# Electronic Supporting information

## Sustainable Polyacetals from Isohexides

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### Contents

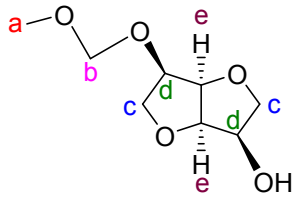
## 1. General methods and materials:-

All manipulations involving moisture sensitive compounds were carried out under inert gas atmosphere using standard Schlenk or glove box techniques. Tetrahydrofuran was distilled from sodium/benzophenone under inert conditions. All other solvents were used as received without further purification. Isomannide, sodium hydride, sodium methoxide, deuterated chloroform, deuterated oxide, deuterated chloride (DCl 35 wt% in $D_2O$) were purchased from Sigma Aldrich and used without further purification. Chloromethyl methyl ether, methane sulphonic acid, p-toluene sulphonic acid monohydrate, trifluromethane sulphonic acid, dimethoxymethane, diethyl azodicarboxylate, triphenyl phosphine, benzoic acid were purchased from Spectrochem Pvt Ltd and used without further purification. NMR spectra were recorded on a Bruker Avance 200, 400, 500 instruments. Chemical shifts are referenced to external reference TMS ($^1$H and $^{13}$C). Coupling constants are given as absolute values. FT-IR spectra were recorded on a Bruker α-T spectrophotometer in the range of 4000-400 $cm^{-1}$. Mass spectra recorded on Thermo scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150 x 4.6 mm diameter 8 um particle size mobile phase used is 90% methanol + 10 % water + 0.1 % formic acid. Differential scanning colorimeter (DSC) was carried out on DSC Q-10 from TA instruments with a heating and cooling rate of 10 K min-1. Thermo gravimetric analysis (TGA) was carried out on PerkinElmer STA 6000 simultaneous thermal analyzer. Elemental analysis was recorded on Flash EA 1112 series. MALDI-TOF was performed on AB SCIEX TOF/TOF ™ 5800 and matrix uesd is Dithranol. GPC measurement was carried out on a Thermo Quest (TQ) GPC at 25$^o$C using chloroform (Merck, Lichrosolv) as the mobile phase. The analysis were carried out at a flow rate 1 mL/min using a set of five μ-styragel HT columns ( HT-2 to HT-6) and a refractive index (RI) detector .This column set enabled the determination of wide range of molecular weight from $10^2$ to $10^6$. Columns were calibrated with polystyrene standard and the molecular weights reported were with respect to polystyrene standard. The wide angle X- ray was performed on Rigaku Micromax-007 HF having high intensity micro focus rotating anode.

# 2. Acid catalyzed synthesis of monoacetal

## *2.1 Isomannide-monoacetal (3a)*

To a tetrahydrofuran suspension ( 15 ml) of isomannide (2 g; 13.69 mmol ) was added dimethoxymethane (15 ml) and trifluromethane sulphonic acid (0.12 ml; 1.369 mmol,10 mol%), and the mixture was stirred over night at room temperature to give a clear solution. Subsequently, the reaction was quenched by adding ammonium hydroxide solution (0.12 ml, 30 % solution), followed by washing with saturated solution of NaCl (30 ml). The aqueous phase was extracted with ethyl acetate (3 x 30 ml) and combined organic phase was dried over $MgSO_4$, filtered and filtrate evaporated to obtain a pale yellow oily liquid. Purification by column chromatography (hexane: ethyl acetate 75:25) yielded (0.5 g; 2.13 mmol) 16 % of diacetal and (0.6 g; 2.56 mmol) 19 % of monoacetal. The same reaction of isomannide is carried out in presence of 40 mol % methane sulphonic acid but the yield of diacetal remained unaffected at 16 %. The spectrum of the major product (i.e. monoacetal) is given below.




**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K ) δ = 4.75-4.67 (dd, $J_{H-H}$ = 6.84 Hz, $2H_b$), 4.52-4.46 (m, $2H_e$), 4.28 (m, $1H_d$) ,4.22-4.17 (m ,$1H_d$ ), 4.10-4.07- (m, $1H_c$), 3.98-3.94 (m, $1H_c$), 3.70-3.63 (m, $2H_c$), 3.38 (s, $3H_a$), 2.85-2.84 (broad peak –OH, 1H). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K) δ = 96.6 (s, $C_b$), 81.5 (s, $C_e$), 81.0 (s, $C_e$), 77.8 (s, $C_d$), 74.6 (s, $C_c$), 72.4 (s, $C_d$), 70.9 (s, $C_c$), 55.8 (s, $C_a$). ESI-MS (+ve) Cal. m/z = 213.07 $[M+Na]^+$; Obs. m/z = 213.07 $[M+Na]^+$. Elemental analysis (%) calculated for $C_8H_{14}O_5$ (190.09): C-50.51%, H-7.36% ; Found : C-49.09% , H-7.69% .

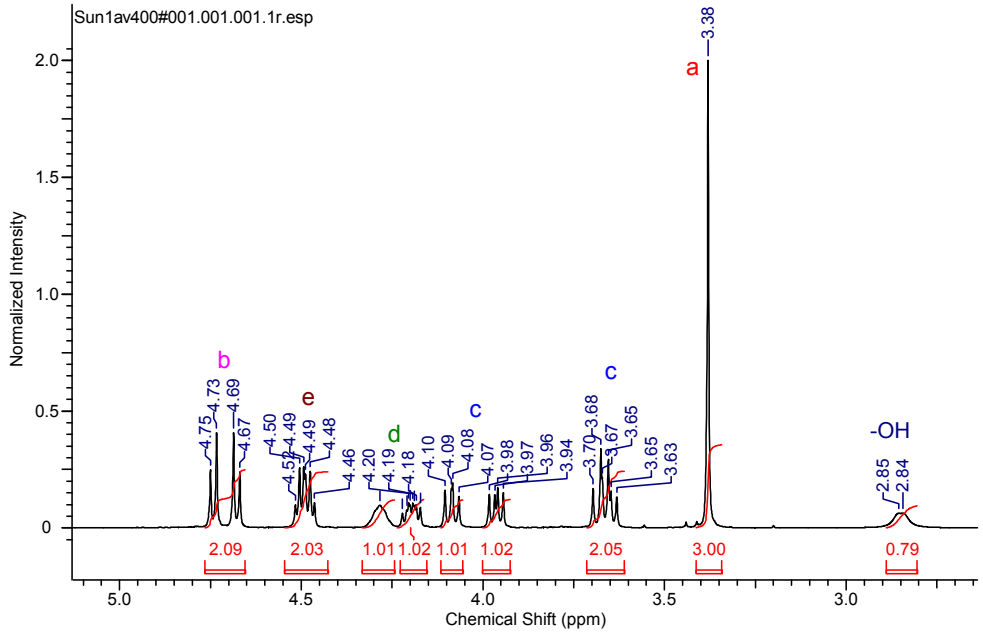



*Figure S1*. $^{1}$H NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz at 298K).

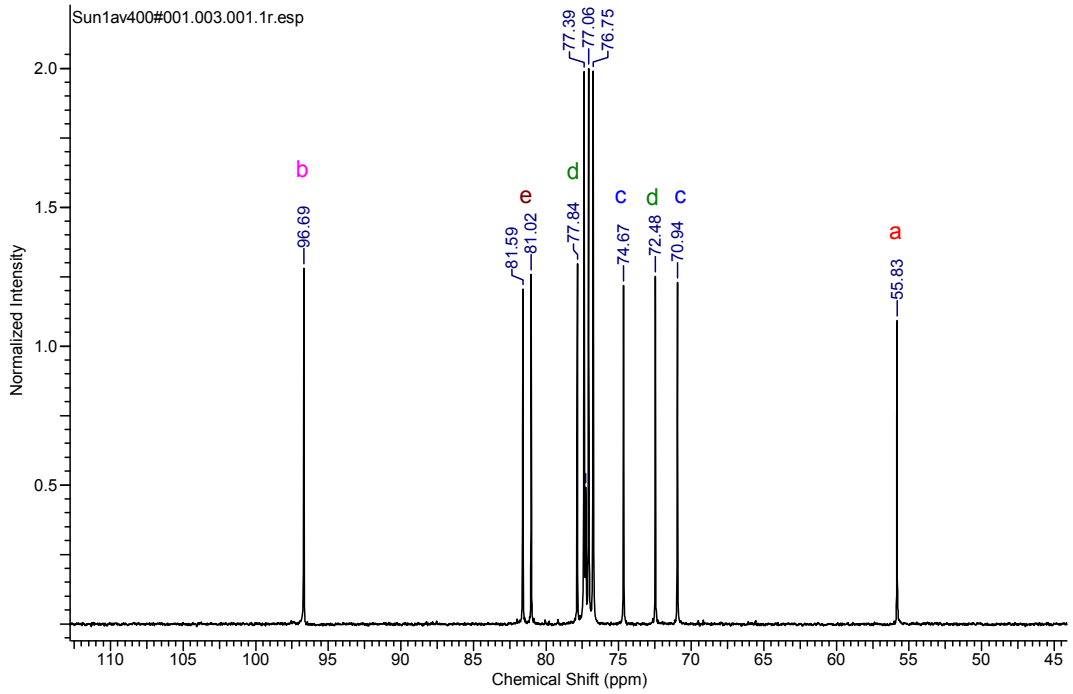



*Figure S2*. $^{13}$C-NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz at 298K).

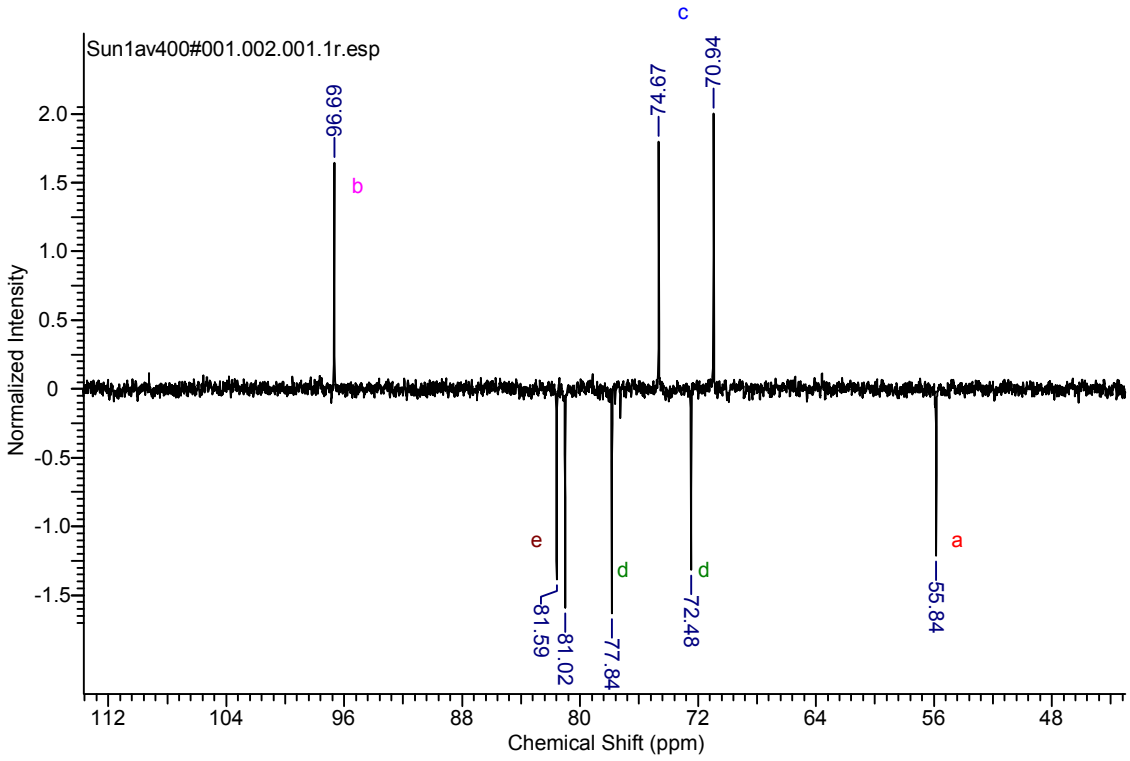



*Figure S3*. 135-DEPT NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz at 298K).

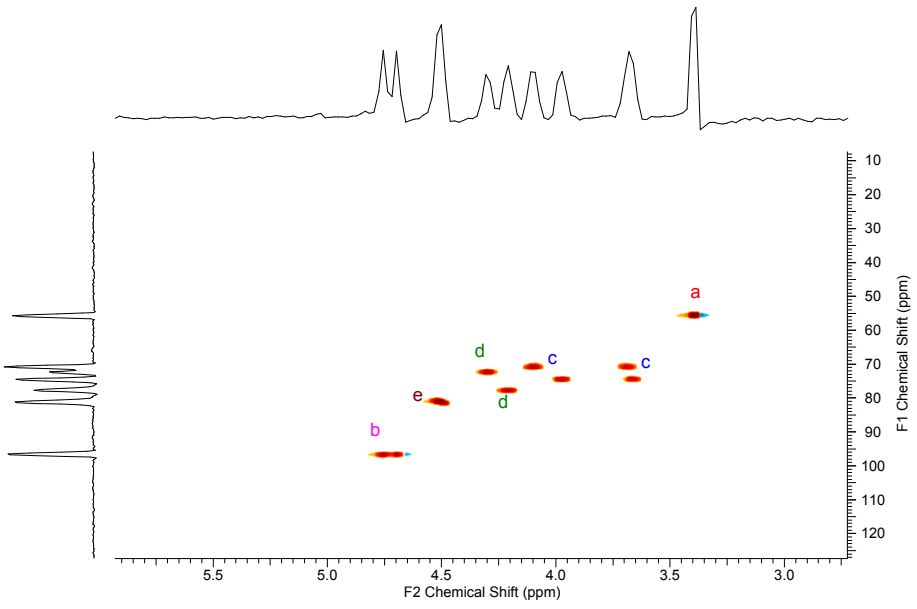



*Figure S4*. HSQC (C-H correlation) spectrum of compound **3a** in $CDCl_3$ (400 MHz at 298K).

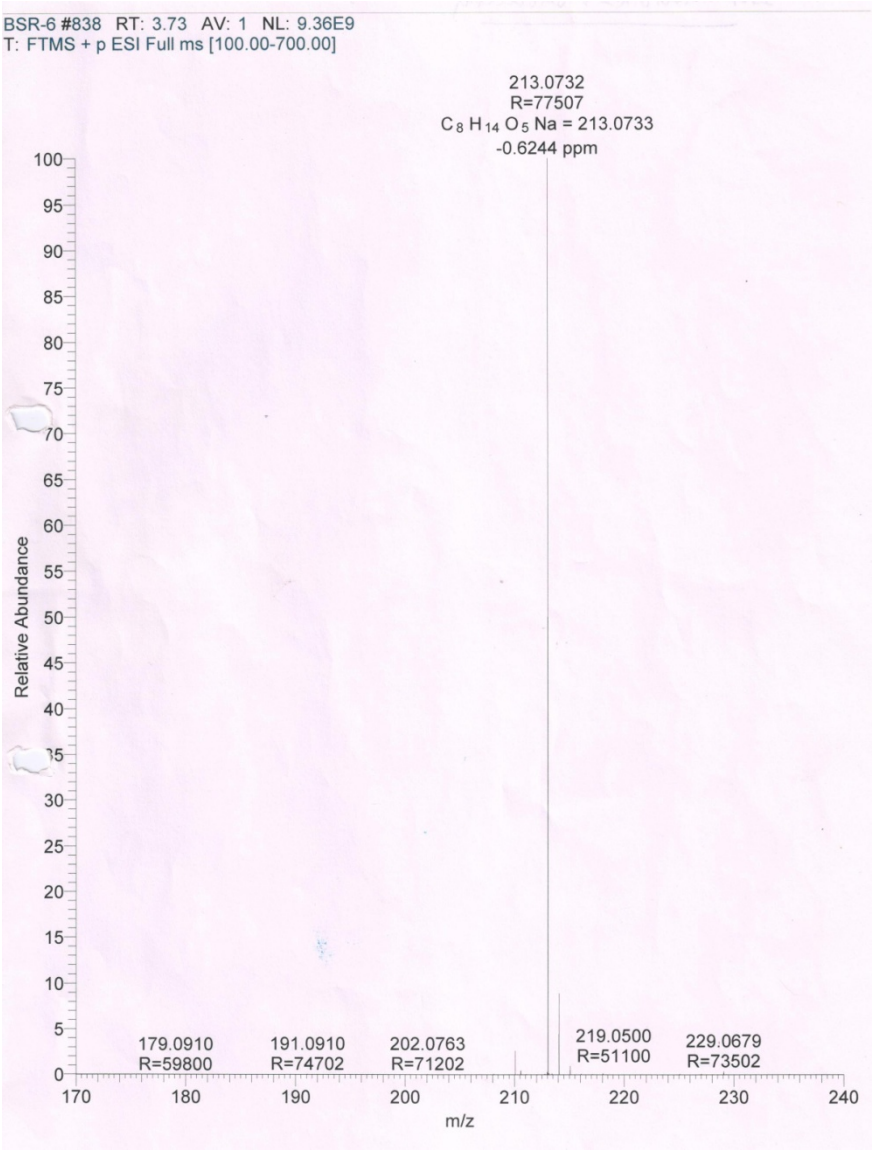
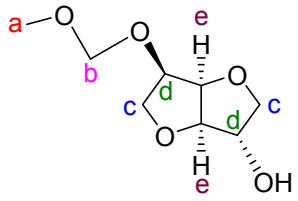



*Figure S5*. ESI-MS (+) spectrum of compound **3a** ($C_8H_{14}O_5$), m/z = 213.07 $[M+Na]^+$.

## *2.2 Isosorbide-monoacetal (3b)*

To a tetrahydrofuran suspension ( 10 ml) of isosorbide (1 g; 6.84 mmol) was added dimethoxymethane (10 ml) and methane sulphonic acid (1.33 ml; 20.52 mmol; 3 equivalent), and the mixture was stirred over night at room temperature to give a clear solution. Subsequently, the reaction was quenched by adding ammonium hydroxide solution (1.33 ml, 30 % solution), followed by washing with saturated solution of NaCl (20

ml). The aqueous phase was extracted with ethyl acetate (3 x 30 ml) and combined organic phase was dried over $MgSO_4$, filtered and filtrate evaporated to obtain a pale yellow oily liquid. Purification by column chromatography (hexane: ethyl acetate75:25), yielded (0.382 g; 1.63 mmol), 24 % of monoacetal and (0.368 g; 1.60 mmol), 23% of diacetal. The spectrum of the major product (i.e. monoacetal) is given below.




**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K ) δ = 4.66-4.62 (dd, $J_{H-H}$ = 6.75 Hz, $2H_b$), 4.56-4.55 (m, $1H_e$), 4.45-4.43 (m, $1H_d$) ,4.24-4.21 (m, $2H_{e,d}$ ), 4.01-3.98 (m, $1H_c$), 3.86-3.80 (m, $2H_c$), 3.52-3.48 (m, $1H_c$), 3.33 (s, $3H_a$), 2.86 (broad peak –OH, 1H). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298K) δ = 95.5 (s, $C_b$), 86.2 (s, $C_e$), 81.7 (s, $C_d$), 81.3 (s, $C_e$), 73.6(s, $C_c$), 73.3 (s, $C_c$), 72.2 (s, $C_d$), 55.5 (s, $C_a$). ESI-MS (+ve) cal. m/z = 213.07 $[M+Na]^+$; Obs. m/z = 213.07 $[M+Na]^+$; Elemental analysis (%) calculated for $C_8H_{14}O_5$ (190.09): C-50.51%, H-7.36% ; Found : C-50.07% , H-7.67% .

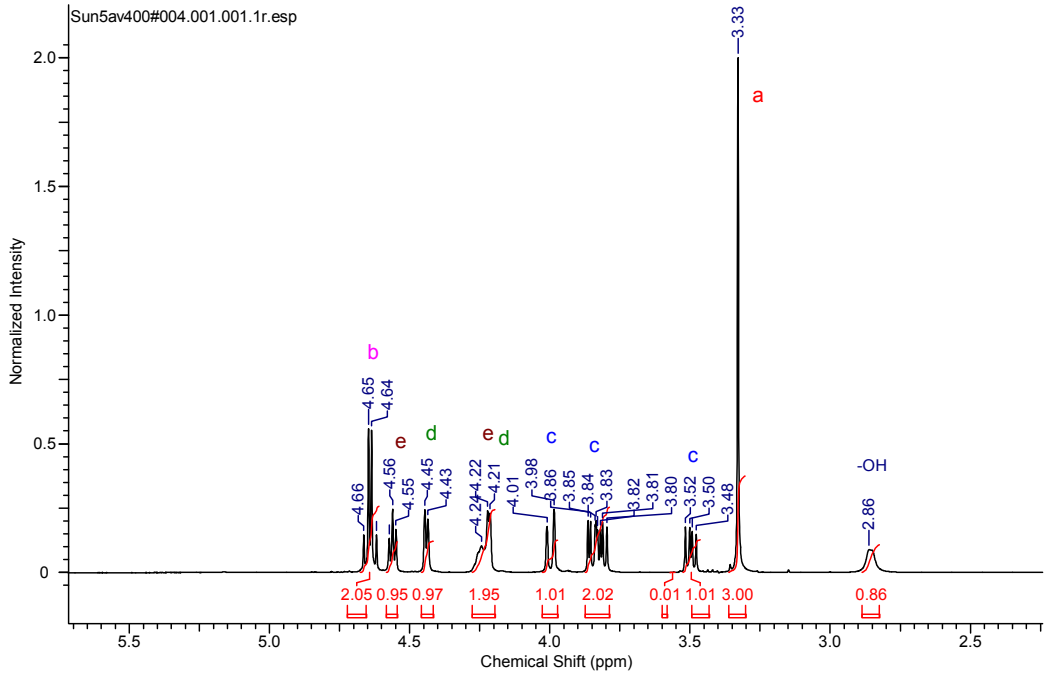


*Figure S6*. $^{1}$H NMR spectrum of compound **3b** in $CDCl_3$ (400 MHz at 298K).

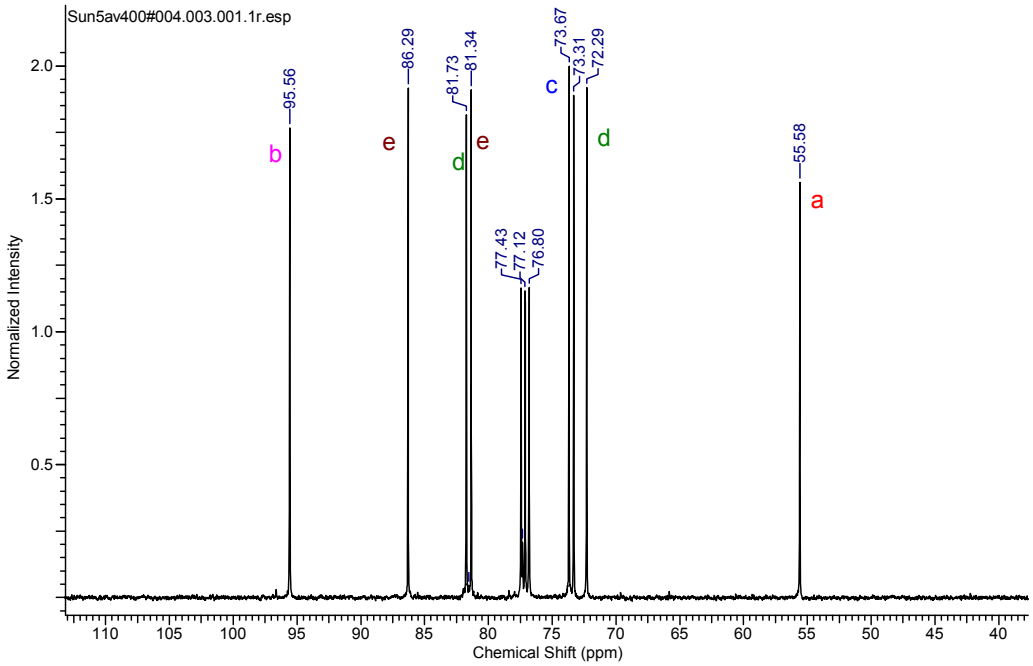



*Figure S7*. $^{13}$C-NMR spectrum of compound **3b** in $CDCl_3$ (400 MHz at 298K).

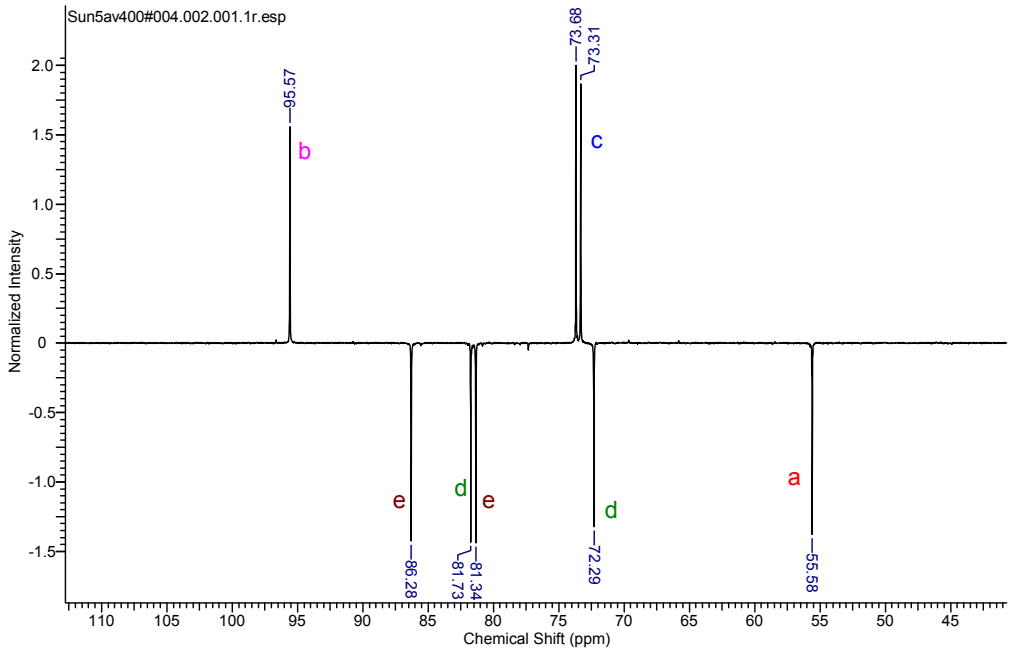



*Figure S8*. 135-DEPT NMR spectrum of compound **3b** in $CDCl_3$ (400 MHz at 298K).

