

# Synthesis of isohexide diyne polymers and hydrogenation to their saturated polyethers

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## I. General Experimental Protocols

**Reagents:** *N,N,N',N'*-Tetramethylethylenediamine (Acros) and triethylamine (Fisher) were purified by vacuum distillation and stored over KOH pellets. Isosorbide was received as a gift chemical in excellent purity from Archer Daniels Midland Co. and was used without purification. Isomannide (98%) was purchased from Acros and used as received. Propargyl bromide was purchased as a 9.0–9.2 M solution in toluene from TCI, stabilized by 0.3% MgO and was filtered before use. Copper iodide was purchased from Sigma as a fine beige-colored powder and used without purification. Nickel (II) chloride hexahydrate (bright green) was purchased from Mallinckrodt and was ground into a fine powder with a mortar and pestle prior to use.

**NMR:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance II or Avance III 500 spectrometer ( $^1\text{H}$  recorded at 500 MHz,  $^{13}\text{C}$  at 125 MHz).  $^1\text{H}$  NMR chemicals shift using,  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  are referenced to TMS at 0.00 ppm and  $\text{CHD}_2\text{SOCD}_3$  at  $\delta$  2.50 ppm, respectively. Multiplets are reported as s (singlet), d (doublet), t (triplet), m (multiplet), and nfm (non-first-order multiplet).

**ATR-FTIR:** An ATR-FTIR instrument (Bruker Alpha Platinum), fitted with a diamond single-bounce crystal, was used to record FT infrared spectra. Measurements were typically recorded with sixteen scans and a four second acquisition time. Samples were deposited as thin films directly onto the diamond window; solids were then also compressed with a pressure anvil.

**MPLC** (medium pressure liquid chromatography) was performed at ca. 25–200 psi on hand-packed silica gel columns (25–35  $\mu\text{m}$ , 40 Å pore size) at a flow rate of ca. 9  $\text{mL min}^{-1}$ . The instrument comprised a Waters HPLC pump and a Waters R401 differential refractive index (RI) detector. The samples were introduced onto the column after as a solution in DCM, and various ratios of hexanes and ethyl acetate were used as the mobile phase. Flash chromatography was carried out on columns packed with a larger size of silica gel particles (40–63  $\mu\text{m}$ ).

**GC-MS:** Low-resolution mass spectra were obtained in electron ionization mode using an Agilent 5975 MSD at 70 eV. This was connected to an Agilent 6953 gas chromatograph outfitted with an Agilent HP-5 column (0.25  $\mu\text{m}$  film thickness, 15 m length  $\times$  0.32 mm ID).

**HRMS:** High-resolution mass spectra (HRMS) were recorded using ESI ionization on a Thermo Orbitrap Velos instrument. An external calibrant (Pierce<sup>TM</sup> LTQ) was used. Samples were directly injected into the ion source.

**SEC-MALS:** Polymer molecular weight ( $M_w$ ,  $M_n$ ) and dispersity ( $\mathcal{D}$ ) were determined by size exclusion chromatography (SEC) using an Agilent 1260 Infinity liquid chromatograph. Dimethylformamide (DMF) containing 0.05 M LiBr was used as the mobile phase. The flow rate was 1.0  $\text{mL min}^{-1}$  at 40 °C. Wyatt Optilab T-rEX refractive index and Wyatt Dawn Heleos II

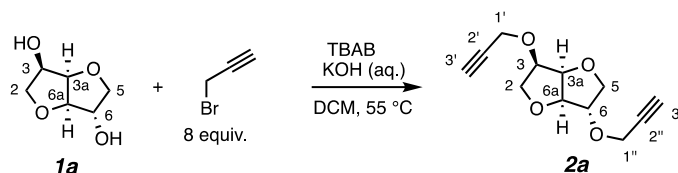
multiangle laser light scattering (MALS) detectors were used. The latter collected scattering from 18 detector angles ranging from 10° to 160° and used a 663.6 nm laser.

**TGA:** TGA (TA Instruments Q500) sample sizes ranged from 4–10 mg. The samples were heated under a mixture of N<sub>2</sub> and air at a heating rate of 10 °C min<sup>-1</sup> from r.t. to 550 °C.

**DSC:** was performed on a TA Instruments Q-1000. Samples were measured in hermetically sealed aluminum pans. Sample sizes ranged from 2–8 mg. Each diyne polymer sample, **poly(2a)**–**poly(2c)** and **poly(2a-RR)**, was equilibrated to –50 °C and ramped at 20 °C min<sup>-1</sup> to the upper temperature limit (150 or 200 °C). Glass transition temperatures were measured during the first and only heating ramp, due to aerobic oxidation at elevated temperatures. The hydrogenated diyne polymers **poly(2a-c)**–[H] were equilibrated to –65 °C and ramped at 10 °C min<sup>-1</sup> to the upper temperature limit (100 °C). Measurements were recorded on the second heating ramp.

## II. Preparation and Characterization of non-Polymeric compounds

### (3*R*,3*aR*,6*S*,6*aR*)-3,6-bis(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan (**2a**).



The following is a representative procedure for the production of the isohexide *bis*-propargyl ethers **2a–2c**. Isosorbide (3.00 g, 20.5 mmol) was dissolved in a potassium hydroxide solution (13.8 g, 247 mmol in 50 mL DI water) in a round-bottom flask equipped with a stir bar. A 9.0 M solution of propargyl bromide in toluene (18.3 mL, 164 mmol) was dissolved in 50 mL of dichloromethane, which was added to the flask, followed by addition of tetrabutylammonium bromide (660 mg, 2.1 mmol). This biphasic mixture was stirred under a reflux condenser at 55 °C for 24 h. The aqueous phase was extracted with 2x50 mL of dichloromethane, and the combined organic layers were washed with satd NH<sub>4</sub>Cl (2x) and brine (2x), dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (3:1 hexanes/EtOAc). The resulting product **2a** was obtained in 66% yield (3.01 g) as a yellow oil. The <sup>1</sup>H NMR data corresponded closely to those reported.<sup>1</sup>

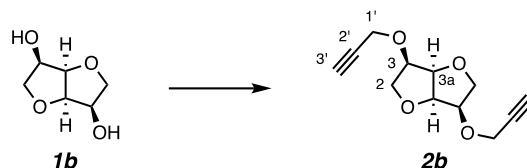
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.58 (dd, *J* = 4.6, 4.6 Hz, 1H, *H*3<sub>a</sub>), 4.48 (dd, *J* = 4.6, 0.9 Hz, 1H, *H*6<sub>a</sub>), 4.27 (dd, *J* = 15.8, 2.4 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.22 (d, *J* = 2.5 Hz, 2H, C1''*H<sub>2</sub>*), 4.18 (dd, *J* = 15.8, 2.4 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.14 (ddd, *J* = 7.2, 6.5, 4.7 Hz, 1H, *H*3), 4.07 (brd, *J* = 4.1 Hz, 1H, *H*6), 3.88 (ddd, *J* = 10.3, 1.2, 1.2 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.82 (dd, *J* = 8.8, 6.5 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.75 (dd, *J* = 10.3, 3.8 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.48 (t, *J* = 2.4 Hz, 1H, *H*3' or *H*3''), 3.47 (t, *J* = 2.4 Hz, 1H, *H*3' or *H*3''), and 3.45 (dd, *J* = 8.8, 7.2 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 4.71 (dd, *J* = 4.5, 4.5 Hz, 1H, *H*3<sub>a</sub>), 4.60 (dd, *J* = 4.3, 0.9 Hz, 1H, *H*6<sub>a</sub>), 4.37 (dd, *J* = 16.0, 2.4 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.31 (dd, *J* = 15.9, 2.4 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.30 (ddd, *J* = 7.2, 6.5, 4.7 Hz, 1H, *H*3), (dd, *J* = 16.0, 2.4 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.07 (brd, *J* = 4.1 Hz, 1H, *H*6), 3.88 (ddd, *J* = 10.3, 1.2, 1.2 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.82 (dd, *J* = 8.8, 6.5 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.75 (dd, *J* = 10.3, 3.8 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.67 (dd, *J* = 8.9, 7.7 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 2.49 (t, *J* = 2.4 Hz, 1H, *H*3' or *H*3''), and 2.48 (t, *J* = 2.4 Hz, 1H, *H*3' or *H*3'').

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 85.6 (C6<sub>a</sub>), 83.0 (C6), 80.6 (C2' or C2''), 80.5 (C2' or C2''), 80.2 (C3<sub>a</sub>), 78.9 (C3), 77.83 (C3' or C3''), 77.80 (C3' or C3''), 72.8 (C5), 69.9 (C2), 57.3 (C1'), and 56.5 (C1'').

**FT-IR** (thin film): 3281, 3274, 2941, 2875, 2116, 1732, 1243, 1062, and 634 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min-1/250 °C) *t*<sub>R</sub> = 7.93 min; MS [70 eV, *m/z* (rel int)]: 222 (1, M<sup>+</sup>), 183 (2, M<sup>+</sup> – CH<sub>2</sub>C≡CH), 82 (33, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), and 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**(3*R*,3*aR*,6*R*,6*aR*)-3,6-bis(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan (**2b**)**

Diyne **2b** was prepared by the same method used to make **2a**, starting with 3.0 g of isomannide (**1b**). The solid crude product was purified by recrystallization in 3:1 hexanes/EtOAc, filtered, washed with cold hexanes, and dried *in vacuo*, yielding **2b** as light-yellow needle-like crystals (2.55 g, 56%). Characterization data closely matched those previously reported.<sup>1</sup>

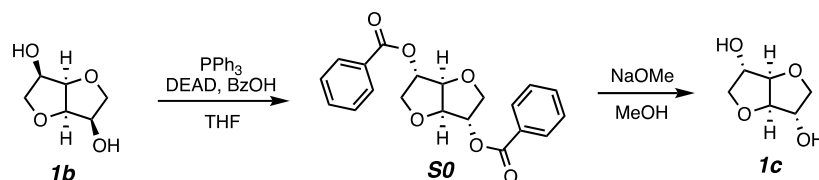
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.53 (nfom, including  $J_{3a/6a} = 4.6$  Hz, *H*3a), 4.26 (dd,  $J = 15.8, 2.4$  Hz, 2H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.16 (dd,  $J = 15.8, 2.4$  Hz, 2H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.13 (dddd,  $J = 8.4, 6.8, 3.6, 1.6$  Hz, 2H, *H*3), 3.91 (dd,  $J = 8.4, 6.8$  Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.47 (t,  $J = 2.4$  Hz, 2H, *H*3'), and 3.46 (dd,  $J = 8.4, 8.4$  Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 80.6, 80.2, 78.9, 77.9, 70.7, and 57.3.

**FT-IR** (thin film): 3232, 2114, 1441, 1327, 1095, 1022, 914, 844, 672 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C) *t<sub>R</sub>* = 7.93 min; MS [70 eV, *m/z* (rel int)]: 183 (2, –CH<sub>2</sub>C≡CH), 82 (39, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), and 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

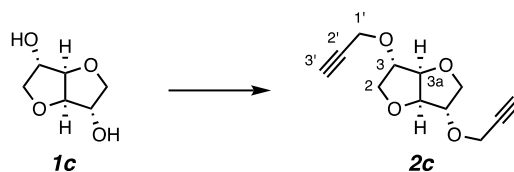
**mp**: 90–93 °C.

**(3*S*,3*aR*,6*S*,6*aR*)-Hexahydrofuro[3,2-*b*]furan-3,6-diol (**1c**)**

Isoidide (**1c**) was prepared according to a procedure adapted from Rajput and Chikkali.<sup>2</sup> Triphenylphosphine (3.59 g, 13.7 mmol), benzoic acid (1.67 g, 13.7 mmol), and isomannide (**1b**, 1.00 g, 6.9 mmol) were dissolved in 20 mL of tetrahydrofuran in an oven-dried round-bottom flask equipped with a stir bar and sealed with a septum. A solution of diethyl azodicarboxylate (2.15 mL, 13.9 mmol) in 20 mL of tetrahydrofuran was added to the round-bottom flask dropwise over a period of 4 hours via syringe pump. The mixture was allowed to stir for 16 hours, at which point additional portions of triphenylphosphine (0.36 g, 1.4 mmol), diethyl azodicarboxylate (0.22 mL, 1.4 mmol), and benzoic acid (0.17 g, 1.4 mmol) were added simultaneously to the flask, and the mixture was allowed to stir for an additional 3 hours.

The solution was concentrated *in vacuo*, and the resulting crude white solid was triturated in 3:1 hexanes/EtOAc, and the byproduct diethyl hydrazine-1,2-dicarboxylate (confirmed by GC-MS) was removed by filtration. The filtrate was concentrated and passed through plugs of silica and basic alumina, removing any excess benzoic acid, benzoic anhydride, and triphenylphosphine oxide. The crude filtrate contained the *exo*-dibenzoate **S0** and some excess triphenyl phosphine. This solution was concentrated *in vacuo*, yielding an off-white solid, which was used in the next sequence without further purification. A portion was subjected to MPLC (3:1 hexanes/EtOAc) to yield a more pure sample of **S0** whose  $^1\text{H}$  NMR data were fully consistent with those reported.<sup>2</sup>

The crude *exo*-dibenzoate **S0**, ca. 1.6 g, was suspended in 30 mL of methanol in a round bottom flask and stirred vigorously at 60 °C for 2 h to fully dissolve the diester. This solution was cooled slowly under vigorous stirring to ~30–40 °C. Sodium methoxide (710 mg, 3.0 equiv., 13 mmol) was added to the tube, which was sealed with a septum and allowed to stir for 3 hours at ambient temperature. The reaction was quenched with Dowex® 50W-X1 resin beads, which was filtered through Celite after stirring for 30 min. The methanolic solution was concentrated *in vacuo* and poured into 40 mL of DI water and extracted 3x with XX mL of dichloromethane (GC-MS analysis of the dichloromethane extract revealed that the residual triphenyl phosphine and methyl benzoate were no longer present). The water-methanol layer was concentrated *in vacuo* and then lyophilized to afford 612 mg isoidide **1c** in (61% yield over two steps).

**(3*S*,3*aR*,6*S*,6*aR*)-3,6-bis(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan (**2c**)**

The residue was purified by MPLC (3:1 hexanes/EtOAc) and concentrated *in vacuo*, yielding **2c** as a light-yellow solid in 55% yield (450 mg). Characterization data closely matched those previously reported.<sup>1</sup>

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.67 (br s, 2H, *H*3*a*), 4.24 (dd, *J* = 16.0, 2.4 Hz, 2H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.23 (dd, *J* = 16.1, 2.4 Hz, 2H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.07 (dd, *J* = 3.8, 1.8 Hz, 2H, *H*3), 3.80 (dd, *J* = 10.2, 1.6 Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.71 (dd, *J* = 10.2, 3.9 Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*), and 3.48 (t, *J* = 2.4 Hz, 2H, *H*3').

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 84.9, 82.5, 80.6, 77.9, 71.7, and 56.6.

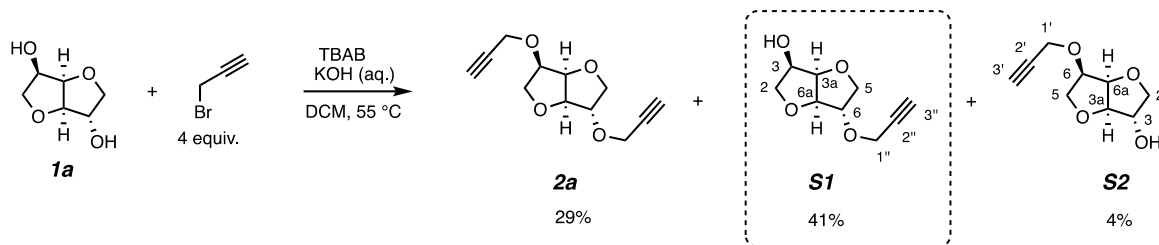
**FT-IR** (thin film): 3251, 2942, 2116, 1731 (w), 1453, 1081, 1022, 839, 780, 672, and 477 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C) *t<sub>R</sub>* = 7.82 min; MS [70 eV, *m/z* (rel int)]: 222 (3, M<sup>+</sup>), 183 (1, -CH<sub>2</sub>C≡CH), 124 (14, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub><sup>+</sup>), 82 (33, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), and 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**mp**: 51–53 °C.



**(3*R*,3*aR*,6*aR*,6*S*)-6-(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan-3-ol (S1) and (3*S*,3*aR*,6*aR*,6*R*)-6-(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan-3-ol (S2)**



Isosorbide (**1a**, 3.00 g, 20.5 mmol) was dissolved in a potassium hydroxide solution (13.8 g, 30.8 mmol) in 30 mL DI water in a round-bottom flask equipped with a stir bar. Tetrabutylammonium bromide (660 mg, 2.1 mmol) was added to the flask. This biphasic mixture was stirred under a reflux condenser at 55 °C. A 9.0 M solution of propargyl bromide in toluene (9.1 mL, 82 mmol) was added to the flask via syringe pump over 4 h, and the mixture was stirred for an additional 20 h under reflux. The aqueous phase was extracted with 2x50 mL of dichloromethane, and the combined organic layers were washed with satd NH<sub>4</sub>Cl (2x) and brine (2x), dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The oily residue was purified by MPLC (3:1 hexanes/EtOAc) to give, in order of elution, **2a** (1.32 g, 29%), **S1** (1.55 g, 41%), and **S2** (150 mg, 4%), whose <sup>1</sup>H NMR data was fully consistent with those reported.<sup>3</sup>

**Characterization Data for S1**

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.83 (br d, *J* = 6 Hz, 1H, C3OH), 4.44 (ddd, *J* = 4.6, 0.9, 0.9 Hz, 1H, H6a), 4.34 (dd, *J* = 4.7, 4.7 Hz, 1H, H3a), 4.22 (dd, *J* = 16.2, 2.4 Hz, 1H, C1''H<sub>a</sub>H<sub>b</sub>), 4.21 (dd, *J* = 16.2, 2.4 Hz, 1H, C1'H<sub>a</sub>H<sub>b</sub>), 4.10 (dddd, *J* = 7.7, 6.4, 6.4, 4.8 Hz, 1H, H3), 4.07 (dddd, *J* = 3.8, 1.5, 1.2, 0.6 Hz, 1H, H6), 3.87 (dddd, *J* = 10.2, 1.4, 0.9, 0.5, 0.5 Hz, 1H, C5H<sub>a</sub>H<sub>b</sub>), 3.77 (dd, *J* = 10.2, 3.9 Hz, 1H, C5H<sub>a</sub>H<sub>b</sub>), 3.72 (dd, *J* = 8.3, 6.5, 0.3 Hz, 1H, C2H<sub>a</sub>H<sub>b</sub>), 3.45 (t, *J* = 2.4 Hz, 1H, H3'), and 3.30 (ddd, *J* = 8.3, 7.7, 0.6 Hz, 1H, C2H<sub>a</sub>H<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 85.3, 83.4, 81.9, 80.6, 77.9, 72.7, 72.5, 71.5, and 56.5.

**FT-IR** (thin film): 3432 (v br), 3275, 2940, 2875, 2116, 1047, 829, and 648 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C *t*<sub>R</sub> = 6.59 min; MS [70 eV, *m/z* (rel int)]: 184 (10, M<sup>+</sup>), 124 (20, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub><sup>+</sup>), 82 (42, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**mp**: 32–34 °C.

**Characterization Data for S2**

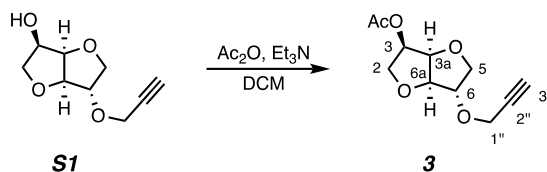
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 5.15 (d, *J* = 3.7 Hz, 1H, C3OH), 4.58 (dd, *J* = 4.3, 4.4 Hz, 1H, H6a), 4.28 (brd, *J* = 4.8 Hz, 1H, H3a), 4.26 (dd, *J* = 15.8, 2.4 Hz, 1H, C1'H<sub>a</sub>H<sub>b</sub>), 4.18 (dd, *J* = 15.8, 2.4 Hz, 1H, C1'H<sub>a</sub>H<sub>b</sub>), 4.14 (ddd, *J* = 7.6, 6.7, 4.6 Hz, 1H, H6), 4.04 (nfom, 1H, H3), 3.81 (dd, *J* = 8.6, 6.7 Hz, 1H, C5H<sub>a</sub>H<sub>b</sub>), 3.73 (dd, *J* = 9.5, 3.4 Hz, 1H, C2H<sub>a</sub>H<sub>b</sub>), 3.70 (brd, *J* = 9.3 Hz, 1H, C2H<sub>a</sub>H<sub>b</sub>), 3.45 (t, *J* = 2.4 Hz, 1H, H3'), and 3.39 (dd, *J* = 8.7, 7.6 Hz, 1H, C5H<sub>a</sub>H<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 88.6, 80.7, 79.9, 79.2, 77.8, 75.9, 75.8, 69.6, and 57.2.

**FT-IR** (thin film): 3409 (v br), 3268, 2942, 2875, 2116, 1447, 1365, 1094, 1022, 914, 844, and 672 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C *t*<sub>R</sub> = 7.02 min; MS [70 eV, *m/z* (rel int)]: 142 (1, C<sub>7</sub>H<sub>10</sub>O<sub>3</sub><sup>+</sup>), 82 (24, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), and 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**HRMS** (ESI) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>12</sub>NaO<sub>4</sub><sup>+</sup> 207.0628; Found 207.0620.

**(3*R*,3*aR*,6*S*,6*aR*)-6-(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan-3-yl acetate (**3**)**

The *exo*-propargyl ether **S1** (150 mg, 0.82 mmol) was dissolved in 5 mL of dichloromethane in a culture tube equipped with a stir bar. Acetic anhydride (205  $\mu$ L, 3.3 mmol) and triethylamine (303  $\mu$ L, 3.3 mmol) were added sequentially via a Wiretrol<sup>TM</sup>. The tube was resealed and allowed to stir at ambient temperature overnight. The reaction mixture was concentrated *in vacuo* and filtered through plugs of silica and basic alumina (1:1 hexanes/EtOAc). The filtrate was concentrated *in vacuo* and acetate **3** was recovered as a pale-yellow oil (180 mg, 98%).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  5.14 (ddd,  $J$  = 6.0, 6.0, 5.2 Hz, 1H,  $H_3$ ), 4.78 (dd,  $J$  = 5.2, 4.6, Hz, 1H,  $H_{3a}$ ), 4.53 (ddd,  $J$  = 4.6, 1.0, 1.0 Hz, 1H,  $H_{6a}$ ), 4.24 (dddd,  $J$  = 3.9, 1.6, 1.0, 0.6 Hz, 1H,  $H_6$ ), 4.22 (dd,  $J$  = 16.1, 2.4 Hz, 1H,  $C1'H_aH_b$ ), 4.18 (dd,  $J$  = 16.1, 2.4 Hz, 1H,  $C1'H_aH_b$ ), 4.02 (ddd,  $J$  = 10.3, 1.4, 0.9 Hz, 1H,  $C5H_aH_b$ ), 3.95 (dd,  $J$  = 9.5, 6.1 Hz, 1H,  $C2H_aH_b$ ), 3.92 (dd,  $J$  = 10.3, 3.8 Hz, 1H,  $C5H_aH_b$ ), 3.75 (ddd,  $J$  = 9.5, 5.9, 0.6 Hz, 1H,  $C2H_aH_b$ ), 2.46 (t,  $J$  = 2.4 Hz, 1H,  $H_{3'}$ ), and 2.12 (s, 3H,  $C3COOCH_3$ ).

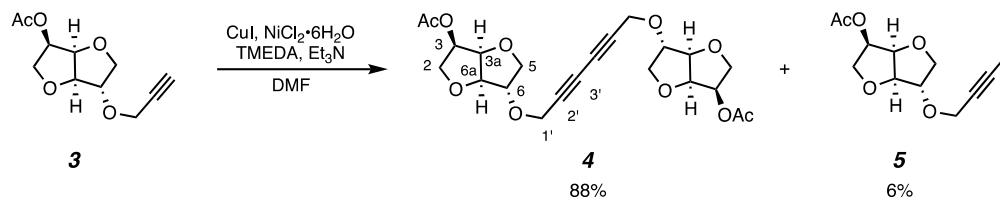
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  170.4, 85.9, 82.8, 80.6, 79.1, 75.1, 74.0, 73.0, 69.9, 56.8, and 20.7.

**FT-IR** (thin film): 3266, 2933, 2873, 1736, 1368, 1232, 1091, 1055, and 645 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C  $t_R$  = 7.76 min; MS [70 eV,  $m/z$  (rel int)]: 226 (1,  $M^+$ ), 166 (11  $C_9H_{10}O_3^+$ ), 82 (76,  $C_5H_6O_2^+$ ), and 69 (100,  $C_4H_5O^+$ , protonated furan).

**HRMS** (ESI)  $m/z$ : [ $M + H$ ]<sup>+</sup> Calcd for  $C_{11}H_{15}O_5^+$  227.0919; Found 227.0907.

**(3*R*,3*aR*,3'*R*,3*a'R*,6*S*,6*aR*,6'*S*,6*a'R*)-(Hexa-2,4-diyne-1,6-diylbis(oxy))bis(hexahydrofuro[3,2-*b*]furan-6,3-diyl) Diacetate (**4**)**



Cuprous iodide (4.2 mg, 0.02 mmol) was suspended in 2 mL of dimethylformamide in a 6-dram vial equipped with a micro stir bar. *N,N,N',N'*-Tetramethylethylenediamine (0.17 mmol, 27  $\mu$ L) was added to the vial under stirring, forming a deep blue homogenous solution, followed by addition of nickel (II) chloride hexahydrate (5.3 mg, 0.02 mmol), turning the solution to a deep green. Triethylamine (0.19 mL, 1.32 mmol) was added dropwise via syringe, and the vial was sealed with a rubber septum and allowed to stir for one hour. A solution of **3** (100 mg, 0.45 mmol) in 0.5 mL of DMF was injected into the vial, which was sealed once again with a septum. The headspace was purged with an oxygen balloon, and the reaction mixture was allowed to stir under oxygen at room temperature for 72 h. The reaction mixture was poured into 10 mL of satd ammonium bicarbonate and extracted 3x with EtOAc. The combined organic layers were washed with DI water (3x) and brine (2x), dried ( $\text{MgSO}_4$ ), and concentrated *in vacuo*. The residue was purified by MPLC (1:1 hexanes/EtOAc) to yield, in order of elution, the alkynyl iodide **5** (5 mg, 6%), containing a similar amount of the coeluting alkyne **3**, and the diyne **4** (87 mg, 88%) as a sticky oil.

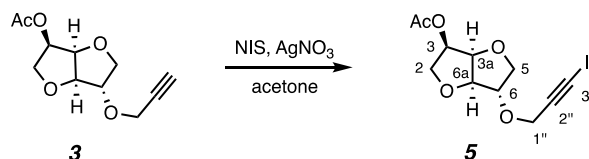
**Characterization data for **4****

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.13 (ddd,  $J = 6.0, 5.9, 5.3$  Hz, 2H,  $H_3$ ), 4.77 (dd,  $J = 5.3, 4.6$  Hz, 2H,  $H_{3a}$ ), 4.50 (ddd,  $J = 4.6, 1.0, 1.0$  Hz, 2H,  $H_{6a}$ ), 4.28 (br d,  $J = 16.8$  Hz, 2H,  $\text{C1}'H_aH_b$ ), 4.27 (br d,  $J = 16.9$  Hz, 2H,  $\text{C1}'H_aH_b$ ), 4.20 (dddd,  $J = 3.9, 1.6, 1.0, 0.6$  Hz, 2H,  $H_6$ ), 4.00 (ddd,  $J = 10.3, 1.5, 0.9$  Hz, 2H,  $\text{C5}H_aH_b$ ), 3.95 (dd,  $J = 9.6, 6.1$  Hz, 2H,  $\text{C2}H_aH_b$ ), 3.91 (dd,  $J = 10.3, 3.9$  Hz, 2H,  $\text{C5}H_aH_b$ ), 3.75 (ddd,  $J = 9.6, 5.8, 0.6$  Hz, 2H,  $\text{C2}H_aH_b$ ), and 2.11 (s, 6H,  $\text{C3COOCH}_3$ ).

**$^{13}\text{C}$  NMR** (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  170.4, 85.8, 83.1, 80.6, 75.0, 74.0, 72.9, 70.7, 70.0, 57.2, and 20.7.

**FT-IR** (thin film): 2932, 2874, 1738, 1367, 1232, 1091, 1055, and 644  $\text{cm}^{-1}$ .

**HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{27}\text{O}_{10}^+$  451.1599; Found 451.1586.

**(3*R*,3*aR*,6*S*,6*aR*)-6-((3-Iodoprop-2-yn-1-yl)oxy)hexahydrofuro[3,2-*b*]furan-3-yl Acetate (**5**)**

*endo*-Acetate **3** (25 mg, 0.11 mmol) was dissolved in 2 mL of acetone in a threaded culture tube fitted with a stir bar. *N*-Iodosuccinimide (30 mg, 1.3 mmol) and silver nitrate (1.9 mg, 0.1 mmol) were added to the culture tube, which was sealed and allowed to stir for 15 h at ambient temperature. The reaction mixture was poured into DI water and extracted 3x with dichloromethane. The combined extracts were dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. The residue was filtered through a short plug of silica (1:1 hexanes/EtOAc) and the filtrate was concentrated *in vacuo* to afford iodoalkyne **5** (31 mg, 81% recovered).

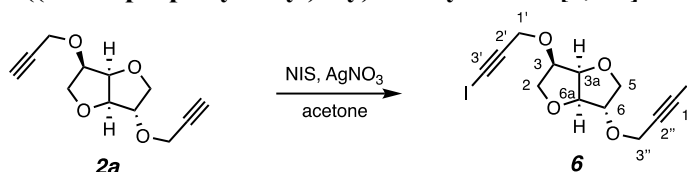
**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.12 (ddd,  $J = 6.0, 5.9, 5.2$  Hz, 1H,  $H_3$ ), 4.76 (dd,  $J = 5.2, 4.6, 0.6$  Hz, 1H,  $H_{3a}$ ), 4.48 (ddd,  $J = 4.6, 1.0, 1.0$  Hz, 1H,  $H_{6a}$ ), 4.35 (d,  $J = 16.0$  Hz, 1H,  $\text{C1}'H_aH_b$ ), 4.34 (d,  $J = 16.0$  Hz, 1H,  $\text{C1}'H_aH_b$ ), 4.21 (dddd,  $J = 3.9, 1.6, 1.0, 0.6$  Hz, 1H,  $H_6$ ), 4.00 (ddd,  $J = 10.3, 1.6, 1.0$  Hz, 1H,  $\text{C5}H_aH_b$ ), 3.94 (dd,  $J = 9.6, 6.1$  Hz, 1H,  $\text{C2}H_aH_b$ ), 3.90 (dd,  $J = 10.3, 3.9$  Hz, 1H,  $\text{C5}H_aH_b$ ), 3.75 (ddd,  $J = 9.5, 5.9, 0.6$  Hz, 1H,  $\text{C2}H_aH_b$ ), and 2.11 (s, 3H,  $\text{C3COOCH}_3$ ).

**$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.4, 89.7, 85.9, 82.8, 80.6, 74.0, 72.9, 69.9, 58.3, 20.7, and 3.9.

**GC-MS** 50  $^\circ\text{C}$ /2.0 min/20  $^\circ\text{C}$  min $^{-1}$ /250  $^\circ\text{C}$   $t_R$  = 10.11 min; MS [70 eV,  $m/z$  (rel int)]: 310 (1,  $\text{M}^+$ ), 224 (38,  $-\text{I}^+$ ), 165 (100,  $^+\text{CH}_2\text{C}\equiv\text{CI}$ ), and 69 (81,  $\text{C}_4\text{H}_5\text{O}^+$ , protonated furan).

**FT-IR** (thin film): 2875, 1736, 1366, 1367, 1232, 1090, 1056, and 732  $\text{cm}^{-1}$ .

**HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{16}\text{IO}_5^+$  352.9886; Found 352.9865.

**(3*R*,3*aR*,6*S*,6*aR*)-3,6-bis((3-Iodoprop-2-yn-1-yl)oxy)hexahydrofuro[3,2-*b*]furan (6)**

*bis*-Propargyl ether **2a** (200 mg, 0.90 mmol) was dissolved in 2 mL of acetone in a screw-cap vial fitted with a stir bar. *N*-Iodosuccinimide (507 mg, 2.3 mmol) and silver nitrate (30 mg, 0.18 mmol) were added to the culture tube, which was sealed and allowed to stir for 15 h at ambient temperature. The reaction mixture was poured into DI water and extracted 3x with dichloromethane. The combined extracts were dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The residue was filtered through a short plug of silica (1:1 hexanes/EtOAc) and the filtrate was concentrated *in vacuo* to afford *bis*-iodoalkyne **6** (239 mg, 56% yield).

