

Supporting information

**MnBr(CO)<sub>5</sub>: a commercially available highly  
active catalyst for olefin hydrosilylation under  
ambient air and green conditions**

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## Equipment and methods

Unless otherwise noted, all reactions were conducted in vials with a magnetic stirring bar under an argon atmosphere or under air. Toluene and mesitylene were distilled from sodium benzophenone ketyl radical and stored under argon in a glovebox or used without any purification depending on the reaction conditions. Other solvents were used without any purification.  $\text{MnBr}(\text{CO})_5$  was used as received, stored under argon in a glovebox or under air. Alkenes were stirred overnight on activated alumina, degassed by freeze-pump-thaw cycles, and stored under argon in a glovebox or used without any purification depending on the reaction conditions. Short-plug column chromatography was performed with Macherey-Nagel Silica 60 M silica gel (0.04–0.063 mm).

$^1\text{H}$  NMR spectra were recorded on a Bruker AC 300 MHz instrument. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) referenced to the appropriate solvent peak ( $^1\text{H}$  NMR:  $\text{CDCl}_3$  at 7.26 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, t = triplet, br. s = broad singlet, m = multiplet), coupling constant  $J$  (Hz), and integration. 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.

Gas chromatography analysis was performed on an Agilent 8890 chromatograph with an HP5 (5% of phenylmethylsiloxane) column (30 m length, 320  $\mu\text{m}$  of diameter, 0.25  $\mu\text{m}$  of thickness) equipped with a flame ionization detector (FID). Throughout the study, mesitylene was used as GC internal standard to obtain the GC yield for all products. The calibration curves were obtained using different known concentrations of both silane and alkene with the following method: flow rate 2.8 mL/min; inlet temperature 250 °C; column temperature 70 °C for 1 min, then 10 °C/min to 120 °C, then 40 °C/min to 300 °C then hold 3 min. Nitrogen was used as carrier gas and air and hydrogen as combustion gasses.

## Solvents and reagents

Toluene, anisole, mesitylene and  $\text{CDCl}_3$  were purchased from Sigma-Aldrich.  $\text{MnBr}(\text{CO})_5$  was purchased from Alfa Aesar. Various alkenes and silanes were purchased from Sigma-Aldrich or Fisher scientific and were used 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 or directly bought from Aldrich (CAS 63148-57-2) and used as received.

## Experimental procedures and spectral data

### General procedure for alkene hydrosilylation under argon

In an argon-filled glovebox, a 4 mL vial was charged with the appropriate alkene (0.94 mmol, 1 equiv.), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol, 1 equiv.), mesitylene (46  $\mu$ L, 0.335 mmol, GC standard), MnBr(CO)<sub>5</sub> catalyst (18.8  $\mu$ mol, 2 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of solvent to reach a total volume of 571  $\mu$ L. The vial was placed to a preheated oil bath at 70 °C and to stir at 500 rpm for 4 h. The catalytic reactions were monitored by GC using mesitylene as internal standard.

### General procedure for alkene hydrosilylation under air

A 4 mL vial under air was charged with the appropriate alkene (0.94 mmol, 1 equiv.), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol, 1 equiv.), mesitylene (46  $\mu$ L, 0.335 mmol, GC standard), MnBr(CO)<sub>5</sub> catalyst (18.8  $\mu$ mol, 2 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of solvent to reach a total volume of 571  $\mu$ L. The vial was placed to a preheated oil bath at 70 °C and to stir at 500 rpm for 4 h. The catalytic reactions were monitored by GC using mesitylene as internal standard.

### General procedure for styrene hydrosilylation with various silanes

A 4 mL vial under argon was charged with styrene (0.94 mmol, 1 equiv.), silane (0.94 mmol, 1 equiv.), mesitylene (46  $\mu$ L, 0.335 mmol, GC standard), MnBr(CO)<sub>5</sub> catalyst (18.8  $\mu$ mol, 2 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of anisole to reach a total volume of 571  $\mu$ L. The vial was placed to a preheated oil bath at 70 °C and to stir at 500 rpm for 4 h. The catalytic reactions were monitored by GC using mesitylene as internal standard.

### General procedure for *n*-octene hydrosilylation with green solvents

A 4 mL vial under air was charged with *n*-octene (74  $\mu$ L, 0.47 mmol, 1 equiv.), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol, 2 equiv.), mesitylene (46  $\mu$ L, 0.335 mmol, GC standard), MnBr(CO)<sub>5</sub> catalyst (9.4  $\mu$ mol, 2 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of solvent to reach a total volume of 571  $\mu$ L. The vial was placed to a preheated oil bath at 70 °C and to stir at 500 rpm for 4 h. The catalytic reactions were monitored by GC using mesitylene as internal standard.

### Radical trapping experiment

In an argon-filled glovebox, a 4 mL vial was charged with *n*-octene (0.94 mmol, 1 equiv.), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol, 1 equiv.), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (5.9 mg, 0.038 mmoles, 8 equiv./Mn), mesitylene (46  $\mu$ L, 0.335 mmol, GC standard), MnBr(CO)<sub>5</sub> catalyst (18.8  $\mu$ mol, 2 mol%), 195  $\mu$ L of toluene and a stirring bar. The vial was placed to a preheated oil bath at 70 °C and to stir at 500 rpm for 4 h. The catalytic reactions were monitored by GC using mesitylene as internal standard.

## Isolation and characterization of the hydrosilylated products

After the desired reaction time, the crude mixture (color variation from pale orange-brown to almost colorless) were passed through a neutral silica column (3 cm in height in a Pasteur pipette) and eluted with pentane. The collected solution was put under vacuum to remove the solvent. Resulting products were colorless or slightly yellow liquids. This purification method is commonly used for the purification of hydrosilylated products in the literature [see the following references as salient examples: M. Jakoobi, V. Dardun, L. Veyre, V. Meille, C. Camp, C. Thieuleux, *J. Org. Chem.* 2020, **85**, 11732; C. C. Hojilla Atienza, A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P. J. Chirik, *ACS Catal.*, 2012, **2**, 2169.]

## General procedure for PMHS functionalization with dienes and alkenes

In an argon-filled glovebox, a 4 mL vial was charged with the corresponding diene (1.7 mmoles, 0.5 equiv.) or alkene (2.4 mmol, 1 equiv.), PMHS (1.0 eq of Si-H),  $\text{MnBr}(\text{CO})_5$  catalyst (7.2  $\mu\text{mol}$ , 0.3 mol%) and a stirring bar. The vial was placed to a preheated oil bath at 70 °C and left for 24 h to stir at 1000 rpm. The samples were further post-cured at 60 °C until the end of 24 h of reaction time.

## General procedure for PMHS functionalization with epoxides

In an argon-filled glovebox, a 4 mL vial was charged with the corresponding or alkene (3.75 mmol, 1 equiv.), PMHS (1.0 eq of Si-H),  $\text{MnBr}(\text{CO})_5$  catalyst (11.4  $\mu\text{mol}$ , 0.3 mol%) and a stirring bar. The vial was placed to a preheated oil bath at 70 °C and left for 24 h to stir at 1000 rpm. The samples were further post-cured at 60 °C until the end of 24 h of reaction time.

## ICPS-MS analysis of $\text{MnBr}(\text{CO})_5$

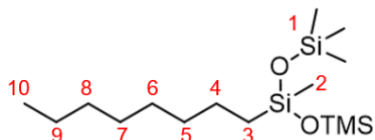
sample: $\text{MnBr}(\text{CO})_5$		
parameter	unit	result
Pt	mg/kg	0,05 0,04

Made by Mikroanalytisches Labor Pascher

## Characterization of the silylated products:

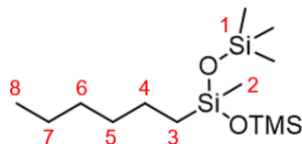
### Alkene functionalization with MD<sup>H</sup>M

#### 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (3a)<sup>1</sup>



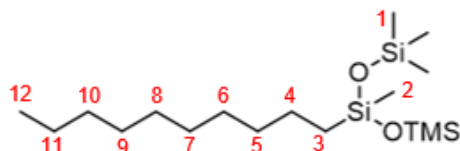
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.26 (br. s, 12H, *H*<sub>4</sub>-*H*<sub>9</sub>), 0.88 (t, *J* = 6.7 Hz, 3H, *H*<sub>10</sub>), 0.43 (t, *J* = 7.7 Hz, 2H, *H*<sub>3</sub>), 0.09 (s, 18H, *H*<sub>1</sub>), -0.01 (s, 3H, *H*<sub>2</sub>).

#### 1,1,1,3,5,5,5-heptamethyl-3-hexyltrisiloxane (3b)<sup>1</sup>



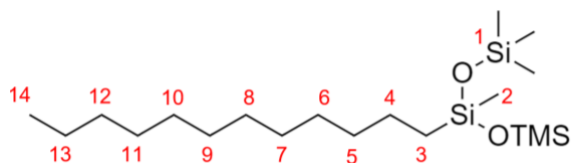
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.28 (br. s, 8H, *H*<sub>4</sub>-*H*<sub>7</sub>), 0.88 (t, *J* = 6.6 Hz, 3H, *H*<sub>8</sub>), 0.45 (t, *J* = 7.5 Hz, 2H, *H*<sub>3</sub>), 0.09 (s, 18H, *H*<sub>1</sub>), -0.01 (s, 3H, *H*<sub>2</sub>).

#### 1,1,1,3,5,5,5-heptamethyl-3-decyltrisiloxane (3c)<sup>2</sup>



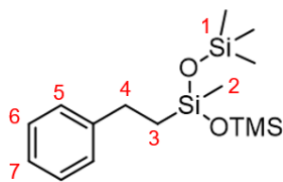
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.26 (m, 16 H, *H*<sub>4</sub>-*H*<sub>11</sub>), 0.88 (t, *J* = 6.7 Hz, 3H, *H*<sub>12</sub>), 0.44 (t, *J* = 7.6 Hz, 2H, *H*<sub>3</sub>), 0.08 (s, 18H, *H*<sub>1</sub>), -0.01 (s, 3H, *H*<sub>2</sub>).

#### 1,1,1,3,5,5,5-heptamethyl-3-dodecyltrisiloxane (3d)<sup>1</sup>



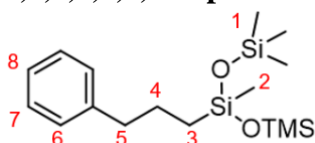
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.31-1.22 (m, 12H, *H*<sub>4</sub>-*H*<sub>13</sub>), 0.88 (t, *J* = 6.7 Hz, 3H, *H*<sub>14</sub>), 0.50-0.39 (t, 2H, *H*<sub>3</sub>), 0.09 (s, 18H, *H*<sub>1</sub>), -0.01 (s, 3H, *H*<sub>2</sub>).

### 1,1,1,3,5,5,5-heptamethyl-3-phenethyltrisiloxane (3e)<sup>1</sup>



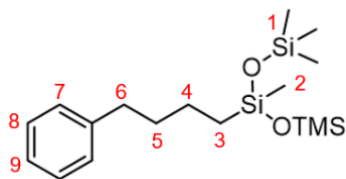
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.27 (m, 2H, *H*6), 7.17 (m, 3H, *H*5+*H*7), 2.64 (m, 2H, *H*4), 0.83 (m, 2H, *H*3), 0.11 (s, 18H, *H*1), 0.02 (s, 3H, *H*2).

### 1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane (3f)<sup>1</sup>



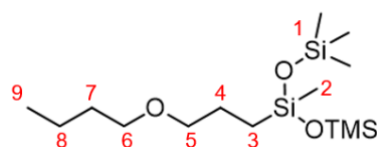
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.26 (m, 2H, *H*7), 7.19 (m, 3H, *H*6+*H*8), 2.62 (t, *J* = 7.7 Hz, 2H, *H*5), 1.65 (m, 2H, *H*4), 0.52 (m, 2H, *H*3), 0.09 (s, 18H, *H*1), -0.01 (s, 3H, *H*2).

### 1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane (3g)<sup>1</sup>



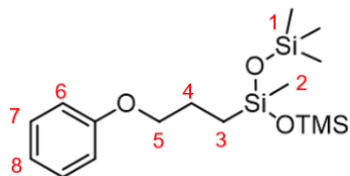
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.26 (m, 2H, *H*8), 7.17 (m, 3H, *H*7+*H*9), 2.60 (t, *J* = 7.5 Hz, 2H, *H*5), 1.62 (m, 2H, *H*5), 1.36 (m, 2H, *H*4), 0.49 (m, 2H, *H*3), 0.07 (s, 18H, *H*1), -0.01 (s, 3H, *H*2).

### 1,1,1,3,5,5,5-heptamethyl-3-(3-butoxypropyl)trisiloxane (3h)<sup>1</sup>



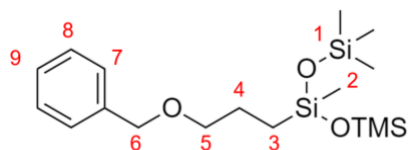
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.38 (t, *J* = 14.2, 6.8 Hz, 4H, *H*5+*H*6), 1.57 (m, 4H, *H*4+*H*7), 1.36 (m, 2H, *H*8), 0.92 (t, *J* = 7.0 Hz, 3H, *H*8), 0.45 (m, 2H, *H*3), 0.09 (s, 18H, *H*1), -0.01 (s, 3H, *H*2).

**1,1,1,3,5,5,5-heptomethyl-3-(3-(phenyloxy)propyl)trisiloxane (3i)<sup>1</sup>**



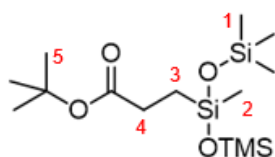
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.26 (m, 2H, *H*7), 6.92 (m, 3H, *H*6+*H*8), 3.92 (t, *J* = 6.9 Hz, 2H, *H*5), 1.82 (m, 2H, *H*4), 0.57 (m, 2H, *H*3), 0.11 (s, 18H, *H*1), 0.05 (s, 3H, *H*2).

**1,1,1,3,5,5,5-heptomethyl-3-(3-(benzyloxy)propyl)trisiloxane (3j)<sup>1</sup>**



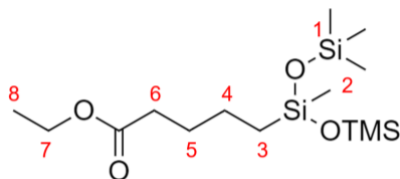
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.26 (m, 2H, *H*7), 6.92 (m, 3H, *H*6+*H*8), 3.92 (t, *J* = 6.9 Hz, 2H, *H*5), 1.82 (m, 2H, *H*4), 0.57 (m, 2H, *H*3), 0.11 (s, 18H, *H*1), 0.05 (s, 3H, *H*2).

**Tert-butyl 3-(1,1,1,3,5,5,5-heptomethyltrisiloxan-3-yl)propanoate (3k)**



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.17 (t, *J* = 6.9 Hz, 2H, *H*4), 1.45 (s, 9H, *H*5), 0.74 (t, *J* = 6.9 Hz, 2H, *H*3), 0.09 (s, 18H, *H*1), 0.02 (s, 3H, *H*2).

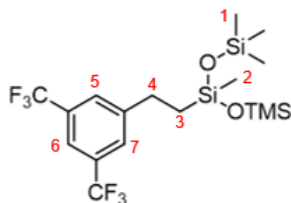
**Ethyl 5-(1,1,1,3,5,5,5-heptomethyltrisiloxan-3-yl)-pentanoate (3l)<sup>1</sup>**



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.13 (q, 2H, *H*8), 2.29 (t, *J* = 7.0 Hz, 2H, *H*6), 1.64 (m, 2H, *H*5), 1.34 (m, 2H, *H*4), 1.26 (t, *J* = 7.0 Hz, 3H, *H*9), 0.46 (m, 2H, *H*3), 0.08 (s, 18H, *H*1), -0.01 (s, 3H, *H*2).

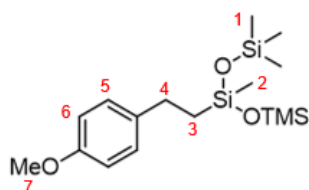


### 3,5-bis(trifluoromethyl)phenethyl-1,1,1,3,5,5,5-heptamethyltrisiloxane (3m)



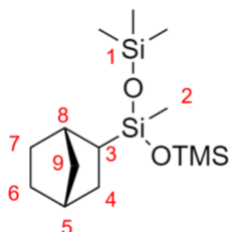
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.98 (s, 2H,  $H5+H7$ ), 7.88 (s, 1H,  $H6$ ), 2.61 (m, 2H,  $H4$ ), 0.82 (m, 2H,  $H3$ ), 0.11 (s, 18H,  $H1$ ), 0.03 (s, 3H,  $H2$ ).

### 3-(4-Methoxyphenethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (3n)<sup>3</sup>



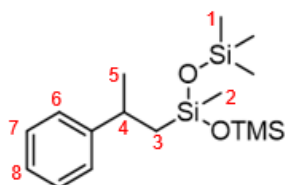
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.12 (d,  $J$  = 8.6 Hz, 2H,  $H5$ ), 6.83 (d,  $J$  = 8.6 Hz, 2H,  $H6$ ), 3.79 (s, 3H,  $H7$ ), 2.60 (m, 2H,  $H4$ ), 0.80 (m, 2H,  $H3$ ), 0.11 (s, 18H,  $H1$ ), 0.03 (s, 3H,  $H2$ ).

### 1-(bicyclo[2.2.1]heptan-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (3o)<sup>4</sup>



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.20 (br. s, 2H), 1.55-1.48 (m, 2H), 1.47-1.39 (m, 1H), 1.34-1.28 (m, 2H), 1.22-1.17 (m, 2H), 1.08 (m, 1H), 0.51-0.40 (m, 1H,  $H5_{\text{endo}}$ ), 0.09 (s, 18H,  $H1$ ), -0.04 (s, 3H,  $H2$ ).

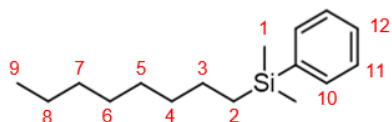
### 1,1,1,3,5,5,5-Heptamethyl-3-(2-phenylpropyl)trisiloxane (3p)<sup>5</sup>



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.27 (t,  $J$  = 6.8 Hz, 2H,  $H7$ ), 7.21 (d,  $J$  = 6.8 Hz, 2H,  $H6$ ), 7.16 (t,  $J$  = 6.8 Hz, 1H,  $H8$ ), 2.92 (m, 1H,  $H4$ ), 1.28 (d,  $J$  = 6.8 Hz, 3H,  $H5$ ), 0.87 (m, 2H,  $H3$ ), 0.08 (s, 18H,  $H1$ ), -0.12 (s, 3H,  $H2$ ).

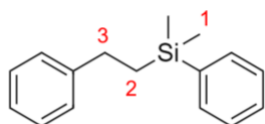
## Alkene functionalization with silanes

### Dimethyl(phenethyl)octylsilane (4a)<sup>6</sup>



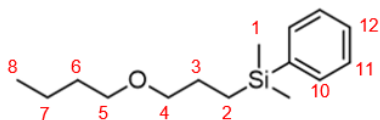
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.51 (m, 2H, *H*11), 7.35 (m, 3H, *H*10+*H*12), 1.22 (m, 12H, *H*3-*H*8), 0.87 (t, *J* = 6.8 Hz, 3H, *H*9), 0.74 (m, 2H, *H*2), 0.25 (s, 6H, *H*1).

### Dimethyl(phenethyl)phenylsilane (4e)<sup>7</sup>



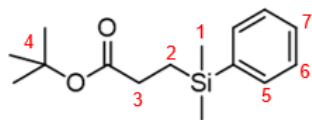
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.58 (m, 2H, *H*-Ar), 7.41 (m, 3H, *H*-Ar), 7.31 (m, 2H, *H*-Ar), 7.20 (m, 3H, *H*-Ar), 2.69 (m, 2H, *H*3), 1.18 (m, 2H, *H*2), 0.34 (s, 6H, *H*1).

