Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Controlling the crystal structure of precisely spaced polyethylene-like polyphosphoesters

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^{1}H, ^{13}C, ^{31}P NMR spectra

NMR spectra o monomers/ precursors

5-(Benzyloxy)pentyl-4-methylbenzenesulfonate (2a)

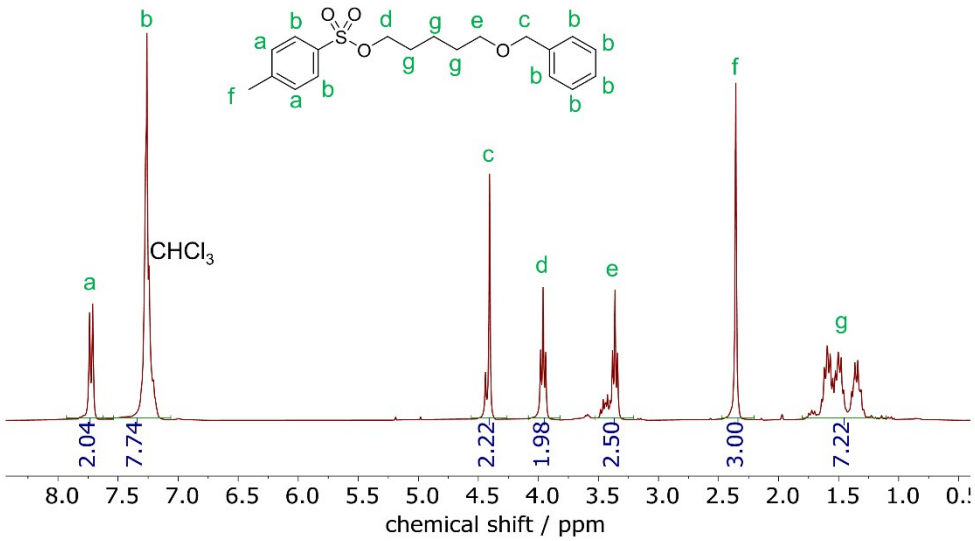

Figure S1: ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 300 MHz at 298 K.

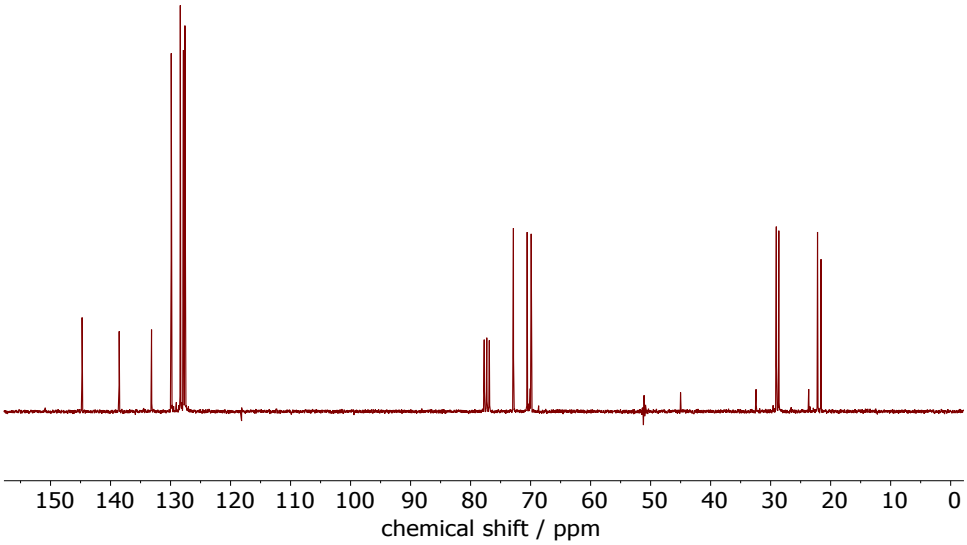

Figure S2: ^{13}C NMR spectrum of **2a** in $CDCl_3$ at 75 MHz at 298 K.

Hexadec-15-enyloxymethyl-benzene **(2b)**

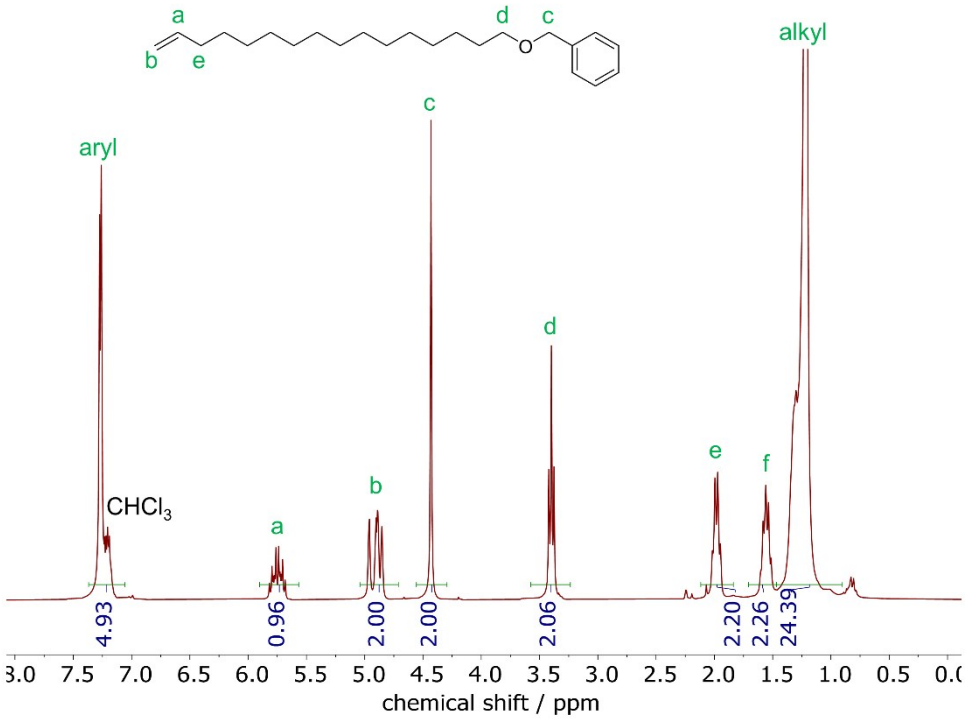

Figure S3: ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 300 MHz at 298 K.

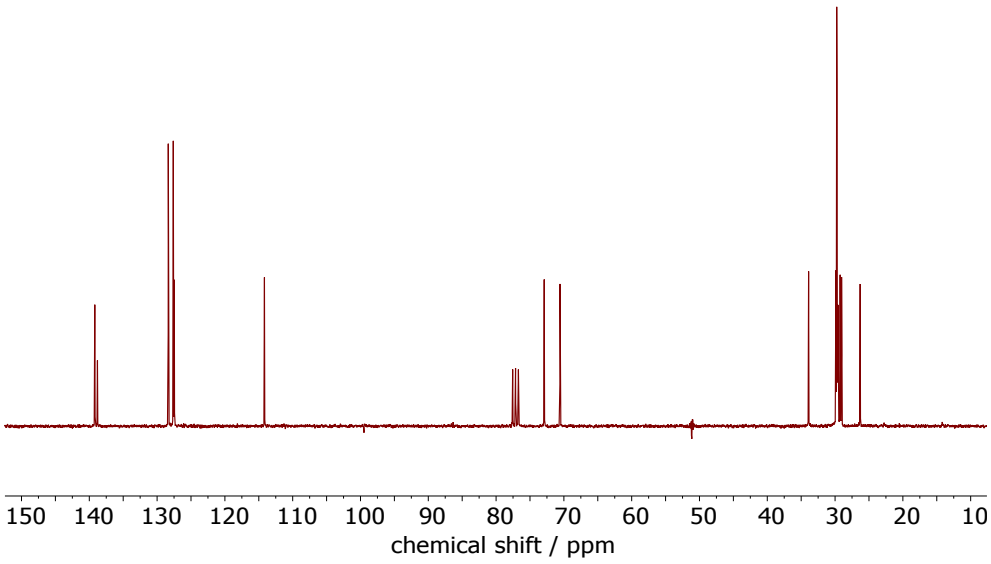

Figure S4: ^{13}C NMR spectrum of **2b** in $CDCl_3$ at 75 MHz at 298 K.

Hexadec-15-en-1-ol **(2c)**

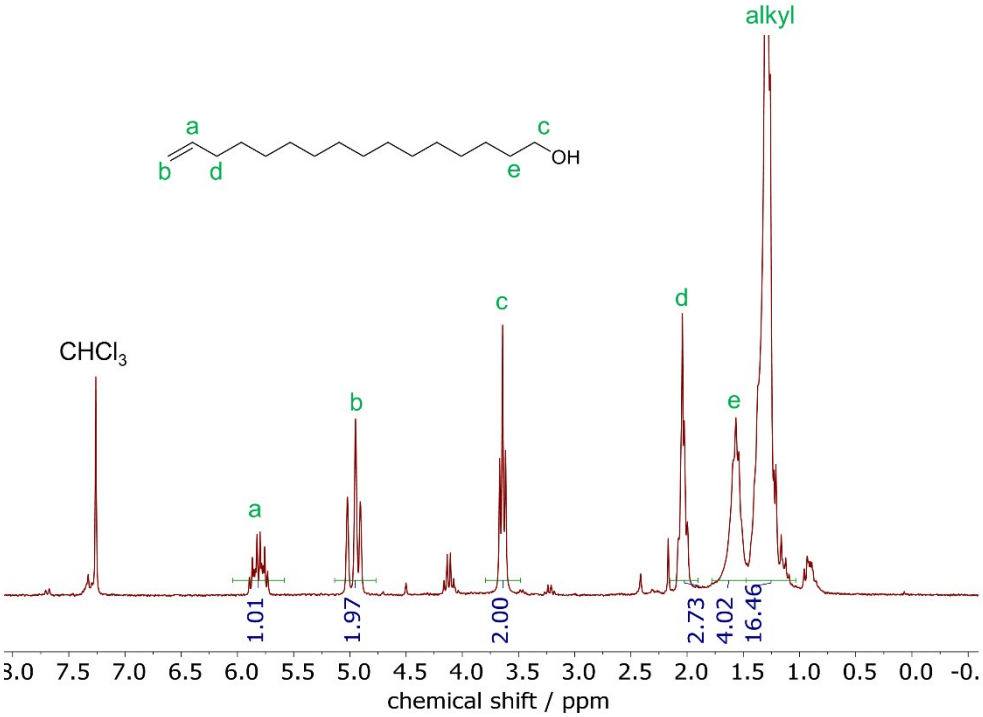

Figure S5: ^{1}H NMR spectrum of **2c** in $CDCl_3$ at 300 MHz at 298 K.

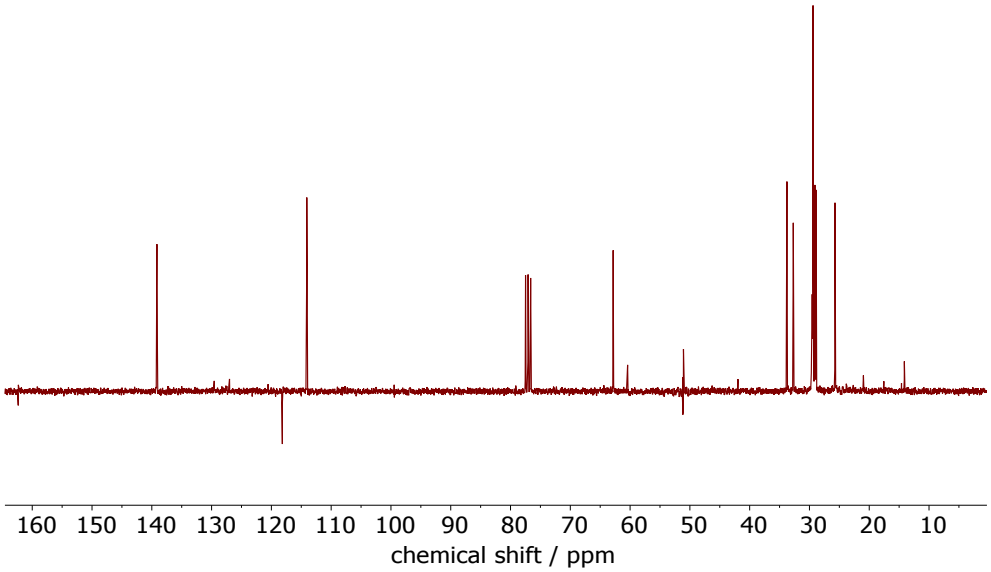

Figure S6: ^{13}C NMR spectrum of **2c** in $CDCl_3$ at 75 MHz at 298 K.

2-Octadecyn-1-ol **(3a)**

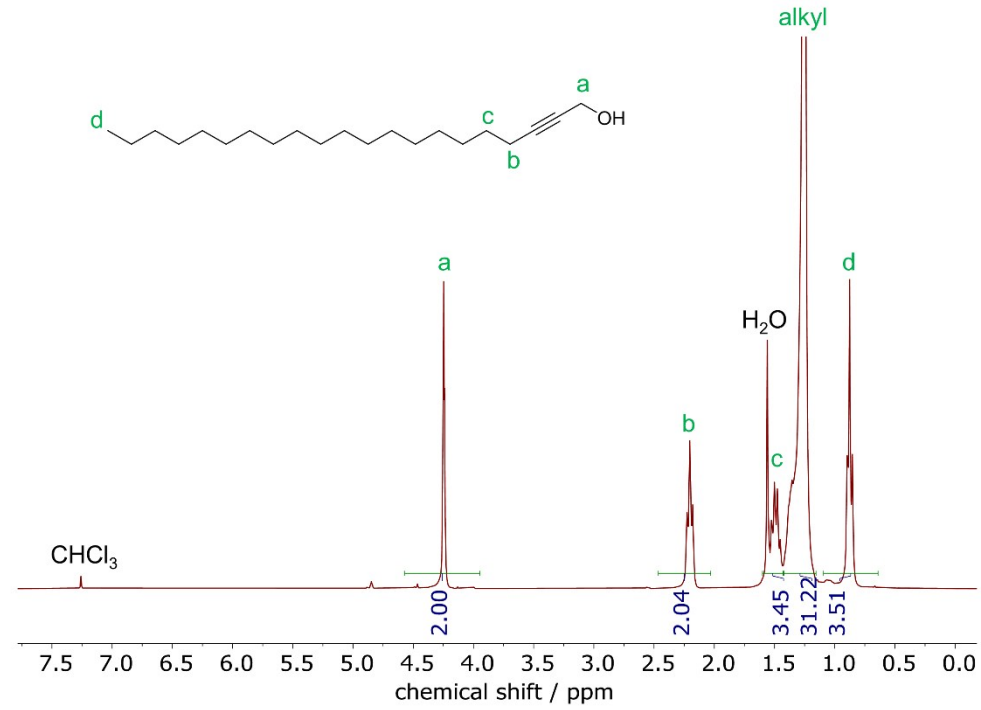

Figure S7: ^{1}H NMR spectrum of **3a** in $CDCl_3$ at 300 MHz at 298 K.

