

Supporting information

# Co<sub>2</sub>(CO)<sub>8</sub> as an efficient catalyst for the synthesis of functionalized polymethylhydrosiloxane oils and unconventional 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), t (triplet), dd (doublet of doublets), dddd (doublet of doublet of doublet of doublets), nfom (non-first order multiplet), br. s (broad singlet), 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 at spinning frequency of 10 kHz. 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 at spinning frequency of 5 kHz.

$^1\text{H}$  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  $-40\text{ }^\circ\text{C}$ . Methyl oleate (from Nu-Check Prep, Inc) was degassed by freeze-pump-thaw cycles, stored for 4 h over Selexsorb® CD and then stirred for 3 days with activated alumina. Various alkenes were purchased from the following vendors, degassed by freeze-pump-thaw cycles and used without further purification:

Aldrich: methylbis(trimethylsilyloxy)vinylsilane ( $\text{MD}^{\text{ViM}}$ ), vinylcyclohexane, oleic acid (90% technical grade), diethyl diallylmalonate (DEDAM).

Sigma Aldrich: 1,1,1,3,5,5,5-heptamethyltrisiloxane ( $\text{MD}^{\text{HM}}$ ), styrene, *tert*-butyl ethylene (TBE), allyl acetate, 1,3-cyclohexadiene

Alfa Aesar: ethyl 4-pentenoate,

TCI: methyl methacrylate (MMA), allyl methacrylate (AMA),

Acros Organics: 1-octene, mesitylene, divinyltetramethyldisiloxane (DVTMS), vinyl acetate,

Jenssen Chimica: 5-hexen-2-one.

Nu-Check Prep, Inc: Methyl oleate

Commercial virgin olive oil was used after freeze-pump-thaw cycles without further purification.

The polymethylhydrosiloxane (PMHS) (internal [Si-H] content 45.5wt%, contains ca. 50 [Si-H] units) was 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 the corresponding alkene (1.0 eq for all entries in Table S1, 0.5 eq for all the entries in Table S2 and S3), PMHS (1.0 eq of Si-H), mesitylene (NMR standard-only for Table S1), 0.1 mol%  $\text{Co}_2(\text{CO})_8$  solution in toluene and a stirring bar, unless noted otherwise. The vial was placed to a preheated oil bath at 60 °C and left for 24 h to stir at 1000 rpm. For corresponding quantities of reagents, NMR standard and catalyst see Tables S1-S4. The wt% of  $\text{Co}_2(\text{CO})_8$  as catalyst in PMHS was calculated to be 0.26 wt% (density(PMHS)=1.006 g/mL).

**Table S1. Quantities of reagents for Table 1 and Scheme 3**

Alkene	Alkene, $\mu\text{L}$	PMHS, $\mu\text{L}$	Mesitylene, $\mu\text{L}$	Volume of 11 mM solution of $\text{Co}_2(\text{CO})_8$ in toluene, $\mu\text{L}$	Expected Co-atom w% compared to PMHS	PMHS oil label	Obtained mass of product in mg
1-octene	147	42	46	84	0.26	<b>1a</b>	54
Vinylcyclohexane	128	42	46	84	0.26	<b>1b</b>	48
TBE	121	42	46	84	0.26	<b>1c</b>	28
Styrene	128 <sup>a</sup>	42	46	84	0.26	<b>1d</b>	35
MD <sup>Vi</sup> M	270	42	46	84	0.26	<b>1e</b>	102
1,3-cyclohexadiene	89	42	46	84	0.26	<b>1f</b>	98
Styrene/MD <sup>Vi</sup> M	64 <sup>b</sup> /163 <sup>b</sup>	42	46	84	0.26	<b>1g</b>	114

[a] 1.2 eq of styrene was used due to formation of small amount of polystyrene. [b] 0.6 eq of styrene and MD<sup>Vi</sup>m were used.

**Table S2. Quantities of reagents for entries in Table 2 and Scheme 4**

Alkene	Alkene, $\mu\text{L}$	PMHS, $\mu\text{L}$	Volume of 11 mM solution of $\text{Co}_2(\text{CO})_8$ in toluene, $\mu\text{L}$	Gel Label	Color of the gel	Color of the silicone polymer after drying overnight at 60 °C under vacuum	Obtained mass of product in mg	Expected Co-atom w% in the product
DEDAM	286	105	210	<b>2a</b>	Dark brown	White-beige	260	0.10
DVTMS	271	105	210	<b>2b</b>	Brownish rose	White	185	0.15
Vinyl acetate	220	210	420	<b>3a</b>	Brown	Slightly pinkish	330	0.16
Allyl acetate	255	210	420	<b>3b</b>	Pink gel	Slightly pinkish	370	0.15
Ethyl 4-pentenoate	334	210	420	<b>3c</b>	Brown	Beige	422	0.13
Methyl methacrylate	252	210	420	<b>3d</b>	Dark Brown	White	390	0.14
Allyl methacrylate	317	210	420	<b>3e</b>	Intense blue	White crystalline	457	0.12
5-Hexen-2-one	272	210	420	<b>3f</b>	Brown	White	422	0.13

**Table S3. Quantities of reagents for entries in Scheme 5**

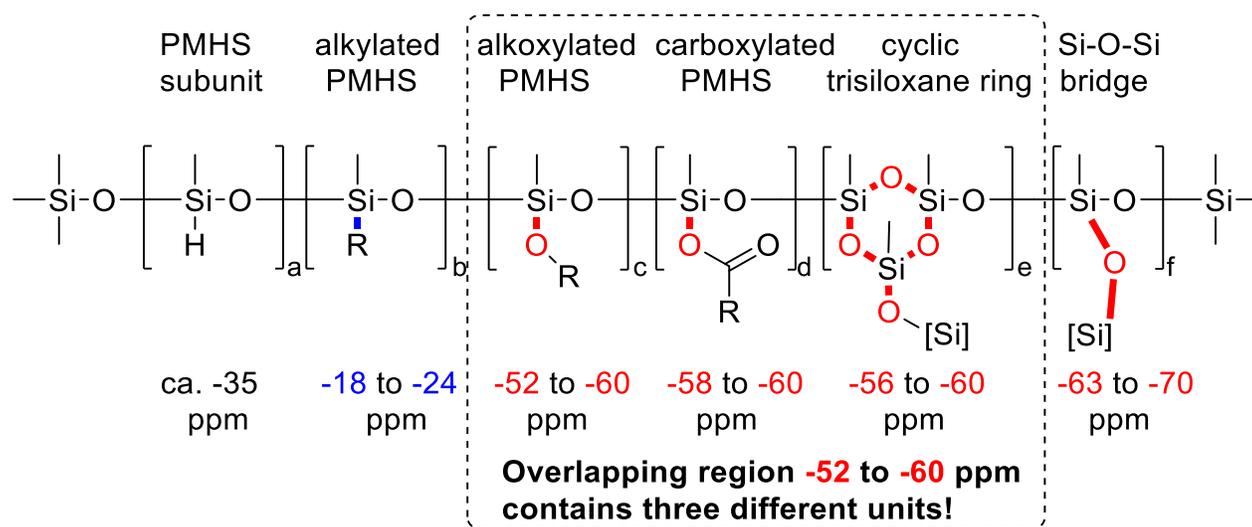
Alkene	Alkene, $\mu\text{L}$	PMHS, $\mu\text{L}$	Volume of 11 mM solution of $\text{Co}_2(\text{CO})_8$ in toluene, $\mu\text{L}$	Gel Label	Color of the gel	Color of the silicone polymer after drying overnight at 60 °C under vacuum	Obtained mass of product in mg	Expected Co-atom w% in the product
Methyl oleate	398	105	210	<b>3h</b>	Brown	White crystalline	420	0.06
Oleic acid (90%, technical grade)	370 <sup>a</sup>	105	210	<b>3i</b>	Brown	White crystalline	396	0.07
Olive oil	1143 <sup>b</sup>	315	630 <sup>c</sup>	<b>3j</b>	brown	dark grey	1284	0.06

[a] For calculations of oleic acid quantity the substrate was considered to be 100% pure. [b] For calculating the quantity the following simplifications were made: i) the olive oil used was considered to contain 100% of trioleylglyceride, ii) the molar ratio of olive oil and PMHS was calculated to match the ratio  $[(\text{C}=\text{C}+\text{C}=\text{O})]/(\text{Si}-\text{H})=1/1$ , iii) the density of olive oil was taken 0.898 g/mL. [c] Volume of 110 mM solution of  $\text{Co}_2(\text{CO})_8$  in toluene was used instead.

## 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>[1]</sup> Si-R (R= Me in PMHS oils having varying length),<sup>[2]</sup> Si-OR (R= linear C1-C10 alkyl, cyclic alkyl, functionalized alkyl and phenyl),<sup>[3,4]</sup> Si-OOCR (only formic, acetic, benzoic and methacrylic acid derivatives have been taken into account),<sup>[5,6]</sup> Si-O-Si bridge<sup>[7-9]</sup> and cyclic trisiloxane ring.<sup>[7,9-12]</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, as part of Si-O-R, Si-OOCR and cyclic trisiloxane ring units, the  $^{29}\text{Si}$  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 C=O or ester functionalities are

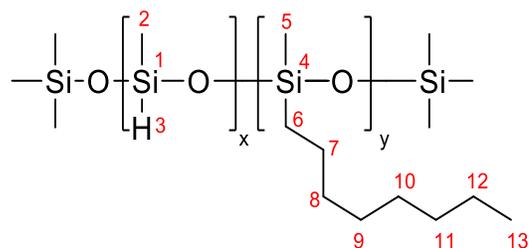
present in the tether used for cross-linking PMHS and therefore the analysis of  $^{29}\text{Si}$  NMR chemical shifts has to be complemented with the use of  $^{13}\text{C}$  SSNMR and DRIFT data.

## 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 eluded with pentane. The collected solutions were 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.

## Functionalization of PMHS with alkenes – formation of functionalized siloxane oils

### Functionalization of PMHS with 1-octene (1a)

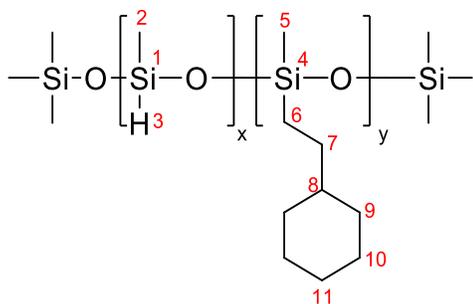


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.71 (s,  $H_3$ ), 1.27 (br. s,  $H_7-H_{12}$ ), 0.89 (s,  $H_{13}$ ), 0.53 (br. s,  $H_6$ ), 0.22-0.02 (m,  $H_2+H_5+\text{SiMe}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  33.5 (br. s), 32.1 (s), 29.5 (br. s), 23.1 (br. m,  $C_7$ ), 22.9 (s), ca. 17.5 (br. m,  $C_6$ ), 14.3 (s,  $C_{13}$ ), ca. 2.0, 1.3 and -0.5 (all br. m, Si-Me).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  -19.2, -19.5, -20.5, -20.9, -21.2, -22.2, -22.5 (all s,  $\text{Si}_4$ ), -36.4, -36.7, -37.7 and -38.8 (all s,  $\text{Si}_1$ ).  $^{29}\text{Si}$  chemical shift for  $\text{Me}_3\text{Si}$ -group was not probably detected due to low S/N ratio. The spectroscopic data contains similar  $^1\text{H}$  and  $^{13}\text{C}$  signals as reported for fully alkylated analogue.<sup>[13]</sup> The product is isolated as colorless liquid (54 mg).

## Functionalization of PMHS with vinylcyclohexane (1b)



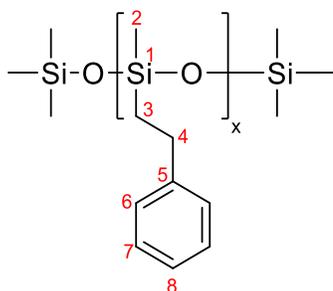
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.70 (s,  $H_3$ ), 1.78-1.59 (m,  $H_8$ - $H_{11}$ ), 1.27-1.07 (m,  $H_8$ - $H_{11}$ ), 0.93-0.76 (m,  $H_7$ ), 0.57-0.43 (m,  $H_6$ ), 0.16-0.11 (m, Si-Me), 0.11-0.02 (m, Si-Me).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  40.6 (s, C8), 33.2 (s, C9 or C10), 30.5 (m, C7), 27.0 (s, C11), 26.6 (s, C10 or C9), 14.6 (m, C6), 2.0, 1.7, -0.3, and -0.5 (all m, Si-Me).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.9 ( $\text{Me}_3\text{Si}$ ), -20.4, -20.7, -21.7, -22.0, -22.3 (all s,  $\text{Si}_4$ ), -37.6 and -37.9 (s,  $\text{Si}_1$ ).

The product is isolated as colorless liquid (48 mg).

## Functionalization of PMHS with styrene (1c)

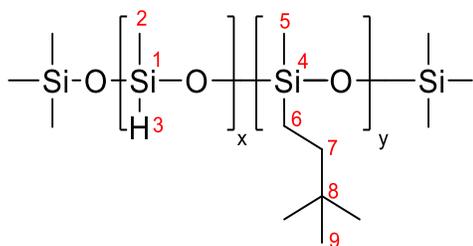


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24-7.02 (m,  $H_6$ - $H_8$ ), 2.67 (br. s,  $H_4$ ), 0.91 (br. s,  $H_3$ ), 0.27 (s,  $\text{Me}_3\text{Si}$ ), 0.12 (br. s,  $H_2$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6 (C5), 128.5 (C6 or C7), 127.8 (C7 or C6), 125.7 (C8), 29.3 (C4), 19.7 (C3), 2.1 ( $\text{Me}_3\text{Si}$ ), 0.0 (C2).

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  -22.9 ( $\text{Si}_1$ ).  $^{29}\text{Si}$  chemical shift for  $\text{Me}_3\text{Si}$ -group was not probably detected due to low S/N ratio. The product is isolated as colorless liquid (35 mg).

## Functionalization of PM<sup>HS</sup> with *tert*-butylethylene (1d)

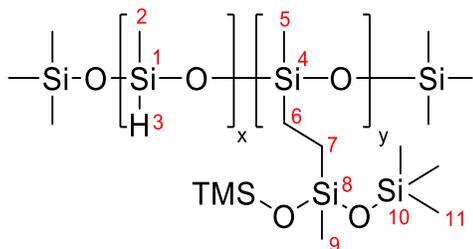


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.72 (s, *H*3), 1.26-1.17 (m, *H*7), 0.84 (s, *H*9), 0.50-0.40 (m, *H*6), 0.17 (d, J 4.8 Hz, *H*2), 0.13-0.03 (m, *H*5).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 36.9 (m, *C*7), 31.0 (s, *C*8), 28.9 (s, *C*9), 11.8 (m, *C*6), 1.7 (br. m, *C*2+*Me*<sub>3</sub>*Si*), -0.6 (m, *C*5).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ -20.0, -21.6 (both s, *Si*4), -36.7 and -37.8 (*Si*1). <sup>29</sup>Si chemical shift for Me<sub>3</sub>Si group was not detected probably due to low S/N ratio. The product is isolated as colorless liquid (20 mg).

## Functionalization of PM<sup>HS</sup> with MD<sup>Vi</sup>M (1e)



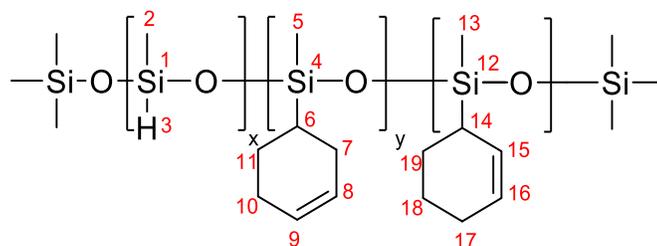
TMS= trimethylsilyl

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.73 (s, *H*3), 0.41 (s, *H*6+*H*7), 0.08 (s, *H*2+*H*6+*SiMe*<sub>3</sub>), -0.01 (s, *H*5).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 8.7 (*C*6+*C*7), 2.02 (*C*2+*C*11+*SiMe*<sub>3</sub>), -1.0 (*C*5).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ 6.7 (*Si*11), -21.1 (*Si*4), -36.6 and -37.5 (*Si*1). <sup>29</sup>Si chemical shift for Me<sub>3</sub>Si group was not detected probably due to low S/N ratio or alternatively it is under *Si*10 peak. The product is isolated as colorless liquid (250 mg).

## Functionalization of PM<sup>HS</sup> with 1,3-cyclohexadiene (1f)



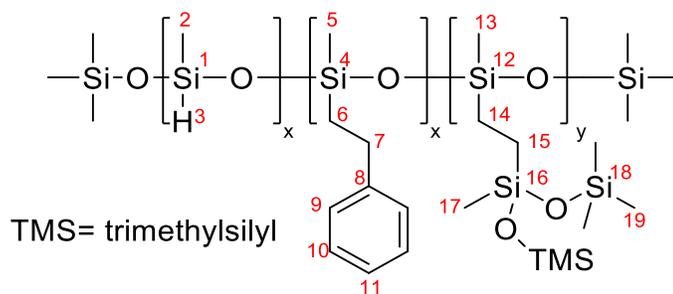
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.70 (br. s, *H*8+*H*9+*H*15+*H*16), 1.99 (br. s, CH), 1.89-1.72 (m, CH), 1.60-1.30 (m, CH), 0.82 (m, *H*6+*H*14), 0.07 (br. s, Si-CH<sub>3</sub>).

Chemical shifts for 1,4-hydrosilylation product are underlined.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 127.8, 127.2, 126.8, 126.2 (all *C*8+*C*9+*C*15+*C*16), 27.6, 25.9, 25.3, 25.2, 23.1, 22.8 (2x*C*), 22.6 (all CH<sub>2</sub> and CH), 2.0 (SiMe<sub>3</sub>), -1.7 (*H*13), -2.0 (*H*5).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ 6.9 (SiMe<sub>3</sub>), -24.4 (*Si*4), -27.0 (*Si*12). The product is isolated as colorless dense liquid (98 mg). The reader might be interested to compare the reported 1,4-hydrosilylation product chemical shifts with the <sup>13</sup>C and <sup>29</sup>Si chemical shifts of similar 1-bis(trimethylsiloxy)methylsilyl-2-cyclohexene.<sup>[14]</sup>

## Functionalization of PM<sup>HS</sup> with styrene and MD<sup>Vi</sup>M (1g)



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.22-7.04 (br. m, *H*9-*H*11), 4.74 (trace *H*3), 2.66 (br. s, *H*7), 0.89 (br. s, *H*6), 0.41 (br. s, *H*14+*H*15), 0.06 (br. s, Si-CH<sub>3</sub>).

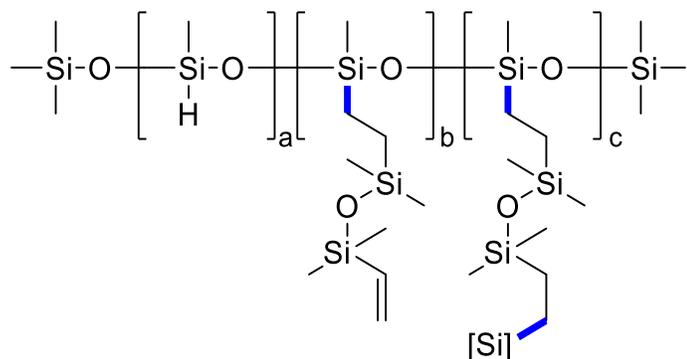
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 128.4 and 127.9 (both *C*9 and *C*10), 126.8 and 125.6 (both *C*8 and *C*11), 29.3 (*C*7), 19.7 (*C*6), 9.0 (*C*14+*C*15), 2.0 (Si-CH<sub>3</sub>), -1.0 (*C*19).

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): δ 6.8 (*Si*18), -21.1, -21.8 and -23.1 (all *Si*4, *Si*16 and *Si*12), -37.8 (trace *Si*1). <sup>29</sup>Si chemical shift for Me<sub>3</sub>Si end-group was not detected probably due to low S/N ratio or alternatively it is under *Si*18 peak. The product is isolated as colorless liquid (114 mg).

## Functionalization of PMHS with alkenes – formation of 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 illustrations of the linked network and how different ester and C=O groups can lead to cross-linking of PMHS chains.  $a+b+c+d+e+f=50$

### Functionalization of PMHS with divinyltetramethyldisiloxane (DVTMS) (2a)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  6.02, 5.89 and 5.69 (all broad olefinic C-H), 4.76 (Si-H), 0.49 (Si-CH<sub>2</sub>), 0.11 (Si-CH<sub>3</sub>).

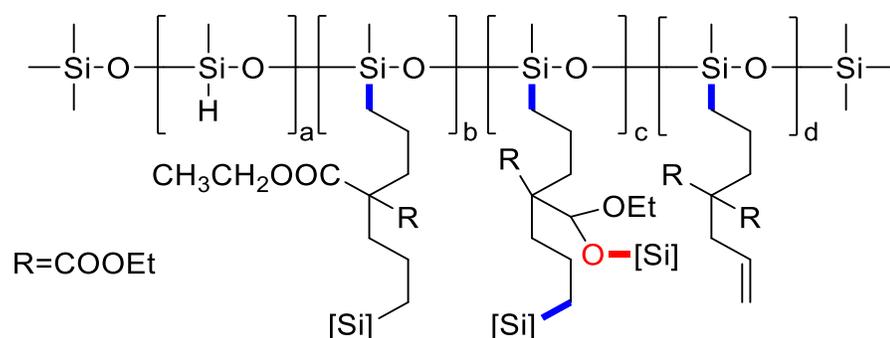
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  131.7 (trace of olefinic C=C), 9.3 (Si-CH<sub>2</sub>), 1.3, -0.1 and -1.1 (all Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  8.3 (-O-Si(Me)<sub>2</sub>-CH<sub>2</sub>- and -O-Si(Me)<sub>2</sub>(CH=CH<sub>2</sub>-), -20.2 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.2 (-O-SiMe(H)-O-).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 3052 (w, alkene C-H), 2958 (m), 2909 (w), 2883 (w), 2792 (w) (all alkane C-H), 2171 (m, Si-H), 1744 (w, ?), 1592 (w, Si-CH=CH<sub>2</sub>), 1409 (m, Si-CH=CH<sub>2</sub>), 1272 (s, Si-CH<sub>3</sub>), 1146 (s) and 1132 (s) (both Si-O-Si, Si-CH<sub>2</sub>CH<sub>2</sub>R), 923 (m, Si-H), 886 (w), 811 (w).

The product is isolated as white solid (185 mg).

## Functionalization of PMHS with diethyl diallylmalonate (DEDAM) (2b)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.93, 5.65 and 5.06 (olefinic C-H), 4.75 (Si-H), 4.14 ([Si]-O-CH(Me)(OR)), 2.59, 1.70 and 1.22 ( $\text{CH}_2$ ), 0.15 (Si- $\text{CH}_3$ ).

$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  171.1 (COOR), 133.5, 128.9, 126.7 and 118.7 (olefinic C=C), 60.9 and 57.7 (O- $\text{CH}_2$ - $\text{CH}_3$ ), 37.4, 18.0 and 14.4 ( $\text{CH}_2$ ), 1.5 to -0.3 (Si- $\text{CH}_2$ , Si- $\text{CH}_3$ ).

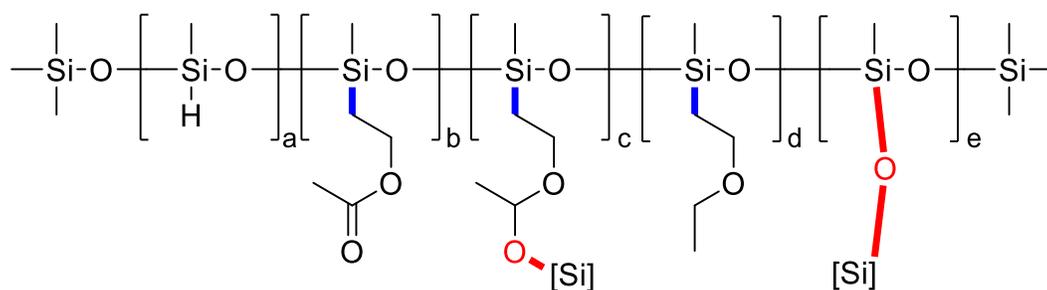
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.2 (-O-Si( $\text{CH}_2$ -R)Me-O-), -36.5 (Si-H), -66.3 (traces of Si-O-Si bridge).

$^{29}\text{Si}$  chemical shift for  $\text{Me}_3\text{Si}$  end-group was not detected probably due to low S/N ratio.

DRIFT (293 K,  $\text{cm}^{-1}$ )  $\nu$  = 3077 (w, alkene C-H), 2983 (m), 2957 (m), 2920 (m), 2880 (m) (all alkane C-H), 2161 (m, Si-H), 1752 (s) and 1718 (s) (both ester C=O), 1641 (w, C=C), 1464 (m, ester/alkane C-H), 1409 (m,  $\text{CH}_3$ ), 1390 (m,  $\text{CH}_3$  in EtO), 1372 (m,  $\text{CH}_2$  in EtO), 1270 (s, Si- $\text{CH}_3$ ), 1252 (s, Si- $\text{CH}_3$ ), 1198 (s, ester C-O), 1164 (s, Si-O-Si), 915 (m, Si-H), 875 (m), 827 (m).

The product is isolated as white-beige solid (260 mg).

## Functionalization of PMHS with vinyl acetate (3a)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  4.99 (traces of olefinic C-H), 4.73 (Si-H), 4.13 ([Si]-O-CH(Me)(OR)), 3.49 (O- $\text{CH}_2$ ), 1.94 ( $\text{CH}_3$ -CO), 0.98 ( $\text{CH}_3$ -CH(OSi)(OR), Si- $\text{CH}_2$ ), 0.12 (Si- $\text{CH}_3$ ).

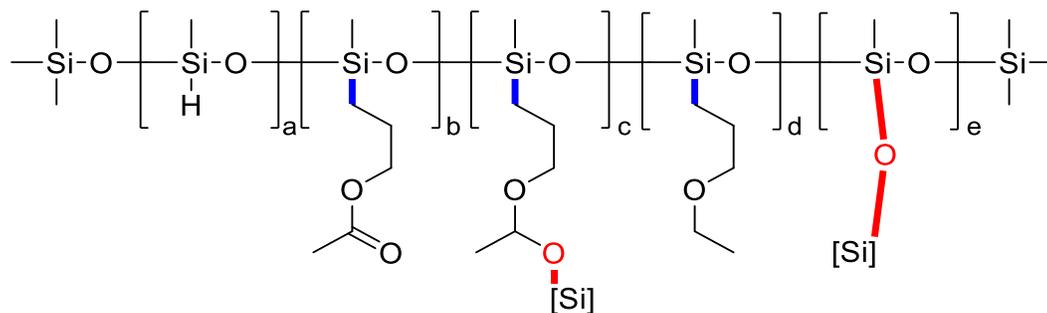
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  170.0 (COOR), 100.4 and 94.8 ([Si]-O-CH(Me)(OR)), 62.9 and 60.9 (OCH<sub>2</sub>), 24.1, 22.3, 20.7, and 18.5 (all CH<sub>3</sub>), 9.1 (Si-CH<sub>2</sub>), 0.2 and -3.0 (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -23.6 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.4 (Si-H), -60.9 (-O-Si(Me)(OR)-O-), -66.4 (traces of Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 3486 (br, m, OH), 2960 (m), 2937 (m), 2906 (m) (all alkane C-H), 2161 (m, Si-H), 1746 (s, ester C=O), 1387 (m) and 1367 (m) (both O-H, acetate), 1278 (s, Si-CH<sub>3</sub>), 1250 (m, Si-CH<sub>3</sub>), 1192 (m, Si-CH<sub>2</sub>-CH<sub>2</sub>R, ester C-O), 1150 (s, Si-O-Si, acetal, aliphatic ether), 1067 (m, Si-O-CH<sub>2</sub>, Si-O-Si, cyclic trimer Si-O-Si), 915 (m, Si-H), 858 (m), 818 (m).

The product is isolated as pale pink solid (330 mg).

### Functionalization of PMHS with allyl acetate (3b)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  6.15 and 5.80 (traces of olefinic C-H), 5.02 ([Si]-O-CH(Me)(OR)), 4.70 (Si-H), 3.93 (O-CH<sub>2</sub>), 1.91, 1.63 and 1.28 (CH<sub>2</sub>), 0.51 (Si-CH<sub>2</sub>), 0.08 (Si-CH<sub>3</sub>).

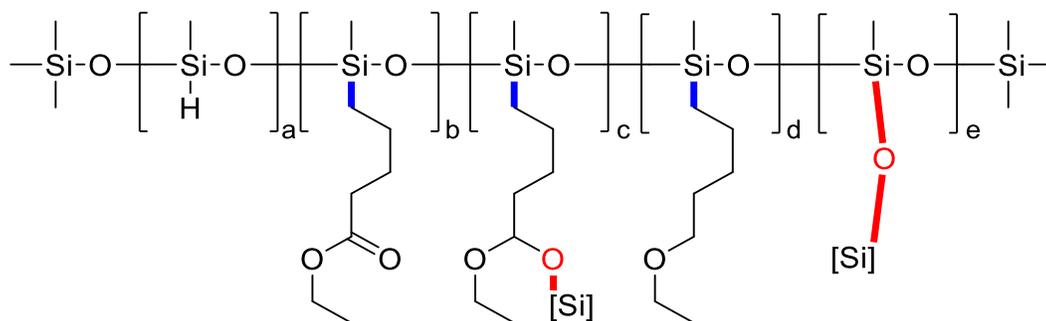
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  169.7 (traces of COOR), 94.7 ([Si]-O-CH(Me)(OR)), 69.2 and 66.3 (both O-CH<sub>2</sub>), 23.8, 22.7 and 20.6 (CH<sub>2</sub>), 13.4 (Si-CH<sub>2</sub>), 1.1, -0.6 and -2.8 (all Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.4 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.6 (Si-H), -61.0 (-O-Si(Me)(OR)-O-), -66.4 (traces of Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 3463 (br. w, O-H), 2986 (m), 2963 (m), 2934 (m), 2889 (m) (all alkane C-H), 2803 (w, aldehyde C-H), 2163 (m, Si-H), 1749 (s, ester C=O), 1444 (m), 1407 (m), 1390 (m), 1367 (m), 1352 (m) (all acetates, CH<sub>2</sub> and CH<sub>3</sub> of EtO), 1275 (s, Si-CH<sub>3</sub>), 1250 (m, Si-CH<sub>3</sub>, Si-CH<sub>2</sub>-CH<sub>2</sub>R), 1198 (m, Si-CH<sub>2</sub>-CH<sub>2</sub>R), 1155 (s, Si-O-Si, acetal), 921 (m, Si-H), 850 (m), 827 (m). NB! Aldehyde C-H IR frequency (2803 cm<sup>-1</sup>) was also detected, which could have occurred via ester reduction to corresponding aldehyde.

The product is isolated as pale pink solid (370 mg).

## Functionalization of PMHS with ethyl 4-pentenoate (3c)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.37 ([Si]-O-CH(Me)(OR)), 4.74 (Si-H), 3.99, 3.67 and 3.32 (OCH<sub>2</sub>), 2.17, 1.54 and 1.13 (CH<sub>2</sub>), 0.47 (Si-CH<sub>2</sub>), 0.05 (Si-CH<sub>3</sub>).

$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  97.8 ([Si]-O-CH(Me)(OR)), 62.3, 59.7 and 57.9 (OCH<sub>2</sub>), 37.2, 33.8, 28.4, 22.7 and 17.2 (all CH<sub>2</sub> and CH<sub>3</sub>), 15.3 (Si-CH<sub>2</sub>), -0.6 and -2.9 (Si-CH<sub>3</sub>).

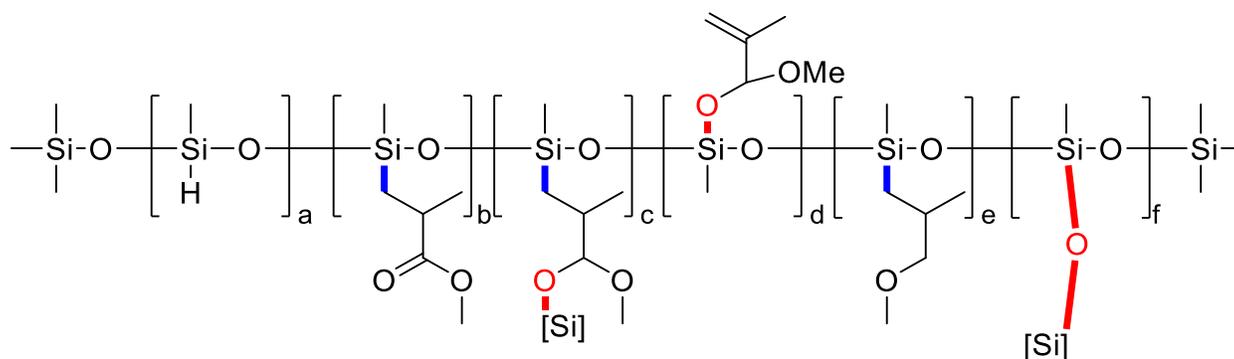
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.5 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.9 (Si-H), -61.2 (-O-Si(Me)(OR)-O-).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 2974 (m), 2934 (m), 2877 (m, all alkane C-H), 2800 (w, aldehyde C-H), 2161 (w, Si-H), 1749 (s, ester C=O), 1467 (m), 1412 (m), 1375 (m), 1352 (m) (all acetates, CH<sub>2</sub> and CH<sub>3</sub> of EtO), 1272 (s, Si-CH<sub>3</sub>), 1192 (s, Si-CH<sub>2</sub>-CH<sub>2</sub>R), 1150 (s, Si-O-Si, acetal), 921 (m), 847 (m), 816 (m). NB! Aldehyde C-H IR frequency (2800 cm<sup>-1</sup>) was also detected, which could have occurred via ester reduction to corresponding aldehyde.

NB! While  $^{13}\text{C}$  NMR demonstrates the absence of carbonyl signals in the spectrum, the DRIFT spectrum has two peaks corresponding to ester carbonyl group (at 1749 cm<sup>-1</sup>). We believe that the lack of signal in  $^{13}\text{C}$  spectrum might be due to insufficient relaxation delay and cross-polarization delay used for this specific sample. However, for all of the other cross-linked products the same parameters were used and in those polymers the expected ester C=O signal was seen in  $^{13}\text{C}$  spectrum.

The product is isolated as beige solid (422 mg).

### Functionalization of PMHS with methyl methacrylate (3d)



$^1\text{H}$  MAS SSNMR (300 MHz) (very broad spectrum, the most intense peaks are presented):  $\delta$  4.7 (Si-H), 3.49 (OCH<sub>3</sub>), 2.54 ([Si]-CH<sub>2</sub>CH(Me)(COOR)), 1.42 and 1.10 (CH<sub>2</sub>, CH<sub>3</sub>), 0.07 (Si-CH<sub>3</sub>).

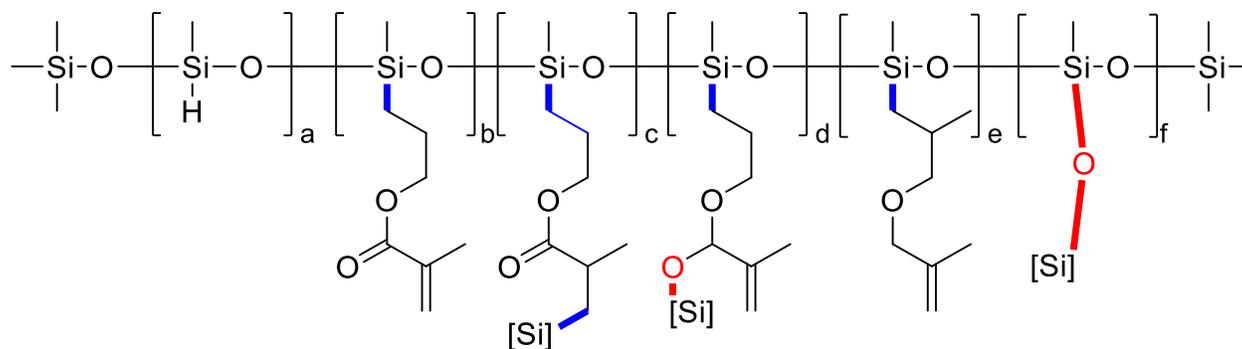
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  176.9 (COOR), 148.9 and 113.2 (both traces of olefinic C=C), 103.0 and 90.9 ([Si]-O-CH(Me)(OR)), 54.9 and 51.7 (OCH<sub>3</sub>), 44.8 (CH), 34.5, 20.3 and 16.8 (CH<sub>2</sub>, CH<sub>3</sub>), 0.5 and -3.3 (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -22.5 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.6 (Si-H), -57.6 and -61.1 (-O-Si(Me)(OR)-O-), -66.8 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 2972 (m), 2912 (m), 2877 (m), 2843 (w) (all alkane C-H), 2169 (w, Si-H), 1749 (m) and 1709 (m) (both ester C=O), 1461 (m) and 1432 (m) (both OCH<sub>3</sub>), 1404 (m), 1381 (m) and 1361 (m) (all ether O-CH<sub>2</sub>), 1272 (s, Si-CH<sub>3</sub>), 1221 (s, Si-CH<sub>2</sub>CH<sub>2</sub>R), 1161 (s, ester C-O, Si-O-CH<sub>2</sub>R), 987 (w), 915 (m), 875 (m), 850 (m), 807 (m).

The product is isolated as white solid (390 mg).

### Functionalization of PMHS with allyl methacrylate (3e)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  very broad spectrum, more intense peaks: 4.7 (br., Si-H), 1.8 (CH<sub>2</sub>, CH<sub>3</sub>), 0.1 (br., Si-CH<sub>3</sub>).

