

## SUPPORTING INFORMATION

### Incorporation of Large Cycloalkene Rings into Alternating Copolymers Allows Control of Glass Transition and Hydrophobicity

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## Materials and Methods

Synthetic procedures were carried out under N<sub>2</sub>, using standard Schlenk or drybox techniques. Dry, oxygen-free solvents, e.g. CH<sub>2</sub>Cl<sub>2</sub> and THF were purified with Pure Process Technology (PPT). Mallinckrodt silica gel-60 (230-400 mesh) was used for column chromatography. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (60F254), and Combi-Flash chromatography on RediSep normal phase silica columns (silica gel-60, 230-400 mesh). Bruker Nanobay 400, Avance III 500 MHz and Avance III 700 MHz NMR instruments were used for analysis. Chemical shifts were calibrated from residual undeuterated solvents; they are denoted in ppm ( $\delta$ ).

Thermal analysis was performed using a TA Instruments Q2000 differential scanning calorimeter. The instrument was calibrated using the Calibration Wizard software (TA Instruments QSeries software). The heat flow (Tzero) calibration was performed using sapphire standards and the temperature (cell constant) was calibrated using indium at a scan rate of 10°C/min. All DSC measurements were performed under a nitrogen flow of 50 ml/min using S5 Tzero aluminum pans and hermetic lids. The sample weight ranged between 4-6 mg. Polymer samples were first heated from 25 °C to 200 °C at a rate of 5 °C/min to erase thermal history. Then samples were cooled to -60 °C at a rate of 5 °C/min, and reheated to 200 °C at a rate of 5°C/min. The second heat runs were used for the thermal analysis of polymers reported in Figure 3 in the main text.

Thermal gravimetric analysis was performed using TA Instruments Q50 Thermogravimetric Analyzer. The sample size ranged between 7-10 mg. Weight loss was collected from 25°C to 550°C at 25°C/min under nitrogen flow of 60 ml/min.

To measure contact angles, polymer thin films were cast on a single side polished, 500  $\mu\text{m}$  thick, small piece ( $1 \times 1 \text{ cm}^2$ ) of silicon wafer (P/B type with orientation of (100)). Fresh sample solution (1 wt% in CH<sub>2</sub>Cl<sub>2</sub>) was filtered with a syringe filter (pore size 0.45 $\mu\text{m}$ ). Prior to spin coating, the silicon wafer was cleaned and dried under vacuum for 16 h. The synthesized copolymers were spin coated at 2000 rpm for 45 s and then 5000 rpm for 5 s. The cast thin films were dried under vacuum for 24 h. The contact angle of pure water was then measured with a

CAM 200 optical Contact Angle Meter. 0.5  $\mu\text{L}$  of water was dispensed onto the surface. Data for thin films fabricated from four different batches of the same copolymer were acquired. For each batch, 2 thin films were fabricated and the static contact angle was measured. The average of all 8 measurements are reported.

## Preparation and Characterization of Bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide

Bicyclo[4.2.0]alkene carboxylic acid (421mg, 2.77mmol)<sup>1</sup>, N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC•HCl) (707.4mg, 3.69mmol), and hexylamine(466.5mg, 4.61mmol) were dissolved in dry  $\text{CH}_2\text{Cl}_2$  in a 100mL flask. The solution was cooled in ice bath and DIPEA (477mg, 3.69mmol) was added. The mixture was stirred for 8 h at 25 °C until the acid was consumed. The reaction mixture was washed sequentially with 5%  $\text{NaHCO}_3$  (3 $\times$ ), 1N HCl (3 $\times$ ) and brine (2 $\times$ ) and dried over anhydrous  $\text{MgSO}_4$ . The solvent was filtered and removed by evaporation. The crude product was subjected to silica flash chromatography.

Chromatography (80:20/hexane:ethyl acetate) yielded amide A (130.3mg, 20%). <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.51 (s, 1H, CONH), 3.33 – 3.19 (m, 2H), 2.85 (dd,  $J = 13.4, 3.2$  Hz, CH), 2.66 (dd,  $J = 11.8, 3.6$  Hz, CH), 2.37 – 2.28 (m, 1H, CH), 2.18 – 2.13 (m, 1H, CH), 2.13 – 1.97 (m, 2H,  $\text{CH}_2$ ), 1.94 – 1.84 (m, 1H, CH), 1.78 – 1.67 (m, 1H, CH), 1.65 – 1.43 (m, 2H,  $\text{CH}_2$ ), 1.40 – 1.17 (m, 8H, side chain  $\text{CH}_2$  and ring  $\text{CH}_2$ ), 1.17 – 1.01 (m, 1H, CH), 0.88 (t,  $J = 6.93$ , 3H,  $\text{CH}_3$ ), with spectra identical to the literature. MS (+EI) calcd. for  $\text{C}_{15}\text{H}_{25}\text{NO}$   $[\text{M}+\text{H}]^+$  236.1, found 236.1.

## General Procedure for AROMP

All reactivity experiments were performed at least twice, and preparative polymerization experiments were performed three times. Under an  $\text{N}_2$  atmosphere, a solution of amide A in  $\text{CDCl}_3$  (100  $\mu\text{L}$ ) was added to the NMR tube. Then 100  $\mu\text{L}$  of 3<sup>rd</sup> generation Grubbs catalyst solution was added to the NMR tube. After complete mix of the solution, NMR spectra were acquired at 25 °C. Cycloalkene was added after the amide was completely initiated as judged by the disappearance of the Ru alkylidene resonance at 19.1 ppm in the <sup>1</sup>H NMR spectrum. When the propagation stopped or A completely ring opened, as judged by a complete upfield shift of proton resonance from 2.9ppm~2.6ppm to 2.6ppm~2.3 ppm, the reaction was quenched with

ethyl vinyl ether and stirred for 30 min. The solvent was evaporated, and alternating copolymer was purified by precipitation in cold diethyl ether. For incomplete reaction, purification was performed through column chromatography (3:97/methanol:CH<sub>2</sub>Cl<sub>2</sub>). The theoretical  $M_{n,theor}$  was calculated from the monomer:catalyst feed ratio.

#### Poly(**A-alt-B1**)<sub>10</sub>

Amide A (30mg, 127.6 $\mu$ mol, 10equiv), catalyst (11.3mg, 12.8 $\mu$ mol, 1equiv), and B1 (10.5mg, 127.6 $\mu$ mol, 10equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 2 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B1**)<sub>10</sub> (33mg, 81% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.15 (d,  $J$  = 6.5 Hz, 8H, =CH), 5.79 (s, 8H, CONH), 5.57 (s, 1H, CONH), 5.41 (m, 2H, =CH), 5.05 (t,  $J$  = 6.6 Hz, 10H, =CH), 3.42 – 3.19 (m, 20H, CH<sub>2</sub>), 2.64 – 2.47 (m, 10H, CH), 2.38 (m, 10H, CH), 2.32 – 1.88 (m, 65H), 1.85 – 1.18 (m, 186H), 0.88 (t,  $J$  = 18.6, 6.7 Hz, 30H, CH<sub>3</sub>).  $M_{n,theor}$ =2.4kDa.  $M_{n,GPC}$ =5.5kDa.  $M_{w,GPC}$  =6.6kDa.  $\bar{D}_M$  =1.2.

#### Poly(**A-alt-B1**)<sub>30</sub>

Amide A (30mg, 127.6 $\mu$ mol, 30equiv), catalyst (3.8mg, 4.3 $\mu$ mol, 1equiv), and B1 (10.5mg, 127.6 $\mu$ mol, 30equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 6 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B1**)<sub>30</sub> (31mg, 77% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.15 (t,  $J$  = 7.1 Hz, 26H, =CH), 5.79 (s, 25H, CONH), 5.57 (s, 6H, CONH), 5.39 (t,  $J$  = 7.2 Hz, 5H, =CH), 5.06 (t,  $J$  = 7.0 Hz, 30H, =CH), 3.52 – 3.14 (m, 60H, CH<sub>2</sub>), 2.65 – 2.48 (m, 31H, CH), 2.46 – 2.32 (m, 27H, CH), 2.28 – 1.82 (m, 190H), 1.78 – 1.21 (m, 562H), 0.90 (t,  $J$  = 6.7 Hz, 90H, CH<sub>3</sub>).  $M_{n,theor}$ =7.3.  $M_{n,GPC}$ =7.9Da.  $M_{w,GPC}$  =9.9kDa.  $\bar{D}_M$  =1.2.

#### Poly(**A-alt-B1**)<sub>50</sub>

Amide A (30mg, 127.6 $\mu$ mol, 50equiv), catalyst (2.3mg, 2.6 $\mu$ mol, 1equiv), and B1 (10.5 mg, 127.6 $\mu$ mol, 50equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 12 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B1**)<sub>50</sub> (30mg, 74% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J$  = 7.1 Hz, 42H, =CH), 5.79 (s, 45H, CONH), 5.57 (s, 8H, CONH), 5.48 – 5.35 (m, 9H, =CH), 5.06 (t,  $J$  = 7.0 Hz, 49H, =CH), 3.50 – 3.15 (m, 99H, CH<sub>2</sub>), 2.67 – 2.47 (m, 55H, CH), 2.47 – 2.34 (m, 42H, CH), 2.29 – 1.88 (m, 306H), 1.87 – 1.15 (m, 953H), 0.90 (t,  $J$  = 6.5 Hz, 143H, CH<sub>3</sub>).  $M_{n,theor}$ =12.2kDa.  $M_{n,GPC}$ =8.8kDa.  $M_{w,GPC}$  =13.3kDa.  $\bar{D}_M$  =1.4.

### Poly(**A-alt-B1**)<sub>100</sub>

Amide A (30mg, 127.6 $\mu$ mol, 100equiv), catalyst (1.2mg, 1.3 $\mu$ mol, 1equiv), and B1 (10.5 mg, 127.6 $\mu$ mol, 100equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 18 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B1**)<sub>100</sub> (28mg, 70% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J$  = 7.1 Hz, 84H, =CH), 5.79 (s, 82H, CONH), 5.57 (s, 10H, CONH), 5.48 – 5.35 (m, 13H, =CH), 5.06 (t,  $J$  = 7.0 Hz, 97H, =CH), 3.50 – 3.15 (m, 200H, CH<sub>2</sub>), 2.67 – 2.47 (m, 101H, CH), 2.47 – 2.34 (m, 86H, CH), 2.29 – 1.88 (m, 684H), 1.87 – 1.15 (m, 1842H), 0.90 (t,  $J$  = 6.5 Hz, 301H, CH<sub>3</sub>).  $M_{n,theor}$ =24.4kDa.  $M_{n,GPC}$ =13.0kDa.  $M_{w,GPC}$ =16.5kDa.  $D_M$ =1.3.

### Poly(**A-alt-B2**)<sub>10</sub>

Amide A (30mg, 127.5 $\mu$ mol, 10equiv), catalyst (11.3mg, 12.8 $\mu$ mol, 1equiv), and B2 (17.6mg, 127.6 $\mu$ mol, 10equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 1 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B2**)<sub>10</sub> (36mg, 76% yield). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J$  = 7.1 Hz, 9H, =CH), 5.67 (s, 8H, CONH), 5.46 (s, 1H, CONH), 5.44 – 5.34 (m, 1H, =CH), 5.06 (t,  $J$  = 7.0 Hz, 10H, =CH), 3.49 – 3.16 (m, 20H, CH<sub>2</sub>), 2.65 – 2.48 (m, 10H, CH), 2.40 (m, 10H, CH), 2.24 – 1.89 (m, 70H), 1.77 – 1.19 (m, 261H), 1.04 – 0.84 (m, 30H, CH<sub>3</sub>).  $M_{n,theor}$ =3.0kDa.  $M_{n,GPC}$ =5.5kDa.  $M_{w,GPC}$ =7.0kDa.  $D_M$ =1.3.

### Poly(**A-alt-B2**)<sub>30</sub>

Amide A (30mg, 127.5 $\mu$ mol, 30equiv), catalyst (3.8mg, 4.3 $\mu$ mol, 1equiv), and B2 (17.6mg, 127.6 $\mu$ mol, 30equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 4 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B2**)<sub>30</sub> (36mg, 76% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J$  = 7.1 Hz, 25H, =CH), 5.75 (s, 25H, CONH), 5.46 (s, 3H, CONH), 5.43 – 5.38 (m, 4H, =CH), 5.06 (t,  $J$  = 7.0 Hz, 30H, =CH), 3.41 – 3.20 (m, 60H, CH<sub>2</sub>), 2.64 – 2.49 (m, 30H, CH), 2.49 – 2.32 (m, 28H, CH), 2.20 – 1.94 (m, 199H), 1.72 – 1.24 (m, 797H), 0.90 (t,  $J$  = 6.6 Hz, 90H, CH<sub>3</sub>).  $M_{n,theor}$ =9.0kDa.  $M_{n,GPC}$ =9.8kDa.  $M_{w,GPC}$ =13.6kDa.  $D_M$ =1.4.

### Poly(**A-alt-B2**)<sub>50</sub>

Amide A (30mg, 127.5 $\mu$ mol, 50 equiv), catalyst (2.3mg, 2.6 $\mu$ mol, 1equiv), and B2 (17.6mg, 127.6 $\mu$ mol, 50equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 6 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B2**)<sub>50</sub> (35mg, 74% yield). <sup>1</sup>H

NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J = 7.2$  Hz, 40H, =CH), 5.67 (s, 41H, CONH), 5.46 (s, 6H, CONH), 5.39 (m, 5H), =CH, 5.06 (t,  $J = 7.1$  Hz, 45H, =CH), 3.38 – 3.21 (m, 95H, CH<sub>2</sub>), 2.60 – 2.48 (m, 47H, CH), 2.50 – 2.29 (m, 47H, CH), 2.25 – 1.87 (m, 374H), 1.75 – 1.14 (m, 1301H), 0.90 (t,  $J = 6.8$  Hz, 150H, CH<sub>3</sub>).  $M_{n,theor}=15.0$ kDa .  $M_{n,GPC}=12.8$ kDa.  $M_{w,GPC} =19.5$ kDa.  $\bar{D}_M = 1.5$ .

#### Poly(**A-alt-B2**)<sub>100</sub>

Amide A (30mg, 127.5 $\mu$ mol, 100 equiv), catalyst (1.2mg, 1.3 $\mu$ mol, 1equiv), and B2 (17.6mg, 127.6 $\mu$ mol, 100equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 12 h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B2**)<sub>100</sub> (33mg, 70% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (t,  $J = 7.1$  Hz, 85H, =CH), 5.75 (s, 82H, CONH), 5.46 (s, 14H, CONH), 5.42 – 5.37 (m, 16H, =CH), 5.06 (t,  $J = 7.0$  Hz, 94H, =CH), 3.41 – 3.17 (m, 199H, CH<sub>2</sub>), 2.62 – 2.47 (m, 97H, CH), 2.46 – 2.33 (m, 90H, CH), 2.21 – 1.88 (m, 711H), 1.71 – 1.23 (m, 2612H), 0.96 – 0.86 (m, 300H, CH<sub>3</sub>).  $M_{n,theor}=30.0$ kDa .  $M_{n,GPC}=26.9$ kDa.  $M_{w,GPC} =38.5$ kDa.  $\bar{D}_M = 1.4$ .

#### Poly(**A-alt-B3**)<sub>10</sub>

Amide A (30mg, 127.5 $\mu$ mol, 10equiv), catalyst (11.3mg, 12.8 $\mu$ mol, 1equiv), and B3 (21.2mg, 127.6 $\mu$ mol, 10 equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 6h, amide A was completely consumed. Precipitation in cold diethyl ether yielded poly(**A-alt-B3**)<sub>10</sub> (36mg, 69% yield). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  6.13 (t,  $J = 7.2$  Hz, 8H,=CH), 5.70 (s, 8H, CONH), 5.49 (s, 1H, CONH), 5.42 – 5.38 (m, 2H, =CH), 5.05 (t,  $J = 7.1$  Hz, 10H, =CH), 3.39 – 3.18 (m, 20H, CH<sub>2</sub>), 2.62 – 2.49 (m, 10H, CH), 2.49 – 2.30 (m, 10H, CH), 2.31 – 1.86 (m, 67H), 1.77 – 1.16 (m, 304H), 0.90 (t,  $J = 6.7$  Hz, 30H).  $M_{n,theor}=3.3$ kDa .  $M_{n,GPC}=6.0$ kDa.  $M_{w,GPC} =7.0$ kDa.  $\bar{D}_M = 1.2$ .

#### Poly(**A-alt-B3**)<sub>30</sub>

Amide A (30mg, 127.5 $\mu$ mol, 30equiv), catalyst (3.8mg, 4.3 $\mu$ mol, 1equiv), and B3 (21.2mg, 127.6 $\mu$ mol, 30equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 20 h, 30% of amide A was consumed. Chromatography (3:97/methanol:dichloromethane) yielded poly(**A-alt-B3**)<sub>30</sub> (10mg, 20% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.13 (t,  $J = 7.1$  Hz, 25H, =CH), 5.70 (s, 25H, CONH), 5.49 (s, 4H, CONH), 5.42 – 5.38 (m, 6H, =CH), 5.05 (t,  $J = 7.1$  Hz, 28H, =CH), 3.39 – 3.18 (m, 59H, CH<sub>2</sub>), 2.53 (m, 28H, =CH), 2.49 – 2.30 (m, 27H, CH), 2.31 – 1.86 (m, 233H), 1.77

– 1.16 (m, 881H), 0.90 (d,  $J = 6.8$  Hz, 91H, CH<sub>3</sub>).  $M_{n,theor}=9.9$ kDa .  $M_{n,GPC}=15.8$ Da.  $M_{w,GPC}=28.0$ kDa.  $\bar{D}_M = 1.8$ .

### Poly(**A-alt-B3**)<sub>50</sub>

Amide A (30mg, 127.6 $\mu$ mol, 50equiv), catalyst (2.3mg, 2.6 $\mu$ mol, 1equiv), and B3 (21.2mg, 127.6 $\mu$ mol, 50equiv) were mixed in CDCl<sub>3</sub> in an NMR tube. After 20 h, 20% of amide A was completely consumed. Chromatography (3:97/methanol:dichloromethane) yielded poly(**A-alt-B3**)<sub>50</sub> (8mg, 16 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.10 (t,  $J = 7.0$  Hz, 46H, =CH), 5.71 (s, 44H, CONH), 5.50 (s, 7H, CONH), 5.38 – 5.32 (m, 6H, =CH), 5.02 (t,  $J = 6.8$  Hz, 50H, =CH), 3.39 – 3.06 (m, 100H, CH<sub>2</sub>), 2.50 (m, 51H, CH), 2.36 (m, 46H, CH), 2.20 – 1.85 (m, 407H), 1.69 – 1.07 (m, 1441H), 0.86 (t,  $J = 6.7$  Hz, 150H, CH<sub>3</sub>).  $M_{n,theor}=16.4$ kDa .  $M_{n,GPC}=11.8$ kDa.  $M_{w,GPC}=28.9$ kDa.  $\bar{D}_M = 2.4$ .





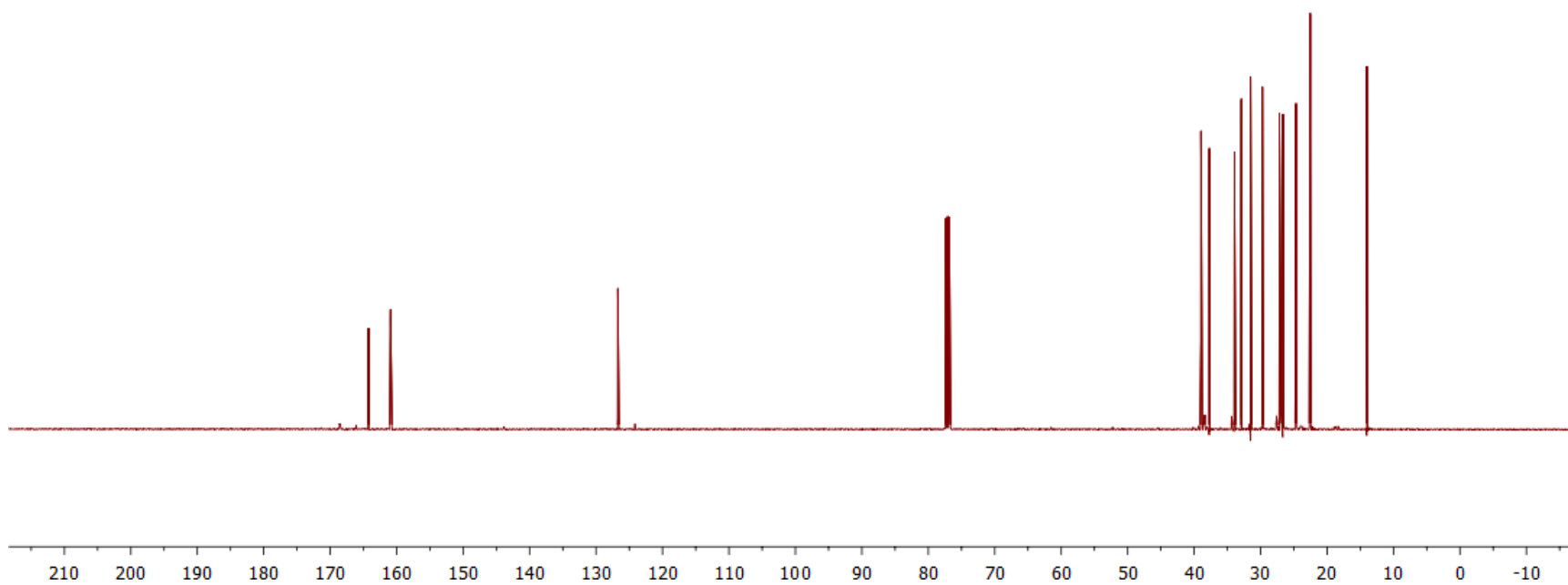
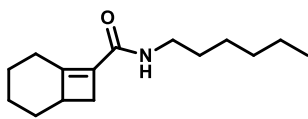
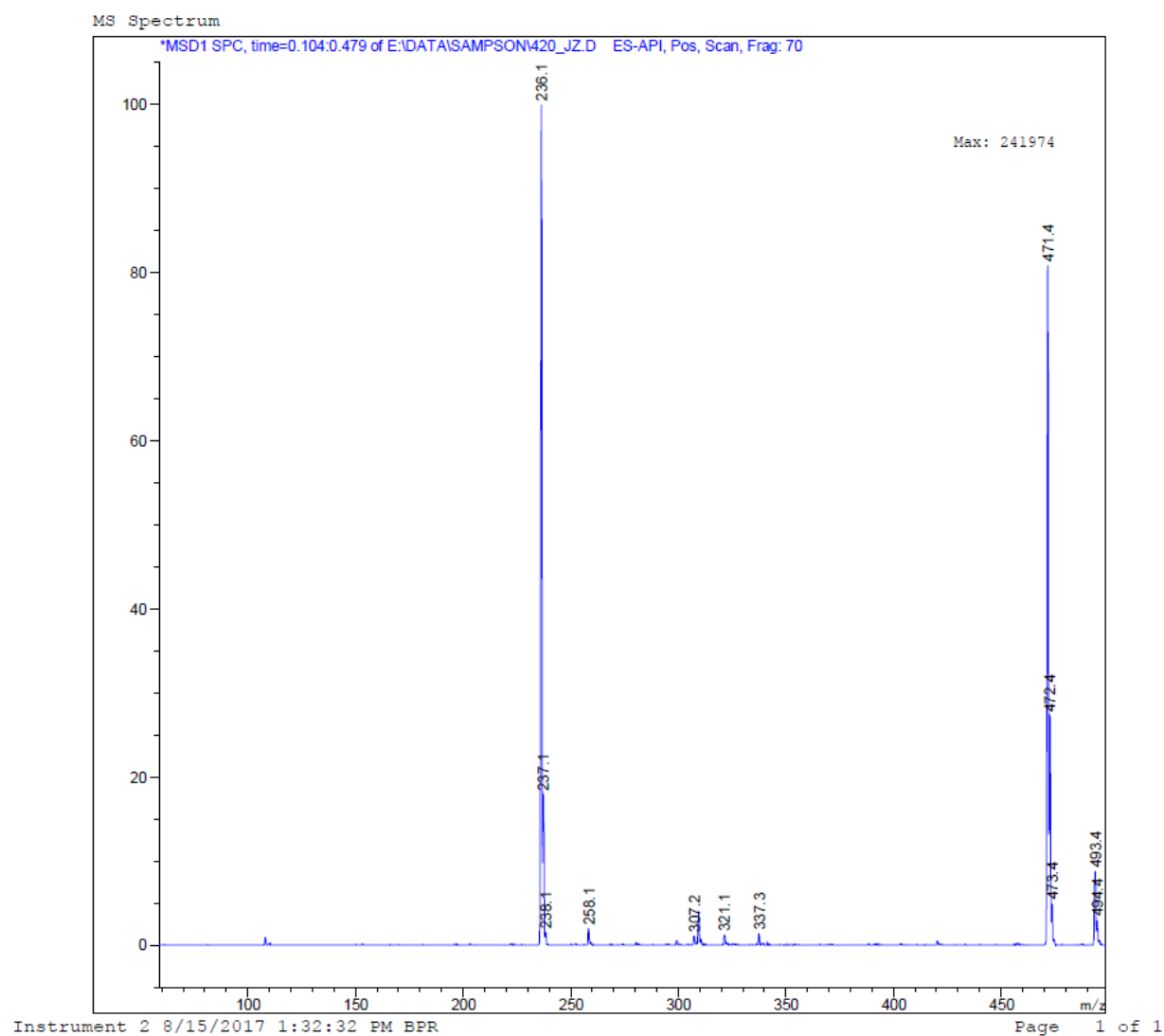


