Supporting Information

for

A Bifunctional Monomer Derived from Lactide for Toughening Polylactide

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Experimental Section

Unless otherwise specified, ACS reagent grade starting materials and solvents were used as received from commercial suppliers without further purification. ^{1}H and ^{13}C NMR analyses were carried out at room temperature on a Varian INOVA-500 spectrometer at 500 and 125 MHz, respectively, with the chemical shifts reported in ppm and referenced to signals from residual protons in the solvent. IR spectra were acquired using a MIDAC M4000 FT-IR spectrometer. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA. High-resolution mass spectral analyses were performed by the Mass Spectrometry Facility at the University of Minnesota, Twin Cities. The reported melting points were measured at 10 °C/min using an Electrothermal MEL-TEMP® 3.0 capillary melting point apparatus and are uncorrected. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter at 589 nm (sodium D line) using a cell with an optical path length of 1.0 dm. Polymer molecular weights and polydispersity indices were determined by size exclusion chromatography (SEC) using three Jordi poly(divinylbenzene) columns of 104, 103, and 500 Å pore sizes and a HP1047A differential refractometer detector at 40 ºC. Chloroform was used as the eluting solvent at a flow rate of 1 mL/min, and monodisperse polystyrene standards were used to calibrate the molecular weights. Differential scanning calorimetry (DSC) measurements were acquired using a TA DSC Q1000. Samples were run under a nitrogen atmosphere at a heating rate of 10 ºC/min, with the temperature calibrated with an indium standard. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed on a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were deposited in a dithranol/potassium trifluoroacetate or 2,5-dihydroxybenzoic acid/potassium trifluoroacetate matrices, and positive ions were detected in either linear or reflectron modes. Small-angle X-ray scattering (SAXS) measurements were performed on a 369 cm custom built beam line at the

University of Minnesota. CuKa X-rays (λ = 1.542 Å) were generated through the use of a rotating anode. Samples were equilibrated under vacuum for 300 s before collection. The 2-D images were azimuthally integrated to a 1-D plot of intensity versus q where $q = 4\pi/\lambda \sin(\theta/2)$ and θ and λ are the scattering angle and X-ray wavelength, respectively. Scanning electron microscopy (SEM) was performed on a Hitachi S-900 FE-SEM using 4.0 kV accelerating voltage. Before SEM analysis, cryo-microtomed polymer surface was stained by 0.5 % RuO_4 solution vapor for 30 min and coated with a ~2 nm thick Pt layer by direct Pt sputtering. Transmission electron microscopy (TEM) analysis of cryo-microtomed polymer thin film (stained by 4% OsO_4 solution vapor) was conducted on a JOEL 1210 transmission electron microscope. Tensile deformation experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was around 0.4 mm.

(3*S*, 6*S*)-3-Bromo-3,6-dimethyl-1,4-dioxane-2,5-dione.[1] To a 2 L three-neck flask were added L-lactide (200.0 g, 1.388 mol), benzene (1 L), and N-bromosuccimide (272.0 g, 1.528 mol). The mixture was brought to reflux under mechanical stirring. Benzoyl peroxide (6.72 g, 27.7 mmol) in benzene (100 mL) was added to the reaction dropwise through a dropping funnel in 20 min. The reaction was monitored by TLC. After the monomer was consumed, the reaction mixture was cooled down to room temperature, and the solid was filtered off. The filtrate was evaporated to dryness and pale yellow solid was formed. The solid was dissolved in dichloromethane (1.5 L), and the solution was washed with saturated sodium bisulfite solution 3 times and saturated NaCl solution once. The organic layer was dried over $MgSO_4$, and the

[1] Scheibelhoffer, A. S.; Blose, W. A.; Harwood, H. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1969**, *10*, 1375-1380.

solution was evaporated to dryness. The orange solid was recrystallized from ethyl acetate and hexanes to give 137.9 g of white crystal. The mother liquor from the filtration was evaporated to dryness, and the solid was recrystallized from ethyl acetate and hexanes to give 54.3 g of white crystal. The yield in total was 192.2 g (62%). ^{1}H NMR ($CDCl_3$): δ 5.48 (q, J = 6.9 Hz, 1H), 2.32 (s, 3H), 1.72 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 164.62, 161.13, 81.33, 73.67, 29.62, 16.40.

(6*S*)-3-Methylene-6-methyl-1,4-dioxane-2,5-dione (1).[1] To a 500 mL three-neck flask were added (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione (31.2 g, 0.140 mol) and dichloromethane (200 mL). The flask was protected under nitrogen and cooled in an ice bath. Triethylamine (21.5 mL, 0.154 mol) was added dropwise through a dropping funnel. After 1 h in the ice bath, the reaction was brought to room temperature and stirred for another 1 h. The reaction mixture was transferred to a separatory funnel, and washed with 1 M HCl solution 3 times and saturated NaCl solution once. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The pale yellow solid was purified by column chromatography on silica gel (dichloromethane, r_f = 0.41) to afford a white solid. The white solid was further purified by sublimation at 45 °C under vacuum to yield 11.88 g (60%) of white crystal. ^{1}H NMR ($CDCl_3$): δ 5.94 (d, J = 2.4 Hz, 1H), 5.54 (d, J = 2.4 Hz, 1H), 5.02 (q, J = 7.0 Hz, 1H), 1.70 (d, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 162.89, 157.71, 142.93, 110.43, 72.41, 17.32. IR (KBr): ν (cm^{-1}) 3142, 3049, 3020, 2942, 1763, 1741, 1648, 1380, 1299, 1252, 1048. Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.26. Found: C, 50.51; H, 4.20. HRMS-CI (*m/z*): $[M+H]^+$ calcd for $C_6H_6O_4$, 143.0344; found, 143.0350. mp 100–102 ºC.

Hydrogenation of (6*S*)-3-Methylene-6-methyl-1,4-dioxane-2,5-dione. (6*S*)-3-Methylene-6-methyl-1,4-dioxane-2,5-dione (2.0 g), 10% Pd/C (0.1 g), and THF (100 mL) were sealed in an autoclave, purged with hydrogen 3 times, and then filled with 400 psig hydrogen gas.

The hydrogenation was run at room temperature for 18 h. The product was filtered to remove the catalyst. After THF was removed in vacuo, the crude product was purified by sublimation at 45 °C under vacuum to give 1.72 g (85%) of white crystal. The product was analyzed by ^{1}H NMR spectroscopy and polarimeter.

Spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (2). To a 250 mL flask were added (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione (15.0 g, 0.106 mol), freshly distilled cyclopentadiene (14.0 g, 0.212 mol), and benzene (100 mL). The reaction mixture was refluxed overnight under Argon. After the reaction was cooled down to room temperature, benzene and extra cyclopentadiene were removed by rotary evaporation. The crude product was purified by column chromatography on silica gel, first by hexanes to remove dicyclopentadiene, then dichloromethane (r_f = 0.31). The white solid was further purified by sublimation at 50 °C under vacuum to give 20.74 g (94%) of white crystal. ^{1}H NMR ($CDCl_3$): δ 6.56–6.34 (m, 1H), 6.32–5.87 (m, 1H), 5.22–4.84 (m, 1H), 3.44–3.16 (m, 1H), 3.09–3.03 (m, 1H), 2.85–2.03 (m, 1H), 2.02–1.85 (m, 1H), 1.82–1.60 (m, 4H), 1.50 (dd, *J* = 12.9 Hz, *J* = 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, shown only the major isomer **2c**): δ 169.15, 167.45, 141.63, 129.99, 88.41, 72.69, 50.52, 47.77, 41.85, 40.33, 16.69. IR (KBr): ν (cm^{-1}) 3091, 2992, 2963, 2905, 1752, 1363, 1336, 1287, 1273, 1263, 1217, 1143, 1101, 1060. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.41; H, 5.78. HRMS-CI (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{12}O_4$, 209.0814; found, 209.0824. mp 126–130 ºC.

Reduction of 2 to Its Diol Derivatives. To a 20 mL flask were added spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (0.50 g, 2.4 mmol) and lithium aluminum hydride (95%, 0.29 g, 7.26 mmol). The flask was purged and protected under nitrogen. Anhydrous diethyl ether (10 mL) was added via syringe through a septum into the flask. The

reaction was run at room temperature overnight. The reaction mixture was then diluted with ethyl acetate, and the solution was washed with saturated NaCl solution and dried over $MgSO_4$. The crude product was analyzed by ^1H NMR without further purification.

General Procedure for the Ring-opening Polymerization of Spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene]. In the dry box, a catalyst/initiator solution was prepared by adding 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 6.7 mg, 48 μmol), benzyl alcohol (10.0 μL, 96 μmol), and anhydrous CH_2Cl_2 (9.6 mL) to a 20 mL vial. To a 20 mL pressure vessel were added spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (0.20 g, 0.96 mmol) and the freshly prepared catalyst/initiator solution (0.96 mL). After 24 h, the reaction was quenched by adding excess amount (>10 equivalents) of benzoic acid. A portion of the solution was evacuated to dryness and analyzed by ^1H NMR and SEC. The remaining polymer solution was precipitated into methanol 3 times. The formed solid polymer sample was vacuum dried overnight and analyzed by NMR, SEC, and DSC.

General Procedure for the Ring-opening Metathesis Polymerization of Spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene]. To a 20 mL vial were added spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (0.20 g, 0.96 mmol) and 3rd generation Grubbs' catalyst (8.5 mg, 9.6 μmol, the catalyst was synthesized according to the literature [2]). The vial was fitted with a septum and purged under nitrogen for 10 min. Dichloromethane (4.8 mL) was added via syringe through the septum to the vial under quick stirring. After 30 min, the reaction was quenched by adding excess amount (>20 equivalents) of ethyl vinyl ether. The polymer solution was precipitated from methanol to remove catalyst and

[2] Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035-4037.

ethyl vinyl ether. The formed solid polymer sample was vacuum dried overnight and analyzed by NMR, SEC, and DSC.

General Procedure for the Ring-opening Metathesis Polymerization with Chain Transfer Agent. In the dry box, a catalyst/CTA solution was prepared by adding *cis*-2-butene-1,4-diol diacetate (301 μL, 1.91 mmol)), 2nd generation Grubbs' catalyst (32.4 mg, 38.2 μmol), and dichloromethane (40 mL) to a vial. To a 150 mL pressure vessel were added spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (0.595 g, 2.86 mmol), 1,5-cyclooctadiene (10.0 g, 92.4 mmol), dichloromethane (30 mL), and a stir bar. 10 mL of the freshly prepared stock solution was added to the pressure vessel to initiate the polymerization at room temperature. After 20 h, the polymerization was quenched by adding excess amount (>20 equivalents) of ethyl vinyl ether. A portion of the solution was evacuated to dryness and analyzed by ^{1}H NMR and SEC. The remaining polymer solution was precipitated from methanol 2 times to remove catalyst and ethyl vinyl ether. The formed solid polymer sample was vacuum dried overnight and analyzed by NMR, SEC, and DSC.

General Procedure for the Ring-opening Polymerization of Poly(COD/2) or PolyCOD with DL-lactide. To a 150 mL pressure vessel were added poly(COD/**2**) (1.0 g), DL-lactide (4.0 g, 27.8 mmol), benzyl alcohol (28.7 μL, 0.277 mmol), dichloromethane (40 mL), and a stir bar. A solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 3.9 mg, 28.0 μmol) in dichloromethane (1 mL) was added to the pressure vessel to initiate the polymerization. The polymerization was run for 1 h in an ice-water bath. The reaction was quenched by adding excess amount (>10 equivalents) of benzoic acid. A portion of the solution was evacuated to dryness and analyzed by ^{1}H NMR and SEC. The remaining polymer solution was precipitated

into cold methanol 2 times. The formed solid polymer sample was vacuum dried overnight and analyzed by NMR, SEC, DSC, and MiniMat.

Determination of the major product in the bromination of L-lactide

Assuming no significant epimerization of the non-brominated methine carbon, bromination of L-lactide can form two diastereomeric products (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione and (3*R*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione. Examining ^{1}H NMR spectrum of the crude bromination product before work-up/recrystallization steps revealed a major (90%) and a minor (10%) product (Figure S3).

The minor product could be removed by recrystallization from ethyl acetate and hexanes. The brominated product after recrystallization, is diastereomerically pure (Figure S1). The specific optical rotation of this compound was measured in chloroform: $[\alpha]^{20}_{D} = -29.7°$ (c = 1.0 g/100mL) consistent with a non-racemic product.

1D nOe NMR spectrum of the major product (Figure S2) was performed to determine the relative position between the 6-methine proton and 3-methyl protons. Saturation of the methine proton resonance enhances the signal of the 3-methyl protons. Therefore the methine proton must be positioned *syn* to the 3-methyl group. These data are consistent with (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione being the major product resulting from bromination of L-lactide.

