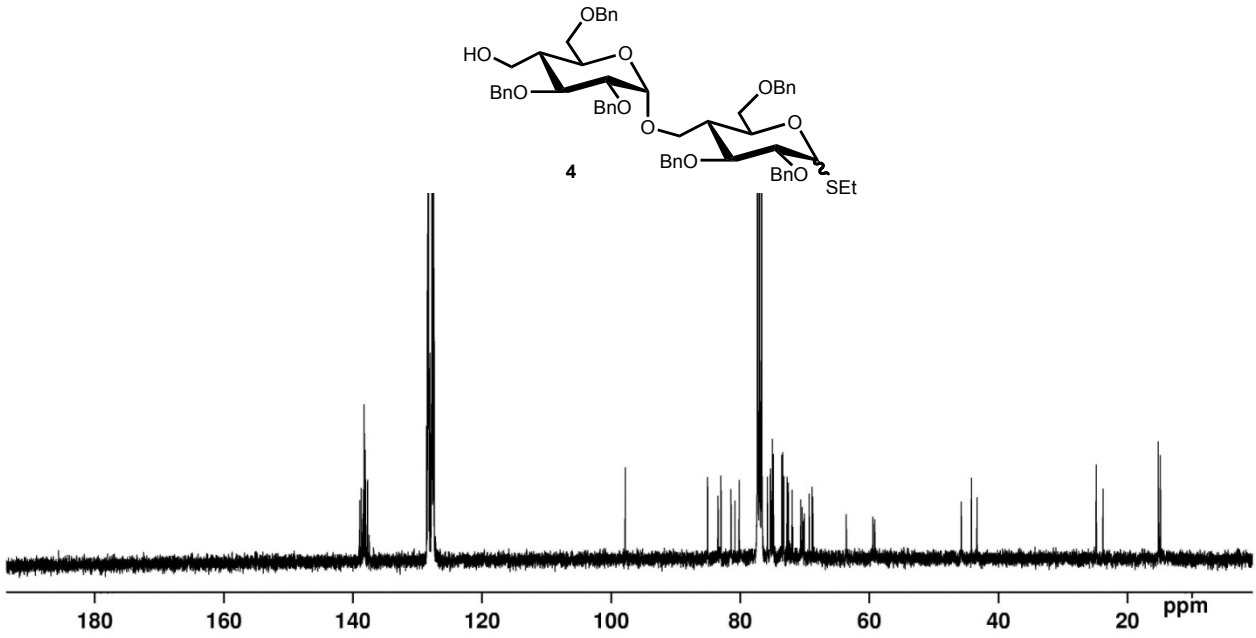


Figure 8. ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

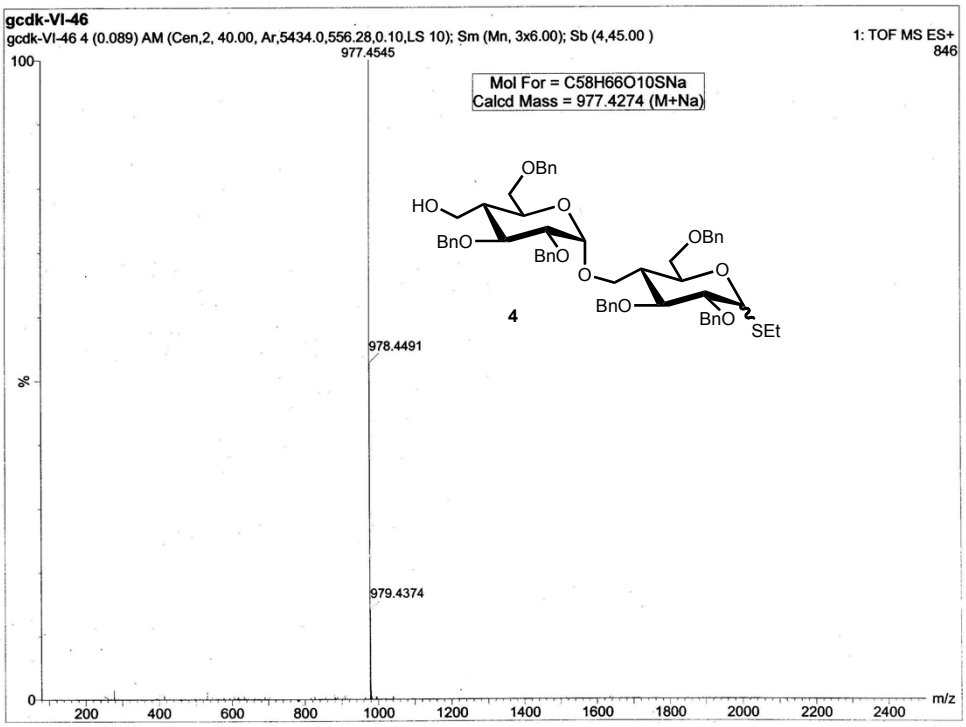


Figure 9. ESI mass spectrum of **4**.

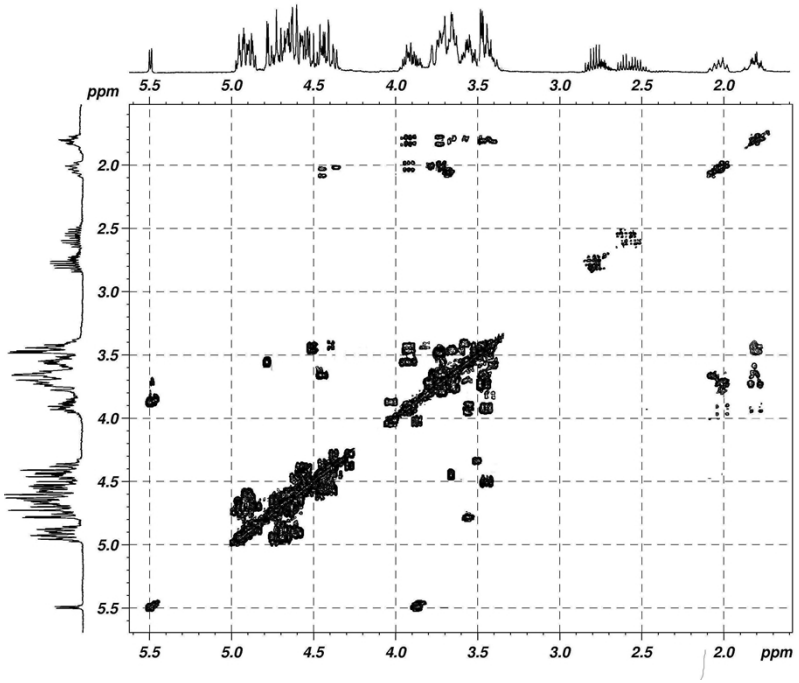


Figure 10. COSY spectrum of **4** (400 MHz, $CDCl_3$).