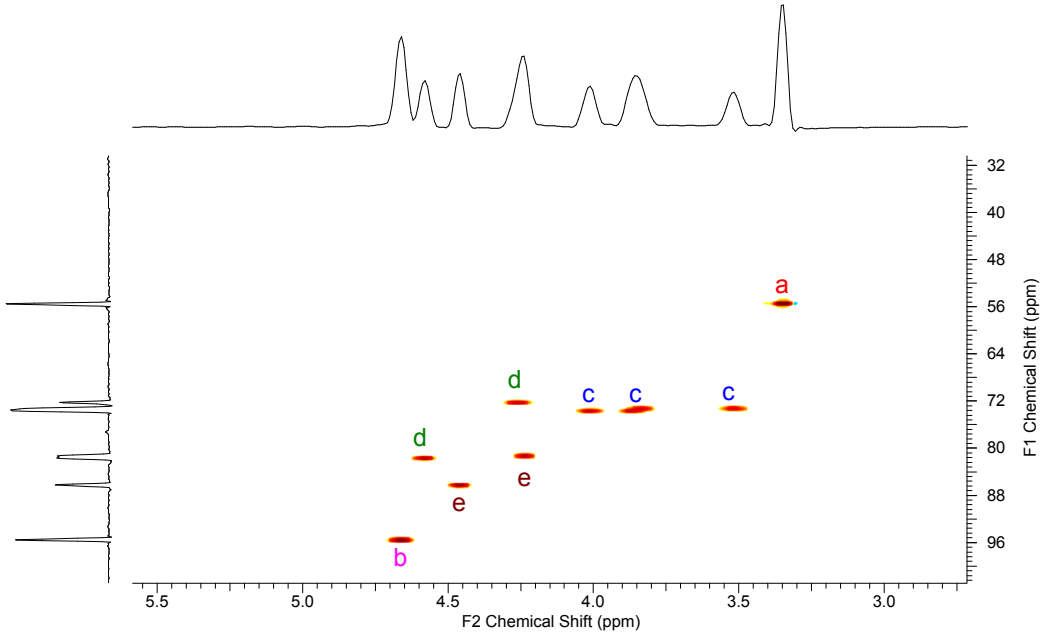



*Figure S9*. HSQC (C-H correlation) spectrum of compound **3b** in $CDCl_3$ (400 MHz at 298K)**.**

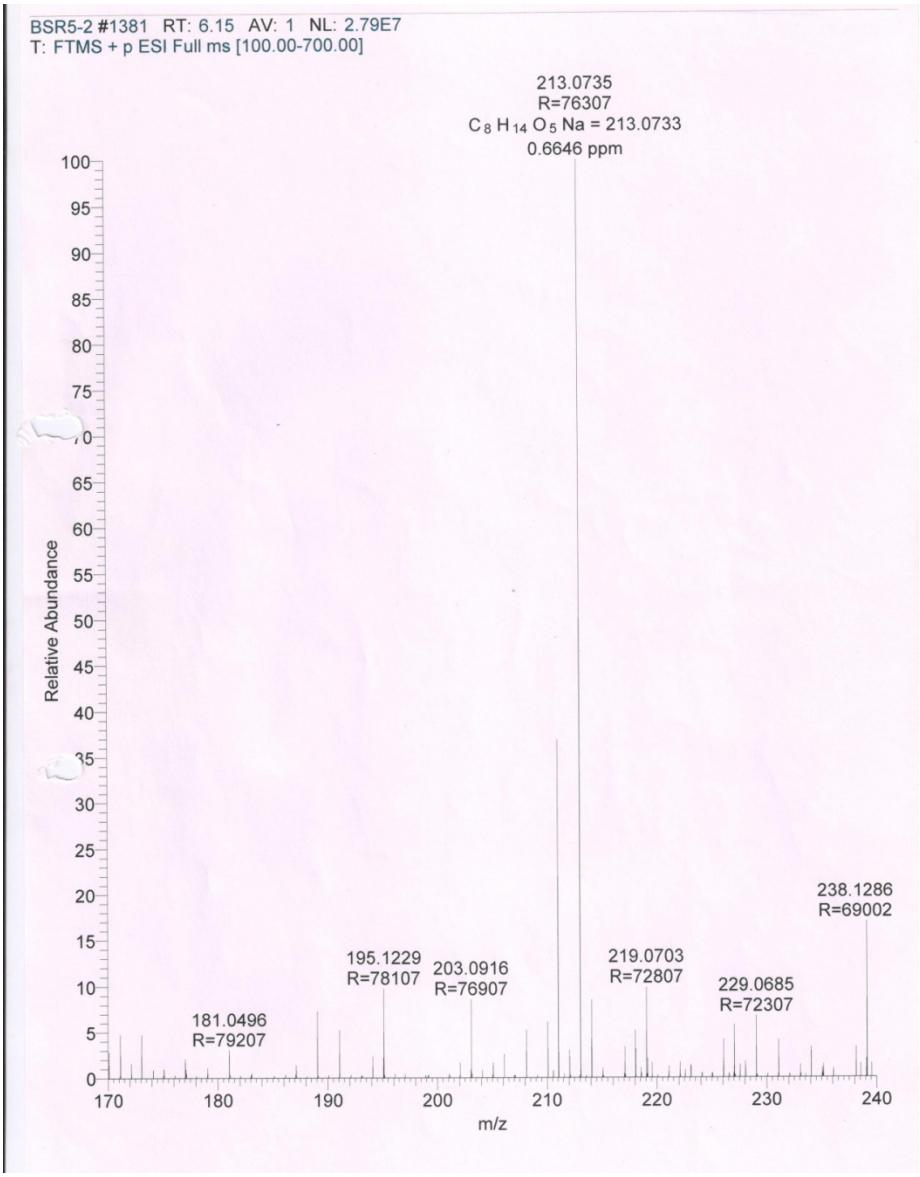
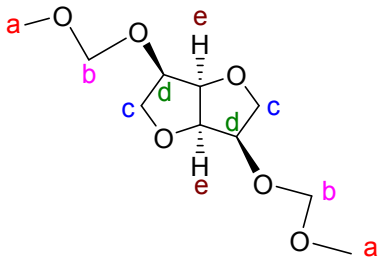



*Figure S10*. ESI-MS (+) spectrum of compound **3b** ($C_8H_{14}O_5$ ), m/z = 213.07 $[M+Na]^+$.

## *2.3 Isoidide-monoacetal (3c)*

As evidenced from the synthesis of **3b** (section 2.2), use of even over stoichiometric amount of acid did not improve the yield of desired diacetal; hence synthesis of isoidide-monoacetal (**3c**) was not attempted.

# 3. Synthesis of isomannide-diacetal (2a)




**$^{1}$H NMR** (200 MHz, $CDCl_3$, 298 K ) δ = 4.71 - 4.61 (dd, $J_{H-H}$ = 6.68 Hz, $4H_b$), 4.50-4.45 (m, $2H_e$), 4.20-4.10 (m, $2H_d$), 4.06-3.98 (m, $2H_c$), 3.69-3.60 (m, $2H_c$), 3.33 (s, 6 $H_a$); **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K) δ = 96.64 (s, $C_b$), 80.80 (s, $C_e$), 78.25 (s, $C_d$), 70.91 (s, $C_c$), 55.72 (s, $C_a$). ESI-MS (+ve mode) Cal. m/z = 257.10 $[M+Na]^+$; Obs. m/z = 257.09 $[M+Na]^+$; Elemental analysis (%) calculated for $C_{10}H_{18}O_6$: C- 51.23%, H-7.69%; Found : C- 51.01%, H- 7.92%, IR ($C_{10}H_{18}O_6$) $cm^{-1}$ =1128, 1080 ( C-H/C-O stretching).

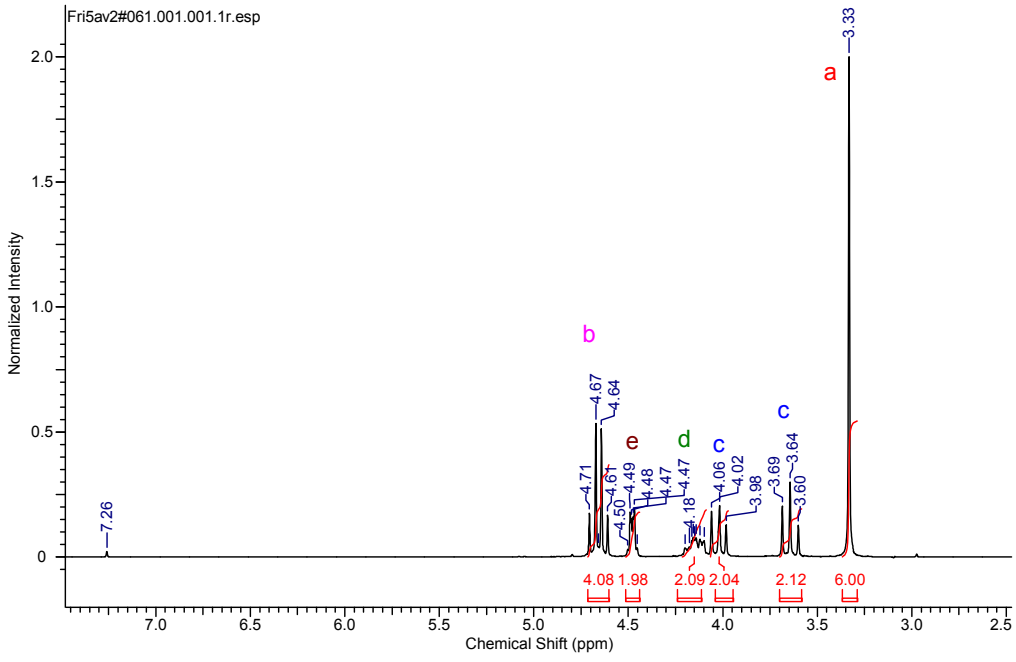


*Figure S11*. $^{1}$H NMR spectrum of compound **2a** in $CDCl_3$ (200 MHz at 298K).

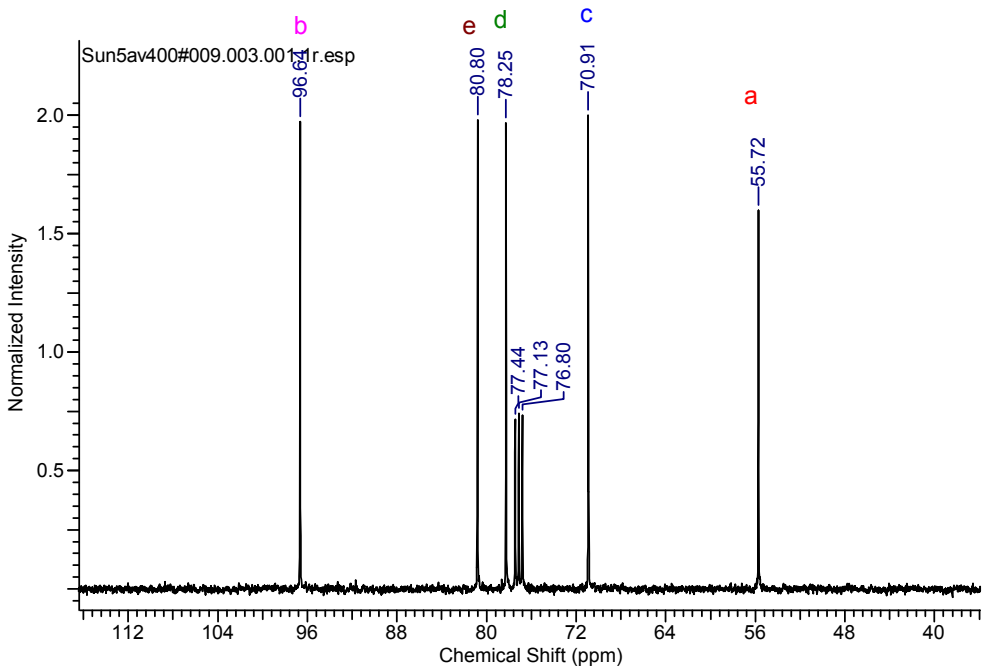



*Figure S12*. $^{13}$C NMR spectrum of compound **2a** in $CDCl_3$ (400 MHz at 298K).

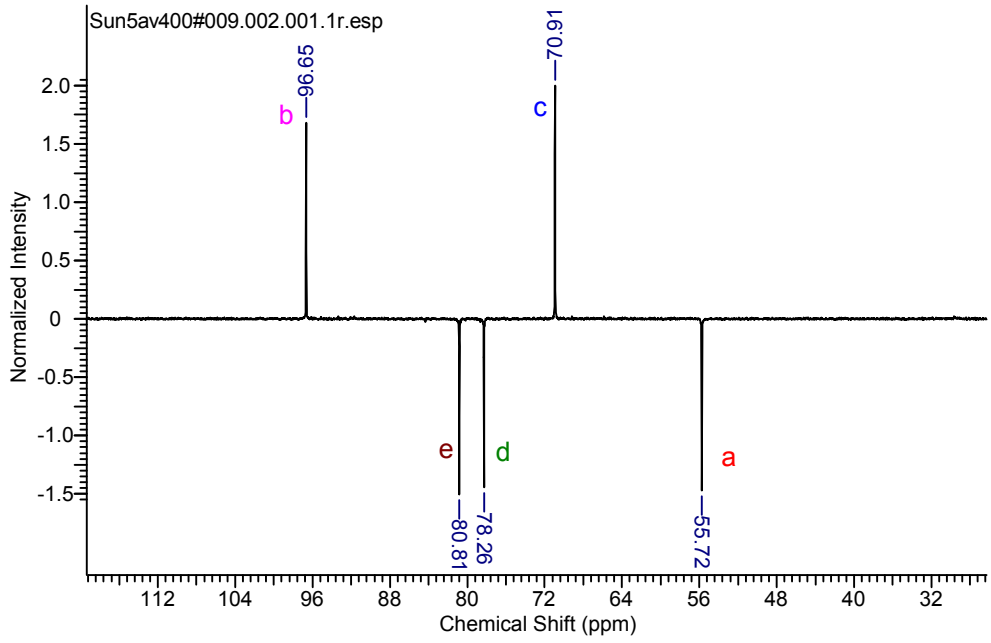



*Figure S13*. 135-DEPT NMR spectrum of compound **2a** in $CDCl_3$ (400 MHz at 298K).

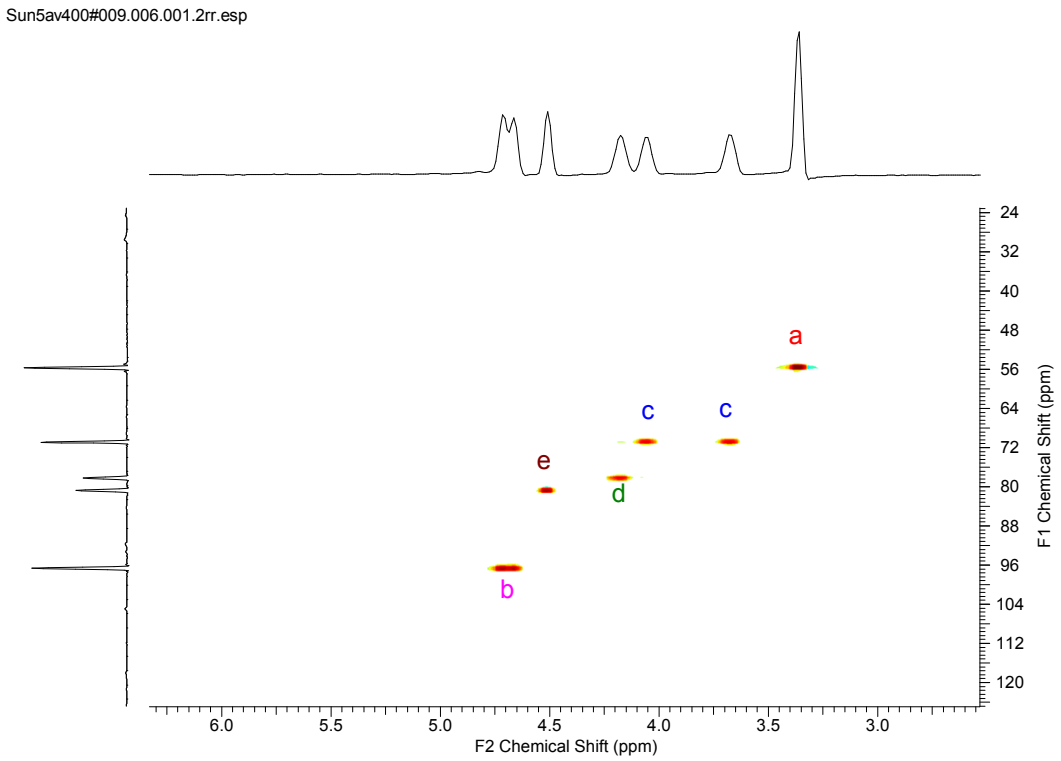



*Figure S14*. HSQC (C-H correlation) - NMR spectrum of compound **2a** in $CDCl_3$ (400 MHz at 298K).

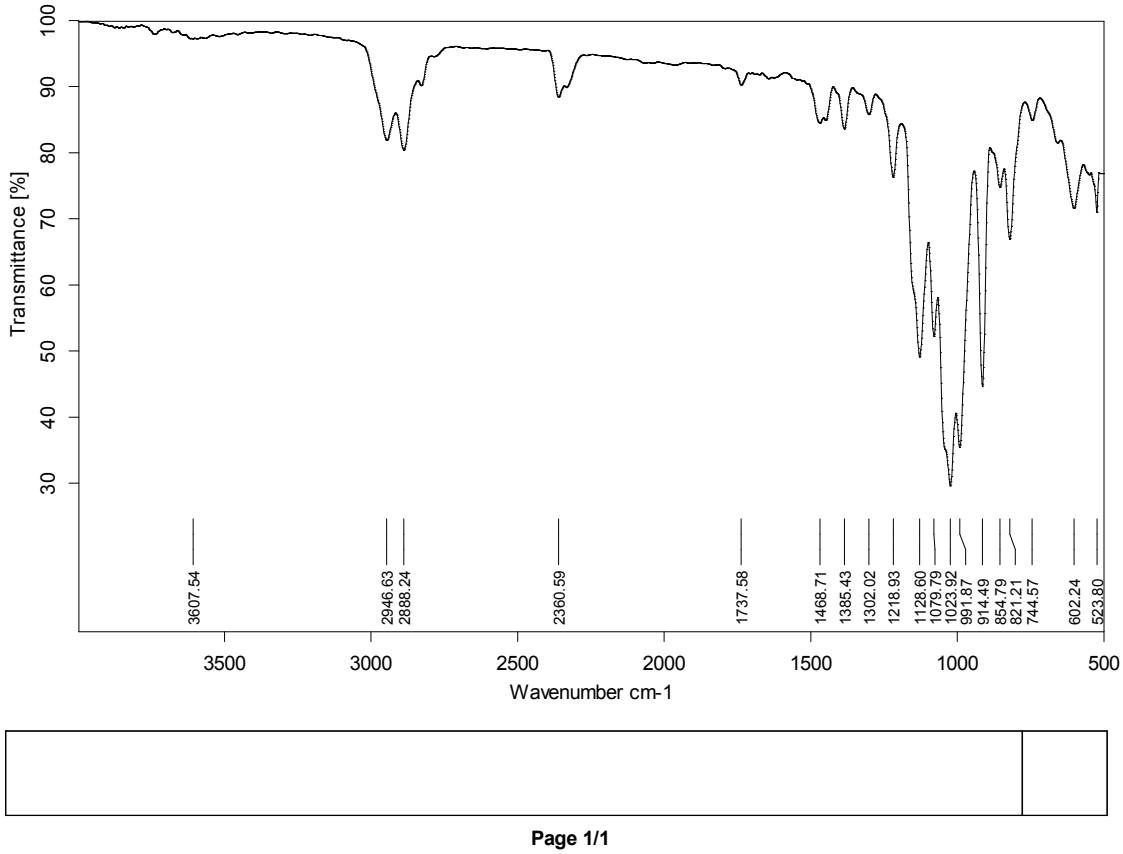



*Figure S15*. IR spectrum of compound **2a**.

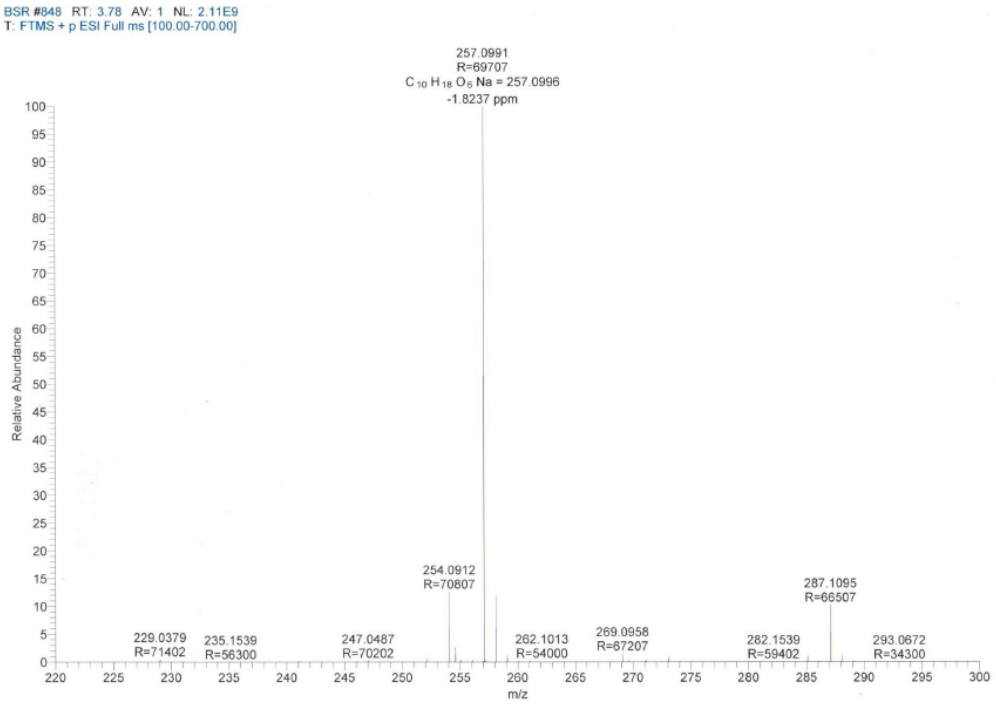
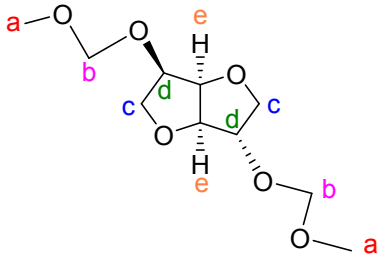



*Figure S16*. ESI-MS (+) spectrum of compound **2a** with a molecular ion peak $[M+Na]^+ = 257.1$ (100%) and 258.1 (10%).

# 4. Synthesis of isosorbide-diacetal (2b)




**$^1$H NMR** (500 MHz, $CDCl_3$, 298 K ) δ = 4.74 - 4.63 (dd, $J_{H-H}$ = 6.94 Hz, $4H_b$), 4.61-4.60 (m, $1H_e$), 4.50 (m, $1H_d$), 4.18-4.16 (m, $1H_e$), 4.16-4.14 (m, $1H_d$), 3.96-3.92 (m, $3H_c$), 3.57-3.53 (m,$1H_c$), 3.37 (s, $3H_a$), 3.34 (s, $3H_a$); **$^{13}$C NMR** (500 MHz, $CDCl_3$, 298 K) δ = 96.6 (s, $C_b$), 95.6 (s, $C_b$), 86.2 (s, $C_e$), 81.6 (s, $C_d$), 80.8 (s, $C_e$), 77.9 (s, $C_d$), 73.7 (s, $C_c$), 69.6 (s, $C_c$), 55.7 (s, $C_a$), 55.5 (s, $C_a$); ESI-MS (+ve mode) Cal. m/z = 257.10 $[M+Na]^+$; Obs. m/z = 257.09 $[M+Na]^+$; Elemental analysis (%) calculated for $C_{10}H_{18}O_6$: C- 51.23 %, H-7.69%; Found: C- 50.95 %, H- 7.84 %, IR ($C_{10}H_{18}O_6$) $cm^{-1}$:1146 ,1104 (C-H/C-O stretching).

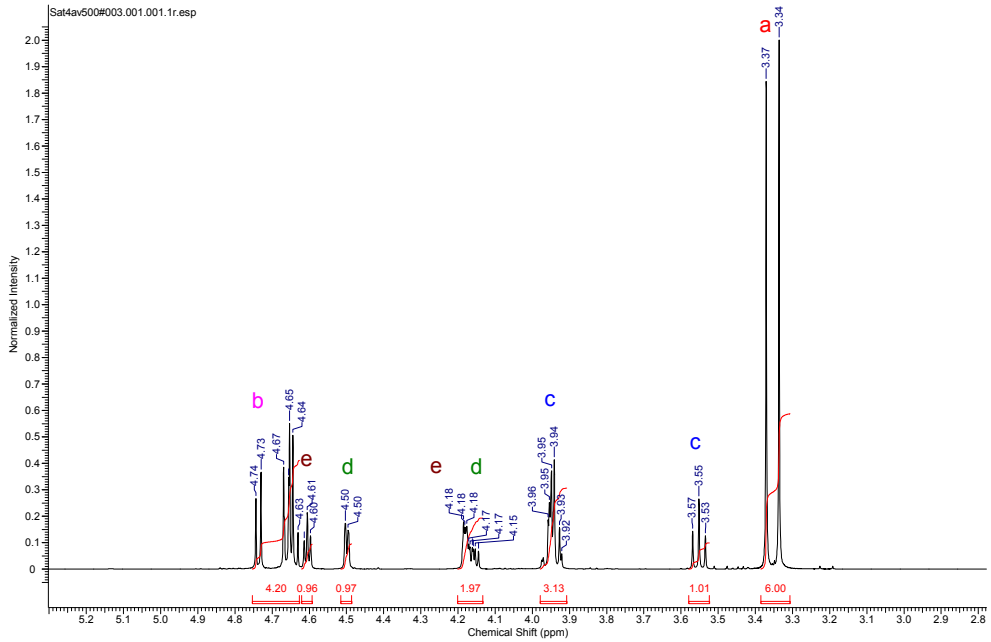



*Figure S17*. $^{1}$H NMR spectrum of **2b** in $CDCl_3$ (500 MHz at 298K).

