Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Variations around the presence and position of sulfur in sugar-derived cyclic monomers: influence on polymerisation thermodynamics, polymer sequence and thermal properties

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Materials and Methods

Unless otherwise stated, all starting materials and reagents were obtained from Sigma-Aldrich, Acros Organics or Alfa Aesar and used without further purification. All solvents were obtained from either Fisher Scientific or VWR Chemicals, except for anhydrous solvents, which were purchased from Sigma-Aldrich or Acros Organics and used without further purification. Tri-*O*-acetyl-D-glucal was purchased from Carbosynth. 4-Methylbenzyl alcohol was recrystallised from dry diethyl ether and stored in a glovebox under Argon prior to use and TBD was recrystallised from dry toluene and dried over CaH_2 prior to use by dissolution in dry THF. Where appropriate, the progress of reactions was monitored by thin layer chromatography using silica coated aluminium plates (Kieselgel 60G F254) purchased from VWR Chemicals and visualized using a potassium permanganate ($KMnO_4$) stain. The purification of intermediates and final products was accomplished by flash column chromatography, using silica gel (Fluka, pore size 60 Å, 70-230 mesh, 63-200 µm), and the purity of the final compounds was determined by NMR spectroscopy.

NMR spectra were recorded on a Brucker 400 and 500 spectrometers operating at a frequencies of 400 MHz (^{1}H) and 101 MHz (^{13}C) and 500 MHz (^{1}H) and 126 MHz (^{13}C) respectively. The NMR spectra were recorded in $CDCl_3$, relative to reference points of the deuterated solvent. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are quoted in Hertz. Abbreviations used to describe the multiplicity of the peaks observed are defined as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets and so on.

Size-exclusion chromatography (SEC) was carried out using a THF or chloroform eluent. Multi analysis software was used to process the data. Polymer samples were dissolved at a concentration of 1 mg mL^{-1}. Samples were recorded on an Agilent 1260 Infinity series instrument at 1 mL min^{-1} at 35 °C using two PLgel 5 µm MIXED-D 300 × 7.5 mm columns in series. Samples were detected with a differential refractive index (RI) detector. Number-average molecular weight ($M_{n,SEC}$), and dispersities, ($Đ_M$ (M_w/M_n)) were calculated against a polystyrene calibration (11 polystyrene standards of narrow molecular weight, ranging from M_w 615–568000 Da).

Differential scanning calorimetry (DSC) was carried out using a MicroSC multicell calorimeter from Setaram; the Calisto program was employed to collect and process the data. The measurement cell and the reference cell were both a 1 mL Hastelloy C cell; a mass of 2–5 mg of polymeric material was loaded into the measurement cell with the reference cell empty. The experiments were performed under N_2 and the sample heated and cooled at a rate of 10 K min^{-1} unless otherwise stated. A second heating and cooling cycle was carried out immediately following completion of the first, unless otherwise stated. Data was plotted using Origin 2018.

Thermogravimetric analysis (TGA) was carried out using a Setsys Evolution TGA 16/18 from Setaram; the Calisto program was employed to collect and process the data. The sample was loaded into a 170 µL alumina crucible

and the analytical chamber purged with argon (200 mL min^{-1}) for 20 minutes prior to starting the analysis. The sample was then heated under an argon flow (20 mL min^{-1}) from 30 to 600 °C at a rate of 10 °C min^{-1}, unless otherwise stated.

FT-IR analysis was carried out using a PerkinElmer Inc. Spectrum 100 FT-IR Spectrometer. Universal ATR enabling wavelengths from 650-4000 cm^{-1} (15 µm to 2.5 µm).

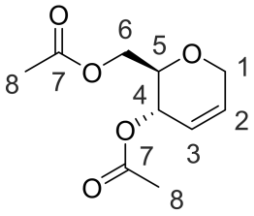
Single-Crystal X-ray Diffraction (XRD) analysis was carried out by Dr Gabriele Kociok-Köhn at 150(2) K on a Rigaku Xcalibur, EosS2 single crystal diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), or on a Rigaku SuperNova, EosS2 single crystal diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.5418 Å). Unit cell determination, data collection and data reduction were performed using the CrysAlisPro software. The structure was solved with SHELXT and refined by a full-matrix least-squares procedure based on F2 (SHELXL-2018/3)7. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed onto calculated positions and refined using a riding model.

General Procedures

1. Monomer Synthesis and Characterisation

Synthesis of (2R,3S)-3-acetoxy-3,6-dihydro-2H-pyran-2-yl)methyl acetate

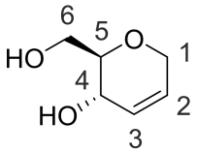
(2R,3S)-3-acetoxy-3,6-dihydro-2H-pyran-2-yl)methyl acetate was synthesised according to the previously reported method, spectroscopic data was consistent with previous literature.[1]



δ_H (400 MHz; chloroform-d): 5.93 (C^3H, 1H, dddd, J_{HH} = 10.3, 2.7, 2.7, 1.8 Hz), 5.74 (C^2H, 1H, dddd, J_{HH} = 10.3, 2.3, 2.3, 2.2 Hz), 5.28-5.19 (C^4H, 1H, m), 4.23-4.18 (C^1H, C^6H, 3H, m), 4.16 (C^6H, 1H, dd, J_{HH} = 12.1, 5.9 Hz), 3.71 (C^5H, 1H, ddd, J_{HH} = 8.6, 5.9, 2.9 Hz), 2.08 (C^7H, 3H, s), 2.06 (C^7H, 3H, s) ppm; δ_C (101 MHz; chloroform-d): 171.0 (C^7), 170.4 (C^7), 129.6 (C^3), 124.3 (C^2), 73.9 (C^5), 65.4 (C^4), 65.2 C^1), 63.4 (C^6), 21.2 (C^8), 20.9 (C^8) ppm.

Synthesis of (2R,3S)-2-(hydroxymethyl)-3,6-dihydro-2H-pyran-3-ol

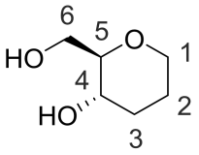
(2R,3S)-2-(hydroxymethyl)-3,6-dihydro-2H-pyran-3-ol was synthesised according to the previously reported method, spectroscopic data was consistent with previous literature.[1]



δ_H (400 MHz; chloroform-d): 5.91-5.74 (C^2H, C^3H, 2H, m), 4.24-4.12 (C^1H, C^4H, 3H, m), 3.89 (C^6H, 1H, dd, J_{HH} = 11.6, 3.8 Hz), 3.80 (C^6H, 1H, dd, J_{HH} = 11.6, 5.5 Hz), 3.34 (C^5H, 1H, ddd, J_{HH} = 8.1, 5.4, 3.9 Hz) ppm; δ_C (101 MHz; chloroform-d): 128.8 (C^3), 127.8 (C^2), 78.8 (C^5), 65.6 (C^4), 64.2 (C^1), 63.1 (C^6) ppm.

Synthesis of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol

Pd/C (10 wt. % loading, 563 mg) was added to a solution of (2R,3S)-2-(hydroxymethyl)-3,6-dihydro-2H-pyran-3-ol (5.63 g, 43.3 mmol, 1.0 equiv.) in anhydrous methanol (100 mL) under argon. The atmosphere of the flask was then exchanged and the solution was saturated with H_2. Under a continuous feed of gas, the reaction mixture was stirred at room temperature for 20 h. Once complete, the mixture was filtered through a pad of celite and concentrated under reduced pressure to afford a colourless oil, which was used directly in the next reaction without further purification (5.61 g, 98 %). Spectroscopic data was consistent with the literature.[2]



δ_H (400 MHz; chloroform-d): 3.89 (C^1H, 1H, ddt, J_{HH} = 11.3, 3.6, 1.8 Hz), 3.80 (C^6H, 1H, dd, J_{HH} = 11.7, 3.8 Hz), 3.75 (C^6H, 1H, dd, J_{HH} = 11.7, 4.8 Hz), 3.52 (C^4H, 1H, ddd, J_{HH} = 11.0, 9.2, 4.7 Hz), 3.38-3.31 (C^1H, 1H, m), 3.10 (C^5H, 1H, dt, J_{HH} = 8.9, 4.3 Hz), 2.12-2.05 (C^3H, 1H, m), 1.73-1.57 (C^2H, 2H, m), 1.49-1.34 (C^3H, 1H, m) ppm; δ_C (101 MHz; chloroform-d): 82.0 (C^5), 67.8 (C^1), 67.3 (C^4), 63.2 (C^6), 32.5 (C^3), 25.5 (C^2) ppm.

NMR analysis of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol

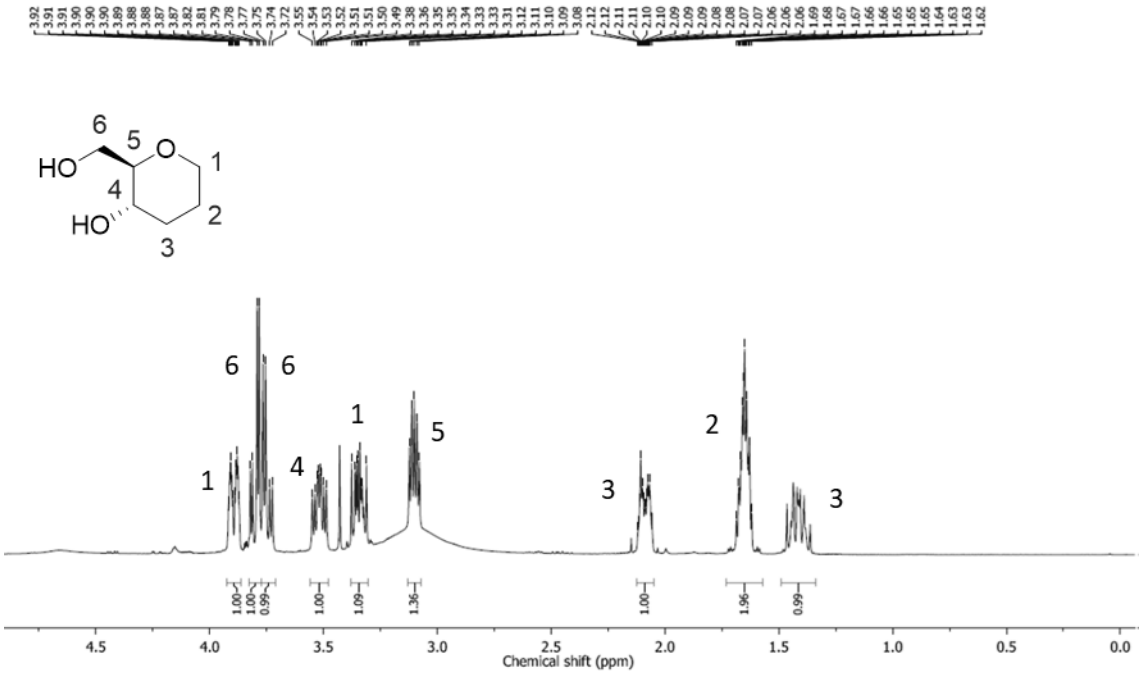


Fig. S1 Annotated ^1H NMR spectrum of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol in chloroform-d.

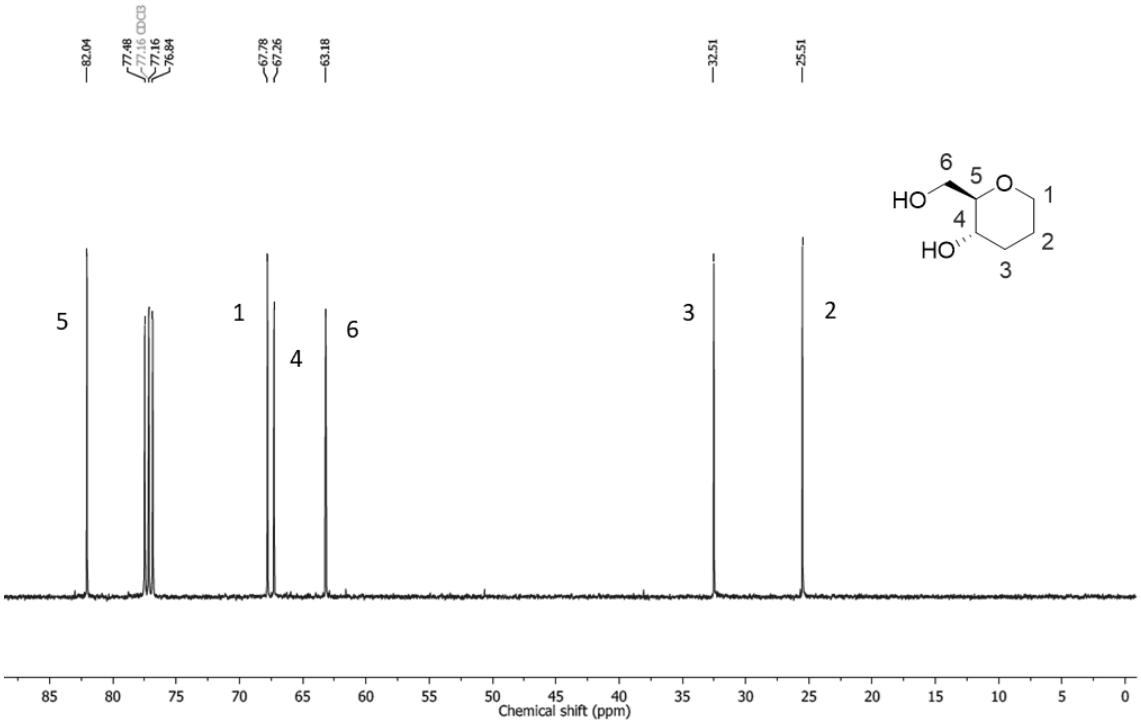


Fig. S2 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol in chloroform-d.

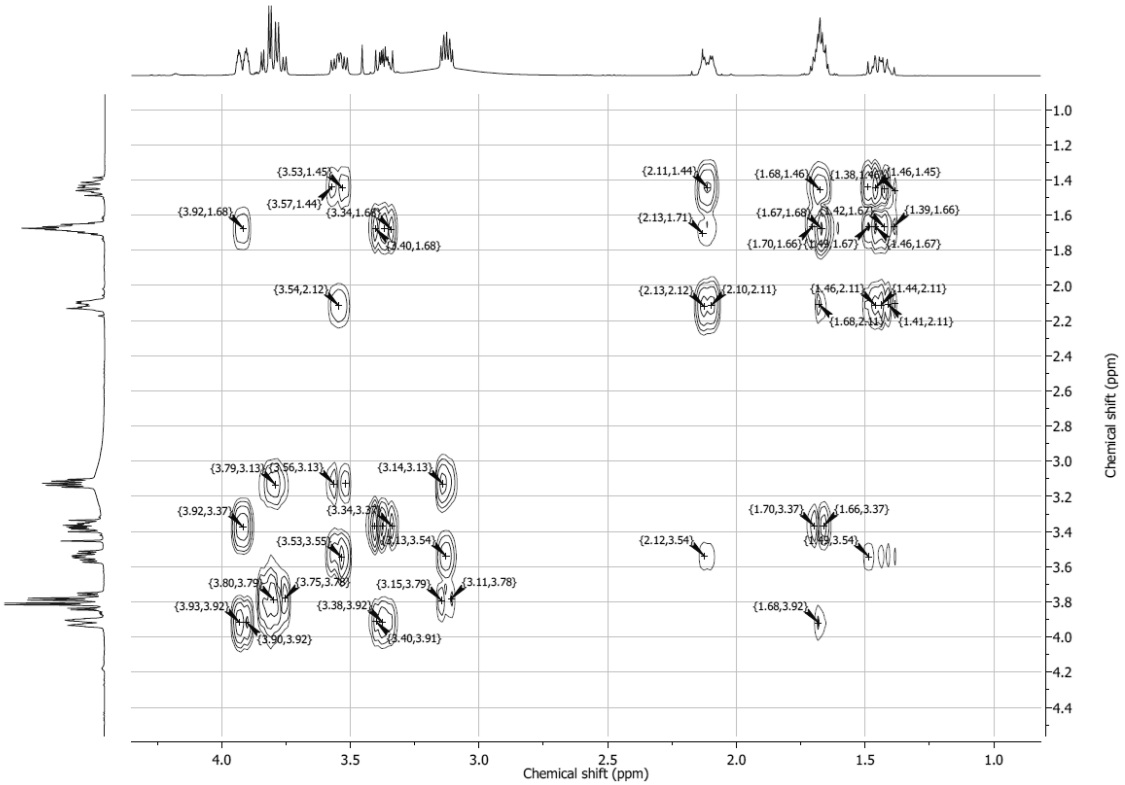


Fig. S3 COSY (^{1}H–^{1}H) NMR spectrum of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol in chloroform-d.

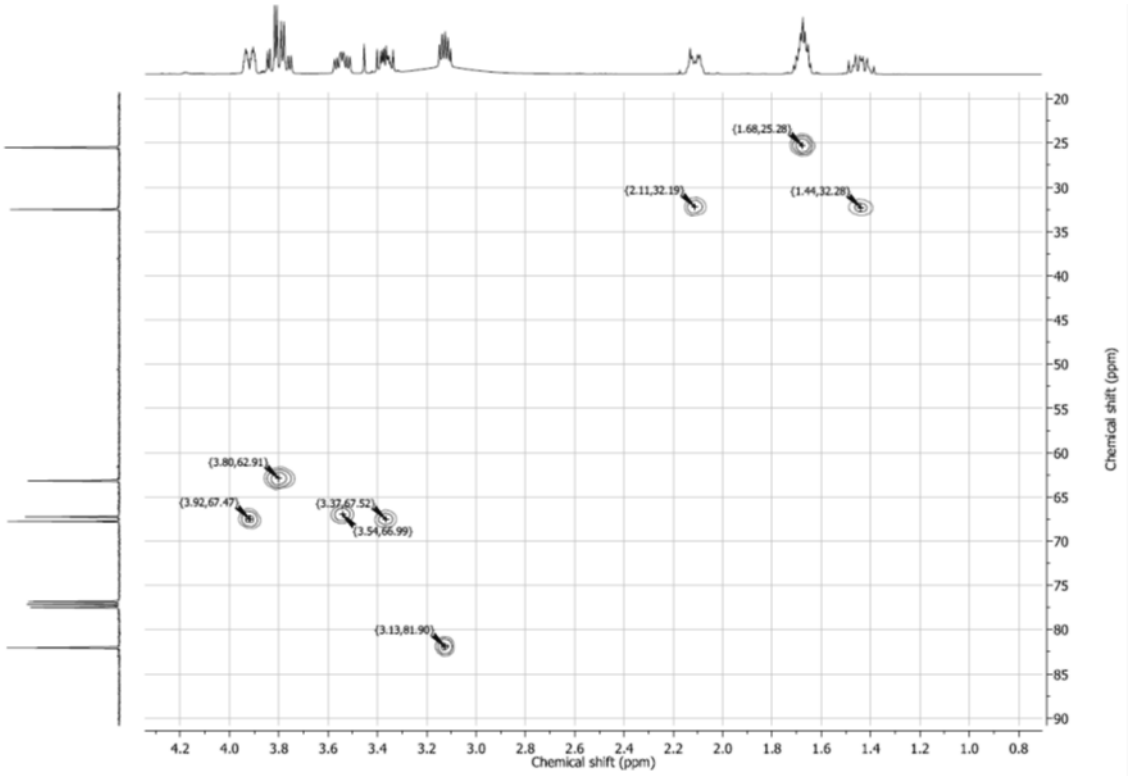
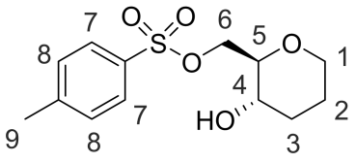


Fig. S4 HSQC (^{1}H–^{13}C) NMR spectrum of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol in chloroform-d.

Synthesis of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate

(2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol (5.28 g, 40.7 mmol, 1.0 equiv.) was dissolved in anhydrous pyridine (42.3 mL) and treated imminently with toluenesulfonyl chloride (7.74 g, 40.7 mmol, 1.0 equiv.) under argon. The reaction mixture was then stirred at room temperature for 20 h. Once complete, DCM (100 mL) and water (100 mL) were added to the reaction mixture. The organic phase was separated from the aqueous phase, dried with $MgSO_4$ and concentrated in *vacuo*. The crude was taken up in DCM (100 mL) and washed with $HCl_{(aq)}$ (ca. 3%, 2 x 25 mL), $NaHCO_3$ (1 mol dm^{-3}, 50 mL) and water (50 mL), dried over $MgSO_4$ and concentrated in *vacuo* to yield an off-white solid, which was used directly in the next reaction without further purification (8.21 g, 70 %).



δ_H (400 MHz; chloroform-d): 7.80 (C^7H, 2H, d, J_{HH} = 8.3 Hz), 7.34 (C^8H, 2H, d, J_{HH} = 7.9 Hz), 4.34 (C^6H, 1H, dd, J_{HH} = 11.0, 4.5 Hz), 4.20 (C^6H, 1H, dd, J_{HH} = 11.0, 2.4 Hz), 3.91-3.85 (C^1H, 1H, m), 3.56 (C^4H, 1H, ddd, J_{HH} = 14.4, 10.7, 5.1 Hz), 3.33-3.25 (C^1H, 1H, m), 3.23-3.18 (C^5H, 1H, m), 2.44 (C^9H, 3H, s), 2.16-2.09 (C^3H, 1H, m), 1.71-1.61 (C^2H, 1H, m), 1.48-1.36 (C^3H, 1H, m) ppm; δ_C (101 MHz; chloroform-d): 145.1 (C^{10}), 133.0 (C^7), 130.0 (C^9), 128.1 (C^8), 80.3 (C^5), 69.9 (C^6), 68.0 (C^1), 66.0 (C^4), 32.5 (C^2), 25.3 (C^3), 21.8 (C^{11}) ppm.

NMR analysis of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate

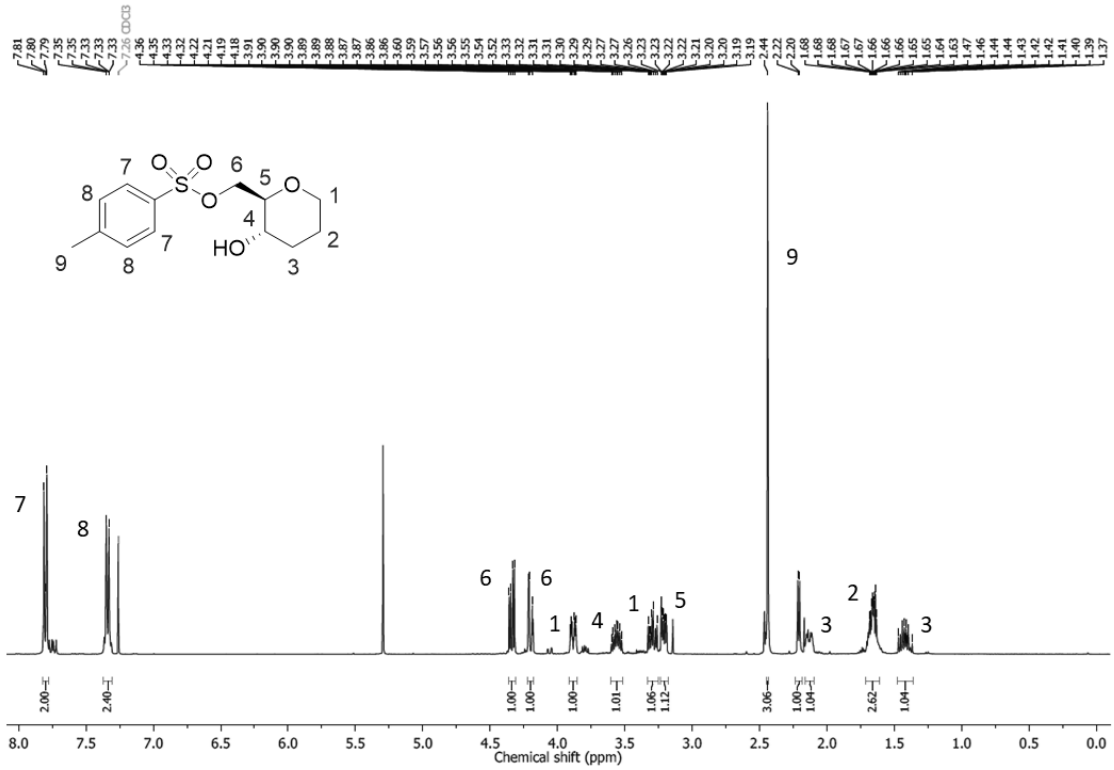


Fig. S5 Annotated ^{1}H NMR spectrum of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate in chloroform-d.

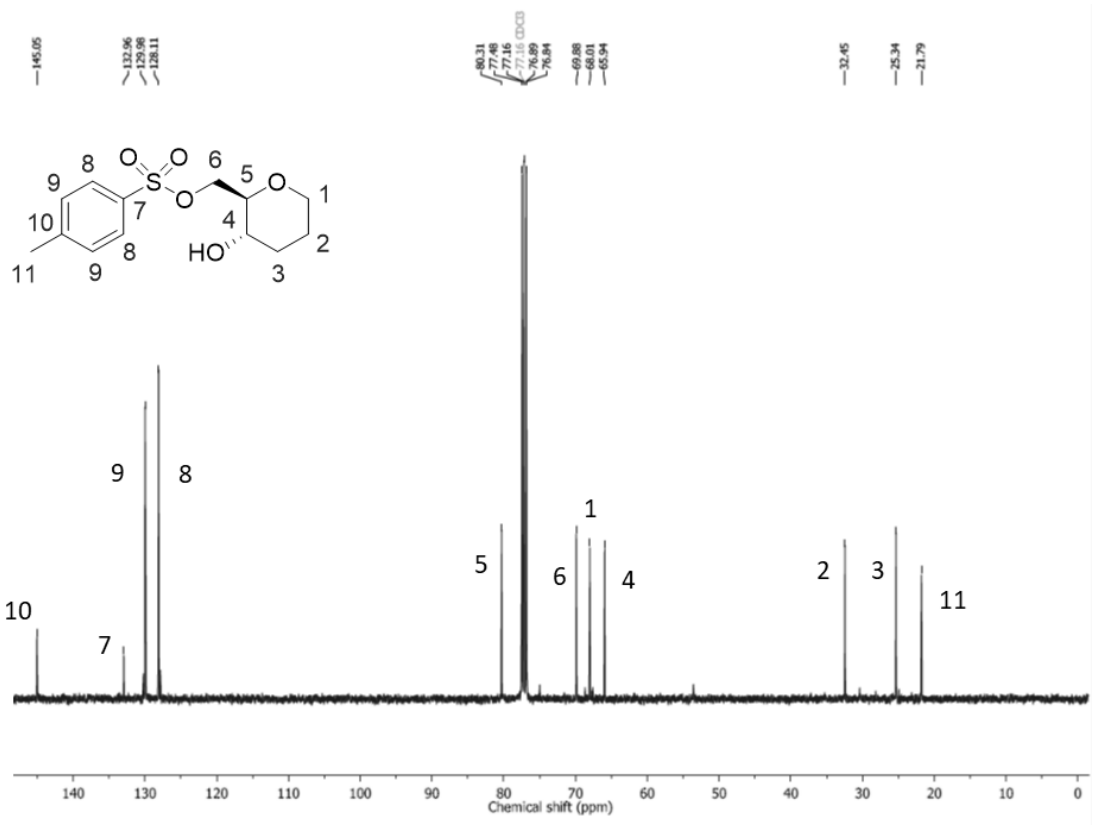


Fig. S6 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate in chloroform-d.

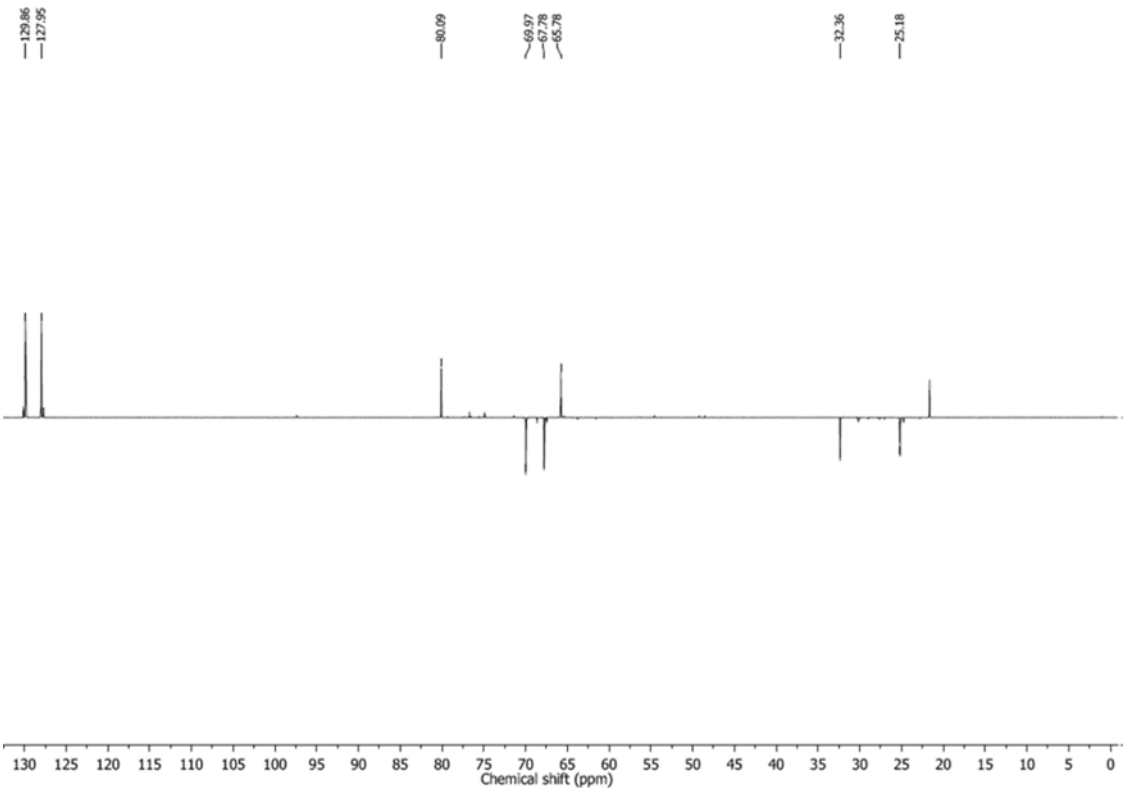


Fig. S7 $^{13}C\{^{1}H\}$ DEPT135 NMR spectrum of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate in chloroform-d.

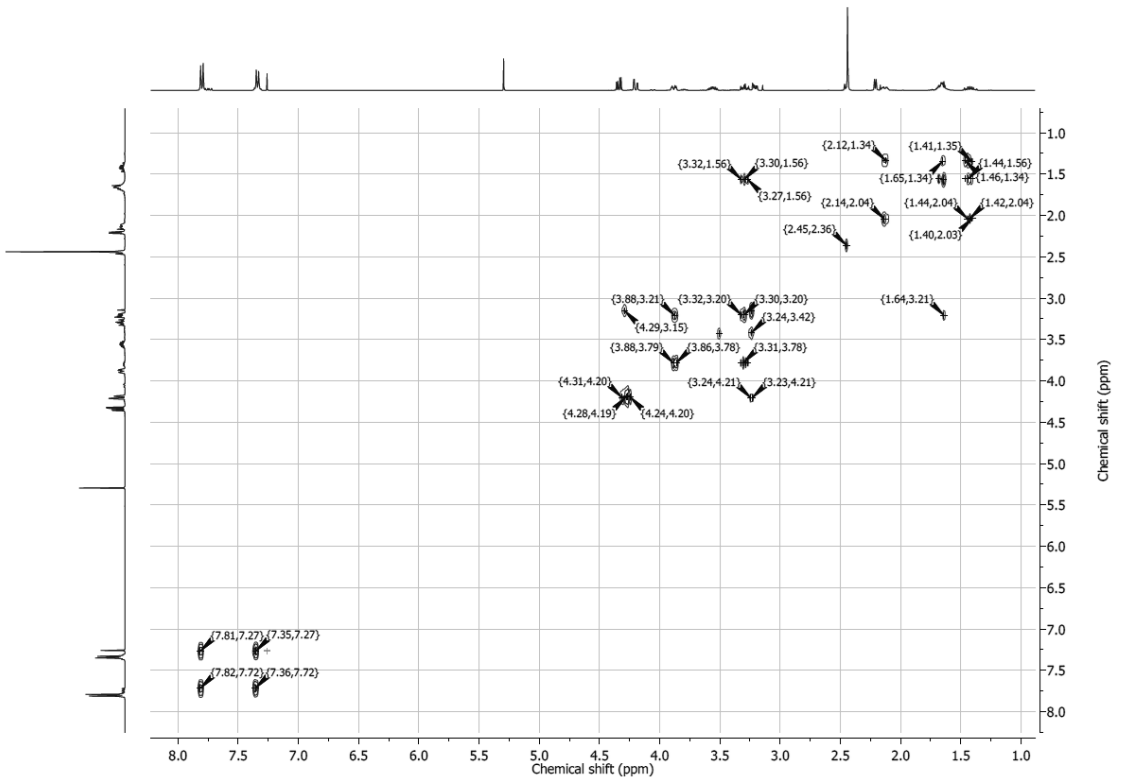


Fig. S8 COSY (^{1}H–^{1}H) NMR spectrum of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate in chloroform-d.

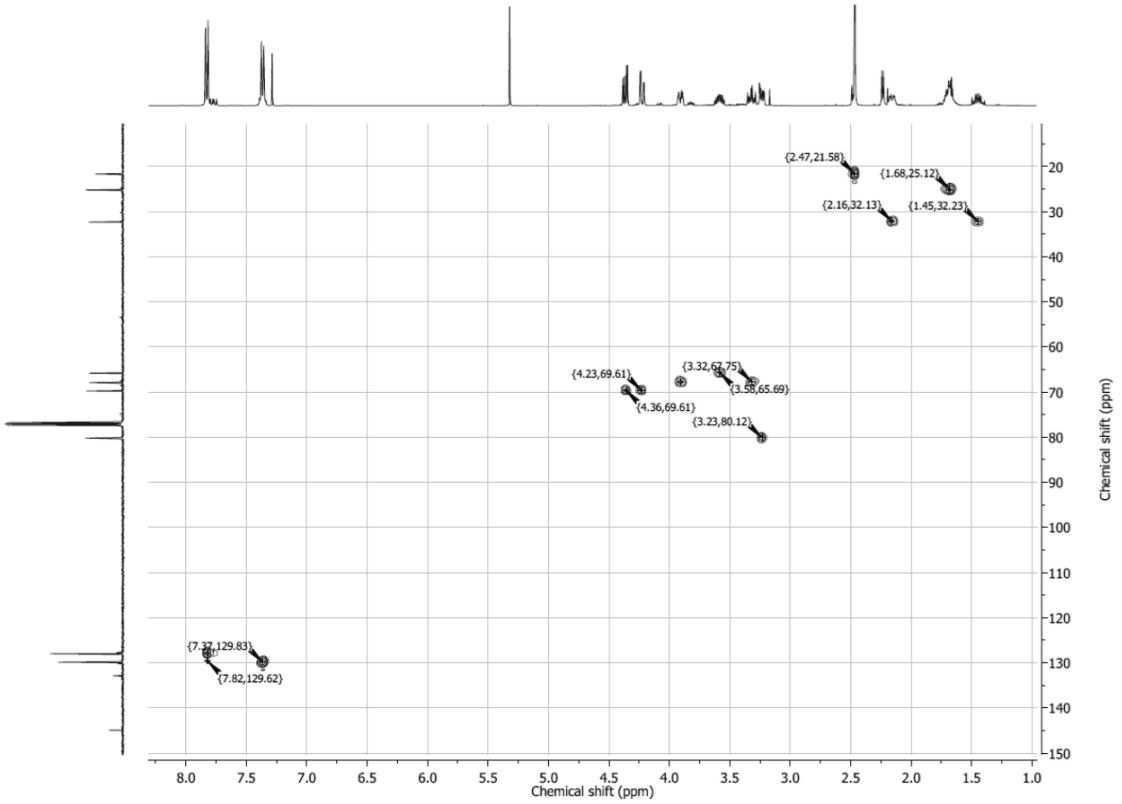
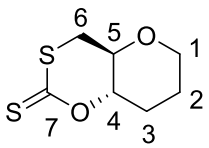


Fig. S9 HSQC (^{1}H–^{13}C) NMR spectrum of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate in chloroform-d.

Synthesis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiine-2-thione (2)

A 0.5 mol L^{-1} solution of ((2R,3S)-3-hydroxytetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate (10.2 g, 35.3 mmol, 1.0 equiv.) in dry THF (70.7 mL) was treated dropwise with a solution of 1 mol L^{-1} potassium tert-butoxide (35.3 mL, 35.3 mmol, 1.0 equiv.) in anhydrous THF at 0 °C under argon. Carbon disulphide (4.27 mL, 70.7 mmol, 2.0 equiv.) was then added dropwise to the reaction mixture and stirred at 0 °C for 3 h. Once complete, Et_2O (100 mL) was added and the reaction mixture was filtered through a celite pad and concentrated in *vacuo* to yield a murky yellow precipitate. The crude product was purified *via* flash column chromatography on SiO_2 using a DCM mobile phase, the filtrate was concentrated in *vacuo* to yield small yellow crystals (5.24 g, 78 %). The product was purified further by recrystallization using absolute ethanol, and isolated *via* filtration as pale-yellow crystals.



δ_H (400 MHz; chloroform-d): 4.21-4.11 (C^4H, 2H, m), 4.01-3.95 (C^1H, 1H, m), 3.69 (C^5H, 1H, ddd, J_{HH} = 10.0, 9.2, 5.7 Hz), 3.51-3.43 (C^1H, 1H, m), 3.08 (C^6H, 1H, dd, J_{HH} = 11.3, 10.0 Hz), 3.02 (C^6H, 1H, dd, J_{HH} = 11.3, 5.7 Hz), 2.45-2.37 (C^3H, 1H, m), 1.86-1.73 (C^2H, C^3H, 3H, m) ppm; δ_C (101 MHz; chloroform-d): 207.5 (C^7), 81.0 (C^4), 71.0 (C^5), 68.0 (C^1), 34.4 (C^6), 29.0 (C^3), 24.9 (C^2) ppm. ν_{max} (cm^{-1}): 2962-2947 (CH), 1250-1173 (C(S)SO), 1050 (C–S).

NMR analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiine-2-thione (2)

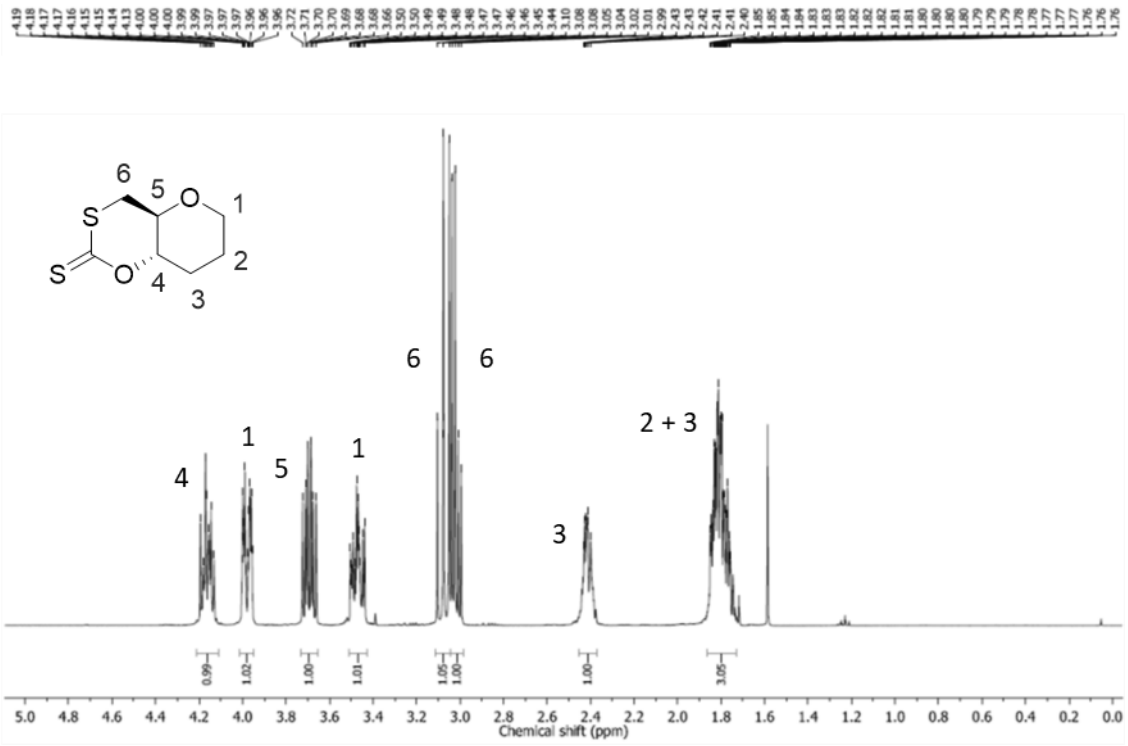


Fig. S10 Annotated ^{1}H NMR spectrum of **2** in chloroform-d.

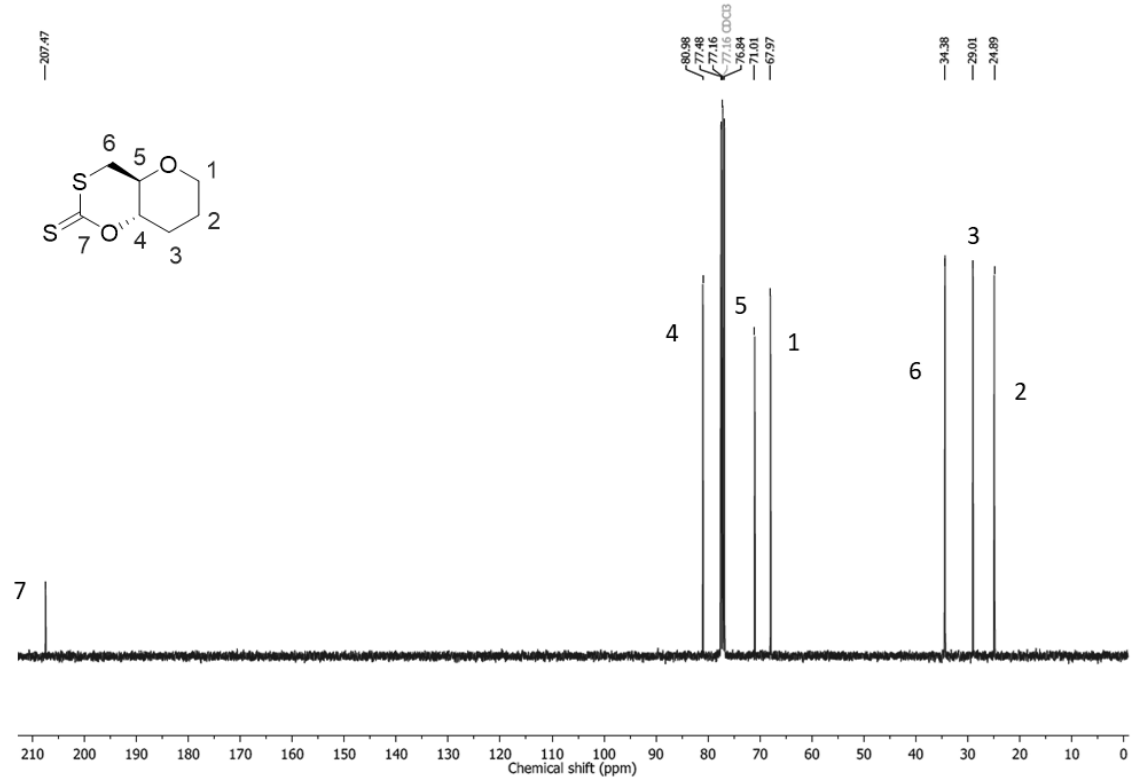


Fig. S11 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of **2** in chloroform-d.

