SUPPORTING INFORMATION

Polymerisation of a terpene-derived lactone: a bio-based alternative to ε-caprolactone

*Helena C. Quilter, Marc Hutchby, Matthew G. Davidson and Matthew D. Jones**

General considerations

All chemicals used were purchased from Aldrich, Alfa Aesar of Fluorochem and used as received except for benzyl alcohol, which was distilled over CaH_2 prior to use. Metal complexes for polymerisation were synthesised as previously reported in literature[1,2] and handled under an inert argon atmosphere using standard Schlenk or glovebox techniques. Toluene used for polymerisations was dry and obtained via SPS (solvent purification system). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. 2D spectra (DOSY) were also recorded on a Bruker 400 MHz instrument.

Electrospray ionisation mass spectra (ESI-MS) were recorded using an electrospray Time-of-Flight MicroTOF mass spectrometer. Samples were prepared in HPLC grade MeOH. Masses were recorded in positive mode and are reported as mass to charge ratios (m/z) in Daltons.

GC-MS were recorded using an Agilent Technologies GC-MS system (GC: 7890B, MS: 5977A, column: capillary nitroterephthalic acid-modified polyethylene glycol column of high polarity DB-FFAP 30 m x 0.250 mm x 0.25 µm). The temperature range was 40 – 250 °C with a heating rate of 20 °C/min and hold time of 5.5 min.

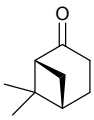
General polymerisation conditions.

Polymerisations were carried out in a Young's ampoule under inert argon conditions. For a typical solution based polymerisation, 4-^{i}PrCL (0.25 g, 1.6 mmol) and the required amount of initiator was dissolved in toluene (3 mL). The ampoule was then placed in a preheated oil bath for the required time. After polymerisation the ampoule was opened to air, quenched with a few drops of MeOH and the solvent removed *in vacuo.* A crude NMR was recorded at this point to determine conversion of monomers from the relative integrals of monomer and polymer resonances. The polymer was then washed with copious amount of MeOH to remove unreacted monomer before thorough drying under vacuum. For solvent-free polymerisations the monomer and initiator were sealed in an ampoule before transferring to a preheated oil bath. For diethylzinc/benzyl alcohol experiments a 1:1 stock solution of $ZnEt_2$ (1M in hexanes) and benzyl alcohol was prepared and the required amount added via syringe. The polymerisation proceeded for the required time or until the solution solidified and stirring was no longer possible. On cooling the polymer was dissolved in CH_2Cl_2, which was then removed *in vacuo* and a crude ^{1}H NMR spectrum obtained. The polymer was purified in the same way. For copolymerisation studies the amount of each monomer was varied to ensure the same quantity was used.

Purified polymers were characterised by gel permeation chromatography (GPC) to determine molecular weight and polydispersity. GPC was carried out on an Agilent Technologies 1260 Infinity instrment with a flow rate of 1 mL min^{-1} at 35 °C with a THF eluent and referenced against polystyrene standards (RI). MALDI ToF mass spectra were determined by the EPSRC MS Service Swansea. Samples were ionised with NaOAc and run on a Bruker ultrafleXtreme.

DSC analysis was recorded on a TA Instruments DSC Q20. For homopolymers the sample was held at -70 °C for 1 minute, heated to 0 °C at 5 °C/min held at this temperature for 1 minute, cooled to -70 °C at 5 °C/min held at this temperature for 1 minute and finally heated to 25 °C at 5 °C/min. For copolymers the range was -70 °C – 220 °C and rate was 10 °C/min. The T_g and T_m values are quoted for the second heating cycle.

Preparation of 4-isopropylcaprolactone from β-pinene



Synthesis of (+)-nopinone (1). A solution of β-pinene (30 g, 0.22 mol) in CH_2Cl_2 (or MeOH) (300 mL) was treated with a flow of ozone at -78 °C until a characteristic blue colour was observed (typically 6 h). The ozone treatment was stopped, and nitrogen was bubbled through the solution to remove excess ozone. The ozonide intermediate was quenched *via* dropwise addition of triethylamine (2 eq.) with stirring while gradually warming to room temperature. The resulting solution was stirred for 18 hr at RT before washing with 1M HCl (5 x 200 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to a pale yellow-green oil which was purified by vacuum distillation (85 °C, 0.45 torr) to yield **1** as a pale yellow-green oil (26.27 g, 0.18 mol, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, s, CH_3), 1.31 (3H, s, CH_3), 1.56 (1H, d, J=10.0 Hz, CH), 1.98 (1H, m, CH), 2.22 (1H, m, CH), 2.32 (1H, m, CH), 2.52 (3H, m, CH_2 + CH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 21.4, 22.1, 25.2, 25.9, 32.7, 40.4, 41.2, 58.0, 214.8 (C=O). GC-MS retention time = 6.2 min.

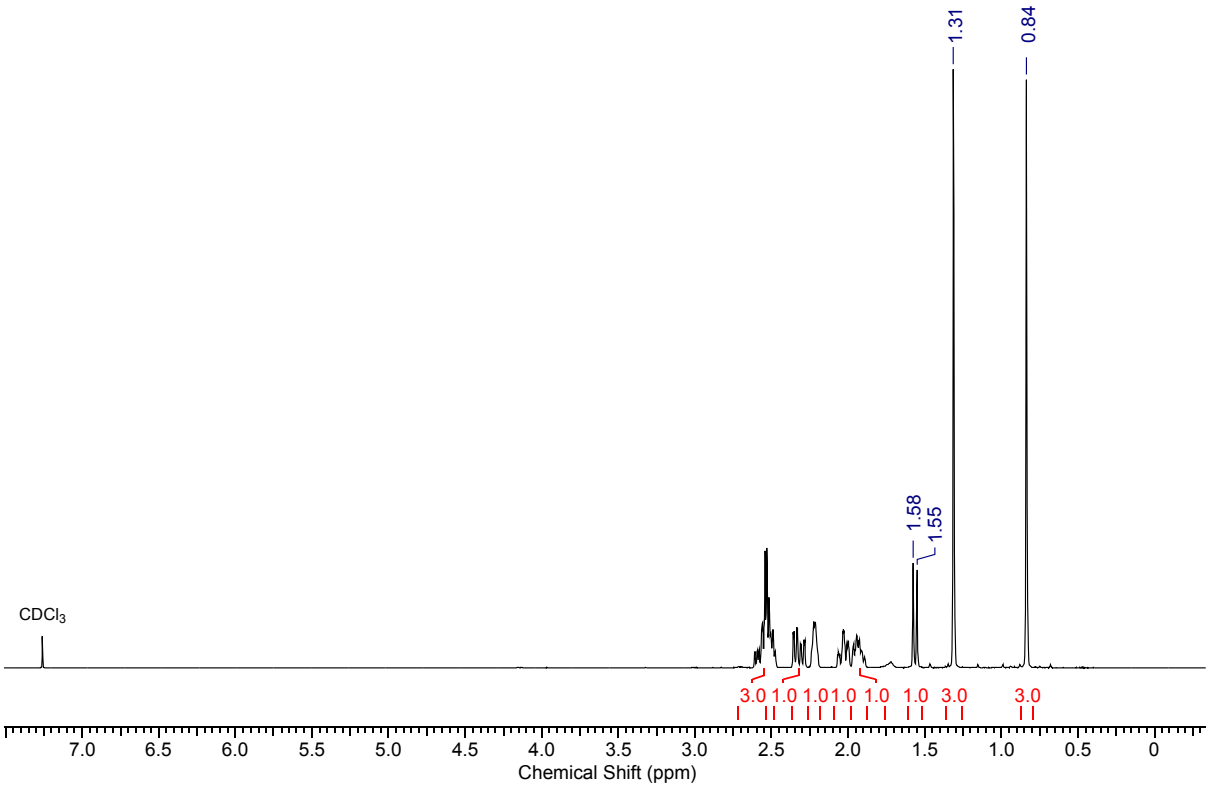


*Figure S1. ^{1}H NMR spectrum of (+)-nopinone (**1**).*

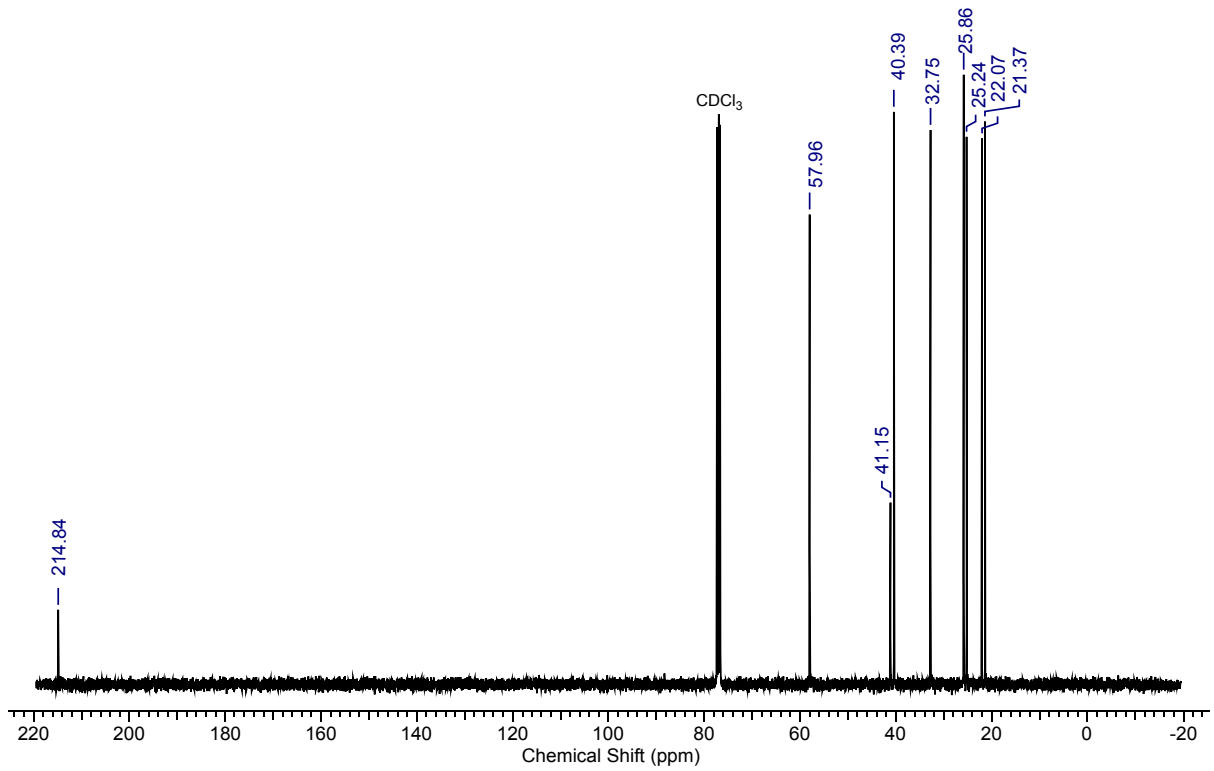
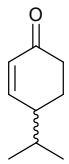


*Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1**.*



Preparation of (±)-cryptone (2).[3] (+)-Nopinone (6.0 g, 43.4 mmol) was dissolved in CH_2Cl_2 (150 mL) under Ar and cooled to 0 °C. $AlCl_3$ (11.6 g, 2 eq.) was added slowly with stirring, and the resulting mixture stirred for 1.5 h. During this time the solution became dark brown. The reaction was quenched by pouring the solution slowly into ice and water (100 mL), and an instant colour change to yellow was observed. The phases were separated, and the organic layer washed with saturated solutions of sodium bicarbonate (100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a brown oil. This was purified by column chromatography on silica (pet ether/Et_2O 95:5) to yield the product as a pale yellow oil (5.53 g, 40.0 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (td, *J* = 1.0 Hz, 6 H, CH_3), 1.61 - 1.87 (m, 2 H, CH_2), 1.91 - 2.12 (m, 1 H, CH), 2.14 - 2.38 (m, 2 H, CH_2), 2.49 (dt, *J* = 1.0 Hz, 1 H), 5.99 (dt, *J* = 10.5, 1.5 Hz, 1 H), 6.88 (dt, *J* = 10.5, 1.5 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.0 (C=O), 154.2 (C=C), 129.6 (C=C), 42.4 (CH), 37.3 (CH_2), 31.4 (CH), 25.2 (CH_2), 19.5 (CH_3), 19.4 (CH_3). GC-MS retention time = 6.8 min.

