

# Supporting Information

## **Polymers from sugars and CS<sub>2</sub>: synthesis and ring-opening polymerisation of sulfur-containing monomers derived from of D-xylose- and 2-deoxy-D-ribose**

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## Experimental Details

### **Materials**

1,2-*O*-Isopropylidene- $\beta$ -D-xylofuranose and 1-*O*-methyl-2-deoxy-D-ribose were purchased from Carbosynth. Carbon disulfide, triethylamine, methanesulfonyl chloride, anhydrous pyridine and 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD) were purchased from Sigma-Aldrich. DBU and *p*-toluenesulfonyl chloride were purchased from Alfa Aesar. 4-Methylbenzyl alcohol was purchased from Acros Organics. Anhydrous solvents were purchased from Alfa Aesar or Sigma-Aldrich. Triethylamine was refluxed and then distilled over CaH<sub>2</sub> prior to use. 4-Methylbenzyl alcohol was recrystallised from dry diethyl ether and stored in a glovebox under Argon prior to use. TBD was dried over CaH<sub>2</sub> immediately prior to use by dissolution in dry THF. Other commercially available reagents and solvents were used without further purification. Dry THF and dry diethyl ether were obtained from an MBraun solvent purification system (SPS) and stored over 3 Å molecular sieves. Column chromatography was performed on silica gel (200-400 mesh particle size, 60 Å pore size), purchased from Sigma Aldrich. Spots were visualised by staining with KMnO<sub>4</sub> solution.

### **Methods**

All **NMR spectra** were recorded in CD<sub>3</sub>CN and CDCl<sub>3</sub> on a Bruker-400 or a Bruker-500 instruments using the deuterated solvent as lock and the residual protiated solvent as internal standard. For CD<sub>3</sub>CN <sup>1</sup>H NMR spectra (400 MHz) <sub>H</sub> = 1.94 ppm and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (101 MHz) <sub>C</sub> = 1.32 and 118.26 ppm. For CDCl<sub>3</sub> <sup>1</sup>H NMR spectra (400 MHz) <sub>H</sub> = 7.26 ppm and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (101 MHz) <sub>C</sub> = 77.16 ppm. Coupling constants are given in Hertz. All polymerisations were carried out under an argon atmosphere. Polymer conversions were determined by <sup>1</sup>H NMR spectroscopy (400 MHz, CDCl<sub>3</sub>).

**CHN microanalysis** was performed by Mr Stephen Boyer of the London Metropolitan University.

**Melting points** were measured on a variable temperature Griffin melting point apparatus.

**Infra-red spectra** were recorded as thin films on a Perkin-Elmer 100 Fourier transform spectrometer. For **mass spectrometry** the flow injection analysis (FIA) was conducted using a MaXis HD quadrupole electrospray time-of-flight (ESI-QTOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). Analyses were performed in both ESI positive and negative-ion modes. The capillary voltage was set to 4500 V, nebulizing gas at 0.4 bar, drying gas at 4 L/min at 200 °C in each case. The TOF scan range was from 75 – 1000 mass-to-charge ratio (*m/z*). The MS instrument was calibrated using sodium formate calibrant solution. The calibrant solution consisted of 3 parts of 1 M NaOH to 97 parts of 50:50 water:isopropanol with 2% formic acid. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula within 2 ppm mass accuracy. Data processing was performed using the Compass Data Analysis software version 4.3 (Bruker Daltonik GmbH, Bremen, Germany).

Number-average molecular weight  $M_n$  and dispersities  $\mathcal{D}$  ( $M_w/M_n$ ) were estimated by **size exclusion chromatography (SEC)** with a differential refractive index (RI) detector (maintained at 35 °C) using a 1260 GPC/SEC MDS instrument from Agilent. The separation was done using two columns PL HFIPgel 300x7.5 mm with a guard column PL HFIPgel 50x7.5 mm. The mobile phase was GPC-grade THF flowing at 1 mL/min. The detection was done using a differential refractive index detector. The columns and the detectors were maintained at 35 °C. The polymeric samples were dissolved in GPC-grade THF at a concentration between 1 mg/mL and 2 mg/mL. The column calibration was done using a set of PS samples.

Glass transition temperatures ( $T_g$ ) were measured by **differential scanning calorimetry (DSC)** using a MicroSC multicell calorimeter from Setaram; the Calisto program was employed to collect and process the data. Both measurement and reference cells were 1 mL Hastelloy C cells, roughly 25-70 mg of polymeric material was loaded into the measurement cell with the reference cell left empty. The experiment was performed under nitrogen gas and the sample heated from 20 to 100 °C at a rate of 1.2 K min<sup>-1</sup> and then cooled at the same rate.

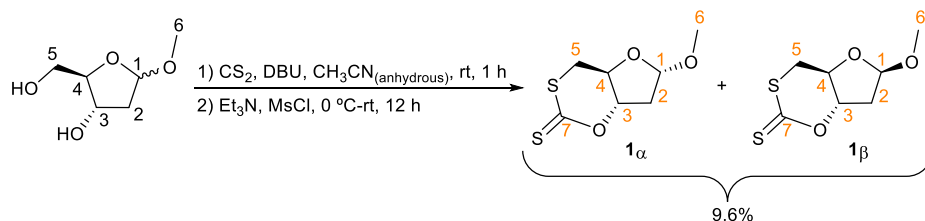
For **thermogravimetric analysis (TGA)** a Setsys Evolution TGA 16/18 instrument from Setaram was used and the Calisto program was employed to collect and process the data. The sample was loaded into a 170  $\mu\text{L}$  alumina crucible and the analytical chamber purged with argon ( $200 \text{ mL min}^{-1}$ ) for 40 min prior to starting the analysis. The sample was then heated under an argon flow ( $20 \text{ mL min}^{-1}$ ) from 30 to 500  $^{\circ}\text{C}$  at a rate of  $2 \text{ K min}^{-1}$ .

Matrix-assisted laser desorption ionisation-time of flight (MALDI-ToF) mass spectrometry was conducted using a Bruker ultrafleXtreme MALDI-TOF/TOF Mass Spectrometer equipped with a 2 kHz Smartbeam-II laser. To the polymer solutions were added solutions of dithranol in THF and KOAc, dithranol in THF and NaOAc or 2,5-dihydroxybenzoic acid (DHB) in THF and KOAc. All the analysis were done in positive-linear mode. A micropipette was used to spot  $\sim 1 \mu\text{L}$  of the solution onto a polished steel MALDI plate and the solvent allowed to evaporate in air. Once loaded, positive ion MALDI spectra were obtained in reflector mode. Laser intensity was varied. The data was analysed using the Flex Analysis software, version 3.4 (build 76). The molecular weight distributions and percentage of each species present were obtained through analysis of the data in the Polytools software package 1.31.

All **single-crystal X-ray diffraction analysis** was carried out by Dr Gabriele Kociok-Köhn on a Nonius Kappa CCD diffractometer using  $\text{Cu-K}_{\alpha}$  radiation at 150 K and  $\lambda = 1.54184 \text{ \AA}$  for monomers **1** and **2** and  $\lambda = 0.71073 \text{ \AA}$  for monomer **3**.

## Synthesis and NMR characterisation

### Synthesis of monomer **1**

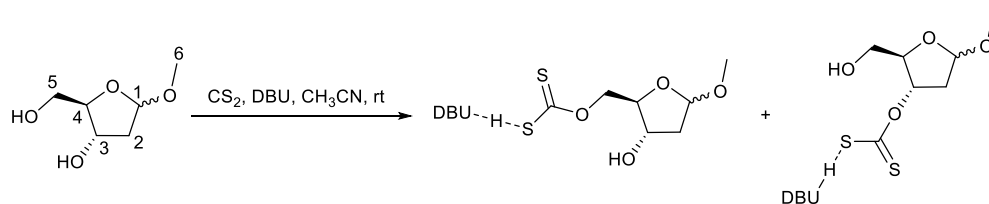


**Scheme S1.** Synthesis of monomer **1**.

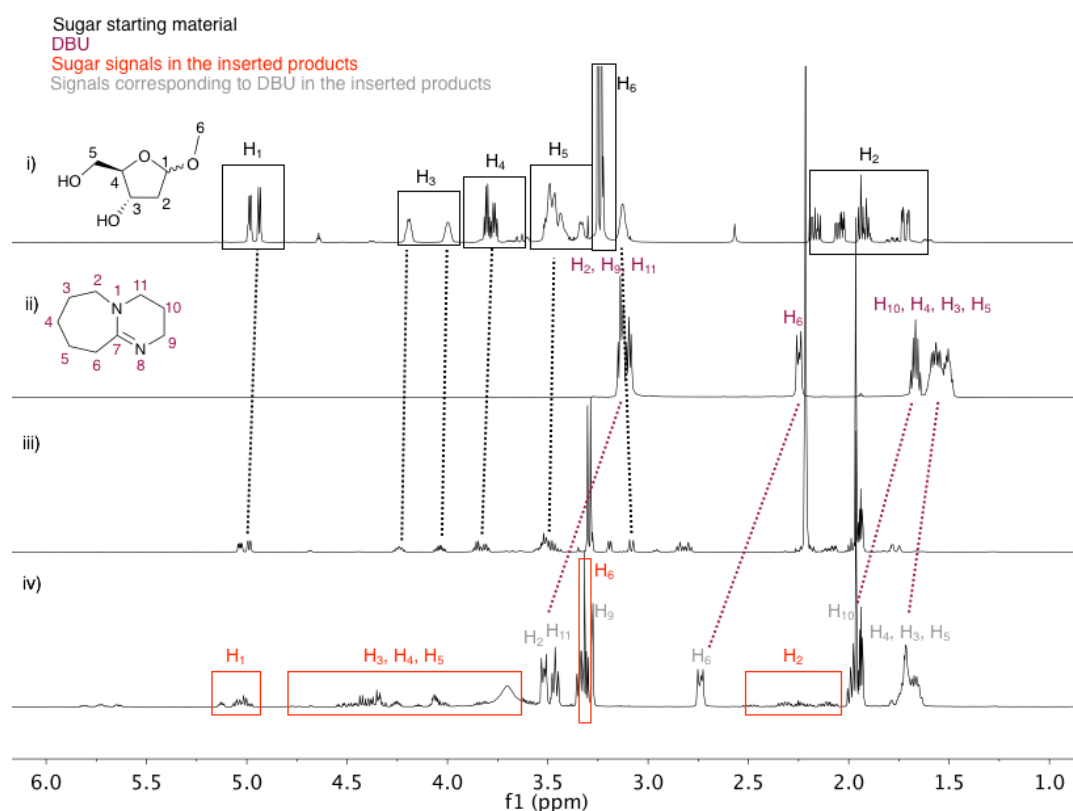
1-*O*-Methyl-2-deoxy-D-ribose (2 g, 13.5 mmol) was put into a Schlenk flask under argon atmosphere. Anhydrous CH<sub>3</sub>CN (135 mL) was added and the sugar was completely dissolved. CS<sub>2</sub> (3.263 mL, 54.0 mmol) was added to the sugar containing solution and the reaction mixture was stirred at room temperature for 5 minutes. DBU (2.02 mL, 13.5 mmol) was added at room temperature and the reaction mixture became yellow. After 1 hour stirring at room temperature the Schlenk flask containing the reaction mixture was put into an ice-water bath and Et<sub>3</sub>N (1.9 mL, 13.5 mmol) was added followed by subsequent addition of methanesulfonyl chloride (1.05 mL, 13.5 mmol). The yellow reaction mixture turned into an intense brown color on stirring overnight at room temperature. Volatiles were then removed under reduced pressure and the crude oil immediately subjected to column chromatography using CHCl<sub>3</sub>. *R<sub>f</sub>* 0.68 (19:1 CHCl<sub>3</sub>/acetone); *R<sub>f</sub>* 0.78 (5:1 CHCl<sub>3</sub>/acetone) using KnMnO<sub>4</sub> stain. The product-containing fractions were combined and the solvents were removed under reduced pressure obtaining **1** as a pale yellow solid (266 mg, 9.6% mixture of  $\alpha$  and  $\beta$  anomers). Several recrystallisations from hexanes yielded pale yellow crystals suitable for single-crystal X-ray diffraction.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) for **1**: = 5.15 (1H, d, *J*=5.3 Hz, H<sub>1 $\beta$</sub> ), 5.11 (1H, dd, *J*=5.8 and 4.2 Hz, H<sub>1 $\alpha$</sub> ), 4.67 (1H, ddd, *J*=10.9, 8.7 and 7.1 Hz, H<sub>3 $\beta$</sub> ), 4.32 (1H, ddd, *J*=9.3, 8.8 and 8.7 Hz, H<sub>3 $\alpha$</sub> ), 4.20 (1H, ddd, *J*=9.8, 8.8 and 6.3 Hz, H<sub>4 $\alpha$</sub> ), 4.11 (1H, ddd, *J*=11.0, 8.7 and 5.4 Hz, H<sub>4 $\beta$</sub> ), 3.40 (3H, s, H<sub>6 $\alpha$</sub> ), 3.35 (3H, s, H<sub>6 $\beta$</sub> ), 3.25 (4H, m, H<sub>5 $\alpha+\beta$</sub> ), 2.80 (1H, ddd, *J*=13.8, 8.7 and 5.8 Hz, H<sub>2 $\alpha$</sub> ), 2.45 (1H, dd, *J*=12.4 and 7.1 Hz, H<sub>2 $\beta$</sub> ), 2.37 (1H, ddd, *J*=12.6, 10.9 and 5.3 Hz, H<sub>2' $\beta$</sub> ), 2.17 (1H, ddd, *J*=13.6, 9.3 and 4.2 Hz, H<sub>2' $\alpha$</sub> ) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 25 °C) for **1**: = 208.1 (C(S)SO, C<sub>7 $\alpha$</sub> ), and 207.8 (C(S)SO, C<sub>7 $\beta$</sub> ), 104.3 (2C<sub>1 $\alpha+\beta$</sub> ), 83.3 (C<sub>3 $\alpha$</sub> ), 83.1 (C<sub>3 $\beta$</sub> ), 72.9 (C<sub>4 $\beta$</sub> ), 69.4 (C<sub>4 $\alpha$</sub> ), 56.1 (C<sub>6 $\alpha$</sub> ), 55.6 (C<sub>6 $\beta$</sub> ), 38.1 (C<sub>5 $\beta$</sub> ), 37.0 (C<sub>2 $\beta$</sub> ), 36.9 (C<sub>2 $\alpha$</sub> ), 36.6 (C<sub>5 $\alpha$</sub> ) ppm. HR-MS (ESI positive mode) in CH<sub>3</sub>CN: *m/z* calculated for [C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>S<sub>2</sub>Na]<sup>+</sup> 228.9964; found: 228.9989. HR-MS (ESI negative mode) in CH<sub>3</sub>CN: *m/z* calculated for [C<sub>7</sub>H<sub>9</sub>O<sub>3</sub>S<sub>2</sub>]<sup>-</sup> 204.9999; found: 204.9968. Elemental analysis: Found: C 40.83%; H 4.74%, C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>S<sub>2</sub> requires C 40.76%; H 4.89%. Melting point of **1** = 90 °C.

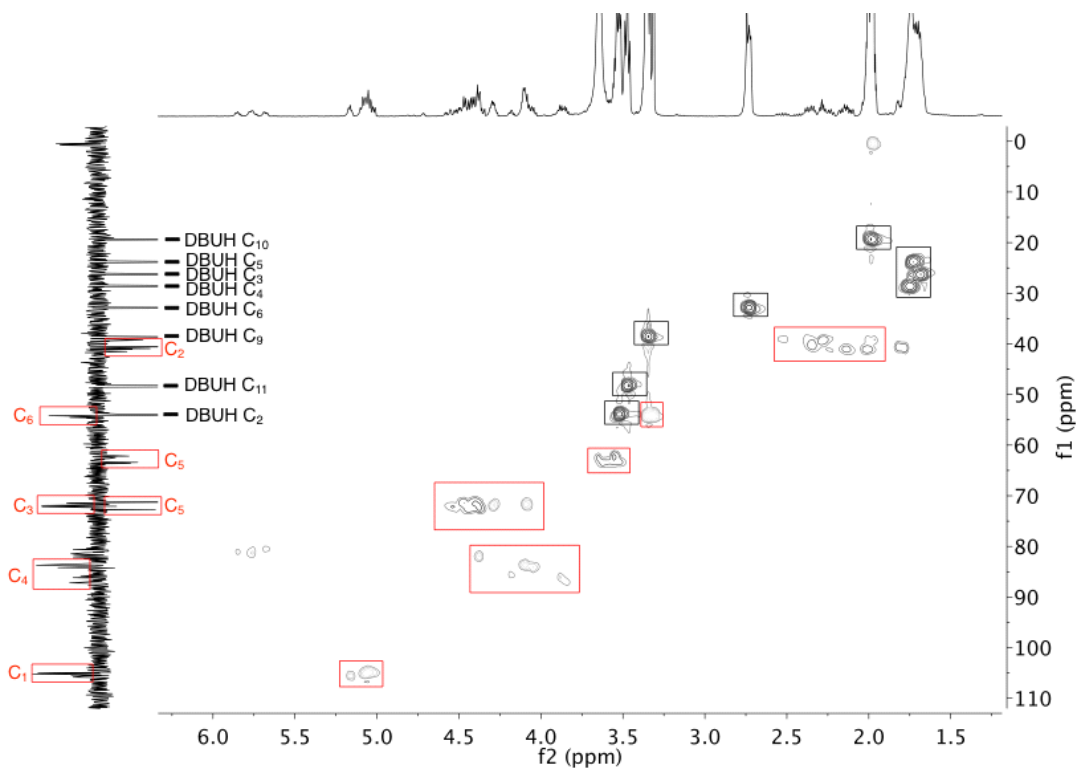
### Insertion of CS<sub>2</sub> into 1-*O*-methyl-2-deoxy-*D*-ribose



**Scheme S2.** Proposed inserted products after addition of CS<sub>2</sub> (4 equivalents) and DBU (1 equivalent) to a solution of 1-*O*-Methyl-2-deoxy-*D*-ribose (0.1 M) in anhydrous CH<sub>3</sub>CN.



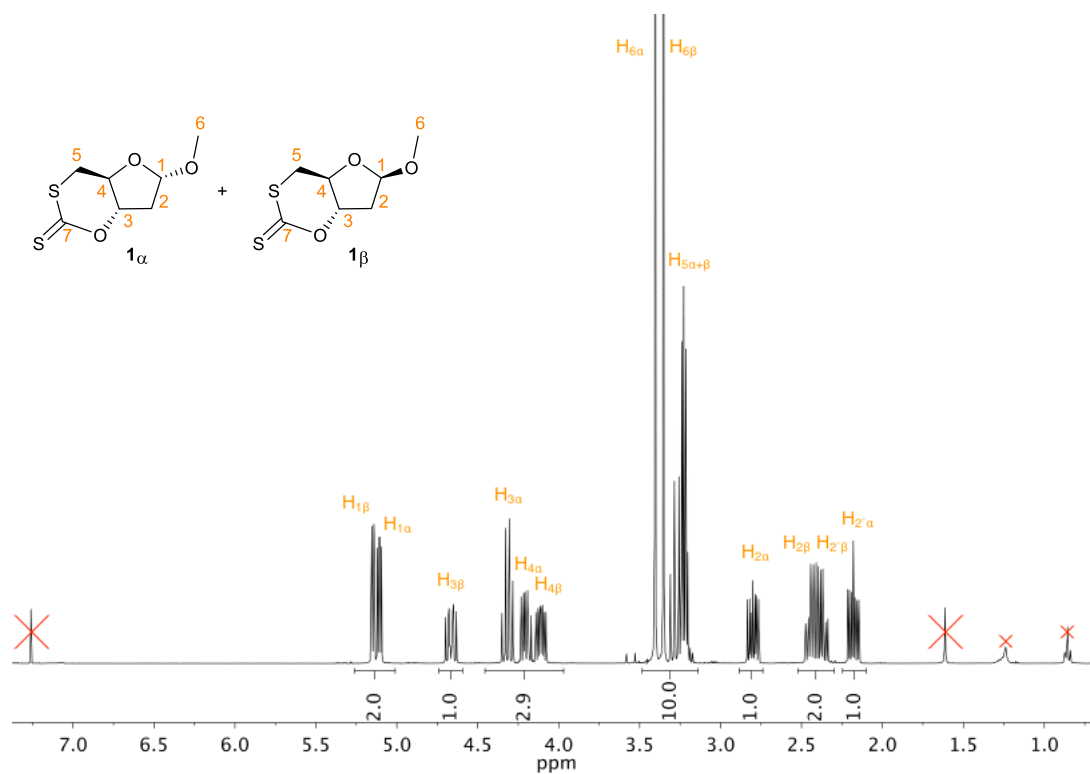
**Figure S1.** <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 25 °C) of: i) 1-*O*-methyl-2-deoxy-*D*-ribose, ii) DBU, iii) reaction mixture containing 1-*O*-methyl-2-deoxy-*D*-ribose (1 equivalent) and CS<sub>2</sub> (4 equivalents), iv) the previous mixture 5 hours after addition of DBU (1 equivalent).



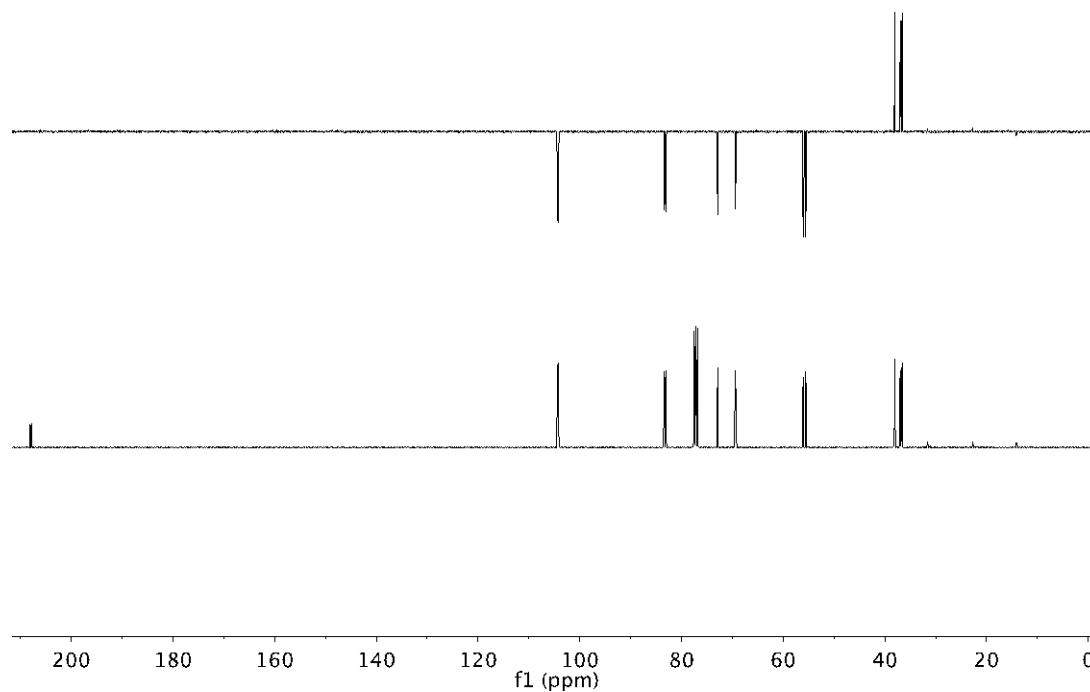
**Figure S2.** HSQC (400 and 101 MHz for <sup>1</sup>H and DEPT-135, CD<sub>3</sub>CN, 25 C) of a reaction mixture containing 1-*O*-methyl-2-deoxy-D-ribose (1 equivalent), CS<sub>2</sub> (4 equivalents) and DBU (1 equivalent) after 5 hours of reaction.



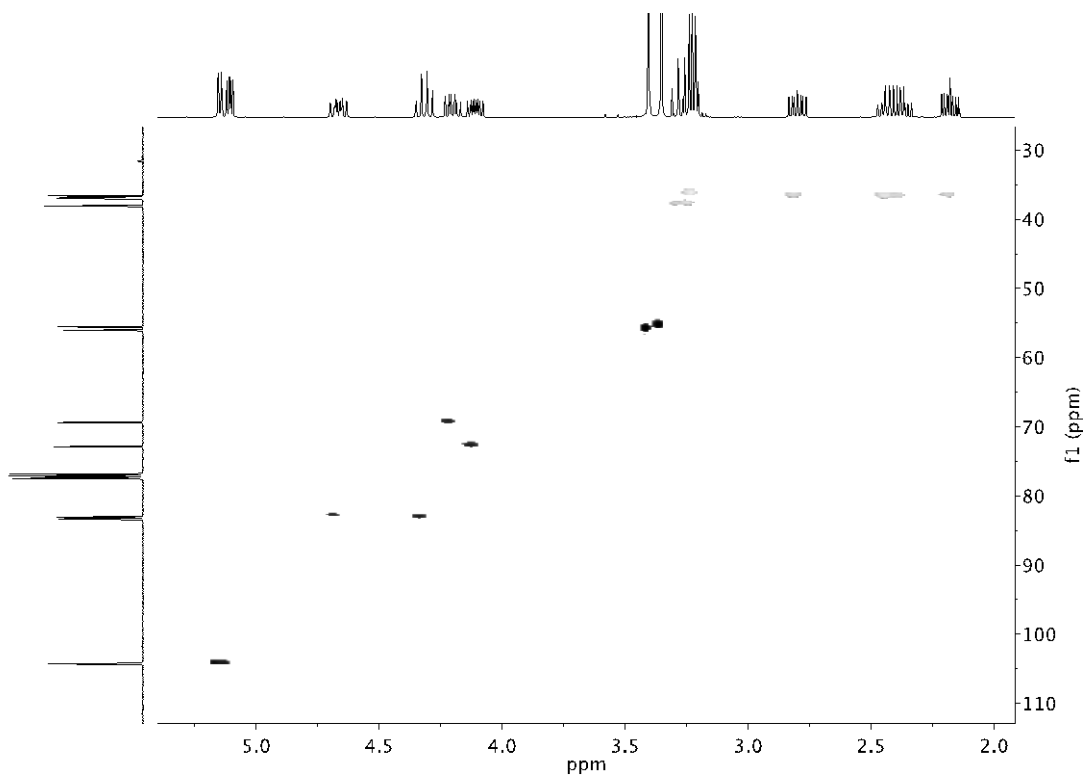
## NMR Characterisation of monomer **1**



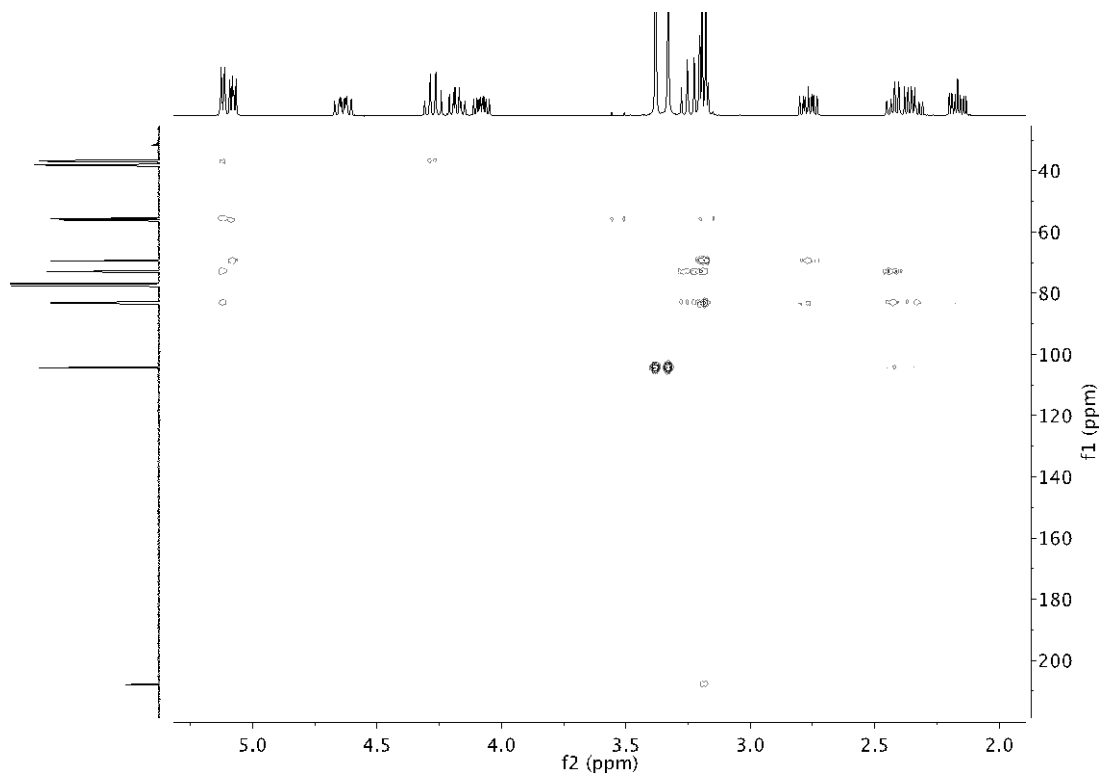
**Figure S3.** Annotated  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 C) of **1** + **1**. Red crosses denote residual  $\text{CHCl}_3$ ,  $\text{H}_2\text{O}$  and *n*-hexane solvent peaks.