Determination of the enantiomeric excess of 1

Based on the structure of its precursor (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione, upon elimination of HBr compound **1** should be (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione. The specific optical rotation of **1** was measured in chloroform: $[\alpha]^{20}_{D} = -6.7°$ (c = 1.0 g/100mL) consistent with a non-racemic product.

To measure its enantiomeric excess, compound **1** was hydrogenated back to lactide. Starting with exclusively (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione, we should get either L-lactide or meso-lactide, depending on the hydrogenation stereoselectivity. The enantiomer (6*R*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione should give either D-lactide or meso-lactide as the hydrogenation product. By measuring the product's optical rotation and the meso-lactide percentage, and assuming that there is no difference in the hydrogenation stereoselectivity between (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione and (6*R*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione, we can then calculate its enantiomeric excess.

The hydrogenation, by using 0.5 wt% (relative to **1**) of 10% Pd/C as the catalyst, favors the formation of L-lactide and D-lactide to meso-lactide (93:7, Figure S5). The hydrogenation product was purified by sublimation and exhibited a specific optical rotation $[\alpha]^{20}_{D} = -242°$ (c = 1.0 g/100mL in chloroform). In a control experiment, L-lactide (purchased from Purac) was hydrogenated and purified the same way, and its specific optical rotation is: $[\alpha]^{20}_{D} = -274°$ (c = 1.0 g/100mL in chloroform; the result is consistent with literature value,[3] and it proves that there is no epimerization taking place in the hydrogenation).

[3] Leemhuis, M.; van Steenis, J. H.; van Uxem, M. J.; van Nostrum, C. F.; Hennink, W. E. *Eur.J. Org. Chem.* **2003**, *17*, 3344-3349.

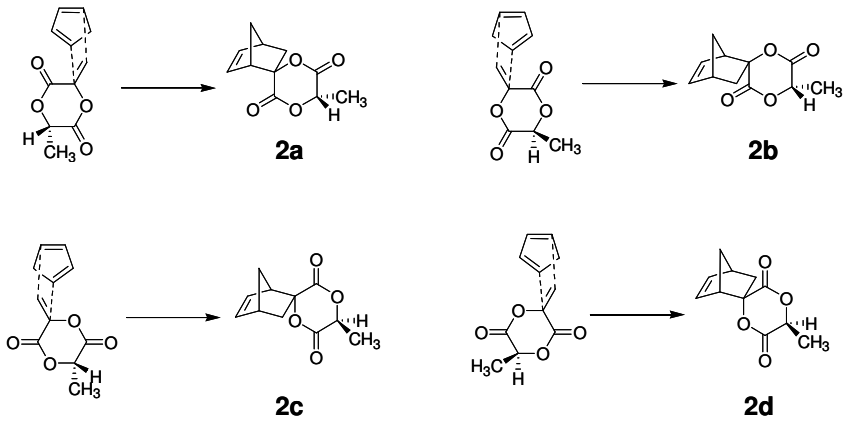
Assuming that there is no difference in the hydrogenation stereoselectivity between (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione and (6*R*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione, the enantiomeric excess of **1** can be calculated:

$$ee = \frac{242/93\%}{274} \times 100\% = 95\%$$

The major isomer is (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione.

This result further corroborates that the epimerization of the non-brominated methine carbon in the bromination of L-lactide, if there is any, should be less than 5%.

Scheme S1. Diastereomeric adducts formed in the Diels-Alder reaction of **1** and cyclopentadiene



Scheme S2. Schematic explanation for the diastereofacial and endo/exo selectivities in the Diels-Alder reaction of **1** and cyclopentadiene

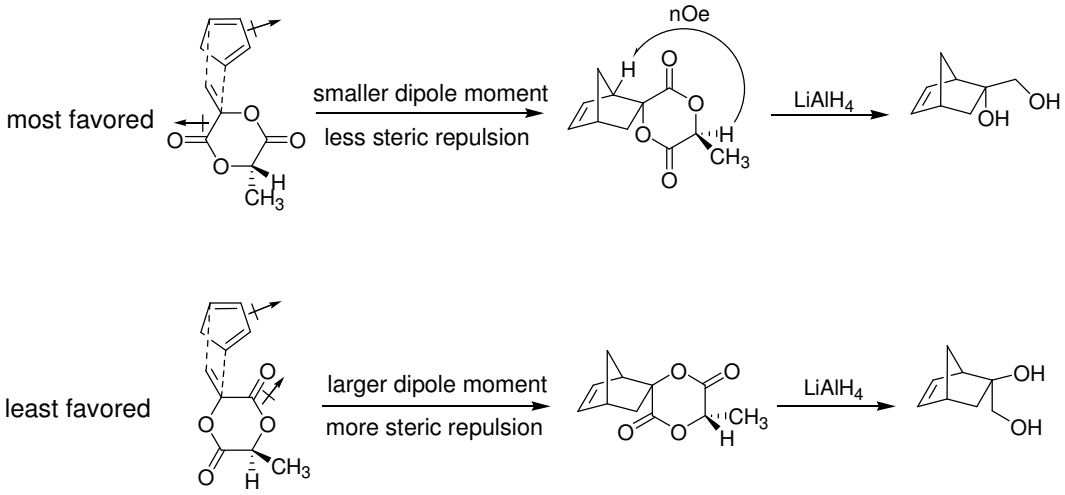


Table S1. ROP of **2** by TBD

$[\mathbf{2}]_0/[I]_0$	Temperature (°C)	Time (h)	Conversion (%)	M_n (kg mol^{-1})	M_w/M_n	T_g (°C)
100	22	1	64	4.6	1.35	N/A
100	22	3	81	5.3	1.59	N/A
100	22	5	82	5.4	1.67	N/A
100	22	11	84	4.9	1.77	N/A
100	22	24	84	4.9	1.85	N/A
100	40	24	74	3.3	1.71	N/A
100	0	24	90	9.0	2.13	N/A
100	–20	24	94	12.2	1.27	108
200	–20	96	95	23.3	1.59	112
300	–20	192	95	30.1	1.69	113

Polymerization conditions: $[\mathbf{2}]_0$ = 1.0 M in CH_2Cl_2, benzyl alcohol was used as the initiator and TBD was used as the catalyst, $[I]_0/[TBD]_0$ = 2/1; reactions were quenched by adding >10 equivalents of benzoic acid.

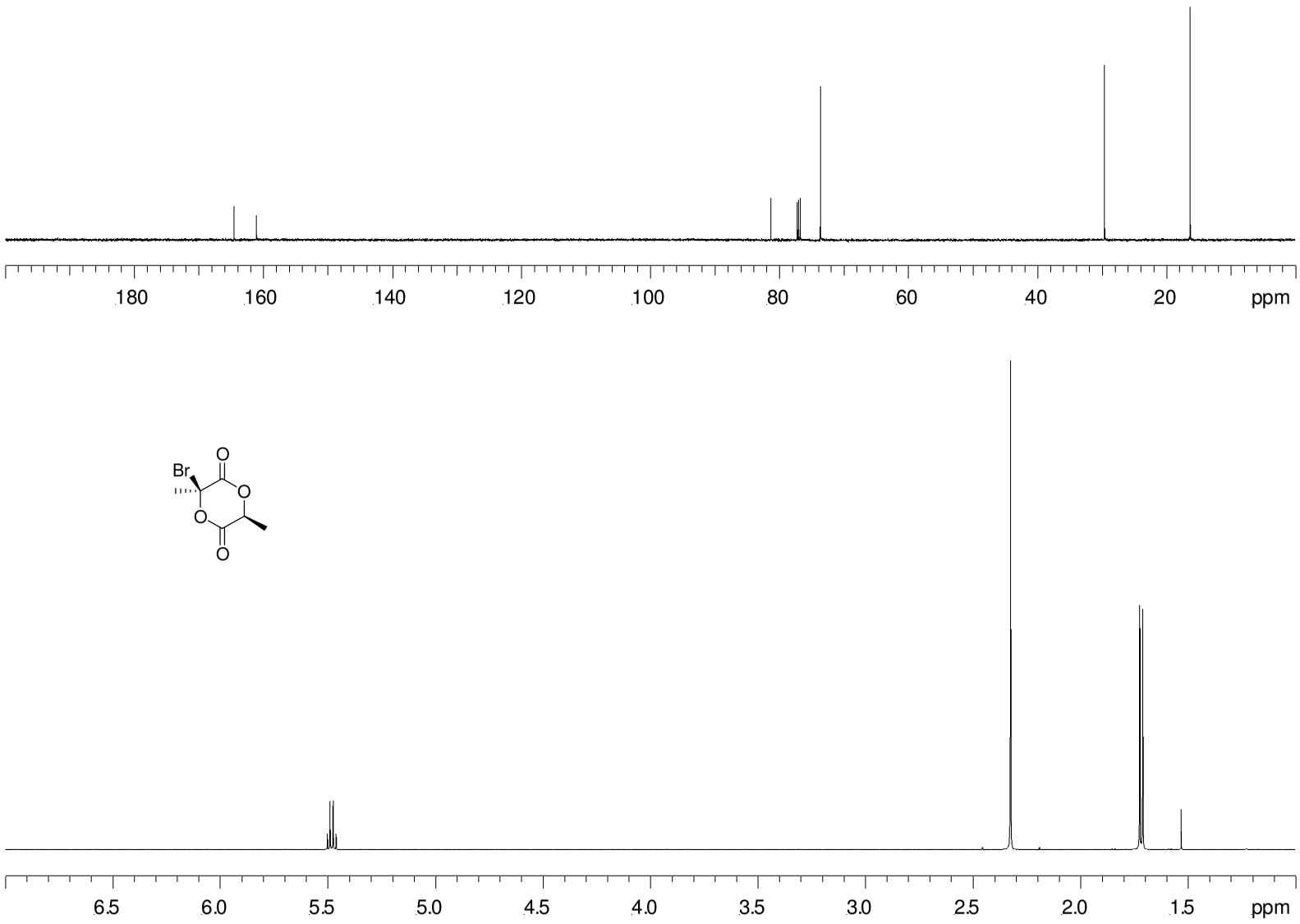


Figure S1. 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra of (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione in $CDCl_3$.

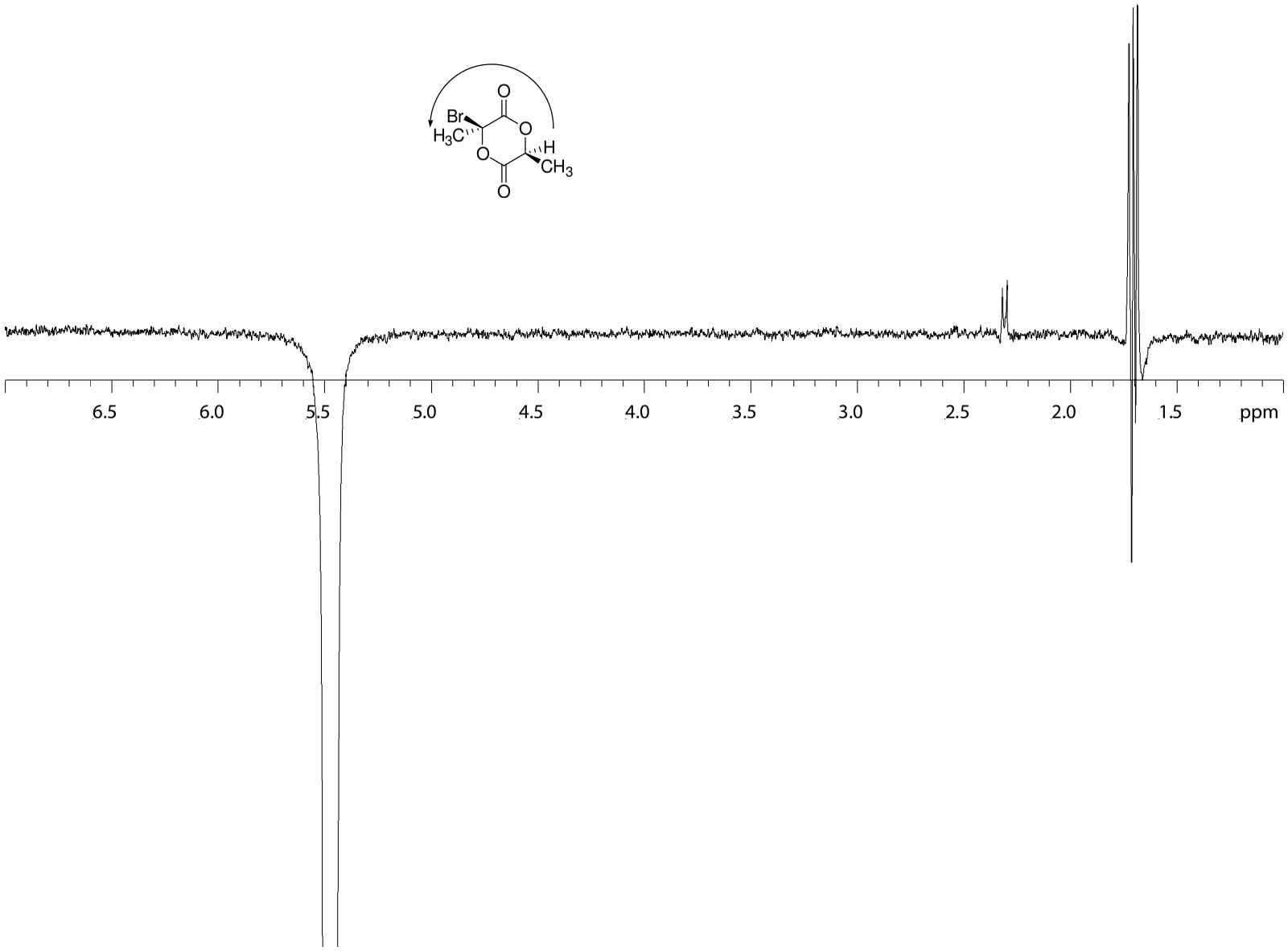


Figure S2. 500 MHz 1D nOe spectrum of (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione in $CDCl_3$.

