

Supporting information

# Co<sub>2</sub>(CO)<sub>8</sub> and unsaturated epoxides as unexpected partners for the preparation of functionalized siloxane oils and cross- linked materials

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## **Equipment and methods**

All air-sensitive manipulations were conducted under an inert atmosphere using an argon-filled MBRAUN Labmaster 130 glovebox or standard Schlenk technique under argon. All glassware was heated in an oven at 110 °C and cooled in an argon atmosphere prior to use. Liquid NMR spectra were acquired on a Bruker AC 300 MHz at ambient temperature unless specified otherwise. Chemical shifts ( $\delta$ ) are reported in ppm.  $^1\text{H}$  NMR spectra are reported relative to the corresponding signals of residual protons in  $\text{CDCl}_3$  ( $\delta$  7.26 ppm). Liquid  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 300 MHz operating at 75 MHz, with complete proton decoupling and are reported relative to the following signals:  $\text{CDCl}_3$   $\delta$  77.16 ppm. Liquid  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker AC 300 MHz operating at 60 MHz, with complete proton decoupling. The splitting patterns are designated as follows: s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublets), ddt (doublet of doublet of triplets), dddd (doublet of doublet of doublet of doublets), nfom (non-first order multiplet), br. m (broad multiplet), m (multiplet). Solid state NMR spectra were acquired on a Bruker AC 300 MHz at ambient temperature unless specified otherwise. All the silicone polymers were dried overnight at 60 °C under vacuum prior of solid-state NMR measurements. The spectra of all silicone polymers were obtained on a Bruker 300 MHz narrow-bore spectrometer using a double resonance 2.5-mm MAS probe. The samples were introduced under air into a zirconia rotor, which was then tightly closed. Dry nitrogen gas was used to spin the samples to avoid sample degradation. The  $^{13}\text{C}$  CPMAS spectra were obtained from cross polarization (CP) from protons using a linear ramped CP to optimize the magnetization transfer efficiency. A proton radio frequency (RF) field of 70 kHz in the center of the ramp was applied, while the RF field on  $^{13}\text{C}$  was adjusted for optimal sensitivity. The experimental conditions that we used for the  $^{29}\text{Si}$  CPMAS techniques are as follows: single-pulse experiment with proton decoupling, 4- $\mu\text{s}$  pulse, recycle delay of 30 s and spinning frequency 5 kHz. The absence of trace amount of Pt in  $\text{Co}_2(\text{CO})_8$  was verified by ICP-MS (inductively coupled plasma mass-spectrometry) analysis (below the 0.05 ppm detection limit of the apparatus and method used).

$^1\text{H}$  MAS 10 kHz, p1= 4 $\mu\text{s}$ , p11= 9dB, d1=5s.  $^{13}\text{C}$  CPMAS 10 kHz, p1=4  $\mu\text{s}$ , p11= 11dB, P30= 8, P31= 8, p112= 9dB, D1=2s.  $^{29}\text{Si}$  CPMAS p1= 5.3  $\mu\text{s}$ , p11= 9dB, P30= 7.2, p112= 9dB, D1= 5s, PCPD2= 7.8  $\mu\text{s}$ , o2= 20, p15= 4000 $\mu\text{s}$

The Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra of solid compounds were collected from a Thermo Scientific Nicolet 6700 FT-IR Spectrometer equipped with an MCT detector. Spectra (64 scans, unless stated otherwise) were measured at 298 K with spectral resolution of 2  $\text{cm}^{-1}$ . The reported spectra are presented in a Kubelka-Munk format and the intensities are designated as following: v. s (very strong), s (strong), m (medium), w (weak).

## Solvents and reagents

Toluene and mesitylene were distilled from sodium benzophenone ketyl and stored under argon in glovebox.  $\text{CDCl}_3$  was purchased from Sigma-Aldrich, degassed by freeze-pump-thaw cycles and stored over 4Å molecular sieves under an argon atmosphere in Rotaflow flasks.  $\text{Co}_2(\text{CO})_8$  (Strem) was used as received and stored in glovebox freezer at  $-40\text{ }^\circ\text{C}$ . Various alkenes were purchased from the following vendors, degassed by freeze-pump-thaw cycles, and used without further purification:

Aldrich: methylbis(trimethylsilyloxy)vinylsilane ( $\text{MD}^{\text{ViM}}$ ), allyl alcohol, allyl benzyl ether (ABE).

Sigma Aldrich: 1,1,1,3,5,5,5-heptamethyltrisiloxane ( $\text{MD}^{\text{HM}}$ ), styrene.

TCI: allyl glycidyl ether (AGE), 4-vinylcyclohexene oxide (VCO), butyl glycidyl ether (BGE).

Strem: 1,1,3,3-tetramethyldisiloxane (TMDS).

Acros Organics: mesitylene.

Alfa Aesar: Mercury

The polymethylhydrosiloxane (PMHS) (internal [Si-H] content 45.5wt%, contains ca. 50 [Si-H] units),  $\text{MD}_{90}\text{D}'_7\text{M}$  (internal [Si-H] content  $\sim 3.02\text{wt}\%$ ) and  $\text{M}'\text{D}_{18}\text{M}'$  (terminal [Si-H] content  $\sim 3.3\text{wt}\%$ ) were generously provided by Elkem Silicones France SAS.

## Catalytic tests

### General procedure and reactant quantities for all the reactions

In an Ar filled glovebox, a 4 mL vial was charged with appropriate volumes of the corresponding alkene (1.0 eq for all entries in Table S1), silane (1.0 eq of Si-H), mesitylene (NMR standard-only for liquid products), the 11 mM stock solution of  $\text{Co}_2(\text{CO})_8$  in toluene and a stirring bar. The vial was placed to a preheated oil bath and left for 24 h to stir at 1000 rpm. At the end of the test, no further purification was performed when dense solids are obtained and the final solids were left to dry under vacuum at 60 °C. When liquids or dense oils were obtained, the crude mixtures were passed through silica column (1.5 cm in height in Pasteur pipette) and eluded with pentane. The collected solution was placed under vacuum to remove the solvent and left to dry under vacuum at 60 °C.

**Table S1. Quantities of reagents for entries in Scheme 2-5.<sup>a</sup>**

Alkene	Alkene, $\mu\text{L}$	silane	Silane quantity, $\mu\text{L}$	Mesitylene, $\mu\text{L}$	Volume of 11 mM solution of $\text{Co}_2(\text{CO})_8$ in toluene, $\mu\text{L}$	ppm catalyst <sup>b</sup>	Product Label	Color of the product	Color of the silicone polymer after drying overnight at 60 °C under vacuum	Isolated yield, mg	Expected Co-atom w% in the product (ICPMS Results)
AGE	446	PMHS	168	-	336	2113	1a	Brown	White	294	0.15 (0.13)
VCO	490	PMHS	168	-	336	2194	1b	Greenish foam	White	303	0.14
Allyl alcohol	80	PMHS	105	-	210	2831	AAP	Colorless or slightly pale-grey	white	141	0.19
AGE	65	MD <sub>90</sub> D <sup>*</sup> M	538 <sup>d</sup>	46	202	-	2a	Colorless	n.a	445	-
AGE	65	M <sup>*</sup> D <sub>18</sub> M <sup>*</sup>	484.5	46	202	-	3a	Colorless	n.a	468	-
AGE	112	TMDS	84	92	84	-	4a	Colorless	n.a	132	-
AGE	56	MD <sup>*</sup> M	128	46	42	-	5a	colorless	n.a	78	-
BGE	335	PMHS	105	46	210	-	n.a	n.a	n.a	n.r, n.a	-
allyl benzyl ether	362	PMHS	105	46	210	-	1c	Colorless	n.a	n.a	-
BGE/ allyl benzyl ether	335/362	PMHS	105	46	210	-	1c	Colorless	n.a	n.a	-
Styrene/ MD <sup>vi</sup> M/AGE <sup>e</sup>	43/109/44	PMHS	42	46	84	1449	1d	Brown	Milky white-pale yellow	171	0.06 (0.08)
Styrene/ MD <sup>vi</sup> M/AGE <sup>f</sup>	121/303/28	PMHS	105	-	210	1567	1d'	Brown	beige	353	0.08

[a] n.a – not applicable, n.r – no reaction. [b] The ppm level of catalyst present is calculated in the same way as reported before.<sup>1</sup> ppm catalyst = (metal complex, mg)/ (reaction mixture, kg), where reaction mixture contains the masses of the alkene substrate and the [Si-H] substrate. [b] 1.1 mM solution was used instead. [c] 0.11 mM solution was used instead. [d] Quantity of MD<sub>90</sub>D<sup>\*</sup>M is in mg instead of  $\mu\text{L}$ . [e] Styrene (0.4): MD<sup>vi</sup>M (0.4 eq): AGE (0.4 eq). [f] Styrene (0.45): MD<sup>vi</sup>M (0.45 eq): AGE (0.10 eq).

**Table S2. Catalyst loading and temperature effects on gel formation.<sup>a</sup>**

Alkene	Temperature (°C)	Reaction time depending on Co <sub>2</sub> (CO) <sub>8</sub> loading (min)					
		0.1 mol%	0.05 mol%	0.033 mol%	0.025 mol%	0.02 mol%	0.01 mol%
AGE	r.t	7	8	13	45	n.r	n.r
	60	3	3	4	7	23	n.r
VCO	r.t	10	n.r	n.r	n.r	n.r	n.r
	60	3	n.r	n.r	n.r	n.r	n.r

[a] n.r – no reaction after 24 h of stirring, r.t – room temperature. The experimental conditions are the same used in table S1 for the synthesis of **1a** and **1b**.

### Mercury tests

As Co nanoparticles may be *in situ* generated during the catalytic tests and active in the targeted reaction, mercury tests were carried out as follows: In an Ar filled glovebox, a 4 mL vial was charged with AGE or VCO (1.0 eq), PMHS (1.0 eq of Si-H), an appropriate volume of the Co<sub>2</sub>(CO)<sub>8</sub> (0.1 mol%) solution and Hg (400 eq compared to Co). The mixture was then stirred at the corresponding temperature. In parallel, the exact same reactions were performed without Hg as depicted in table S1. Results are shown in Table S3 and Figure S1

**Table S3. Gelation time with and without Hg.**

Alkene	Temperature (°C)	Reaction time with Hg (min)	Reaction time without Hg (min)
AGE	r.t	7	7
	60	3	3
VCO	r.t	10	10
	60	3	3

## Procedure for the synthesis of functionalized PMHS with AGE catalyzed by Karstedt catalyst (APK)

Outside the glovebox, a 4 mL vial was charged with AGE (145  $\mu$ L, 1.22 mol, 1.3 eq), PMHS (42  $\mu$ L, 1.0 eq of [Si-H]), and Karstedt catalyst in toluene (50  $\mu$ L, 0.2 mol% of Karstedt catalyst in toluene) and a stirring bar. The vial was placed to a preheated oil bath at 60 °C and to stir at 1000 rpm for 24 h. At the end of the reaction, the crude mixture was passed through silica column (1.5 cm in height in Pasteur pipette) and eluded with pentane. The collected solution was placed under vacuum to remove the solvent and left to dry under vacuum at 60 °C. No efforts were made to optimize the reaction conditions.

## Current examples of non-precious metal catalyzed PMHS cross-linking

**Table S4. Comparison of catalyst loadings in ppm under the same conditions<sup>a</sup>**

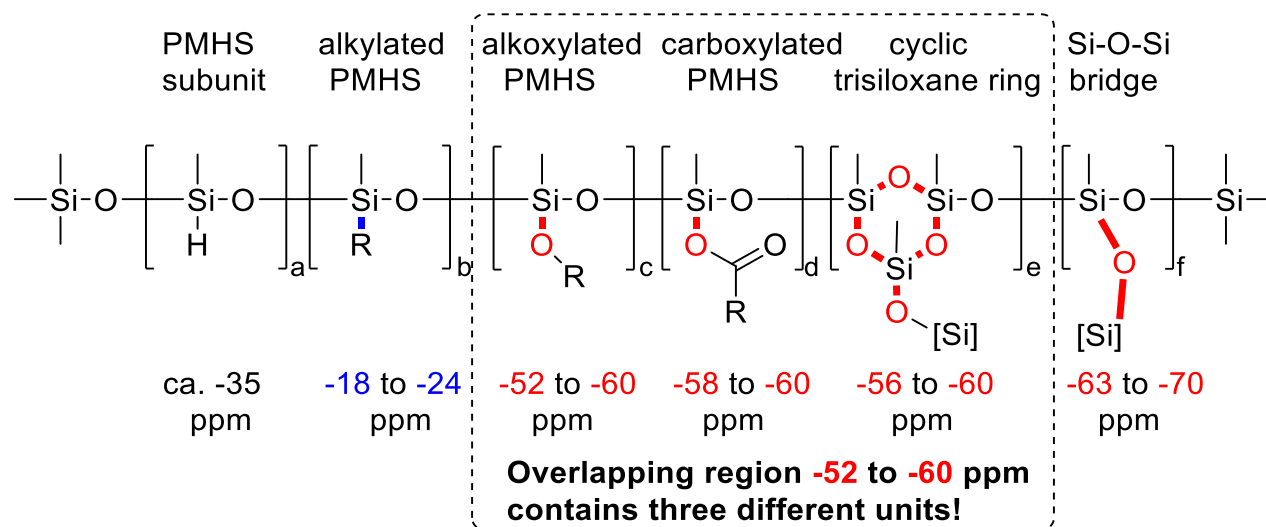
Catalyst	Fe-dimer <sup>1</sup>	Fe-dimer <sup>1</sup>	Fe-dimer <sup>1</sup>	Co-dimer <sup>2</sup>	Mn-dimer <sup>3</sup>	Fe-dimer <sup>4</sup>	Fe-dimer <sup>4</sup>	Ni <sup>5</sup>	Co <sup>6</sup>	Co <sup>6</sup>	Co <sup>6</sup>	Co <sup>6</sup>
m(catalyst), mg	0.52	0.5	1	6.4	4	32.6 <sup>b</sup>	32.6 <sup>b</sup>	6.7 <sup>c</sup>	2	2	2	2
Alkene substrate	vPDMS	vPDMS	vPDMS	vPDMS	vPDMS	vPDMS	vPDMS	vPDMS	1-octene	1-dodecene	1-octene	1-dodecene
m(alkane substrate), g	1000	1000	1000	2870	1072 <sup>d</sup>	10000	10000	500	750	965	485	672
[Si-H] substrate	Different PMHS analogues											
m([Si-H] substrate), mg	44	44	44	130	65 <sup>d</sup>	660	1330	220	500	285	825	580
<b>ppm (catalyst)</b>	<b>498</b>	<b>479</b>	<b>958</b>	<b>2133</b>	<b>3516</b>	<b>3061</b>	<b>2880</b>	<b>1284</b>	<b>1600</b>	<b>1600</b>	<b>1527</b>	<b>1597</b>
<b>ppm (catalyst) range</b>	<b>498-3516</b>											
<b>ppm range reported in this work</b>	<b>1449-2831</b>											

[a] The ppm level of catalyst present is calculated in the same way as reported before.<sup>1</sup> ppm catalyst = (metal complex, mg)/ (reaction mixture, kg), where reaction mixture contains the masses of the alkene substrate and the [Si-H] substrate. vPDMS – vinyl terminated polydimethylsiloxane. [b] Based on complex **1** with MW=326.27 g/mol. [c] Based on the Ni-precursor and added ligand. [d] Alkene substrate and [Si-H] substrate masses were calculated using densities of 0.98 g/mL and 1.006 g/mL, respectively.

## Assigning $^{29}\text{Si}$ chemical shifts to the PMHS backbone units

Here in this section, we would like to draw the reader's attention to the use of  $^{29}\text{Si}$  SSNMR chemical shifts as simple means to assign the newly formed Si-X bond in cross-linked polysiloxane materials. Additionally, we will highlight the situations where  $^{29}\text{Si}$  SSNMR chemical shifts alone cannot distinguish between Si-OR, Si-OOCR and cyclic trisiloxane ring, in which case  $^{13}\text{C}$  SSNMR and DRIFT spectra have to be used as complementary data to justify the presence of these three groups.

### $^{29}\text{Si}$ chemical shifts in functionalized and cross-linked PMHS



**Scheme S1.** Typical  $^{29}\text{Si}$  SSNMR chemical shifts of Si-H, Si-R, Si-OR, Si-OOCR, cyclic trisiloxane ring and Si-O-Si bridge present in cross-linked PMHS. All the chemical shifts have been rounded to the closest digit. References to the reported  $^{29}\text{Si}$  chemical shifts: Si-H,<sup>7</sup> Si-R (R= Me in PMHS oils having varying length),<sup>8</sup> Si-OR (R= linear C1-C10 alkyl, cyclic alkyl, functionalized alkyl and phenyl),<sup>9,10</sup> Si-OOCR (only formic, acetic, benzoic and methacrylic acid derivatives have been taken into account),<sup>11,12</sup> Si-O-Si bridge<sup>13-15</sup> and cyclic trisiloxane ring.<sup>13,15-18</sup>

### Issues related with characterization of functionalized cross-linked PMHS

On Scheme S1,  $^{29}\text{Si}$  SSNMR chemical shifts of three types of Si-X units (Si-H, Si-R and Si-O-Si bridge) in PMHS chain are well separated from each other and pose no issues to their assignment to respective units. However, when new Si-O bond is formed in the cross-linked material, the Si-O-R and cyclic trisiloxane ring unit  $^{29}\text{Si}$  SSNMR chemical shifts cannot be unambiguously assigned to their respective units as they overlap in region -52 to 60 ppm. The latter situation occurs in this work when i) epoxide ring functionality is present and can undergo

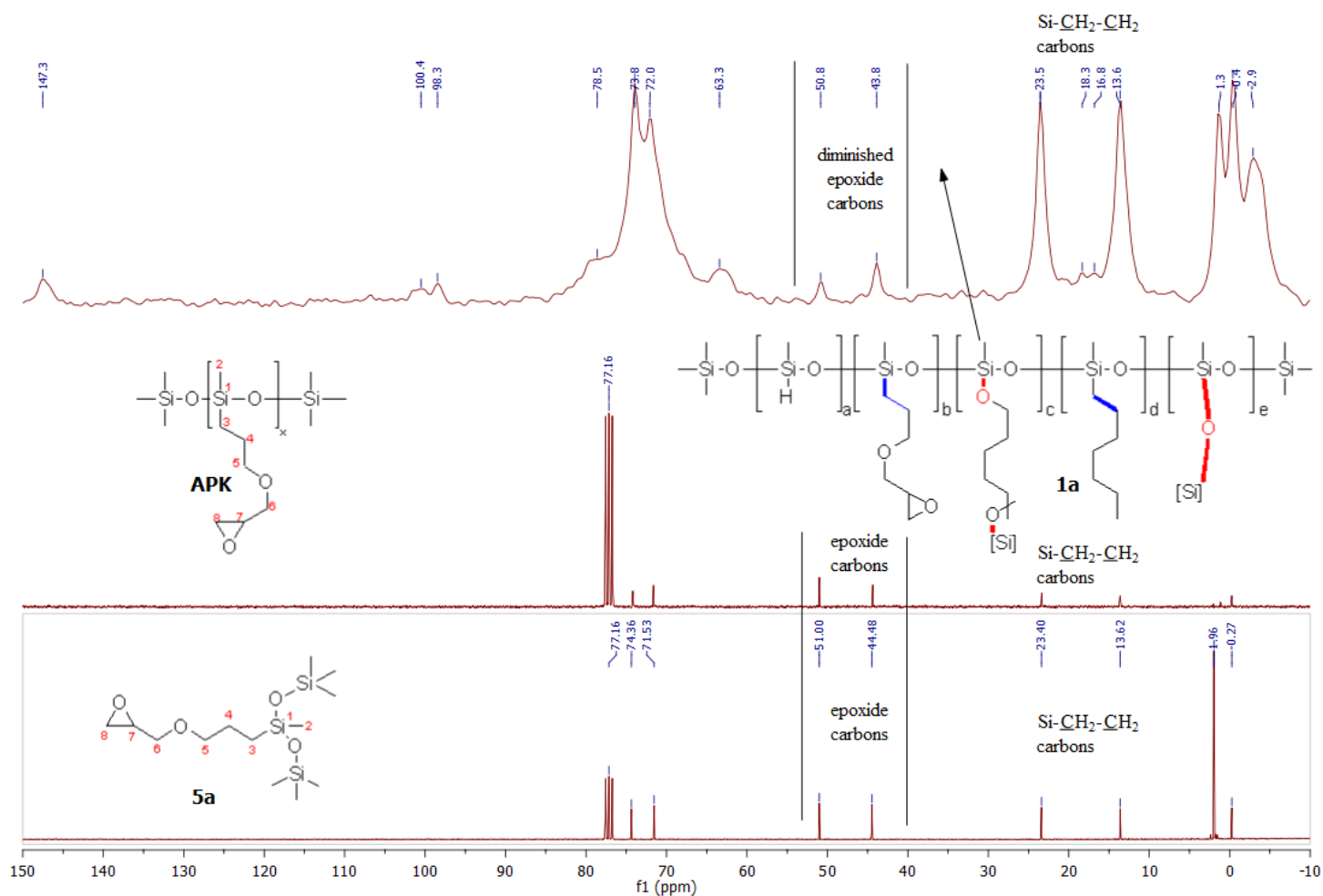


isomerization to ketone or aldehyde, after which reduction of C=O group to CH-OSi bond can occur, ii) epoxide ring opening occurs to form Si-O-C bond. In these two cases the tether can additionally undergo O-C bond cleavage in Si-O-C bond to form Si-O-Si and reduced sidechain. Further information regarding the nature of cross-linking of PMHS via Si-O-Si and/or via standard C=C bond hydrosilylation followed by epoxide ring opening cannot therefore be analyzed only by  $^{29}\text{Si}$  NMR chemical shifts, but has to be complemented with the use of  $^{13}\text{C}$  SSNMR and DRIFT data.

### **Analysis of NMR spectra from “Cross-linking of PMHS with AGE”**

#### **Discussion of chemical shifts from Figure S1:**

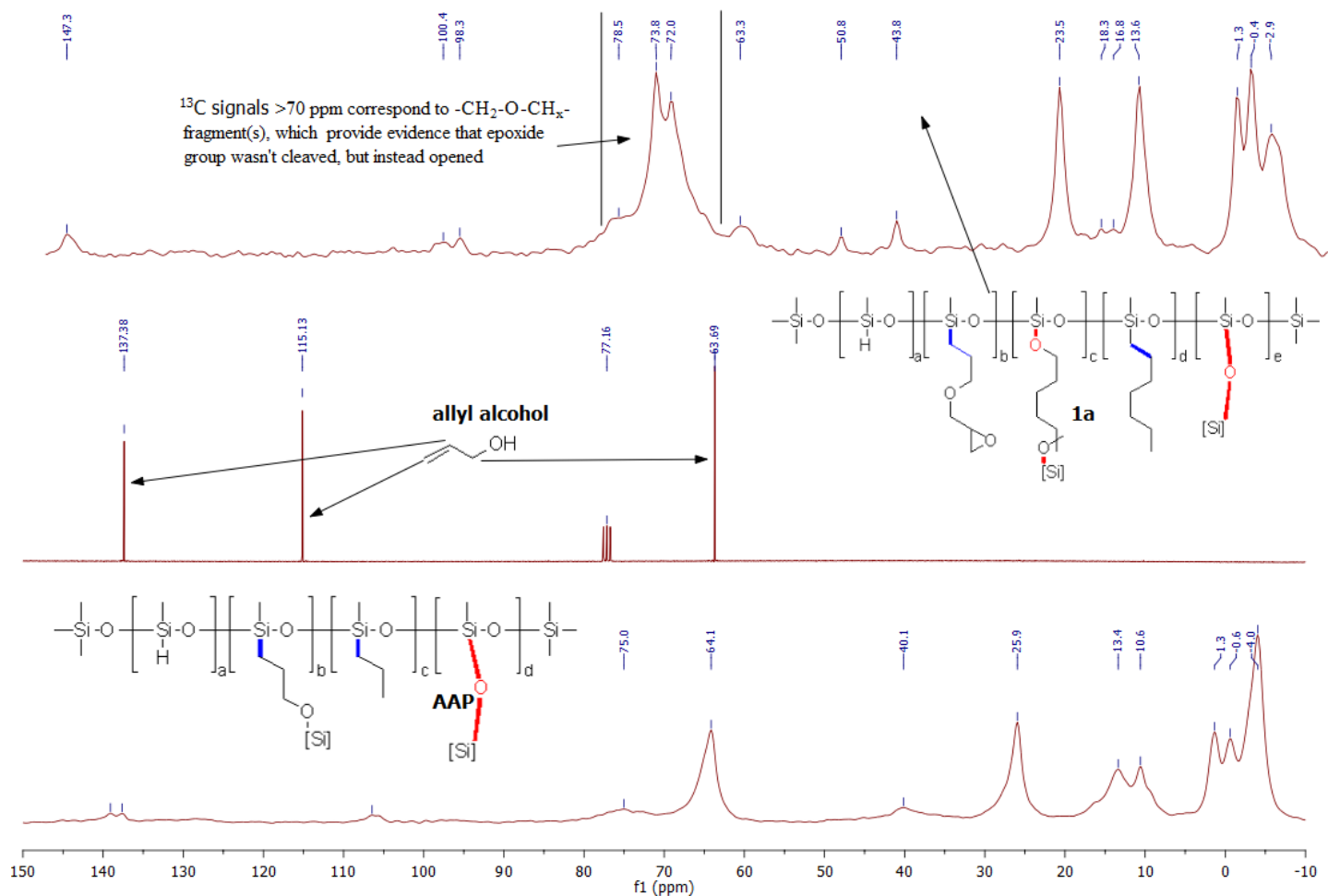
Products **1a**, **APK** and **4a** all contain hydrosilylated allyl group having distinct chemical shifts in range of 13-14 ppm and 23-24 ppm corresponding to carbon signals of Si-CH<sub>2</sub> and Si-CH<sub>2</sub>-CH<sub>2</sub> moieties, respectively. Additional similarities are seen in the range of 43-51 ppm, where the epoxide carbon signals can be found. For **1a** the epoxide carbon signals have diminished considerably compared to Si-CH<sub>2</sub> and Si-CH<sub>2</sub>-CH<sub>2</sub> peaks, which suggests epoxide ring opening. Further evidence to the presence of opened epoxide ring is provided in the region of 71-75 ppm. If the cross-linking reaction would have occurred by the cleavage of O-C bond in the -O-CH<sub>2</sub>-epoxide fragment, then in the newly formed Si-O-C bond the  $^{13}\text{C}$  chemical shift of the carbon would be ca. 64 ppm (as will be further demonstrated on Figure S2). However, two distinguishable peaks at 72.0 and 73.8 ppm for **1a** are in good agreement with  $^{13}\text{C}$  spectra of other hydrosilylated AGE products on Scheme 1a, providing evidence that epoxide ring opening had occurred giving linear Si-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-Si or branched Si-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH(O-Si)-CH<sub>3</sub> cross-linker with the underlined  $^{13}\text{C}$  signals having chemical shift >70 ppm.



**Figure S1.** Comparison of  $^{13}\text{C}$  chemical shifts of **1a** (top), AGE functionalized PMHS using Karstedt catalyst (**APK**) (middle) and MDM functionalized AGE (**5a**) (bottom).