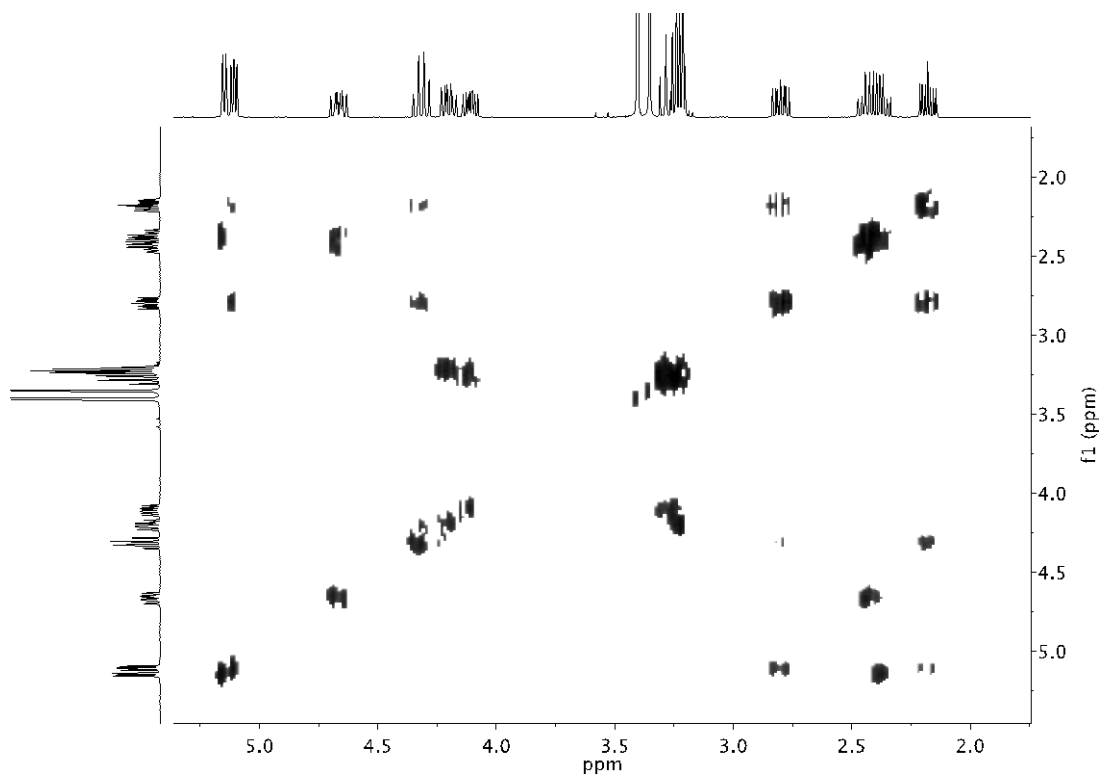
**Figure S4.**  $^{13}\text{C}$  NMR and DEPT-135 spectra (101 MHz,  $\text{CDCl}_3$ , 25 C) of **1** + **1**.



**Figure S5.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **1 + 1**.

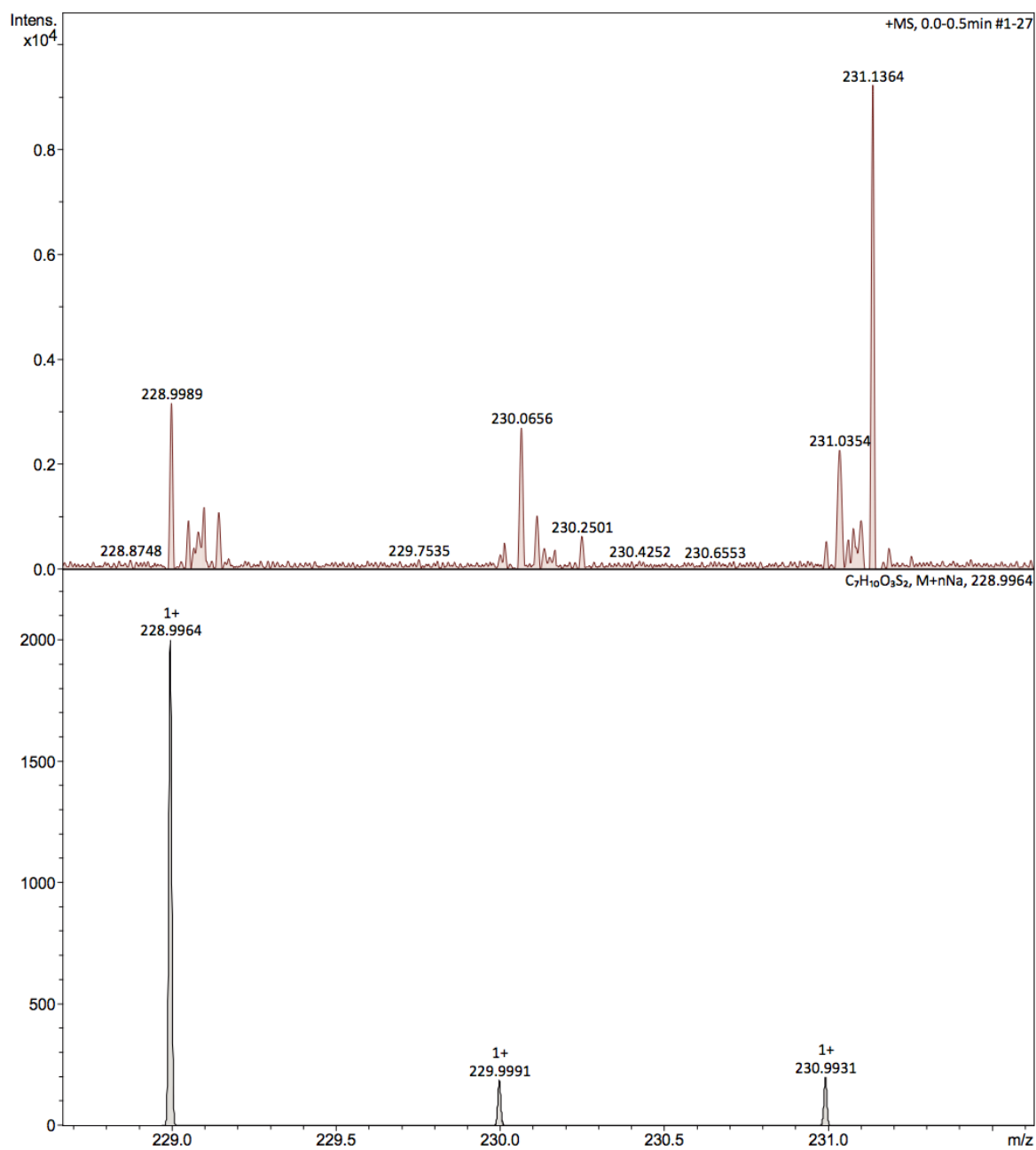


**Figure S6.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **1 + 1**.

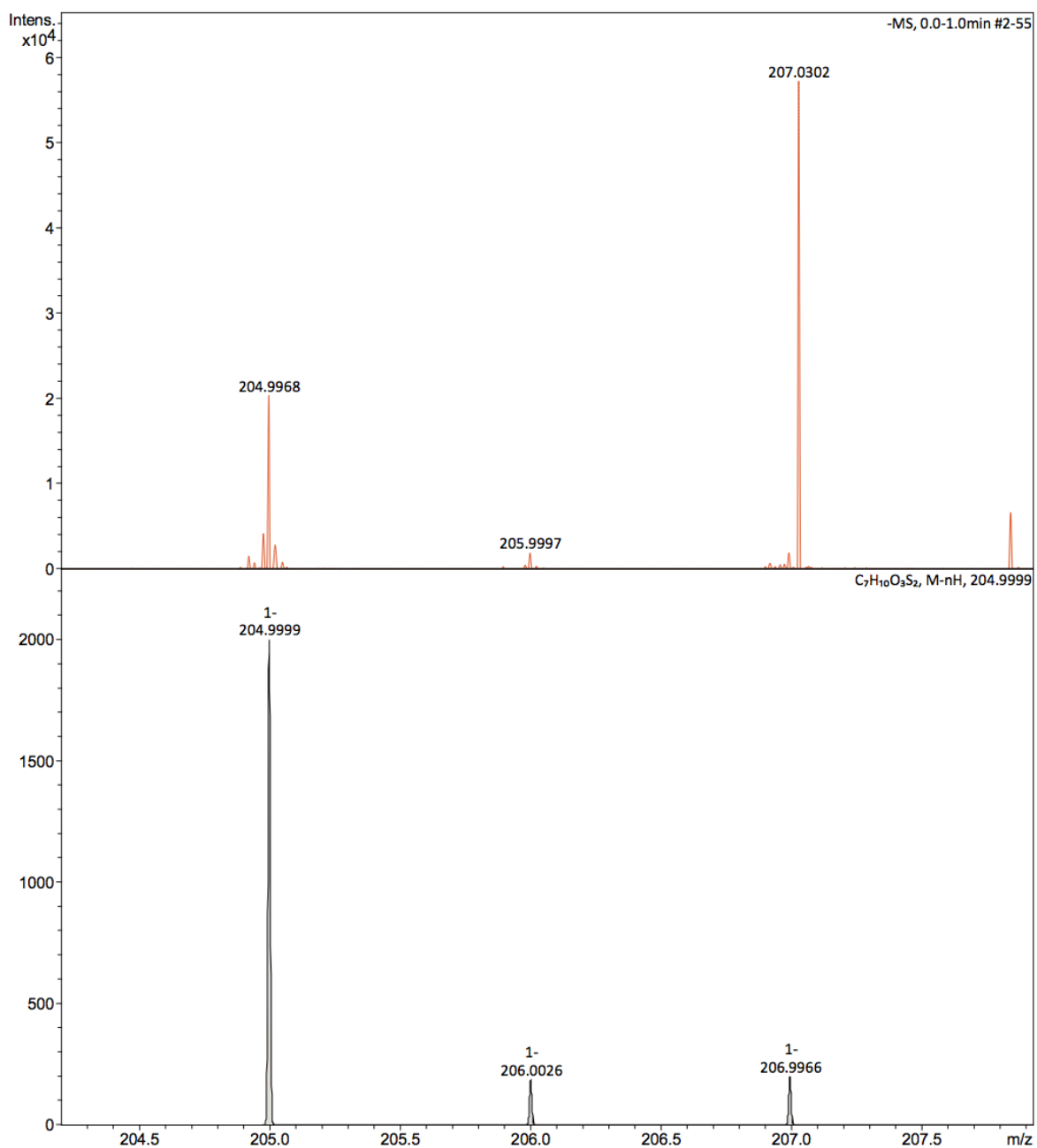


**Figure S7.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of **1 + 1**.

## MS Characterisation of monomer 1

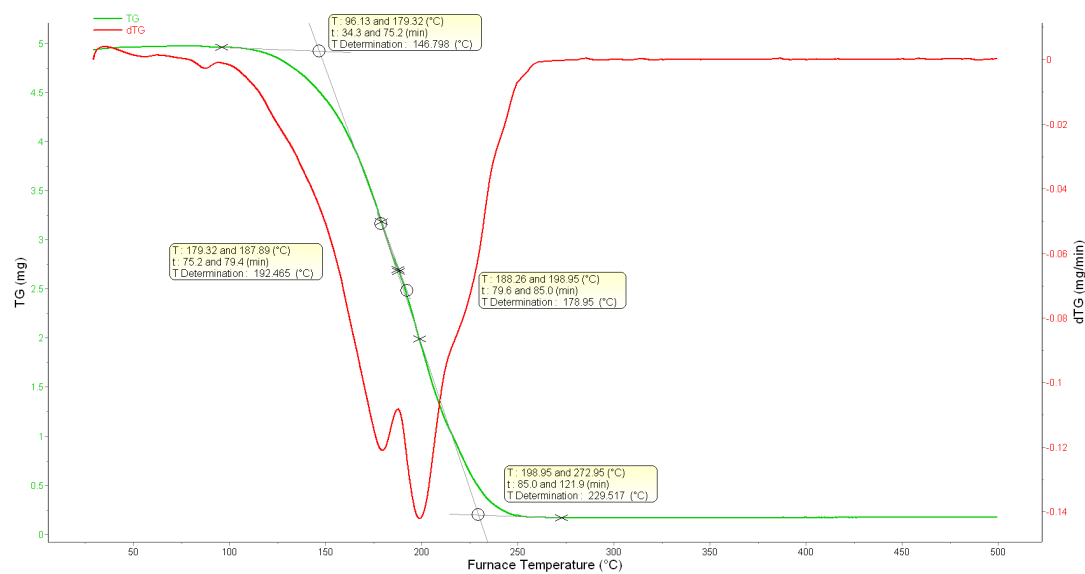


**Figure S8.** HR-MS (ESI positive mode) for [C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>S<sub>2</sub>Na]<sup>+</sup> (top) found 228.9989, (bottom) calculated 228.9964.



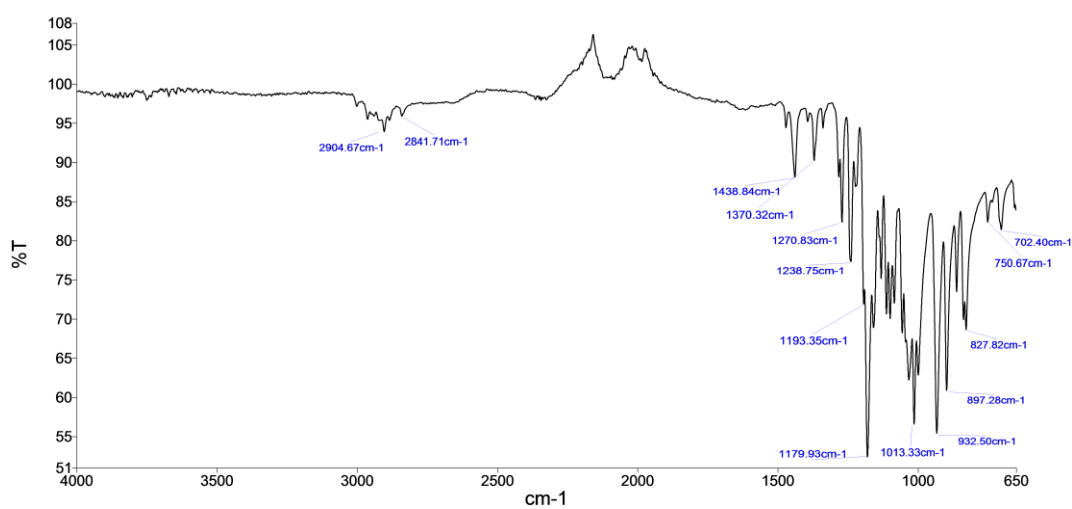
**Figure S9.** HR-MS (ESI negative mode) for  $[C_7H_9O_3S_2]^-$  (top) found 204.9968, (bottom) calculated 204.9999.

## TGA of monomer 1



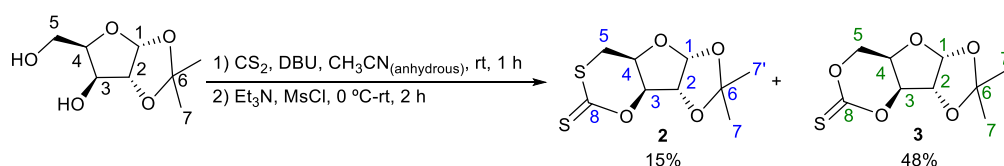
**Figure S10.** TGA of monomer 1. The monomer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

## FT-IR of monomer 1



**Figure S11.** FT-IR of monomer 1.

### Synthesis of monomers **2** and **3**



**Scheme S3.** Synthesis of monomers **2** and **3**.

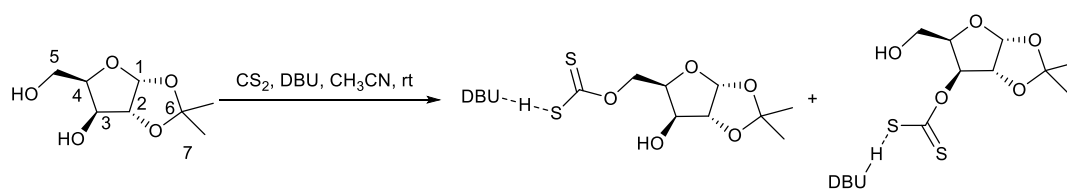
1,2-*O*-Isopropylidene-D-xylofuranose (2 g, 10.52 mmol) was put into a Schlenk flask under argon atmosphere. Anhydrous CH<sub>3</sub>CN (105 mL) was added and the sugar was completely dissolved. Under argon atmosphere CS<sub>2</sub> (2.542 mL, 42.06 mmol) was added while stirring the reaction mixture at room temperature for 5 minutes. DBU (1.572 mL, 10.52 mmol) was added and the reaction mixture changed from colorless to yellow instantly. After 1 hour stirring at room temperature the Schlenk flask containing the reaction mixture was put into an ice-water bath and Et<sub>3</sub>N (1.464 mL, 10.52 mmol) was added to the reaction mixture. After 5 minutes, methanesulfonyl chloride (0.814 mL, 10.52 mmol) was added to the reaction mixture and it was left stirring for 2 hours enabling the reaction mixture to reach room temperature. The crude reaction mixture was subjected to column chromatography using chloroform as eluent. The product-containing fractions were combined and subjected to a second column chromatography. *R<sub>f</sub>* for **2**: 0.69 (19:1 CHCl<sub>3</sub>/acetone); *R<sub>f</sub>* for **3**: 0.5 (19:1 CHCl<sub>3</sub>/acetone) using KnMnO<sub>4</sub> stain. The solvents were removed under reduced pressure obtaining **2** as a pale yellow solid (380 mg, 15%) and **3** as a colorless solid (1.164 g, 48%). Several recrystallisations from hexanes yielded pale yellow crystals of **2** and colorless crystals of **3** suitable for single-crystal X-ray diffraction.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) for **2**: = 6.03 (1H, d, *J*=3.7 Hz, H<sub>1</sub>), 4.92 (1H, d, *J*=3.2 Hz, H<sub>2</sub>), 4.88 (1H, td, *J*=5.1 and 3.3 Hz, H<sub>4</sub>), 4.80 (1H, d, *J*=3.2 Hz, H<sub>3</sub>), 3.37 (1H, dd, *J*=5.5 and 13.6 Hz, H<sub>5</sub>), 3.17 (1H, dd, *J*=4.9 and 13.6 Hz, H<sub>5'</sub>), 1.54 (3H, s, H<sub>7</sub>), 1.36 (3H, s, H<sub>7'</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 25 °C) for **2**: = 208.6 (C(S)SO, C<sub>8</sub>); 113.1 (C, C<sub>6</sub>); 105.3 (CH, C<sub>1</sub>); 87.2 (CH, C<sub>3</sub>); 83.7 (CH, C<sub>2</sub>); 70.5 (CH, C<sub>4</sub>); 31.3 (CH<sub>2</sub>, C<sub>5</sub>); 26.9 (CH<sub>3</sub>, C<sub>7</sub>); 26.4 (CH<sub>3</sub>, C<sub>7'</sub>) ppm. HR-MS (ESI positive mode) of **2** in CH<sub>3</sub>CN: *m/z* calculated for [C<sub>9</sub>H<sub>13</sub>O<sub>4</sub>S<sub>2</sub>]<sup>+</sup> 249.0250; found: 249.0294; *m/z* calculated for [C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub>Na]<sup>+</sup> 271.0069; found: 271.0104. Elemental analysis of **2**: Found: C 43.50%, H 4.98%, C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub> requires C 43.53%, H 4.87%. Melting point of **2** = 120 °C.

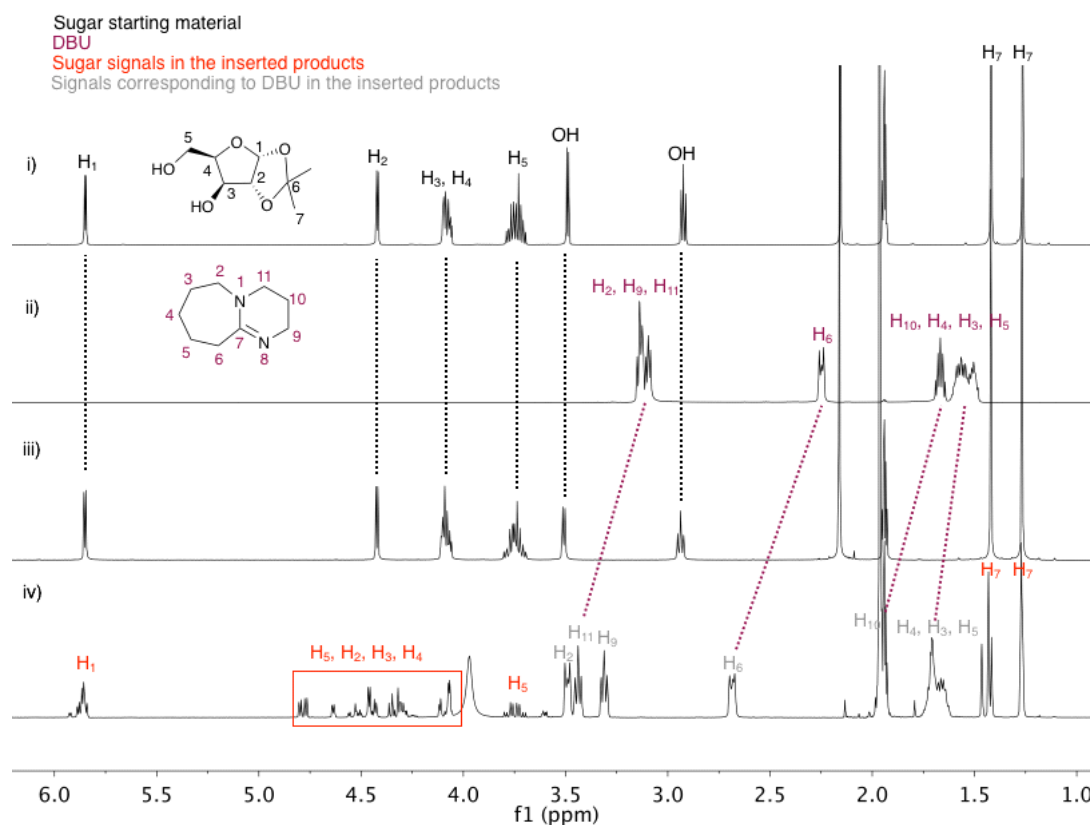
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) for **3**: = 6.03 (1H, d, *J*=3.6 Hz, H<sub>1</sub>), 4.85 (1H, d, *J*=3.3 Hz, H<sub>3</sub>), 4.83 (1H, d, *J*=3.6 Hz, H<sub>2</sub>), 4.68 (1H, m, H<sub>4</sub>), 4.66-4.63 (1H, dd, *J*=1.9 and 12.6 Hz, H<sub>5</sub>), 4.53-4.49 (1H, dd, *J*=2 and 12.8 Hz, H<sub>5'</sub>), 1.52 (3H, s, H<sub>7</sub>), 1.35 (3H, s, H<sub>7'</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 25 °C) for **3**: = 187.4 (C(S)O<sub>2</sub>, C<sub>8</sub>); 113.4 (C, C<sub>6</sub>); 105.4 (CH, C<sub>1</sub>); 83.6 (CH, C<sub>3</sub>); 82.6 (CH, C<sub>2</sub>); 69.4 (CH, C<sub>4</sub>); 67.6 (CH<sub>2</sub>, C<sub>5</sub>); 26.8 (CH<sub>3</sub>, C<sub>7</sub>); 26.4 (CH<sub>3</sub>, C<sub>7'</sub>) ppm. HR-MS (ESI positive mode) of **3** in CH<sub>3</sub>CN: *m/z* calculated for [C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>SNa]<sup>+</sup> 255.0298; found: 255.0334. HR-MS (ESI negative mode) of **3** in CH<sub>3</sub>CN: *m/z* calculated for [C<sub>9</sub>H<sub>11</sub>O<sub>5</sub>S]<sup>-</sup> 231.0333; found: 231.0301. Elemental analysis of **3**: Found: C 46.42%, H 5.27%, C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>S requires C, 46.54%, H 5.21%. Melting point of **3** = 130 °C.

Monomer **3** can also be prepared using the reporting method.<sup>1</sup>

### Insertion of CS<sub>2</sub> into 1,2-*O*-isopropylidene-*D*-xylofuranose

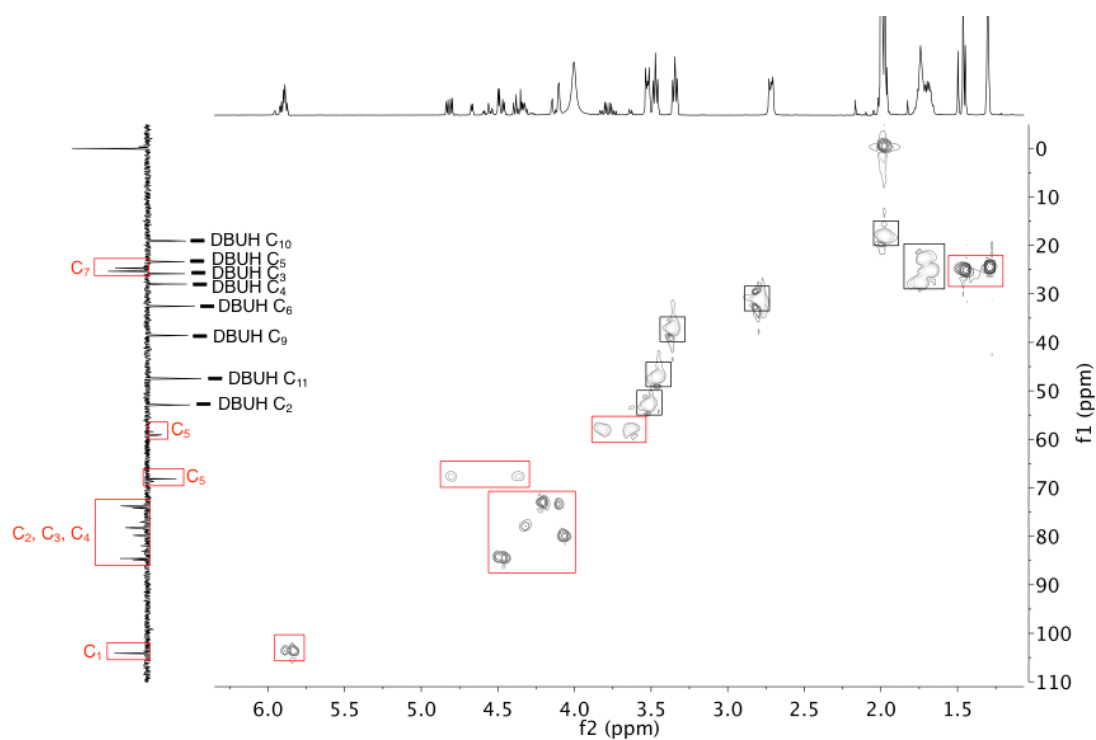


**Scheme S4.** Proposed inserted products after addition of CS<sub>2</sub> (4 equivalents) and DBU (1 equivalent) to a solution of 1,2-*O*-isopropylidene-*D*-xylofuranose (0.1 M) in anhydrous CH<sub>3</sub>CN.



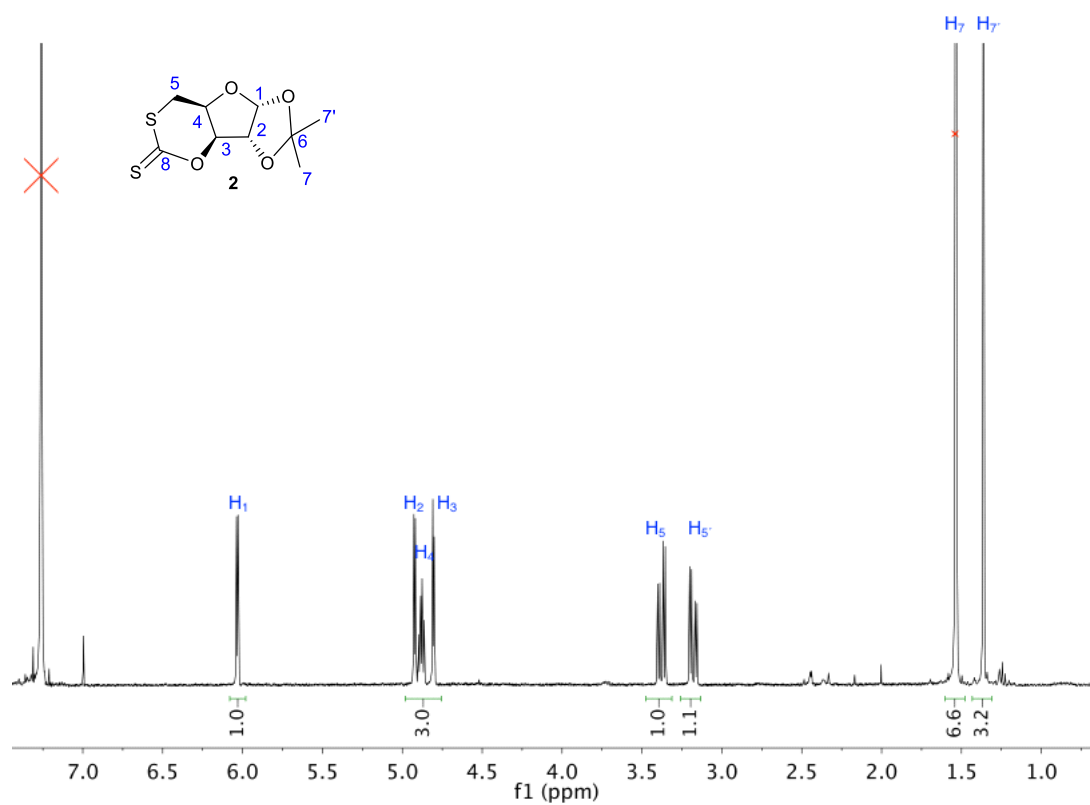
**Figure S12.** <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 25 C) of: i) 1,2-*O*-isopropylidene-*D*-xylofuranose, ii) DBU, iii) reaction mixture containing 1,2-*O*-isopropylidene-*D*-xylofuranose (1 equivalent) and CS<sub>2</sub> (4 equivalents), iv) the previous mixture 5 hours after addition of DBU (1 equivalent).



