

Supplementary information

The use of silanols as initiators for the ROP of hexamethylcyclotrisiloxane in ammonia – from linear functional polymers to silicones of complex structure

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Experimental

Toluene was dried and distilled over CaH₂ as described earlier.¹

Anhydrous ammonia was purchased from Spectra Gases Inc.

2,2,4,4,6,6-Hexamethylcyclotrisiloxane (D₃), Chlorodimethylvinylsilane, Triphenylsilanol (Ph₃SiOH), Diphenylsilanediol (Ph₂Si(OH)₂) were purchased from abcr GmbH.

Pyridine was purchased from Acros Organics.

Phenylsilanetriol (PhSi(OH)₃), *cis*-Tetra[(phenyl)(hydroxy)]cyclotetrasiloxane (*cis*-[PhSi(O)OH]₄) were synthesized according to the reported procedure.^{2,3}

The NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (at 300 and 59.6 MHz for ¹H and ²⁹Si respectively), the internal standard was tetramethylsilane, and the solvents were C₃D₆O and CDCl₃.

SEC analysis was performed on a Shimadzu chromatograph using a RID - 20A refractometer as the detector, a PSS SDV analytical 10³ Å column (Size 300 x 8 mm), and toluene as the eluent.

MALDI mass spectra were recorded on the Axima Confidence time-of-flight spectrometer (Shimadzu Biotech) with nitrogen laser ($\lambda = 337$ nm).

Dithranol was used as a matrix for all experiments. Addition of AgTFA salt used as electrolyte. The target was prepared as follows. Polymers were dissolved in THF to give a concentration 7 mg/ml. 20 µl of the obtained solutions were mixed with 20 µl of the 25 mg/ml matrix solution in THF and 10 µl of the 1 mg/ml AgTFA solution in THF. Resulting mixtures were deposited on a stainless-steel target and dried in air. The mass spectra were obtained in the reflectron mode with 5 laser shots per scan.

General procedure for polymerization of hexamethylcyclotrisiloxane (D_3) in ammonia

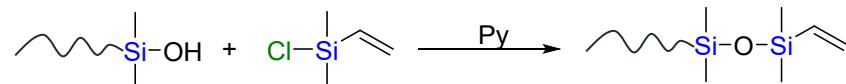
Required amount of D_3 and initiator were loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with required amount of NH_3 under chill-down using an INFLOW mass flow meter (Bronkhorst, Netherlands). Next, the autoclave was thermostated at 30 °C. After that, if necessary, the temperature was increased. After the end of the reaction, decompression was performed at room temperature and the target polymers were isolated. Reagents loadings are presented in the table S1.

Table S1.

Experiment	Initiator	Reagents loadings					Reaction conditions		Conversion of D_3 , %			
		D_3 , g	D_3 , mmol	Silanol, g	Silanol, mmol	NH_3 , g	Time, h	Temperature, °C				
1	Ph_3SiOH	1	4.5	0.031	0.11	5	4	30	21			
2				0.047	0.17		8		27			
3				0.091	0.33		24		51			
4				0.276	0.99	5			79			
5				0.031	0.11				93			
6									98			
7									60			
8	$Ph_2Si(OH)_2$	1	4.5			5	4	30	29			
9				0.024	0.11		8		62			
10							24		68			

Experiment	Initiator	Reagents loadings					Reaction conditions		Conversion of D ₃ , %
		D ₃ , g	D ₃ , mmol	Silanol, g	Silanol, mmol	NH ₃ , g	Time, h	Temperature, °C	
11	PhSi(OH) ₃	1	4.5	0.017	0.11	5	4	30	42
12							8		60
13							24		88
14				0.172	1.1	5	24	30	100
15	<i>cis</i> -[PhSi(O)OH] ₄	1	4.5	0.031	0.06	5	24	30	81
16				0.062	0.11				97
17				0.124	0.22				100

General procedure for end-capping of the terminal silanol groups of the polymers



After decompression, the reaction mixture was dissolved in dry toluene and dripped to a solution of required amount vinyldimethylchlorosilane with pyridine in dry toluene (table S2). The loading of chlorosilane was calculated based on the fact that for one mole of polymer (molar mass was calculated by SEC) containing one, two, three and four hydroxy groups for polymers 3-6, 10, 13 and 16 respectively. For the reaction, chlorosilane was taken in a twofold excess. The end-capping reaction was carried out for 2 hours. Then the reaction mixture was washed with water. The organic phase was separated, dried over Na_2SO_4 , and filtered. The solvent was distilled off on a rotary vacuum evaporator at $50^\circ\text{C}/77\text{ mbar}$. An excess of D_3 was removed at $80^\circ\text{ C}/1\text{ mbar}$.

Table S2.

Experiment	Polymer, g	Vin(Me) ₂ SiCl, mL	Vin(Me) ₂ SiCl, mmol	Py, mL	Py, mmol	Toluene, mL	Yield, g	Yield, %
3b	0.51	0.02	0.17	0.01	0.17	5.5	0.48	92
4b	0.61	0.03	0.22	0.02	0.27	6.5	0.35	57
5b	0.94	0.06	0.43	0.05	0.62	6.5	0.86	91
6b	0.56	0.18	1.29	0.11	1.36	6.5	0.35	63
10b	0.68	0.04	0.27	0.02	0.27	7.5	0.59	86
13b	0.88	0.1	0.72	0.06	0.72	10.5	0.87	94
16b	0.97	0.22	1.58	0.13	1.58	13.5	0.88	83

Characterization of the compounds obtained

PhSi(OH)₃: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.73-7.71 (d, 2H, -C₆H₅); 7.39-7.31 (m, 3H, -C₆H₅); 5.52 (s, 3H, -OH).

cis-[PhSi(O)OH]₄: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.54-7.52 (d 8H, -C₆H₅); 7.37-7.34 (t, 4H, -C₆H₅); 7.23-7.20 (t, 8H, -C₆H₅).

3b: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.65-7.62 (d, 6H, -C₆H₅); 7.49-7.41 (m, 9H, -C₆H₅); 6.24-6.12 (dd, 1H, -CH=CH₂); 6.00-5.94 (dd, 1H, -CH=CH₂); 5.84-5.76 (dd, 1H, -CH=CH₂); 0.14 (s, 360H, -SiCH₃).

²⁹Si NMR (59.6 MHz, C₃D₆O, ppm): δ -4.15, -20.02, -20.95, -21.98.

MALDI-ToF *m/z* calcd for C₁₂₄H₃₃₀KO₅₂Si₅₃ ([M+K⁺]): 4179.06, found 4179.68.

4b: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.65-7.64 (d 6H, -C₆H₅); 7.63-7.49 (t, 3H, -C₆H₅); 7.47-7.42 (t, 6H, -C₆H₅); 6.21-6.15 (dd, 1H, -CH=CH₂); 5.99-5.96 (dd, 1H, -CH=CH₂); 5.82-5.78 (dd, 1H, -CH=CH₂); 0.15 (s, 414H, -SiCH₃).

5b: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.64-7.63 (d 6H, -C₆H₅); 7.49-7.47 (t, 3H, -C₆H₅); 7.44-7.42 (t, 6H, -C₆H₅); 6.21-6.15 (dd, 1H, -CH=CH₂); 5.99-5.96 (dd, 1H, -CH=CH₂); 5.82-5.78 (dd, 1H, -CH=CH₂); 0.14 (s, 251H, -SiCH₃).

6b: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.62-7.60 (d 6H, -C₆H₅); 7.47-7.39 (m, 9H, -C₆H₅); 6.20-6.11 (dd, 1H, -CH=CH₂); 5.97-5.92 (dd, 1H, -CH=CH₂); 5.80-5.74 (dd, 1H, -CH=CH₂); 0.11 (s, 81H, -SiCH₃).

10b: ¹H NMR (300 MHz, C₃D₆O, ppm): δ 7.69-7.67 (d, 4H, -C₆H₅); 7.46-7.39 (m, 6H, -C₆H₅); 6.24-6.12 (dd, 2H, -CH=CH₂); 6.00-5.94 (dd, 2H, -CH=CH₂); 5.84-5.76 (dd, 2H, -CH=CH₂); 0.14 (s, 738H, -SiCH₃).

²⁹Si NMR (59.6 MHz, C₃D₆O, ppm): δ -4.17, -20.85, -20.96, -21.99.

MALDI-ToF *m/z* calcd for C₁₈₄H₅₂₀KO₈₄Si₈₅ ([M+K⁺]): 6501.64, found 6503.67.

13b: ^1H NMR (300 MHz, $\text{C}_3\text{D}_6\text{O}$, ppm): δ 7.73-7.68 (m, 2H, $-\text{C}_6\text{H}_5$); 7.46-7.39 (m, 3H, $-\text{C}_6\text{H}_5$); 6.22-6.15 (dd, 3H, $-\text{CH}=\text{CH}_2$); 5.99-5.96 (dd, 3H, $-\text{CH}=\text{CH}_2$); 5.83-5.78 (dd, 3H, $-\text{CH}=\text{CH}_2$); 0.15 (s, 225H, $-\text{SiCH}_3$).

^{29}Si NMR (59.6 MHz, $\text{C}_3\text{D}_6\text{O}$, ppm): δ -4.17, -21.11, -22.06, -80.58.

MALDI-ToF m/z calcd for $\text{C}_{132}\text{H}_{374}\text{KO}_{60}\text{Si}_{61}$ ($[\text{M}+\text{K}^+]$): 4671.18, found 4670.90.

16b: ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.68-7.66 (d, 8H, $-\text{C}_6\text{H}_5$); 7.41-7.24 (m, 12H, $-\text{C}_6\text{H}_5$); 6.20-6.12 (dd, 4H, $-\text{CH}=\text{CH}_2$); 5.98-5.94 (dd, 4H, $-\text{CH}=\text{CH}_2$); 5.80-5.74 (dd, 4H, $-\text{CH}=\text{CH}_2$); 0.12 (s, 1776H, $-\text{SiCH}_3$).

^{29}Si NMR (59.6 MHz, CDCl_3 , ppm): δ -4.21, -21.05, -22.05, -79.24.

MALDI-ToF m/z calcd for $\text{C}_{112}\text{H}_{273}\text{O}_{44}\text{Si}_{44}$ ($[\text{M}+\text{H}^+]$): 3558.90, found 3556.85.

SEC data

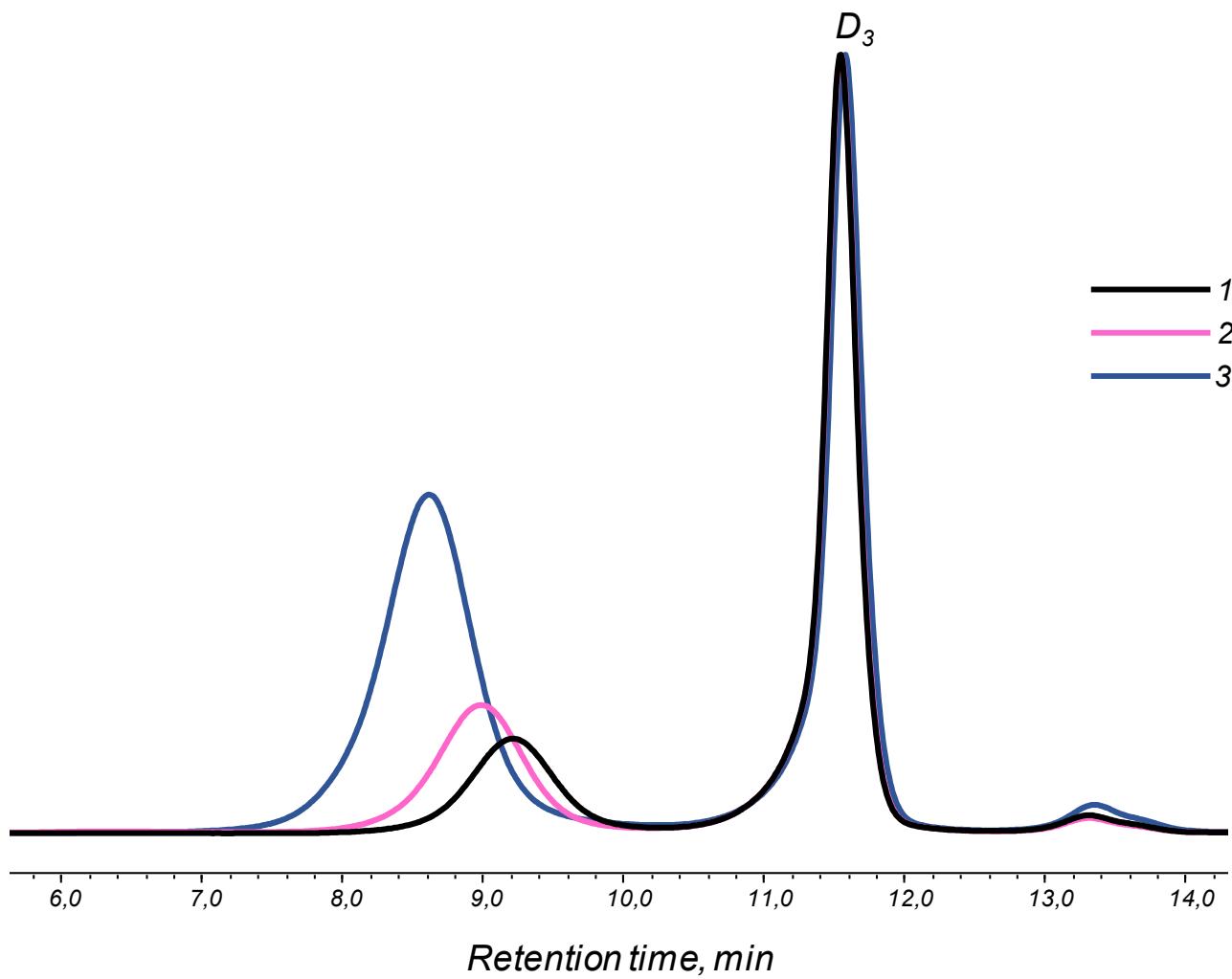


Fig. S1 SEC curves of polymers 1-3 after ammonia decompression (initiator – Ph₃SiOH)

