

# Supplementary Materials

## Controlled Synthesis of Linear Polyamidoamino Acids

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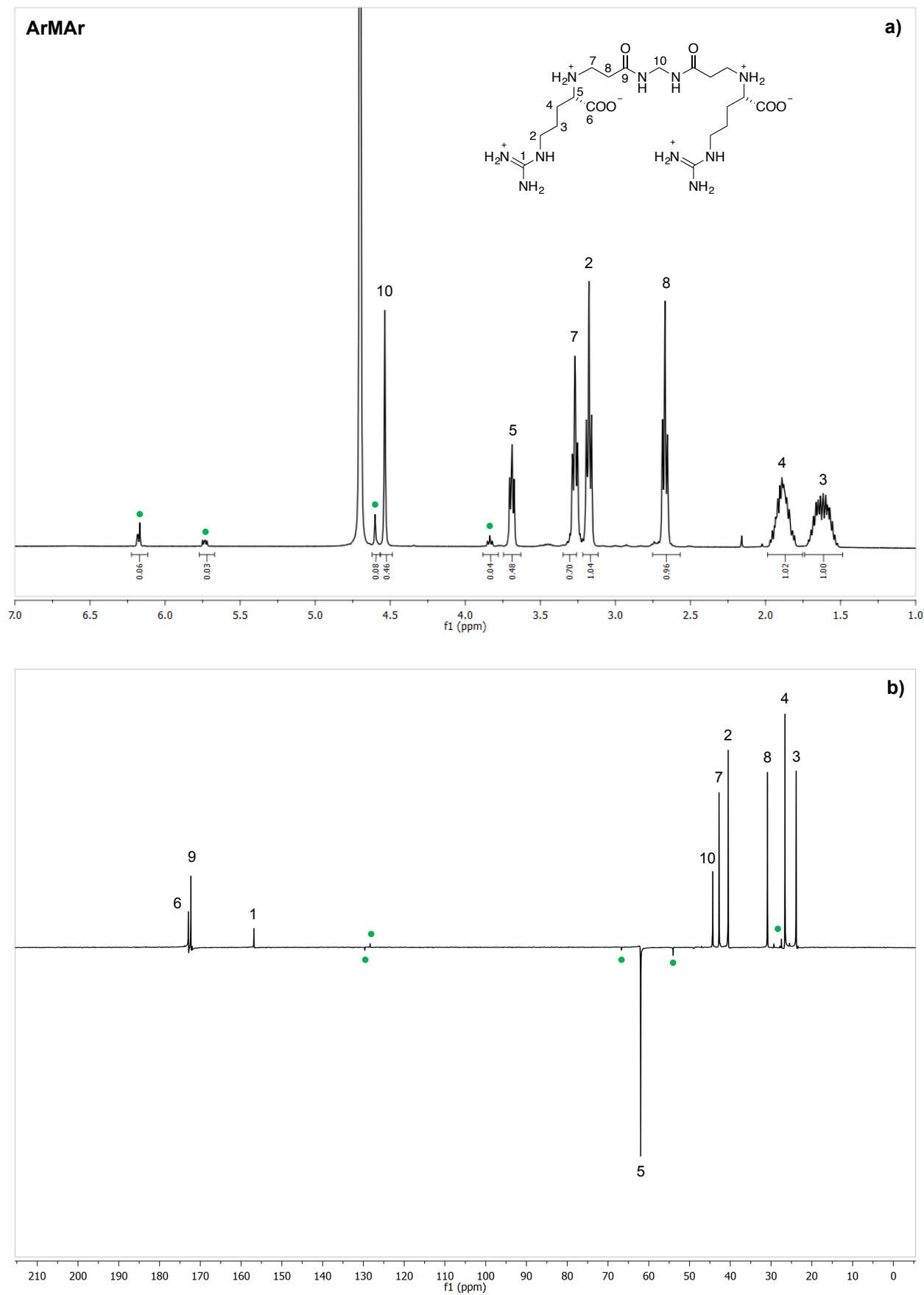
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**Figures S1-S10.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra.

**Figure S11.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra.

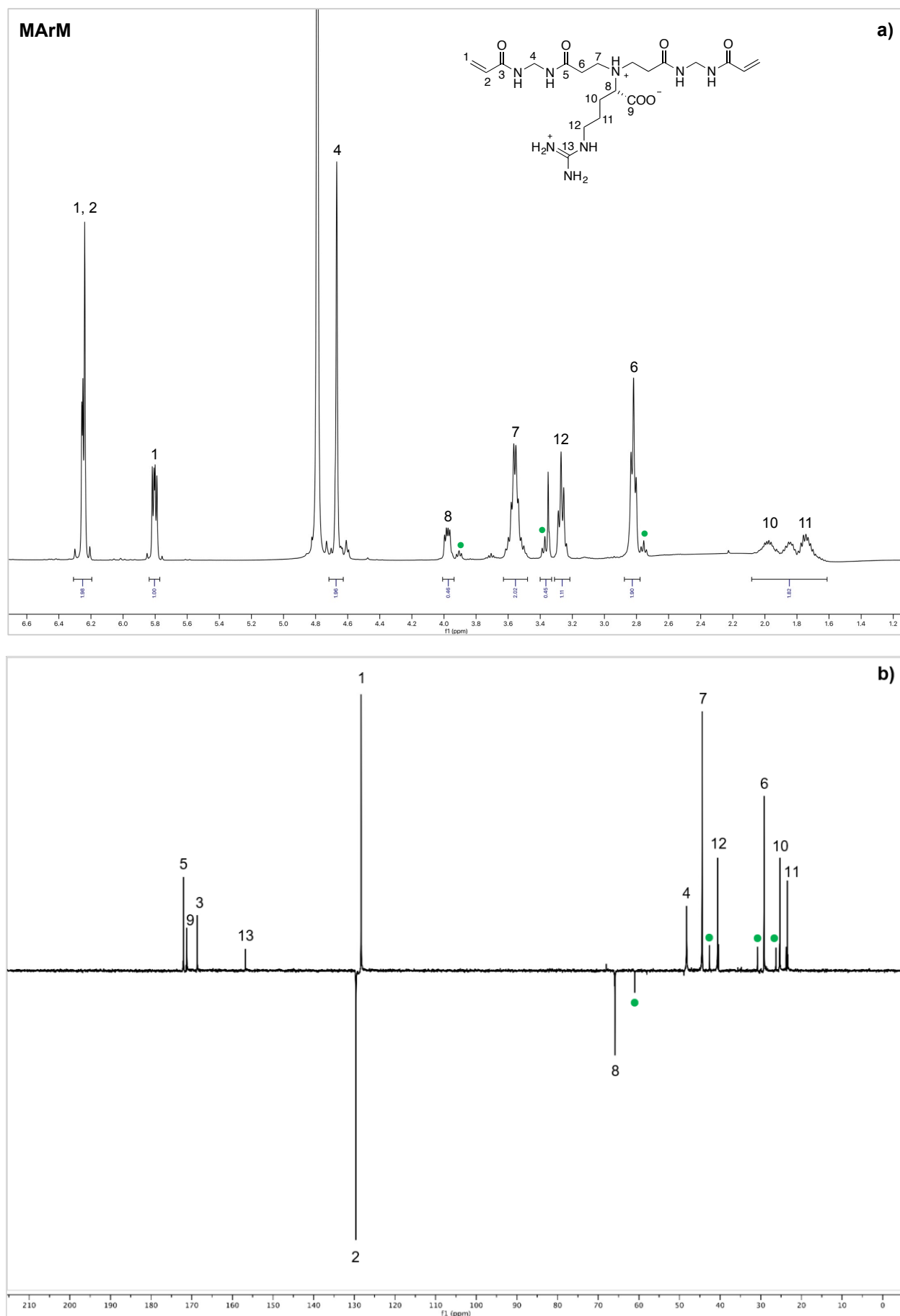
**Figures S12-S17.** ESI-MS spectra.