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.55 (dd, *J* = 4.6, 4.6 Hz, 1H, *H*3a), 4.45 (ddd, *J* = 4.6, 1.1, 1.1 Hz, 1H, *H*6a), 4.39 (d, *J* = 15.9 Hz, 1H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.34 (s, 2H, C1''*H*<sub>2</sub>), 4.31 (d, *J* = 15.9 Hz, 1H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.10 (ddd, *J* = 7.2, 6.4, 4.7 Hz, 1H, *H*3), 4.02 (br d, *J* = 4.1 Hz, 1H, *H*6), 3.86 (ddd, *J* = 10.3, 1.2, 1.2 Hz, 1H, C5*H*<sub>a</sub>*H*<sub>b</sub>), 3.82 (dd, *J* = 8.8, 6.5 Hz, 1H, C2*H*<sub>a</sub>*H*<sub>b</sub>), 3.75 (dd, *J* = 10.3, 3.8 Hz, 1H, C5*H*<sub>a</sub>*H*<sub>b</sub>), and 3.45 (dd, *J* = 8.8, 7.2 Hz, 1H, C2*H*<sub>a</sub>*H*<sub>b</sub>).

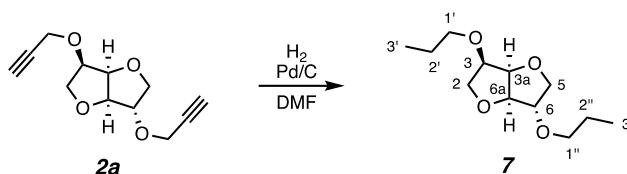
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 89.8, 85.6, 83.0, 80.2, 78.9, 72.9, 72.8, 69.9, 58.9, 58.1, 13.7, and 13.6.

**FT-IR** (thin film): 2931, 2872, 2182, 1077, 1059, and 832 cm<sup>-1</sup>.

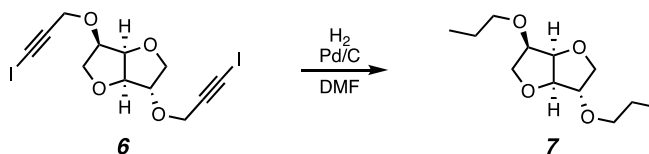
**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C) *t*<sub>R</sub> = 12.33 min; MS [70 eV, *m/z* (rel int)]: 165 (100,

<sup>+</sup>CH<sub>2</sub>C≡CI), 127 (30, I<sup>+</sup>), and 69 (40, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**HRMS** (ESI) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>12</sub>I<sub>2</sub>NaO<sub>4</sub><sup>+</sup> 496.8717; Found 496.8696.

**(3*R*,3*aR*,6*S*,6*aR*)-3,6-Dipropoxyhexahydrofuro[3,2-*b*]furan (7)**

**Preparation of 7:** To a solution of diyne **2a** (100 mg, 0.43 mmol) dissolved in 1 mL of *N,N*-dimethylformamide was added Pd/C (10 wt%, ca. 10 mg) inside an open 6 dram vial. The vial was placed into a 100 mL Fischer-Porter vessel, which was then sealed and twice pressurized with hydrogen gas and vented. The vessel was again pressurized to 80 psi, and the black suspension was magnetically stirred for 24 h at ambient temperature. The pressure was vented, and the suspension was filtered through a pad of Celite®. The filtrate was concentrated *in vacuo* to afford 91 mg of the *bis*-propyl ether **7** in 92% isolated yield.



**Hydrogenation of 6 to 7:** To a solution of diyne **6** (50 mg, 0.11 mmol) dissolved in 1 mL of *N,N*-dimethylformamide was added Pd/C (10 wt%, ca. 10 mg) inside an open 6 dram vial. A portion of solid sodium bicarbonate (ca. 20 mg) was also added to the suspension. The vial was placed into a 100 mL Fischer-Porter vessel, which was then sealed and twice pressurized with hydrogen gas and vented. The vessel was again pressurized to 80 psi, and the black suspension was magnetically stirred for 24 h at ambient temperature. The pressure was vented and the suspension was filtered through a pad of Celite®. The filtrate was concentrated *in vacuo* to afford 21 mg of the *bis*-propyl ether **7** in 92% isolated yield. This material was judged to be substantially identical to that made from **2a** by <sup>1</sup>H NMR and GC-MS analyses.

**Characterization Data for 7:**

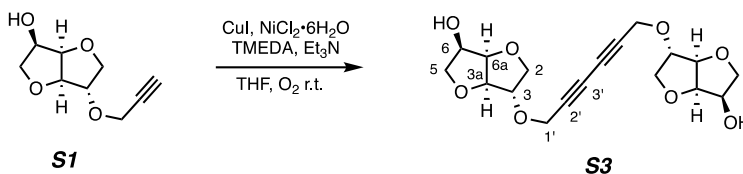
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.53 (dd, *J* = 4.6, 4.6 Hz, 1H, *H*3<sub>a</sub>), 4.40 (ddd, *J* = 4.4, 0.8, 0.8 Hz, 1H, *H*6<sub>a</sub>), 3.94 (ddd, *J* = 7.7, 6.6, 4.6 Hz, 1H, *H*3), 3.86 (nfom, 1H, *H*6), 3.79 (dd, *J* = 8.4, 6.5 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.81–3.77 (m, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.76 (dd, *J* = 9.9, 3.9 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.52 (ddd, *J* = 9.1, 6.7, 6.7 Hz, 1H, OCH*aH<sub>b</sub>Et*), 3.40 (ddd, *J* = 9.1, 6.6, 6.6 Hz, 1H, OCH*aH<sub>b</sub>Et*'), 3.39 (m, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.36 (ddd, *J* = 9.1, 6.6, 6.6 Hz, 1H, OCH*aH<sub>b</sub>Et*'), 3.35 (ddd, *J* = 9.2, 6.6, 6.6 Hz, 1H, OCH*aH<sub>b</sub>Et*'), 1.50 (overlapping m, 4H, OCH<sub>2</sub>CH<sub>2</sub>Me and OCH<sub>2</sub>CH<sub>2</sub>Me'), 0.860 (t, *J* = 7.4 Hz, 3H, O(CH<sub>2</sub>)<sub>2</sub>C3'*H*<sub>3</sub>), and 0.856 (t, *J* = 7.4 Hz, 3H, O(CH<sub>2</sub>)<sub>2</sub>C3'*H*<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 86.0, 84.2, 80.2, 80.1, 73.0, 71.6, 70.7, 69.8, 23.1, 23.0, and 11.0(2x).

**FT-IR** 2961, 2935, 2874, 1447, 1370, 1093, 1074, and 1015 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C *t*<sub>R</sub> = 7.55 min; MS [70 eV, *m/z* (rel int)]: 230 (19, M<sup>+</sup>), 127 (39, C<sub>7</sub>H<sub>11</sub>O<sub>2</sub><sup>+</sup>), 103 (39, M C<sub>5</sub>H<sub>11</sub>O<sub>2</sub><sup>+</sup>), 86 (25, C<sub>5</sub>H<sub>10</sub>O<sup>+</sup>), and 69 (100, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**HRMS** (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>23</sub>O<sub>4</sub><sup>+</sup> 231.1591; Found 231.1583.

**(3*R*,3*aR*,3'*R*,3*a'R*,6*S*,6*aR*,6'*S*,6*a'R*)-6,6'-(Hexa-2,4-diyne-1,6-diylbis(oxy))bis(hexahydro-furo[3,2-*b*]furan-3-ol) (S3)**

Cuprous iodide (51 mg, 0.27 mmol) was suspended in 3 mL of tetrahydrofuran in a round-bottom flask equipped with a stir bar. *N,N,N',N'*-Tetramethylethylenediamine (250  $\mu$ L, 1.7 mmol) was added to the vial under stirring, forming a light green homogenous solution, followed by addition of nickel (II) chloride hexahydrate (65 mg, 0.27 mmol), turning the solution to a deep green. Triethylamine (1.0 mL, 1.4 mmol) was added dropwise via syringe, and the vial was sealed with a rubber septum and allowed to stir for one hour. A solution of **S1** (991 mg, 5.4 mmol) in 0.5 mL of THF was injected into the vial, which was sealed once again with a septum. The solution and headspace were gently sparged with oxygen (balloon) fitted with a long needle over the course of ca. one hour, and the reaction mixture was stirred at room temperature for 48 h. The crude reaction mixture was filtered through a short plug of silica (100% EtOAc as the eluent). The filtrate was concentrated *in vacuo* and purified by MPLC (100% EtOAc) to afford the *exo/exo*-diyne **S3** (845 mg, 86%) as a yellow viscous oil.

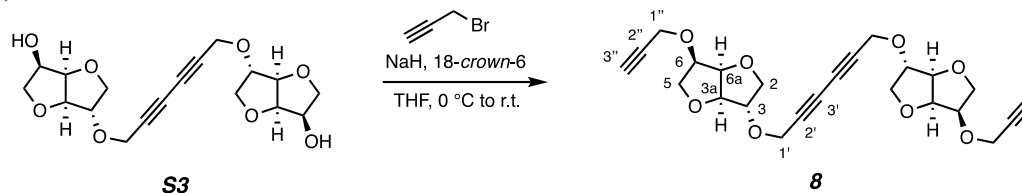
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.83 (dd,  $J$  = 6.5, 0.6 Hz, 2H, C6OH), 4.44 (ddd,  $J$  = 4.4, 1.1, 1.1 Hz, 2H, H3a), 4.38 (s, 4H, C1'*H*<sub>2</sub>), 4.34 (dd,  $J$  = 4.7, 4.7 Hz, 2H, H6a), 4.10 (dddd,  $J$  = 7.8, 6.4, 6.4, 4.8 Hz, 2H, H6), 4.05 (dddd,  $J$  = 3.8, 1.9, 1.4, 0.6 Hz, 2H, H3), 3.88 (ddd,  $J$  = 10.3, 1.3, 1.3, Hz, 2H, C2H<sub>a</sub>H<sub>b</sub>), 3.77 (dd,  $J$  = 10.3, 3.8 Hz, 2H, C2H<sub>a</sub>H<sub>b</sub>), 3.72 (dd,  $J$  = 8.4, 6.5 Hz, 2H, C5H<sub>a</sub>H<sub>b</sub>), and 3.30 (ddd,  $J$  = 8.3, 7.7, 0.6 Hz, 2H, C5H<sub>a</sub>H<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  84.9, 83.5, 81.6, 76.7, 72.3, 72.1, 71.2, 69.6, and 56.6.

**FT-IR** (thin film): 3421 (v br), 2933, 2872, 1657, 1387, 1046, 914, and 661 cm<sup>-1</sup>.

**HRMS** (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>O<sub>8</sub><sup>+</sup> 367.1387; Found 367.1374.

**1,6-bis(((3*S*,3*aR*,6*R*,6*aR*)-6-(Prop-2-yn-1-yloxy)hexahydrofuro[3,2-*b*]furan-3-yl)oxy)hexa-2,4-diyne (2*a*-RR\*)**



To a solution of crude **S3** (600 mg, 1.6 mmol) in 10 mL of tetrahydrofuran was added 18-*crown*-6 (22 mg, 0.08 mmol) and a 60 wt.% dispersion in mineral oil of sodium hydride (180 mg, 4.3 mmol). The reaction mixture was concentrated, dissolved in DCM, and filtered through a plug of silica (100% EtOAc as the eluent), and the resulting filtrate was concentrated to afford a brown residue. This was purified by MPLC (2:1 hexanes/EtOAc) to afford the  $\alpha,\omega$ -propargylated *exo/exo*-diyne **2a-RR** as a light-yellow oil (442 mg, 61% yield).

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.58 (dd,  $J$  = 4.6, 4.6 Hz, 2H, *H*<sub>6a</sub>), 4.48 (ddd,  $J$  = 4.5, 1.0, 1.0 Hz, 2H, *H*<sub>3a</sub>), 4.39 (s, 4H, C1'*H*<sub>2</sub>), 4.27 (dd,  $J$  = 15.8, 2.4 Hz, 2H, C1''*H*<sub>a</sub>*H*<sub>b</sub>), 4.18 (dd,  $J$  = 15.8, 2.4 Hz, 2H, C1''*H*<sub>a</sub>*H*<sub>b</sub>), 4.14 (ddd,  $J$  = 7.3, 6.3, 4.7 Hz, 2H, *H*<sub>6</sub>), 4.06 (dddd,  $J$  = 3.7, 1.2, 1.2, 0.6 Hz, 2H, *H*<sub>3</sub>), 3.88 (ddd,  $J$  = 10.3, 1.1, 1.1 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>), 3.82 (dd,  $J$  = 8.8, 6.4 Hz, 2H, C5*H*<sub>a</sub>*H*<sub>b</sub>), 3.75 (dd,  $J$  = 10.3, 3.7 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>), 3.47 (t,  $J$  = 2.4 Hz, 2H, *H*<sub>3</sub>''), and 3.45 (ddd,  $J$  = 8.8, 7.2 Hz, 0.6 Hz 2H, C5*H*<sub>a</sub>*H*<sub>b</sub>).

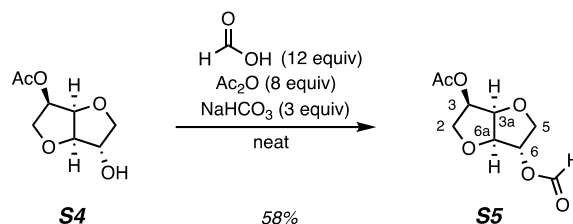
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  85.6, 83.5, 80.7, 80.3, 78.9, 77.9, 77.0, 72.8, 70.0, 69.9, 57.3, and 57.0.

**FT-IR** (thin film): 3269, 2923, 2871, 1449, 1362, 1127, 1060, 1020, and 664 cm<sup>-1</sup>.

**HRMS** (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>27</sub>O<sub>8</sub><sup>+</sup> 443.1700; Found 443.1691; [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>26</sub>NaO<sub>8</sub><sup>+</sup> 465.1520; Found 465.1508.

\* the descriptor "RR" in **2a-RR** [and **poly(2a-RR)**] designates that this is a regioregular monomer (and polymer)



**(3*R*,3*aR*,6*S*,6*aR*)-6-(Formyloxy)hexahydrofuro[3,2-*b*]furan-3-yl acetate (S5)**

Formic acid (580  $\mu$ L, 9.4 mmol, 88% aq soln) and acetic anhydride (864  $\mu$ L, 6.2 mmol) were added to a threaded culture tube fitted with a stir bar and PTFE-lined cap were heated at 60 °C for 90 minutes. The solution of mixed anhydride was cooled to 0 °C in an ice water bath, and then added via pipet to the neat *endo*-acetate **S4**<sup>†</sup> (146 mg, 0.78 mmol) in a separate vial, followed by addition of solid sodium bicarbonate (197 mg, 2.3 mmol). This mixture was allowed to warm to ambient temperature and stirred overnight, at which point the reaction mixture was quenched by dropwise addition to a solution of aq sodium bicarbonate. This was extracted 3x with dichloromethane. The combined organic layers were washed with brine, dried with anhyd MgSO<sub>4</sub>, and concentrated *in vacuo* to afford the formate ester **S5** (98 mg, 58% recovered), which gave the following data without further purification.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (ddd,  $J$  = 0.9, 0.9, 0.9 Hz, 1H, C6COH), 5.33–5.31 (nfom, 1H, *H*6), 5.16 (ddd,  $J$  = 6.1, 5.3, 5.3 Hz, 1H, *H*3), 4.85 (dd,  $J$  = 5.3, 4.7 Hz, 1H, *H*3a), 4.52 (ddd,  $J$  = 4.6, 0.8, 0.8 Hz, 1H, *H*6a), 4.03 (ddd,  $J$  = 10.8, 3.0, 0.9 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 4.01 (dd,  $J$  = 10.8, 1.8 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.96 (dd,  $J$  = 9.8, 6.0 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.81 (ddd,  $J$  = 9.8, 5.5, 0.6 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), and 2.12 (s, 3H, C3COOCH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  170.3, 159.8, 85.7, 80.8, 77.6, 73.9, 73.3, 70.4, and 20.7.

**FT-IR** (thin film): 2882, 2875, 1731, 1714, 1370, 1233, 1165, 1090, and 849 cm<sup>-1</sup>.

**GC-MS** 50 °C/2.0 min/20 °C min<sup>-1</sup>/250 °C)  $t_R$  = 7.10 min; MS [70 eV,  $m/z$  (rel int)]: 170 (5, M–HCO<sub>2</sub>H), 156 (10, M–H<sub>3</sub>CCO<sub>2</sub>H), 110 (98, C<sub>6</sub>H<sub>6</sub>O<sub>2</sub><sup>+</sup>), and 69 (64, C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>, protonated furan).

**HRMS** (ESI)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>13</sub>O<sub>6</sub><sup>+</sup> 217.0712; Found 217.0697.

**mp**: 42–44 °C.

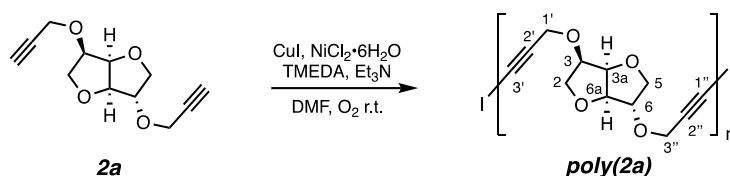
<sup>†</sup> Kindly provided by Dr. Derek Saxon.

### III. Preparation and Characterization of Polymers

#### Typical procedure for the Glaser oxidative polymerization of isohexide *bis*-propargyl ethers **2a–c**.

Cuprous iodide (56 mg, 0.30 mmol) was suspended in 2 mL of dimethylformamide in a 6-dram vial equipped with a micro stir bar. *N,N,N',N'*-Tetramethylethylenediamine (2.4 mmol, 360  $\mu$ L) was added to the vial under stirring, forming a deep blue homogenous solution. Nickel (II) chloride hexahydrate (71 mg, 0.30 mmol) was added, and the solution turned to a deep green. Triethylamine (1.0 mL, 1.32 mmol) was added dropwise via syringe, and the vial was sealed with a rubber septum and allowed to stir for one hour. Diyne **2a** (1.3 g, 0.45 mmol) was injected into the vial, which was sealed once again with a septum. The solution and headspace were sparged with an oxygen balloon fitted with a long needle, and the reaction mixture was allowed to stir under oxygen at room temperature for 48 h. The polymer was precipitated by dropwise addition of the reaction mixture into 100 mL of a stirred satd ammonium chloride solution at ambient temperature. The resulting suspension was allowed to settle, and the supernatant liquid removed by decantation. The residual solid was washed with DI water (2x10 mL). The vial was wrapped in foil, and the remaining wet solids were frozen in liquid nitrogen and the remaining water was removed on a lyophilizer. The **poly(2a)** was obtained as a fluffy, off-white powder (936 mg, 72% yield).

#### Poly(**2a**)



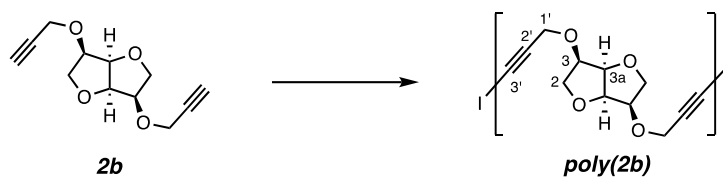
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.60 (dd,  $J$  = 4.7, 4.7 Hz, 1H, *H*3a), 4.48 (brd,  $J$  = 4.7 Hz, 1H, *H*6a), 4.43 (d  $J$  = 16.6 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.40 (s, 1H, C1'*H<sub>2</sub>*), 4.36 (d,  $J$  = 16.6 Hz, 1H, C1'*H<sub>a</sub>H<sub>b</sub>*), 4.14 (ddd,  $J$  = 6.7, 4.7, 4.7 Hz, 1H, *H*3), 4.06 (brd,  $J$  = 3.7 Hz, 1H, *H*6), 3.89 (brd,  $J$  = 10.3 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.82 (dd,  $J$  = 8.9, 6.4 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.76 (dd,  $J$  = 10.3, 3.7 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), and 3.46 (dd,  $J$  = 8.9, 6.5 Hz, 1H, C2*H<sub>a</sub>H<sub>b</sub>*).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  85.6, 83.4, 80.3, 79.3, 77.2–76.9 (ca. 4 br singlets, C2' and C2''), 72.8, 70.06 (C1' or C1''), 70.02, 69.98 (C1' or C1''), 57.8, and 57.0.

**SEC-MALS**  $M_n$  = 12.5 kDa,  $\bar{D}$  = 1.3.

**DSC**  $T_g$  = 55 °C.

**TGA**  $T_{d5\%}$  = 253 °C.

**Poly(2b)**

**Poly(2b)** was recovered as a fluffy, off-white powder (176 mg from 200 mg of **2c**; 87% yield).

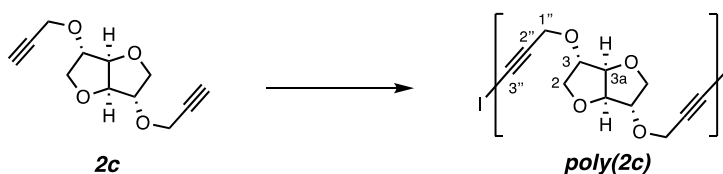
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.54 (nfom, 2H, *H*3a), 4.42 (nfod, *J*<sub>app</sub> = 16.2 Hz, 2H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.34 (nfod, *J*<sub>app</sub> = 16.0 Hz, 2H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.14 (dddd, *J* = 8.2, 6.8, 3.6, 1.6 Hz, 2H, *H*3), 3.91 (dd, *J* = 8.4, 6.9 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>), and 3.46 (dd, *J* = 8.3, 8.3 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 80.3, 79.3, 77.1(C<sub>alkyne</sub>), 70.7, 70.1(C<sub>alkyne</sub>), and 57.8(CH<sub>2</sub>).

**SEC-MALS** *M*<sub>n</sub> = 9.1 kDa, *D* = 1.5.

**DSC** *T*<sub>g</sub> = 64 °C.

**TGA** *T*<sub>d5%</sub> = 171 °C.

**Poly(2c)**

**Poly(2c)** was recovered as a fluffy, off-white powder (164 mg from 200 mg of **2c**; 82% yield).

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.52 (nfom, 2H, *H*3a), 4.41 (s, 4H, C1''*H*<sub>2</sub>), 4.07 (dd, *J* = 3.8, 1.3 Hz, 2H, *H*3), 3.80 (dd, *J* = 10.3, 1.4 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>), and 3.46 (dd, *J* = 10.3, 3.8 Hz, 2H, C2*H*<sub>a</sub>*H*<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 84.9, 82.9, 77.0(C<sub>alkyne</sub>), 71.7, 70.0(C<sub>alkyne</sub>), and 57.1(CH<sub>2</sub>).

**SEC-MALS** *M*<sub>n</sub> = 8.9 kDa, *D* = 1.5.

**DSC** *T*<sub>g</sub> = 56 °C.

**TGA** *T*<sub>d5%</sub> = 178 °C.

**Poly(2a-RR)<sup>‡</sup>**

**Poly(2a-RR)** was recovered as a fluffy, off-white powder (155 mg from 200 mg of **8**; 78% yield).

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.60 (dd, *J* = 4.7, 4.7 Hz, 1H, *H*3a), 4.48 (ddd, *J* = 4.4, 1.0, 1.0 Hz, 1H, *H*6a), 4.43 (d, *J* = 16.6 Hz, 1H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.40 (s, 1H, C1'*H*<sub>2</sub>), 4.36 (d, *J* = 16.6 Hz, 1H, C1'*H*<sub>a</sub>*H*<sub>b</sub>), 4.14 (ddd, *J* = 6.7, 4.7, 4.7 Hz, 1H, *H*3), 4.06 (ddd, *J* = 3.8, 1.9, 1.2 Hz, 1H, *H*6), 3.89 (ddd, *J* = 10.4, 1.2, 1.2 Hz, 1H, C5*H*<sub>a</sub>*H*<sub>b</sub>), 3.82 (dd, *J* = 8.9, 6.4 Hz, 1H, C2*H*<sub>a</sub>*H*<sub>b</sub>), 3.76 (dd, *J* = 10.3, 3.7 Hz, 1H, C5*H*<sub>a</sub>*H*<sub>b</sub>), and 3.46 (dd, *J* = 8.9, 6.5 Hz, 1H, C2*H*<sub>a</sub>*H*<sub>b</sub>).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 85.6, 83.4, 80.3, 79.3, 77.1(C2' or C2''), 77.0(C2' or C2''), 72.8, 70.06(C1' or C1''), 70.02, 69.98(C1' or C1''), 57.8, and 57.0.

**SEC-MALS** *M*<sub>n</sub> = 15.7 kDa, *Đ* = 1.7.

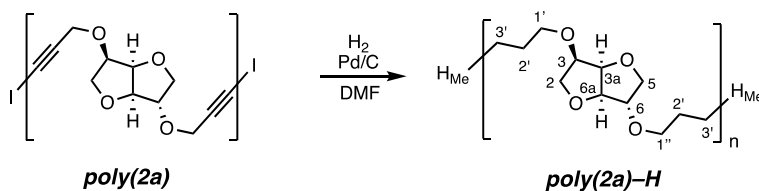
**DSC** *T*<sub>m</sub> = −28 °C, *T*<sub>g</sub> = 23 °C.

**TGA** *T*<sub>d5%</sub> = 178 °C.

<sup>‡</sup> the descriptor “RR” in **2a-RR** [and **poly(2a-RR)**] designates that this is a regioregular monomer (and polymer)

**Typical procedure for the hydrogenation of polymeric diynes poly(2a–c).**

To a solution of **poly(2a)** (100 mg) in 2 mL of dimethylformamide in a small vial equipped with a stir bar was added Pd/C (20 wt%, ca. 20 mg) and potassium carbonate (50 wt%, 50 mg). The vial was placed into a 100 mL Fischer-Porter vessel, which was sealed and twice pressurized with hydrogen gas and vented. The vessel was again pressurized to 80 psi, and the black suspension was allowed to stir for 1 week. The pressure was vented, and the suspension was filtered through a pad of Celite<sup>®</sup>, and the pad was washed with a small amount of additional DMF. The filtrate was concentrated *in vacuo* to afford **poly(2a)–H** as a sticky, lightly colored solid (87 mg, 89% isolated yield).

**Poly(2a)–[H]**

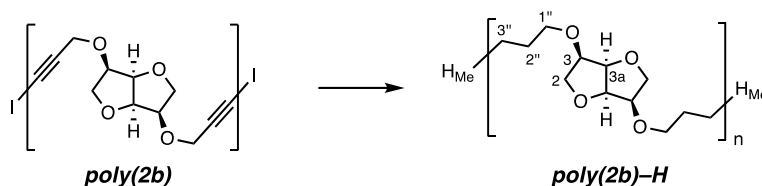
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.52 (dd, *J* = 4.6, 4.6 Hz, 1H, *H*3a), 4.39 (brd, *J* = 4.4 Hz, 1H, *H*6a), 3.93 (ddd, *J* = 7.0, 7.0, 4.5, Hz, 1H, *H*3), 3.85 (brd, *J* = 3.6 Hz, 1H, *H*6), 3.79 (brd, *J* = 8.9 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.76 (dd, *J* = 9.9, 3.8 Hz, 1H, C5*H<sub>a</sub>H<sub>b</sub>*), 3.55 (dddd, *J* = 9.1, 6.7, 6.7, 0.6 Hz, 1H, OC1'*H<sub>a</sub>H<sub>b</sub>*), 3.43–3.38 (m, 3H, OC1''*H<sub>2</sub>* and C5*H<sub>a</sub>H<sub>b</sub>*), 3.37 (ddd, *J* = 8.8, 6.6, 6.6 Hz, 1H, OC1'*H<sub>a</sub>H<sub>b</sub>*), 1.51–1.46 (m, 4H, C2'*H<sub>2</sub>* and C2''*H<sub>2</sub>*), and 1.32–1.27 (m, 4H, C3'*H<sub>2</sub>* and C3''*H<sub>2</sub>*). Resonances for the two methyl end groups were observed at 0.860 (t, *J* = 7.4 Hz, 0.12H, C3'*H<sub>3</sub>* or C3''*H<sub>3</sub>*) and 0.856 (t, *J* = 7.4 Hz, 0.12H, C3'*H<sub>3</sub>* or C3''*H<sub>3</sub>*).

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 86.0, 84.2, 80.2, 80.1, 73.0, 69.9(C1' or C1''), 69.8(C1' or C1''), 69.0, 29.8, 29.7, and 25.9.

**SEC-MALS** *M<sub>n</sub>* = 9.7 kDa, *Đ* = 1.6.

**DSC** *T<sub>g</sub>* = -10 °C.

**TGA** *T<sub>d5%</sub>* = 289 °C.

**Poly(2b)–[H]**

**Poly(2b)–H** was recovered as a sticky, lightly colored solid (88% isolated yield).

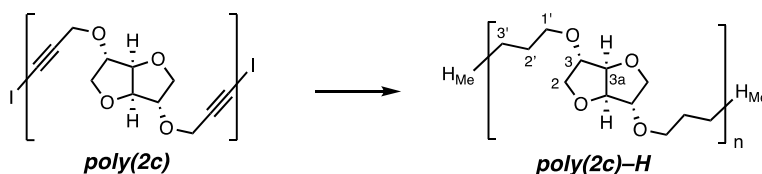
**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.48 (nfom, 2H, *H*3a), 3.93 (dddd, *J* = 8.3, 7.0, 3.4, 1.6 Hz, 2H, *H*3), 3.87 (dd, *J* = 8.2, 6.9 Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.52 (dt, *J* = 15.7, 6.7 Hz, 2H, C1'*H<sub>a</sub>H<sub>b</sub>*), 3.41 (dd, *J* = 8.2, 8.2 Hz, 2H, C2*H<sub>a</sub>H<sub>b</sub>*), 3.37 (dt, *J* = 15.7, 6.5 Hz, C1'*H<sub>a</sub>H<sub>b</sub>* 2H), 1.51–1.46 (m, 4H, C2'*H*<sub>2</sub>), and 1.32–1.27 (m, 4H, C3'*H*<sub>2</sub>). Resonances for the two methyl endgroups were observed at 0.860 (t, *J* = 7.4 Hz, 0.20H, C3'*H*<sub>3</sub> or C3''*H*<sub>3</sub>)

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 80.3, 80.2, 70.8, 69.9(C1''), 29.8, and 25.9.

**SEC-MALS** *M<sub>n</sub>* = 4.3 *D* = 1.3.

**DSC** *T<sub>g</sub>* = -2 °C.

**TGA** *T<sub>d5%</sub>* = 208 °C.

**Poly(2c)–[H]**

**Poly(2c)–H** was recovered as a sticky, lightly colored solid (72% isolated yield).

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>): δ 4.41 (br s, 2H, *H*3a), 3.86–3.83 (m, 2H, *H*3), 3.71–3.67 (m, 4H, C2*H*<sub>2</sub>), 3.47–3.42 (m, 4H, C1'*H*<sub>2</sub>), 3.39 (dt, *J* = 15.7, 6.5 Hz, C1'*H<sub>a</sub>H<sub>b</sub>* 2H), 1.53–1.45 (m, 4H, C2'*H*<sub>2</sub>), and 1.34–1.28 (m, 4H, C3'*H*<sub>2</sub>). Resonances for the methyl end groups were observed at 0.86 (t, *J* = 7.4 Hz, 0.14H, C3'*H*<sub>3</sub>).

