

# Supporting Information

## Water-soluble Random and Alternating Copolymers of Styrene Monomers with Adjustable Lower Critical Solution Temperature

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## Experimental

### Methods

<sup>1</sup>H-NMR spectra were recorded on Bruker DPX-400 operating at 400 MHz with CDCl<sub>3</sub> as a solvent at room temperature.

Molar masses and molar mass distributions were determined by SEC. For homo- and copolymers of **1** and **2**, SEC was run in THF as eluent at 25 °C and using three 5 μ-MZ-SDV columns with pore sizes of 10<sup>3</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å (flow rate 1 mL·min<sup>-1</sup>). The detection was performed with a RI-(Shodex RI-71). For copolymers of **3**, SEC was run in DMF+0.1% LiBr. For calibration, linear polystyrene standards (PSS, Germany) were used.

Turbidity measurements were performed on a Tepper TP1 photometer (Mainz, Germany). Transmittance of polymer solutions in pure deionized water or buffer solutions were monitored at 670 nm as a function of temperature (cell path length: 12 mm; one heating/cooling cycle at rate of 1 °C·min<sup>-1</sup>). Polymer solutions with a concentration of 1 g·L<sup>-1</sup> or 3 g·L<sup>-1</sup> were used. The temperature value at the onset of turbidity upon heating was defined as the transition temperature.

Dynamic light scattering was performed on a Malvern HPPS-ET equipped with a He-Ne laser (λ = 633 nm) at concentrations of 1g·L<sup>-1</sup>, using the backscattering mode at a fixed angle of 173°.

Dynamic light scattering measurements were performed on a high-performance particle sizer (HPPS-ET, Malvern Instruments, UK) using a light scattering apparatus equipped with a He-Ne laser (λ = 633 nm) and a thermoelectric Peltier temperature controller (temperature control range: 10-90 °C). All polymer solutions were filtered by microfilter before measurements.

## Materials

### Chemicals used

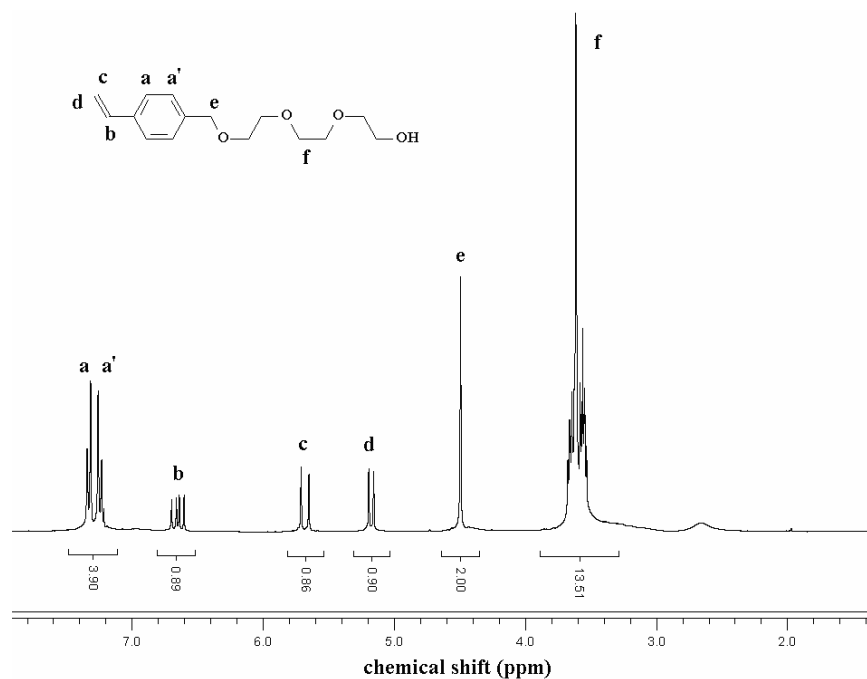
Tri(ethylene glycol) (99%), tetra(ethylene glycol) (99.5%), triethylamine (99%), copper(I) bromide (98%), copper(II) bromide (99%), were purchased from Acros Organics and used without further purification. 4-Vinylbenzyl chloride (technical-grade, 90%), 2, 2'-bipyridyl (98%) and phosphate buffered saline were obtained from Fluka. NaH (95% powder), 2-bromoisobutyl bromide (98%), 1, 1, 4, 7, 10, 10-hexamethyl-triethylenetetramine (97%), (1-bromoethyl) benzene (97%), ethyl 2-bromoisobutyrate (98%), sodium L-ascorbate (99%), hexamethyldisilazane (97%), maleic anhydride (99%), N-methylmaleimide (**4**) (97%), and N-propylmaleimide (**5**) (94%), were purchased from Aldrich and used as received. N-[methoxyoligo(ethyleneglycol)]maleimide (**11**, bearing PEG750) was obtained from Rapp Polymere. 3-Trimethylsilylpropylamine (95%) was purchased from ABCR.

Tetrahydrofuran (THF) (J.T.Baker) was distilled from sodium and benzophenone and stored in a solvent storage bottle before use. Silica gel (0.06-0.2 mm, 60A) (Acros Organics), hexane (technical-grade), ethyl acetate (Chem Solute), acetic anhydride (99%), zinc bromide (98%), sodium acetate (99%), and sodium chloride (Chem Solute) were used as received. N-Decylmaleimide (**6**) was a gift from Peter Hendlinger, and 4-cyano-4-(dodecylsulfanylthiocarbonylsulfanyl)pentanoic acid (**CTA1**) was a gift from Achille M. Bivigou Koumba.

### Synthesis of triethyleneglycol-mono-4-vinylbenzylether (**1**)

Following a literature procedure,<sup>[1]</sup> tri(ethylene glycol) (30.93 g, 0.2062 mol) and dry THF (35 mL) were added to a three-necked flask, followed by the gradual addition of NaH (95%) (2.22 g, 0.0924 mol). The mixture was stirred under an N<sub>2</sub> atmosphere for 1 h. A solution of 4-vinylbenzyl chloride (6.36 g, 0.040 mol) in dry THF (15 mL) was added dropwise. After being refluxed at 65 °C bath temperature overnight, the reaction mixture was quenched with water (100 mL) and poured into a separatory funnel. The organic layer was separated, and the aqueous layer was extracted four times with chloroform. The organic phases were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporating the solvents, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1v:1v) as eluent, affording a slightly yellow liquid. Yield 8.97 g (84.3%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.36 (d, 2H, aromatic), 7.28 (d, 2H, aromatic), 6.68 (dd, 1H,  $\text{CH}_2=\text{CH-}$ ), 5.72 (dd, 1H,  $\text{CHH}=\text{CH-}$ ), 5.21 (dd, 1H,  $\text{CHH}=\text{CH-}$ ), 4.53 (s, 2H,  $(\text{CH}_2)_2\text{CCH}_2\text{O-}$ ), 3.56–3.70 (m, 12H,  $-\text{OCH}_2\text{CH}_2\text{O-}$ ), 3.11 (br, 1H,  $-\text{OH}$ ).

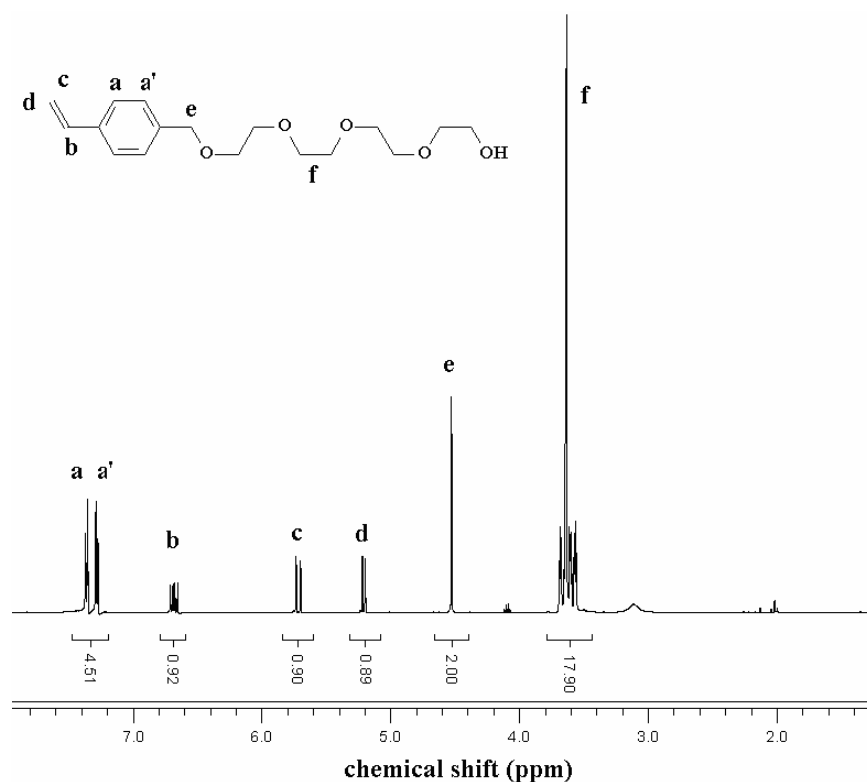


**Fig. S1.**  $^1\text{H-NMR}$  spectrum of monomer **1** in  $\text{CDCl}_3$ . Values given under the signals give the integral of corresponding groups.

### Synthesis of tetraethyleneglycol-mono-4-vinylbenzylether (**2**)

Following a literature procedure,<sup>[1]</sup> tetra(ethylene glycol) (40.0 g, 0.206 mol) and dry THF (35 mL) were added to a three-necked flask, followed by the gradual addition of NaH (95%) (2.22 g, 0.0924 mol). The mixture was stirred in an  $\text{N}_2$  atmosphere for 1 h. A solution of 4-vinylbenzyl chloride (6.36 g, 0.040 mol) in dry THF (15 mL) was added dropwise. After being refluxed at 65 °C bath temperature overnight, the reaction mixture was quenched with water (100 mL) and poured into a separatory funnel. The organic layer was separated, and the aqueous layer was extracted four times with chloroform. The organic phases were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporating the solvents, the crude product was purified by column chromatography on silica gel with ethyl acetate as eluent, affording a slightly yellow liquid. Yield 10.3 g (82.7%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.36 (d, 2H, aromatic), 7.30 (d, 2H, aromatic), 6.69 (dd, 1H,  $\text{CH}_2=\text{CH-}$ ), 5.72 (dd, 1H,  $\text{CHH}=\text{CH-}$ ), 5.21 (dd, 1H,  $\text{CHH}=\text{CH-}$ ), 4.53 (s, 2H,  $(\text{CH}_2)_2\text{CCH}_2\text{-}$ ), 3.57–3.70 (m, 16H,  $-\text{OCH}_2\text{CH}_2\text{O-}$ ), 3.10 (br, 1H,  $-\text{OH}$ ).