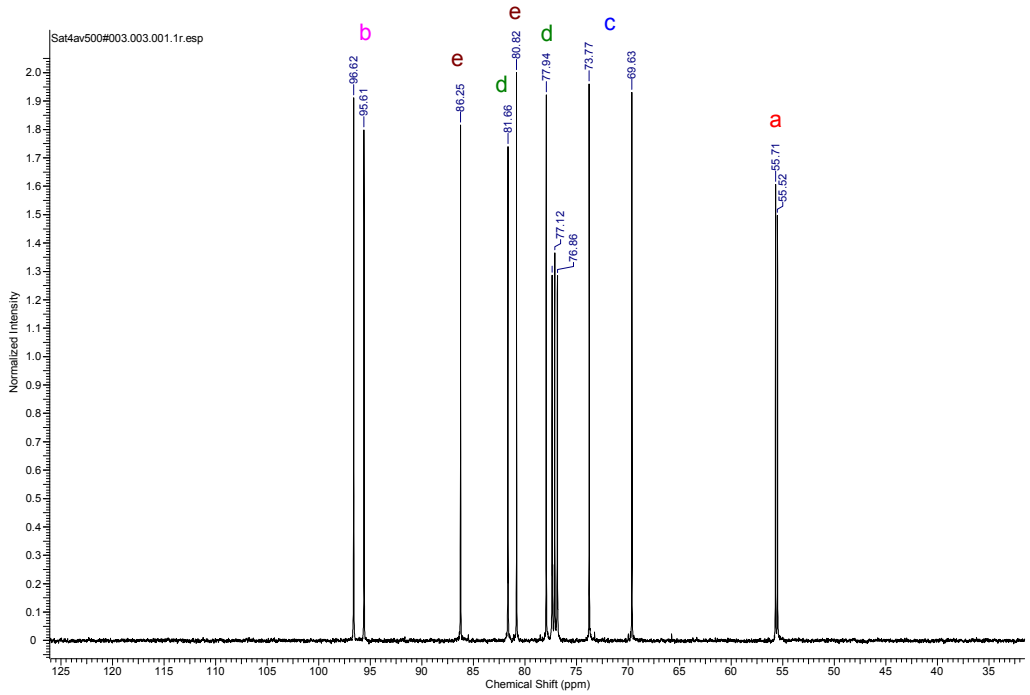



*Figure S18*. $^{13}$C NMR spectrum of **2b** in $CDCl_3$ (500 MHz at 298K).

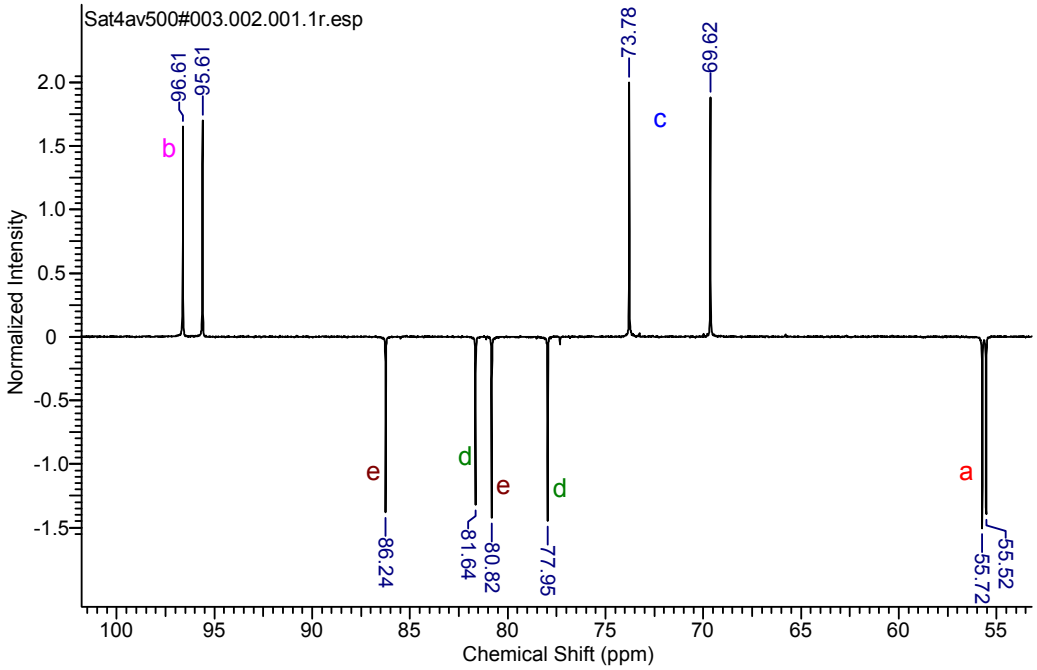



*Figure S19*. 135-DEPT NMR of compound **2b** in $CDCl_3$ (500 MHz at 298K).

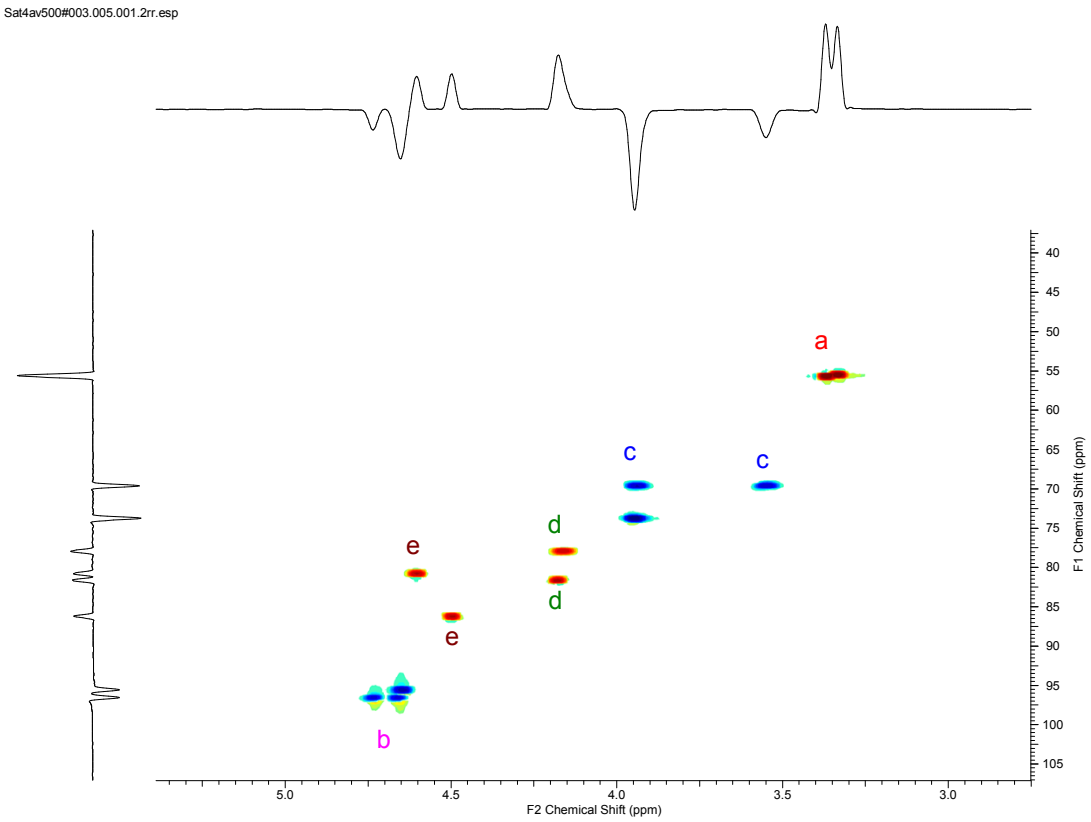


*Figure S20*. HSQC (C-H correlation) NMR spectrum of compound **2b** in $CDCl_3$ (500 MHz at 298K).

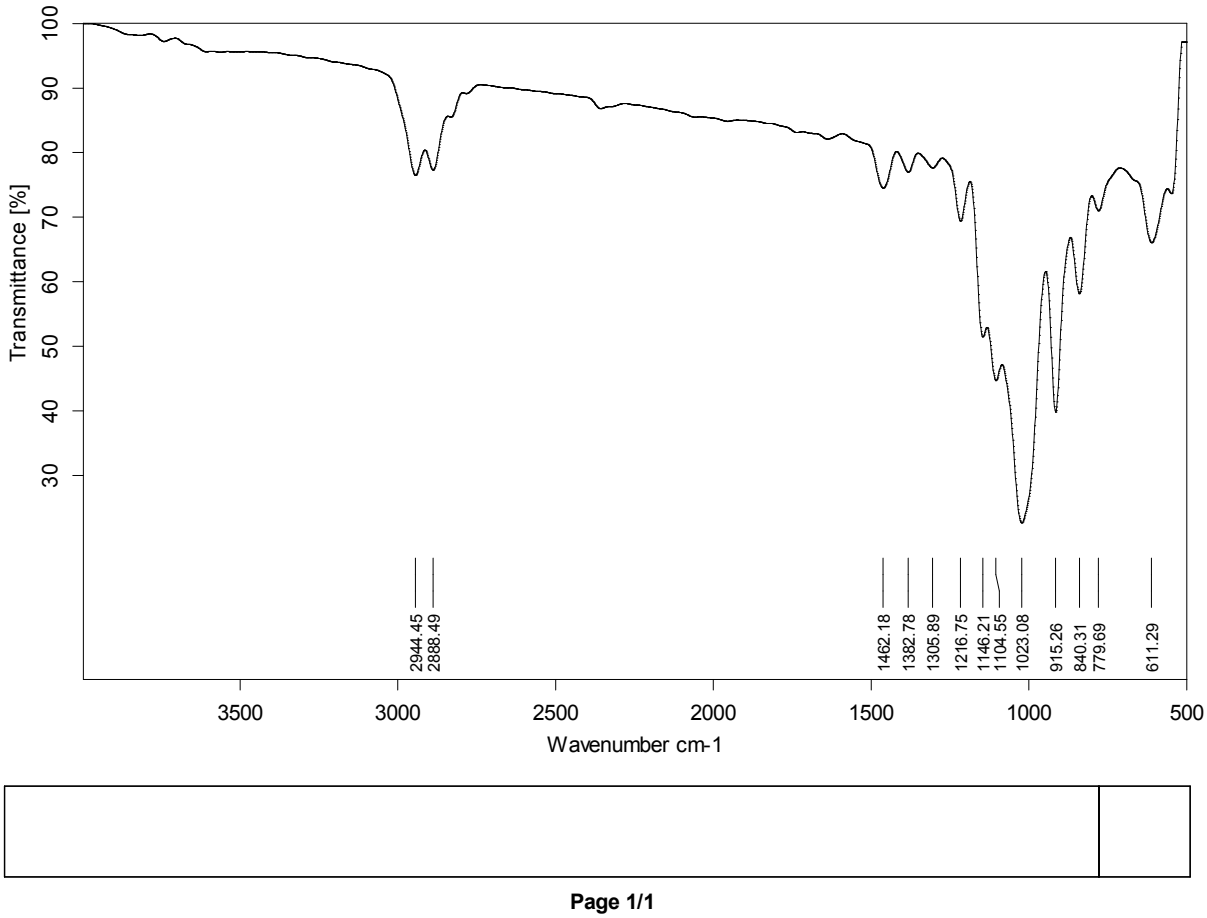



*Figure S21*. IR spectrum of compound **2b**.

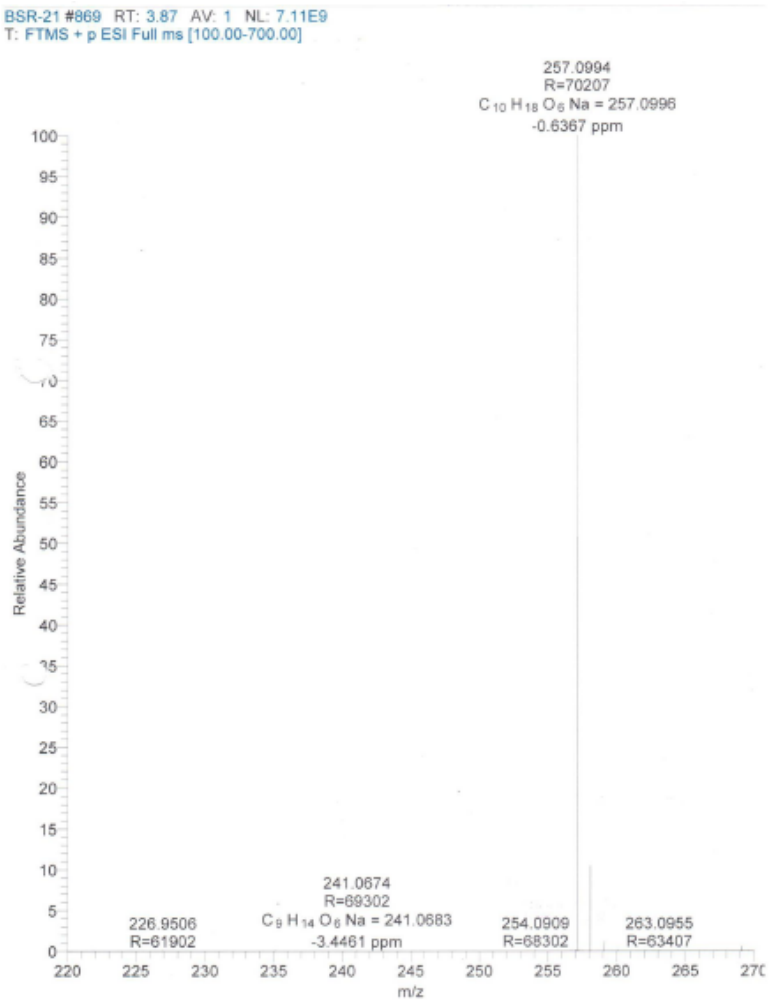


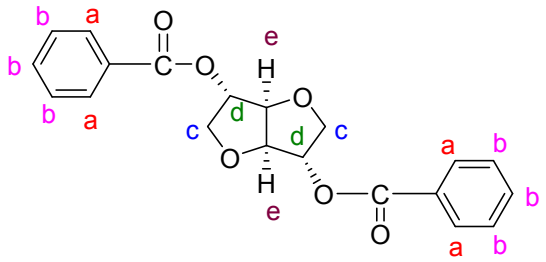

*Figure S22*. ESI-MS(+) spectrum of **2b** with a molecular ion peak $[M+Na]^+$ = 257.1 (100%) and 258.1 (10%).

# 5. Synthesis of isoidide (1c):-

## A. Synthesis of (3*S*,3a*R*,6*S*,6a*R*)-hexahydrofuro[3,2-*b*]-furan-3,6-diyl dibenzoate:-

The titled compound was synthesized following a earlier report with slight modifications.[1] Isomannide (4 g, 27.37 mmol) and triphenylphosphine (14.35 g, 54.74 mmol) were dissolved in tetrahydrofuran (80 ml). To this solution was added benzoic acid (6.68 g, 54.74 mmol) and diethyl azodicarboxyate (8.58 ml, 54.74 mmol) in tetrahydrofuran (80 ml) over a period of 3 hours at ambient temperature. Water bath was used to maintain the temperature of

the reaction mixture during the addition. The reaction mixture was stirred for 15 hours and then additional benzoic acid (0.66 g, 5.474 mmol), triphenylphosphine (1.435 g, 5.474 mmol), diethyl azodicarboxylate (0.85 mL, 5.474 mmol) were added and the mixture was stirred for 3 hours. After completion of the reaction, volatiles were evaporated in vacuo and the residue was subjected to column chromatography (hexane:ethyl acetate 80:20). This procedure resulted into a white solid of **(**3*S*,3a*R*,6*S*,6a*R*)-hexahydrofuro[3,2-*b*]-furan-3,6-diyl dibenzoate (8.5 g, 88 % ).




**$^{1}$H NMR** (200 MHz, $CDCl_3$, 298 K): δ = 8.06-8.01 (m, $4H_a$ ), 7.63-7.41 (m, $6H_b$ ), 5.52-5.51 (m, $2H_e$), 4.94-4.88 (m, $2H_d$), 4.13-4.12 (m, $4H_c$). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K): 165.3 (s, $C_a$), 133.2 (s, $C_b$), 130.0 (s, $C_c$), 129.5 (s, $C_d$), 128.3 (s, $C_e$), 85.4 (s, $C_f$), 77.8 (s, $C_g$), 72.5 (s, $C_h$).

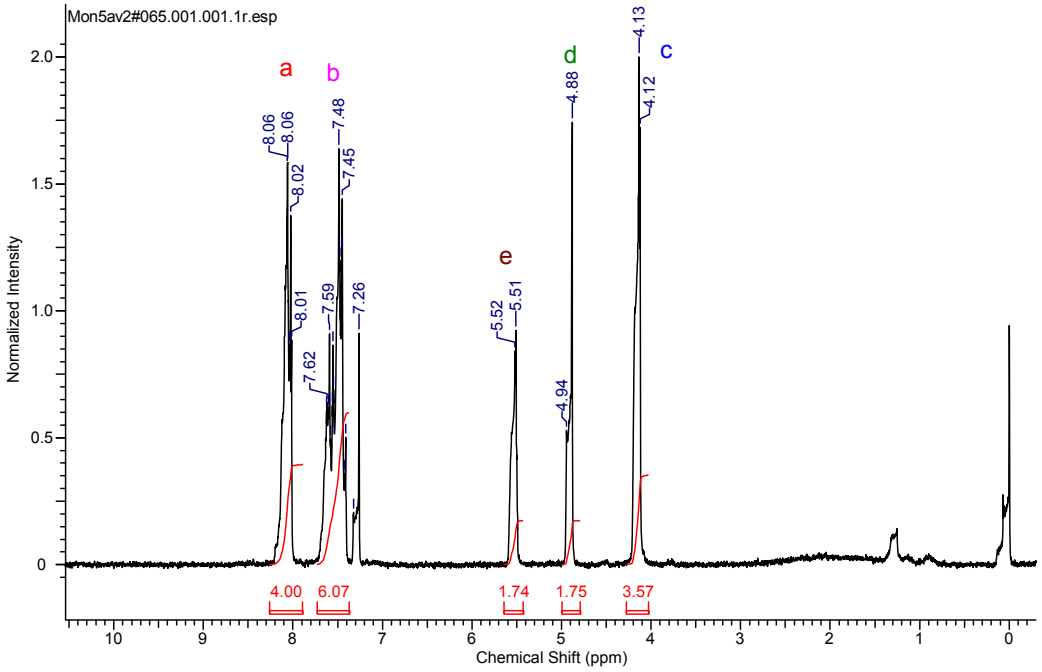
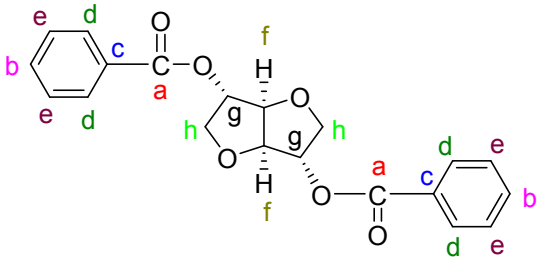
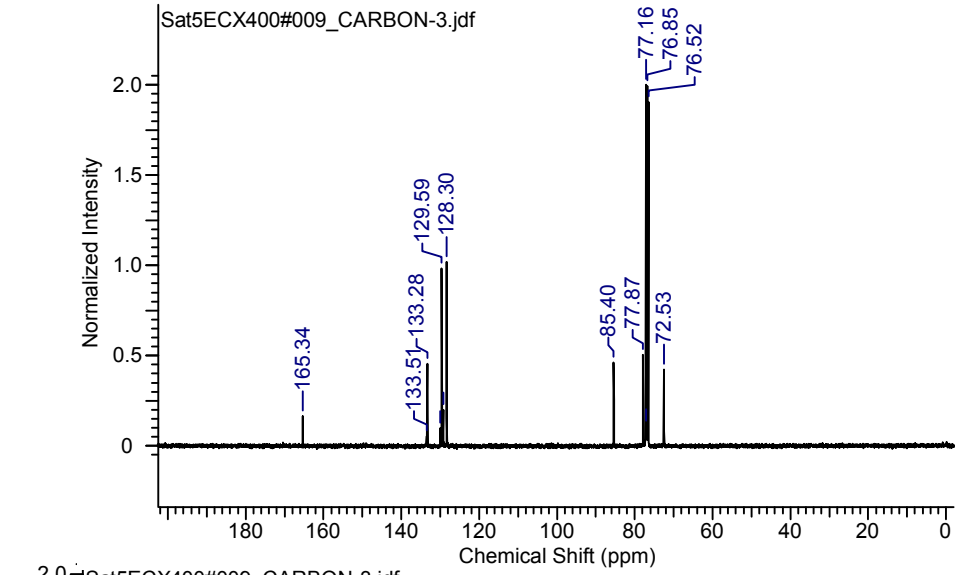
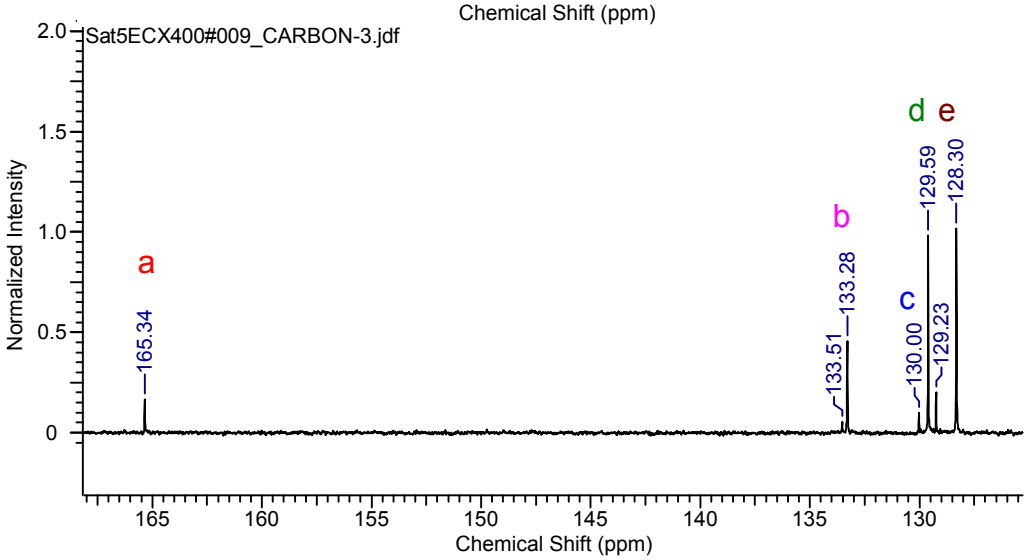



*Figure S23*. $^{1}$H NMR of (3*S*,3a*R*,6*S*,6a*R*)-hexahydrofuro[3,2-*b*]-furan-3,6-diyl dibenzoate in $CDCl_3$ (200 MHz at 298K).




Sat5ECX400#009_CARBON-3.jdf
Normalized Intensity
Chemical Shift (ppm)
165.34
133.51
133.28
129.59
128.30
85.40
77.87
77.16
76.85
76.52
72.53


Sat5ECX400#009_CARBON-3.jdf
Normalized Intensity
Chemical Shift (ppm)
a
b
c
d
e
165.34
133.51
133.28
130.00
129.23
129.59
128.30

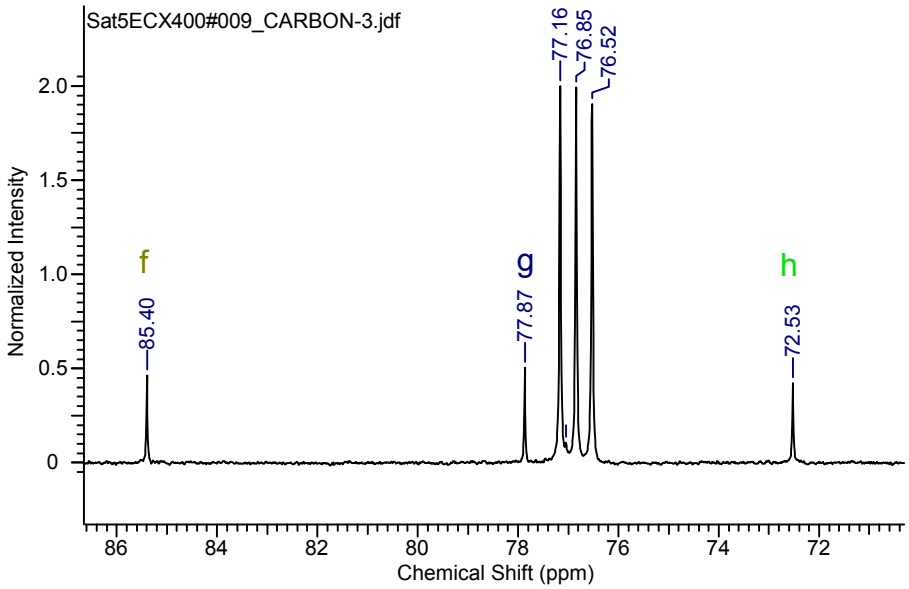
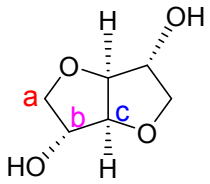

Sat5ECX400#009_CARBON-3.jdf
Normalized Intensity
Chemical Shift (ppm)
f
g
h
85.40
77.87
77.16
76.85
76.52
72.53

*Figure S24*. $^{13}C$ NMR of 3*S*,3a*R*,6*S*,6a*R*)-hexahydrofuro[3,2-*b*]-furan-3,6-diyl dibenzoate in $CDCl_3$ (400 MHz at 298K).

## B. Synthesis of isoidide {(3*S*,3a*R*,6*S*,6a*R*)-Hexahydrofuro[3,2-b] furon-3-6 diol} from the exo-dibenzoate :-




**Procedure:-** A methanol (200 ml) suspension of 3*S*,3a*R*,6*S*,6a*R*)-hexahydrofuro[3,2-*b*]-furan-3,6-diyl dibenzoate (4 g; 11.30 mmol) was gently heated (50-60 $^{o}$C for 2 h) and was allowed to cool to room temperature with constant stirring. Sodium methoxide (200 mg; 3.70 mmol) was added to the above solution and the reaction mixture was stirred for 22 hours at room temperature. The clear solution was neutralized with DOWEX (50 x 2) and filtered through a celite bed. The filtrate was diluted with dichloromethane (100 ml) and the organic phase was extracted with distilled water (3 x 50 ml). The combined methanol-water phase was concentrated in vacuo and the residue was subjected to column chromatography (dichloromethane/methanol 9:1) leading to semisolid product (1.3 g; 8.90mmol) 78 %.

**$^{1}$H NMR** (400 MHz, $D_2O$, 298 K): δ = 4.57 (s, $2H_b$), 4.28 (m, $2H_c$), 3.84-3.74 (dd, 9.96 Hz, $4H_a$). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K): δ = 86.37 (s, $C_b$), 74.67 (s, $C_c$), 73.75 (s, $C_a$).

