Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Aerobic Co or Cu / NHPI - catalyzed oxidation of hydride siloxanes: synthesis of siloxanols

AUTHORS

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1. Materials and methods

^{1}H, ^{13}C, ^{29}Si and HMBC NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer in $CDCl_3$, chemical shifts are referenced to residual chloroform (7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad).

Analytical gas-liquid chromatography (GLC) was performed using a «Krystall-2000M» chromatograph: the detector is catarometer; helium as carrier gas; sorbent is Chromaton-H-AW with 5% silicon SE-30; 1m long column with 0.003 m diameter; temperature in the column 50-330 °C and hexamethyldisiloxane as internal standart.

GPC analysis was performed on the "Shimadzu" (Japan, Germany), the detector - refractometer RID - 20A, the column – Phenogel 5u 500A, 1000A (Size (300 x 7,8 mm)); standart – polystyrene, eluent – toluene; temperature - 40°C; speed of flow 1ml/sec.

Preparative chromatography was performed using «Reverelis Prep» (Buchi). Column: C18, 40 µm, lot #17042635, flow rate 32 ml/min.

High resolution mass spectra (HRMS) were registered on a Bruker Daltonics micrOTOF-Q II instrument using electrospray ionization (ESI). The measurements were acquired in a positive ion mode with the following parameters: interface capillary voltage 4500 V; mass range from m/z 50 to 3000; external calibration (Electrospray Calibrant Solution, Fluka); nebulizer pressure 0.4 Bar; flow rate 3 µL/min; nitrogen was applied as a dry gas (6L/min); interface temperature was set at 180°C.

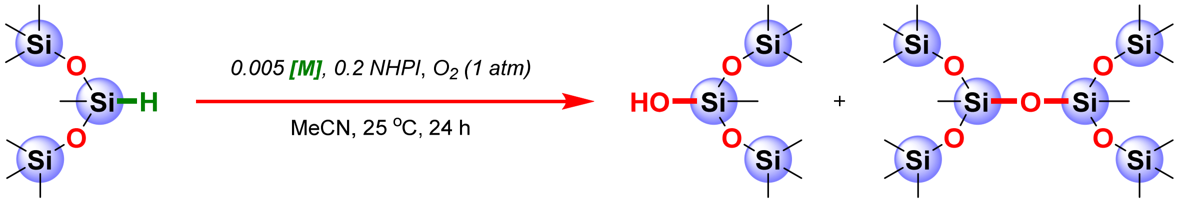
Samples were introduced into the mass spectrometer chamber via syringe injection, compounds were dissolved in acetonitrile.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker “Tensor 37”. Spectra were taken from thin films and CCl_4 solution.

All starting reagents and materials (incl. triethylsilane **1j**, 1,1,1,3,5,5,5-heptamethyltrisiloxane **1a**, heptamethylcyclotetrasiloxane **1c**, N-hydroxyphtalimide, metal salts (incl. cobalt acetate tetrahydrate and copper acetate monohydrate)) were purchased from Sigma Aldrich, Acros and ABCR. Solvents were dried and purified according to standard procedures.

2. Screening of Reaction Conditions

Table 2.1. The effect of [M]-catalyst[a]



1a **2a** **3a**

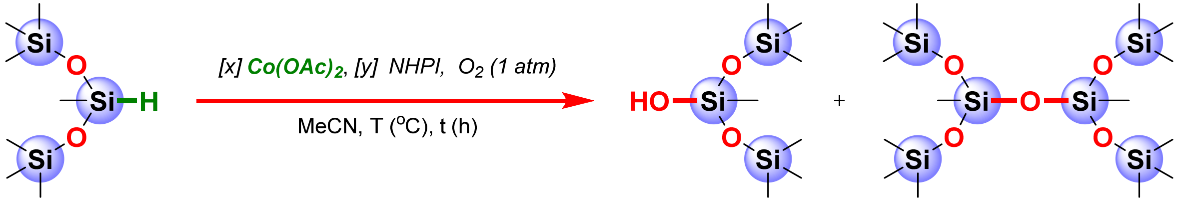
[M]	**$Co(OAc)_2$**	**$Co(acac)_2$**	**$Cu(OAc)_2$**	**$CuCl_2$**	**$CuCO_3$**	**$Cu(acac)_2$**	**CAN**	**$Cr(OAc)_3$**	**$Fe(acac)_3$**	**$Fe(OAc)_2$**	**$Ni(OAc)_2$**	**$Mn(OAc)_2$**
Yield of 2a, %	**60, 82^{b}, 16^{c}**	<1	**57, 11^{b}, 80^{c}**	5, 16^{c}	17, 62^{c}	0, 2^{c}	15	3	<1, 10^{c}	2	<1	<1
1a/2a/3a, %	**3/60/37, 16/82/2^{b}, 0/16/84^{c}**	99/1/0	**43/57/0, 89/11/0^{b}, 12/80/8^{c}**	95/5/0 77/16/7^{c}	82/17/1 35/62/3^{c}	100/0/0 96/2/2^{c}	70/15/15	97/3/0	99/1/0 90/10/0^{c}	98/2/0	99/1/0	99/1/0

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), [M] (2.25 µmol, 0.005 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 °C for 24 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

[b] 8 hours.

[c] 72 hours (3 days).

Table 2.2. The effect of Co(OAc)$_2$-, NHPI-loading, t (h) and T (°C)[a]

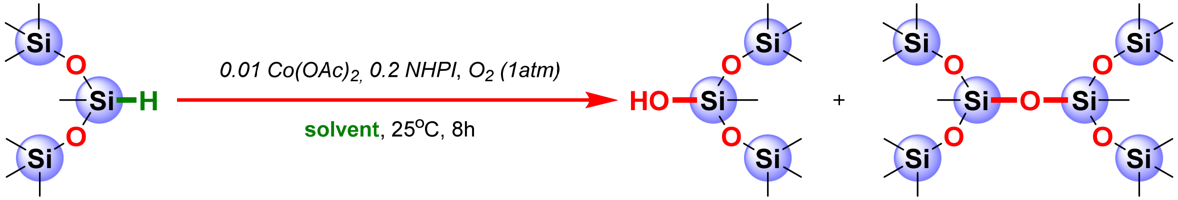


1a **2a** **3a**

№	[x]	[y]	T, °C	t, h	Yield, %	1a/2a/3a, %
1	0.005	*0.1*	25	8	75	21/75/4
2	0.005	*0.2*	25	8	82	16/82/2
3	0.005	*0.3*	25	8	56	41/56/3
4	***0.01***	**0.2**	**25**	**8**	**90**	**3/90/7**
5	*0.02*	0.2	25	8	84	15/84/1
6	0.01	0.2	*40*	4	85	3/85/12
7	0.01	0.2	*40*	8	64	1/64/35
8	0.01	0.2	*60*	4	86	1/86/13
9	0.01	0.2	*60*	8	56	0/56/44

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), NHPI (0.045 – 0.135 mmol, 0.1 - 0.3 eq.), Co(OAc)$_2$ (2.25 – 9 µmol, 0.005 - 0.02 eq.) and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 - 60 °C for 4 - 8 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

Table 2.3. The effect of solvent[a]

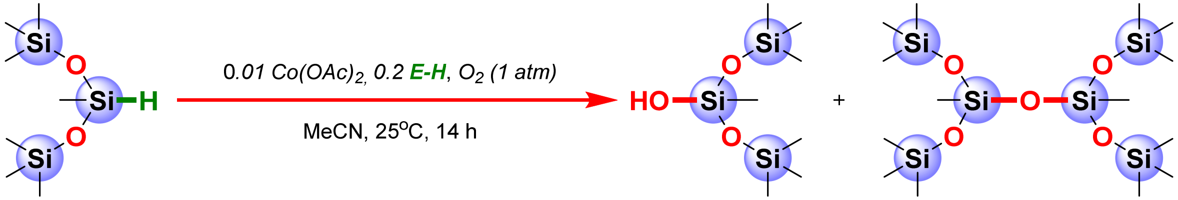


1a **2a** **3a**

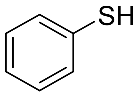
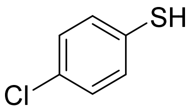
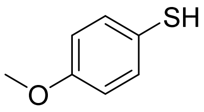
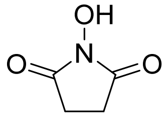
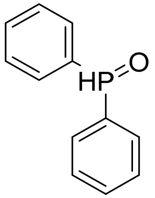
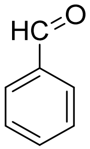
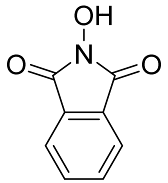
Solvent	THF	Et_2O	$MeNO_2$	DCM	DCE	PhH	TolH-F8	EtOAc	$Me_2C(O)$	MeCN
Yield of 2a, %	2	<1	<1	3	<1	1	<1	19	58	**90**
1a/2a/3a, %	26/2/72	99/1/0	98/1/1	92/3/5	97/1/2	99/1/0	97/1/2	78/19/3	37/58/5	**3/90/7**

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), $Co(OAc)_2$ (4.503 µmol, 0.01 eq.), and solvent (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 °C for 8 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

Table 2.4. The effect of organocatalyst (E-H reagent) [a]



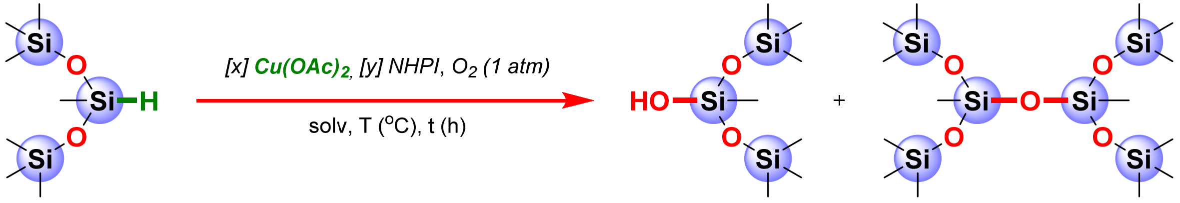
1a **2a** **3a**

Organocatalyst (E-H reagent)	PhSH 	*p*-Cl-C_6H_4-SH 	*p*-MeO-C_6H_4-SH 	NHS 	$Ph_2P(O)H$ 	PhC(O)H 	NHPI[b] 
Yield of 2a, %	3	2	3	2	10	27	**90**
1a / 2a / 3a, %	96/3/1	98/2/0	96/3/1	98/2/0	90/10/0	66/27/7	**3/90/7**

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), organocat. (0.090 mmol, 0.2 eq.), $Co(OAc)_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 °C for 14 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

[b] 8 hours

Table 2.5. The effect of $Cu(OAc)_2$-, NHPI-loading, t (h) and T (^{o}C)[a]



1a **2a** **3a**

№	[x]	[y]	T, °C	t, h	Yield of 2a, %	1a / 2a / 3a, %
1	0.005	*0.1*	25	48	56	42/56/2
2	0.005	*0.2*	25	48	67	27/67/6
3	0.005	*0.3*	25	48	51	44/51/5
4	0.005	*0.4*	25	48	43	54/43/3
5	*0.005*	0.2	25	72	80	12/80/8
6	*0.01*	0.2	25	72	83	8/83/9
7	*0.02*	0.2	25	72	78	9/78/13
9	0.01	0.2	*40*	9 – 12	85	8/85/7
10	**0.01**	**0.2**	***60***	**6 – 9**	**95, 70[b]**	**2/95/3**

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), NHPI (0.045 – 0.18 mmol, 0.1 - 0.4 eq.), [M] (2.25 – 9 μmol, 0.005 - 0.02 eq.) and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 - 60 °C for 6 - 72 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

[b] Separated yield.

Summary

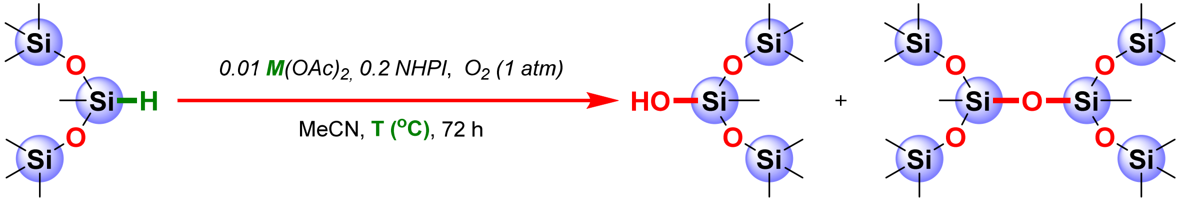
It was shown that in the case of the [Co]-catalyst the reduction of the reaction time from 24 to 8 hours led to the increase of **2a** yield from 60 to 82 % on account of the decrease of byproducts (siloxanes) production. In the case of the [Cu]-catalyst, the yield of **2a**, on the contary, decreased from 57% to 11% at 24 and 8 hours respectively (Table 2.1, notes *a* and *b*).

Prolongation of the reaction time from 24 hours to 3 days using [Cu] as a catalyst led to the increase in **2a** yield up to 80% without changes in the siloxanes formation (8%). While using [Co] at the same conditions, process almost completely ended in the siloxane formation (up to 84%) with only 16% yield of **2a** (Table 2.1, notes *a* and *c*).

This optimization indicates a slightly different behavior of the two most active catalysts at different times and temperatures. The above described experiments have shown, that there are at least two optimal variants of **2a** oxidation. The combination of three main parameters ([M], temperature, time) allows to determine optimal conditions for other substrates of different reactivity.

3. Optimization of synthesis and characterization data for 2a

Table 3.1. Optimization of 1a aerobic oxidation[a]



1a **2a** **3a**

	Cu(OAc)$_2$			Co(OAc)$_2$		
T, °C	**25**	**40**[b]	**60**[c]	**25**[c]	**40**[d]	**60**[d]
Yield of 2a, %	83	85	**95**	**90**	85	86
1a / 2a / 3a, %	8/83/9	8/85/7	**2/95/3**	**3/90/7**	3/85/12	1/86/13

[a] Reaction conditions: **1a** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), M(OAc)$_2$ (4.503 μmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 - 60 °C for 72 h under the oxygen static atmosphere. The yield of **2a** was determined by GLC.

[b] 9 – 12 hours.

[c] 6 – 9 hours.

[d] 4 hours

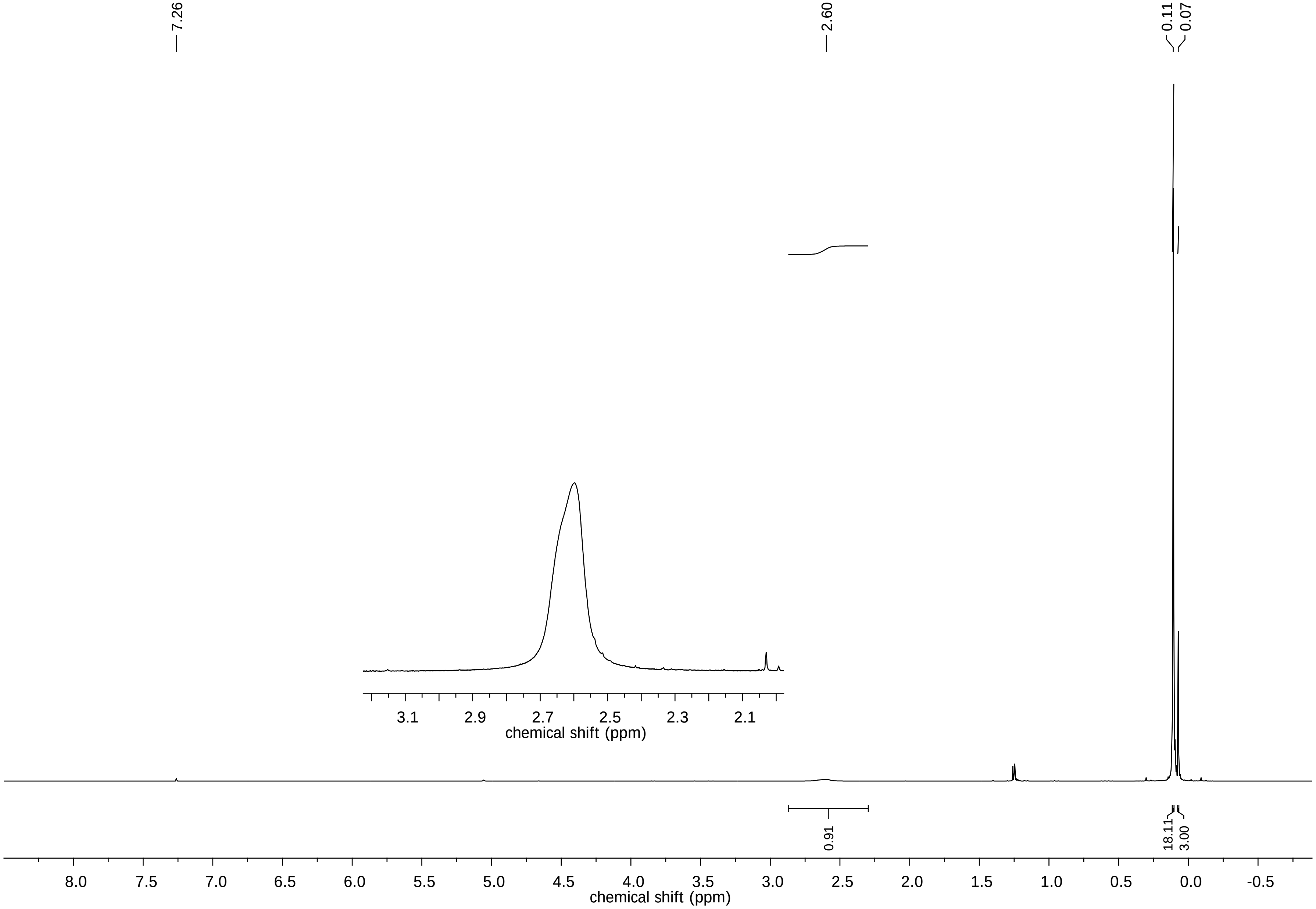
Method of ***2a*** *synthesis***:** **1a** (15 g, 67.5 mmol, 1 eq), NHPI (2.20 g, 13.5 mmol, 0.2 eq), Cu(OAc)$_2$×H$_2$O (0.13 g, 0.675 mmol, 0.01 eq) and MeCN (150 mL) were stirred in a 1000 ml round bottomed flask at 60 °C for 8 h under oxygen flow. According to GLC the yield of **2a** was 93-97%. 80-90% of the solvent was evaporated (180-200 mbar, T_{bath} = 40 °C). Then pentane (140-160 ml) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and solvents were evaporated (700 – 800 mbar, T_{bath} = 40 °C). Product **2a** was obtained as colorless oil by distillation under reduced pressure (BP = 76-78 °C at 23 mbar). The separated yield was 70% (11.25 g).

Characterization data for 1,1,1,3,5,5,5-Heptamethyltrisiloxanol (**2a**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3H); δ = 0.11 (s, 18H); 2.50 – 2.74 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = -2.98; 1.60. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -54.73; 8.55. IR (cm^{-1}): 3373, 2960, 1256, 1060. HRMS (ESI) m/z $[M - H]^-$: calcd for $[C_7H_{21}O_3Si_3]^-$, 237.0793; found, 237.0813; $[M + Na]^+$: calcd for $[C_7H_{22}O_3Si_3 + Na]^+$, 261.0769; found, 261.0765; $[M + NH_4]^+$: calcd for $[C_7H_{22}O_3Si_3 + NH_4]^+$, 256.1215; found, 256.1209.

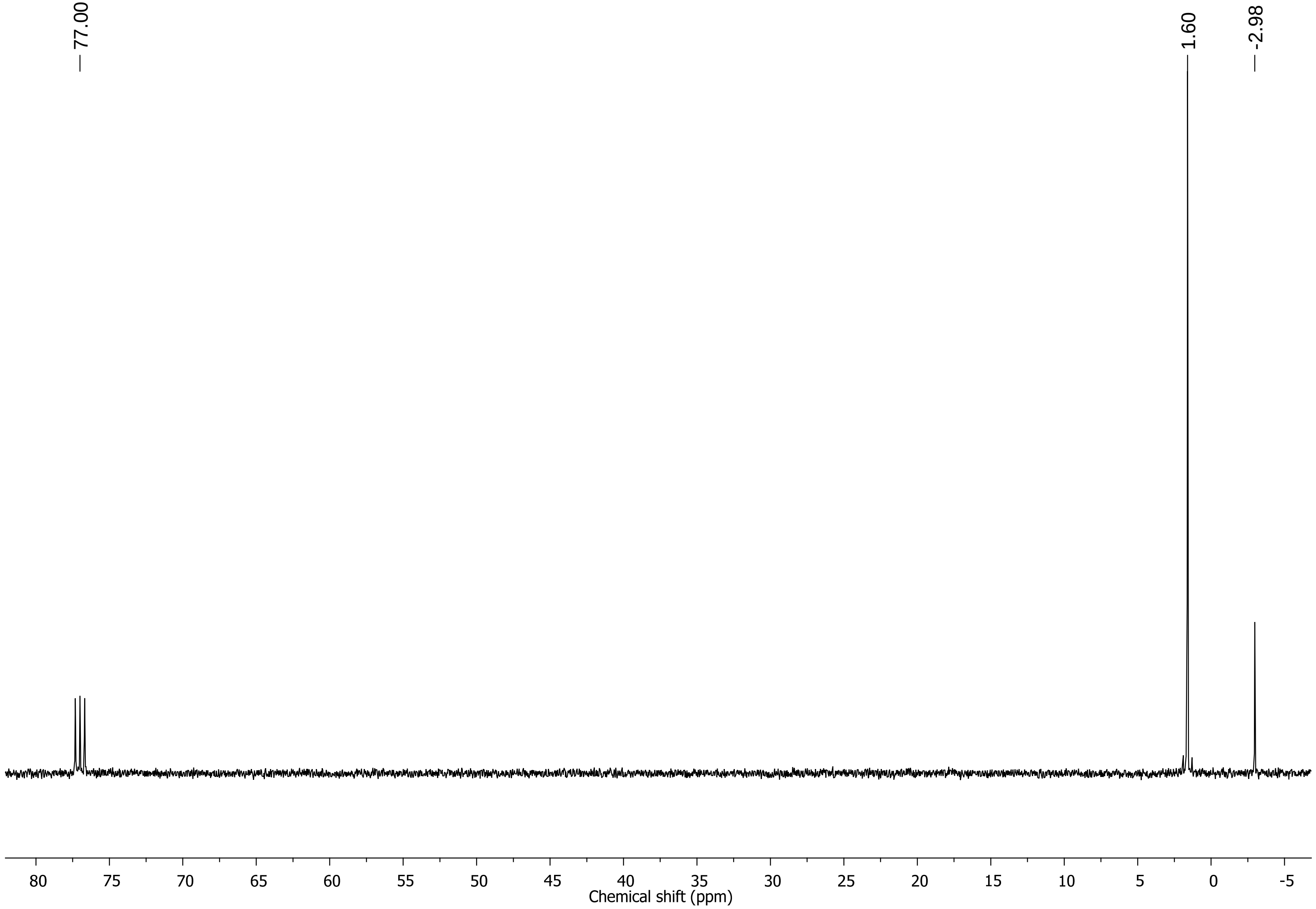
^{1}H NMR

(400 MHz, $CDCl_3$)



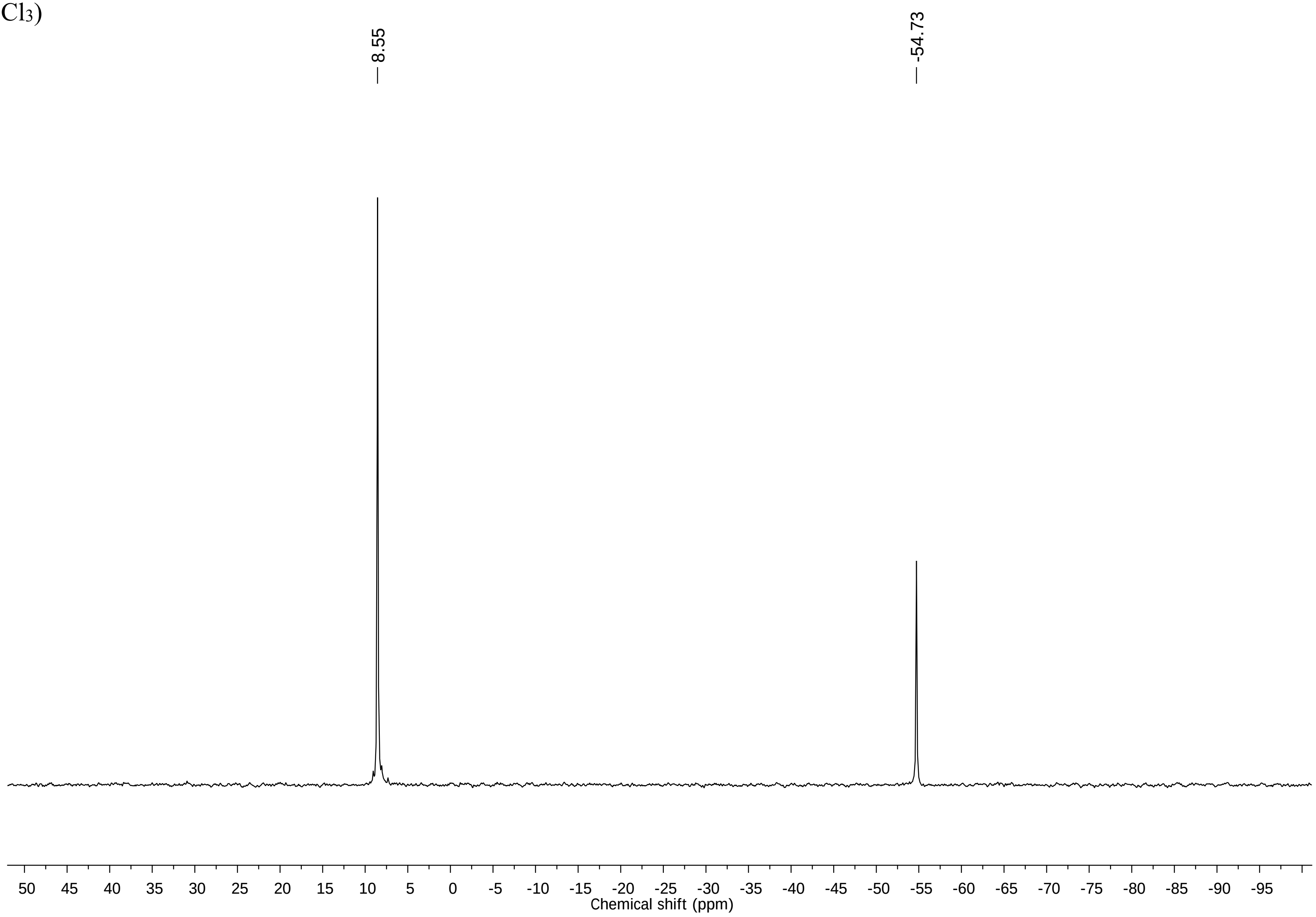
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

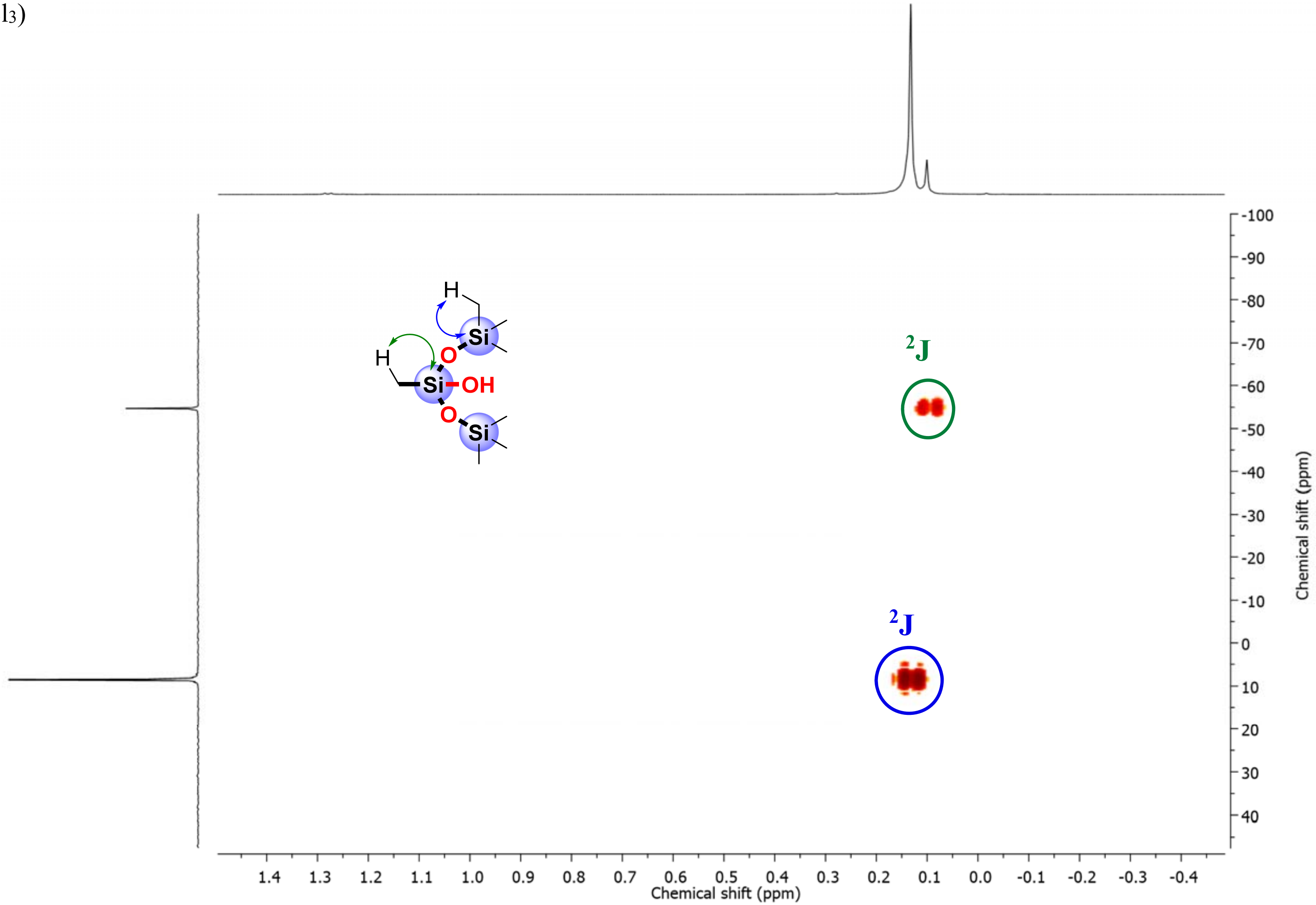
(80 MHz, $CDCl_3$)



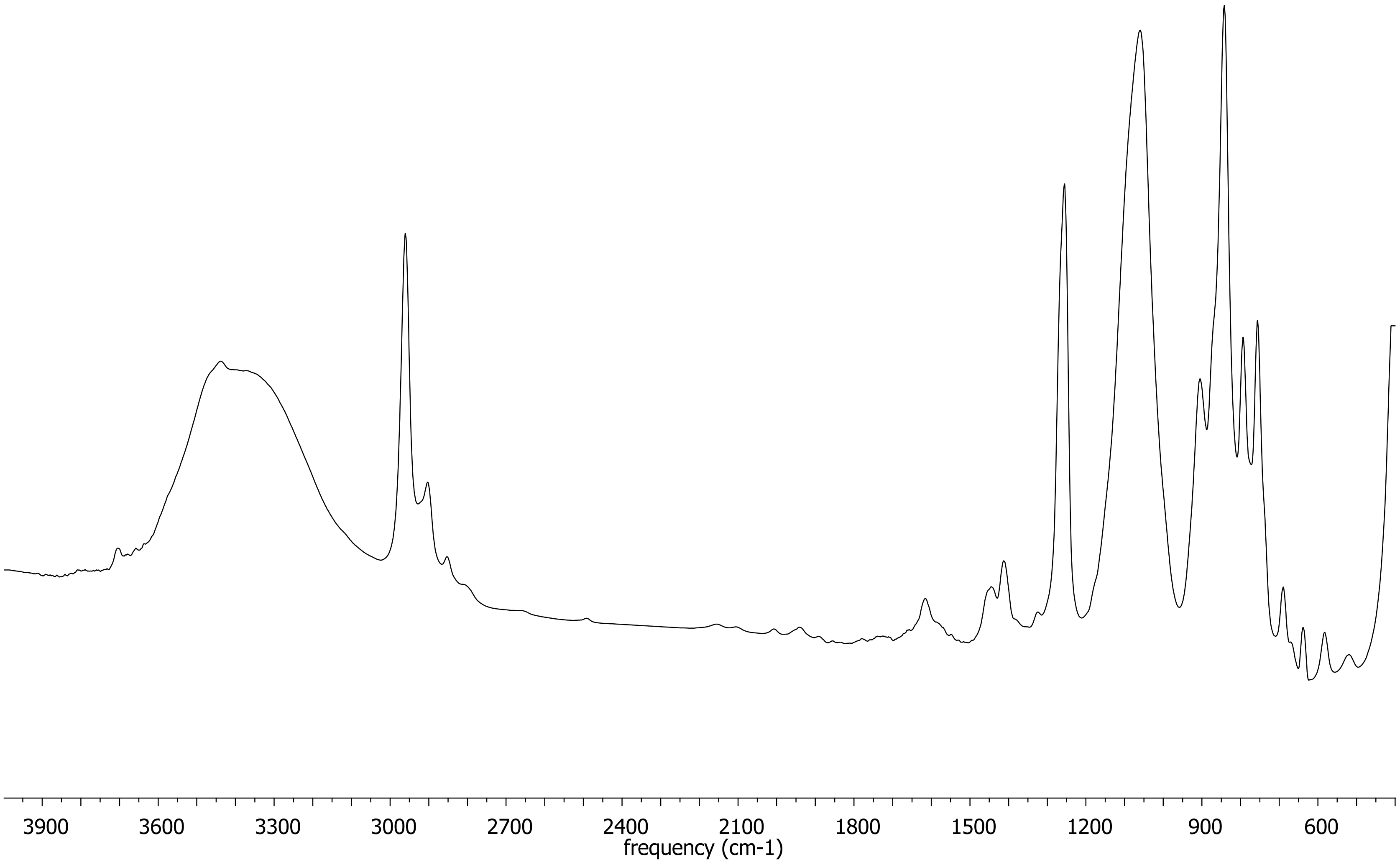
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)



IR-spectrum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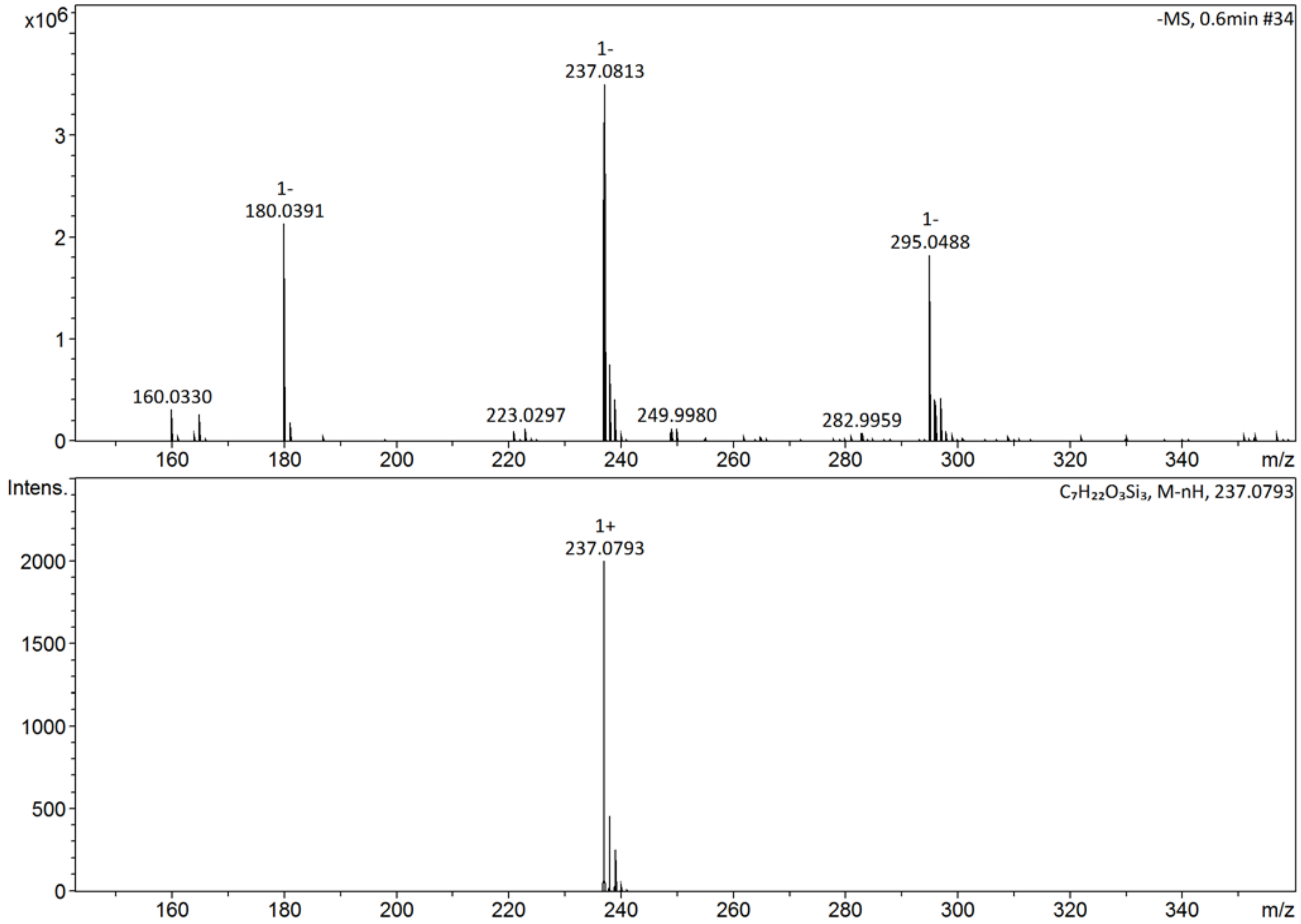
frequency (cm-1)

ESI-HRMS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1-
180.0391
1-
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249.9980
282.9959
0
1
2
3
160
180
200
220
240
260
280
300
320
340
m/z
Intens.
C₇H₂₂O₃Si₃, M-nH, 237.0793
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237.0793
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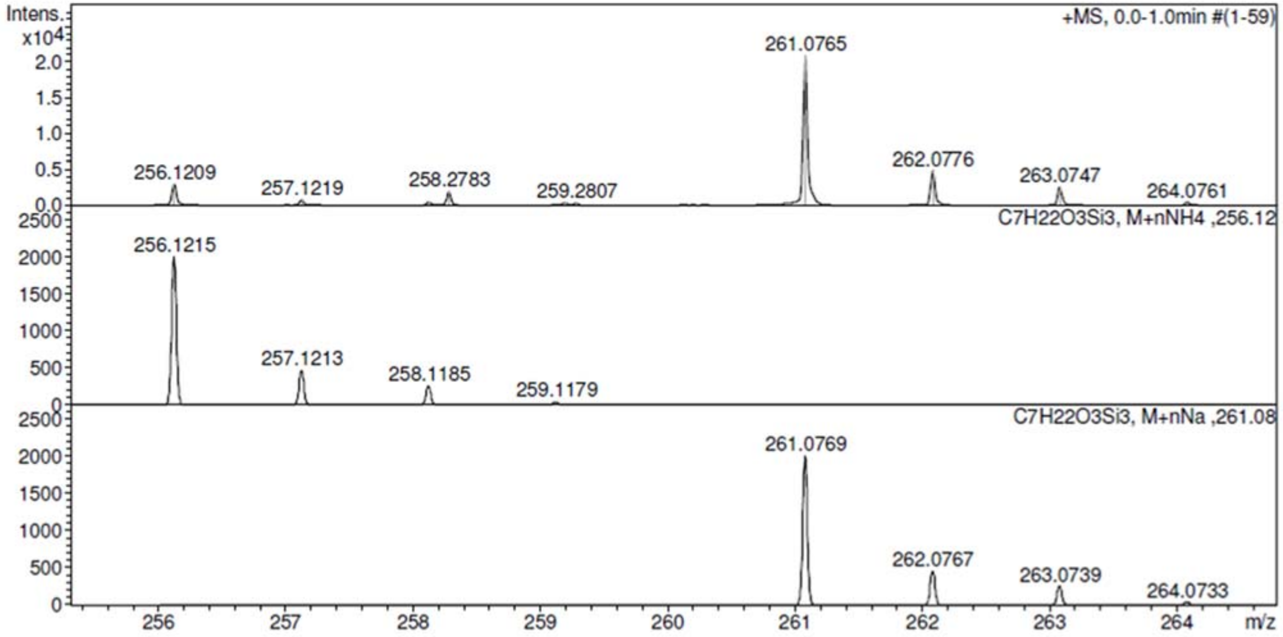
m/z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1500
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262.0767
263.0739
264.0733
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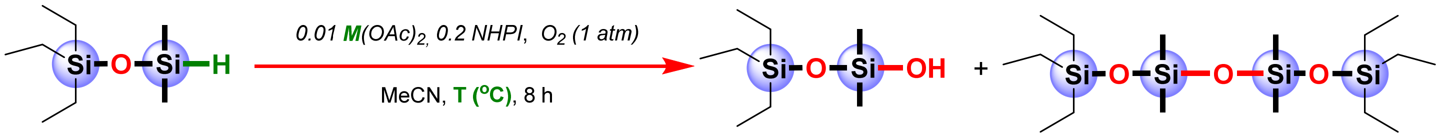
258
259
260
261
262
263
264
m/z

4. Optimization of synthesis and characterization data for 2b

Table 4.1. Optimization of 1b aerobic oxidation[a]



1b **2b** **3b**

	Cu(OAc)₂			**Co(OAc)₂**		
T, °C	**25**	**40**	**60**	**25** [b]	**40**	**60**
Yield of 2b, %	5	73	60	**77**	39	48
1b / 2b / 3b, %	95/5/0	15/73/12	26/60/14	**7/77/14**	41/39/20	43/48/9

[a] Reaction conditions: **1b** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.),M(OAc)$_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25 - 60 °C for 8 h under the oxygen static atmosphere. The yield of **2b** was determined by GLC.