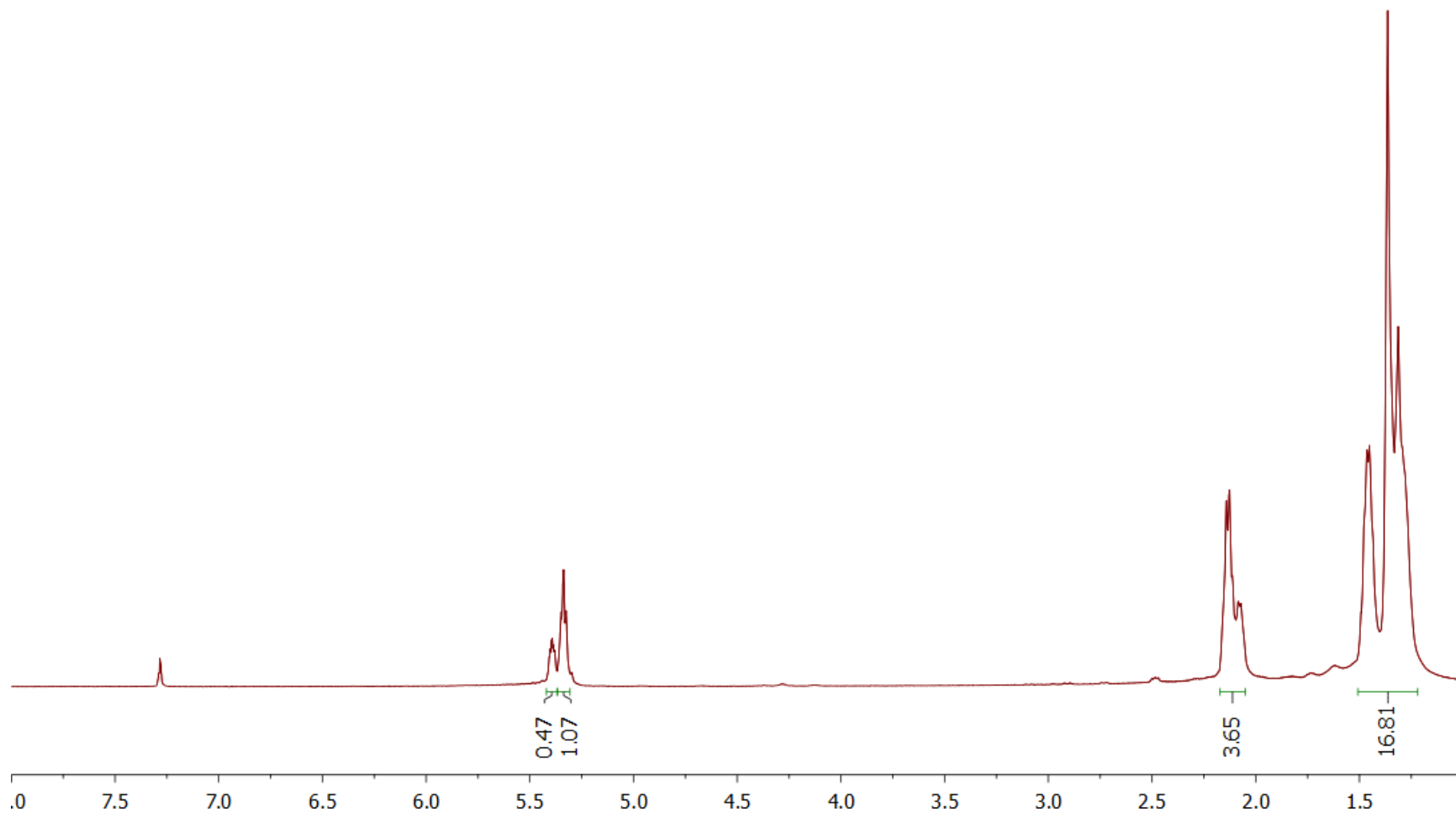
Figure S2  $^{13}\text{C}$  spectrum of Monomer A

Print of window 80: MS Spectrum  
Data File : E:\DATA\SAMPSON\420\_JZ.D  
Sample Name : 420\_JZ

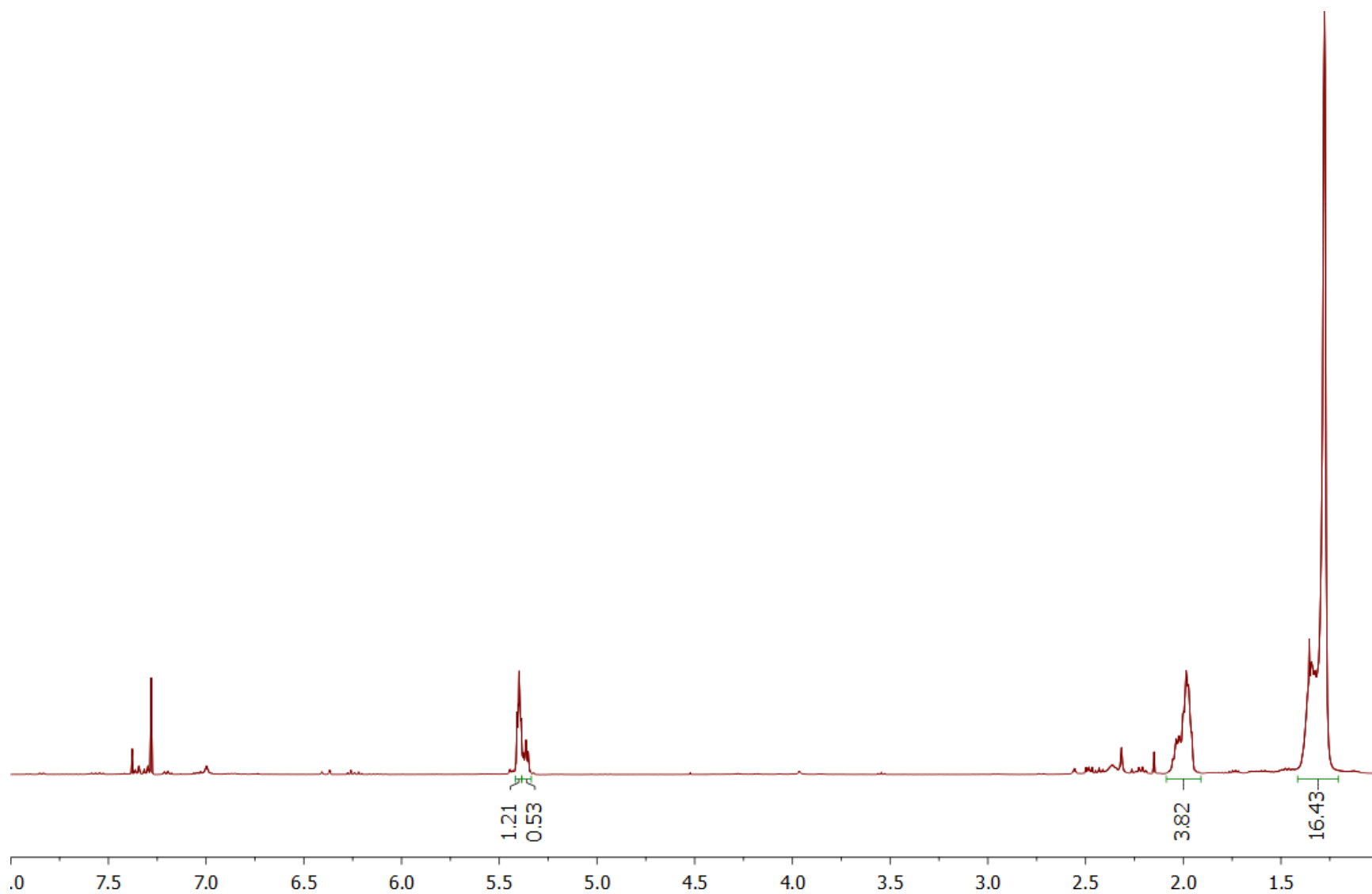
=====  
Acq. Operator : RUDY  
Acq. Instrument : Instrument 2 Location : P1-F-01  
Injection Date : 8/15/2017 1:29:42 PM Inj : 1  
Inj Volume : 1.0 µl  
  
Acq. Method : E:\METHODS\DIRINJ-POS.M  
Last changed : 8/15/2017 1:28:39 PM by RUDY  
(modified after loading)  
Analysis Method : E:\METHODS\BPR\FIA-DA.M  
Last changed : 5/4/2017 10:39:58 AM by BPR  
Method Info : FIA positive  
  
Sample Info : POS\_cdcl3



**Figure S3 Mass Spectrum of Monomer A**



**Figure S4** <sup>1</sup>H spectrum of Monomer B3



**Figure S5**  $^1\text{H}$  spectrum of Monomer B3 after treated with catalyst

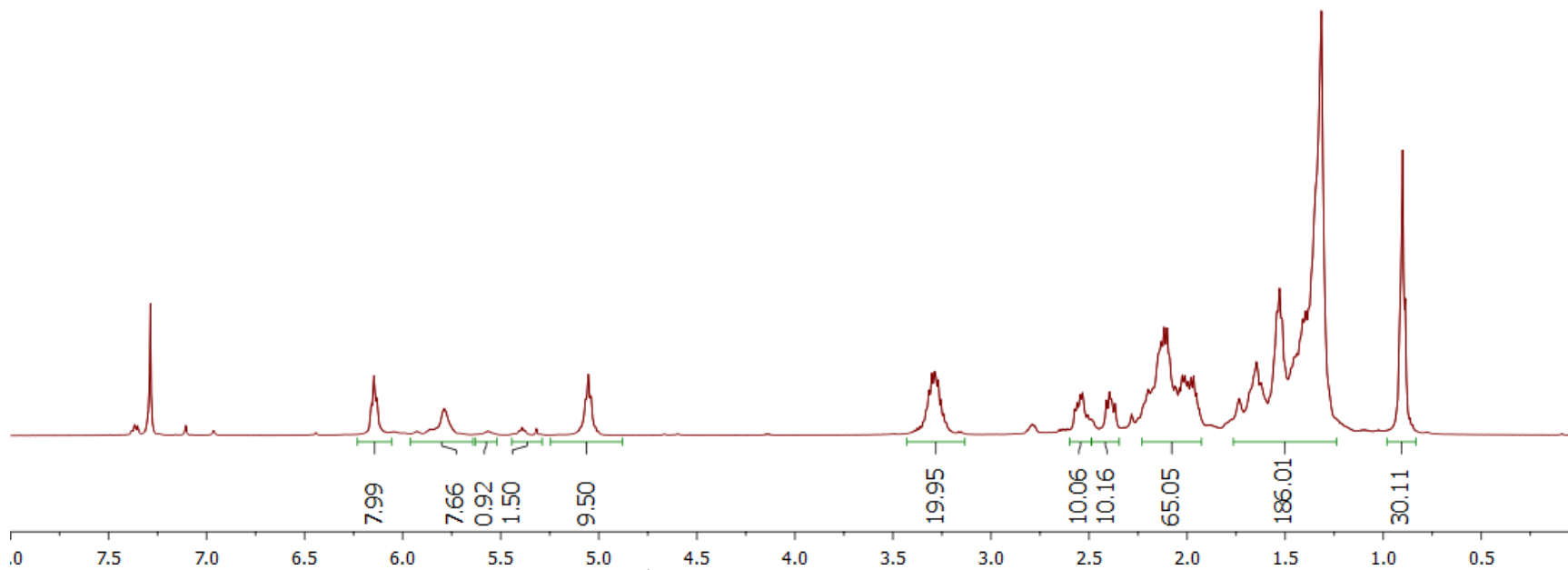
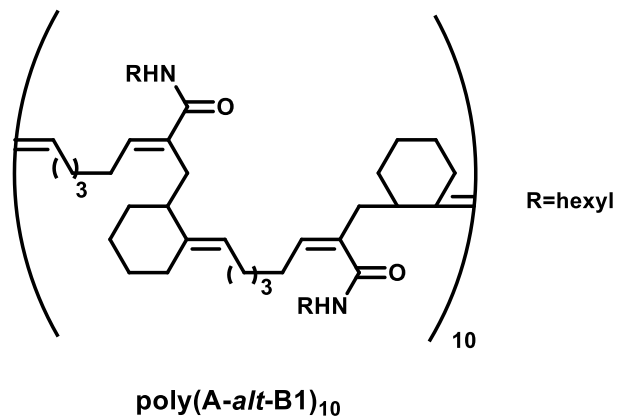


Figure S6 <sup>1</sup>H spectrum of poly(A-*alt*-B1)<sub>10</sub>

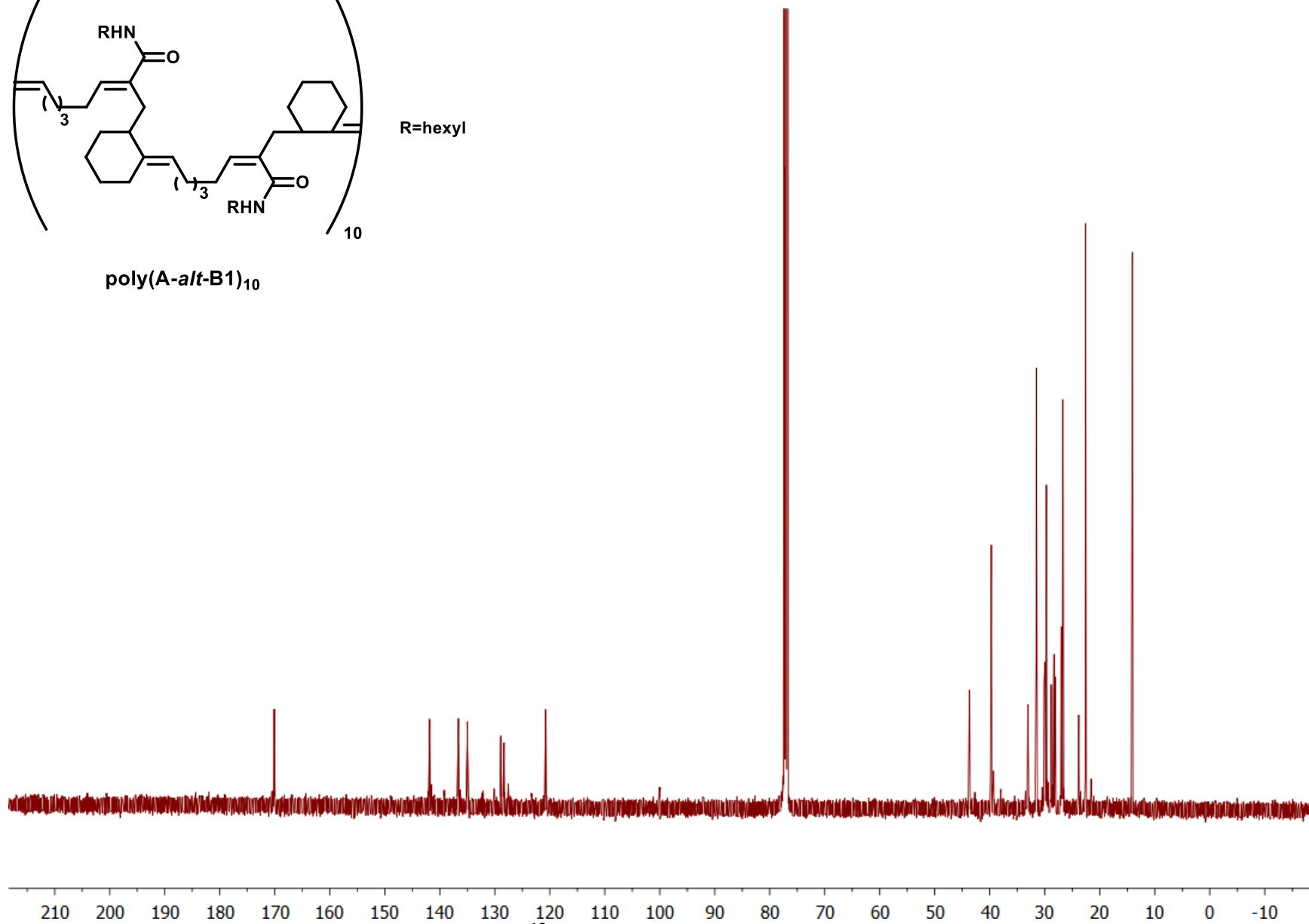
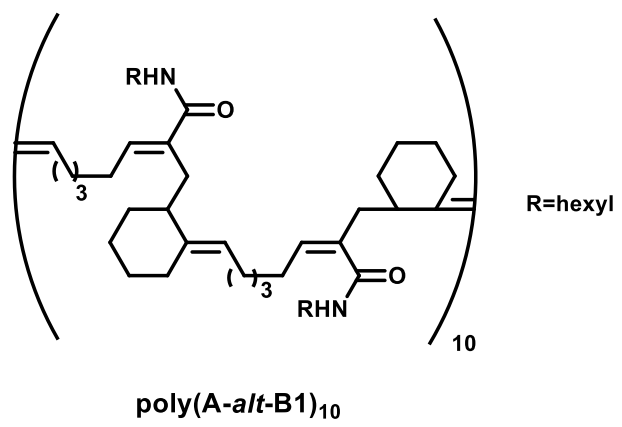