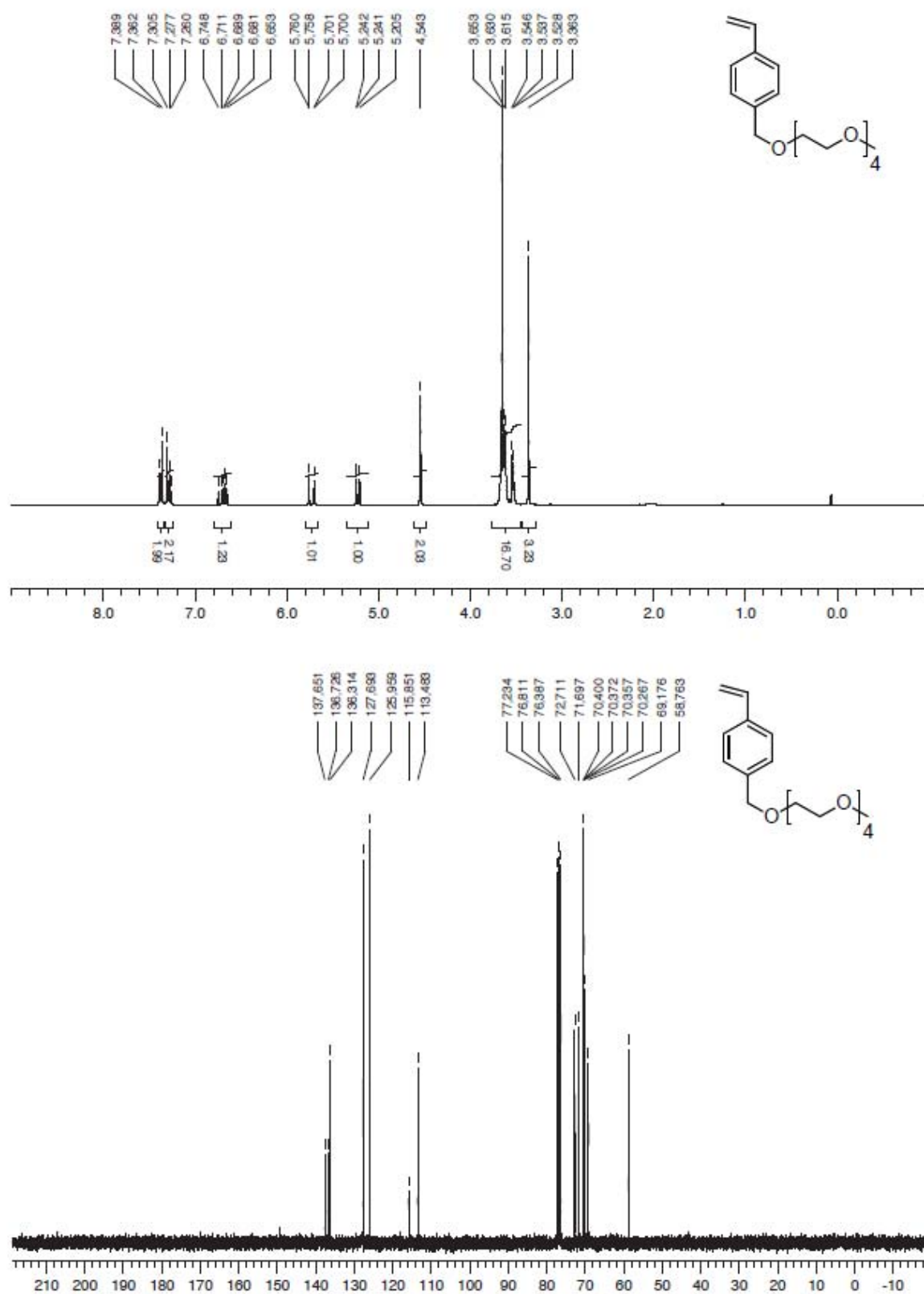


**Fig. S2.** <sup>1</sup>H-NMR spectrum of monomer **2** in CDCl<sub>3</sub>. Values given under the signals give the integral of corresponding groups.

#### 4-Vinylbenzyl methoxytetra(oxyethylene) ether (**3**).

Following a literature procedure,<sup>[2]</sup> tetra(ethylene glycol) monomethyl ether (10.0 g, 48 mmol), NaH (1.8 g, 71 mmol), and dry THF (100 ml) were placed in a 250 ml Schlenk flask. After stirring the mixture for 1 h at ambient temperature, 4-vinylbenzyl chloride was added dropwise and the mixture was stirred at 75°C over night. The reaction was quenched with water, extracted three times with CHCl<sub>3</sub> and concentrated in vacuo. The crude product was purified by column chromatography (ethylacetate:hexane 10v:1v) to yield 4-vinylbenzyl methoxytetra(oxyethylene) ether as slightly yellow oil. Yield 11.8 g (76%).

<sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>): δ = 3.36 (s, 3H, OCH<sub>3</sub>), 3.52-3.65 (m, 16H, 8 OCH<sub>2</sub>), 4.54 (s, 2H, ArCH<sub>2</sub>), 5.22 (dd, J = 10.95Hz, 1H, CH<sub>2</sub>CH), 5.73 (dd, J = 17.55Hz, 1H, CH<sub>2</sub>CH), 6.69 (dd, J = 17.7Hz, 1H, CH<sub>2</sub>CH), 7.28 (d, J = 8.1Hz, 2H, ArH), 7.37 (d, J = 8.1Hz, 2H, ArH). <sup>13</sup>C NMR (75 Mhz, CDCl<sub>3</sub>): δ = 59.0 (OCH<sub>3</sub>), 69.4-70.6 (7 CH<sub>2</sub>), 71.9 (CH<sub>2</sub>OMe), 72.9 (ArCH<sub>2</sub>), 113.7 (CH<sub>2</sub>CH), 126.2 (2 ArC), 127.9 (2 ArC), 136.5 (ArCCH), 136.9 (ArCCH<sub>2</sub>), 137.9 (CH<sub>2</sub>CH). R<sub>f</sub>: 0.3 (ethylacetate).



**Fig. S3.** <sup>1</sup>H (top, in acetone *d*<sub>6</sub>) and <sup>13</sup>C NMR (bottom, in CDCl<sub>3</sub>) spectra of monomer **3**.

Values given under the signals give the integral of corresponding groups.

### **N-(3-trimethylsilyl)propyl maleamic acid.**

Maleic anhydride (1.9 g, 19.5mmol) was dissolved in DMF (5mL) and aminopropyl-trimethylsilane (2.5 g, 19.1mmol) was added. The solution was stirred at room temperature over night, precipitated into H<sub>2</sub>O, filtrated and washed thrice with H<sub>2</sub>O. The crude product was recrystallized thrice from H<sub>2</sub>O to yield N-(3-trimethylsilyl)propyl maleic acid as colorless solid (4.35 g, 100%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.01 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.48-0.54 (m, 2H, CH<sub>2</sub>Si), 1.53-1.63 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.30-3.37 (m, 2H, NCH<sub>2</sub>), 6.30 (d, J = 12.9 Hz, 1H, CHCOOH), 6.51 (d, J = 12.6 Hz, 1H, CHCO), 8.12 (bs, 1H, NH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = -1.7 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.9 (CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 23.5 (NHCH<sub>2</sub>CH<sub>2</sub>), 43.7 (NHCH<sub>2</sub>), 132.4 (CHCO), 135.7 (CHCOOH), 166.2 (COOH), 166.5 (CO). Anal. calcd for C<sub>10</sub>H<sub>19</sub>NO<sub>3</sub>Si: C, 52.37 %; H, 8.35 %; N, 6.11 %; found: C, 51.70 %; H, 8.89 %; N, 6.09 %. HRMS (ESI): calcd for C<sub>10</sub>H<sub>20</sub>NO<sub>3</sub>Si ([MH<sup>+</sup>]) 230.1212; found 230.1216.

### **N-(3-trimethylsilyl)propyl maleimide (7).**

Adapting a literature procedure,<sup>[3]</sup> N-(3-trimethylsilyl)propyl maleic acid (500 mg, 2.2 mmol) was dissolved in toluene (20 mL) under argon atmosphere. The solution was heated to 80°C and ZnBr<sub>2</sub> (500 mg, 2.2 mmol) was added. Then, hexamethyl disilazane (720 mg, 4.4 mmol) in toluene (10 mL) was added dropwise and the reaction mixture was stirred at 80°C for 6 h and at room temperature for 15 h. The solution was concentrated in vacuo and the crude product was purified by column chromatography (DCM:MeOH 24:1) to yield N-(3-trimethylsilyl)propyl maleimide (410 mg, 89%) as slightly brown solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = -0.03 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.42-0.47 (m, 2H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 1.50-1.61 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>), 3.49 (t, J = 7.35 Hz, 2H, NHCH<sub>2</sub>), 6.68 (s, 2H, 2 CHCO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = -2.1 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.4 (CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 23.0 (NHCH<sub>2</sub>CH<sub>2</sub>), 40.7 (NCH<sub>2</sub>), 133.8 (2 CH), 170.7 (2 CO). Anal. calcd for C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub>Si: C, 56.83%; H, 8.04%; N, 6.62%; found: C, 56.30%; H, 8.02%; N, 6.36%. HRMS (ESI): calcd for C<sub>10</sub>H<sub>18</sub>NO<sub>2</sub>Si ([MH<sup>+</sup>]) 212.1107; found 212.1122. R<sub>f</sub>: 0.8 (DCM/MeOH 10:1).

### **N,N-maleoyl-L-glycine tert.-butylester (8).**

Adapting a literature procedure,<sup>[3]</sup> L-glycine tert.-butylester (500 mg, 3.0 mmol) and triethylamine (300 mg, 3.0 mmol) in toluene (20 mL) were placed in a 50 mL round bottom flask, maleic anhydride (293 mg, 2.99 mmol) was added and the reaction mixture as stirred at

60°C for 6 h and at room temperature for 15 h. ZnBr<sub>2</sub> (685 mg, 3.0 mmol) was added in one portion, the solution was heated to 80°C and hexamethyl disilazane (1.04 g, 6.4 mmol) in toluene (10 mL) was added dropwise. The reaction mixture was stirred at 80°C for 6 h and at room temperature for 20 h. The solution was concentrated in vacuo and the crude product was purified by column chromatography (DCM:MeOH 24:1) to yield N,N-maleoyl-L-glycine *tert.*-butylester (430 mg, 68%) as colorless solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.45 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 4.16 (s, 2H, CH<sub>2</sub>), 6.77 (s, 2H, 2 CH). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ = 27.7 (C(CH<sub>3</sub>)<sub>3</sub>), 39.2 (CH<sub>2</sub>), 82.6 (C(CH<sub>3</sub>)<sub>3</sub>), 134.2 (2 CH), 165.9 (COO), 169.7 (2 CO). Anal. calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>4</sub>: C, 56.87%; H, 6.20%; N, 6.63%; found: C, 56.75%; H, 6.01%; N, 6.64%. HRMS (ESI): calcd for C<sub>10</sub>H<sub>14</sub>NO<sub>4</sub> ([MH<sup>+</sup>]) 212.0923; found 212.0930. R<sub>f</sub>: 0.7 (DCM/MeOH 10:1).