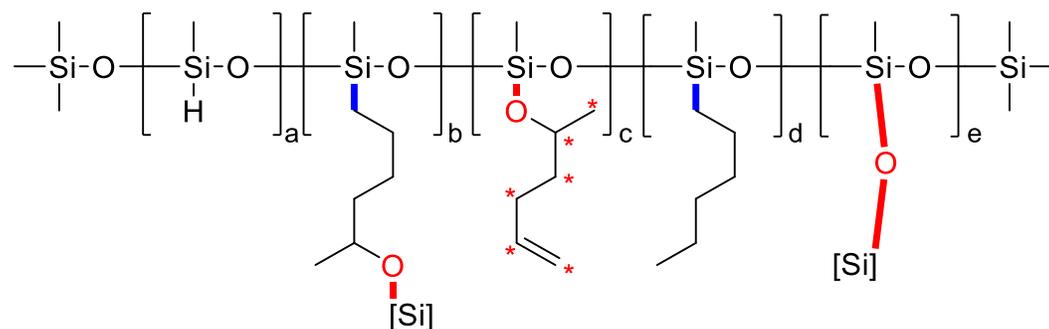
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  176.7 and 166.4 (COOR), 136.9, 132.7, 124.5 and 118.3 (all olefinic C=C), 66.5 and 55.6 (OCH<sub>2</sub>), 45.2 (CH<sub>2</sub>), 22.4, 18.3 and 14.1 (CH<sub>2</sub>, CH<sub>3</sub>), 1.1 (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  7.9 (end-group SiMe<sub>3</sub>), -20.9 (-O-Si(CH<sub>2</sub>-R)Me-O-), -35.7 (Si-H), -58.2 (very low intensity -O-Si(Me)(OR)-O-), -65.2 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>)  $\nu$  = 3080 (w, alkene C-H), 2966 (m), 2886 (m) (all m, alkane C-H), 2166 (m, Si-H), 1744 (s, ester C=O), 1649 (w, methacrylate C=C), 1478 (m) and 1452 (m) (both ether O-CH<sub>2</sub> and ester CH<sub>2</sub>), 1415 (m) and 1395 (m) (both methacrylate =CH<sub>2</sub>), 1270 (s, Si-CH<sub>3</sub>), 1238 (m, Si-CH<sub>2</sub>CH<sub>2</sub>R), 1204 (s, Si-CH<sub>2</sub>CH<sub>2</sub>R), 1127 (s, Si-O-Si, Si-O-CH<sub>2</sub>R, acetal), 978 (m), 918 (m), 881 (m), 818 (m).

The product is isolated as white crystalline solid (457 mg).

### Functionalization of PMHS with 5-hexen-2-one (3f)



The unreacted C=C bond has isomerized throughout the marked (\*) chain.

$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.74 and 5.39 (olefinic C-H), 4.74 (Si-H), 4.34 and 4.01 ([Si]-O-CH(Me)(OR)), 1.99, 1.81, 1.60, 1.31, 1.14 and 0.8 (CH<sub>2</sub> and CH<sub>3</sub>), 0.11 (Si-CH<sub>3</sub>).

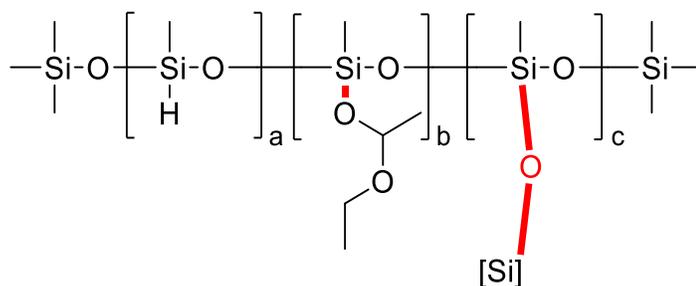
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  128.0 and 126.9 (both olefinic C=C), 108.6 and 91.3 ([Si]-O-CH(Me)(OR)), 68.6 (-O-CH), 42.9, 39.3, 36.1, 29.4, 23.4, 17.5 and 14.0 (all CH<sub>2</sub> and CH<sub>3</sub>), 1.1, -0.6 and -3.3 (all Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.1 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.8 (Si-H), -60.5 (-O-Si(Me)(OR)-O-), -63.4 and -66.4 (both Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 3026 (w, alkene C-H), 2969 (m), 2937 (m), 2874 (m) (all alkane C-H), 2166 (m, Si-H), 1724 (w, C=O), 1684 (w), 1644 (w) (both C=C), 1455 (m, CH<sub>3</sub> group C-H), 1415 (m, Si-CH<sub>3</sub>), 1378 (m, Si-O-CH(Me)R), 1278 (s, Si-CH<sub>3</sub>), 1161 (s, Si-O-CH(Me)R), 970 (m), 924 (m), 878 (m), 853 (m), 807 (m).

The product is isolated as white solid (422 mg).

### Functionalization of PMHS with EtOAc (3g)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.58 (?), 5.01 ([Si]-O-CH(Me)(OR)), 4.70 (Si-H), 3.72 and 3.32 (O-CH<sub>2</sub>), 1.11 (CH<sub>2</sub> and CH<sub>3</sub>), 0.06 (Si-CH<sub>3</sub>).

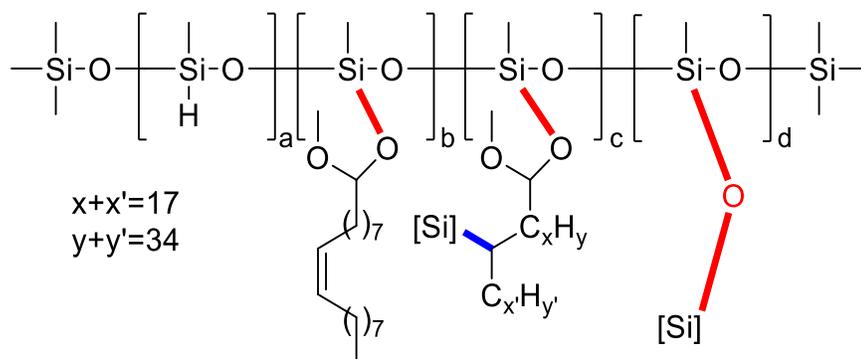
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  100.3, 94.7 and 89.5 ([Si]-O-CH(Me)(OR)), 62.1 and 57.9 (O-CH<sub>2</sub>), 26.6, 23.9, 18.2 and 15.3 (all CH<sub>2</sub> + CH<sub>3</sub>), 1.3 and -4.1 (all Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -36.7 (Si-H), -59.2 and -61.7 (both -O-Si(Me)(OR)-O-), -66.4 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 2983 (m), 2926 (m), 2886 (m) (all alkane C-H), 2172 (w, Si-H), 1489 (w, OEt), 1444 (w, OEt), 1395 (m, OEt), 1344 (w, OEt), 1278 (v. s, Si-CH<sub>3</sub>) and 1187 (v. s, Si-OCH(Me)OEt), 1115 (m, CH<sub>2</sub>-O-CH), 1064 (w, OEt), 995 (w), 910 (w), 853 (m) and 824 (m).

The product is isolated as grey solid (302 mg).

### Functionalization of PMHS with methyl oleate (3h)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.32 ([Si]-O-CH(Me)(OR)), 4.75 (Si-H), 3.52 and 3.25 (both O-CH<sub>2</sub>), 2.17, 1.93, 1.25 and 0.85 (CH<sub>2</sub> and CH<sub>3</sub>), 0.08 (all Si-CH<sub>3</sub>).

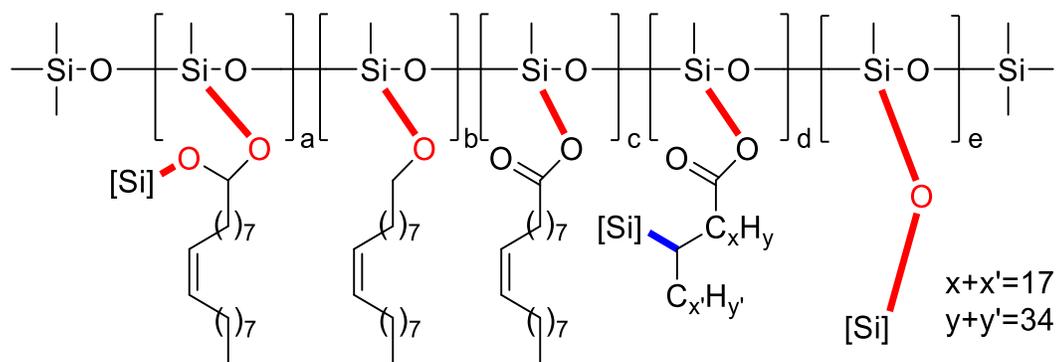
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  99.2 ([Si]-O-CH(Me)(OR)), 62.4 and 54.1 (O-CH<sub>2</sub>), 49.7, 37.3, 33.4, 30.0, 24.6, 23.2 and 17.5 (CH<sub>2</sub> and CH<sub>3</sub>), -0.6 and -3.0 (both Si-CH<sub>3</sub>)

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.2 (-O-Si(CH<sub>2</sub>-R)Me-O-), -36.6 (Si-H), -57.5 and -61.4 (-O-Si(Me)(OR)-O-), -66.6 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 3457 (br. w, O-H), 2943 (s) and 2857 (s) (both alkane C-H), 2680 (w, aldehyde C-H), 2169 (w, Si-H), 1746 (s) and 1718 (s) (both C=O), 1632 (w, C=C), 1467 (m, alkane C-H, OEt), 1441 (m, OEt), 1412 (m, Si-CH<sub>3</sub>), 1372 (m, OEt), 1270 (s, Si-CH<sub>3</sub>), 1141 (s, ester C-O, ether C-O), 1058 (s, Si-O-Si), 908 (m), 847 (m), 801 (m). NB! Aldehyde C-H IR frequency (2680 cm<sup>-1</sup>) was also detected, which could have occurred via ester reduction to corresponding aldehyde.

The product is isolated as white crystalline solid (420 mg).

### Functionalization of PMHS with oleic acid (3i)



$^1\text{H}$  MAS SSNMR (300 MHz):  $\delta$  5.31 (olefinic C-H), 4.71 (Si-H), 2.25, 2.00, 1.56, 1.28 (all CH<sub>2</sub>), 0.88 (CH<sub>3</sub>), 0.12 (Si-CH<sub>3</sub>).

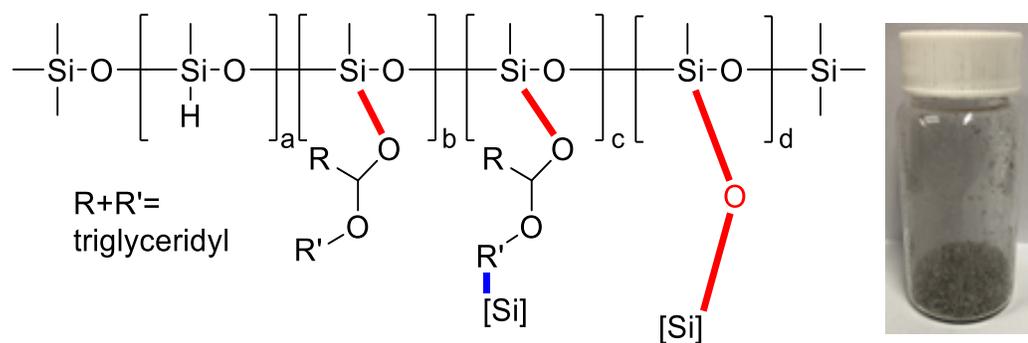
$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  181.5 and 171.8 (both COOR), 130.2 (olefinic C=C), 92.9 ([Si]-O-CH(Me)(OR)), 39.9, 35.6, 32.6, 29.7, 24.9 (all CH<sub>2</sub>), 14.3 (Si-CH<sub>2</sub> and/or CH<sub>3</sub>), 0.8 and -3.3 (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -23.1 (-O-Si(CH<sub>2</sub>-R)Me-O-), -35.4 (Si-H), -59.3 (-O-Si(Me)(OR)-O-), -66.2 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 3014 (s, alkene C-H), 2969 (s), 2943 (s) and 2860 (s) (all alkane C-H), 2181 (m, Si-H), 1741 (s) and 1721 (s) (both ester C=O), 1609 (w, C=C), 1467 (s, alkane C-H), 1418 (s, carboxylic acid O-H), 1384 (s, O-H), 1275 (s, Si-CH<sub>3</sub>), 1164 (s, Si-OCH<sub>x</sub>R), 915 (s), 855 (s), 810 (s).

The product is isolated as white crystalline solid (396 mg).

### Functionalization of PMHS with olive oil (3j)



$^1\text{H}$  MAS SSNMR (300 MHz) (very broad spectrum, more intense peaks):  $\delta$  5.27 (olefinic C-H), 4.17 and 3.99 (both O-CH or O-CH<sub>2</sub>), 1.87 and 1.21 (both CH<sub>2</sub>), 0.14 (Si-CH<sub>3</sub>)

$^{13}\text{C}$  CPMAS SSNMR (75 MHz):  $\delta$  173.3 (traces of ester C=O), 130.3 (olefinic C=C), 98.4 ([Si]-O-CH(Me)(OR)), 71.2 and 62.3 (O-CH<sub>x</sub>), 37.3, 32.5, 29.9 and 24.8 (all CH<sub>2</sub>), 14.1 (CH<sub>3</sub>), 1.1 and -3.2 (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta$  -21.1 and -23.9 (both -O-Si(CH<sub>x</sub>-R)Me-O-), -36.4 (Si-H), -58.3 and -60.7 (both -O-Si(Me)(OR)-O-), -66.1 (Si-O-Si bridge).

DRIFT (293 K, cm<sup>-1</sup>):  $\nu$  = 2961 (s), 2935 (s) and 2861 (s) (all alkane C-H), 2683 (w, aldehyde C-H), 2168 (s, Si-H), 2034 (w), 1999 (w), 1750 (s, ester C=O), 1470 (s, alkane C-H), 1418 (m, methyl ester CH<sub>3</sub>), 1378 (m, aldehyde C-H, alcohol O-H), 1272 (s, Si-CH<sub>3</sub>), 1158 (s, Si-OCH<sub>x</sub>), 969 (m), 920 (s), 877 (m), 849 (m), 800(m). **NB!** Aldehyde C-H IR frequency (2683 cm<sup>-1</sup>) was also detected, which could have occurred via ester reduction to corresponding aldehyde.

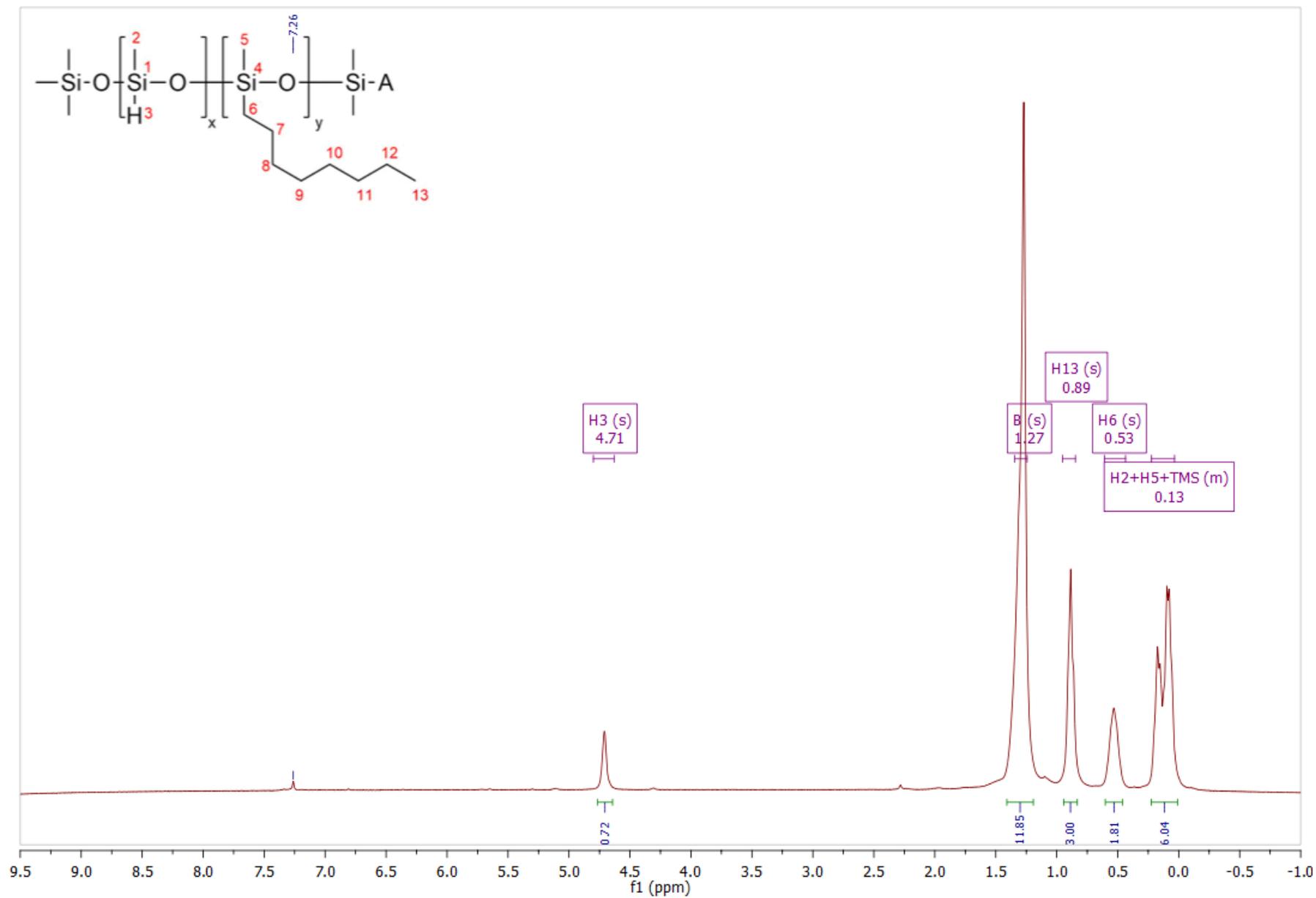
The product is isolated as dark-grey solid (1284 mg).

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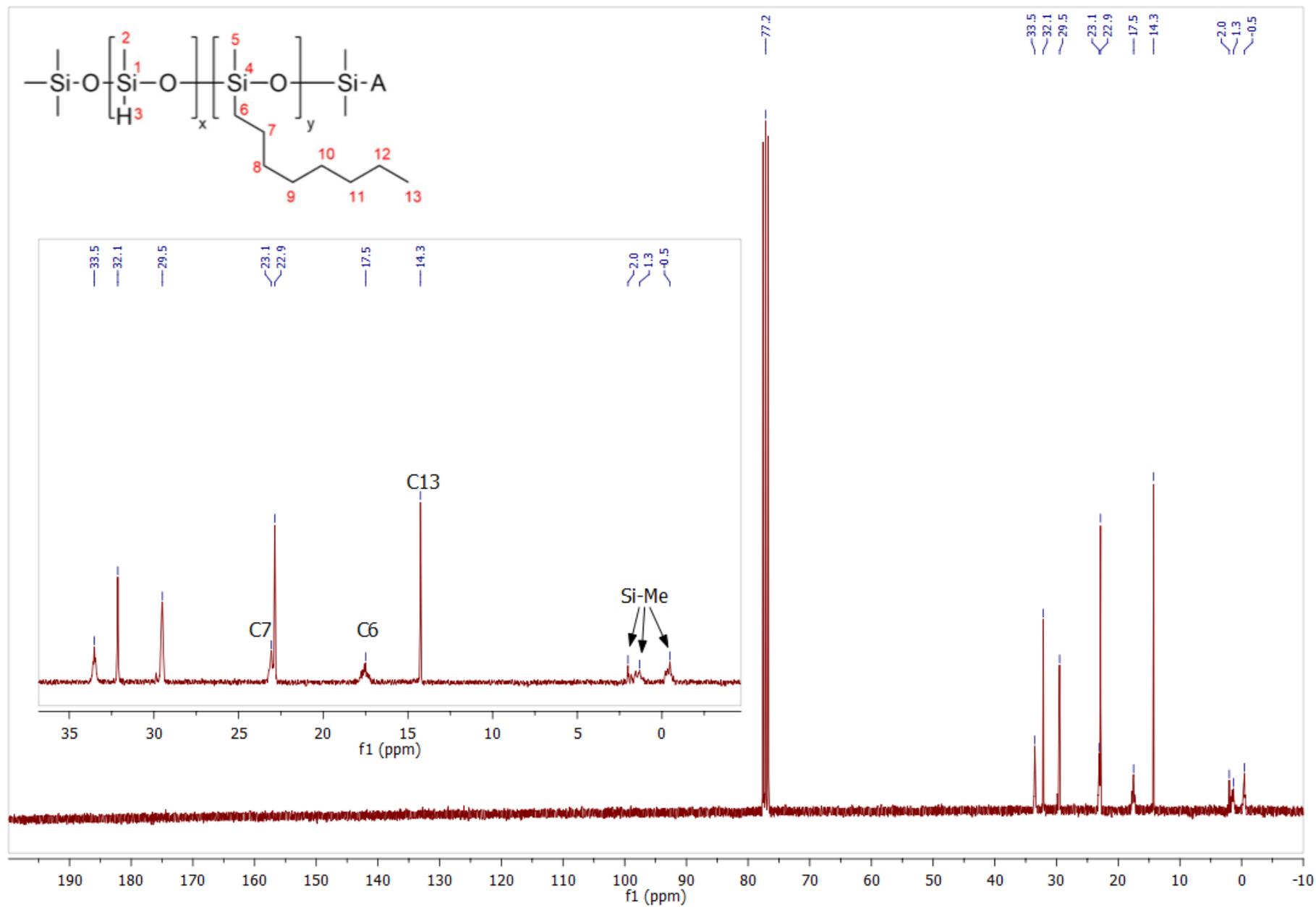
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## NMR spectra

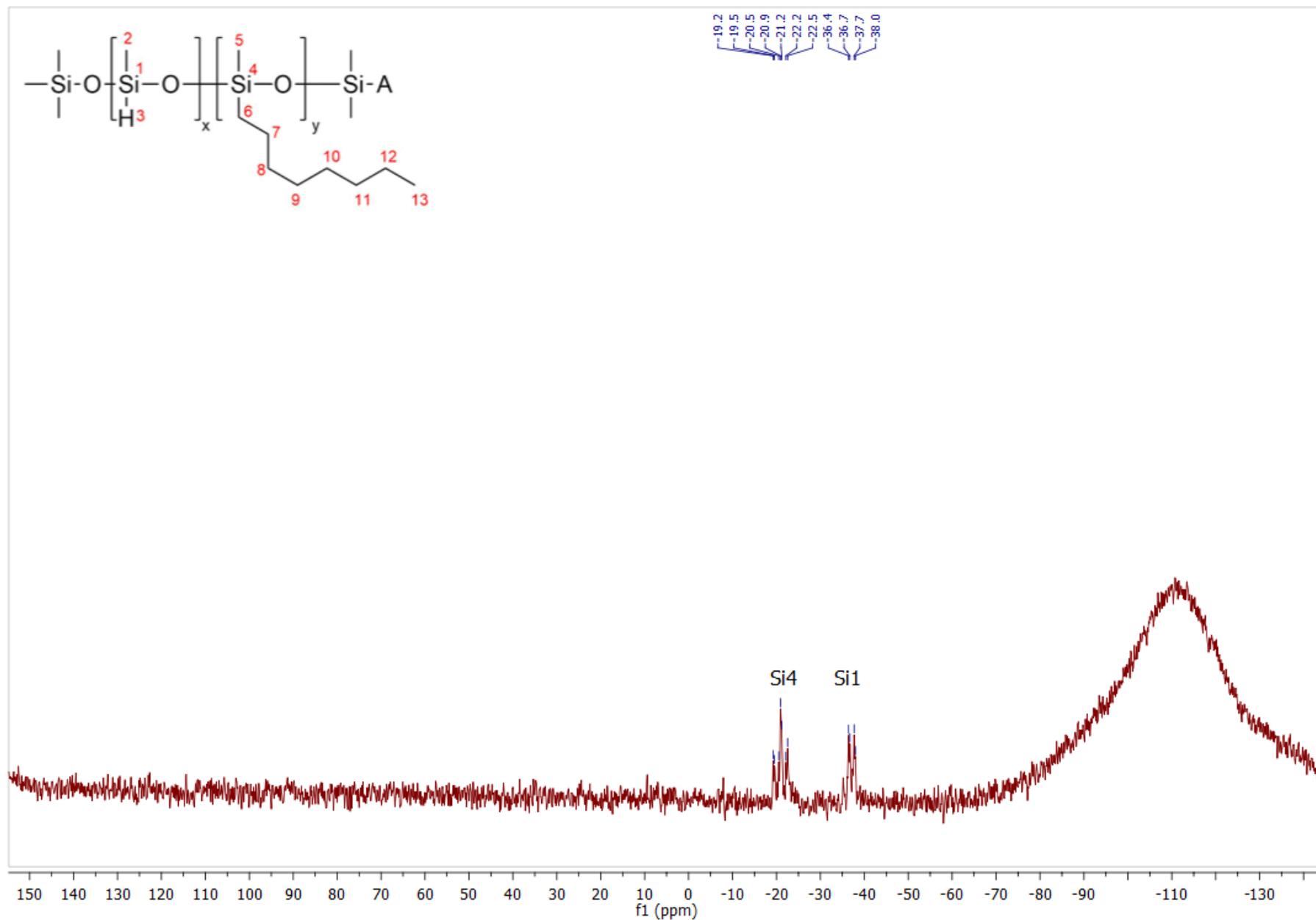
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of 1a



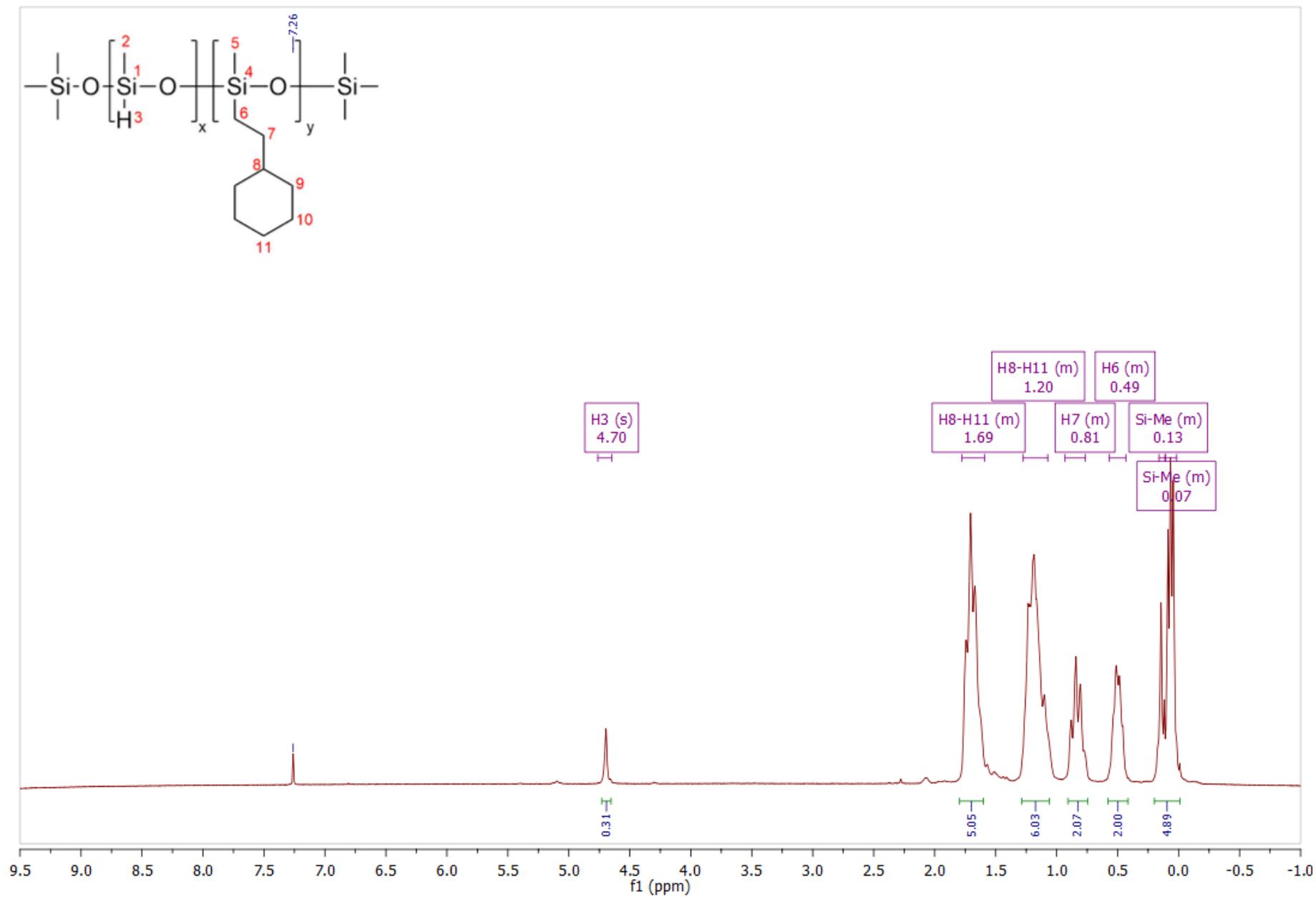
$^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz,  $\text{CDCl}_3$ ) of 1a



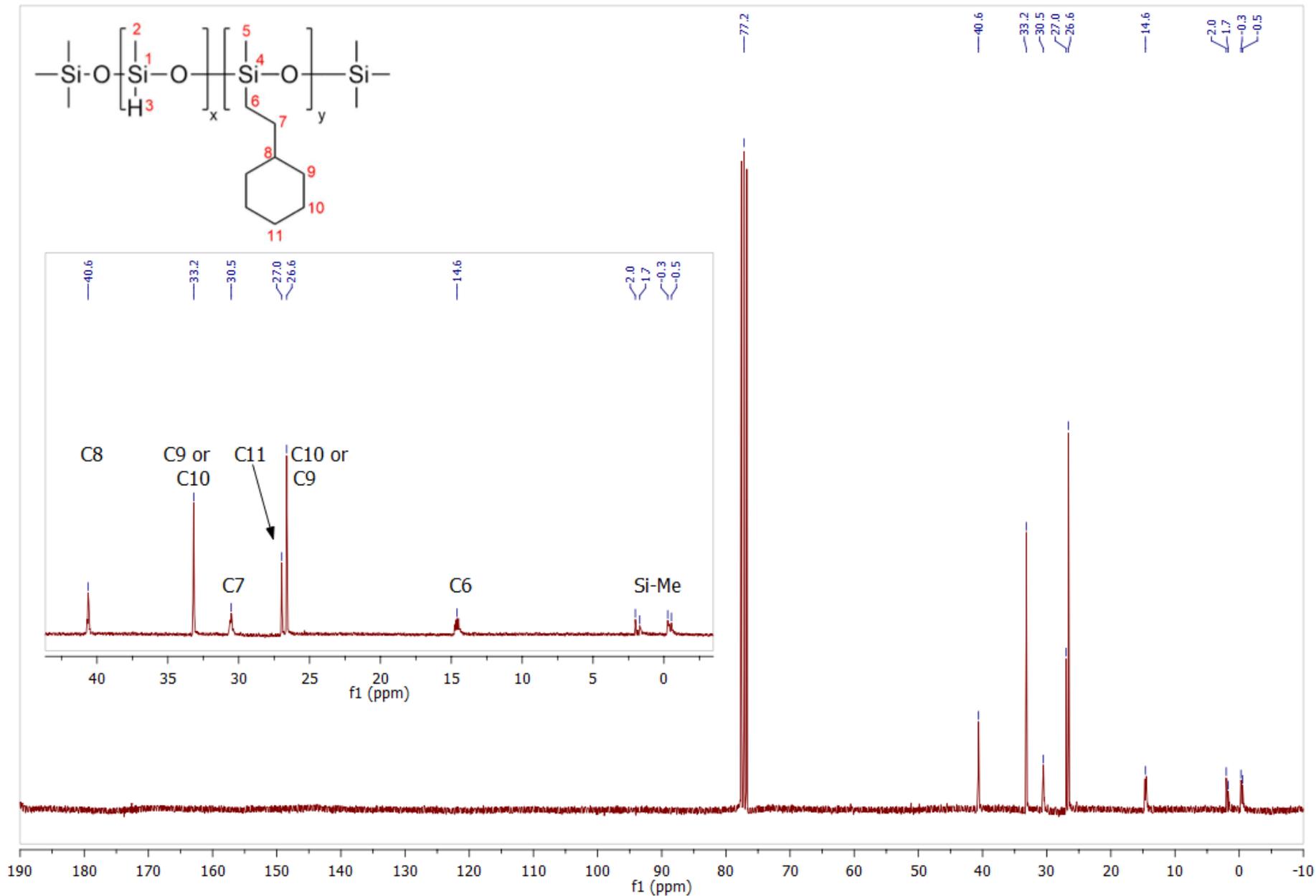
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 1a



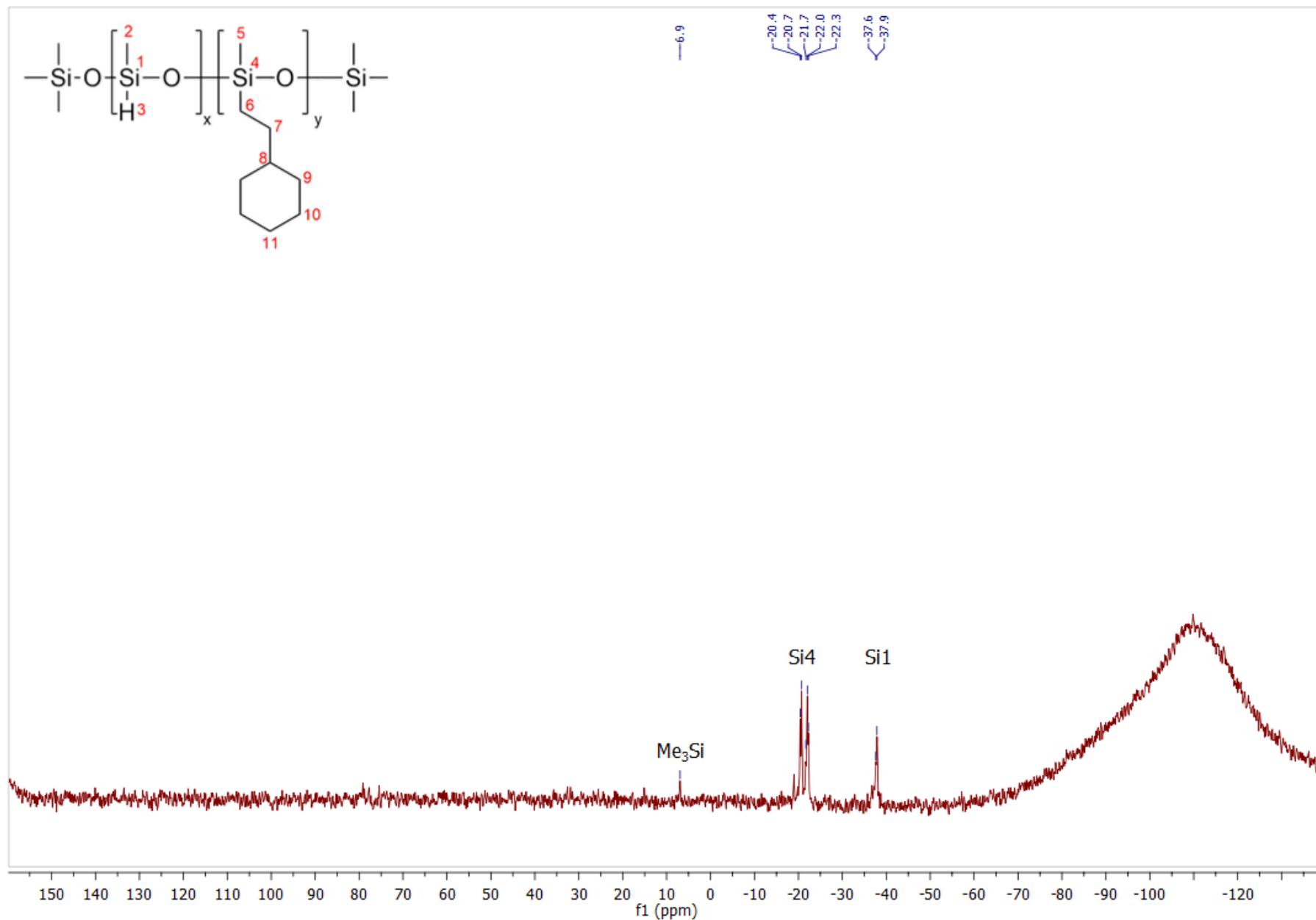
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1b



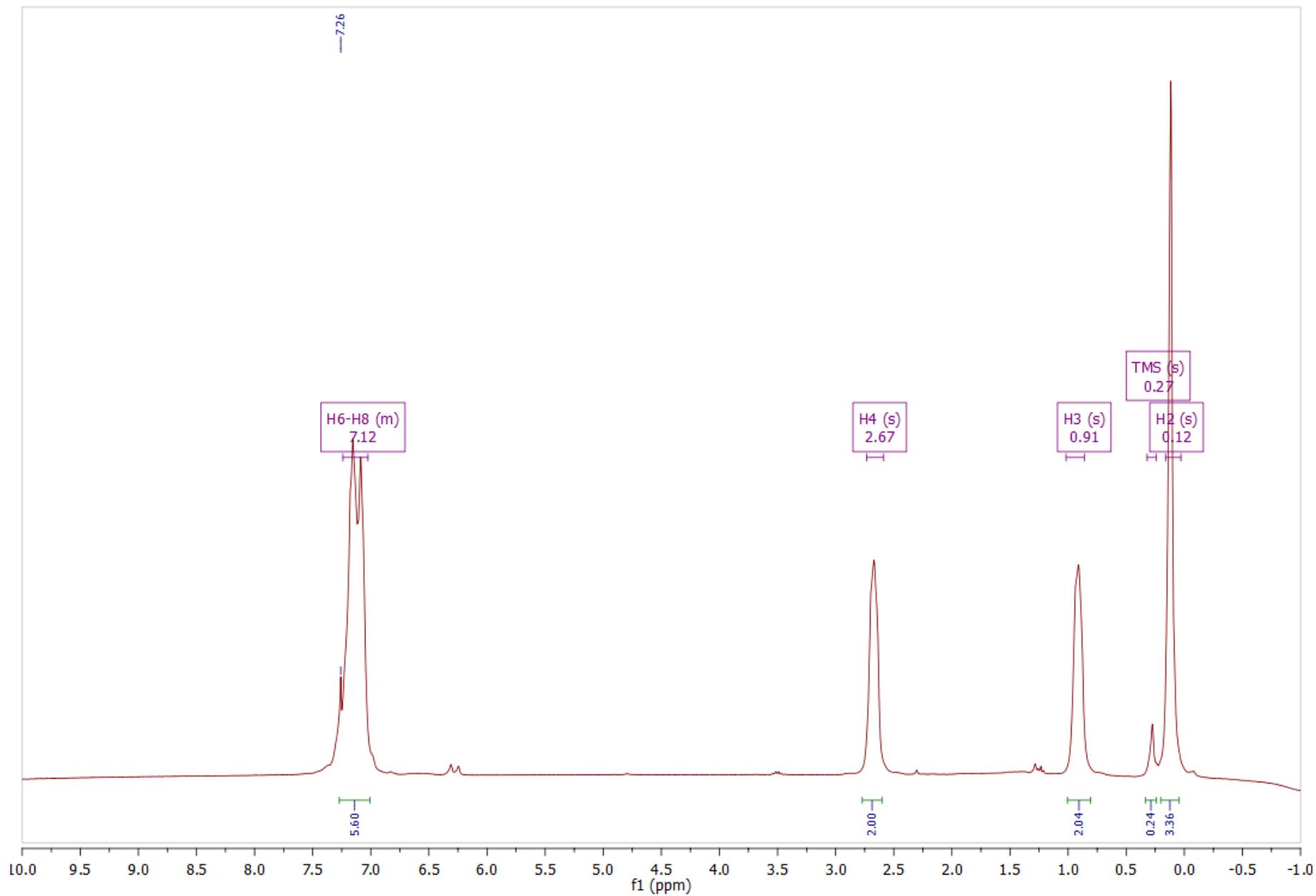
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 1b