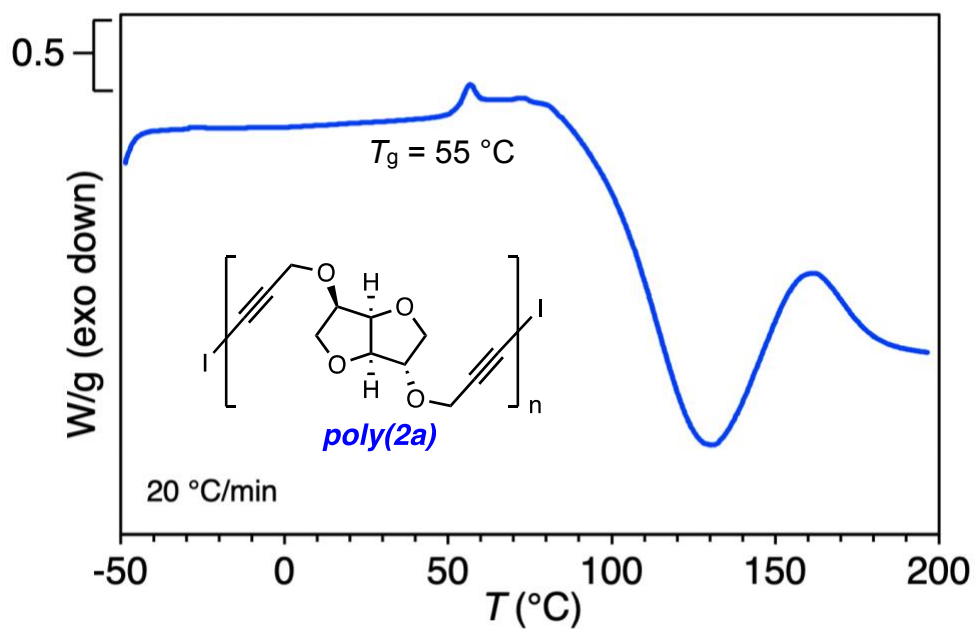
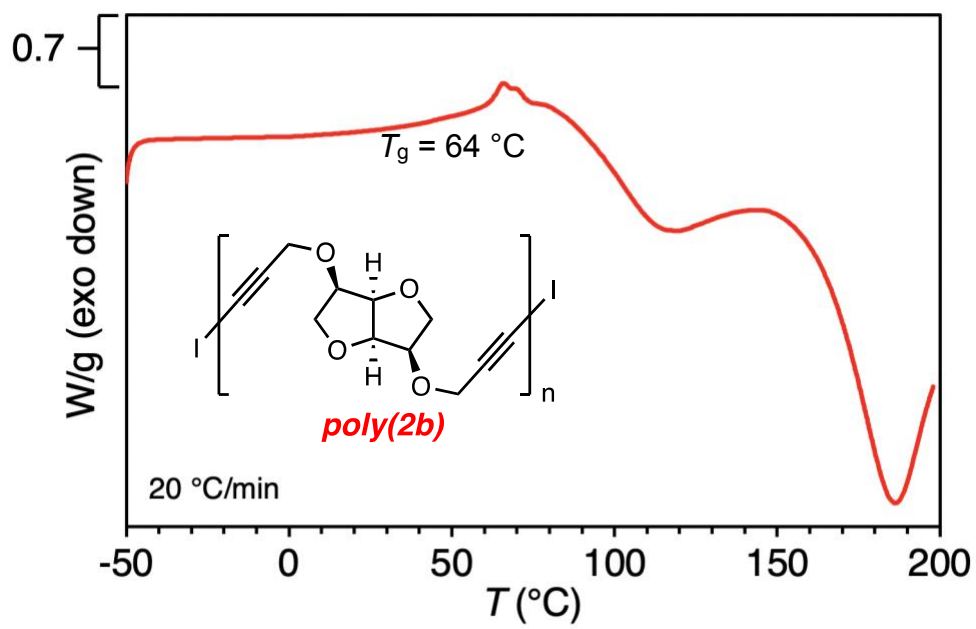
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>): δ 85.3, 83.4, 71.8, 69.1, 29.7, and 25.9.

**SEC-MALS** *M<sub>n</sub>* = 5.5 kDa, *D* = 1.8.

**DSC** *T<sub>g</sub>* = -9 °C; *T<sub>m</sub>*<sup>1</sup> = -29 °C; *T<sub>m</sub>*<sup>2</sup> = 83 °C.

**TGA** *T<sub>d5%</sub>* = 248 °C.

## IV. Polymer DSC, TGA, SEC traces:

Figure S1. DSC thermogram for **poly(2a)**Figure S2. DSC thermogram for **poly(2b)**

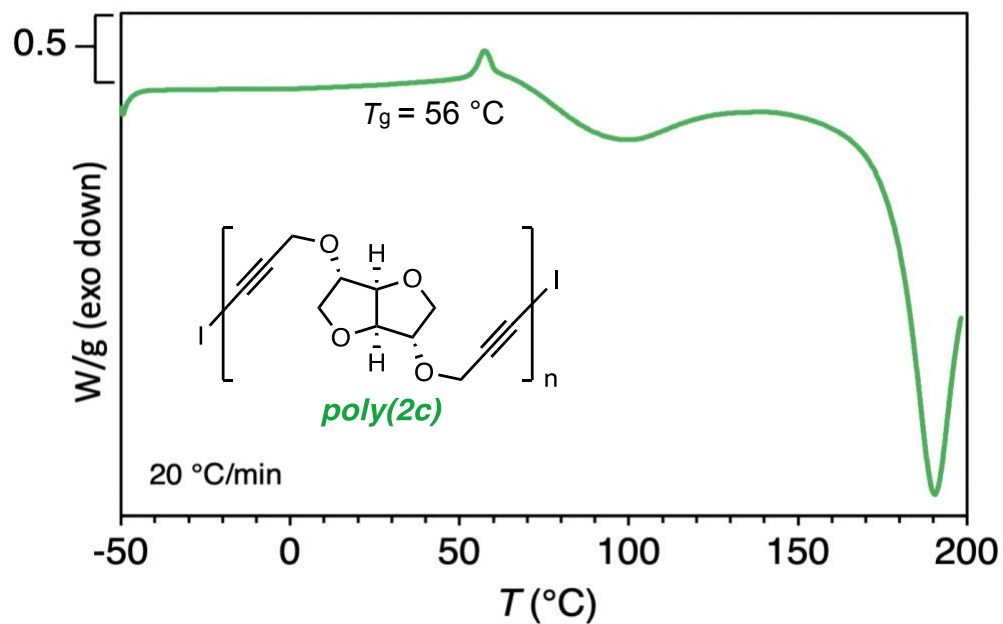


Figure S3. DSC thermogram for **poly(2c)**

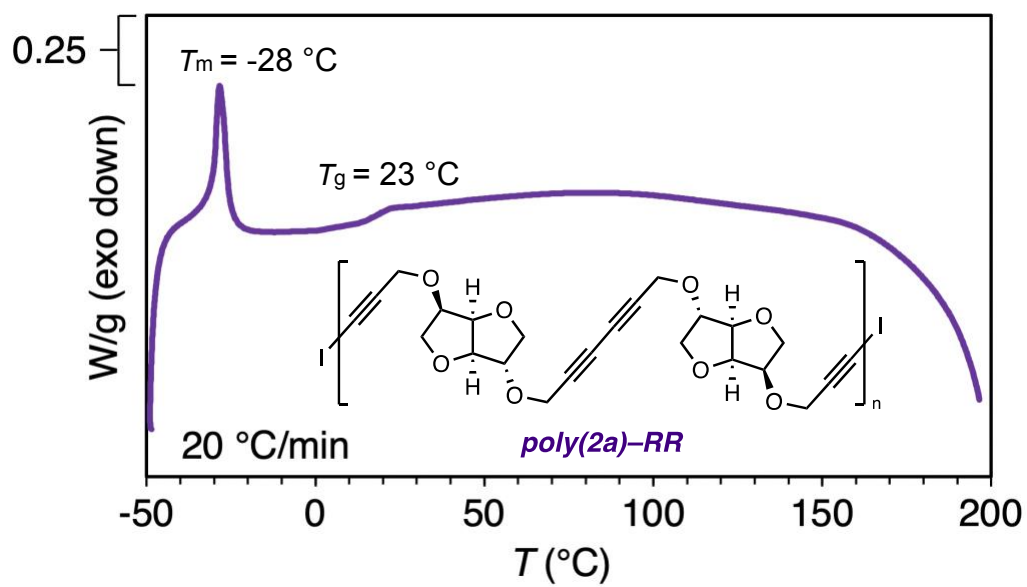


Figure S4. DSC thermogram for **poly(2a-RR)**



**Brief discussion of the thermal properties (DSC) of Poly(2a-RR)**

We also explored the effects of regioregularity on the isosorbide-based diyne polymer. That is, what effect would an all-*head-to-head* orientation of the diynes in the polyne backbone have on the thermal properties? To that end, we prepared the bis-terminal diyne monomer **2a-RR** already containing a pre-formed *exo/exo* 1,3-diyne linking the two isosorbide units. This can only polymerize through its terminal *endo*-propargyl ethers, resulting in alternating *exo/exo*- and *endo/endo*-2,4-hexadiynyl subunits between its isosorbide linkages. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral properties of **poly(2a)** and **poly(2a-RR)** are nearly identical, except for subtle, but diagnostic, differences in the diyne carbon resonances, but the thermal behaviors of these two polymers are remarkably different. While **poly(2a)** displays no  $T_m$  and a  $T_g$  of 55 °C (Figure S1), **poly(2a-RR)** displays a strong melting transition at -28 °C and a much lower  $T_g$  of 23 °C (Figure S4). Although we do not have a strong rationale to offer in way of explanation, these data highlight the profound effect that subtle changes in polymer microstructure can have on the thermal properties of the material, at least in the context of isosorbide-based polymers.

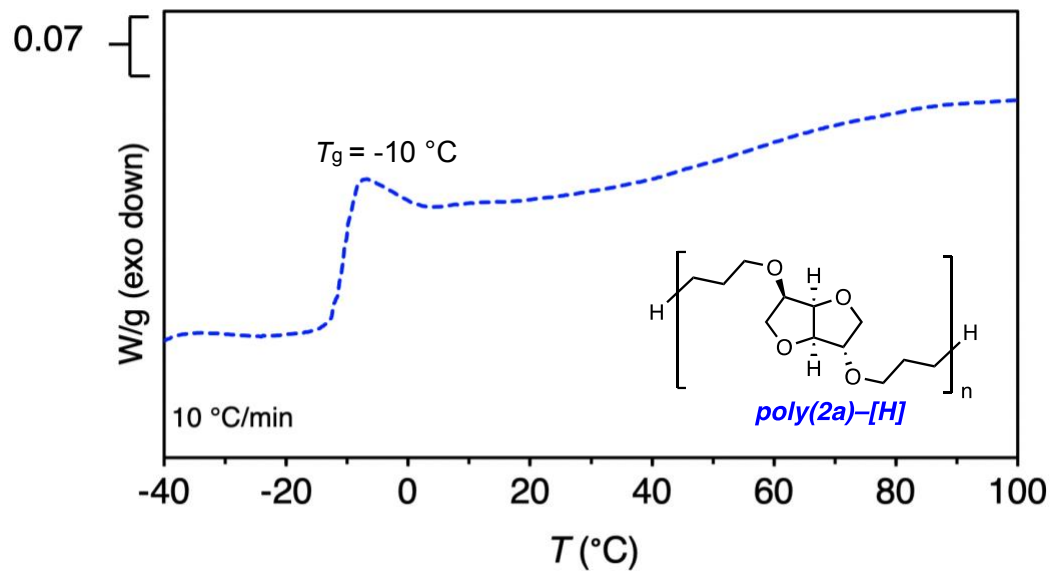


Figure S5. DSC thermogram for **poly(2a)-[H]**

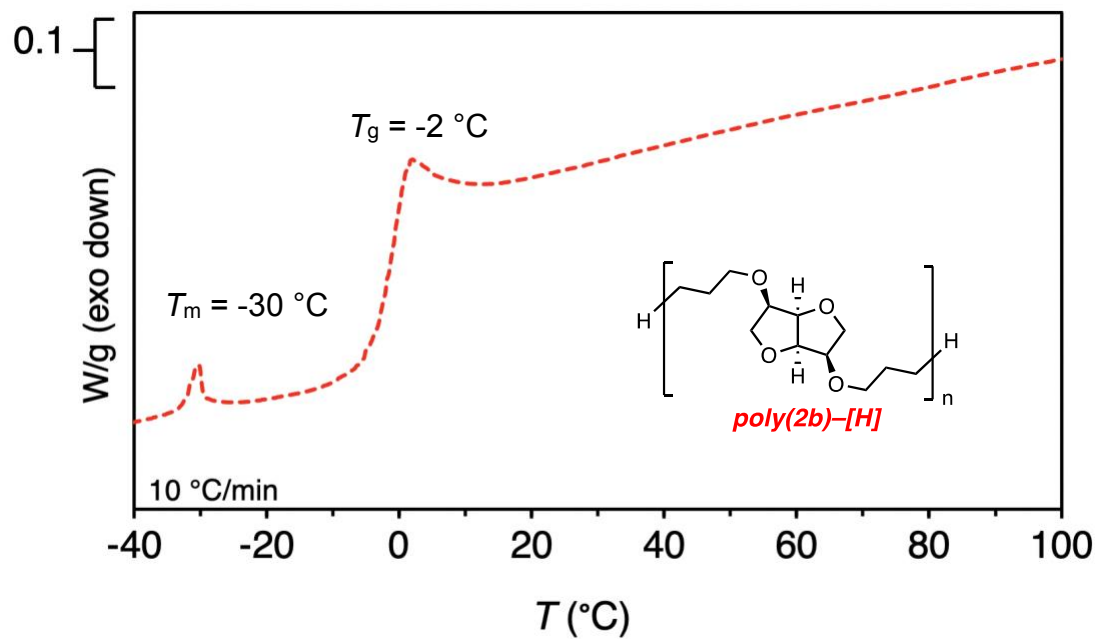
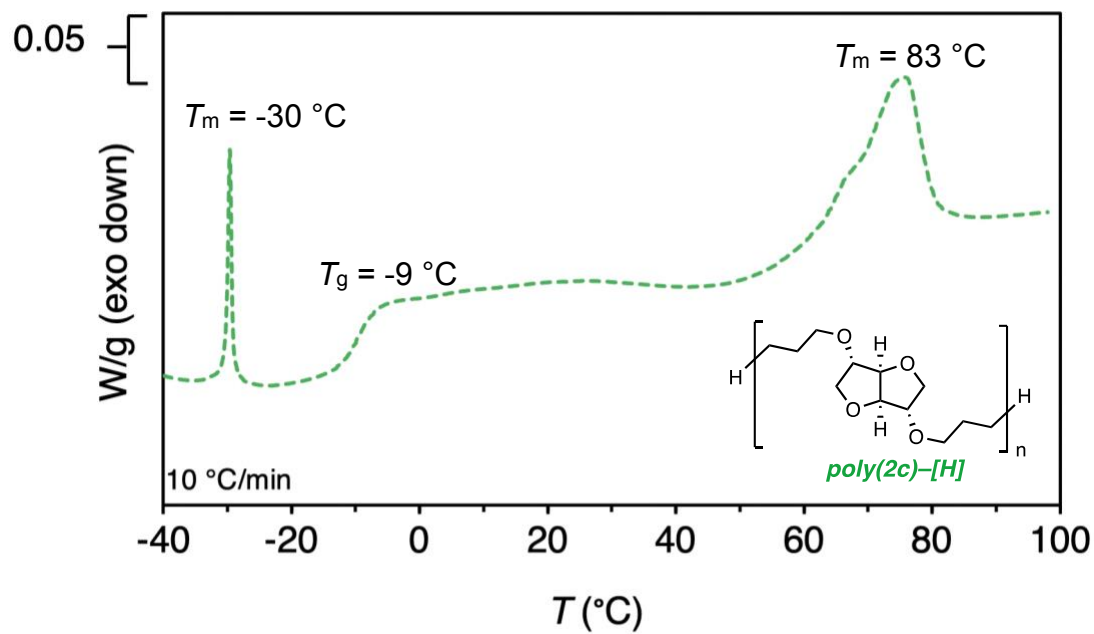
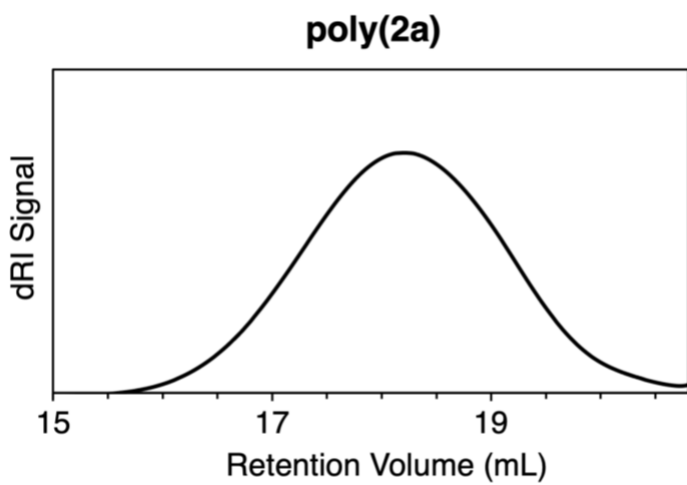


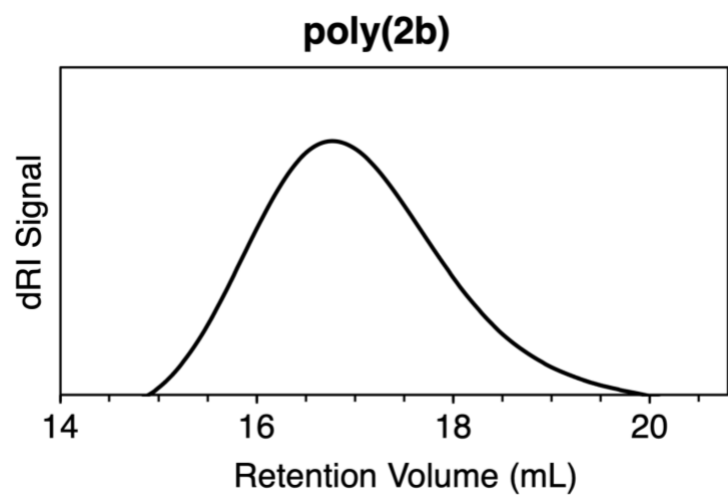
Figure S6. DSC thermogram for **poly(2b)-[H]**



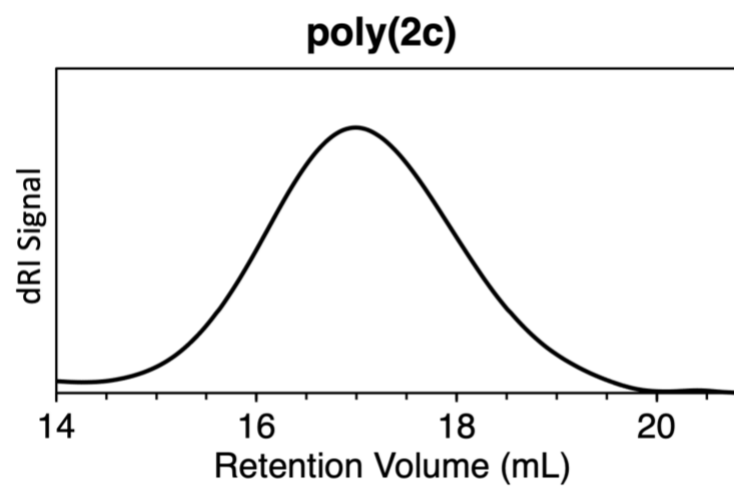
**Figure S7.** DSC thermogram for **poly(2c)-[H]**



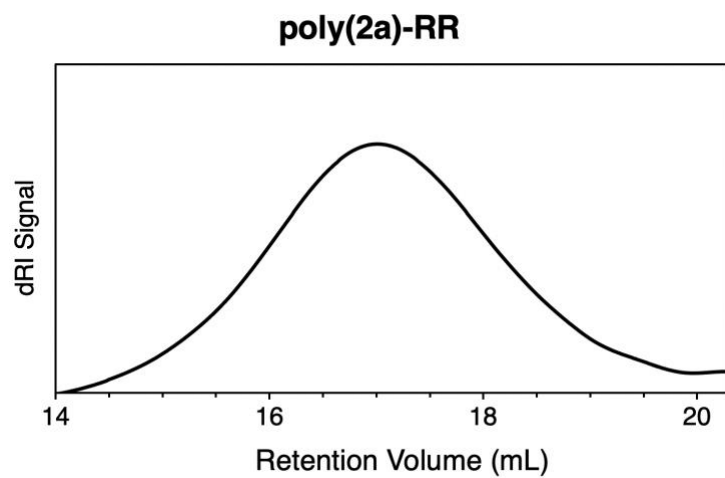
**Figure S8.** SEC chromatogram (DMF mobile phase) for **poly(2a)**



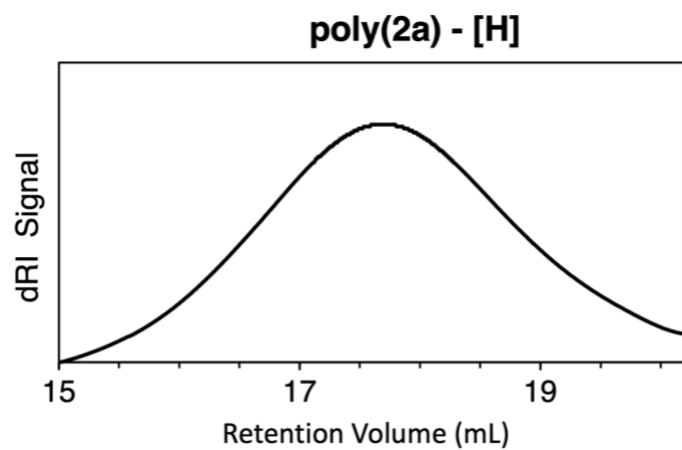
**Figure S9.** SEC chromatogram (DMF mobile phase) for **poly(2b)**



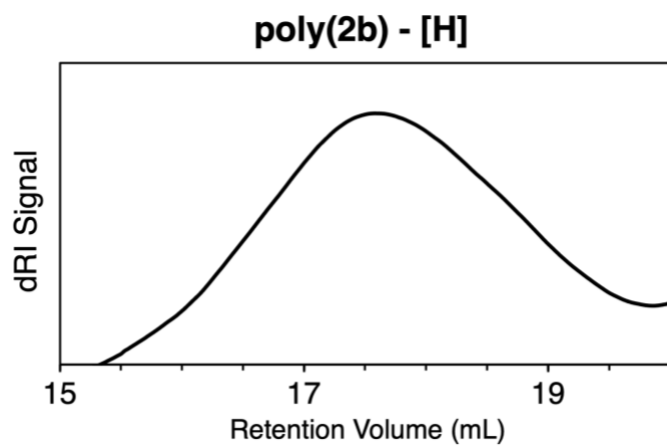
**Figure S10.** SEC chromatogram (DMF mobile phase) for **poly(2c)**



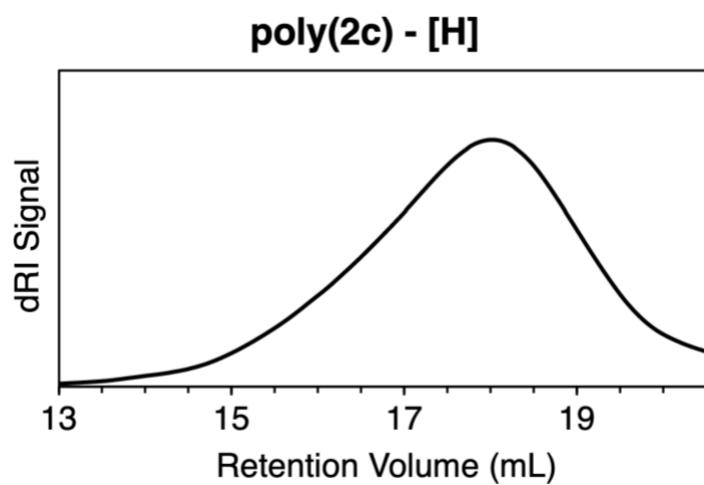
**Figure S11.** SEC chromatogram (DMF mobile phase) for **poly(2a-RR)**



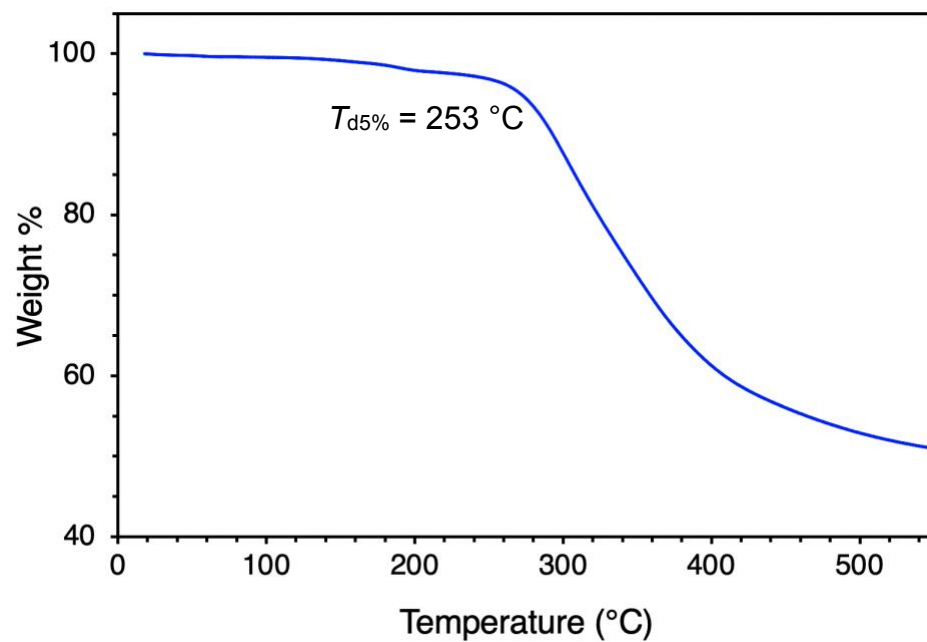
**Figure S12.** SEC chromatogram (DMF mobile phase) for **poly(2a)-[H]**



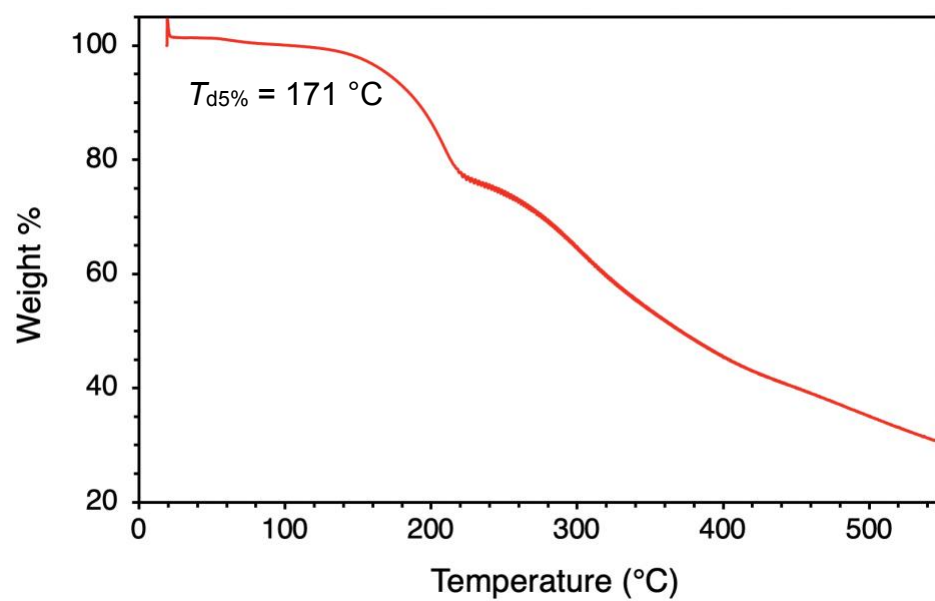
**Figure S13.** SEC chromatogram (DMF mobile phase) for **poly(2b)–[H]**



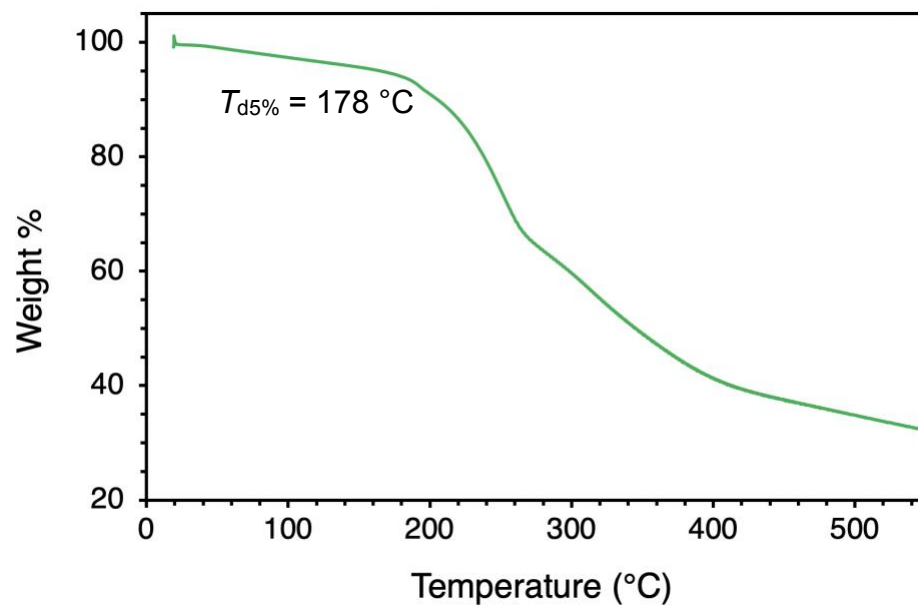
**Figure S14.** SEC chromatogram (DMF mobile phase) for **poly(2c)–[H]**



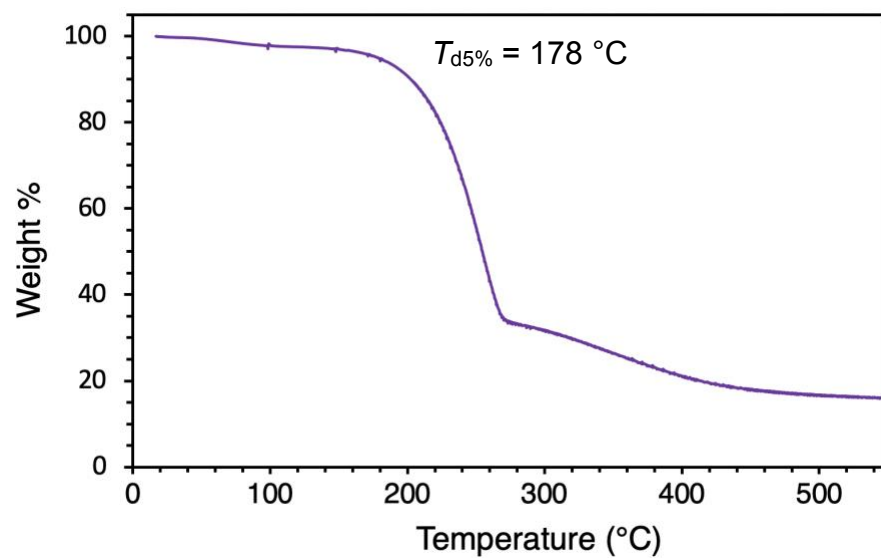
**Figure S15.** TGA thermogram for **poly(2a)**



