

# Supporting Information

## Revealing the Physical Properties of Chlorine-substituted Poly(acetylene)

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## General Methodology

Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. 1,3,5,7-Cyclooctatetraene (COT) was purchased from Matrix Scientific. Carbon tetrachloride, sulfuryl chloride, Hoveyda-Grubbs 2<sup>nd</sup> generation (HG2) catalyst, and the Grubbs 2<sup>nd</sup> generation (G2) catalyst were purchased from Sigma-Aldrich. The Grubbs 3<sup>rd</sup> generation (G3) catalyst was synthesized and isolated from the Grubbs 2<sup>nd</sup> generation (G2) catalyst by following a previously reported procedure.<sup>1</sup> Methanol, 1,4-dioxane, and sodium carbonate anhydrous were purchased from Daejung Chemicals & Metals. Triethylamine was purchased from Alfa Aesar. Dimethyl acetylenedicarboxylate was purchased from Tokyo Chemical Industry Co., Ltd. Anhydrous tetrahydrofuran was purchased from Acros Organics.

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded in THF-*d*<sub>8</sub> (<sup>1</sup>H: 3.58 and 1.73 ppm; <sup>13</sup>C: 67.6 ppm) or chloroform-*d*<sub>1</sub> (<sup>1</sup>H: 7.26 ppm; <sup>13</sup>C: 77.2 ppm) using a Bruker 400 MHz spectrometer. Solid-state CP-MAS <sup>13</sup>C NMR spectra were recorded at 125 MHz using a Bruker 500 MHz spectrometer. Coupling constants (*J*) are expressed in hertz (Hz). Splitting patterns are indicated as follows: bm, broad multiplet; br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were obtained from a Xevo G2-XS QToF Quadrupole Time-of-Flight Mass Spectrometer (Waters Inc.) and a Clarus SQ 8S GC/Mass Spectrometer (PerkinElmer Inc.) Size exclusion chromatography (SEC) was performed on a Malvern GPCmax Solvent/Sample Module system with internally equipped refractive index (RI), viscometer, and light scattering detectors. An external UV-vis detector was connected to the system and the corresponding data were treated independently. THF was used as the eluent at a flow rate of 0.8 mL min<sup>-1</sup>. Molecular weight and polydispersity data are reported relative to poly(styrene) standards using conventional and/or universal calibration. Mark-Houwink parameters were calculated using the Malvern OmniSEC software package (ver. 5.12). Infrared (IR) spectra were recorded on a Agilent Cary-630 FT-IR spectrometer. Raman spectra were recorded on a WITec confocal Raman Microscope System alpha 300M. Conductivity measurements were conducted using

an Advanced Instrument Technology CMT-SR200N Sheet Resistance / Resistivity Measurement System. Thermogravimetric analyses (TGA) were performed on a Thermal Advantages (TA) Q500 at a heating rate of 10 °C min<sup>-1</sup> under an atmosphere of nitrogen. X-ray photoelectron spectroscopy were performed using an Escalab 250Xi (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromated aluminum K $\alpha$  source (1486.6 eV). UV-vis spectroscopy data were recorded using an Agilent Cary 100 UV-visible Spectrometer.

### **Additional Synthetic Details**

#### *Synthesis of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (3).*

A previously reported procedure<sup>2</sup> was modified to synthesize this compound. Briefly, an oven-dried three-neck 100 mL round bottom flask purged with nitrogen was charged with cyclooctatetraene (**2**) (16.9 mL, 150 mmol) in carbon tetrachloride (45 mL). Thereafter, the temperature was kept constant (25 °C) in a water bath, and sulfuryl chloride (15.8 mL, 195 mmol) was added dropwise via syringe pump over 1 h while stirring. After the addition of sulfuryl chloride, an oil bubbler was connected to monitor the progress of reaction. The reaction was completed when no bubbling was observed in the oil bubbler (approximately 15 h). Sodium carbonate (5.0 g, 47 mmol) was added to quench the reaction, and the resulting suspension was stirred for 30 min before filtration. The filtrate was evaporated under reduced pressure to obtain crude **3** which was subsequently used without further purification.

#### *Synthesis of cis-, and trans- 7,8-dimethyl 3,4-dichlorotricyclo[4.2.2.0<sup>2,5</sup>]deca-7,9-diene-7,8-dicarboxylate (4).*

A previously reported procedure<sup>2,3</sup> was modified to synthesize this compound. Briefly, a three-neck 100 mL round bottom flask was charged with crude **3** in carbon tetrachloride (45 mL) and dimethylacetylene dicarboxylate (16.5 mL, 135 mmol). The mixture was then refluxed at 90 °C. After 3 h, the residual solvent was evaporated under reduced pressure and the crude ester product was

purified using column chromatography (silica gel, 15 : 1 v/v *n*-hexane/ethyl acetate as an eluent) to afford **4** as an off-white solid (28.5 g, 60% yield over two steps; *cis* : *trans* = 4 : 1 as determined by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR (*cis* isomer, 400 MHz, CDCl<sub>3</sub>): δ 6.63 – 6.56 (m, 2H), 4.29 – 4.23 (m, 2H), 3.89 – 3.84 (m, 2H), 3.78 (s, 6H), 2.84 – 2.77 (m, 2H). <sup>1</sup>H NMR (*trans* isomer, 400 MHz, CDCl<sub>3</sub>): δ 6.72 – 6.66 (m, 1H), 6.54 – 6.48 (m, 1H), 4.41 – 4.35 (m, 1H), 4.28 – 4.21 (m, 2H), 3.93 – 3.88 (m, 1H), 3.78 (d, 6H, *J* = 1.4 Hz), 3.08 – 3.00 (m, 1H), 2.78 – 2.71 (m, 1H). <sup>13</sup>C NMR (*cis* isomer, 100 MHz, CDCl<sub>3</sub>): δ 165.64, 142.09, 134.49, 53.99, 52.46, 48.82, 41.58. <sup>13</sup>C NMR (*trans* isomer, 100 MHz, CDCl<sub>3</sub>): δ 165.89, 165.65, 143.35, 142.73, 135.80, 134.40, 59.77, 58.53, 52.53, 47.73, 44.89, 41.45, 40.95. HR-MS (ESI) calcd. for C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub> [M + Na]<sup>+</sup> 339.0161, found 339.0165.

#### *Synthesis of cis-3,4-dichlorocyclobutene (I).*

A previously reported procedure<sup>3</sup> was modified to synthesize this compound. Briefly, crude **4** was transferred to a 100 mL pressure equalizing dropping funnel attached to a 100 mL three-neck round bottom flask, which was equipped with a distillation head, a condenser, and a 100 mL receiving flask. The reaction flask was immersed in an oil bath (200 °C) and the pressure of the setup was reduced to 15 mbar. Crude **4** was added dropwise to the pyrolysis flask with vigorous stirring, and the pyrolysate was collected in the receiving flask at -78 °C. After the addition was complete, the pyrolysis was continued for another 30 min. Subsequent purification using column chromatography (silica gel, *n*-hexane as an eluent) and Kugelrohr distillation (25 °C, 0.1 mbar) afforded **1** as a clear liquid (1.8 g, 10% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.28 (t, 2H, *J* = 1.2 Hz), 5.15 (t, 2H, *J* = 1.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.66, 61.09. GC-MS (EI) calcd. for C<sub>4</sub>H<sub>4</sub>Cl<sub>2</sub> [M]<sup>+</sup> 121.9685, found 121.9466.

#### *Synthesis of poly(I).*

*cis*-3,4-Dichlorocyclobutene (0.20 g, 1.63 mmol) and anhydrous tetrahydrofuran (2.8 mL) were added to an air-free reaction flask (25 mL) at room temperature under a positive flow of nitrogen. A solution

of G3 (11.8 mg, 0.013 mmol) in anhydrous tetrahydrofuran (0.5 mL) was injected and the mixture was gently stirred for 1 h at room temperature. The reaction was quenched upon the addition of ethyl vinyl ether (ca. 50  $\mu$ L) and the resulting mixture was poured into methanol (ca. 100 mL). An off-white precipitate formed and was subsequently collected via filtration and then dried under reduced pressure to afford poly(**1**) (0.18 g, 90% yield).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  6.10 – 5.70 (bm, 2H), 5.20 – 4.60 (bm, 2H).  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta$  133.7 – 132.5, 132.2 – 131.3, 64.1 – 63.6, 59.0 – 58.3. Using the reaction conditions and the procedure described above, the ROMP of **1** was also accomplished using the HG2 catalyst; key data are summarized in Table S1.

**Table S1.** ROMP of **1** using HG2.

Run	$[\mathbf{1}]_0/[\text{HG2}]_0$	Isolated yield (%)	$M_n$ (kDa)	$\mathcal{D}$
1	122	96	41	1.3
2	61	91	31	1.4

*Synthesis of chlorine-substituted poly(acetylene) (5).*

Triethylamine (1.35 mL, 9.7 mmol) was added to a reaction flask containing poly(**1**) (0.12 g, 0.97 mmol) in anhydrous tetrahydrofuran (9.7 mL) at 60  $^\circ\text{C}$  under a nitrogen atmosphere and in the dark. After 24 h, the reaction mixture was poured into methanol and the precipitated solids were subsequently collected via filtration and then dried under reduced pressure to afford **5** (84.1 mg, >99% yield). Solid-state CP-MAS  $^{13}\text{C}$  NMR (125 MHz):  $\delta$  133.58. The methanol filtrate was then concentrated and poured into excess diethyl ether. The precipitate was washed with diethyl ether, collected as a white solid and later identified as triethylammonium chloride (133 mg, >99% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.02 (s, 1H), 3.15 – 3.04 (m, 6H), 1.40 (t, 9H,  $J = 7.3$  Hz). HR-MS (DART) calcd. for  $\text{C}_6\text{H}_{16}\text{N}^+ [\text{M}]^+$  102.1277, found 102.1278.

#### *Preparation of a film of 5.*

A glass substrate (2.5 cm × 2.5 cm) was first cleaned with acetone and isopropanol. A reaction vial was charged with poly(**1**) (8.6 mg, 0.070 mmol), 1,4-dioxane (0.86 mL) and triethylamine (0.1 mL, 0.7 mmol). The resulting mixture (0.4 mL) was then drop-casted onto the glass substrate which was previously heated to 40 °C using a hot plate and placed in a chamber that was designed for solvent vapor annealing. The chamber was wrapped with aluminum foil to minimize exposure to ambient light. After 20 min, the reaction temperature was increased to 60 °C. After 24 h, the resulting film was washed with methanol and dried under nitrogen for 2 h followed by vacuum until 0.05 torr was achieved at room temperature.

#### *Doping of a film of 5 with iodine.*

Iodine (10 g) was placed at the bottom of a chamber subjacent to a glass substrate supporting a film of **5**. Evacuation of the chamber (0.10 torr) facilitated iodine sublimation at room temperature and in the dark. After 3 h, the chamber was entombed in a glove bag filled with nitrogen and the conductivity of the sample was measured.

#### *Doping of a film of 5 with sodium naphthalenide.*

A sodium naphthalenide / THF solution was prepared by modifying a previously reported procedure.<sup>4</sup> An oven-dried 50 mL Schlenk flask was charged with naphthalene (0.65 g, 5.1 mmol) in anhydrous tetrahydrofuran (5 mL). Sodium (0.13 g, 5.6 mmol) was then slowly added to the reaction flask. The reaction mixture was stirred for 3 h at 25 °C under an atmosphere of nitrogen. The dark green sodium naphthalenide solution was then drop-casted on the polymer film under an atmosphere of nitrogen and in the dark. After 3 h, the film was washed with degassed methanol followed by tetrahydrofuran. The doped film was dried under vacuum and the conductivity of the material was measured.

#### *Synthesis of dimethyl bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate (6)*

A modified literature procedure was used to prepare **6**.<sup>5</sup> An oven-dried 50 mL Schlenk flask was charged with cyclopentadiene (0.69 g, 10.5 mmol) that was freshly cracked from dicyclopentadiene and dimethyl fumarate (1.44 g, 10.0 mmol) in anhydrous tetrahydrofuran (4.4 mL). The reaction mixture was stirred for 17 h at 25 °C, and the solvent removed under reduced pressure to afford **6** as a clear oil (2 g, 93% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.33 – 6.25 (m, 1H), 6.11 – 6.04 (m, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 3.42 – 3.36 (m, 1H), 3.30 – 3.25 (m, 1H), 3.16 – 3.11 (m, 1H), 2.73 – 2.67 (m, 1H), 1.66 – 1.59 (m, 1H), 1.50 – 1.44 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.99, 173.81, 137.67, 135.26, 52.21, 51.94, 47.97, 47.73, 47.44, 47.20, 45.74. HR-MS (ESI) calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> [M + Na]<sup>+</sup> 233.0784, found 233.0782.

#### *Synthesis of poly(6).*

Dimethyl bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate (0.10 g, 0.48 mmol) and anhydrous tetrahydrofuran (0.55 mL) were added to a 25 mL air-free reaction flask at room temperature under a positive flow of nitrogen. A solution of G3 (8.9 mg, 0.010 mmol) in anhydrous tetrahydrofuran (0.4 mL) was injected and the mixture was gently stirred for 30 min at room temperature. The reaction was quenched upon the addition of ethyl vinyl ether (ca. 50 μL) and the resulting mixture was eluted with tetrahydrofuran through a filter funnel packed with basic alumina. The filtrate was then poured into cold hexane (ca. 50 mL) which caused a precipitate to form. The precipitate was subsequently collected via filtration and dried under vacuum to afford poly(**6**) (90 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 5.65 – 5.13 (bm, 2H), 3.75 – 3.54 (m, 6H), 3.46 – 2.65 (bm, 4H), 2.10 – 1.85 (br, 1H), 1.62 – 1.37 (br, 1H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>): δ 174.9 – 173.4, 134.8 – 130.5, 54.6 – 51.4, 48.6 – 47.3, 46.3 – 45.5, 43.6 – 39.6.