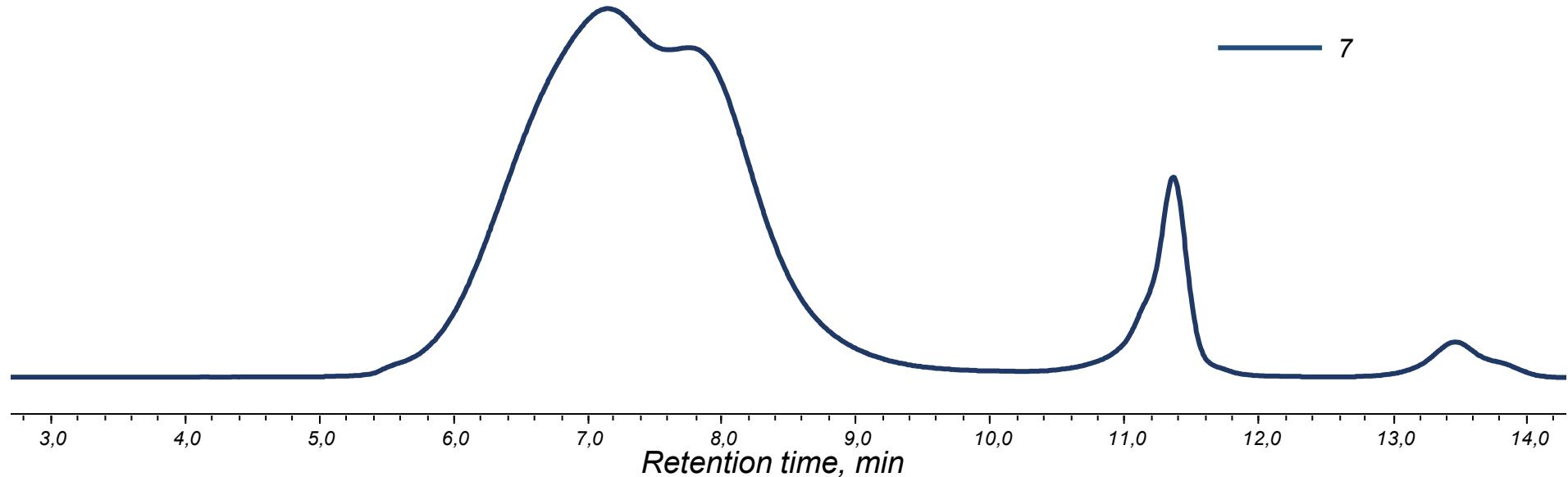


Fig. S2 SEC curve of polymer 7 after ammonia decompression (initiator – Ph₃SiOH)

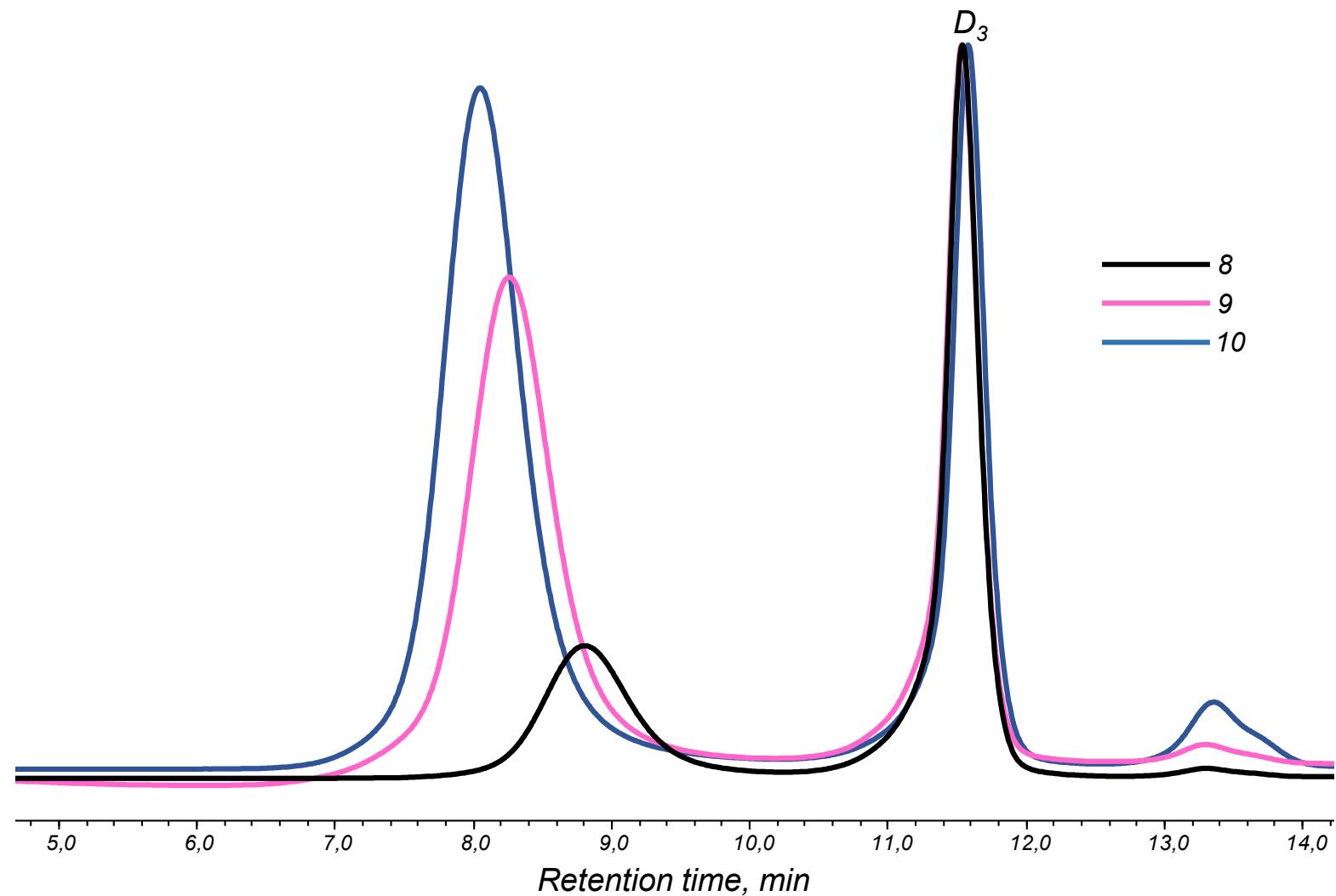


Fig. S3 SEC curves of polymers 8-10 after ammonia decompression (initiator – $\text{Ph}_2\text{Si}(\text{OH})_2$)

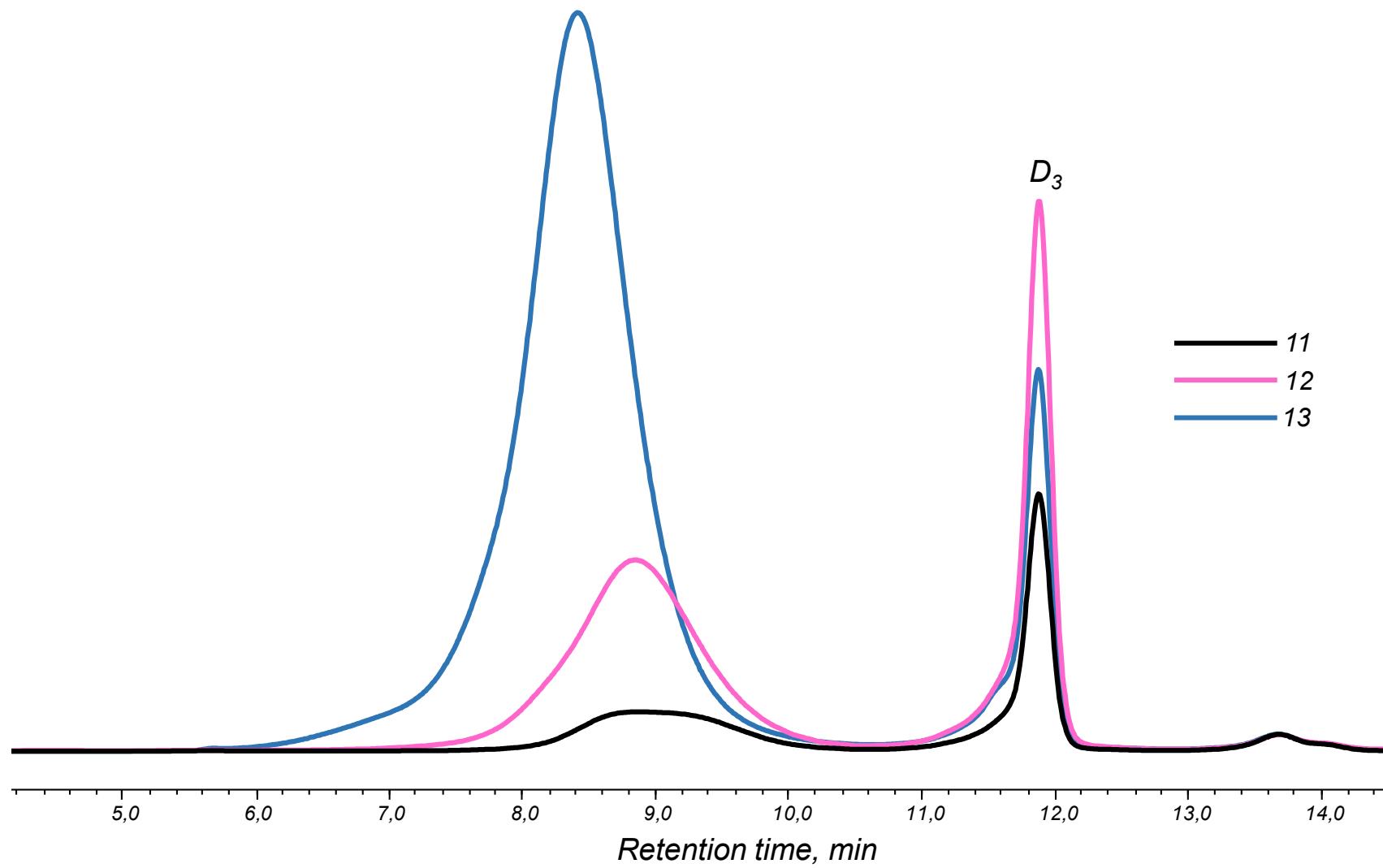


Fig. S4 SEC curves of polymers 11-13 after ammonia decompression (initiator – PhSi(OH)₃)