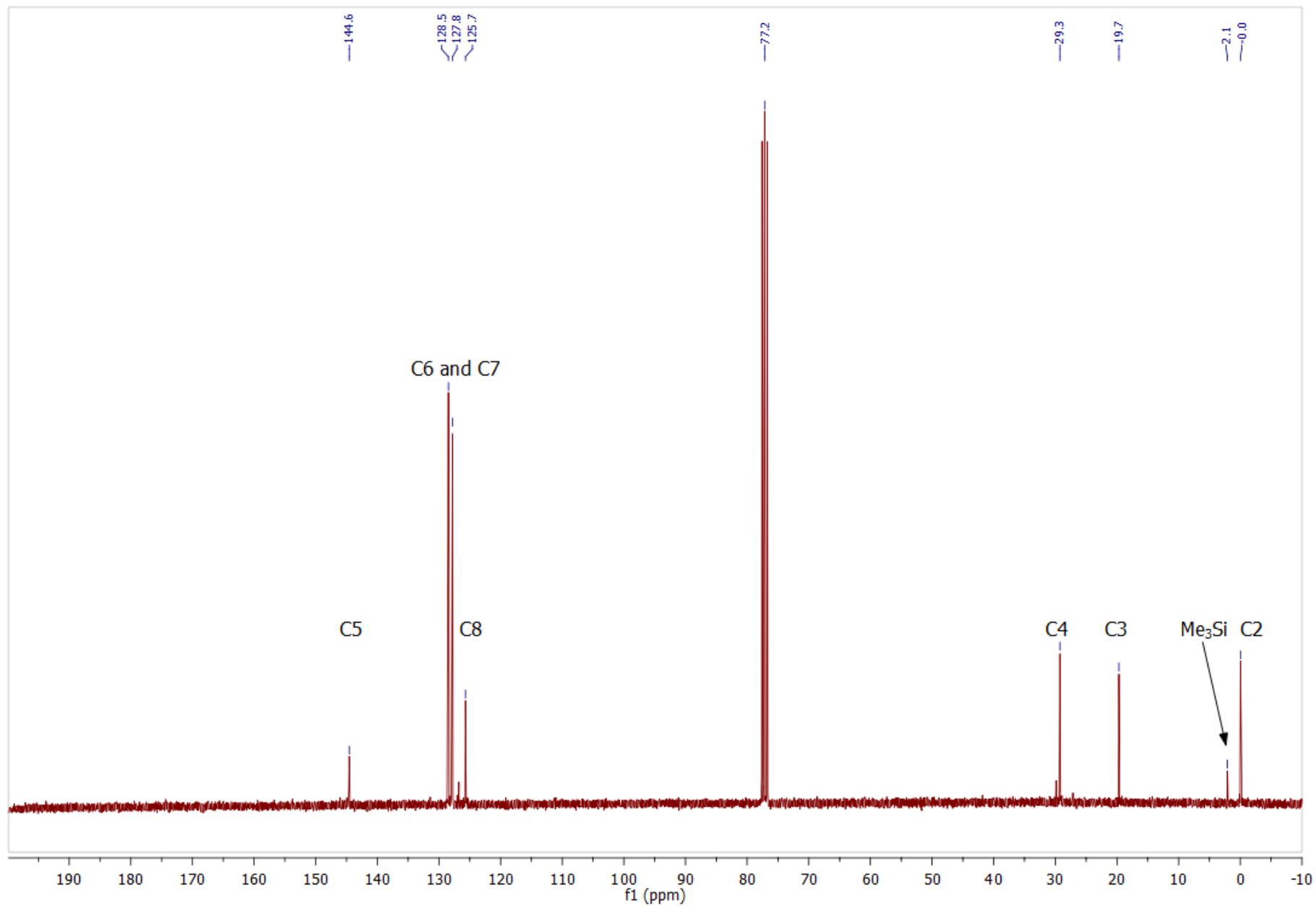
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 1b



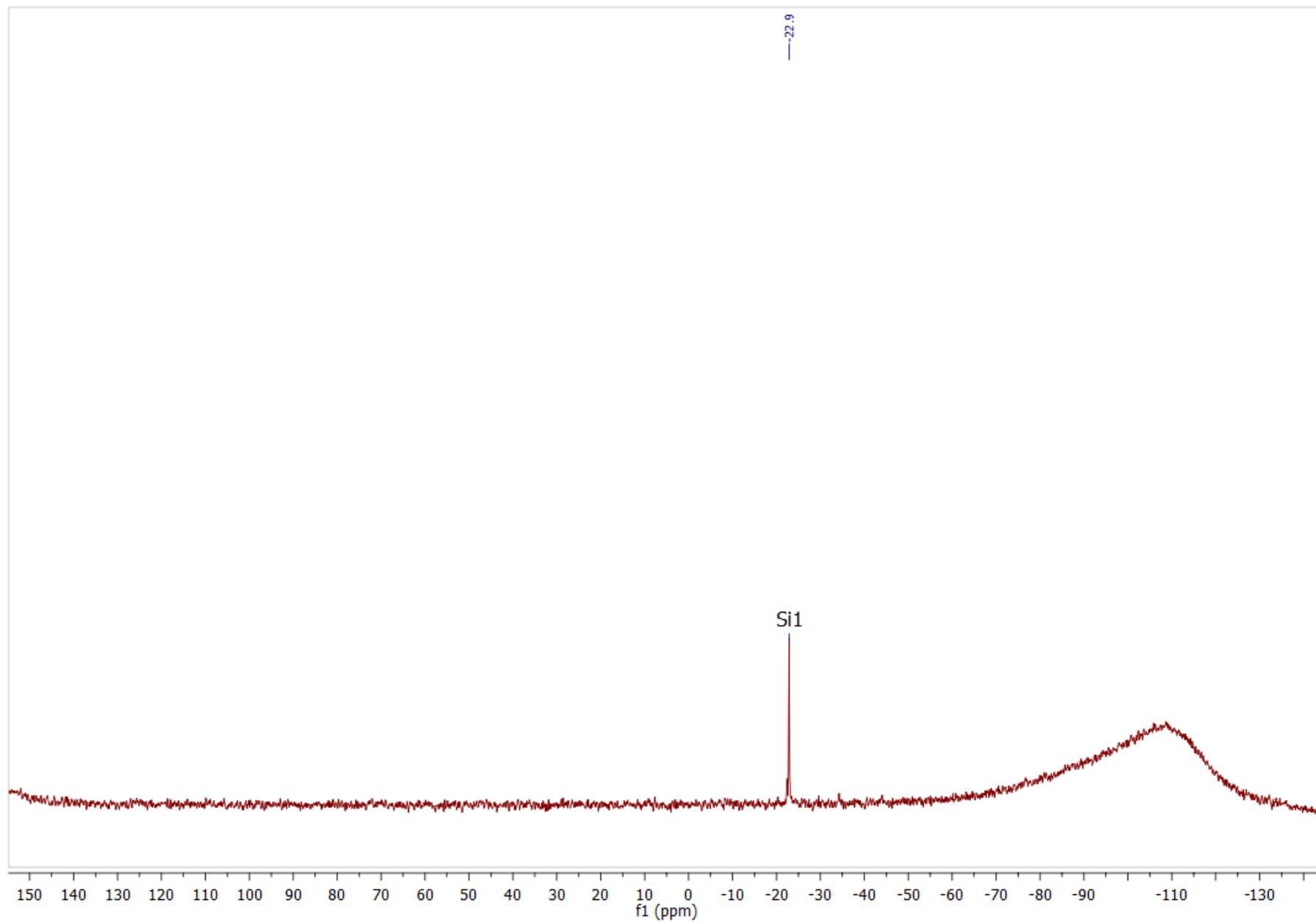
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1c



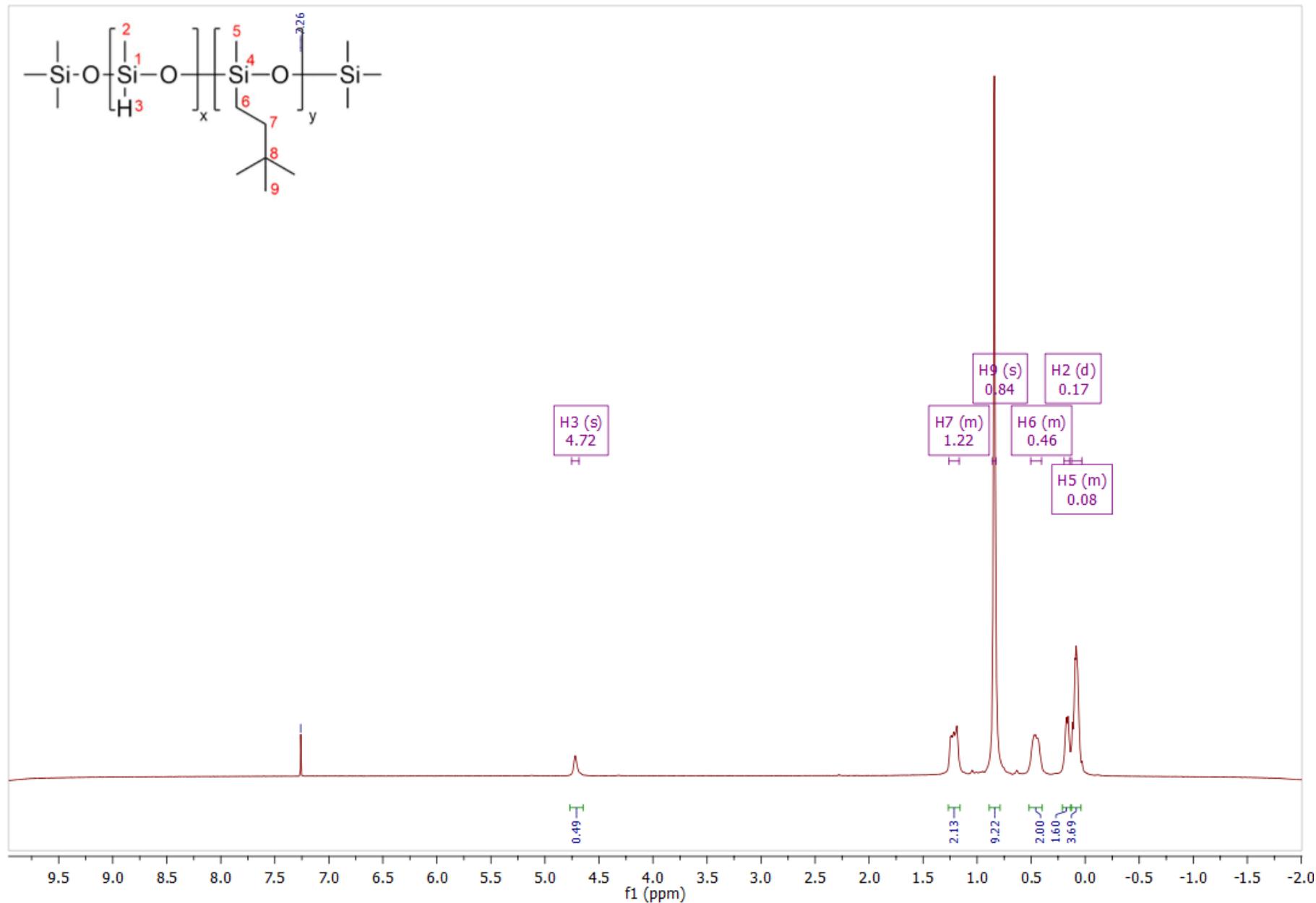
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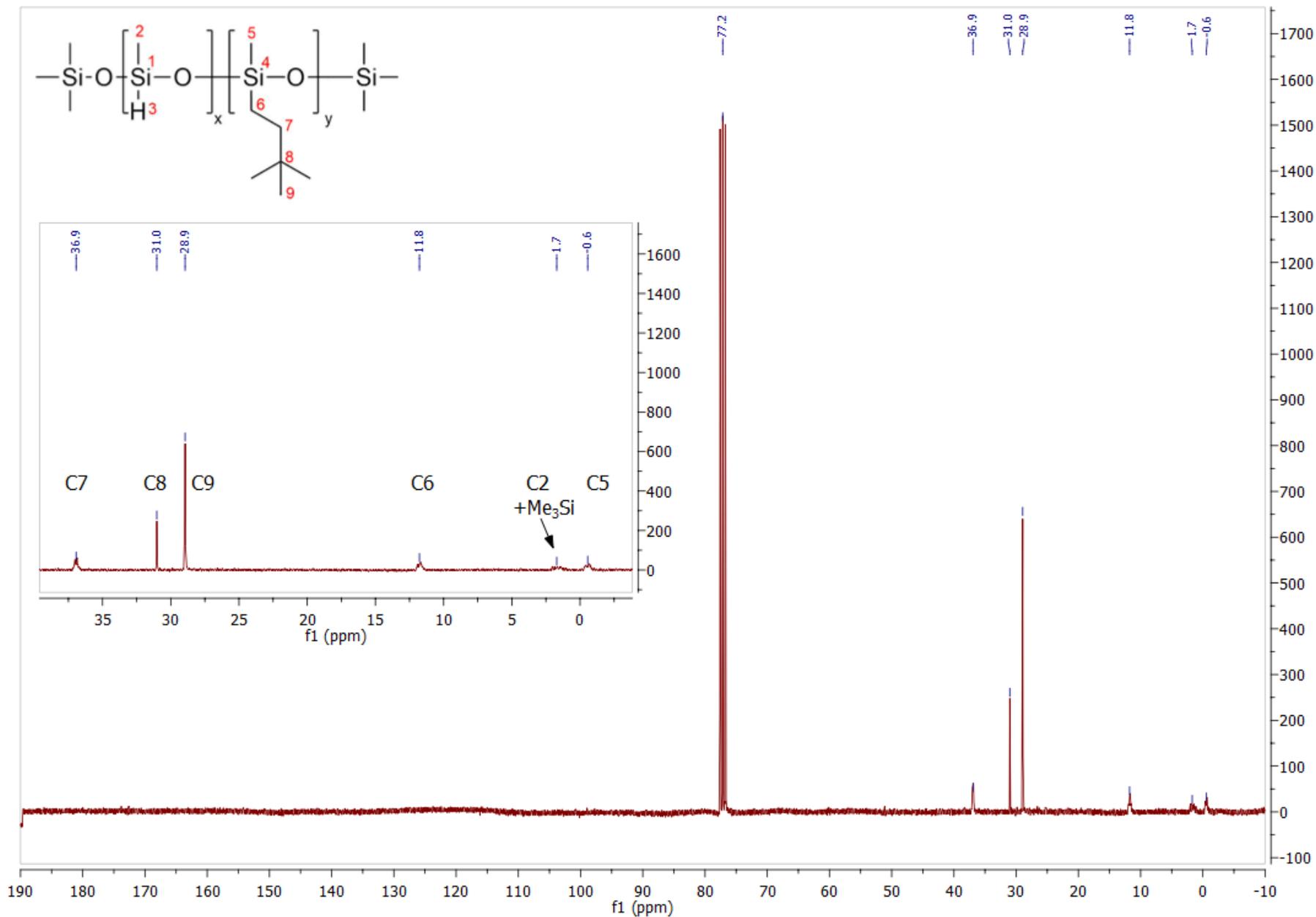
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 1c



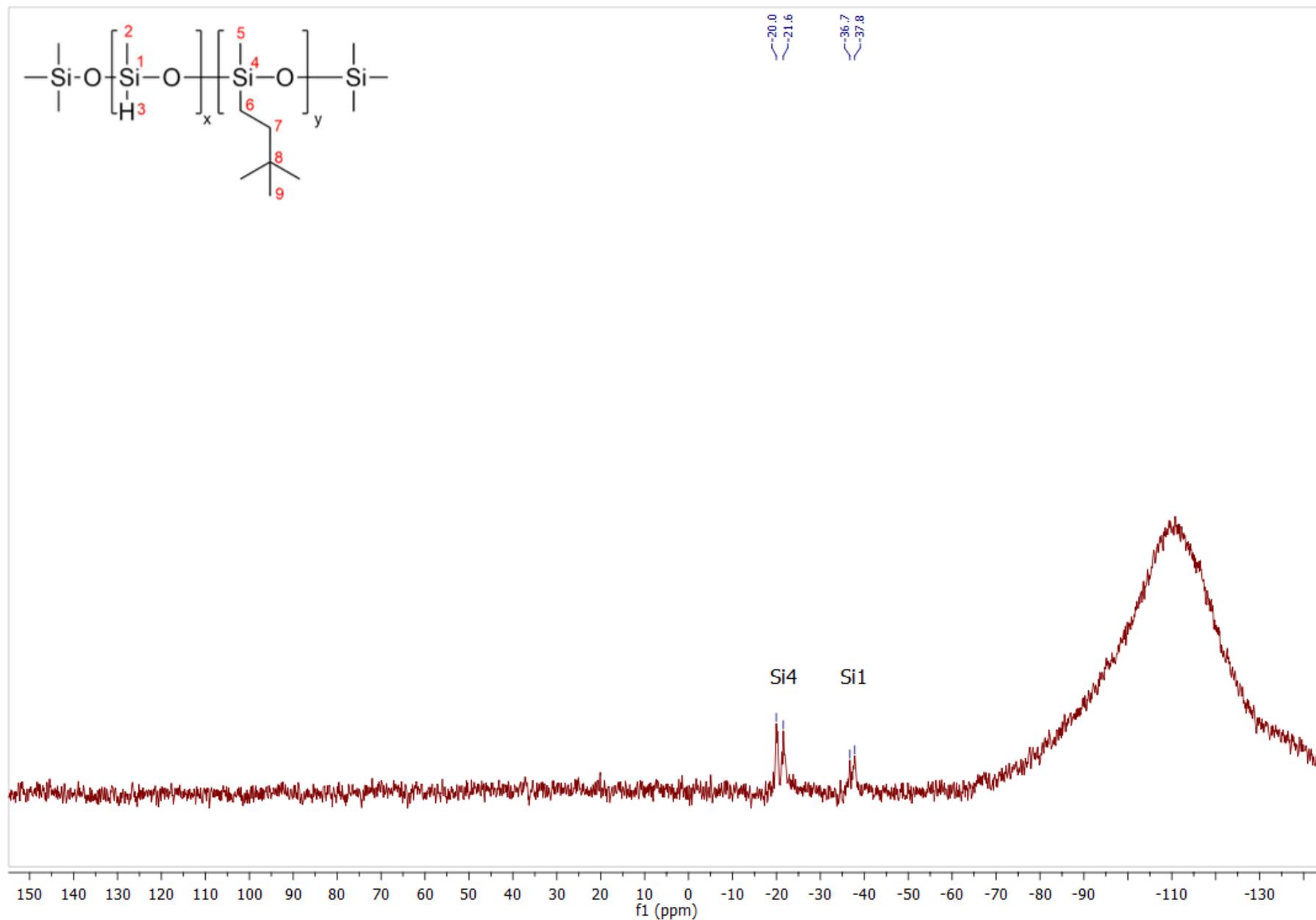
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1d



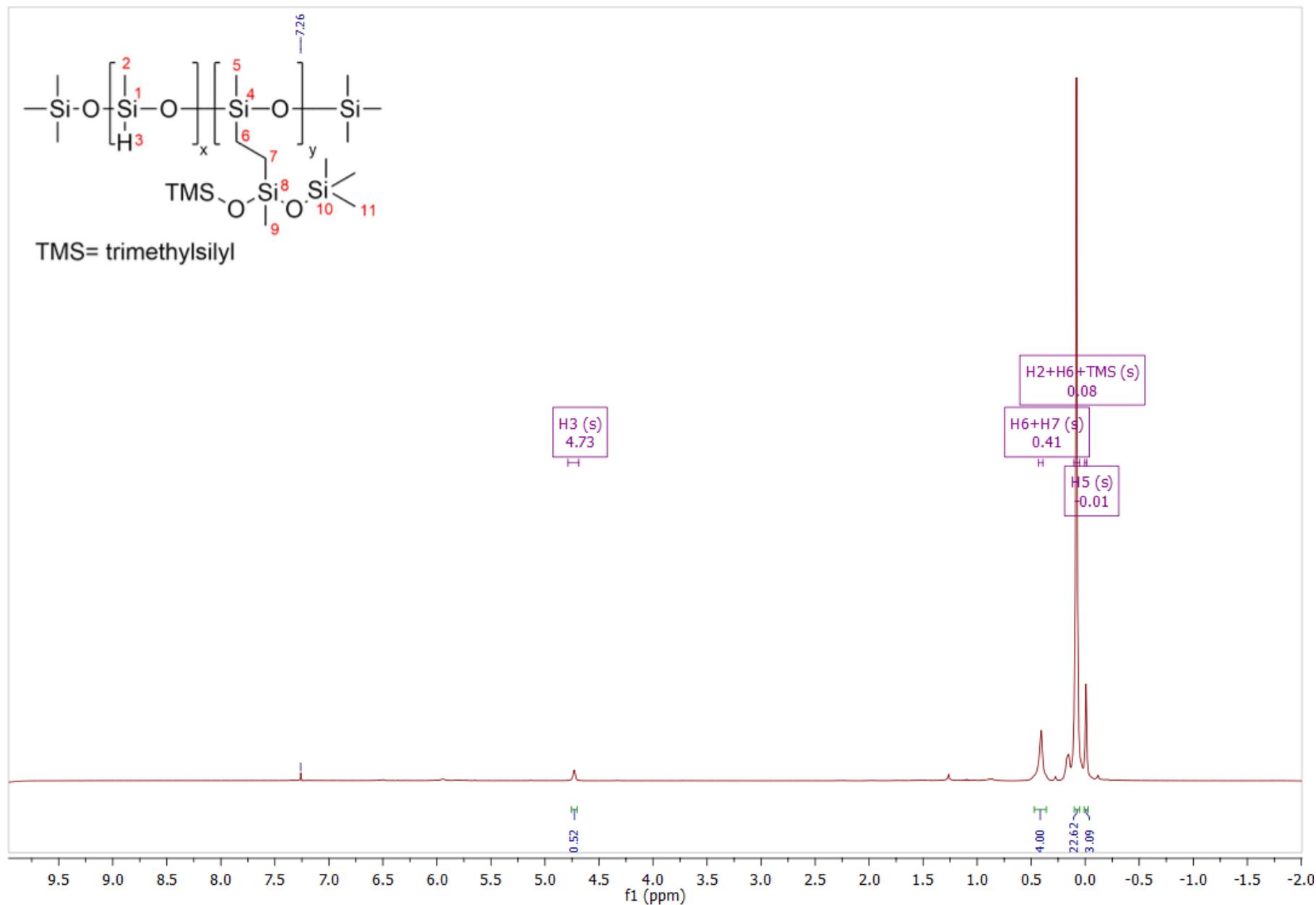
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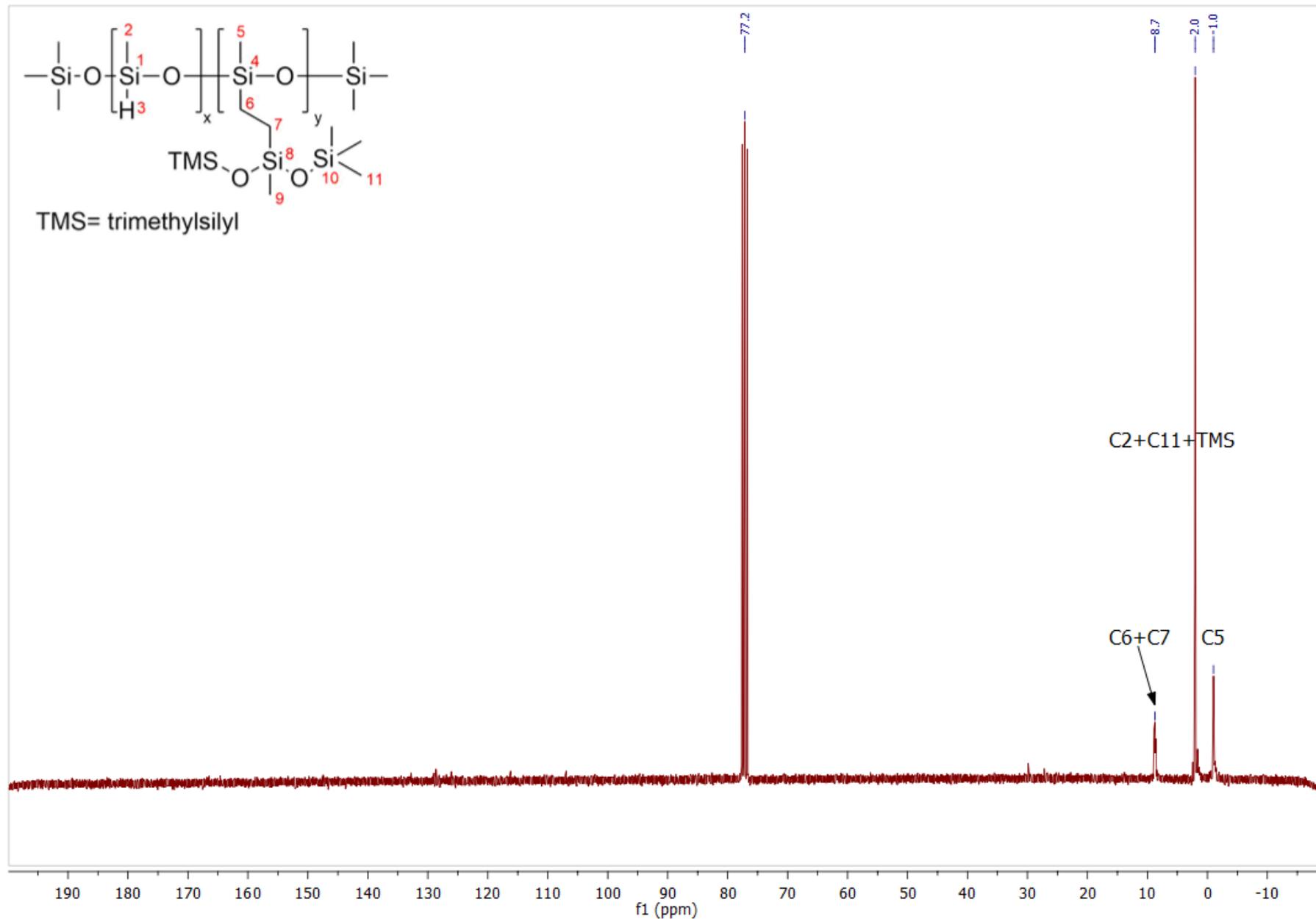
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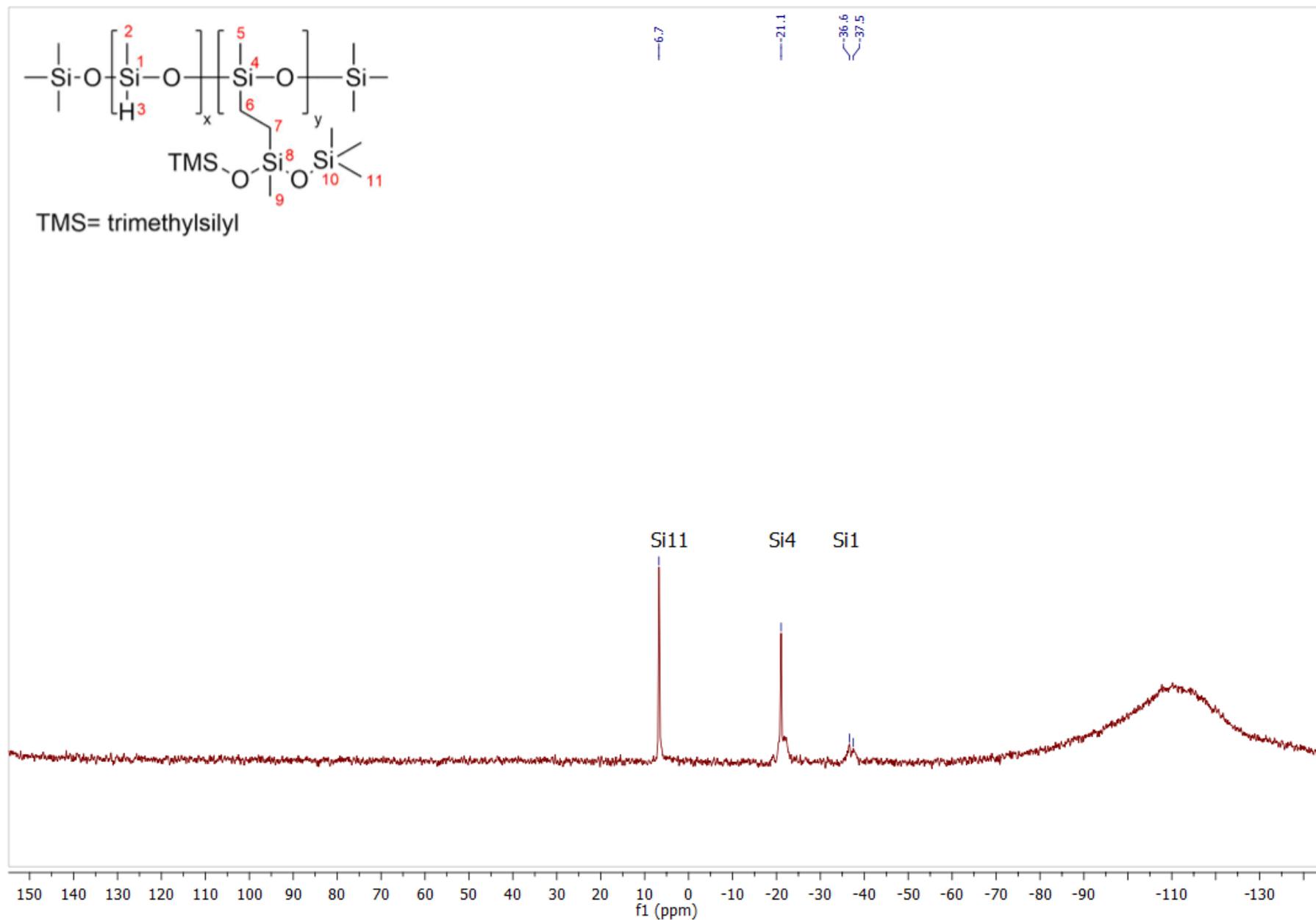
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1e



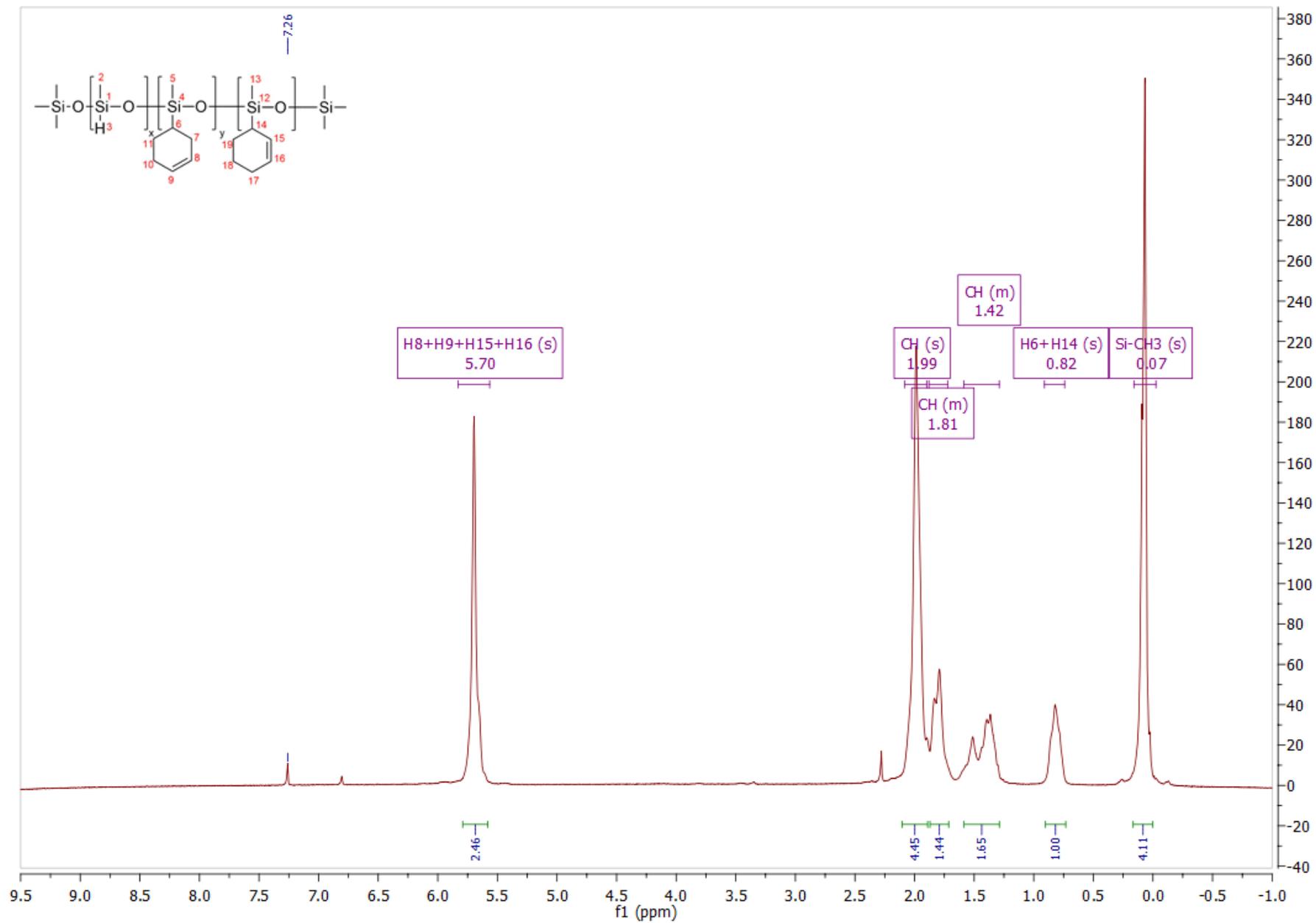
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 1e



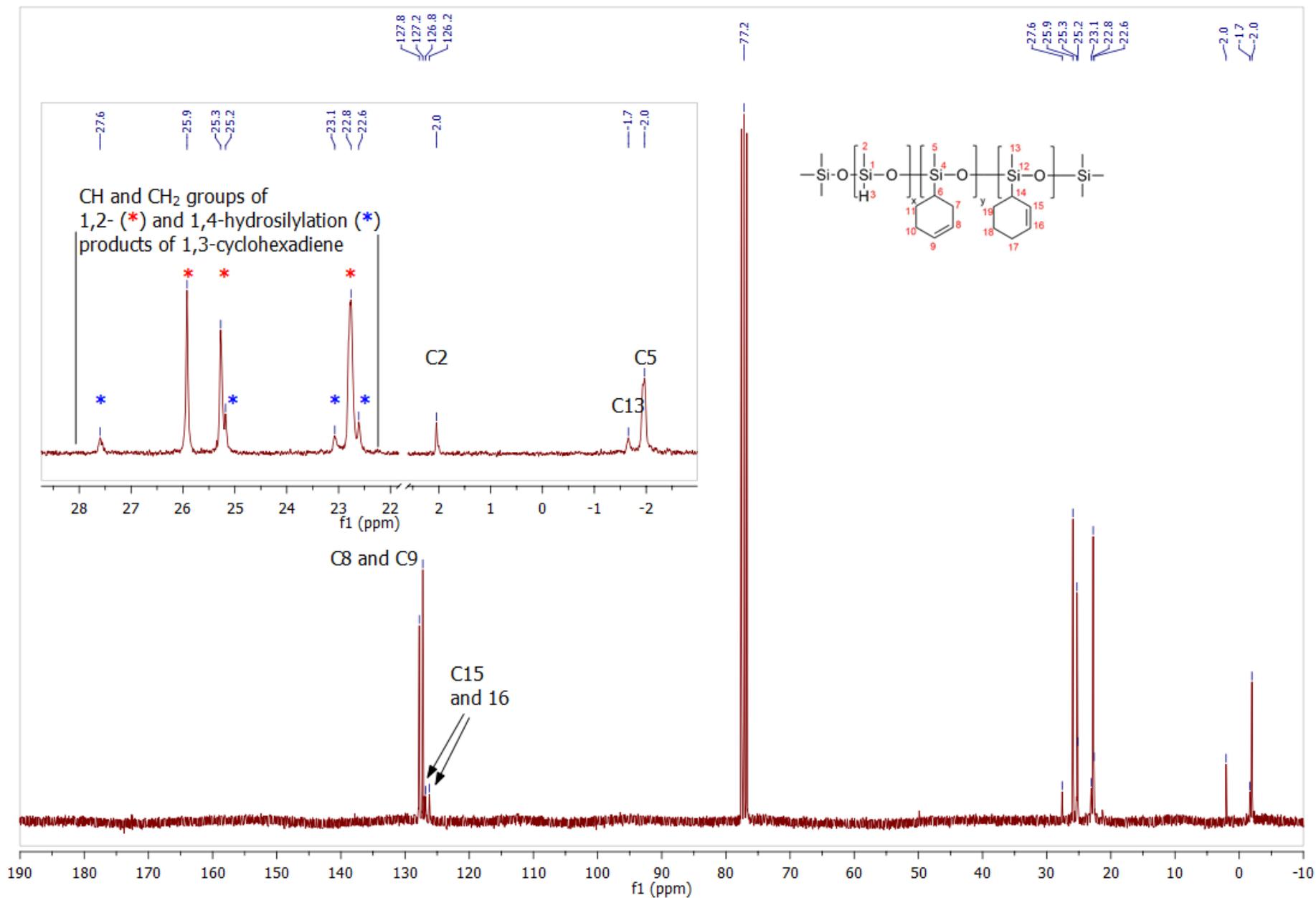
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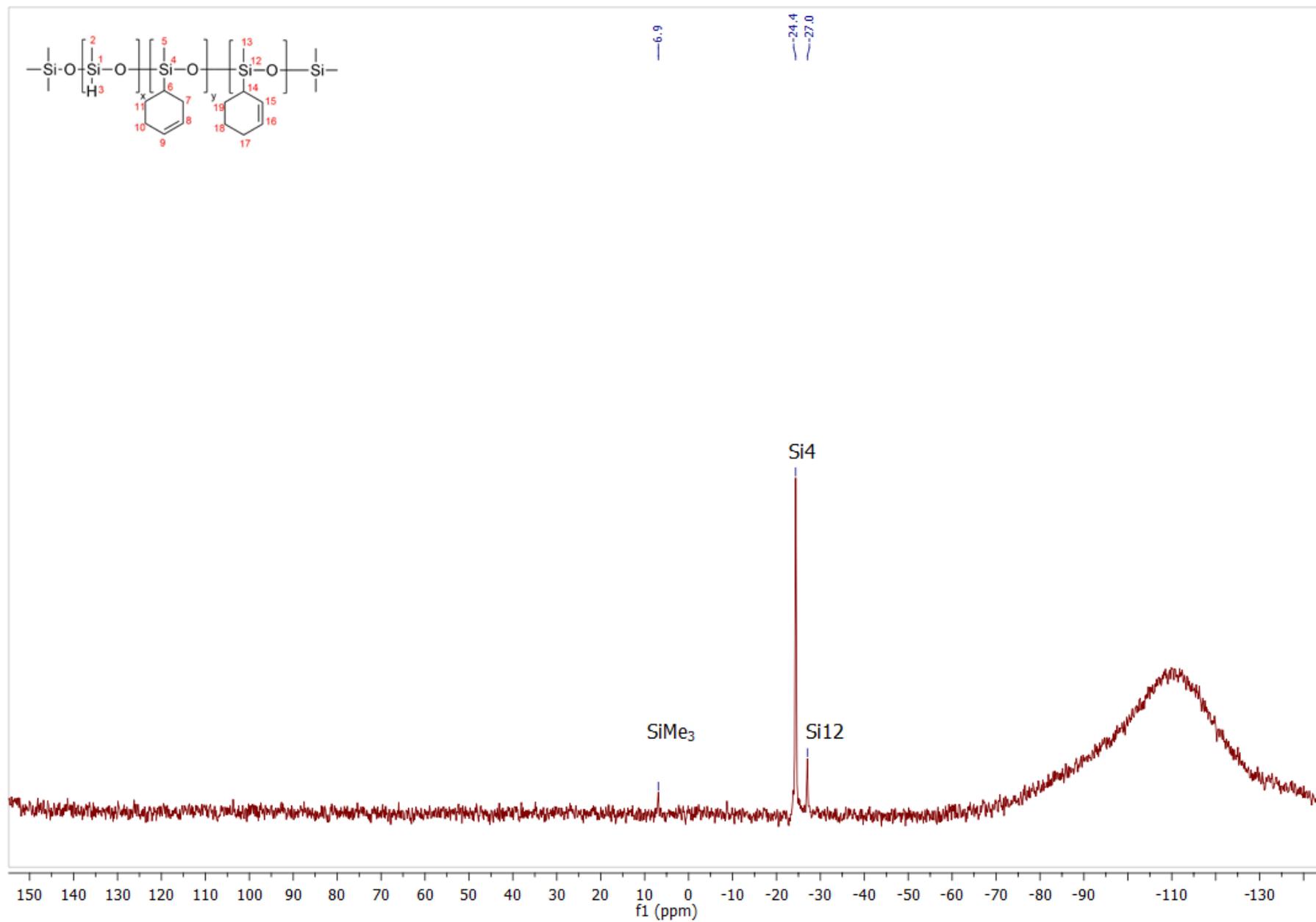
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1f