#### *Synthesis of poly(6)-block-poly(1).*

Monomer **6** (105 mg, 0.5 mmol) was dissolved in anhydrous tetrahydrofuran (0.6 mL). Subsequent injection of pre-determined quantities of G3 (13.6 mg, 0.015 mmol) dissolved in anhydrous

tetrahydrofuran (0.4 mL) followed by stirring at room temperature for 30 min initiated the polymerization of the monomer. A small aliquot was removed from the reaction vessel, filtered through a filter funnel packed with basic alumina using tetrahydrofuran, and then analyzed by SEC. A solution of monomer **1** (45 mg, 0.37 mmol) in anhydrous tetrahydrofuran (0.75 mL) was then injected into the reaction vessel and the resulting reaction mixture was stirred for an additional 30 min. Excess ethyl vinyl ether (ca. 50  $\mu$ L) was added to quench the reaction and then the resulting mixture was eluted using tetrahydrofuran through the filter funnel packed with basic alumina. The filtrate was concentrated under reduced pressure and poured into cold hexane (ca. 100 mL) to induce precipitation. The precipitate was collected via filtration and dried under reduced pressure to afford poly(**6**)-*block*-poly(**1**) (142 mg, 95% yield).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  6.13 – 5.65 (bm, 4H), 5.59 – 5.16 (bm, 6H), 5.16 – 4.52 (bm, 4H), 3.73 – 3.51 (m, 18H), 3.43 – 2.63 (bm, 12H), 2.10 – 1.82 (br, 3H), 1.58 – 1.35 (br, 3H).  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta$  174.9 – 173.4, 134.8 – 130.5, 64.2 – 63.5, 59.2 – 58.3, 54.6 – 51.5, 48.6 – 47.3, 46.3 – 45.5, 43.6 – 39.2. SEC data using conventional calibration:  $M_{n, \text{conv.}} = 10.1$  kDa,  $D_{\text{conv.}} = 1.10$ ; universal calibration:  $M_{n, \text{univ.}} = 8.3$  kDa,  $D_{\text{univ.}} = 1.05$ .

#### *Synthesis of block copolymer 7.*

Triethylamine was added (1.0 mL) to a stirred solution of poly(**6**)-*block*-poly(**1**) (0.15 g) in anhydrous tetrahydrofuran (8.7 mL) at 60  $^{\circ}\text{C}$  under an atmosphere of nitrogen and in the dark. The reaction mixture was poured into excess methanol after 24 h. The precipitated solids were subsequently collected and dried under reduced pressure to afford **7** (116 mg, 85% yield).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  6.13 – 5.65 (bm, 4H), 5.59 – 5.16 (bm, 6H), 5.16 – 4.52 (bm, 4H), 3.73 – 3.51 (m, 18H), 3.43 – 2.63 (bm, 12H), 2.10 – 1.82 (br, 3H), 1.58 – 1.35 (br, 3H). SEC data using conventional calibration:  $M_{n, \text{conv.}} = 7.7$  kDa,  $D_{\text{conv.}} = 1.17$ ; universal calibration:  $M_{n, \text{univ.}} = 33.4$  kDa,  $D_{\text{univ.}} = 1.06$ .

#### *Synthesis of poly(**1**)-random-poly(*cis*-2-ethylhexyl 4-chlorocyclobut-2-ene-1-carboxylate) (**9**).*

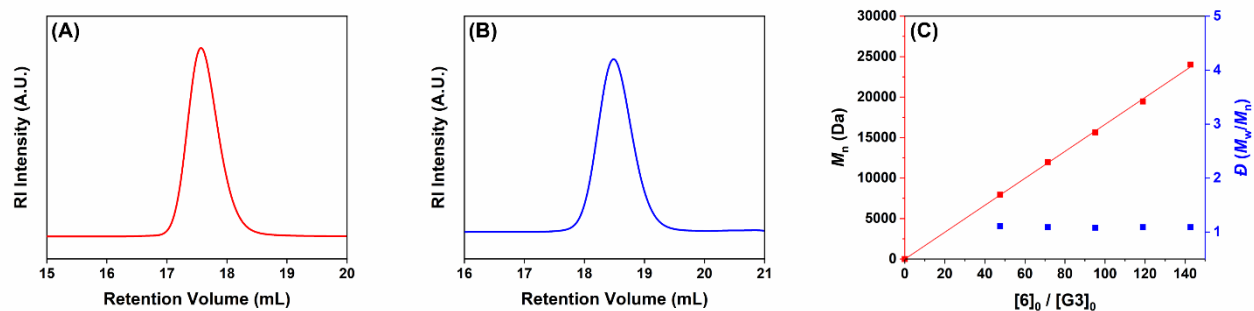


Monomer **1** (24 mg, 0.20 mmol), *cis*-2-ethylhexyl 4-chlorocyclobut-2-ene-1-carboxylate (**8**)<sup>6</sup> (76 mg, 0.31 mmol), and anhydrous tetrahydrofuran (0.6 mL) were added to an air-free reaction flask (25 mL) at room temperature under a positive flow of nitrogen. A solution of HG2 (4.7 mg, 0.0075 mmol) in anhydrous tetrahydrofuran (0.4 mL) was injected into the reaction vessel and the resulting mixture was gently stirred for 1 h at room temperature. The reaction was quenched upon the addition of ethyl vinyl ether (ca. 50  $\mu$ L) and the resulting mixture was filtered through acidic alumina. The filtrate was dried under reduced pressure to afford **9** as a brown viscous gel (70 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.23 – 5.40 (bm, 3H), 5.19 – 4.34 (bm, 2H), 4.16 – 3.86 (br, 2H), 3.86 – 3.08 (bm, 1H), 1.62 – 1.50 (br, 1H), 1.43 – 1.20 (bm, 8H), 0.93 – 0.63 (bm, 6H). SEC data using conventional calibration:  $M_{n, \text{conv.}} = 17.9$  kDa,  $D_{\text{conv.}} = 1.21$ ; universal calibration:  $M_{n, \text{univ.}} = 10.0$  kDa,  $D_{\text{univ.}} = 1.10$ .

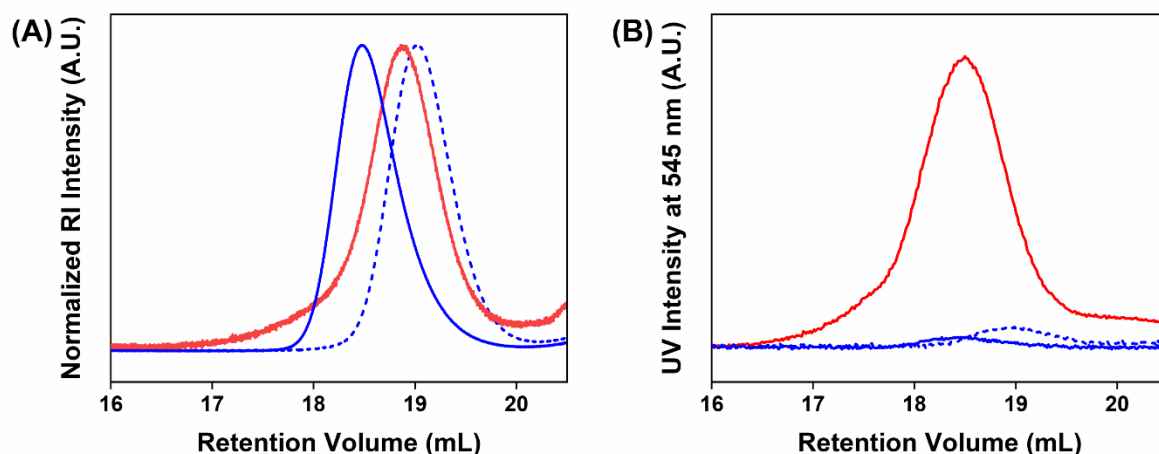
#### *Synthesis of 10.*

Triethylamine was added (0.4 mL) to a stirred solution of copolymer **9** (54 mg) in anhydrous tetrahydrofuran (2.7 mL) at 60 °C under an atmosphere of nitrogen and in the dark. The reaction mixture was poured into excess methanol after 24 h. The precipitated solids were subsequently collected and dried under reduced pressure to afford random copolymer **10** (35 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>):  $\delta$  9.12 – 5.46 (bm, 9H), 4.28 – 3.89 (br, 4H), 1.41 – 1.26 (br, 16H), 0.95 – 0.85 (br, 12H). SEC data using conventional calibration:  $M_{n, \text{conv.}} = 6.2$  kDa,  $D_{\text{conv.}} = 1.72$ ; universal calibration:  $M_{n, \text{univ.}} = 7.5$  kDa,  $D_{\text{univ.}} = 1.53$ .

## SEC Data

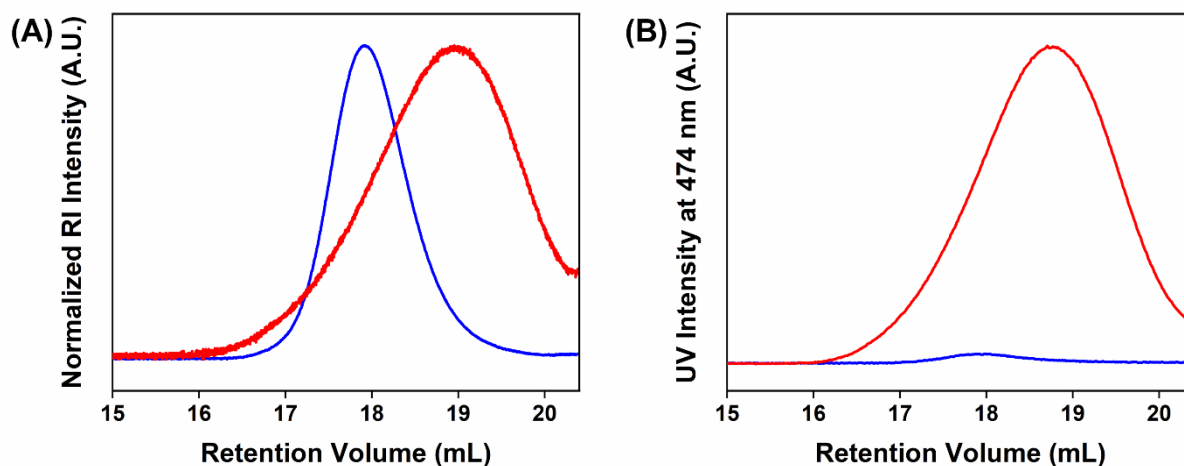


**Figure S1.** Representative SEC data that were collected for poly(**1**) and poly(**6**). Conditions: G3 as initiator, THF as solvent, N<sub>2</sub> atmosphere, 25 °C; [1]<sub>0</sub> = 0.5 M, 1 h, isolated yields were typically >90%; [6]<sub>0</sub> = 0.5 M, 30 min, isolated yields were typically >90%. (A) Poly(**1**) ([1]<sub>0</sub> / [Ru]<sub>0</sub> = 122; M<sub>n</sub> = 20.4 kDa, Đ = 1.05, M<sub>n, theoretical</sub> = 15.0 kDa) and (B) poly(**6**) ([6]<sub>0</sub> / [Ru]<sub>0</sub> = 47; M<sub>n</sub> = 7.9 kDa, Đ = 1.11, M<sub>n, theoretical</sub> = 9.8 kDa). (C) Plot of M<sub>n</sub> (red) and Đ (blue) versus the [6]<sub>0</sub> to [Ru]<sub>0</sub> feed ratio.



**Figure S2.** SEC data that were recorded for poly(**6**) (blue dotted line), poly(**6**)-*block*-poly(**1**) (blue solid line), and **7** (red solid line) using a (A) RI or (B) UV detector (545 nm). Conditions and data for poly(**6**) and poly(**6**)-*block*-poly(**1**): G3 as catalyst, THF as solvent, N<sub>2</sub> atmosphere, 25 °C, 30 min for each block. [6]<sub>0</sub> / [Ru]<sub>0</sub> = 33.3; M<sub>n</sub> = 6.1 kDa, Đ = 1.13 (blue dotted line); ([6]<sub>0</sub> + [1]<sub>0</sub>) / [Ru]<sub>0</sub> = 57.0; M<sub>n</sub> = 10.0 kDa, Đ = 1.14 (blue solid line); 95% yield. Conditions and data for **7**: excess triethylamine,

THF as solvent, N<sub>2</sub> atmosphere, 60 °C, dark, 24 h. 85% yield.  $M_{n, \text{conv. using RI}} = 7.7 \text{ kDa}$ ,  $D_{\text{conv. using RI}} = 1.17$ ;  $M_{n, \text{univ.}} = 33.4 \text{ kDa}$ ,  $D_{\text{univ.}} = 1.06$ ;  $M_{n, \text{conv. using UV}} = 9.5 \text{ kDa}$ ,  $D_{\text{conv. using UV}} = 1.29$ .

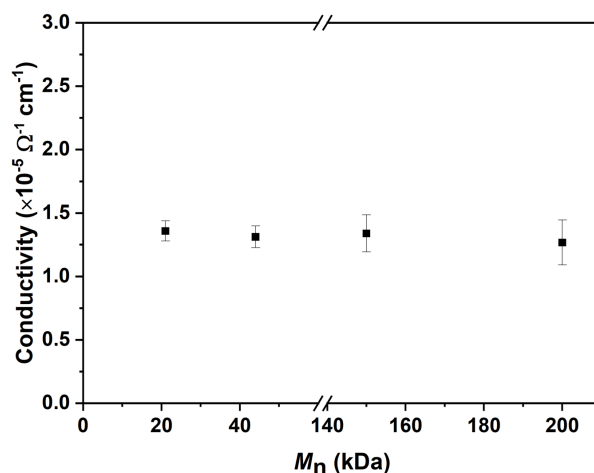


**Figure S3.** SEC data recorded for **9** (blue) and **10** (red) as visualized with a (A) RI or (B) UV detector (474 nm). Conditions and data for **9**: HG2 as catalyst, THF as solvent, N<sub>2</sub> atmosphere, 25 °C, 1 h, 70% yield; **8** : **1** = 1.5;  $([\mathbf{1}]_0 + [\mathbf{8}]_0) / [\text{HG2}]_0 = 68$ ;  $M_n = 17.9 \text{ kDa}$ ,  $D = 1.21$ . Conditions and data for **10**: excess triethylamine, THF as solvent, N<sub>2</sub> atmosphere, 60 °C, dark, 24 h, 80% yield;  $M_{n, \text{conv. using RI}} = 6.2 \text{ kDa}$ ,  $D_{\text{conv. using RI}} = 1.72$ ;  $M_{n, \text{univ.}} = 7.5 \text{ kDa}$ ,  $D_{\text{univ.}} = 1.53$ ;  $M_{n, \text{conv. using UV}} = 6.1 \text{ kDa}$ ,  $D_{\text{conv. using UV}} = 1.90$ .

