

Copper(II) Triflate-Mediated Synthesis of Functionalized Silsesquioxanes *via* Dehydrogenative Coupling of POSS Silanols with Hydrosilanes

Joanna Kaźmierczak ^{*a} and Grzegorz Hreczycho ^{*a}

^a Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614

Poznań (Poland)

*g.h@amu.edu.pl

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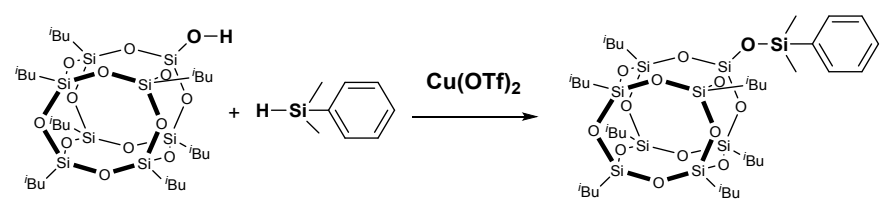
1. Optimization of reaction conditions

Table 1 Investigating the catalytic activity of different triflates in dehydrogenative coupling reaction of POSS silanols with silanes

$M(OTf)_n$	Catalyst loading ^a	Conversion ^b (%)
no catalyst	-	0
Sc(OTf) ₃	4 mol%	traces
Zn(OTf) ₂	4 mol%	traces
Ca(OTf) ₂	4 mol%	traces
Mg(OTf) ₂	4 mol%	traces
Fe(OTf) ₂	4 mol%	traces
AgOTf	4 mol%	40
AgOTf	8 mol%	85
Cu(OTf)₂	4 mol%	99

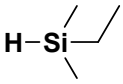
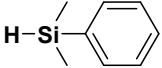
^a Reaction conditions: toluene, argon atmosphere, 80°C, 24 h, molar ratio of reagents POSS monosilanol:silane = 1.0:3.0; ^b Conversion determined by crude NMR.

Table 2 Optimization of reaction conditions for functionalization of POSS monosilanol

					
[POSS silanol:silane]	Solvent	Catalyst loading Cu(OTf) ₂	Temperature (°C)	Time (h)	Conversion ^a (%)
1.0:3.0	toluene	2 mol%	80	24	traces
		2 mol%	110	24	traces
		4 mol%	60	24	20
		4 mol%	80	16	85
		4 mol%	80	24	99
	THF	4 mol%	60	24	traces
1.0:1.5	toluene	4 mol%	80	24	30

^a Conversion determined by crude NMR.

Table 3 Optimization of reaction conditions for dehydrogenative coupling of POSS disilanol with silanes mediated by $\text{Cu}(\text{OTf})_2$

Solvent	Silane	[POSS disilanol:silane]	Catalyst loading $\text{Cu}(\text{OTf})_2$	Temperature ($^{\circ}\text{C}$)	Time (h)	Conversion ^a (%)
toluene		1.0:6.0	6 mol%	80	24	traces
			6 mol%	110	24	traces
			8 mol%	80	24	85
		1.0:6.0	6 mol%	80	24	traces
			8 mol%	80	24	90

^a Conversion determined by crude NMR.

2. Experimental Section

Materials and Procedures

Cu(OTf)₂ was purchased from ABCR GmbH & Co. KG. Other reagents as well as solvents were purchased from Sigma-Aldrich Co. or ABCR GmbH & Co. KG. They were used for experiments without further purification. Toluene was dried using benzophenone/sodium procedure prior to use. POSS compounds were obtained from Hybrid Plastics. Reactions were carried out under argon atmosphere. The structure of products was determined by NMR spectroscopy. The spectra ¹H NMR (400 MHz), ¹³C NMR (101 MHz), ²⁹Si NMR (79 MHz) were recorded on a Bruker Avance III HD NanoBay spectrometer, using CDCl₃ as solvent. Whereas, mechanistic study was performed in Young NMR tubes, using toluene-d₈ as solvent. All spectra were acquired at 298 K. GC-MS-analysis was performed on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finnigan Mat 800 ion trap detector.

Synthetic procedures

General procedure for the synthesis of compound 1-12:

To a 25 mL Schlenk flask equipped with a stirring bar, POSS monosilanol (1.0 mmol, 1.0 equiv.), silane (3.0 mmol, 3.0 equiv.) and 2 mL of toluene were added under argon atmosphere. Subsequently, copper(II) trifluoromethanesulfonate (0.04 mmol, 4 mol %) was added and the reaction mixture was stirred at 80°C for 24 h. After this time, the product was separated from the catalyst by filtration. Next, the solvent and all volatiles were evaporated under reduced pressure and subsequently the excess of silane was separated from the product by adding acetonitrile. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give the corresponding compounds **1-12**.

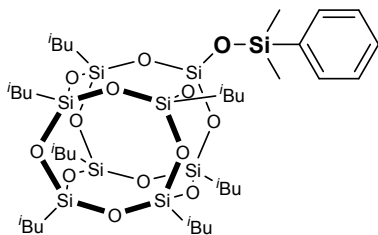
General procedure for the synthesis of compounds 13-16:

To a 25 mL Schlenk flask equipped with a stirring bar, POSS disilanol (1.0 mmol, 1.0 equiv.), silane (6.0 mmol, 6.0 equiv.) and 2 mL of toluene were added under argon atmosphere. Subsequently, copper(II) trifluoromethanesulfonate (0.08 mmol, 8 mol %) was added and the reaction mixture was stirred at 80°C for 24 h. After this time, the product was separated from the catalyst by filtration. Next, the solvent and all volatiles were evaporated under reduced pressure and subsequently the excess of silane was separated from the product by adding acetonitrile. The product was obtained as oil which was separated from acetonitrile to give the corresponding compounds **13-16**.

General procedure for closing the cage of POSS disilanol and obtaining compound 17:

To a 25 mL Schlenk flask equipped with a stirring bar, POSS disilanol (1.0 mmol, 1.0 equiv.), silane (1.5 mmol, 1.5 equiv.) and 2 mL of toluene were added under argon atmosphere. Subsequently, copper(II) trifluoromethanesulfonate (0.08 mmol, 8 mol %) was added and the reaction mixture was stirred at 80°C for 24 h. After this time, the product was separated from the catalyst by filtration. Next, the solvent and all volatiles were evaporated under reduced pressure and subsequently the excess of silane was separated from the product by adding acetonitrile. The product was obtained as oil which was separated from acetonitrile to give the product **17** in 85% yield.

3. The spectroscopic data of obtained silsesquioxane derivatives



Compound **(1)** was obtained as solid in 97% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.35-0.41 (m, 6H), 0.59-0.65 (m, 14H), 0.95-1.01 (m, 42H), 1.84-1.93 (m, 7H), 7.34-7.42 (m, 3H), 7.55-7.64 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 0.4, 22.4, 22.5, 23.8, 23.9, 25.7, 25.7, 127.6, 129.3, 133.1, 139.0.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 0.7, -67.0, -67.9, -109.6.

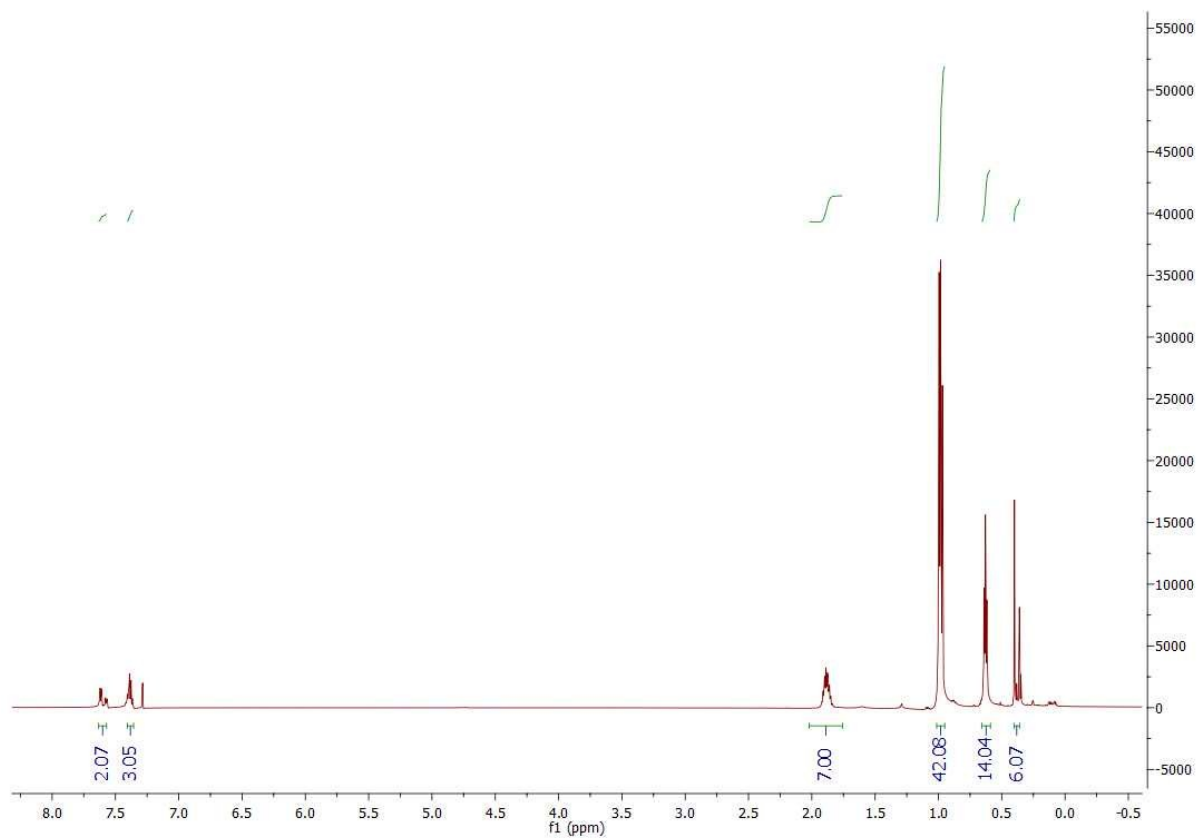


Figure 1 ¹H NMR (400 MHz) of compound (1).

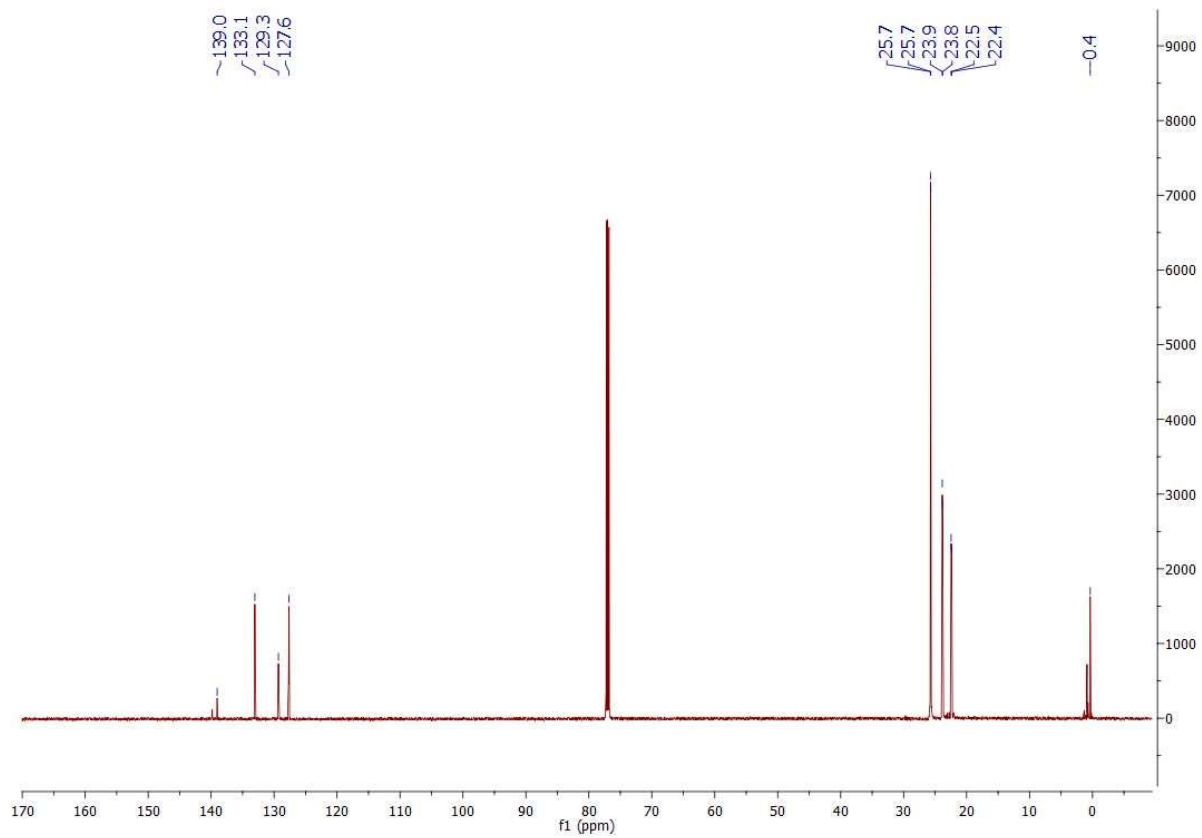


Figure 2 ^{13}C NMR (101 MHz) of compound (1).

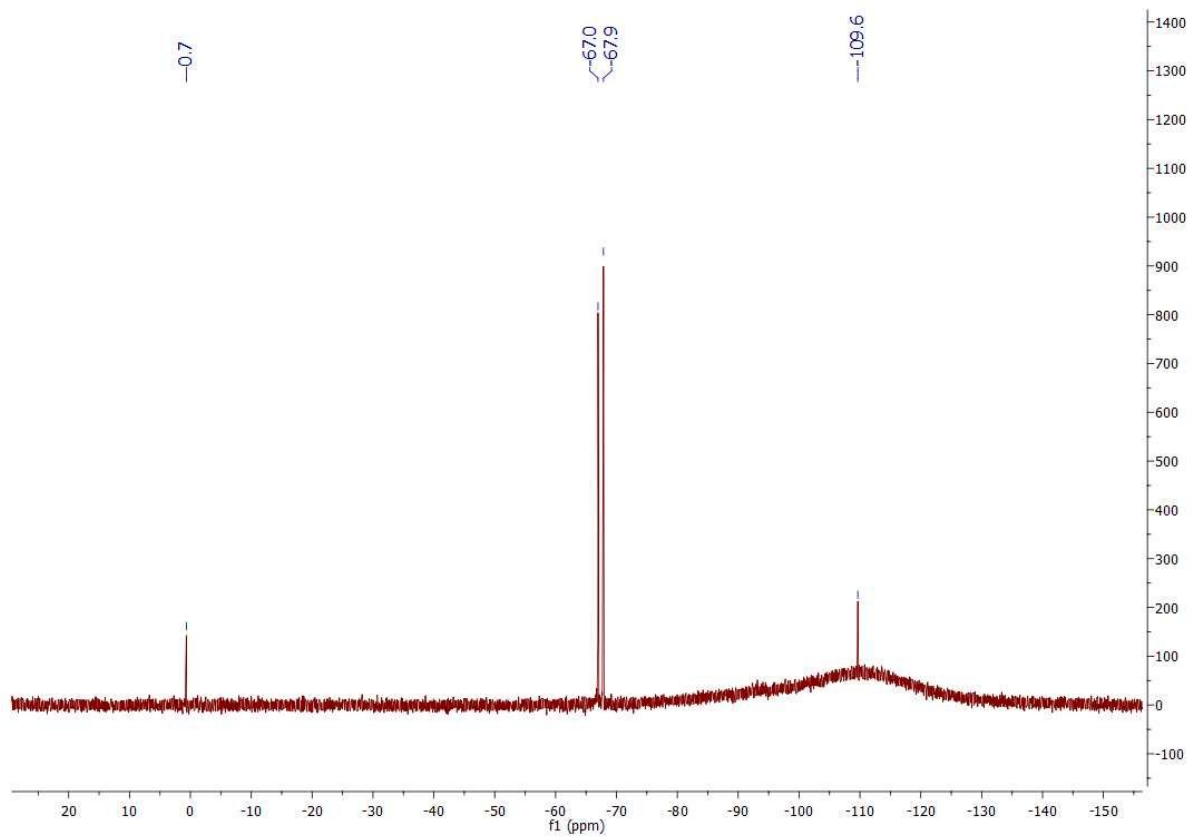
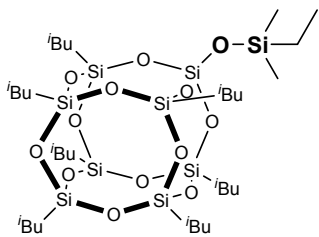


Figure 3 ^{29}Si NMR (79 MHz) of compound (1).



Compound **(2)** was obtained as solid in 95% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.12 (s, 6H), 0.53-0.60 (m, 2H), 0.60-0.67 (m, 14H), 0.93-1.05 (m, 45H), 1.80-1.96 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = -0.9, 6.5, 9.5, 22.4, 22.5, 22.5, 23.8, 23.9, 25.7.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 12.4, -67.1, -67.9, -109.7.

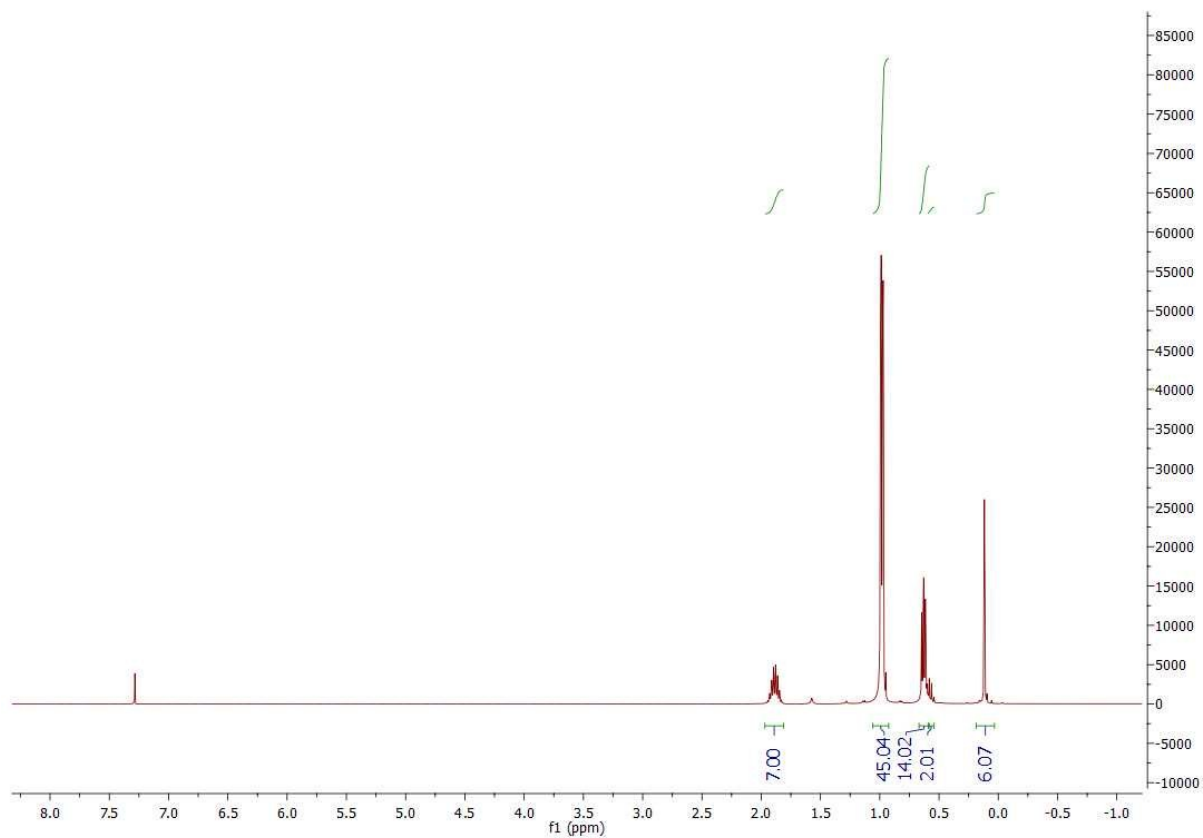


Figure 4 ¹H NMR (400 MHz) of compound (2).

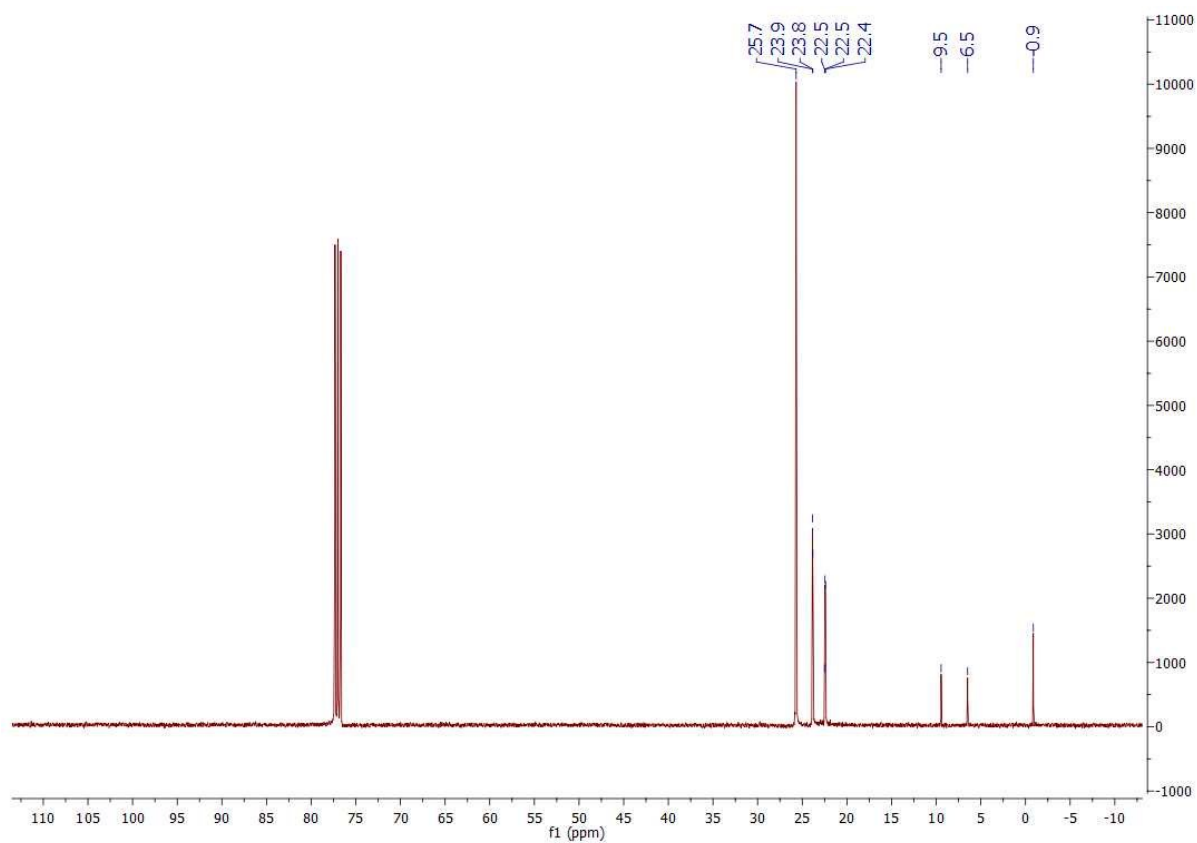


Figure 5 ^{13}C NMR (101 MHz) of compound (2).

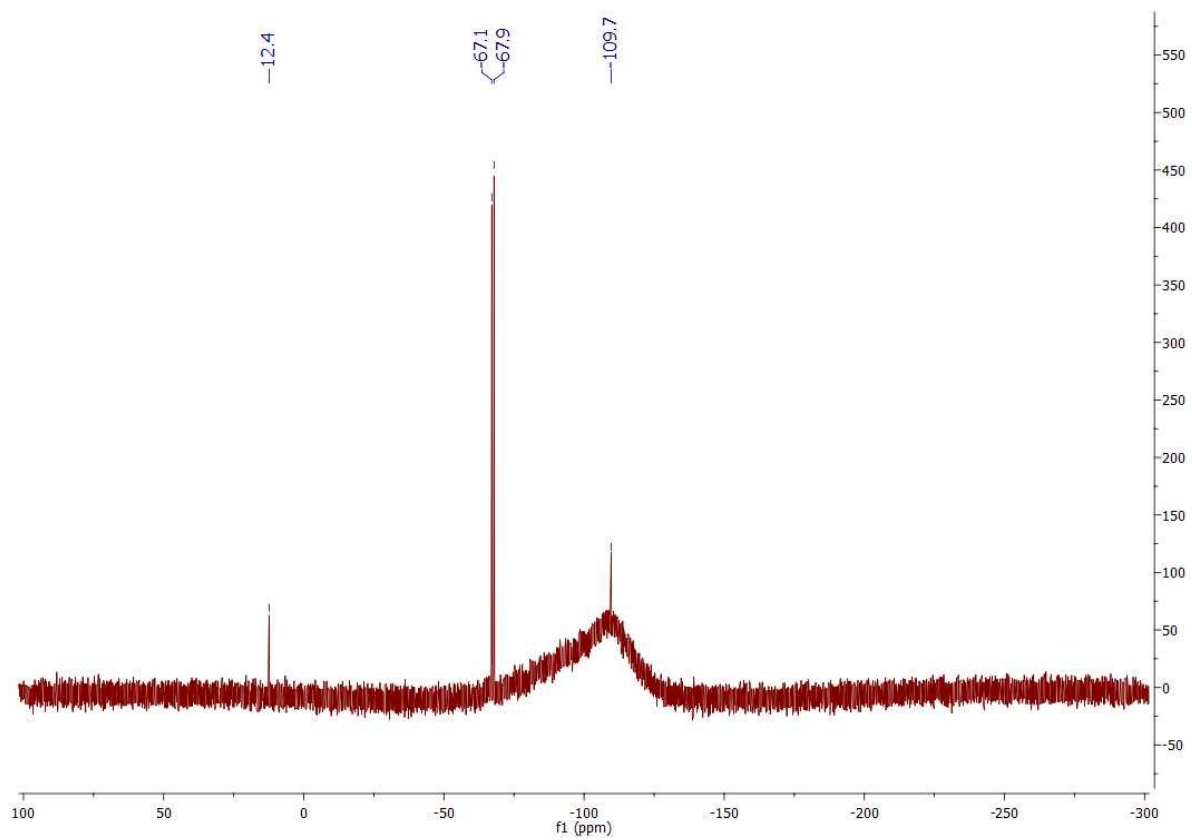
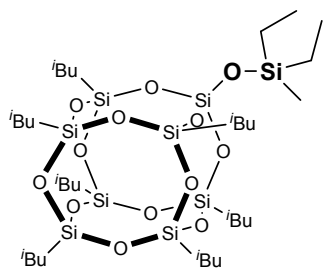


Figure 6 ^{29}Si NMR (79 MHz) of compound (2).



Compound **(3)** was obtained as solid in 98% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.09 (s, 3H), 0.53-0.60 (m, 4H), 0.61-0.66 (m, 14H), 0.95-1.01 (m, 48H), 1.84-1.94 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = -3.1, 6.5, 7.6, 22.4, 22.5, 22.5, 23.8, 23.9, 25.7.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 13.1, -67.1, -67.9, -109.8.