#### **N,N-maleoyl-L-alanine *tert.*-butylester (9).**

Adapting a literature procedure,<sup>[3]</sup> L-alanine *tert.*-butylester (2.0 g, 11.3 mmol) and triethylamine (1.1 g, 11.2 mmol) in toluene (80 mL) were stirred for 30 min at room temperature. The solution was heated to 60°C, maleic anhydride (1.1 g, 11.3 mmol) was added and the reaction mixture was stirred for 8 h at 60°C, and for additional 12 h at room temperature. After adding ZnBr<sub>2</sub>, the solution was heated to 80°C, and hexamethyl disilazane (3.6 g, 22.4 mmol) in toluene (20 mL) was added dropwise. The mixture was continued for 6 h, cooled to room temperature and stirred for another 12 h. The solution was concentrated in vacuo and the crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 24:1) to yield N,N-maleoyl-L-alanine *tert.*-butylester (1.75 g, 69%) as colorless solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.42 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.58 (d, J = 7.5 Hz, 3H, CHCH<sub>3</sub>), 4.67 (q, J = 7.2 Hz, 1H, CHCH<sub>3</sub>), 6.71 (s, 2H, 2 CHCO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 14.9 (CH<sub>3</sub>CH), 27.6 (C(CH<sub>3</sub>)<sub>3</sub>), 48.0 (CHCH<sub>3</sub>), 82.1 (C(CH<sub>3</sub>)<sub>3</sub>), 134.0 (2 CHCO), 168.3 (2 NCO), 169.8 (COO).

#### **N-2-(methylthio)ethyl maleimide.**

Adapting a literature procedure,<sup>[3]</sup> methylthioethylamine (2.5 g, 27.4 mmol) and maleic anhydride (2.7 g, 27.4 mmol) were dissolved in toluene (150 mL), stirred at 60°C for 8 h, and at room temperature for additional 12 h. ZnBr<sub>2</sub> (6.2 g, 27.4 mmol) was added, the reaction mixture was heated to 80°C and hexamethyl disilazane (8.85 g, 54.8 mmol) was added dropwise. The solution was stirred for 12 h, cooled to room temperature and stirred for



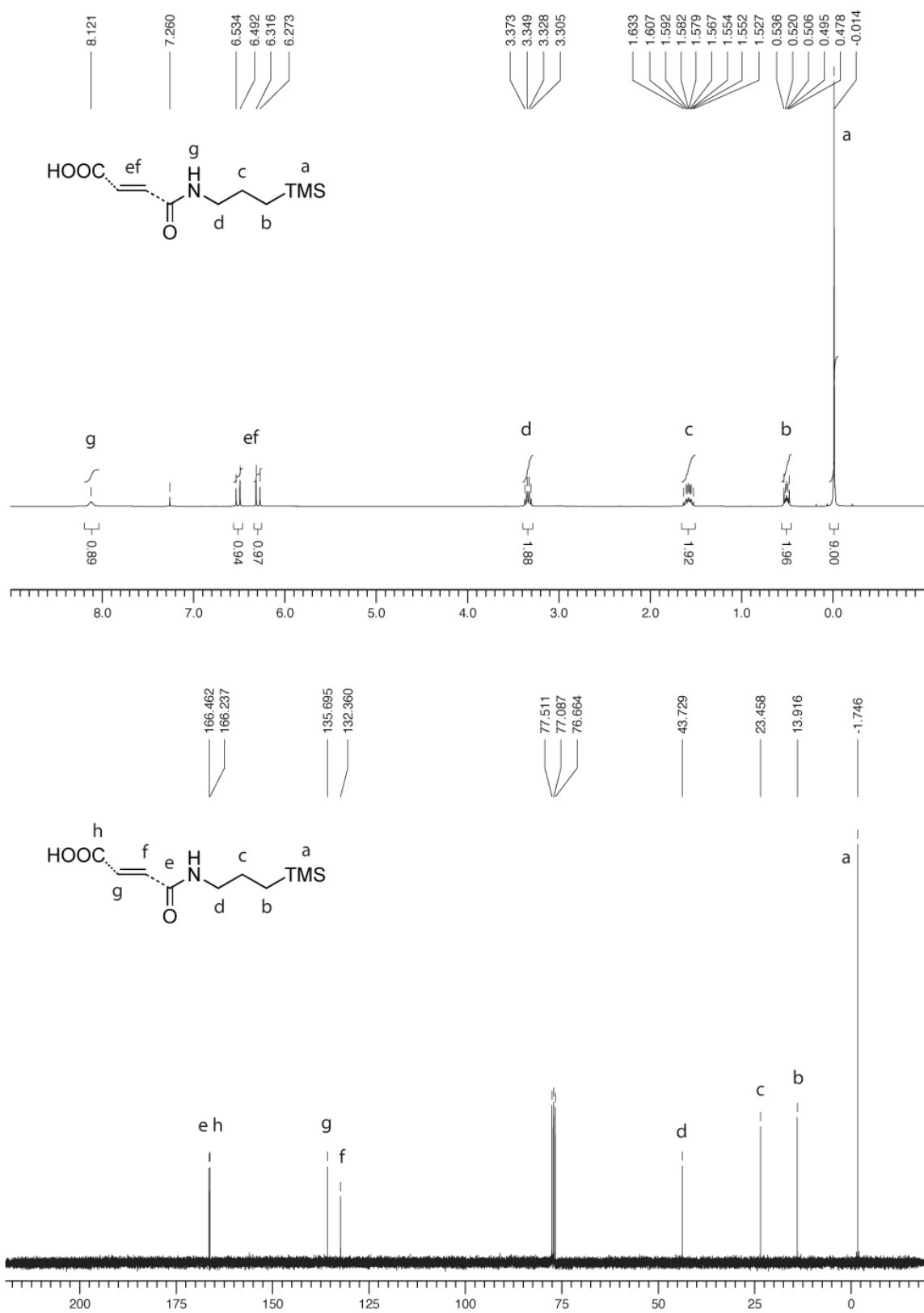
another 12 h. The solvent was removed in vacuo and the crude reaction mixture was purified by column chromatography (DCM:MeOH 24:1) to yield N-ethylthiomethyl maleimide (1.1 g, 24%) as yellow oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.12 (s, 3H,  $\text{SCH}_3$ ), 2.70 (t,  $J$  = 6.9 Hz, 2H,  $\text{SCH}_2$ ), 3.73 (t,  $J$  = 6.9 Hz, 2H,  $\text{NCH}_2$ ), 6.70 (s, 2H, 2  $\text{CHCO}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.8 ( $\text{SCH}_3$ ), 31.9 ( $\text{SCH}_2$ ), 36.0 ( $\text{NCH}_2$ ), 133.9 (2  $\text{COCH}$ ), 170.3 (2  $\text{CO}$ ).  $R_f$ : 0.8 (DCM/MeOH 10:1).

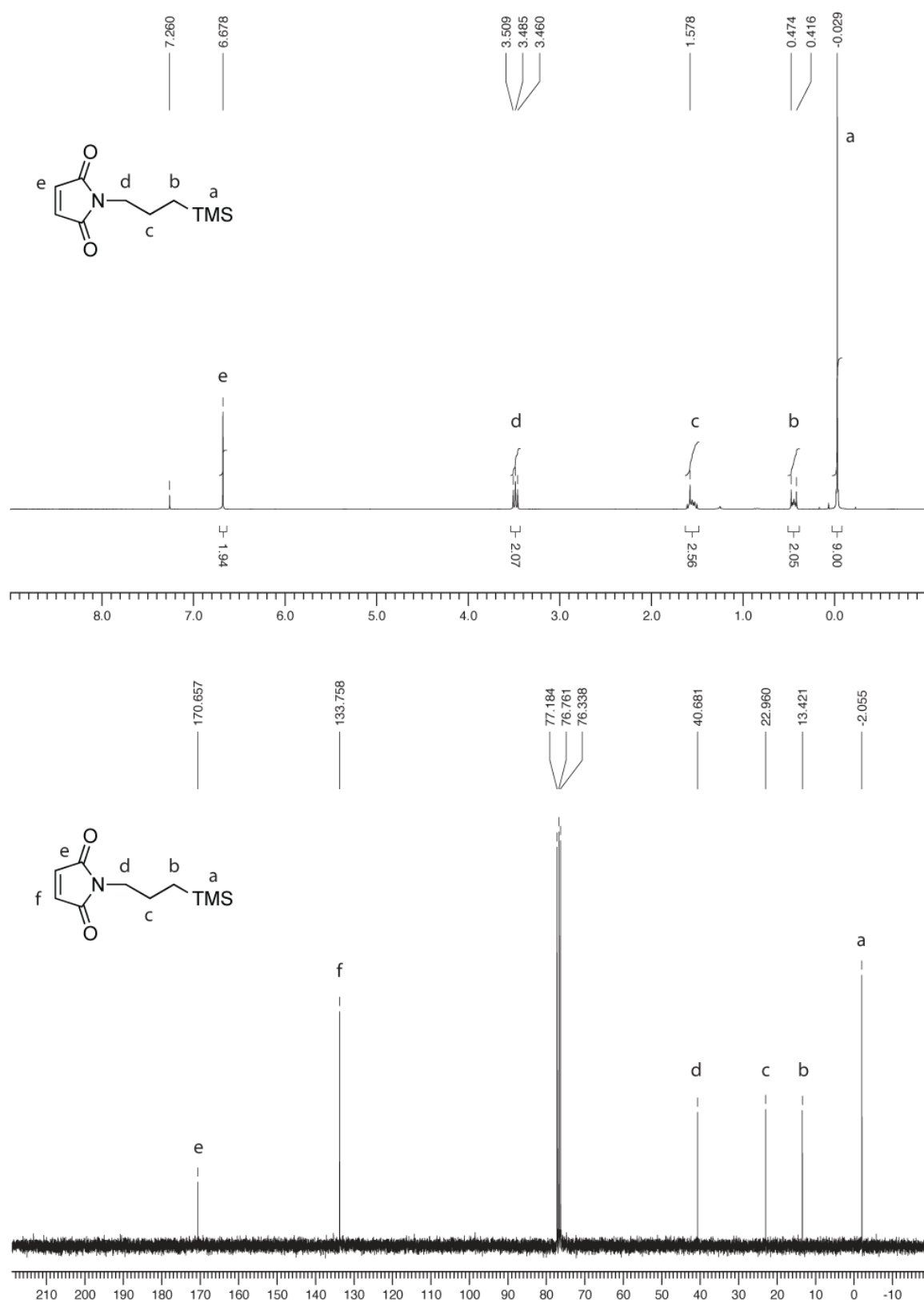
#### **N-2(methylsulfoxy)ethyl maleimide (10).**

Adapting a literature procedure,<sup>[4]</sup> N-ethylthiomethyl maleimide (500 mg, 2.9 mmol) was added to a 0.5 M solution of  $\text{NaIO}_4$  in methanol/water (8 mL/22 mL) and stirred at room temperature over night. Then, the solvent was removed in vacuo and the crude reaction mixture was purified by column chromatography (DCM:MeOH 24:1) to yield N-ethylsulfoxymethyl maleimide (170 mg, 31%) as colorless solid.