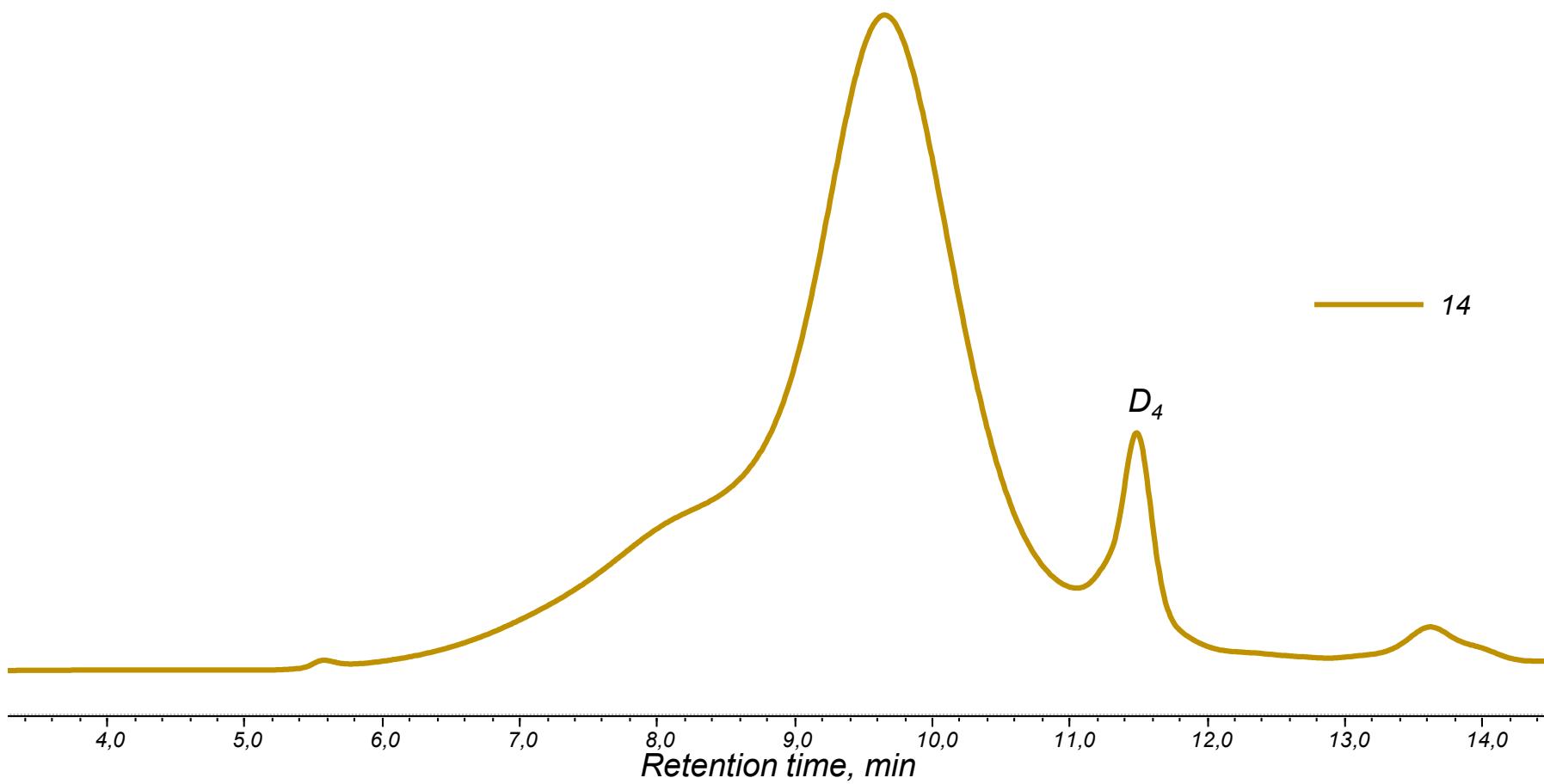


Fig. S5 SEC curve of polymer 14 after ammonia decompression (initiator – PhSi(OH)₃)

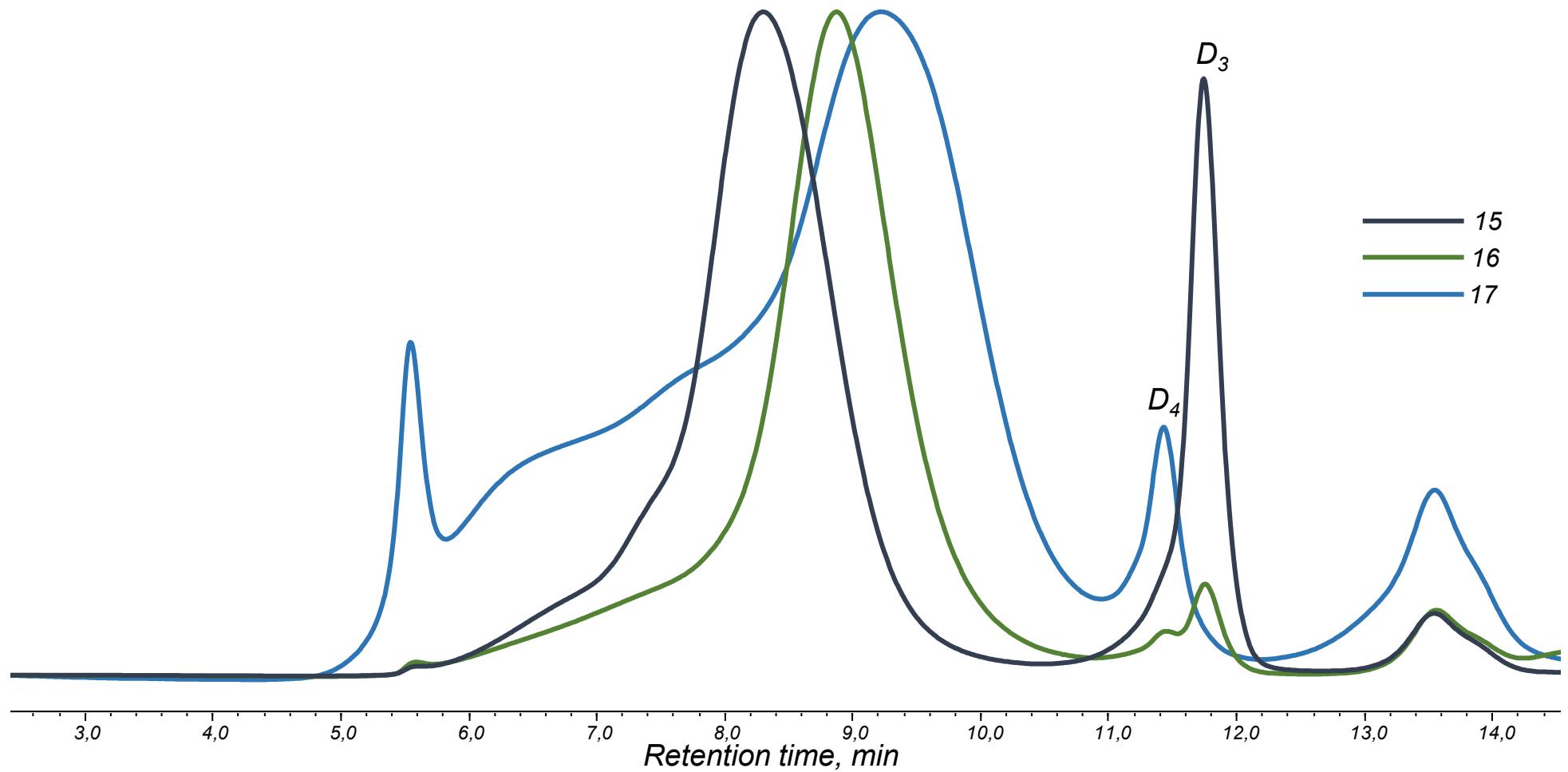


Fig. S6 SEC curves of polymers 15-17 after ammonia decompression (initiator – *cis*-[PhSi(O)OH]₄)

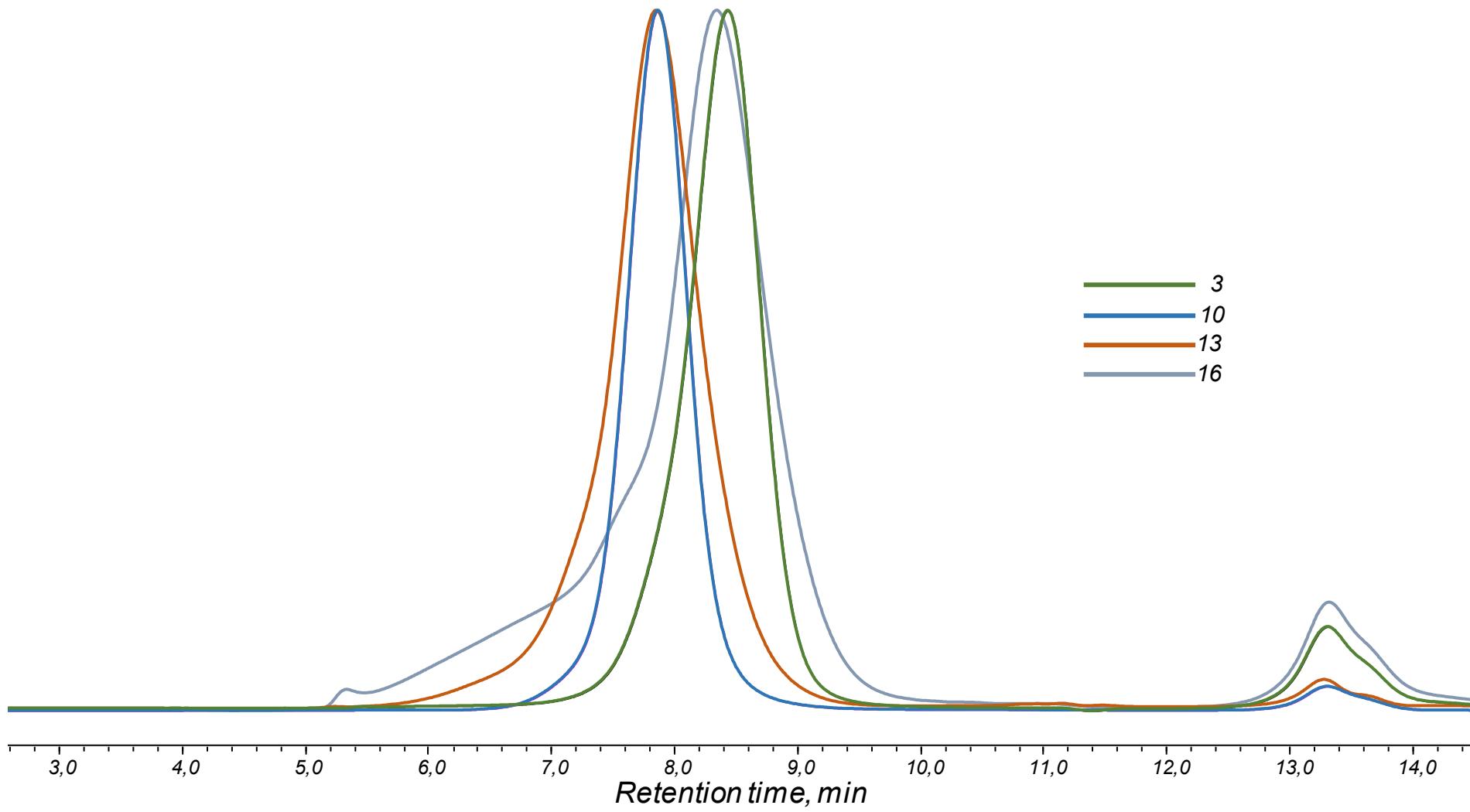


Fig. S7 SEC curves of polymers 3, 10, 13 and 16 after end-capping of the terminal -SiOH groups