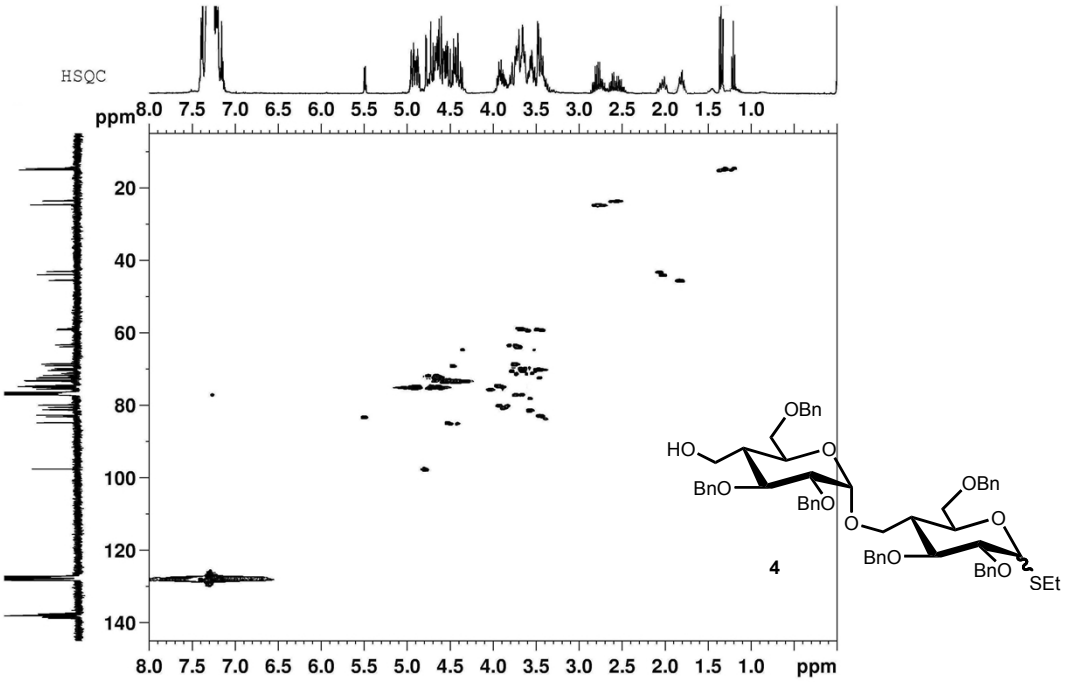


Figure 11. HMQC spectrum of **4** (400 MHz, $CDCl_3$).

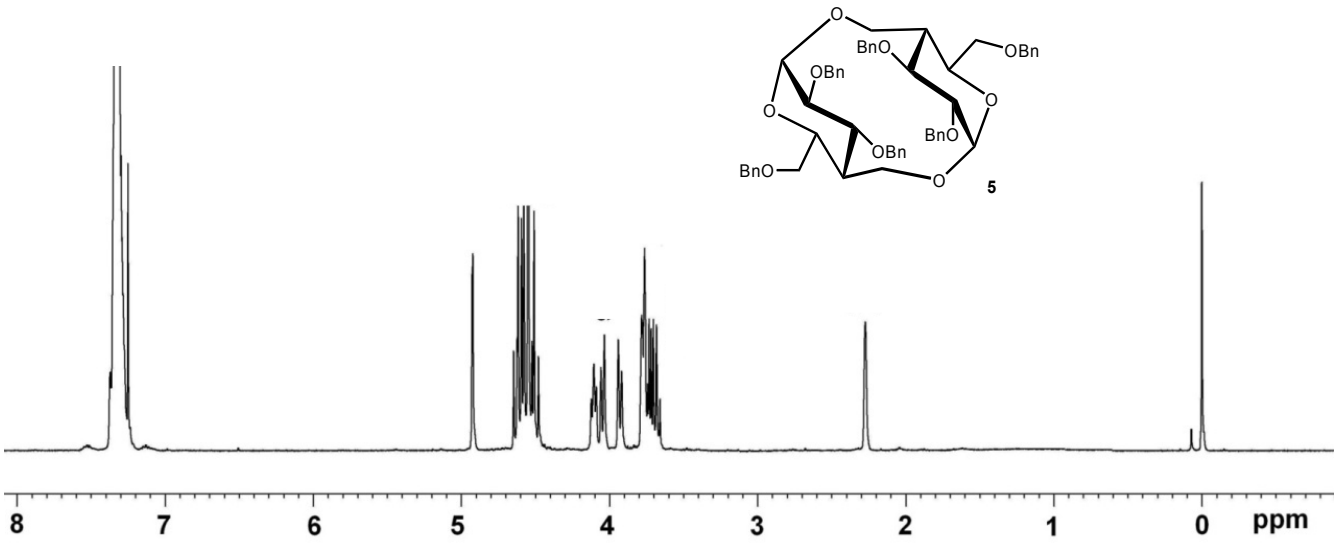


Figure 12. ^1H NMR spectrum of **5** (400 MHz, $CDCl_3$).