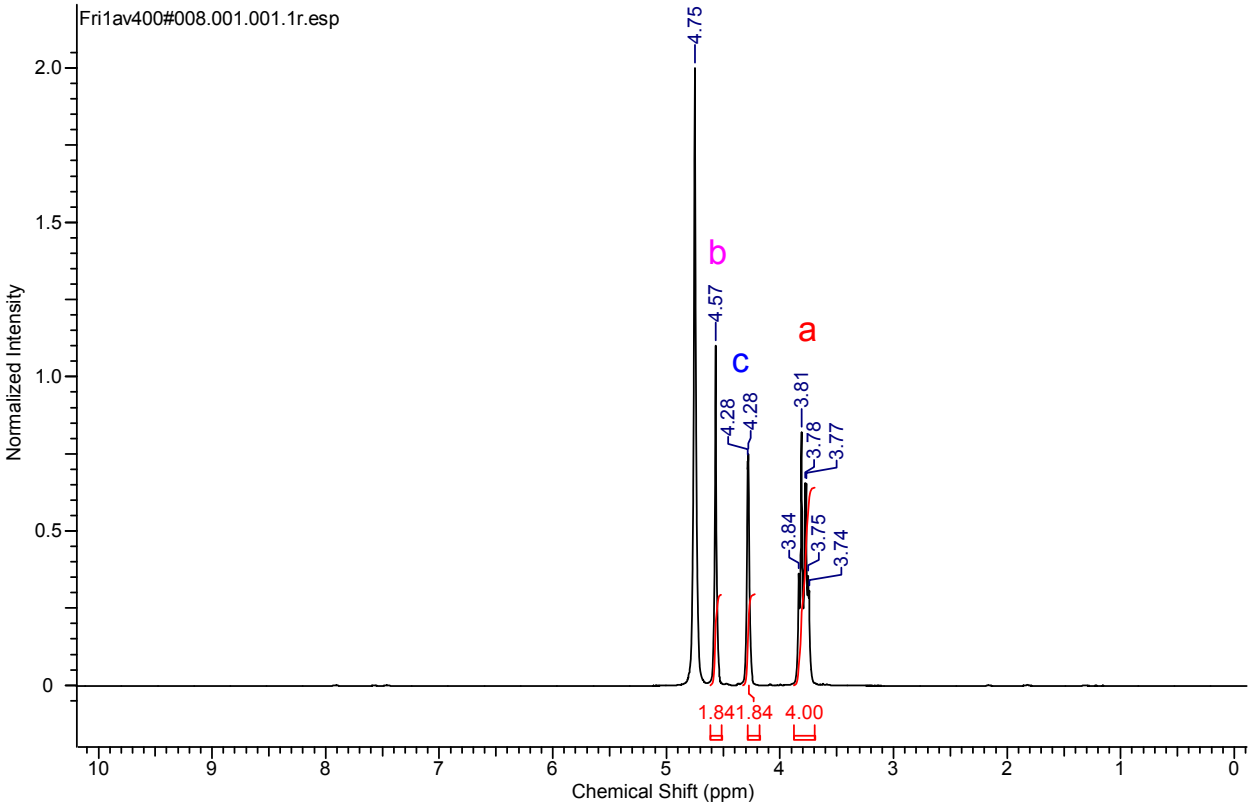



*Figure S25*. $^{1}$H NMR of compound **1c** in $D_2O$ (400 MHz at 298K).

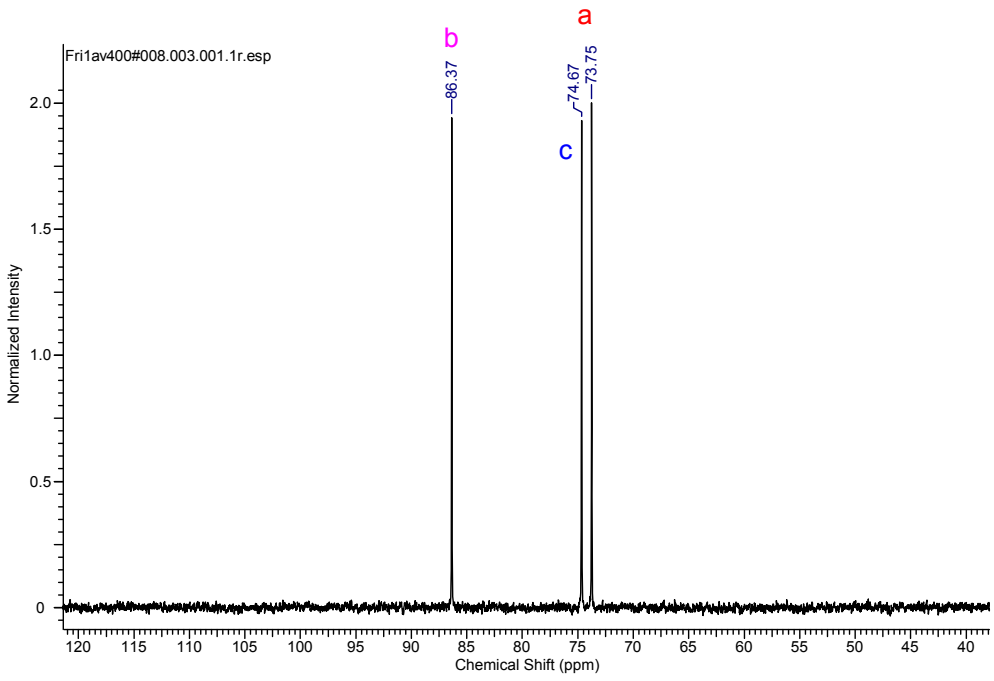


*Figure S26*. $^{13}C$ NMR of compound **1c** in $D_2O$ (400 MHz at 298K).

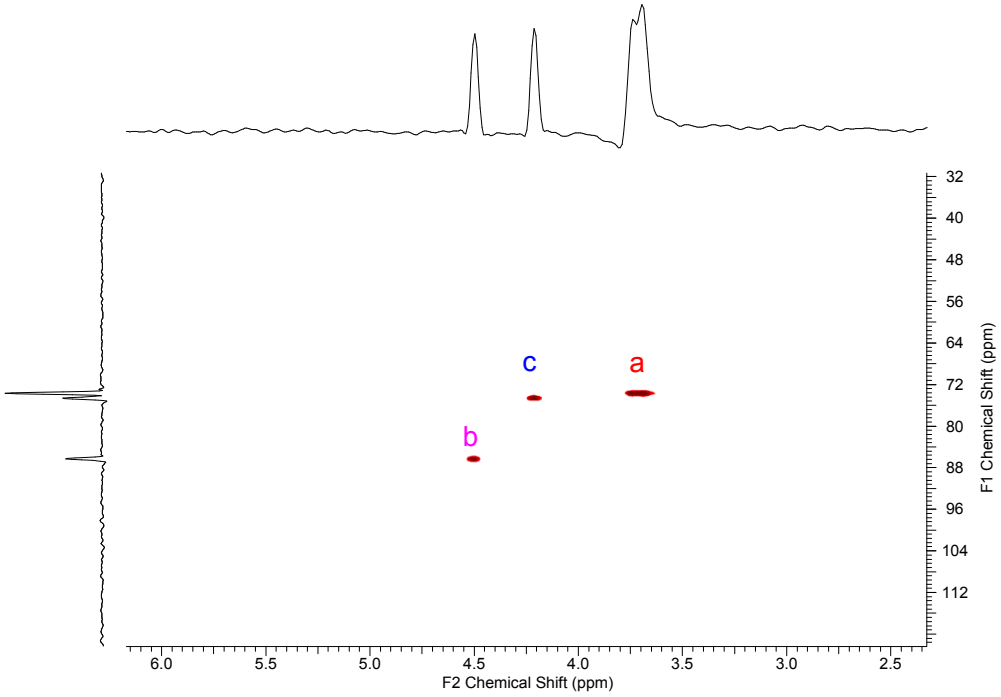
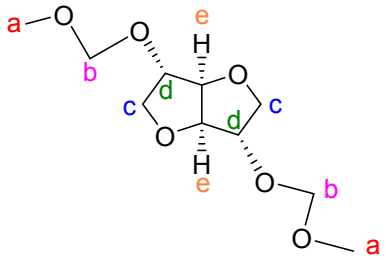



*Figure S27*. HSQC spectrum of compound **1c** in $D_2O$ (400 MHz at 298K).

# 6. Synthesis of isoidide-diacetal (2c)




**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K ) δ = 4.71 - 4.65 (dd, $4H_b$), 4.62 (m, $2H_e$), 4.20 (m, $2H_d$), 3.90-3.79 (m, $4H_c$), 3.36 (s, 6 $H_a$ ; **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K) δ = 95.6 (s, $C_b$), 85.9 (s, $C_e$), 80.8 (s, $C_d$), 72.5 (s, $C_c$), 55.5 (s, $C_a$). ESI-MS (+ve mode) Cal. m/z = 257.10

$[M+Na]^+$; Obs. m/z = 257.10 $[M+Na]^+$; Elemental analysis (%) calculated for $C_{10}H_{18}O_6$: C-51.23, H-7.69; Found: C-51.51, H-8.35, IR ($C_{10}H_{18}O_6$) $cm^{-1}$ 1150, 1078.

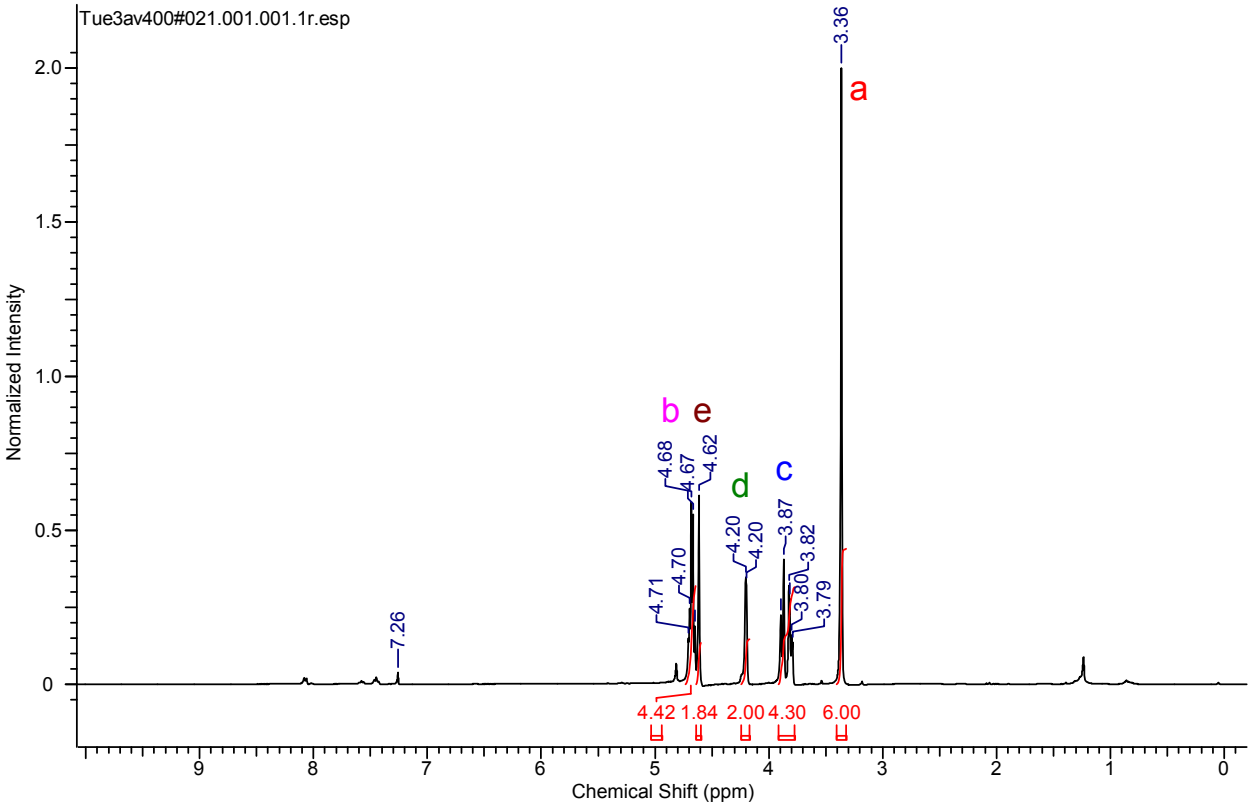



*Figure S28*. $^1$H NMR spectrum of compound **2c** in $CDCl_3$ (400 MHz at 298K).

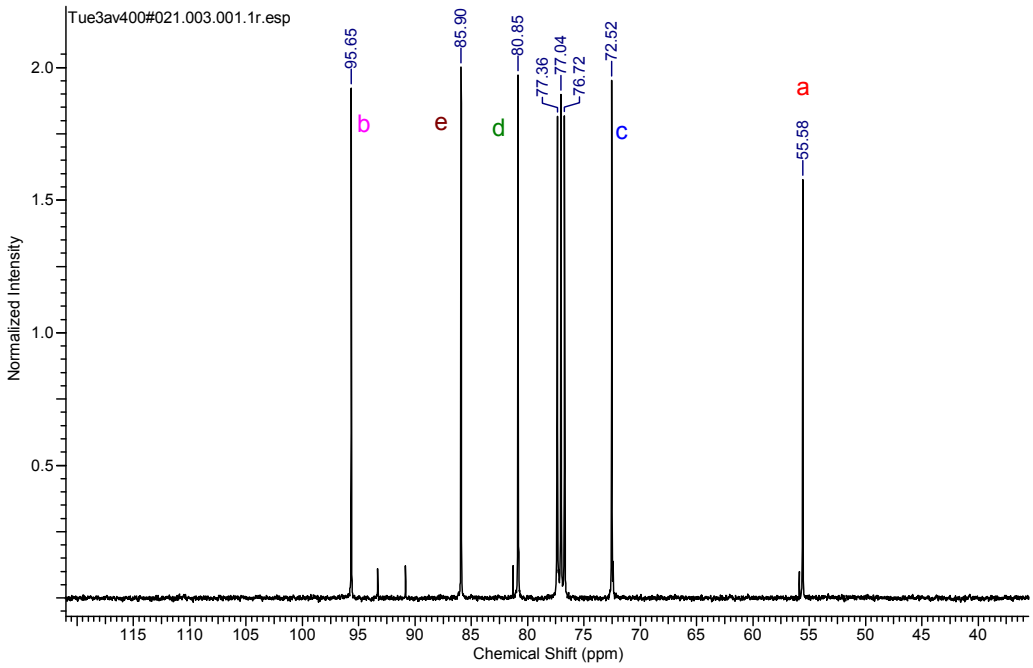



*Figure S29*. $^{13}$C NMR spectrum of compound **2c** in $CDCl_3$ (400 MHz at 298K).

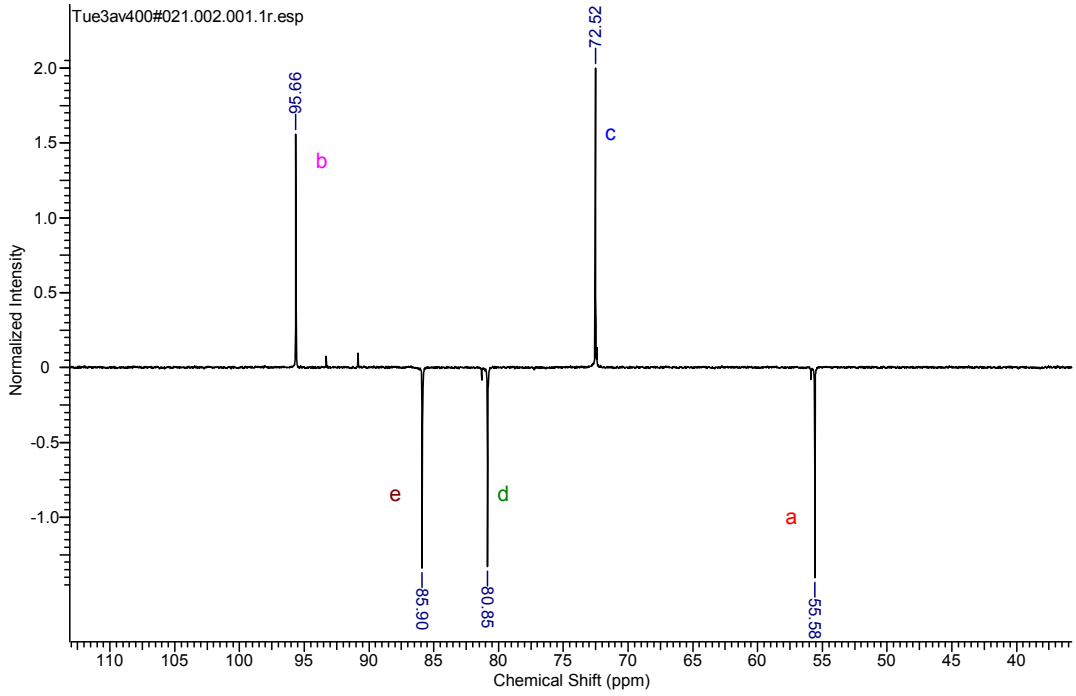



*Figure S30*. 135-DEPT NMR spectrum of compound **2c** in $CDCl_3$ (400 MHz at 298K).

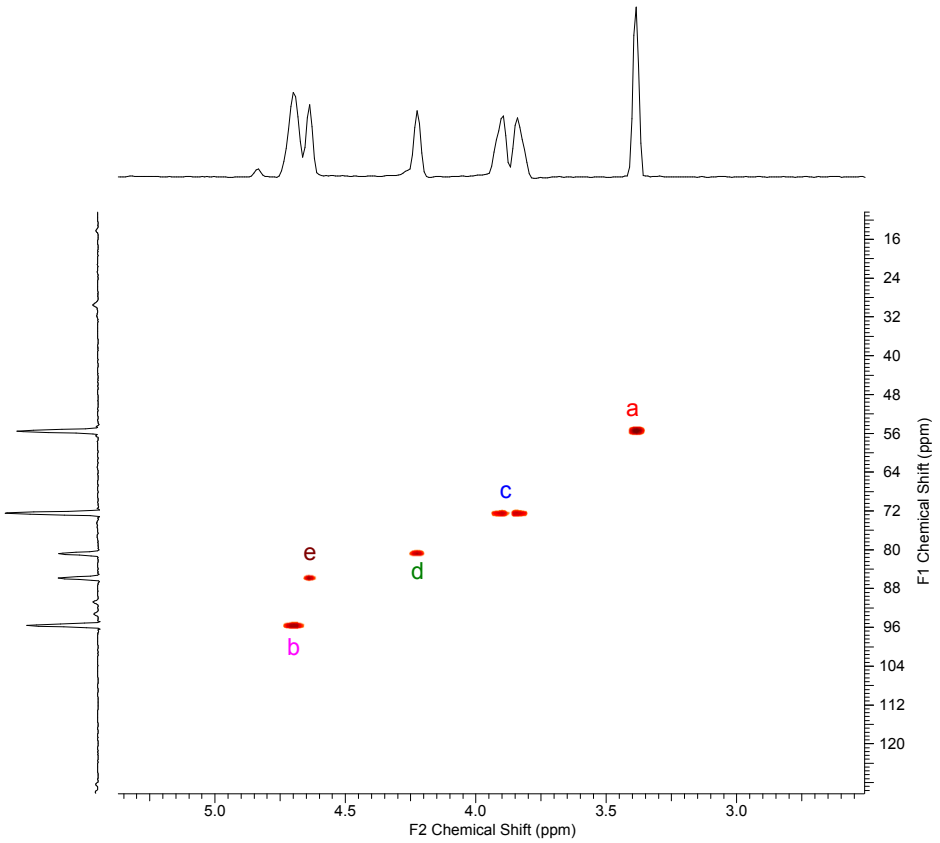



*Figure S31*. HSQC (C-H correlation) NMR spectrum of compound **2c** in $CDCl_3$ (400 MHz at 298K).

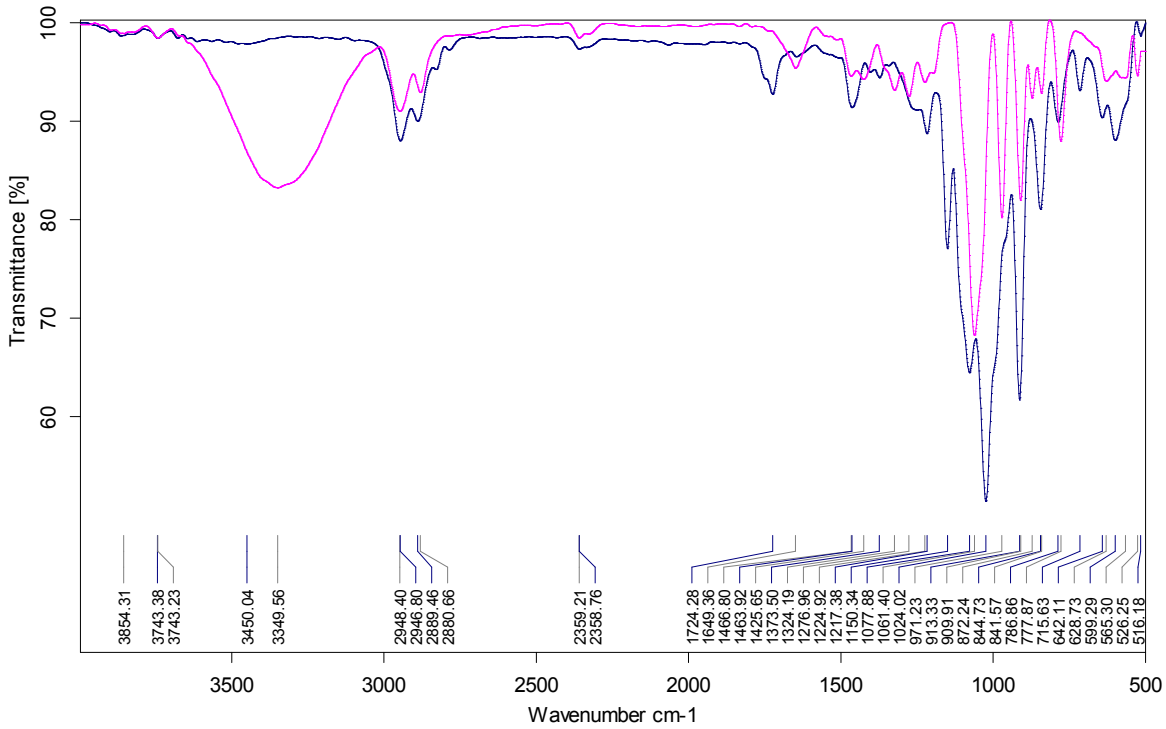



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*Figure S32*. Overlap of IR spectrum of **2c** (black) with the isoidide **1c** (pink).

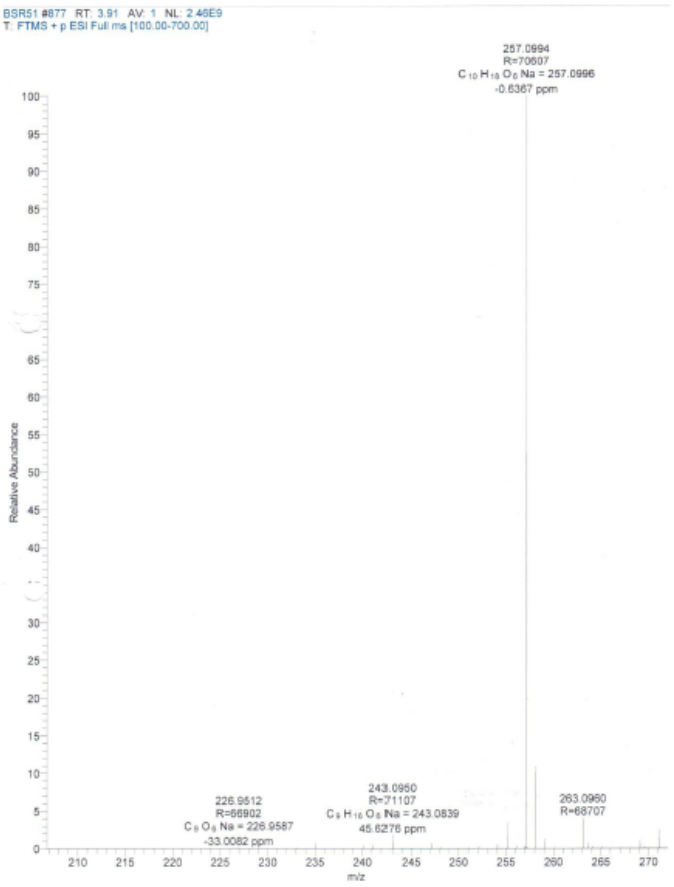



*Figure S33*. ESI-MS(+) spectrum of **2c** with a molecular ion peak $[M+Na]^+ = 257.1$ (100%) and 258.1 (10%).

## Polycondensation of isohexides 2a-c:

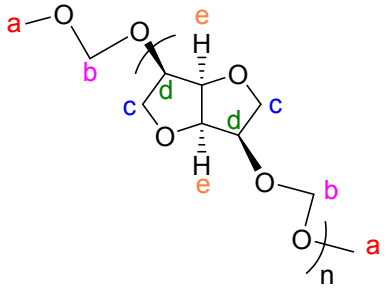
**Polycondensation Method A**: The polymerization was run in a 70 ml Schlenk tube equipped with air-tight high torque overhead mechanical stirrer. The **P2a-c** was prepared by heating neat **2a-c** with $_P$TSA at 60°C which was raised to 90/120/140 °C over a defined period. The byproduct (dimethoxymethane) was continuously removed on vacuum. The polymerization was terminated after desired time, the vessel was cooled down and the solid polymer was dissolved in minimum amount of chloroform. Re-precipitation from methanol produced desired polymers as white solid materials. See the following table S1 for polymerization details.

**Polycondensation Method B**: The polymerization was run in a 50 ml round bottom flask which was connected to rotary evaporator under argon. The polymer was prepared by heating neat **2a-c** with $_P$TSA at 60°C under argon flush, followed by increased temperature (70-140 $^oC$) over desired time under 0.01 mbar vacuum. The byproduct (dimethoxymethane) was continuously removed on vacuum. The polymerization was terminated after desired time, the vessel was cooled down and the solid polymer was dissolved in minimum amount of chloroform. Re-precipitation from methanol produced desired polymers as white solid materials. See the following table S1 for polymerization details.

**Table S1: Polymerization of isohexide diacetals under different polymerization conditions.**

| Run | Polymerization Condition |
|---|---|
| **P2a-2** Method B | Temperature was increased from 60°C-70°C over 25 mins. with a vacuum-argon purge cycles. This was followed by increase in temperature from 70°C-140°C with 0.01 mbar vacuum for next 35 mins to give solid polymer. |
| **P2a-3** Method A | Temperature was raised from 60°C-80°C for 15 min with regular vacuum-argon purge cycles. This was followed by increase in temperature from 80°C-130°C with 0.01 mbar vacuum for next 25 min resulting into solid mass. |
| **P2b-1** Method A | Temperature was raised from 60°C-90°C for 1 h with regular vacuum-argon purge cycles. This was followed by 0.01 mbar vacuum for next 2 h. Solid polymer was observed after cooling. |
| **P2b-3** Method A | Temperature was raised from 60°C-90°C for 1 h with regular vacuum-argon purge cycles. This was followed by 0.01 mbar vacuum for next 11 h. Solid polymer was observed after cooling. |
| **P2c-2** Method A | Temperature was raised from 60°C-80°C for 30 min with regular vacuum-argon purge cycles. This was followed by heating from 80°C-138°C under 0.01 mbar vacuum for next 30 mins. leading to solid polymer material. |
| **P2c-3** Method A | Polymerization was started at 60°C under argon atmosphere. In the first step the reaction vessel was heated from 60°C-80°C for 30 min with regular vacuum-argon purge cycles. This was followed by heating from 80°C-117°C under 0.01 mbar vacuum for next 30 mins. Finally the polymer was obtained as solid material. |

# 7. Polycondensation of isomannide-diacetal to P2a-1:




**$^{1}$H NMR** (400 MHz, $CDCl_3$, 298 K) δ = 4.84 - 4.83 (m, 94$H_b$), 4.54-4.51 (m, 103$H_e$), 4.28-4.25 (m, 102$H_d$), 4.05-3.93 (m, 105$H_c$), 3.67 -3.61 (m, 101$H_c$), 3.37 (s, 6$H_a$). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K) δ = 96.0-95.0 (s, $C_b$), 81.6-80.7 (s, $C_e$), 78.1-77.9 (s, $C_d$), 74.6 (s, $C_c$), 72.3 (s, $C_d$) 70.9 (s, $C_c$), 55.7 (s, $C_a$).