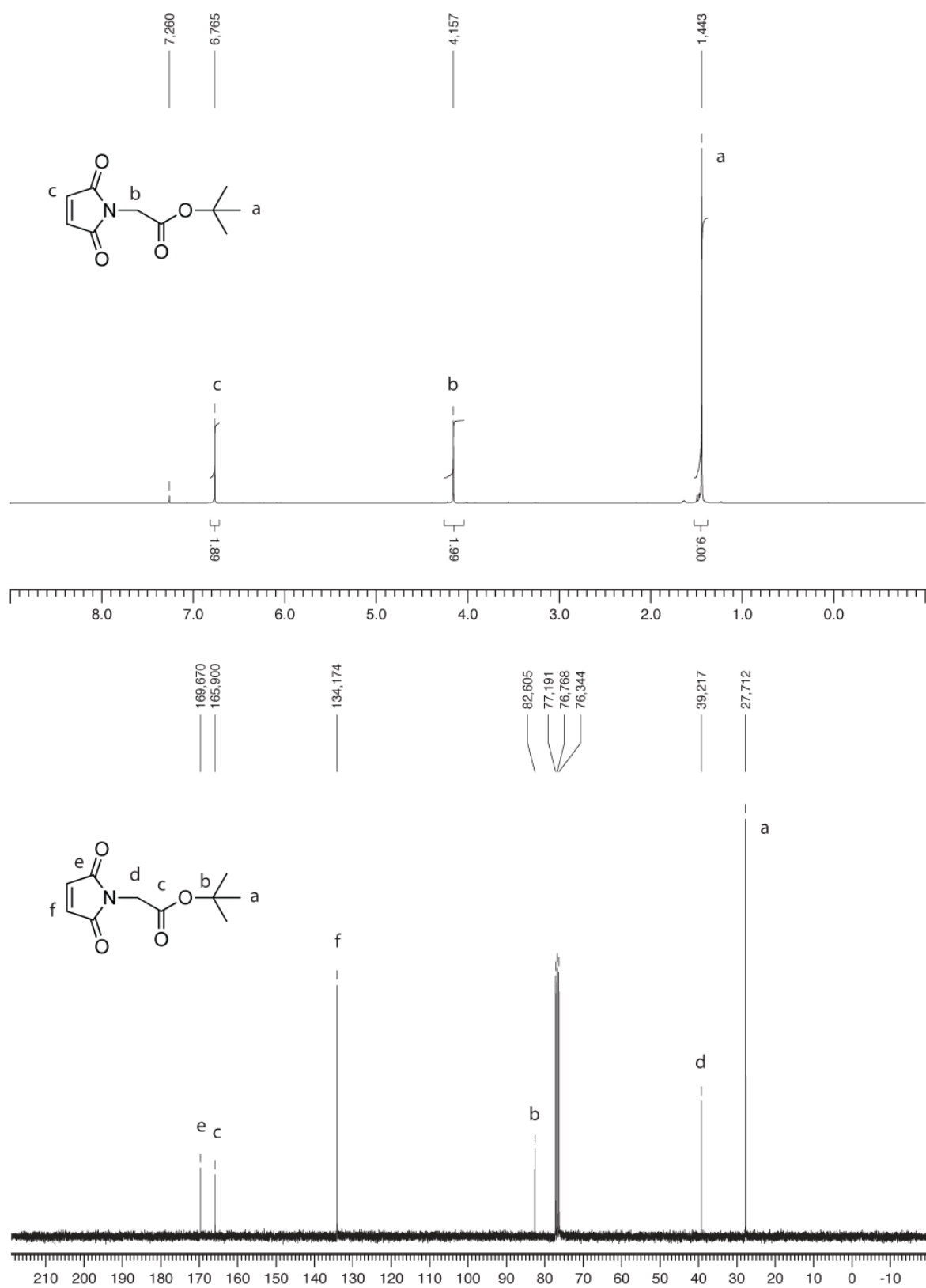
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.99 (s, 3H,  $\text{SOCH}_3$ ), 3.33 (t,  $J$  = 6.6 Hz, 2H,  $\text{SOCH}_2$ ), 4.04 (t,  $J$  = 6.6 Hz, 2H,  $\text{NCH}_2$ ), 6.76 (s, 2H, 2  $\text{CHCO}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 31.3 ( $\text{SOCH}_3$ ), 40.4 ( $\text{SOCH}_2$ ), 51.3 ( $\text{NCH}_2$ ), 134.3 (2  $\text{COCH}$ ), 169.7 (2  $\text{CO}$ ).



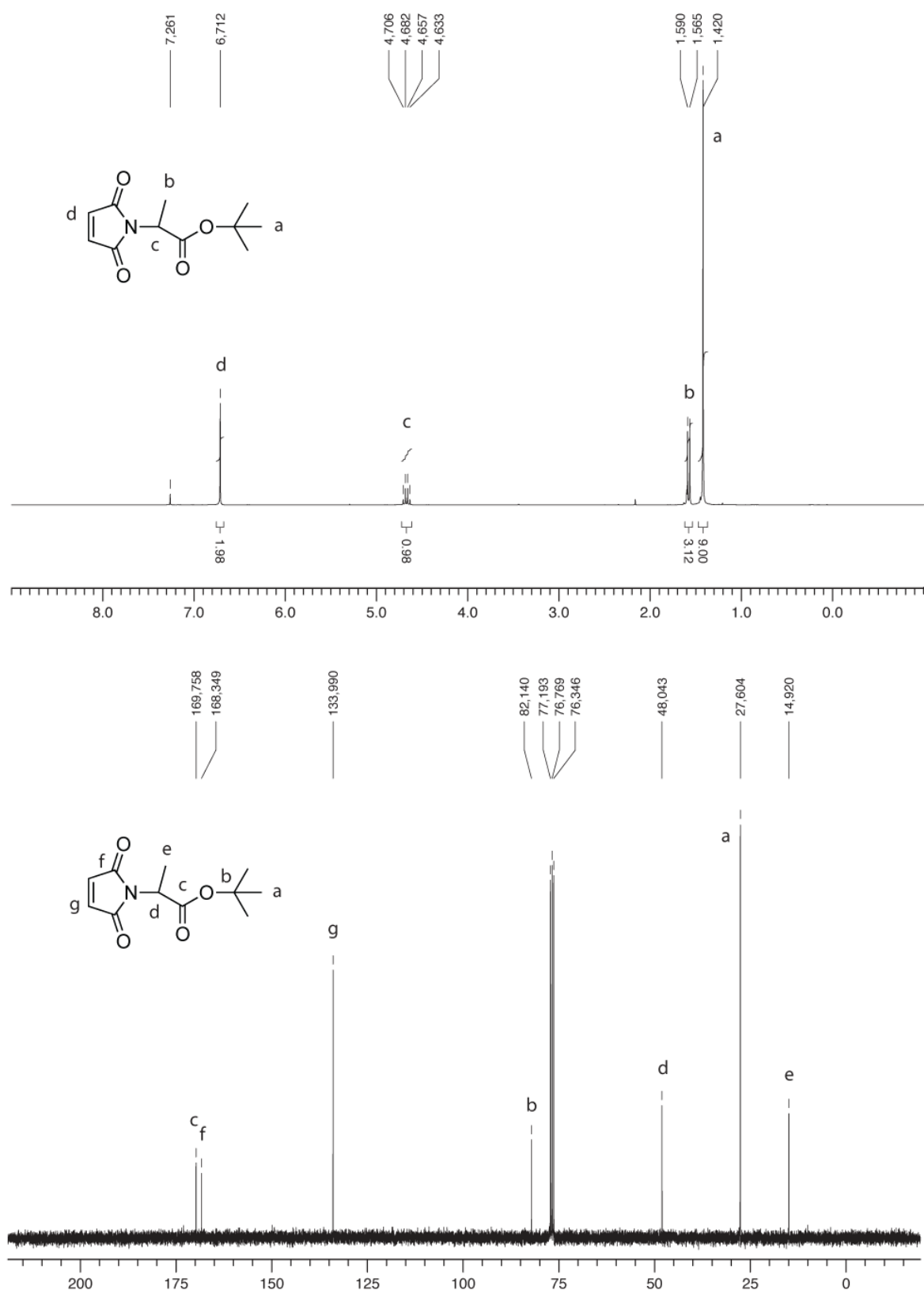
**Figure S4:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of N-(3-trimethylsilyl)propyl maleamic acid in CDCl<sub>3</sub>.



**Figure S5:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of N-(3-trimethylsilyl)propyl maleimide (**7**) in CDCl<sub>3</sub>.