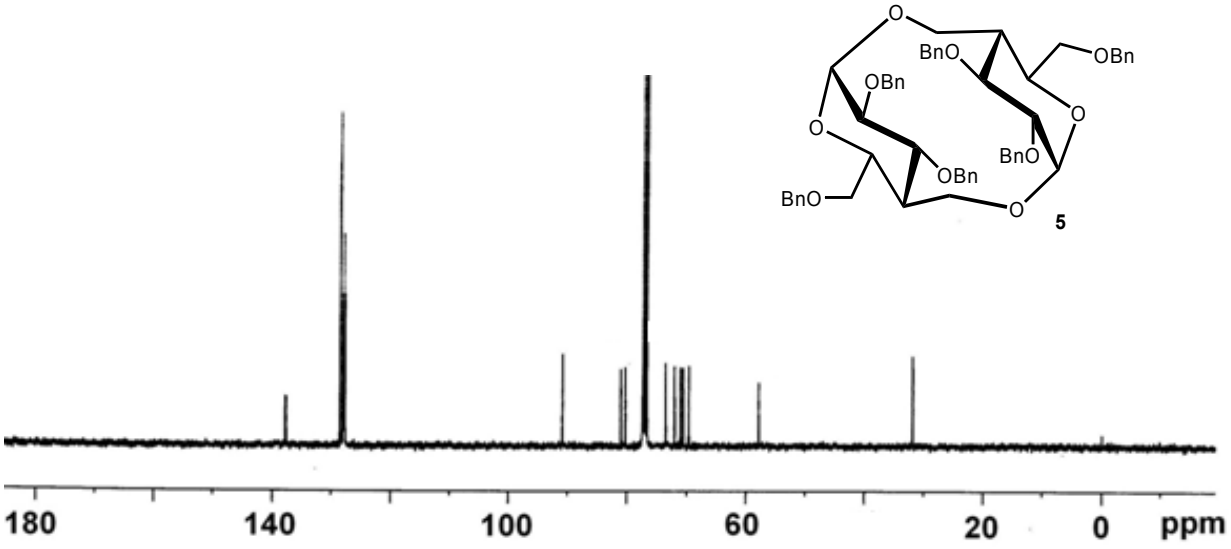


Figure 13. ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

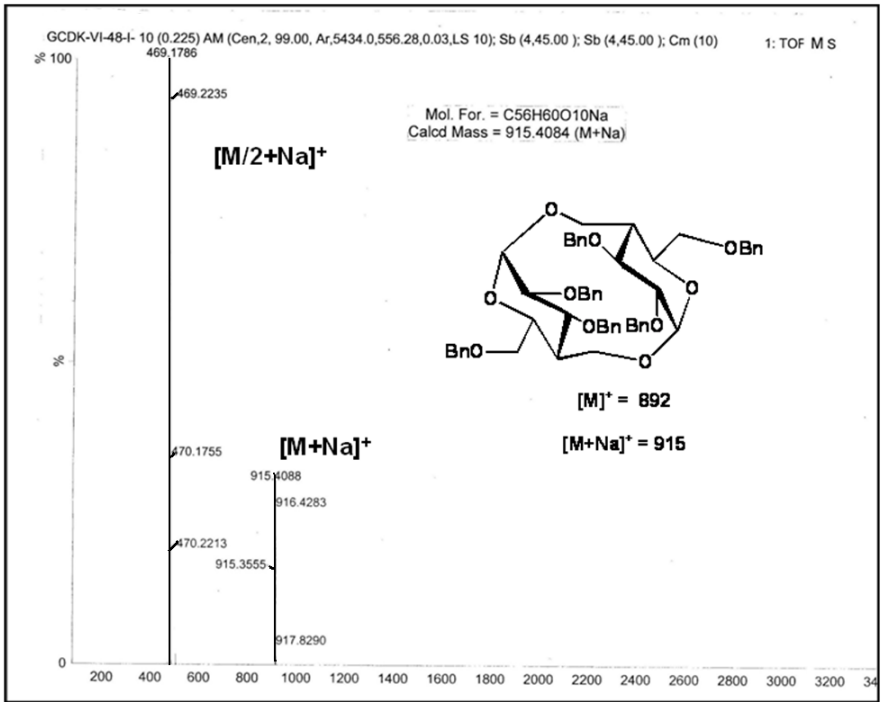


Figure 14. ESI mass spectrum of **5**.

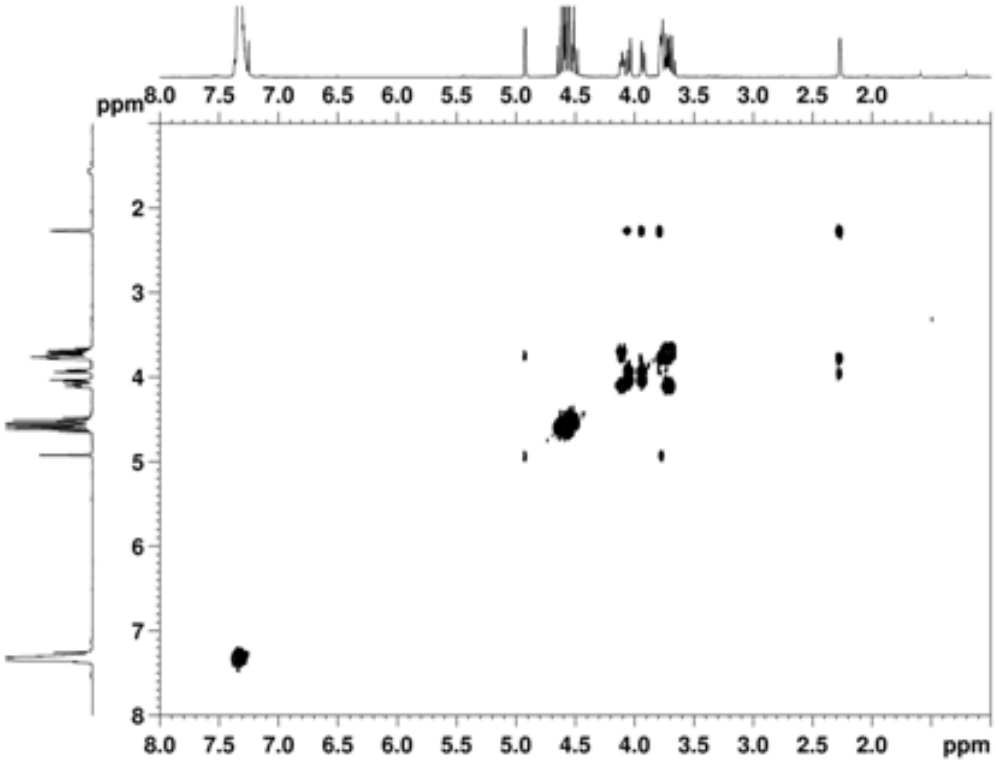


Figure 15. COSY spectrum of **5** (400 MHz, $CDCl_3$).

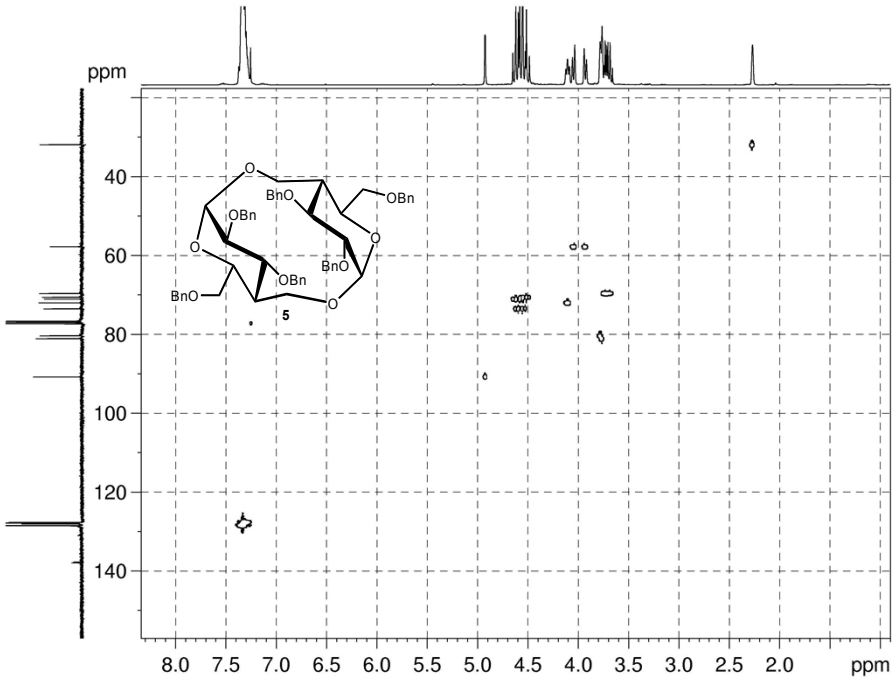


Figure 16. HSQC spectrum of **5** (400 MHz, $CDCl_3$).