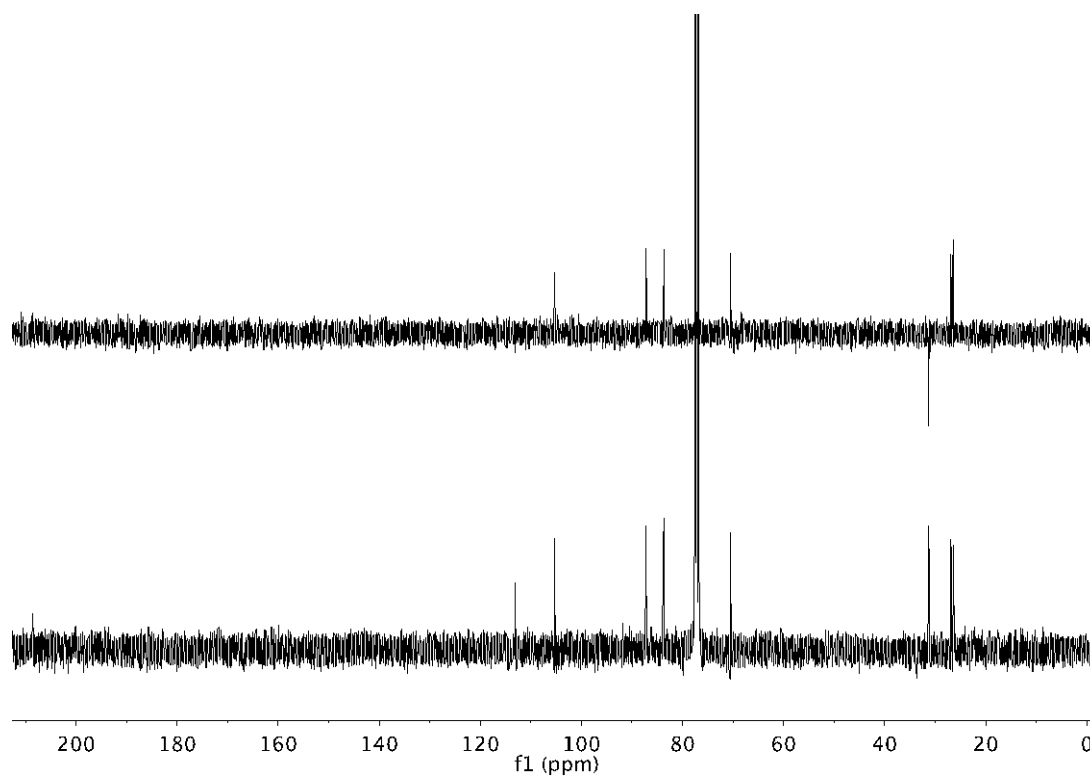


**Figure S13.** HSQC (400 and 101 MHz for  $^1\text{H}$  and DEPT-135,  $\text{CD}_3\text{CN}$ , 25 C) of a reaction mixture containing 1,2-*O*-isopropylidene-D-xylofuranose (1 equivalent),  $\text{CS}_2$  (4 equivalents) and DBU (1 equivalent) after 5 hours of reaction.

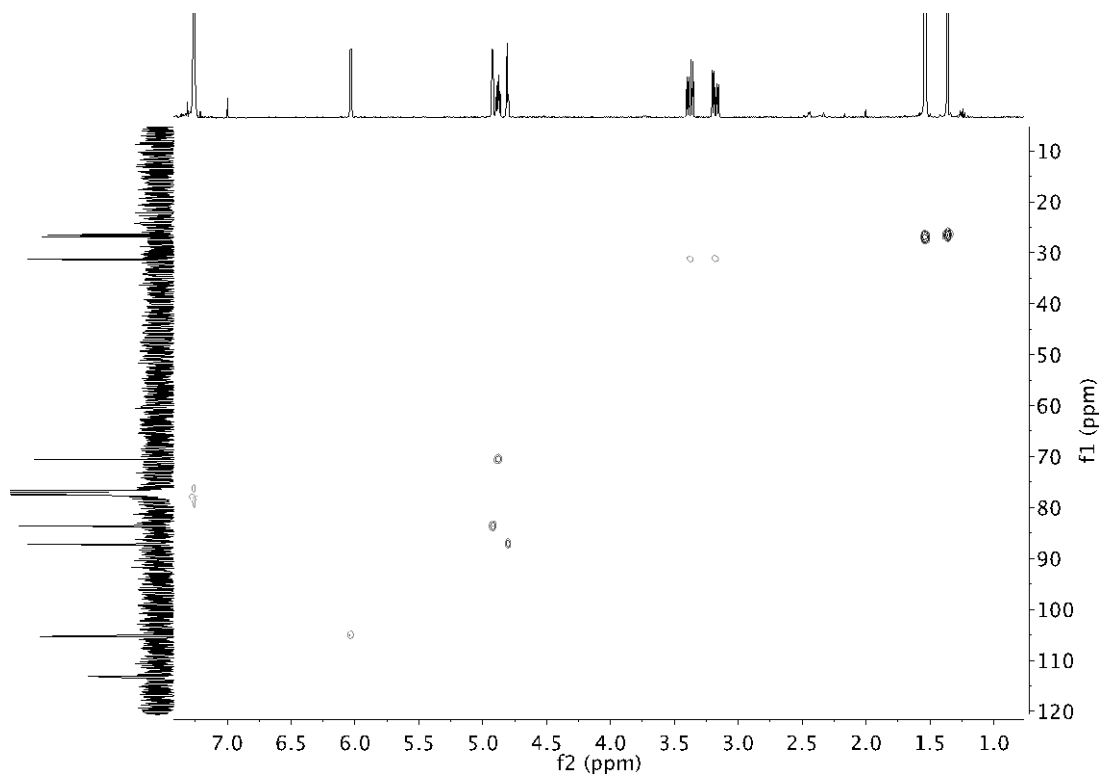
## NMR Characterisation of monomer 2



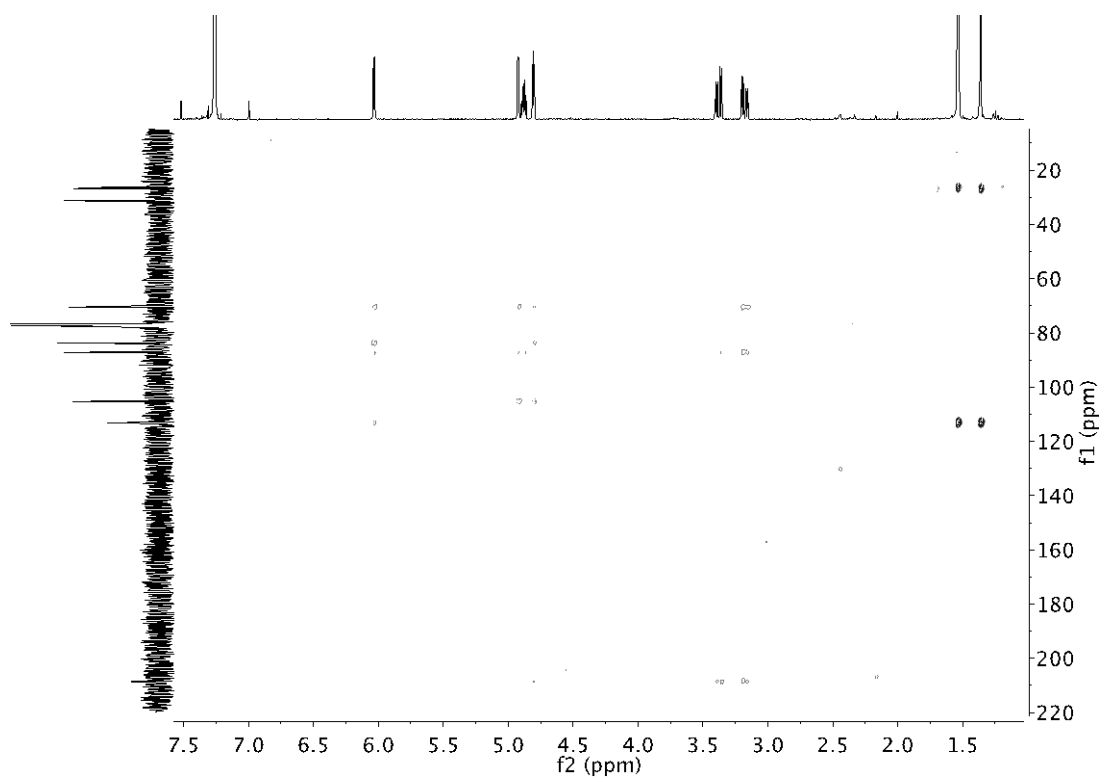
**Figure S14.** Annotated  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 C) of **2**. Red crosses denote residual  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  solvent peaks. The  $\text{H}_2\text{O}$  peak is overlapped with the  $\text{H}_7$  signal.



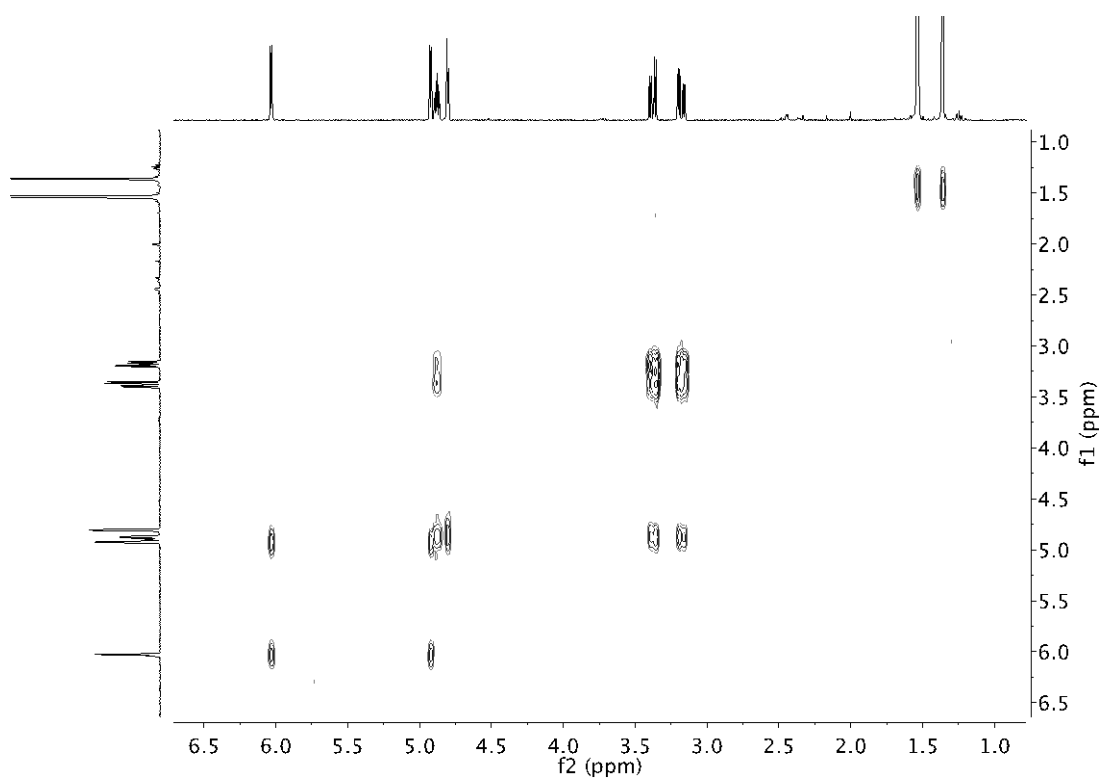
**Figure S15.**  $^{13}\text{C}$  NMR and DEPT-135 spectra (101 MHz,  $\text{CDCl}_3$ , 25 C) of **2**.



**Figure S16.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **2**.

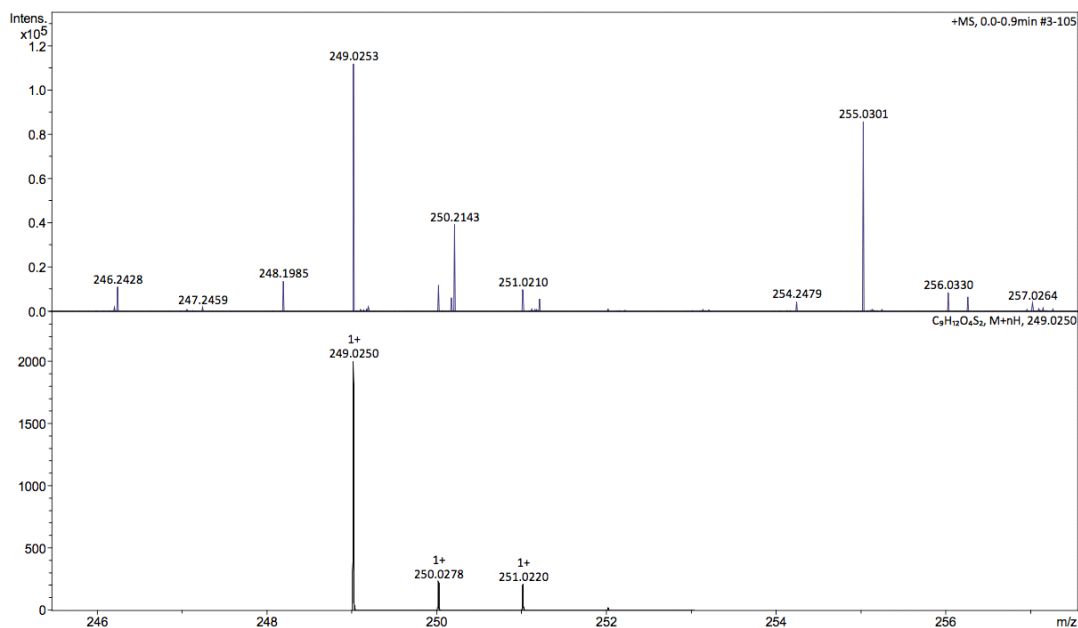


**Figure S17.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **2**.

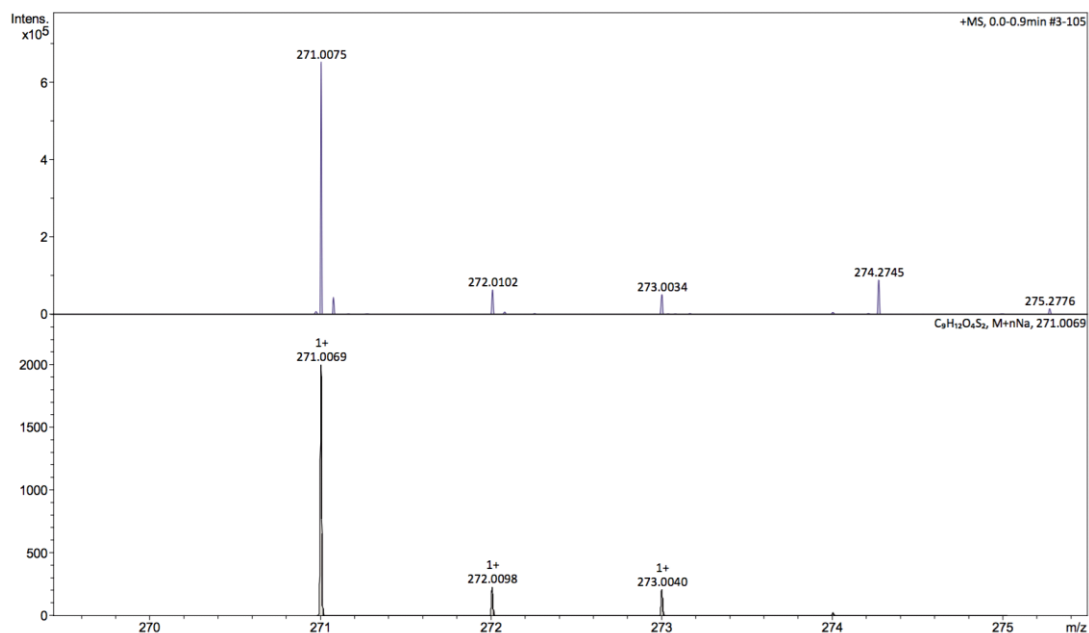


**Figure S18.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of **2**.

## MS Characterisation of monomer 2

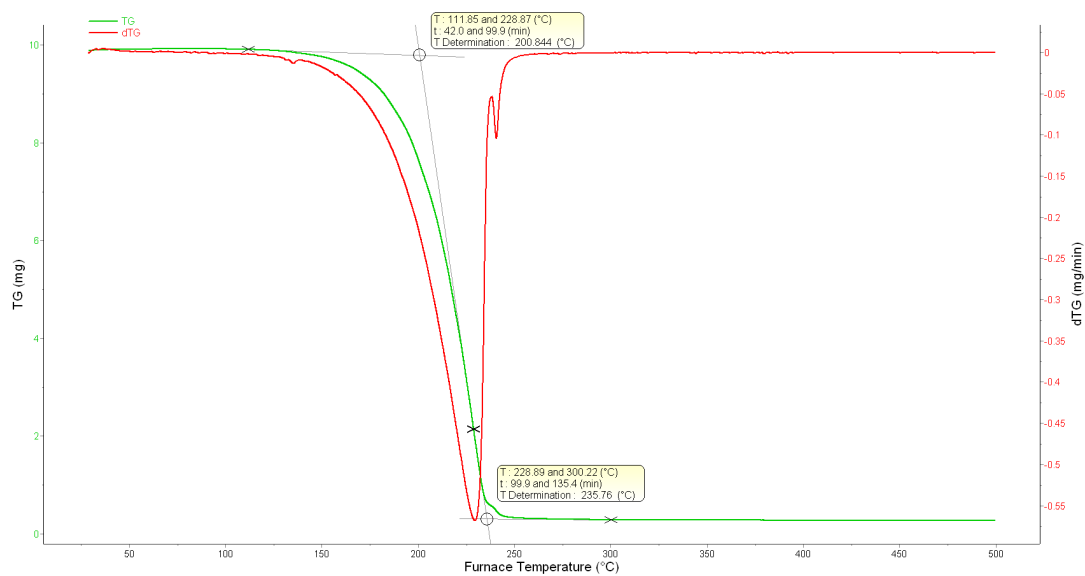


**Figure S19.** HR-MS (ESI positive mode) for  $[C_9H_{13}O_4S_2]^+$  (top) found 249.0253, (bottom) calculated 249.0250.



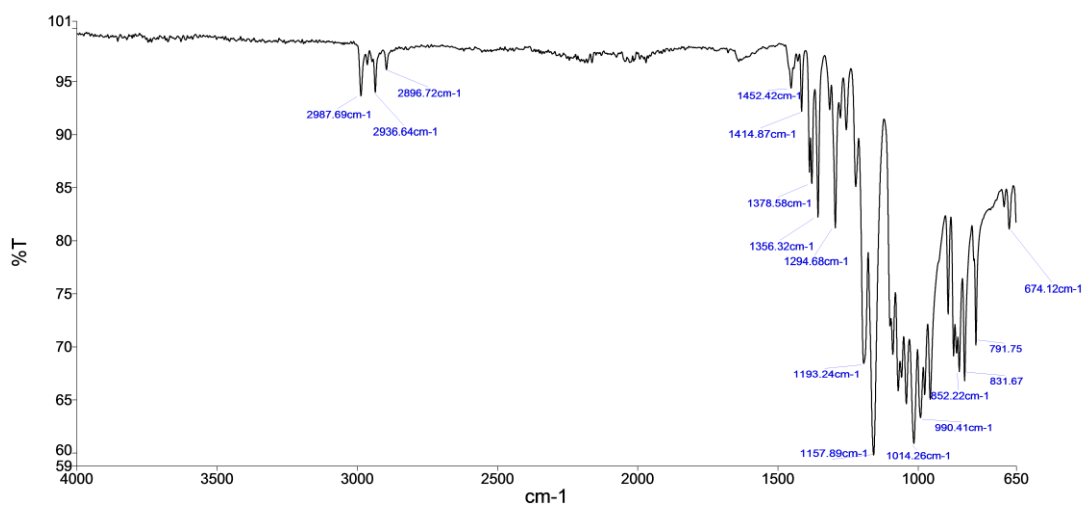
**Figure S20.** HR-MS (ESI positive mode) for  $[C_9H_{12}O_4S_2Na]^+$  (top) found 271.0075, (bottom) calculated 271.0069.

## TGA of monomer 2



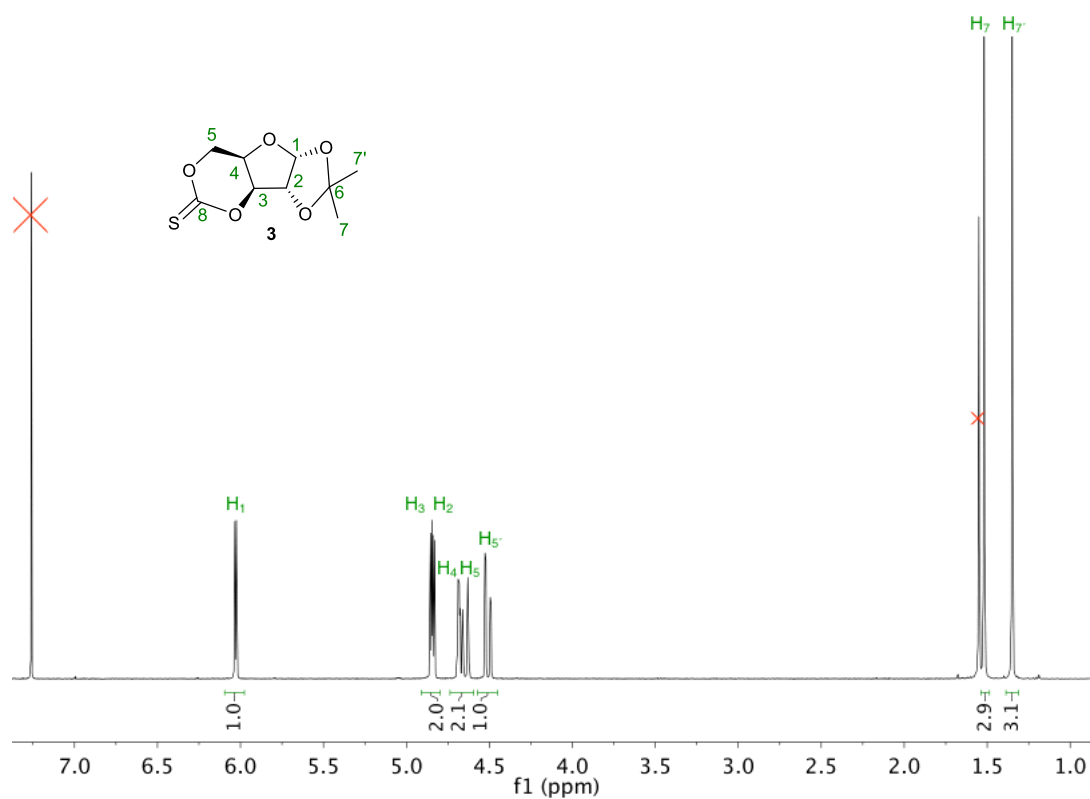
**Figure S21.** TGA of monomer 2. The monomer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

## FT-IR of monomer 2

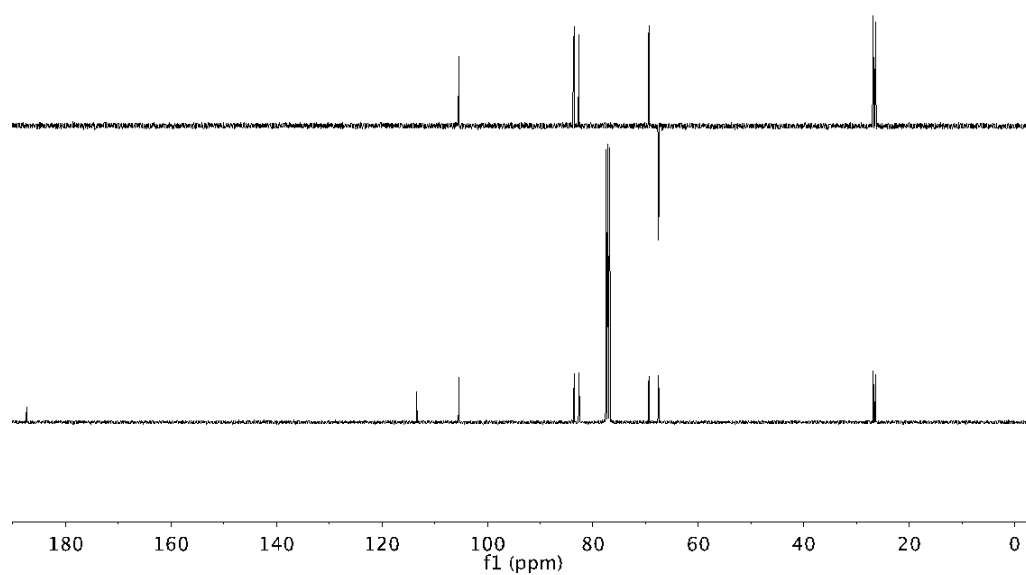


**Figure S22.** FT-IR of monomer 2.

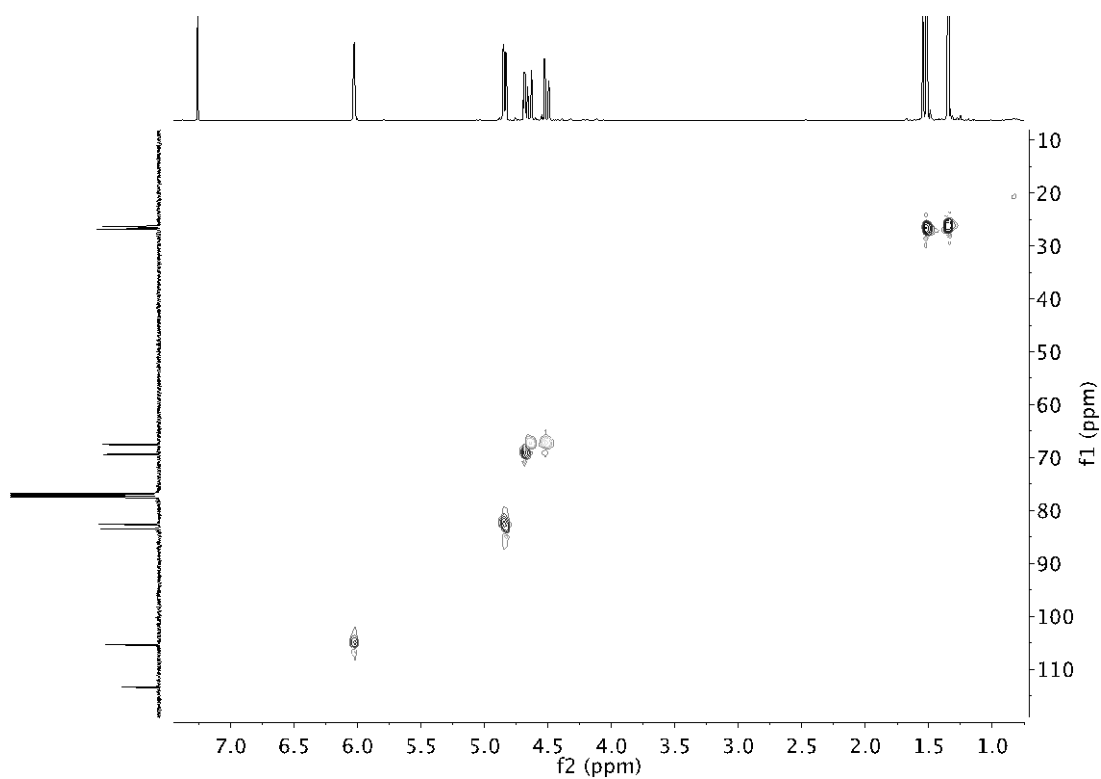
### NMR Characterisation of monomer 3



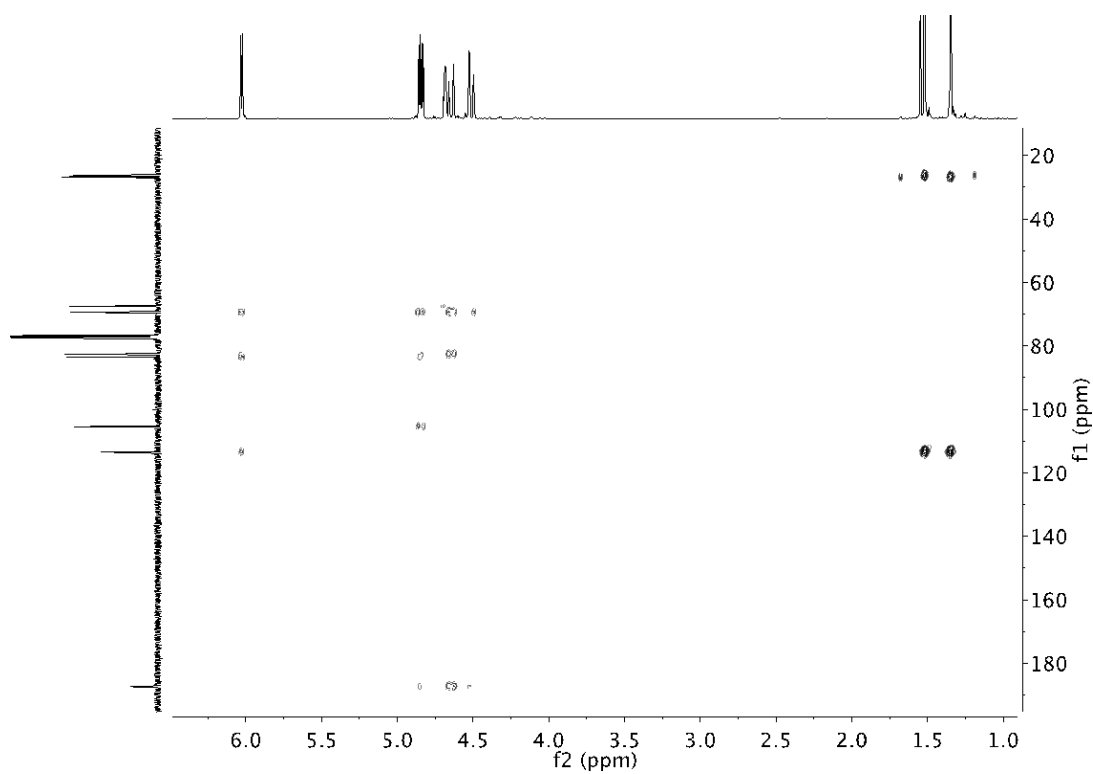
**Figure S23.** Annotated  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 C) of **3**. Red crosses denote residual  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  solvent peaks.