### 3-(n-Butoxy)-1-(dimethyl(phenyl)silyl)-1-propene (4h)



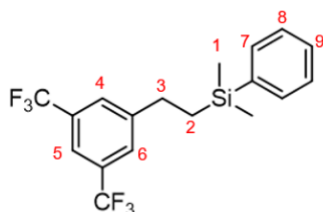
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55 (m, 2H, *H*11), 7.37 (m, 3H, *H*10+*H*12), 3.36 (m, 4H, *H*4+*H*5), 1.58 (m, 4H, *H*3+*H*6), 1.36 (m, 2H, *H*7), 0.93 (t, *J* = 7.0 Hz, 3H, *H*8), 0.75 (m, 2H, *H*2), 0.29 (s, 6H, *H*1).

### Tert-butyl 3-(dimethyl(phenyl)silyl)propanoate (4k)<sup>8</sup>



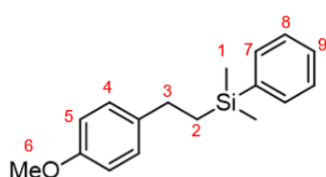
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.51 (m, 2H, *H*6), 7.37 (m, 3H, *H*5+*H*7), 2.19 (m, 2H, *H*3), 1.43 (s, 9H, *H*4), 1.05 (m, 2H, *H*2), 0.29 (s, 6H, *H*1).

**(1,3-bis(trifluoromethyl)phenethyl)dimethyl(phenyl)silane (4m)**



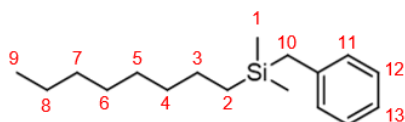
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.68 (s, 1H,  $H_5$ ), 7.61 (s, 2H,  $H_4+H_6$ ), 7.53 (m, 2H,  $H_8$ ), 7.40 (m, 3H,  $H_7+H_9$ ), 2.76 (m, 2H,  $H_3$ ), 1.17 (m, 2H,  $H_2$ ), 0.32 (s, 6H,  $H_1$ ).

**(4-methoxyphenethyl)dimethyl(phenyl)silane (4n)<sup>8</sup>**



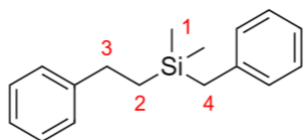
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.58 (m, 2H,  $H_8$ ), 7.40 (m, 3H,  $H_7+H_9$ ), 7.10 (m, 2H,  $H_4$ ), 6.82 (m, 2H,  $H_5$ ), 3.76 (s, 3H,  $H_6$ ), 2.60 (m, 2H,  $H_3$ ), 1.09 (m, 2H,  $H_2$ ), 0.30 (s, 6H,  $H_1$ ).

**Octyldimethyl(benzyl)silane (5a)<sup>9</sup>**



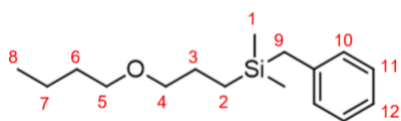
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.21 (m, 2H,  $H_{12}$ ), 7.07 (m, 1H,  $H_{13}$ ), 6.98 (m, 2H,  $H_{11}$ ), 2.05 (m, 2H,  $H_{10}$ ), 1.27 (brs, 12H,  $H_3-H_8$ ), 0.91 (m, 3H,  $H_9$ ), 0.41 (m, 2H,  $H_2$ ), -0.03 (s, 6H,  $H_1$ ).

**Benzyl dimethyl(benzyl)silane (5e)<sup>7</sup>**



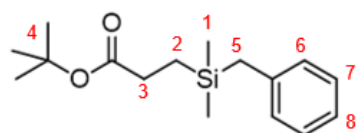
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 (m, 7H,  $H\text{-Ar}$ ), 7.11 (m, 1H,  $H\text{-Ar}$ ), 7.02 (m, 2H,  $H\text{-Ar}$ ), 2.62 (m, 2H,  $H_3$ ), 2.13 (s, 2H,  $H_4$ ), 0.91 (m, 2H,  $H_2$ ), 0.02 (s, 6H,  $H_1$ ).

### 3-(n-Butoxy)-1-(dimethyl(benzyl)silyl)-1-propene (5h)



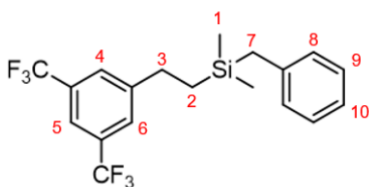
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22 (m, 2H,  $H_{11}$ ), 7.07 (m, 3H,  $H_{10}+H_{12}$ ), 3.38 (m, 4H,  $H_4+H_5$ ), 2.08 (m, 2H,  $H_9$ ), 1.56 (m, 4H,  $H_3+H_6$ ), 1.34 (m, 2H,  $H_7$ ), 0.93 (t,  $J$  = 7.2 Hz, 3H,  $H_8$ ), 0.50 (m, 2H,  $H_2$ ), 0.03 (s, 6H,  $H_1$ ).

### Tert-butyl 3-(dimethyl(benzyl)silyl)propanoate (5k)



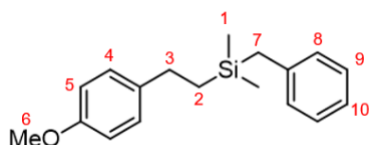
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.20 (m, 2H,  $H_7$ ), 7.07 (m, 3H,  $H_6+H_8$ ), 2.19 (m, 2H,  $H_3$ ), 2.02 (m, 2H,  $H_5$ ), 1.44 (s, 9H,  $H_4$ ), 0.86 (m, 2H,  $H_2$ ), 0.09 (s, 6H,  $H_1$ ).

### Benzyl(3,5-bis(trifluoromethyl)phenethyl)dimethylsilane (5m)<sup>7</sup>



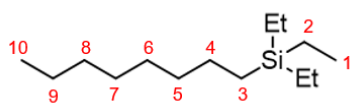
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.67 (s, 1H,  $H_5$ ), 7.57 (s, 2H,  $H_4+H_6$ ), 7.23 (t,  $J$  = 7.0 Hz, 2H,  $H_9$ ), 7.10 (t,  $J$  = 7.4 Hz, 1H,  $H_{10}$ ), 7.02 (d,  $J$  = 7.3 Hz, 2H,  $H_8$ ), 2.65 (m, 2H,  $H_3$ ), 2.15 (s, 2H,  $H_7$ ), 0.91 (m, 2H,  $H_2$ ), 0.05 (s, 6H,  $H_1$ ).

### Benzyl(4-methoxyphenethyl)dimethylsilane (5n)<sup>7</sup>



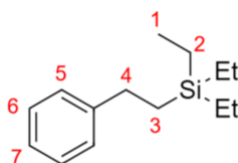
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22 (t,  $J$  = 7.5 Hz, 2H,  $H_9$ ), 7.09 (m, 3H,  $H_8+H_{10}$ ), 7.01 (d,  $J$  = 7.7 Hz, 2H,  $H_4$ ), 6.82 (d,  $J$  = 8.4 Hz, 2H,  $H_5$ ), 3.79 (s, 3H,  $H_6$ ), 2.51 (m, 2H,  $H_3$ ), 2.11 (s, 2H,  $H_7$ ), 0.89 (m, 2H,  $H_2$ ), -0.01 (s, 6H,  $H_1$ ).

### Octyltriethylsilane (6a)<sup>10</sup>



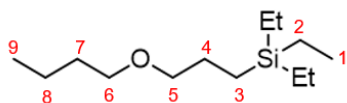
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.26 (brs, 12H, *H4-H9*), 0.91 (m, 12H, *H1+H10*), 0.63 (m, 8H, *H2+H3*).

### Phenethyltriethylsilane (6e)<sup>11</sup>



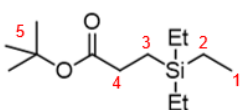
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.30 (m, 2H, *H6*), 7.19 (m, 3H, *H5+H7*), 2.64 (m, 2H, *H4*), 0.99 (m, 9H, *H1*), 0.91 (m, 2H, *H3*), 0.59 (m, 6H, *H2*).

### (3-butoxypropyl)triethylsilane (6h)<sup>12</sup>



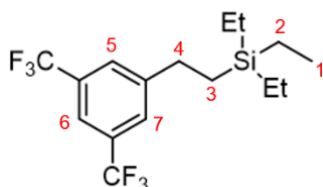
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.37 (m, 4H, *H5+H6*), 1.54 (m, 6H, *H4+H7+H8*), 1.34 (m, 2H, *H3*), 0.92 (m, 12H, *H1+H9*), 0.50 (m, 6H, *H2*).

### Tert-butyl 3-(triethyl)propanoate (6k)



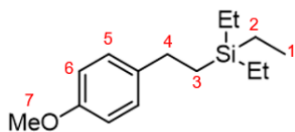
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.17 (m, 2H, *H4*), 1.44 (s, 9H, *H5*), 0.93 (t, *J* = 7.7 Hz, 9H, *H1*), 0.81 (m, 2H, *H3*), 0.51 (dd, *J* = 15.5 Hz, 7.7 Hz, 6H, *H2*).

### Triethyl(1,3-bis(trifluoromethyl)phenethyl)silane (6m)<sup>13</sup>



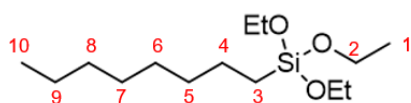
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.69 (s, 1H, *H6*), 7.65 (s, 2H, *H5+H7*), 2.75 (m, 2H, *H4*), 0.98 (t, *J* = 8.0 Hz, 9H, *H1*), 0.92 (m, 2H, *H3*), 0.59 (m, 6H, *H2*).

### Triethyl(4-methoxyphenethyl)silane (6n)<sup>14</sup>



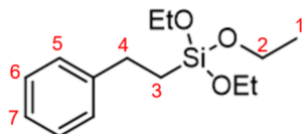
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.11 (m, 2H, *H*5), 6.83 (m, 2H, *H*6), 3.79 (s, 3H, *H*7), 2.56 (m, 2H, *H*4), 0.95 (t, *J* = 7.9 Hz, 9H, *H*1), 0.85 (m, 2H, *H*3), 0.56 (m, 6H, *H*2).

### Tri(ethoxy)octylsilane (7a)<sup>15</sup>



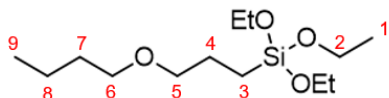
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.83 (m, 6H, *H*2), 1.25 (m, 21H, *H*1+*H*4-*H*9), 0.88 (m, 3H, *H*10), 0.63 (m, 2H, *H*3).

### Tri(ethoxy)phenylsilane (7e)<sup>16</sup>



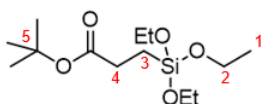
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.28 (m, 2H, *H*6), 7.22 (m, 3H, *H*5+*H*7), 3.83 (m, 6H, *H*2), 2.75 (m, 2H, *H*4), 1.24 (t, *J* = 7.0 Hz, 9H, *H*1), 1.02 (m, 2H, *H*3).

### (3-butoxypropyl)triethoxysilane (7h)<sup>17</sup>



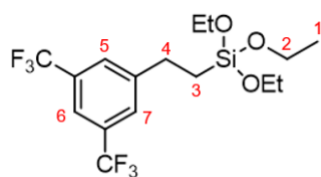
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.48 (m, 6H, *H*2), 3.36 (m, 4H, *H*5+*H*6), 1.56 (m, 4H, *H*4+*H*7), 1.34 (m, 2H, *H*8), 1.23 (m, 9H, *H*1), 0.91 (m, 3H, *H*9), 0.63 (m, 2H, *H*3).

### Tert-butyl 3-(triethoxysilyl)propanoate (7k)<sup>18</sup>



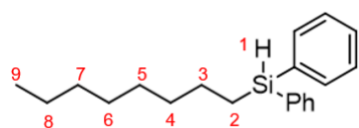
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.49 (m, 6H, *H*2), 2.17 (m, 2H, *H*4), 1.54 (m, 9H, *H*5), 1.21 (m, 9H, *H*1), 0.92 (m, 2H, *H*3).

**(1,3-bis(trifluoromethyl)phenethyl)triethoxysilane(7m)**



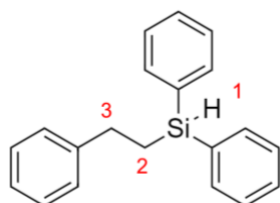
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.97$  (s, 1H,  $H_6$ ),  $7.71$  (s, 2H,  $H_5+H_7$ ),  $3.47$  (m, 6H,  $H_2$ ),  $2.78$  (m, 2H,  $H_4$ ),  $1.25$  (m, 9H,  $H_1$ ),  $0.88$  (m, 2H,  $H_3$ ).

**Octyldiphenylsilane (8a)<sup>19</sup>**



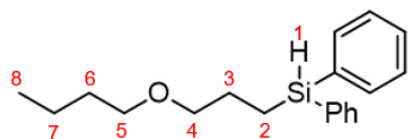
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.56$  (m, 4H,  $H\text{-Ar}$ ),  $7.39$  (m, 6H,  $H\text{-Ar}$ ),  $4.86$  (m, 1H,  $H_1$ ),  $1.48\text{-}1.16$  (m, 12H,  $H_3+H_8$ ),  $1.16$  (m, 2H,  $H_2$ ),  $0.86$  (m, 3H,  $H_9$ ).

**Phenethyldiphenylsilane (8e)<sup>20</sup>**



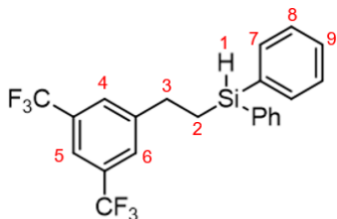
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.55$  (m, 4H,  $H\text{-Ar}$ ),  $7.34$  (m, 6H,  $H\text{-Ar}$ ),  $7.22$  (m, 2H,  $H\text{-Ar}$ ),  $7.15$  (m, 3H,  $H\text{-Ar}$ ),  $4.87$  (t,  $J = 3.6$  Hz, 1H,  $H_1$ ),  $2.74$  (m, 2H,  $H_3$ ),  $1.48$  (m, 2H,  $H_2$ ).

**(3-Butoxypropyl)diphenylsilane (8h)**



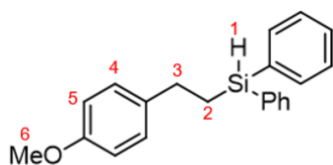
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.58$  (m, 4H,  $H\text{-Ar}$ ),  $7.37$  (m, 6H,  $H\text{-Ar}$ ),  $4.88$  (t,  $J = 3.5$  Hz, 1H,  $H_1$ ),  $3.79$  (m, 4H,  $H_4+H_5$ ),  $1.53\text{-}1.13$  (m, 8H,  $H_2+H_3+H_6+H_7$ ),  $0.96$  (t,  $J = 7.4$  Hz, 3H,  $H_8$ ).

**(1,3-bis(trifluoromethyl)phenethyl)diphenylsilane (8m)**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.82\text{-}7.41$  (s, 13H, *H-Ar*), 4.89 (t,  $J = 3.5$  Hz, 1H, *H1*), 2.88 (m, 2H, *H3*), 1.17 (m, 2H, *H2*).

**(2-(4-methoxyphenyl)ethyl)diphenylsilane (8n)<sup>21</sup>**

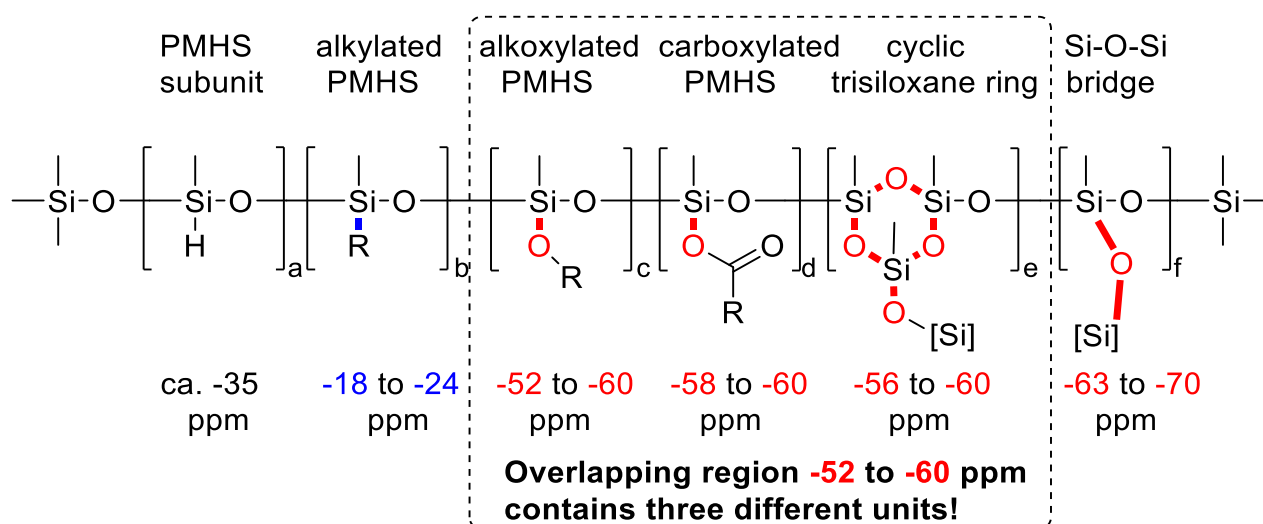


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.62$  (m, 4H, *H-Ar*), 7.45 (m, 6H, *H-Ar*), 7.08 (m, 2H, *H4*), 6.86 (m, 2H, *H5*), 4.90 (t,  $J = 3.6$  Hz, 1H, *H1*), 3.79 (s, 3H, *H6*), 2.73 (m, 2H, *H3*), 1.48 (m, 2H, *H2*).



## PMHS functionalization

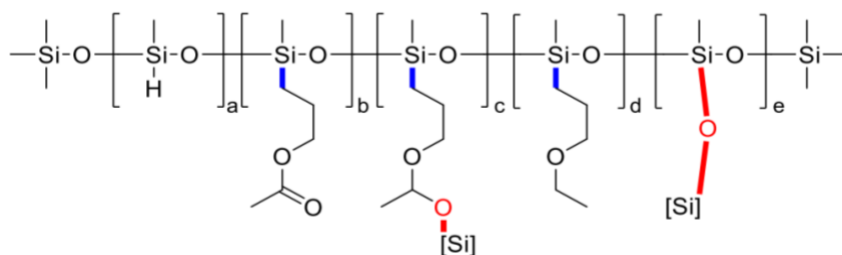
### <sup>29</sup>Si chemical shifts evidence for C=O bond activation for functionalized and cross-linked PMHS



**Scheme S1.** Typical <sup>29</sup>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 <sup>29</sup>Si chemical shifts: Si-H,<sup>22</sup> Si-R (R= Me in PMHS oils having varying length),<sup>23</sup> Si-OR (R= linear C1-C10 alkyl, cyclic alkyl, functionalized alkyl and phenyl),<sup>24,25</sup> Si-OOCR (only formic, acetic, benzoic and methacrylic acid derivatives have been taken into account),<sup>26,27</sup> Si-O-Si bridge,<sup>28,29,30</sup> and cyclic trisiloxane ring.<sup>8,10</sup>

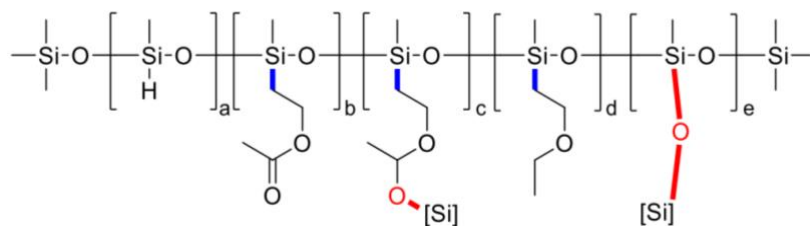
All polysiloxanes are already described in the literature.<sup>31</sup>

### **Functionalization of PMHS with allyl acetate (4c)**



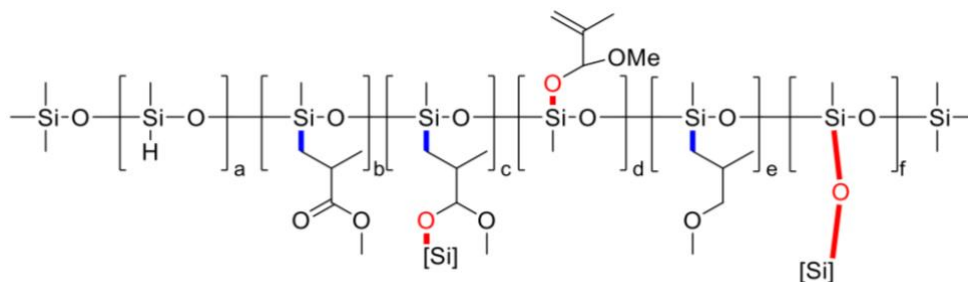
<sup>29</sup>Si CPMAS SSNMR (60 MHz):  $\delta = -20.99$  (Si-R),  $-36.30$  (Si-H),  $-57.35$  (Si-O),  $-61.50$  (Si-O),  $-66.78$  (Si-O-Si bridge).