**Figure S6.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of N,N-maleoyl-L-glycine *tert.*-butylester (**8**).



**Figure S7.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of N,N-maleoyl-L-alanine *tert.*-butylester (9).

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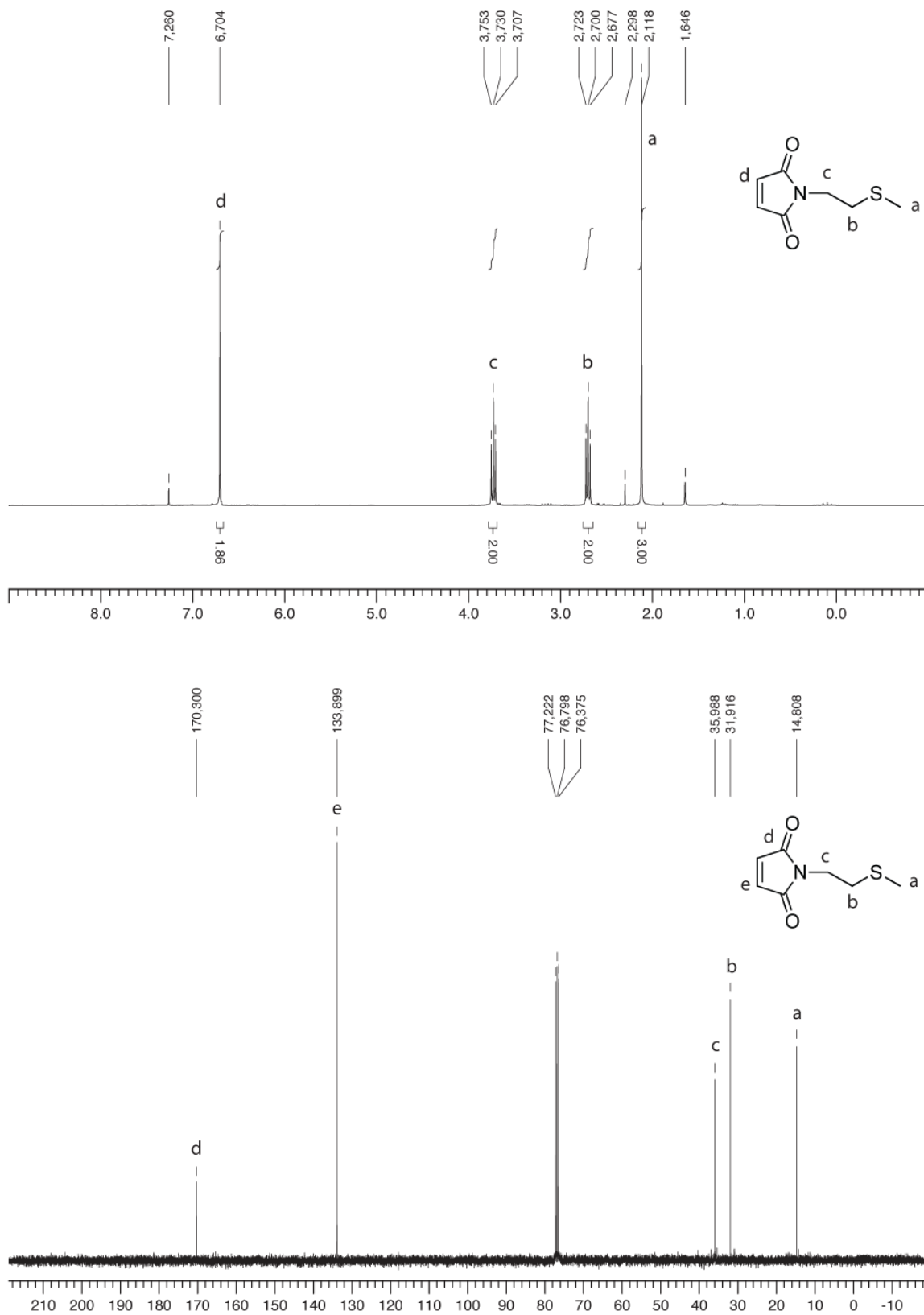
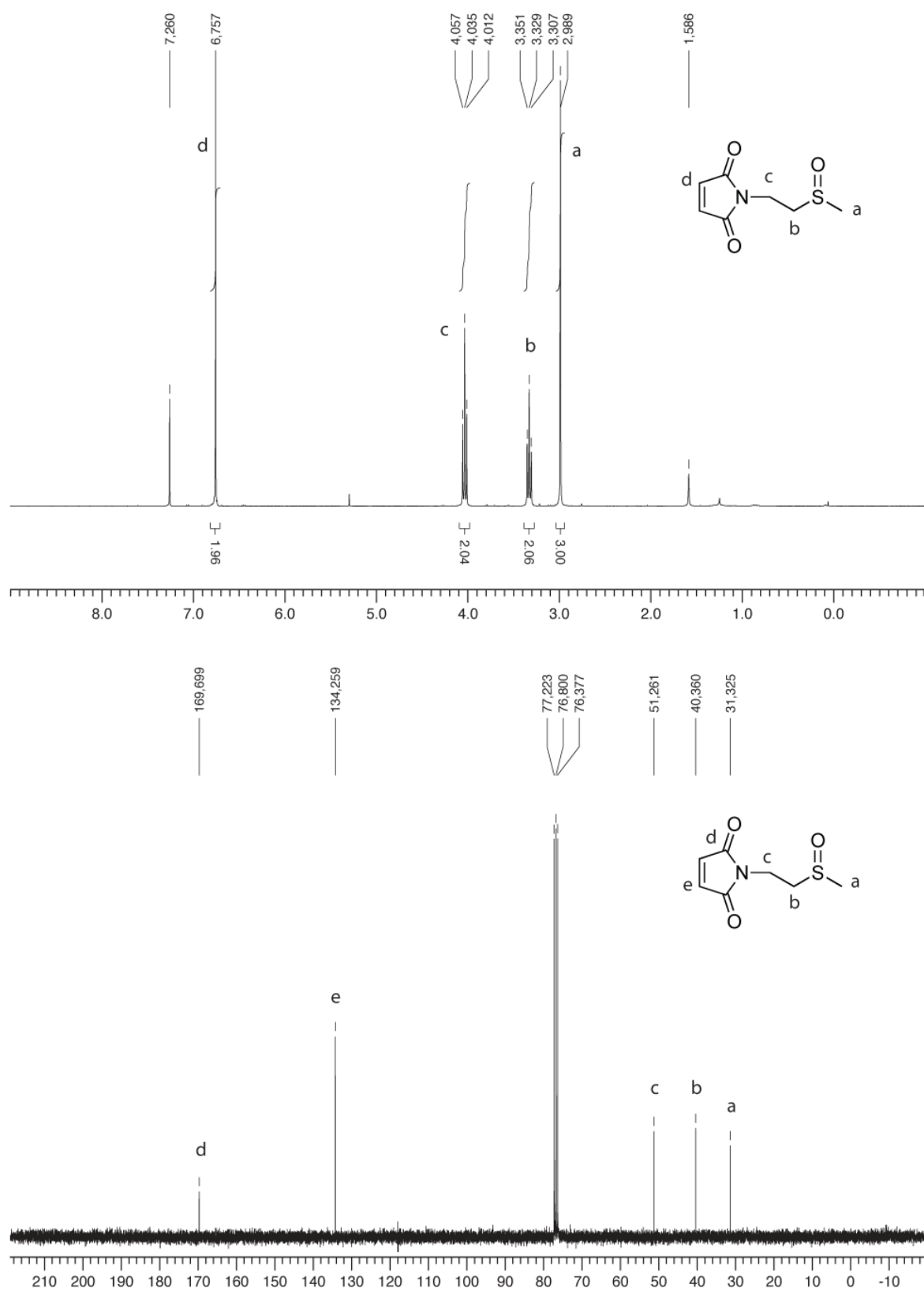
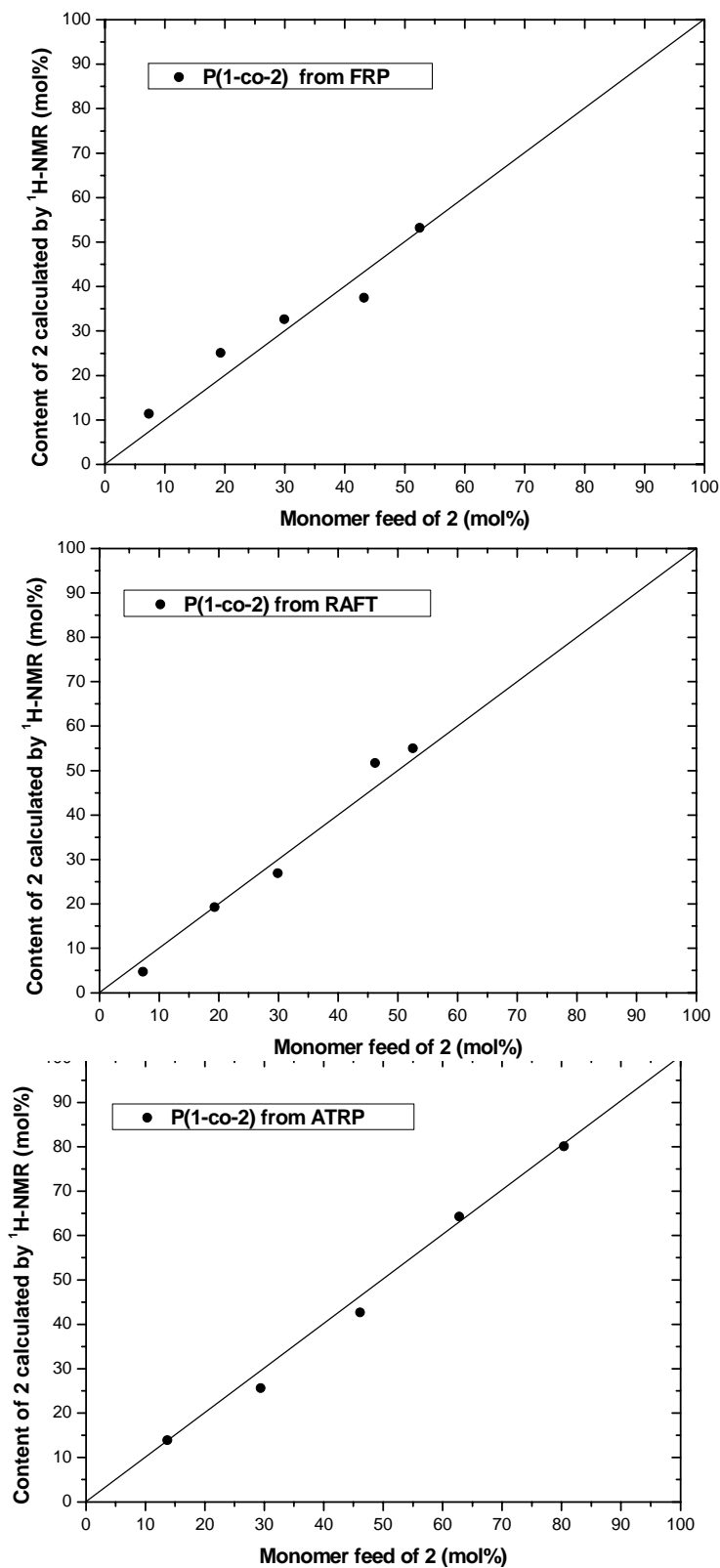


Figure S8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of N-2-(methylthio)ethyl maleimide.