**Figure S24.**  $^{13}\text{C}$  NMR and DEPT-135 spectra (101 MHz,  $\text{CDCl}_3$ , 25 C) of **3**.

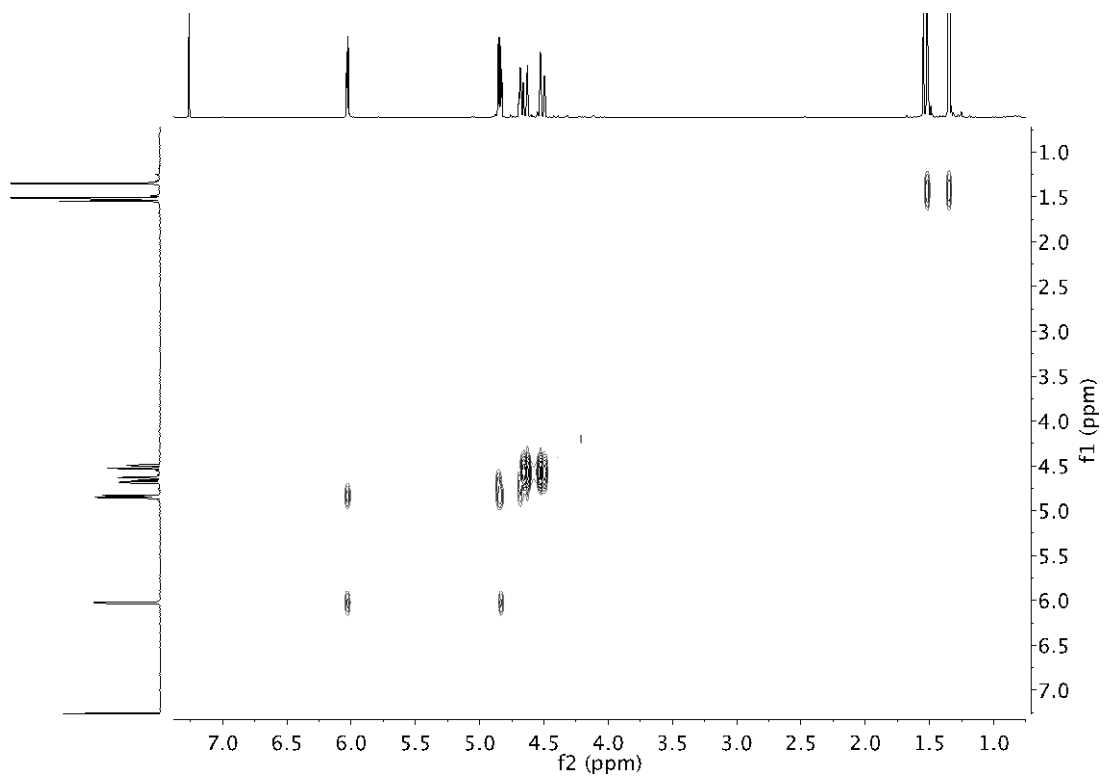


**Figure S25.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **3**.



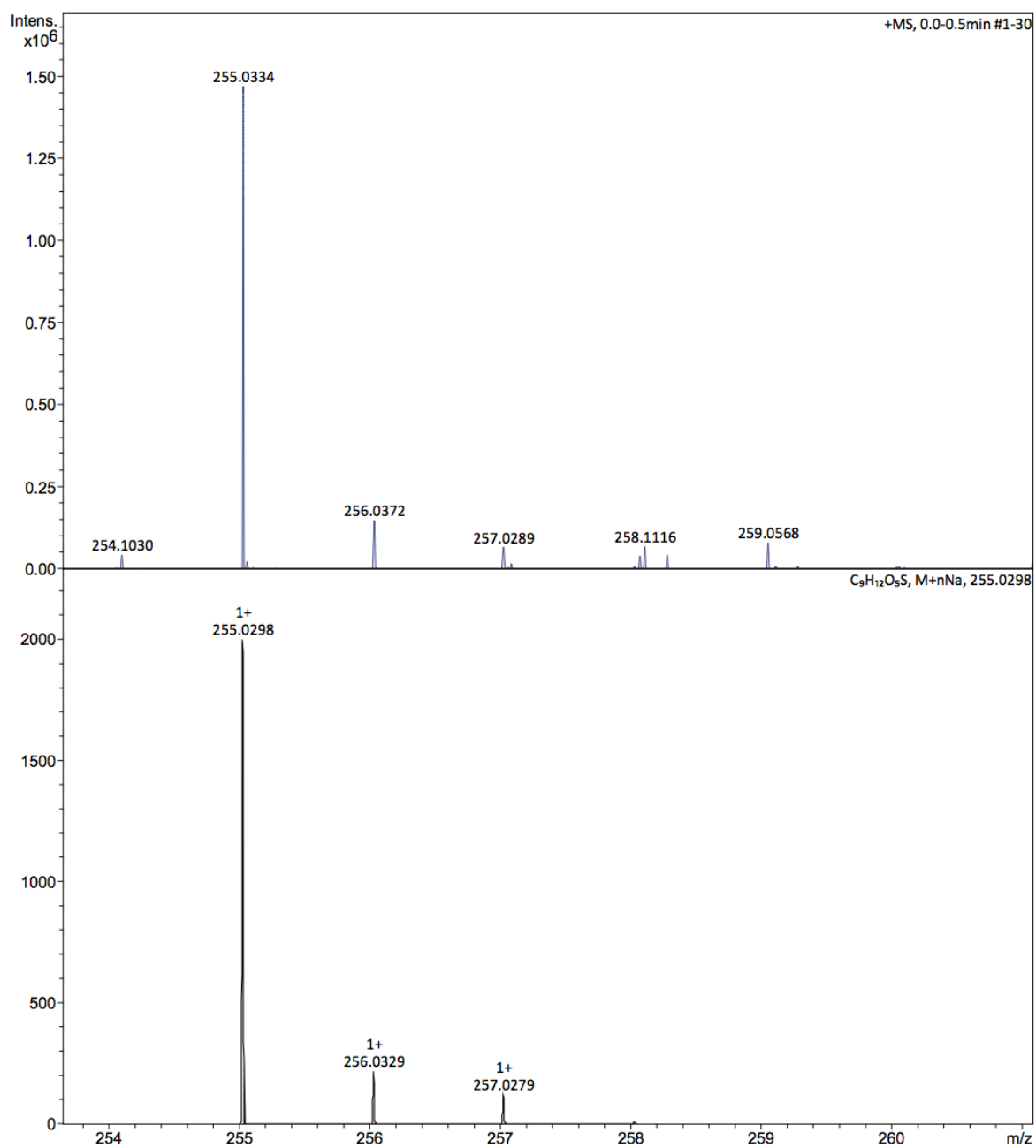
**Figure S26.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **3**.



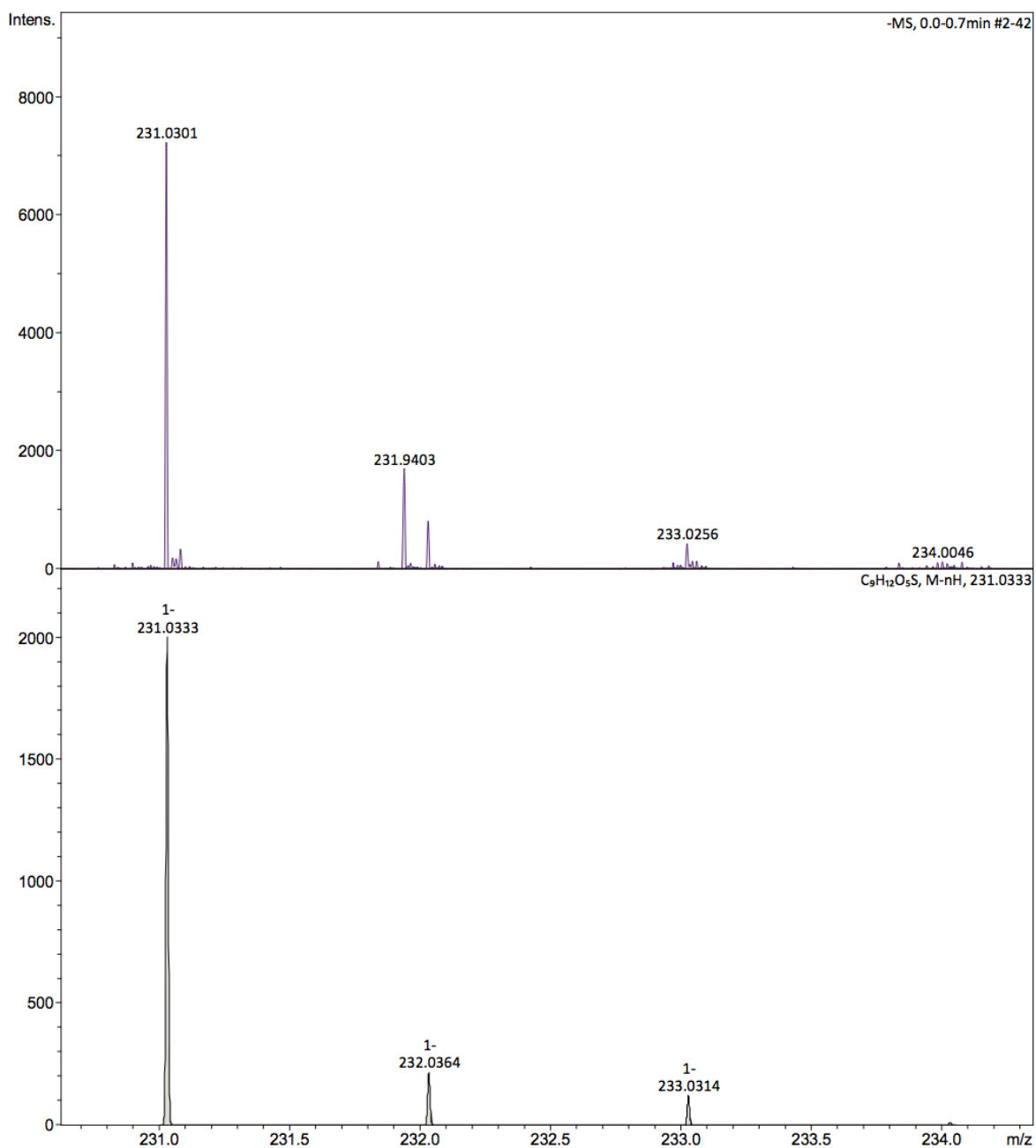


**Figure S27.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of **3**.

### MS Characterisation of monomer 3

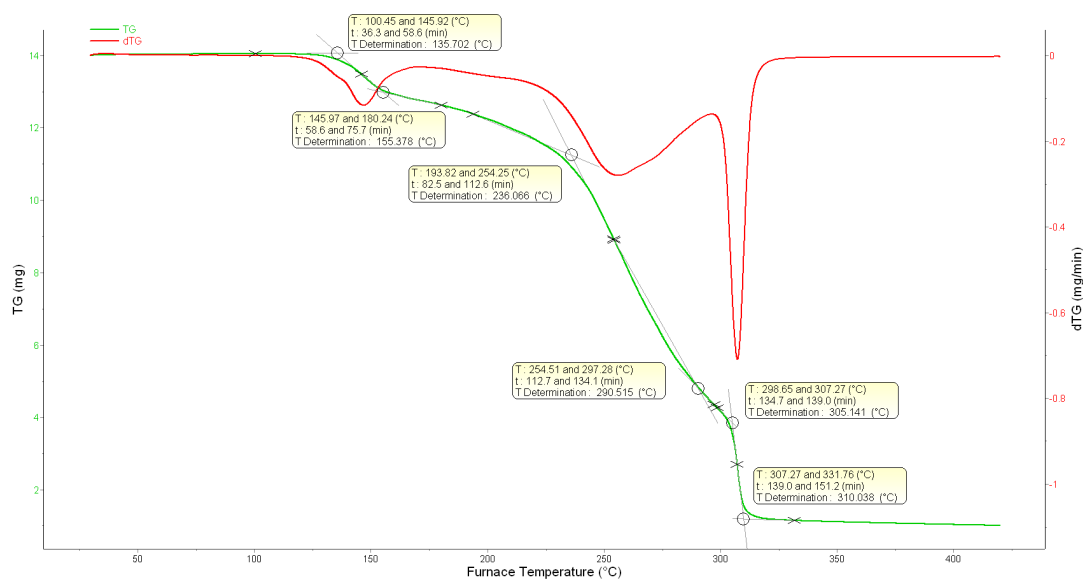


**Figure S28.** HR-MS (ESI positive mode) for  $[C_9H_{12}O_5SNa]^+$  (top) found 255.0334, (bottom) calculated 255.0298.



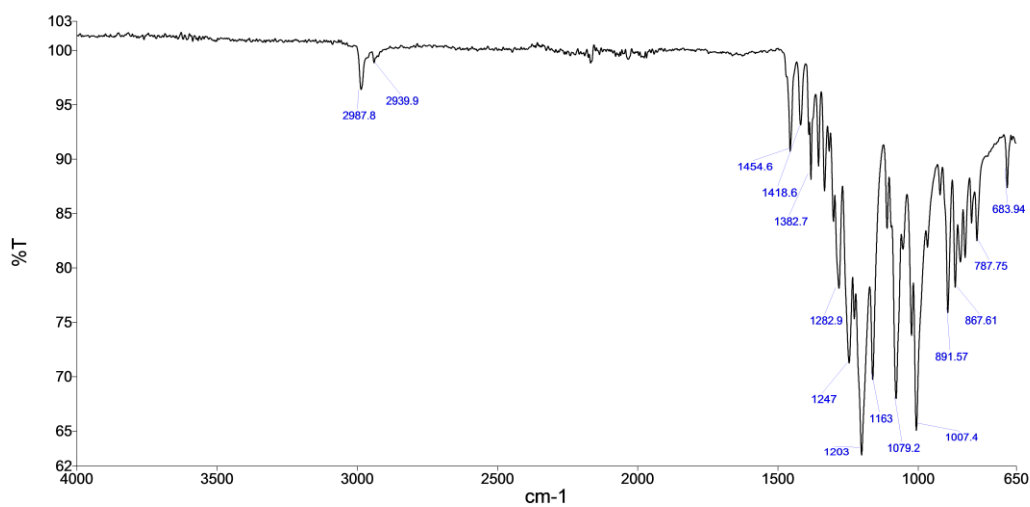
**Figure S29.** HR-MS (ESI negative mode) for  $[C_9H_{11}O_5S]^-$  (top) found: 231.0301, (bottom) 231.0333.

### TGA of monomer 3



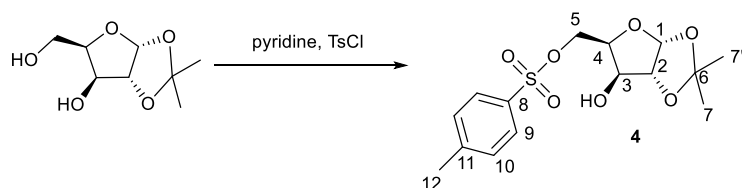
**Figure S30.** TGA of monomer 3. The monomer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

### FT-IR of monomer 3



**Figure S31.** FT-IR of monomer 3.

### Synthesis of intermediate 4

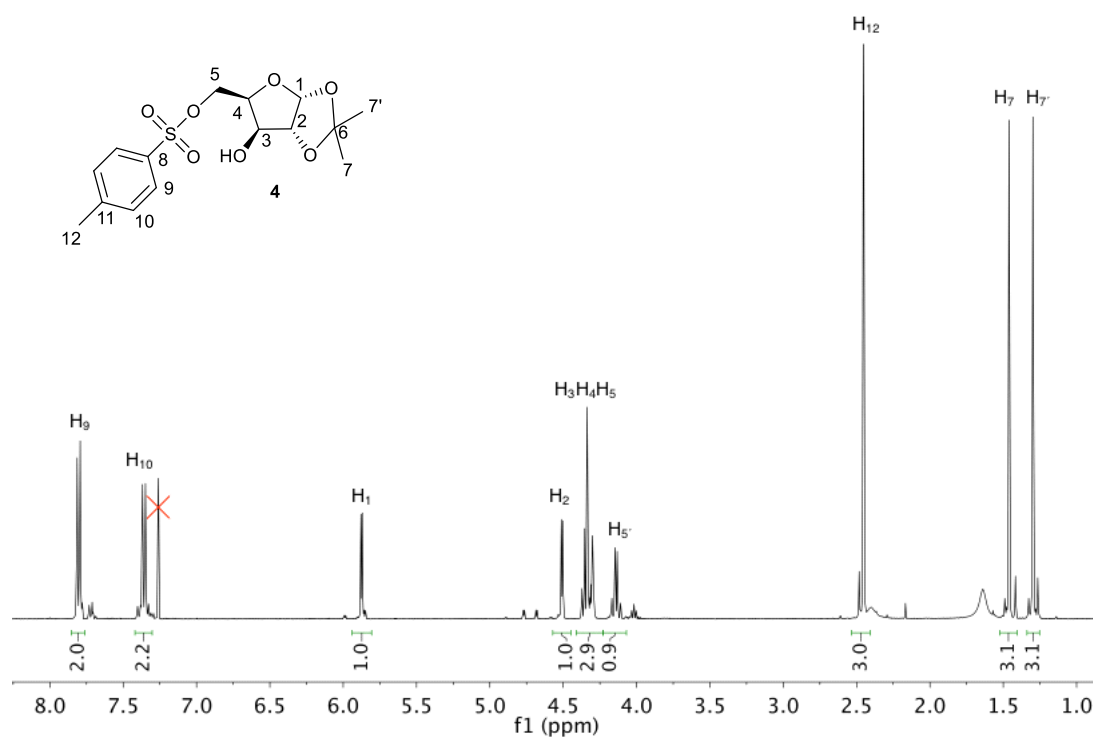


**Scheme S5.** Synthesis of intermediate **4**.

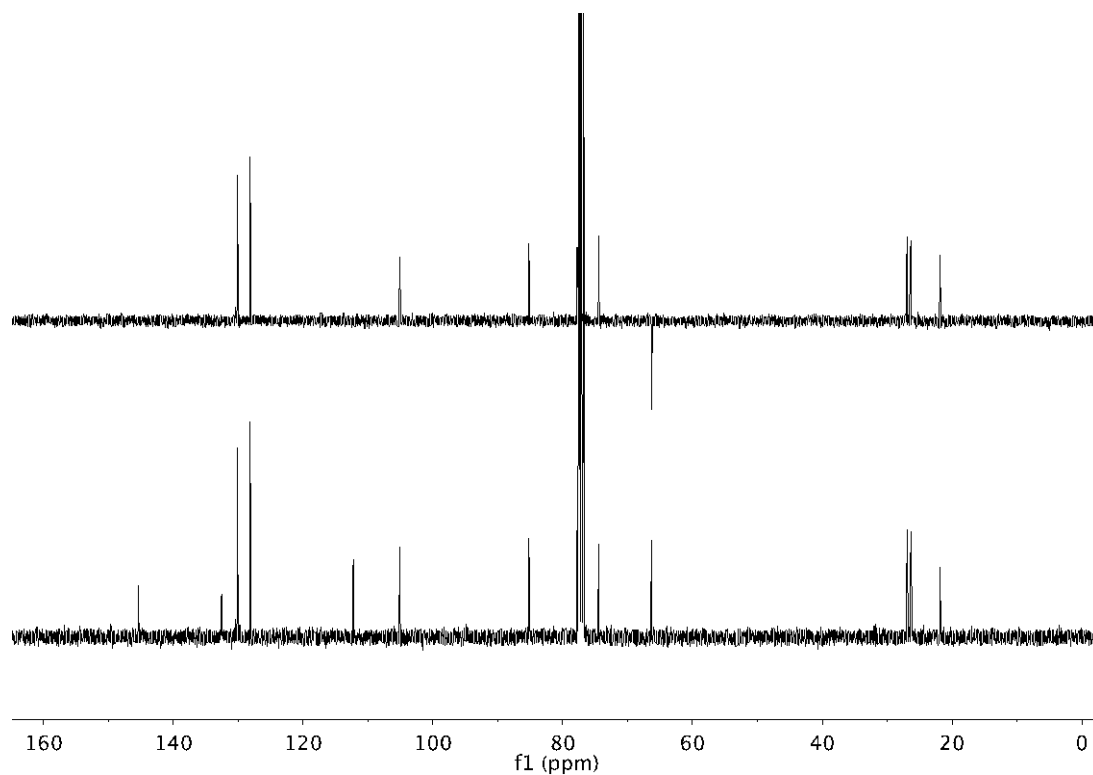
1,2-*O*-Isopropylidene-*D*-xylofuranose (1.00 g, 5.26 mmol) was put into a round bottom flask. Pyridine (6 mL) and *p*-toluenesulfonyl chloride (1.10 g, 5.78 mmol) were added and the mixture was stirred at room temperature for 4 hours. Dichloromethane (10 mL) and water (10 mL) were added to the reaction mixture. The organic phase was separated from the aqueous phase and dried with MgSO<sub>4</sub>. The organic phase was filtrated through cotton and the solvent was removed under reduced pressure obtaining the tosylated xylofuranose **4** as a white solid (1.47 g, 81%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): = 7.80 (2H, d, *J*=8.4 Hz, H<sub>9</sub>), 7.35 (2H, d, *J*=8.1 Hz, H<sub>10</sub>), 5.87 (1H, d, *J*=3.6 Hz, H<sub>1</sub>), 4.51 (1H, d, *J*=3.6 Hz, H<sub>2</sub>), 4.37-4.30 (3H, m, *J*=5.5, H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub>), 4.17-4.11 (1H, dd, *J*=9.1 and 14.4 Hz, H<sub>5'</sub>), 2.45 (3H, s, H<sub>12</sub>), 1.46 (3H, s, H<sub>7</sub>), 1.30 (3H, s, H<sub>7'</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): = 145.4 (C, C<sub>8</sub>); 132.6 (C, C<sub>11</sub>); 130.2 (CH, C<sub>10</sub>); 128.2 (CH, C<sub>9</sub>); 112.3 (C, C<sub>6</sub>); 105.1 (CH, C<sub>1</sub>); 85.2 (CH, C<sub>2</sub>); 77.8 (CH, C<sub>3</sub>); 74.5 (CH, C<sub>4</sub>); 66.3 (CH, C<sub>5</sub>); 26.9 (CH<sub>2</sub>, C<sub>7</sub>); 26.4 (CH<sub>3</sub>, C<sub>7'</sub>); 21.8 (CH<sub>3</sub>, C<sub>12</sub>) ppm. HR-MS (ESI positive mode) of **4** in CH<sub>3</sub>OH: *m/z* calculated for [C<sub>15</sub>H<sub>21</sub>O<sub>7</sub>S]<sup>+</sup> 345.1003; found: 345.1026; *m/z* calculated for [C<sub>15</sub>H<sub>20</sub>O<sub>7</sub>SnNa]<sup>+</sup> 367.0822; found: 367.0889. Elemental analysis of **4**: Found: C 52.23%, H 5.85%, C<sub>15</sub>H<sub>20</sub>O<sub>7</sub>S requires C, 52.32%, H 5.85%. Melting point of **4** = 105 °C.

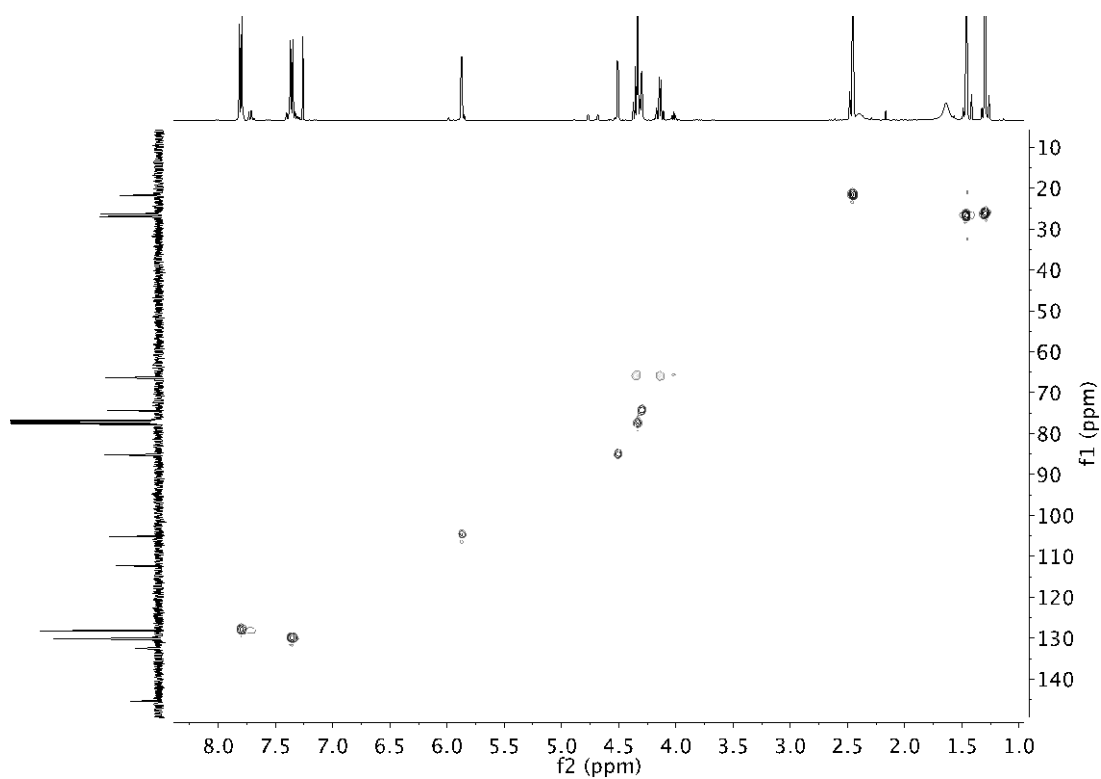
### NMR Characterisation of intermediate 4



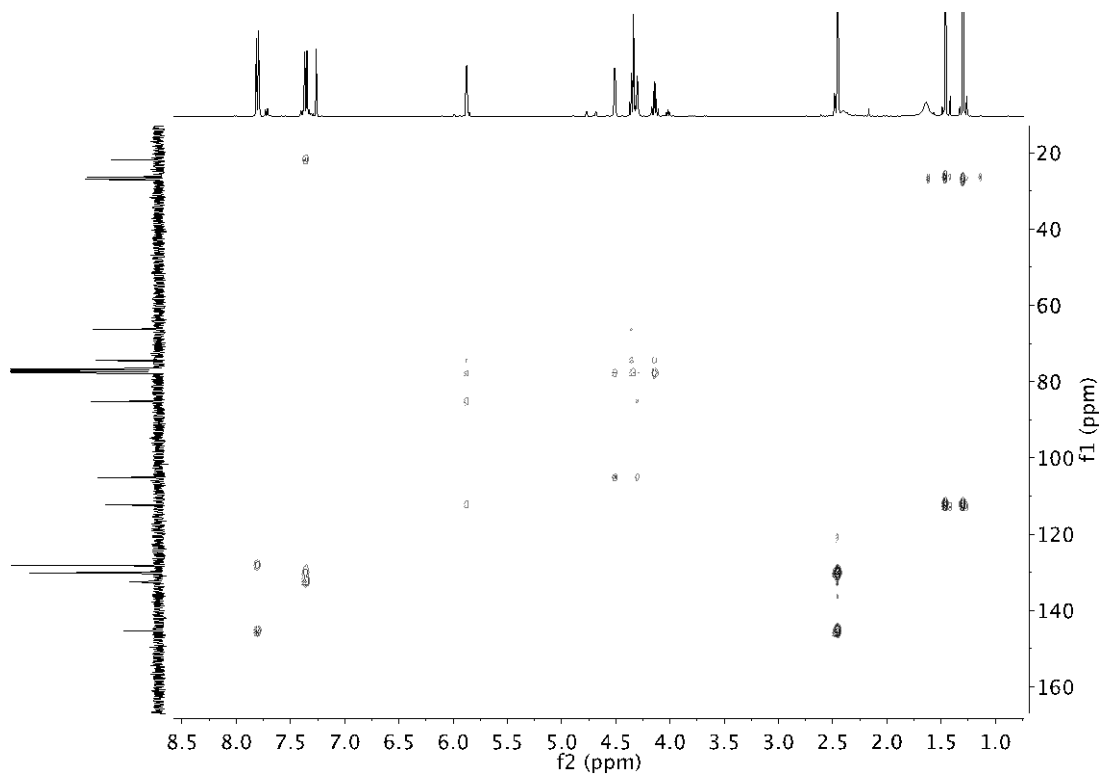
**Figure S32.** Annotated  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 C) of **4**. Red cross denotes residual  $\text{CHCl}_3$  solvent peak.



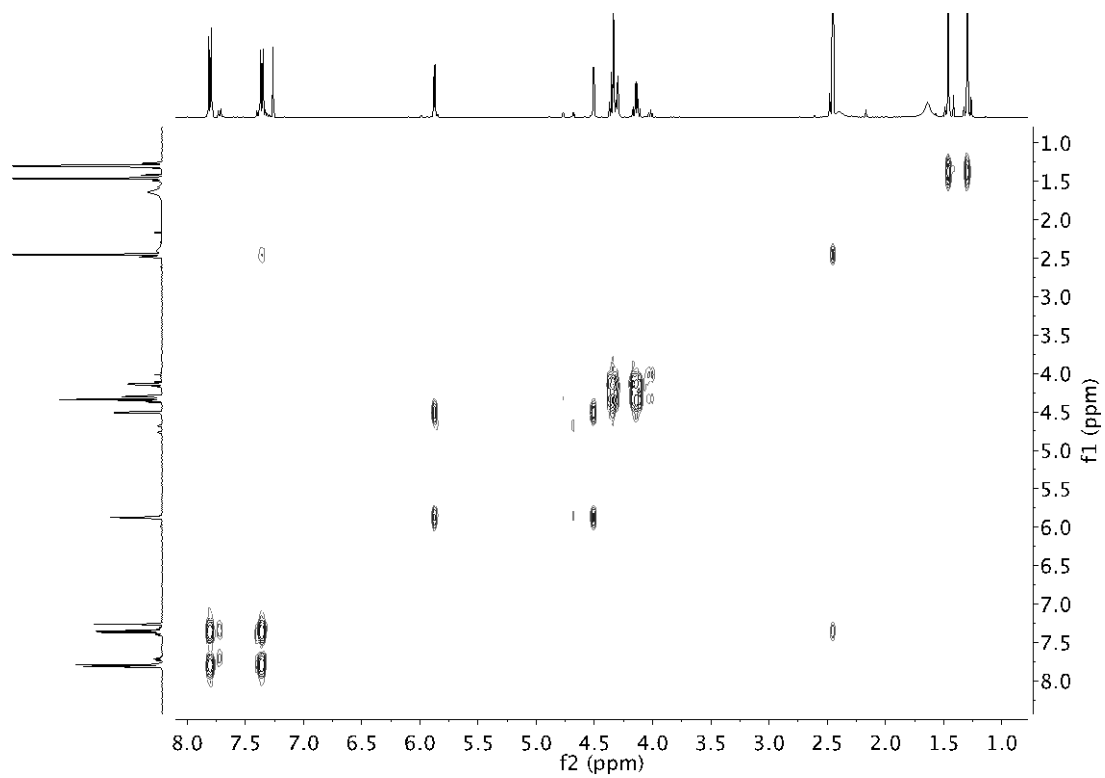
**Figure S33.**  $^{13}\text{C}$  NMR and DEPT-135 spectra (101 MHz,  $\text{CDCl}_3$ , 25 C) of **4**.