#### Discussion of chemical shifts from Figure S2:

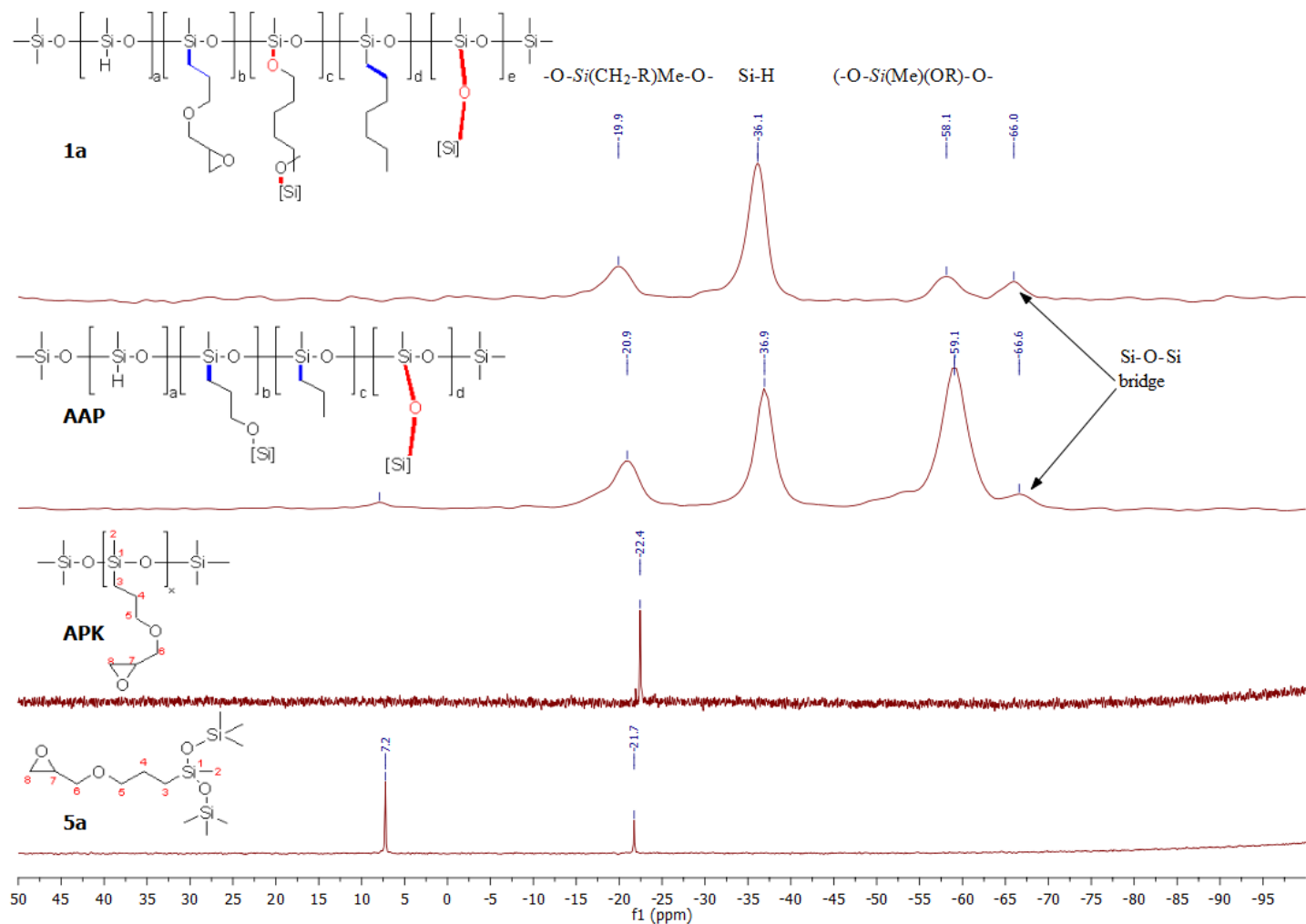
Further proof to the fact that epoxide ring was not cleaved during the cross-linking can be obtained from  $^{13}\text{C}$  signals in Figure S2. In theory, if the cleavage of epoxide group could have happened, then we would obtain allyloxy fragment capable of cross-linking PMHS chains via  $\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-Si}$  bridge. The same outcome can however be reached by using allyl alcohol as the tether to form cross-linked material **AAP**. In the latter case, similar  $\text{Si-CH}_2$  and  $\text{Si-CH}_2\text{-CH}_2$  chemical shifts can be seen between **1a** and **AAP**. However, the striking difference in reactivity between AGE and allyl alcohol becomes evident when we compare the respective  $\text{CH}_2\text{-O-Si}$  chemical shifts. In case of **AAP** the  $\text{CH}_2\text{-O-Si}$  carbon signal is at ca. 64 ppm (as  $\text{CH}_2\text{-O-H}$  carbon signal in its apparent tether, allyl alcohol), while for **1a** the respective signal lies between 72-74 ppm.



**Figure S2.** Comparison of <sup>13</sup>C chemical shifts of **1a** (top), allyl alcohol (middle) and cross-linked material from allyl alcohol and PMHS (**AAP**) (bottom).

Discussion of chemical shifts from Figure S3:

Excerpt of <sup>29</sup>Si NMR chemical shifts in region 50 to -100 ppm shows that **1a** is cross-linked via hydrosilylation of C=C bond and epoxide ring opening to form new Si-C and Si-O-C bonds, respectively. In addition to that, cross-linked material **1a** contains Si-O-Si bridge at ca. -66 ppm formed from the reduction of Si-O-C bond by another Si-H bond. Comparing the relative peak heights of Si-O-C and Si-O-Si peaks between **1a** and **AAP**, we can say that in case of the latter further reduction of Si-O-C bond to Si-O-Si bridge was much slower than in the case of **1a**, where the peak intensities of Si-O-C bond and Si-O-Si bridge are practically equal.

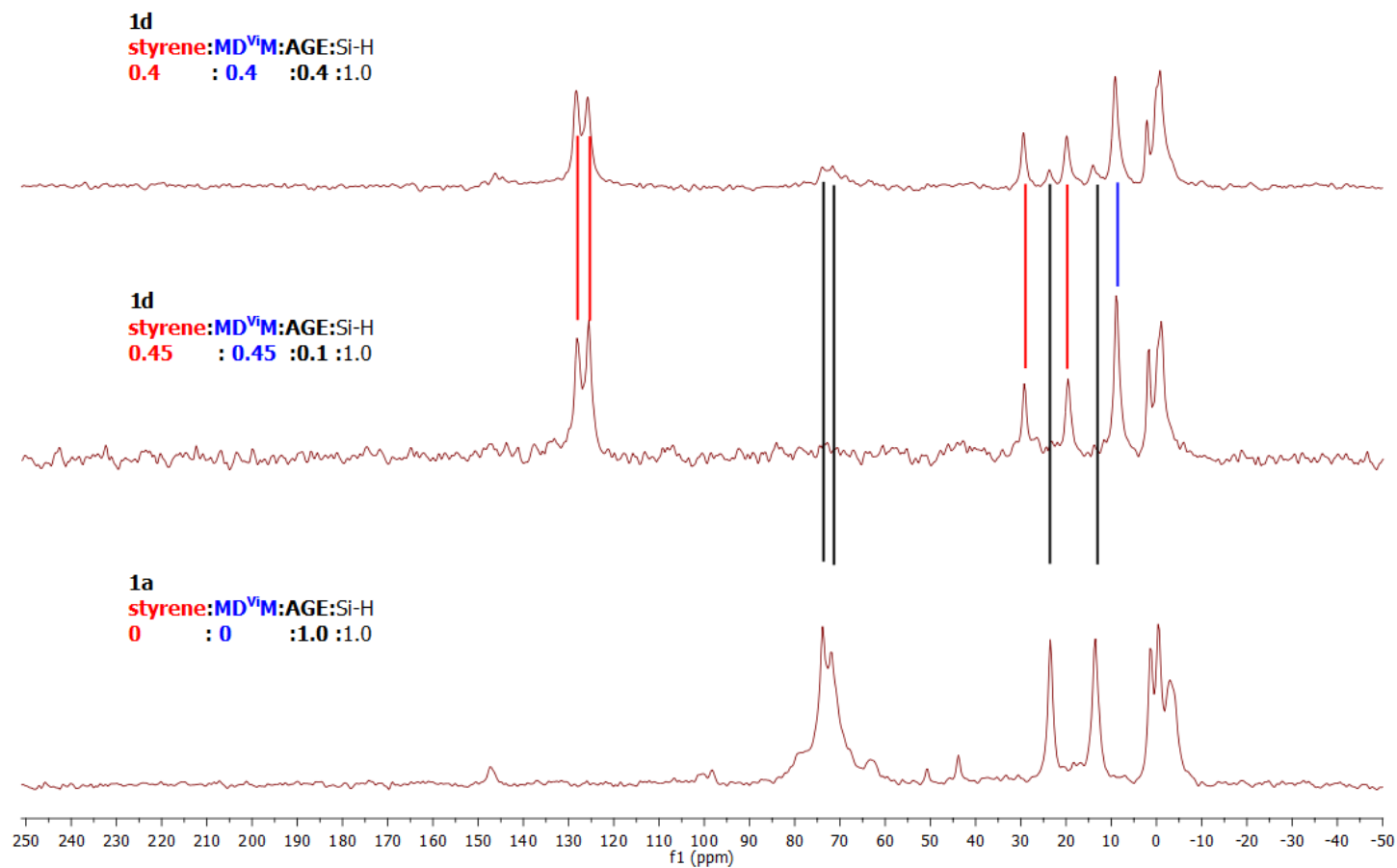


**Figure S3.** Comparison of  $^{29}\text{Si}$  chemical shifts of **1a** (top), **AAP** (second from the top), **APK** (second from the bottom) and **5a** (bottom).

## Comparison of $^{13}\text{C}$ and $^{29}\text{Si}$ CPMAS spectra of **1d** and **1d'** with **1a**

Discussion of chemical shifts from Figure S4:

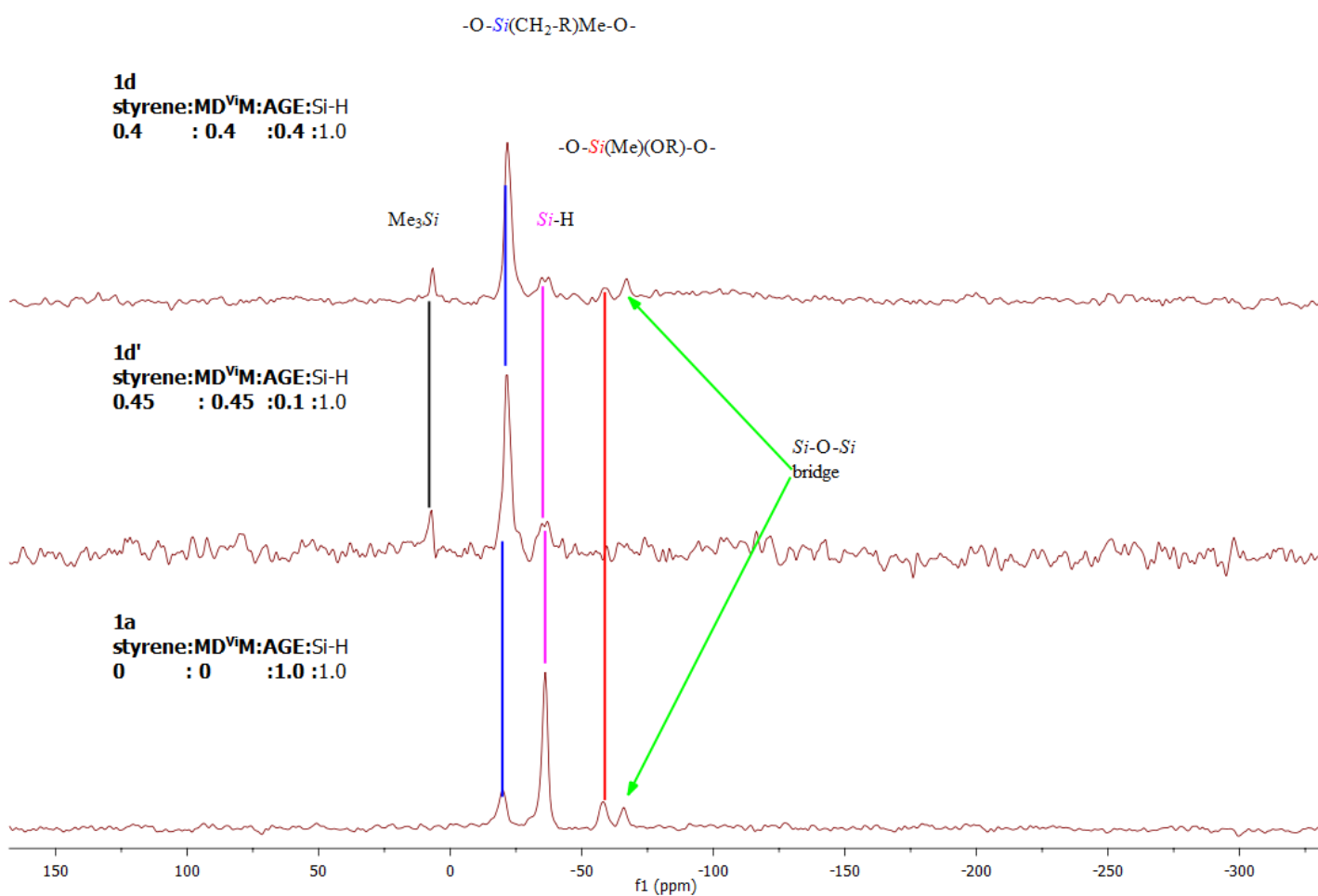
The  $^{13}\text{C}$  spectra of **1d** and **1d'** are practically identical, as the signals corresponding to incorporated styrene and MD<sup>Vi</sup>M are present in both spectra. The only differences are based on the  $^{13}\text{C}$  chemical shifts of AGE, which in case of **1d'** are non-visible due to low concentration of AGE in the starting mixture.



**Figure S4.** Comparison of  $^{13}\text{C}$  chemical shifts of **1d** (top), **1d'** (middle) and **1a** (bottom).

## Discussion of chemical shifts from Figure S5:

Similarly to Figure S4, the  $^{29}\text{Si}$  signals corresponding to formation of Si-C bonds (noted in blue, at ca. -20 to -22 ppm) via hydrosilylation of styrene and MD<sup>Vi</sup>M, and incorporated MD<sup>Vi</sup>M (noted in black, Me<sub>3</sub>Si signal at 6-7 ppm) are present in both spectra. The only observable differences arise from the quantity of AGE used in both reaction mixtures, as with higher AGE amount in **1d** the Si-O-C bond and Si-O-Si bridge  $^{29}\text{Si}$  signals are visible in the spectrum, while for **1d'** those signals are not observed due to low concentration.



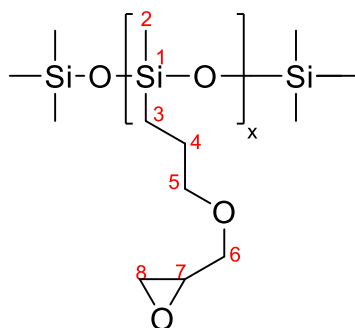
**Figure S5.** Comparison of  $^{29}\text{Si}$  chemical shifts of **1d** (top), **1d'** (middle) and **1a** (bottom).

## Isolation and characterization of PMHS oils and cross-linked materials

After the designated reaction time the crude mixtures from Table S1 and all entries without PMHS in Table S4 (color varied from pale orange-brown to almost colorless) were passed through silica column (1.5 cm in height in Pasteur pipette) and eluted with pentane. The collected solution was placed under vacuum to remove the solvent and left to dry under vacuum at 60 °C. Remaining non-cross-linked products were colorless viscous oils.

## Synthesis of test-reaction products

### Functionalization of PMHS with AGE using Karstedt catalyst (APK)



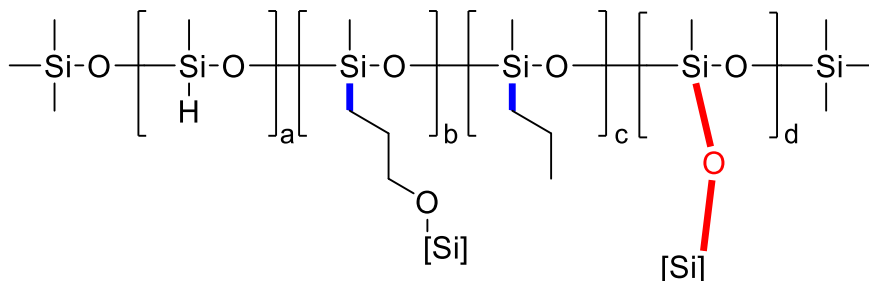
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.69 (dd, J 11.5, 3.0 Hz, *H*6), 3.47-3.32 (m, *H*5 and *H*6), 3.12 (ddt, J 5.8, 4.1, 2.9 Hz, *H*7), 2.77 (dd, *H*8), 2.58 (dd, J 5.0, 2.7 Hz, *H*8), 1.60 (m, *H*4), 0.55-0.44 (mfom, *H*3), 0.08, 0.07, 0.06 (s, all Si-CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 74.19 (*C*5/*C*6), 71.62 (*C*6/*C*5), 50.99 (*C*7), 44.36 (*C*8), 23.37 (*C*4), 13.63 (*C*3), 2.02, 1.15, -0.26 (all Si-CH<sub>3</sub>).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ -22.4 (*Si*1).

The product is isolated as colorless liquid (147 mg).

### Functionalization of PMHS with allyl alcohol (AAP)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  7.12 (traces of toluene), 6.12 (traces of olefinic C-H), 4.57 (Si-H), 3.55 (O-CH<sub>2</sub>), 1.41 (CH<sub>2</sub>), 0.78 (CH<sub>2</sub>, Si-CH<sub>2</sub>), 0.03 (Si-CH<sub>3</sub>).

$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  139.1 and 137.6 (olefinic C=C), 106.4 (O-CH=CH-, from isomerization of allyl alcohol), 75.0 and 64.1 (both O-CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 25.9 (Si-CH<sub>2</sub>-CH<sub>2</sub>), 13.4 and 10.6 (both Si-CH<sub>2</sub>-CH<sub>2</sub>), 1.3, -0.6 and -4.0 (all Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  7.9 (end-group SiMe<sub>3</sub>), -20.9 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.9 (Si-H), -59.1 (-O-Si(Me)(OR)-O-), -66.6 (Si-O-Si bridge).

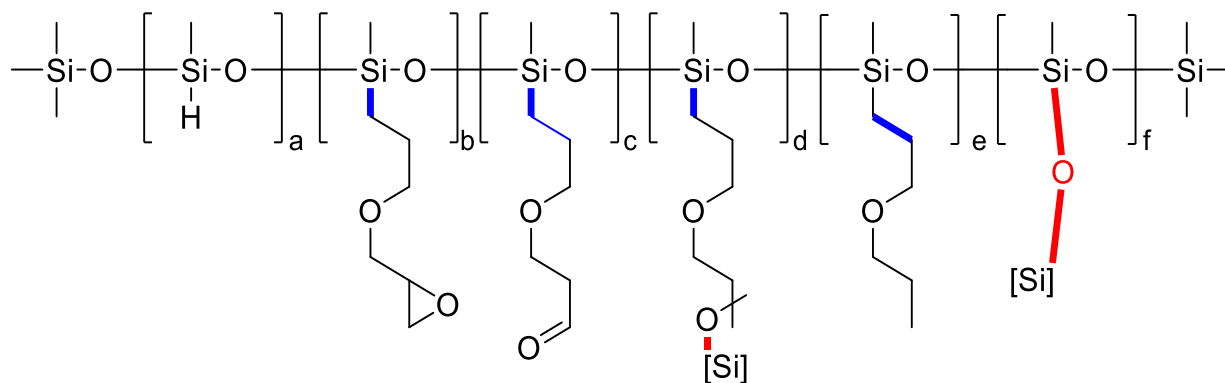
DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 2968 (m), 2942 (w), 2879 (w) (all alkane C-H), 2167 (w, Si-H), 1666 (w, alkane CH<sub>2</sub>), 1464 (w, alkane CH<sub>2</sub>), 1407 (w, Si-CH<sub>3</sub>), 1391 (w), 1271 (s, Si-CH<sub>3</sub>), 1157 (s, Si-O-(CH<sub>2</sub>)<sub>3</sub>, Si-O-Si, Si-CH<sub>2</sub>(CH<sub>2</sub>)<sub>x</sub>R), C-O), 919 (m), 850 (m), 796 (m).

The product is isolated as white solid (141 mg).

### Functionalization of PMHS with alkenes – formation of functionalized siloxane oils and cross-linked silicone materials

NB! The structures proposed here represent general structure of the formed polymers. They do not correspond to block-polymers as drawn but should be viewed as illustration of the linked network and how different ester, C=O and epoxide groups can lead to cross-linking of PMHS chains. a+b+c+d+e+f+g=50

#### Functionalization of PMHS with allyl glycidyl ether (1a)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  6.24 and 6.00 (olefinic C-H), 4.78 (Si-H), 4.33, 3.65 and 3.46 (O-CH<sub>2</sub>, O-CH), 3.05, 2.69, 2.51, 1.58, 1.16, 0.95, 0.63 (CH<sub>2</sub>, CH), 0.18 (Si-CH<sub>3</sub>).



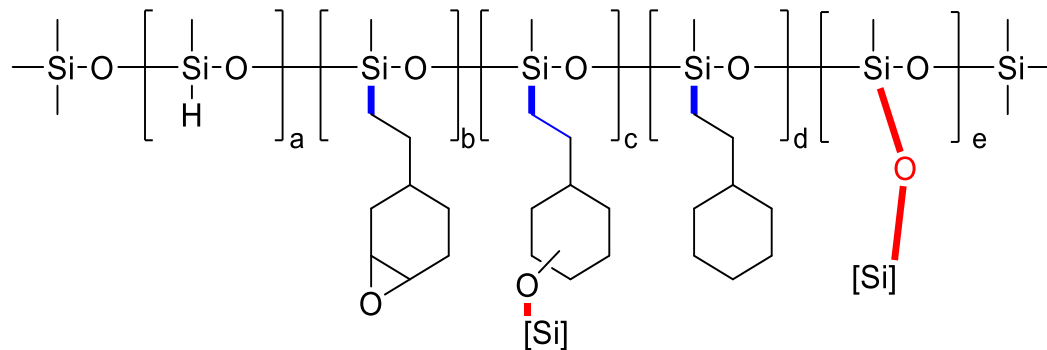
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  147.3 (olefinic  $\text{C}=\text{C}$ ), 100.4 and 98.3 (acetal C or  $\text{Si}-\text{O}-\text{CH}=\text{CH}-$  from isomerization of AGE), 78.5, 73.8, 72.0, 63.3, 50.8 ( $\text{O}-\text{CH}_2$ ), 43.8, 23.5, 18.3 and 16.8 ( $\text{CH}_2$ ), 13.6 ( $\text{CH}_2-\text{Si}$ ), 1.3, -0.4 and -2.9 ( $\text{Si}-\text{CH}_3$ ).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -20.1 ( $-\text{O}-\text{Si}(\text{CH}_2-\text{R})\text{Me}-\text{O}-$ ), -36.3 ( $\text{Si}-\text{H}$ ), -58.3 ( $-\text{O}-\text{Si}(\text{Me})(\text{OR})-\text{O}-$ ), -66.2 ( $\text{Si}-\text{O}-\text{Si}$  bridge).

DRIFT (293 K,  $\text{cm}^{-1}$ ):  $\nu$  = 3488 (m, O-H), 3052 (m, C-H of epoxide ring), 2960 (s), 2932 (s) and 2874 (s) (all alkane C-H), 2803 (m, aldehyde C-H), 2746 (w, aldehyde C-H), 2161 (s, Si-H), 1735 (m, aldehyde  $\text{C}=\text{O}$ ), 1664 (m), 1458 (m, alkane  $\text{CH}_2$ ), 1409 (m, O-H, epoxide ring C-H) and 1378 (m, epoxide ring C-H), 1338 (m, ether  $\text{CH}_2$ ), 1281 (s, Si- $\text{CH}_3$ , epoxide ring C-O), 1190 (s,  $\text{Si}-\text{CH}_2(\text{CH}_2)_x\text{R}$ ), 1155 (s, C-O), 918, 861, 813 (m).

The product is isolated as white-beige solid (294 mg). NB! Aldehyde C-H IR frequencies and acetal peaks may result from the epoxide group isomerization to aldehyde, which is described in the recent review.<sup>19</sup>

### Functionalization of PMHS with 1,2-Epoxy-4-vinylcyclohexane (1b)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  7.00 (trace of toluene), 5.62 (olefinic C-H), 4.67 ( $\text{Si}-\text{H}$ ), 2.88 ( $\text{O}-\text{CH}$ ), 1.85 and 1.18 ( $\text{CH}_2$ ), 0.08 ( $\text{Si}-\text{CH}_3$ )

$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  143.9 and 112.5 (unreacted  $\text{C}=\text{C}$  bond), 75.6, 73.4 and 70.1 (all three  $\text{CH}-\text{O}$  from opened epoxide ring), 51.0 (epoxide  $\text{C}-\text{O}$ ), 35.2, 32.0, 30.2, 27.2, 25.7 and 24.2 (all  $\text{CH}_2$ ), 14.2 ( $\text{Si}-\text{CH}_2$ ), 1.2, -0.5 and -3.1 (all three  $\text{Si}-\text{CH}_3$ ).

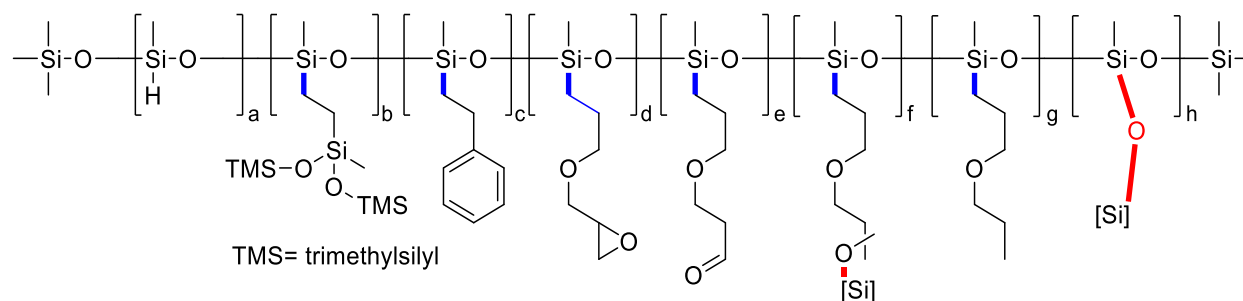
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -19.1 ( $-\text{O}-\text{Si}(\text{CH}_2-\text{R})\text{Me}-\text{O}-$ ), -35.9 ( $\text{Si}-\text{H}$ ), -58.9 ( $-\text{O}-\text{Si}(\text{Me})(\text{OR})-\text{O}-$ ), -65.8 ( $\text{Si}-\text{O}-\text{Si}$  bridge).