NMR data

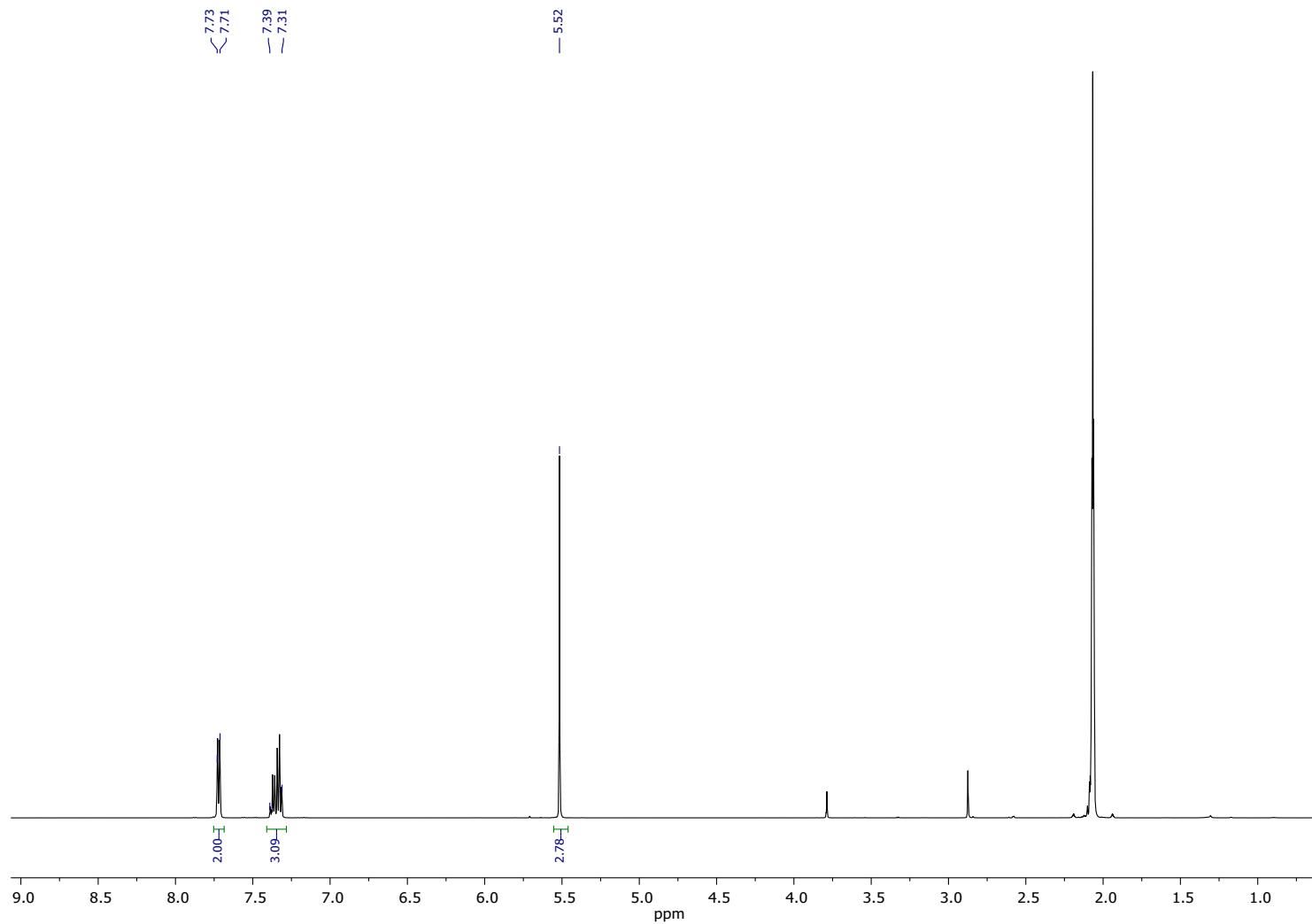


Fig. S8 ^1H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of $\text{PhSi}(\text{OH})_3$

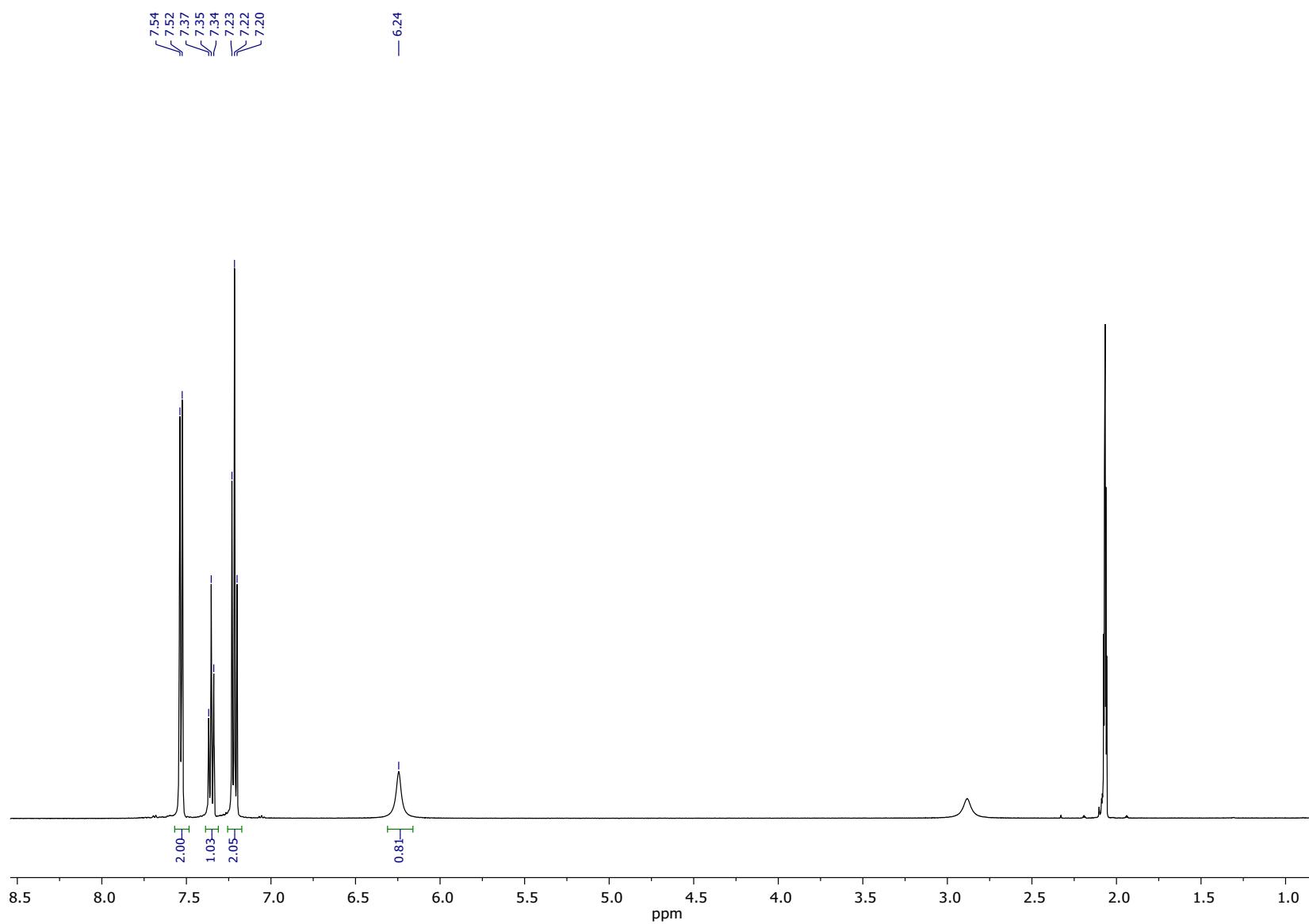


Fig. S9 ^1H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of *cis*-[PhSi(O)OH]₄

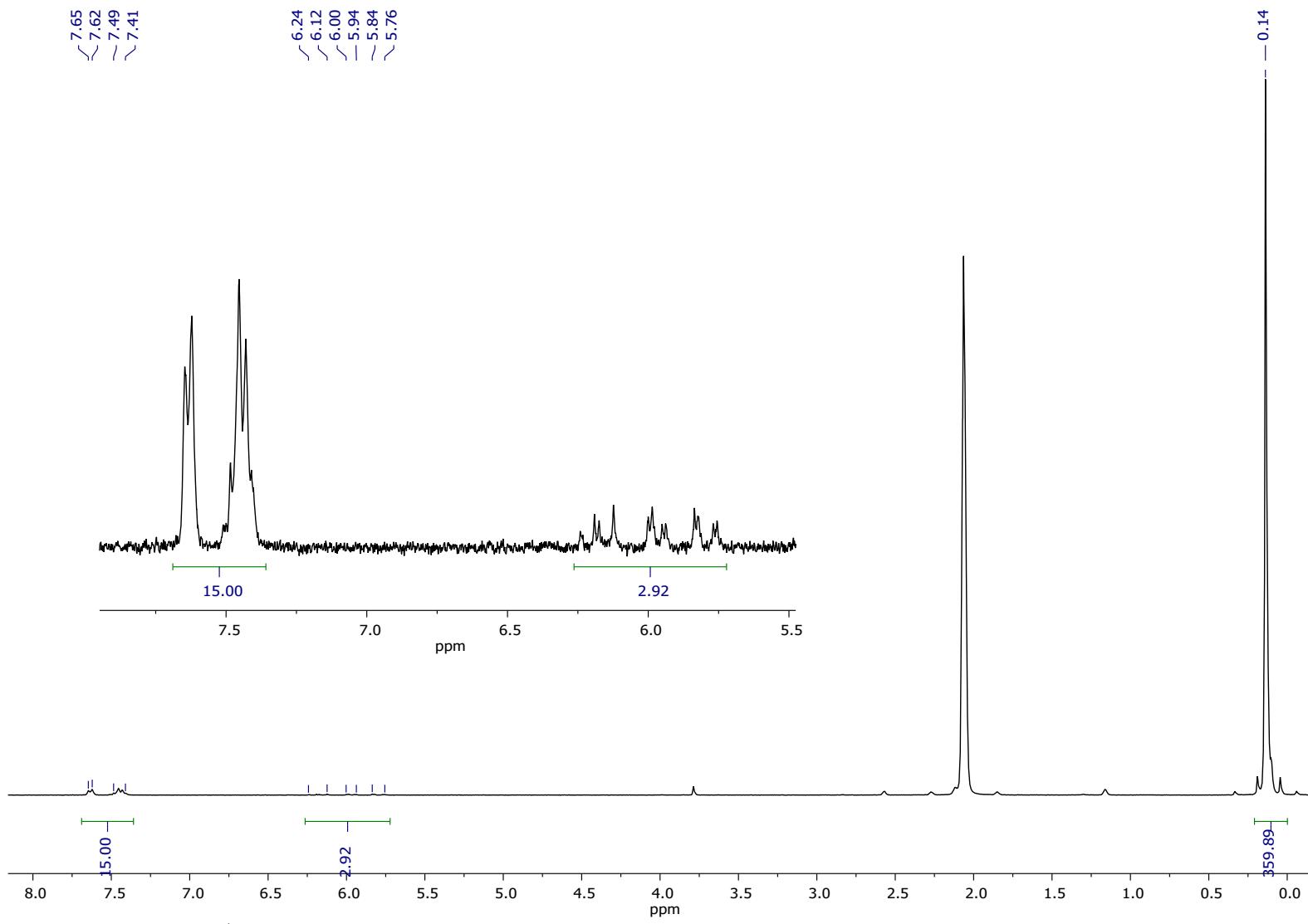


Fig. S10 ^1H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of polymer 3(b) after end-capping of the terminal -SiOH group