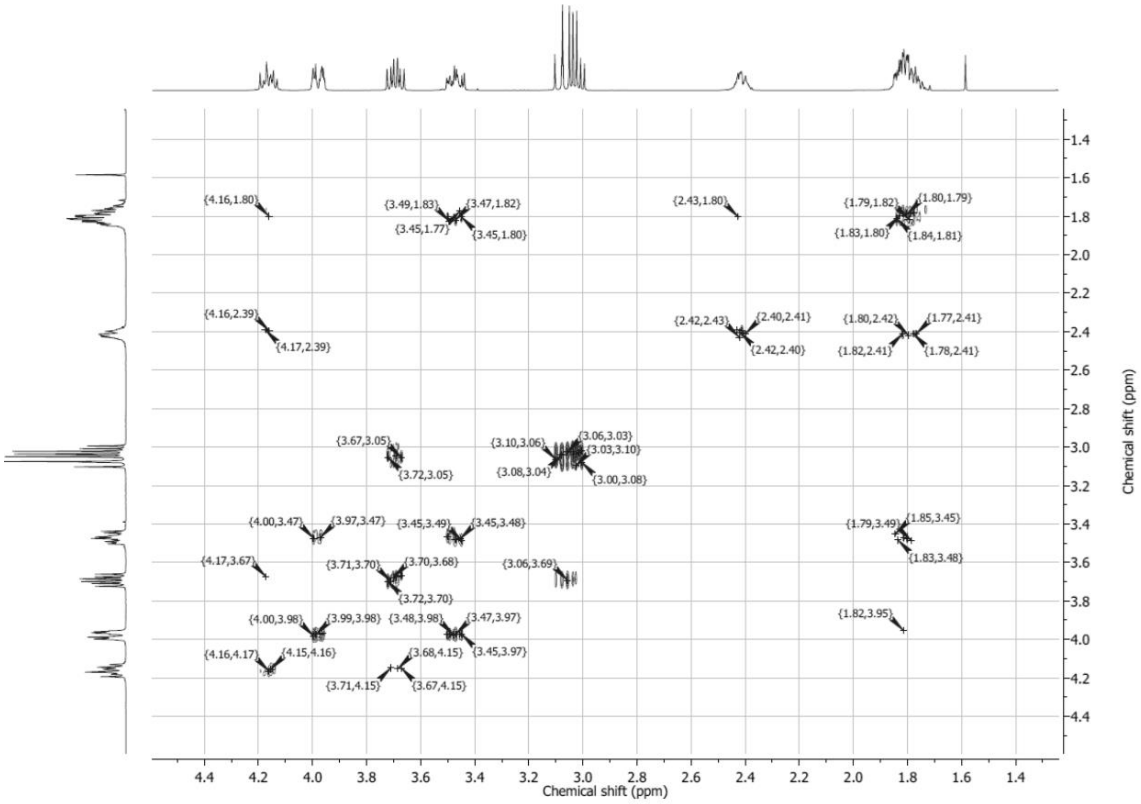


Fig. S12 COSY (^{1}H–^{1}H) NMR spectrum of **2** in chloroform-d.

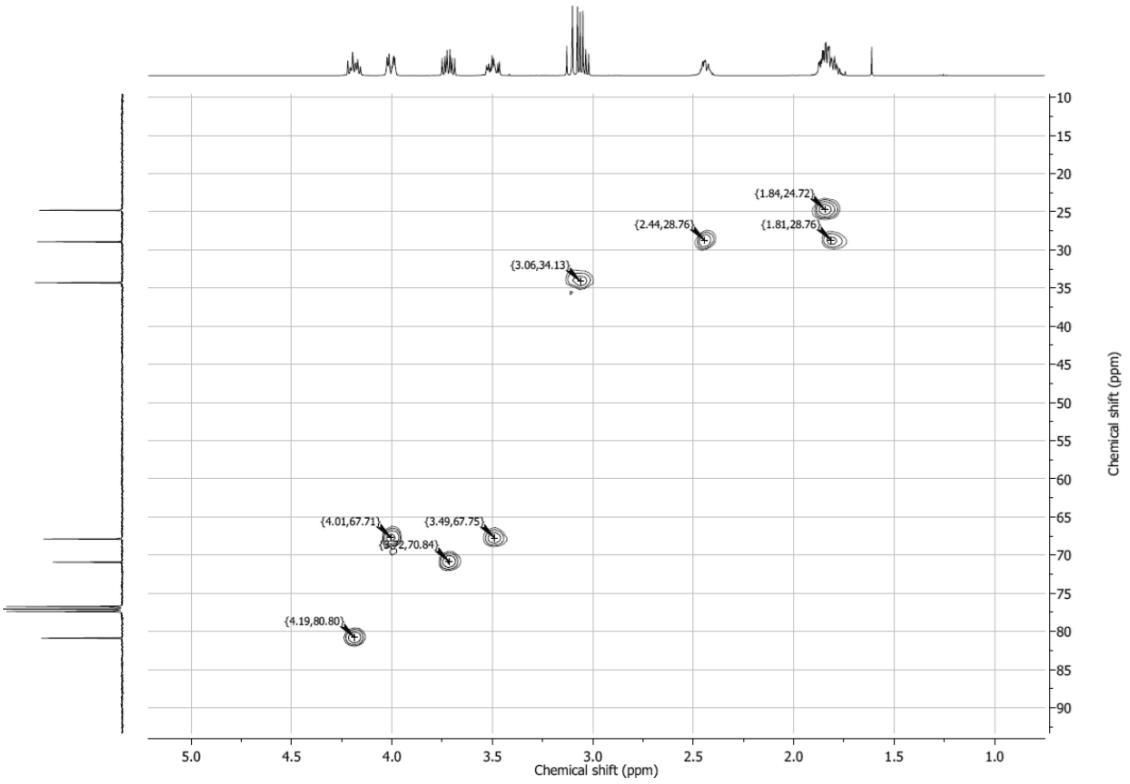


Fig. S13 HSQC (^{1}H–^{13}C) NMR spectrum of **2** in chloroform-d.

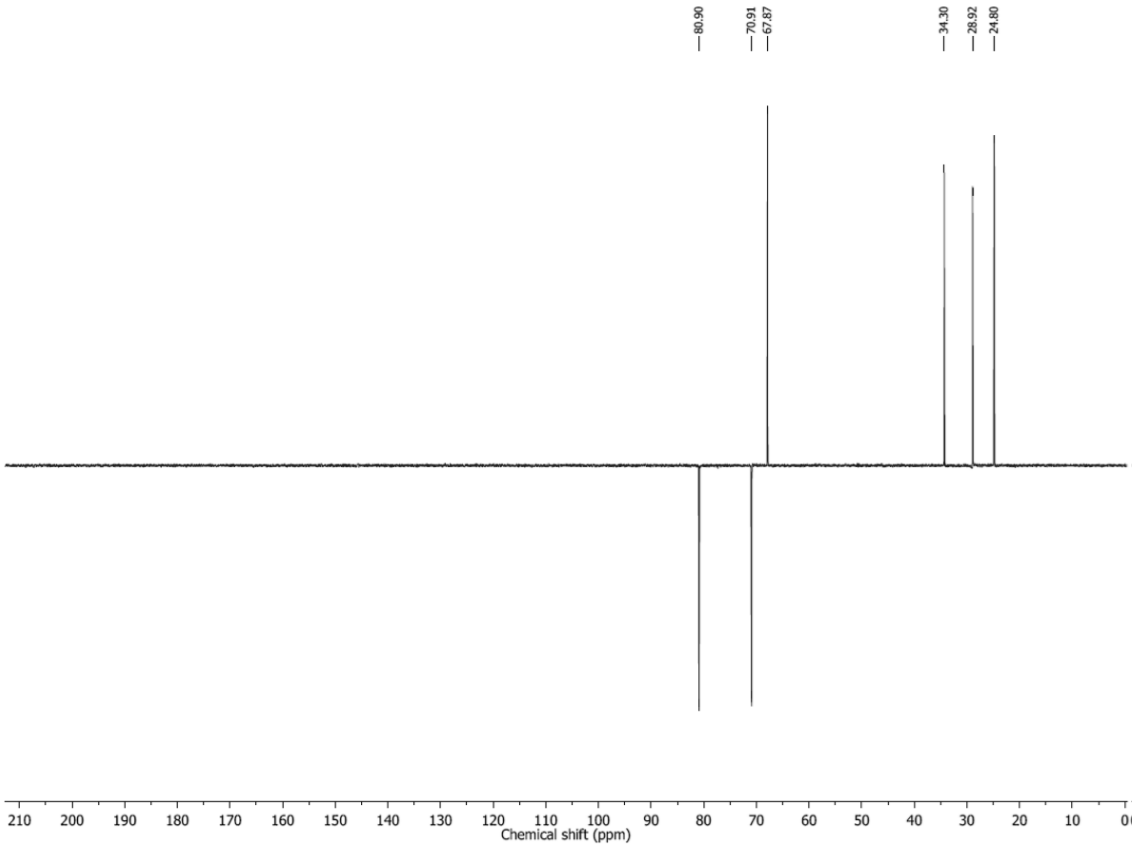


Fig. S14 $^{13}C\{^{1}H\}$ DEPT135 NMR spectrum of **2** in chloroform-d.

DSC analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiine-2-thione (2)

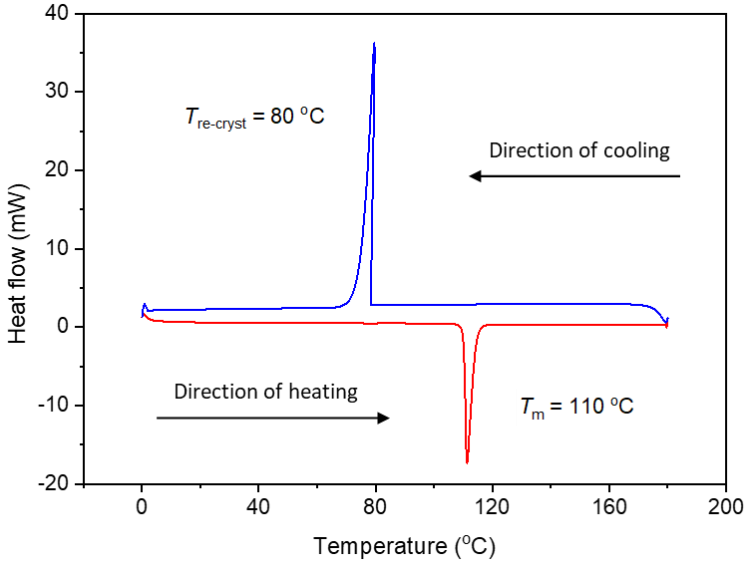


Fig. S15 DSC trace of the monomer **2**, first heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the melting temperature (T_m) ≈ 110 °C of the monomer. Single endothermic peak, corresponding to the recrystallisation temperature ($T_{recryst}$) ≈ 80 °C of the monomer.

TGA analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiine-2-thione (2)

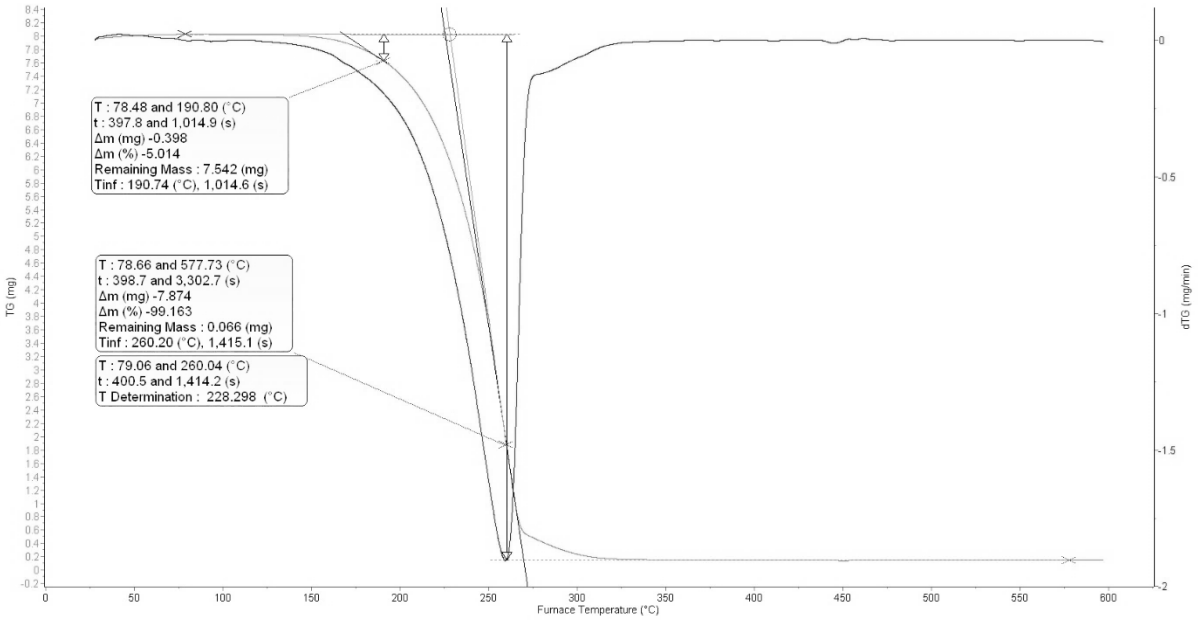


Fig. S16 TGA trace of the monomer **2**. The monomer was heated from 0 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 191 °C; $T_{d,max}$ = 260 °C with 1 % char remaining at 600 °C.

FT-IR analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiine-2-thione (2)

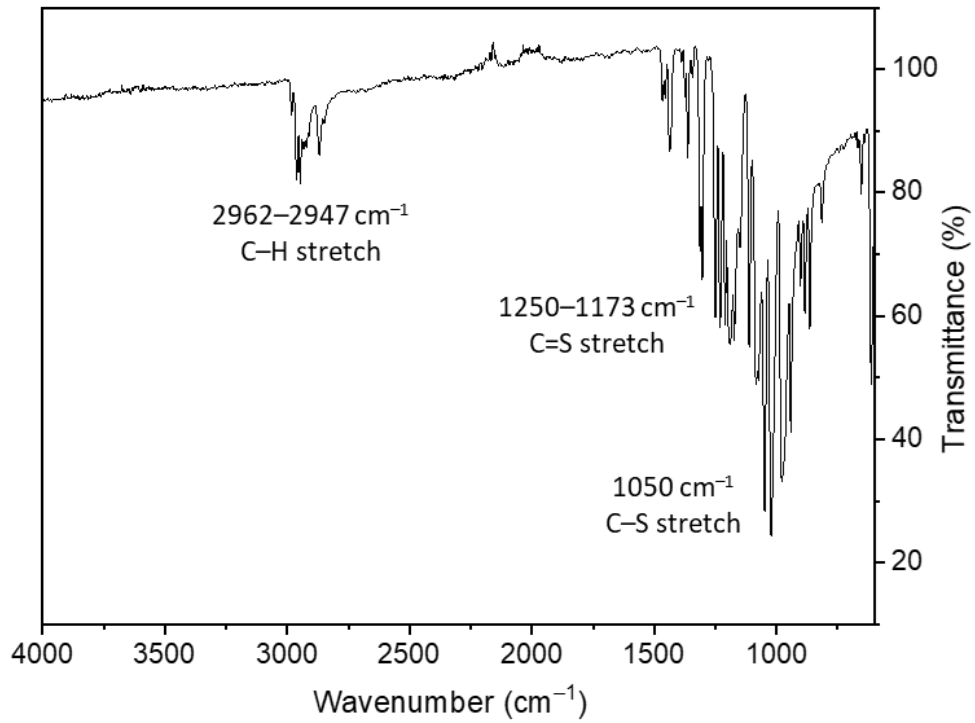


Fig. S17 Labelled FT-IR spectrum of **2**.

Crystal Diffraction Data and Structure Refinement for 2 (CCDC Number – 2095960)

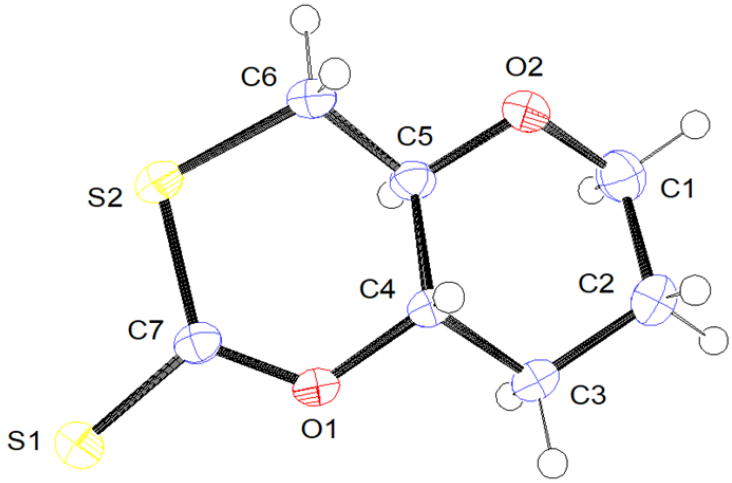


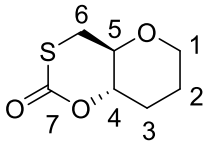
Fig. S18 ORTEP drawing of the crystal structure of **2** with thermal ellipsoids at the 50% probability level. Selected bond lengths and dihedral angles (°): S(1)–C(7) 1.655 (2), S(2)–C(7) 1.726 (2), S(2)–C(6) 1.810 (2), O(1)–C(7) 1.324 (2), O(2)–C(1) 1.464 (2), C(2)–C(3) 1.509 (3), C(7)–S(2)–C(6) 105.34 (9), C(7)–O(1)–C(4) 123.46 (16), O(1)–C(7)–S(1) 118.56 (15), O(1)–C(7)–S(2) 123.92 (15), S(1)–C(7)–S(2) 117.49 (12), C(5)–C(6)–S(2) 110.44 (16).

Identification code	s21ab1	
Empirical formula	C7 H10 O2 S2	
Formula weight	190.27	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.33251(11) Å	α = 90°.
	b = 7.69444(17) Å	β = 96.8866(17)°.
	c = 8.95591(16) Å	γ = 90°.
Volume	433.229(15) $Å^3$	
Z	2	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	5.163 mm^{-1}	
F(000)	200	
Crystal size	0.503 x 0.394 x 0.107 mm^3	
Theta range for data collection	4.974 to 73.426°.	
Index ranges	-7<=h<=7, -9<=k<=7, -11<=l<=11	
Reflections collected	6162	
Independent reflections	1504 [R(int) = 0.0243]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.136	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1504 / 1 / 100
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0281, wR2 = 0.0738
R indices (all data)	R1 = 0.0281, wR2 = 0.0738
Absolute structure parameter	0.014(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.353 and -0.330 e.$Å^{-3}$

Synthesis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiin-2-one (3)

A stream of ozone diluted in oxygen was bubbled through a 0.1 mol L^{-1} solution of **2** (1.0 g, 5.74 mmol, 1.0 equiv.) in dry DCM (57.4 mL) at -78 °C for several minutes. The solution turned a blue after several minutes, due to ozone saturation. The ozone generator was turned off and oxygen was allowed to pass through the solution for a few minutes to flush out any remaining ozone. Once complete, the solvent was removed from the reaction mixture in *vacuo* to yield an off-white solid. The crude product was purified *via* column chromatography on SiO_2 using a hexane:EtOAc (4:1) mobile phase, all fractions containing the product were combined and concentrated in *vacuo* to yield a fluffy white powder (0.66 g, 72 %).



δ_H (500 MHz; chloroform-d): 4.13 (C^4H, 1H, ddd, J_{HH} = 10.5, 9.2, 5.0 Hz), 3.98-3.93 (C^1H, 1H, m), 3.60 (C^5H, 1H, ddd, J_{HH} = 9.7, 9.7, 5.6 Hz), 3.44 (C^1H, 1H, ddd, J_{HH} = 11.3, 11.3, 3.4 Hz), 3.15-3.03 (C^6H, 2H, m), 2.29-2.23 (C^2H, 1H, m), 1.81-1.62 (C^2H, C^3H, 3H, m) ppm; δ_C (126 MHz; chloroform-d): 165.7 (C^7), 79.3 (C^4), 72.8 (C^5), 69.0 (C^1), 32.1 (C^6), 30.4 (C^3), 25.6 (C^2) ppm. ν_{max} (cm^{-1}): 2954-2868 (CH), 1671 (C(O)SO), 1149-1017 (C–O), 1149-1017 (C–S).

NMR analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiin-2-one (3)

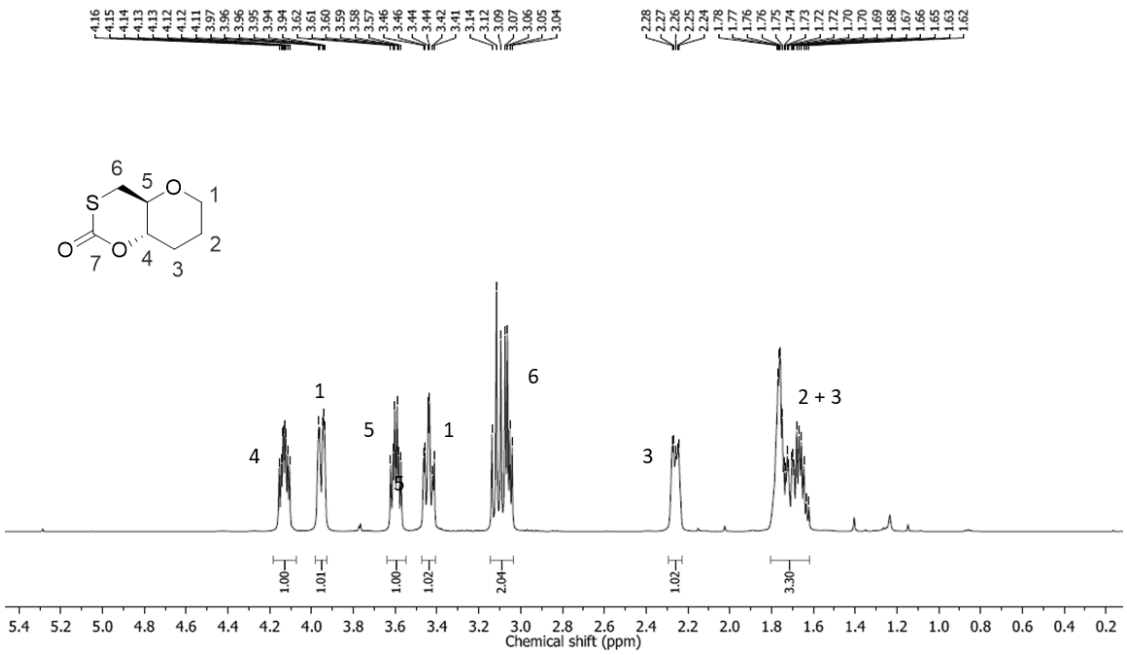


Fig. S19 Annotated ^1H NMR spectrum of **3** in chloroform-d.

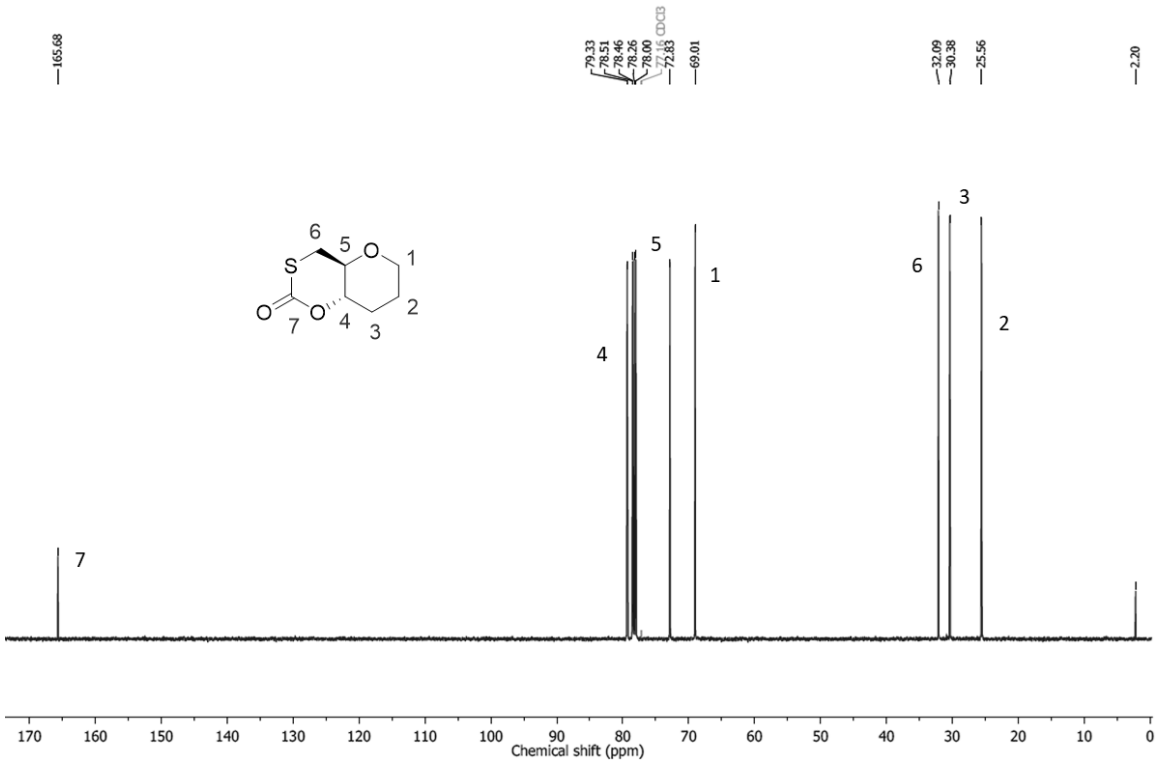


Fig. S20 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of **3** in chloroform-d.

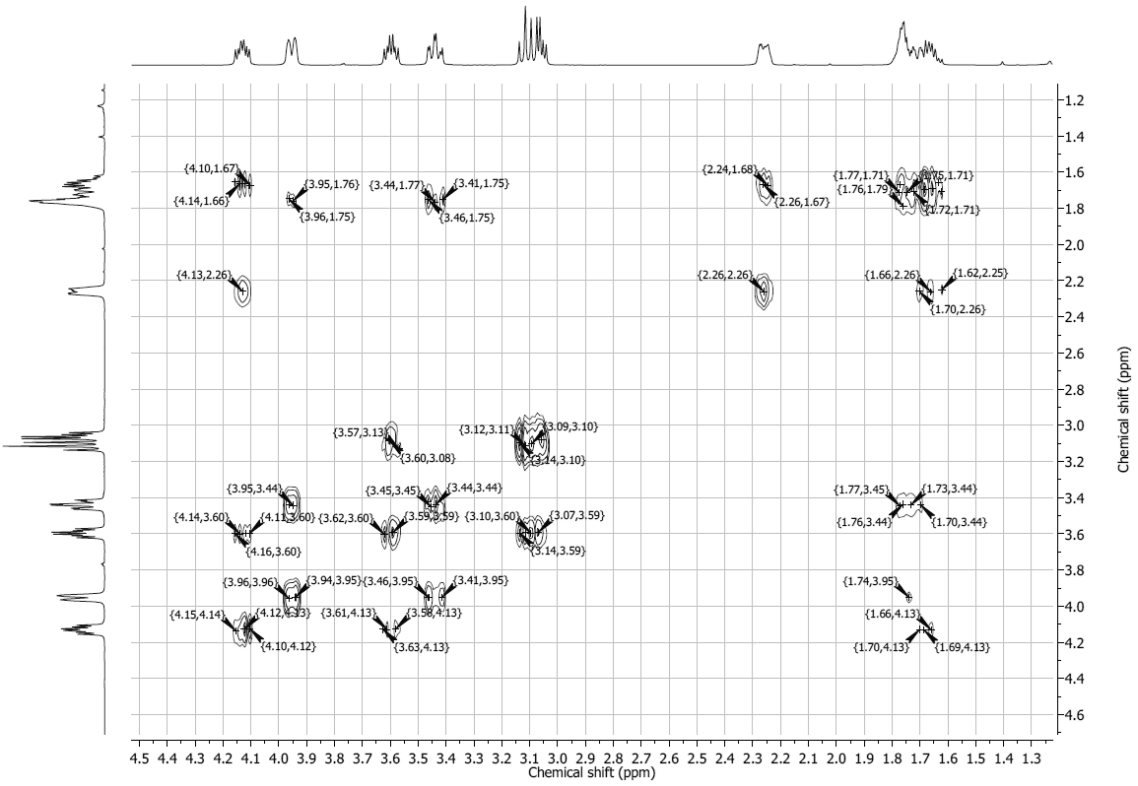


Fig. S21 COSY (^{1}H–^{1}H) NMR spectrum of **3** in chloroform-d.

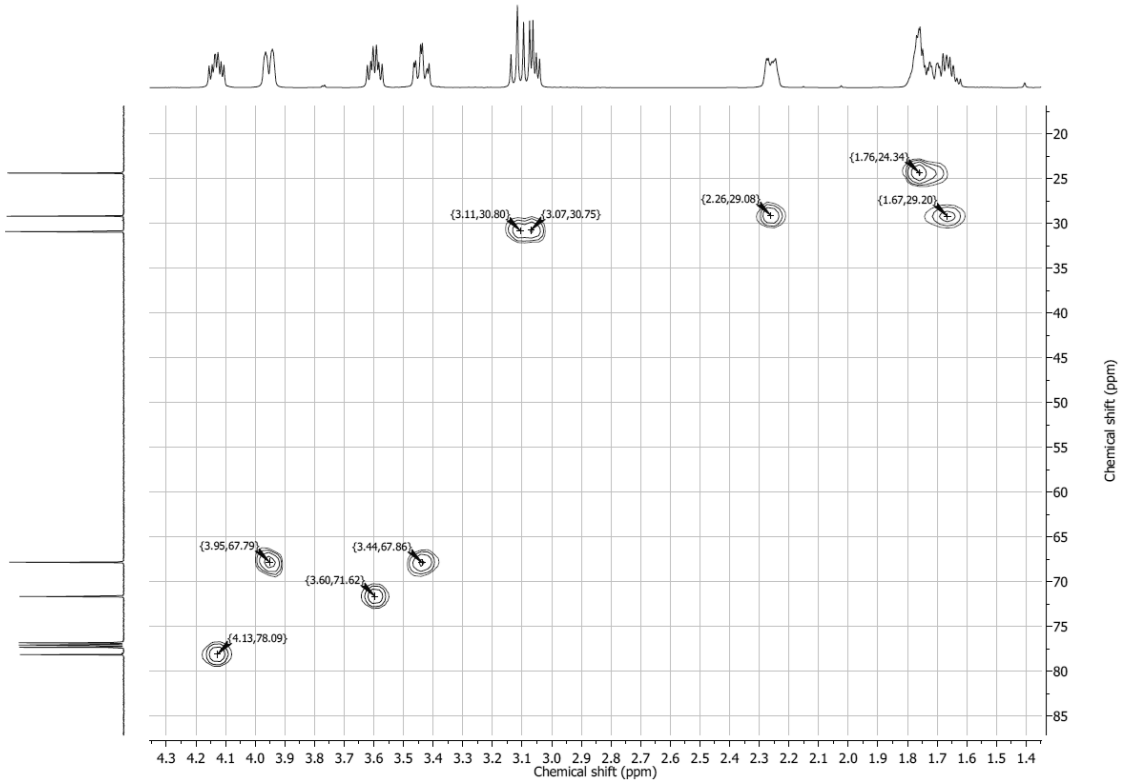


Fig. S22 HSQC (^{1}H–^{13}C) NMR spectrum of **3** in chloroform-d.

DSC analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiin-2-one (3)

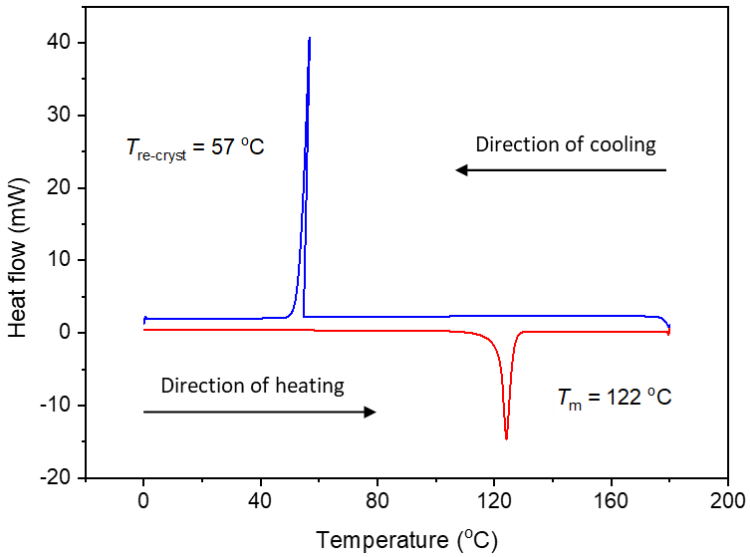


Fig. S23 DSC trace of the monomer **3**, first heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the melting temperature (T_m) ≈ 122 °C of the monomer. Single endothermic peak, corresponding to the recrystallisation temperature ($T_{recryst}$) ≈ 57 °C of the monomer.

TGA analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiin-2-one (3)

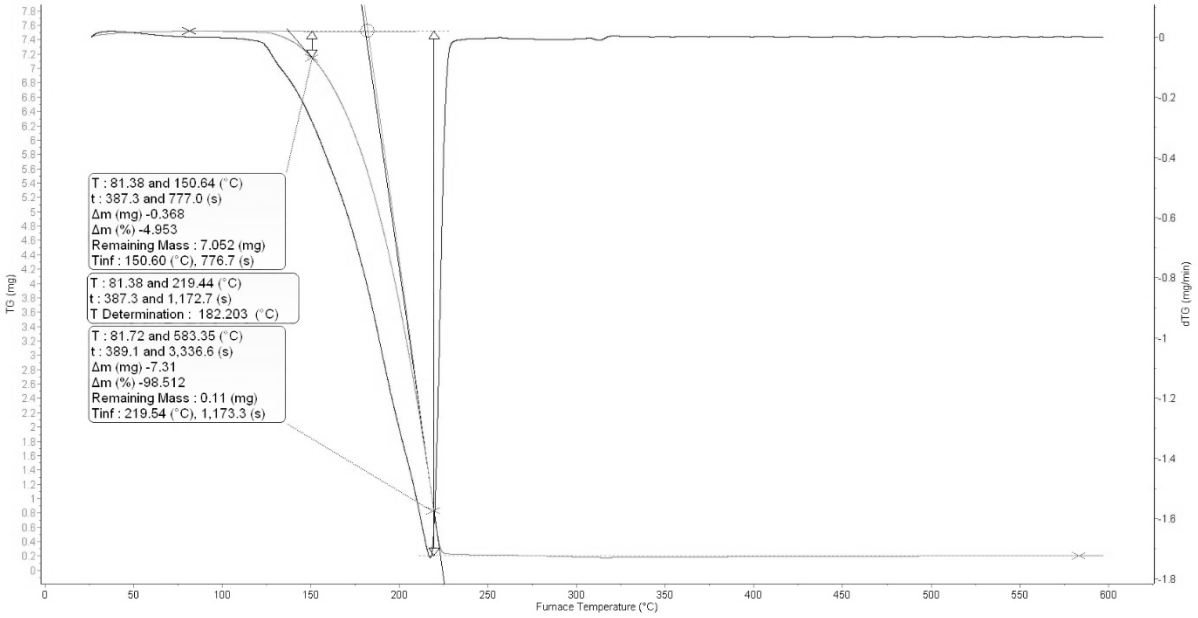


Fig. S24 TGA trace of the monomer **3**. The monomer was heated from 0 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 150 °C; $T_{d,max}$ = 219 °C with 1 % char remaining at 600 °C.

FT-IR analysis of (4aS,8aS)-hexahydropyrano[2,3-e][1,3]oxathiin-2-one (3)

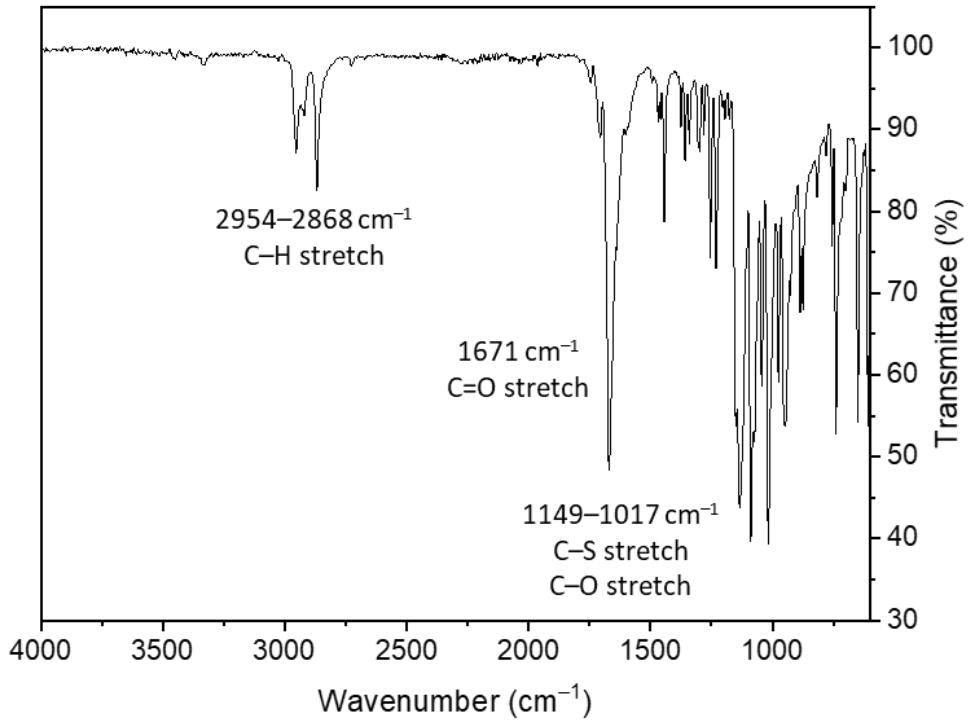


Fig. S25 Labelled FT-IR spectrum of **3**.

Crystal Diffraction Data and Structure Refinement for 3 (CCDC Number – 2177255)

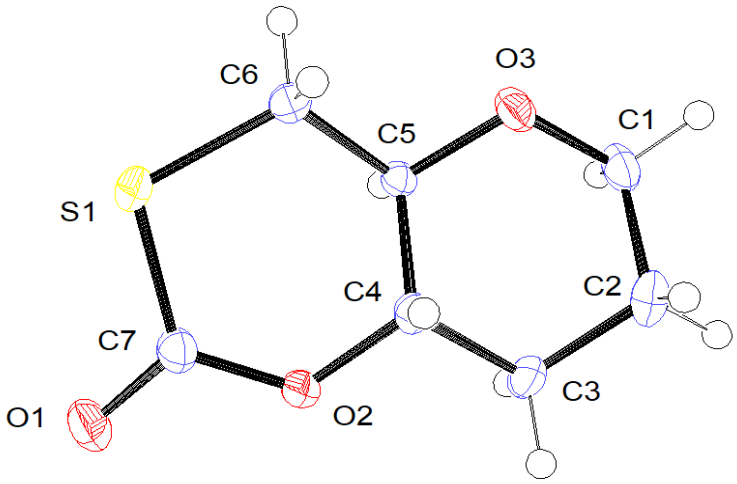


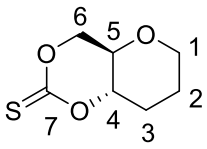
Fig. S26 ORTEP drawing of the crystal structure of **3** with thermal ellipsoids at the 50% probability level. Selected bond lengths and dihedral angles (°): S–C(7) 1.761 (16), S–C(6) 1.812 (16), O(1)–C(7) 1.207 (19), O(2)–C(7) 1.335 (18), O(2)–C(4) 1.452 (18), C(6)–C(5) 1.513 (19), C(7)–S–C(6) 105.90 (7), C(7)–O(2)–C(5) 122.40 (11), O(1)–C(7)–S 119.53 (14), O(1)–C(7)–O(2) 119.53 (14), O(1)–C(7)–S 117.93 (17), O(2)–C(7)–S 122.46 (11).

Identification code	e22ab1	
Empirical formula	C7 H10 O3 S	
Formula weight	174.21	
Temperature	149.9(6) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.0382(2) Å	α = 90°.
	b = 6.9857(2) Å	β = 90°.
	c = 18.8158(6) Å	γ = 90°.
Volume	793.67(4) $Å^3$	
Z	4	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.361 mm^{-1}	
F(000)	368	
Crystal size	0.696 x 0.550 x 0.448 mm^3	
Theta range for data collection	3.111 to 30.232°.	
Index ranges	-7<=h<=8, -9<=k<=9, -24<=l<=25	
Reflections collected	13165	
Independent reflections	2192 [R(int) = 0.0200]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92518	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2192 / 0 / 100
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0643
R indices (all data)	R1 = 0.0248, wR2 = 0.0648
Absolute structure parameter	0.041(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.212 and -0.232 e.$Å^{-3}$

Synthesis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxine-2-thione (4)

An excess of 1,1′-thiocarbonyldiimidazole (TCDI) (1.48 g, 8.32 mmol, 1.1 equiv.) was added gradually, over the course of 1 h, to a solution of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol (1.0 g, 7.57 mmol, 1.0 equiv.) in dry DCM (30 mL) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for a further 1.5 h. The reaction progress was monitored by thin layer chromatography using an EtOAc (100 %) mobile phase. After completion, the reaction mixture was immediately washed with $HCl_{(aq)}$ (ca. 3%, 30 mL) and $NaHCO_3$ (1 mol L^{-1}, 30 mL), dried over $MgSO_4$ and concentrated in *vacuo* to yield a white powder (0.90 g, 68 %). The product was purified further by recrystallization using absolute ethanol, and isolated *via* filtration as white crystals.



δ_H (500 MHz; chloroform-d): 4.51 (C^6H, 1H, dd, J_{HH} = 10.5, 6.0 Hz), 4.15 (C^6H, 1H, t, J_{HH} = 10.4 Hz), 4.08 (C^4H, 1H, ddd, J_{HH} = 11.2, 9.5, 4.7 Hz), 3.98-3.90 (C^1H, 1H, m), 3.60 (C^5H, 1H, ddd, J_{HH} = 9.9, 9.8, 6.0 Hz), 3.47 (C^1H, 1H, ddd, J_{HH} = 11.5, 11.5, 3.4 Hz), 2.33-2.26 (C^3H, 1H, m), 1.84-1.72 (C^2H, 2H, m), 1.72-1.62 (C^3H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 189.2 (C^7), 77.6 (C^4), 71.7 (C^6), 69.6 (C^5), 67.9 (C^6), 27.5 (C^3), 24.5 (C^2) ppm. ν_{max} (cm^{-1}): 2955-2875 (CH), 1256-1188 ($C(S)O_2$), 1016 (C–O).

NMR analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxine-2-thione (4)

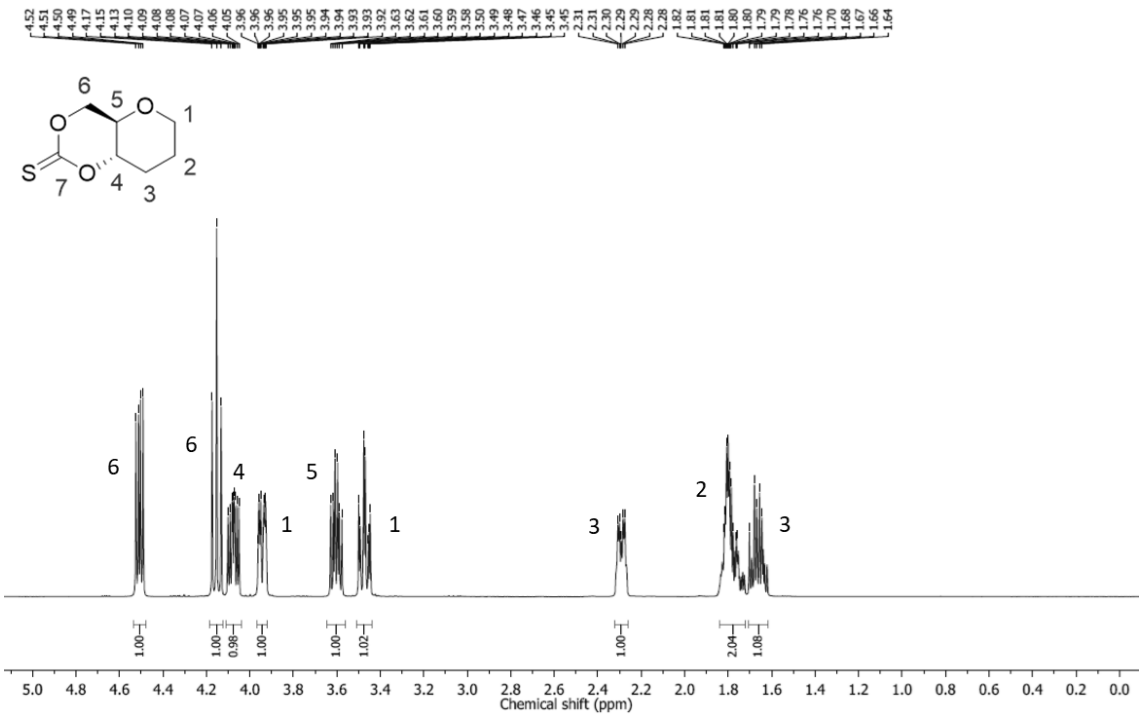


Fig. S27 Annotated ^1H NMR spectrum of **4** in chloroform-d.

