

## Supporting Information for:

### Biomaterials from sugars: ring-opening polymerization of a carbohydrate lactone.

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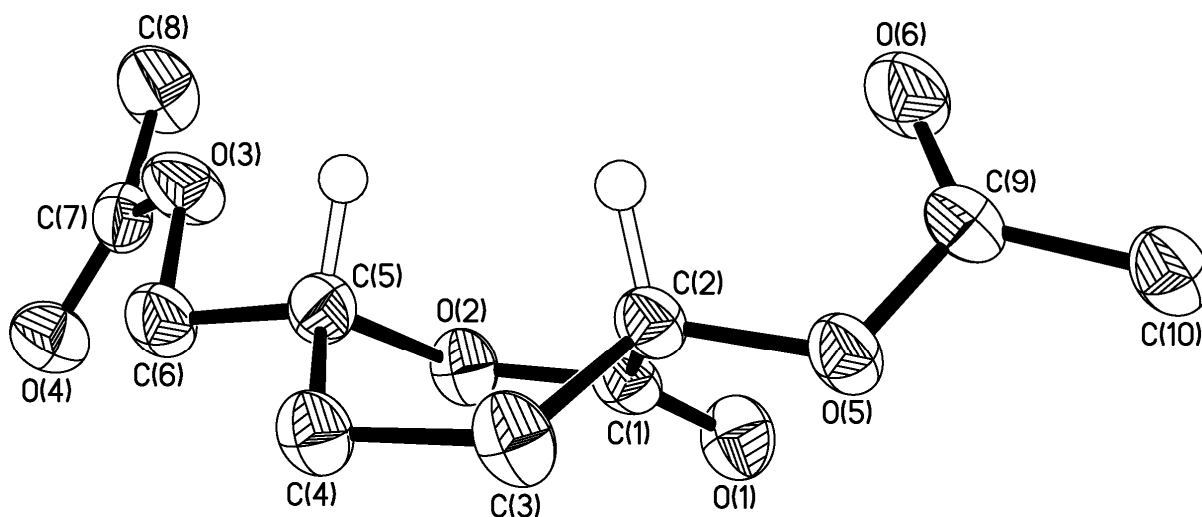
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### X-ray crystallography

Crystal data for **3**: C<sub>10</sub>H<sub>14</sub>O<sub>6</sub>, *M* = 230.21, monoclinic, *P*2<sub>1</sub>/*c* (no. 14), *a* = 7.19184(19), *b* = 14.5149(4), *c* = 11.0204(3) Å, β = 104.825(3)°, *V* = 1112.11(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.375 g cm<sup>-3</sup>, μ(Mo-Kα) = 0.115 mm<sup>-1</sup>, *T* = 173 K, colourless plates, Oxford Diffraction Xcalibur 3 diffractometer; 3718 independent measured reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.042, *wR*<sub>2</sub> = 0.121, 2332 independent observed absorption-corrected reflections [*|F<sub>o</sub>*| > 4σ(*|F<sub>o</sub>*)], 2θ<sub>max</sub> = 65°, 147 parameters. CCDC 680953.



**Figure S1:** The molecular structure of **3** (50% probability ellipsoids).

## ***Experimental Section***

### ***Materials***

The tin(II) butoxide ( $\text{Sn}(\text{OBu})_2$ ) and zinc ( $\text{LZnOEt}$ ) initiators (Fig. S1) were prepared and used according to the literature.<sup>1, 2</sup> Diethyl ether was dried by distillation from sodium, ethyl acetate and *d*-chloroform were dried by distillation from calcium hydride. All other reagents and chemicals were purchased from Aldrich Chemical Co. and used as received. All manipulations were carried out under a dry nitrogen atmosphere either on a Schlenk line or in an MBraun nitrogen filled glove box.

### ***Measurements***

NMR spectra were performed on Bruker AV400 and AV500 instruments.  $\text{CDCl}_3$  was used as the NMR solvent and reference compound. Elemental analyses were conducted by Mr Stephen Boyer, London Metropolitan University, Holloway Rd, London. The SEC measurements were performed on a Polymer labs SEC 60 instrument with two Polymer labs mixed B columns and  $\text{CHCl}_3$  at a flow rate of 1  $\text{mLmin}^{-1}$  as the eluent. Narrow molecular weight polystyrene standards were used to calibrate the instrument. The MALDI-ToF mass spectra were recorded on samples which had been quenched (by exposure to air) at the EPSRC National mass spectrometry service at Swansea University using a Voyager instrument. The dithranol matrix was dissolved in THF and mixed with the sample in a ratio of 1:5 (sample: matrix). The additive was sodium acetate. The static water contact angle was determined on films of **4** which were coated on clean glass slides (13 mm diameter, VWR International, PA, USA) using a dip coater (KSV Instrument, Finland). The slides were completely dipped into a 5 mg/mL solution of polymer at a velocity of 85 mm/min and withdrawn at 5 mm/min to allow the formation of a thin

polymer film on the glass slide. Static water contact angles were measured using a Drop Shape Analysis System (EasyDrop, Krüss, Germany). A 30  $\mu\text{L}$  drop of ultra-pure water (MilliQ water, Millipore, MA, USA) was placed on the film surfaces and static water contact angle was measured. The measurements were performed on three different areas of each slide, repeated on two slides and the values averaged. The thermal properties were measured using differential scanning calorimetry (Diamond DSC, PerkinElmer, UK). Scans were performed from  $-70$  to  $170$   $^{\circ}\text{C}$ , at a controlled heating rate of  $10$   $^{\circ}\text{C}/\text{min}$ . A sealed empty crucible was used as a reference and the DSC was calibrated using indium. The thermal gravimetric analysis (Pyris 1 TGA, PerkinElmer UK) was carried out in flowing air, at a heating rate of  $10$   $^{\circ}\text{C}/\text{min}$ .

### 3-Acetoxy-6-acetoxymethyl-pyran-2-one (**2**)<sup>3,4</sup>

D-Glucono-1,5-lactone **1** (6.00 g, 33.7 mmol) was stirred with acetic anhydride (20 mL) and anhydrous pyridine (20 mL) at  $80$   $^{\circ}\text{C}$  for 1 hour. The mixture was poured onto crushed ice (400 mL) and extracted with  $\text{CHCl}_3$  ( $2 \times 300$  mL). The combined organic layers was washed with ice-cold water ( $2 \times 200$  mL), dried ( $\text{MgSO}_4$ ) and filtered. The solution was treated with activated carbon, filtered and concentrated. The product was dried *in vacuo* and yielded a yellow syrup (7.30 g, 32.3 mmol, 96%), which is in accordance with the literature.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.10 (1H, d,  $^3J_{\text{H-H}} = 7.09$  Hz, H-3), 6.28 (1H, d,  $^3J_{\text{H-H}} = 7.16$  Hz, H-4), 4.86 (2H, s, H-6, H-6'), 2.33, 2.15 ( $2 \times 3\text{H}$ , 2 x s,  $\text{COCH}_3$ ) ppm.

### Acetic acid 5-acetoxy-6-oxo-tetrahydro-pyran-2-ylmethyl ester (**3**)

3-Acetoxy-6-acetoxymethyl-pyran-2-one (**2**) (4.80 g, 21.2 mmol) was dissolved in ethyl acetate (50 mL) and added to a Parr reactor, followed by a spatula of Pd/C (5%). The mixture was stirred under hydrogen ( $5 \times 10^6$  Pa) and heated to 75 °C for 4 hours. The product was filtered through celite and concentrated to yield colorless syrup (4.83 g, 21.0 mmol, 99%). The crude product was purified by repeated recrystallization from diethyl ether and dried *in vacuo* to yield white crystals (2.44 g, 10.6 mmol, 50%).