**Table S2.** Mark-Houwink Parameters.

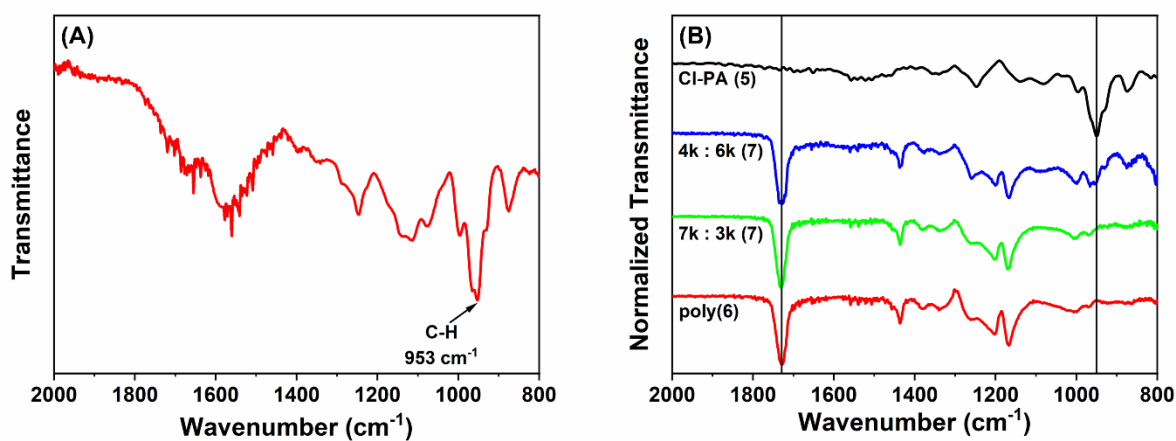
polymer	a	Log K	K ( $\times 10^{-3} \text{ mL/g}$ )
<b>7</b>	0.78	-4.59	10.1
poly( <b>6</b> )- <i>block</i> -poly( <b>1</b> )	0.53	-2.57	76.5
poly( <b>6</b> )	0.46	-2.29	101.2

## Additional Conductivity Measurement Data

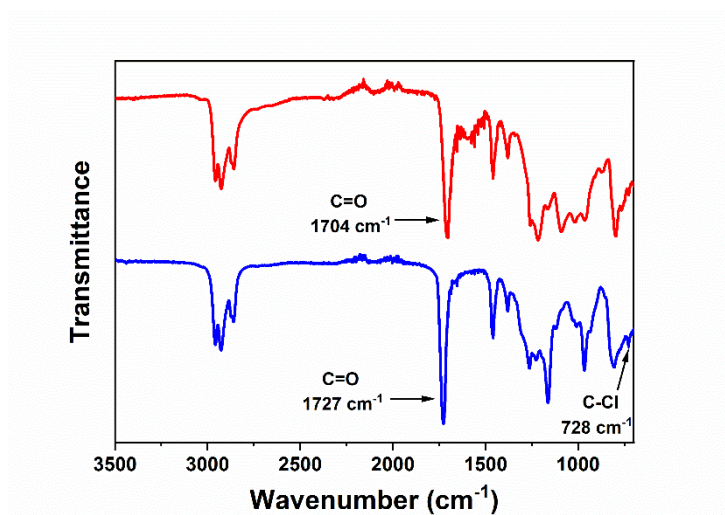


**Figure S4.** Conductivity data recorded for films of **5** as prepared from poly(**1**) with different molecular weights (20 kDa, 44 kDa, 150 kDa, or 200 kDa). Each sample was measured at least three times and the results obtained from each set of experiments were averaged.

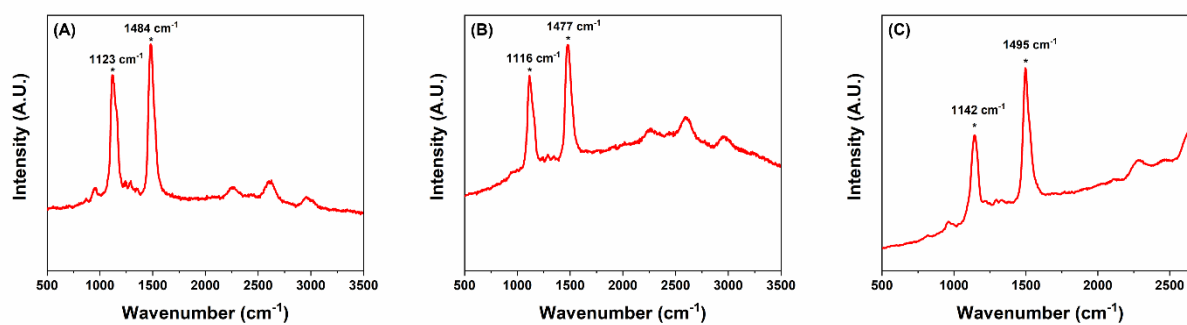
## Infrared and Raman Spectra



**Figure S5.** Infrared spectra recorded for (A) a film of **5** and (B) **5** as a powder, different ratios of block copolymer **7**, and poly(**6**) (indicated). Note: the peaks at 1729  $\text{cm}^{-1}$  and 950  $\text{cm}^{-1}$  are indicative of a  $\nu_{\text{C=O}}$  for poly(**6**) and a  $\nu_{\text{C-H}}$  for **5**, respectively.

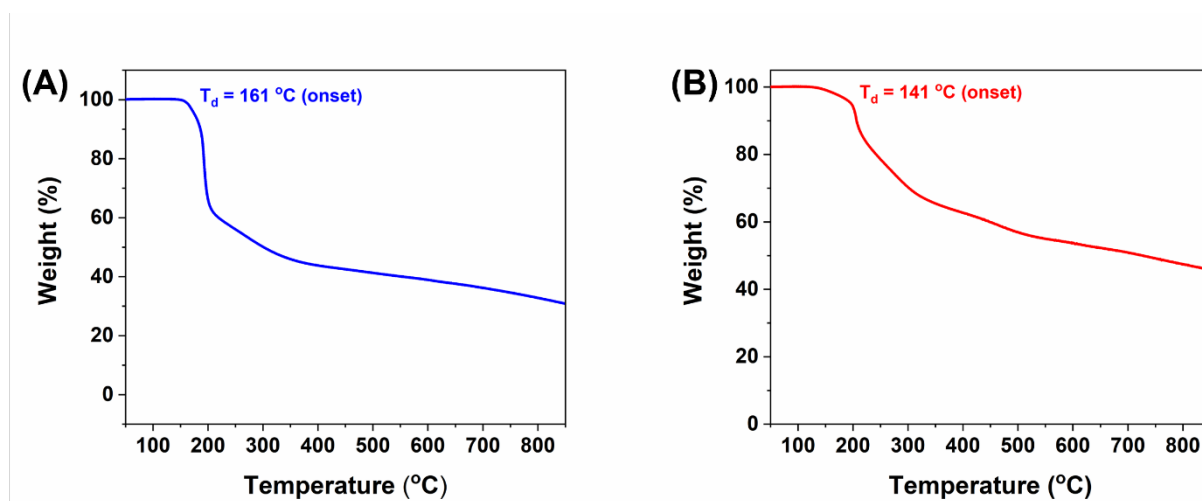


**Figure S6.** Infrared spectra recorded for random copolymer **9** (blue) and **10** (red).



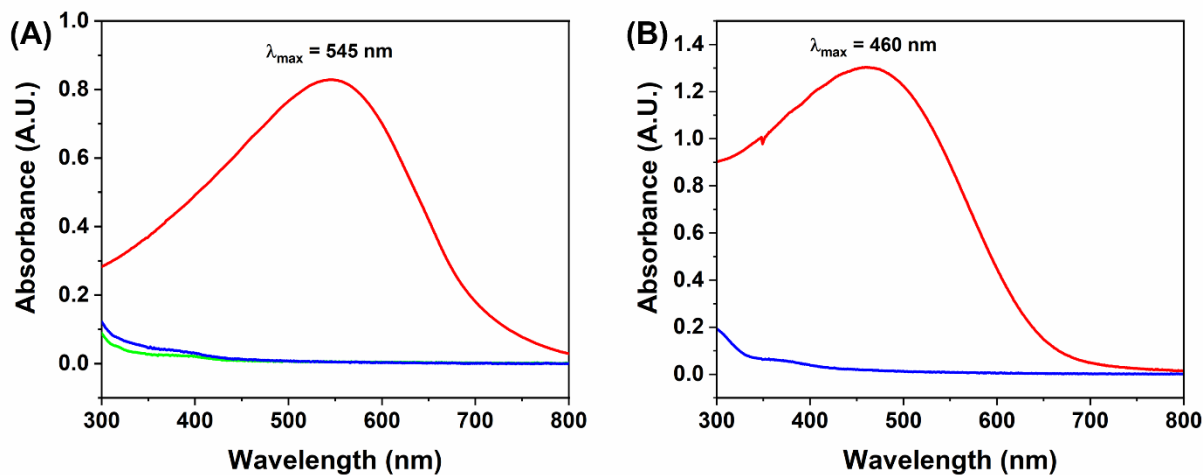
**Figure S7.** Raman spectra recorded for (A) a film of **5**, (B) block copolymer **7** and (C) random copolymer **10**.

## TGA Data



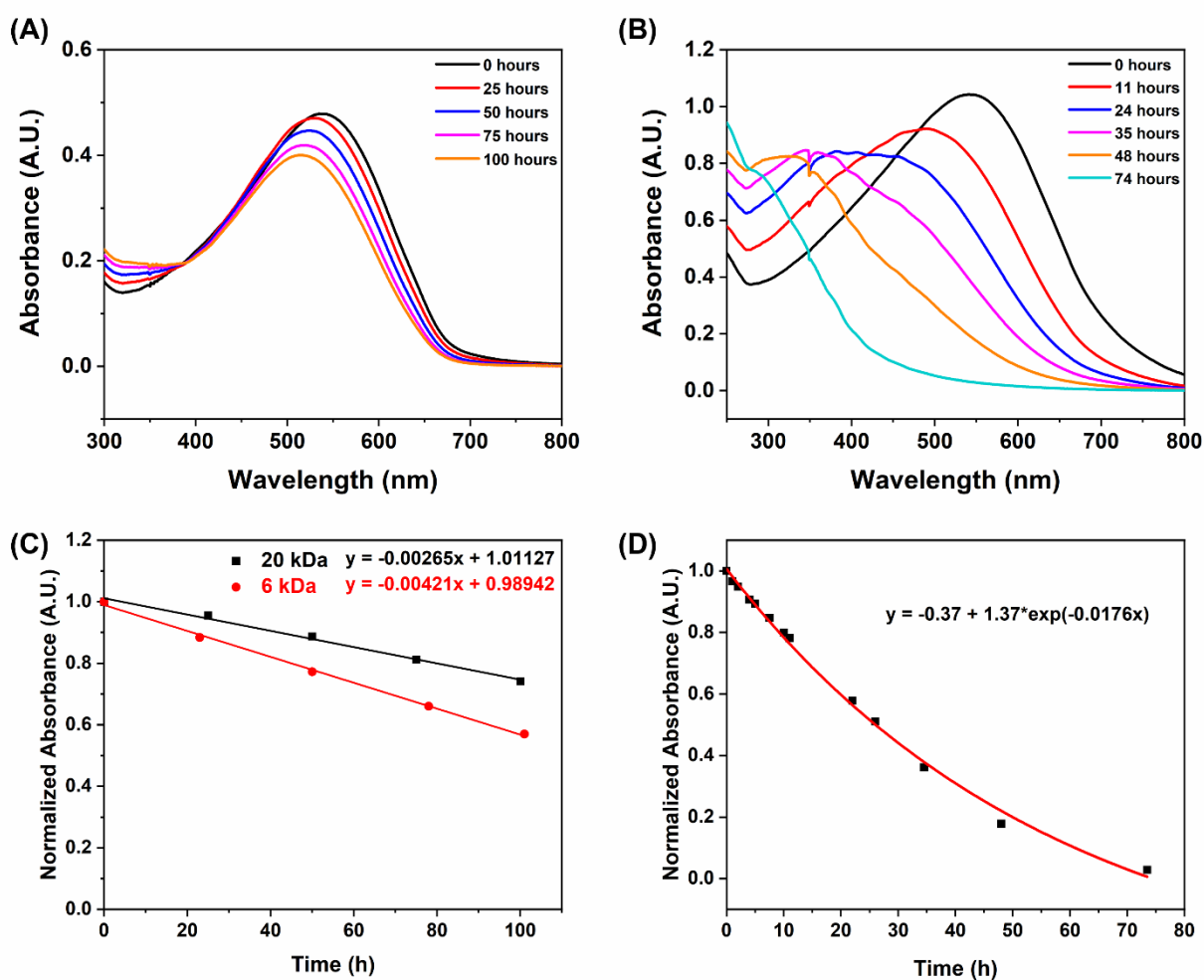
**Figure S8.** TGA data recorded for (A) poly(1) and (B) **5** as obtained under an atmosphere of nitrogen and at a heating rate of 10 °C min<sup>-1</sup>.

## UV-vis Data



**Figure S9.** UV-vis absorption spectra recorded for tetrahydrofuran solutions of (A) poly(6) (green), poly(6)-*block*-poly(1) (blue) and **7** (red) and (B) random copolymer **9** (blue) and **10** (red). [poly(6)]<sub>0</sub> = [poly(6)-*block*-poly(1)]<sub>0</sub> = 1 mM, [**7**]<sub>0</sub> = 0.3 mM, [**9**]<sub>0</sub> = 0.84 mM, [**10**]<sub>0</sub> = 0.24 mM.

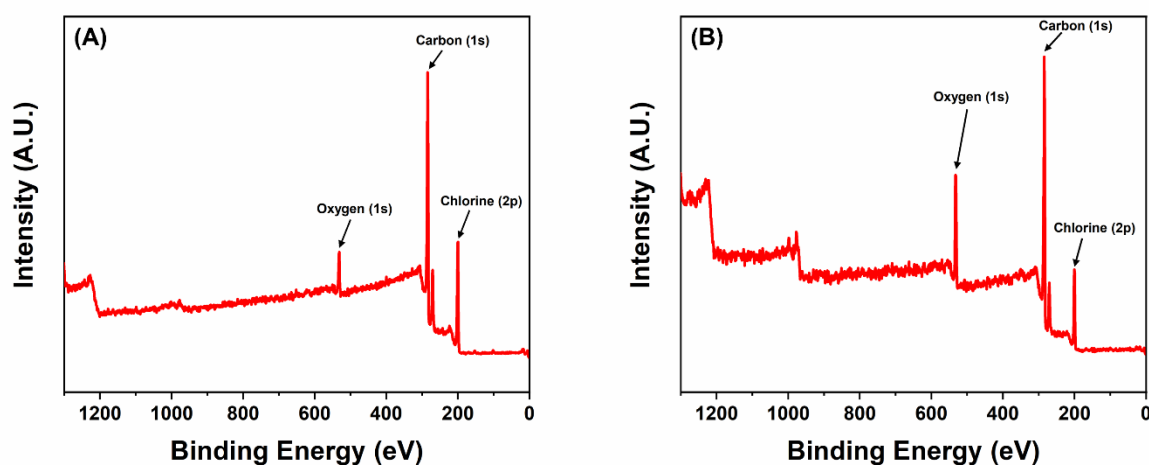
The UV-vis absorption profiles for homopolymer **5** and block copolymer **7** were separately monitored over time in tetrahydrofuran at room temperature and under ambient conditions. To minimize undesired light scattering, suspensions or solutions of the polymer ( $[\text{polymer}]_0 = 1 \text{ mg / mL}$ ) were filtered through a  $0.2 \mu\text{m}$  PTFE filter prior to analysis. Data are shown below.