[b] – 16 h.

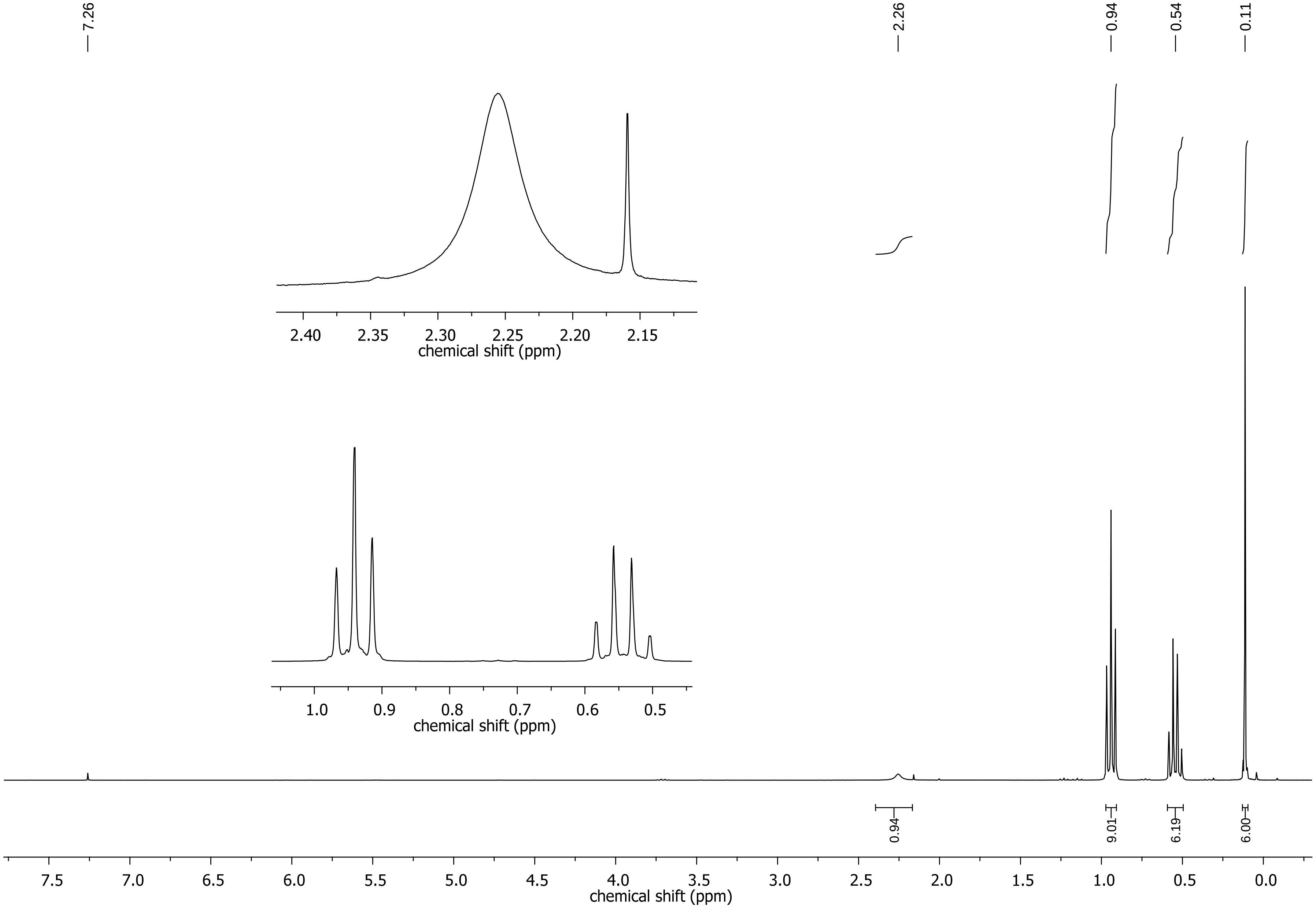
Method of ***2b*** *synthesis***:** **1b** (4.22 g, 22.16 mmol, 1 eq.), NHPI (0.72 g, 4.44 mmol, 0.2 eq.), Co(OAc)$_2$×4H$_2$O (0.055 g, 0.22 mmol, 0.01 eq.), and MeCN (50 mL) were stirred in a 500 ml round bottomed flask at 25 °C for 15 h under the oxygen static atmosphere. According to GLC the yield of **2a** was 75–79 %. 80-90% of the solvent was evaporated (180-200 mbar, T_{bath} = 40 °C). Then pentane (60-80 mL) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite and then solvents were evaporated (700-800 mbar, T_{bath} = 40 °C). Product **2b** was obtained as colorless oil by distillation under reduced pressure (BP = 61-62 °C at 1 mbar). The separated yield was 40% (1.83 g).

Characterization data for 3,3,3-triethyl-1,1-dimethyldisiloxan-1-ol (**2b**):

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.11 (s, 6H); δ = 0.54 (q, J = 10.4 Hz, 6H); 0.94 (t, J = 10.4 Hz, 9H); 2.26 (br, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 0.34; 6.16; 6.65. ^{29}Si NMR (80 MHz, CDCl$_3$): δ = -11.34; 10.65. IR (cm^{-1}): 3344, 2958, 1258, 1077. HRMS (ESI) m/z [M – H]$^-$: calcd for [$C_8H_{22}O_2Si_2$ – H]$^-$, 205,1075; found, 205,1075

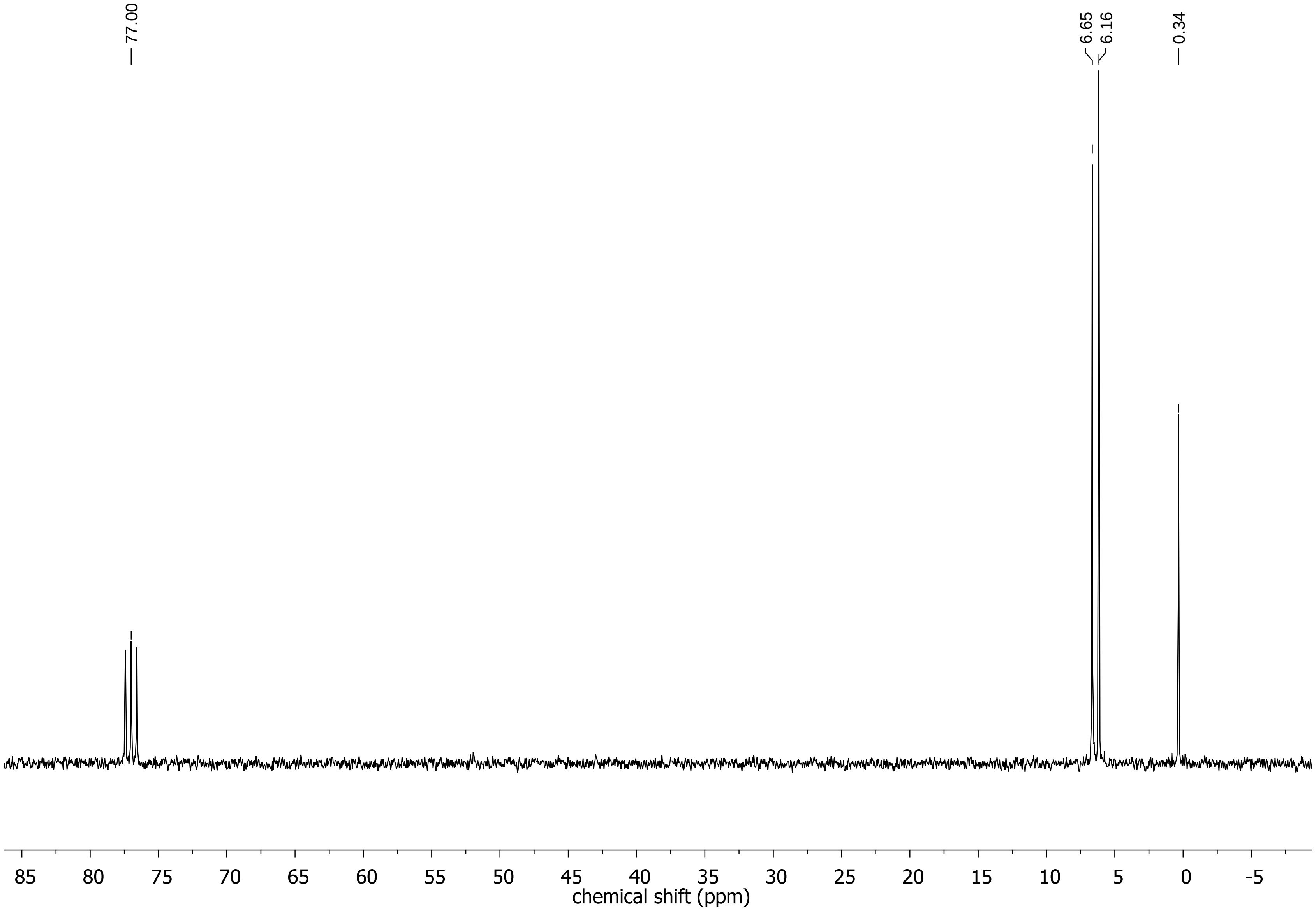
^{1}H NMR

(400 MHz, $CDCl_3$)



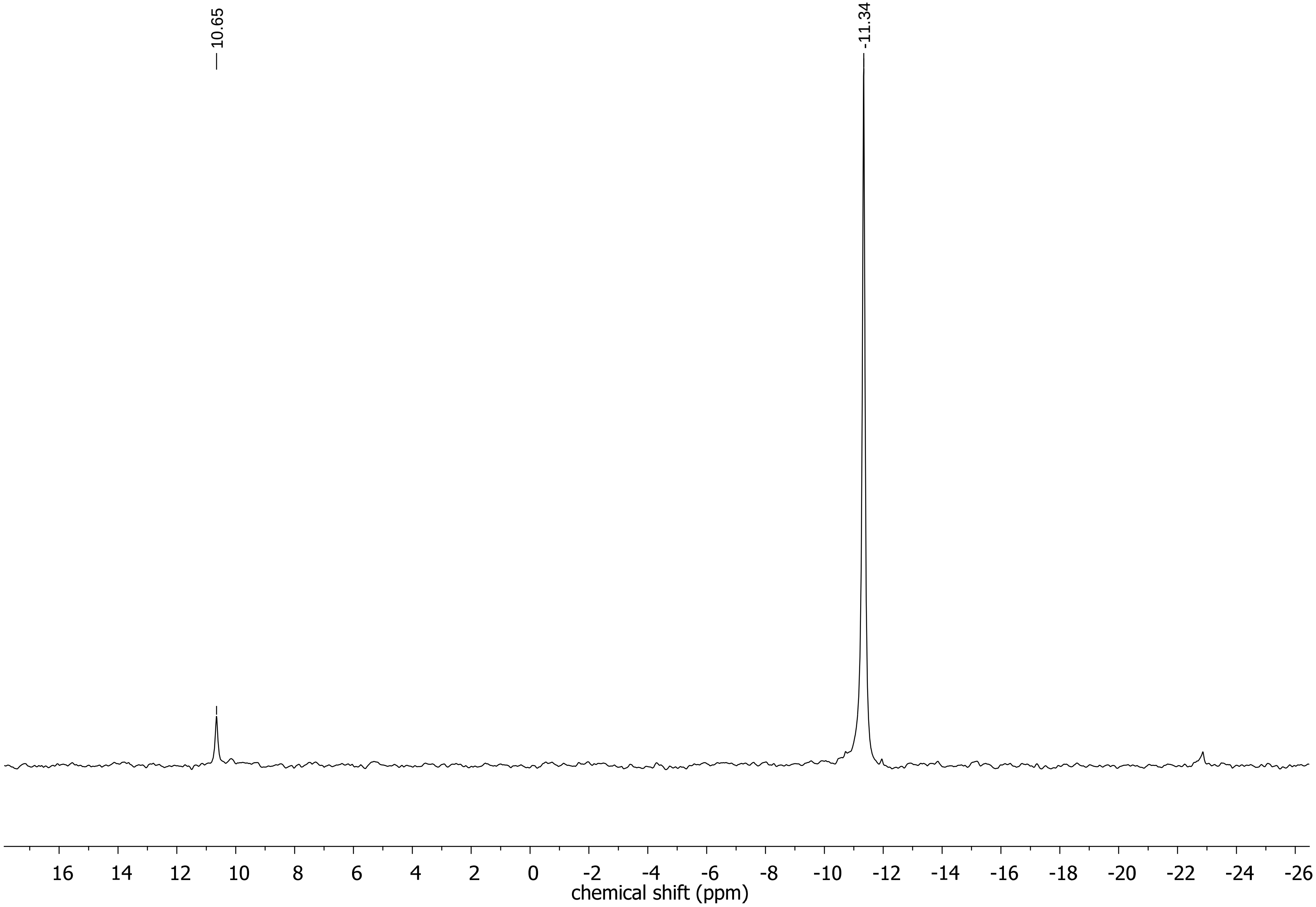
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

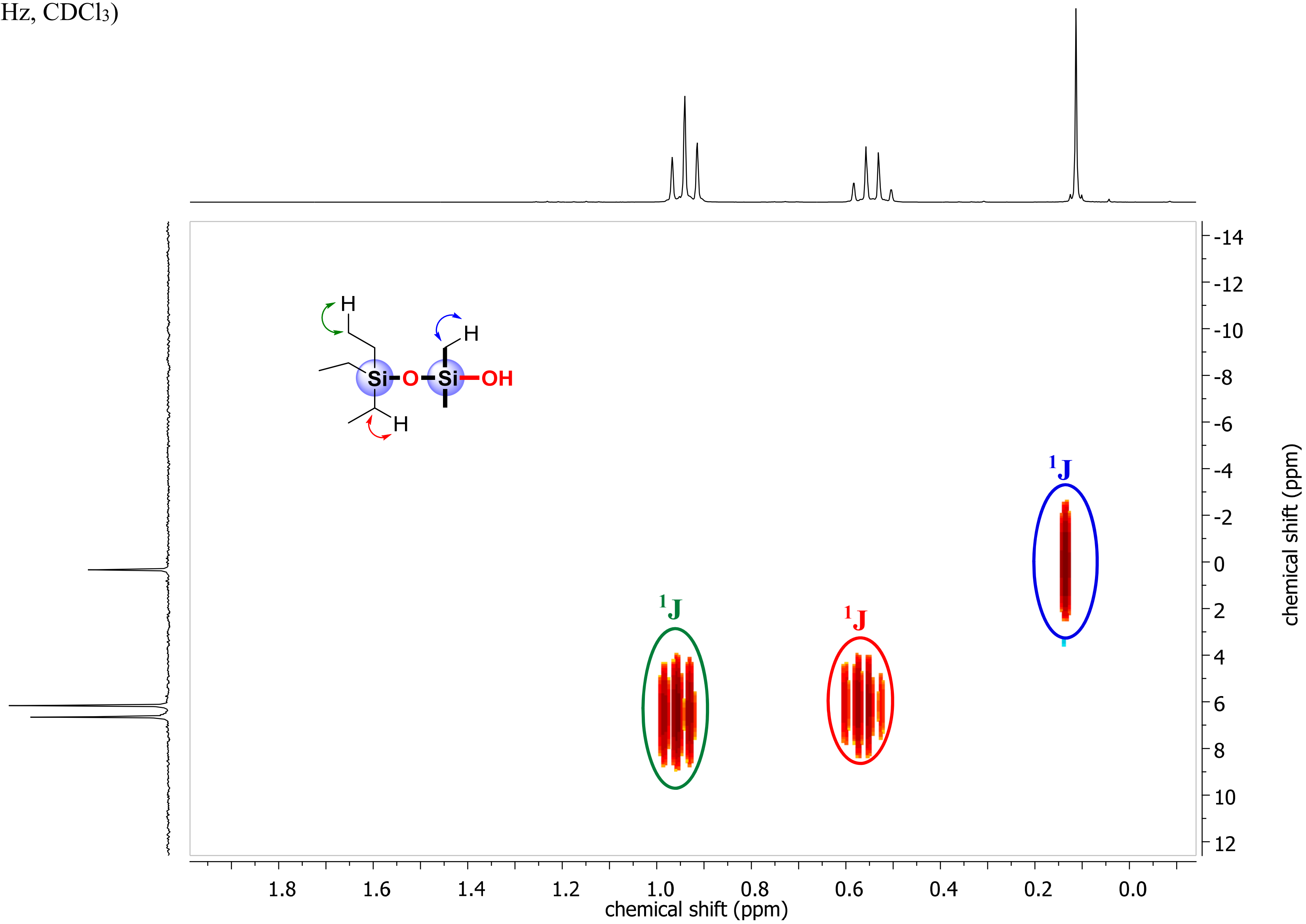
(80 MHz, $CDCl_3$)



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

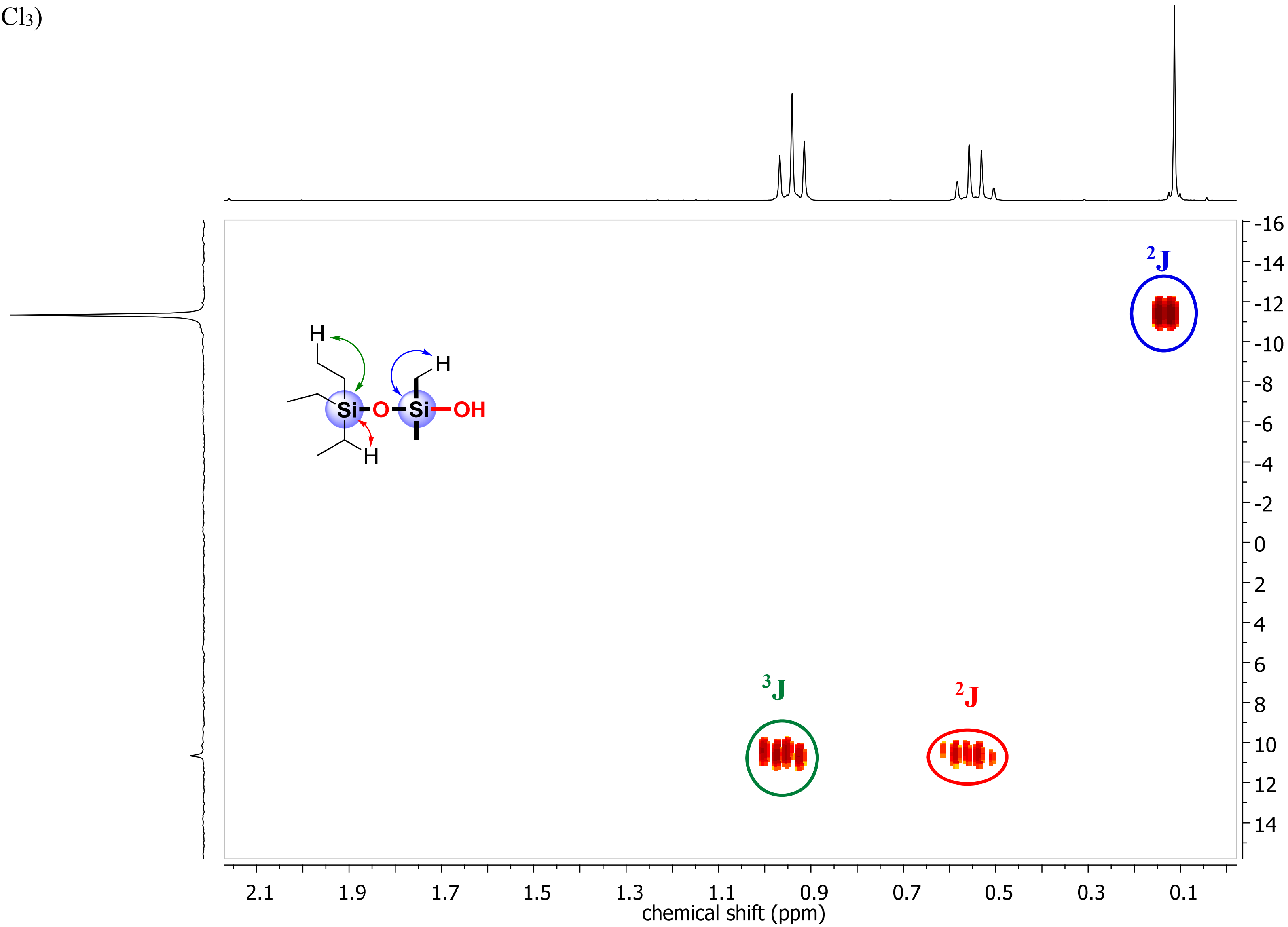
^{13}C: 100 MHz, $CDCl_3$)



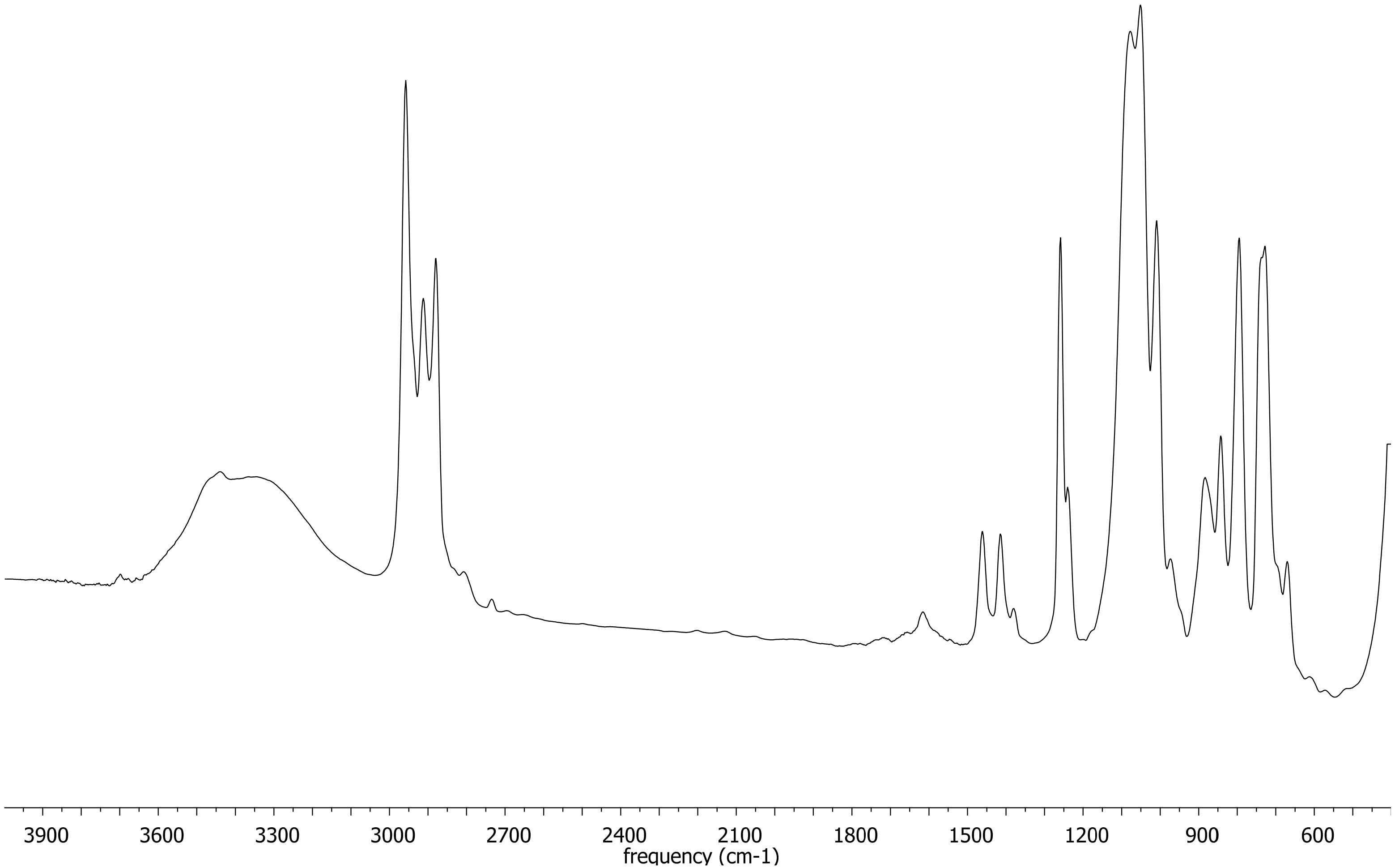
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

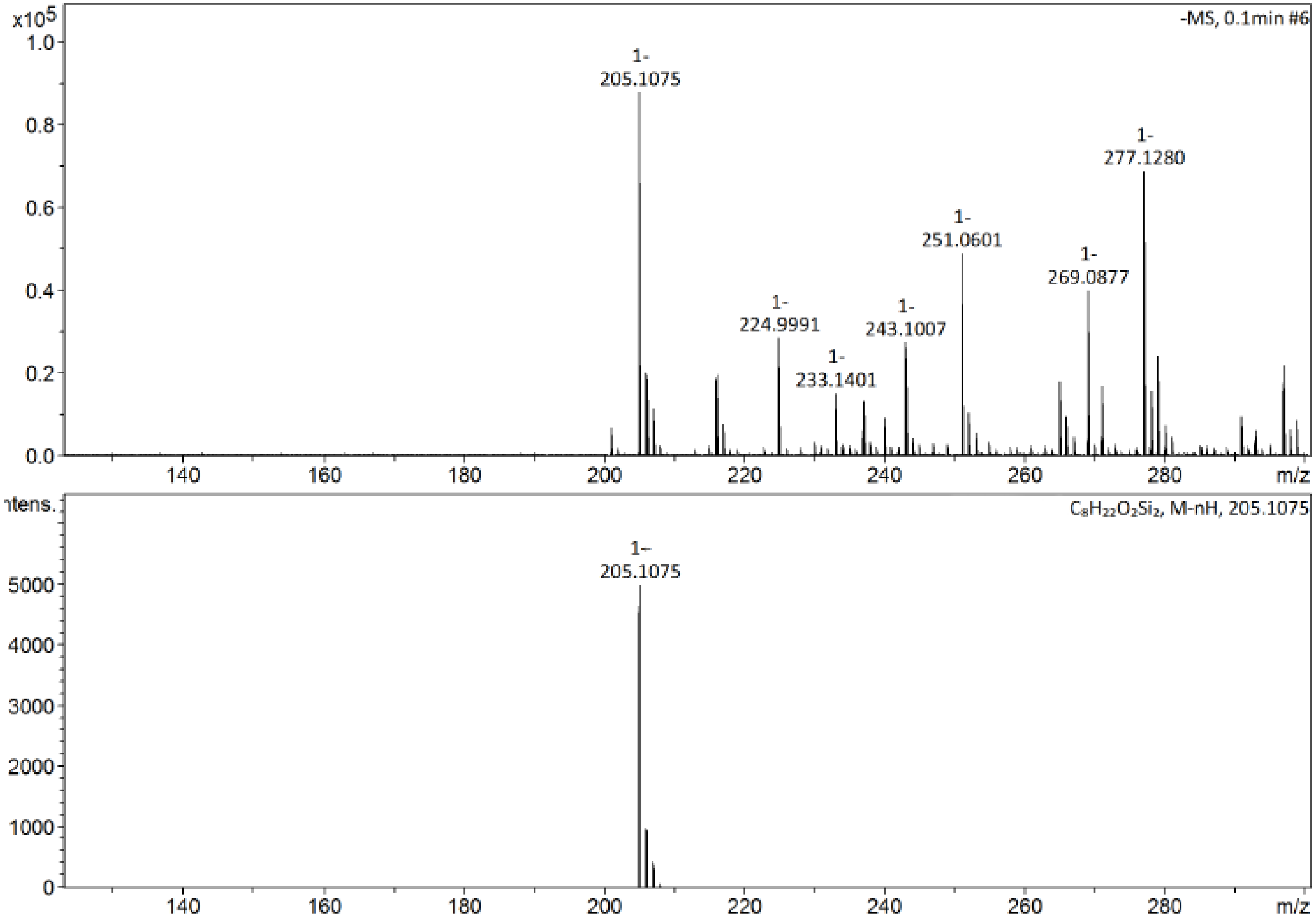
^{29}Si: 80 MHz, $CDCl_3$)



IR-spectrum

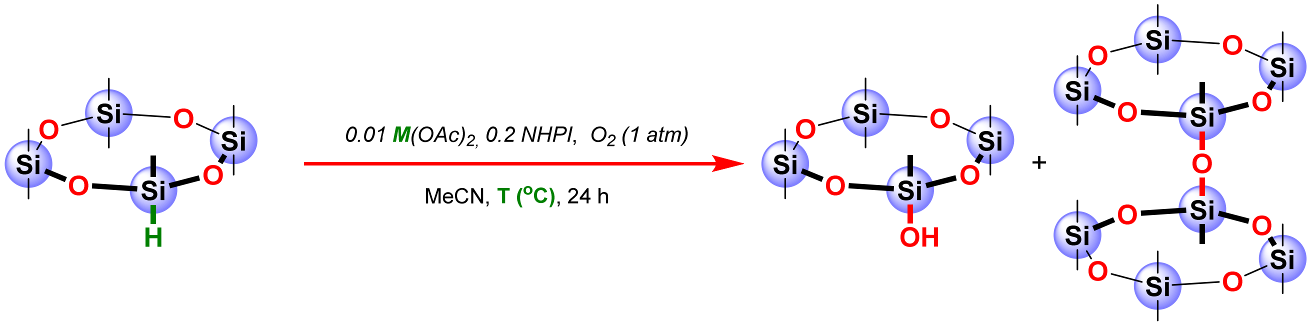

3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

ESI-HRMS


x10^5
1.0
0.8
0.6
0.4
0.2
0.0
-MS, 0.1min #6
1- 205.1075
1- 224.9991
1- 233.1401
1- 243.1007
1- 251.0601
1- 269.0877
1- 277.1280
140
160
180
200
220
240
260
280
m/z
Intens.
5000
4000
3000
2000
1000
0
C₈H₂₂O₂Si₂, M-nH, 205.1075
1– 205.1075
140
160
180
200
220
240
260
280
m/z

5. Optimization of synthesis and characterization data for 2c

Table 5.1. Optimization of 1c aerobic oxidation [a]



1c **2c** **3c**

T, °C	Cu(OAc)$_2$		Co(OAc)$_2$	
	40	**60**	**40**	**60**
Yield of 2c, %	24	23	75	83
1c / 2c / 3c, %	72/24/4	34/23/43	18/75/7	13/83/4

[a] Reaction conditions: **1c** (0.450 mmol, 1 eq.), NHPI (0.0905mmol, 0.2 eq.), M(OAc)$_2$ (4.525 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 8 h under the oxygen static atmosphere. The yield of **2c** was determined by GLC.

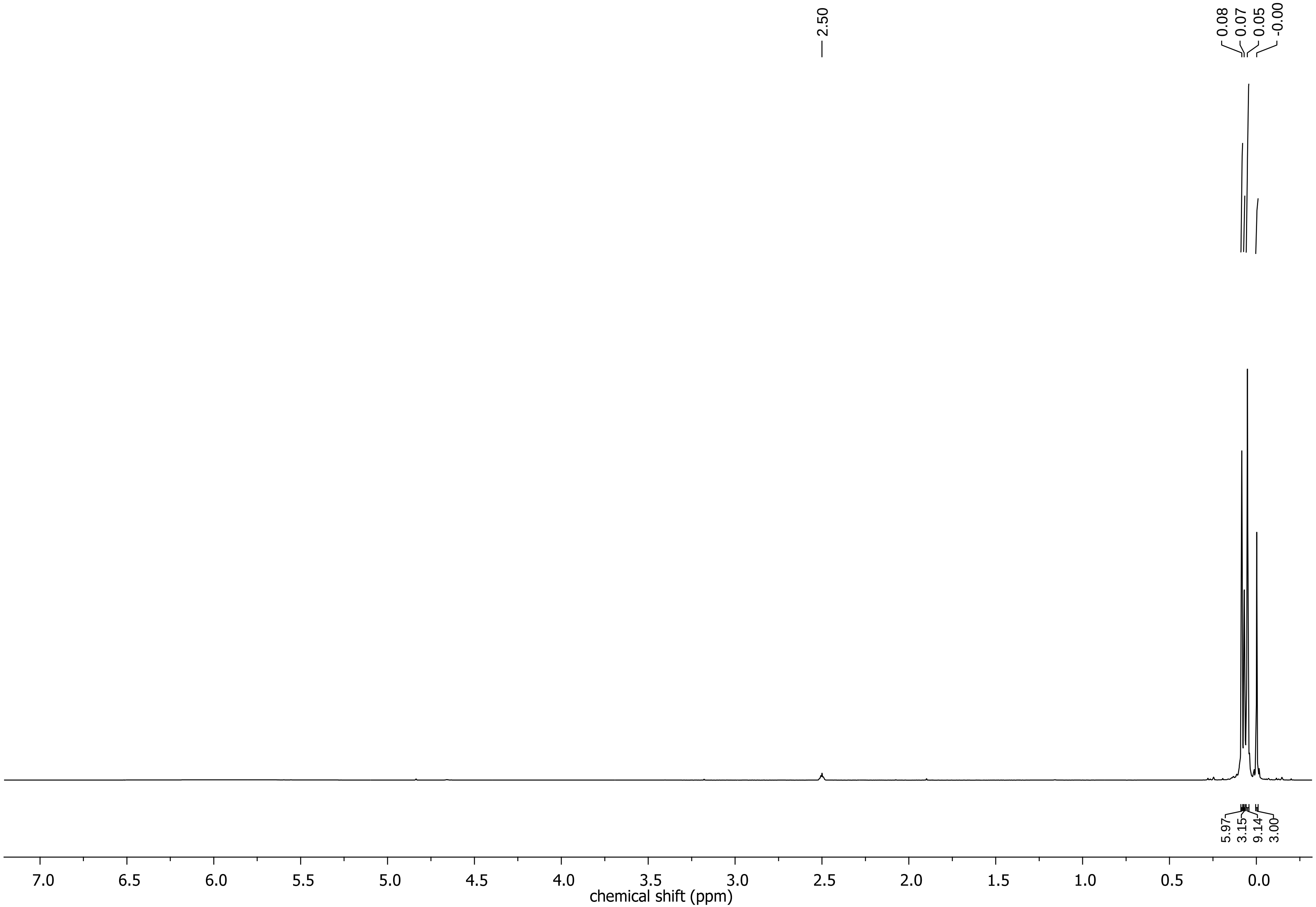
Method of ***2c*** *synthesis***:** **1c** (8g, 28.4 mmol, 1 eq.), NHPI (0.925 g, 5.67 mmol, 0.2 eq.), Co(OAc)$_2$×4H$_2$O (0.071 g, 0.284 mmol, 0.01 eq.), and acetonitrile (60 mL) were stirred in a 500 ml round bottomed flask at 60 °C for 8 h under the oxygen static atmosphere. According to GLC the yield of **2c** was 82–85 %. 80-90% of the solvent was evaporated (180-200 mbar, T$_{bath}$ = 40 °C). Then pentane (60-70 mL) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and solvents were evaporated (700 – 800 mbar, T$_{bath}$ = 40 °C). Product **2c** was obtained as colorless oil by distillation under reduced pressure (BP = 60-61 °C at 2 mbar). The separated yield was 56% (4.74 g).

Characterization data for 1,3,3,5,7,7-heptamethylcyclotetrasiloxane-1-ol (**2c**):

^{1}H NMR (400 MHz, DMSO-D$_6$): δ = 0.00 (s, 3H); δ = 0.05 (s, 9H); 0.07(s, 3H), 0.08 (s, 6H), 5-7 (br, 1H). ^{13}C NMR (100 MHz, DMSO-D$_6$): δ = -2.37, 0.97, 1.07, 1.12. ^{29}Si NMR (80 MHz, DMSO-D$_6$): δ = -56.18; -19.46, -19.04. IR (cm^{-1}): 3327, 2965, 1262, 1077. HRMS (ESI) m/z [M + H]$^+$: calcd for [$C_7H_{22}O_5Si_4$ + H]$^+$, 299.0617; found, 299.0612; [M + Na]$^+$: calcd for [$C_7H_{22}O_5Si_4$ + Na]$^+$, 321.0437; found, 321.0435; [M + NH$_4$]$^+$: calcd for [$C_7H_{22}O_5Si_4$ + NH$_4$]$^+$, 316.0883; found, 316.0878.