DRIFT (293 K,  $\text{cm}^{-1}$ ):  $\nu$  = 3084 (w, C-H of epoxide ring), 2969 (m), 2949 (m) and 2858 (m) (all three alkane C-H), 2677 (w), 2185 (m, Si-H), 1824 (w), 1733 (w, aliphatic ketone  $\text{C}=\text{O}$ ), 1670 (w, unreacted  $\text{C}=\text{C}$ ), 1641 (w, unreacted  $\text{C}=\text{C}$ ), 1455 (m) and 1435 (m) (both alkane C-H), 1415 (m) and 1381 (m) (both epoxide C-H), 1358

(m), 1341 (m), 1275 (s, Si-CH<sub>3</sub>, epoxide ring C-O), 1249 (m, Si-CH<sub>2</sub>(CH<sub>2</sub>)<sub>x</sub>R), 1160 (s, Si-O-(CH<sub>2</sub>)<sub>x</sub>R), 1143 (s, Si-O-Si), 926 (m), 820 (w).

The product is isolated as white solid (303 mg). NB! Ketone C-H IR frequencies may result from the epoxide group isomerization to ketone, which is described in the recent review.<sup>19</sup>

### Functionalization of PMHS with styrene, MD<sup>Vi</sup>M and allyl glycidyl ether (1d)



<sup>1</sup>H MAS SSNMR (300 MHz):  $\delta$  6.92 (aromatic C-H), 6.15, 5.96, 5.76 (all traces of olefinic C-H), 4.48 (Si-H), 3.23 (O-CH<sub>x</sub>), 2.54, 2.29, 2.21, 1.31 and 0.77 (all CH<sub>2</sub> and CH<sub>3</sub>), 0.34 and -0.08 (Si-CH<sub>3</sub>).

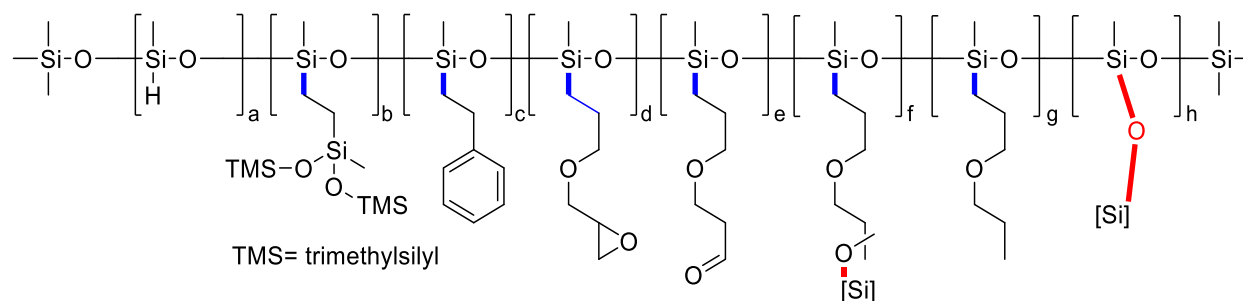
<sup>13</sup>C CPMAS SSNMR (75 MHz):  $\delta$  146.2 (*i*-C), 128.3 and 125.8 (*o*- and *m*-C), 73.9 and 71.6 (O-CH<sub>2</sub>), 29.4 (-CH<sub>2</sub>-Ph), 23.7 (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 19.9 (-CH<sub>2</sub>-CH<sub>2</sub>-Ph), 14.0 (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 9.1 (Si-CH<sub>2</sub>-CH<sub>2</sub>-Si), 2.1 and -0.8 (Si-CH<sub>3</sub>).

<sup>29</sup>Si CPMAS SSNMR (60 MHz):  $\delta$  6.7 (end-group SiMe<sub>3</sub>), -21.7 (Si-CH<sub>2</sub>-CH<sub>2</sub>-), -34.9 and -37.4 (both Si-H), -58.5 (-O-Si(Me)(OR)-O-), -67.0 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 3794 (w), 3740 (w), 3706 (w), 3648 (w), 3574 (w) (all alcohol O-H), 3112 (m), 3092 (m), 3066 (m), 3032 (m) (all aromatic C-H and epoxide ring C-H), 2974 (m), 2917 (m), 2795 (m) (all alkane C-H), 2666 (w), 2486 (w), 2163 (w, Si-H), 2103 (w, Si-H), 2021 (w), 1938 (m), 1878 (w), 1787 (w), 1749 (w, aldehyde C=O), 1655 (m), 1609 (m), 1578 (m), 1492 (m), 1455 (m) (all aromatic C=C), 1418 (m, O-H, epoxide ring C-H), 1267 (s, Si-CH<sub>3</sub>), 1235 (m, Si-CH<sub>2</sub>CH<sub>2</sub>-), 1144 (s) and 1127 (s) (both Si-O-Si), 878 (s), 861 (s), 804 (m).

The product is isolated as a milky white solid (171 mg). NB! Aldehyde C-H IR frequencies may result from the epoxide group isomerization to aldehyde, which is described in the recent review.<sup>19</sup>

## Functionalization of PMHS with styrene, MD<sup>vi</sup>M and allyl glycidyl ether (1d')



<sup>1</sup>H MAS SSNMR (300 MHz):  $\delta$  6.93 (aromatic C-H), 2.56 (-CH<sub>2</sub>-Ph), 0.79 (-CH<sub>2</sub>-CH<sub>2</sub>-Ph), 0.37 and -0.1 (Si-CH<sub>3</sub>).

<sup>13</sup>C CPMAS SSNMR (75 MHz):  $\delta$  128.2 and 125.7 (aromatic C=C), 29.3 (-CH<sub>2</sub>-Ph), 19.7 (-CH<sub>2</sub>-CH<sub>2</sub>-Ph), 9.0 (Si-CH<sub>2</sub>), 1.8 and -0.9 (Si-CH<sub>3</sub>).

<sup>29</sup>Si CPMAS SSNMR (60 MHz):  $\delta$  7.2 (end-group SiMe<sub>3</sub>), -21.5 (Si-CH<sub>2</sub>-CH<sub>2</sub>-Ph), -35.0 and -36.9 (Si-H).

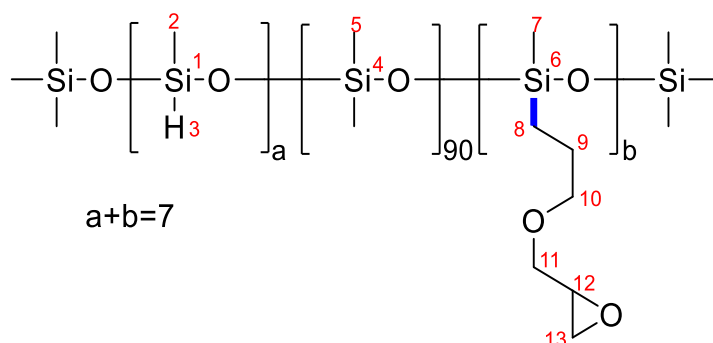
DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 3797 (w), 3734 (w), 3706 (w), 3654 (w) (all alcohol O-H), 3112 (m), 3086 (m), 3063 (m), 3032 (m) (all aromatic C-H and epoxide ring C-H), 2966 (m), 2926 (m), 2792 (m) (all alkane C-H), 2675 (w), 2498 (w), 2152 (w, Si-H), 2006 (w), 1944 (w), 1884 (w), 1801 (w), 1744 (w, aldehyde C=O), 1664 (m), 1607 (m), 1575 (m), 1504 (m), 1452 (m) (all aromatic C=C), 1412 (m, O-H, epoxide ring C-H), 1270 (s, Si-CH<sub>3</sub>), 1235 (m, Si-CH<sub>2</sub>CH<sub>2</sub>-), 1187 (s, Si-(CH<sub>2</sub>)<sub>x</sub>), 1150 (s) and 1132 (s) (both Si-O-Si), 881 (s), 861 (s), 804 (m).

The product is isolated as beige solid (353 mg). NB! Aldehyde C-H IR frequencies may result from the epoxide group isomerization to aldehyde, which is described in the recent review.<sup>19</sup>

## Functionalization of MD<sub>90</sub>D'<sub>7</sub>M, M'D<sub>18</sub>M', TMDS and MD'M with alkenes

NB! The structure proposed here for **2a** represents general structure of the functionalized polymer. It does not correspond to block-polymers as drawn, but should be viewed as illustration.

### Functionalization of MD<sub>90</sub>D'<sub>7</sub>M with AGE (**2a**)

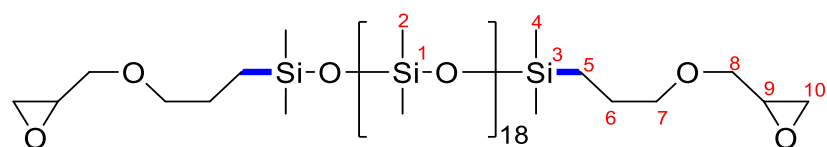


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.68 (s, *H*3), 3.68 (d, *J* 9.2 Hz, *H*11), 3.51-3.32 (m, *H*10 and *H*11), 3.14 (s, *H*12), 2.79 (m, *H*13), 2.60 (br. s, *H*13), 1.63 (m, *H*9), 0.50 (nfom, *H*8), 0.07 (s, *H*2+*H*5+*H*7).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 74.3 and 71.5 (*C*10 and *C*11), 51.0 (*C*12), 44.5 (*C*13), 25.4, 23.3, 13.5 (*C*8), 1.9, 1.2 and 1.0 (*C*5), 0.4 (*C*7).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ 7.3 (*Si*Me<sub>3</sub>), -20.5, -21.6, -21.9 and -22.6 (*Si*4+*Si*6), -37.5 (*Si*1) The product is isolated as colorless liquid (445 mg).

### Functionalization of M'D<sub>18</sub>M' with AGE (**3a**)

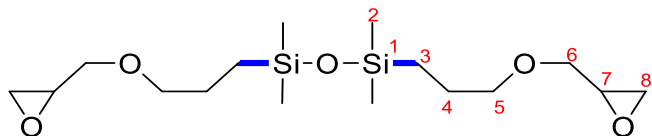


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.69 (d, *J* 11.1 Hz, 1H, *H*8), 3.53-3.32 (m, 3H, *H*7+*H*8), 3.14 (br. s, 1H, *H*9), 2.79 (m, 1H, *H*10), 2.65-2.57 (m, 1H, *H*10), 1.66-1.55 (m, 2H, *H*6), 0.56-0.48 (nfom, 2H, *H*5), 0.07 and 0.06 br. (s, *Si*-*CH*<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 74.5 and 71.6 (*C*7 and *C*8), 51.0 (*C*9), 44.5 (*C*10), 23.6 (*C*6), 14.2 (*C*5), 1.3 (*C*2), 1.2 (*C*2), 0.2 (*C*4).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.7 (*SiMe*<sub>2</sub>R), -21.3 and -21.9 (*SiI*). The product is isolated as colorless liquid (468 mg).

### 1,1,3,3-tetramethyl-1,3-bis(3-(oxiran-2-ylmethoxy)propyl)disiloxane (4a)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.69 (dd,  $J = 11.5, 3.1$  Hz, 1H, *H*<sub>6</sub>), 3.50-3.39 (m, 2H, *H*<sub>5</sub>), 3.37 (dd,  $J = 11.5, 5.8$  Hz, 1H, *H*<sub>6</sub>), 3.14 (m, 1H, *H*<sub>7</sub>), 2.78 (dd,  $J = 5.0, 4.2$  Hz, 1H, *H*<sub>8</sub>), 2.59 (dd,  $J = 5.0, 2.7$  Hz, 1H, *H*<sub>8</sub>), 1.64-1.52 (m, 2H, *H*<sub>4</sub>), 0.49 (nfom, 2H, *H*<sub>3</sub>), 0.04 (s, 12H, *SiMe*<sub>2</sub>).

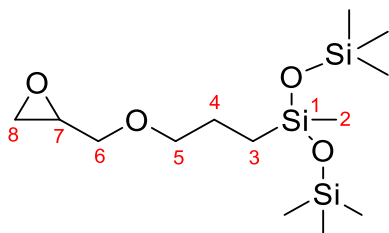
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  74.44 (*C*<sub>5</sub>/*C*<sub>6</sub>), 71.54 (*C*<sub>6</sub>/*C*<sub>5</sub>), 50.98 (*C*<sub>7</sub>), 44.45 (*C*<sub>8</sub>), 23.59 (*C*<sub>4</sub>), 14.32 (*C*<sub>3</sub>), 0.37 (*C*<sub>2</sub>).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.8 (*SiI*).

HRMS (ESI+)  $m/z$ : [*M*+Na]<sup>+</sup> Calcd for  $\text{C}_{16}\text{H}_{34}\text{Si}_2\text{O}_5\text{Na}$  385.1837, Found 385.1836.

The product is a colorless liquid (132 mg) obtained in 77% isolated yield.

### 1,1,1,3,5,5,5-heptamethyl-3-(3-(oxiran-2-ylmethoxy)propyl)trisiloxane (5a)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.70 (dd,  $J = 11.5, 3.2$  Hz, 1H, *H*<sub>6</sub>), 3.51-3.35 (m, 3H, *H*<sub>5</sub>+*H*<sub>6</sub>), 3.15 (dddd,  $J = 5.8, 4.1, 3.2, 2.7$  Hz, 1H, *H*<sub>7</sub>), 2.79 (dd,  $J = 5.1, 4.1$  Hz, 1H, *H*<sub>8</sub>), 2.61 (dd,  $J = 5.1, 2.7$  Hz, 1H, *H*<sub>8</sub>), 1.61 (nfom, 2H, *H*<sub>4</sub>), 0.45 (nfom, 2H, *H*<sub>3</sub>), 0.08 (s, 18H, *SiMe*<sub>3</sub>), 0.01 (s, 3H, *H*<sub>2</sub>). The spectroscopic data correspond to the reported data.<sup>20</sup>

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  77.16 (*C*<sub>5</sub>/*C*<sub>6</sub>), 74.36 (*C*<sub>6</sub>/*C*<sub>5</sub>), 51.00 (*C*<sub>7</sub>), 44.48 (*C*<sub>8</sub>), 23.4 (*C*<sub>4</sub>), 13.62 (*C*<sub>3</sub>), 1.96 (*Si*(*CH*<sub>3</sub>)<sub>3</sub>), -0.27 (*C*<sub>2</sub>).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.2 (*SiMe*<sub>3</sub>), -21.7 (*SiI*).

The product is a colorless liquid (78 mg) obtained in 49% isolated yield.

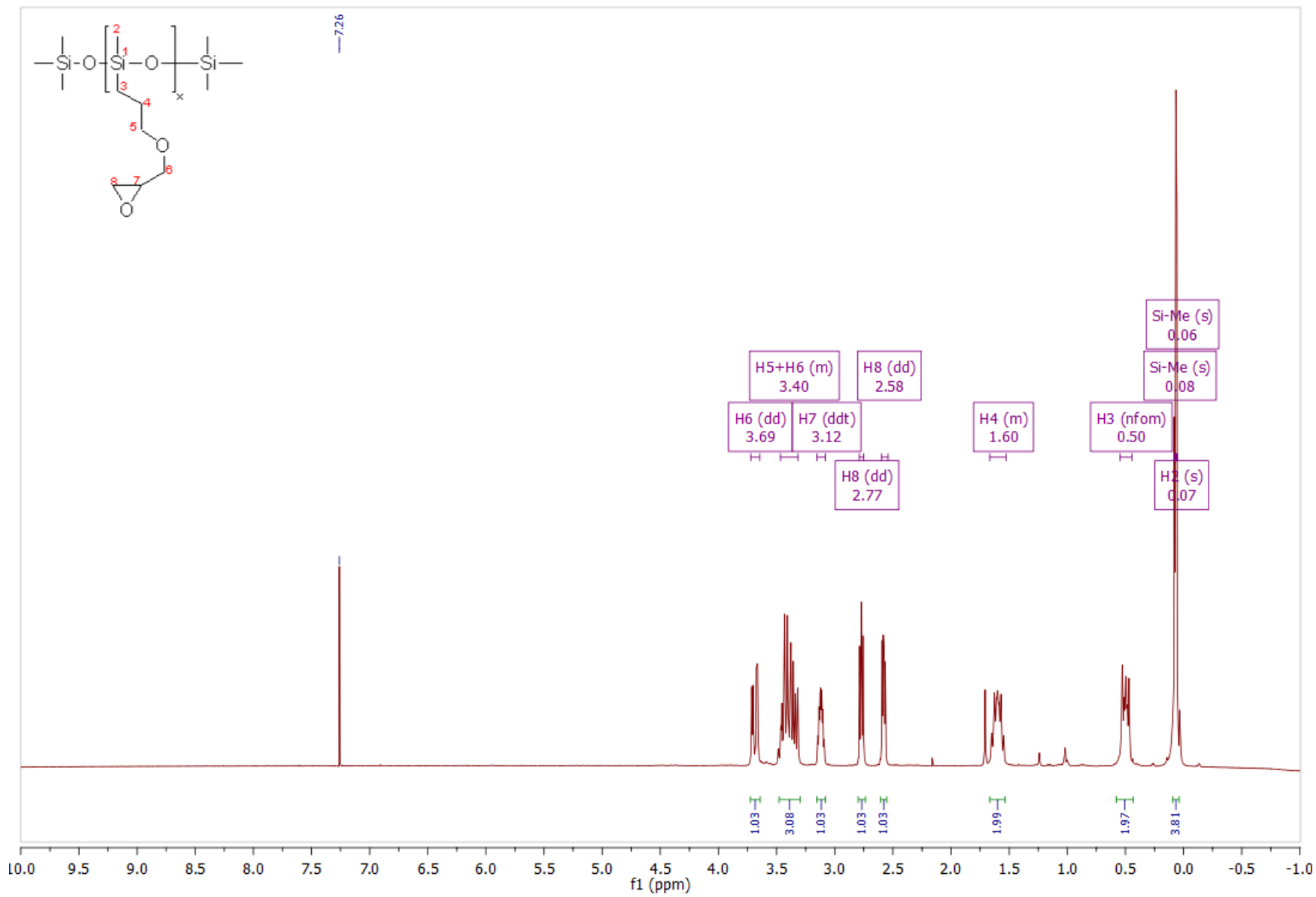
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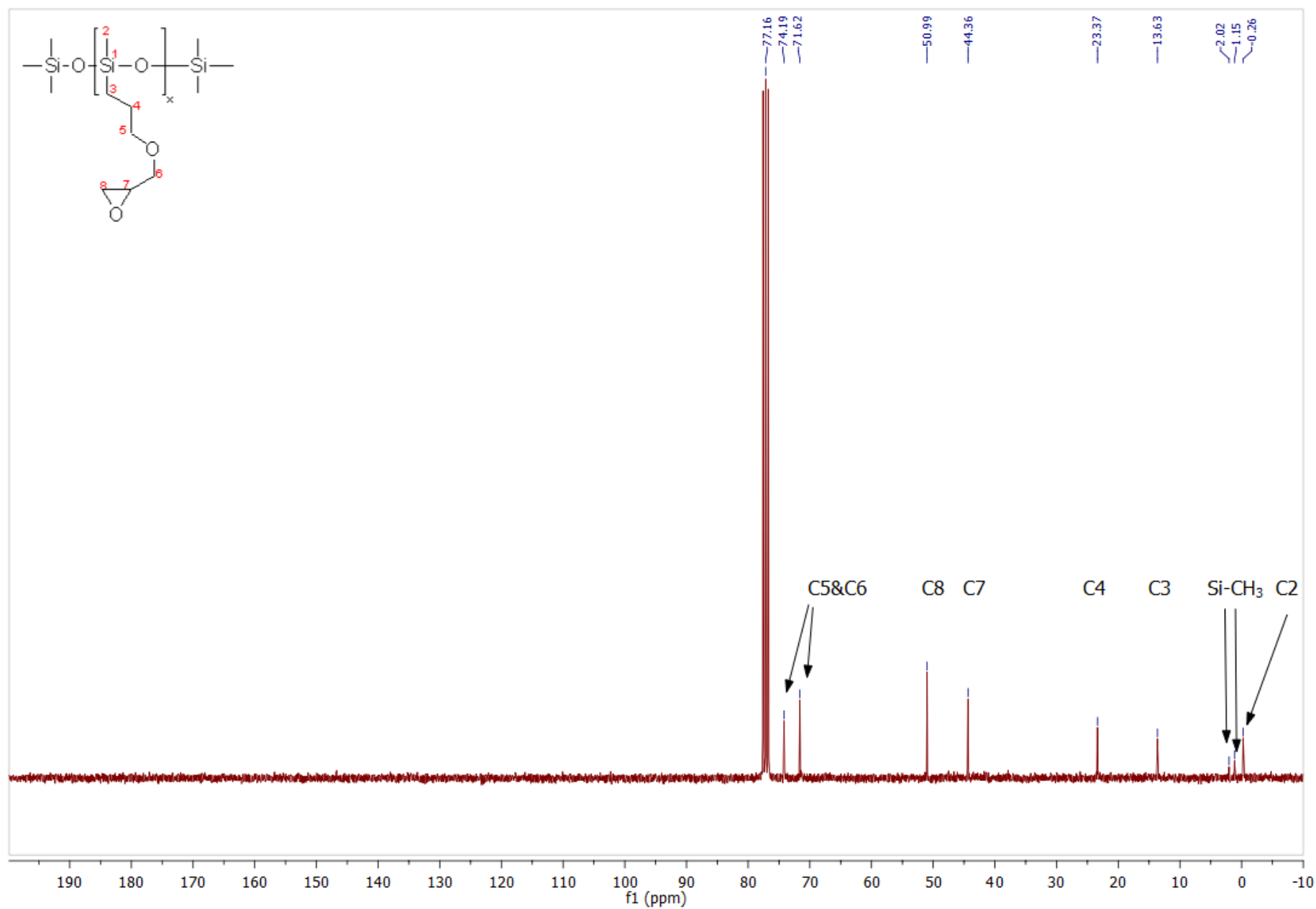
## NMR spectra

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of APK

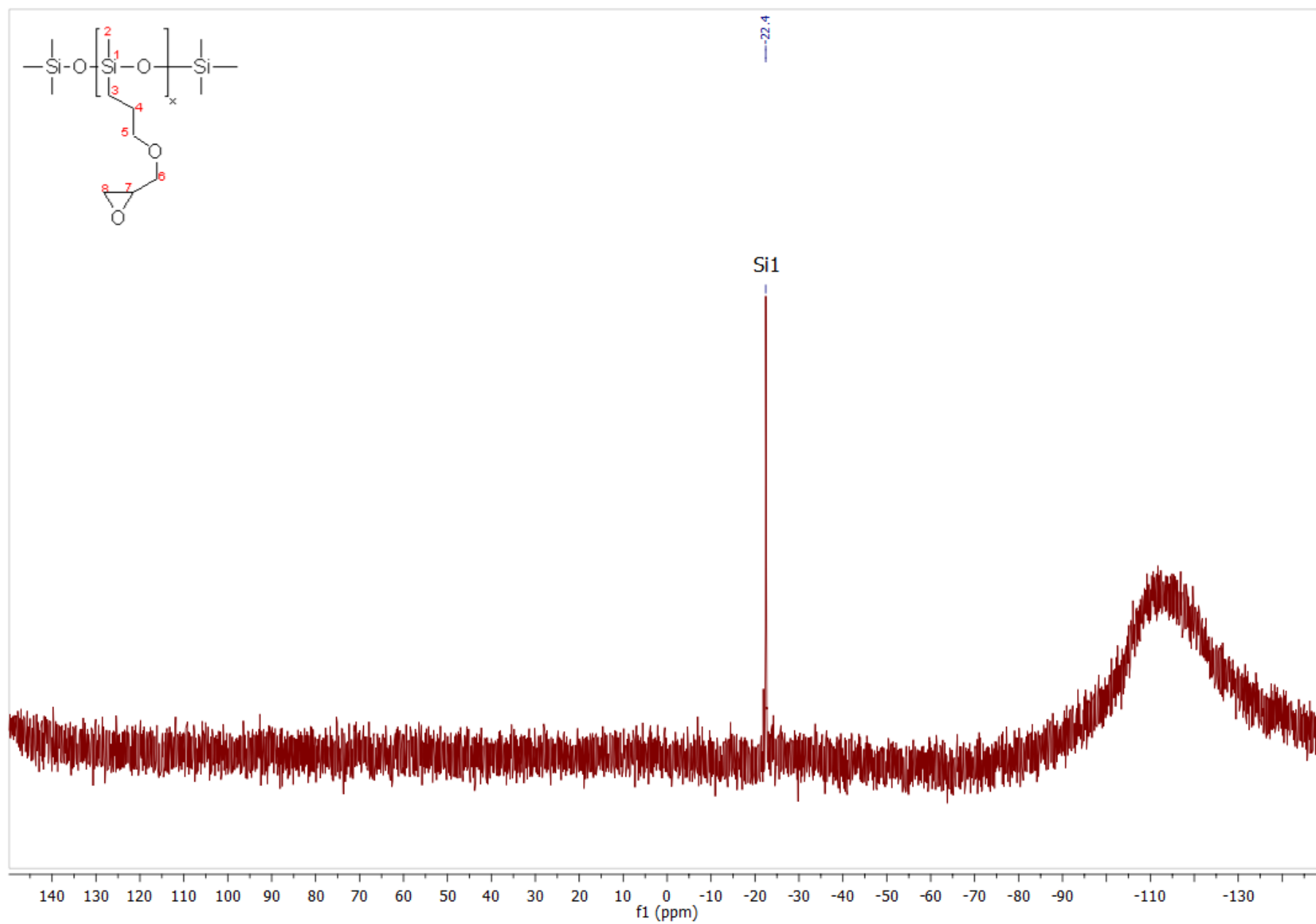




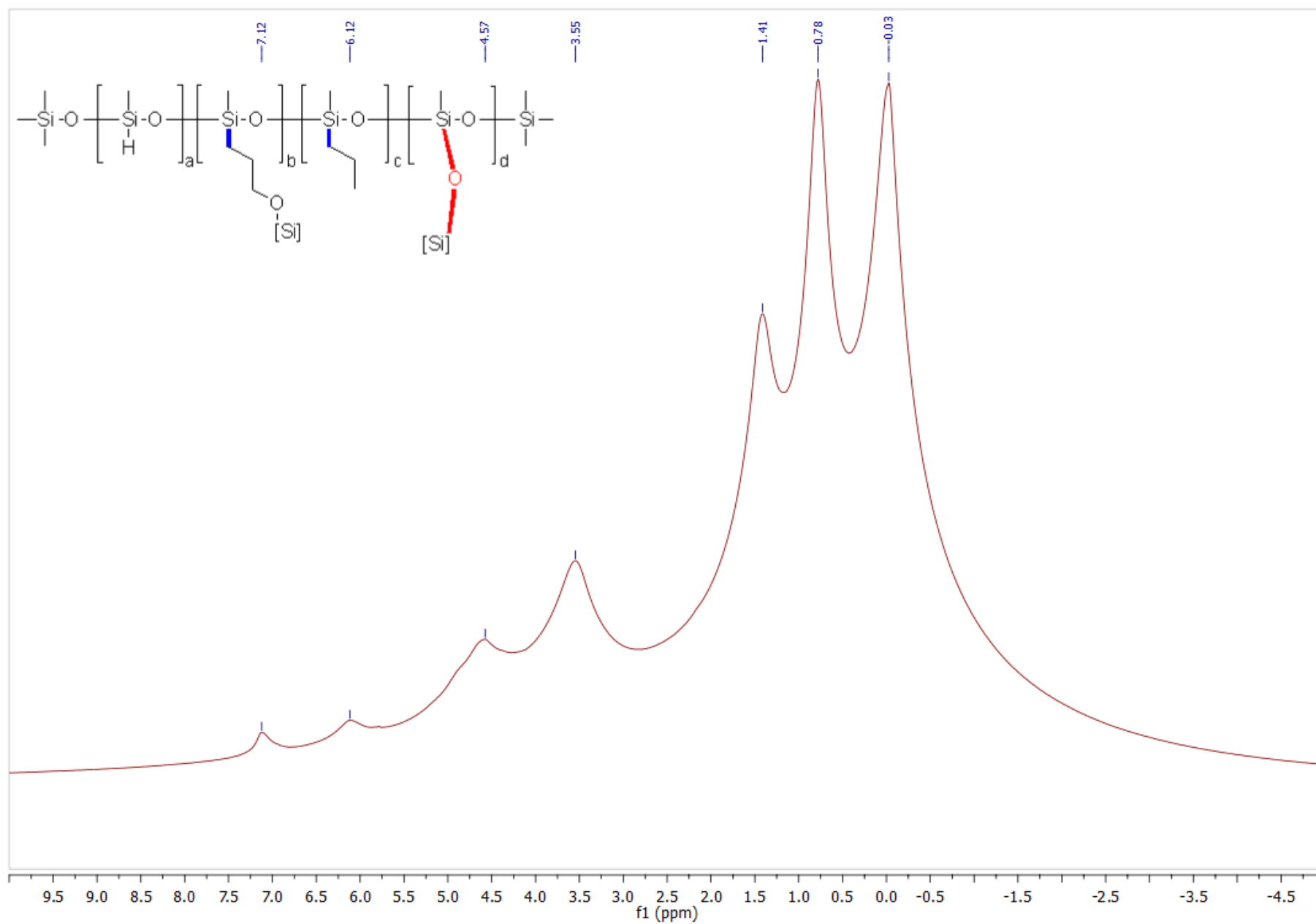
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of APK