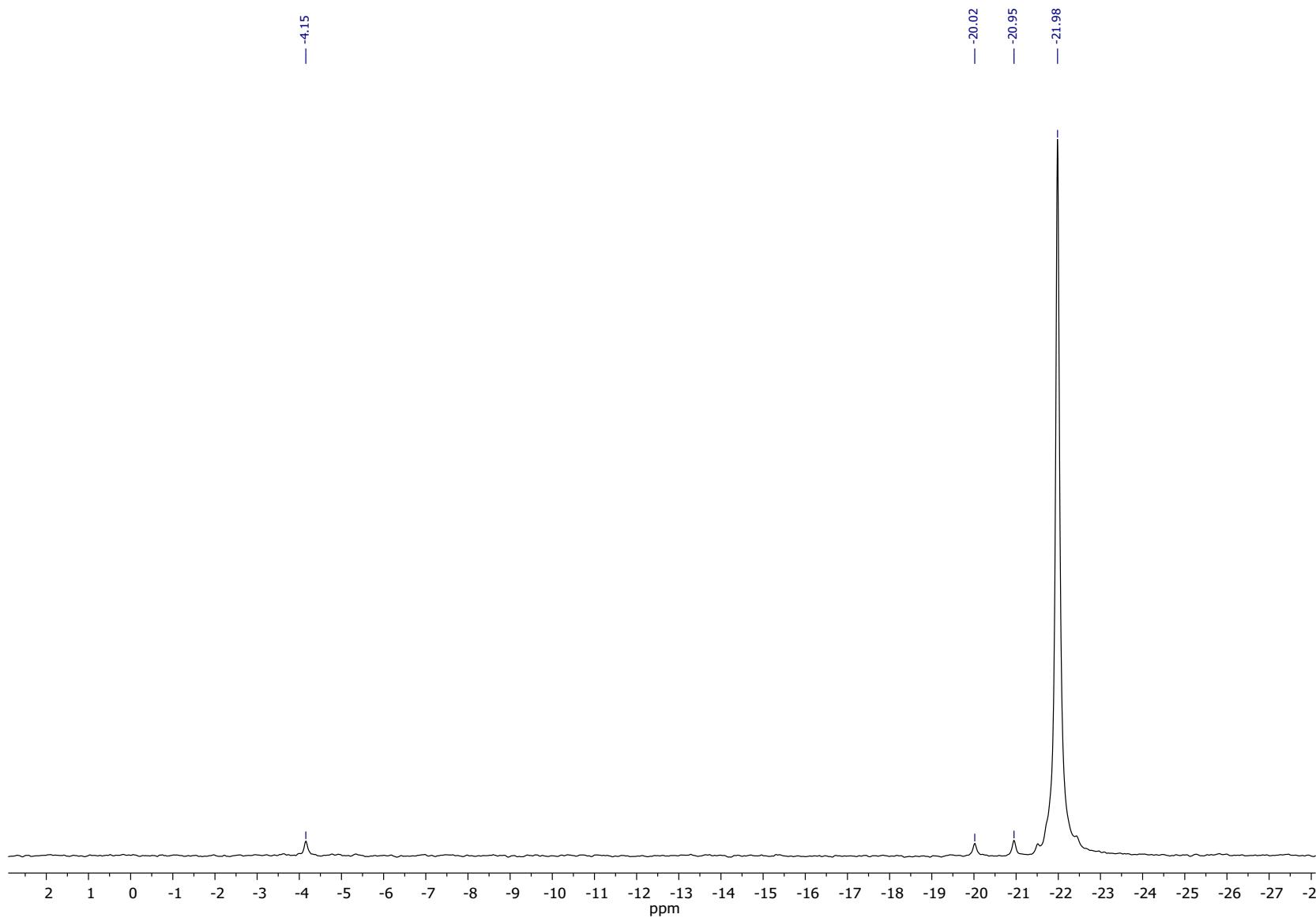


Fig. S11 ^{29}Si NMR spectrum of polymer 3(b) after end-capping of the terminal -SiOH group

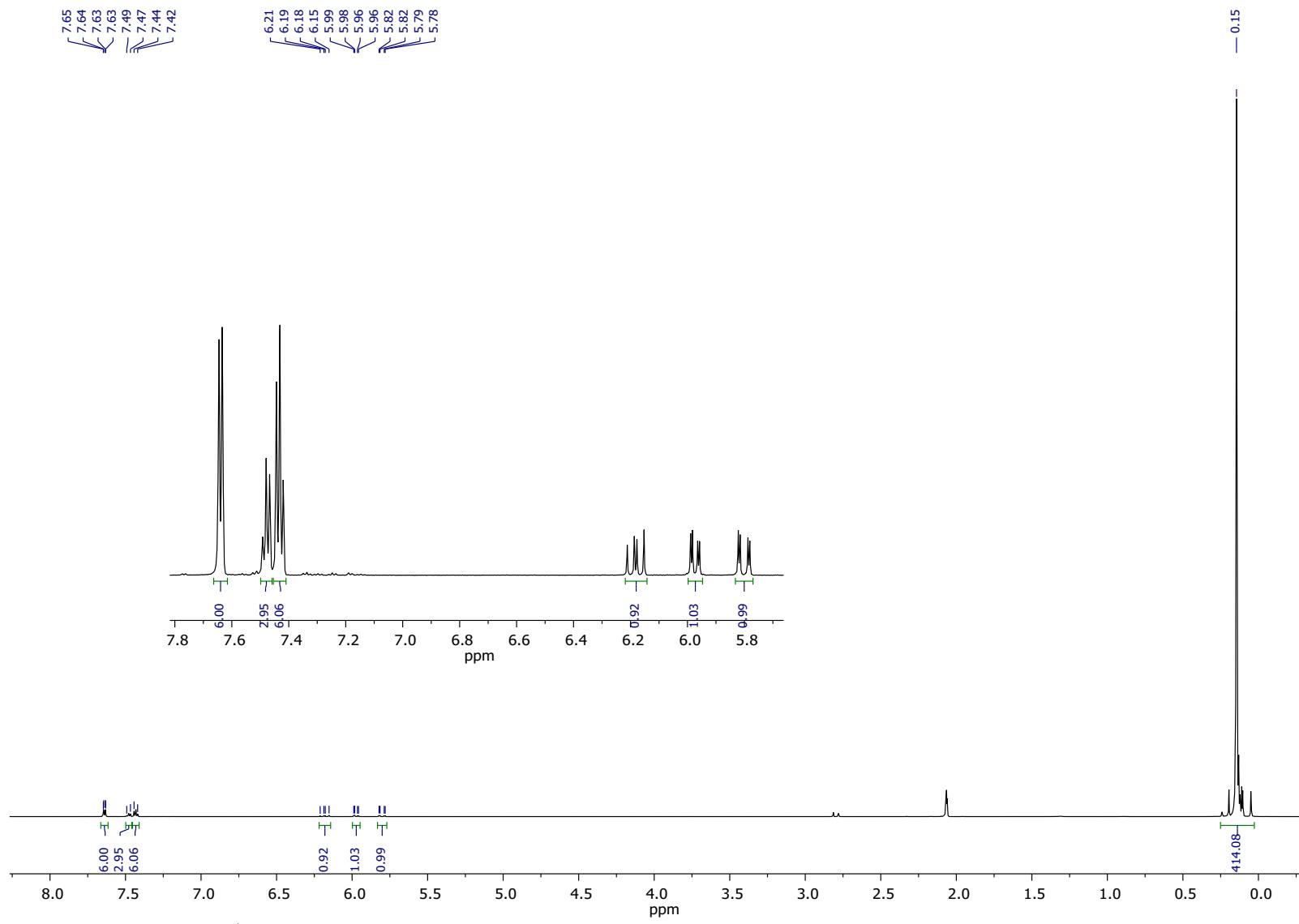


Fig. S12 ¹H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of polymer 4(b) after end-capping of the terminal -SiOH group

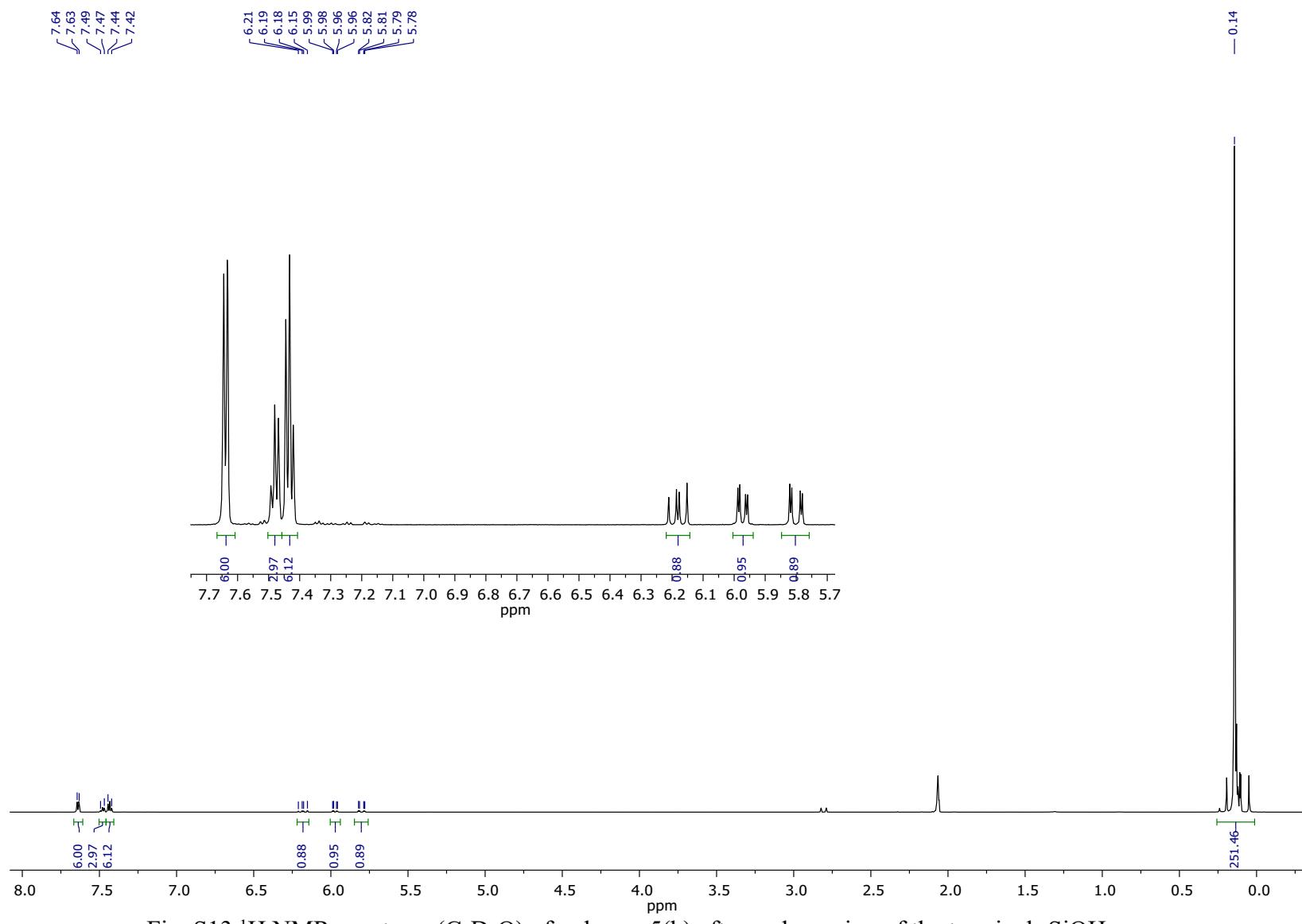
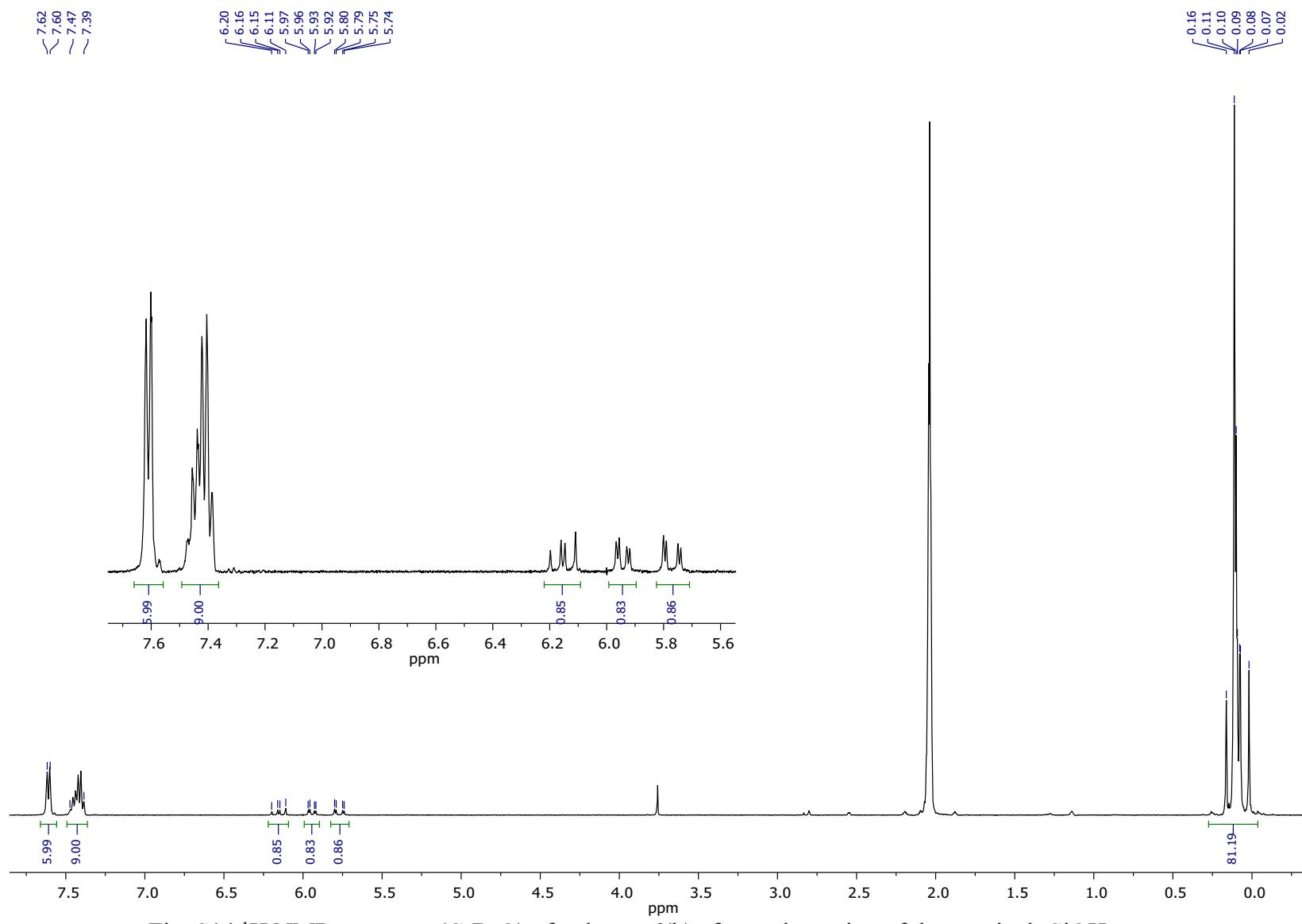