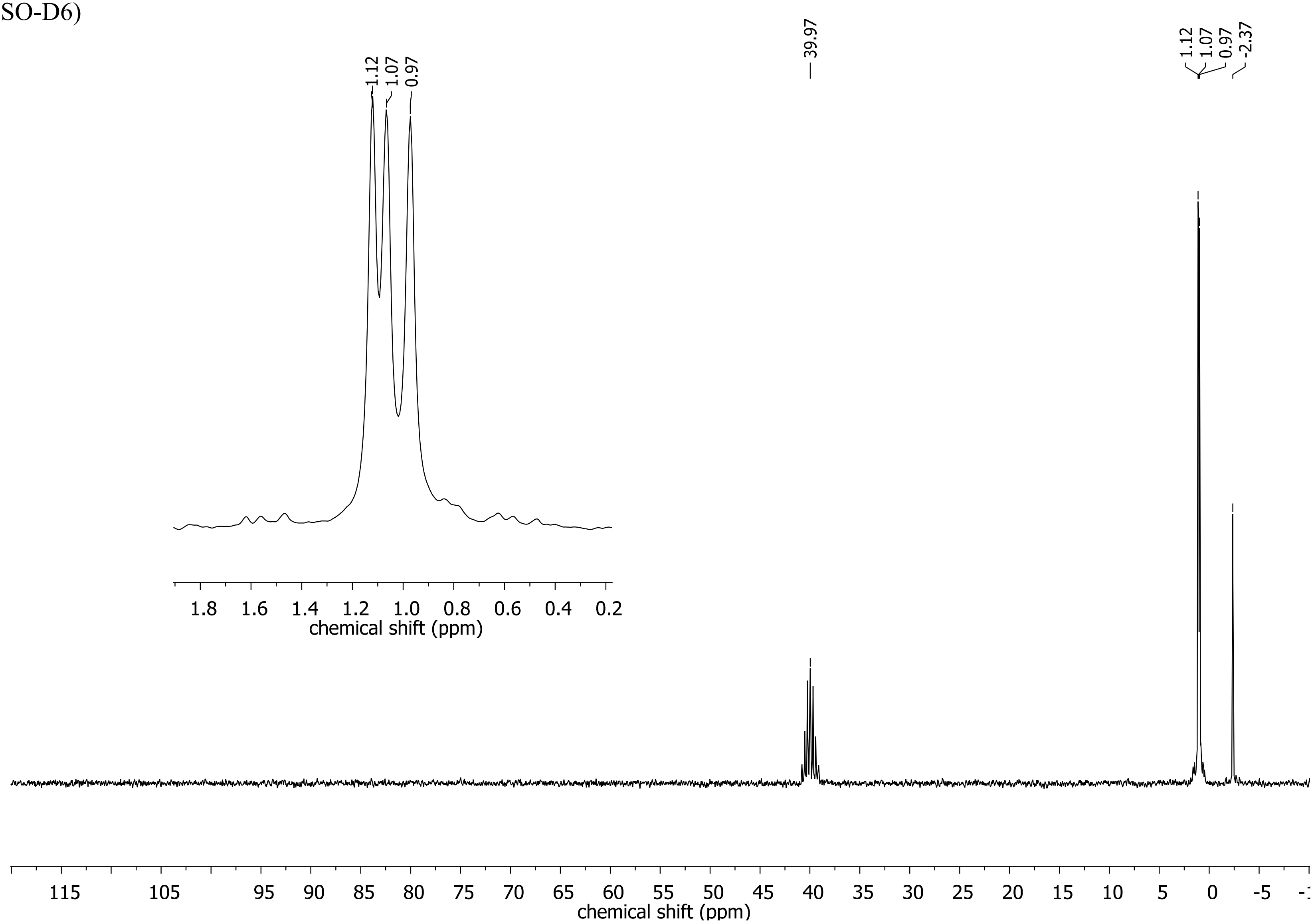
^{1}H NMR

(400 MHz, DMSO-D6)



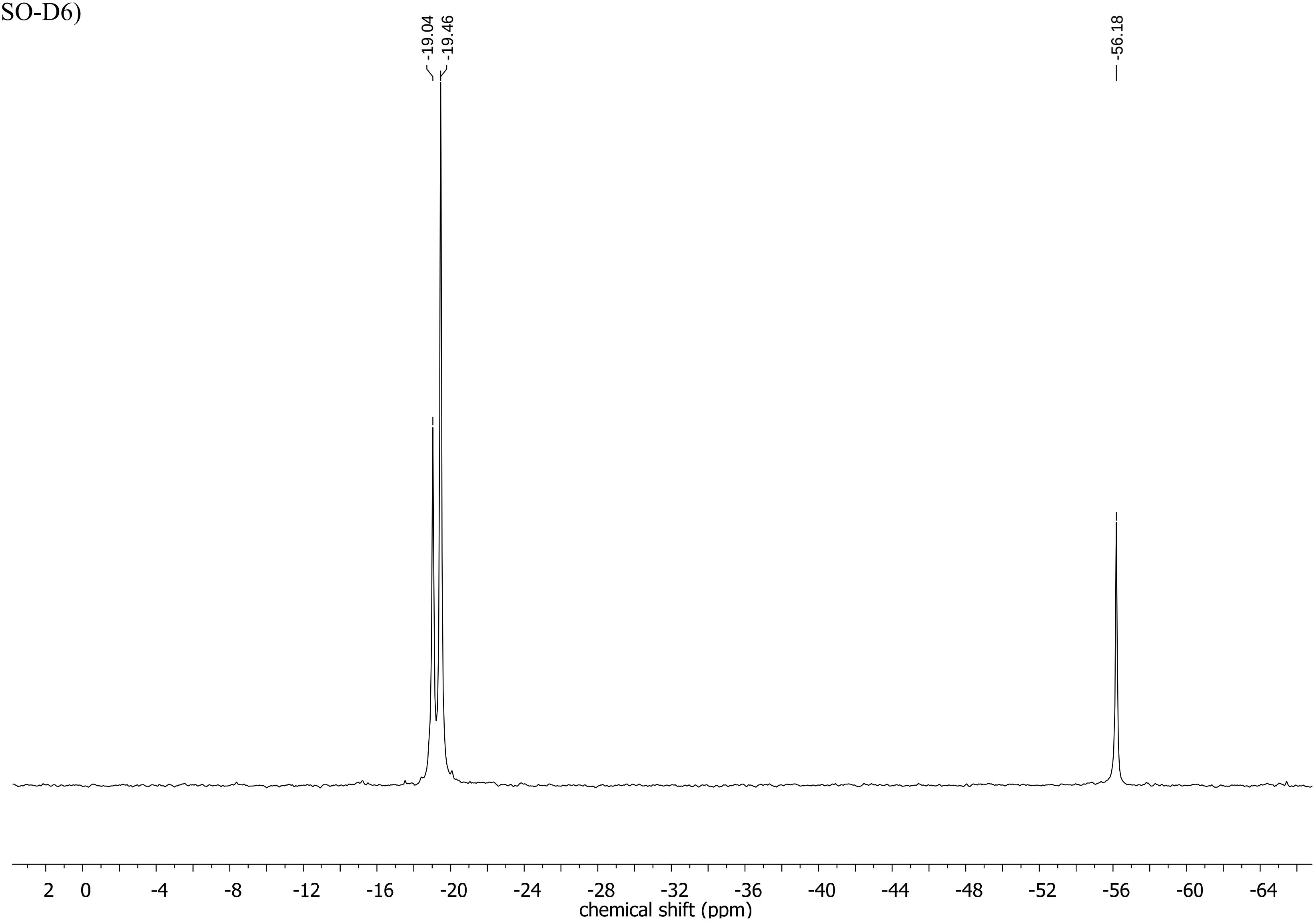
^{13}C NMR

(100 MHz, DMSO-D6)



^{29}Si NMR

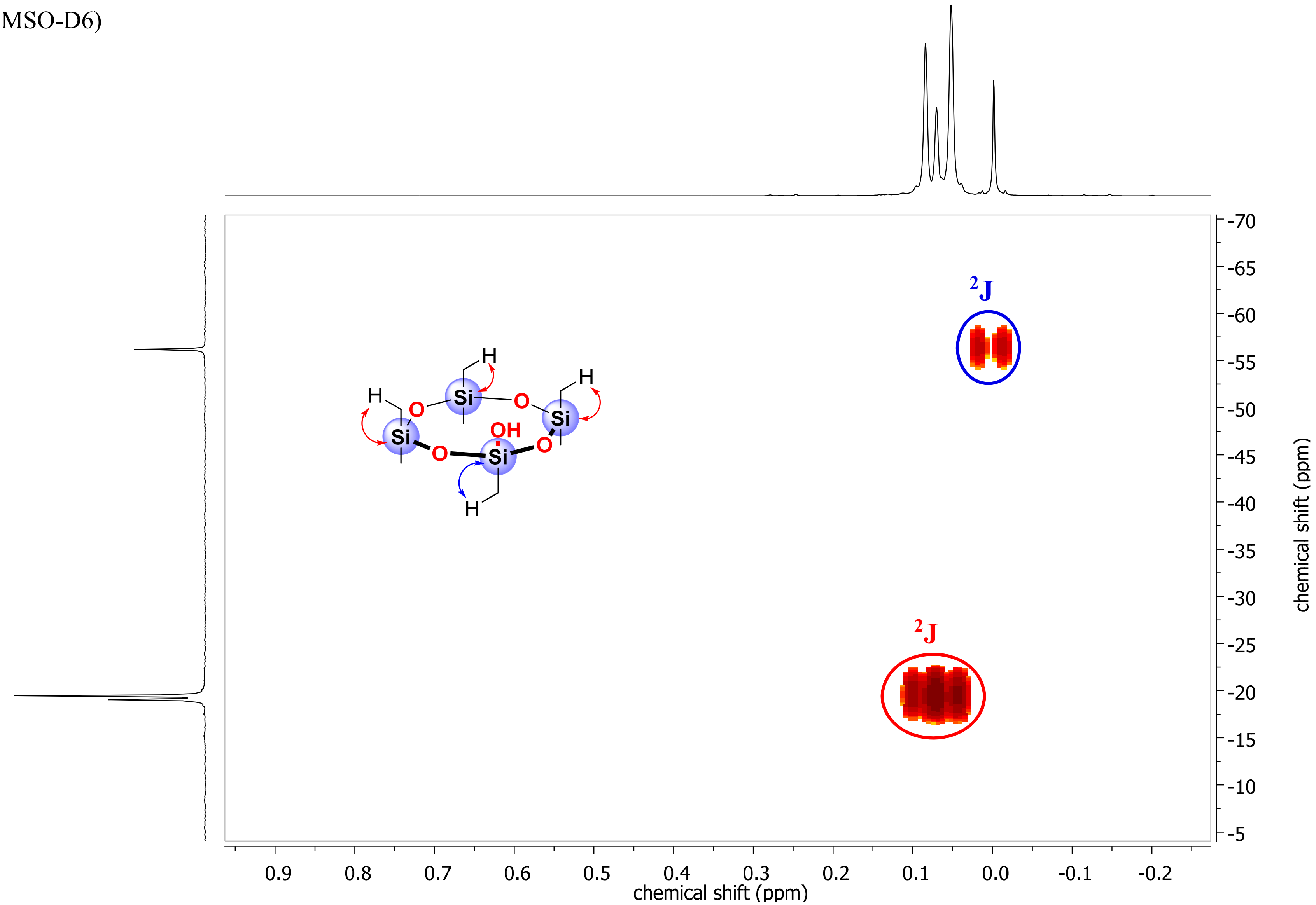
(80 MHz, DMSO-D6)



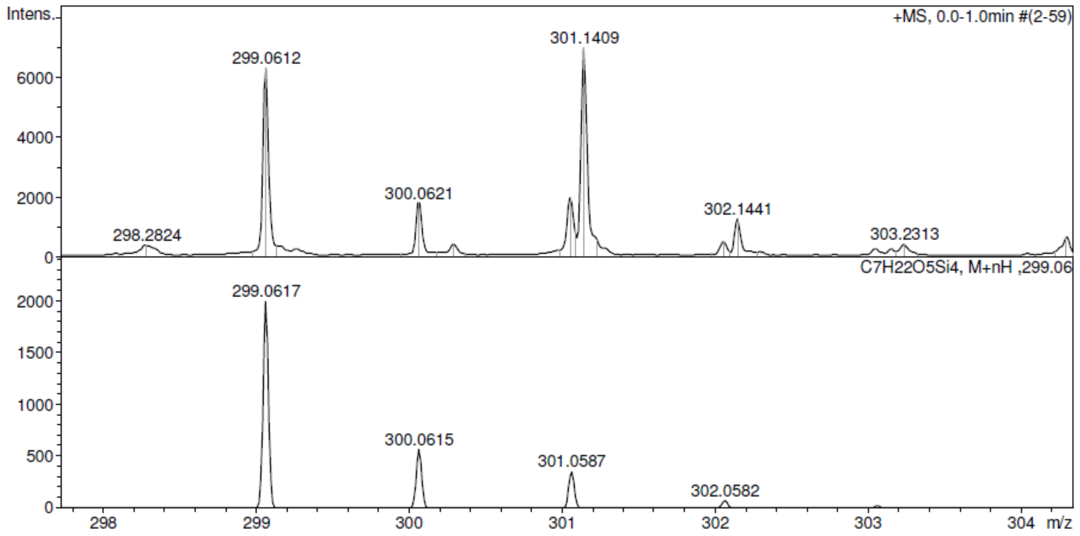
^{1}H, ^{29}Si –HMBC NMR

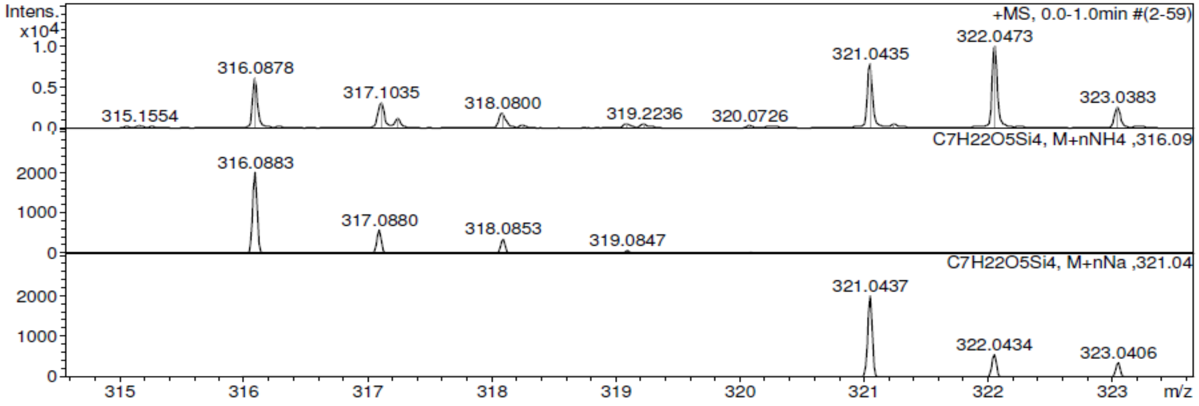
(^{1}H: 400 MHz,

^{29}Si: 80 MHz, DMSO-D6)



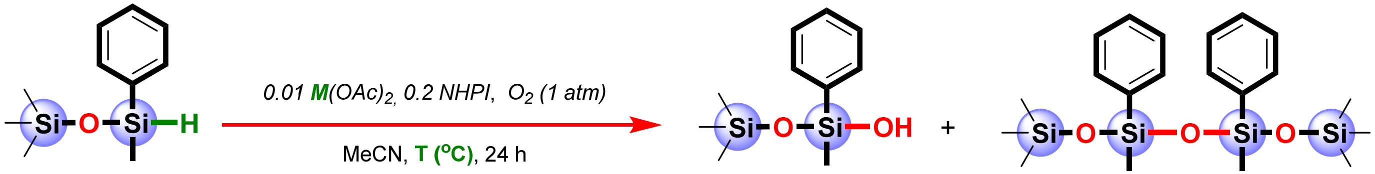
ESI-HRMS


Intens.
+MS, 0.0-1.0min #(2-59)
6000
4000
2000
0
298.2824
299.0612
300.0621
301.1409
302.1441
303.2313
C7H22O5Si4, M+nH ,299.06
2000
1500
1000
500
0
299.0617
300.0615
301.0587
302.0582
298
299
300
301
302
303
304
m/z


Intens.
x10^4
1.0
0.5
0.0
+MS, 0.0-1.0min #(2-59)
315.1554
316.0878
317.1035
318.0800
319.2236
320.0726
321.0435
322.0473
323.0383
C7H22O5Si4, M+nNH4 ,316.09
2000
1000
0
316.0883
317.0880
318.0853
319.0847
C7H22O5Si4, M+nNa ,321.04
2000
1000
0
321.0437
322.0434
323.0406
315
316
317
318
319
320
321
322
323
m/z

6. Optimization of synthesis and characterization data for 2d

Table 6.1. Optimization of 1d aerobic oxidation[a]



1d **2d** **3d**

	$Cu(OAc)_2$			$Co(OAc)_2$		
T, °C	**25**	**40**	**60**	**25**[b]	**40**[b]	**60**[c]
Yield of 2d, %	1	10	3	**74**	54	49
1d / 2d / 3d, %	99/1/0	88/10/1	97/3/0	**26/58/16**	22/54/24	26/49/25

[a] Reaction conditions: **1d** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), $M(OAc)_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 24 h under the oxygen static atmosphere. The yield of **2d** was determined by GLC.

[b] 9 hours.

[c] 6hours.

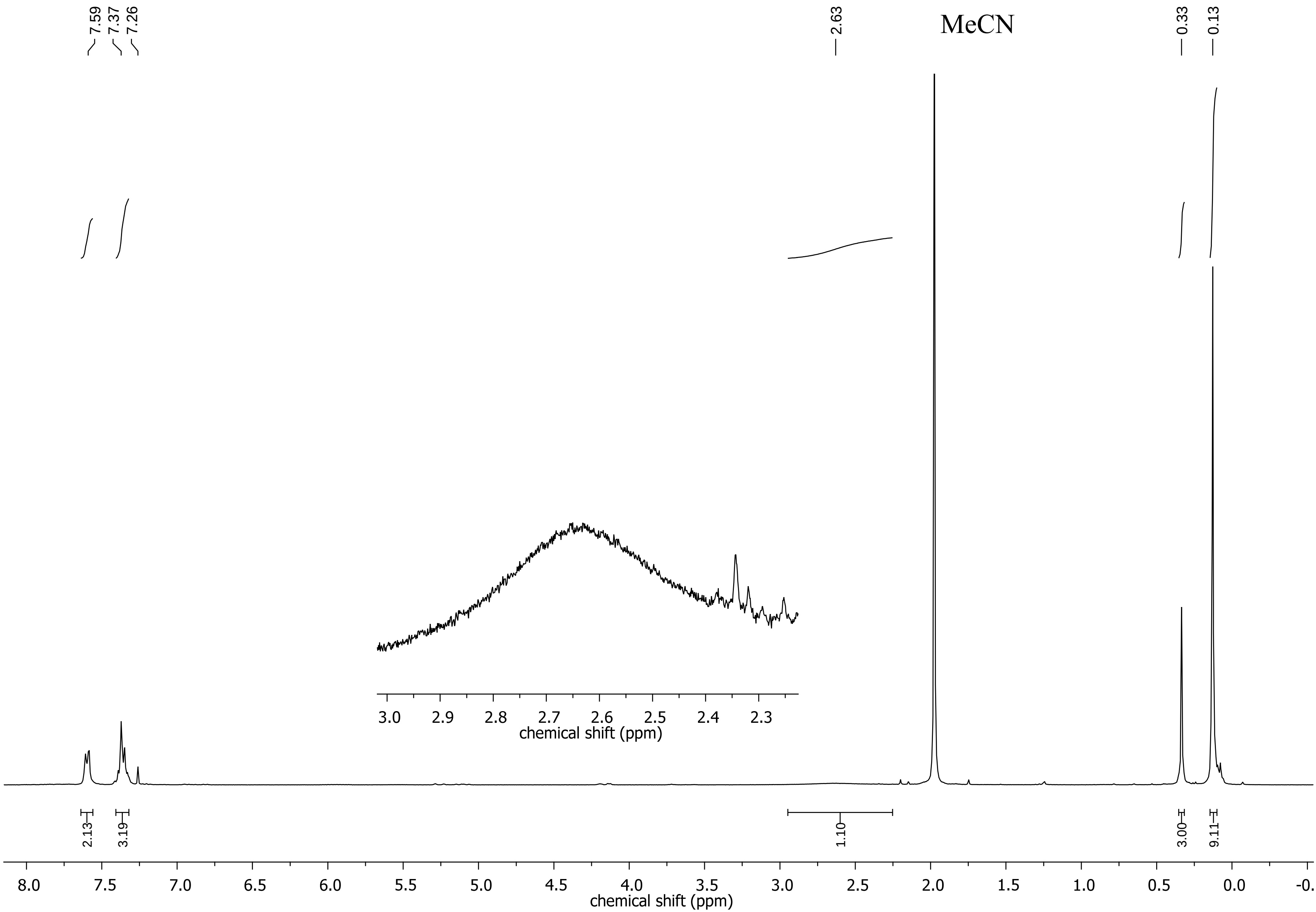
*Method of **2d** synthesis*: **1d** (0.474 g, 2.26 mmol, 1 eq.), NHPI (0.072 g, 0.44 mmol, 0.2 eq.), $Co(OAc)_2 \times 4H_2O$ (0.005 g, 22.6 µmol, 0.01 eq.), and MeCN (5 mL) were stirred in a 50 ml round bottomed flask at 40 °C for 7 h under the oxygen static atmosphere. According to GLC the yield of **2d** was 56 – 58%. Product **2d** was obtained as colorless oil by flash reversed phase chromatography (MeCN as eluent). The separated yield was 20% (0.099 g).

Characterization data for 1,3,3,3-tetramethyl-1-phenyldisiloxan-1-ol (**2d**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 9H); δ = 0.33 (s, 3H); 2.30 – 3.10 (br, 1H); 7.37 (m, 3H); 7.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = -1.05; 1.72; 116.38; 127.67; 129.71; 133.25. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -24.42; 9.42. IR (cm^{-1}): 3464; 3071; 2960; 1257; 1061. HRMS (ESI) m/z $[M - H]^-$: calcd for $[C_{10}H_{18}O_2Si_2 - H]^-$, 225.0762; found, 225.0781.

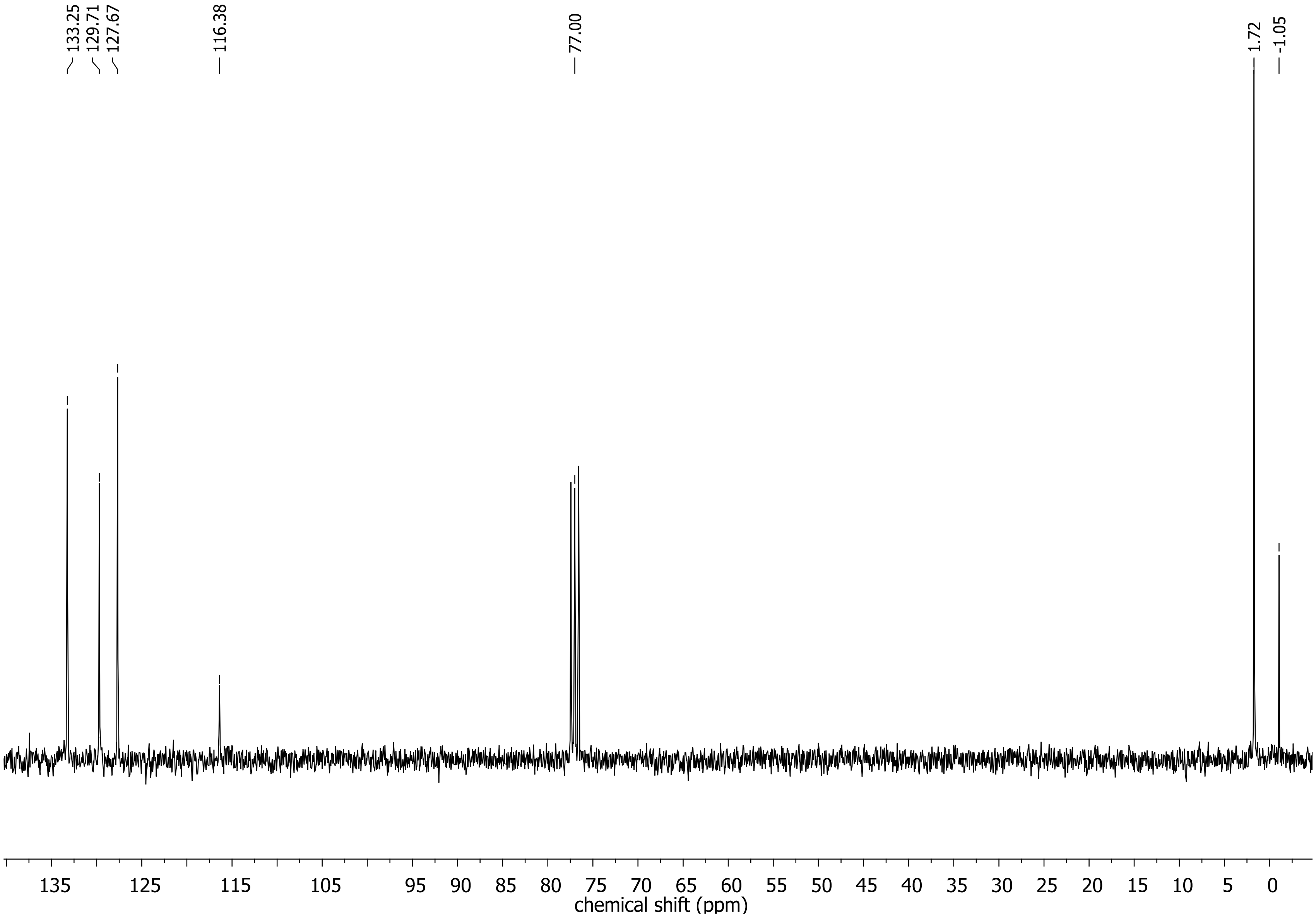
^{1}H NMR

(400 MHz, $CDCl_3$)



^{13}C NMR

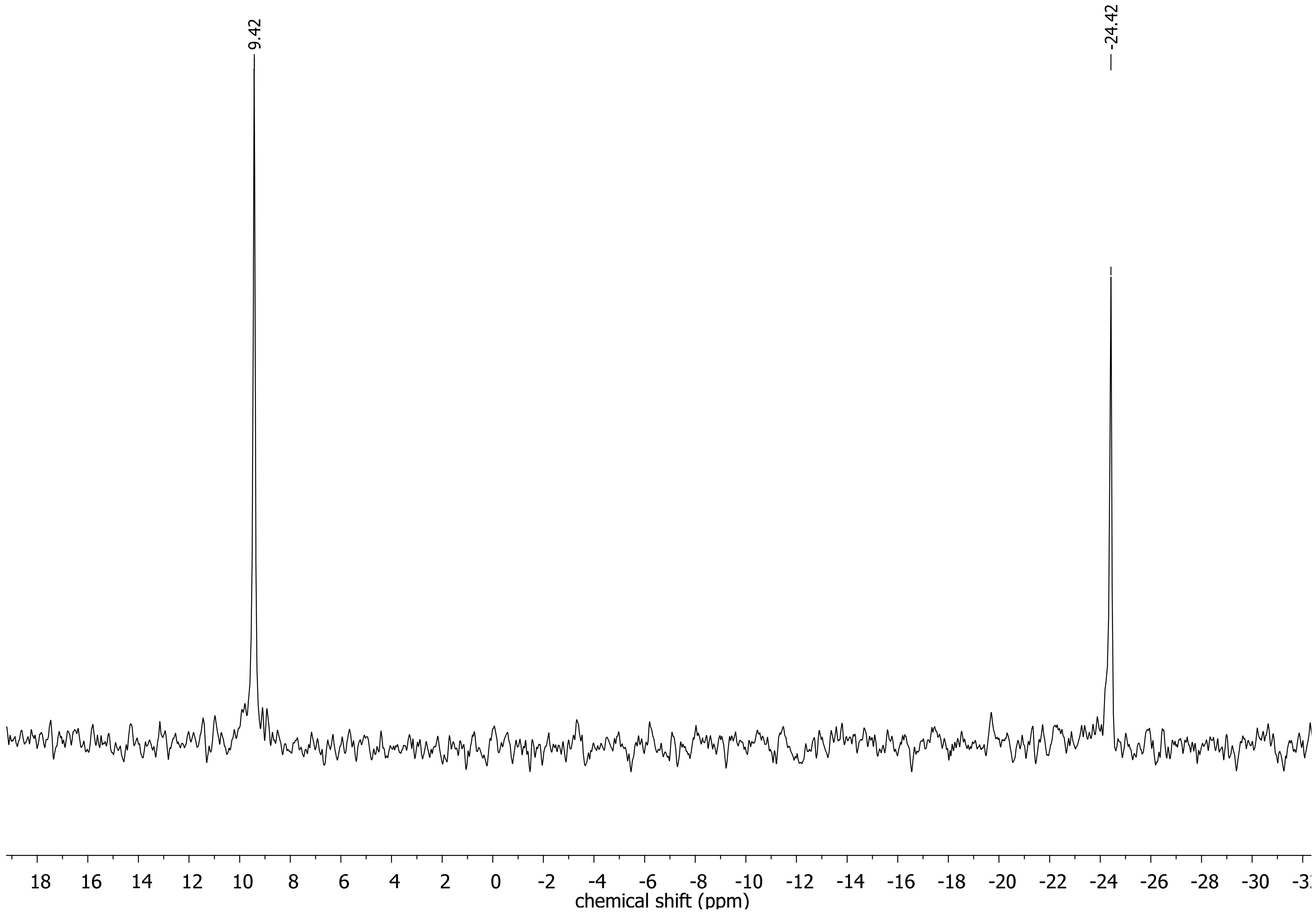
(100 MHz, $CDCl_3$)



^{29}Si NMR

(80 MHz, $CDCl_3$)

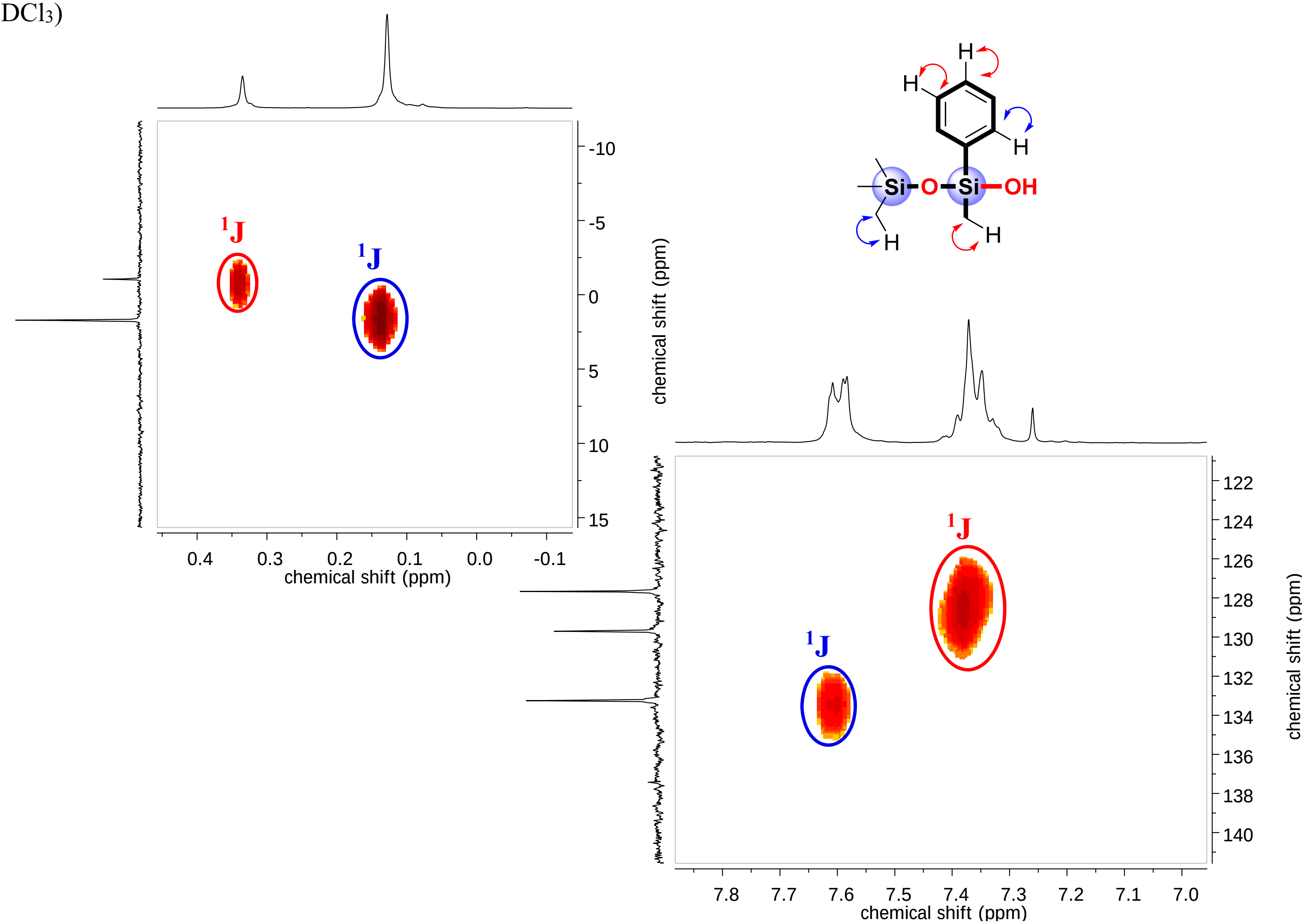
45



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

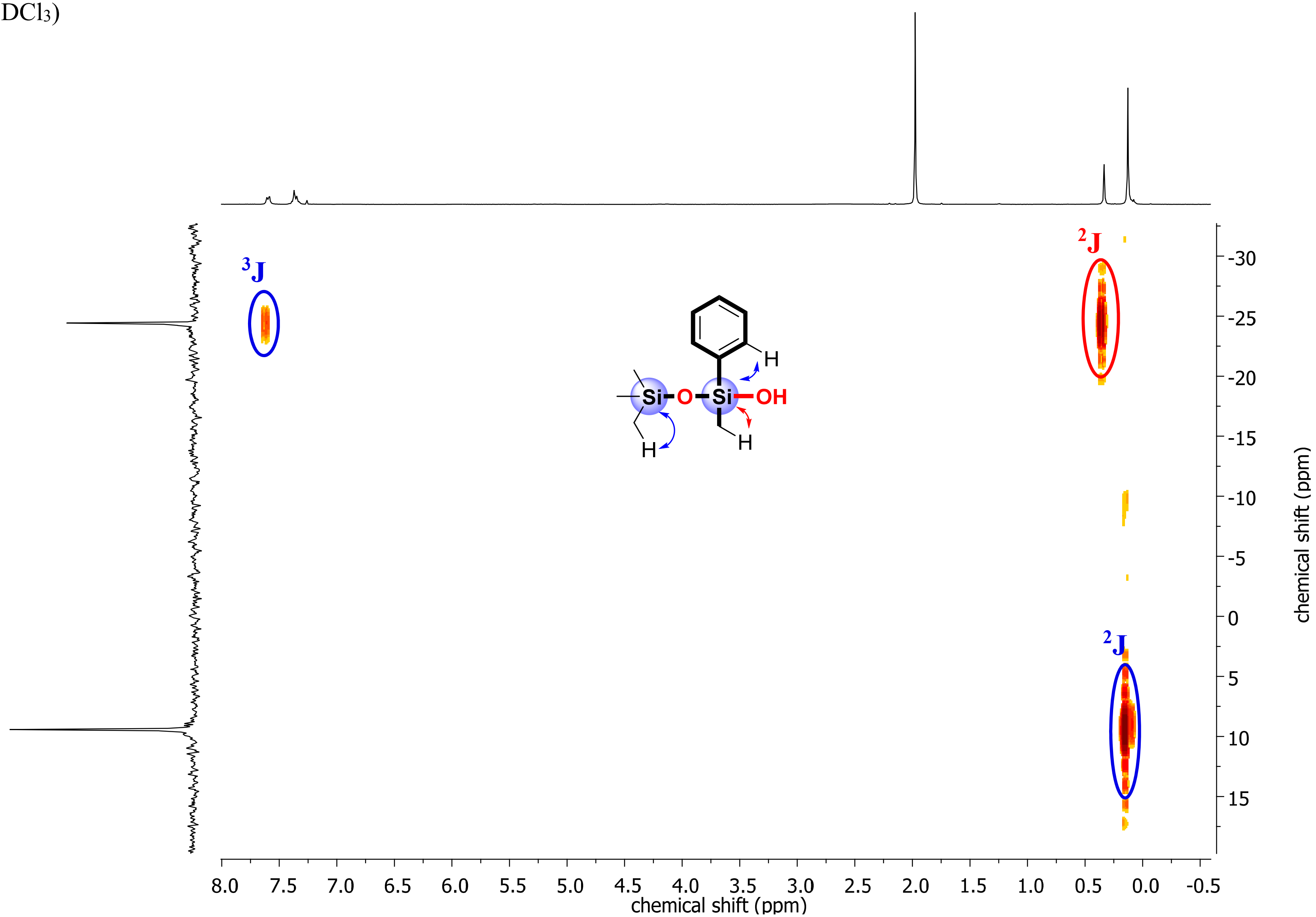
^{13}C: 100 MHz, $CDCl_3$)



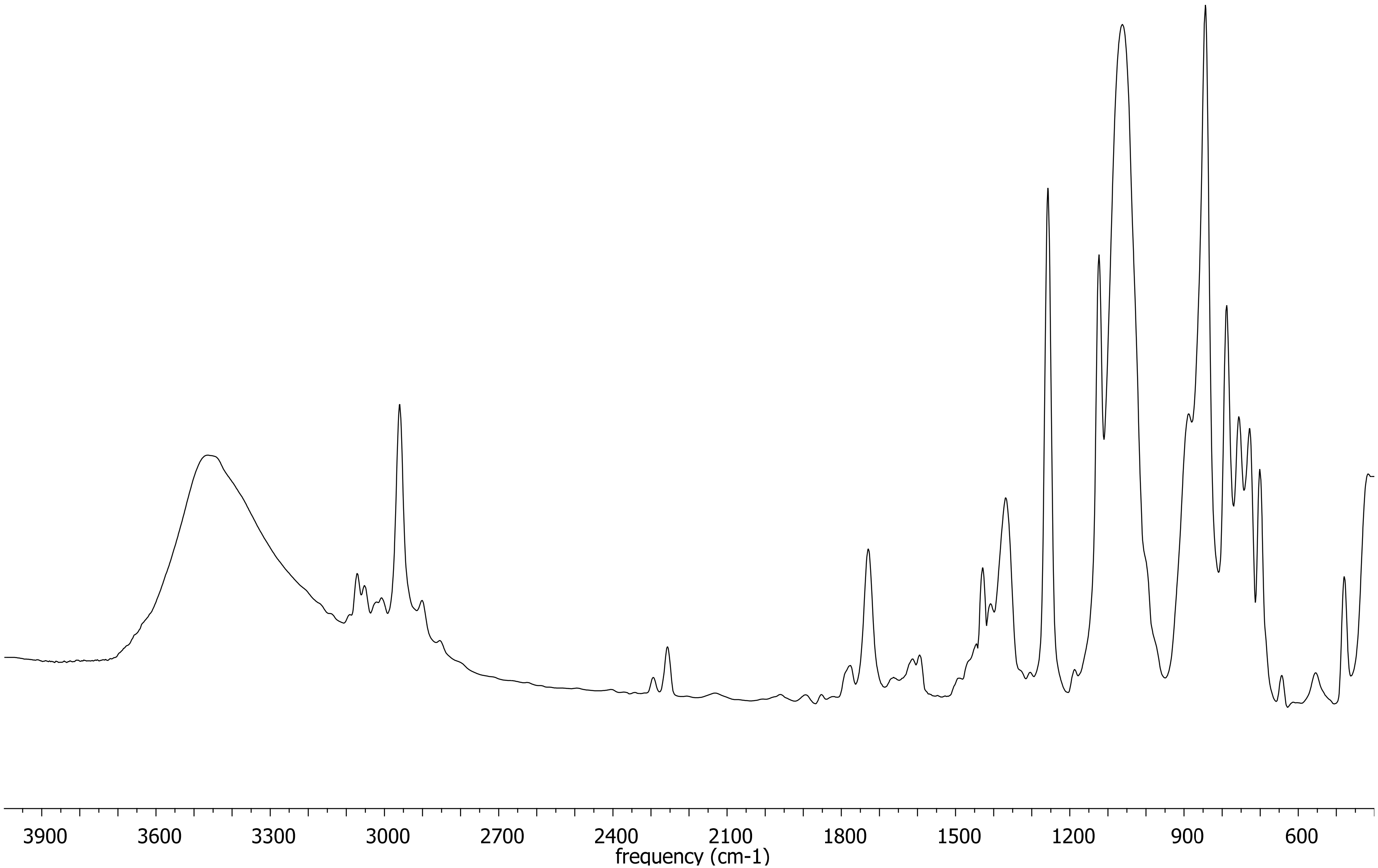
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)

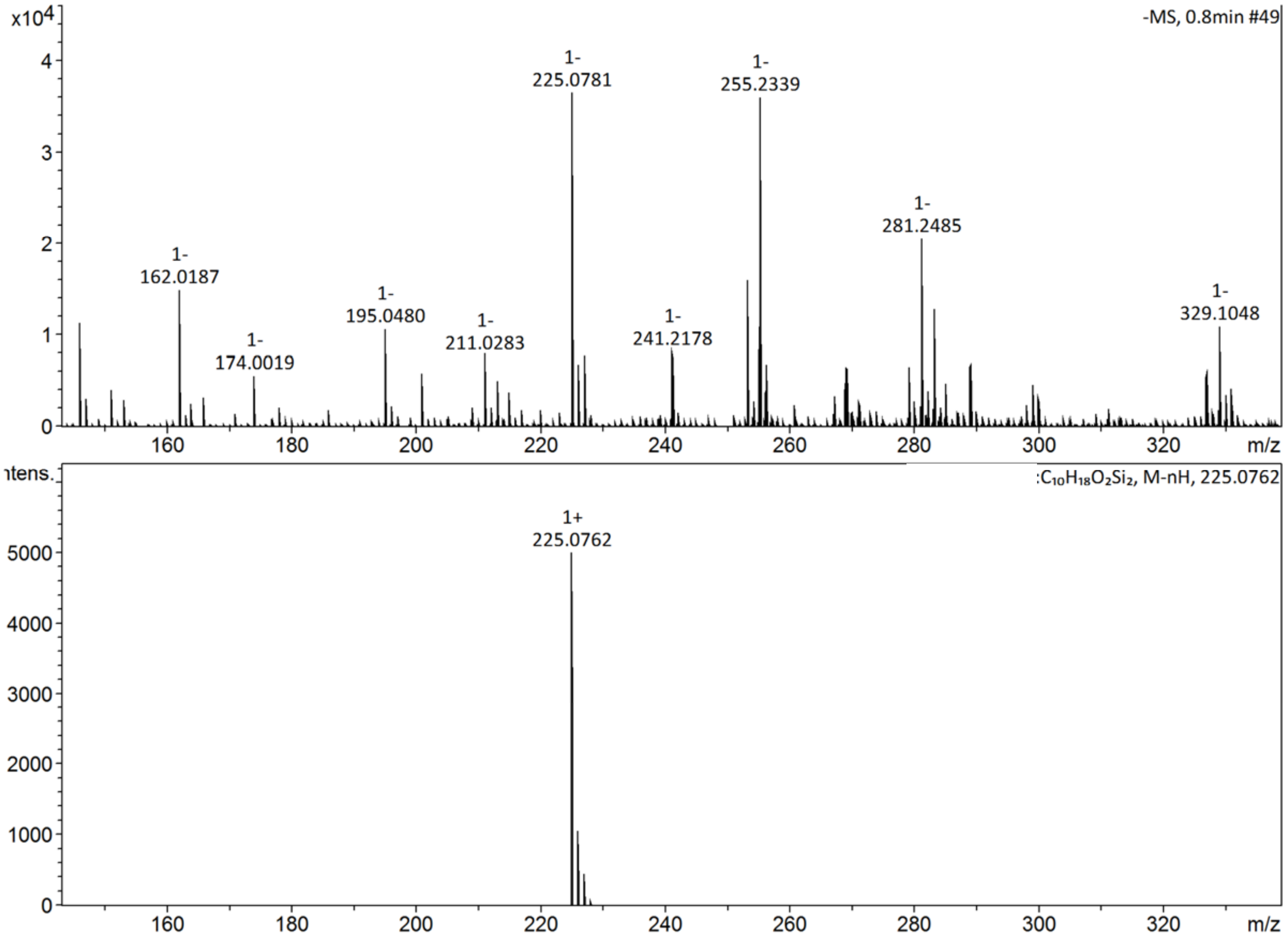


IR-spectrum


3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

ESI-HRMS

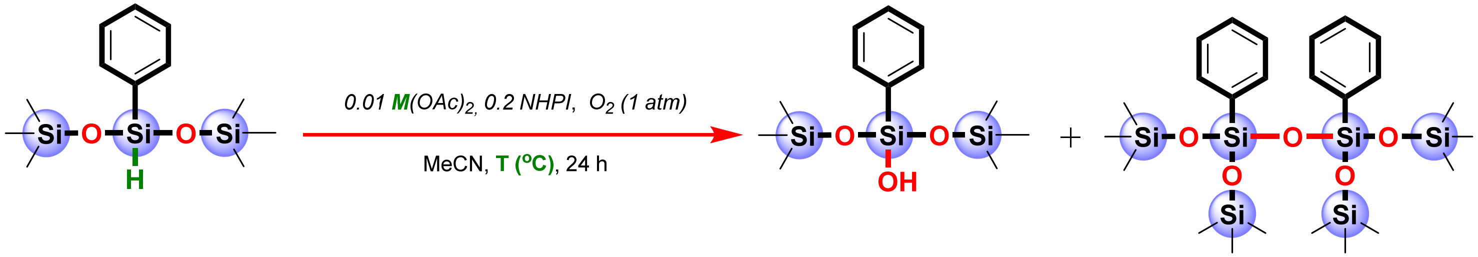
49



x10^4
Intens.
-MS, 0.8min #49
1- 162.0187
1- 174.0019
1- 195.0480
1- 211.0283
1- 225.0781
1- 241.2178
1- 255.2339
1- 281.2485
1- 329.1048
0
1
2
3
4
160
180
200
220
240
260
280
300
320
m/z
:C₁₀H₁₈O₂Si₂, M-nH, 225.0762
1+ 225.0762
0
1000
2000
3000
4000
5000
160
180
200
220
240
260
280
300
320
m/z

7. Optimization of synthesis and characterization data for 2e

Table 7.1. Optimization of 1e aerobic oxidation[a]



1e **2e** **3e**

	Cu(OAc)$_2$			**Co(OAc)$_2$**		
T, °C	**25**	**40**	**60** [b]	**25** [b]	40 [b]	**60** [b]
Yield of 2e, %	58	37	28	**76**	72	84
1e / 2e / 3e, %	41/58/1	61/37/2	70/28/2	**10/76/14**	8/72/20	8/67/25

[a] Reaction conditions: **1e** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), M(OAc)$_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 24 h under the oxygen static atmosphere. The yield of **2e** was determined by GLC.