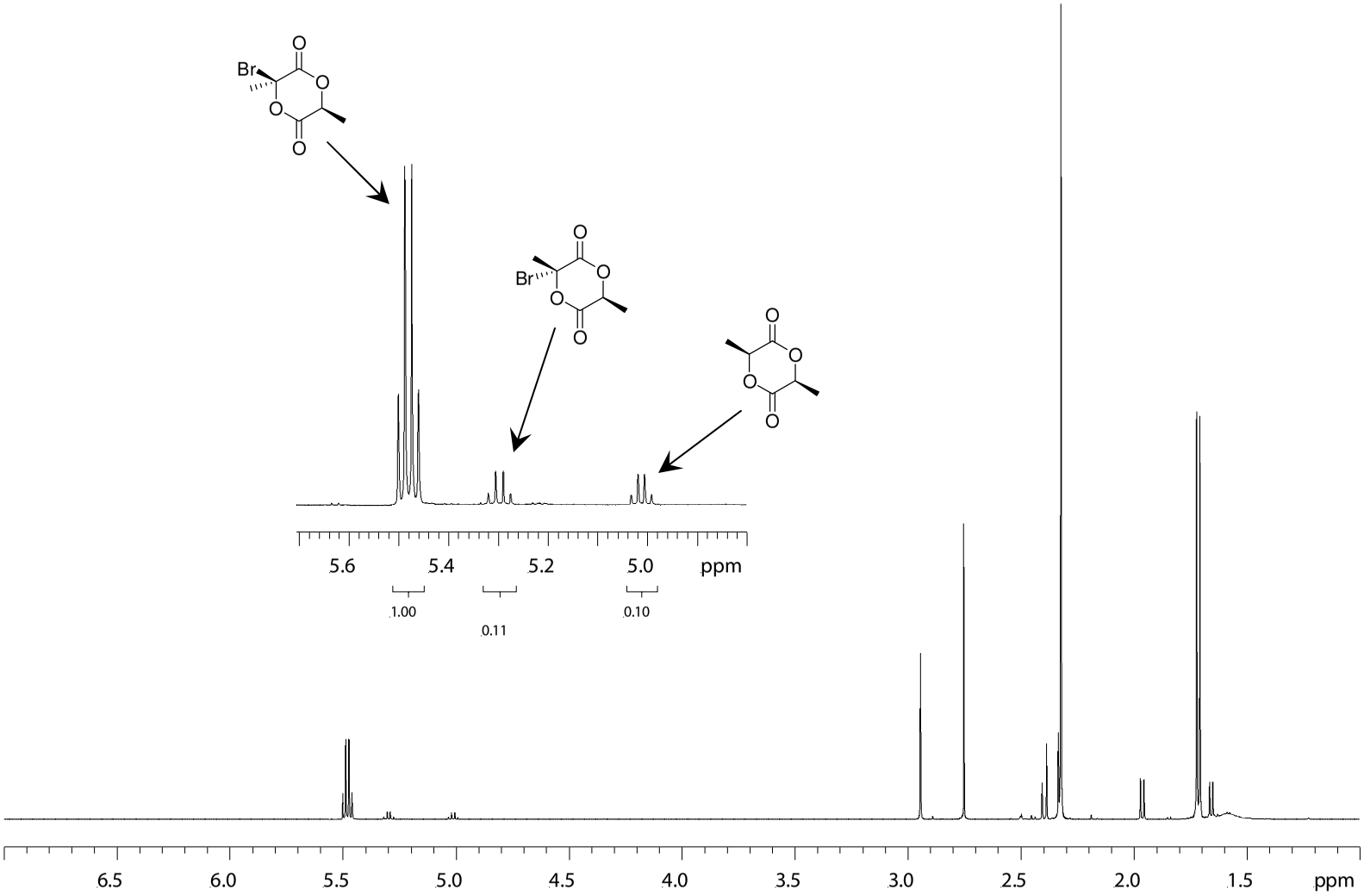


Figure S3. 500 MHz ^{1}H NMR spectrum (in $CDCl_3$) of the crude product formed in the bromination reaction of L-lactide.

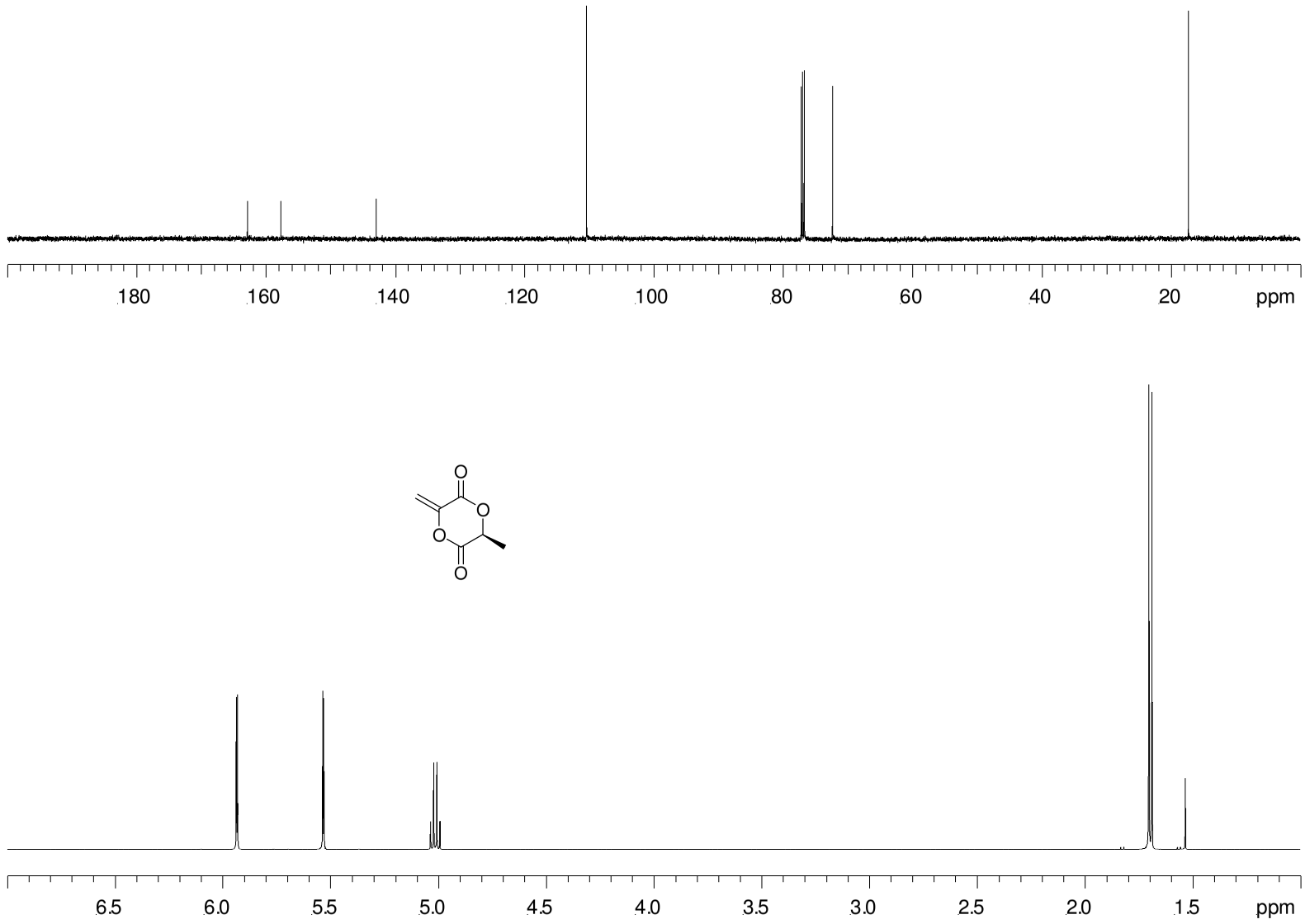


Figure S4. 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra of (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione in $CDCl_3$.

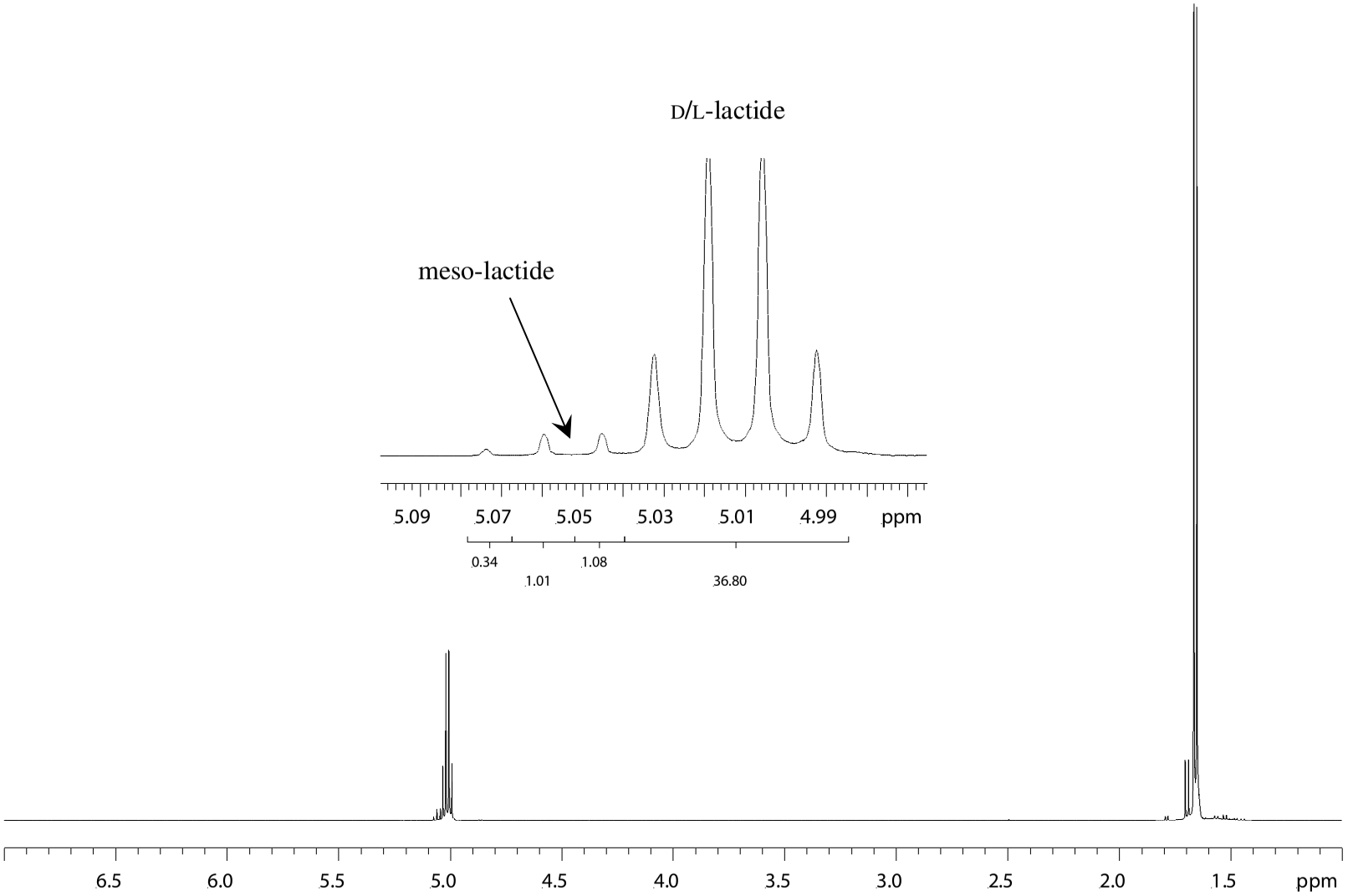


Figure S5. 500 MHz ^{1}H NMR spectrum (in $CDCl_3$) of the product via hydrogenation of compound **1**. Reaction condition: 2.0 g of compound **1** in 100 mL THF, 0.1 g of Pd/C (10%), 400 psig H_2, 18 h at RT.