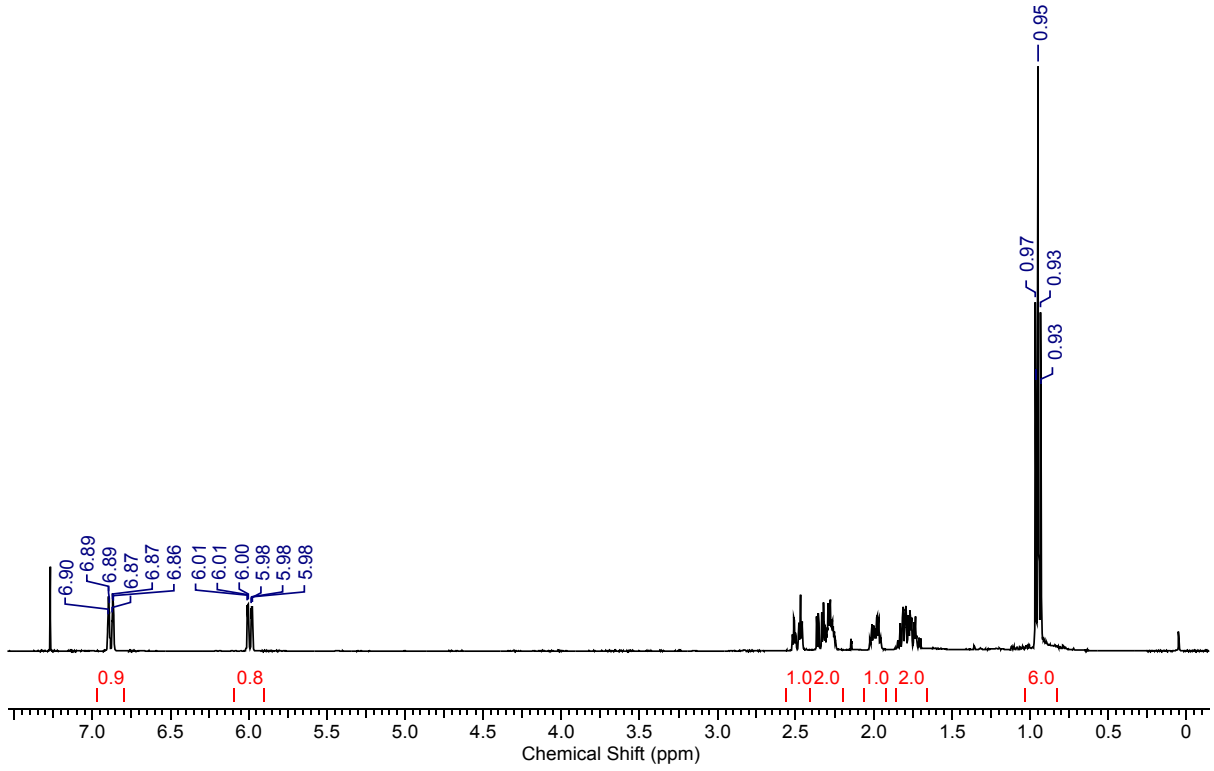


*Figure S3. ^{1}H NMR spectrum of (+)-cryptone (**2**).*

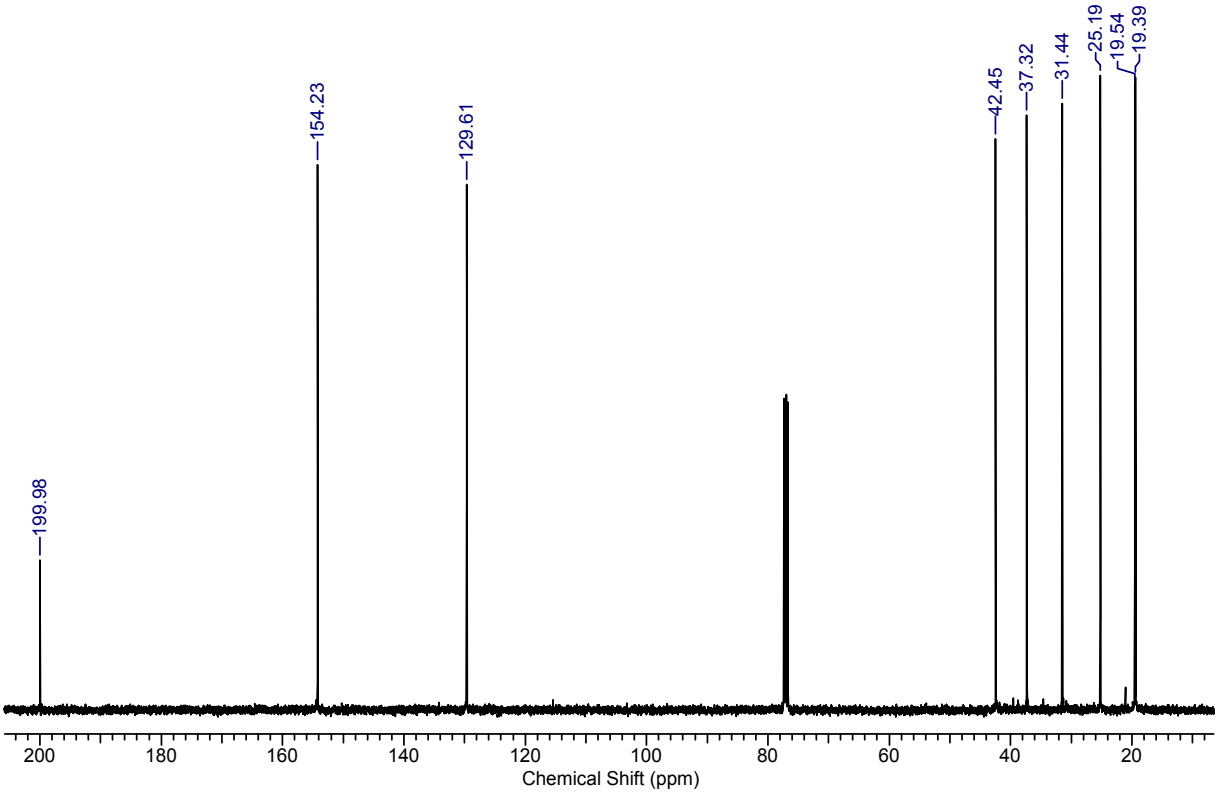


*Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.*

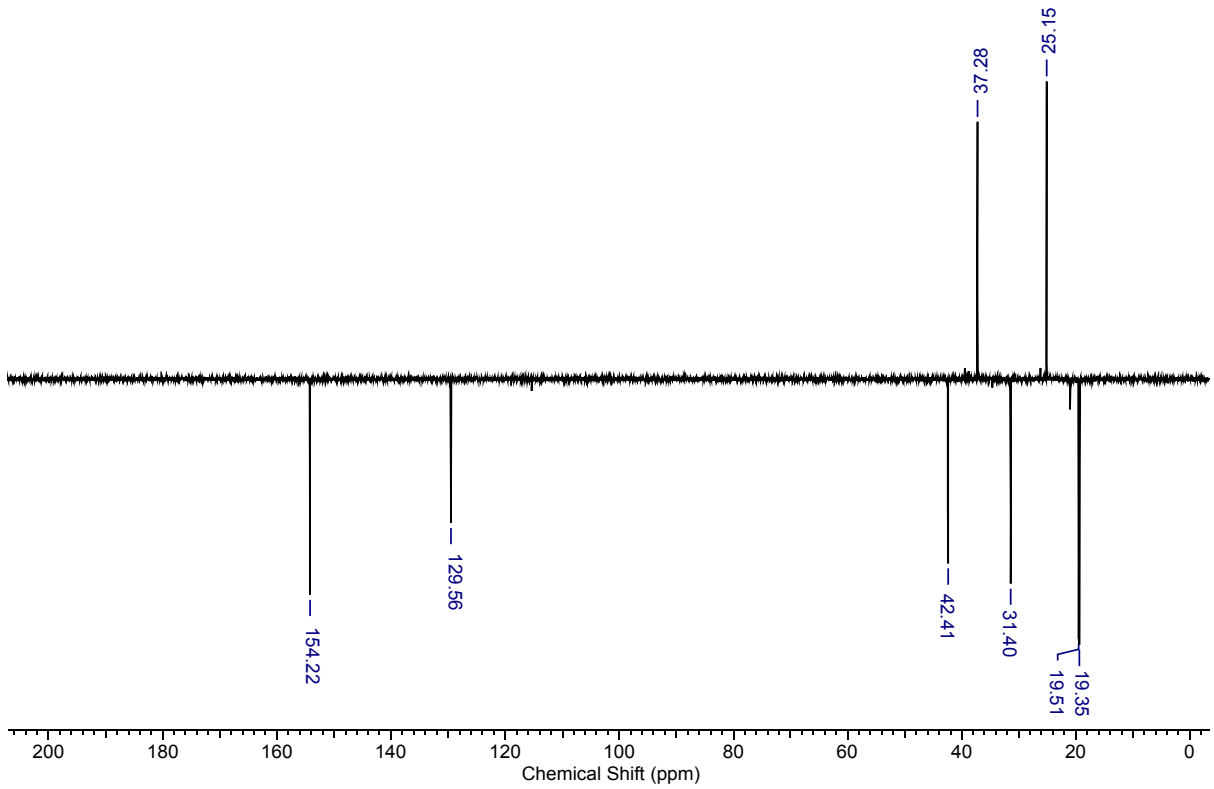
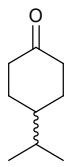


*Figure S5. DEPT-135 $^{13}C\{^{1}H\}$ NMR spectrum of **2**.*



Preparation of 4-isopropylcyclohexanone (3). A Parr 5500 high pressure reactor was charged with cryptone (**2**) (1.0 g, 7.24 mmol), $Rh(PPh_3)_3Cl$ (Wilkinson's catalyst, 5 wt%, 50 mg) and EtOAc (20 mL). The reactor was flushed with hydrogen (10 bar) before sealing and heating at 40 °C for 24 h with stirring. After this time the rector was vented, allowed to cool and the solution was passed over Celite before removing the solvent, giving a brown oil. Purified by vacuum distillation to yield **3** as a colourless oil (0.96 g, 6.88 mmol, 95 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (6H, d, J=6.5 Hz, 2 x CH_3), 1.49 (4H, m, J=5.0 Hz, 2 x CH_2), 1.98 (2H, m, J=2.5 Hz, 2 x CH), 2.31 (4H, m, J=6.5 Hz, 2 x CH_2-C(O)). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 18.9 (2 x CH_3), 28.6 (2 x CH_2), 30.8 (CH), 40.0 (2 x CH_2), 41.5 (CH), 211.6 (C=O). GC-MS retention time = 6.1 min.

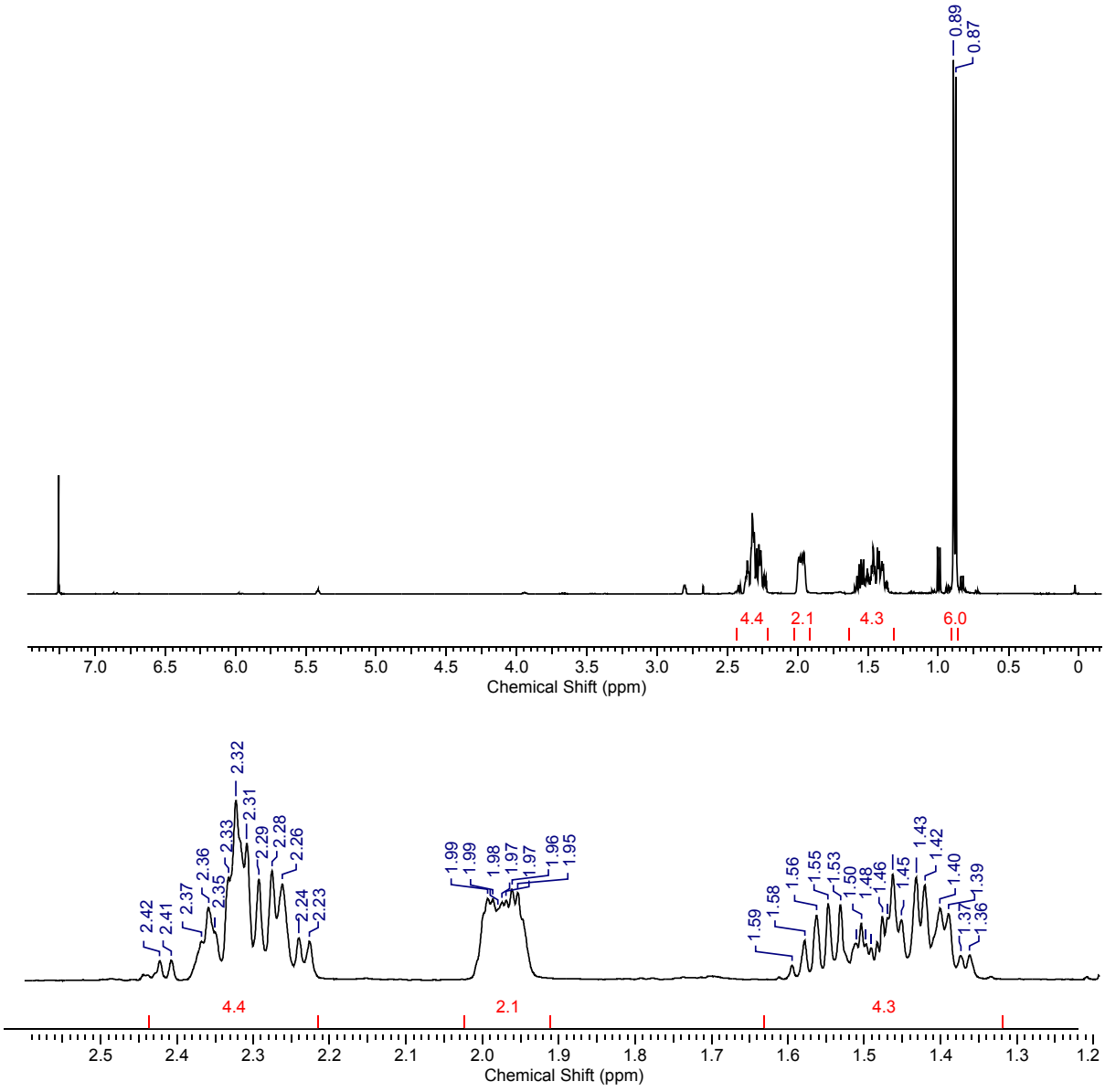


*Figure S6. ^{1}H NMR spectrum of **3**, with expanded aliphatic region.*

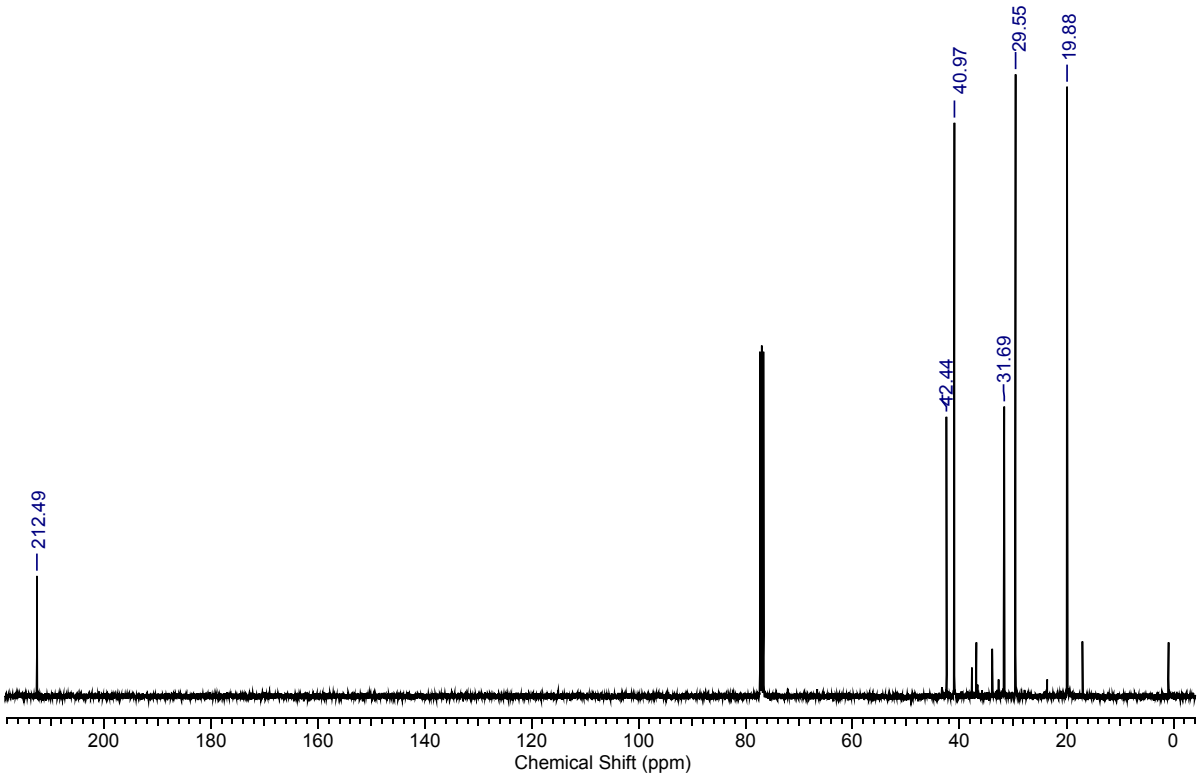


*Figure S7. $^{13}C\{^{1}H\}$ spectrum of **3**.*

Preparation of 4-isopropylcaprolactone (4^{i}PrCL) (4). To a stirred solution of 4-isopropylcyclohexanone (Fluorochem, 10.0 g, 70 mmol, or **3**) in CH_2Cl_2 (150 mL) under Ar at 0 °C was added m-CPBA in portions (14.8 g, 84 mmol, 1.2 eq.). On warming to RT a white precipitate formed, and the suspension was stirred for 48 h. The precipitate was removed by vacuum filtration and the solution was washed with Na_2SO_3 (10% aq., 200 mL), and saturated solutions of sodium bicarbonate (200 mL) and brine (200 mL). The organic fraction was dried over $MgSO_4$ and concentrated to a yellow oil (10.32 g). This was purified *via* column chromatography on silica (hexane/EtOAc 6:1) and dried by vacuum distillation (bpt = 239 °C, 1 atm, 95 °C, 0.45 torr) over CaH_2 to yield **3** as a colourless oil (9.7 g, 62 mmol, 89%).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.85 (6H, dd, J=2.5 Hz, 2 x CH_3), 1.46 (4H, m, 2 CH, CH_2), 1.85 (2H, m, CH_2), 2.59 (2H, m, CH_2), 4.20 (2H, m, C(O)-CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 19.1 (CH_3), 19.2 (CH_3), 25.6 (CH_2), 31.9 (CH_2), 32.4 (CH), 33.3 (CH_2), 46.4 (CH), 68.4 (CH_2-O), 176.0 (C=O). m/z calc. for $C_9H_{16}O_2Na$ $[M+Na]^+$: 179.1048, found 179.1083. GC-MS retention time = 9.4 min.