[b] 7 hours.

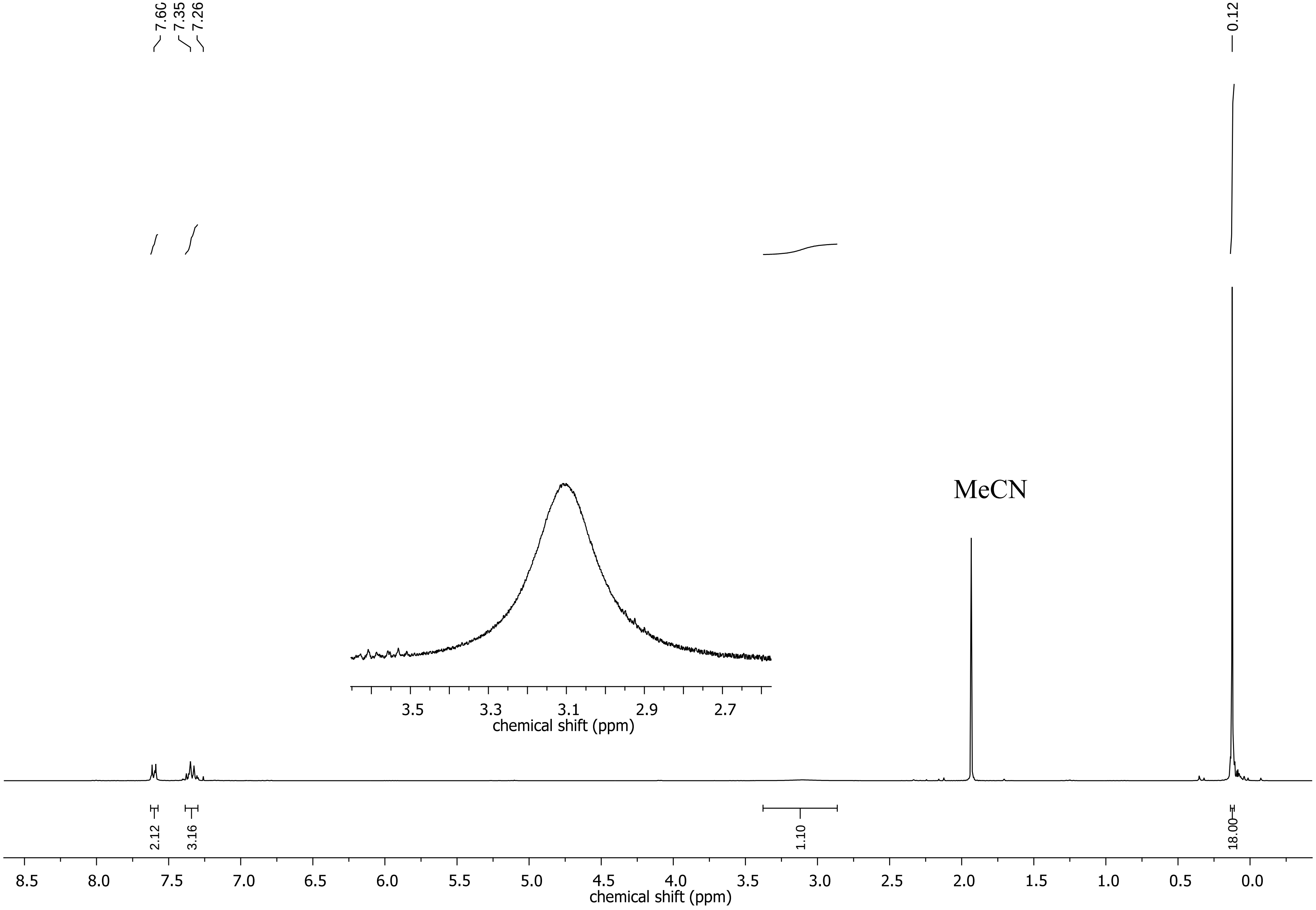
Method of ***2e*** *synthesis***:** **1e** (0.512 g, 1.80 mmol, 1 eq.), NHPI (0.059 g, 0.36 mmol, 0.2 eq.), Co(OAc)$_2$×4H$_2$O (0.004 g, 18.02 µmol, 0.01 eq.), and MeCN (4 mL) were stirred in a 50 ml round bottomed flask at 25 °C for 8 h under the oxygen static atmosphere. According to GLC the yield of **2e** was 74 – 77%. Product **2e** was obtained as colorless oil by flash reversed phase chromatography (MeCN as eluent). The separated yield was 35% (0.189 g).

Characterization data for 1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxan-3-ol (**2e**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 18H); 2.90 – 3.30 (br, 1H); 7.35 (m, 3H); 7.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.49; 116.31; 127.46; 129.65; 133.82. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -68.770; 9.71. IR (cm^{-1}): 3381; 3073; 2960; 1255; 1070. HRMS (ESI) m/z $[M - H]^-$: calcd for $[C_{12}H_{24}O_3Si_3 - H]^-$, 299.0950; found, 299.0950.

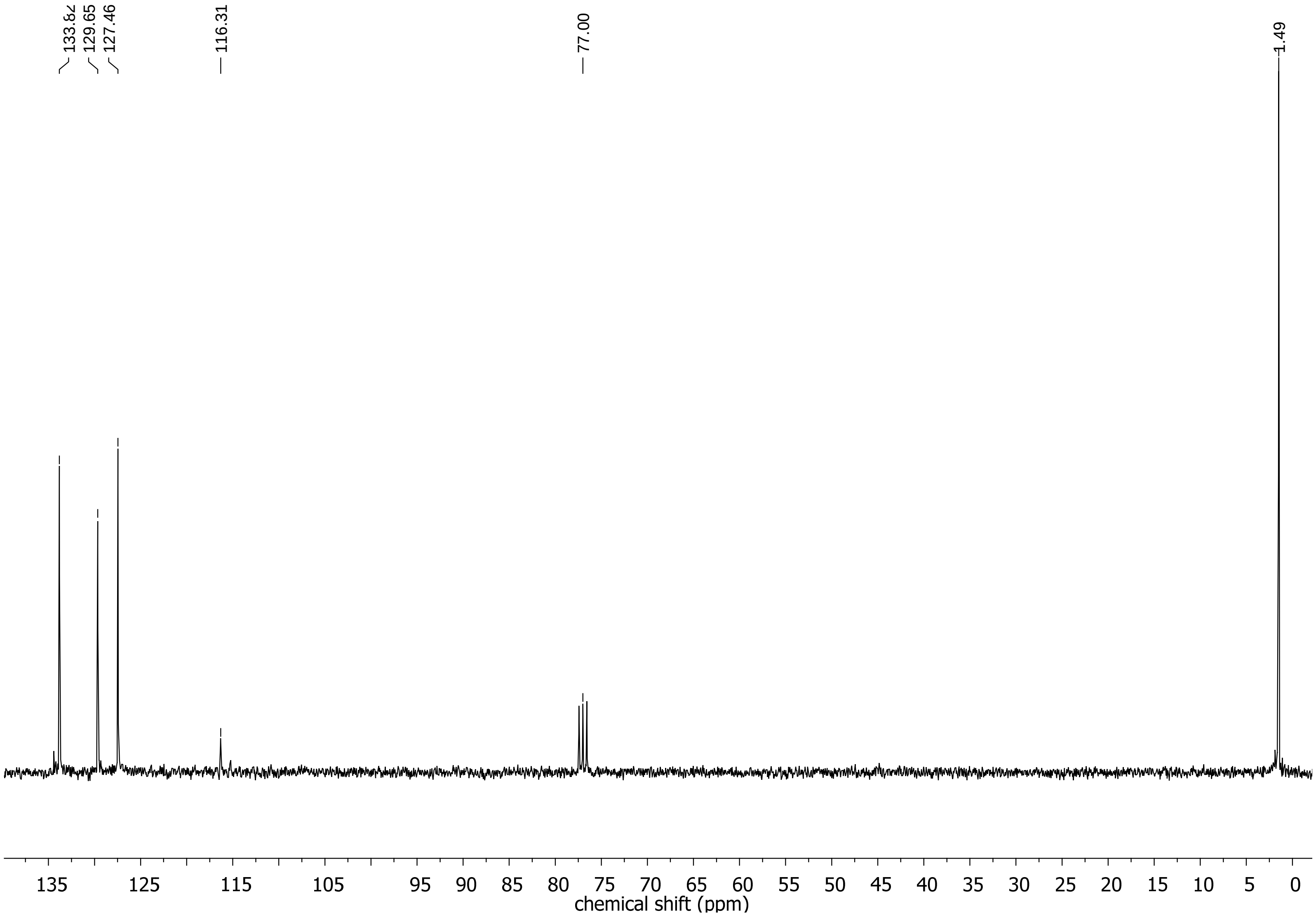
^{1}H NMR

(400 MHz, $CDCl_3$)



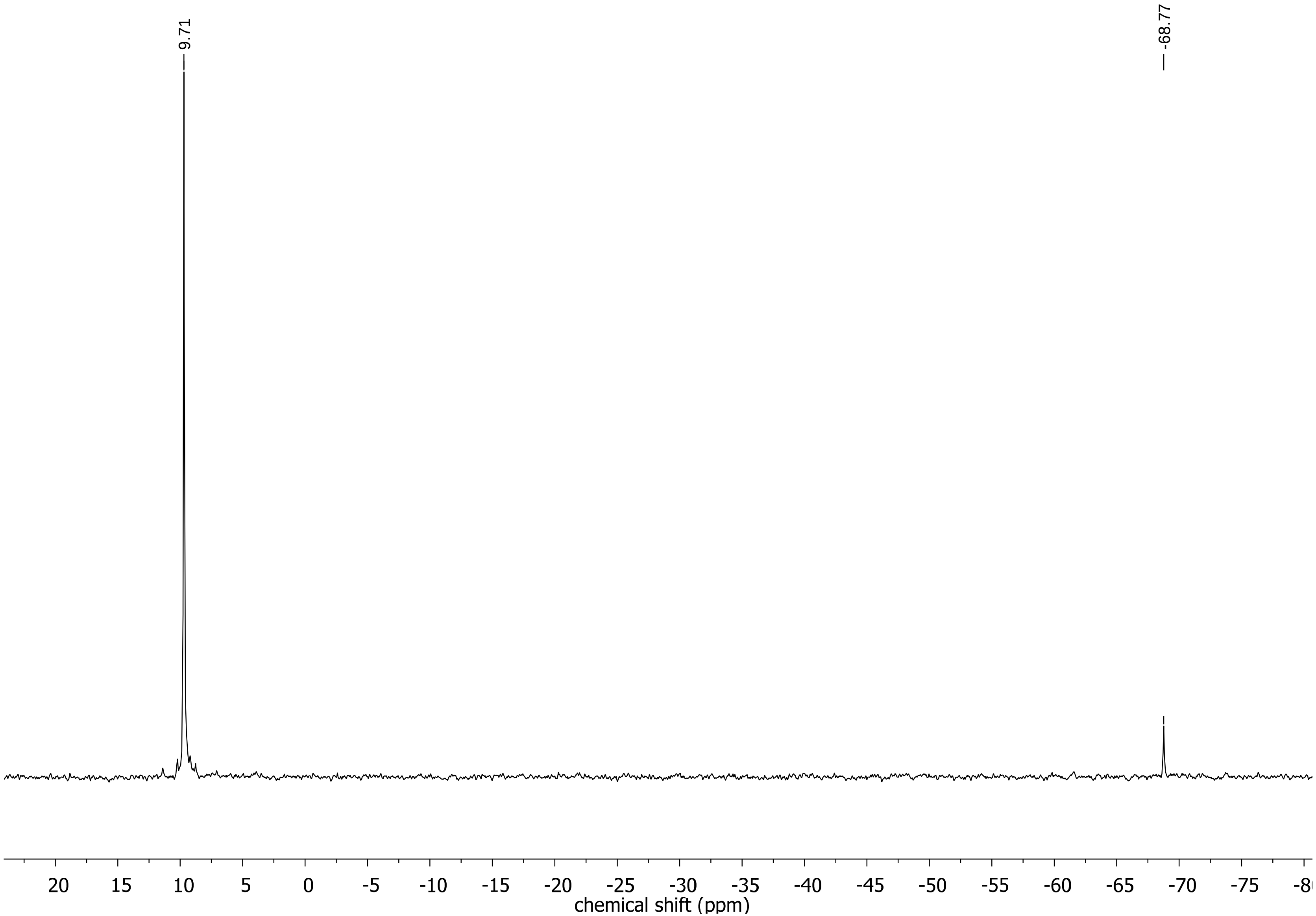
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

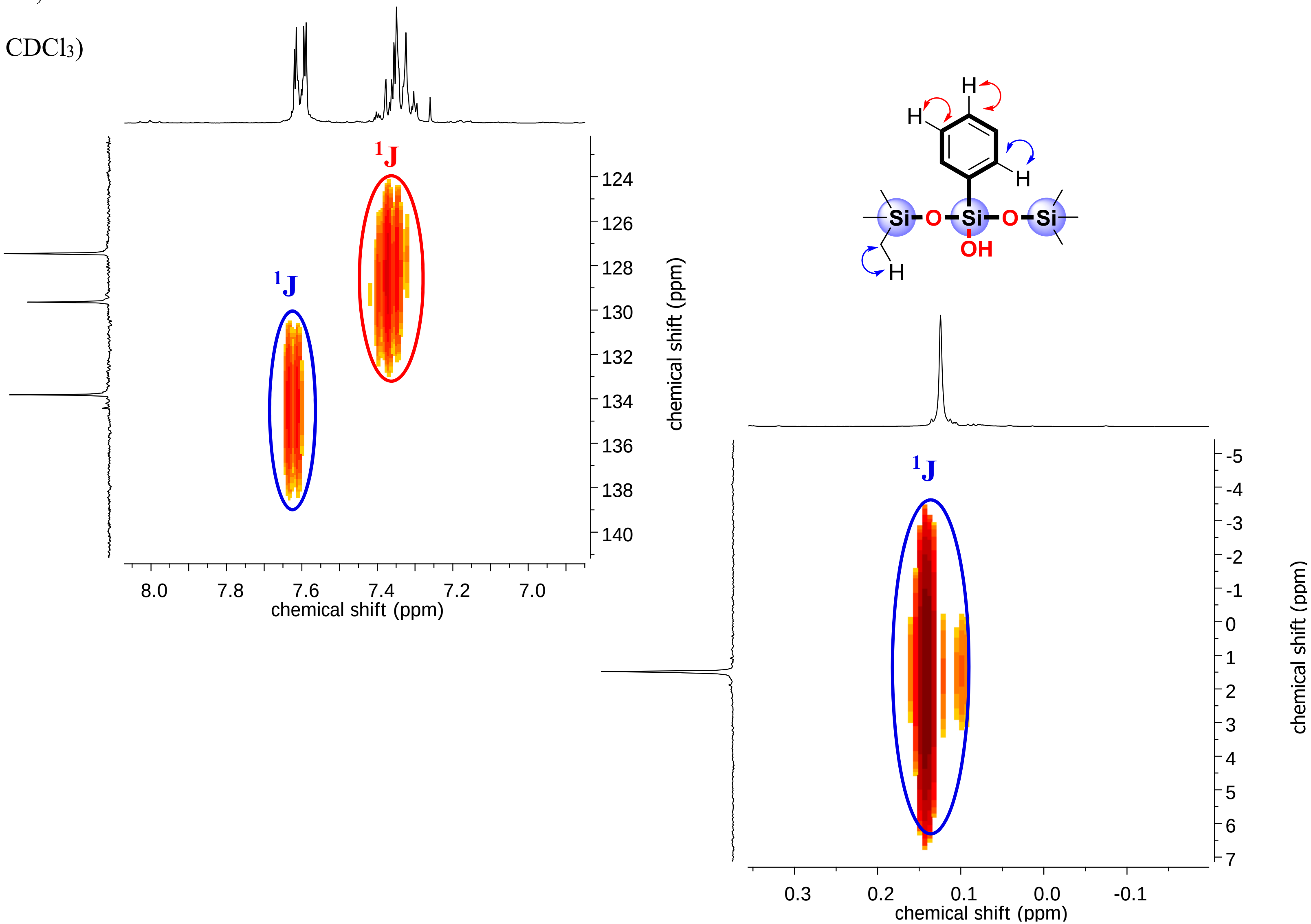
(80 MHz, $CDCl_3$)



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

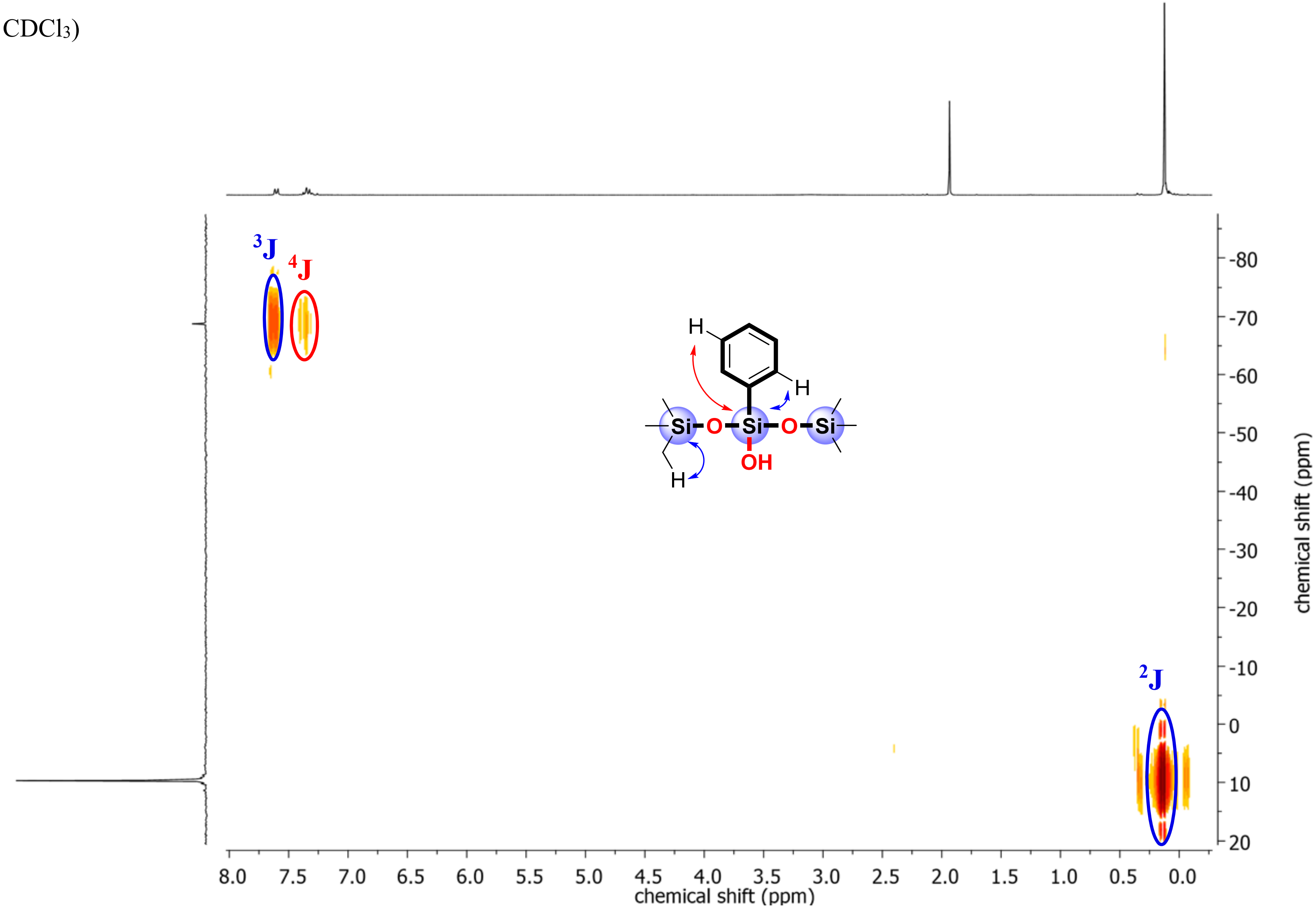
^{13}C: 100 MHz, $CDCl_3$)



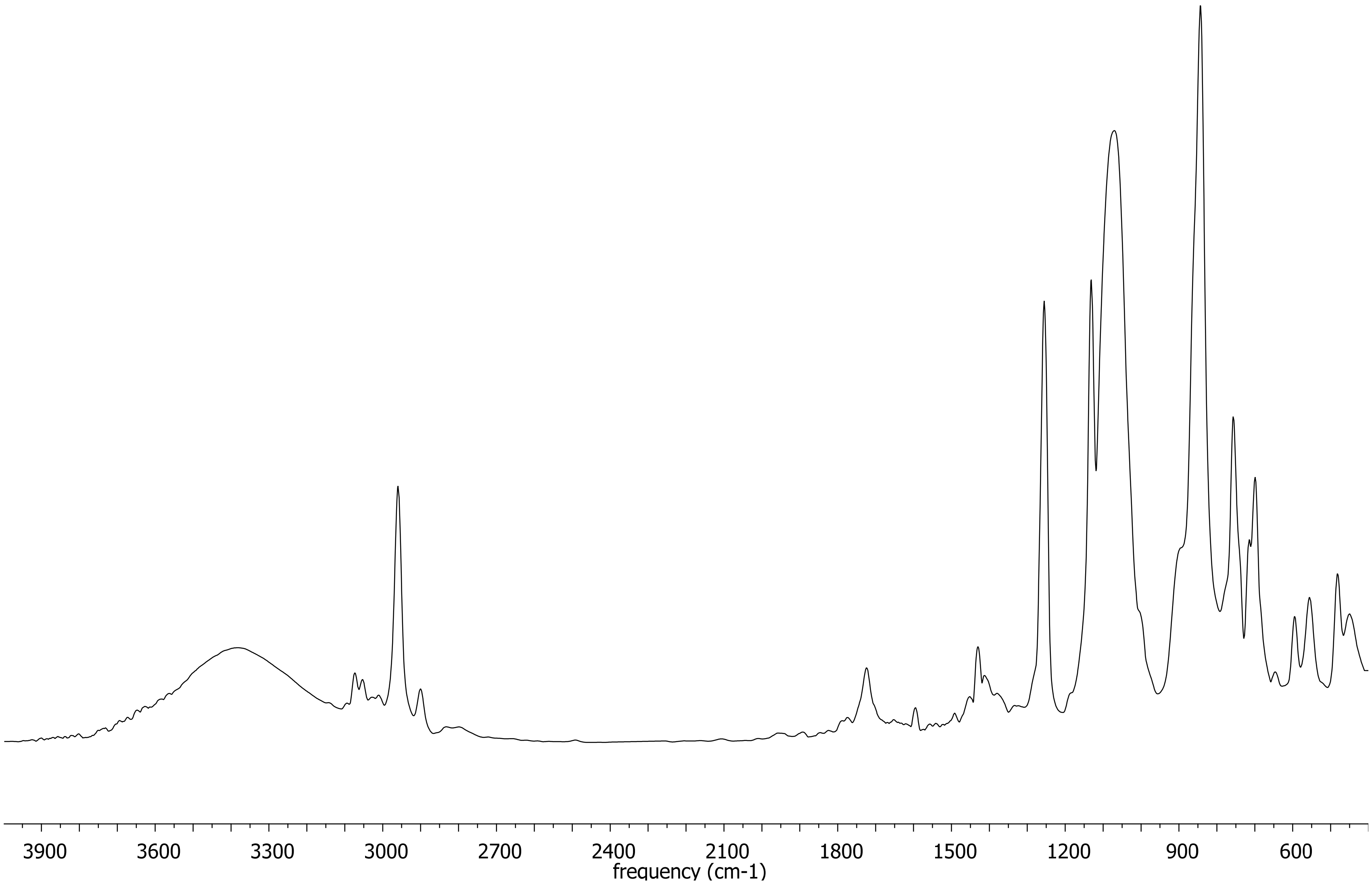
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

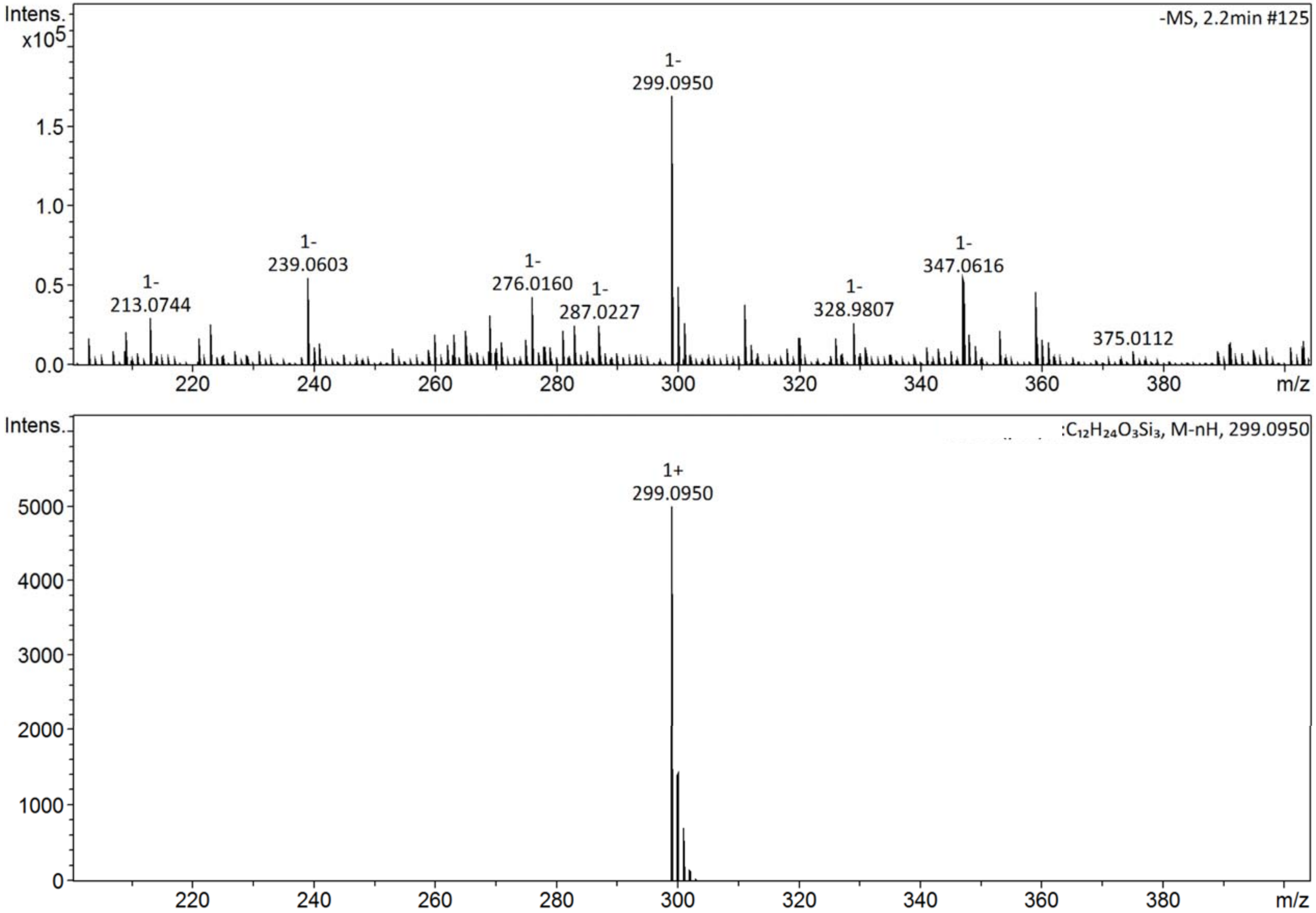
^{29}Si: 80 MHz, $CDCl_3$)



IR-spectrum

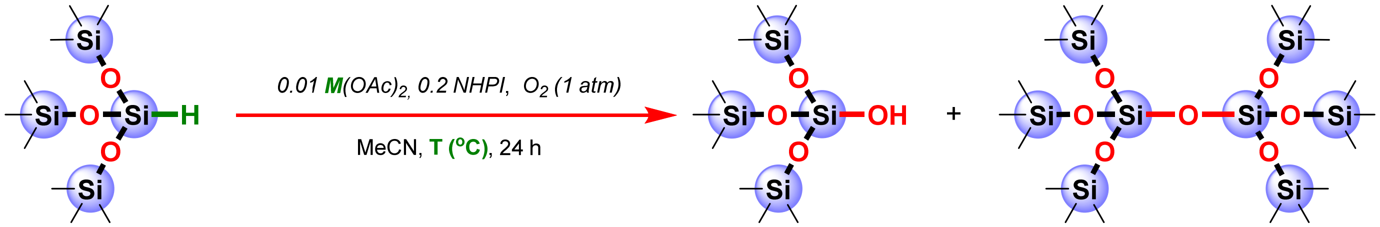

3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

ESI-HRMS


Intens.
x10^5
-MS, 2.2min #125
1-
299.0950
1-
239.0603
1-
276.0160
1-
287.0227
1-
213.0744
1-
328.9807
1-
347.0616
375.0112
1.5
1.0
0.5
0.0
220
240
260
280
300
320
340
360
380
m/z
Intens.
:C₁₂H₂₄O₃Si₃, M-nH, 299.0950
1+
299.0950
5000
4000
3000
2000
1000
0
220
240
260
280
300
320
340
360
380
m/z

8. Optimization of synthesis and characterization data for 2f

Table 7.1. Optimization of 1f aerobic oxidation [a]



1f **2f** **3f**

	Cu(OAc)$_2$			Co(OAc)$_2$		
T, °C	**25**	**40**	**60**	**25**	**40**	**60**
Yield of 2f, %	3	12	**59**	0	0	21
1f / 2f / 3f, %	97/3/0	88/12/0	**29/59/12**	100/0/0	100/0/0	74/21/5

[a] Reaction conditions: **1f** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), M(OAc)$_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 24 h under the oxygen static atmosphere. The yield of **2f** was determined by GLC.

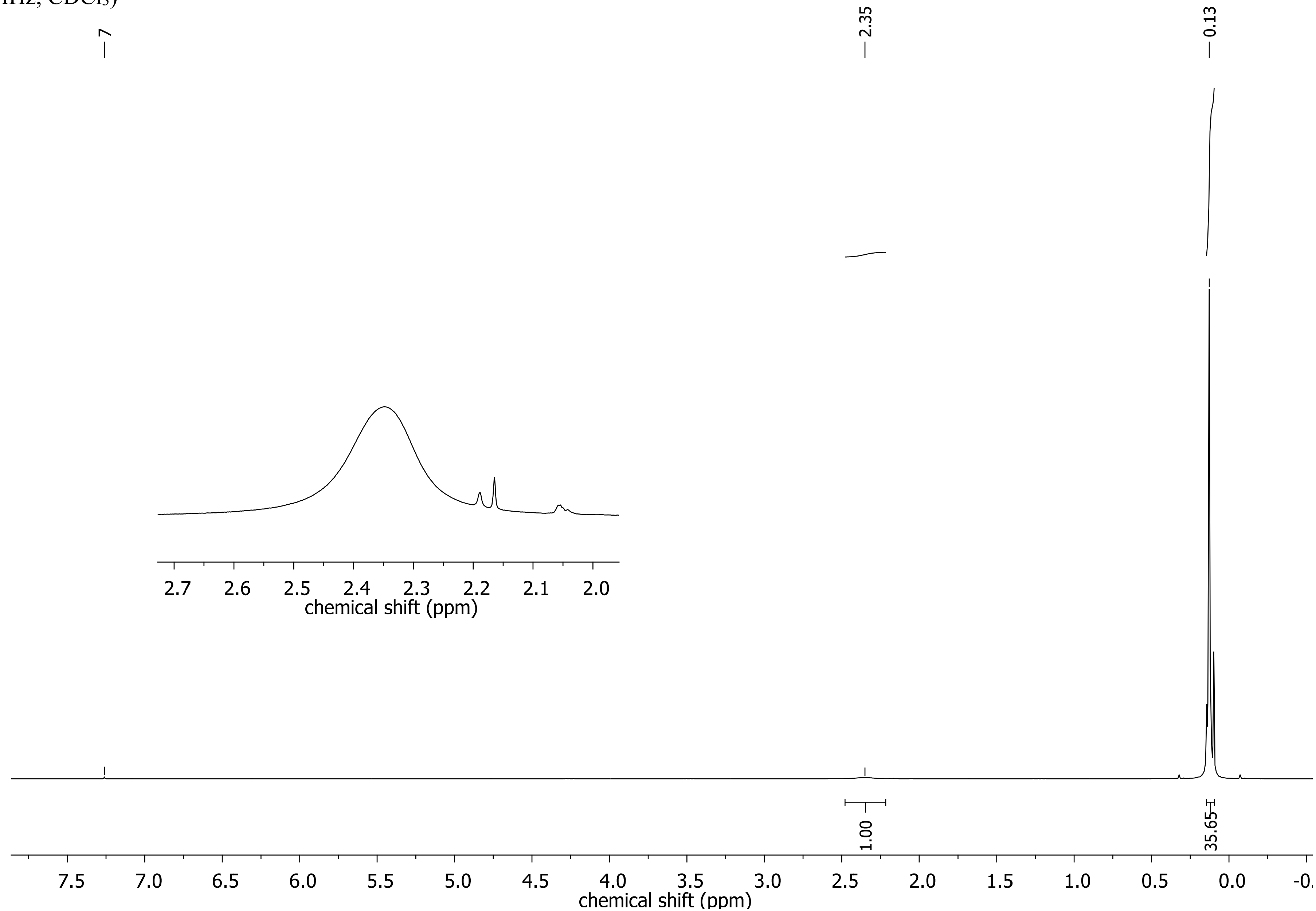
Method of ***2f*** *synthesis*: **1f** (8.57 g, 28.94 mmol, 1 eq.), NHPI (0.944 g, 5.79 mmol, 0.2 eq.), Cu(OAc)$_2$×H$_2$O (0.058 g, 0.289 mmol, 0.01 eq.), and MeCN (65 mL) were stirred in a 500 ml round bottomed flask at 60 °C for 24 – 36 h under the oxygen static atmosphere. According to GLC the yield of **2f** was 58 – 60 %. 80-90% of the solvent was evaporated (180-200 mbar, T$_{bath}$ = 40 °C). Then pentane (60-70 mL) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and solvents were evaporated (700 – 800 mbar, T$_{bath}$ = 40 °C). Product **2f** was obtained as colorless oil by distillation under reduced pressure (BP = 64-65 °C at 1 mbar). The separated yield was 40% (3.62 g).