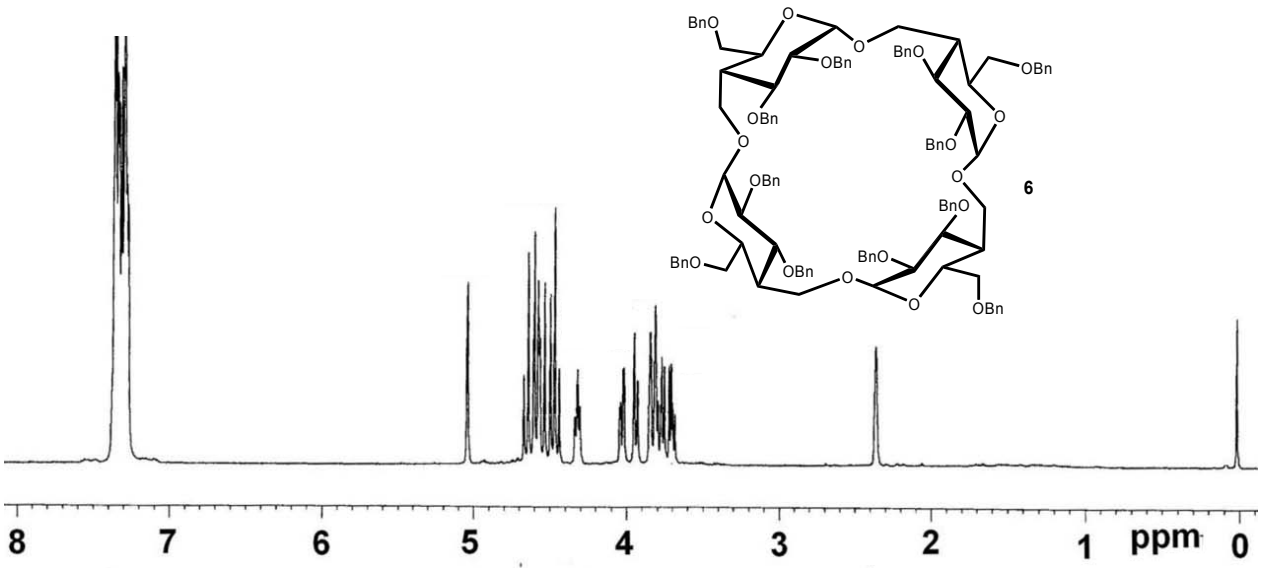


Figure 17. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

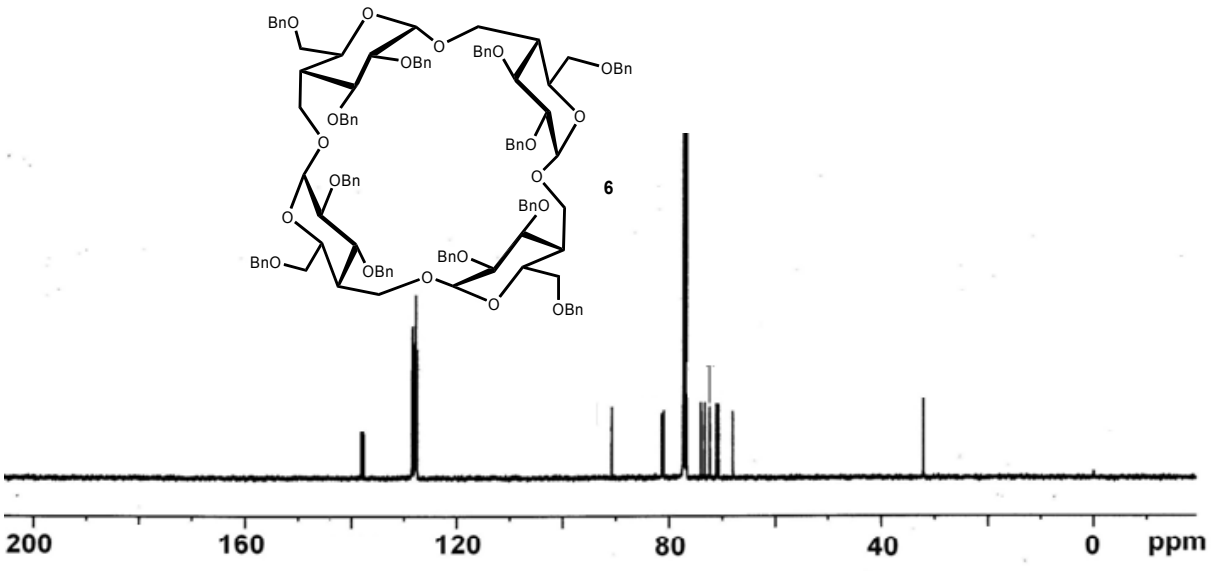


Figure 18. ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

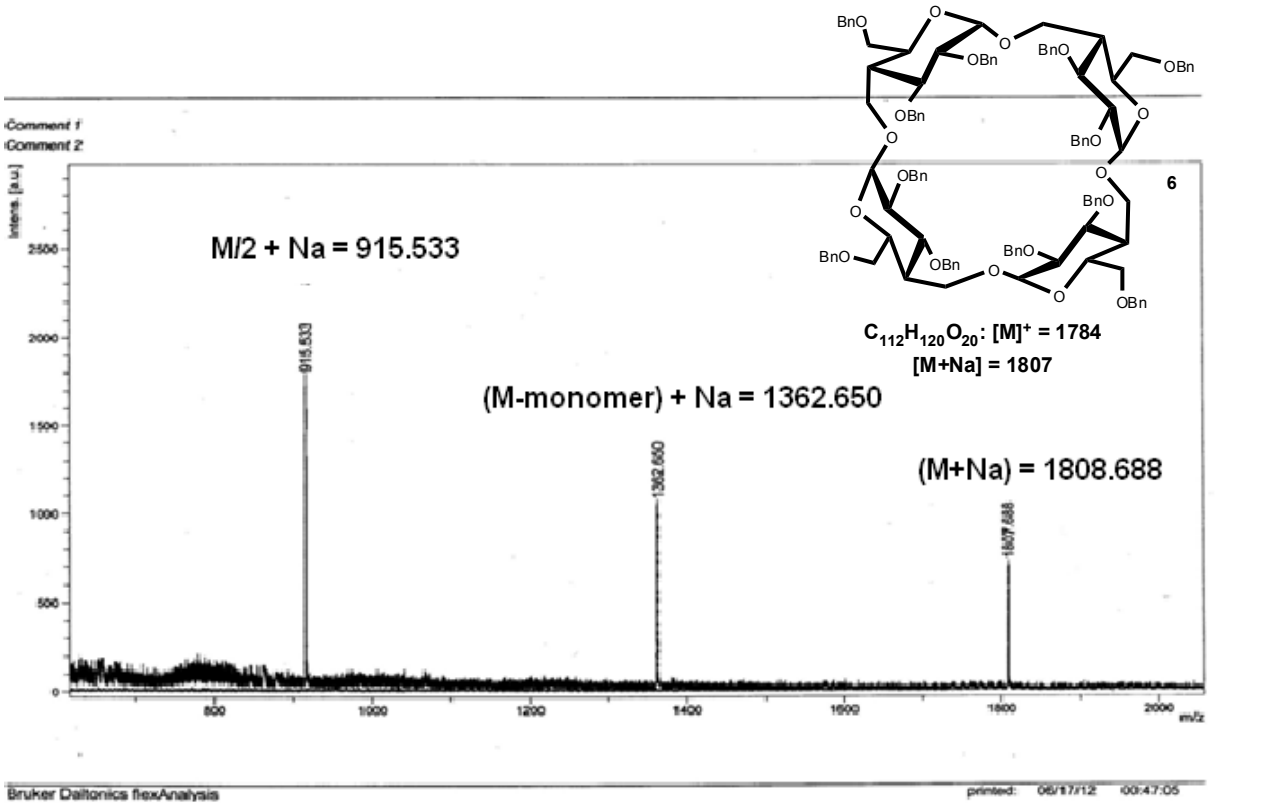


Figure 19. MALDI-TOF mass spectrum of **6**.