**Figure S10.** UV-vis absorption spectra recorded for THF solutions of (A) homopolymer **5** (20 kDa) or (B) block copolymer **7** (7.7 kDa) over time. Plots of normalized  $\lambda_{\text{max}}$  absorbance values versus time for (C) homopolymer **5** with different molecular weights (20 kDa or 6 kDa as indicated) or (D) block copolymer **7** (7.7 kDa).

## XPS Measurement Details and Data

A XPS survey spectrum of **5** was recorded using a Thermo Fisher Scientific Escalab 250Xi. The charge compensated measurement was taken over a spot size of 500  $\mu\text{m}$  at an angle normal to the surface using a combined/flood gun operating at a current of 50  $\mu\text{A}$  and an ion voltage of 2 V. The spectrum was shifted and referenced to the peak position of the C 1s spectrum (284.8 eV). The shifted value was applied to the spectrum recorded for **5**. The survey spectrum was taken at a pass energy of 100 eV (5 scans).



**Figure S11.** XPS survey spectra recorded for **5** as a (A) powder and (B) film.



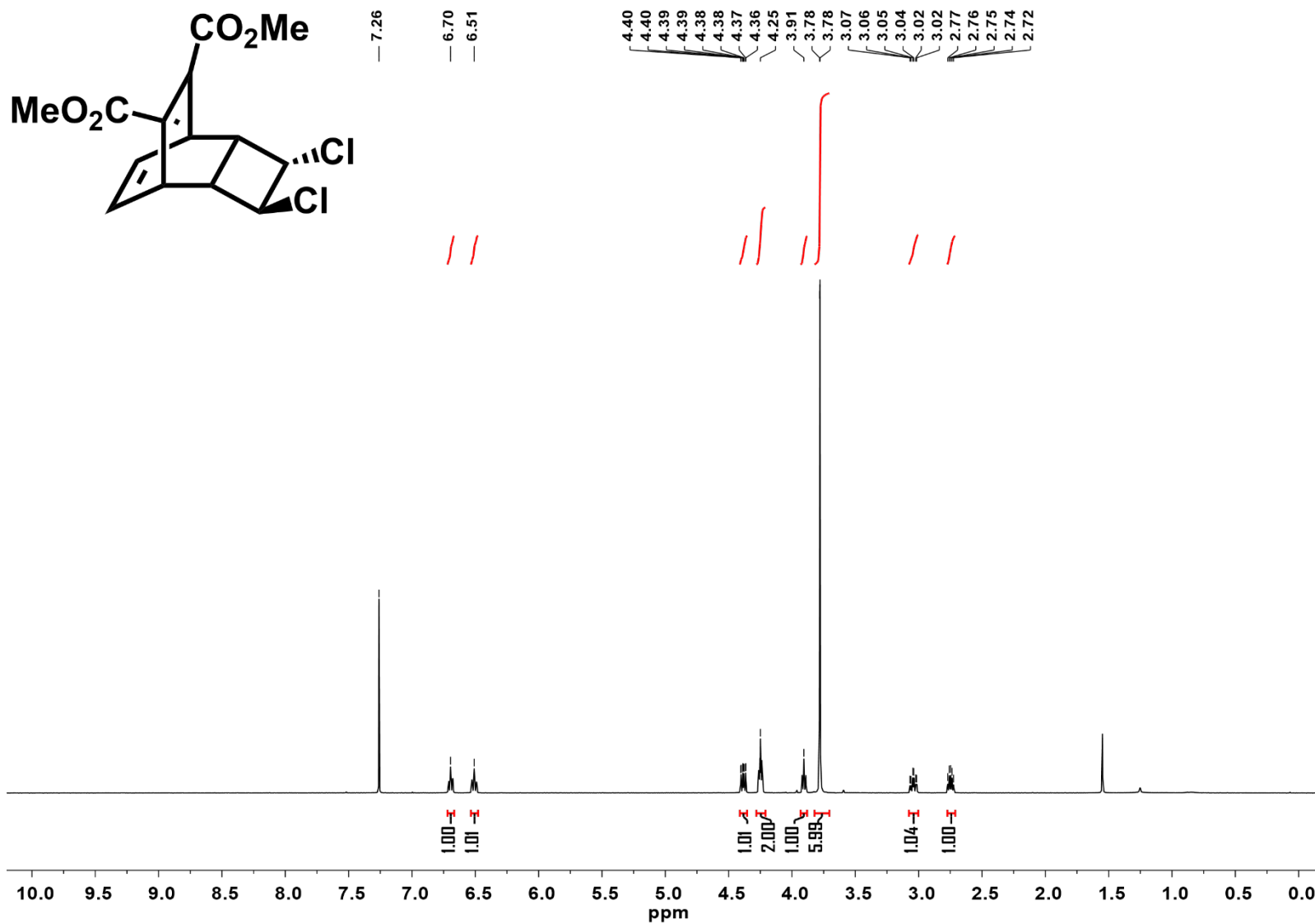


Figure S12. <sup>1</sup>H NMR spectrum recorded for *trans*-4 at 25 °C in chloroform-*d*<sub>1</sub>.

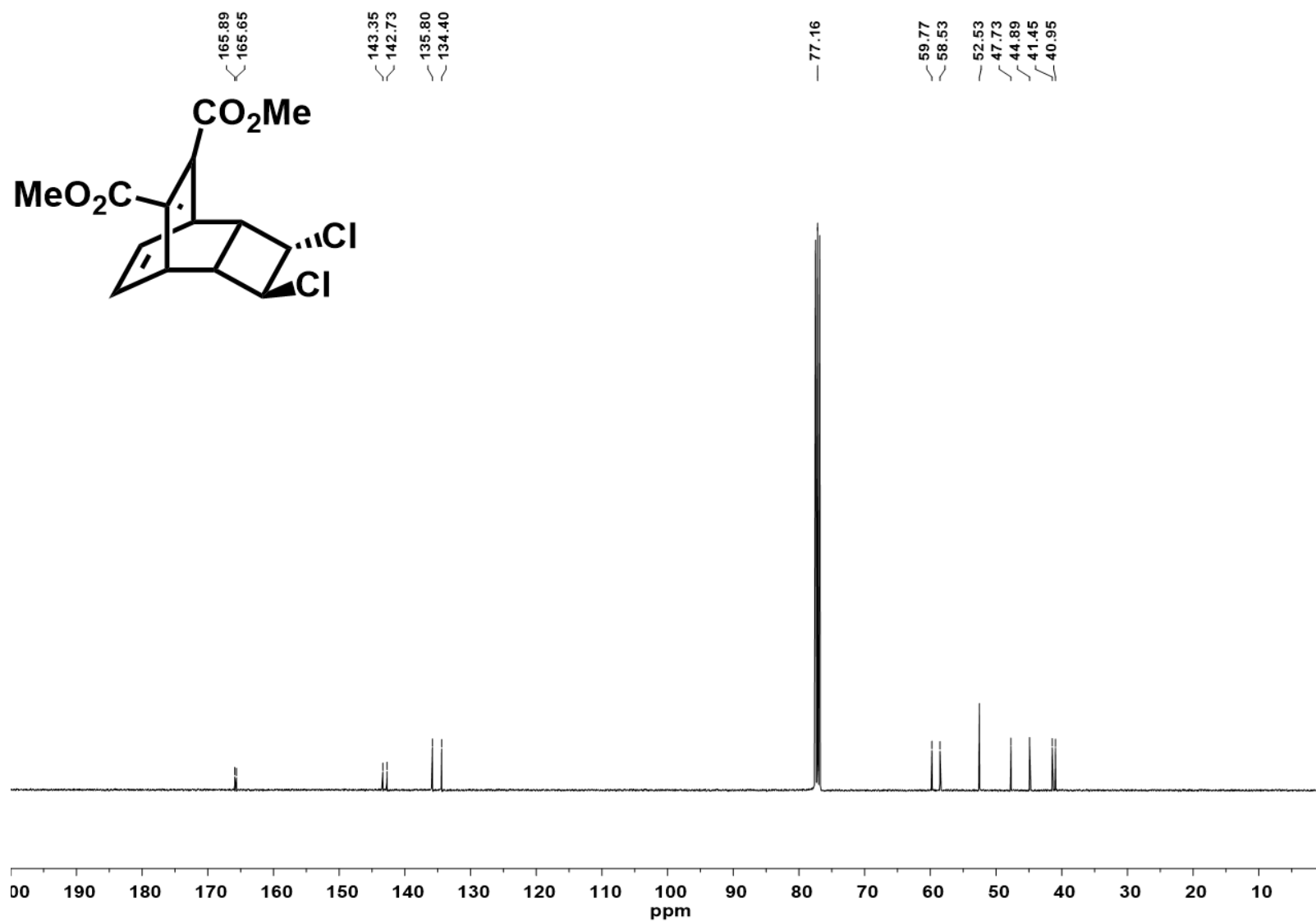


Figure S13. <sup>13</sup>C NMR spectrum recorded for *trans*-4 at 25 °C in chloroform-*d*<sub>1</sub>.

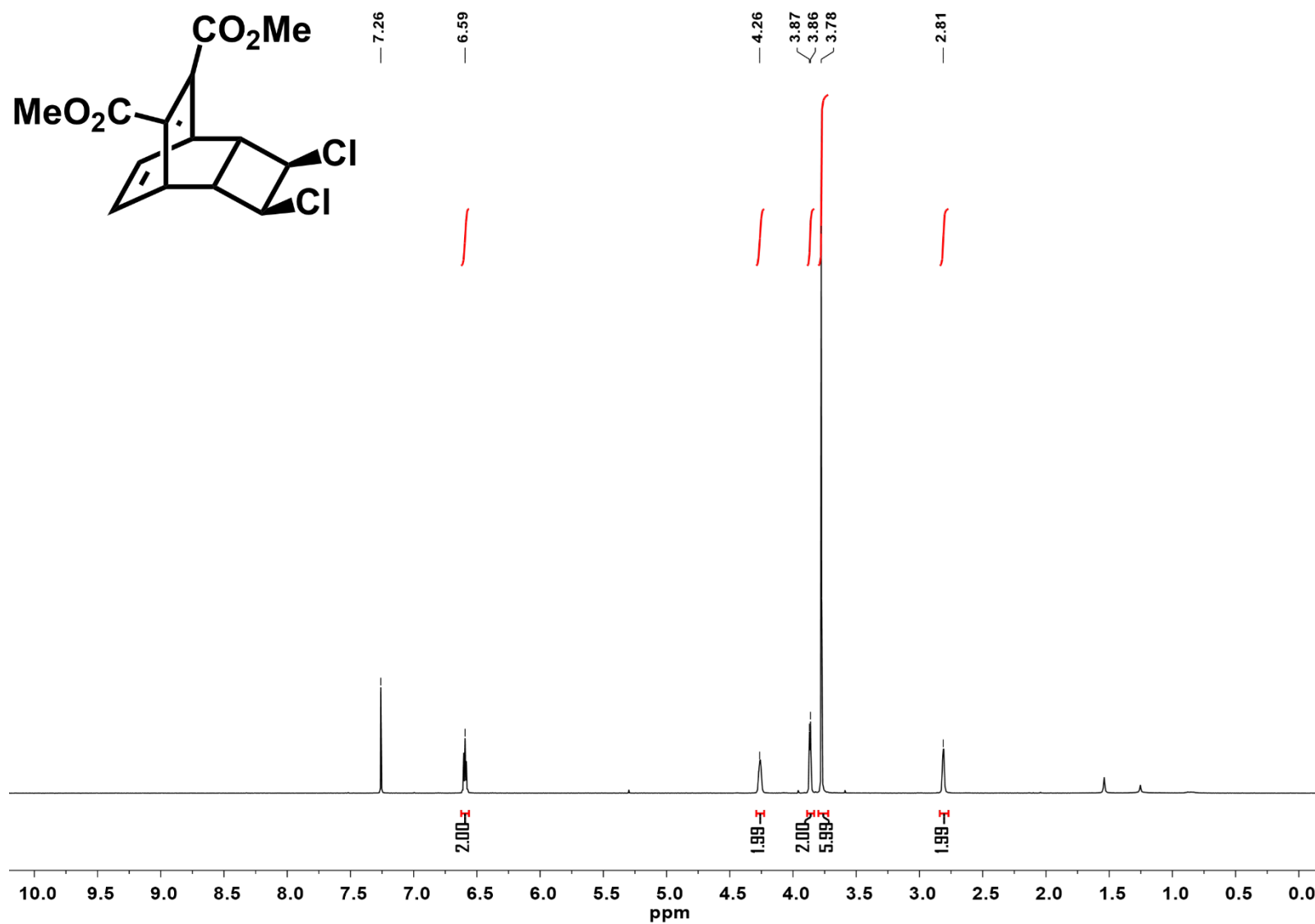


Figure S14. <sup>1</sup>H NMR spectrum recorded for *cis*-4 at 25 °C in chloroform-*d*<sub>1</sub>.