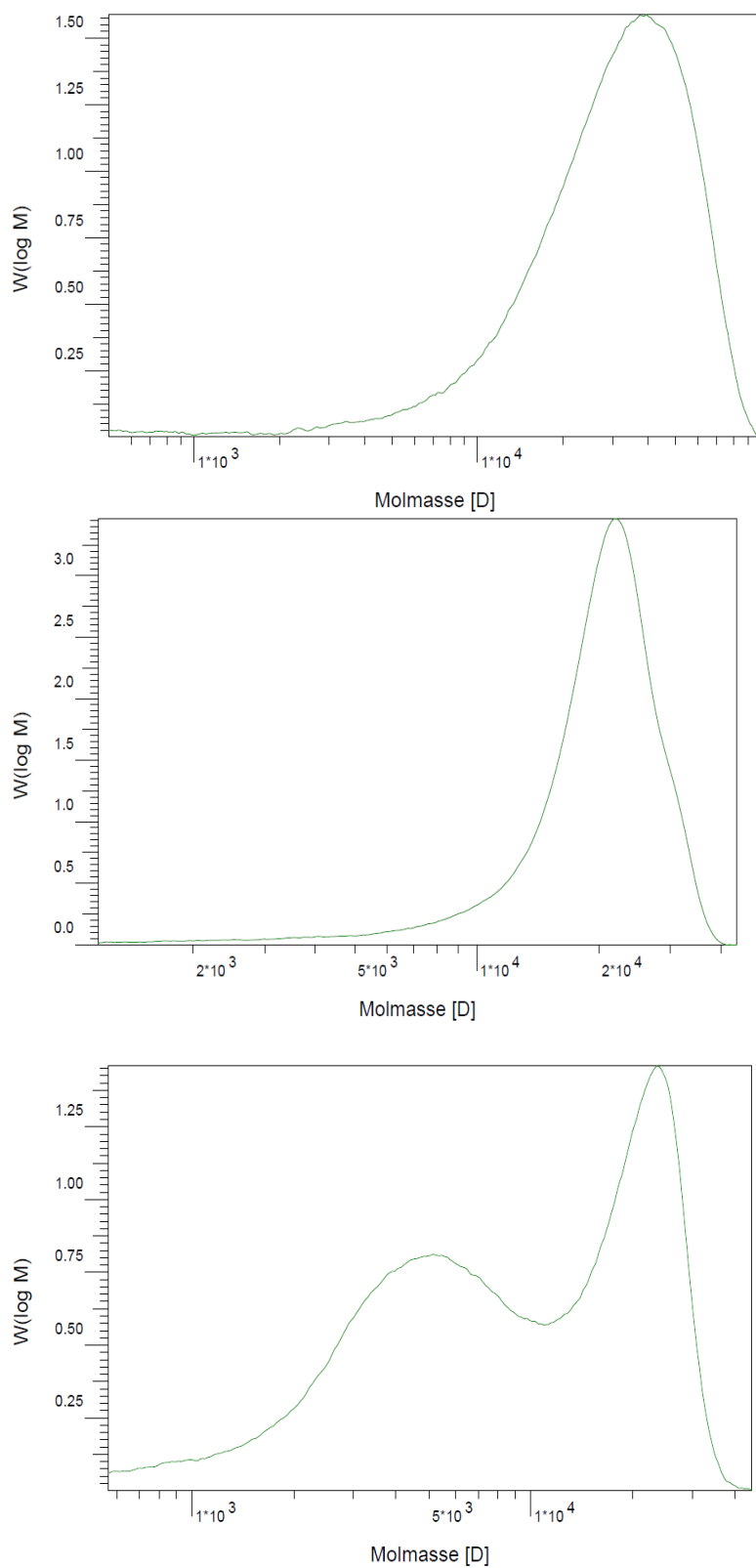


**Fig. S9.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of N-2-(methylsulfoxy)ethyl maleimide (**10**).

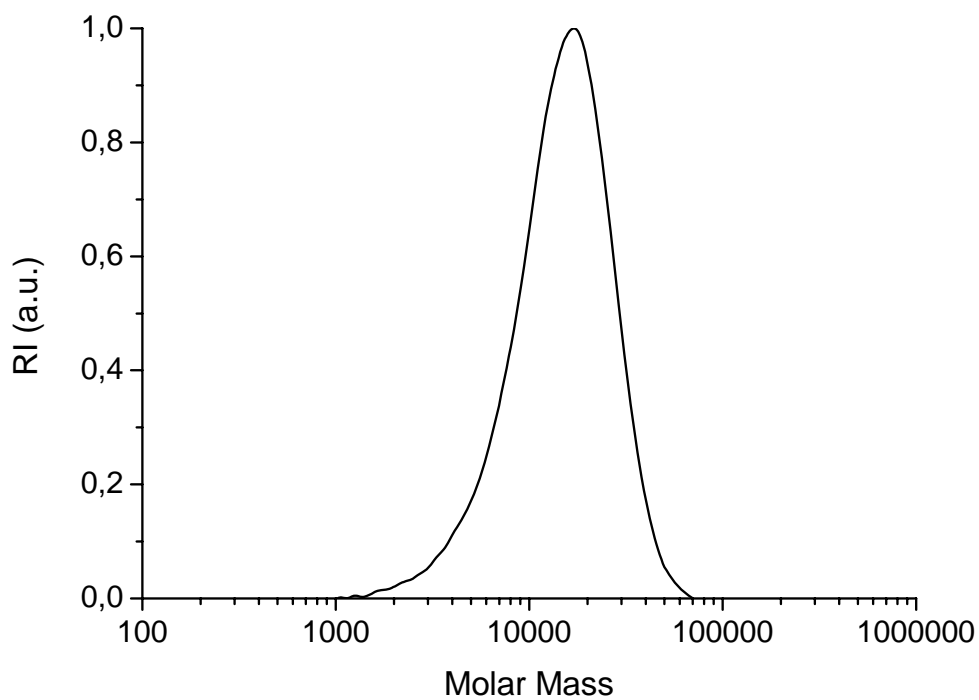


**Fig. S10.** Composition of copolymers **P(1-co-2)** in dependence on the monomer feed ratio using various free radical polymerization techniques. From top to bottom: classical free radical polymerization, RAFT, and ATRP (determined by <sup>1</sup>H-NMR).

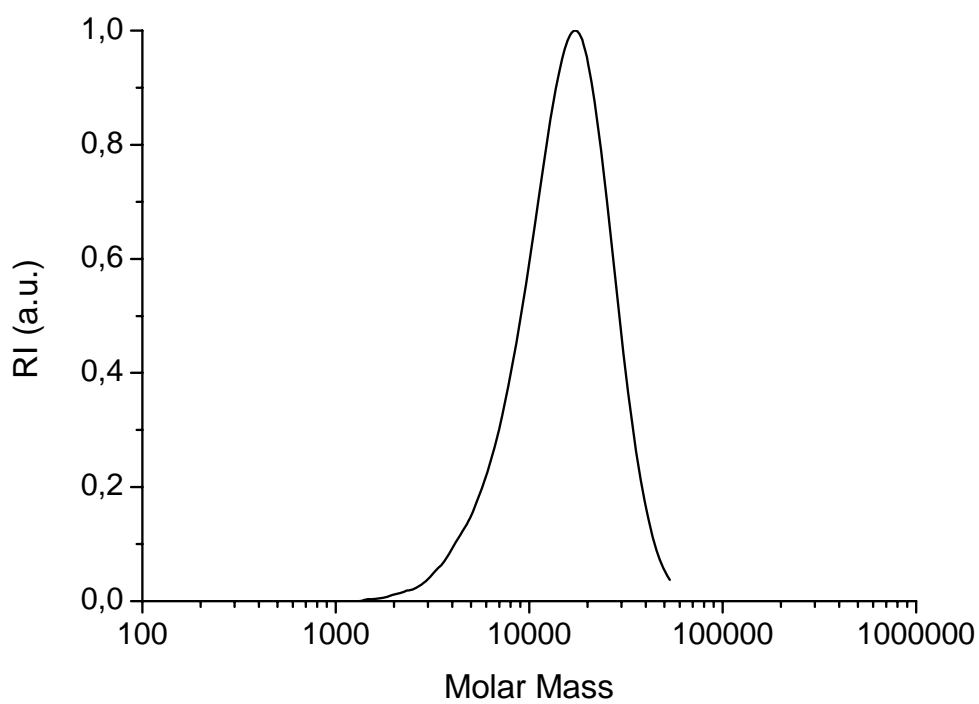




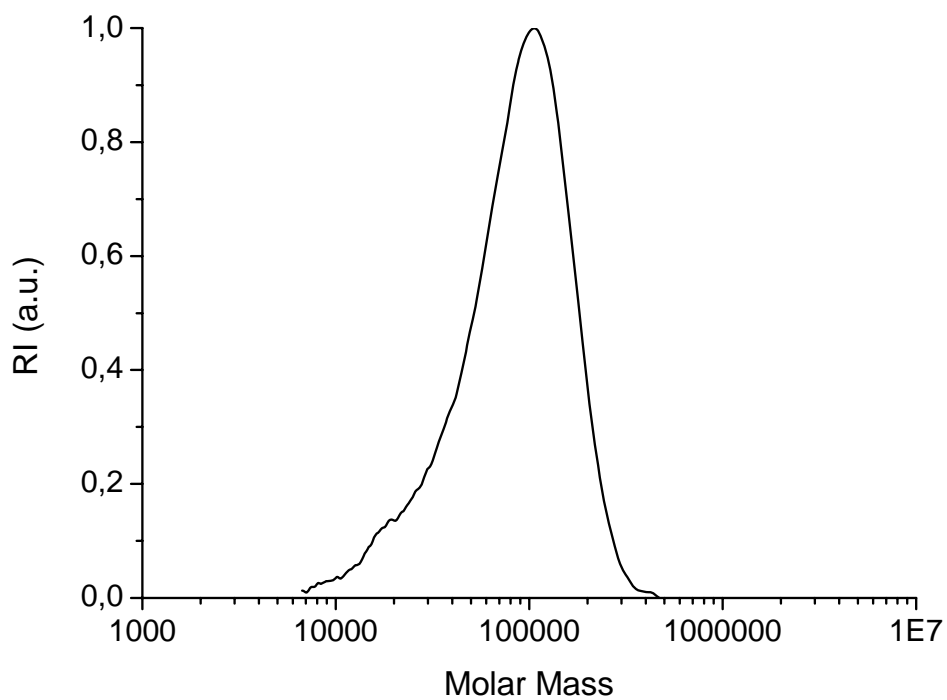
**Fig. S11.** representative SEC elugrams of copolymer series **P(1-co-2)**. From top to bottom:  
**P(1-co-2)-7f** made by FRP, **P(1-co-2)-46r** made by RAFT, **P(1-co-2)-80a** made by ATRP.



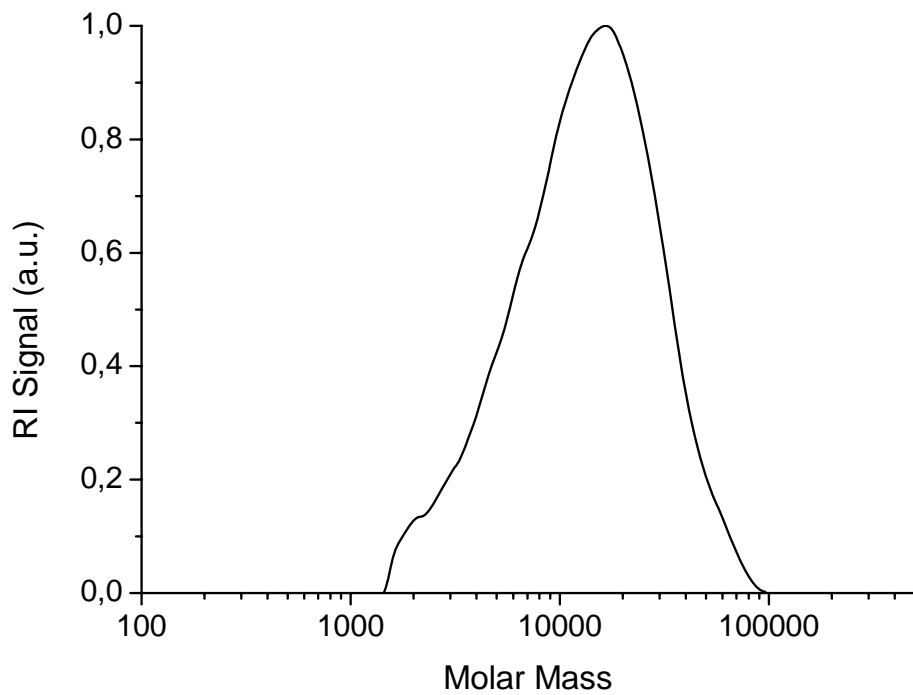
**Fig. S12.** SEC of P(3-alt-4)<sub>45</sub> in DMF+LiBr (0.1%).