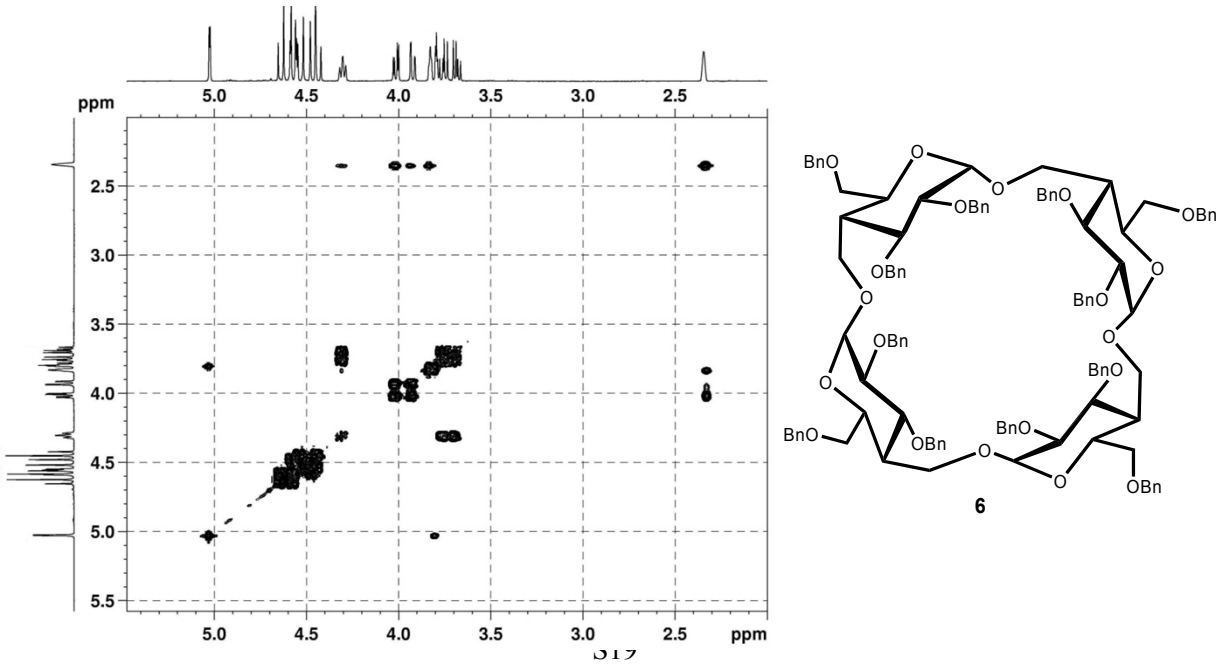


Figure 20. CC

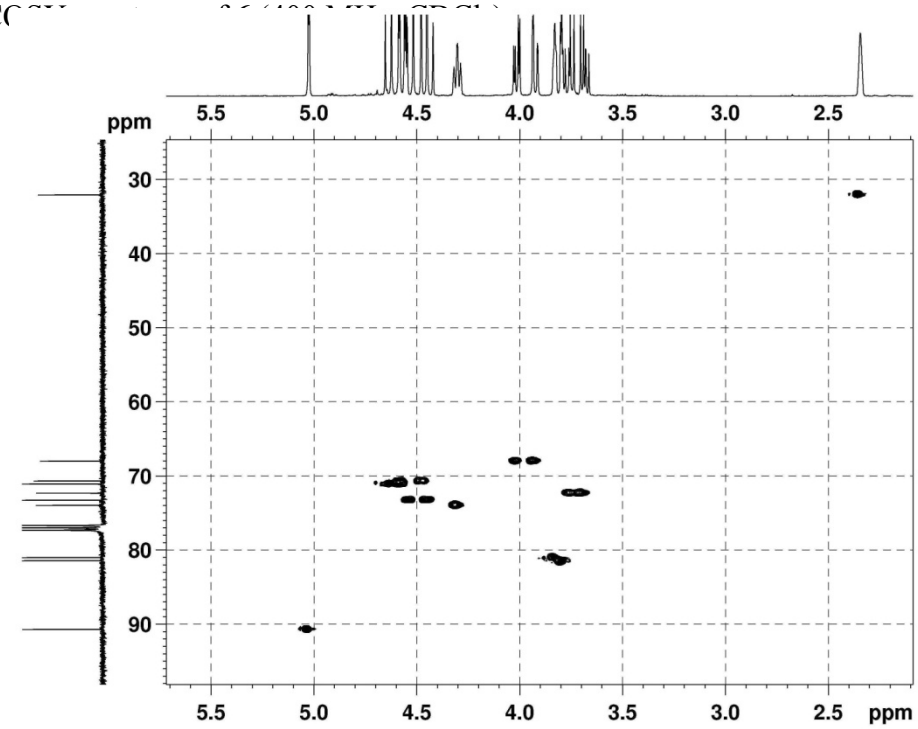
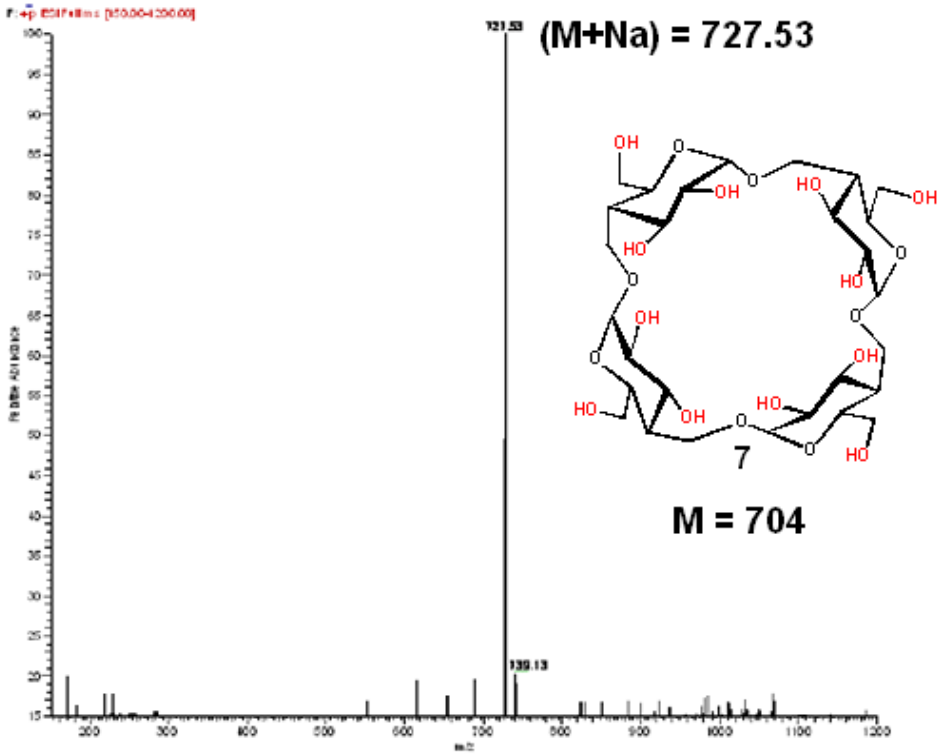


Figure 21. HSQC spectrum of **6** (400 MHz, $CDCl_3$).



