Supporting Information

Biologically Active Branched Polysaccharide Mimetics: Synthesis via Ring-opening Polymerization of a Maltose-based β-Lactam

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General methods, materials, and instrumentation

Materials and chemicals were purchased from Sigma Aldrich or Alfa Aesar, and were used as received unless otherwise noted. 2,3,6,2',3',4',6'-hepta-*O*-acetyl-α-D-maltosyl bromide and 3,4,6-tri-*O*-benzyl-D-glucal starting materials were purchased from Carbosynth, LLC (San Diego, California). Solvents used for the polymerization reactions were dried and freshly distilled prior to use. All reactions were carried out under nitrogen using standard techniques, unless otherwise noted. Lyophilization was performed using a Virtis Benchtop 4K freeze dryer Model 4BT4K2L-105 at -40 °C. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 500MHz spectrometer. Infrared spectroscopy (FT-IR) was performed on a Nicolet FT-IR with a horizontal attenuated total reflectance (ATR) adapter plate. Specific optical rotations were determined at 25 °C using a Rudolph Autopol II polarimeter operating at 589 nm in a 50 mm pathlength cell. The molecular weights of benzylated polymers were determined by gel permeation chromatography (GPC) against polystyrene standards using THF as the eluent at a flow rate of 1.0 mL/min through two Jordi columns (Jordi Gel DVB 10^5 Å and Jordi Gel DVB 10^4 Å, 7.8 x 300 mm) at 25 °C with a refractive index detector. The molecular weights of the deprotected polymers were determined by GPC versus dextran standards using aqueous buffer (0.2 M $NaNO_3$, 0.010 M phosphate buffer, pH 7.5) as the eluent at a flow rate of 0.50 mL/min through two Agilent PL aquagel columns (OH MIXED-M and OH 30, 7.5 x 300 mm) at 25 °C with a refractive index detector. Circular dichroism (CD) studies were performed in a 1 mm path length cuvette using an Applied Photophysics CS/2Chirascan with a standard Mercury lamp.

Turbidimetric Assay

The turbidimetric assay was performed in pH 7.4 HEPES-buffered saline (HEPES) containing HEPES 10 mM, NaCl 150 mM, $CaCl_2$ 1 mM, and $MnCl_2$ 1 mM, according to the literature with minor modifications.[1] The Con A stock solution was freshly prepared by dissolving Con A in HEPES buffer and adjusted to the concentration of 0.104 mg/mL determined by the UV absorbance at 280 nm (based on A_{280}=1.37x [mg/mL Con A]). The Con A solution (570 μL) was transferred to a 1 cm cuvette. Then the solution of PASs in HEPES buffer was added [30 μL at 0.351mg/mL for Mal-PASs (1.0 mM based on maltose residue), and 30 μL at 1.0 mg/mL for alt-PASs and glc-PASs (5.3 mM based on sugar residue)]. The final concentrations of Con A and Mal-PASs were 1.0 μM based on Con A tetramer and 50.0 μM based on maltose residue, respectively. The solution was mixed vigorously for 10 seconds using a micropipette before the absorbance was recorded at 420nm for 20 min at 25 °C. At the 16 min timepoint, 66 μL of a 10 mg/mL α-methyl mannose solution (50 mM) was added. Each sample was run three times and the curves shown were the average of all three runs.

Dynamic light scattering measurements

Dynamic light scattering (DLS) measurements were conducted on a Brookhaven 90 plus nano-particle sizer. For size determination, polymer samples were prepared in MilliQ water at concentration of 0.50 and 0.05 mg/mL and then filtered through a 0.45 μm filter to remove any dust particulates just before sample measurement. Each sample was measured 10 times and averaged to give the listed values.

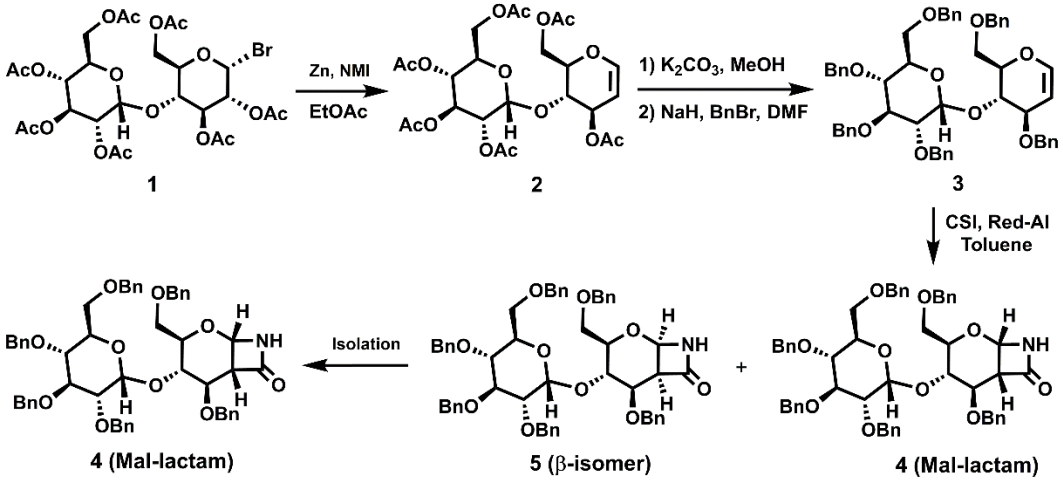
DLS data show that while glc-PASs (**P5**) aggregate into structures with diameter of about 100 nm, alt-PAS (**P6**) and Mal-PASs (**P1**-**P4**) do not form nano-scaled structures in aqueous solutions. However, the aggregation of glc-PAS is not likely the major reason for the weak binding with Con A: First, in the turbidity assay, the final concentration of glc-PAS (**P5**) was 0.05mg/mL (265μM based on the glucose repeating unit), while the final concentration of Con A was 1.0μM. Despite of the aggregation of glc-PAS (**P5**), there should be still enough sugar residues on surface for binding if they could bind to Con A. Second, it has been reported that nanoscale structures derived from glycopolymers tend to display much higher affinity towards binding lectins, since spherical and three dimensioned structures provide greater surface area for lectins to access their binding ligands.[2] In contrast, studies have shown that the internal glucose residues of linear polysaccharides could not be recognized by Con A.[3] Therefore, we proposed that the weak binding between glc-PAS (**P5**) and Con A was due to the lack of of terminal glucose residues.

Cell Culture and *In Vitro* Cell Viability Assay

The cytotoxicity of Mal-PASs was evaluated using an MTS cell proliferation assay in three cell lines: human embryonic kidney (HEK293), human cervix adenocarcinoma (HeLa), and mouse embryonic fibroblast (NIH3T3) cells *in vitro*. The rationale for selecting these three cell lines was to assess toxicity against: 1) cells originating from

two different species (human and mouse); 2) a human healthy, normal cell line versus a cell line derived from a cancer cells (HEK293 vs. HeLa); and 3) a cell line used in standard pre-clinical FDA biocompatibilty/safety testing (NIH3T3).[4] HEK293, NIH3T3 and HeLa cells (ATCC) were maintained at 37 °C under 5% CO_2 using DMEM media containing 10% fetal bovine serum and 1% glutamine–penicillin–streptomycin. Cytotoxicity of Mal-PASs were evaluated using an MTS assay (CellTiter 96 Aqueous One, Promega, Madison, WI). Briefly, cells were cultured in a 96-well plate at 3000 cells/well for 1 day, after which the media was exchanged for media containing either no treatment or 0, 50, 250, 500 or 1000μg/mL of polymers. The cells were then incubated with treatment for 24 hours, after which cell viability was quantified relative to the no treatment control, after correcting for background absorbance. Three wells per treatment concentration were used, and the assay was repeated three times.

Small Molecule Synthetic Procedures



Scheme S1. Synthetic route for Mal-lactam (4)

3,6,2',3',4',6'-hexo-*O*-acetyl-D-maltal (2). The procedure was adapted from the literature with minor changes.[5] 2,3,6,2',3',4',6'-hepta-*O*-acetyl-α-D-maltosyl bromide (**1**) (25.0 g, 35.7 mmol) was dissolved in EtOAc (350 mL), then activated Zn powder (14.0 g, 214.1 mmol) and *N*-methylimidazole (3.0 mL, 37.7 mmol) were added. The mixture was refluxed for 3 hours. After cooling to room temperature, the mixture was filtered through Celite and the filtrate washed with 10% HCl (200 mL), sat. $NaHCO_3$ (200 mL) and brine (200 mL), then dried with sodium sulfate (Na_2SO_4). After filtration, the solvent was evaporated under vacuum. The crude product was purified by flash chromatography (EtOAc-hexane, 1:2) to afford compound **2** (13.5 g, 67%) as a white solid. ^{1}H NMR (500 MHz, CDCl3): δ 6.40 (d, *J* = 6.2 Hz, 1H), 5.47 (d, *J* = 4.0 Hz, 1H), 5.38 (t, *J* = 9.9 Hz, 1H), 5.15 (m, 1H), 5.03 (t, *J* = 9.8 Hz, 1H), 4.80 (m, 2H), 4.34 (m, 2 H), 4.27 (m, 1 H), 4.21 (dd, *J* = 12.4, 4.2 Hz, 1H), 4.07 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.00 (m, 2H), 2.03 (m, 18H); ^{13}C NMR (125 MHz, CDCl3): δ 170.5, 170.4, 170.3, 170.0, 169.5 145.5, 98.6, 95.8, 74.0, 72.4, 70.4, 69.5 (2), 68.2, 68.1, 61.8, 61.6, 21.0, 20.8, 20.6 (2), 20.5 (2) ; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{32}O_{15}Na$, 583.1639; found, 583.1628.

3,6,2',3',4',6'-hexo-*O*-benzyl-D-maltal (3). To a solution of compound **2** (13.5 g, 24.1 mmol) in methanol (200 mL), K_2CO_3 (500 mg, 3.61 mmol) was added. The mixture was stirred at room temperature for 12 hours. The solvent was then evaporated and D-maltal was used in the next step without further purification.

To the solution of D-maltal (7.42 g, 24.1 mmol) in DMF (300 mL), NaH (4.74 g, 188.0 mmol) was added slowly at 0 °C. The solution was stirred for 30 minutes at room temperature. After cooling down to 0 °C, benzyl bromide (22.3 mL, 188.0 mmol) was added dropwise and the reaction mixture was warmed up to room temperature and stirred for 36 hours. After quenching the reaction with water, 300 mL ethyl acetate was added to the solution. The organic phase was washed with water and brine, and dried over Na_2SO_4. After filtration, the solvent was evaporated under vacuum. The crude was purified by silica gel flash chromatography (EtOAc–hexane from 1: 20 to 1: 5) and yielded compound **3** as colorless oil (18.7g, 92%). ^{1}H NMR (500 MHz, CDCl3): δ 7.34-7.08 (m, 30 H), 6.47 (dd, *J* = 6.2, 1.2 Hz, 1H), 5.45 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.89 (dd, *J* = 6.2, 3.2 Hz, 1H), 4.79 (dd, *J* = 10.8, 9.6 Hz, 1H), 4.66-4.48 (m, 7H), 4.46 (d, *J* = 3.2Hz, 1H), 4.43 (d, *J* = 4.0 Hz, 1H), 4.35 (d, *J* = 12.2 Hz, 1H), 4.26 (m, 1H), 4.23 (m, 1H), 4.17 (dd, *J* = 6.9, 5.0 Hz, 1H), 3.89 (t, *J* = 9.35 Hz, 1H), 3.82 (m, 2H), 4.72 (dd, *J* = 10.8, 3.4 Hz, 1H), 3.66 (dd, *J* = 10.2, 9.0 Hz, 1H), 3.60 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.54 (dd, *J* = 9.8, 3.7 Hz, 1H), 3.48 (dd, *J* = 10.8, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl3): δ 145.3, 138.9, 138.4, 138.2, 138.1, 138.0, 137.9, 128.4 (2), 128.3 (3), 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (2), 127.4, 99.3, 96.3, 81.8, 79.7, 77.56, 76.4, 75.6, 75.0, 74.4,

73.4, 73.3, 72.8, 70.8, 70.3, 68.9, 68.3, 68.2; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{54}H_{56}O_9Na$, 871.3822; found, 871.3817.

Mal-lactam (4). The procedure was adapted from the literature with minor changes.[6] At room temperature, 3.20 mL (5.17 g, 36.5 mmol) of chlorosulfonyl isocyanate (CSI), which had previously been stored over oven-dried sodium carbonate for more than one week at 4 °C, was dissolved in 30 mL of anhydrous toluene over 2.0 g of oven-dried Na_2CO_3 under nitrogen. The solution was cooled to -78 °C in a dry ice/acetone bath and a solution of 15.5 g (18.2 mmol) of compound **3** in 30 mL of anhydrous toluene was slowly added. The solution was warmed to -61 °C by transferring the reaction flask to a dry ice/chloroform cooling bath. After 6 hours at -61 °C, the reaction was cooled to -78 °C and diluted with an additional 80 mL of anhydrous toluene and 13.3 mL of Red-Al (>60 wt% solution in toluene) was added slowly. After 20 minutes at -78 °C, the reaction was warmed to -61 °C for 20 minutes and then warmed to -10 °C in an ice/saturated ammonium chloride bath. After 5 minutes at -10 °C, 3.0 mL of water was added and reaction was stirred for an additional 30 minutes while warming to 0 °C. Then the solution was filtered to remove solids. After the addition of 100 mL of diethyl ether, the organic phase was washed with saturated bicarbonate and brine, dried over Na_2SO_4, and the solvent was removed. The crude was purified by silica gel flash chromatography (EtOAc–hexane from 1: 5 to 1: 1), giving a β-lactam product containing 93% of monomer **4** and 7% of distereomer (**5**) (8.40g, 51%). This product was further purified by repeated flash chromatography with 1: 20 to 1: 10 EtOAc: CH_2Cl_2, affording diastereopure monomer **4** as a colorless semisolid (5.3g, 32%). ^{1}H NMR (500 MHz, CDCl3): δ 7.33-7.10 (m, 30 H), 6.02 (d, *J* = 2.6 Hz, 1H), 5.56 (d, *J* = 4.4 Hz, 1H), 5.43 (d, *J* = 3.6 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.56-4.47 (m, 5H), 4.44 (d, *J* = 5.7 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.34 (d, *J* = 12.2 Hz, 1H), 4.21 (dd, *J* = 6.4, 3.0 Hz, 1H), 4.16 (ddd, *J* = 8.6, 5.1, 2.8 Hz, 1H), 4.01 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.85 (dd, *J* = 9.9, 8.9 Hz, 1H), 3.71 (m, 3H), 3.61 (dd, *J* = 10.2, 9.0 Hz, 1H), 3.52 (t, *J* = 2.9 Hz, 1H), 3.50 (dd, *J* = 3.3, 2.0 Hz, 1H), 3.40 (m, 2H); ^{13}C NMR (125 MHz, CDCl3): δ 166.4, 138.7, 138.4, 137.9, 137.8 (2), 137.4, 128.4, 128.3 (3), 128.2, 128.0, 127.8 (3), 127.6 (2), 127.5, 127.2, 96.2, 81.8, 79.4, 77.4, 77.1, 76.2, 75.6, 75.0, 73.4 (2), 72.8, 71.9, 71.1, 70.6, 69.6, 69.5, 68.2, 54.6; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{55}H_{57}O_{10}N$, 914.3880; found, 914.3887.

General Procedure for Polymerization

In an oven-dried flask, Mal-lactam (0.400 g, 0.448 mmol) and *t*-butylacetyl chloride (10.0 mol% for $DP_{(theo)}$ = 10, 6.67 mol% for $DP_{(theo)}$ = 15, 5.0 mol% for $DP_{(theo)}$ = 20, and 3.33 mol% for $DP_{(theo)}$ = 30) were dissolved in 5.0 mL of freshly distilled tetrahydrofuran (THF, without BHT) which had been dried over molecular sieves. Because small quantities of initiator were required, a stock solution of *t*-butylacetyl chloride in tetrahydrofuran was prepared immediately before use and the appropriate volume was added to the reaction flask. The reaction flask was cooled to 0°C in an ice bath. Next, an appropriate volume of a 0.25 M solution of LiHMDS in THF (25.0 mol% for $DP_{(theo)}$ = 10, 16.7 mol% for $DP_{(theo)}$ = 15, 12.5 mol% for $DP_{(theo)}$ = 20, and 8.32 mol% for $DP_{(theo)}$ = 30) was added and the solution was stirred 1-2 hours, and the reaction was monitored by GPC. To quench the reaction, a drop of saturated NH_4Cl aqueous solution was added to the reaction. The solvent was removed and the resultant solid was redissolved in dichloromethane (25 mL) and washed with 1 M HCl, saturated $NaHCO_3$, and brine. After drying over Na_2SO_4, the solvent was removed under vacuum. The product was dissolved in minimal dichloromethane and precipitated by adding dropwise into a flask of stirred, cold hexane (50 mL). The resultant solid was collected by filtration, redissolved in dichloromethane, and precipitated in cold methanol and dried. The precipitate was collected by filtration and dried under high vacuum (83-91%). Spectral data is listed for **P4'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-6.75 (br m, 30H), 5.41 (br s, 1H), 4.92-2.60 (br m, 26H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 138.8, 138.6, 138.5, 138.1, 137.7, 128.1 (3), 127.8, 127.7, 127.4, 127.0, 95.7, 82.1, 79.0, 75.4, 74.8, 74.1, 73.2, 72.9, 72.2, 71.6, 70.8, 69.3, 68.0, 51.6. IR (ATR): 3347 br (NH), 1700 (amide I), 1496 br (amide II), 1069 cm^{-1}.

General procedure for Debenzylation

To a polymer (0.30-0.36 g depending on the sample) solution in 5.0 mL of tetrahydrofuran, 1.5 equivalent of LiHMDS was added and the solution was stirred for 5 minutes at room temperature. The solution was then added into a rapidly stirred solution of sodium in anhydrous liquid ammonia (100 mL) at −60 °C under nitrogen (sodium was washed in cyclohexane and cut into small pieces before addition). The solution's deep blue color was maintained by adding additional sodium. After 1 hour at −60 °C, saturated ammonium chloride solution was added until the blue color disappeared. After evaporation of the ammonia in a water bath (room temperature), the resulting aqueous layer was washed with diethyl ether. The aqueous solution was dialyzed at room temperature for 2 days with six water changes (Spectrum labs dialysis tubing, MWCO 2000). The solutions were lyophilized to give deprotected Mal-PASs as white fluffy solids (76-92%). Spectral data is listed for **P4**: ^{1}H NMR (500 MHz, D_2O) δ

5.75 (d, *J*= 5.0 Hz, 1H), 5.40 (m, 1H), 4.40 (t, *J*= 9.9 Hz, 1H), 3.87 (d, *J*= 11.7 Hz, 1H), 3.75 (m, 6H), 3.60 (m, 1H), 3.52 (m, 1H), 3.43 (t, *J*= 9.4 Hz, 1H), 3.09 (m, 1H); ^{13}C NMR (125 MHz, D_2O) δ 172.7, 102.7, 80.0, 77.4, 75.7, 75.5, 74.6, 74.5, 72.2, 71.8, 63.4, 63.2, 53.9. IR (ATR): 3350 br, 1680 (amide I), 1540 (amide II), 1032 cm^{-1}. The DPs determined by proton NMR are 12.3, 19.6, 26.4, 37.5 for **P1**, **P2**, **P3**, and **P4**, respectively.