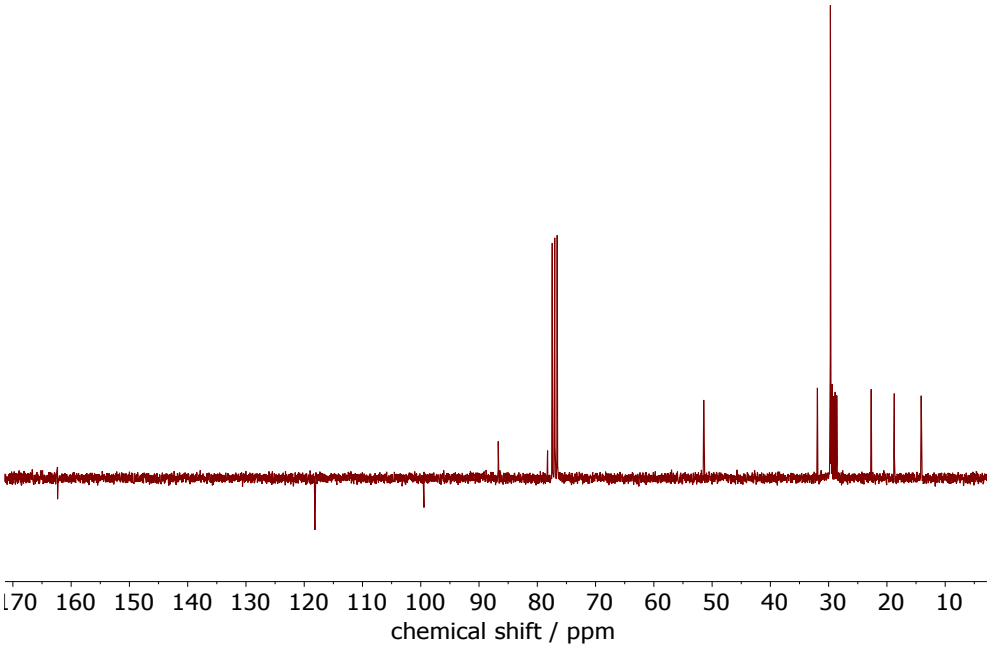

Figure S8: ^{13}C NMR spectrum of **3a** in $CDCl_3$ at 75 MHz at 298 K.

20-Henicosyn-1-ol **(3b)**

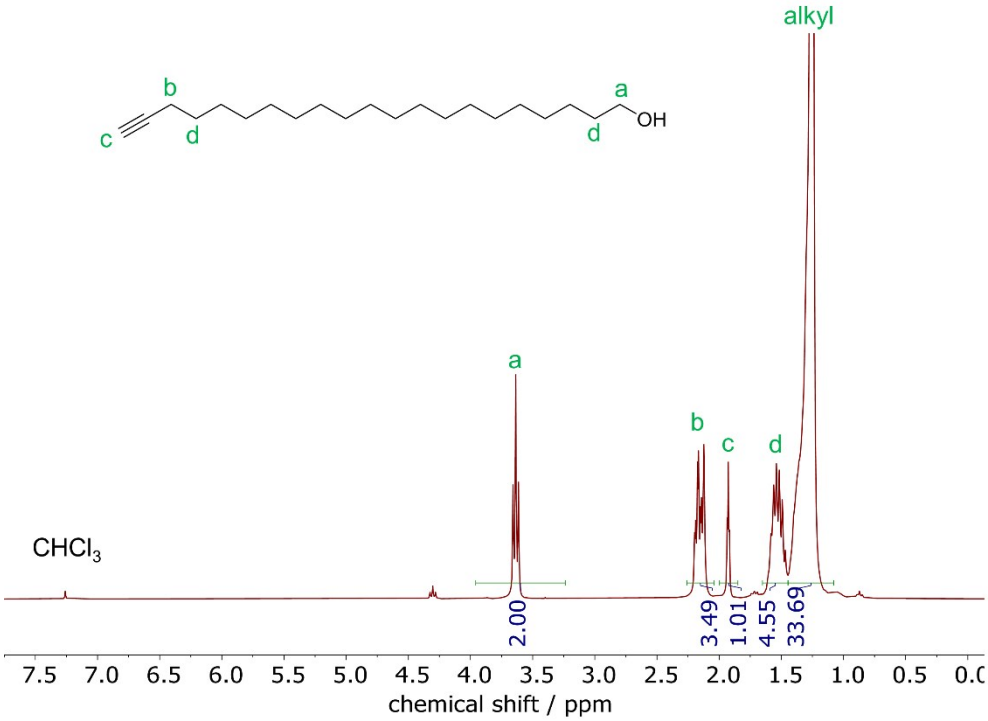

Figure S9: ^{1}H NMR spectrum of **3b** in $CDCl_3$ at 300 MHz at 298 K.

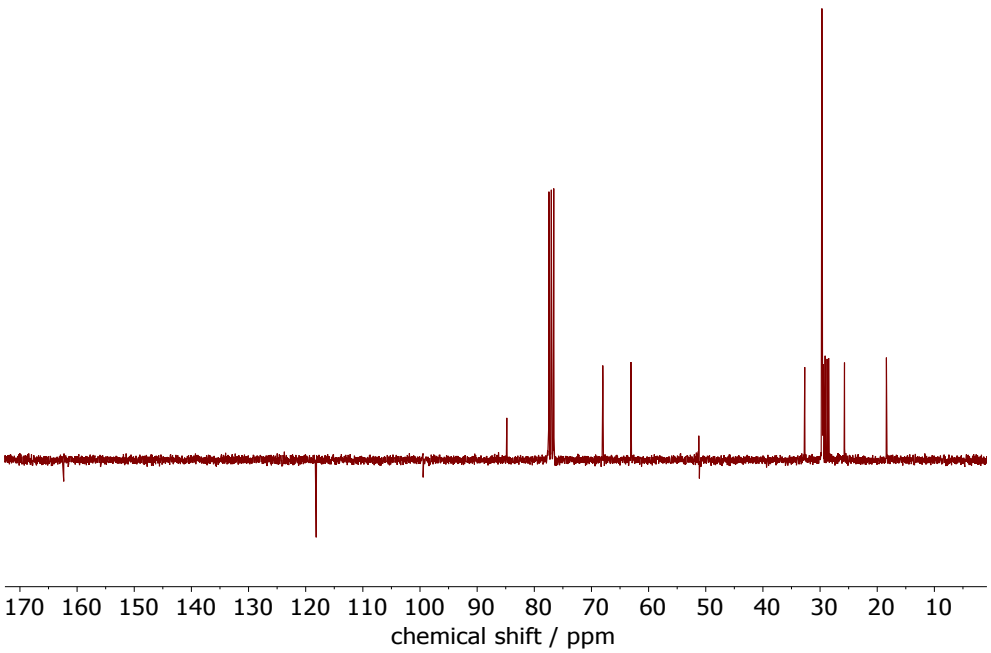

Figure S10: ^{13}C NMR spectrum of **3b** in $CDCl_3$ at 75 MHz at 298 K.

20-Henicosen-1-ol **(3c)**

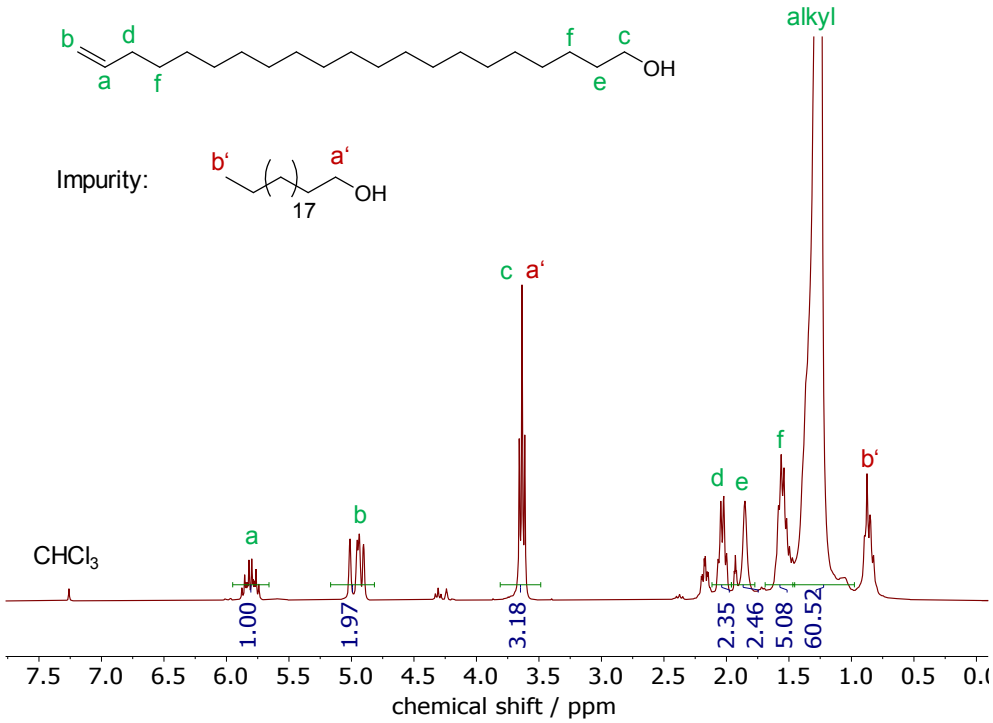

Figure S11: ^{1}H NMR spectrum of **3c** in $CDCl_3$ at 300 MHz at 298 K.

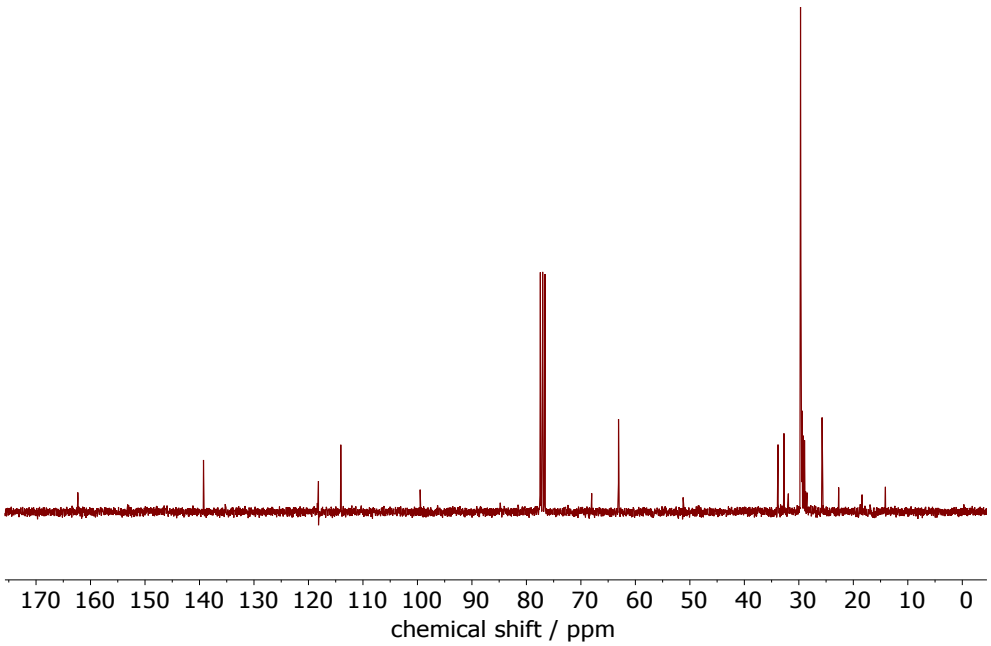

Figure S12: ^{13}C NMR spectrum of **3c** in $CDCl_3$ at 75 MHz at 298 K.