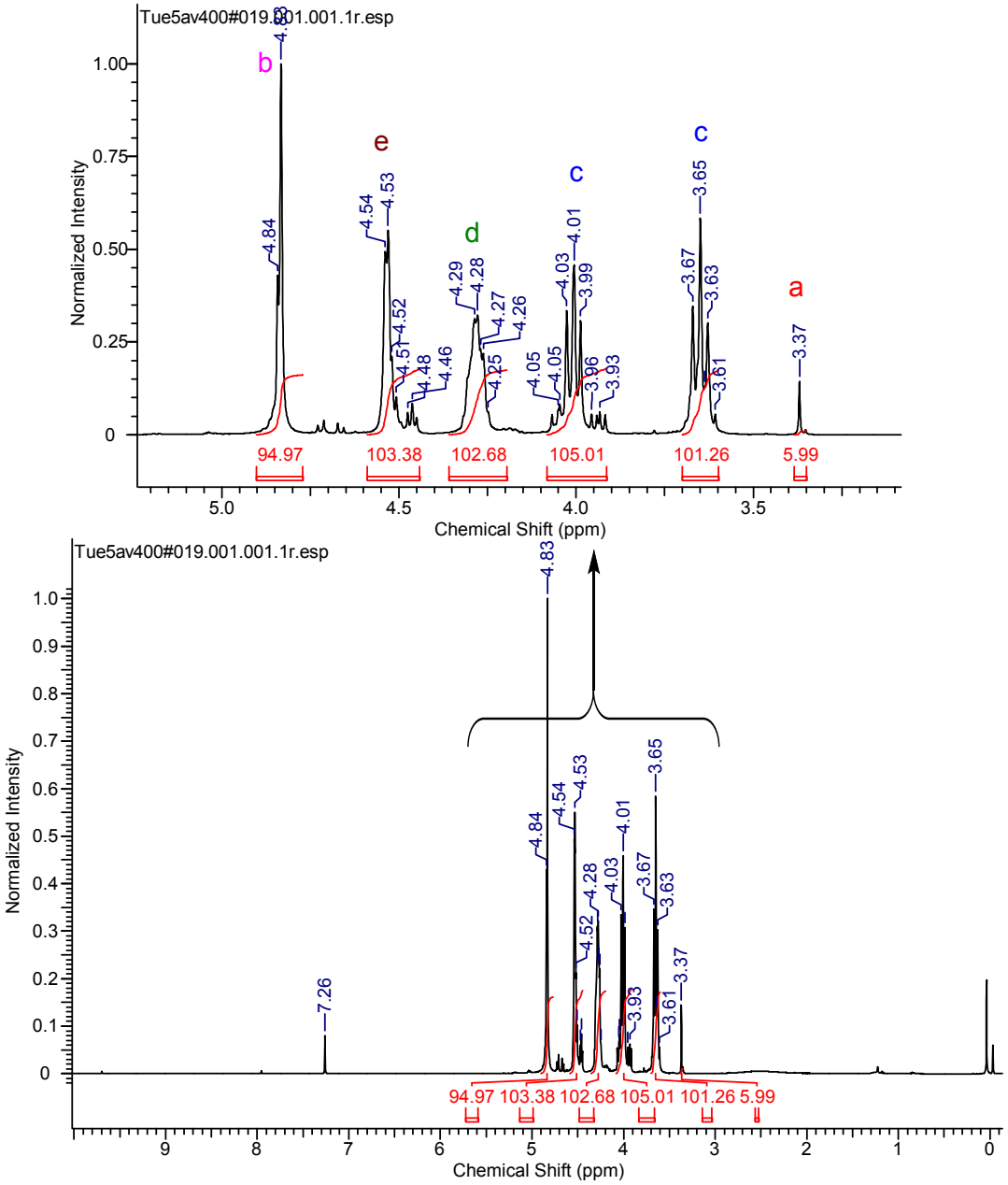



*Figure S34*. $^{1}$H NMR spectrum of **P2a-1** in $CDCl_3$ (400 MHz at 298K).

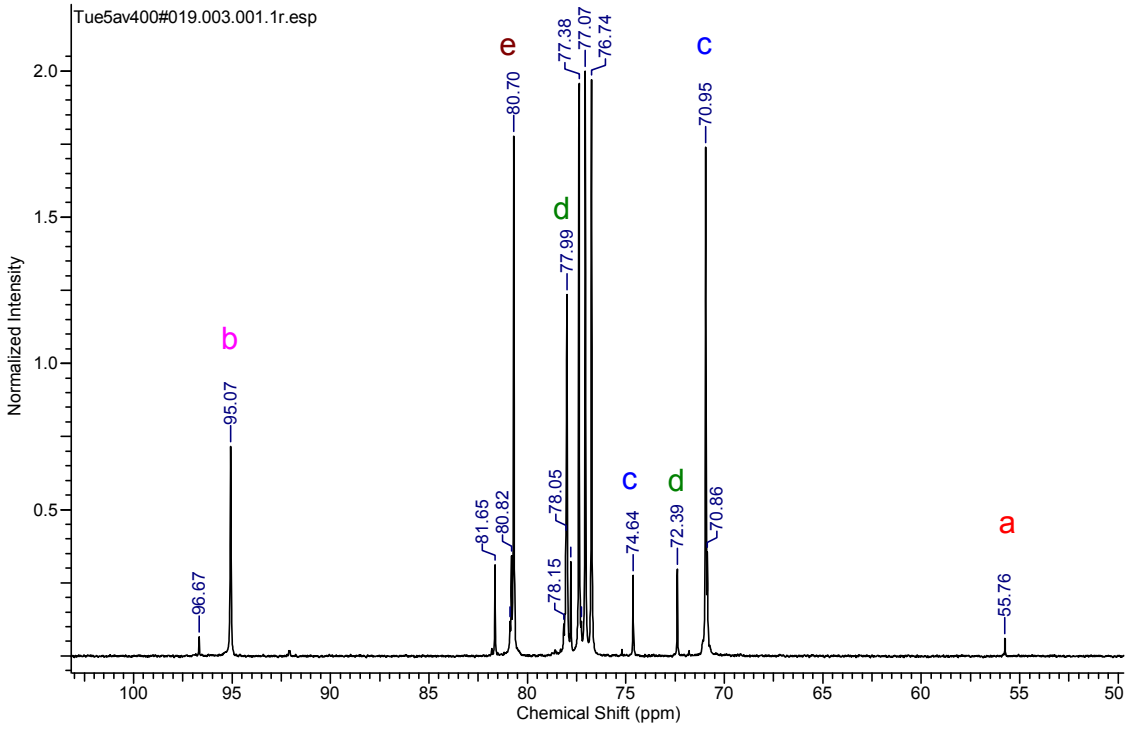



*Figure S35*. $^{13}$C NMR spectrum of **P2a-1** in $CDCl_3$ (400 MHz at 298K).

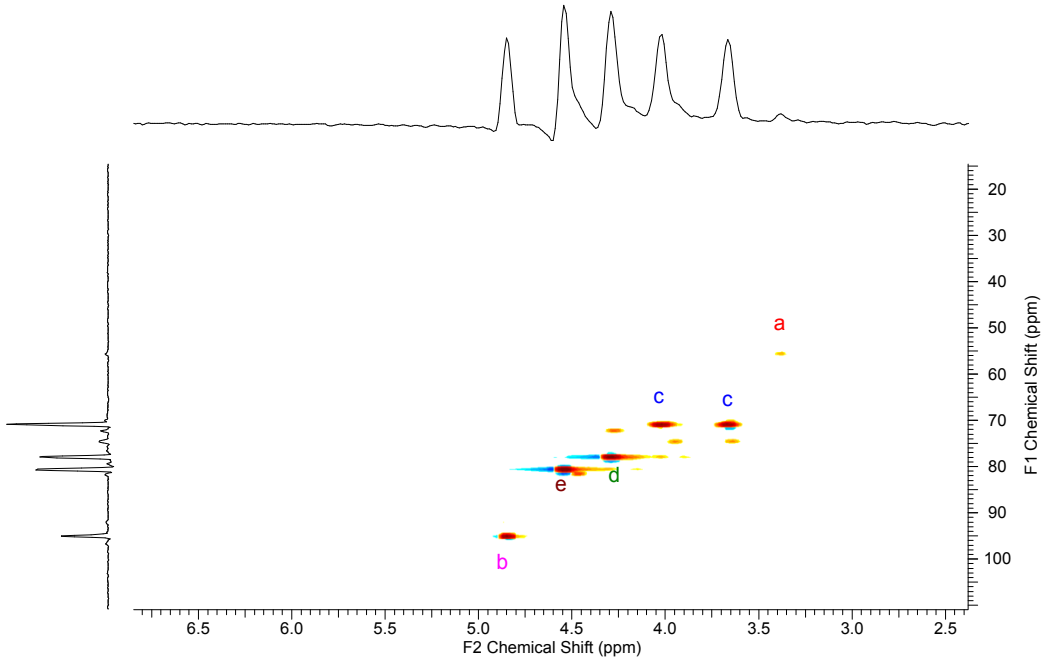



*Figure S36*. HSQC ($^1J_{C\text{-}H}$ correlation) NMR spectrum of **P2a-1** in $CDCl_3$ (400 MHz at 298K).

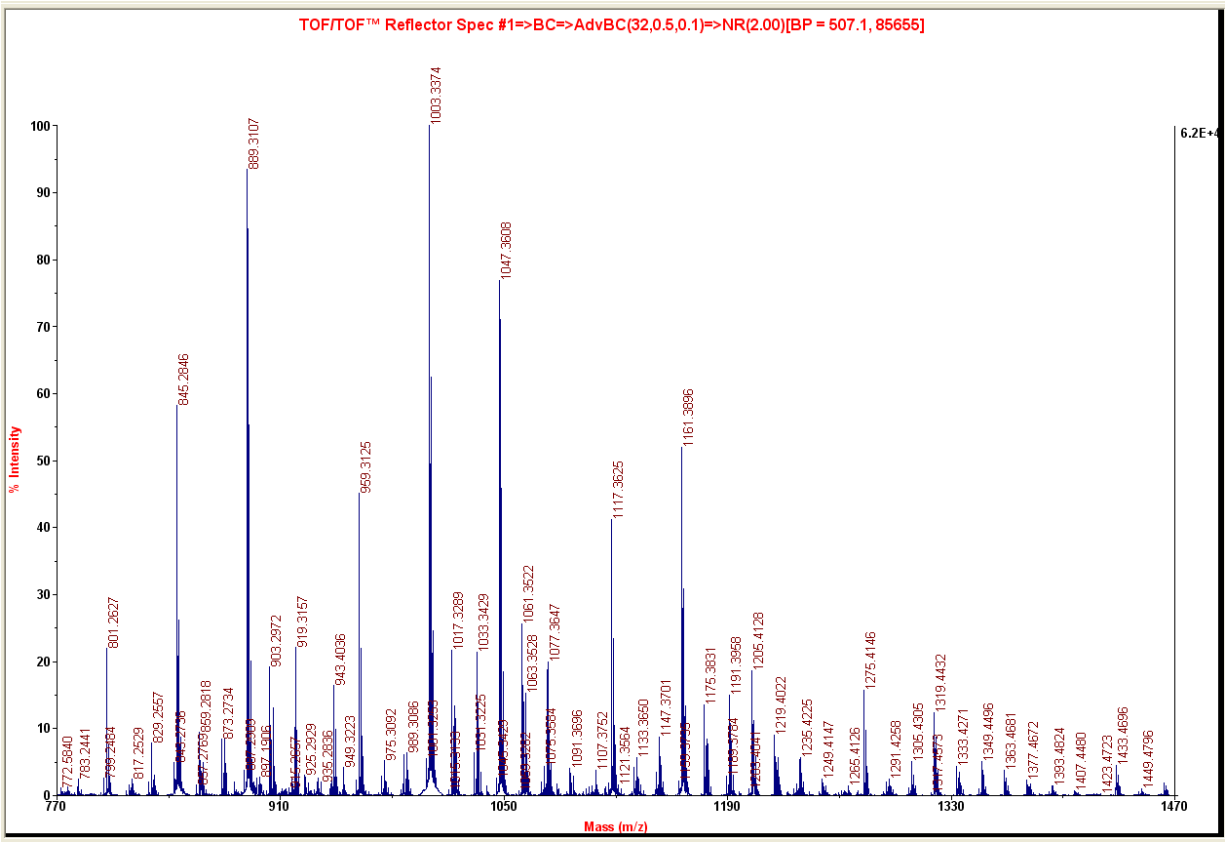



*Figure S37*. MALDI-ToF-MS spectra of **P2a-1** displaying a repeat unit of 158Da (1161-1003; 1117-959; 1047-889).

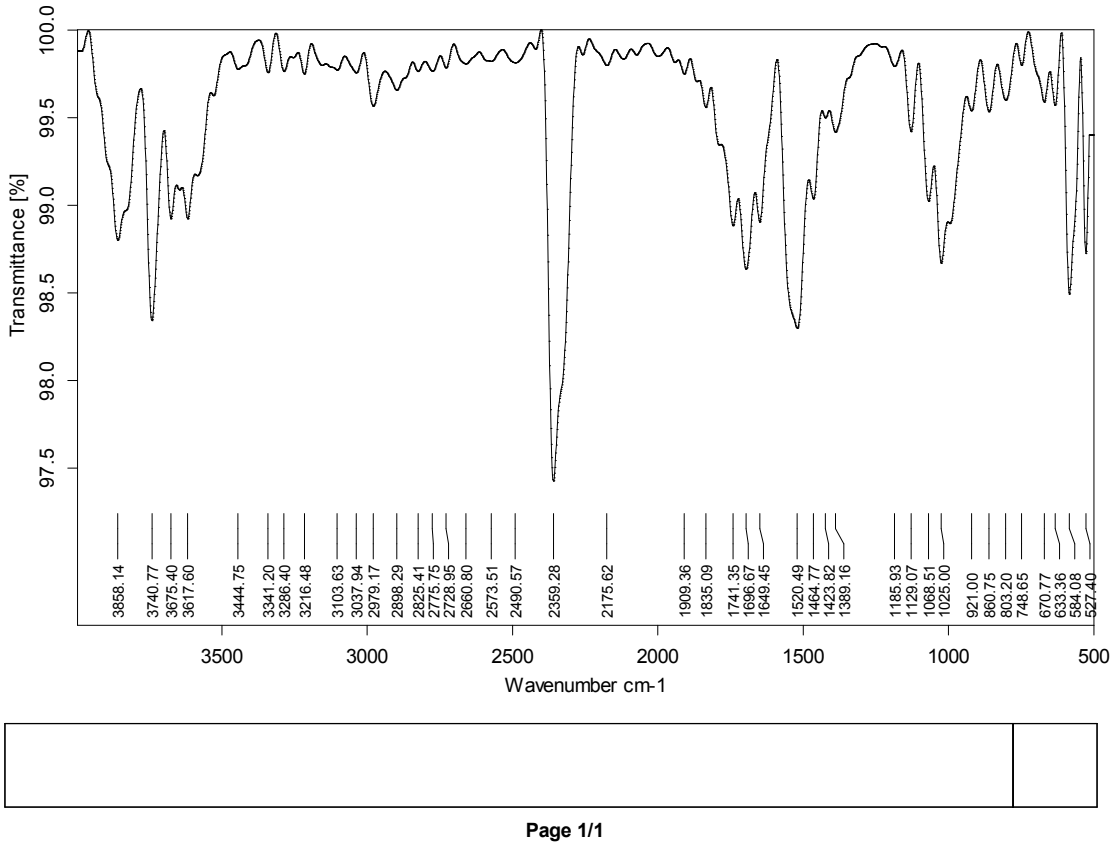



*Figure S38*. IR spectrum of **P2a-1**.

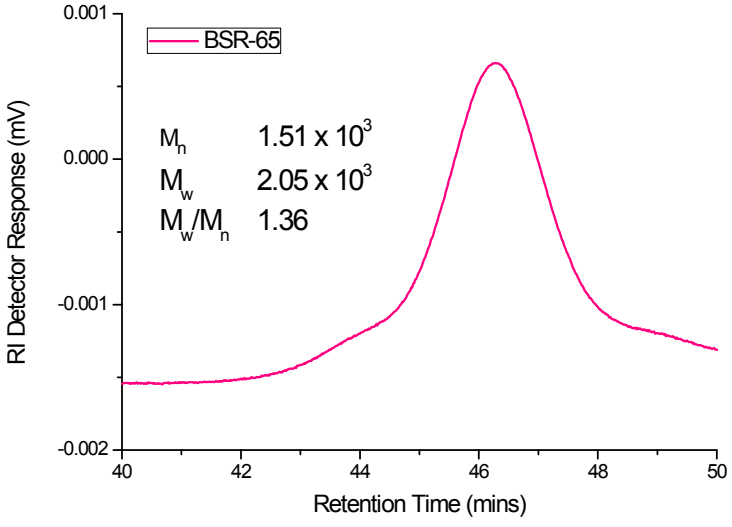



*Figure S39a*. GPC chromatogram of **P2a-1** (in chloroform at room temperature).

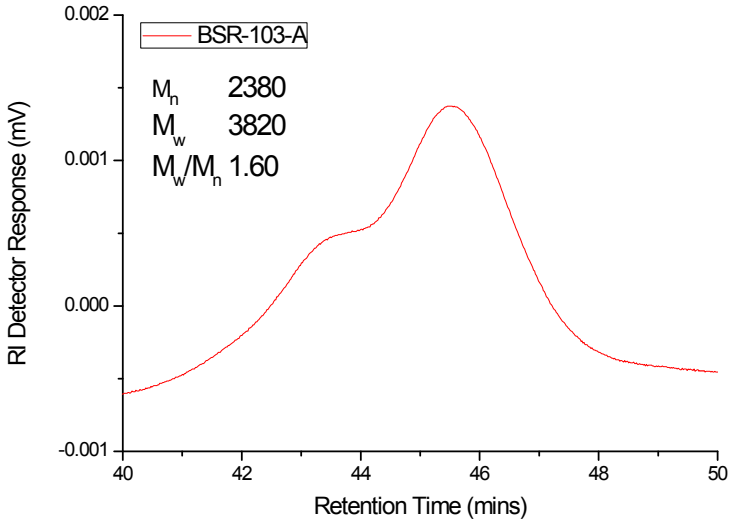



*Figure S39b*. GPC chromatogram of **P2a-2** (in chloroform at room temperature).

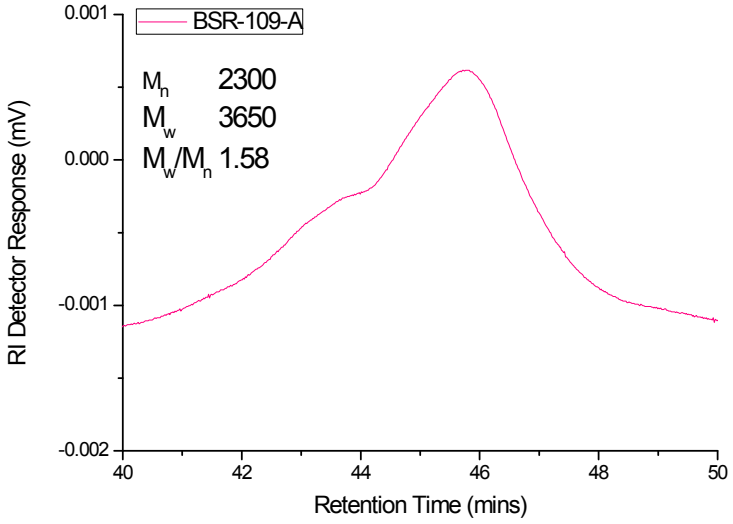
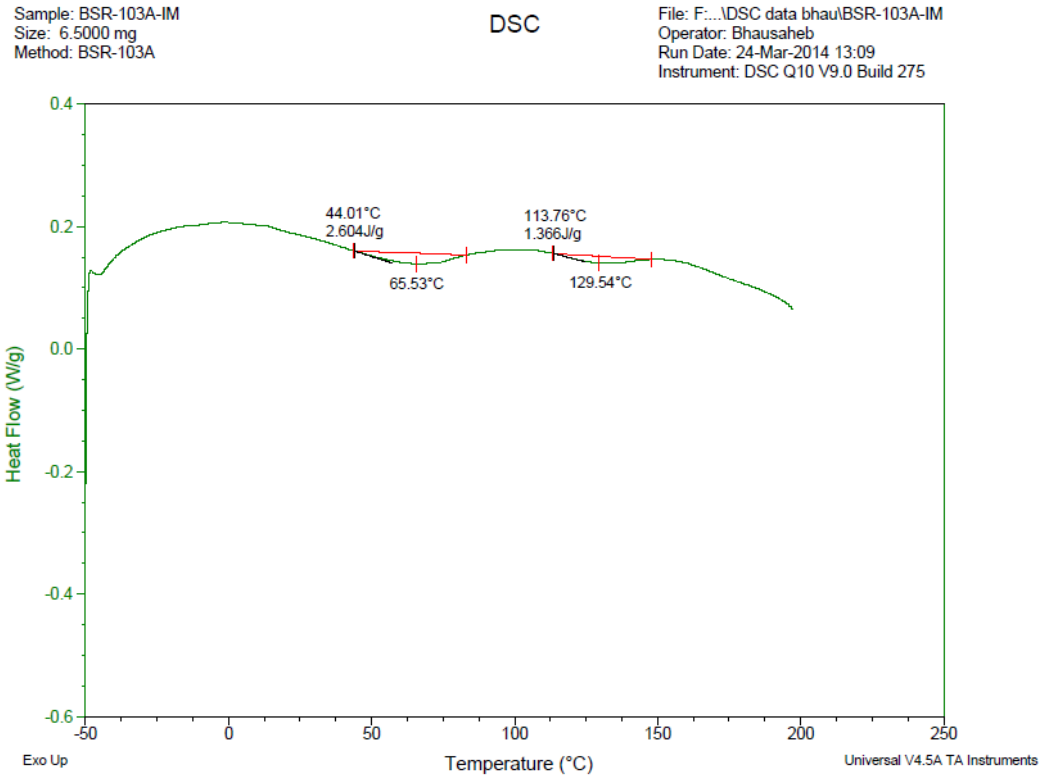



*Figure S39c*. GPC chromatogram of **P2a-3** (in chloroform at room temperature).


Sample: BSR-103A-IM
Size: 6.5000 mg
Method: BSR-103A
DSC
File: F:...\DSC data bhau\BSR-103A-IM
Operator: Bhausaheb
Run Date: 24-Mar-2014 13:09
Instrument: DSC Q10 V9.0 Build 275
44.01°C
2.604J/g
65.53°C
113.76°C
1.366J/g
129.54°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

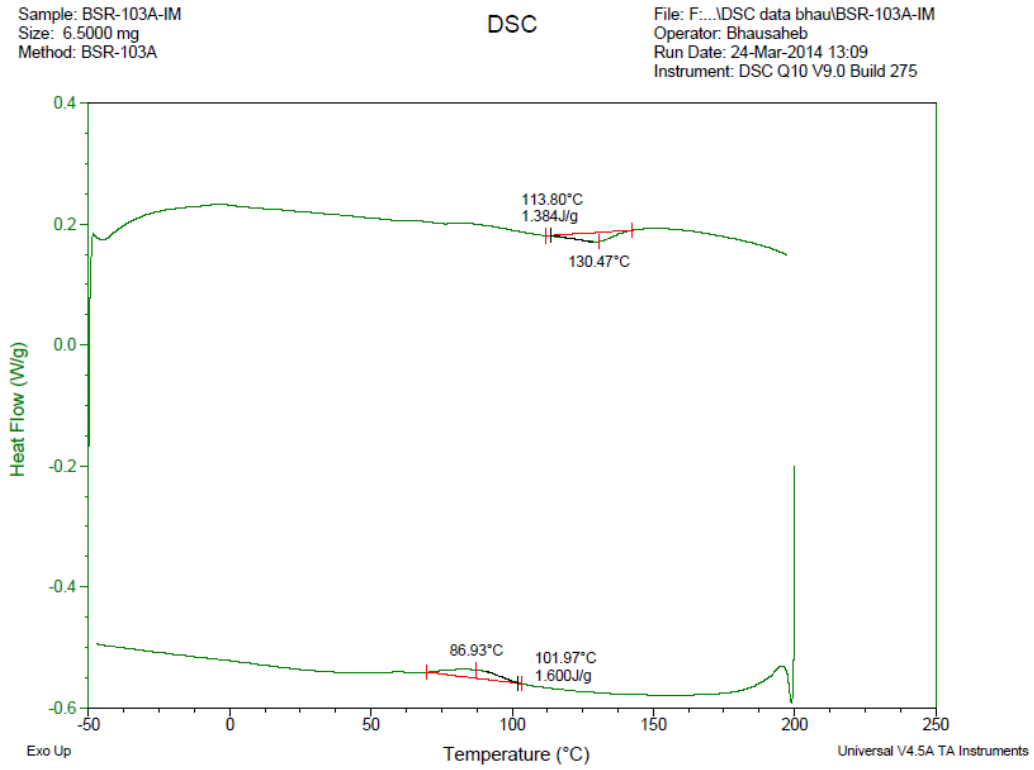

Sample: BSR-103A-IM
Size: 6.5000 mg
Method: BSR-103A
DSC
File: F:...\DSC data bhau\BSR-103A-IM
Operator: Bhausaheb
Run Date: 24-Mar-2014 13:09
Instrument: DSC Q10 V9.0 Build 275
113.80°C
1.384J/g
130.47°C
86.93°C
101.97°C
1.600J/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

*Figure S40*. DSC heating and cooling curves of **P2a-2;** first heating (top), cooling and second heating (bottom).