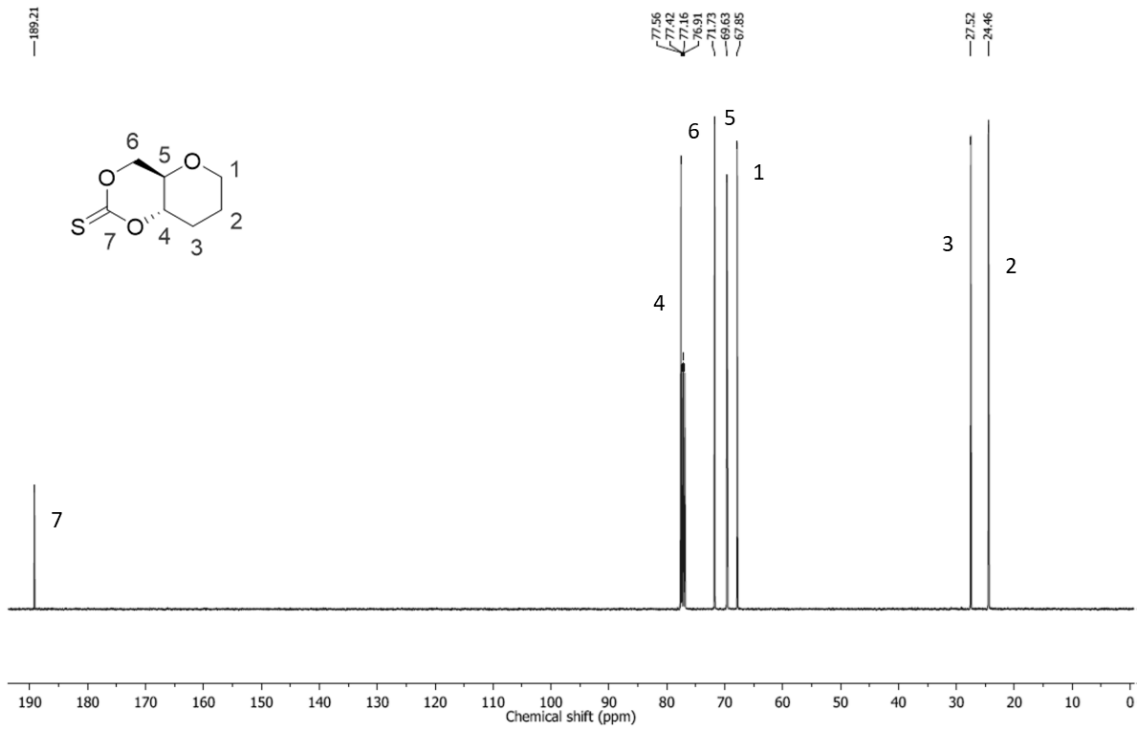


Fig. S28 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of **4** in chloroform-d.

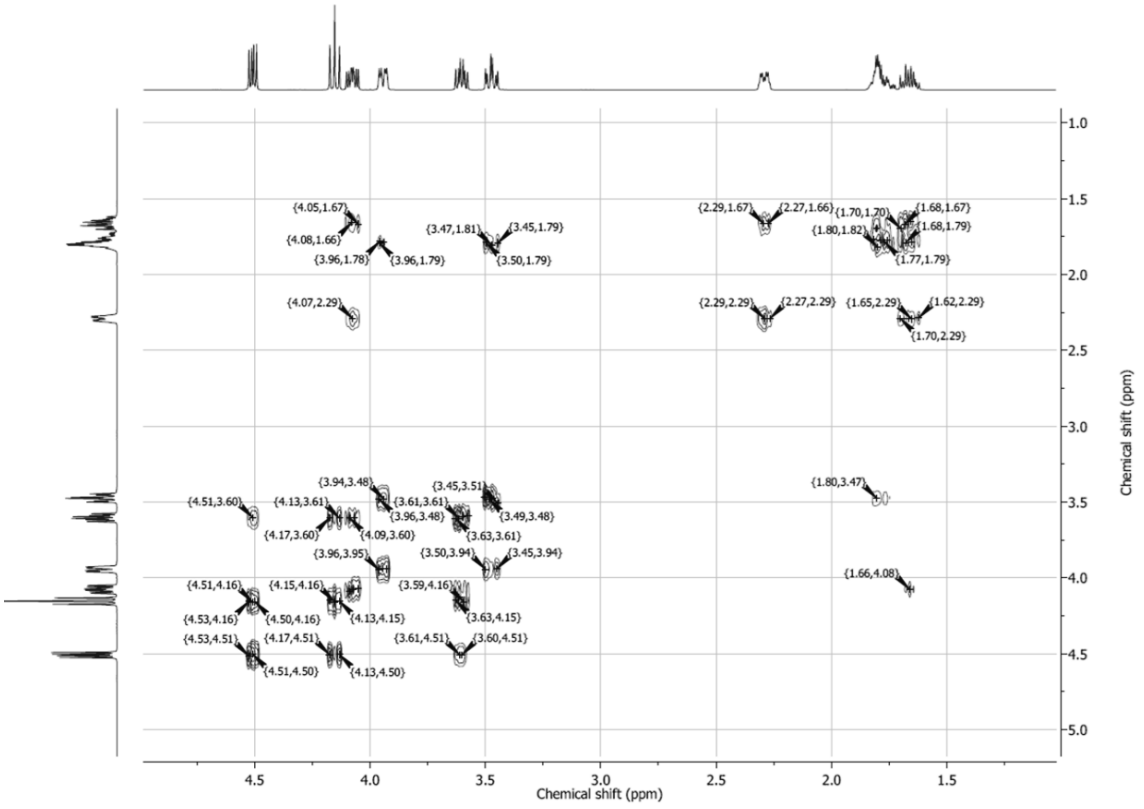


Fig. S29 COSY (^{1}H–^{1}H) NMR spectrum of **4** in chloroform-d.

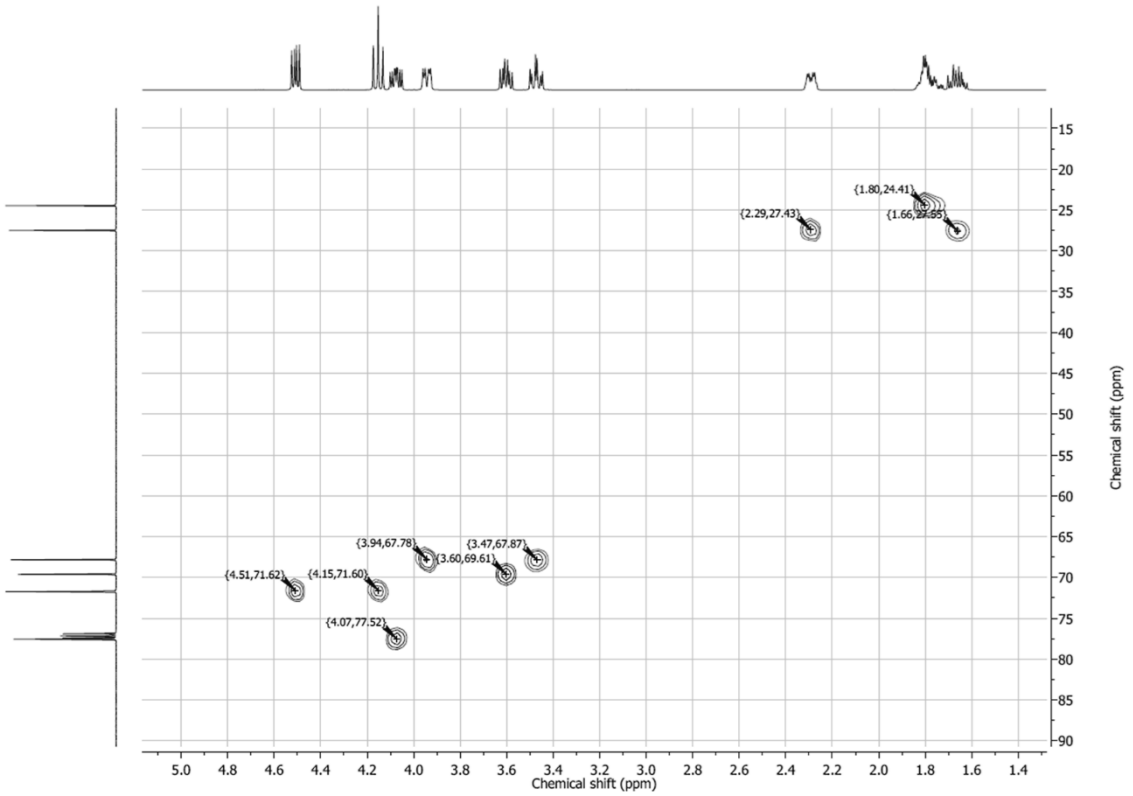


Fig. S30 HSQC (^{1}H–^{13}C) NMR spectrum of **4** in chloroform-d.

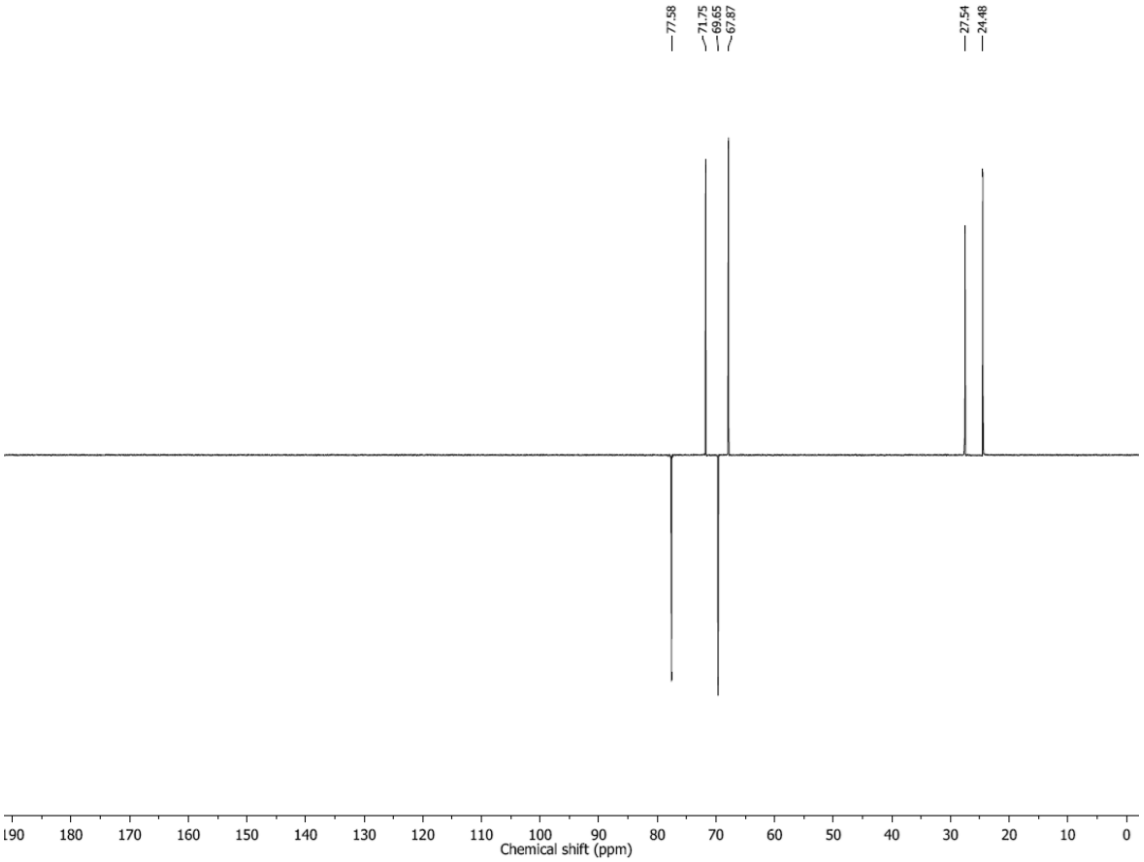


Fig. S31 $^{13}C\{^{1}H\}$ DEPT135 NMR spectrum of **4** in chloroform-d.

DSC analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxine-2-thione (4)

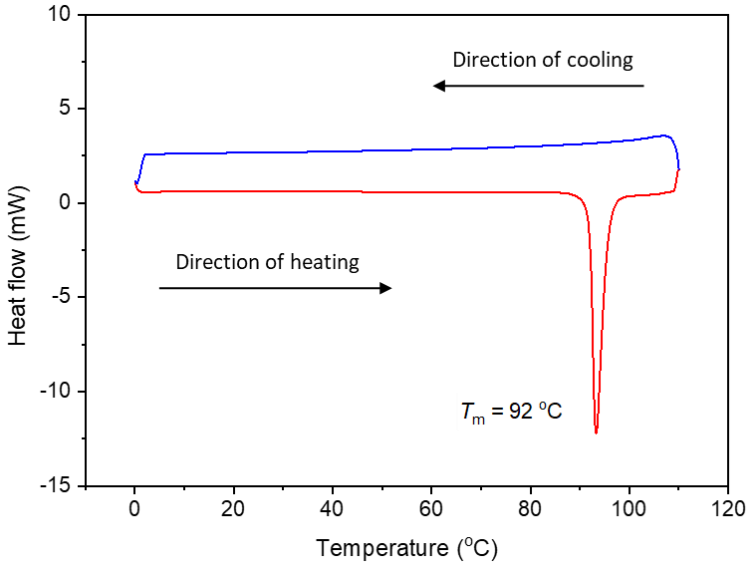


Fig. S32 DSC trace of the monomer **4**, first heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the melting temperature (T_m) ≈ 92 °C of the monomer.

TGA analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxine-2-thione (4)

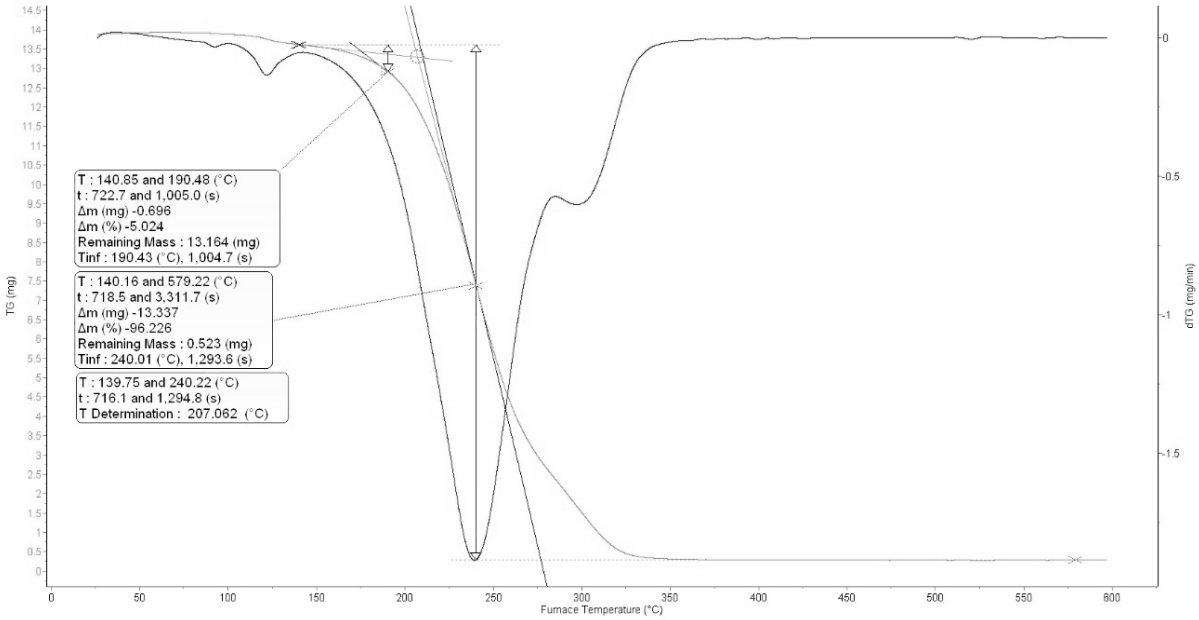


Fig. S33 TGA trace of the monomer **4**. The monomer was heated from 0 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 190 °C; $T_{d,max}$ = 240 °C with 4 % char remaining at 600 °C.

FT-IR analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxine-2-thione (4)

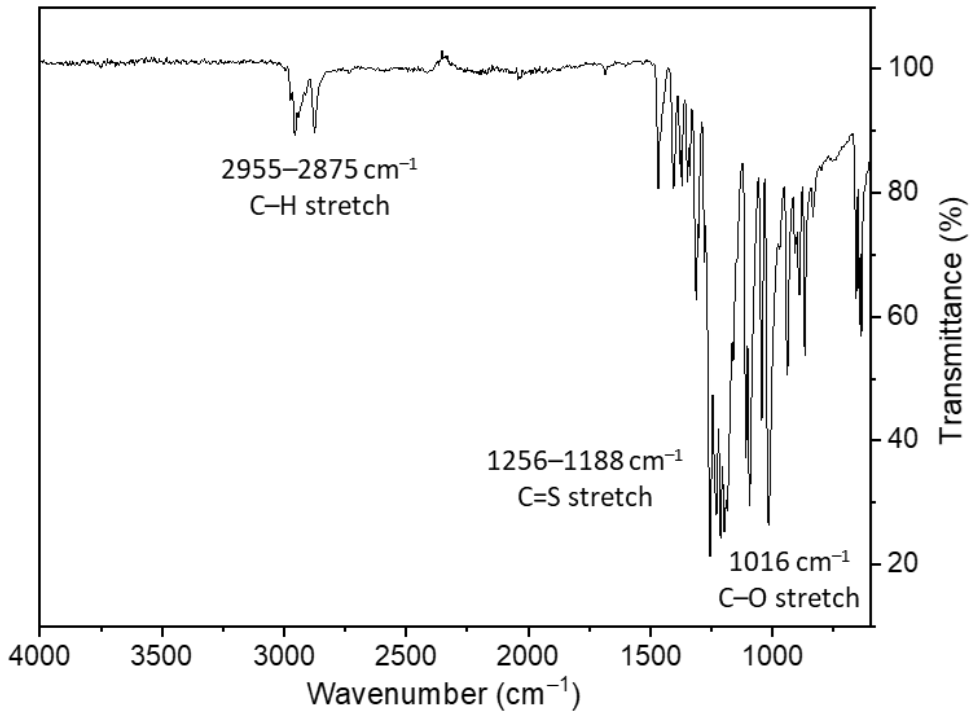


Fig. S34 Labelled FT-IR spectrum of **4**.

Crystal Diffraction Data and Structure Refinement for 4 (CCDC Number – 2177256)

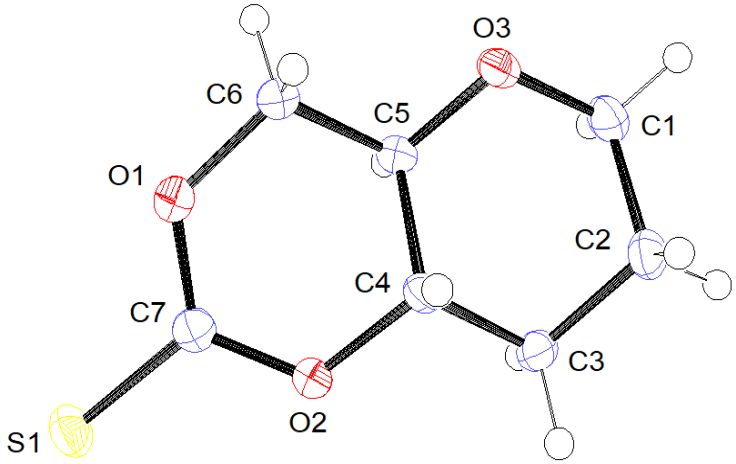
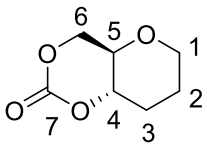


Fig. S35 ORTEP drawing of the crystal structure of **4** with thermal ellipsoids at the 50% probability level. Selected bond lengths and dihedral angles (°): S–C(7) 1.649 (2), O(1)–C(7) 1.327 (2), O(1)–C(6) 1.462 (3), O(2)–C(7) 1.324 (2), O(2)–C(4) 1.464 (2), C(6)–C(5) 1.505 (3), C(7)–S–C(6) 105.90 (7), C(7)–O(1)–C(6) 123.57 (15), C(7)–O(2)–C(4) 120.38 (14), O(2)–C(7)–O(1) 120.50 (17), O(2)–C(7)–S(1) 119.93 (14), O(1)–C(7)–S(1) 119.57 (14), O(1)–C(6)–C(5) 110.34 (16).

Identification code	e22ab3	
Empirical formula	C7 H10 O3 S	
Formula weight	174.21	
Temperature	149.9(6) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2	
Unit cell dimensions	a = 12.5990(3) Å	α = 90°.
	b = 6.90114(15) Å	β = 102.949(3)°.
	c = 18.8705(5) Å	γ = 90°.
Volume	1599.02(7) $Å^3$	
Z	8	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	0.358 mm^{-1}	
F(000)	736	
Crystal size	0.700 x 0.550 x 0.400 mm^3	
Theta range for data collection	3.153 to 27.483°.	
Index ranges	-16<=h<=16, -8<=k<=8, -24<=l<=24	
Reflections collected	12814	
Independent reflections	3659 [R(int) = 0.0244]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.94340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3659 / 1 / 199	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0603	
R indices (all data)	R1 = 0.0264, wR2 = 0.0608	
Absolute structure parameter	0.00(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.205 and -0.172 $e.Å^{-3}$	

Synthesis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxin-2-one (5)

An excess of 1,1′-carbonyldiimidazole (CDI) (1.35 g, 8.32 mmol, 1.1 equiv.) was added gradually, over the course of 1 h, to a solution of (2R,3S)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-ol (1.0 g, 7.57 mmol, 1.0 equiv.) in dry DCM (30 mL) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for a further 1.5 h. The reaction progress was monitored by thin layer chromatography using an EtOAc (100 %) mobile phase. After completion, the reaction mixture was immediately washed with $HCl_{(aq)}$ (ca. 3%, 30 mL) and $NaHCO_3$ (1 mol L^{-1}, 30 mL), dried over $MgSO_4$ and concentrated in *vacuo* to yield a white powder (0.78 g, 65 %). The product was purified further by recrystallization using diethyl ether, and isolated *via* filtration as white crystals.



δ_H (500 MHz; chloroform-d): 4.46 (C^6H, 1H, dd, J_{HH} = 10.1, 5.9 Hz), 4.15 (C^6H, 1H, t, J_{HH} = 10.2 Hz), 4.06 (C^4H, 1H, ddd, J_{HH} = 11.2, 9.5, 4.6 Hz), 4.02-3.97 (C^1H, 1H, m), 3.54 (C^5H, 1H, ddd, J_{HH} = 10.1, 10.1, 5.9 Hz), 3.49 (C^1H, 1H, ddd, J_{HH} = 11.8, 11.8, 3.5 Hz), 2.30-2.24 (C^3H, 1H, m), 1.85-1.70 (C^2H, 2H, m), 1.69-1.58 (C^3H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 148.1 (C^7), 76.1 (C^4), 70.2 (C^5), 69.9 (C^6), 68.0 (C^6), 28.2 (C^3), 24.3 (C^2) ppm. ν_{max} (cm^{-1}): 2964-2877 (CH), 1729 ($C(O)O_2$), 1091 (C–O).

NMR analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxin-2-one (5)

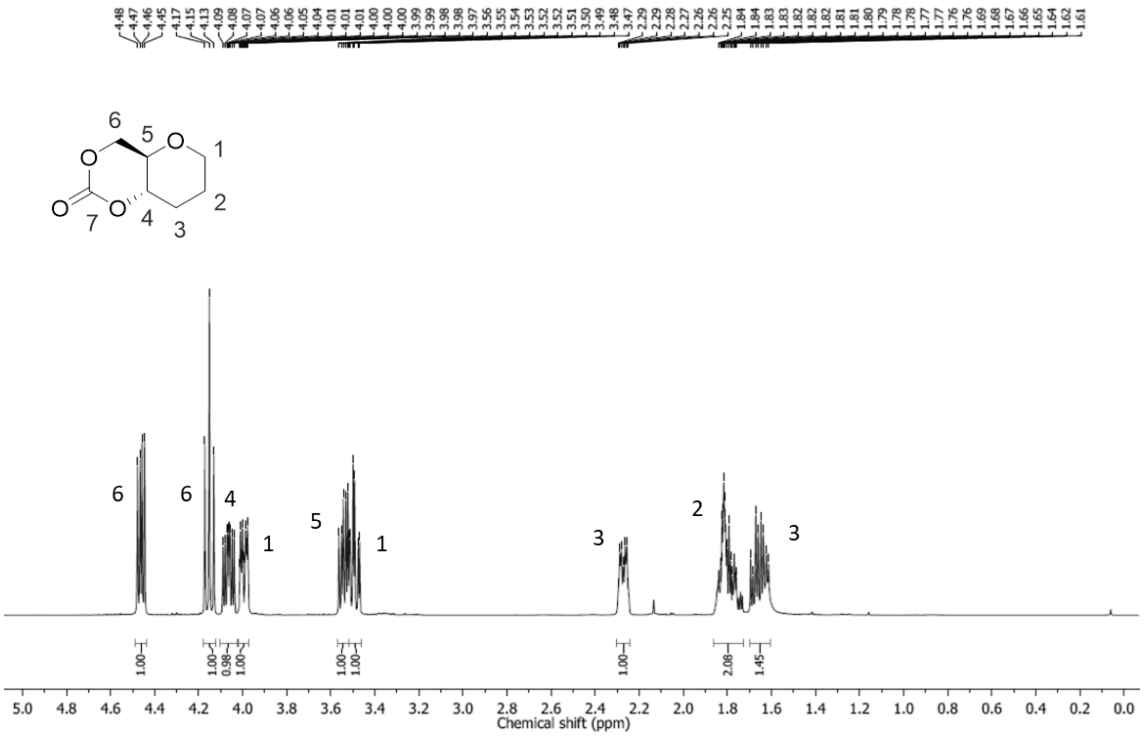


Fig. S36 Annotated ^1H NMR spectrum of **5** in chloroform-d.

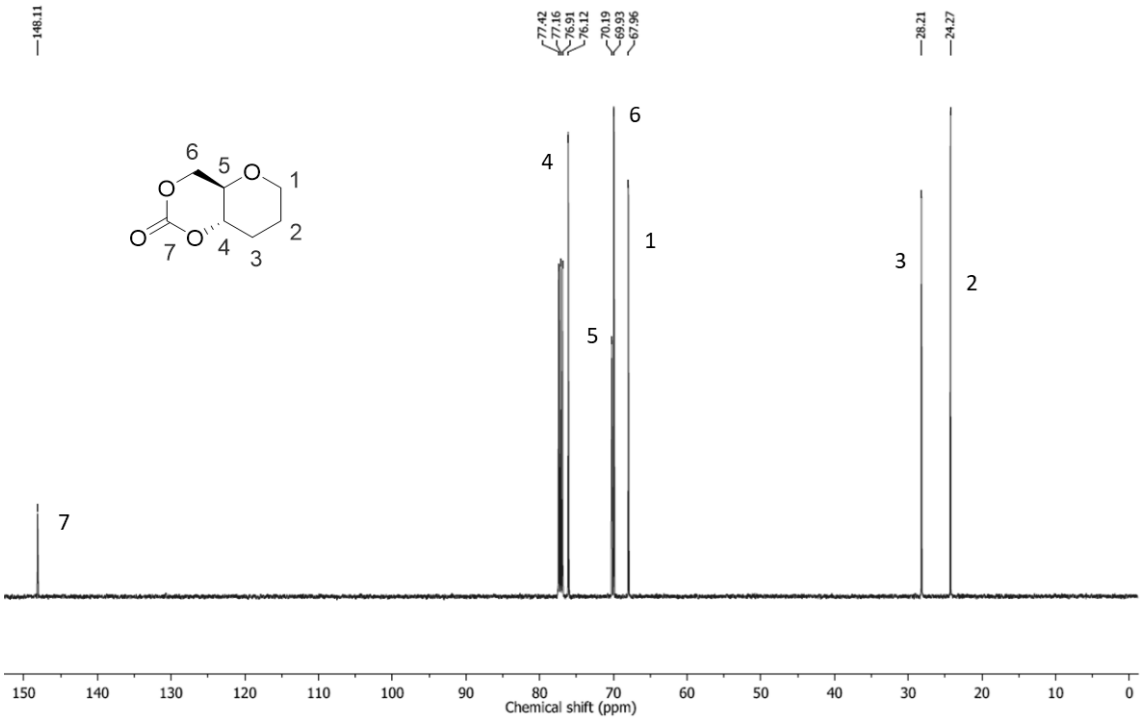


Fig. S37 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of **5** in chloroform-d.

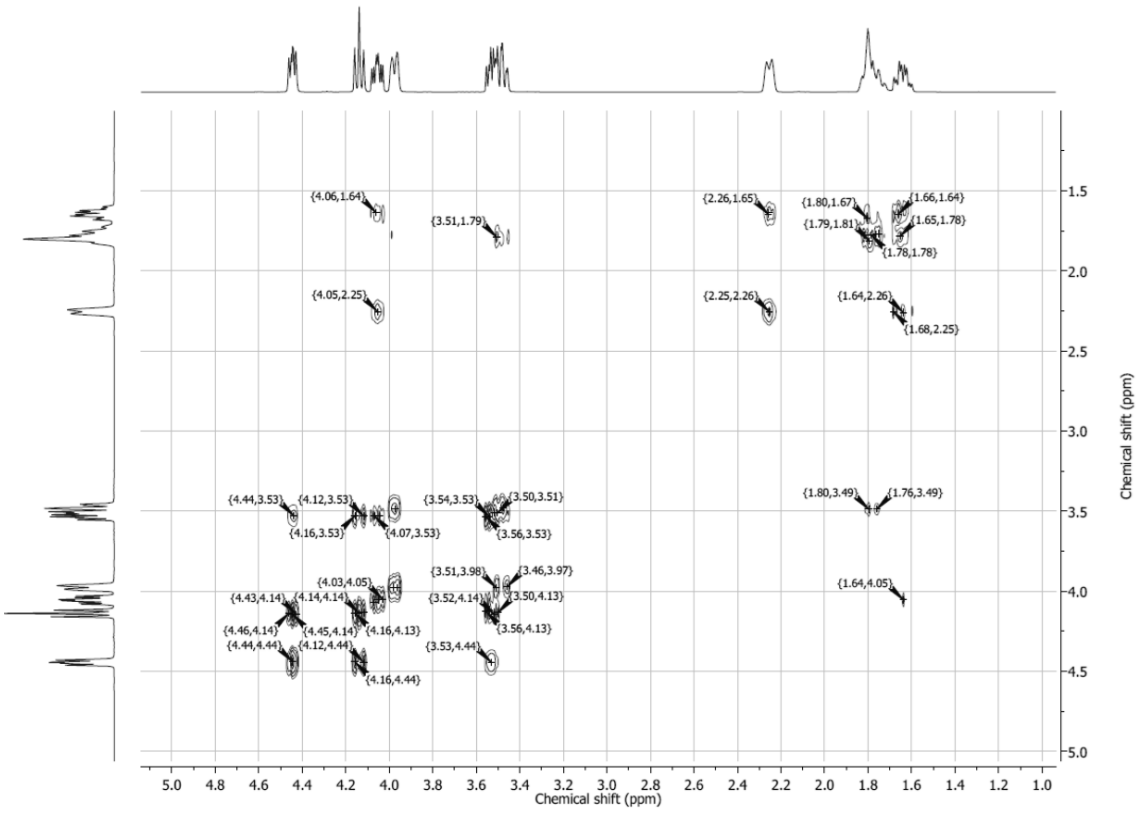


Fig. S38 COSY (^{1}H–^{1}H) NMR spectrum of **5** in chloroform-d.

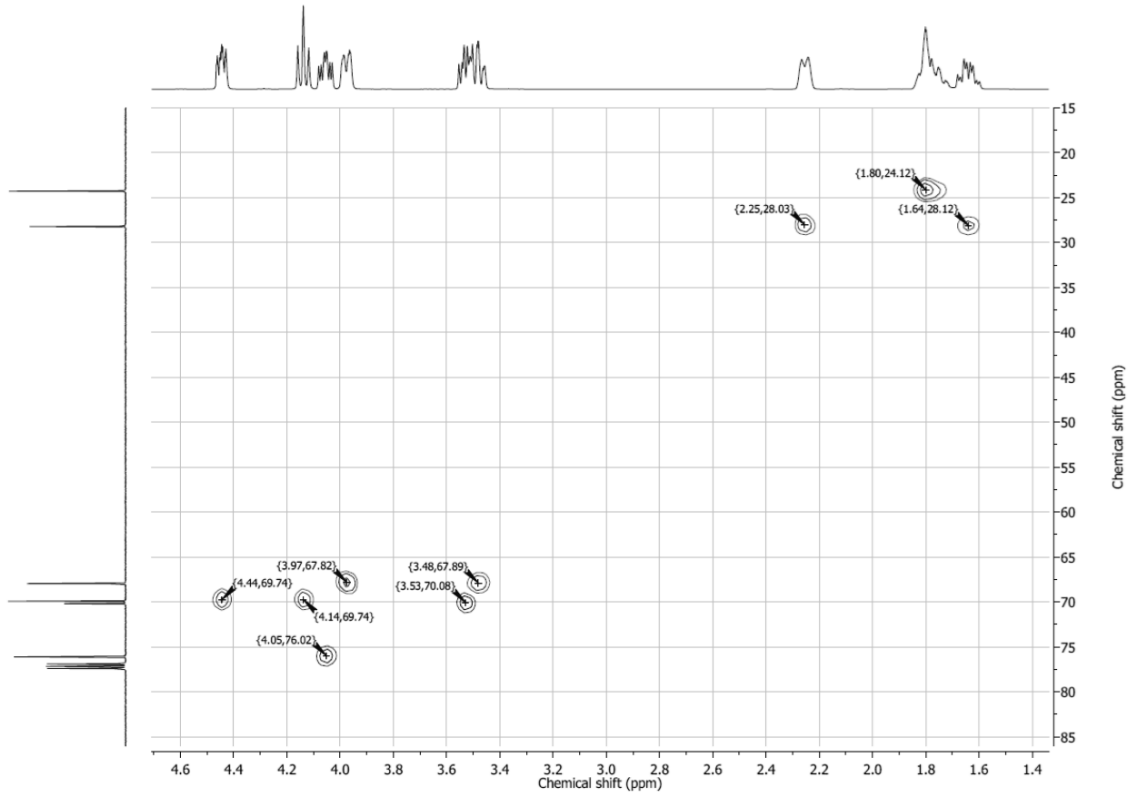


Fig. S39 HSQC (^{1}H–^{13}C) NMR spectrum of **5** in chloroform-d.

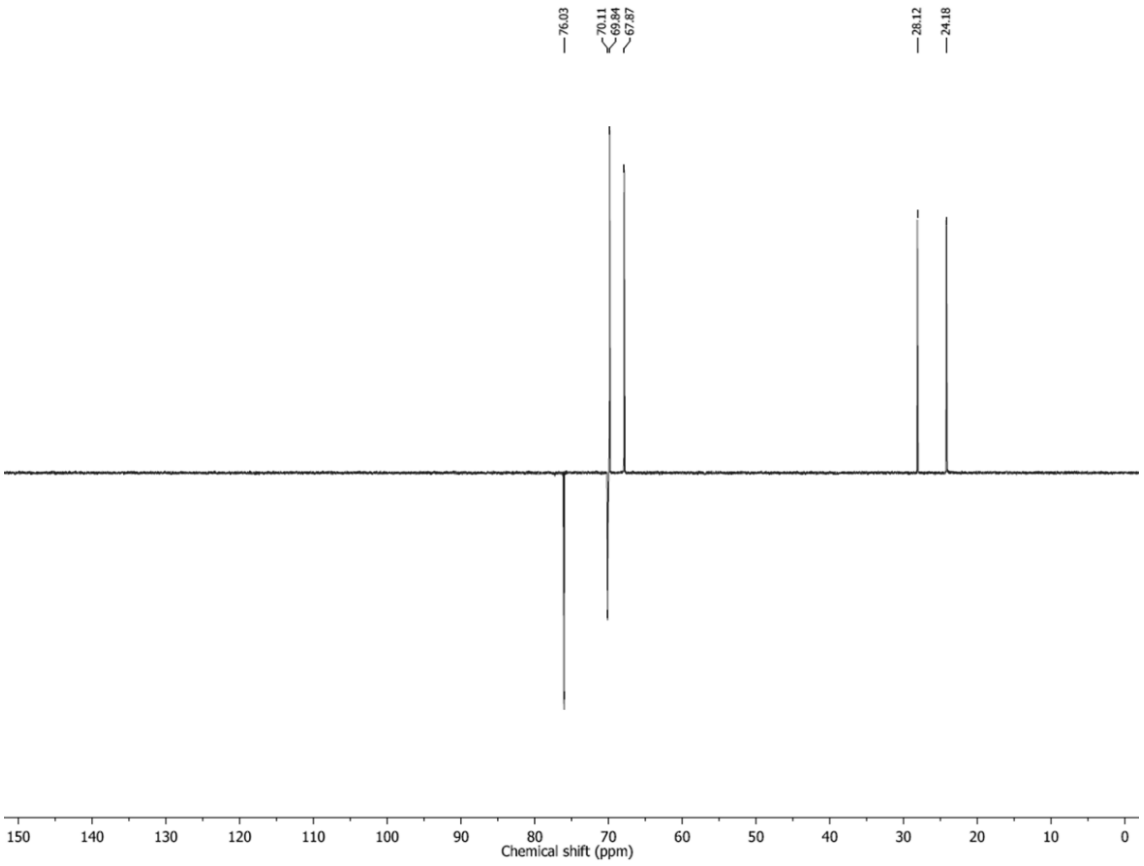


Fig. S40 ^{13}C{^{1}H} DEPT135 NMR spectrum of **5** in chloroform-d.

DSC analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxin-2-one (5)

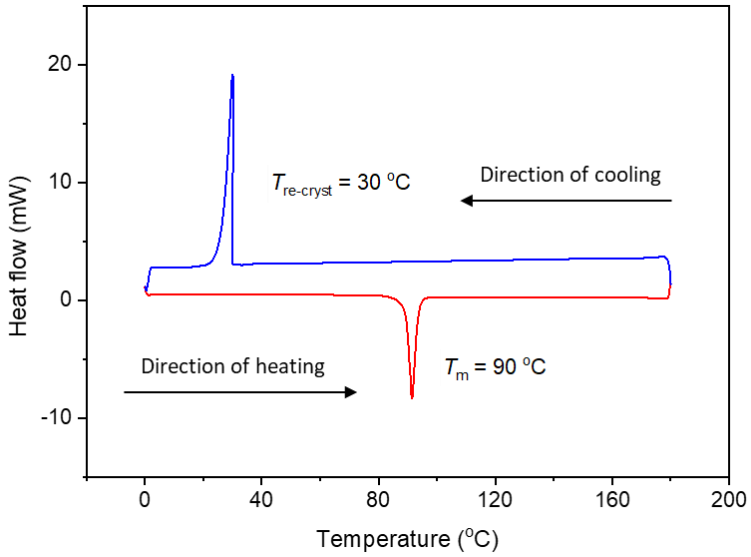


Fig. S41 DSC trace of the monomer **5**, first heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the melting temperature (T_m) ≈ 88 °C of the monomer. Single endothermic peak, corresponding to the recrystallisation temperature ($T_{recryst}$) ≈ 20 °C of the monomer.

TGA analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxin-2-one (5)

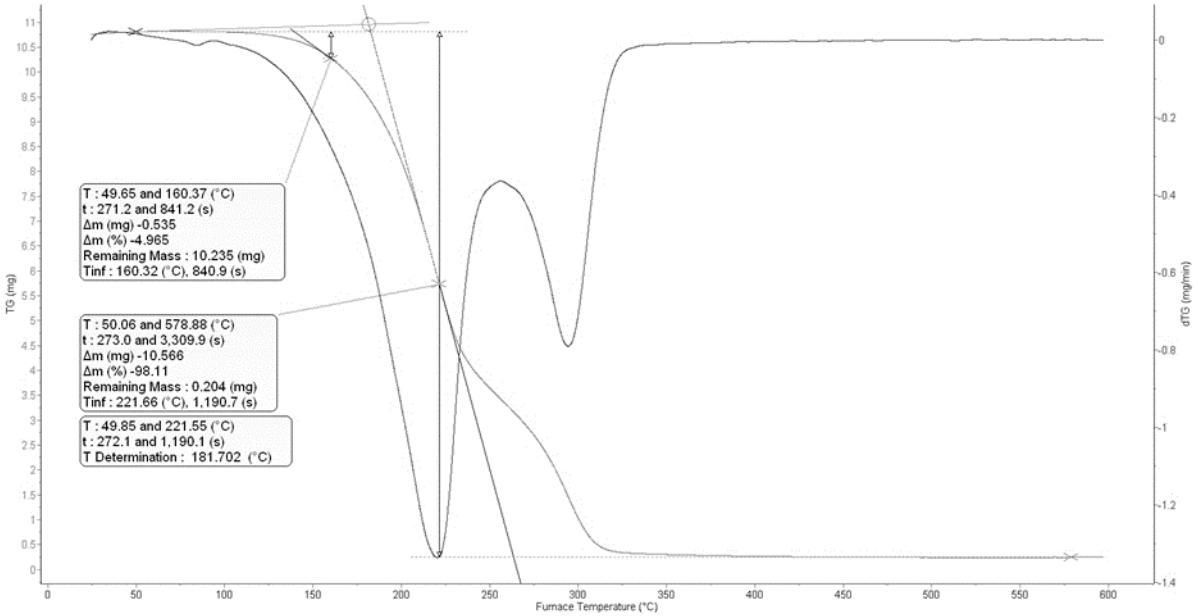


Fig. S42 TGA trace of the monomer **5**. The monomer was heated from 0 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 160 °C; $T_{d,max}$ = 222 °C with 2 % char remaining at 600 °C.

FT-IR analysis of (4aR,8aS)-hexahydropyrano[3,2-d][1,3]dioxin-2-one (5)

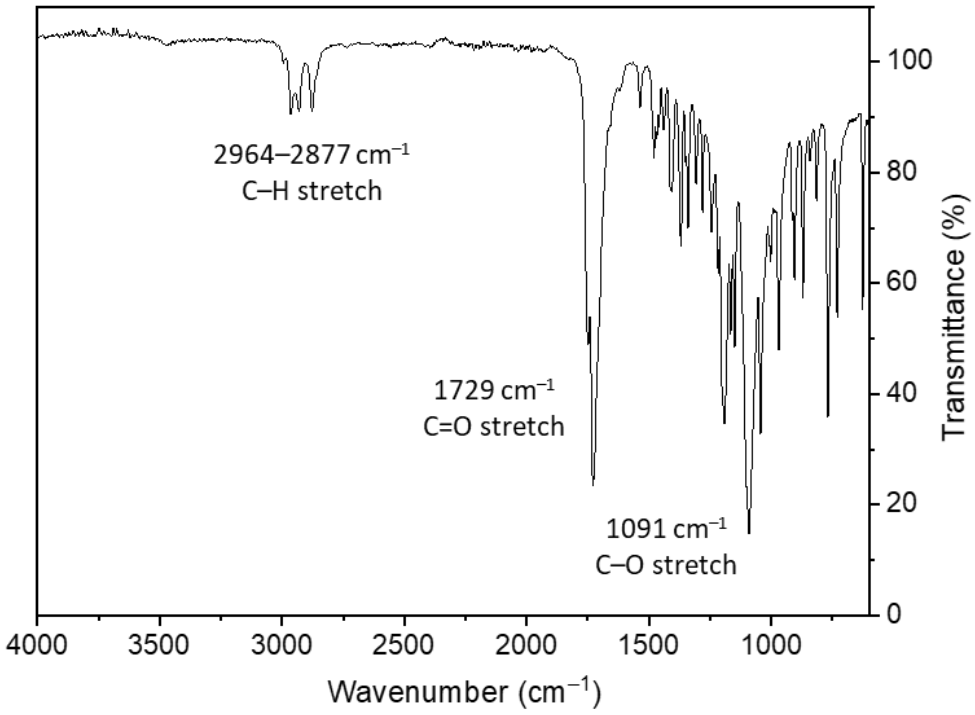


Fig. S43 Labelled FT-IR spectrum of **5**.