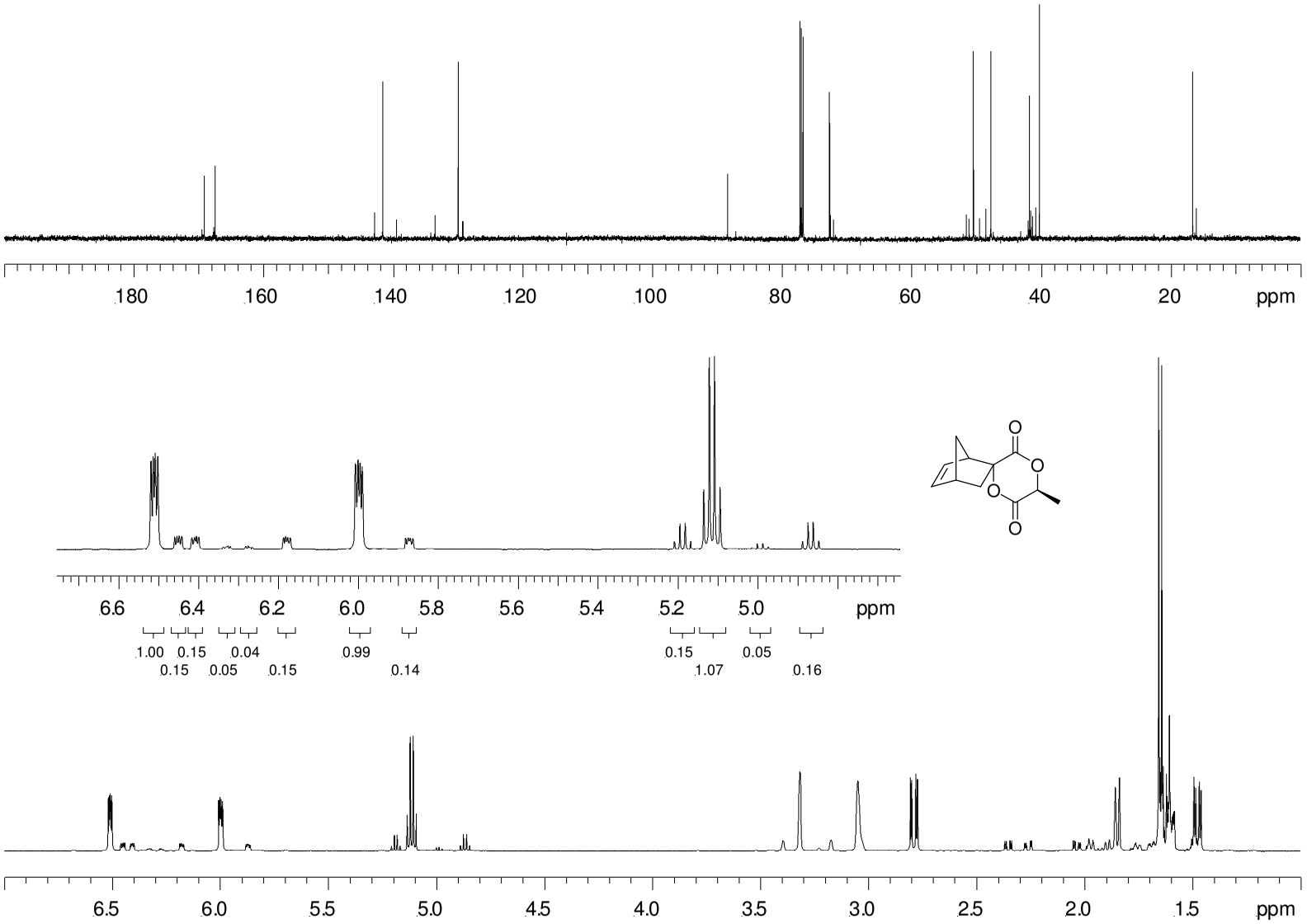


Figure S6. 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo [2.2.1]hept[5]ene] in $CDCl_3$.

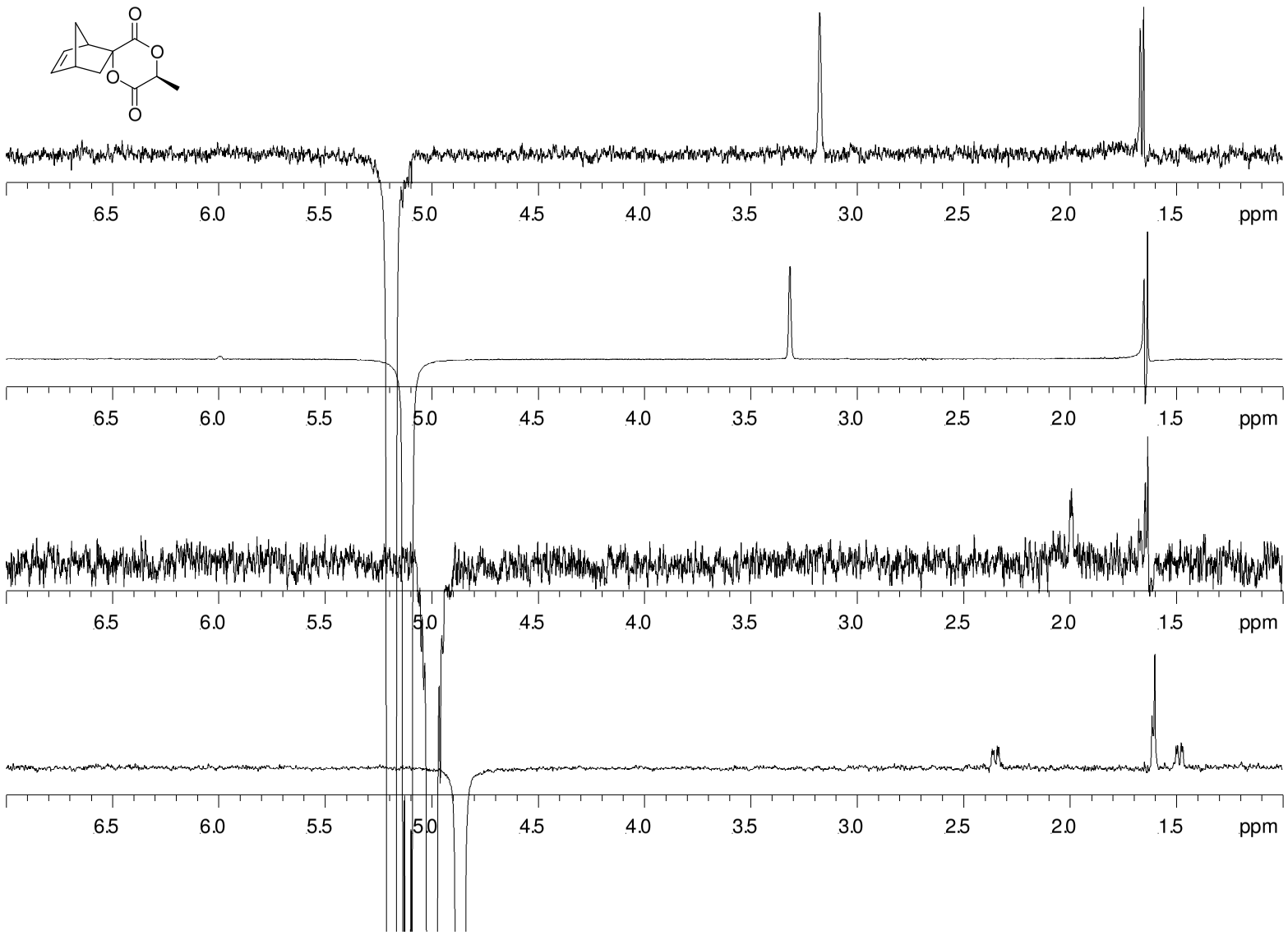


Figure S7. 500 MHz 1D nOe spectrum of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] in $CDCl_3$.

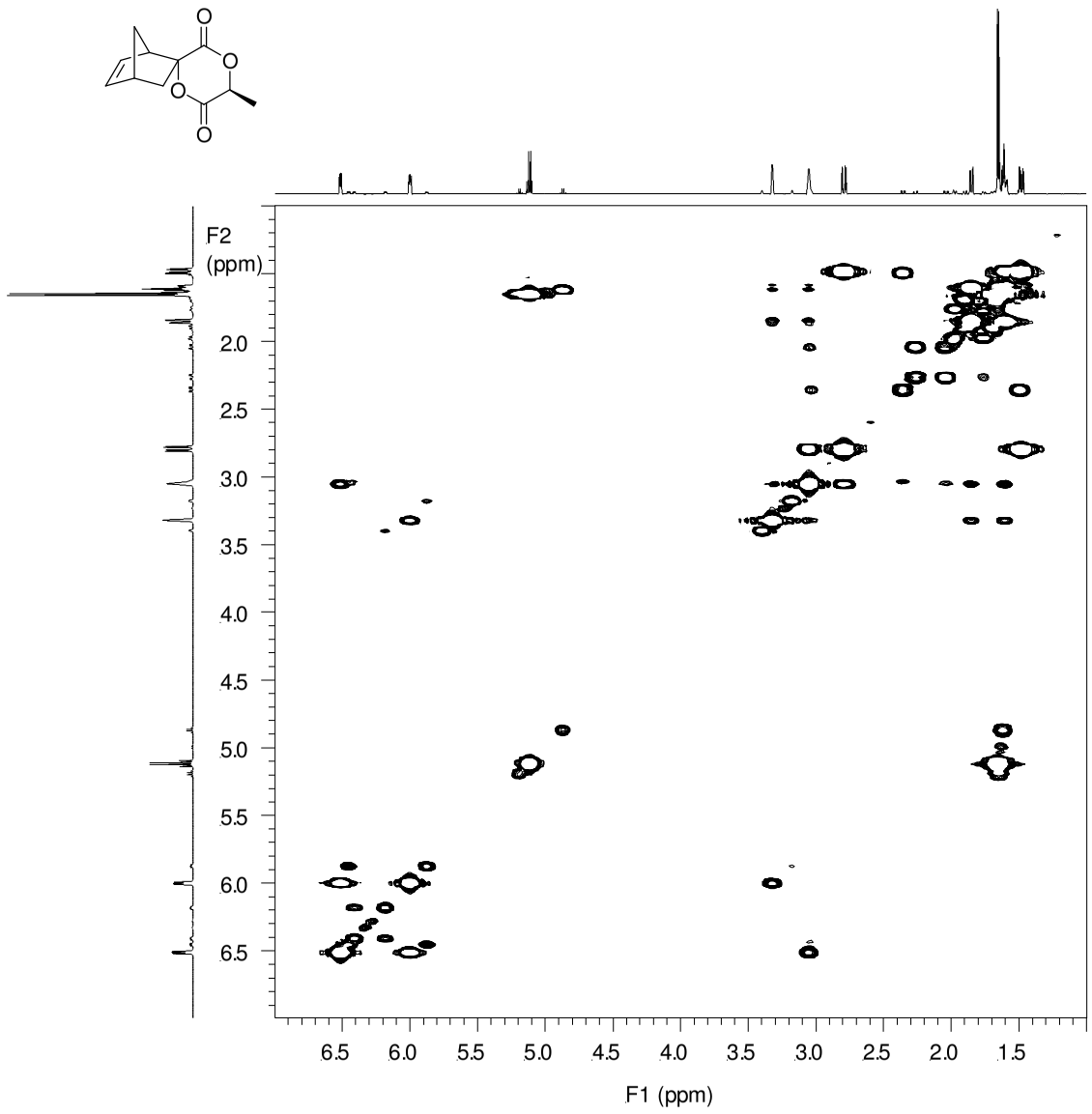


Figure S8. 500 MHz ^{1}H–^{1}H COSY spectrum of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] in $CDCl_3$.