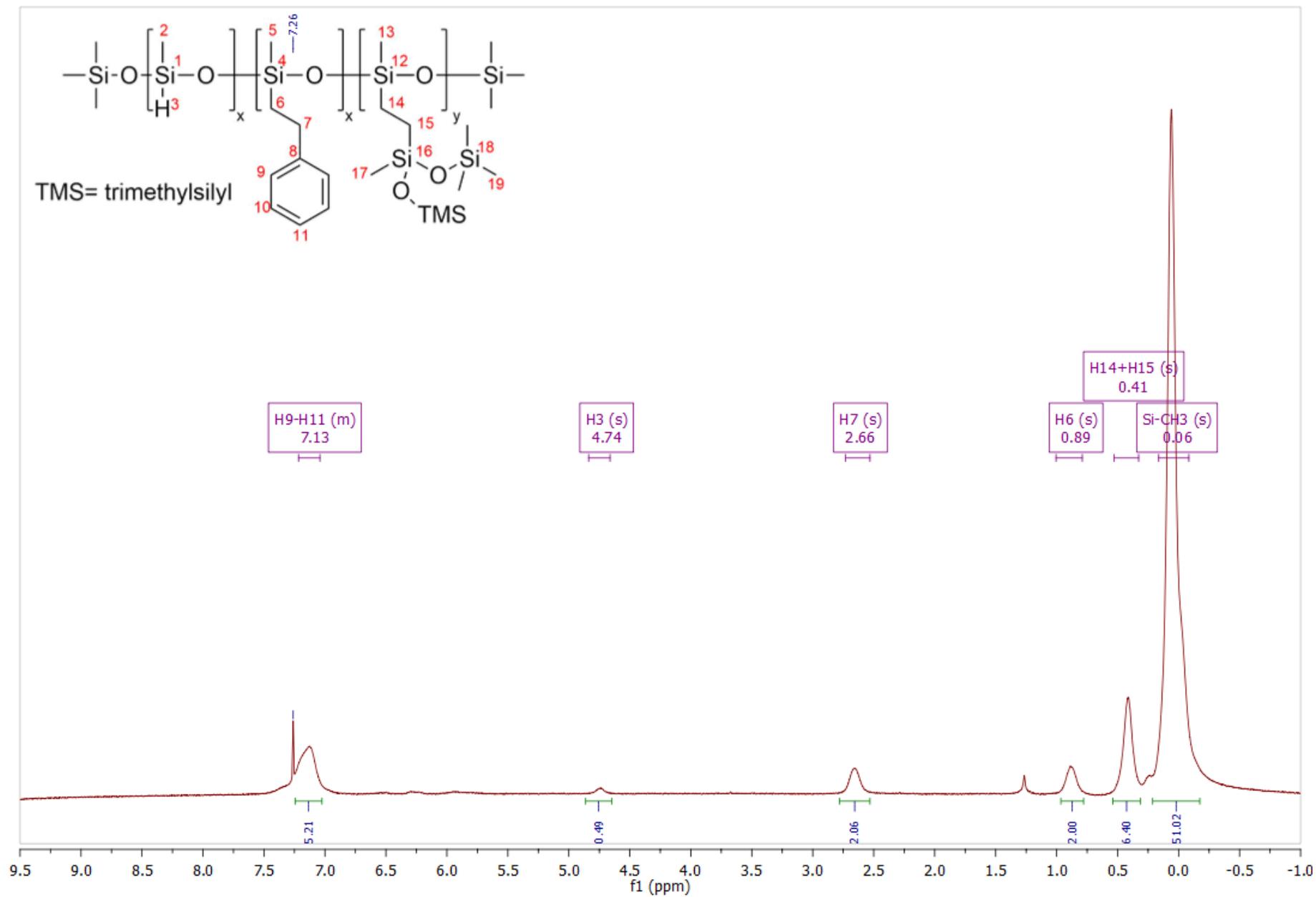
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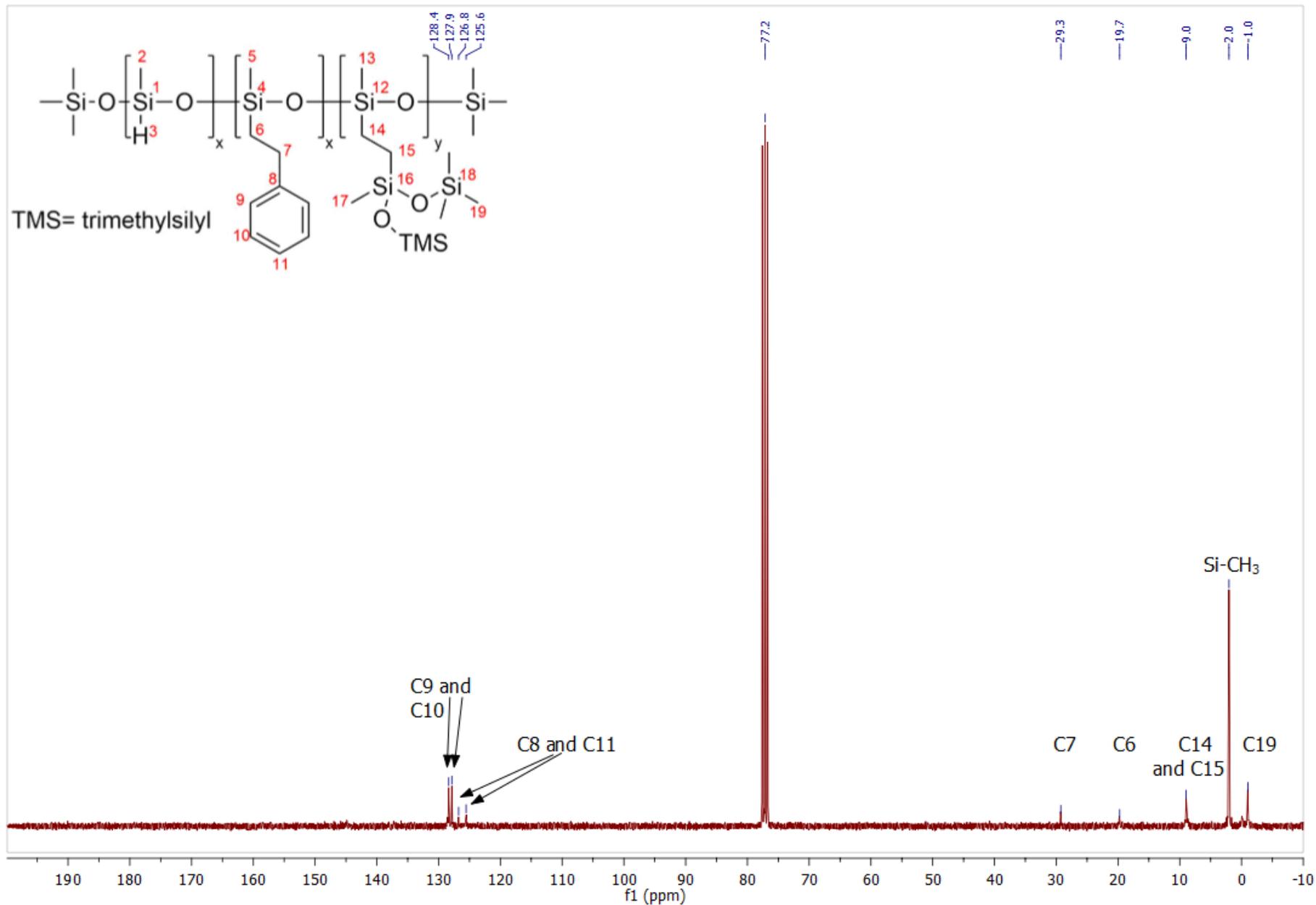
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 1f



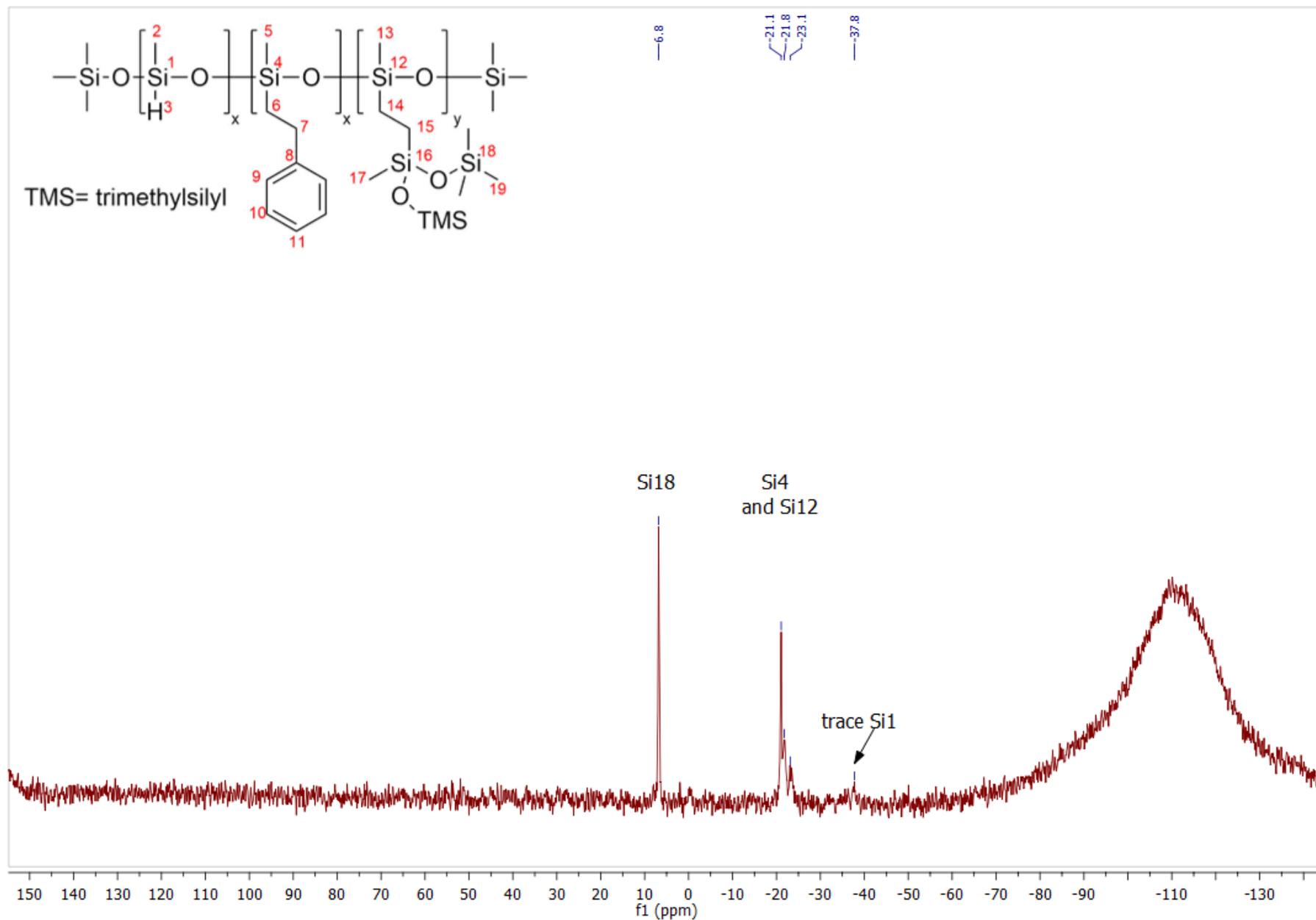
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 1g



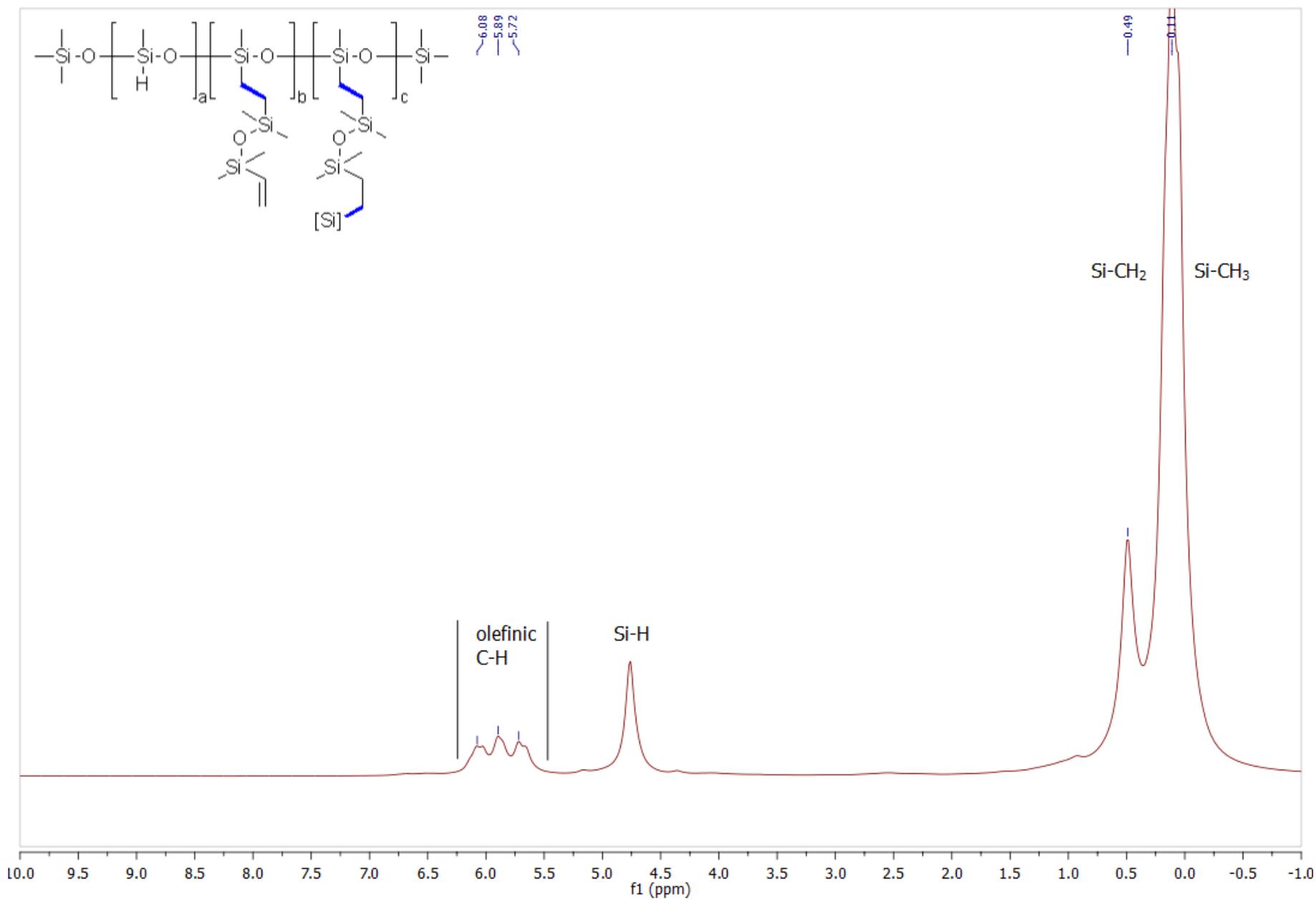
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **1g**



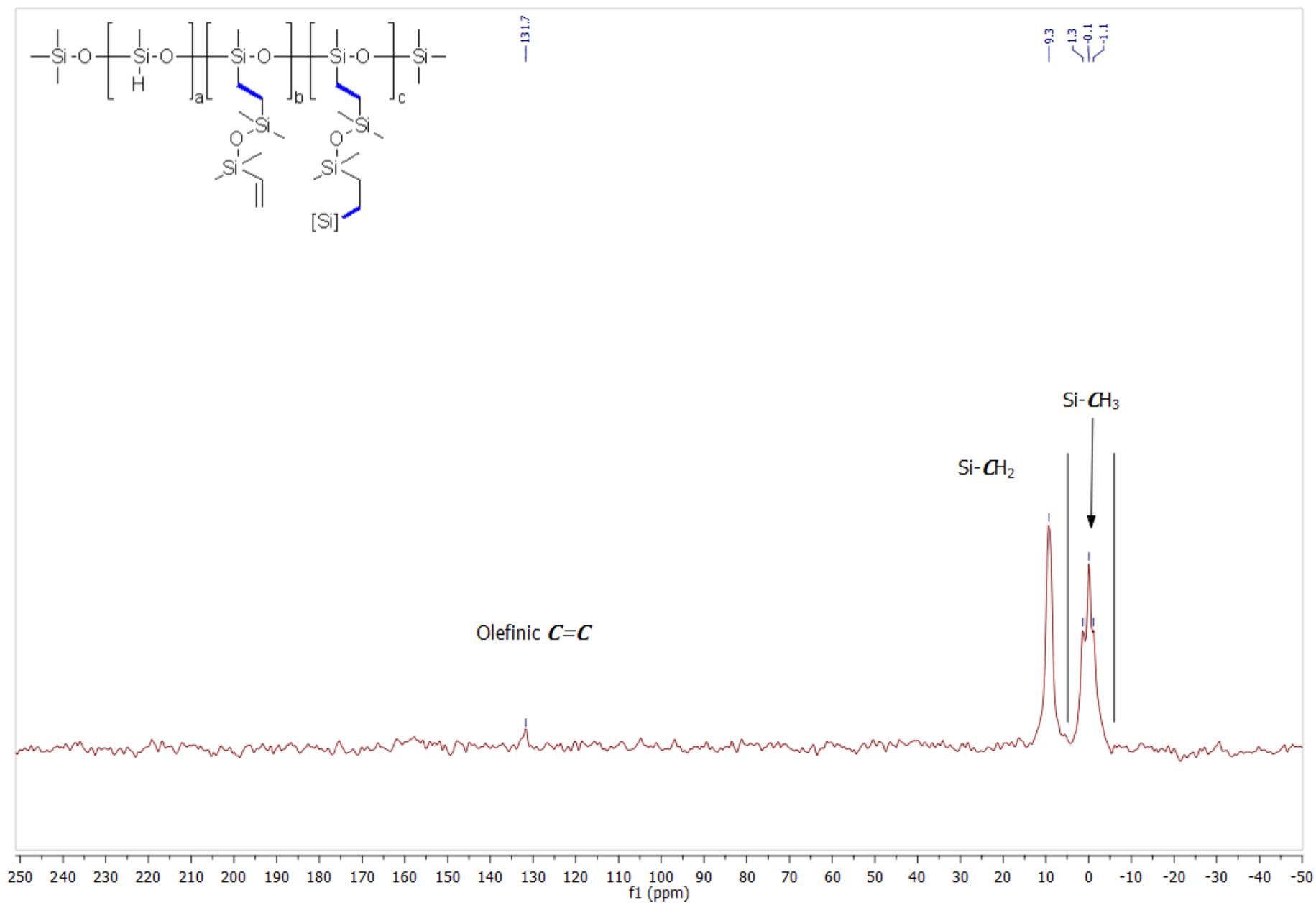
$^{29}\text{Si} \{^1\text{H}\}$  NMR (60 MHz,  $\text{CDCl}_3$ ) of 1g



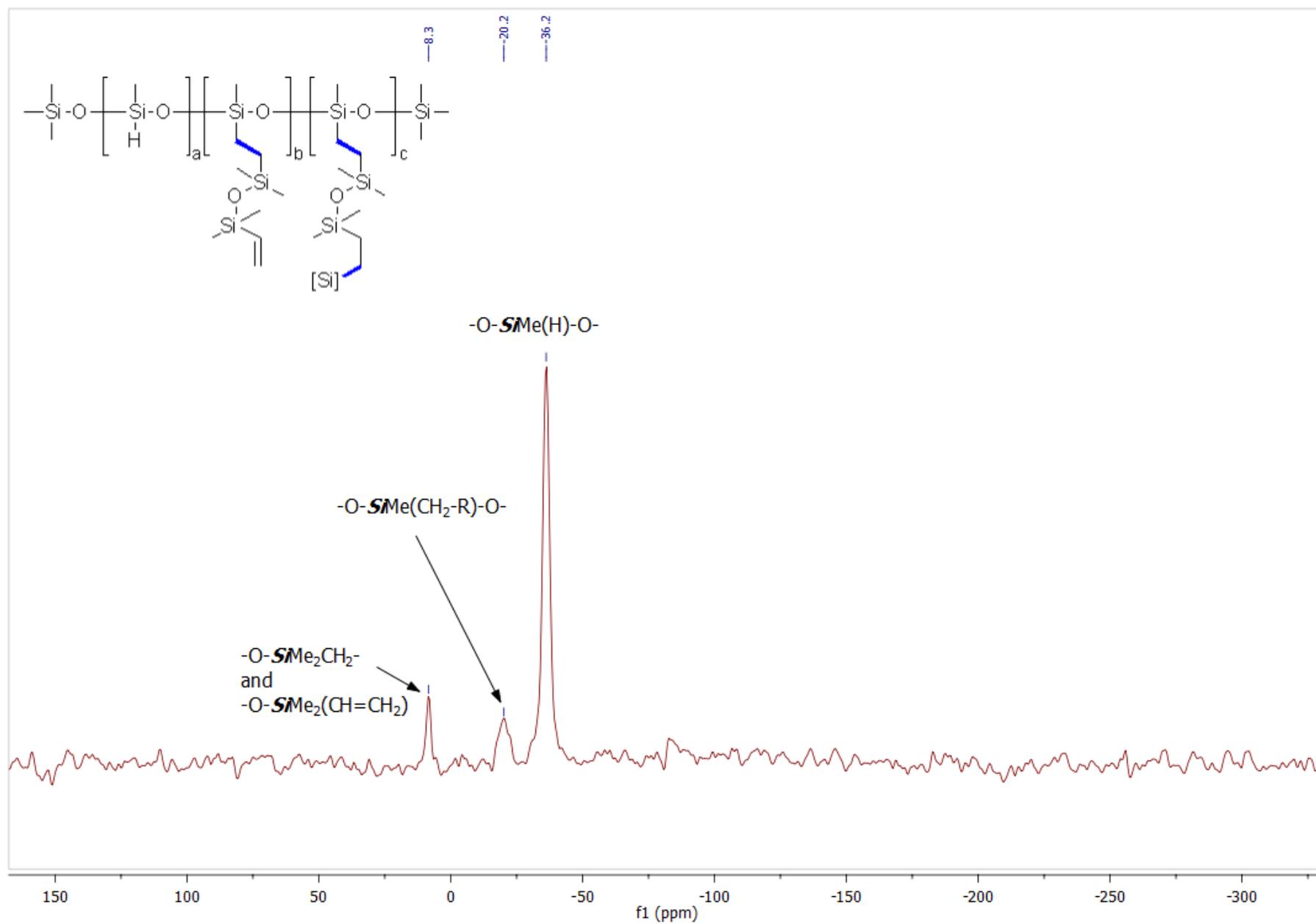
**<sup>1</sup>H MAS SS-NMR of 2a**



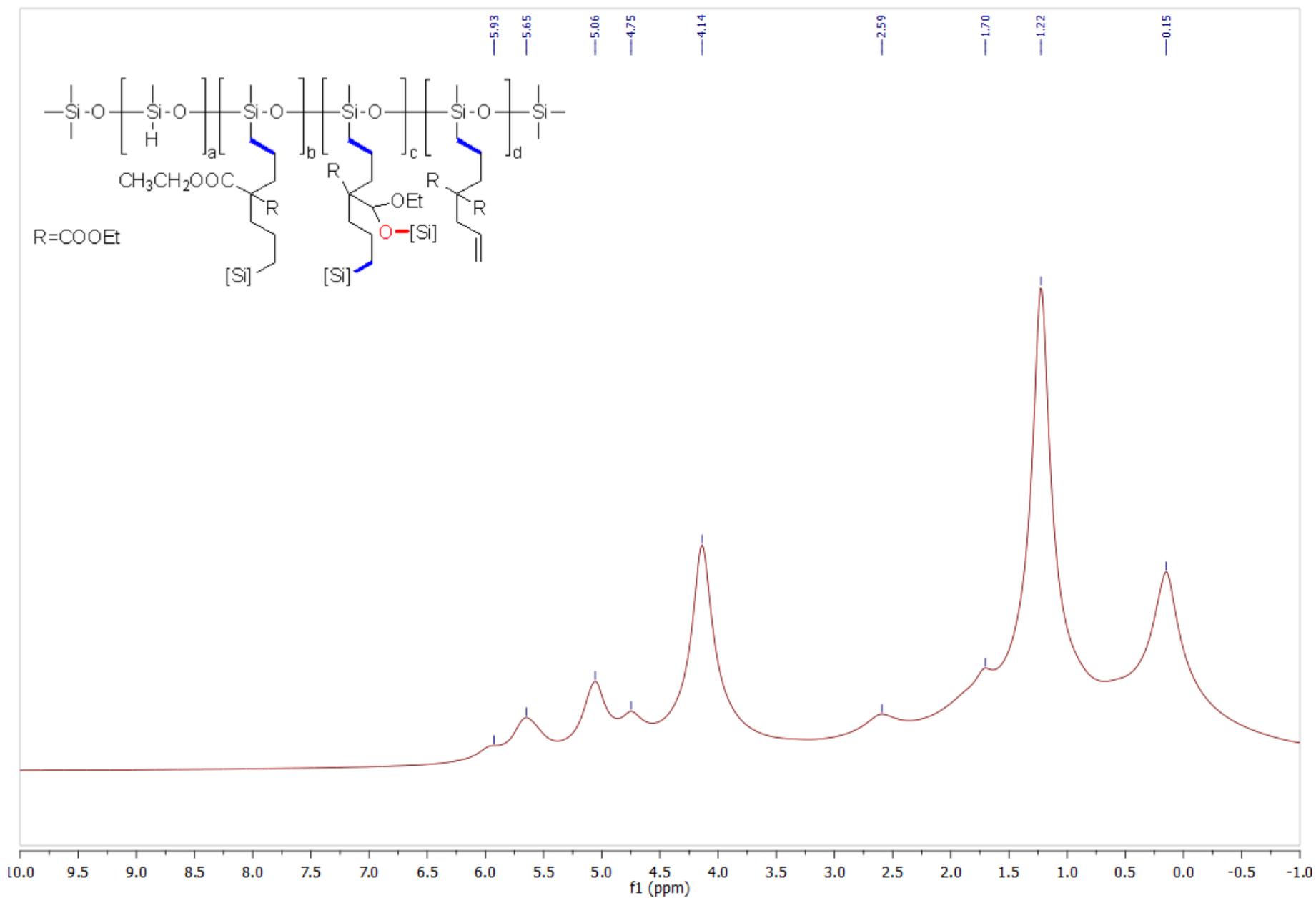
# $^{13}\text{C}$ CPMAS SS-NMR of 2a



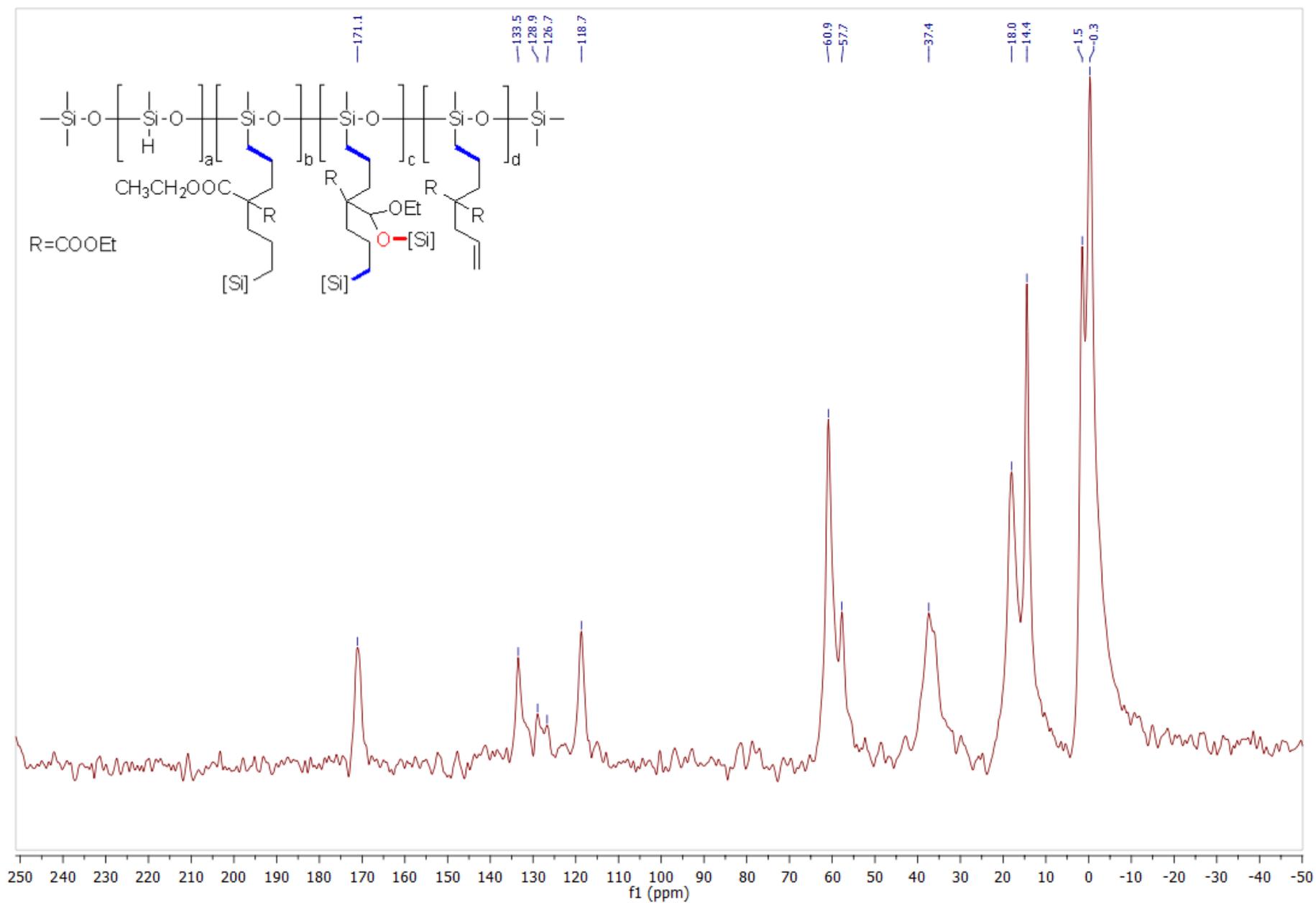
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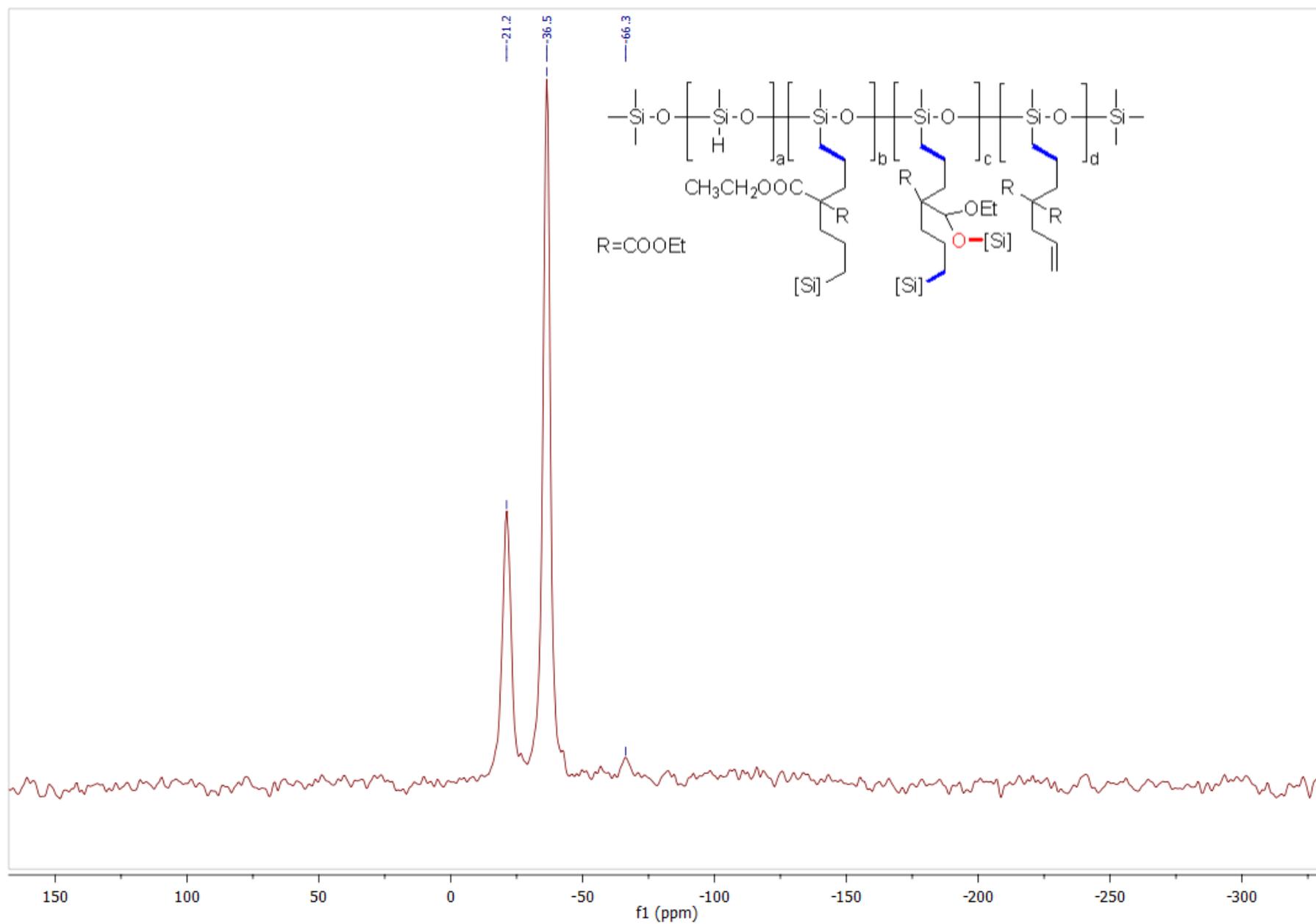
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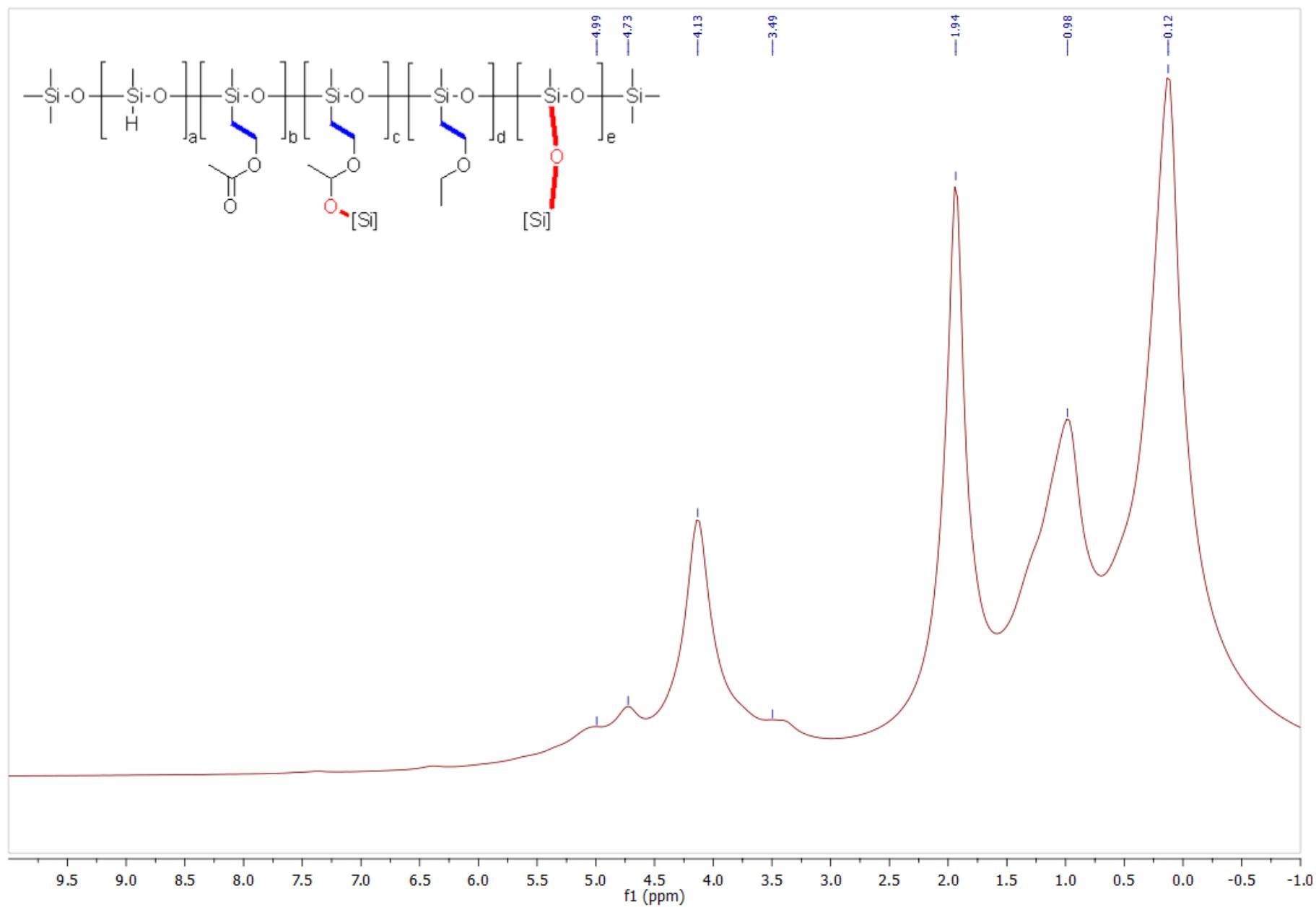
# <sup>13</sup>C CPMAS SS-NMR of 2b