M. pt. 93.5-94.5 °C. Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>6</sub>: C, 52.17%; H, 6.13%. Found: C, 52.11%; H, 6.17%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.44 (1H, dd, <sup>3</sup>J<sub>H-H</sub> = 17.08 Hz, <sup>3</sup>J<sub>H-H</sub> = 8.55 Hz, H-2), 4.65 (1H, m, H-5), 4.26 (1 H, dd, <sup>2</sup>J<sub>H-H</sub> = 12.13 Hz, <sup>3</sup>J<sub>H-H</sub> = 3.54 Hz, H-6), 4.18 (1 H, dd, <sup>2</sup>J<sub>H-H</sub> = 12.16, <sup>3</sup>J<sub>H-H</sub> = 6.32 Hz, H-6'), 2.36 (1H, m, H-3), 2.19 (3H, s, COCH<sub>3</sub>), 2.12 (3H, s, COCH<sub>3</sub>), 2.07-1.88 (3H, m, H-3', H-4, H-4') ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ: 170.6, 169.8, 168.6 (2 × COCH<sub>3</sub>, C-1), 74.9 (C-5), 65.9 (C-2), 64.9 (C-6), 22.7, 22.4 (C-3, C-4), 20.7 (2 × COCH<sub>3</sub>) ppm. *m/z* (CI-ammonia gas): 248 [M+NH<sub>4</sub><sup>+</sup>]. [ $\alpha_D^{20}$ ] = 0° (CHCl<sub>3</sub>, 10 mg/mL). IR (paraffin)  $\nu$ : 2959, 1766, 1732, 1457, 1377, 1348, 1099, 1059, 1036, 976 cm<sup>-1</sup>.

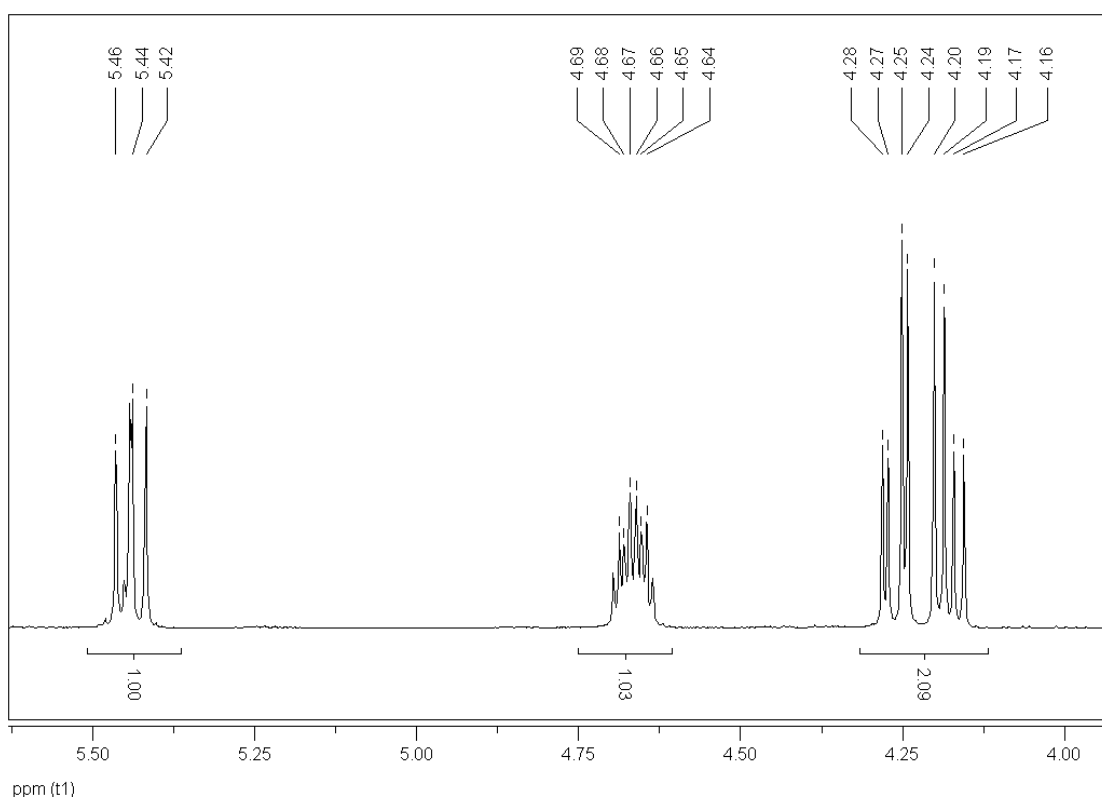
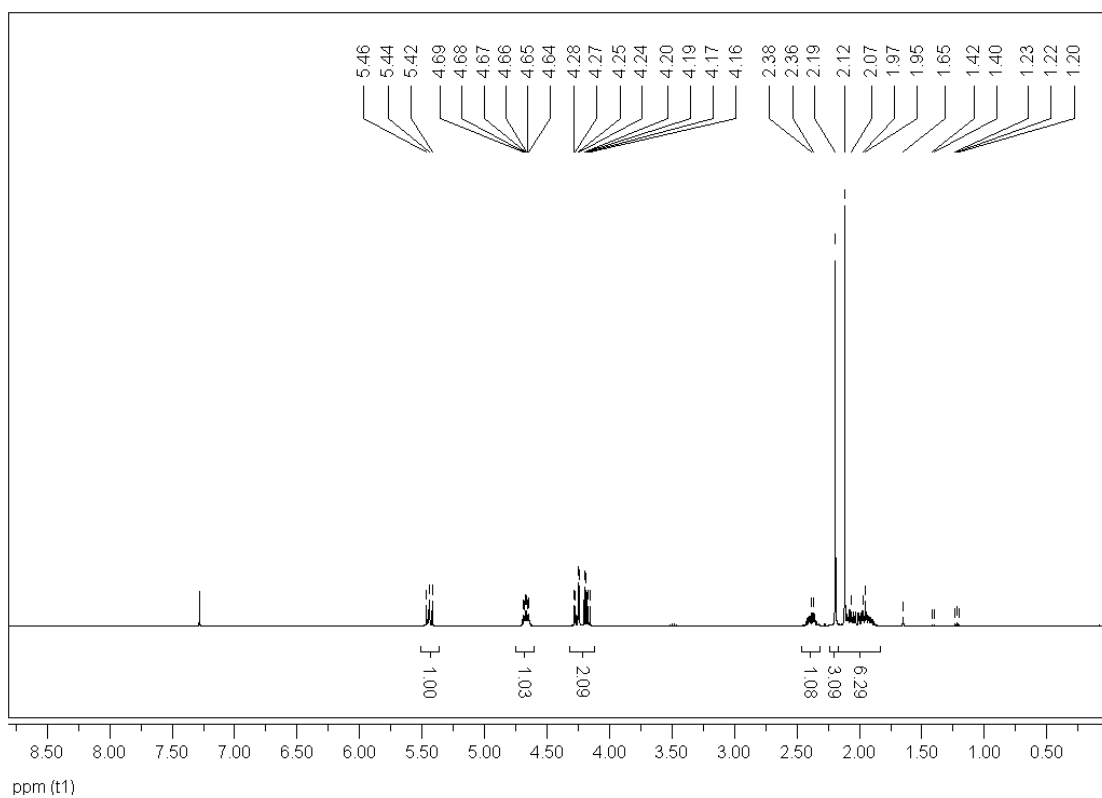
Poly(acetic acid-5-acetoxy-6-oxo-tetrahydro-pyran-2-yl-methyl ester) (**4**)