**Figures S18-S19.** SEC traces.



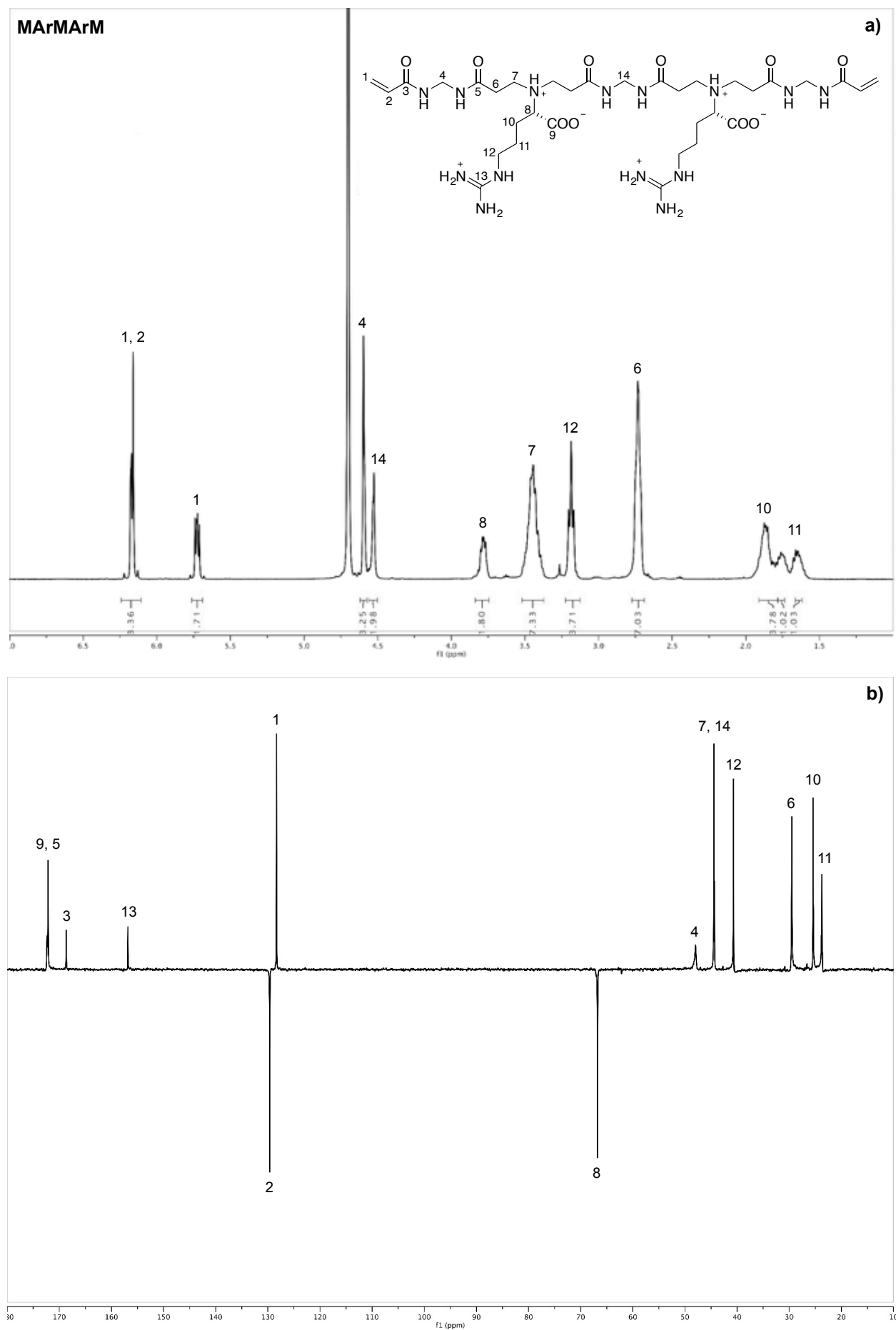
**Figure S1.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of ArMAr recorded in  $\text{D}_2\text{O}/\text{DCl}$  at  $\text{pH} = 4.5$ .

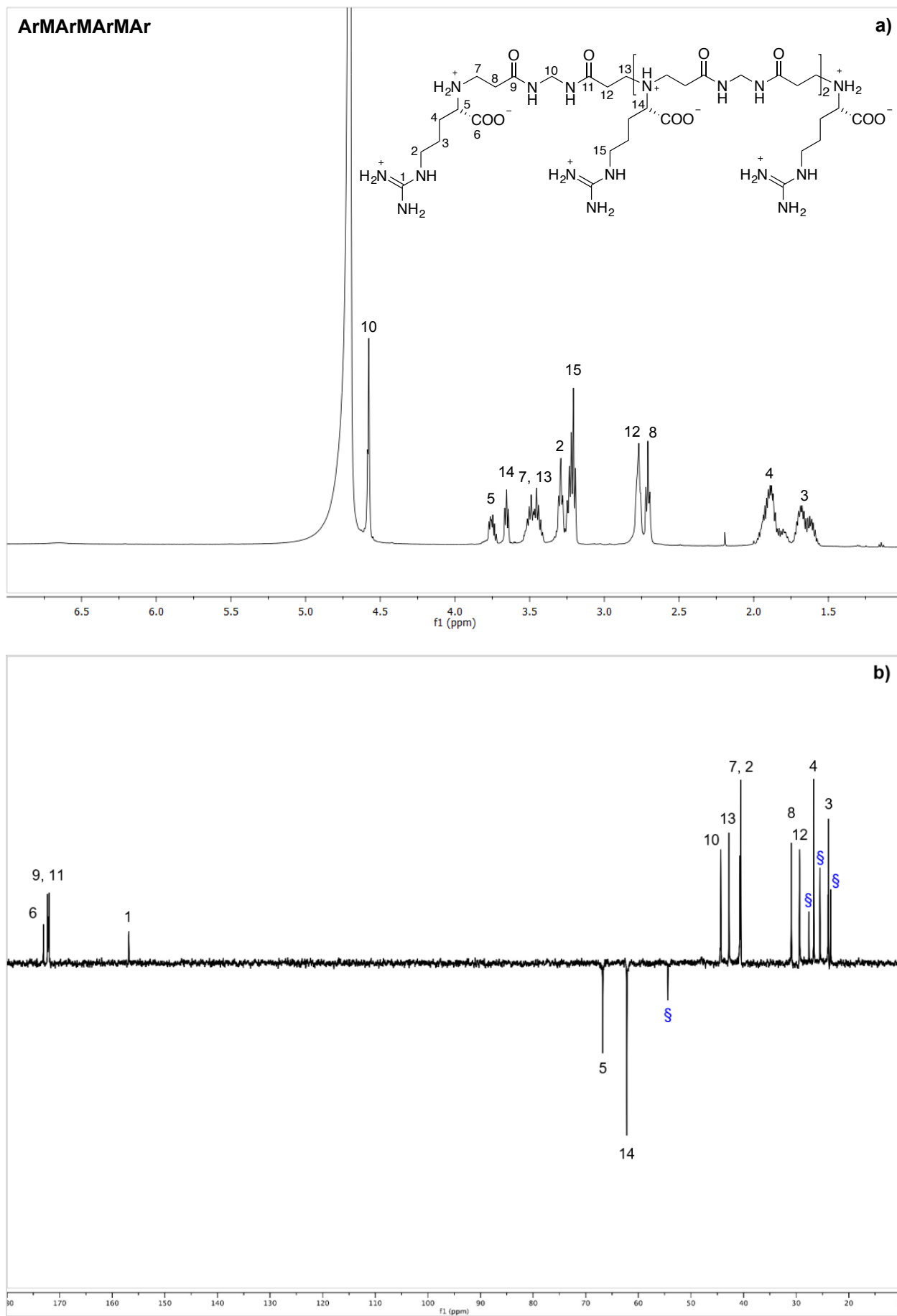
• ArM dimer impurity



**Figure S2.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of MArM recorded in  $\text{D}_2\text{O}/\text{DCl}$  at pH = 4.5.