### Functionalization of PMHS with vinyl acetate (4d)



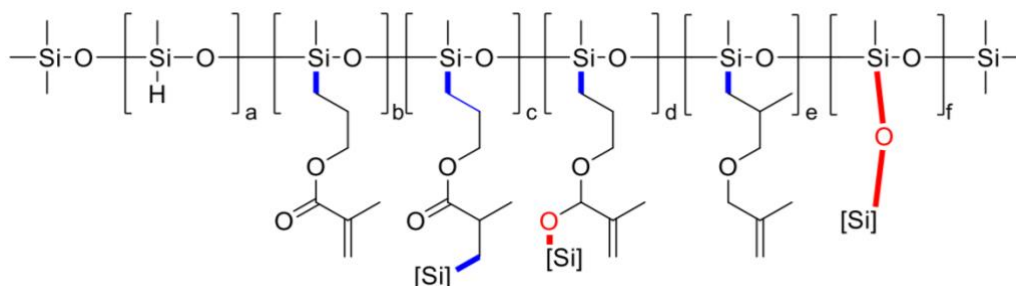
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = 8.21$  (Si-PMHS),  $-4.77$  (Si-PMHS),  $-23.6$  (Si-R),  $-36.4$  (Si-H),  $-59.30$  (Si-O),  $-66.26$  (Si-O-Si bridge).

### Functionalization of PMHS with methyl methacrylate (4e)



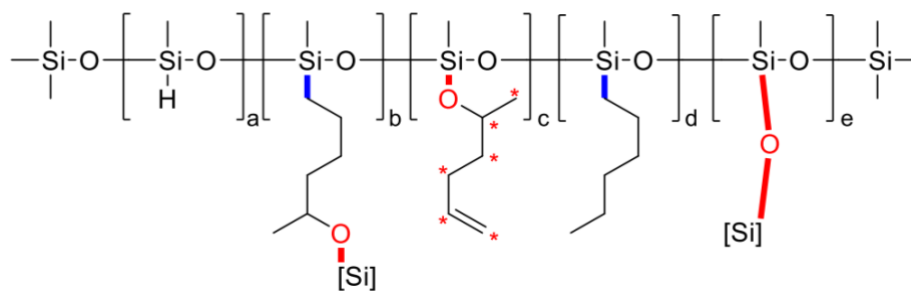
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = -22.15$  (Si-R),  $-35.85$  (Si-H),  $-57.09$  (Si-O),  $-66.8$  (Si-O-Si bridge).

### Functionalization of PMHS with allyl methacrylate (4f)



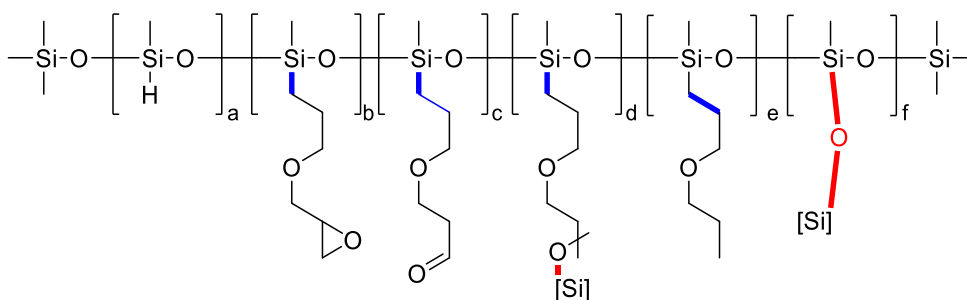
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = 9.92$  (Si-PMHS),  $-20.68$  (Si-R),  $-35.12$  (Si-H),  $-57.63$  (Si-O),  $-65.96$  (Si-O-Si bridge).

### Functionalization of PMHS with 5-hexen-2-one (4g)



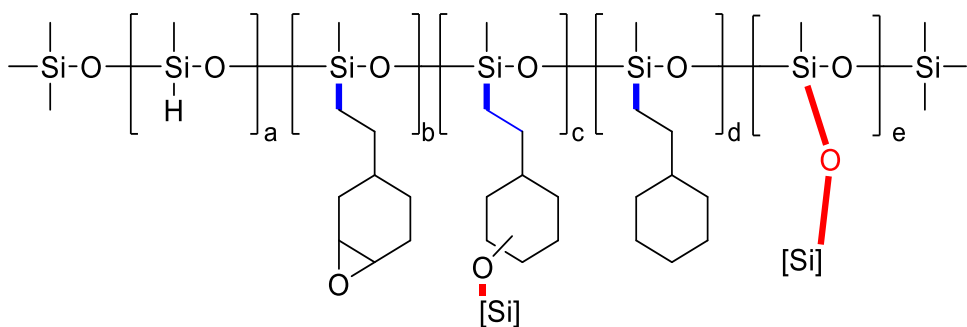
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = -22.02$  (Si-R),  $-36.82$  (Si-H),  $-60.81$  (Si-O).

### Functionalization of PMHS with allyl glycidyl ether (4h)



$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = -17.97$  (Si-R),  $-21.24$  (Si-R),  $-25.14$  (Si-R),  $-36.06$  (Si-H),  $-49.31$  (Si-O),  $-58.07$  (Si-O)  $-66.36$  (Si-O-Si bridge).

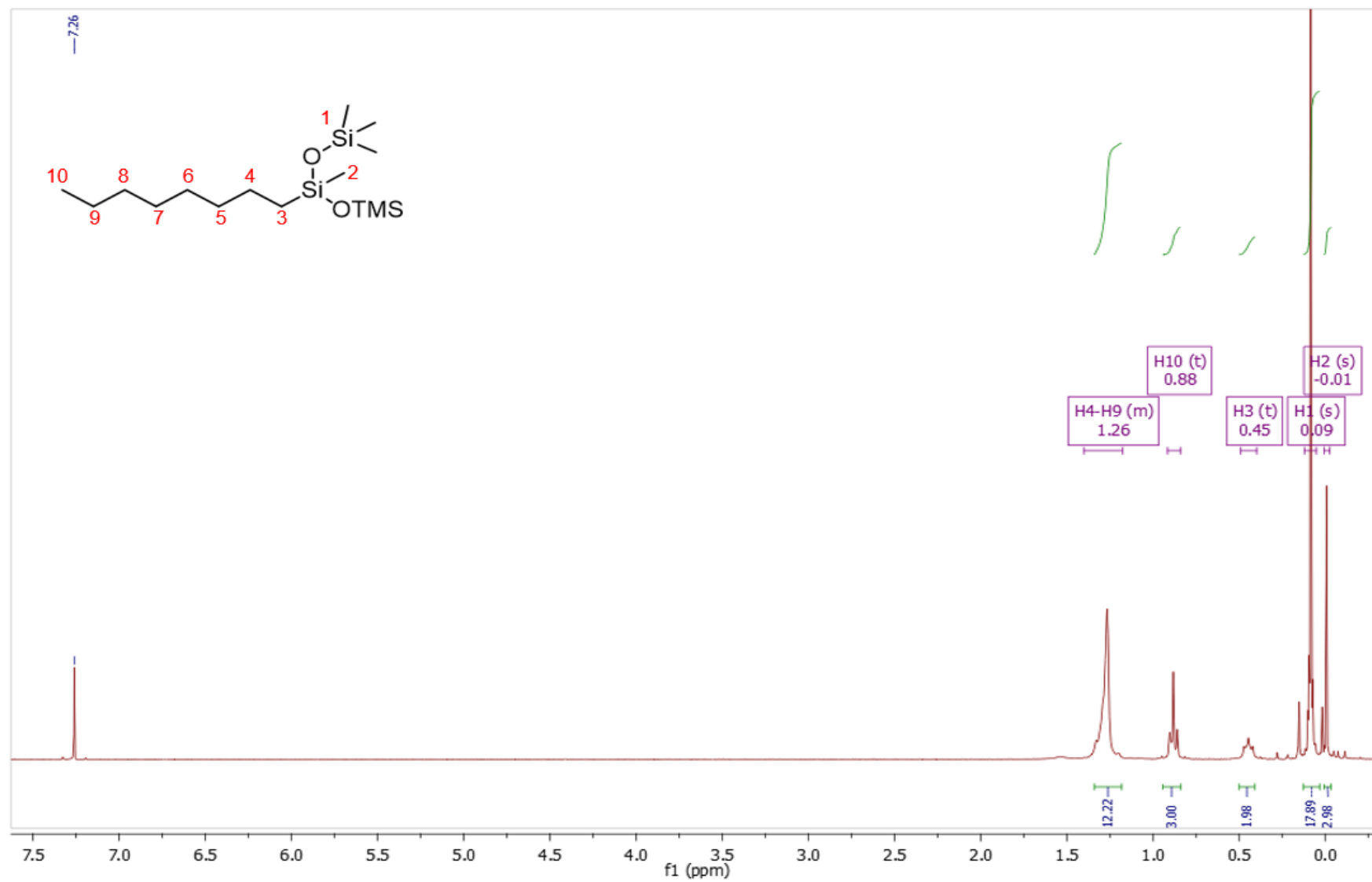
### Functionalization of PMHS with 1,2-epoxy-4-vinylcyclohexane (4i)



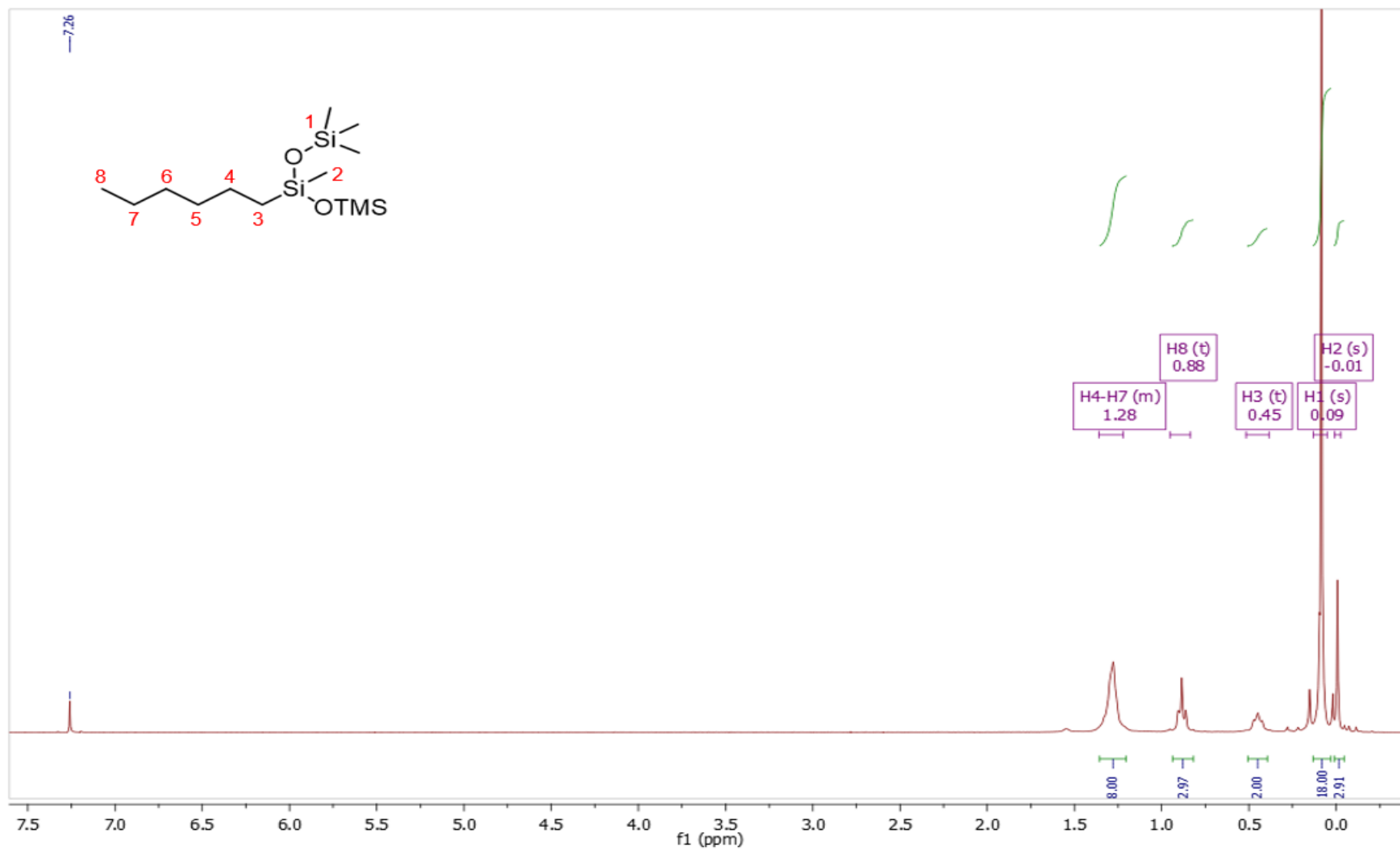
$^{29}\text{Si}$  CPMAS SSNMR (60 MHz):  $\delta = -9.69$  (Si-R),  $-20.08$  (Si-R),  $-35.03$  (Si-H),  $-58.79$  (Si-O),  $-65.26$  (Si-O-Si bridge).

$^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ , 25 °C) of purified hydrosilylated products

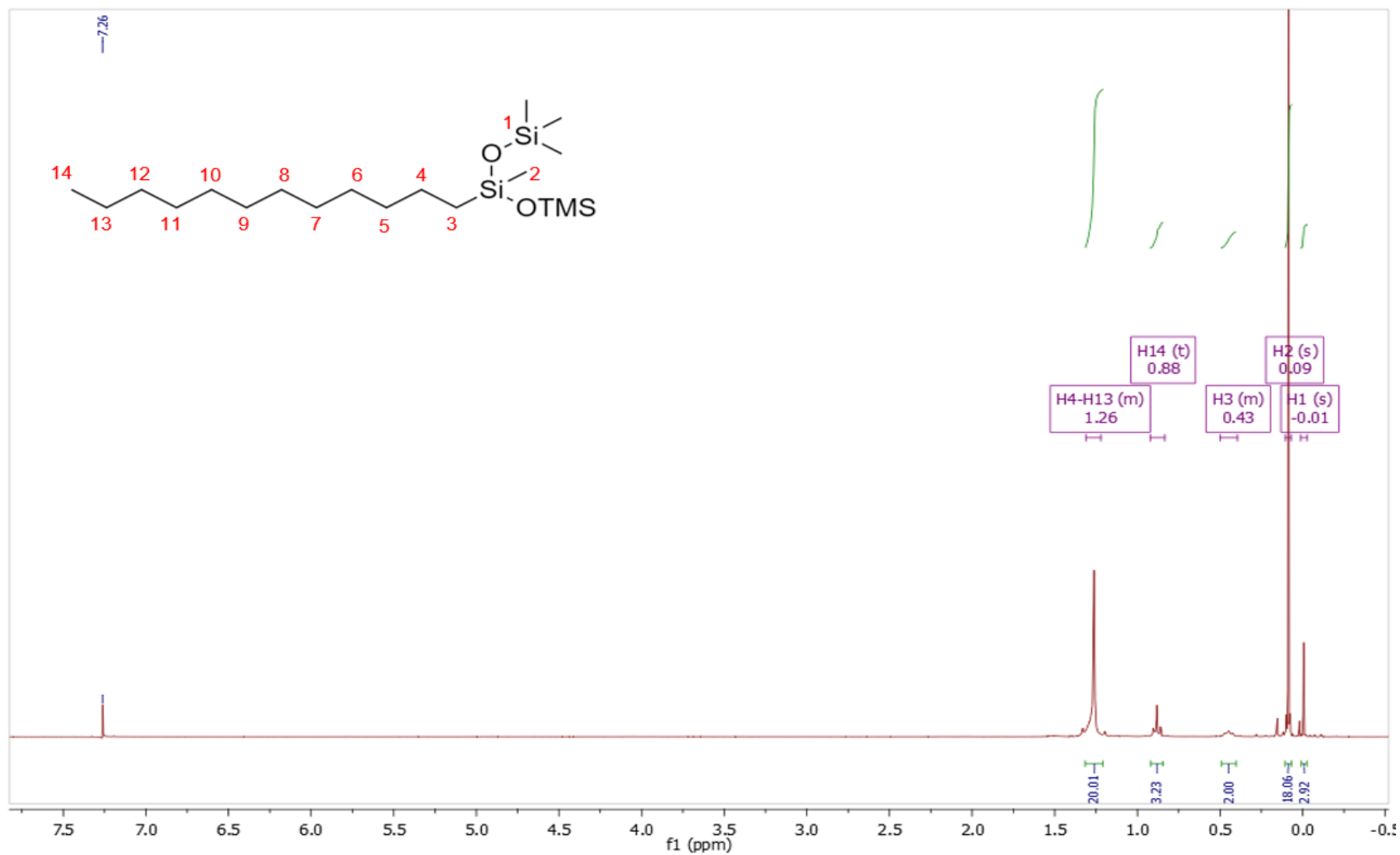
1,1,1,3,5,5,5-heptomethyl-3-octyltrisiloxane (3a)



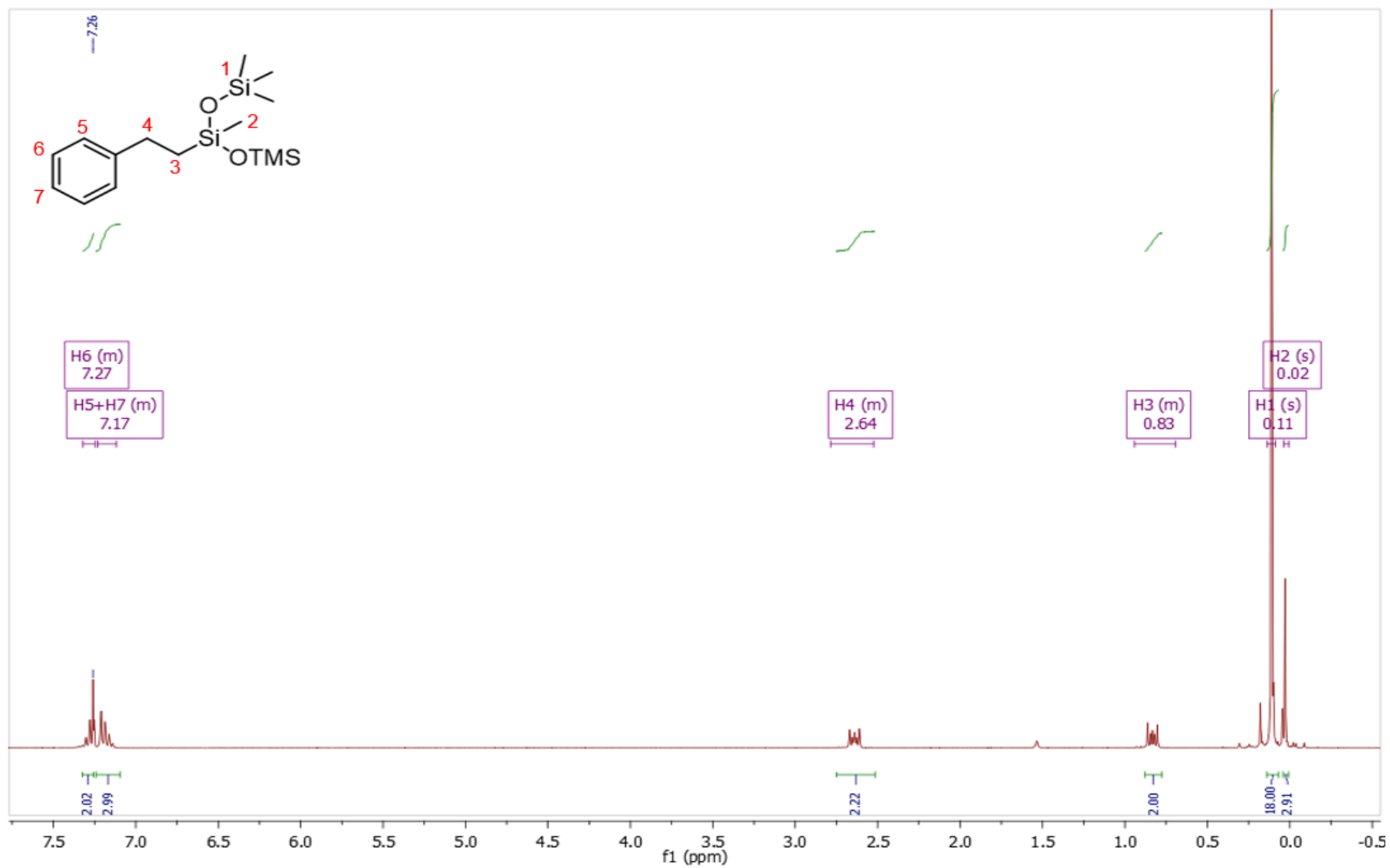
1,1,1,3,5,5,5-heptomethyl-3-hexyltrisiloxane (3b)