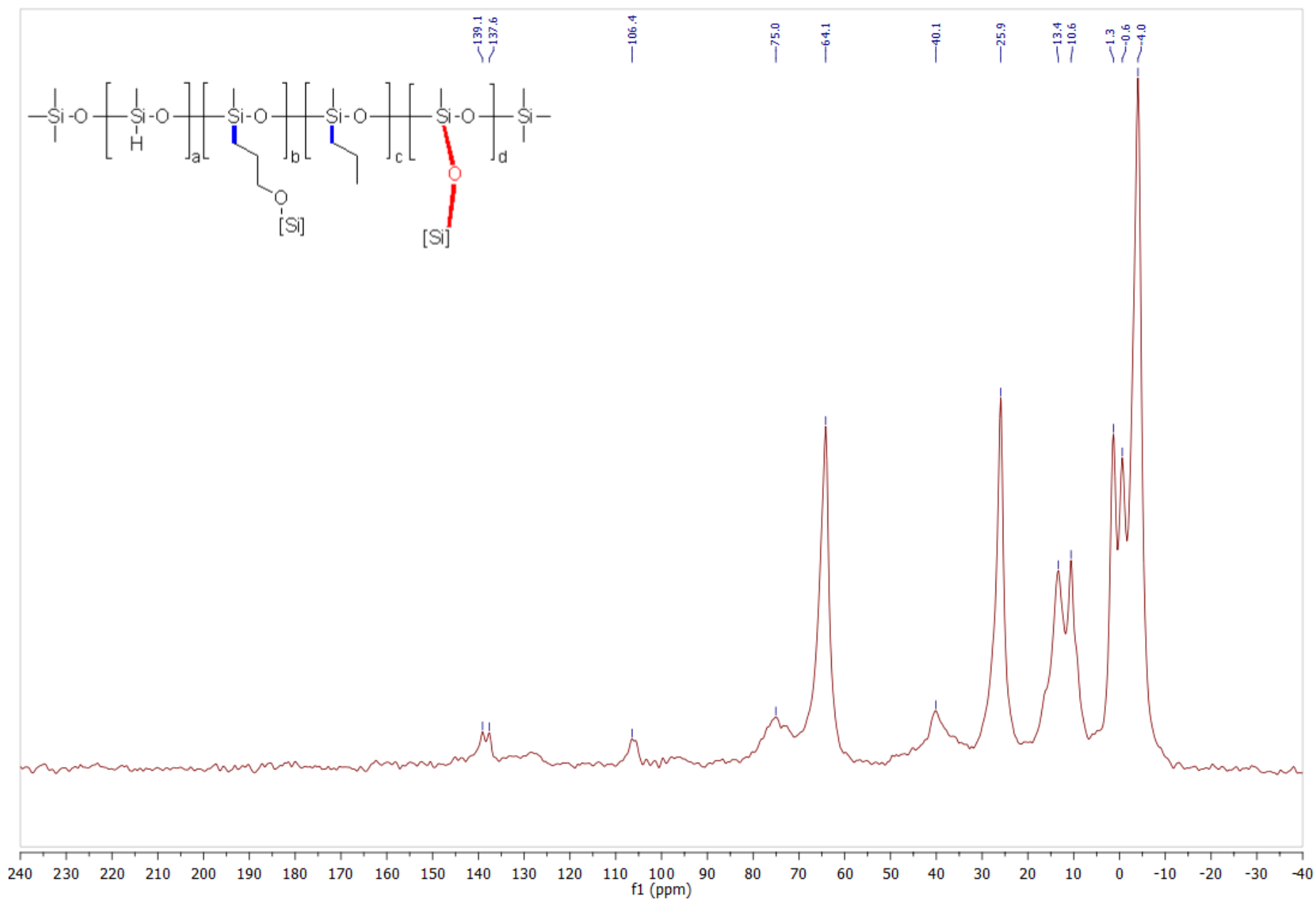
$^{29}\text{Si}$  {1H} NMR (60 MHz,  $\text{CDCl}_3$ ) spectrum of APK