Crystal Diffraction Data and Structure Refinement for 5 (CCDC Number – 2177257)

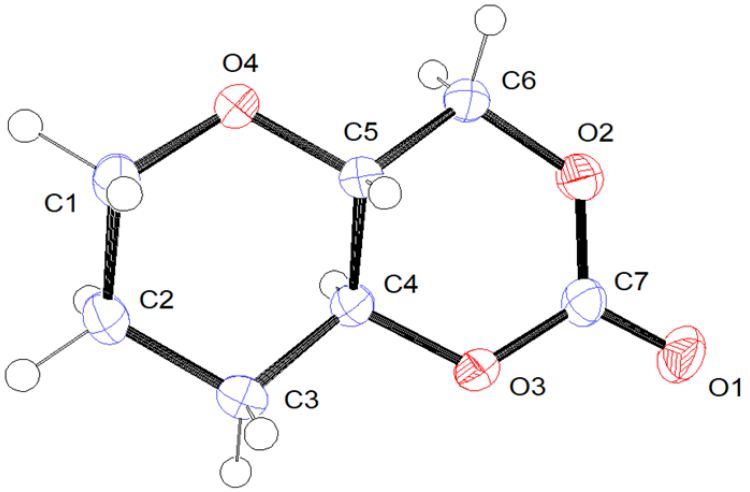
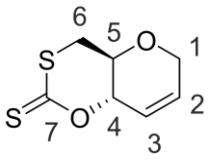


Fig. S44 ORTEP drawing of the crystal structure of **5** with thermal ellipsoids at the 50% probability level. Selected bond lengths and dihedral angles (°): O(1)–C(7) 1.204 (2), O(2)–C(7) 1.333 (2), O(2)–C(6) 1.456 (2), O(3)–C(7) 1.336 (19), O(3)–C(4) 1.454 (18), C(6)–C(5) 1.503 (2), C(7)–O(2)–C(6) 123.87 (14), C(7)–O(3)–C(4) 119.57 (12), O(1)–C(7)–O(2) 119.72 (15), O(1)–C(7)–O(3) 120.18 (16), O(2)–C(7)–O(3) 120.08 (15), O(2)–C(6)–C(5) 120.19 (14)

Identification code	s22ab1	
Empirical formula	C7 H10 O4	
Formula weight	158.15	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.79278(12) Å	α = 90°.
	b = 6.11294(9) Å	β = 90.4175(12)°.
	c = 13.39685(18) Å	γ = 90°.
Volume	720.058(17) $Å^3$	
Z	4	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	1.029 mm^{-1}	
F(000)	336	
Crystal size	0.320 x 0.250 x 0.050 mm^3	
Theta range for data collection	5.030 to 72.888°.	
Index ranges	-10<=h<=10, -7<=k<=7, -16<=l<=16	
Reflections collected	11144	
Independent reflections	2780 [R(int) = 0.0213]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.67311	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2780 / 1 / 199	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0668	
R indices (all data)	R1 = 0.0261, wR2 = 0.0671	
Absolute structure parameter	-0.03(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.194 and -0.179 $e.Å^{-3}$	

Synthesis of (4aS,8aS)-4,4a,6,8a-tetrahydropyrano[2,3-e][1,3]oxathiine-2-thione (1)

1 was synthesised according to the previously reported method, spectroscopic data shown is consistent with previous literature.[1]



δ_H (400 MHz; chloroform-d): 6.07-5.9 (C^2H, C^3H, 2H, m), 4.82-4.75 (C^4H, 1H, m), 4.36-4.30 (C^1H, 1H, m), 4.30-4.24 (C^1H, 1H, m), 3.89 (C^5H, 1H, ddd, J_{HH} = 10.1, 8.4, 6.2 Hz), 3.18-3.10 (C^6H, 2H, m) ppm; δ_C (101 MHz; chloroform-d): 207.6 (C^7), 130.4 (C^2), 122.8 (C^3), 77.8 (C^4), 68.4 (C^5), 66.2 (C^1), 35.0 (C^6) ppm. ν_{max} (cm^{-1}): 2895-2820 (CH), 1180 (C(S)SO), 1010 (C–S).

NMR analysis of (4aS,8aS)-4,4a,6,8a-tetrahydropyrano[2,3-e][1,3]oxathiine-2-thione (1)

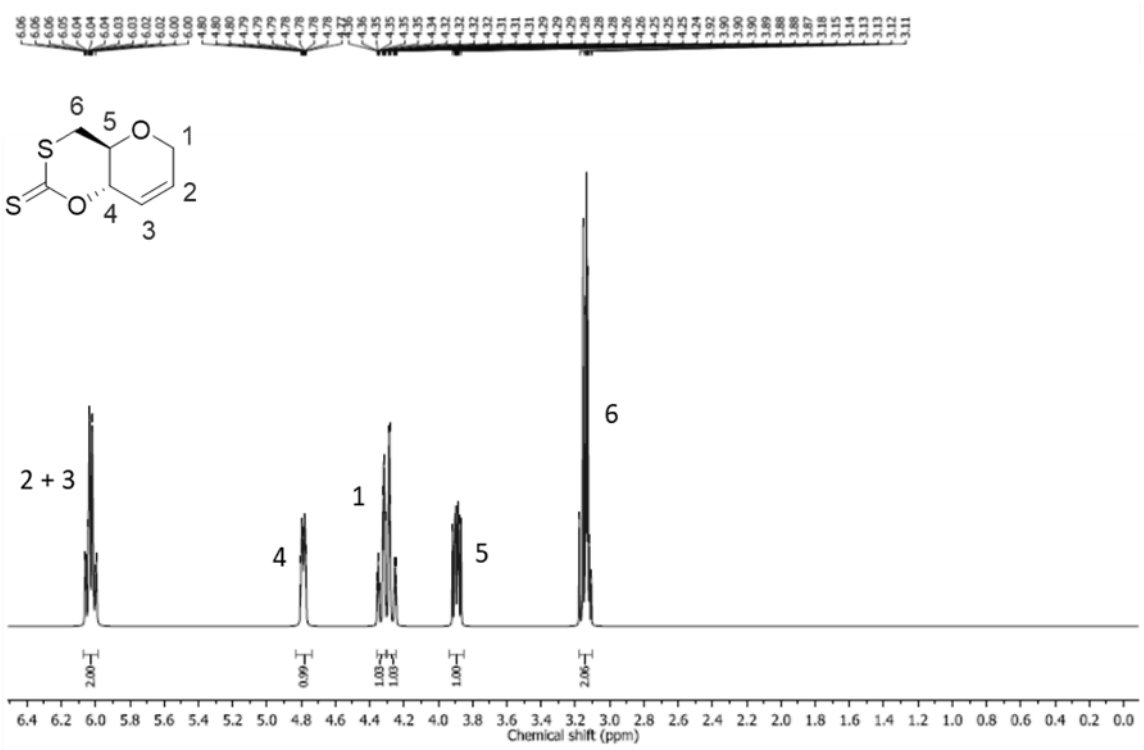


Fig. S45 Annotated ^1H NMR spectrum of **1** in chloroform-d.

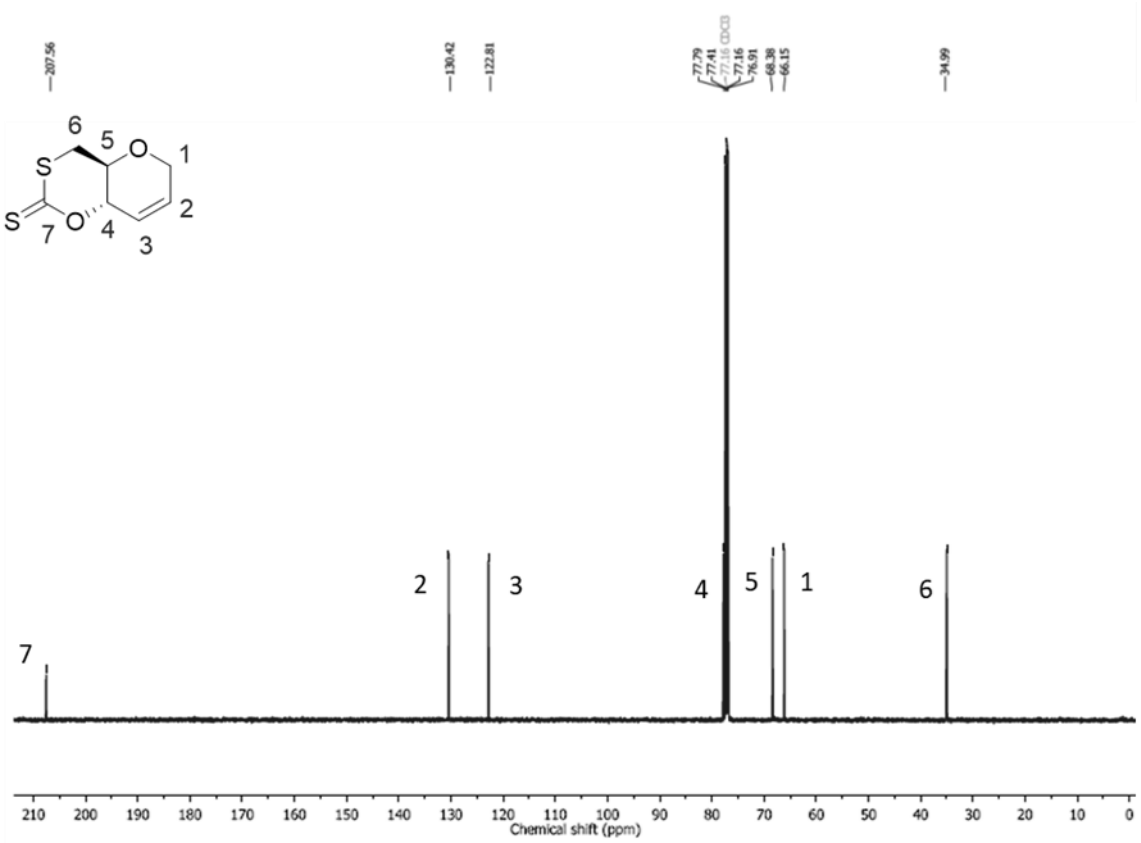


Fig. S46 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of **1** in chloroform-d.

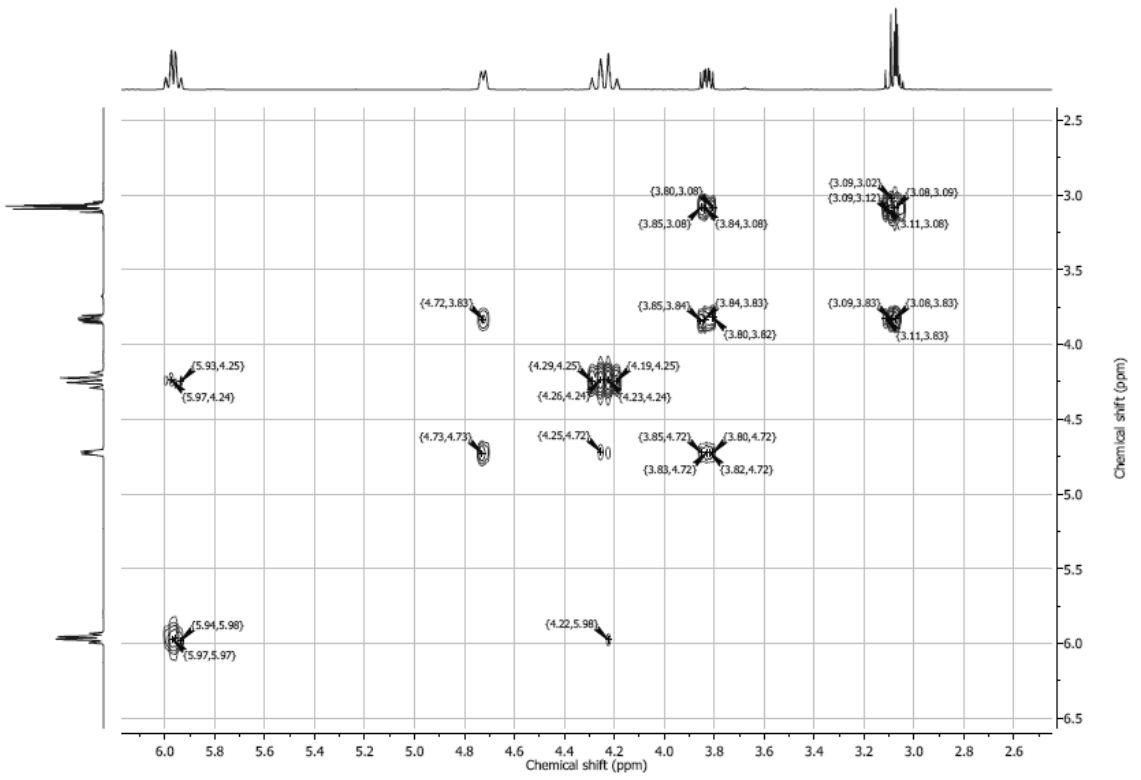


Fig. S47 COSY (^{1}H–^{1}H) NMR spectrum of **1** in chloroform-d.

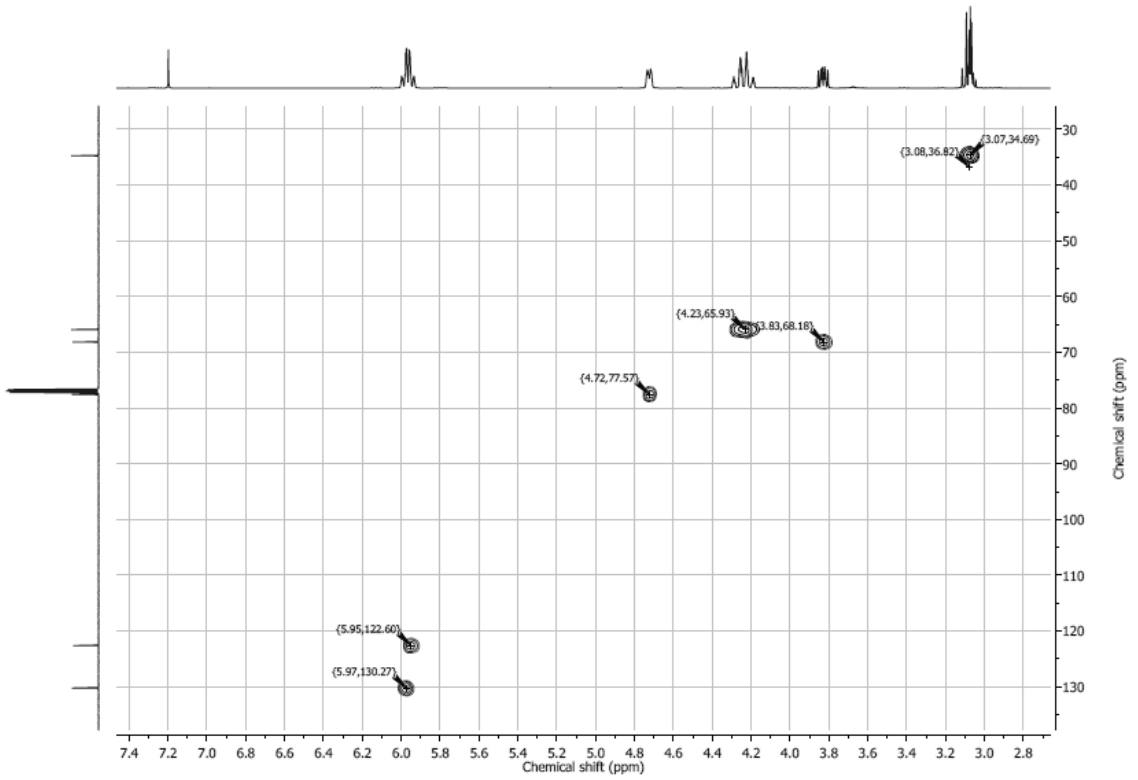


Fig. S48 HSQC (^{1}H–^{13}C) NMR spectrum of **1** in chloroform-d.

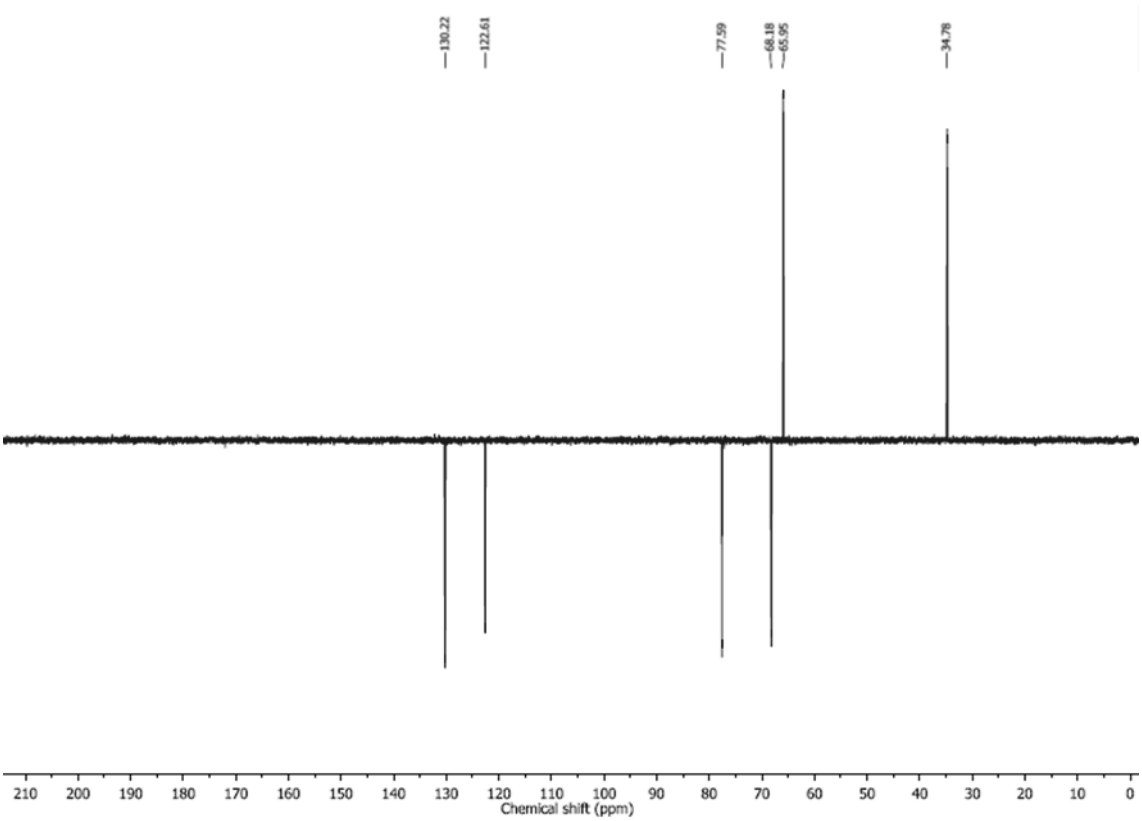


Fig. S49 ^{13}C{^{1}H} DEPT135 NMR spectrum of **1** in chloroform-d.

DSC analysis of (4aS,8aS)-4,4a,6,8a-tetrahydropyrano[2,3-e][1,3]oxathiine-2-thione (1)

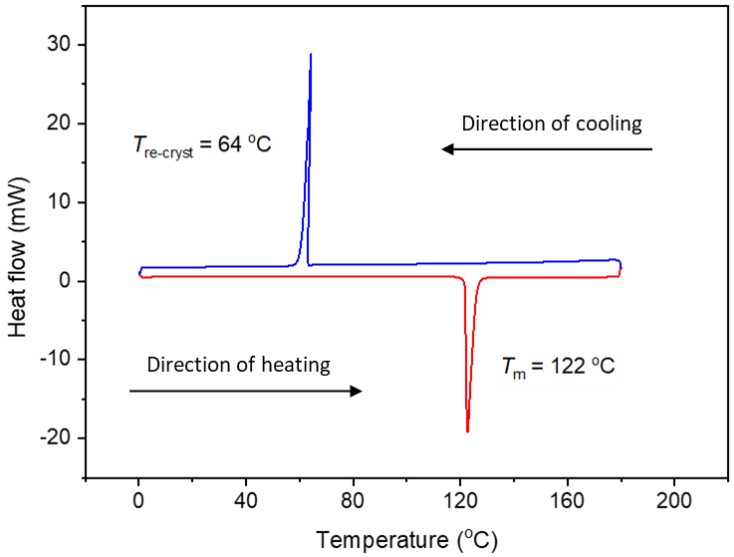


Fig. S50 DSC trace of monomer **1**, first heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the melting temperature (T_m) ≈ 122 °C of the monomer. Single endothermic peak, corresponding to the re-crystallisation temperature ($T_{recryst}$) ≈ 64 °C of the monomer.

TGA analysis of (4aS,8aS)-4,4a,6,8a-tetrahydropyrano[2,3-e][1,3]oxathiine-2-thione (1)

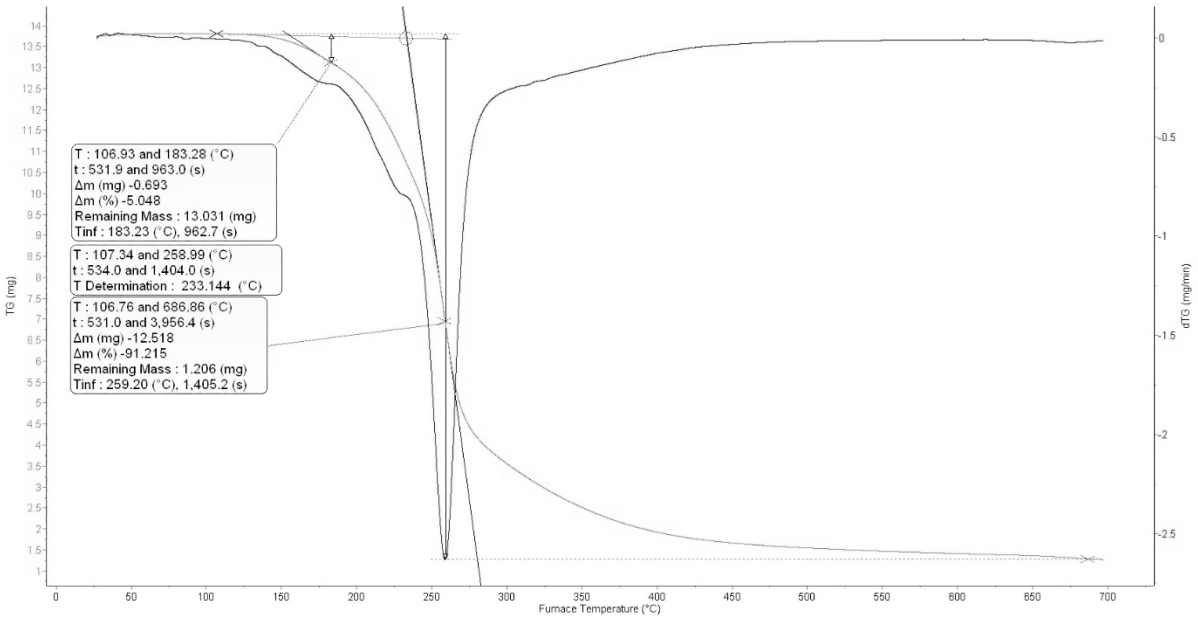


Fig. S51 TGA trace of monomer **1**. The monomer was heated from 30 to 700 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 183 °C and $T_{d,max}$ = 259 °C with 9 % char remaining at 700 °C.

FT-IR analysis of (4aS,8aS)-4,4a,6,8a-tetrahydropyrano[2,3-e][1,3]oxathiine-2-thione (1)

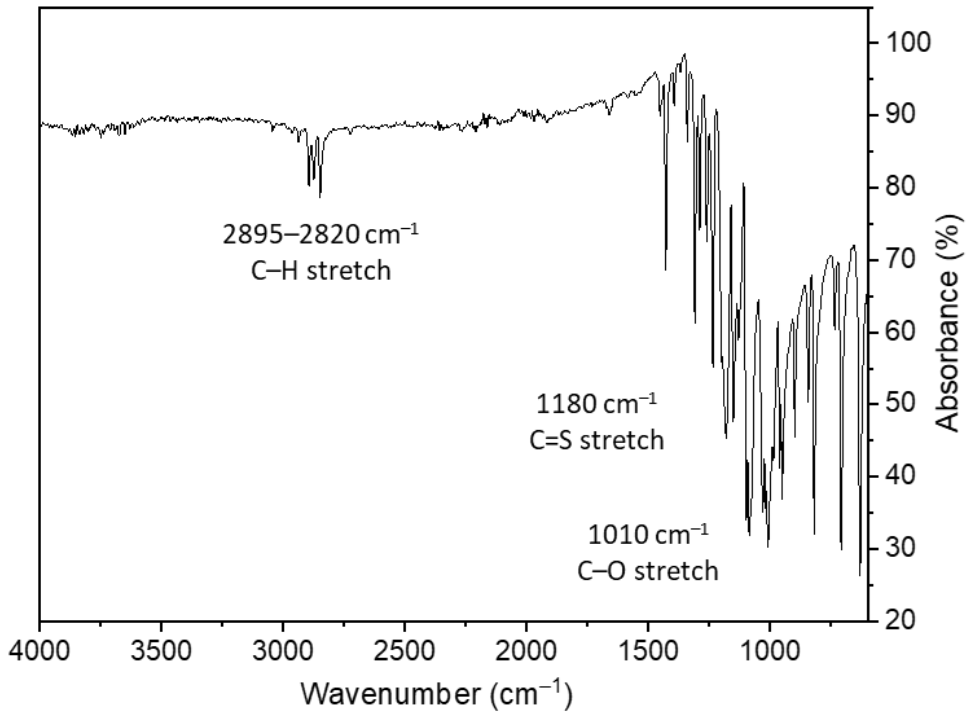


Fig. S52 Labelled FT-IR spectrum of **1**.

Crystal Diffraction Data and Structure Refinement for 1 (CCDC Number – 2089243)

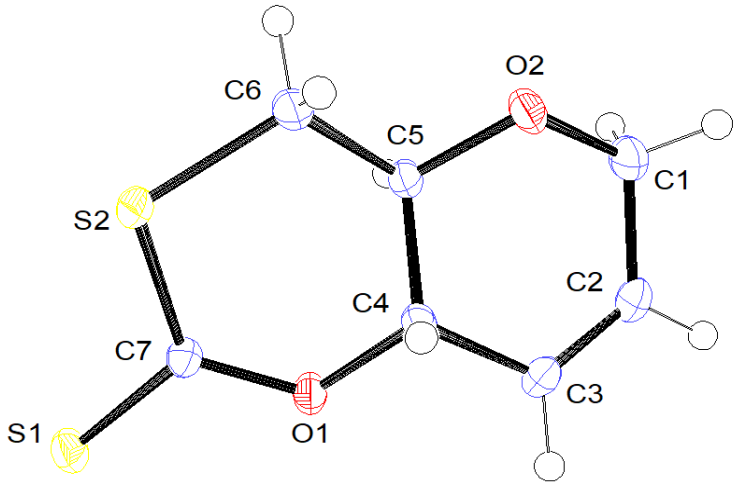


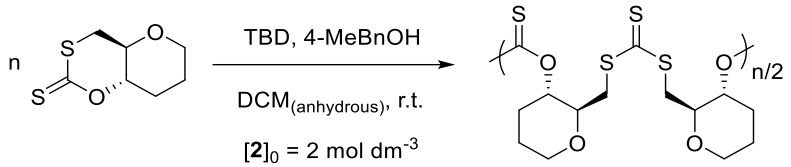
Fig. S53 ORTEP drawing of the crystal structure of **1** with thermal ellipsoids at the 50% probability level. Selected bond lengths and dihedral angles (°): S(1)–C(7) 1.646 (2), S(2)–C(7) 1.733 (2), S(2)–C(6) 1.819 (2), O(1)–C(7) 1.333 (2), O(1)–C(4) 1.458 (3), C(7) –S(2)–C(6) 106.63 (10), C(7)–O(1)–C(4) 120.23 (16), O(1)–C(7)–S(1) 119.06 (15), O(1)–C(7)–S(2) 122.85 (15), S(1)–C(7)–S(2) 118.08 (12).

Identification code	e20ab1
Empirical formula	C7 H8 O2 S2
Formula weight	188.25

Temperature	150.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.2400(3) Å	α = 90°.
	b = 7.3164(4) Å	β = 90°.
	c = 17.7083(8) Å	γ = 90°.
Volume	808.46(7) $Å^3$	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	0.601 mm^{-1}	
F(000)	392	
Crystal size	0.429 x 0.327 x 0.101 mm^3	
Theta range for data collection	3.462 to 30.268°.	
Index ranges	-8<=h<=8, -8<=k<=10, -25<=l<=24	
Reflections collected	7475	
Independent reflections	2183 [R(int) = 0.0277]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.90790	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2183 / 0 / 100	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0673	
R indices (all data)	R1 = 0.0382, wR2 = 0.0692	
Absolute structure parameter	-0.02(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.388 and -0.337 $e.Å^{-3}$	
Independent reflections	1504 [R(int) = 0.0243]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.136	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1504 / 1 / 100	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0281, wR2 = 0.0738	
R indices (all data)	R1 = 0.0281, wR2 = 0.0738	
Absolute structure parameter	0.014(17)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.353 and -0.330 $e.Å^{-3}$	

2. General Polymerisation Procedures

Ring opening polymerisation of 2



Under an argon atmosphere 4-MeBnOH (16 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.008 mmol, 1.0 equiv.) and TBD (16 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.008 mmol, 1.0 equiv.) were added to a solution of monomer **2** (0.150 g, 0.788 mmol, 100 equiv.) in anhydrous DCM (0.39 mL, 2.0 mol dm^{-3}). The mixture was stirred at room temperature for 6 h and quenched by the addition of a benzoic acid solution (≈ 30 equiv.). The solvent was removed under reduced pressure and the crude solid was dissolved in $CHCl_3$ and precipitated from Et_2O. The product was isolated by centrifugation (3500 rpm, 2 x 5 minutes), washed twice with Et_2O and dried under vacuum. The polymer was isolated as a pale-yellow solid.

δ_H (500 MHz; chloroform-d): 5.18-5.06 (C^4H, 1H, m), 3.93 (C^1H, 1H, d, J_{HH} = 11.1 Hz), 3.80 (C^6H, 1H, d, J_{HH} = 12.5 Hz), 3.69-3.52 (C^5H, C^6H, 2H, m), 3.45-3.35 (C^1H, 1H, m), 2.46-2.33 (C^3H, 1H, m), 1.83-1.69 (C^2H, 2H, m), 1.63-1.51 (C^3H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 223.8 (C^7), 193.5 (C^8), 79.2 (C^4), 77.6 (C^5), 68.0 (C^1), 39.0 (C^6), 25.1 (C^3), 25.0 (C^2) ppm. ν_{max} (cm^{-1}): 2942-2851 (CH), 1268-1226 ($C(S)O_2$), 1268-1226 ($C(S)S_2$), 1090-1033 (C–S).

NMR analysis of the polymer derived from 2

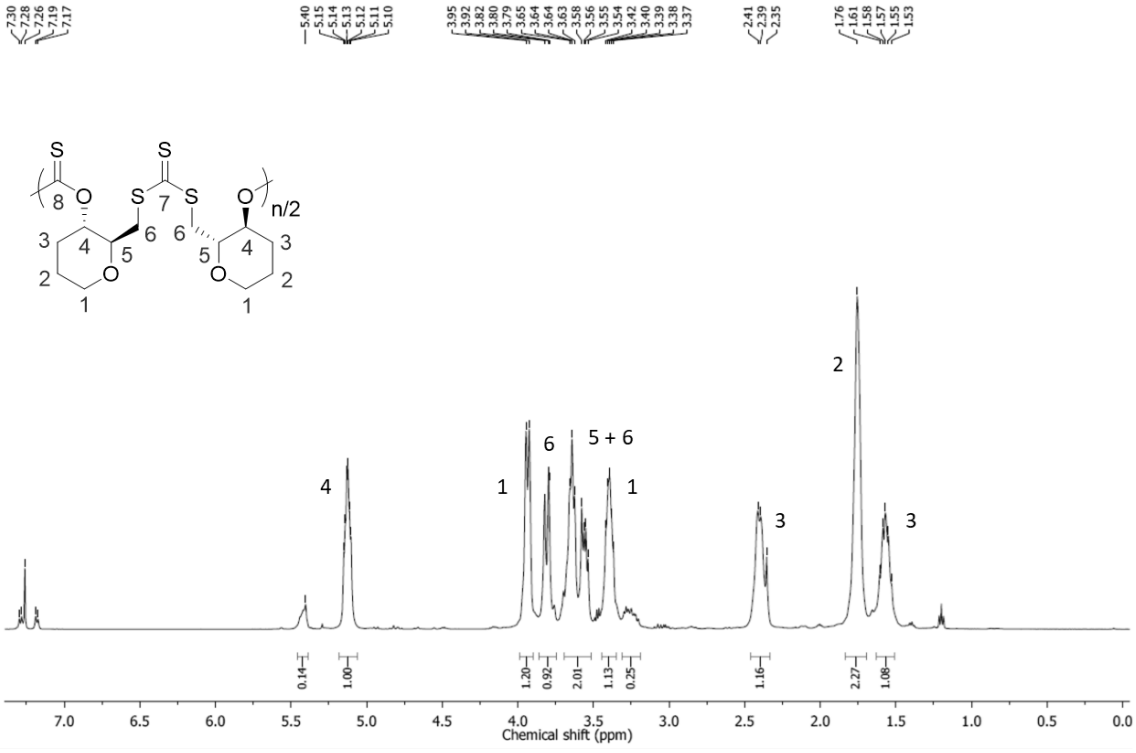


Fig. S54 Annotated ^1H NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)) in chloroform-d.

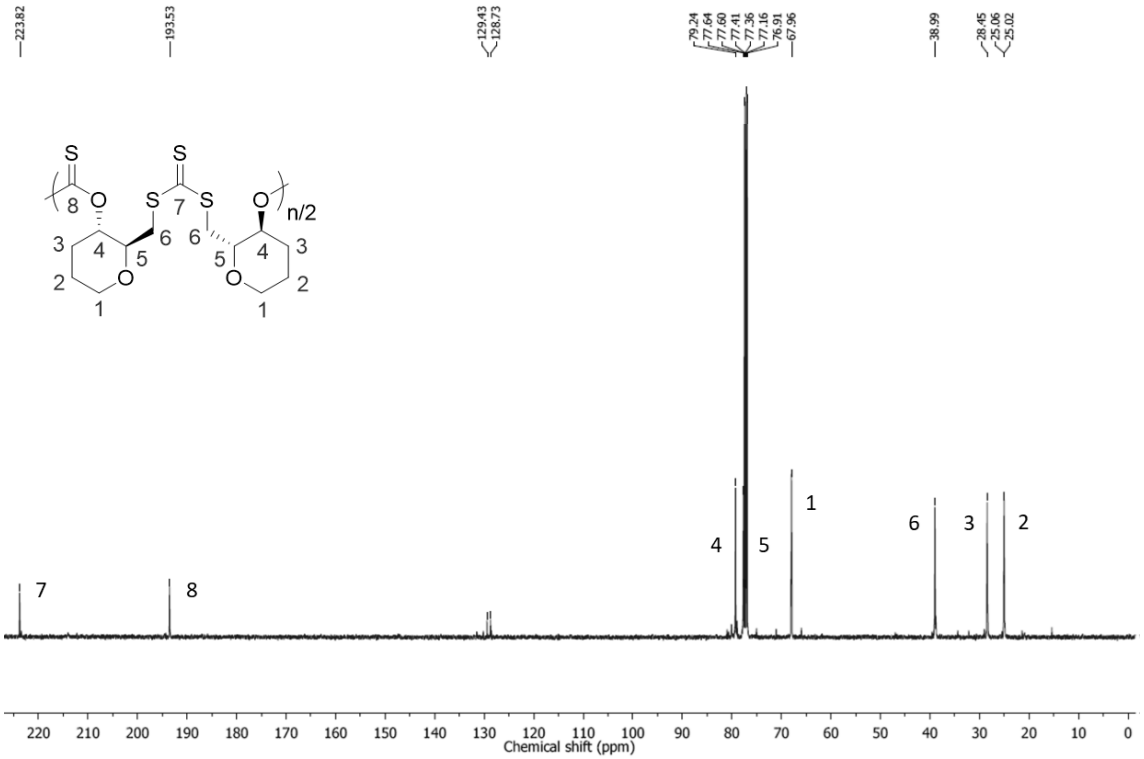


Fig. S55 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)) in chloroform-d.

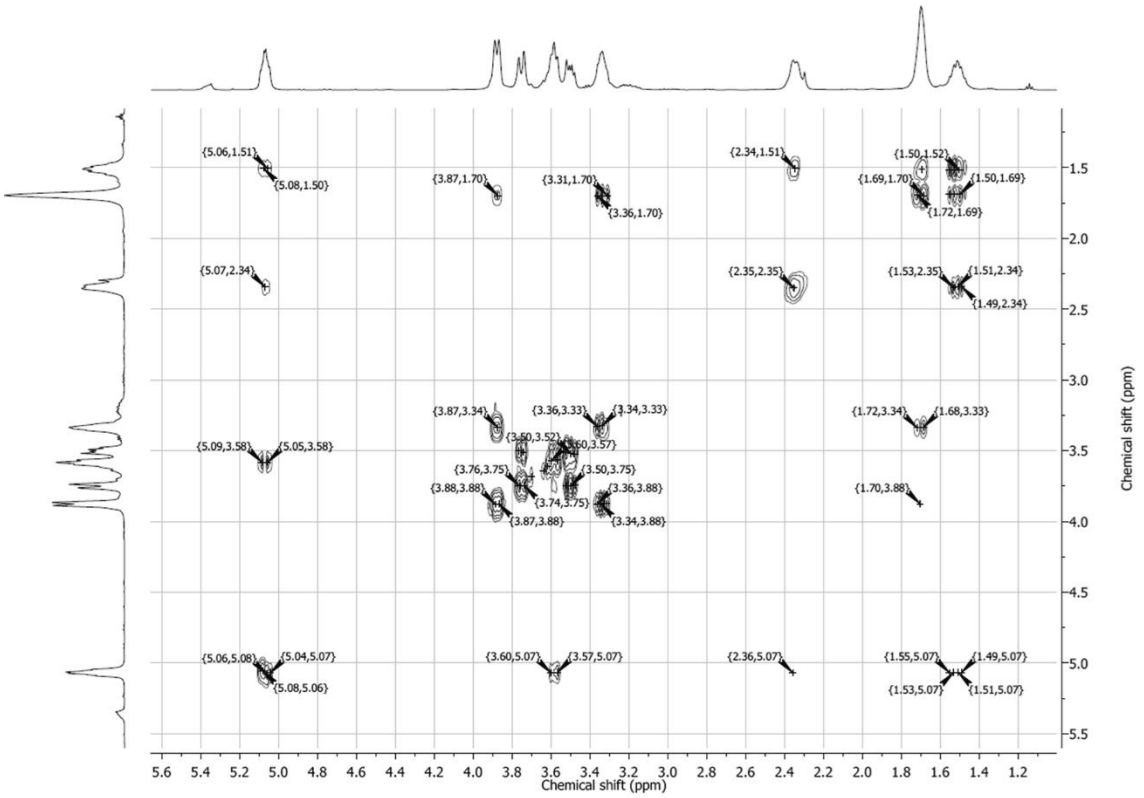


Fig. S56 COSY (^{1}H–^{1}H) NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)) in chloroform-d.

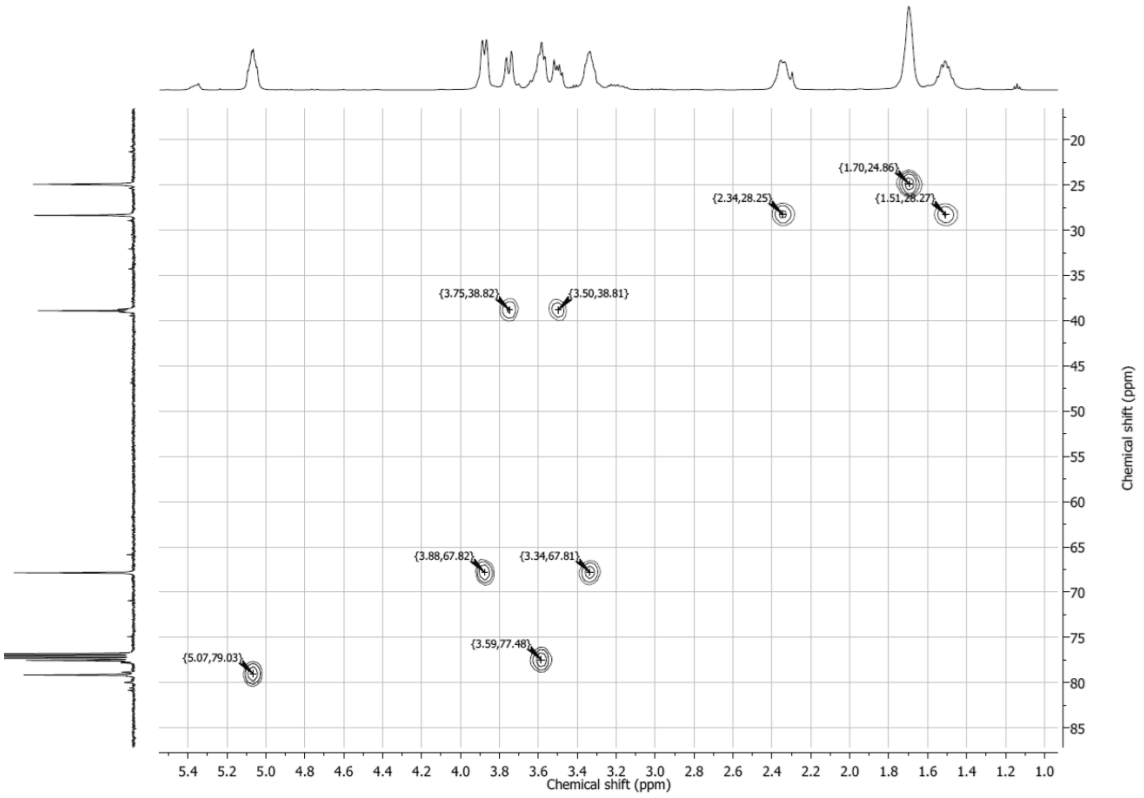


Fig. S57 HSQC (^{1}H–^{13}C) NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)) in chloroform-d.

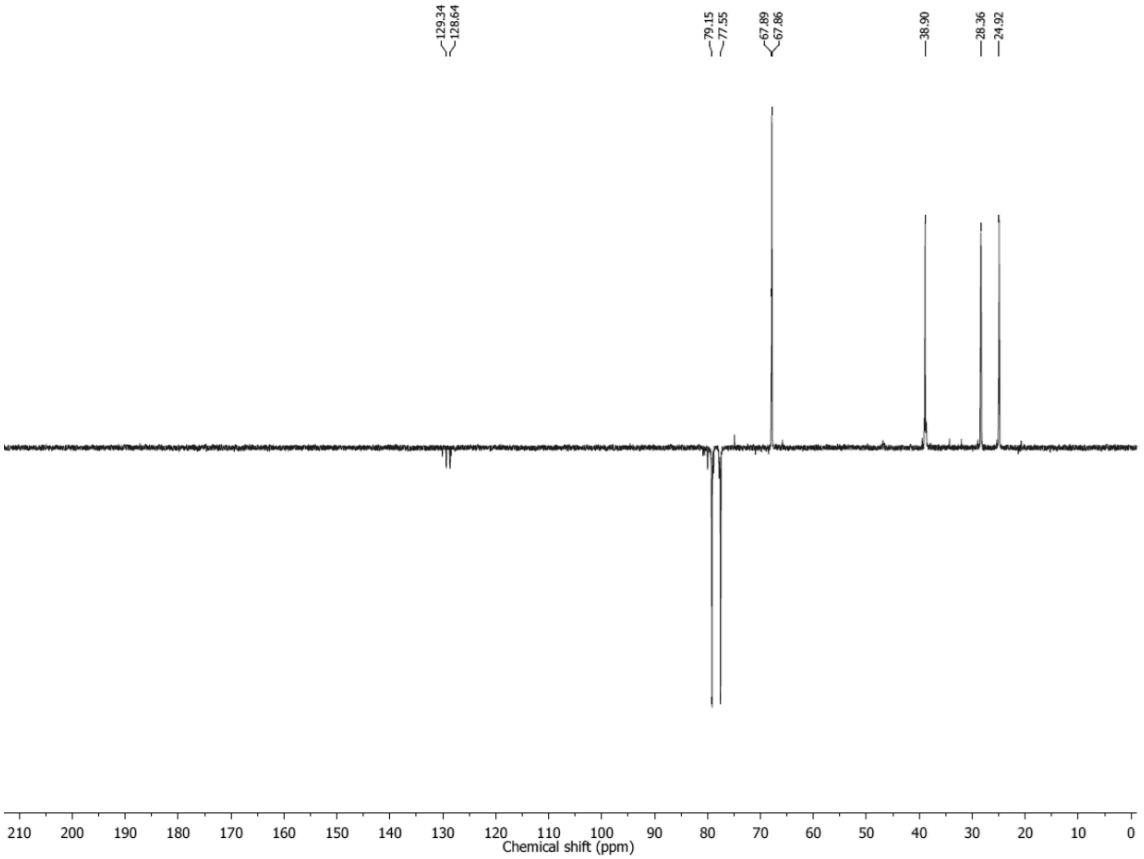


Fig. S58 ^{13}C{^{1}H} DEPT135 NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)) in chloroform-d.