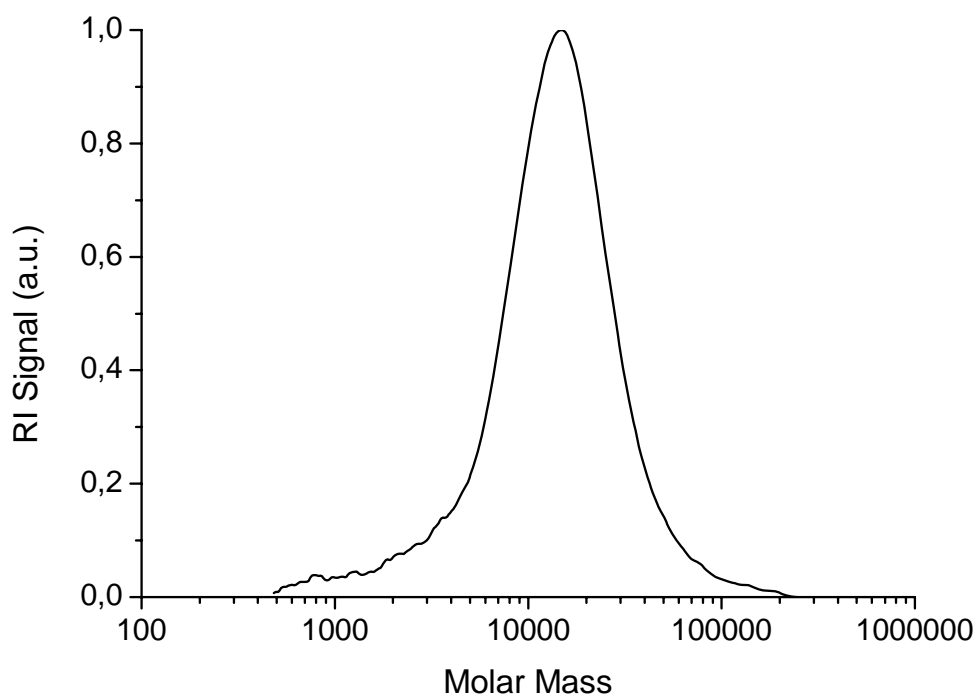
**Fig. S13.** SEC of P(3-alt-5)<sub>43</sub> in DMF+LiBr (0.1%).



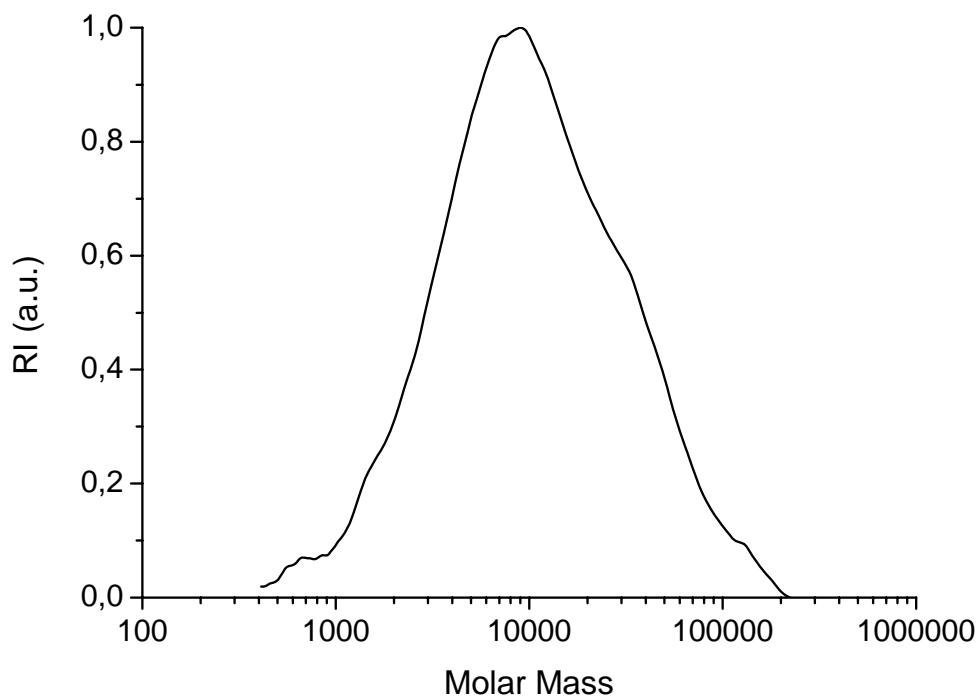
**Fig. S14.** SEC of  $P(3\text{-alt-}7)_{34}$  in DMF+LiBr (0.1%).



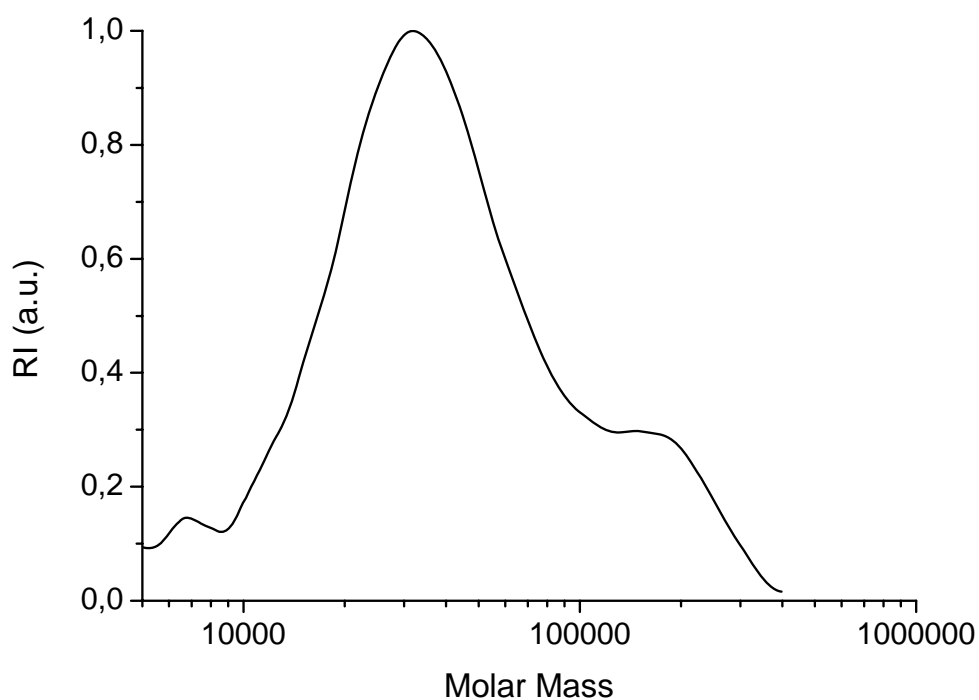
**Fig. S15.** SEC of  $P(3\text{-alt-}8)_{34}$  in DMF+LiBr (0.1%).



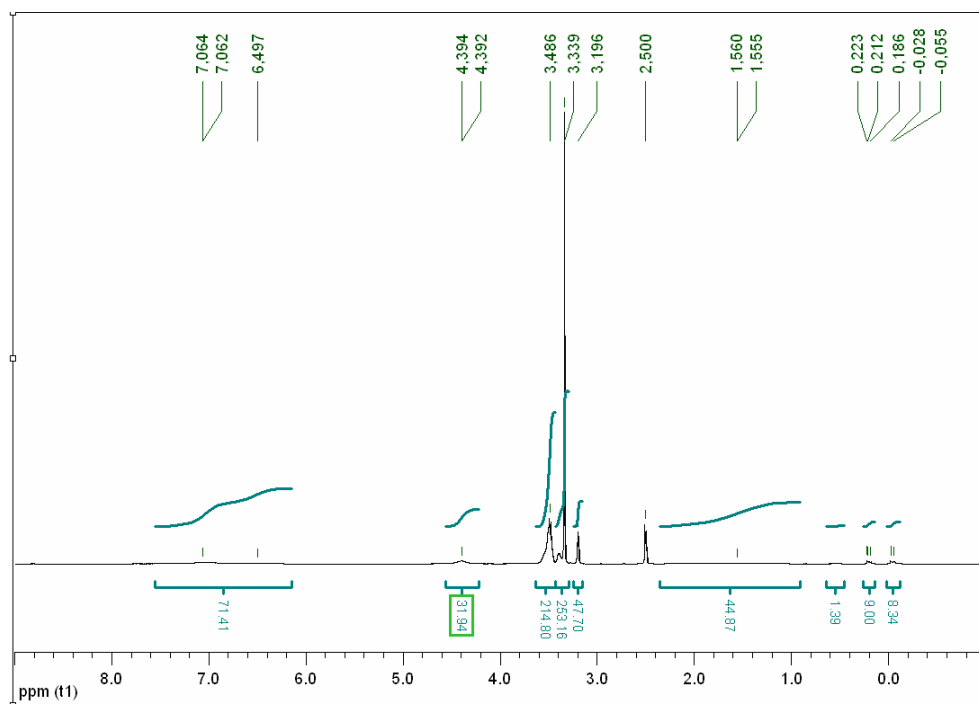
**Fig. S16.** SEC of **P(3-alt-9)<sub>23</sub>** in DMF+LiBr (0.1%).