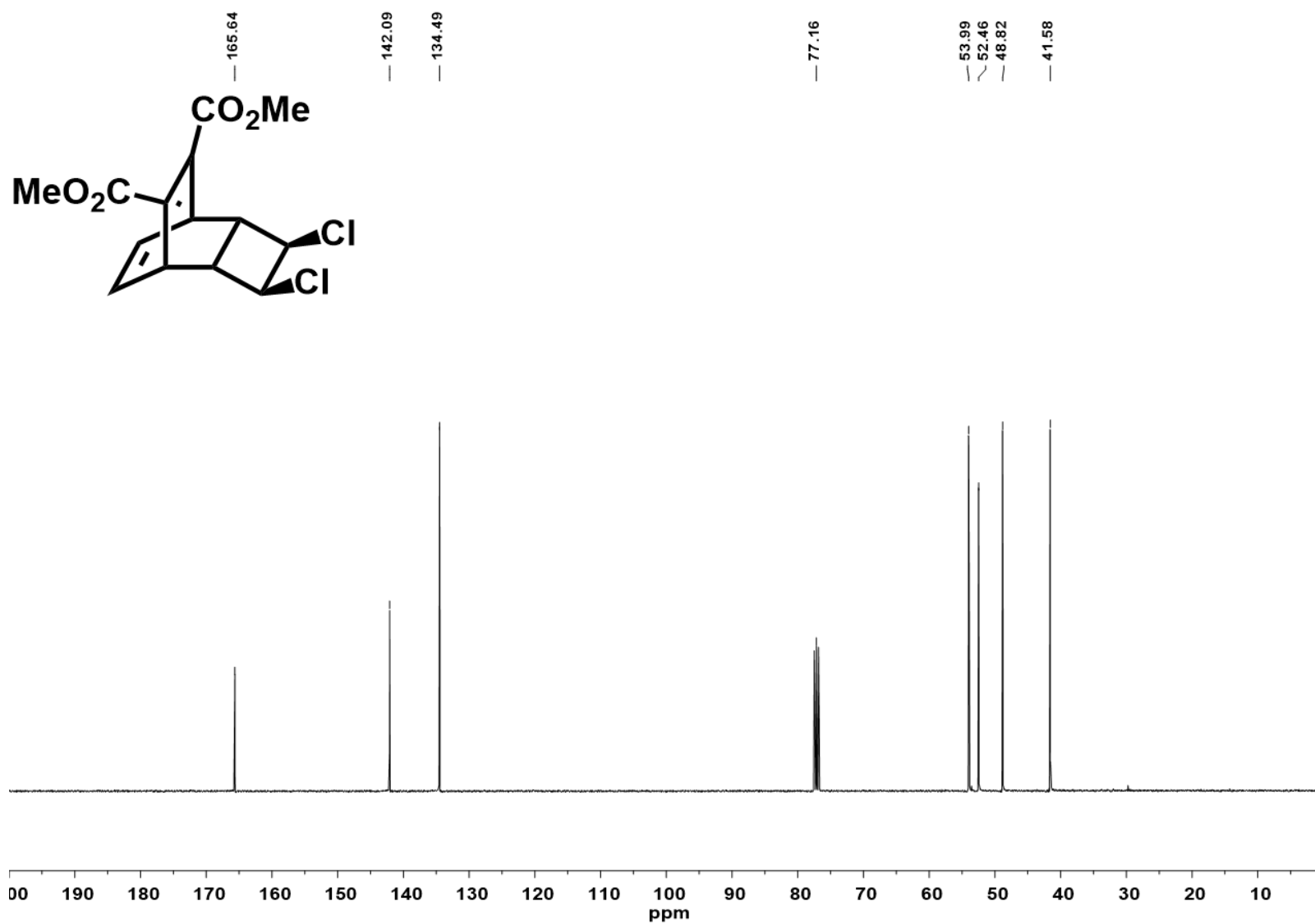


Figure S15. <sup>13</sup>C NMR spectrum recorded for *cis-4* at 25 °C in chloroform-*d*<sub>1</sub>.

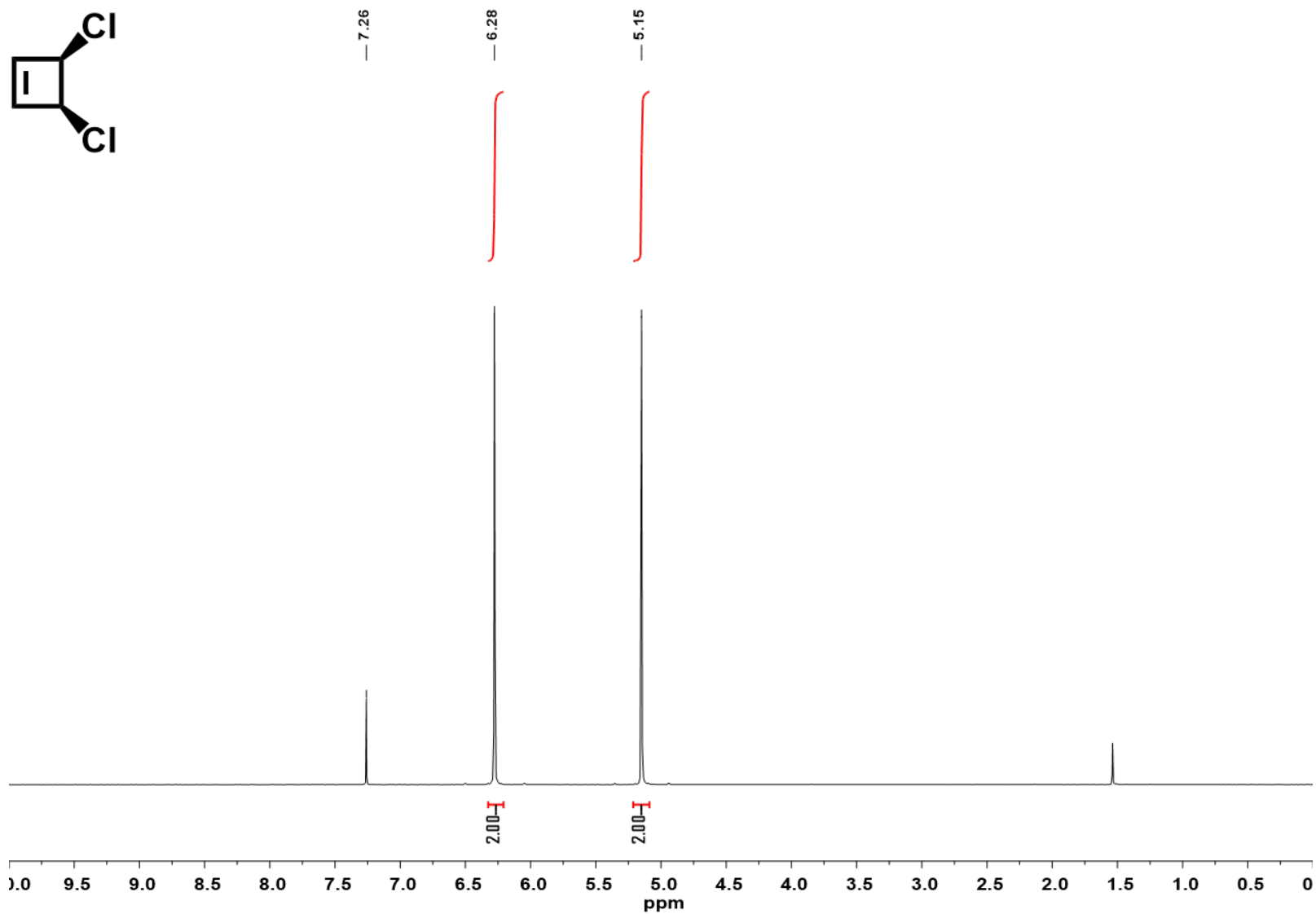
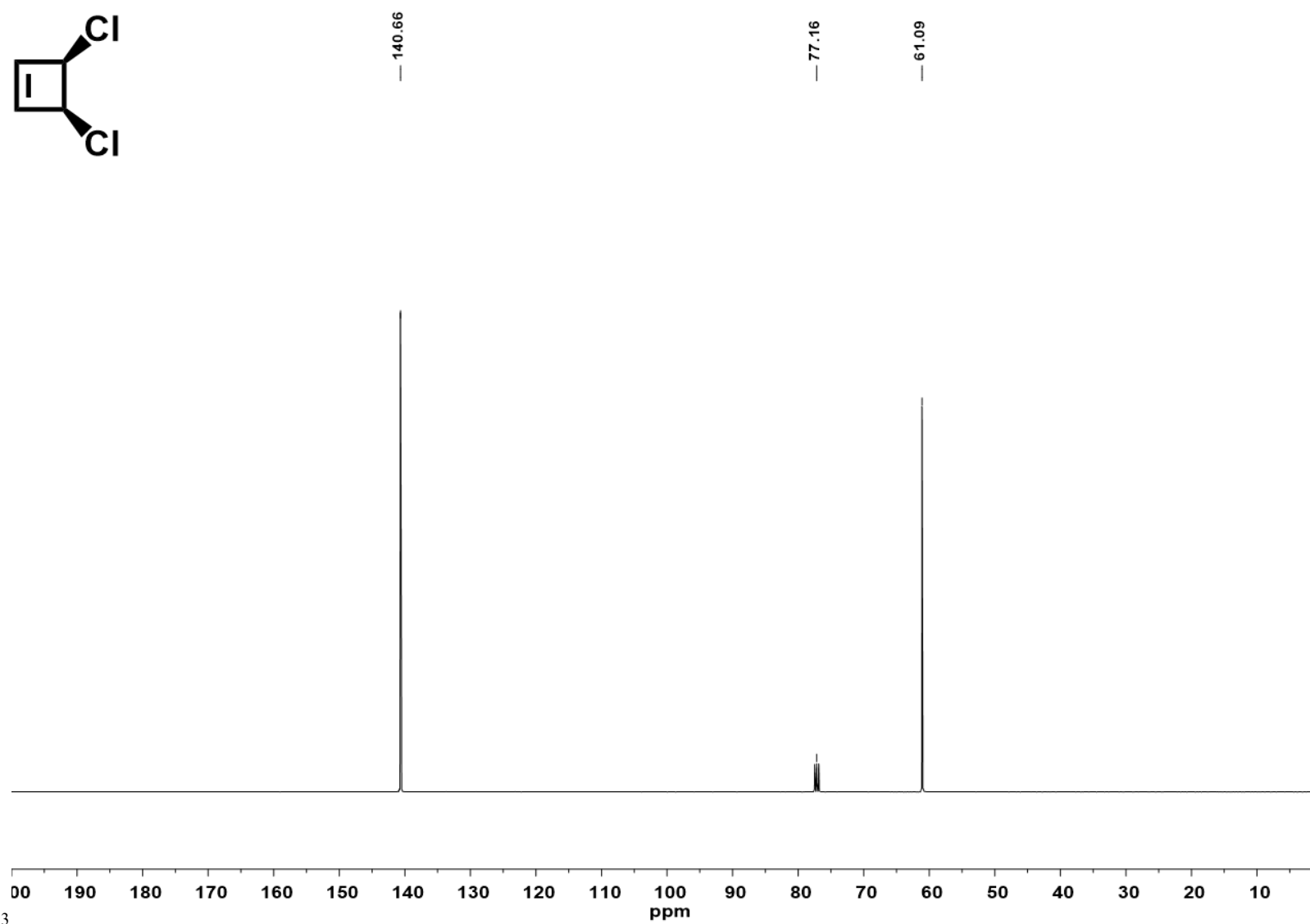
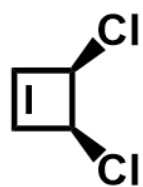


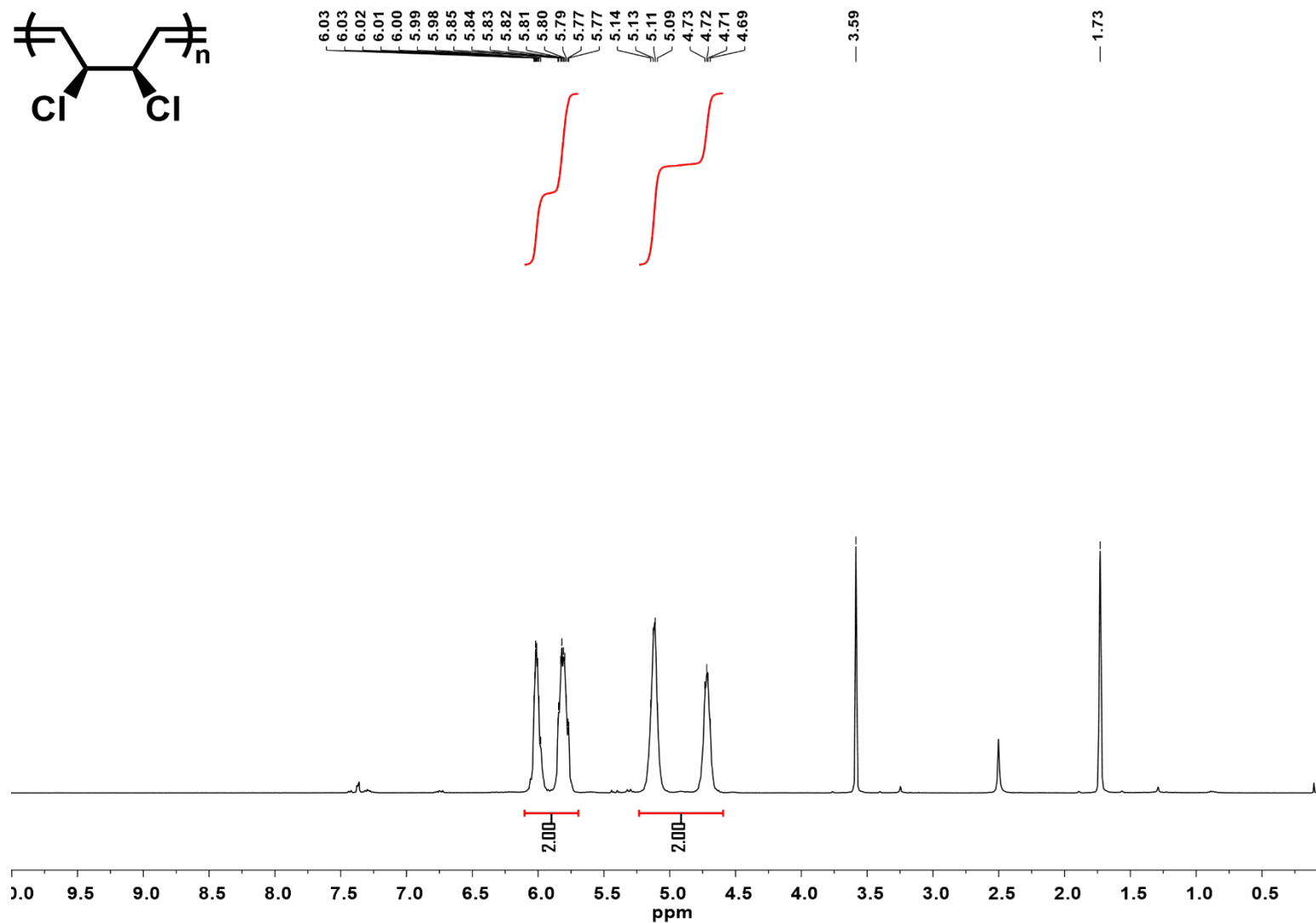
Figure S16.  $^1\text{H}$  NMR spectrum recorded for **1** at 25 °C in chloroform- $d_1$ .