Figure S7 <sup>13</sup>C spectrum of poly(A-*alt*-B1)<sub>10</sub>

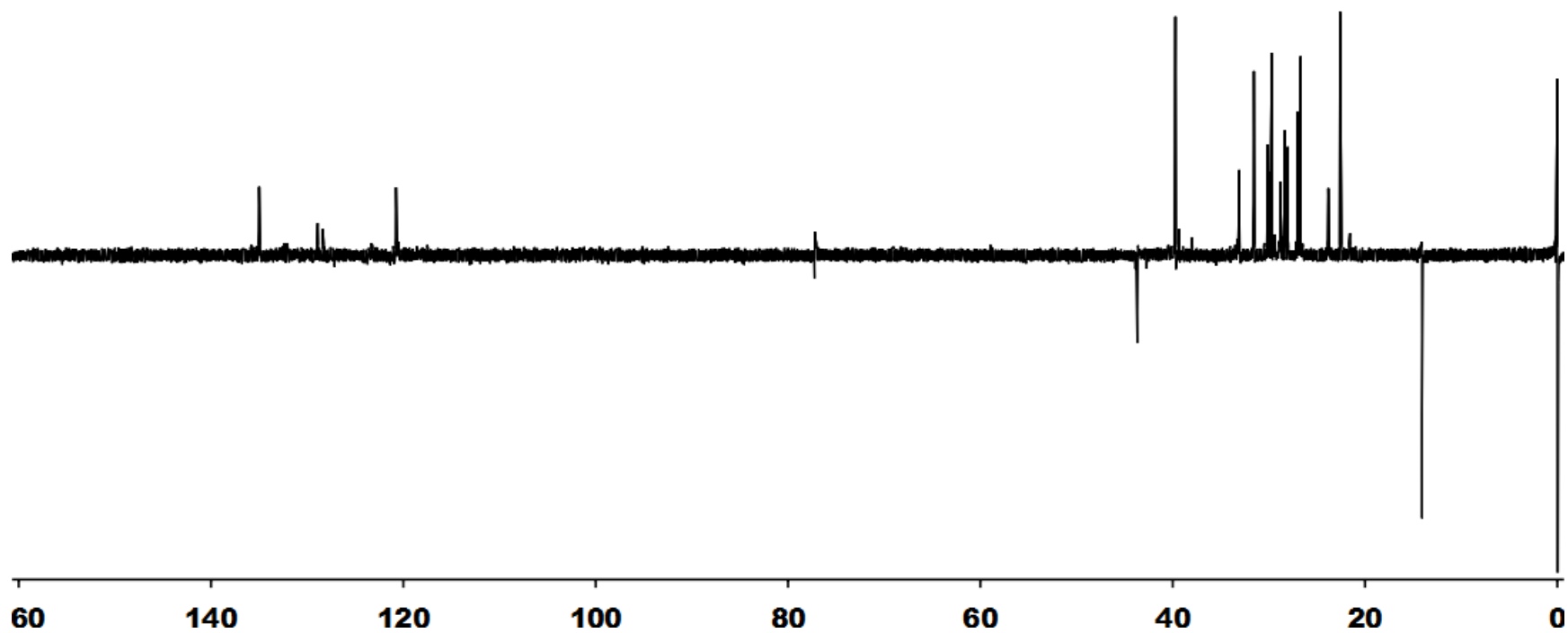
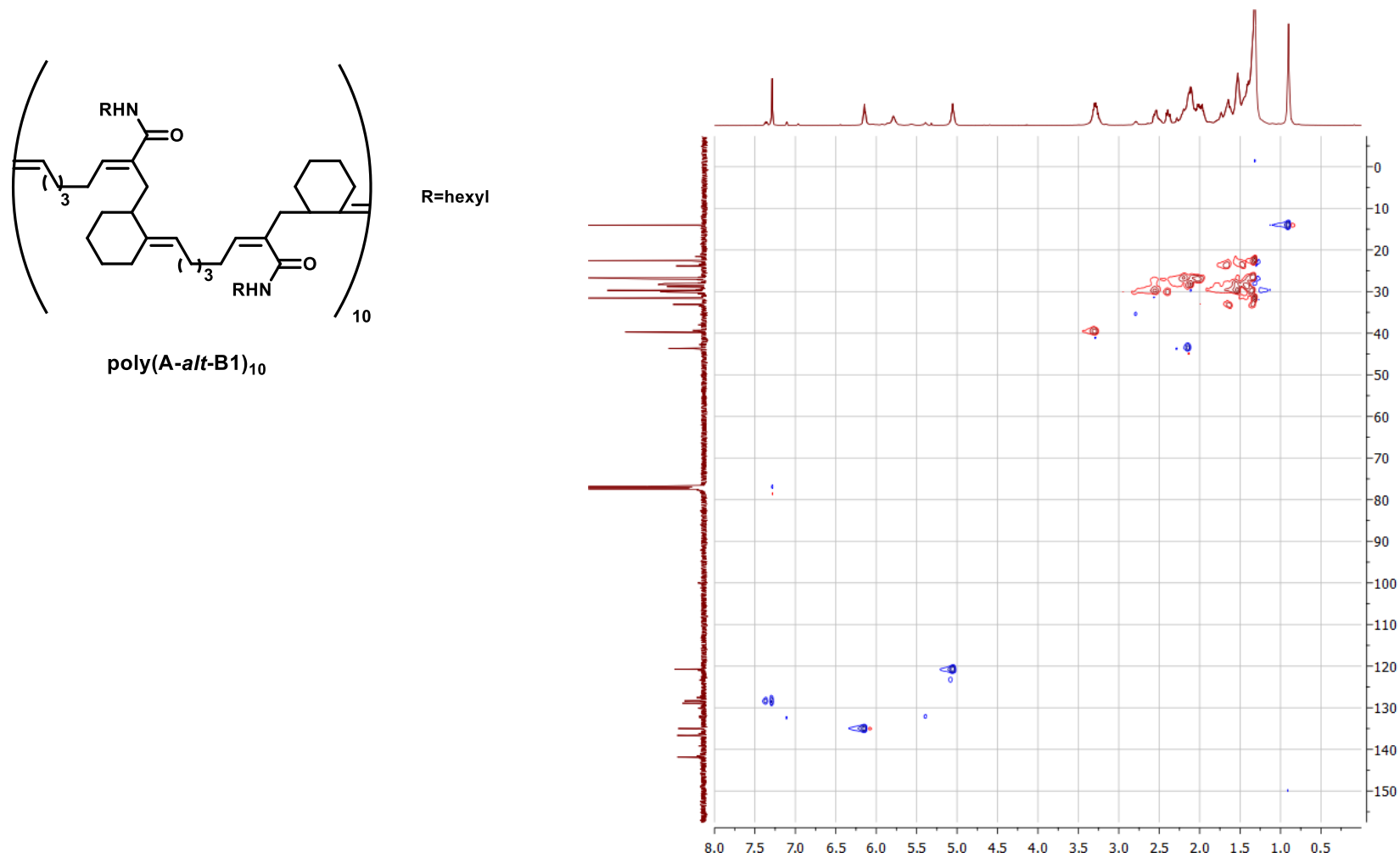
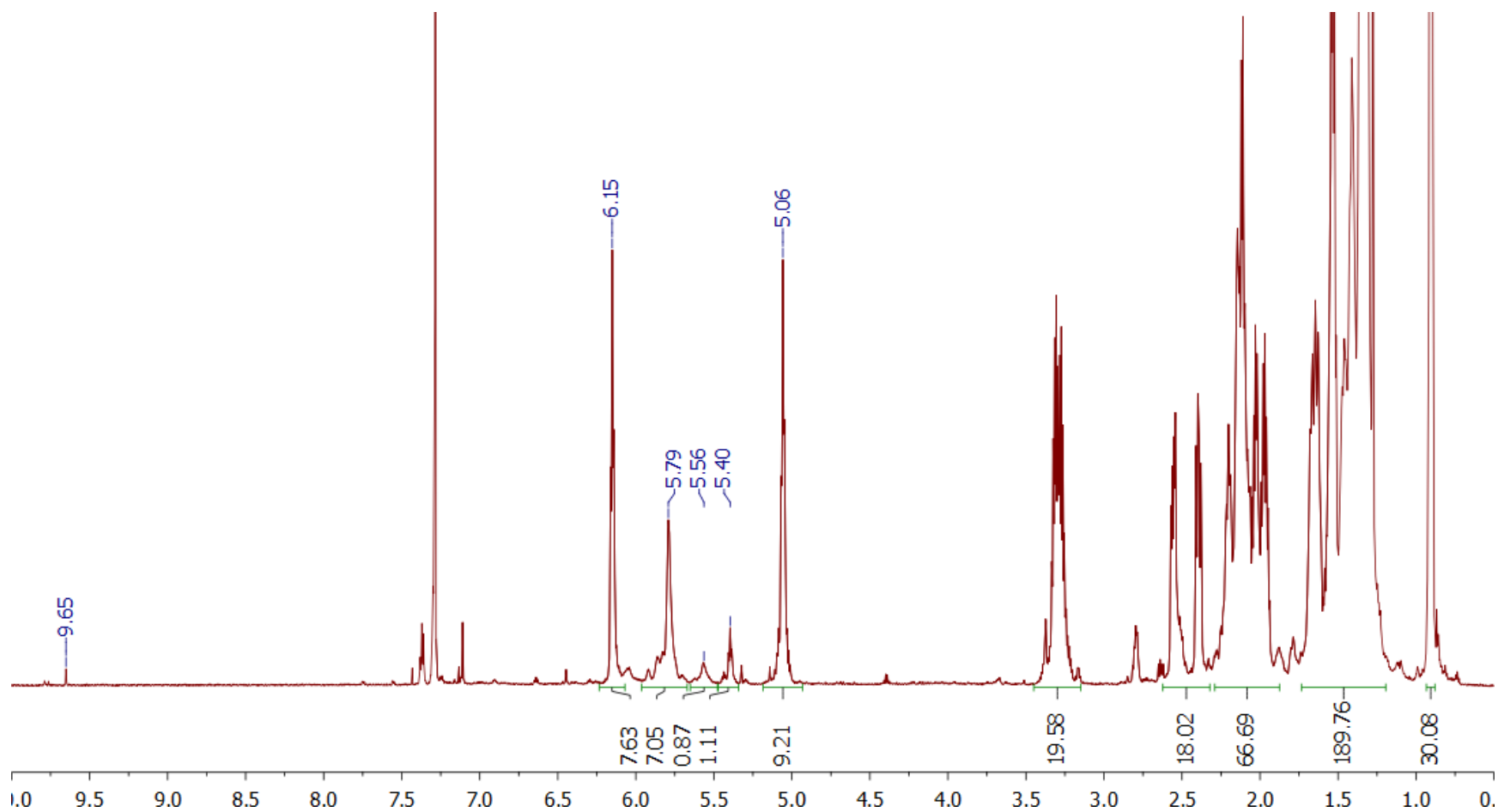


Figure S8  $^{13}\text{C}$  DEPT of poly(A-*alt*-B1)<sub>10</sub>



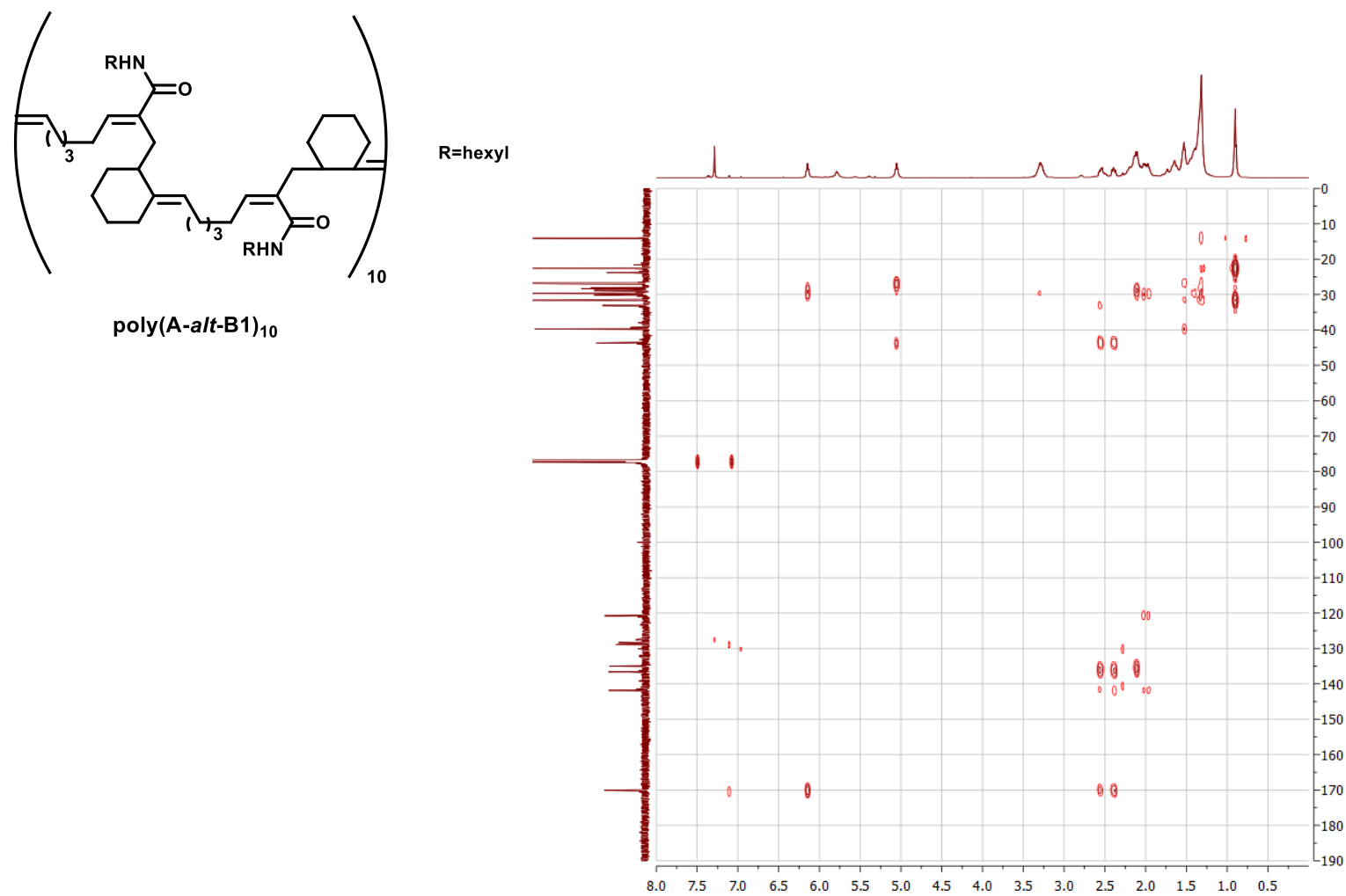
Figure S9 HSQC spectrum of poly(A-*alt*-B1)<sub>10</sub>





**Figure S10**  $^1\text{H}$  spectrum of poly(A-alt-B1)<sub>10</sub> quenched with vinylene carbonate

Figure S11 HMBC spectrum of poly(A-*alt*-B1)<sub>10</sub>



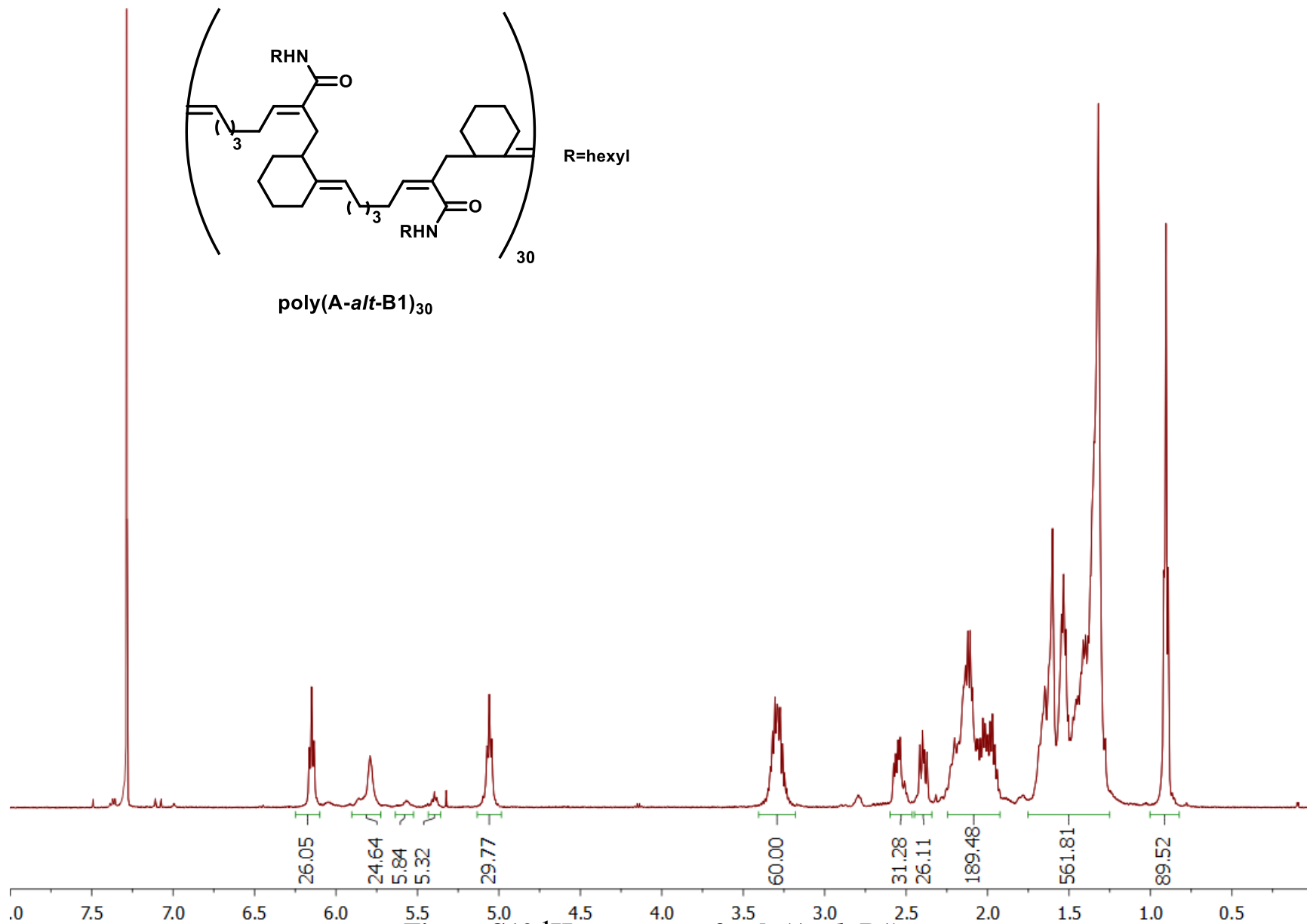
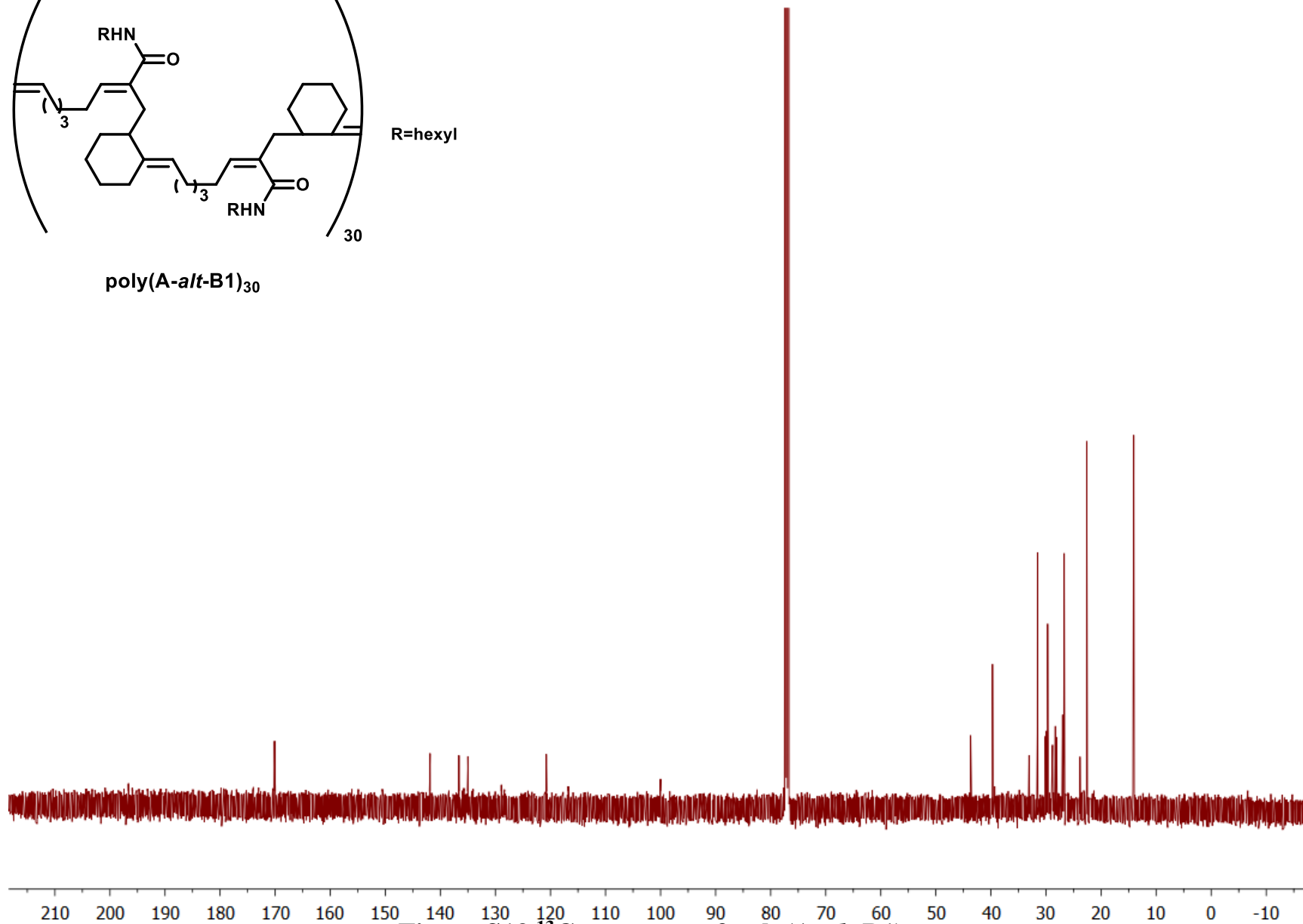
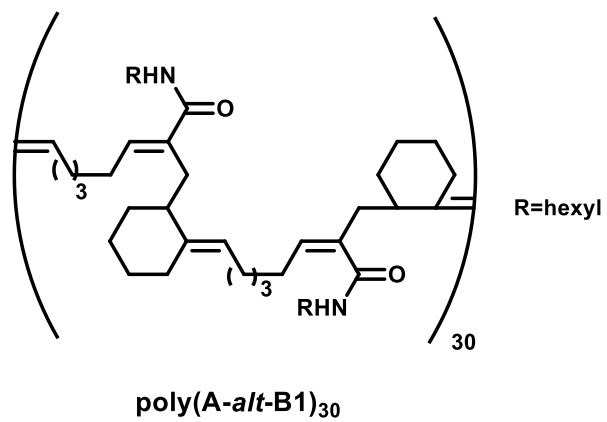


Figure S12 <sup>1</sup>H spectrum of poly(A-alt-B1)<sub>30</sub>



**Figure S13**  $^{13}\text{C}$  spectrum of poly(A-*alt*-B1)<sub>30</sub>

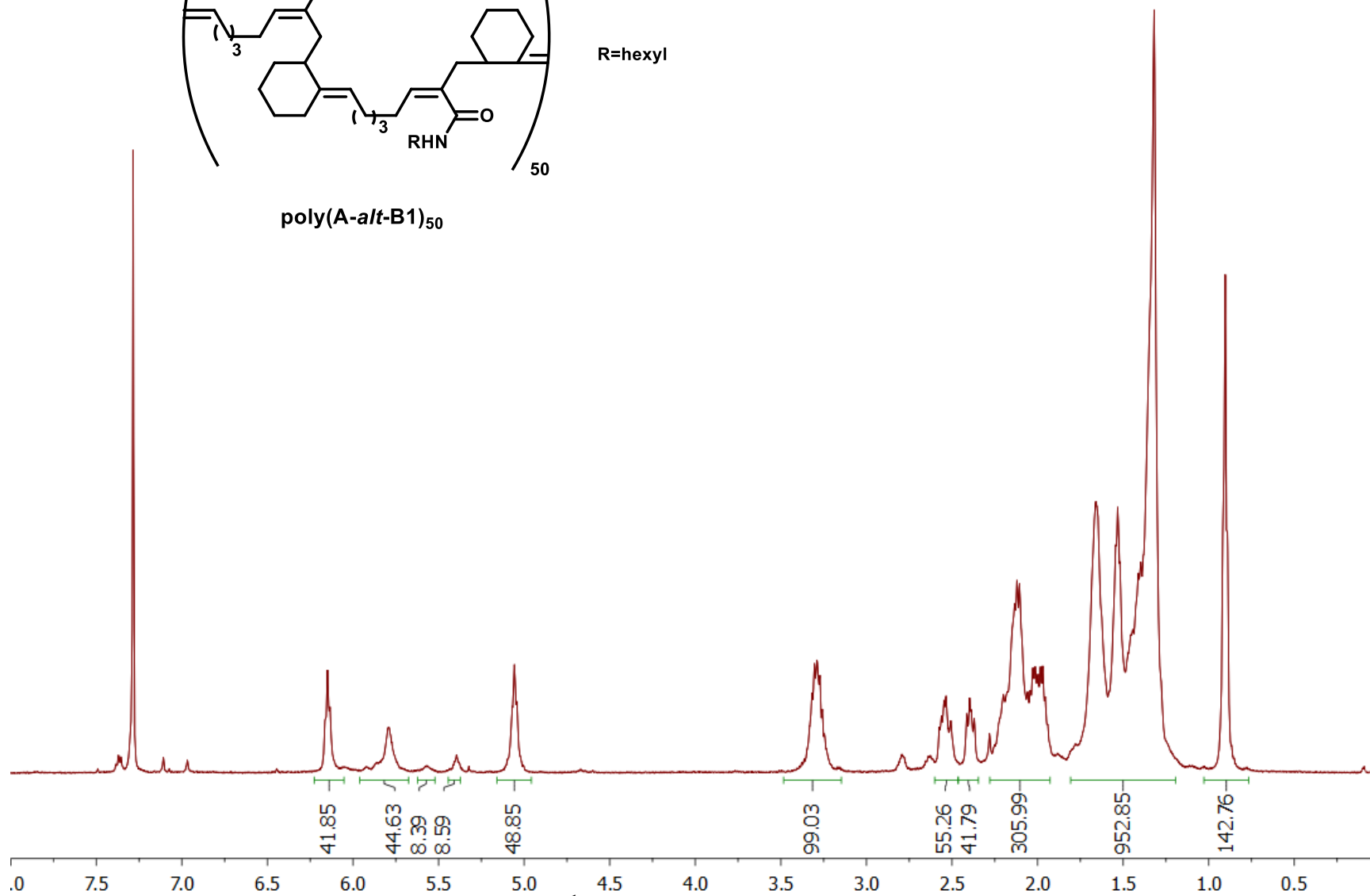
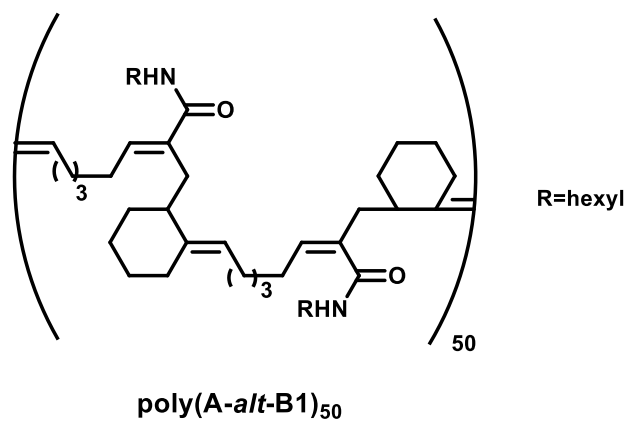