Glc-PAS (**P5**) and Alt-PAS (**P6**) were obtained according to previously reported procedures.[4,7]

Glc-PAS (**P5**): ^{1}H NMR (500 MHz, D_2O) δ 5.75 (d, J = 5.1 Hz, 1H), 4.12 (t, J = 10.1, 1H, H3), 3.75 (br s, 2H), 3.45(m, 2H), 3.05 (dd, J = 11.2, 5.1, 1H); ^{13}C NMR (125 MHz, D_2O) δ 170.1, 74.6, 73.0, 69.9, 68.3, 60.2, 51.0. IR (ATR): 3612-3111 br, 1672 (amide I), 1522 br (amide II), 1059 cm^{-1}.

Alt-PAS (**P6**): ^{1}H NMR (500 MHz, D_2O) δ 5.65 (br s, 1H), 4.60-4.14 (br m, 1H), 4.12-3.52 (br m, 4H), 3.20-2.58 (br m, 1H); ^{13}C NMR (125 MHz, D_2O) δ 171.1, 75.0, 73.8, 68.9, 66.3, 64.8, 61.4, 50.7. IR (ATR): 3605-3121 br, 1666 (amide I), 1532 br (amide II), 1057 cm^{-1}.

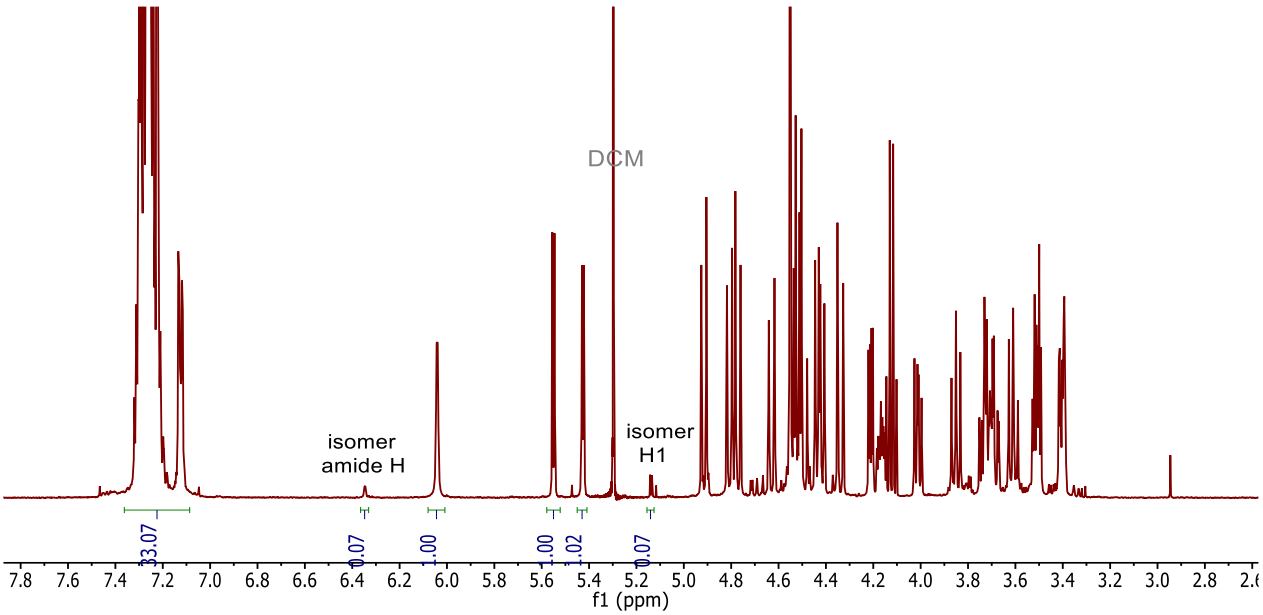


Figure S1. ^{1}H NMR of cycloaddition product with diastereomeric impurity

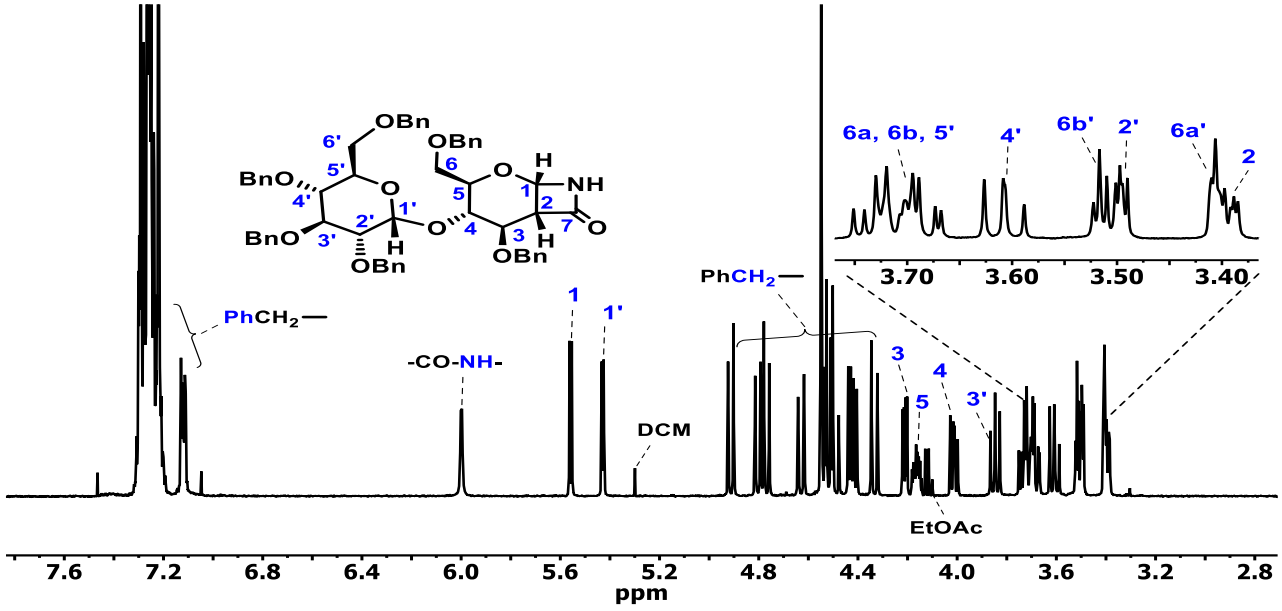
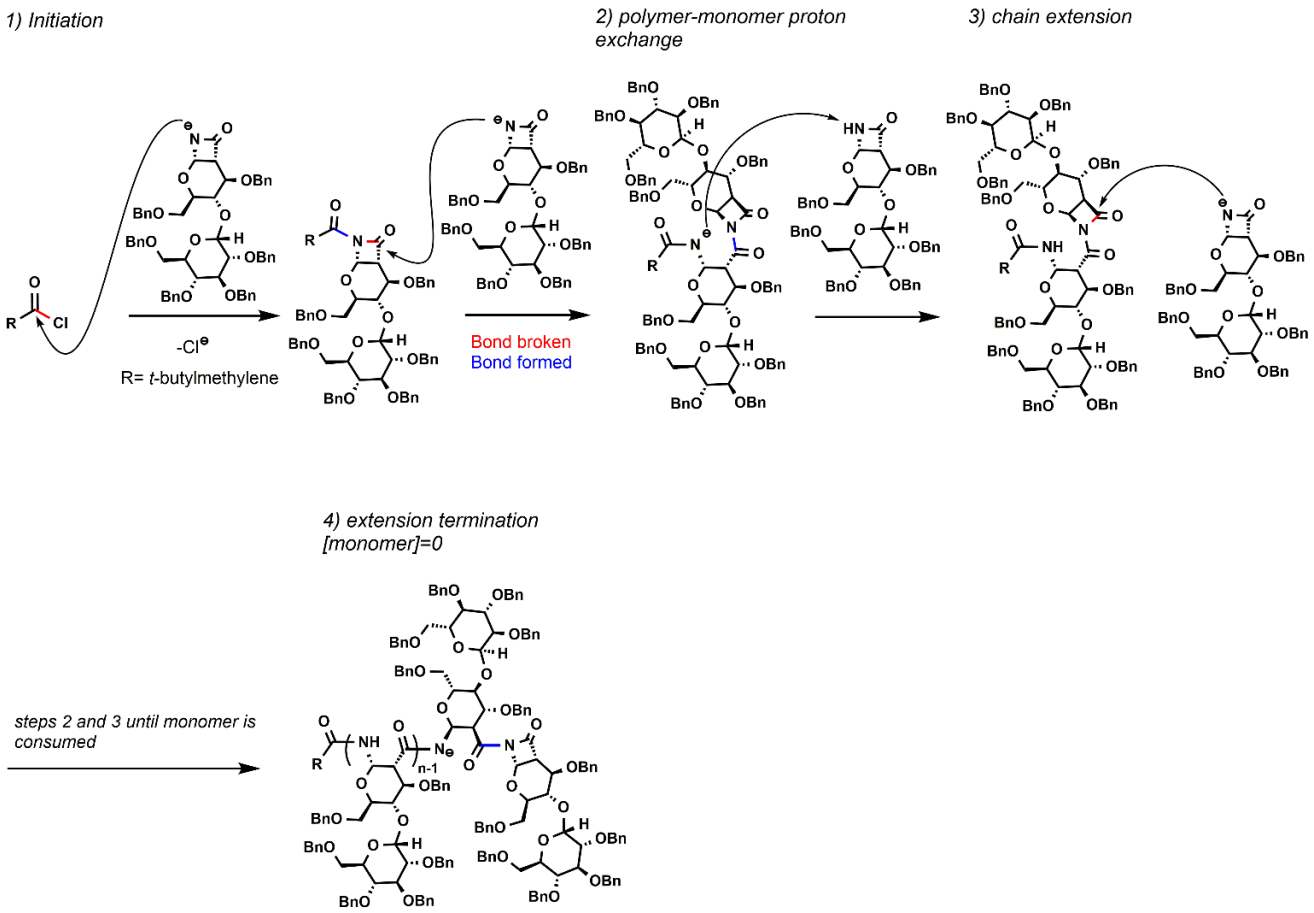


Figure S2. ^{1}H NMR of diastereopure Mal-lactam (**4**)



Scheme S2. Polymerization mechanism of Mal-lactam (monomer is deprotonated by LiHMDS).

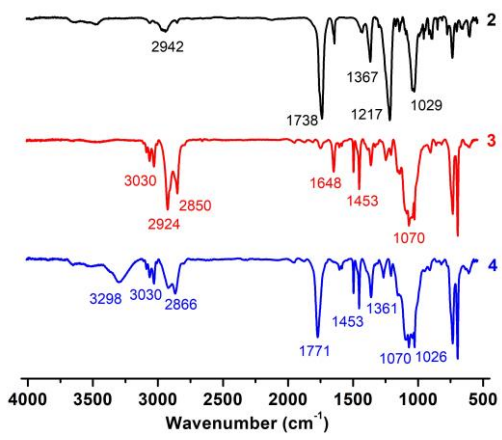


Figure S3. IR of small molecules

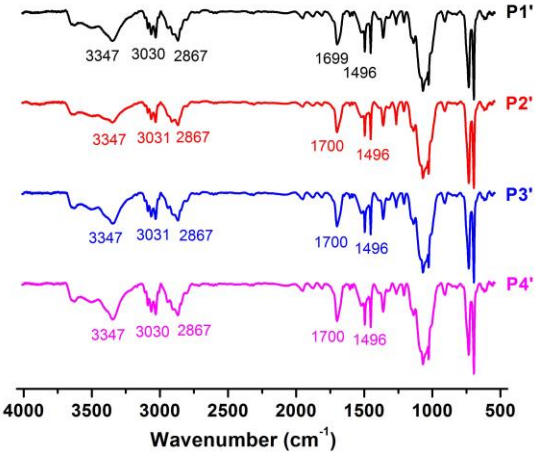


Figure S4. IR of Mal-PASs-Bn (**P1'**-**P4'**)

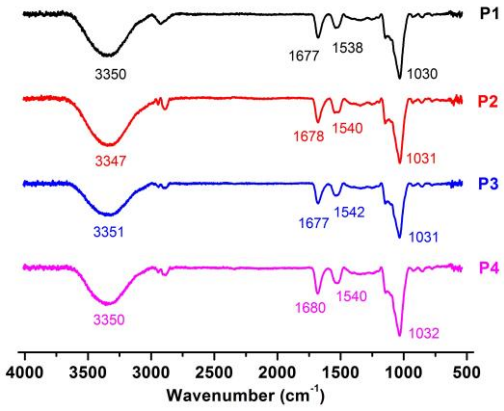


Figure S5. IR of Mal-PASs (**P1**-**P4**).

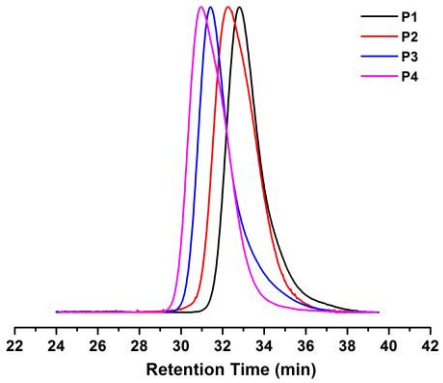


Figure S6. GPC traces of Mal-PASs (**P1**-**P4**).

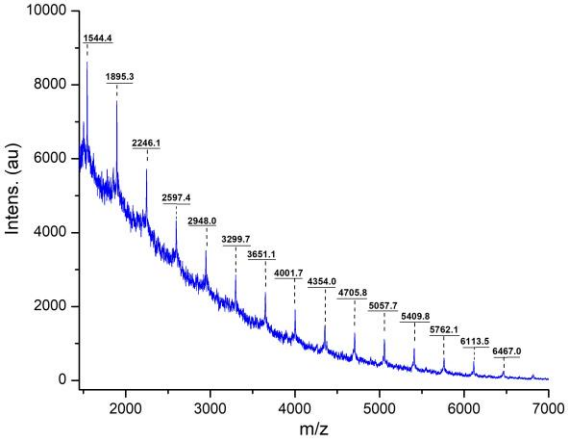


Figure S7. MALDI-TOF spectrum of **P1**.

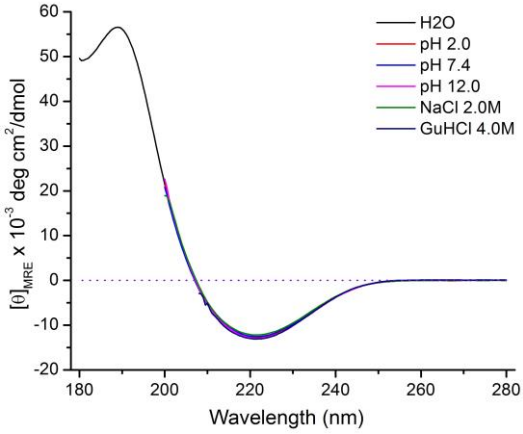


Figure S8. CD of **P4** in various solutions.

Table S1. Average Length of Mal-PASs and Initial Rate of Con A Clustering.

Entry	$DP_{(GPC)}$	Length (nm) according to $DP_{(GPC)}$[a]	$DP_{(NMR)}$	Length (nm) according to $DP_{(NMR)}$[a]	k_i (10^{-3} au/min)[b]
P1	12.4	3.8	12.3	3.7	0.803
P2	17.3	5.1	19.6	5.8	4.35
P3	23.4	6.8	26.4	7.7	34.7
P4	32.3	9.3	37.5	10.8	84.7

[a] Estimated based on the length of 10 mer of Glc-PAS (2.8 nm), which was calculated based on molecular dynamics (MD) simulation of an all-atom (AA) model produced using a modified CHARMM force field. [b] Determined by a linear fit to the steepest part of the binding curve.

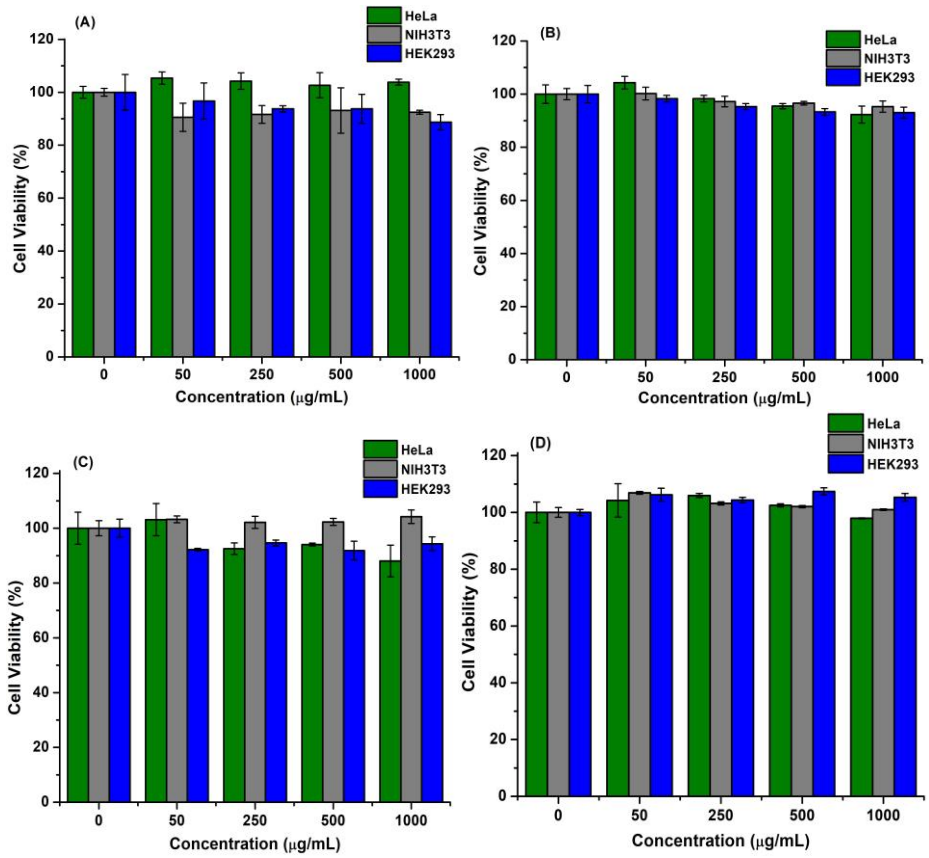
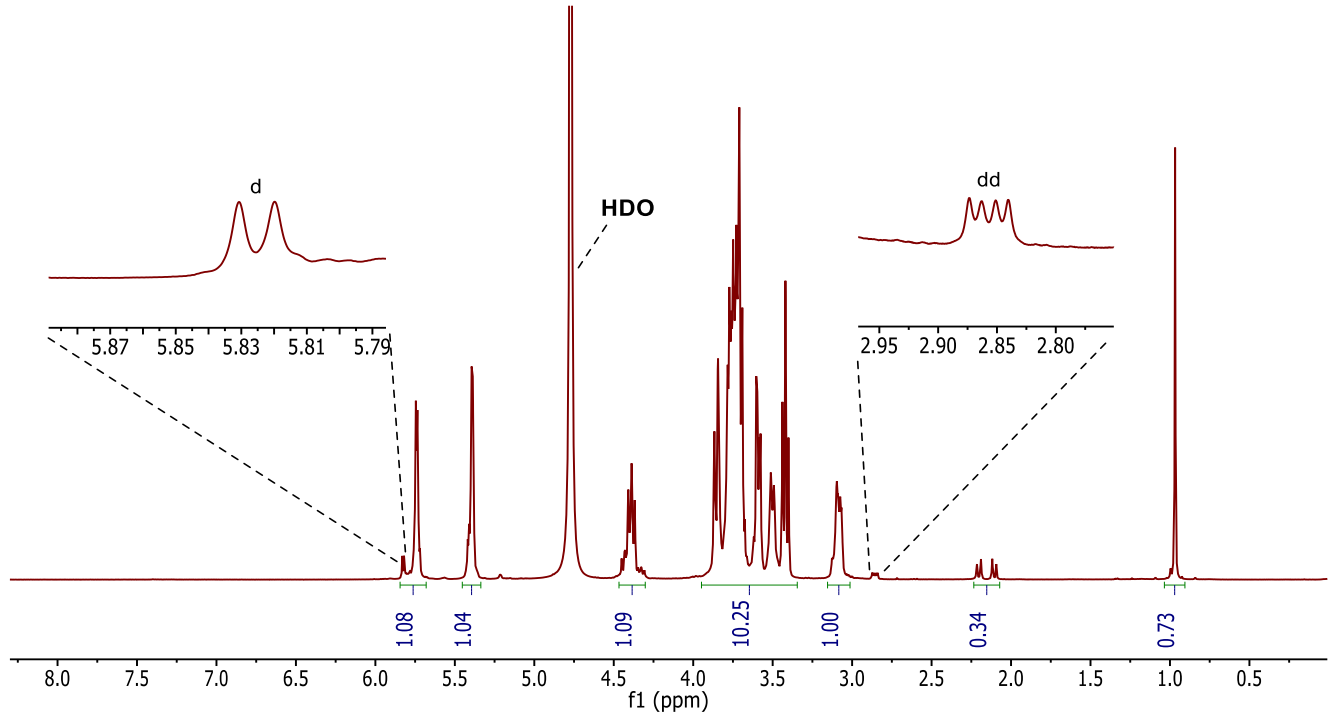


Figure S9. Cytotoxicity of **P1** (A), **P2** (B), **P3** (C), and **P4** (D).