Characterization data for tris(trimethylsilyloxy)silanol (**2f**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 27H); 2.20 – 2.50 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.47. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -96.25; 9.70. IR (cm^{-1}): 3702, 2959, 1252, 1069. HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_9H_{28}O_4Si_4 + Na]^+$, 335.0957; found, 335.0969.

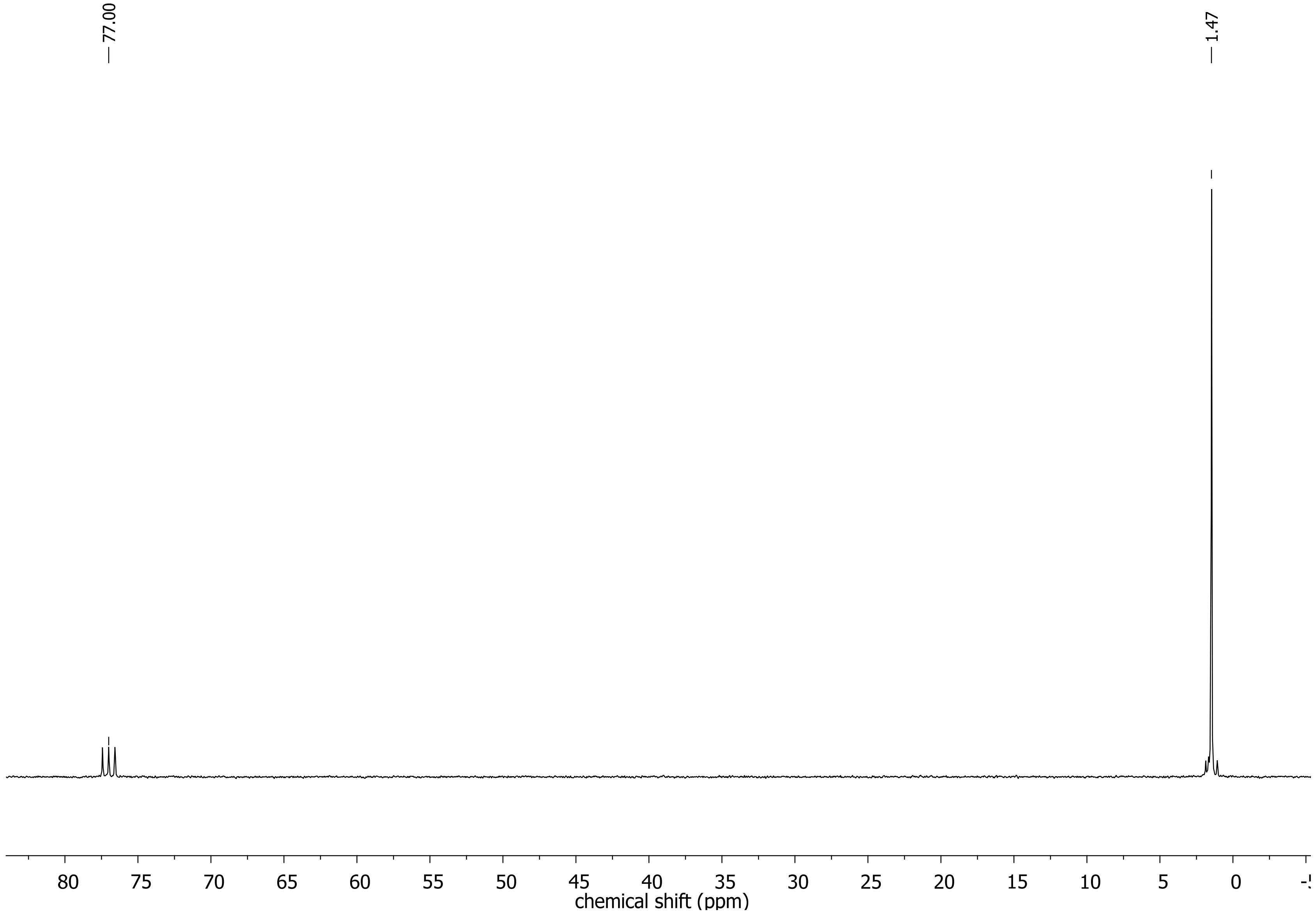
^{1}H NMR

(400 MHz, $CDCl_3$)



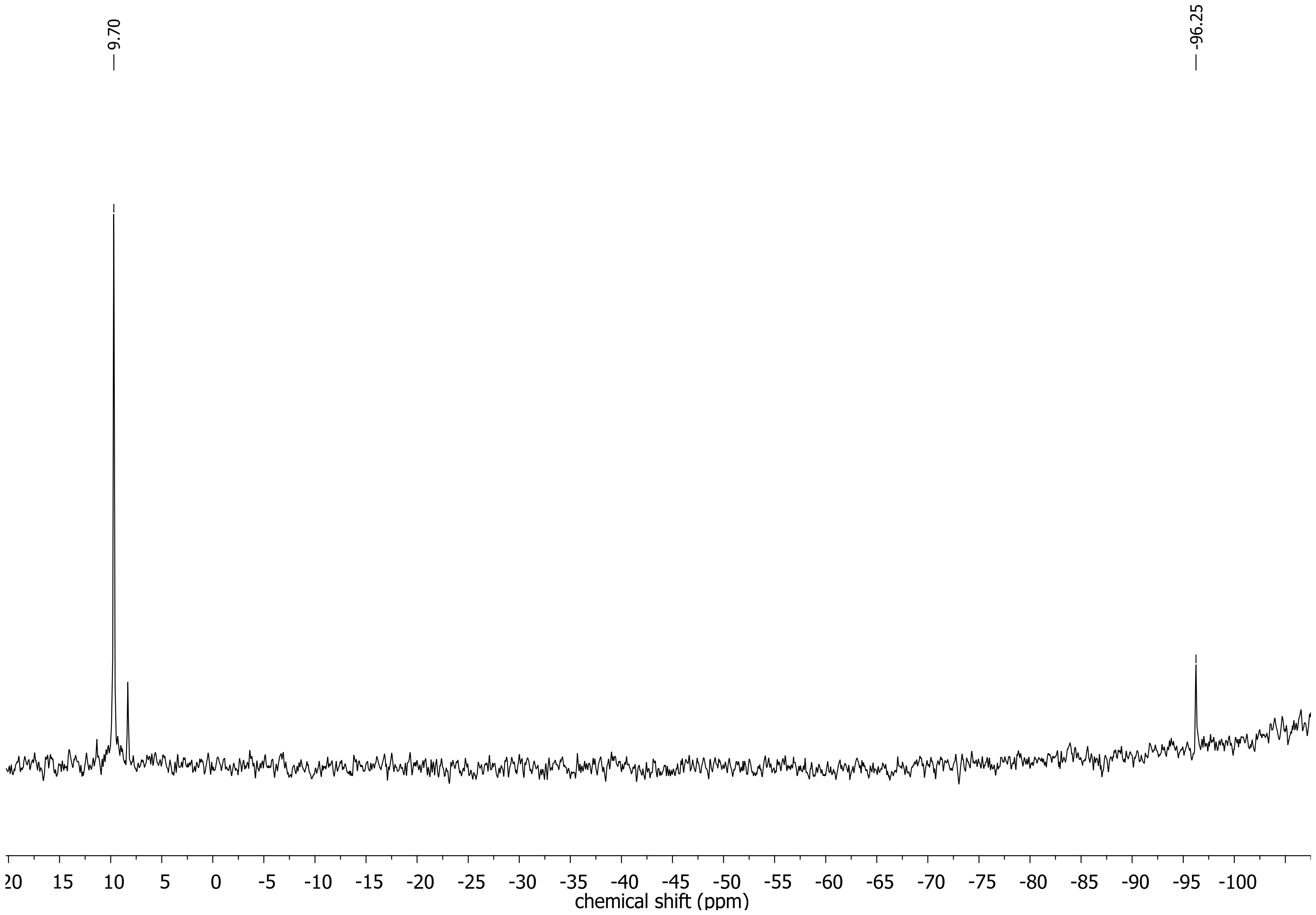
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

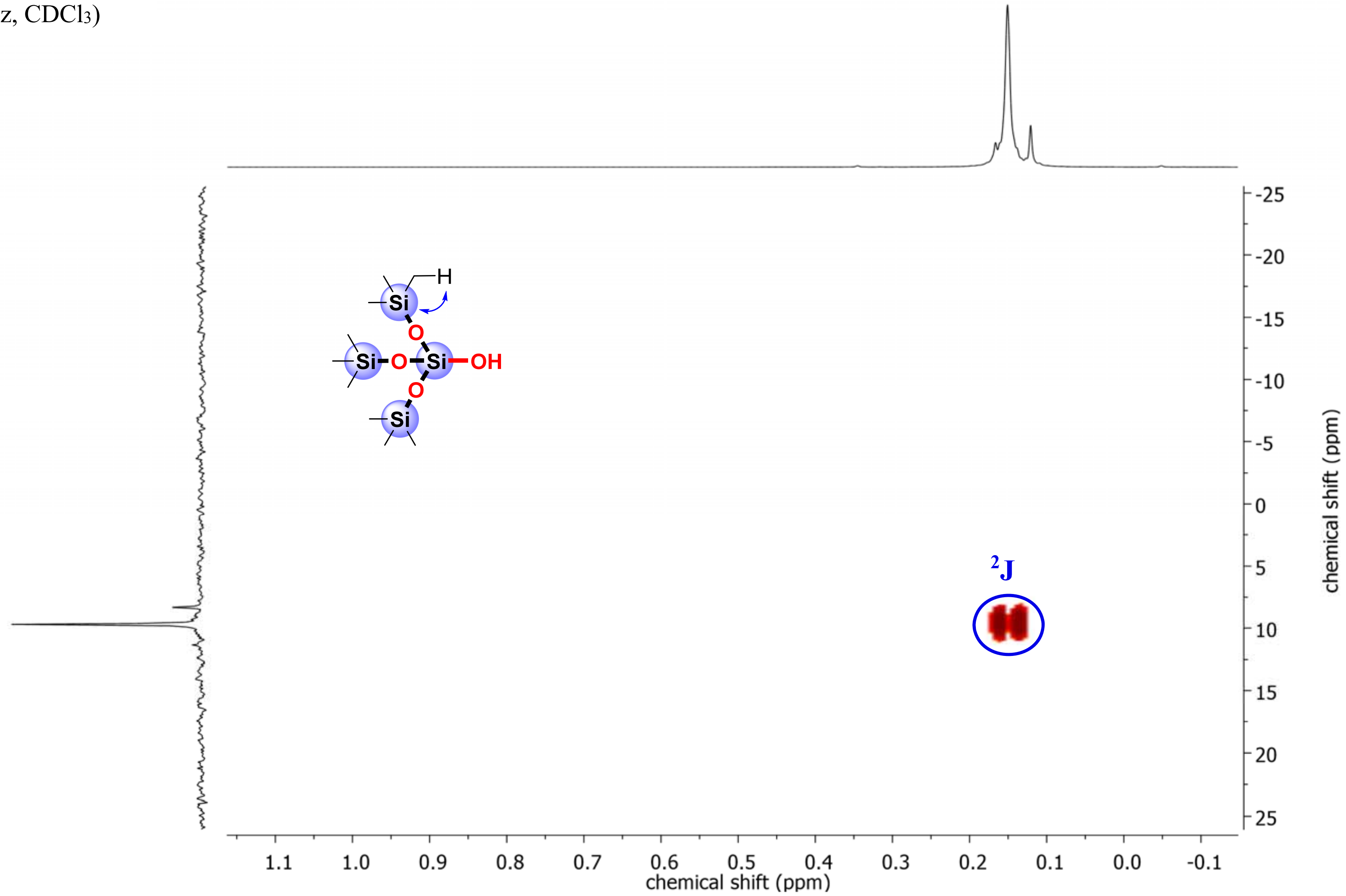
(80 MHz, $CDCl_3$)



^{1}H, ^{29}Si –HMBC NMR

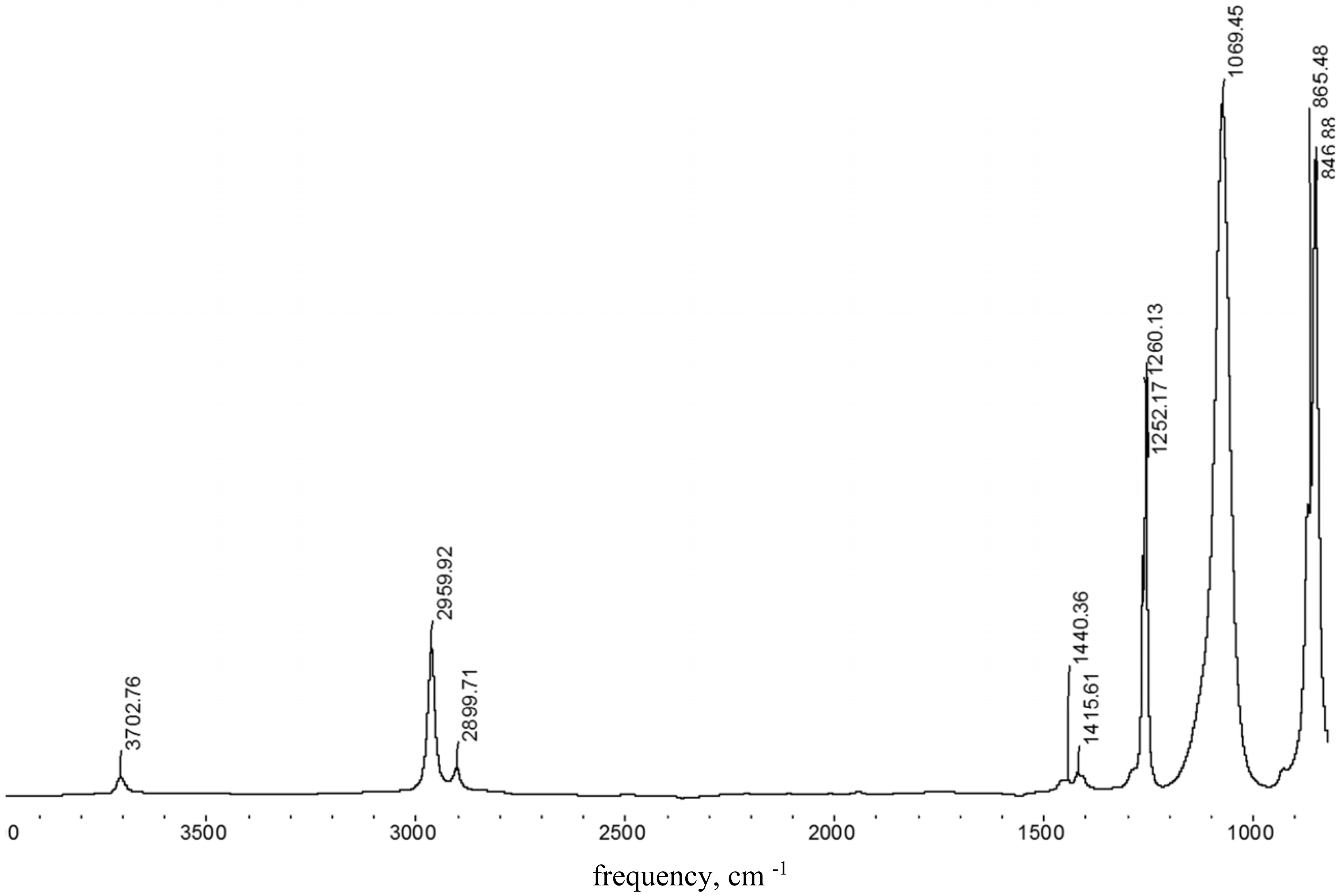
(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)

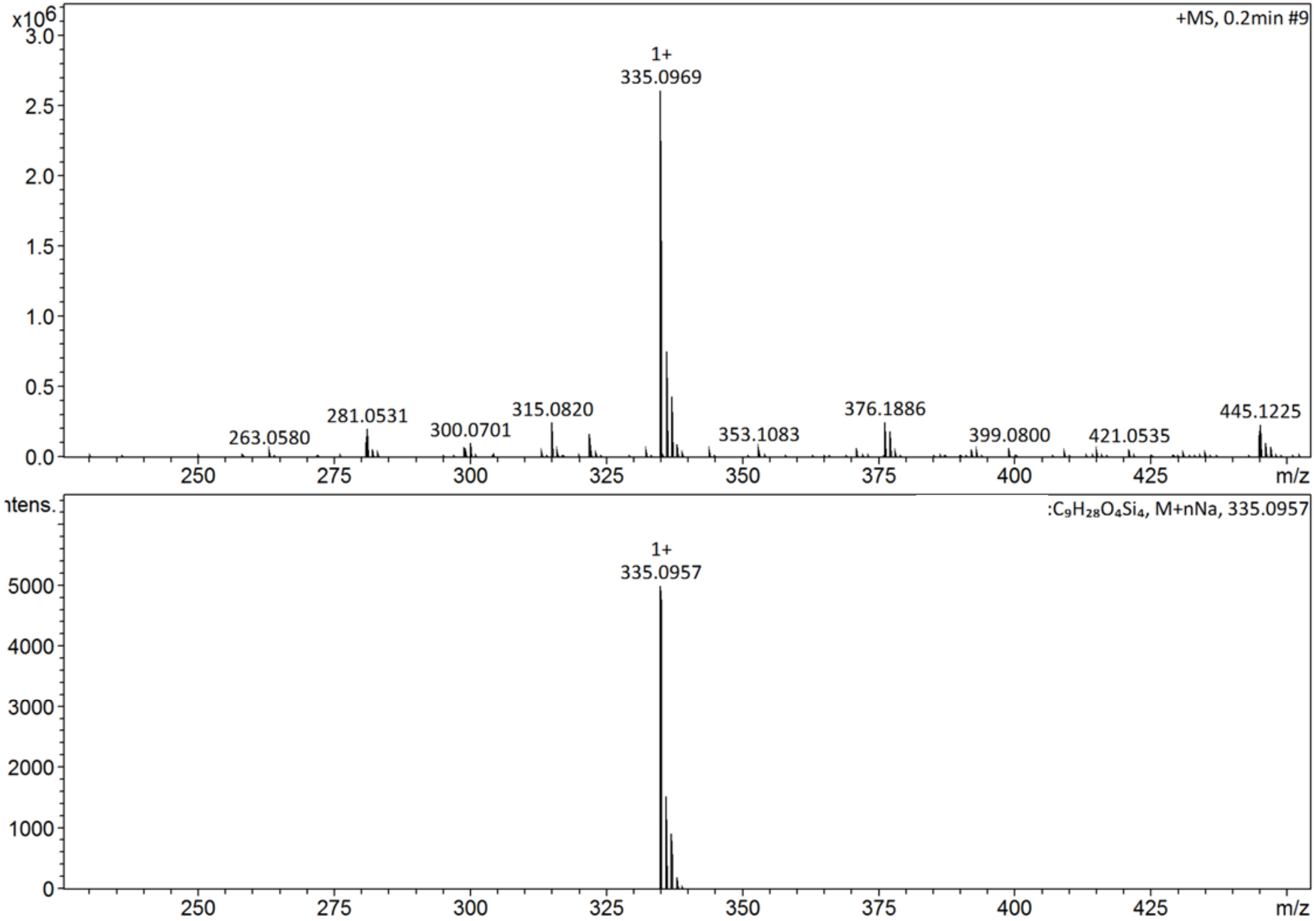


IR-spectrum

(CCl_4 solution)



ESI-HRMS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2.5
2.0
1.5
1.0
0.5
0.0
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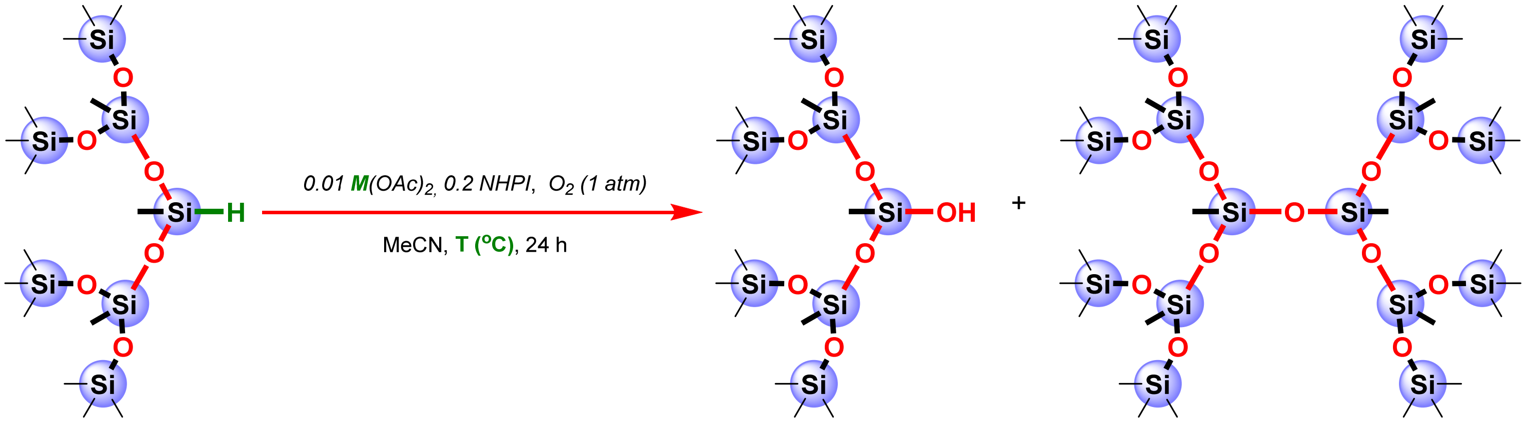
263.0580
281.0531
300.0701
315.0820
353.1083
376.1886
399.0800
421.0535
445.1225
250
275
300
325
350
375
400
425
m/z
ntens.
:C₉H₂₈O₄Si₄, M+nNa, 335.0957
1+
335.0957
5000
4000
3000
2000
1000
0
250
275
300
325
350
375
400
425
m/z

9. Optimization of synthesis and characterization data for 2g

Table 9.1. Optimization of 1g aerobic oxidation [a]



1g **2g** **3g**

	$Cu(OAc)_2$		$Co(OAc)_2$		
T, °C	**40**[c]	**60**[b]	**25**	**40**	**60** [b]
Yield of 2g, %	57	**81**	11	45	59
1g / 2g / 3g, %	33/57/10	**19/81/0**	89/11/0	50/45/5	39/59/2

[a] Reaction conditions: **1g** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), $M(OAc)_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 24 h under the oxygen static atmosphere. The yield of **2f** was determined by GLC.

[b] 12 hours.

[c] 36 hours.

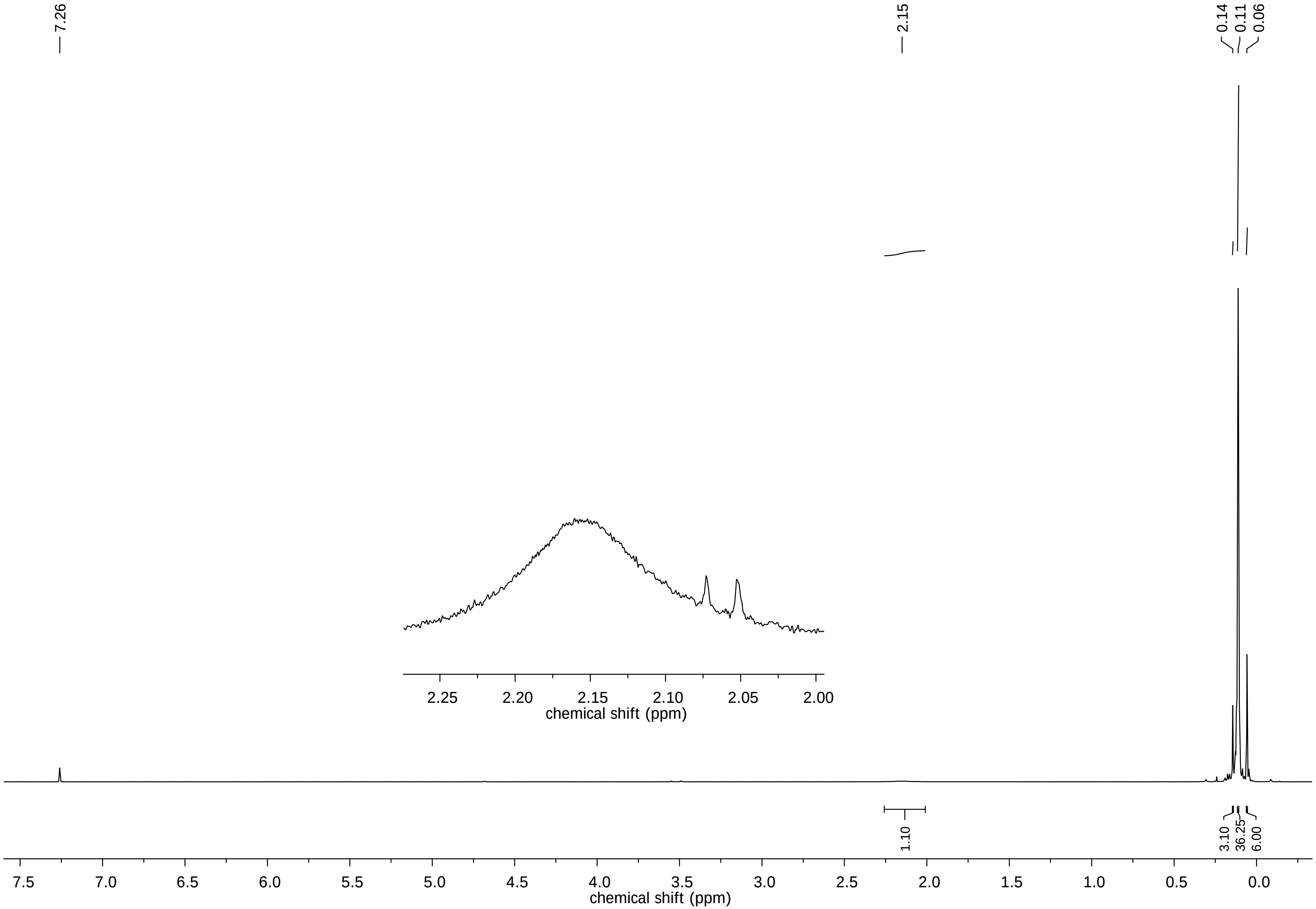
Method of **2g** *synthesis***:** **1g** (5.859 g, 11.31 mmol, 1 eq.), NHPI (0.368 g, 2.26 mmol, 0.2 eq.), $Cu(OAc)_2 \times H_2O$ (0.022 g, 0.113 mmol, 0.01 eq.), and MeCN (25 mL) were stirred in a 500 ml round bottomed flask at 60 °C for 12 h under oxygen flow. According to GLC the yield of **2g** was 80 – 82%. 80-90% of the solvent was evaporated (180-200 mbar, T_{bath} = 40 °C). Then pentane (30-35 ml) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and solvents were evaporated (300 – 350 mbar, T_{bath} = 40 °C). Product **2g** was obtained as colorless oil by distillation under reduced pressure (BP = 128-129 °C at 1 mbar). The separated yield was 52% (3.15 g).

Characterization data for 1,1,1,3,5,7,9,9,9-nonamethyl-3,7-bis(trimethylsilyloxy)pentasiloxan-5-ol (**2g**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 6H); δ = 0.11 (m, 36H); 0.14 (s, 3H); 2.00 – 2.30 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = -3.37; -2.33; 1.64. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -65.00; -56.58; 8.16. IR (cm^{-1}): 3496; 2960; 1252; 1057. HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{15}H_{46}O_7Si_7 + H]^+$, 535.1701; found, 535.1698; $[M + NH_4]^+$: calcd for $[C_{15}H_{46}O_7Si_7 + NH_4]^+$, 552.1967; found, 552.1956.

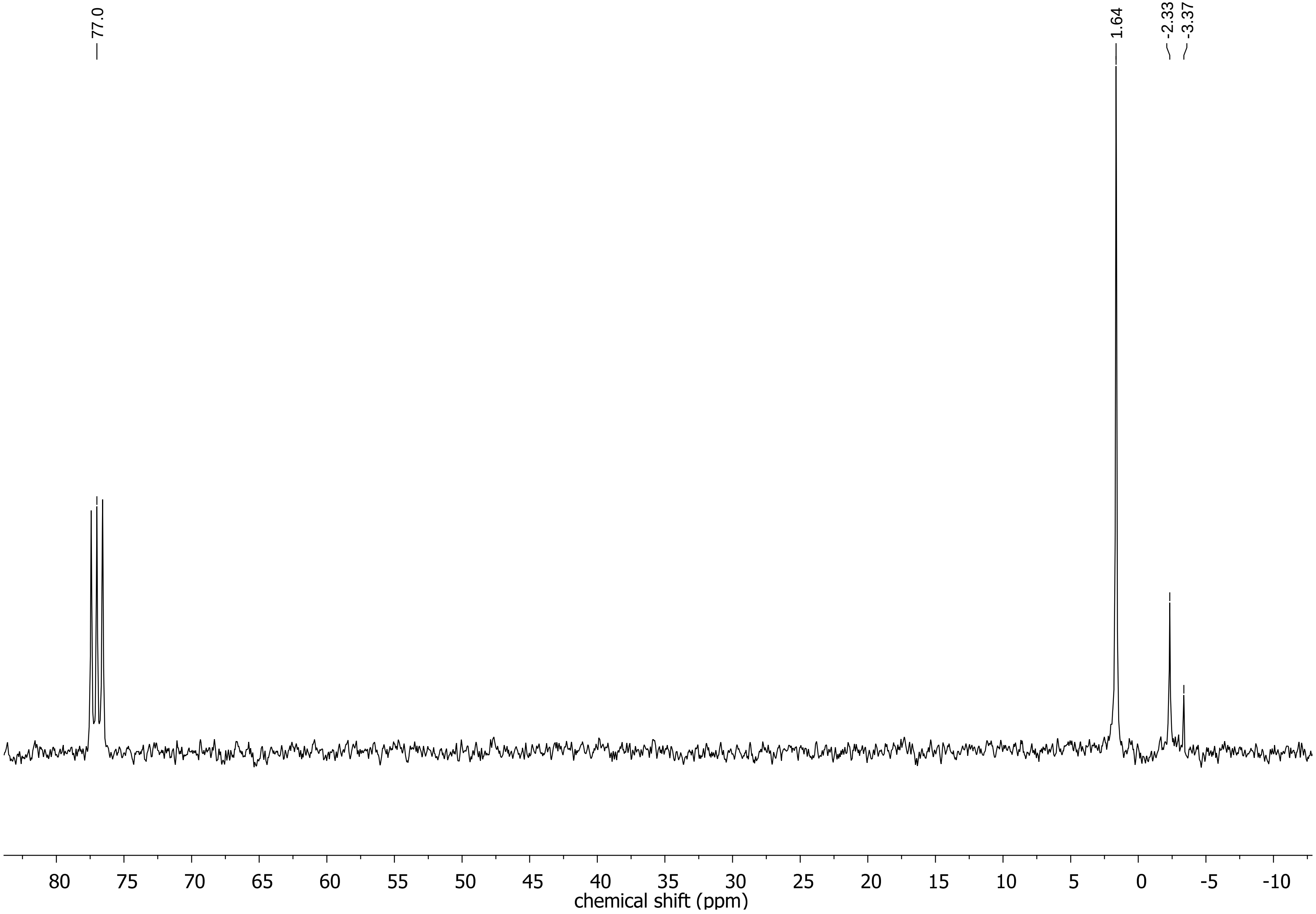
^{1}H NMR

(400 MHz, $CDCl_3$)



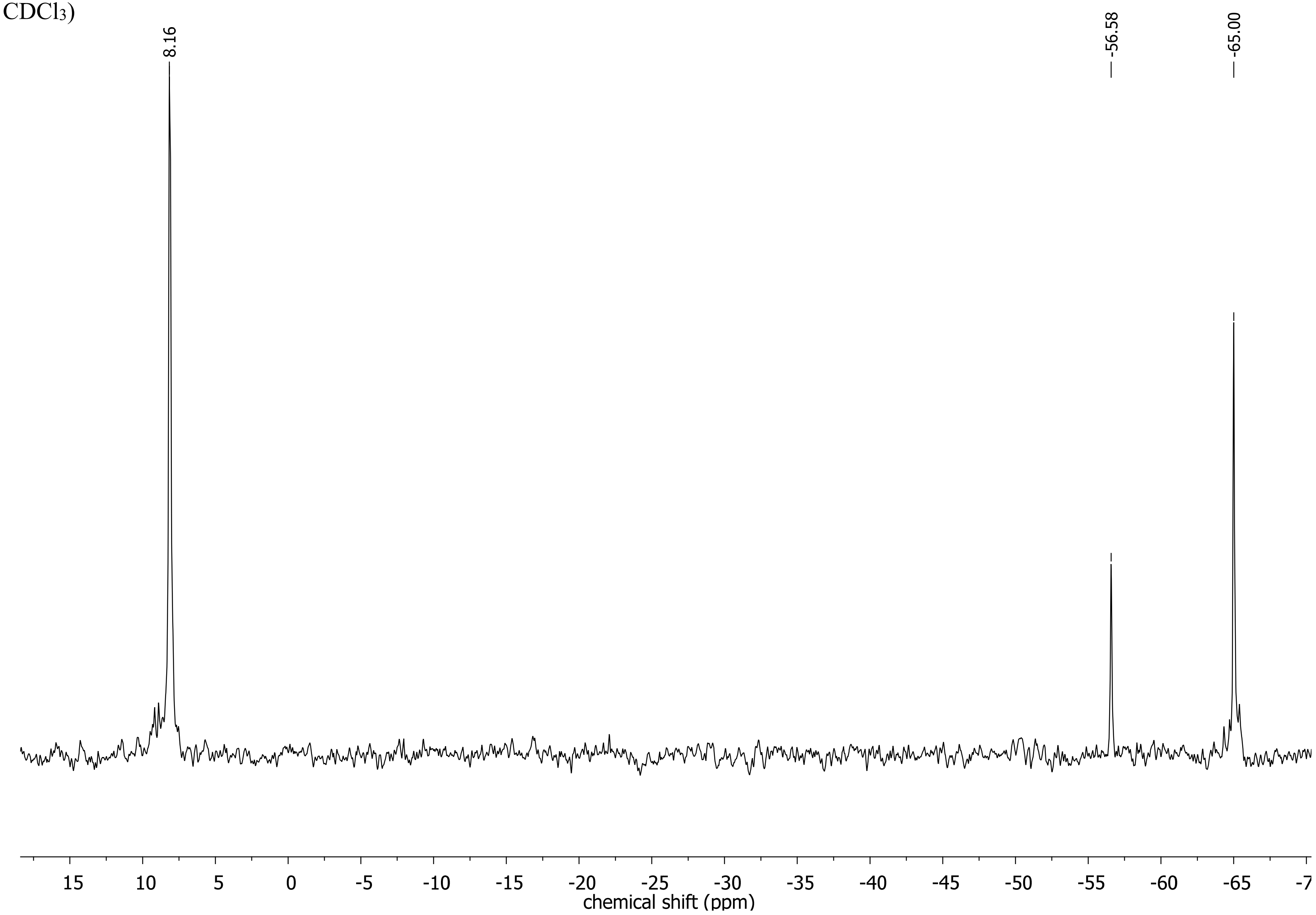
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

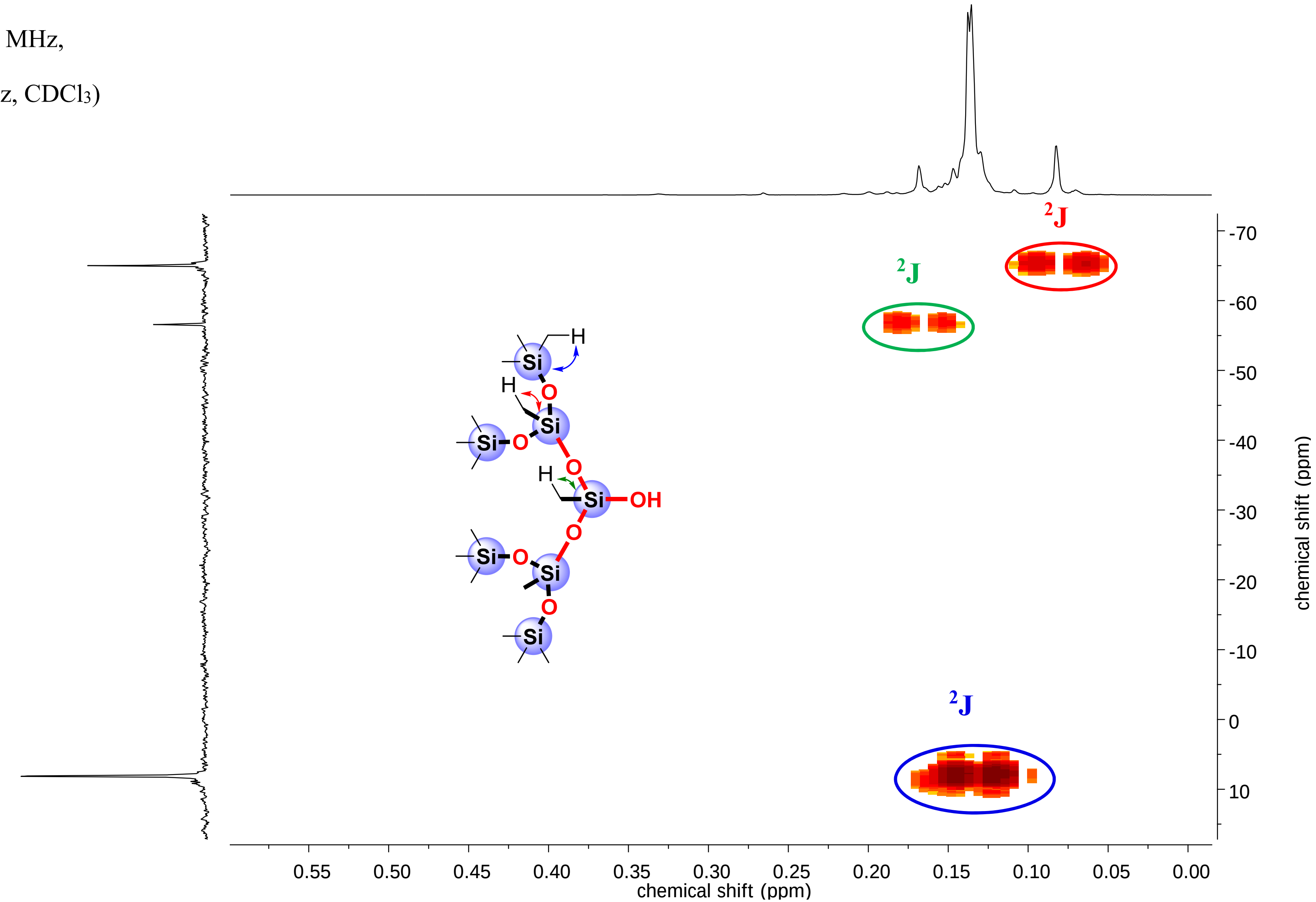
(80 MHz, $CDCl_3$)