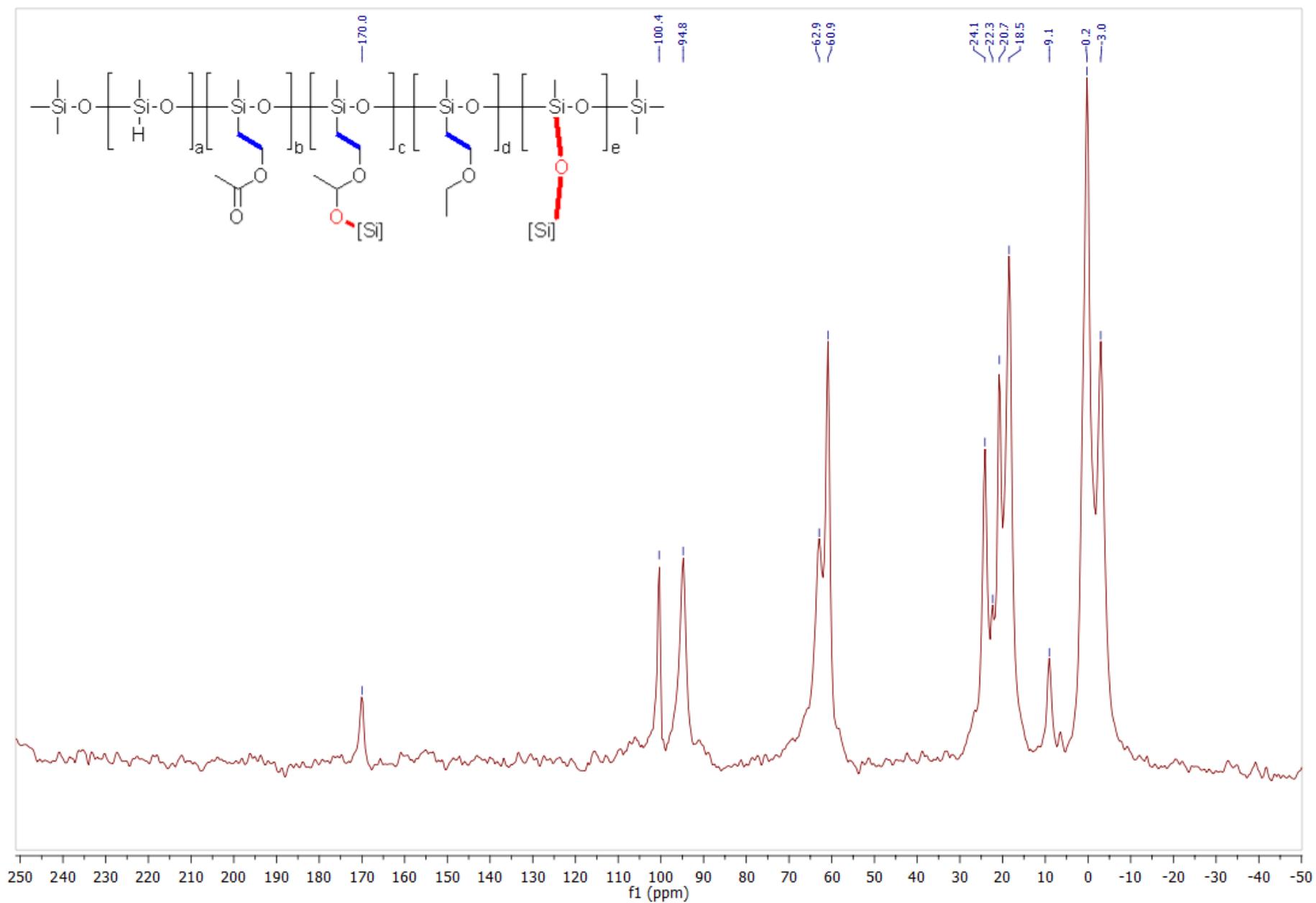
$^{29}\text{Si}$  CPMAS SS-NMR of 2b



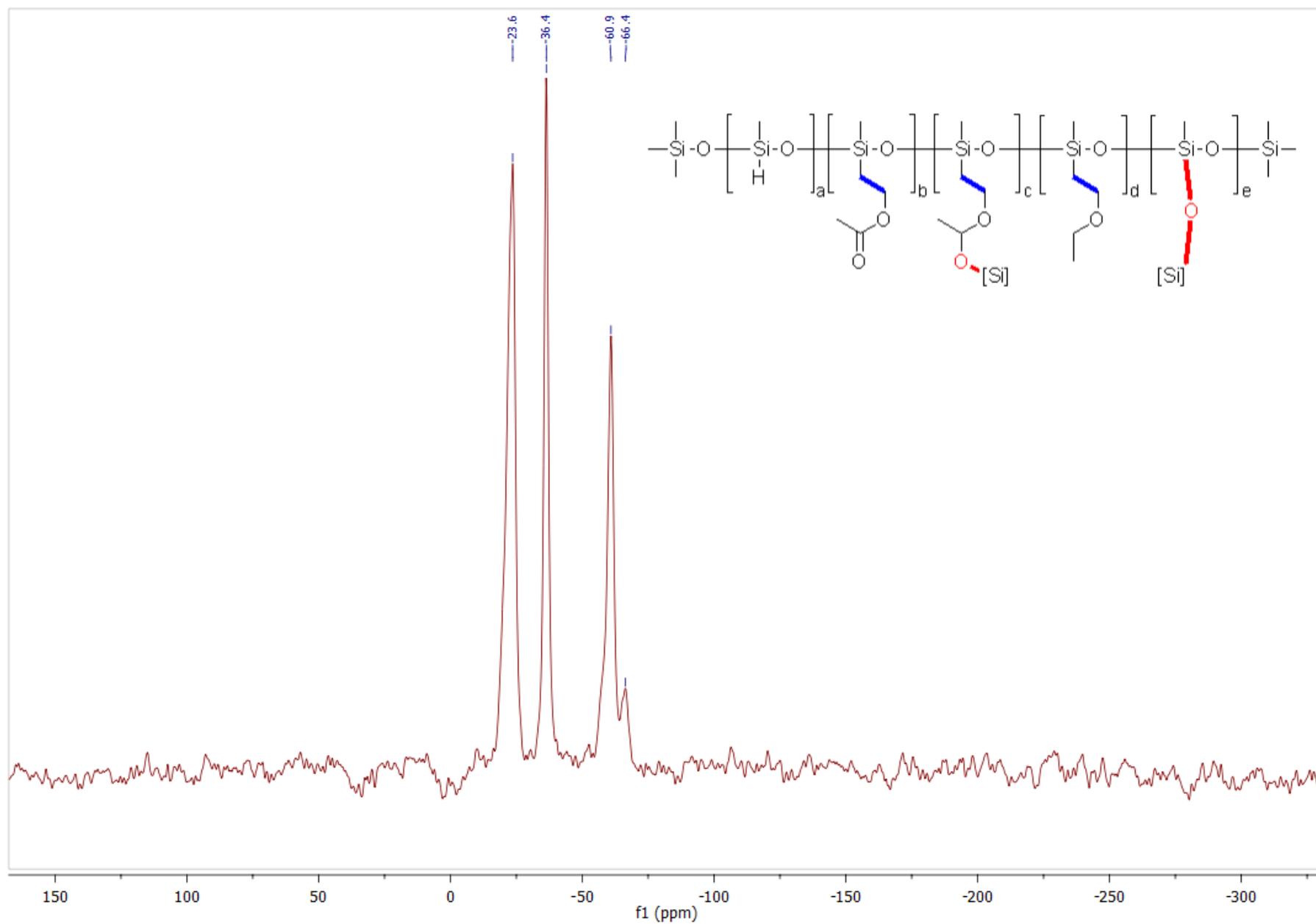
**<sup>1</sup>H MAS SS-NMR of 3a**



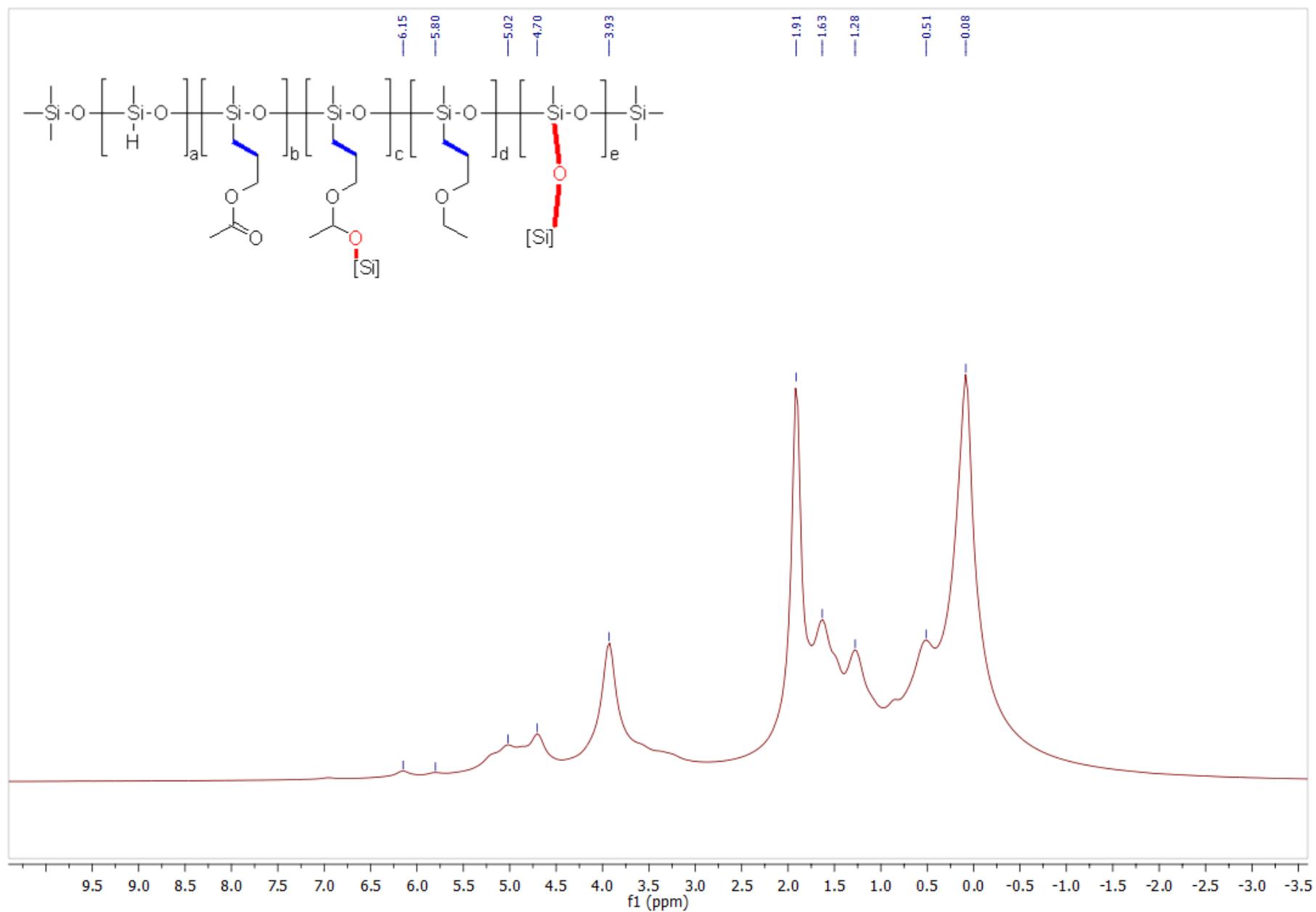
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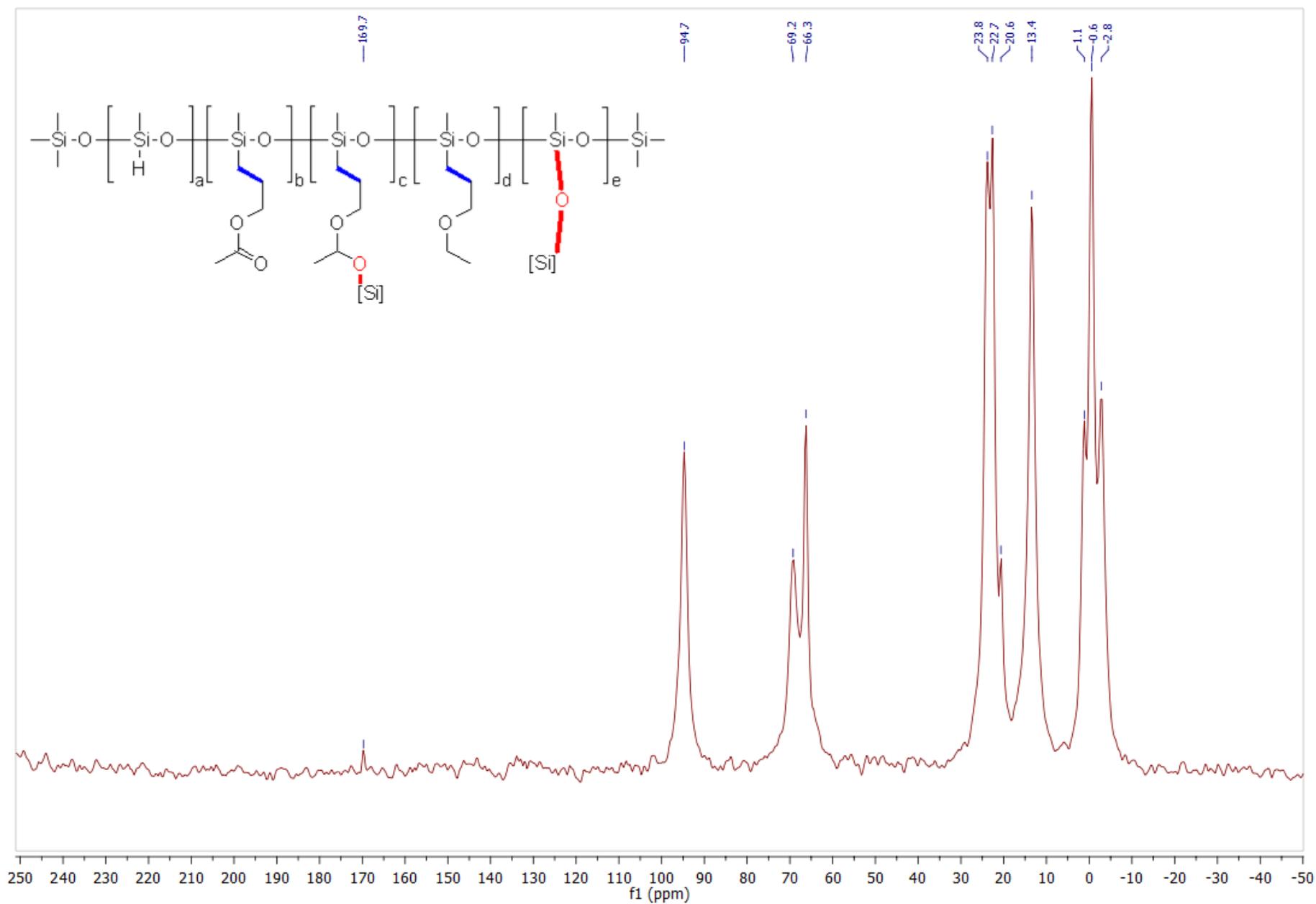
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**$^1\text{H}$  MAS SS-NMR of 3b**

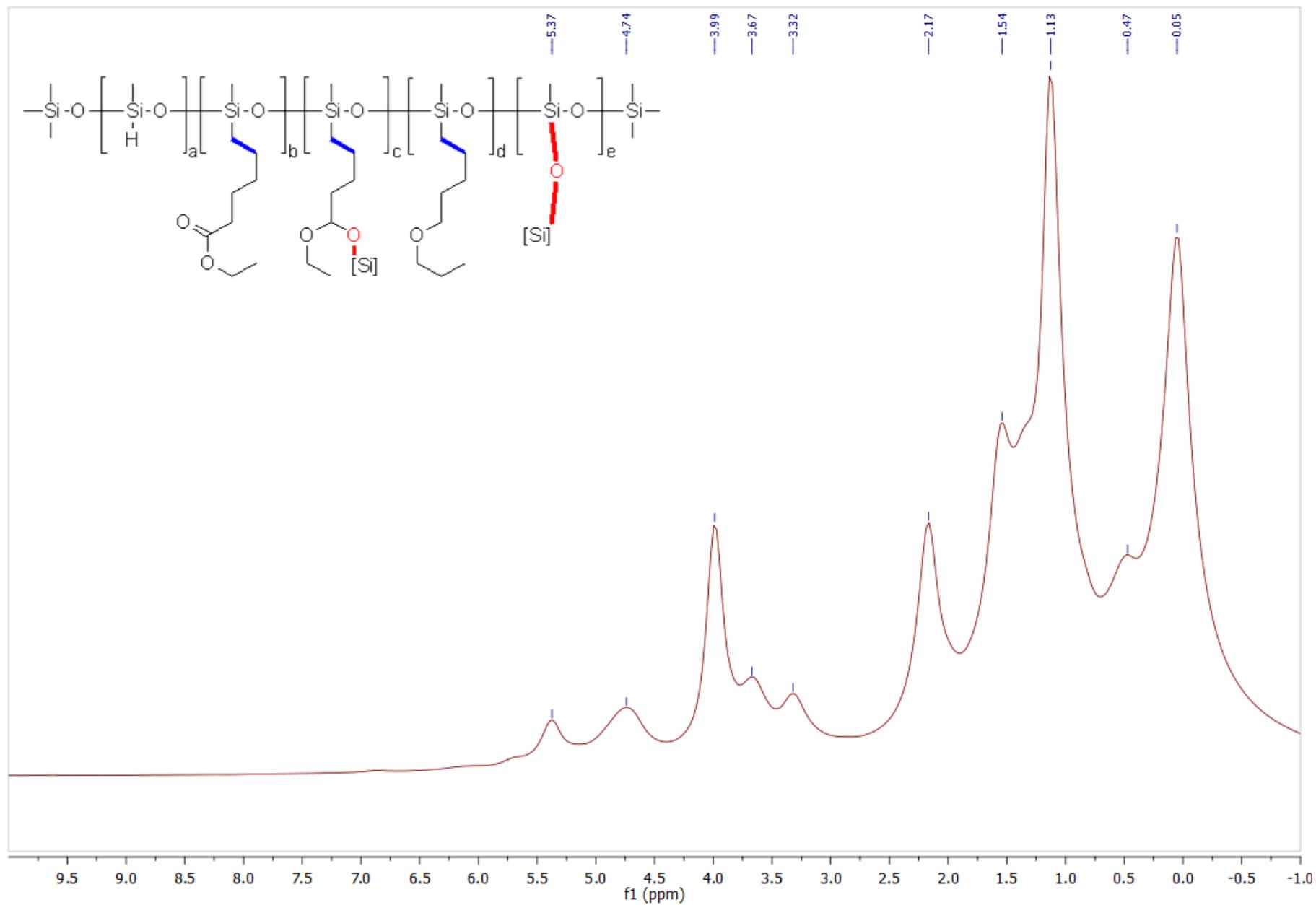


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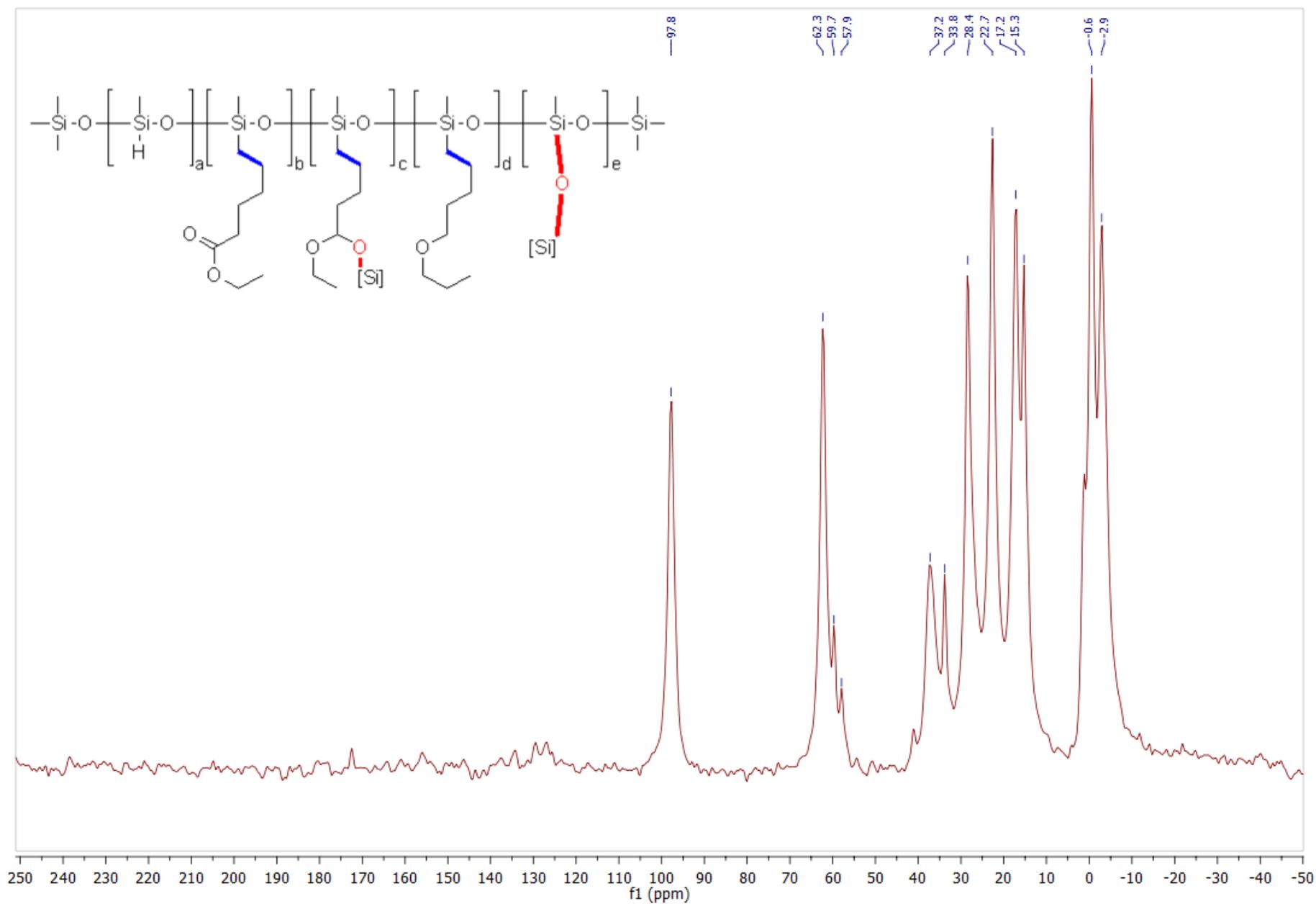




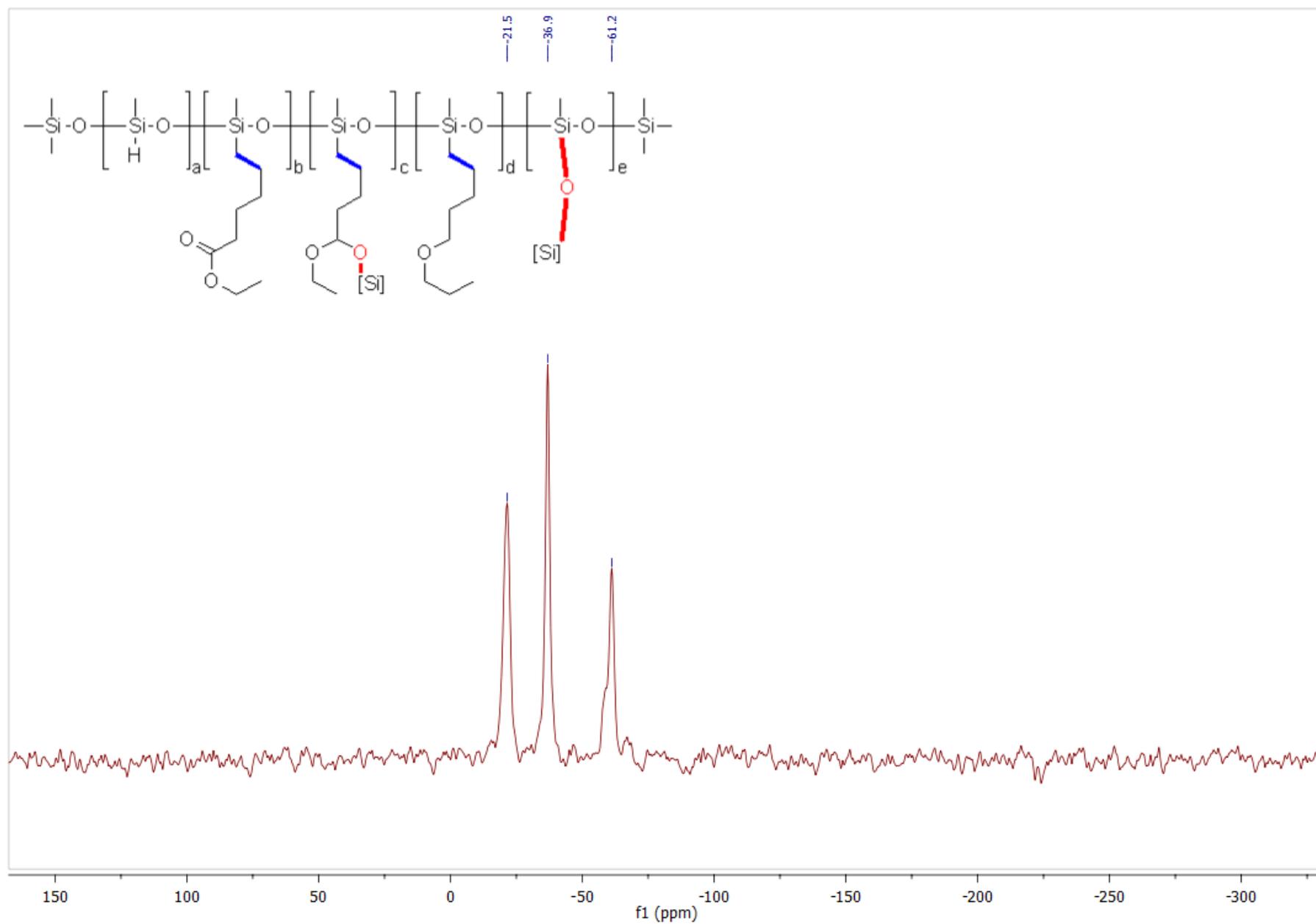
**<sup>1</sup>H MAS SS-NMR of 3c**



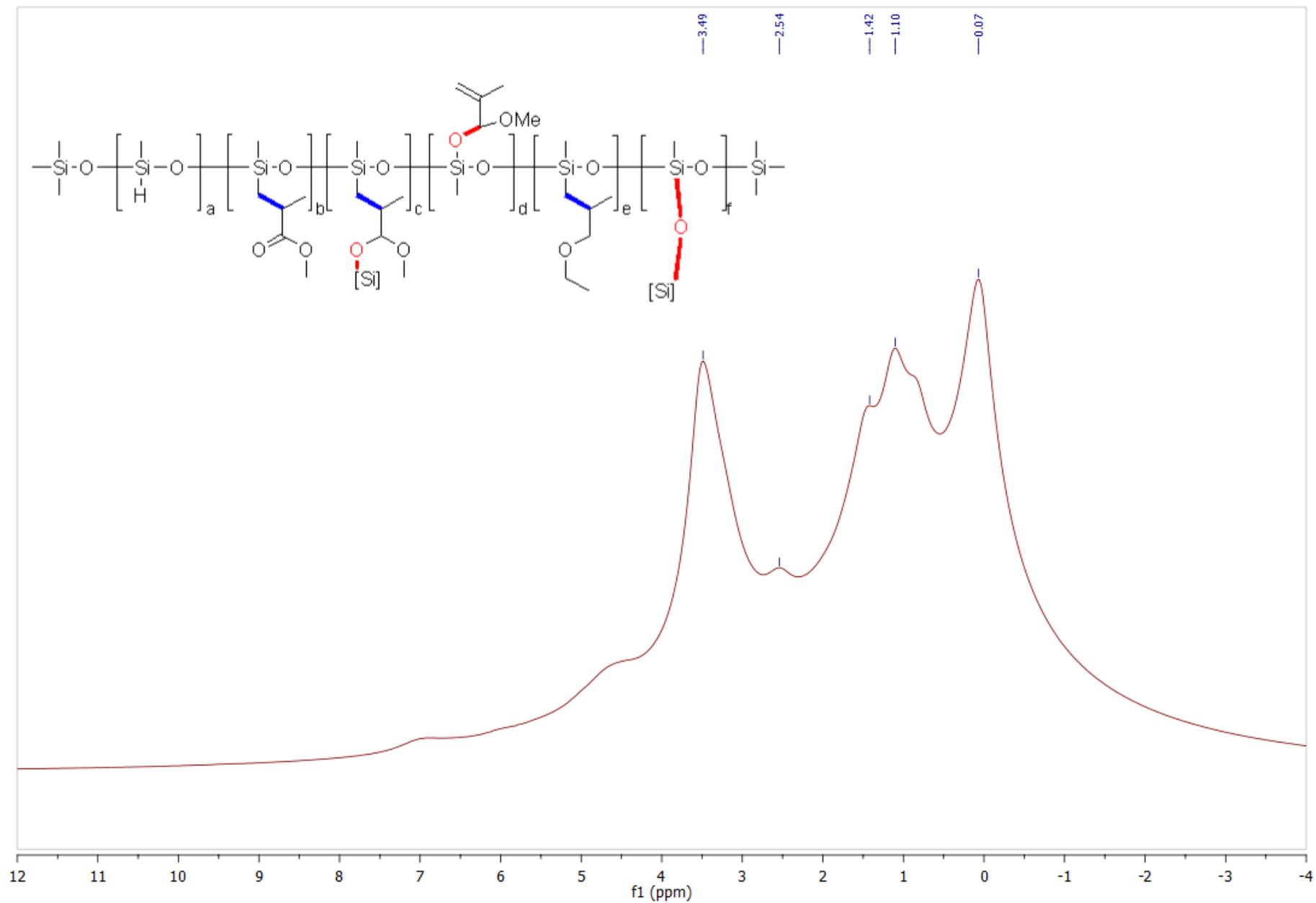
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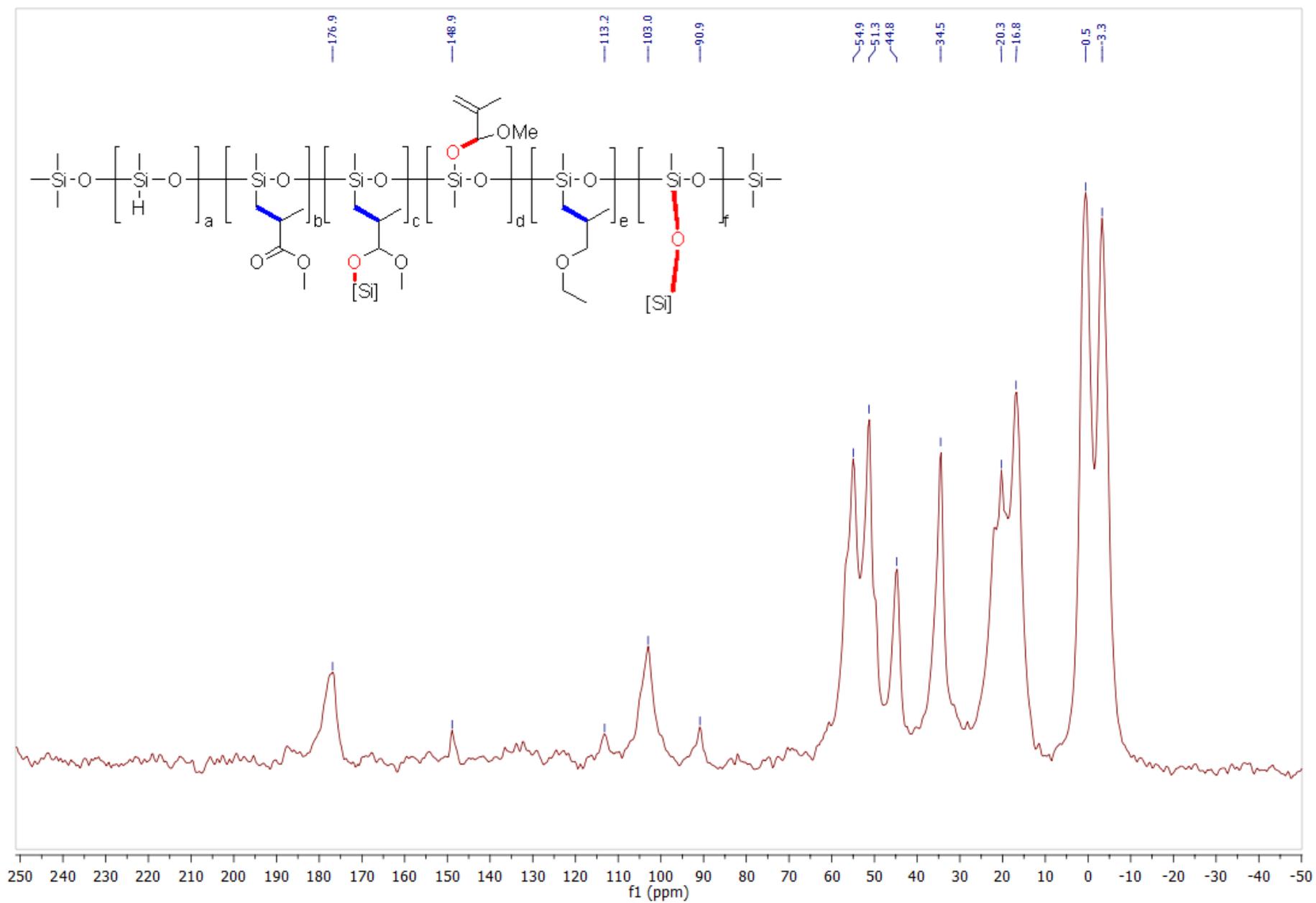
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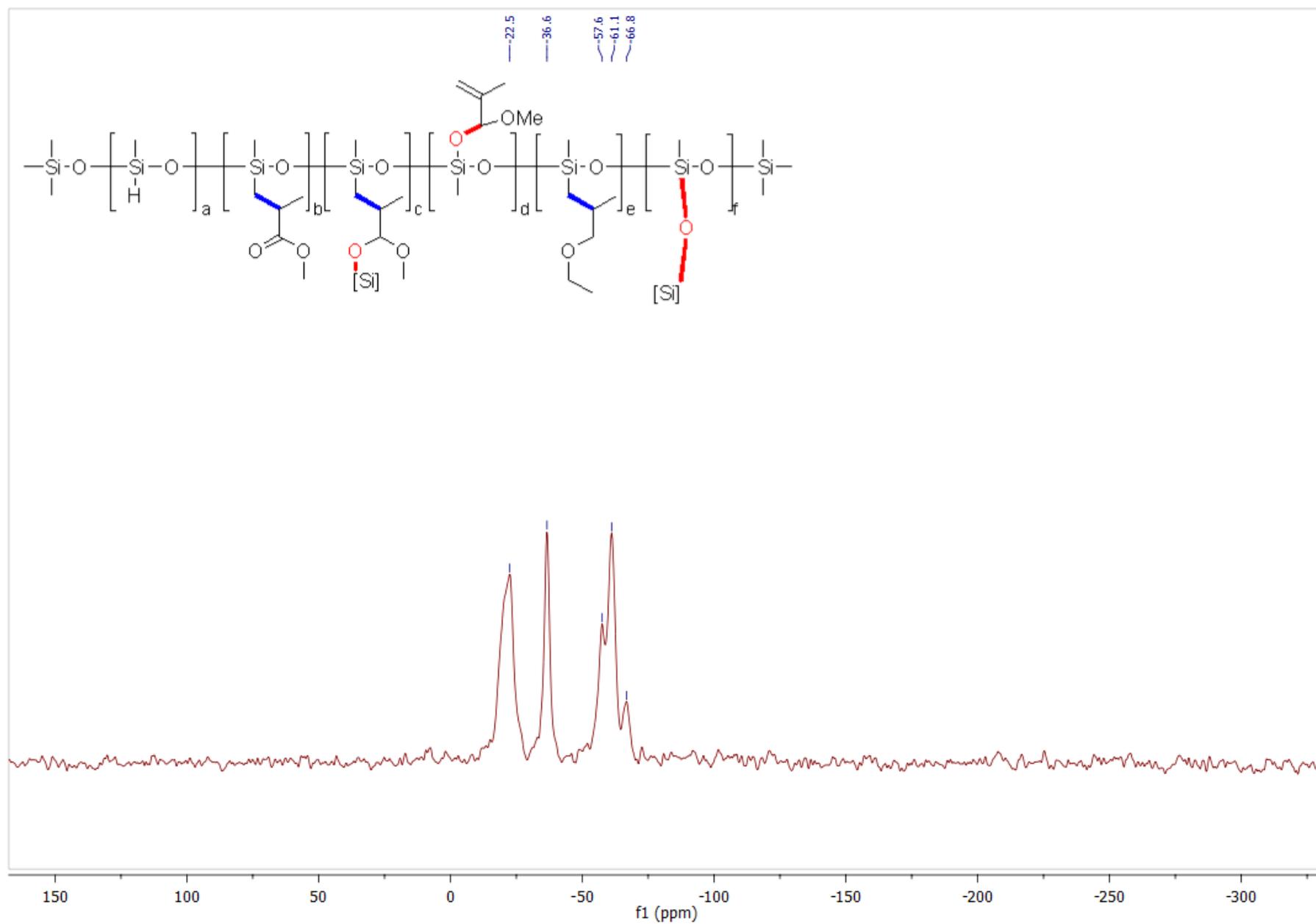
**<sup>1</sup>H MAS SS-NMR of 3d**