3

**Figure S17.**  $^{13}\text{C}$  NMR spectrum recorded for **1** at 25 °C in chloroform- $d_1$ .

S22



**Figure S18.** <sup>1</sup>H NMR spectrum recorded for poly(1) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

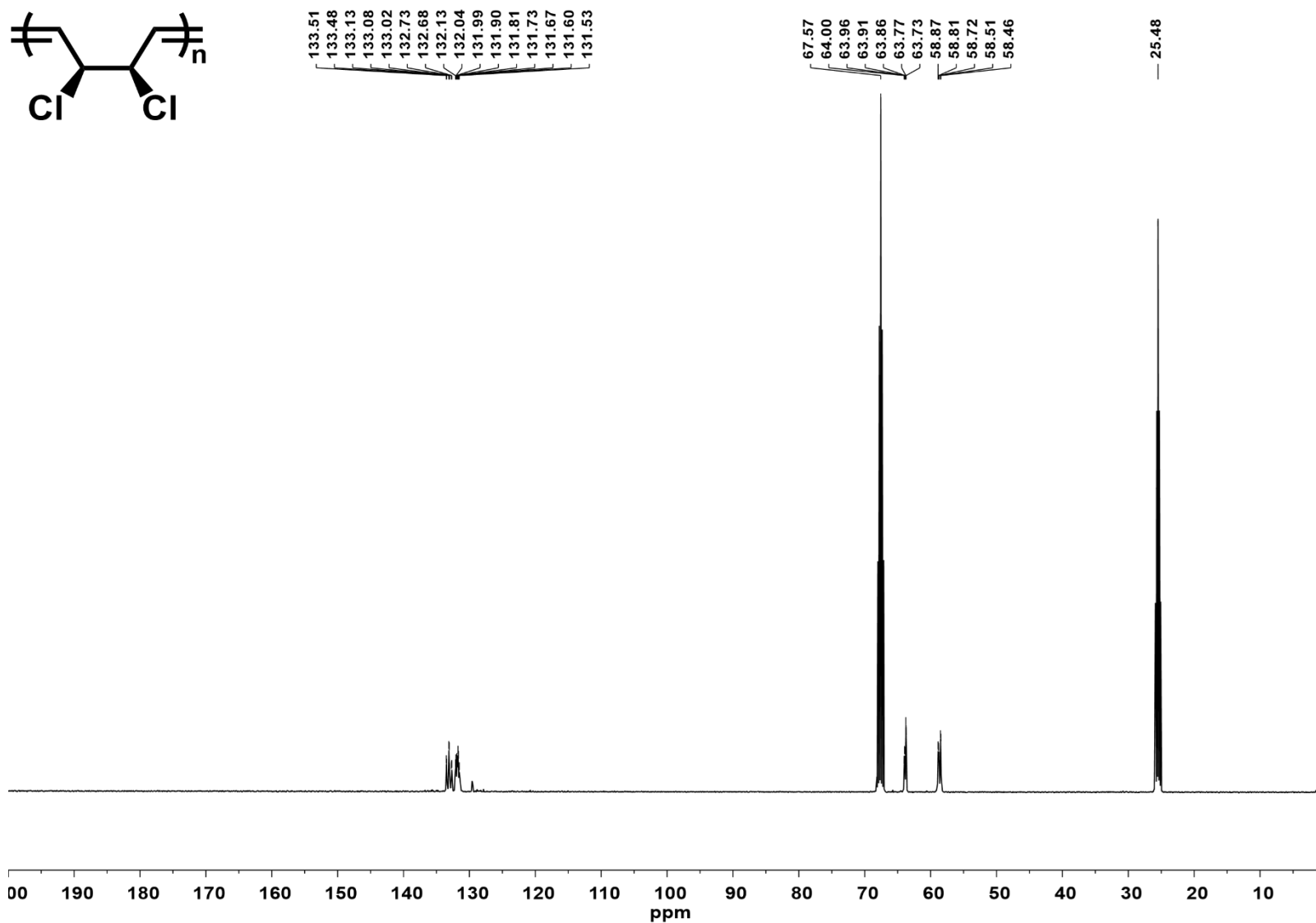


Figure S19. <sup>13</sup>C NMR spectrum recorded for poly(1) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.



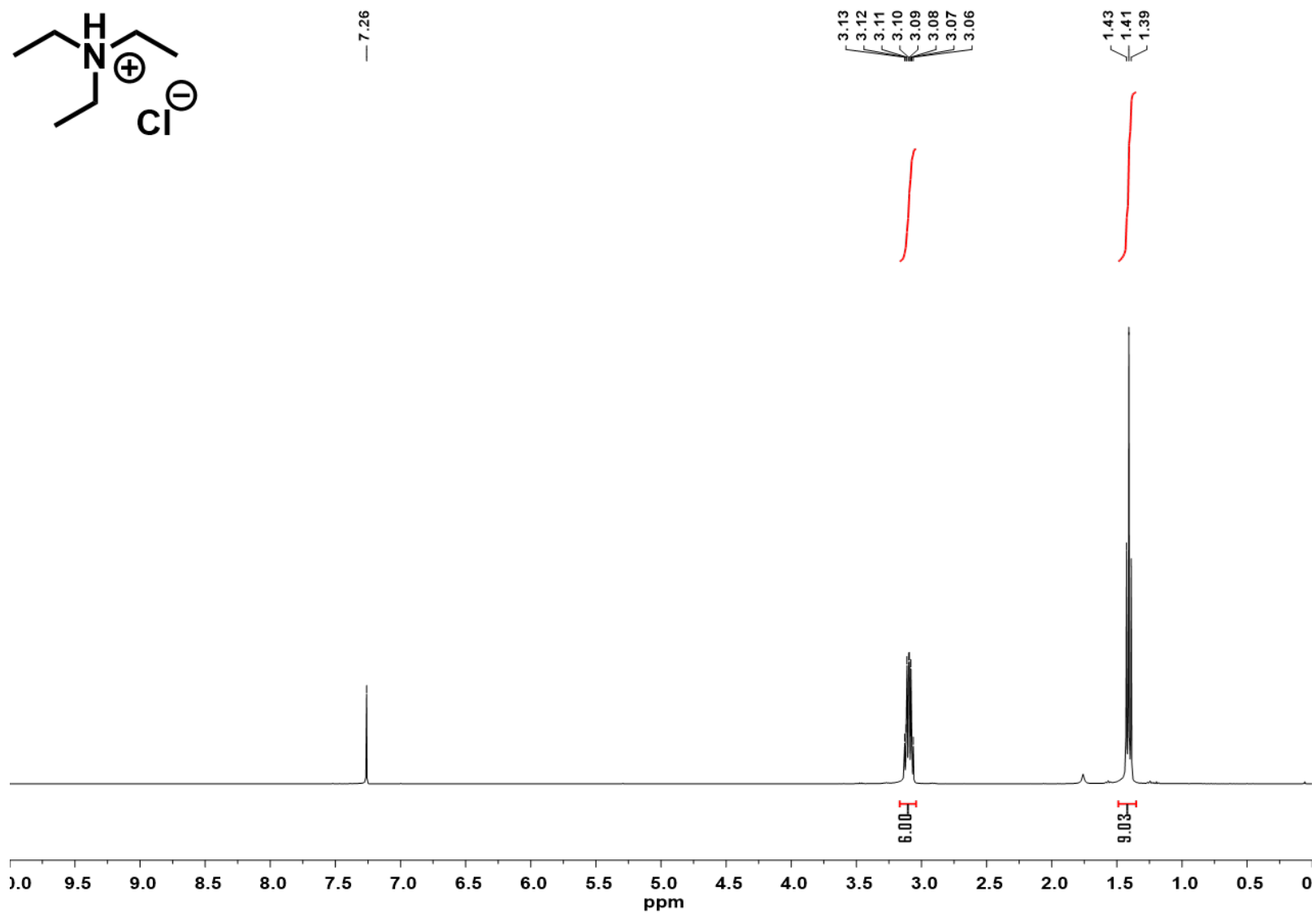


Figure S20.  $^1\text{H}$  NMR spectrum recorded for triethylammonium chloride at 25 °C in chloroform- $d_1$ .

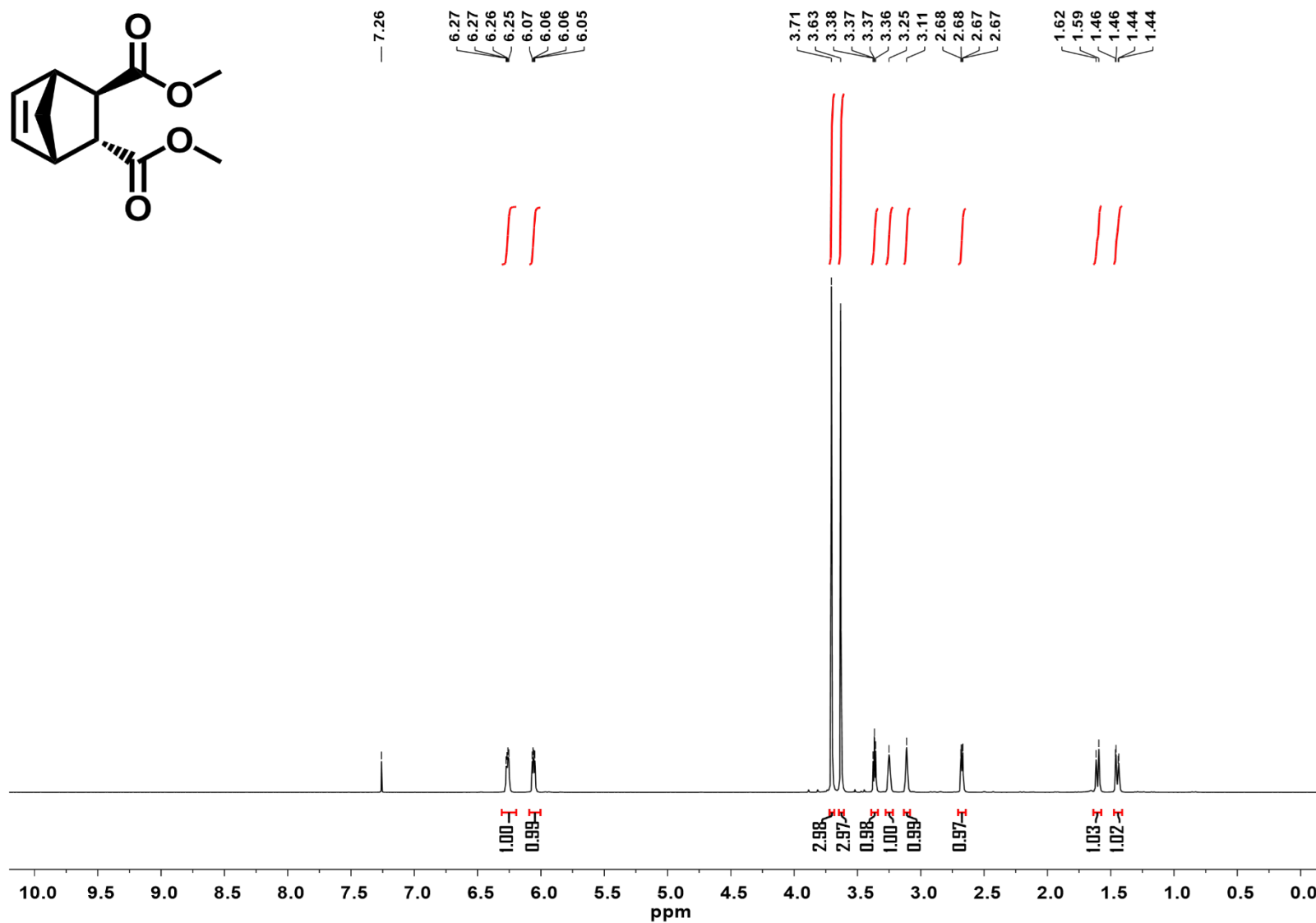


Figure S21. <sup>1</sup>H NMR spectrum recorded for **6** at 25 °C in chloroform-*d*<sub>1</sub>.

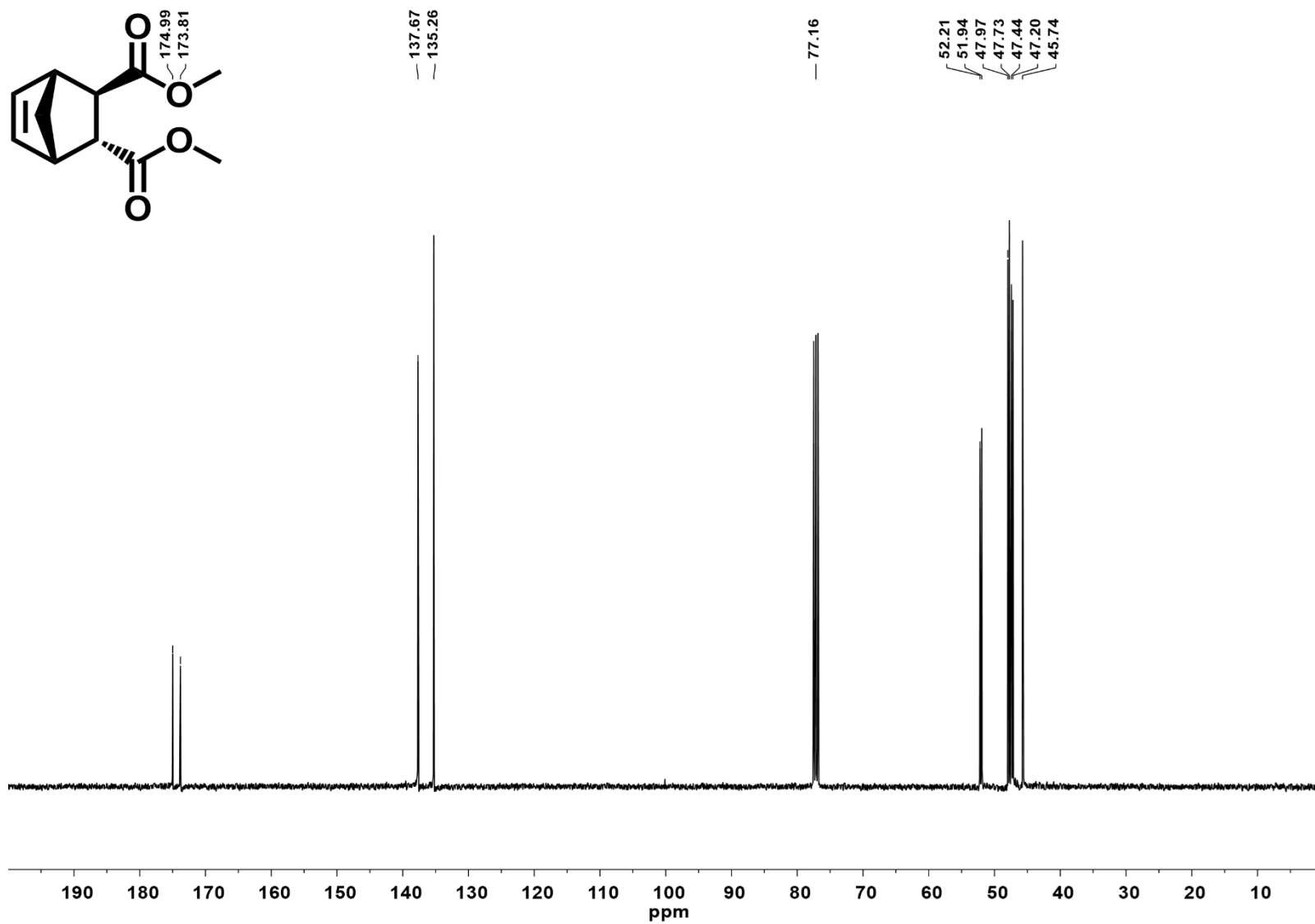


Figure S22.  $^{13}\text{C}$  NMR spectrum recorded for **6** at 25 °C in chloroform- $d_1$ .