**Figure S16.** TGA thermogram for **poly(2b)**

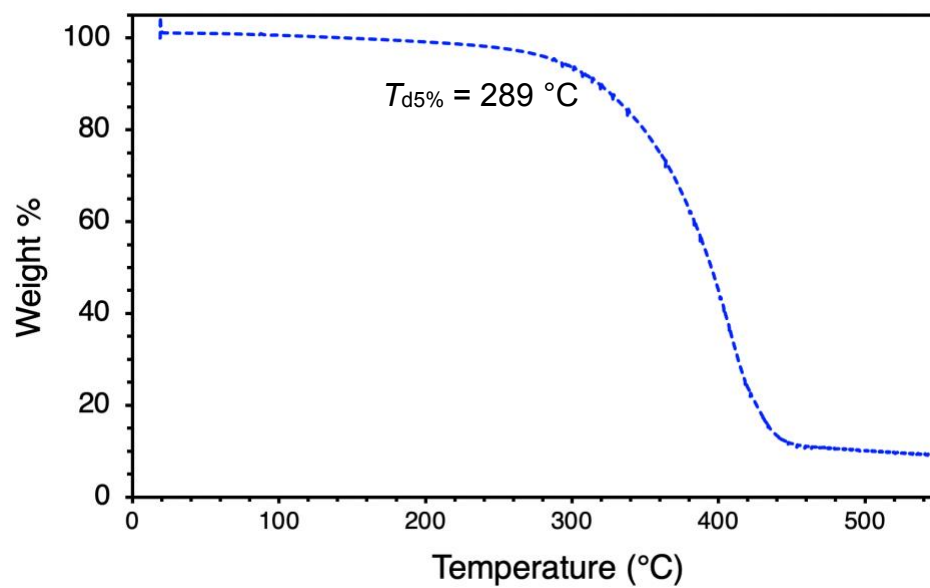


**Figure S17.** TGA thermogram for **poly(2c)**

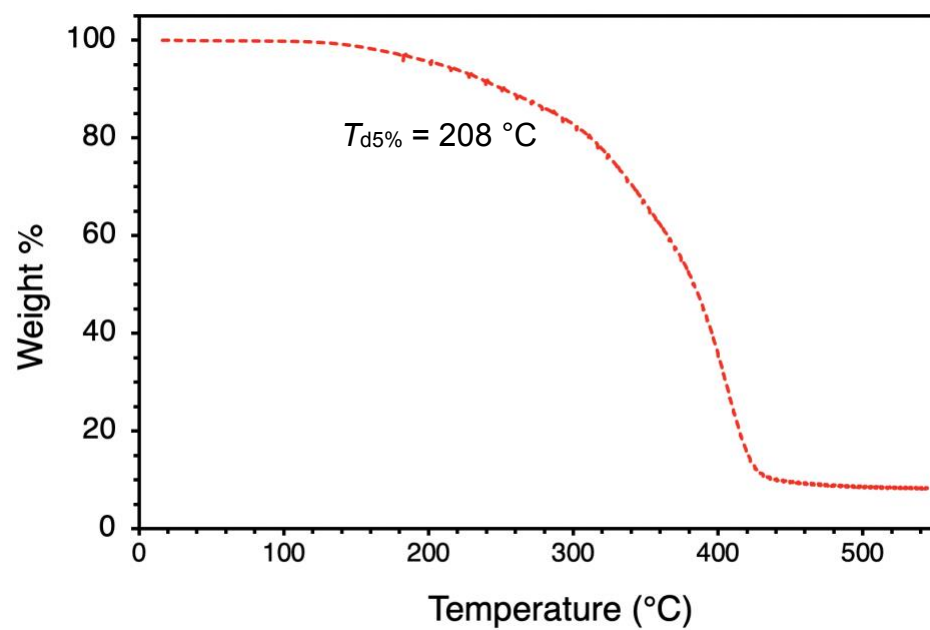


**Figure S18.** TGA thermogram for **poly(2a-RR)**

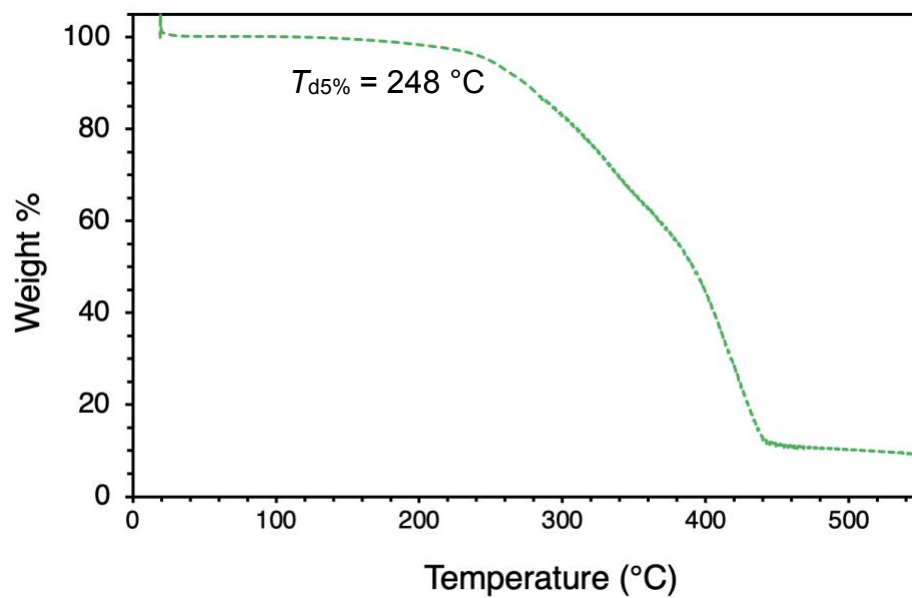




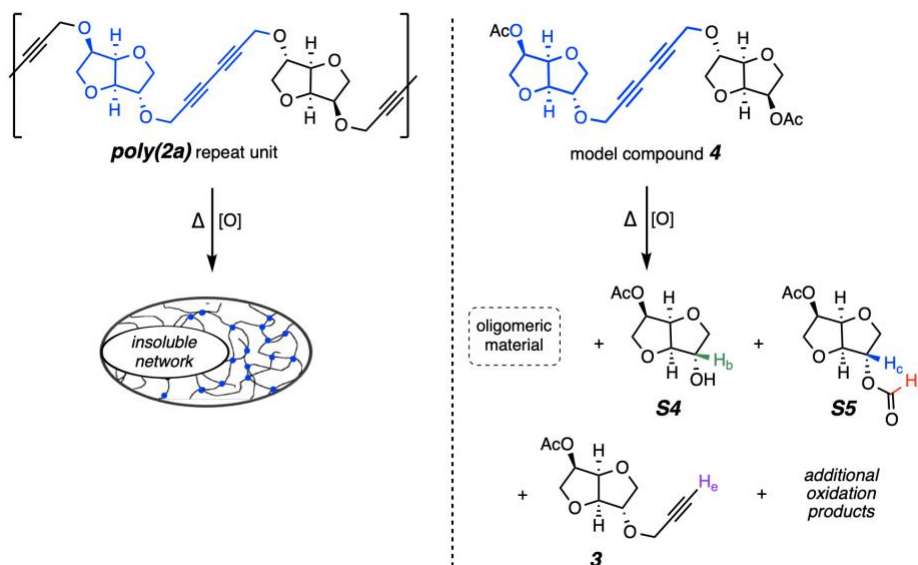
**Figure S19.** TGA thermogram for **poly(2a)-[H]**



**Figure S20.** TGA thermogram for **poly(2b)-[H]**

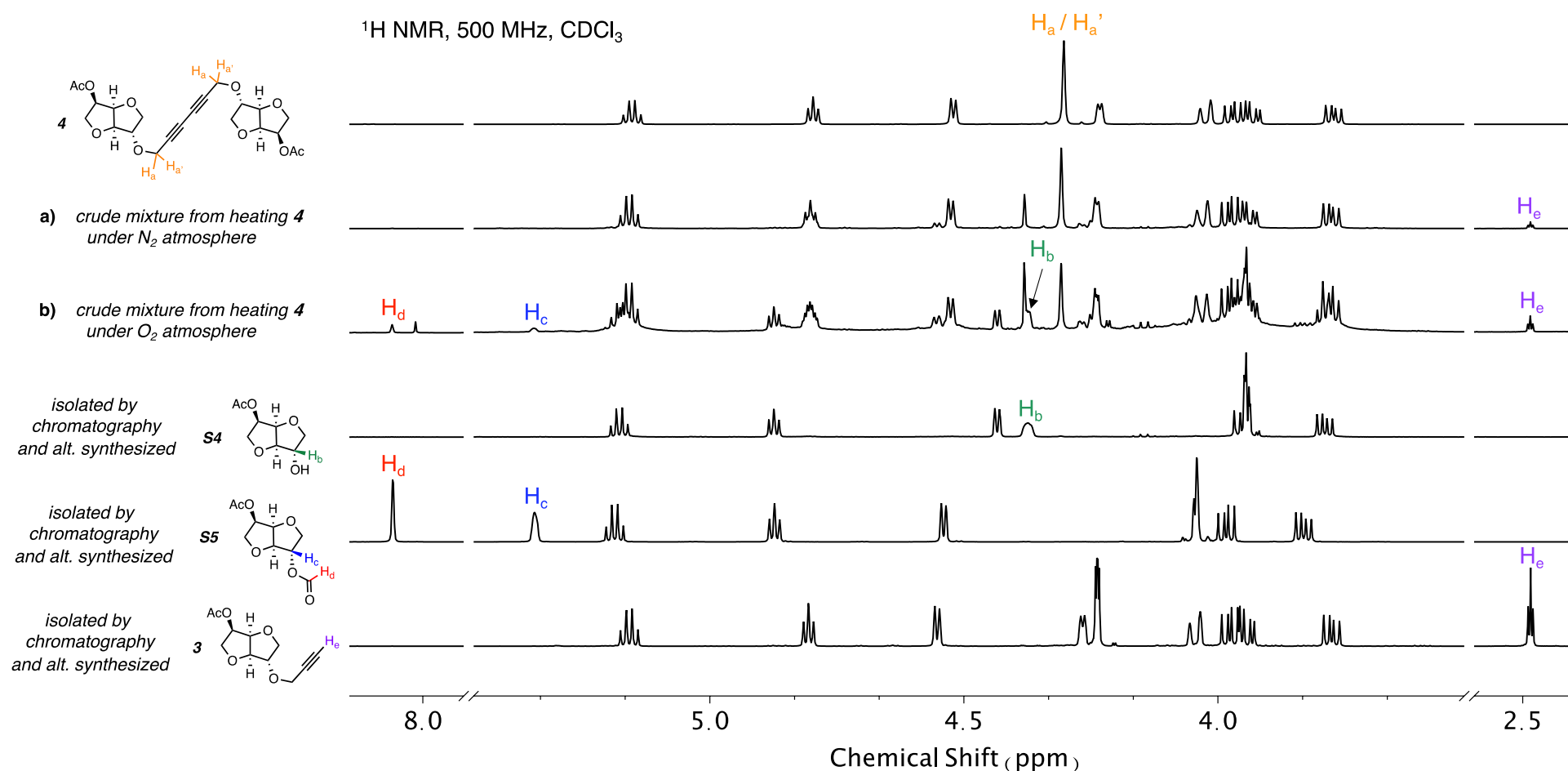
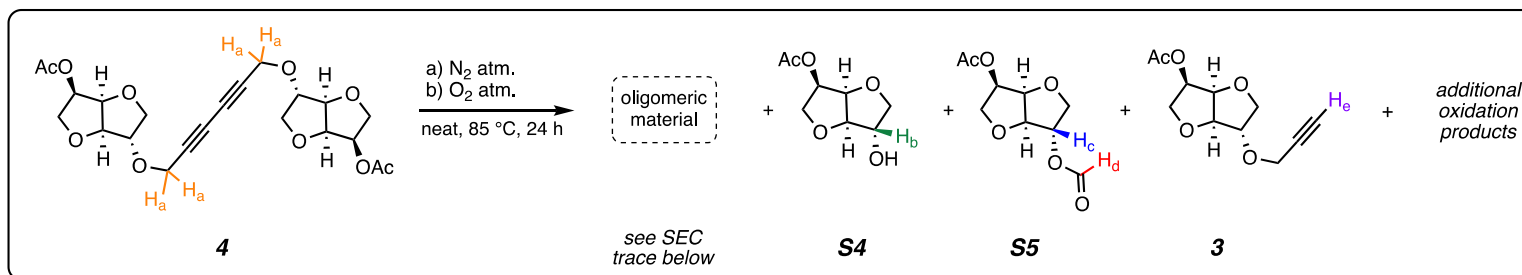


**Figure S21.** TGA thermogram for **poly(2c)-[H]**

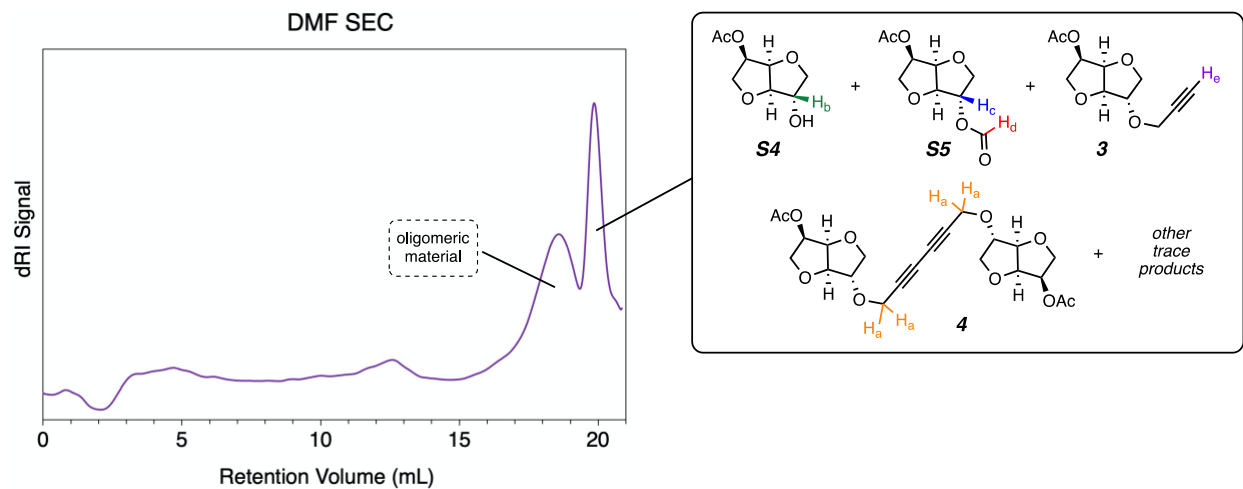
V. Model study of aerobic oxidation of **4**

**Figure S22.** Model study for oxidation of **poly(2a)** using model compound **4**.

The DSC thermograms of **poly(2a–c)** displayed large, irreversible exothermic events following the  $T_g$ , beginning between 70–90 °C (see **S23**). The materials recovered from the DSC pans were insoluble in any organic solvent, and therefore challenging to characterize. In order to investigate the nature of this phenomenon, we devised a study using acetate-protected diyne **4**, meant to simulate one repeat unit of the polymer, highlighted in blue (Figure S1). The model substrate was heated in bulk under a) a nitrogen atmosphere and b) an oxygen atmosphere for 24 hours. The crude products were dissolved in  $CDCl_3$  analyzed by GC-MS and  $^1H$  NMR spectroscopy and then subjected to column chromatography. The suspected degradation products were then alternatively synthesized and fully characterized.



**Figure S23.** <sup>1</sup>H NMR spectra of products **S4**, **S5**, and **3** resulting from thermal and/or oxidative decomposition of **4**.



**Figure S24.** SEC analysis (DMF mobile phase) of the oxidation products obtained from heating **4**.

## VI. References for Supporting Information

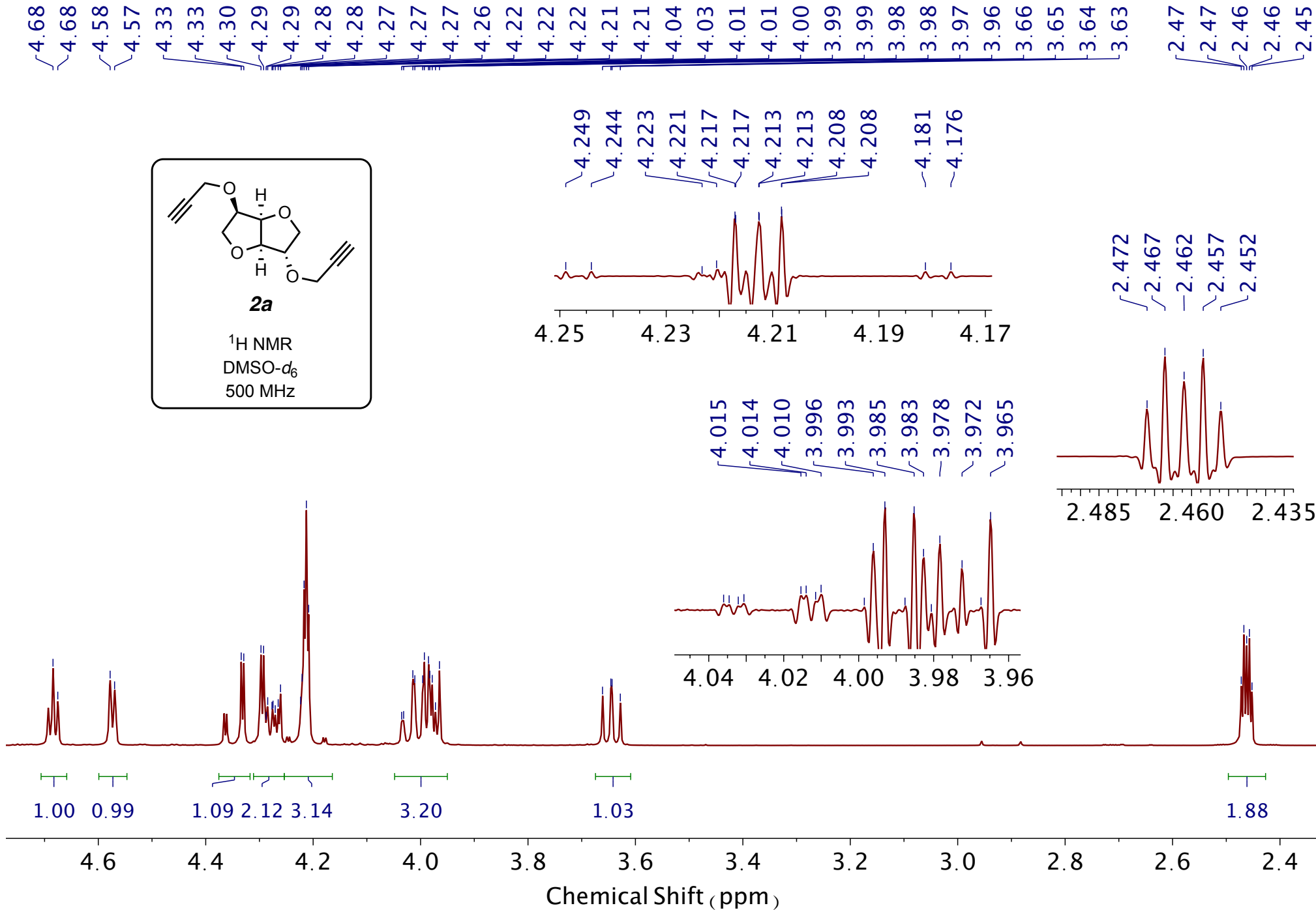
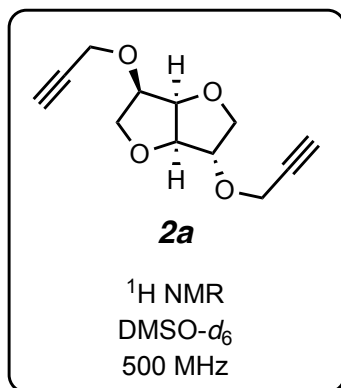
<sup>1</sup> *Biomacromolecules* **2010**, *11*, 2797–2803

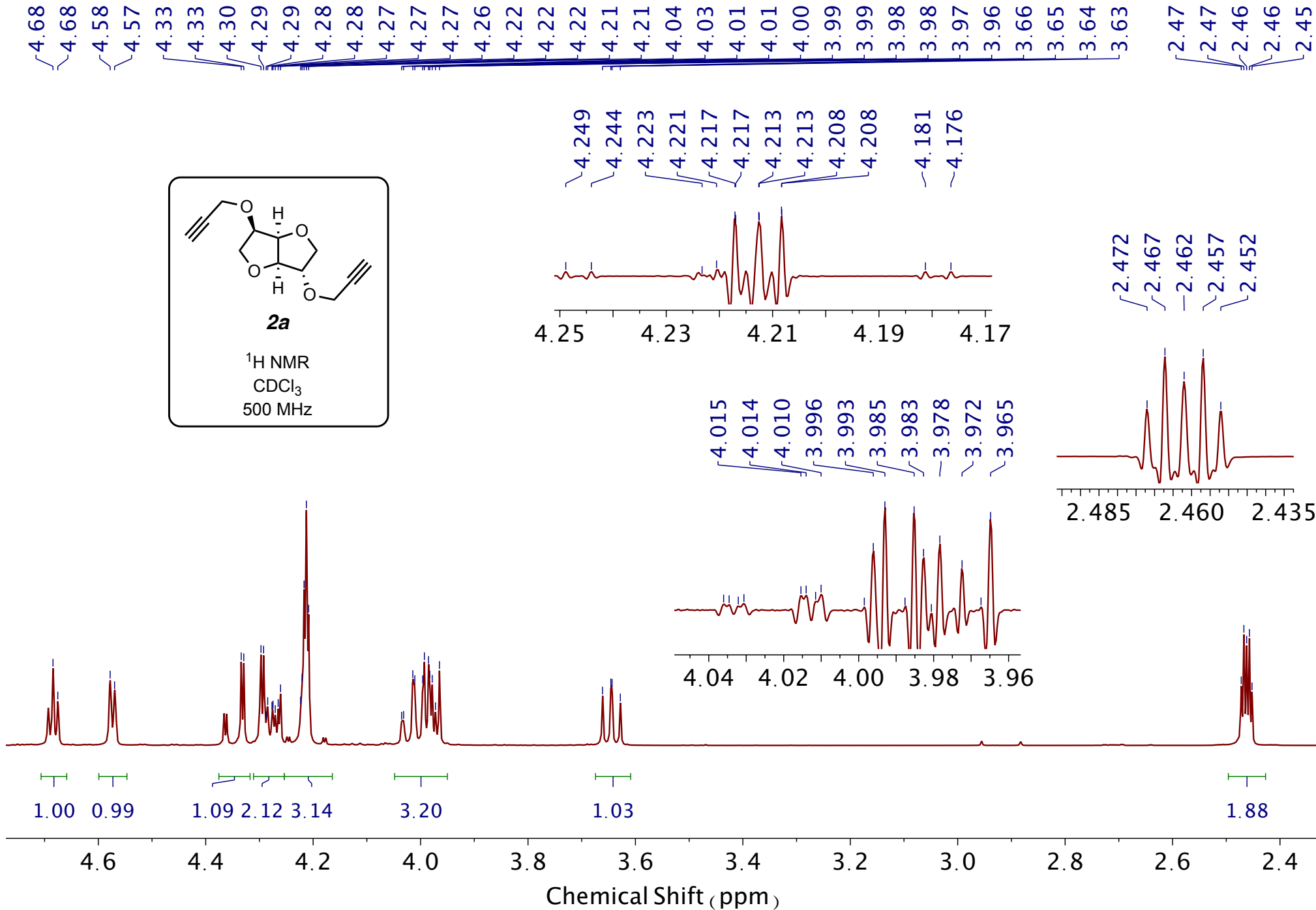
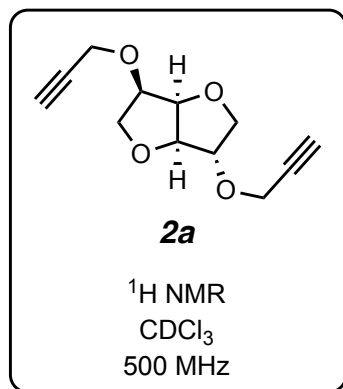
<sup>2</sup> *Green Chem.* **2014**, *16*, 3810–3818

<sup>3</sup> *Biomacromolecules* **2012**, *13*, 4138–4145

<sup>4</sup> *J. Am. Chem. Soc.* **2019**, *13*, 5107–5111

## VII. Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra





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83.01  
80.66  
80.53  
80.23  
78.93  
77.90  
77.85

72.81

69.90

57.33

56.46

40.50

40.33

40.26

40.16

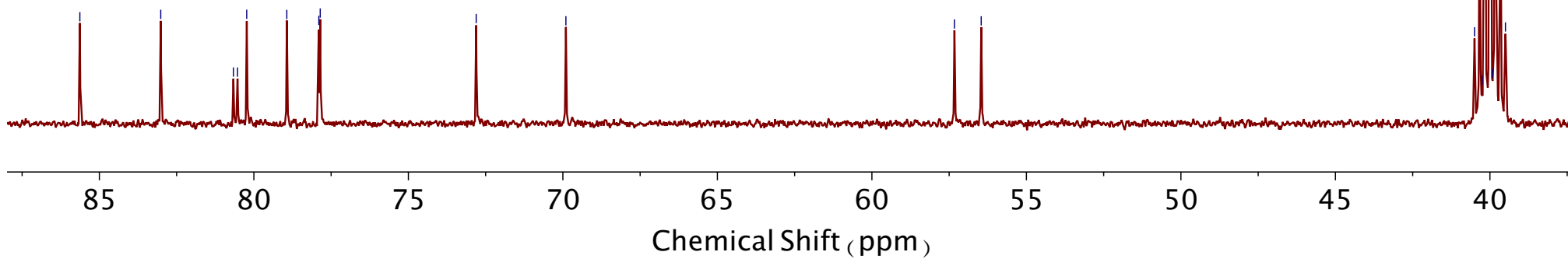
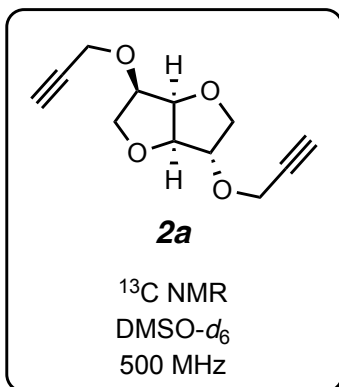
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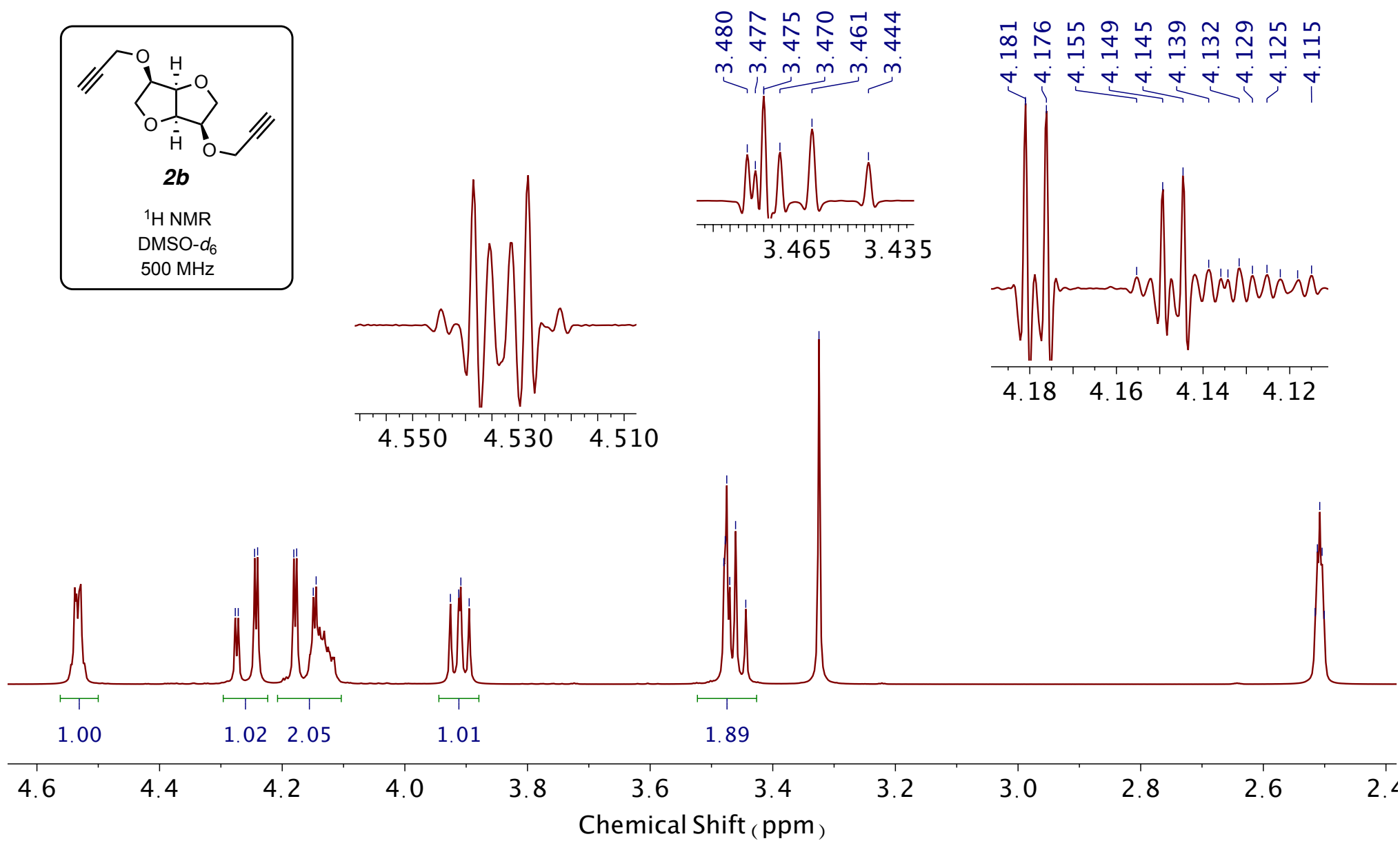
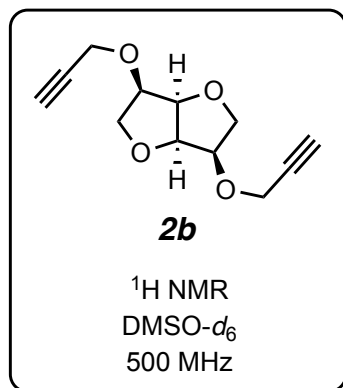




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4.27  
4.25  
4.24  
4.18  
4.18  
4.15  
4.14  
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3.91  
3.90

3.48  
3.48  
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3.32

2.52  
2.51  
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2.50  
2.50

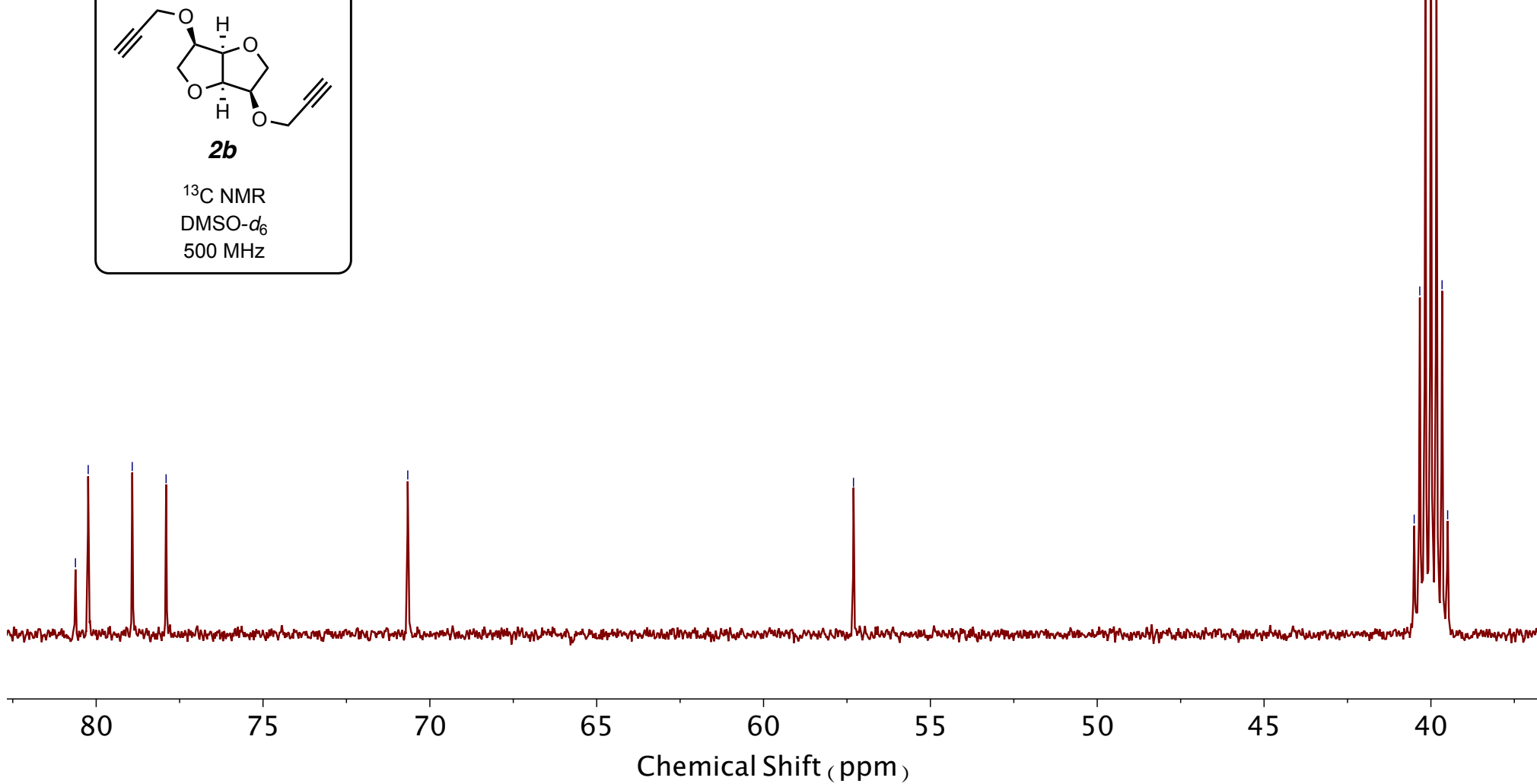
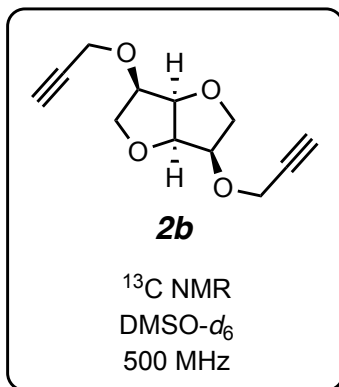