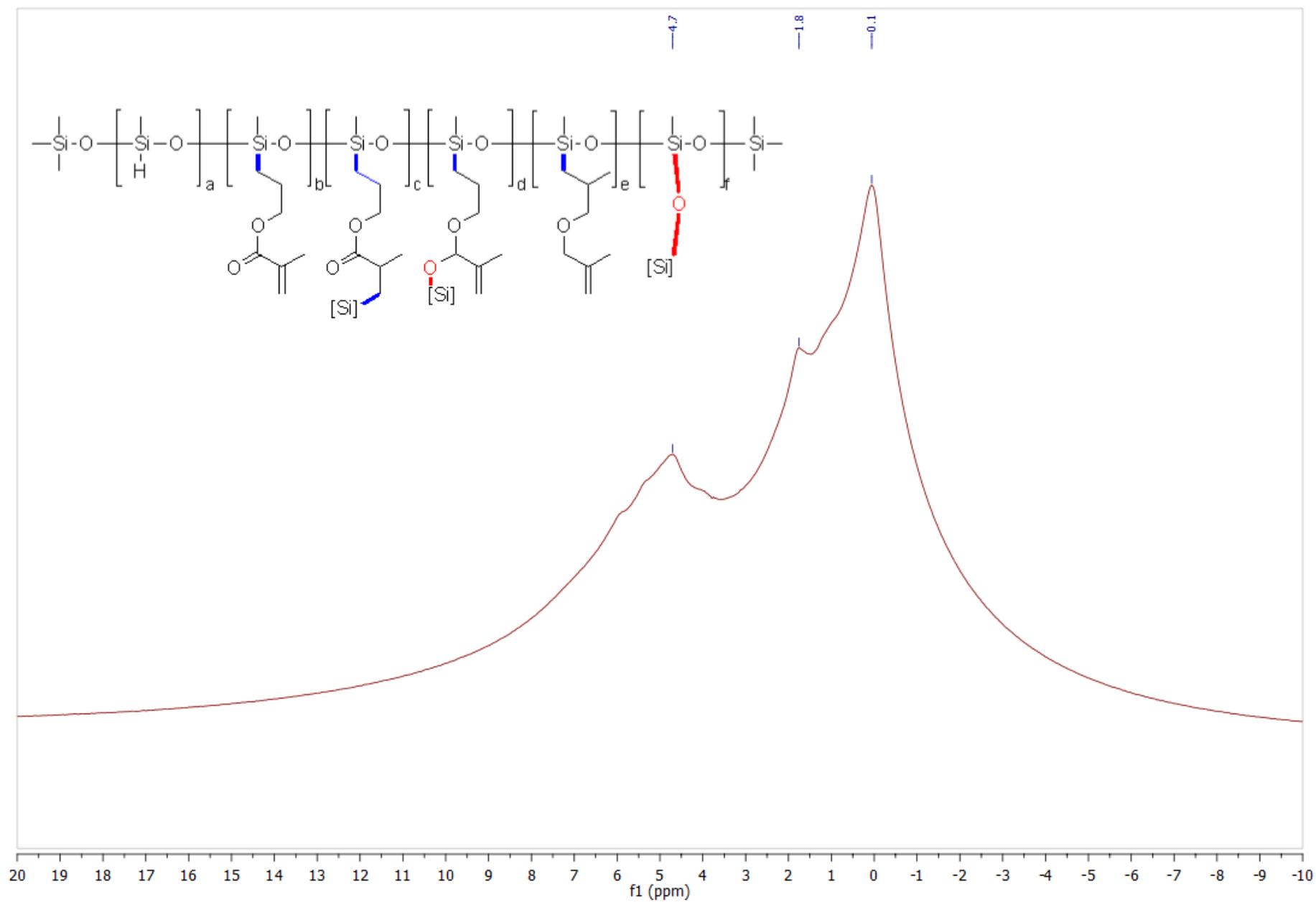
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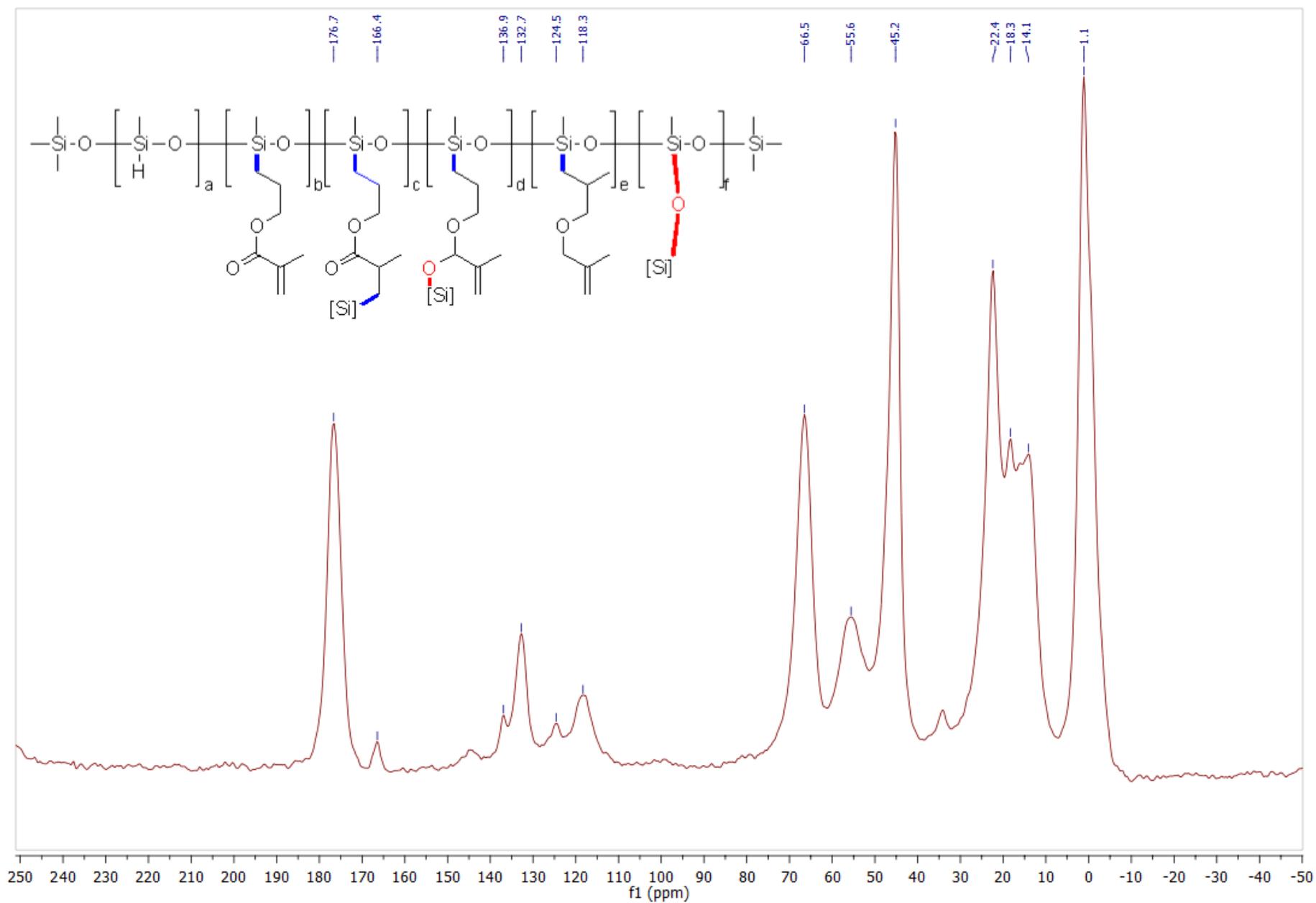
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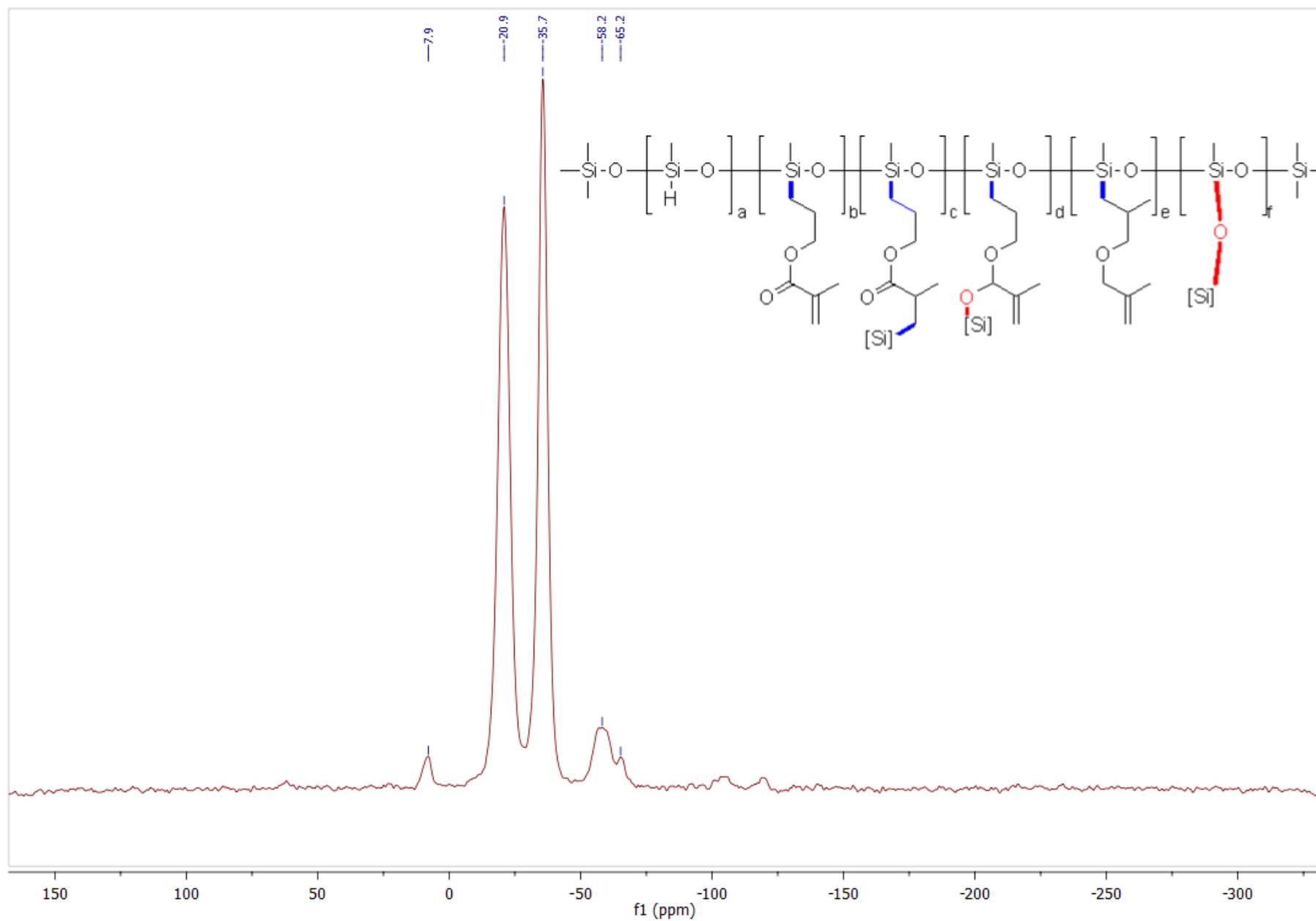
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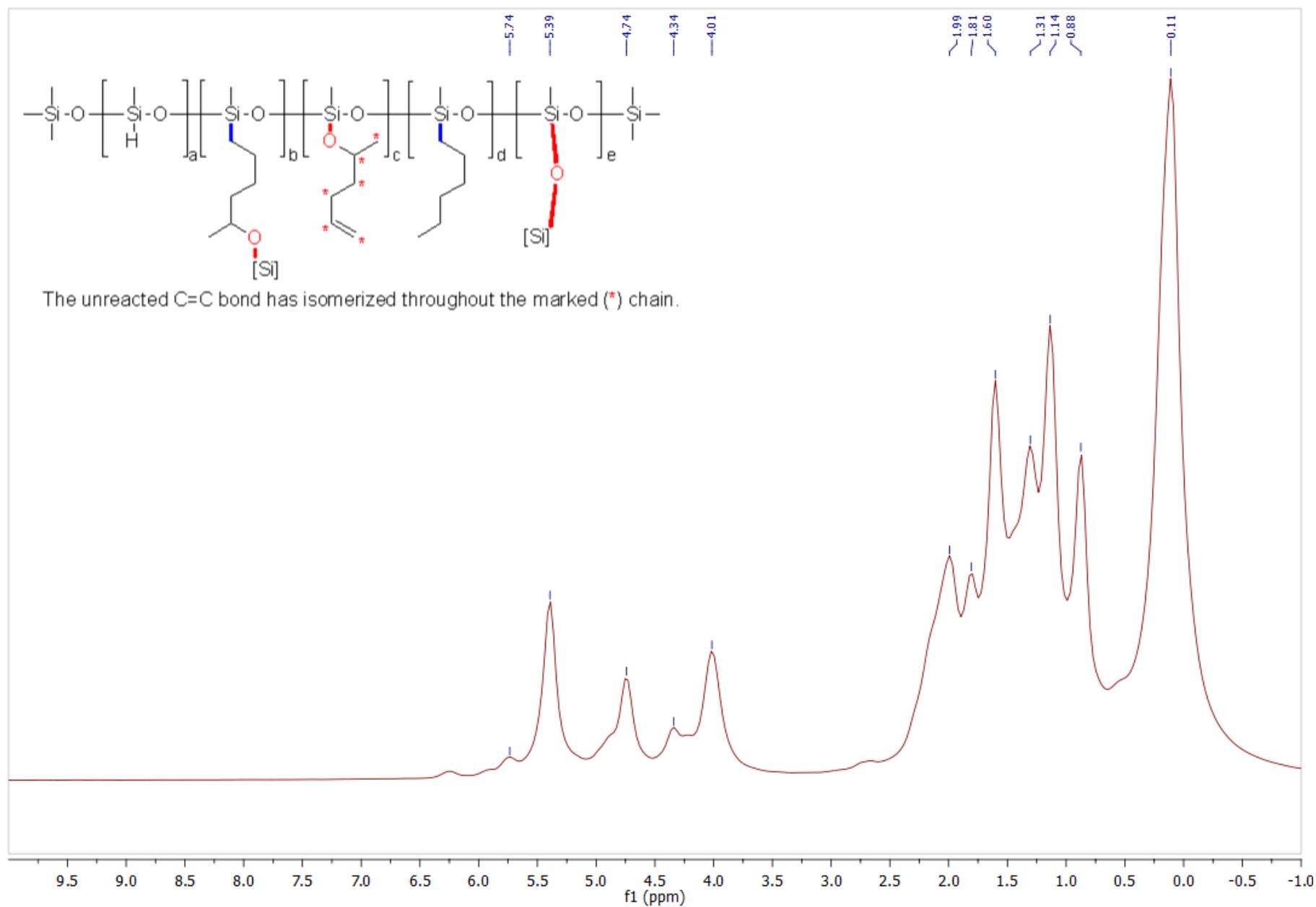
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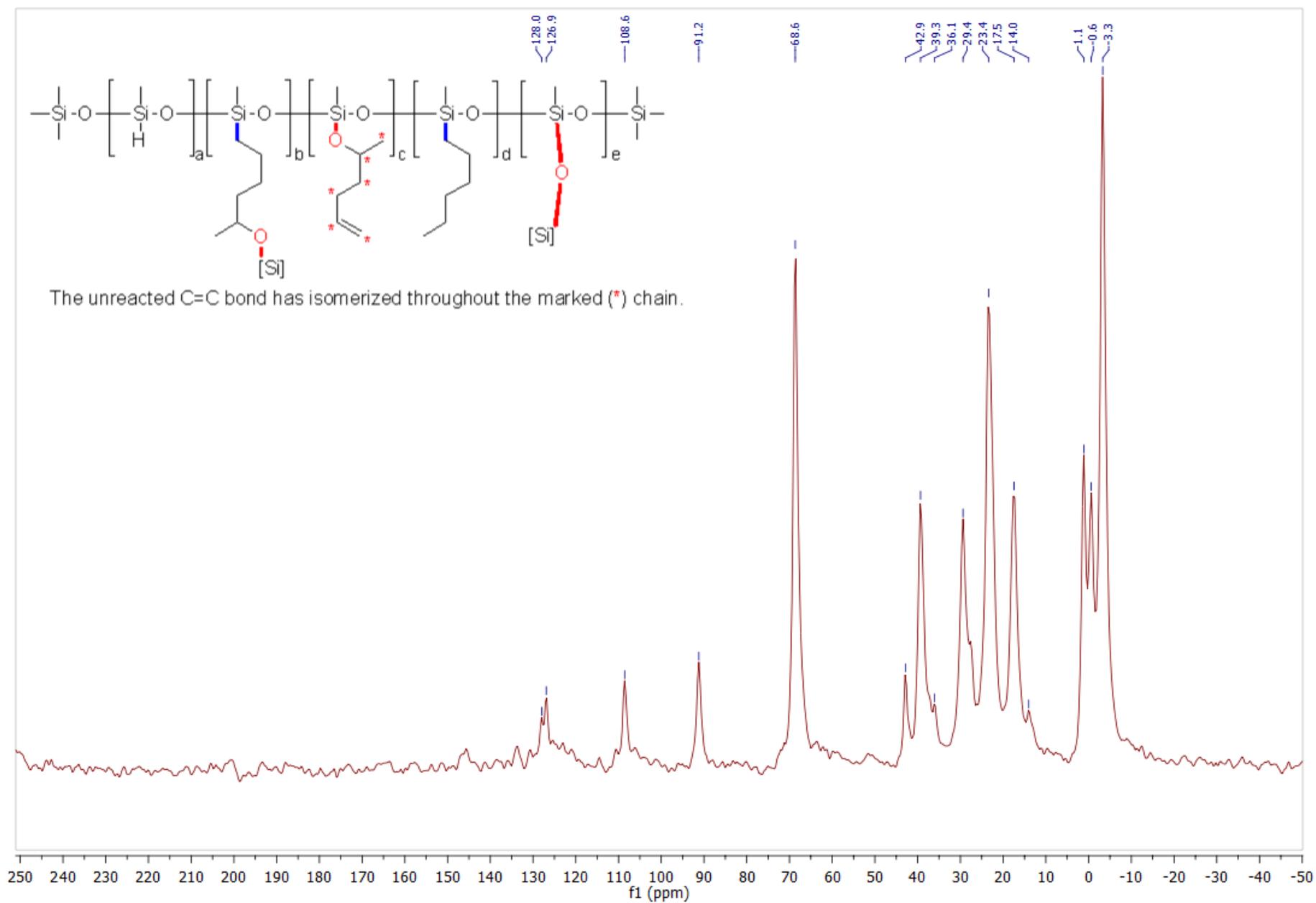
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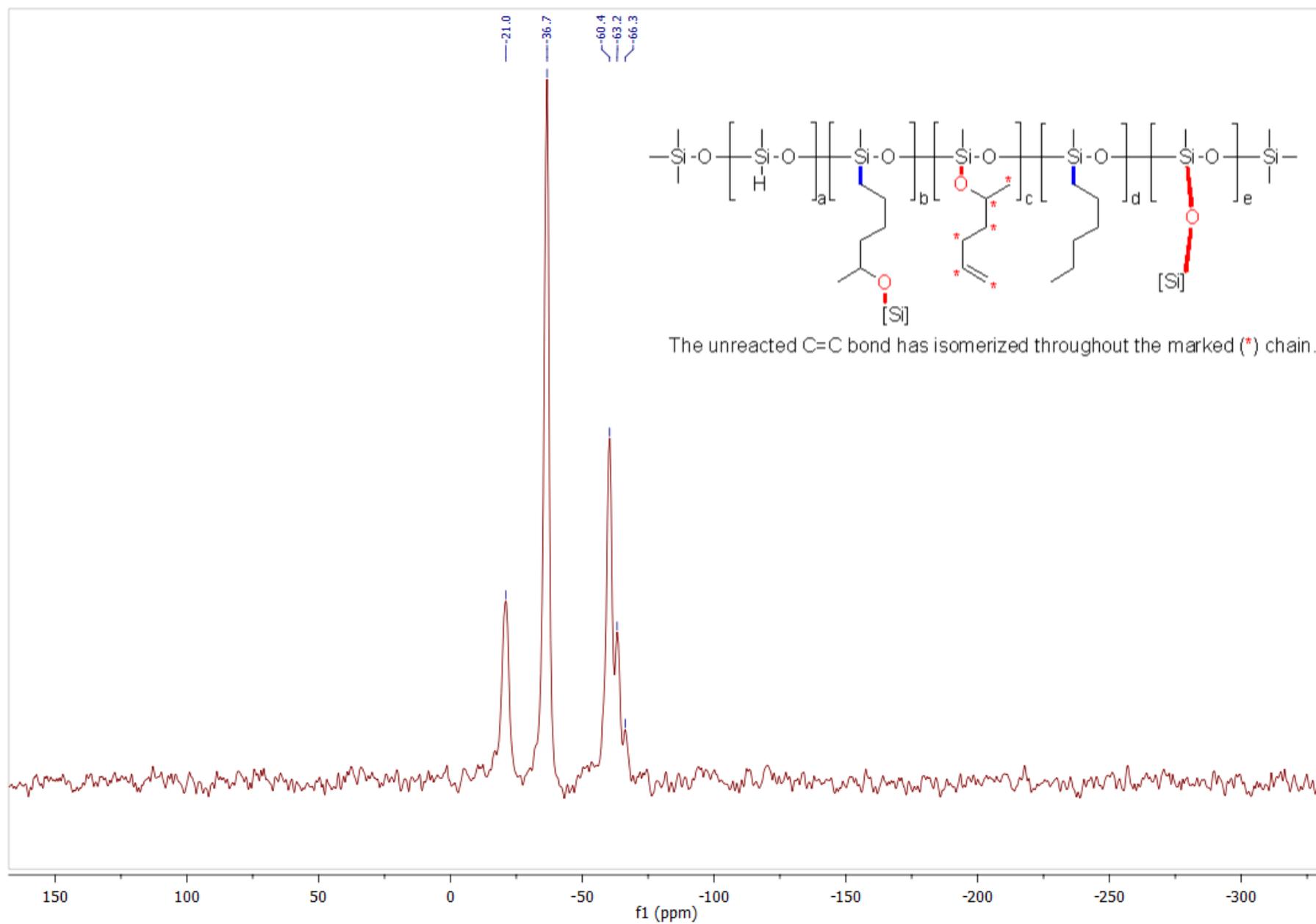
# <sup>1</sup>H MAS SS-NMR of 3f



# $^{13}\text{C}$ CPMAS SS-NMR of 3f

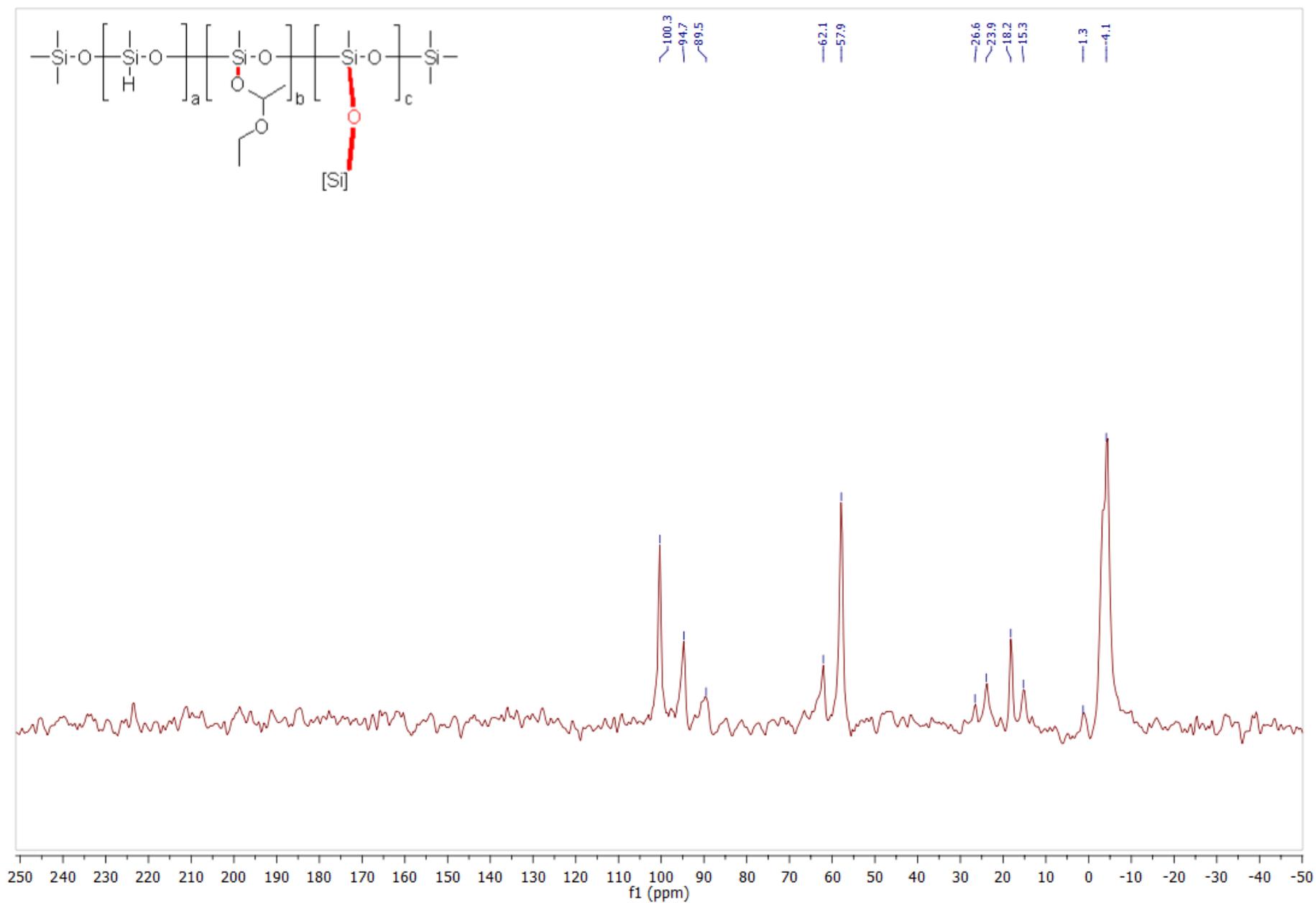


$^{29}\text{Si}$  CPMAS SS-NMR of 3f

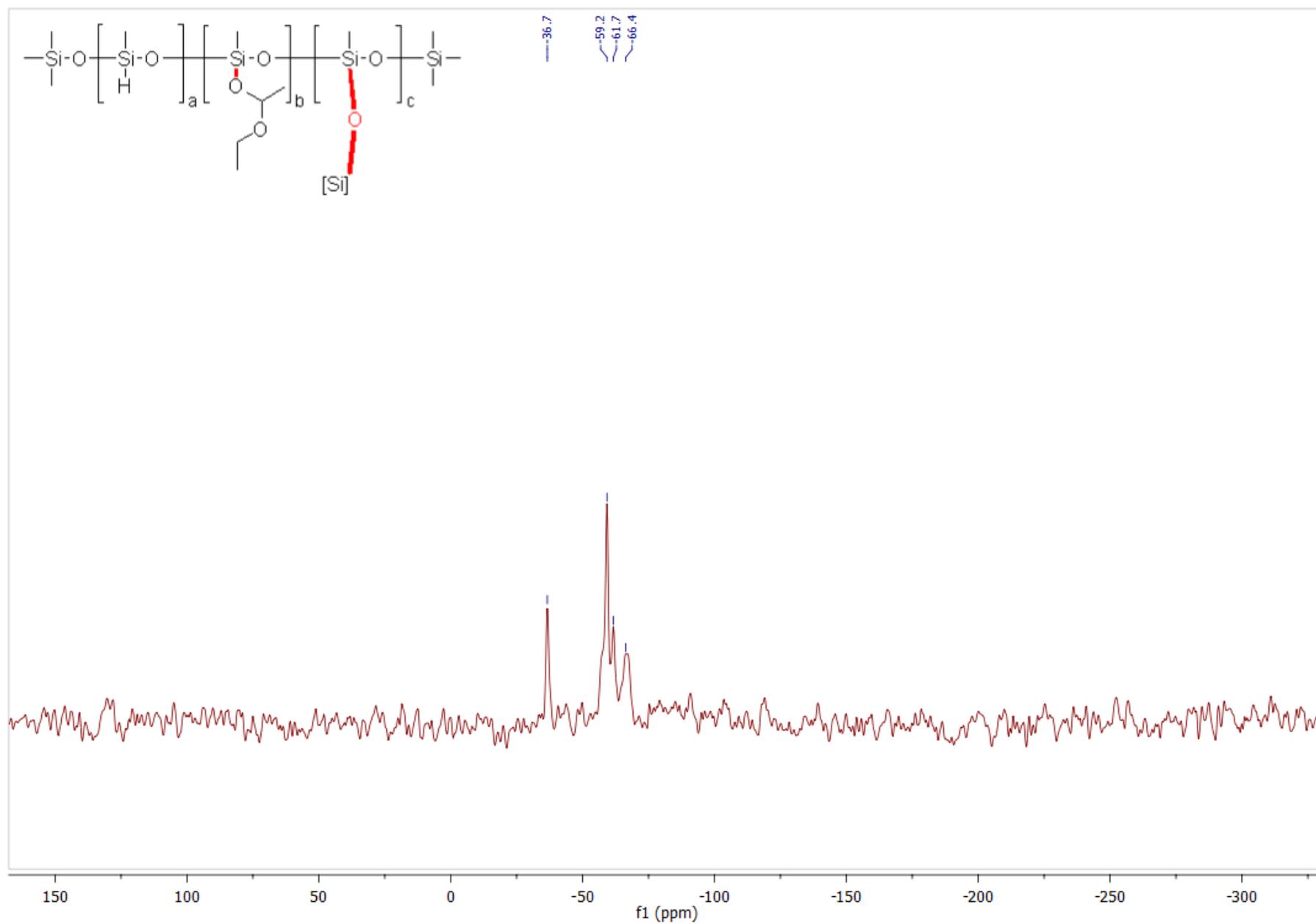




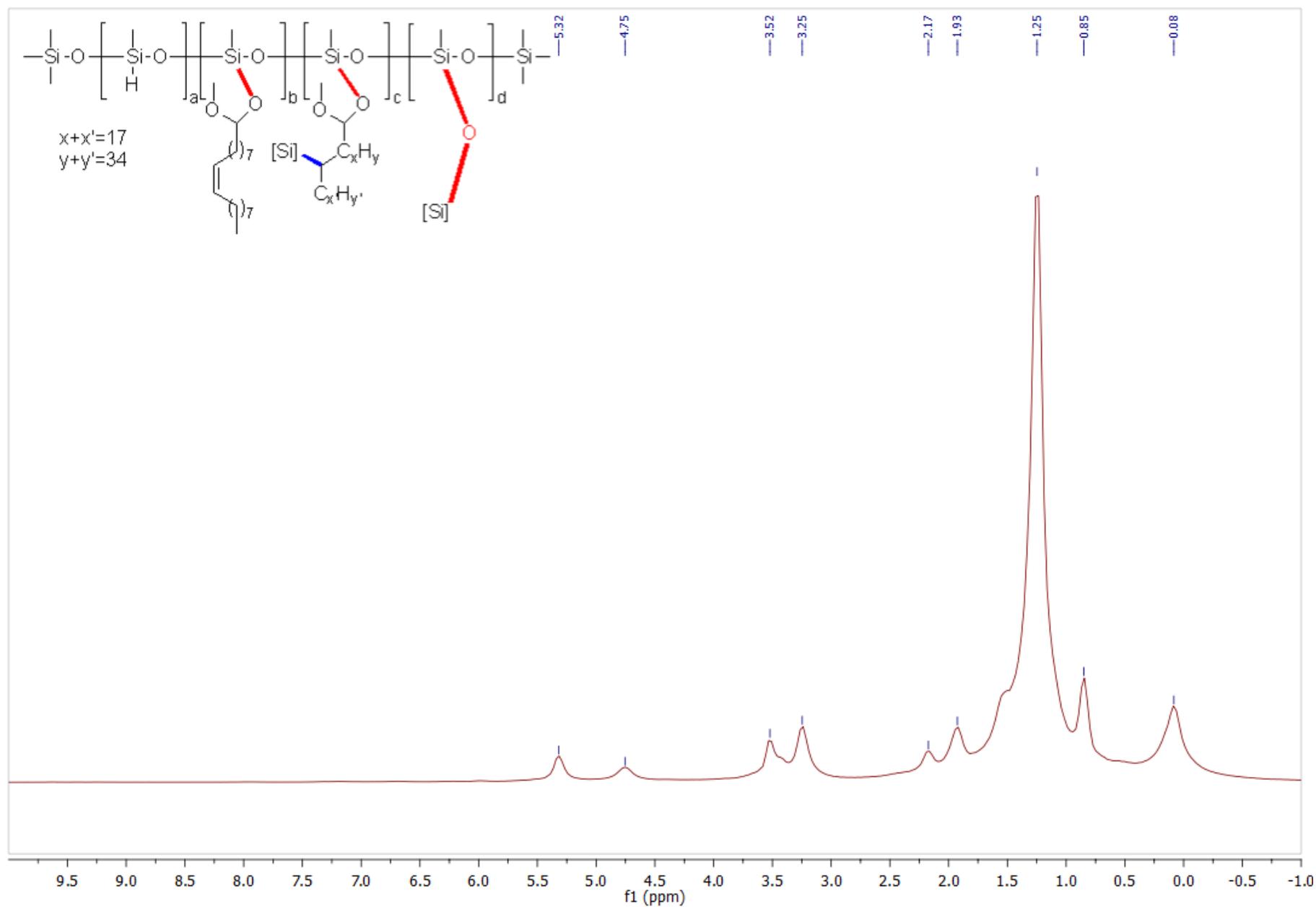
# $^{13}\text{C}$ CPMAS SS-NMR of 3g



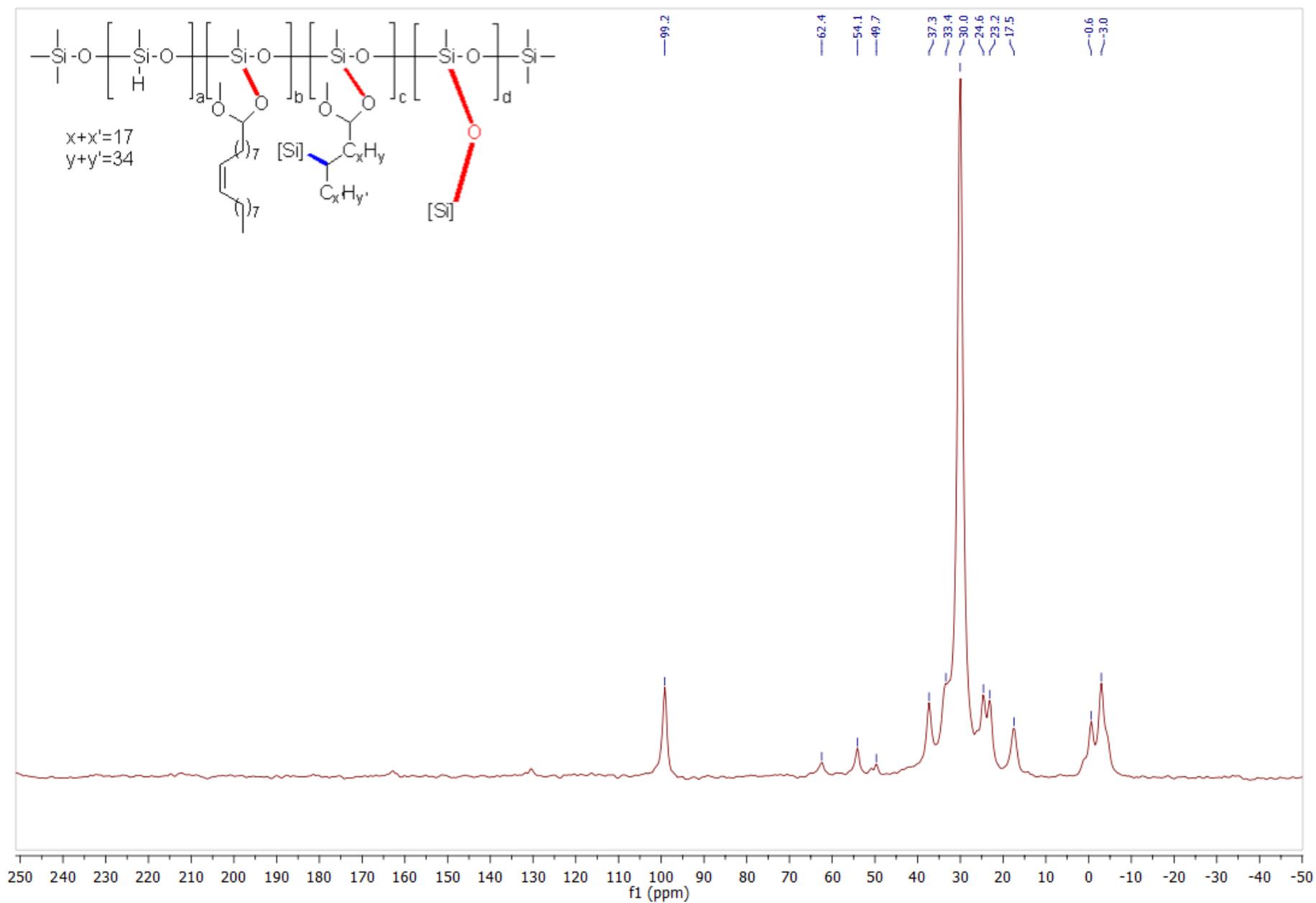
**$^{29}\text{Si}$  CPMAS SS-NMR of 3g**