Figure S14 <sup>1</sup>H spectrum of poly(A-*alt*-B1)<sub>50</sub>

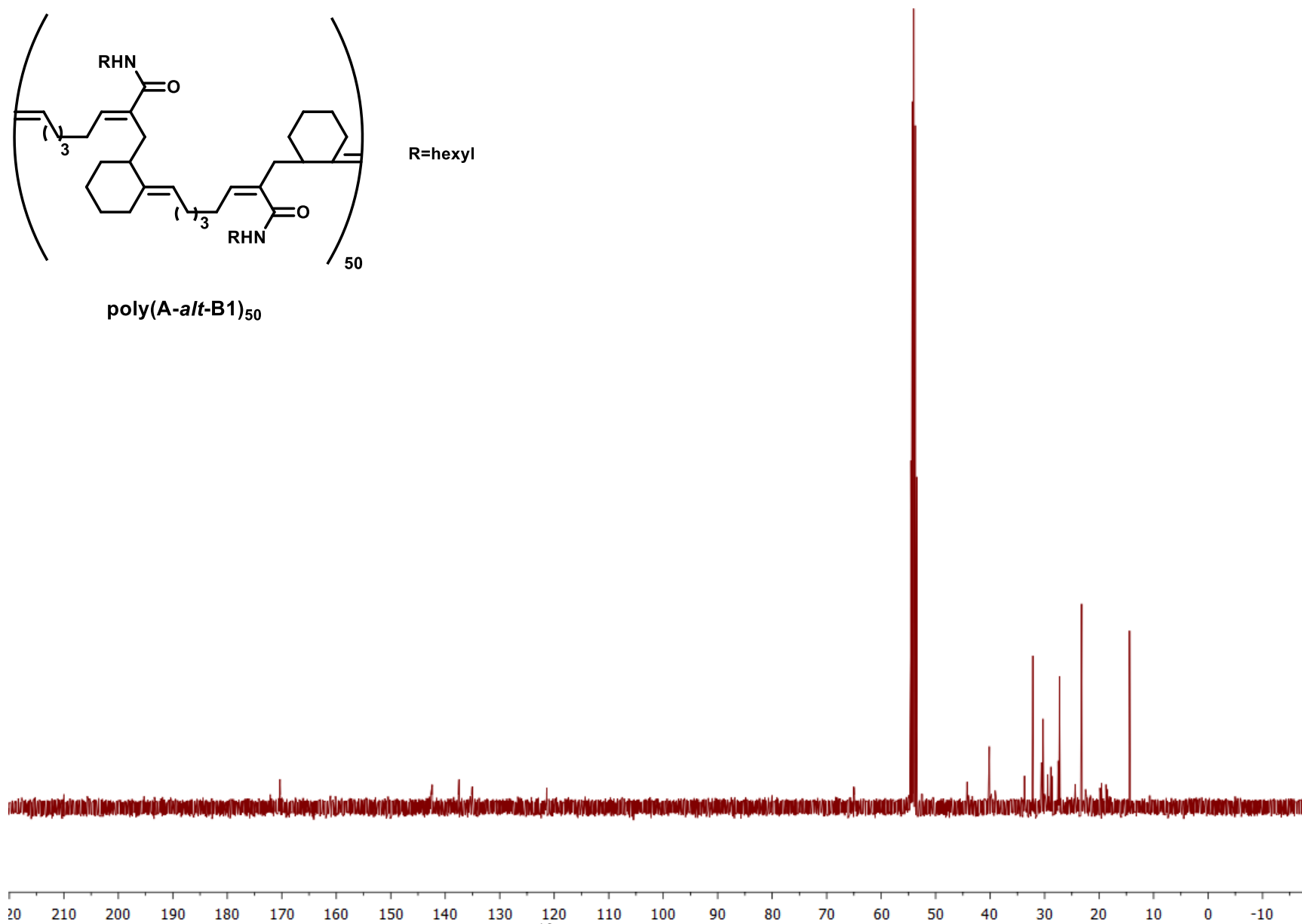
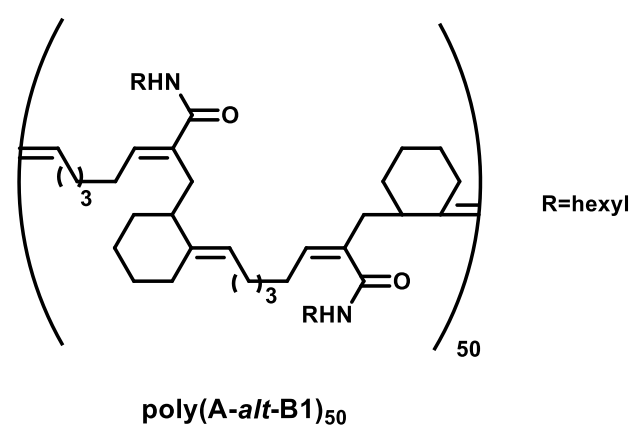


Figure S15 <sup>13</sup>C spectrum of poly(A-*alt*-B1)<sub>50</sub>

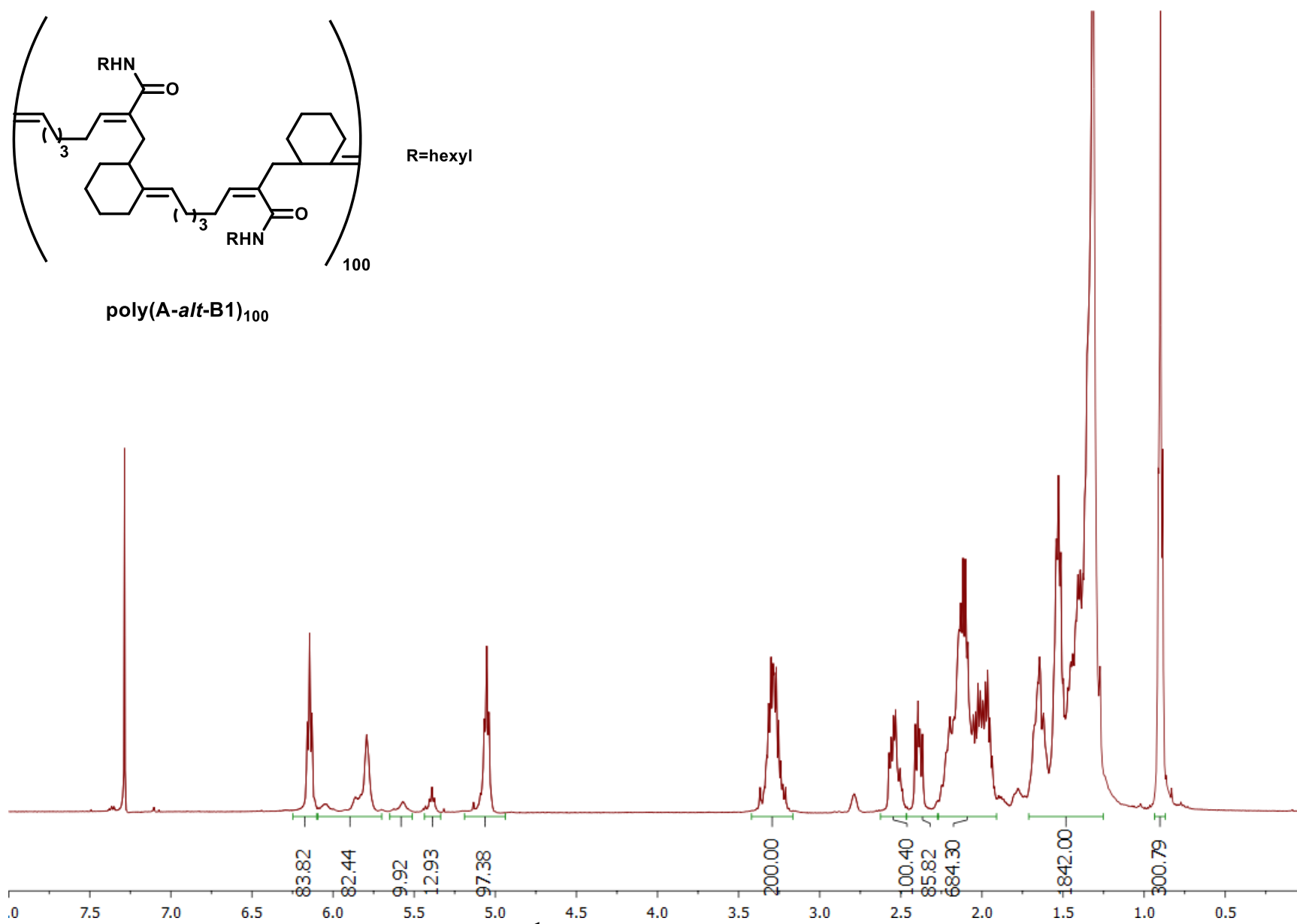
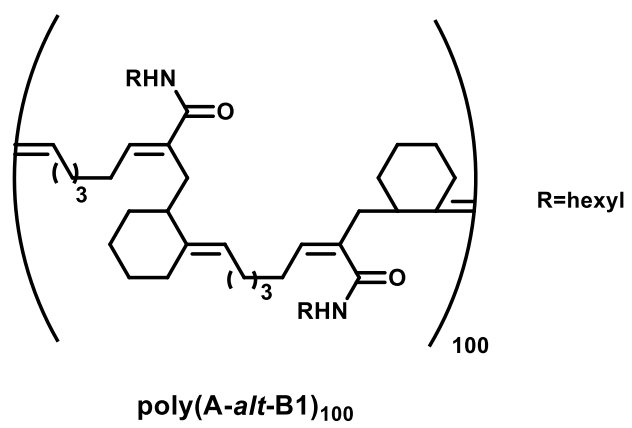


Figure S16  $^1\text{H}$  spectrum of poly(A-alt-B1) $_{100}$



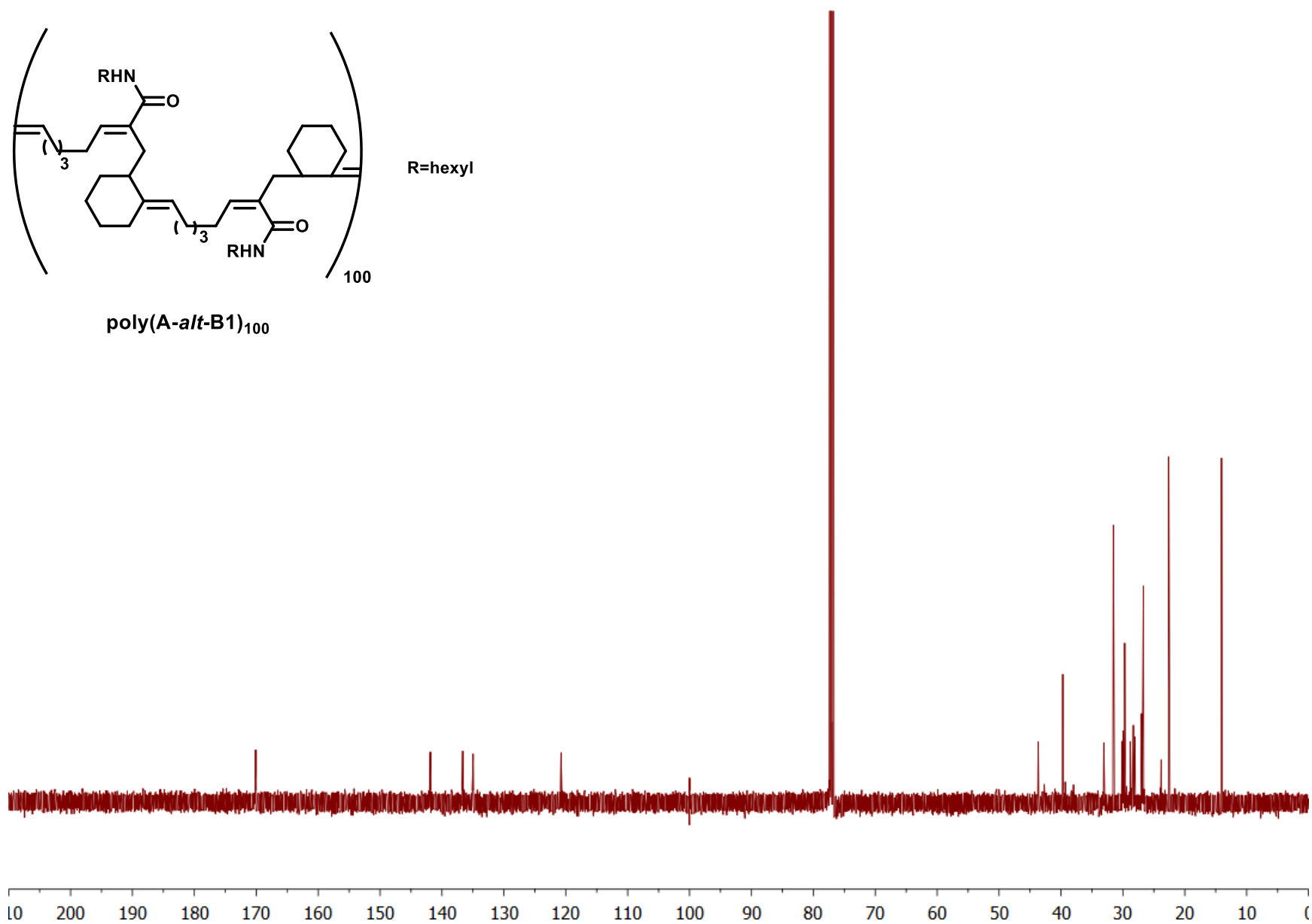


Figure S17 <sup>13</sup>C spectrum of poly(A-alt-B1)<sub>100</sub>

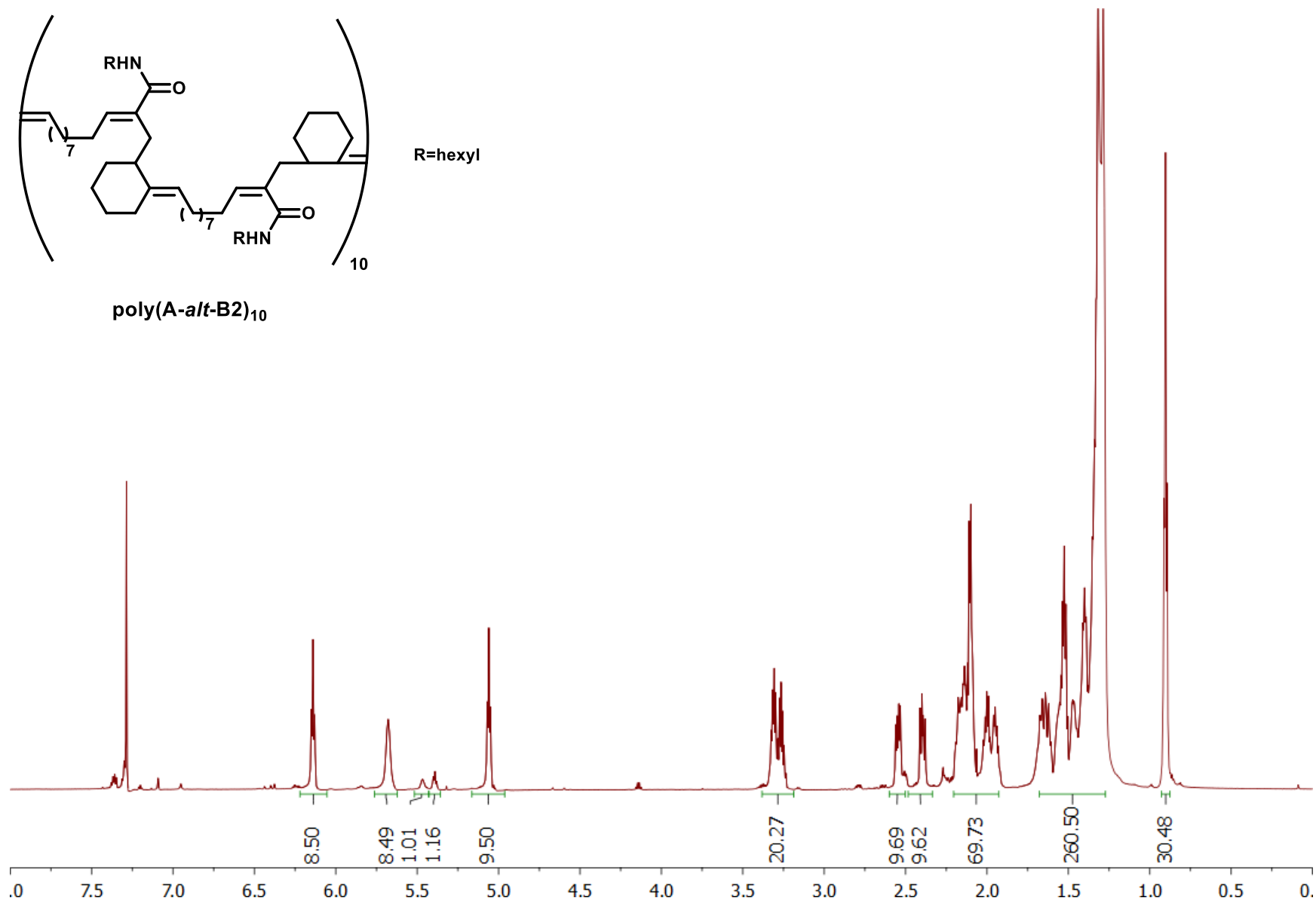
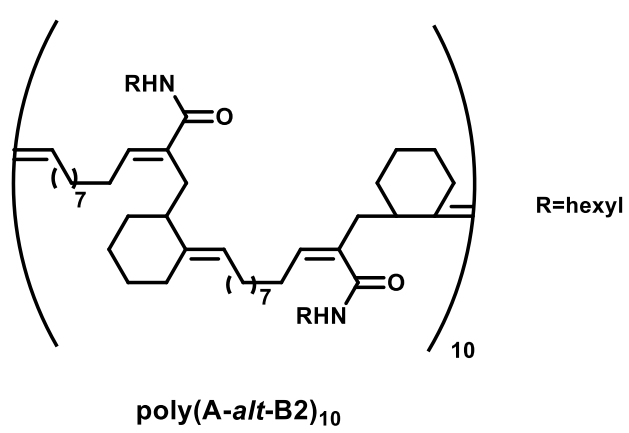


Figure S18 <sup>1</sup>H spectrum of poly(A-*alt*-B2)<sub>10</sub>

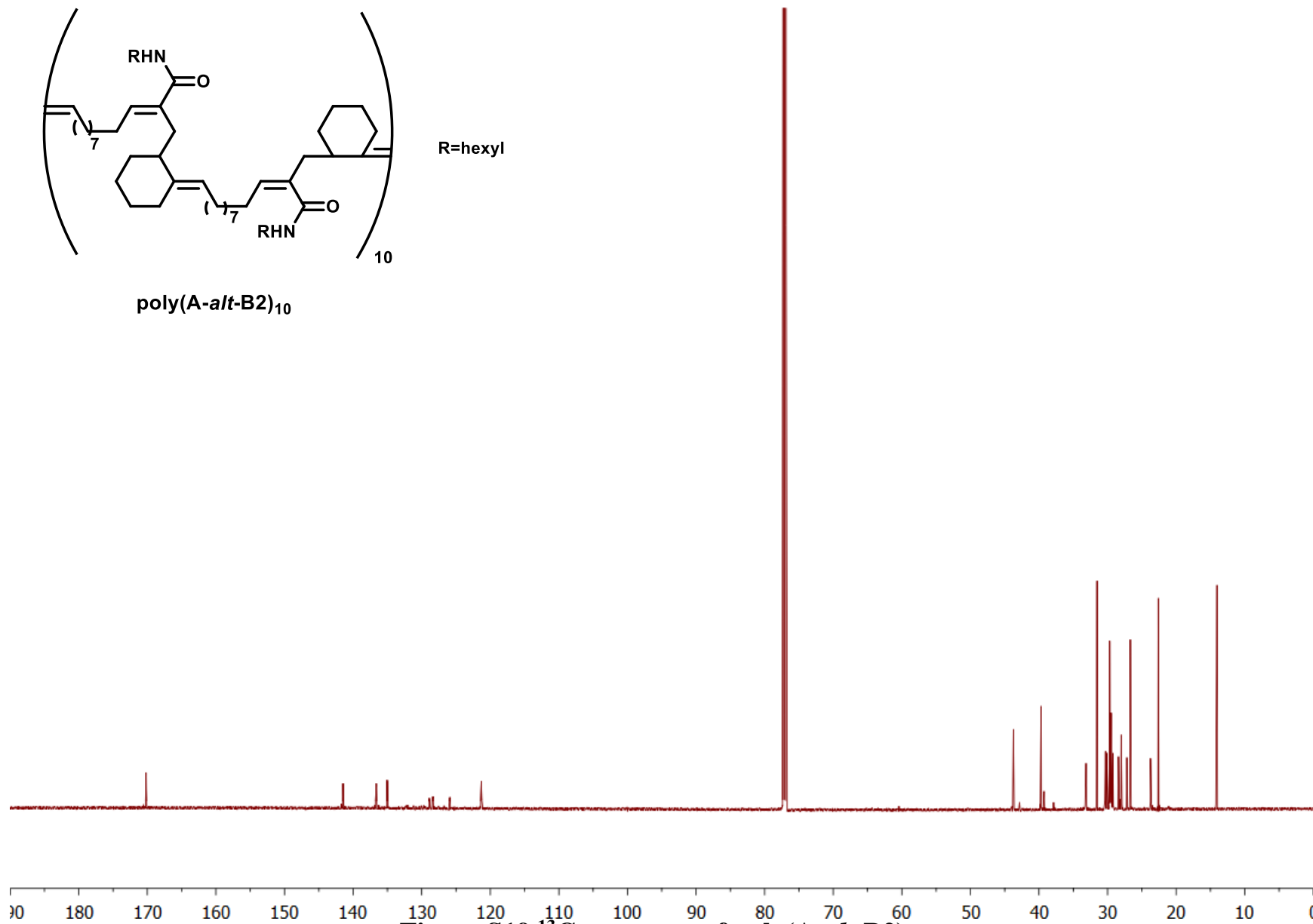
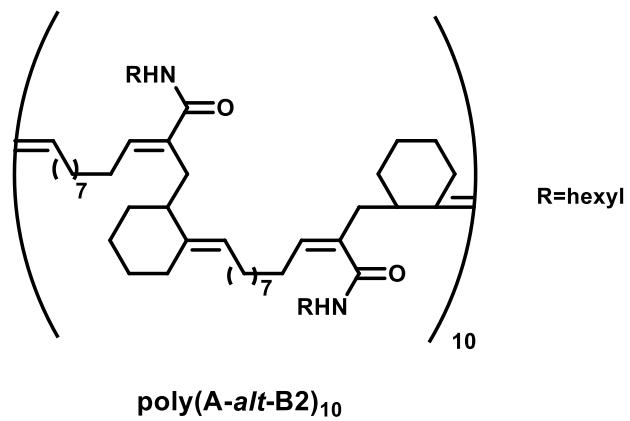
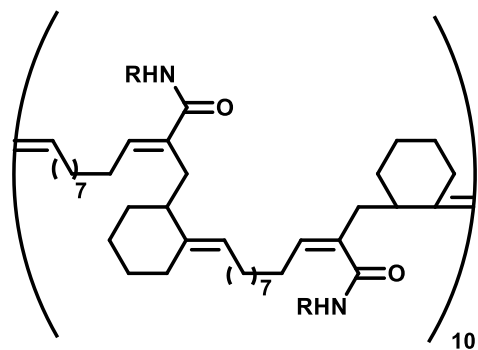