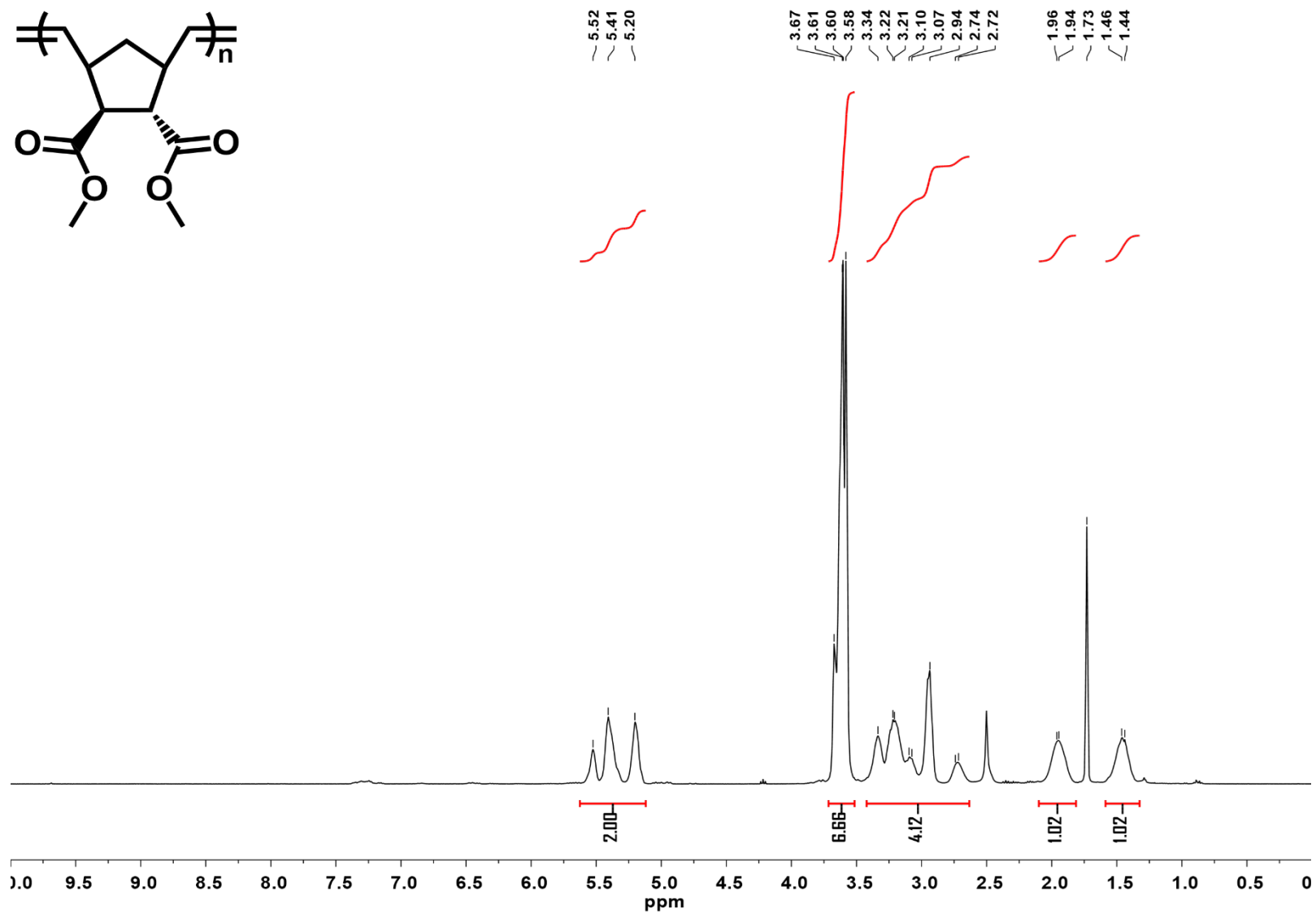


Figure S23. <sup>1</sup>H NMR spectrum recorded for poly(6) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

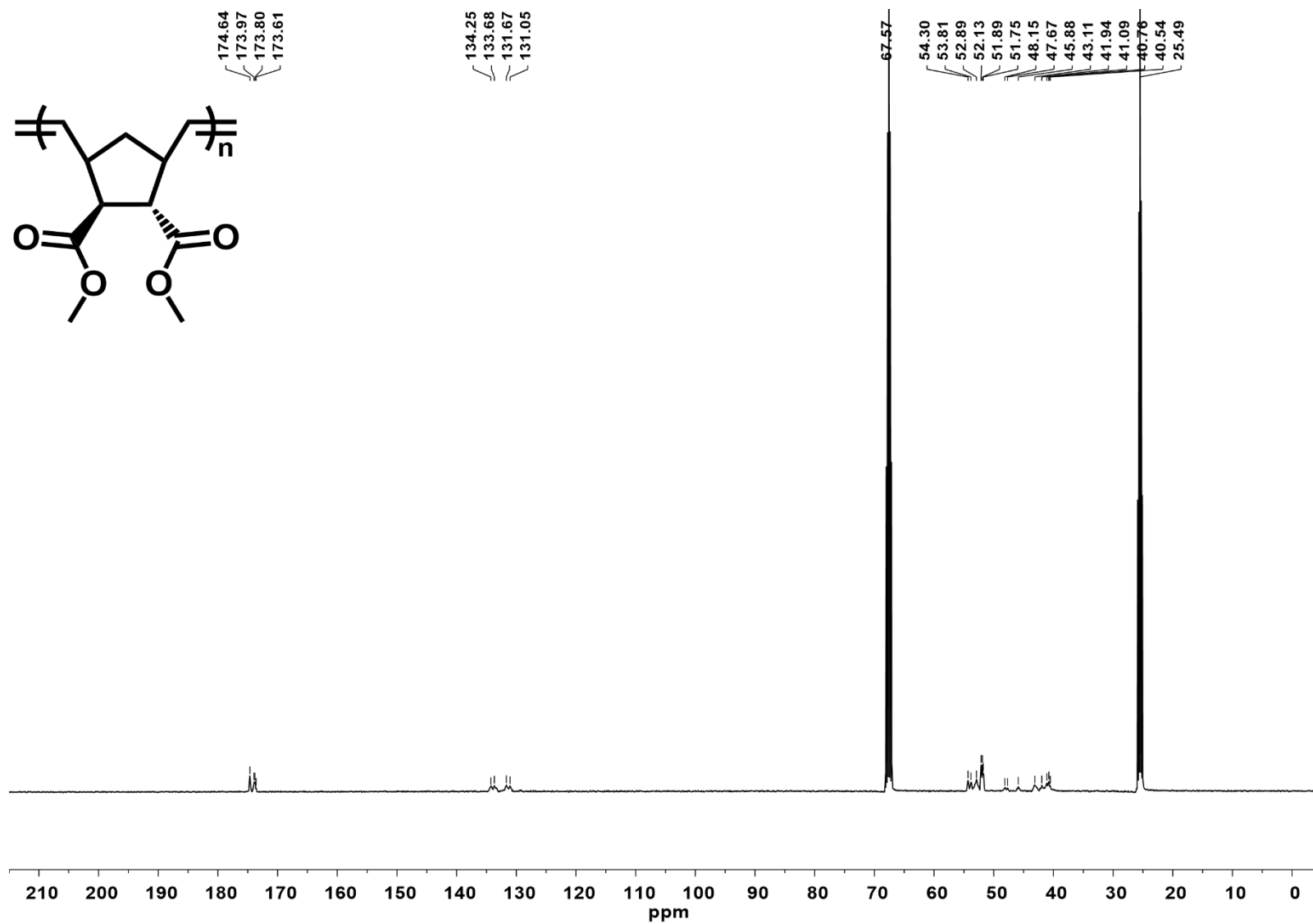


Figure S24. <sup>13</sup>C NMR spectrum recorded for poly(6) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

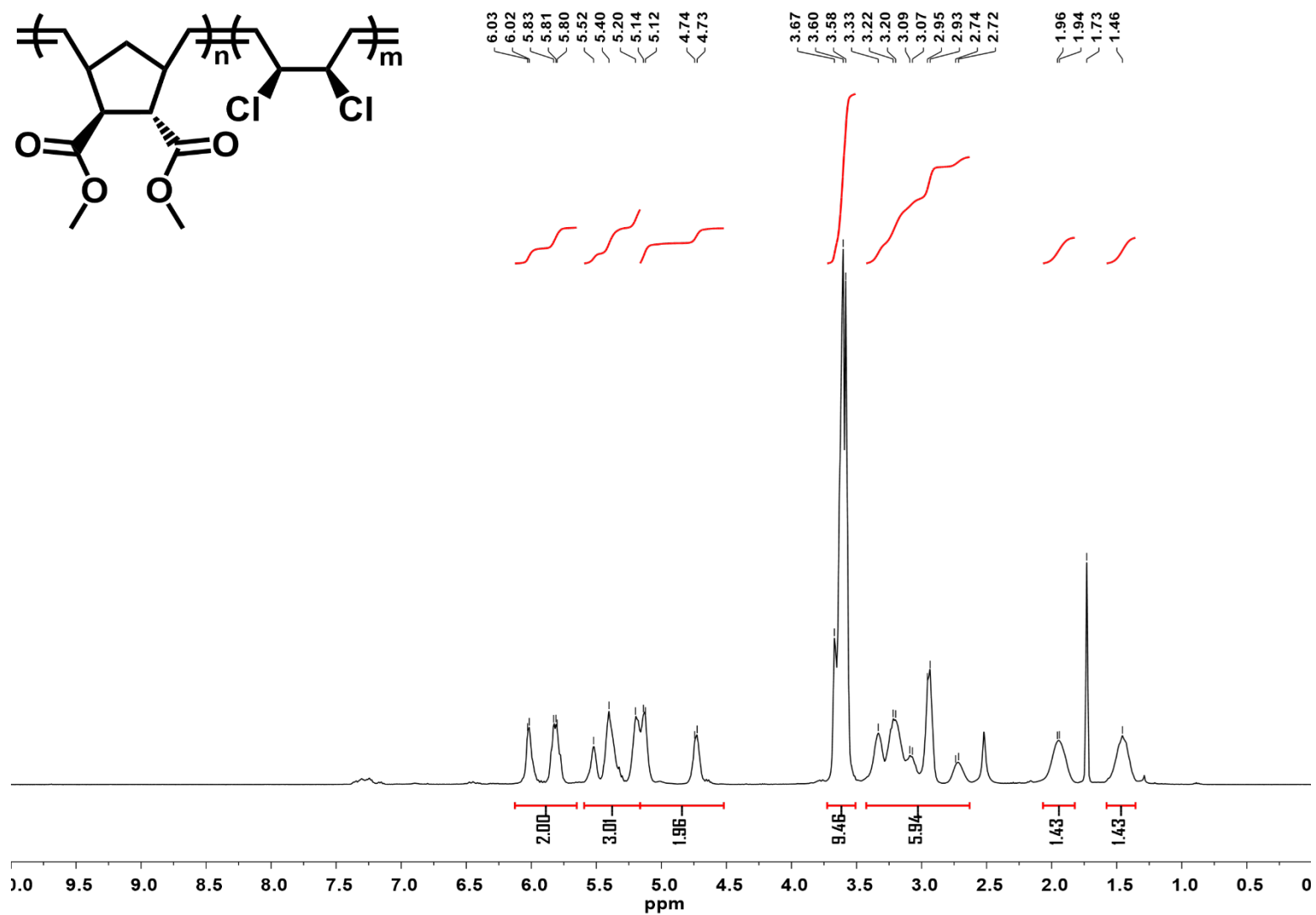


Figure S25. <sup>1</sup>H NMR spectrum recorded for poly(6)-*block*-poly(1) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