Figure

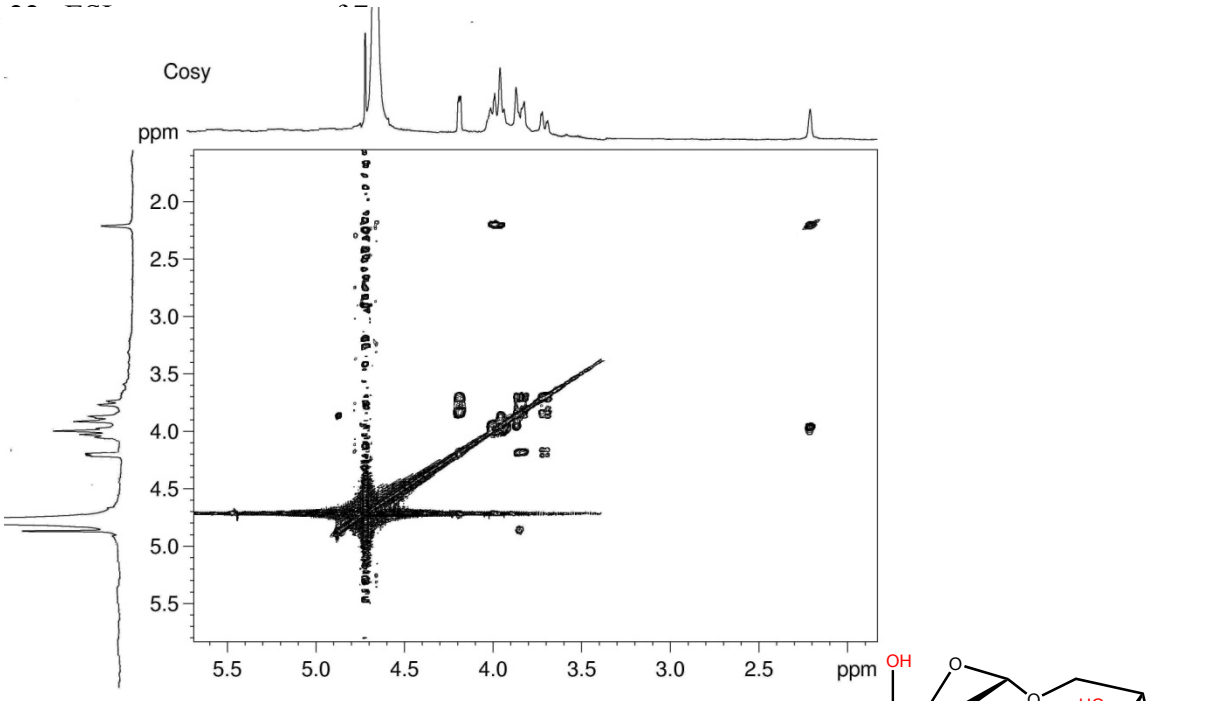


Figure 23. COSY spectrum of **7** (400 MHz, D_2O).

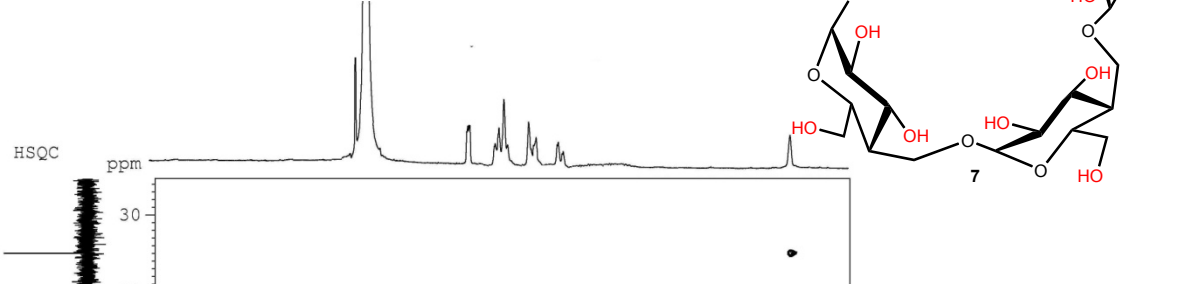


Figure 24. HSQC spectrum of **7** (400 MHz, D_2O).