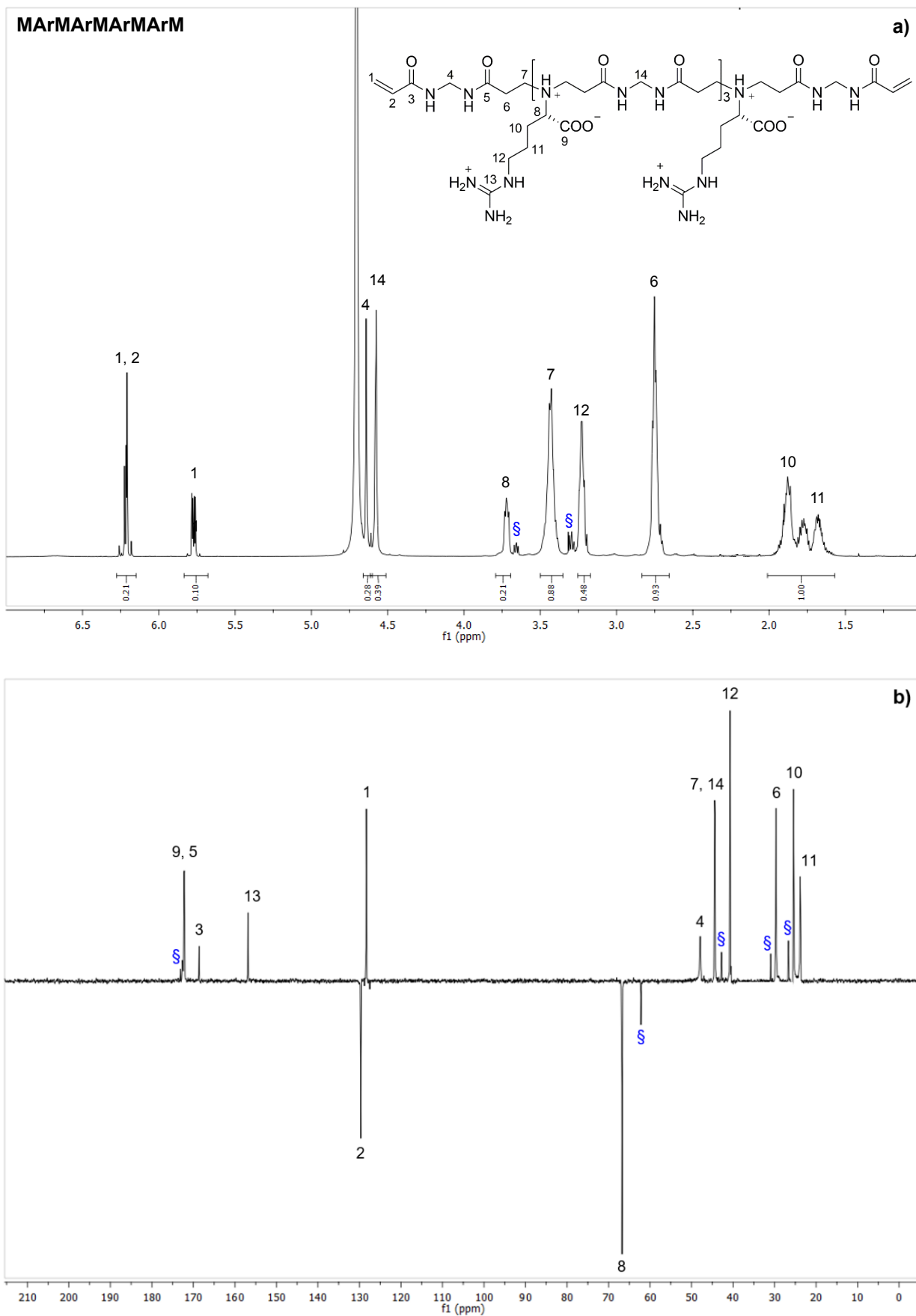
• MArMArM pentamer impurity





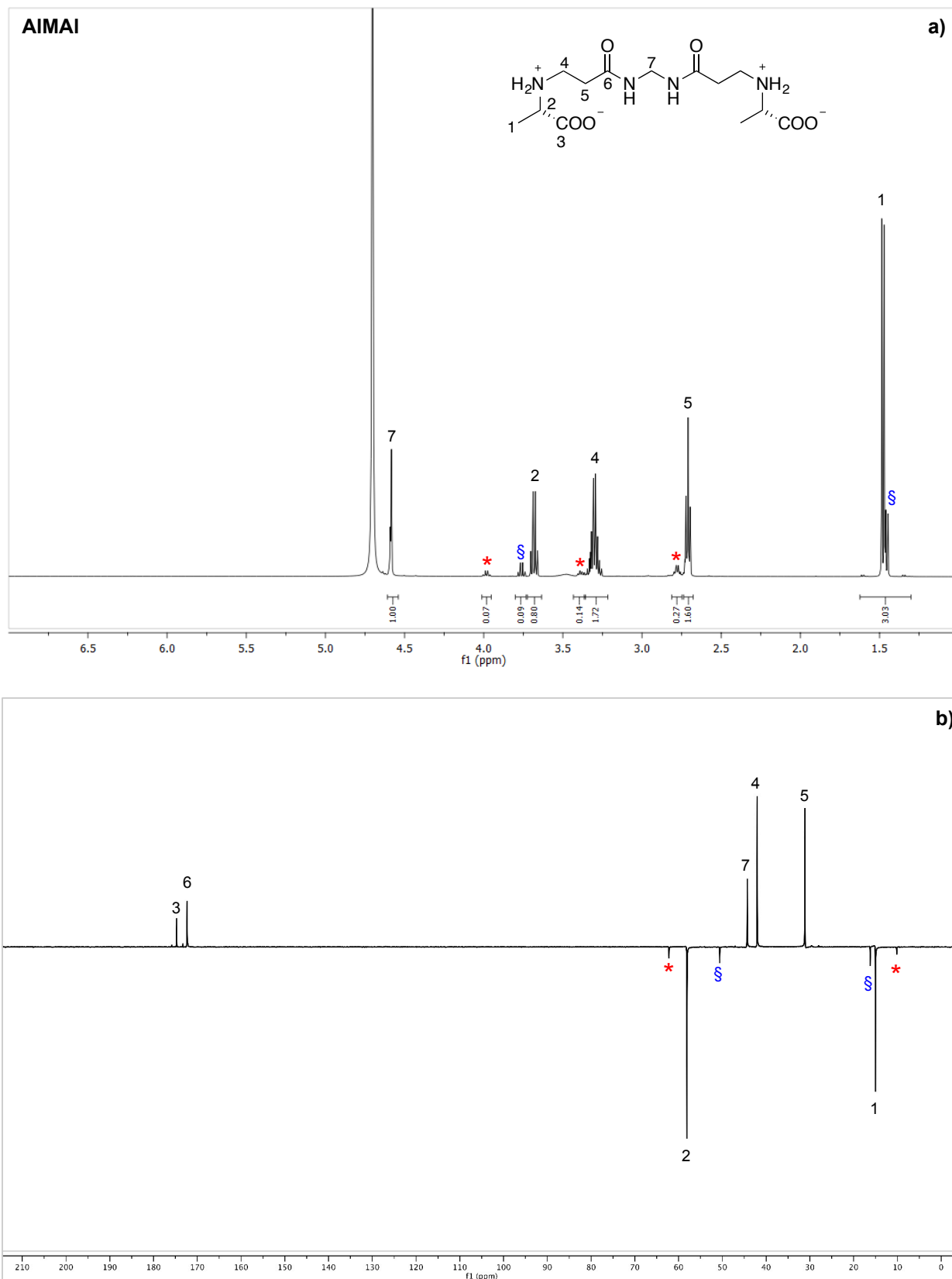
**Figure S4.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of ArMArMArMAr recorded in  $\text{D}_2\text{O}/\text{DCl}$  at pH = 4.5.

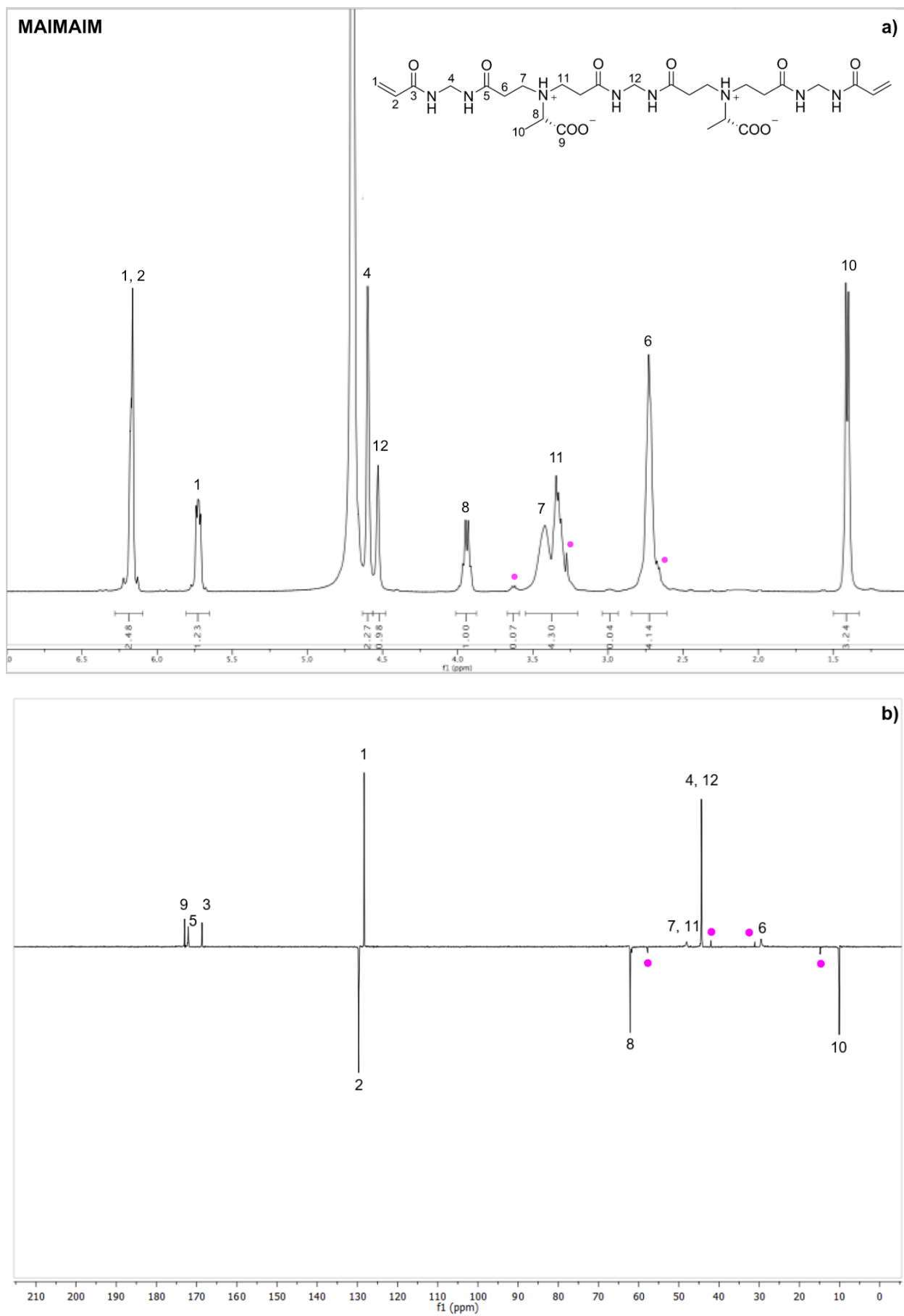
§ *L*-Arginine impurity



**Figure S5.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of MArMArMArMArM recorded in  $\text{D}_2\text{O}/\text{DCl}$  at  $\text{pH} = 4.5$ .