Size-Exclusion Chromatography analysis of the polymer derived from 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	7805	5729	8887	12829	17113	12227	1.551

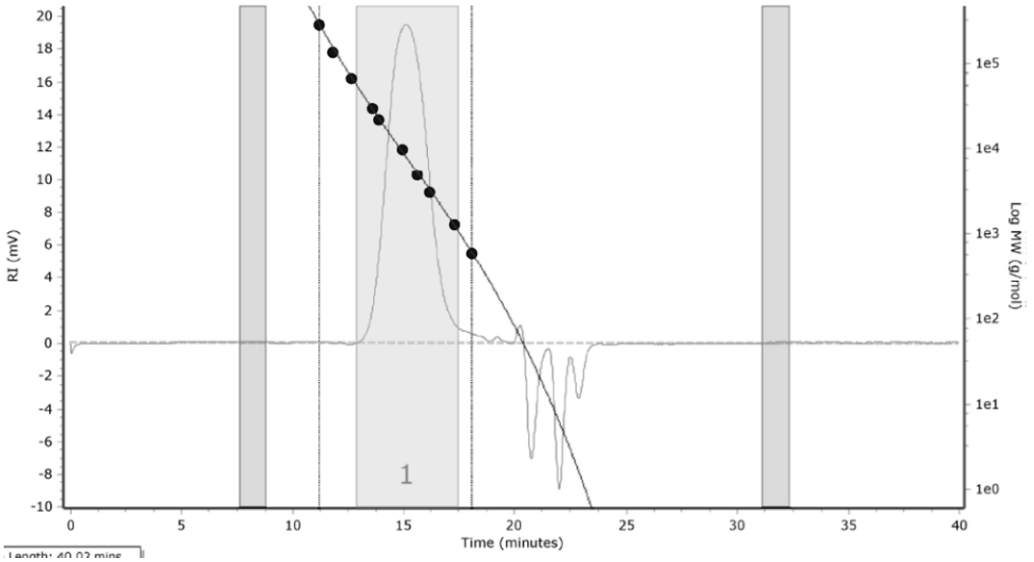


Fig. S59 SEC trace of poly(**2**) (M_n 5700 g mol^{-1} ($Đ$ 1.55)).

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	10077	7652	12010	17442	23226	16620	1.57

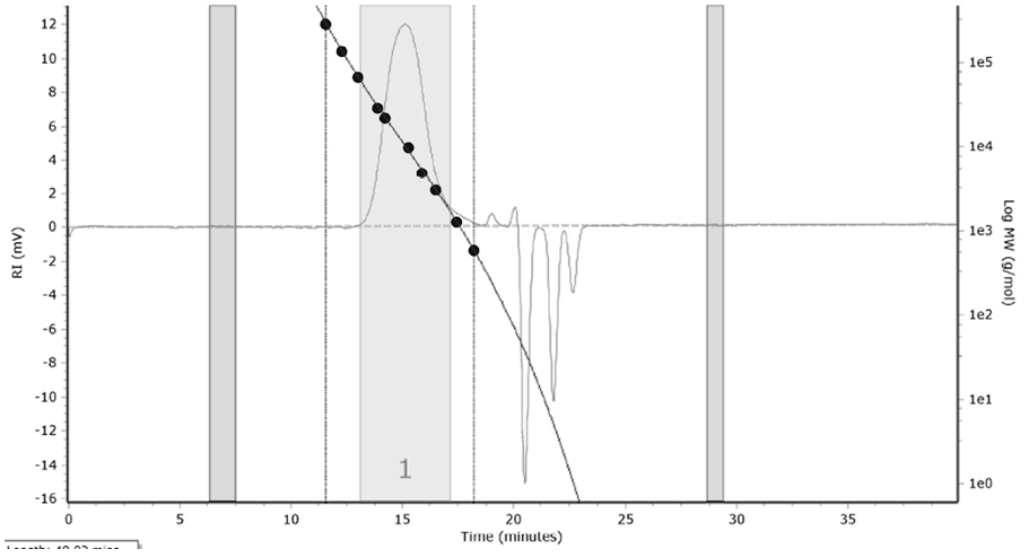


Fig. S60 SEC trace of poly(**2**) (M_n 7700 g mol^{-1} ($Đ$ 1.57)).

DSC analysis of the polymer derived from 2

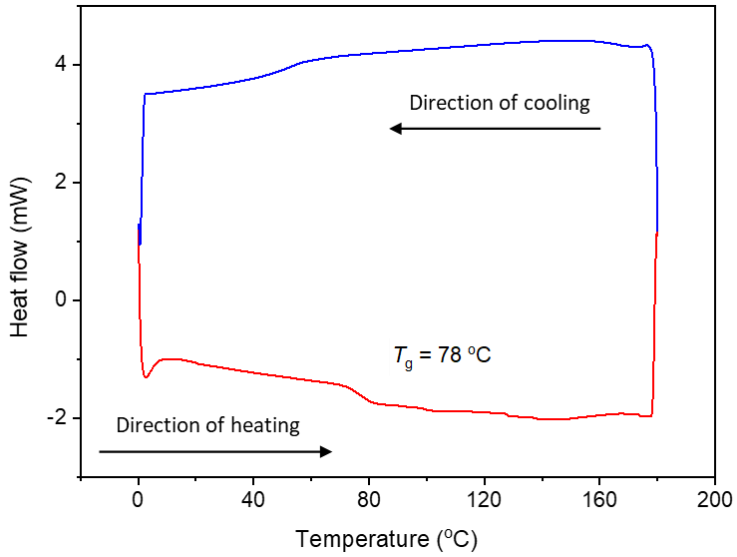


Fig. S61 DSC trace of poly(**2**) (M_n 5700 g mol^{-1} ($Đ$ 1.55)), first heating and cooling cycle between 20 and 180 °C. Single exothermic peak, corresponding to the glass transition temperature (T_g) ≈ 78 °C of the polymer.

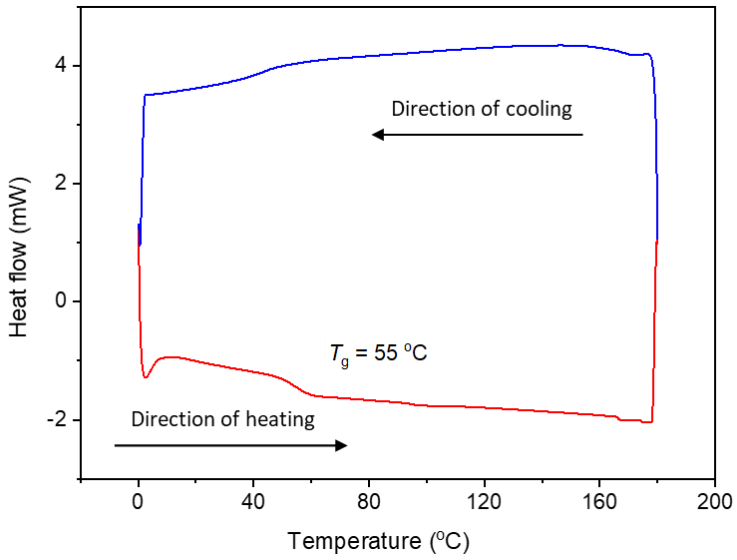


Fig. S62 DSC trace of poly(**2**) (M_n 5700 g mol^{-1} ($Đ$ 1.55)), second heating and cooling cycle between 0 and 180 °C. Single transition, corresponding to the glass transition temperature (T_g) ≈ 55 °C of the polymer.

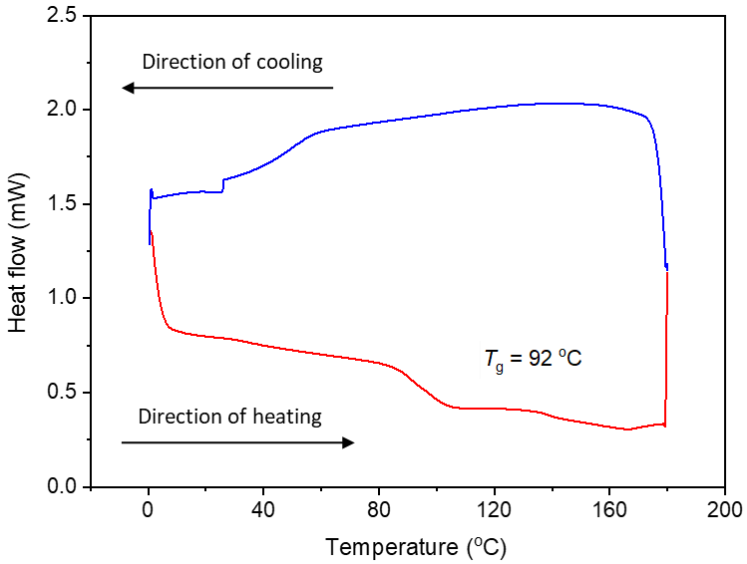


Fig. S63 DSC trace of poly(**2**) (M_n 7700 g mol^{-1} ($Đ$ 1.57)), second heating and cooling cycle between 0 and 180 °C. Single transition, corresponding to the glass transition temperature (T_g) ≈ 92 °C of the polymer.

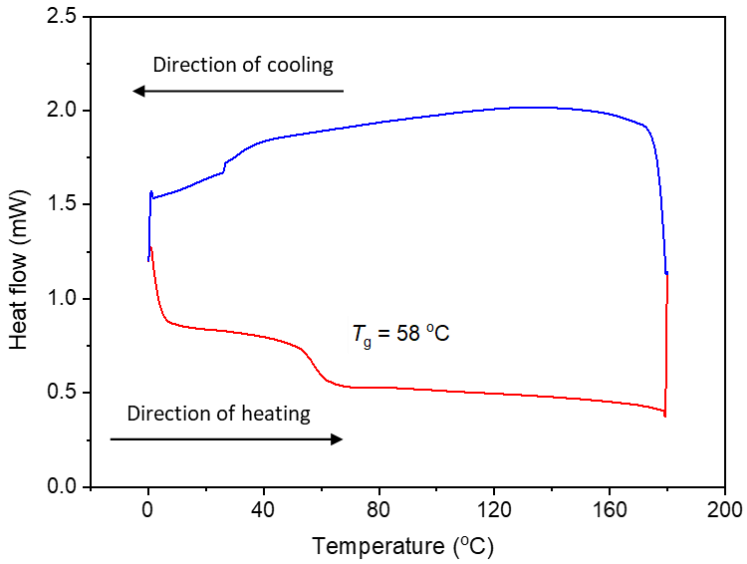


Fig. S64 DSC trace of poly(**2**) (M_n 7700 g mol^{-1} ($Đ$ 1.57)), second heating and cooling cycle between 0 and 180 °C. Single transition, corresponding to the glass transition temperature (T_g) ≈ 58 °C of the polymer.

TGA analysis of the polymer derived from 2

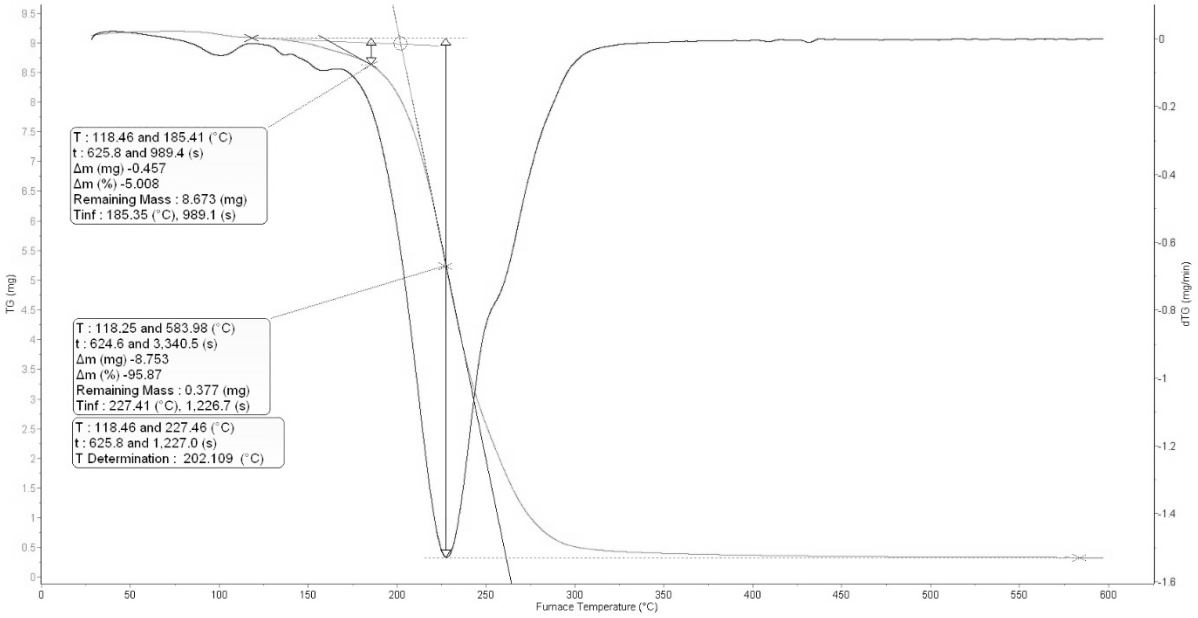


Fig. S65 TGA trace of poly(**2**) (M_n 5700 g mol^{-1} ($Đ$ 1.55)). The monomer was heated from 30 to 800 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$= 195 °C; $T_{d,max}$ = 232 °C with 3 % char remaining at 800 °C.

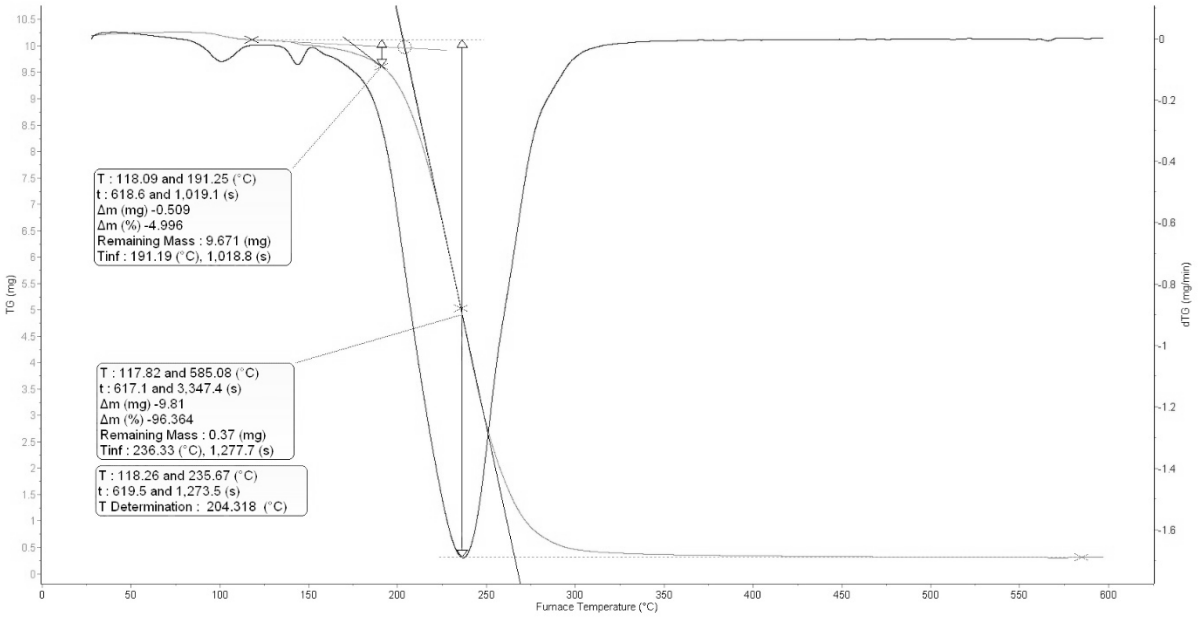


Fig. S66 TGA trace of poly(**2**) (M_n 7700 g mol^{-1} ($Đ$ 1.57)). The monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$= 191 °C; $T_{d,max}$ = 204 °C with 4 % char remaining at 600 °C.

FT-IR analysis of the polymer derived from 2

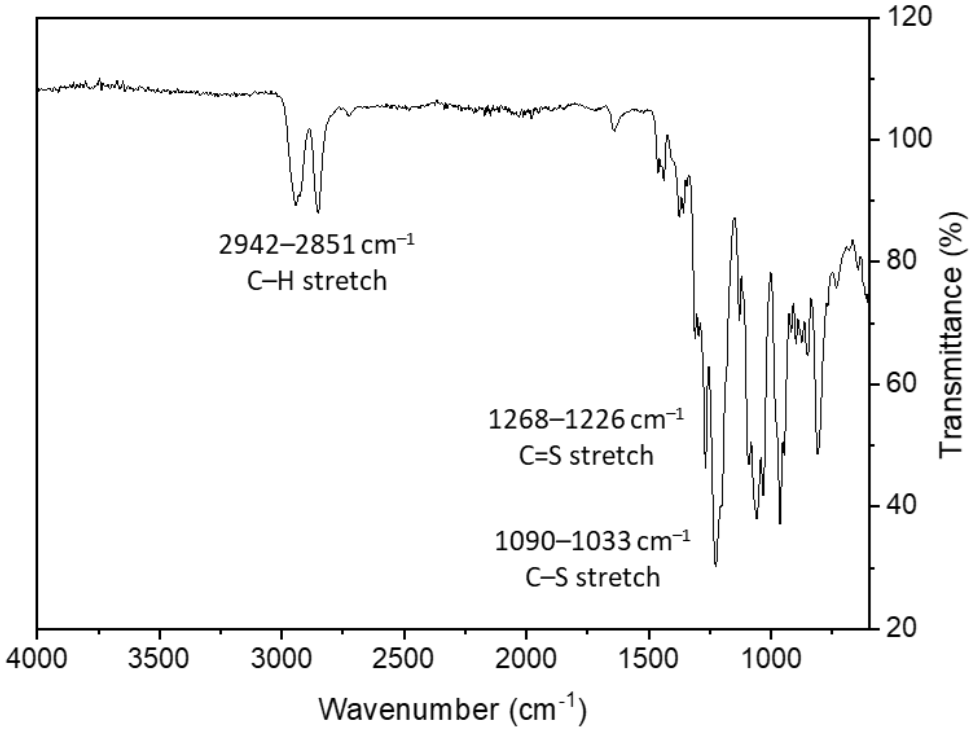


Fig. S67 Labelled FT-IR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)).

Influence of concentration on the ROP of 2

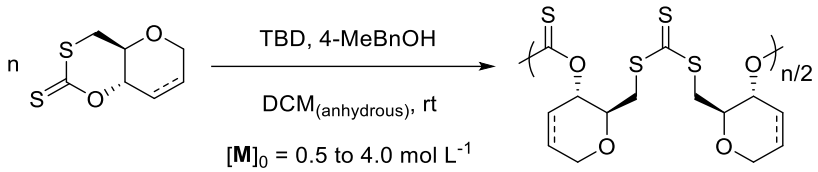


Table S1 Ring-opening polymerisation of **1** and **2** over different initial monomer concentrations.[a]

Entry	M	$[\mathbf{M}]_0$ (mol L^{-1})	Time (h)	Conv.[b] (%)	$[M]_{eq}$ (mol L^{-1})
1[1]	**1**	0.5	6	58	0.21
2[1]	**1**	1.0	6	78	0.22
3[1]	**1**	2.0	6	90	0.20
4	**2**	1.0	6	28	0.72
5	**2**	2.0	6	54	0.92
6	**2**	3.0	6	59	1.22
7	**2**	4.0	6	65	1.40

[a]Polymerisations were carried out at room temperature under an argon atmosphere, in anhydrous DCM solvent with [**M**]:[TBD]:[I] of 100:1:1 (I = 4-methylbenzylalcohol); [b]Monomer conversion to polymer, calculated based on the relative integration of the monomer proton signals and polymer signals, in the ^{1}H NMR spectrum.

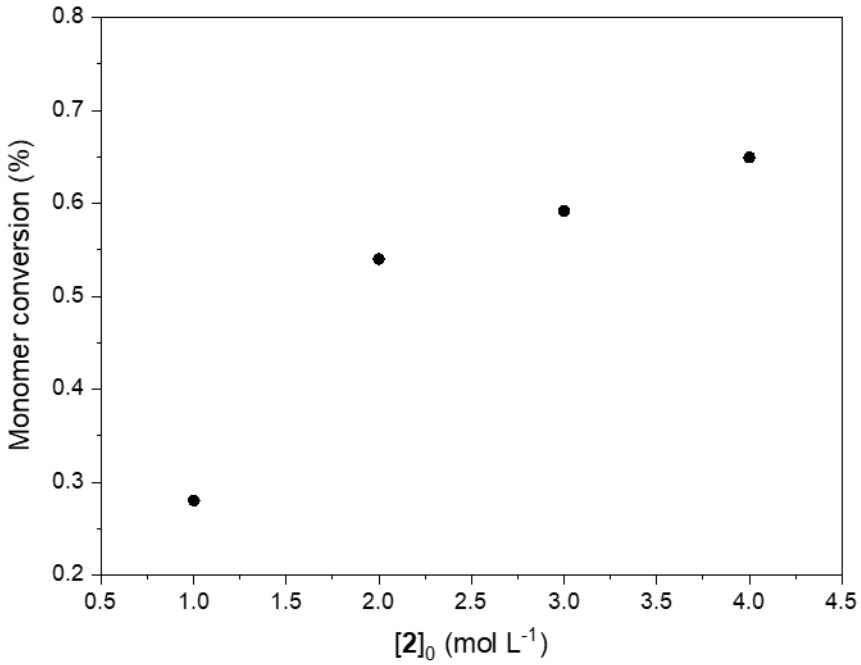


Fig. S68 Plot of monomer conversion at equilibrium *versus* $[\mathbf{2}]_0$ for the ROP of **2** with 4-MeBnOH and TBD catalyst. Carried out in DCM at room temperature, for $[\mathbf{2}]_0$ = 1.0–4.0 mol L^{-1} and $[\mathbf{2}]_0$:$[TBD]_0$:$[4\text{-MeBnOH}]_0$ = 100:1:1.

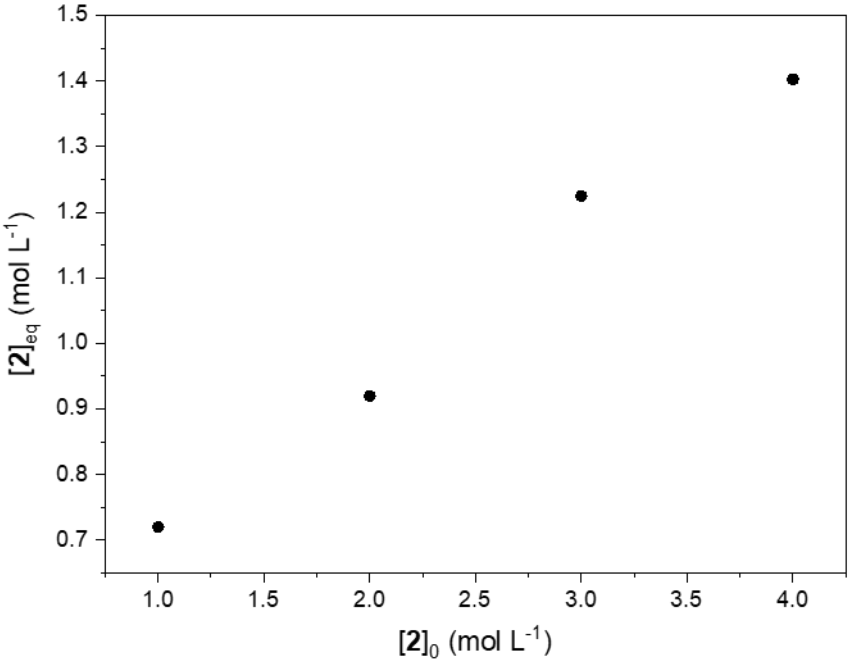


Fig. S69 Plot of $[\mathbf{2}]_{eq}$ against $[\mathbf{2}]_0$ for the ROP of **2** with 4-MeBnOH and TBD catalyst. Carried out in DCM at room temperature, for $[\mathbf{2}]_0$ = 1.0–4.0 mol L^{-1} and $[\mathbf{2}]_0$:$[TBD]_0$:$[4\text{-MeBnOH}]_0$ = 100:1:1.

Determination of ROP thermodynamic parameters of 2

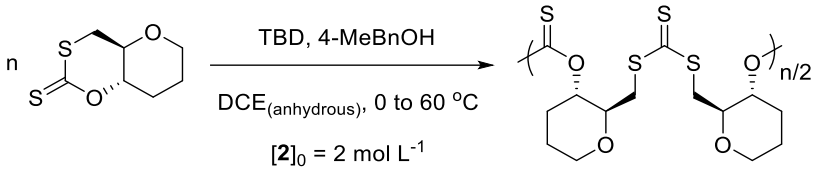


Table S2 Ring-opening polymerisation of **2** over a 0–60 °C temperature range.[a]

Entry	Temp. (°C)	$[\mathbf{1}]_0$:$[TBD]_0$:$[I]_0$[b]	Time (h)	Conv.[c] (%)	$M_{n,CALC}$[d]	$M_{n,SEC}$[e]	$M_{w,SEC}$[e]	$Đ_M$ [e]
1	0	100:1:1	20	27	5260	4700	6500	1.35
3	20	100:1:1	20	19	3740	4200	5400	1.27
5	40	100:1:1	20	14	2410	4100	5000	1.23
7	60	100:1:1	20	3	690	-	-	-

[a]Polymerisations were carried out at different temperatures, under an argon atmosphere, in anhydrous 1,2-dichloroethane solvent with initial $[\mathbf{2}]_0$ = 2 mol L^{-1} (**2** = monomer); [b]I = 4-methylbenzylalcohol; [c]Monomer conversion to polymer, calculated based on the relative integration of the H-4' proton signal of **2** (δ_H = 4.21-4.11) and poly(**2**) (δ_H = 5.18-5.06), in the ^{1}H NMR spectrum; [d]Number-average molecular weight as calculated using $M_r(I)+(M_r(monomer) \times [monomer]_0/[I]_0 \times conv/100\%)$, units given in g mol^{-1}; [e]Number-average molecular weight and dispersity ($M_{n,SEC}$, $M_{w,SEC}$, $Đ_M$), calculated by SEC relative to polystyrene standards in THF eluent, units given in g mol^{-1}.

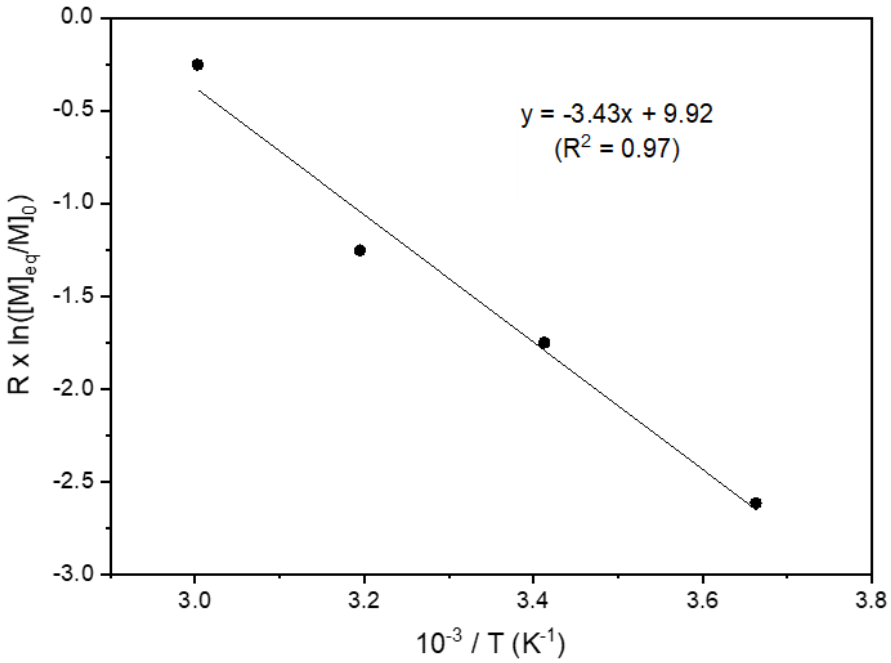


Fig. S70 ROP of **2** with 4-MeBnOH and TBD catalyst: calculation of the thermodynamic parameters from a plot of R x $\ln([\mathbf{M}]_{eq}/[\mathbf{M}]_0)$ as a function of 1/T, where T is the absolute temperature. Carried out in 1,2-dichloroethane, over a temperature range of 0–60 °C for $[\mathbf{2}]_0$ = 2.0 mol L^{-1} and $[\mathbf{2}]_0$:$[TBD]_0$:$[4\text{-MeBnOH}]_0$ = 100:1:1.

$$R \times \ln\left(\frac{\mathrm{M_{eq}}}{\mathrm{M_0}}\right) = \frac{\Delta H_\mathrm{p}}{\mathrm{T}} - \Delta S_\mathrm{p}$$

$$R \times \ln\left(\frac{\mathrm{M_{eq}}}{\mathrm{M_0}}\right) = -3.43\mathrm{x} + 9.92$$

$$T_\mathrm{c} = \frac{\Delta H_\mathrm{p}}{\Delta S_\mathrm{p}} = \frac{-3430\ \mathrm{J\ mol^{-1}}}{-9.92\ \mathrm{J\ K^{-1} mol^{-1}}} = 346\ \mathrm{K} = 73\ ^\circ\mathrm{C}$$

Standardised entropy of polymerisation for different concentrations

$$\Delta S_\mathrm{p} = \Delta S_\mathrm{p}^0 + (\mathrm{R} \times \ln([\mathrm{M}]))$$

$$\Delta S_\mathrm{p}^0 = \Delta S_\mathrm{p} - (\mathrm{R} \times \ln([\mathrm{M}]))$$

$$\Delta S_\mathrm{p}^0 = -9.92 - (8.3145 \times \ln(2)) = -15.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Property	Value	Unit	Property	Value	Unit
[M]	2	mol L^{-1}	[M]	1	mol L^{-1}
ΔH_p	-3.43	kJ mol^{-1}	ΔH_p	-3.43	kJ mol^{-1}
ΔS_p (2 M)	-9.92	J mol^{-1} K^{-1}	ΔS_p (1 M)	-15.7	J mol^{-1} K^{-1}

NMR analysis of poly(2) after heating to 180 °C

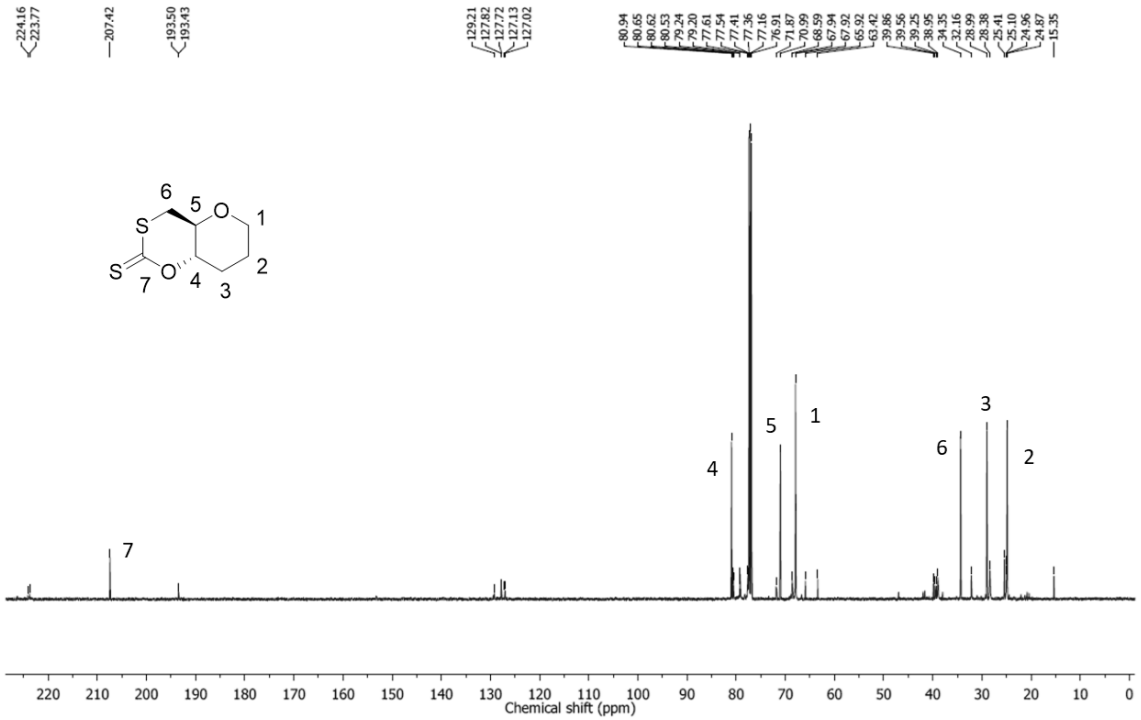


Fig. S71 Annotated $^{13}C\{^1H\}$ NMR spectrum of poly(**2**) (M_n 6400 g mol^{-1} ($Đ$ 1.60)), after heating to 180 °C, in chloroform-d.

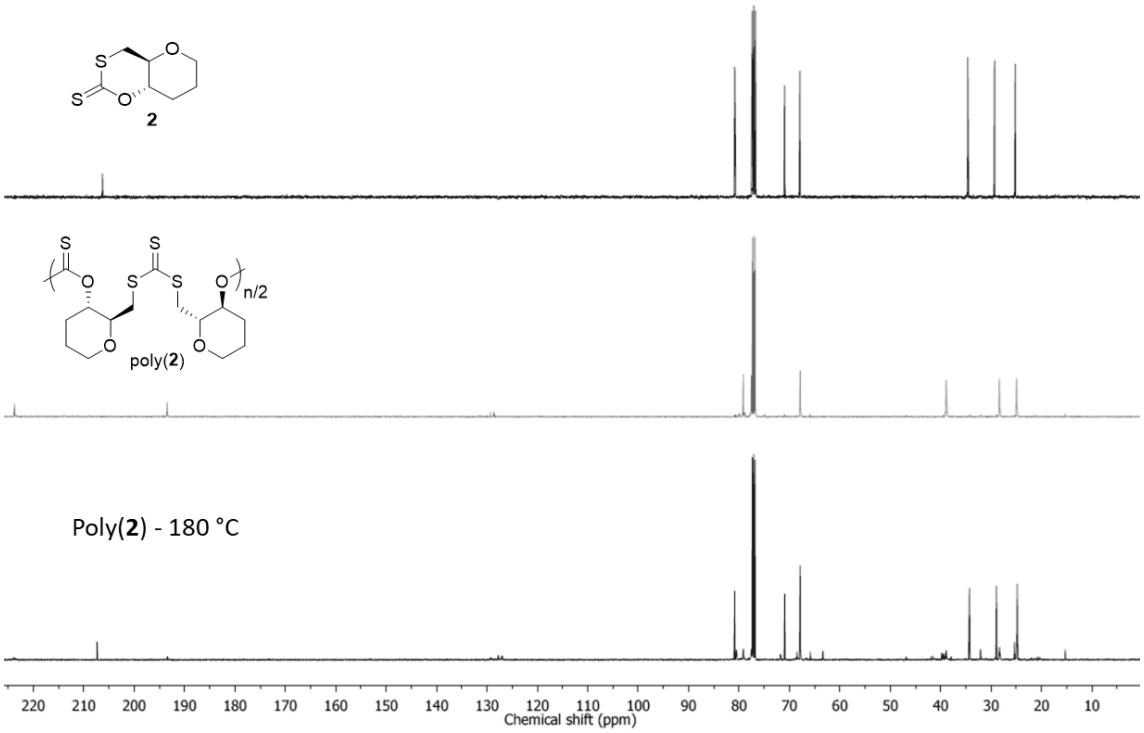


Fig. S72 Stacked $^{13}C[^{1}H]$ NMR spectra of monomer **2** (top), poly(**2**) (middle) and poly(**2**) once heated to 180 °C for 5 minutes (bottom). Poly(**2**) was placed in a sample vial and heated without solvent, NMR spectra indicates an almost quantitative recovery of the xanthate monomer.

Size-Exclusion Chromatography analysis of poly(2) after heating to 180 °C

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	908	606	989	1457	1938	1388	1.632

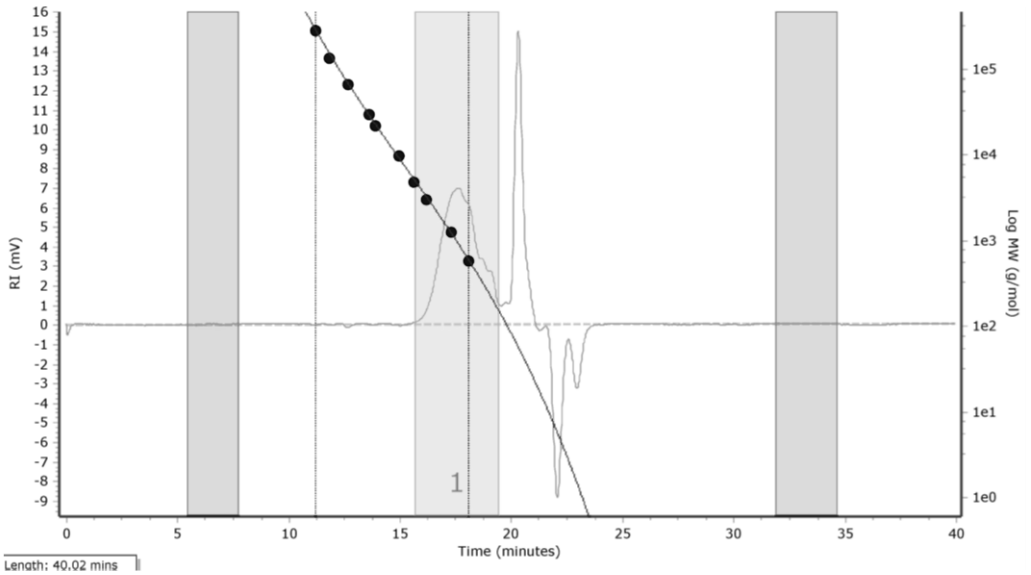


Fig. S73 SEC trace of supernatant obtained from precipitating poly(**2**) (M_n 5500 g mol^{-1} ($Đ$ 1.54)) after heating to 180 °C.

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	2376	1979	2401	2842	3293	2776	1.213

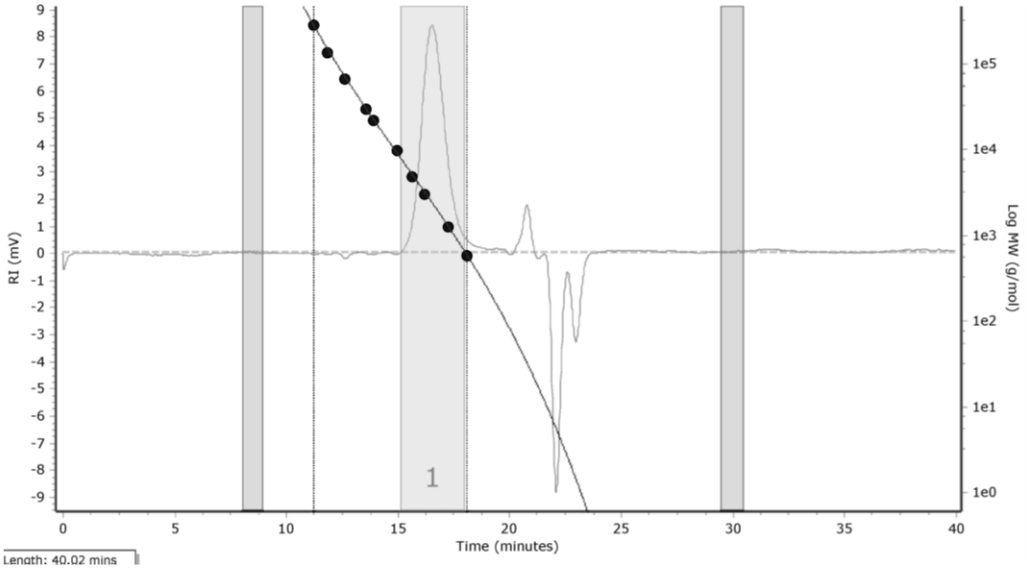
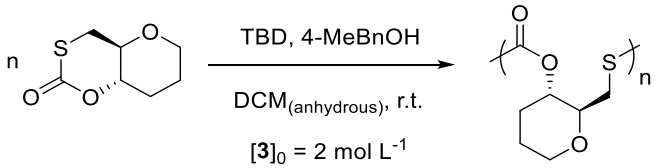


Fig. S74 SEC trace of solid obtained from precipitating poly(**2**) (M_n 5500 g mol^{-1} ($Đ$ 1.54)) after heating to 180 °C.

Ring opening polymerisation of 3



Under an argon atmosphere 4-MeBnOH (11.5 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.0057 mmol, 1.0 equiv.) and TBD (11.5 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.0057 mmol, 1.0 equiv.) were added to a solution of monomer **3** (0.100 g, 0.574 mmol, 10 equiv.) in anhydrous DCM (0.58 mL, 1.0 mol dm^{-3}). The mixture was stirred at room temperature for 6 h and quenched by the addition of a benzoic acid solution (≈ 30 equiv.). The solvent was removed under reduced pressure and the crude solid was mixed with $CHCl_3$ and precipitated from Et_2O. The product was isolated by centrifugation (3500 rpm, 2 x 5 minutes), washed twice with Et_2O and dried under vacuum. The polymer was isolated as a white solid.

δ_H (500 MHz; chloroform-d): 4.71-4.58 (C^{4}H, 1H, m), 3.93 (C^{1}H, 1H, d, J_{HH} = 11.5 Hz), 3.54-3.36 (C^{5}H, C^{1}H, 2H, m), 3.25 (C^{6}H, 1H, d, J_{HH} = 12.5 Hz), 2.92 (C^{6}H, 1H, dd, J_{HH} = 14.2, 7.8 Hz), 2.25 (C^{3}H, 1H, d, J_{HH} = 8.7 Hz), 1.80-1.66 (C^{2}H, 2H, m), 1.63-1.49 (C^{3}H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 171.2 (C^7), 78.2 (C^5), 74.7 (C^4), 68.1 (C^1), 33.1 (C^6), 29.0 (C^3), 24.8 (C^2) ppm. ν_{max} (cm^{-1}): 2954-2861 (CH), 1710 (C(O)SO), 1147-1061 (C–O), 1147-1061 (C–S).

NMR analysis of the polymer derived from 3

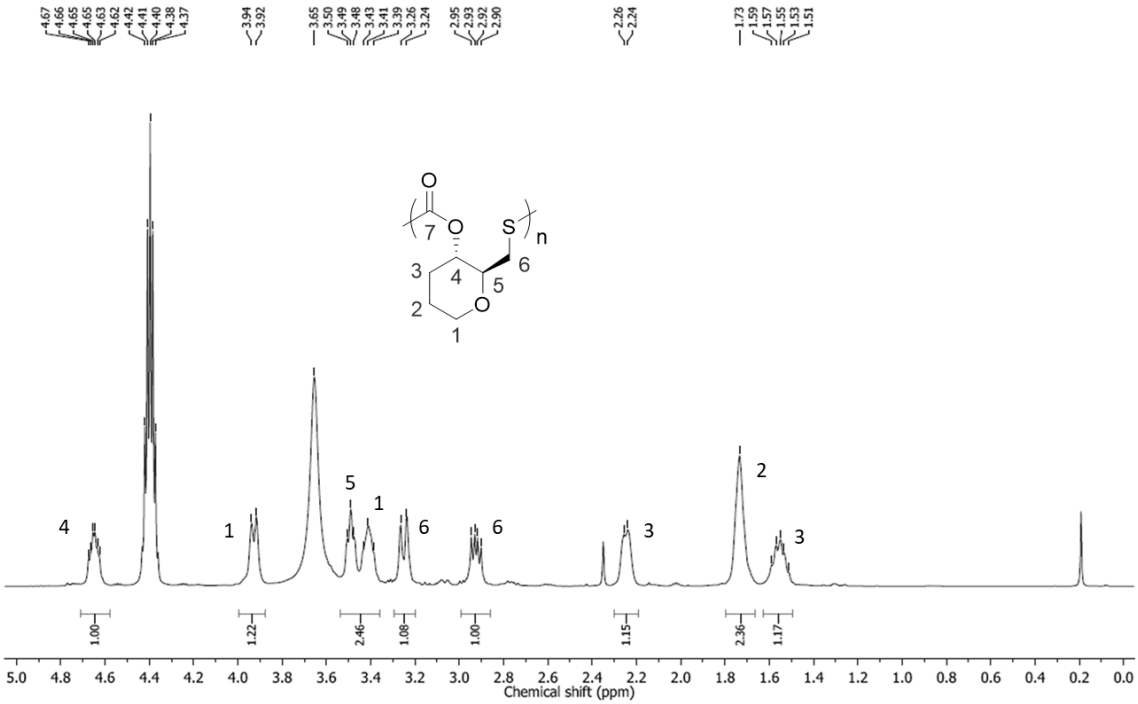


Fig. S75 Annotated ^{1}H NMR spectrum of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)) in chloroform-d. Peaks due to HFIP visible at 4.40 (q), 3.65 (s, br) ppm.