Fig. S13 ^1H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of polymer 5(b) after end-capping of the terminal -SiOH group



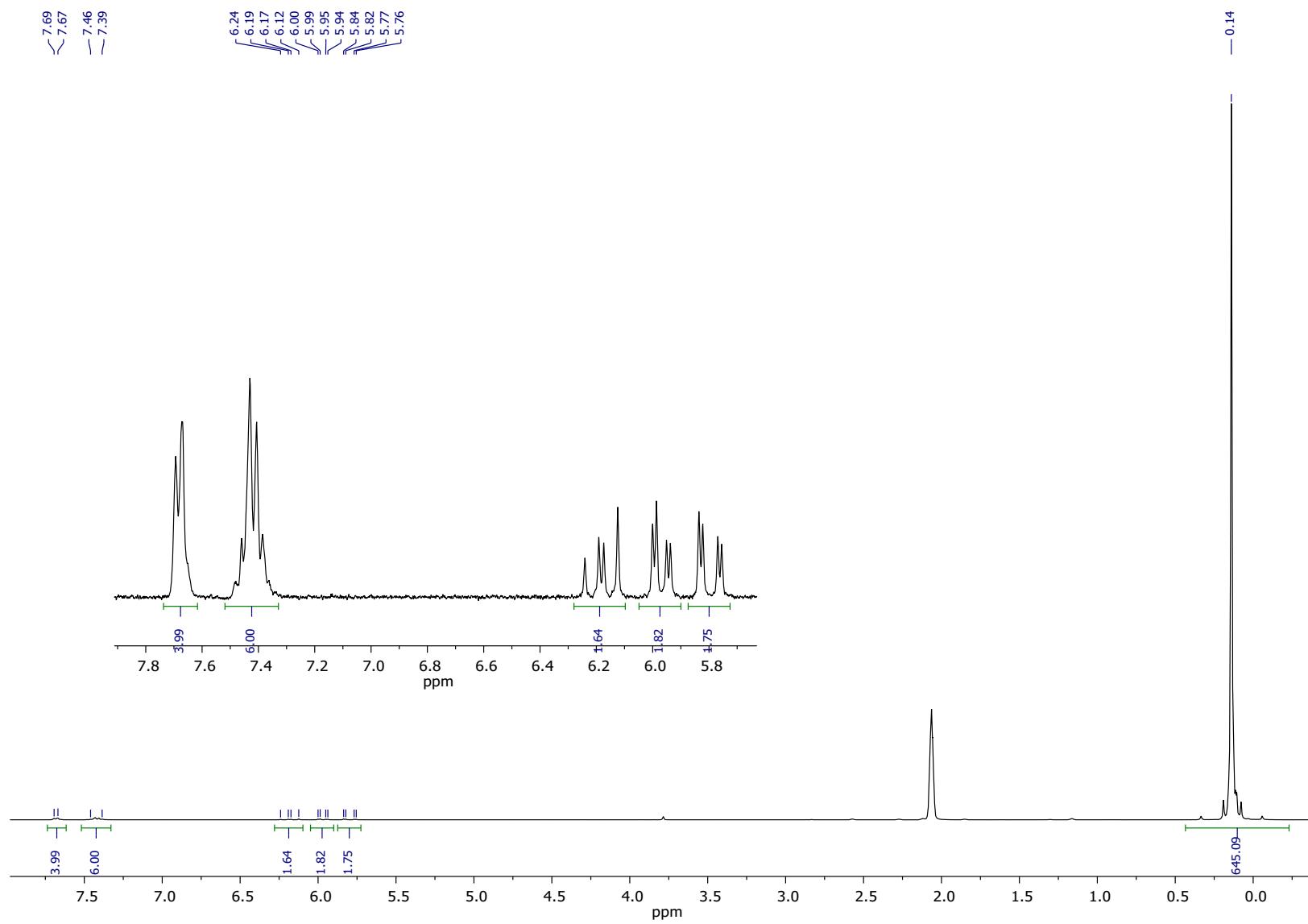


Fig. S15 ${}^1\text{H}$ NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of polymer 10(b) after end-capping of the terminal $-\text{SiOH}$ groups

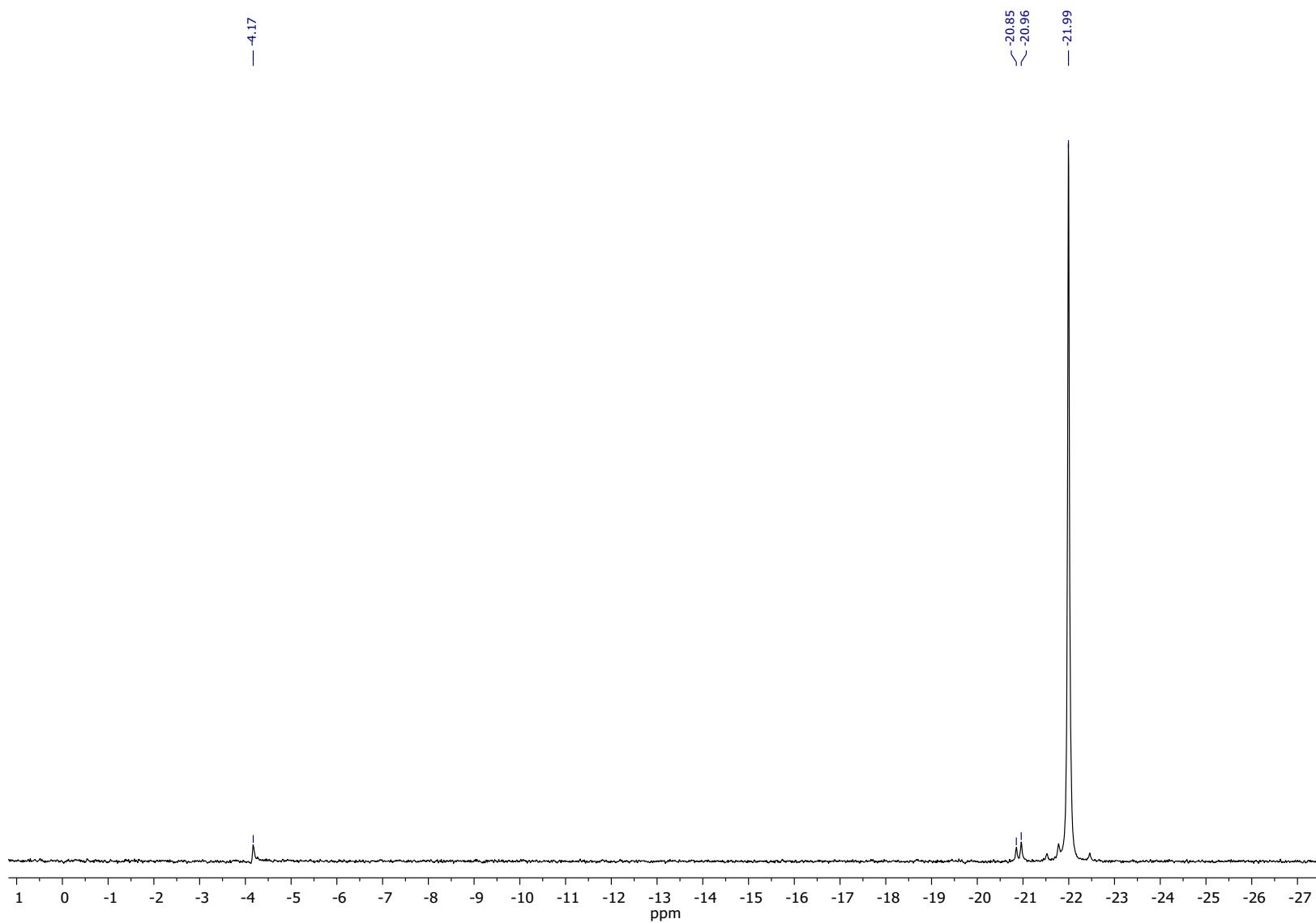


Fig. S16 ^{29}Si NMR spectrum of polymer 10(b) after end-capping of the terminal $-\text{SiOH}$ groups

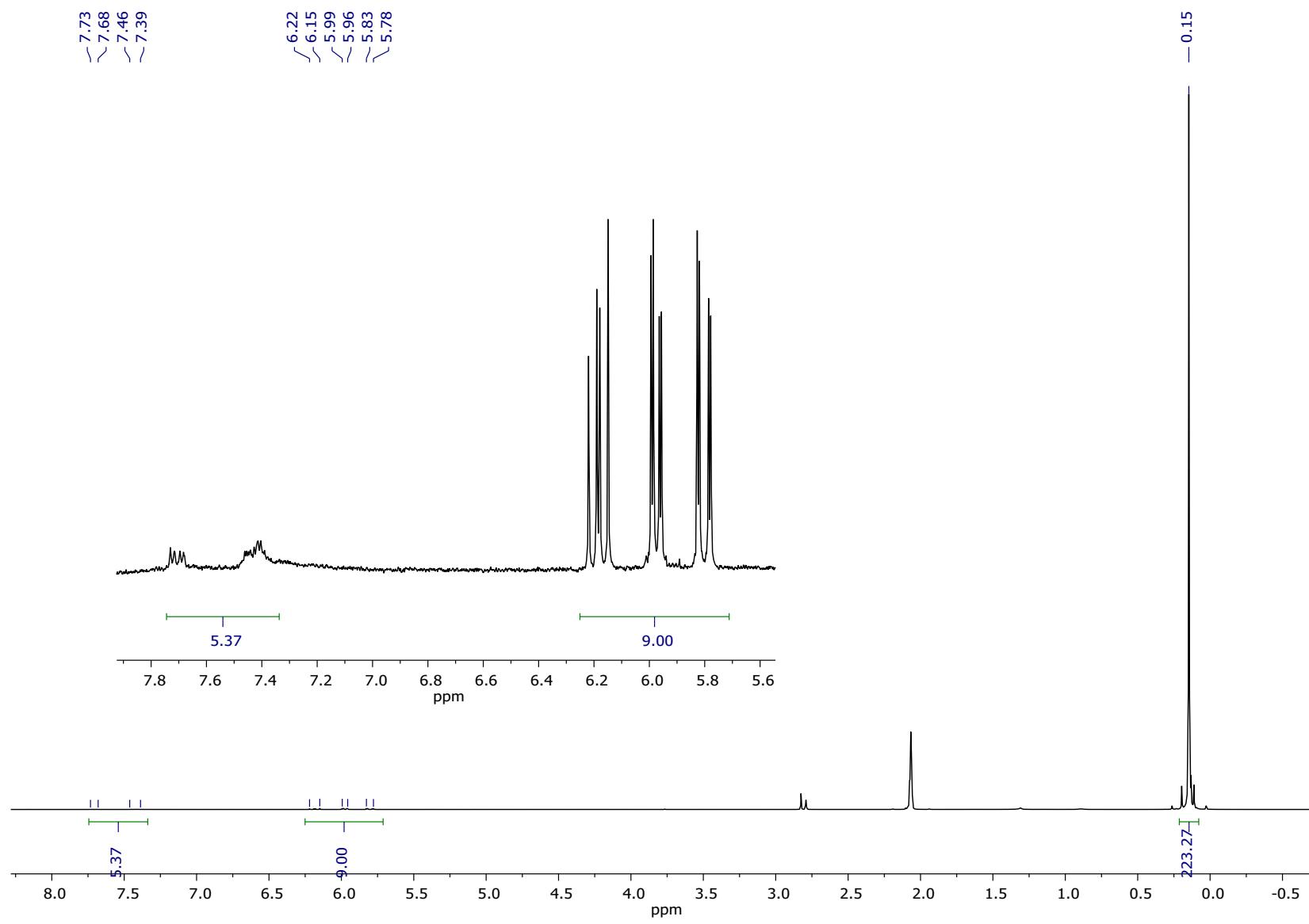


Fig. S17 ¹H NMR spectrum ($\text{C}_3\text{D}_6\text{O}$) of polymer 13(b) after end-capping of the terminal -SiOH groups