$\text{S}$  *L*-Arginine impurity

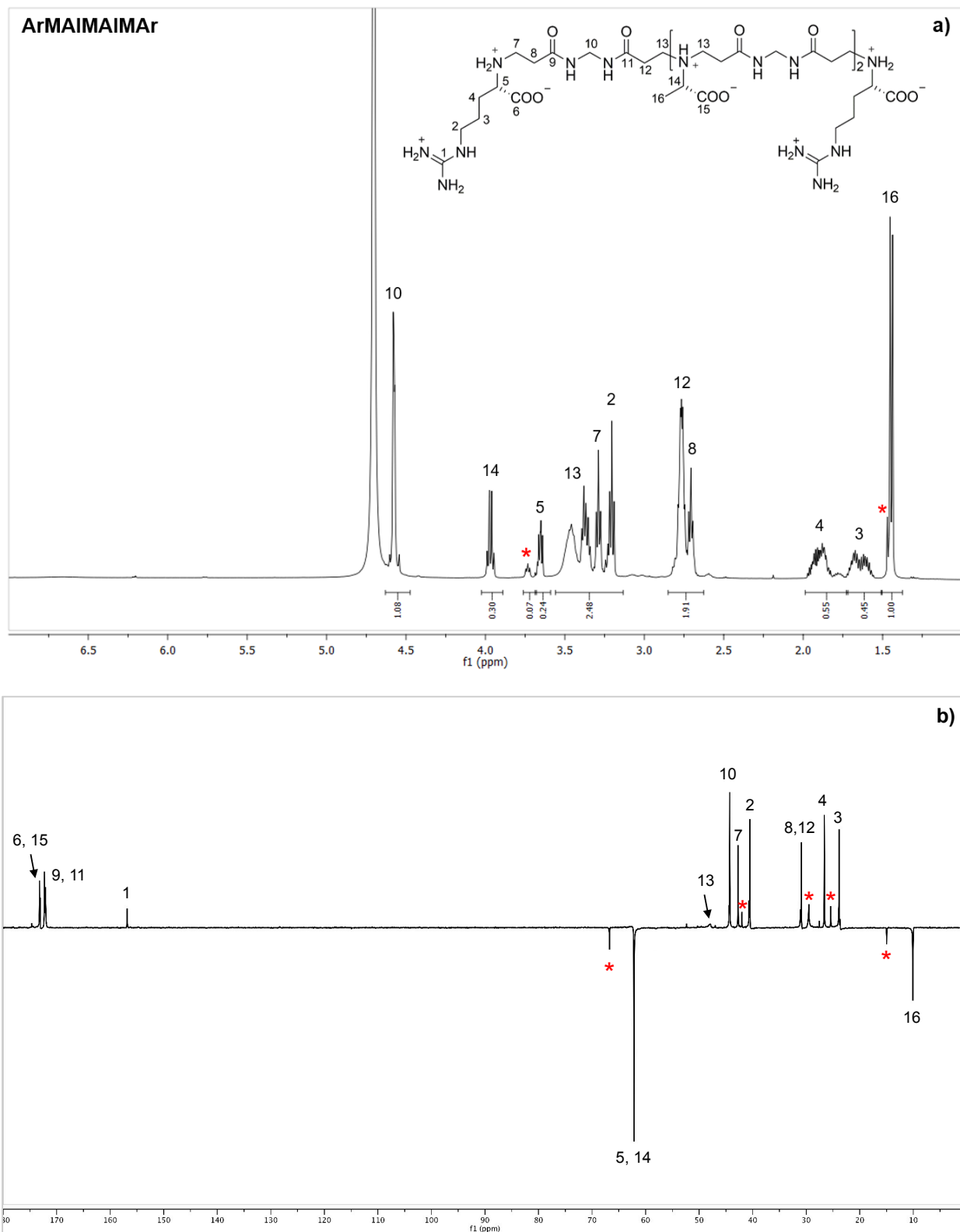




**Figure S7.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of MAIMAIM recorded in  $\text{D}_2\text{O}/\text{DCl}$  at  $\text{pH} = 4.5$ .

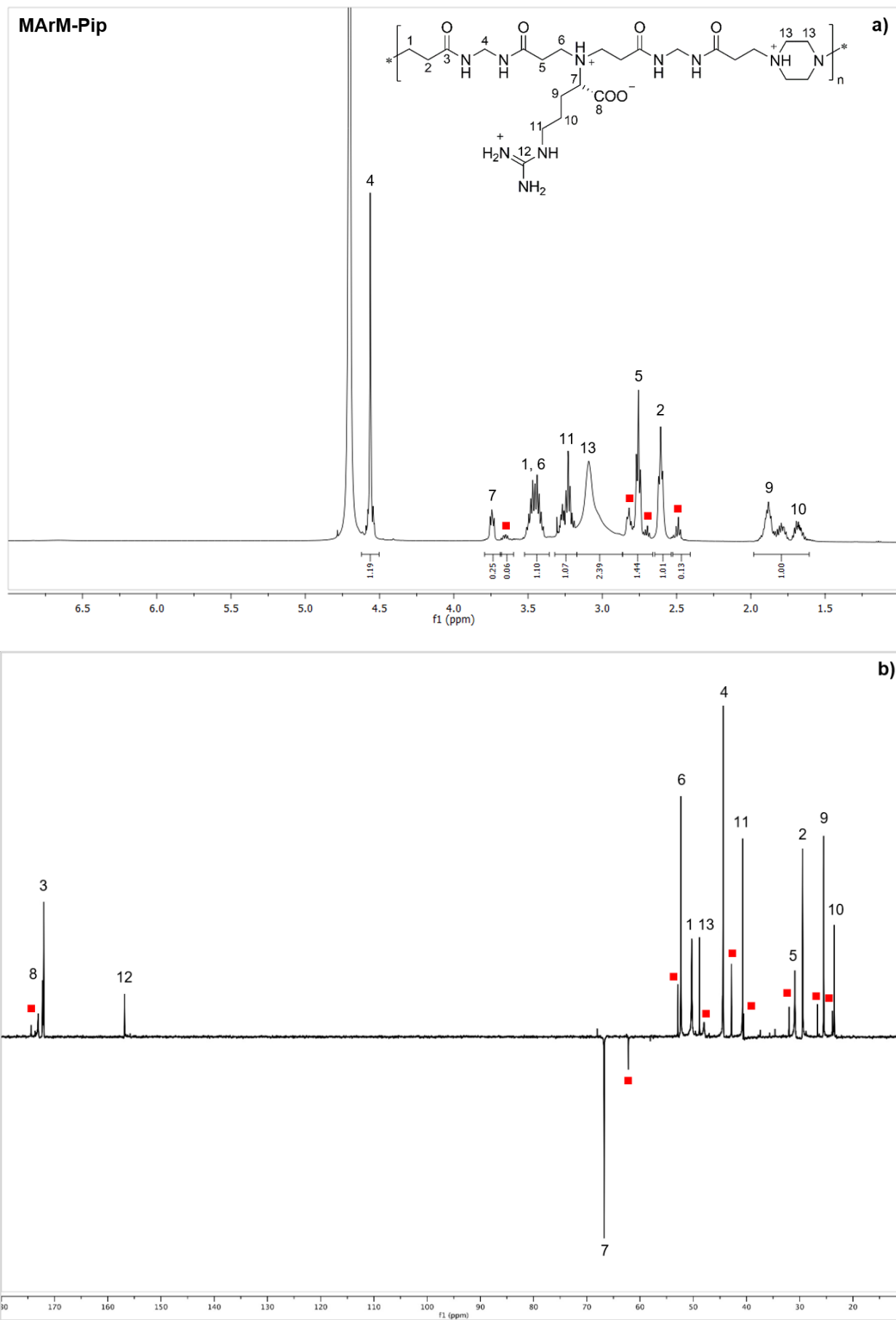
• Other oligomers of the homologous series

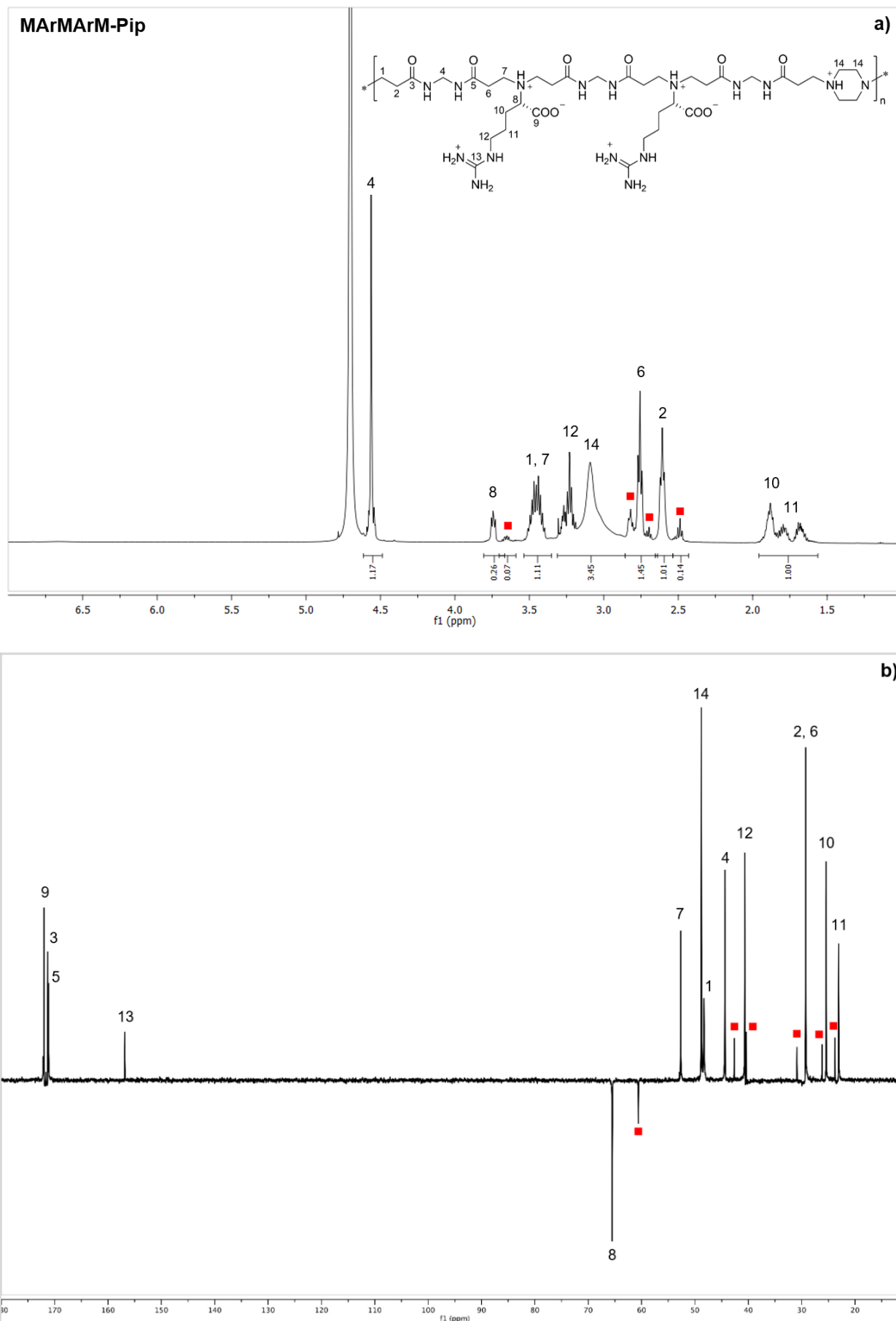




**Figure S8.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of ArMAIMAIMAr recorded in  $\text{D}_2\text{O}/\text{DCl}$  at  $\text{pH} = 4.5$ .