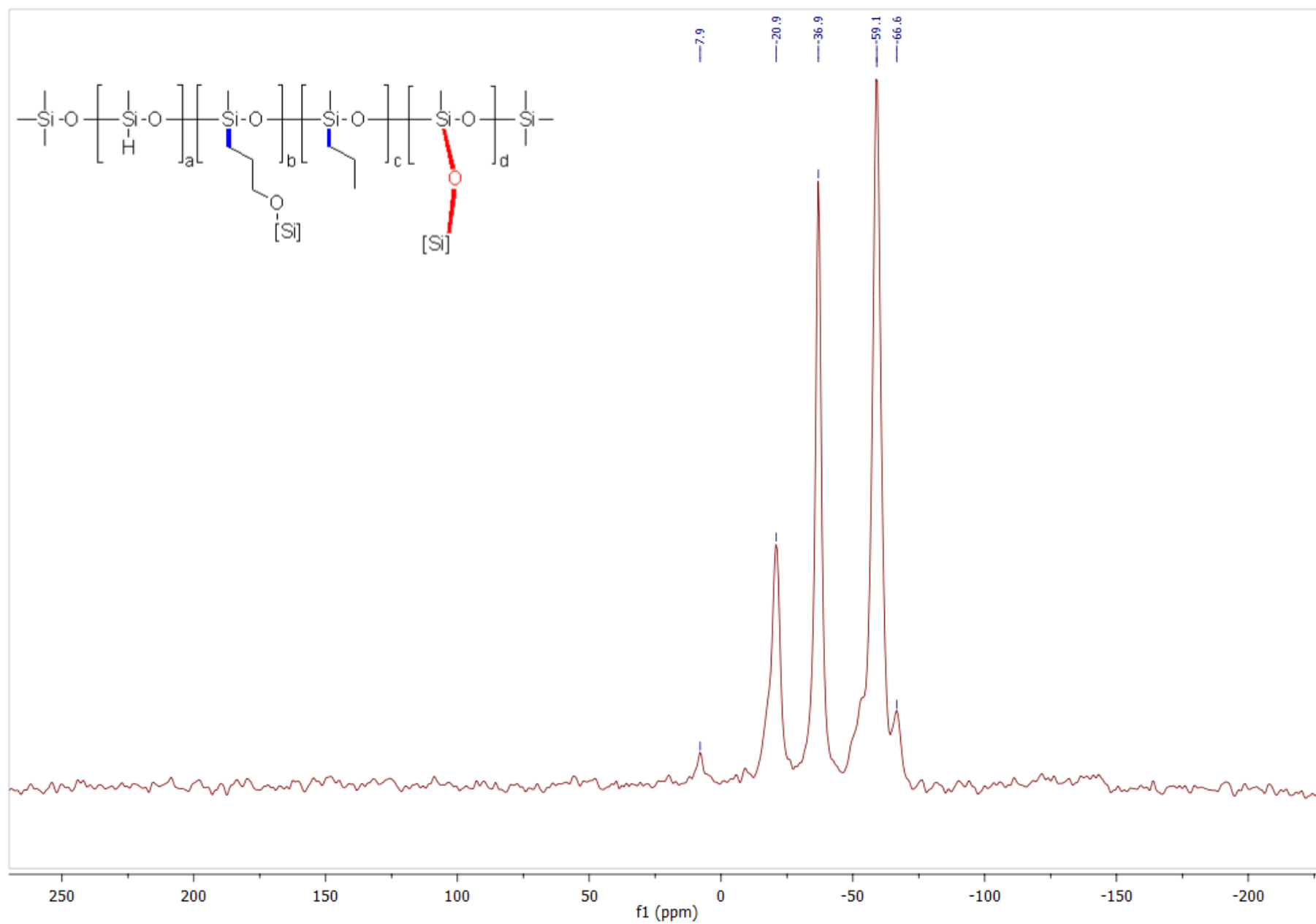
# $^1\text{H}$ MAS SS-NMR of AAP



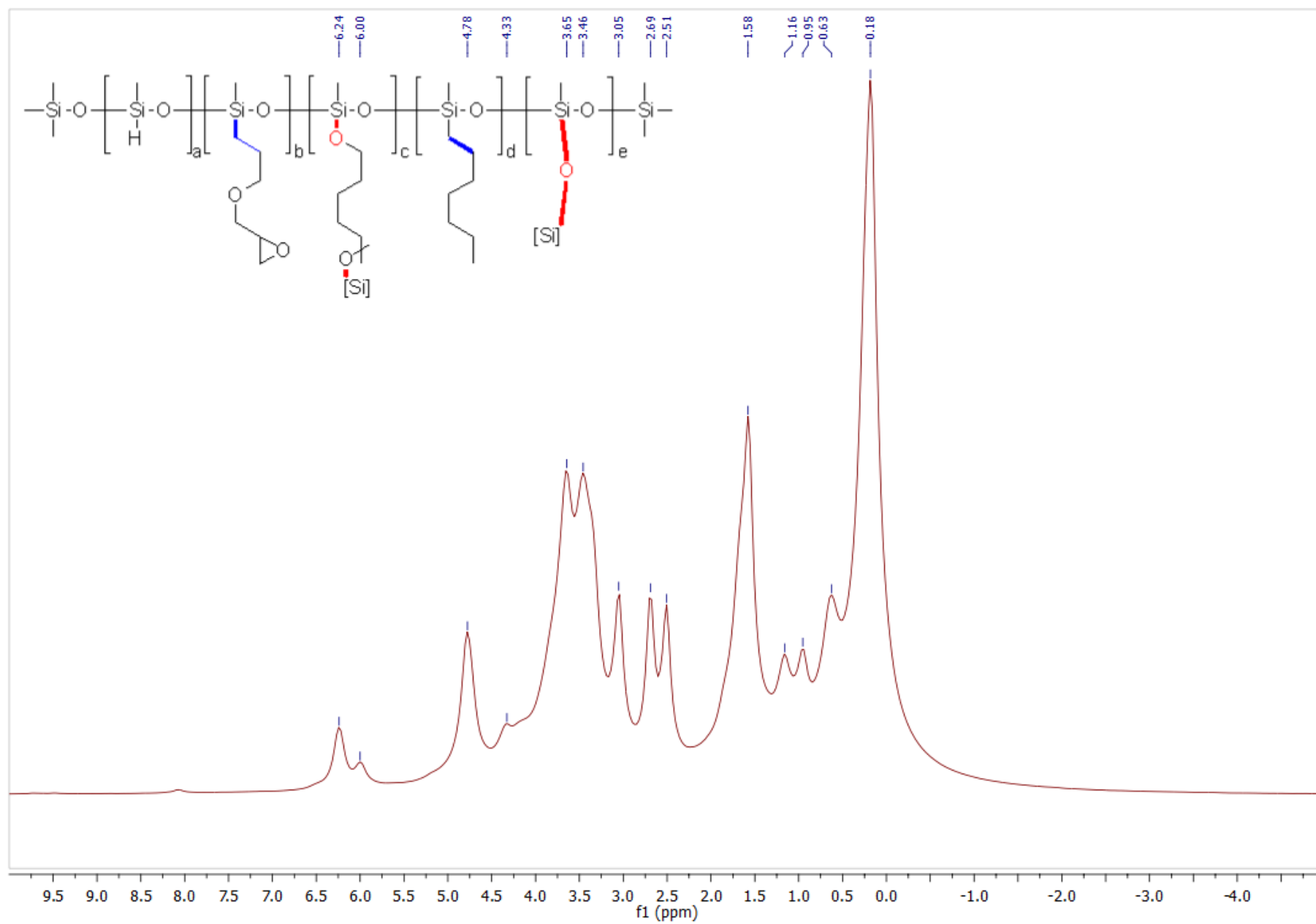
# $^{13}\text{C}$ CPMAS SS-NMR of AAP



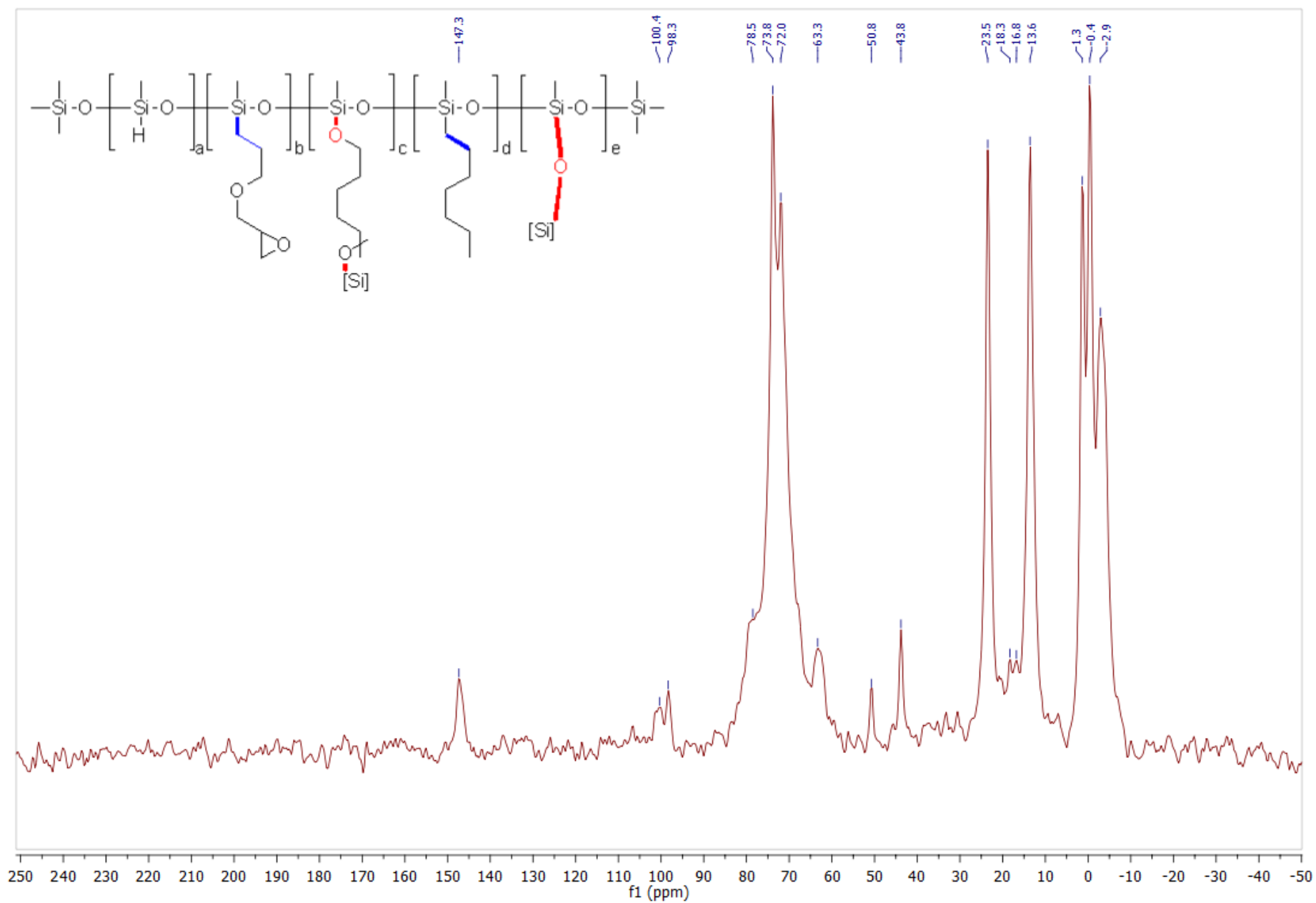
# $^{29}\text{Si}$ CPMAS SS-NMR of AAP



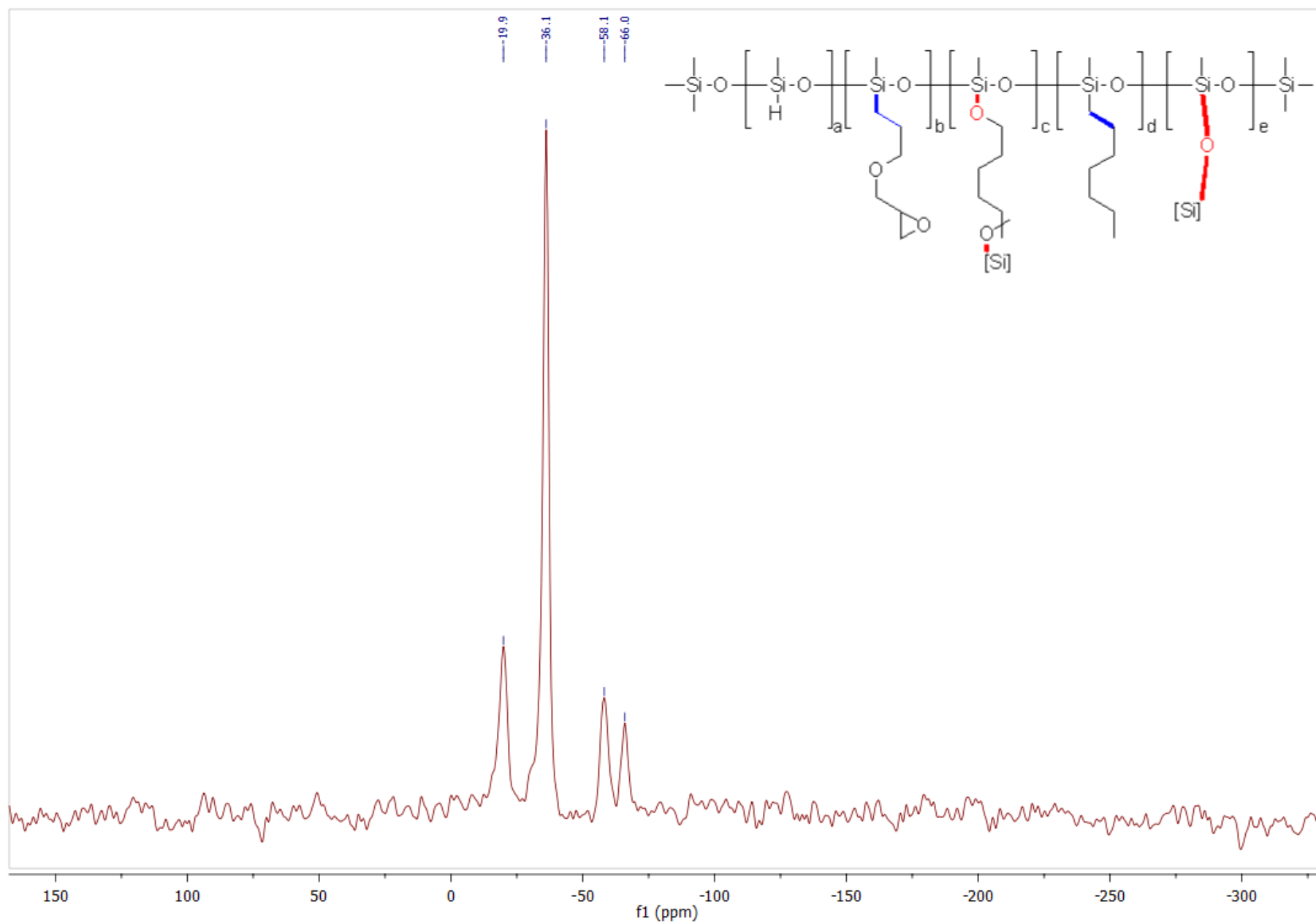
**<sup>1</sup>H MAS SS-NMR of 1a**



# <sup>13</sup>C CPMAS SS-NMR of 1a

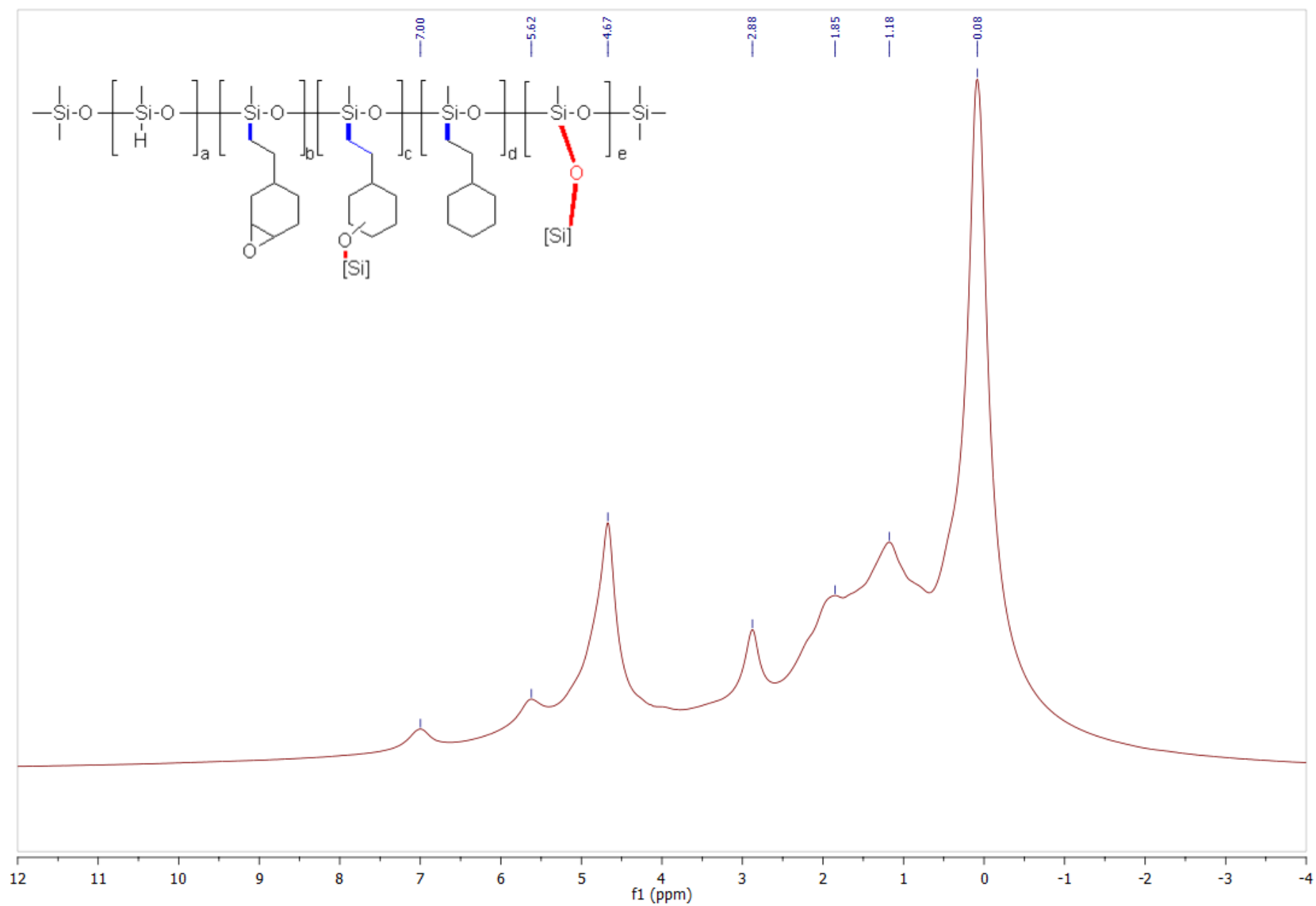


<sup>29</sup>Si CPMAS SS-NMR of 1a

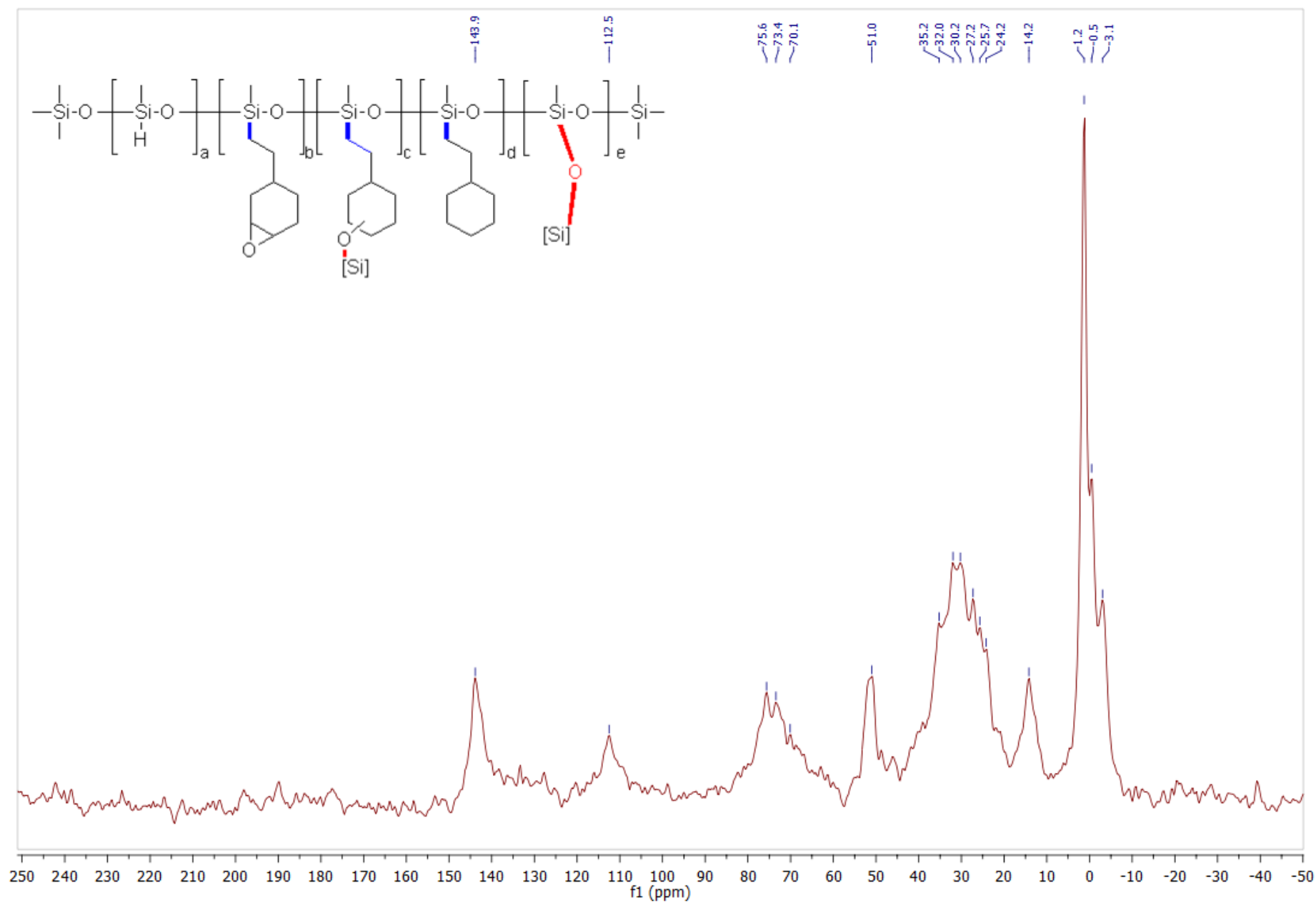




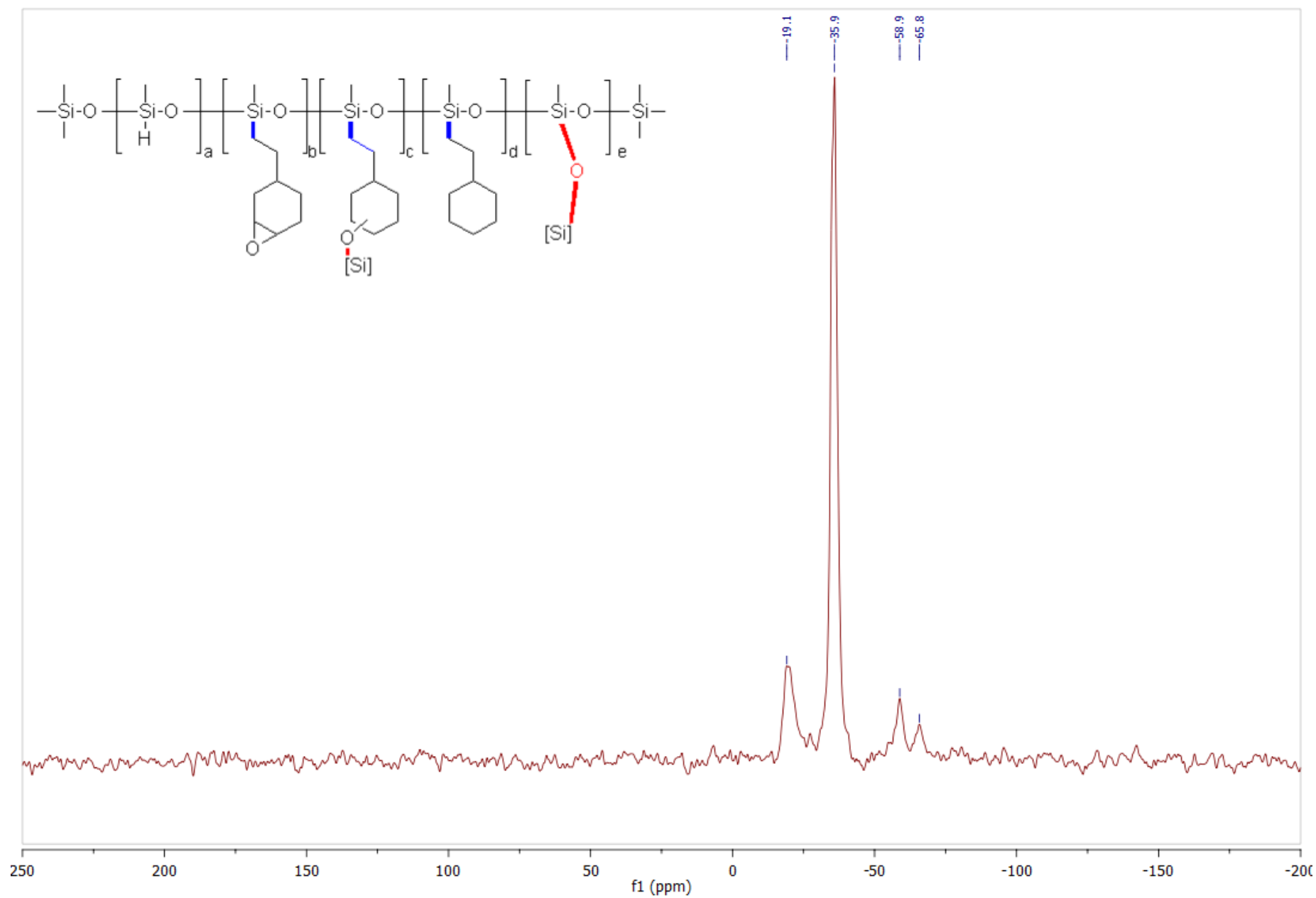
**<sup>1</sup>H MAS SS-NMR of 1b**



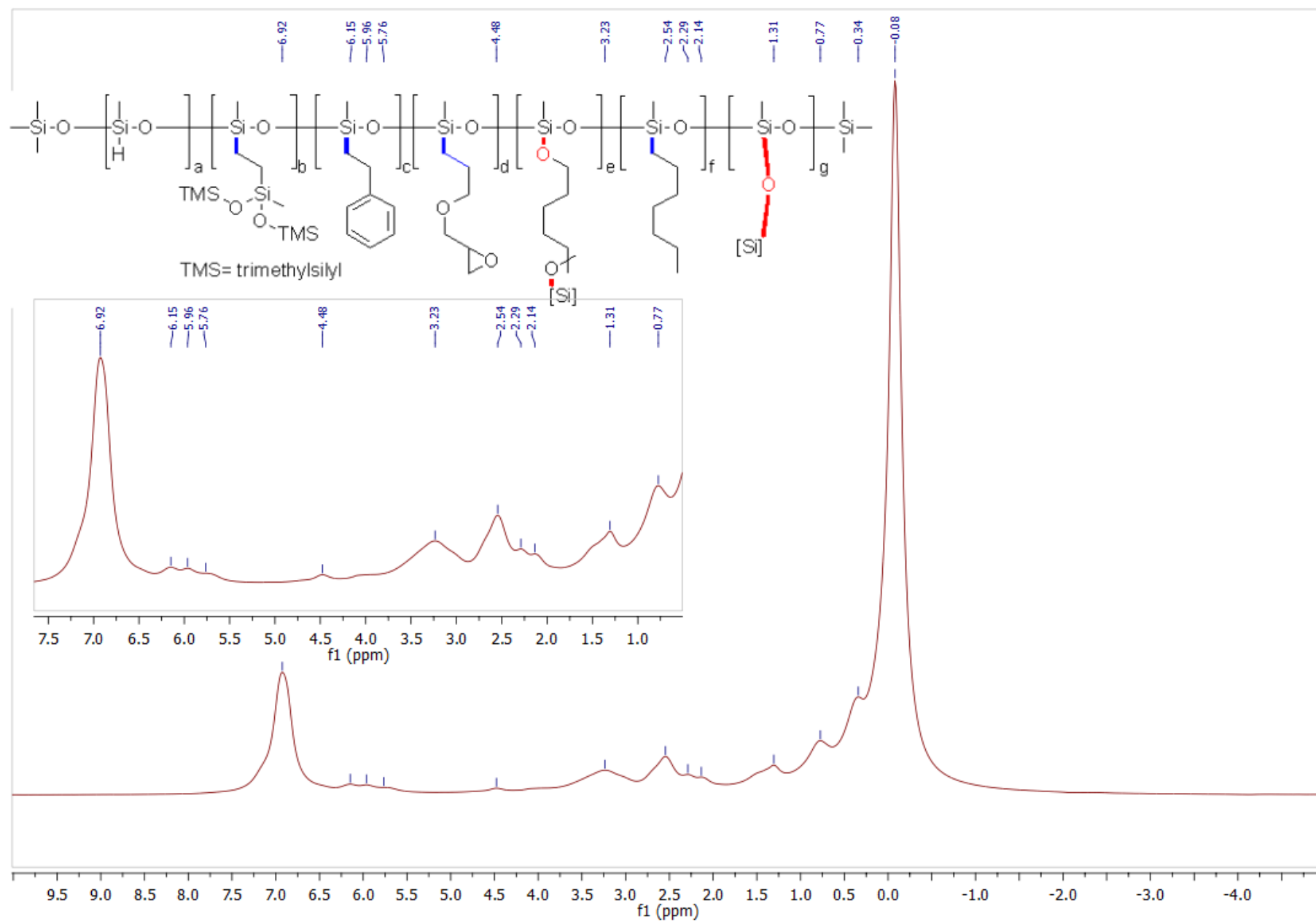
# <sup>13</sup>C CPMAS SS-NMR of epoxide 1b



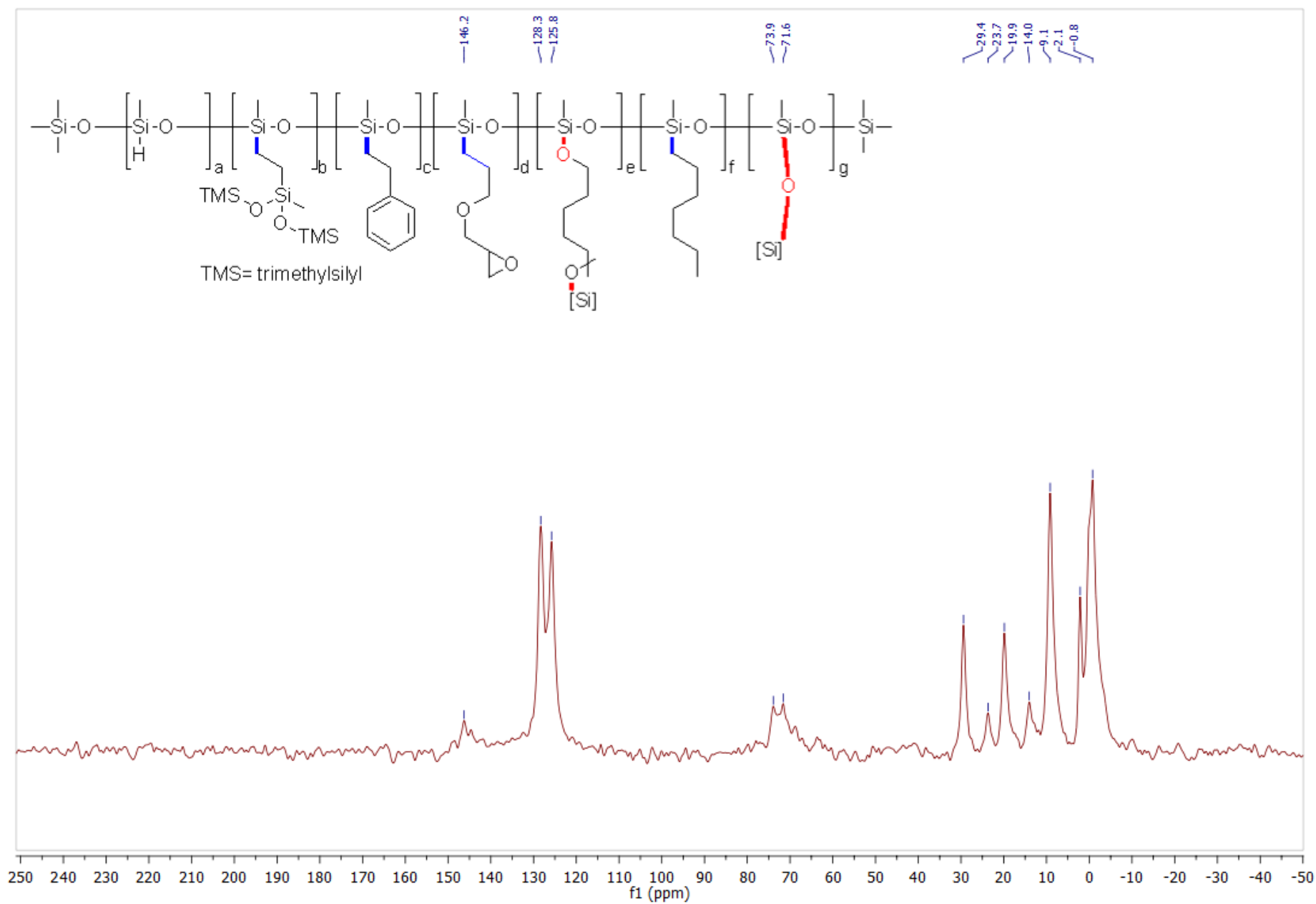
**$^{29}\text{Si}$  CPMAS SS-NMR of 1b**