**Figure S34.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **4**.



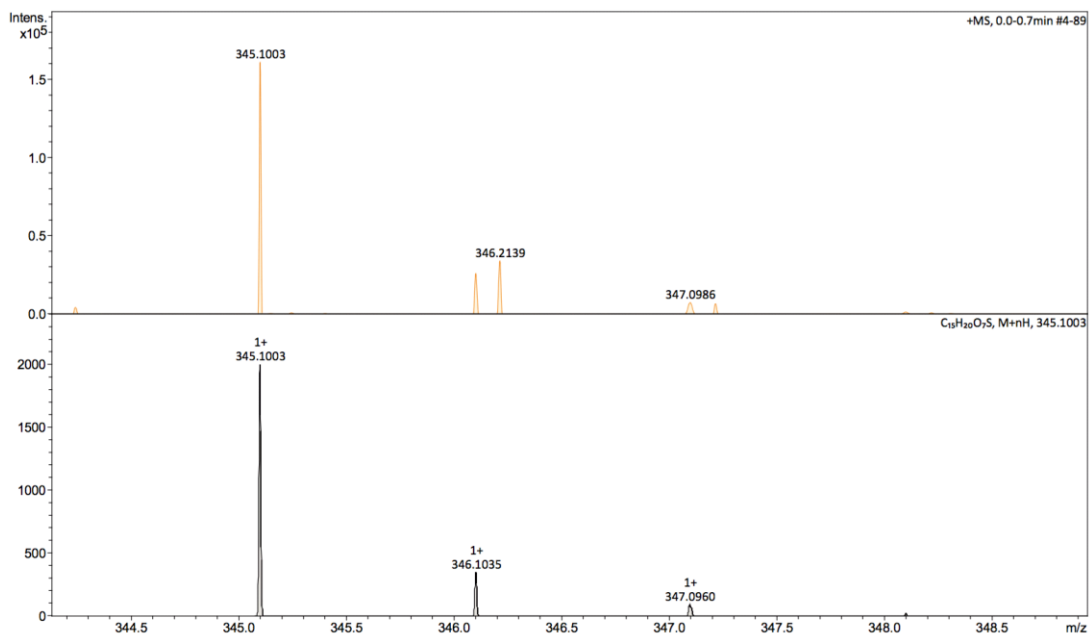
**Figure S35.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of **4**.



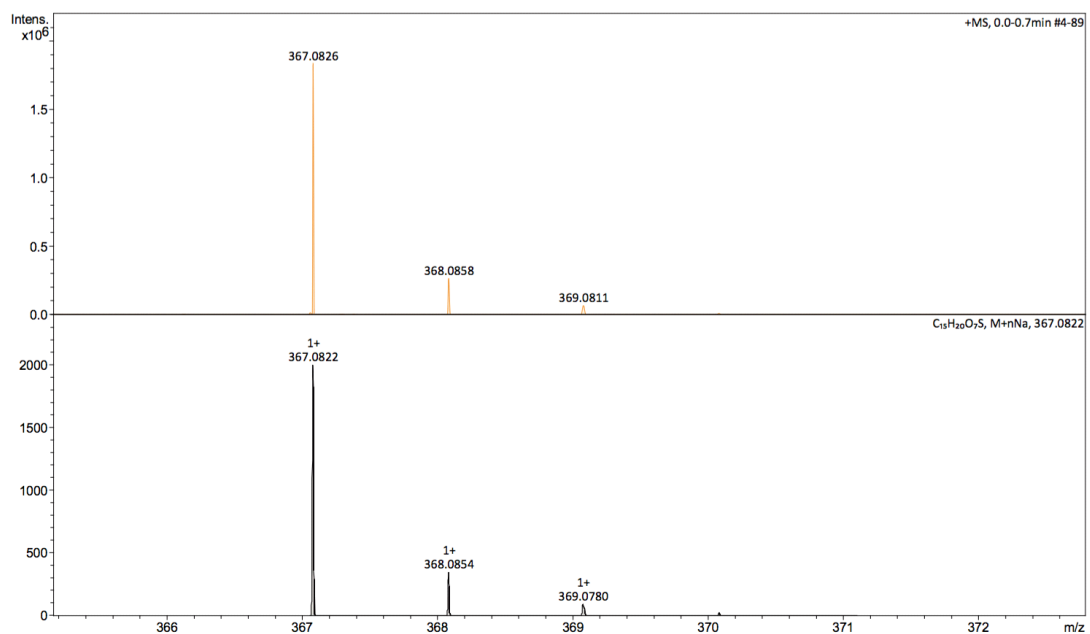
**Figure S36.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of **4**.



### MS Characterisation of intermediate 4

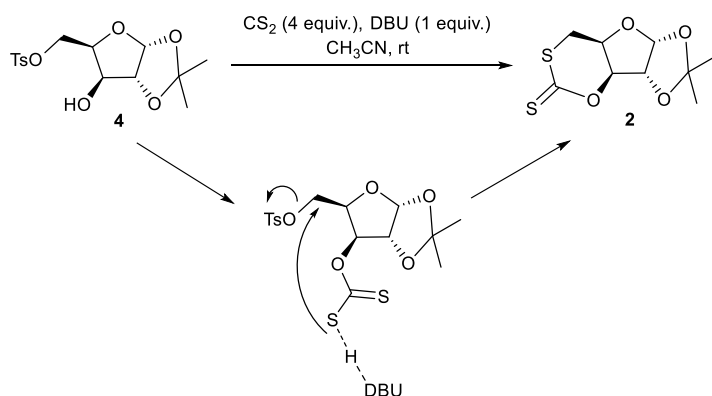


**Figure S37.** HR-MS (ESI positive mode) for  $[C_{15}H_{21}O_7S]^+$  (top) found 345.1003, (bottom) calculated 345.1003.



**Figure S38.** HR-MS (ESI positive mode) for  $[C_{15}H_{20}O_7SNa]^+$  (top) found 367.0826, (bottom) calculated 367.0822.

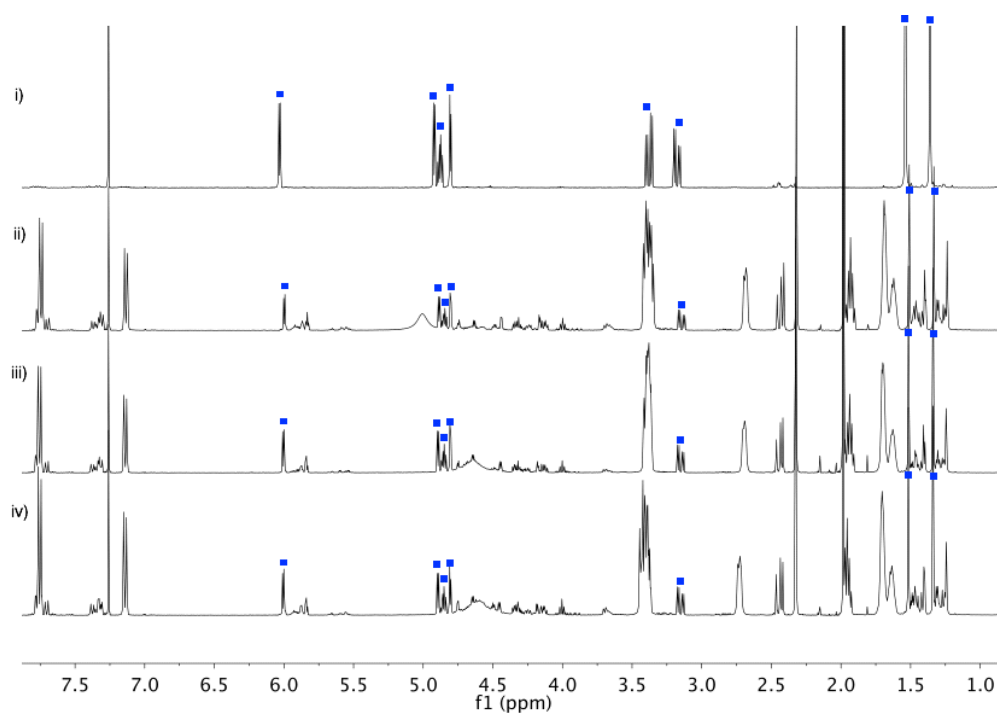
### Investigation into the reaction mechanism of formation of monomer 2



**Scheme S6.** Synthesis of monomer **2** from **4** through a S<sub>N</sub>2-like reaction.

The tosylated sugar derivative **4** (0.635 g, 1.843 mmol) was put into a Schlenk flask under argon atmosphere. Anhydrous CH<sub>3</sub>CN (18 mL) was added and the sugar was completely dissolved. CS<sub>2</sub> (0.445 mL, 7.375 mmol) was added under argon atmosphere while stirring the reaction mixture at room temperature for 5 minutes. DBU (0.276 mL, 1.843 mmol) was added and the reaction mixture became yellow. The reaction mixture was monitored by <sup>1</sup>H NMR at different times observing 50% conversion, already after 30 minutes, based on the integration of de OTs signals *versus* the H<sub>1</sub> signal in **2**. The reaction mixture was left stirring at room temperature overnight but conversion didn't change.

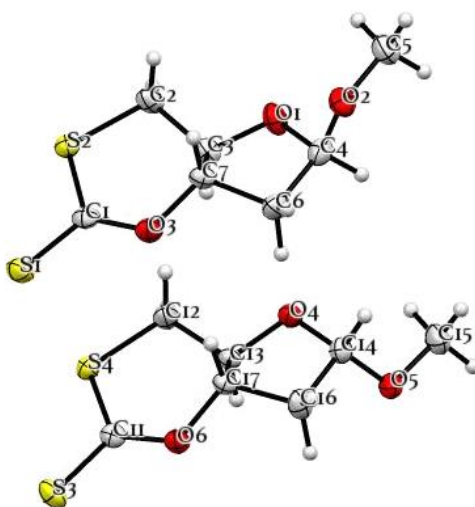
*NMR monitoring of the formation of monomer 2 from intermediate 4*



**Figure S39.** <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 25 °C) of: i) **2**; reaction mixture containing **4** (1 equivalent), CS<sub>2</sub> (4 equivalents) and DBU (1 equivalent) after: ii) 30 min, iii) 2 hours and iv) overnight. In blue squares are highlighted the signals corresponding to **2**.

## Crystal data

### *Crystal data and structure refinement for monomer 1*

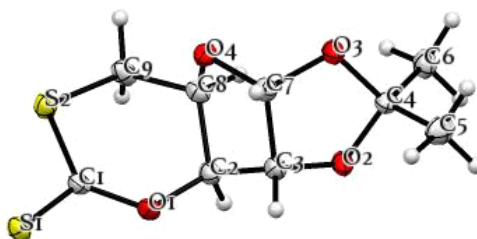


**Figure S40.** ORTEP<sup>2</sup> view of the crystal structure of monomer **1**. Key atoms labelled and displacement ellipsoids at the 50% probability level. Co-crystallised  $\beta$ -anomer (top); selected bond lengths ( $\text{\AA}$ ) and dihedral angles ( $^\circ$ ): S(1)-C(1) 1.645(2), S(2)-C(1) 1.742(2), S(2)-C(2) 1.831(2), O(3)-C(1) 1.329(3), O(3)-C(7) 1.447(2), C(4)-C(6)-C(7)-C(3) 39.3(2), O(1)-C(3)-C(7)-C(6) -41.6(2), C(4)-O(1)-C(3)-C(7) 27.0(2), C(3)-O(1)-C(4)-C(6) 1.5(2), O(1)-C(4)-C(6)-C(7) -24.1(2). Co-crystallised  $\alpha$ -anomer (bottom); selected bond lengths ( $\text{\AA}$ ) and dihedral angles ( $^\circ$ ): S(3)-C(11) 1.642(2), S(4)-C(11) 1.742(2), S(4)-C(12) 1.823(2), C(14)-C(16)-C(17)-C(13) 33.5(2), O(4)-C(13)-C(17)-C(16) -45.4(2), C(14)-O(4)-C(13)-C(17) 39.5(2), C(13)-O(4)-C(14)-C(16) -18.0(2), O(4)-C(14)-C(16)-C(17) -10.7(2).

Empirical formula	C <sub>7</sub> H <sub>10</sub> O <sub>3</sub> S <sub>2</sub>	
Formula weight	206.27	
Temperature	150.00(10) K	
Wavelength	1.54184 $\text{\AA}$	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 7.55350(10) $\text{\AA}$	$\alpha = 90^\circ$
	b = 12.29650(10) $\text{\AA}$	$\beta = 90^\circ$
	c = 19.9749(2) $\text{\AA}$	$\gamma = 90^\circ$
Volume	1855.30(3) $\text{\AA}^3$	
Z	8	
Density (calculated)	1.477 Mg/m <sup>3</sup>	
Absorption coefficient	4.954 mm <sup>-1</sup>	
F(000)	864	
Crystal size	0.250 x 0.100 x 0.040 mm <sup>3</sup>	
Theta range for data collection	4.222 to 73.152 $^\circ$	
Index ranges	-9 $\leq$ h $\leq$ 8, -15 $\leq$ k $\leq$ 14, -24 $\leq$ l $\leq$ 24	
Reflections collected	17053	
Independent reflections	3697 [R(int) = 0.0346]	
Completeness to theta = 1.000 $^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.36298	

Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3697 / 0 / 219
Goodness-of-fit on $F^2$	1.073
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0244, wR2 = 0.0630
R indices (all data)	R1 = 0.0254, wR2 = 0.0637
Absolute structure parameter	-0.014(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.213 and -0.263 e. $\text{\AA}^{-3}$

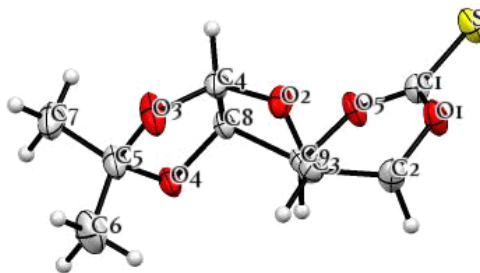
*Crystal data and structure refinement for monomer 2*



**Figure S41.** ORTEP<sup>2</sup> view of the crystal structure of monomer **2**. Key atoms labelled and displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and dihedral angles (°): C(1)-S(1) 1.647(1), C(1)- S(2) 1.723(7), C(1)-O(1) 1.325(9), S(1)-C(1)-S(2) 116.76, S(1)-C(1)-O(1) 118.91, S(2)-C(1)-O(1) 124.33, O(1)-C(2)-C(8)-C(9) -49.64.

Empirical formula	C <sub>9</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	248.31
Temperature	150.01(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub>
Unit cell dimensions	a = 7.5406(2) Å      α = 90° b = 7.8875(3) Å    β = 95.198(3)° c = 8.9868(3) Å      γ = 90°
Volume	532.31(3) Å <sup>3</sup>
Z	2
Density (calculated)	1.549 Mg/m <sup>3</sup>
Absorption coefficient	4.499 mm <sup>-1</sup>
F(000)	260
Crystal size	0.300 x 0.300 x 0.200 mm <sup>3</sup>
Theta range for data collection	4.941 to 72.997°
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -11 ≤ l ≤ 11
Reflections collected	7772
Independent reflections	2069 [R(int) = 0.0224]
Completeness to theta = 1.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.66292
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2069 / 1 / 138
Goodness-of-fit on F <sup>2</sup>	1.069
Final R indices [I > 2σ(I)]	R1 = 0.0236, wR2 = 0.0624
R indices (all data)	R1 = 0.0237, wR2 = 0.0624
Absolute structure parameter	-0.014(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.264 and -0.205 e.Å <sup>-3</sup>

*Crystal data and structure refinement for monomer 3*

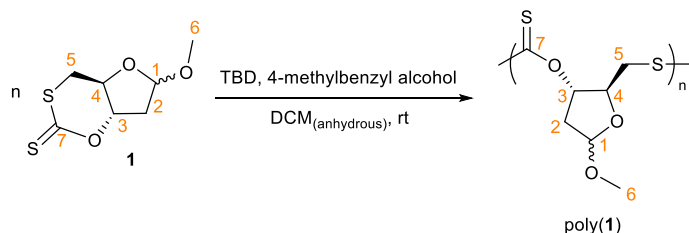


**Figure S42.** ORTEP<sup>2</sup> view of the crystal structure of monomer **3**. Key atoms labelled and displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and dihedral angles (°): C(1)-S 1.646(7), C(1)-O(1) 1.314(0), C(1)-O(5) 1.328(1), S-C(1)-O(1) 119.40, O(1)-C(1)-O(5) 120.95, S-C(1)-O(5) 119.65, C(2)-C(3)-C(9)-O(5) -42.59.

Empirical formula	C <sub>9</sub> H <sub>12</sub> O <sub>5</sub> S
Formula weight	232.25
Temperature	150.00(10) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	a = 6.0784(3) Å      α = 90° b = 9.8330(4) Å      β = 90° c = 17.9994(9) Å      γ = 90°
Volume	1075.80(9) Å <sup>3</sup>
Z	4
Density (calculated)	1.434 Mg/m <sup>3</sup>
Absorption coefficient	0.299 mm <sup>-1</sup>
F(000)	488
Crystal size	0.300 x 0.200 x 0.100 mm <sup>3</sup>
Theta range for data collection	3.538 to 30.251°
Index ranges	-4 ≤ h ≤ 8, -13 ≤ k ≤ 11, -25 ≤ l ≤ 24
Reflections collected	9690
Independent reflections	2841 [R(int) = 0.0329]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94457
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2841 / 0 / 138
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indices [I > 2σ(I)]	R1 = 0.0422, wR2 = 0.0792
R indices (all data)	R1 = 0.0514, wR2 = 0.0833
Absolute structure parameter	0.01(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.278 e.Å <sup>-3</sup>

## Polymerisation studies

### **Polymerisation of monomer 1**



**Scheme S7.** Polymerisation of monomer **1** using TBD as catalyst and 4-methylbenzyl alcohol as initiator.

The procedure for a typical polymerisation experiment (Entry 4 in Table S1) is as follows: Under an argon atmosphere 4-MeBnOH (15  $\mu$ L, 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0076 mmol, 1 equiv.) and TBD (15  $\mu$ L, 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0076 mmol, 1 equiv.) were added to a solution of monomer **1** (0.156 g, 0.76 mmol, 100 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (0.755 mL, 1 M). The mixture was stirred at room temperature. After 15 minutes the polymerisation was quenched by addition of a solution of benzoic acid (~30 equiv.) and the solvent removed under reduced pressure. The crude solid was then dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and precipitated from  $\text{Et}_2\text{O}$ . The product was isolated by centrifugation (3000 rpm, 10 minutes), washed twice with  $\text{Et}_2\text{O}$  and dried under vacuum. The polymer was isolated as a yellow solid (70 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 C):  $\delta$  = 5.88, 5.66 (2H, br,  $\text{H}_{3\alpha+\beta}$ ), 5.21-5.19, 5.10-5.08 (2H, m,  $\text{H}_{1\alpha+\beta}$ ), 4.54-4.48 (2H, m,  $\text{H}_4$ ), 3.61-3.27 (10H, m,  $\text{H}_{5\alpha+\beta}$ ,  $\text{H}_{6\alpha+\beta}$ ), 2.54-2.11 (4H, m,  $\text{H}_{2\alpha+\beta}$ ) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 C) for **3**:  $\delta$  = 213.0 (C(S)SO,  $\text{C}_{7\alpha+\beta}$ ), 106.2, 105.0 ( $\text{C}_{1\alpha+\beta}$ ), 86.1, 84.7 ( $\text{C}_{3\alpha+\beta}$ ), 81.6 ( $\text{C}_{4\alpha+\beta}$ ), 55.8, 55.3 ( $\text{C}_{6\alpha+\beta}$ ), 39.9-38.9 ( $\text{C}_{2\alpha+\beta}$ ,  $\text{C}_{5\alpha+\beta}$ ) ppm.

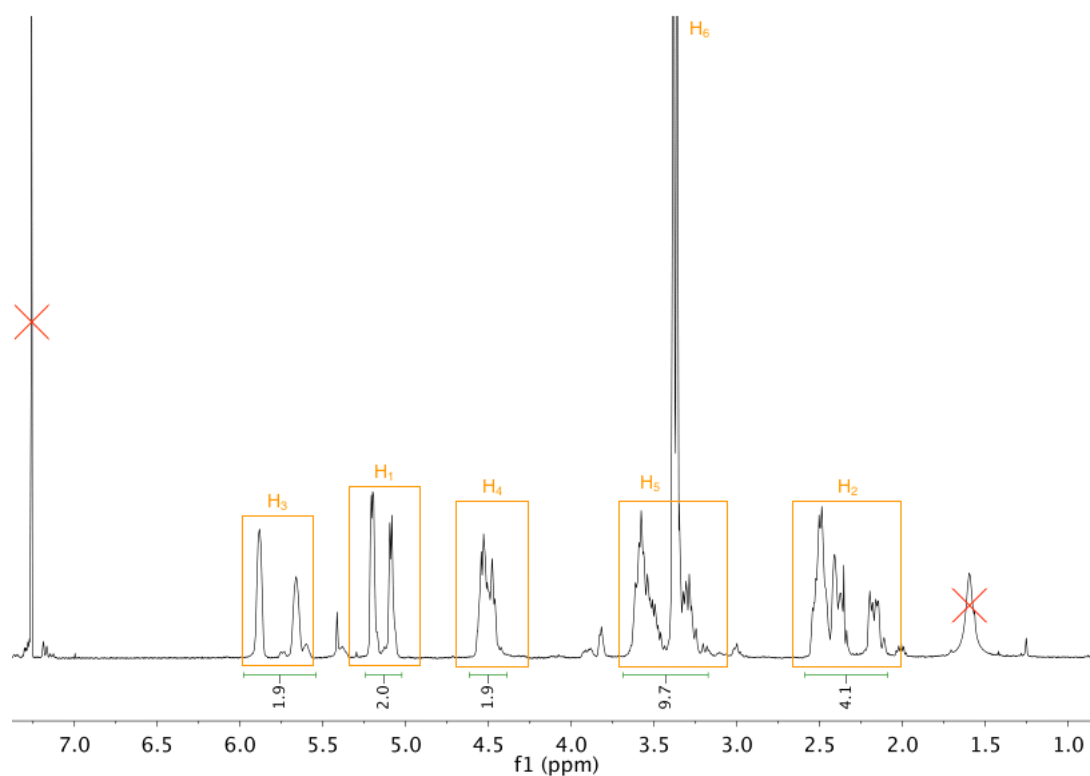
**Table S1.** Polymerisation tests performed with monomer **1**.<sup>a</sup>

Entry	[M]:[C]:[I] <sup>b</sup>	Time (h)	Conv. <sup>c</sup> (%)	$M_n$ (SEC) <sup>d</sup> (kDa)	$M_n$ (calc) <sup>e</sup> (kDa)	$M_w$ (SEC) <sup>d</sup> (kDa)	$\bar{D}$ <sup>f</sup>	Type of polymer linkages <sup>g</sup>
1	25:1:1	0.25	>99	5.1	5.3	7.9	1.6	C(S)SO
2	50:1:1	0.25	>99	5.2	10.4	9.1	1.8	C(S)SO
3	50:1:1	2	>99	7.4	10.4	11.4	1.5	C(S)SO
4	100:1:1	0.25	>99	11.3	20.7	24.6	2.2	C(S)SO

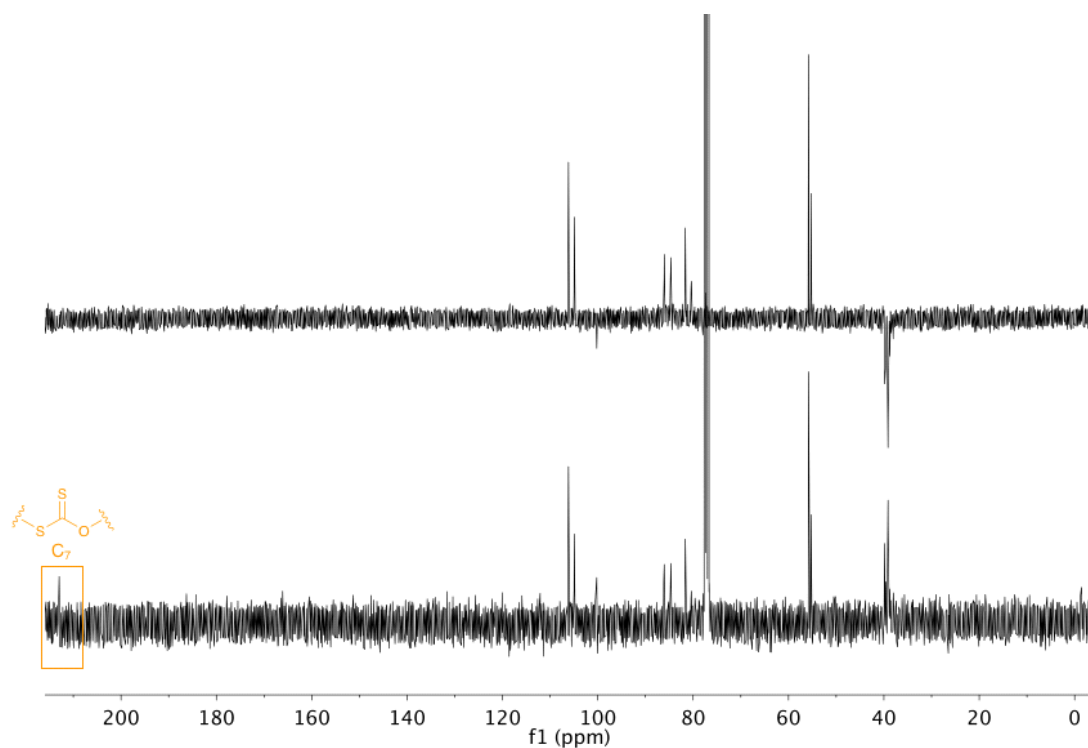
<sup>a</sup> Polymerizations carried out at room temperature in anhydrous  $\text{CH}_2\text{Cl}_2$  as solvent with  $[\mathbf{1}]_0 = 1$  M; <sup>b</sup> C is the catalyst, TBD, and I is the initiator, 4-MeBnOH; <sup>c</sup> conversion measured by  $^1\text{H}$  NMR determined by relative integration of the anomeric proton in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ ; <sup>d</sup> estimated by SEC (RI detector) versus polystyrene standards with THF as eluent; <sup>e</sup> calculated as  $M_r(I) + (M_r(\text{monomer}) \times [\text{monomer}]_0 / [I]_0 \times \text{conv} / 100\%)$ ; <sup>f</sup>  $\bar{D} = M_n / M_w$ ; <sup>g</sup> determined by  $^{13}\text{C}$  NMR.



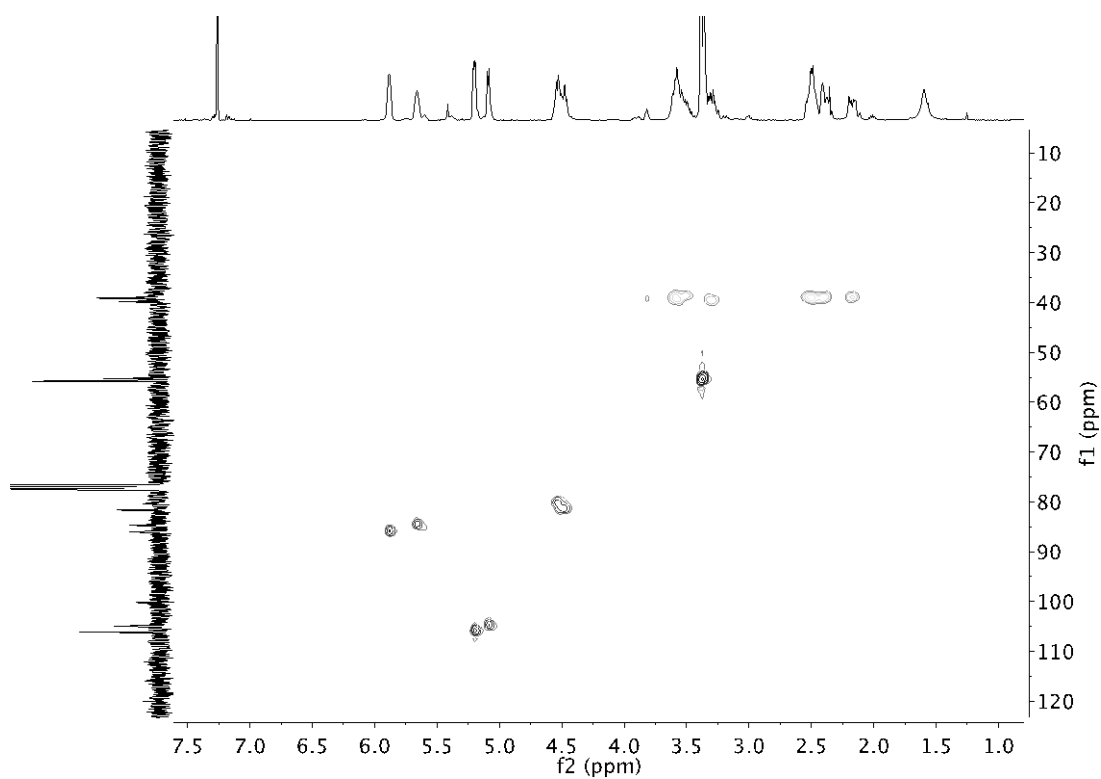
### NMR Characterisation of the polymer derived from monomer 1



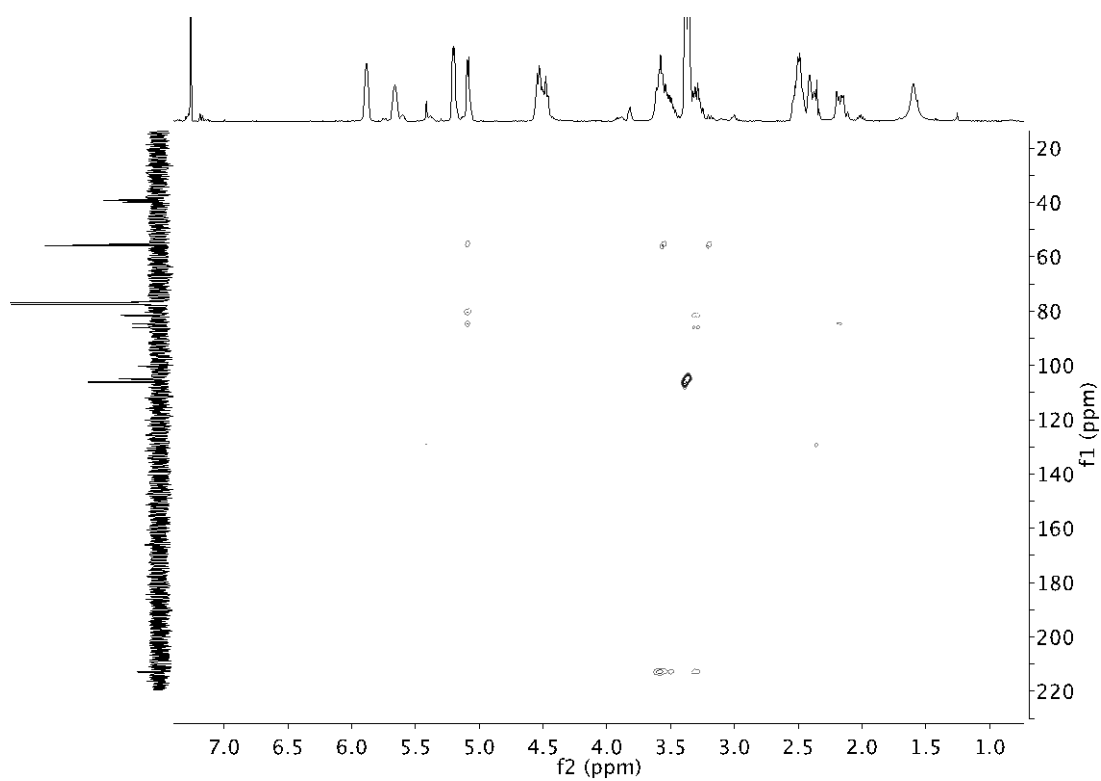
**Figure S43.** Annotated <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 C) of poly(**1**)  $M_n$  7 402 g mol<sup>-1</sup>, Đ 1.5 (Entry 3 in Table S1). Red crosses denote residual CHCl<sub>3</sub> and water solvent peaks.