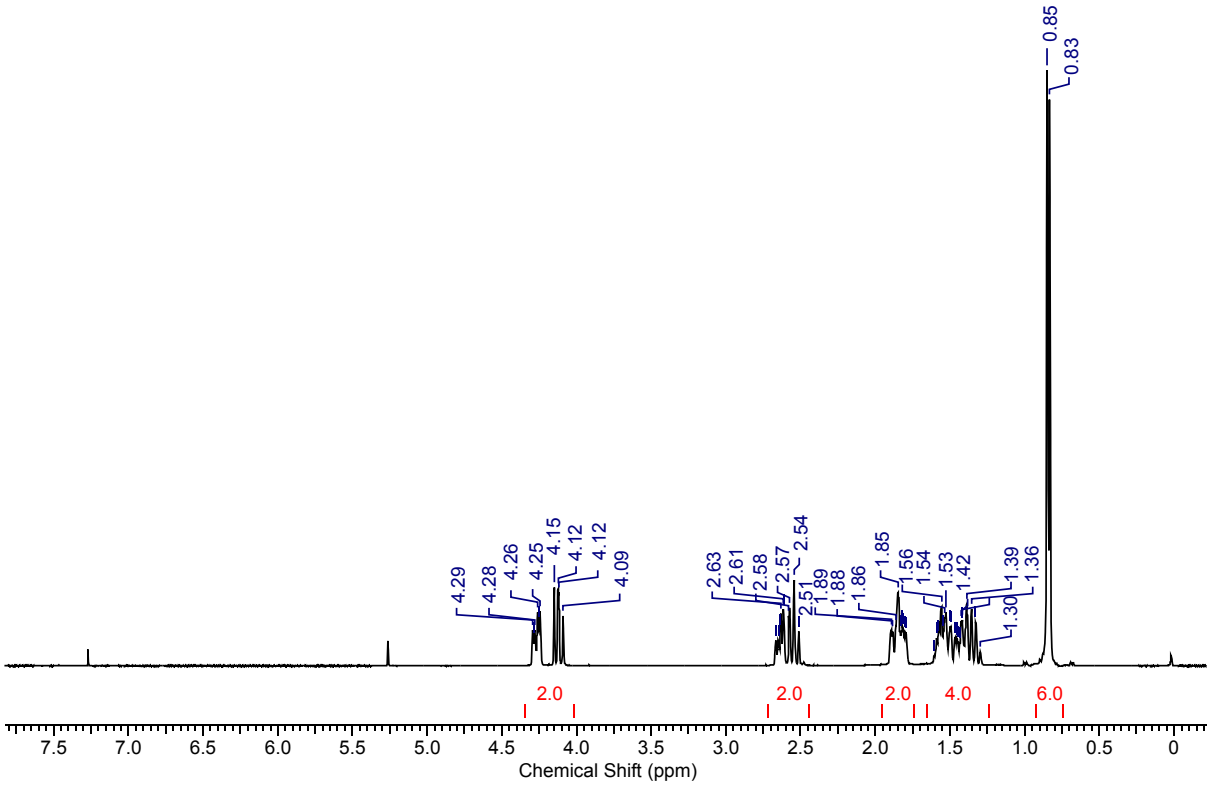


*Figure S8. ^{1}H NMR spectrum for 4-isopropylcaprolactone (**4**).*

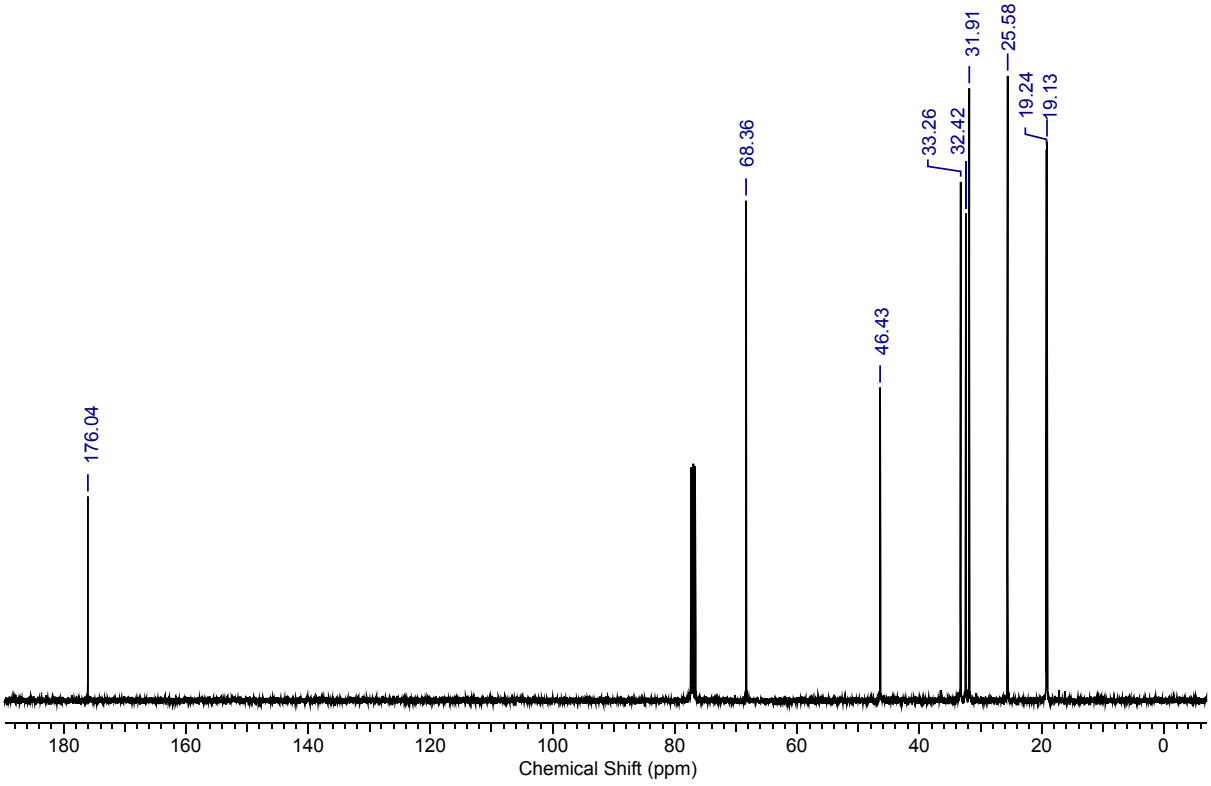


*Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum for **4**.*

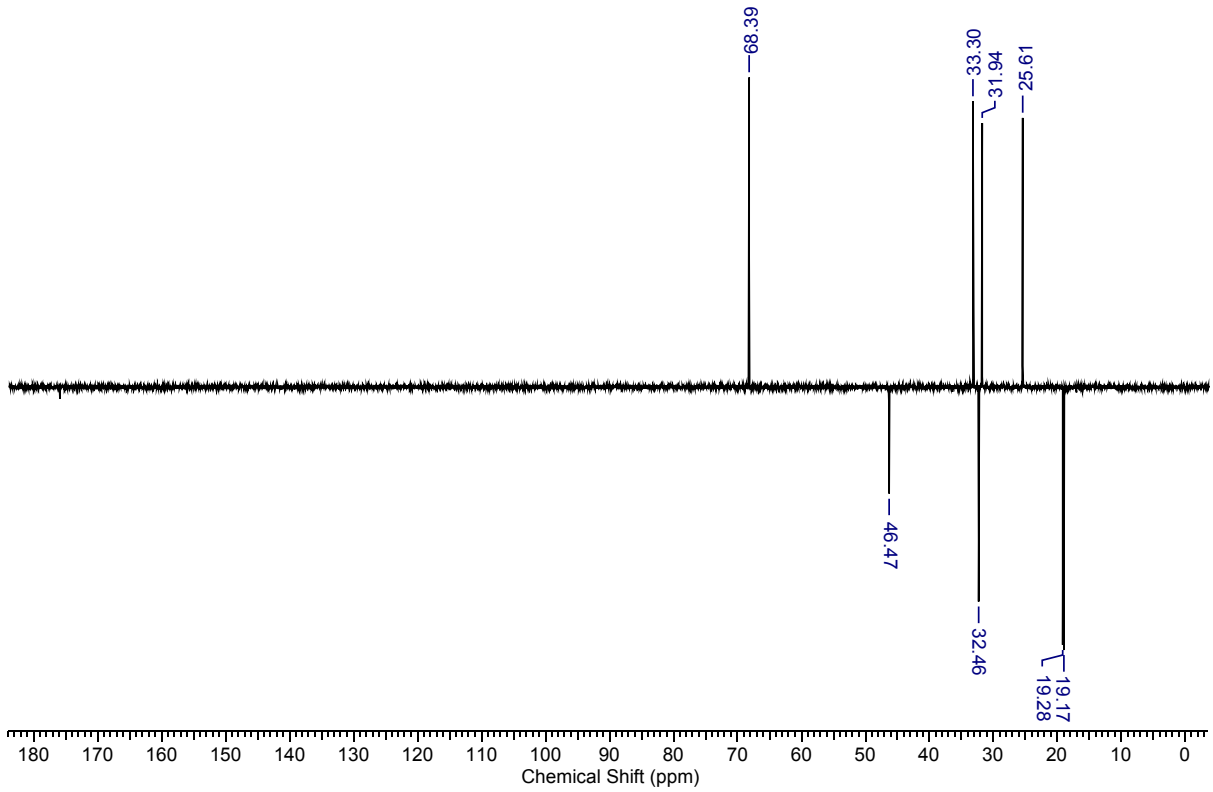
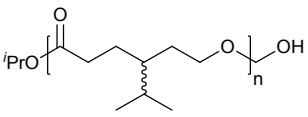


*Figure S10. DEPT-135 $^{13}C\{^{1}H\}$ NMR spectrum for **4**.*



Poly(4-isopropylcaprolactone). Thick, colourless gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (dd, *J* = 7.0 3.5 Hz, 6H, 2 x CH_3), 1.18 - 1.31 (m, 1H), 1.40 - 1.59 (m, 2H, CH_2), 1.59 - 1.76 (m, 3H, CH + CH_2), 2.17 - 2.37 (m, 2H, CH_2), 3.99 - 4.15 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl) δ 18.6 (CH_3), 19.1 (CH_3), 25.9 (CH_2), 29.1 (CH_2), 29.2 (CH), 32.5(CH_2), 40.3 (CH), 63.3 (CH_2-O), 173.6 (C=O).