Bis-(undec-10-en-1-yl) ethylphosphate **(1)**

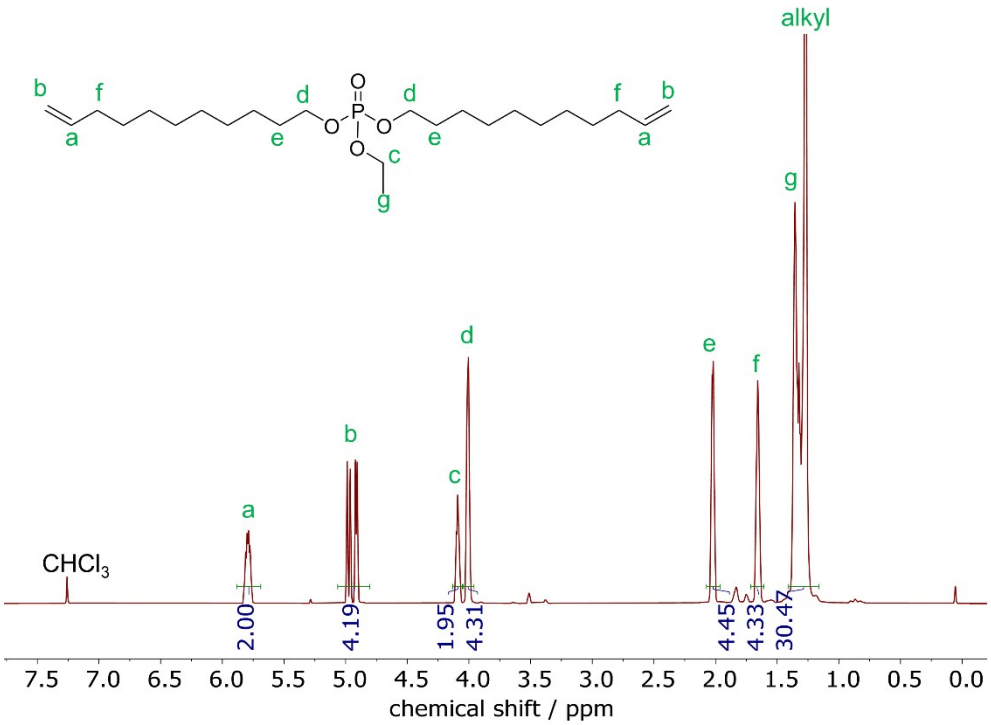

Figure S13: ^{1}H NMR spectrum of **1** in $CDCl_3$ at 300 MHz at 298 K.

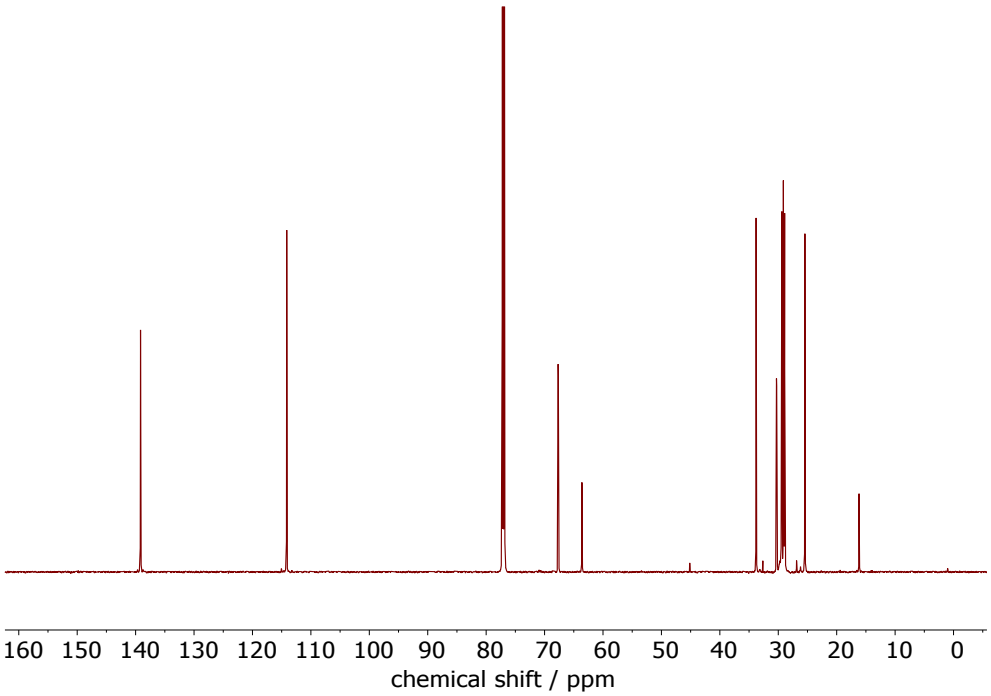

Figure S14: ^{13}C NMR spectrum of **1** in $CDCl_3$ at 75 MHz at 298 K.

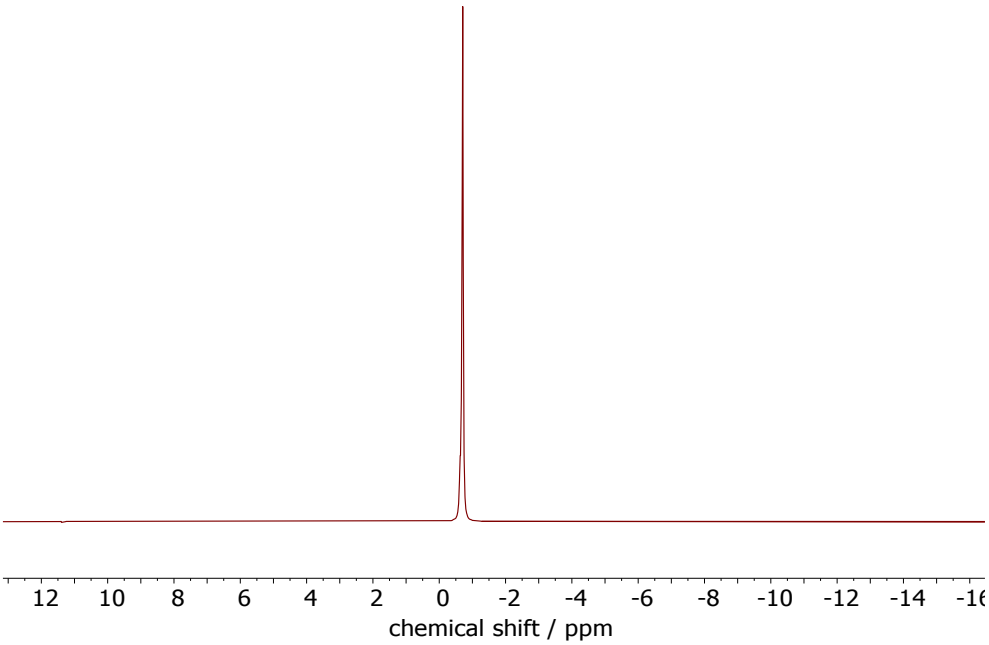

Figure S15: ^{31}P NMR spectrum of **1** in $CDCl_3$ at 121 MHz at 298 K.

Ethyl di(hexadec-15-en-1-yl) phosphate **(2)**

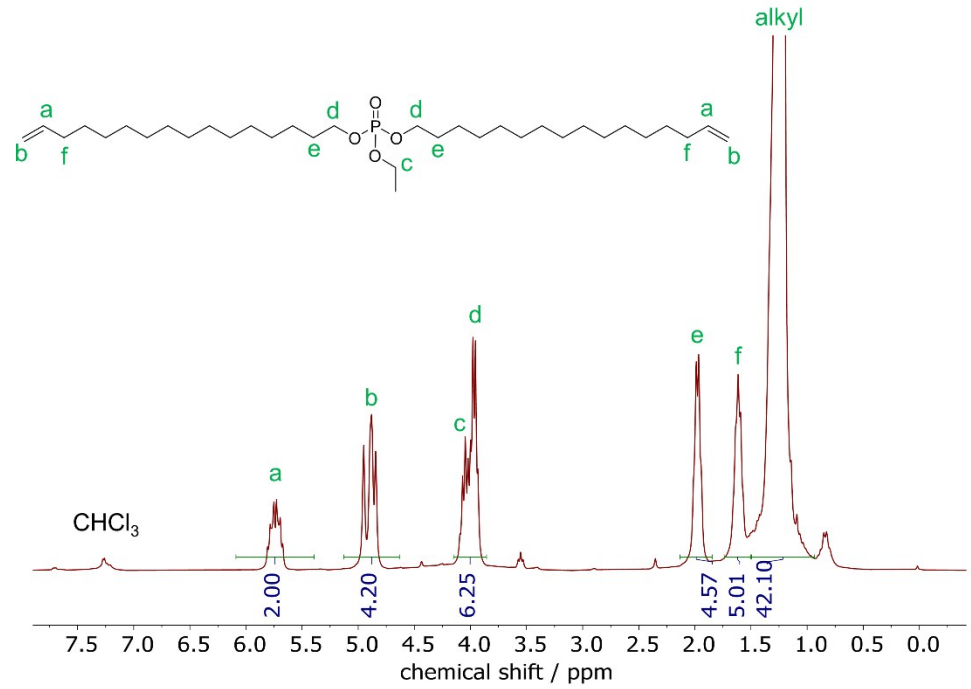

Figure S16: ^{1}H NMR spectrum of **2** in $CDCl_3$ at 300 MHz at 298 K.

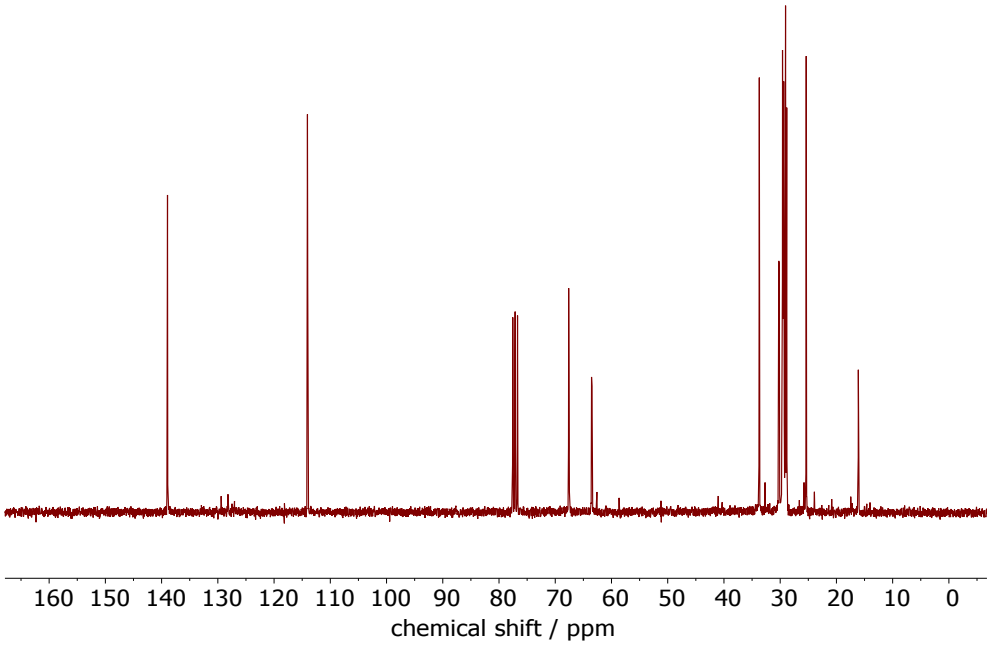

Figure S17: ^{13}C NMR spectrum of **2** in $CDCl_3$ at 75 MHz at 298 K.

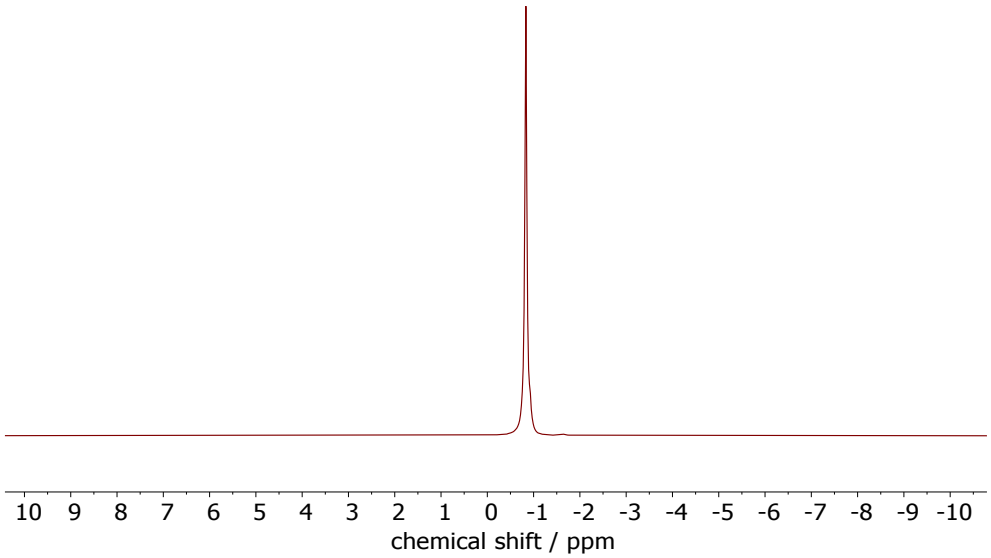

Figure S18: ^{31}P NMR spectrum of **2** in $CDCl_3$ at 121 MHz at 298 K.

Ethyl di(henicos-20-en-1-yl) phosphate **(3)**

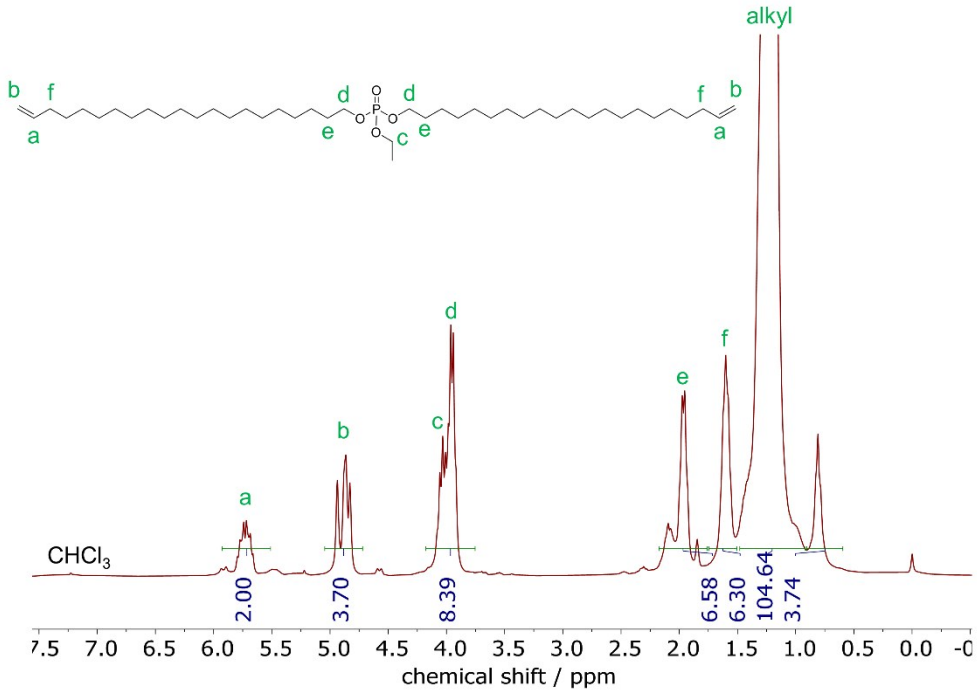

Figure S19: ^{1}H NMR spectrum of **3** in $CDCl_3$ at 300 MHz at 298 K.