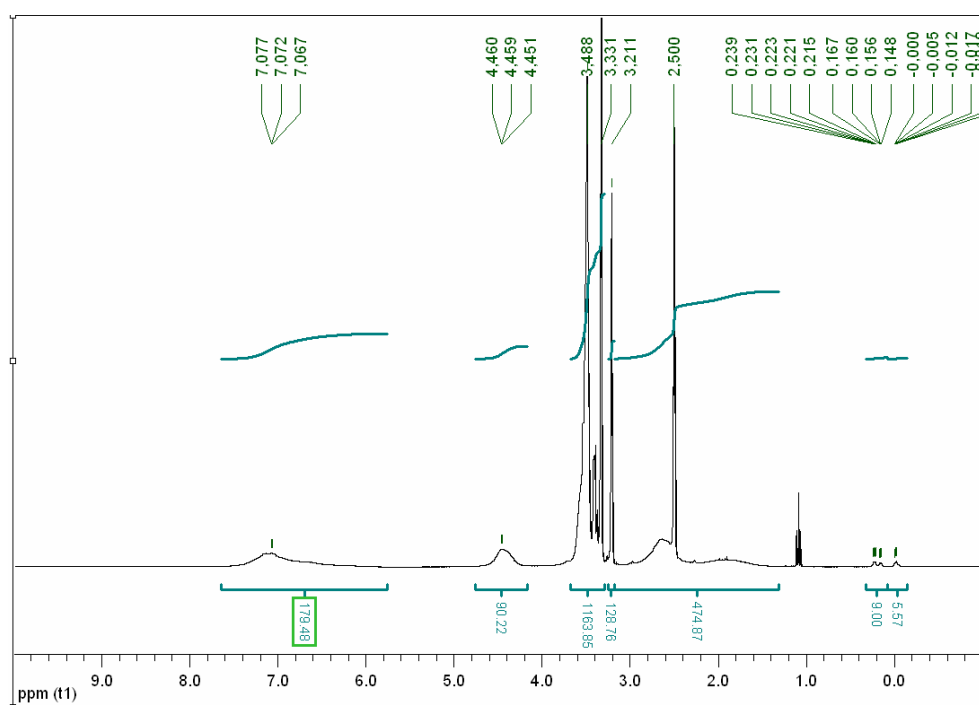
**Fig. S17.** SEC of **P(3-alt-10)<sub>9</sub>** in DMF+LiBr (0.1%).



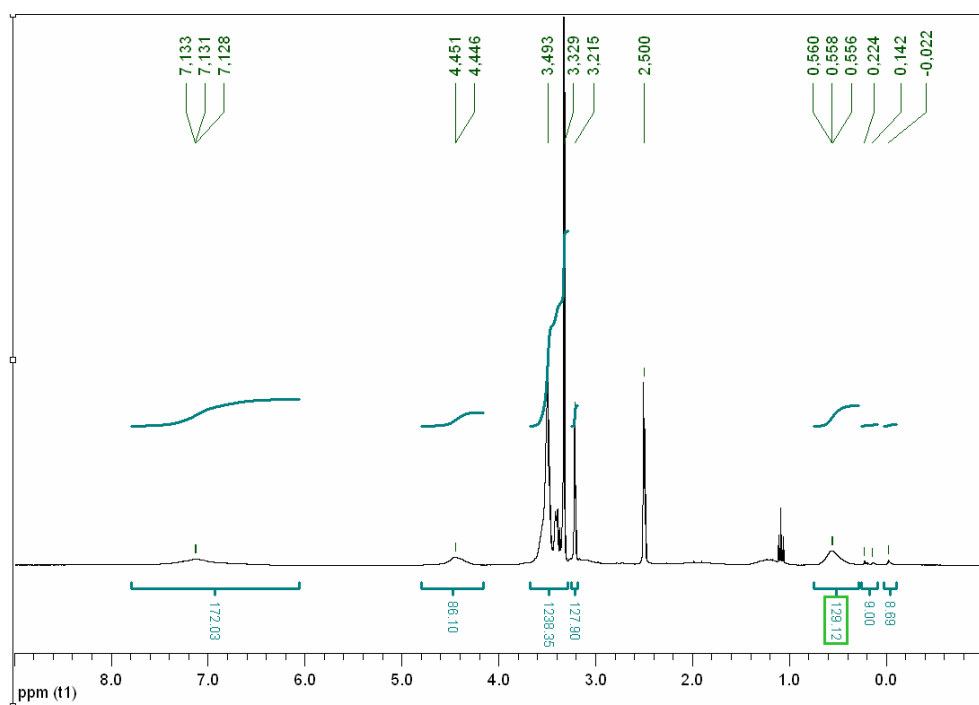
**Fig. S18.** SEC of **P(3-alt-11)<sub>24</sub>** in DMF+LiBr (0.1%).



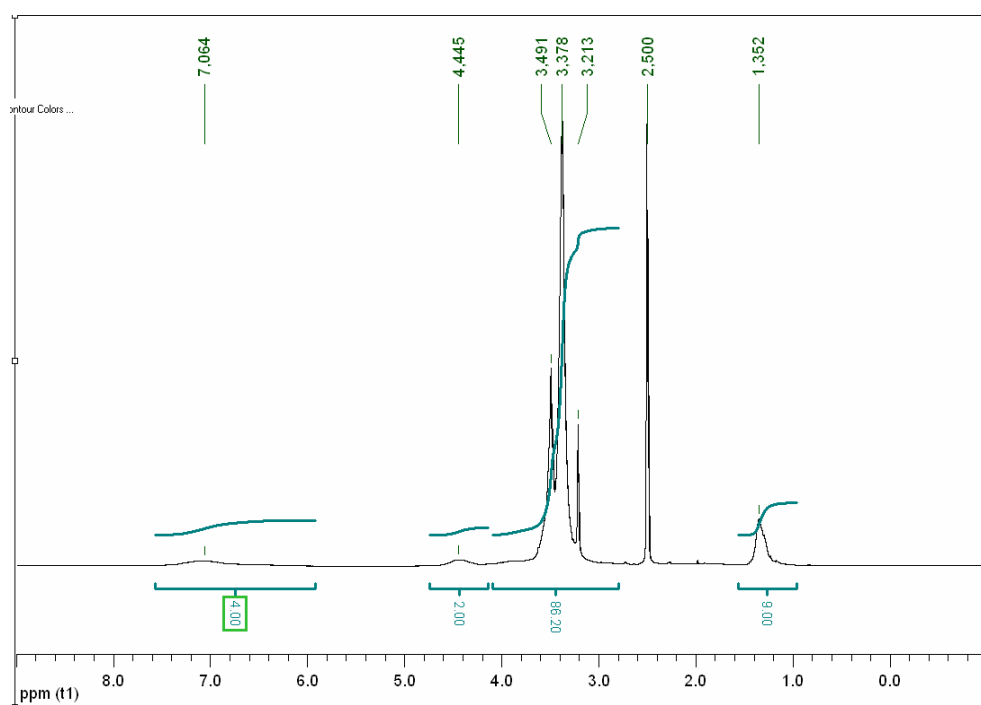
**Fig. S19.** <sup>1</sup>H NMR of polymer **P3<sub>16</sub>** in DMSO-d<sub>6</sub>.



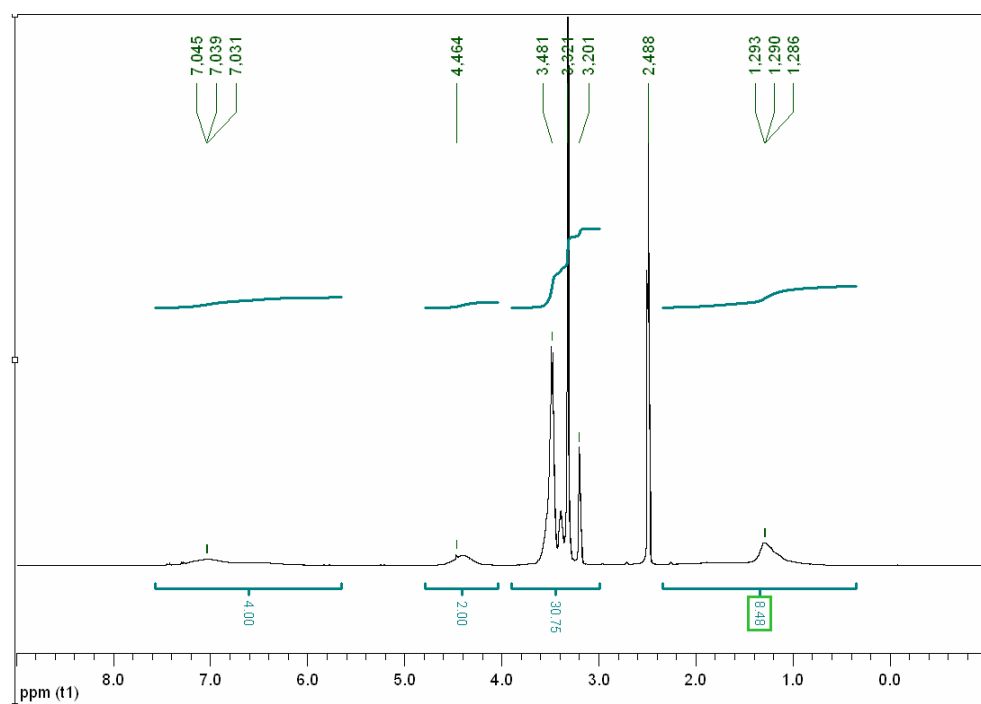
**Fig. S20.**  $^1\text{H}$  NMR of  $\text{P}(\mathbf{3}\text{-alt-}\mathbf{4})_{45}$  in  $\text{DMSO-d}_6$ .



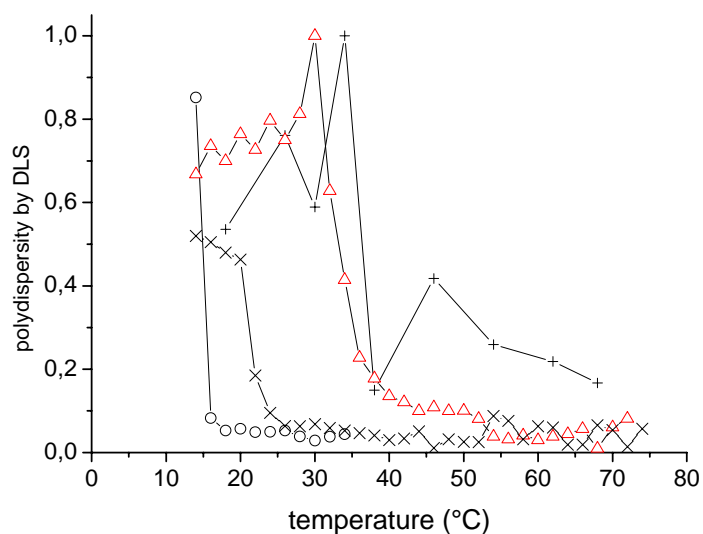
**Fig. S20.**  $^1\text{H}$  NMR of  $\text{P}(\mathbf{3}\text{-alt-}\mathbf{5})_{43}$  in  $\text{DMSO-d}_6$ .



**Fig. S20.**  $^1\text{H}$  NMR of  $\text{P}(\mathbf{3-alt-8})_{34}$  in  $\text{DMSO-d}_6$ .



**Fig. S21.**  $^1\text{H}$  NMR of  $\text{P}(\mathbf{3-alt-9})_{23}$  in  $\text{DMSO-d}_6$ .



**Figure S22.** Evolution of the polydispersity of the average hydrodynamic diameters of alternating copolymers in aqueous solutions ( $1.0 \text{ g}\cdot\text{L}^{-1}$ ), measured by DLS: **P(3-alt-4)<sub>45</sub>** (+), **P(3-alt-5)<sub>43</sub>** (O), **P(3-alt-8)<sub>34</sub>** (X), and **P(3-alt-9)<sub>23</sub>** ( $\Delta$ ). Lines are meant as guide to the eyes.

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