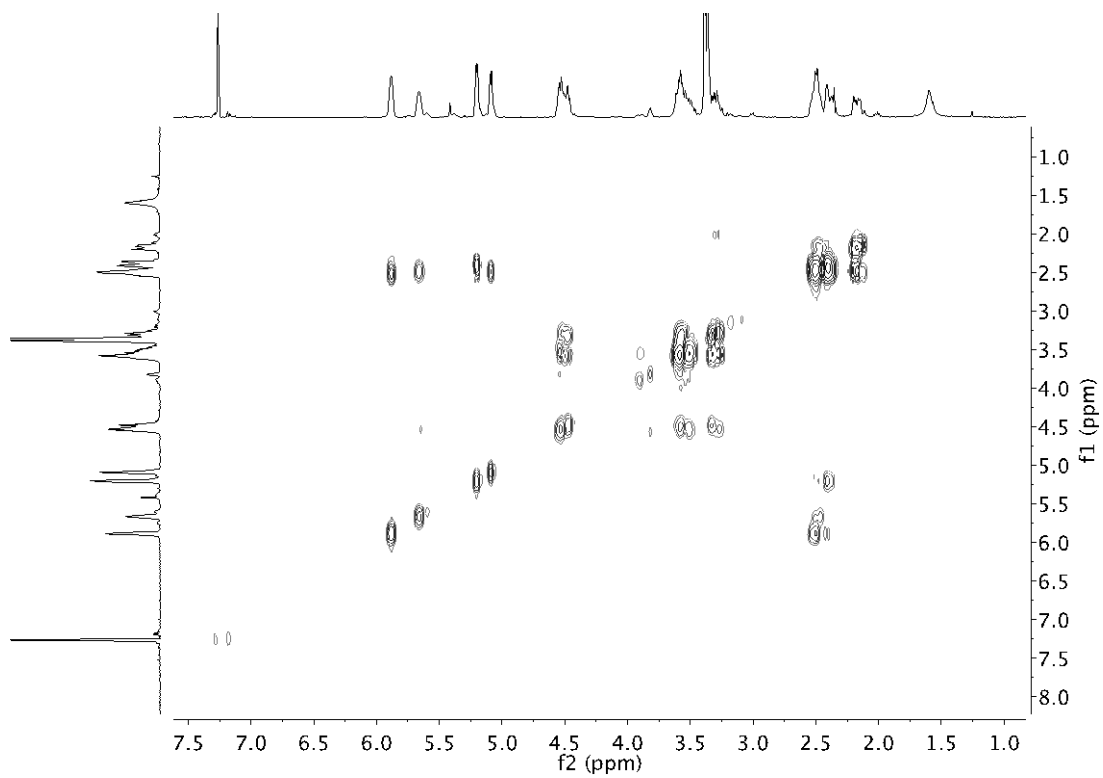
**Figure S44.** <sup>13</sup>C NMR and DEPT-135 spectra (101 MHz, CDCl<sub>3</sub>, 25 C) of poly(**1**)  $M_n$  7 402 g mol<sup>-1</sup>, Đ 1.5 (Entry 3 in Table S1).



**Figure S45.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**1**)  $M_n$  7 402 g mol $^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S1).



**Figure S46.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**1**)  $M_n$  7 402 g mol $^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S1).

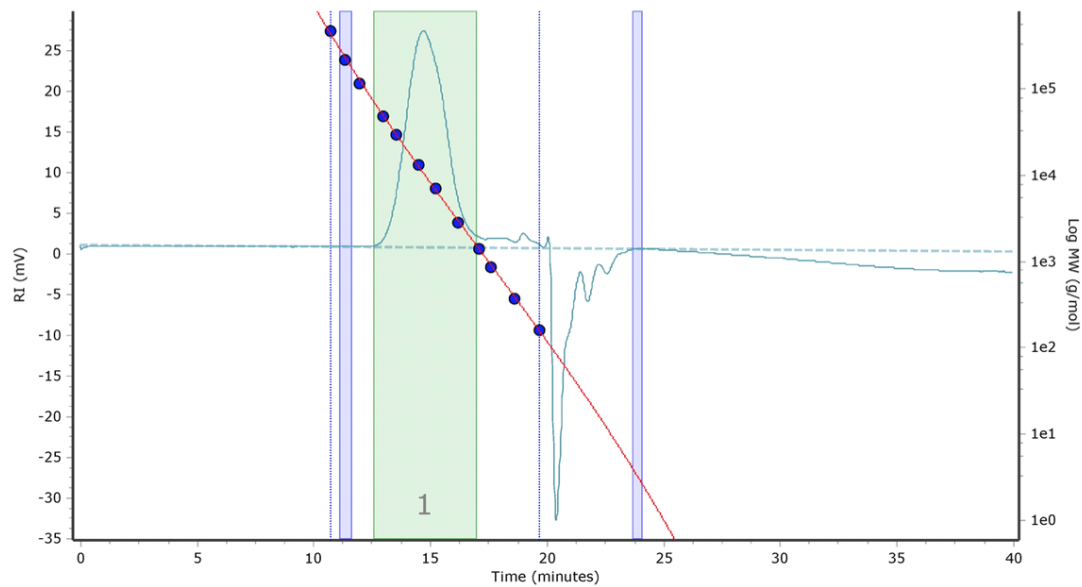


**Figure S47.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of poly(**1**)  $M_n$  7 402 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S1).

## Size-Exclusion Chromatography of poly(1)

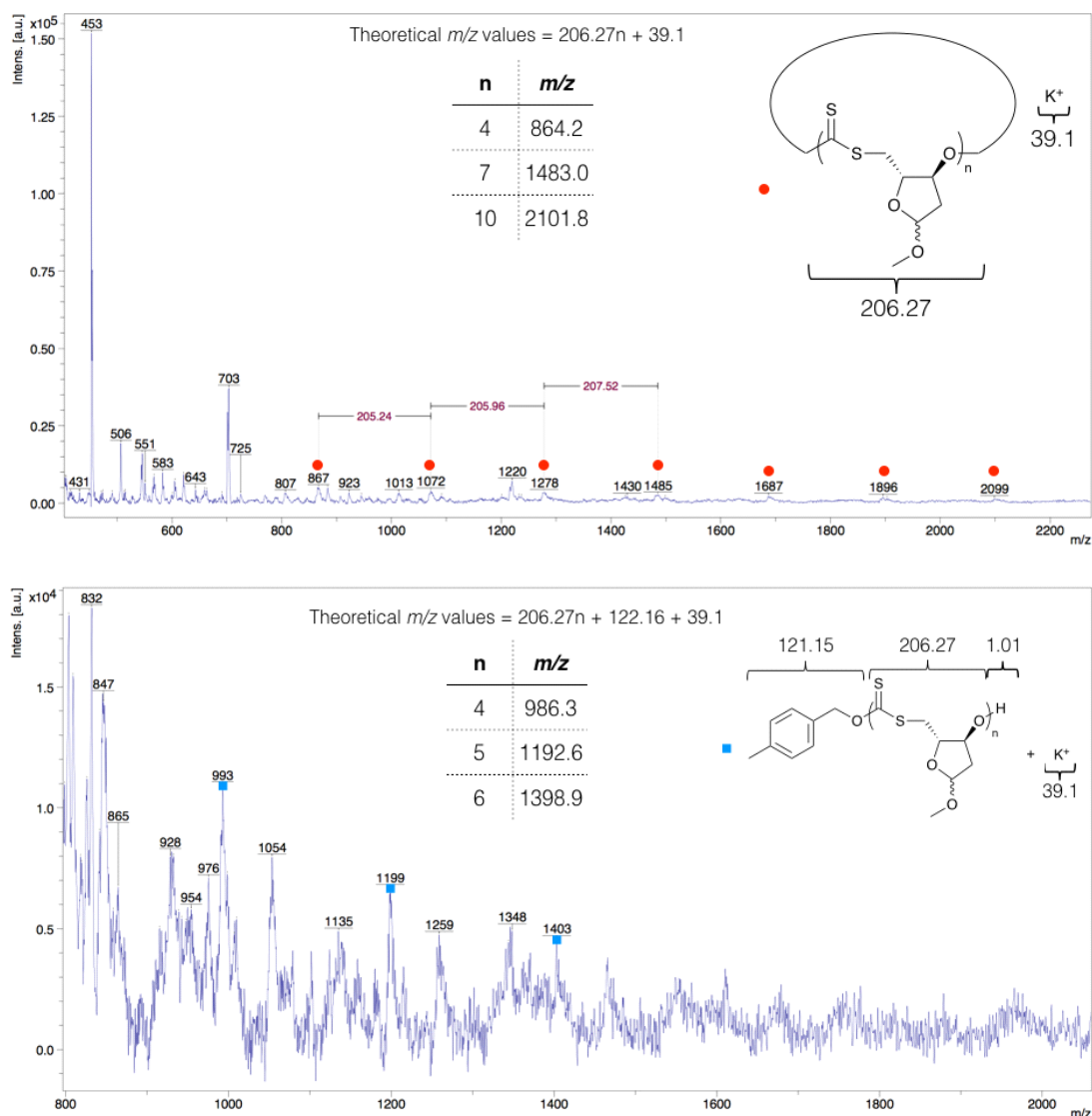
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	10393	7402	11381	16669	22870	15828	1.538



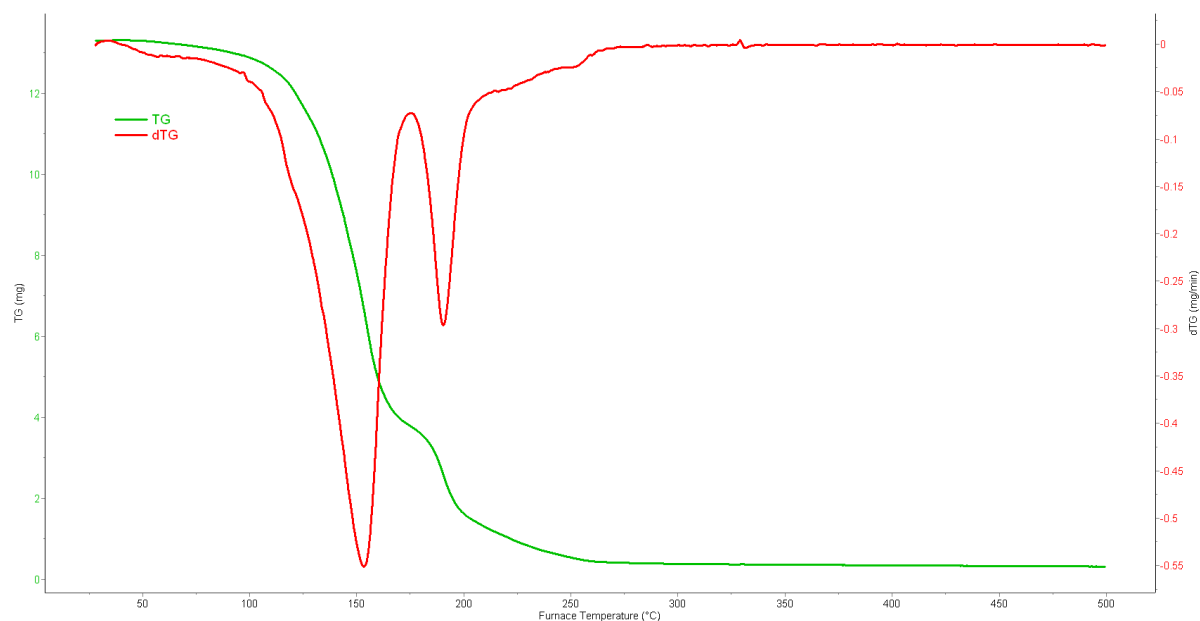
**Figure S48.** SEC trace of polymer showing  $M_n$  7 402 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S1).

## End-group Determination with MALDI-ToF Mass Spectrometry

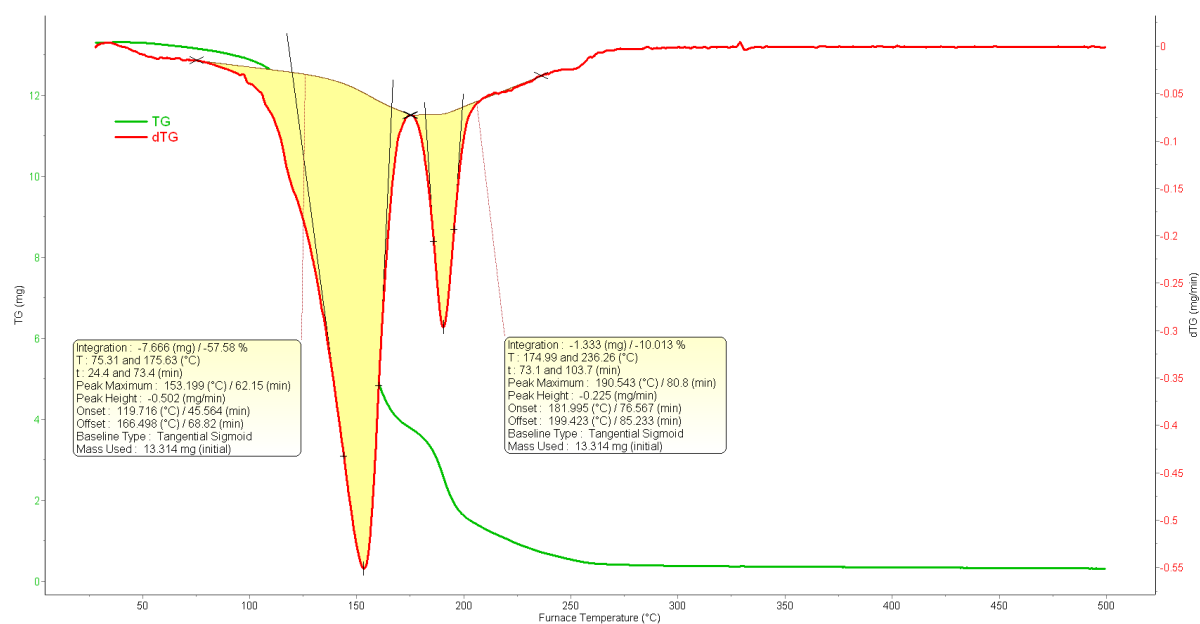


**Figure S49.** MALDI-ToF of two different samples of poly(1): on the top,  $M_{n,SEC} 5067 \text{ g mol}^{-1}$ ,  $\text{Đ} 1.6$  (Dithranol/THF (1:5) + KOAc) (Entry 1 in Table S1); at the bottom,  $M_{n,SEC} 7402 \text{ g mol}^{-1}$ ,  $\text{Đ} 1.5$  (Dithranol/THF (1:24) + NaOAc) (Entry 3 in Table S1). In red circles are highlighted the signals corresponding to potassium adduct of cyclic polymer which is due to backbiting of the polymer chain. In blue squares with same repeat unit  $206.27 \text{ m/z}$  are highlighted the signals corresponding to potassium adduct of linear polymer with OH and 4-methylbenzyl alcohol end-groups.

## TGA of poly(1)

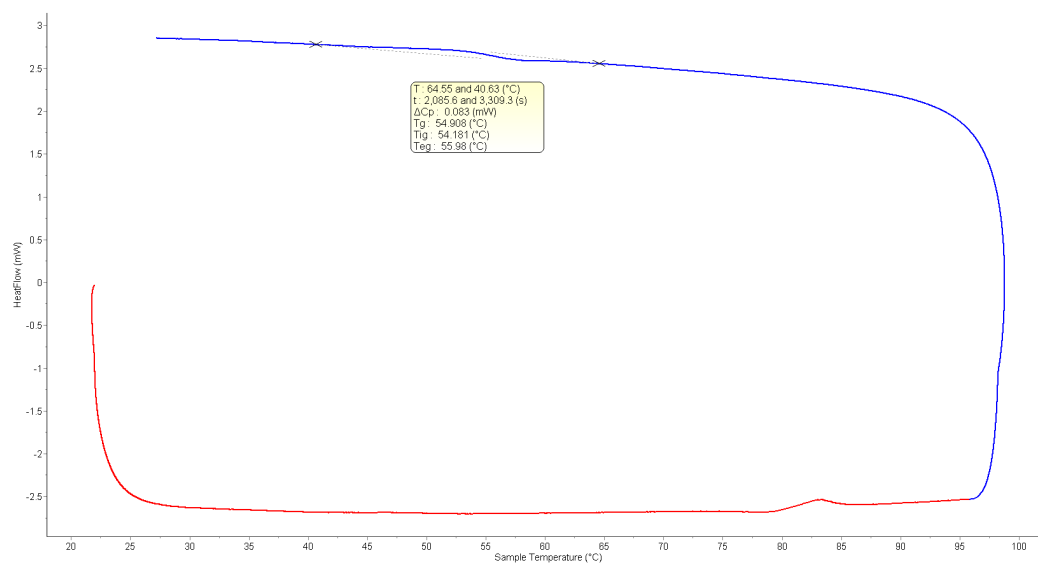


**Figure S50.** TGA analysis of poly(1)  $M_n$  11 327 g mol<sup>-1</sup>,  $\bar{D}$  2.2 (Entry 4 in Table S1). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.



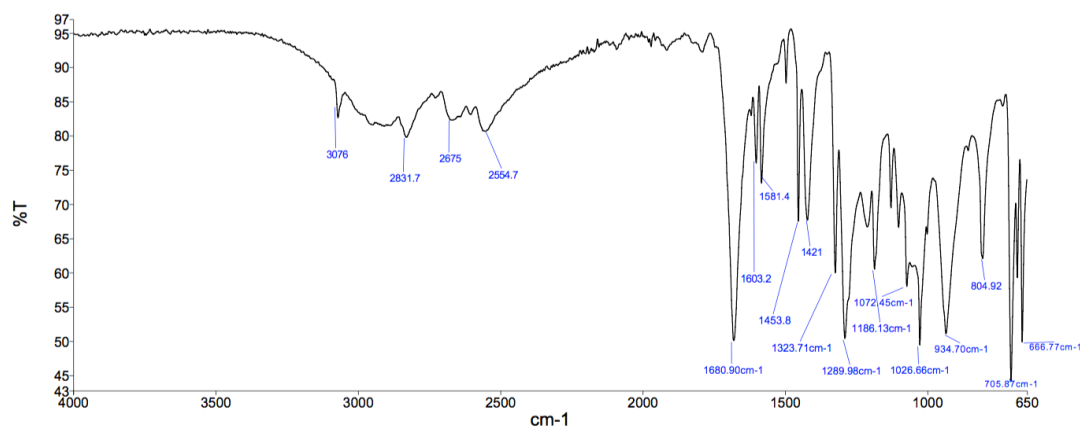
**Figure S51.** Processed TGA analysis of poly(1)  $M_n$  11 327 g mol<sup>-1</sup>,  $\bar{D}$  2.2 (Entry 4 in Table S1). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

### DSC of poly(**1**)



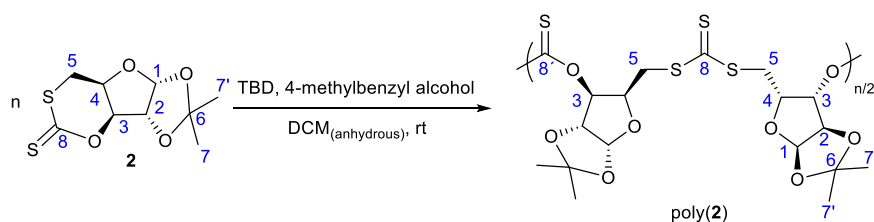
**Figure S52.** DSC traces of poly(**1**). Heating (red) and cooling (blue) cycles between 20 and 100 °C for poly(**1**)  $M_n$  11 327 g mol<sup>-1</sup>, Đ 2.2 (Entry 4 in Table S1).

### FT-IR of poly(**1**)



**Figure S53.** FT-IR of poly(**1**)  $M_n$  11 327 g mol<sup>-1</sup>, Đ 2.2 (Entry 4 in Table S1).

## Polymerisation of monomer 2



**Scheme S8.** Polymerisation of monomer **2** using TBD as catalyst and 4-methylbenzyl alcohol as initiator.

The procedure for a typical polymerisation experiment (Entry 4 in Table S2) is as follows: Under an argon atmosphere 4-MeBnOH (13  $\mu$ L, 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0065 mmol, 1 equiv.) and TBD (13  $\mu$ L, 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0065 mmol, 1 equiv.) were added to a solution of monomer **2** (0.162 mg, 0.652 mmol, 100 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (0.652 mL, 1 M). The mixture was stirred at room temperature. After 15 minutes the polymerisation was quenched by addition of a solution of benzoic acid (~30 equiv.) and the solvent removed under reduced pressure. The crude solid was then dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and precipitated from  $\text{Et}_2\text{O}$ . The product was isolated by centrifugation (3000 rpm, 10 minutes) and washed twice with  $\text{Et}_2\text{O}$ . The polymer was isolated as a yellow solid (0.127 g, 79%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 C): = 5.96-5.92 (1H, m,  $\text{H}_1$ ), 5.63-5.60 (1H, m,  $\text{H}_3$ ), 4.70-4.66 (1H, m,  $\text{H}_2$ ), 4.62-4.58 (1H, m,  $\text{H}_4$ ), 3.72-3.63 (2H, m,  $\text{H}_{5,5'}$ ), 1.53-1.47 (3H, br. s,  $\text{H}_7$ ), 1.34-1.30 (3H, br. s,  $\text{H}_{7'}$ ) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 C): = 222.5 (C(S) $\text{S}_2$ ,  $\text{C}_8$ ); 193.1 (C(S) $\text{O}_2$ ,  $\text{C}_8$ ); 112.8 (C,  $\text{C}_6$ ); 104.9 (CH,  $\text{C}_1$ ); 85.3 (CH,  $\text{C}_3$ ); 83.3 (CH,  $\text{C}_2$ ); 76.8 (CH,  $\text{C}_4$ ); 34.5 ( $\text{CH}_2$ ,  $\text{C}_5$ ); 26.8 ( $\text{CH}_3$ ,  $\text{C}_7$ ); 26.5 ( $\text{CH}_3$ ,  $\text{C}_{7'}$ ) ppm.

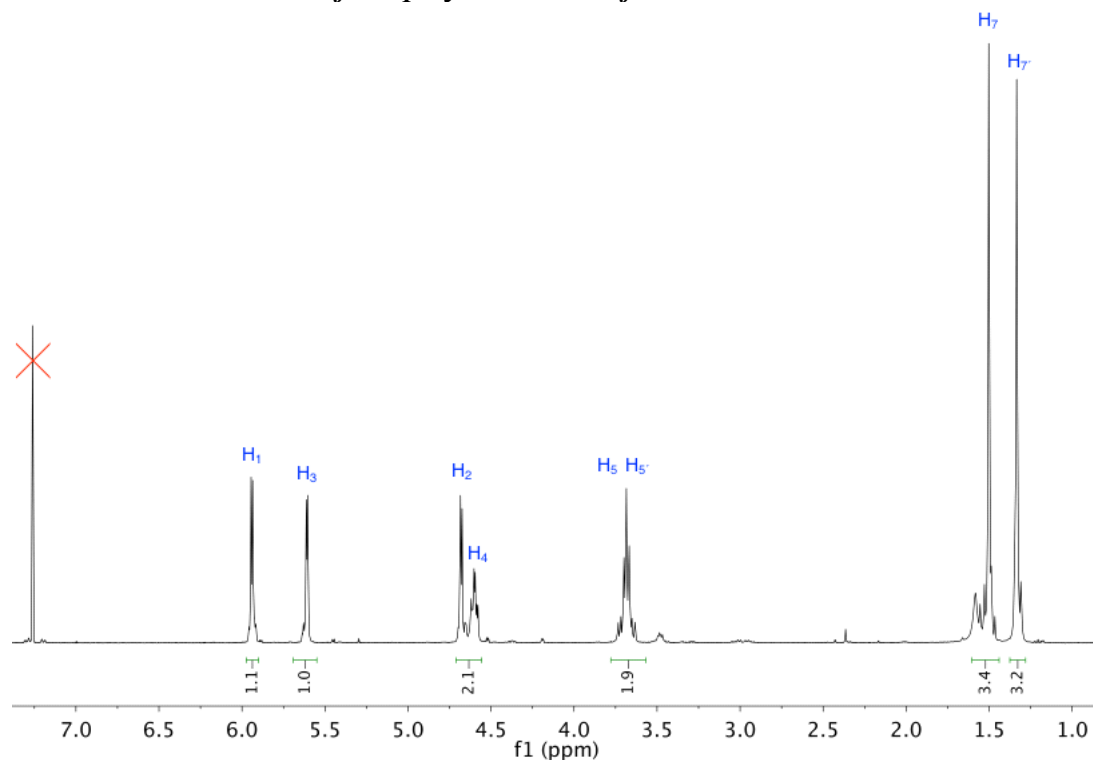
**Table S2.** Polymerisation tests performed with monomer **2**.<sup>a</sup>

Entry	[M]:[C]:[I] <sup>b</sup>	Time (h)	Conv. <sup>c</sup> (%)	$M_n$ (SEC) <sup>d</sup> (kDa)	$M_n$ (calc) <sup>e</sup> (kDa)	$M_w$ (SEC) <sup>d</sup> (kDa)	$\bar{D}$ <sup>f</sup>	Type of polymer linkage(s) <sup>g</sup>
1	25:1:1	0.25	86	6.0	5.5	9.2	1.5	Alternating C(S) $\text{S}_2$ and C(S) $\text{O}_2$
2	50:1:1	0.25	87	5.3	10.9	11.5	2.2	Alternating C(S) $\text{S}_2$ and C(S) $\text{O}_2$
3	50:1:1	2	>99	12.6	12.5	18.3	1.5	Alternating C(S) $\text{S}_2$ and C(S) $\text{O}_2$
4	100:1:1	0.25	86	15.7	21.5	26.5	1.7	Alternating C(S) $\text{S}_2$ and C(S) $\text{O}_2$

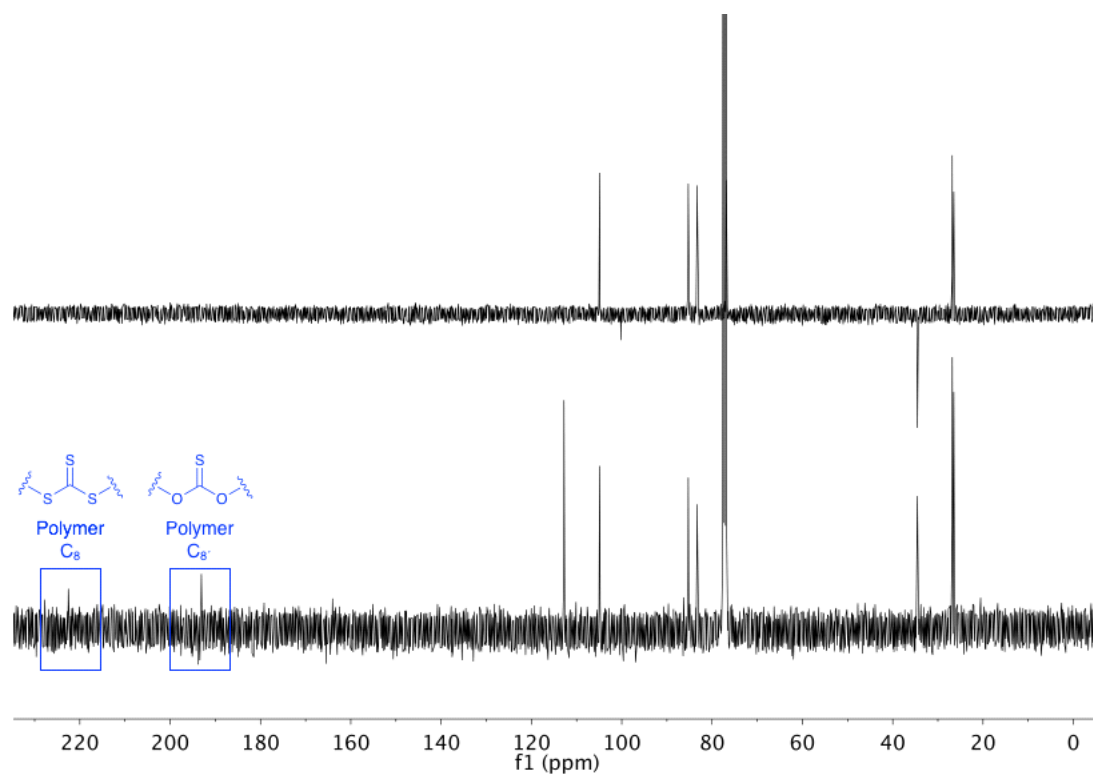
<sup>a</sup> Polymerizations carried out at room temperature in anhydrous  $\text{CH}_2\text{Cl}_2$  as solvent with  $[\mathbf{2}]_0 = 1$  M; <sup>b</sup> C is the catalyst, TBD, and I is the initiator, 4-MeBnOH; <sup>c</sup> conversion measured by  $^1\text{H}$  NMR determined by relative integration of the anomeric proton in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ ; <sup>d</sup> estimated by SEC (RI detector) versus polystyrene standards with THF as eluent; <sup>e</sup> calculated as  $M_r(\text{I}) + (M_r(\text{monomer}) \times [\text{monomer}]_0 / [\text{I}]_0 \times \text{conv} / 100\%)$ ; <sup>f</sup>  $\bar{D} = M_w / M_n$ ; <sup>g</sup> determined by  $^{13}\text{C}$  NMR.