# 1,1,1,3,5,5,5-heptomethyl-3-dodecyltrisiloxane (3c)

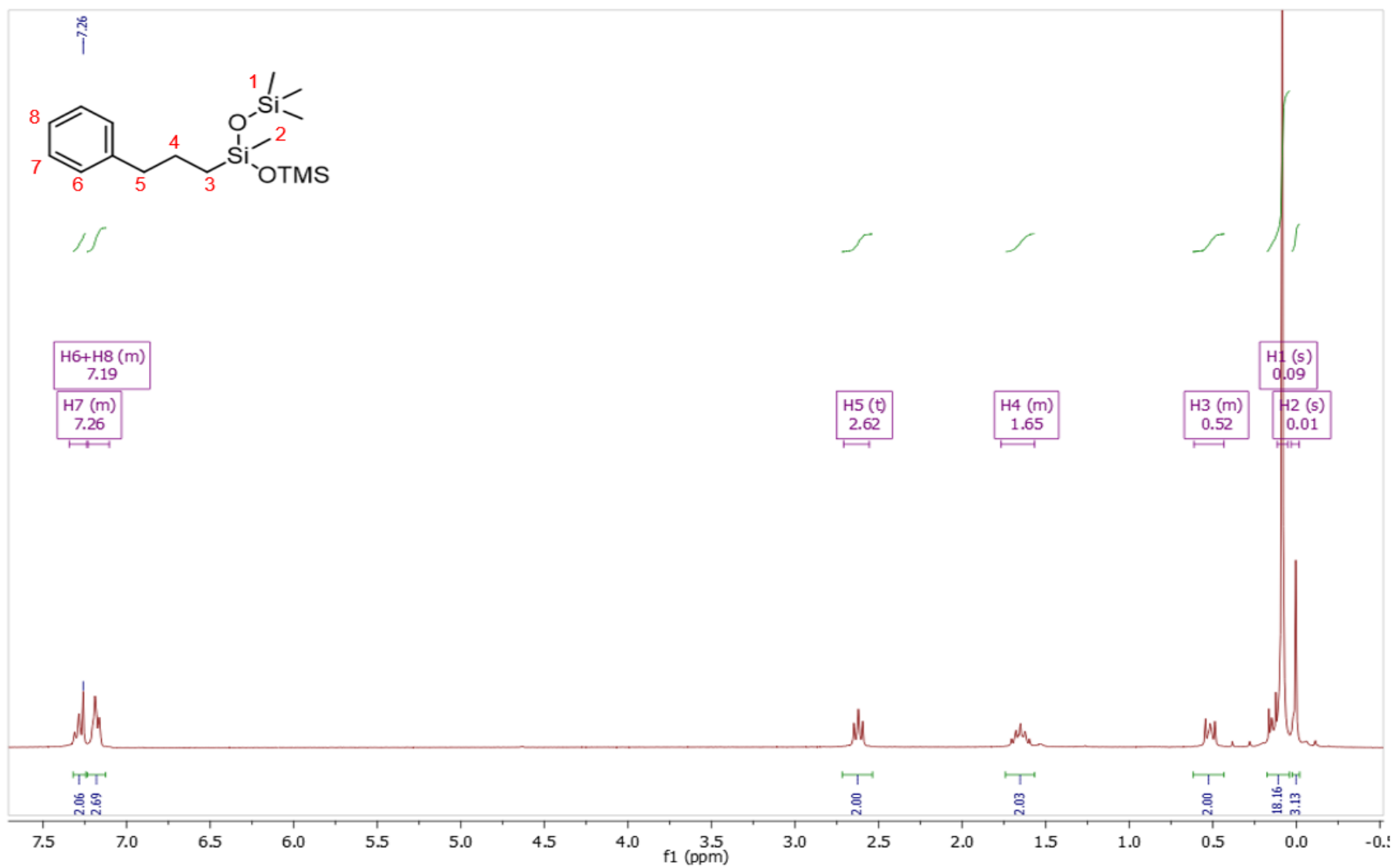


1,1,1,3,5,5,5-heptomethyl-3-phenethyltrisiloxane (3d)

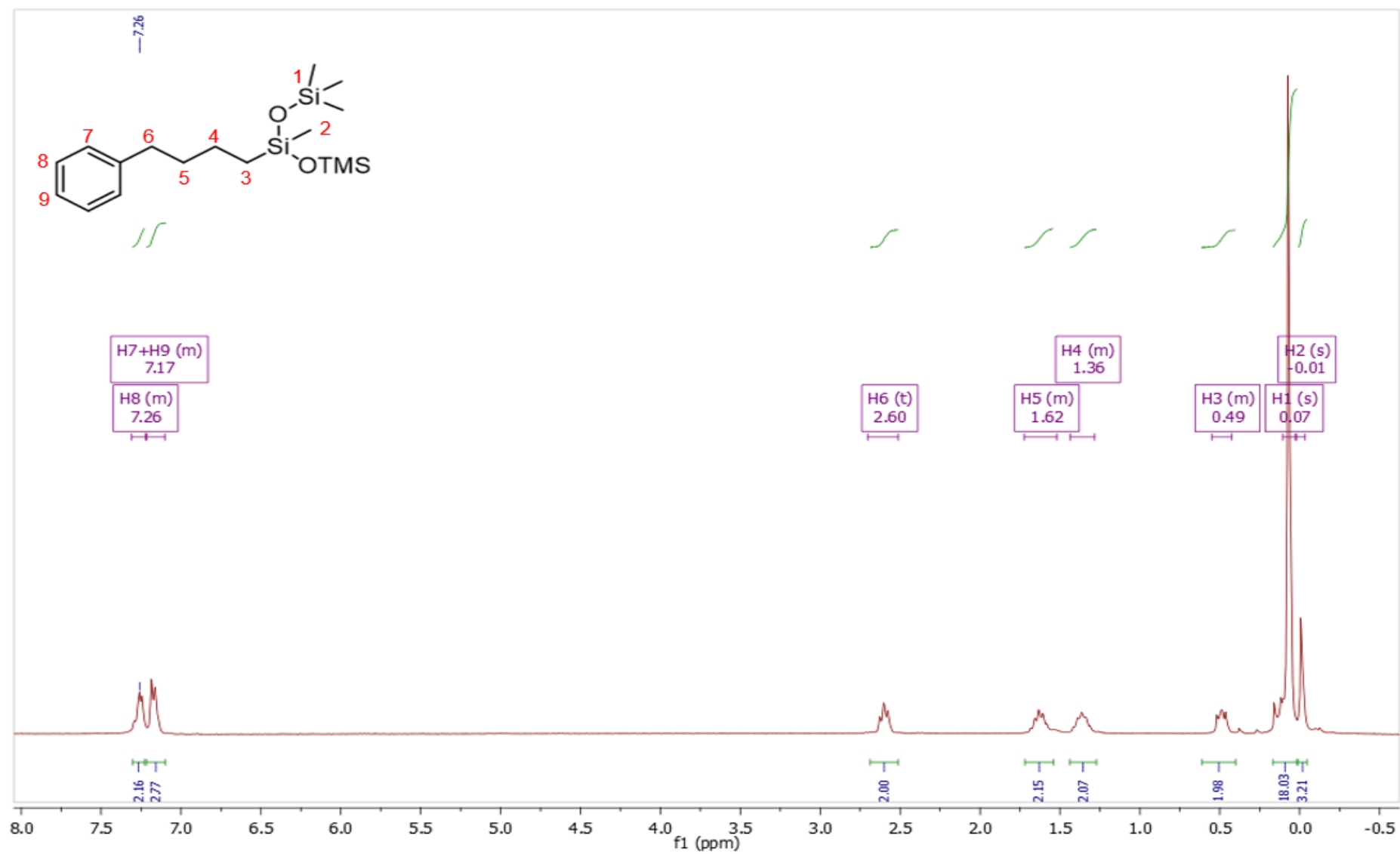




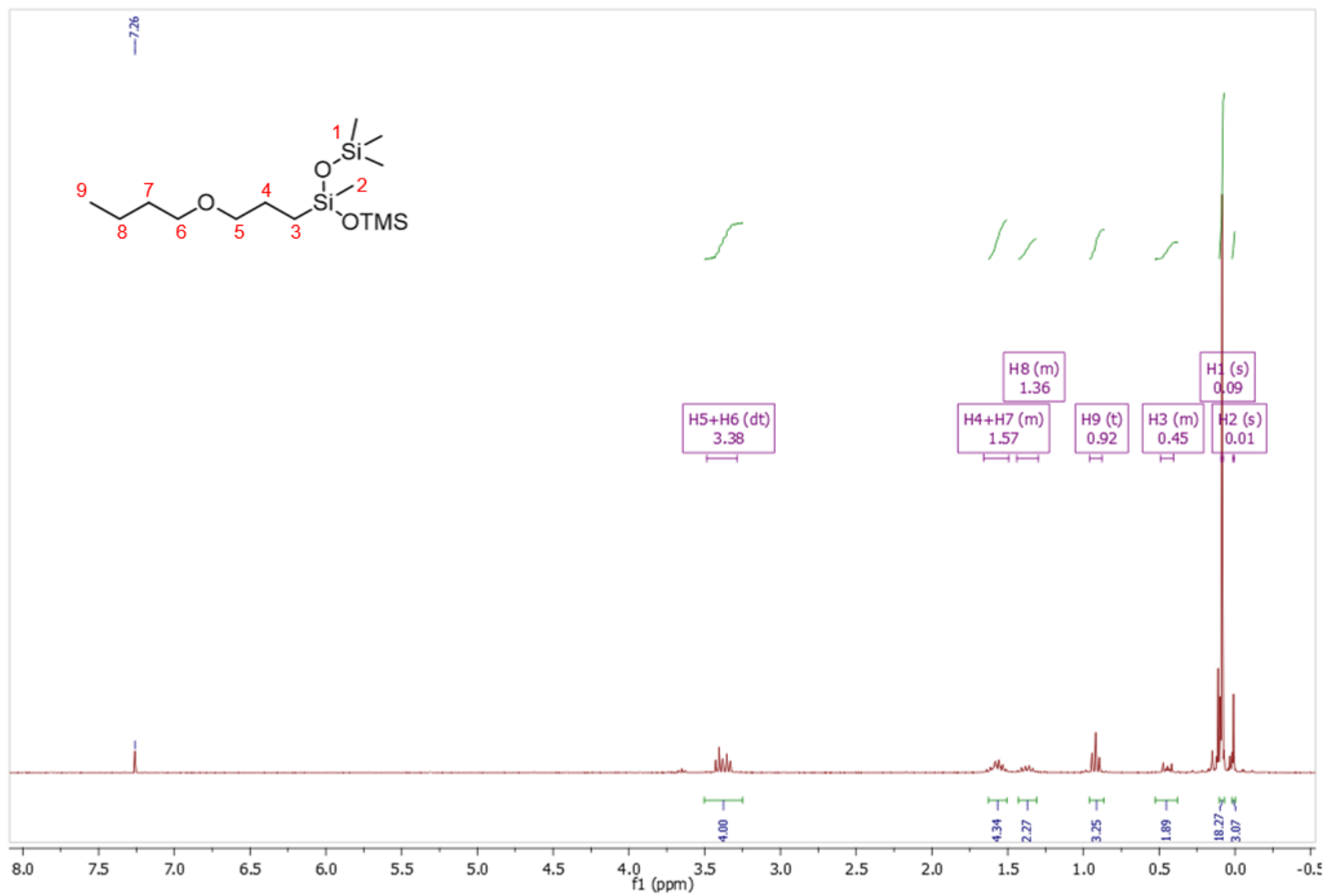
1,1,1,3,5,5,5-heptomethyl-3-(4-phenylbutyl)trisiloxane (3e)



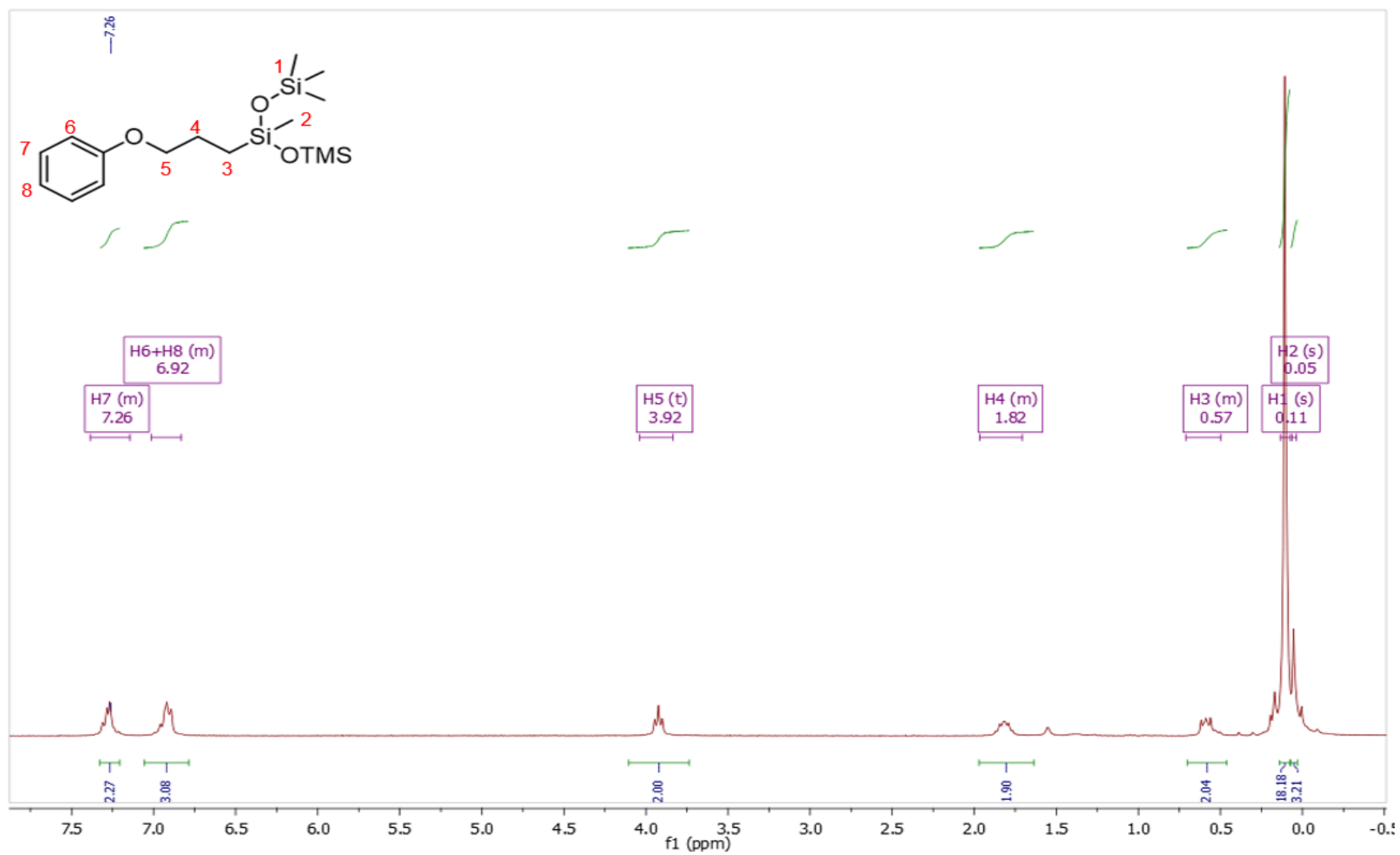
1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane (3f)



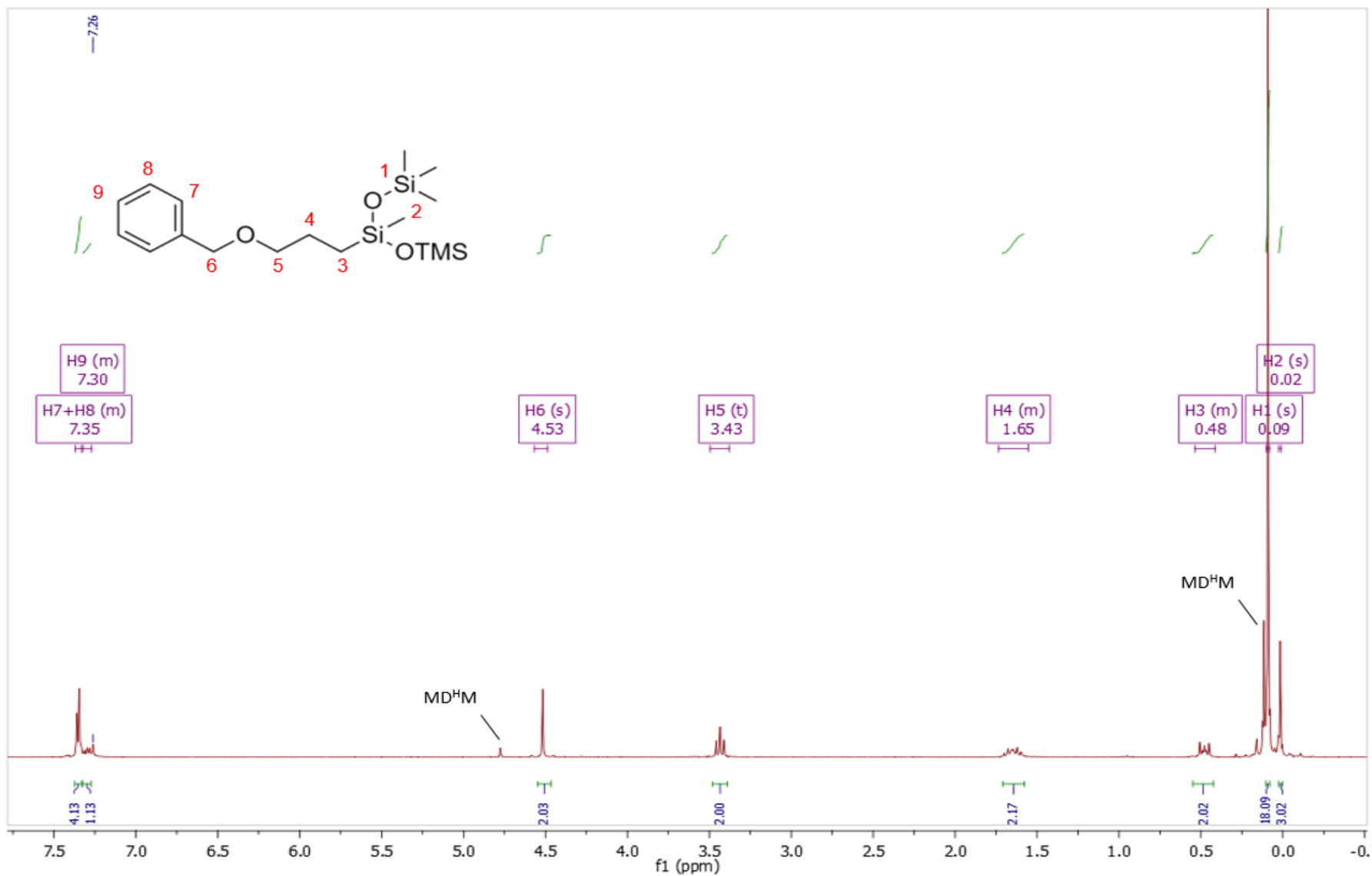
1,1,1,3,5,5,5-heptomethyl-3-(3-Butoxypropyl)trisiloxane (3g)