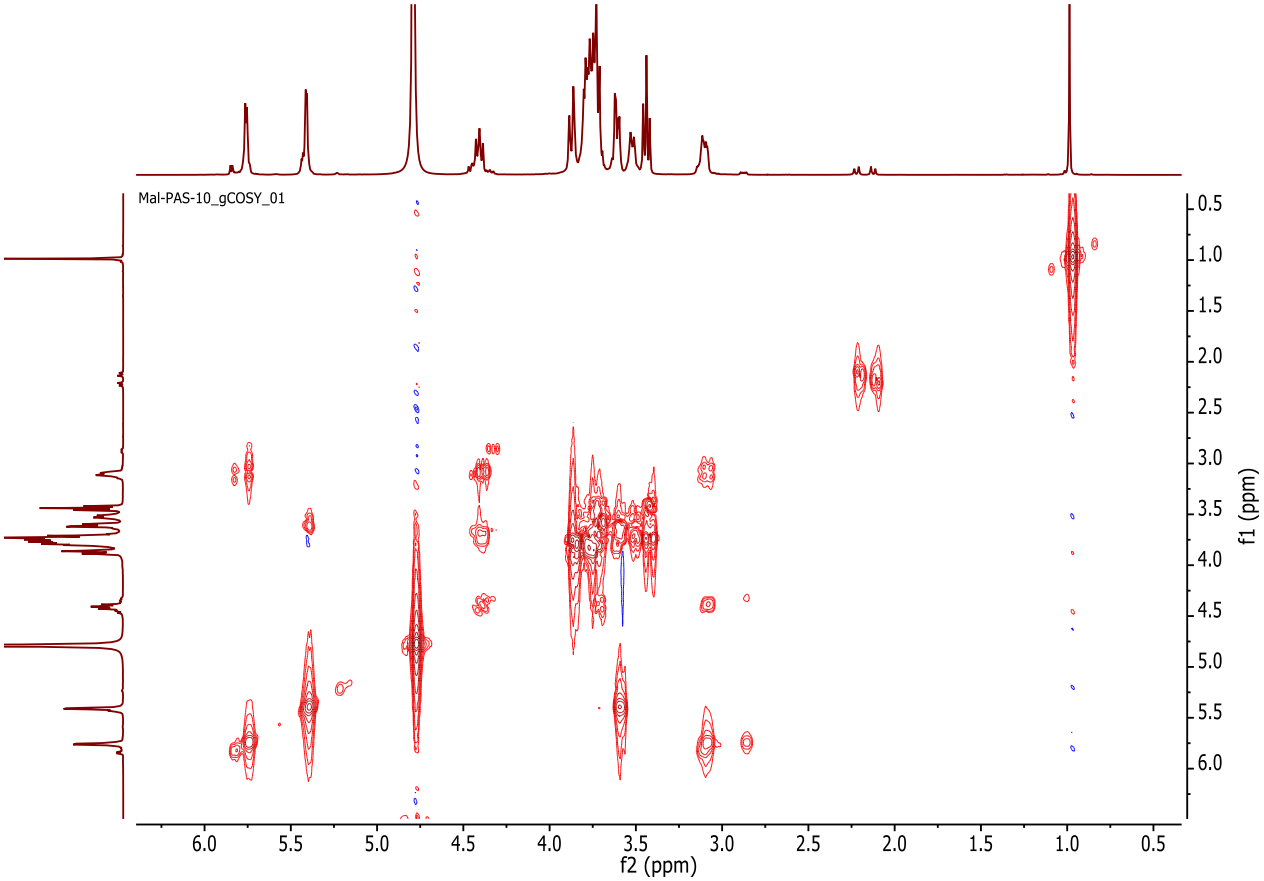
Table S2. Polymer Characterization using DLS.

Entry	Concentration (mg/mL)	Eff. Diam. (nm)	Polydispersity
P1	0.50	0.0	0.000
P2	0.50	0.0	0.000
P3	0.50	0.0	0.000
P4	0.50	0.0	0.000
P5	0.50	101.7	0.192
P6	0.50	0.2	0.044
P1	0.05	0.0	0.000
P2	0.05	0.0	0.000
P3	0.05	0.0	0.000
P4	0.05	0.0	0.000
P5	0.05	114.8	1.026
P6	0.05	0.0	0.000