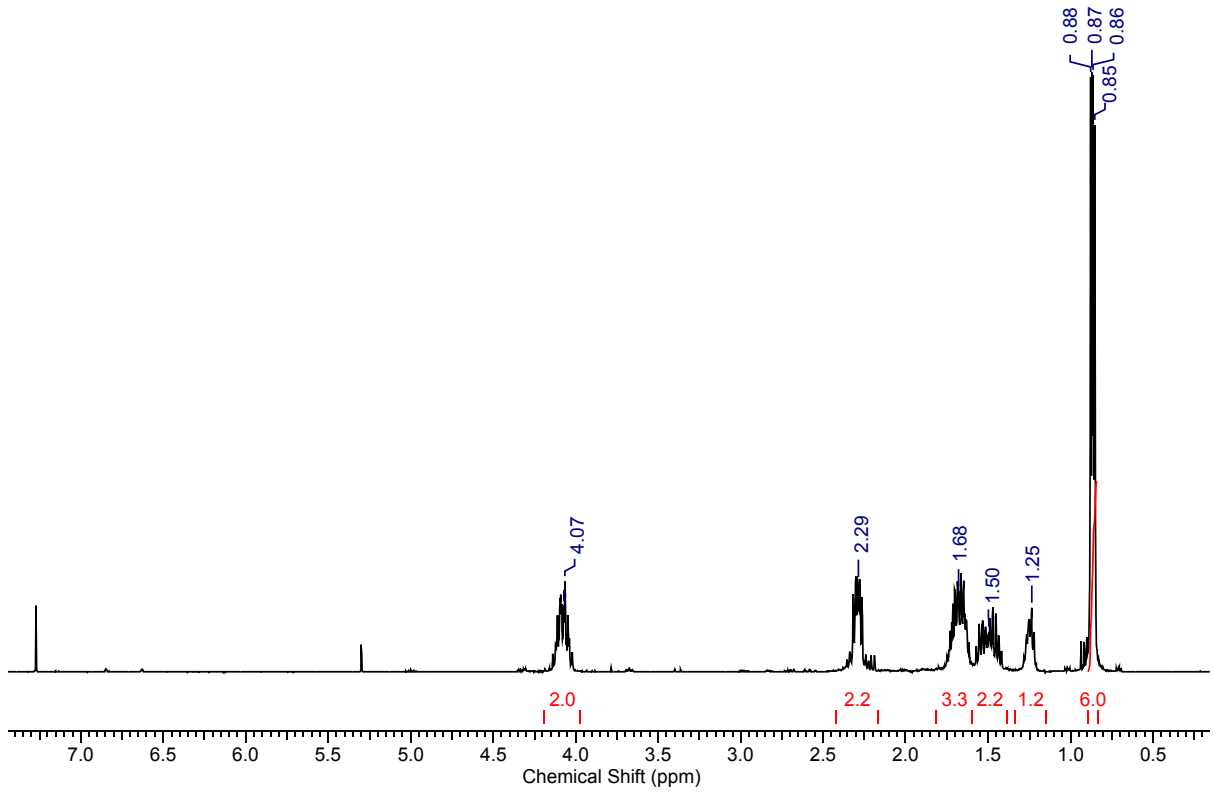


*Figure S11. ^{1}H NMR spectrum of poly(**4**) ($CDCl_3$, 400 MHz).*

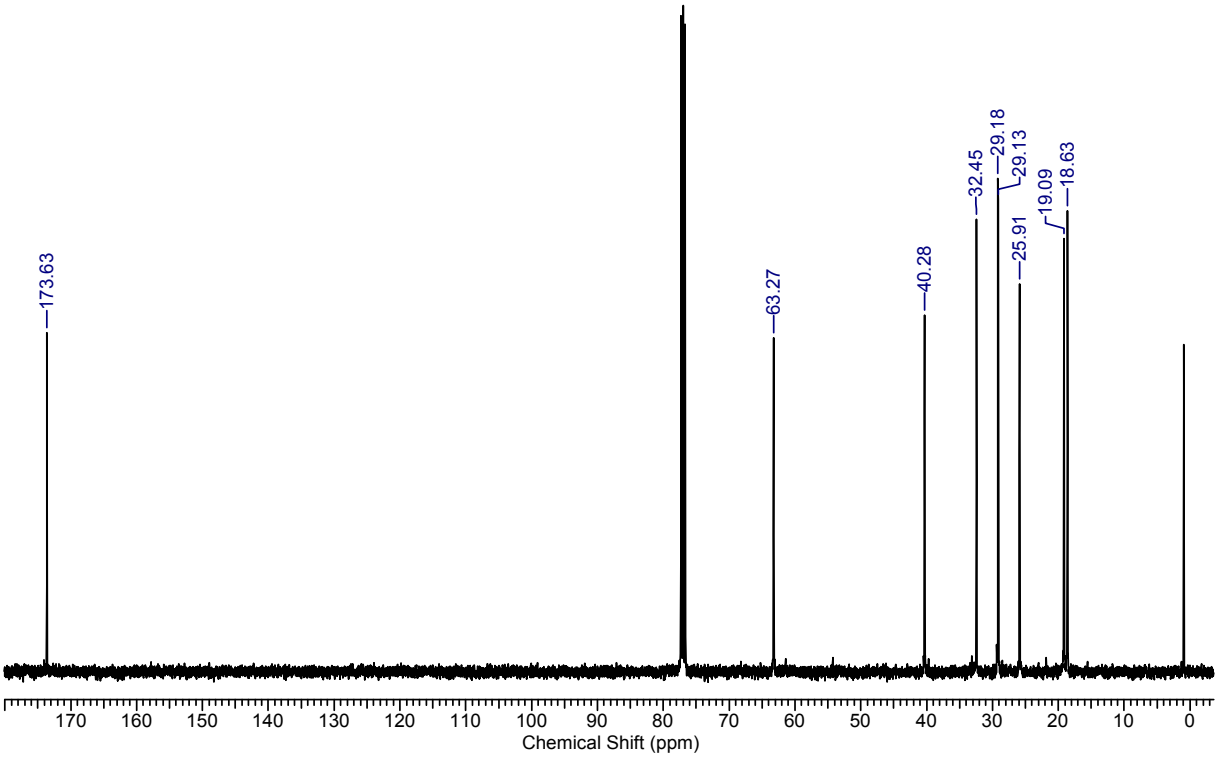


*Figure S12.. $^{13}C\{^{1}H\}$ NMR spectrum of poly(**4**) ($CDCl_3$, 101 MHz).*

Selected polymer characterisation

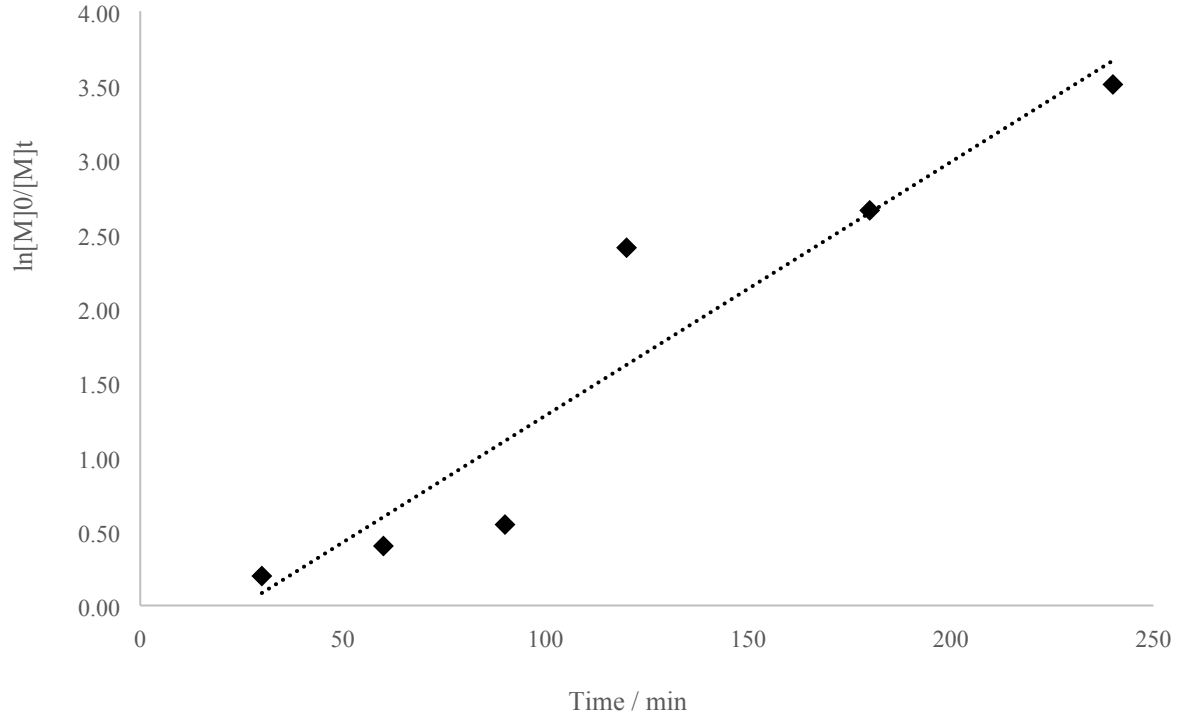


Figure S13. Kinetic plot for homopolymerisation with $ZnEt_2$/BnOH. [M]:[Zn]:[BnOH] = 100:1:1, 100 °C, solvent free.

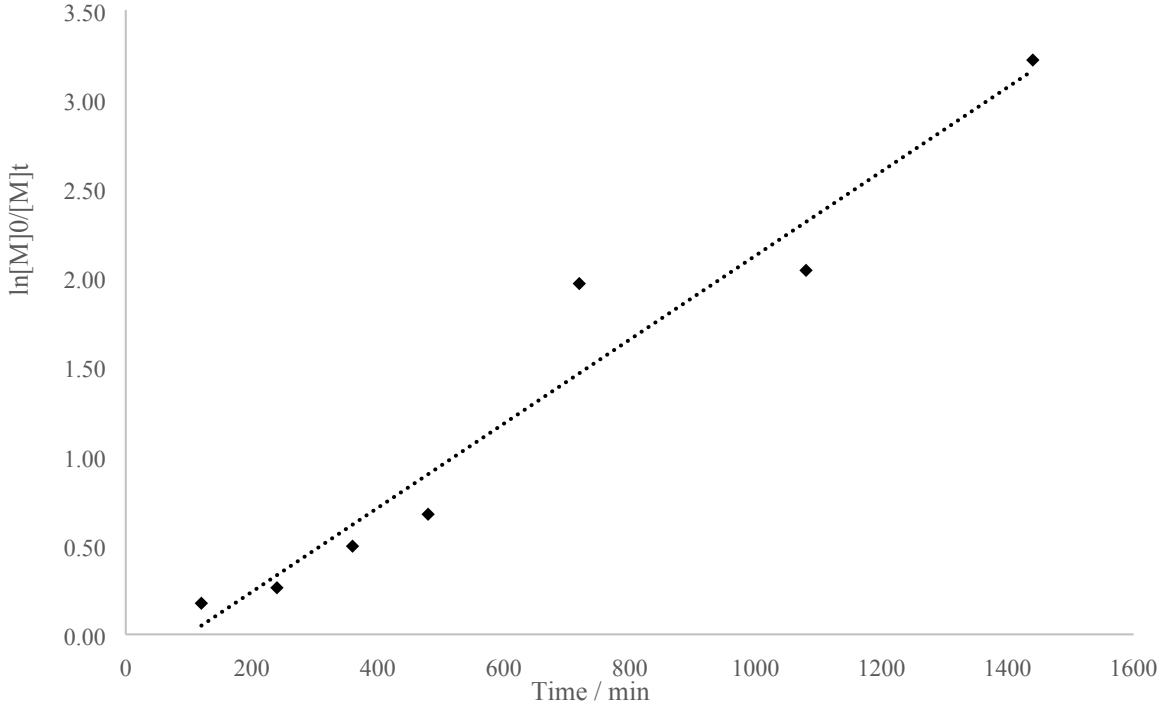


*Figure S14. Kinetic plot for homopolymerisation of **4** with Zr(tris)(O^{i}Pr), [M]:[Zr] = 100:1, 100 °C, solvent free.*

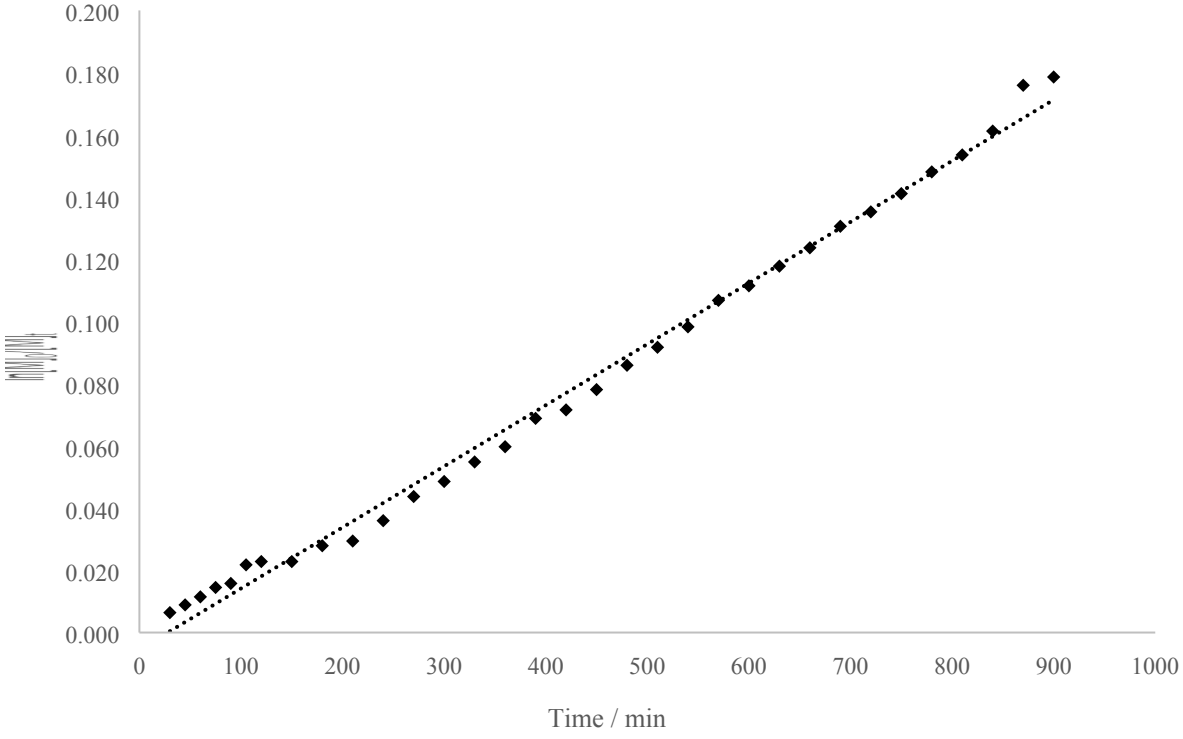


*Figure S15. Kinetic plot for solution kinetics for homopolymerisation of **4** with Zr(tris)(O^{i}Pr), [M]:[Zr] = 100:1, d^{8} toluene, 80 °C.*

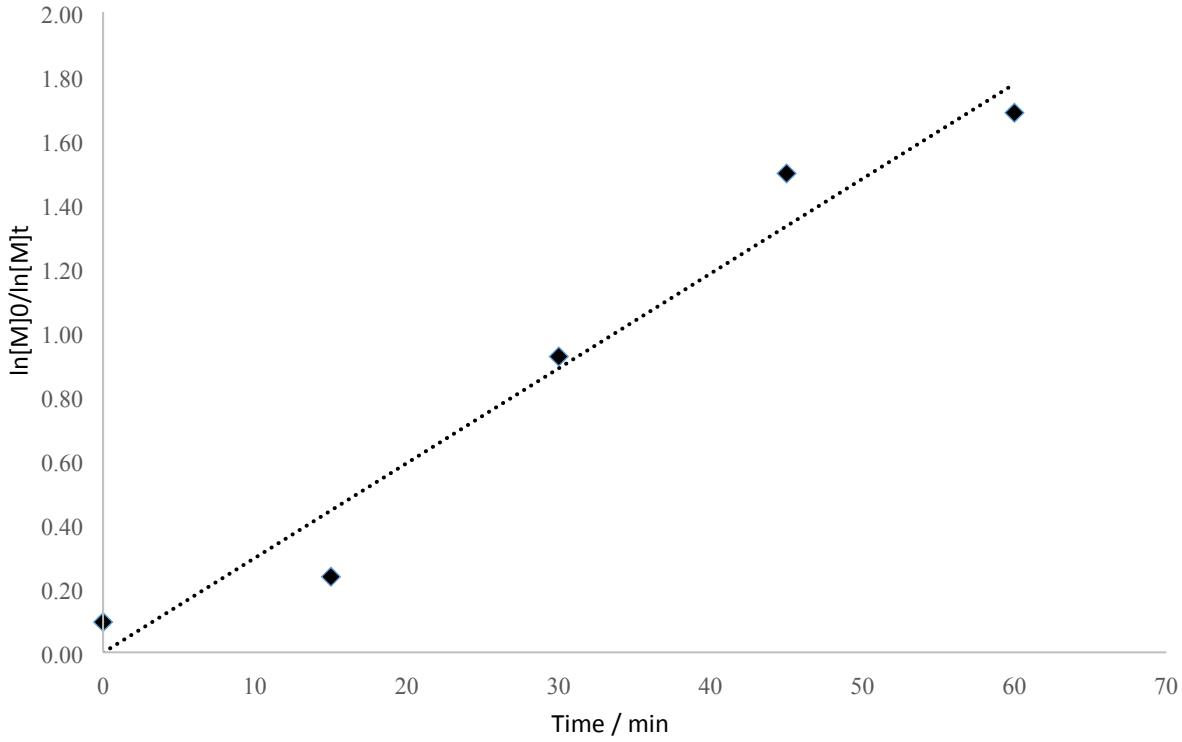


*Figure S16.Kinetic plot for solution kinetics of homopolymerisation of **4** with Zr(bis)(O^{i}Pr)$_{2,}$ [M]:[Zr] = 100, d^{8} toluene, 60 °C.*