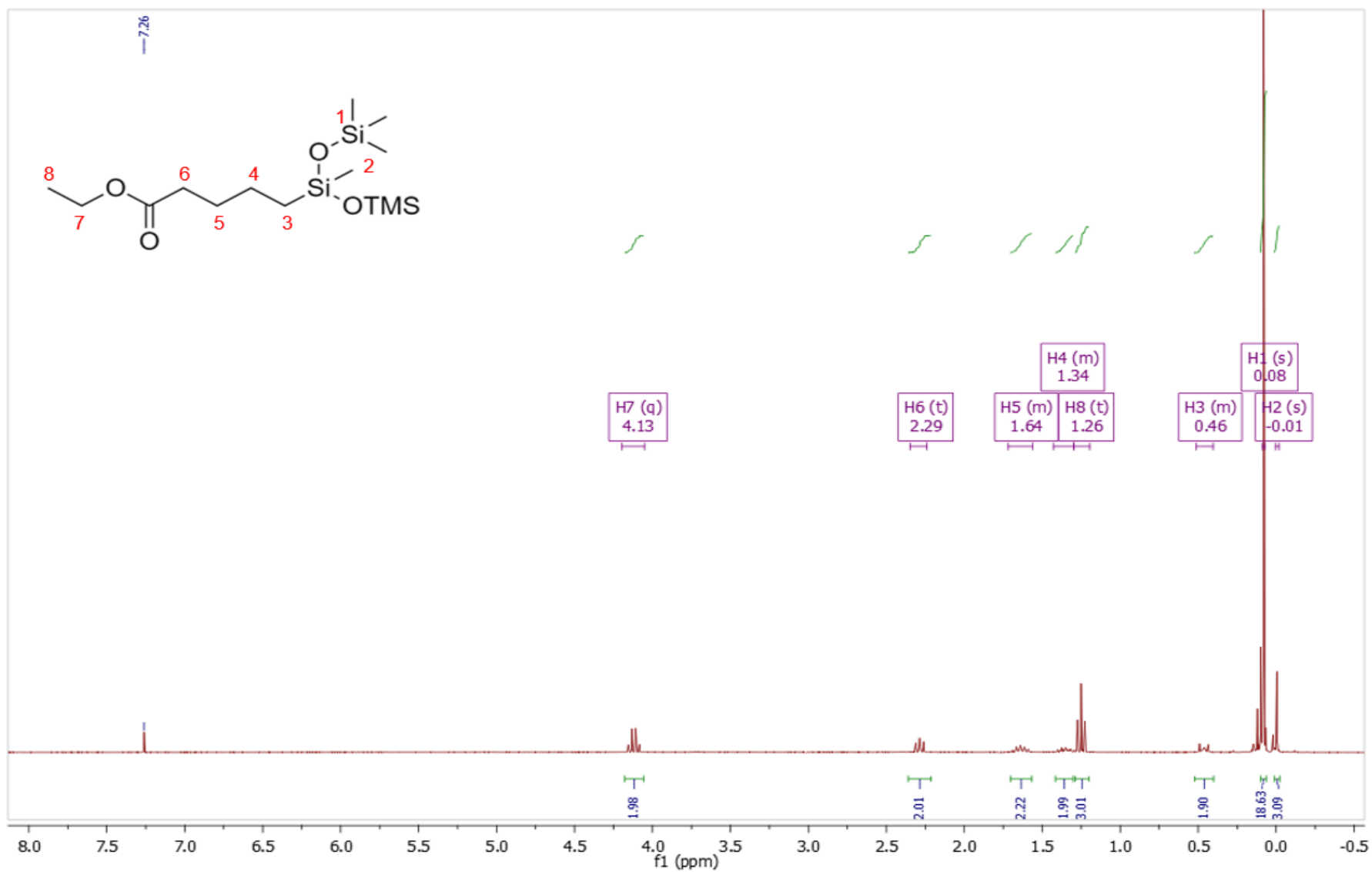
1,1,1,3,5,5,5-heptomethyl-3-(3-(phenyloxy)propyl)trisiloxane (3h)



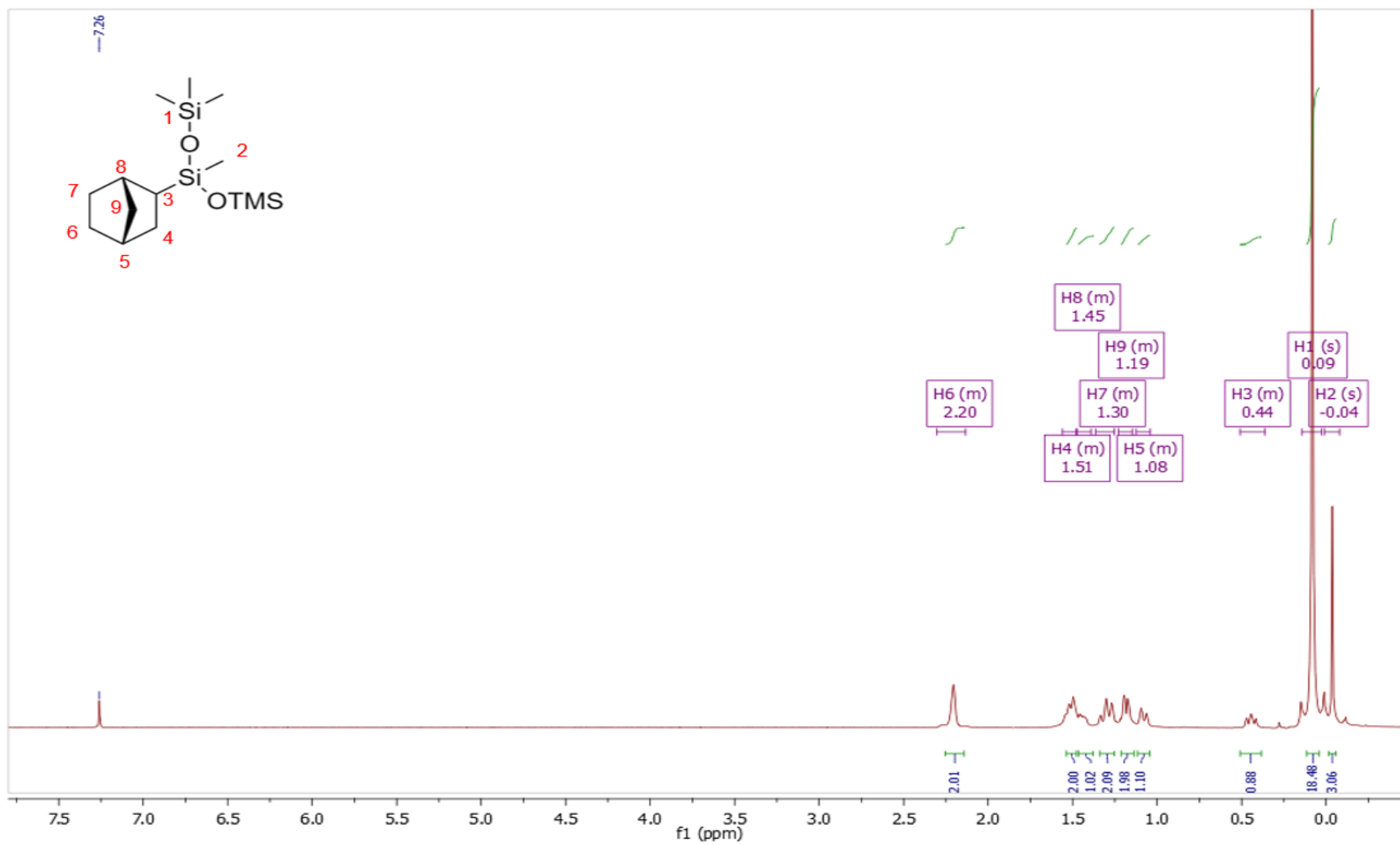
1,1,1,3,5,5,5-heptomethyl-3-(3-(benzyloxy)propyl)trisiloxane (3i)



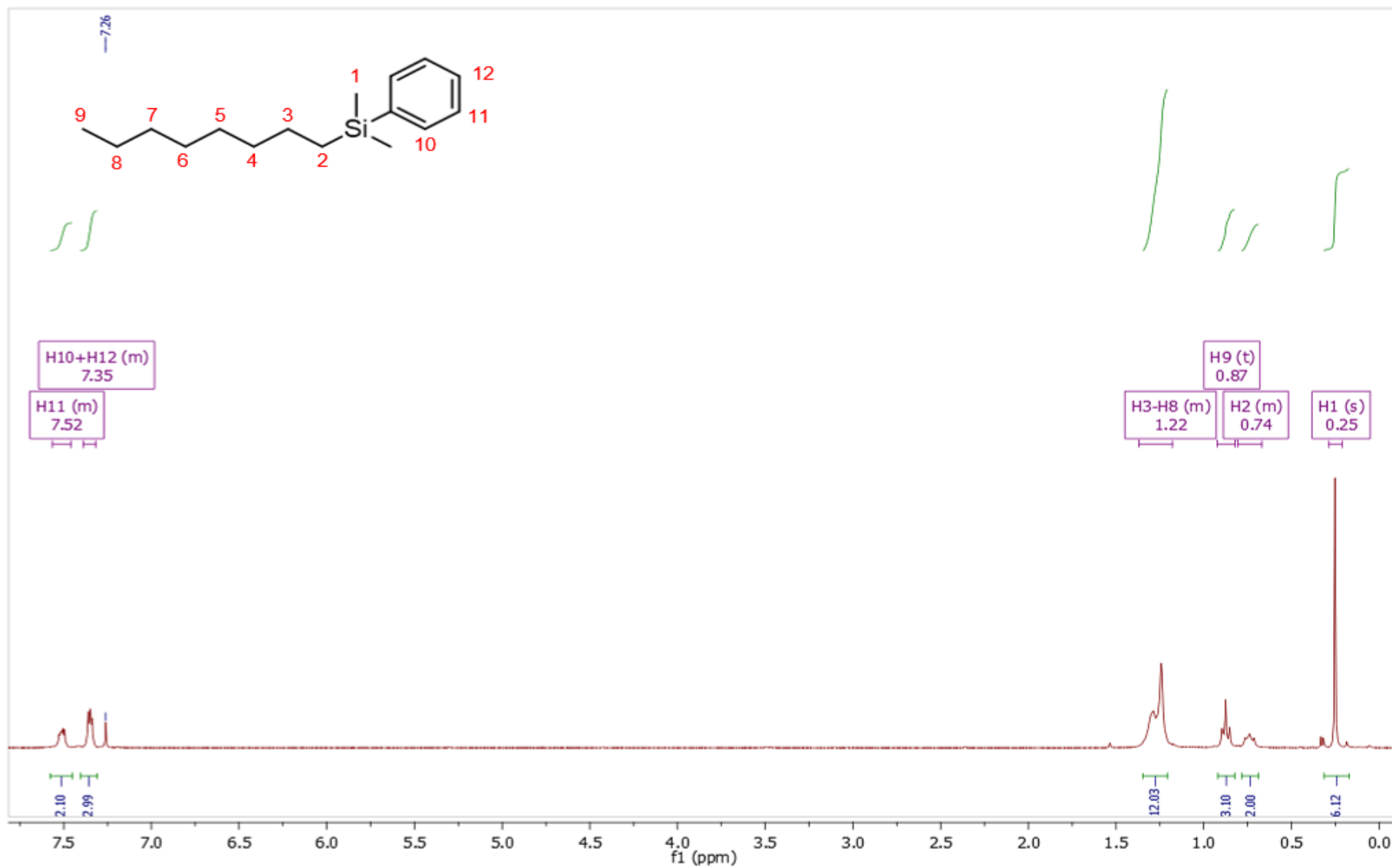
Ethyl 5-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-pentanoate (3j)



1-(bicyclo[2.2.1]heptan-2-yl)-1,1,1-3-5,5,5-heptamethyltrisiloxane (3k)