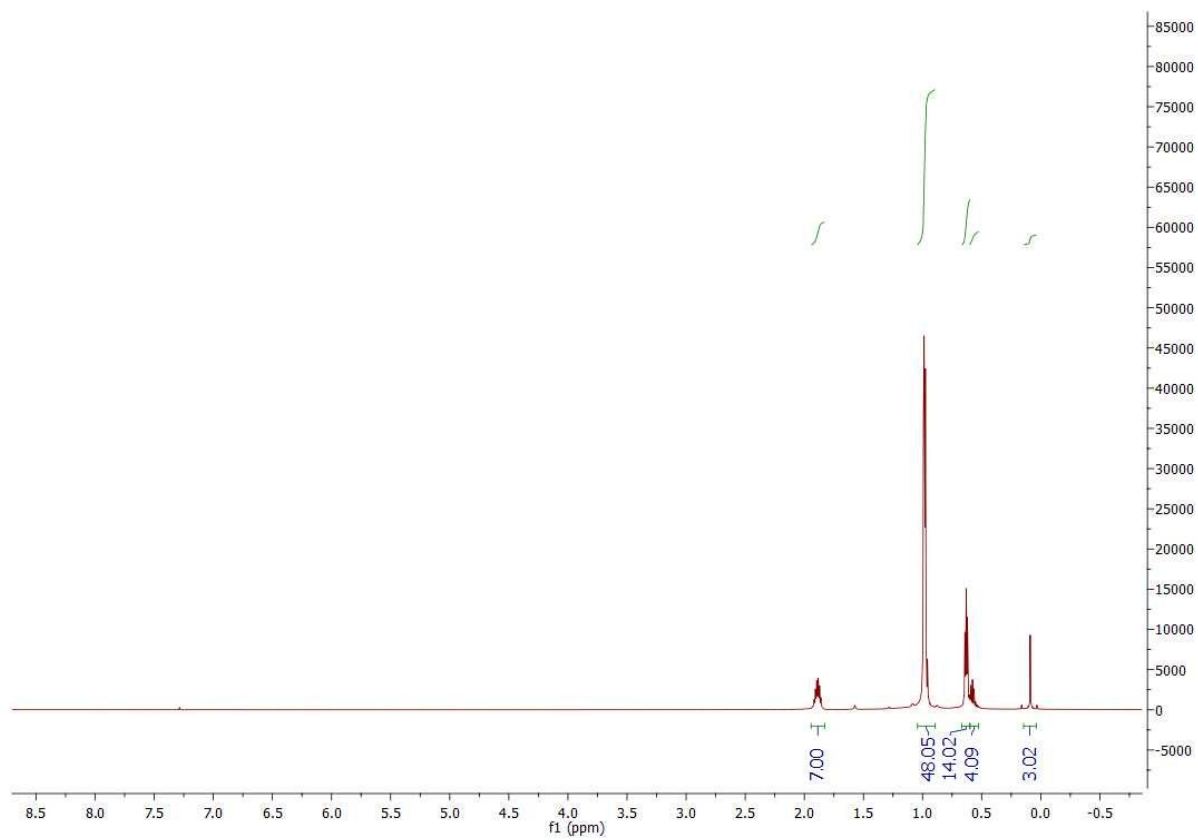


Figure 7 ^1H NMR (400 MHz) of compound (3).

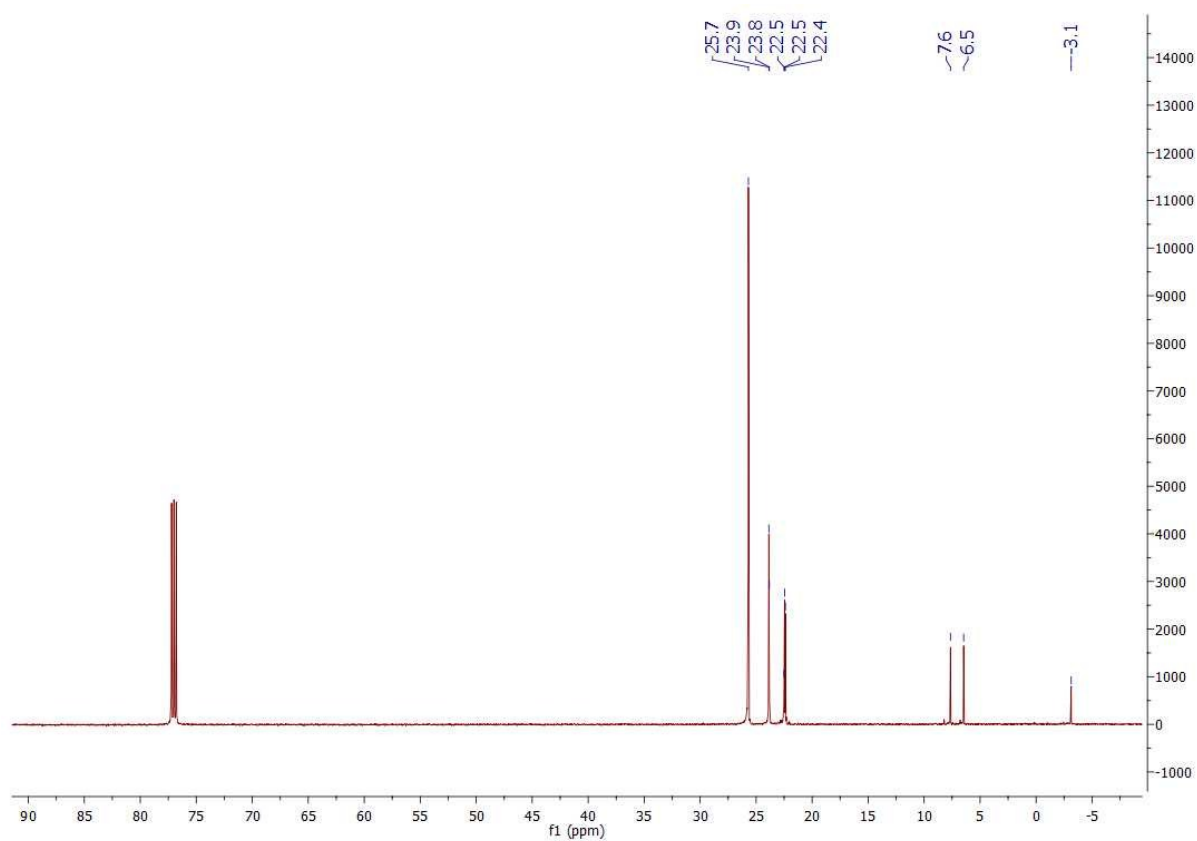


Figure 8 ^{13}C NMR (101 MHz) of compound (3).

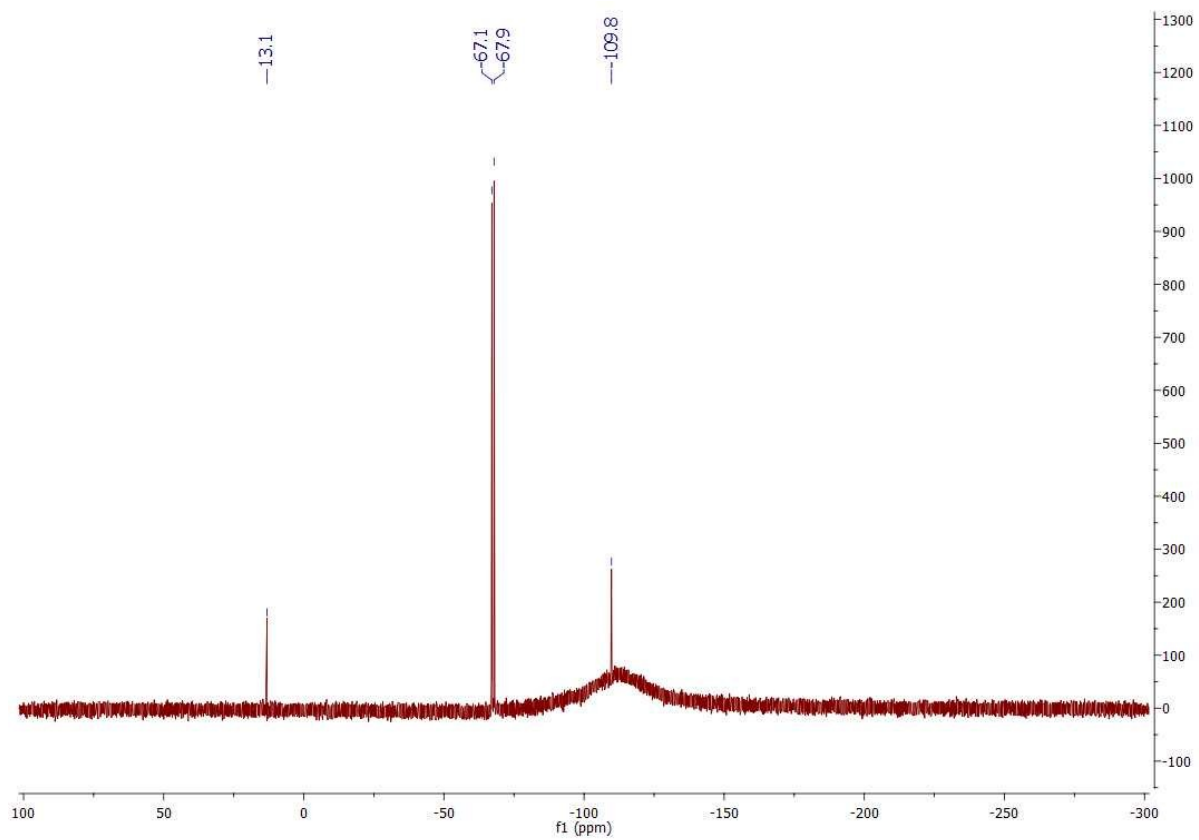
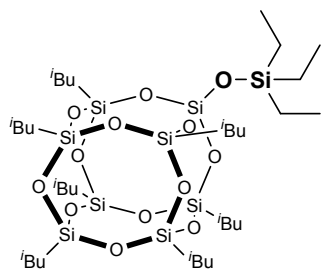


Figure 9 ^{29}Si NMR (79 MHz) of compound (3).



Compound **(4)** was obtained as solid in 90% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.52-0.58 (m, 6H), 0.60-0.65 (m, 14H), 0.94-1.02 (m, 51H), 1.82-1.94 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 5.8, 6.5, 22.4, 22.5, 22.5, 23.8, 23.9, 25.7.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 13.1, -67.1, -67.9, -109.9.

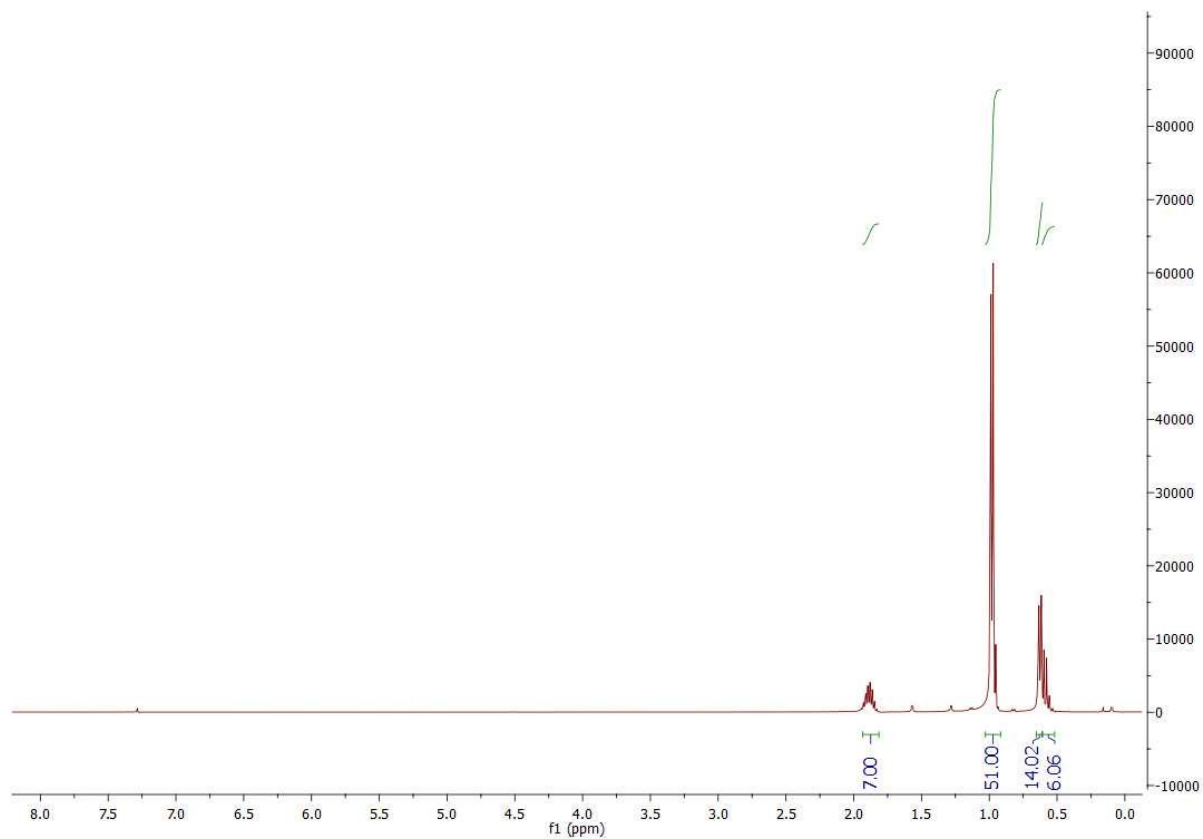


Figure 10 ^1H NMR (400 MHz) of compound (4).

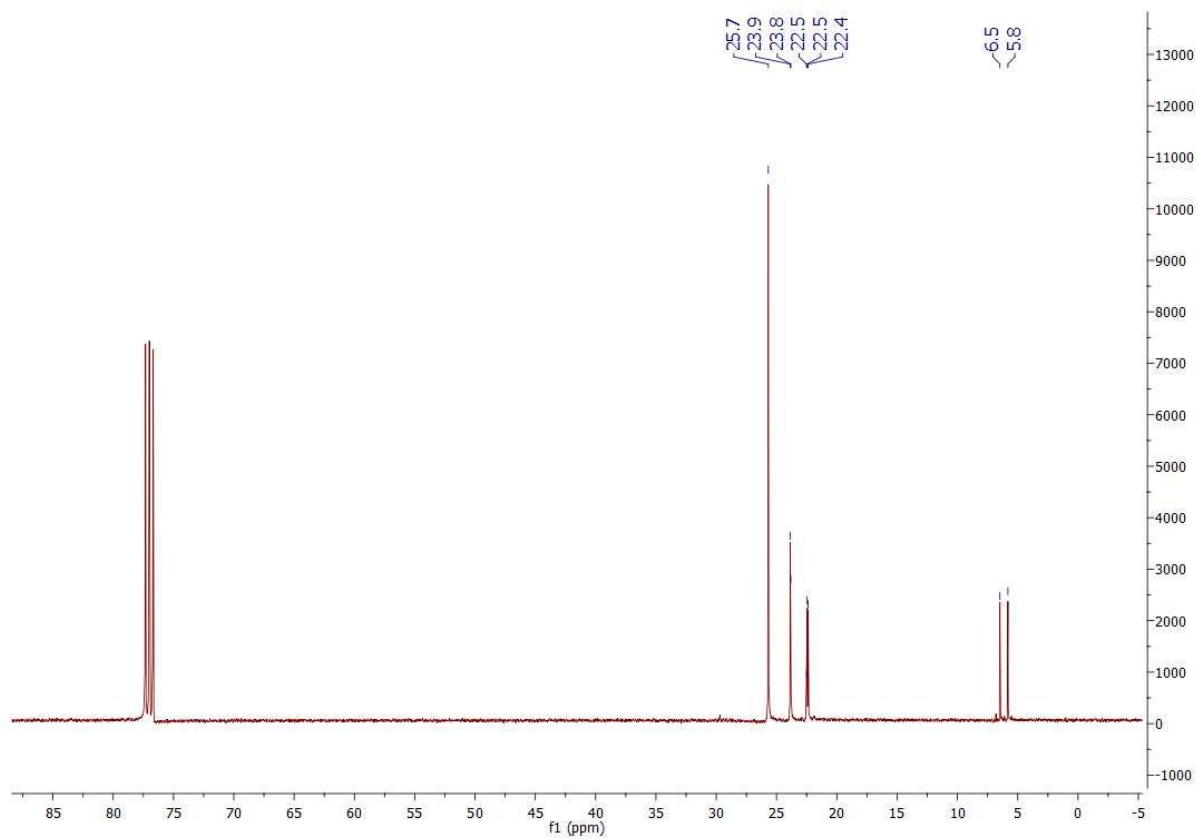


Figure 11 ^{13}C NMR (101 MHz) of compound (4).

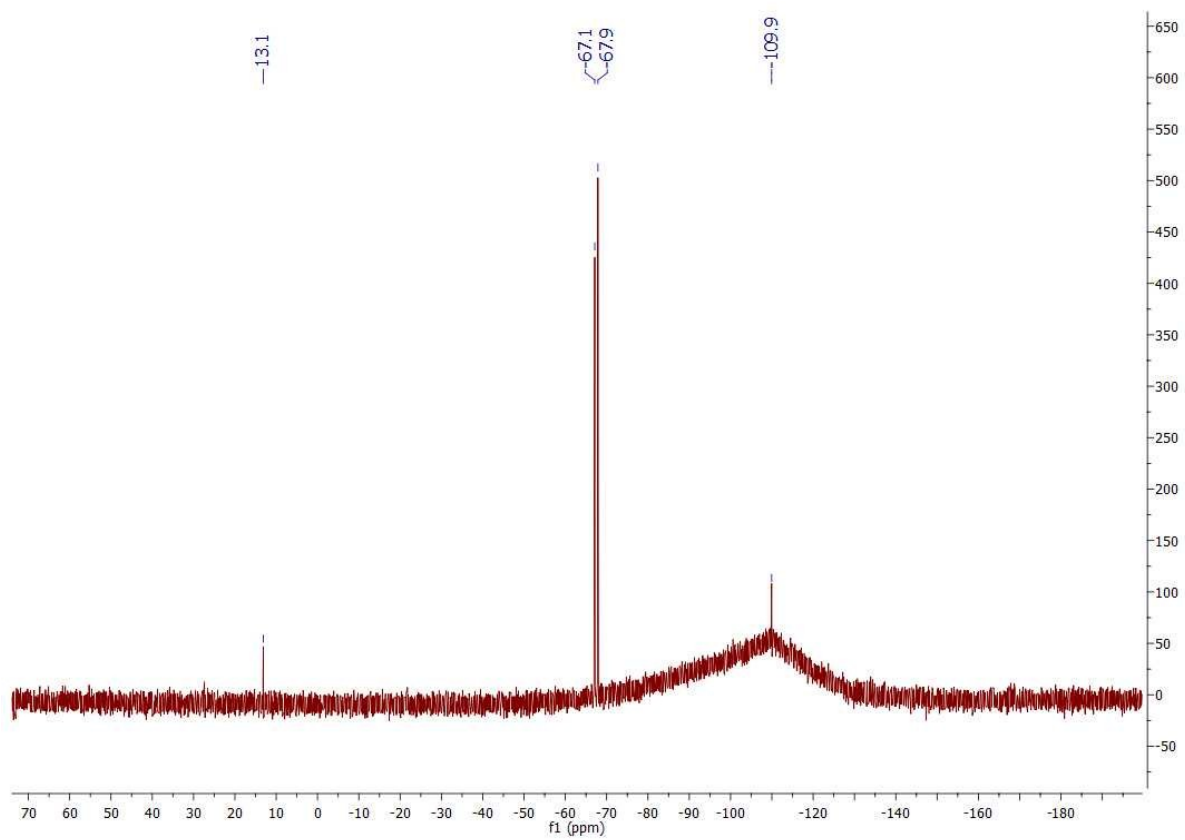
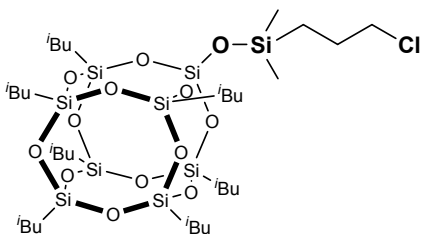


Figure 12 ^{29}Si NMR (79 MHz) of compound (4).



Compound **(5)** was obtained as oil in 88% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.10-0.20 (m, 6H), 0.58-0.66 (m, 14H), 0.66-0.73 (m, 12H), 0.93-1.03 (m, 42H), 1.50-1.60 (m, 2H), 1.82-1.94 (m, 7H), 3.52 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = -0.4, 15.5, 22.4, 22.4, 22.5, 23.8, 23.9, 25.7, 26.8, 47.8.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 10.8, -67.0, -67.9, -109.6.

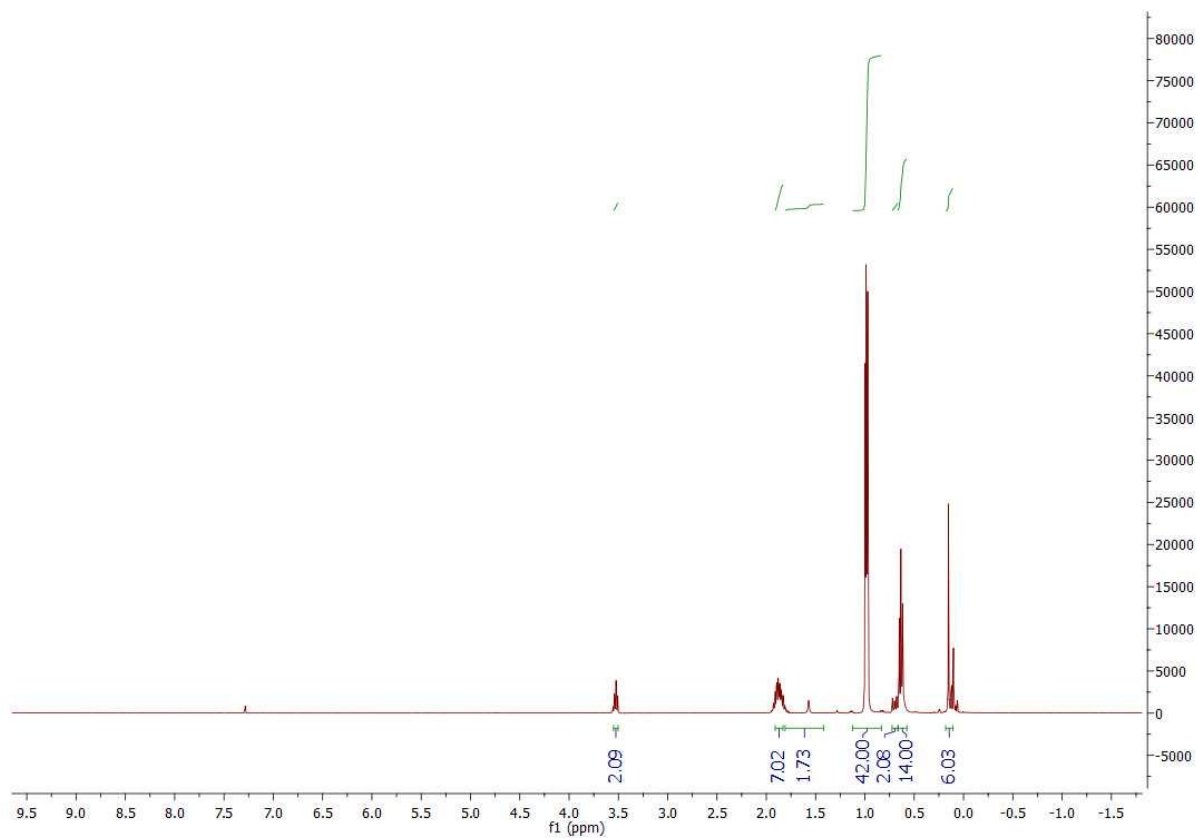


Figure 13 ^1H NMR (400 MHz) of compound (5).

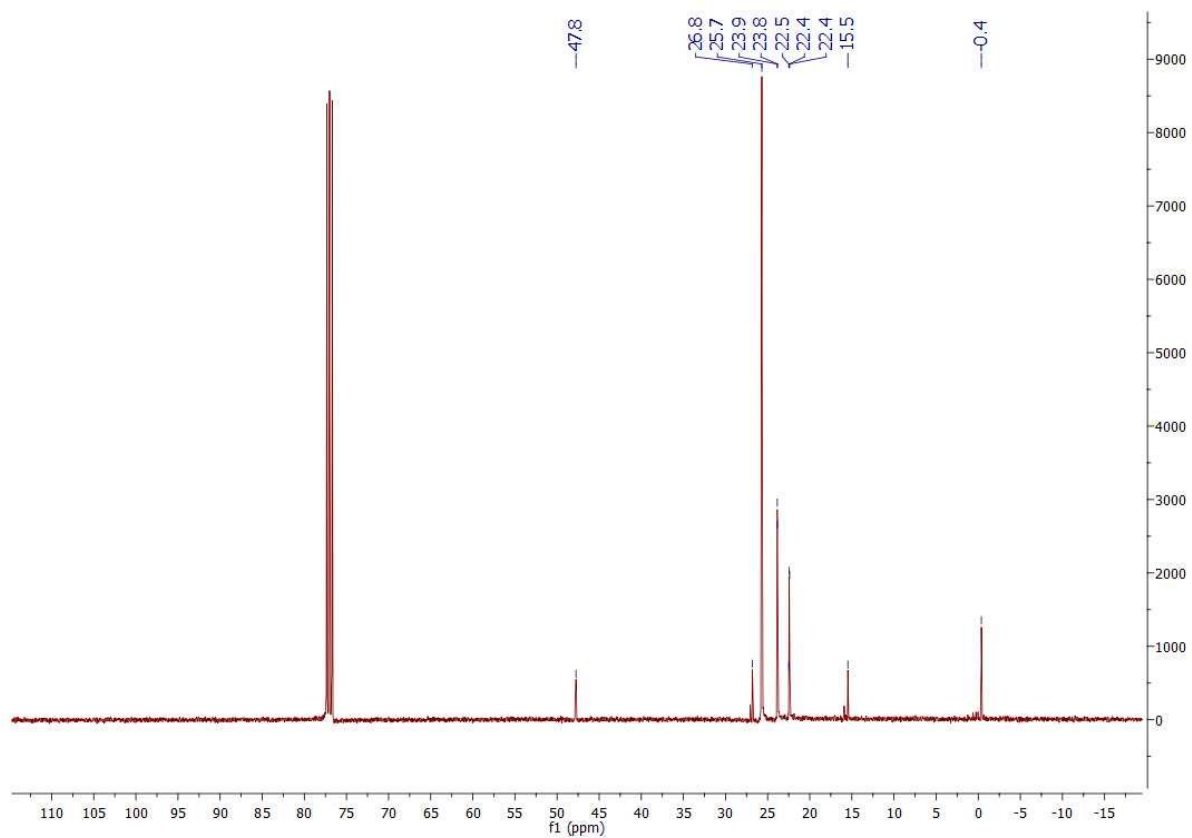


Figure 14 ^{13}C NMR (101 MHz) of compound (5).