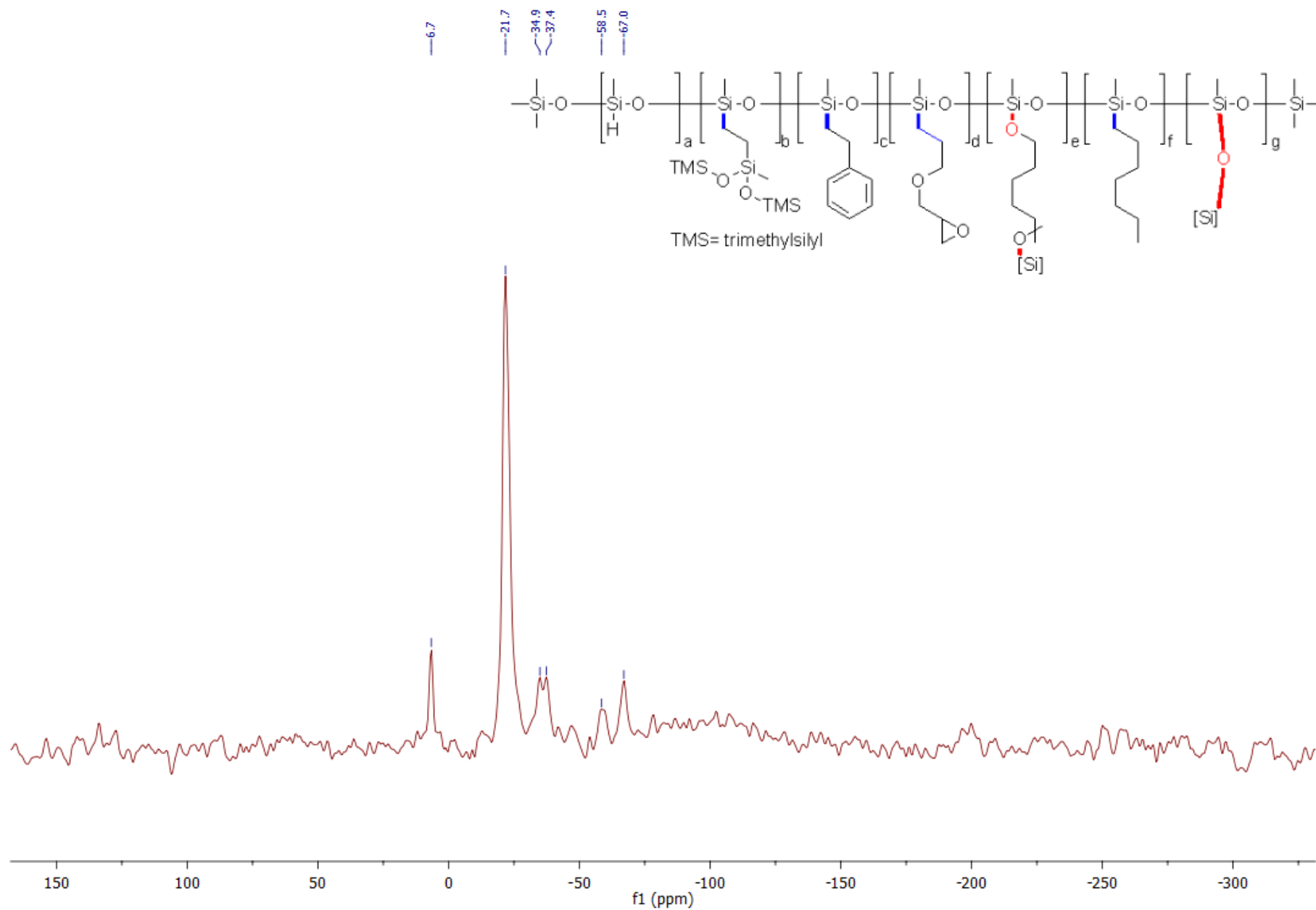
# $^1\text{H}$ MAS SS-NMR of 1d



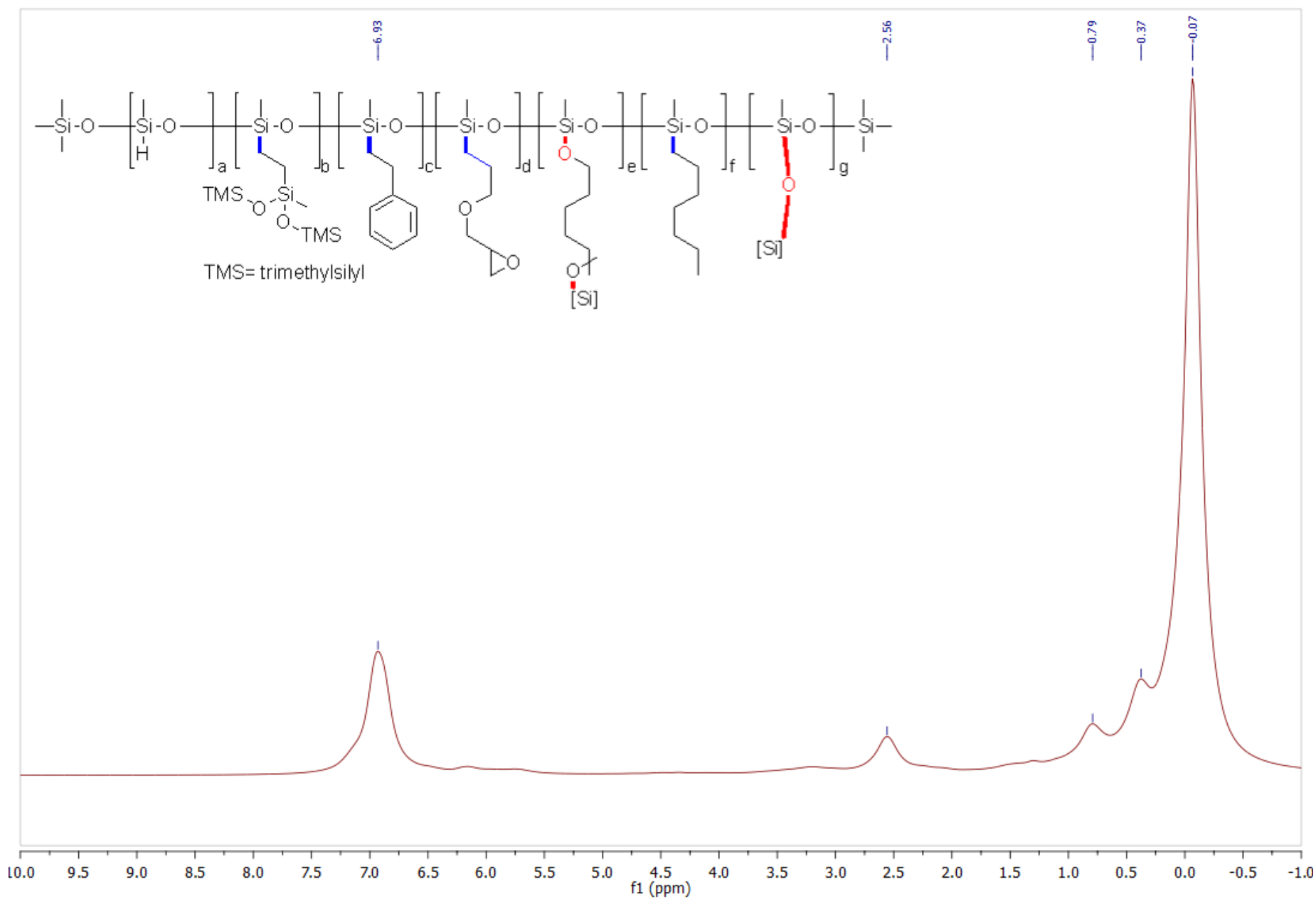
# $^{13}\text{C}$ CPMAS SS-NMR of 1d



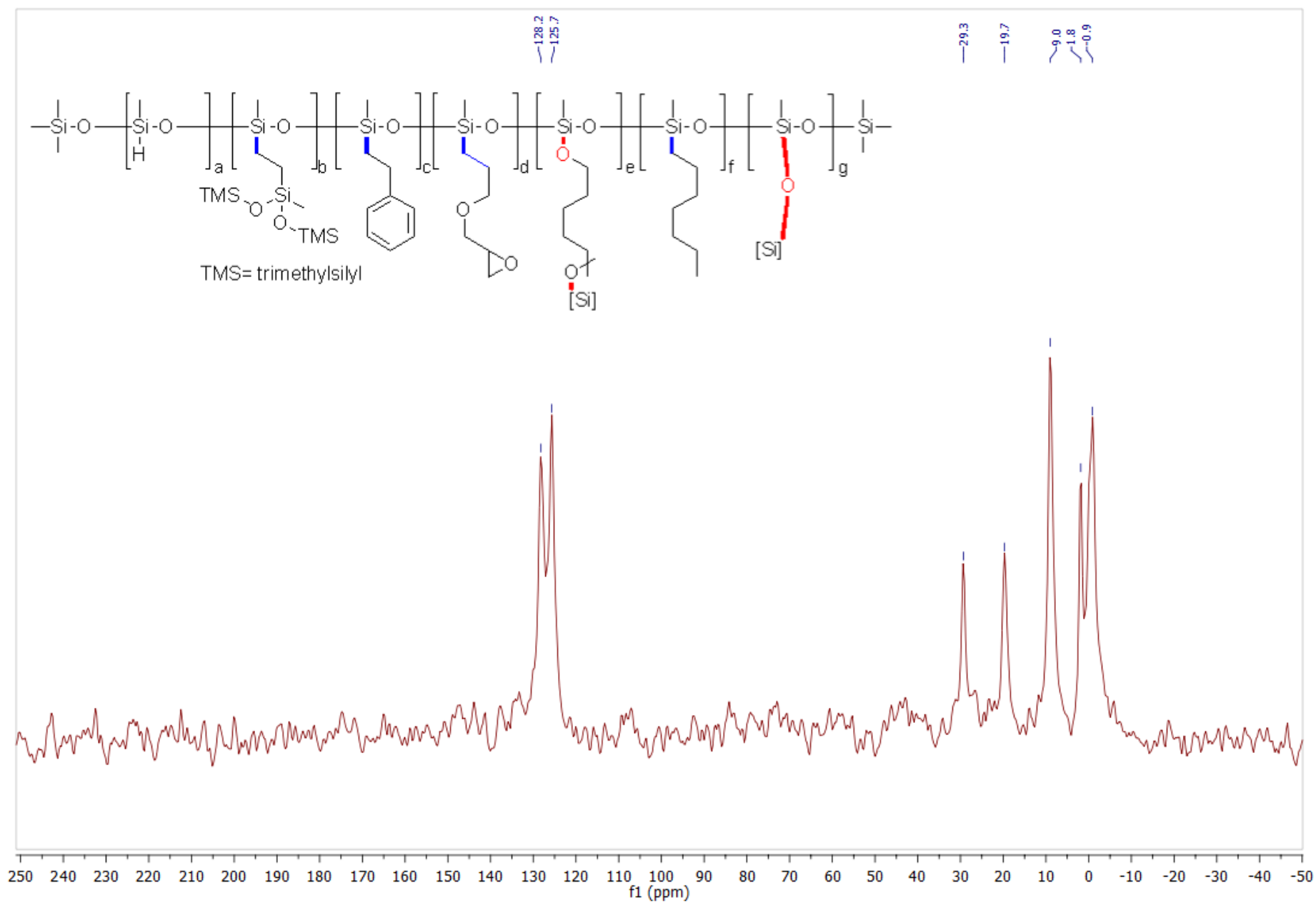
# $^{29}\text{Si}$ CPMAS SS-NMR of 1d



**<sup>1</sup>H MAS SS-NMR of 1d'**

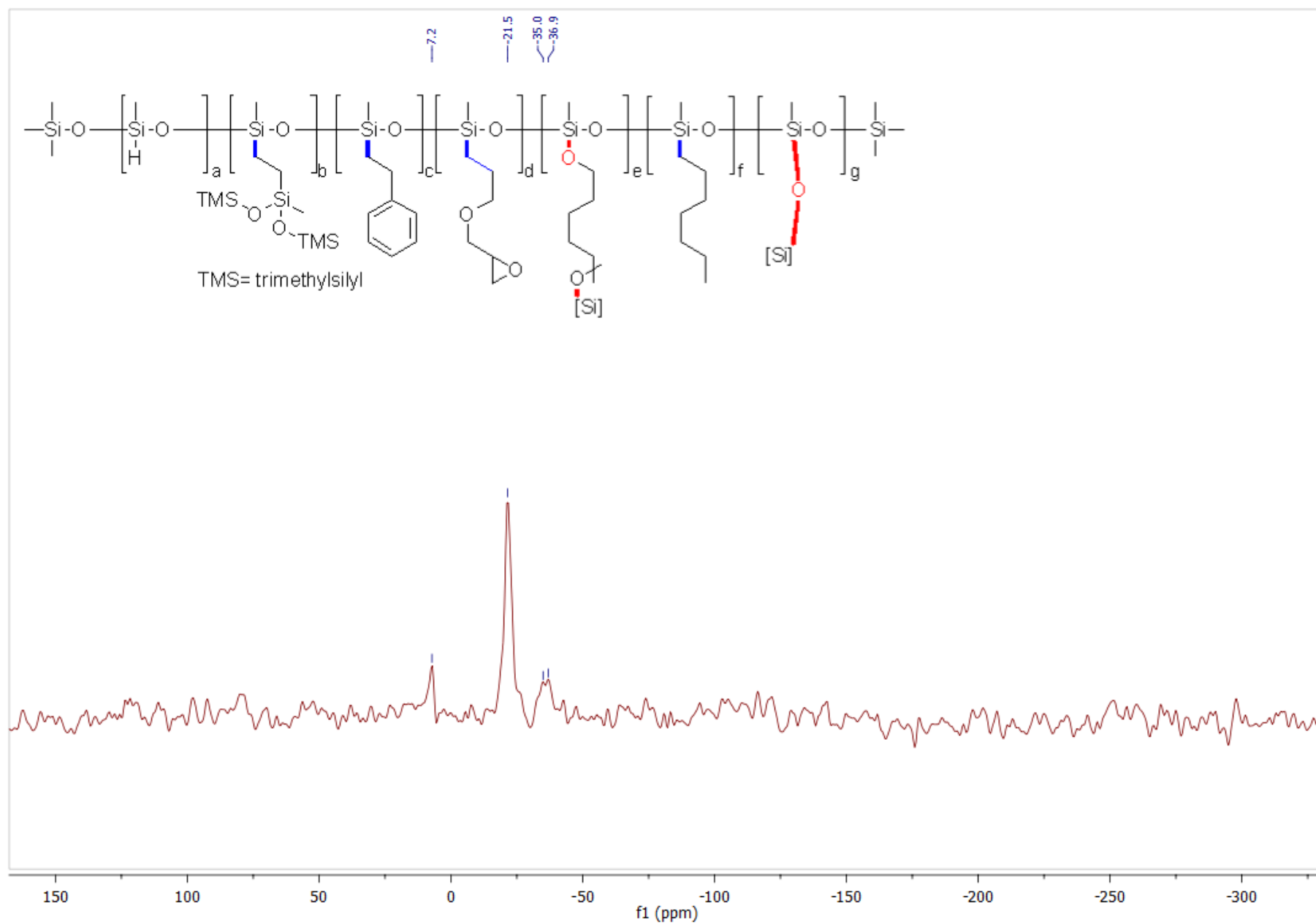


# $^{13}\text{C}$ CPMAS SS-NMR of 1d'

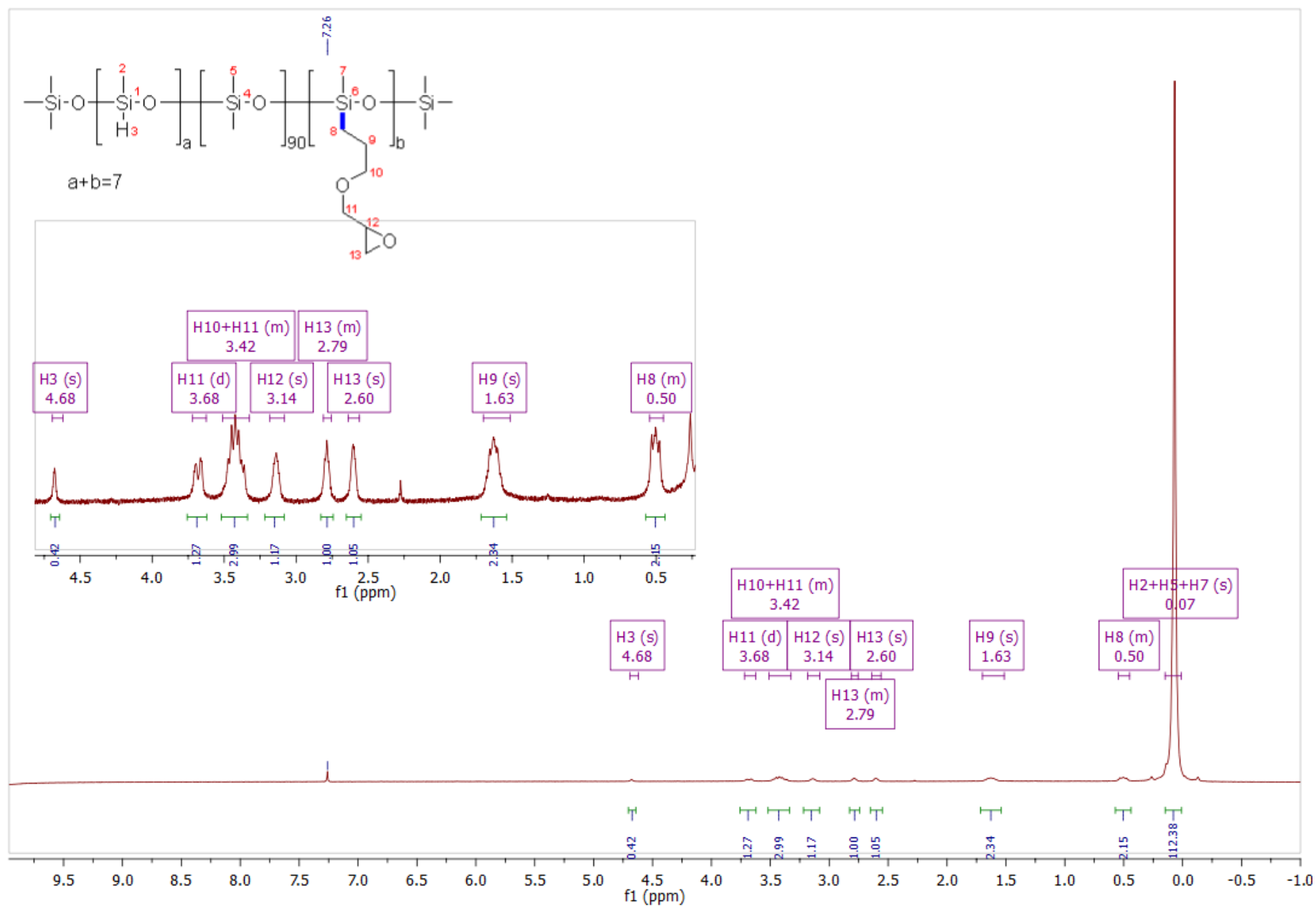




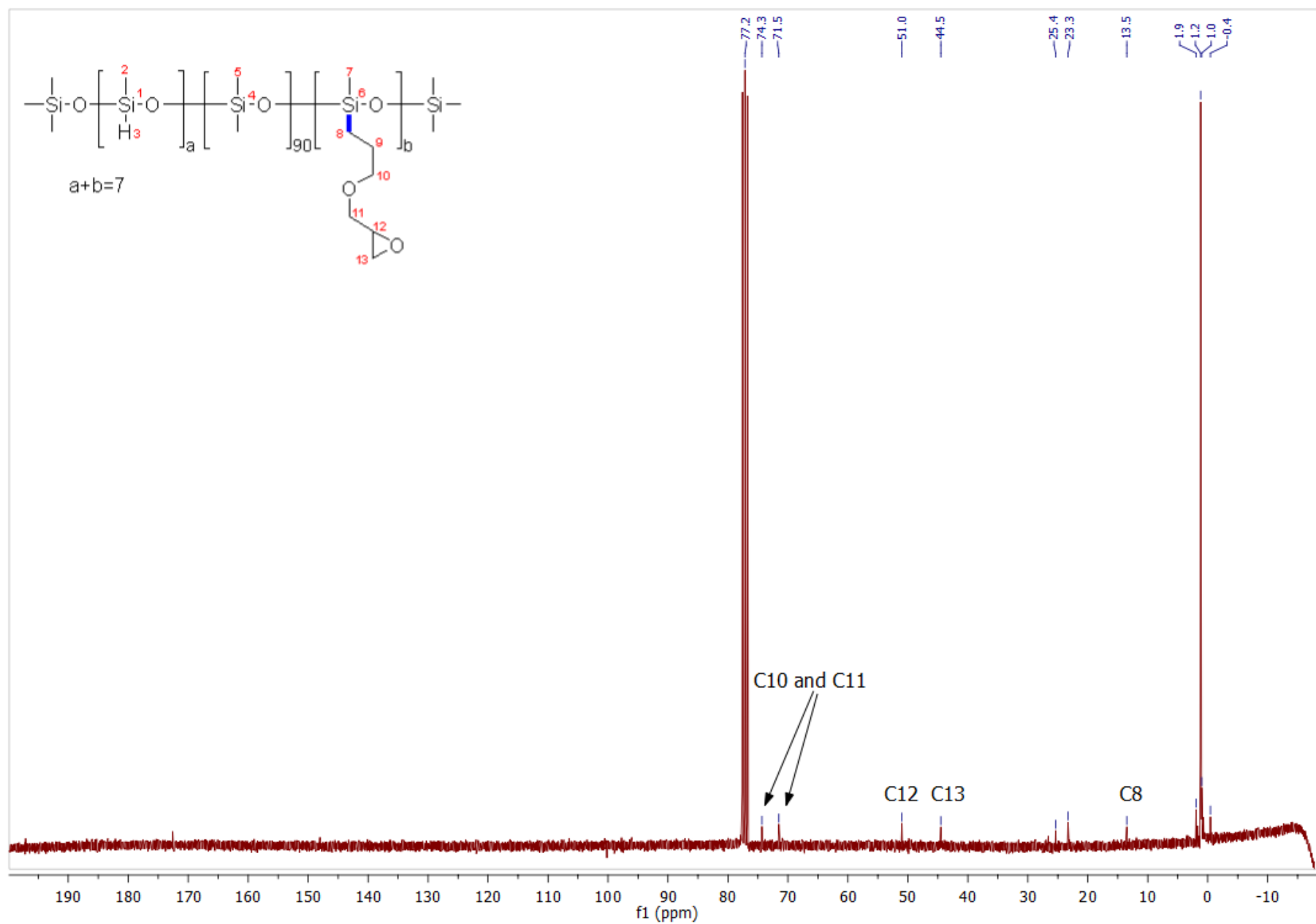
**$^{29}\text{Si}$  CPMAS SS-NMR of 1d'**



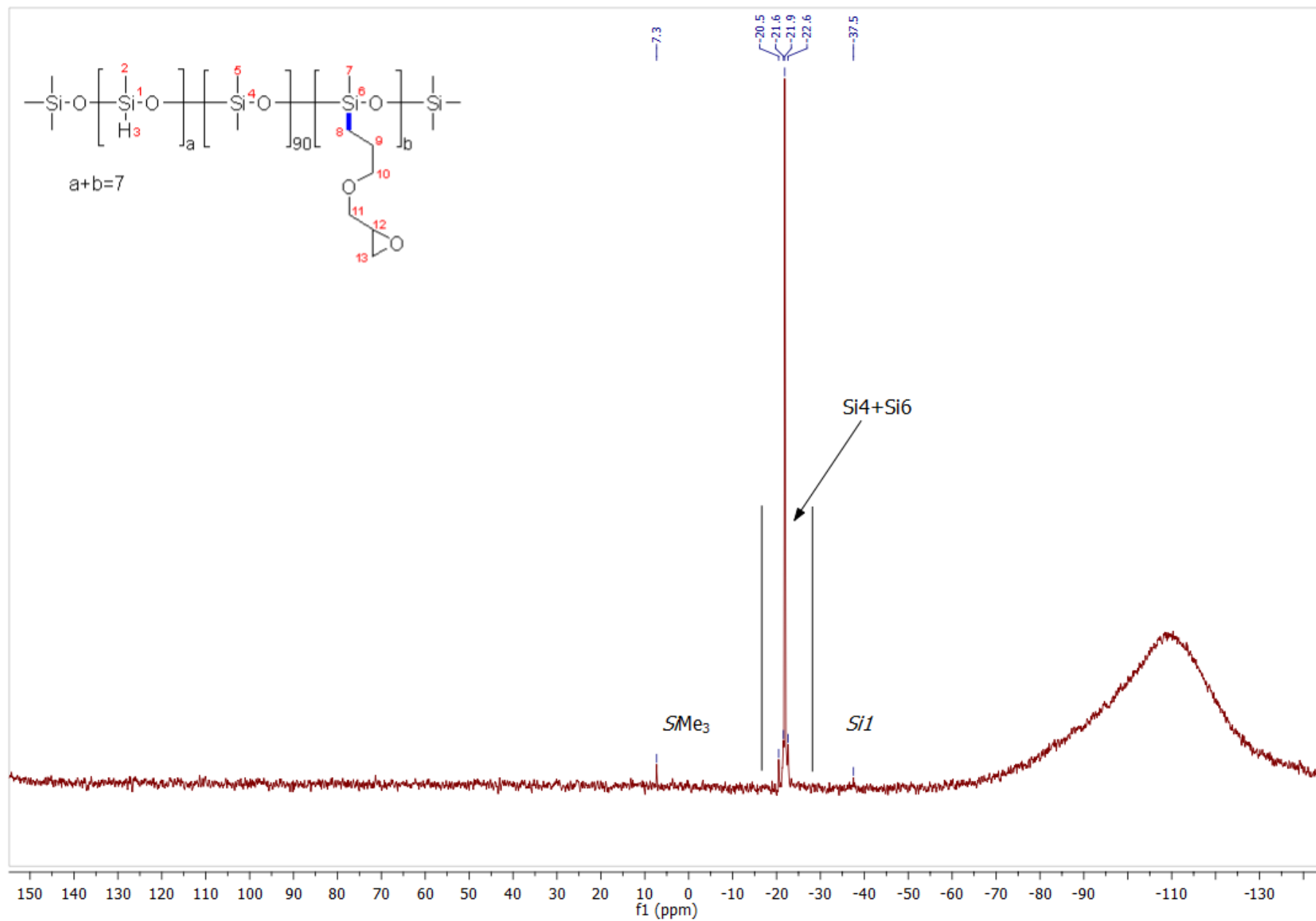
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **2a**



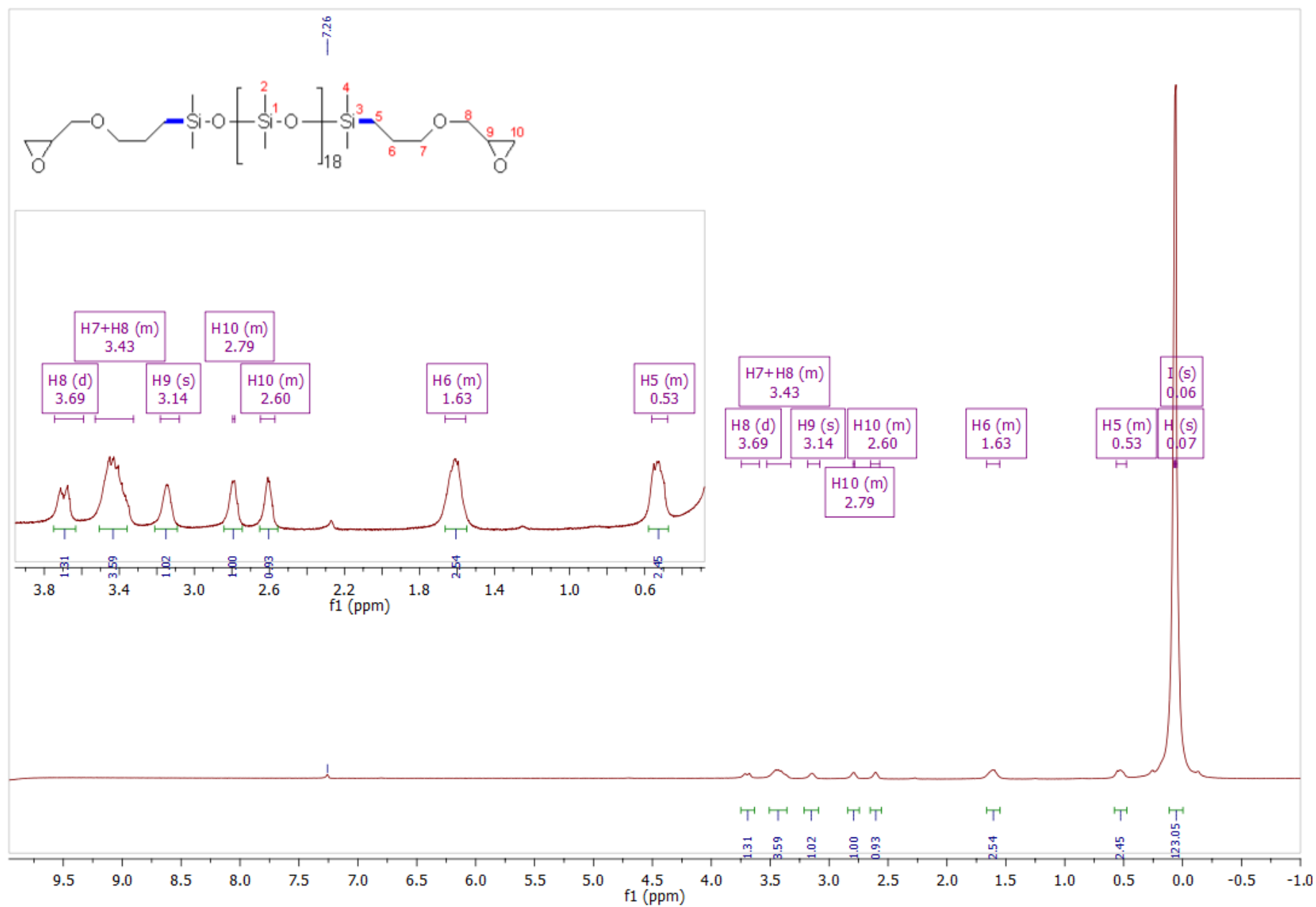
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **2a**



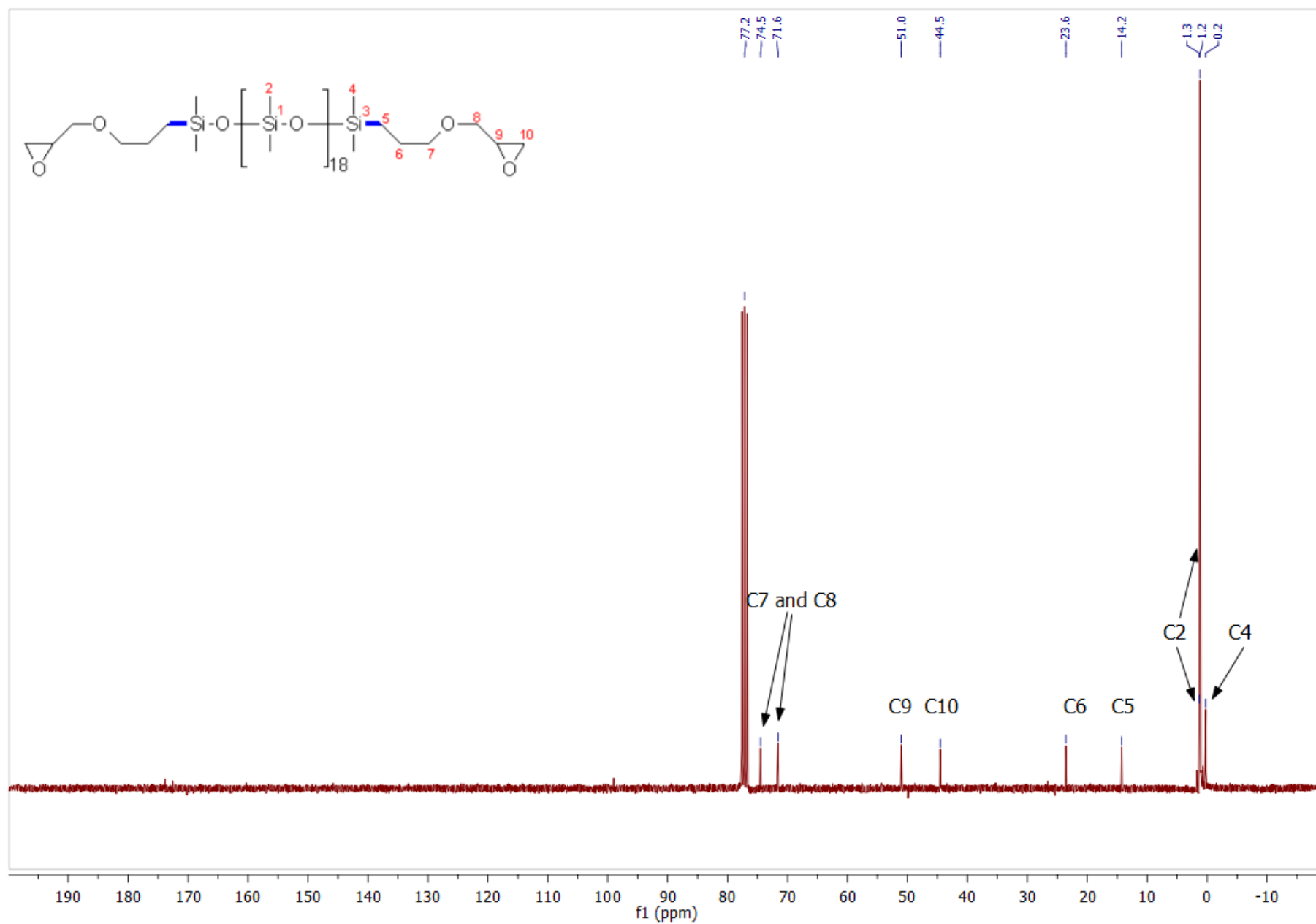
$^{29}\text{Si}$  {1H} NMR (60 MHz,  $\text{CDCl}_3$ ) spectrum of **2a**



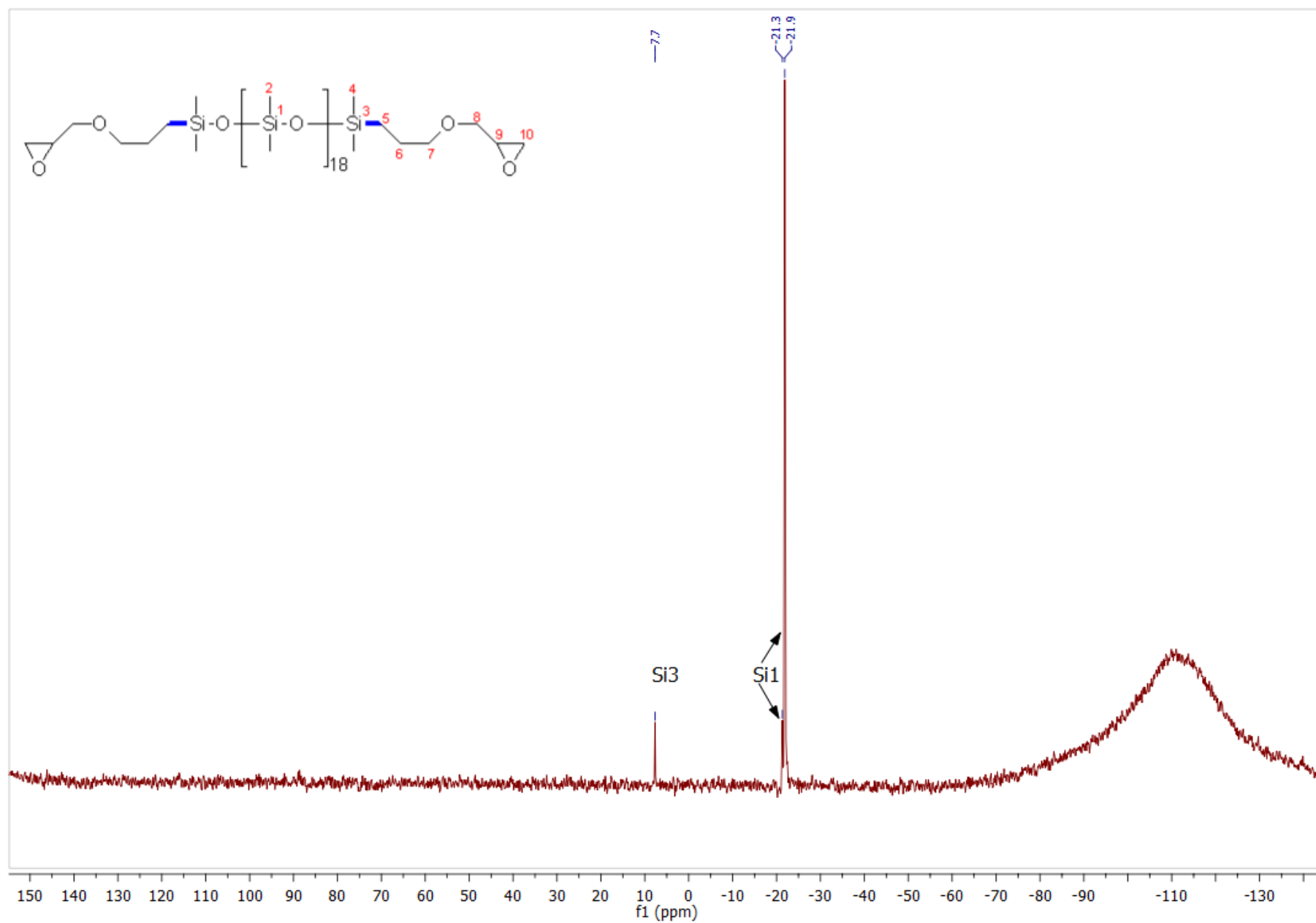
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **3a**



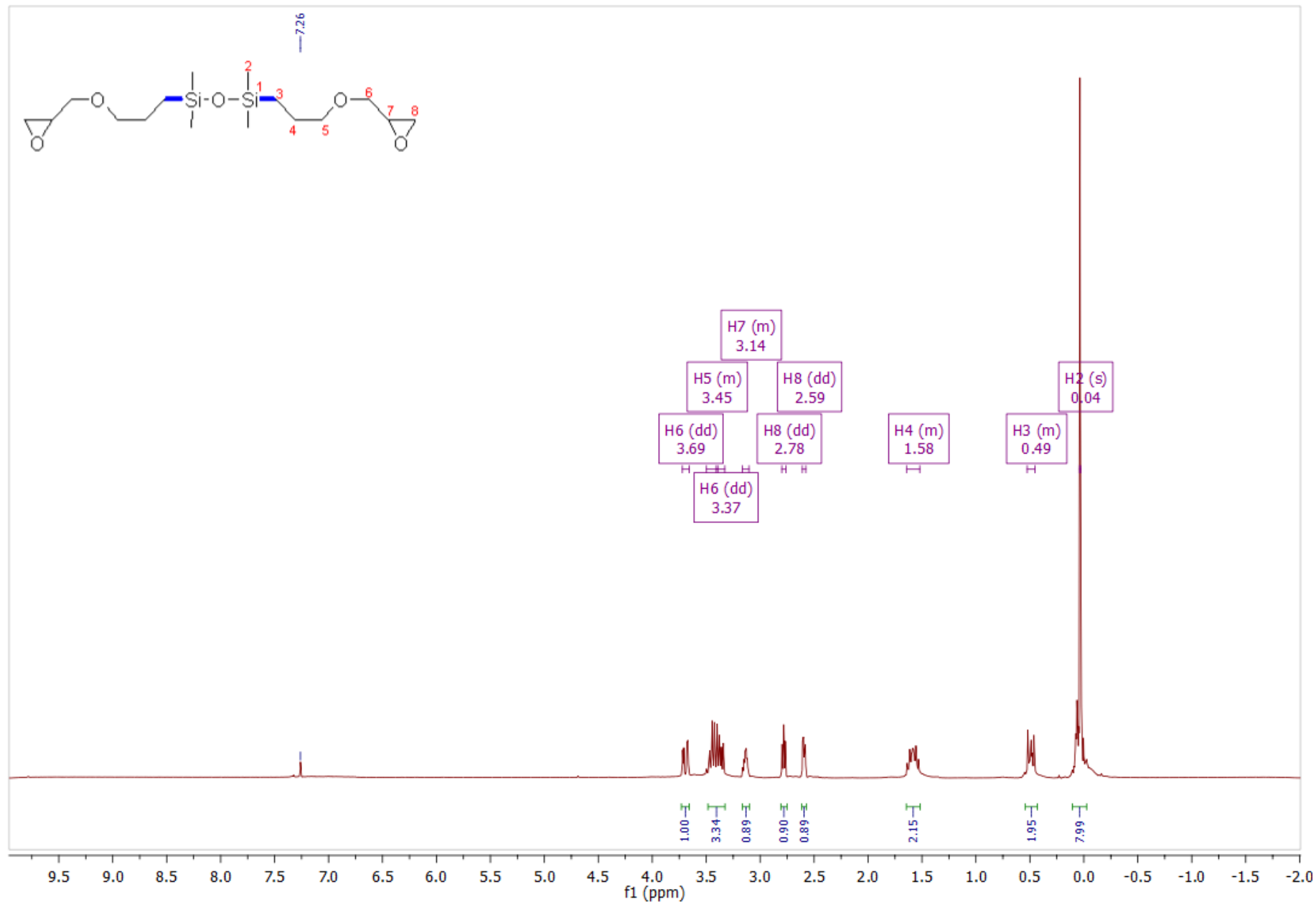
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **3a**