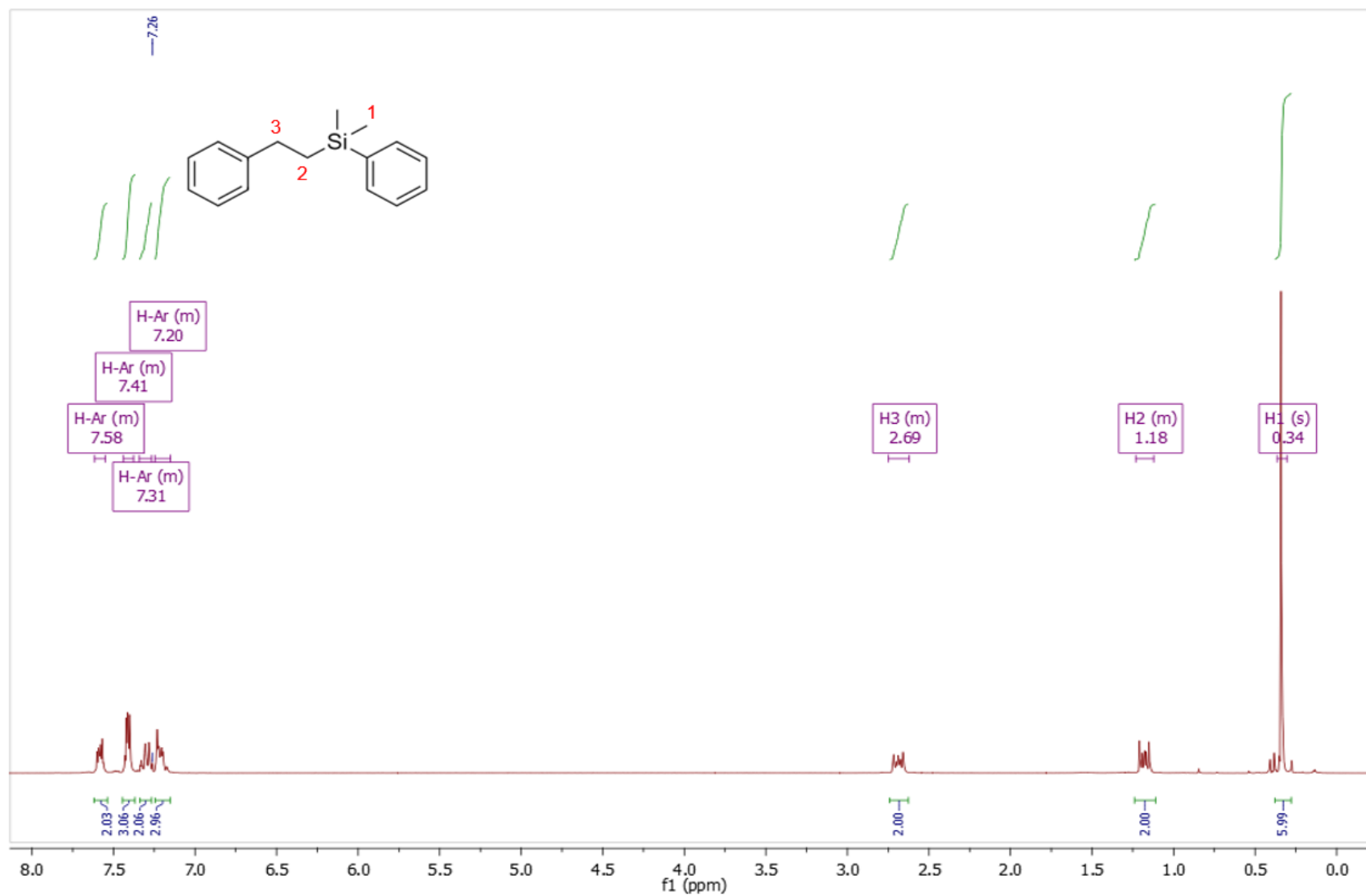


# Dimethyl(phenethyl)octylsilane (4a)

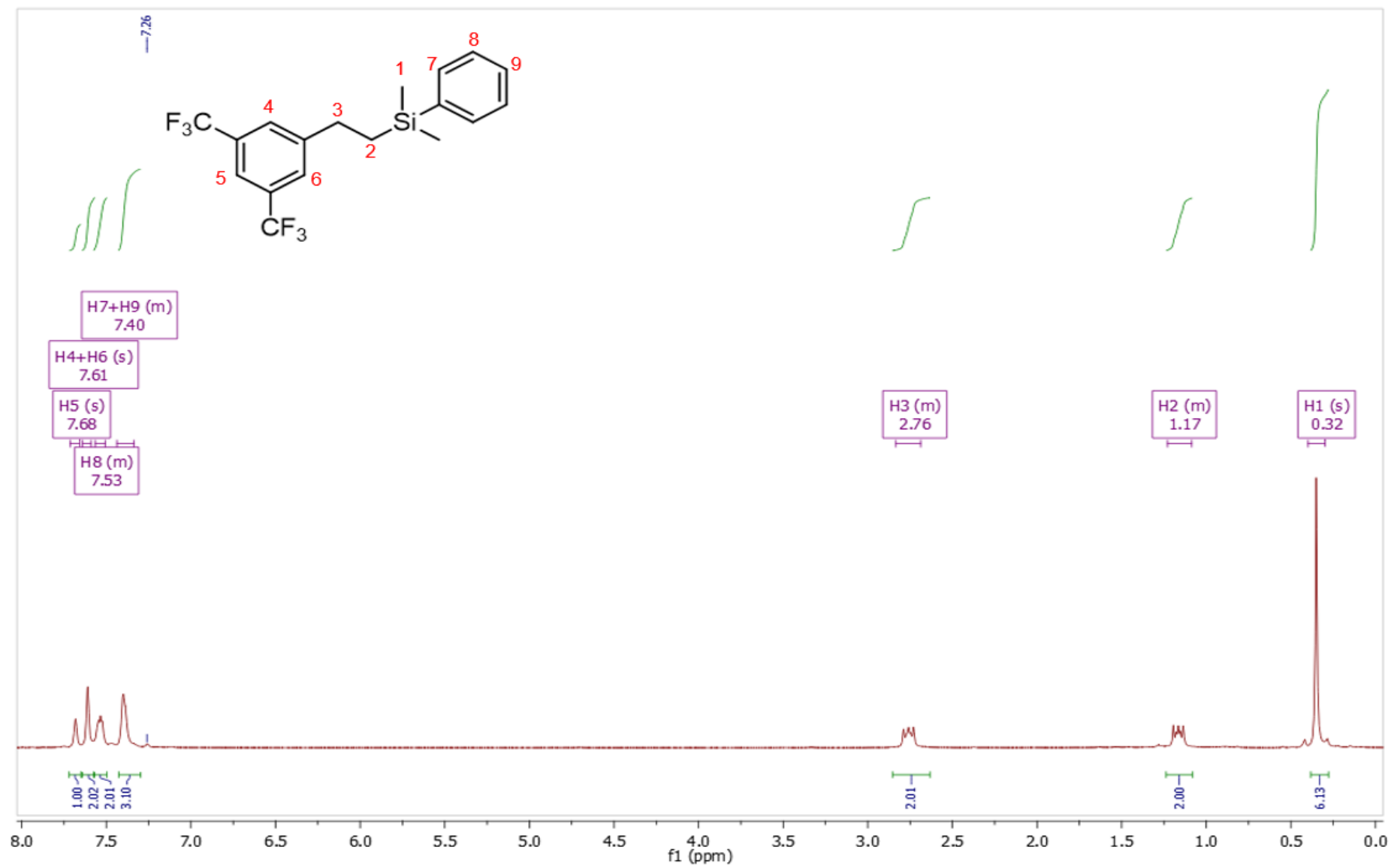




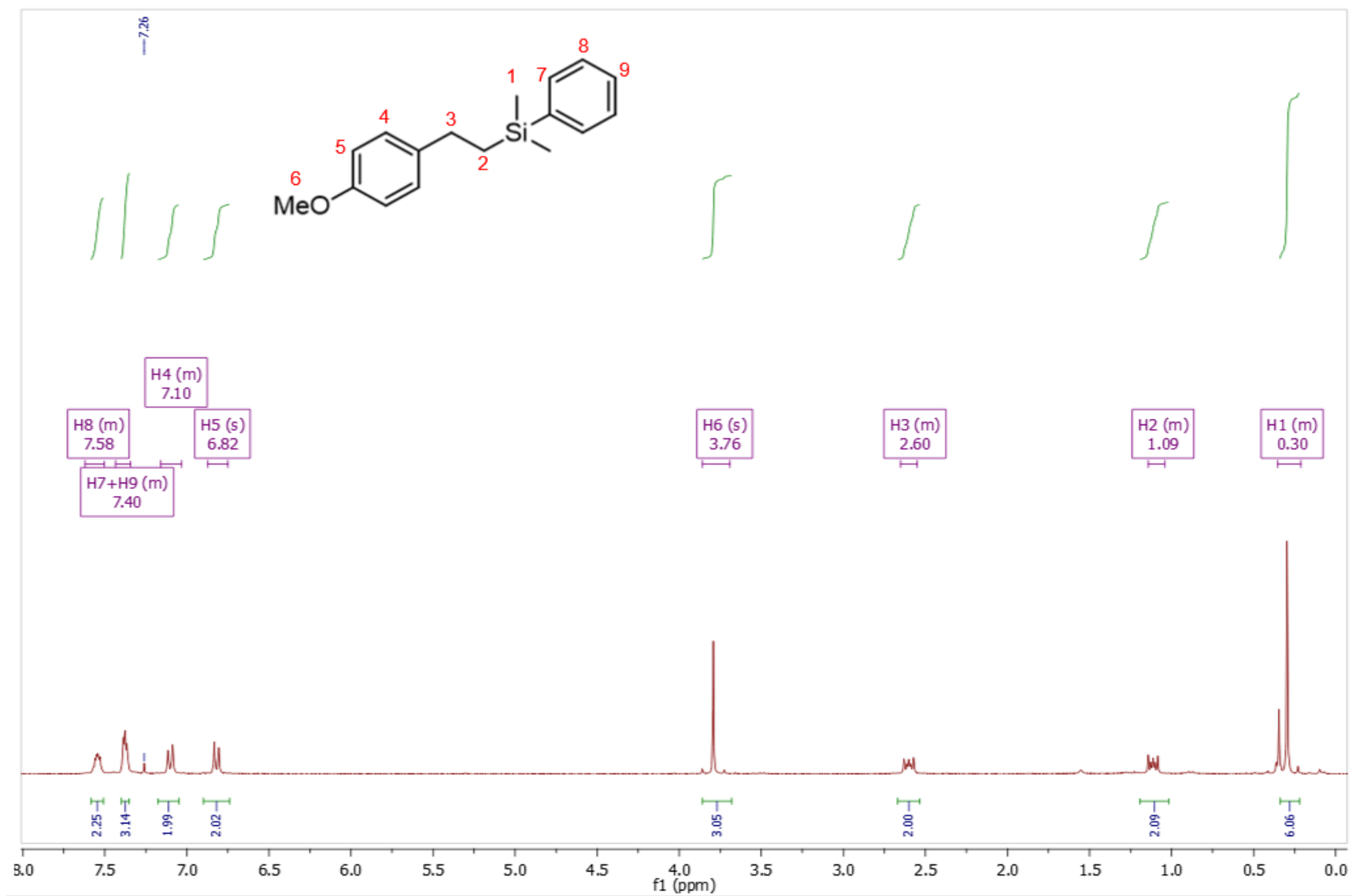
# Dimethyl(phenethyl)(phenyl)silane (4e)



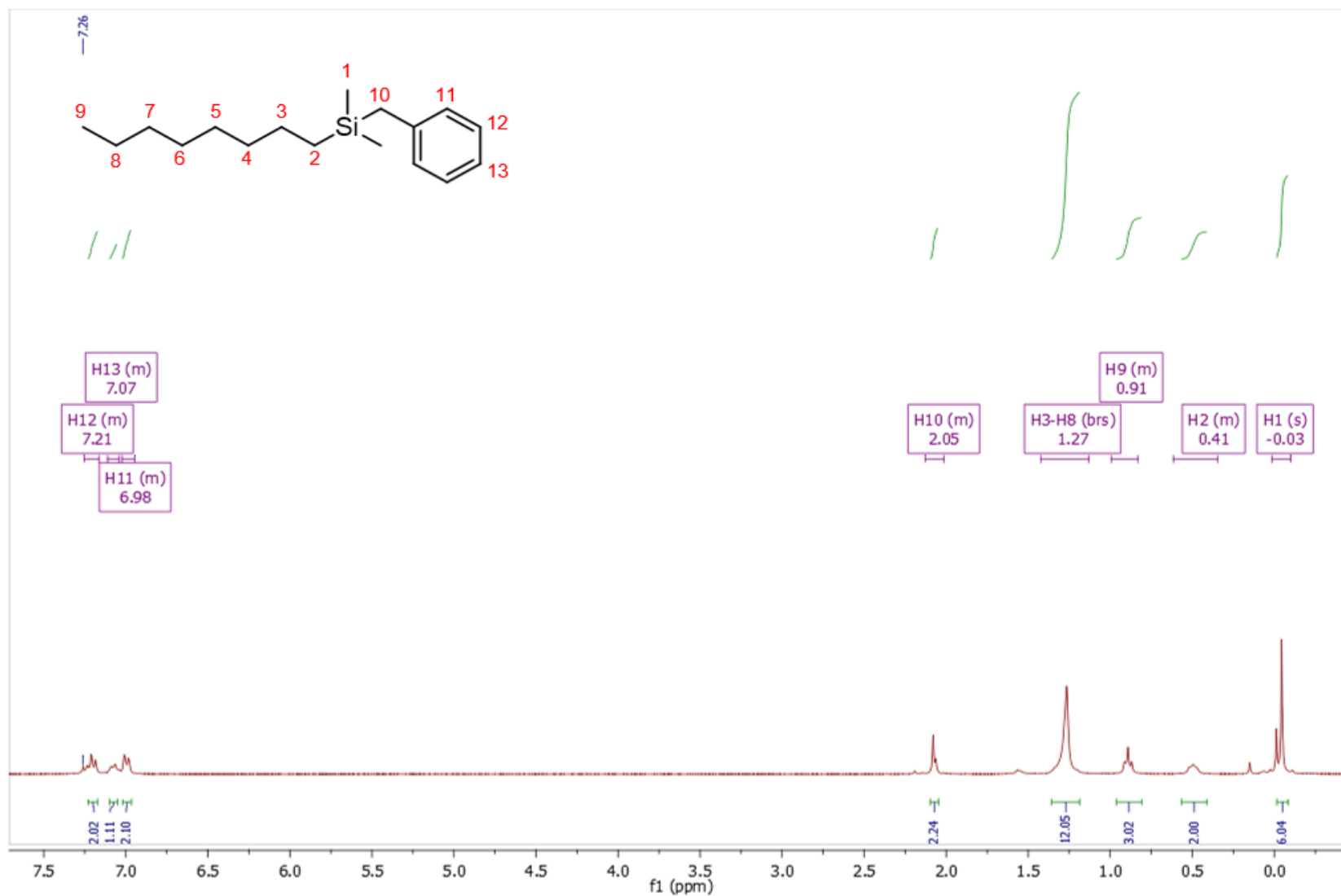
**(1,3-bis(trifluoromethyl)phenethyl)dimethyl(phenyl)silane (4m)**



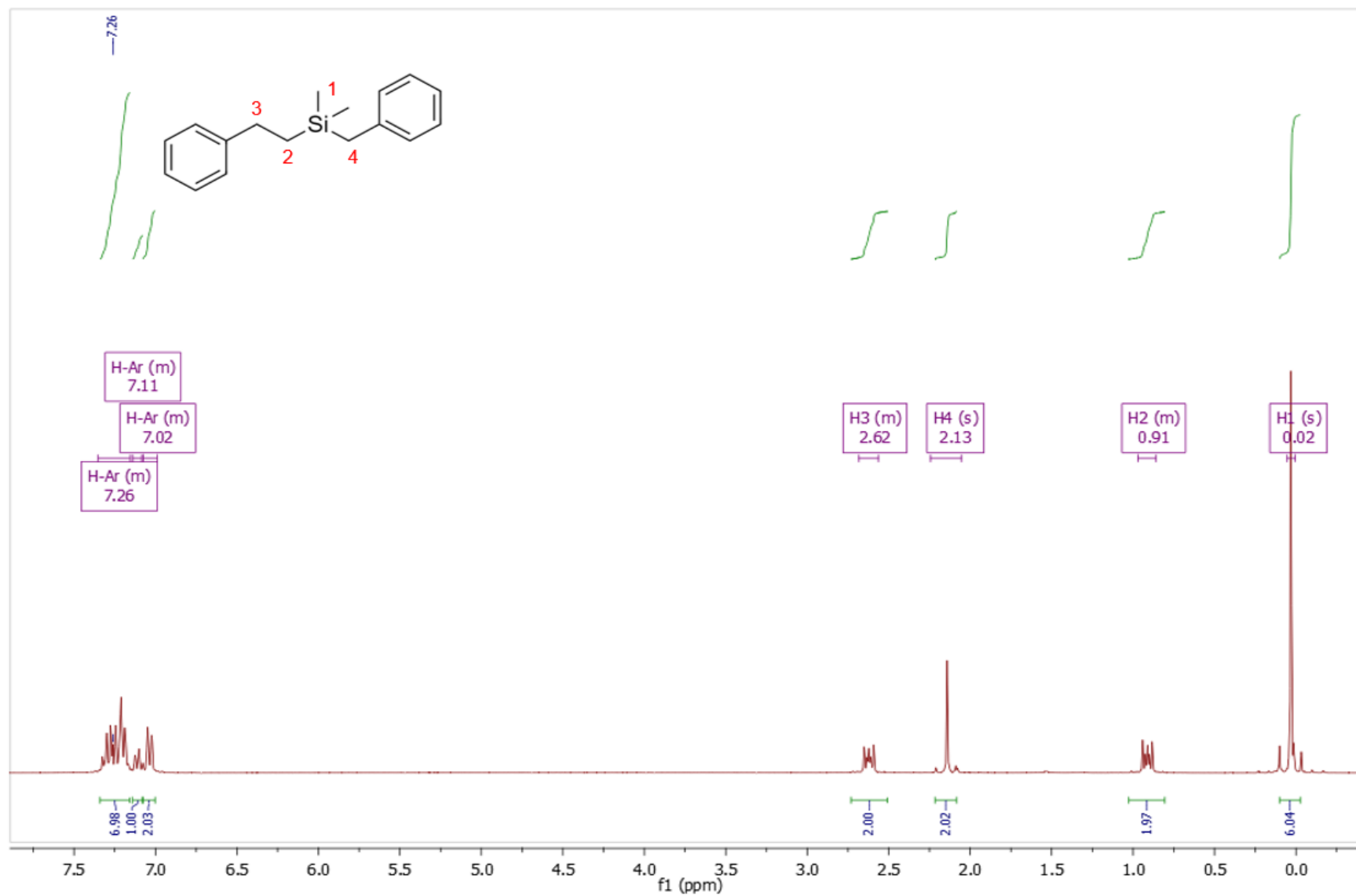
**(4-methoxyphenethyl)dimethyl(phenyl)silane (4n)**



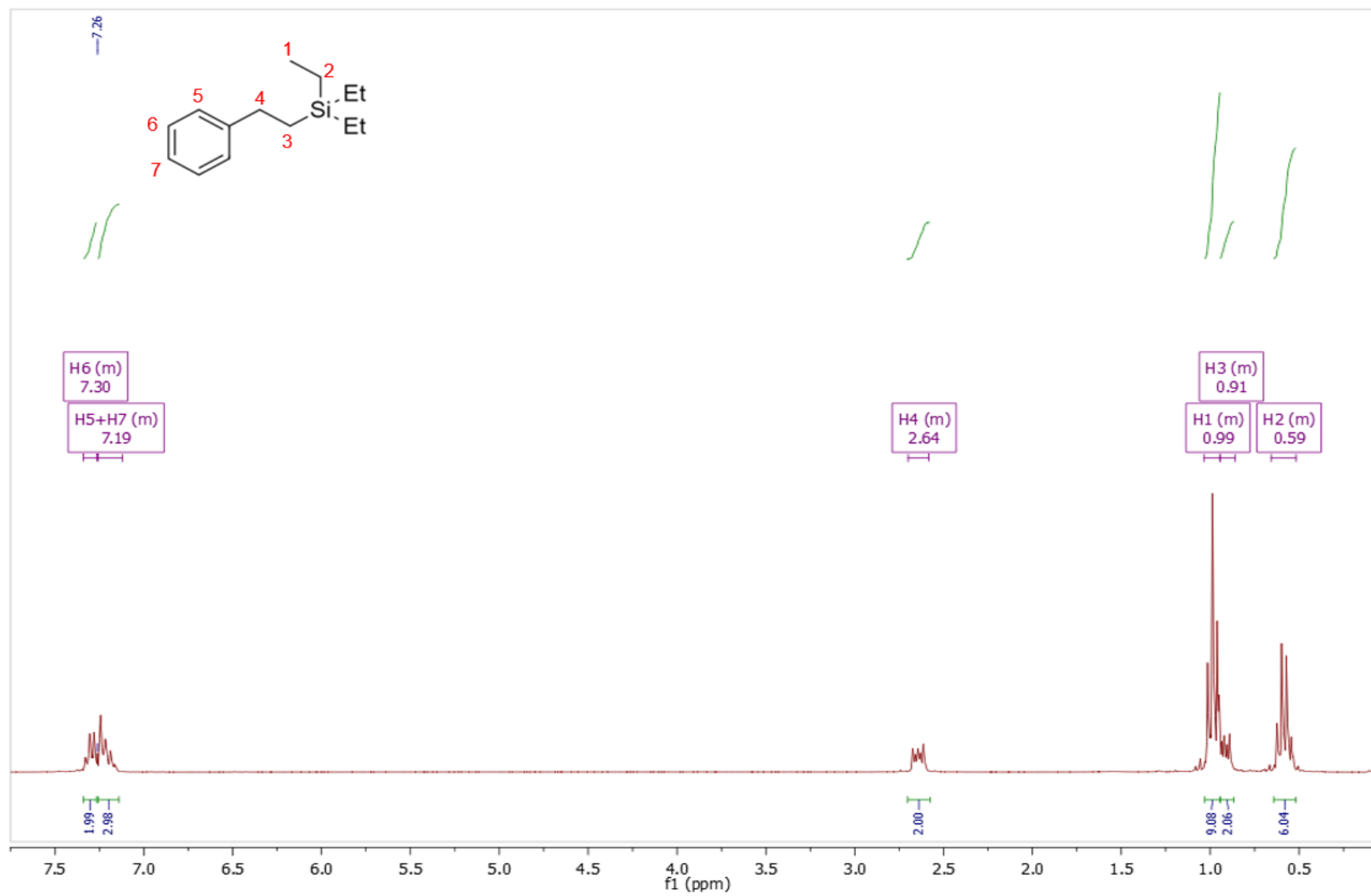
# Octyldimethyl(phenethyl)silane (5a)



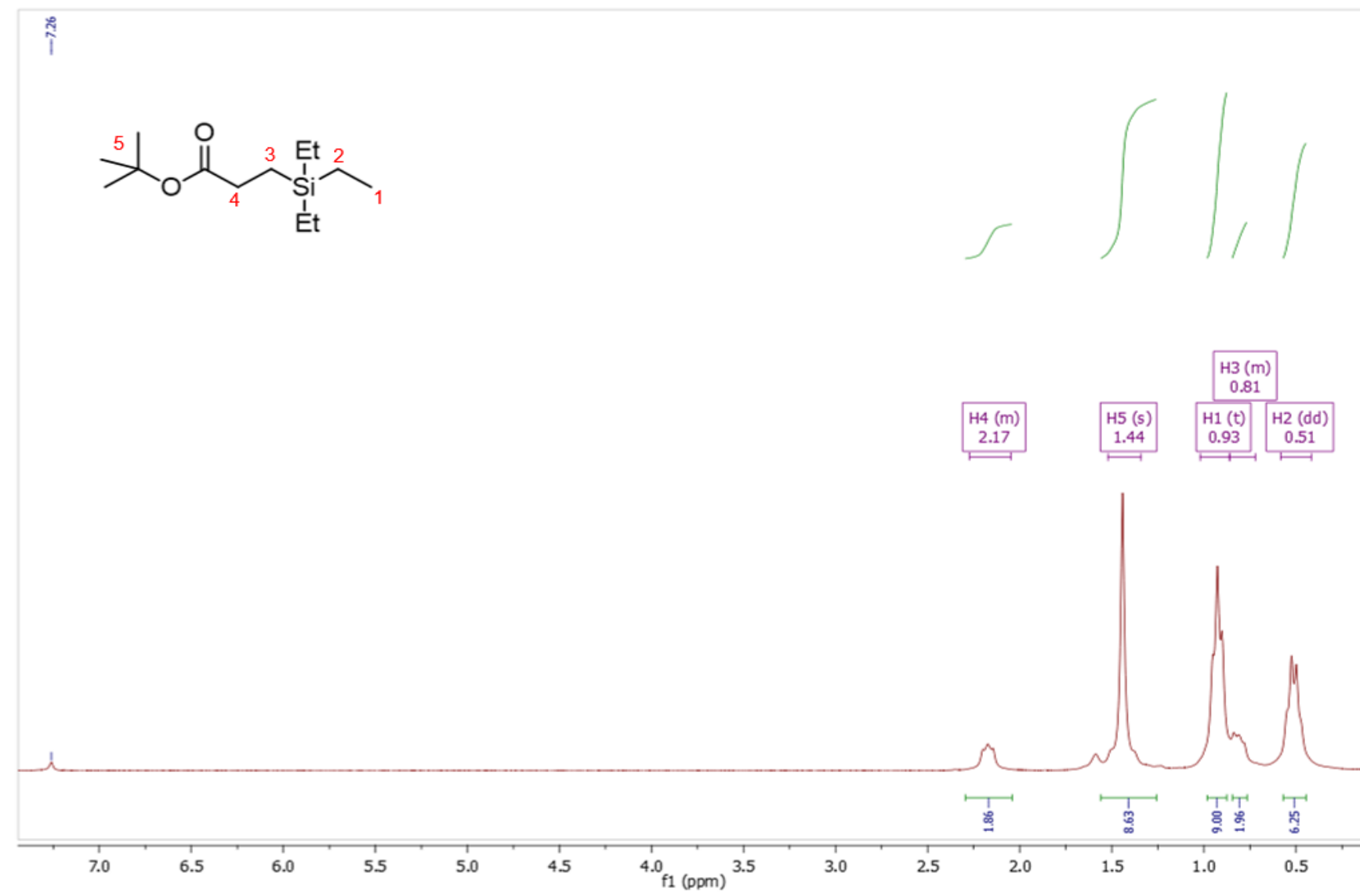
# Benzyldimethyl(phenethyl)silane (5e)