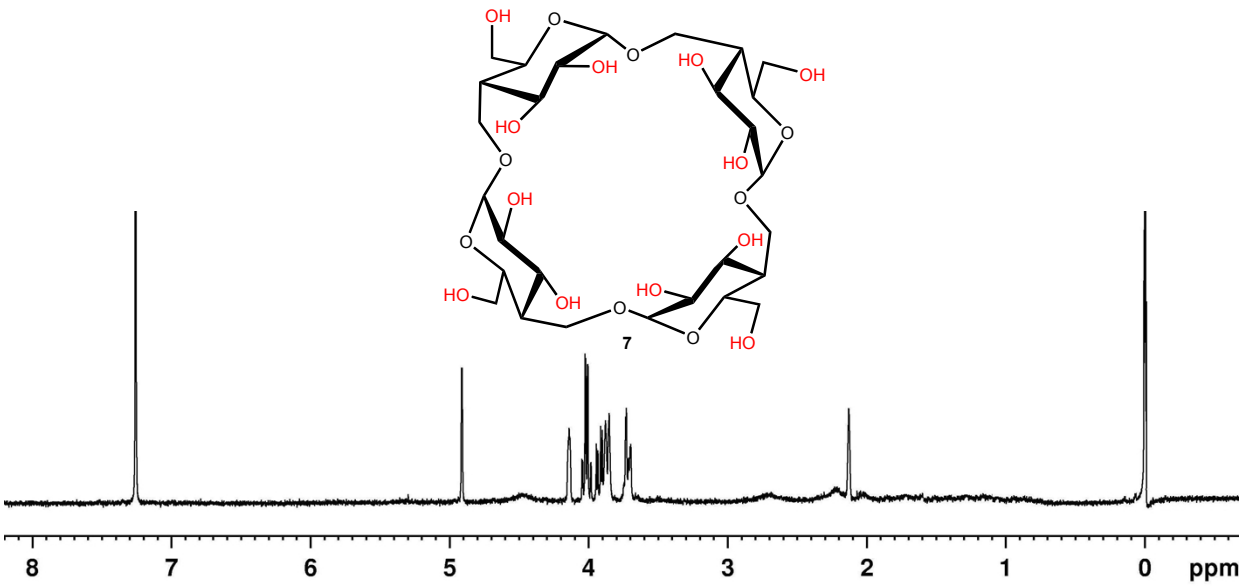


Figure 25. ^1H NMR spectrum of **7** in $CDCl_3$ (400 MHz).

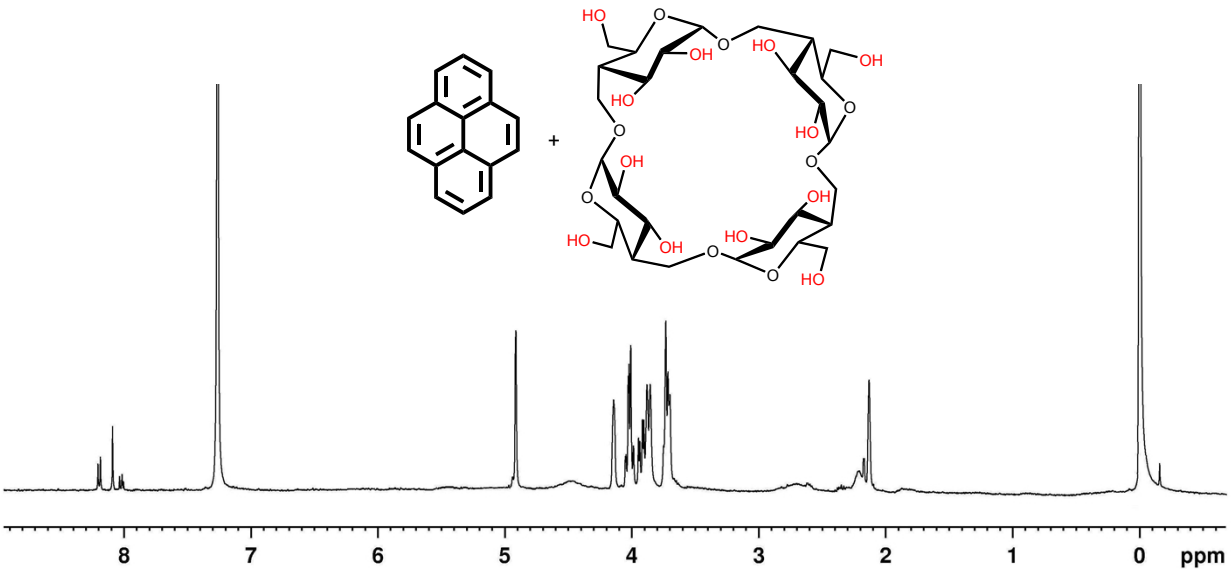


Figure 26. ^{1}H NMR spectrum of **7** (0.9 mM) with pyrene (400 MHz, $CDCl_3$).

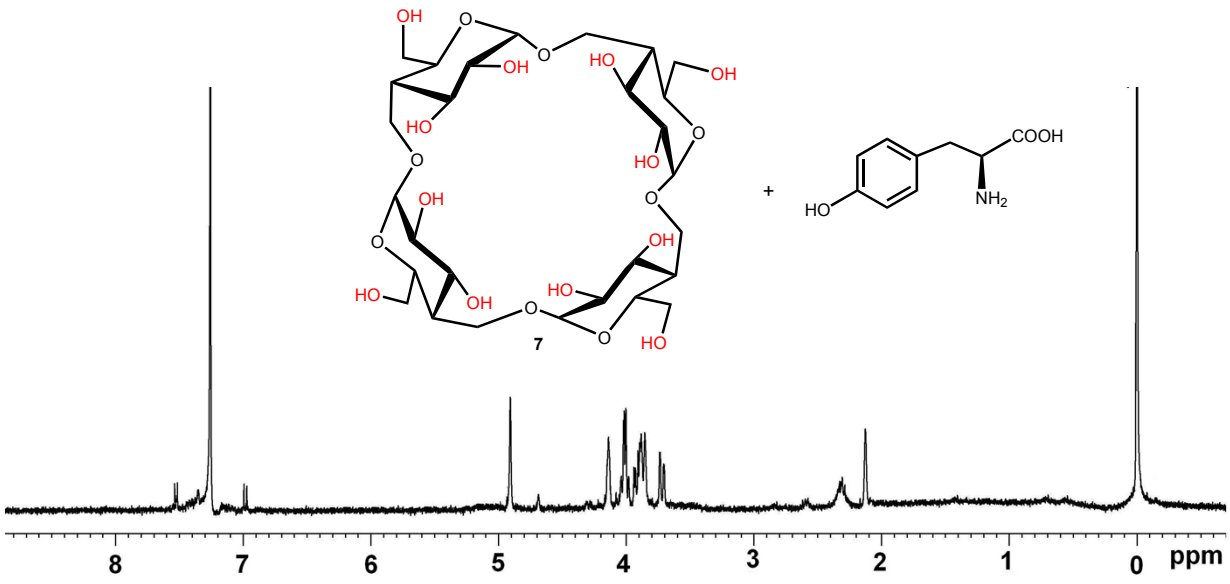


Figure 27. ^{1}H NMR spectrum of **7** with L-tyrosine (400 MHz, $CDCl_3$).