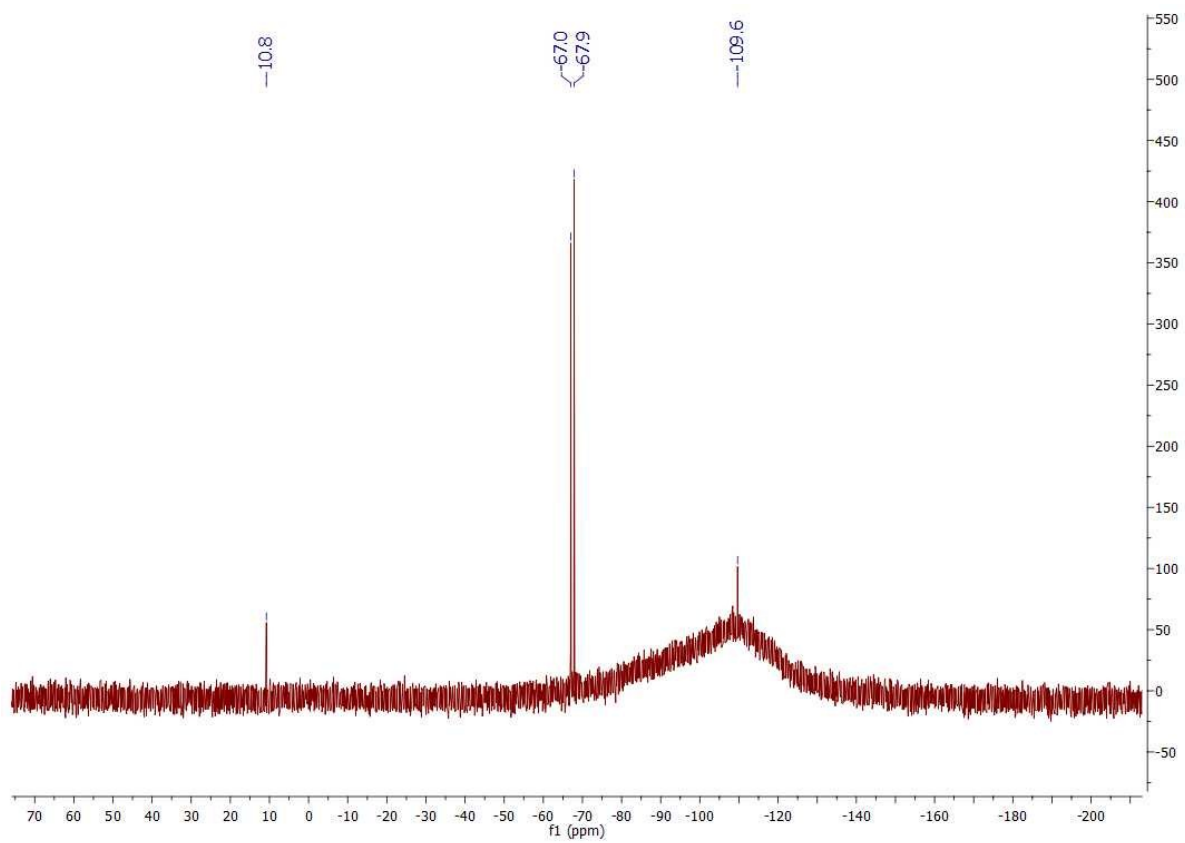
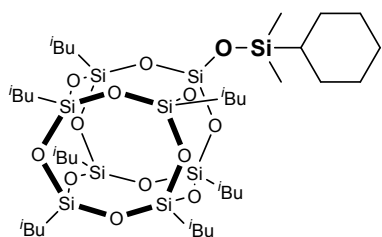


Figure 15 ^{29}Si NMR (79 MHz) of compound (5).



Compound **(6)** was obtained as oil in 91% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.01-0.11 (m, 6H), 0.57-0.69 (m, 14H), 0.90-1.15 (m, 42H), 1.20-1.30 (m, 6H), 1.70-1.77 (m, 5H), 1.82-1.96 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = -2.3, -1.6, 22.5, 23.9, 25.7, 26.4, 26.8, 26.9, 27.0, 27.4, 27.9, 28.0.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 10.7, -67.1, -67.9, -109.9.

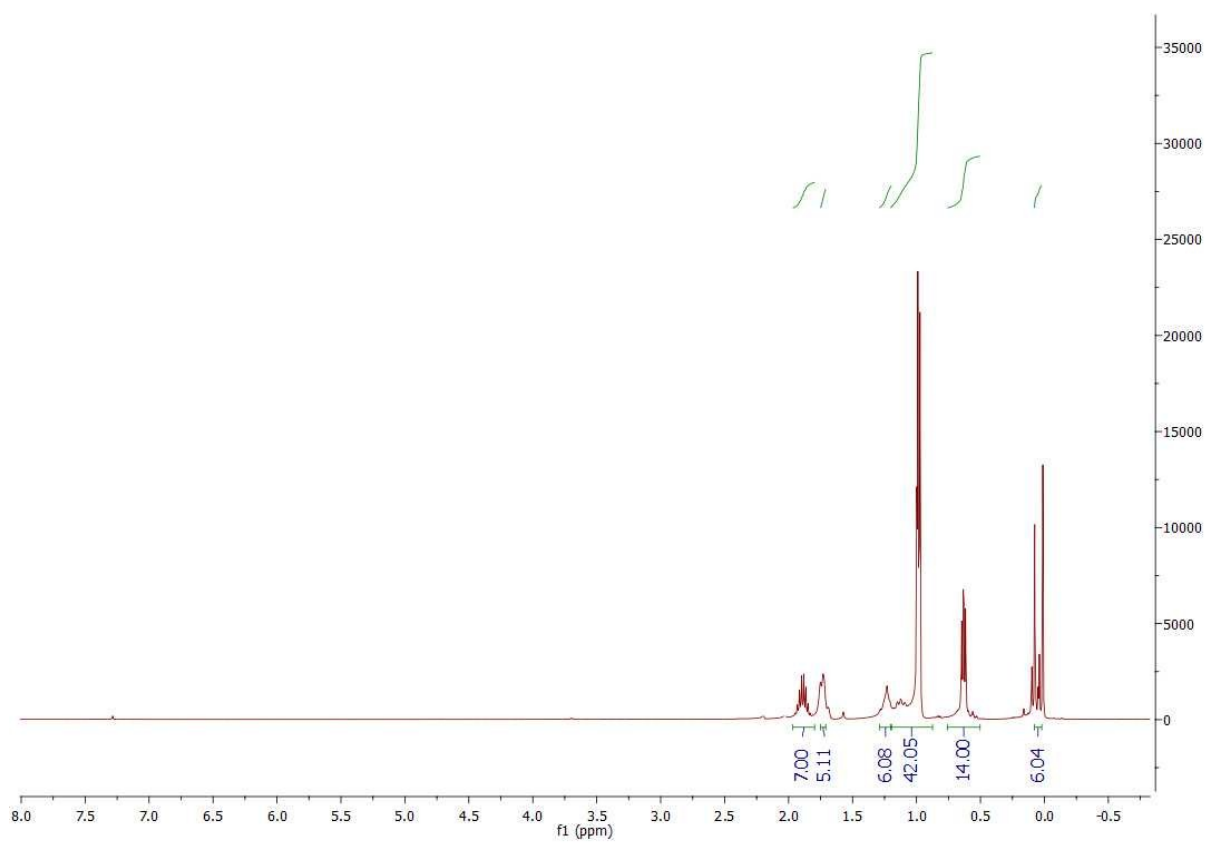


Figure 16 ^1H NMR (400 MHz) of compound (6).

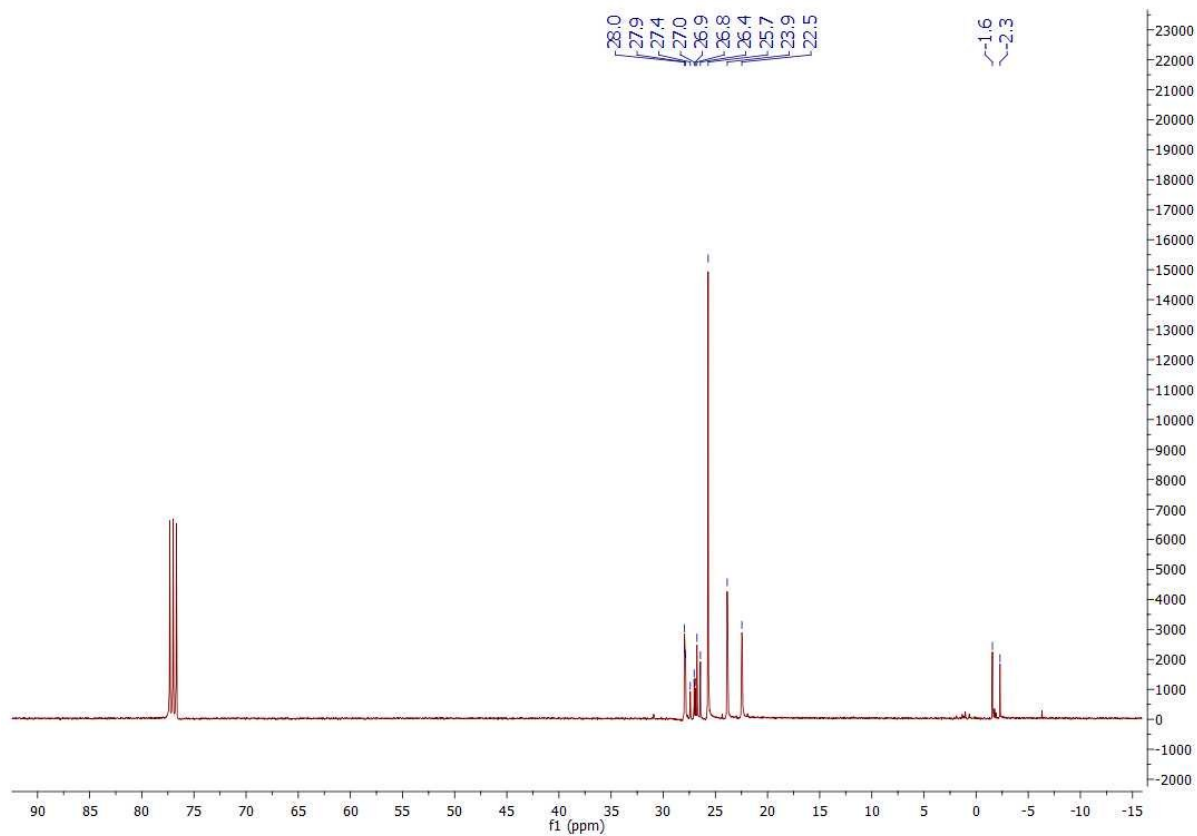


Figure 17 ^{13}C NMR (101 MHz) of compound (6).

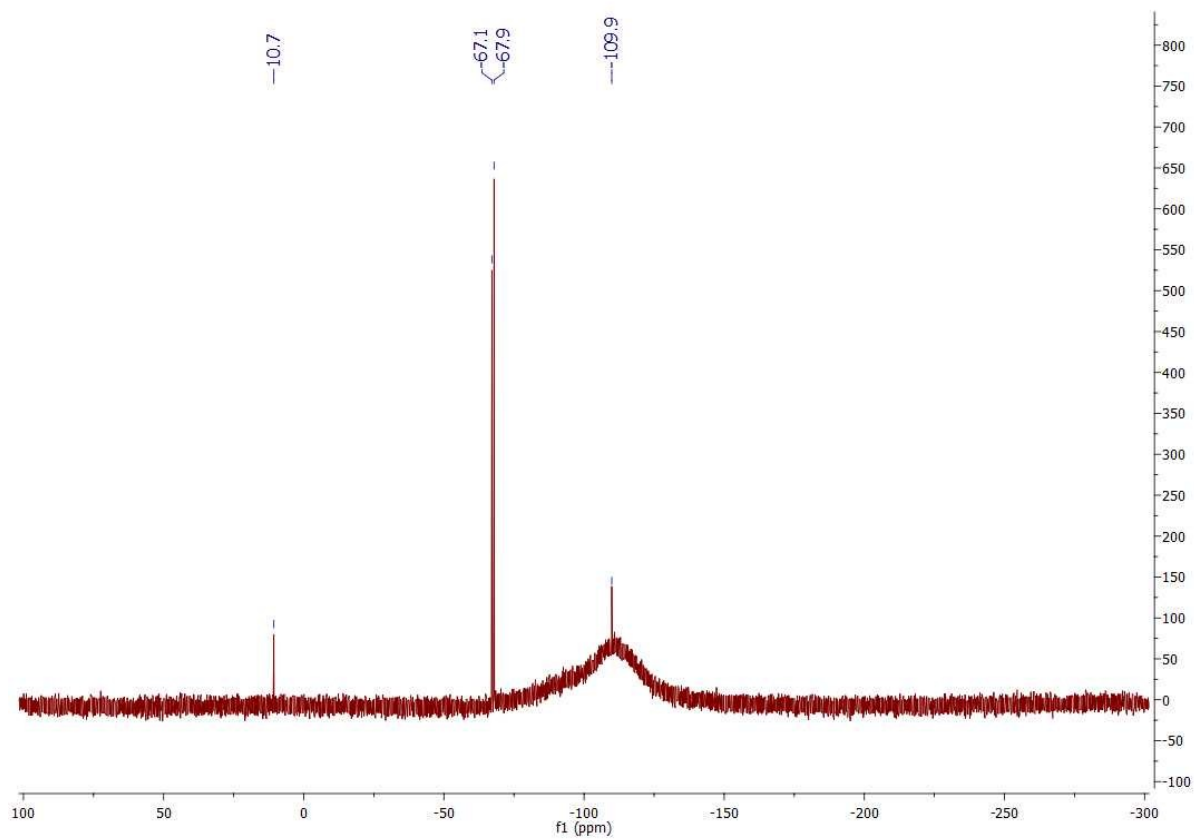
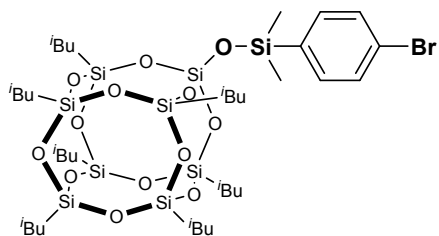


Figure 18 ^{29}Si NMR (79 MHz) of compound (6).



Compound **(7)** was obtained as solid in 87% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.05-0.45 (m, 6H), 0.58-0.68 (m, 14H), 0.93-1.05 (m, 42H), 1.79-1.99 (m, 7H), 7.37-7.54 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 0.3, 22.3, 22.4, 22.5, 23.8, 23.9, 25.7, 124.2, 130.8, 134.7, 137.8.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = -0.8, -67.0, -67.9, -109.6.

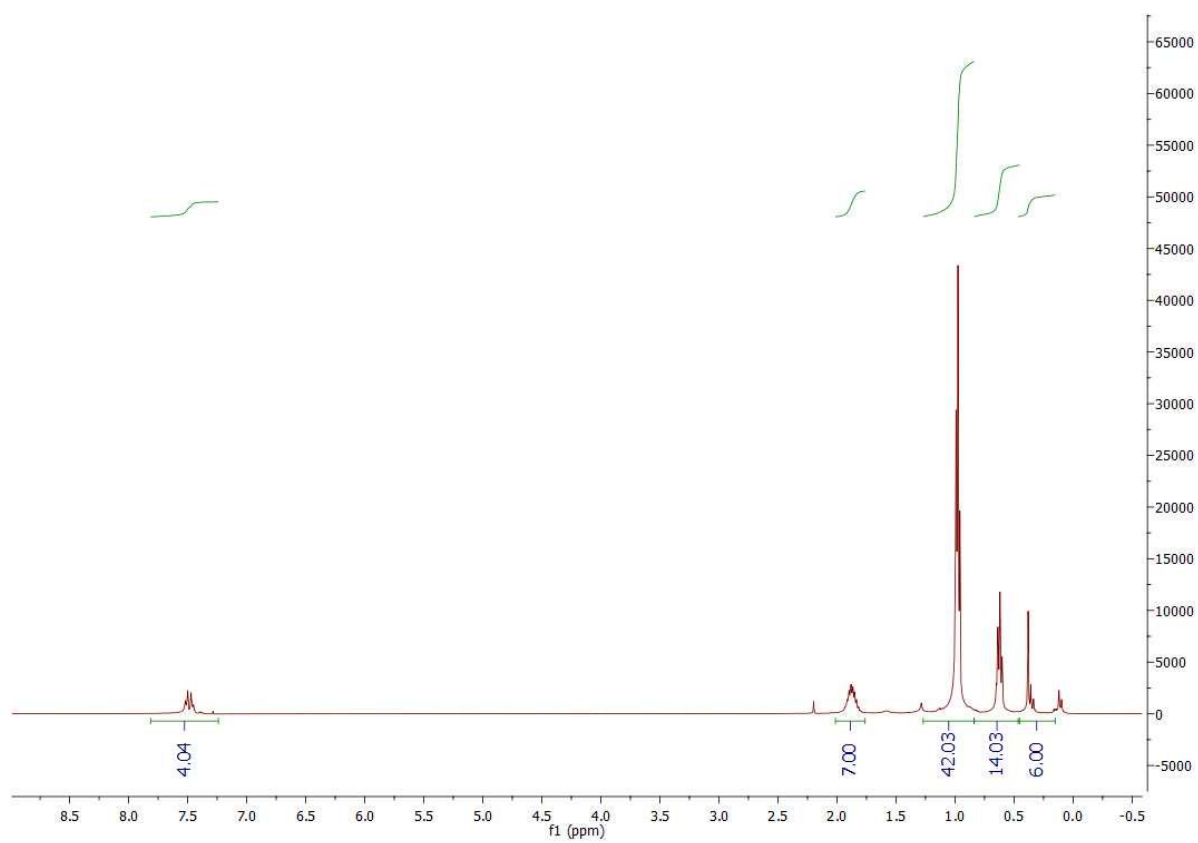


Figure 19 ^1H NMR (400 MHz) of compound (7).

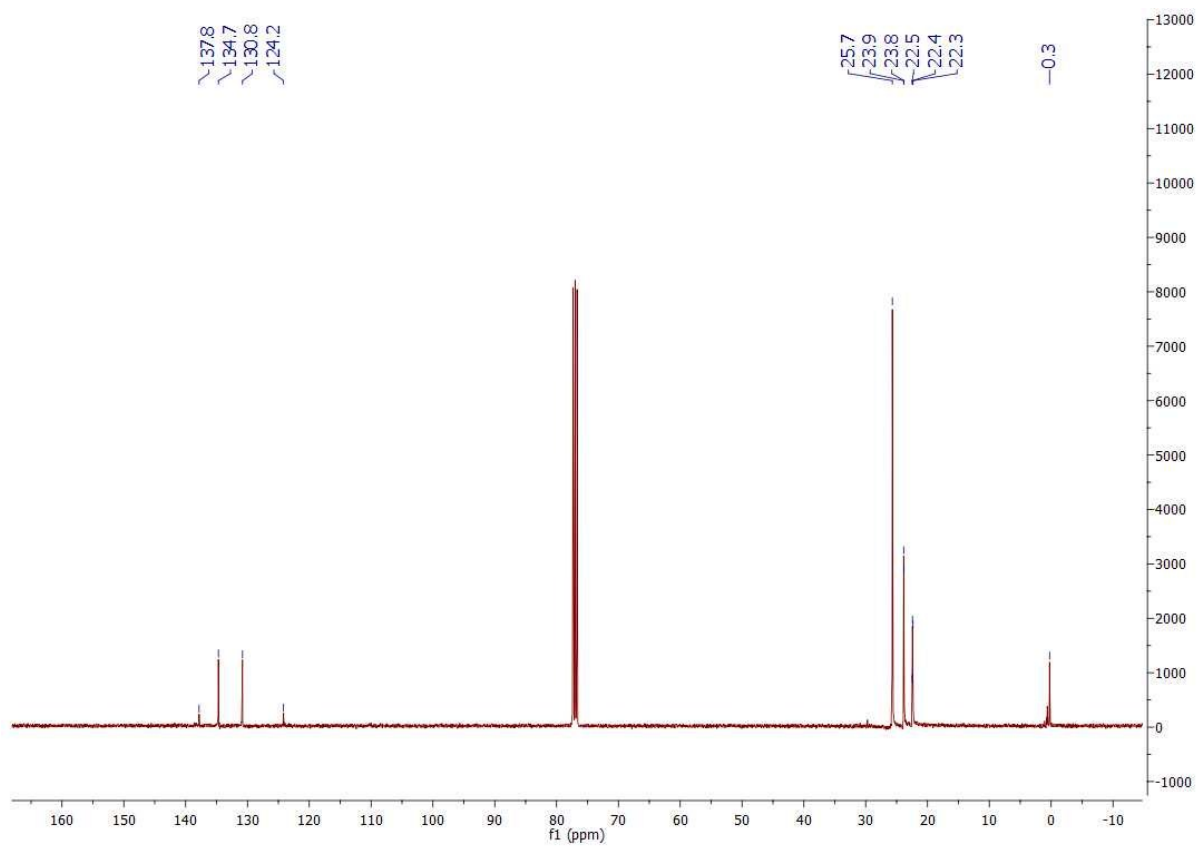


Figure 20 ^{13}C NMR (101 MHz) of compound (7).

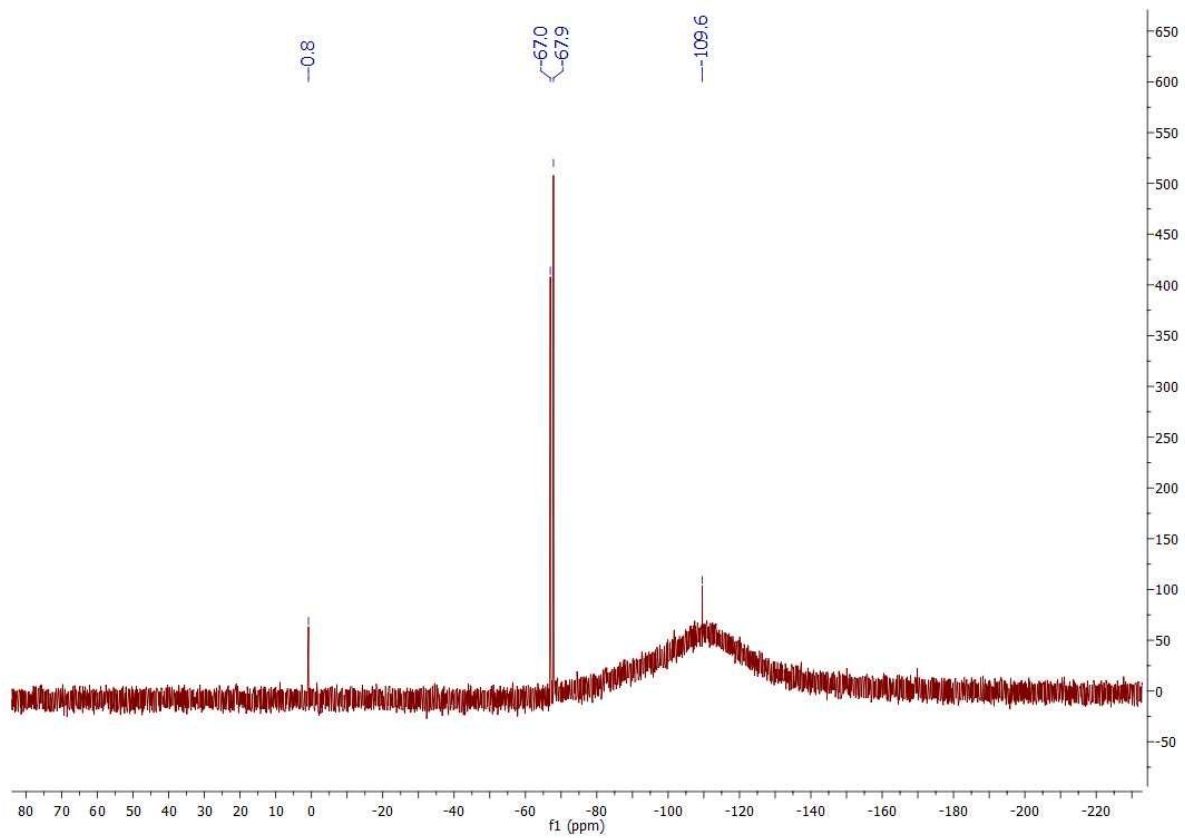
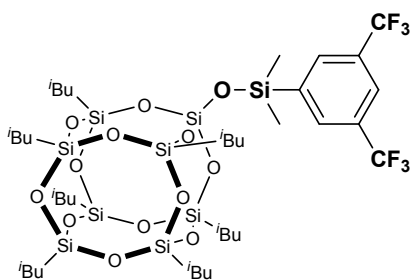


Figure 21 ^{29}Si NMR (79 MHz) of compound (7).



Compound **(8)** was obtained as oil in 95% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.45-0.48 (m, 6H), 0.57-0.67 (m, 14H), 0.90-1.06 (m, 42H), 1.76-1.98 (m, 7H), 7.85-8.05 (m, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 0.2, 22.2, 22.4, 23.8, 23.8, 25.5, 25.7, 119.5, 122.2, 123.1, 124.9, 127.7, 130.3, 130.6, 130.9, 131.2, 132.8, 142.5.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 0.4, -66.8, -67.8, -109.2.

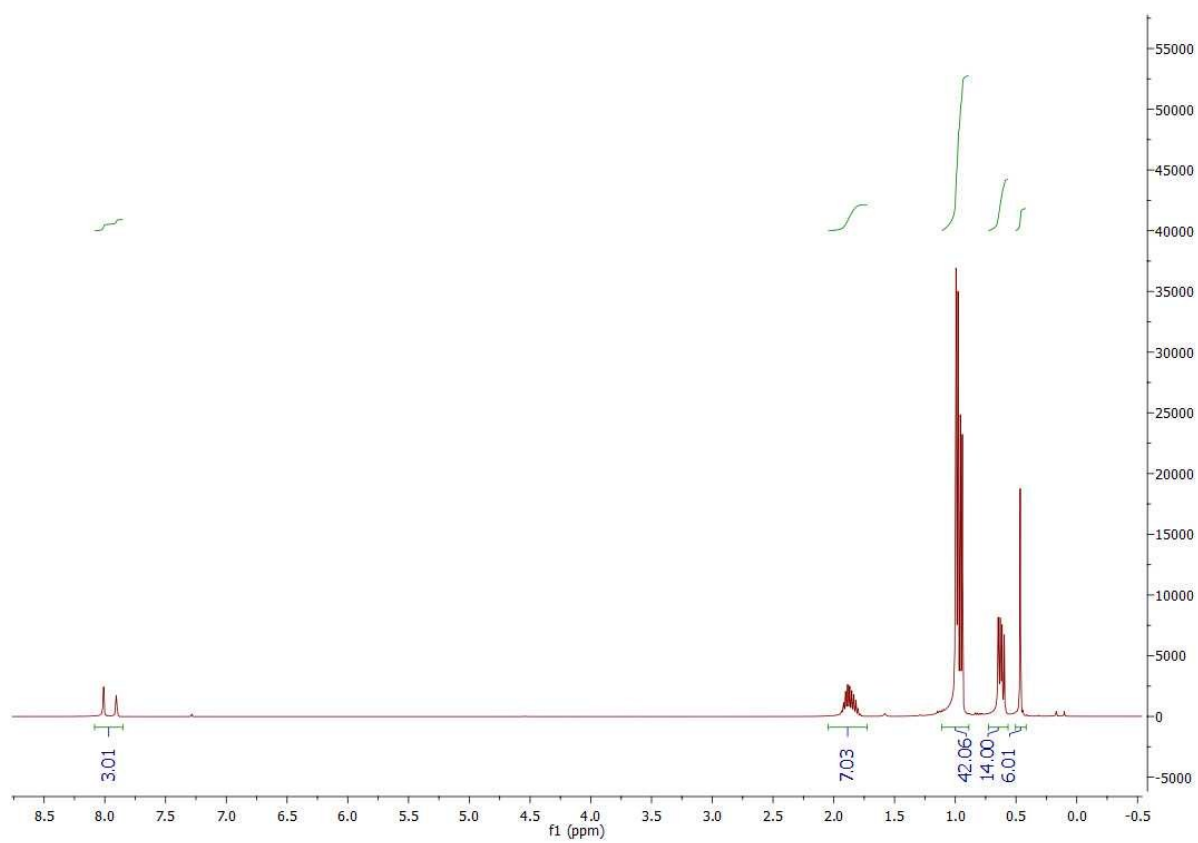


Figure 22 ^1H NMR (400 MHz) of compound (8).