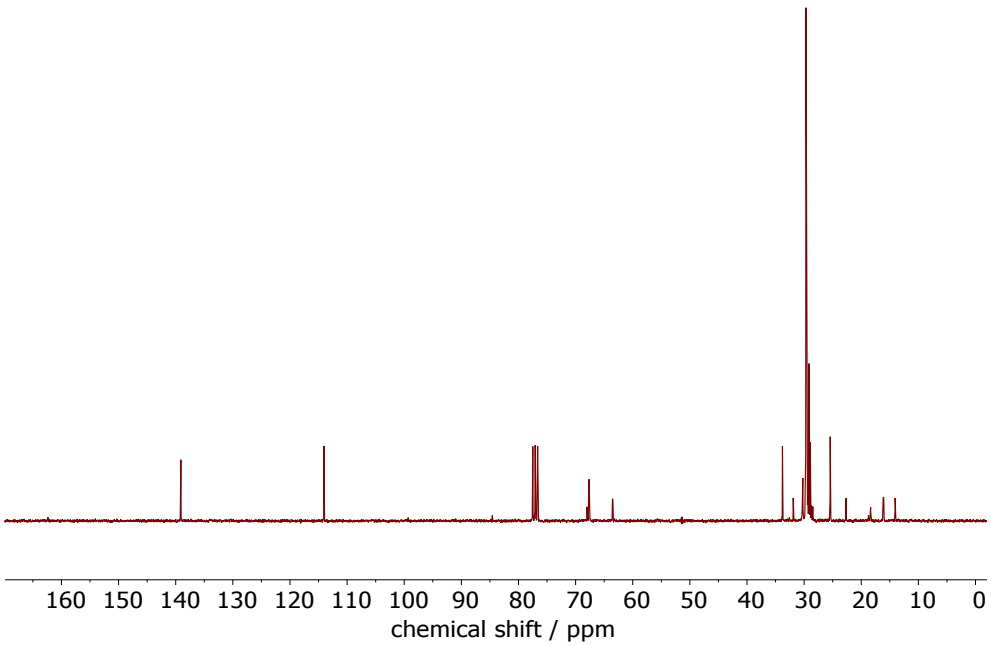

Figure S20: ^{13}C NMR spectrum of **3** in $CDCl_3$ at 75 MHz at 298 K.

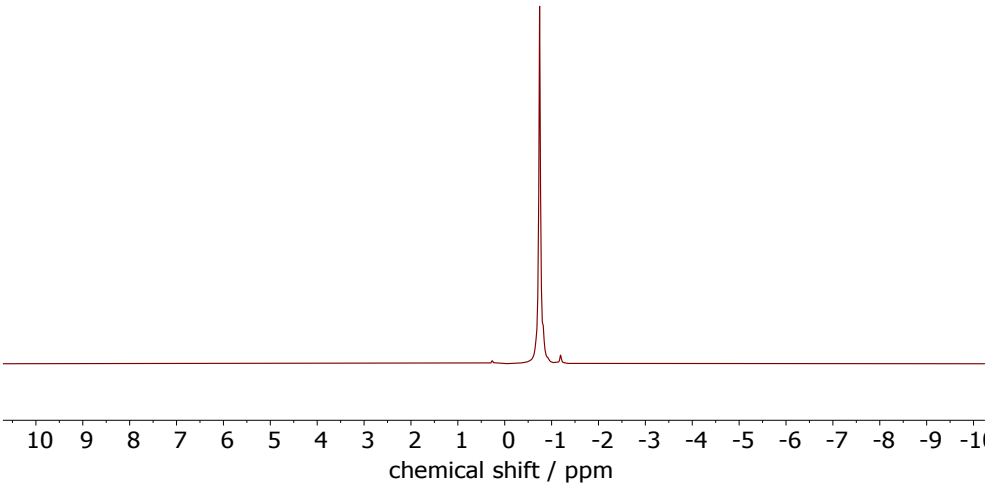

Figure S21: ^{31}P NMR spectrum of **3** in $CDCl_3$ at 121 MHz at 298 K.

NMR spectra of polymer samples

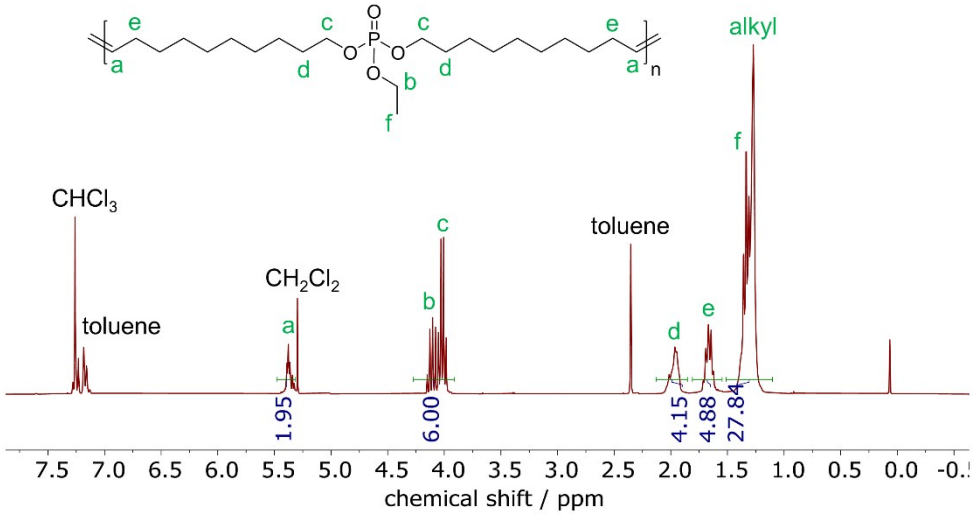

Figure S22: ^{1}H NMR spectrum of **poly(1)** in $CDCl_3$ at 300 MHz at 298 K.

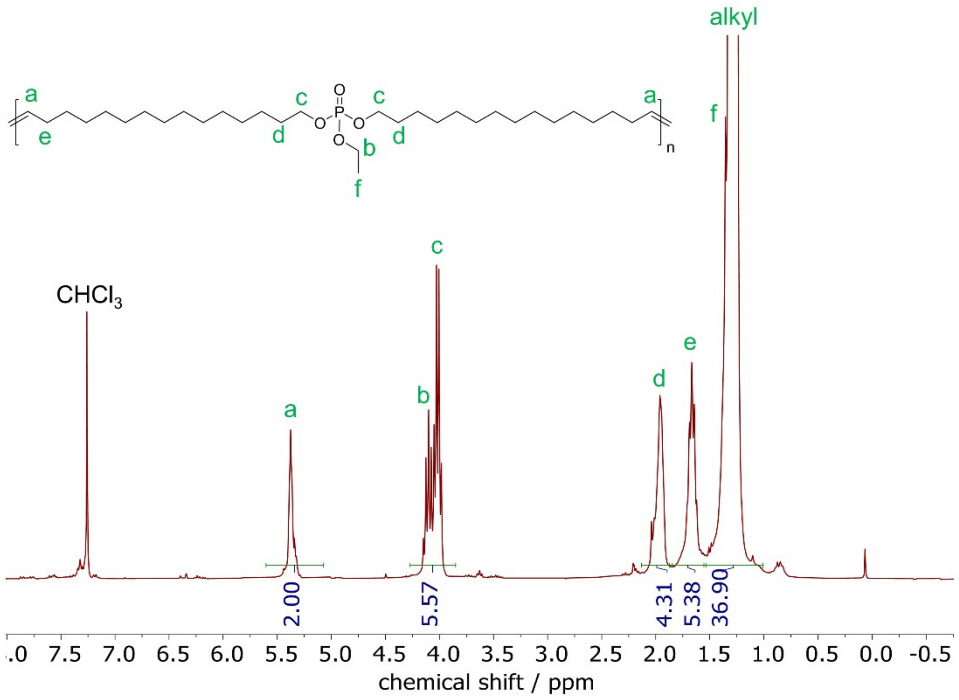

Figure S23: ^{1}H NMR spectrum of **poly(2)** in $CDCl_3$ at 300 MHz at 298 K.

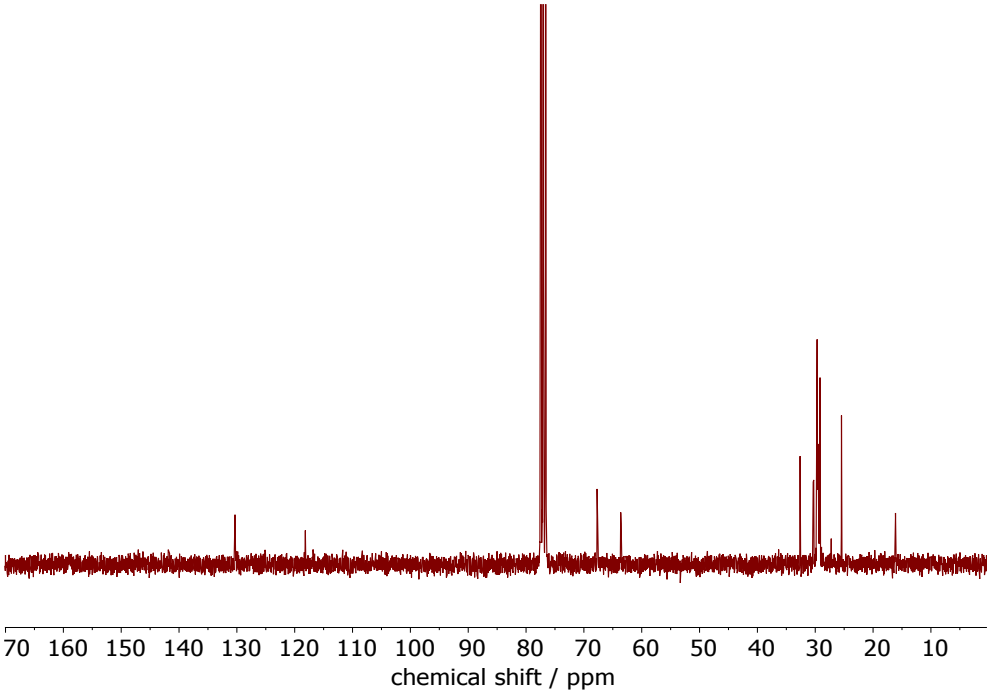

Figure S24: ^{13}C NMR spectrum of **poly(2)** in $CDCl_3$ at 75 MHz at 298 K.

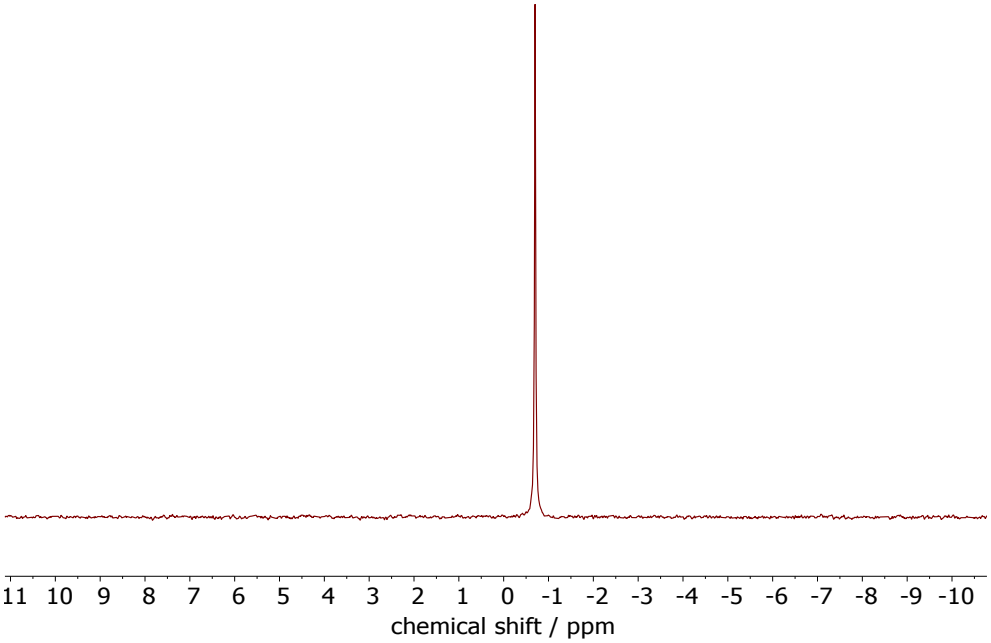

Figure S25: ^{31}P NMR spectrum of **poly(2)** in $CDCl_3$ at 121 MHz at 298 K.