Table S1. Polymerisation data for living character tests with Zr(tris)(O^{i}Pr)

[M]:[I]	t	T	Conversion %	Mn $_{calc}$	Mn	PDI	Tg / °C
50	24	100	94	7392	10100	1.58	-50.1
100	24	100	96	15036	11400	1.42	-50.9
200	24	100	79	24708	13500	1.18	-52.6
300	24	100	54	25332	9800	1.14	-
400	24	100	37	23148	7100	1.14	-
300	72	100	87	40776	14100	1.47	-51.6
400	72	100	55	34380	9200	1.30	-47.5

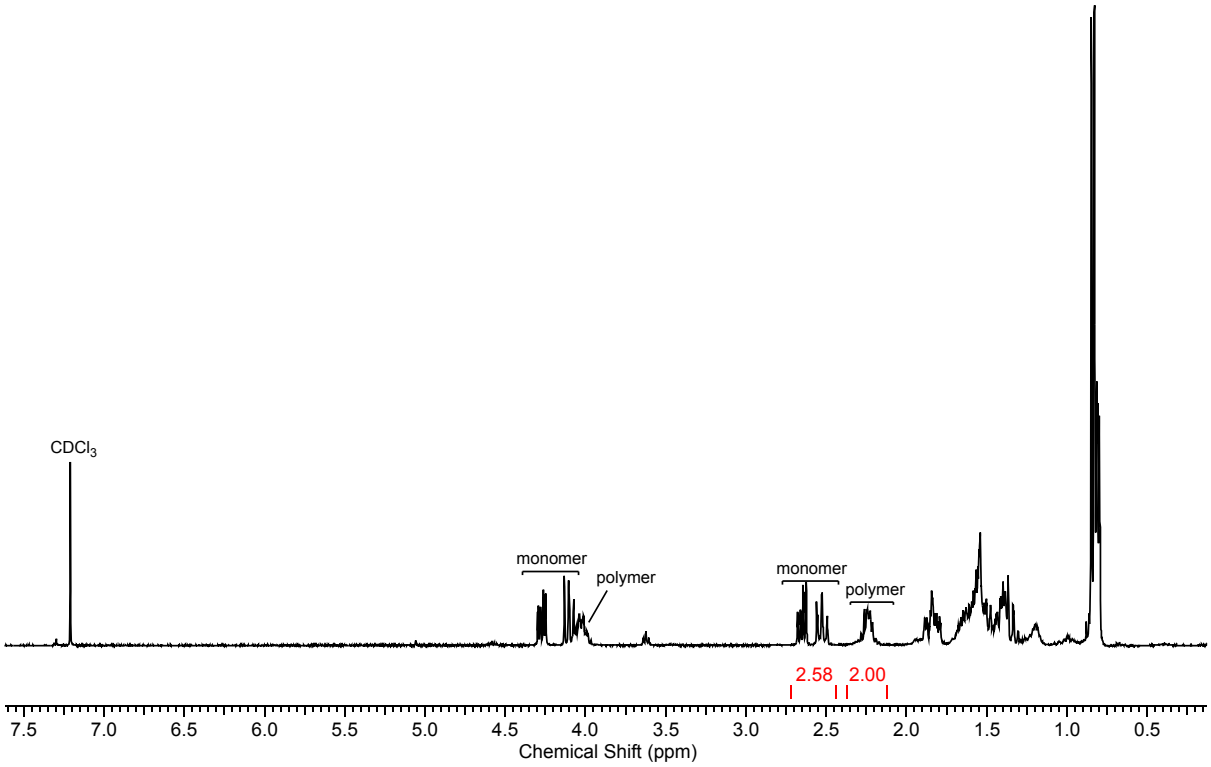


Figure S17. Example crude NMR spectrum showing conversion (table 1, entry 2).

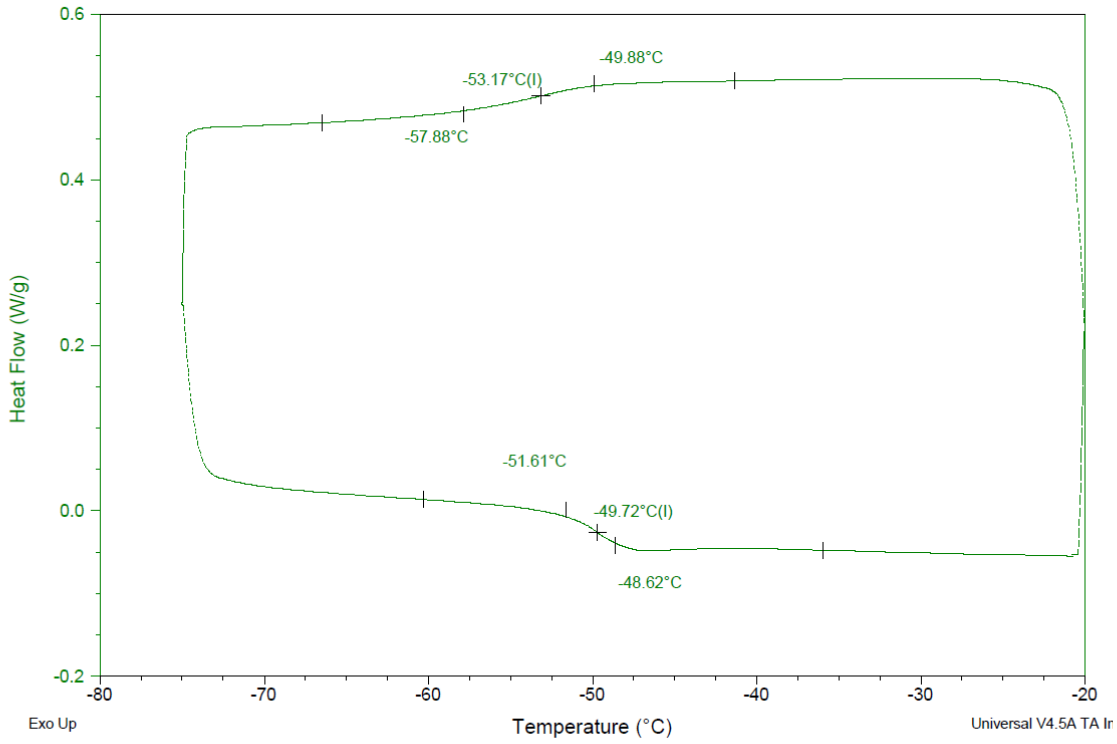


Figure S18. DSC trace for homopolymer showing glass transition at -49.72 °C (table 1, entry 6).

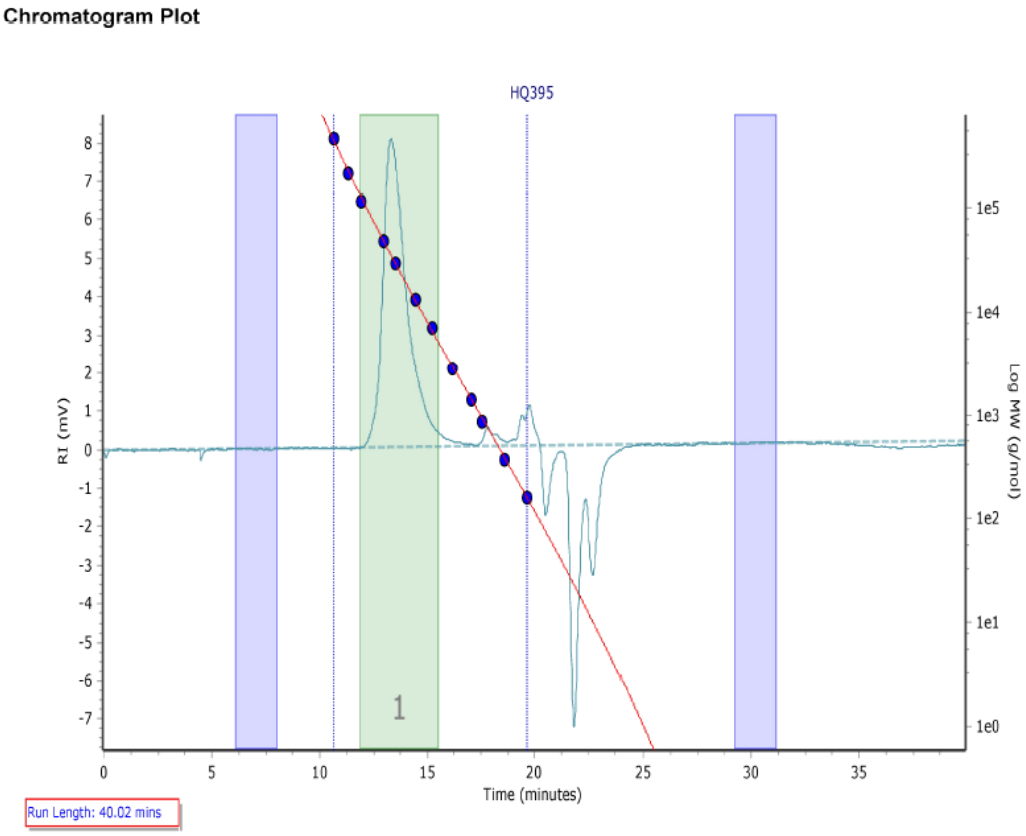


Figure S19. GPC trace for Table 1, Entry 1

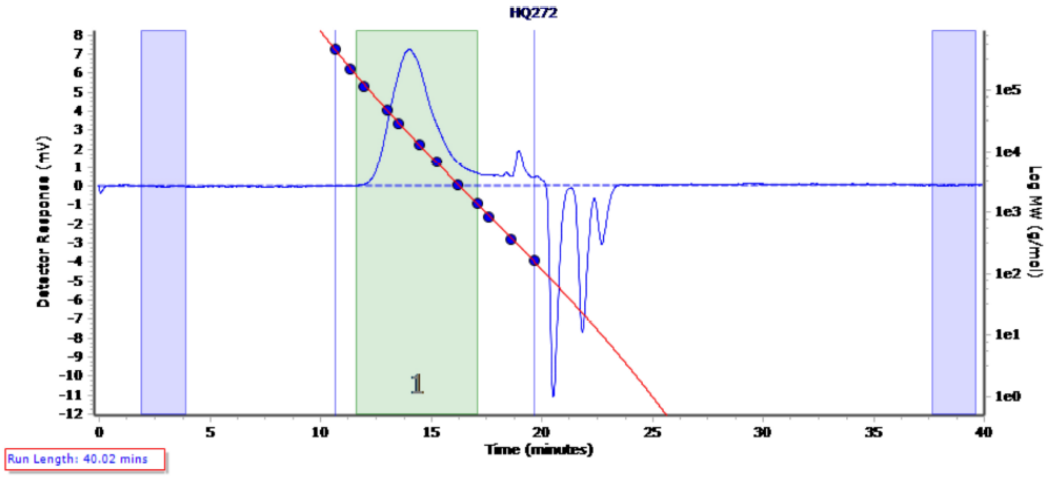


Figure S20. GPC trace for Table 1 Entry 5.

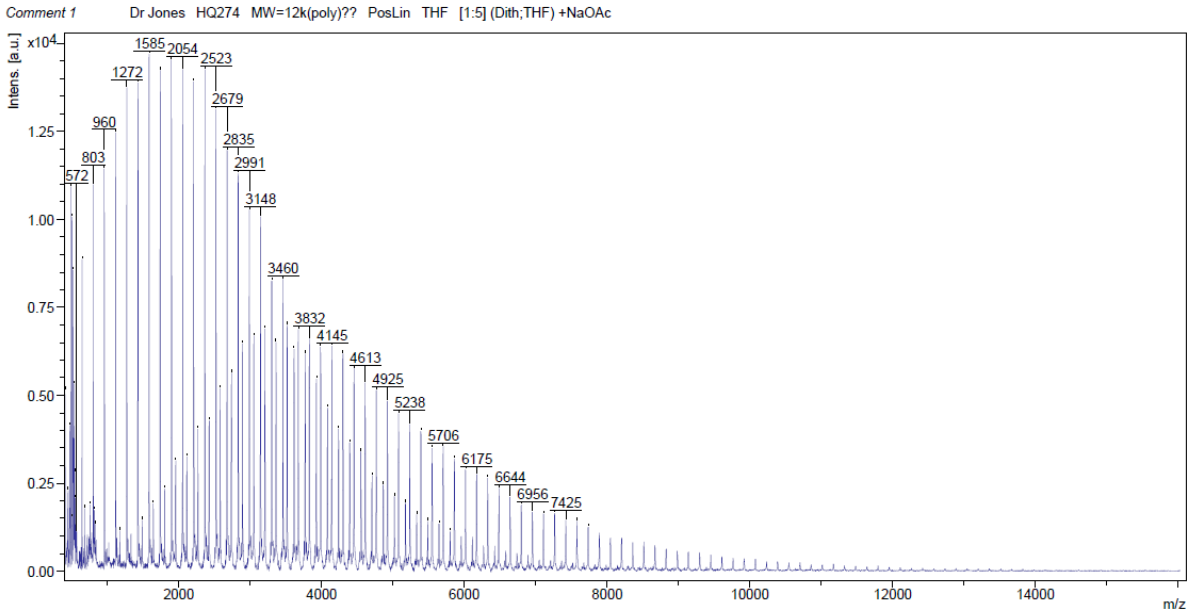


Figure S21. MALDI-TOF spectrum for Table 1, entry 6. Series A is cyclic polymer; series B is linear (HO^{i}Pr capped).