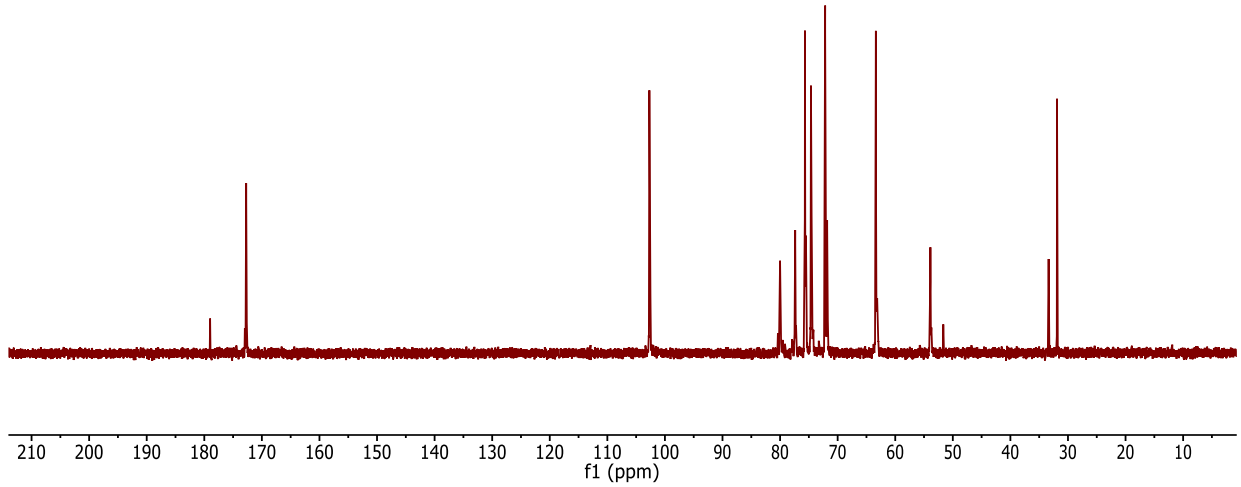
^{1}H NMR of **P1**



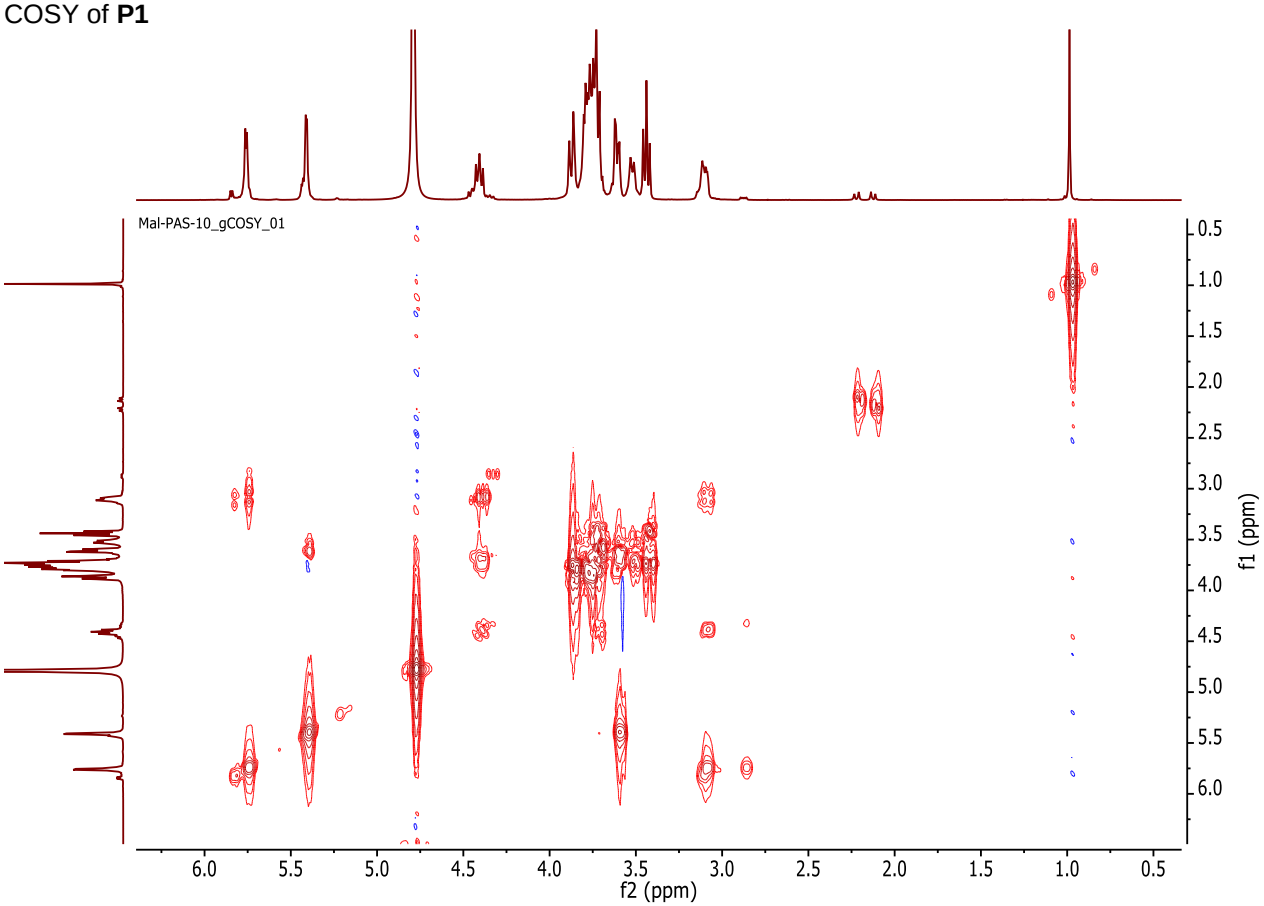
COSY of **P1**



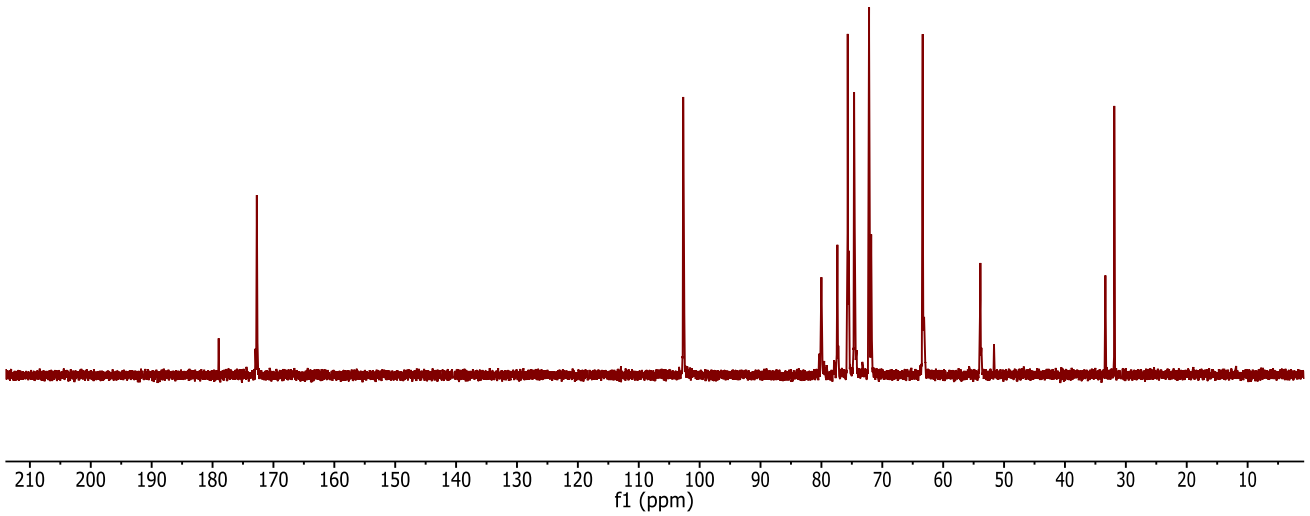
^{13}C NMR of **P1**



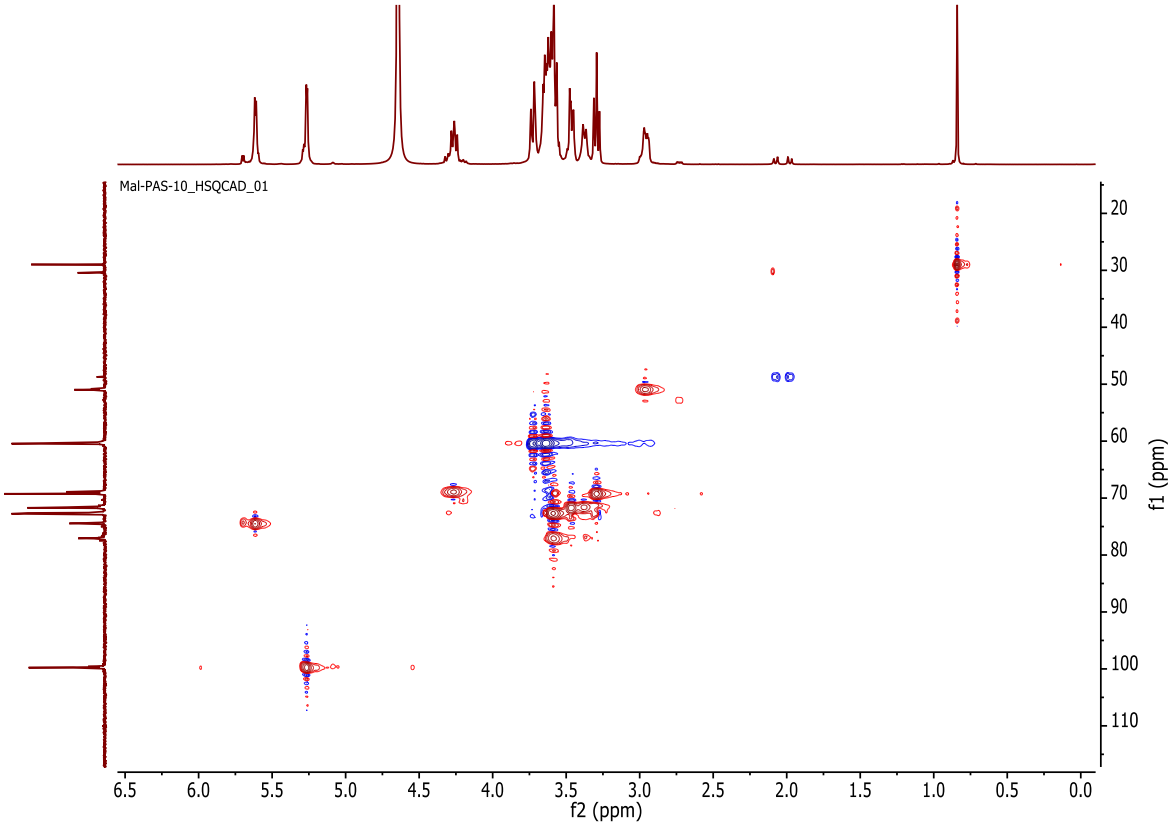
COSY of **P1**



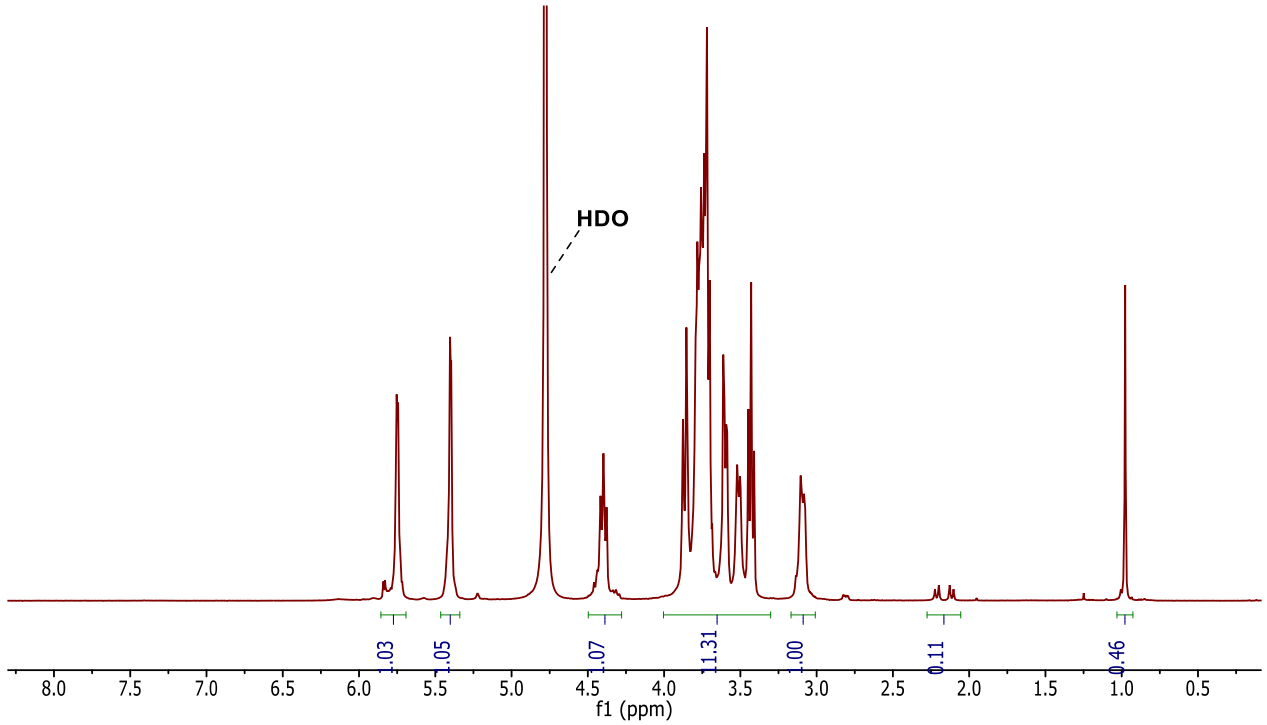
^{13}C NMR of **P1**



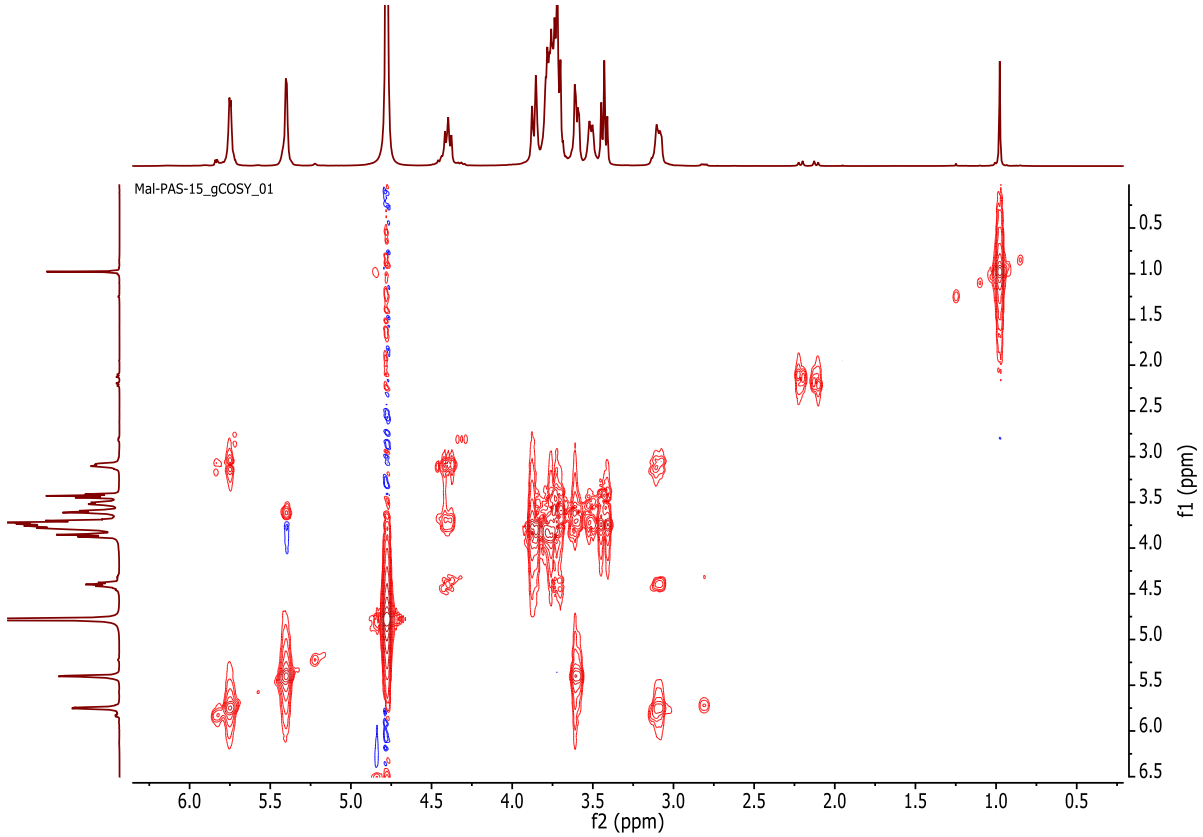
HSQC of **P1**



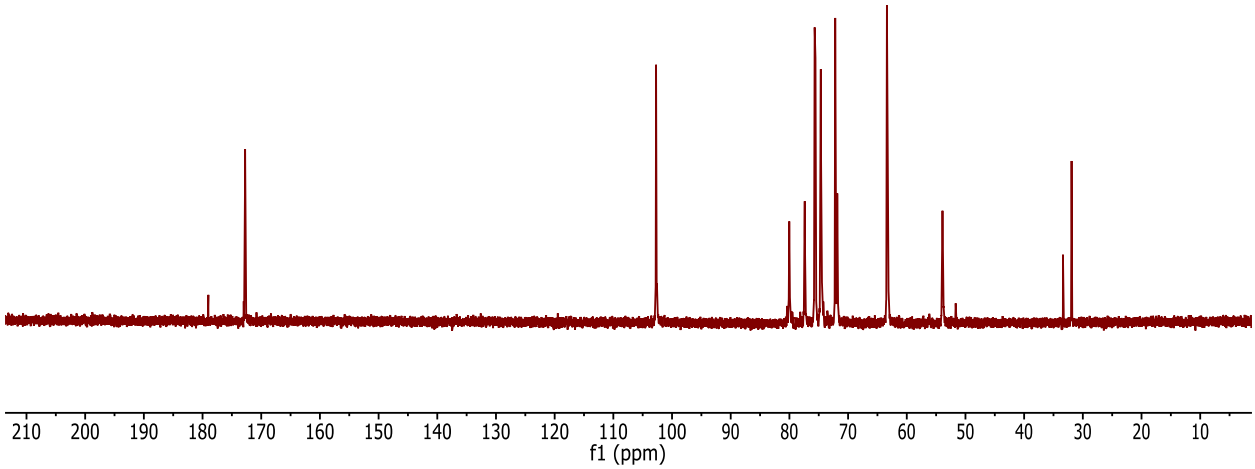
^{1}H NMR of **P2**



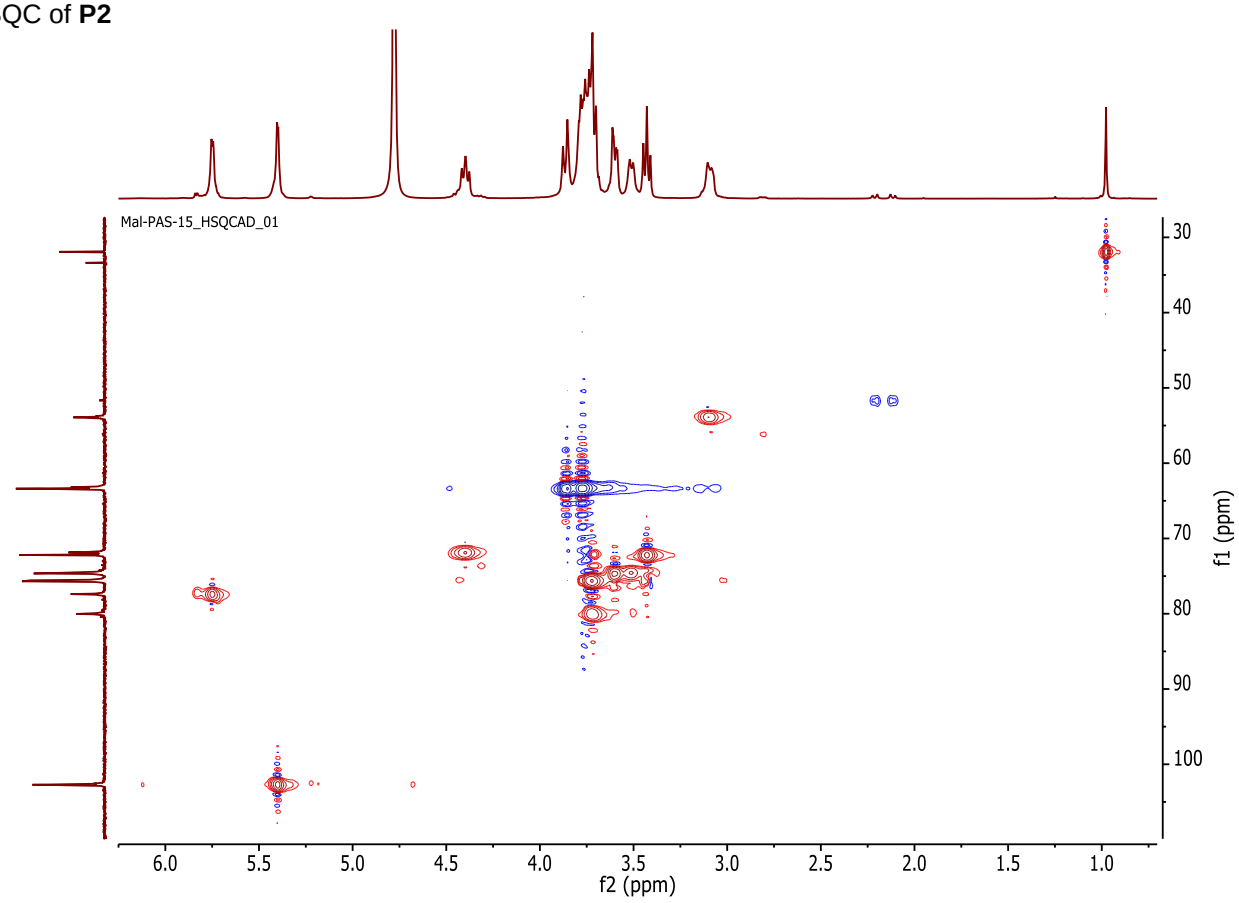
COSY of **P2**