$^{29}\text{Si}$   $\{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) spectrum of **3a**

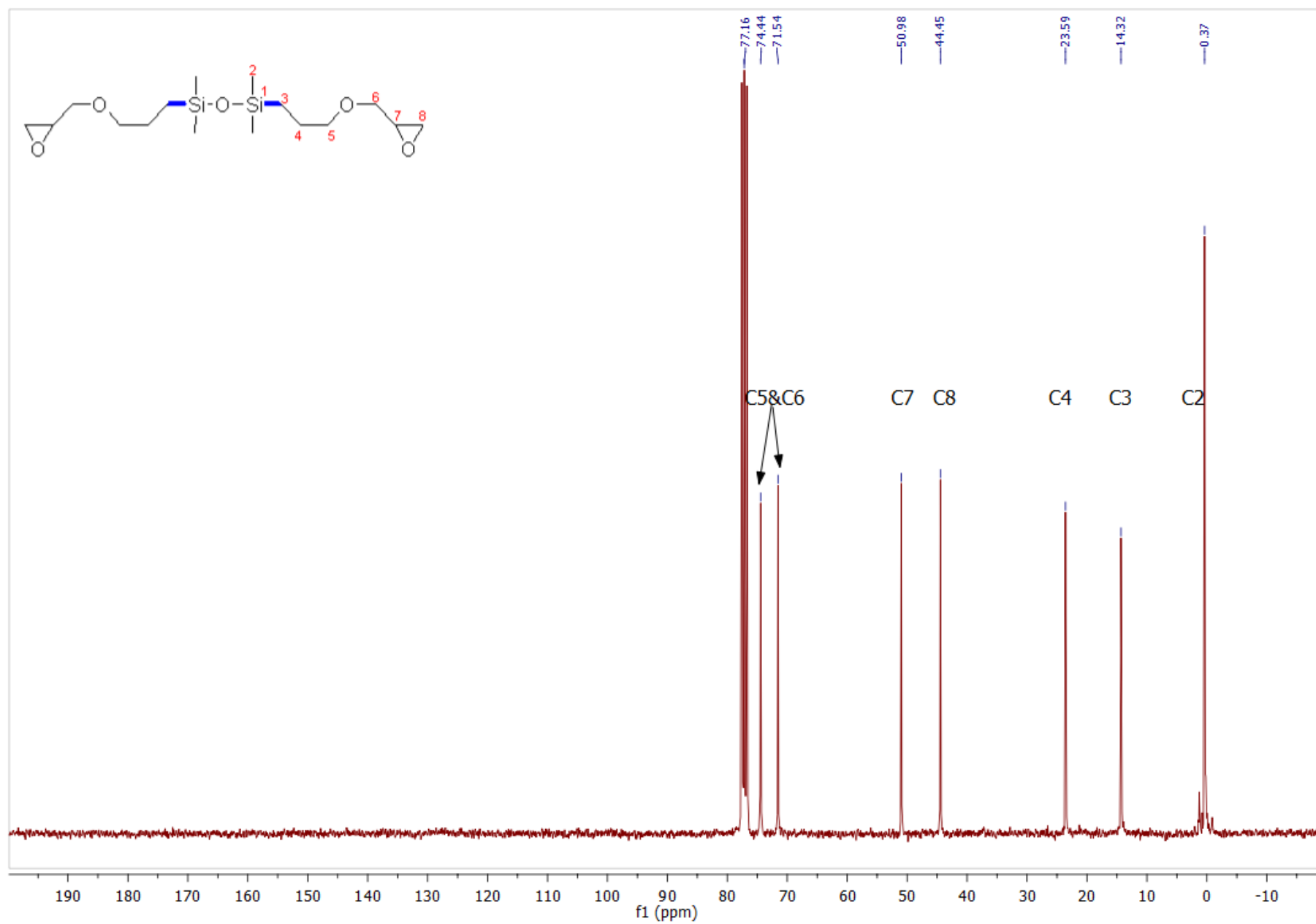


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 4a

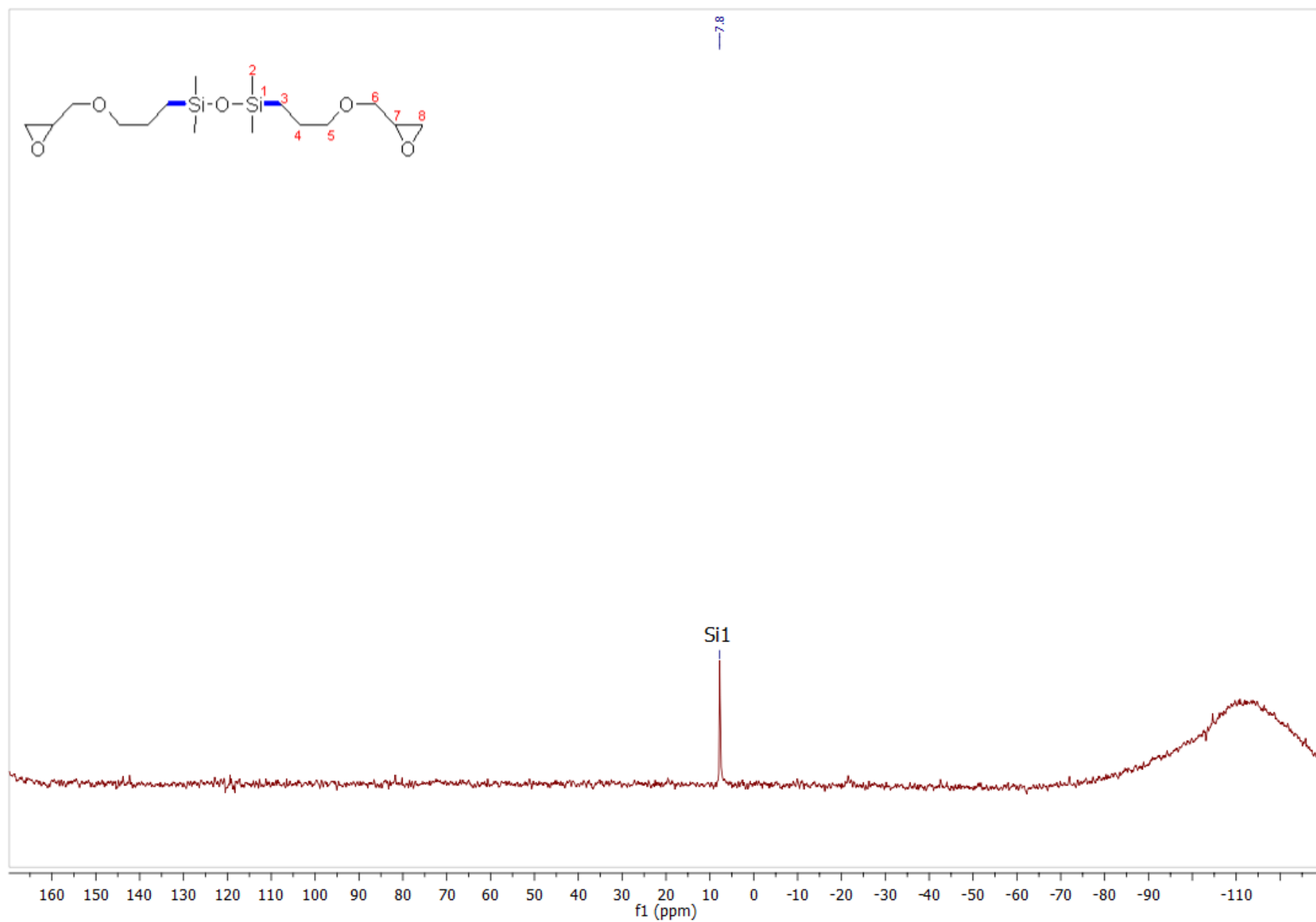




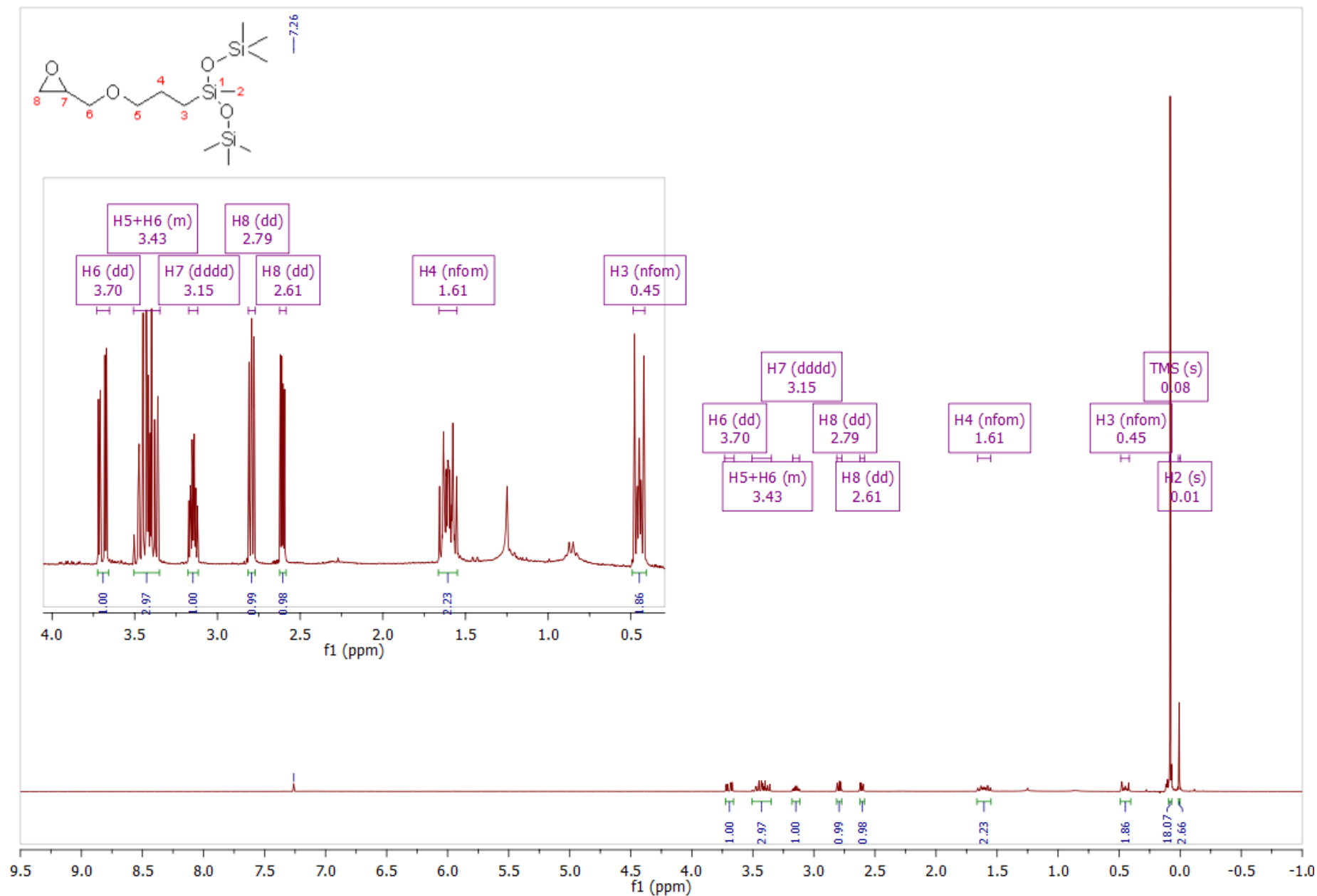
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 4a



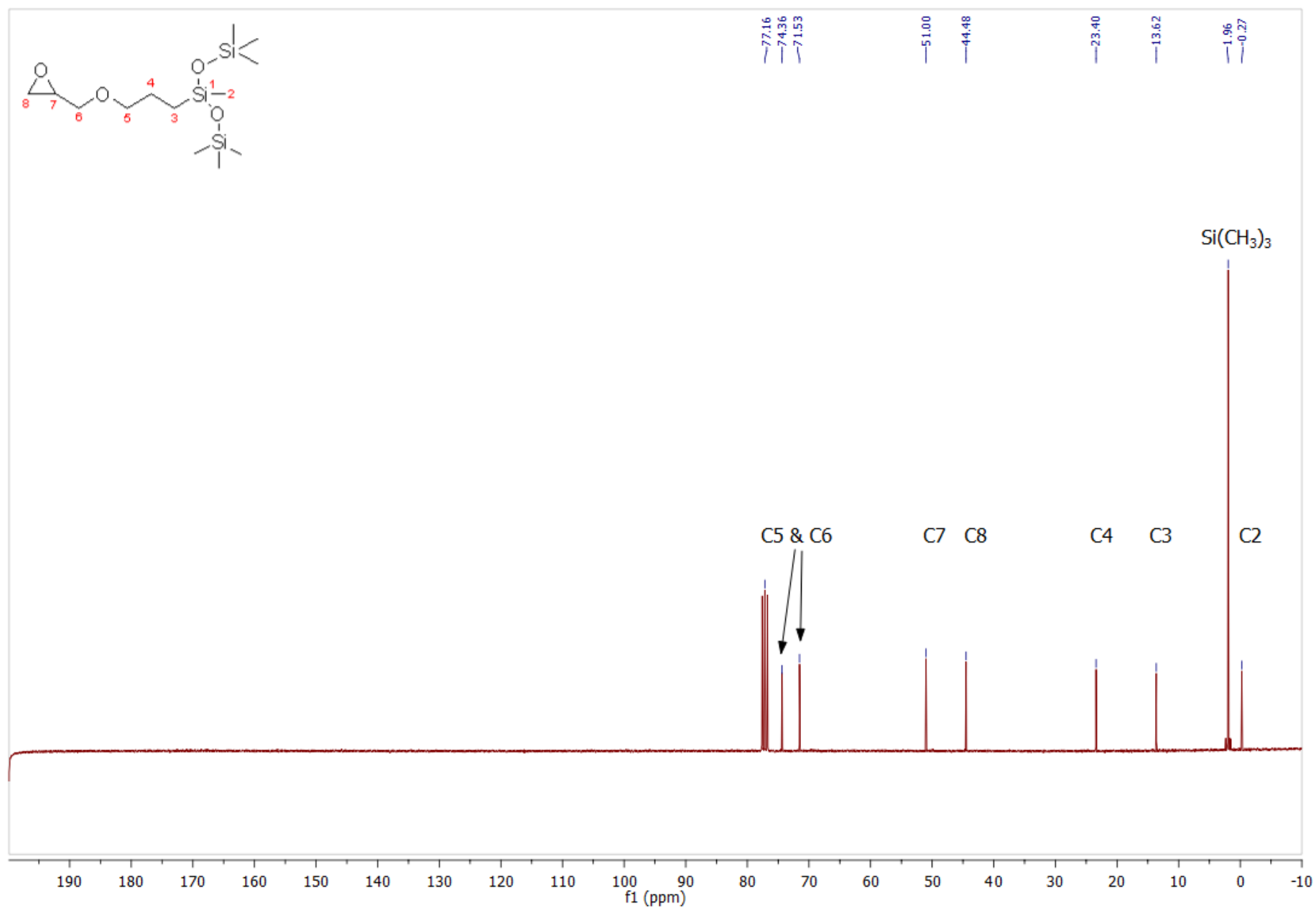
$^{29}\text{Si}$  { $^1\text{H}$ } NMR (60 MHz,  $\text{CDCl}_3$ ) of 4a



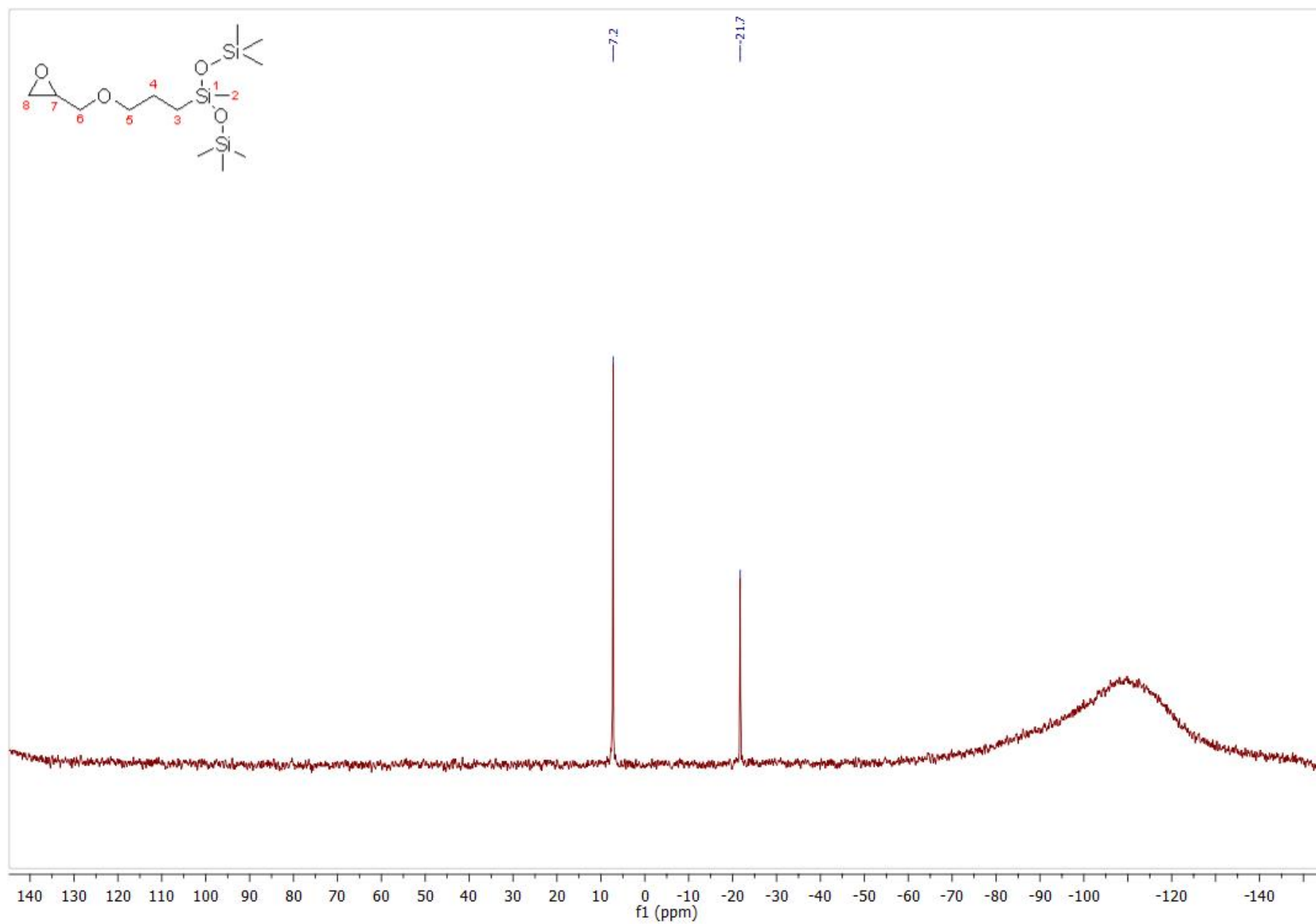
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 5a



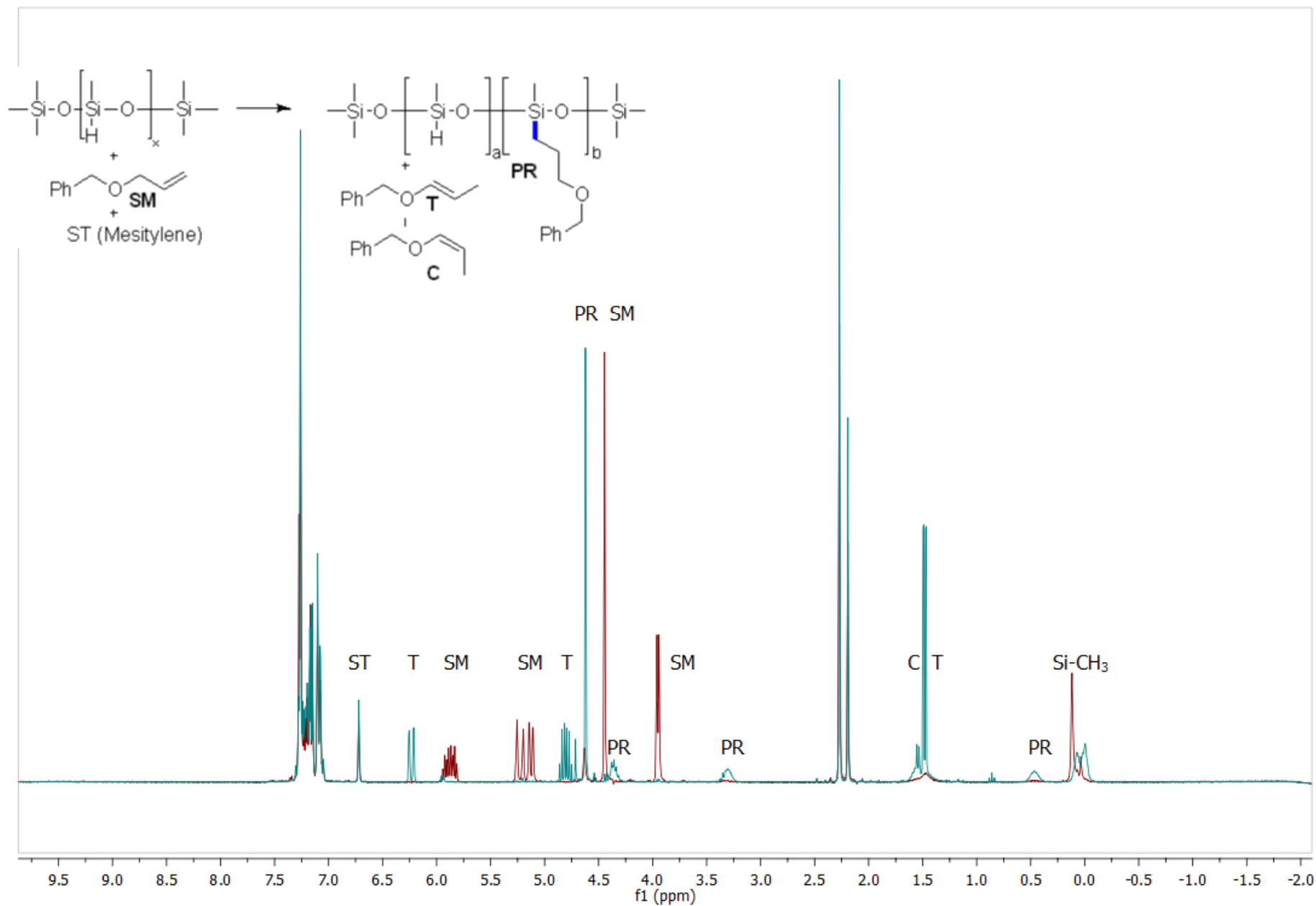
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 5a



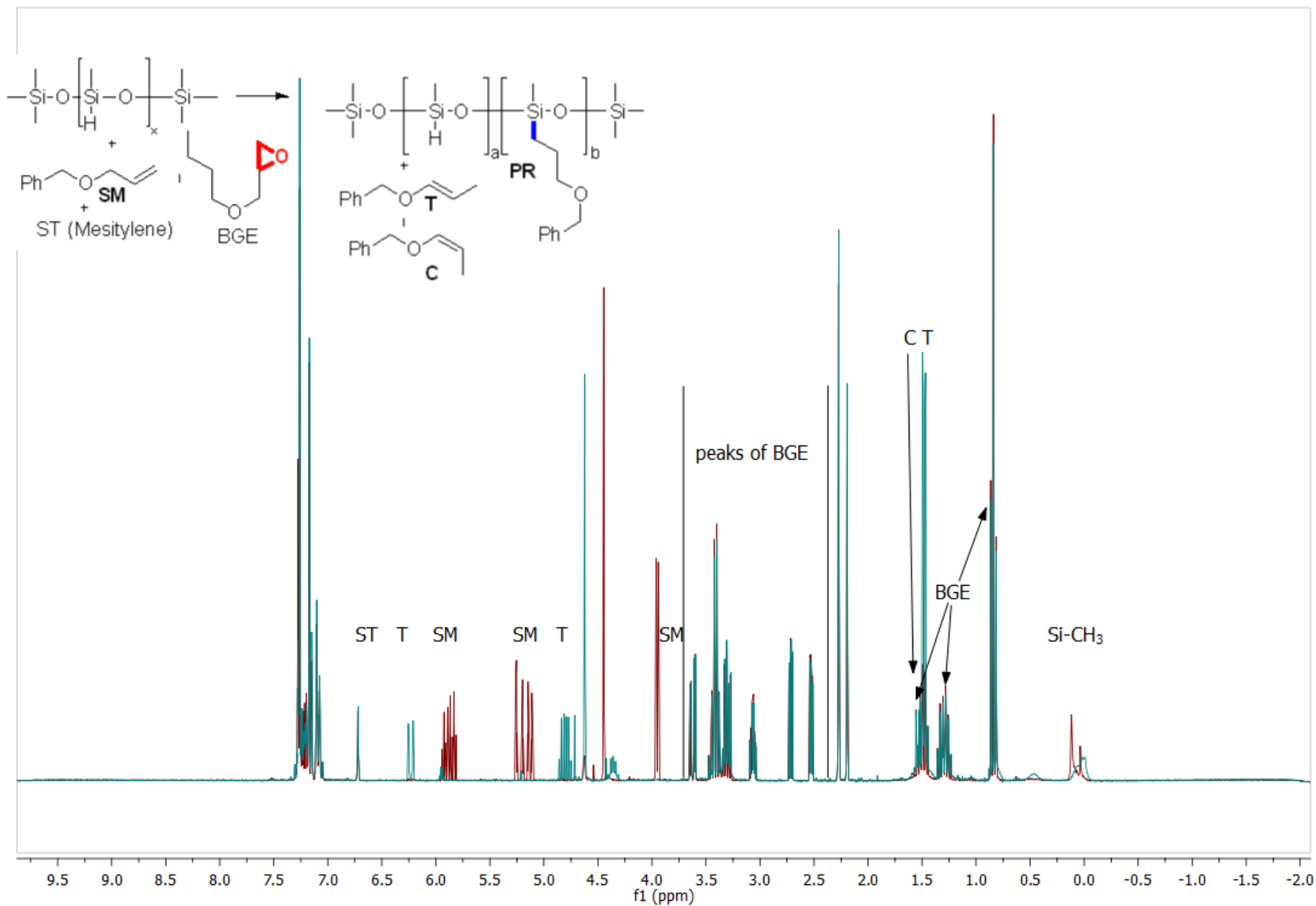
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 5a