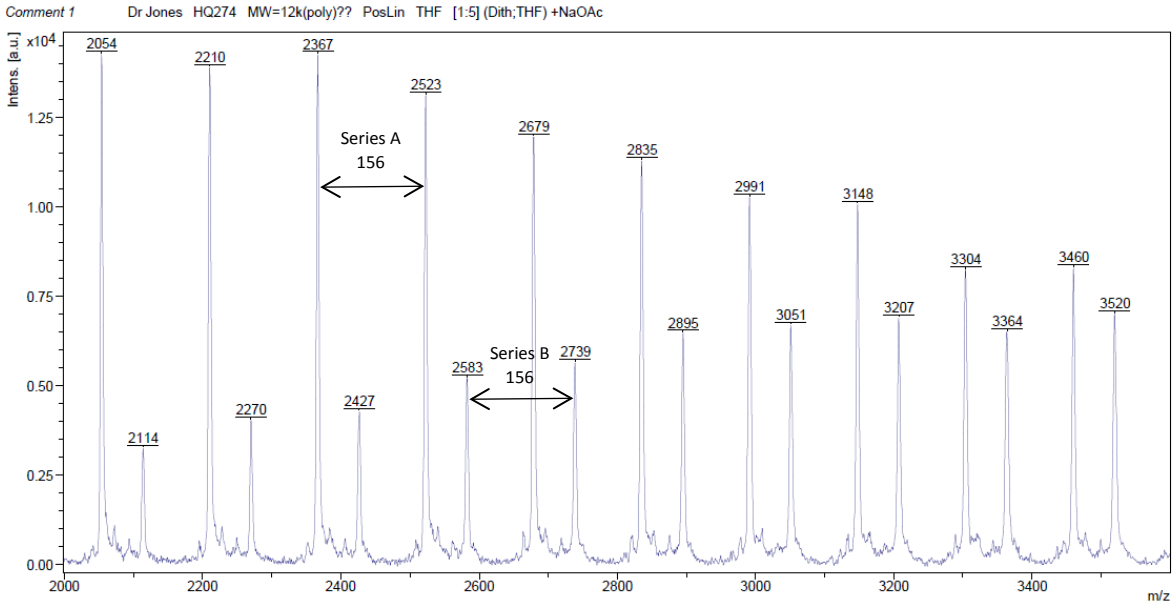


Figure S22. MALDI-TOF spectrum for Table 1, entry 6 showing polymer repeat units of 156 gmol^{-1}. Series A is cyclic polymer; series B is linear.