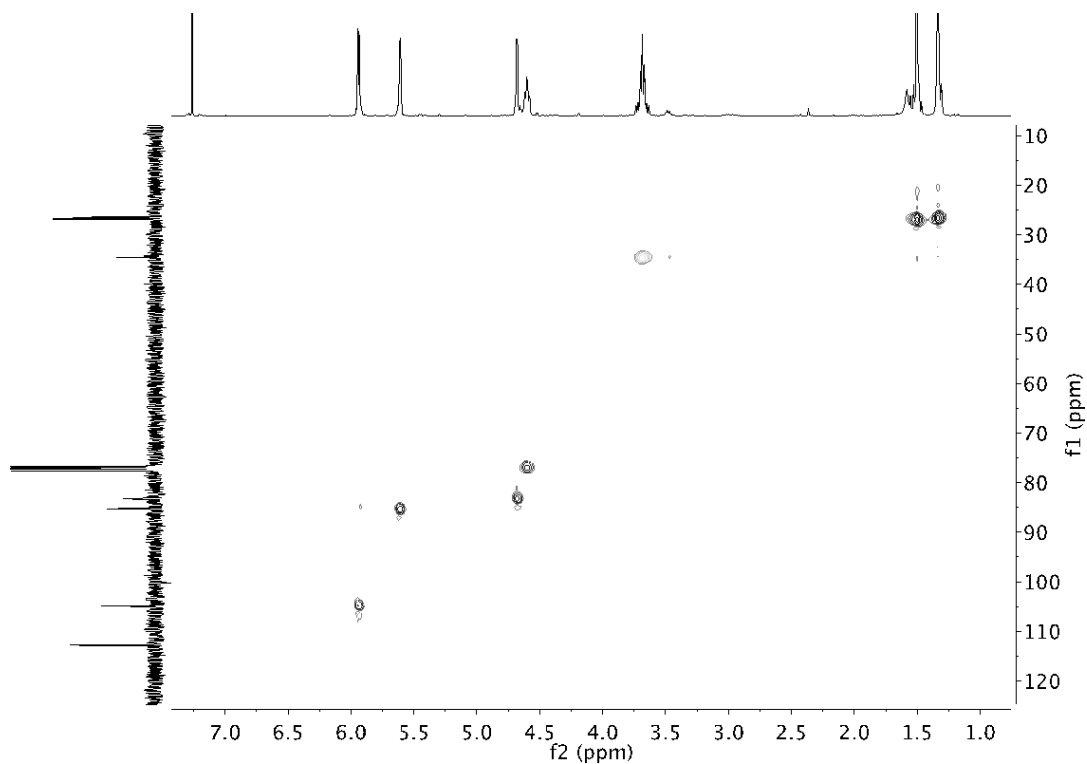
## NMR Characterisation of the polymer derived from monomer 2



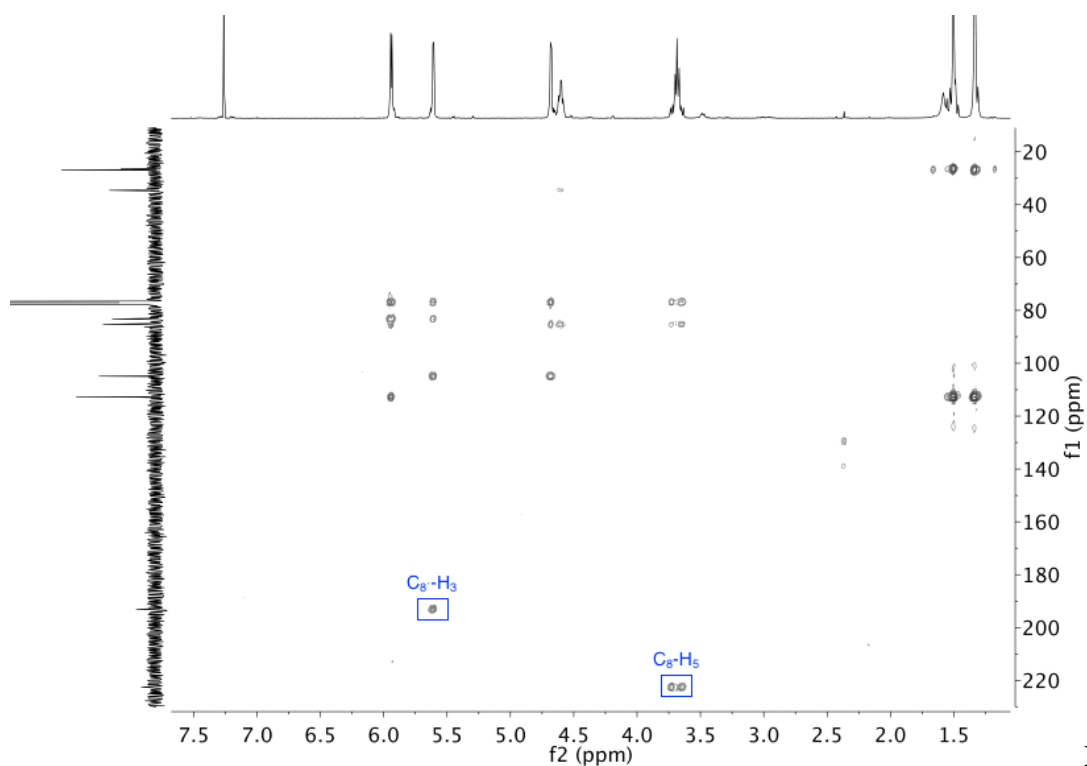
**Figure S54.** Annotated  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 C) of poly(**2**)  $M_n$  12 550  $\text{g mol}^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S2). Red cross denotes residual  $\text{CHCl}_3$  solvent peak.



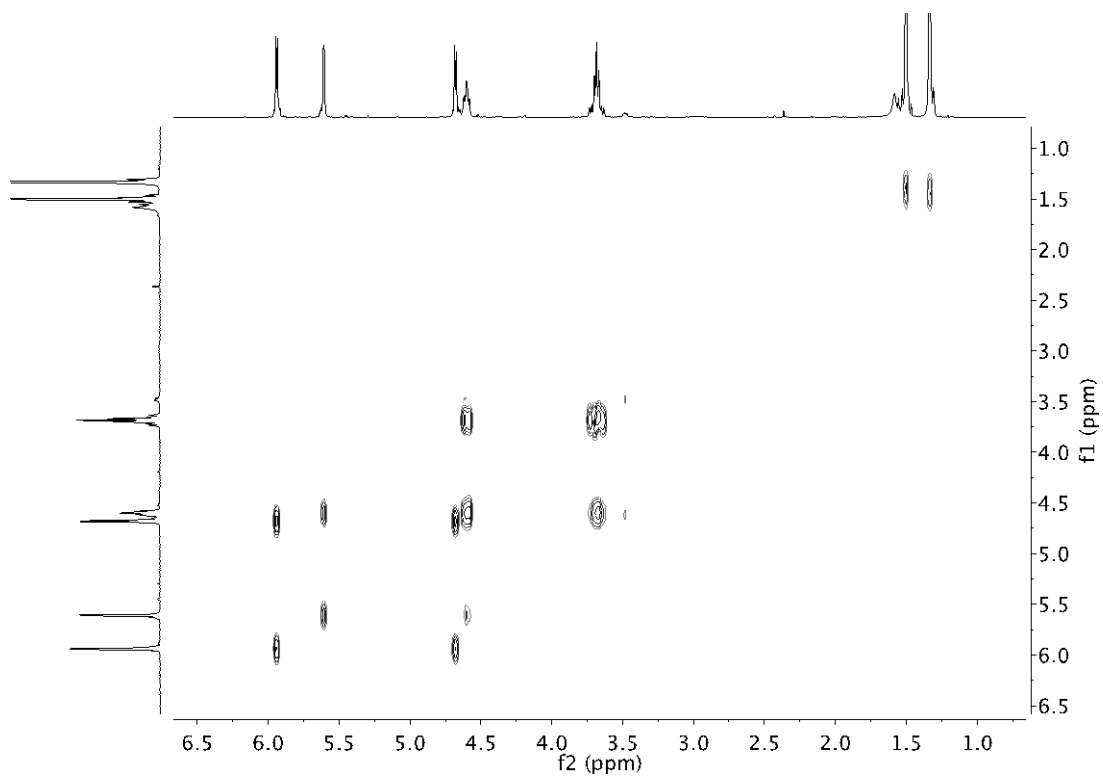
**Figure S55.**  $^{13}\text{C}$  NMR and DEPT-135 spectra (101 MHz,  $\text{CDCl}_3$ , 25 C) of poly(**2**)  $M_n$  12 550  $\text{g mol}^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S2).



**Figure S56.** HSQC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**2**)  $M_n$  12 550  $\text{g mol}^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S2).



**Figure S57.** HMBC (400 and 101 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**2**)  $M_n$  12 550  $\text{g mol}^{-1}$ ,  $\text{D}$  1.5 (Entry 3 in Table S2).

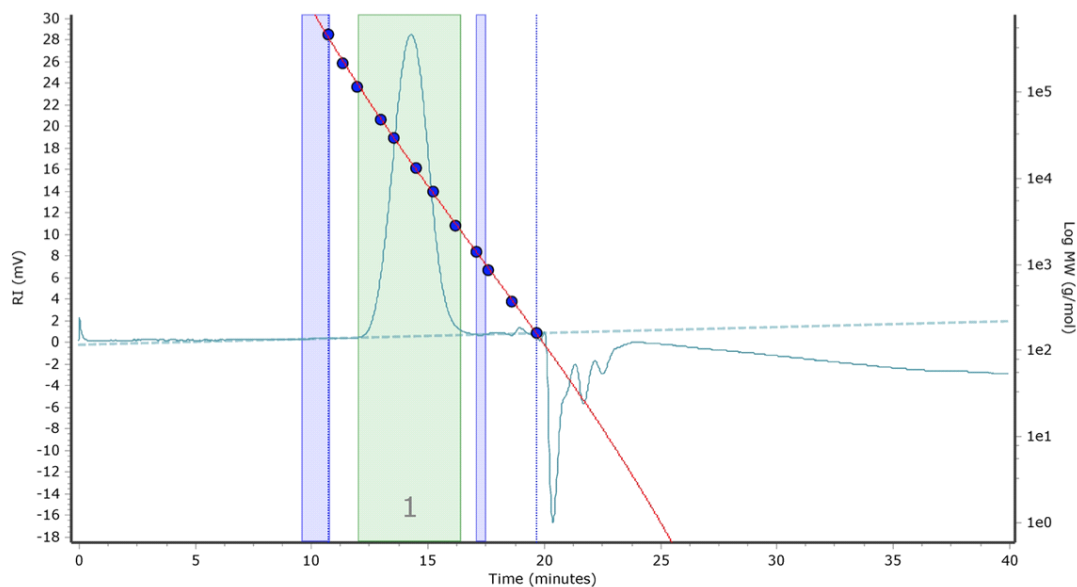


**Figure S58.** COSY (400 MHz, CDCl<sub>3</sub>, 25 C) of poly(**2**)  $M_n$  12 550 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S2).

## Size-Exclusion Chromatography of poly(2)

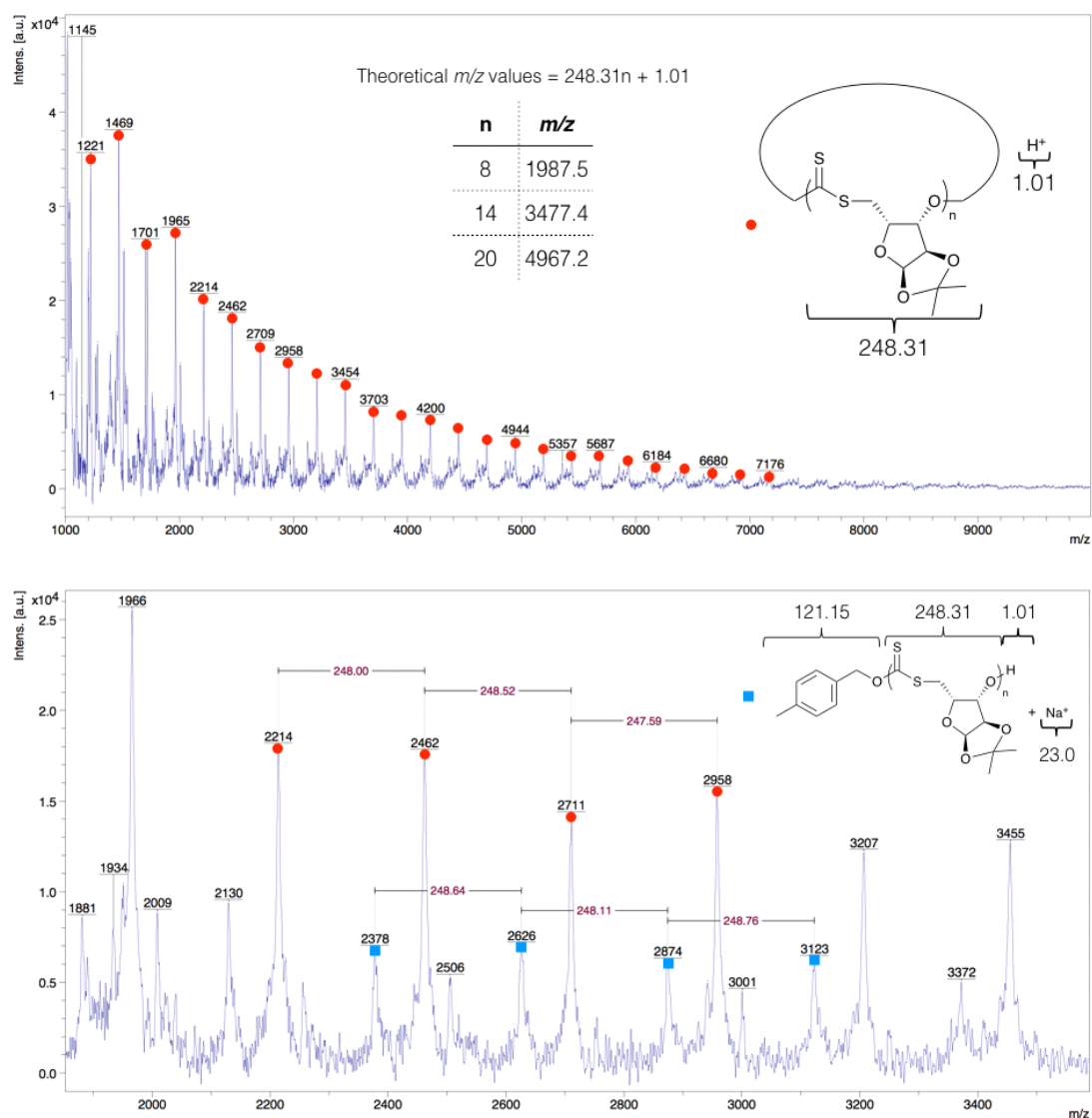
### Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	14942	12550	18311	26233	35883	24938	1.459



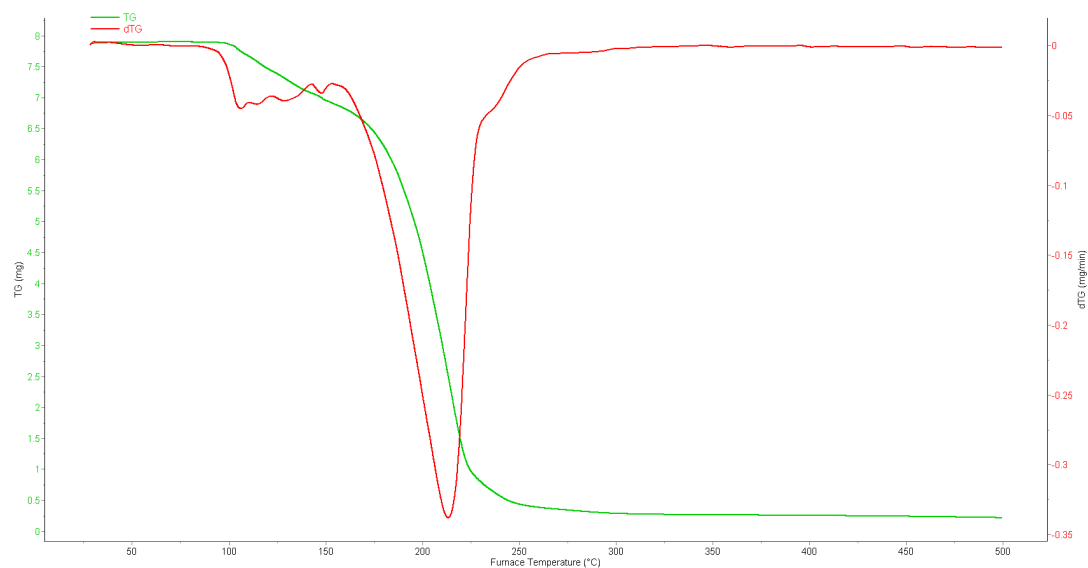
**Figure S59.** SEC trace of polymer showing  $M_n$  12 550 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S2).

## End-group Determination with MALDI-ToF Mass Spectrometry

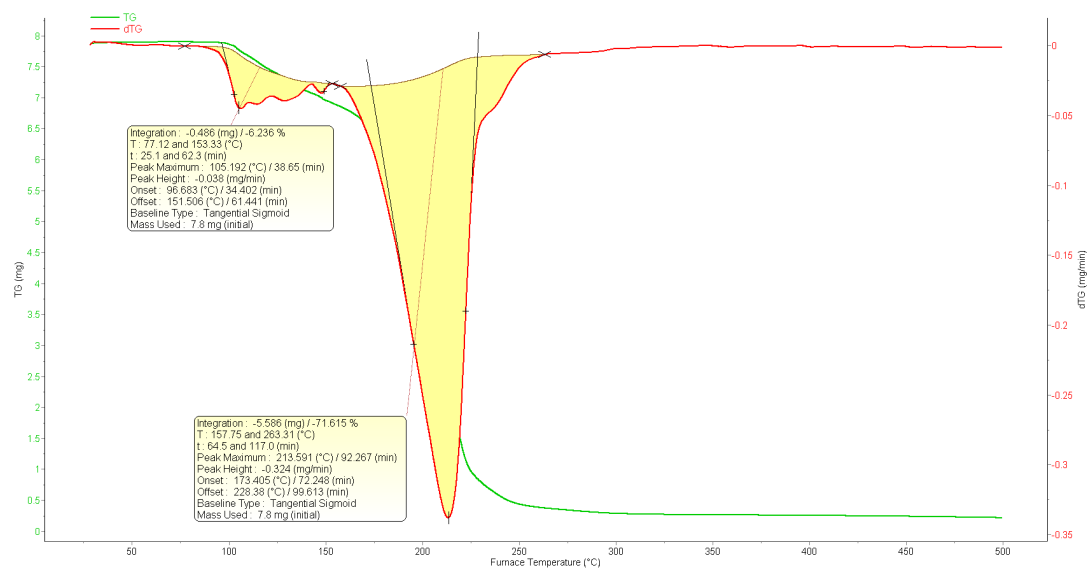


**Figure S60.** MALDI-ToF of two different samples of poly(2) (Dithranol/THF (1:5) + NaOAc): on the top,  $M_{n,SEC}$  12 550 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S2); at the bottom,  $M_{n,SEC}$  6 043 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 1 in Table S2). In red circles are highlighted the signals corresponding to cyclic polymer which is due to backbiting of the polymer chain. In blue squares with same repeat unit 248.31  $m/z$  are highlighted the signals corresponding to sodium adduct of linear polymer with OH and 4-methylbenzyl alcohol end-groups.

## TGA of poly(2)

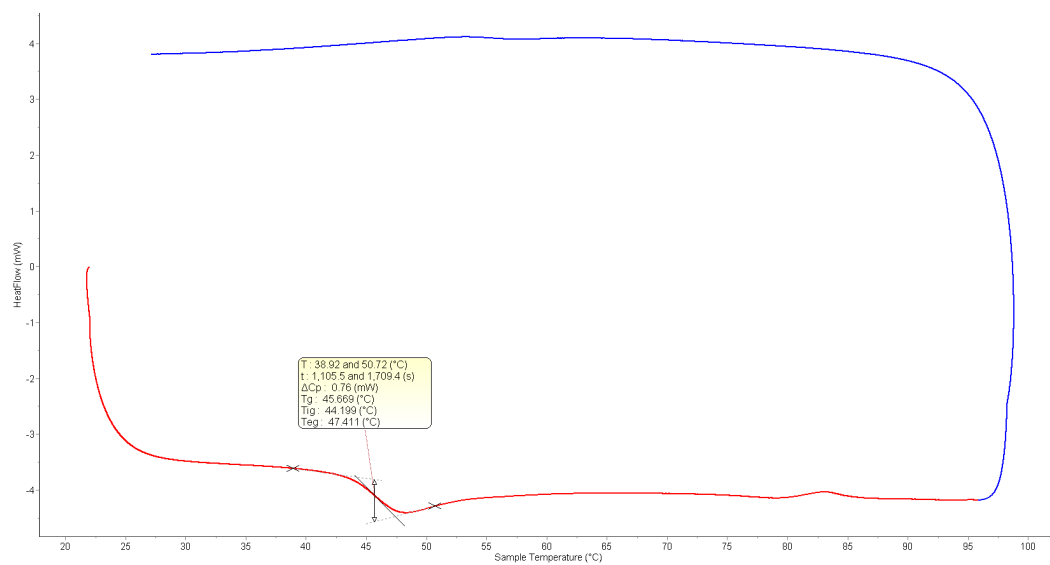


**Figure S61.** TGA analysis of poly(2)  $M_n$  12 550 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S2). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.



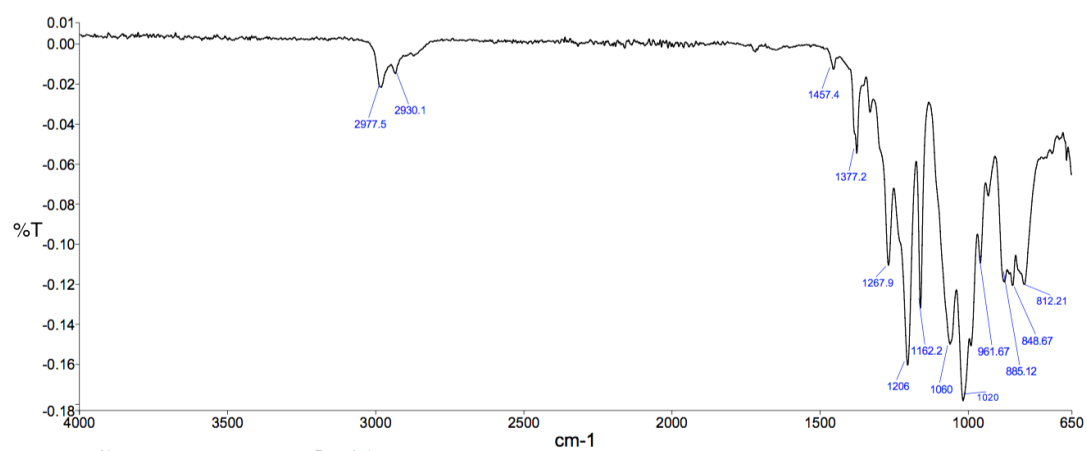
**Figure S62.** Processed TGA analysis of poly(2)  $M_n$  12 550 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 3 in Table S2). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

### DSC of poly(2)



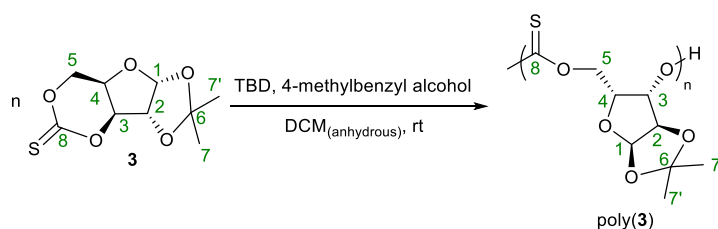
**Figure S63.** DSC traces of poly(2). Heating (red) and cooling (blue) cycles between 20 and 100 °C for poly(2)  $M_n$  15 657 g mol<sup>-1</sup>, Đ 1.7 (Entry 4 in Table S2).

### FT-IR of poly(2)



**Figure S64.** FT-IR of poly(2)  $M_n$  15 657 g mol<sup>-1</sup>, Đ 1.7 (Entry 4 in Table S2).

### Polymerisation of monomer **3**



**Scheme S9.** Polymerisation of monomer **3** using TBD as catalyst and 4-methylbenzyl alcohol as initiator.

The procedure for a typical polymerisation experiment (Entry 9 in Table S3) is as follows: Under an argon atmosphere 4-MeBnOH (31.6  $\mu\text{L}$ , 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0158 mmol, 1 equiv.) and TBD (31.6  $\mu\text{L}$ , 0.5 M in anhydrous  $\text{CH}_2\text{Cl}_2$ , 0.0158 mmol, 1 equiv.) were added to a solution of monomer **3** (0.367 g, 1.58 mmol, 100 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.0 mL, 1.58 M). The mixture was stirred at room temperature. After 15 minutes the polymerisation was quenched by addition of a solution of excess benzoic acid (~30 equiv.) and the solvent removed under reduced pressure. The crude solid was then dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and precipitated from  $\text{Et}_2\text{O}$ . The product was isolated by centrifugation (3000 rpm, 10 minutes) and washed twice with  $\text{Et}_2\text{O}$ . The polymer was isolated as a white solid (0.121 g, 33%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 C): = 6.00-5.95 (1H, br,  $\text{H}_1$ ), 5.75-5.63 (1H, m,  $\text{H}_4$ ), 4.76-4.50 (4H, m,  $\text{H}_2$ ,  $\text{H}_3$ ,  $\text{H}_5$ ), 1.54 (3H, br,  $\text{H}_7$ ) 1.33 (3H, br,  $\text{H}_{7'}$ ) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 C): = 194.8, 193.8, 193.0 (3  $\text{C}(\text{S})\text{O}_2$ ,  $\text{C}_8$ ); 112.8 (C,  $\text{C}_6$ ); 105.0 (CH,  $\text{C}_1$ ); 84.5, 83.1, 76.2 (3 CH,  $\text{C}_{2,3,4}$ ); 69.6 ( $\text{CH}_2$ ,  $\text{C}_5$ ); 26.8 ( $\text{CH}_3$ ,  $\text{C}_7$ ); 26.4 ( $\text{CH}_3$ ,  $\text{C}_{7'}$ ) ppm.