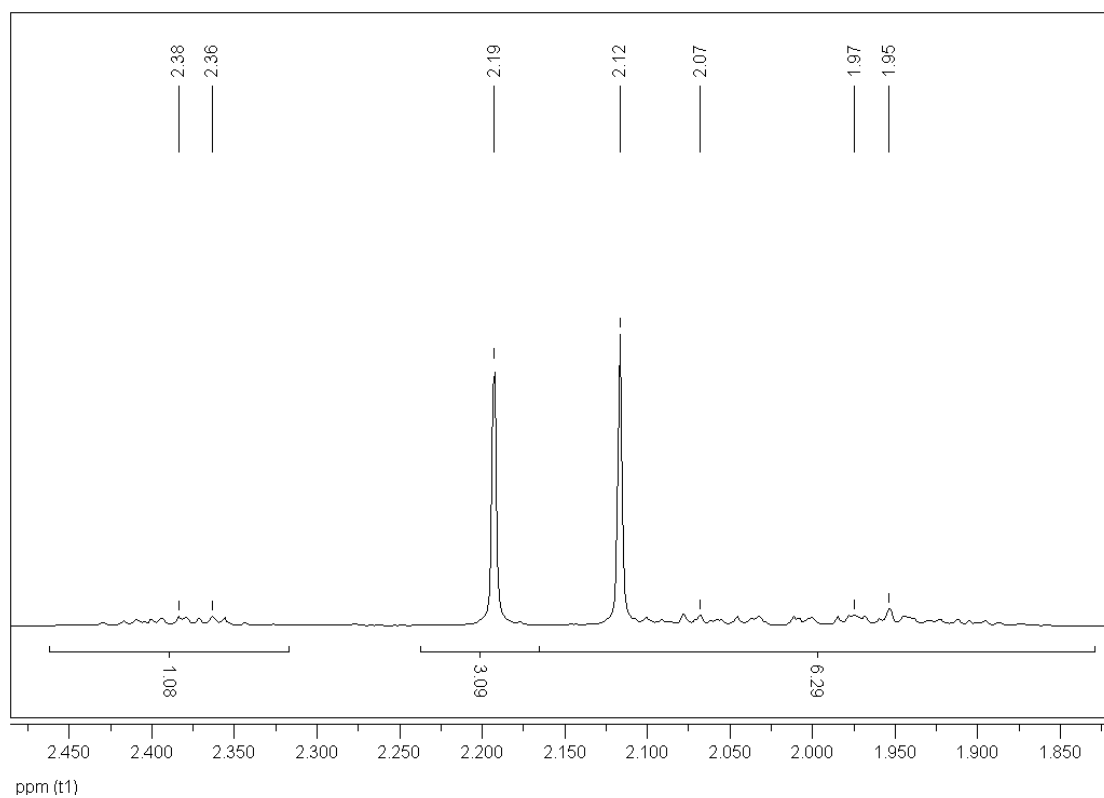
In an oven dried ampule, monomer **3** (0.138 g, 0.6 mmol, 1 eq) was dissolved in toluene (0.45 mL) at 80 °C. To it was added a volume of the stock solution of Sn(OBu)<sub>2</sub> (0.15 mL of a 0.04 M solution in toluene, 0.01 eq). The polymerization was monitored by taking aliquots at regular time intervals, quenching them by addition of wet hexane (to destroy the tin alkoxide propagating species) and drying the resulting mixture *in vacuo*. The percentage conversion was determined using <sup>1</sup>H

NMR spectroscopy: by integration of the H-2 signals, at 5.45 ppm for **3** and 5.00 ppm for **4**, and the H-5 signals, at 4.65 ppm for **3** and 5.14 ppm for **4**. Once the polymerization reached equilibrium, **4** was purified by repeated precipitation in diethyl ether (3 x 30 mL) and dried *in vacuo* (0.06 g, 44 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.14 (1H, bs, H-5), 5.00 (1H, H-2), 4.28-4.05 (2H, H-6), 2.15 (3H, s, COCH<sub>3</sub>), 2.09 (3H, s, COCH<sub>3</sub>), 1.89 (2H, H-3), 1.72 (2H, H-4) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 171.2-169.4 (C=O), 71.9-71.4 (C-2), 70.2-70.1 (C-5), 65.6-64.4 (C-6), 26.6-26.2 (C-3, C-4), 20.9-20.5 (3 × COCH<sub>3</sub>) ppm.