Calculation of the binding constant of 7-pyrene complex:

The following table provides the concentration of pyrene solubilized in varying concentration of **7** in aqueous solution, as determined by UV-Vis absorption spectra.

Table 1.

[**7**] (M)	Concentration of solubilized pyrene (α) (M)	$\alpha/(1-\alpha)$
0.2×10^{-3}	1.5×10^{-6}	2.14
0.5×10^{-3}	2.3×10^{-6}	3.28
0.7×10^{-3}	7.7×10^{-6}	11
0.9×10^{-3}	14.7×10^{-6}	21

$1-\alpha$ = aqueous solubility of pyrene without host = 0.7×10^{-6} M

A plot of $\alpha/(1-\alpha)$ *vs* [**7**] (Figure 28) showed an exponential increase in the solubilization of pyrene, from which a critical concentration (cc) of 7 required to enhance pyrene solubilization was adjudged to be 0.43 mM.

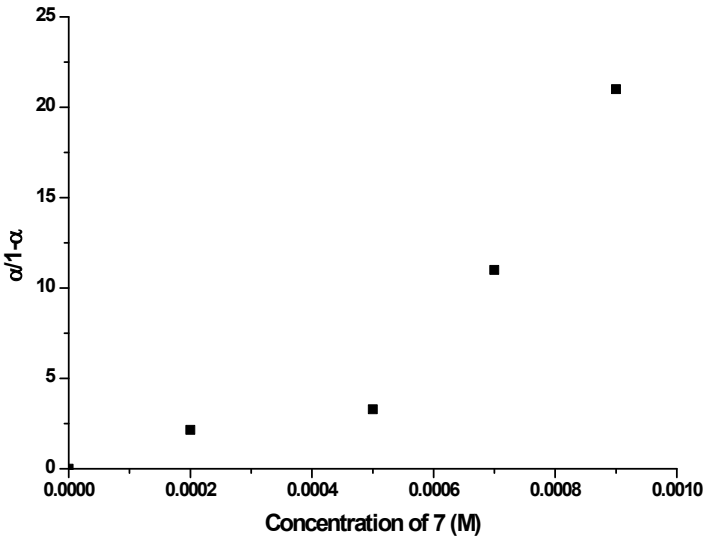


Figure 28. A plot of the ratio of solubilized pyrene in varying concentration of 7.

Calculation of the binding constant. For calculating the binding constant, the model of micelle-guest interaction was utilized. Micelle forming systems have been studied for their solubilization properties of pyrene.[3] Accordingly, an attempt to determine the association constant (K_a) was undertaken by using the following equation

$$\alpha/1\text{-}\alpha = K_a\{[\mathbf{7}] - cc/n\} \qquad (1)$$

where cc is the critical concentration of **7** required for enhanced solubility of pyrene and n is the aggregation number (mole ratio) of **7** at the critical concentration. The mole ratio was determined to be 4 from the NMR studies for 0.5, 0.7 and 0.9 mM solutions of **7**, solubilizing pyrene as given in Table 1. From the above equation, a K_a of $1.77 \times 10^5\ M^{-1}$ was derived for **7**-pyrene complexation.

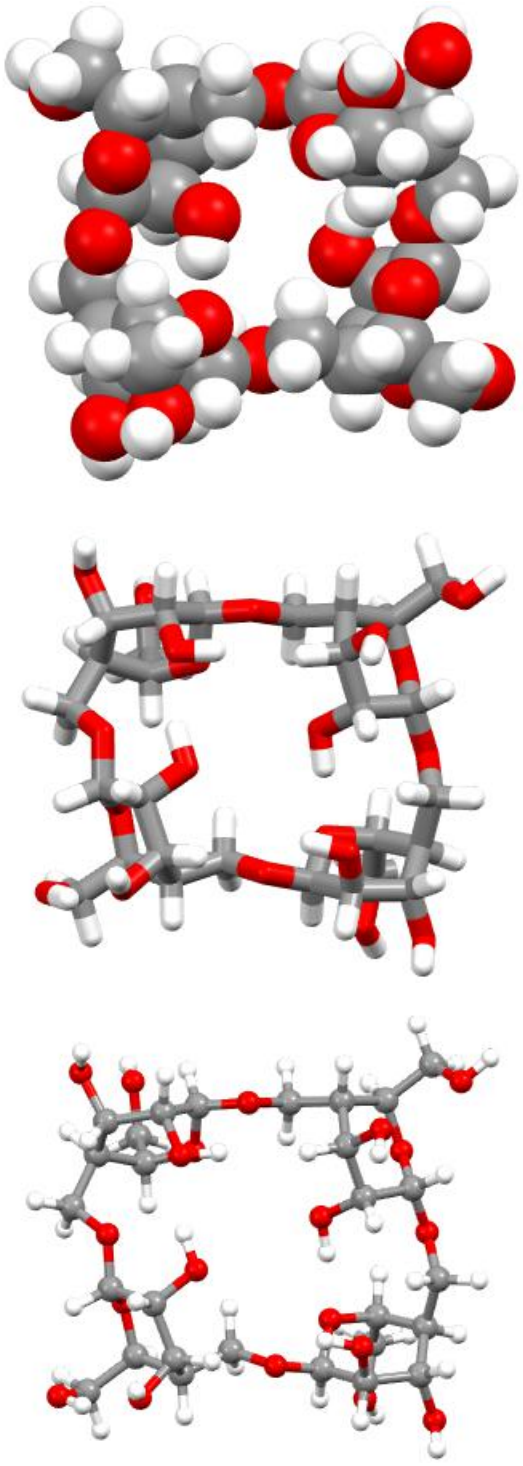


Figure 29. Few more energy minimized molecular modeling structures of host **7**.

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3. A. V. Sapre, K. V. S. Rama Rao and K. N. Rao, *J. Phys. Chem.*, 1980, **84**, 2261-2267, and references cited therein.