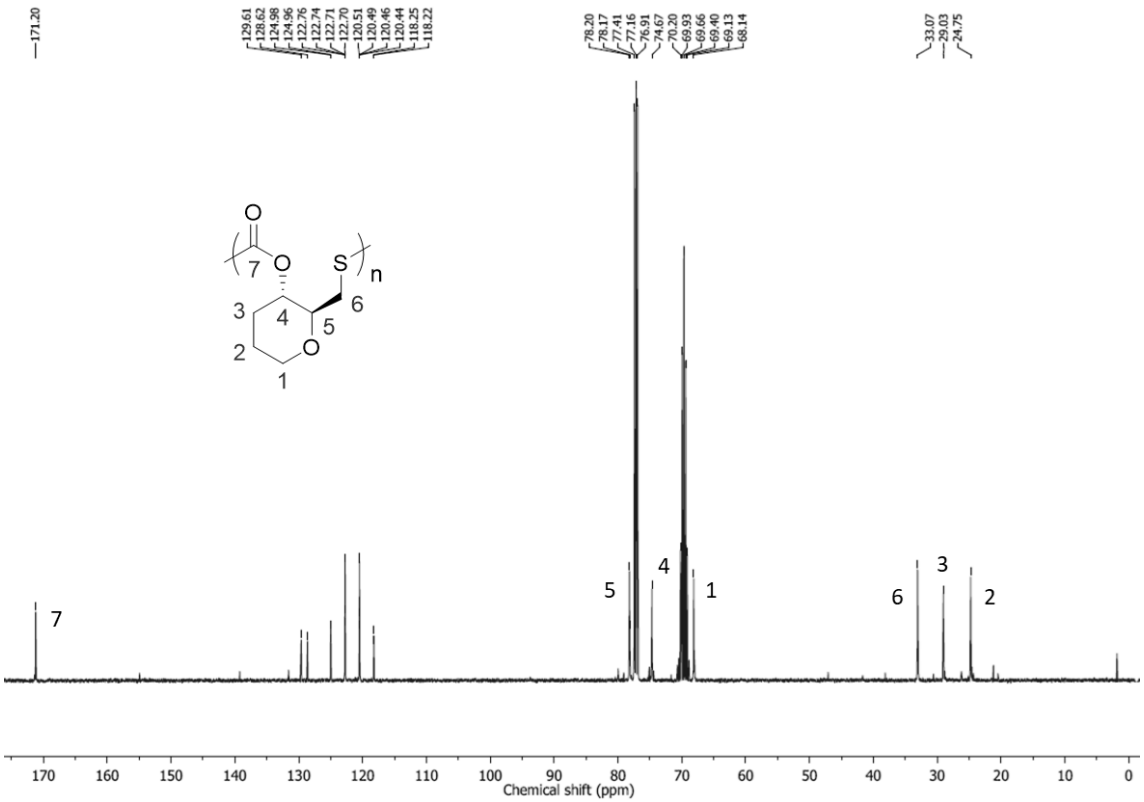


Fig. S76 Annotated ^{13}C{^{1}H} NMR spectrum of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)) in chloroform-d. Peaks due to HFIP visible at 121.5 (q), 69.7 (m) ppm.

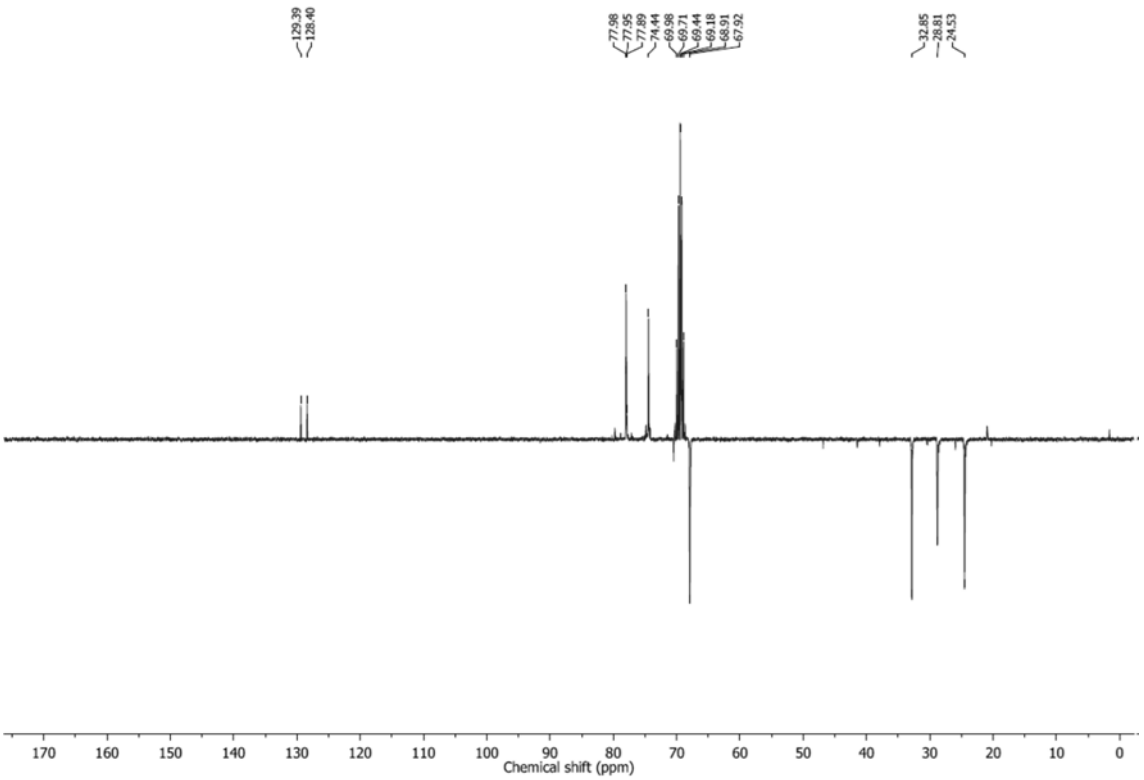


Fig. S77 $^{13}C\{^{1}H\}$ DEPT135 NMR spectrum of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)) in chloroform-d.

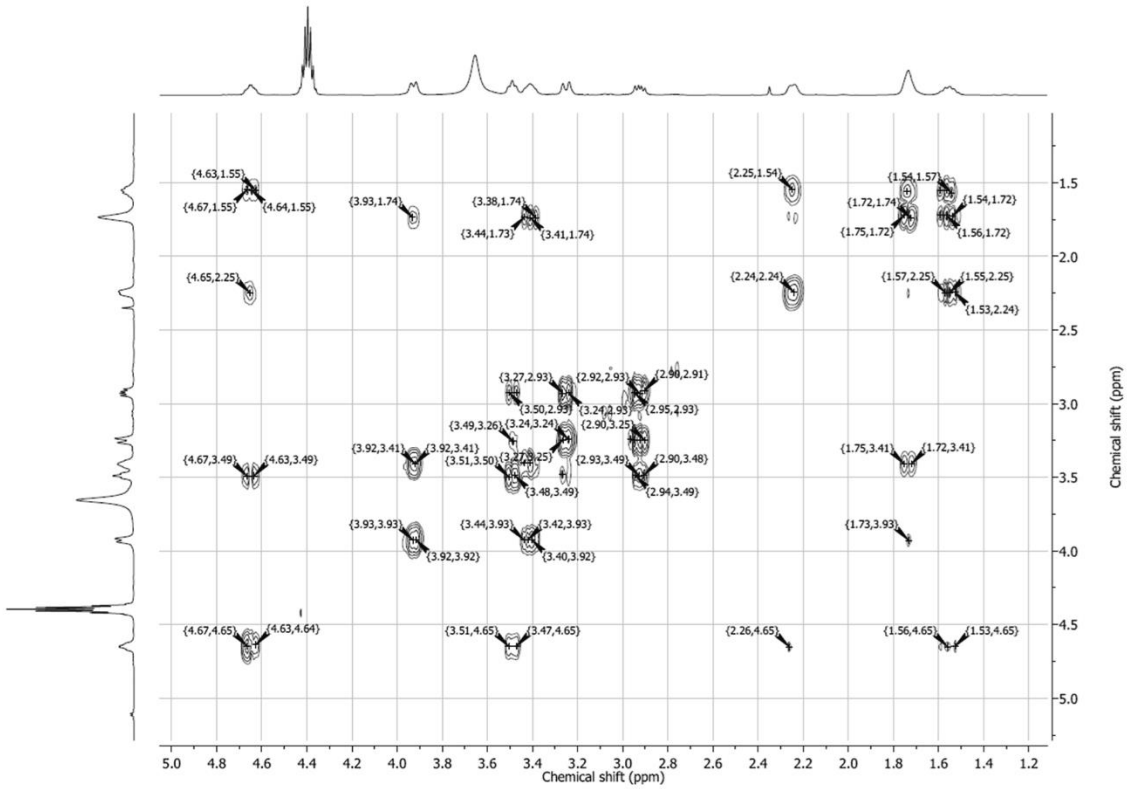


Fig. S78 COSY (^{1}H–^{1}H) NMR spectrum of poly(**3**) (M_n 2600 g mol^{-1} (Đ 1.50)) in chloroform-d.

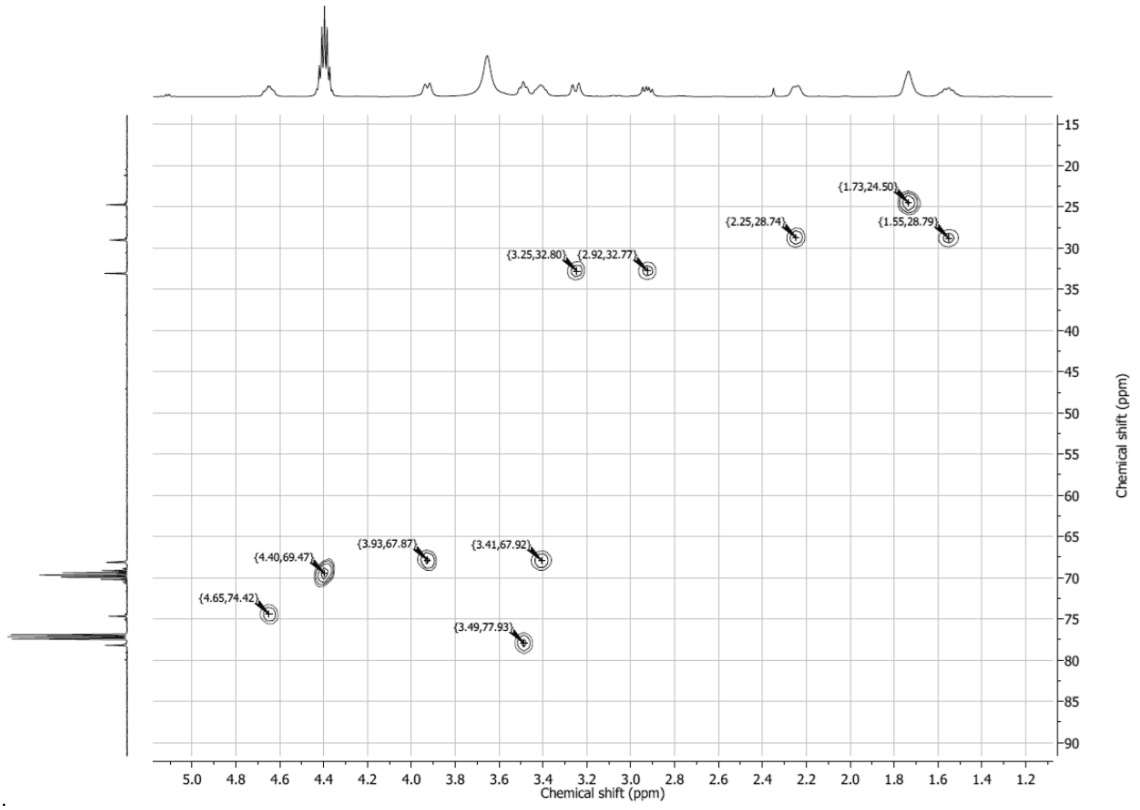


Fig. S79 HSQC ($^{1}H–^{13}C$) NMR spectrum of poly(**3**) (M_n 2600 g mol–1 (*Đ* 1.50)) in chloroform-d.

Size-Exclusion Chromatography analysis of the polymer derived from 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	4126	2645	3957	5650	7529	5387	1.496

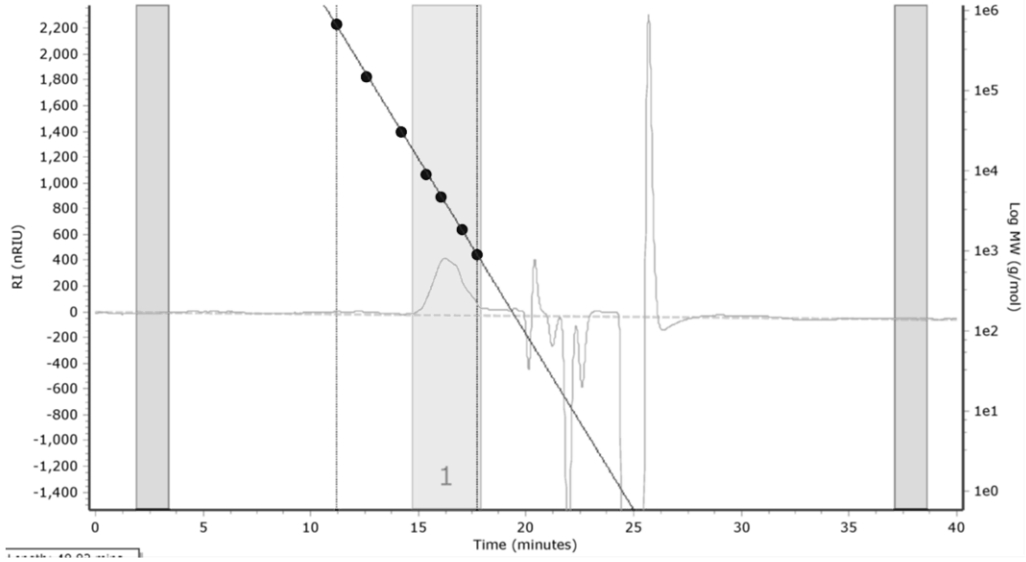


Fig. S80 SEC trace of poly(**3**) (M_n 2600 g mol^{-1} (*Đ* 1.50)).

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	4267	2830	4124	5635	7154	5413	1.457

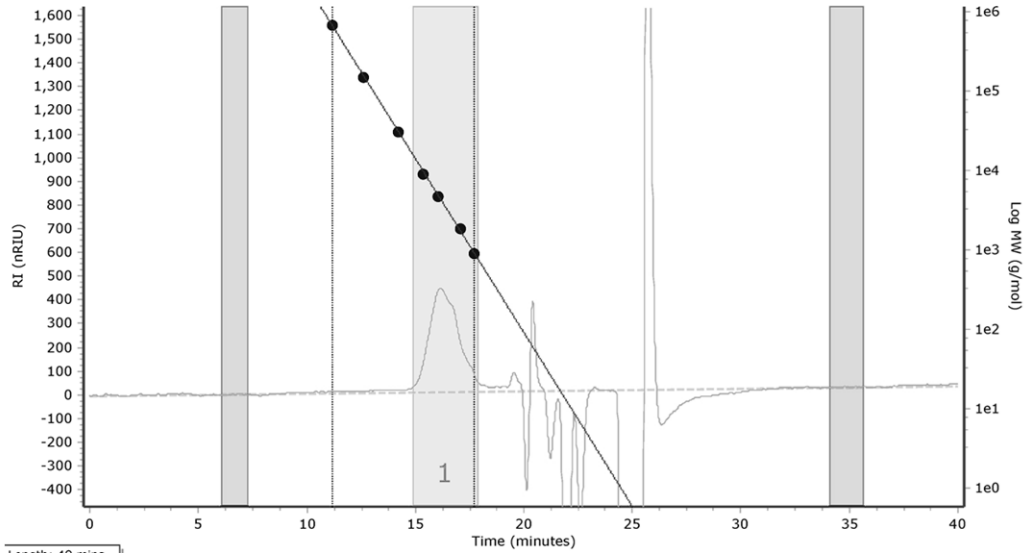


Fig. S81 SEC trace of poly(**3**) (M_n 2800 g mol^{-1} ($Đ$ 1.46)).

DSC analysis of the polymer derived from 3

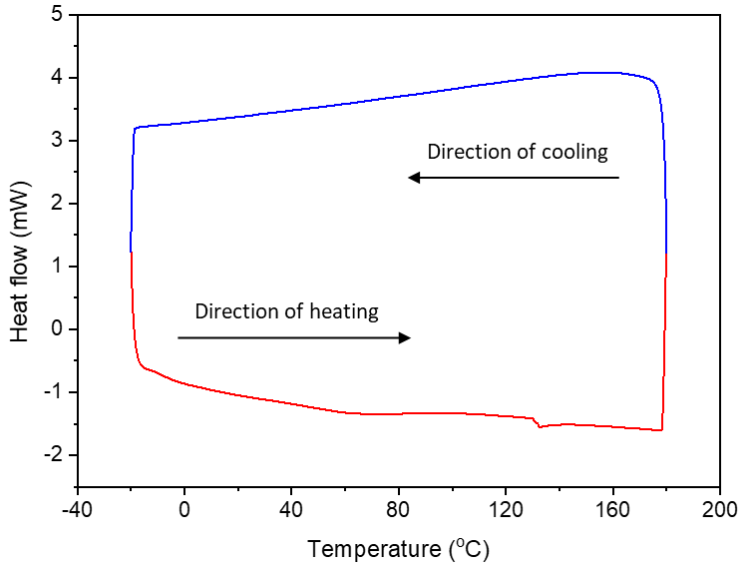


Fig. S82 DSC trace of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)), first heating and cooling cycle between -20 and 180 °C. No peaks visible in DSC thermogram.

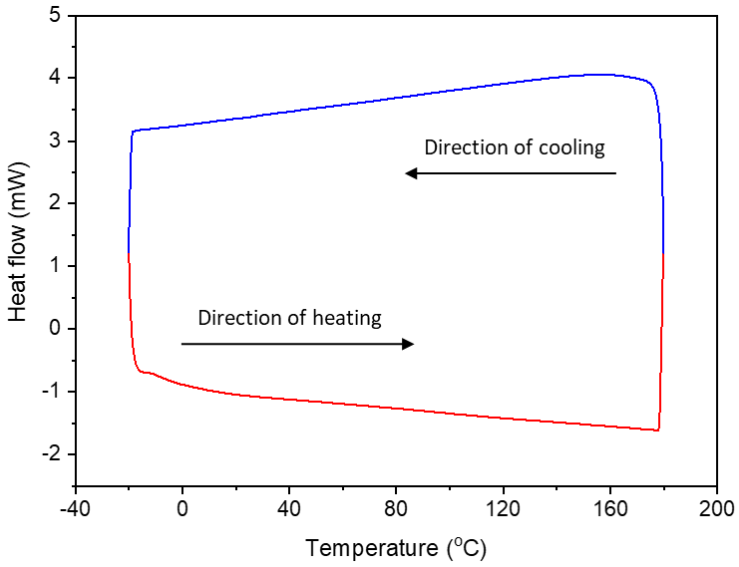


Fig. S83 DSC trace of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)), second heating and cooling cycle between -20 and 180 °C. No peaks visible in DSC thermogram.

TGA analysis of the polymer derived from 3

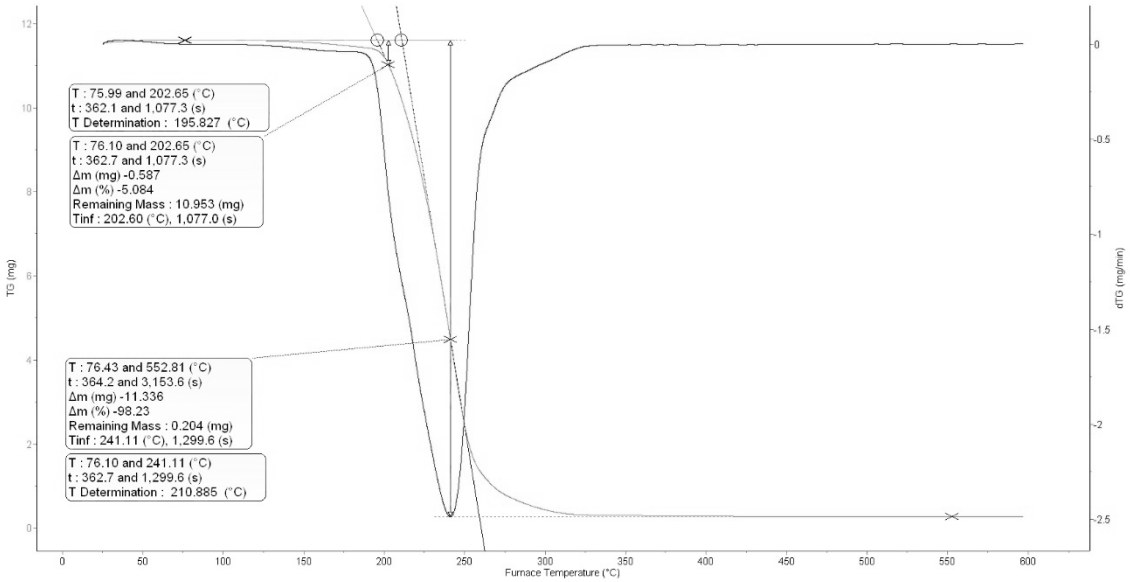


Fig. S84 TGA trace of poly(**3**) (M_n 2800 g mol^{-1} ($Đ$ 1.46)). The monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 203 °C; $T_{d,max}$ = 241 °C with 2 % char remaining at 600 °C.

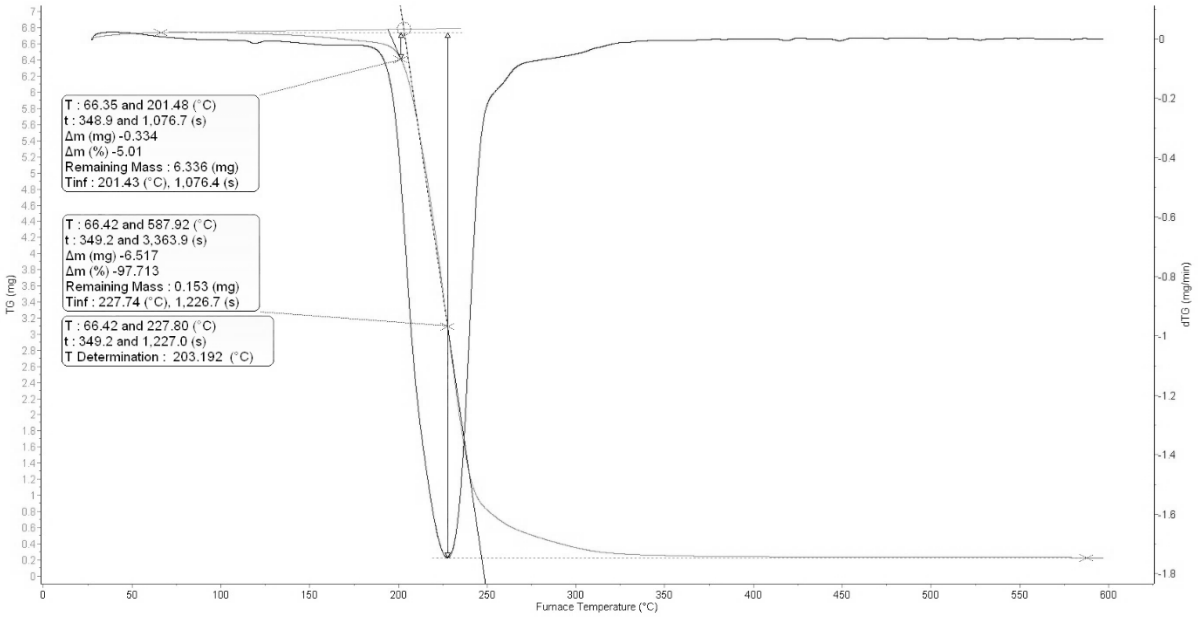


Fig. S85 TGA trace of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)). The monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 202 °C; $T_{d,max}$ = 228 °C with 2 % char remaining at 600 °C.

DMA analysis of the polymer derived from 3

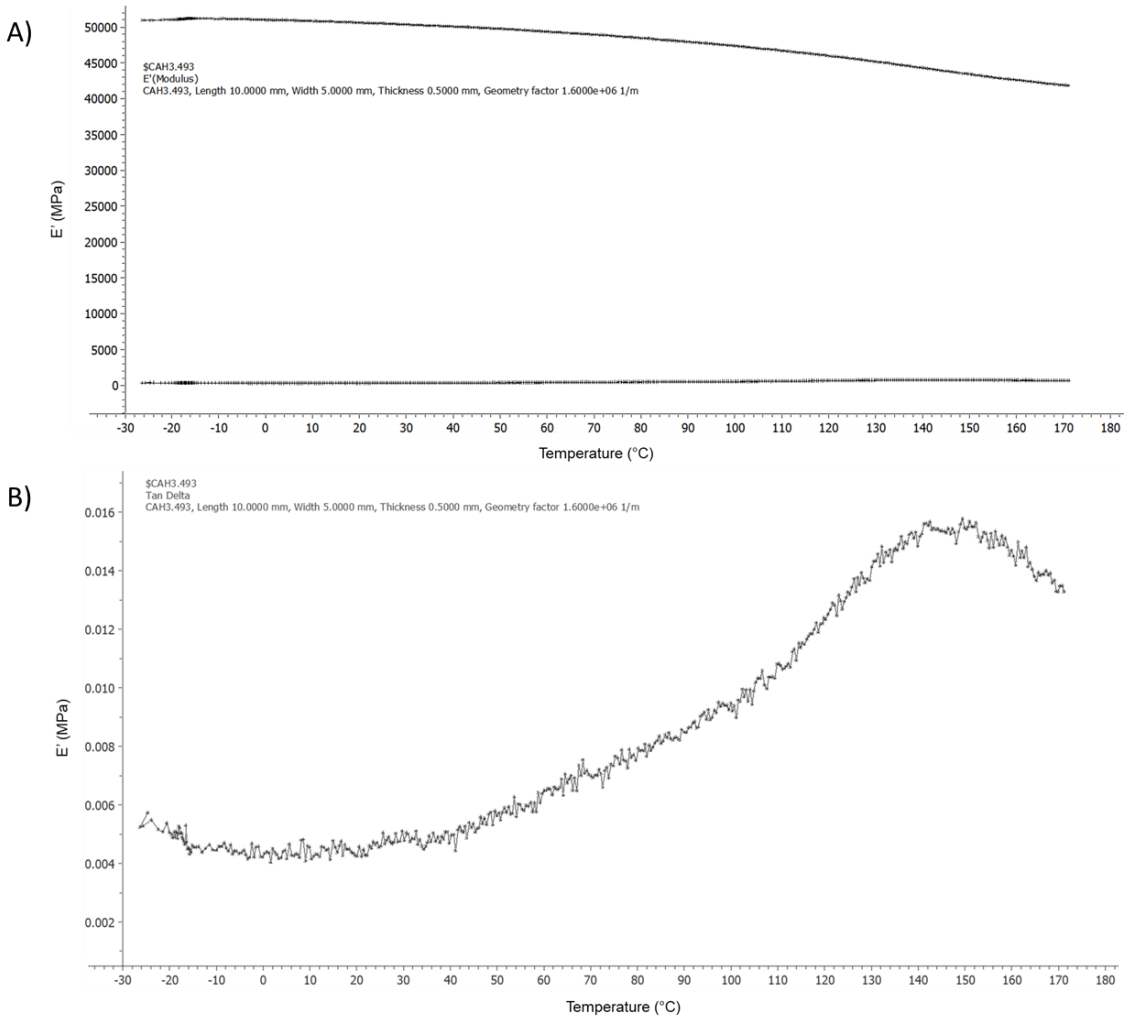


Fig. S86 DMA temperature sweep test of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50)): A) Storage modulus; B) Loss modulus. The monomer was heated from -20 to 180 °C under argon at 3 °C min^{-1}. Single transition observed corresponding to an unknown alteration to the polymer structure T_{max} = 150 °C.

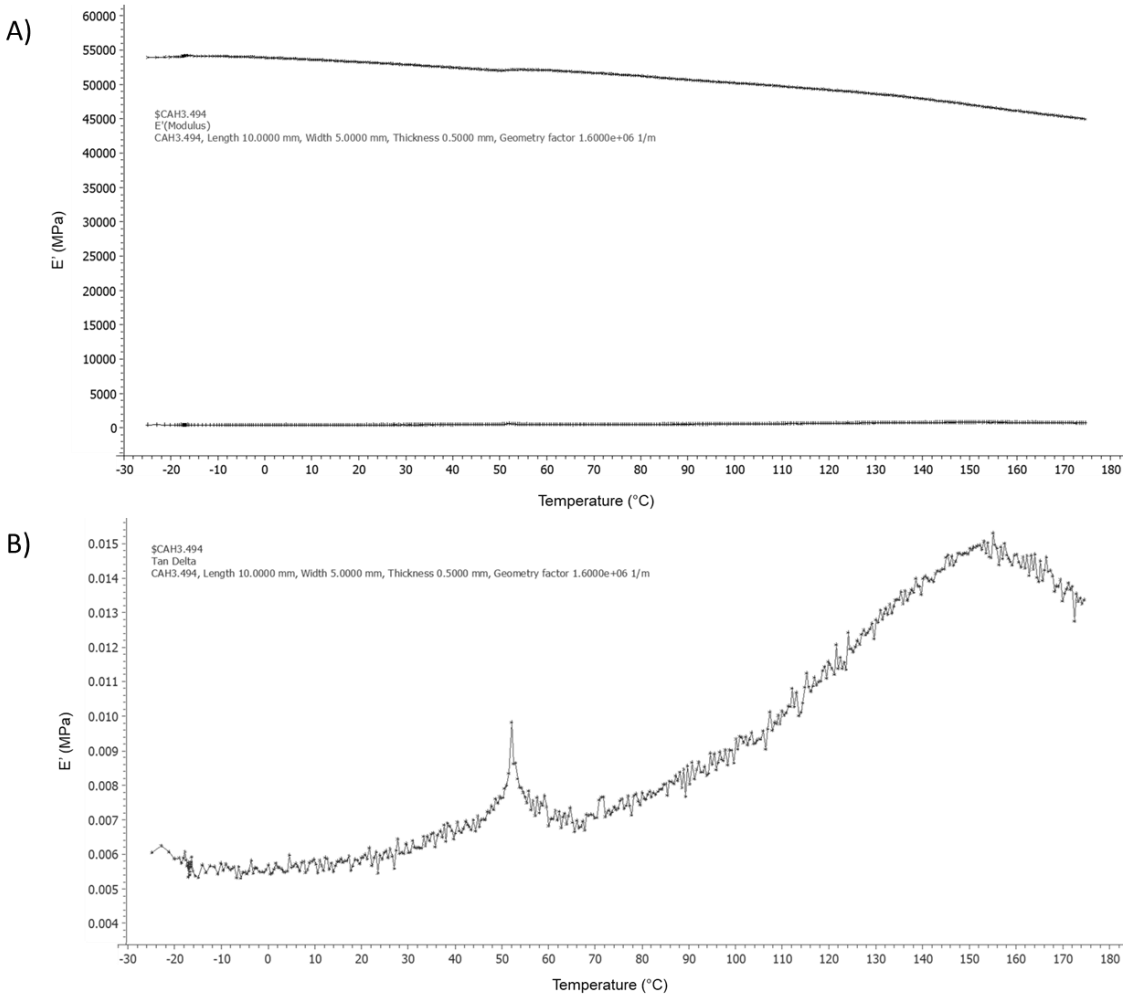


Fig. S87 DMA temperature sweep test of poly(**3**) (M_n 2800 g mol^{-1} ($Đ$ 1.46)):)): A) Storage modulus; B) Loss modulus. The monomer was heated from -20 to 180 °C under argon at 3 °C min^{-1}. Single transition observed corresponding to an unknown alteration to the polymer structure T_{max} = 155 °C.

FT-IR analysis of the polymer derived from 3

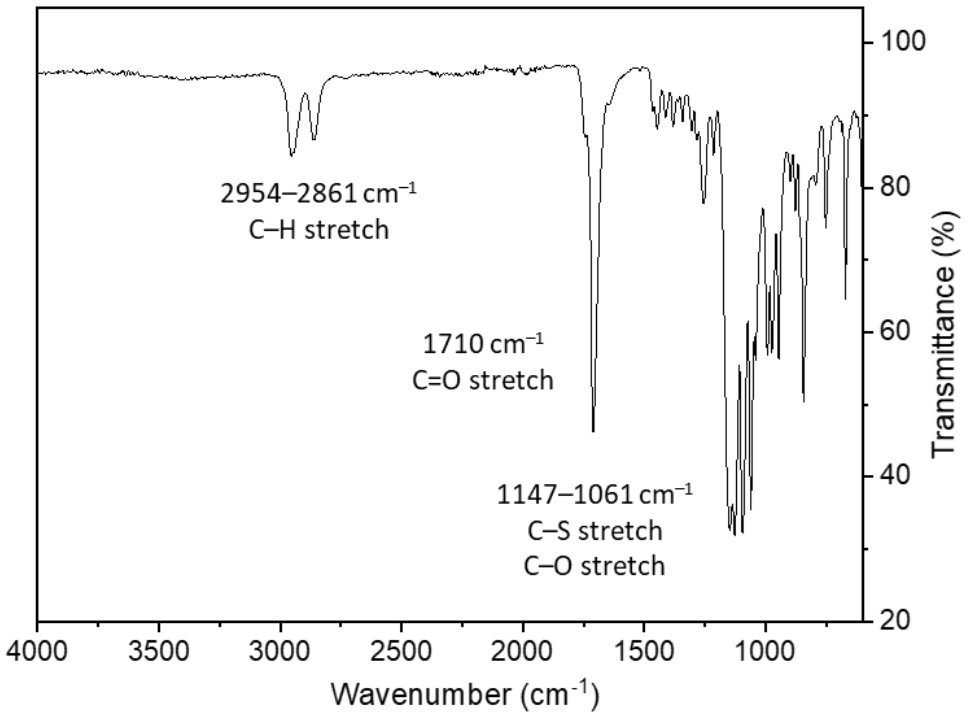
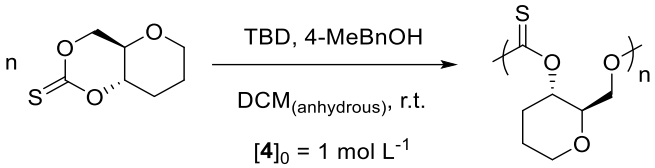


Fig. S88 Labelled FT-IR spectrum of poly(**3**) (M_n 2600 g mol^{-1} ($Đ$ 1.50))**.**

Ring opening polymerisation of 4



Under an argon atmosphere 4-MeBnOH (11.5 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.006 mmol, 1.0 equiv.) and TBD (11.5 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.006 mmol, 1.0 equiv.) were added to a solution of monomer **4** (0.100 g, 0.574 mmol, 100 equiv.) in anhydrous DCM (0.57 mL, 1.0 mol L^{-1}). The mixture was stirred at room temperature for 1 h and quenched by the addition of a benzoic acid solution (≈ 30 equiv.). The solvent was removed under reduced pressure and the crude solid was dissolved in $CHCl_3$ and precipitated from Et_2O. The product was isolated by centrifugation (3500 rpm, 2 x 5 minutes), washed twice with Et_2O and dried under vacuum. The polymer was isolated as a white solid.

δ_H (500 MHz; chloroform-d): 5.17-5.04 (C^4H, 1H, m), 4.68-4.38 (C^6H, 2H, m), 4.01-3.91 (C^1H, 1H, m), 3.78-3.64 (C^5H, 1H, m), 3.44-3.35 (C^1H, 1H, m), 2.46-2.34 (C^3H, 1H, m), 1.84-1.67 (C^2H, 2H, m), 1.61-1.48 (C^3H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 195.4 (C^7), 194.1 (C^7), 193.1 (C^7), 76.7 (C^5), 76.6 (C^4), 72.2 (C^1), 67.8 (C^6), 28.3 (C^3), 24.8 (C^2) ppm. ν_{max} (cm^{-1}): 2948-2854 (CH), 1220 ($C(S)O_2$), 1098 (C–O).

NMR analysis of the polymer derived from 4

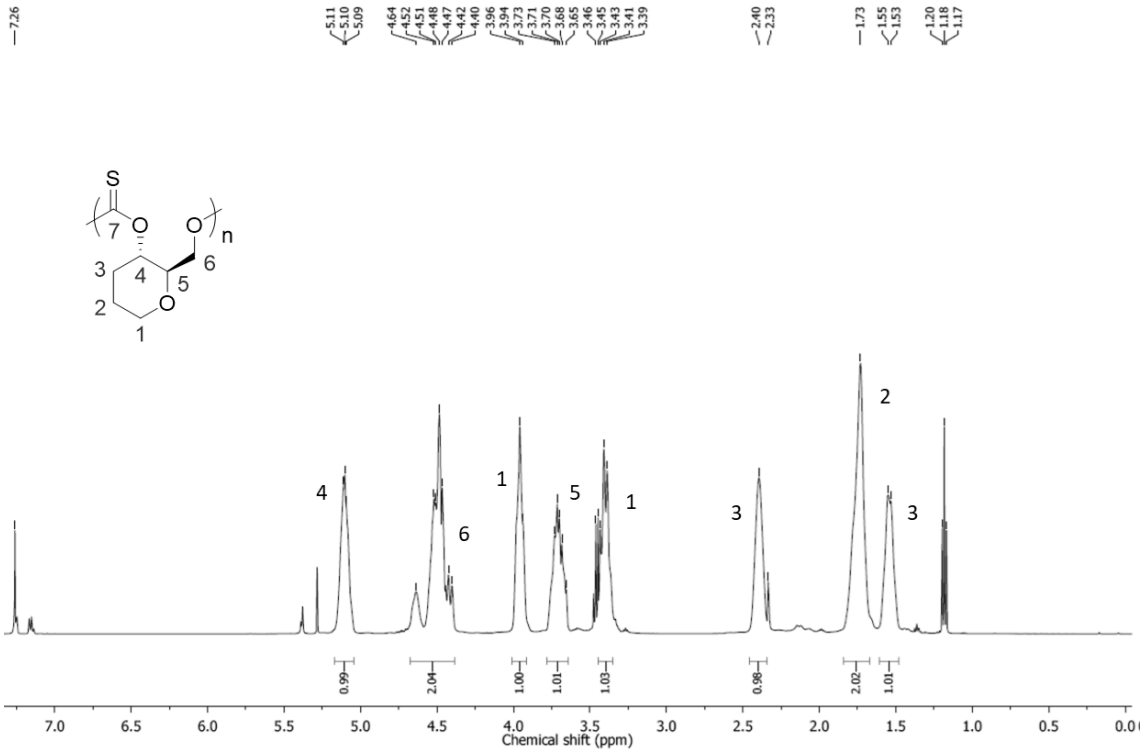


Fig. S89 Annotated ^1H NMR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)) in chloroform-d.

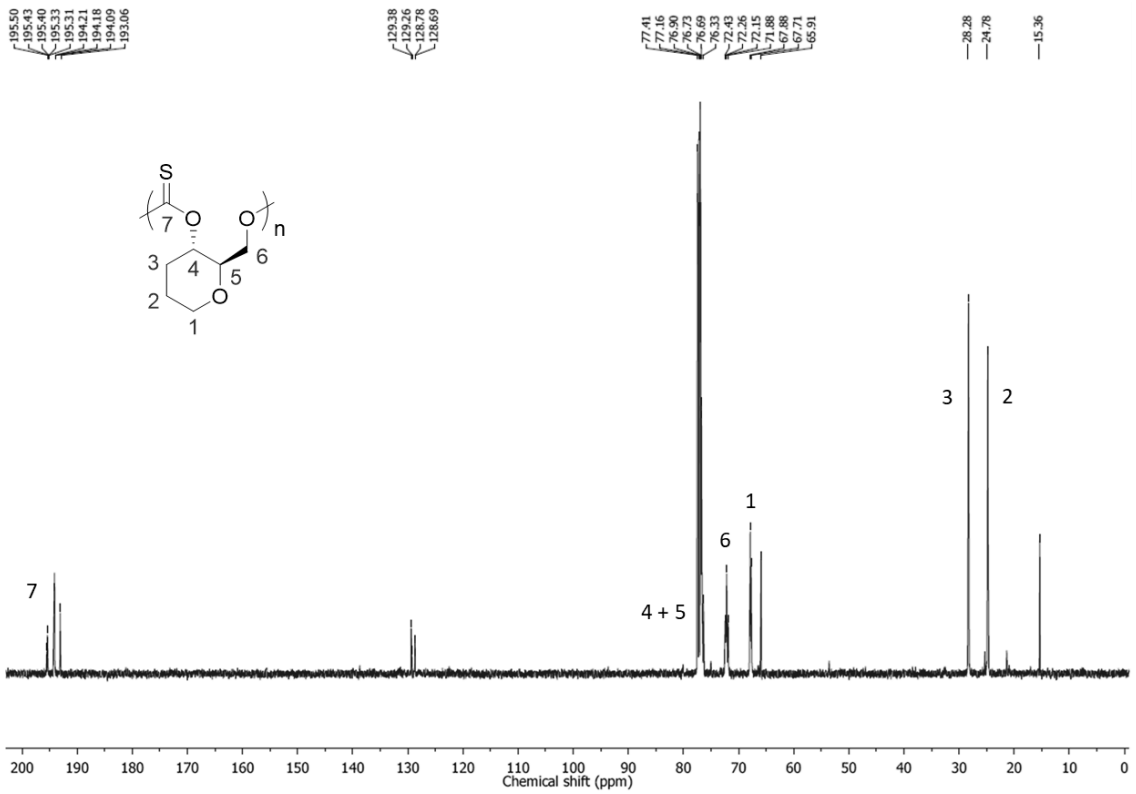


Fig. S90 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)) in chloroform-d.

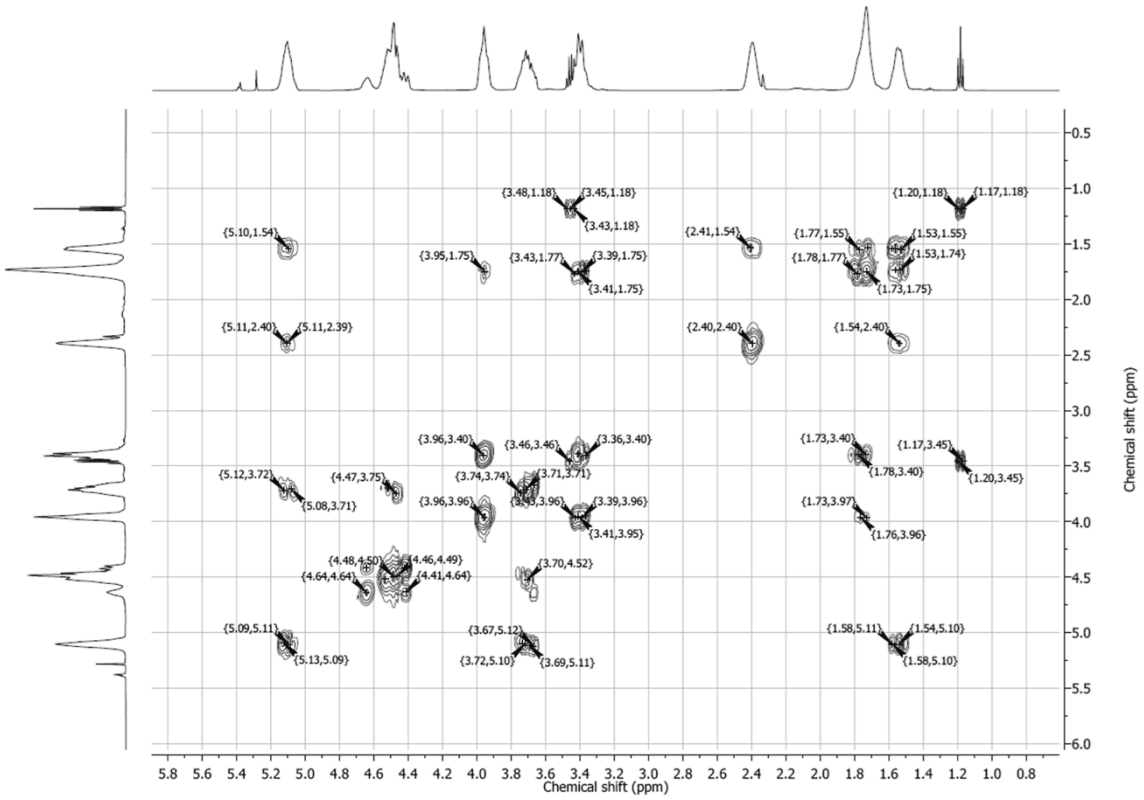


Fig. S91 COSY (^{1}H–^{1}H) NMR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)) in chloroform-d.