Figure S19 <sup>13</sup>C spectrum of poly(A-*alt*-B2)<sub>10</sub>

Figure S20 HSQC spectrum of poly(A-*alt*-B2)<sub>10</sub>



poly(A-*alt*-B2)<sub>10</sub>

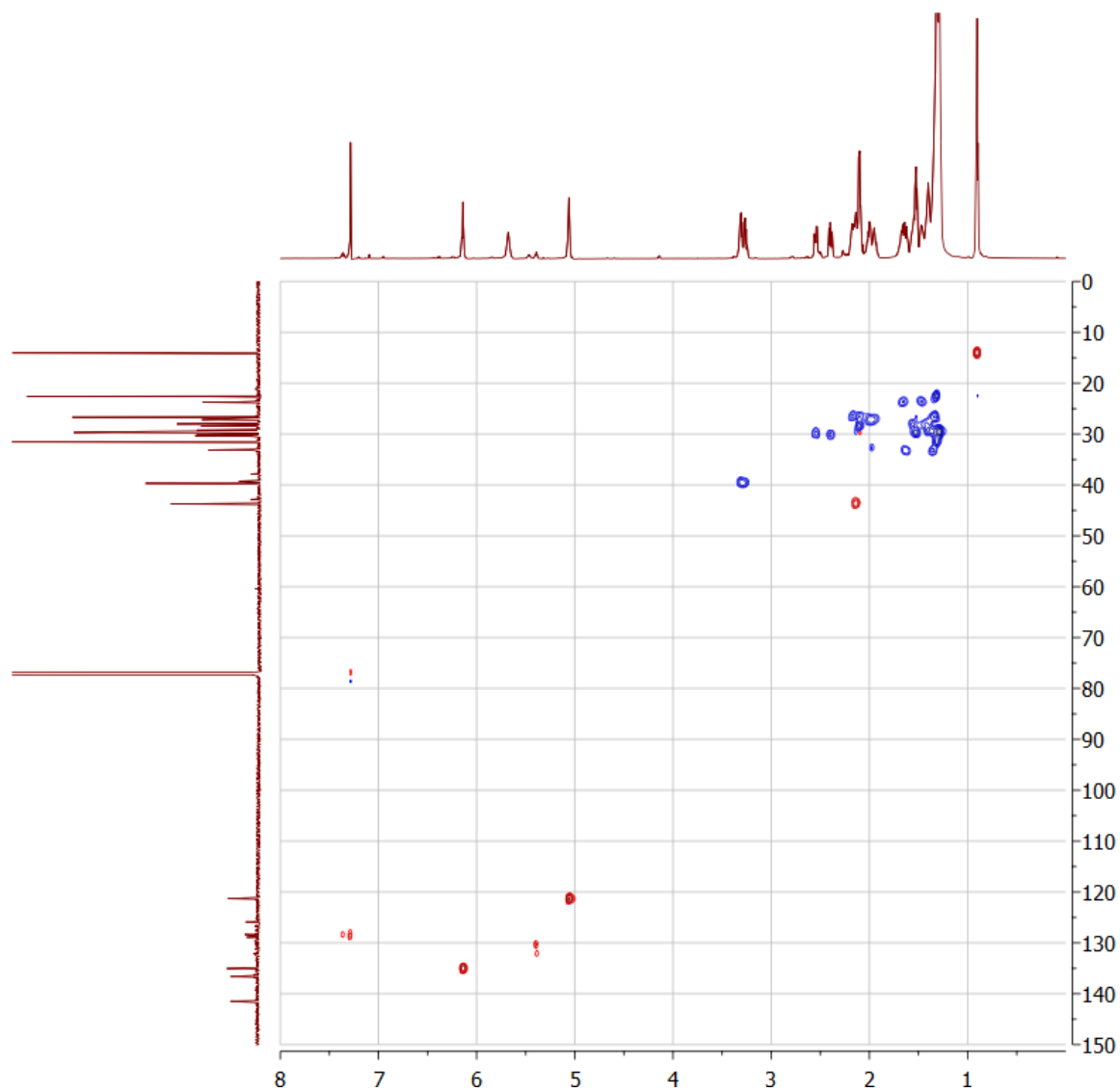
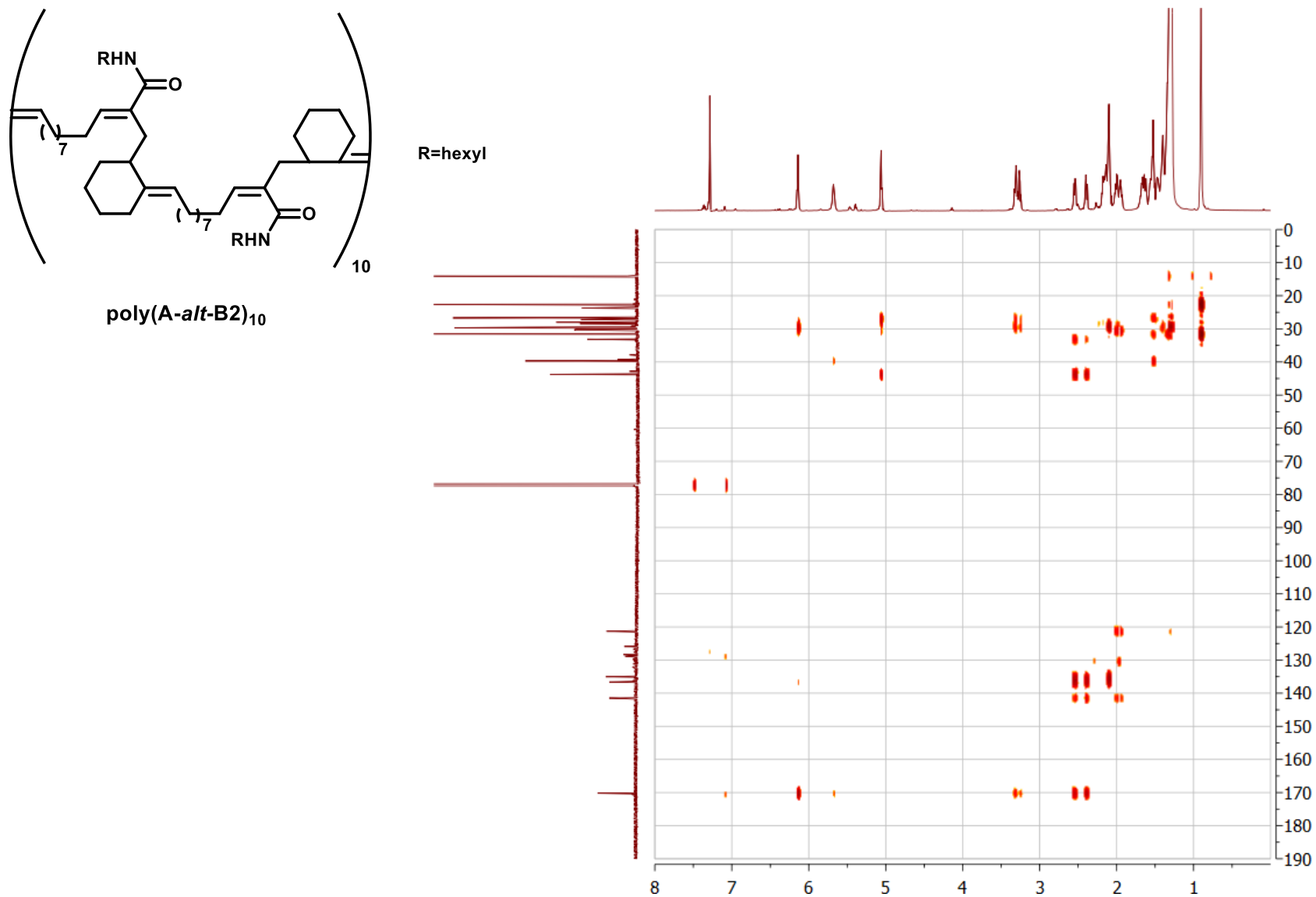


Figure S21 HMBC spectrum of poly(A-*alt*-B2)<sub>10</sub>



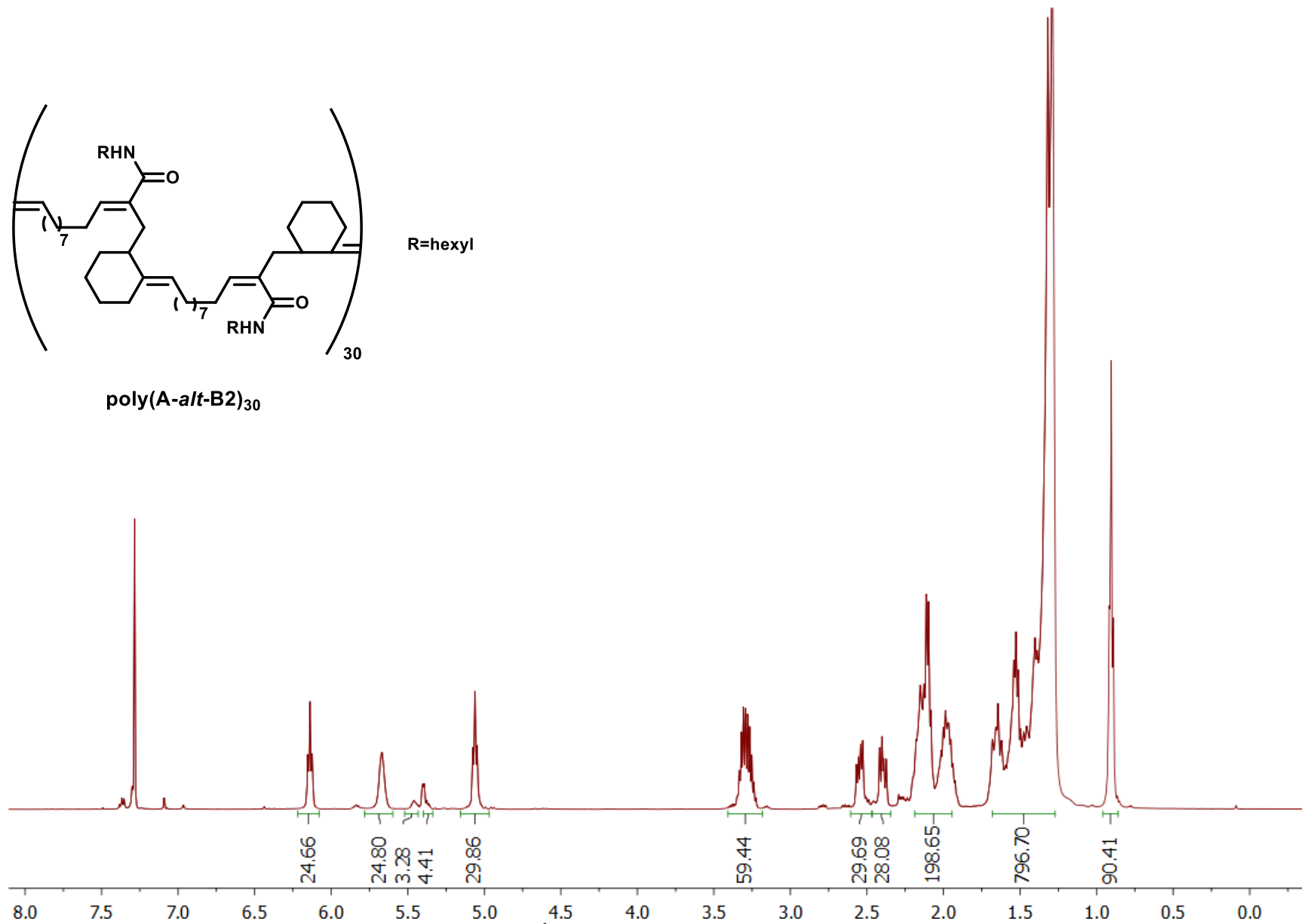
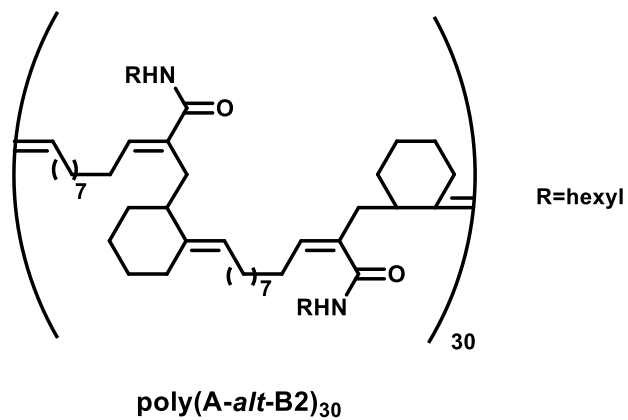
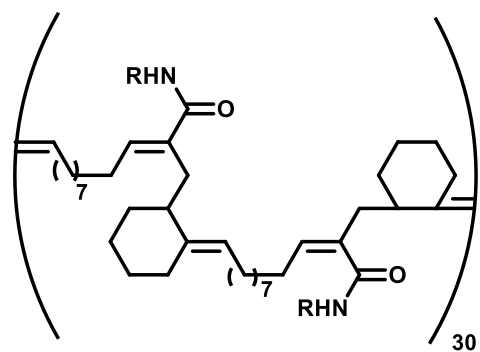


Figure S22 <sup>1</sup>H spectrum of poly(A-*alt*-B2)<sub>30</sub>



R=hexyl

poly(A-*alt*-B2)<sub>30</sub>

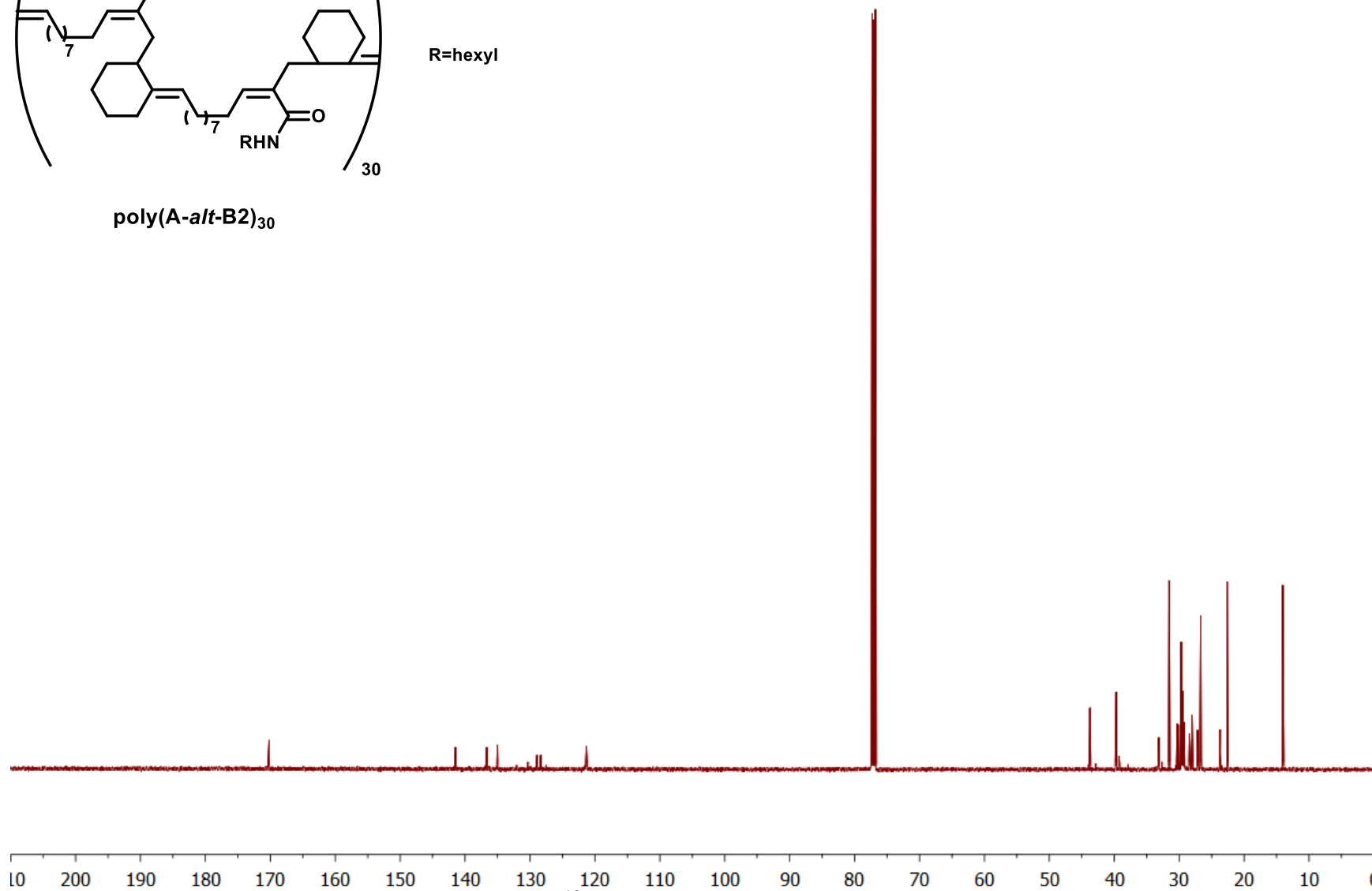


Figure S23 <sup>13</sup>C spectrum of poly(A-*alt*-B2)<sub>30</sub>

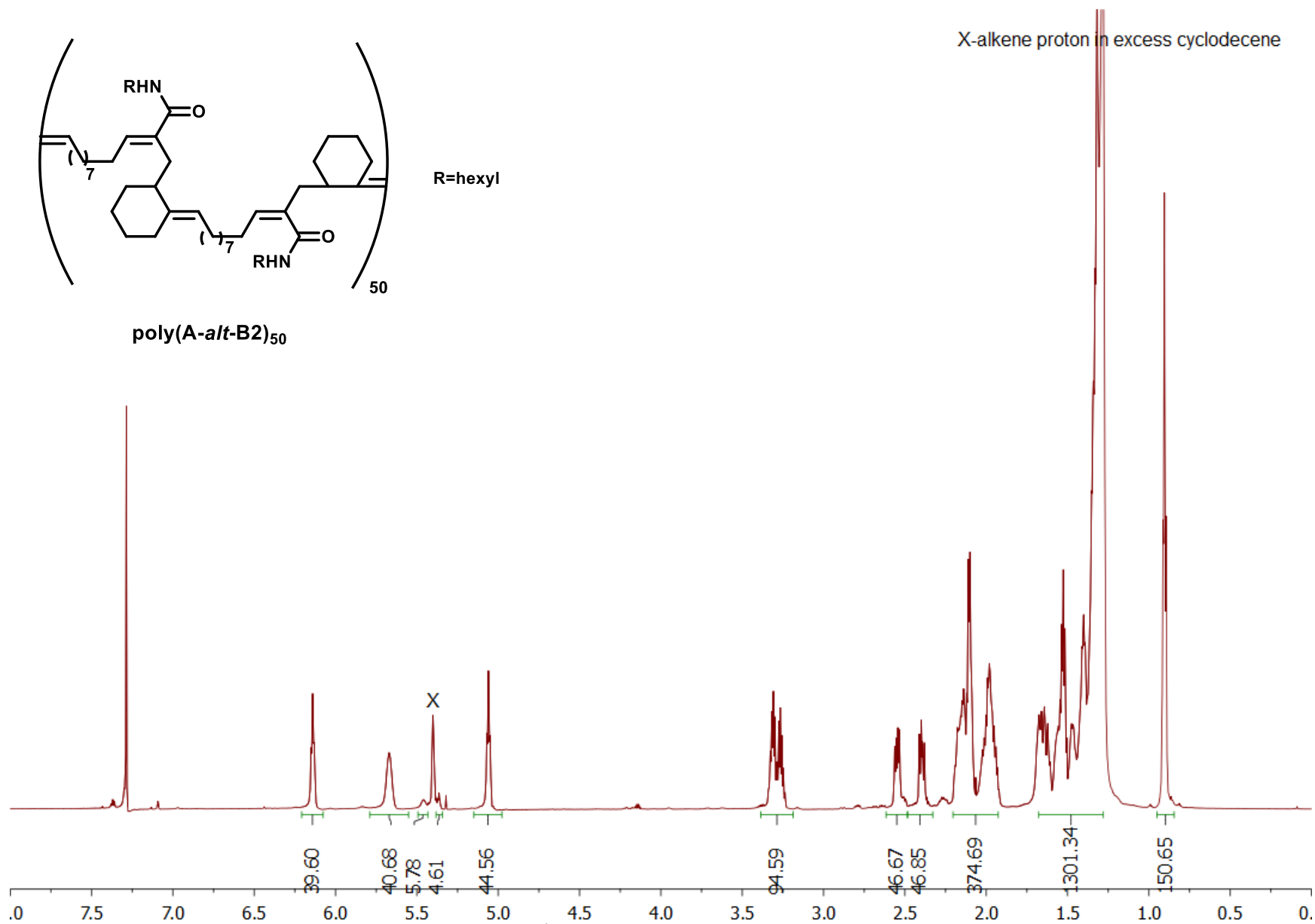
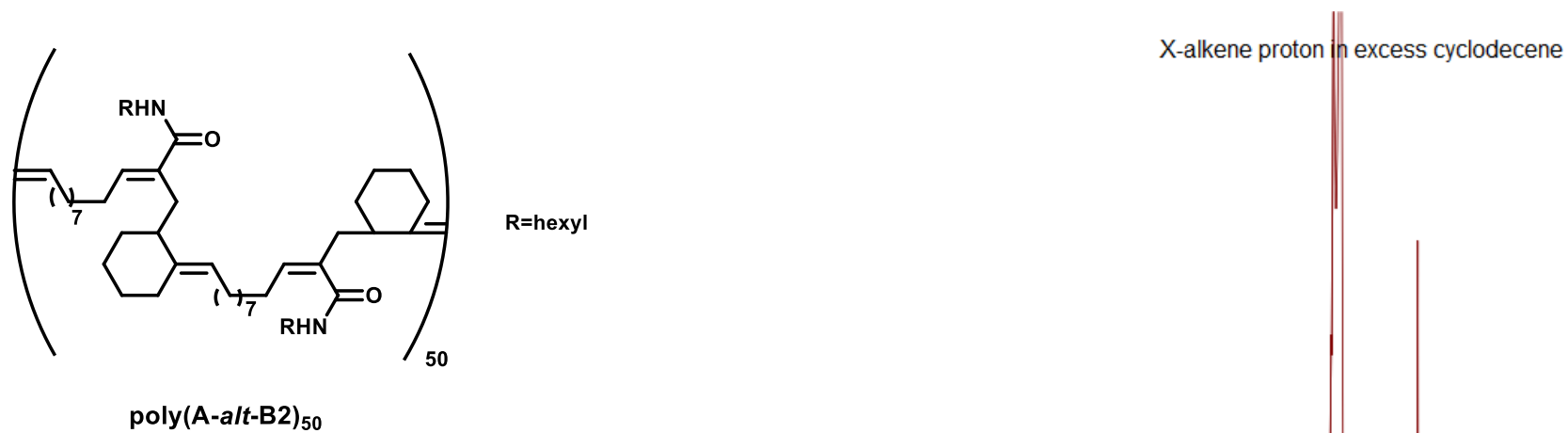
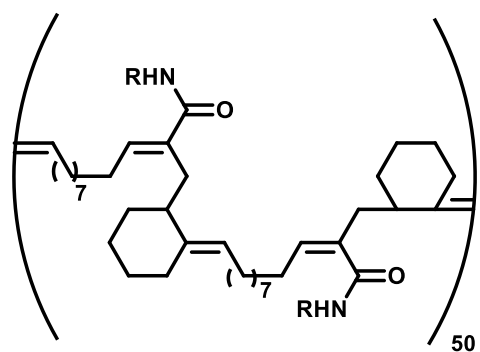