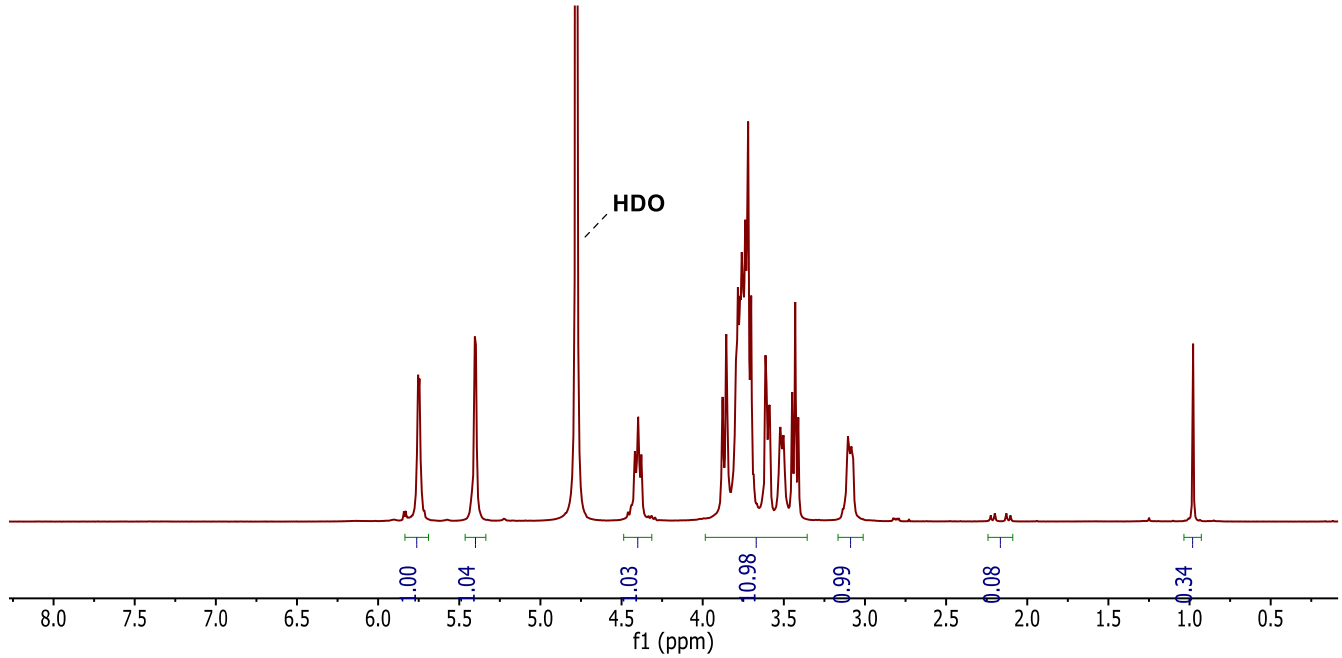
^{13}C NMR of **P2**



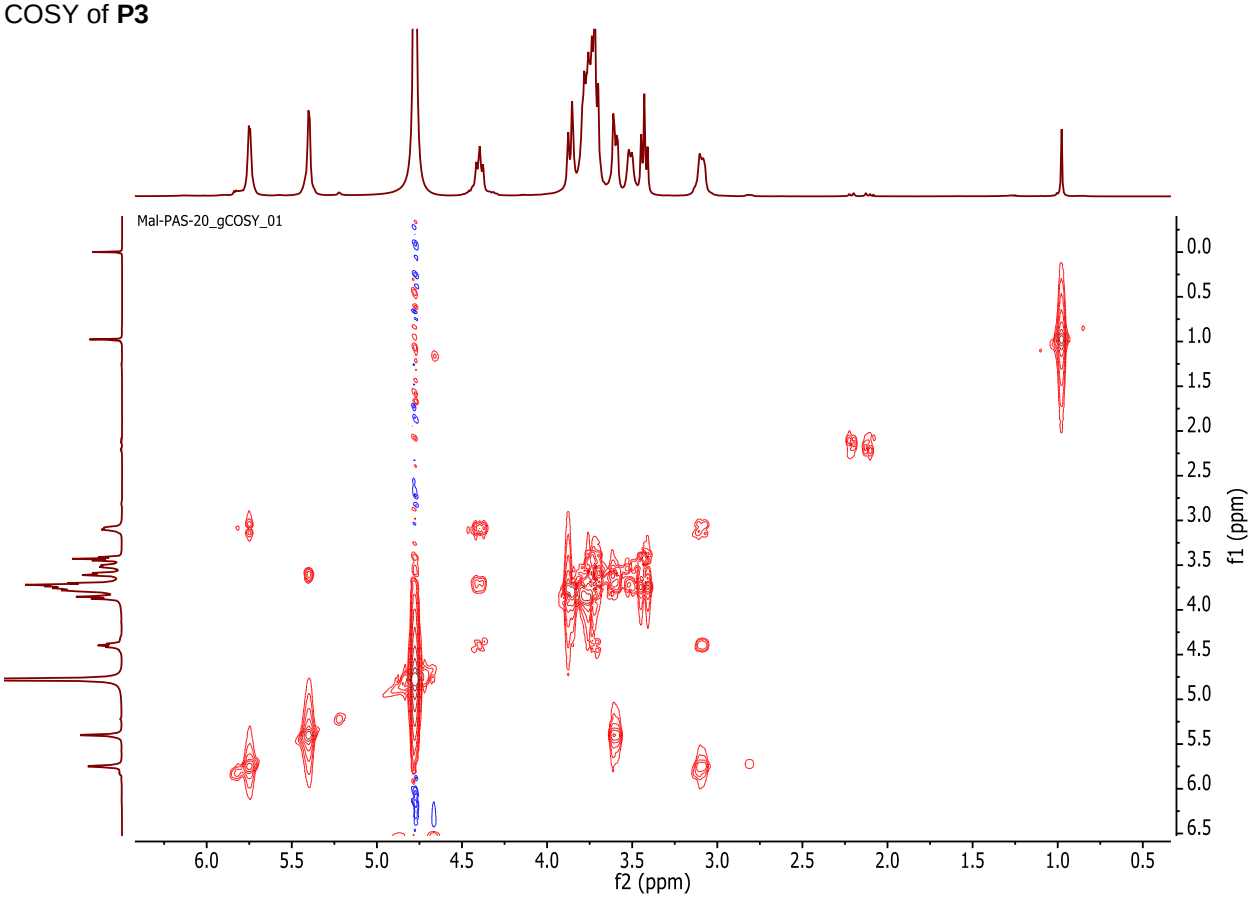
HSQC of **P2**



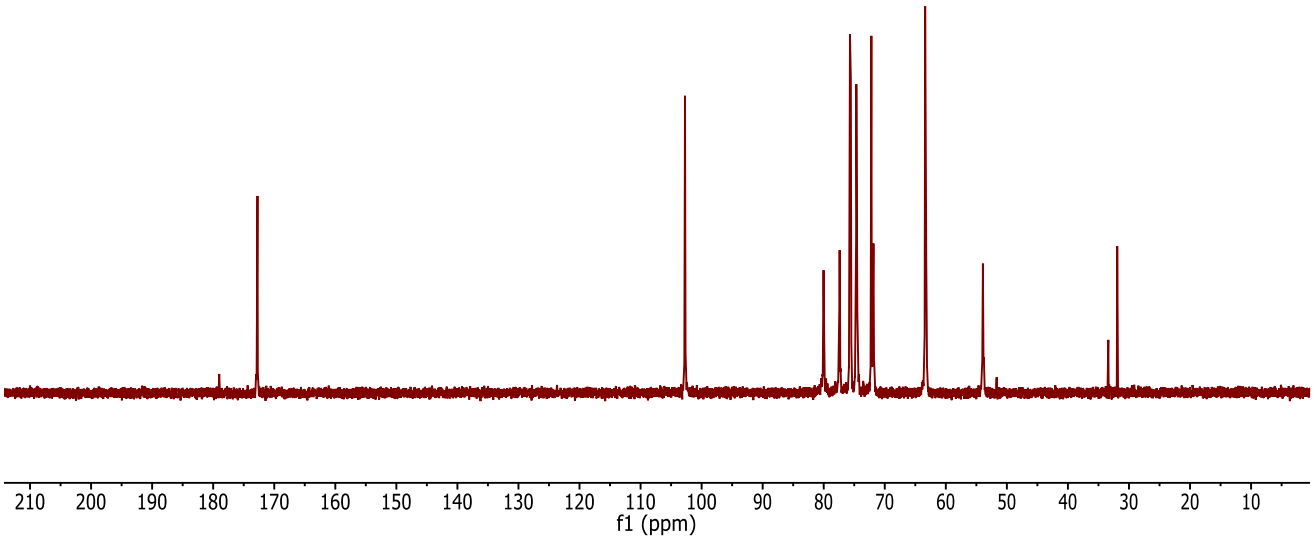
^{1}H NMR of **P3**



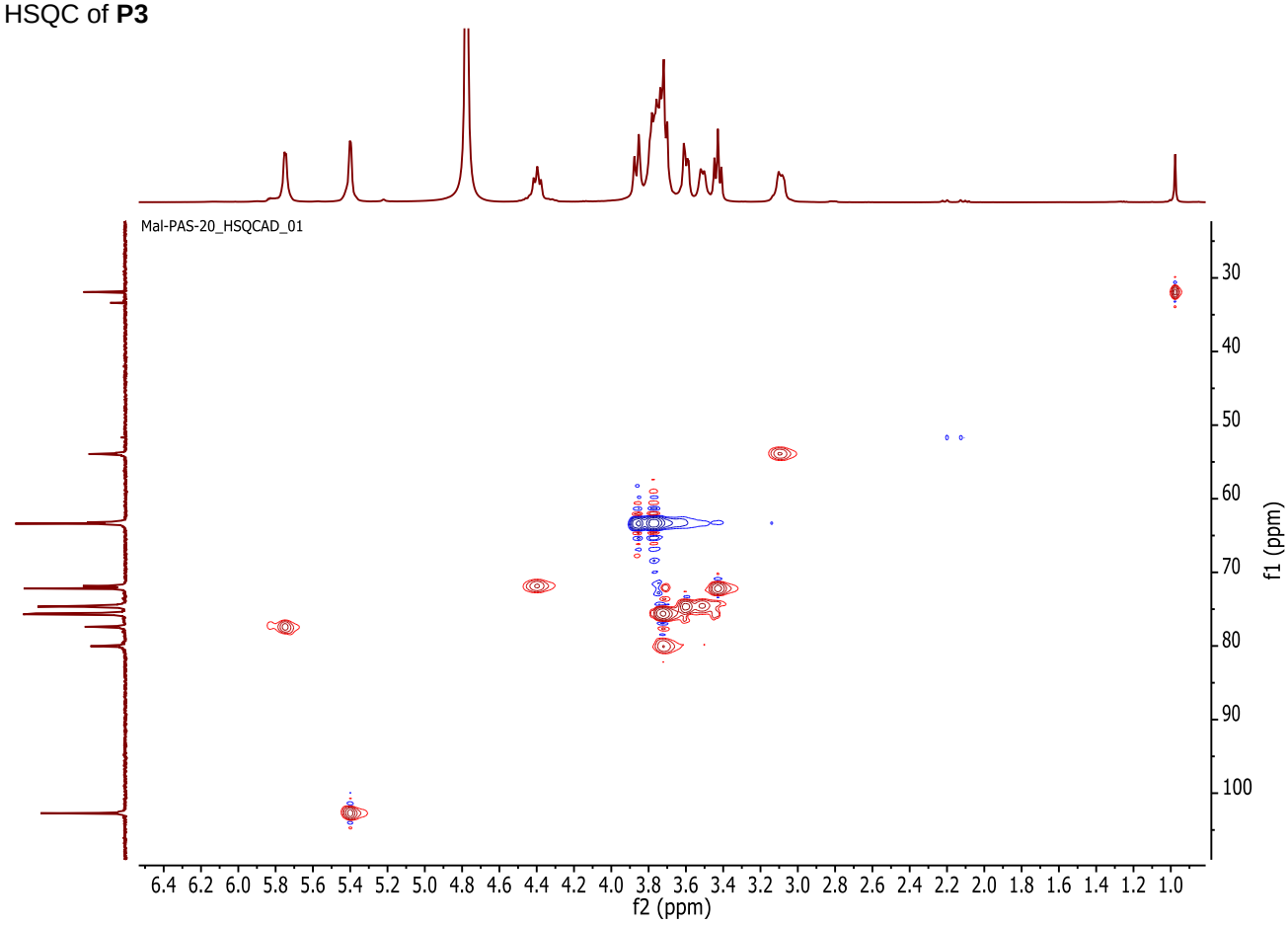
COSY of **P3**



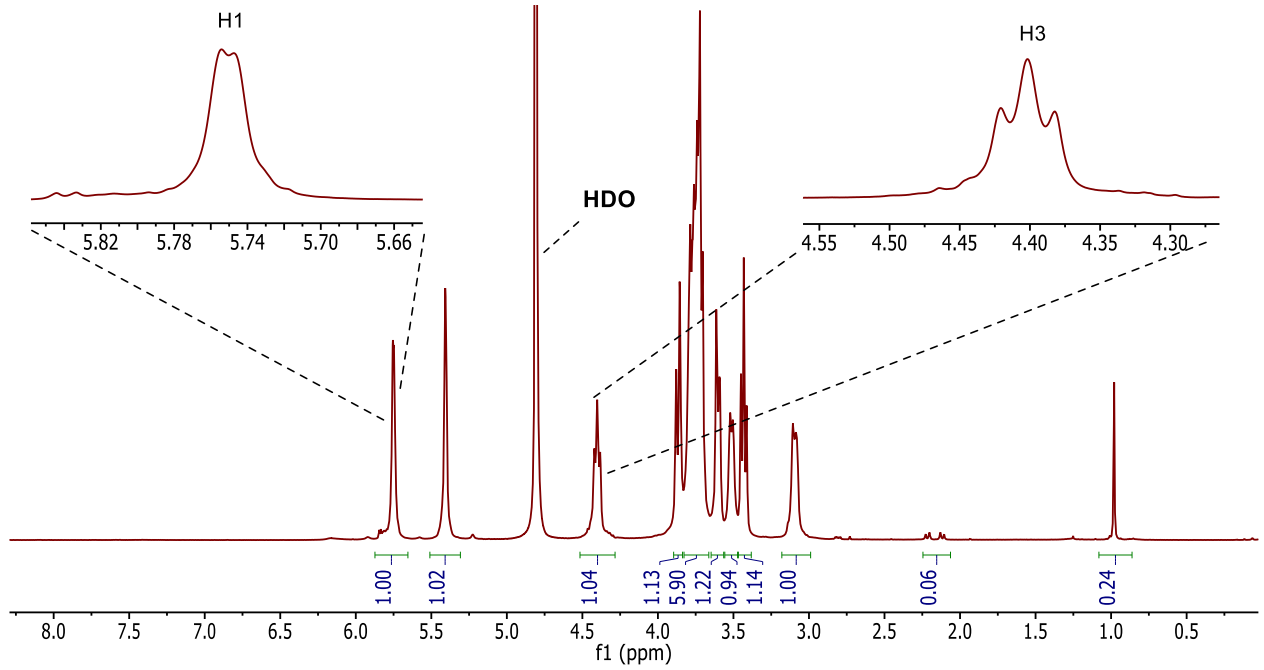
^{13}C NMR of **P3**



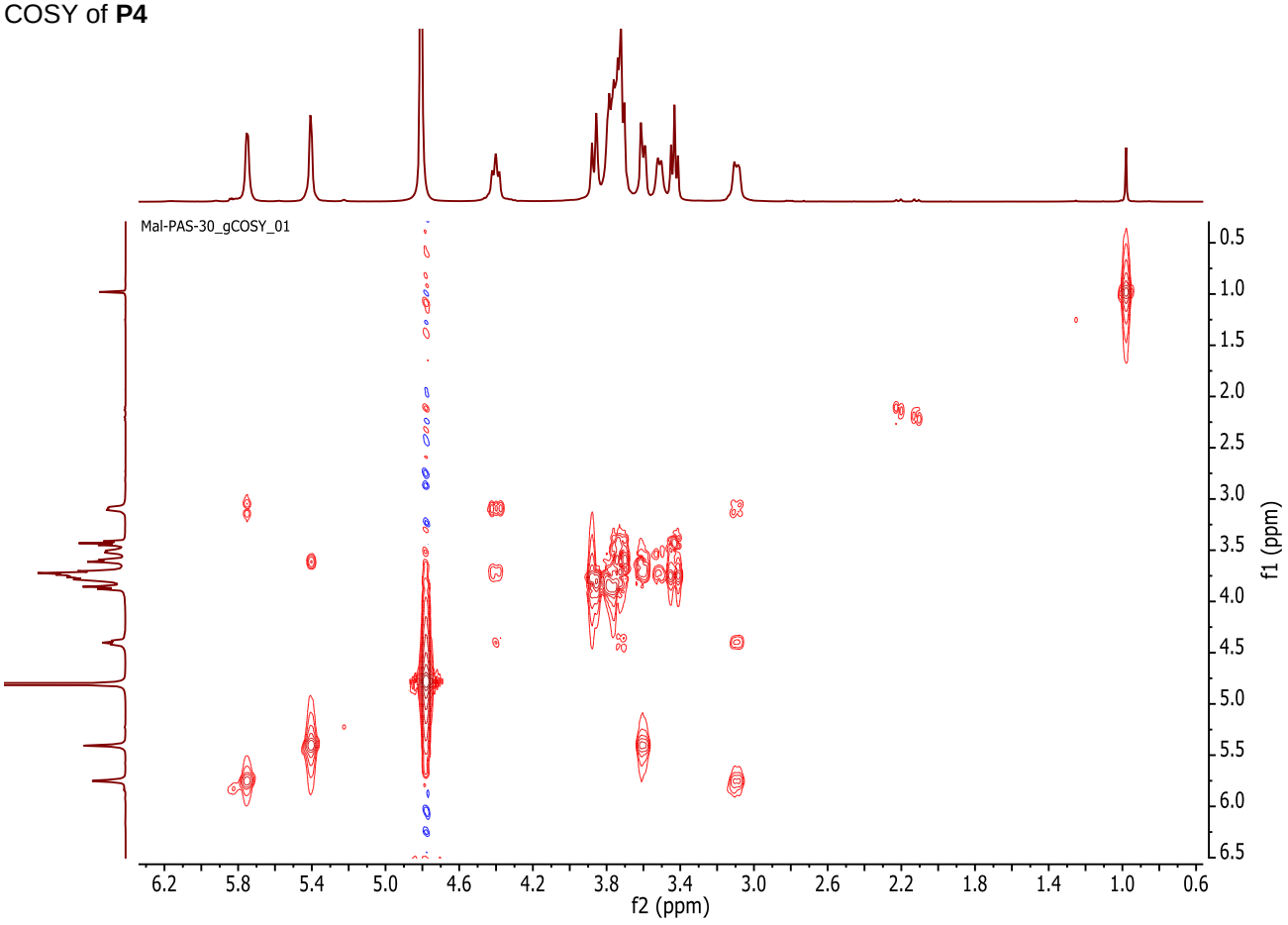
HSQC of **P3**



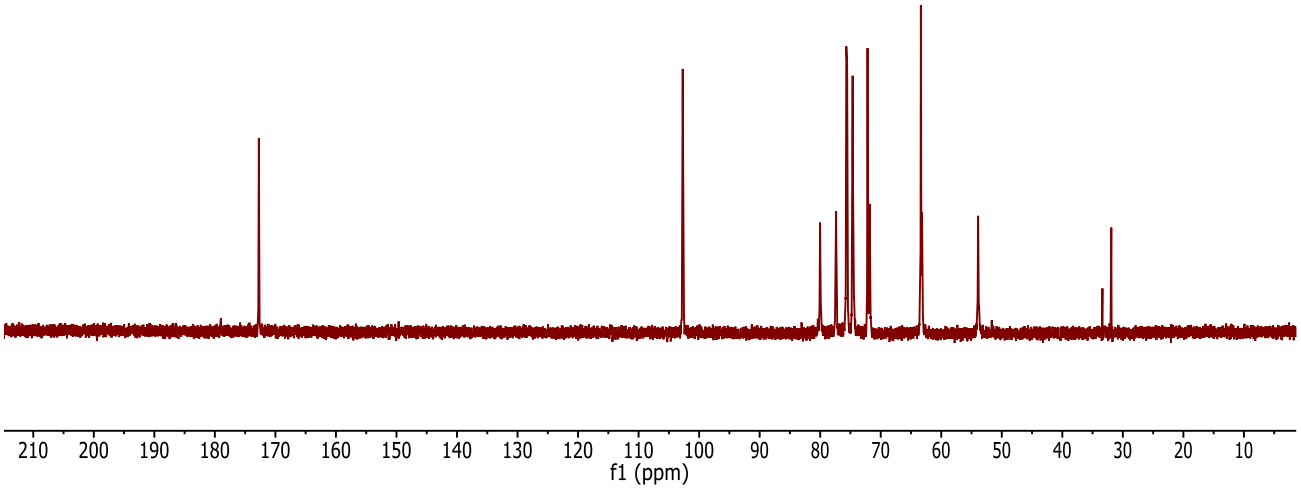
^{1}H NMR of **P4**



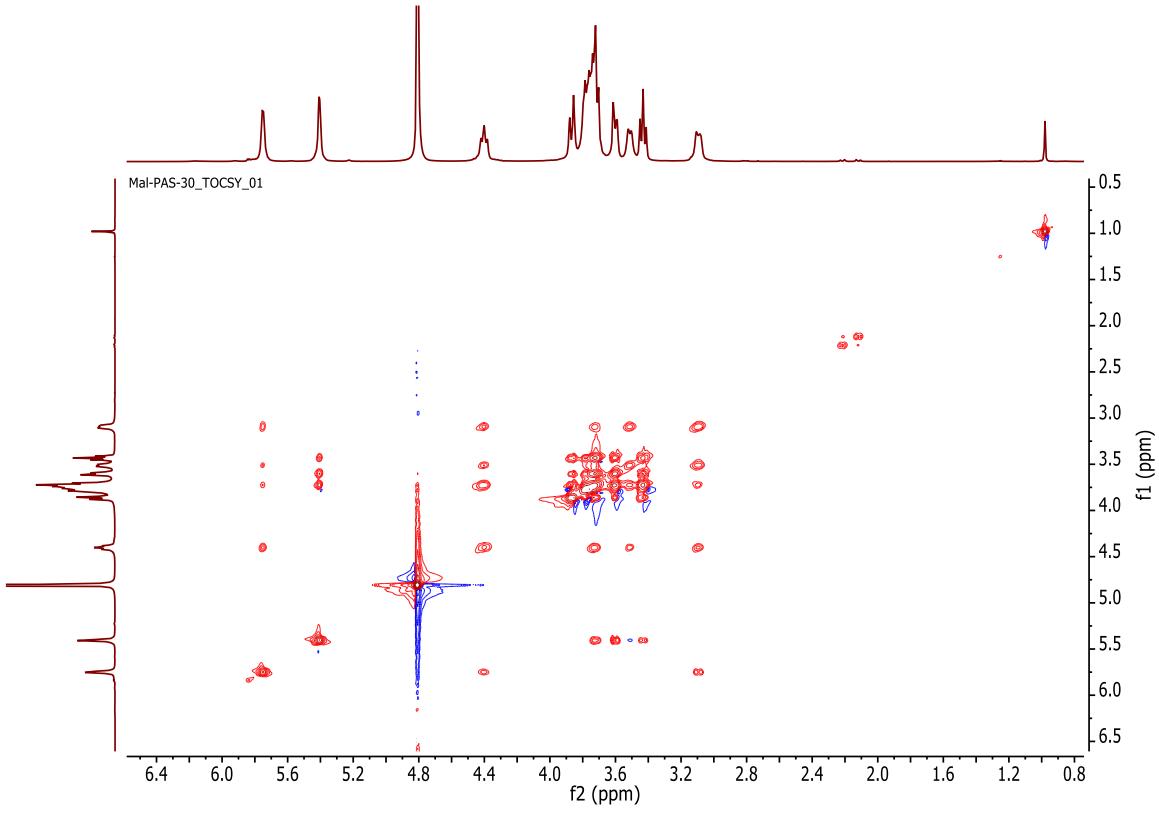
COSY of **P4**