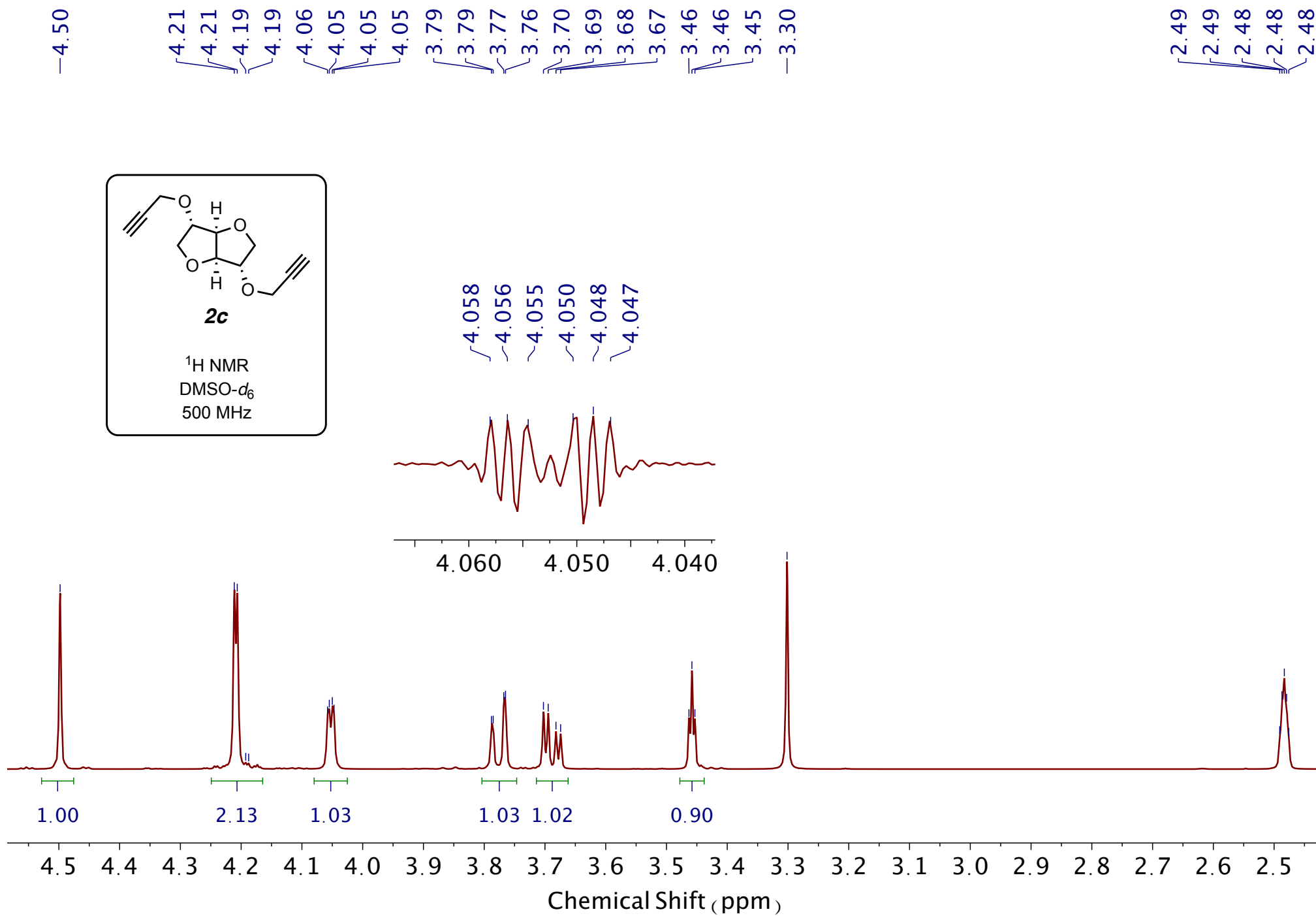
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70.66

57.30

40.50  
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39.67  
39.50



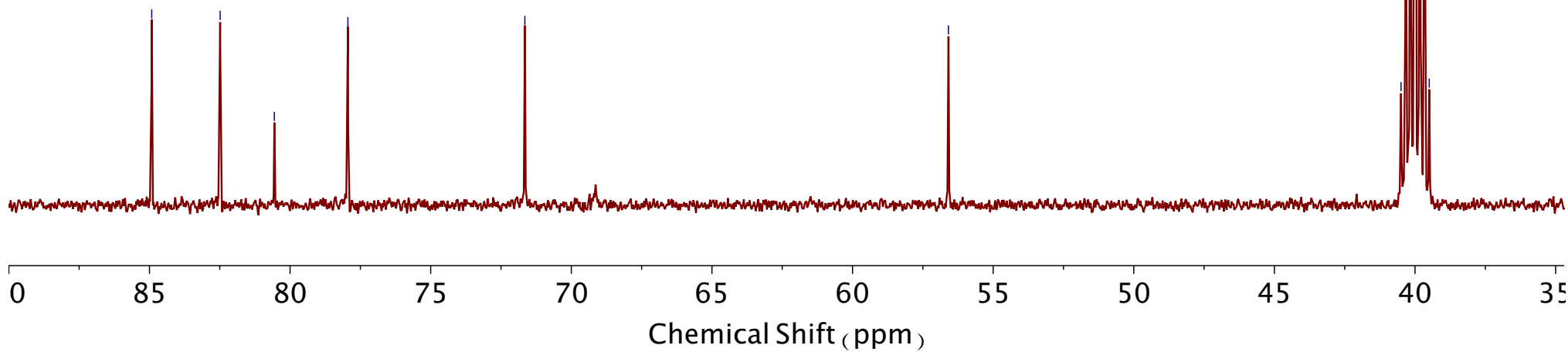
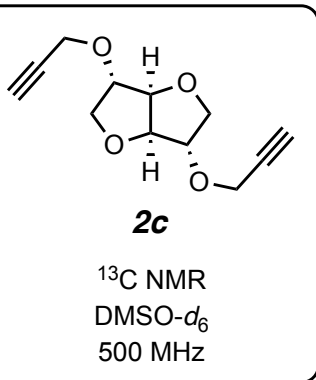


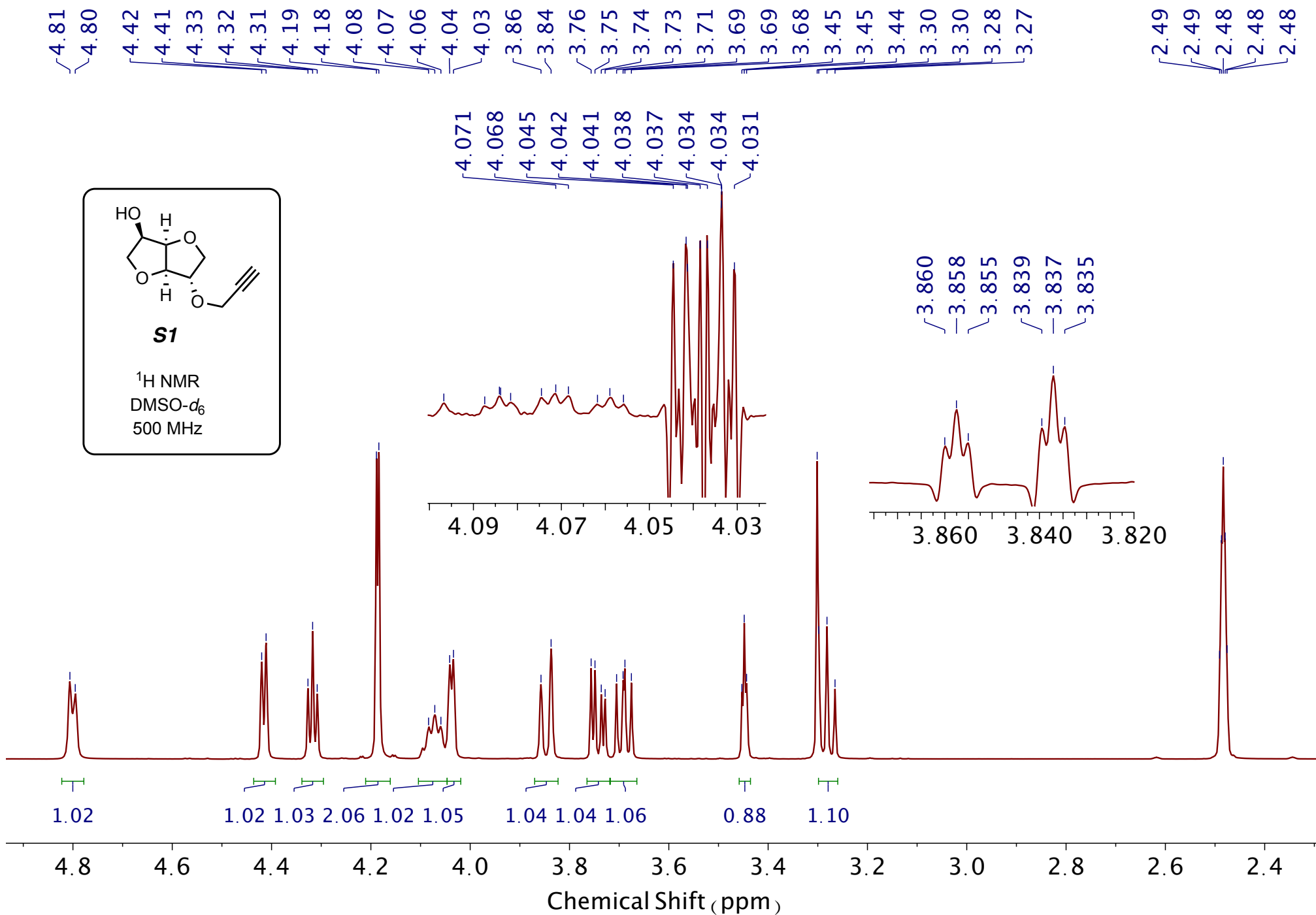
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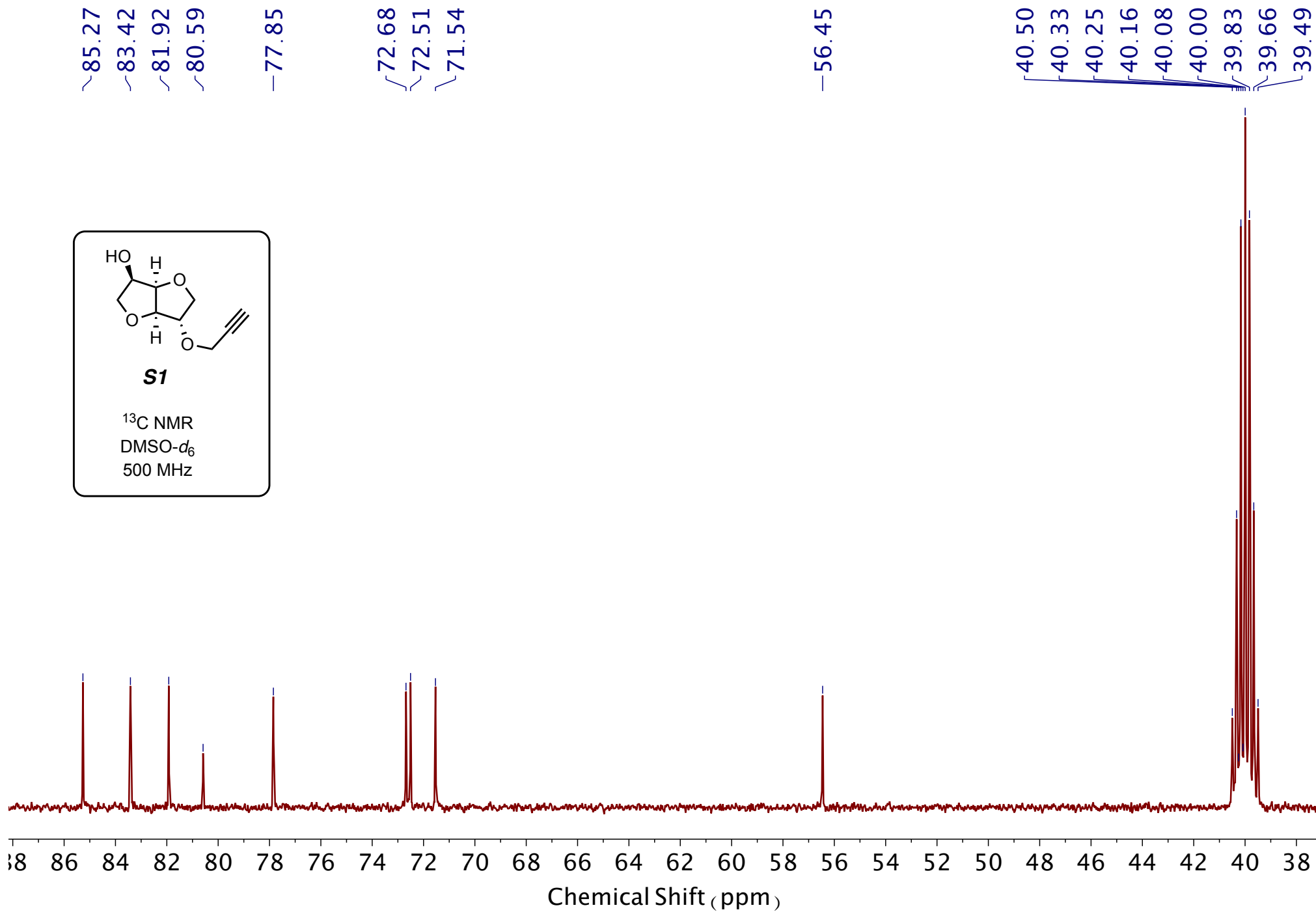
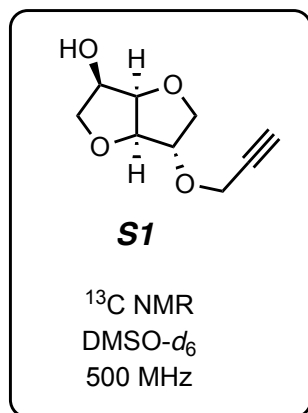
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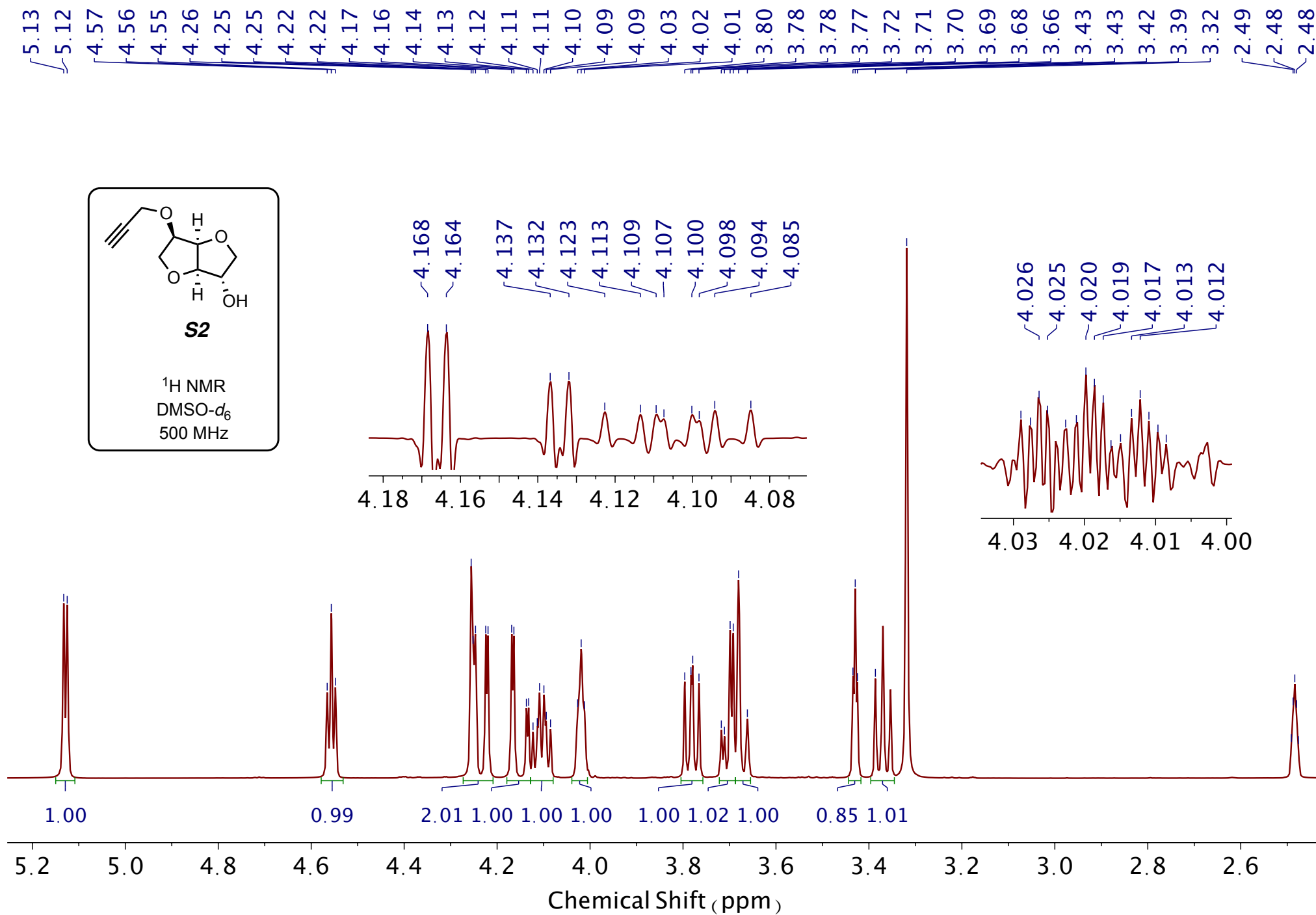
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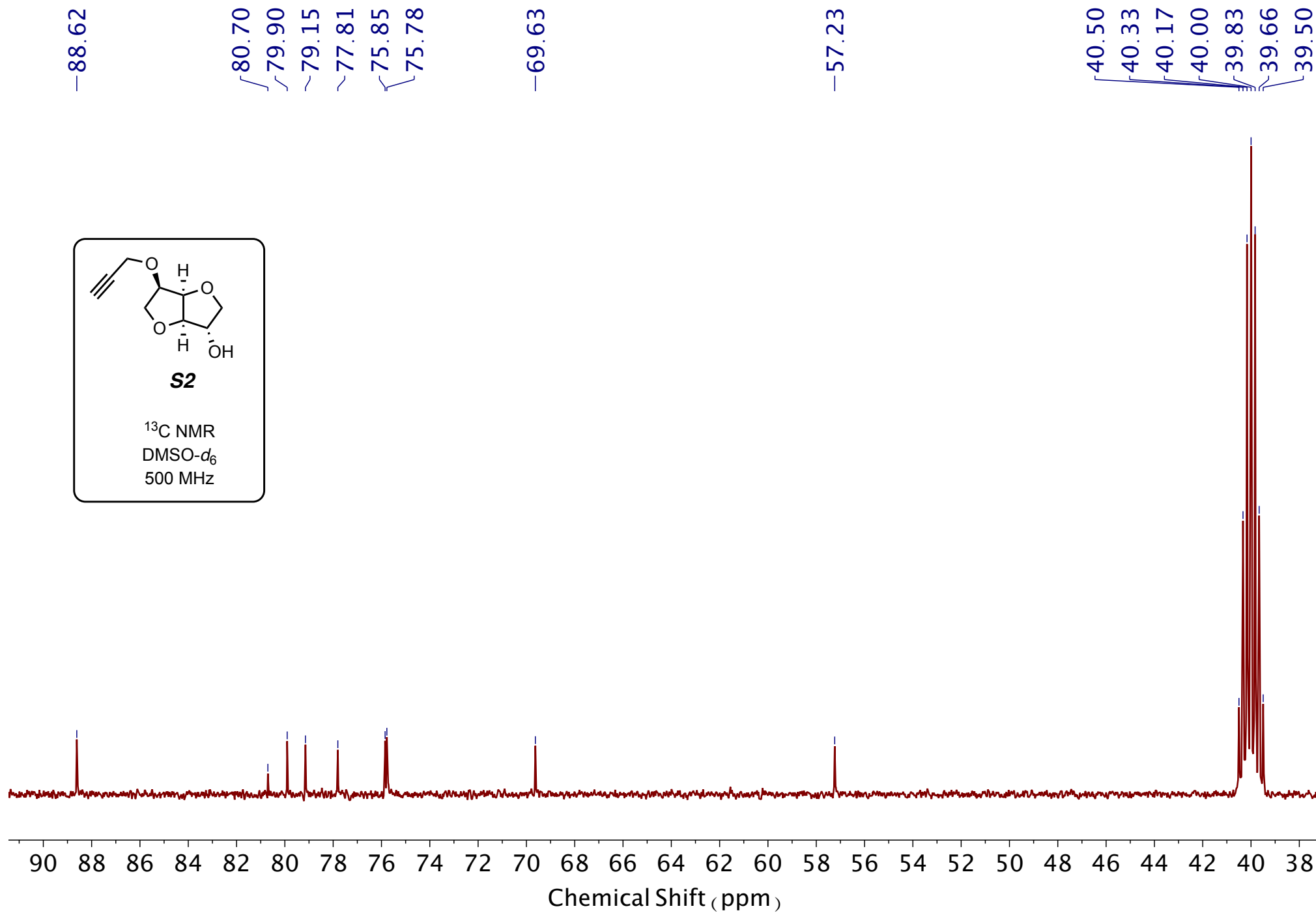
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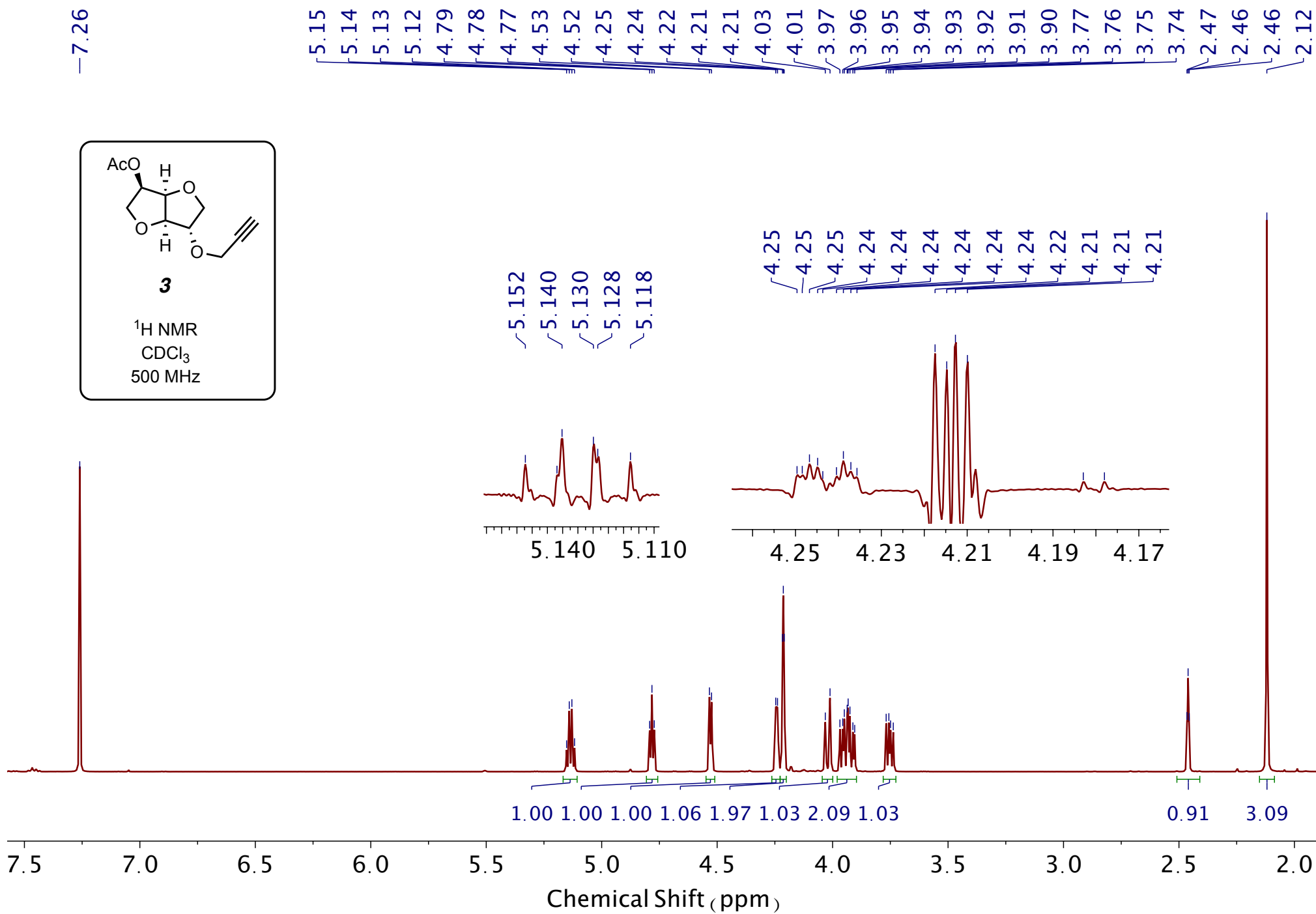