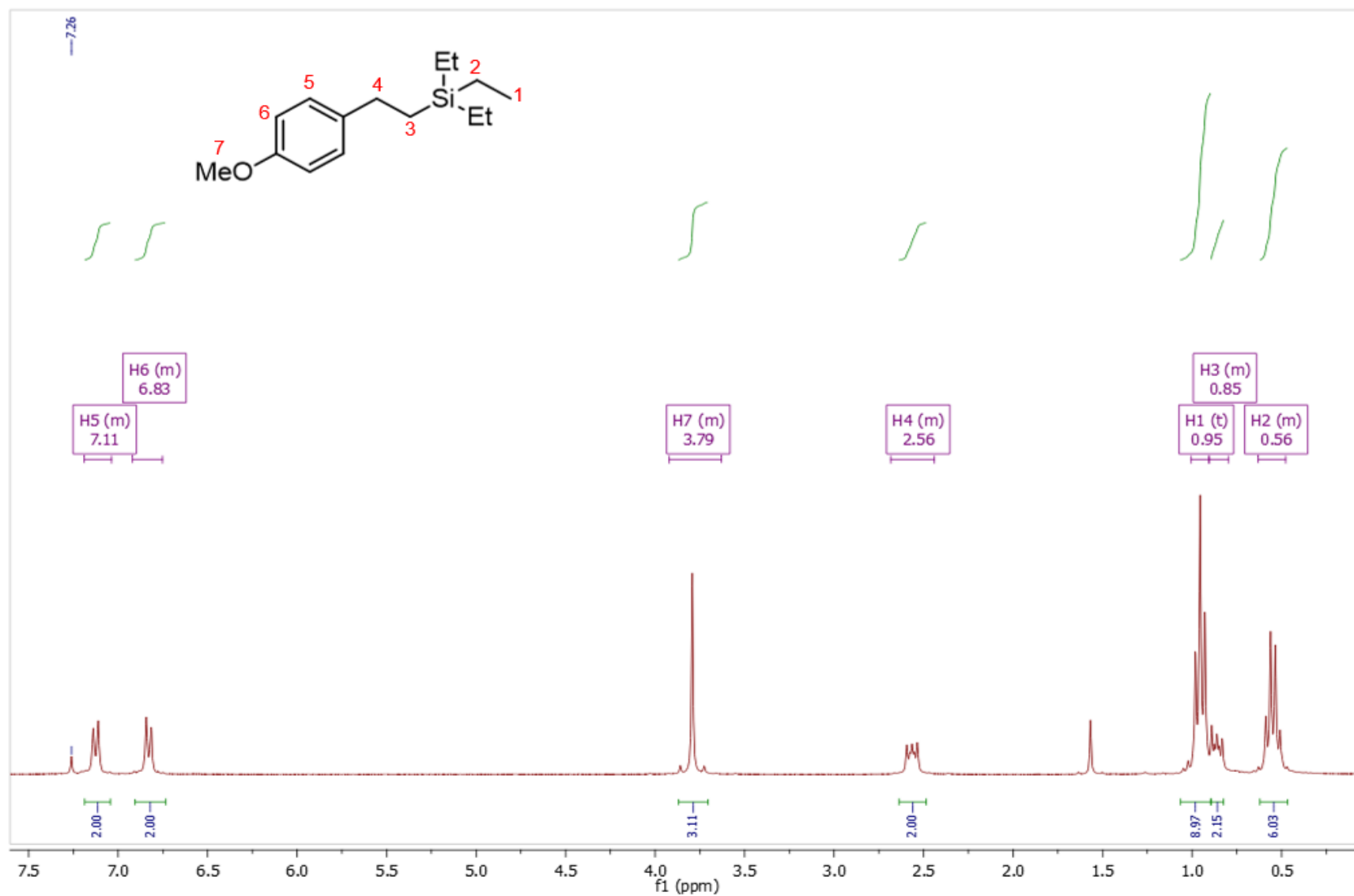
# Phenyltriethylsilane (6e)



# Tert-butyl 3-(triethoxysilyl)propanoate (6h)

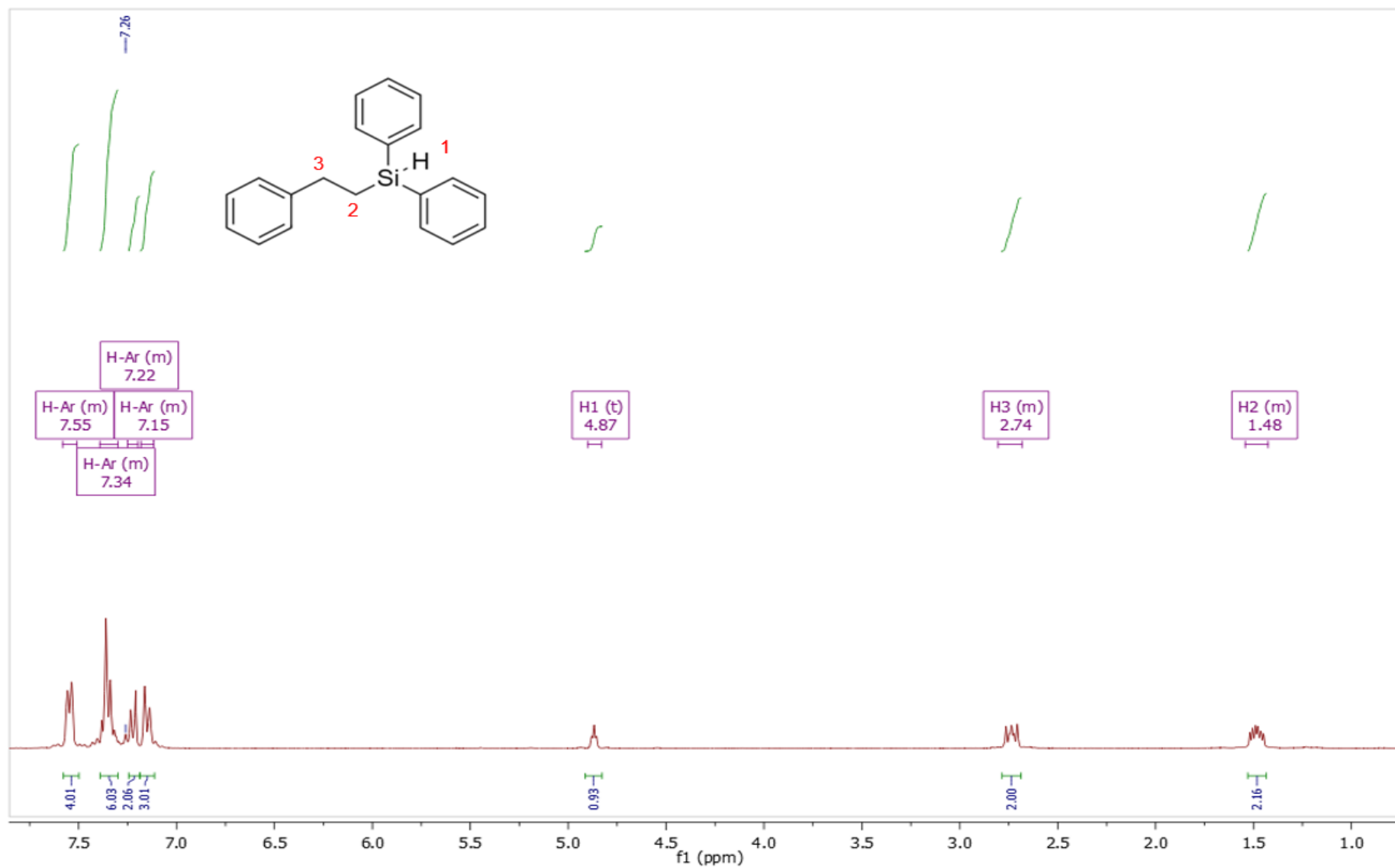


# Triethyl(4-methoxyphenethyl)silane (6n)



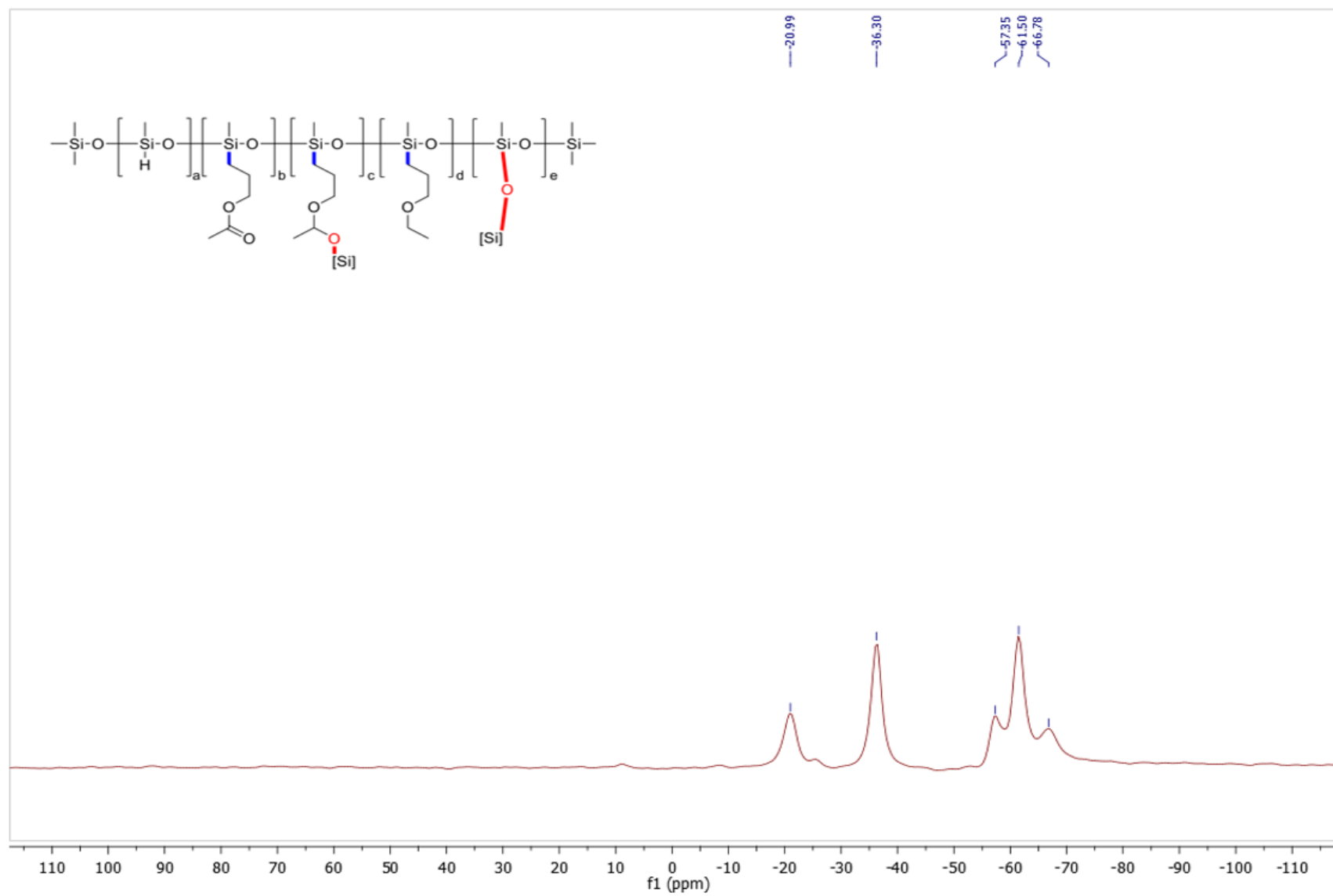


# Phenethyldiphenylsilane (8e)

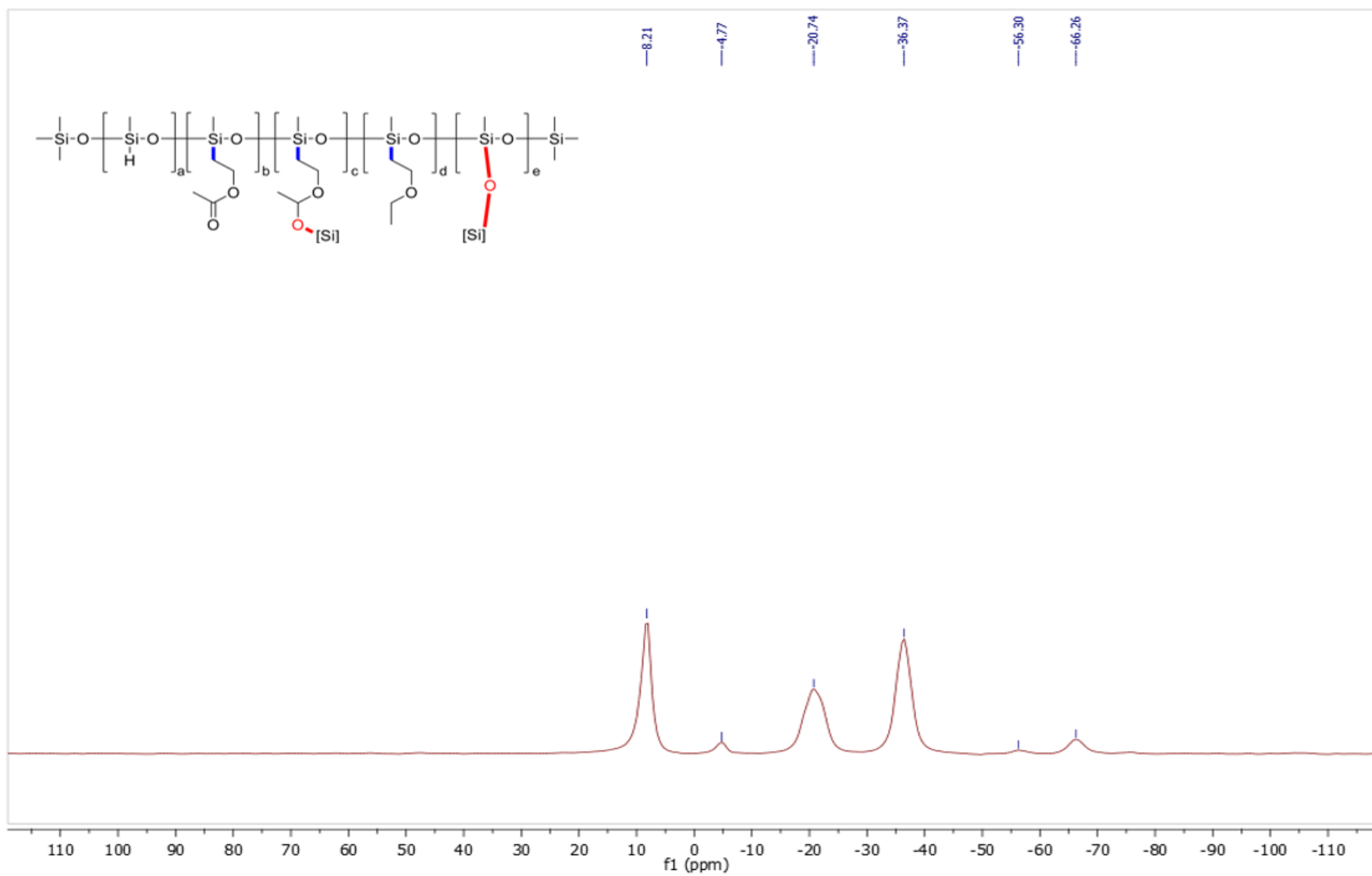


$^{29}\text{Si}$  CPMAS SS NMR spectra (60 MHz, 25 °C) of purified hydrosilylated polysiloxanes

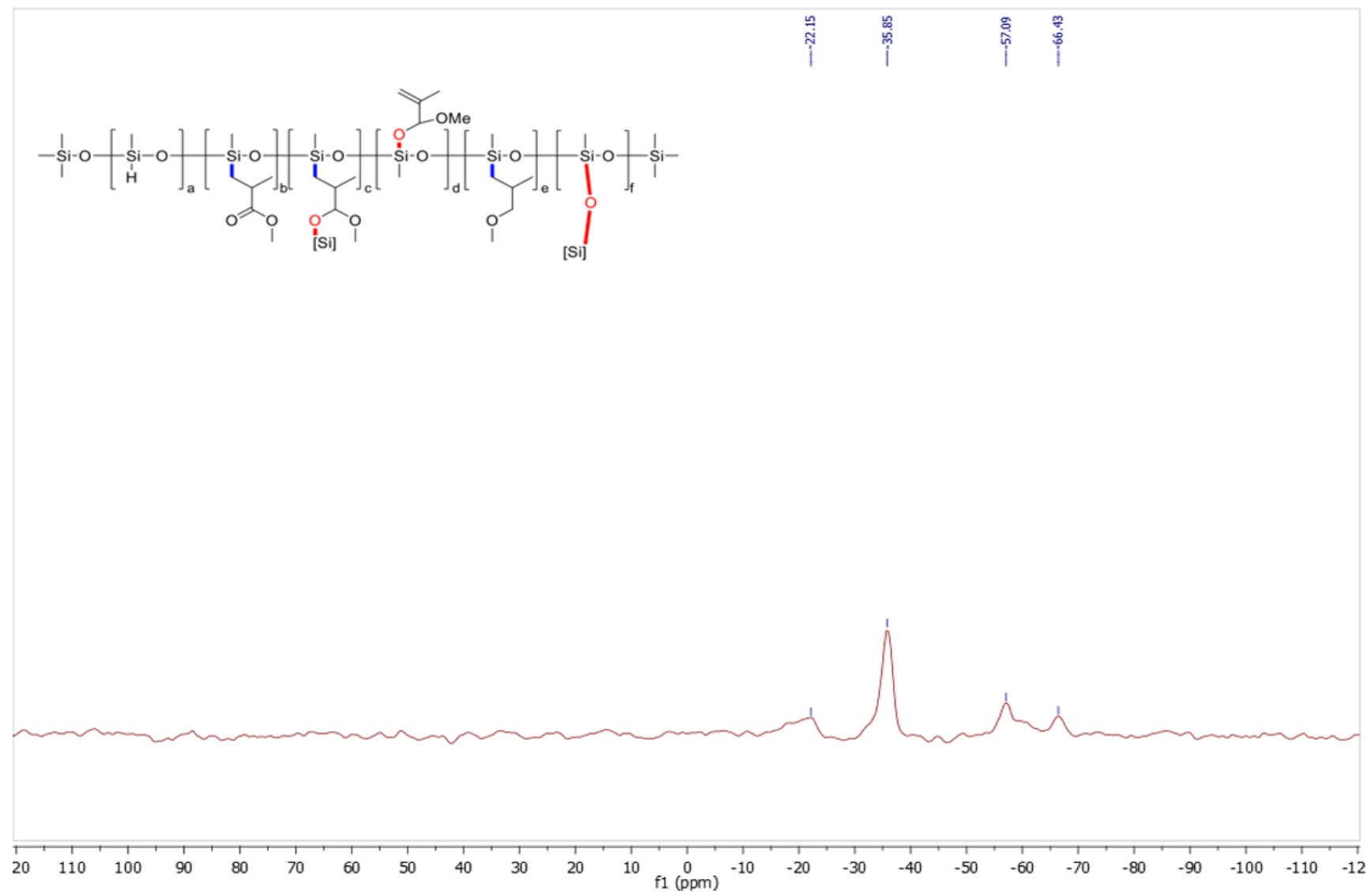
**$^{29}\text{Si}$  CPMAS SS-NMR of 4c**