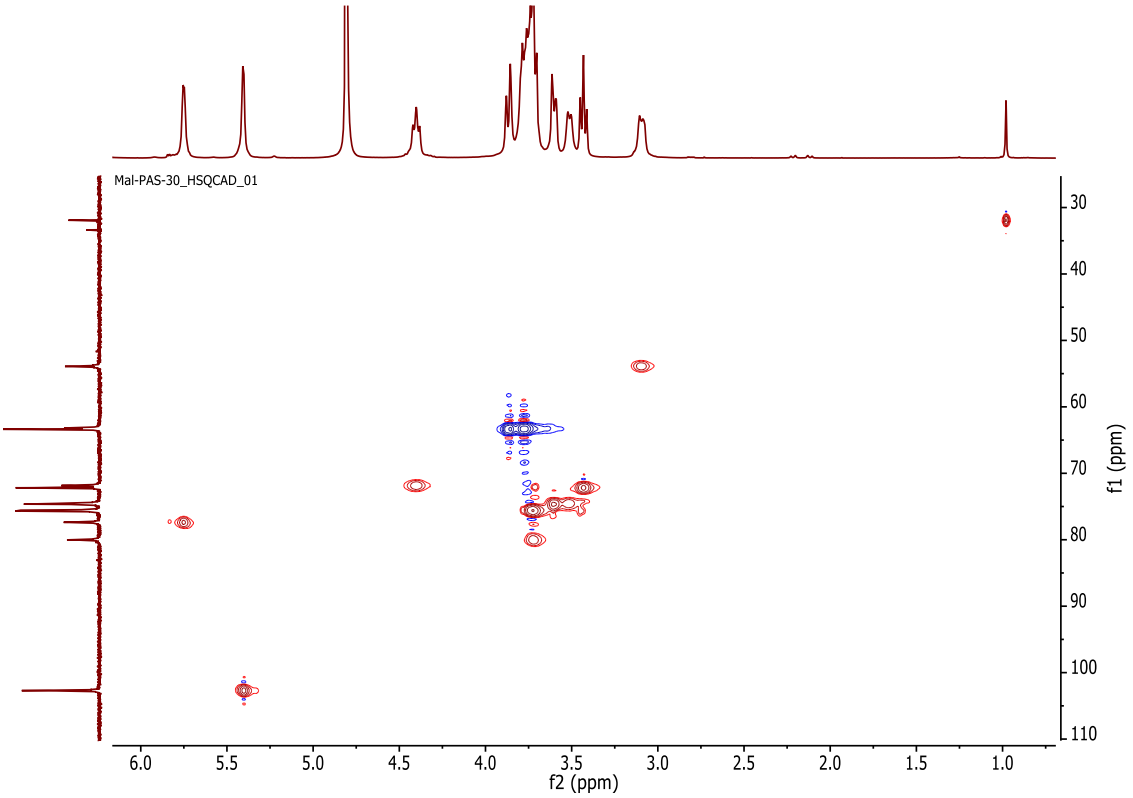
^{13}C NMR of **P4**



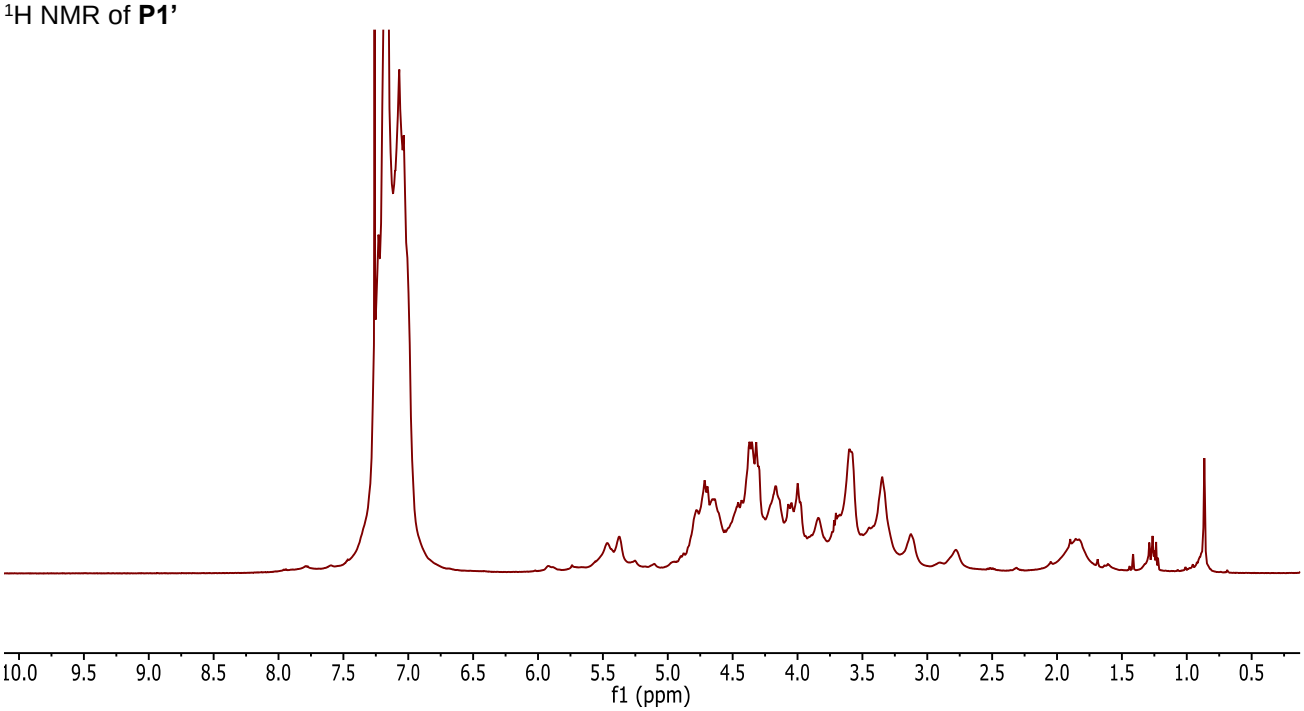
TOCSY of **P4**



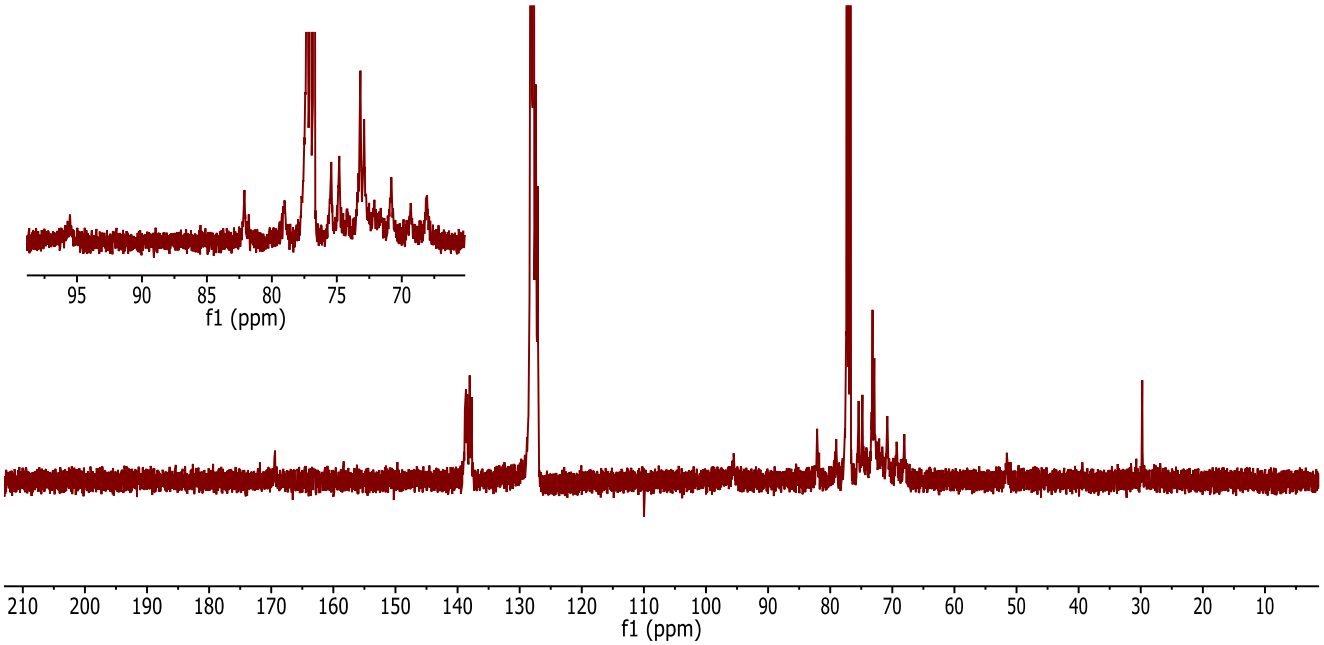
HSQC of **P4**



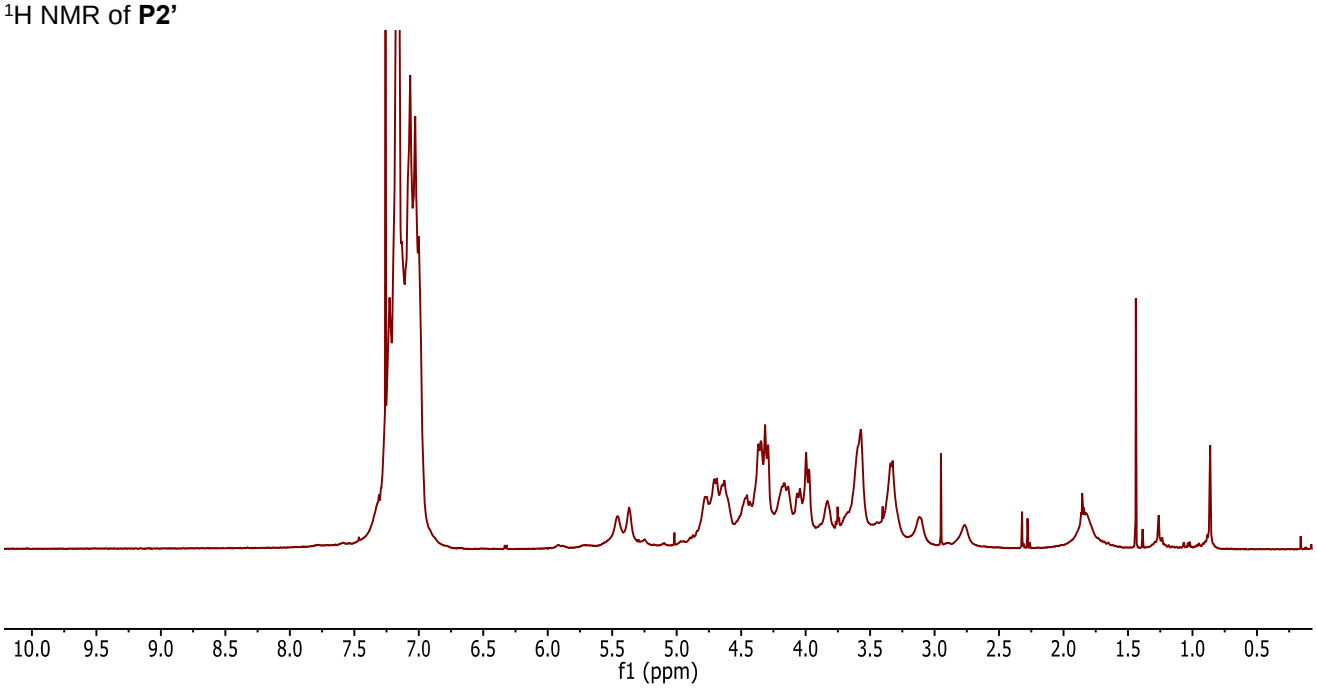
^{1}H NMR of **P1'**



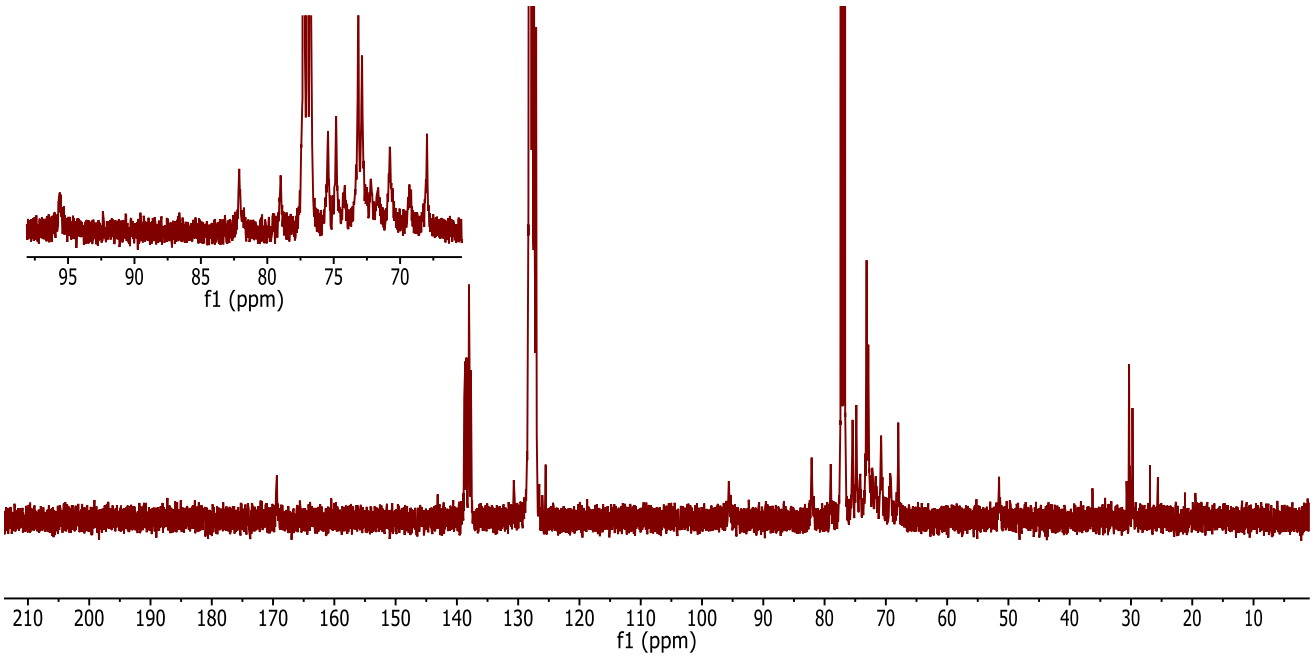
^{13}C NMR of **P1'**



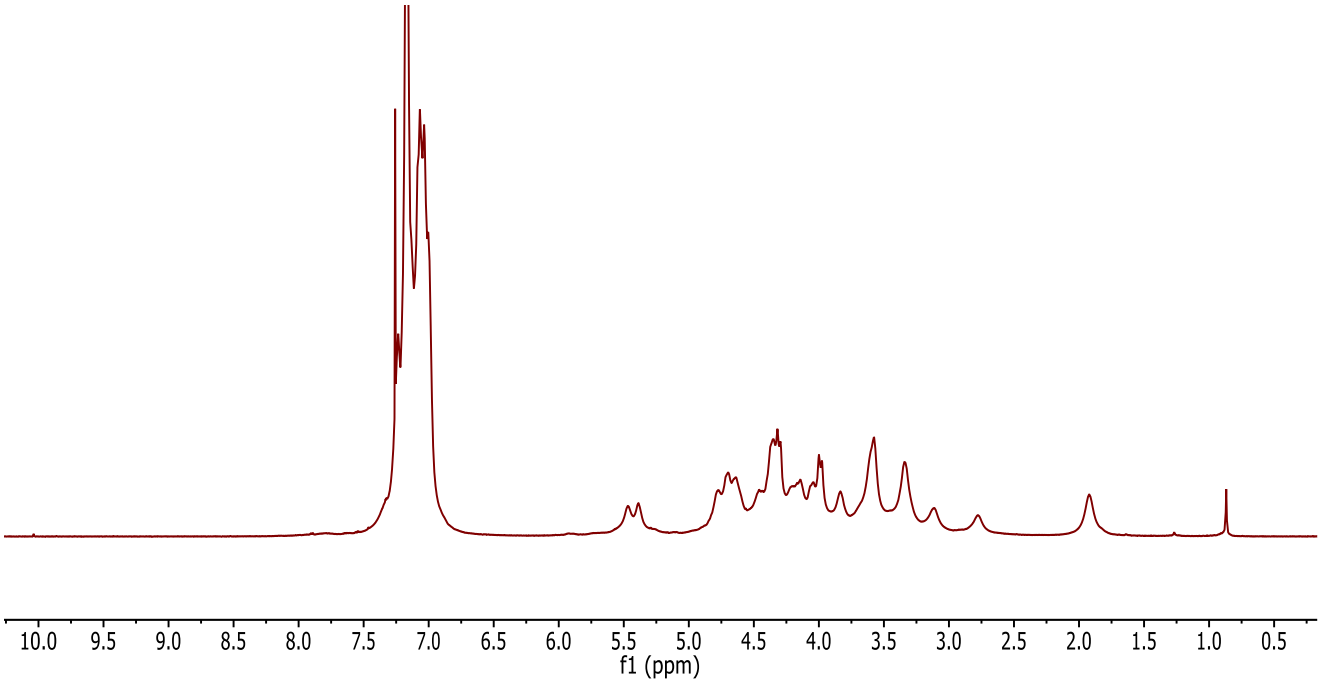
^{1}H NMR of **P2'**



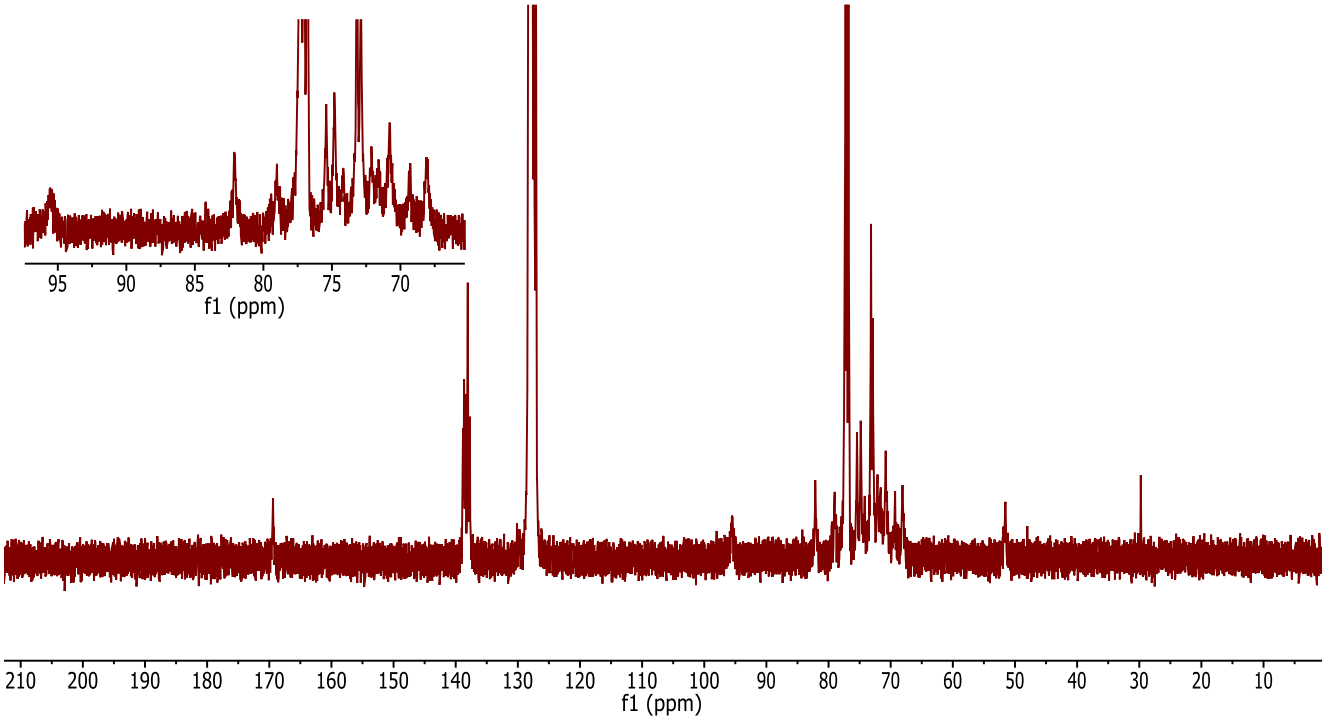
^{13}C NMR of **P2'**



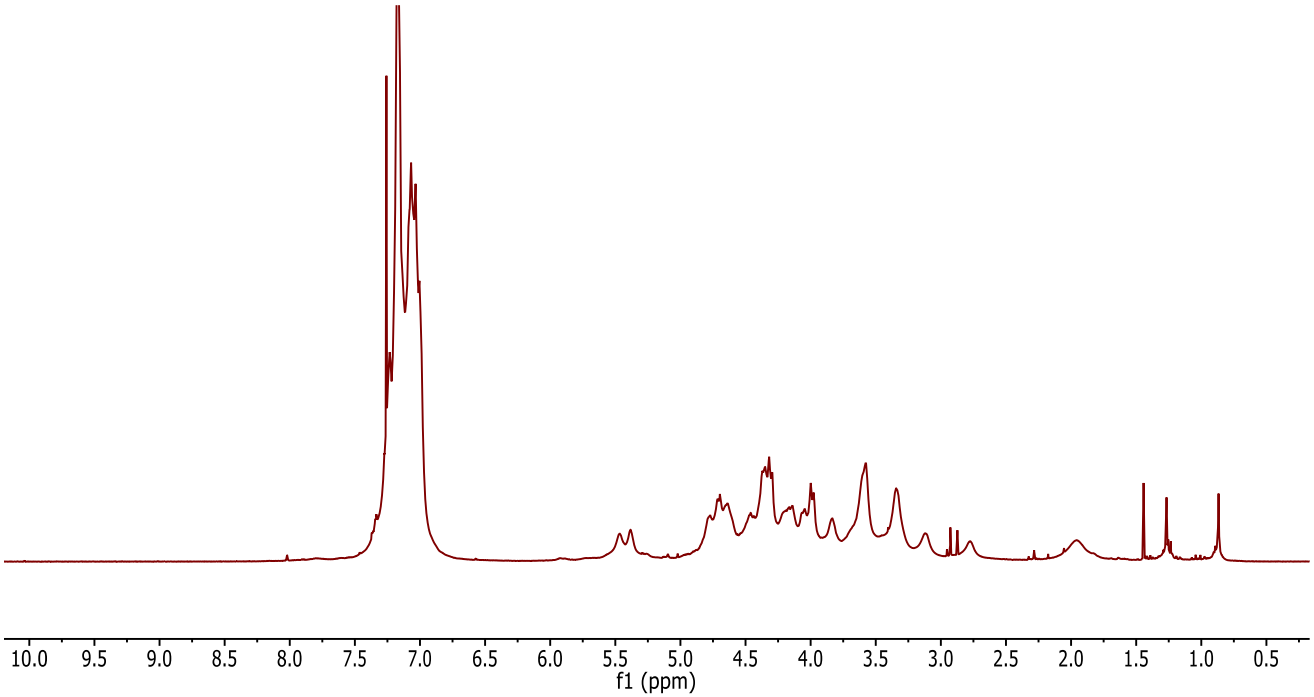
^{1}H NMR of **P3'**