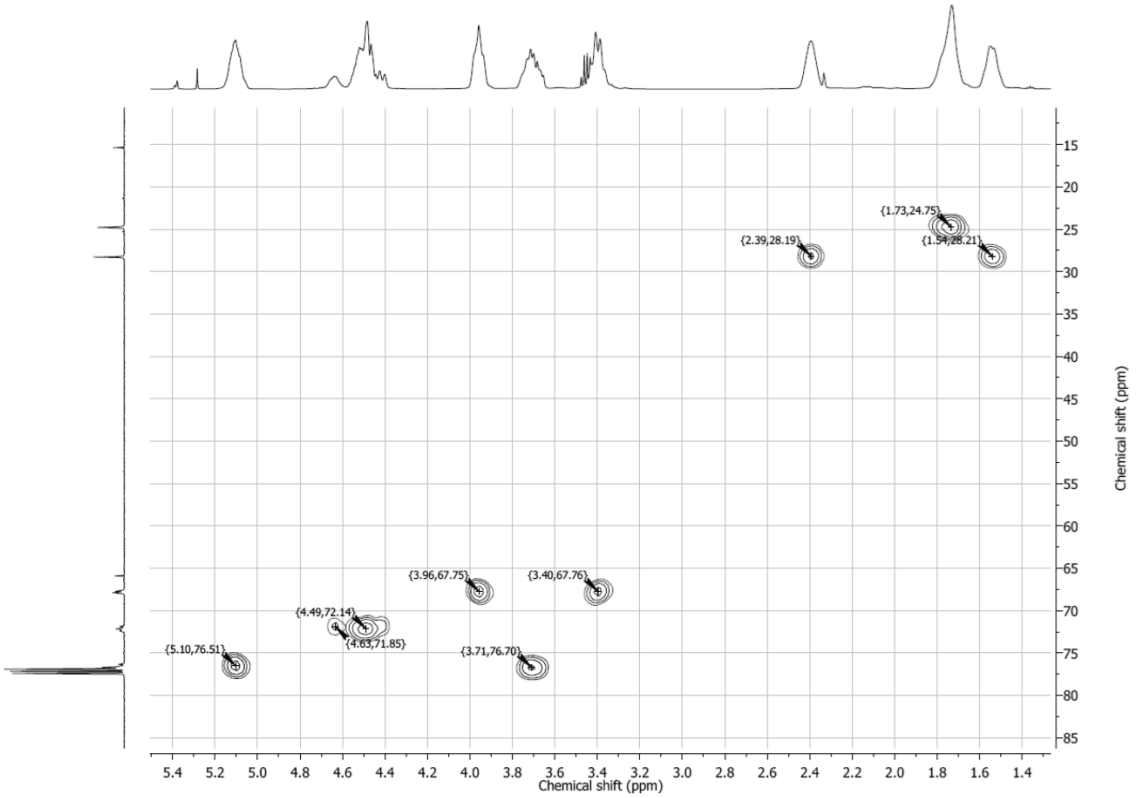


Fig. S92 HSQC (^{1}H–^{13}C) NMR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)) in chloroform-d.

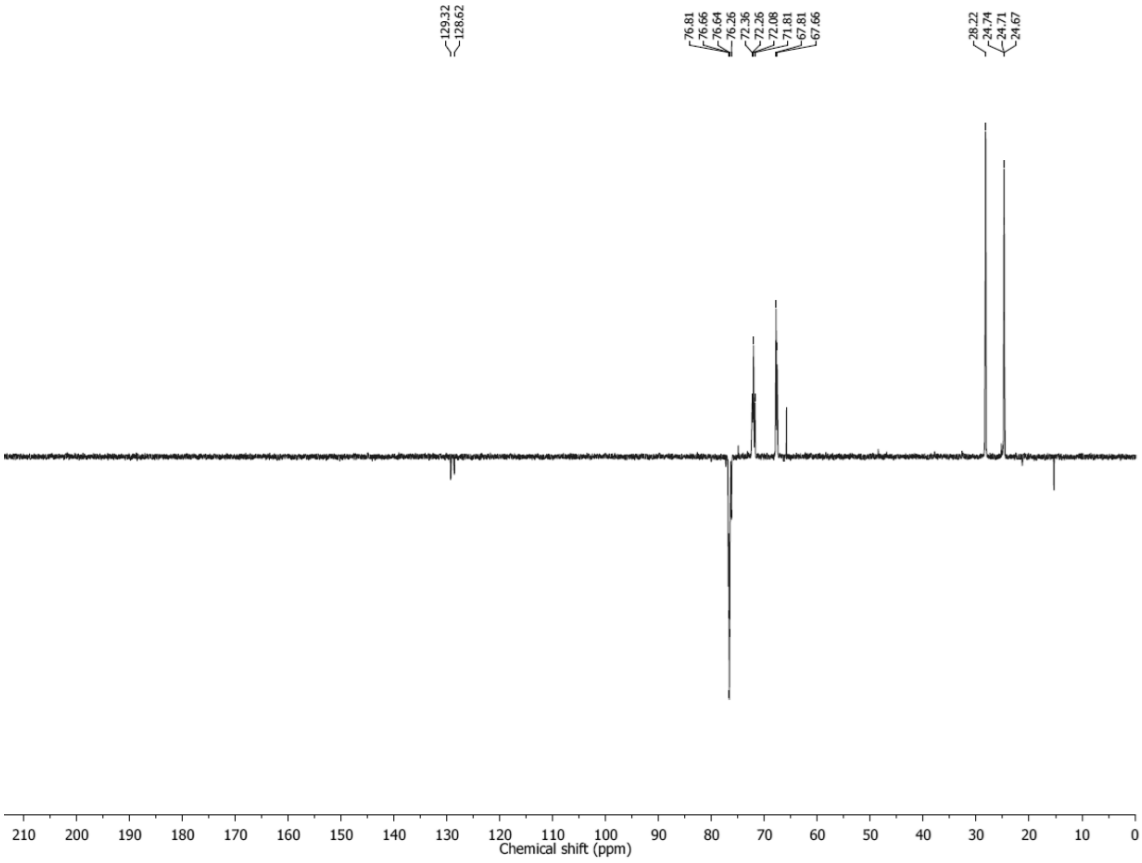


Fig. S93 ^{13}C{^{1}H} DEPT135 NMR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)) in chloroform-d.

Size-Exclusion Chromatography analysis of the polymer derived from 4

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	7974	7110	9416	12366	15860	11888	1.324

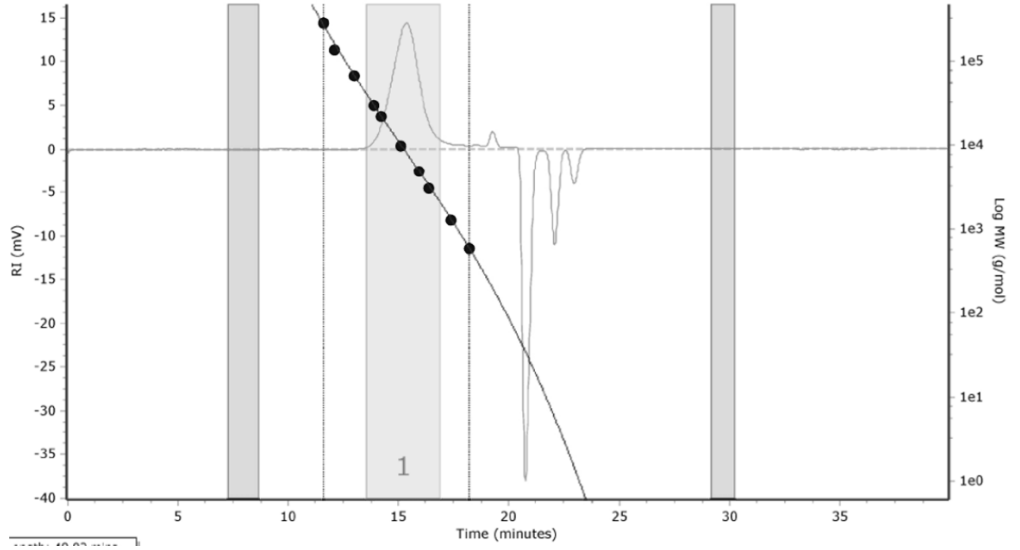


Fig. S94 SEC trace of poly(**4**) (M_n 8000 g mol^{-1} ($Đ$ 1.32)).

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	6985	5706	7850	10453	13398	10045	1.376

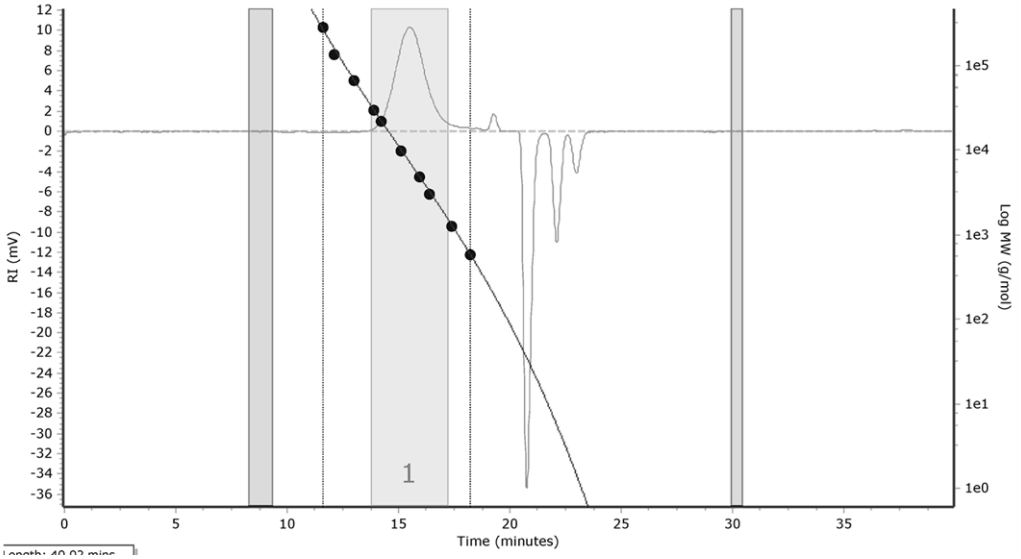


Fig. S95 SEC trace of poly(**4**) (M_n 5700 g mol^{-1} ($Đ$ 1.38)).

DSC analysis of the polymer derived from 4

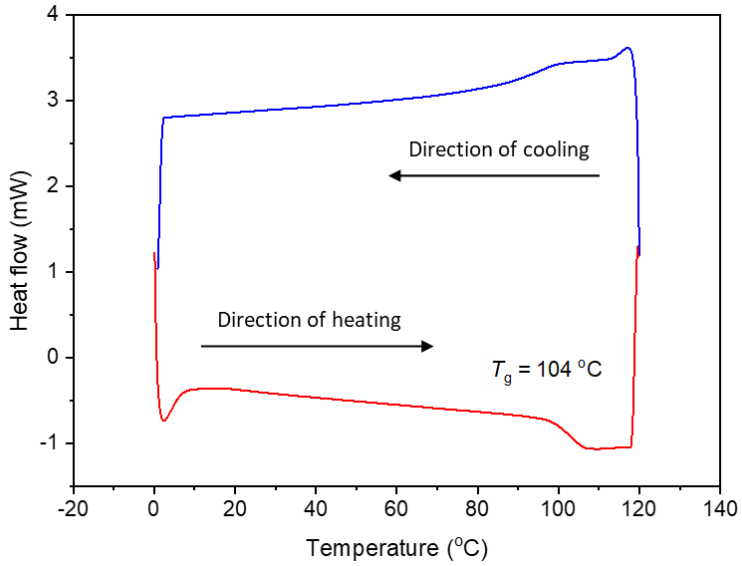


Fig. S96 DSC trace of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)), second heating and cooling cycle between 0 and 120 °C. Single exothermic peak, corresponding to the glass transition temperature (T_g) ≈ 104 °C of the polymer.

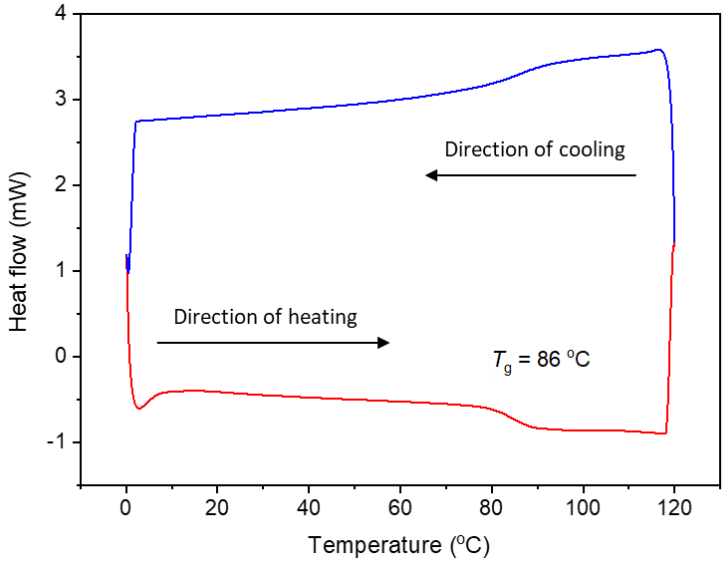


Fig. S97 DSC trace of poly(**4**) (M_n 5700 g mol^{-1} ($Đ$ 1.38)), second heating and cooling cycle between 0 and 120 °C. Single transition, corresponding to the glass transition temperature (T_g) ≈ 86 °C of the polymer.

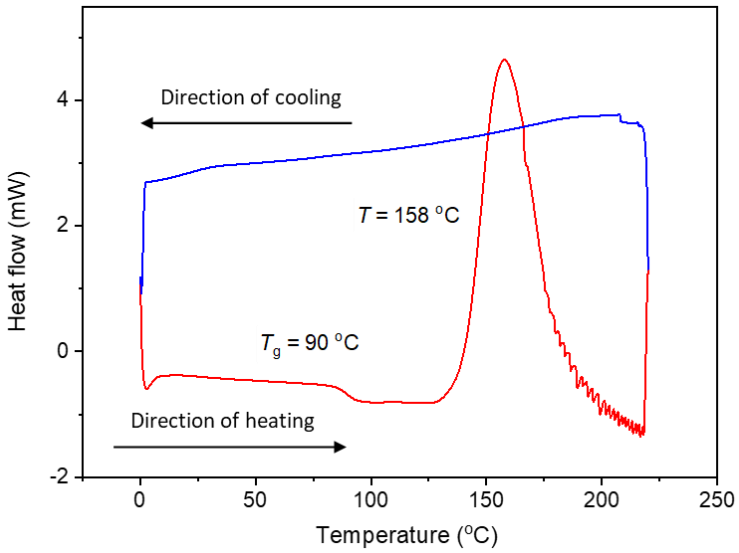


Fig. S98 DSC trace of poly(**4**) (M_n 5700 g mol^{-1} ($Đ$ 1.38)), third heating and cooling cycle between 0 and 220 °C. Two transitions, corresponding to the glass transition temperature (T_g) ≈ 90 °C and the suspected degradation temperature T ≈ 158 °C of the polymer.

TGA analysis of the polymer derived from 4

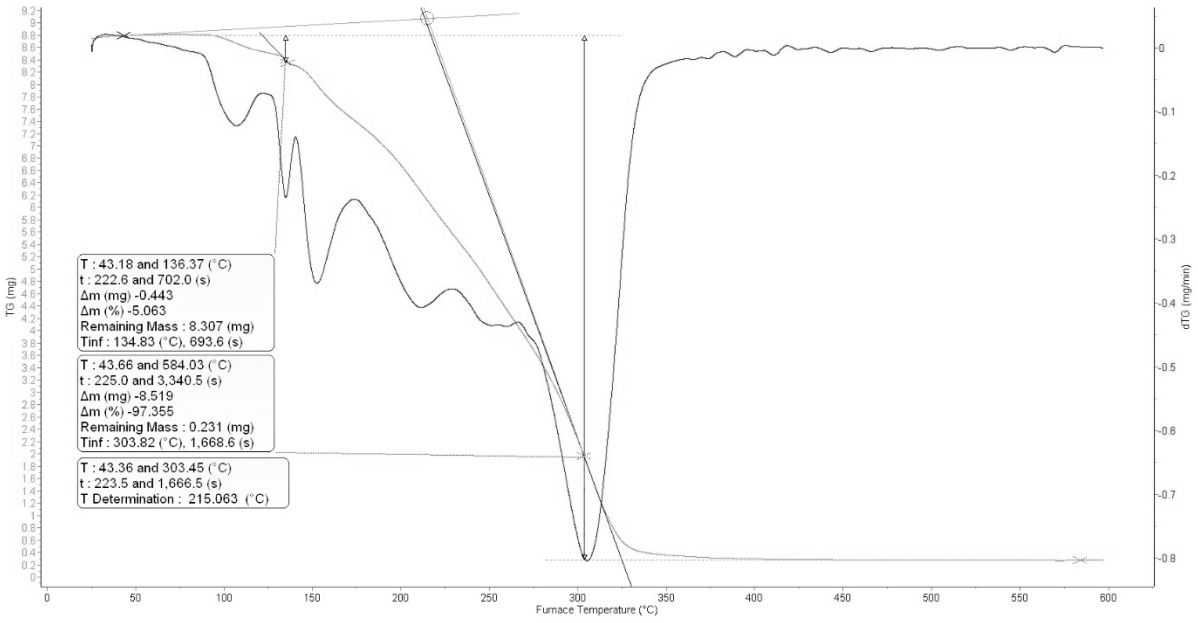


Fig. S99 TGA trace of poly(**4**) (M_n 5700 g mol^{-1} ($Đ$ 1.38)). The monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 136 °C; $T_{d,max}$ = 303 °C with 3 % char remaining at 600 °C.

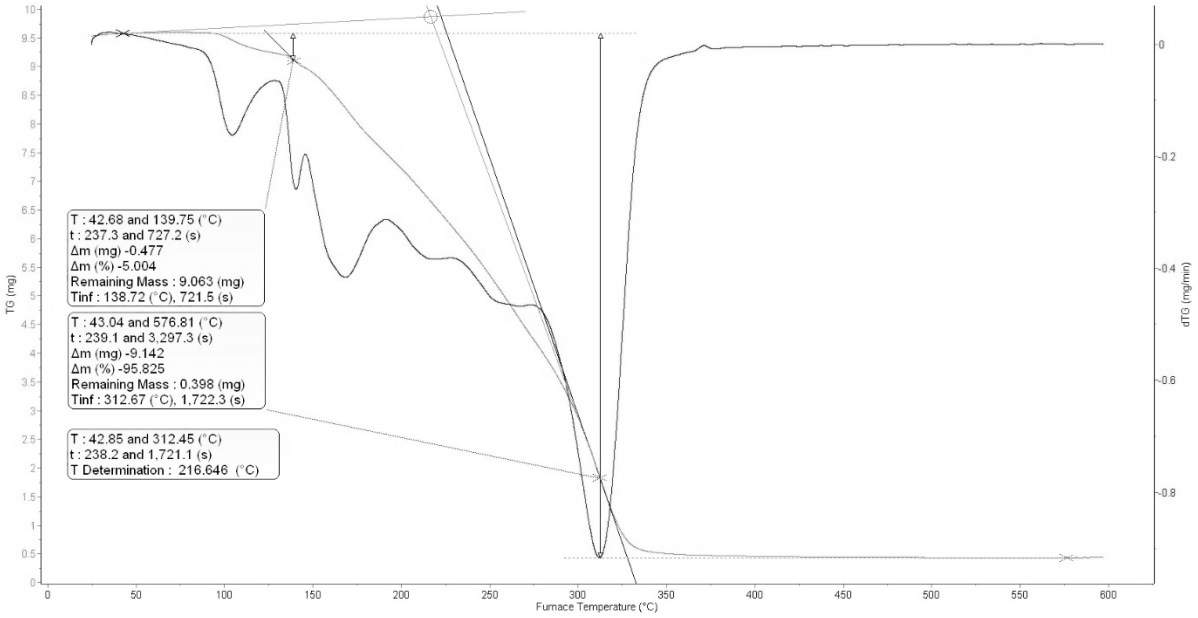


Fig. S100 TGA trace of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)). The monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 140 °C; $T_{d,max}$ = 312 °C with 4 % char remaining at 600 °C.

FT-IR analysis of the polymer derived from 4

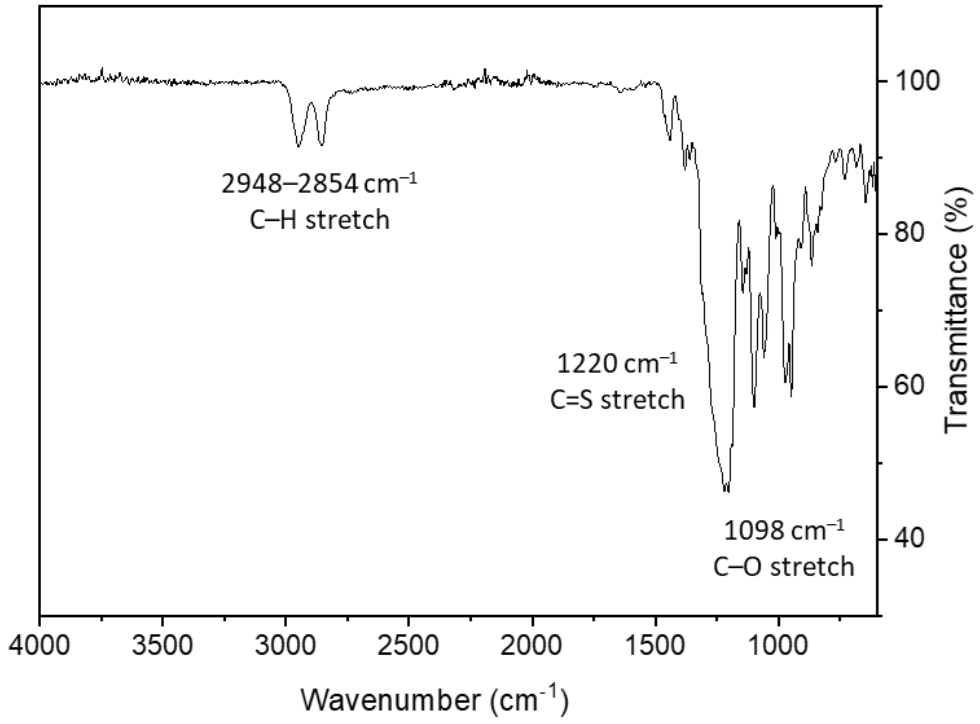
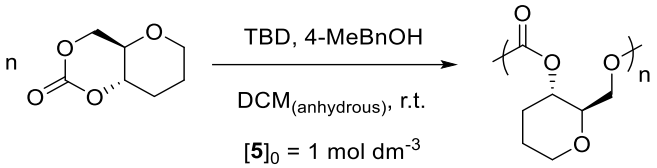


Fig. S101 Labelled FT-IR spectrum of poly(**4**) (M_n 7100 g mol^{-1} ($Đ$ 1.32)).

Ring opening polymerisation of 5



Under an argon atmosphere 4-MeBnOH (12.6 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.006 mmol, 1.0 equiv.) and TBD (12.6 µL, 0.5 mol dm^{-3} in anhydrous DCM, 0.006 mmol, 1.0 equiv.) were added to a solution of monomer **5** (0.100 g, 0.632 mmol, 100 equiv.) in anhydrous DCM (0.63 mL, 1.0 mol L^{-1}). The mixture was stirred at room temperature for 0.15 h and quenched by the addition of a benzoic acid solution (≈ 30 equiv.). The solvent was removed under reduced pressure and the crude solid was dissolved in $CHCl_3$ and precipitated from Et_2O. The product was isolated by centrifugation (3500 rpm, 2 x 5 minutes), washed twice with Et_2O and dried under vacuum. The polymer was isolated as a white solid.

δ_H (500 MHz; chloroform-d): 4.47-4.41 (C^4H, 1H, m), 4.32-4.14 (C^6H, 2H, m), 3.98-3.88 (C^1H, 1H, m), 3.54-3.45 (C^5H, 1H, m), 3.41-3.31 (C^1H, 1H, m), 2.34-2.24 (C^3H, 1H, m), 1.80-1.64 (C^2H, 2H, m), 1.59-1.47 (C^3H, 1H, m) ppm; δ_C (126 MHz; chloroform-d): 155.2 (C^7), 154.2 (C^7), 153.3 (C^7), 77.1 (C^5), 72.1 (C^4), 67.8 (C^1), 67.1 (C^6), 29.1 (C^3), 24.8 (C^2) ppm. ν_{max} (cm^{-1}): 2956-2860 (CH), 1741 ($C(O)O_2$), 1233 (C–O).

NMR analysis of the polymer derived from 5

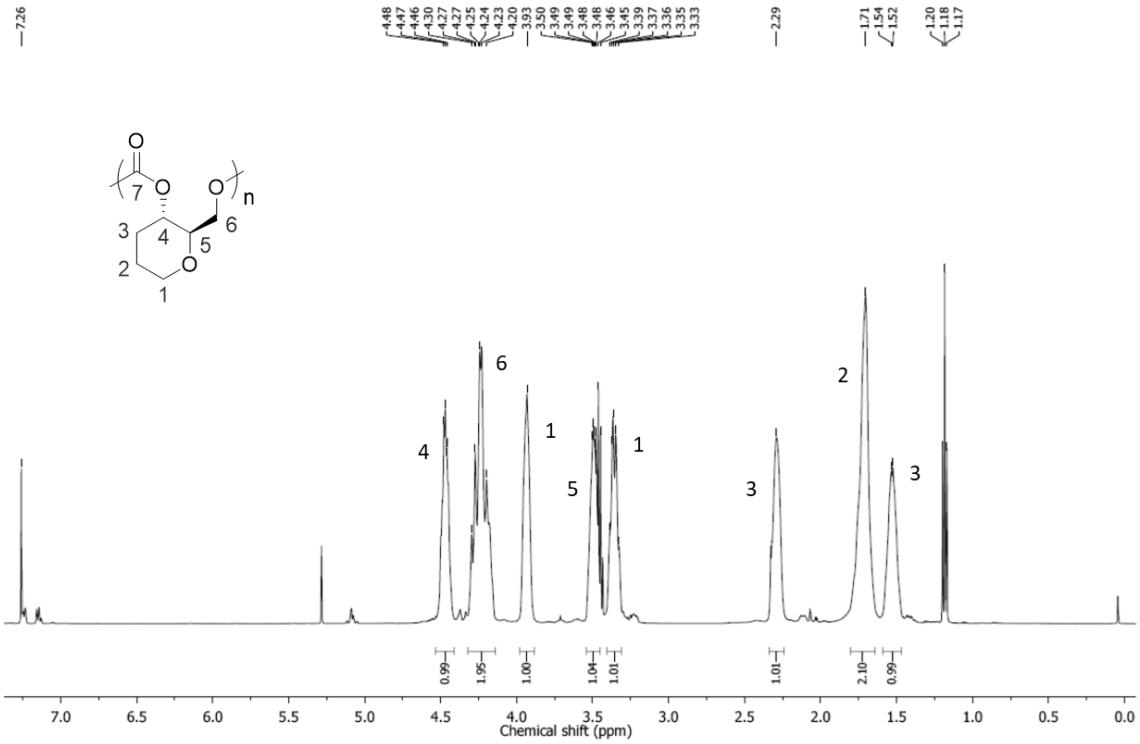


Fig. S102 Annotated ^{1}H NMR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)) in chloroform-d.

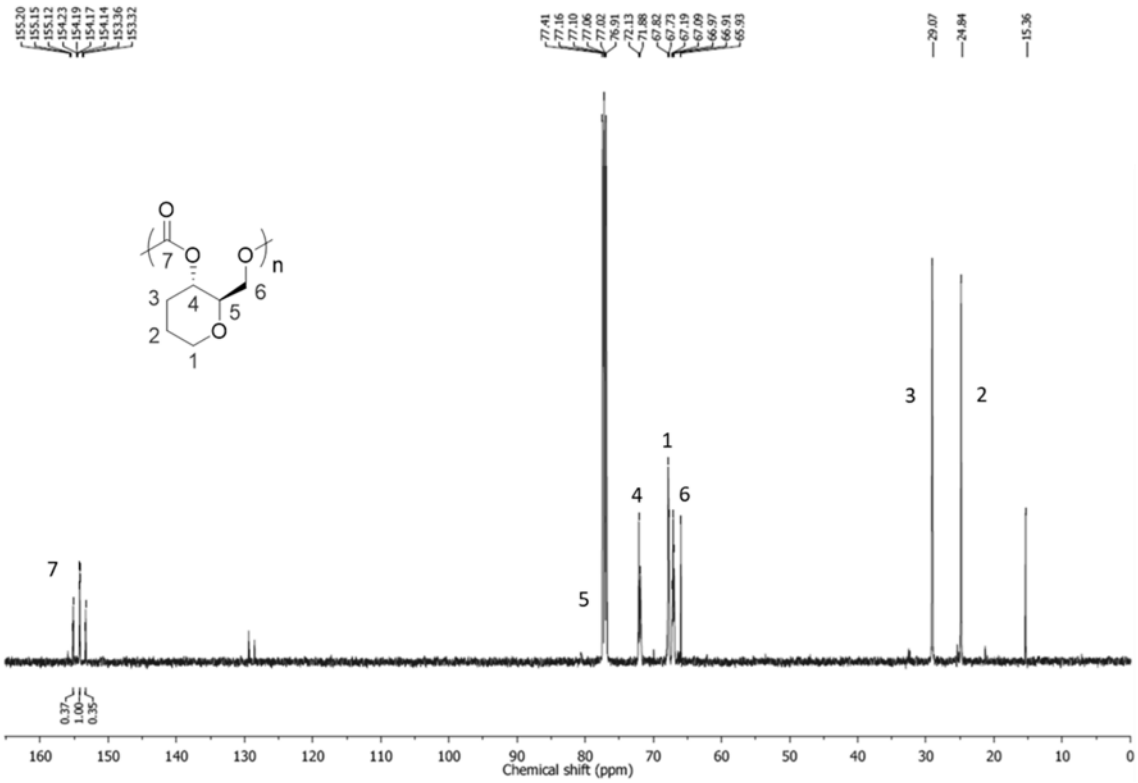


Fig. S103 Annotated $^{13}C\{^{1}H\}$ NMR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)) in chloroform-d.

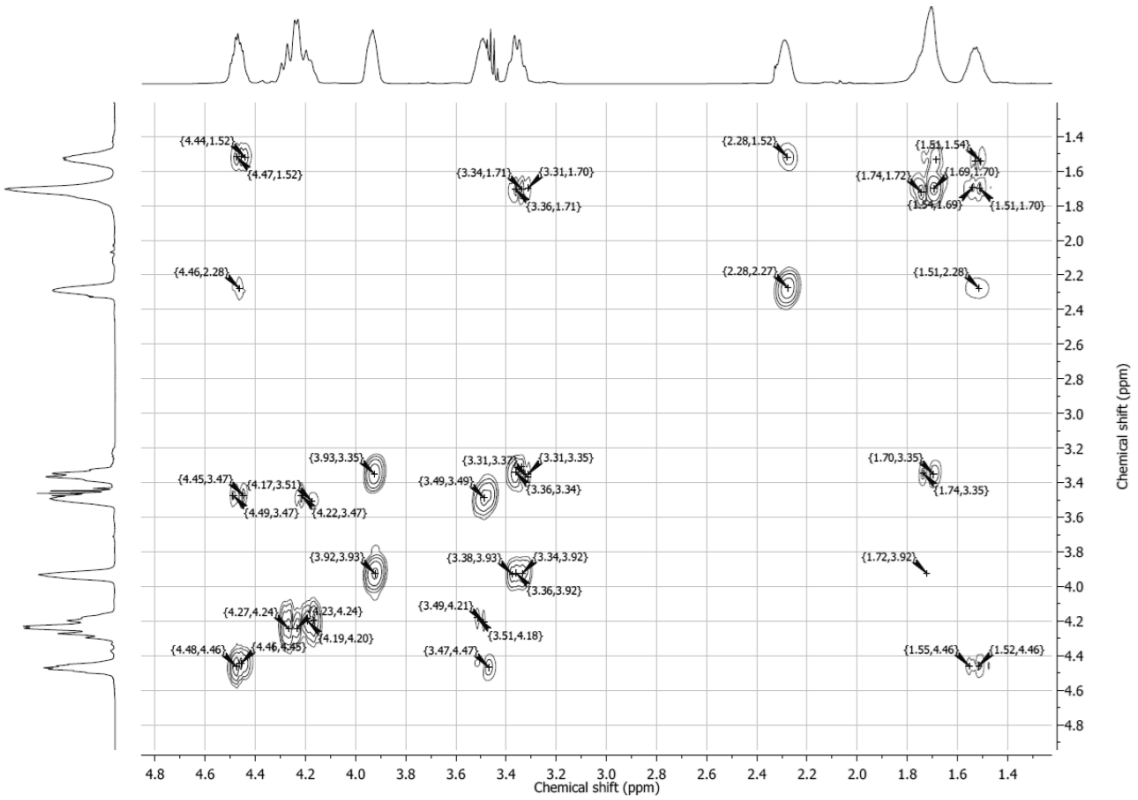


Fig. S104 COSY (^{1}H–^{1}H) NMR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)) in chloroform-d.

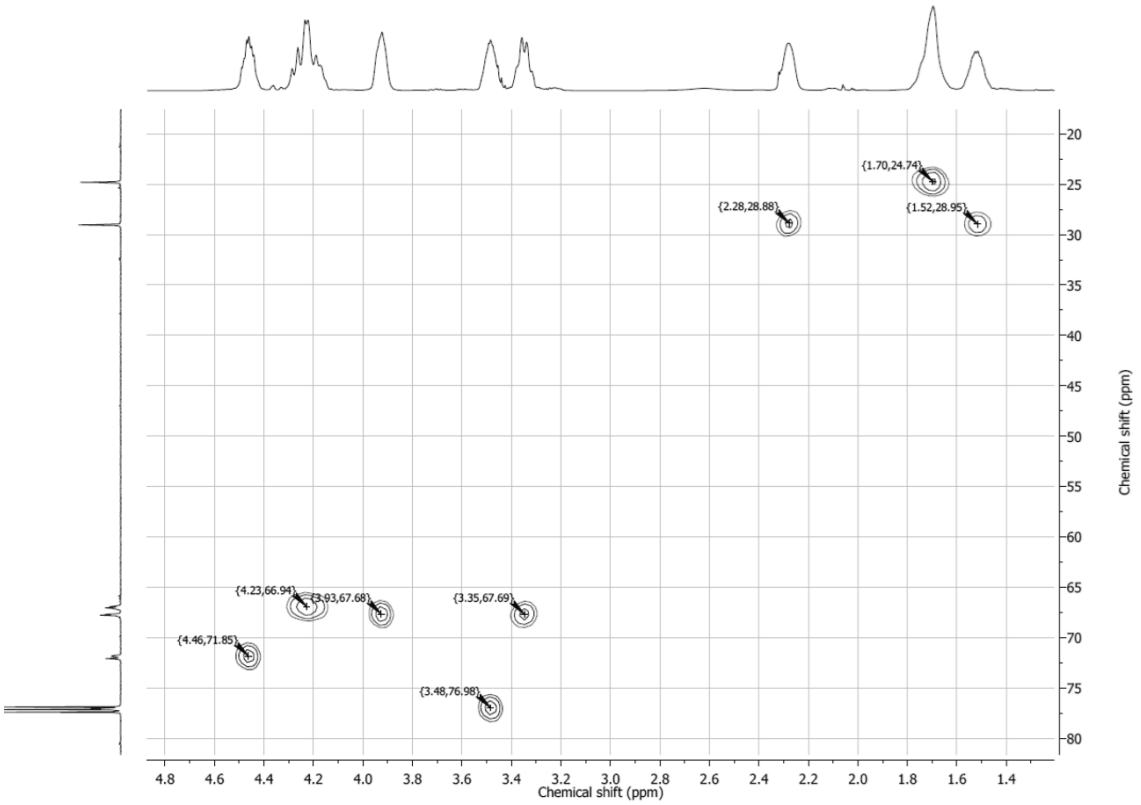


Fig. S105 HSQC (^{1}H–^{13}C) NMR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)) in chloroform-d.

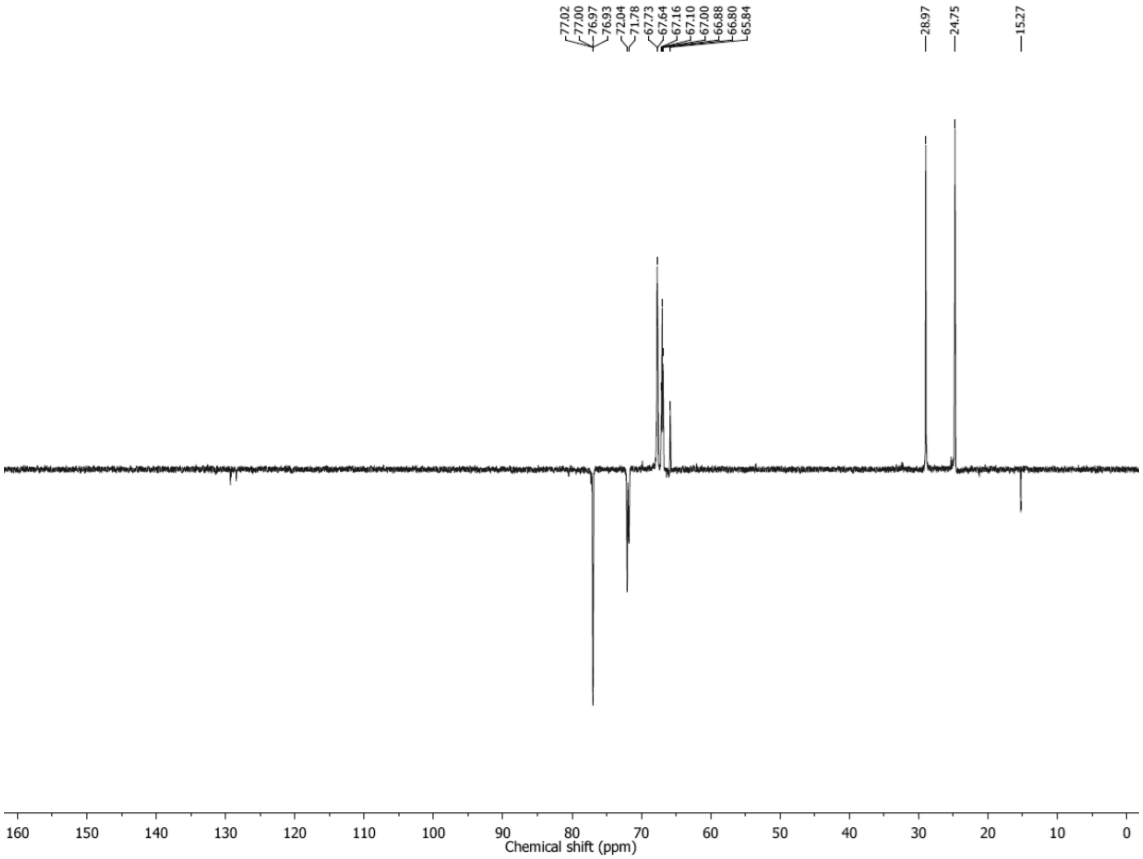


Fig. S106 ^{13}C{^{1}H} DEPT135 NMR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)) in chloroform-d.

Size-Exclusion Chromatography analysis of the polymer derived from 5

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	4901	4940	6250	8011	10135	7721	1.265

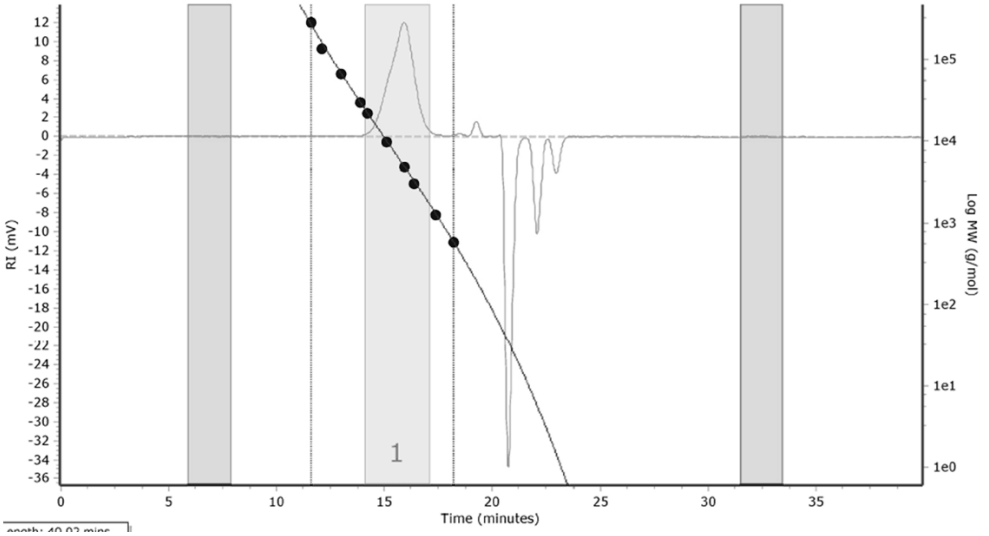


Fig. S107 SEC trace of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)).

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	5356	6040	7450	9283	11391	8987	1.233

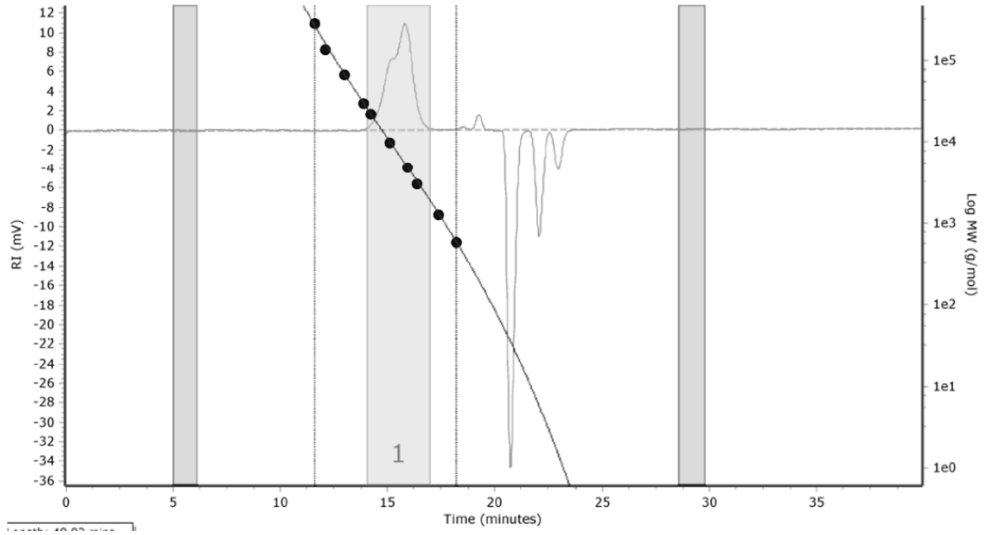


Fig. S108 SEC trace of poly(**5**) (M_n 6000 g mol^{-1} ($Đ$ 1.23)) with a bimodal distribution.