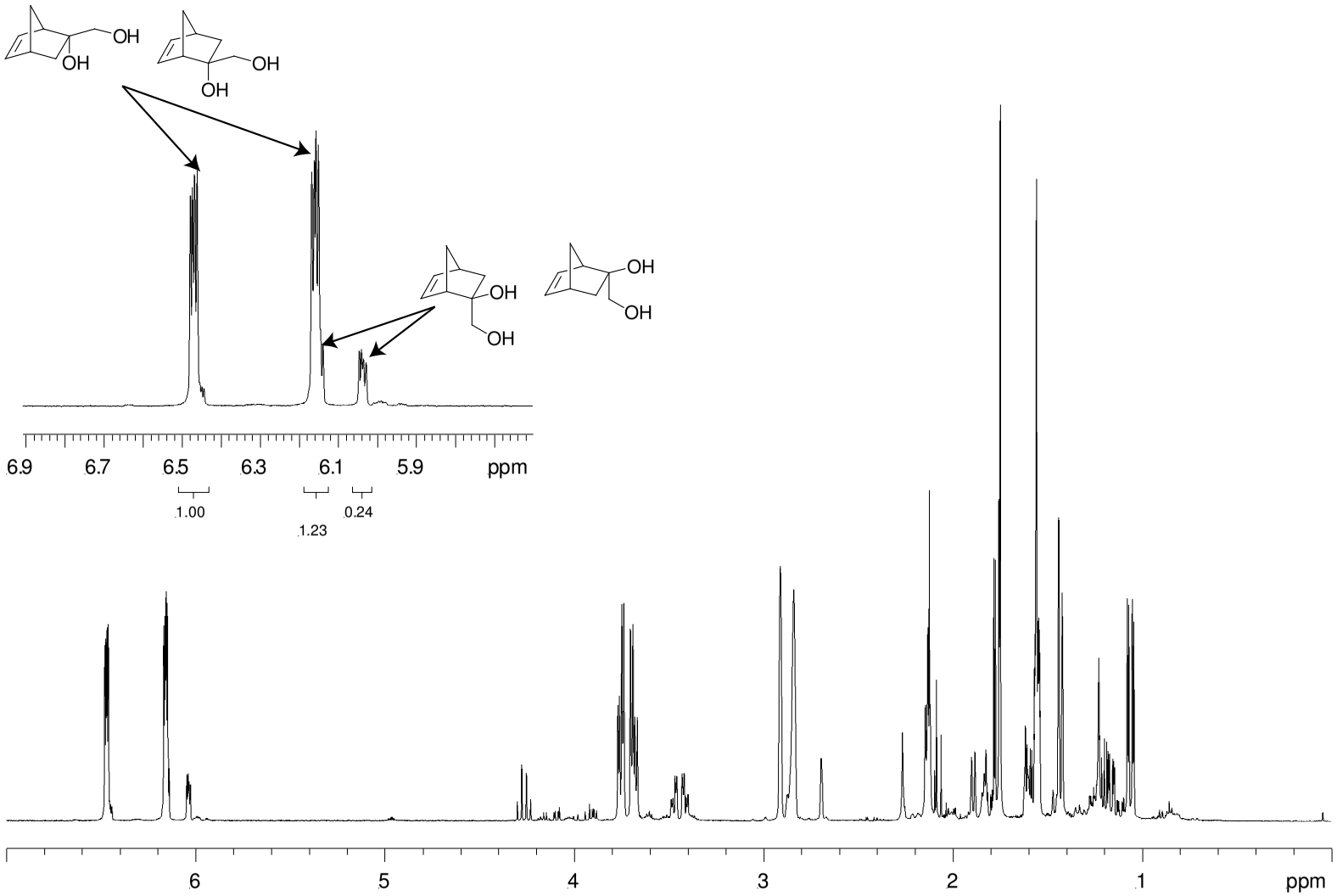


Figure S9. 500 MHz ^{1}H NMR spectrum of 2-hydroxybicyclo[2.2.1]hept[5]ene-2-methanol in $CDCl_3$.

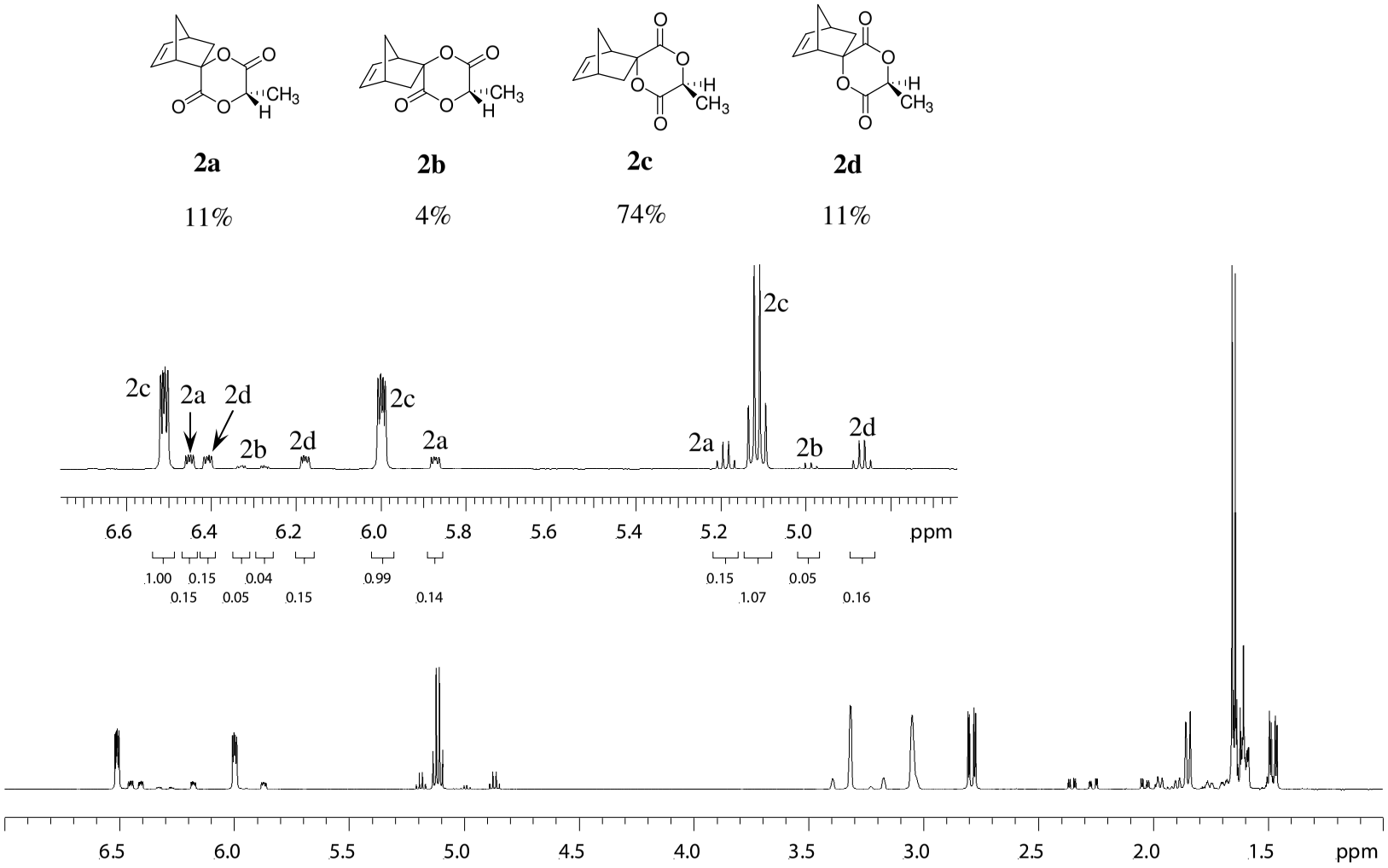


Figure S10. 500 MHz ^{1}H NMR spectrum of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo [2.2.1]hept[5]ene] and the assignment of its isomers.

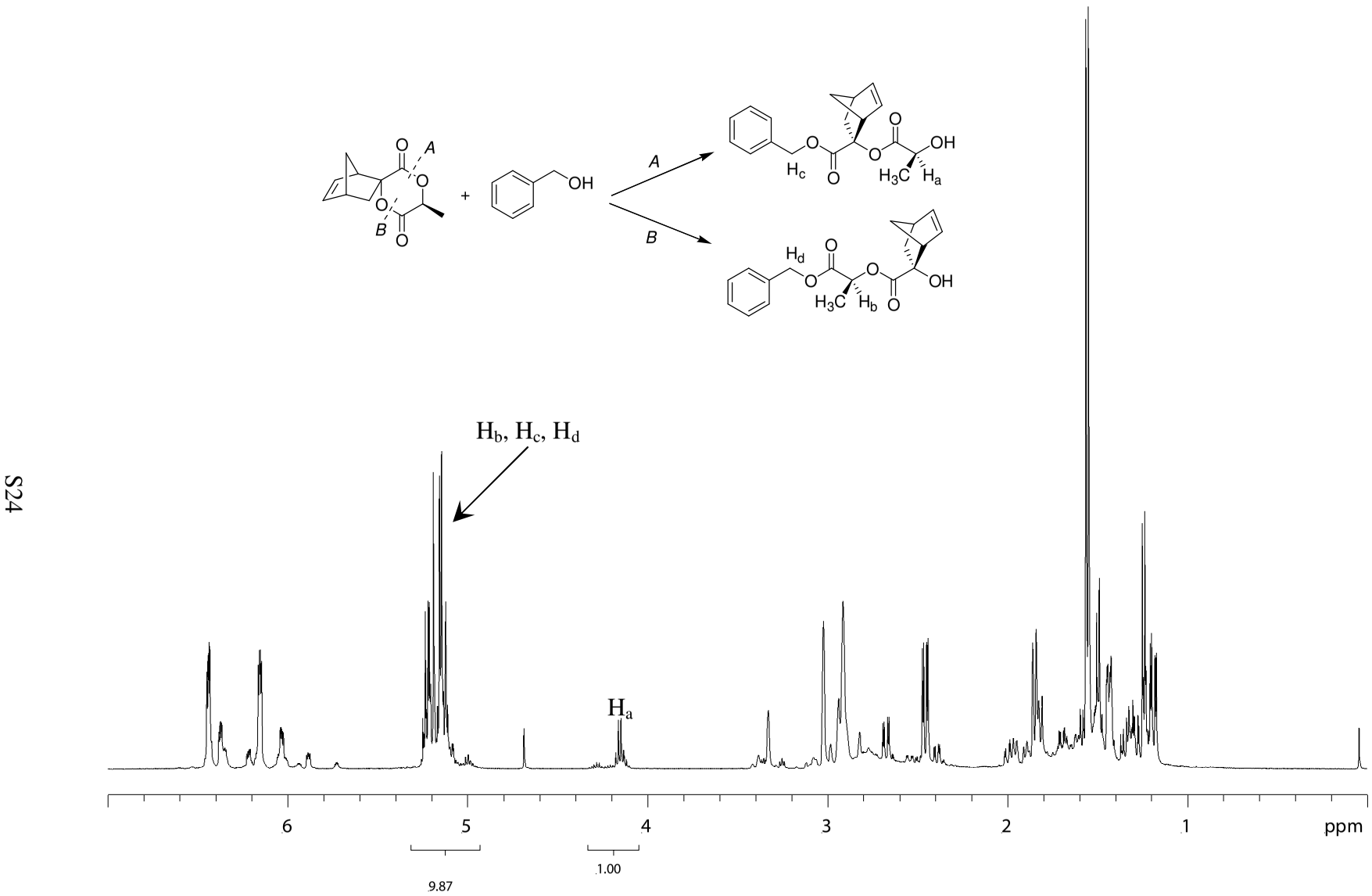


Figure S11. 500 MHz ^{1}H NMR spectrum (in $CDCl_3$) of the ring-opened adduct of compound **2** with 1 eq. of benzyl alcohol. Reaction condition: [**2**]:[benzyl alcohol]:[TBD] = 1:1:0.005, −20 °C in dichloromethane, under nitrogen, 30 min. The C-O bond B was cleaved preferentially to C-O bond A (78:22).