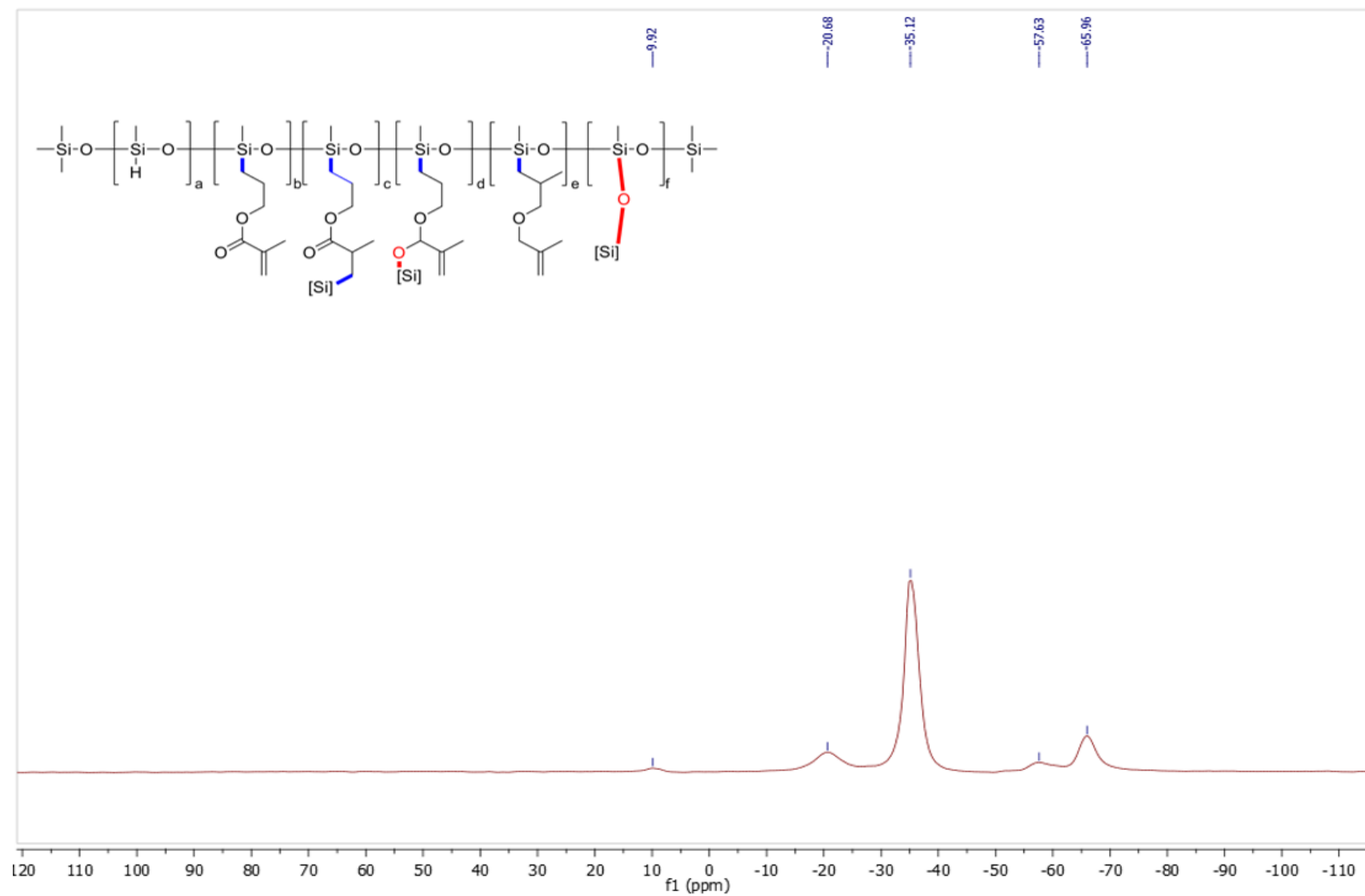
**$^{29}\text{Si}$  CPMAS SS-NMR of 4d**



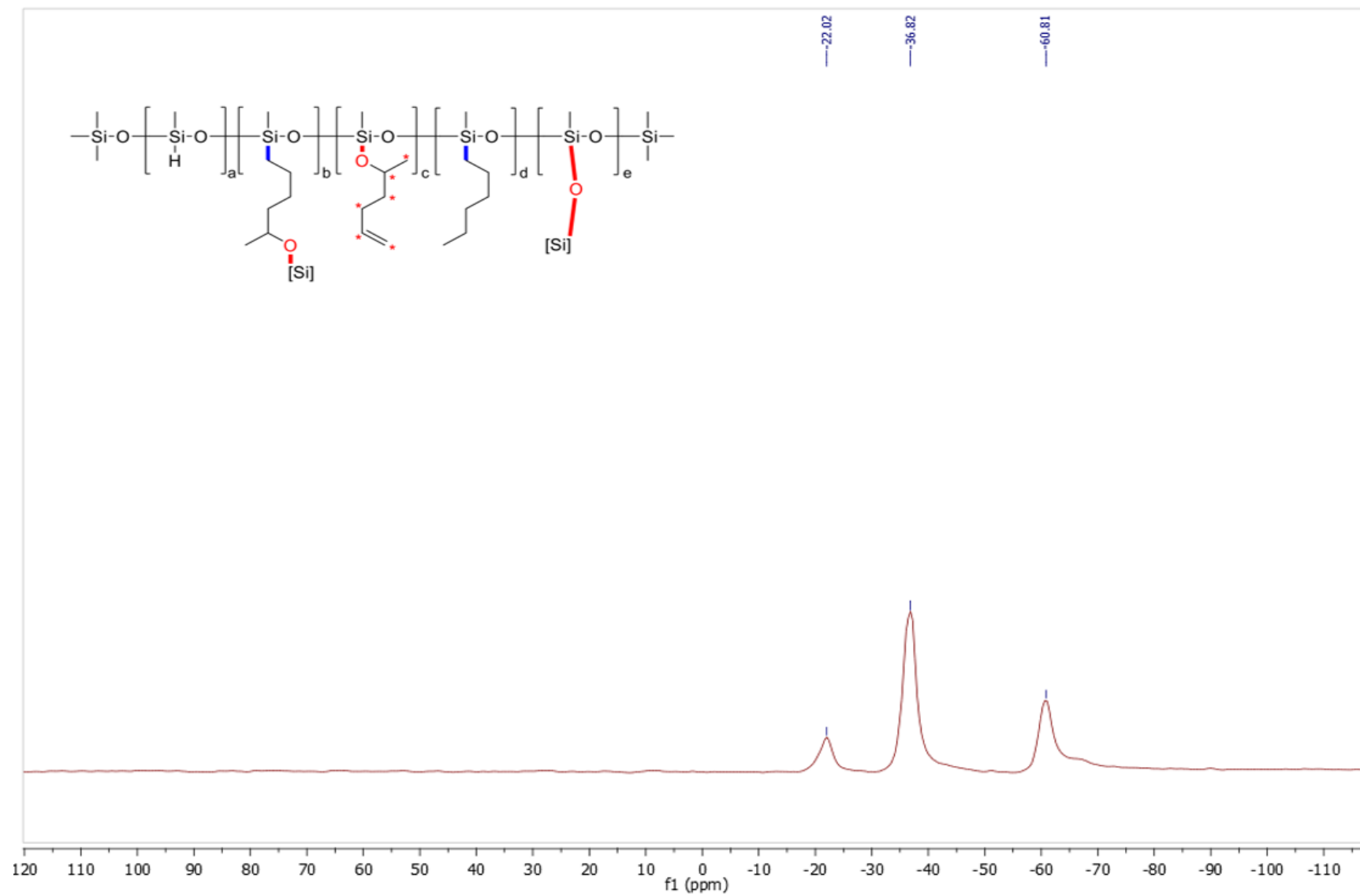
**$^{29}\text{Si}$  CPMAS SS-NMR of 4e**



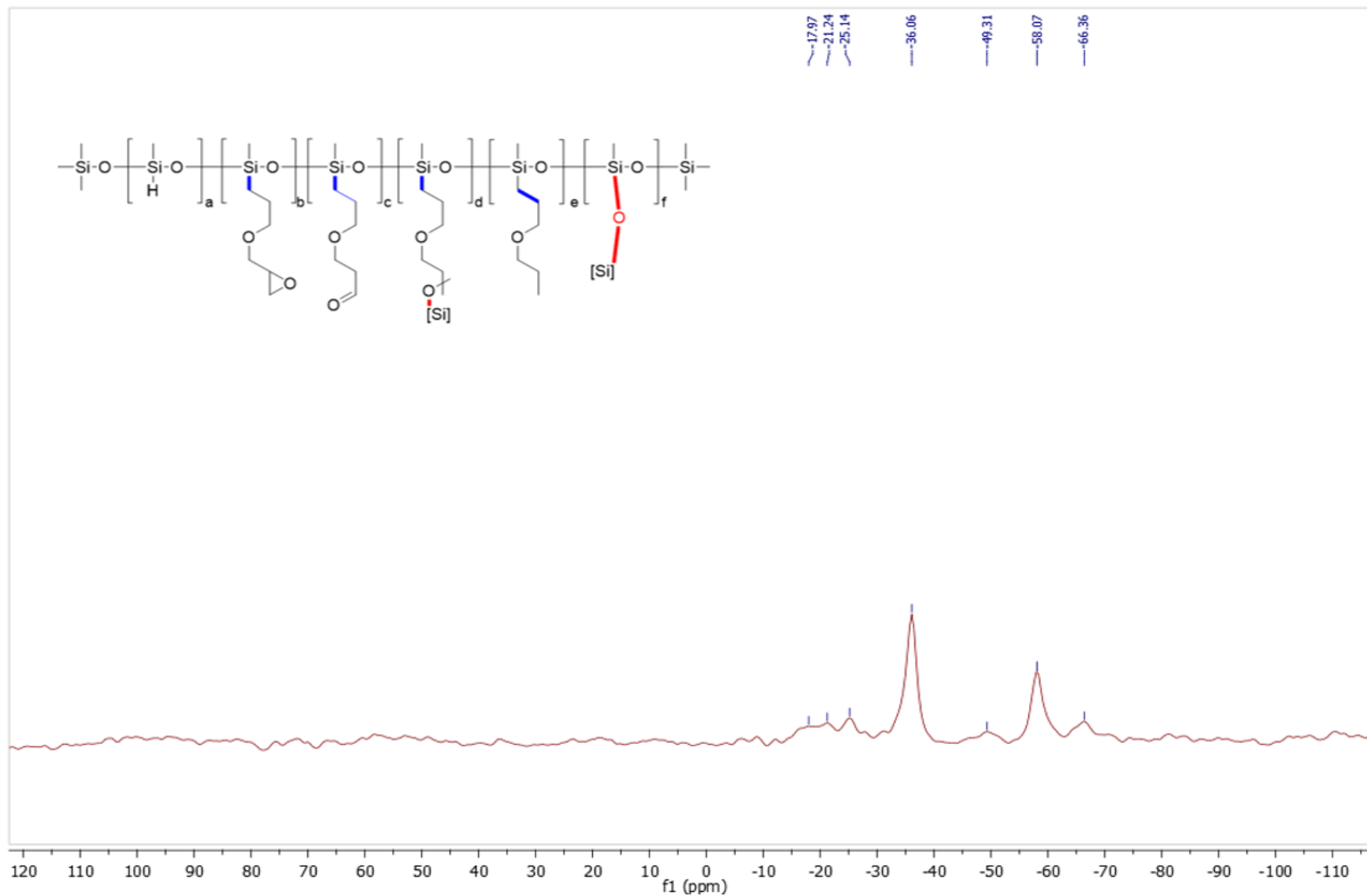
**$^{29}\text{Si}$  CPMAS SS-NMR of 4f**



**$^{29}\text{Si}$  CPMAS SS-NMR of 4g**

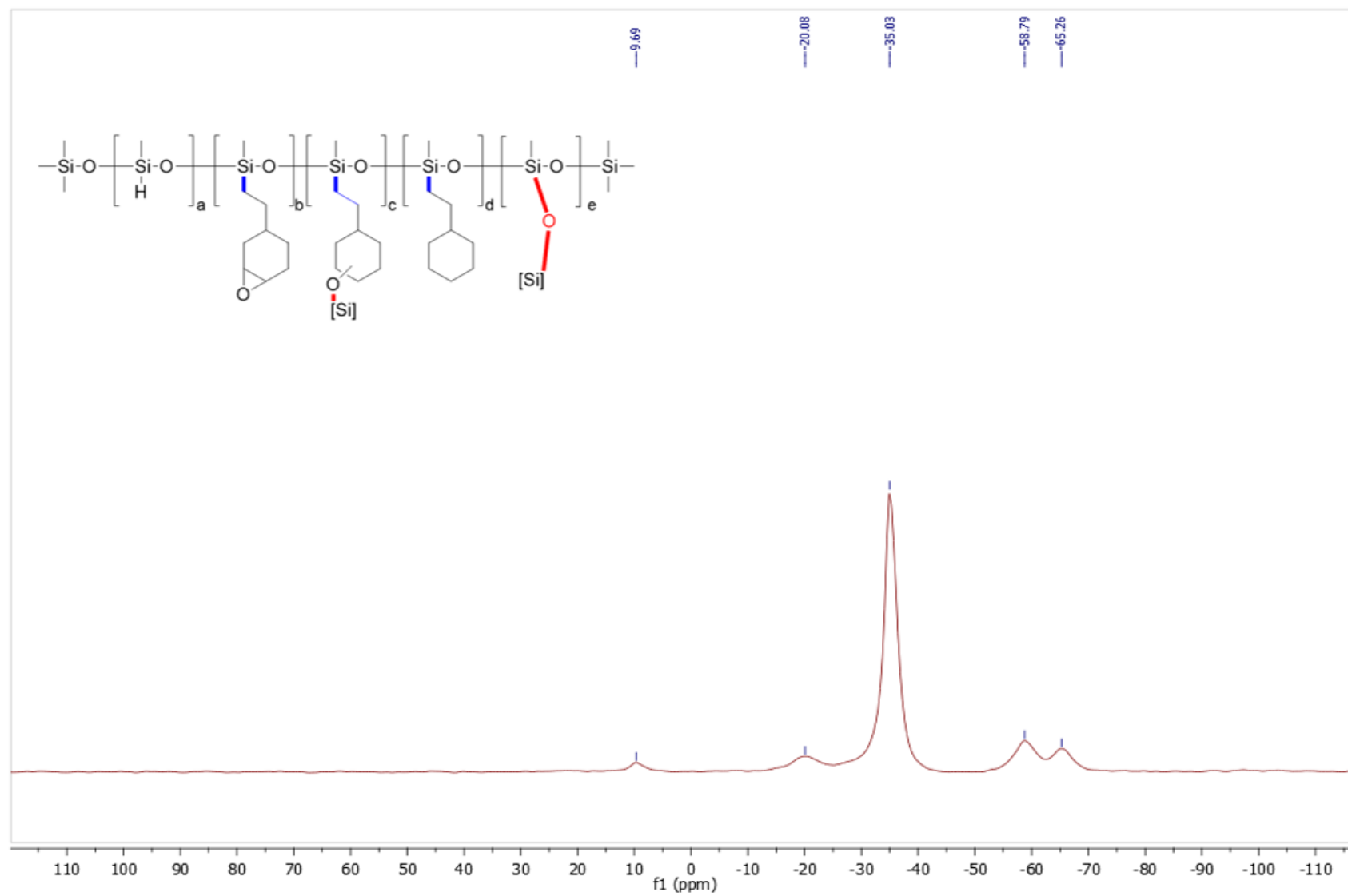


# $^{29}\text{Si}$ CPMAS SS-NMR of 4h





$^{29}\text{Si}$  CPMAS SS-NMR of 4i



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- <sup>1</sup> A. Vivien, L. Veyre, R. Mirgalet, C. Camp and C. Thieuleux, *Chem. Commun.*, 2022, **58**, 4091-4094.
- <sup>2</sup> D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, and Z. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 19154-19166.
- <sup>3</sup> A. Bokka and J. Jeon, *Org. Lett.*, 2016, **18**, 5324-5327.
- <sup>4</sup> R. Srivastava, M. Jakoobi, C. Thieuleux, E. A. Quadrelli and C. Camp. *Dalton Trans.*, 2021, **50**, 869-879.
- <sup>5</sup> A. Sanagawa and H. Nagashima, *Organometallics*, 2018, **37**, 2859-2871.
- <sup>6</sup> K. Itami, K. Mitsudo, A. Nishino, and J-I. Yoshida, *Chemistry Letters*, 2001, **30**, 1088-1089.
- <sup>7</sup> X. Yang, and C. Wang, *C. Chin. J. Chem.*, 2018, **36**, 1047-1051.
- <sup>8</sup> Y. Zhao, Y. Wan, Q. Yuan, J. Wei, and Y. Zhang, *Organic Letters*, 2023, **25** (9), 1386-1391.
- <sup>9</sup> Y. Yuan, Y. Gu, Y-E. Wang, J. Zheng, J. Ji, D. Xiong, F. Xue, and J. Mao, *Org. Chem.*, 2022, **87**, 21, 13907-13918.
- <sup>10</sup> J. Dong, X-A. Yuan, Z. Yan, L. Mu, J. Ma, C. Zhu and J. Xie. *Nat. Chem.*, 2021 **13**, 182-190.
- <sup>11</sup> M. P. Doyle, G. A. Devora, A. O. Nefedov, and K. G. High *Organometallics* 1996, **15**, 8, 2098-2102.
- <sup>12</sup> M. P. Doyle, G. A. Devora, A. O. Nefedov, and K. G. High, *Organometallics* 1992, **11**, 2, 549-555.
- <sup>13</sup> J. S. Bair, Y. Schramm, A. G. Sergeev, E. Clot, O. Eisenstein, and J. F. Hartwig, *J. Am. Chem. Soc.* 2014, **38**, 13098-13101.
- <sup>14</sup> Y. Jiang, O. Blacque, T. Fox, C.M. Frech, and H. Berke, *Chem. Eur J.*, 2007, **15**, 2121-2128.
- <sup>15</sup> A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, and P. J. Chirik, *Science*, 2012, **335**, 567-570.
- <sup>16</sup> C. H. Schuster, T. Diao, I. Pappas, and P. J. Chirik, *ACS Catal.* 2016, **6**, 2632-2636.
- <sup>17</sup> New heterogenized rhodium complexes, methods of their synthesis and application as hydrosilylation catalysts. Marciniak *et al.* 2007, Patent No.: US 8,049,024 B2.
- <sup>18</sup> Polysiloxane, method of manufacturing same, silicon-containing alicyclic compound, and radiation-sensitive resin compounds Iwasawa *et al.* 2001, Patent No.: EP 1 142 928 A.
- <sup>19</sup> I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, and X. Hu, *Angew. Chem. Int. Ed.* 2015, **54**, 14523-14526.
- <sup>20</sup> A. Kuznetsov and V. Gevorgyan, *Org. Lett.* 2012, **14**, 914-917.
- <sup>21</sup> Y. Gao, L. Wang, and L. Deng, *ACS Catal.* 2018, **8**, 9637-9646.
- <sup>22</sup> B. Arkles and G. Larson, *Silicon Compounds: Silanes & Silicones*, 2013.
- <sup>23</sup> H.-G. Horn and H. C. Marsmann, *Die Makromol. Chemie*, 1972, **162**, 255-267.
- <sup>24</sup> B. P. S. Chauhan, J. S. Rathore and N. Giloxhani, *Appl. Organomet. Chem.*, 2005, **19**, 542-550.
- <sup>25</sup> K. D. Safa, S. Tofangdarzadeh and A. Hassanpour, *J. Organomet. Chem.*, 2009, **694**, 4107-4115.
- <sup>26</sup> M. Chauhan, B. P. S. Chauhan and P. Boudjouk, *Org. Lett.*, 2000, **2**, 1027-1029.
- <sup>27</sup> B. Boutevin, F. Guida-Pietrasanta and A. Ratsimihety, *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 3722-3728.
- <sup>28</sup> H. Jancke, G. Engelhardt and H. Grosse-Ruyken, *J. Organomet. Chem.*, 1983, **247**, 139-148.
- <sup>29</sup> H. Jancke, J. Schulz, E. Popowski and H. Kelling, *J. Organomet. Chem.*, 1988, **354**, 23-29.
- <sup>30</sup> G. Engelhardt, H. Jancke, E. Lippmaa and A. Samoson, *J. Organomet. Chem.*, 1981, **210**, 295-301.
- <sup>31</sup> A) M. Jakoobi, V. Dardun, C. Camp and C. Thieuleux, *Catal. Sci. Technol.*, 2021, **11**, 3176-3181. B) M. Jakoobi, A. Vivien, C. Camp and C. Thieuleux, *Catal. Sci. Technol.*, 2021, **11**, 4714-4718.