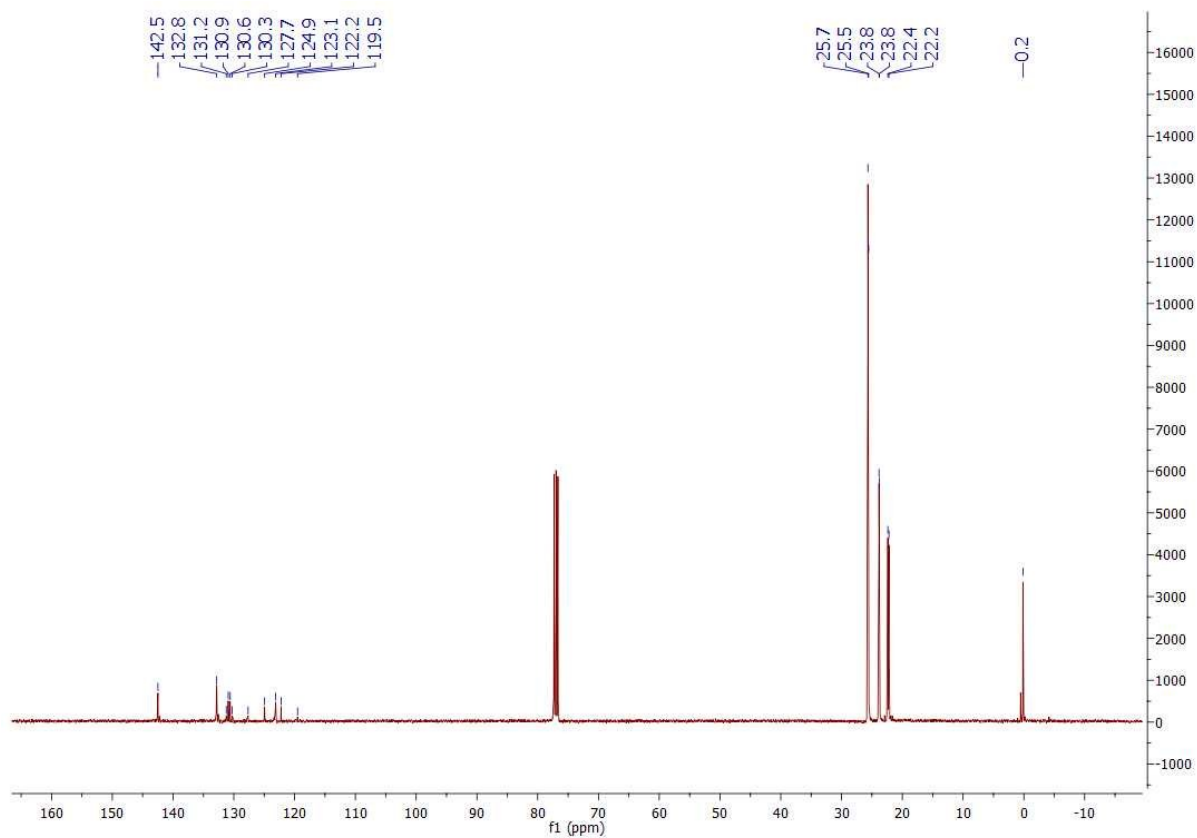
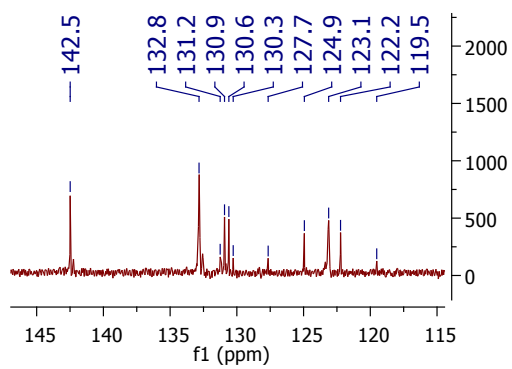


Figure 23 ^{13}C NMR (101 MHz) of compound **(8)**.



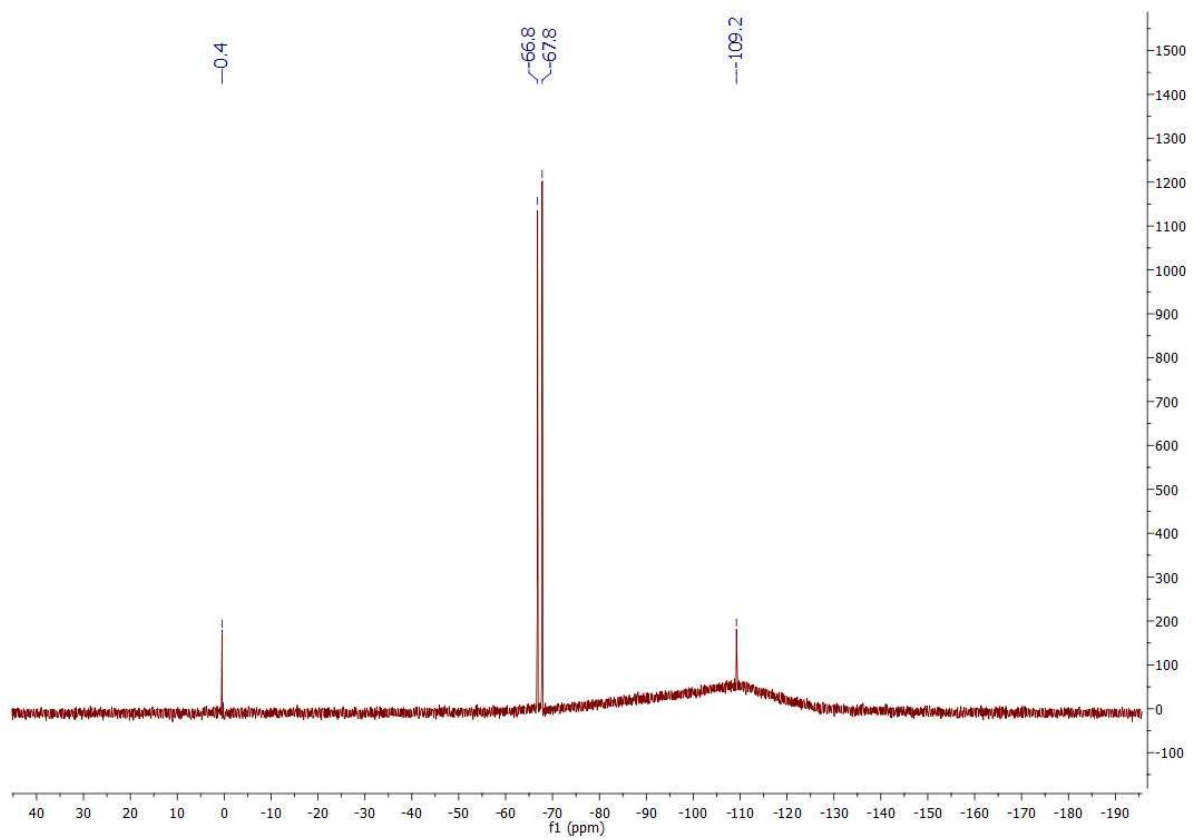
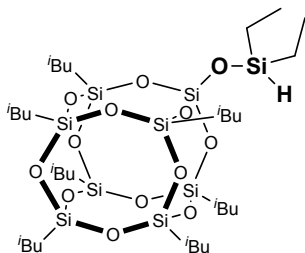


Figure 24 ^{29}Si NMR (79 MHz) of compound (8).



Compound (**9**) was obtained as solid in 94% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.58-0.72 (m, 18H), 0.95-1.04 (m, 48H), 1.82-1.96 (m, 7H), 4.48-4.54 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 6.3, 6.5, 22.3, 22.4, 22.5, 23.8, 23.9, 25.7.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 2.6, -67.0, -67.9, -109.2.

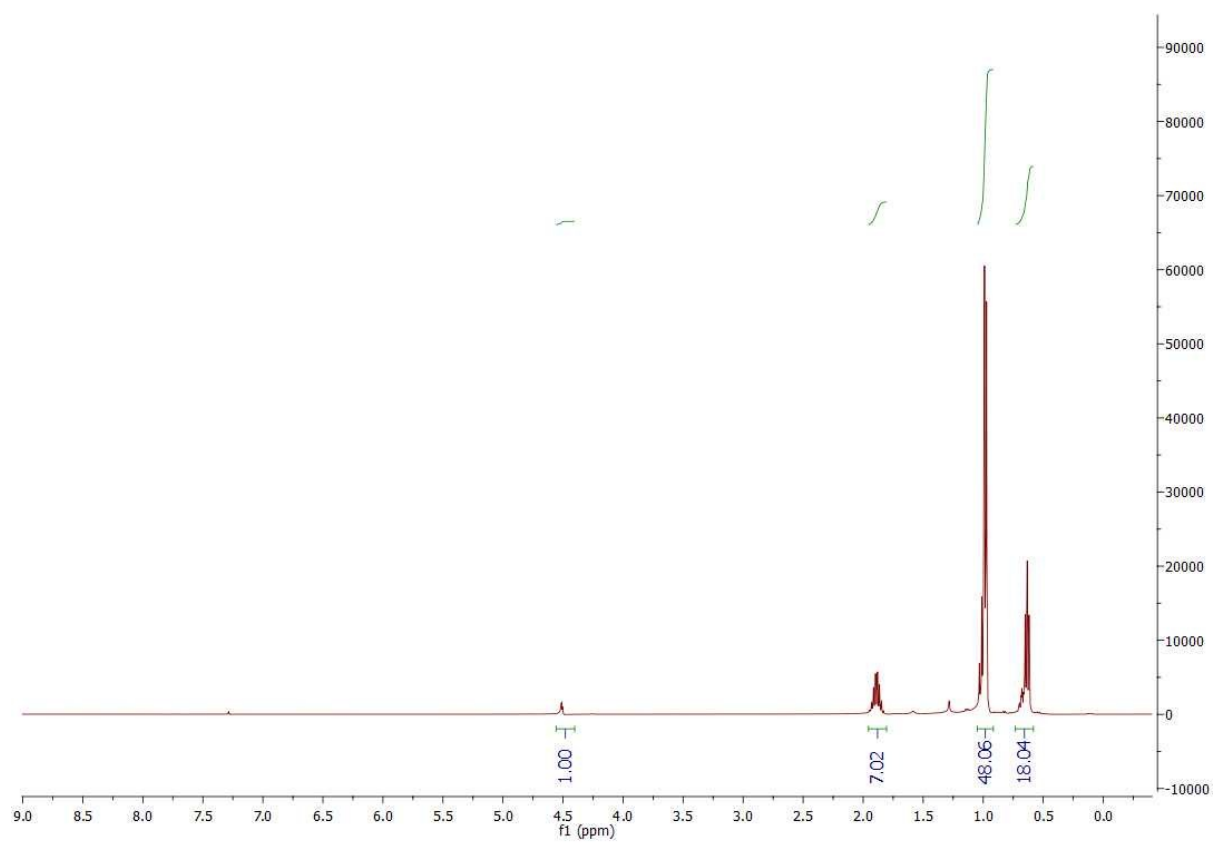


Figure 25 ^1H NMR (400 MHz) of compound (9).

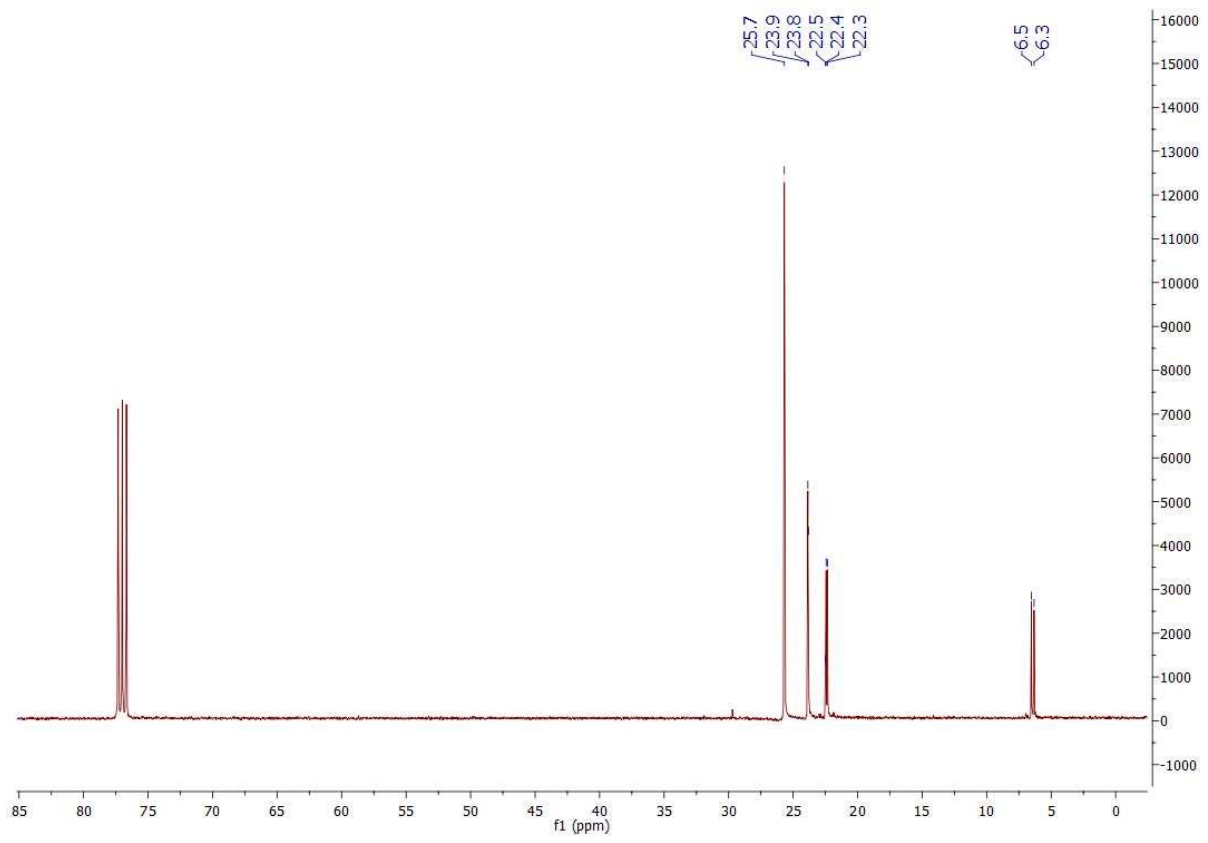


Figure 26 ¹³C NMR (101 MHz) of compound (9).

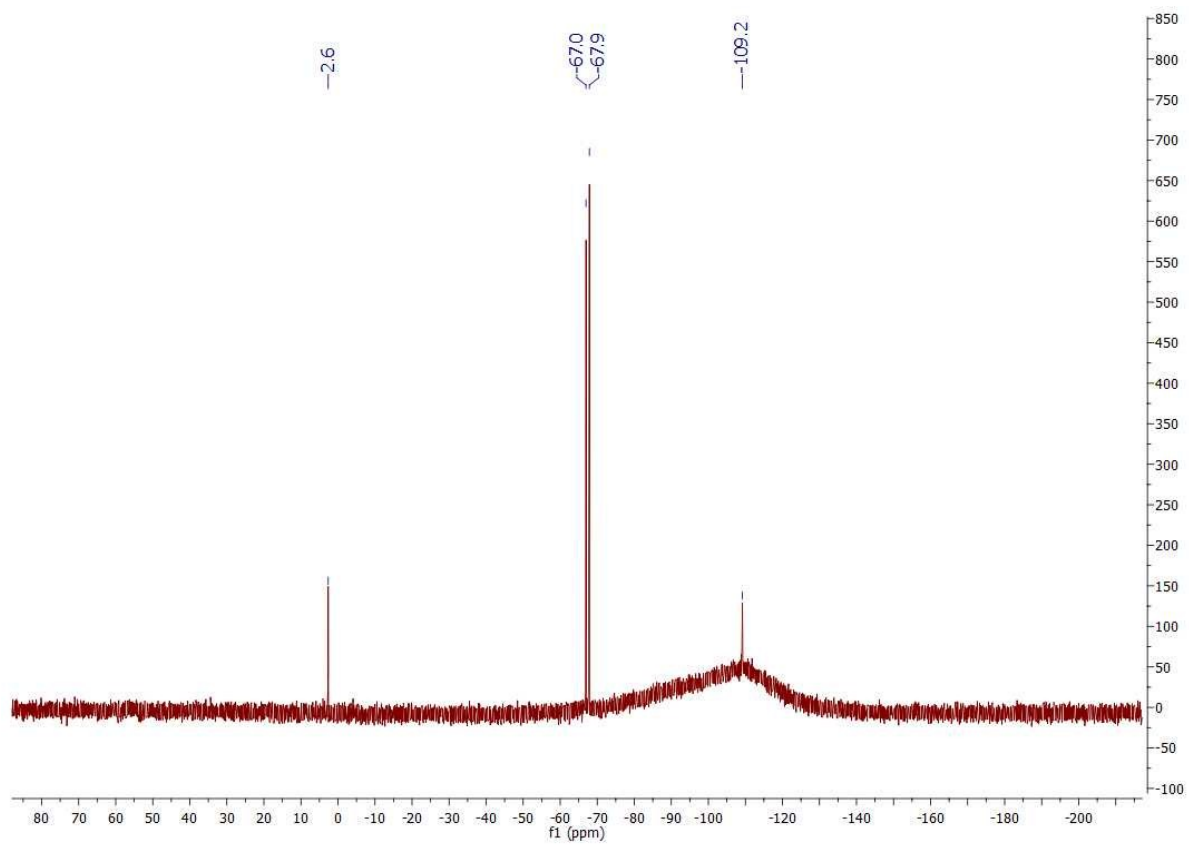
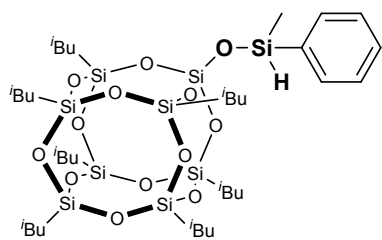


Figure 27 ^{29}Si NMR (79 MHz) of compound (9).



Compound **(10)** was obtained as oil in 97% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.46-0.50 (m, 3H), 0.59-0.67 (m, 14H), 0.93-1.02 (m, 42H), 1.79-1.95 (m, 7H), 5.11-5.17 (m, 1H), 7.35-7.56 (m, 5H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = -0.9, 22.3, 22.4, 23.8, 23.9, 25.7, 25.7, 127.8, 129.9, 133.4, 136.7.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = -12.2, -66.9, -67.9, -109.1.

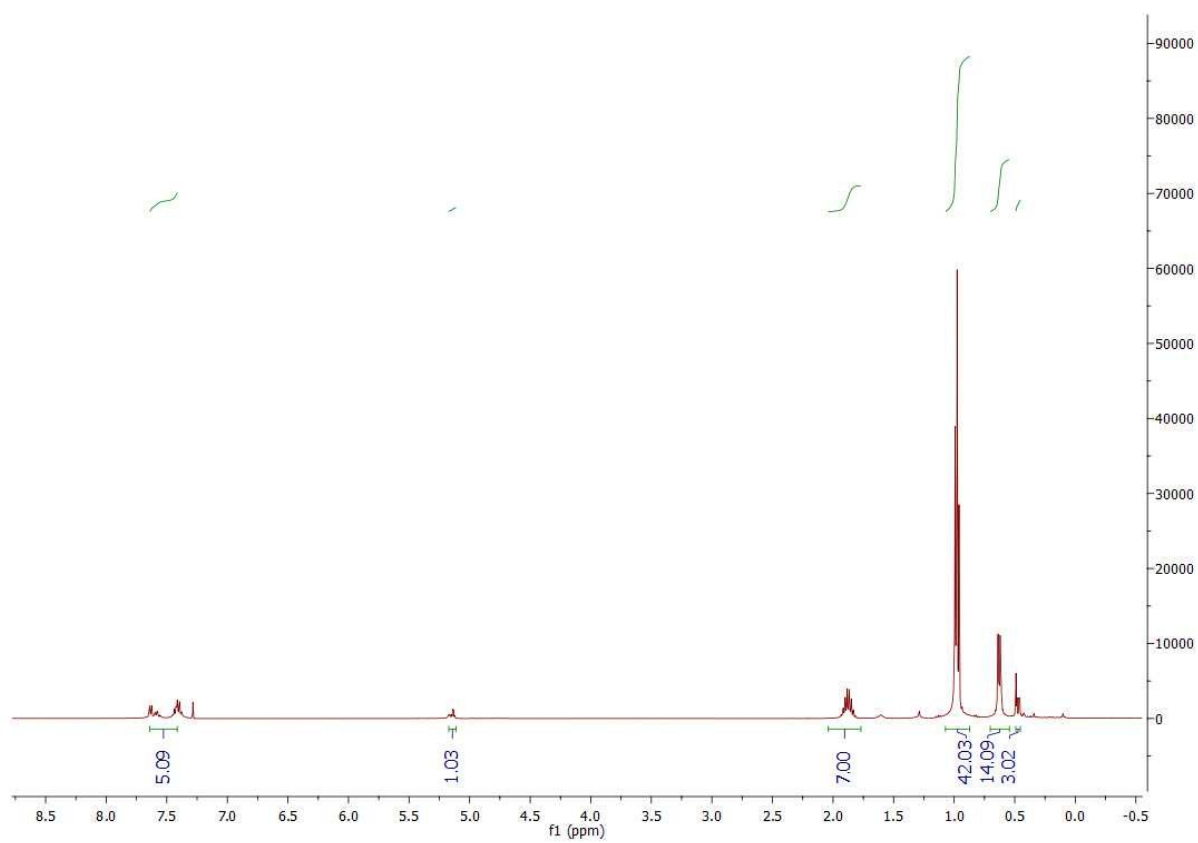


Figure 28 ^1H NMR (400 MHz) of compound (10).

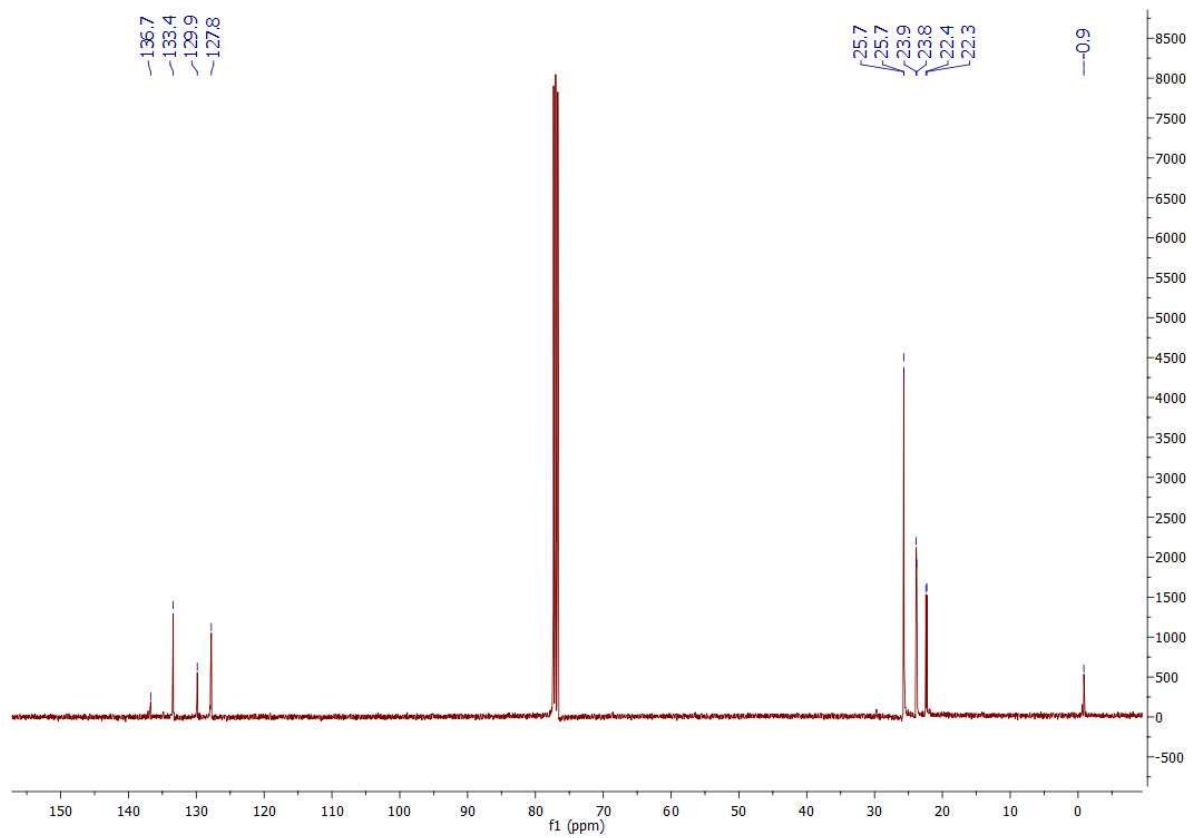


Figure 29 ^{13}C NMR (101 MHz) of compound (10).

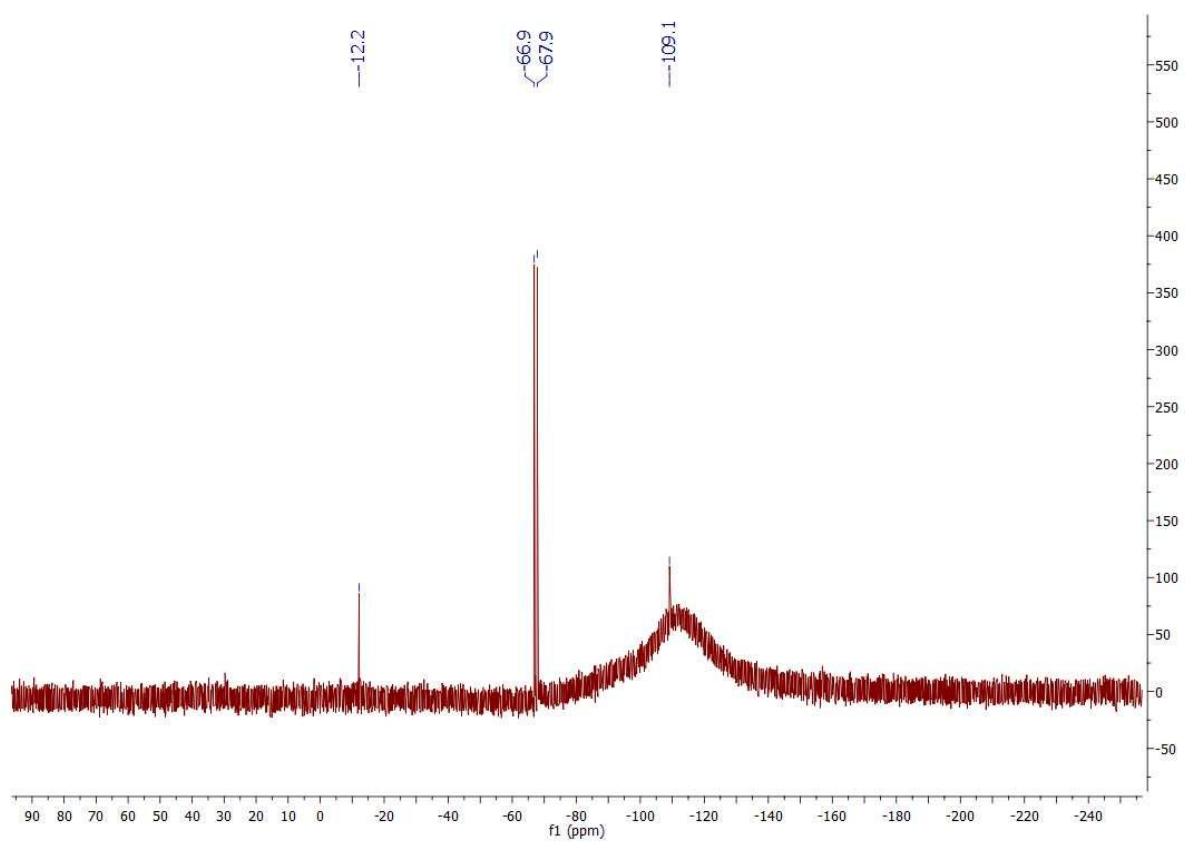
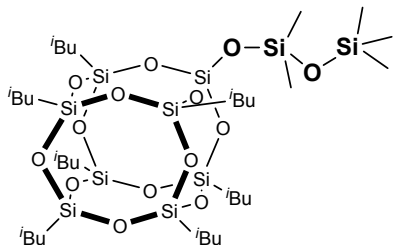


Figure 30 ^{29}Si NMR (79 MHz) of compound (10).