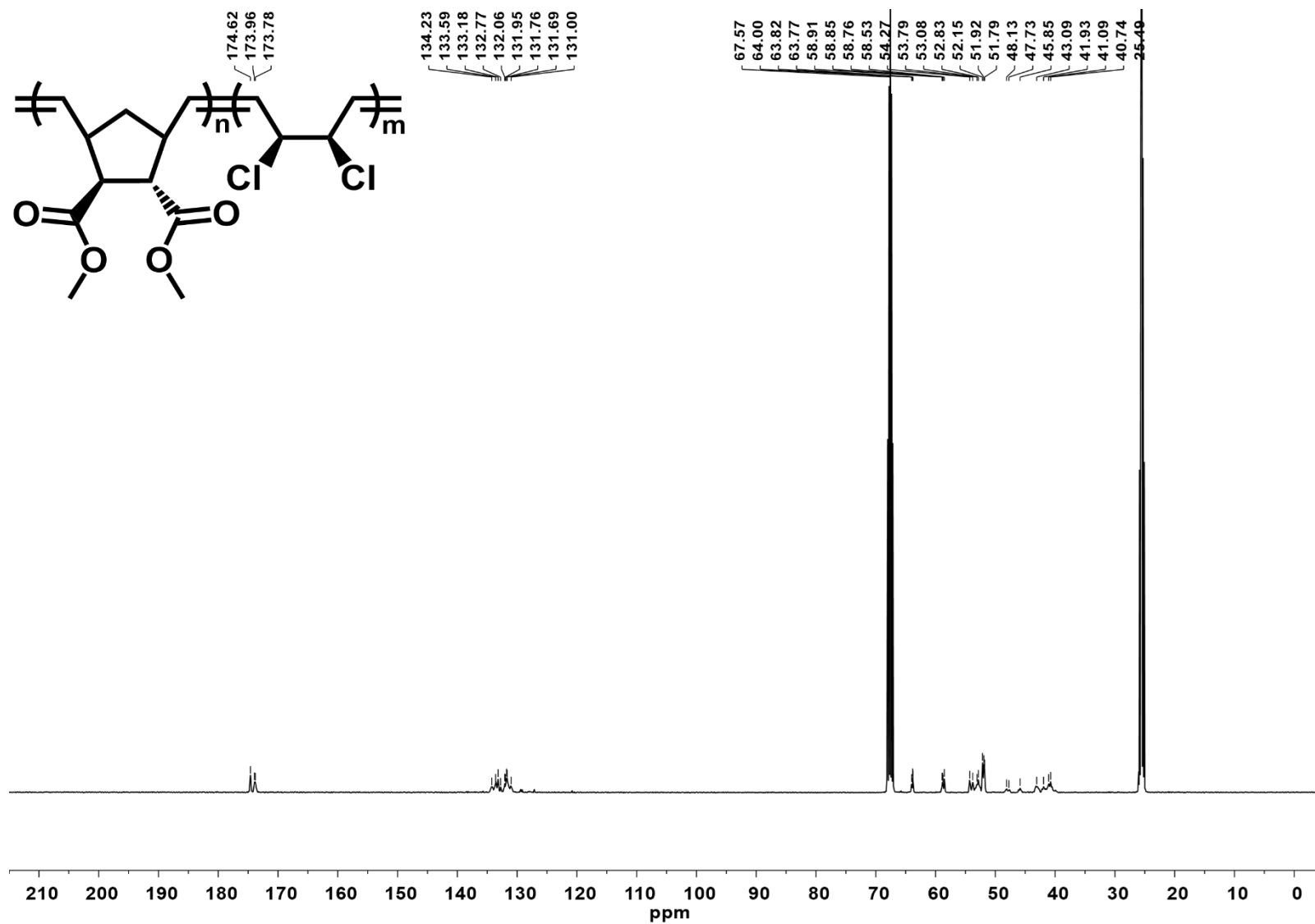


Figure S26. <sup>13</sup>C NMR spectrum recorded for poly(6)-*block*-poly(1) at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

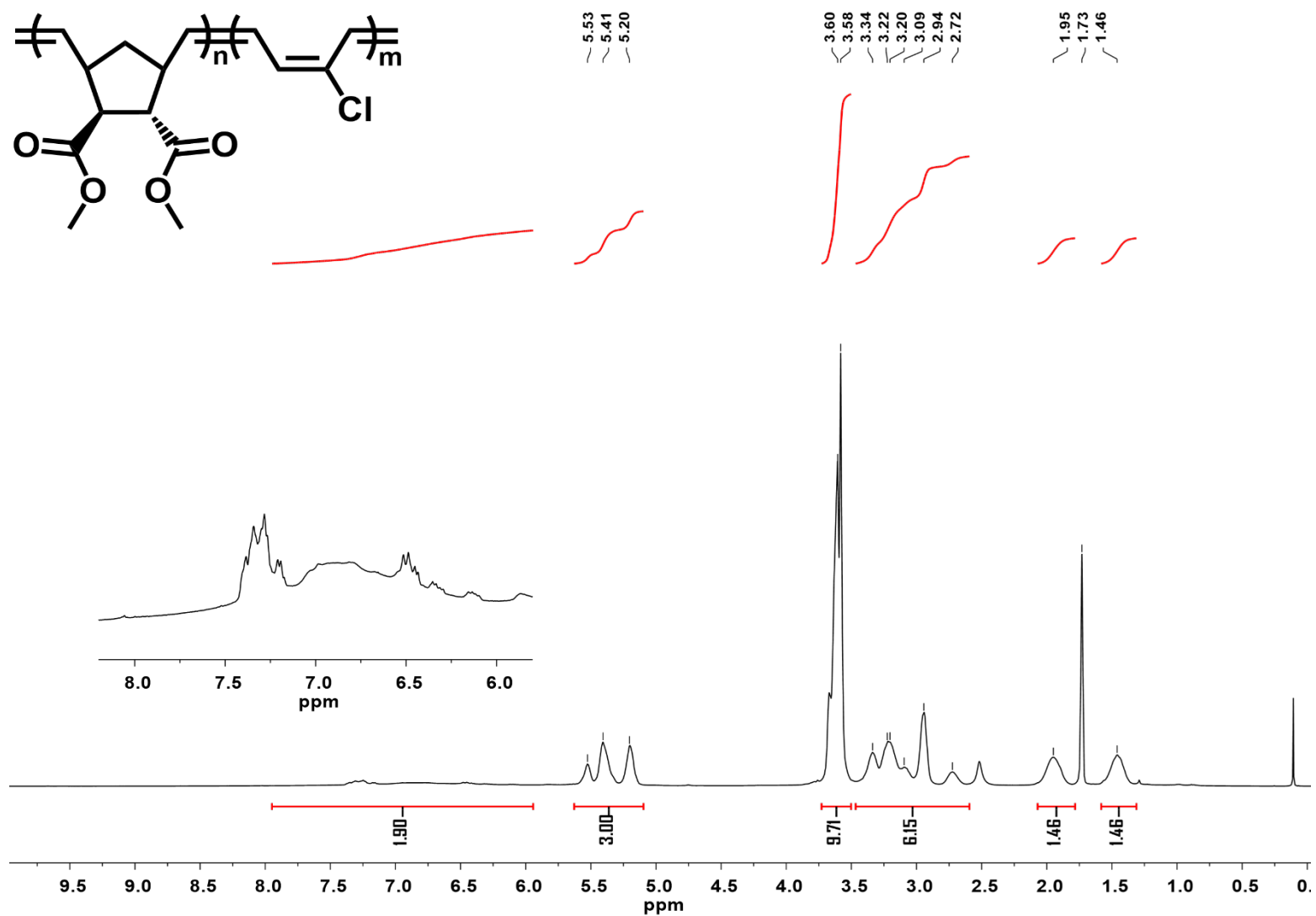


Figure S27.  $^1\text{H}$  NMR spectrum recorded for 7 at 25 °C in tetrahydrofuran- $d_8$ .



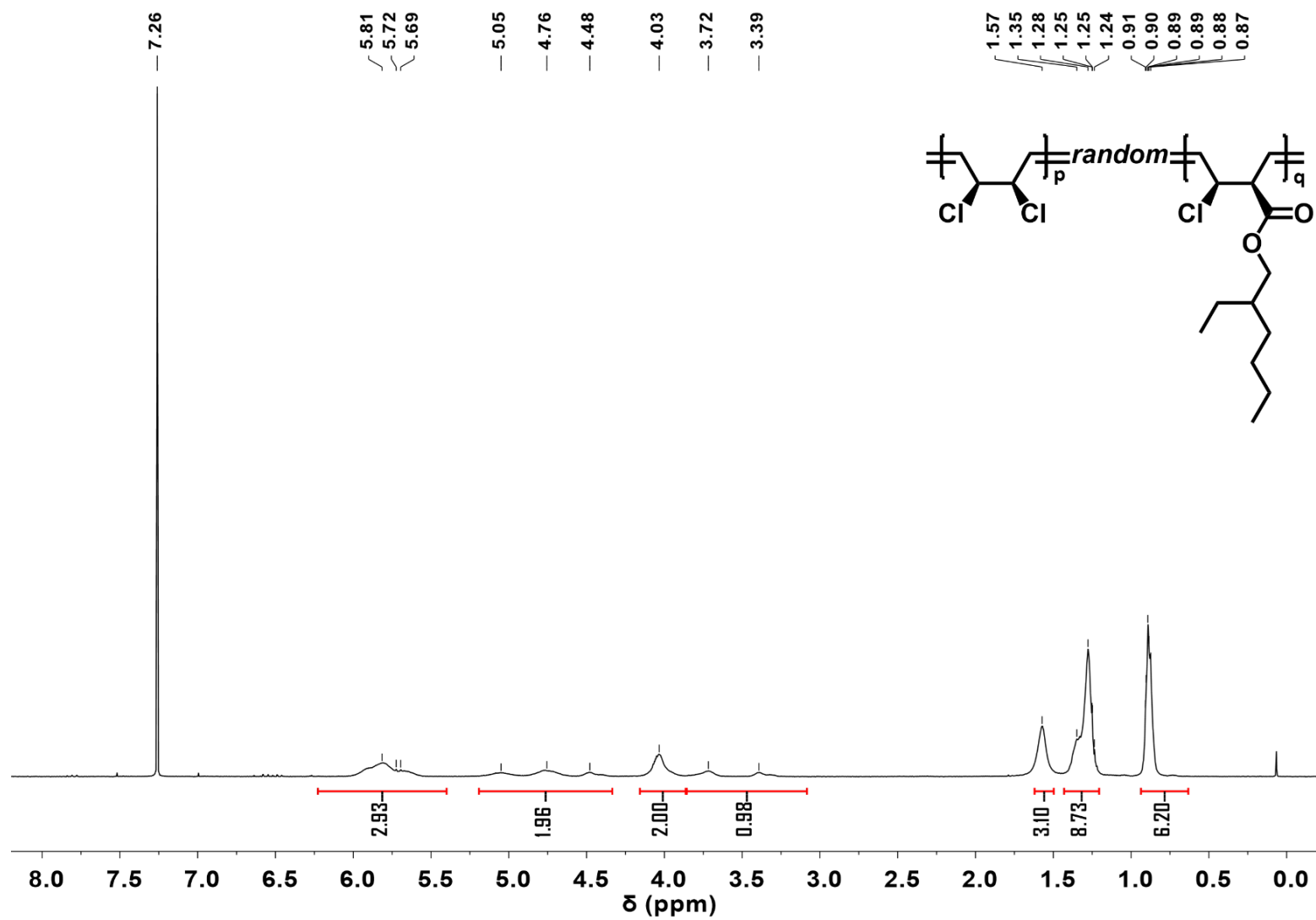


Figure S28.  $^1\text{H}$  NMR spectrum recorded for **9** at 25 °C in chloroform- $d_1$ .

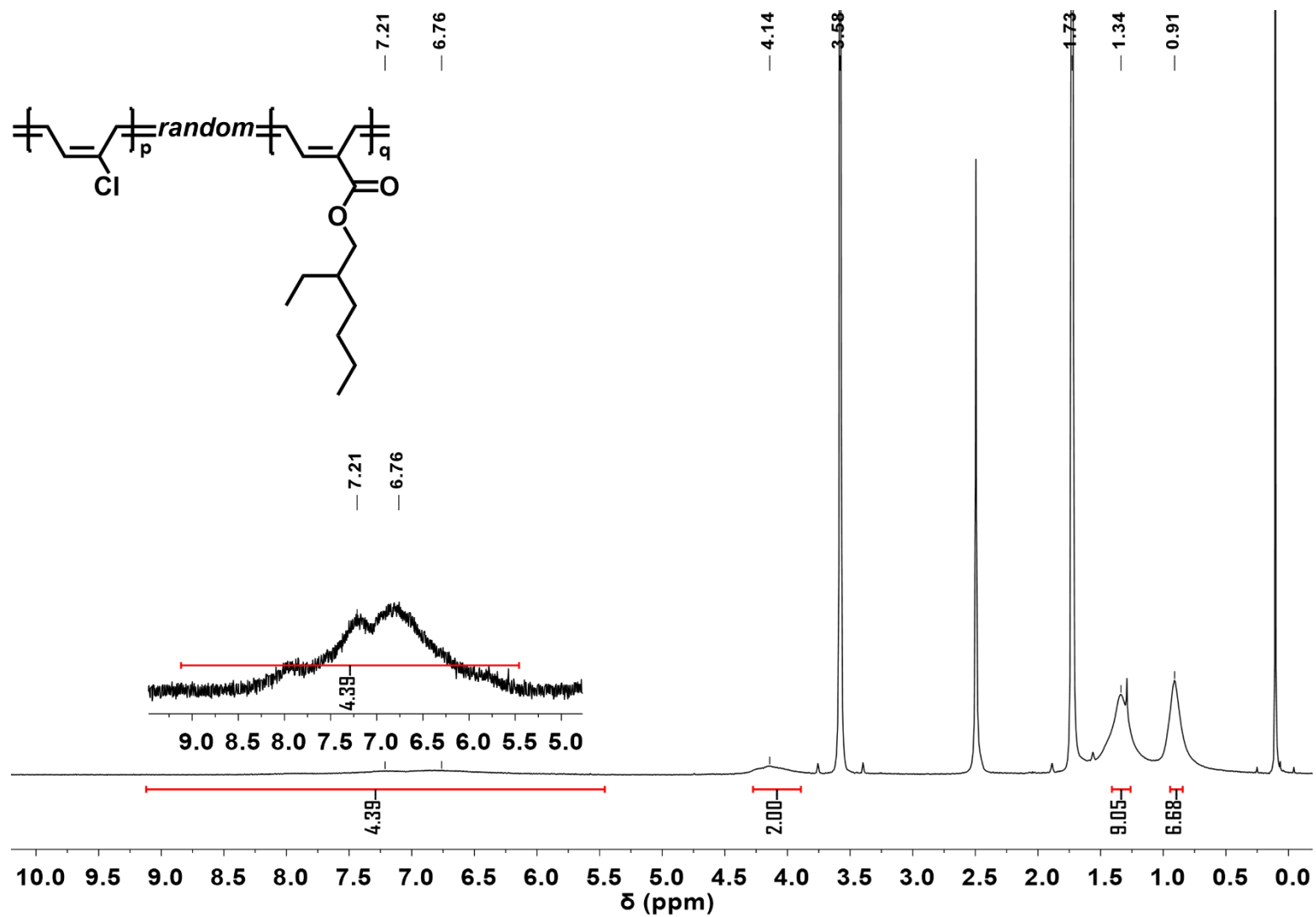


Figure S29. <sup>1</sup>H NMR spectrum recorded for **10** at 25 °C in tetrahydrofuran-*d*<sub>8</sub>.

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