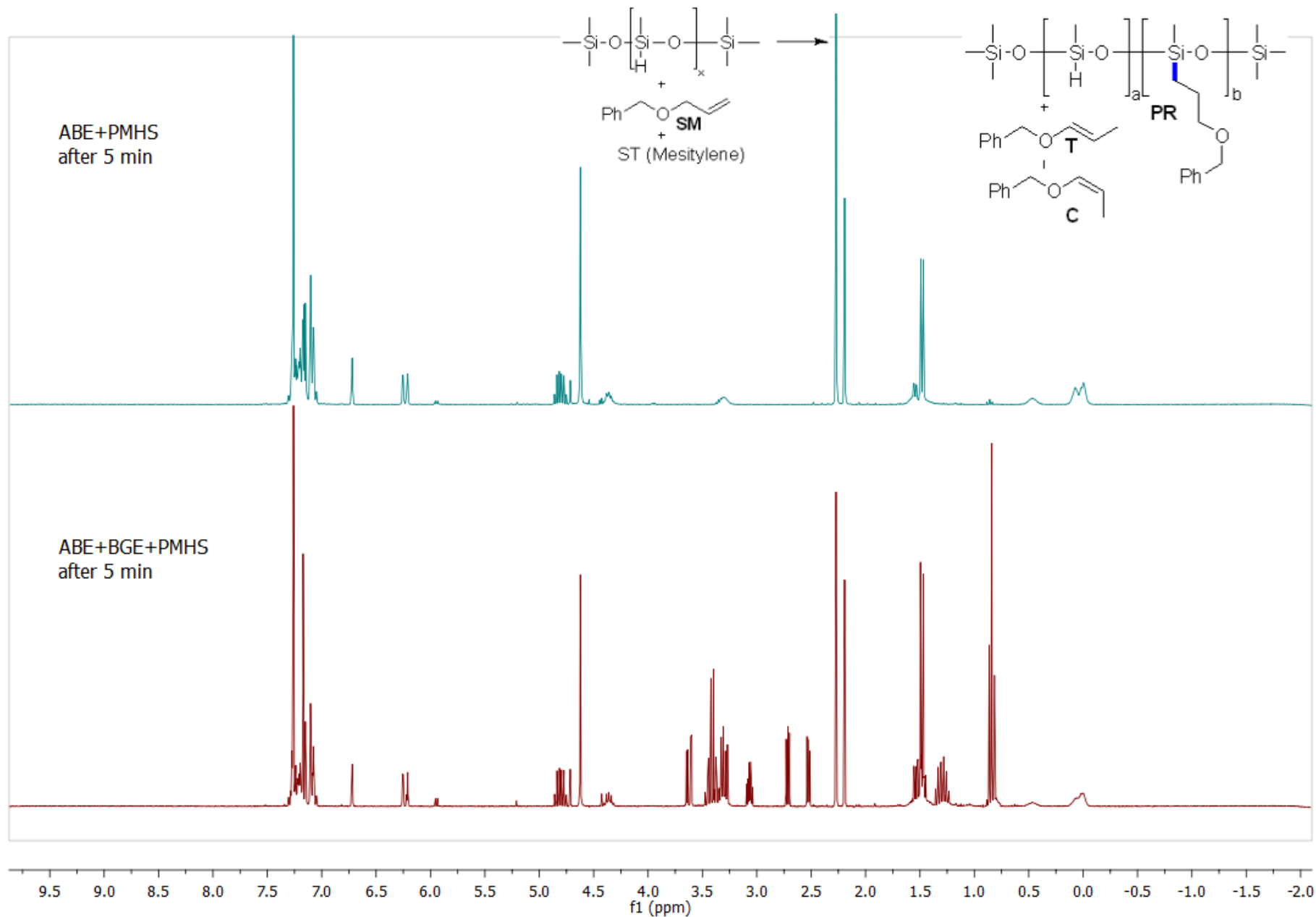
Crude  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of reaction between ABE and PMHS after 0 (red) and 5 (turquoise) minutes



Crude  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of reaction between allyl benzyl ether, BGE and PMHS after 0 (red) and 5 (turquoise) minutes



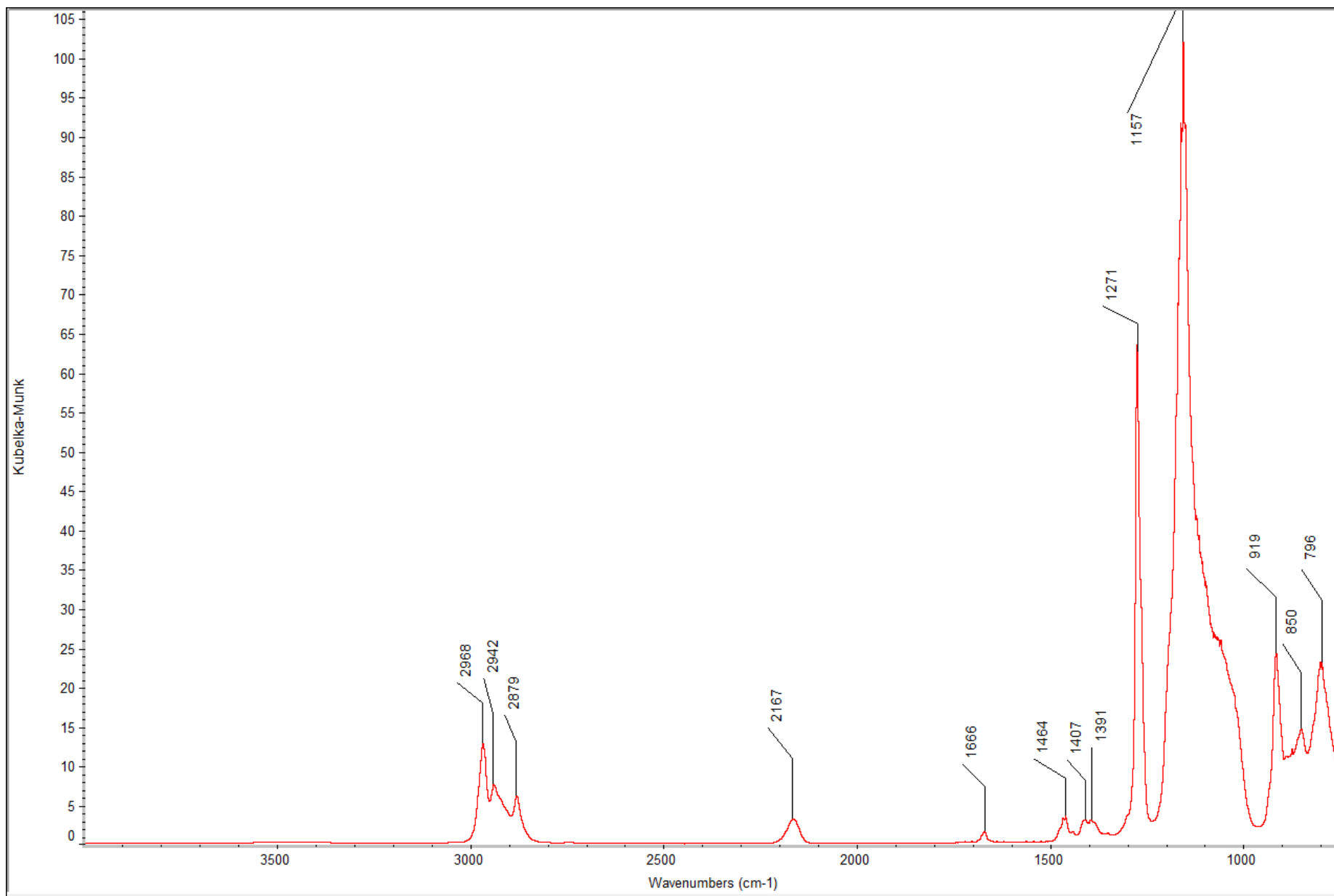
Comparison of  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) crude reaction mixture (5 min) spectra of reaction on Scheme 4b (red) and 4c (turquoise)



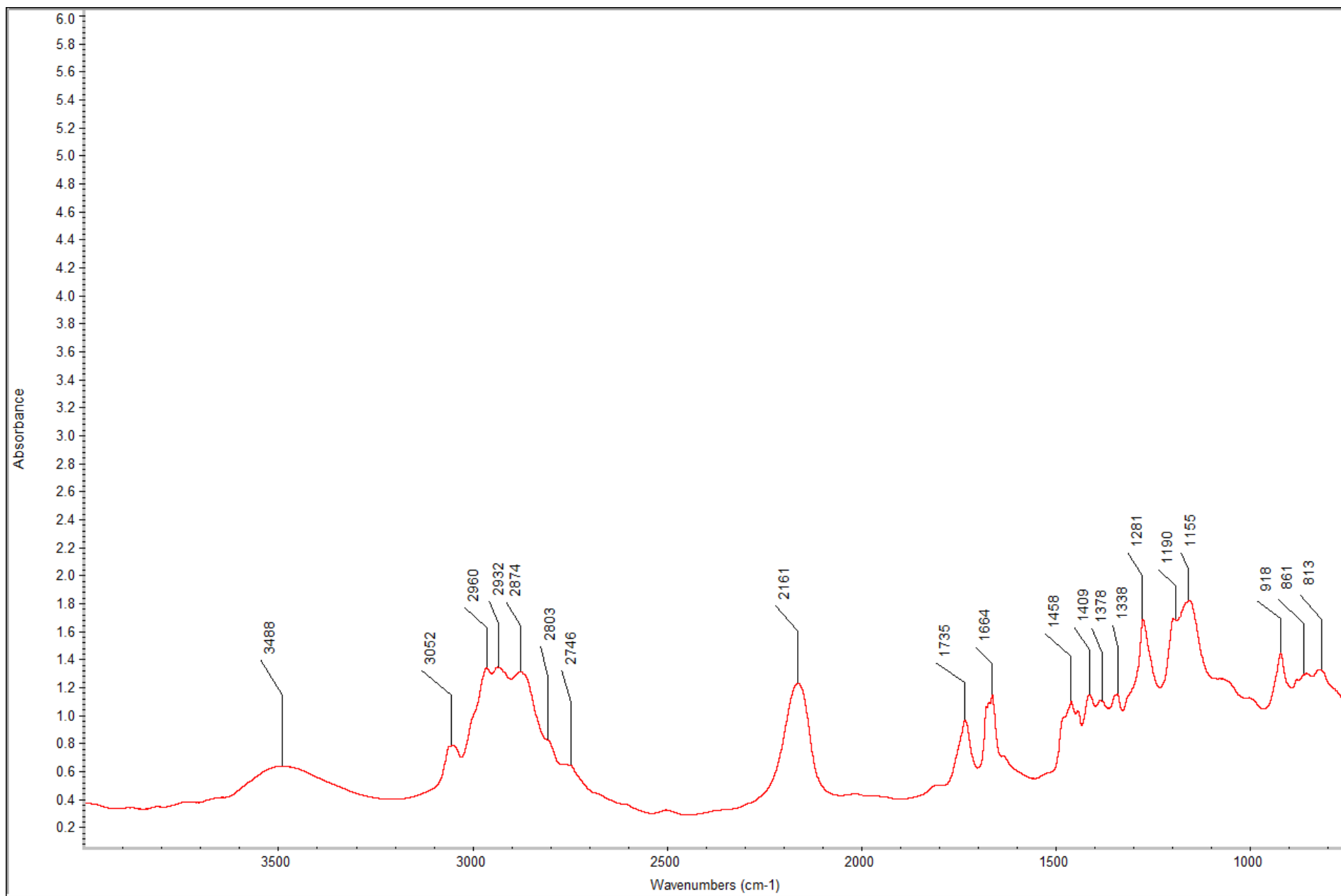


## DRIFT spectra

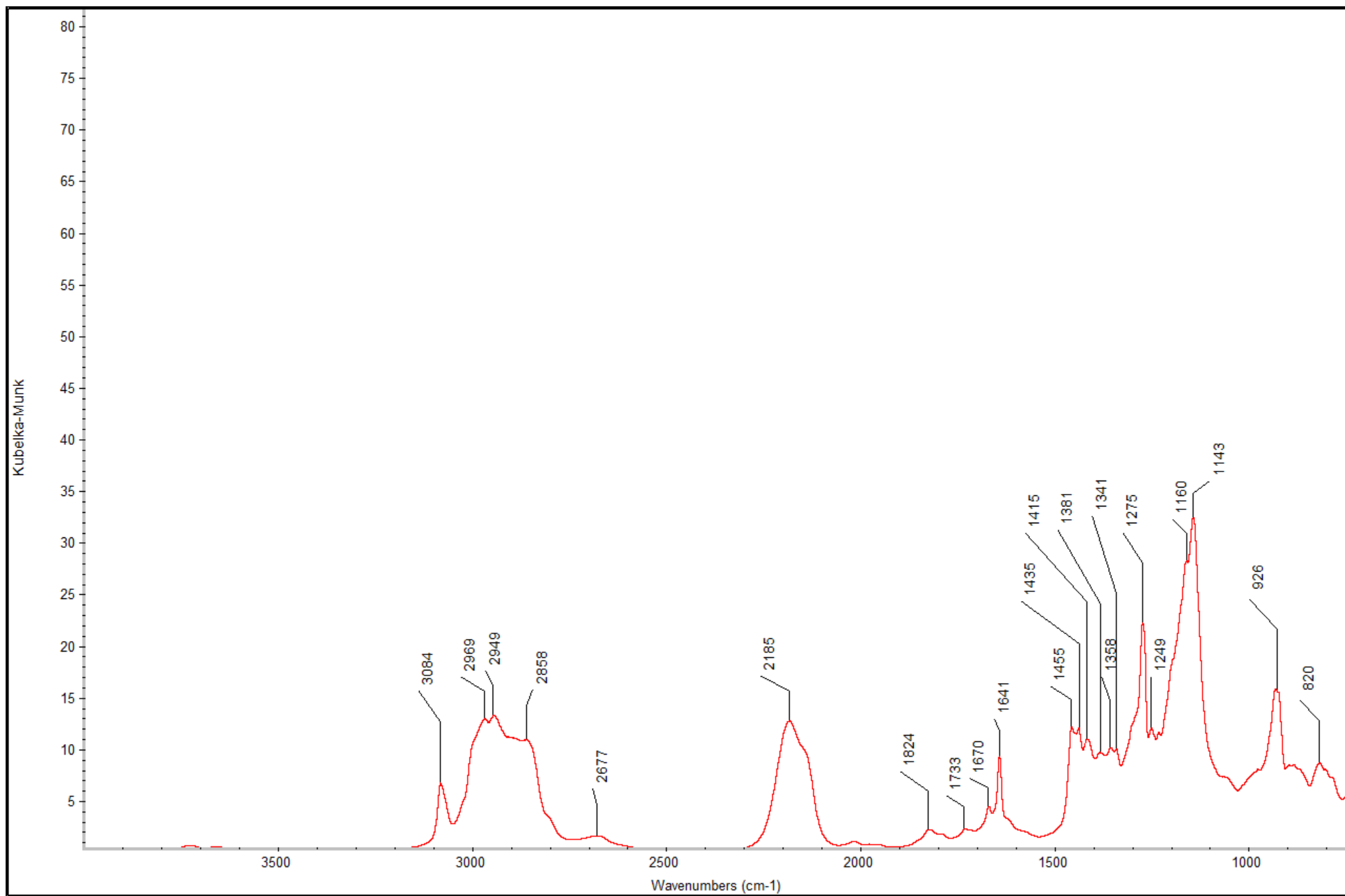
### DRIFT spectrum of AAP



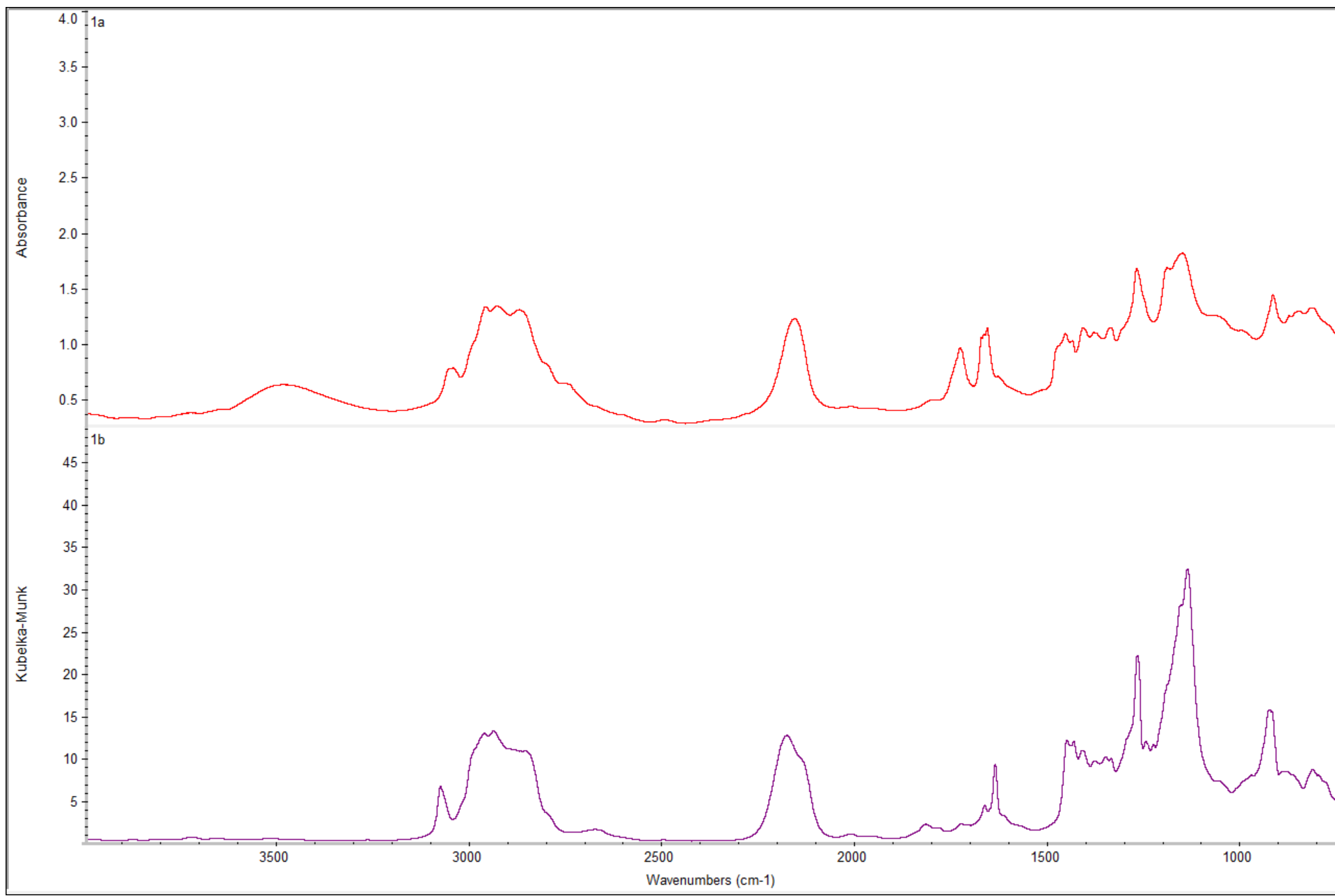
# DRIFT spectrum of 1a



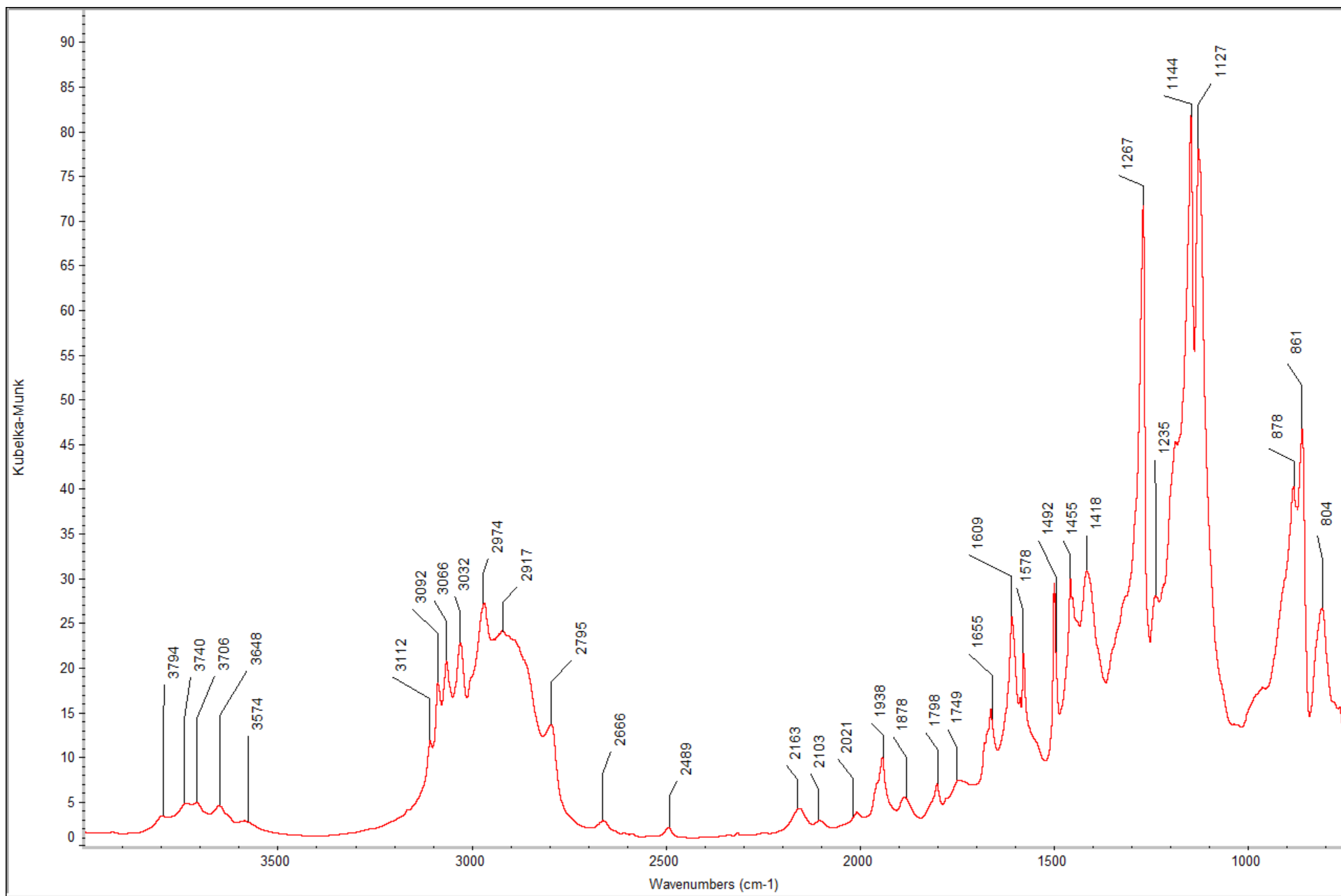
# DRIFT spectrum of 1b



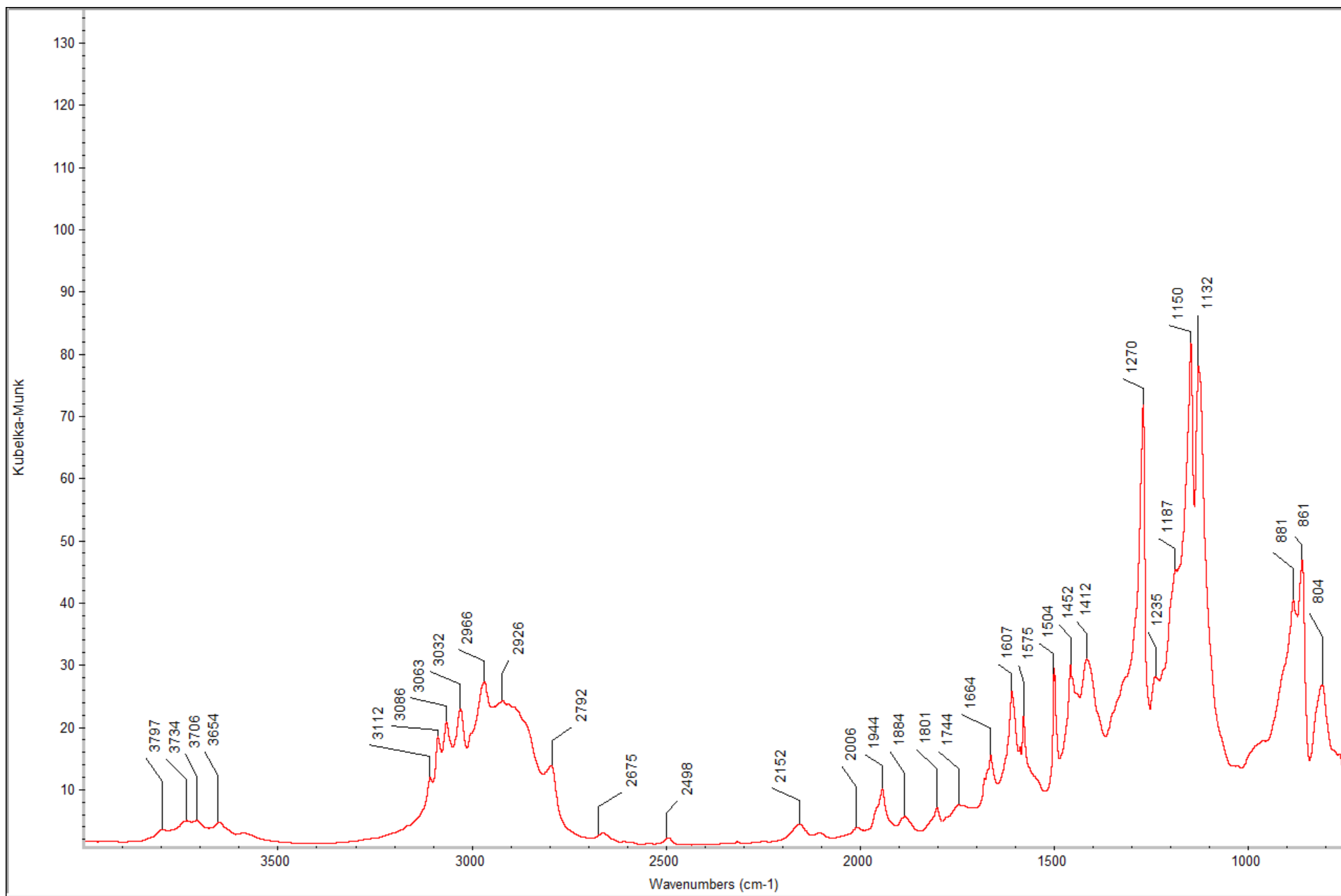
**DRIFT spectra: Comparison of DRIFT spectra between 1a and 1b.**



# DRIFT spectrum of 1d



# DRIFT spectrum of 1d'



**DRIFT spectra: Comparison of DRIFT spectra between 1a, 1d and 1d'.**