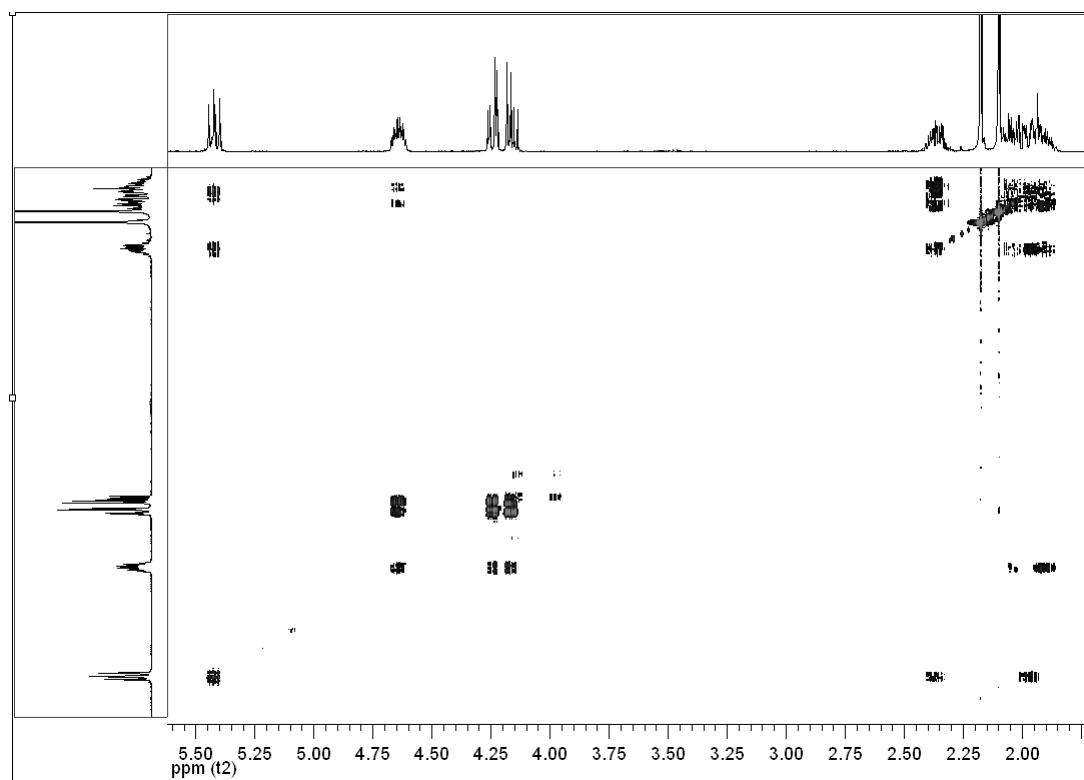
## Spectra



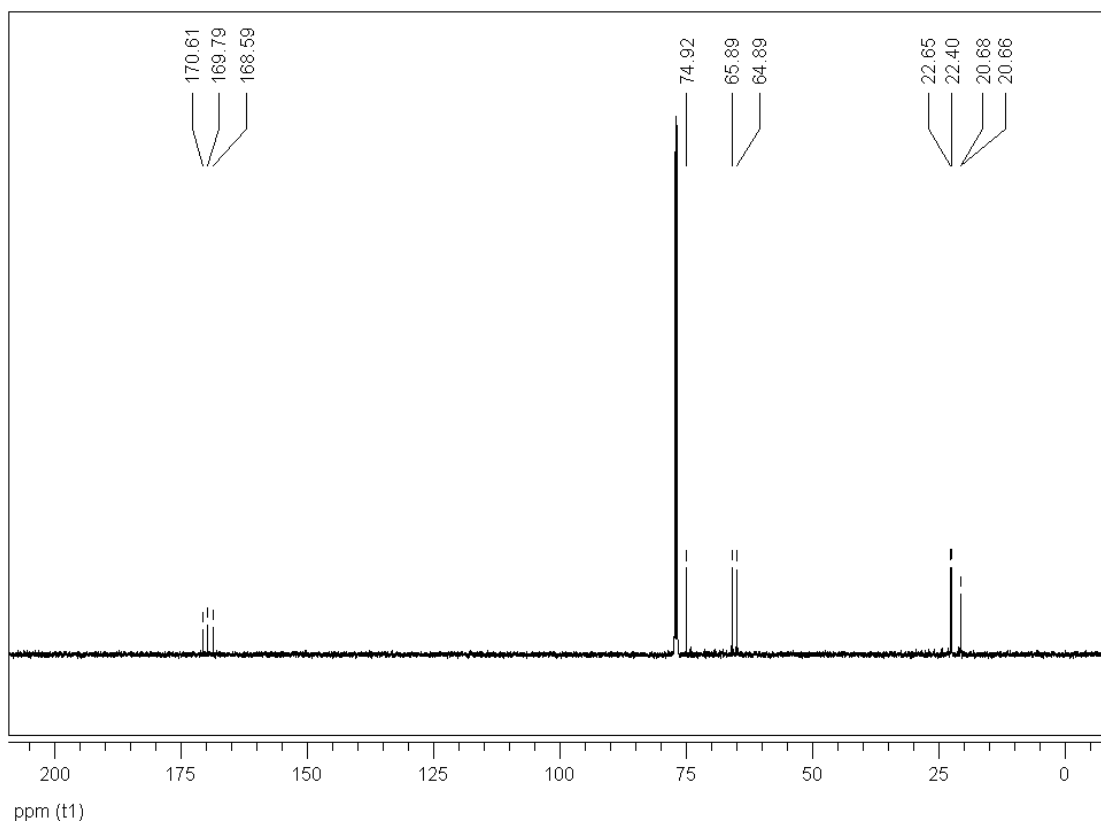


**Figure S2:** <sup>1</sup>H NMR spectrum of **3**.

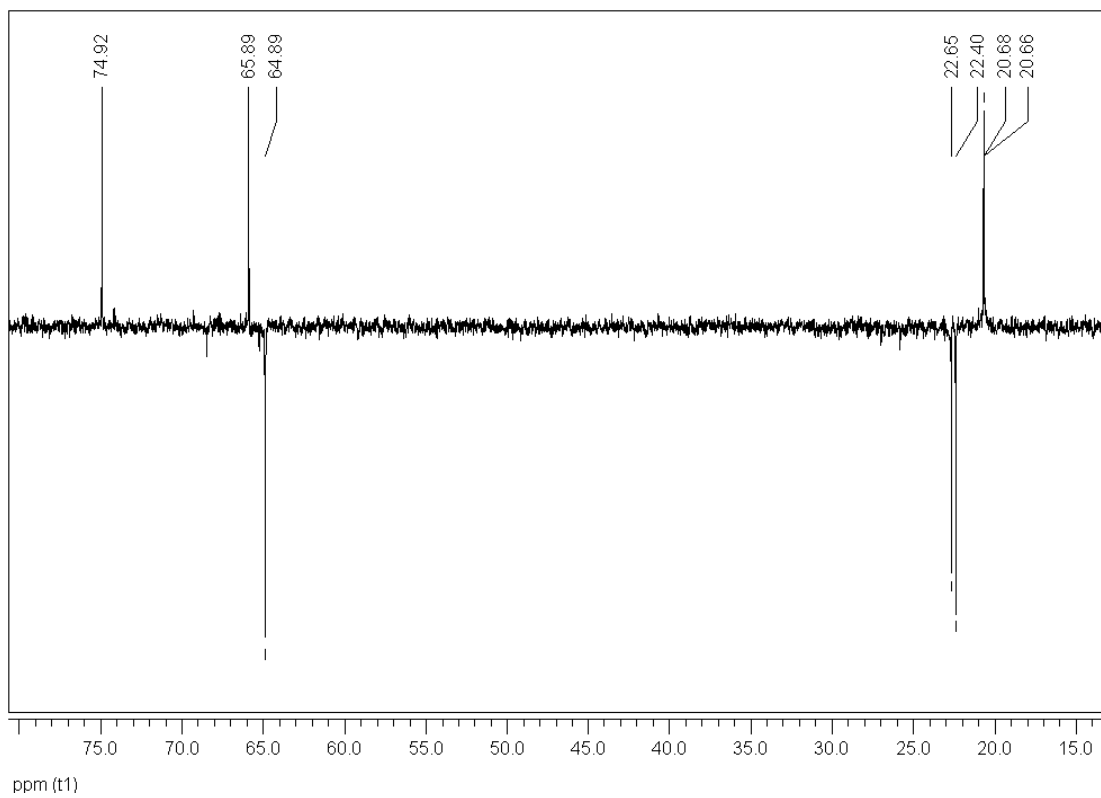




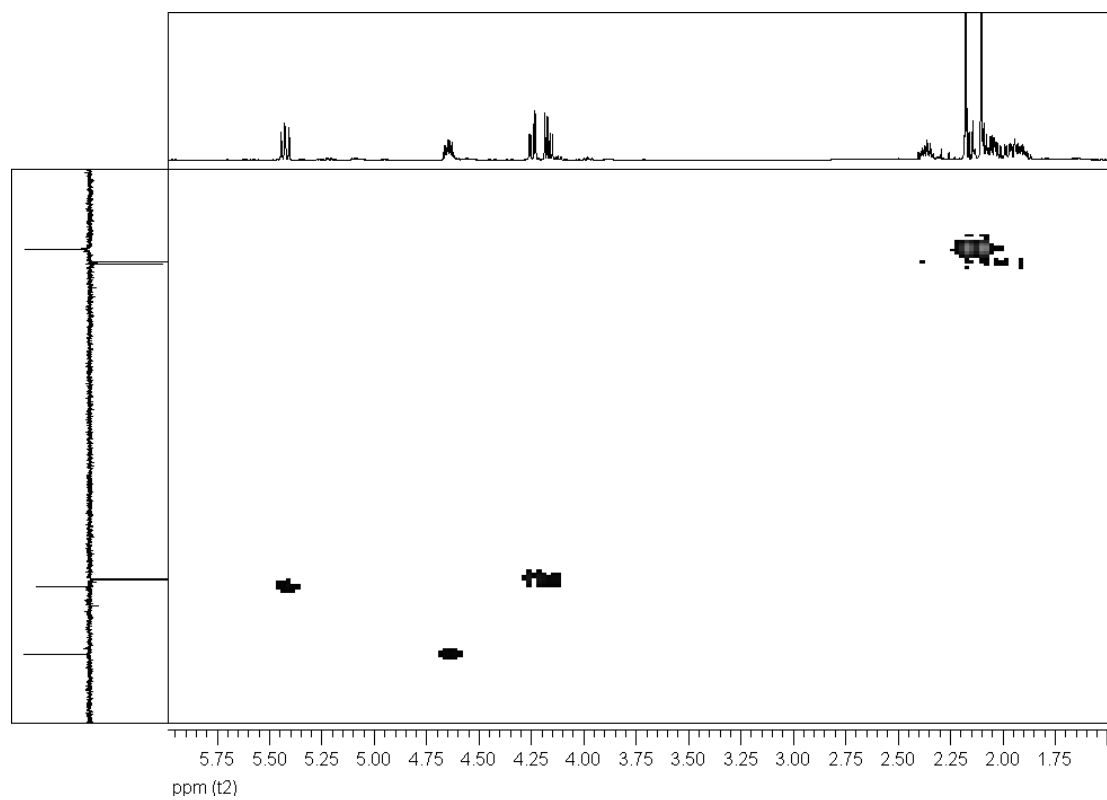
**Figure S3:** COSY spectrum of **3**.