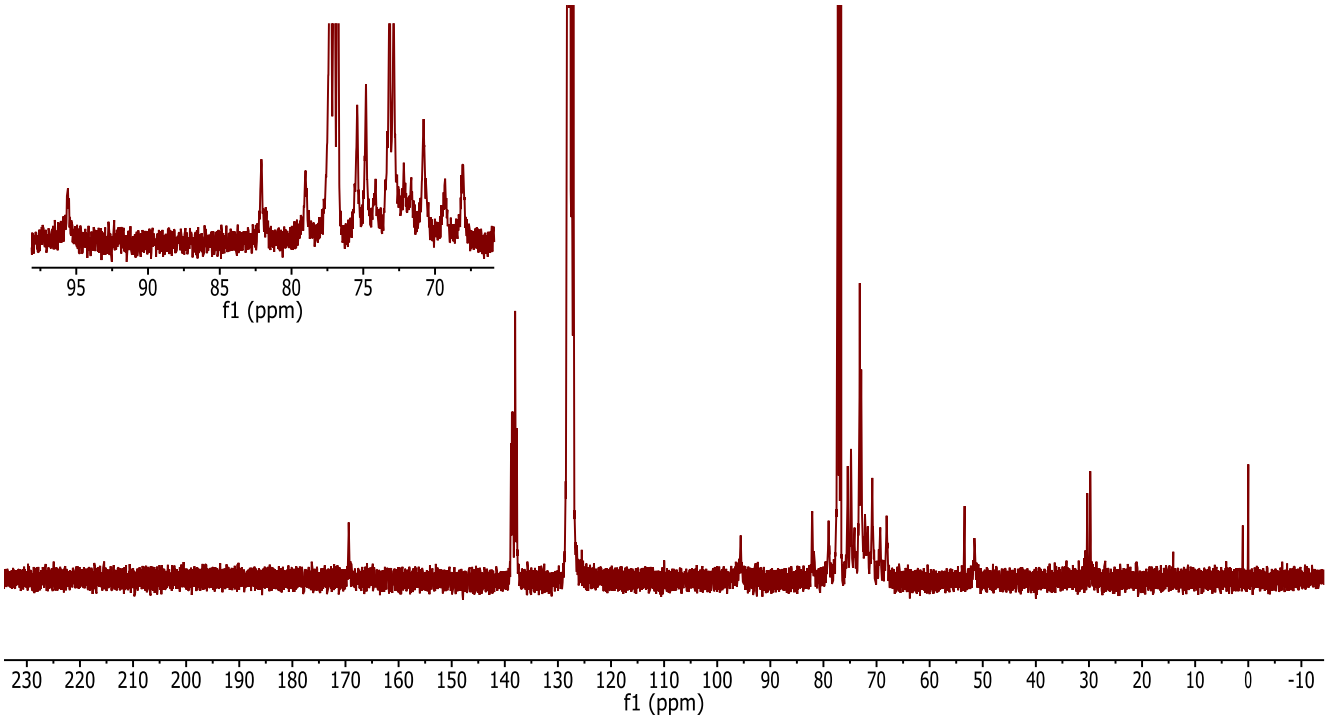
^{13}C NMR of **P3'**



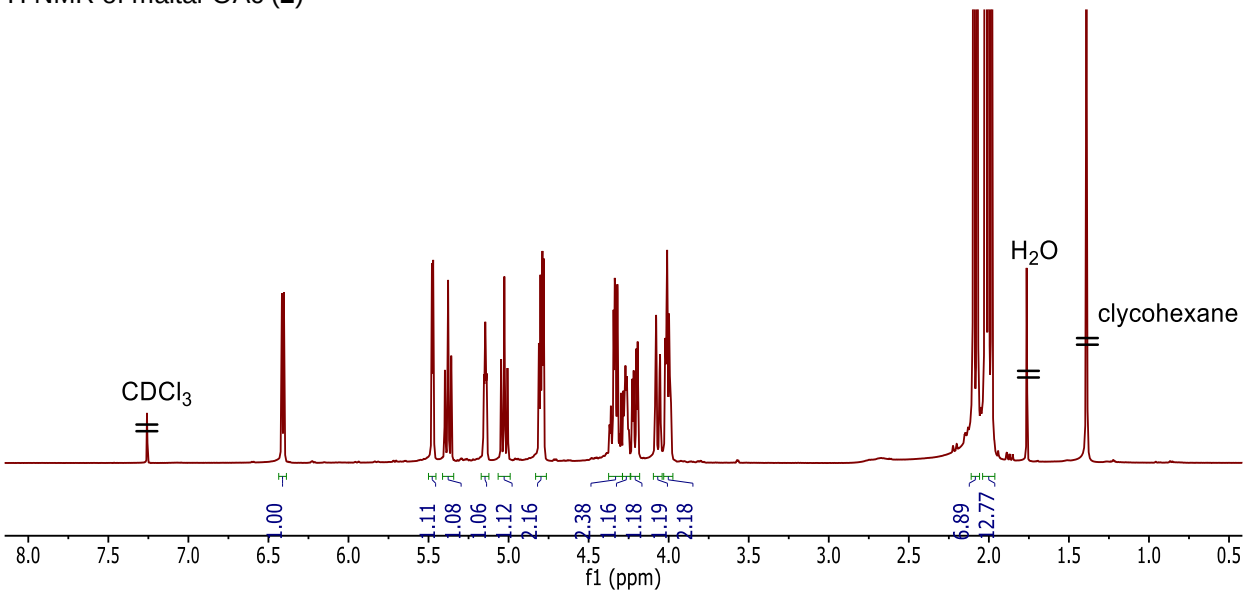
^{1}H NMR of **P4'**



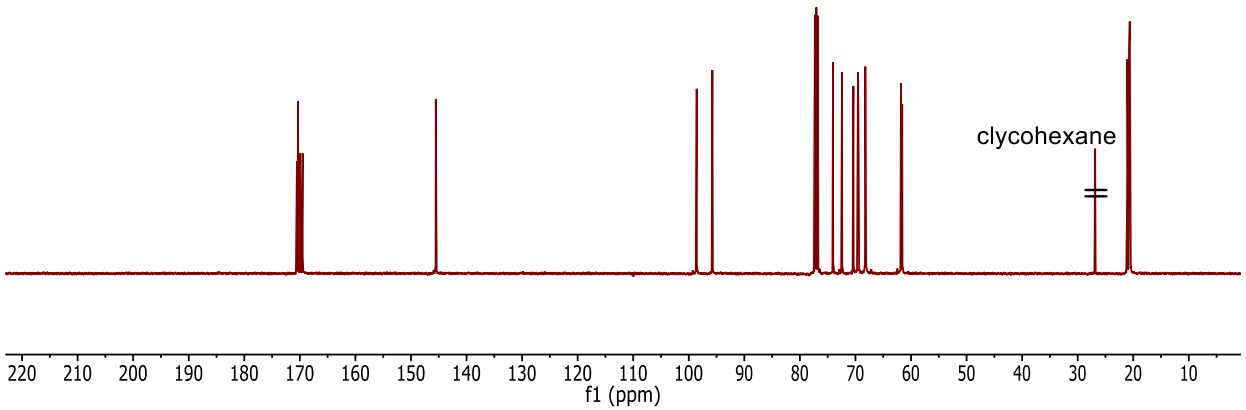
^{13}C NMR of **P4'**



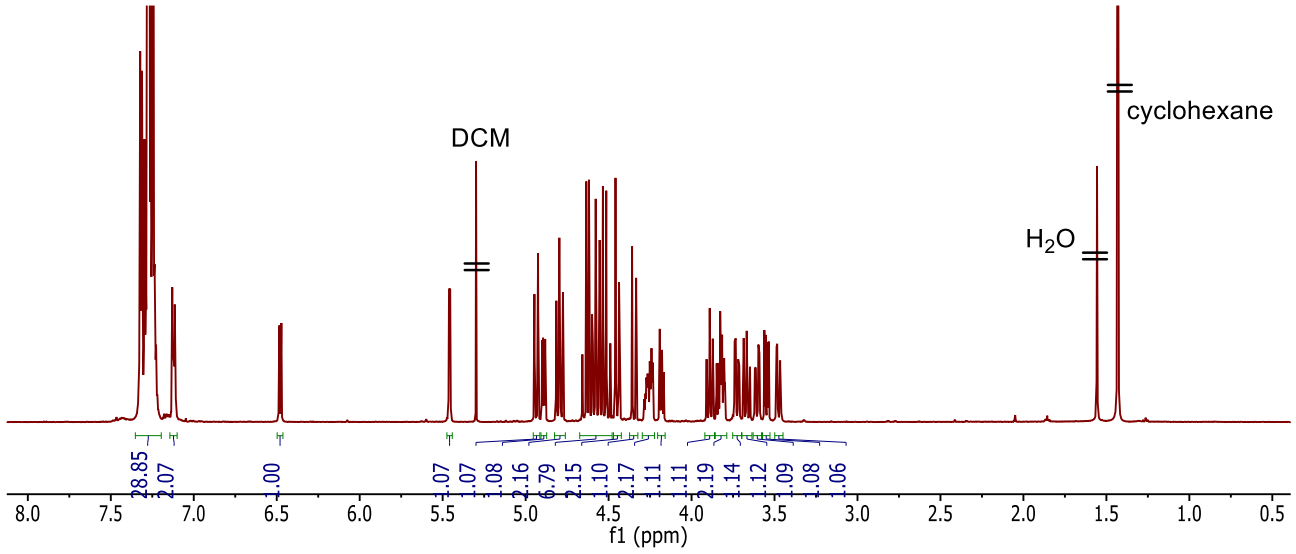
^{1}H NMR of maltal-OAc (**2**)



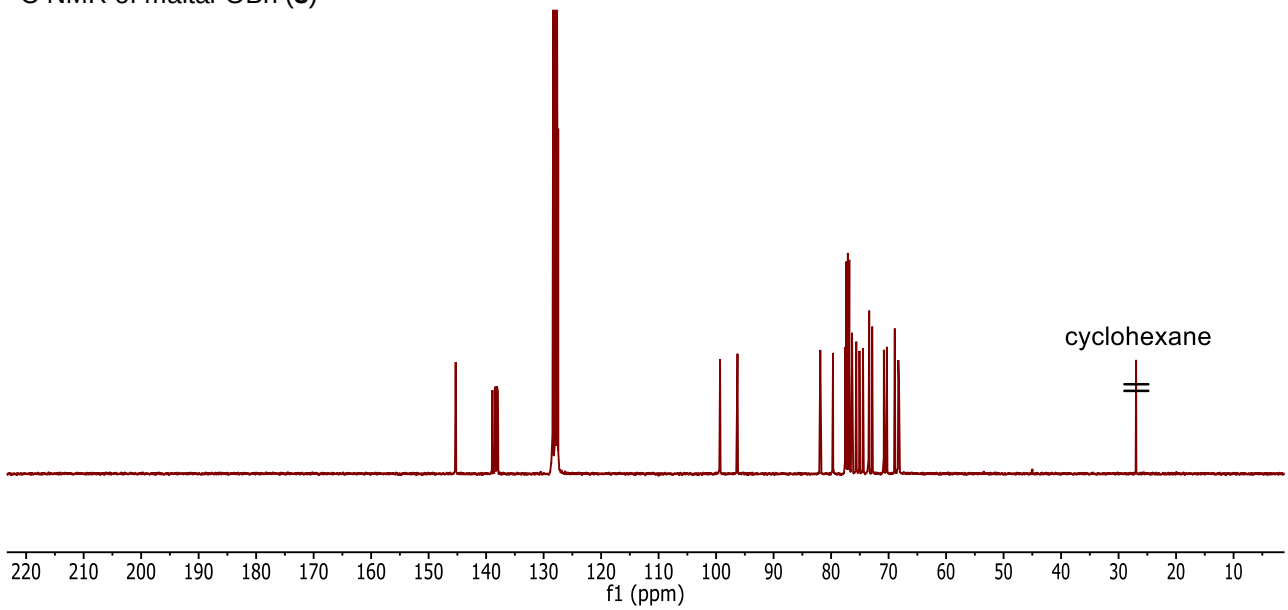
^{13}C NMR of maltal-OAc (**2**)



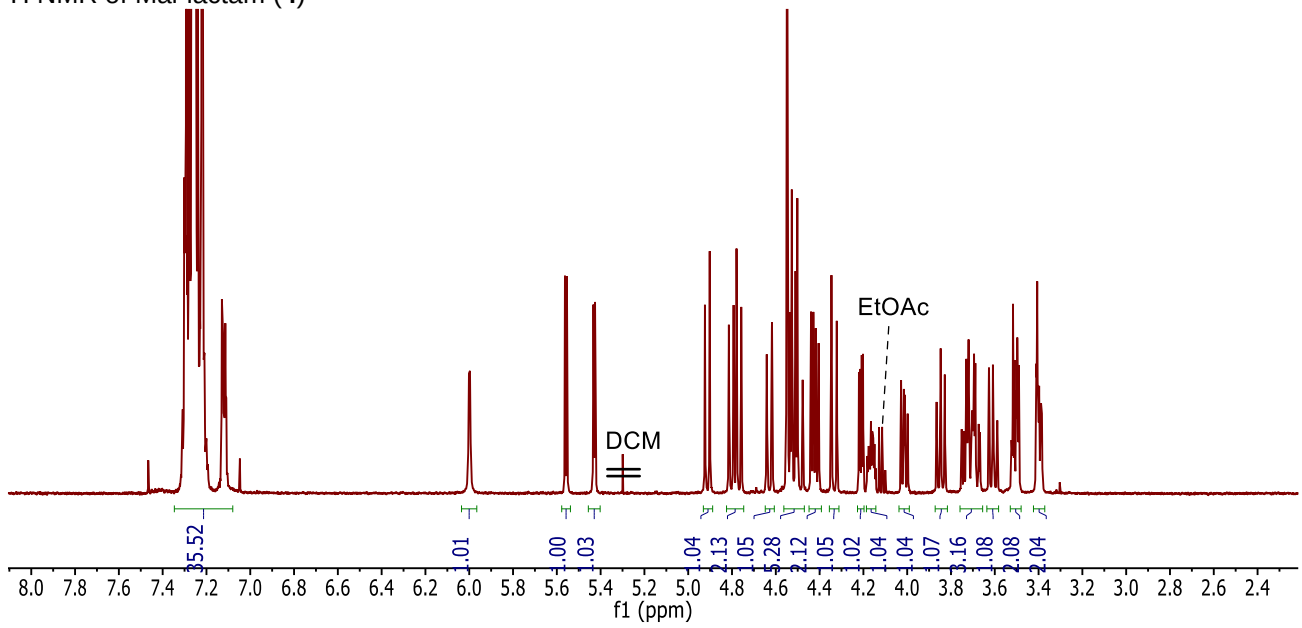
^{1}H NMR of maltal-OBn (**3**)



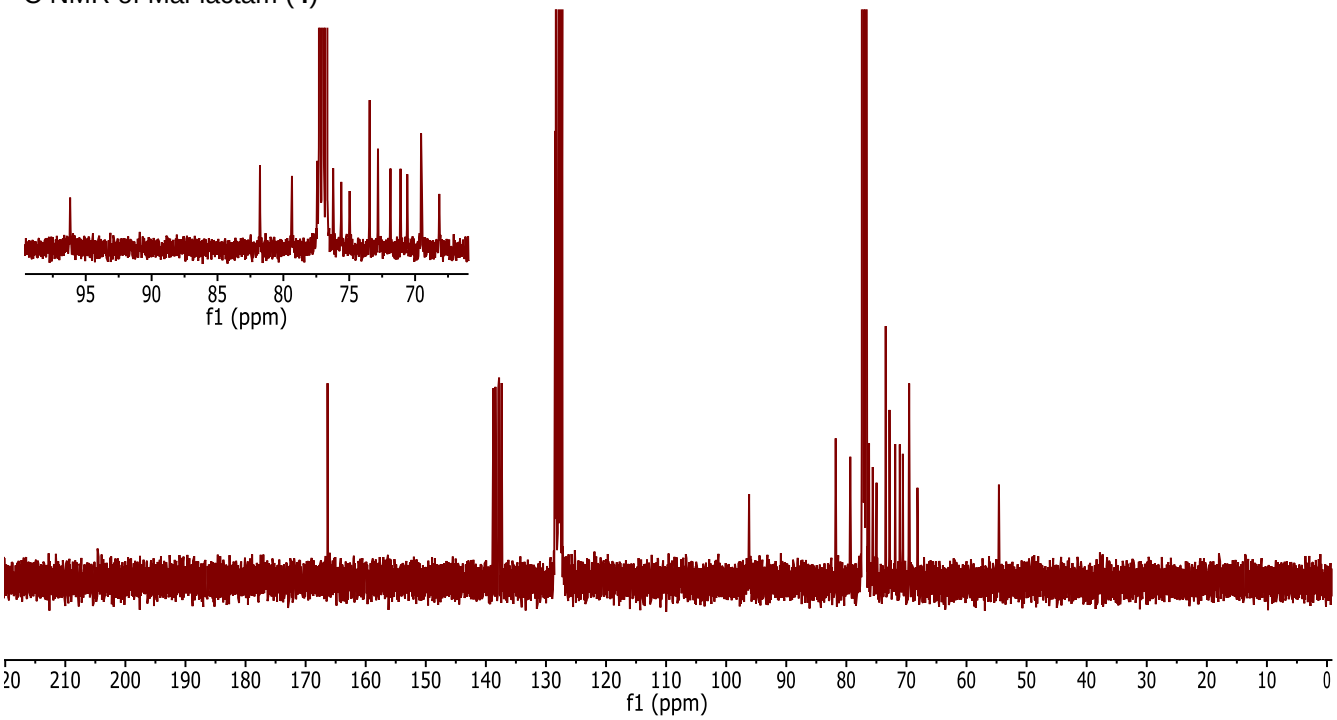
^{13}C NMR of maltal-OBn (**3**)