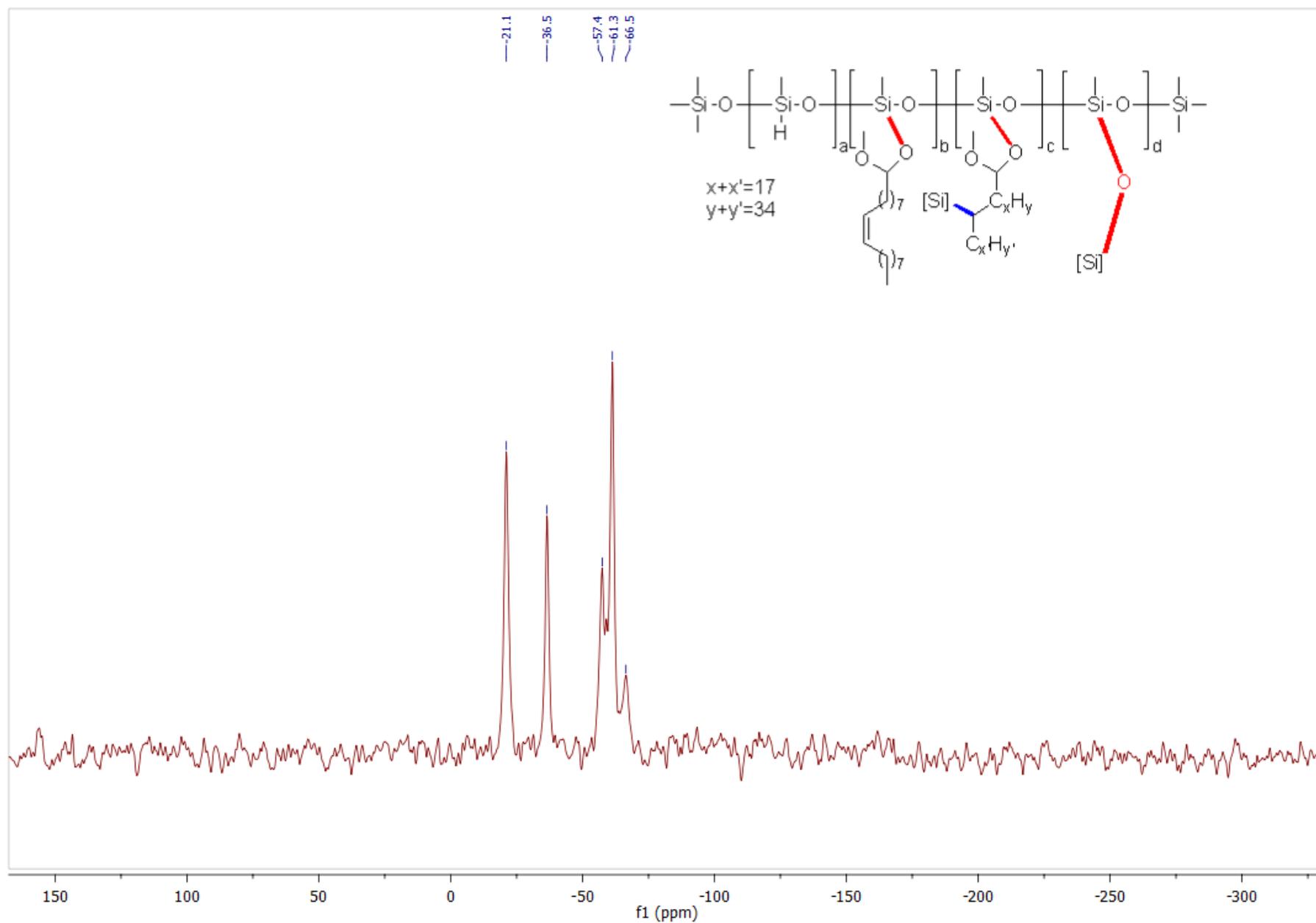
**<sup>1</sup>H MAS SS-NMR of 3h**



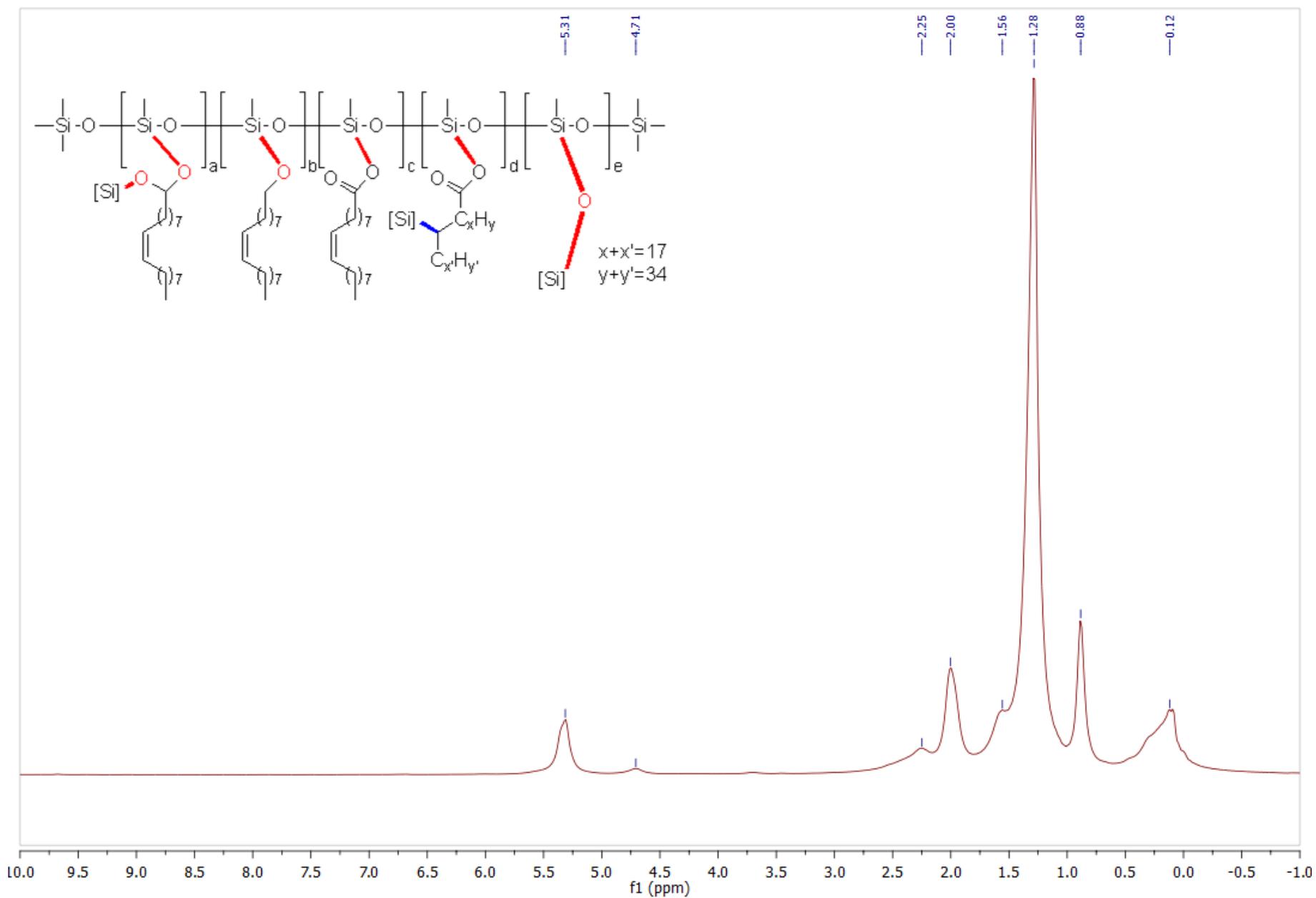
# <sup>13</sup>C CPMAS SS-NMR of 3h



<sup>29</sup>Si CPMAS SS-NMR of 3h

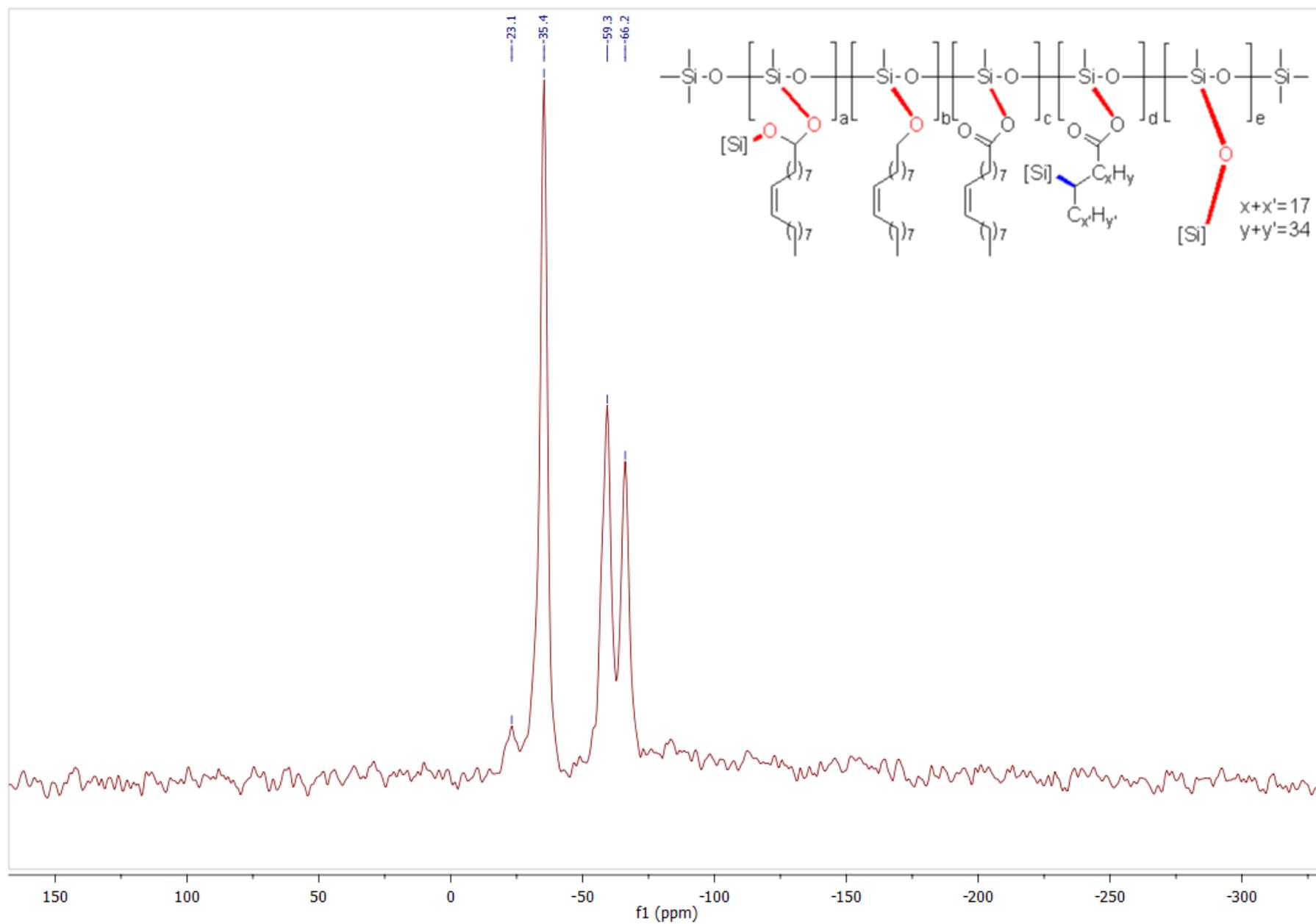


**<sup>1</sup>H MAS SS-NMR of 3i**

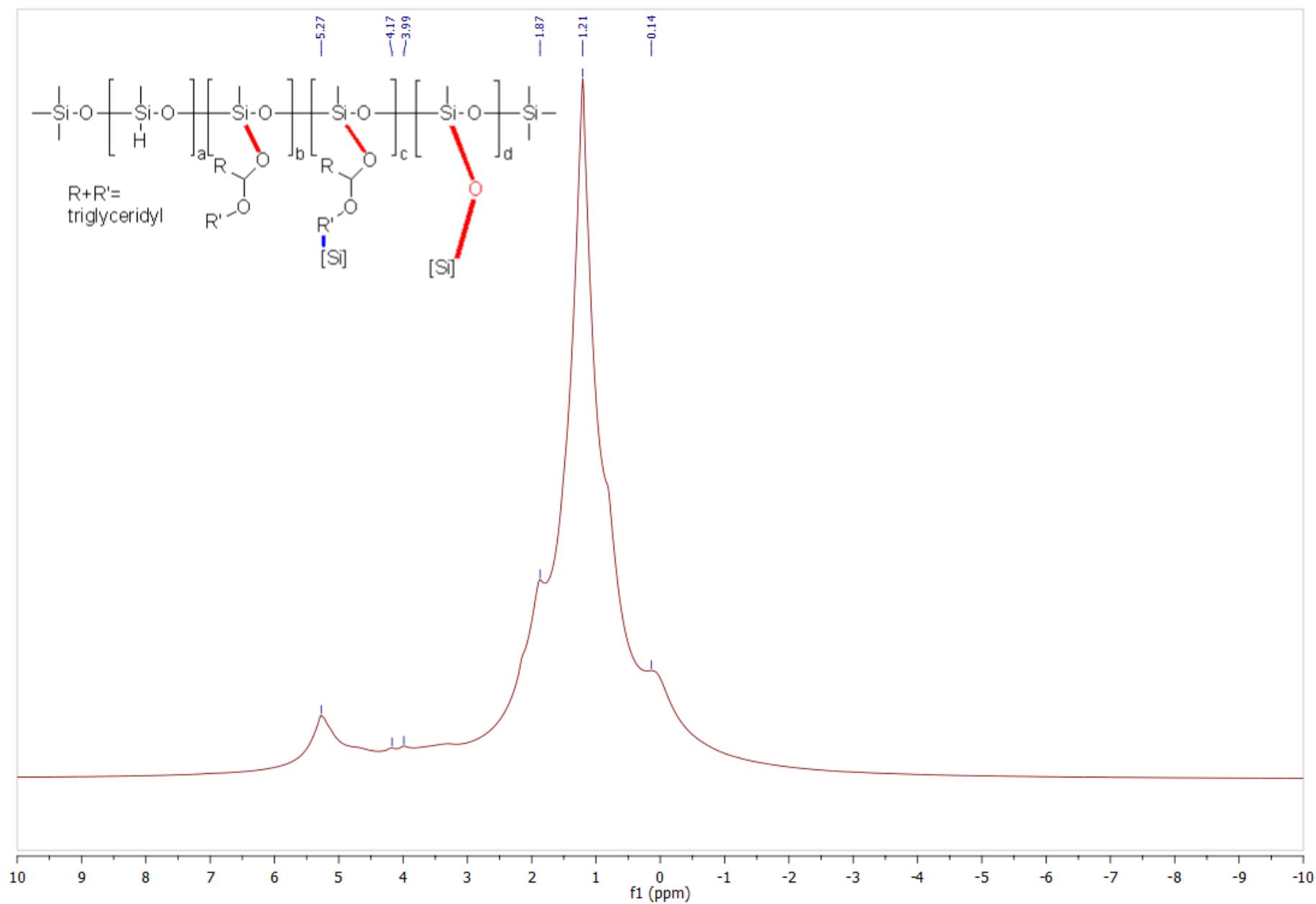




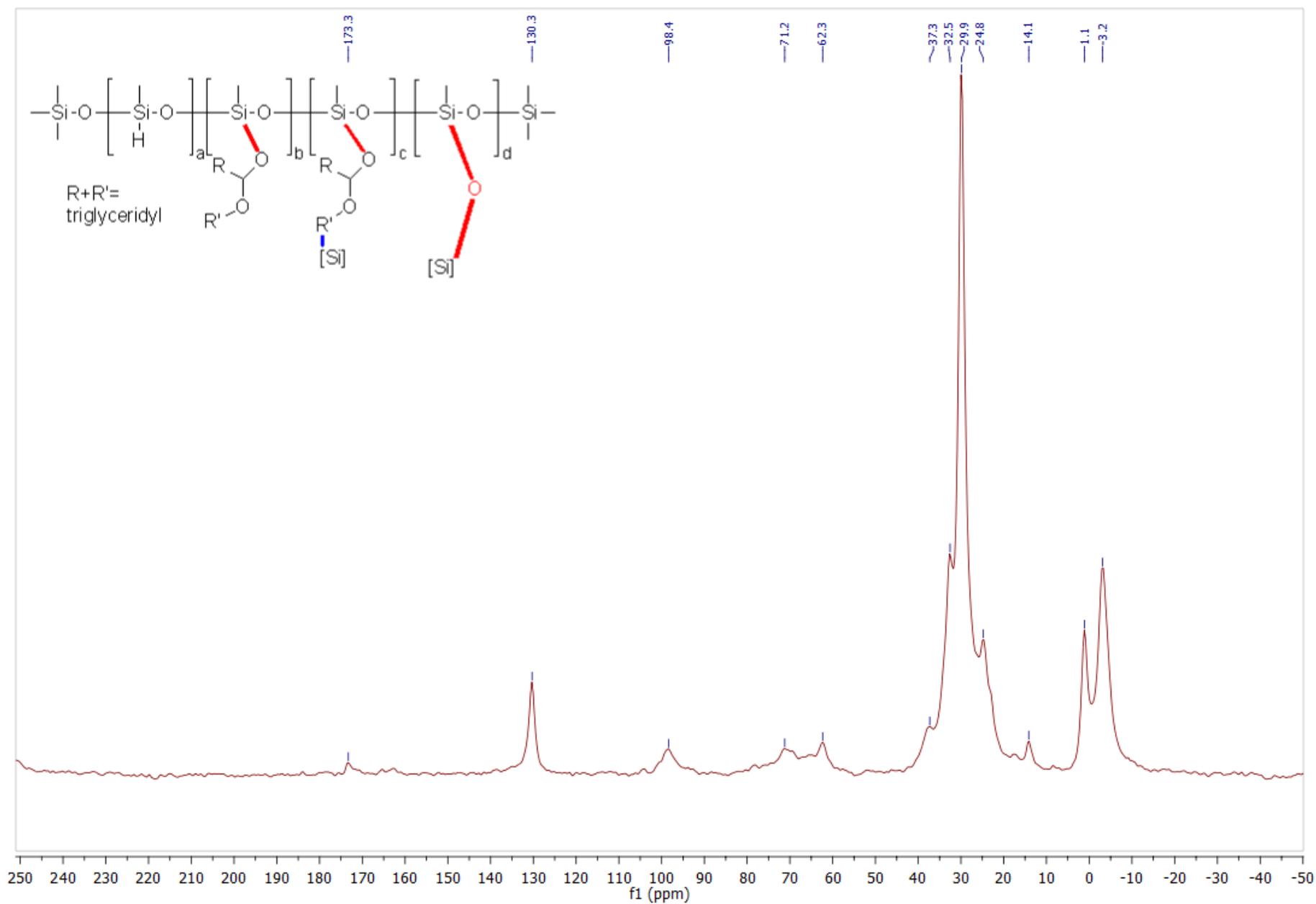
$^{29}\text{Si}$  CPMAS SS-NMR of 3i



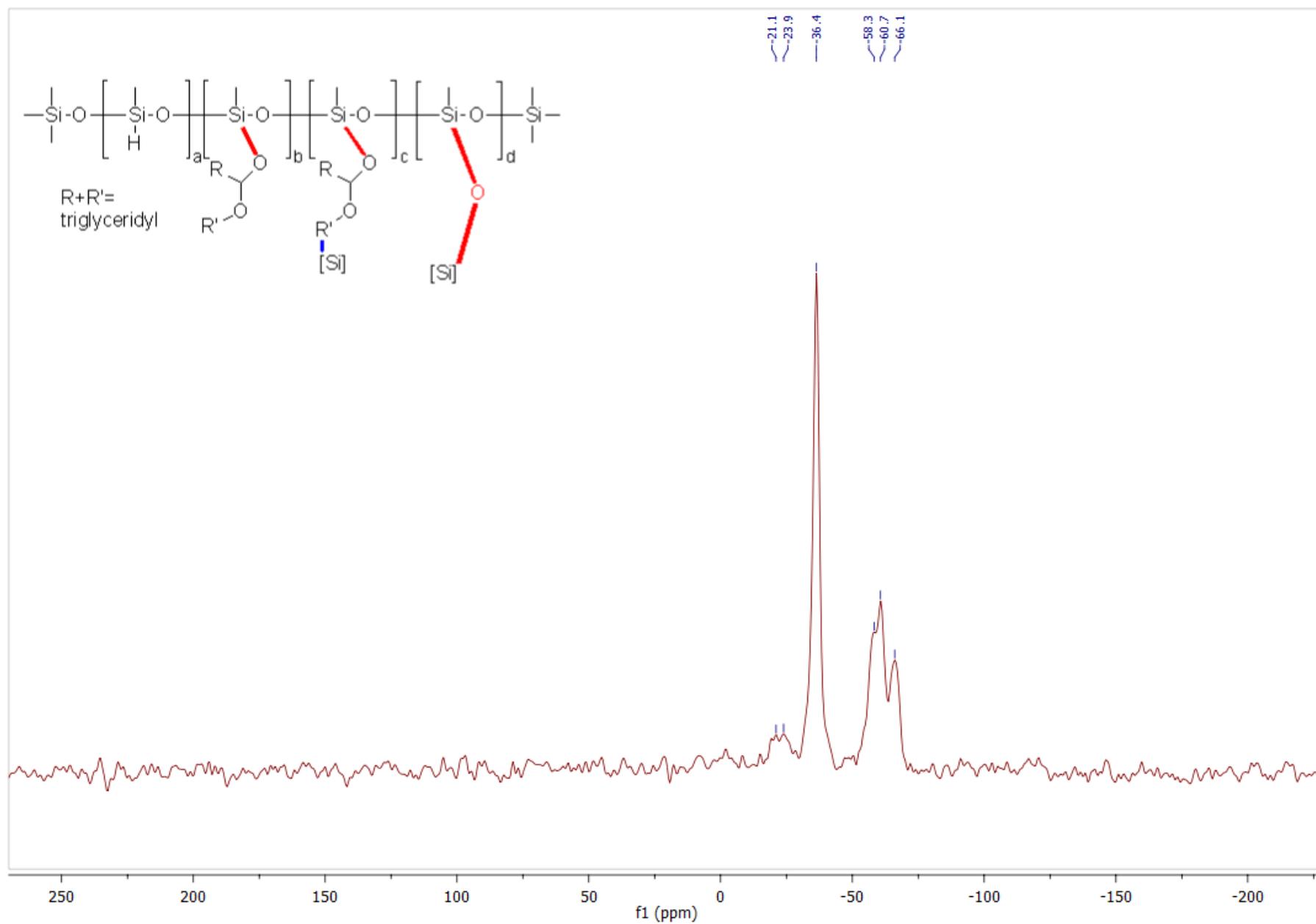
# $^1\text{H}$ MAS SS-NMR of 3j



# $^{13}\text{C}$ CPMAS SS-NMR of 3j

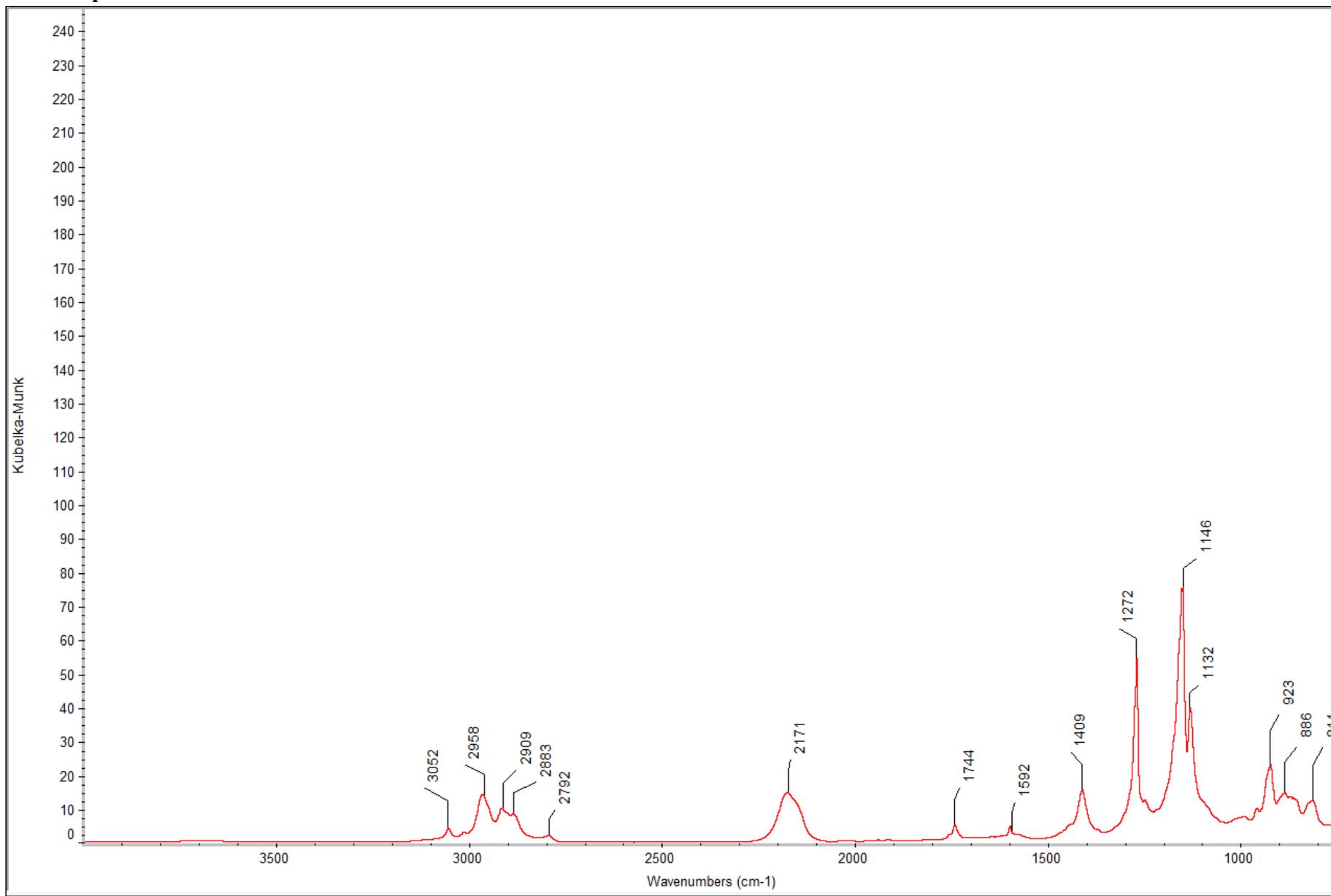


# $^{29}\text{Si}$ CPMAS SS-NMR of 3j

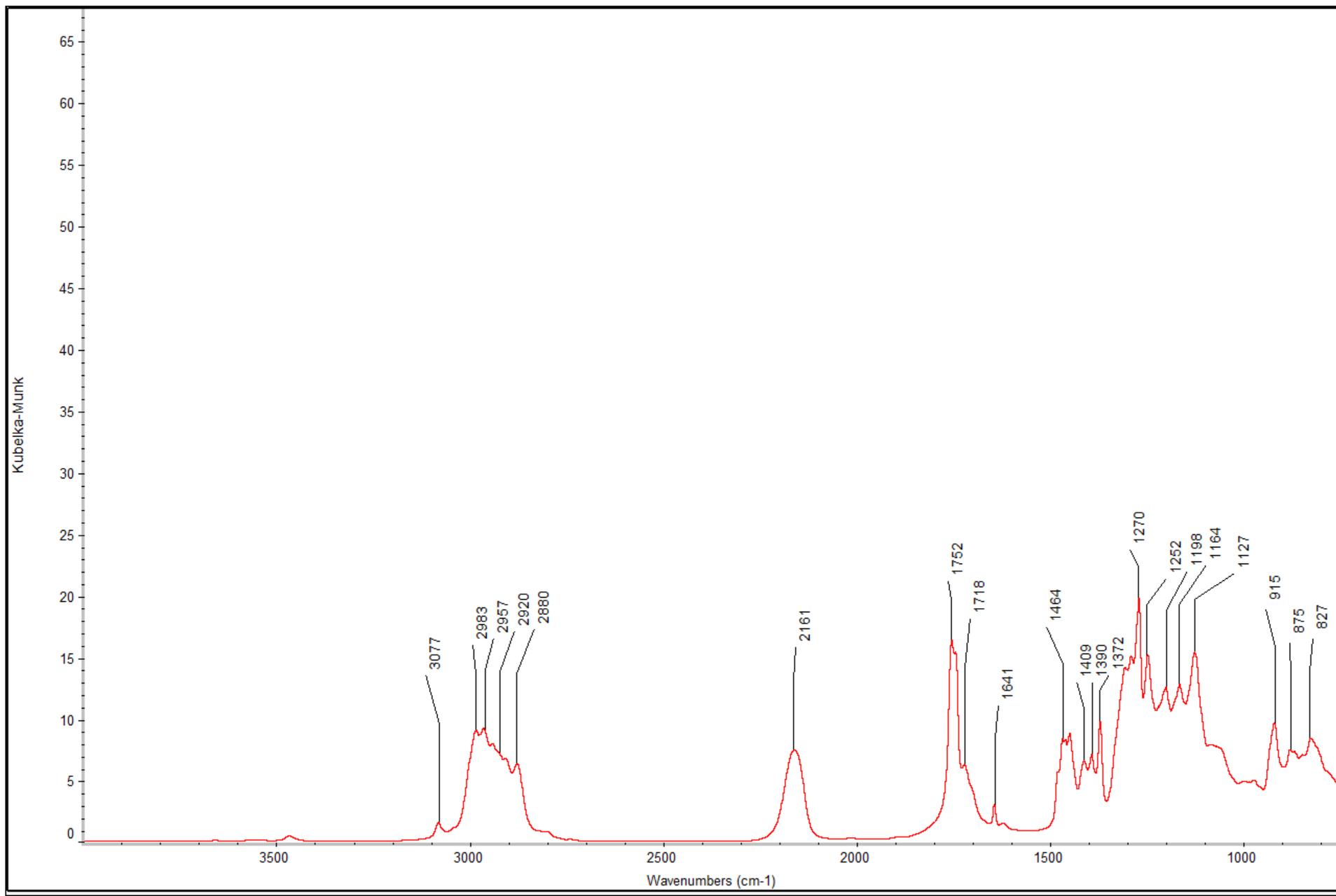


## DRIFT spectra

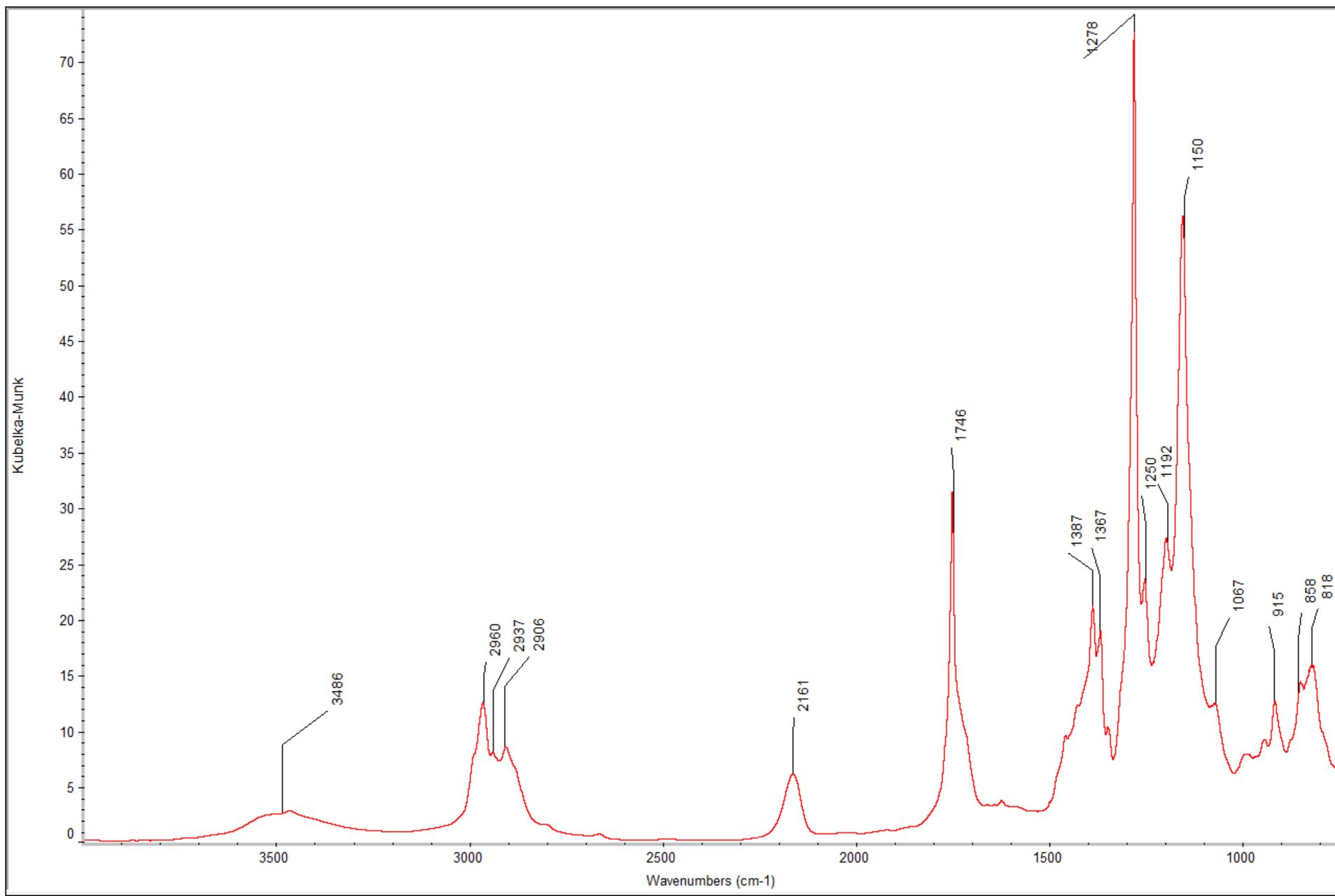
### DRIFT spectrum of 2a



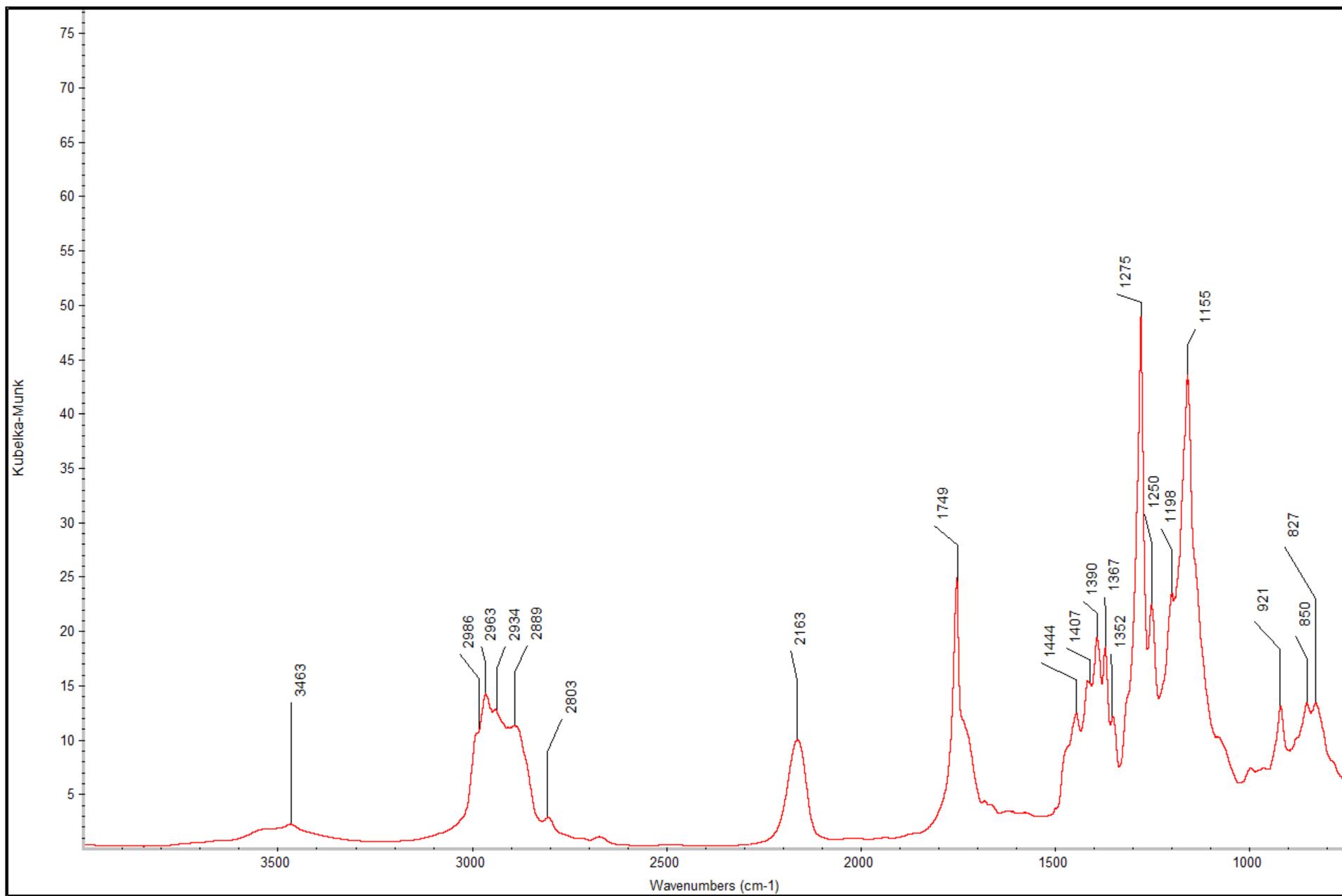
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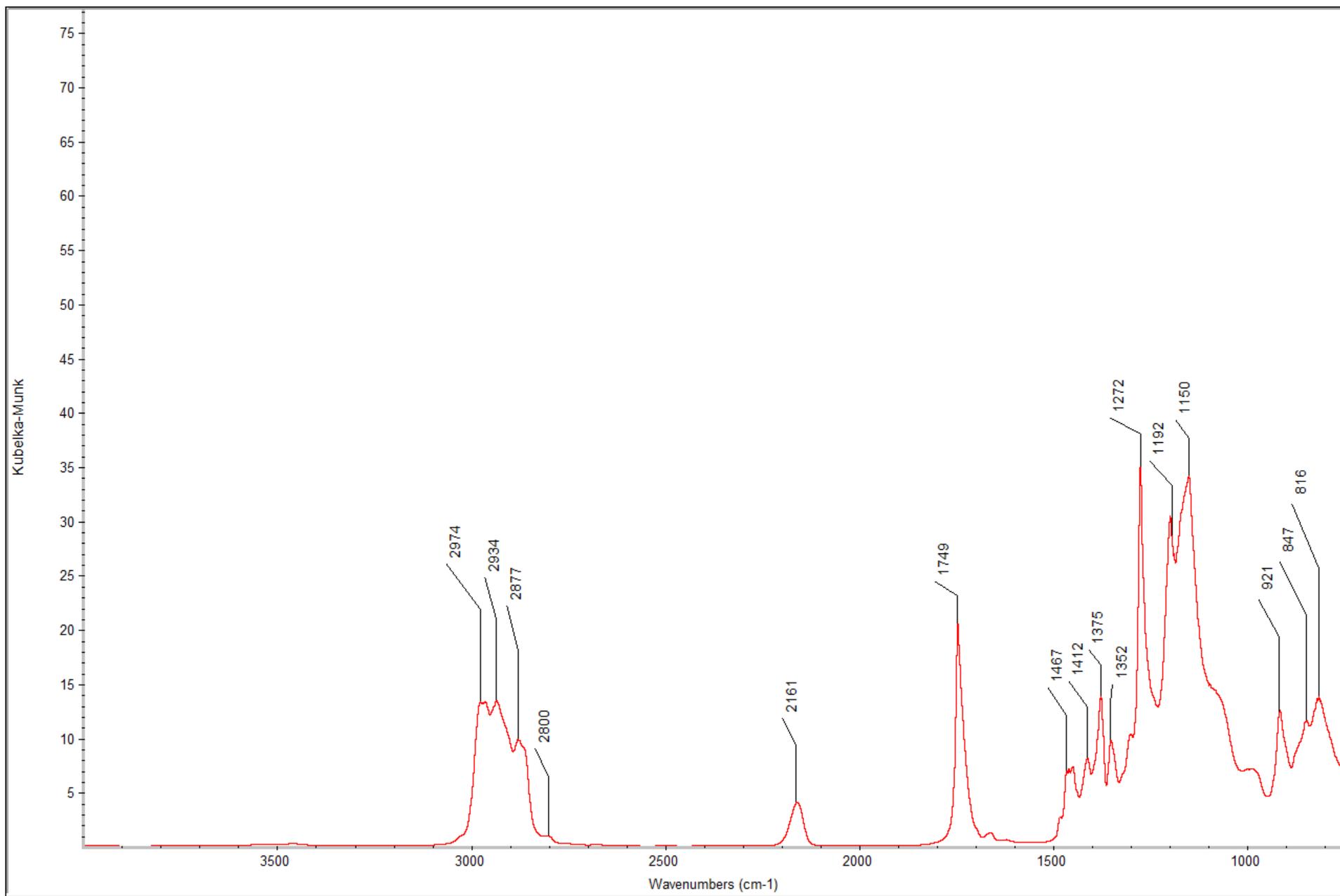
# DRIFT spectrum of 3a