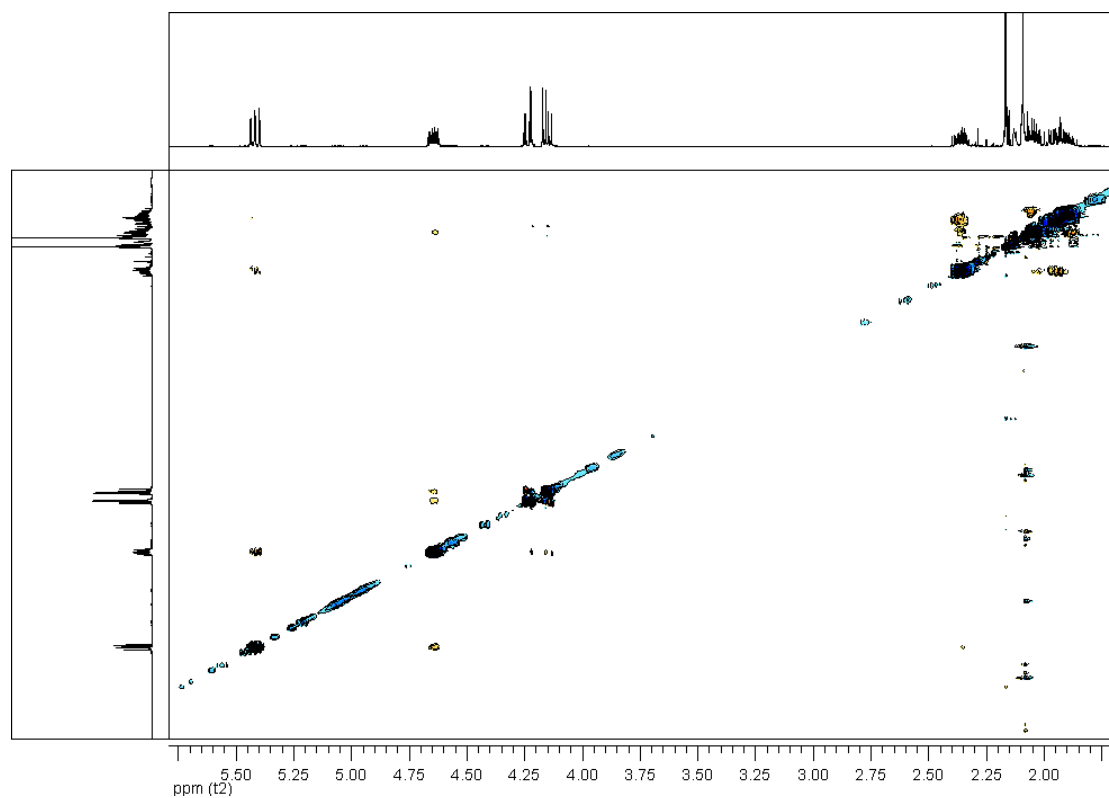
**Figure S4:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



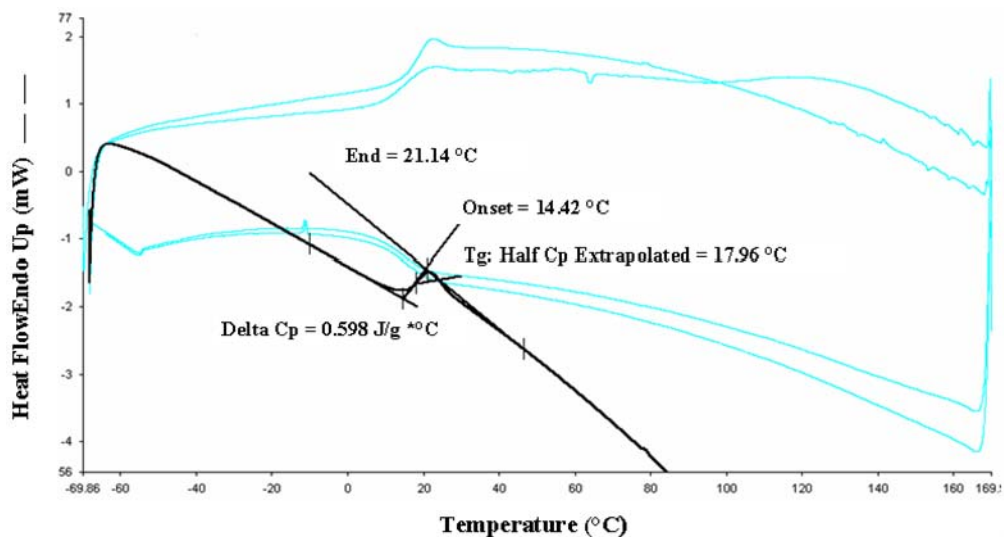
**Figure S5:** DEPT-135 spectrum of **3**.



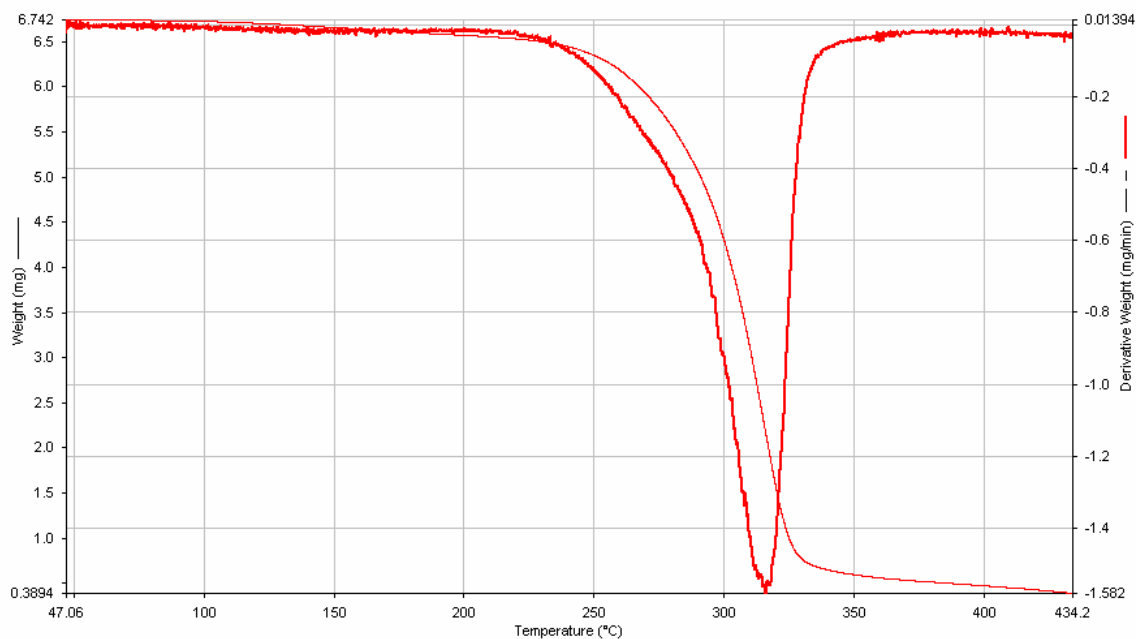
**Figure S6:** HMQC spectrum of **3**.