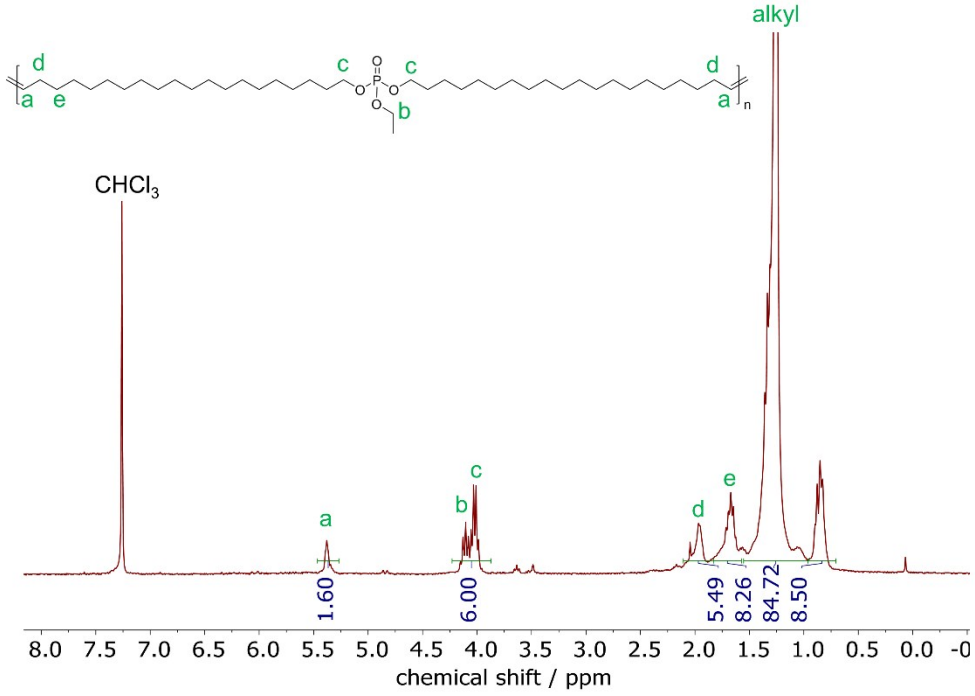

Figure S26: ^{1}H NMR spectrum of **poly(3)** in $CDCl_3$ at 300 MHz at 298 K.

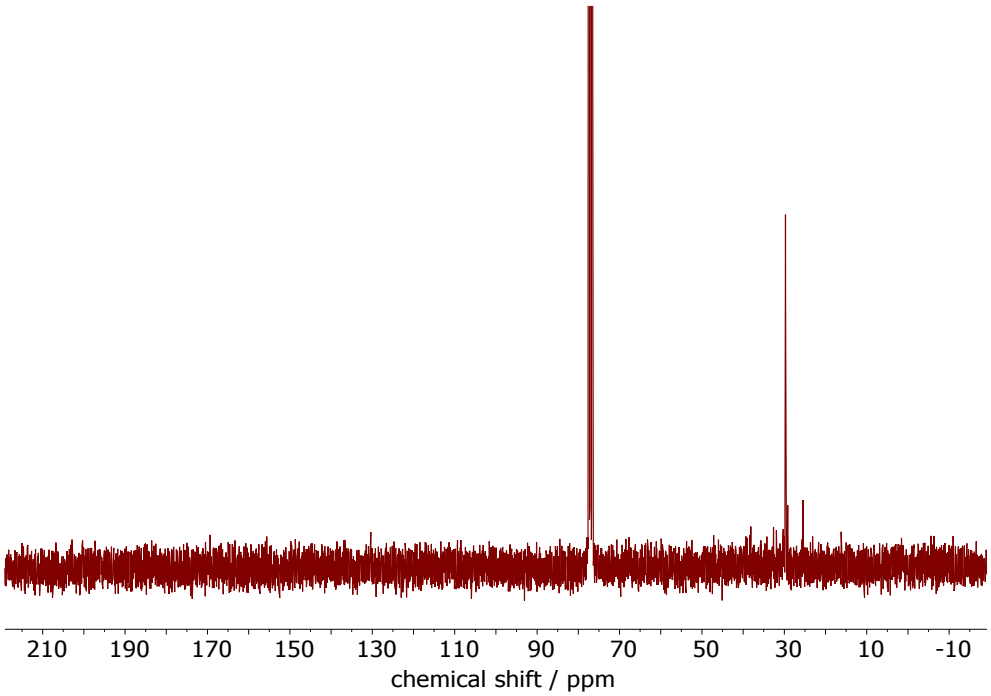

Figure S27: ^{13}C NMR spectrum of **poly(3)** in $CDCl_3$ at 75 MHz at 298 K.

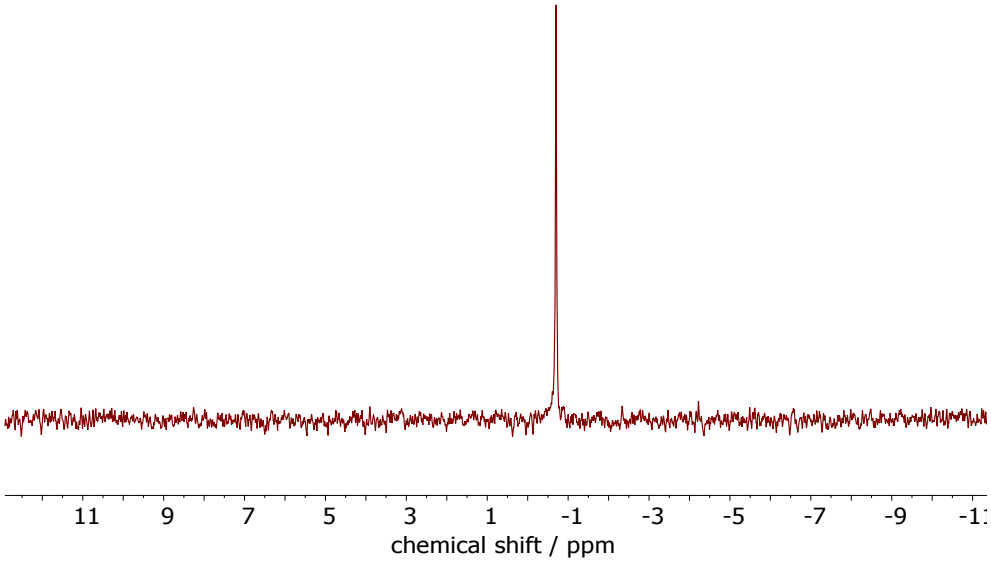

Figure S28: ^{31}P NMR spectrum of **poly(3)** in $CDCl_3$ at 121 MHz at 298 K.

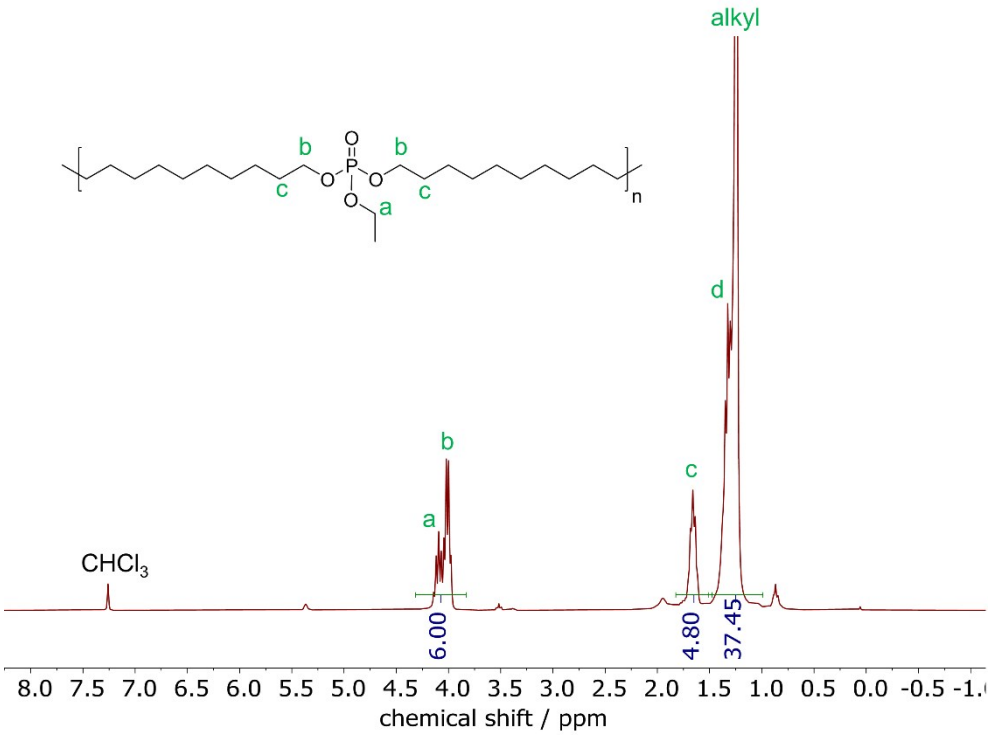

Figure S29: ^{1}H NMR spectrum of **poly(1)-H** in $CDCl_3$ at 300 MHz at 298 K.

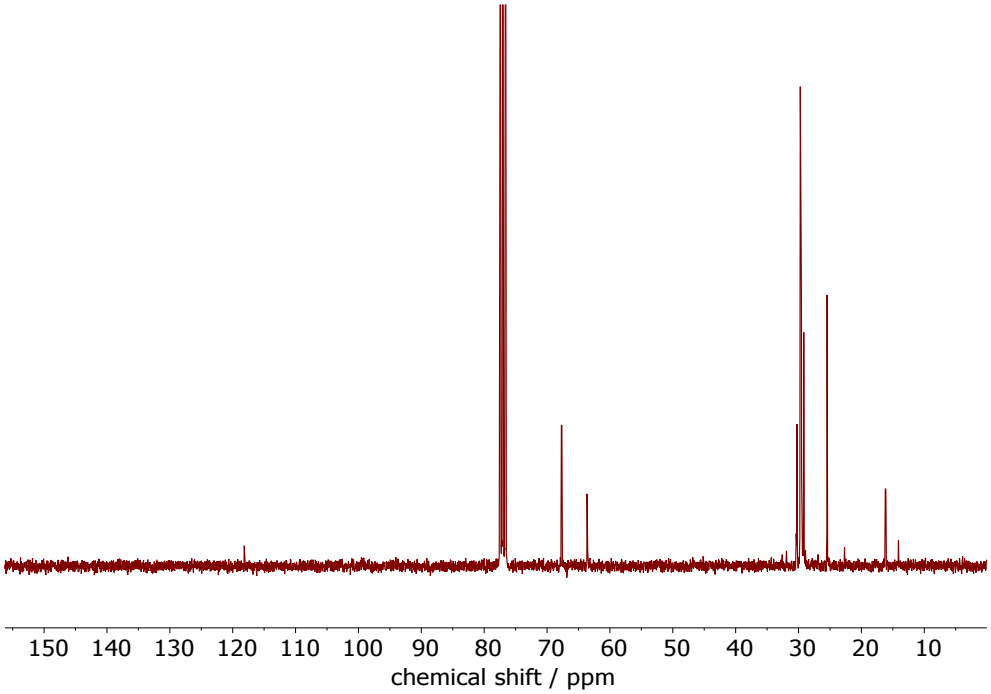

Figure S30: ^{13}C NMR spectrum of **poly(1)-H** in $CDCl_3$ at 75 MHz at 298 K.

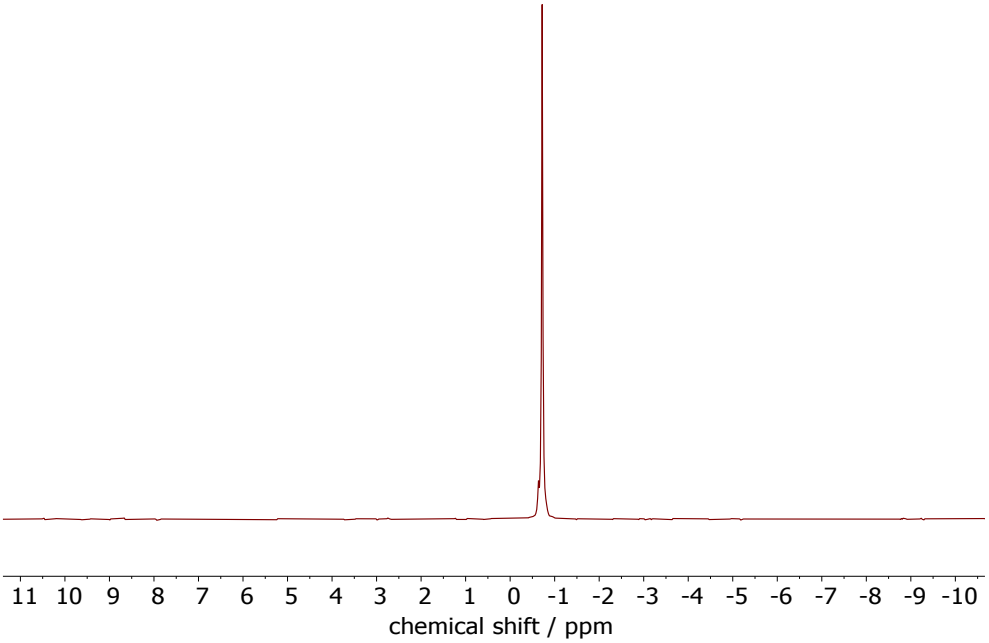

Figure S31: ^{31}P NMR spectrum of **poly(1)-H** in $CDCl_3$ at 121 MHz at 298 K.