Compound **(11)** was obtained as oil in 89% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.08-0.16 (m, 15H), 0.60-0.67 (m, 14H), 0.96-1.01 (m, 42H), 1.81--1.95 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 1.0, 1.3, 22.4, 22.5, 22.5, 23.8, 23.9, 25.7.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 11.3, -21.9, -67.1, -67.9, -109.6.

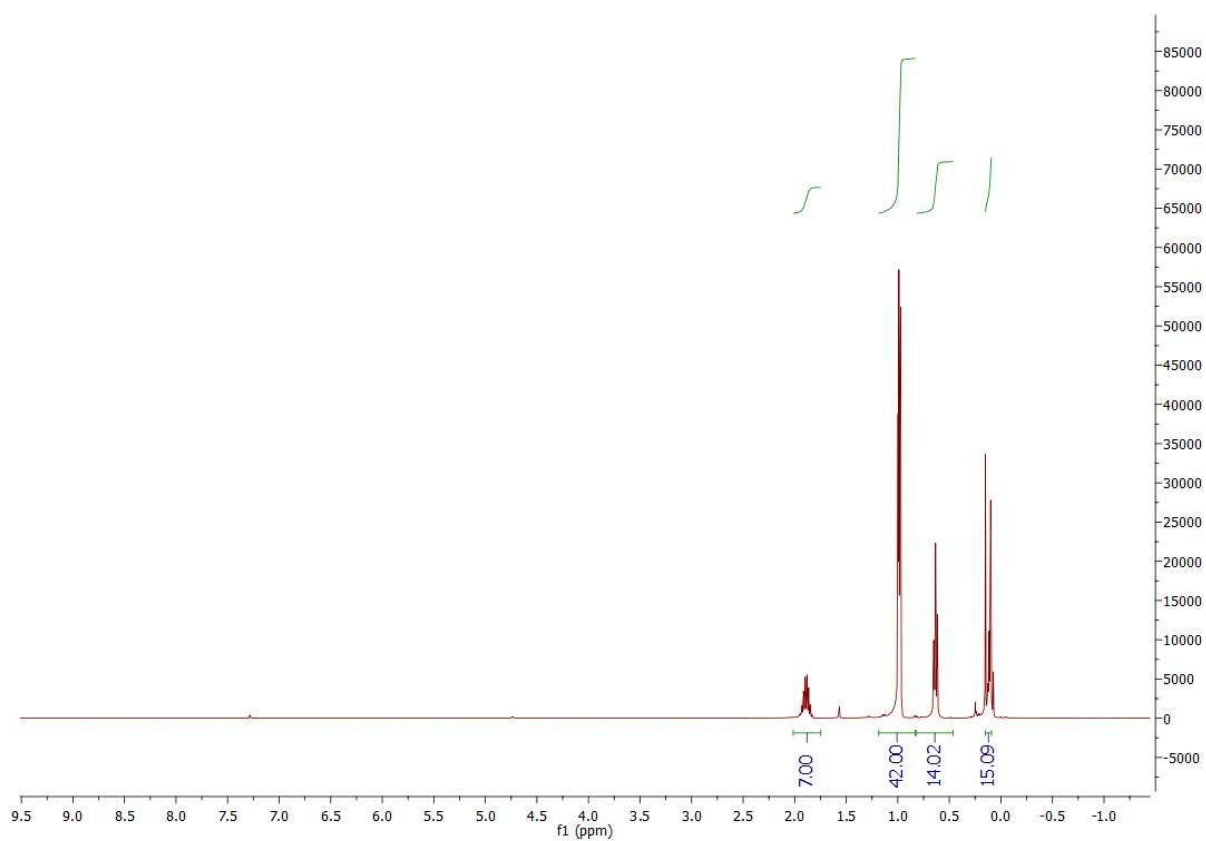


Figure 31 ^1H NMR (400 MHz) of compound (**11**).

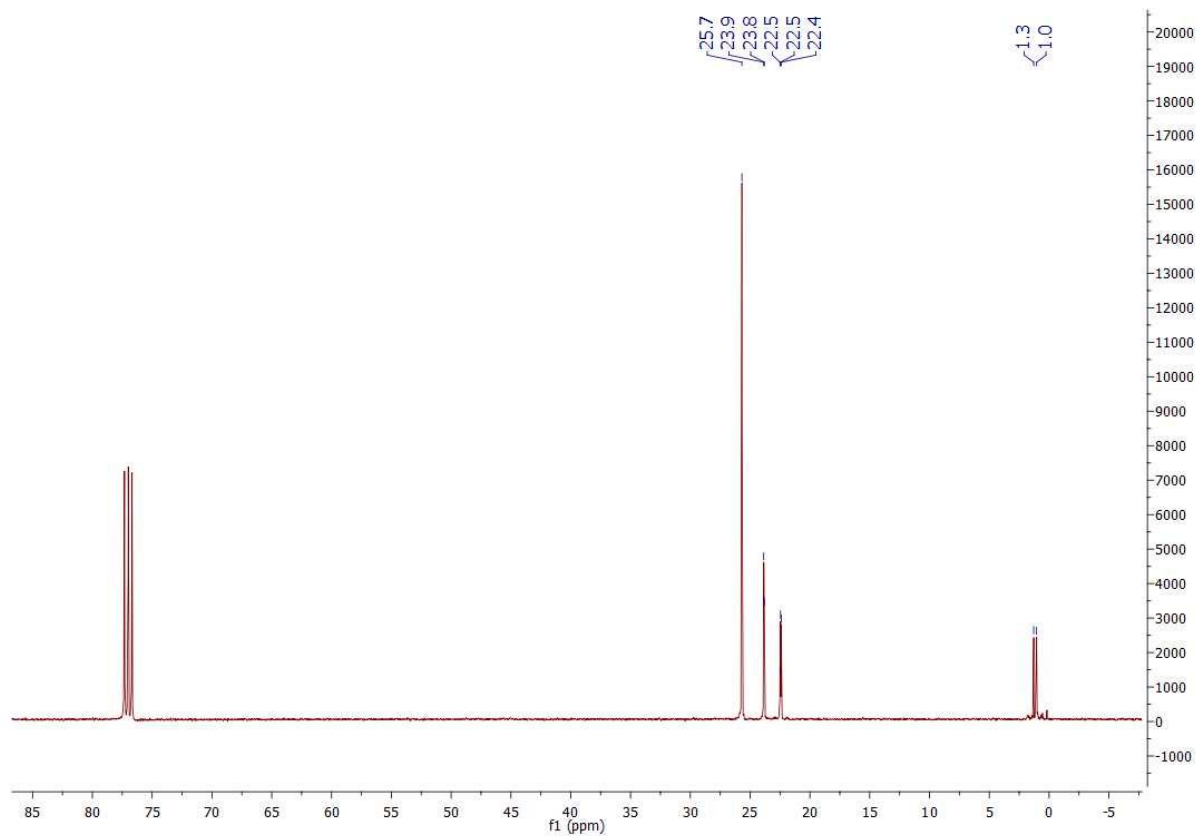


Figure 32 ^{13}C NMR (101 MHz) of compound (11).

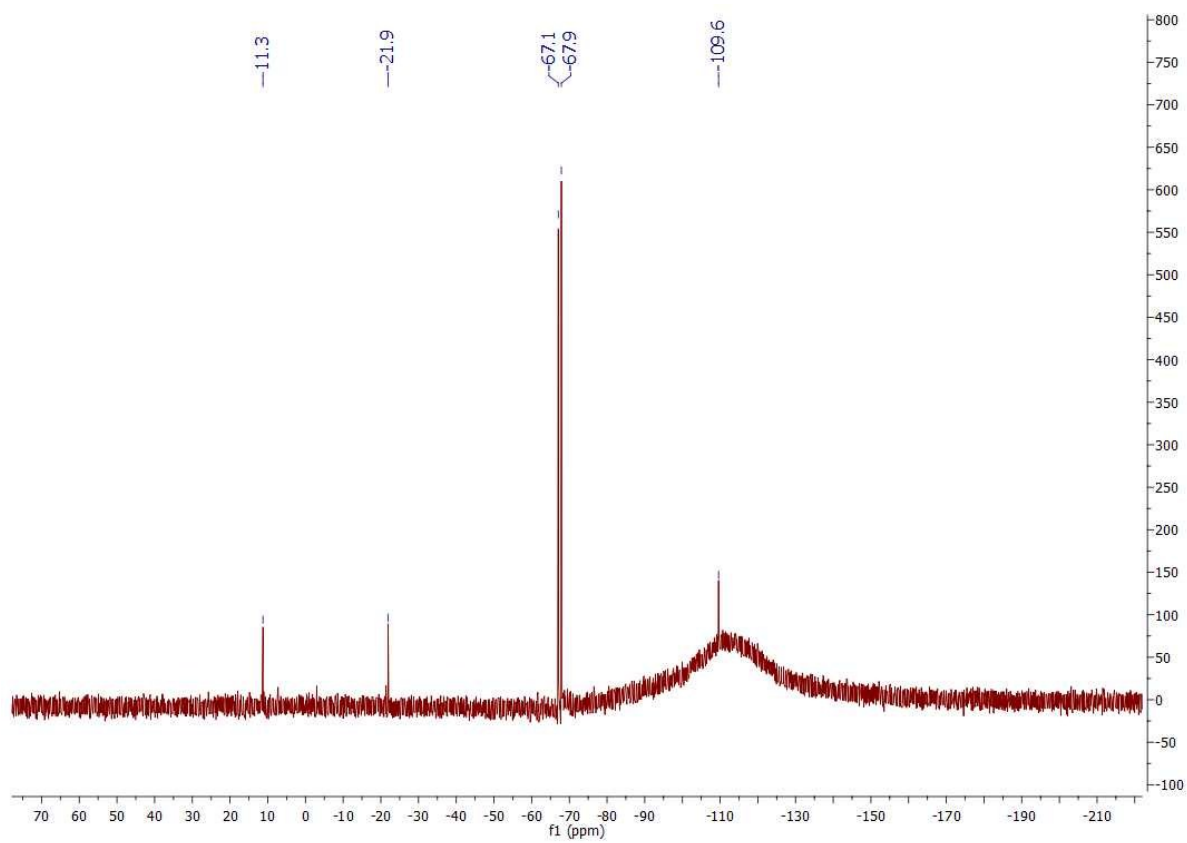
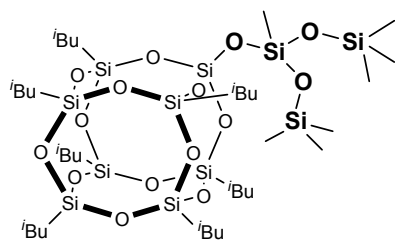


Figure 33 ^{29}Si NMR (79 MHz) of compound (11).



Compound **(12)** was obtained as oil in 90% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.07-0.26 (m, 21H), 0.59-0.67 (m, 14H), 0.93-1.02 (m, 42H), 1.83-1.94 (m, 7H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 1.3, 1.6, 22.4, 22.5, 22.5, 23.8, 23.9, 25.7.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 11.3, -66.9, -67.1, -67.9, -109.6.

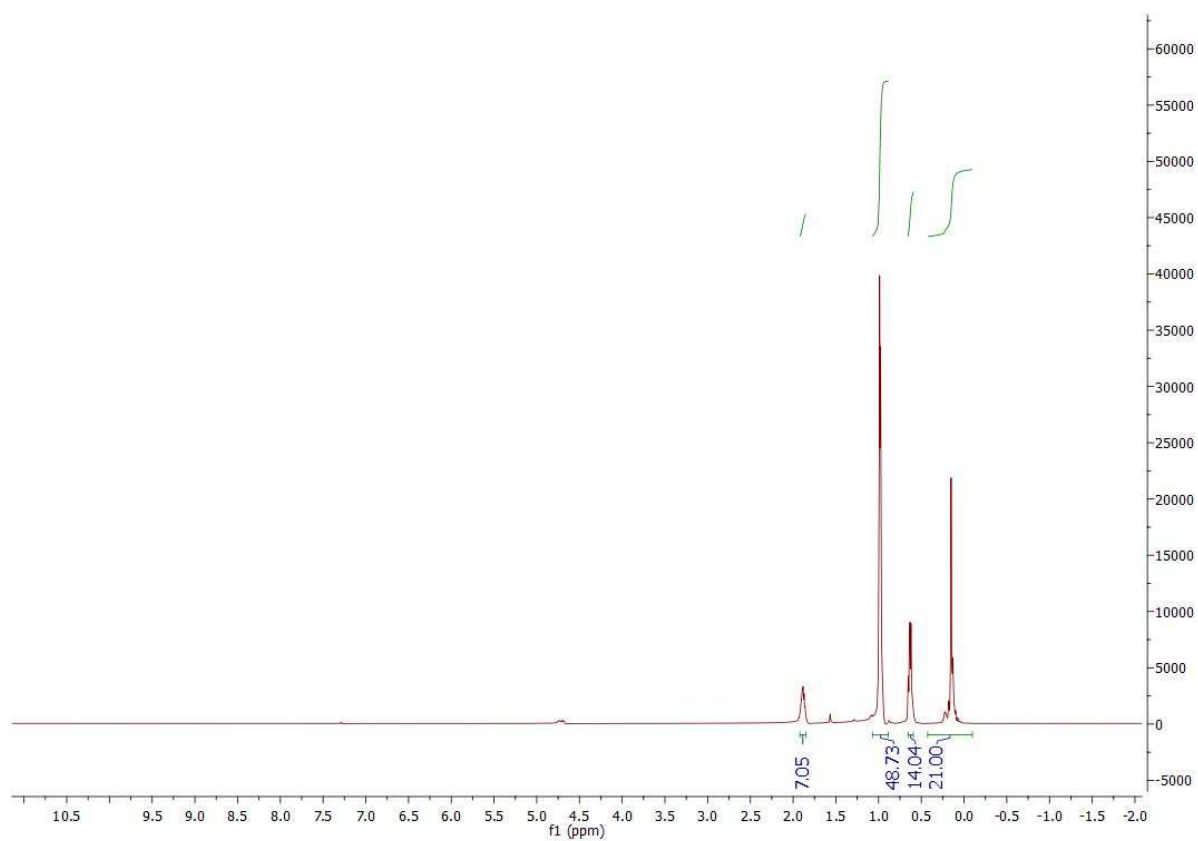


Figure 34 ^1H NMR (400 MHz) of compound (12).

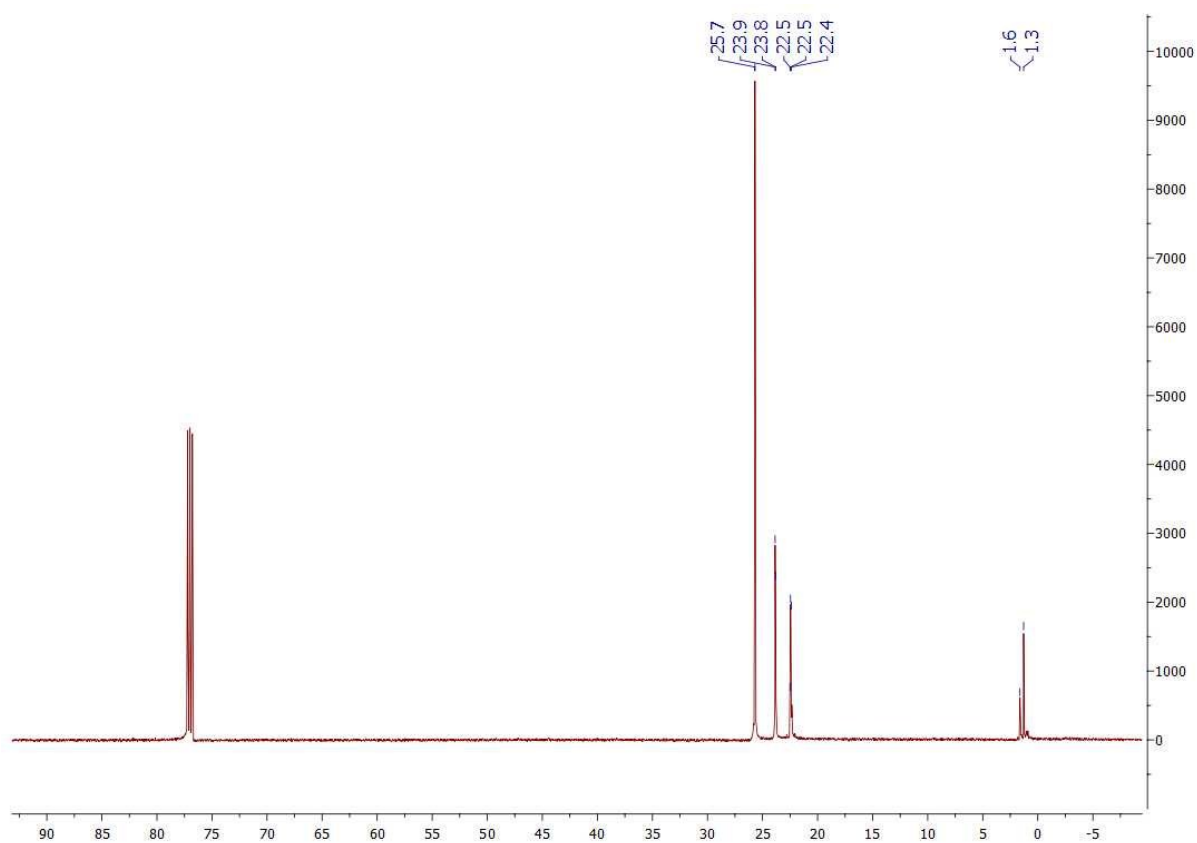


Figure 35 ^{13}C NMR (101 MHz) of compound (12).

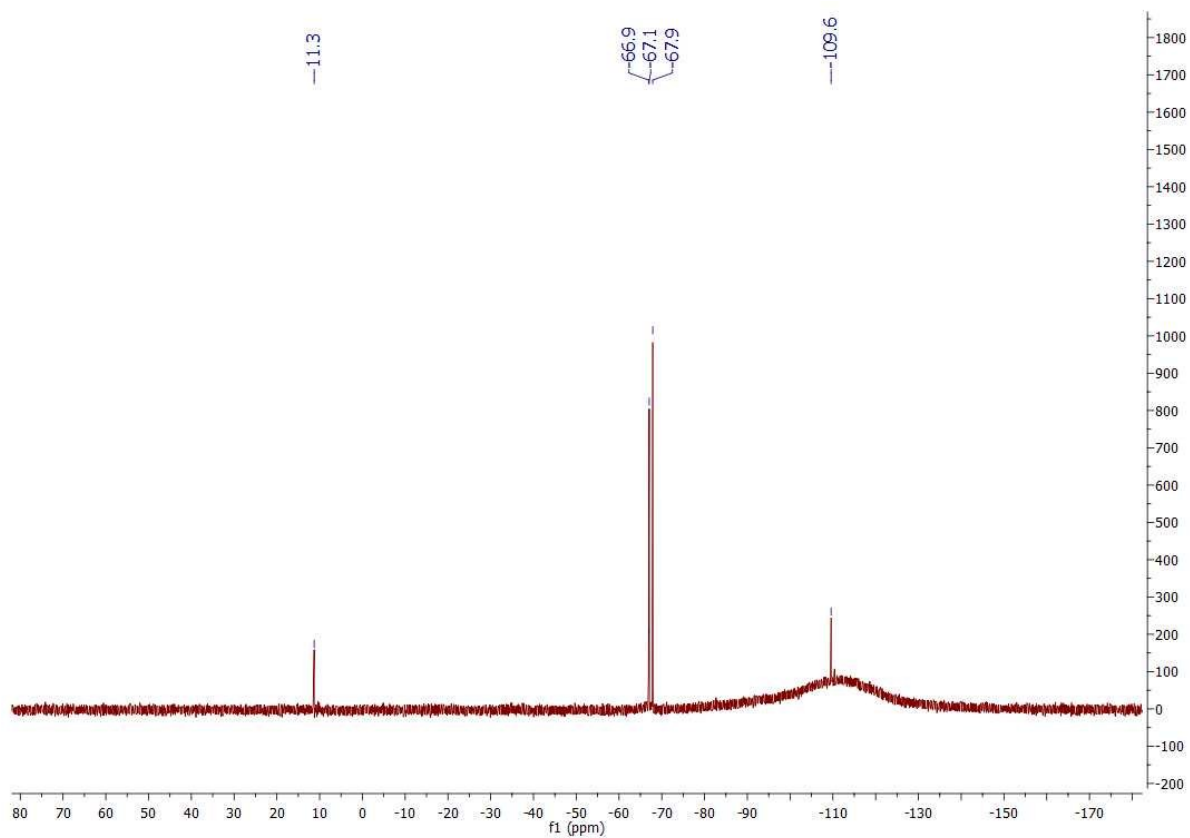
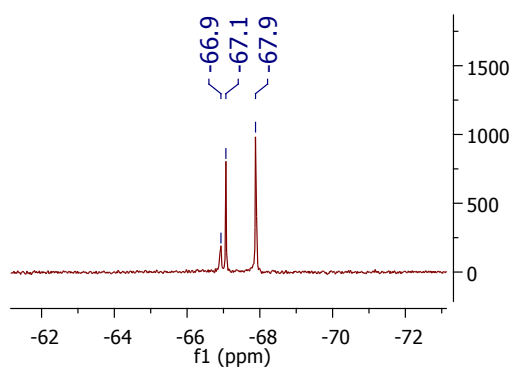
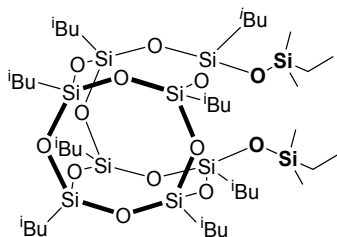


Figure 36 ^{29}Si NMR (79 MHz) of compound (12).





Compound **(13)** was obtained as oil in 82% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.04-0.20 (m, 12H), 0.53-0.65 (m, 16H), 0.67-0.71 (m, 4H), 0.95-1.03 (m, 54H), 1.82-1.96 (m, 8H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = -0.6, 6.6, 9.7, 21.8, 22.5, 22.9, 23.0, 23.6, 23.7, 23.8, 23.9, 25.7.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 9.6, -55.1, -57.4, -57.6.

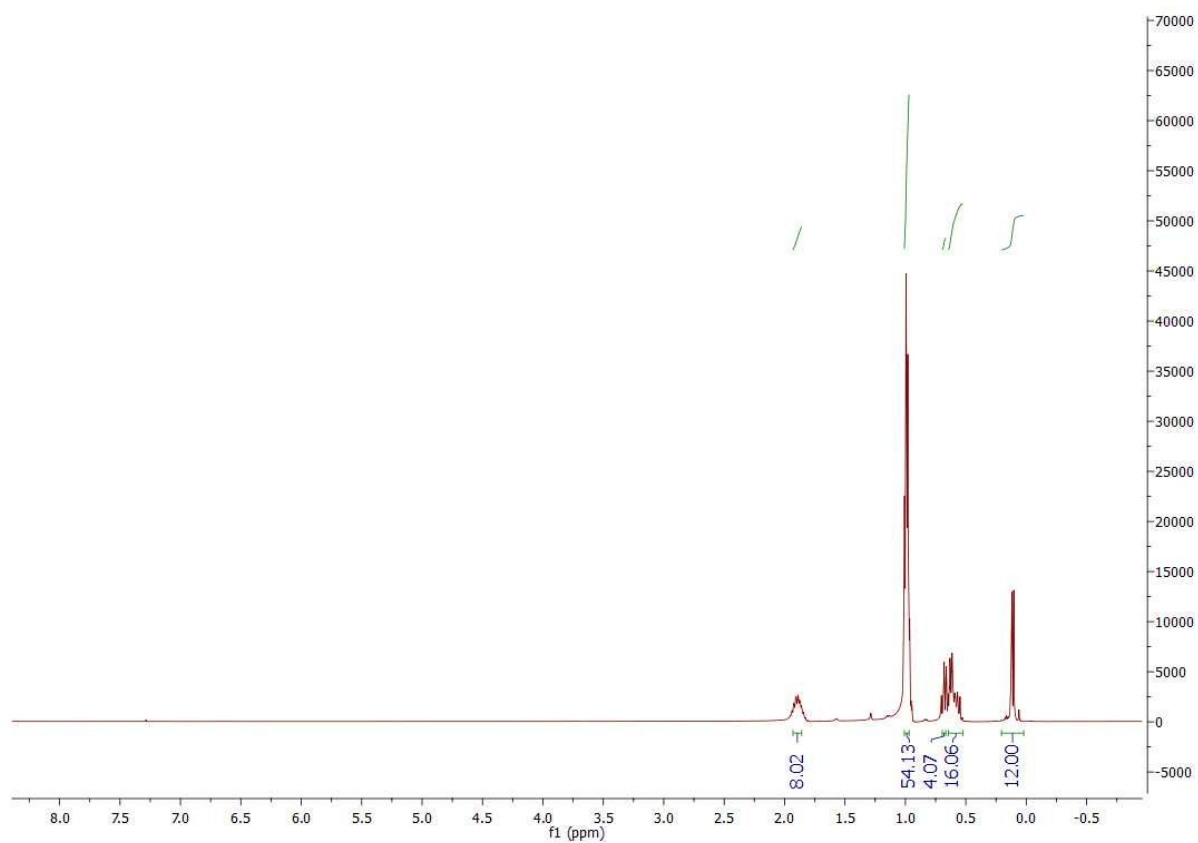


Figure 37 ^1H NMR (400 MHz) of compound (13).