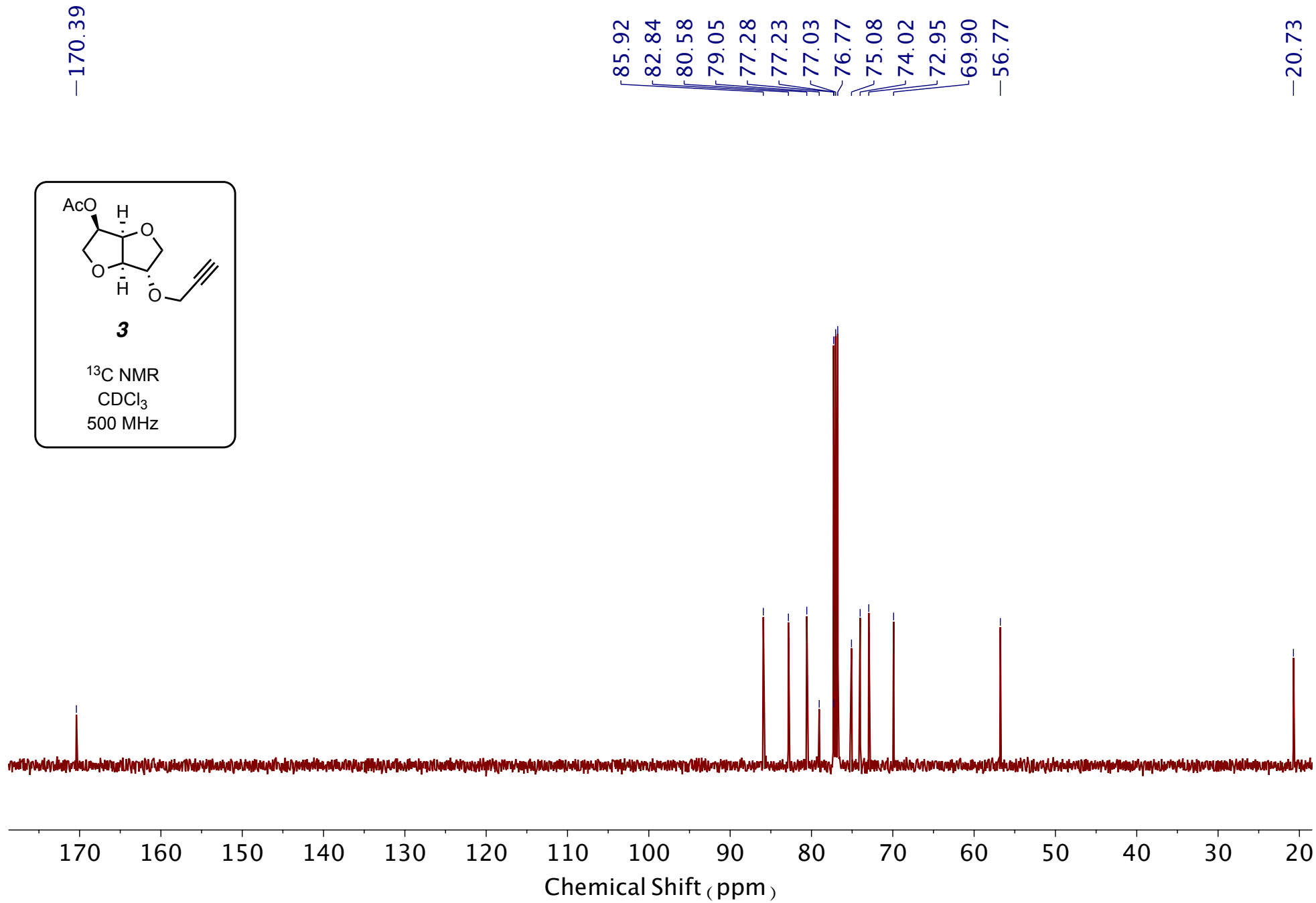












-7.26

5.15

5.13

5.12

5.11

4.78

4.77

4.76

4.50

4.49

4.28

4.21

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4.01

3.99

3.96

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3.94

3.93

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3.91

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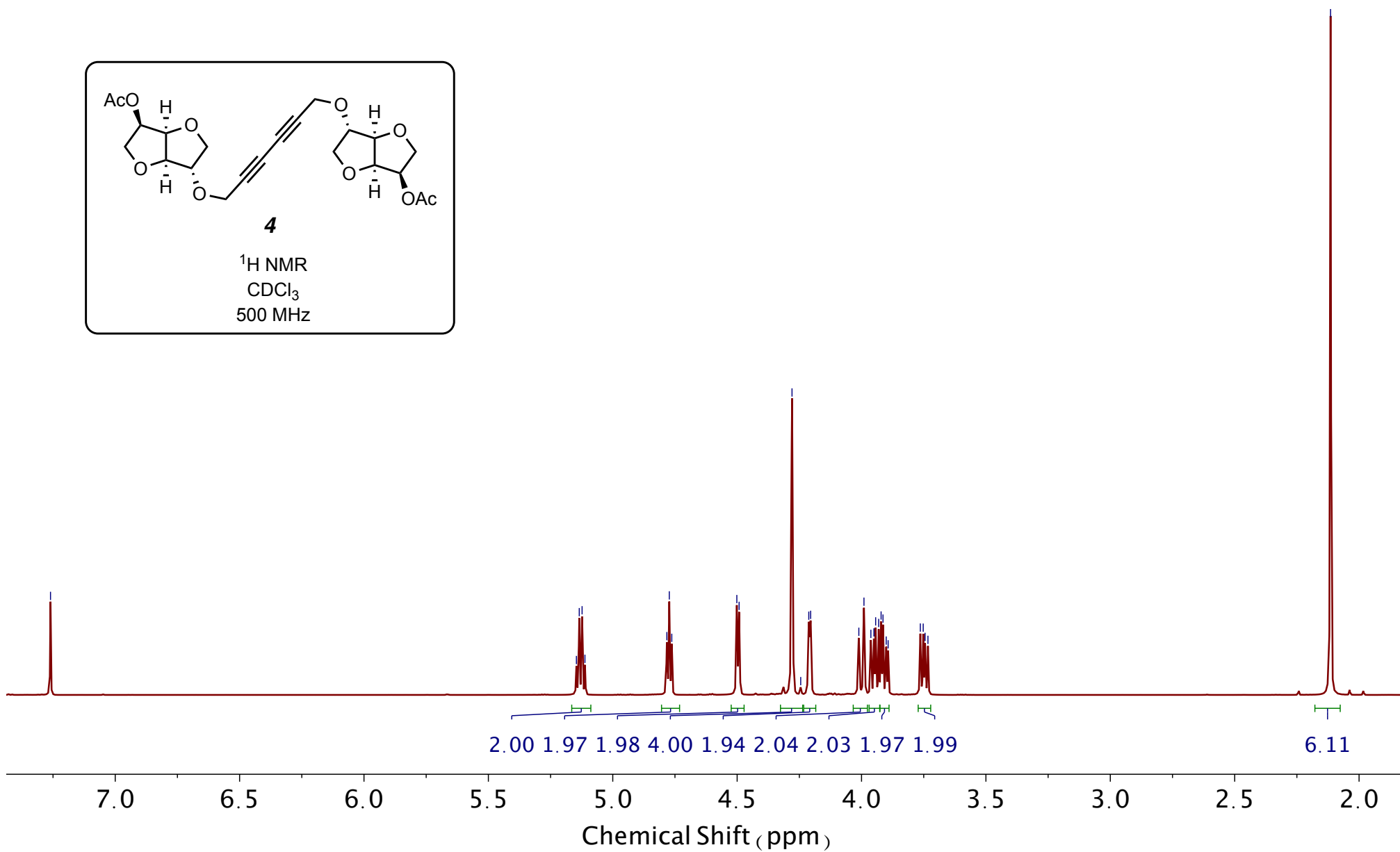
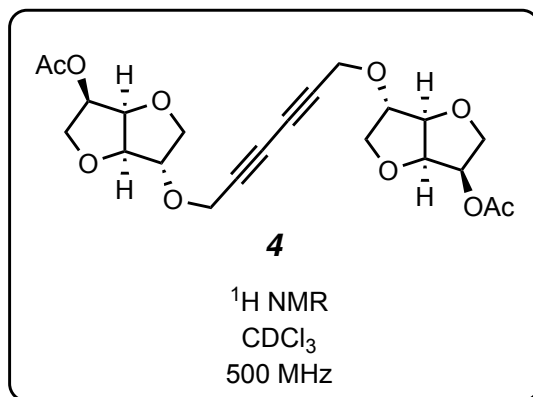
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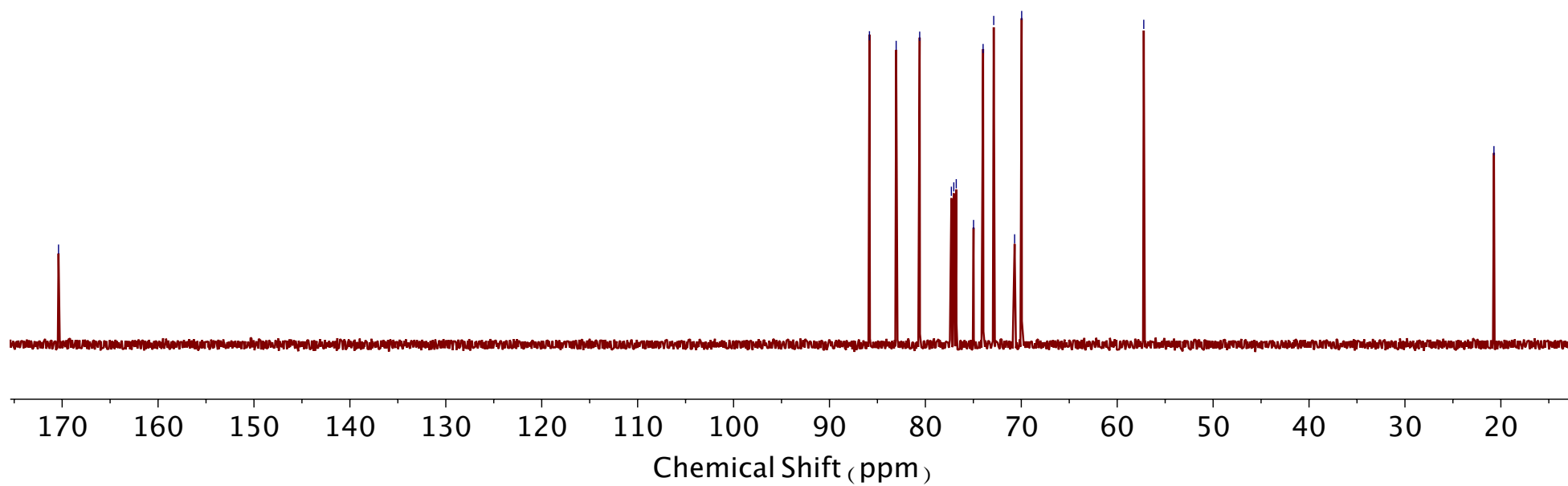
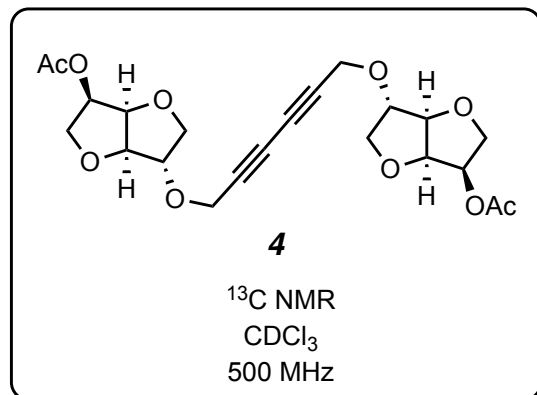
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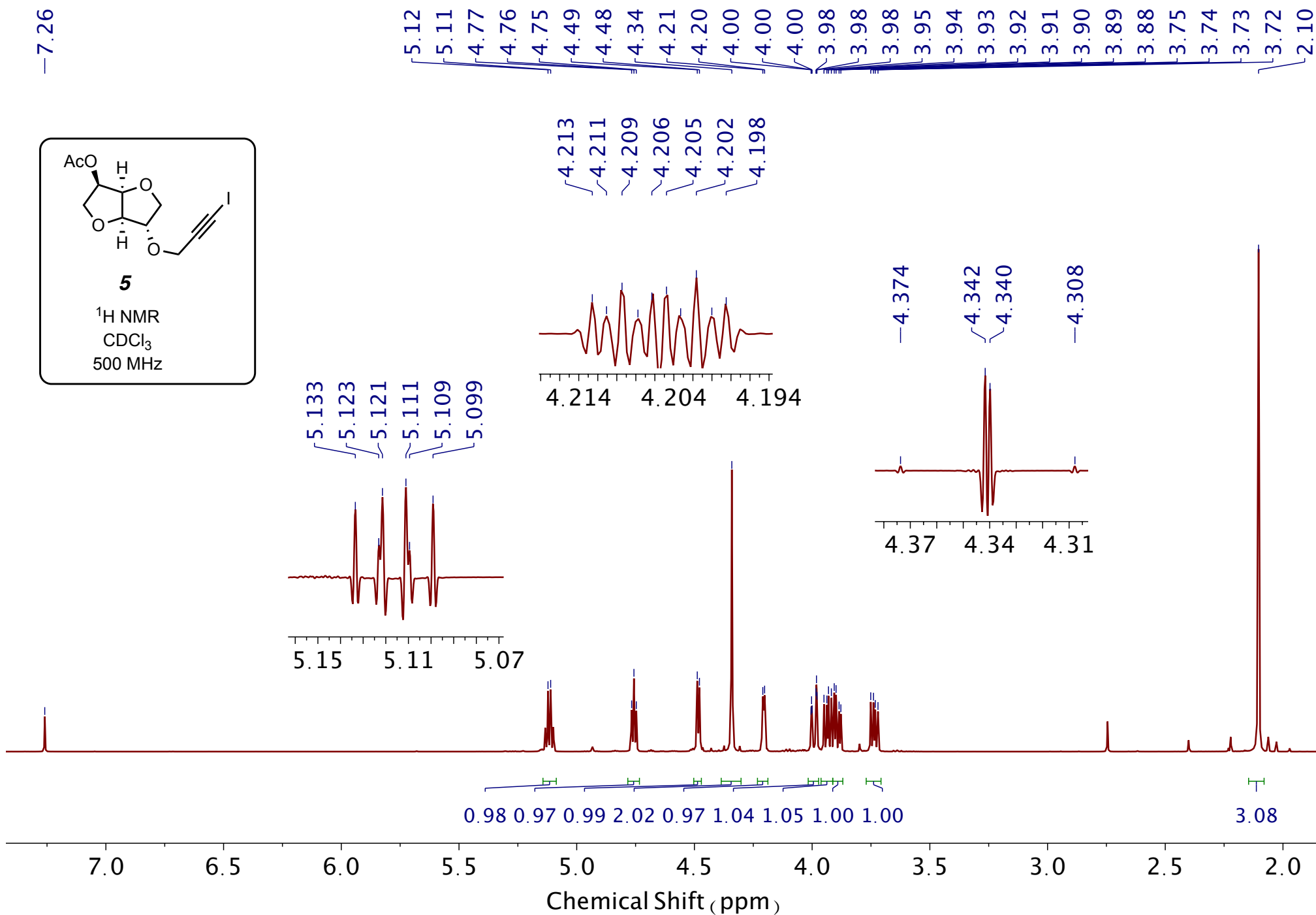


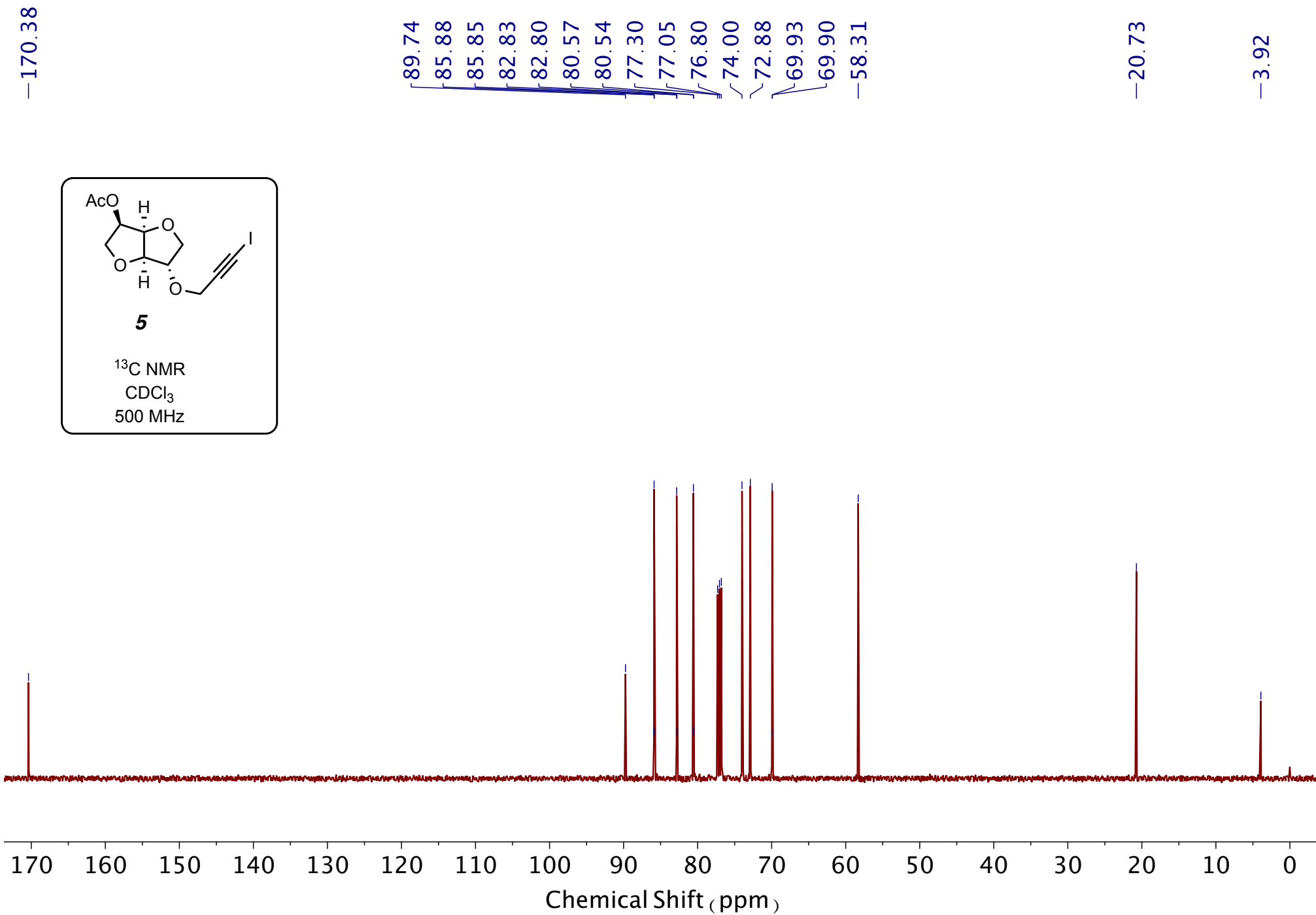
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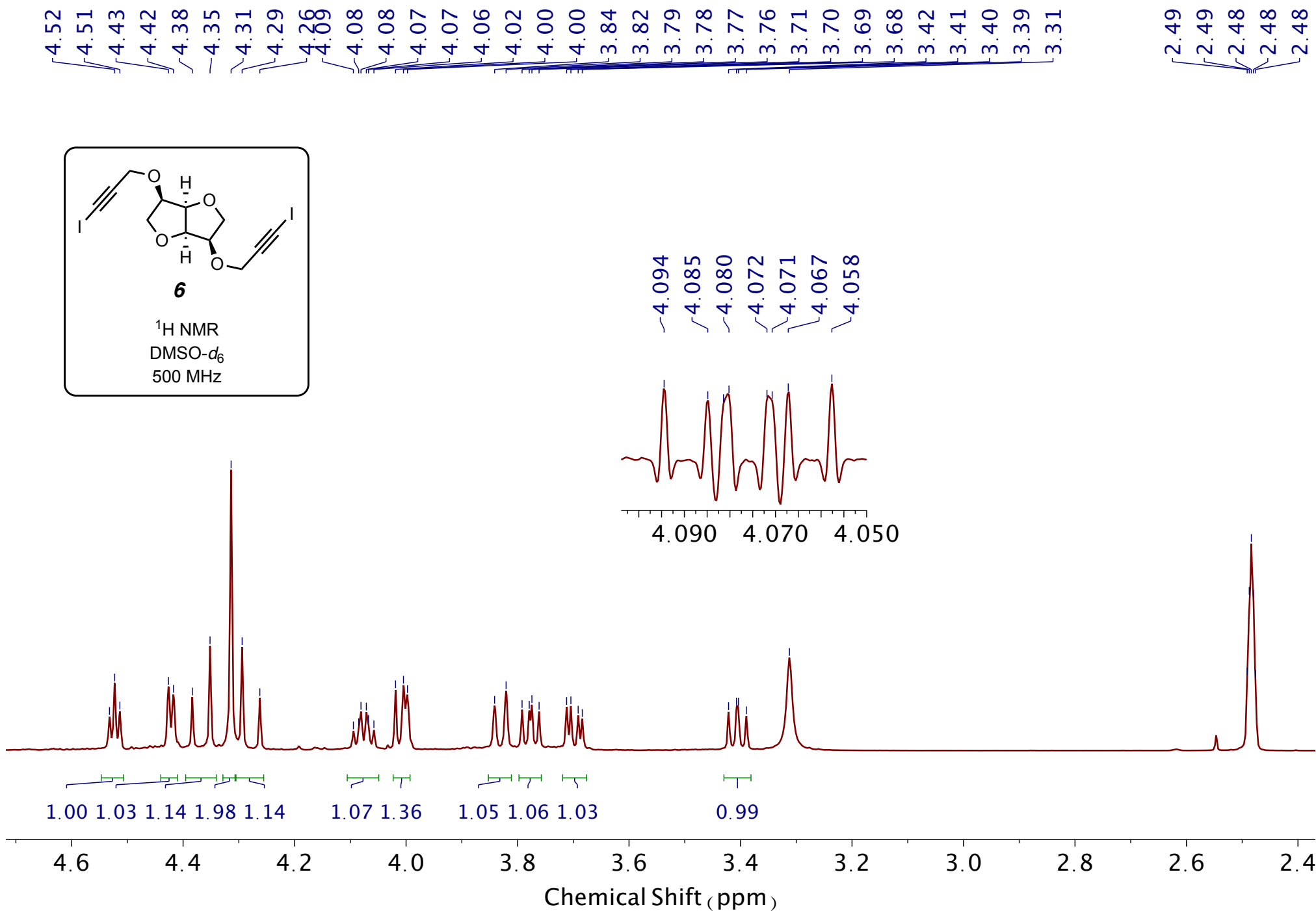
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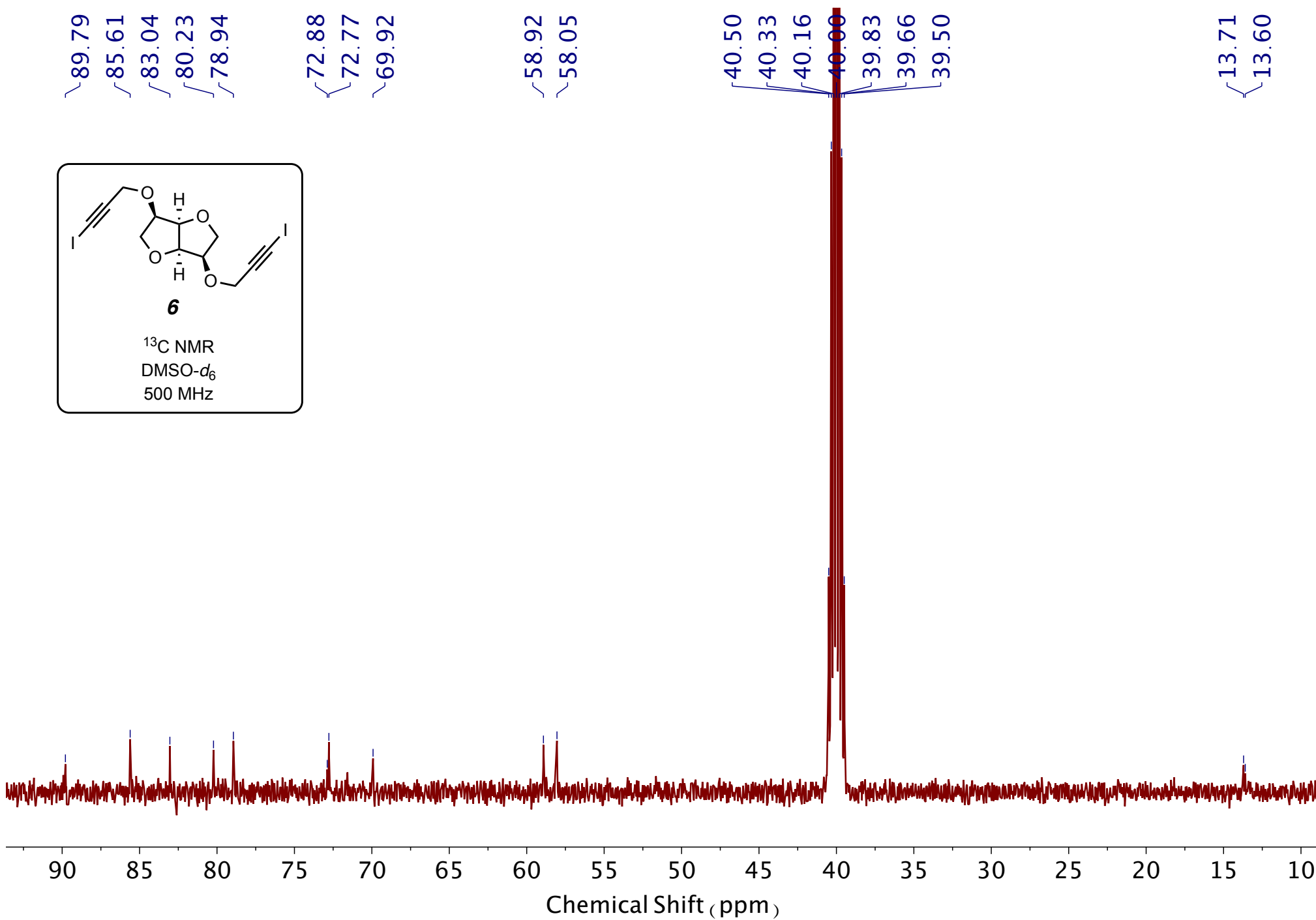
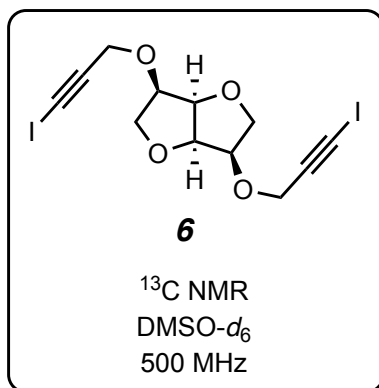
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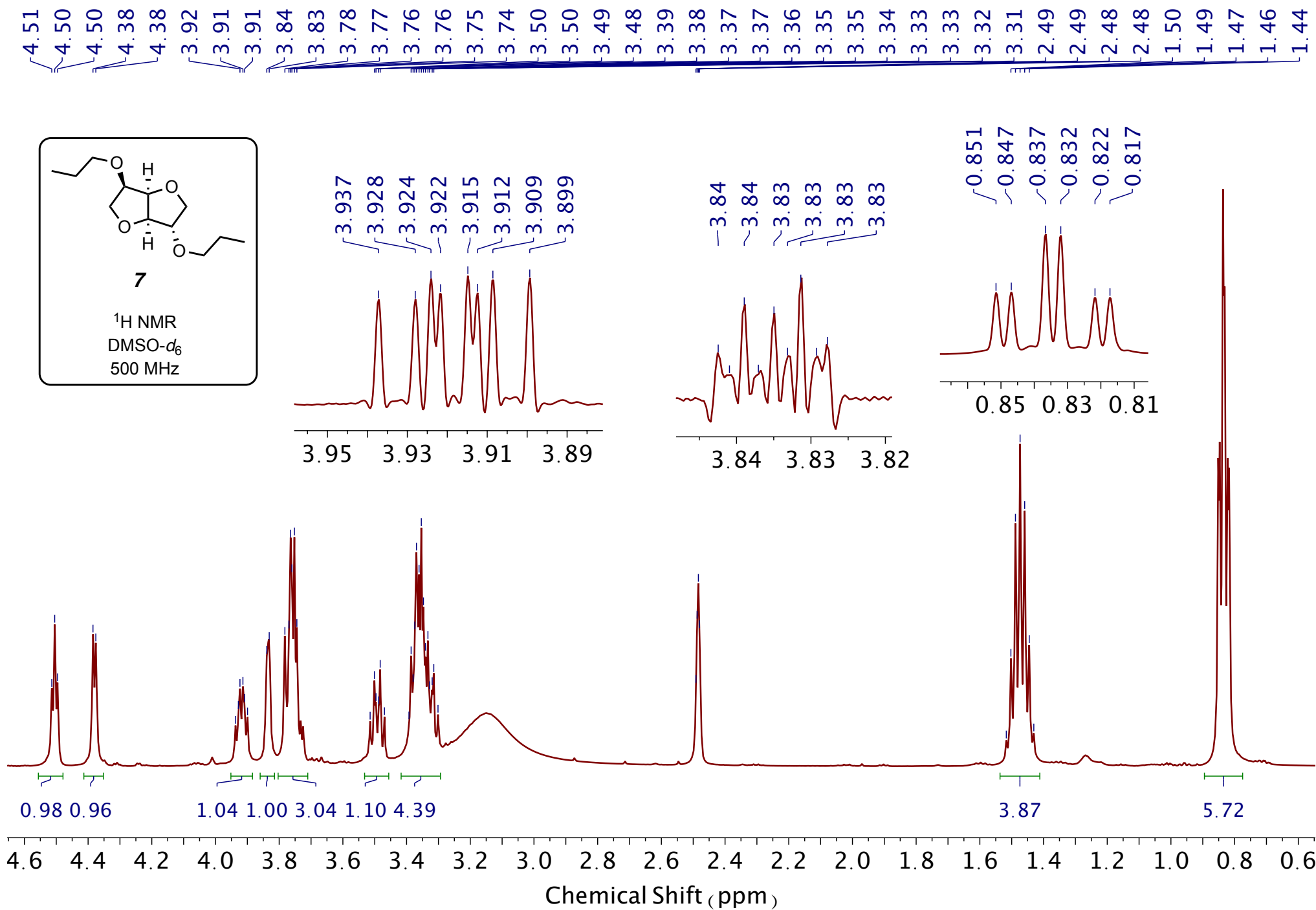


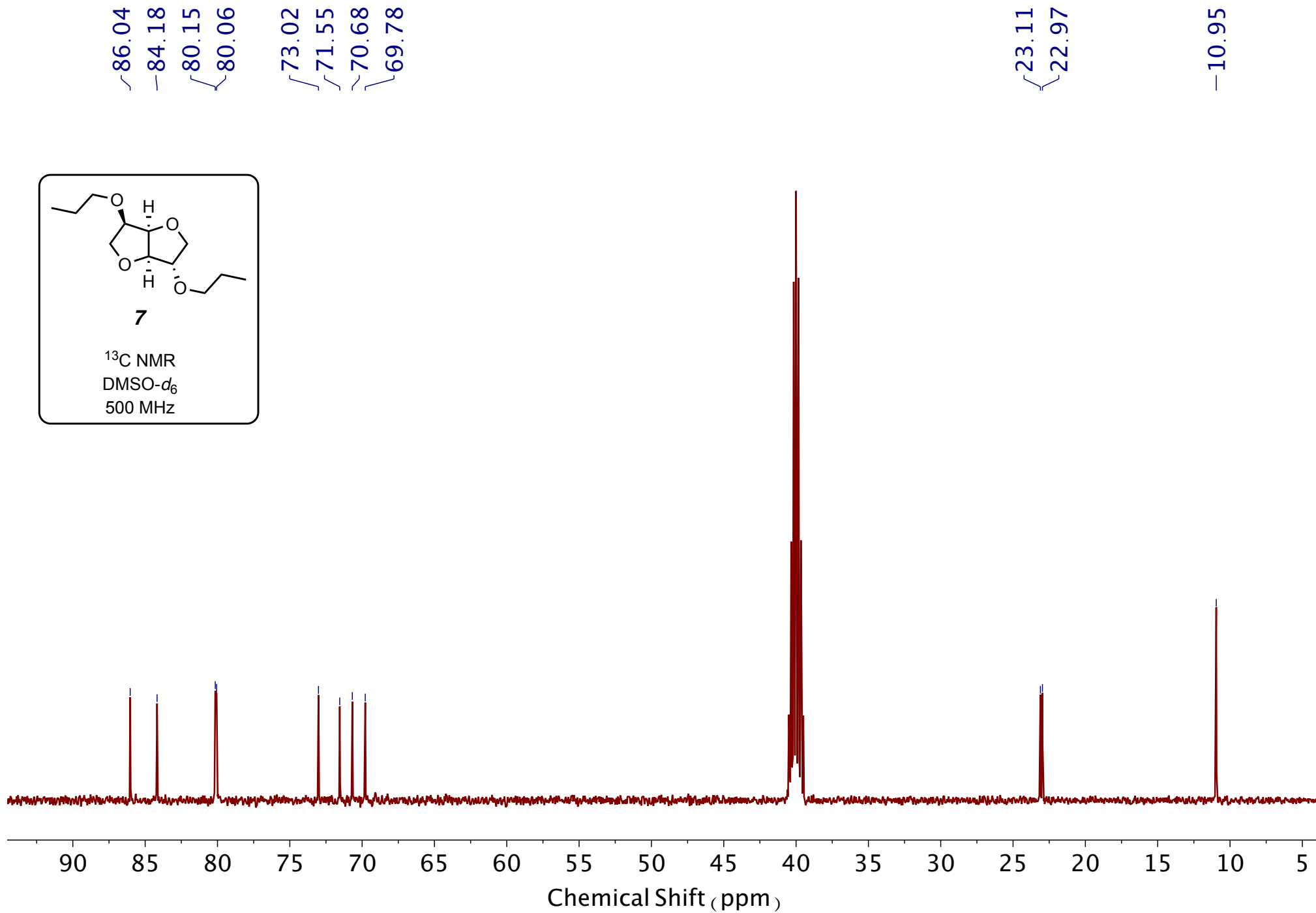
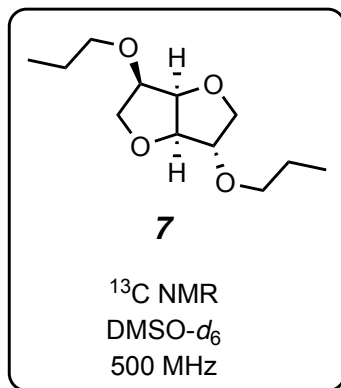