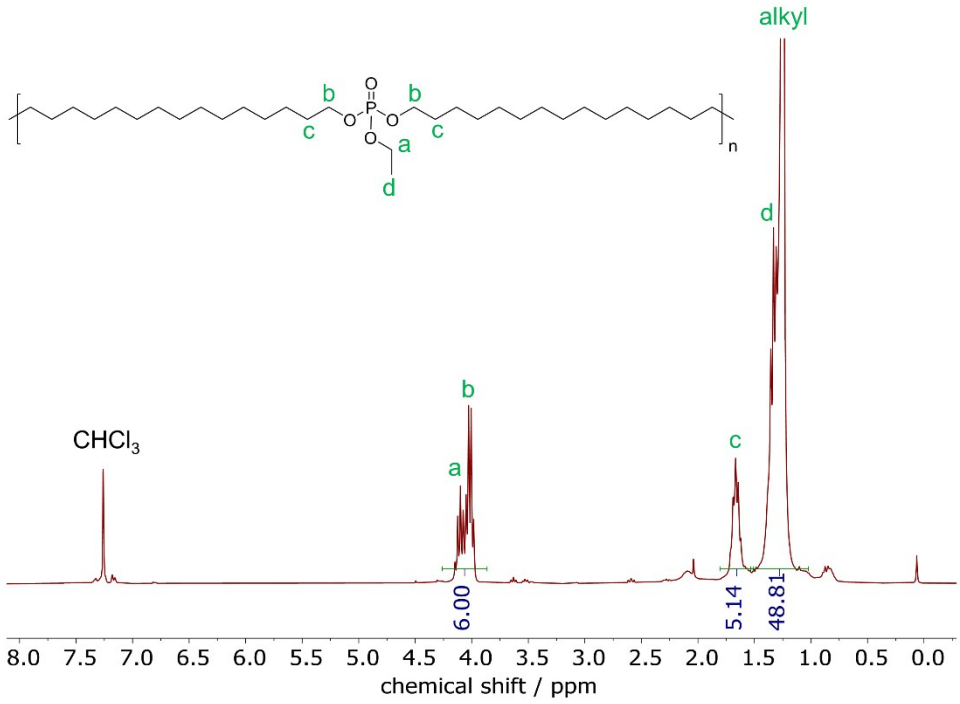

Figure S32: ^{1}H NMR spectrum of **poly(2)-H** in $CDCl_3$ at 300 MHz at 298 K.

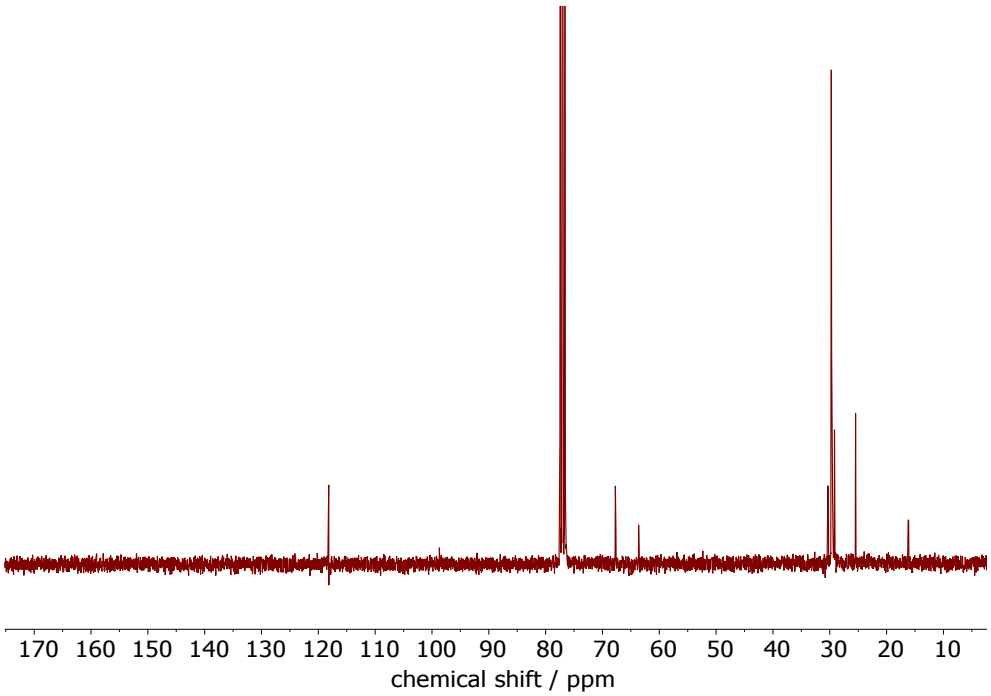

Figure S33: ^{13}C NMR spectrum of **poly(2)-H** in $CDCl_3$ at 75 MHz at 298 K.

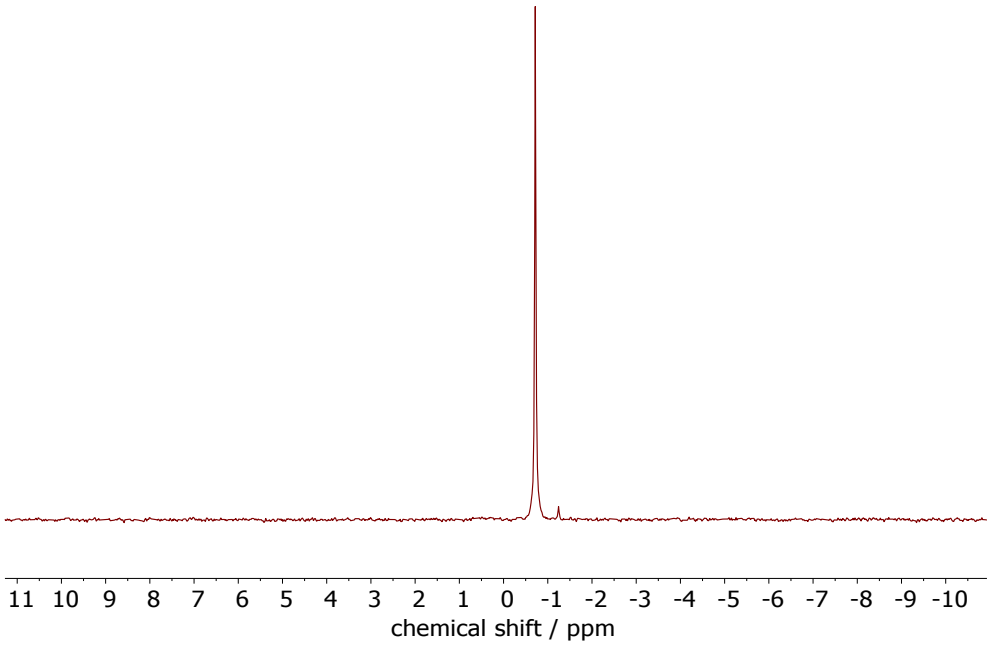

Figure S34: ^{31}P NMR spectrum of **poly(2)-H** in $CDCl_3$ at 121 MHz at 298 K.

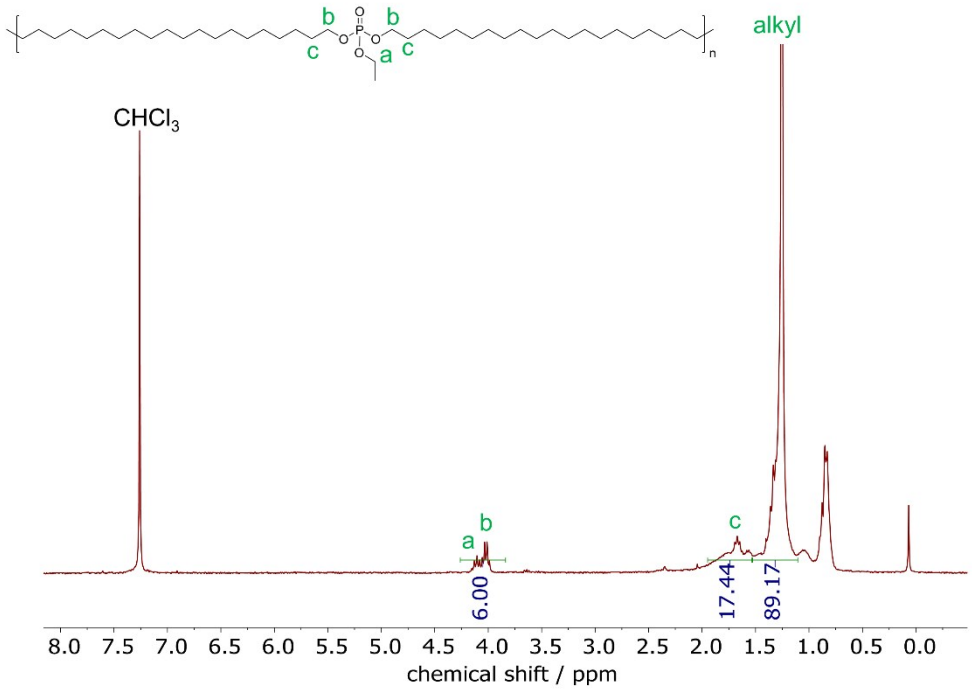

Figure S35: ^{1}H NMR spectrum of **poly(3)-H** in $CDCl_3$ at 300 MHz at 298 K.

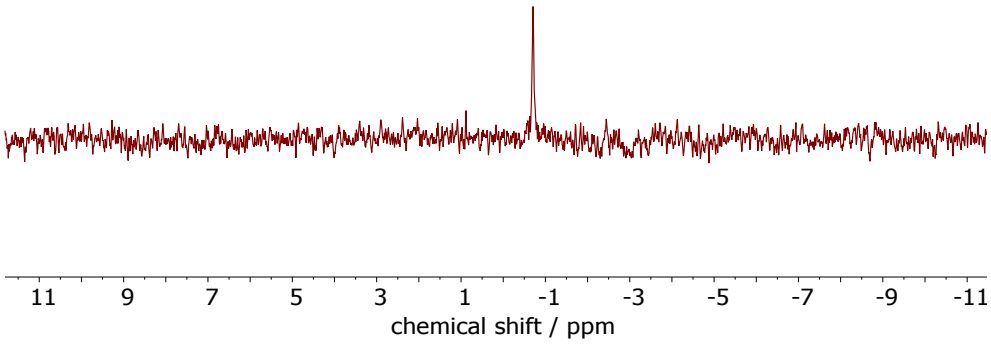

Figure S36: ^{31}P NMR spectrum of **poly(3)-H** in $CDCl_3$ at 121 MHz at 298 K.

Mass spectrometry

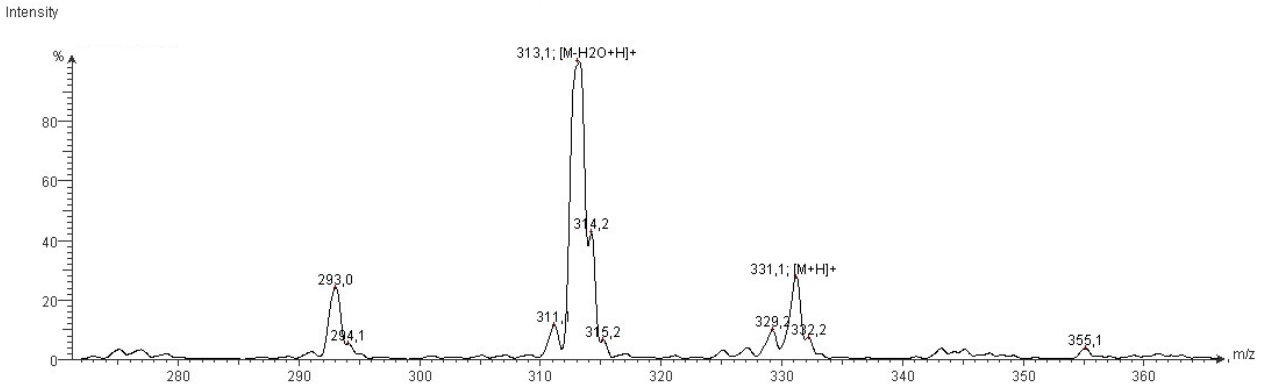

Figure S37: Mass spectrogram of **2b** (atmospheric-pressure chemical ionization).

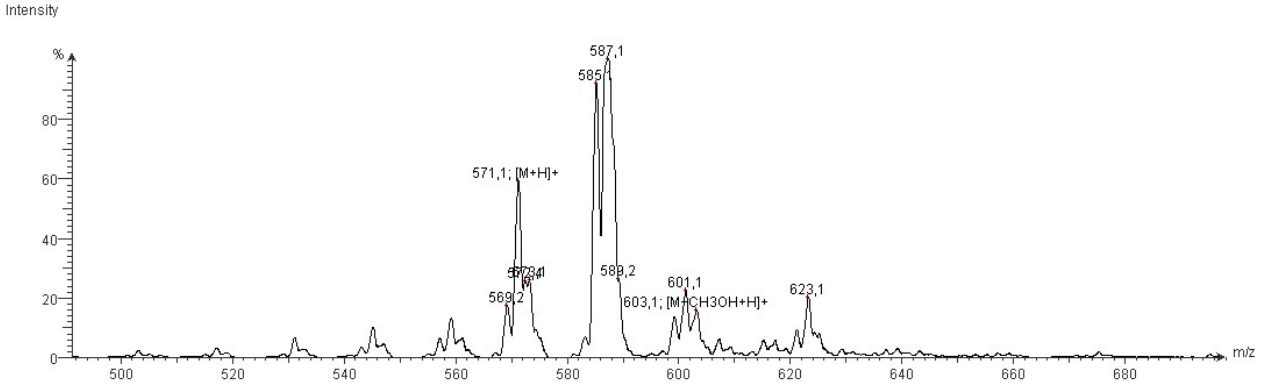

Figure S38: Mass spectrogram of **2** (atmospheric-pressure chemical ionization).

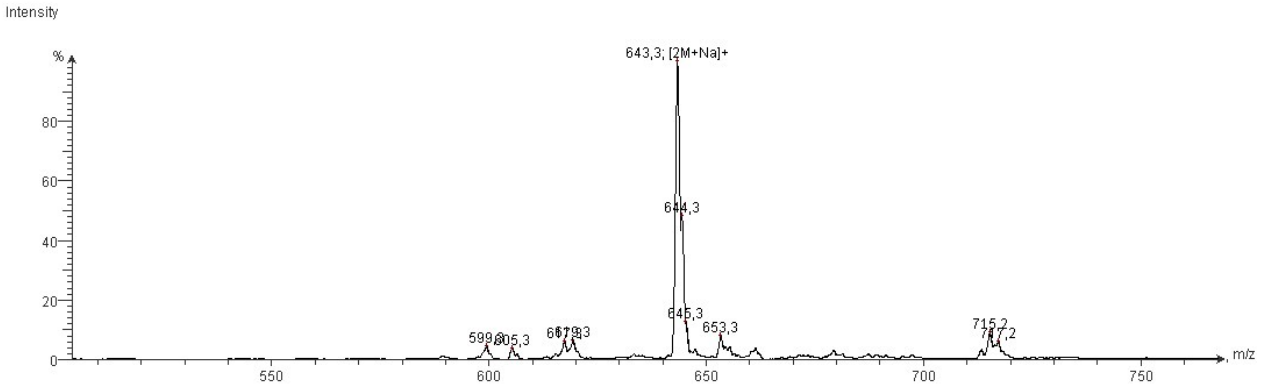

Figure S39: Mass spectrogram of **3c** (atmospheric-pressure chemical ionization).