DSC analysis of the polymer derived from 5

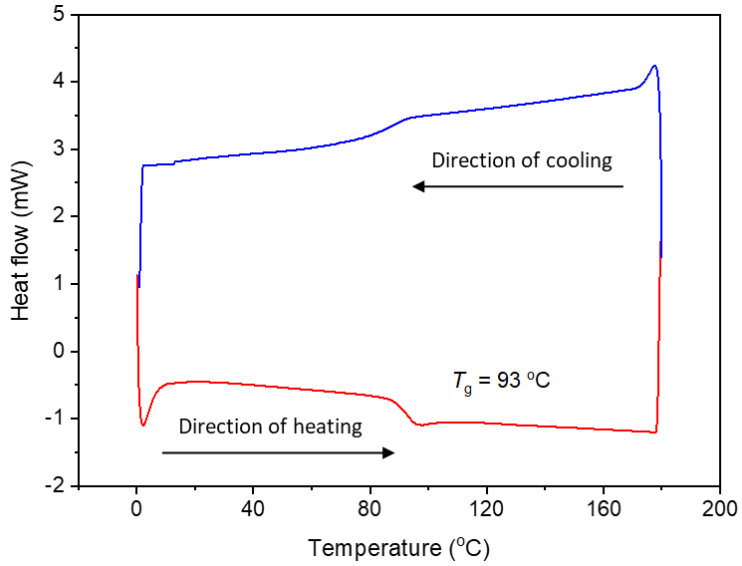


Fig. S109 DSC trace of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)), second heating and cooling cycle between 0 and 180 °C. Single exothermic peak, corresponding to the glass transition temperature (T_g) ≈ 93 °C of the polymer.

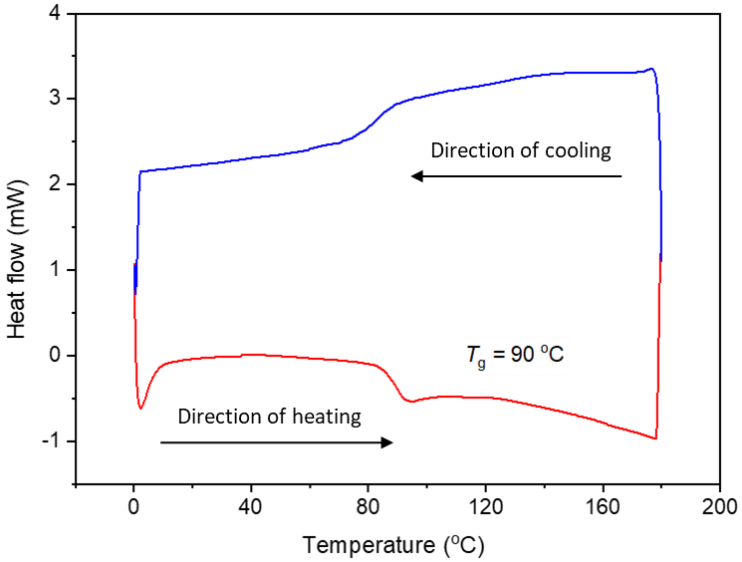


Fig. S110 DSC trace of poly(**5**) (M_n 6000 g mol^{-1} ($Đ$ 1.23)), second heating and cooling cycle between 0 and 180 °C. Single transition, corresponding to the glass transition temperature (T_g) ≈ 90 °C of the polymer.

TGA analysis of the polymer derived from 5

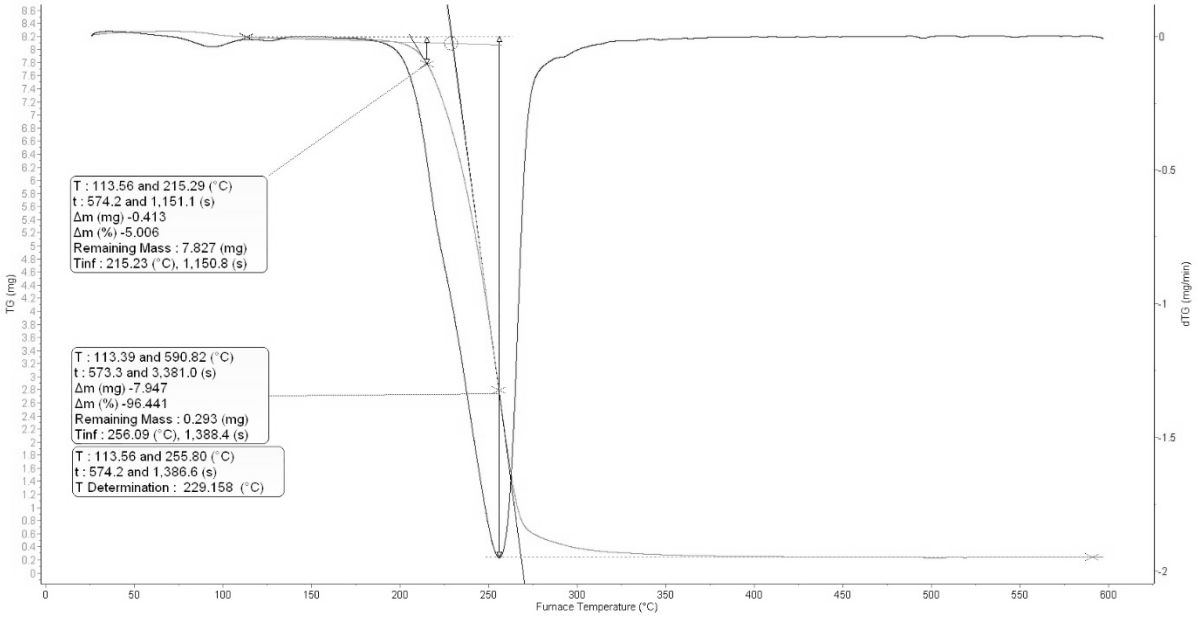


Fig. S111 TGA trace of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)), the monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 215 °C; $T_{d,max}$ = 256 °C with 4 % char remaining at 600 °C.

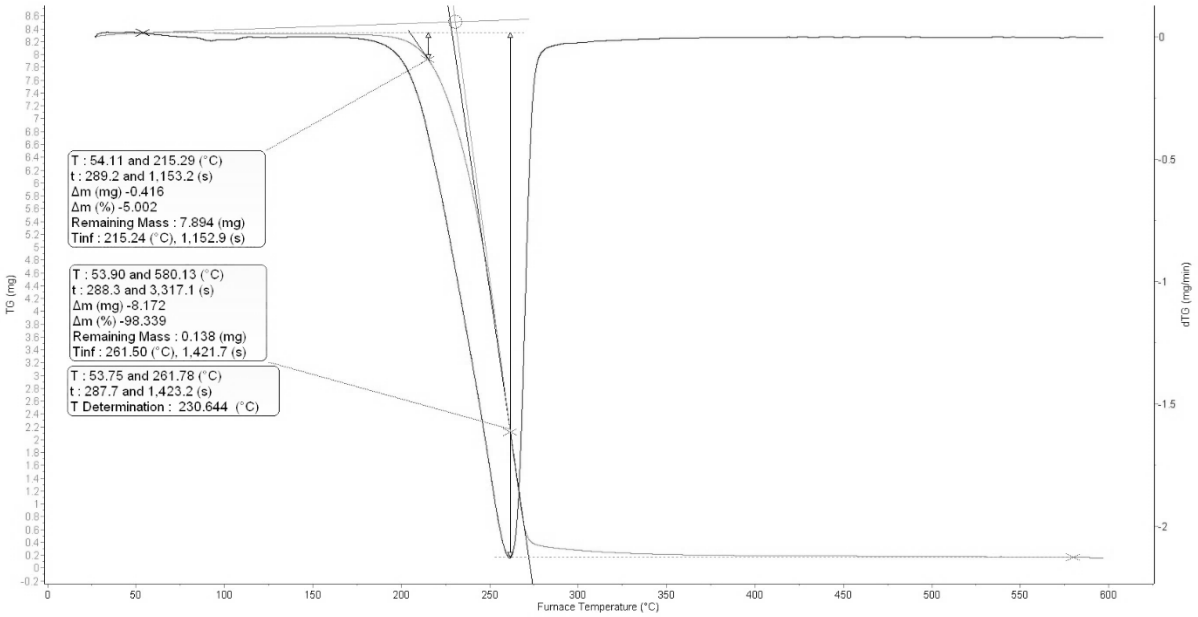


Fig. S112 TGA trace of poly(**5**) (M_n 6000 g mol^{-1} ($Đ$ 1.23)), the monomer was heated from 30 to 600 °C under argon at 10 °C min^{-1}. Obtained values: $T_{d5\%}$ = 215 °C; $T_{d,max}$ = 262 °C with 2 % char remaining at 600 °C.

FT-IR analysis of the polymer derived from 5

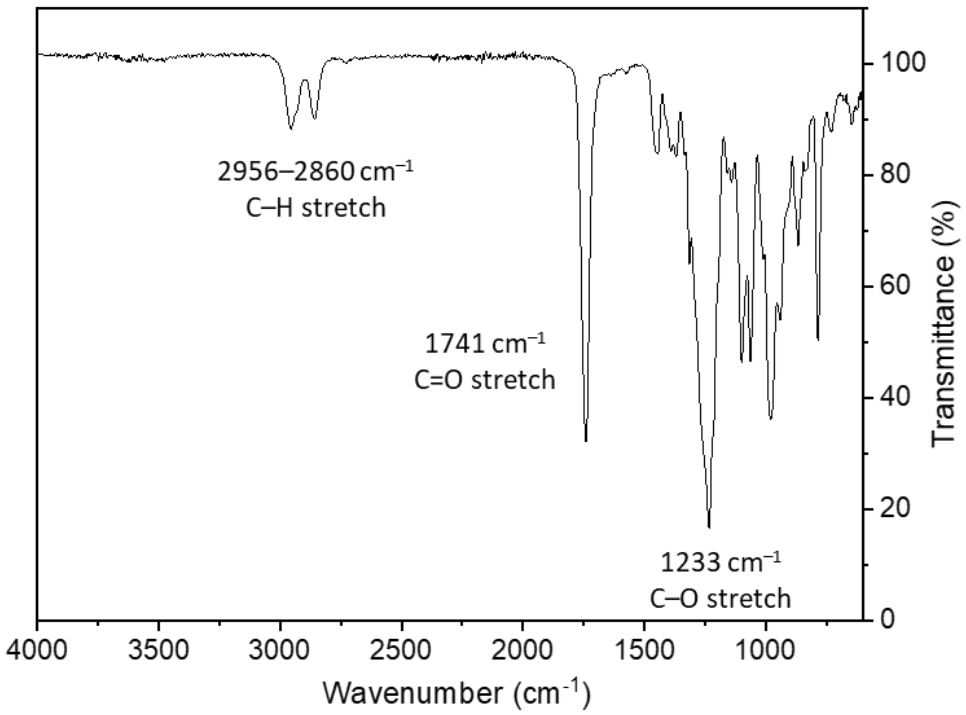


Fig. S113 Labelled FT-IR spectrum of poly(**5**) (M_n 4900 g mol^{-1} ($Đ$ 1.27)).

3. DFT Computational Studies

All calculations were performed using the Gaussian16 suite of codes (revision D.01).[3] Geometries were fully optimised without any symmetry or geometry constraints using the rωB97XD LC hybrid functional developed by Chai and Head-Gordon. This includes an empirical dispersion correction and has been shown to effectively reproduce thermodynamic and kinetic experimental data. Calculations were carried out using a temperature of 298K and solvent effects in dichloromethane considered using a conductor-like polarisable continuum model (CPCM).[4, 5]

The nature of all the stationary points as minima was verified by calculations of the vibrational frequency spectrum. Only the most stable conformational isomers are reported for all intermediates. Free energies were calculated within the harmonic approximation for vibrational frequencies.

DFT Modelling of the isodesmic ring opening for all monomers

An isodesmic reaction is a chemical reaction in which the type of chemical bonds broken in the reactant are the same as the type of bonds formed in the reaction product and is commonly used as a hypothetical reaction in thermochemistry to calculate the ring-strain of cyclic molecules.[6] The reaction between a dimethyl substituted carbonate or the appropriate sulfur-containing carbonate and one molecule of the corresponding cyclic monomer (**1**, **2**, **3**, **4** or **5**) was examined using DFT calculations. A split-valence double ζ with polarization and diffuse functions 6-31+G(d,p) basis set was used and the addition of the dimethyl carbonate or the appropriate sulfur-containing carbonate to either side of the carbonate/thiocarbonate/thionocarbonate/xanthate linkage was considered.

Full coordinates for all the stationary points, together with computed free Gibbs energy and vibrational frequency data, are available *via* the corresponding Gaussian16 output files, stored in the digital repository: DOI:10.6084/m9.figshare.21411687.

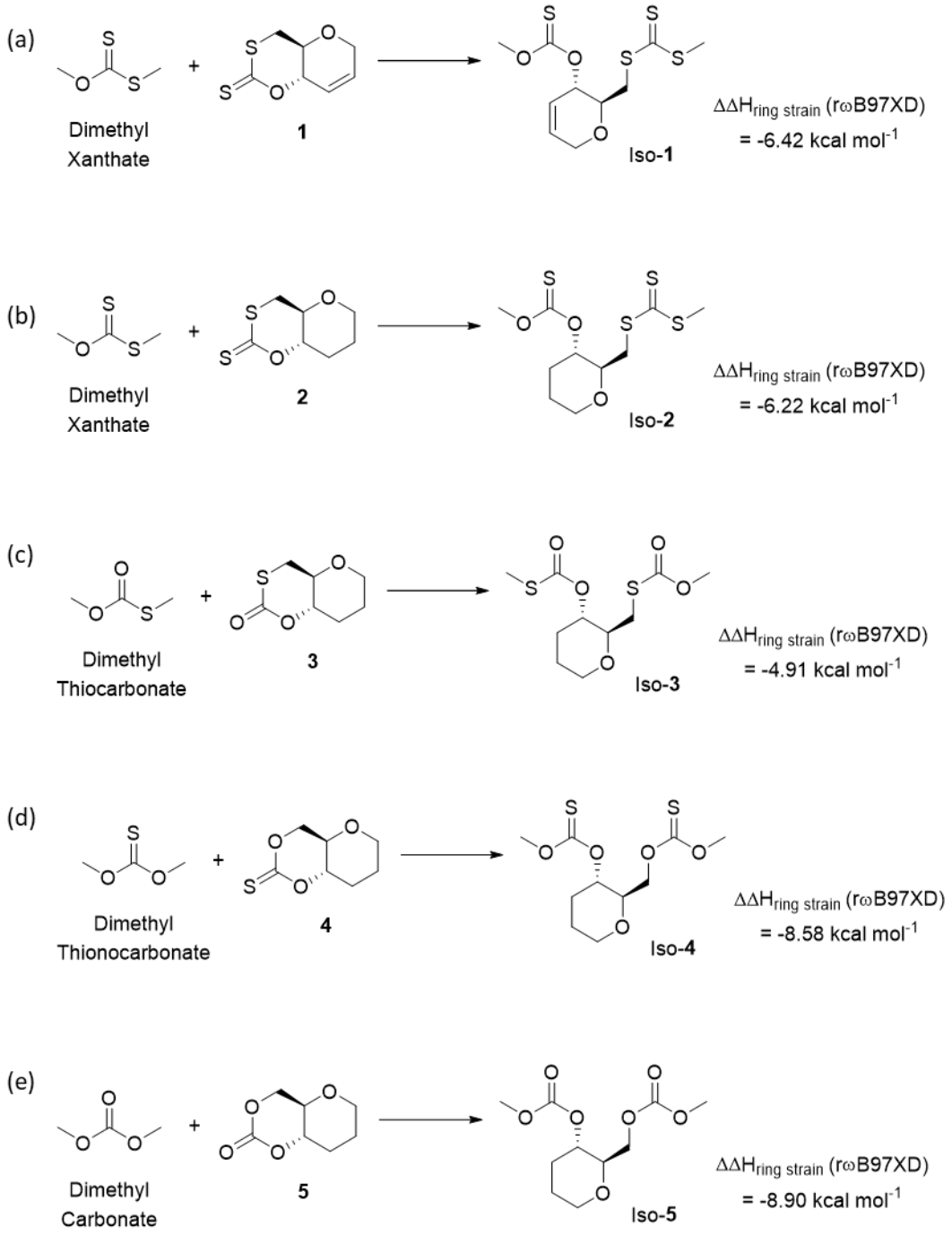


Fig. S114 Isodesmic reactions between (a) dimethyl xanthate and unsaturated xanthate monomer **1**; (b) dimethyl xanthate and saturated xanthate monomer **2**; (c) dimethyl thiocarbonate and saturated thiocarbonate monomer **3**; (d) dimethyl thionocarbonate and saturated thionocarbonate monomer **4** and (e) dimethyl carbonate and saturated carbonate monomer **5**.

Table S3 Computed Gibbs Free Energies at the rωB97XD/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening of **1** with dimethyl xanthate.

	Structure	***G (Hartree)***	***ΔG (kcal/mol)***	***H (Hartree)***	***ΔH (kcal/mol)***
	1	-1218.094826	-	-1218.048719	-
	$C(S)SOMe_2$	-989.383343	-	-989.342094	-
	1 + $C(S)SOMe_2$	-2207.478169	0.00	-2207.390813	0.00
Isodesmic	Iso-**1**	-2207.47285	3.337720	-2207.40104	-6.417535
Ring Strain					

Table S4 Computed Gibbs Free Energies at the rωB97XD/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening of **2** with dimethyl xanthate.

	Structure	***G (Hartree)***	***ΔG (kcal/mol)***	***H (Hartree)***	***ΔH (kcal/mol)***
	2	-1219.313862	-	-1219.267059	-
	$C(S)SOMe_2$	-989.383343	-	-989.342094	-
	2 + $C(S)SOMe_2$	-2208.697205	0.00	-2208.609153	0.00
Isodesmic	Iso-**2**	-2208.689133	5.065253	-2208.619061	-6.217359
Ring Strain					

Table S5 Computed Gibbs Free Energies at the rωB97XD/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening of **3** with dimethyl thiocarbonate.

	Structure	***G (Hartree)***	***ΔG (kcal/mol)***	***H (Hartree)***	***ΔH (kcal/mol)***
	3	-896.364993	-	-896.319519	-
	$C(O)SOMe_2$	-666.435850	-	-666.395148	-
	3 + $C(O)SOMe_2$	-1562.800843	0.00	-1562.714667	0.00
Isodesmic	Iso-**3**	-1562.790318	6.604532	-1562.722493	-4.910885
Ring Strain					

Table S6 Computed Gibbs Free Energies at the rωB97XD/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening of **4** with dimethyl thionocarbonate.

	Structure	***G (Hartree)***	***ΔG (kcal/mol)***	***H (Hartree)***	***ΔH (kcal/mol)***
	4	-896.336981	-	-896.291623	-
	$C(S)O_2Me_2$	-666.407026	-	-666.367840	-
	4 + $C(S)O_2Me_2$	-1562.744007	0.00	-1562.659463	0.00
Isodesmic	Iso-**4**	-1562.738663	3.353408	-1562.673133	-8.578048
Ring Strain					

Table S7 Computed Gibbs Free Energies at the rωB97XD/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening of **5** with dimethyl carbonate.

	Structure	***G (Hartree)***	***ΔG (kcal/mol)***	***H (Hartree)***	***ΔH (kcal/mol)***

	5	-573.390562	-	-573.346563	-
	$C(O)O_2Me_2$	-343.461260	-	-343.422684	-
	5 + $C(O)O_2Me_2$	-916.851822	0.00	-916.769247	0.00
Isodesmic	Iso-**5**	-916.847473	2.729037	-916.783428	-8.898705
Ring Strain					

Plots of ΔH^{ROP} versus monomer conversion

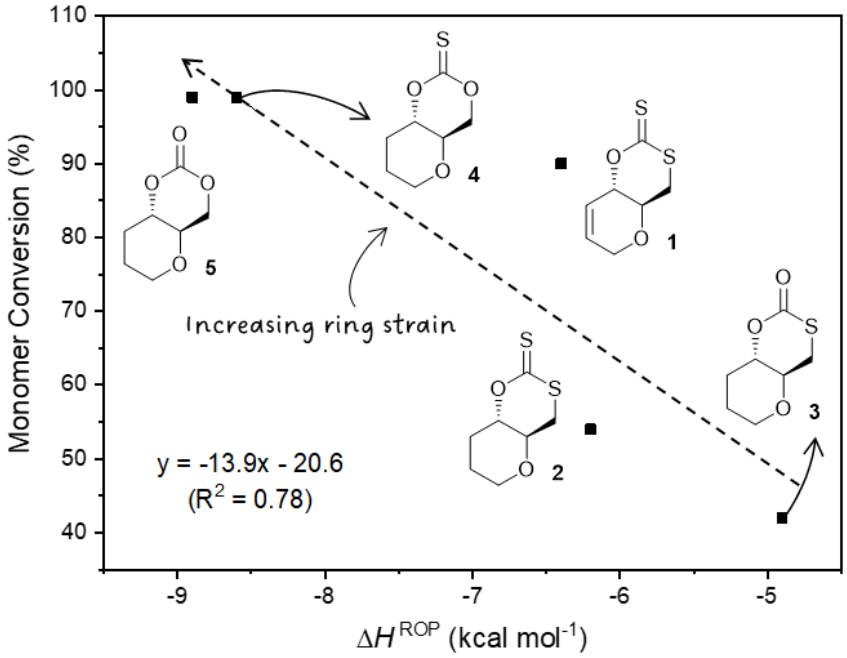


Fig. S115 Plot of ΔH^{ROP}, calculated as a representation of ring strain, versus monomer conversion (including monomer **1**).

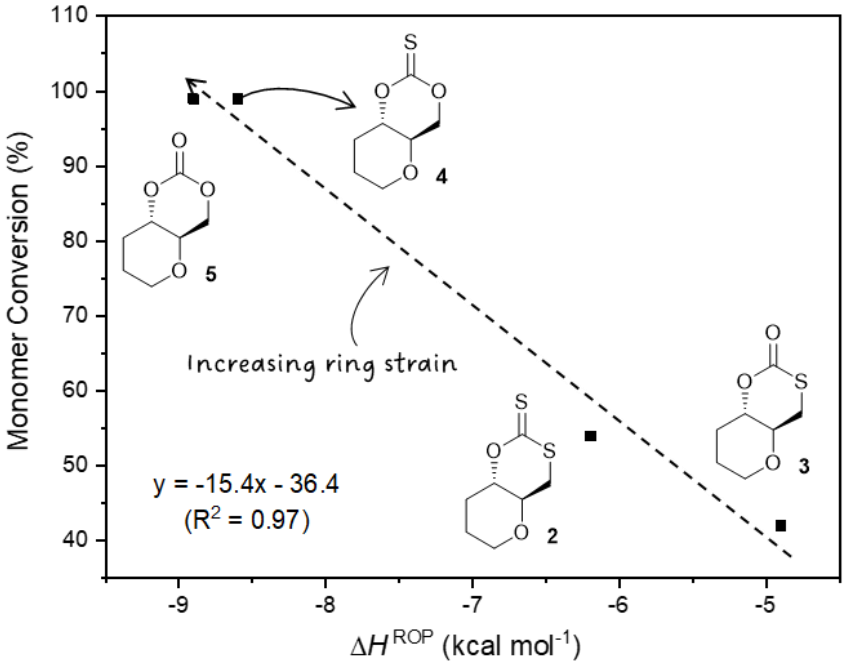
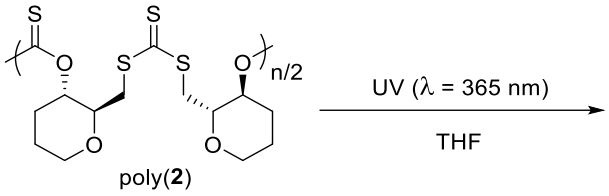


Fig. S116 Plot of ΔH^{ROP}, calculated as a representation of ring strain, versus monomer conversion (excluding monomer **1**).

4. Polymer Degradation

UV degradation of poly(2)



Under an argon atmosphere, a solution of poly(**2**) (0.030 g, 0.158 mmol, 1.0 equiv.) in THF (3.5 mL) was divided equally between 5 vacuum-tight vials. The vials were placed under UV light (λ = 365 nm) and taken off at predetermined intervals. All crude reaction mixtures were then subjected to ^{1}H NMR spectroscopy and SEC analysis.

Table S8 UV degradation of poly(**1**).

Entry	Time (h)	$M_{n,SEC}$[(a)]	$M_{w,SEC}$[(a)]	% M_n[(b)]	$Đ$[(a)]
1	0	5500	8500	100	1.54
2	0.5	2900	5500	53	1.92
3	1	2500	4900	45	1.94
4	2	1600	3300	29	2.07
6	3	1400	2700	25	1.90
7	4	1200	2500	22	2.02
8	6	970	1700	18	1.78

[a]Number-average molecular weight and Dispersity ($M_{n,SEC}$, $M_{w,SEC}$, $Đ$), calculated by SEC relative to polystyrene standards in THF eluent, units given in g mol^{-1}; [b]Percentage of the original $M_{n,SEC}$.

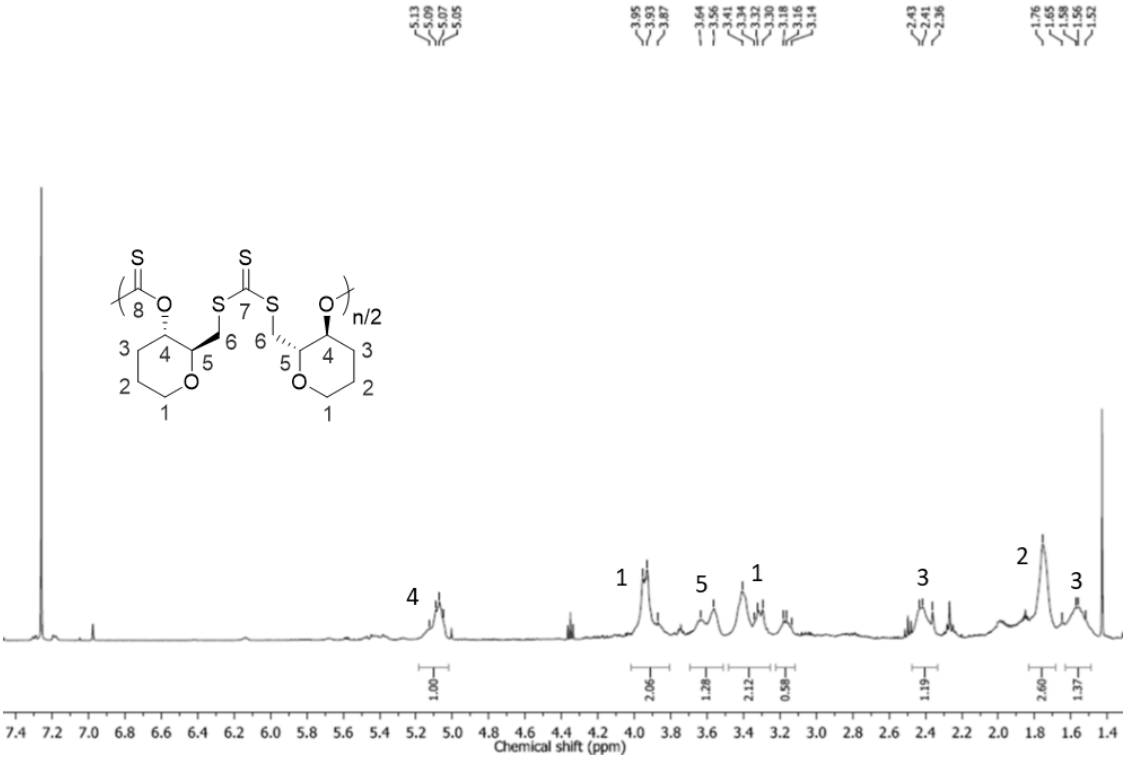


Fig. S117 Annotated ^{1}H NMR spectra of poly(**2**) in chloroform-d, after 6 hours of UV exposure. Loss of H-6' proton environments observed, as well as changes to integrations.

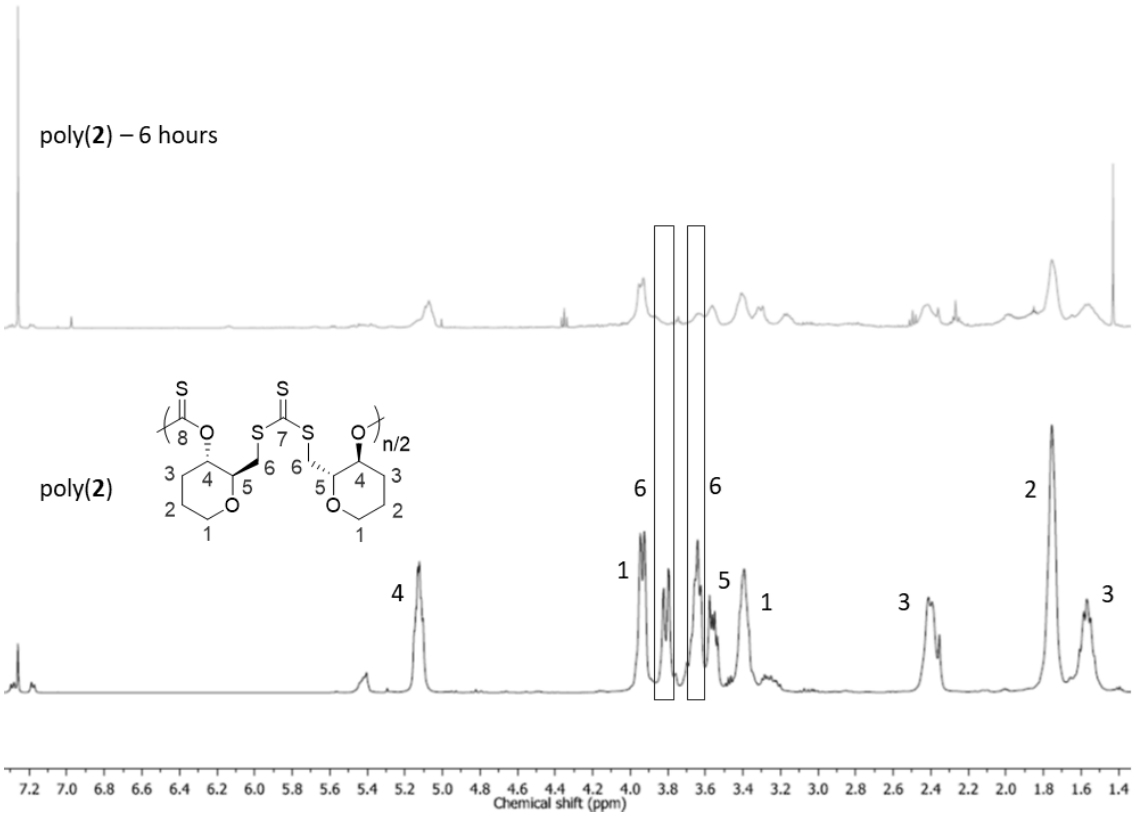
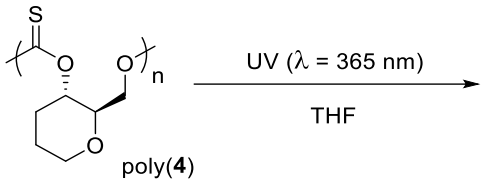


Fig. S118 Stacked ^{1}H NMR spectra of poly(**2**) before (bottom) and after (top) 6 hours of UV irradiation (λ = 365 nm). Loss of H-6' environments have been highlighted.

UV degradation of poly(4)



Under an argon atmosphere, a solution of poly(**4**) (0.030 g, 0.172 mmol, 1.0 equiv.) in THF (3.5 mL) was divided equally between 5 vacuum-tight vials. The vials were placed under UV light (λ = 365 nm) and taken off at predetermined intervals. All crude reaction mixtures were then subjected to ^{1}H NMR spectroscopy and SEC analysis.

Table S9 UV degradation of poly(**4**).

Entry	Time (h)	$M_{n,SEC}$[(a)]	$M_{w,SEC}$[(a)]	% M_n[(b)]	$Đ$[(a)]
1	0	6300	8200	100	1.30
2	1	6500	8400	103	1.28
3	2	6300	8200	100	1.29
4	3	6300	8100	100	1.29
5	4	6000	7600	95	1.28
6	6	5600	7400	89	1.32

[a]Number-average molecular weight and Dispersity ($M_{n,SEC}$, $M_{w,SEC}$, $Đ$), calculated by SEC relative to polystyrene standards in THF eluent, units given in g mol^{-1}; [b]Percentage of the original $M_{n,SEC}$.

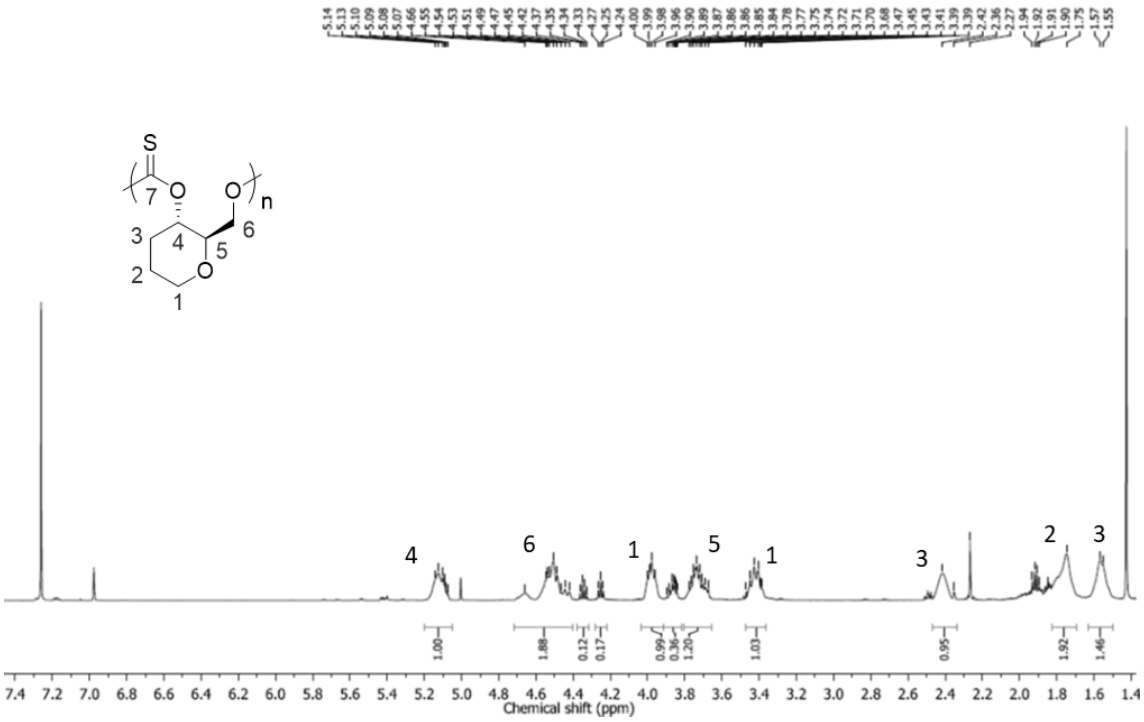


Fig. S119 Annotated ^{1}H NMR spectra of poly(**4**) in chloroform-d, after 6 hours of UV exposure. Reduced integration observed for the H-6' proton environment.

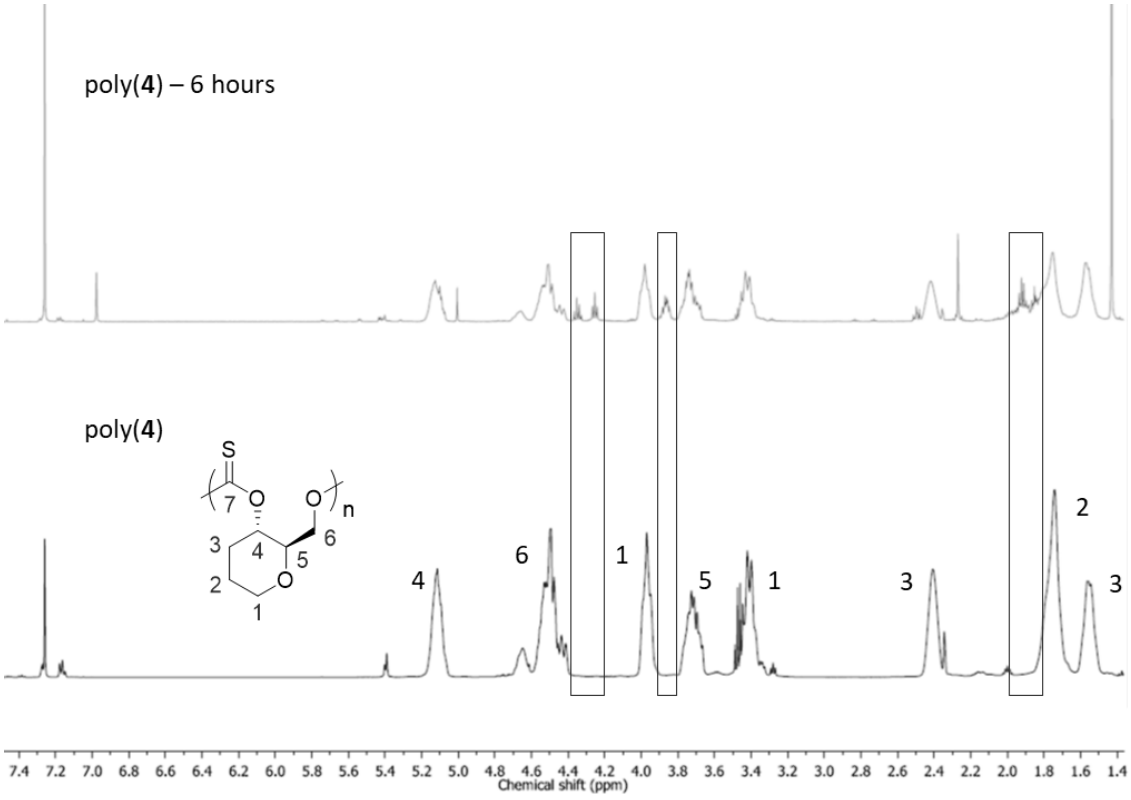
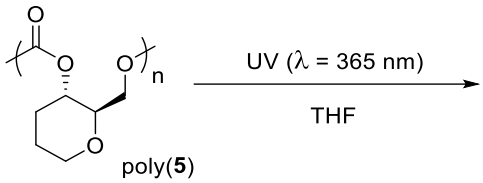


Fig. S120 Stacked ^{1}H NMR spectra of poly(**4**) before (bottom) and after (top) 6 hours of UV irradiation (λ = 365 nm). New proton environments have been highlighted; however, characterisation was not possible.

UV degradation of poly(5)



Under an argon atmosphere, a solution of poly(**5**) (0.030 g, 0.189 mmol, 1.0 equiv.) in THF (3.5 mL) was divided equally between 5 vacuum-tight vials. The vials were placed under UV light (λ = 365 nm) and taken off at predetermined intervals. All crude reaction mixtures were then subjected to ^{1}H NMR spectroscopy and SEC analysis.

Table S10 UV degradation of poly(**5**)

Entry	Time (h)	$M_{n,SEC}$[(a)]	$M_{w,SEC}$[(a)]	% M_n[(b)]	$Đ$[(a)]
1	0	4900	5700	100	1.16
2	1	4900	5800	100	1.17
3	2	4900	5800	100	1.17
4	3	4900	5800	100	1.18
5	4	4900	5700	100	1.17
6	6	4900	5700	100	1.17

[a]Number-average molecular weight and Dispersity ($M_{n,SEC}$, $M_{w,SEC}$, $Đ$), calculated by SEC relative to polystyrene standards in THF eluent, units given in g mol^{-1}; [b]Percentage of the original $M_{n,SEC}$.

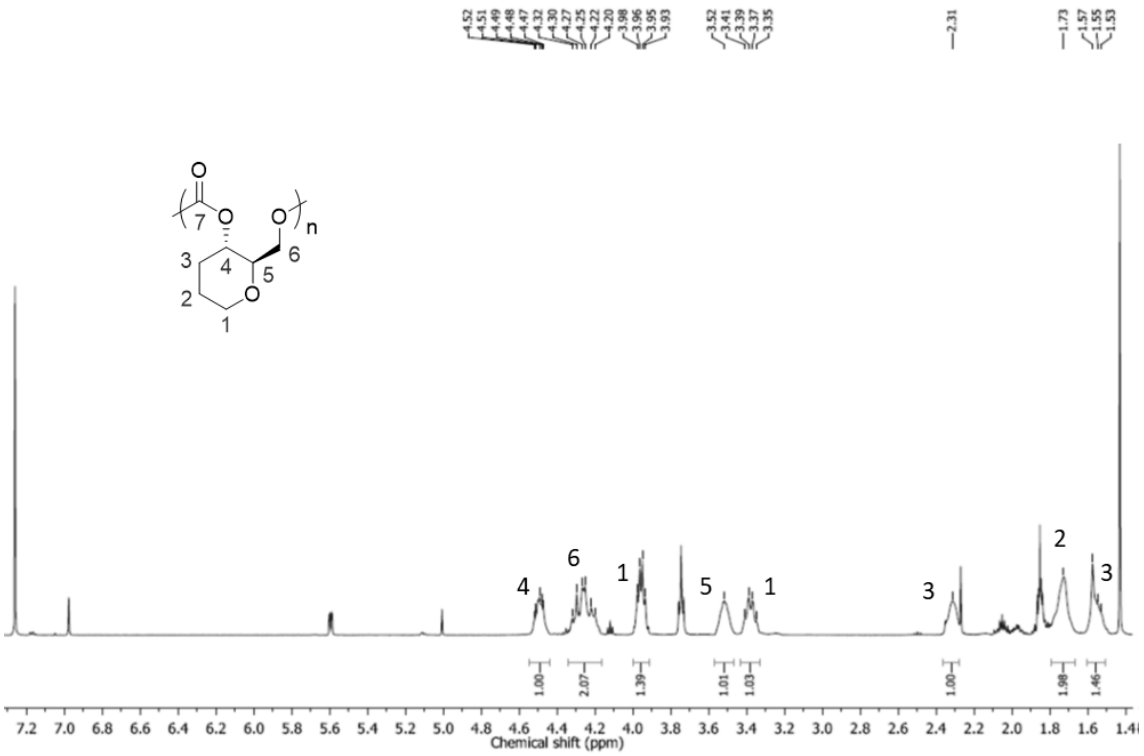


Fig. S121 Annotated ^{1}H NMR spectra of poly(**5**) in chloroform-d, after 6 hours of UV exposure.

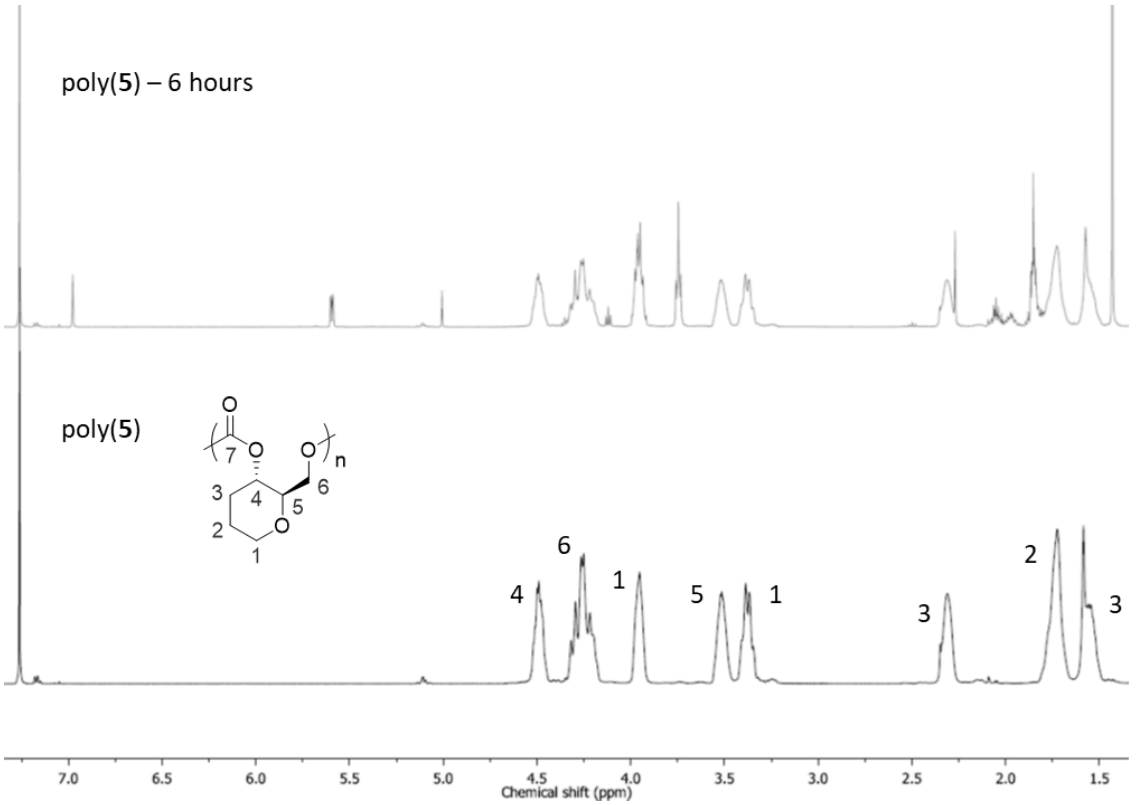


Fig. S122 Stacked ^{1}H NMR spectra of poly(**5**) before (bottom) and after (top) 6 hours of UV irradiation (λ = 365 nm).

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