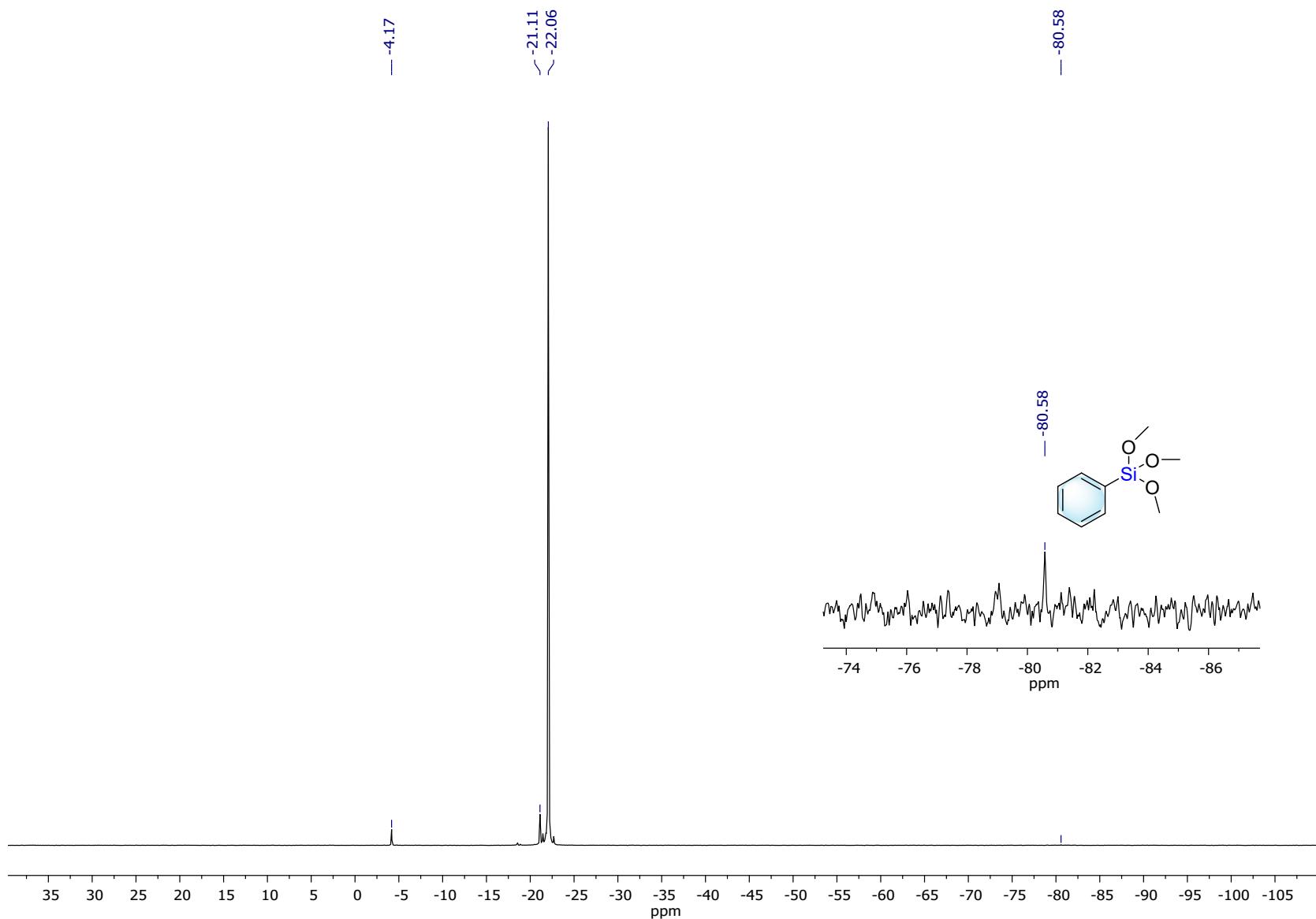


Fig. S18 ^{29}Si NMR spectrum of polymer 13(b) after end-capping of the terminal -SiOH groups

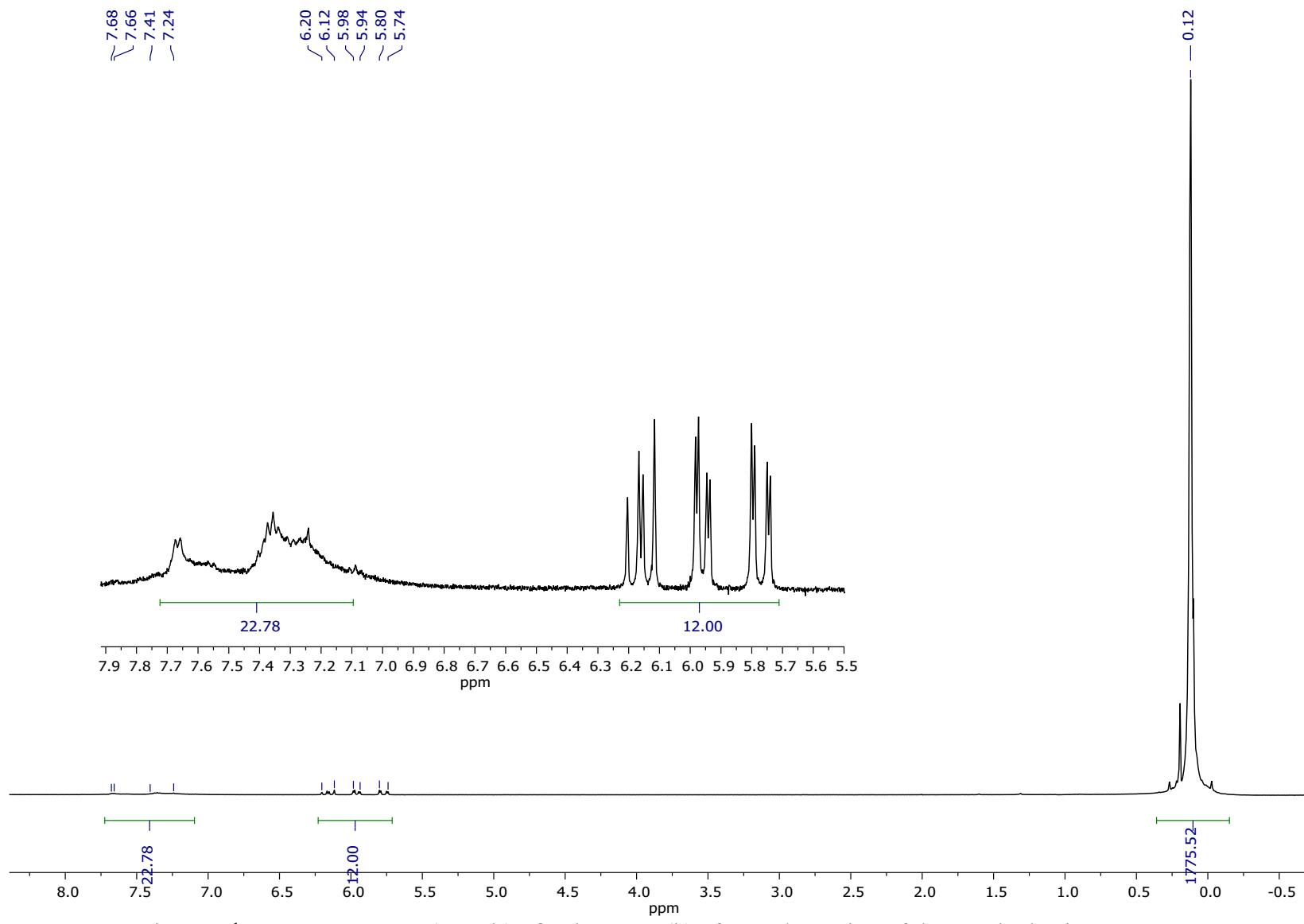


Fig. S19 ^1H NMR spectrum (CDCl_3) of polymer 16(b) after end-capping of the terminal $-\text{SiOH}$ groups

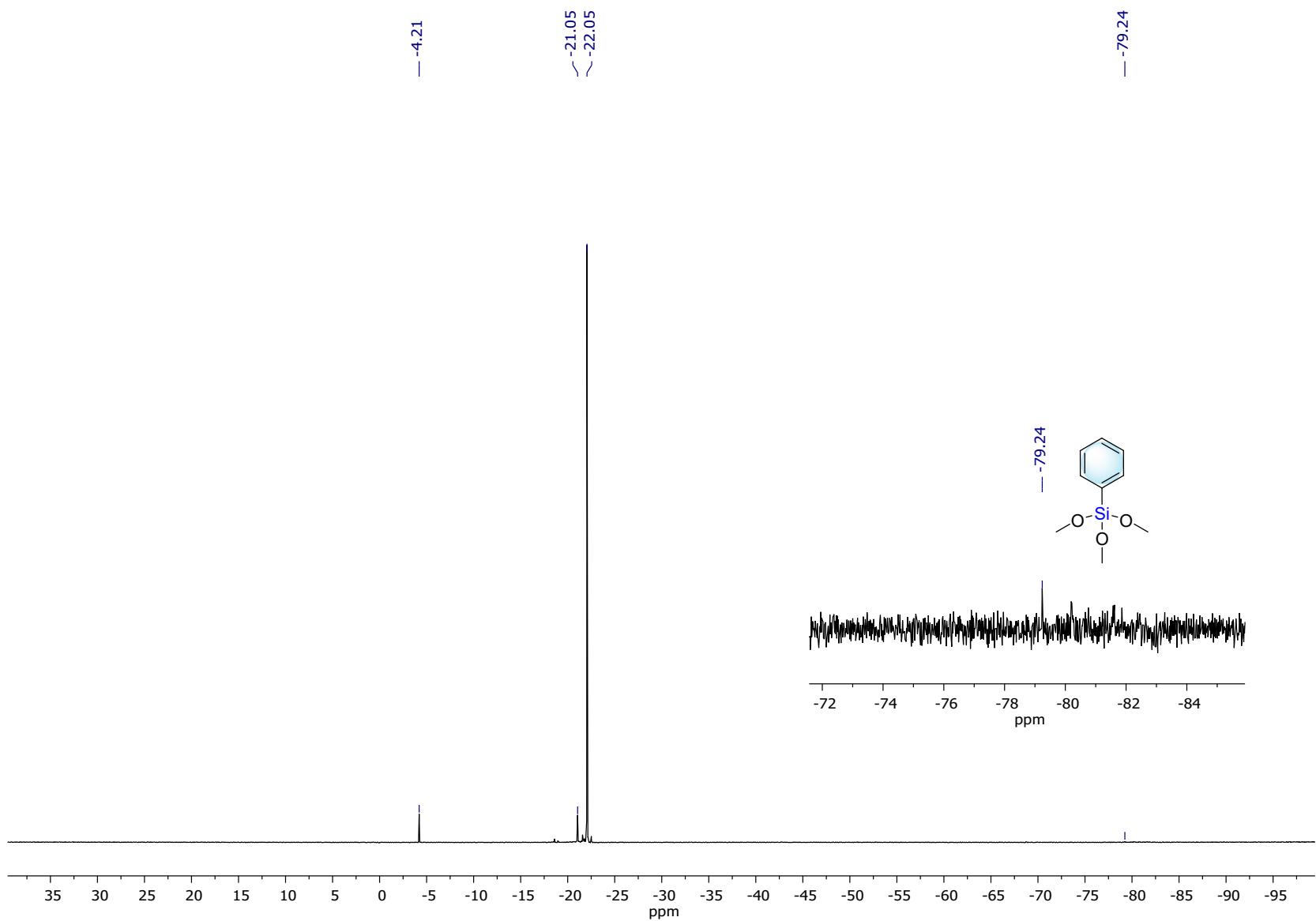


Fig. S20 ^{29}Si NMR spectrum of polymer 16(b) after end-capping of the terminal -SiOH groups