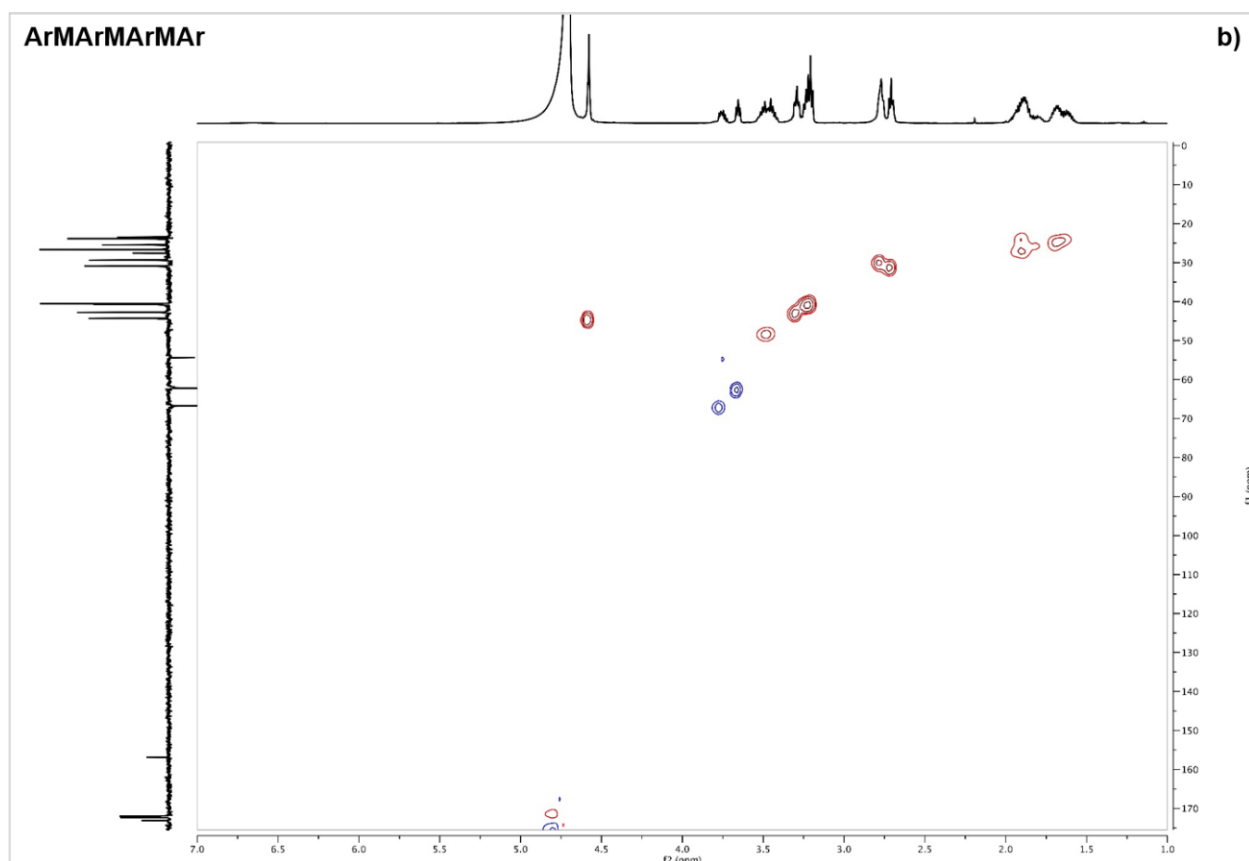
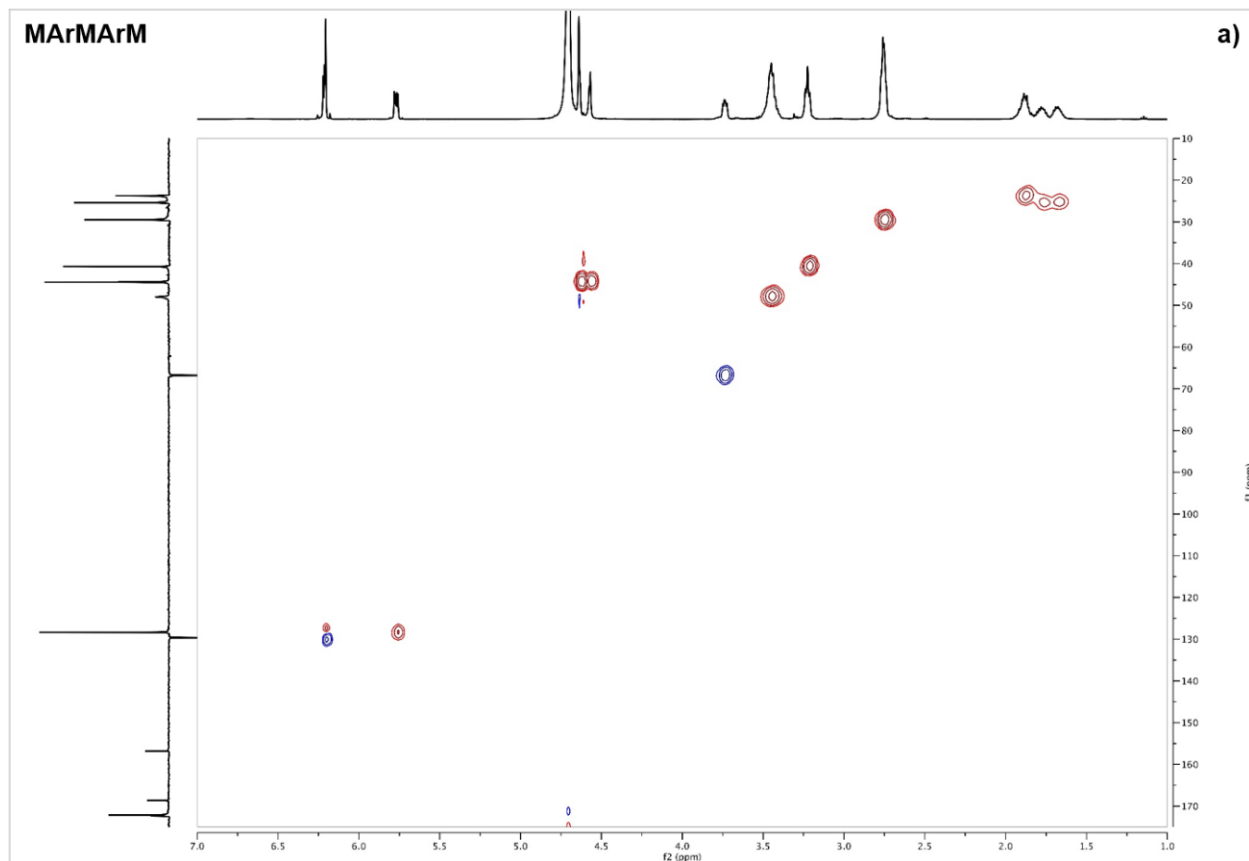
\* Differently protonated species or other oligomers of the homologous series.