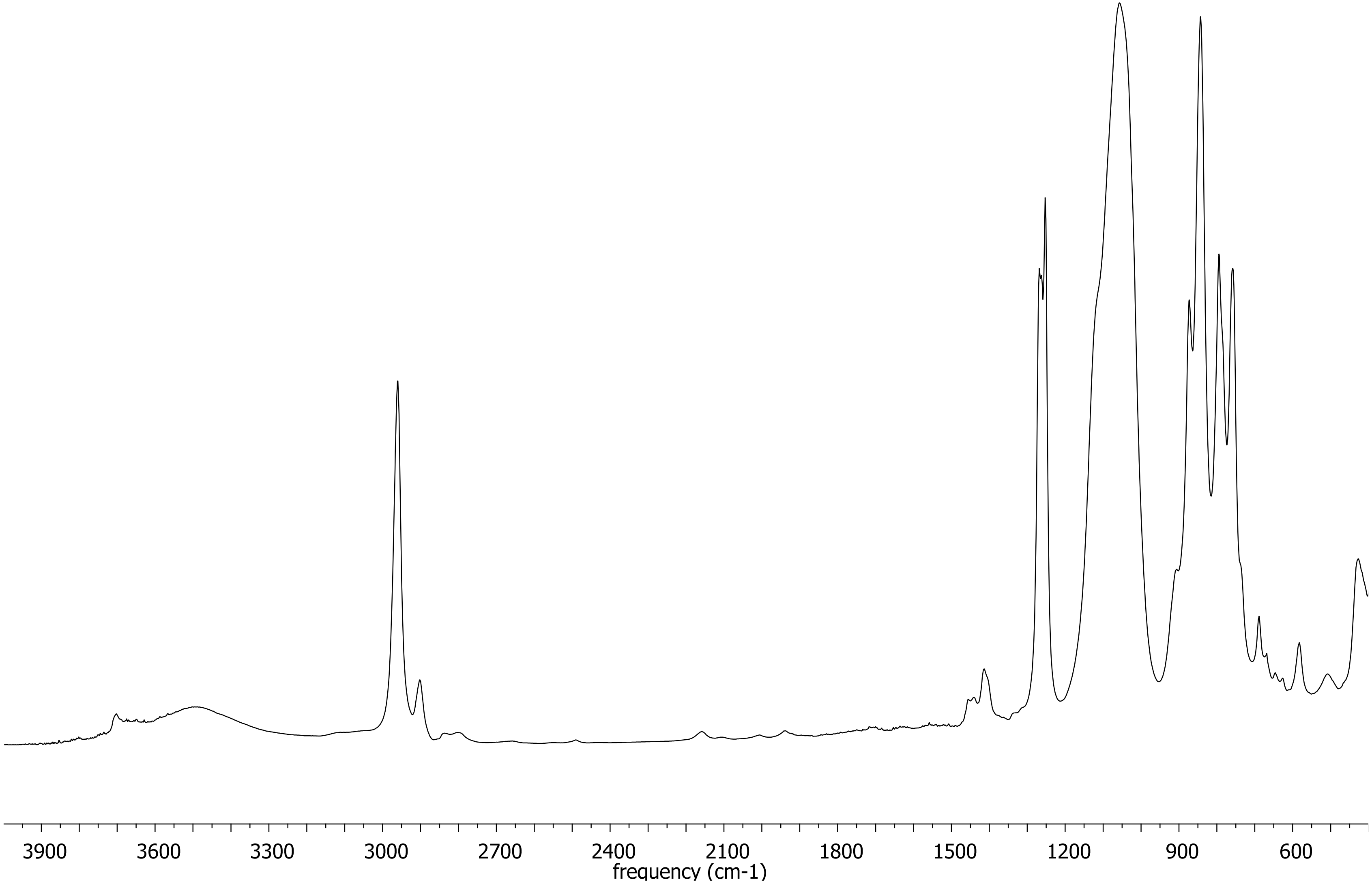
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)



IR-spectrum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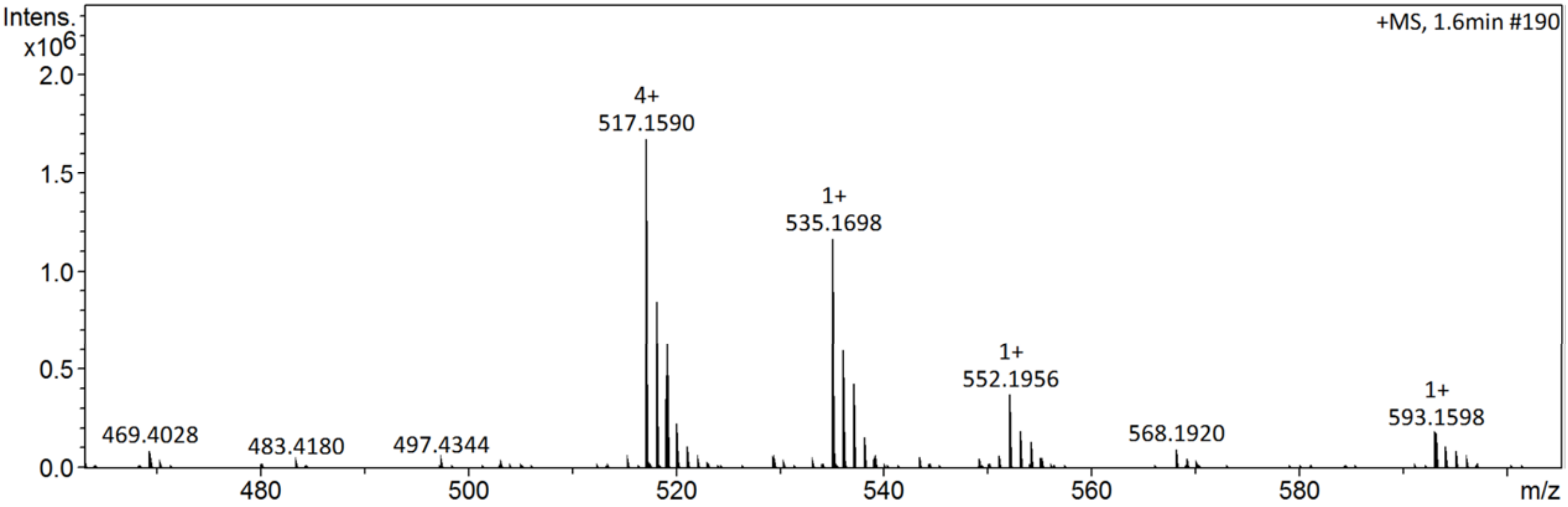
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

ESI-HRMS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1.0
0.5
0.0
+MS, 1.6min #190
4+
517.1590
1+
535.1698
1+
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469.4028
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497.4344
568.1920
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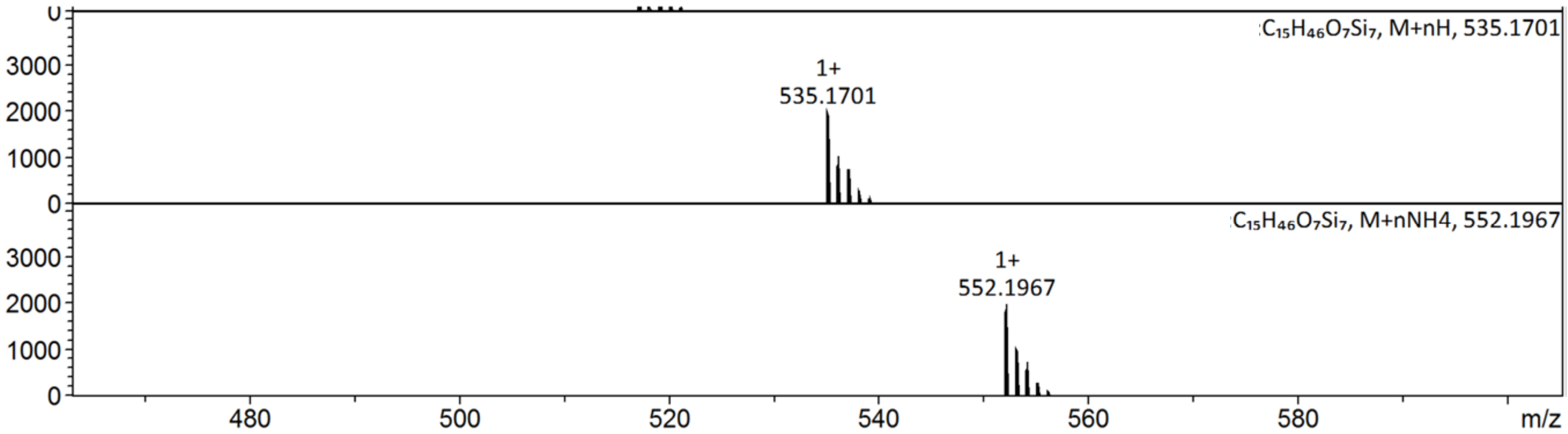
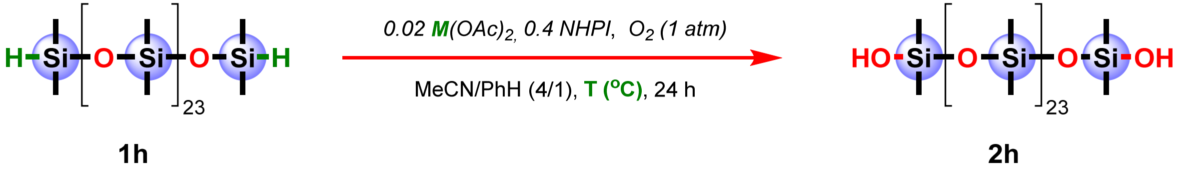
500
520
540
560
580
m/z


3000
2000
1000
0
C₁₅H₄₆O₇Si₇, M+nH, 535.1701
1+
535.1701
C₁₅H₄₆O₇Si₇, M+nNH4, 552.1967
1+
552.1967
480
500
520
540
560
580
m/z

10. Optimization of synthesis and characterization data for 2h

Table 10.1. Optimization of 1h aerobic oxidation[a]



	Cu(OAc)$_2$		Co(OAc)$_2$		
T, °C	**40** [b]	**60**	**30**	**40** [b]	**60** [b]
Yield of 2h, %	92	**98**	0	45	26
1h / 2h, %	8/92	**2/98**	100/0	55/45	73/26

[a] Reaction conditions: **1h** (0.450 mmol, 1 eq.), NHPI (0.18mmol, 0.4 eq.), M(OAc)$_2$ (9.0 µmol, 0.02 eq.), PhH (0.4 mL) and MeCN (1.6 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 30-60 °C for 24 h under the oxygen static atmosphere. The yield of **2h** was determined by ^{1}H MNR.

[b] 5 days.

*Method of **2h** synthesis*: **1h** (2.89 g, 1.56 mmol, 1 eq.), NHPI (0.102 g, 0.62 mmol, 0.4 eq.), $Cu(OAc)_2 \times H_2O$ (0.062 g, 0.031 mmol, 0.02 eq.), PhH (1.4 mL) and MeCN (5.6 mL) were stirred in a 500 ml round bottomed flask at 60 °C for 24 h under the oxygen flow. According to ^{1}H NMR the yield of **2h** was 96 – 98 %. Then the solvents were evaporated (180-200 mbar, T_{bath} = 40 °C). Then pentane (10-15 ml) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and pentane was evaporated (700 – 800 mbar, T_{bath} = 40 °C). Product **2h** was obtained as colorless liquid. The separated yield was 96% (2.82 g).

The length (a degree of polymerization) of the macromolecule after oxidation was calculated as a ratio of signal integral intensities of terminal to internal CH_3-groups for **2h** (^{1}H NMR).

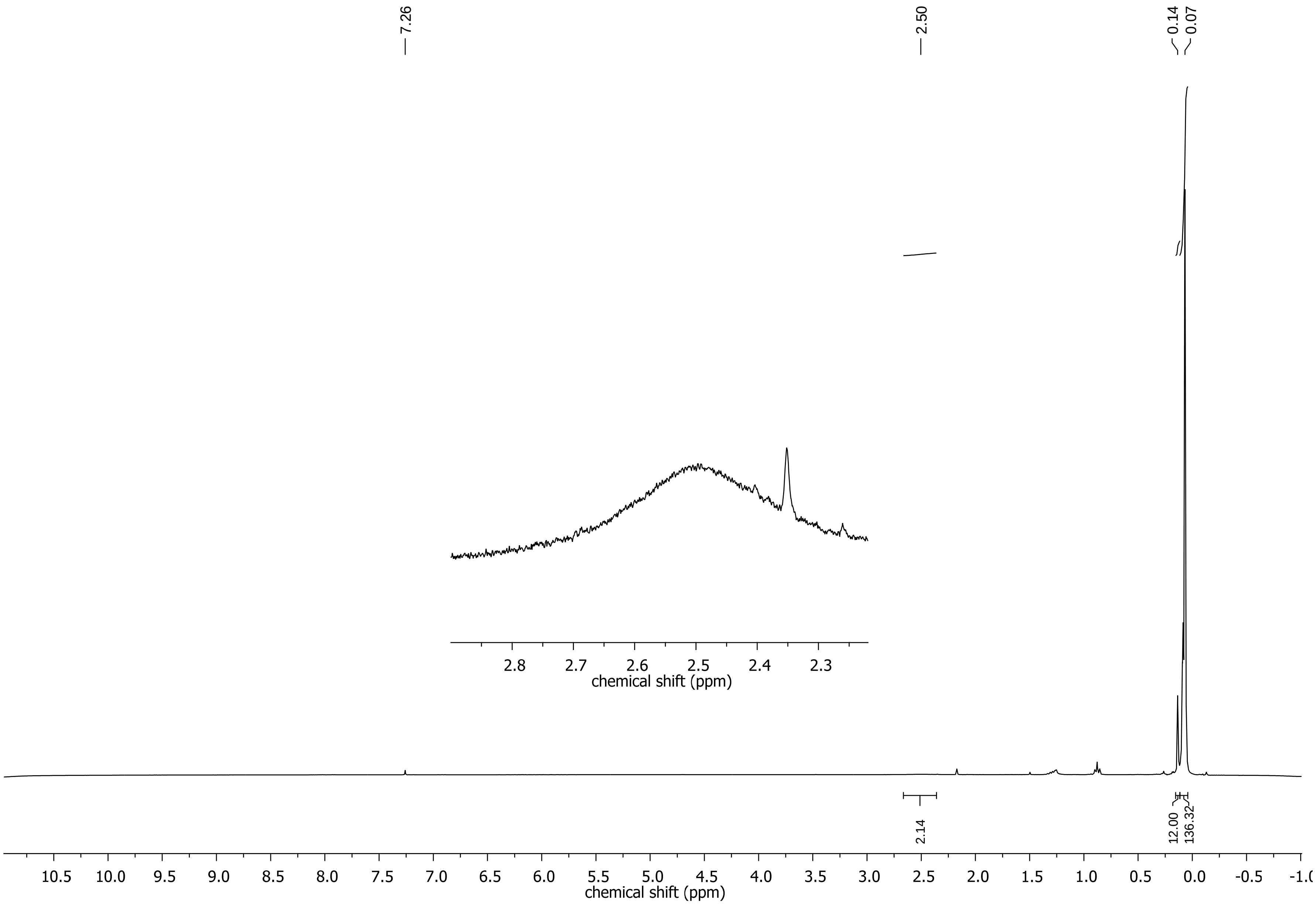
Characterization data for **2h**:

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.05 – 0.10 (br, 136H); 0.12 – 0.14 (br, 12H); 2.35 – 2.65 (br, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 1.02 (br). ^{29}Si NMR (80 MHz, CDCl$_3$): δ = -21.89 – -20.81;-10.40. IR (cm^{-1}): 3312; 2964; 1261; 1091; 1022. GPC (500A): M_w (pss) = 4688; M_n (pss) = 2953; PDI = 1.59.

To have additional prove of Si-OH groups existence oxidation of **1h** was followed by silylation (see **13.2**).

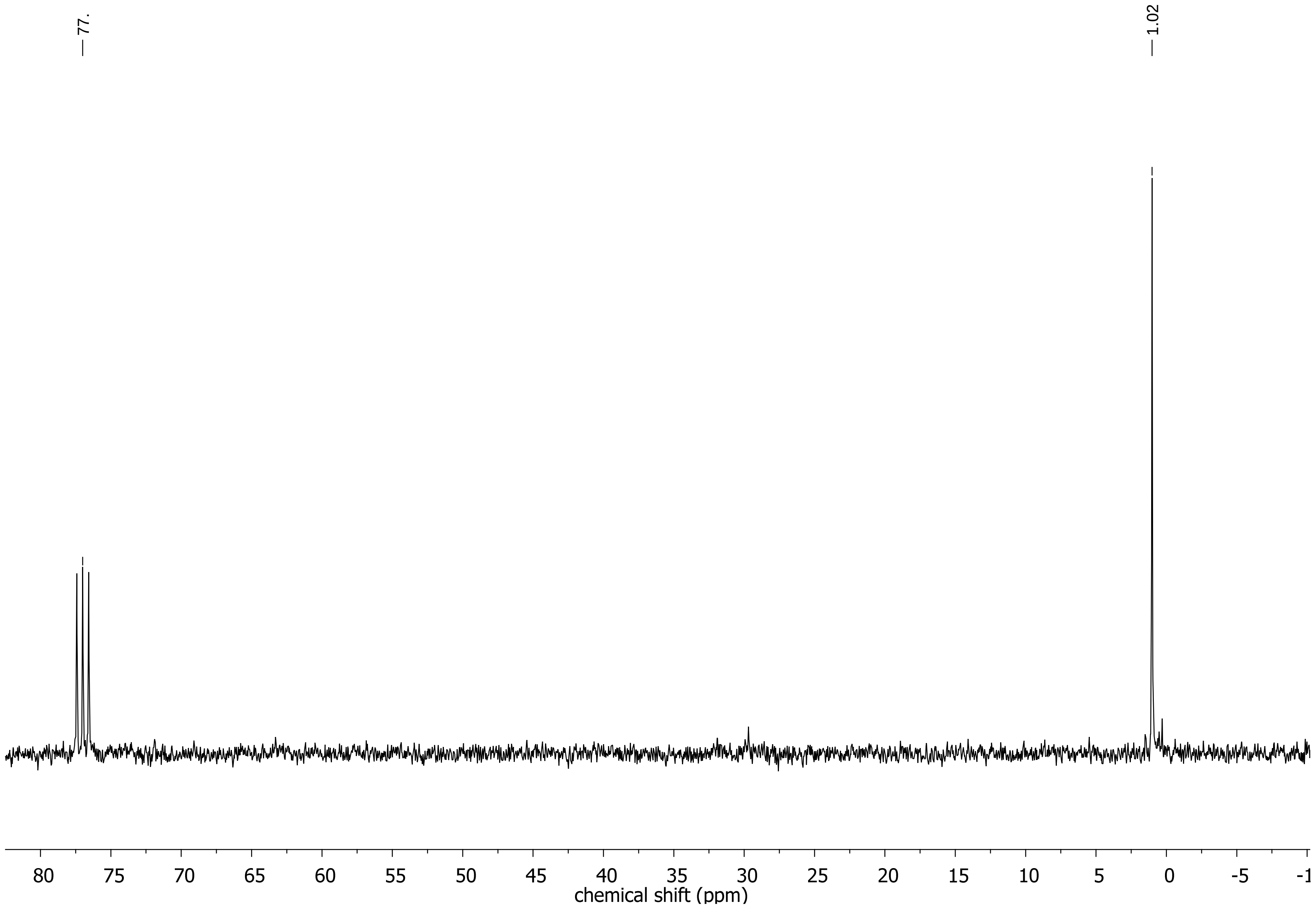
^{1}H NMR

(400 MHz, $CDCl_3$)



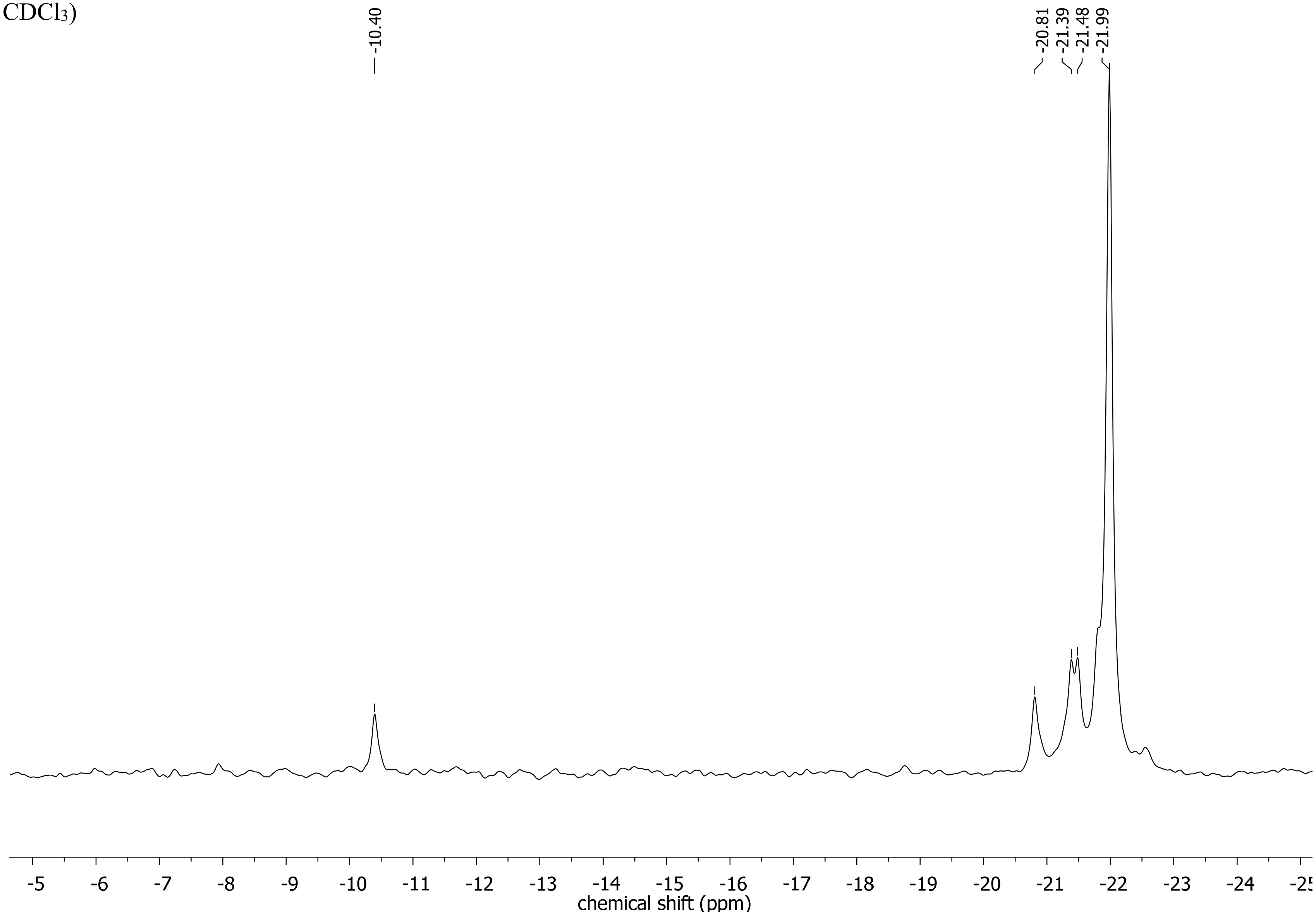
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

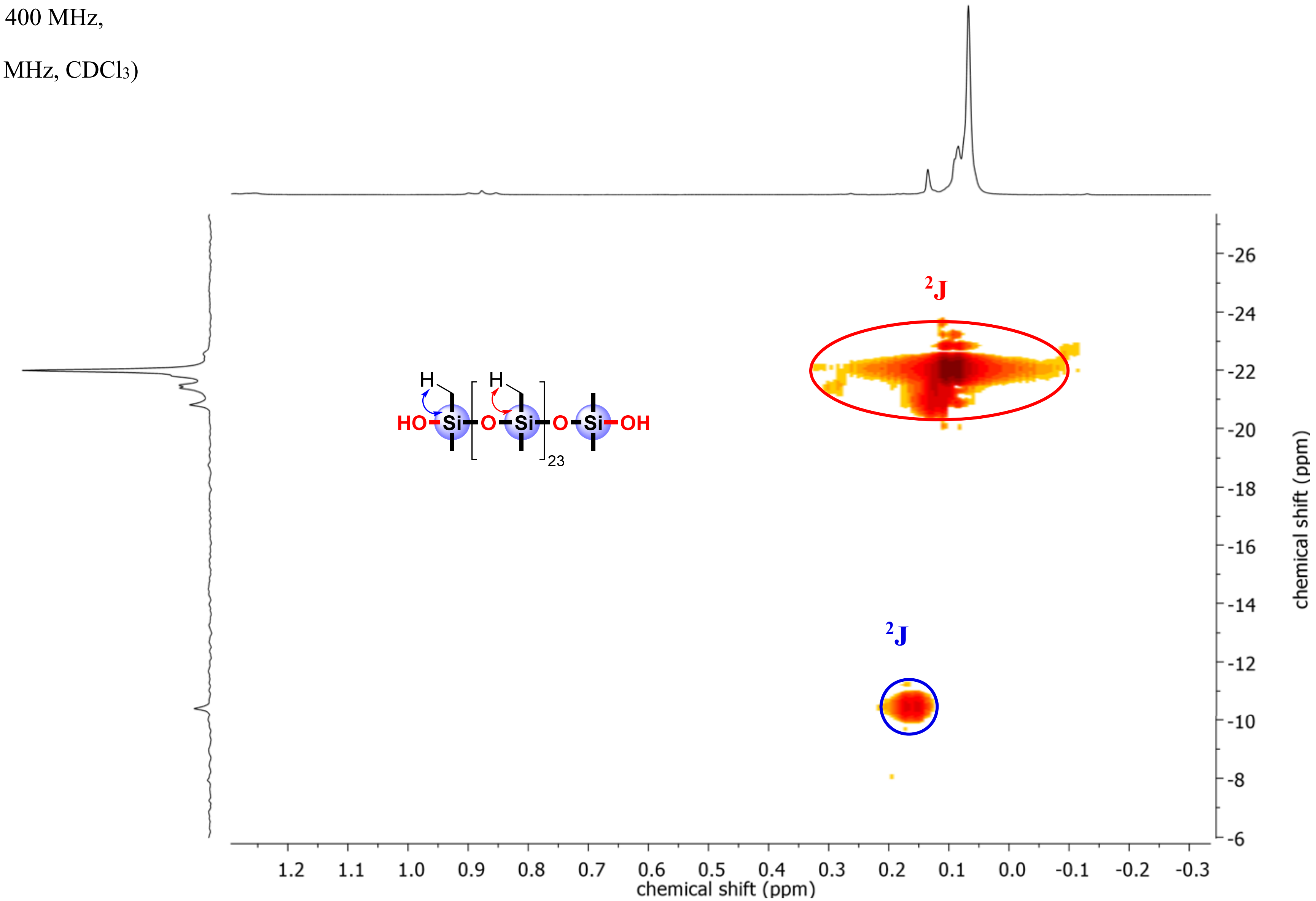
(80 MHz, $CDCl_3$)



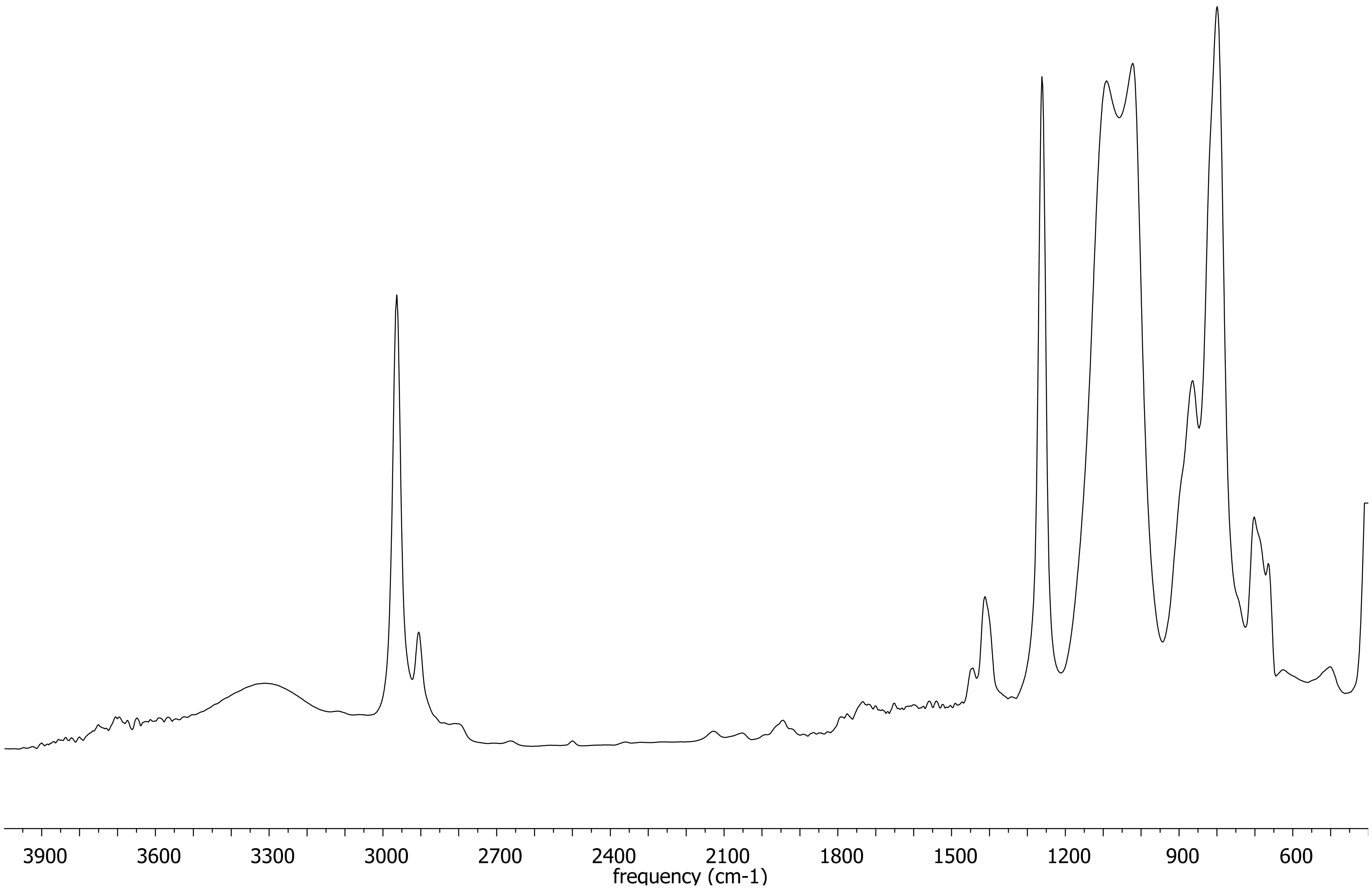
^1H, ^{29}Si –HMBC NMR

(^1H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)

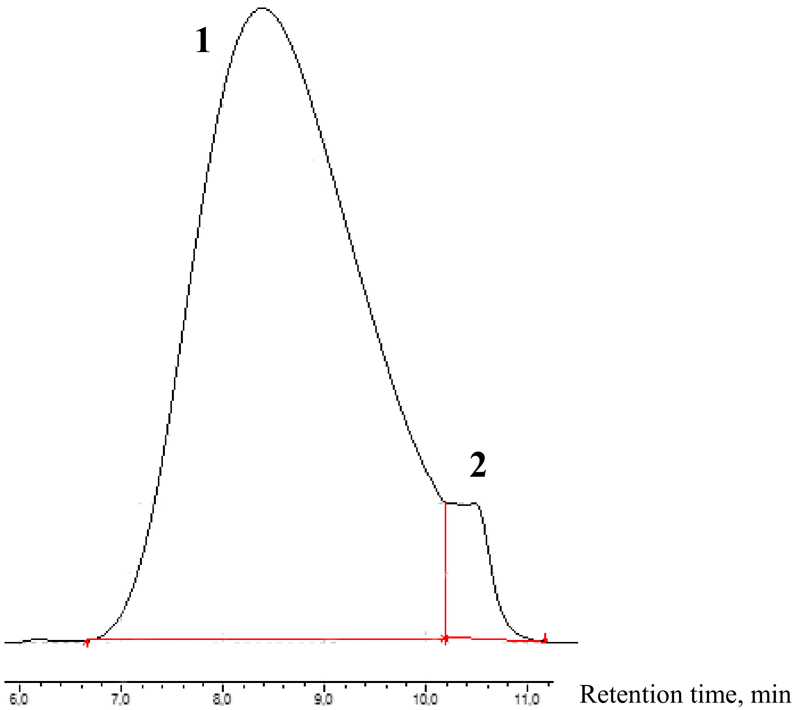


IR-spectrum


3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

GPC curve

500A



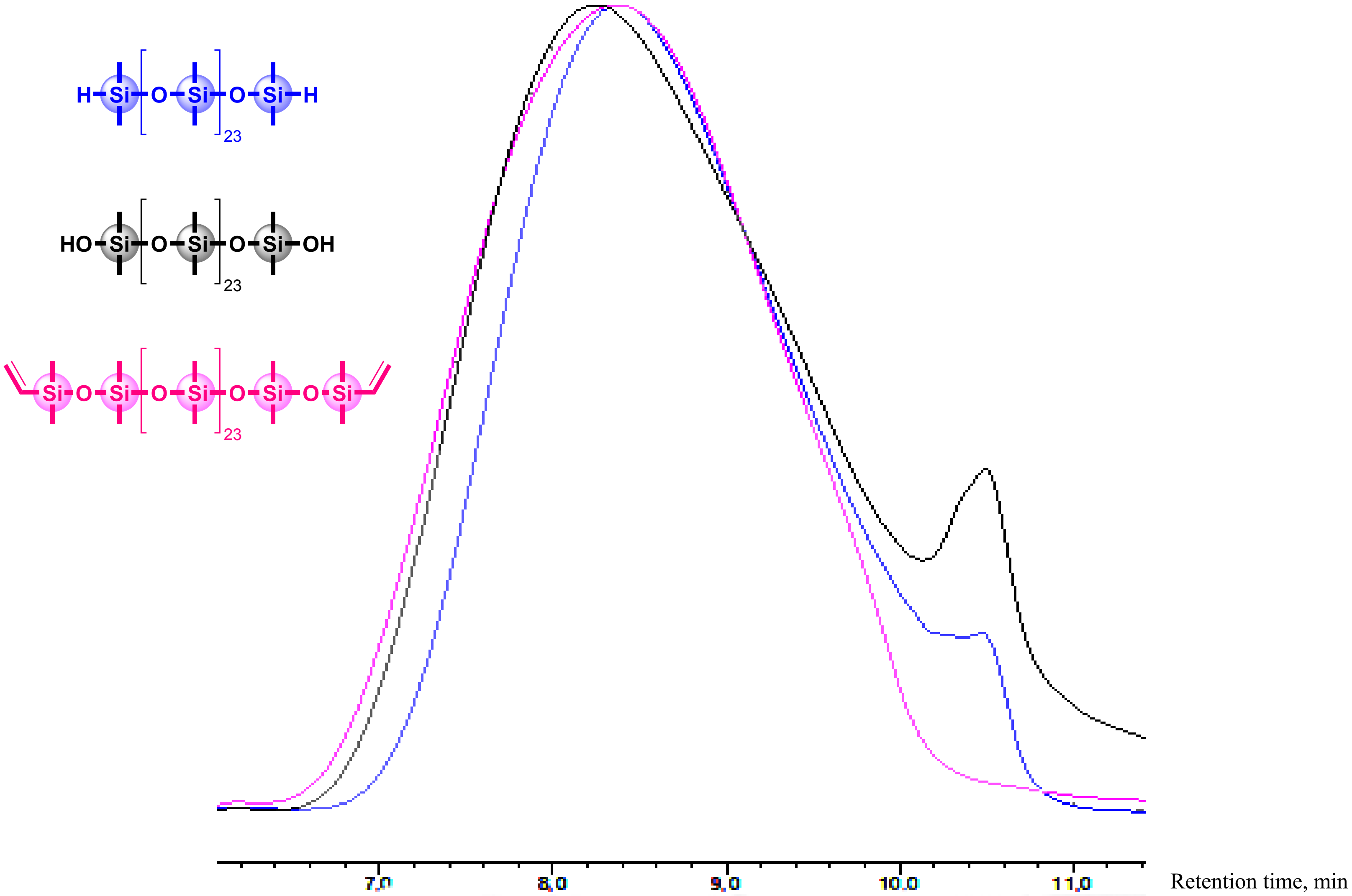
Peak 1. M_w (pss) = 4688;

M_n (pss) = 2953;

PDI = 1.59

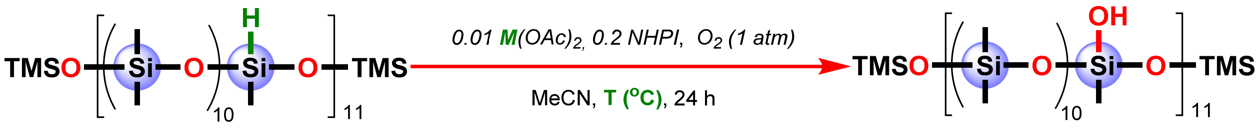
GPC comparison

500A



11. Optimization of synthesis and characterization data for 2i

Table 11.1. Optimization of 1i aerobic oxidation[a]



1i **2i**

T, °C	**Cu(OAc)$_2$**			**Co(OAc)$_2$**
	40	**60**	**60** [b]	**60** [b]
Yield of 2i, %	51	**98**	83	16
1i / 2i, %	49/51	**2/98**	17/83	84/16

[a] Reaction conditions: **1i** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), M(OAc)$_2$ (4.503 µmol, 0.01 eq.) and MeCN (1 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 40-60 °C for 48 h under the oxygen static atmosphere. The yield of **2i** was determined by ^{1}H MNR.

[b] A mixture of MeCN (0.8 ml) and PhH (0.2 mL) was used as a solvent, 2 days.

*Method of **2i** synthesis*: **1i** (1.8 g, 2.25 mmol, 1 eq. per [(Me$_2$SiO)$_{10}$Me***SiH***]-unit), NHPI (0.073 g, 0.45 mmol, 0.2 eq. per [(Me$_2$SiO)$_{10}$Me***SiH***]-unit), Cu(OAc)$_2$×H$_2$O (0.004 g, 0.022 mmol, 0.01 eq. per [(Me$_2$SiO)$_{10}$Me***SiH***]-unit) and MeCN (5 mL) were stirred in a 250 ml round bottomed flask at 60 °C for 3 days under oxygen flow. According to ^{1}H NMR the yield of **2i** was 97 – 99 %. Then the solvent was evaporated (180-200 mbar, T$_{bath}$ = 40 °C). Then pentane (7-10 ml) was added. The reaction mixture was filtered through a short pad (0.4 – 0.5 cm) of Celite, and pentane was evaporated (700 – 800 mbar, T$_{bath}$ = 40 °C). Product **2i** was obtained as colorless liquid. The separated yield was 92% (1.69 g).

The SiMe$_2$ / MeSi***OH***-blocks ratio was determined after silylation (see **13.3**).