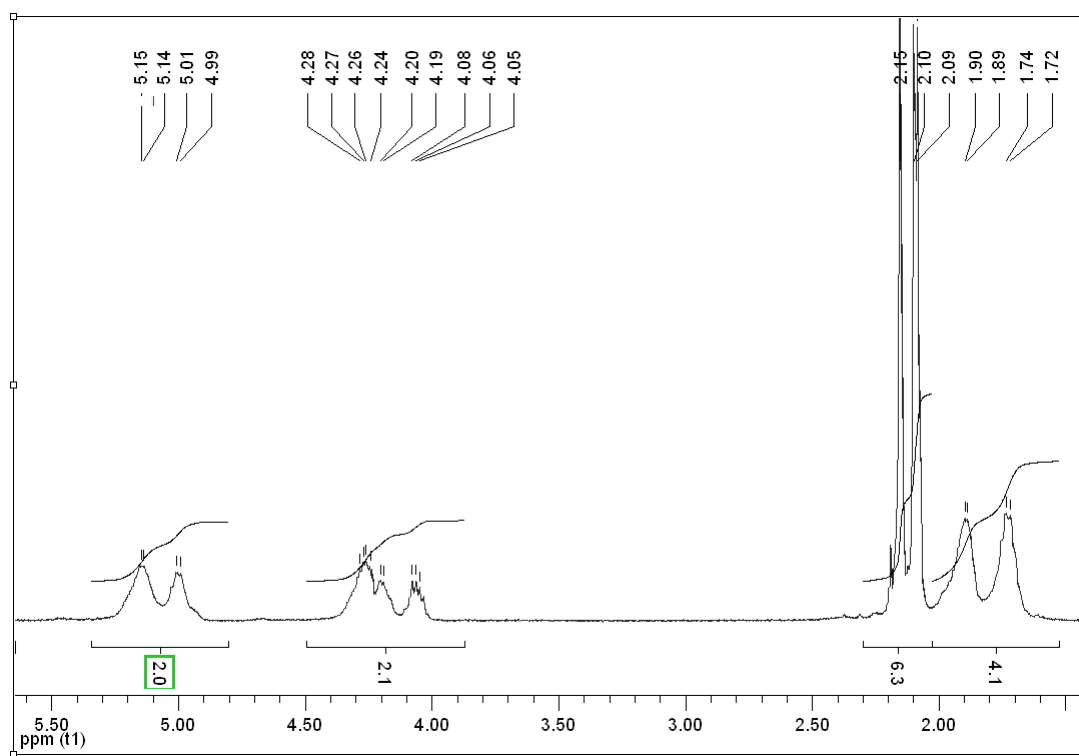
**Figure S7:** NOESY spectrum of **3**.



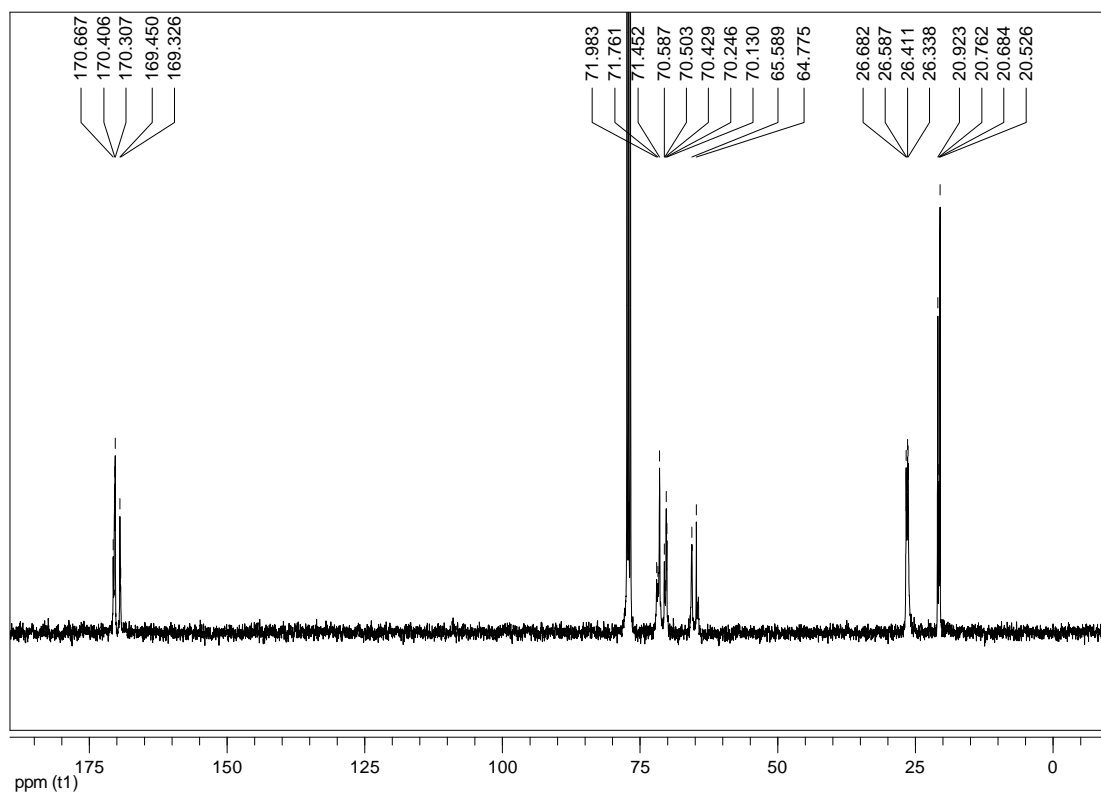
**Figure S8:** DSC plot for **4**, the  $T_g$  is 18 °C ( $M_n = 2900$ , PDI = 1.26).

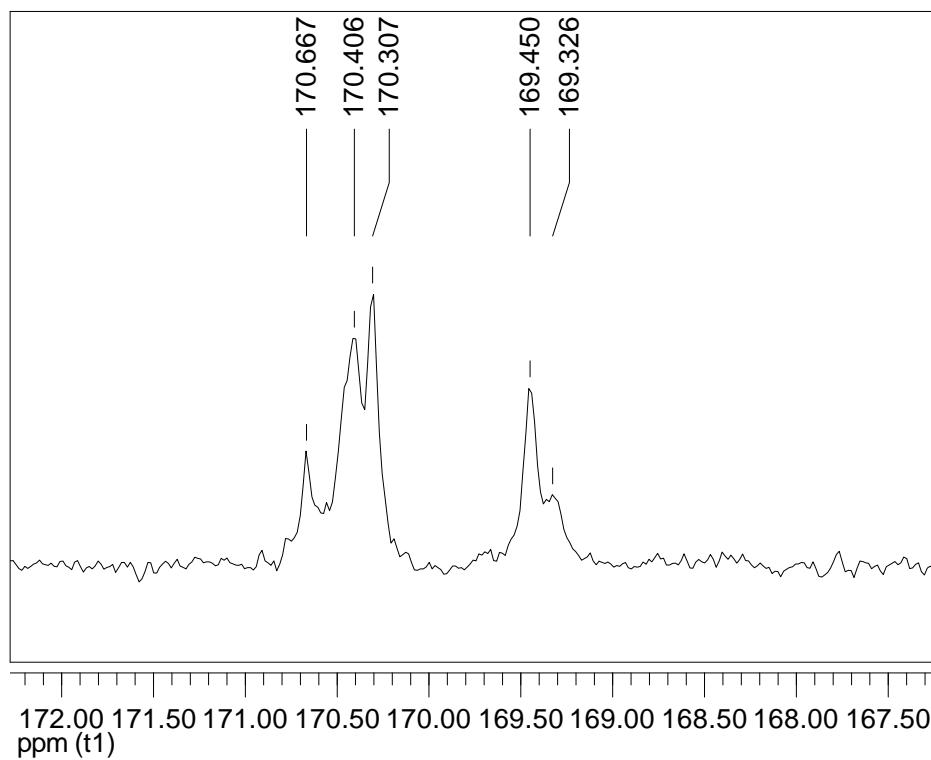


**Figure S9:** TGA plot for **4** ( $M_n = 2900$ , PDI = 1.26).



**Figure S10:**  $^1\text{H}$  NMR spectrum of **4**.





**Figure S11:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4**, including the expanded carbonyl region (166-173 ppm).