MALDI-ToF data

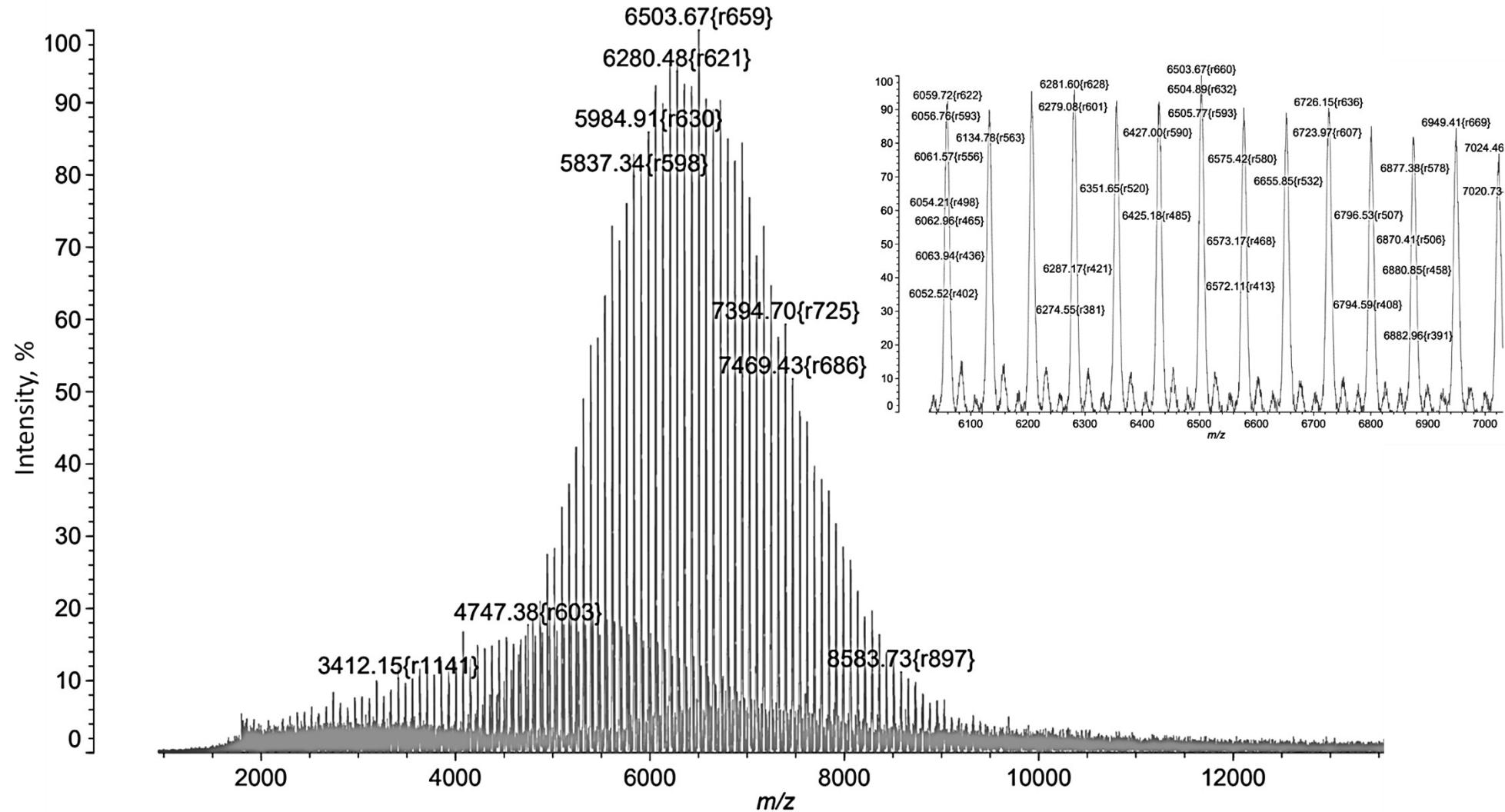


Fig. S21 Mass spectrum of polymer 10(b) after end-capping of the terminal -SiOH groups

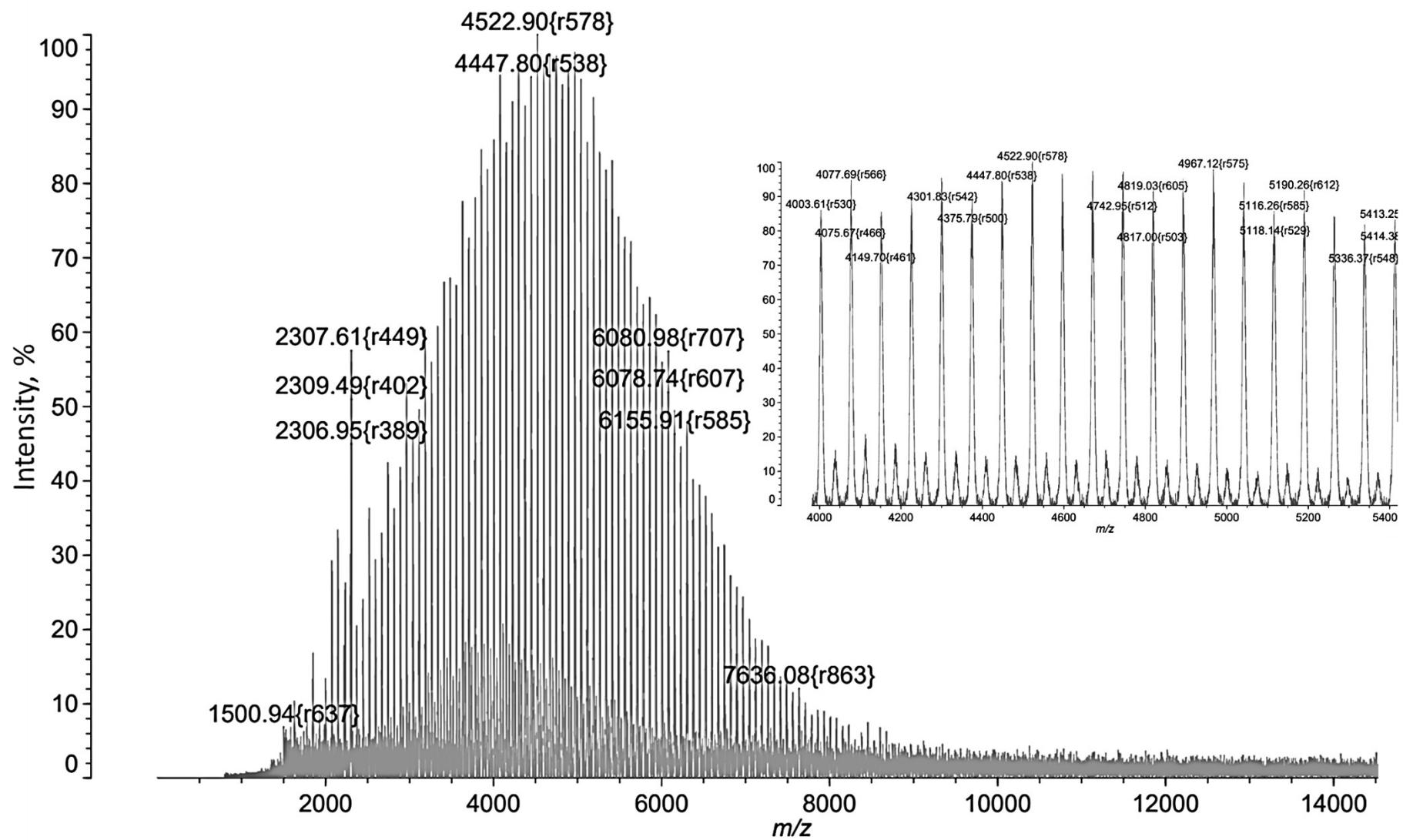


Fig. S22 Mass spectrum of polymer 13(b) after end-capping of the terminal -SiOH groups

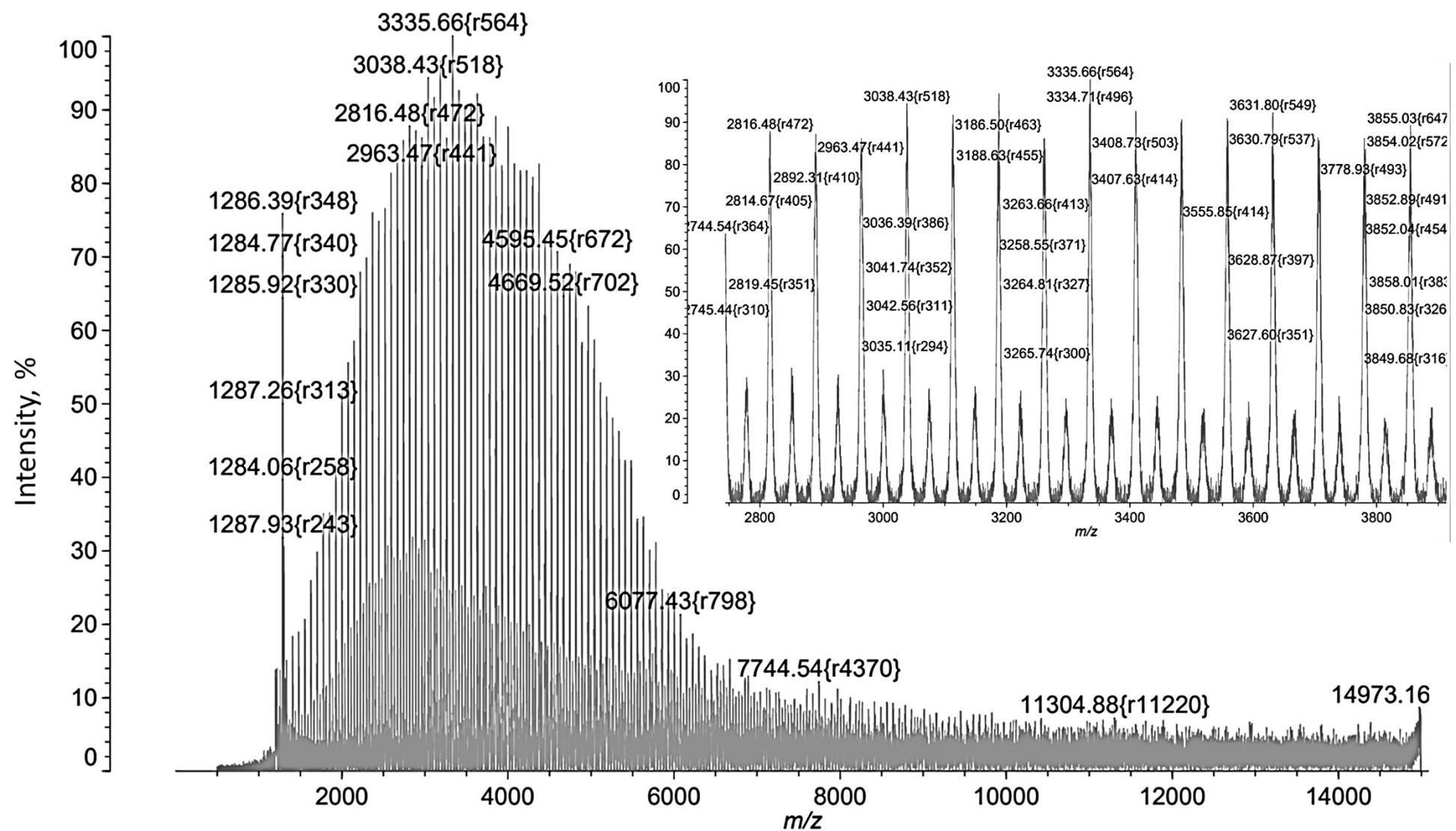


Fig. S23 Mass spectrum of polymer 16(b) after end-capping of the terminal -SiOH groups

References

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