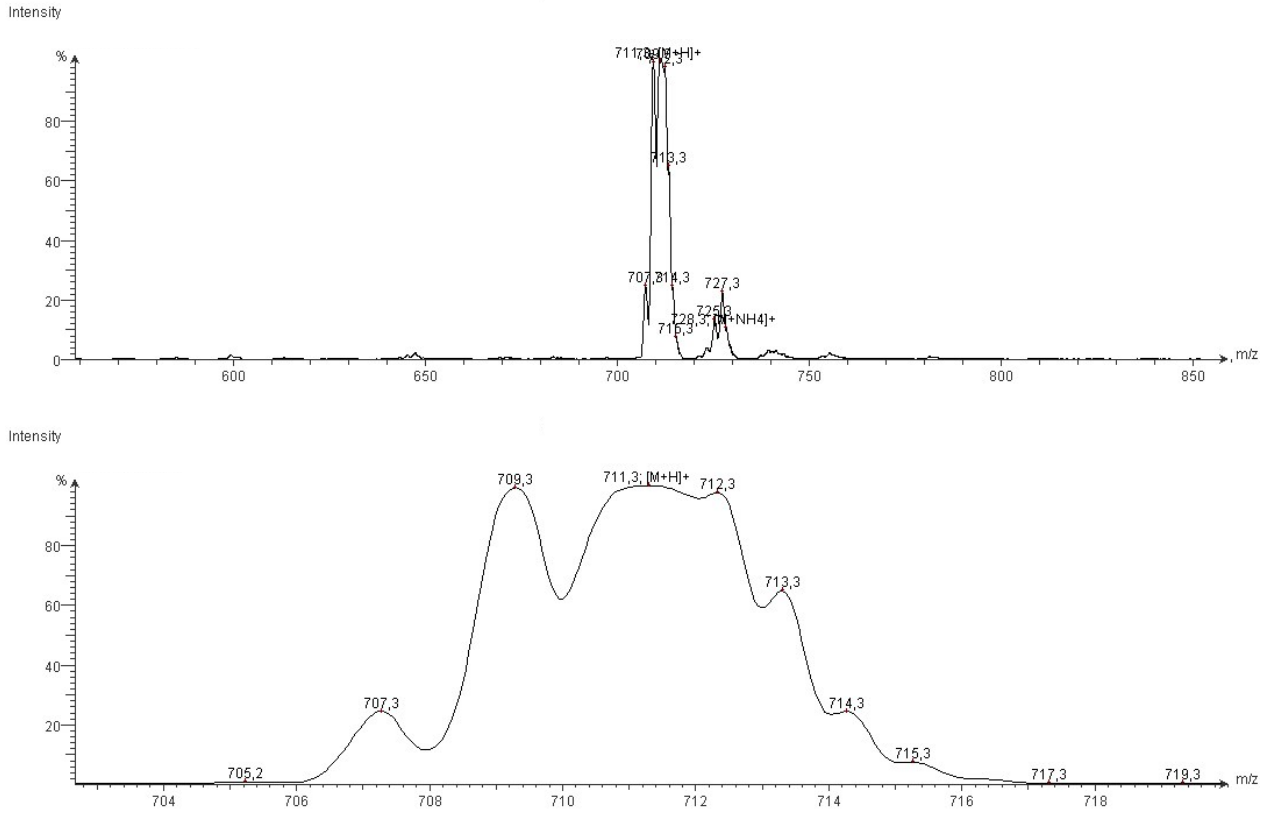

Figure S40: Mass spectrogram of **3** (atmospheric-pressure chemical ionization). Top: range from 500 to 850 m/z. Bottom: Zoom-in of molpeak.

Size exclusion chromatography (SEC)

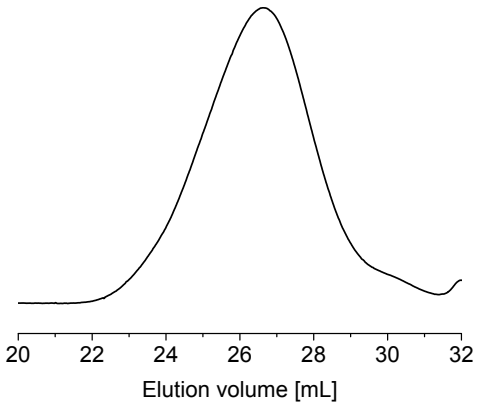

Figure S41: SEC elugram of **poly(2)** in THF.

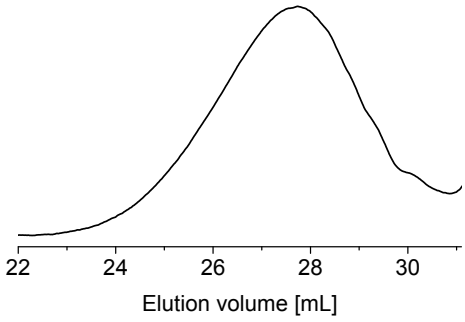

Figure S42: SEC elugrams of **poly(3)** in THF.

Transmission electron microscopy (TEM) of bulk samples

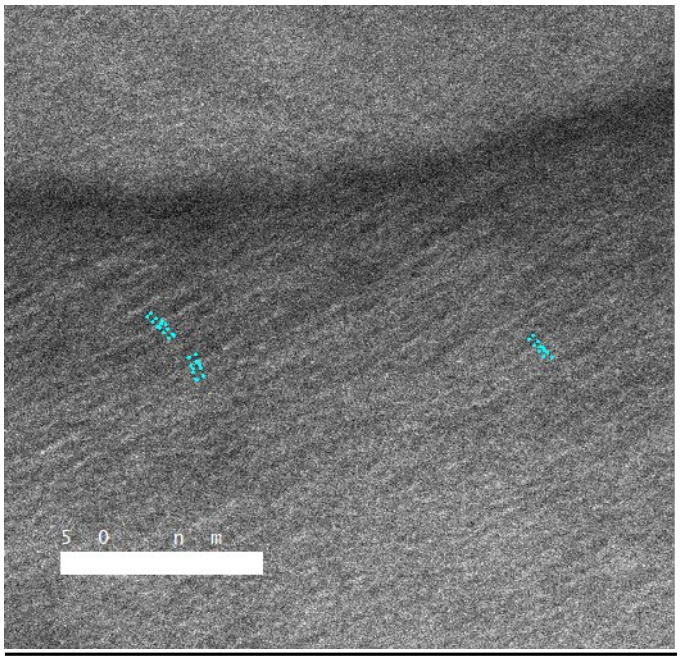

Figure S43: TEM image of **poly(1)-H**.

Figure S44: TEM thickness mapping of **poly(1)-H**.

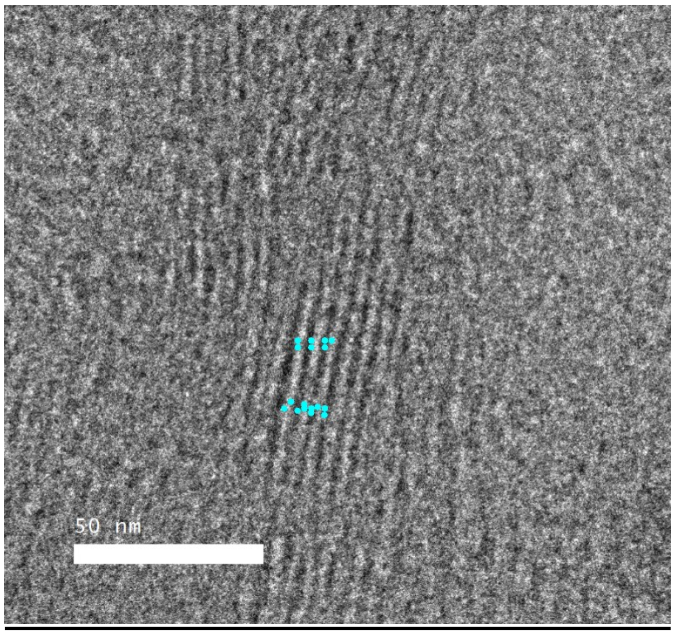

Figure S45: TEM image of **poly(2)-H**.

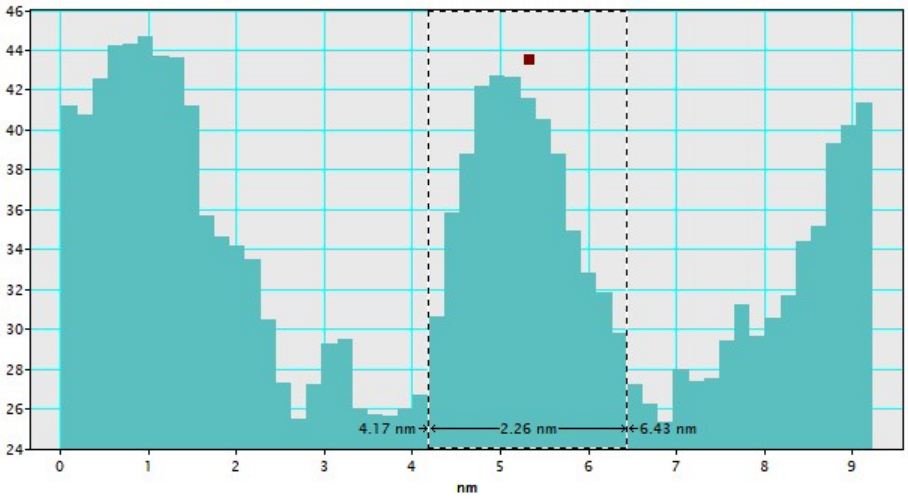

Figure S46: TEM thickness mapping of **poly(2)-H**.

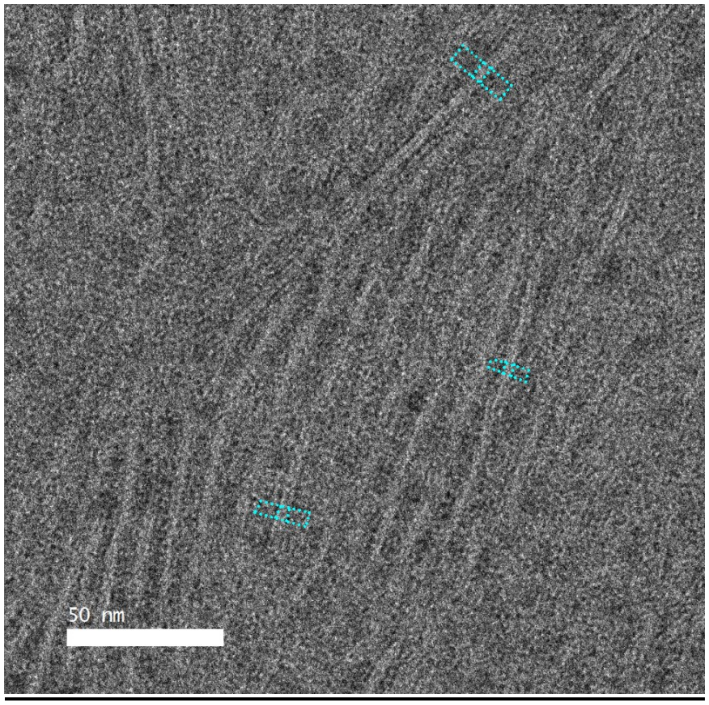

Figure S47: TEM image of **poly(3)-H**.

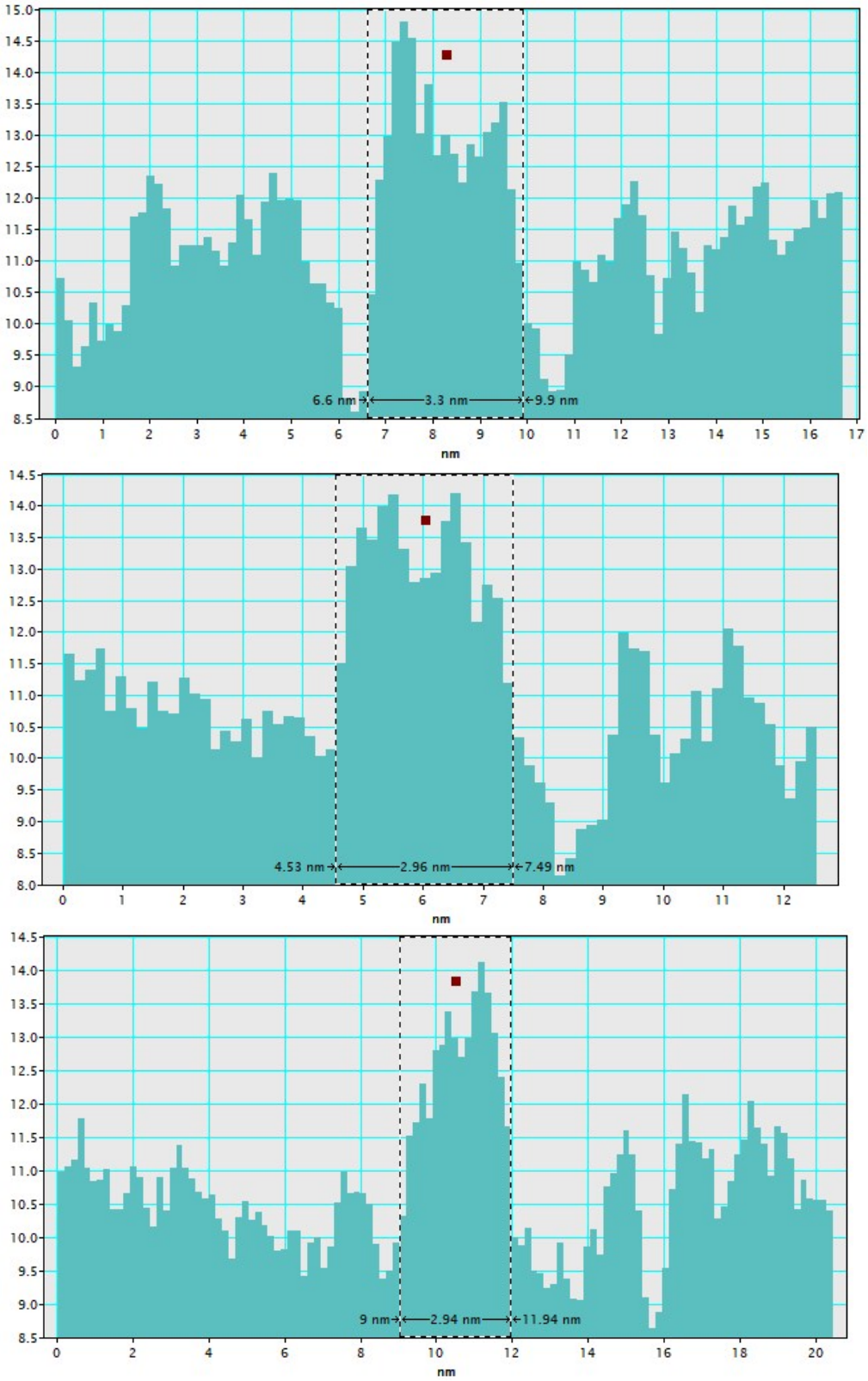

Figure S48: TEM thickness mapping of **poly(3)-H**.