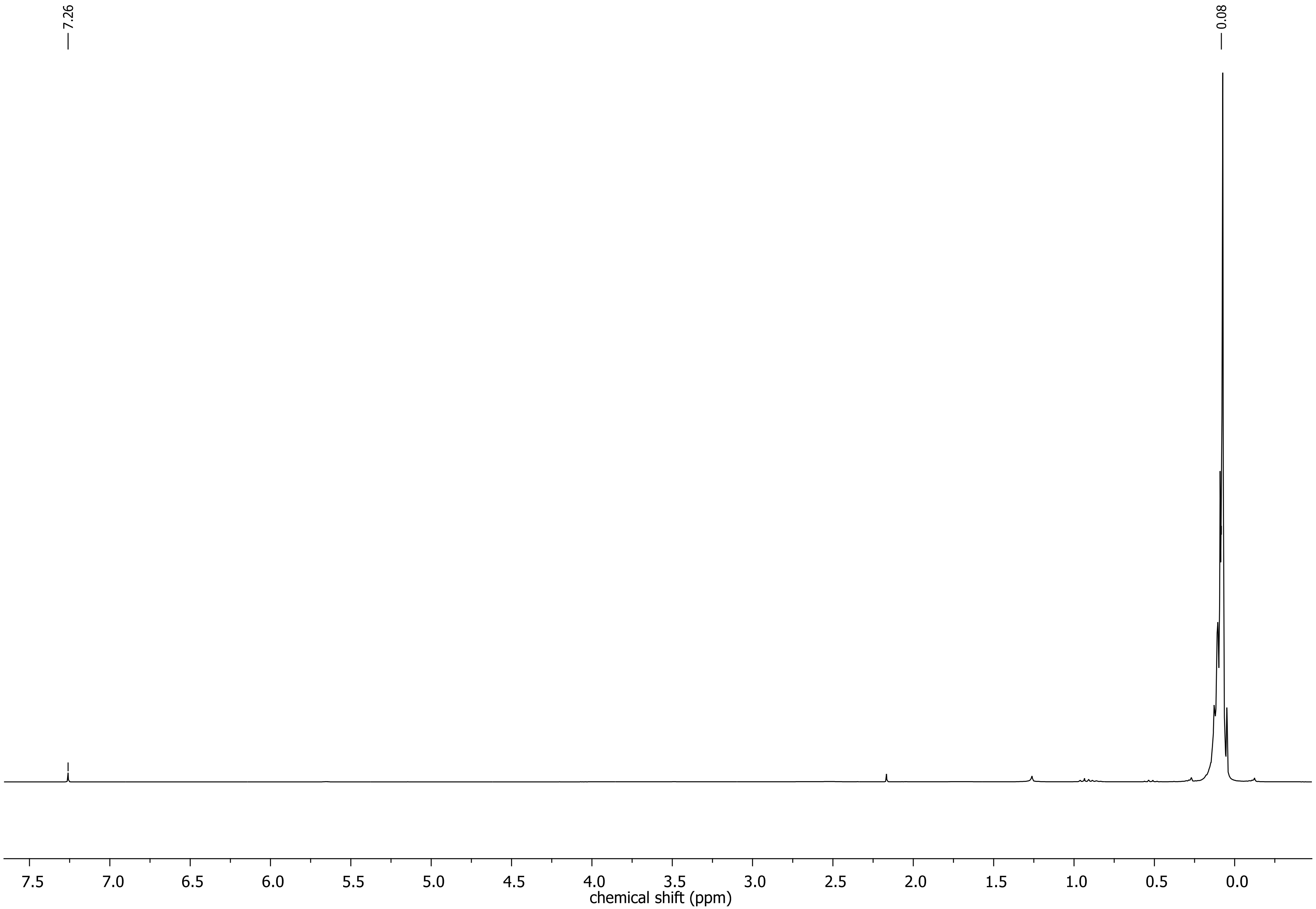
Characterization data for **2i**:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (br) ^{13}C NMR (100 MHz, $CDCl_3$): δ = -3.16; 0.85; 1.02; 1.12; 1.77. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -55.96; -22.0 – -20.92; 7.19. IR (cm^{-1}): 3618; 2963; 1260; 1086; 1022. GPC (1000A): M_w (pss) = 10994; M_n (pss) = 3981; PDI = 2.76.

To have additional prove of Si-OH groups existence oxidation of **1h** was followed by silylation (see **13.3**).

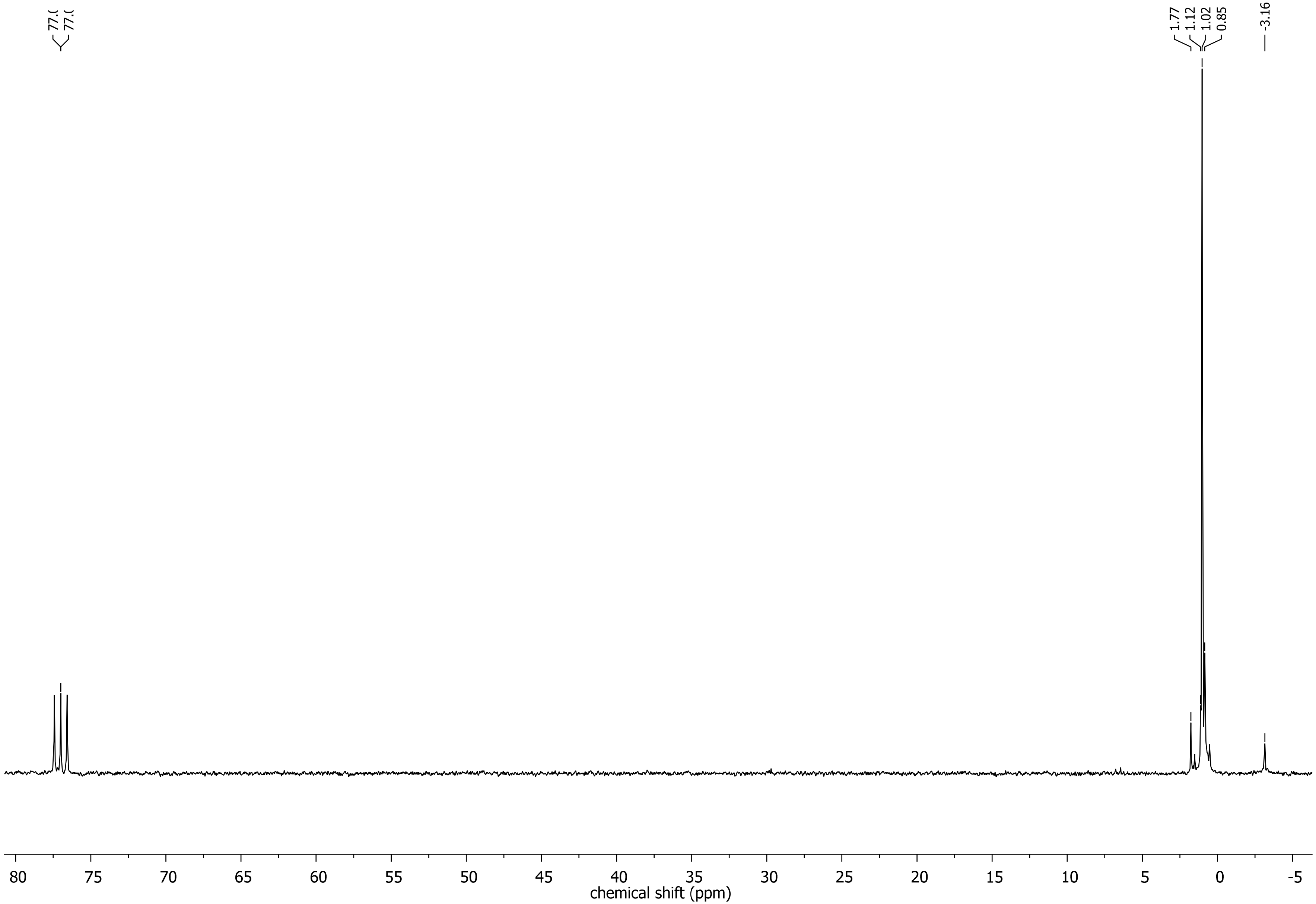
^{1}H NMR

(400 MHz, $CDCl_3$)



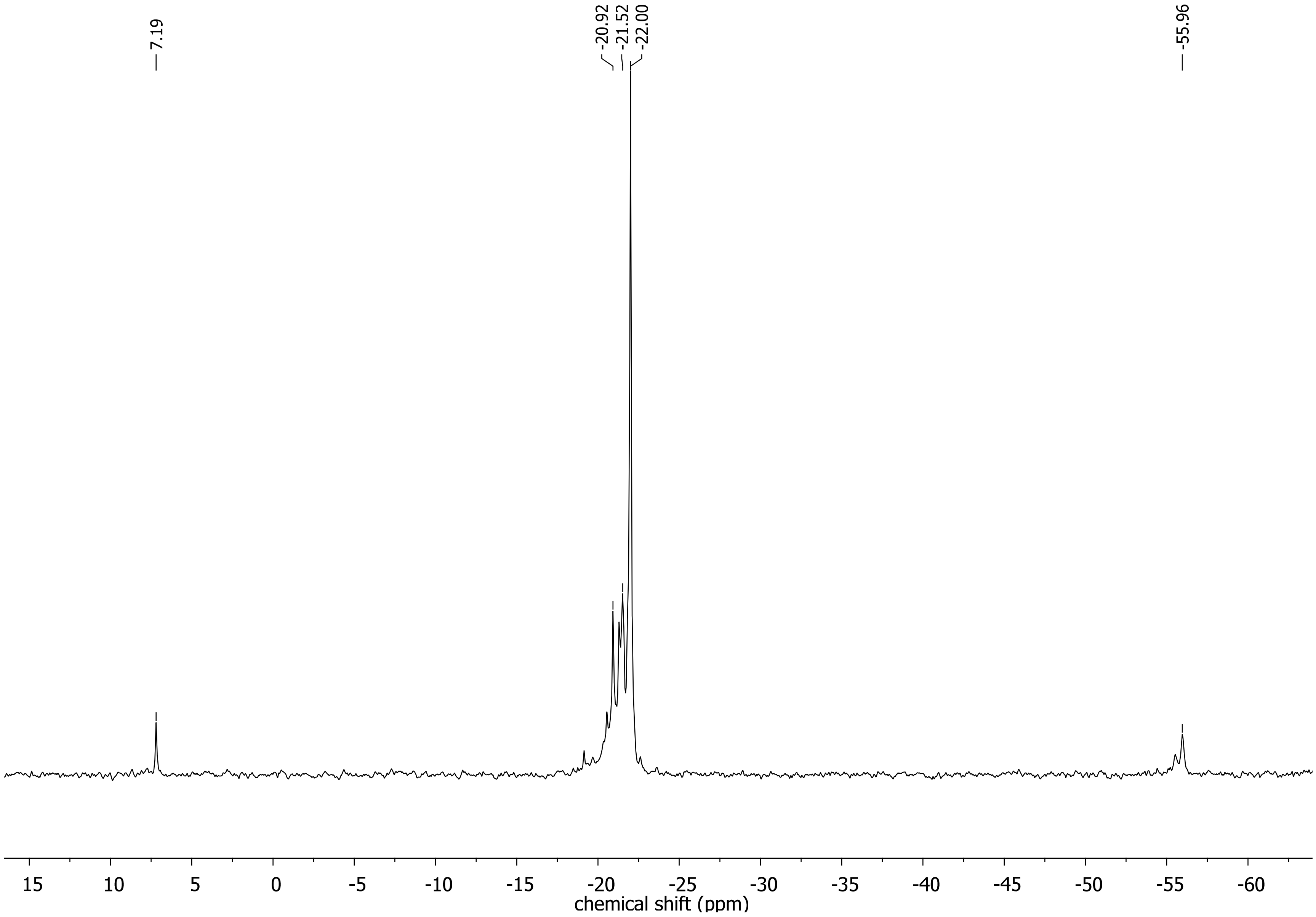
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

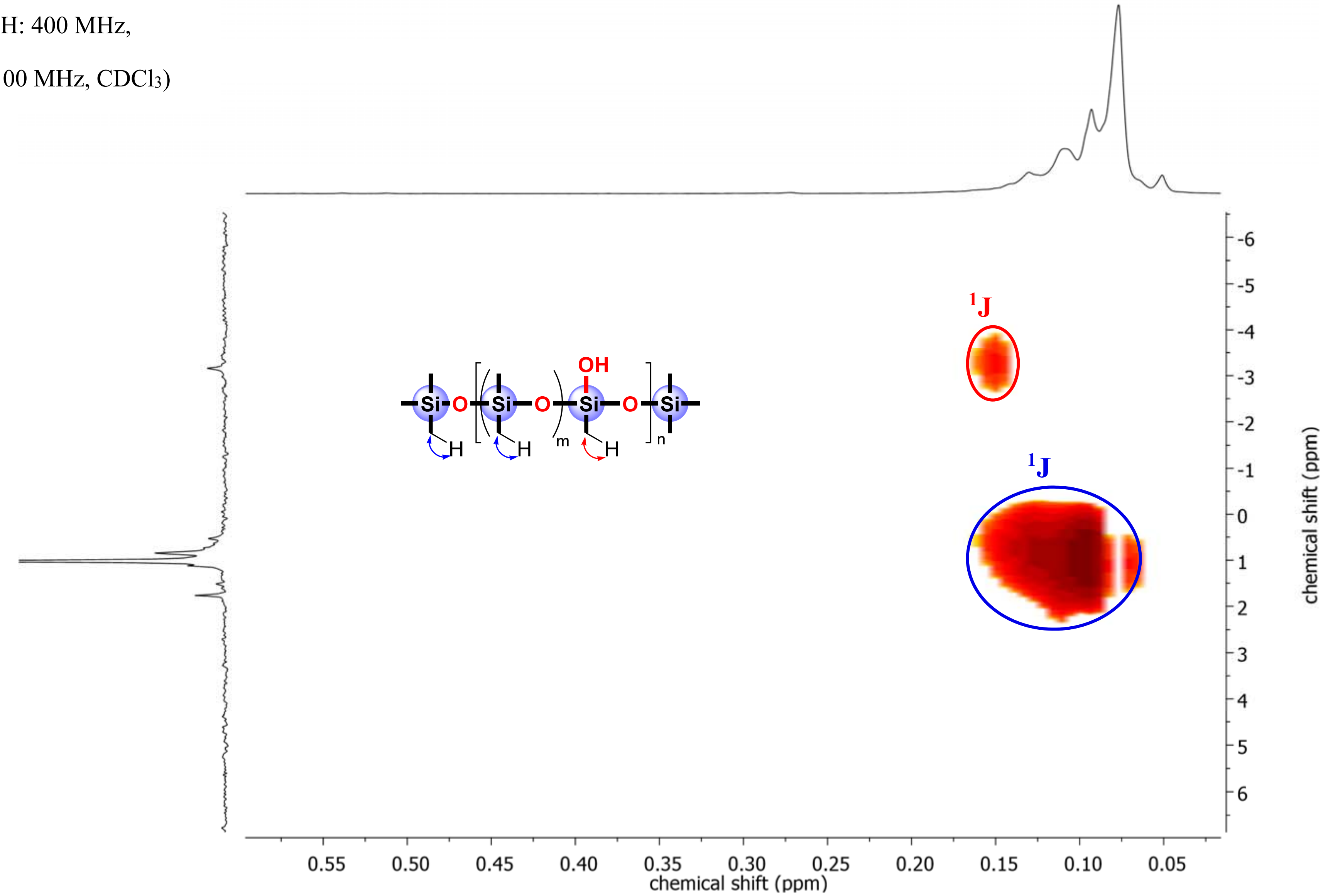
(80 MHz, CDCl$_3$)



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

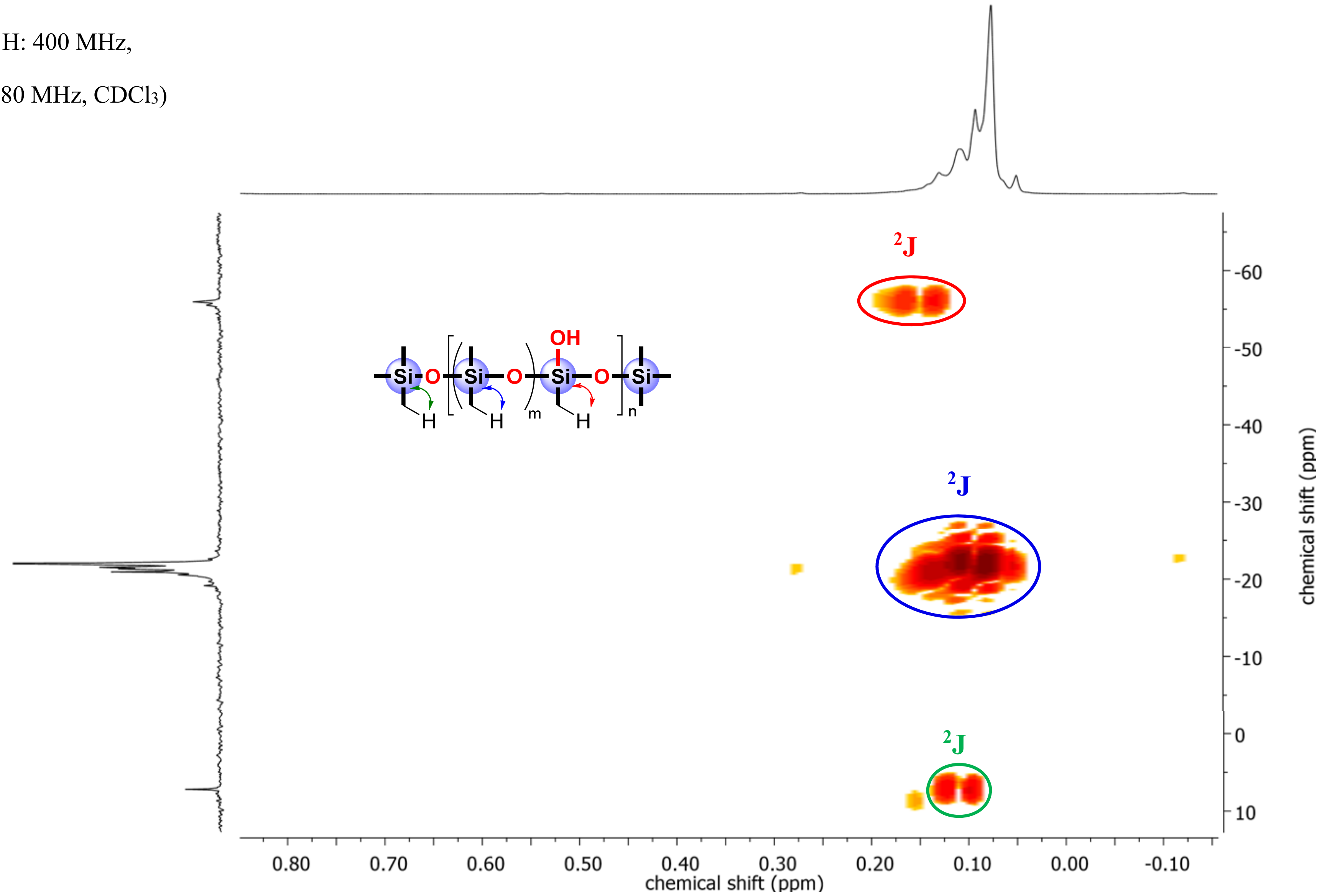
^{13}C: 100 MHz, CDCl$_3$)



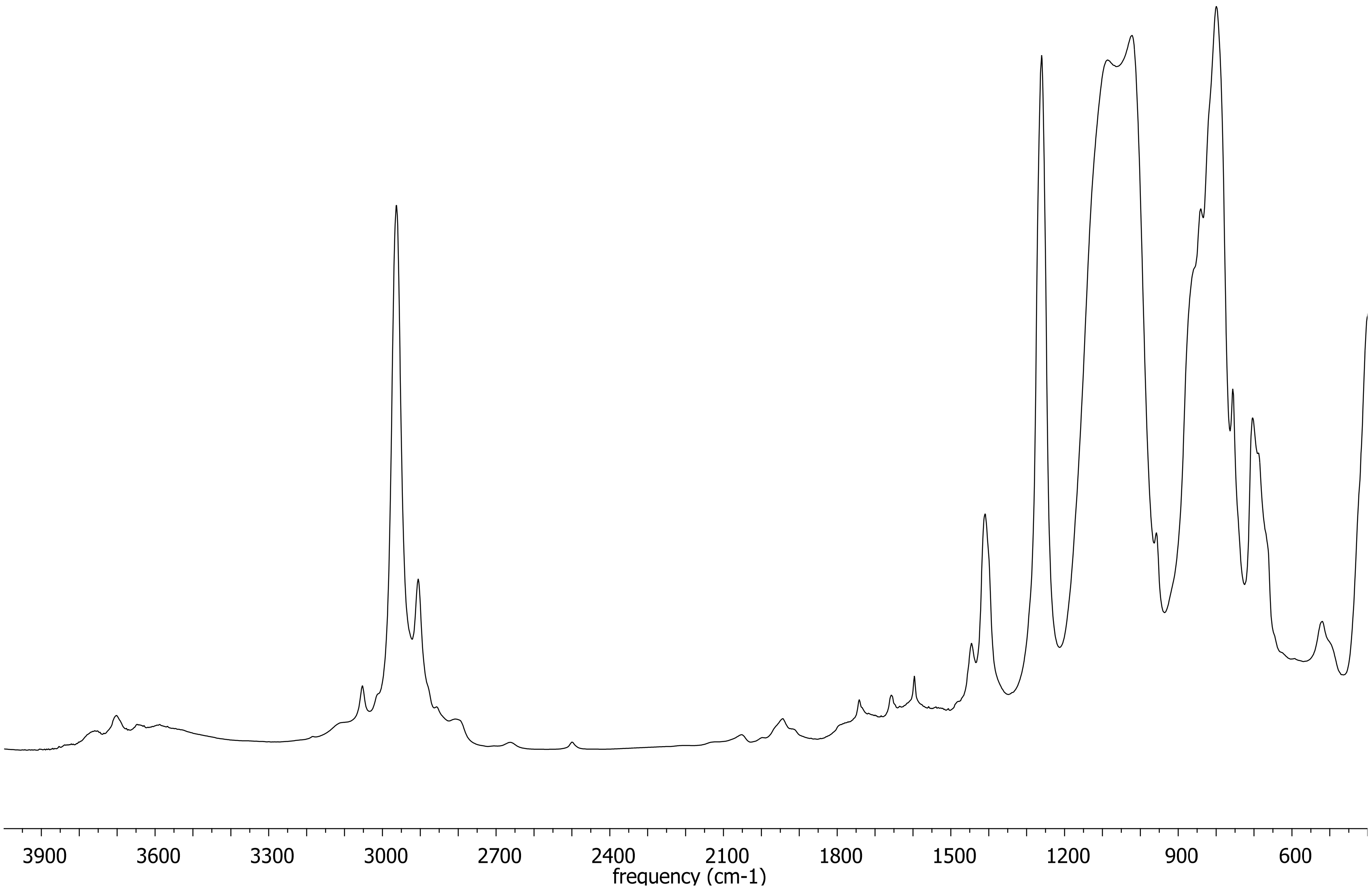
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)



IR-spectrum


3900
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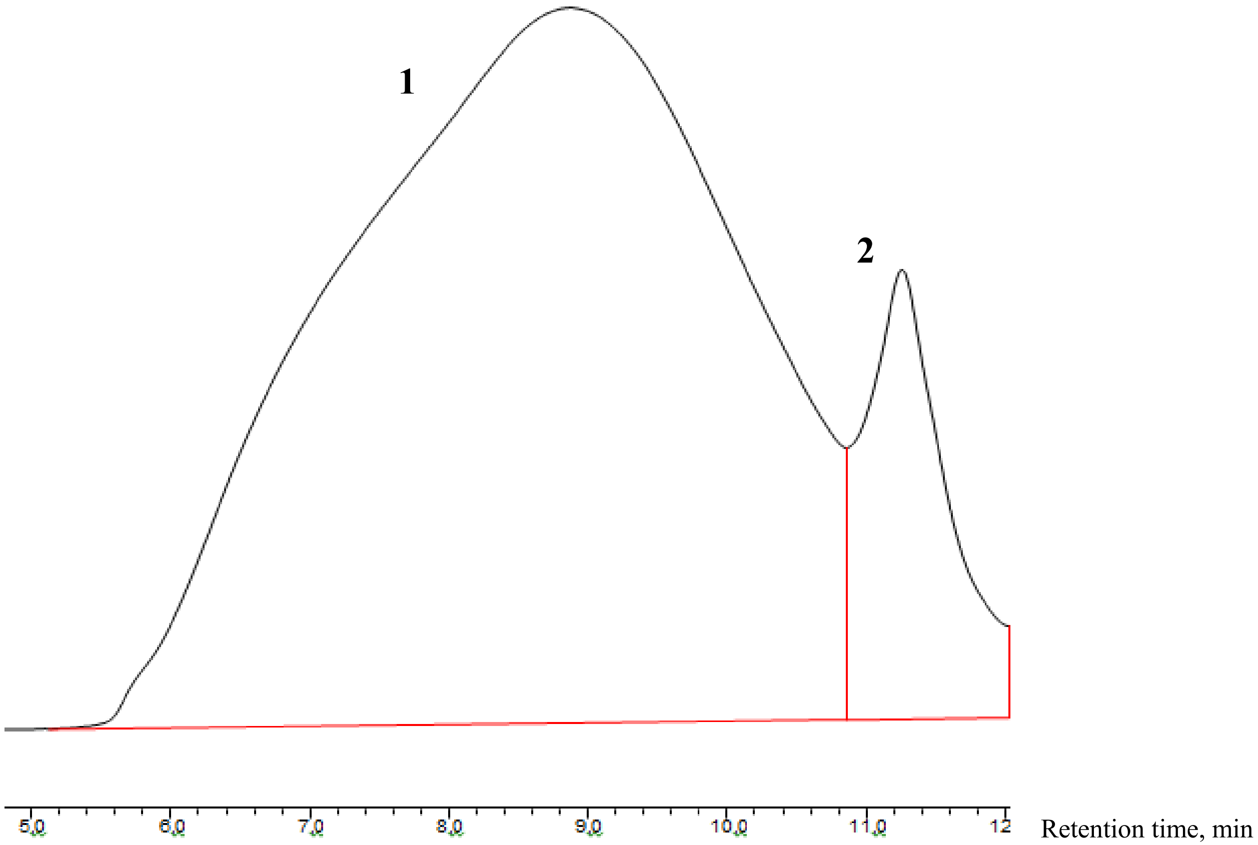
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

GPC curve

1000A



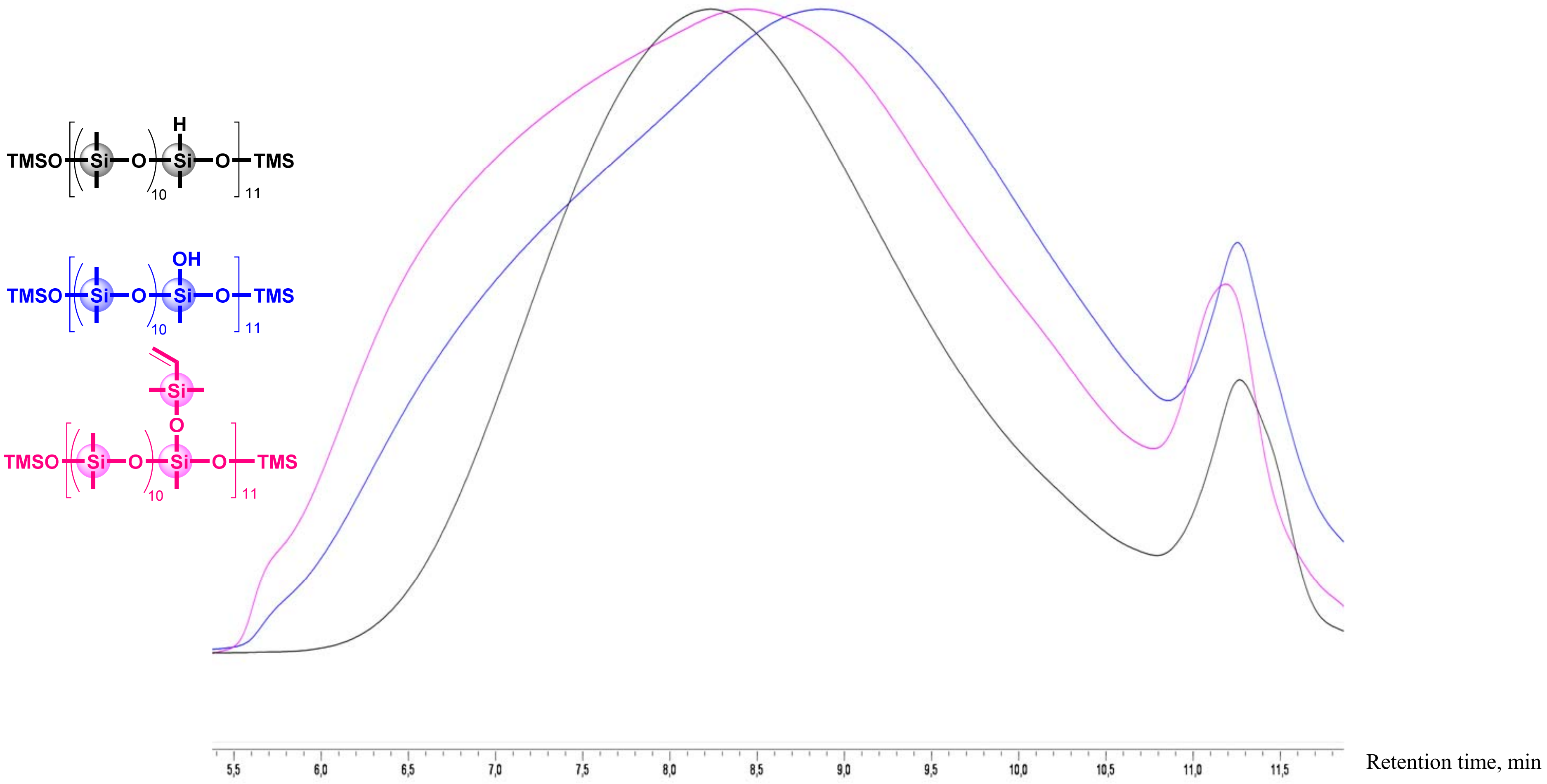
Peak 1. M_w (pss) = 10994;

M_n (pss) = 3981;

PDI = 2.76.

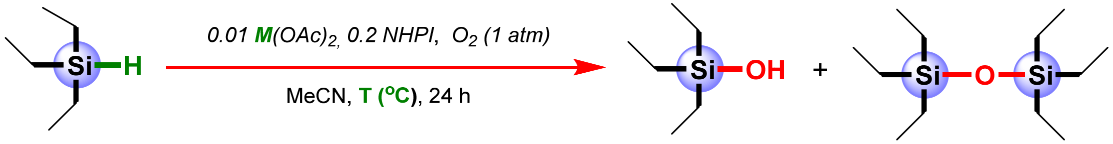
GPC comparison

1000A



12. Optimization of synthesis and characterization data for 2j

Table 12.1. Optimization of 1j aerobic oxidation[a]



1j **2j** **3j**

	Cu(OAc)₂			Co(OAc)₂		
T, °C	**25**	**40**	**60**[b]	**25**[b]	**40**[c]	**60**[c]
Yield of 2j, %	11	89	69	**90**	75	70
1j / 2j / 3j, %	80/11/9	2/89/9	22/69/9	**2/91/7**	6/75/19	5/70/25

[a] Reaction conditions: **1j** (0.450 mmol, 1 eq.), NHPI (0.090 mmol, 0.2 eq.), $M(OAc)_2$ (4.503 µmol, 0.01 eq.), and MeCN (1.00 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 25-60 °C for 24 h under the oxygen static atmosphere. The yield of **2j** was determined by GLC.

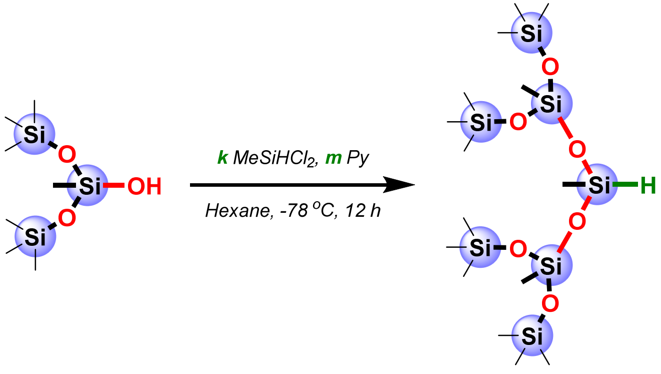
[b] 8 – 10 hours.

[c] 1 – 2 hours.

13. Optimization of 2a silylation, methods of synthesis and characterization data for 1b, g; 4c-e, g-i.

As was mentioned earlier, siloxanols serve as good building blocks for synthesis of well-defined structures, e.g. dendrimers. It is an urgent need to optimize ways of synthesis of these structures. The proposed earlier method based on the condensation with chlorosilane and oxidation steps allows to synthesize such structures. It is necessary to develop an effective and universal method for hydrosilanes synthesis by the chlorosilane condensation with silanol to use this procedure for the multi-step synthesis of complex siloxanol. So we have performed a short optimization of siloxanol silylation using **2a** as a model compound. As a result, we proposed two pathways: (a) step-by-step silylation including oxidation of **1a** followed by the product separation and subsequent condensation; (b) *in situ* silylation without the inermediate purification of **2a.** The second one allows to synthesize the desired product in high yields and exclude one mechanical step.

Table 13.1.1. The 2a silylation optimization. The effect of components ratio[a]

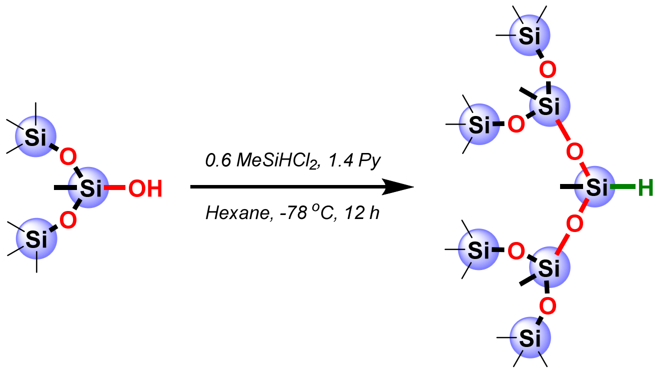


2a 1g

2a / $MeSiHCl_2$ / Py	1 / 0.6 / 1.4	1 / 0.5 / 1.2	1 / 0.45 / 1
Yield of 1g, %	74	59	48

[a] Reaction conditions: a solution of $MeSiHCl_2$ (0.159 – 0.213 g, 1.39 – 1.85 mmol, 0.45 – 0.6 eq.) in hexane (1 mL) and a solution of pyridine (0.243 – 0.341 g, 3.08 – 4.31 mmol, 1 – 1.4 eq.) in hexane (1 mL) were synchronously dropwise added (up to 5 min) to a solution of **2a** (0.735 g, 3.08 mmol, 1 eq.) in hexane (5 mL) under Ar at -78 °C under stirring. Then the reaction mass was slowly heated to 25 °C and stirred for 12 – 15 h. Next hexane (20 mL) was added and this mixture was washed with water (3×15 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). The yield of **1g** was determined by ^1H NMR using DCE as an internal standart.

Table 13.1.2. The 2a silylation optimization. The effect of mixing order[a]



2a **1g**

Method	1 [b]	2 [c]	3 [d]	4 [e]
Yield of 1g, %	**74**	**58**	**41**	**86**

[a] Reaction conditions: **2a** (0.735 g, 3.08 mmol, 1 eq.), $MeSiHCl_2$ (0.213 g, 1.85 mmol, 0.6 eq.), pyridine (0.341 g, 4.31 mmol, 1.4 eq.) and hexane (7 mL) were mixed under Ar at -78 °C under stirring. Then the reaction mass was slowly heated to 25 °C and stirred for 12 – 15 h. Next hexane (20 mL) was added and this mixture was washed with water (3×15 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). The yield of **1g** was determined by ^1H NMR using DCE as an internal standart.

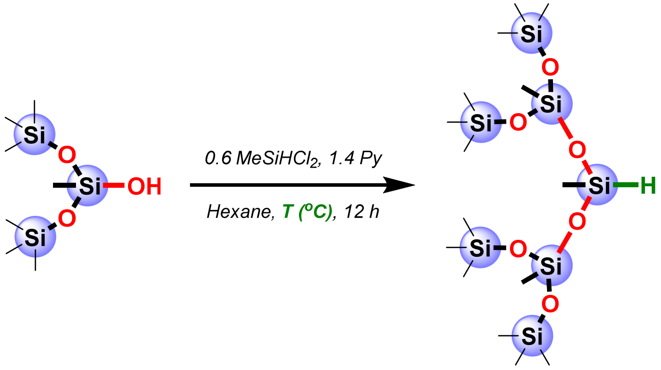
[b] A solution of $MeSiHCl_2$ in hexane (1 mL) and a solution of pyridine in hexane (1 mL) were synchronously dropwise added (up to 5 min) to a solution of **2a** in hexane (5 mL) under Ar at -78 °C under stirring.

[c] A solution of $MeSiHCl_2$ in hexane (1 mL) followed by solution of pyridine in hexane (1 mL) were added to a solution of **2a** in hexane (5 mL) under Ar at -78 °C under stirring.

[d] A solution of pyridine in hexane (1 mL) followed by solution of $MeSiHCl_2$ (1 mL) in hexane were added to a solution of **2a** in hexane (5 mL) under Ar at -78 °C under stirring.

[e] A solution of **2a** in hexane (5 mL) was dropwise added (up to 5 min) to a solution of pyridine with $MeSiHCl_2$ in hexane (2 mL) under Ar at -78 °C under stirring.

Table 13.1.3. The 2a silylation optimization. The effect of temperature[a]

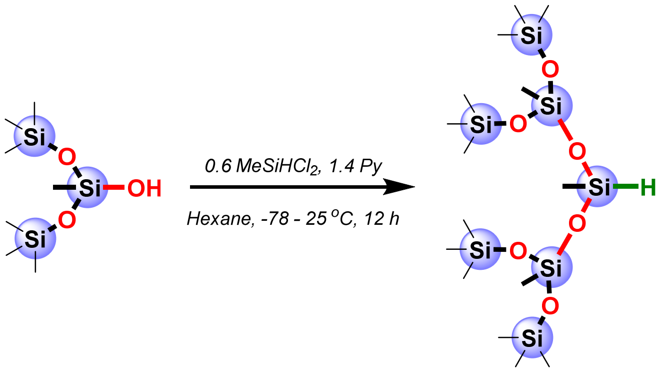


2a **1g**

T, ºC	-78	-20	+4	+25
Yield of 1g, %	86	77	72	61

[a] Reaction conditions: a solution of **2a** (0.735 g, 3.08 mmol, 1 eq.) in hexane (5 mL) was dropwise added (up to 5 min) to a solution of pyridine (0.341 g, 4.31 mmol, 1.4 eq.) with $MeSiHCl_2$ (0.213 g, 1.85 mmol, 0.6 eq.) in hexane (2 mL) under Ar at -78 – 25 ºC under stirring. Then the reaction mass was slowly heated to 25 ºC and stirred for 12 – 15 h. Next hexane (20 mL) was added and this mixture was washed with water (3×15 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). The yield of **1g** was determined by ^{1}H NMR using DCE as an internal standart.

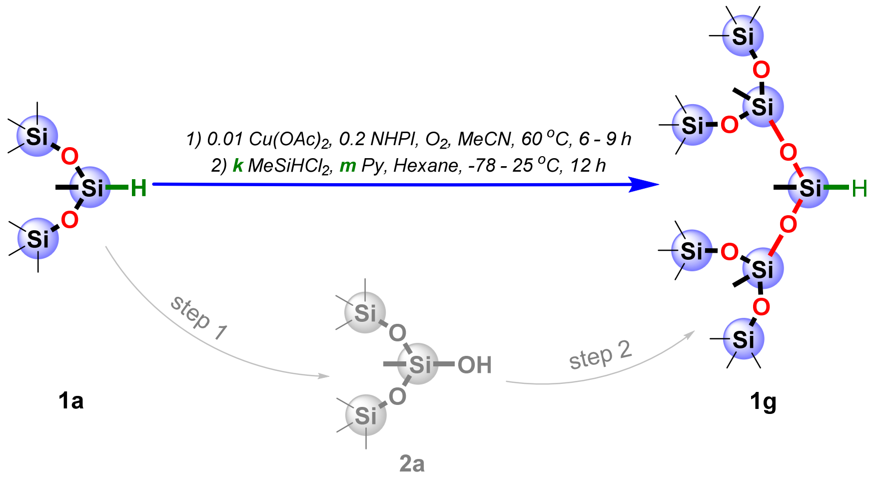
13.1.5. Method for 2a silylation



2a **1g**

Reaction conditions: a solution of **2a** (10 g, 41.93 mmol, 1 eq.) in hexane (70 mL) was dropwise added (up to 5 min) to a solution of pyridine (4.64 g, 58.7 mmol, 1.4 eq.) with $MeSiHCl_2$ (2.89 g, 25.16 mmol, 0.6 eq.) in hexane (25 mL) under Ar at -78 – 25 ºC under stirring. Then the reaction mass was slowly heated to 25 ºC and stirred for 12 – 15 h. Hexane (250 mL) was added, and this mixture was washed with water (3×200 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **1g** was obtained as a liquid. The separated yield was 73% (7.94 g).

Table 13.1.4. Optimization of *in situ* 2a silylation. The effect of components ratio[a].