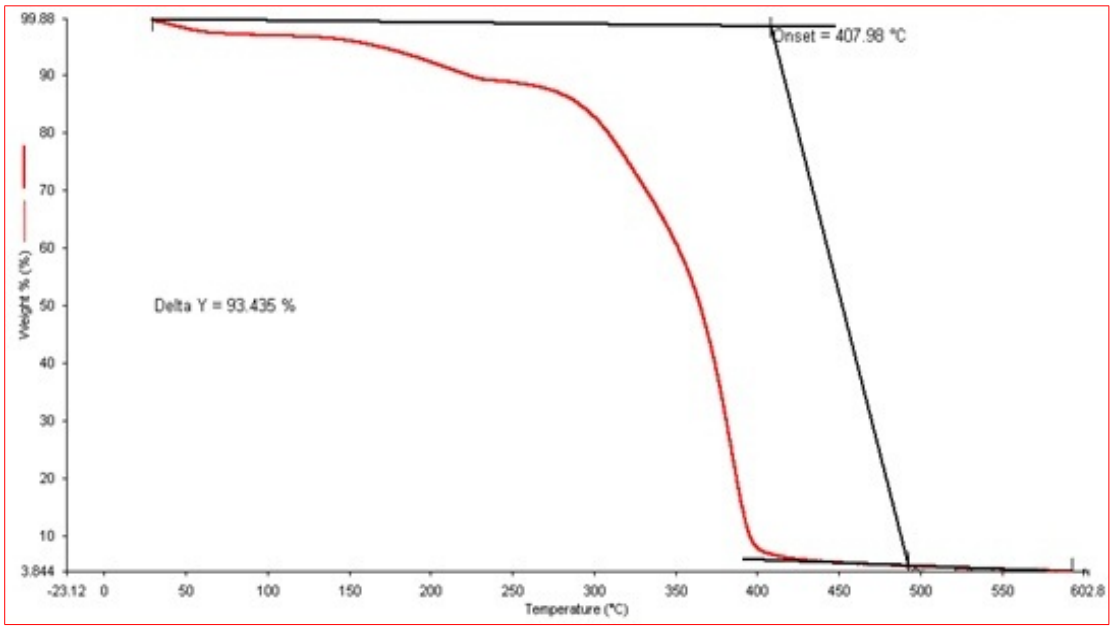



*Figure S41*. TGA trace of **P2a-1** recorded between 0-600°C in $N_2$ atmosphere.

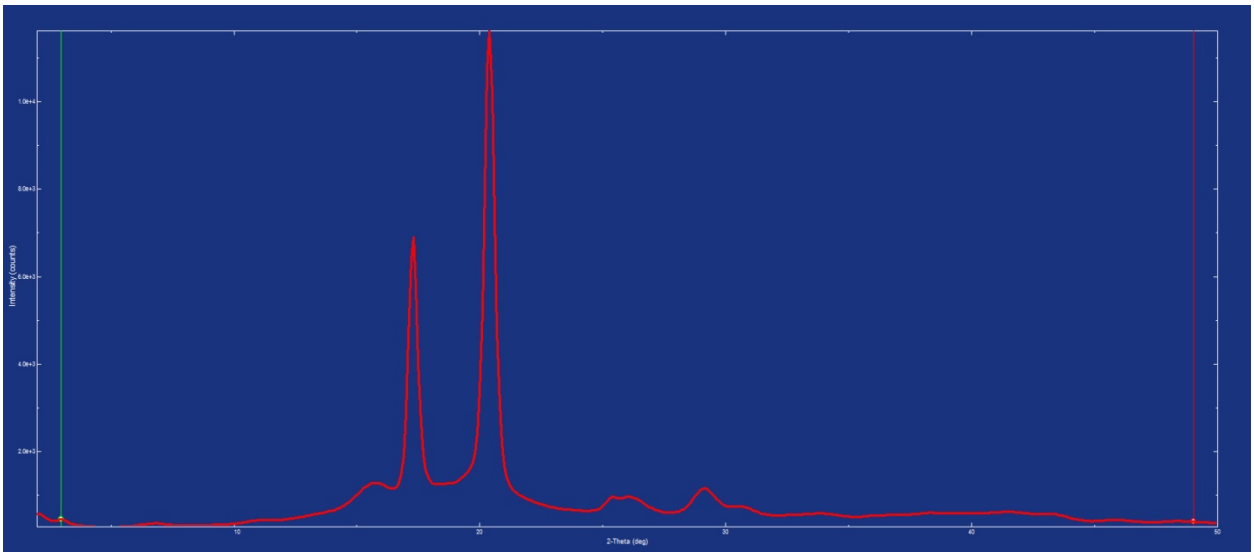
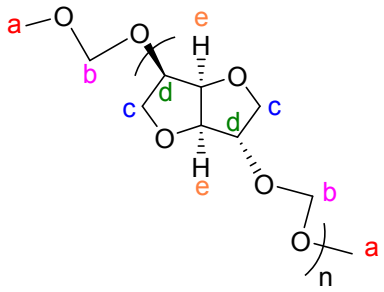


*Figure S42*. X-ray powder diffraction profile of **P2a-1**.

## 8. Polycondensation of isosorbide-diacetal to P2b-2:




**$^{1}$H NMR** (400 MHz, $CDCl_3$, 298 K) δ = 4.85 - 4.75 (m, 342$H_b$), 4.62-4.59 (m, 185$H_e$), 4.46 (m, 173$H_d$), 4.30-4.17 (m, 347$H_{e,d}$) , 3.95 -3.92 (m, 527$H_c$), 3.60-3.52 (m, 176$H_c$), 3.38-3.34 (s, 6$H_a$). **$^{13}$C NMR** (400 MHz, $CDCl_3$, 298 K) δ = 94.9-93.3 (s ,$C_b$), 88.0 (s, $C_e$), 86.2-86.1 (s, $C_d$), 81.9-80.7 (s, $C_e$), 78.2-78.0 (s, $C_d$), 73.4 (s, $C_c$), 69.8 (s, $C_c$).

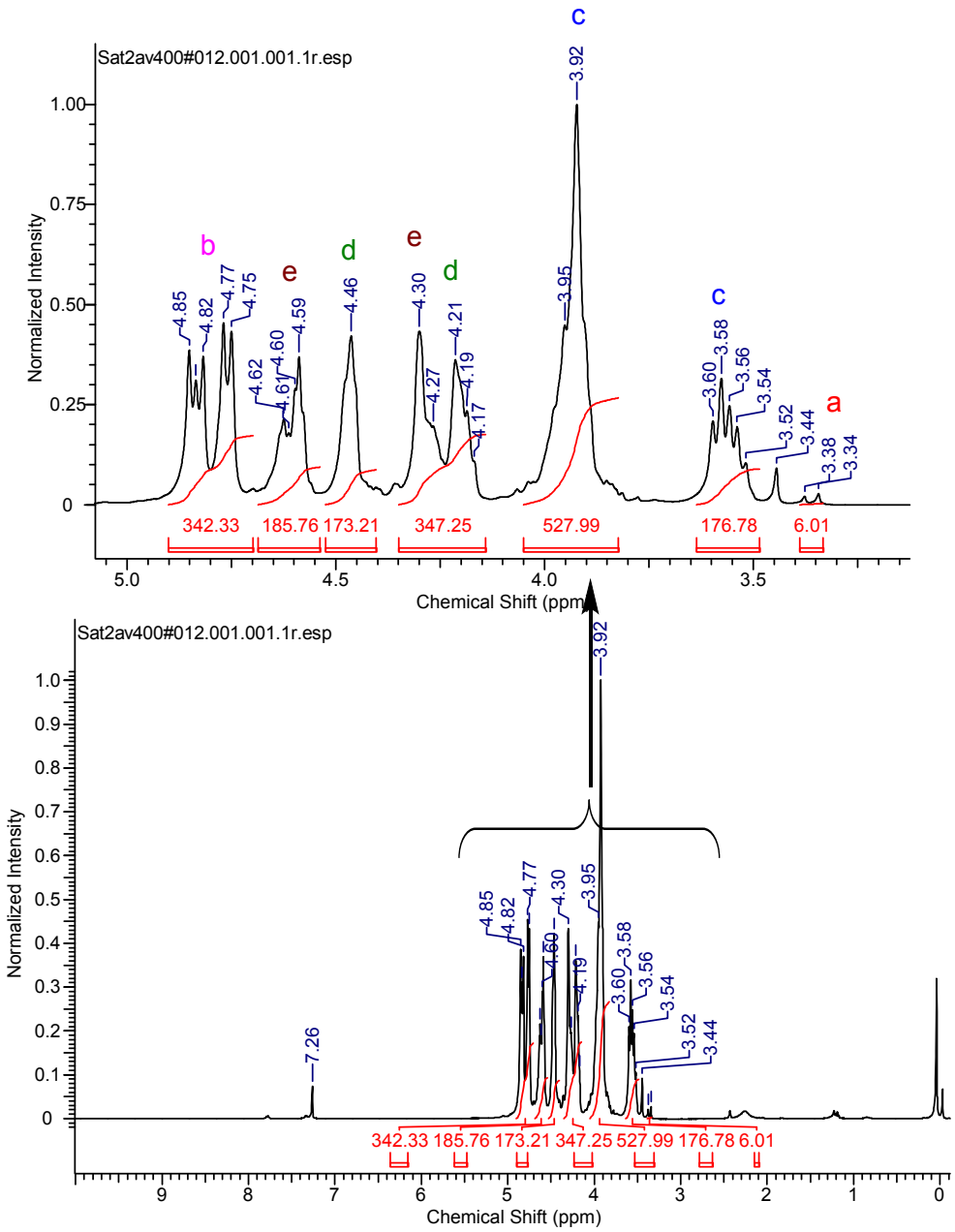



*Figure S43*. $^{1}$H NMR spectrum of **P2b-2** in $CDCl_3$ (400 MHz at 298K).

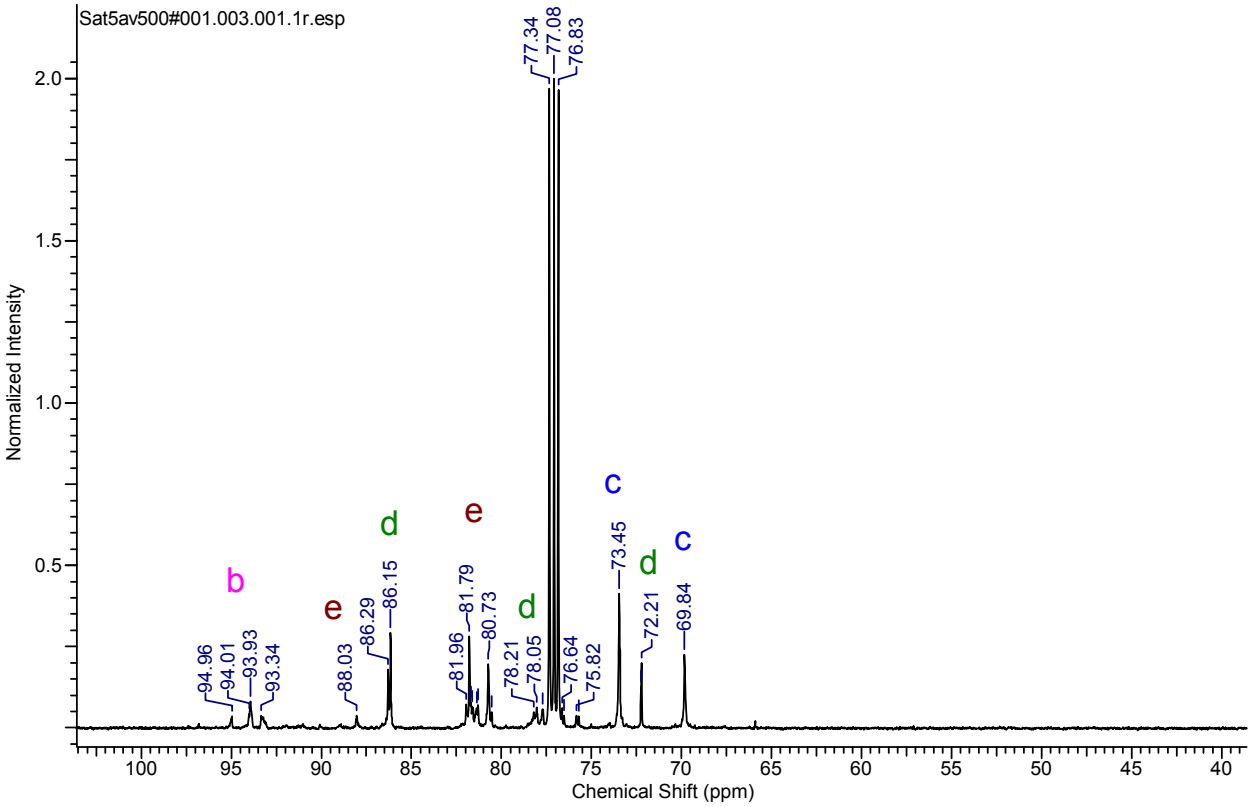



*Figure S44*. $^{13}$C NMR spectrum of **P2b-2** in $CDCl_3$ (400 MHz at 298K).

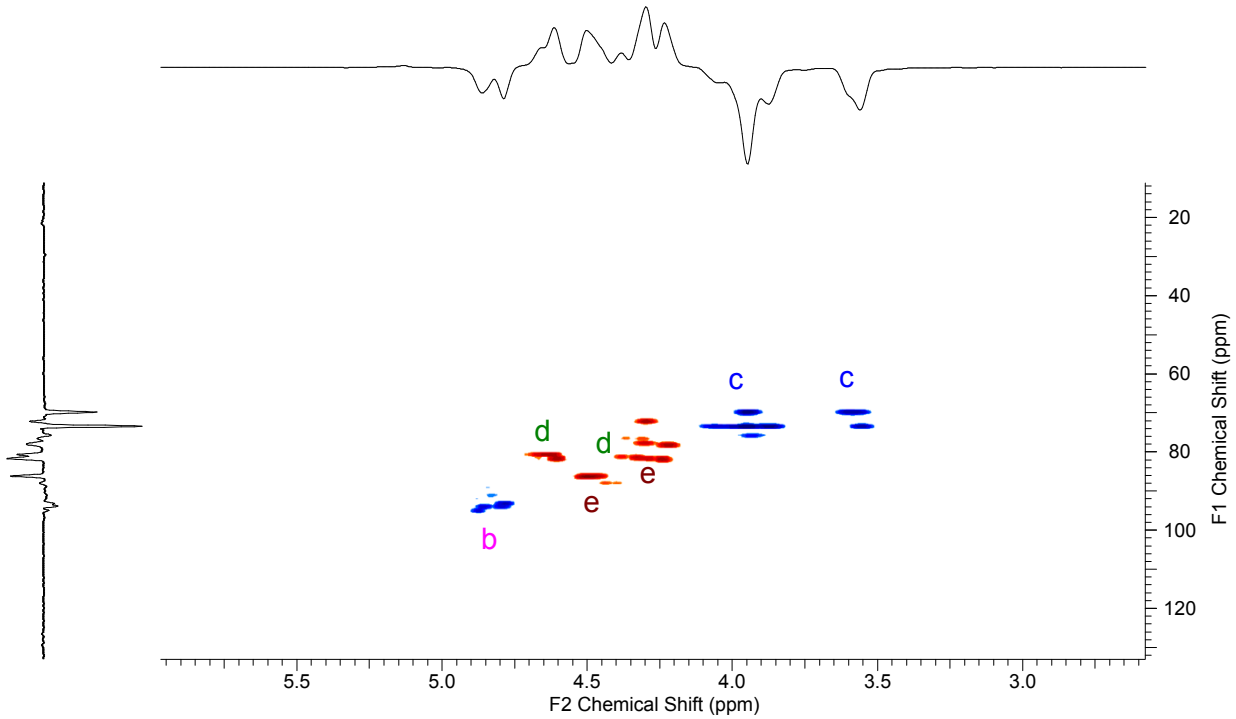


*Figure S45*. HSQC ($^{1}J_{C\text{-}H}$ correlation) NMR spectrum of **P2b-2** in $CDCl_3$ (400 MHz at 298K).

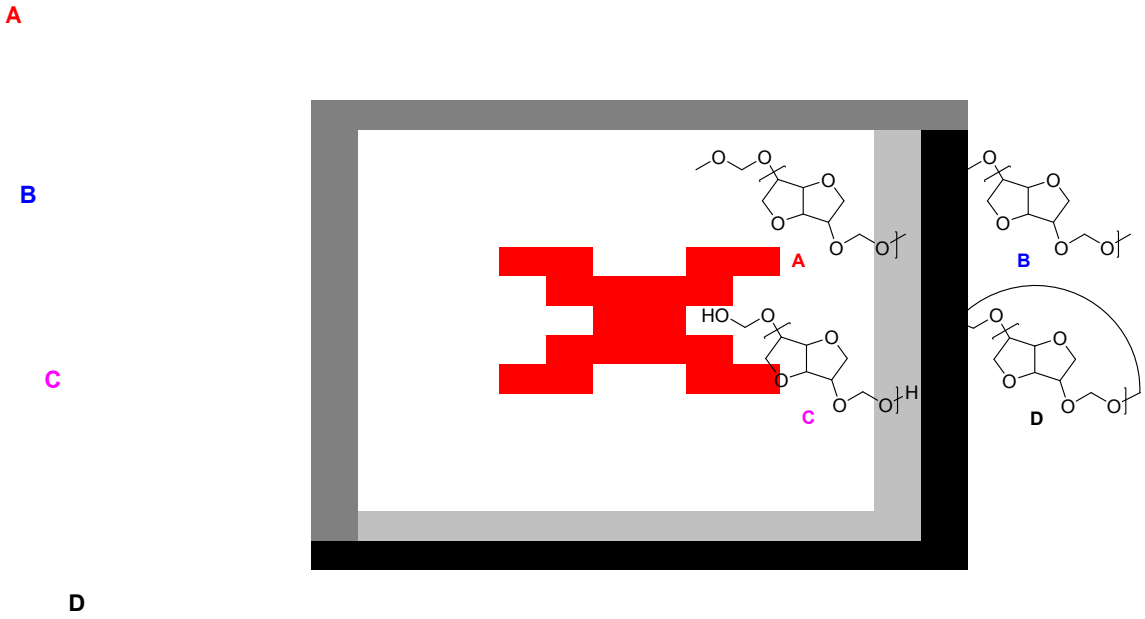



*Figure S46*. MALDI-ToF-MS spectra of **P2b-2**.

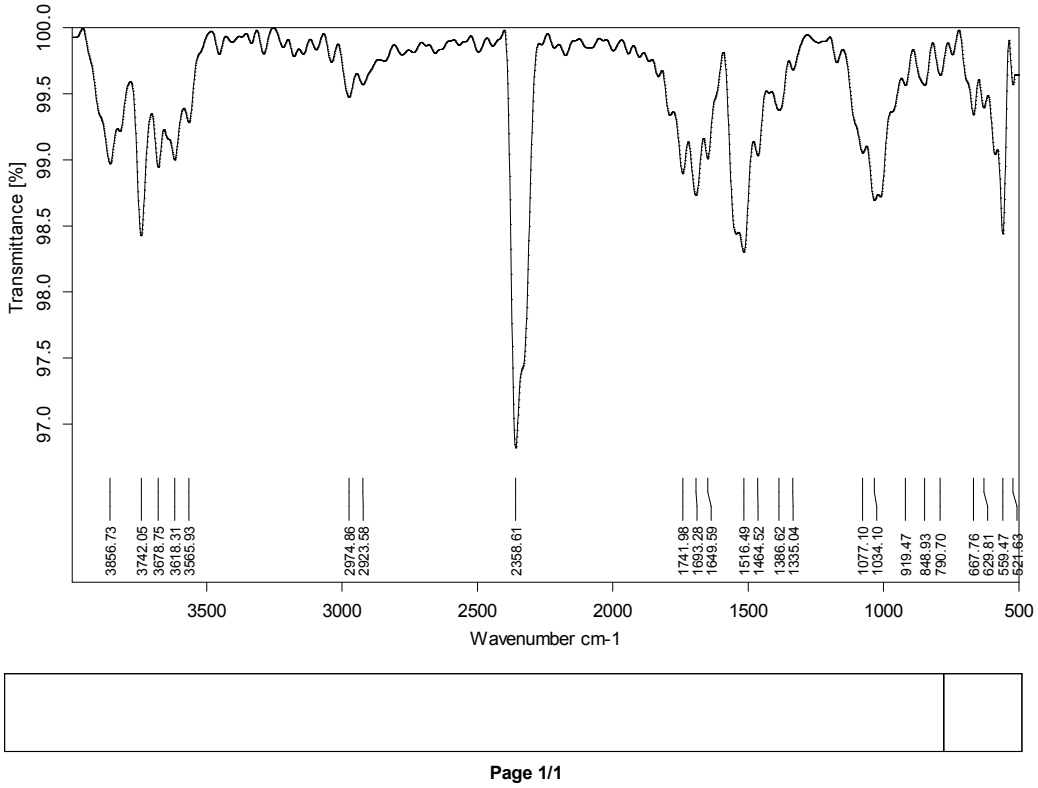



*Figure S47*. IR spectrum of **P2b-2**.

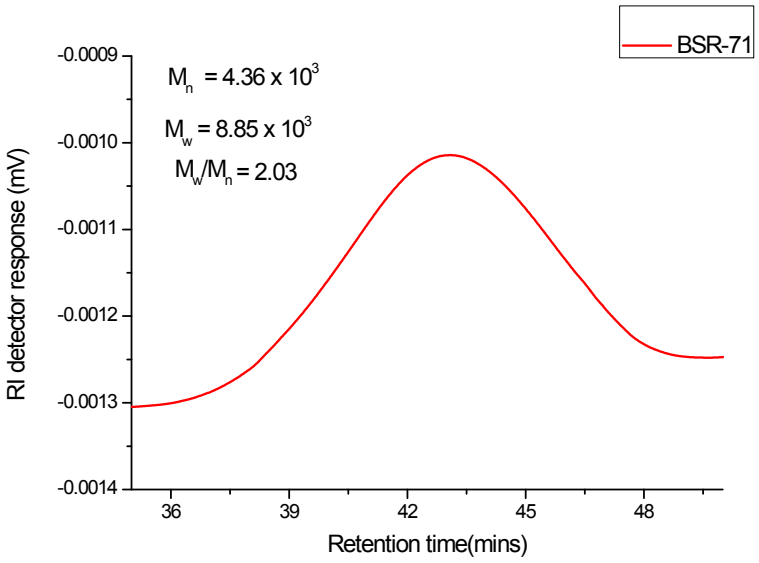



*Figure S48a*. GPC chromatogram of **P2b-2** (in chloroform at room temperature).

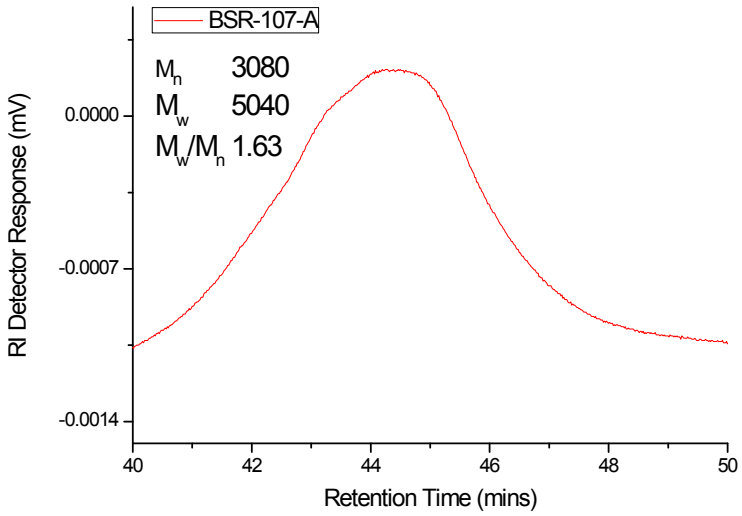



*Figure S48b*. GPC chromatogram of **P2b-1** (in chloroform at room temperature).

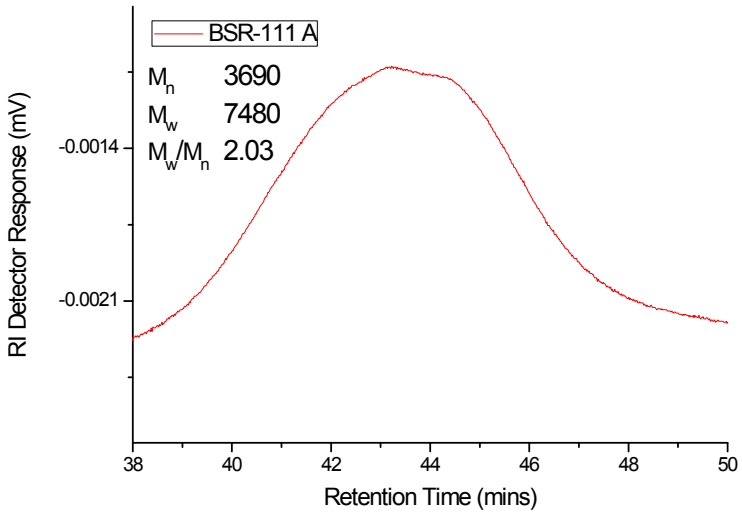



*Figure S48c*. GPC chromatogram of **P2b-3** (in chloroform at room temperature).

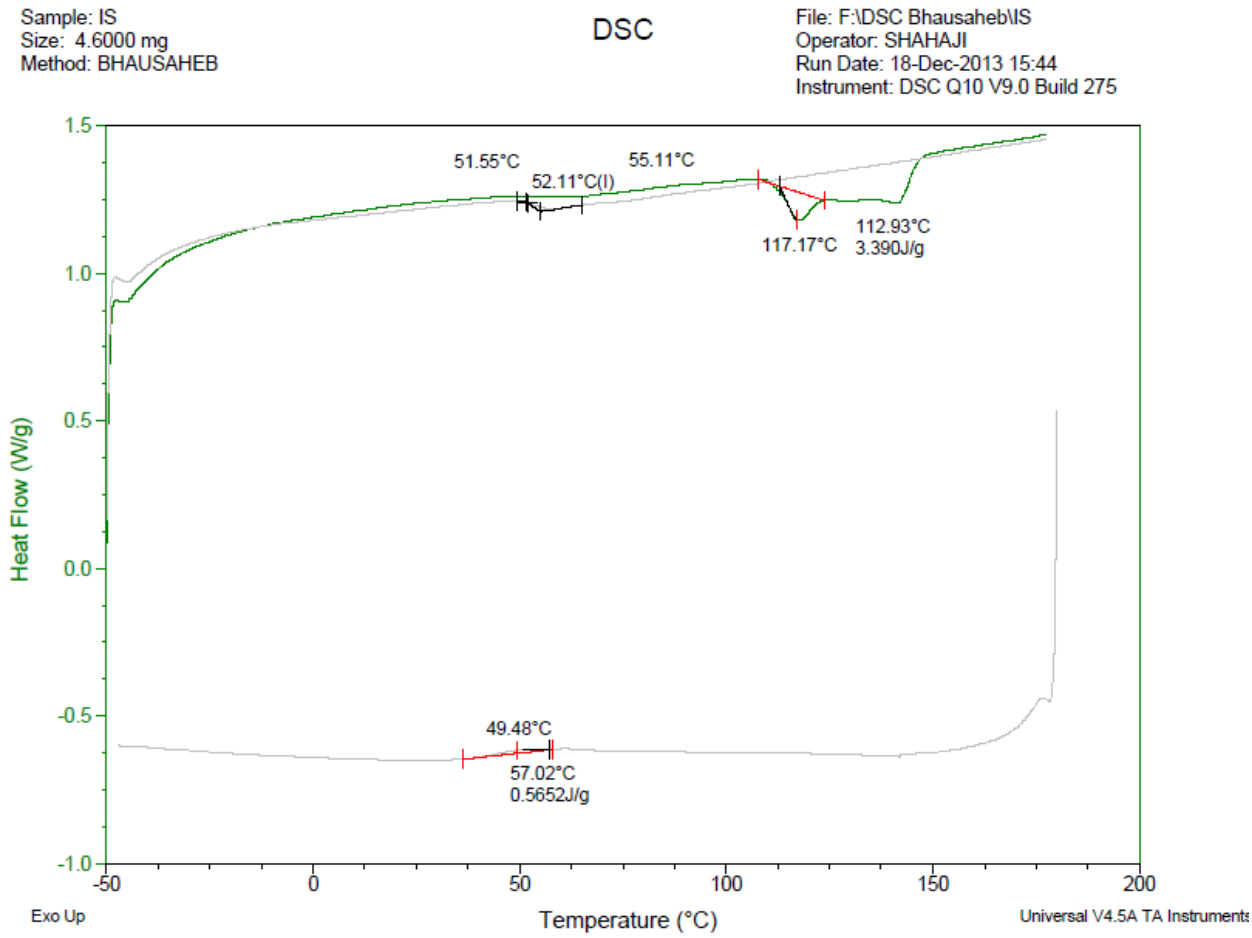



*Figure S49*. DSC heating ( 1st heating green, 2nd heating black) and cooling curves of **P2b-2**.