Copolymers

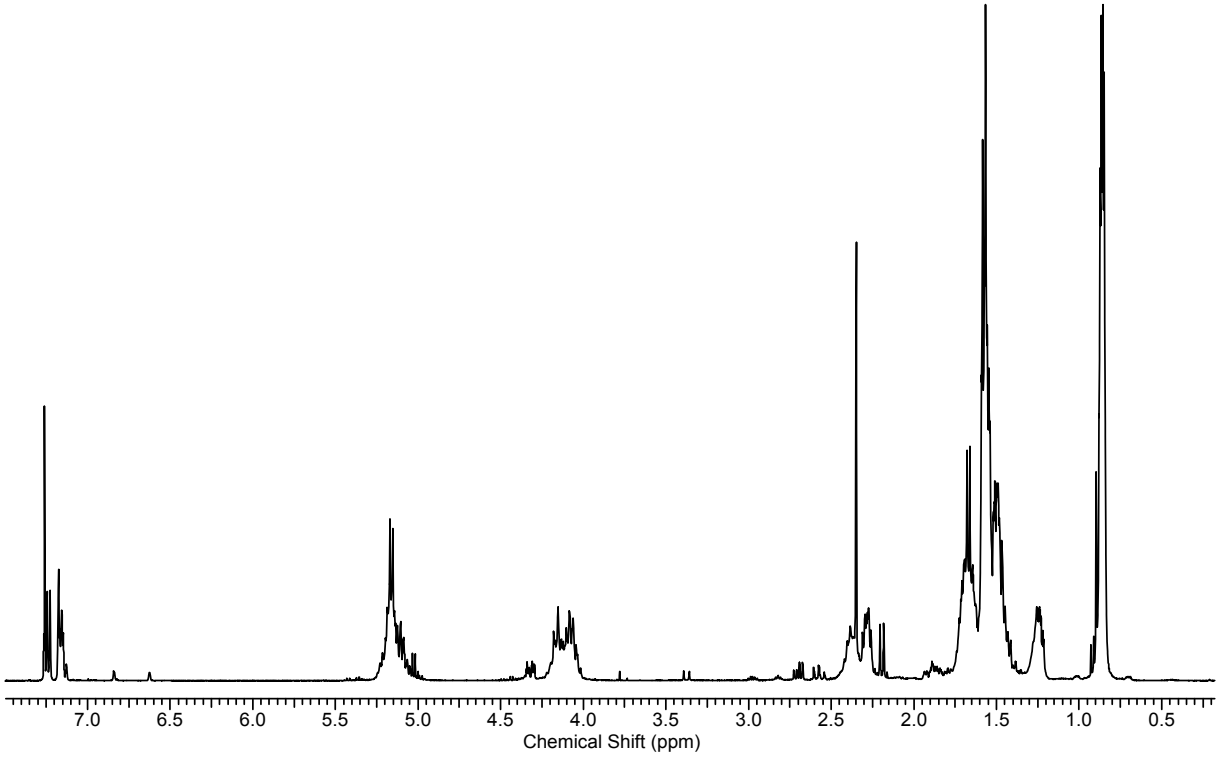


Figure S23. ^{1}H NMR spectrum for Table 2 Entry 14

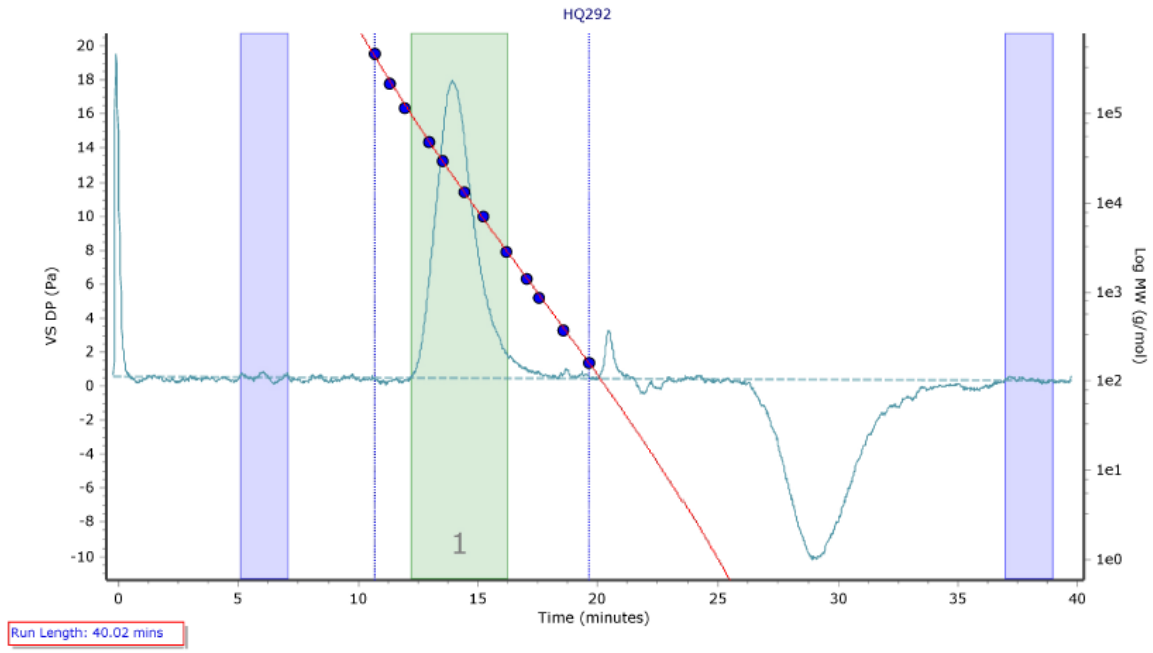


Figure S24. GPC trace for Table 2 Entry 14

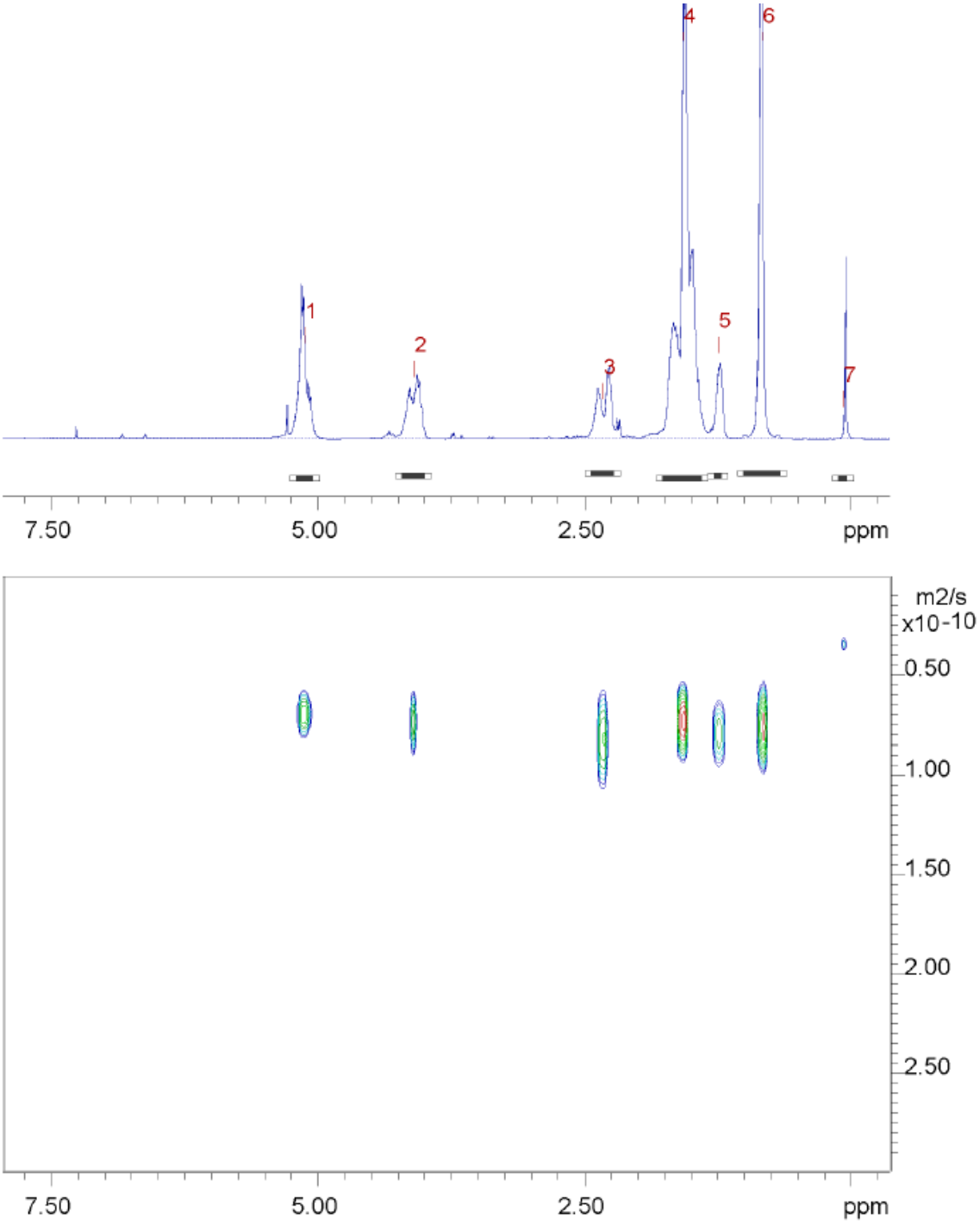


Figure S25. DOSY for Table 2, Entry 14

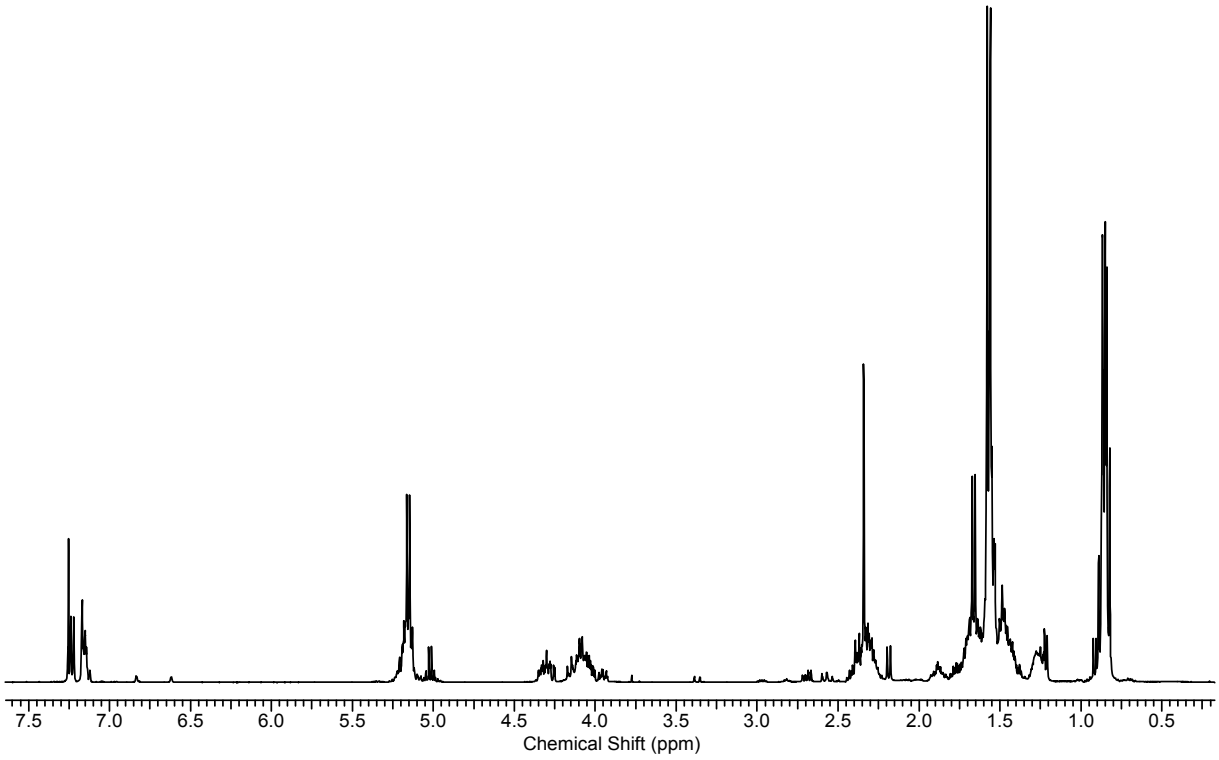


Figure S26. ^{1}H NMR spectrum for Table 2 Entry 13

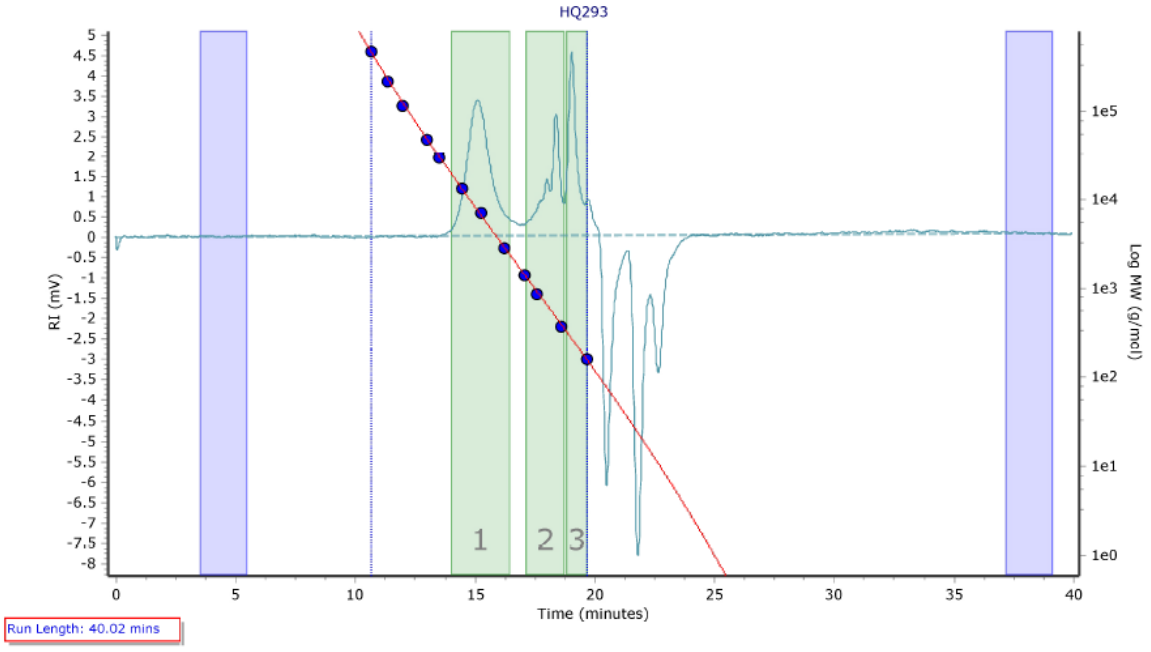


Figure S27. GPC trace for Table 2 Entry 13.

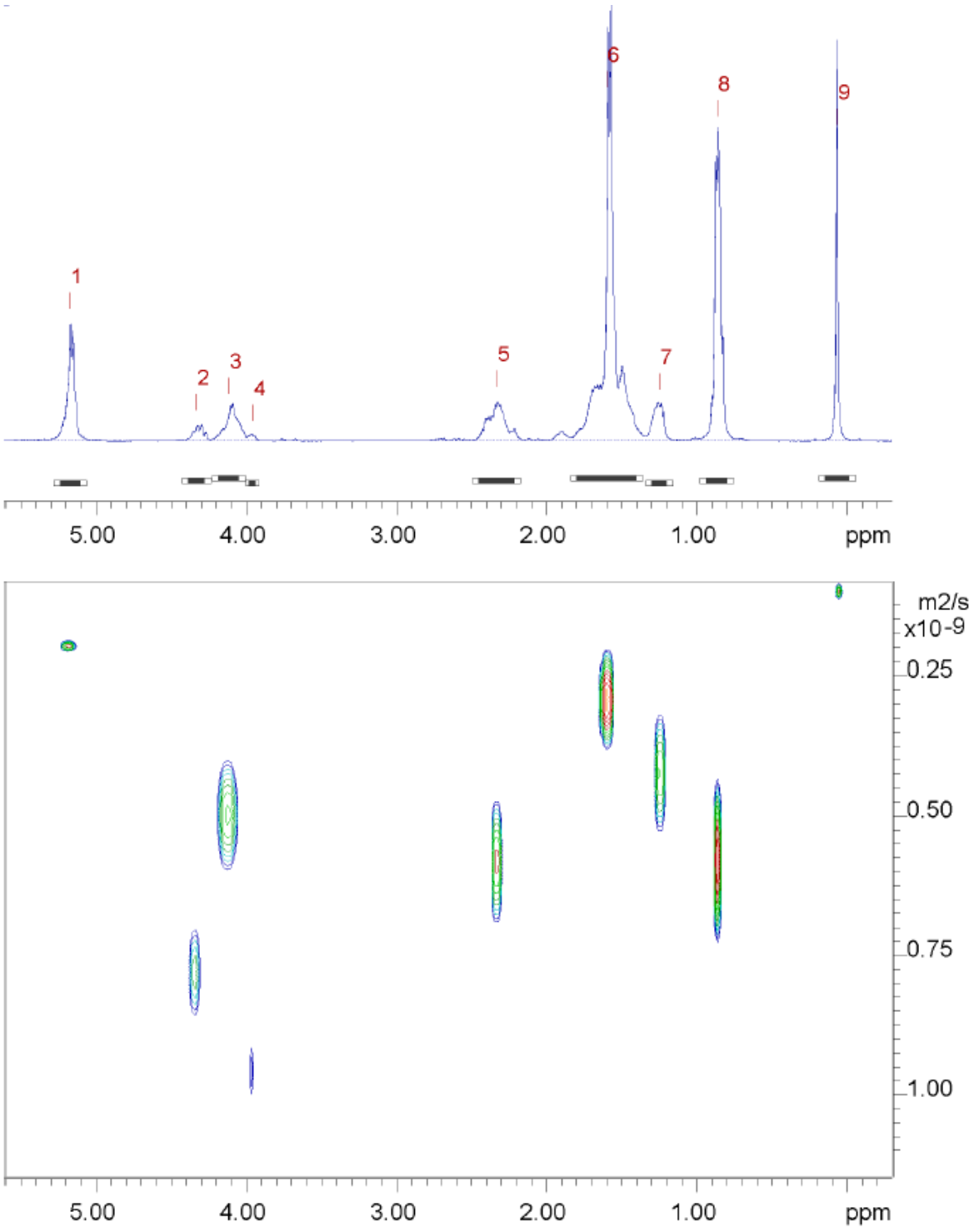


Figure S28. DOSY for Table 2, Entry 13

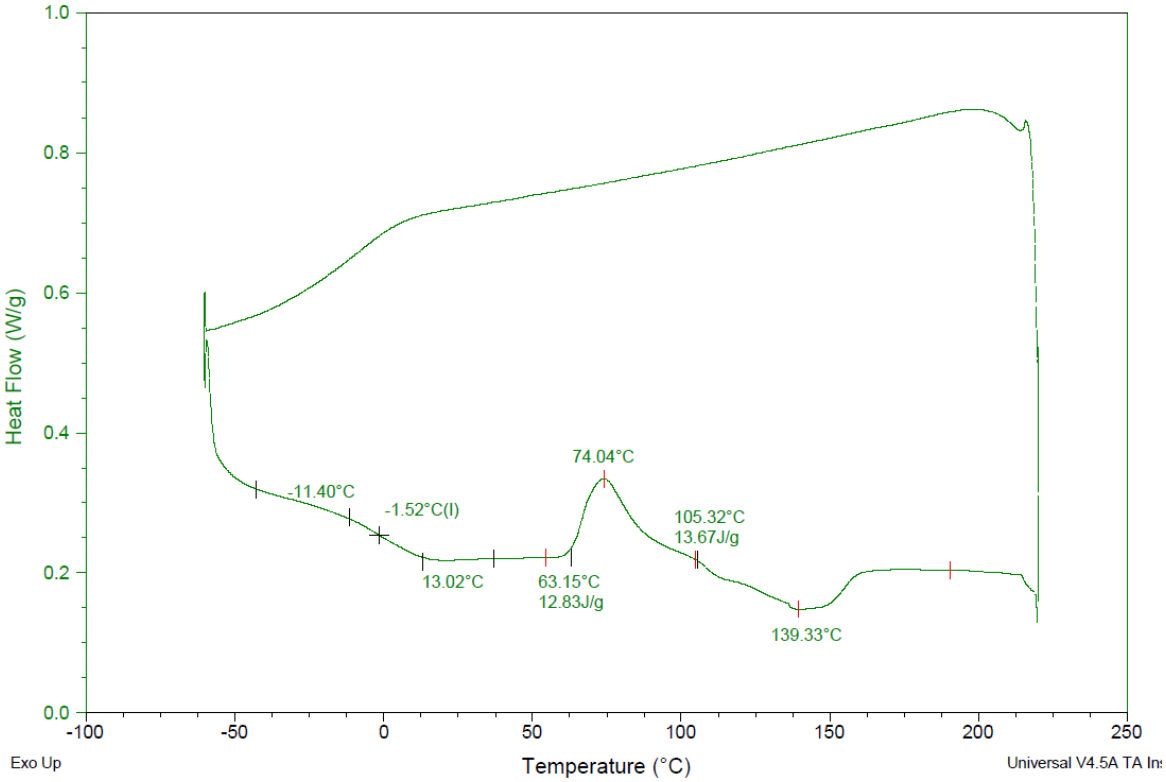


Figure S29. DSC trace for polymer sample (table 2, entry 13) showing T_g, T_c and T_m thermal events.

4-Isopropylcaprolactam synthesis:

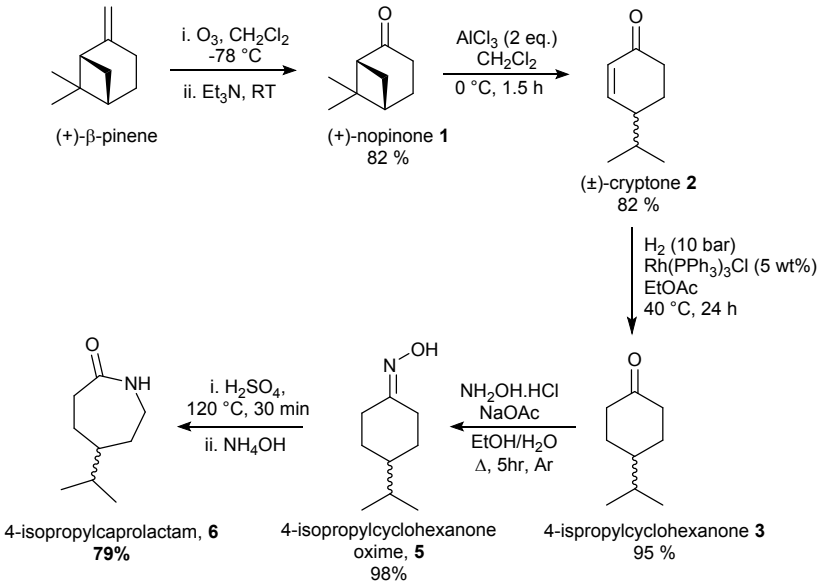


Figure S30. Preparation of 4-isopropylcaprolactam in 5 steps from (+)-β-pinene.

Preparation of 4-isopropylcyclohexanone oxime (5). 4-isopropropylcyclohexanone (**3**) (1.0 g, 7.2 mmol) was mixed with hydroxylamine hydrochloride ($NH_2OH.HCl$, 0.75 g, 10.8 mmol, 1.5 eq.) and sodium acetate (NaOAc, 1.1 g, 13 mmol, 1.8 eq.) in a mixture of ethanol (10 mL) and water (7 mL). The mixture was refluxed for 5 h under Ar before cooling to room temperature and stirring overnight. The solvent was removed *in vacuo* and the residue was taken up in EtOAc (25 mL),

washed with water (25 mL) and brine (sat., 25 mL). The organic phase was dried over Na_2SO_4 and the solvent removed to yield the product (**5**) as a thick, yellow oil (1.0 g, 0.70 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.78 Hz, 6 H, 2 x CH_3), 1.11 - 1.37 (m, 3 H, CH_2 + CH), 1.43 - 1.56 (m, 1 H, CH), 1.68 - 1.81 (m, 1 H, CH_2), 1.81 - 1.93 (m, 2 H, CH_2), 2.08 (dt, *J* = 13.40 Hz, 1 H, CH_2), 2.37 - 2.47 (m, 1 H, CH_2), 3.25 - 3.38 (m, 1 H, CH_2), 8.96 (br. s., 1 H, OH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 19.8 (CH_3), 19.8 (CH_3), 28.4 (CH_2), 29.6 (CH_2), 31.6 (CH_2), 32.1 (CH), 43.3 (CH), 160.9 (C=N). m/z calc for $C_9H_{18}NO$ $[M+H]^+$ = 156.1388, found 156.1397.