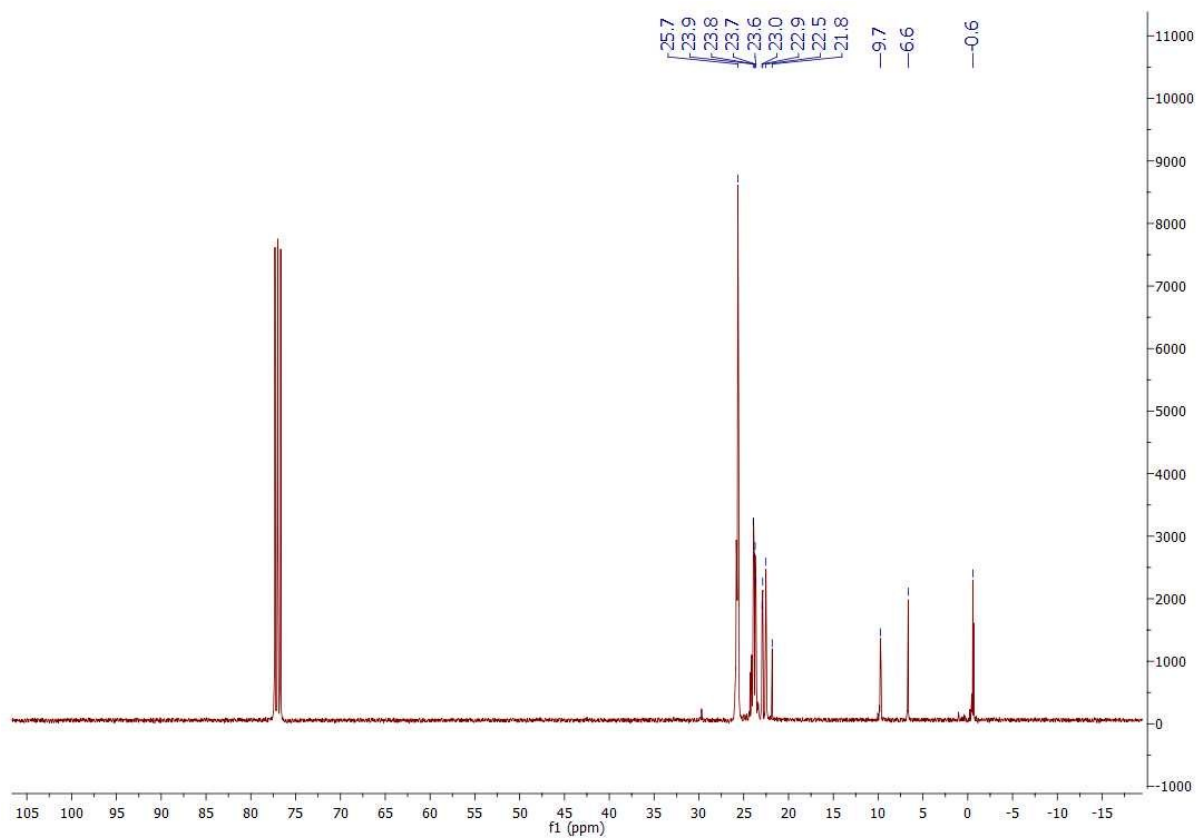


Figure 38 ^{13}C NMR (101 MHz) of compound (13).

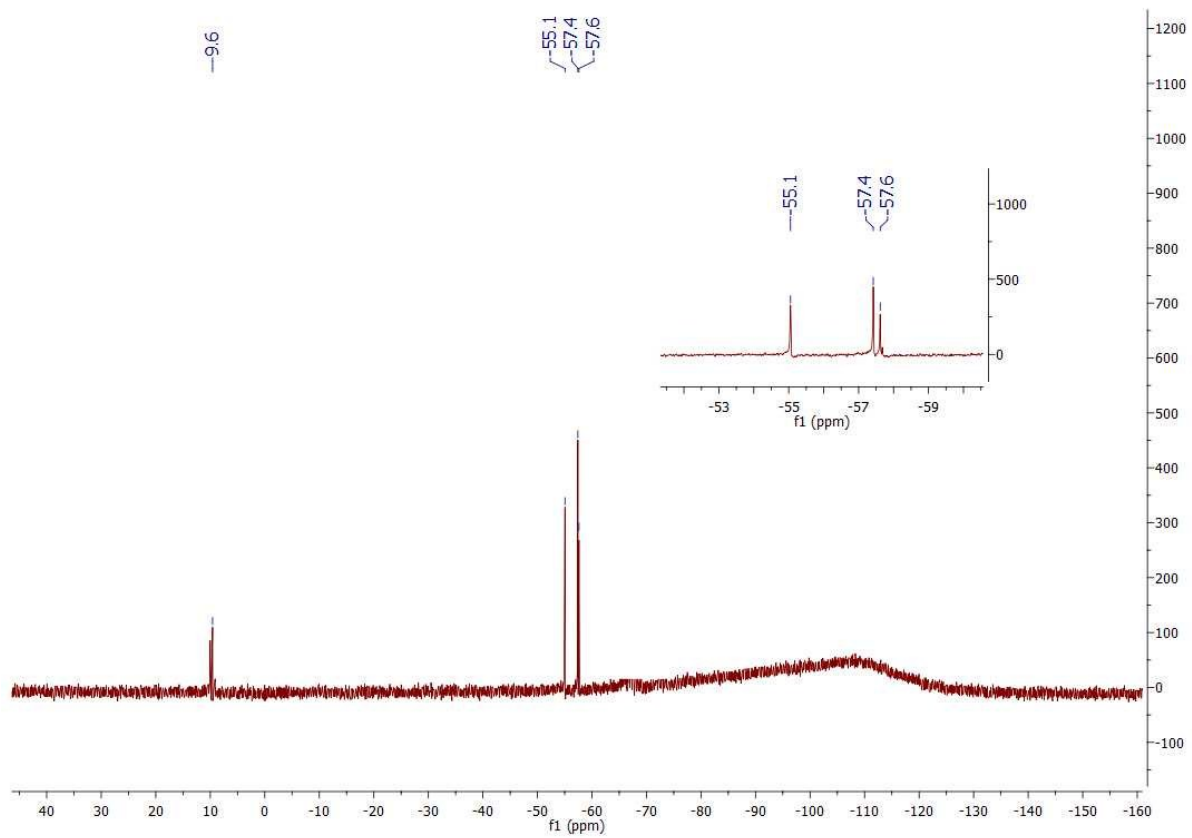
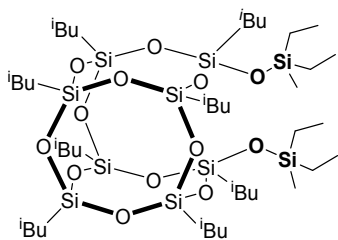


Figure 39 ^{29}Si NMR (79 MHz) of compound (13).



Compound **(14)** was obtained as oil in 81% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.04-0.13 (m, 6H), 0.48-0.62 (m, 16H), 0.64-0.72 (m, 8H), 0.75-1.08 (m, 60H), 1.82-1.97 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = -2.8, 1.1, 6.7, 21.8, 22.5, 22.5, 22.9, 23.0, 23.7, 23.9, 25.6, 25.7.

²⁹Si NMR (79 MHz, CDCl₃) δ (ppm) = 10.6, -66.2, -67.3, -68.2.

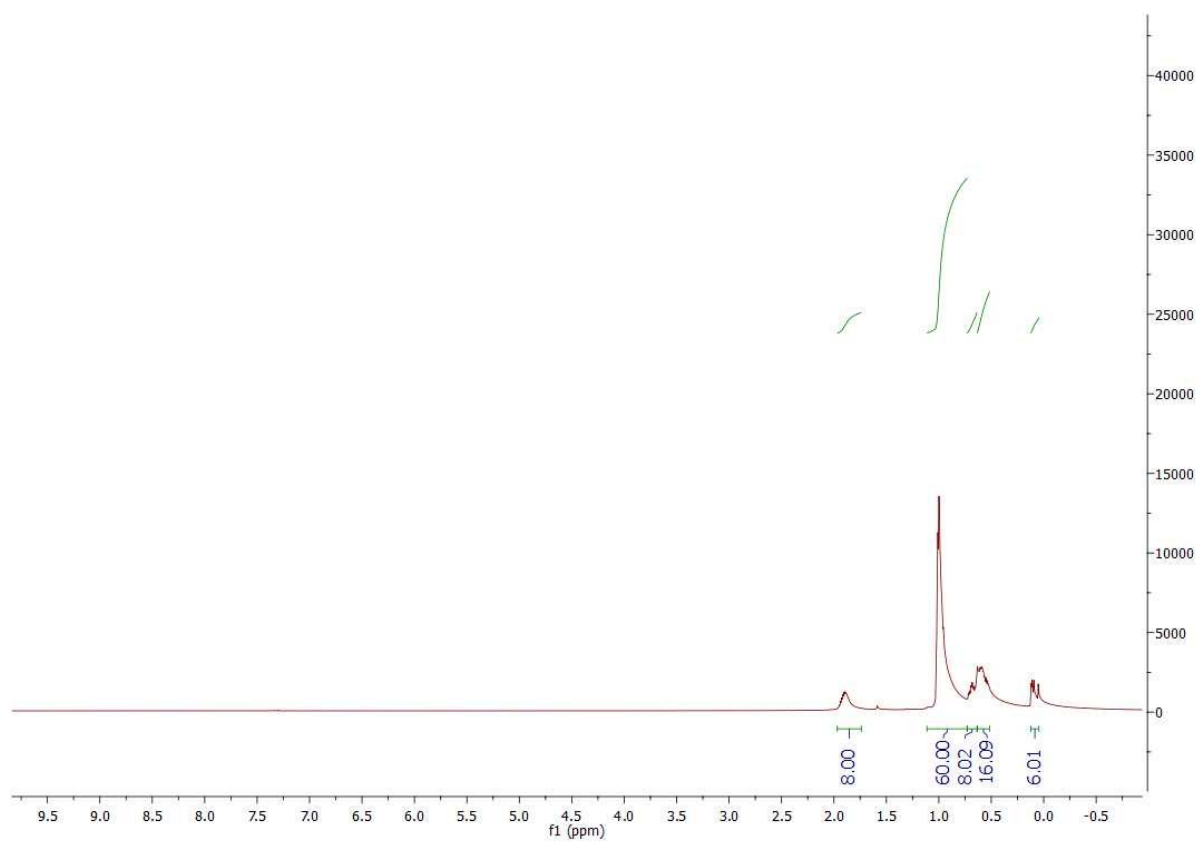


Figure 40 ^1H NMR (400 MHz) of compound (**14**).

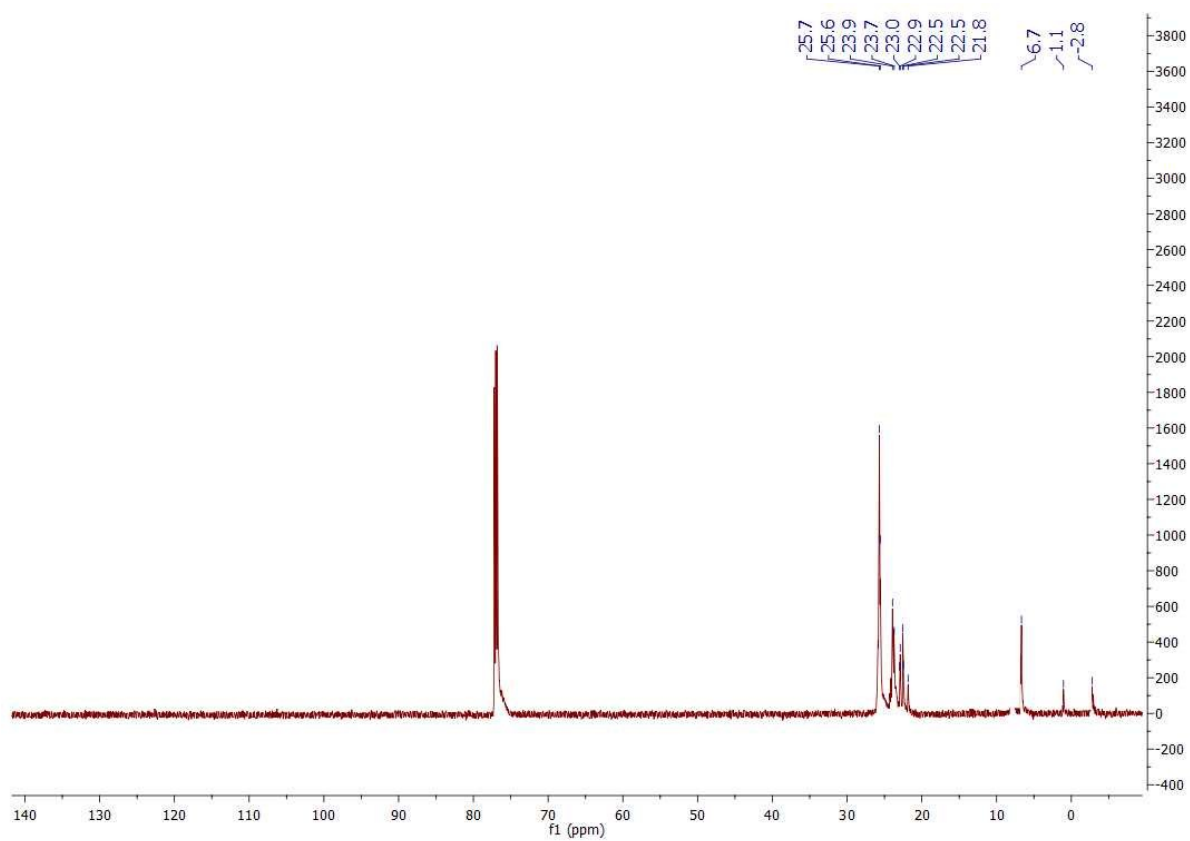


Figure 41 ^{13}C NMR (101 MHz) of compound (14).

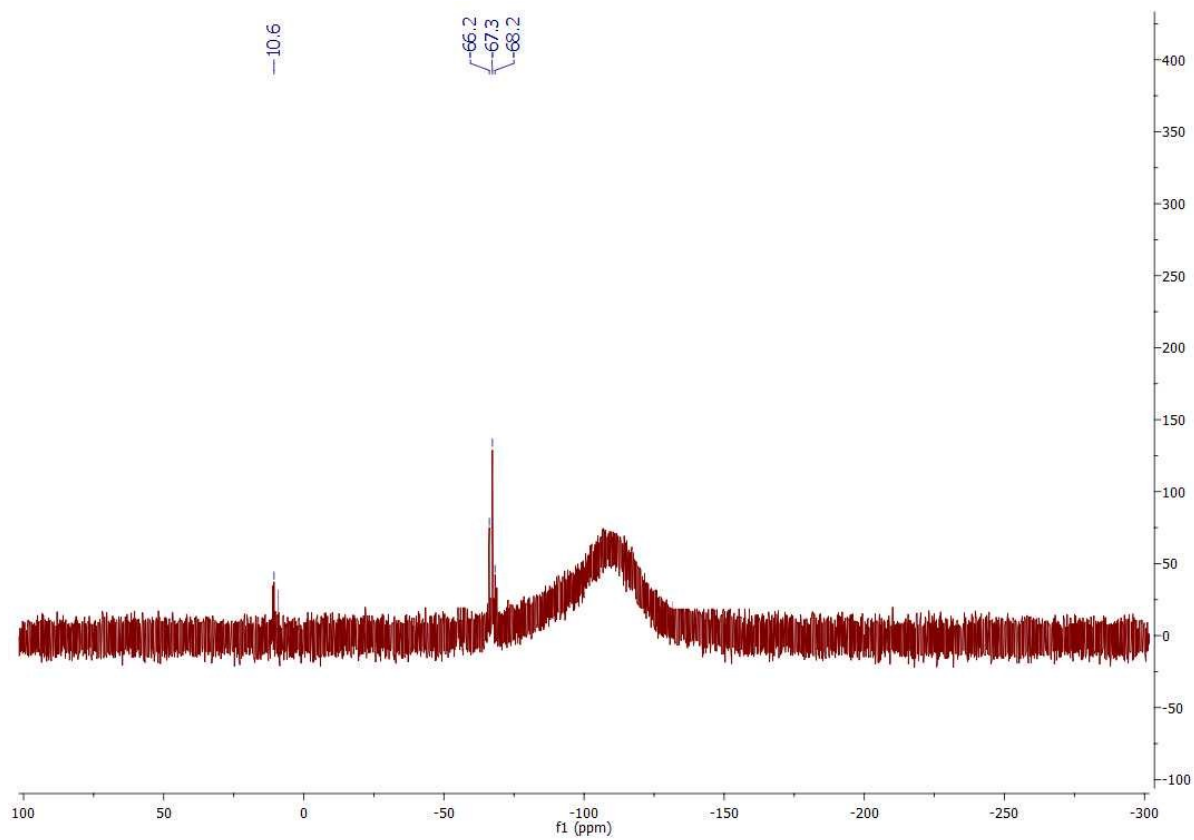
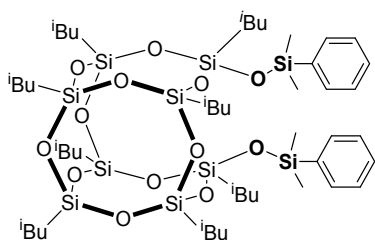


Figure 42 ^{29}Si NMR (79 MHz) of compound (**14**).



Compound **(15)** was obtained as oil in 85% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.33-0.44 (m, 12H), 0.55-0.74 (m, 16H), 0.95-1.05 (m, 48H), 1.82-1.96 (m, 8H), 7.25-7.50 (m, 6H), 7.55-7.70 (m, 4H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 0.6, 21.9, 22.4, 22.5, 22.9, 23.7, 23.9, 25.6, 25.7, 25.8, 127.6, 129.1, 133.0, 139.8.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = -1.4, -66.0, -67.2, -67.4.

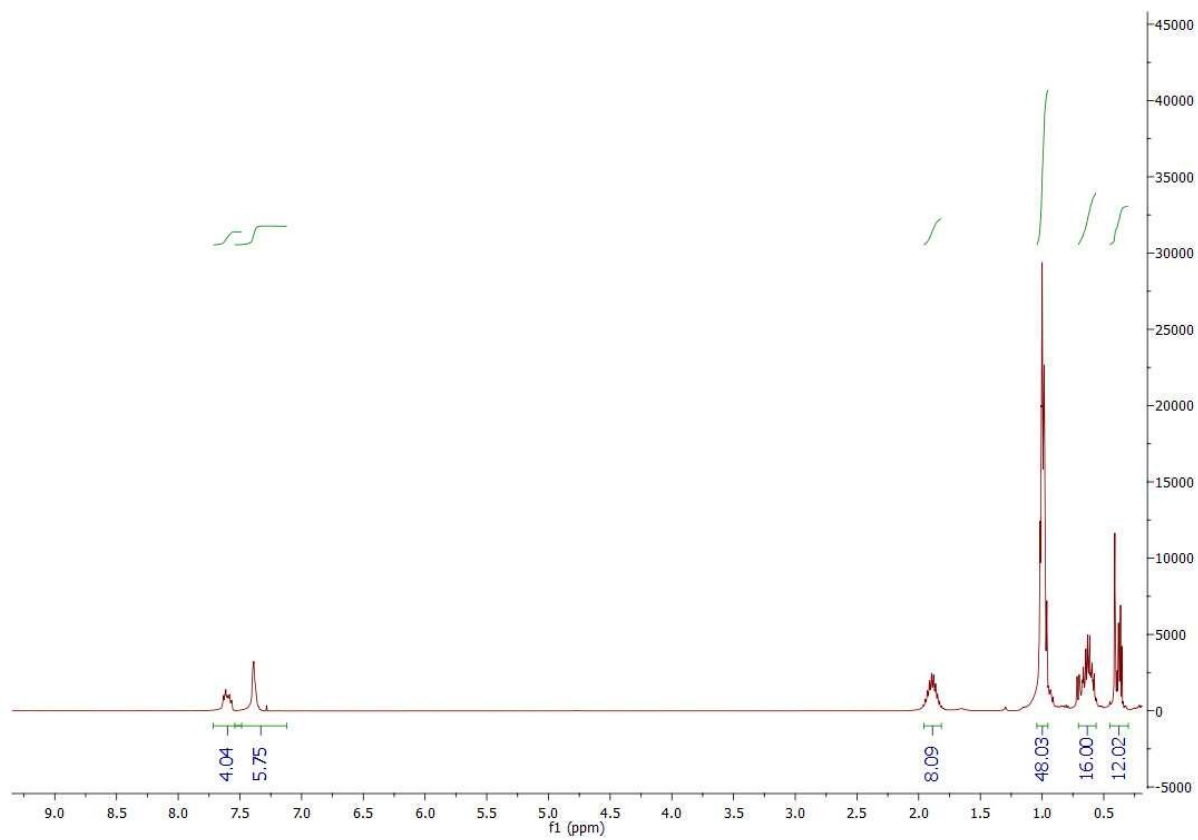


Figure 43 ^1H NMR (400 MHz) of compound (15).

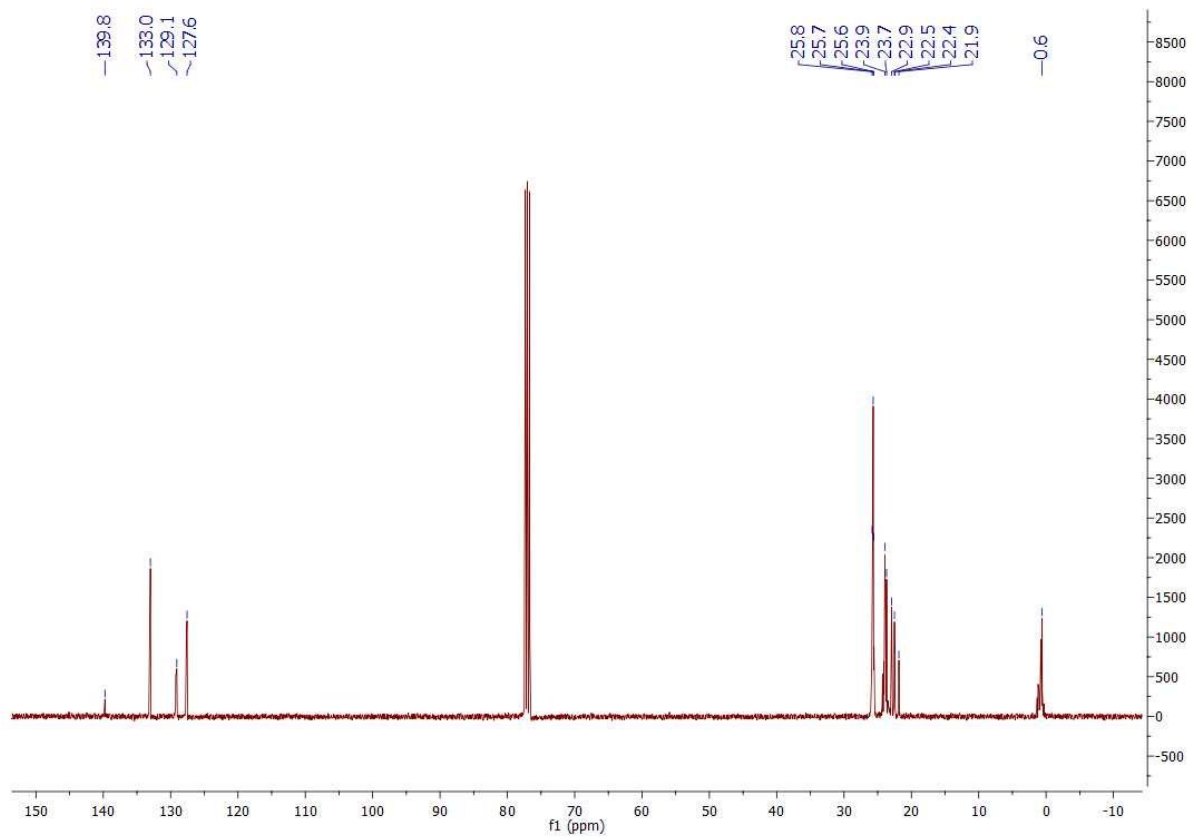


Figure 44 ^{13}C NMR (101 MHz) of compound (15).

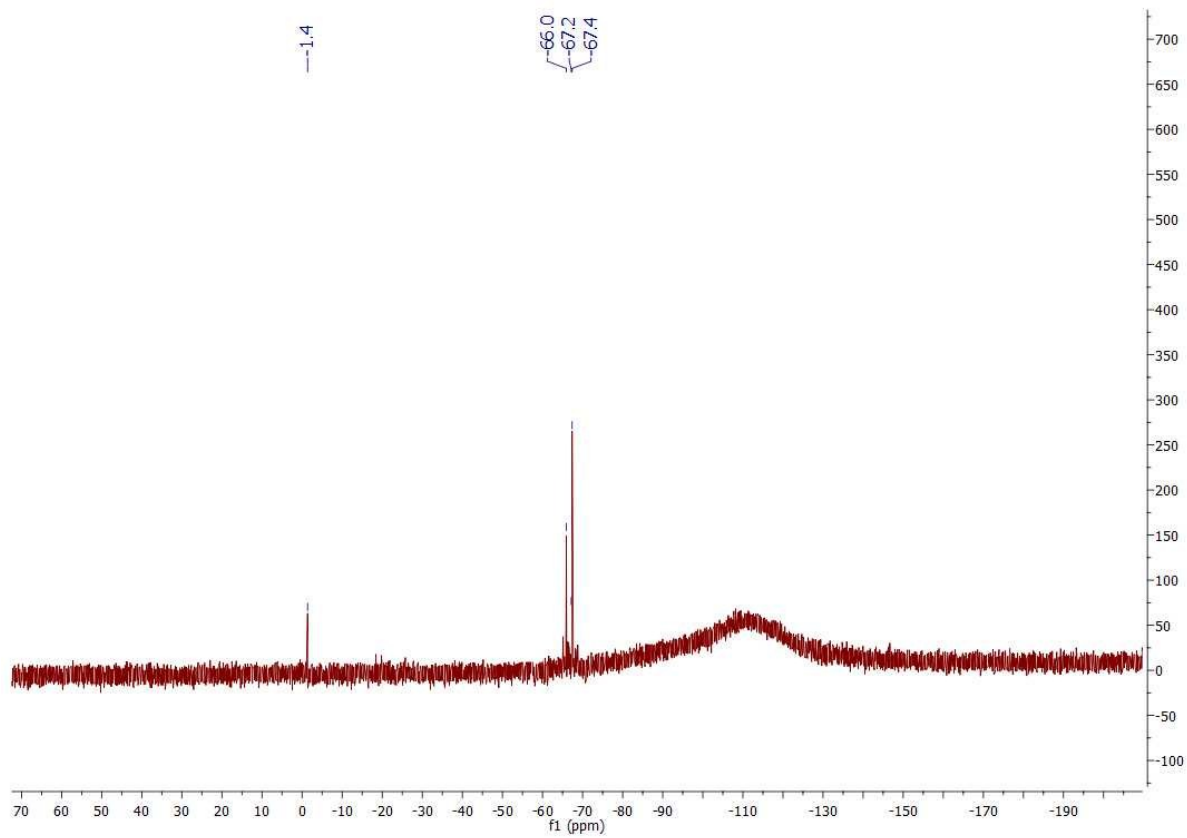
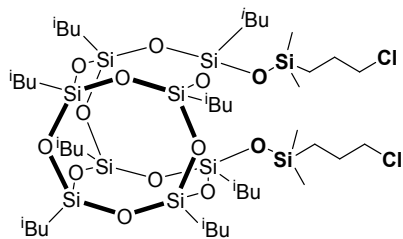


Figure 45 ^{29}Si NMR (79 MHz) of compound (15).



Compound **(16)** was obtained as oil in 80% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.05-0.20 (m, 12H), 0.57-0.73 (m, 20H), 0.96-1.02 (m, 48H), 1.78-1.96 (m, 8H), 3.50-3.55 (m, 4H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = -0.1, 0.3, 15.9, 21.8, 22.6, 22.9, 23.6, 23.7, 23.9, 24.1, 25.6, 25.8, 25.9, 27.0, 47.8.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = 8.5, 7.6, -65.9, -67.4, -68.4.