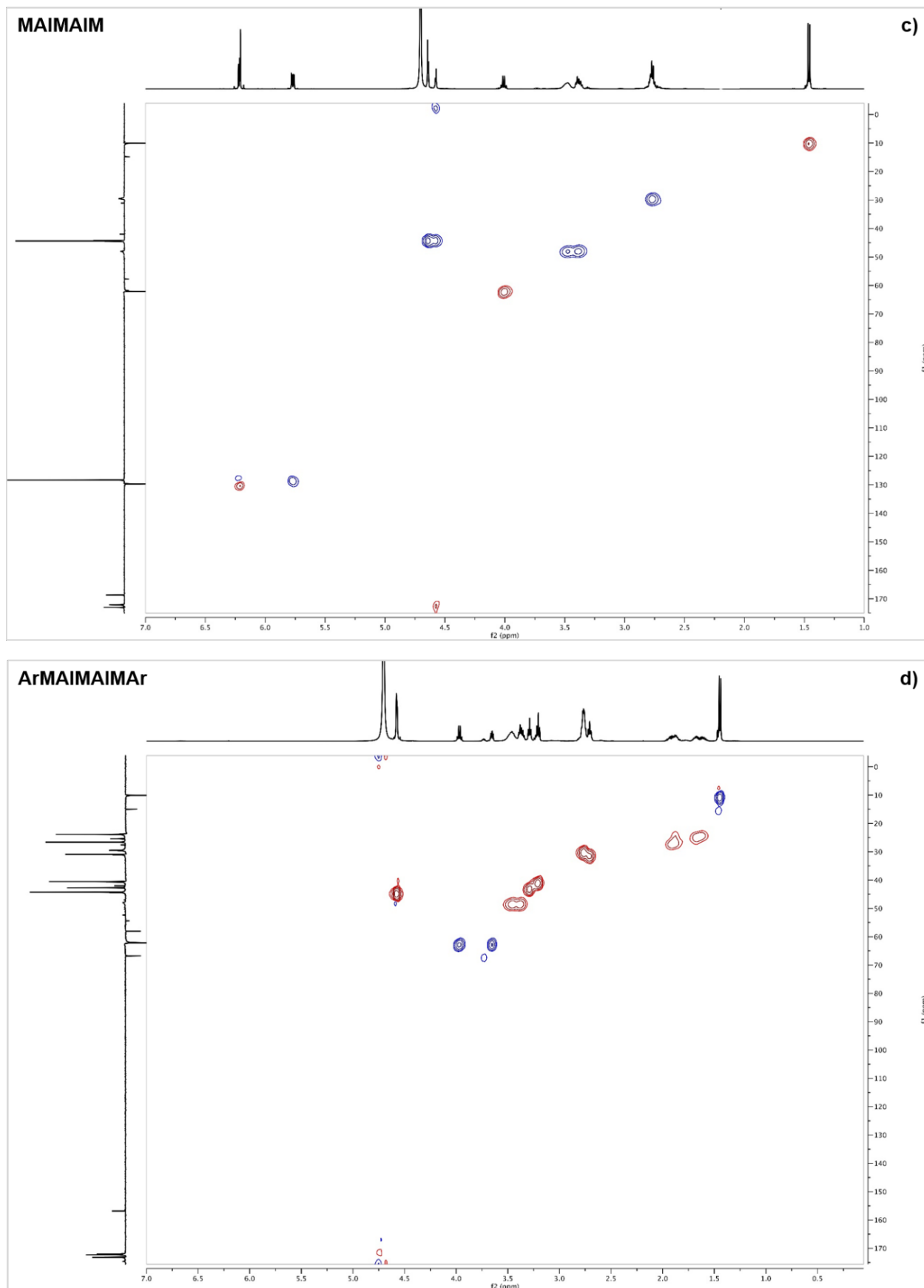




**Figure S10.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  APT NMR (b) spectra of  $[\text{MArMArM-Pip}]_n$  recorded in  $\text{D}_2\text{O}/\text{DCl}$  at pH = 4.5.

■ Copolymer terminals





**Figure S11.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of MArMArM (a); ArMArMArAr (b); MAIMAIM (c); ArMAIMAIMAr (d) recorded in  $\text{D}_2\text{O}/\text{DCl}$  at pH = 4.5.

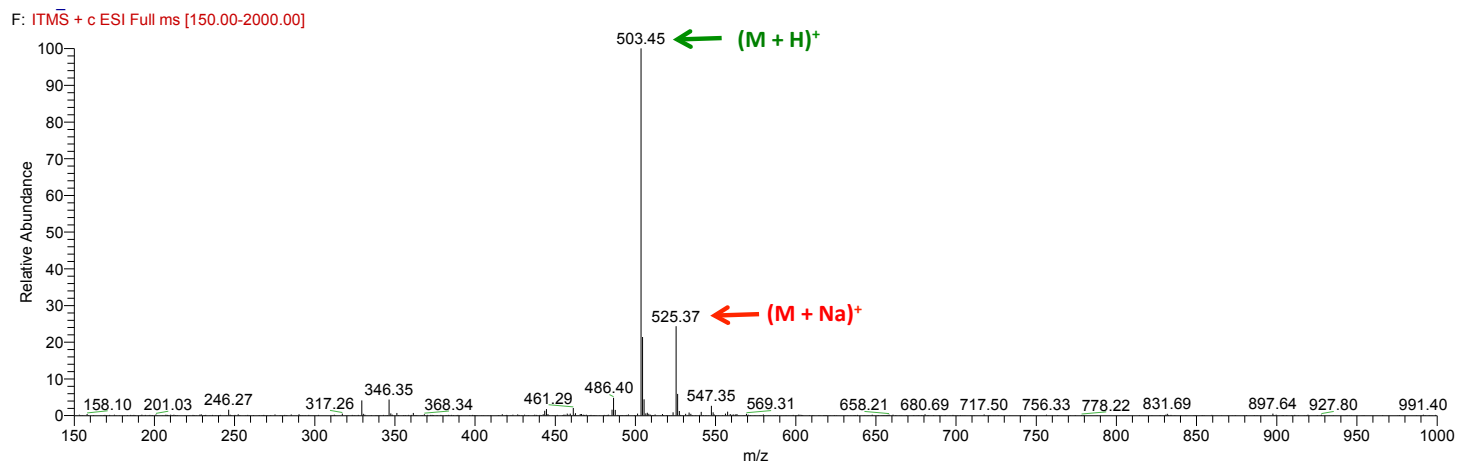


Figure S12. Positive ionization mode ESI-MS spectrum of ArMAr.

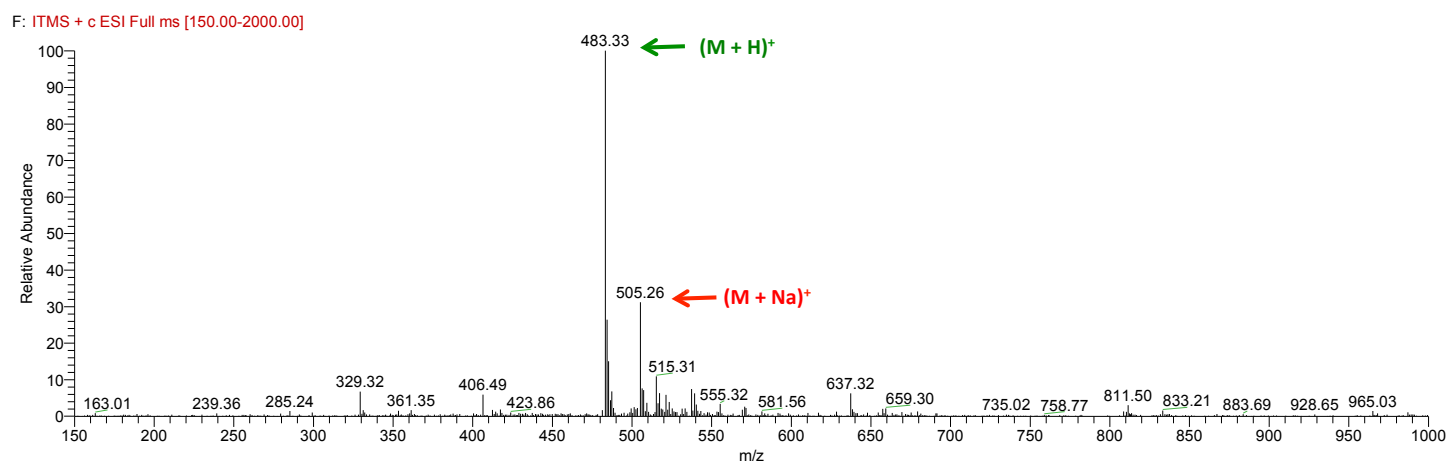


Figure S13. Positive ionization mode ESI-MS spectrum of MArM.

F: ITMS + c ESI Full ms [150.00-2000.00]

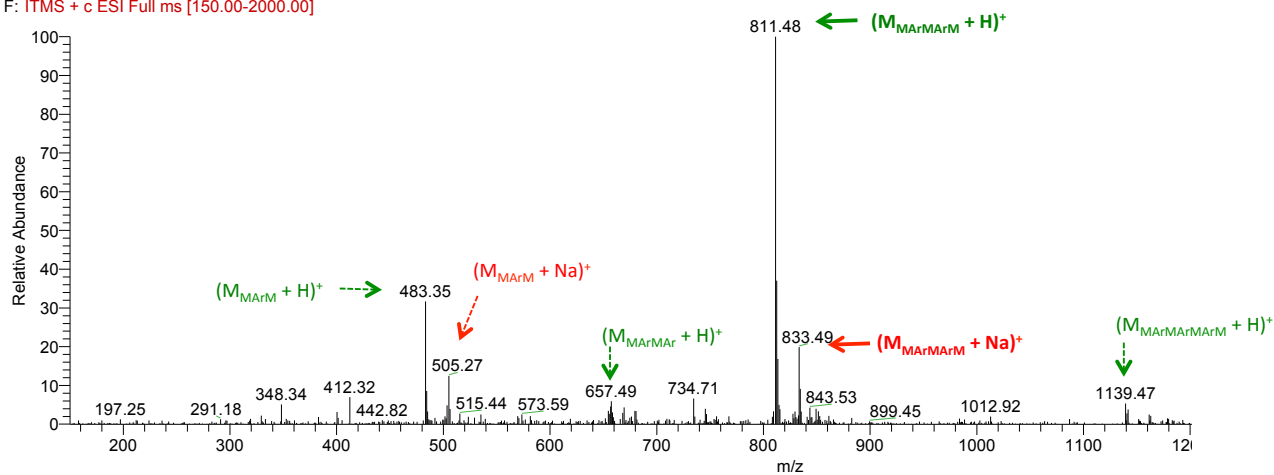


Figure S14. Positive ionization mode ESI-MS spectrum of MARMAR.