Figure S24 <sup>1</sup>H spectrum of poly(A-*alt*-B2)<sub>50</sub>





R=hexyl

poly(A-*alt*-B2)<sub>50</sub>

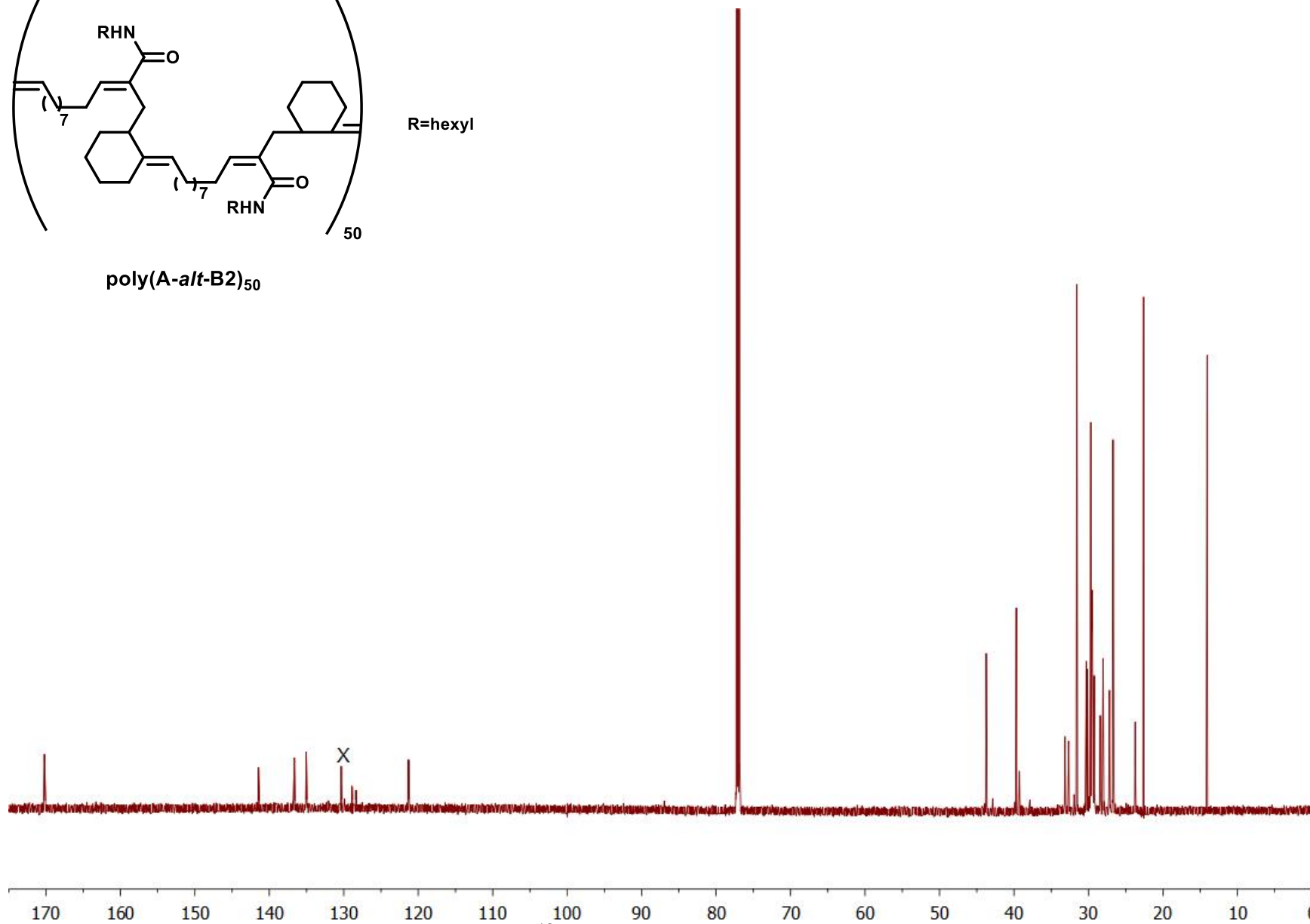


Figure S25 <sup>13</sup>C spectrum of poly(A-*alt*-B2)<sub>50</sub>

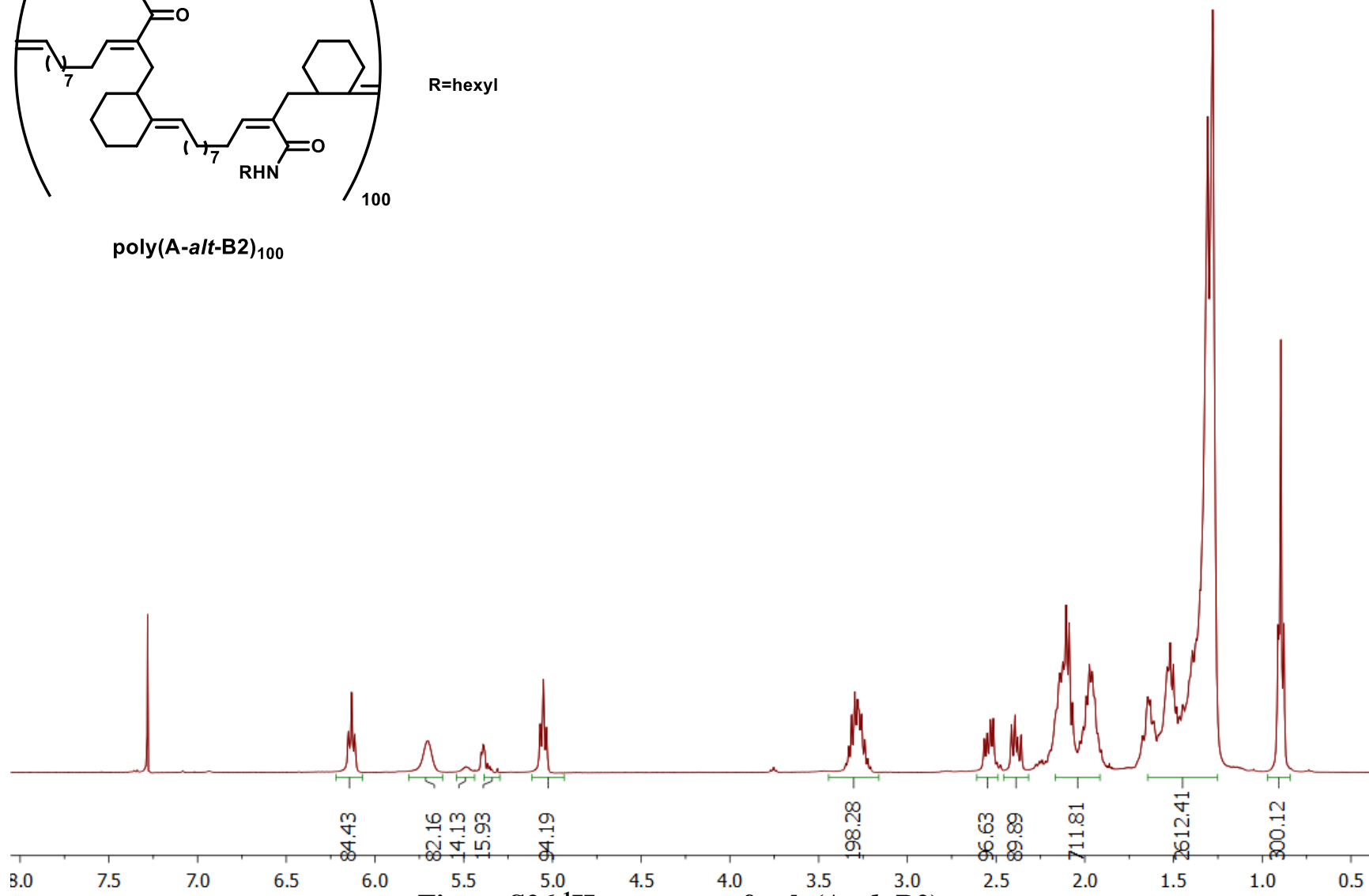
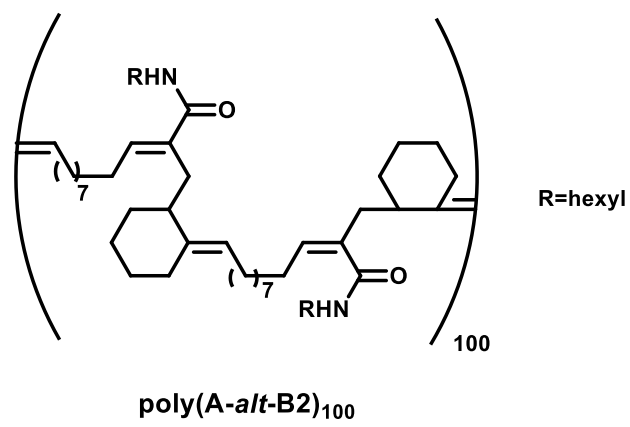


Figure S26 <sup>1</sup>H spectrum of poly(A-*alt*-B2)<sub>100</sub>

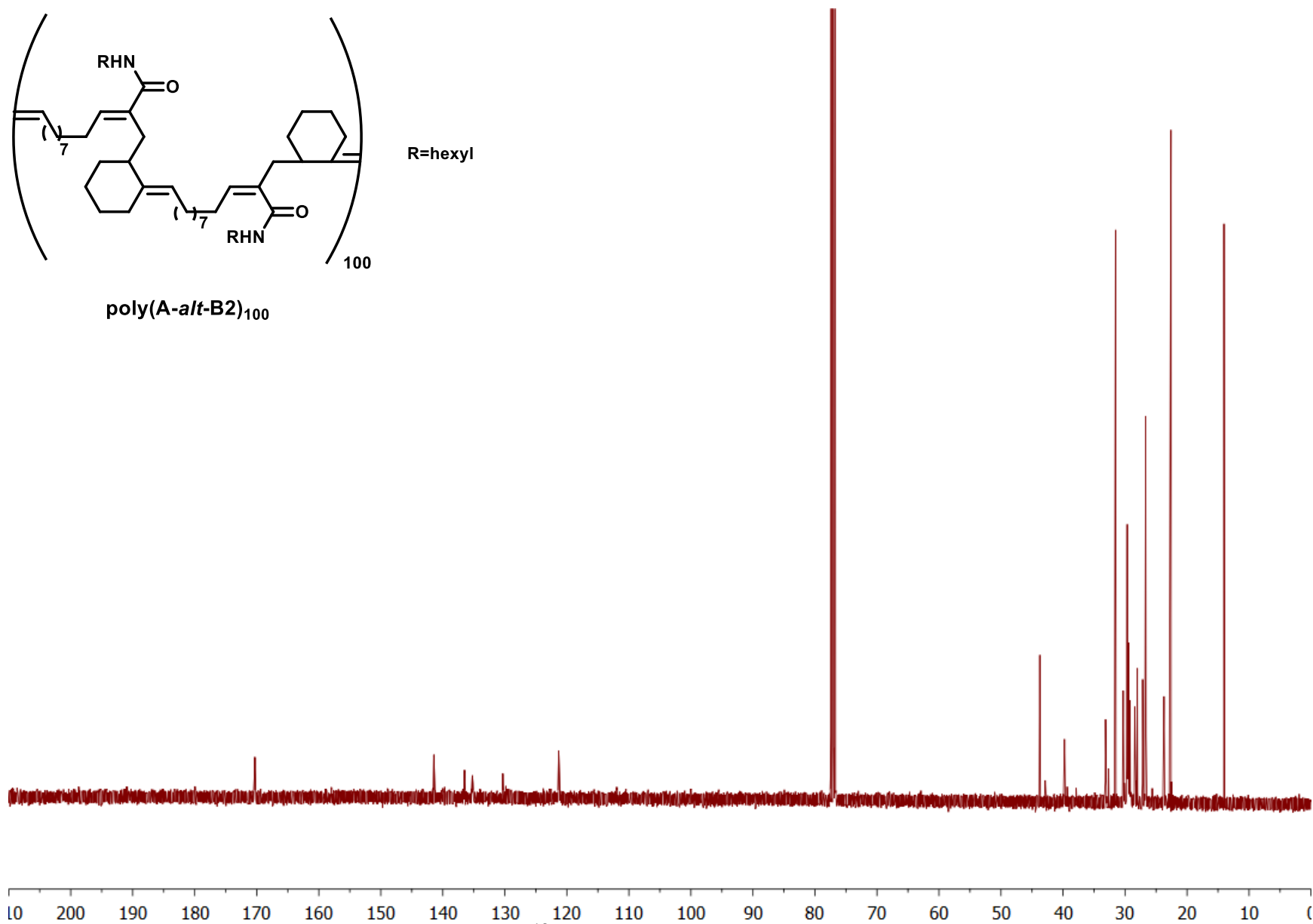
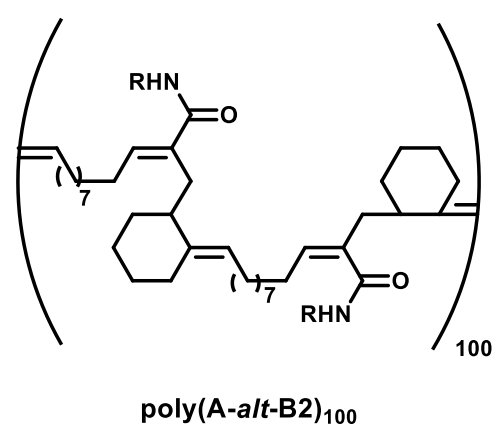


Figure S27 <sup>13</sup>C spectrum of poly(A-*alt*-B2)<sub>100</sub>

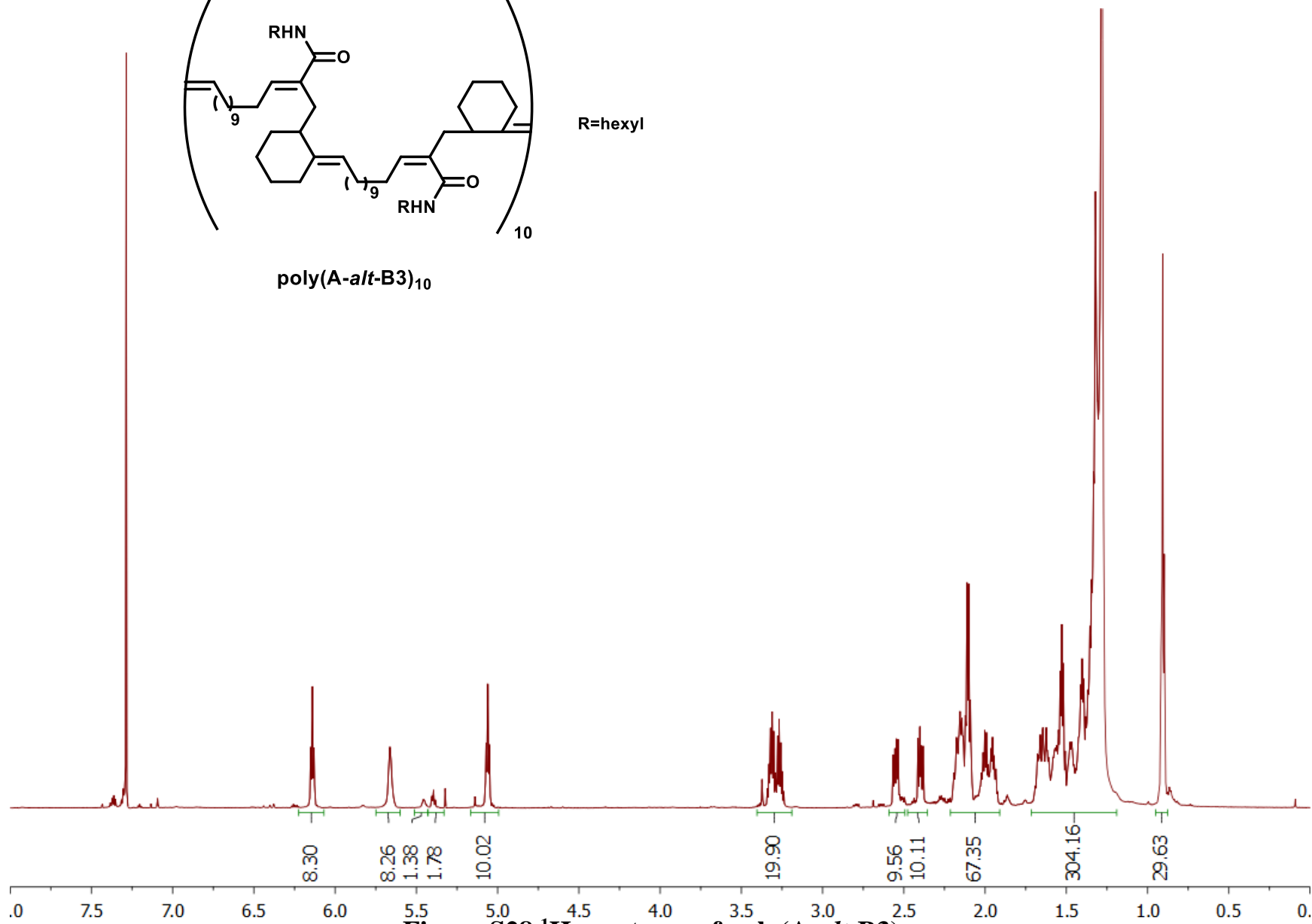
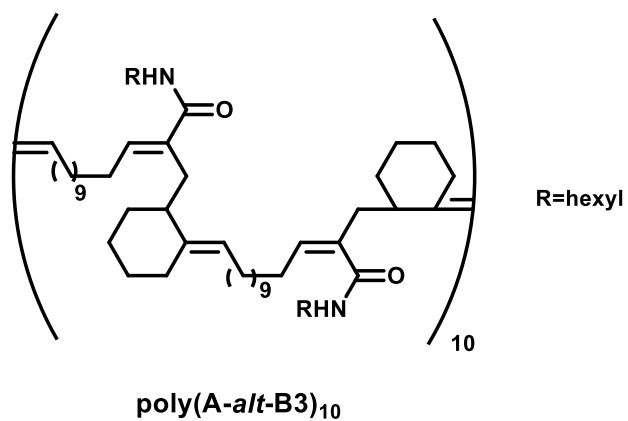


Figure S28 <sup>1</sup>H spectrum of poly(A-*alt*-B3)<sub>10</sub>

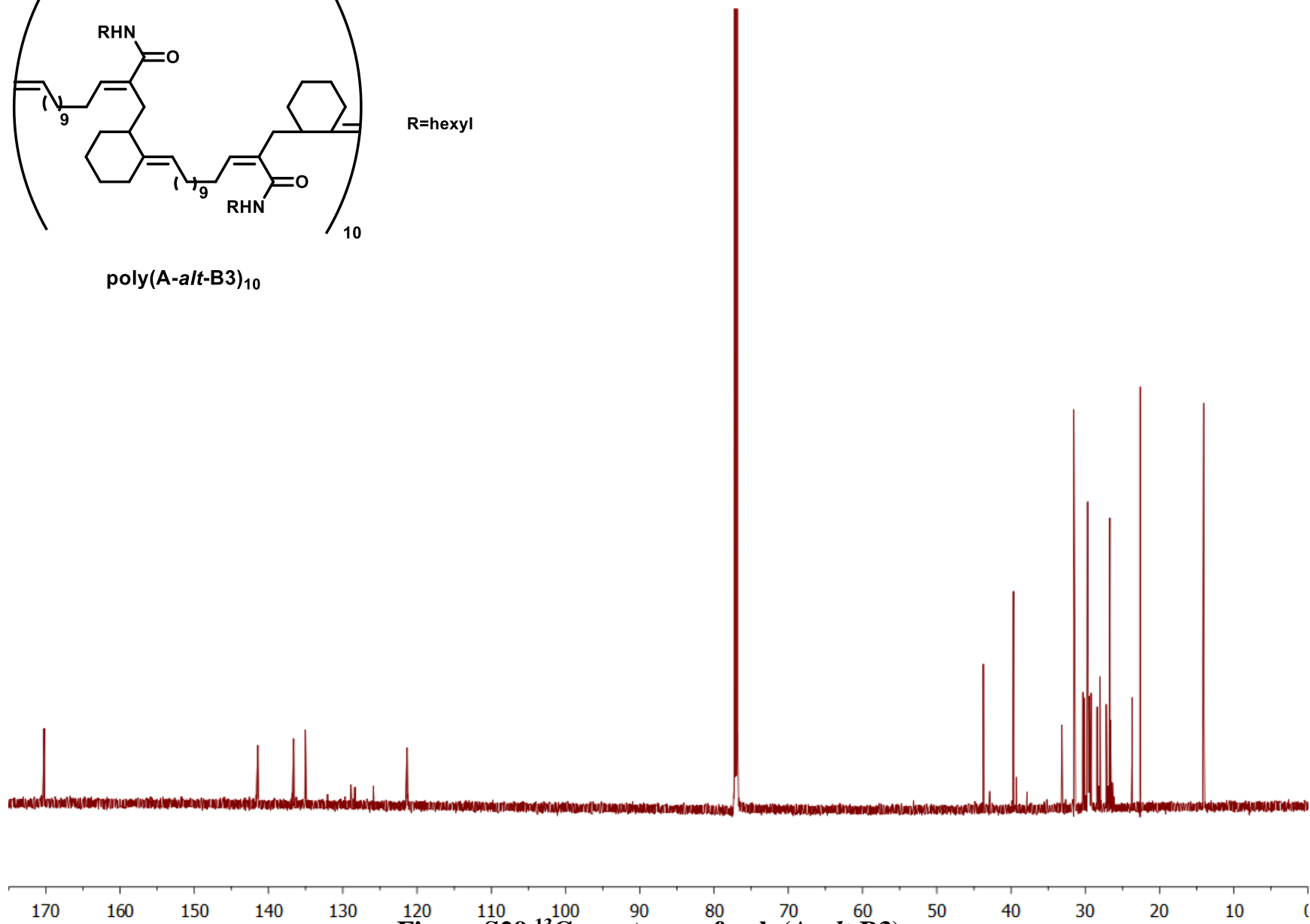
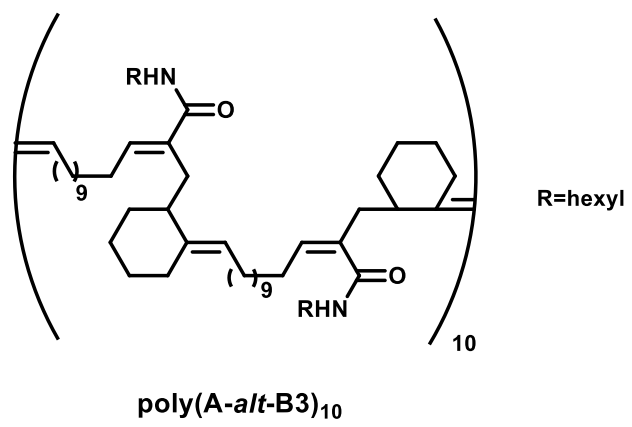