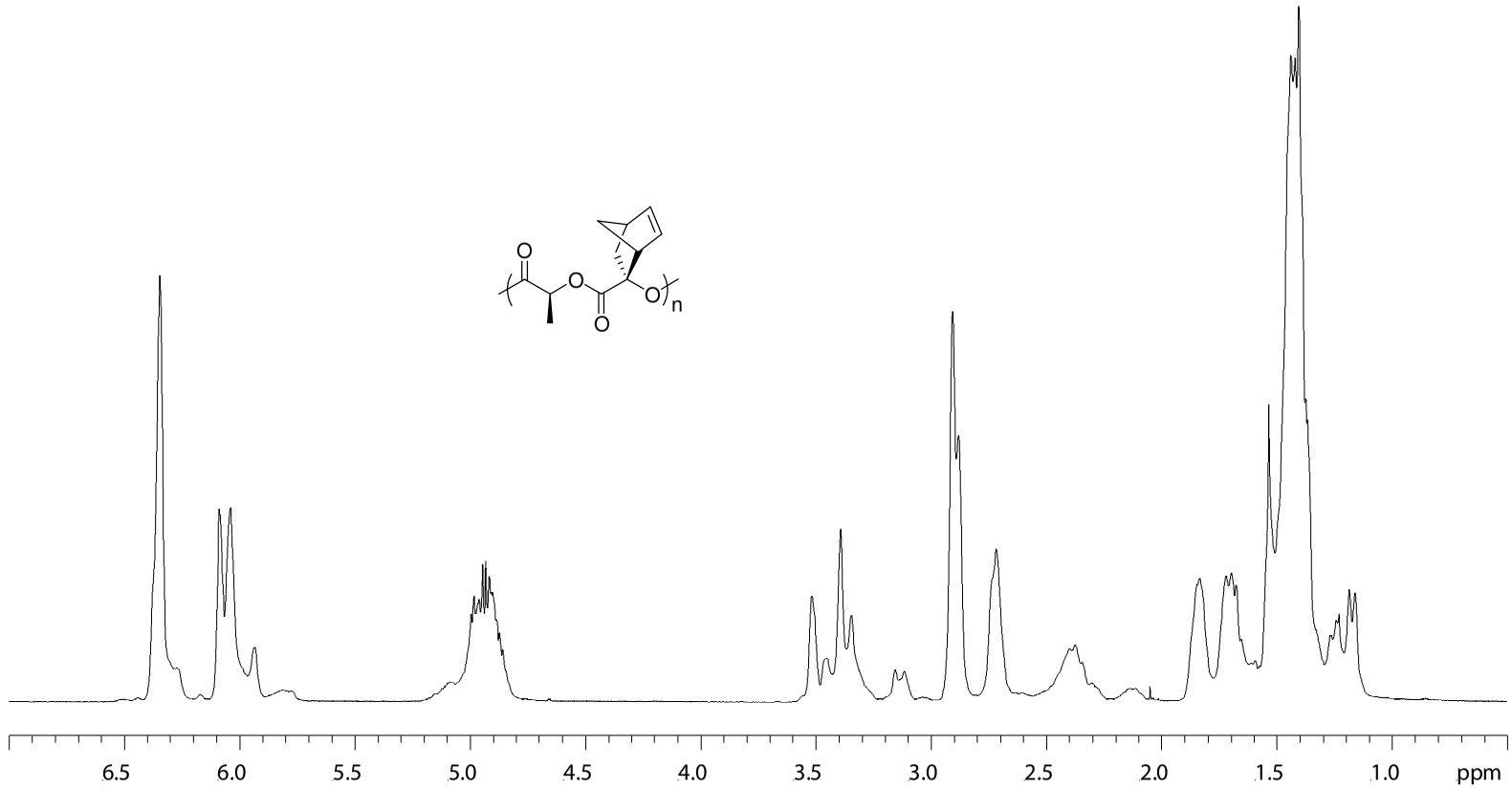


Figure S12. 500 MHz ^{1}H NMR spectrum of poly**2-L** in $CDCl_3$.

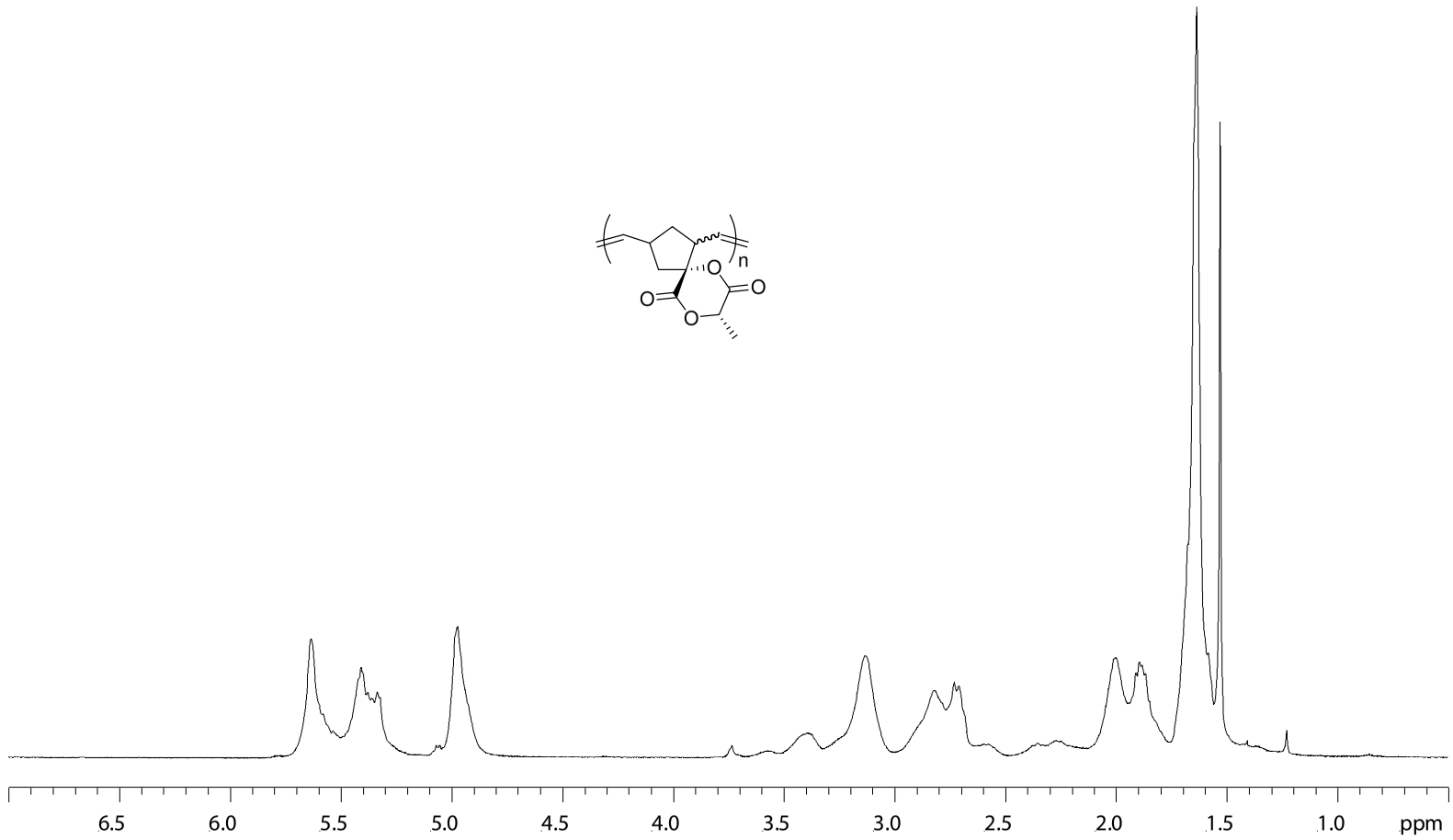


Figure S13. 500 MHz ^{1}H NMR spectrum of poly**2-N** in $CDCl_3$.

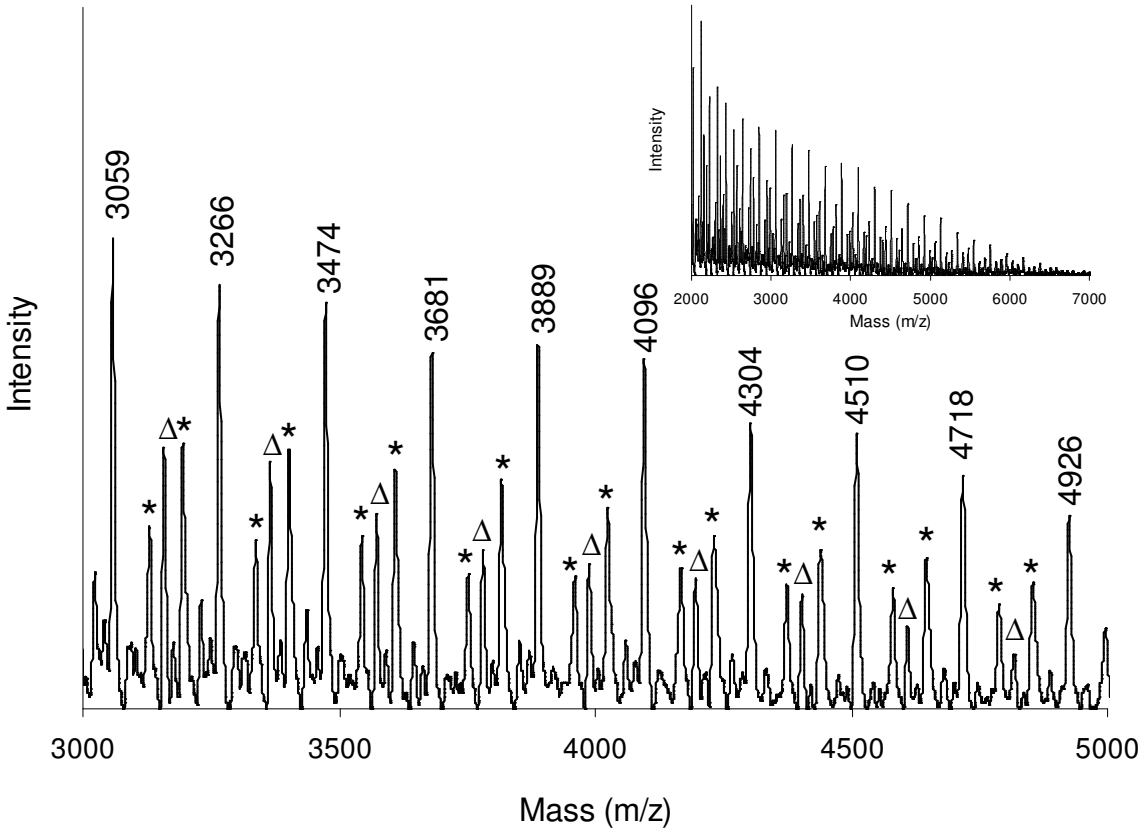


Figure S14. MALDI-TOF spectrum of poly**2-L** (SEC, PS stnd: M_n = 7,900, M_w/M_n = 1.63) taken in linear mode. Samples were dissolved in THF. 2,5-Dihydroxybenzoic acid was used as the matrix, potassium trifluoroacetate was used as the salt, and poly(ethylene glycol) was used as the calibration standard.(∗ = loss or gain of one lactic acid repeat unit –$COCHCH_3O$– due to intermolecular transesterifications; Δ = loss of benzyl alcohol, possibly due to intramolecular transesterifications).