F: ITMS - c ESI Full ms [150.00-2000.00]

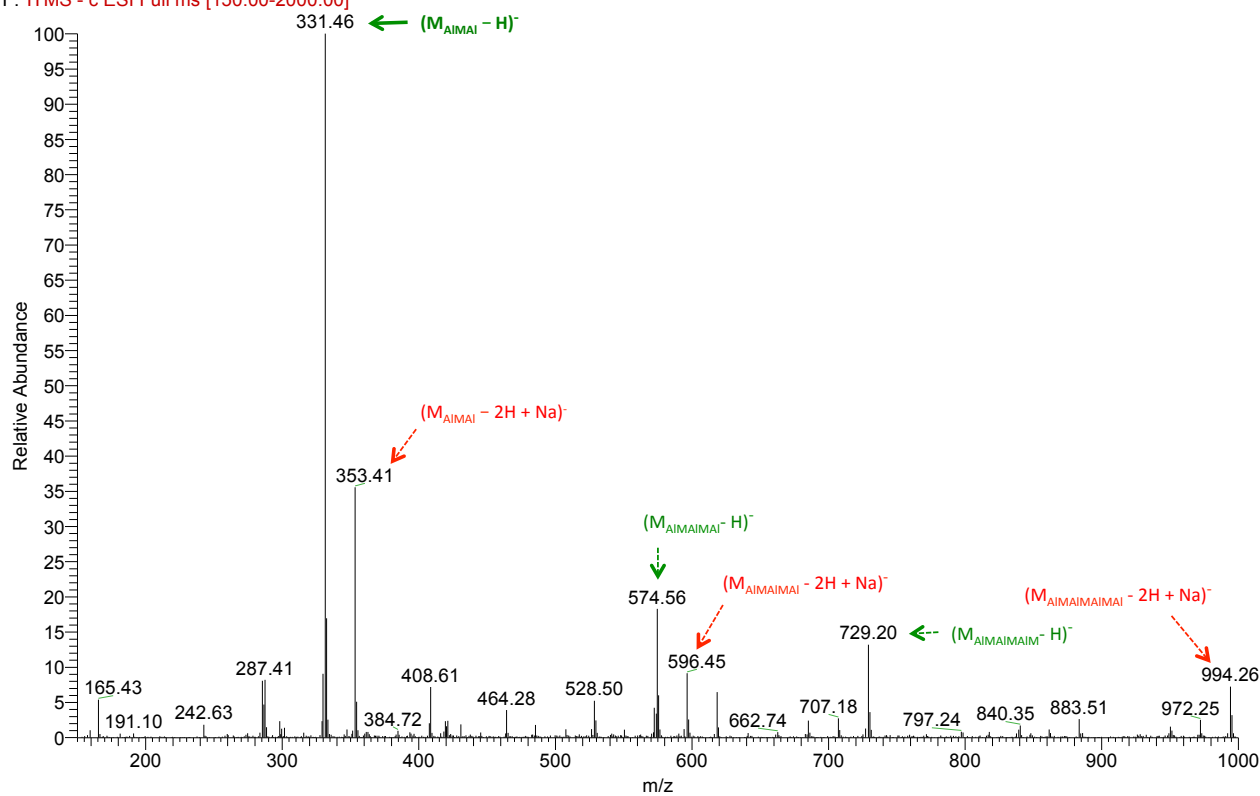


Figure S15. Negative ionization mode ESI-MS spectrum of AIMAI.

F: ITMS - c ESI Full ms [150.00-2000.00]

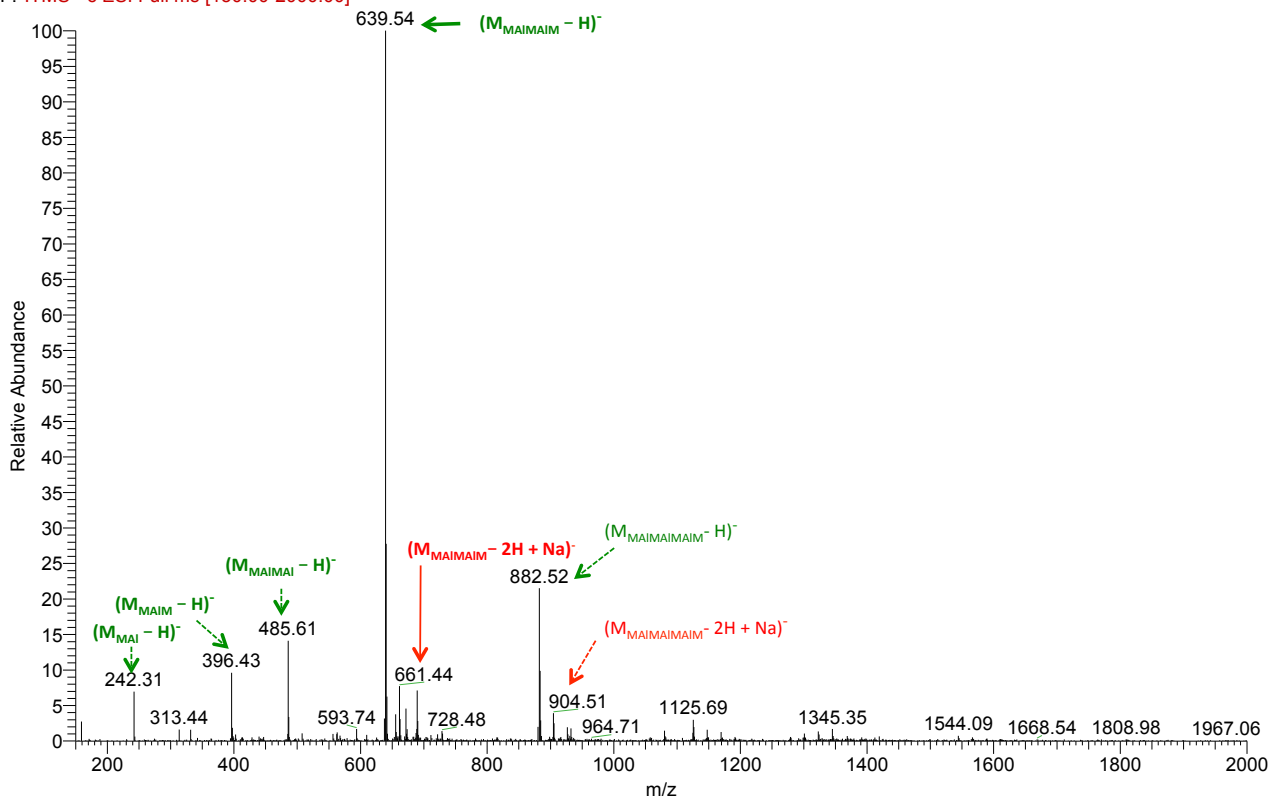


Figure S16. Negative ionization mode ESI-MS spectrum of MAIMAIM.

F: ITMS - c ESI Full ms [150.00-2000.00]