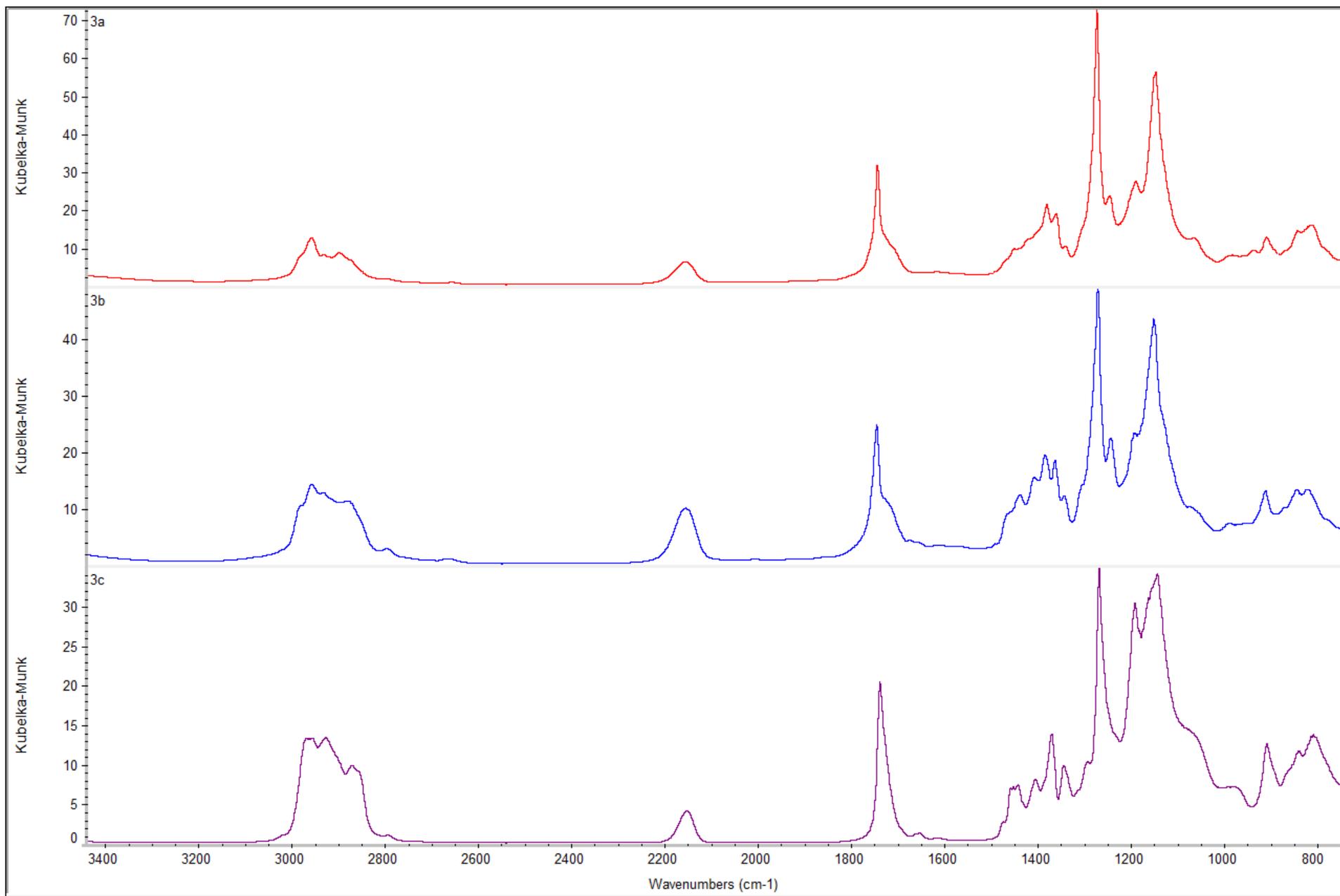
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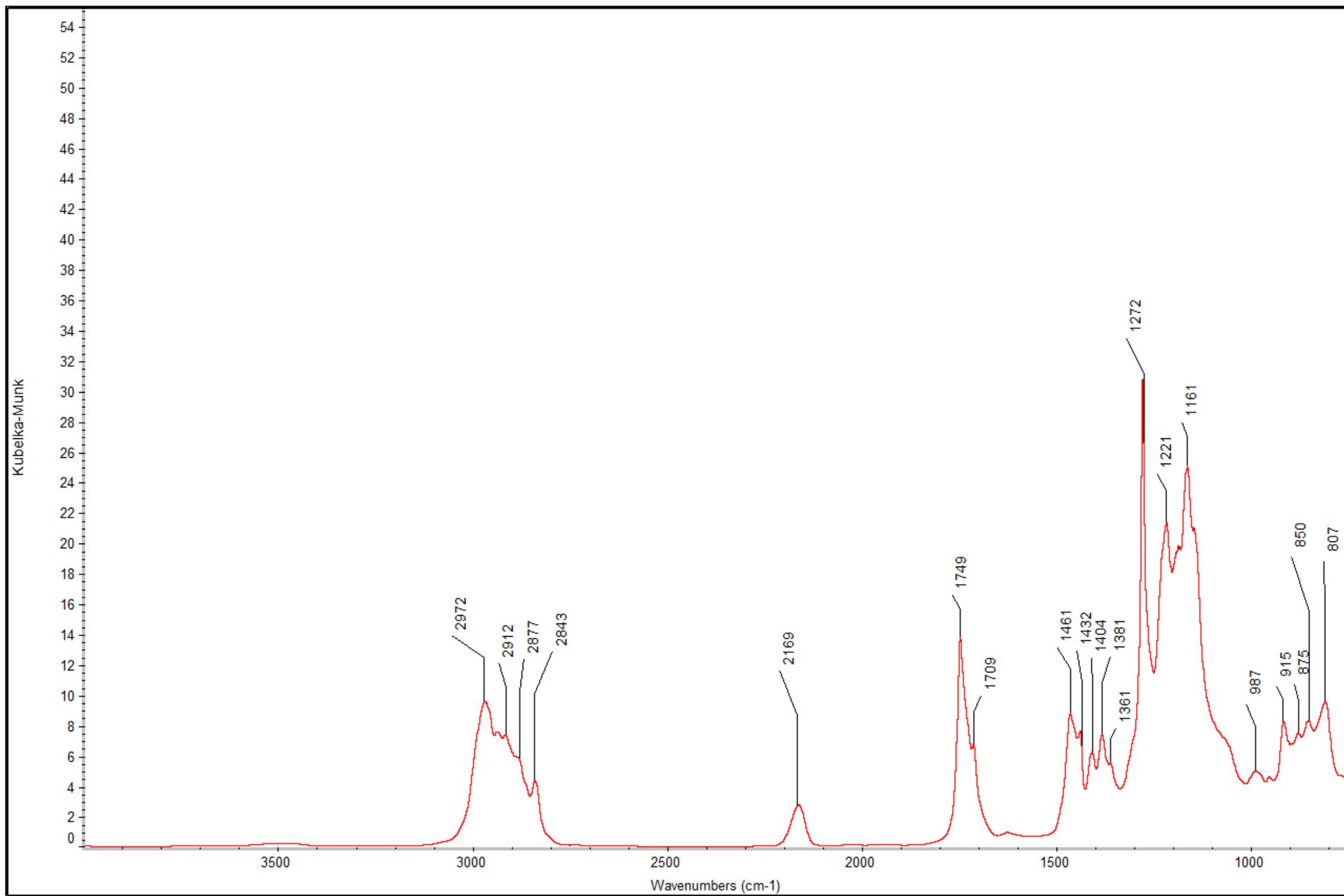
# DRIFT spectrum of 3c



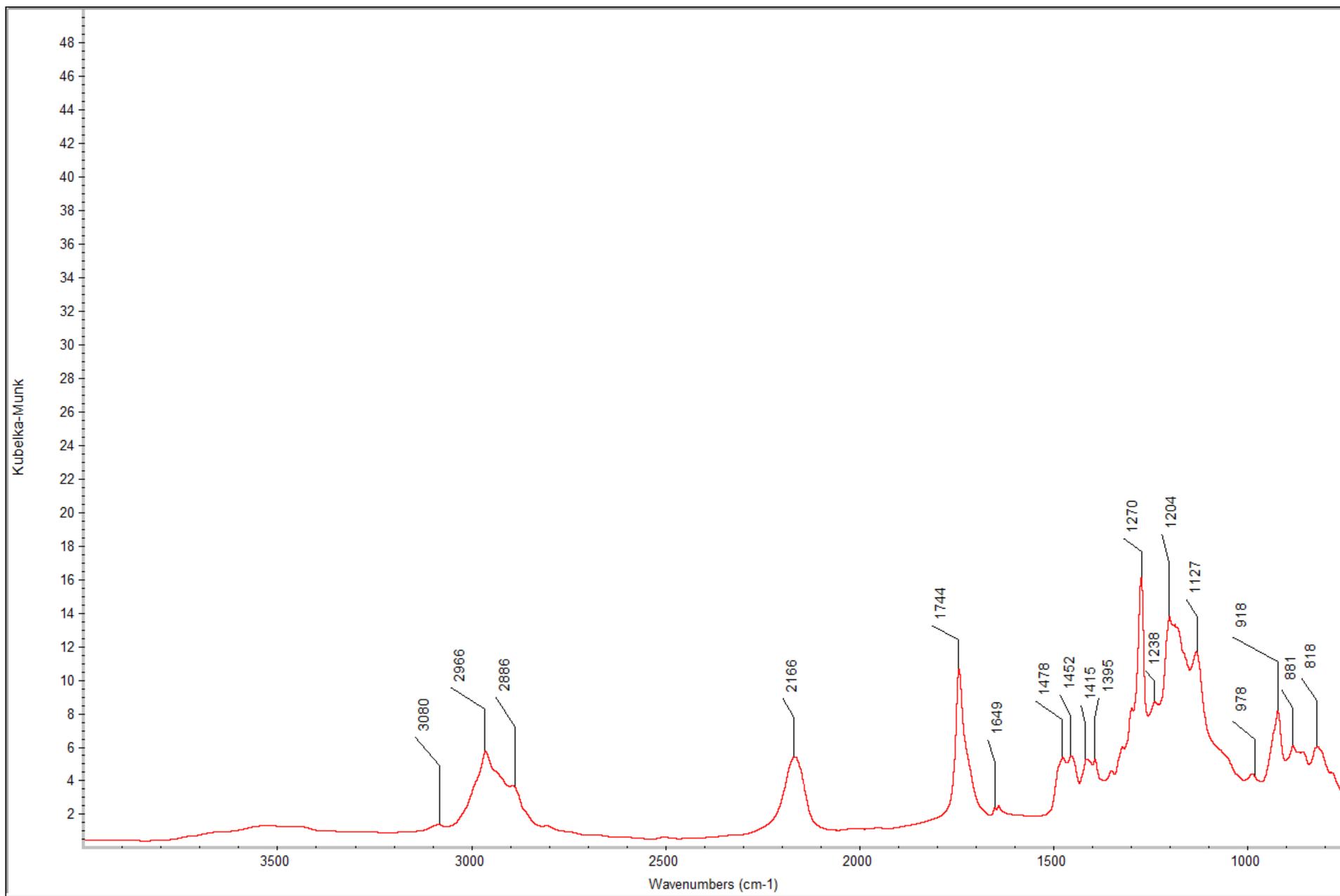
## DRIFT spectra: Comparison of DRIFT spectra between 3a-3c



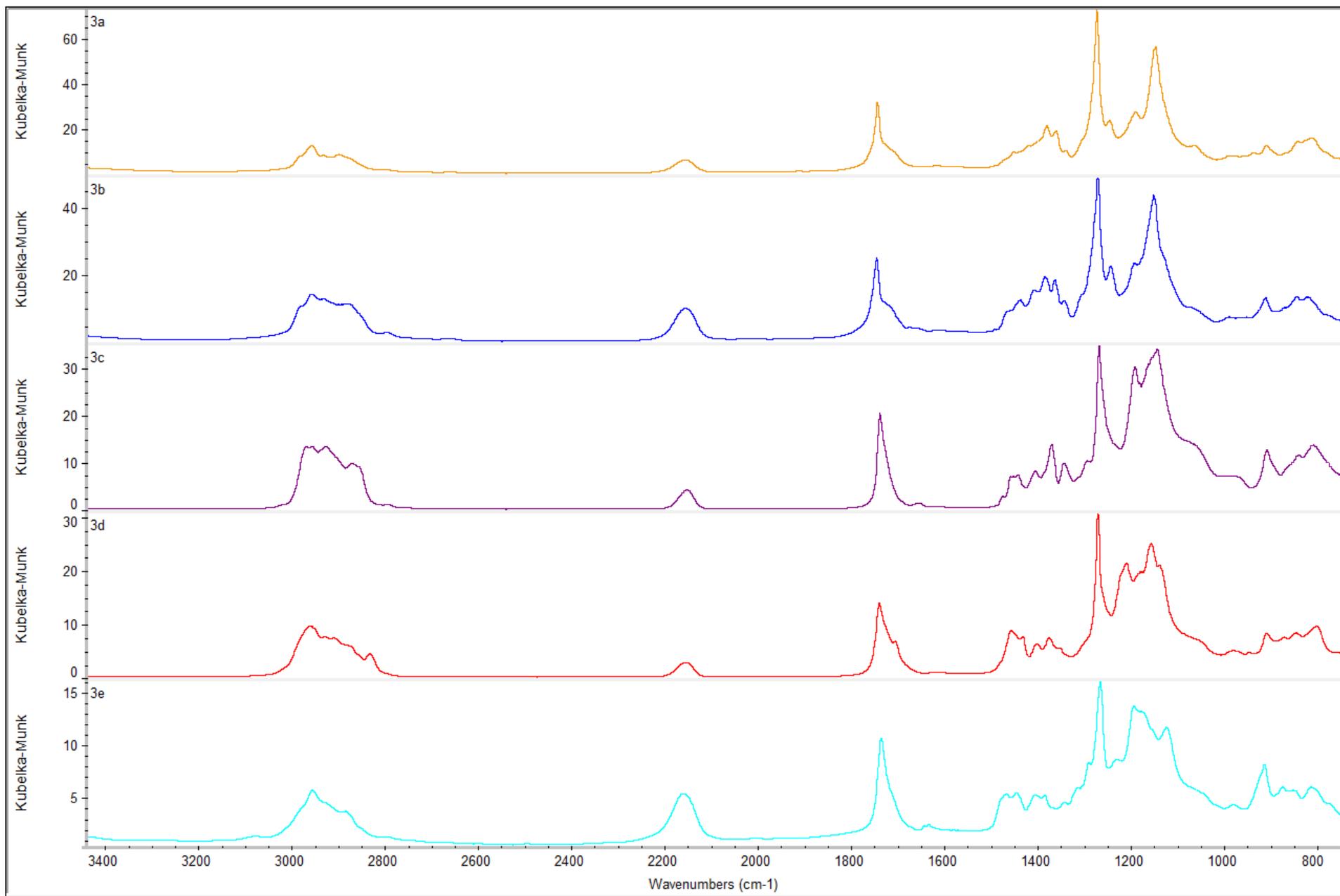
# DRIFT spectrum of 3d



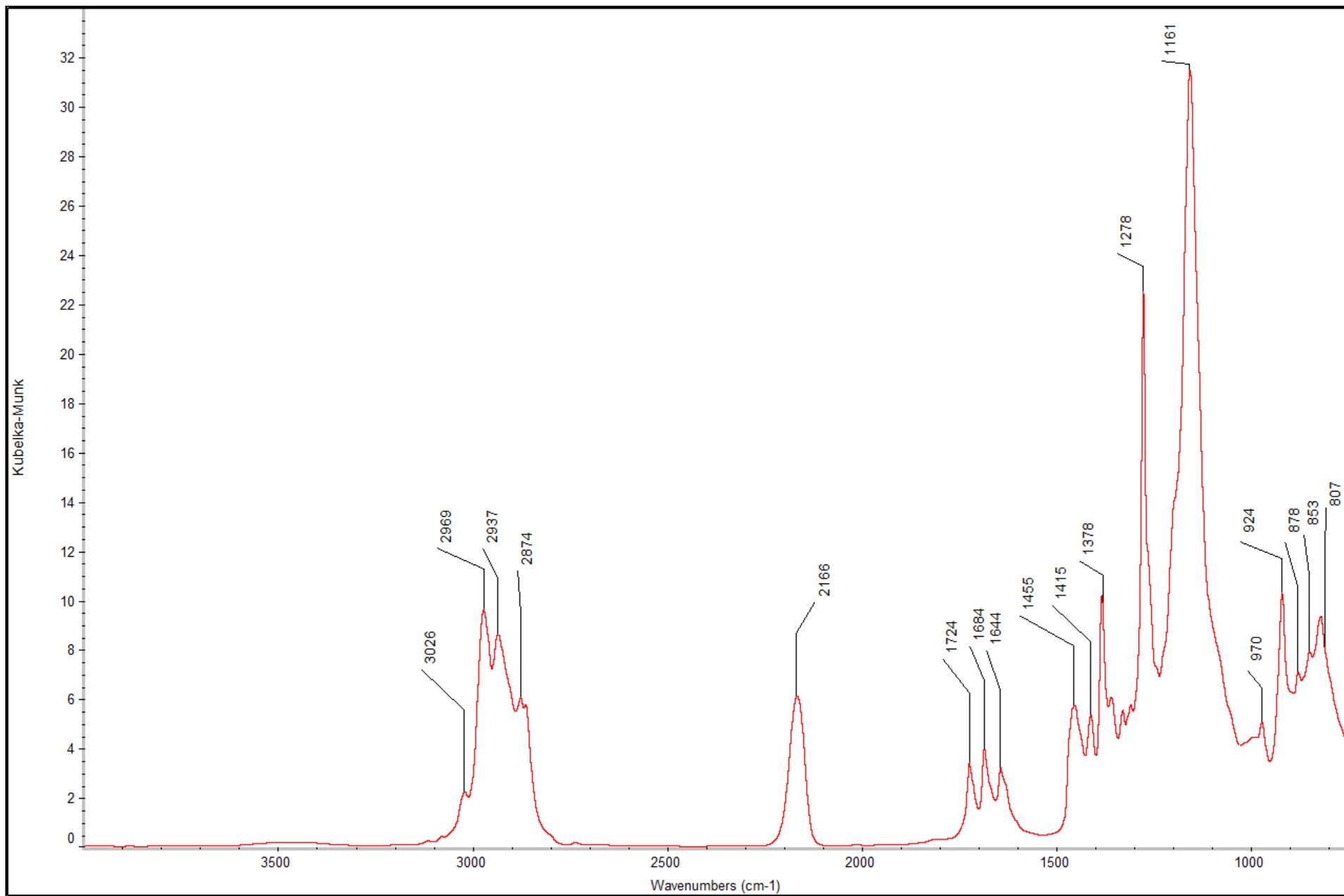
# DRIFT spectrum of 3e



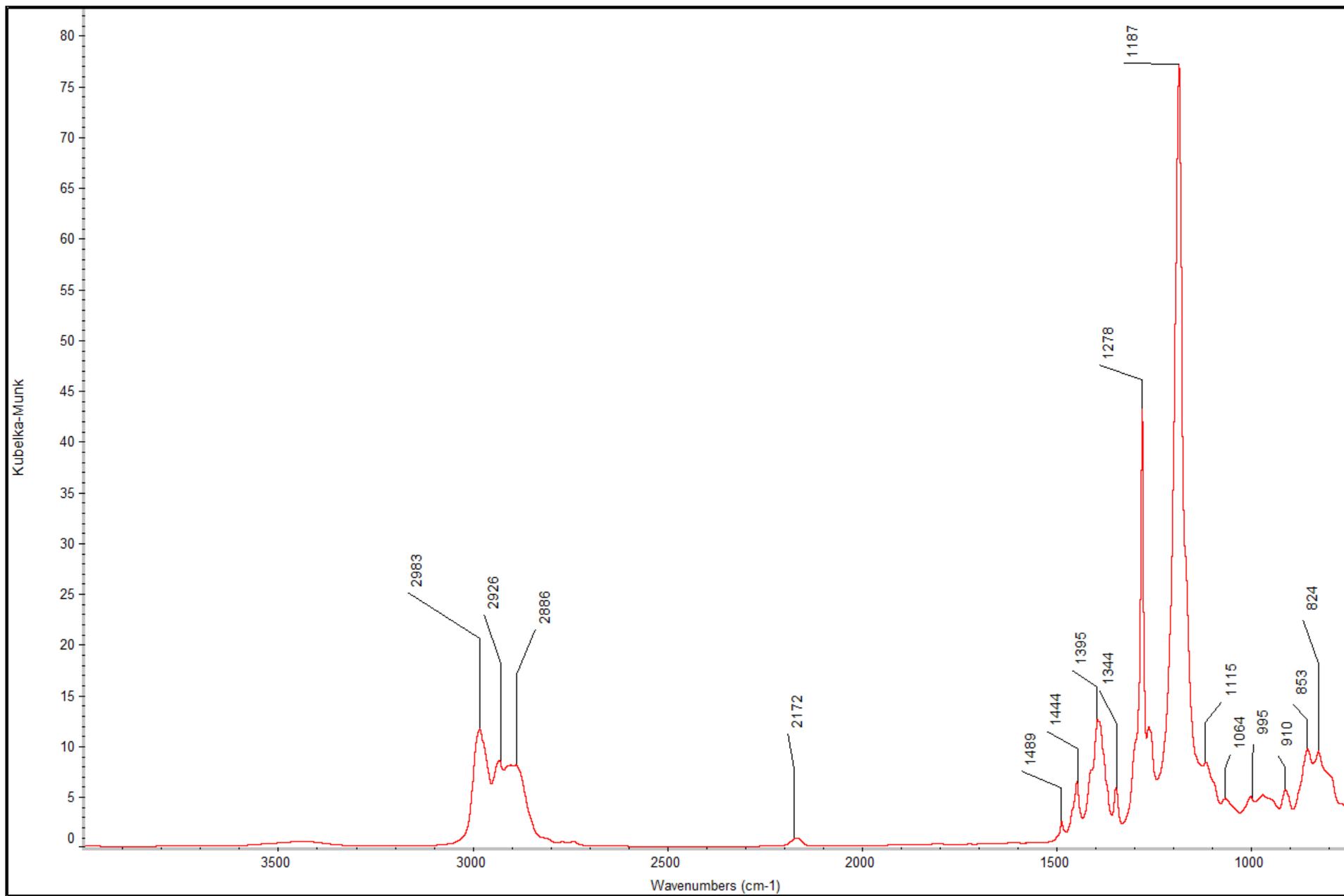
## DRIFT spectra: Comparison of DRIFT spectra between 3a-3e



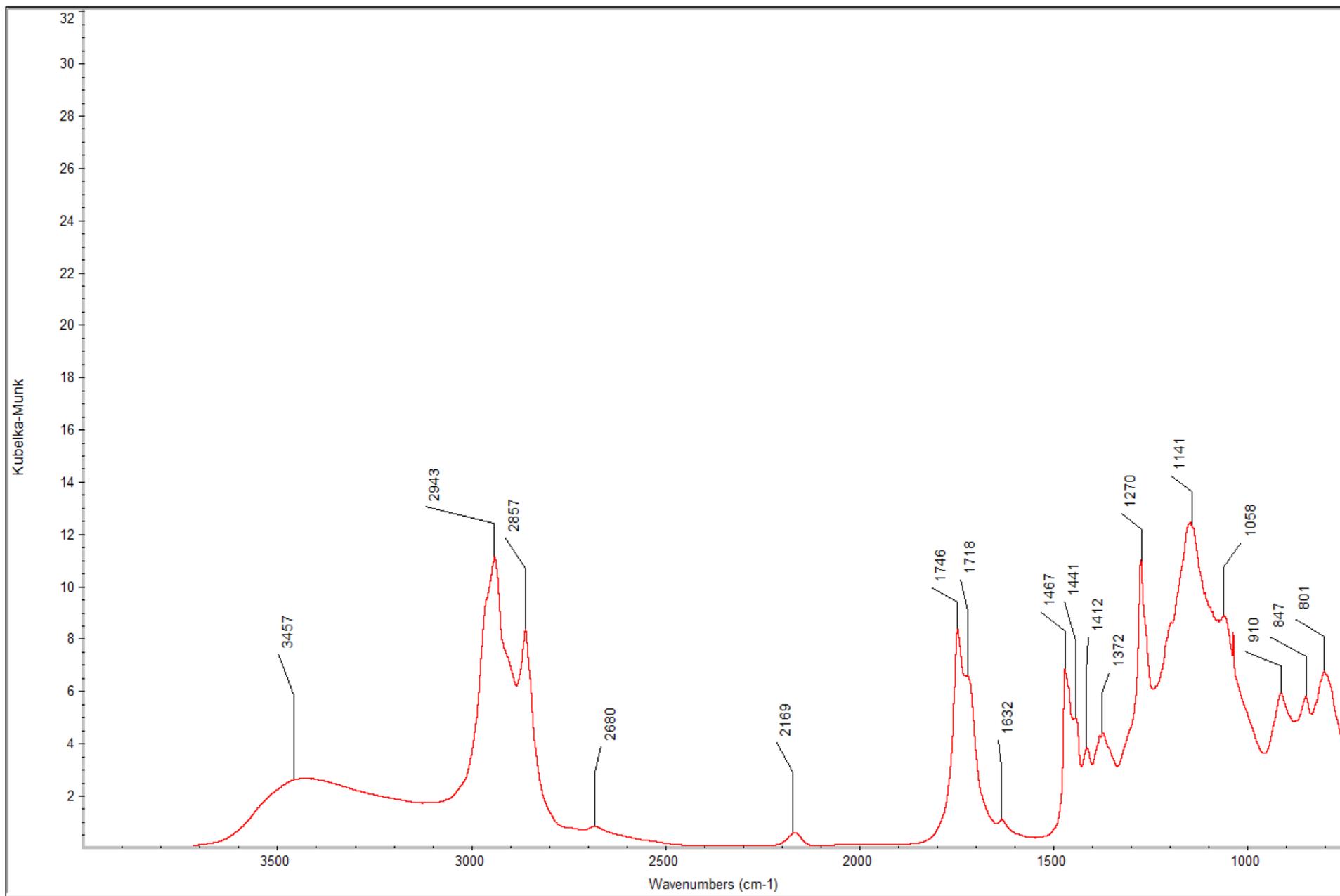
# DRIFT spectrum of 3f



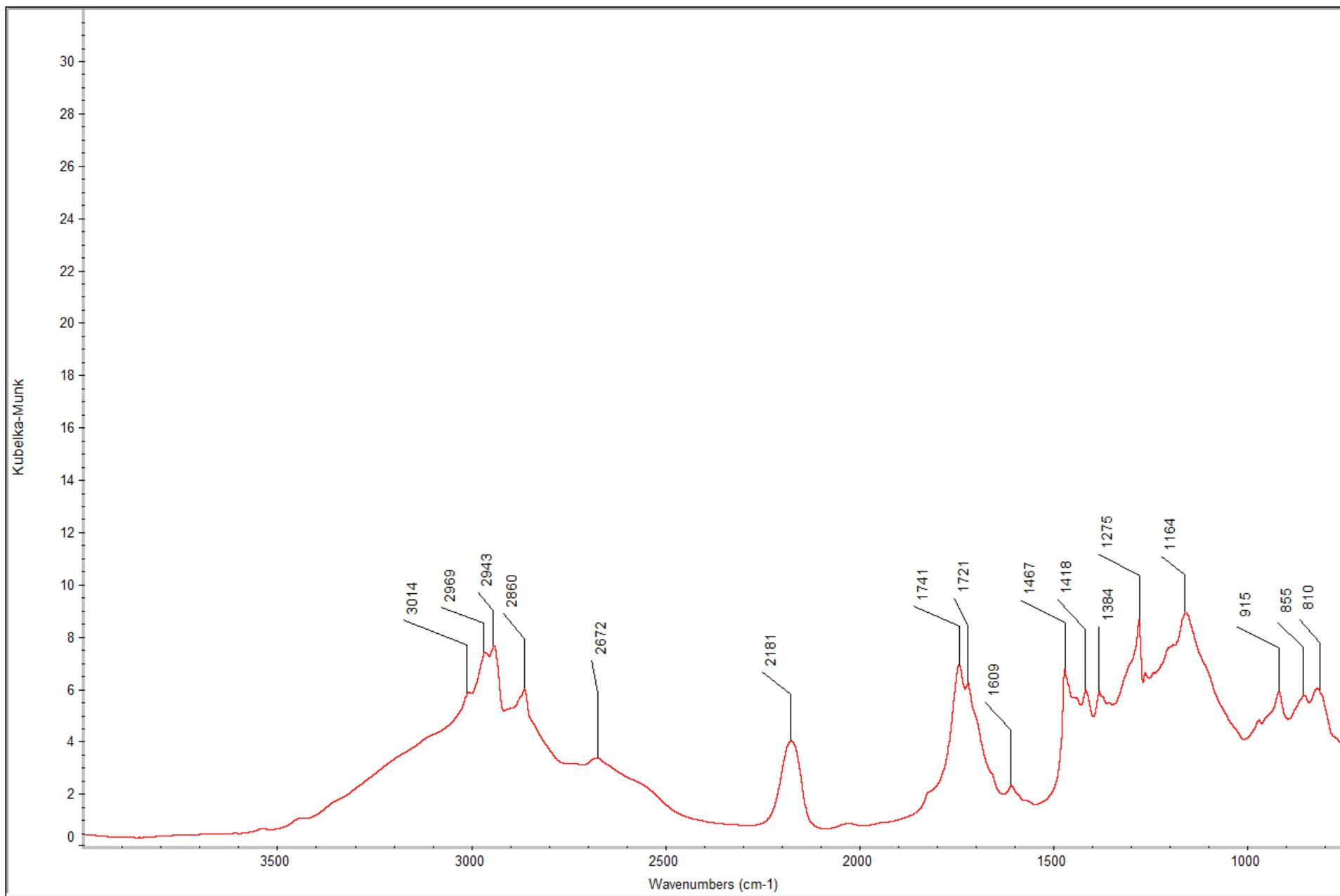
# DRIFT spectrum of 3g



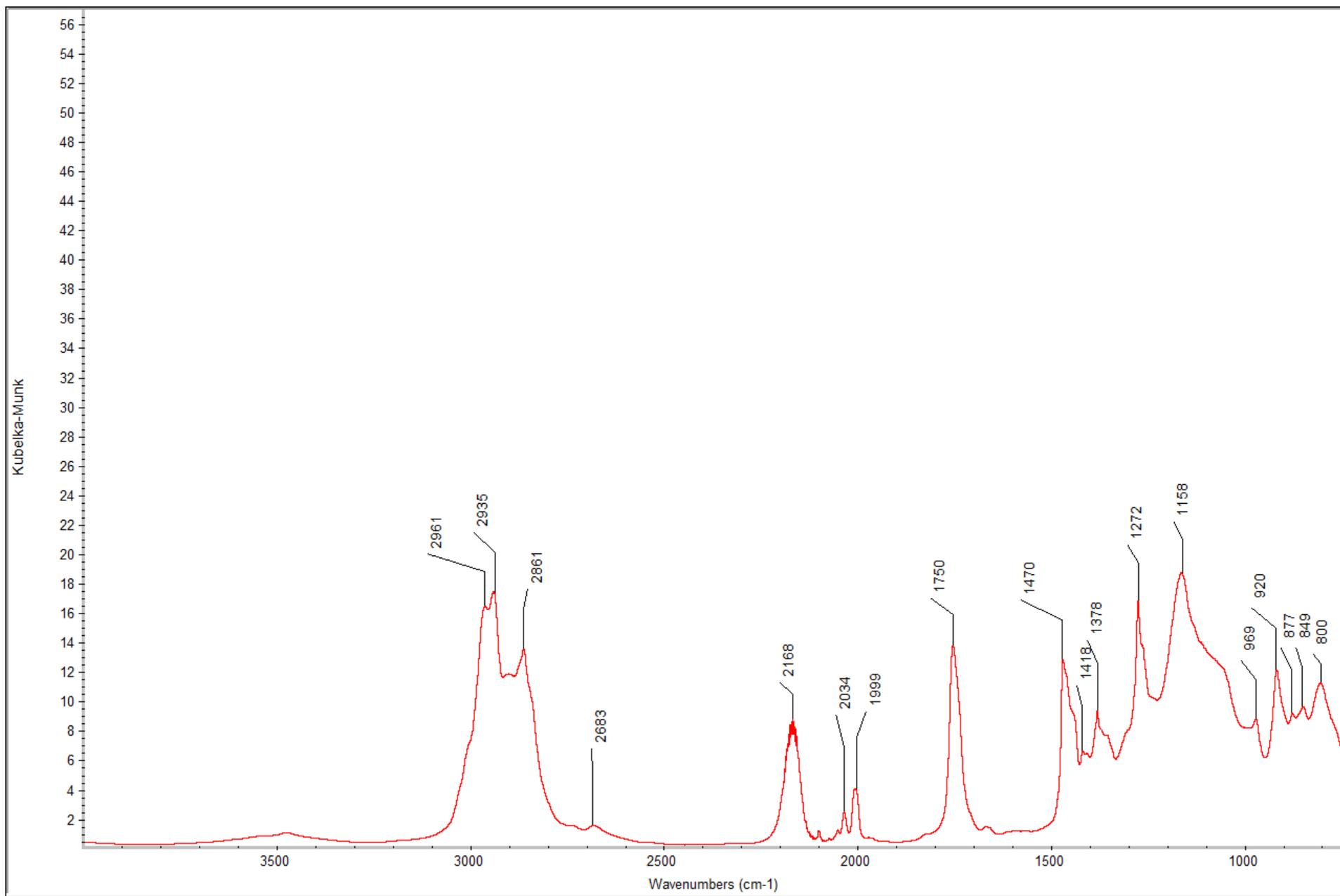
# DRIFT spectrum of 3h



# DRIFT spectrum of 3i



# DRIFT spectrum of 3j



## DRIFT spectra: Comparison of DRIFT spectra between 3h, 3i and 3j