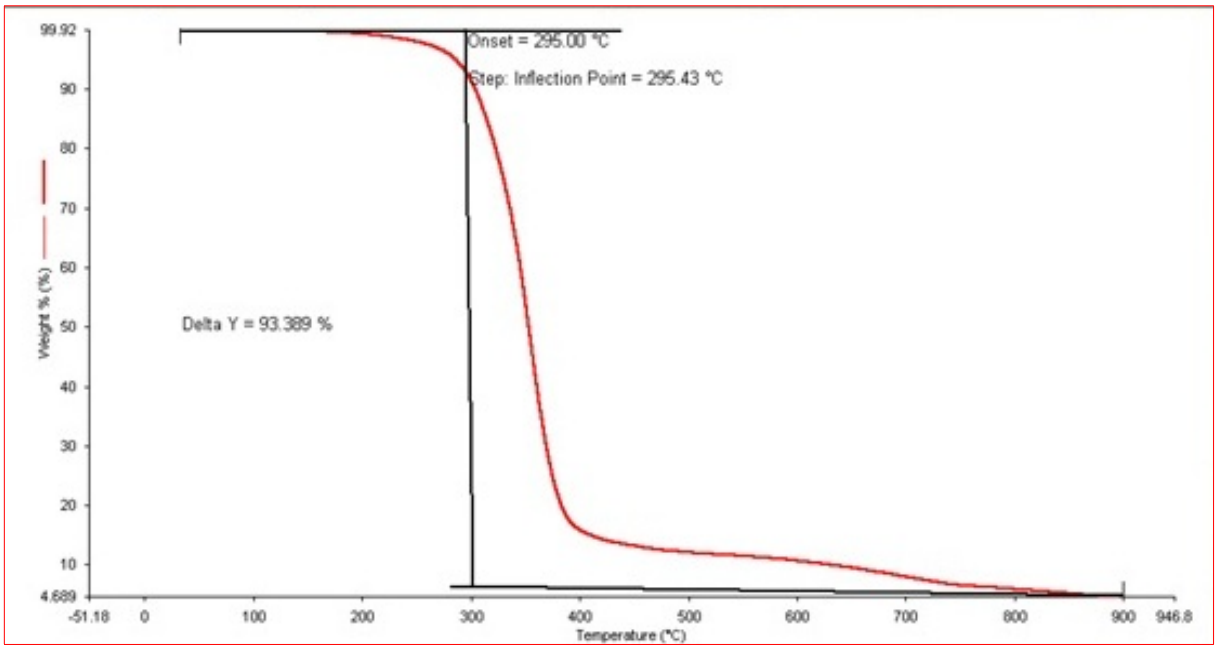



*Figure S50*. TGA trace of **P2b-2** recorded between 0-600°C in $N_2$ atmosphere.

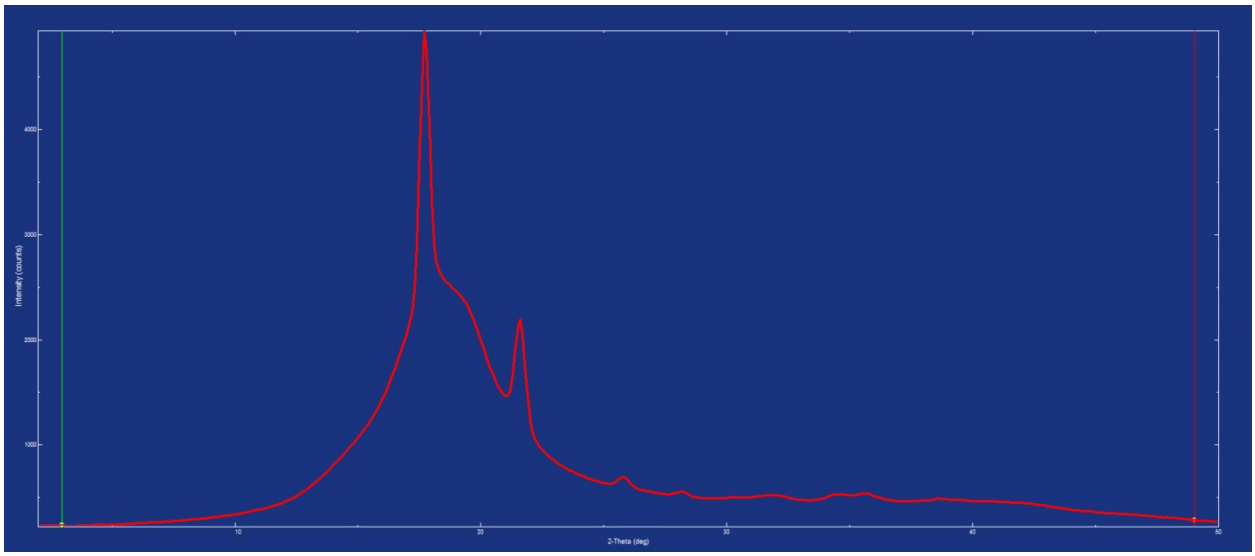
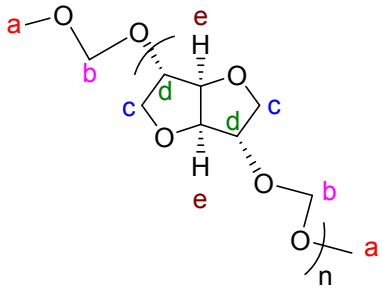


*Figure S51*. X-ray powder diffraction profile of **P2b-2**.

# 9. Polycondensation of isoidide-diacetal to P2c-1:




**$^{1}$H NMR** (500 MHz, $CDCl_3$, 298 K) δ = 4.80 - 4.57 (m, $130H_{b,e}$), 4.28-4.21 (m, $61H_d$), 3.87-3.80 (m, $127H_c$), 3.36 (s, $6H_a$). **$^{13}$C NMR** (500 MHz, $CDCl_3$, 298 K) δ = 95.6-93.1 (s, $C_b$), 87.6-85.7 (s, $C_e$), 80.9 (s, $C_d$), 74.4 (s, $C_c$), 72.37 (s, $C_d$), 72.30 (s, $C_c$), 55.6 (s, $C_a$).

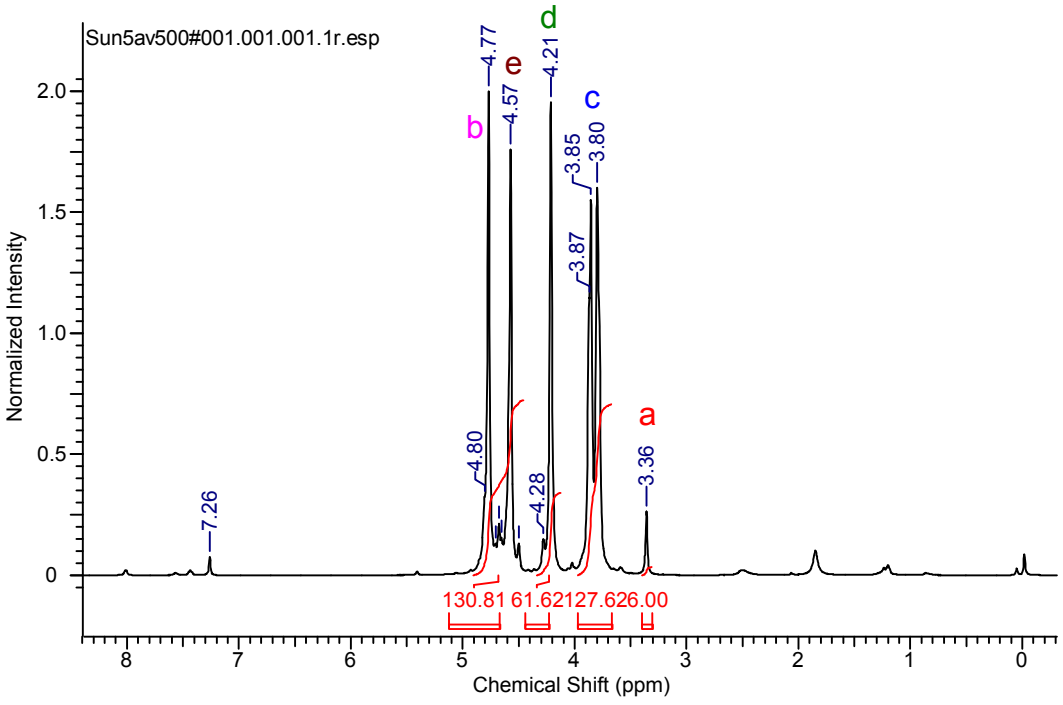



*Figure S52*. $^{1}$H NMR spectrum of **P2c-1** in $CDCl_3$ (500 MHz at 298K).

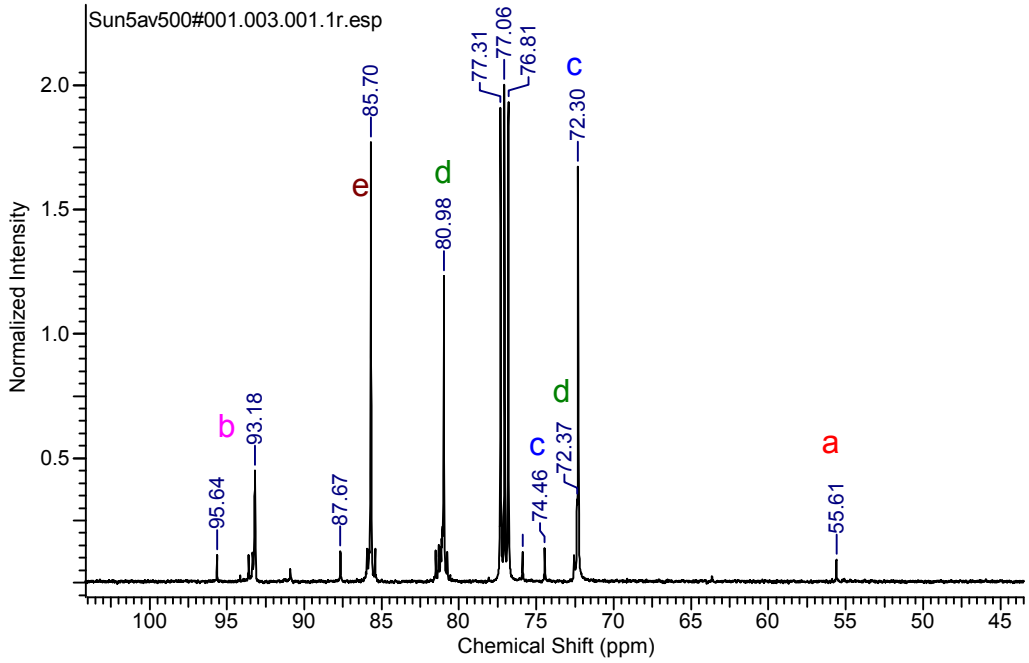



*Figure S53*. $^{13}$C NMR spectrum of **P2c-1** in $CDCl_3$ (500 MHz at 298K).

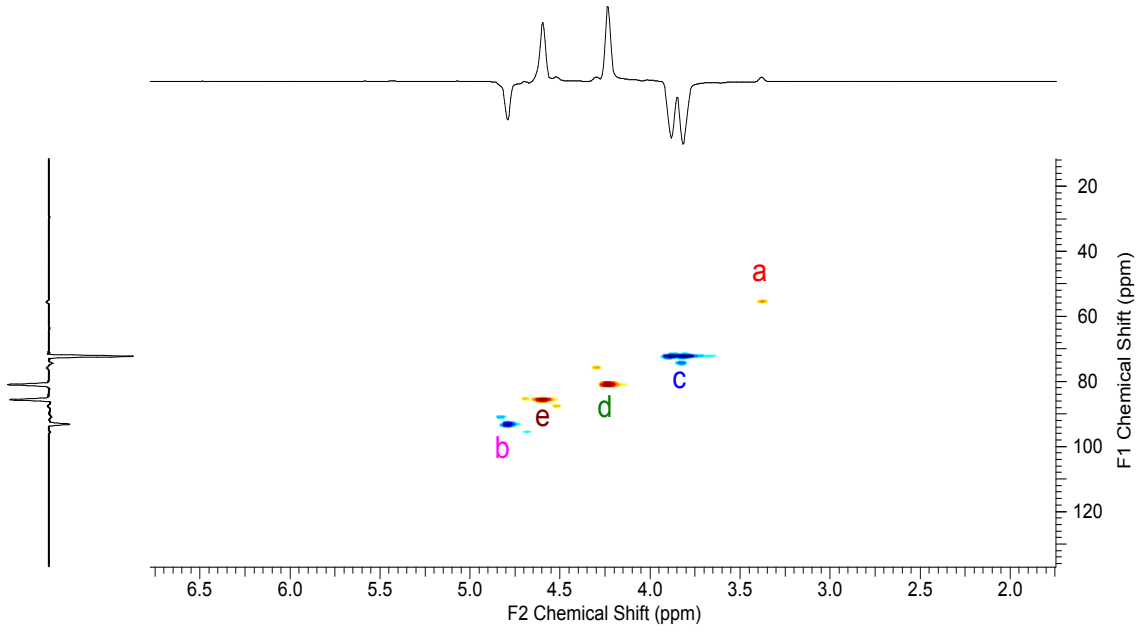



*Figure S54*. HSQC ($^1J_{C\text{-}H}$ correlation) NMR spectrum of **P2c-1** in $CDCl_3$ (400 MHz at 298K).

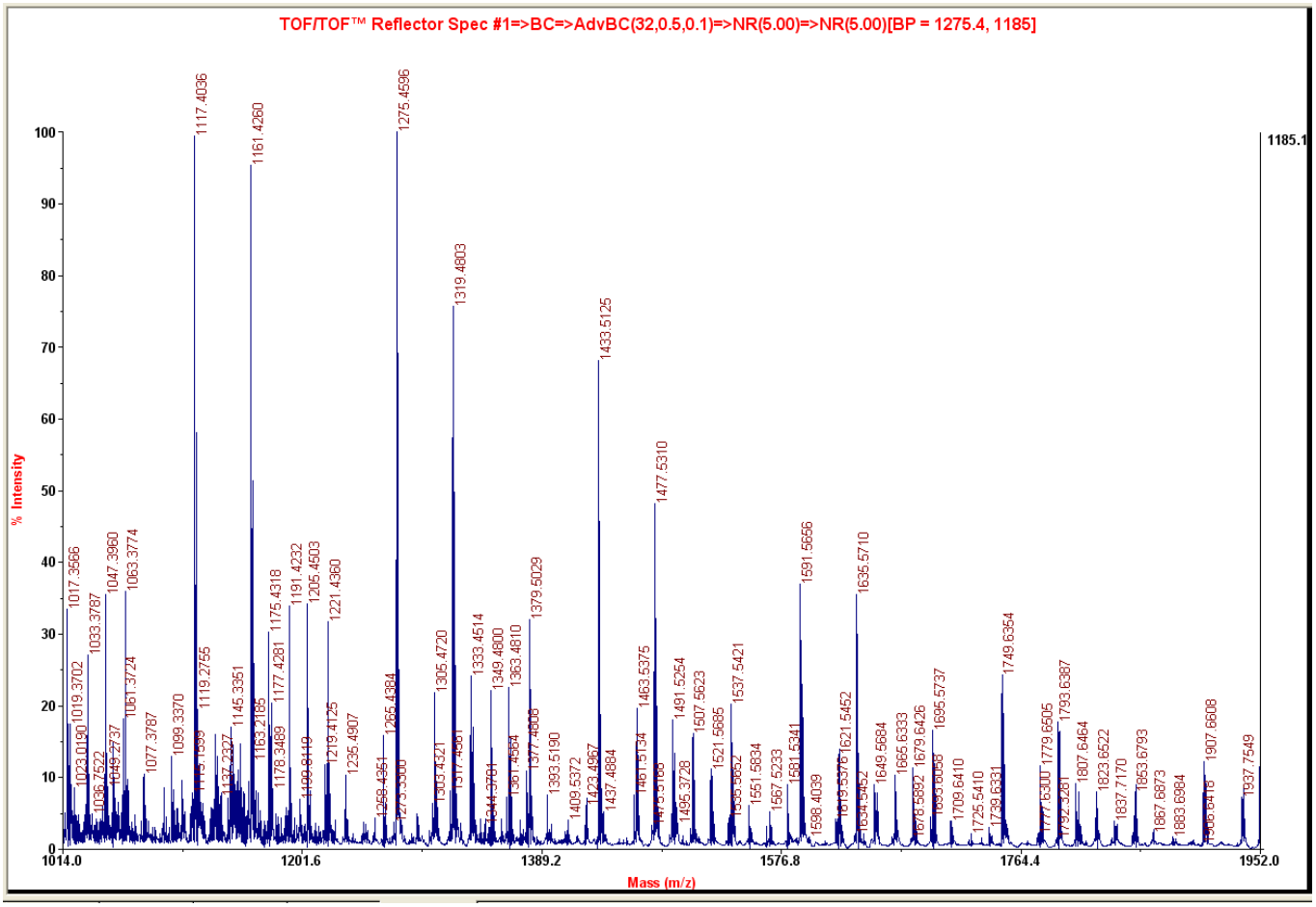



*Figure S55*. MALDI-ToF-MS spectra of **P2c-1** recorded in chloroform.

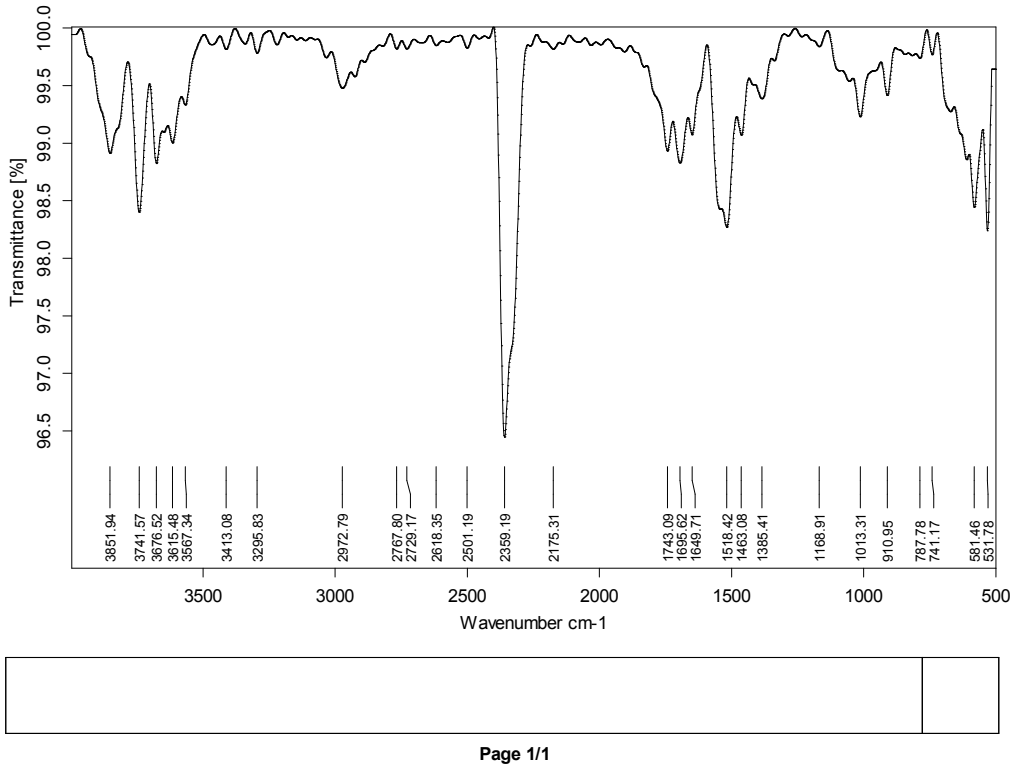



*Figure S56*. IR spectrum of **P2c-1**.

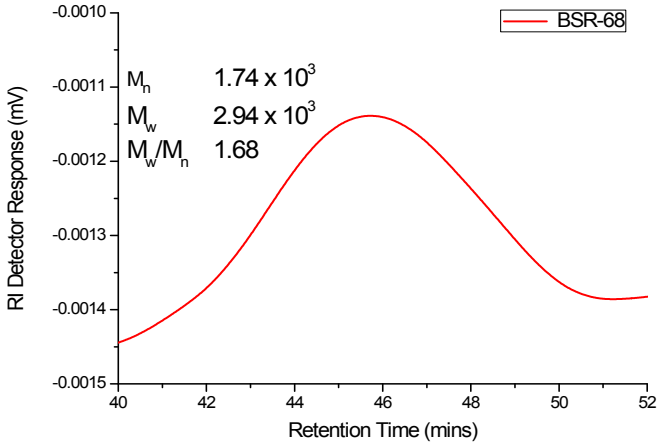



*Figure S57a*. GPC chromatogram of **P2c-1** (in chloroform at room temperature).

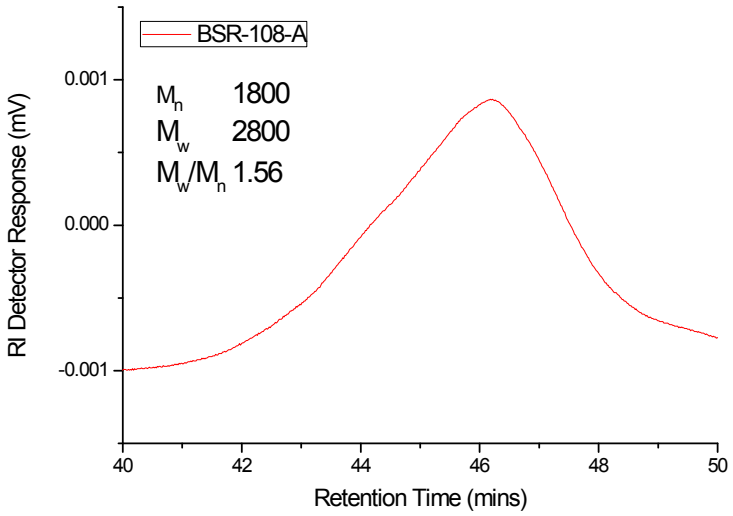



*Figure S57b*. GPC chromatogram of **P2c-2** (in chloroform at room temperature).

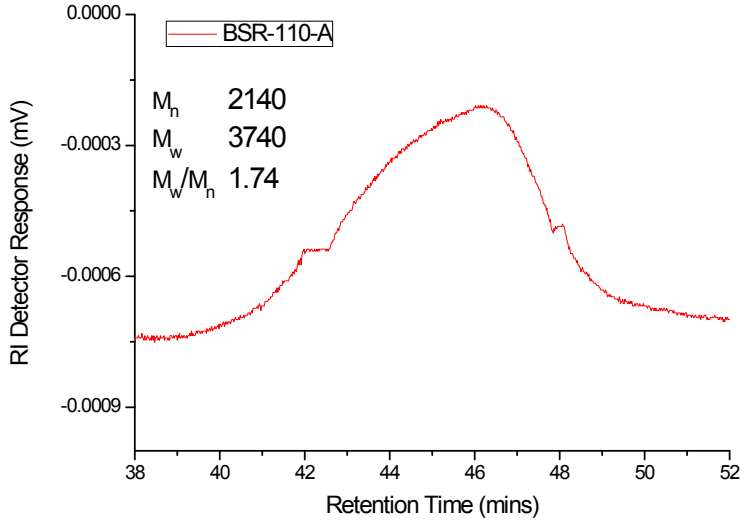



*Figure S57c*. GPC chromatogram of **P2c-3** (in chloroform at room temperature).

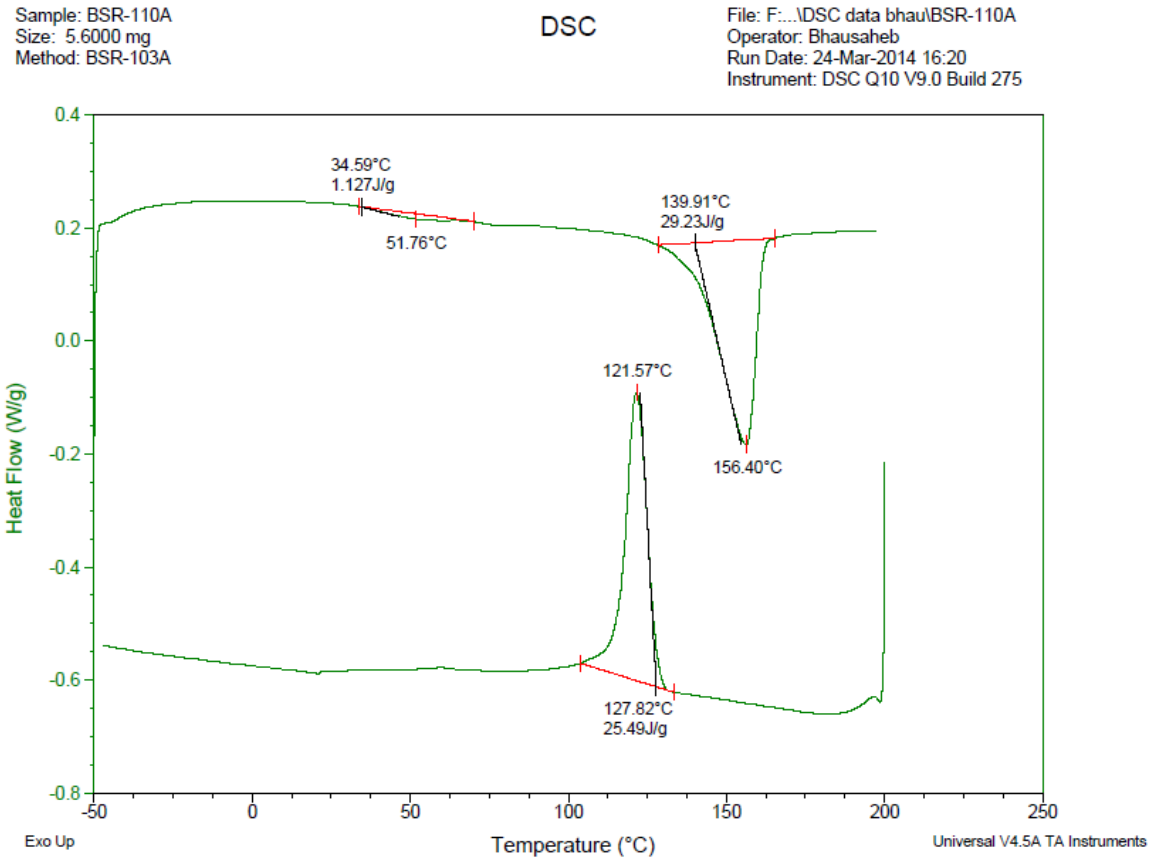



*Figure S58*. DSC heating and cooling curves of **P2c-3**.