Fig. S12a

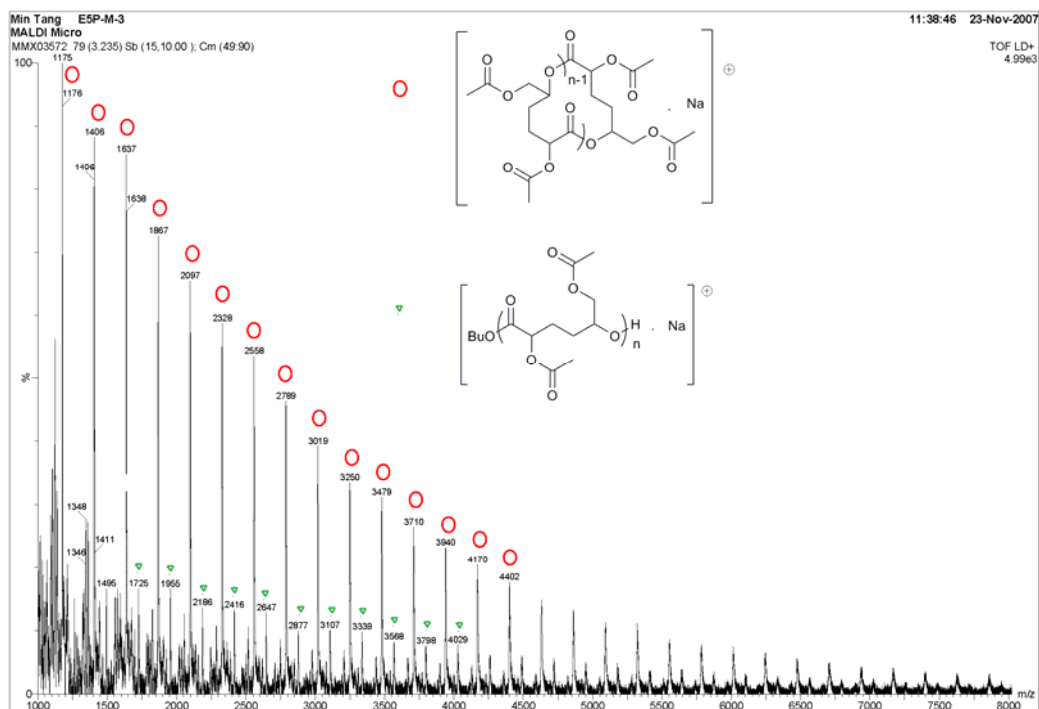
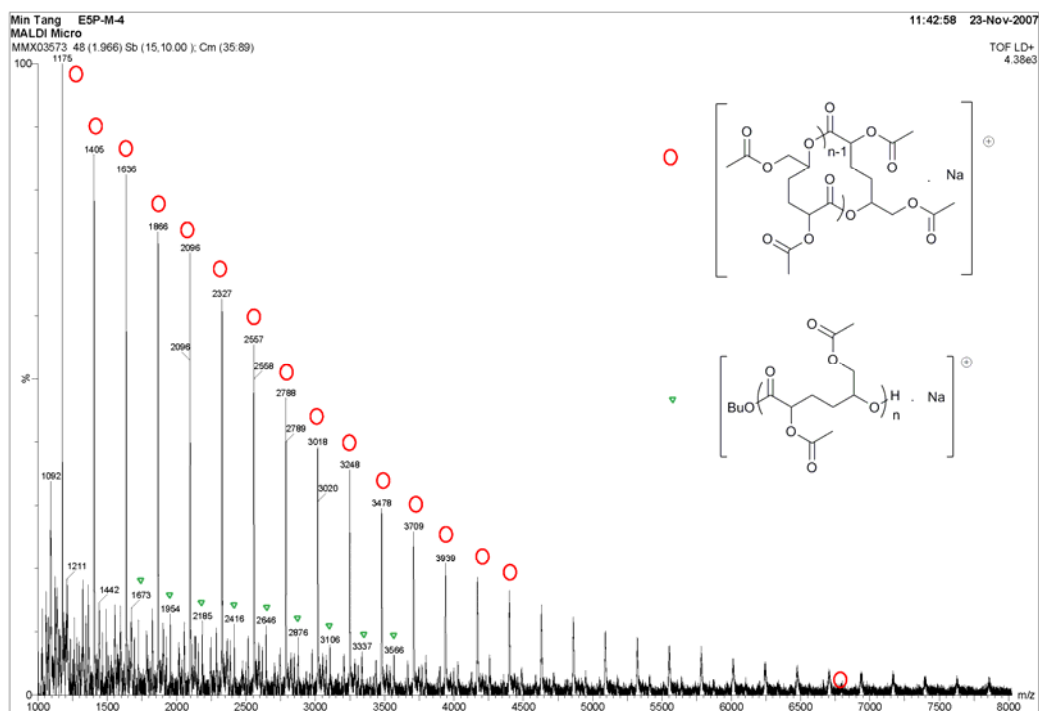