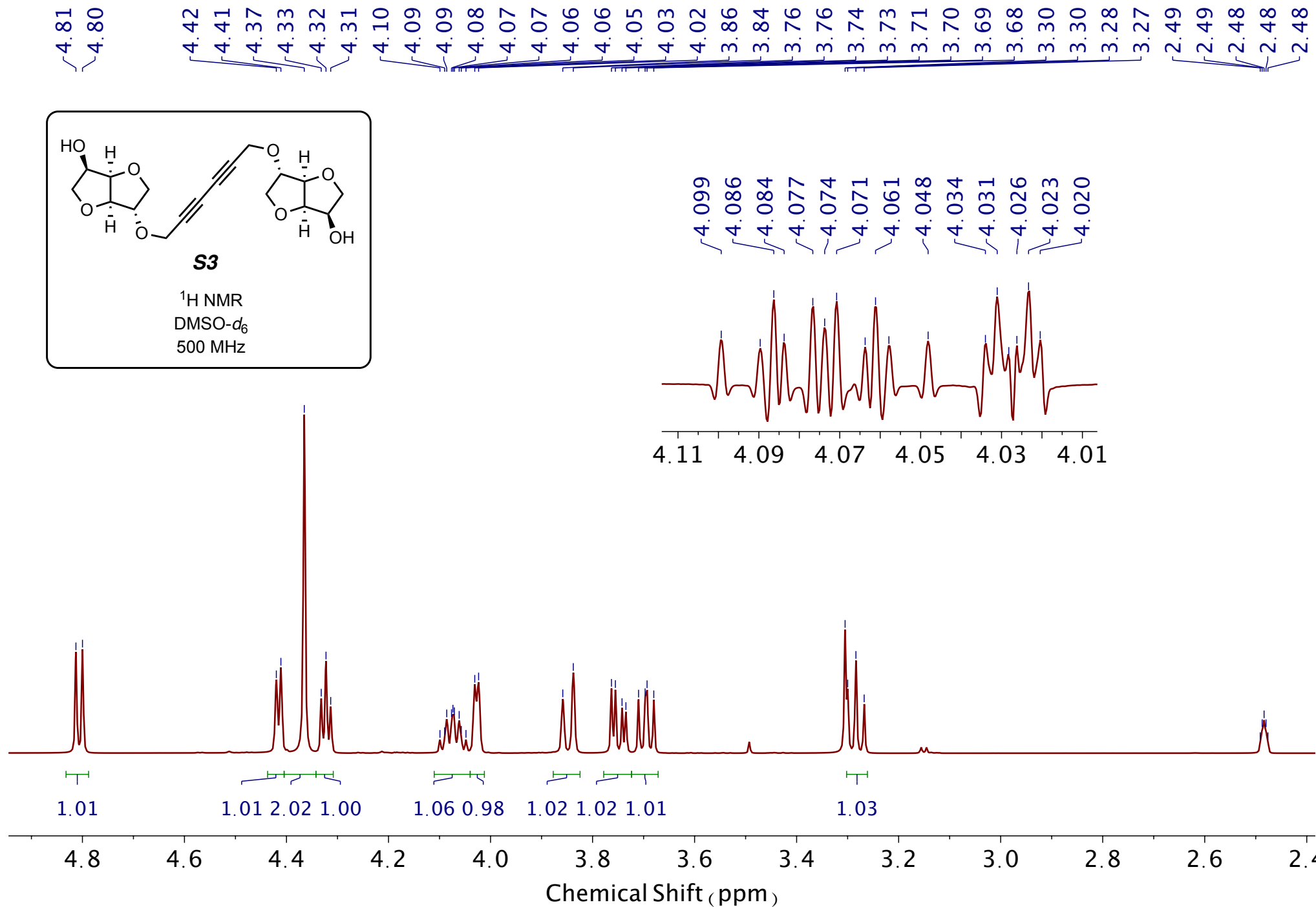


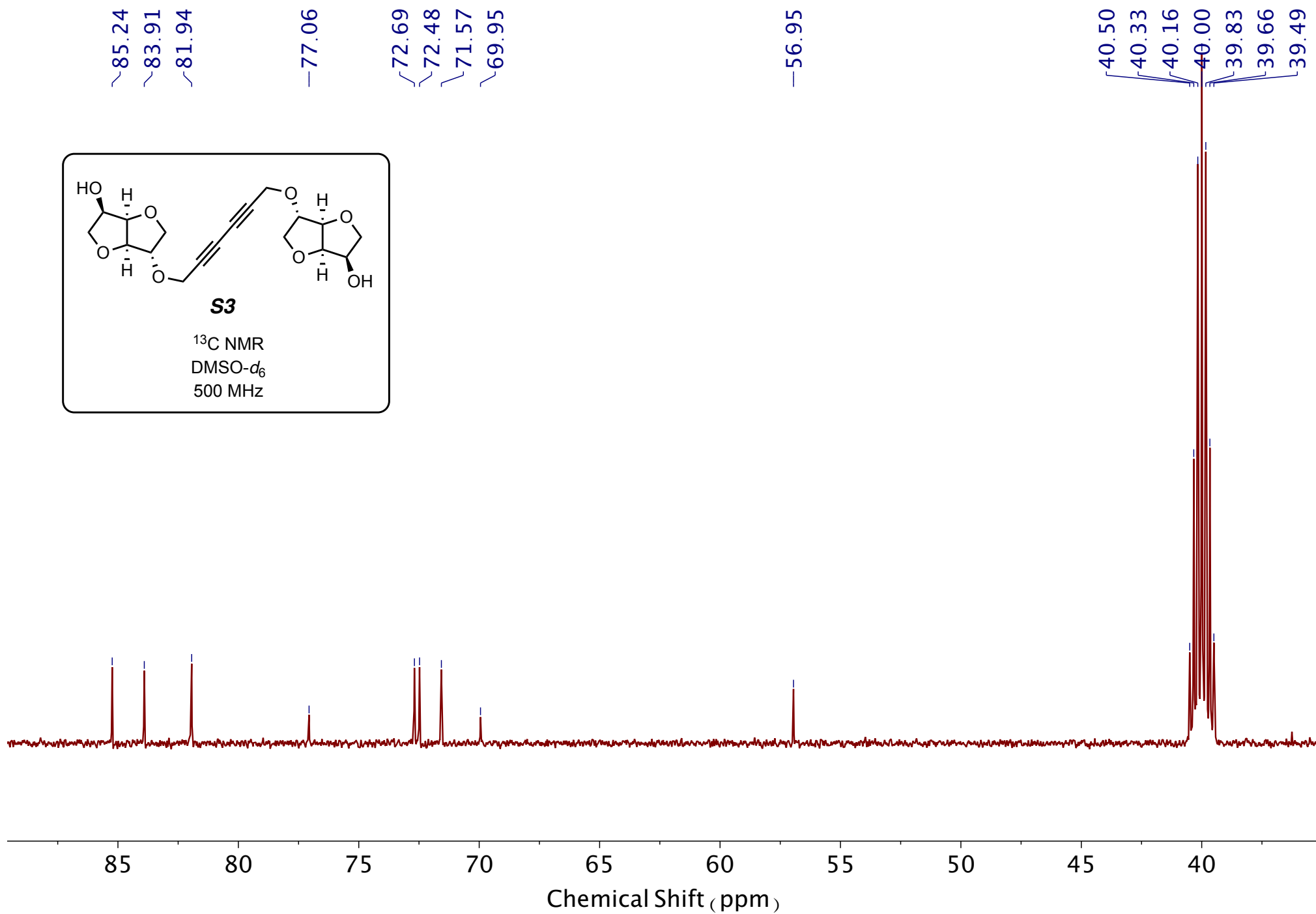


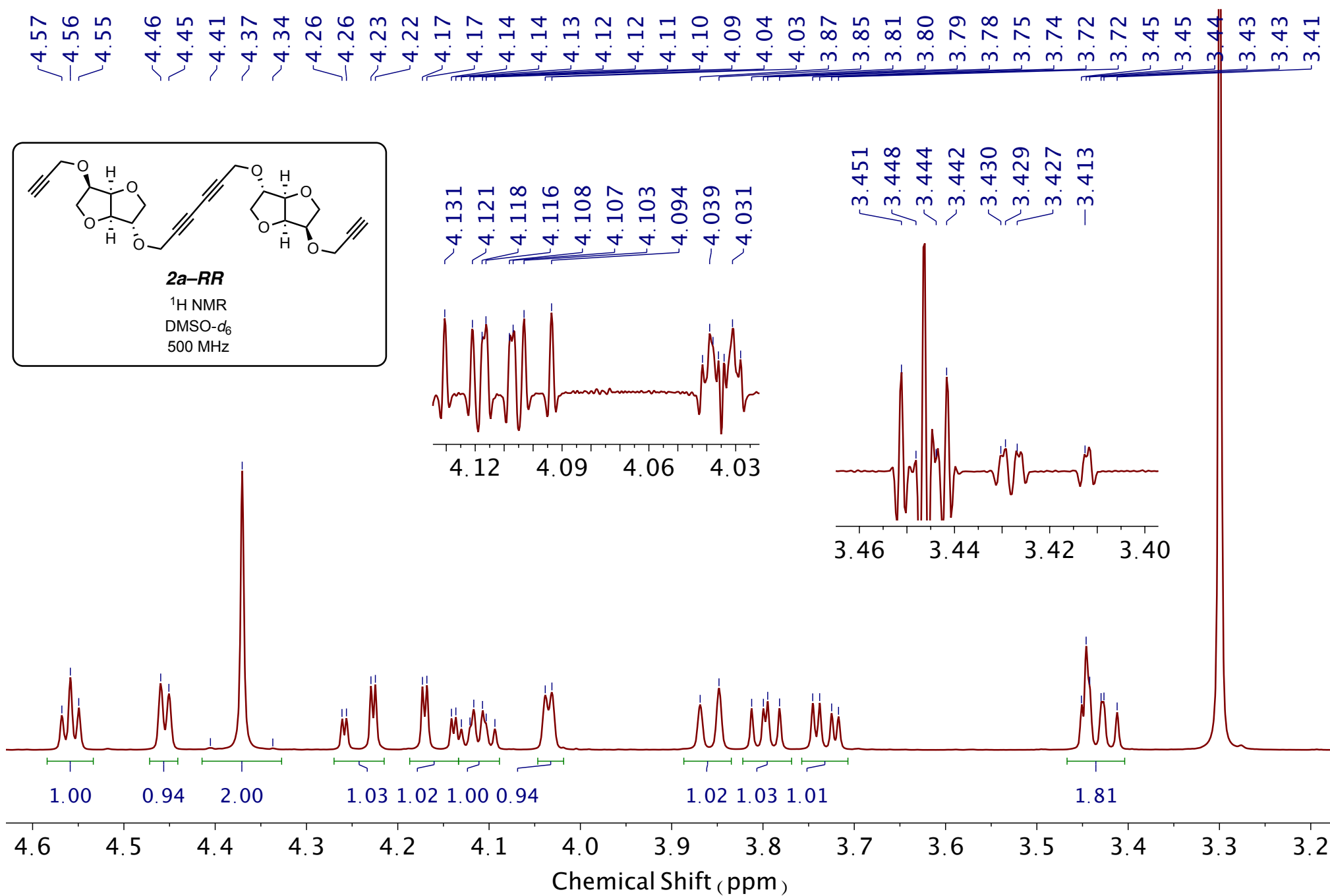


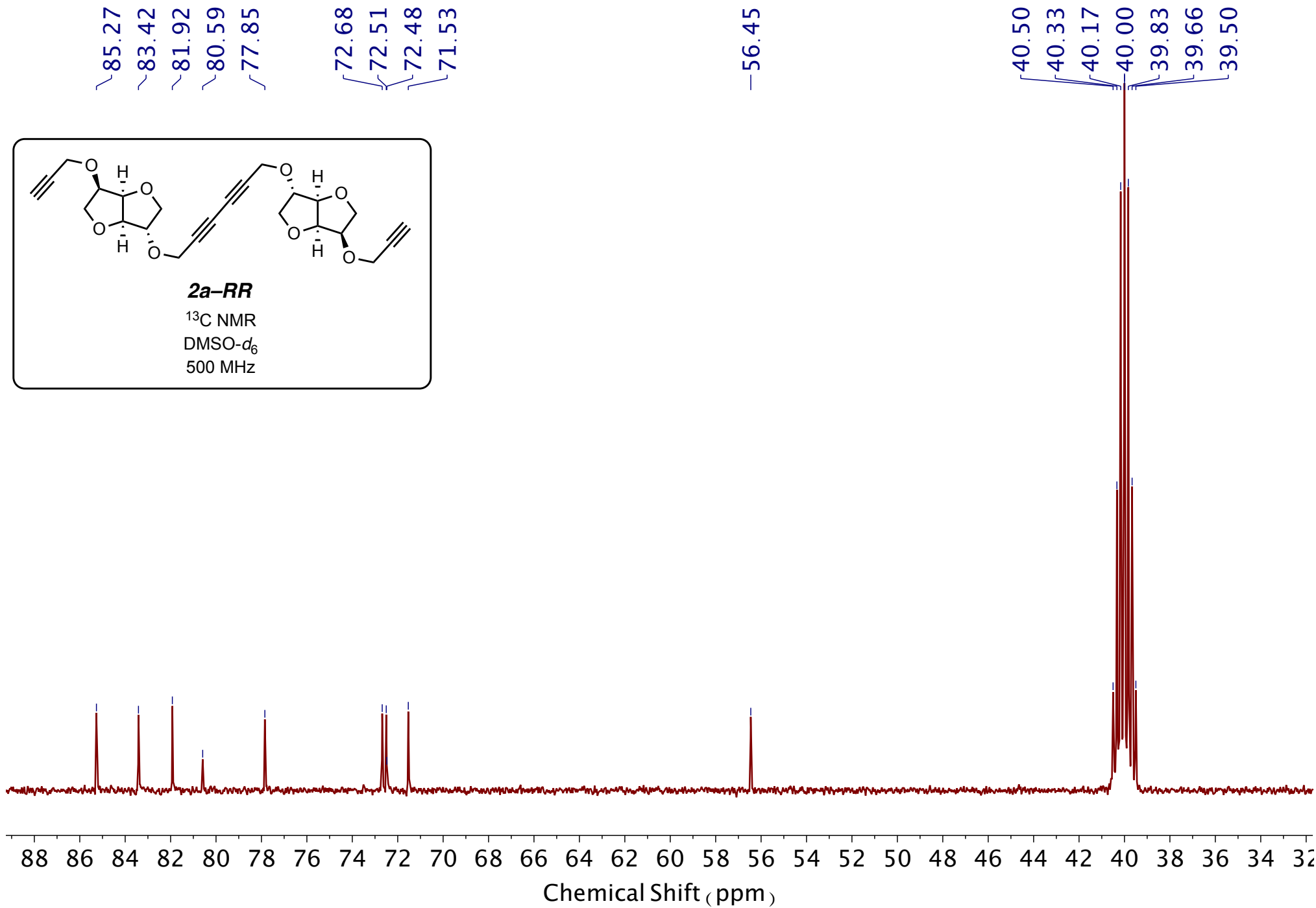
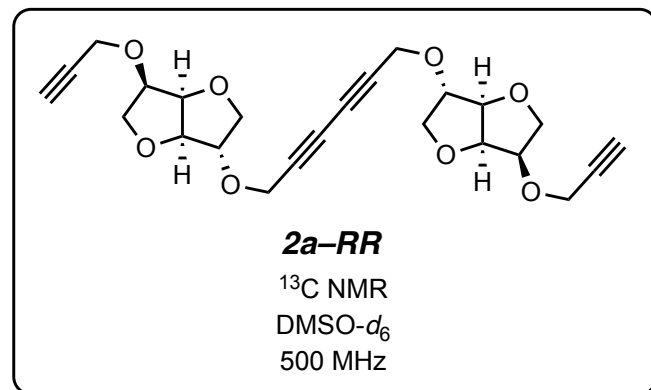


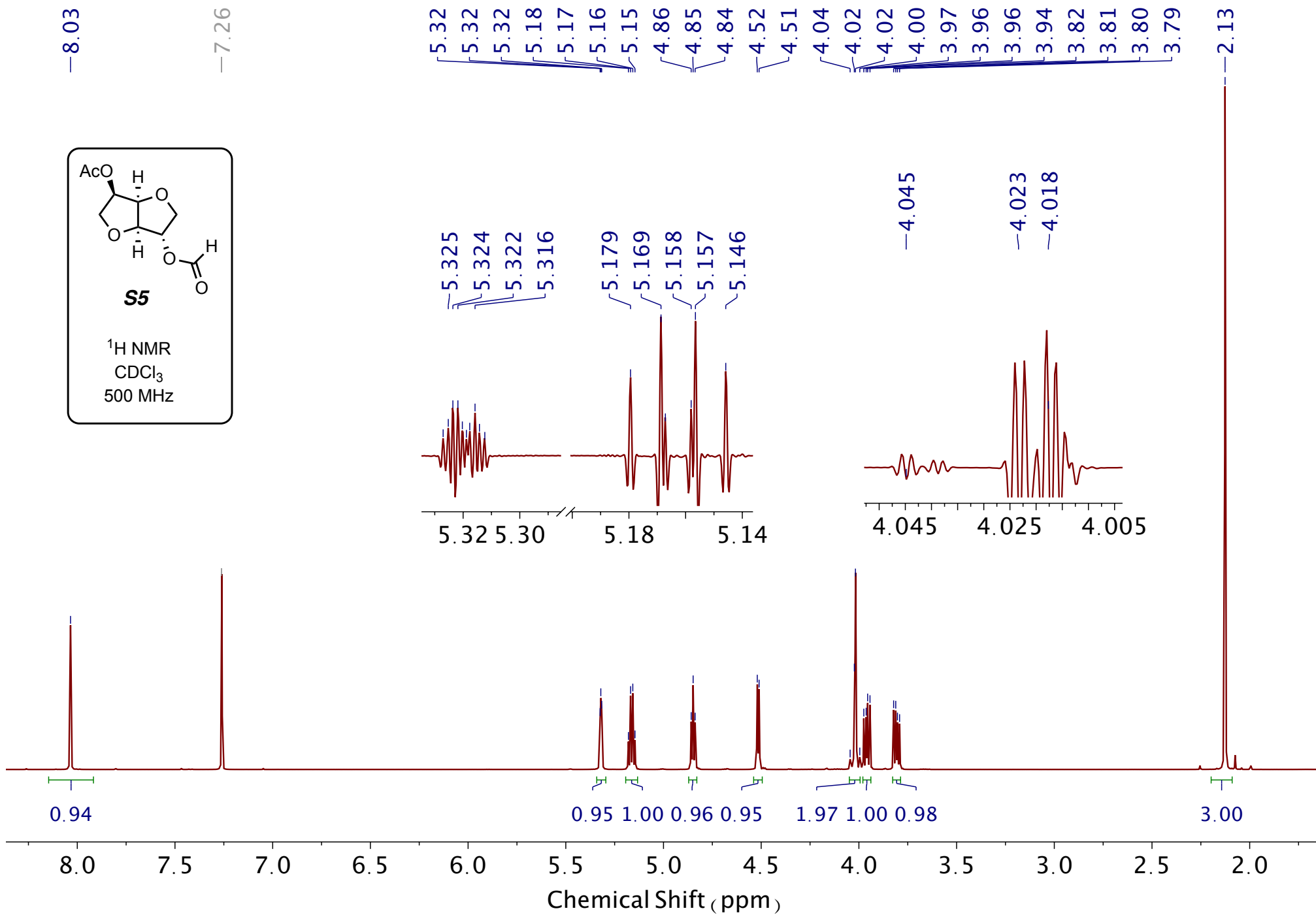












—170.32

—159.77

85.74

80.81

77.57

77.28

77.23

77.03

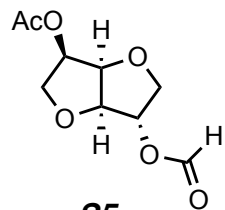
76.77

73.86

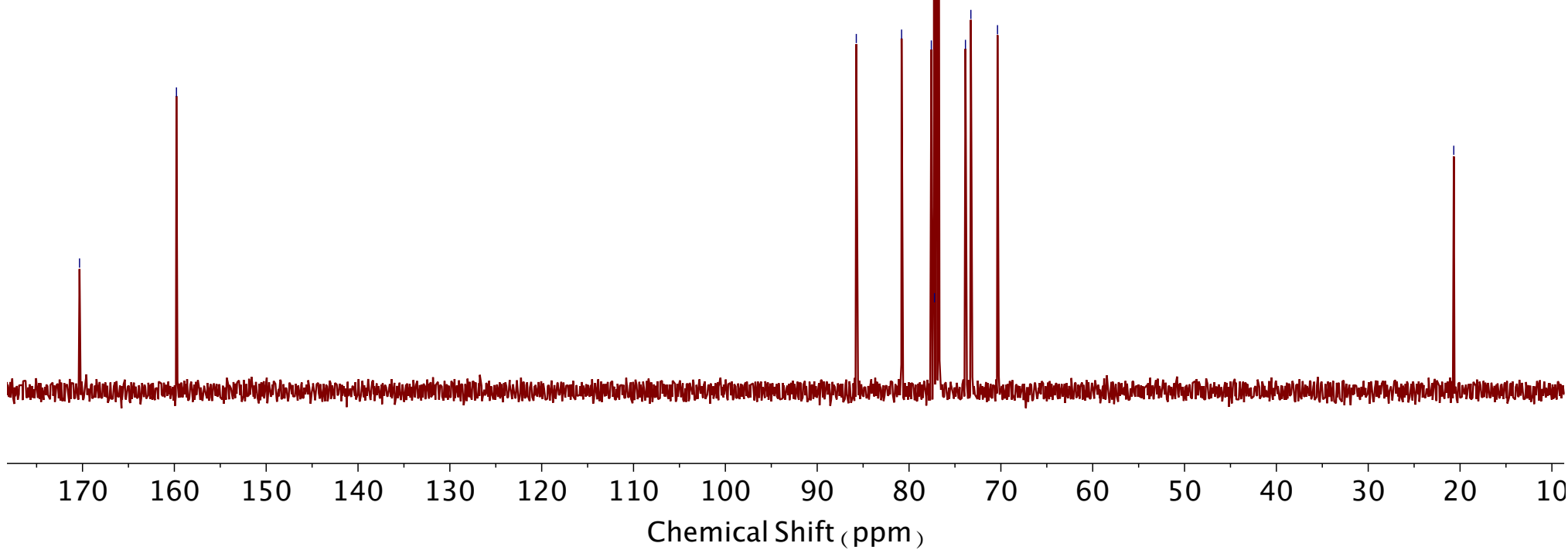
73.27

70.37

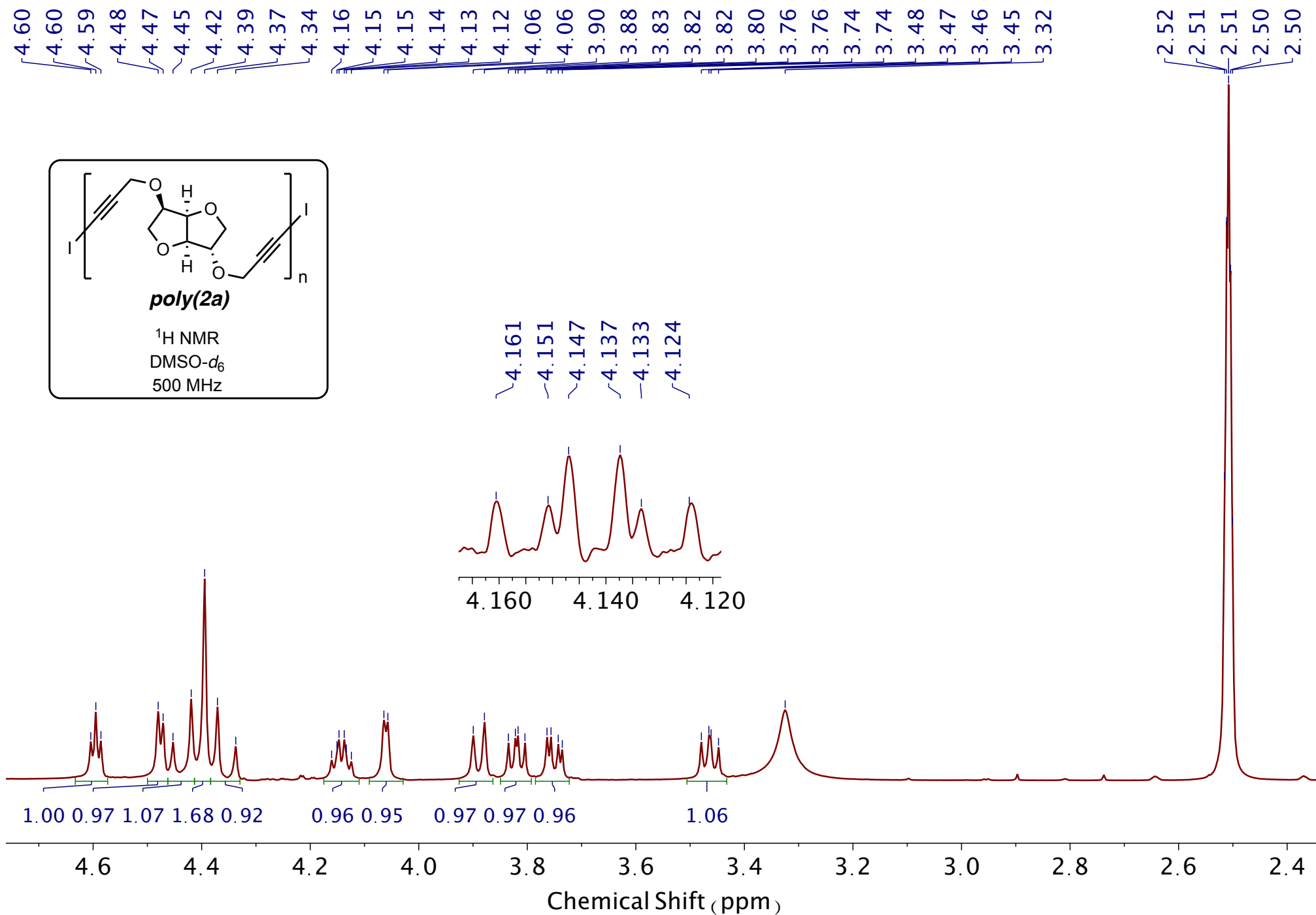
—20.68

**S5**

$^{13}\text{C}$  NMR  
 $\text{CDCl}_3$   
500 MHz



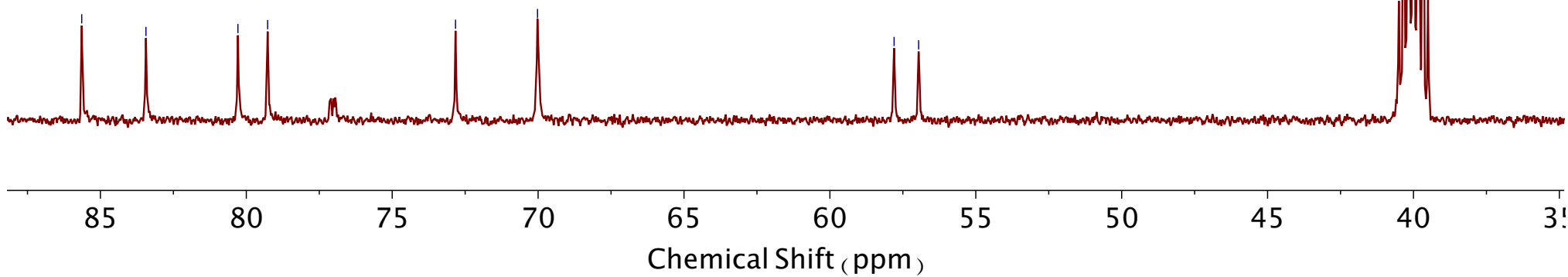
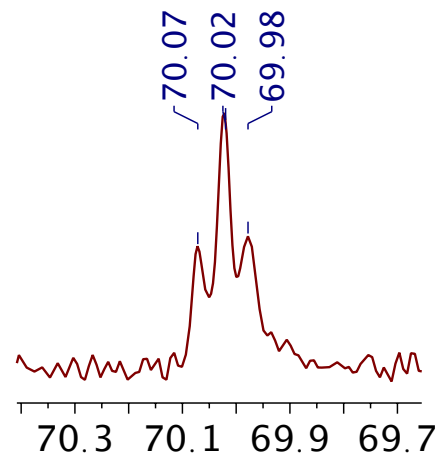
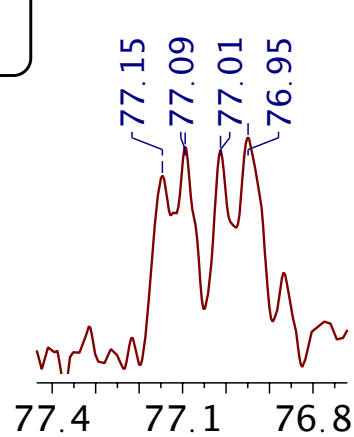
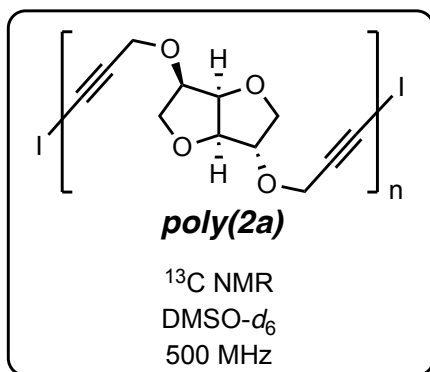


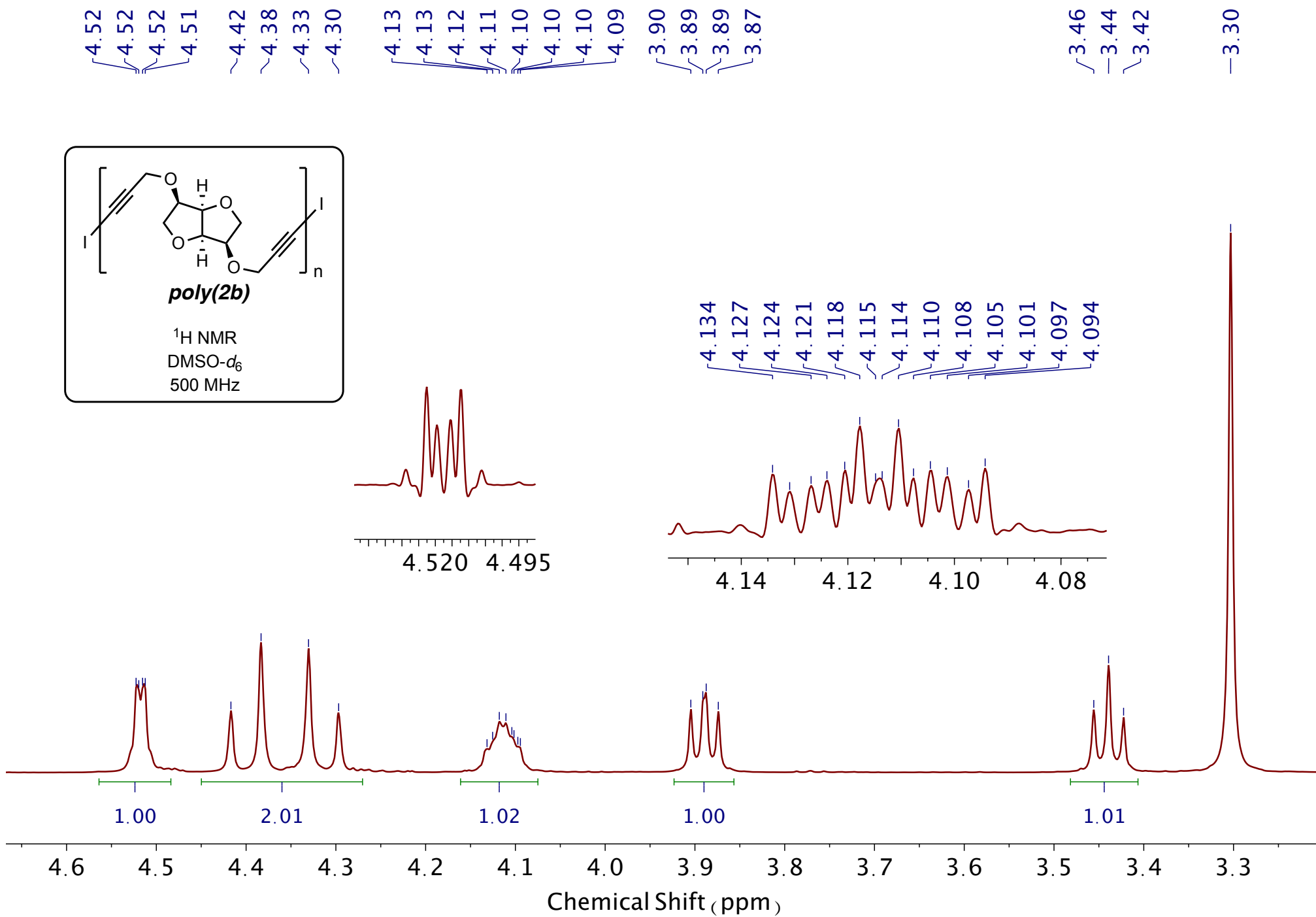


—85.64  
—83.44  
~80.29  
~79.27

—72.83  
—70.02

~57.80  
~56.96



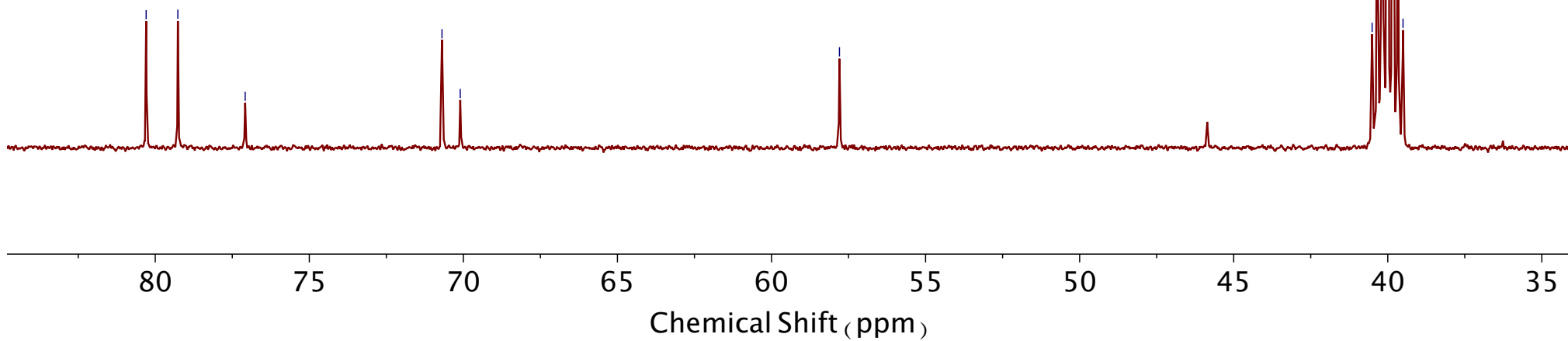
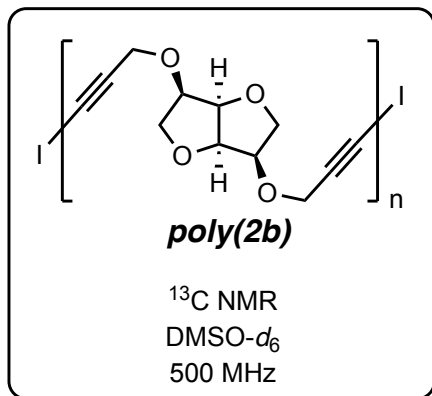


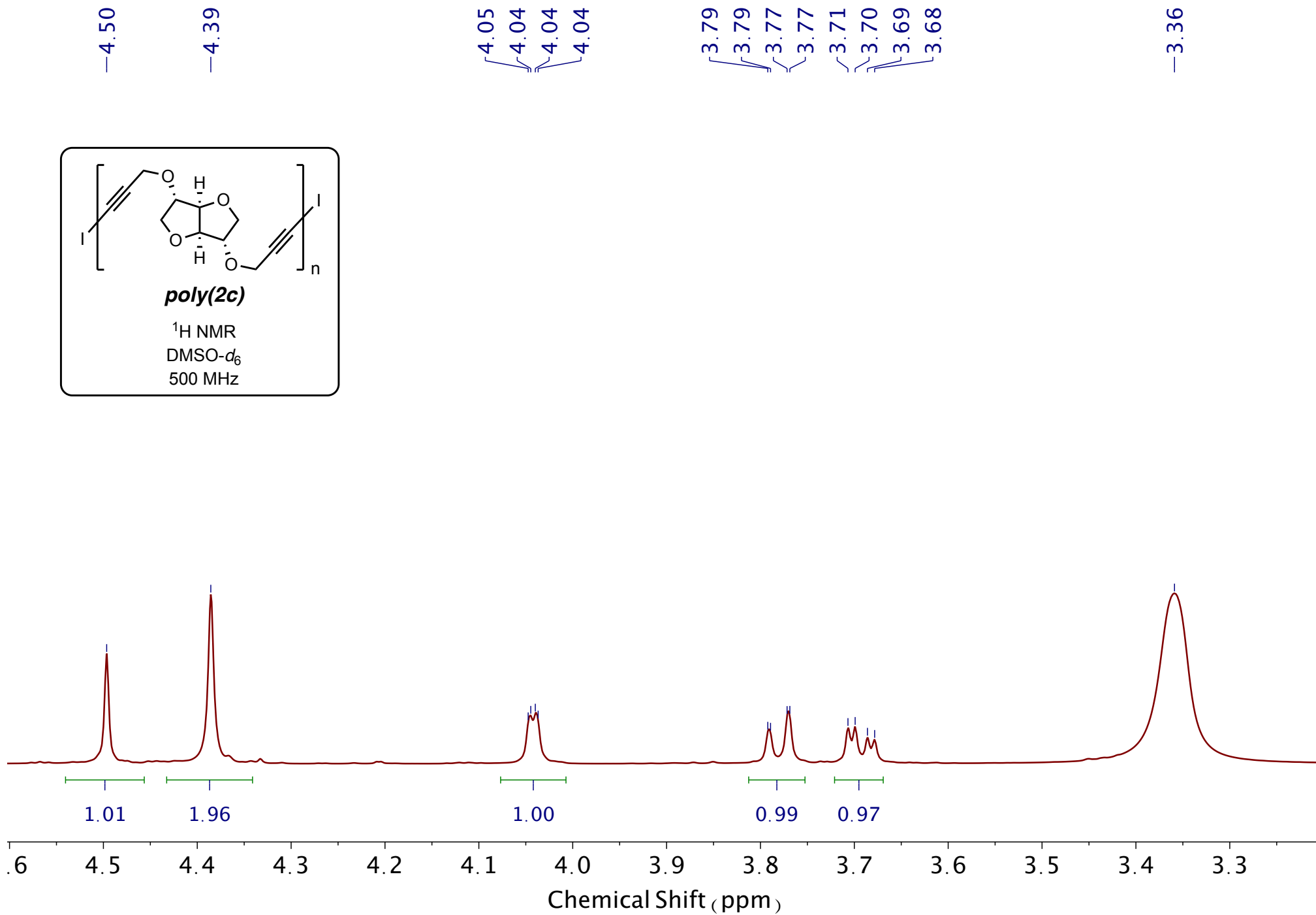
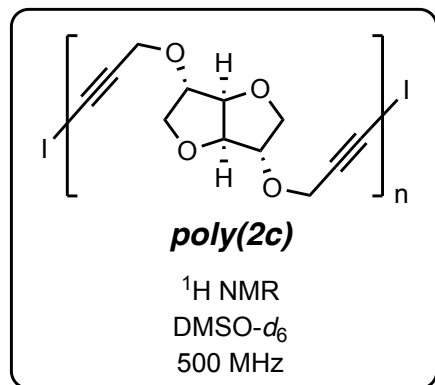
80.29  
79.27  
77.08