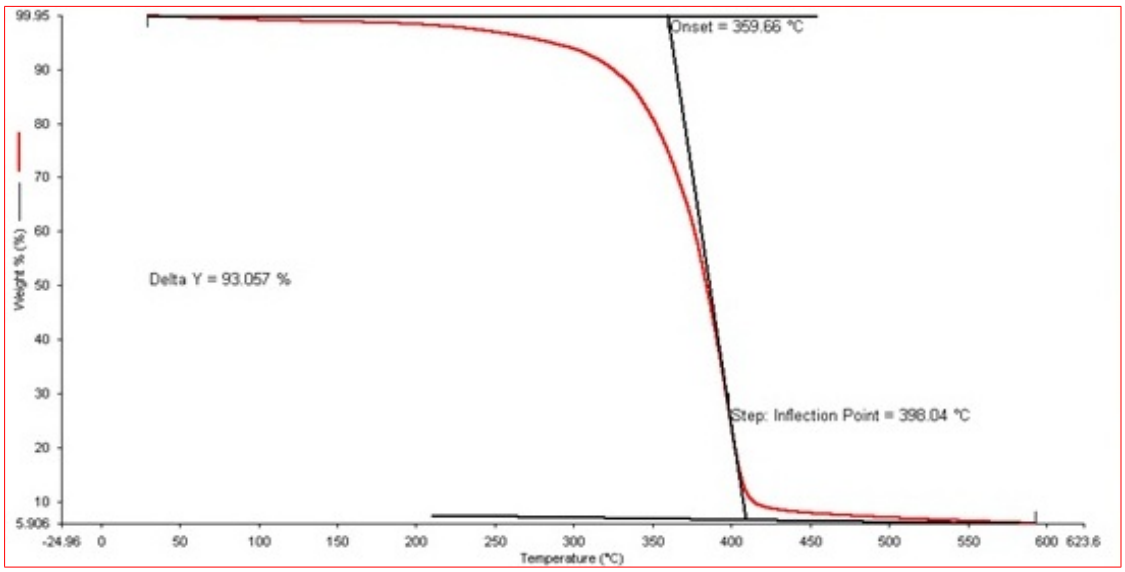



*Figure S59*. TGA trace of **P2c-3** recorded between 0-600°C in $N_2$ atmosphere.

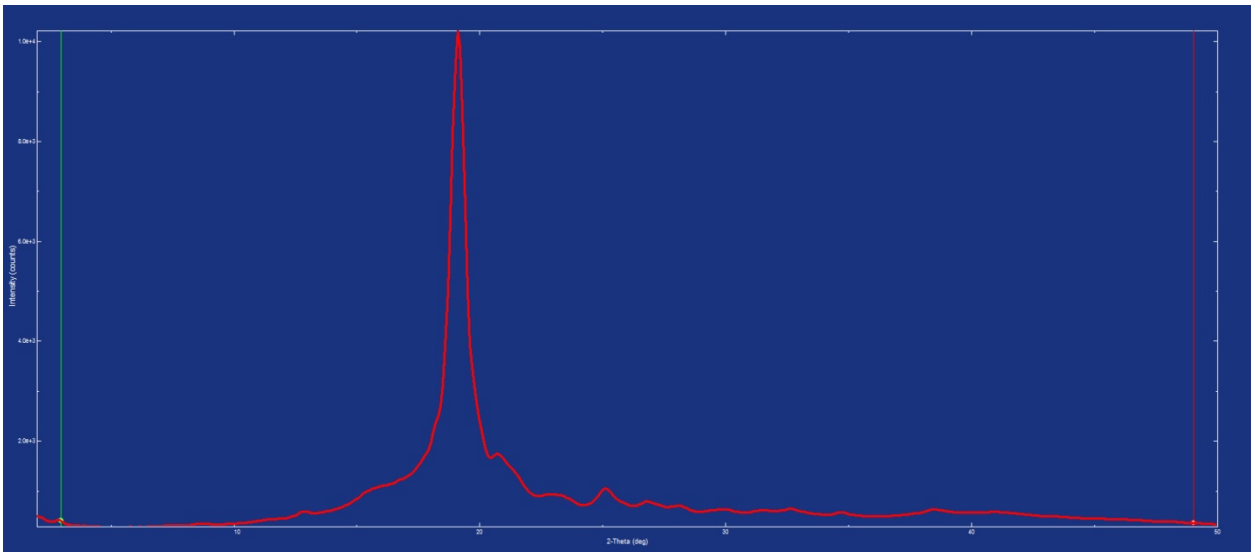


*Figure S60*. X-ray powder diffraction profile of **P2c-3**.

## 10. Molecular weight determination by End Group Analysis (NMR):

Polymerization experiments were performed at different time intervals to establish the exact chemicals shift of the end groups (in this case the $–OCH_3$ groups). Thus, it was established that the methoxy end groups appear at 3.35 ppm (Figure S62 bottom) and the signal disappears if the polymerization is run for 24 hours, indicating high molecular weight polymers with negligible amount of end-groups (Figure S62 top). An exemplary molecular weight calculation is given below.

Addition of total number of backbone protons = 1750, Then divide total number of backbone protons by the number of protons in single repeat unit of the polymer (i.e. 10). So 1750/10 = 175. The number of repeat units (175) is multiplied by 158 (Where 158 is the molecular weight of repeating unit). Hence, 175 x 158 = 27,600 (see figure S61 **P2b**).

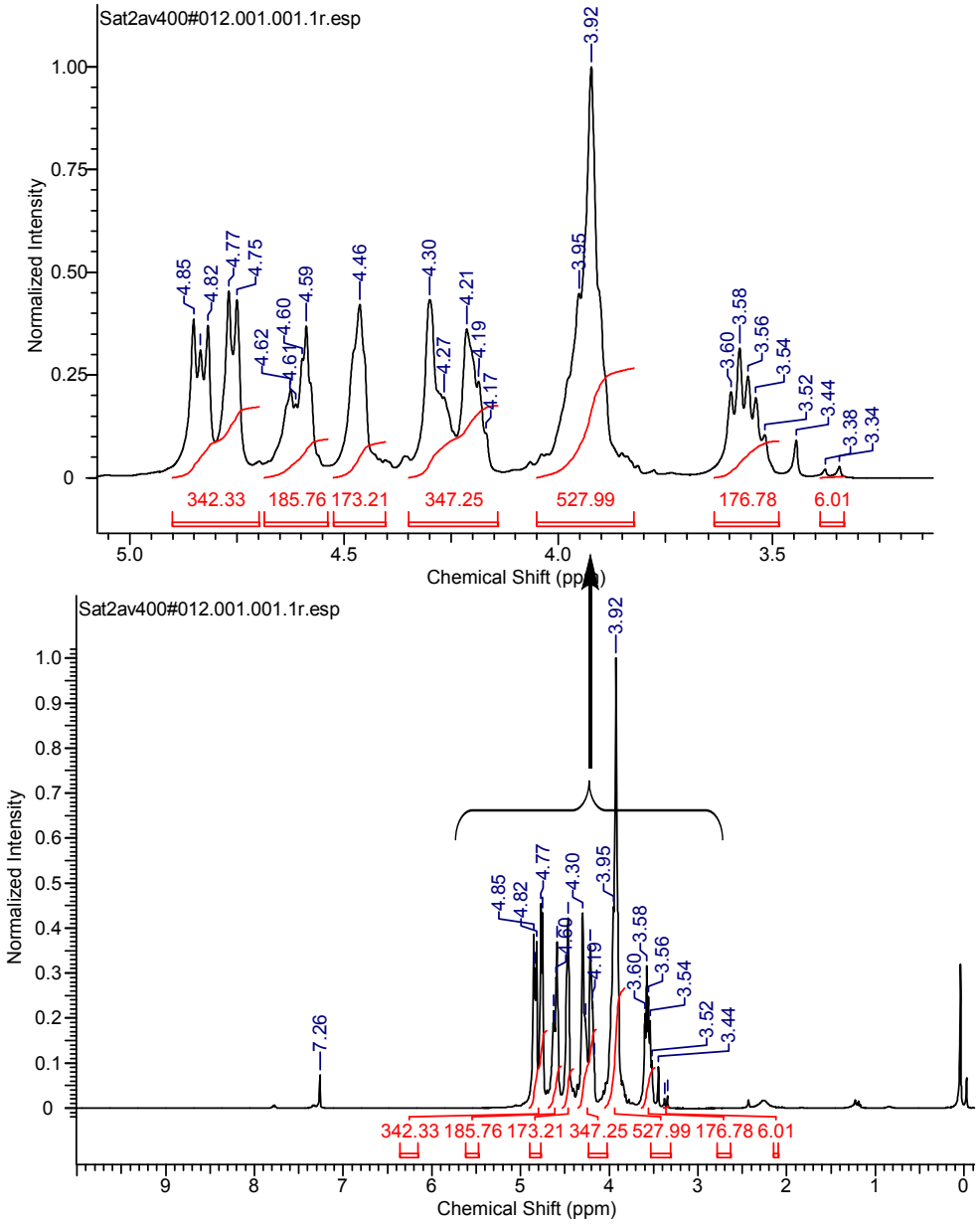



*Figure S61.* $^{1}$H NMR of **P2b-2** in $CDCl_3$ (400 MHz at 298K).

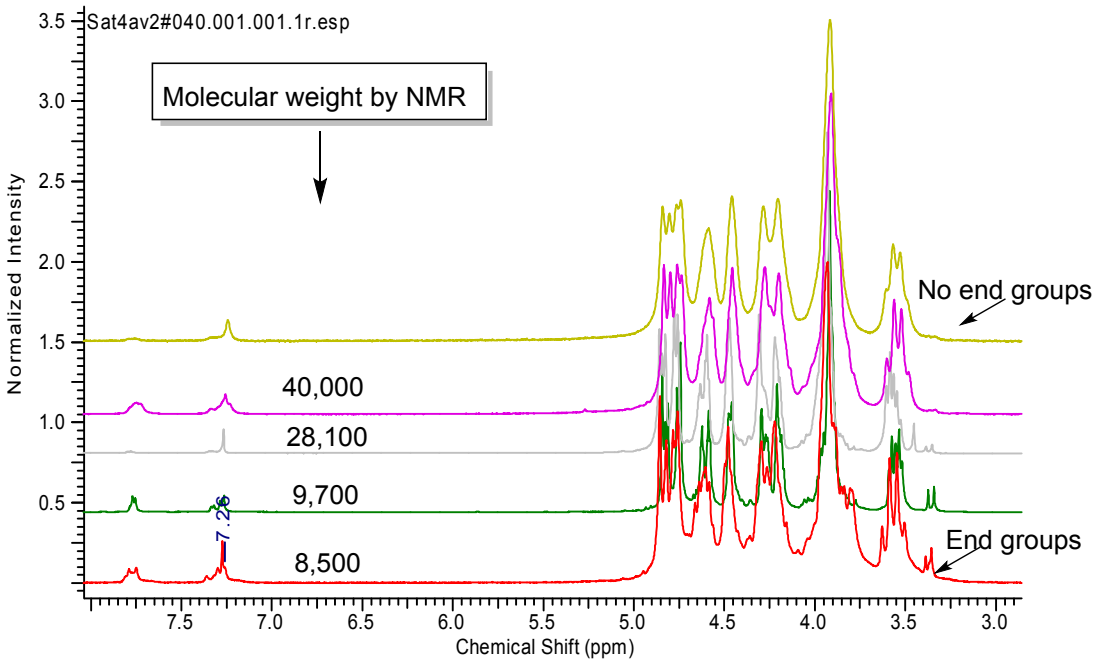



*Figure S62*. $^{1}$H NMR of **P2b** at different time intervals.


*Figure S63*. Isolated polyacetals IS (**P2b**), IM (**P2a**) and II (**P2c**).

# 11. Degradation of P2b:

## *A) Hydrolytic degradation:*

The polyacetal **P2b** was selected as the most relevant representative of the three polymers for degradation studies. 40 mg of **P2b** was taken in a frit and was washed with 0.8 ml of $D_2O$. Proton NMR of the washing displayed only solvent ($D_2O$) signal (see Figure S64), indicating that the polyacetal is stable under washing conditions. However, a clear solution was obtained when the same polymer was transferred to a round bottom flask and stirred with $D_2O$ (total 0.2 ml; 35% DCl in $D_2O$ solution) over a period of 54 hours. $^1H$ NMR of initial mixture (solid polymer was visible) displayed a spectrum similar to neat **P2b** (see Figure S65-bottom). Whereas, after acid treatment a clear solution was obtained; with sharp proton signal corresponding to the bicyclic skeleton (see Figure S65, 5, 20, 33 and 54 hours). These findings were further supported by the $^{13}C$ NMR (Figure S66); suggesting that the polymer breaks down to the isosorbide backbone.

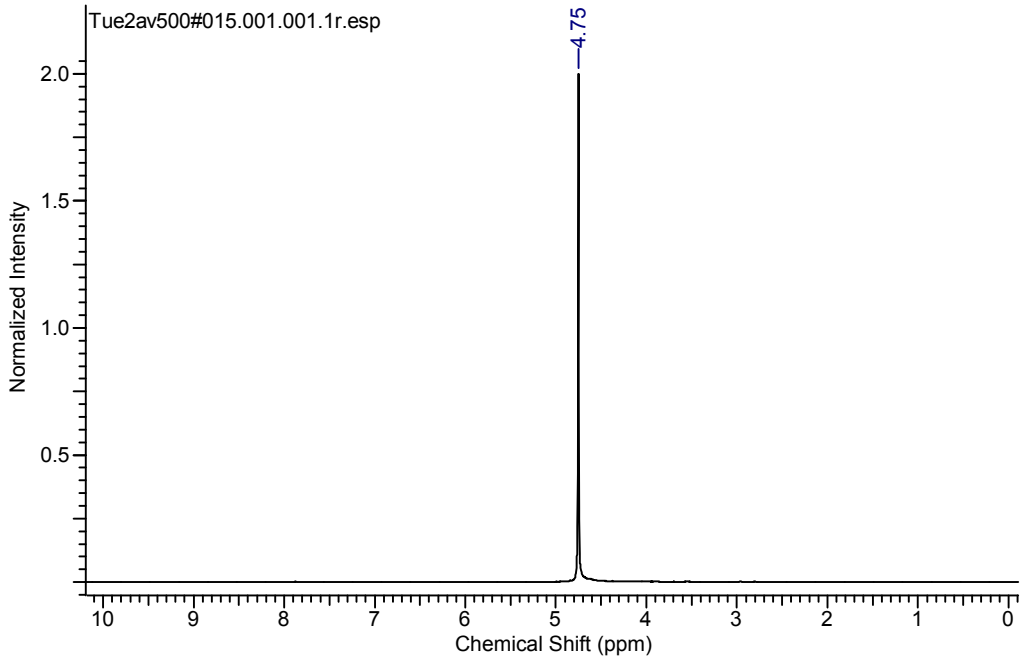


*Figure S64*. $^1$H NMR of **P2b** after rinsing with $D_2O$ (500 MHZ, 298K).

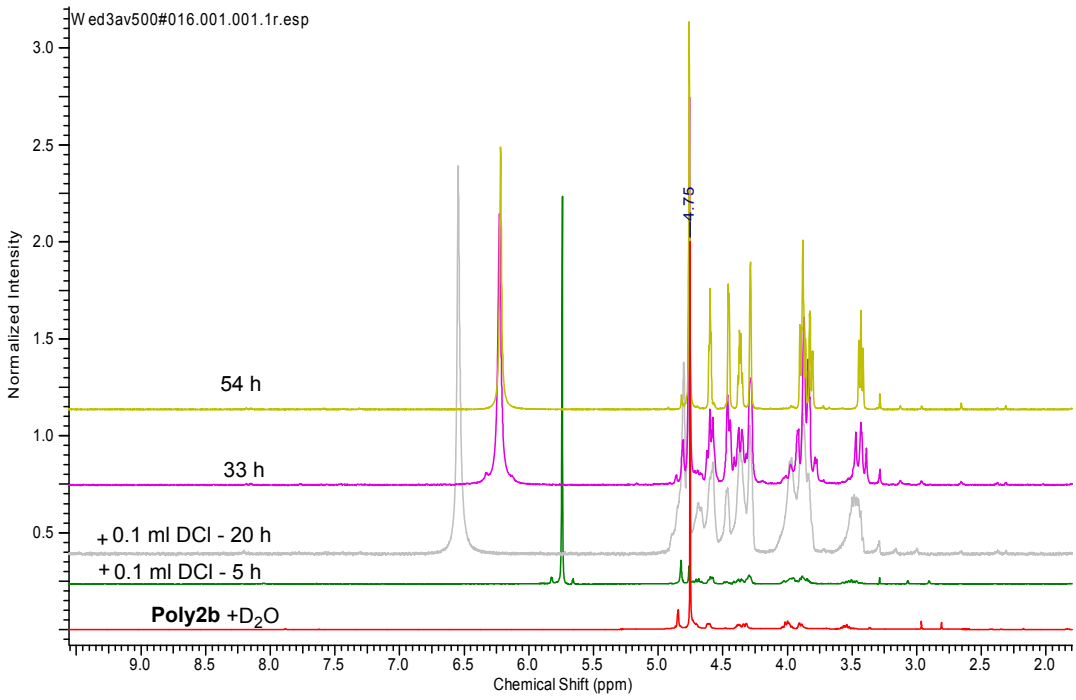



*Figure S65*. Time dependent $^1$H NMR of **P2b-2** in acidic media (in $D_2O$).

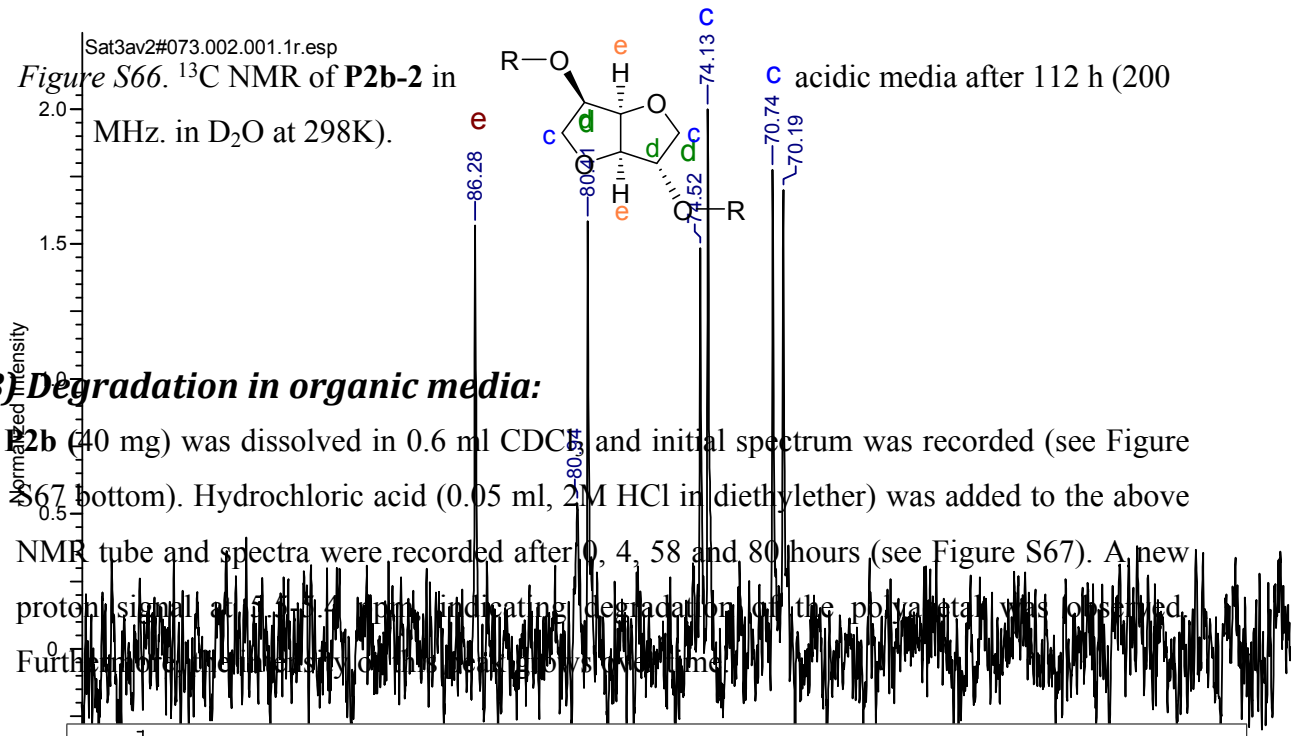



*Figure S66.* $^{13}C$ NMR of **P2b-2** in acidic media after 112 h (200 MHz. in $D_2O$ at 298K).

## *B) Degradation in organic media:*

**P2b** (40 mg) was dissolved in 0.6 ml $CDCl_3$ and initial spectrum was recorded (see Figure S67 bottom). Hydrochloric acid (0.05 ml, 2M HCl in diethylether) was added to the above NMR tube and spectra were recorded after 0, 4, 58 and 80 hours (see Figure S67). A new proton signal at 5.5-5.4 ppm indicating degradation of the polyacetal was observed. Furthermore the intensity of this peak grows over time.

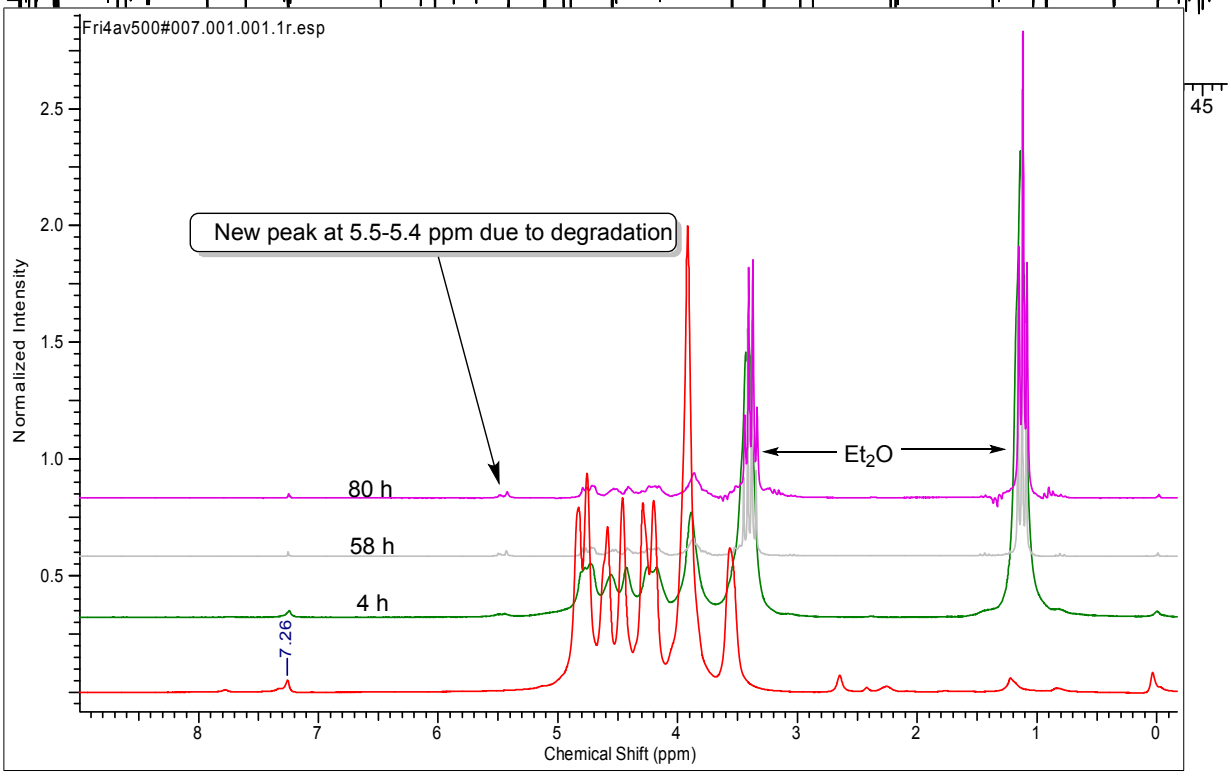



*Figure S67.* Variable time $^1H$ NMR (stacked) of **P2b** in acidic media (in $CDCl_3$)

## *C) Monitoring the acid induced degradation by GPC:*

**P2b (**20 mg) was dissolved in 4 ml chloroform and 0.2 ml HCl (2M in diethylether) was added. The solution was allowed to stand for 1 hour and was filtered through a bed of basic alumina. The filtrate was collected and the GPC was recorded (see Figure S68 right). The parent polyacetal with a Mw of 8900 (poly2b; figure S68 left) degrades to low molecular weight fragments of about 741 (Figure S68 right). Although such low molecular weights from GPC measurement are unreliable (lower detection limits of GPC), these observations indicate that the polymer chain degrades to low molecular weight fragments.

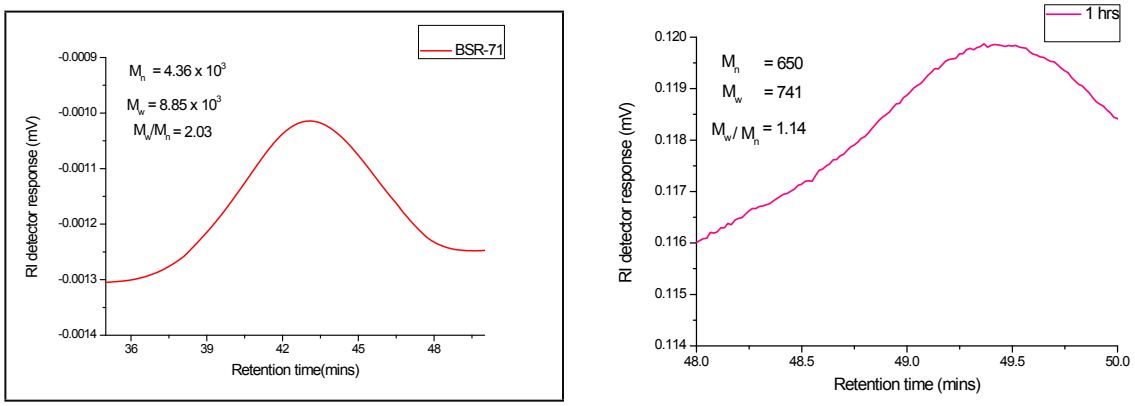



*Figure S68.* Time resolved GPC curve of **P2b** (Left) and GPC after acidic degradation (Right), in chloroform, against PS standard.

[1] G. de Coster, K. Vandyck, E. van der Eycken, J. van der Eycken, M. Elseviers, H. Roper, T*etrahedron: Asymmetry* **2002**, *13*, 1673-1679