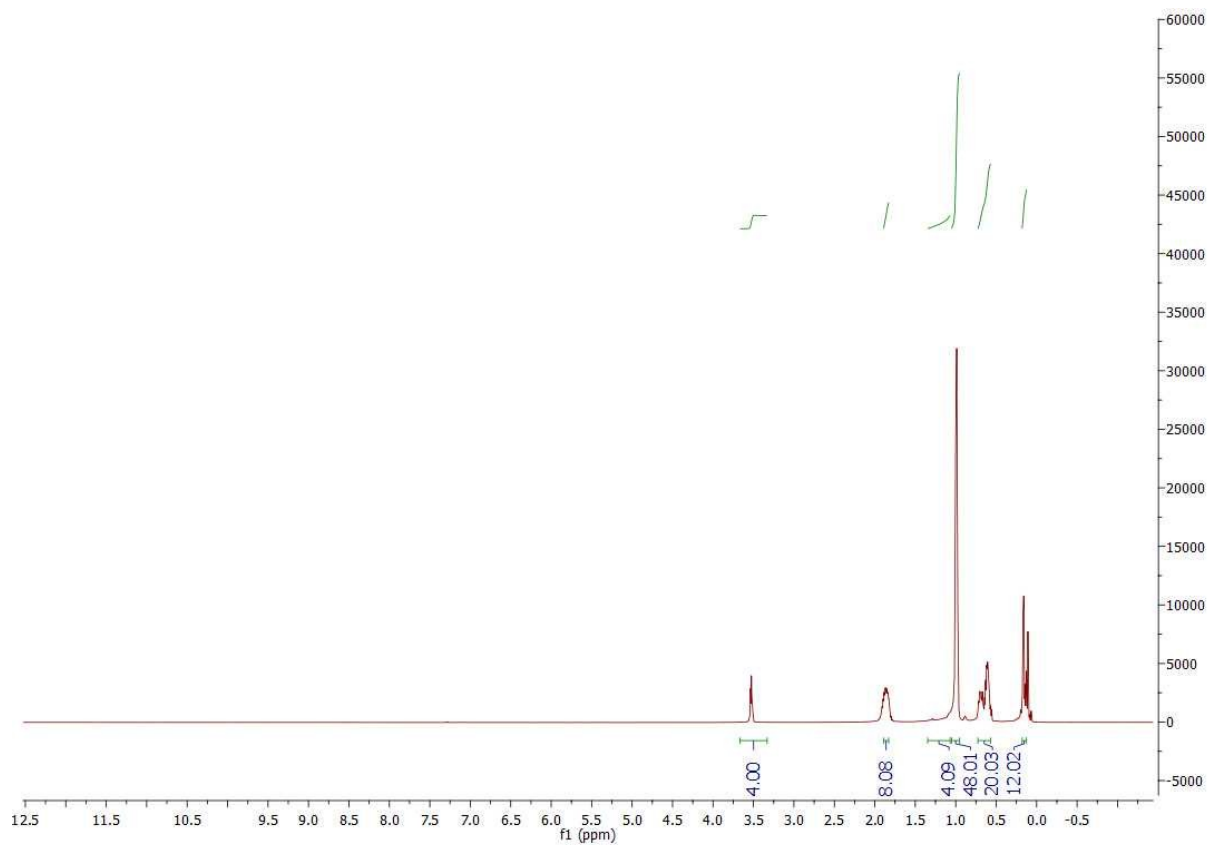


Figure 46 ^1H NMR (400 MHz) of compound (16).

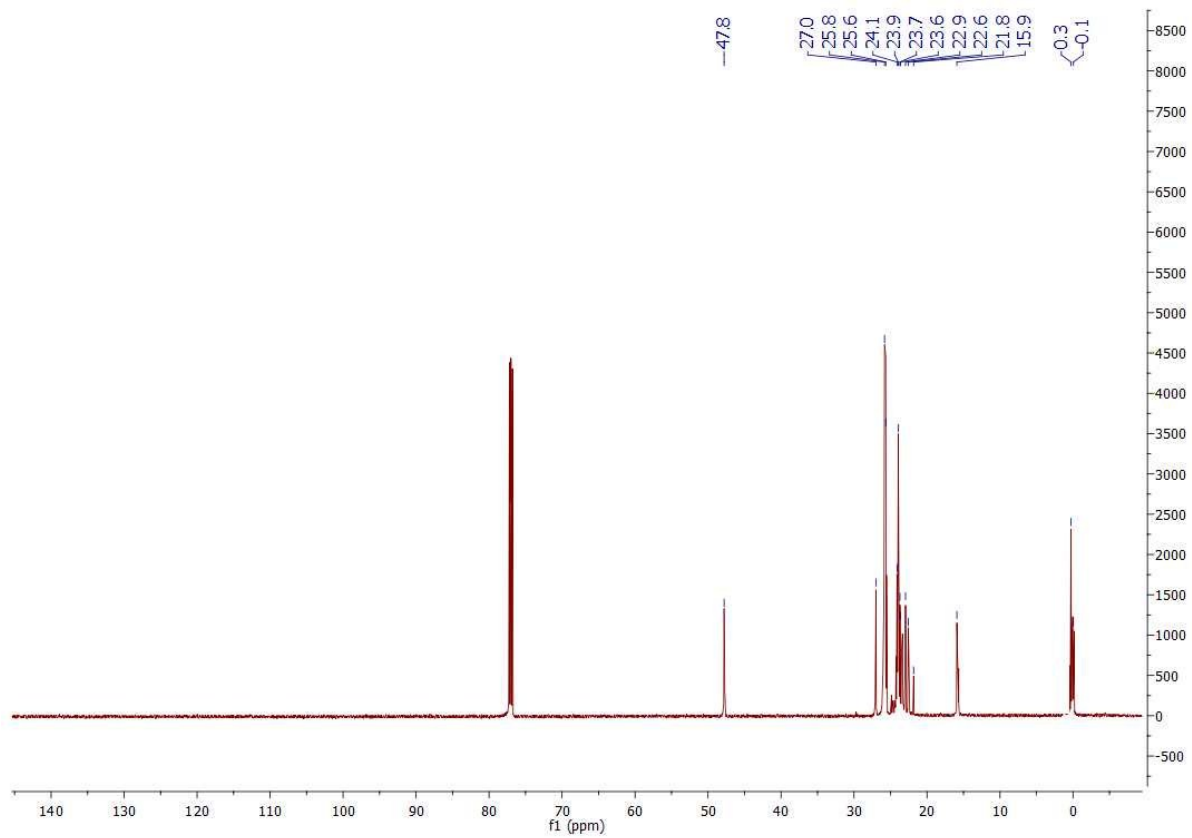


Figure 47 ^{13}C NMR (101 MHz) of compound (16).

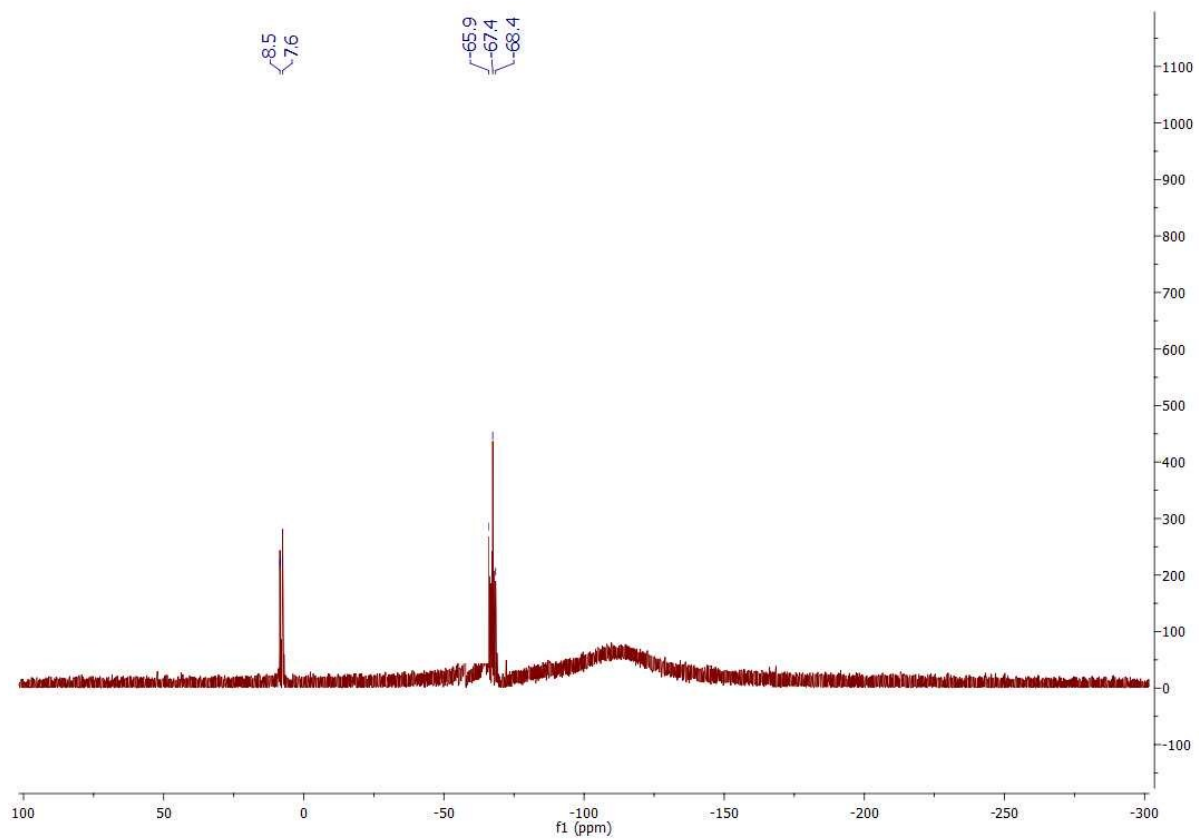
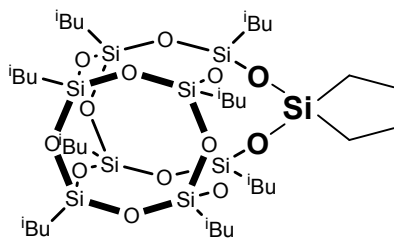


Figure 48 ^{29}Si NMR (79 MHz) of compound (16).



Compound **(17)** was obtained as oil in 85% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 0.53-0.58 (m, 4H), 0.60-0.65 (m, 16H), 0.96-1.01 (m, 54H), 1.82-1.96 (m, 8H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 6.3, 6.5, 6.8, 7.2, 22.5, 23.1, 23.7, 23.9, 24.0, 24.1, 25.7, 25.8.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ (ppm) = -20.4, -67.1, -67.9, -69.2.

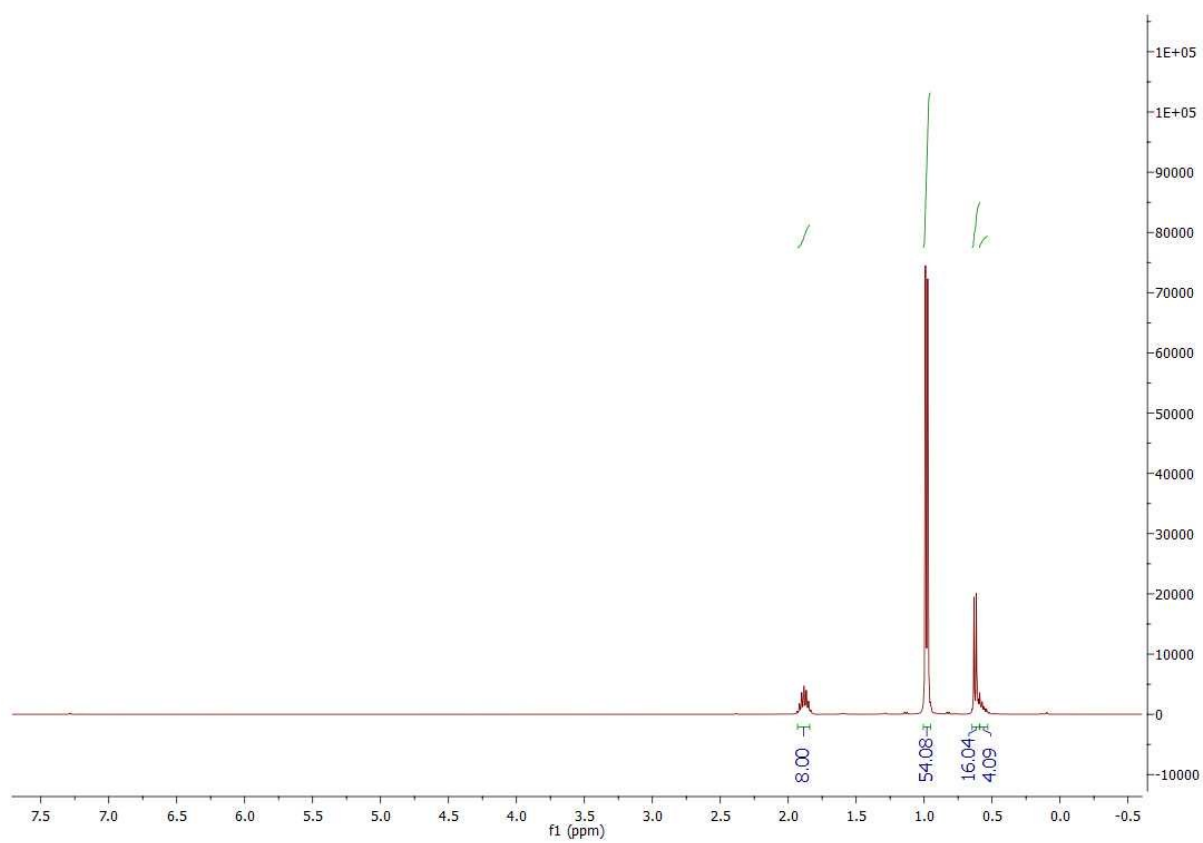


Figure 49 ^1H NMR (400 MHz) of compound (17).

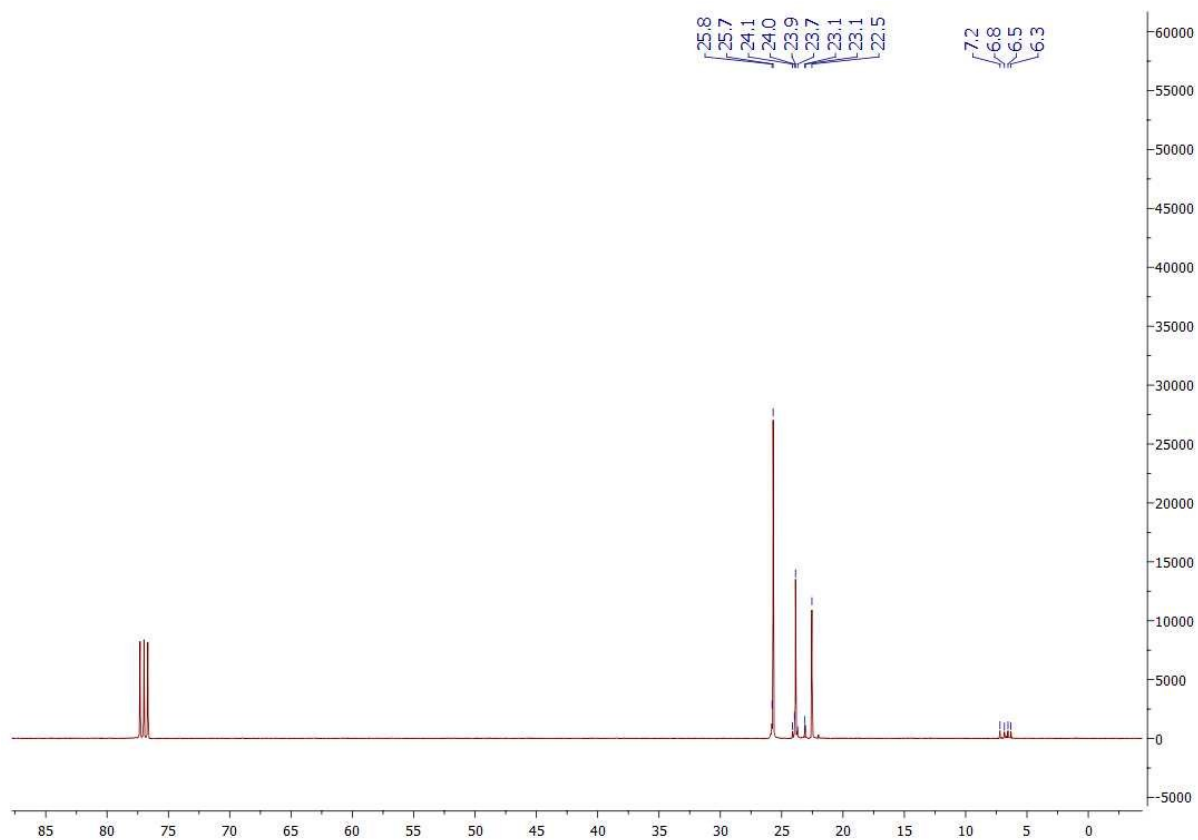


Figure 50 ^{13}C NMR (101 MHz) of compound (**17**).

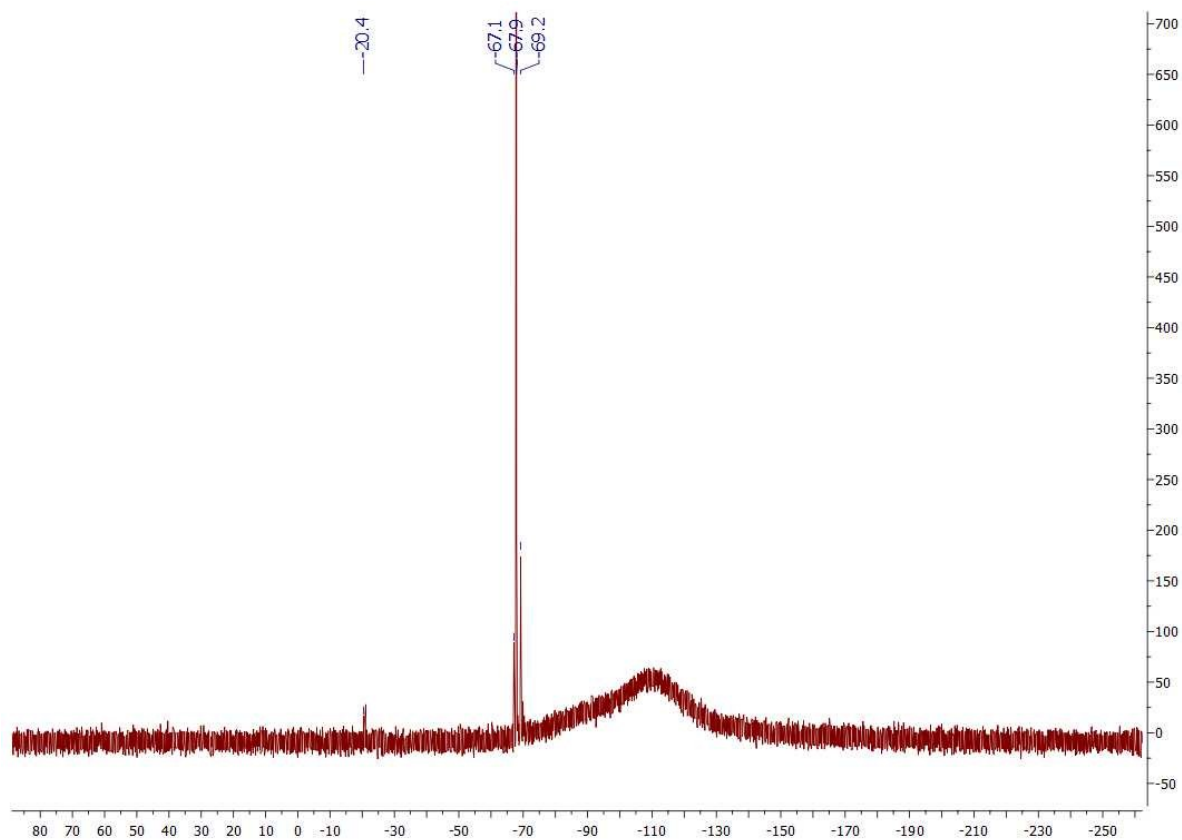


Figure 51 ^{29}Si NMR (79 MHz) of compound (17).

4. The results of the mechanistic study on dehydrogenative coupling reaction of POSS silanols with silanes mediated by $\text{Cu}(\text{OTf})_2$

4.1. ^1H NMR spectrum (400 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of POSS monosilanol with phenyldimethylsilane mediated by $\text{Cu}(\text{OTf})_2$ performed in toluene- d_8 (80°C , 24h) and detection of hydrogen as by-product in this process (at 4.50 ppm):

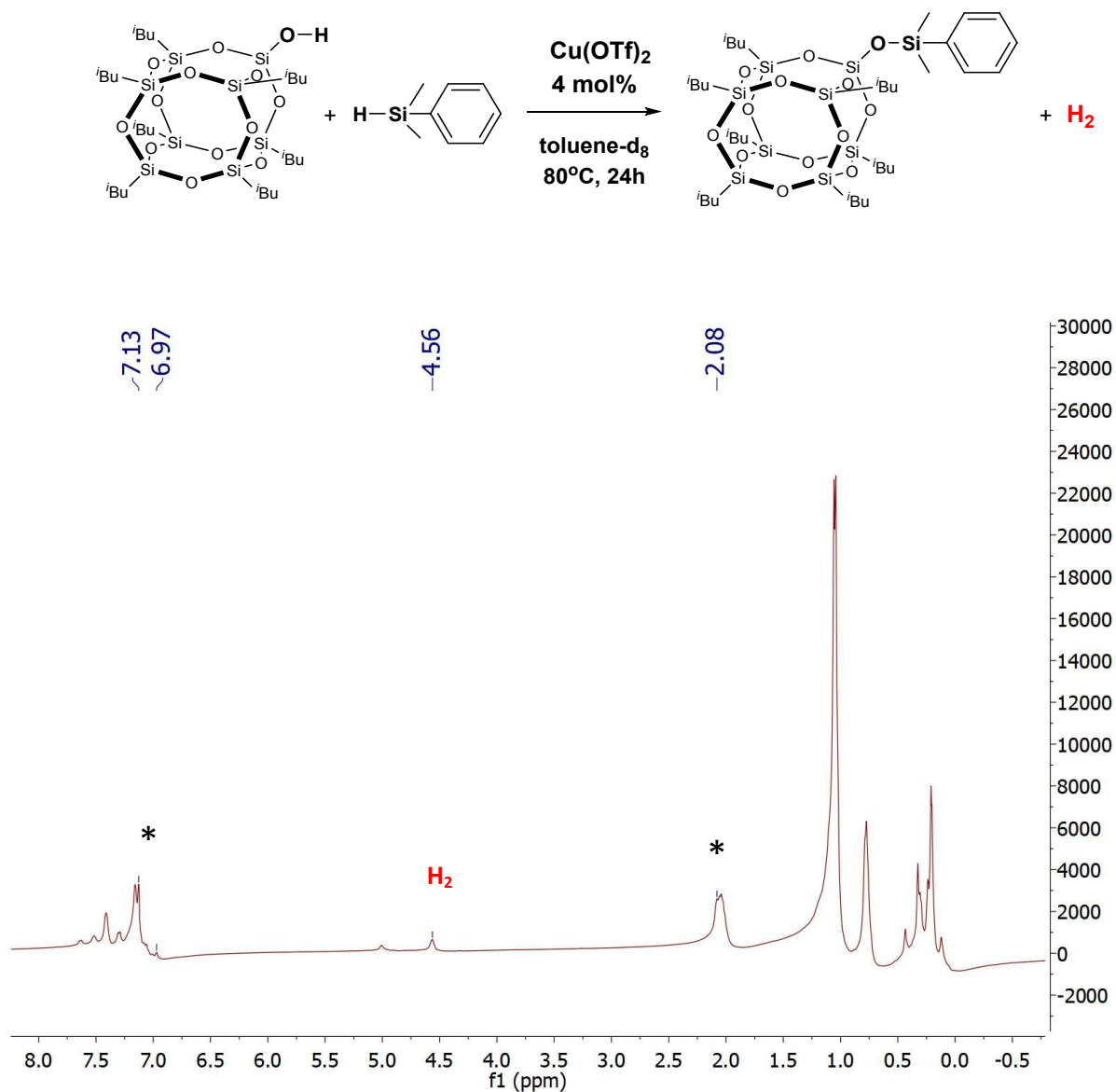


Figure 52 ^1H NMR spectrum (400 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of POSS monosilanol with phenyldimethylsilane mediated by $\text{Cu}(\text{OTf})_2$ performed in toluene- d_8 (80°C , 24h)

*solvent peaks (toluene- d_8)

4.2. ^{29}Si NMR spectrum (79 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of **phenyldimethylsilane** with **$\text{Cu}(\text{OTf})_2$** performed in toluene- d_8 (80°C , 24h) in Young NMR tube:

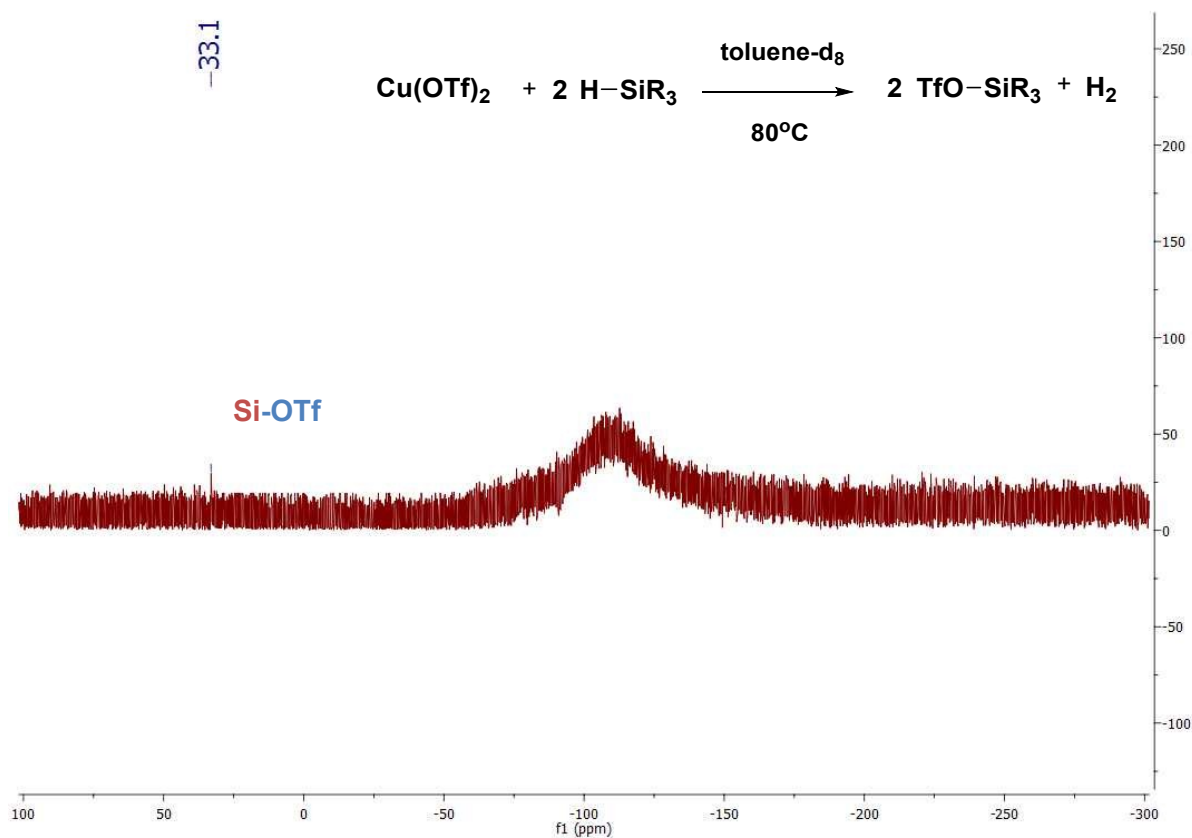


Figure 53 ^{29}Si NMR spectrum (79 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of **phenyldimethylsilane** with **$\text{Cu}(\text{OTf})_2$** performed in toluene- d_8 (80°C , 24h) in Young NMR tube

The formation of $\text{PhMe}_2\text{Si}-\text{OTf}$ was confirmed by GC-MS analysis.

Mass spectral characteristic of $\text{PhMe}_2\text{Si}-\text{OSO}_2\text{CF}_3$; m/z : 284 (M^+), 268 (M^+-CH_3), 253 (M^+-2CH_3), 199 ($\text{M}^+-\text{CH}_3-\text{CF}_3$), 135 (PhMe_2Si), 77 (Ph).