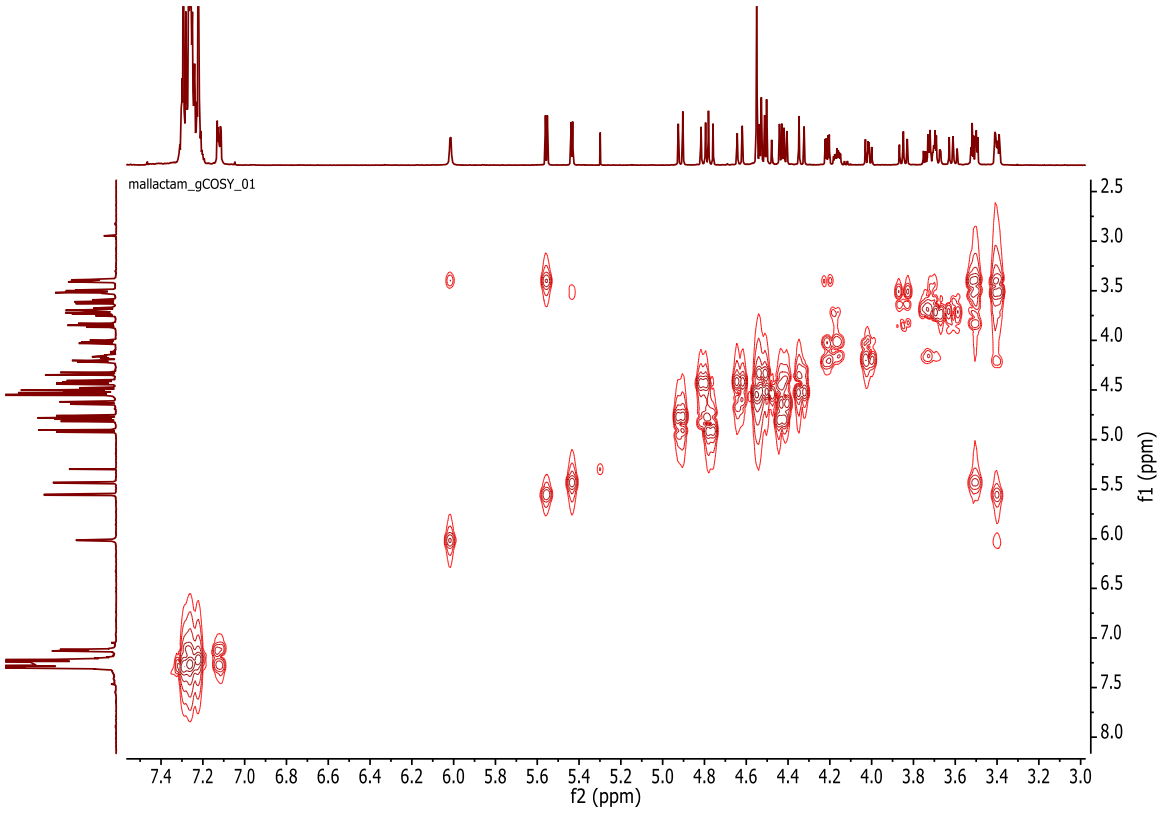
^{1}H NMR of Mal-lactam (**4**)



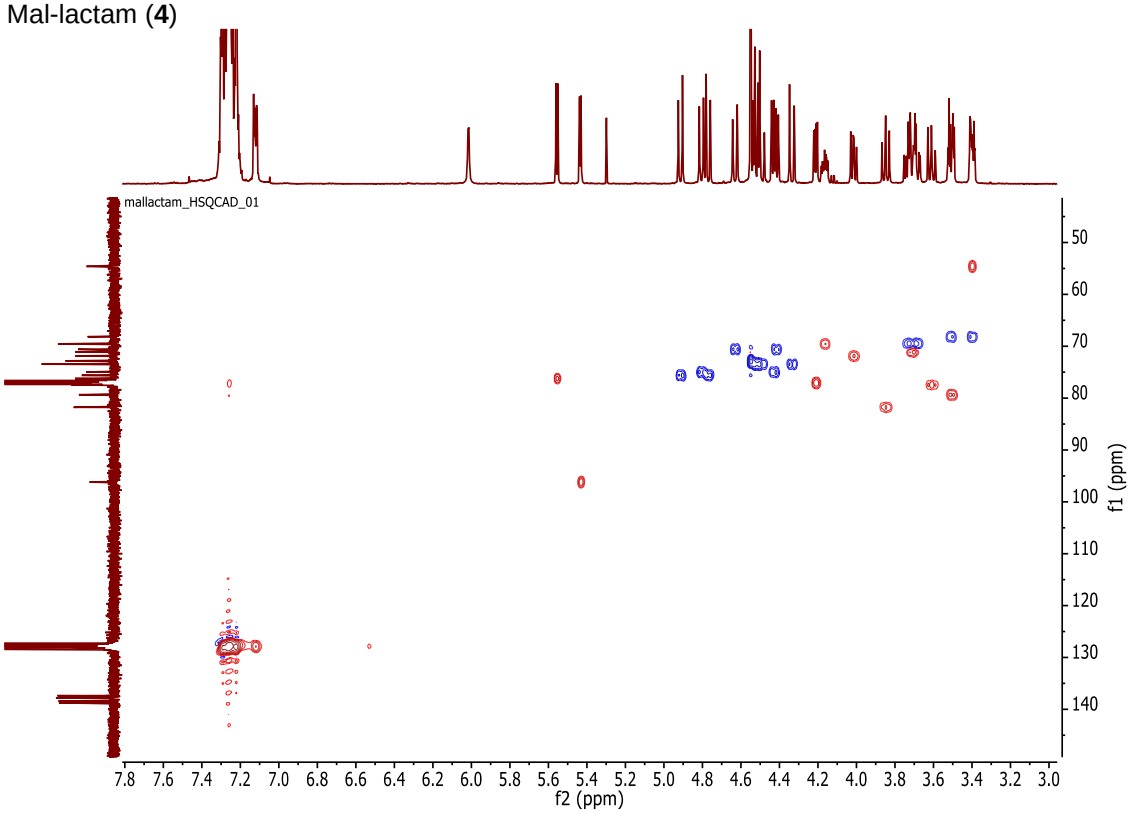
^{13}C NMR of Mal-lactam (**4**)



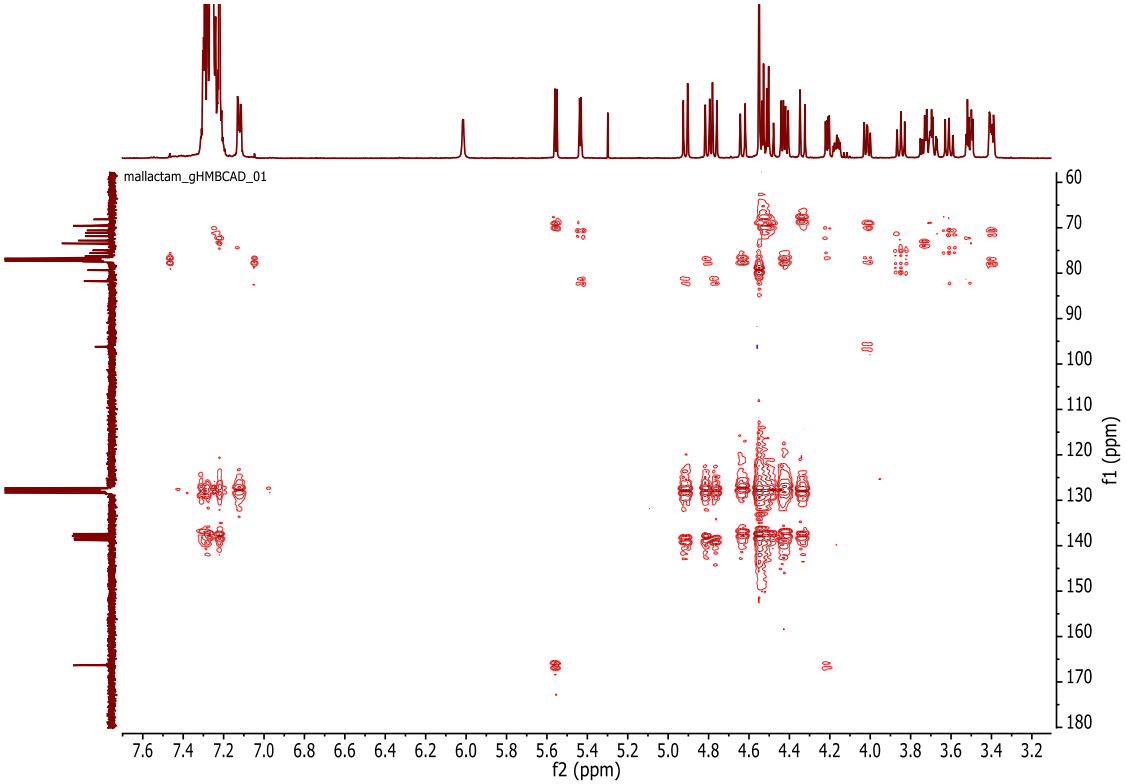
COSY of Mal-lactam (**4**)



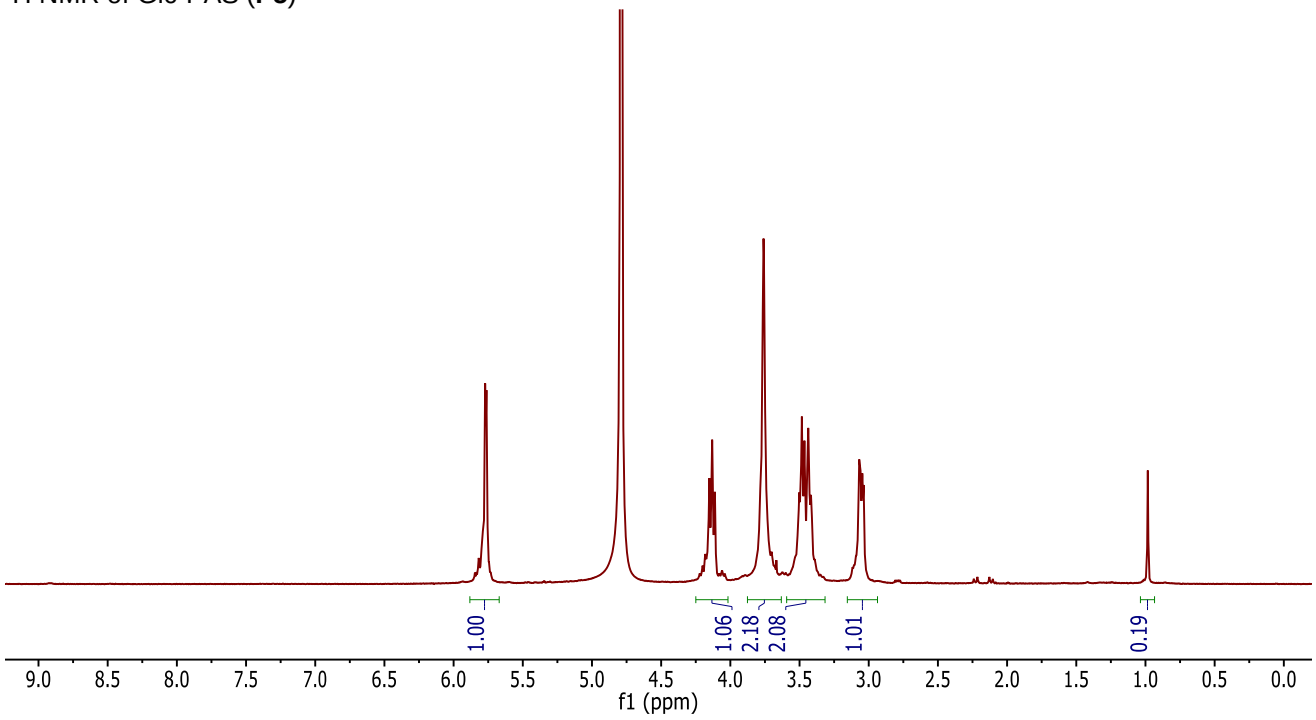
HSQC of Mal-lactam (**4**)



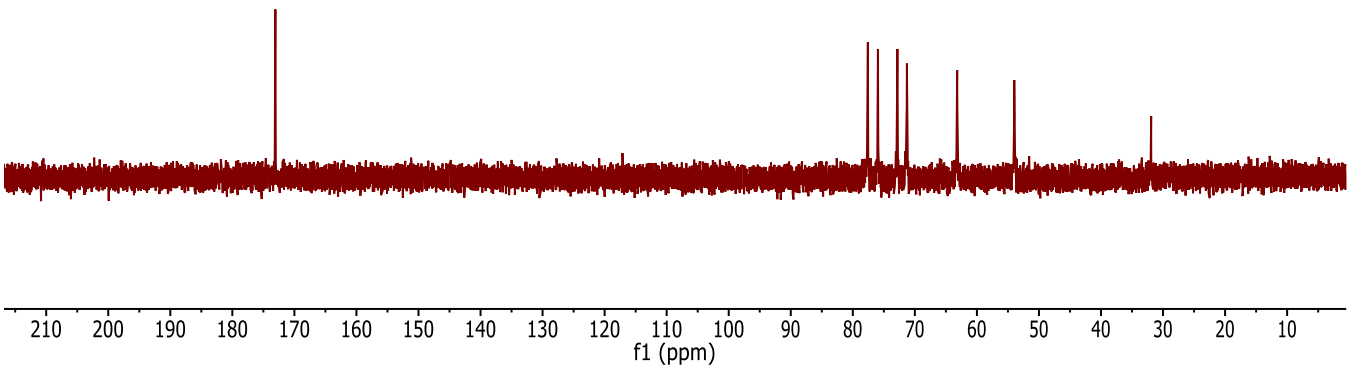
HMBC of Mal-lactam (**4**)



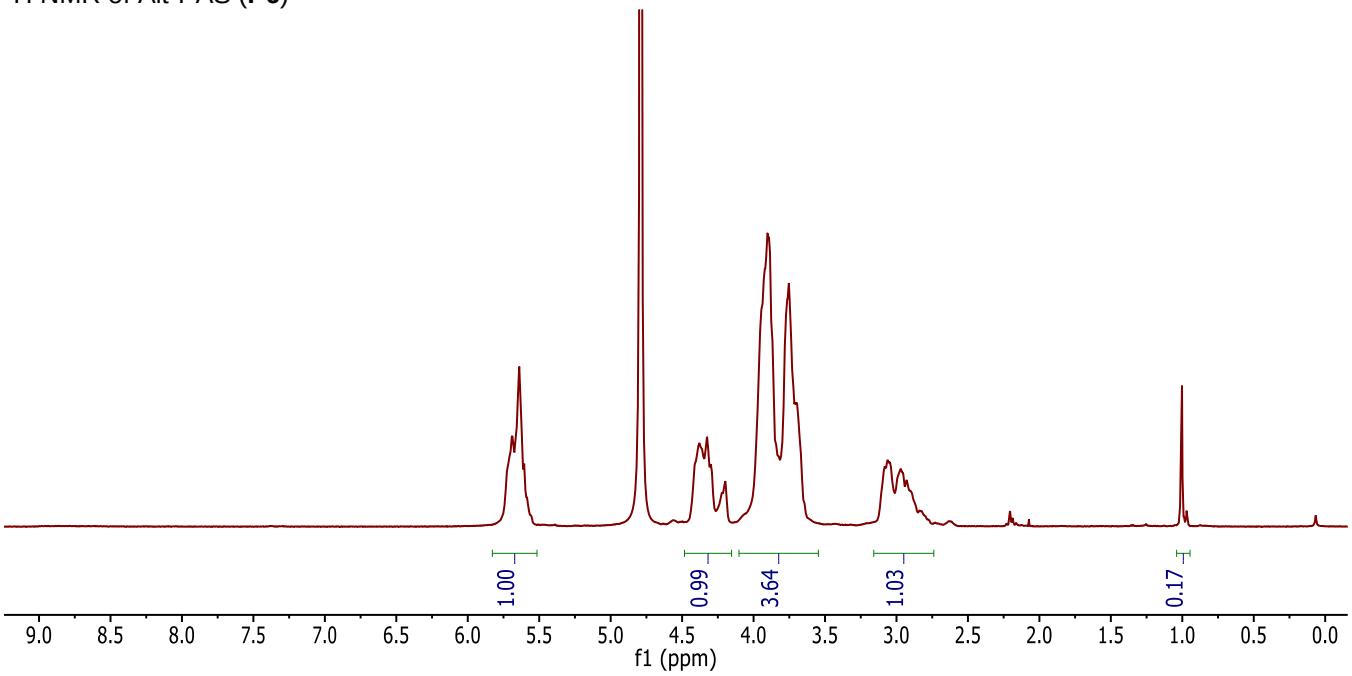
^{1}H NMR of Glc-PAS (**P5**)



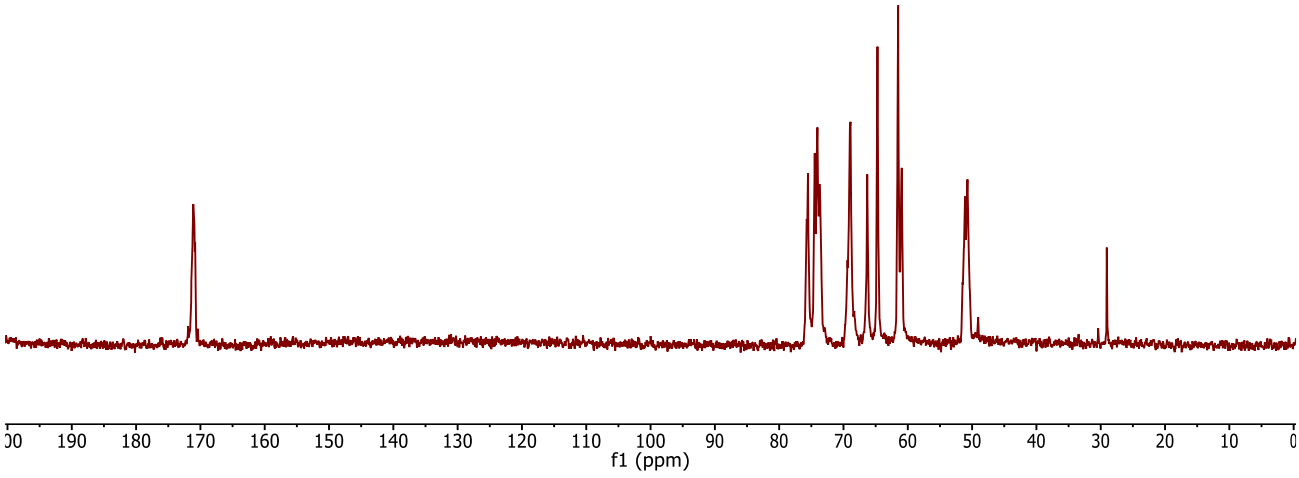
^{13}C NMR of Glc-PAS (**P5**)



^{1}H NMR of Alt-PAS (**P6**)



^{13}C of Alt-PAS (**P6**)



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