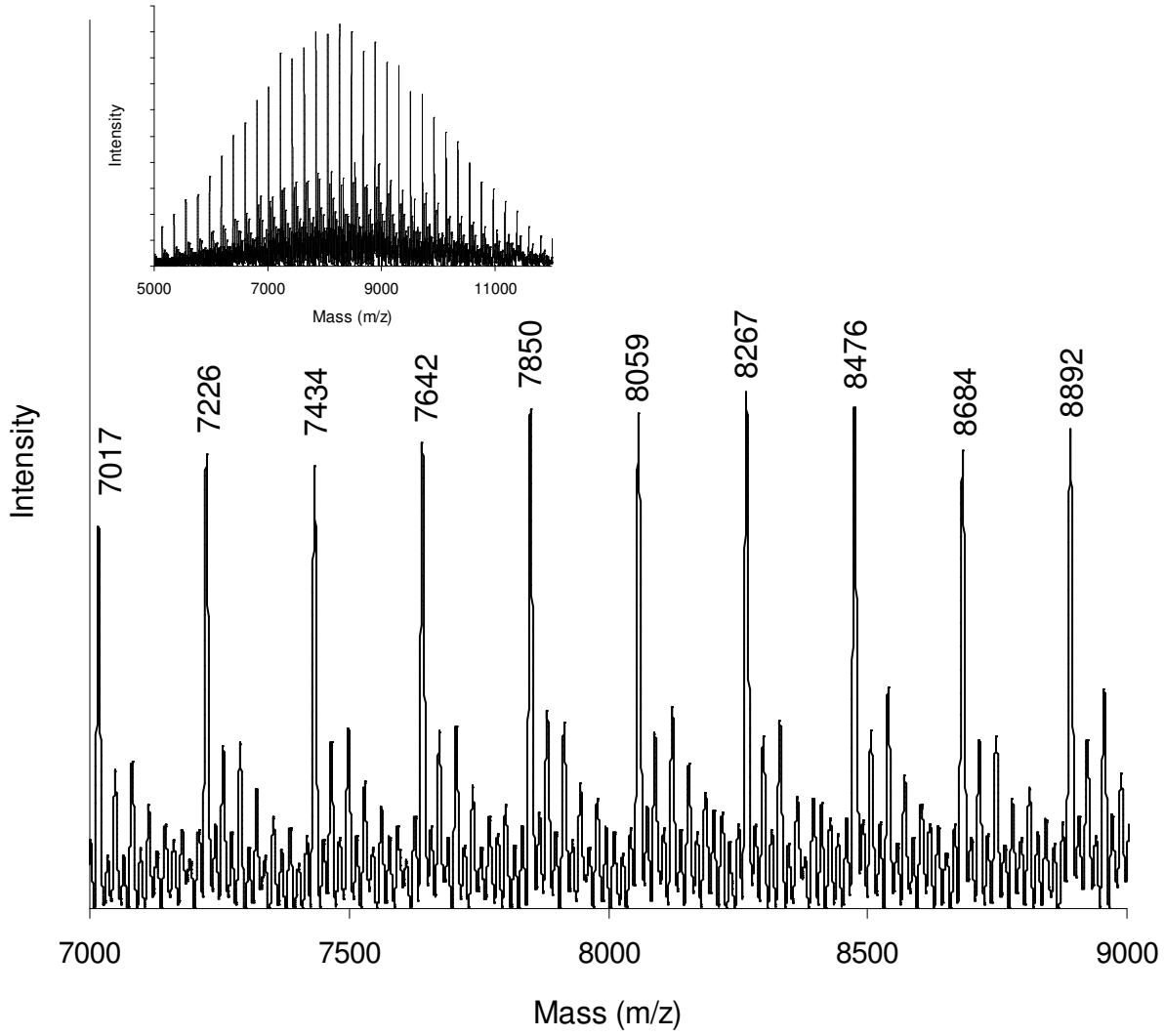


Figure S15. MALDI-TOF spectrum of poly**2-N** (SEC, PS stnd: M_n = 14,000, M_w/M_n = 1.04) taken in reflectron mode. Samples were dissolved in THF. Dithranol was used as the matrix, potassium trifluoroacetate was used as the salt, and poly(ethylene glycol) was used as the calibration standard.

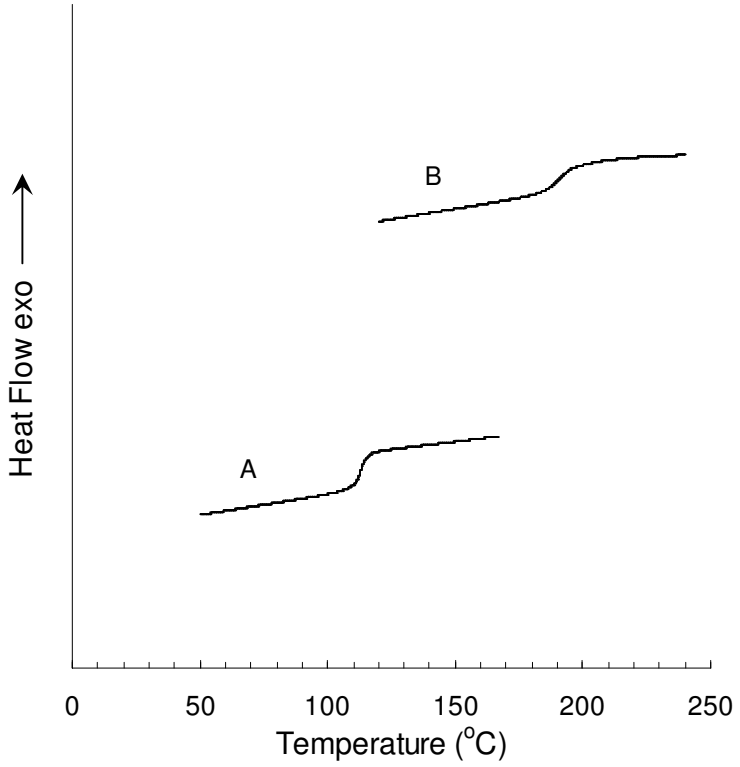


Figure S16. DSC traces of poly**2-L** (trace A, SEC: M_n = 33,600, M_w/M_n = 1.63) and poly**2-N** (trace B, SEC: M_n = 62,800, M_w/M_n = 1.16).

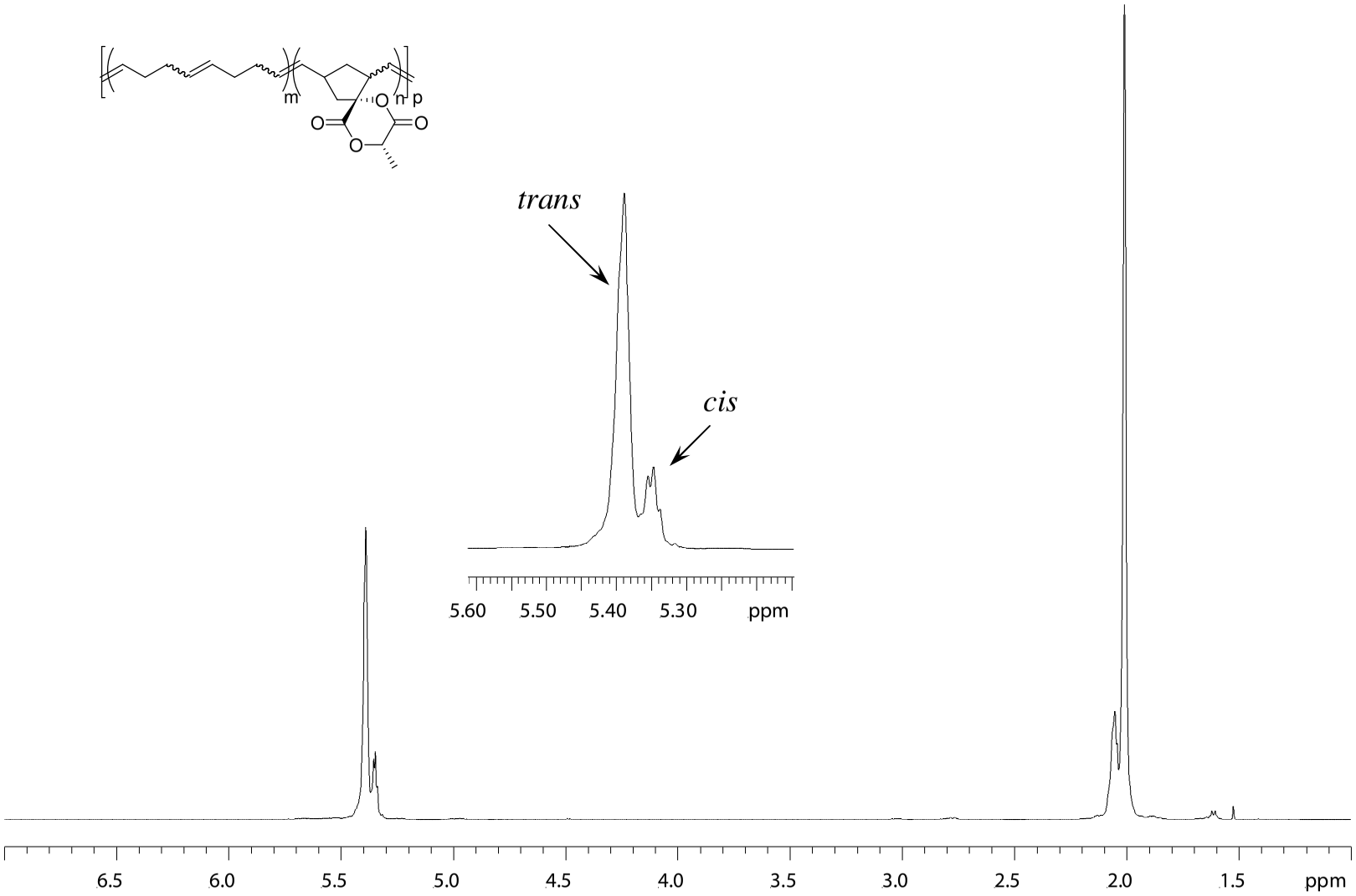
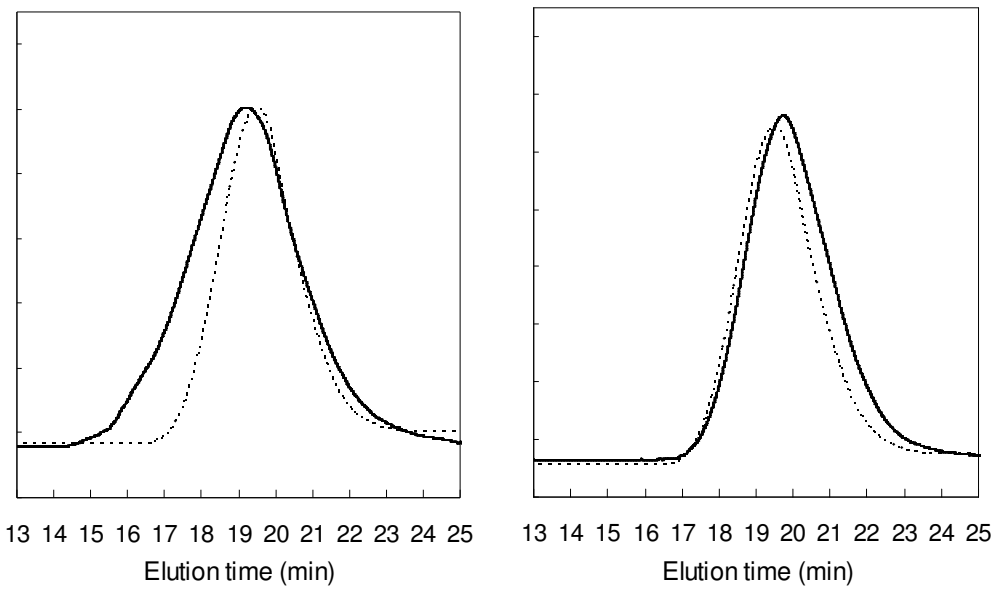


Figure S17. 500 MHz ^{1}H NMR spectrum of poly(COD/**2**) in $CDCl_3$.



A B

Figure S18. A: SEC traces of composite **C1** (solid line) and its precursor COD/**2** copolymer (dotted line); B: SEC traces of composite **C2** (solid line) and its precursor polyCOD (dotted line).

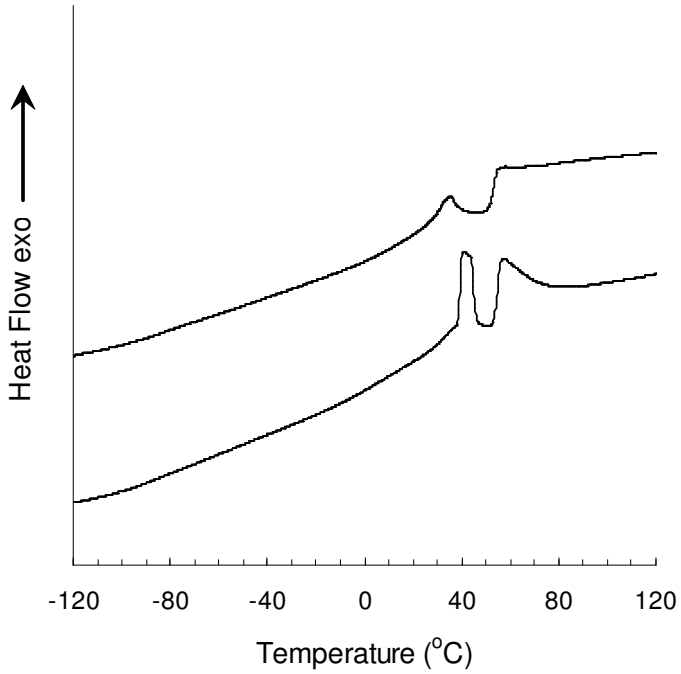


Figure S19. DSC traces of composite **C1** (top trace) and **C2** (bottom trace). Heating rate: 10 °C/min under nitrogen. The samples were held at 150 °C for 2 min to erase thermal history and cooled down to −150 °C at 10 °C/min before the measurement.