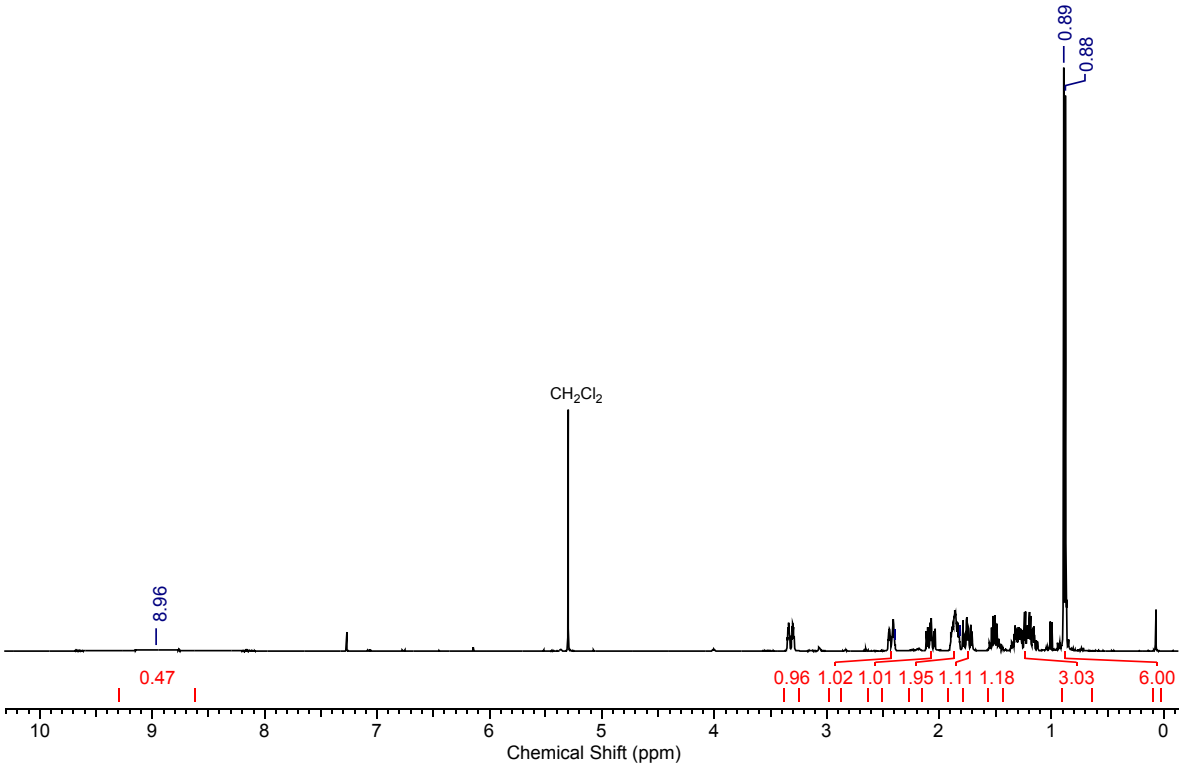


*Figure S31. ^{1}H NMR spectrum of **5***

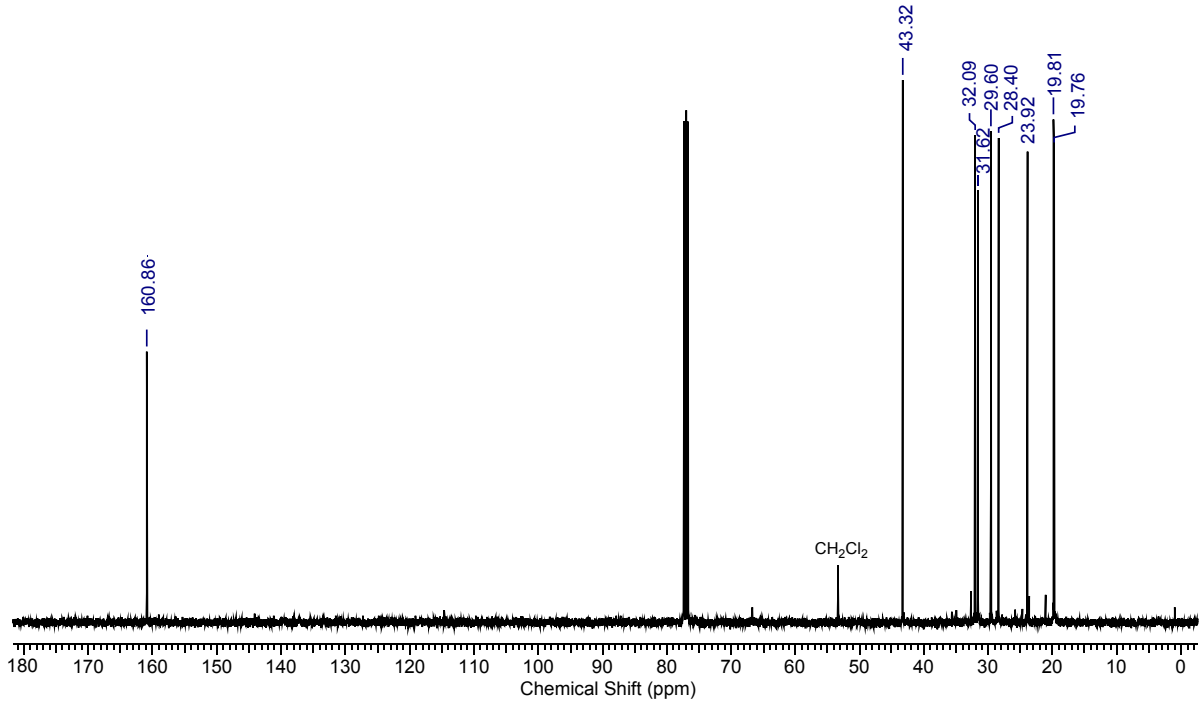


*Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **5***

Preparation of 4-isopropylcaprolactam (6). 4-isopropylcycohexanone oxime, **5** (1.0 g, 0.70 mmol) was dissolved in 80% H_2SO_4 (10 mL) and heated to 120 °C. The mixture was refluxed for 30 minutes before cooling to room temperature. Water was added (20 mL) to dilute the solution, and then NH_4OH was added to dropwise to bring the mixture to pH 6. The product was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases washed with brine (sat., 50 mL), dried with Na_2SO_4 and concentrated *in vacuo* to yield **6** as a pale brown solid (0.86 g, 5.5 mol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.90 Hz, 6 H, 2 x CH_3), 1.16 - 1.46 (m, 3 H, CH_2 + CH), 1.49 - 1.68 (m, 1 H, CH), 1.68 - 1.87 (m, 2 H, CH_2), 2.31 - 2.57 (m, 2 H, CH_2), 3.09 - 3.38 (m, 2 H, CH_2), 6.68 (br. s., 1 H, NH). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 19.2 (CH_3), 19.3 (CH_3), 25.9 (CH_2), 32.4 (CH_2), 33.1 (CH), 35.6 (CH_2), 42.0 (CH_2), 48.0 (CH), 179.0 (C=O). m/z calc for $C_9H_{17}NONa$ $[M+Na]^+$ = 178.1208, found 178.1217.

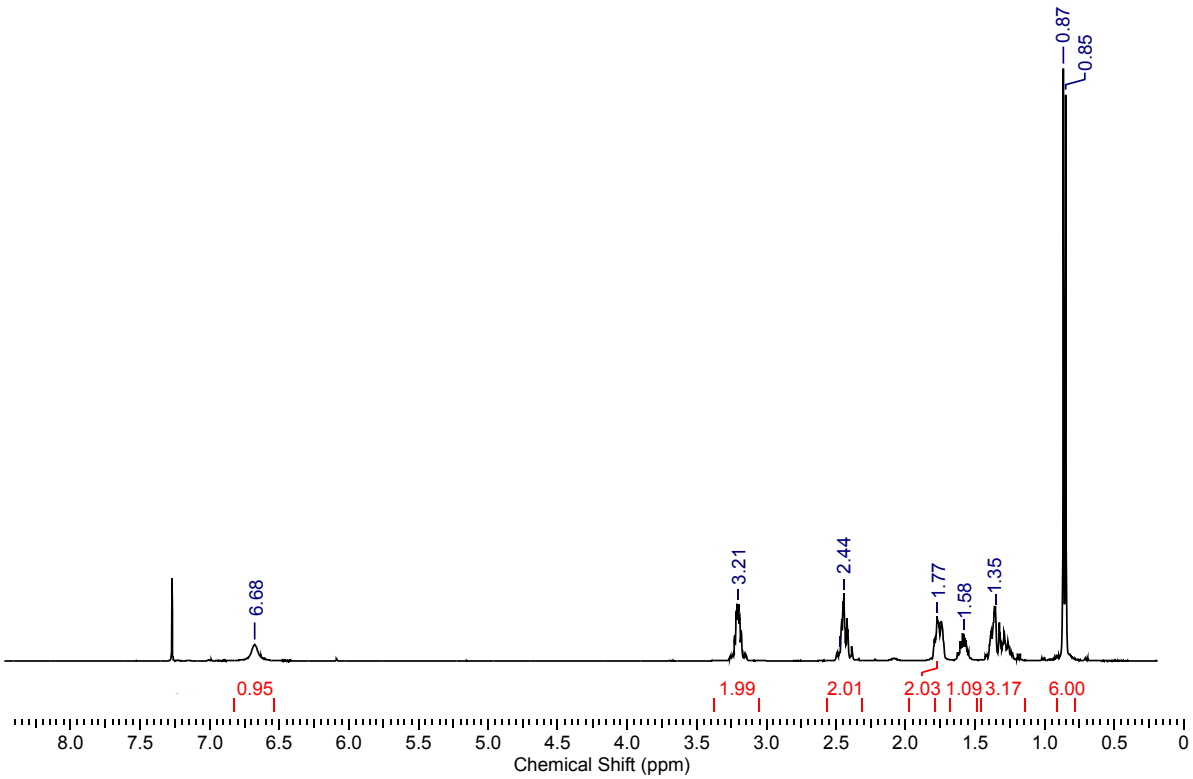


*Figure S33. ^{1}H NMR spectrum of **6***

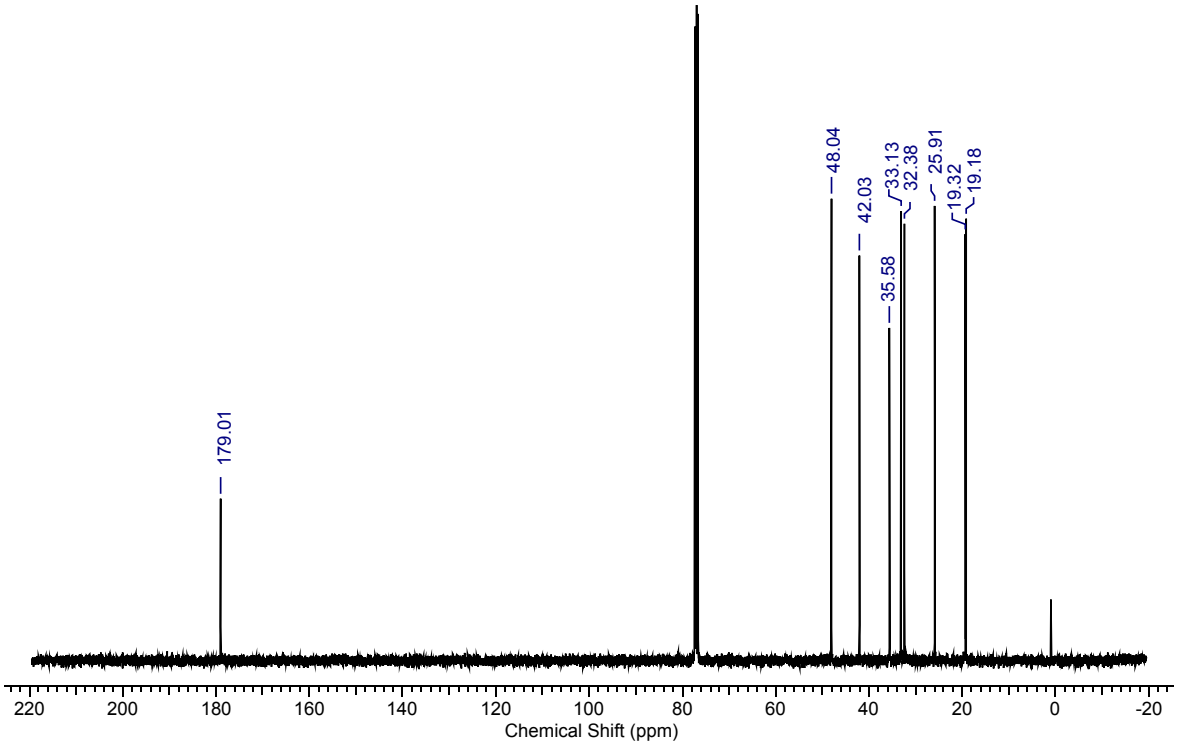


*Figure 34. $^{13}C\{^{1}H\}$ NMR of **6***

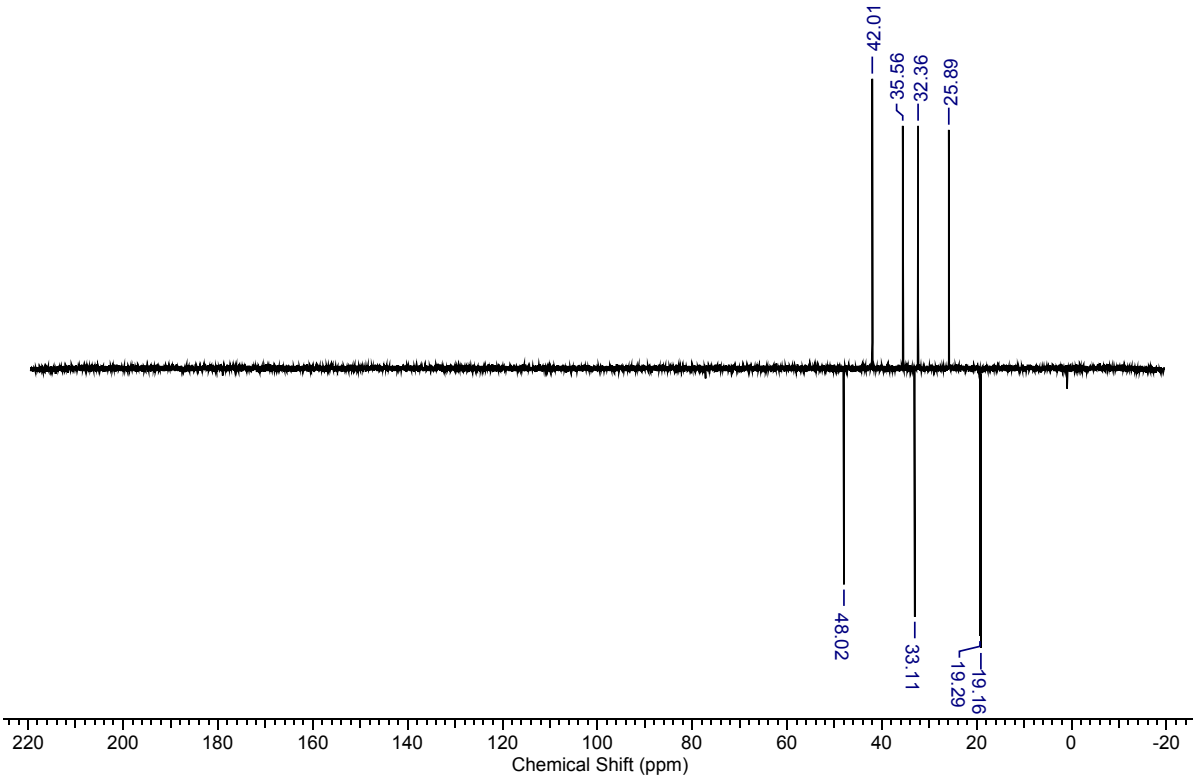


*Figure S35. DEPT-135 $^{13}C\{^{1}H\}$ NMR spectrum of **6***

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2 M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schäfer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.*, 2014, **50**, 15967–15970.

3 K. Mori, *Tetrahedron: Asymmetry*, 2006, **17**, 2133–2142.