4.3. ^{29}Si NMR spectrum (79 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) of phenyldimethylsilane as comparison for mechanistic studies:

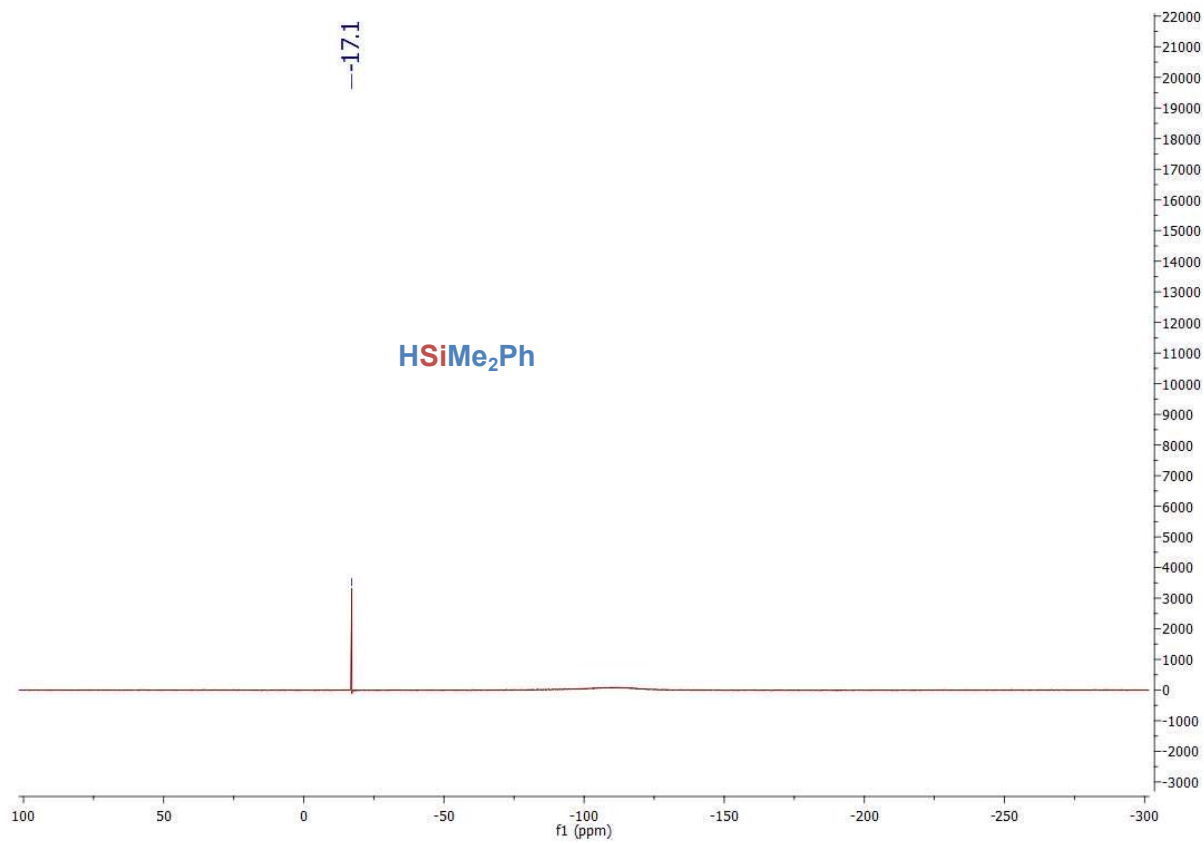


Figure 54 ^{29}Si NMR spectrum (79 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) of phenyldimethylsilane

4.4. ^1H NMR spectrum (400 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of **phenyldimethylsilane** with **$\text{Cu}(\text{OTf})_2$** performed in toluene- d_8 (80°C , 24h) in Young NMR tube

The conformation for the evolution of H_2 in this process:

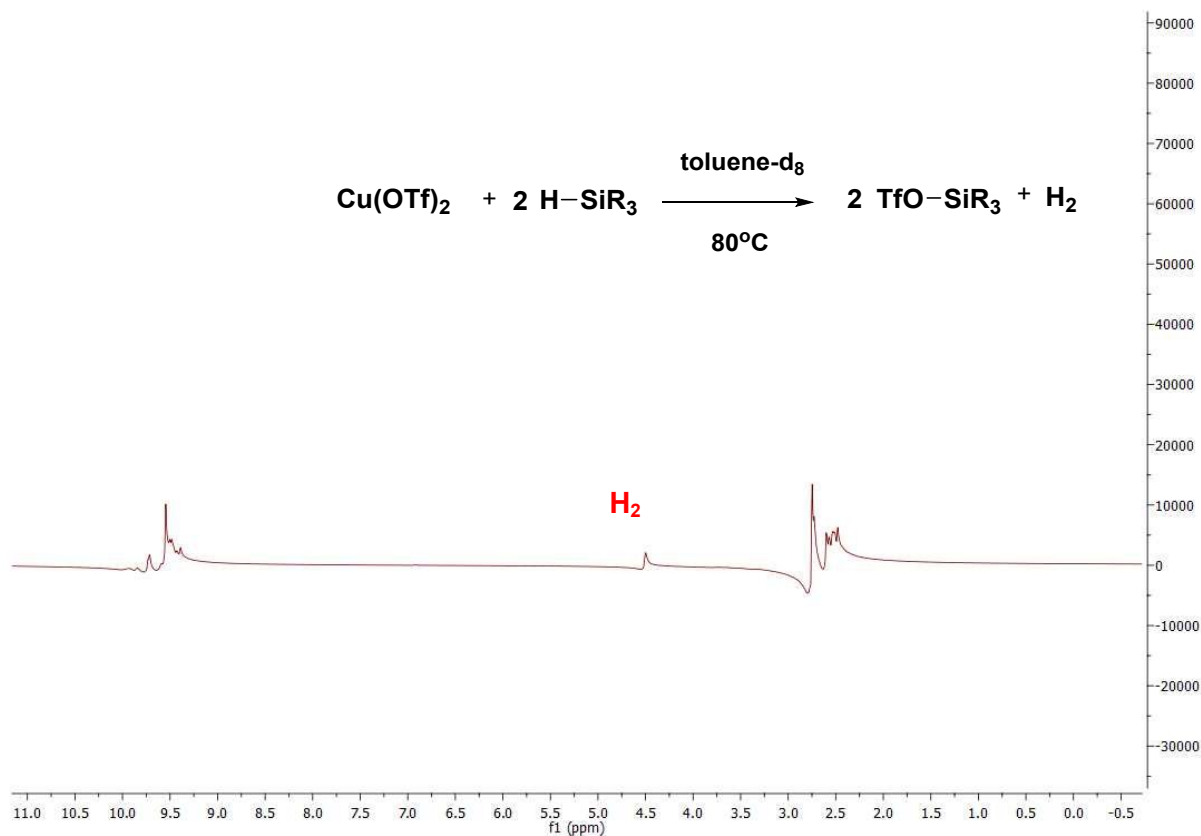
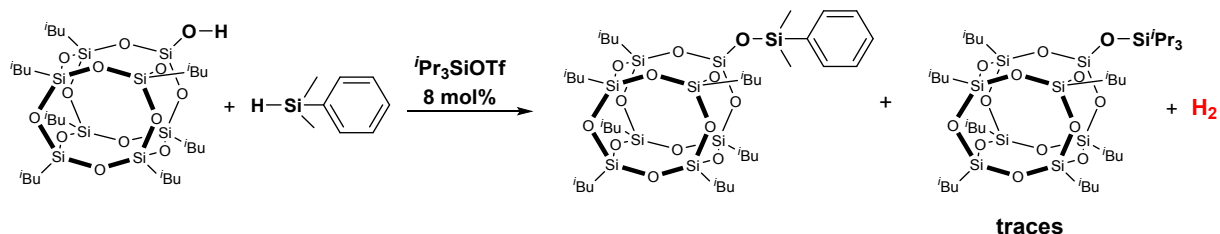


Figure 55 ^1H NMR spectrum (400 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) for the reaction of phenyldimethylsilane with $\text{Cu}(\text{OTf})_2$ performed in toluene- d_8 (80°C , 24h) in Young NMR tube

4.5. The use of silyl triflate $i\text{Pr}_3\text{SiOTf}$ as catalyst of dehydrogenative coupling reaction of POSS silanols with silanes

4.5.1.



The obtained mixture of two products: the desired product and the SSQ derivative substituted with tri-*iso*-propylsilyl moiety from catalyst, was observed in NMR spectra (especially in ^{13}C NMR spectrum).

Furthermore, hydrogen as by-product detected in ^1H NMR spectrum:

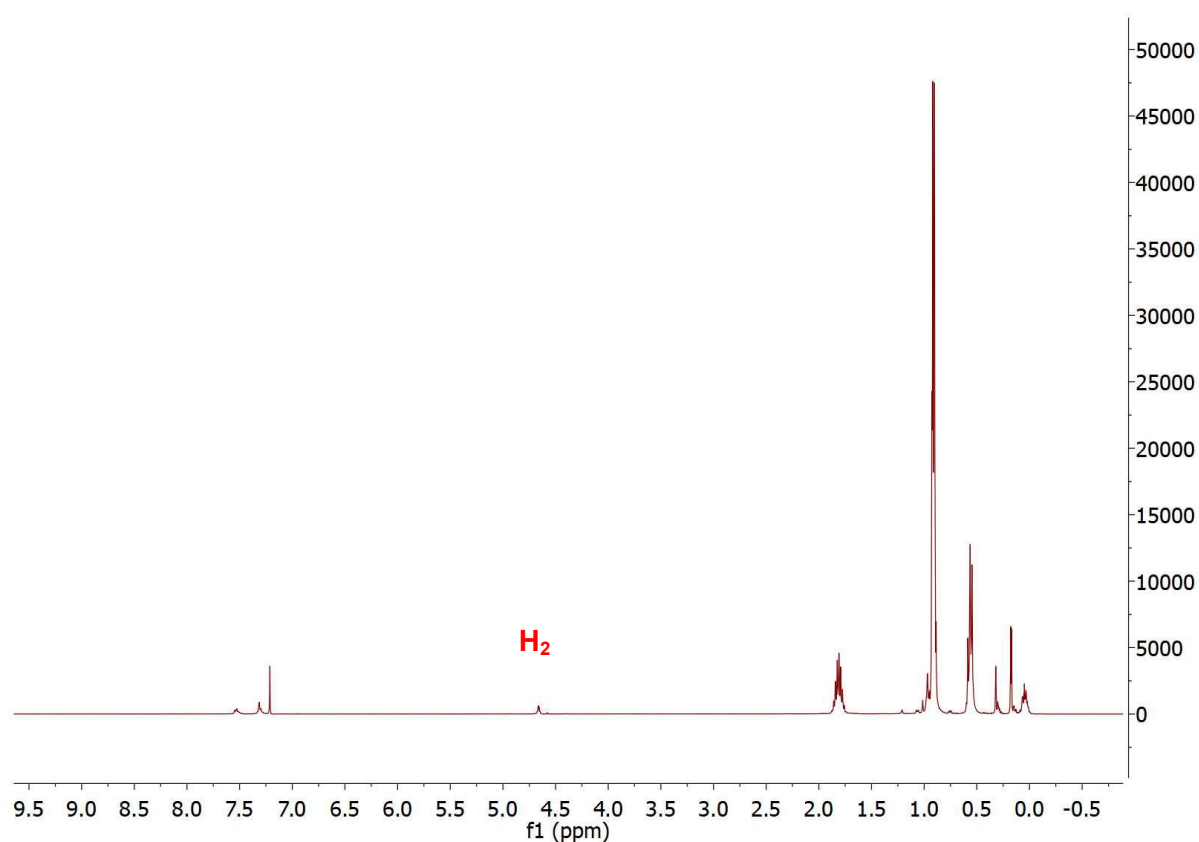
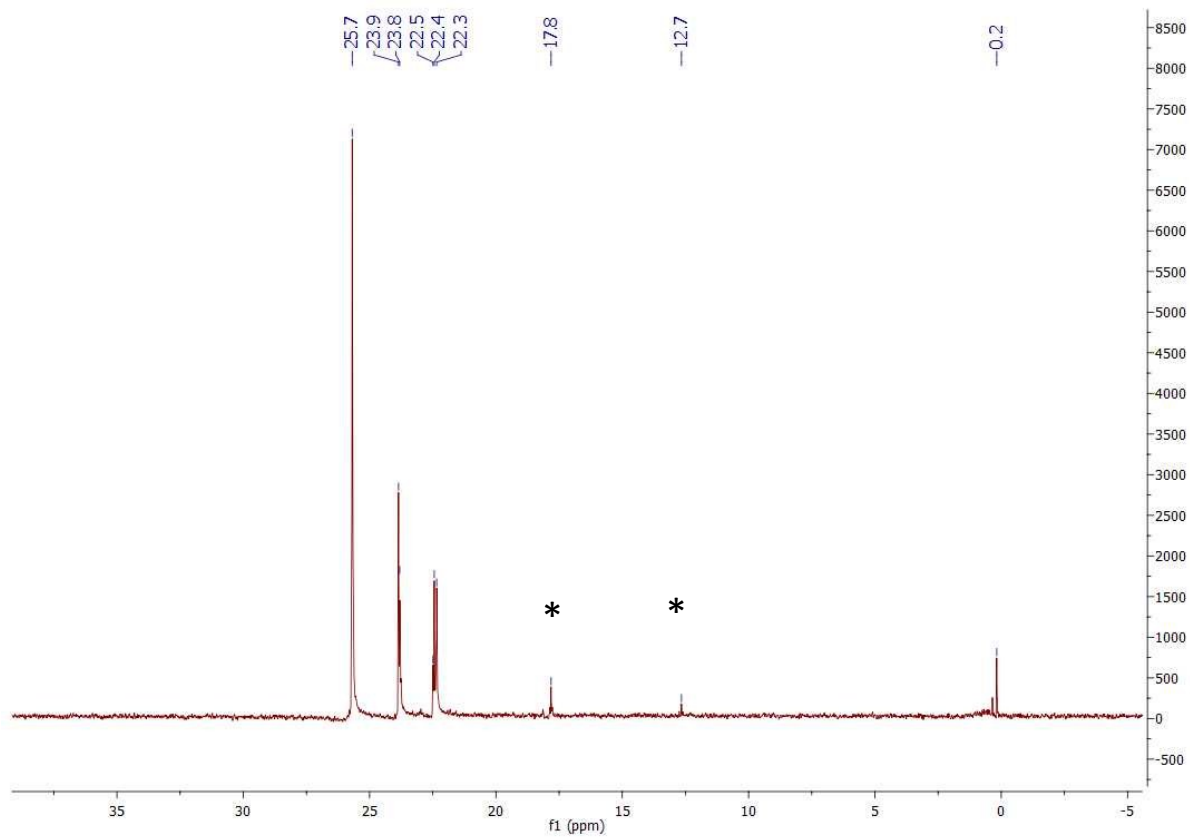


Figure 56 ^1H NMR (400 Hz) for the results of the reaction between POSS monosilanol with phenyldimethylsilane catalyzed by $i\text{Pr}_3\text{SiOTf}$



*additional peaks from $i\text{Pr}_3\text{Si}$ moiety: $((\text{CH}_3)_2\text{CH})_3\text{-Si}$

Figure 57 ^{13}C NMR (101 Hz) for the results of the reaction between POSS monosilanol with phenyldimethylsilane catalyzed by $i\text{Pr}_3\text{SiOTf}$

4.5.2. Analogous experiment using ethyldimethylsilane

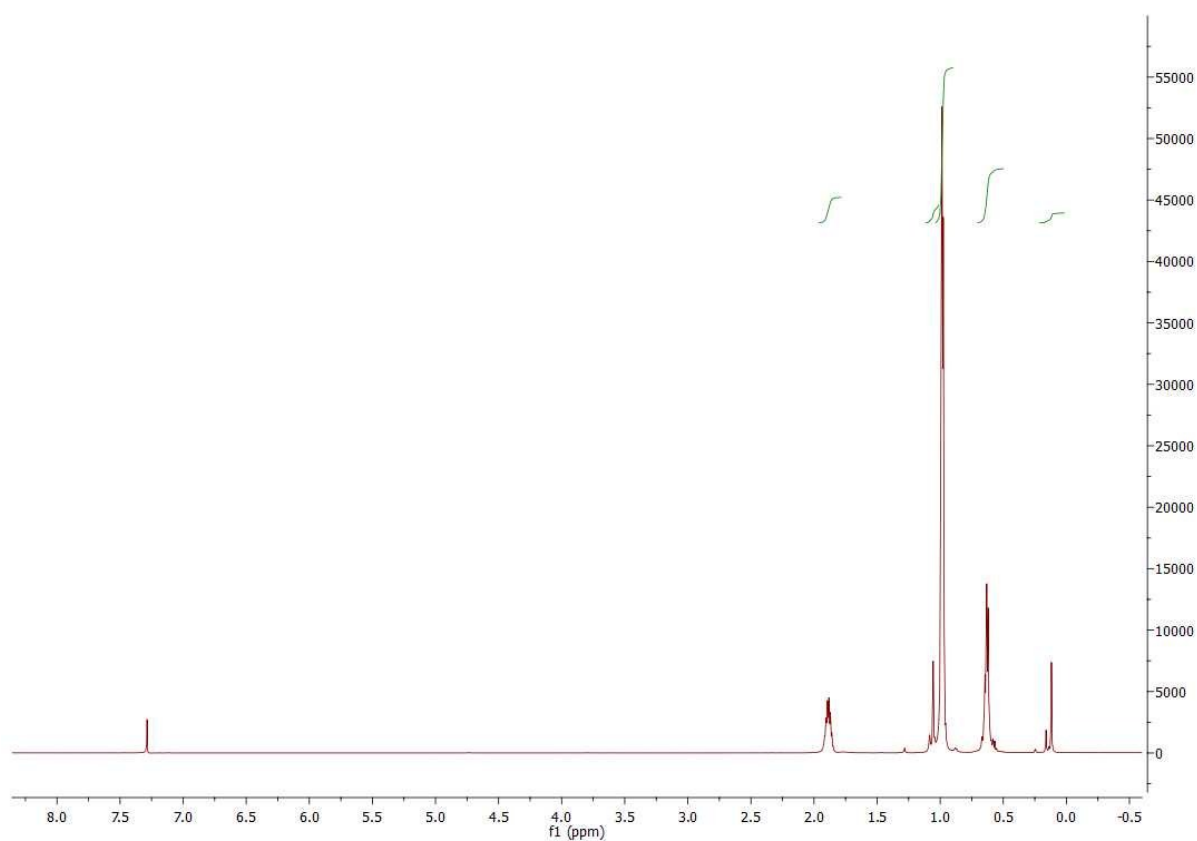
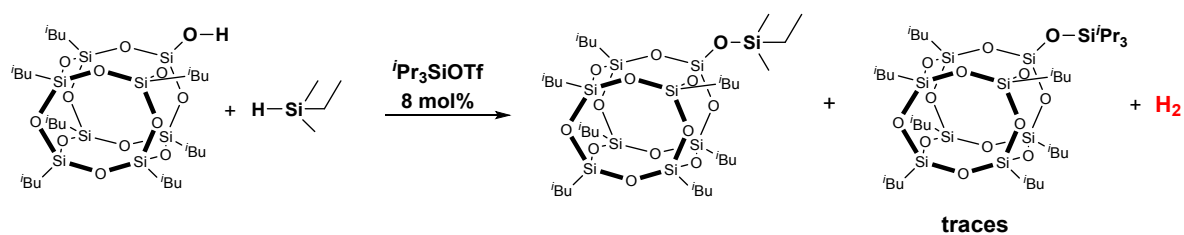
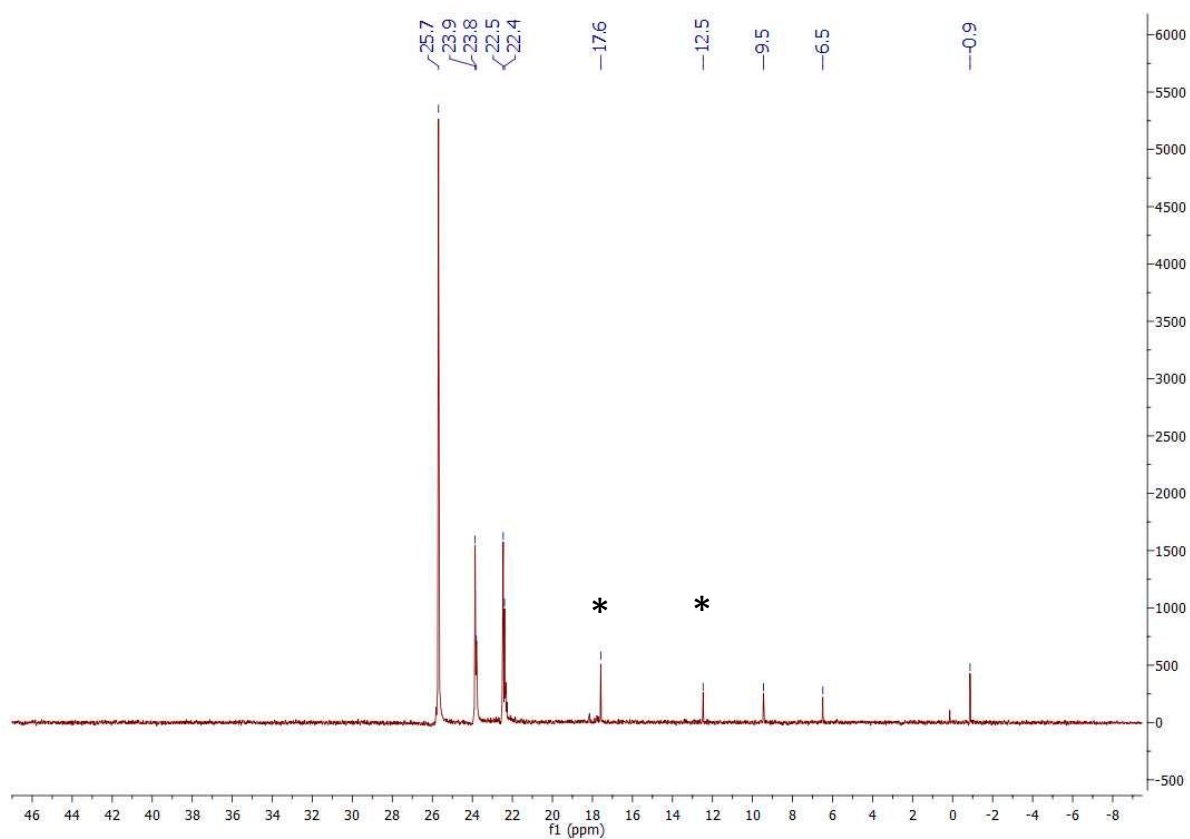


Figure 58 ^1H NMR (400 Hz) for the results of the reaction between POSS monosilanol with ethyldimethylsilane catalyzed by $i\text{Pr}_3\text{SiOTf}$



*additional peaks from $i\text{Pr}_3\text{Si}$ moiety: $((\text{CH}_3)_2\text{CH})_3\text{-Si}$

Figure 59 ^{13}C NMR (101 Hz) for the results of the reaction between POSS monosilanol with ethyldimethylsilane catalyzed by $i\text{Pr}_3\text{SiOTf}$

4.6. The results for coupling reaction between POSS monosilanol and phenyldimethylsilane catalyzed by silyl triflate ester generated *in situ* from 0.04 equiv. of TfOH and phenyldimethylsilane

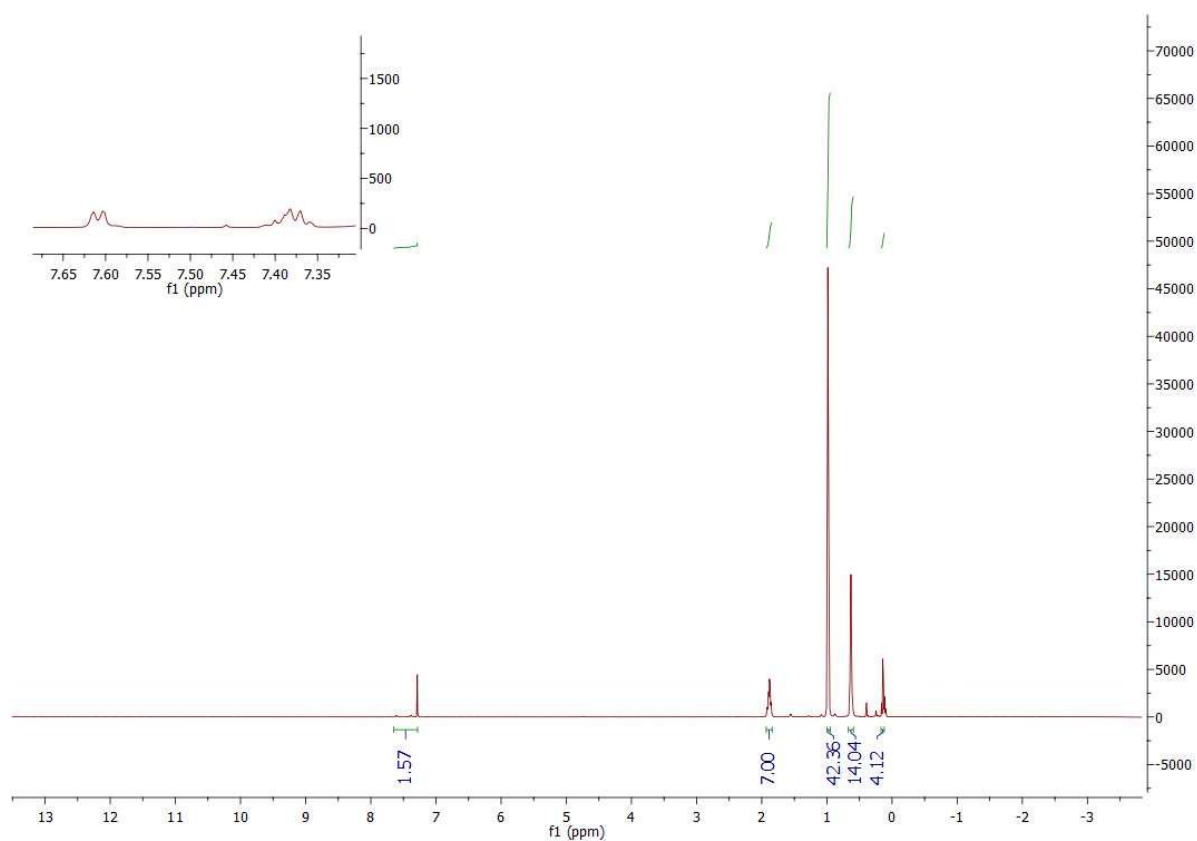
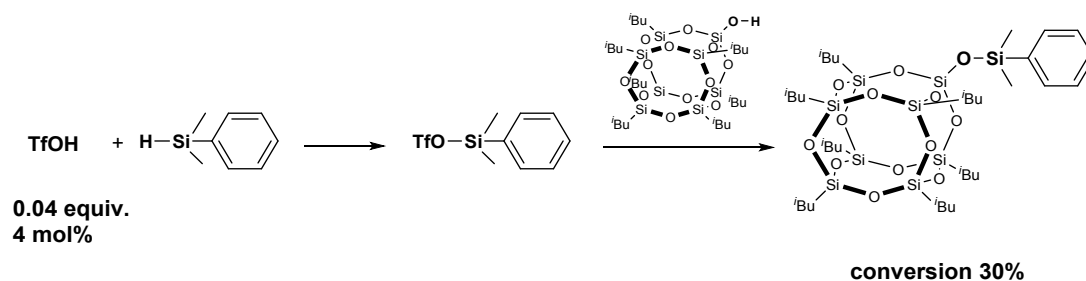


Figure 60 ^1H NMR (400 Hz) for the results of the reaction between POSS monosilanol with phenyldimethylsilane catalyzed by silyl ester generated *in-situ*.