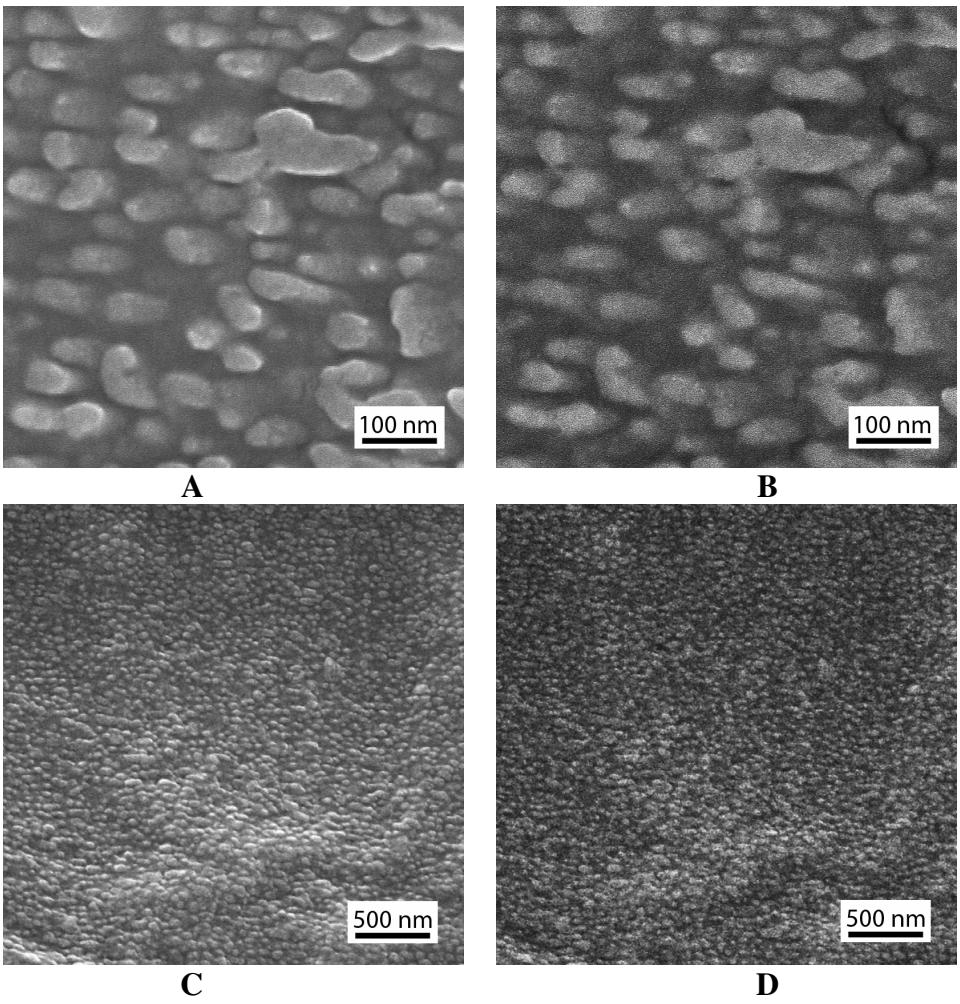


Figure S20. SEM images of composite **C1** (A, C: secondary electron images, B, D: backscattered electron images). The surface was cryo-microtomed, stained by 0.5% RuO_4 solution vapor for 30 min, and then coated with ~2 nm of Pt by direct Pt sputtering.

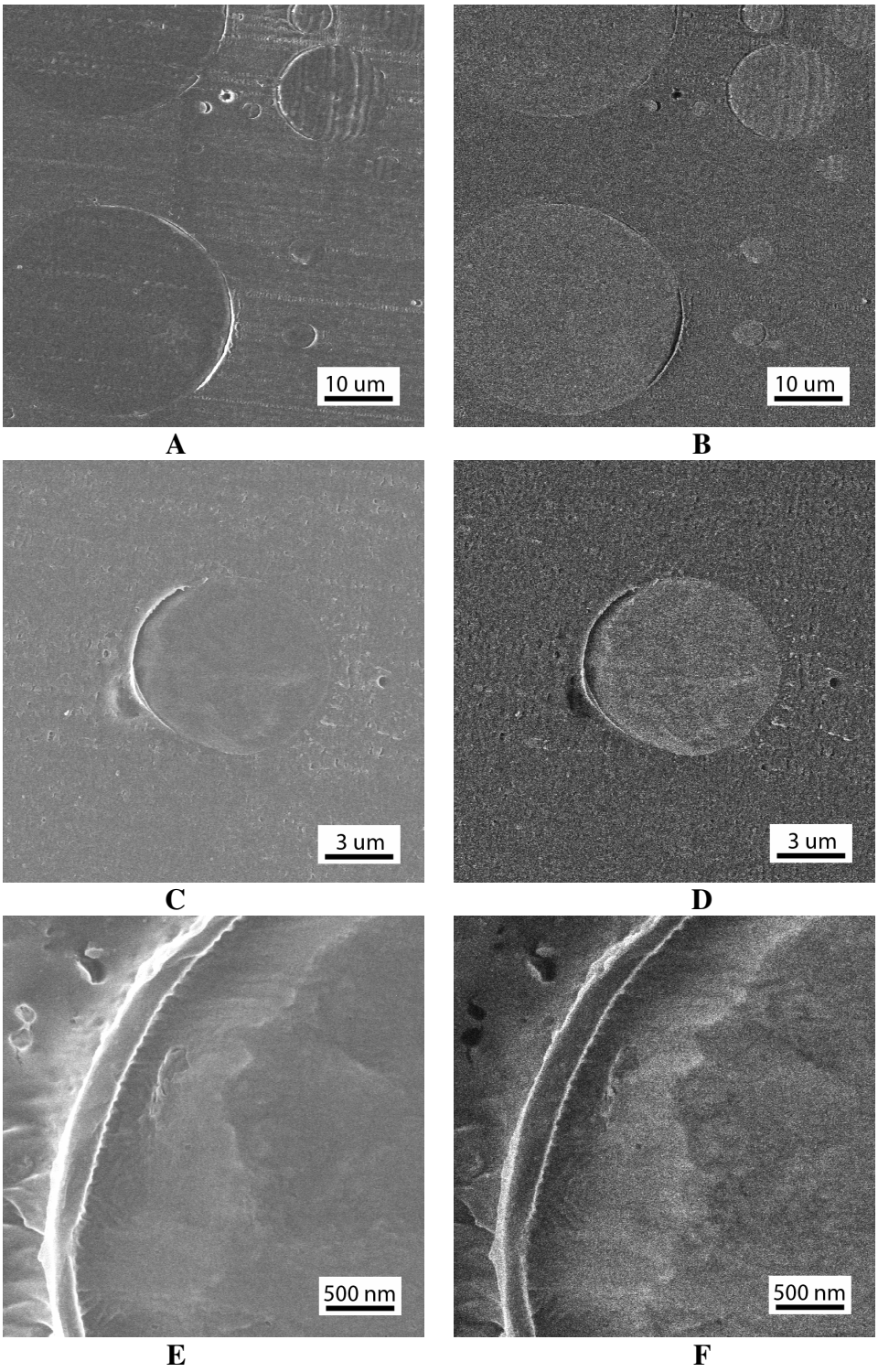


Figure S21. SEM images of composite **C2** (A, C, E: secondary electron images, B, D, F: backscattered electron images). The surface was cryo-microtomed, stained by 0.5% RuO_4 solution vapor for 30 min, and then coated with ~2 nm of Pt by direct Pt sputtering.

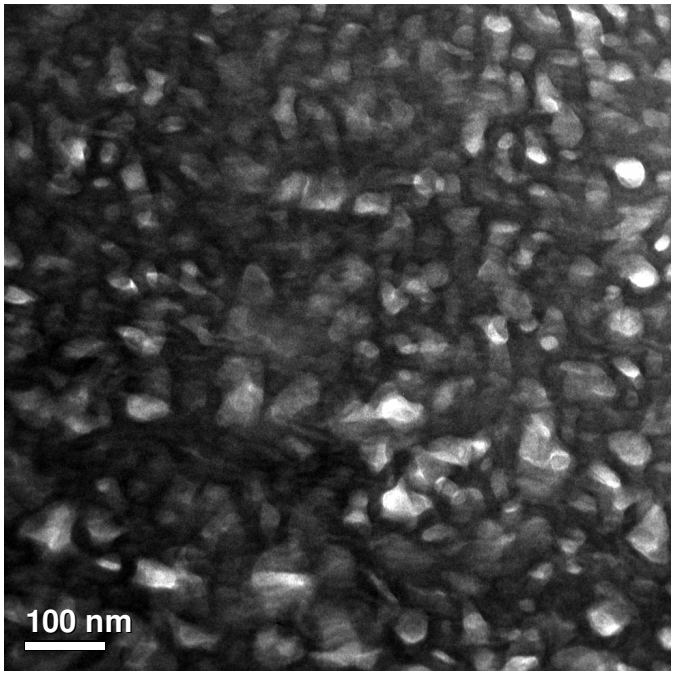


Figure S22. TEM image of composite **C1**. The thin film was stained by 4% OsO_4 solution vapor for 15 min before imaging.

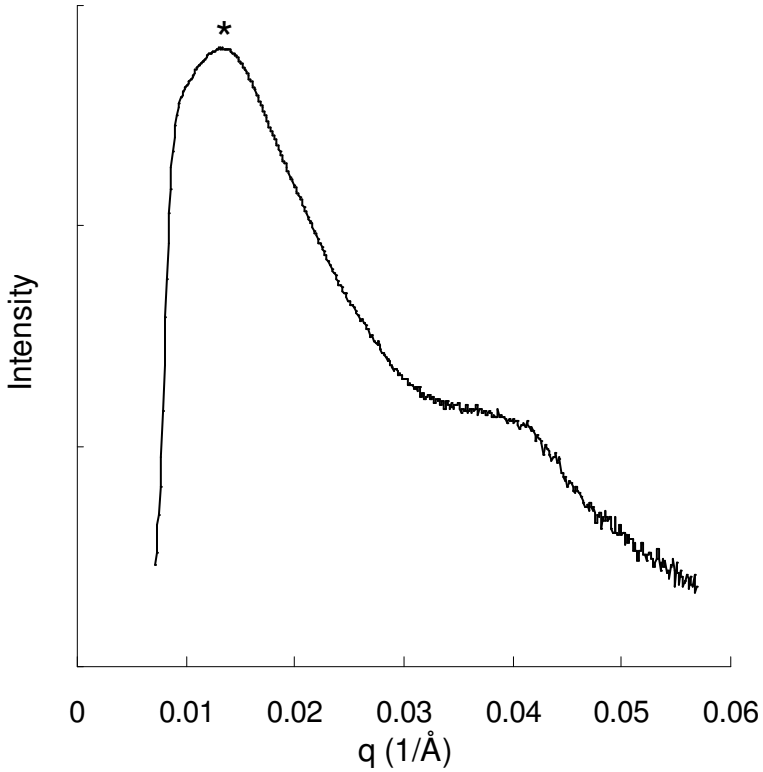


Figure S23. SAXS of composite **C1** at 100 °C. Domain spacing (D) was calculated by $D = 2\pi/q^*$. q* was marked with an asterisk.

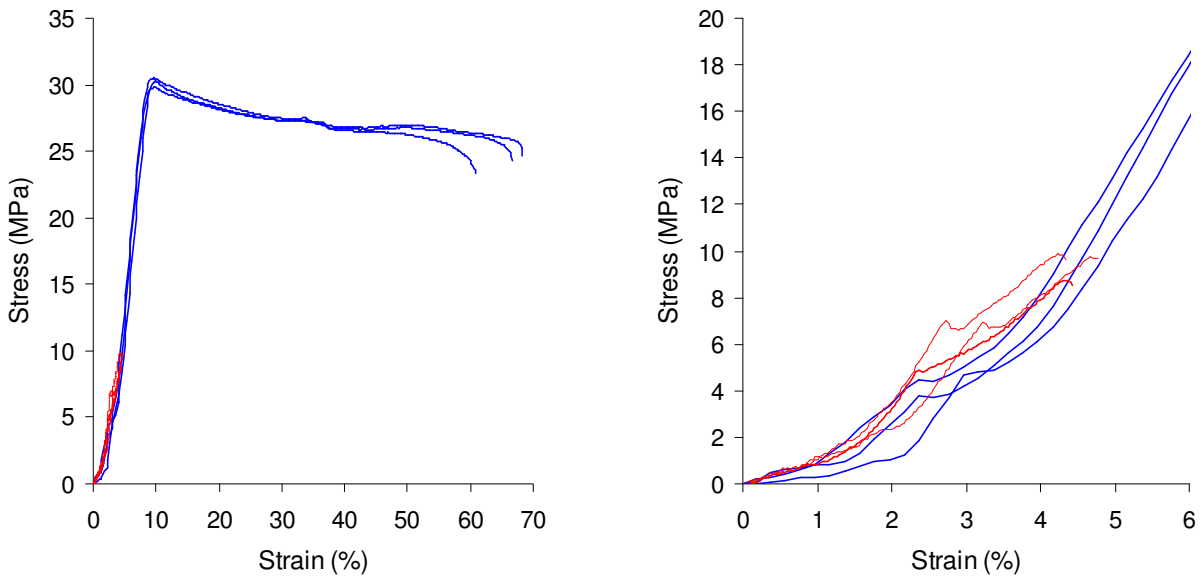


Figure S24. Tensile tests on composite **C1** (blue) and **C2** (red).