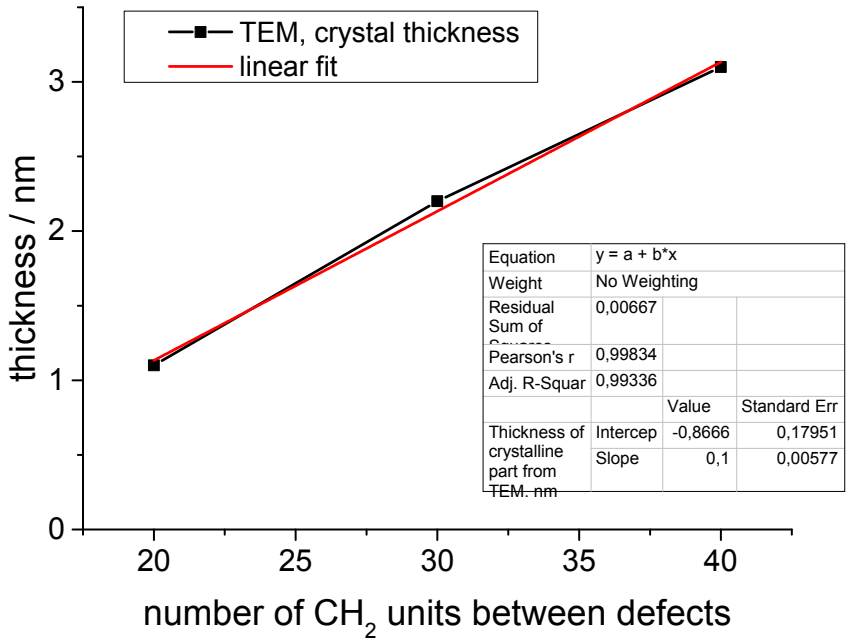

Figure S49: Crystal thickness determined by TEM plotted against the number of CH_2 units between phosphate defects with a linear fit.

Atomic force microscopy (AFM) thickness mapping of solution-grown polymer crystals

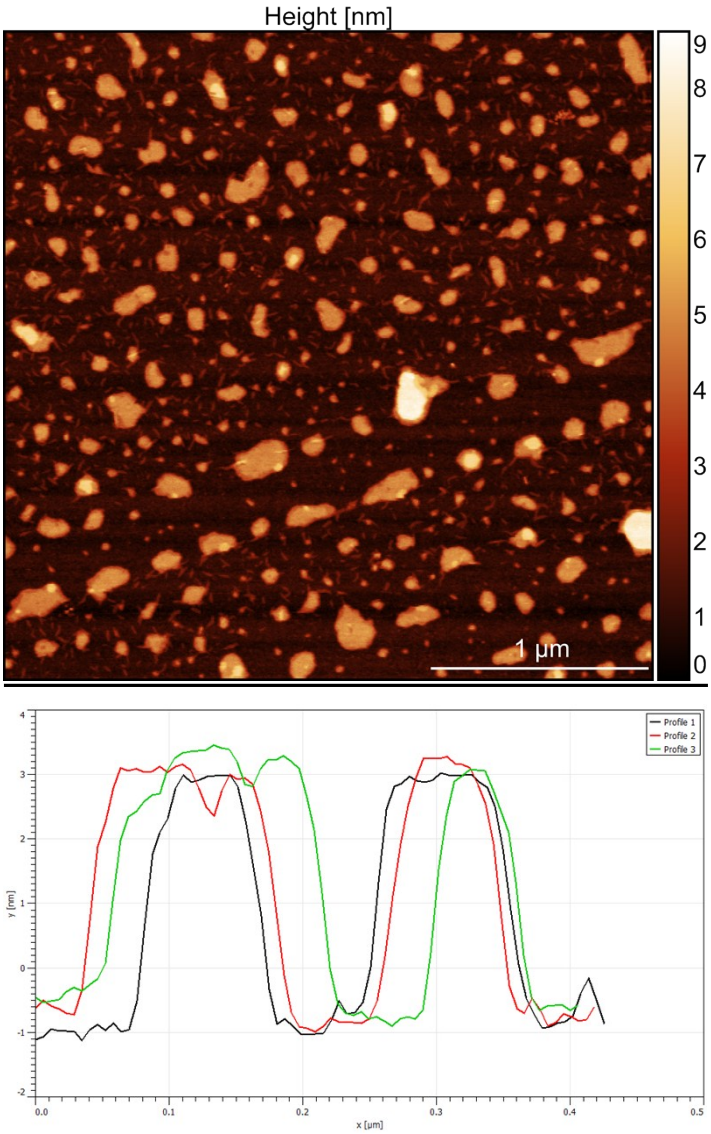

Figure S50: AFM image of **poly(1)-H**.

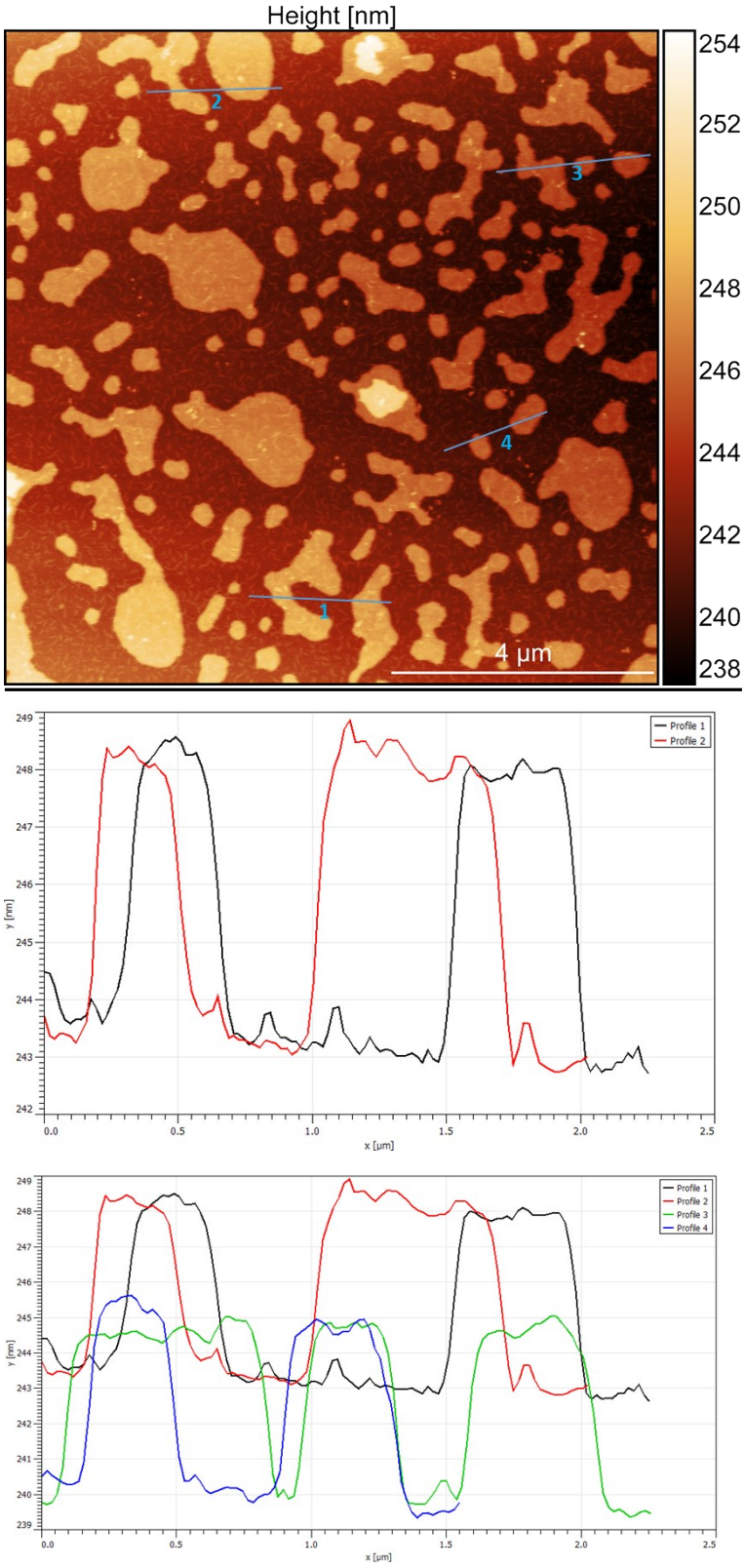

Figure S51: AFM image of **poly(2)-H**.

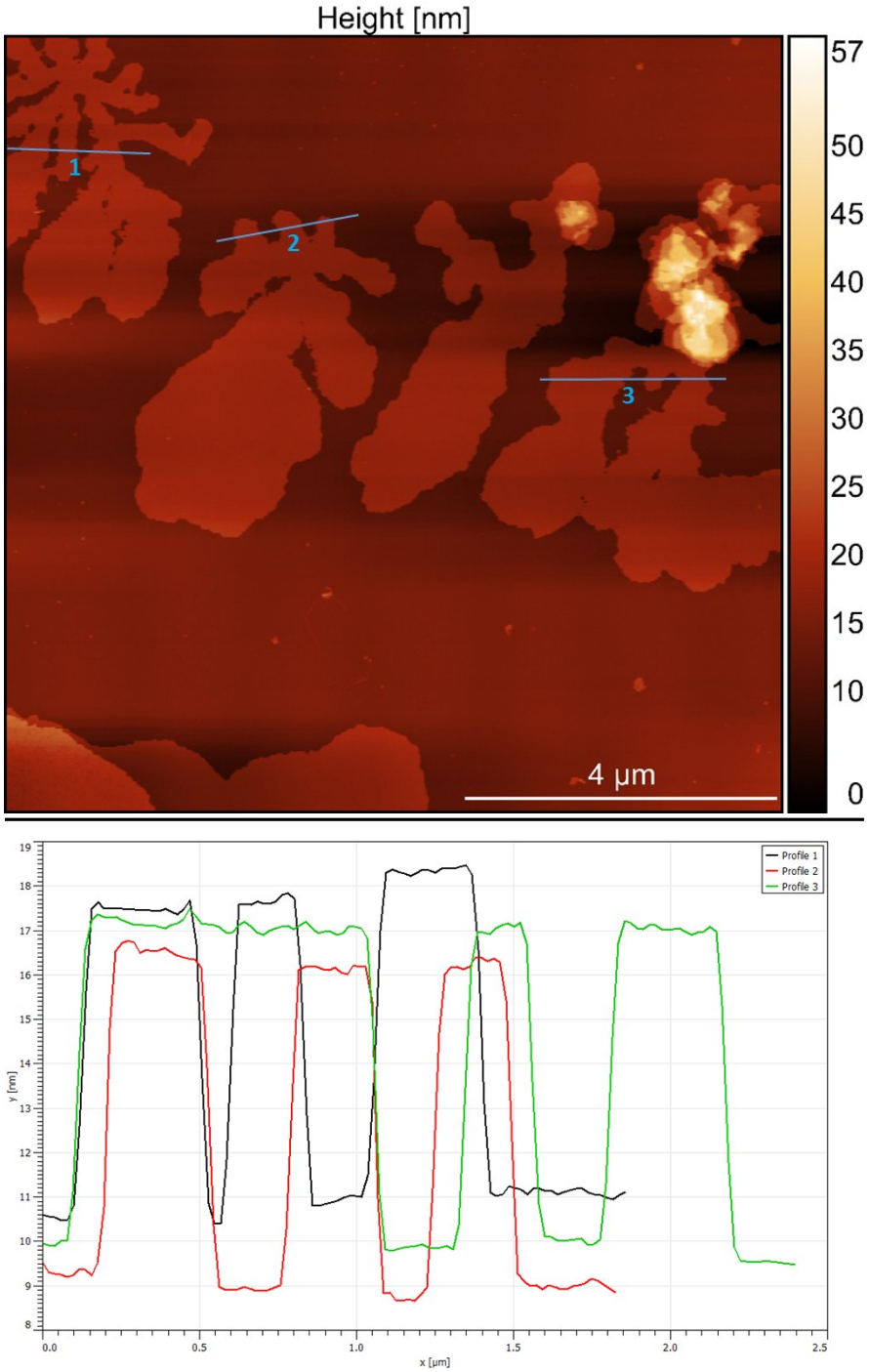

Figure S52: AFM image of **poly(3)-H**.