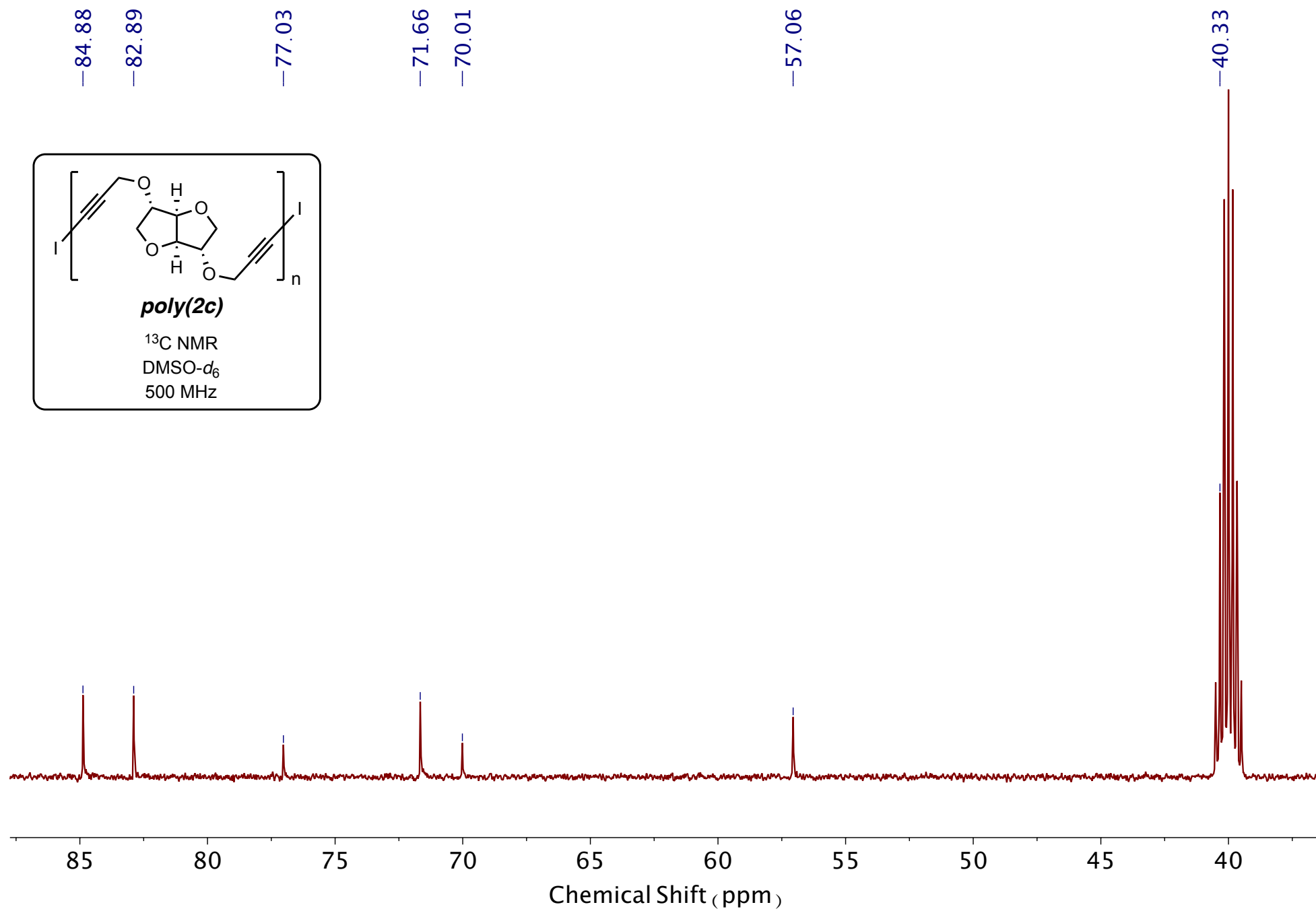
70.69  
70.10

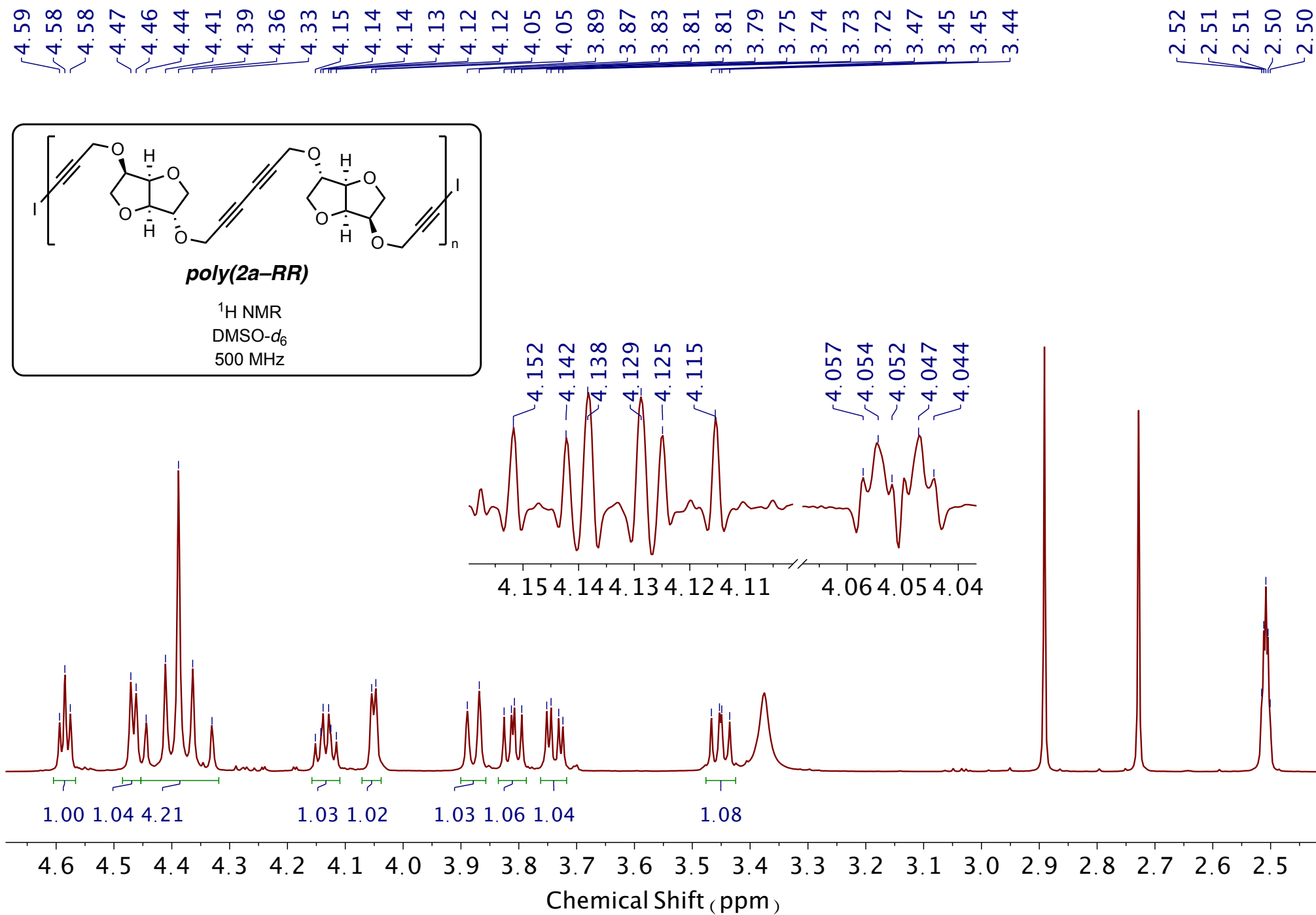
57.79

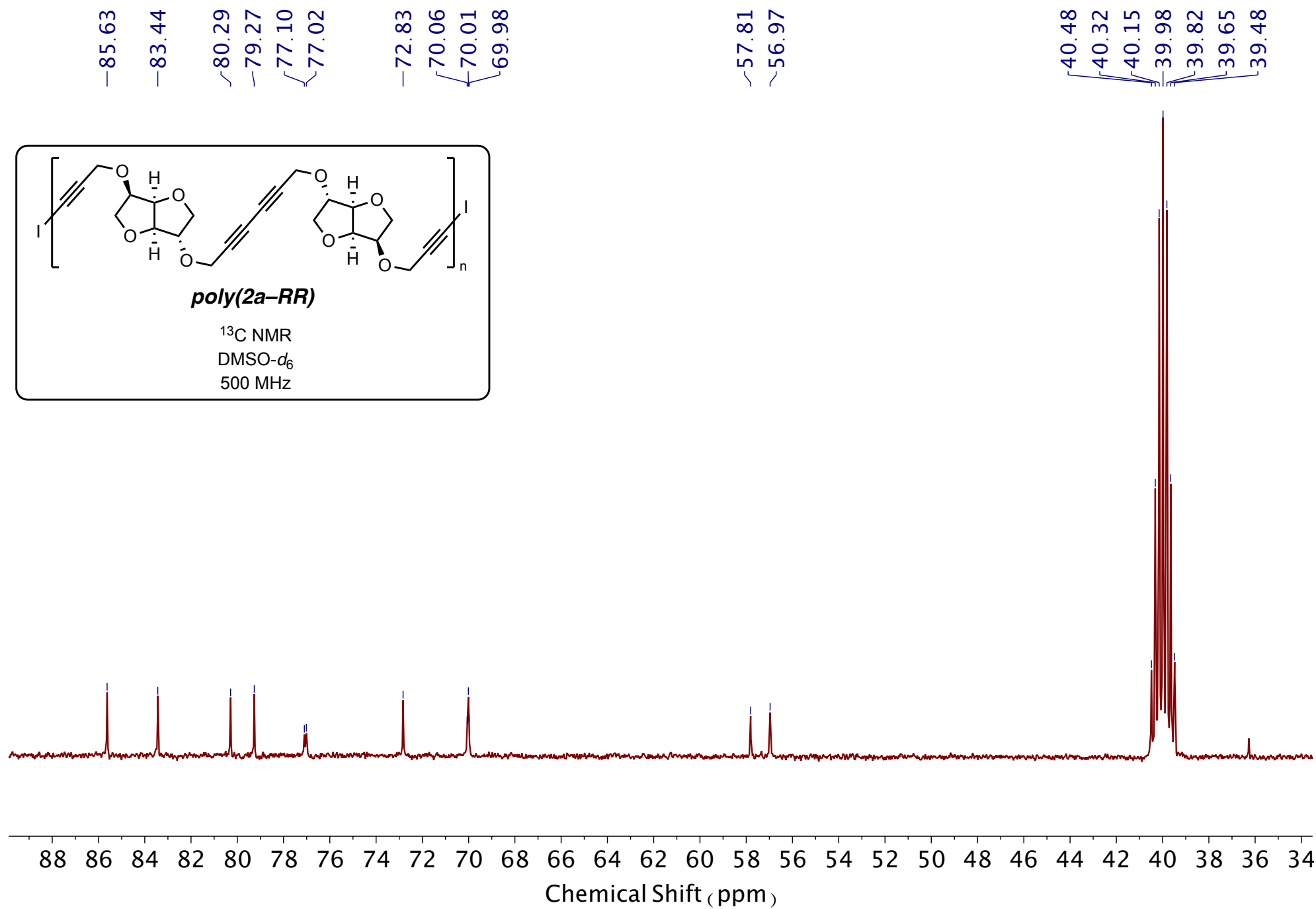
40.51  
40.34  
40.17  
40.01  
39.84  
39.67  
39.50



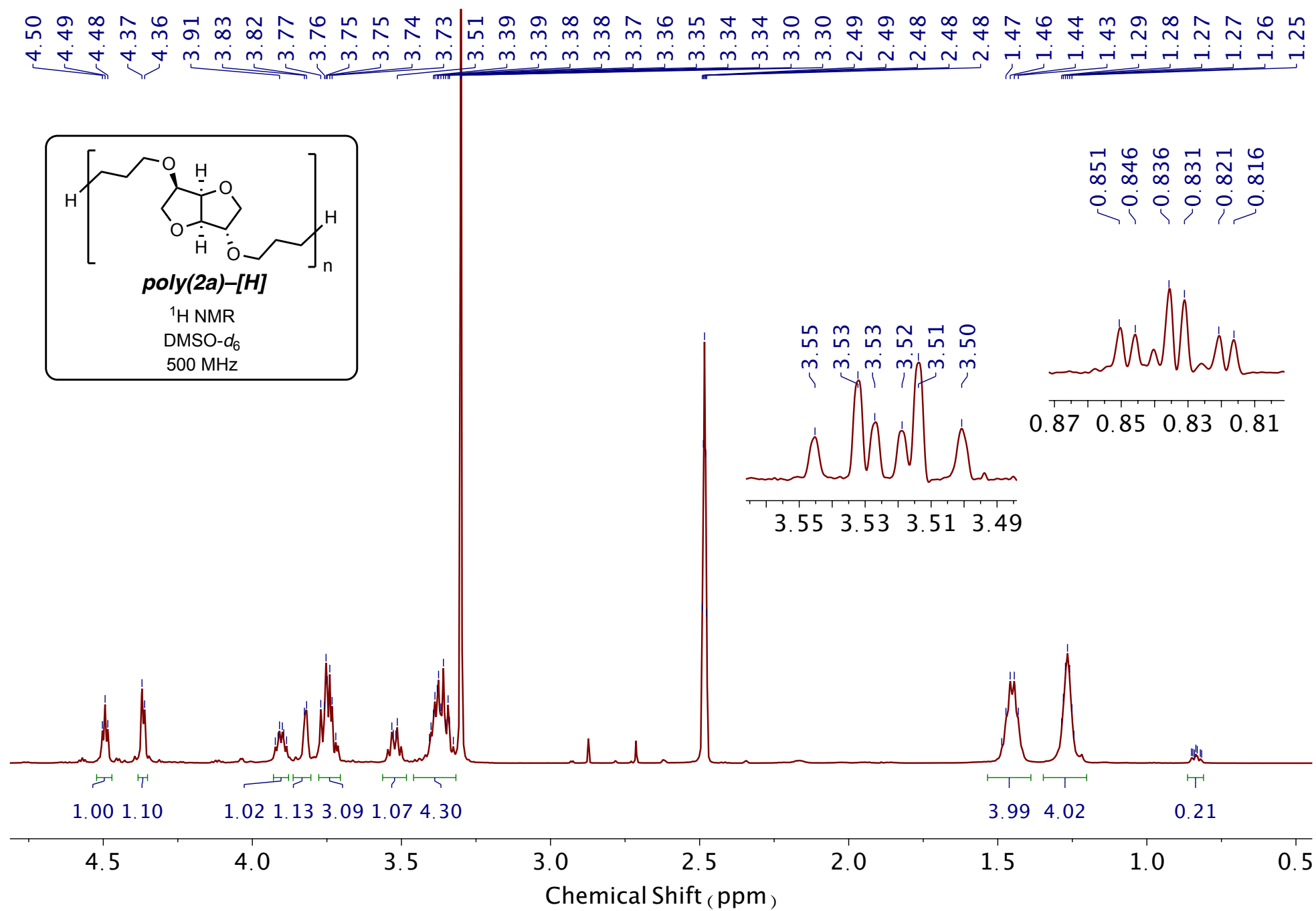


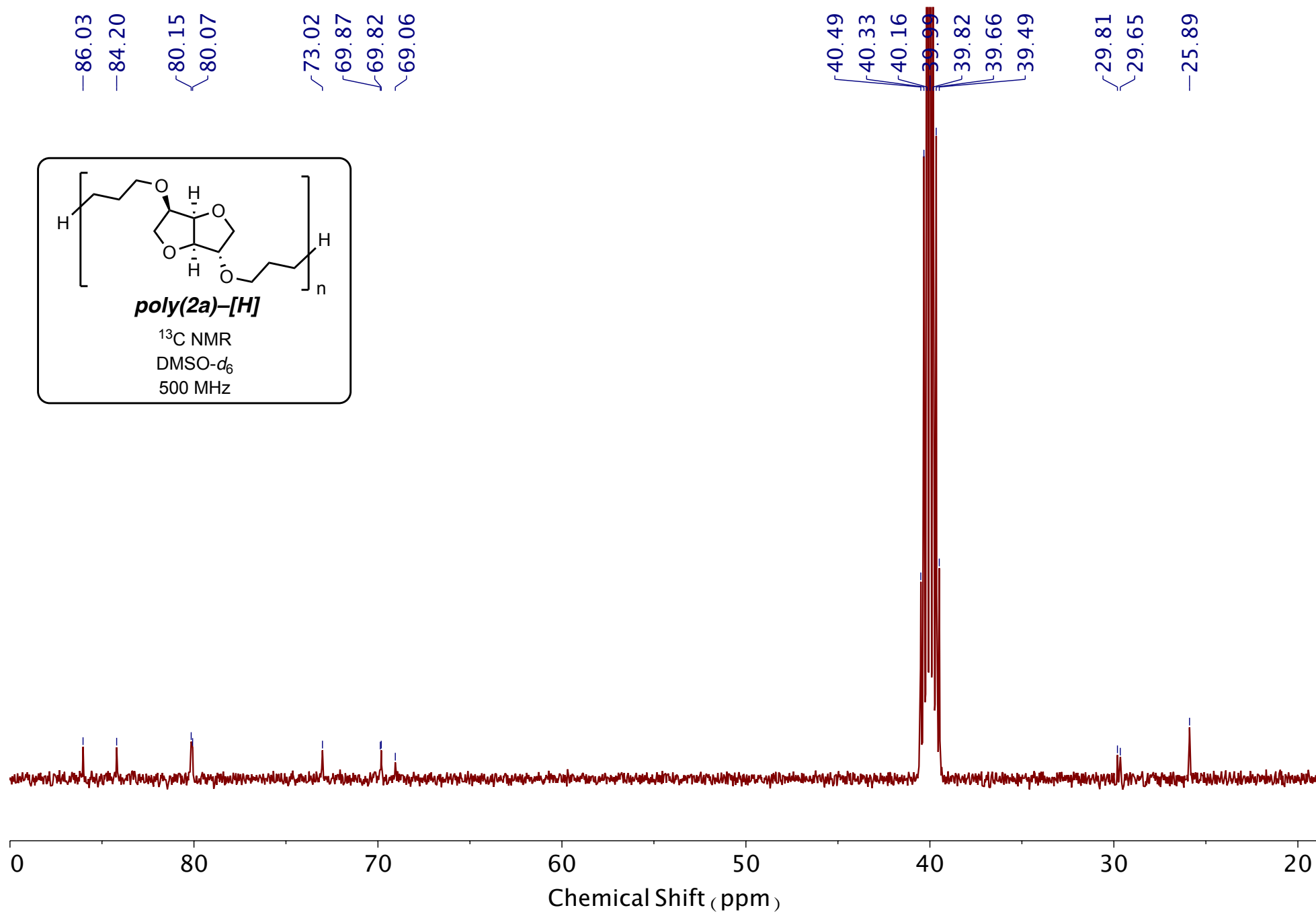


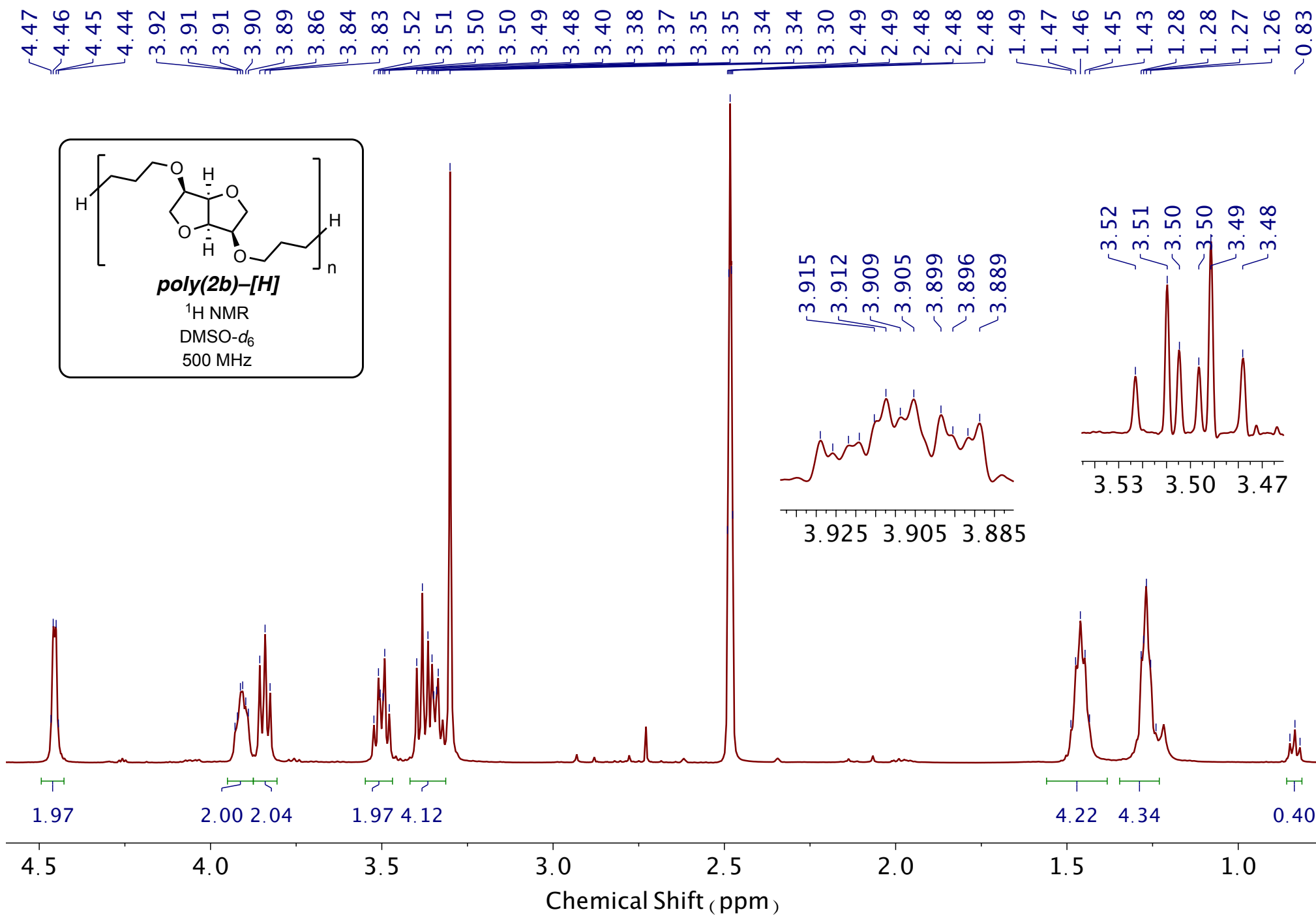












—80.28

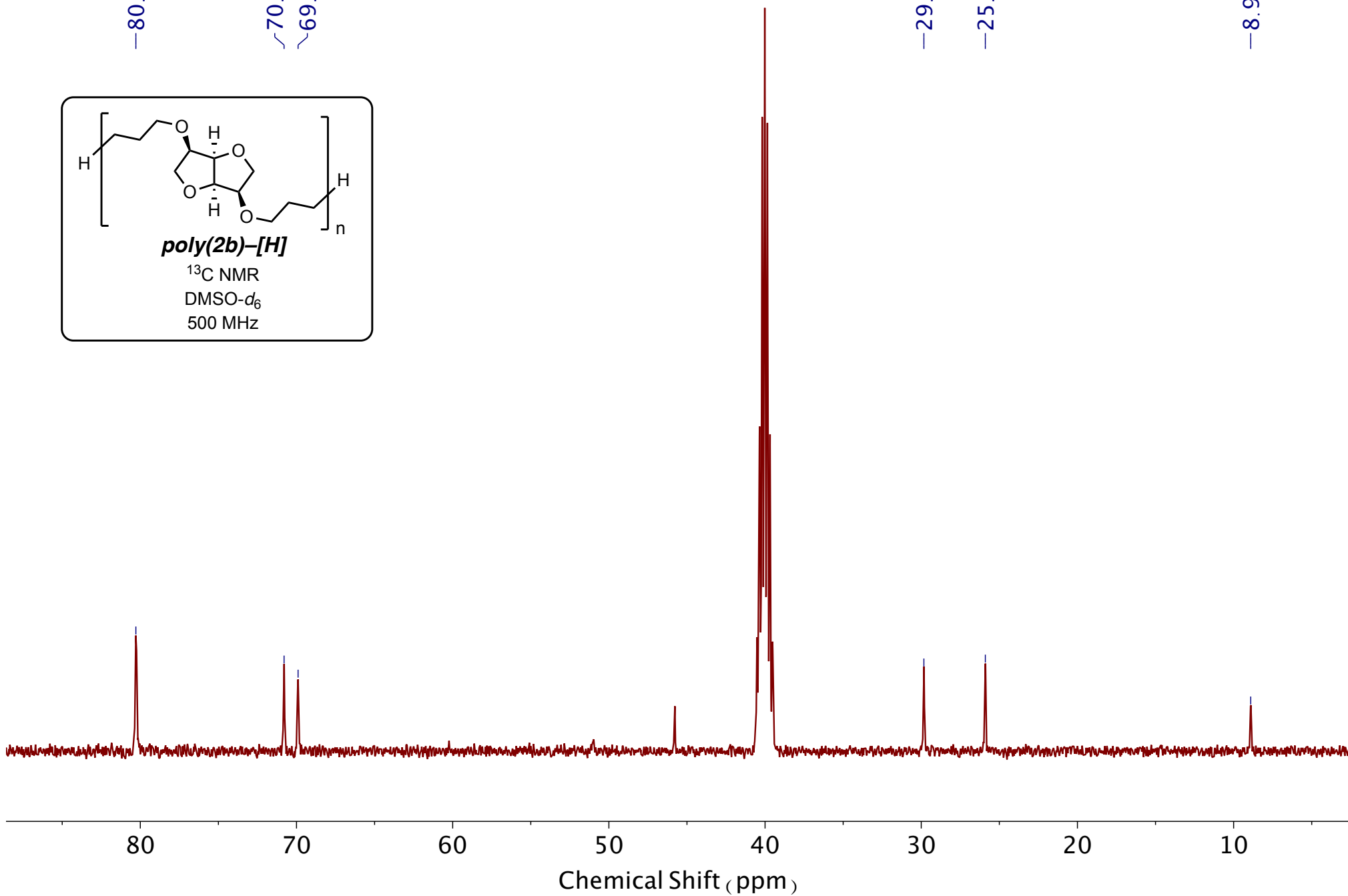
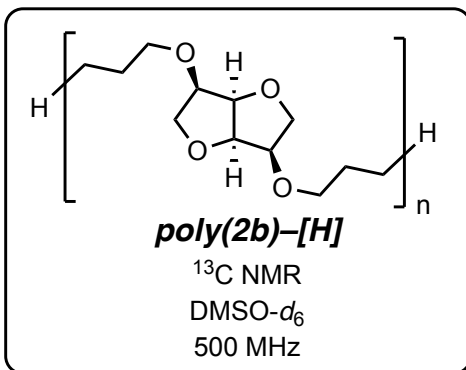
~70.80

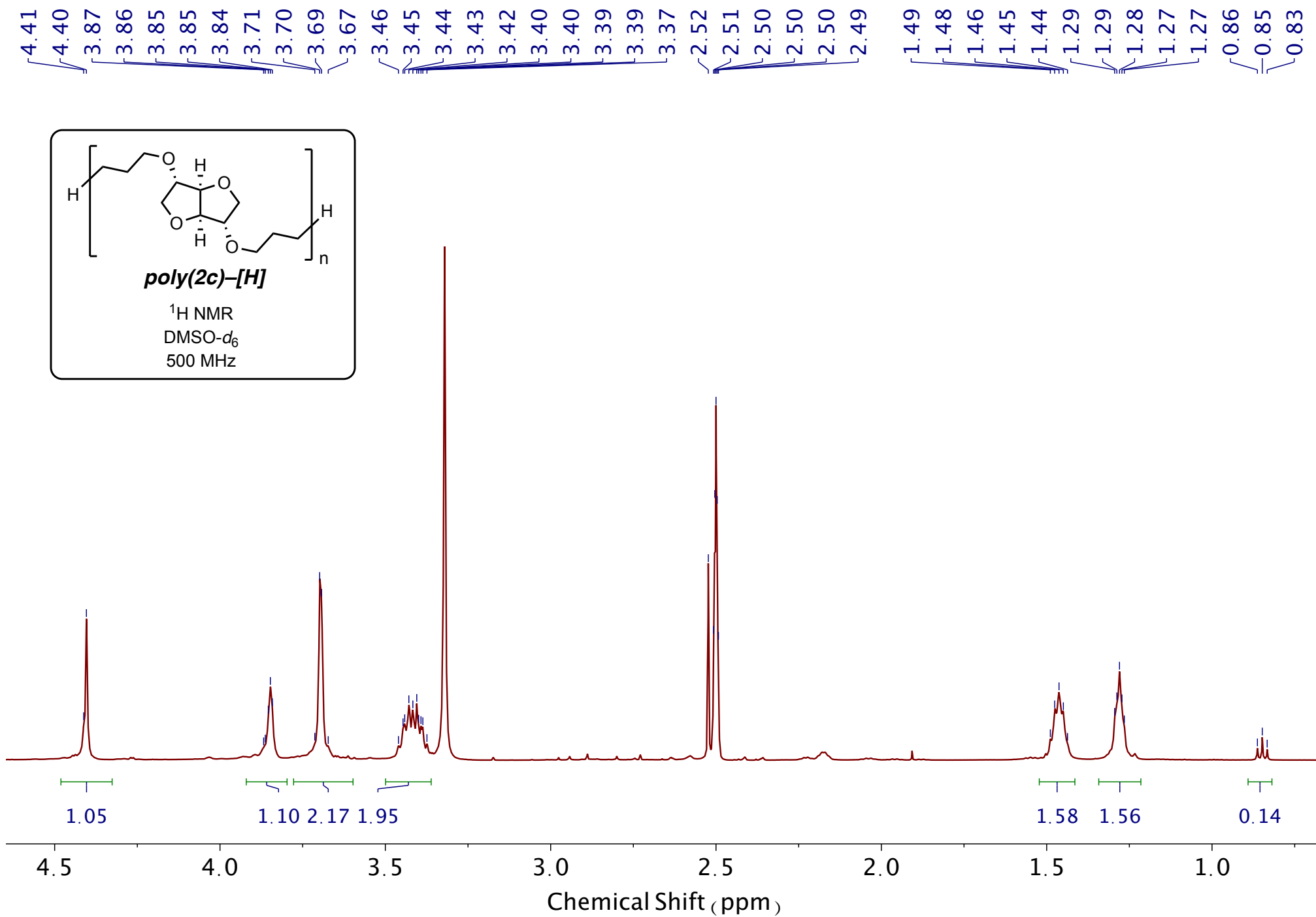
~69.90

—29.83

—25.90

—8.90





—85.31  
—83.40

—71.84  
—69.13

40.50  
40.33  
40.26  
40.17  
40.09  
40.00  
39.92  
39.83  
39.66  
39.50

—29.66

—25.89