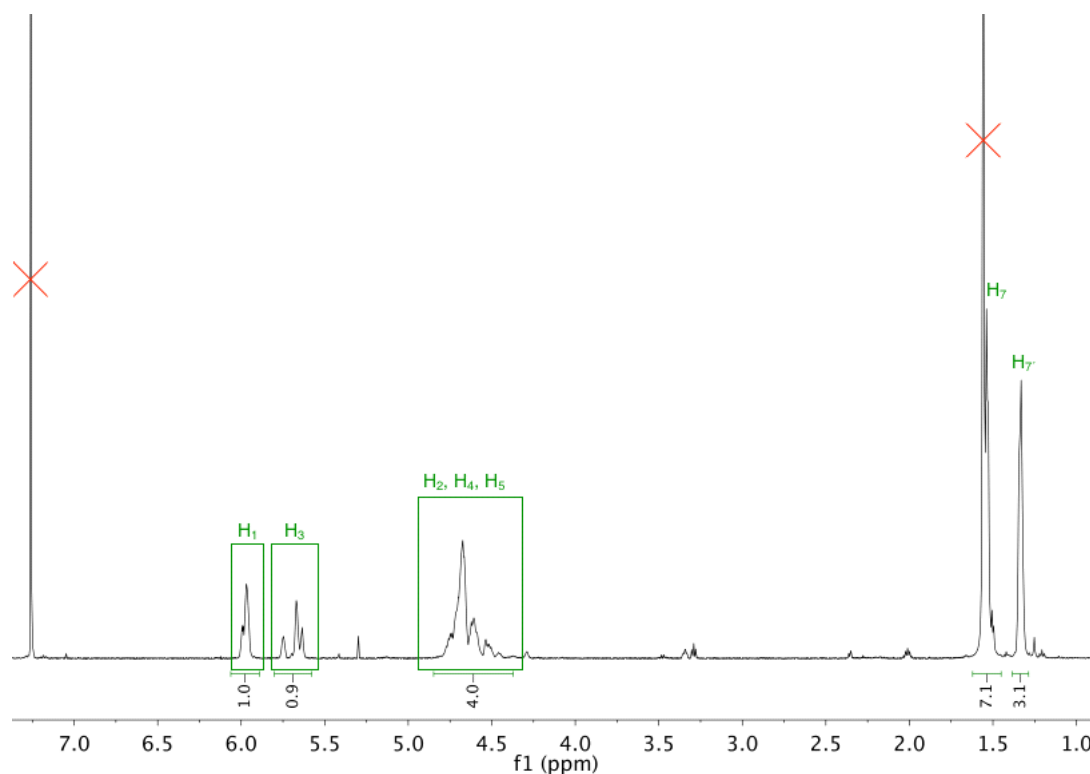
**Table S3.** Polymerisation tests performed with monomer **3**.<sup>a</sup>

Entry	[M]:[C]:[I] <sup>b</sup>	Time (h)	Conv. <sup>c</sup> (%)	$M_n$ (SEC) <sup>d</sup> (kDa)	$M_n$ (calc) <sup>e</sup> (kDa)	$M_w$ (SEC) <sup>d</sup> (kDa)	$\bar{D}$ <sup>f</sup>	Type of polymer linkage <sup>g</sup>
1	25:1:1	0.25	42	5.2	2.6	7.6	1.5	C(S)O <sub>2</sub>
2	50:1:1	0.25	40	7.4	4.8	9.3	1.3	C(S)O <sub>2</sub>
3	50:1:1	2	66	6.7	7.8	8.3	1.2	C(S)O <sub>2</sub>
4	50 <sup>h</sup> :1:1	0.25	52	7.5	6.2	11.1	1.5	C(S)O <sub>2</sub>
5	50 <sup>h</sup> :1:1	0.5	61	10.0	7.2	12.9	1.3	C(S)O <sub>2</sub>
6	50 <sup>h</sup> :1:1	3	62	10.3	7.3	13.3	1.3	C(S)O <sub>2</sub>
7	100 <sup>h</sup> :1:1	0.25	44	10.6	10.3	15.9	1.5	C(S)O <sub>2</sub>

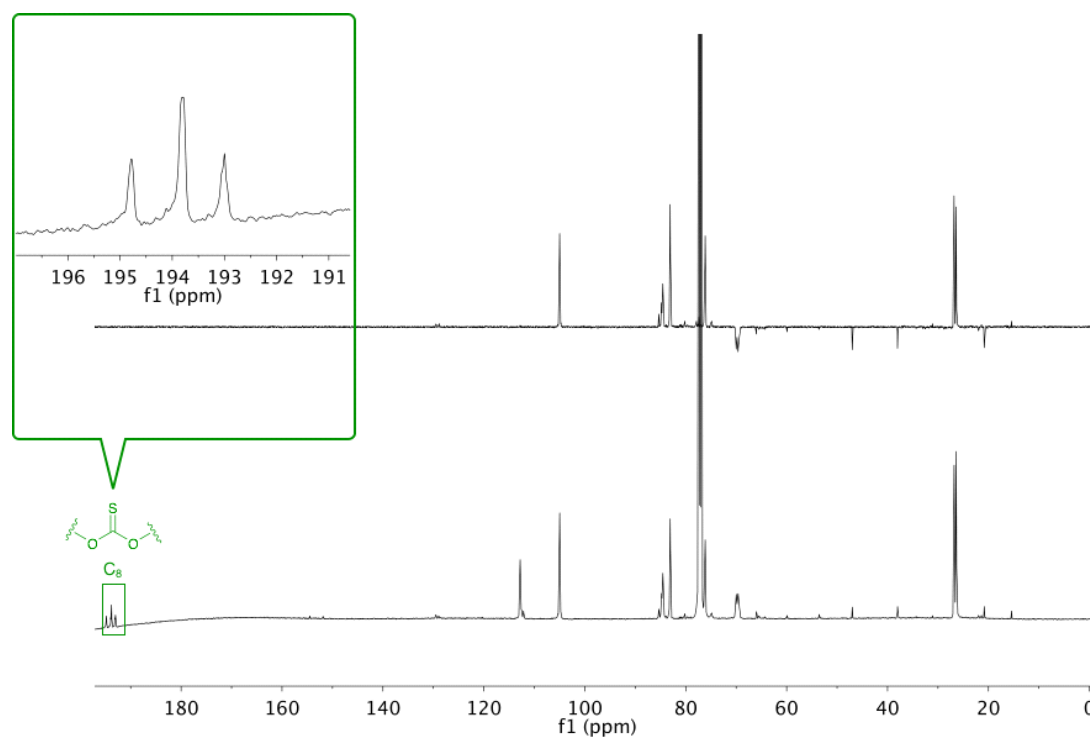
<sup>a</sup> Polymerizations carried out at room temperature in anhydrous  $\text{CH}_2\text{Cl}_2$  as solvent with  $[\mathbf{3}]_0 = 1$  M, unless stated otherwise; <sup>b</sup> C is the catalyst, TBD, and I is the initiator, 4-MeBnOH; <sup>c</sup> conversion measured by  $^1\text{H}$  NMR determined by relative integration of the anomeric proton in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ ; <sup>d</sup> estimated by SEC (RI detector) versus polystyrene standards with THF as eluent; <sup>e</sup> calculated as  $M_r(\text{I}) + (M_r(\text{monomer}) \times [\text{monomer}]_0 / [\text{I}]_0 \times \text{conv} / 100\%)$ ; <sup>f</sup>  $\bar{D} = M_n / M_w$ ; <sup>g</sup> determined by  $^{13}\text{C}$  NMR; <sup>h</sup>  $[\mathbf{3}] = 1.58$  M.



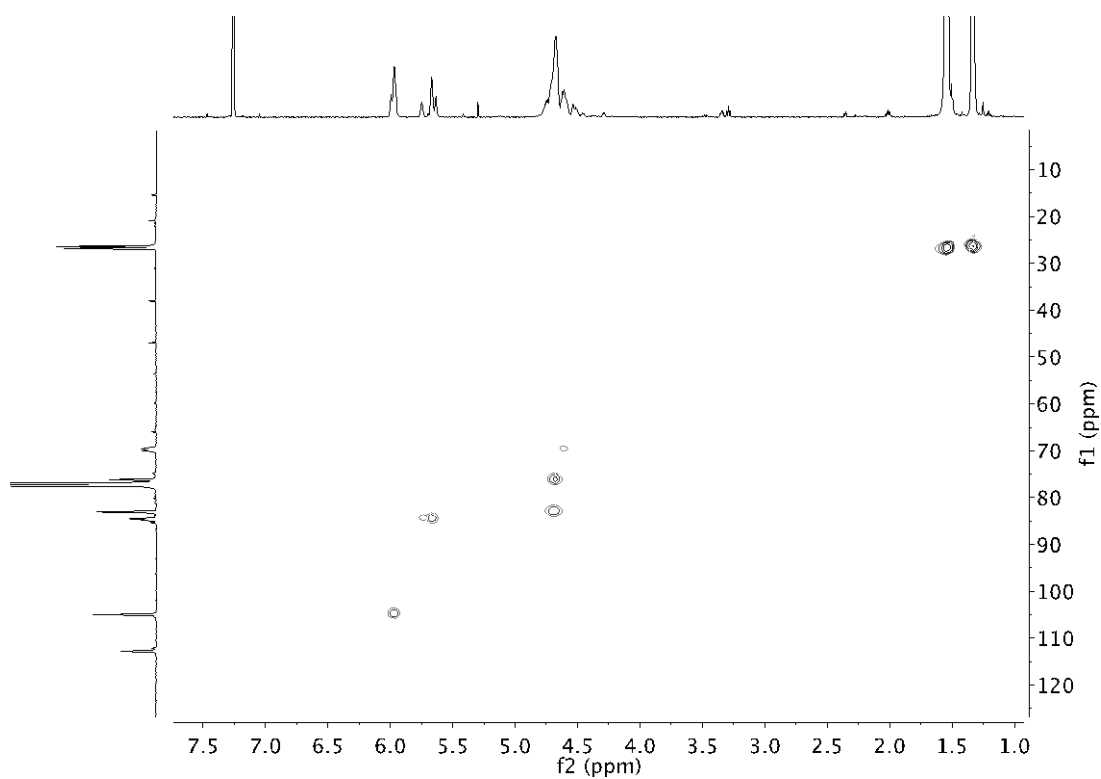
### NMR Characterisation of the polymer derived from monomer 3



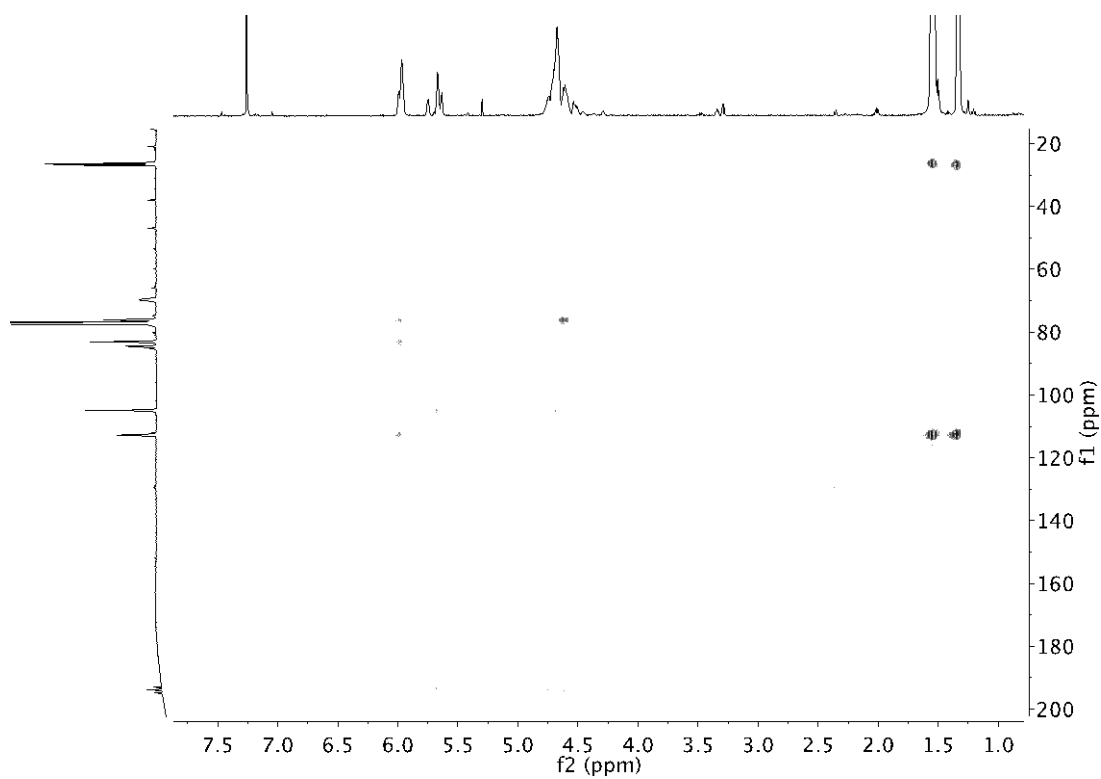
**Figure S65.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25 C) of poly(**3**)  $M_n$  10 269 g mol<sup>-1</sup>, Đ 1.3 (Entry 6 in Table S3). Red crosses denote residual CHCl<sub>3</sub> and H<sub>2</sub>O solvent peaks. The H<sub>2</sub>O peak is partially overlapped with the H<sub>7</sub> signal.



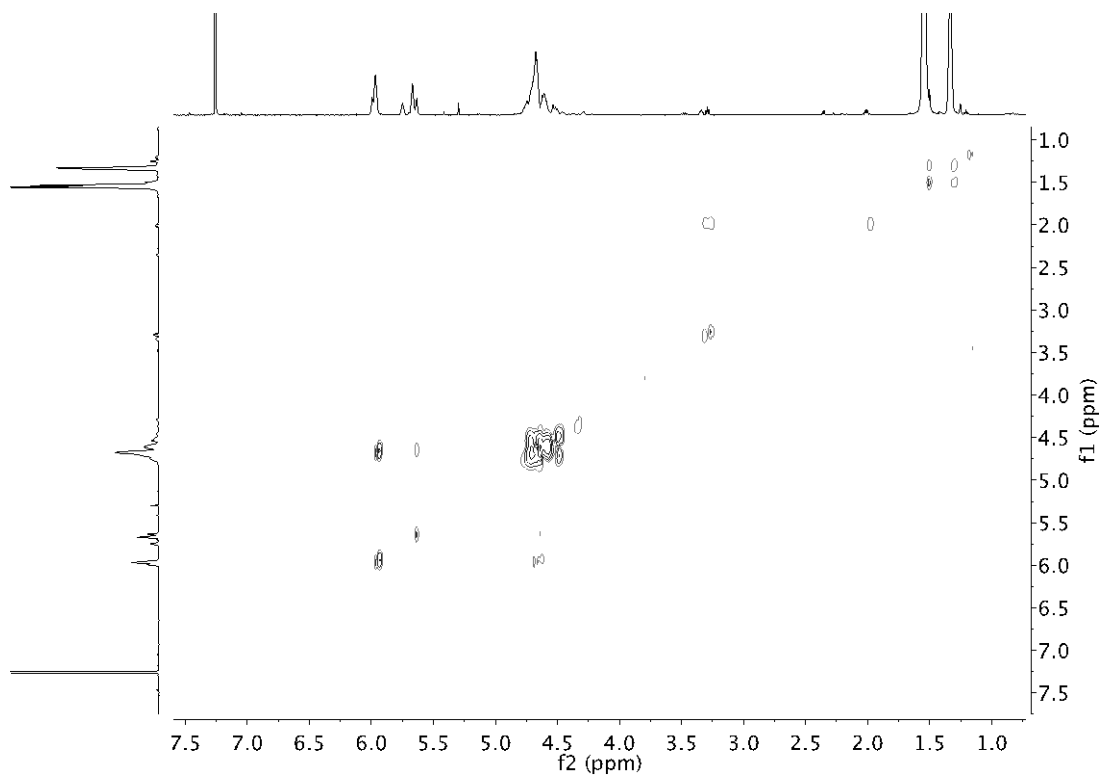
**Figure S66.** <sup>13</sup>C NMR and DEPT-135 spectra (125 MHz, CDCl<sub>3</sub>, 25 C) of poly(**3**)  $M_n$  10 269 g mol<sup>-1</sup>, Đ 1.3 (Entry 6 in Table S3).



**Figure S67.** HSQC (500 and 125 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**3**)  $M_n$  10 269  $\text{g mol}^{-1}$ ,  $\text{D}$  1.3 (Entry 6 in Table S3).



**Figure S68.** HMBC (500 and 125 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 25 C) of poly(**3**)  $M_n$  10 269  $\text{g mol}^{-1}$ ,  $\text{D}$  1.3 (Entry 6 in Table S3).

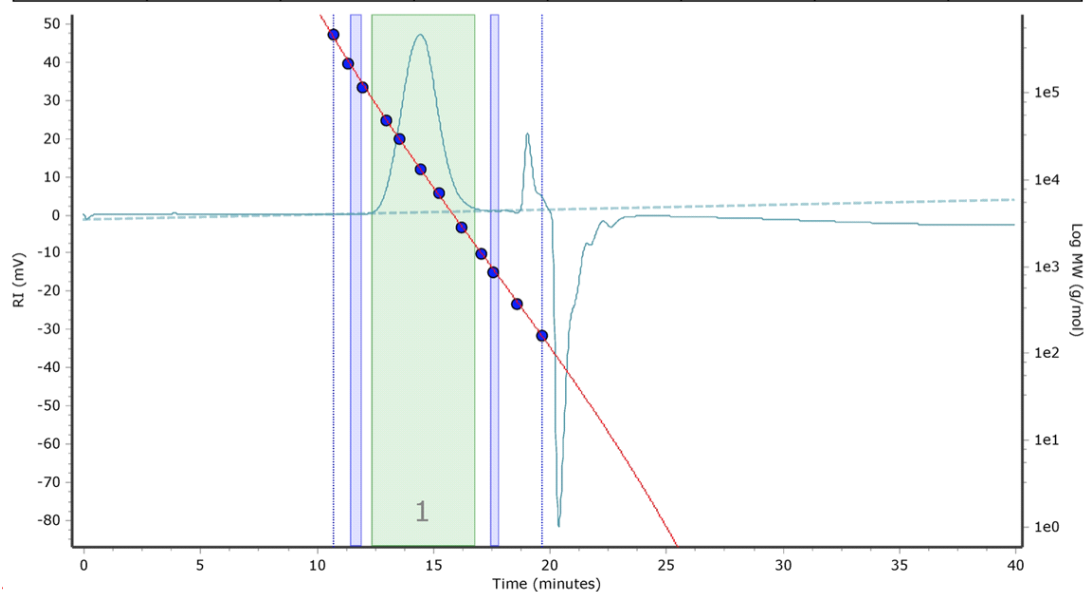


**Figure S69.** COSY (500 MHz, CDCl<sub>3</sub>, 25 C) of poly(**3**)  $M_n$  10 269 g mol<sup>-1</sup>,  $\delta$  1.3 (Entry 6 in Table S3).

## Size-Exclusion Chromatography of poly(3)

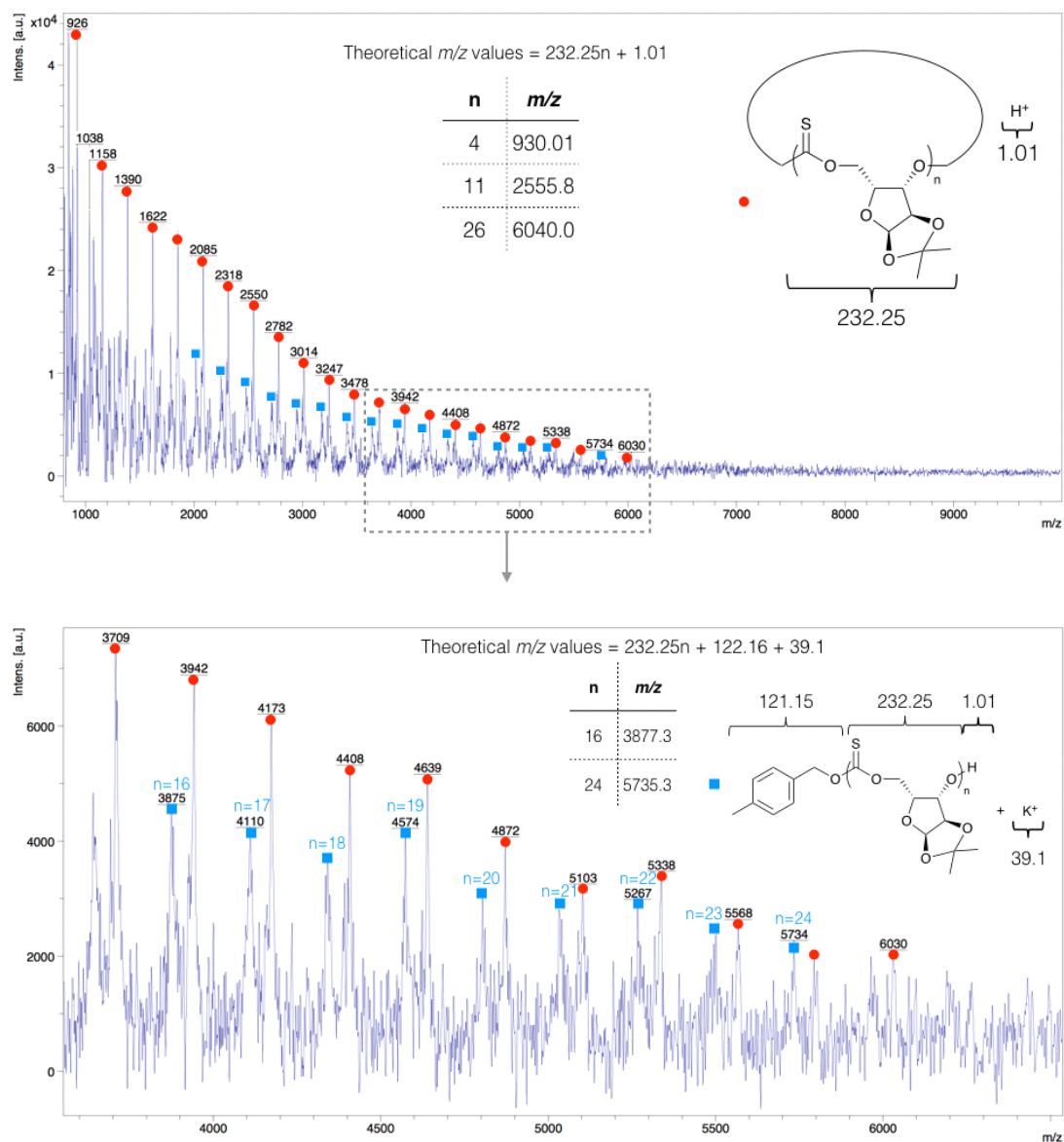
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13105	10594	15909	22846	30850	21745	1.502



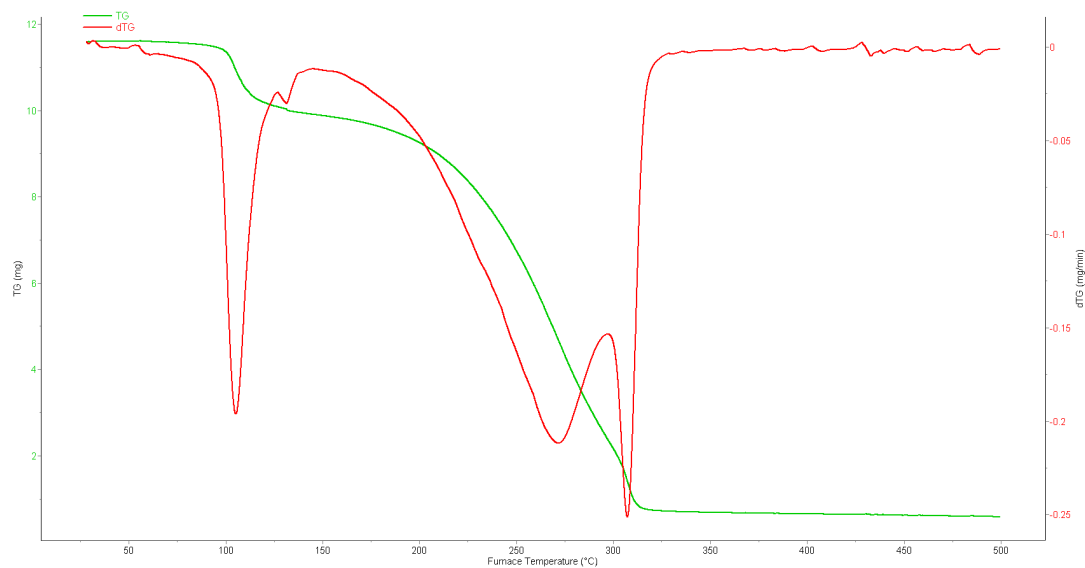
**Figure S70.** SEC trace of polymer showing  $M_n$  10 594 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 7 in Table S3).

## End-group Determination with MALDI-ToF Mass Spectrometry

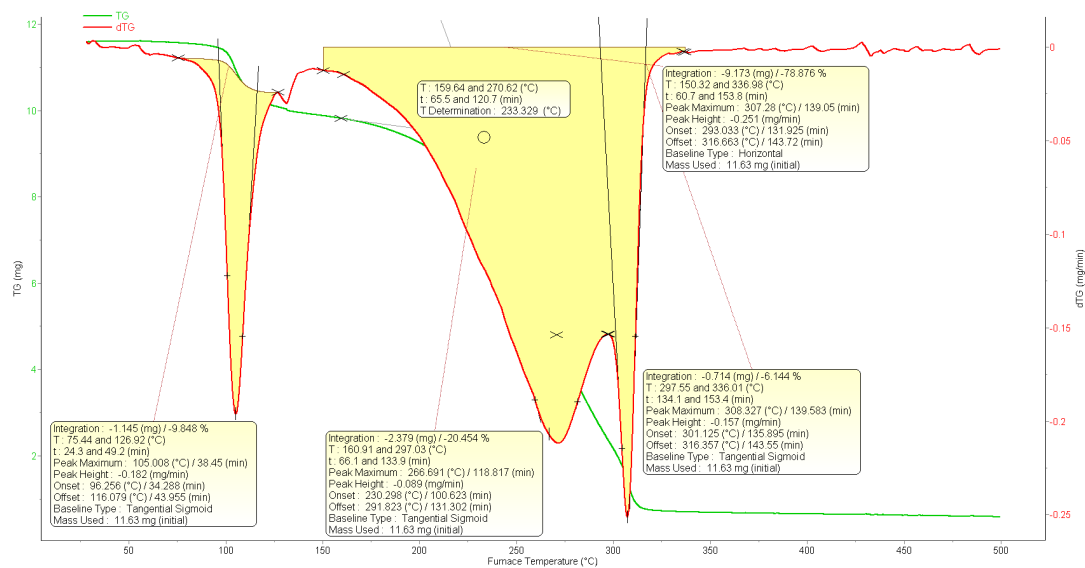


**Figure S71.** MALDI-ToF of poly(3)  $M_{n,SEC}$  7 488 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (DHB/THF (1:2) + KOAc) (Entry 4 in Table S3). Major series (red circles) corresponds to proton adduct of cyclic polymer is due to backbiting of the polymer chain. Minor series (blue squares) with same repeat unit 232.25 m/z, corresponds to potassium adduct of linear polymer with OH and 4-methylbenzyl alcohol end-groups, for example  $n=16$  gives  $m/z$   $232.25 \times 16 + 122.16 + 39.1 = 3877.26$ .

## TGA of poly(3)

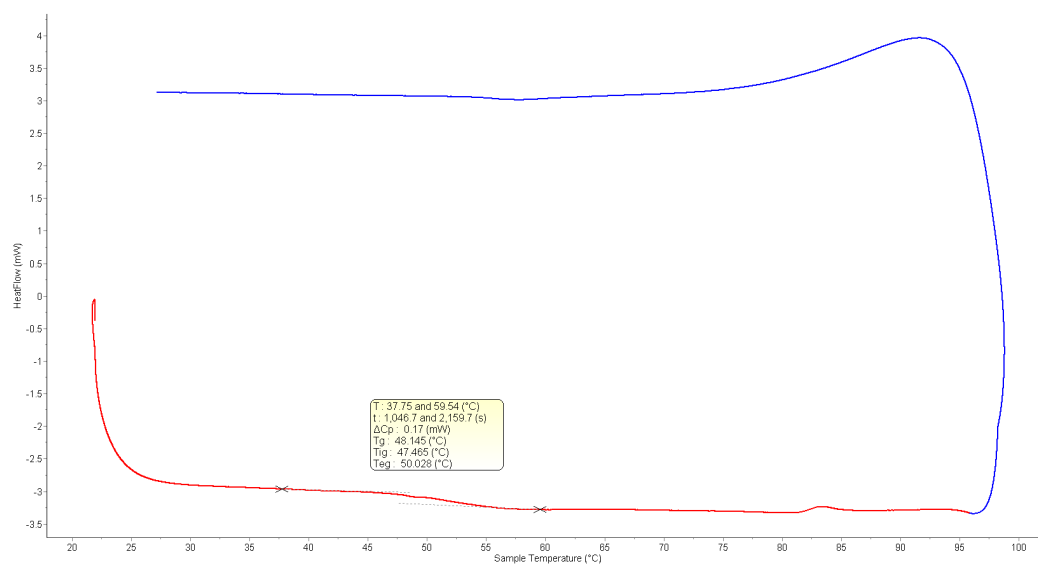


**Figure S72.** TGA analysis of poly(3)  $M_n$  10 594 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 7 in Table S3). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.



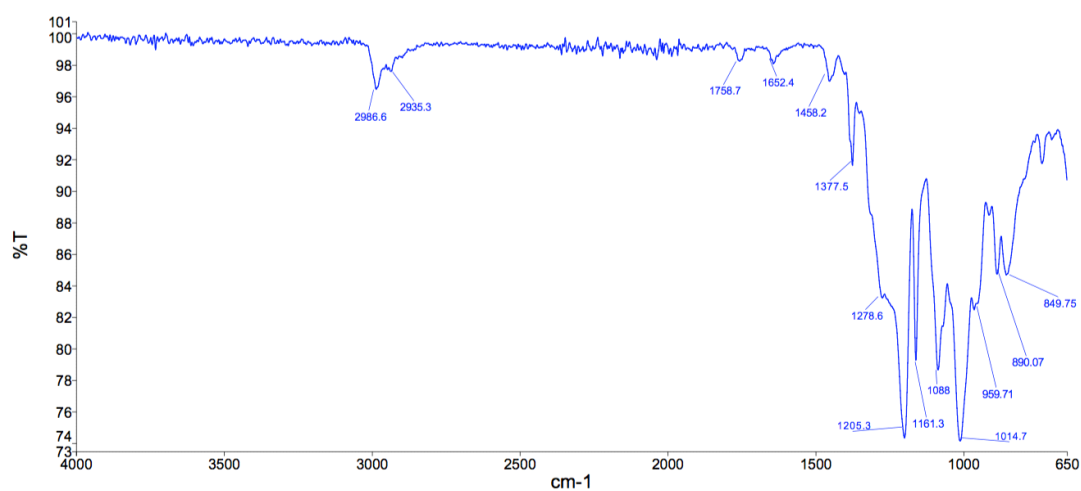
**Figure S73.** Processed TGA analysis of poly(3)  $M_n$  10 594 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 7 in Table S3). The polymer was heated from 30 to 500 °C under argon at 2 K min<sup>-1</sup>.

### DSC of poly(3)



**Figure S74.** DSC traces of poly(3). Heating (red) and cooling (blue) cycles between 20 and 100 °C for poly(3)  $M_n$  7 488 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 4 in Table S3).

### FT-IR of poly(3)



**Figure S75.** FT-IR of poly(3)  $M_n$  7 488 g mol<sup>-1</sup>,  $\bar{D}$  1.5 (Entry 4 in Table S3).

## **References**

- <sup>1</sup> M. Adiyaman, S. P. Khanapure, S. W. Hwang and J. Rokach, *Tetrahedron Lett.*, 1995, **36**, 7367-7370.
- <sup>2</sup> L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849-854.