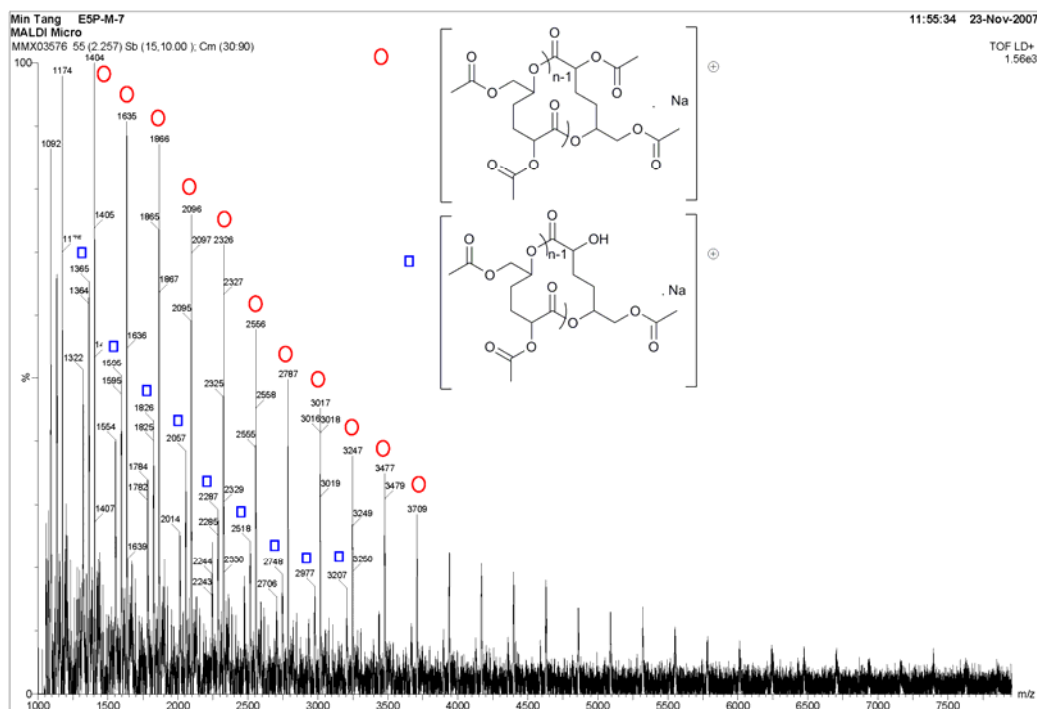
Fig. S12b



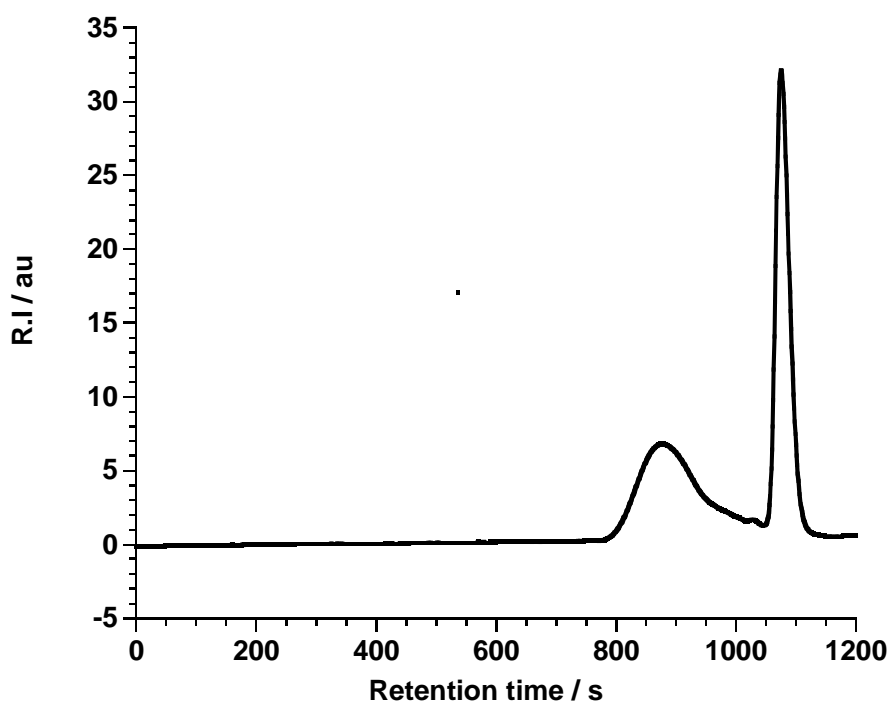




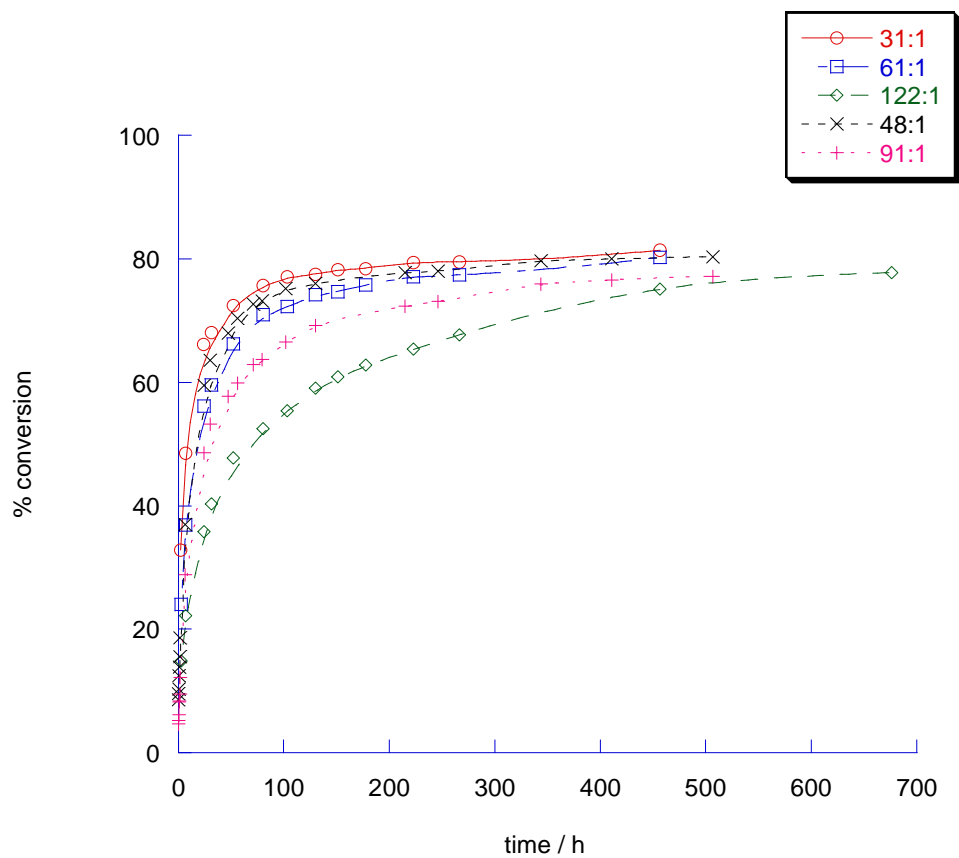
**Fig. S12e**



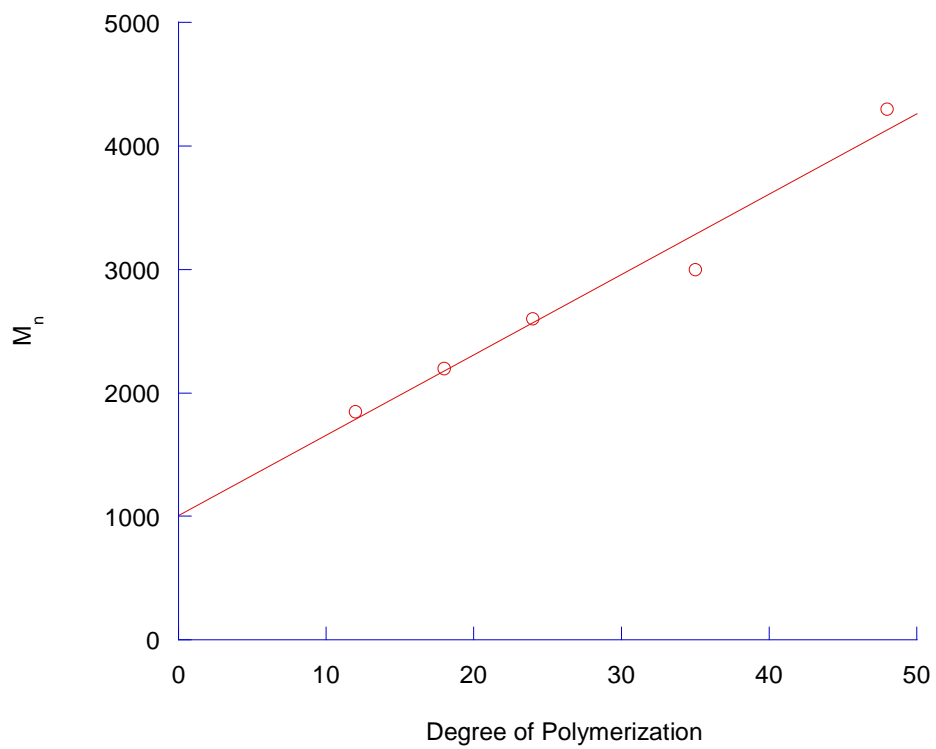
**Figure S12a-e:** MALDI-TOF mass spectra of **4** at various conversions (a = 47%, b=60%, c=76%, d=76% after 48 h, e=76% after 70h. The spectra were run using a dithranol matrix in THF using a NaOAc additive. Polymerization conditions:  $[3]_0 = 1$  M,  $[\text{Sn}(\text{O}i\text{Bu})_2]_0 = 0.01$  M, toluene, 80 °C.



**Figure S13:** SEC trace for **4**, trace shows the signal due to the polymer (retention time: 800-1000 s) and monomer (1100 s). Polymerization conditions:  $[3]_0 = 1 \text{ M}$ ,  $[\text{Sn}(\text{OBu})_2]_0 = 0.01 \text{ M}$ , toluene,  $80 \text{ }^\circ\text{C}$ . SEC conditions:  $\text{CHCl}_3$ ,  $1 \text{ mLmin}^{-1}$ , two mixed B columns, polystyrene standards.

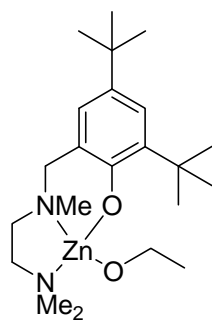


**Figure S14:** Plots of % conversion versus time at various loadings of Sn(OBu)<sub>2</sub> initiator. Polymerization conditions: [3]<sub>0</sub> = 1 M, toluene, 80 °C.



**Figure S15:** Plot of DP vs.  $M_n$  using the  $\text{Sn}(\text{O}i\text{Bu})_2$  initiators. Polymerization conditions:  $[\mathbf{3}]_0 = 1 \text{ M}$ , toluene,  $80 \text{ }^\circ\text{C}$ .

**Figure S16:** Structure of the initiator LZnOEt used.



## References

1. R. Gsell and M. Zeldin, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1133-1137.
2. C. K. Williams, L. E. Breyfogle, S. K. Choi, W. W. Nam, V. G. Young Jr., M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **123**, 11350-11359.
3. J. S. Gratzl and C. R. Nelson, *Carbohydr. Res.*, 1978, **60**, 267-273.
4. C. Pederson, *Carbohydr. Res.*, 1999, **315**, 192-197.