Figure S29 <sup>13</sup>C spectrum of poly(A-*alt*-B3)<sub>10</sub>

Figure S30 HSQC spectrum of poly(A-*alt*-B3)<sub>10</sub>

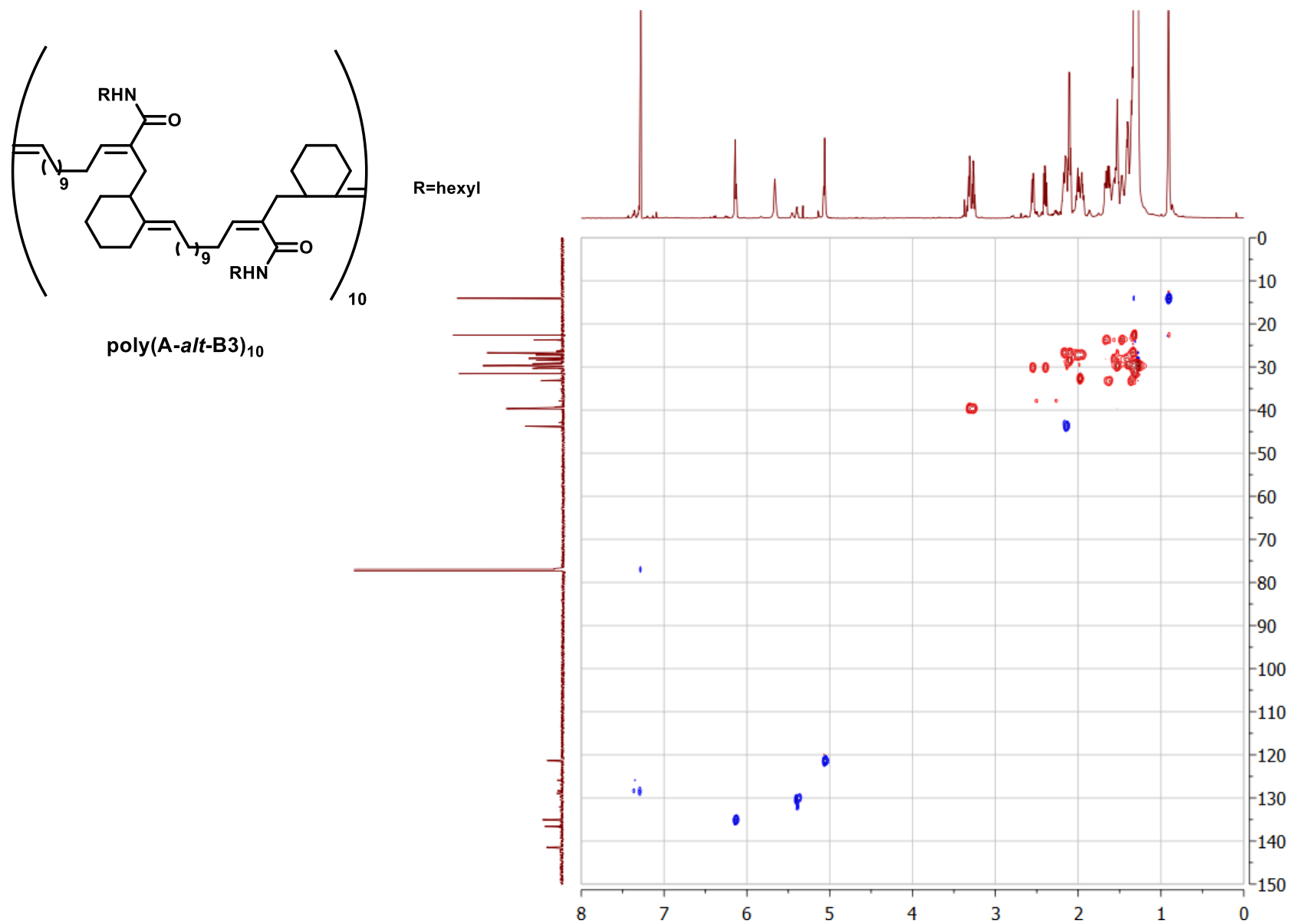
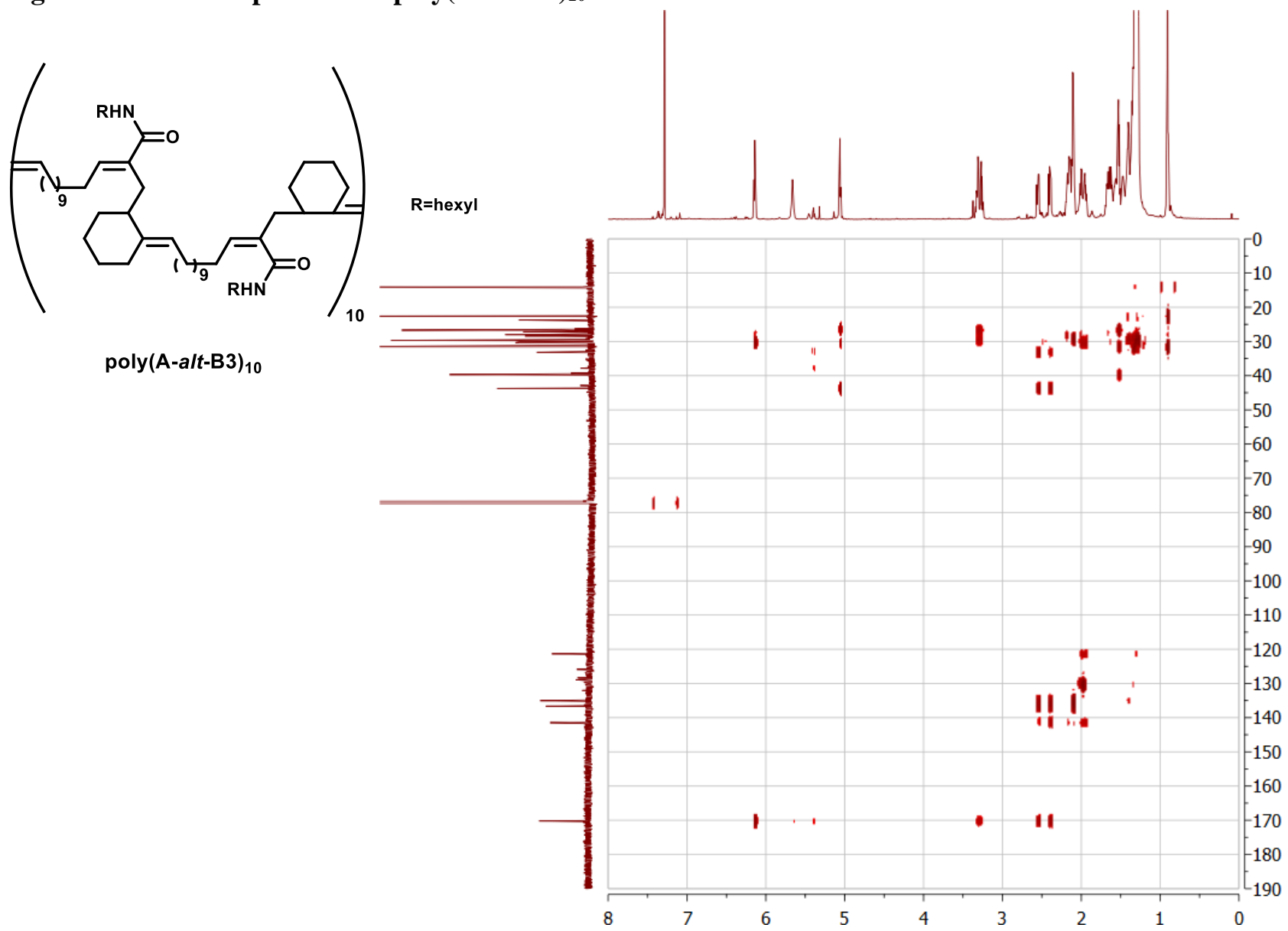
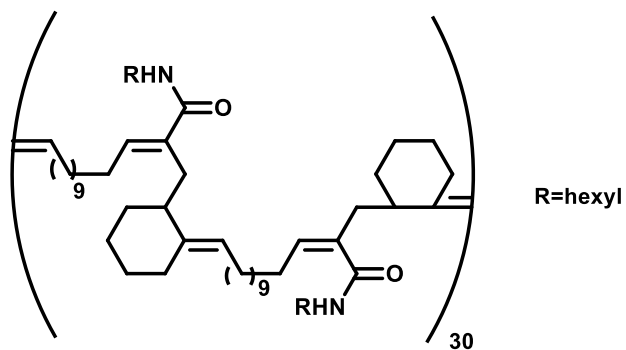


Figure S31 HMBC spectrum of poly(A-*alt*-B3)<sub>10</sub>





x- alkene proton of excess cyclododecene

poly(A-*alt*-B3)<sub>30</sub>

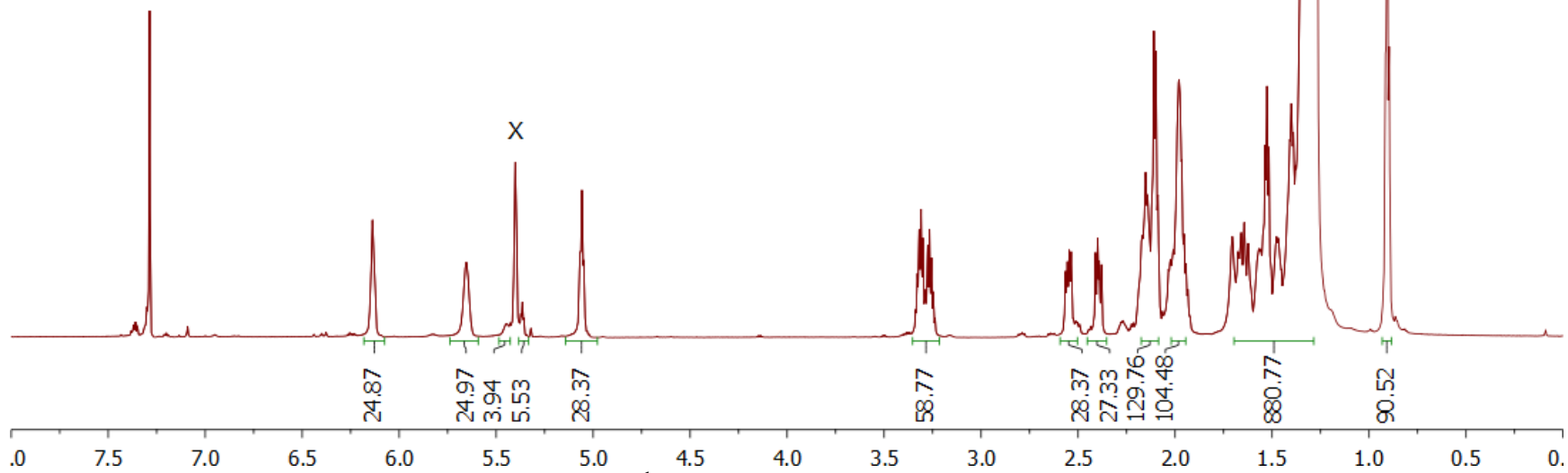
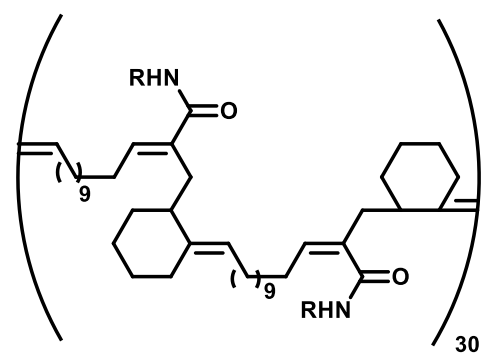


Figure S32 <sup>1</sup>H spectrum of poly(A-*alt*-B3)<sub>30</sub>





R=hexyl

poly(A-*alt*-B3)<sub>30</sub>

x-alkene carbon of excess cyclododecene

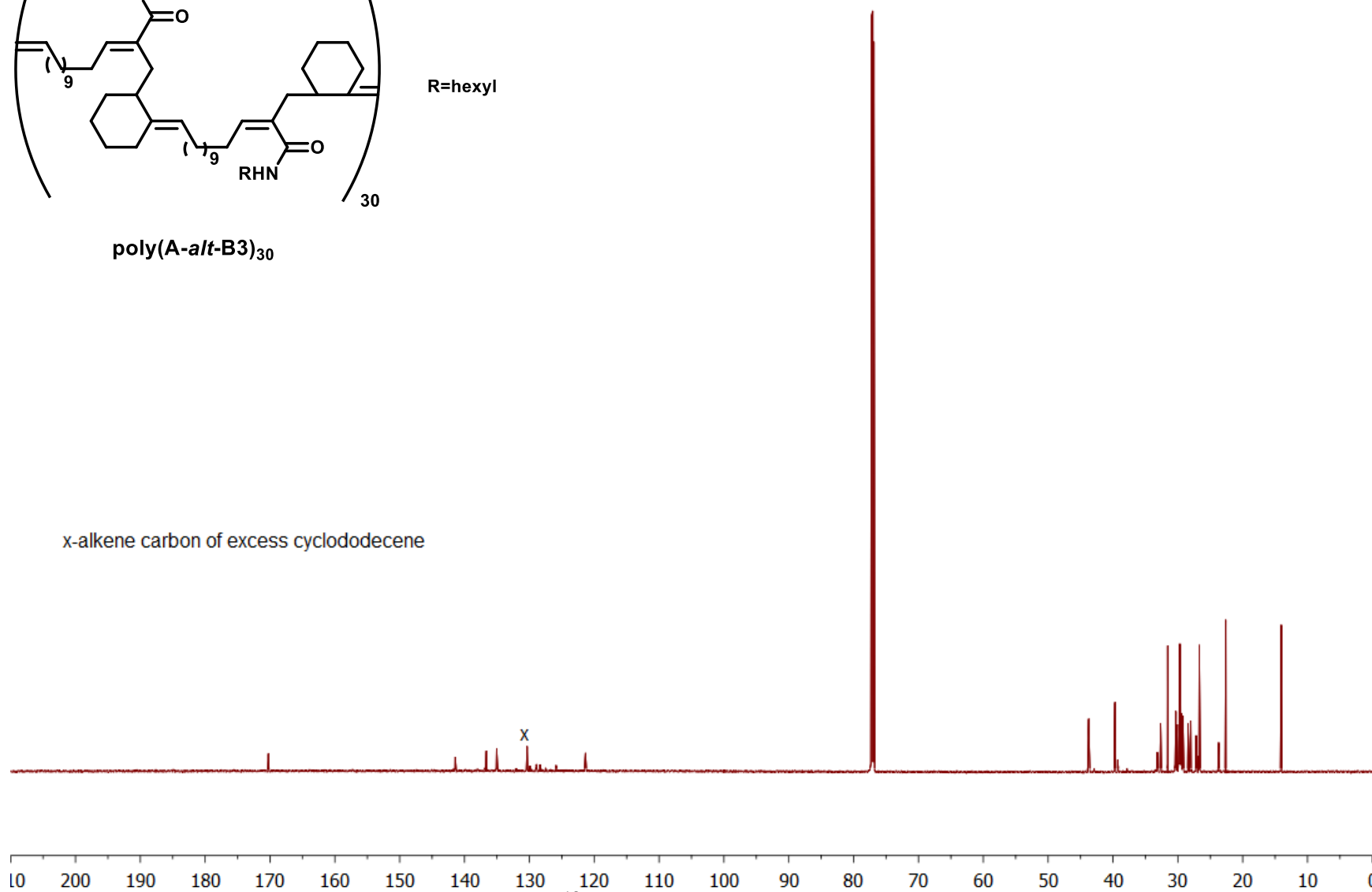


Figure S33 <sup>13</sup>C spectrum of poly(A-*alt*-B3)<sub>30</sub>

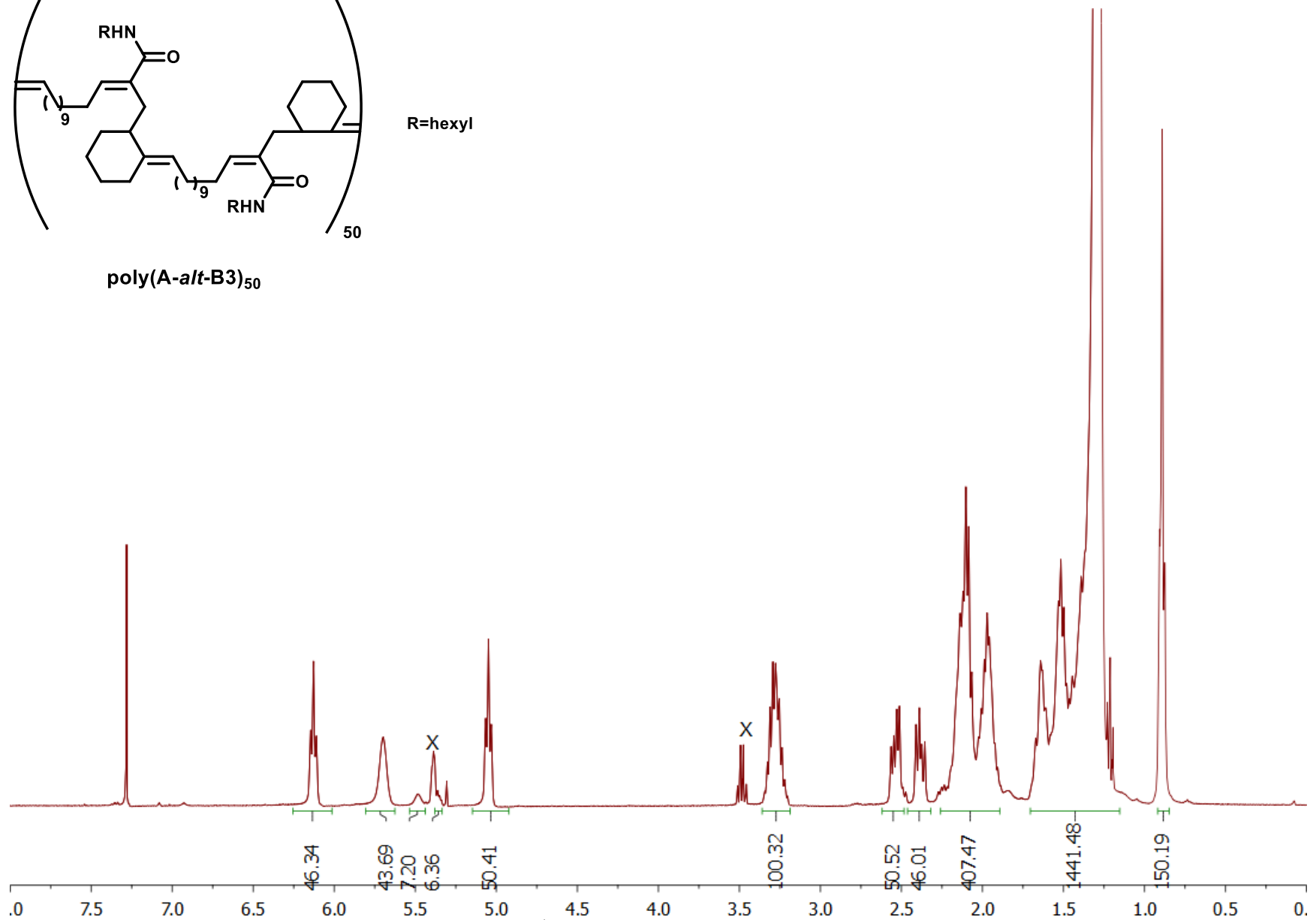
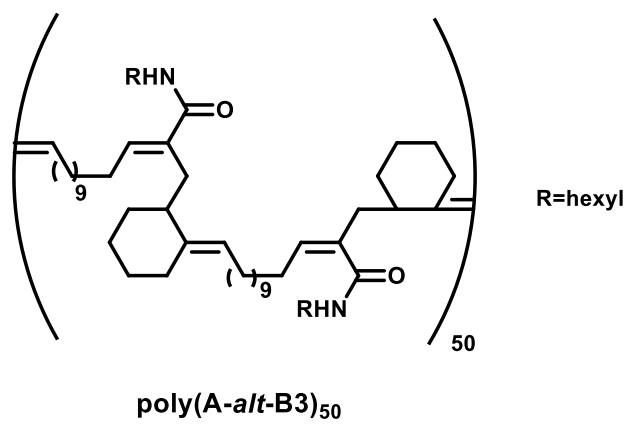
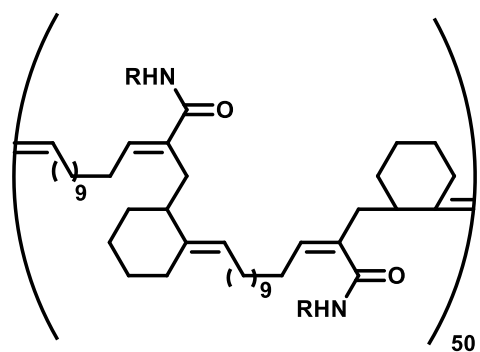