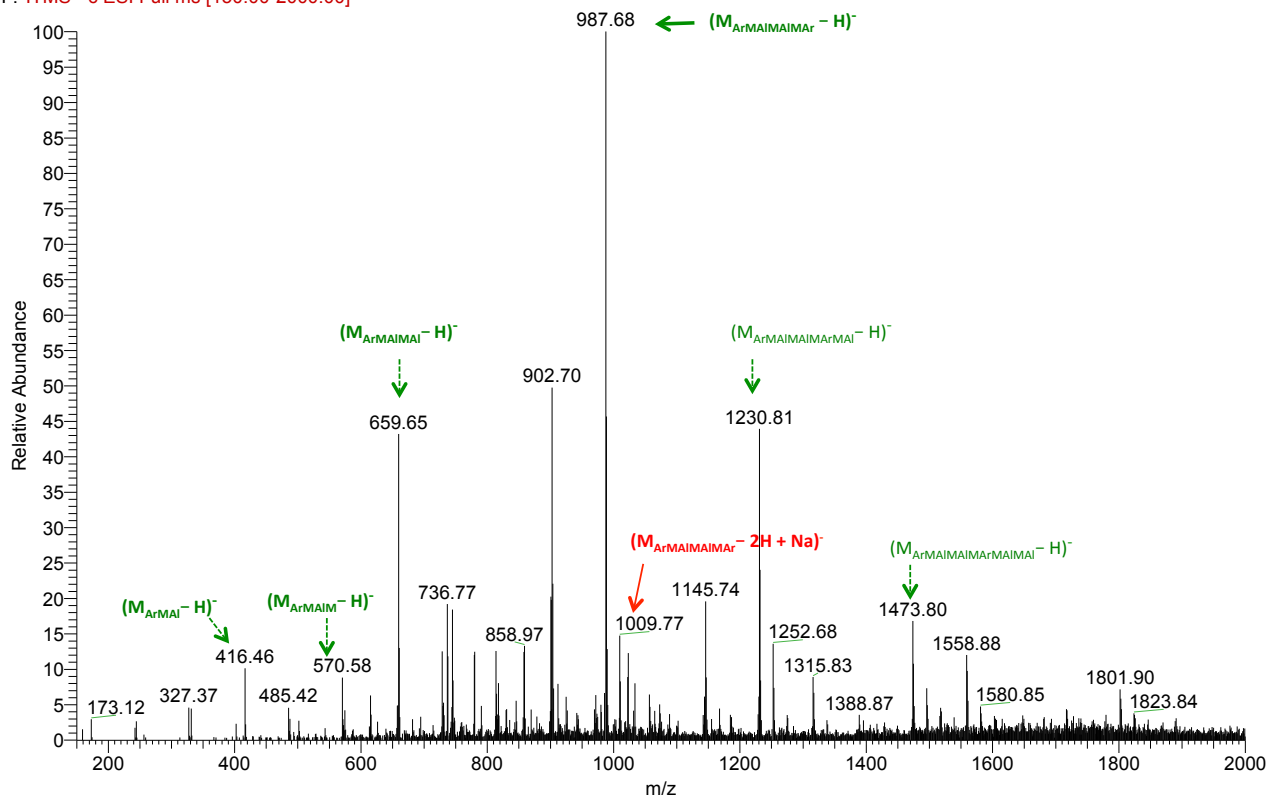
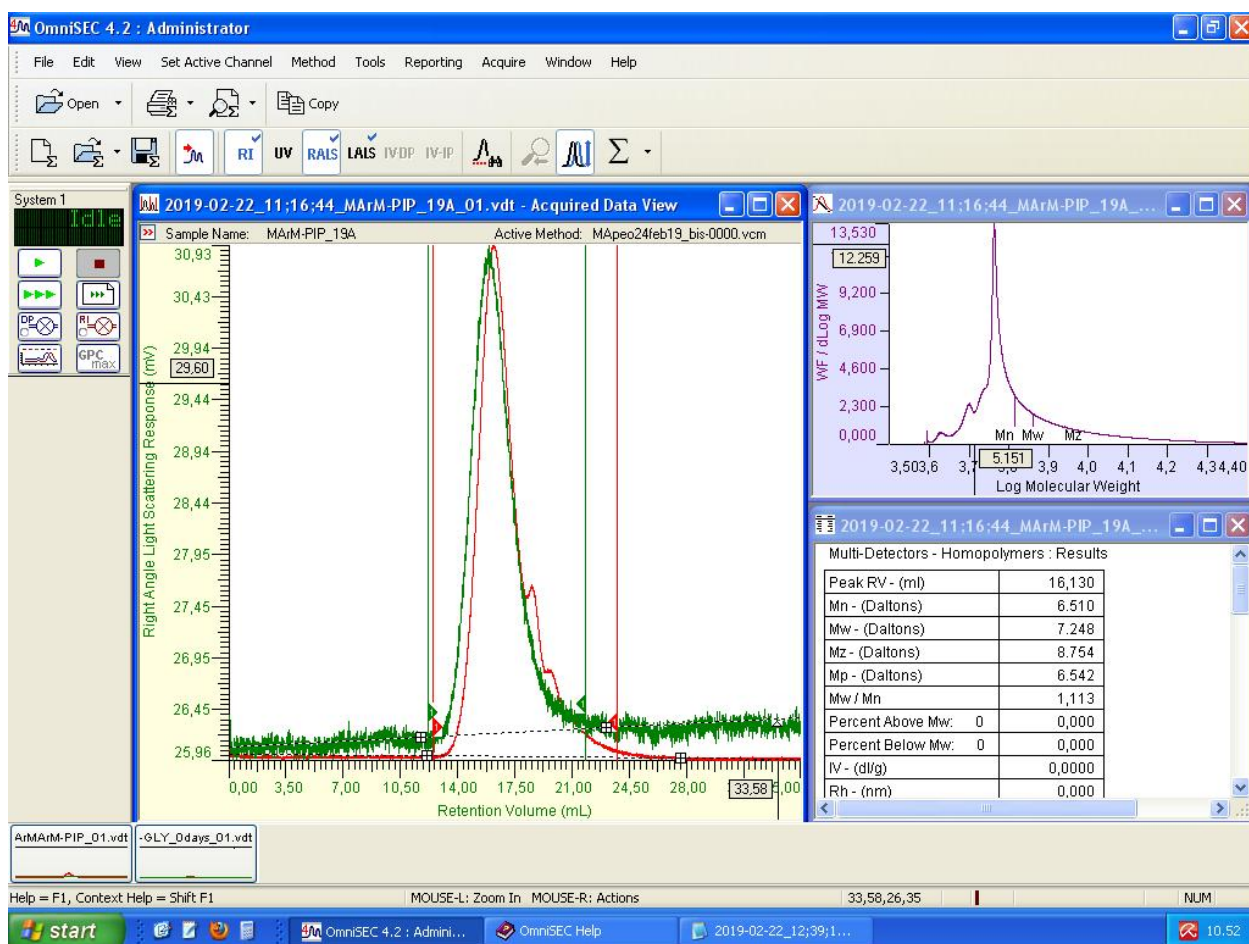
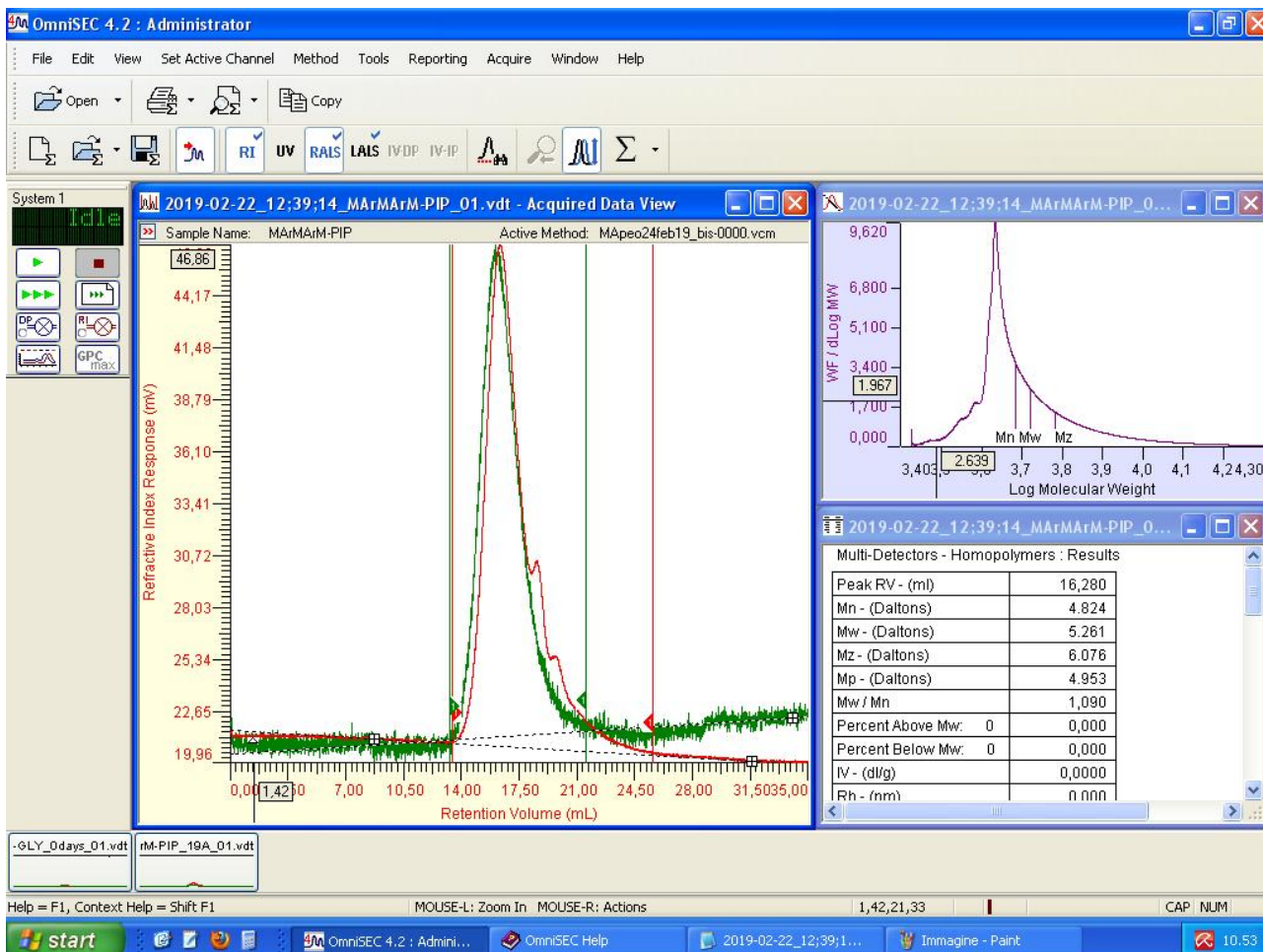


Figure S17. Negative ionization mode ESI-MS spectrum of ArMAIMAIMAr.





**Figure S18.** Snapshot of the OmniSEC 4.2 software output showing the results of SEC analysis of the  $[\text{MArM-Pip}]_n$  copolymer carried out at  $\text{pH } 8.00 \pm 0.05$  0.1 M Tris buffer solution with 0.2 M sodium chloride. The operational conditions were: sample concentration  $20 \text{ mg mL}^{-1}$ ; flow rate  $1 \text{ mL min}^{-1}$ ; injection volume  $20 \mu\text{L}$ ; column dimensions  $300 \times 7.5 \text{ mm}^2$ , temperature  $25 \text{ }^\circ\text{C}$ .  
Green line: light scattering trace, red line: refractive index trace.



**Figure S19.** Snapshot of the OmniSEC 4.2 software output showing the results of SEC analysis of the  $[\text{MArMArM-Pip}]_n$  copolymer carried out at  $\text{pH } 8.00 \pm 0.05$  0.1 M Tris buffer solution with 0.2 M sodium chloride. The operational conditions were: sample concentration  $20 \text{ mg mL}^{-1}$ ; flow rate  $1 \text{ mL min}^{-1}$ ; injection volume  $20 \text{ }\mu\text{L}$ ; column dimensions  $300 \times 7.5 \text{ mm}^2$ , temperature  $25 \text{ }^\circ\text{C}$ .  
Green line: light scattering trace, red line: refractive index trace.