Figure S34 <sup>1</sup>H spectrum of poly(A-*alt*-B3)<sub>50</sub>



R=hexyl

poly(A-*alt*-B3)<sub>50</sub>

x-excess cyclododecene

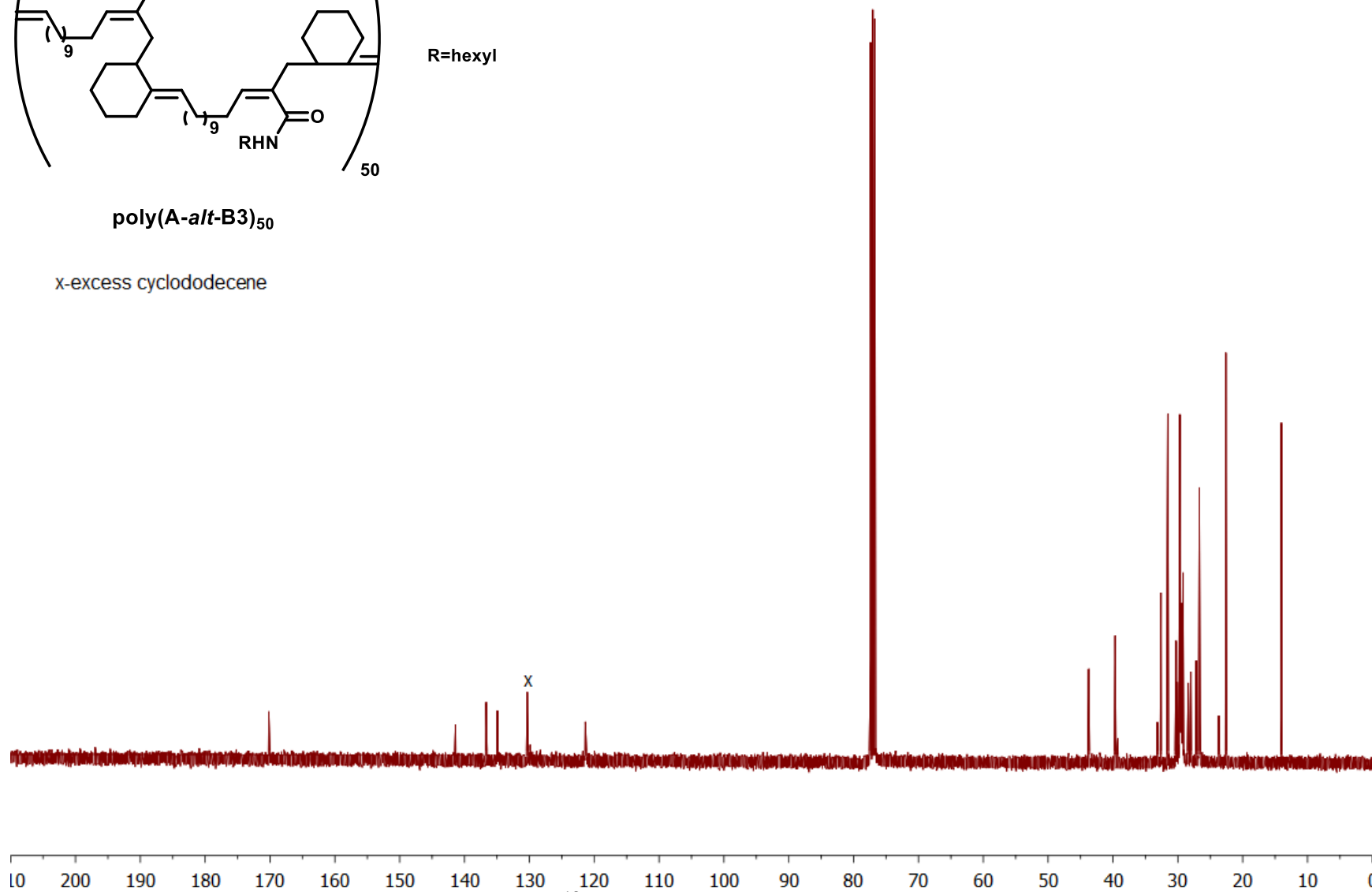
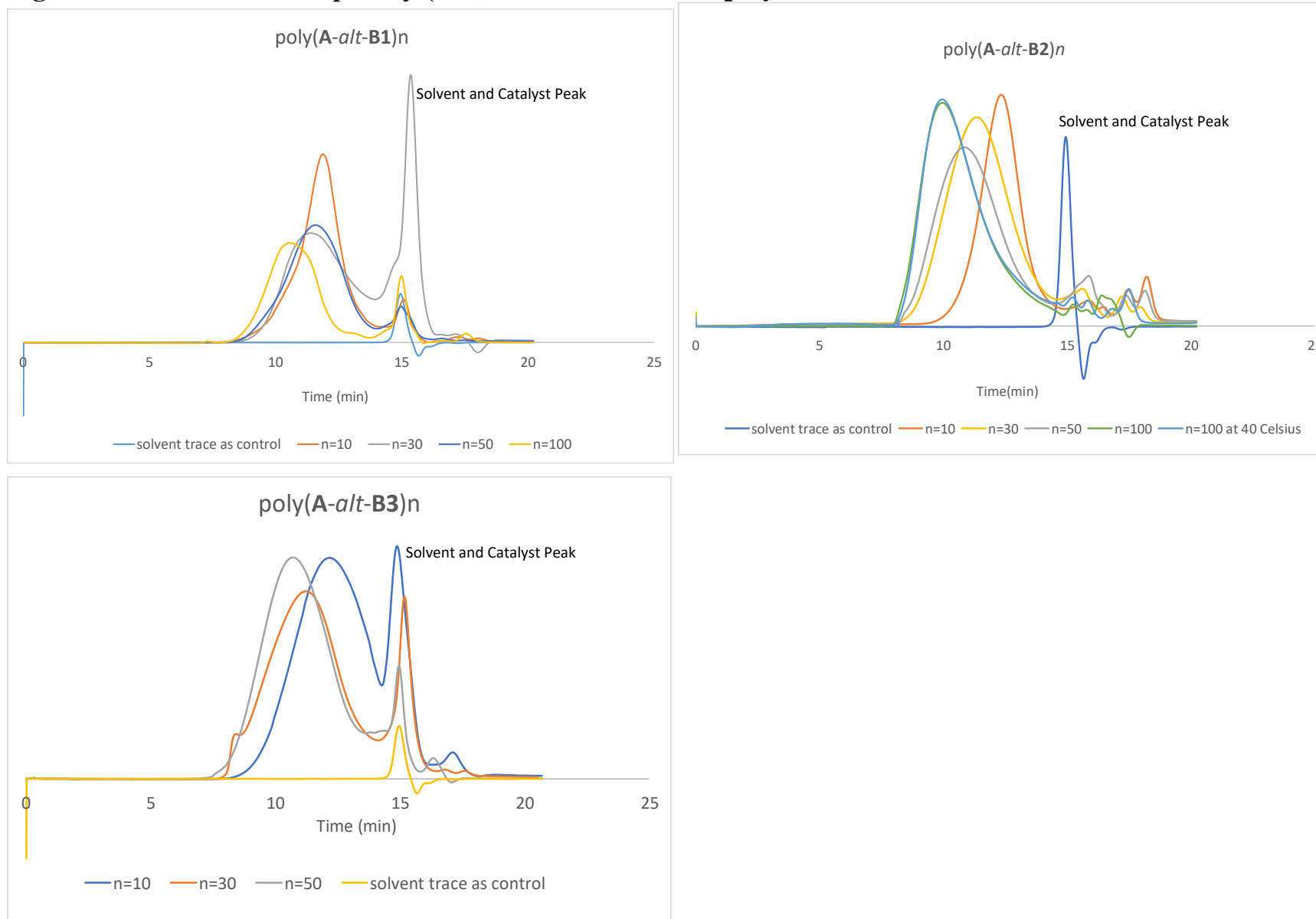
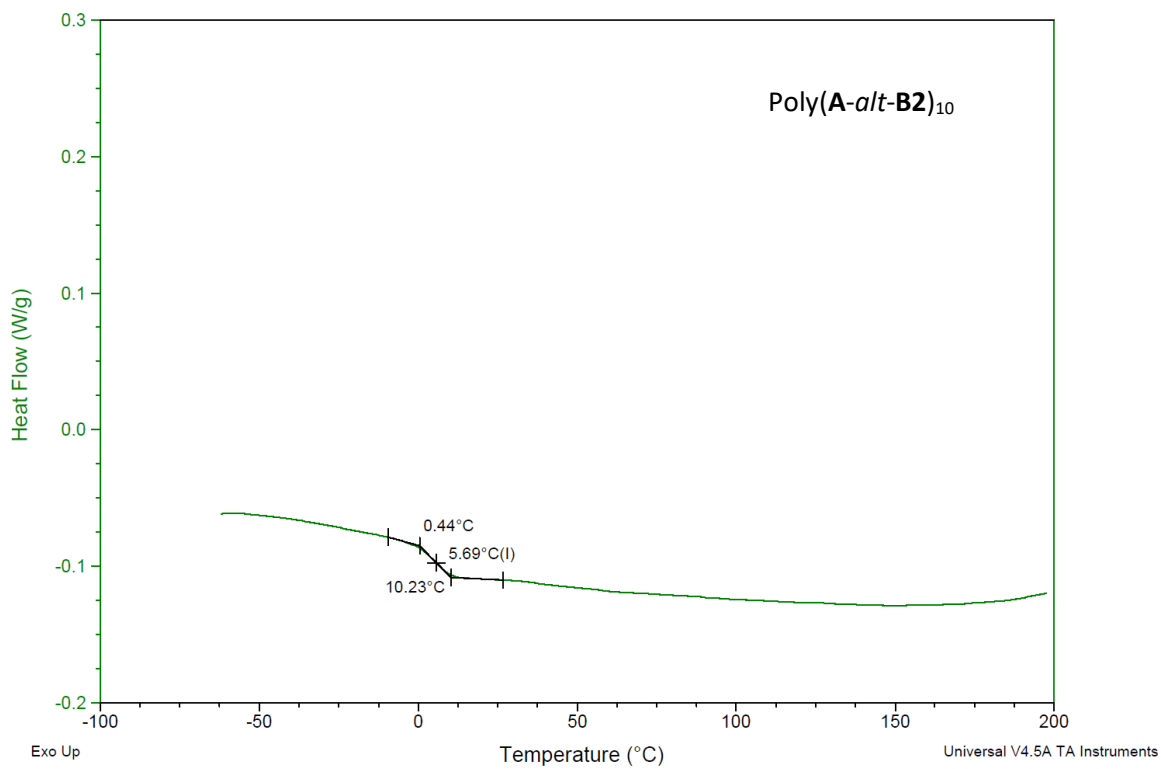
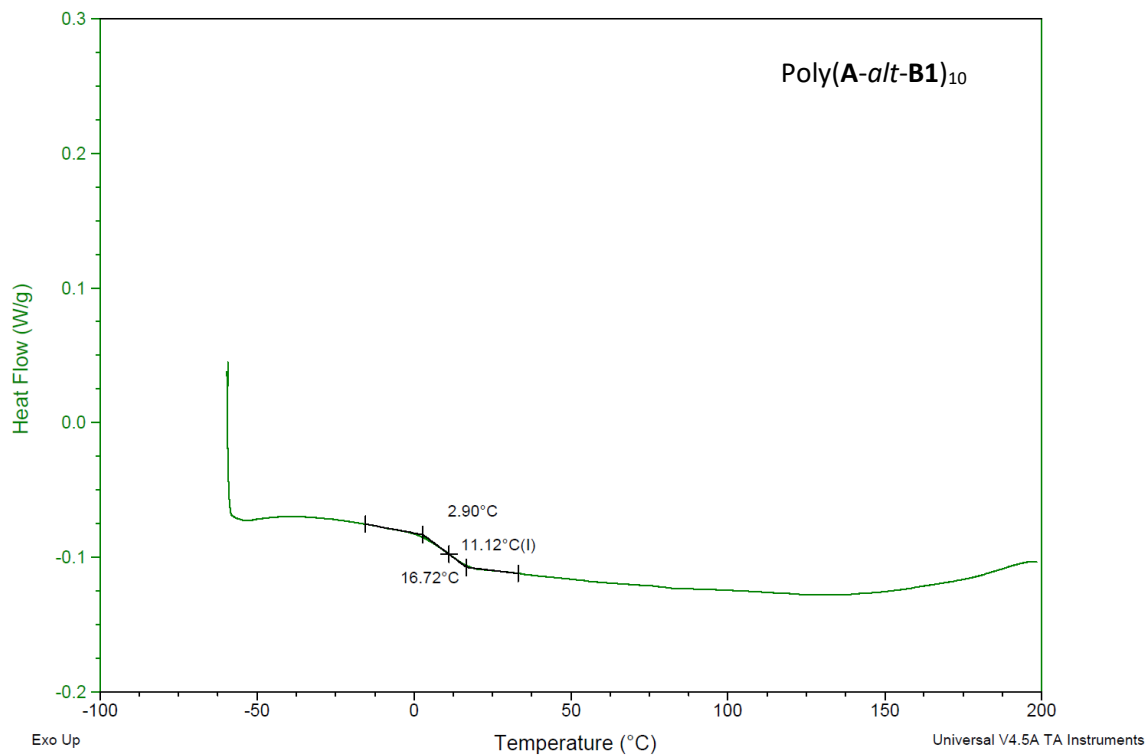


Figure S35 <sup>13</sup>C spectrum of poly(A-*alt*-B3)<sub>50</sub>

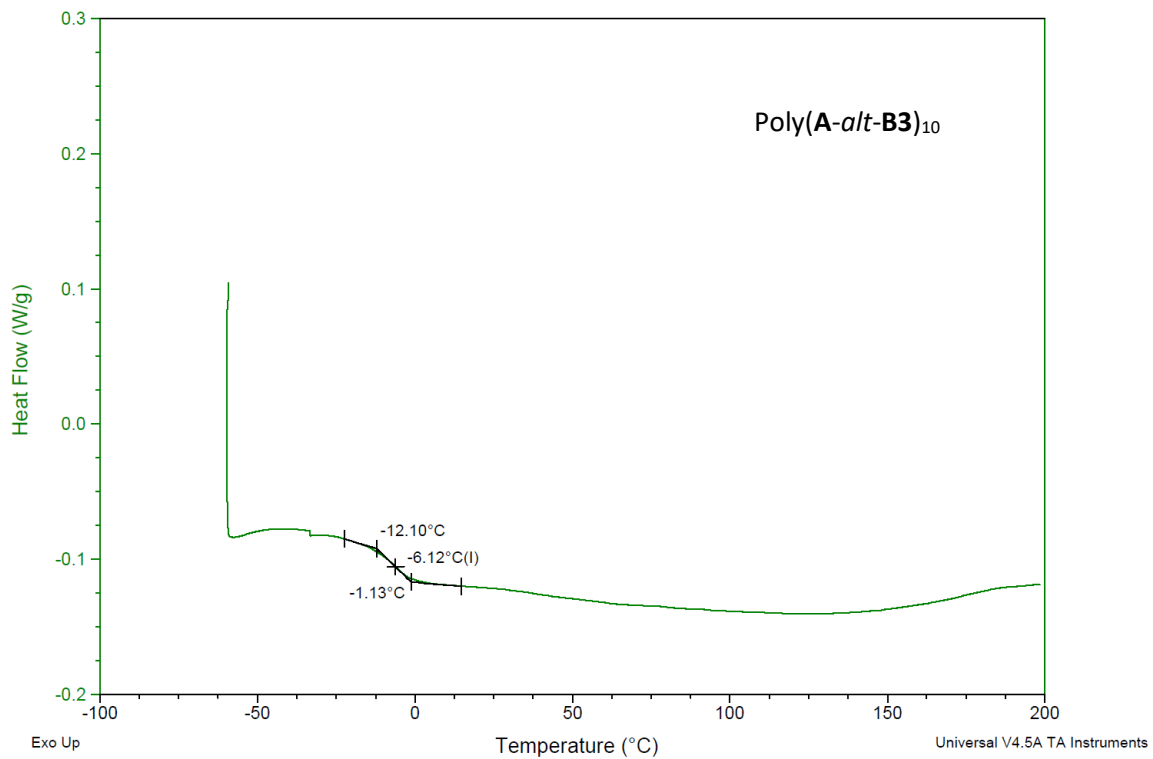
**Figure S36 Molar mass dispersity ( $\overline{M}_w/\overline{M}_n$ ) traces of AROMP polymers**



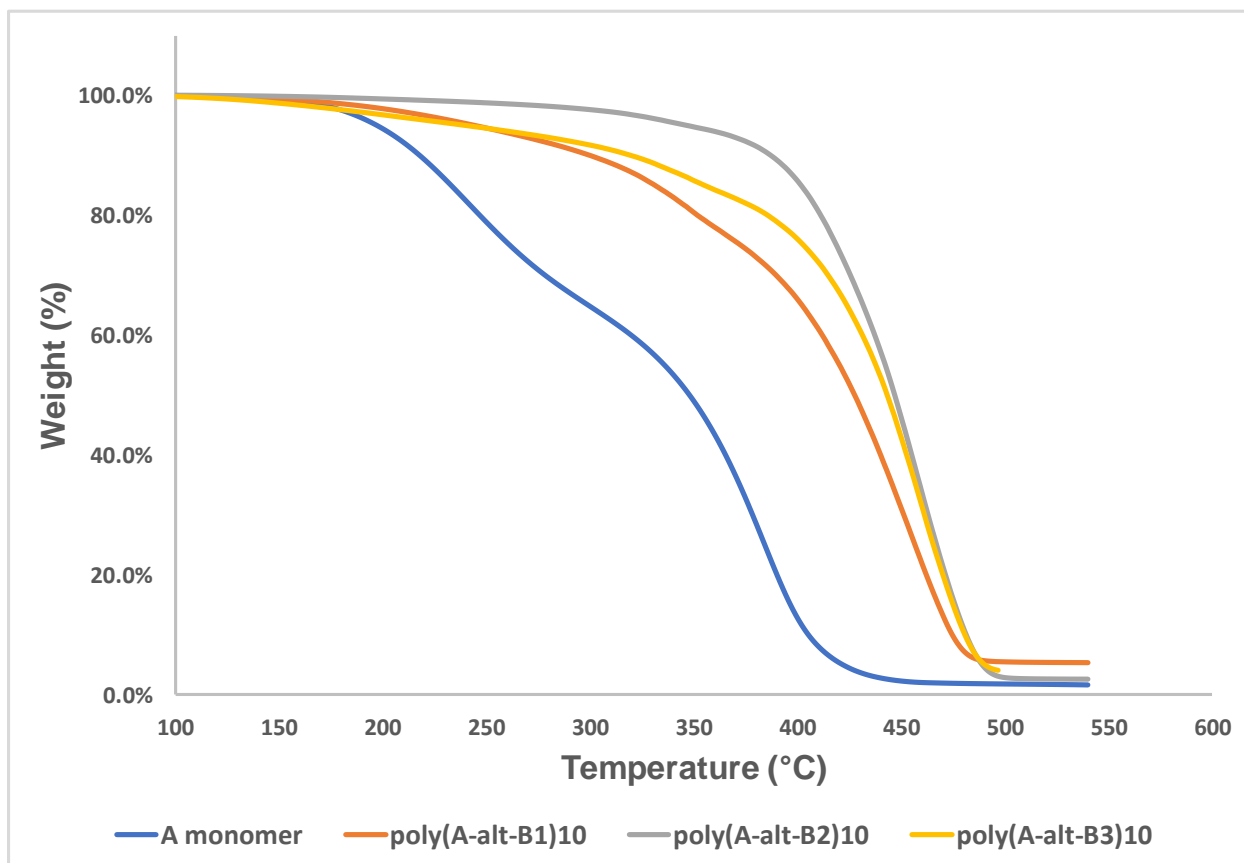
**Figure S37 DSC traces of AROMP polymers**



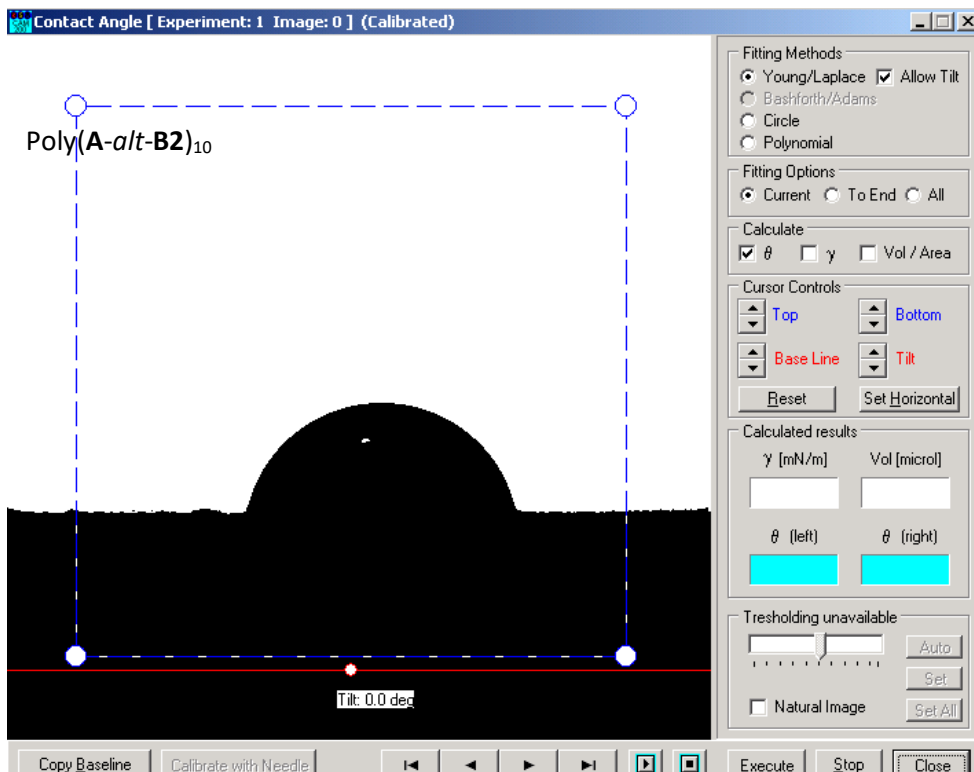
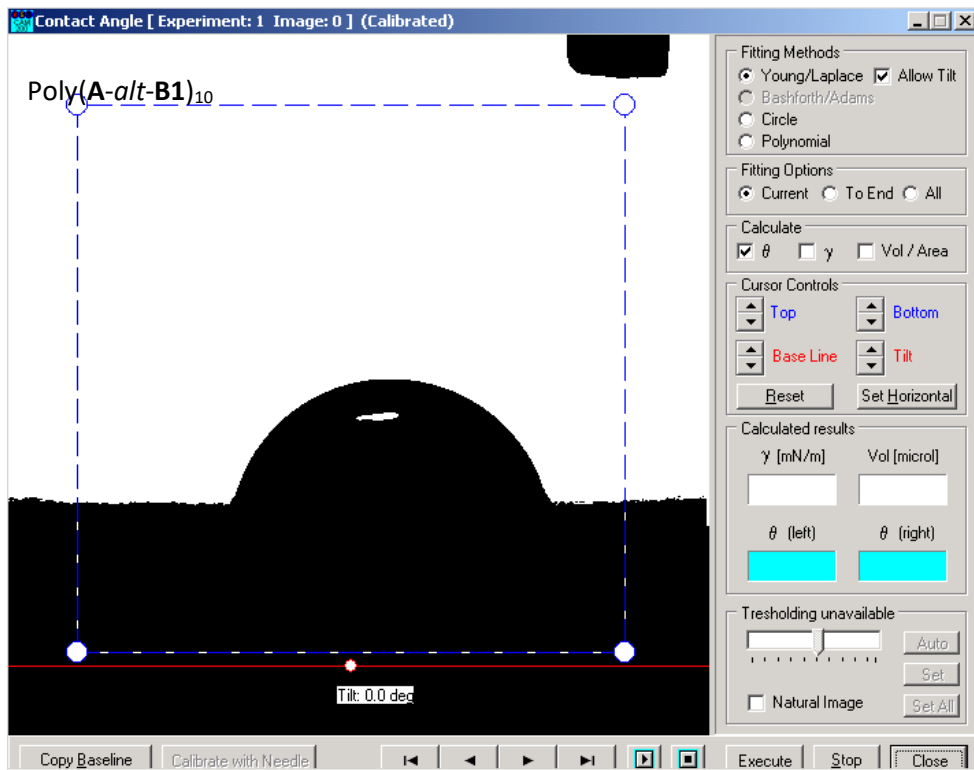
**Figure S38 DSC traces of AROMP polymers (Continued)**



**Figure S39 TGA traces of AROMP polymers**

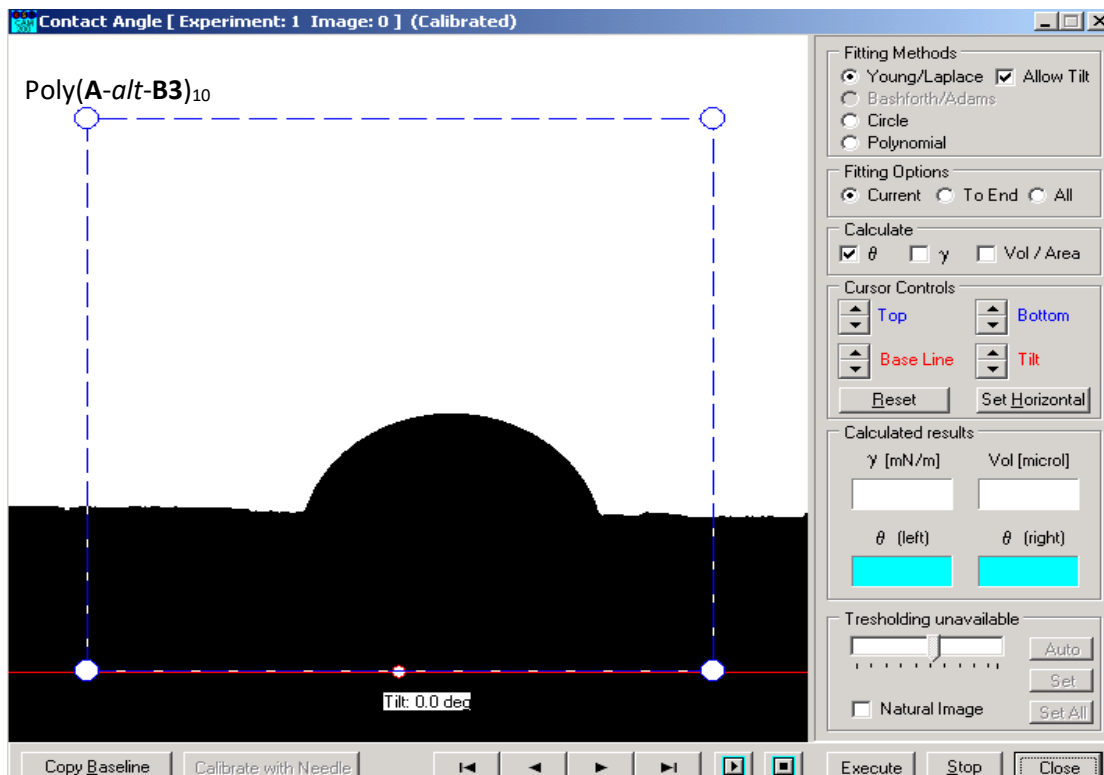


**Figure S40 Representative water droplet contact angle image of copolymer thin films on silicon wafer**





**Figure S41 Representative water droplet contact angle image of copolymer thin films on silicon wafer (Continued)**



## Reference

1. Chen, L.; Li, L.; Sampson, N. S. Access to bicyclo[4.2.0]octene monomers to explore the scope of alternating ring-opening metathesis polymerization. *The Journal of Organic Chemistry* **2018**, 83 (5), 2892-2897 DOI: 10.1021/acs.joc.8b00054.