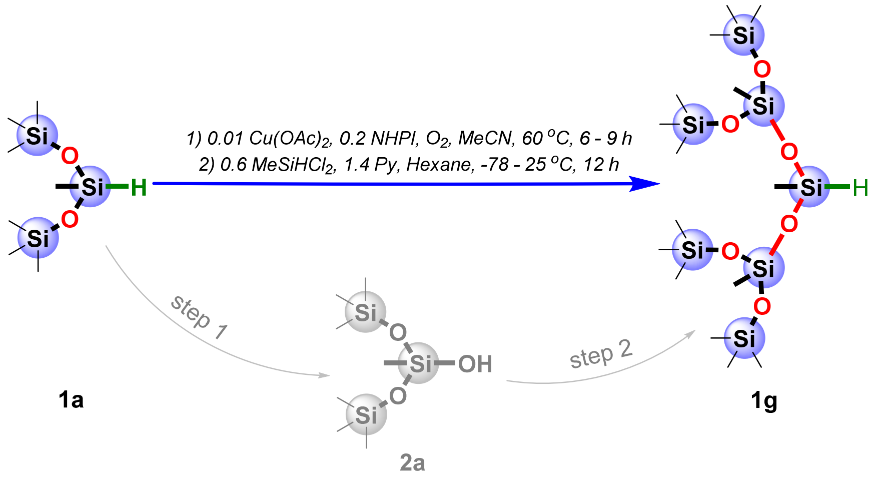
2a / MeSiHCl$_2$ / Py	**1 / 0,6 / 1,4**	**1 / 0,5 / 1,2**	**1 / 0,45 / 1**
Yield of 1g, %	**67**	53	26

[a] Reaction conditions:

Step 1. **1a** (0.933 g, 4.20 mmol, 1 eq.), NHPI (0.137 g, 0.84 mmol, 0.2 eq.), Cu(OAc)$_2$ (8.4 mg, 42 μmol, 0.01 eq.) and MeCN (9 mL) were stirred in a 100 ml round bottomed flask at 60 °C for 6-9 h under the oxygen static atmosphere. 80-90 % of the solvent was evaporated (190-200 mbar, T_{bath} = 40 °C). The yield of **2a** was 90 –95% (determined by GLC).

Step 2. Hexane (6 mL) was added to the reaction mixture. A solution of pyridine (0.332 – 0.465 g, 4.20 – 5.88 mmol, 1 – 1.4 eq.) in hexane (2 mL) and a solution of MeSiHCl$_2$ (0.217 – 0.290 g, 1.89 – 2.52 mmol, 0.45 – 0.6 eq.) in hexane (2 mL) were synchronously dropwise added (up to 5 min) under Ar at -78 °C under stirring. Then it was slowly heated to 25°C and stirred for 12 – 15 hours. Hexane (40 mL) was added and this mixture was filtered through a short pad (0.4 – 0.5 cm) of SiO$_2$ and then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). The yield of **1g** was determined by ^{1}H NMR using DCE as an internal standart.

13.1.5. Method for 2a *in situ* silylation



Step 1. **1a** (15 g, 67.41 mmol, 1 eq.), NHPI (2.20 g, 13.48 mmol, 0.2 eq.), $Cu(OAc)_2 \times H_2O$ (0.13 g, 0.67 mmol, 0.01 eq.) and MeCN (150 mL) were stirred in 1000 mL round bottomed flask at 60 °C for 8 h under the oxygen static atmosphere. 80-90 % of the solvent was evaporated (180-200 mbar, T_{bath} = 40 °C) resulting in 5-7% silanol solution (in MeCN).

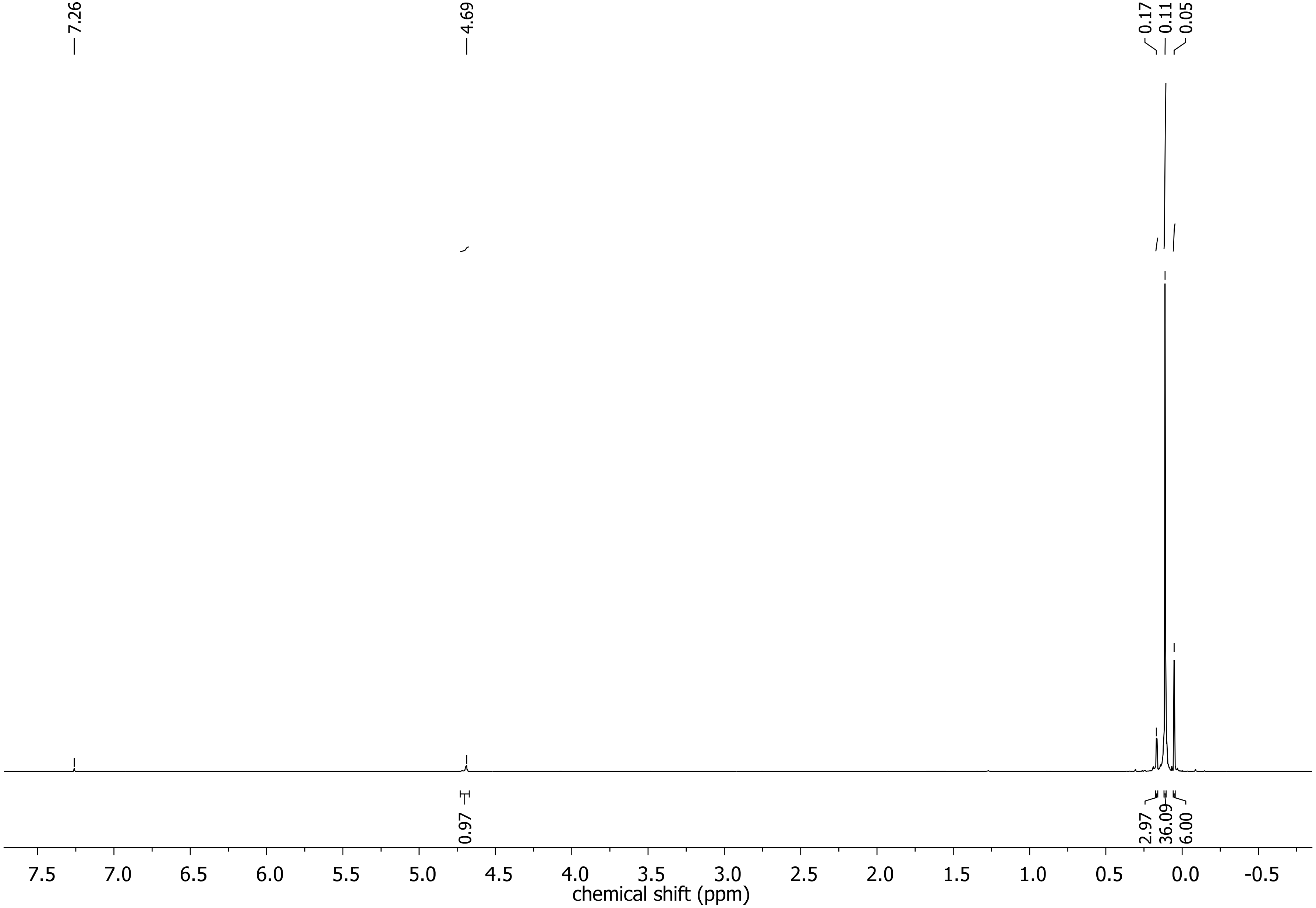
Step 2. Hexane (110 mL) was added to the reaction mixture. A solution of pyridine (7.46 g, 94.37 mmol, 1.4 eq.) in hexane (25 mL) and a solution of $MeSiHCl_2$ (4.65 g, 40.45 mmol, 0.6 eq.) in hexane (25 mL) were synchronously dropwise added (up to 5 min) under Ar at -78 °C under stirring. Then it was slowly heated to 25ºC and stirred for 12 – 15 hours. Next hexane (500 mL) was added, and this mixture was washed with water (3×300 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **1g** was obtained as a liquid. The separated yield was 55% (9.92 g).

Characterization data for 1,1,1,3,5,7,9,9,9-nonamethyl-3,7-bis((trimethylsilyl)oxy)pentasiloxane (**1g**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 6H); 0.11 (s, 36H); 0.17 (d, J = 2 Hz, 3H), 4.69 (m, 1H). ^{13}C NMR (100 Hz, $CDCl_3$): –2.29; 1.16; 1.65. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = –64.74; –38.19; 7.90. IR (cm^{-1}): 2960; 2159; 1252; 1057.

^{1}H NMR

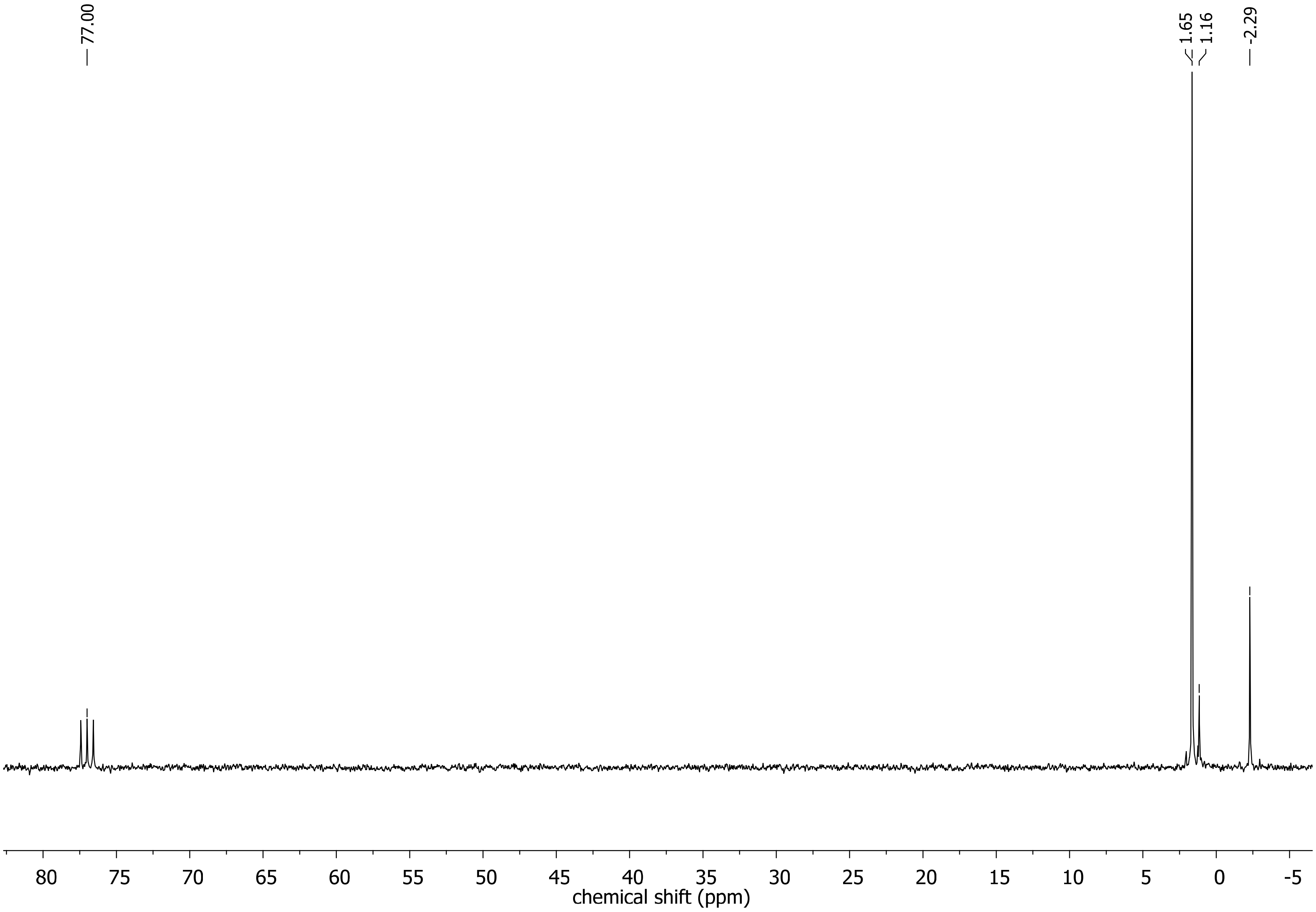
(400 MHz, $CDCl_3$)



^{13}C NMR

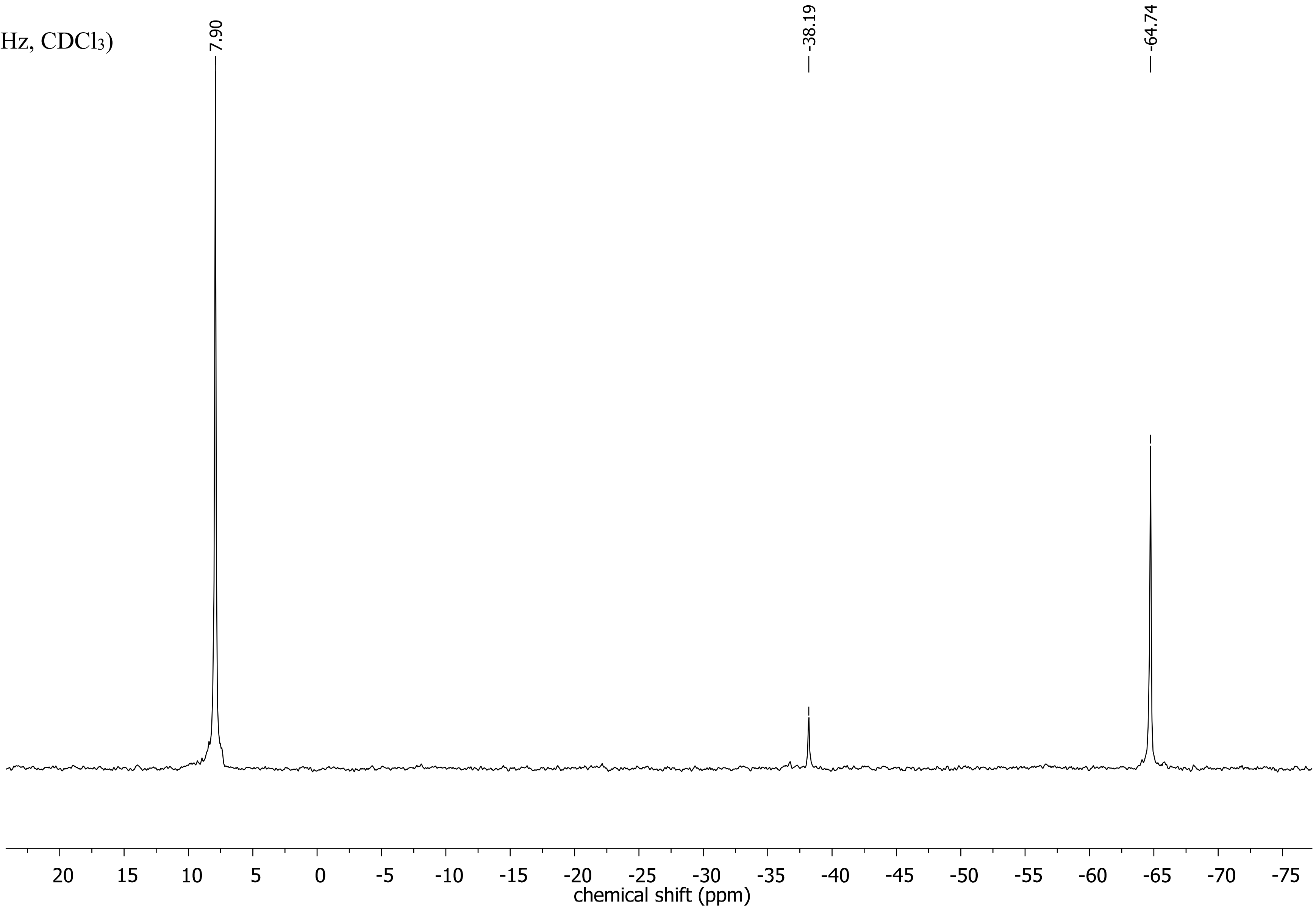
(100 MHz, $CDCl_3$)

110



^{29}Si NMR

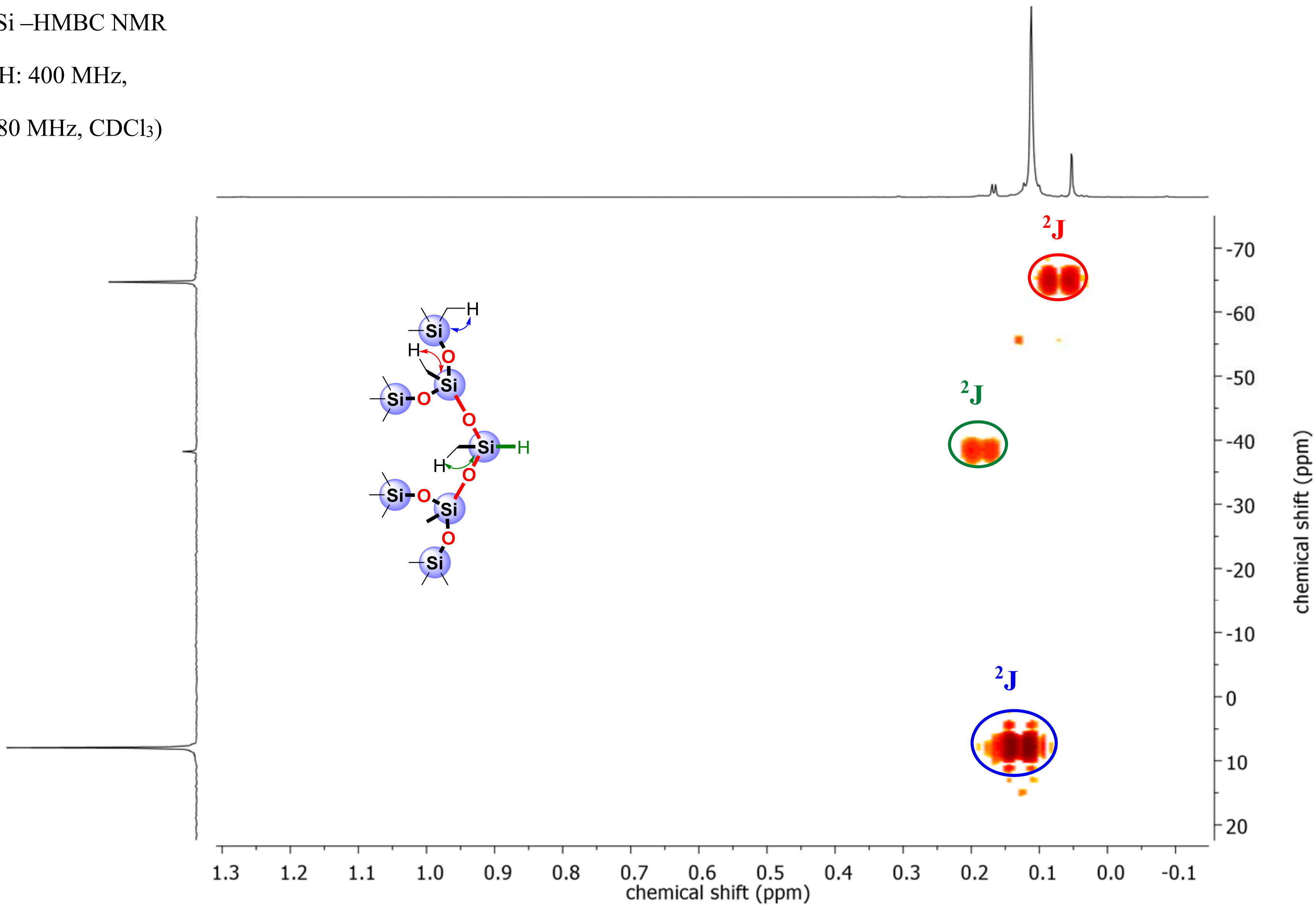
(80 MHz, $CDCl_3$)



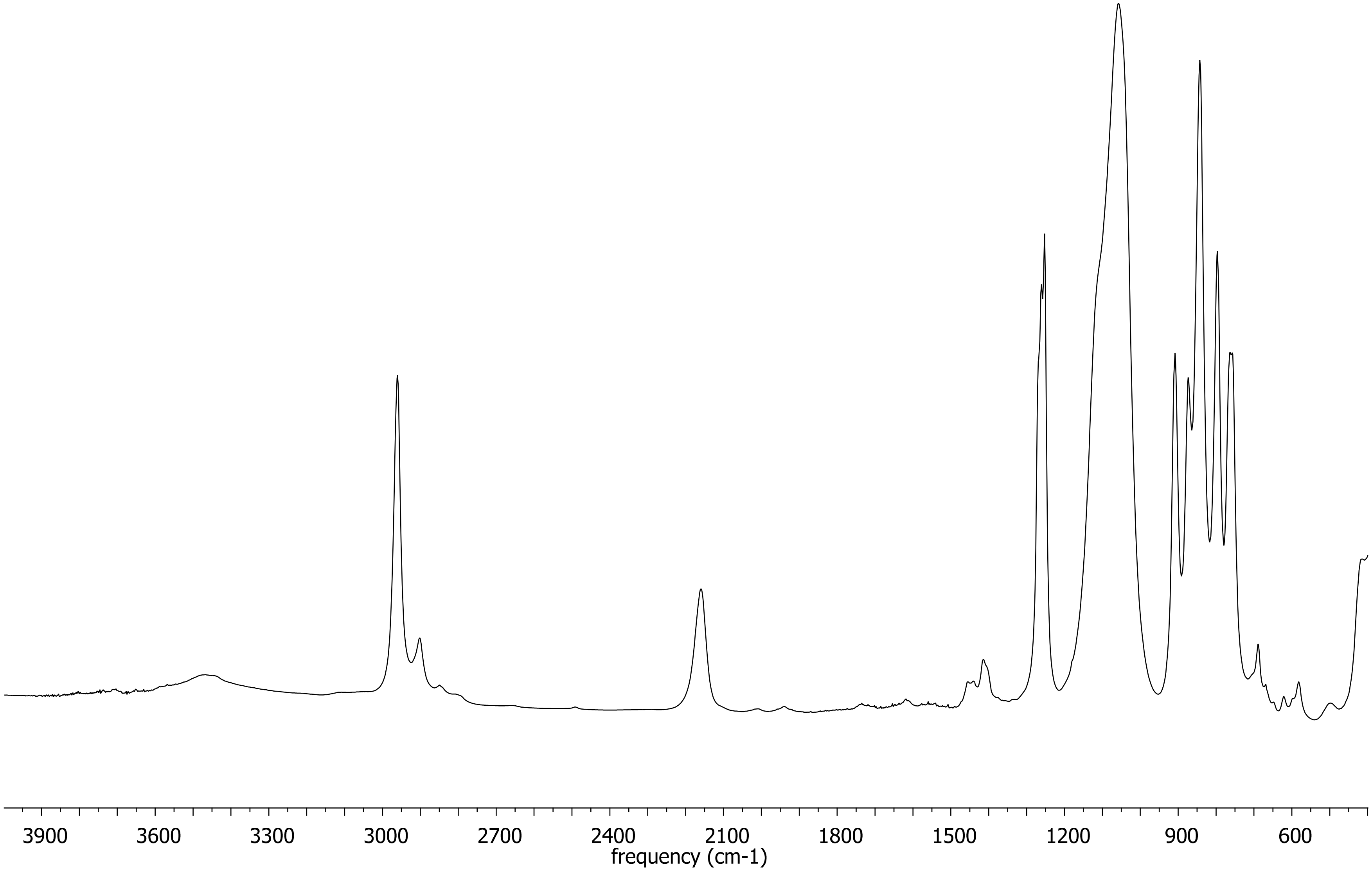
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

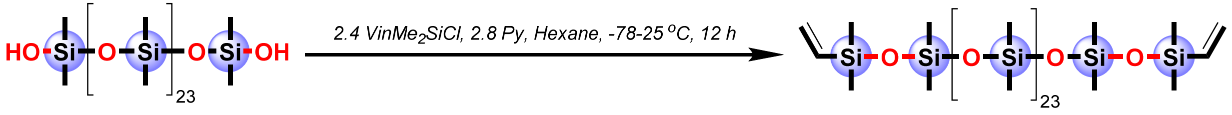
^{29}Si: 80 MHz, $CDCl_3$)



IR spectrum


3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

13.2. Method for 2h silylation



2h **4h**

A solution of **2h** (0.5 g, 0.268 mmol, 1 eq.) in hexane (3.5 mL) was dropwise added (up to 5 min) to a solution of pyridine (0.059 g, 0.75 mmol, 2.8 eq) and $VinMe_2SiH$ (0.077 g, 0.643 mmol, 2.4 eq.) in hexane (1.5 mL) under Ar at -78 ºC under stirring. Then the reaction mass was slowly heated to 25ºC and stirred for 12 – 15 hours. Next hexane (15 mL) was added and this mixture was washed with water (3×15 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **4h** was obtained as a liquid. The separated yield was 72% (0.392 g).

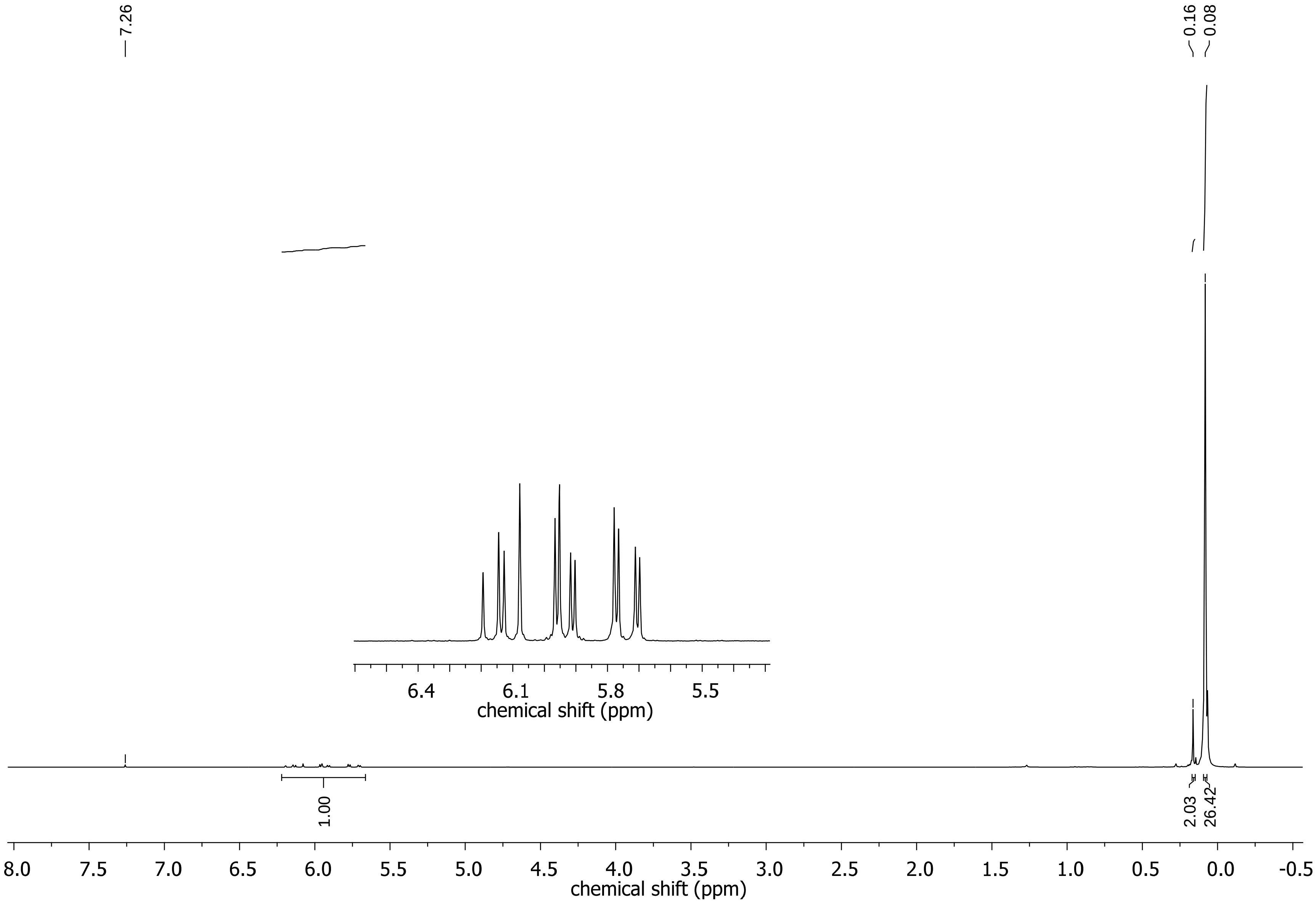
The length (a degree of polymerization) of the macromolecule after silylation was calculated as a ratio of signal integral intensities of terminal to internal CH_3-groups (^1H NMR).

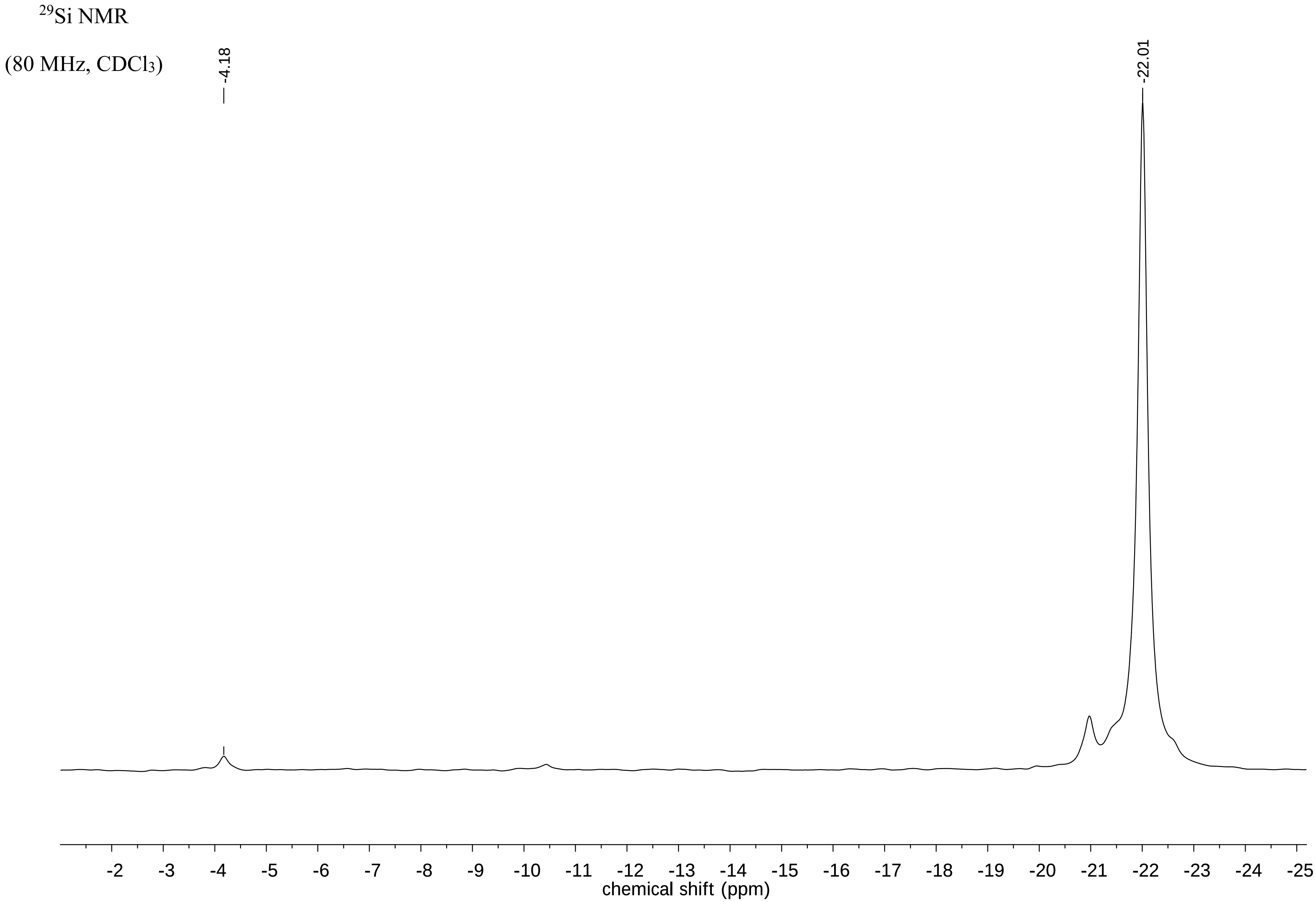
<u>Characterization data for **4h**:</u>

^1H NMR (400 MHz, $CDCl_3$): δ = 0.08 (br, 173H); 0.16 (br, 12H); 5.67-6.20 (m, 6H). ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -23.0 – -22.01; -10.43; -4.18; IR (cm^{-1}): 2963; 1261; 1093; 1023. GPC (500A): M_w (pss) = 4920; M_n (pss) = 3076; PDI = 1.60.

^{1}H NMR

(400 MHz, $CDCl_3$)

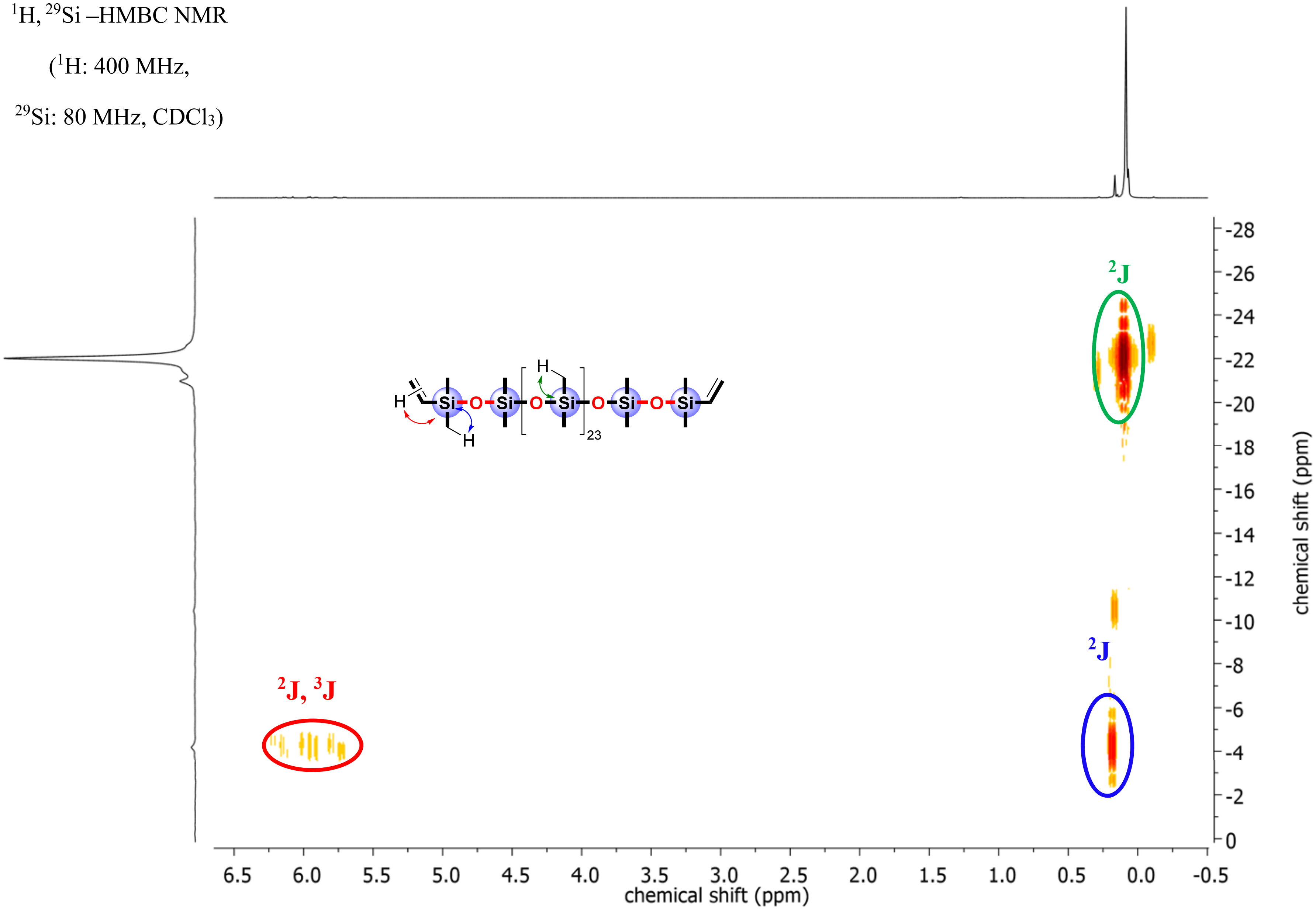



^{29}Si NMR
(80 MHz, CDCl$_3$)
-4.18
-22.01
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
chemical shift (ppm)

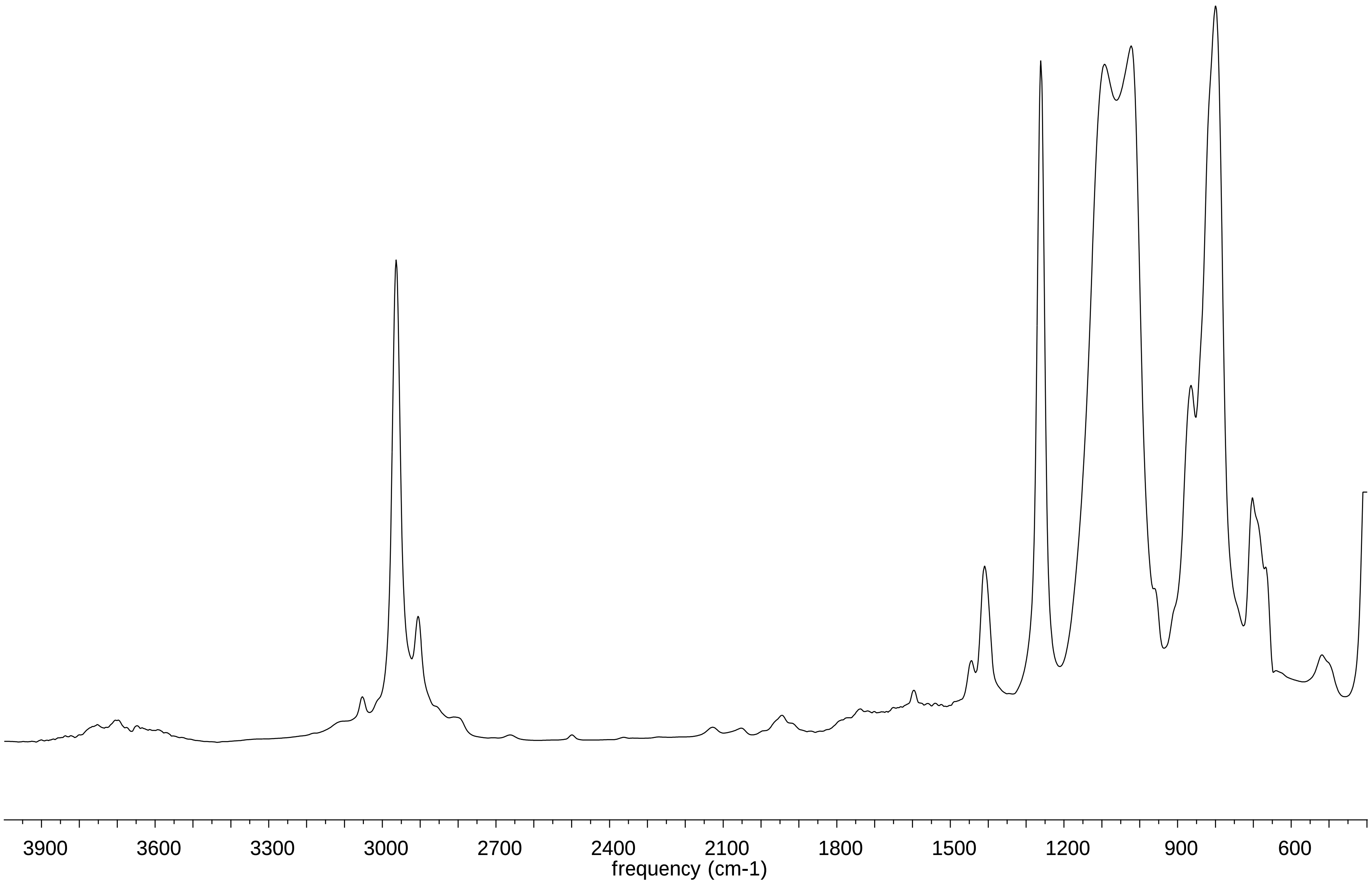
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)

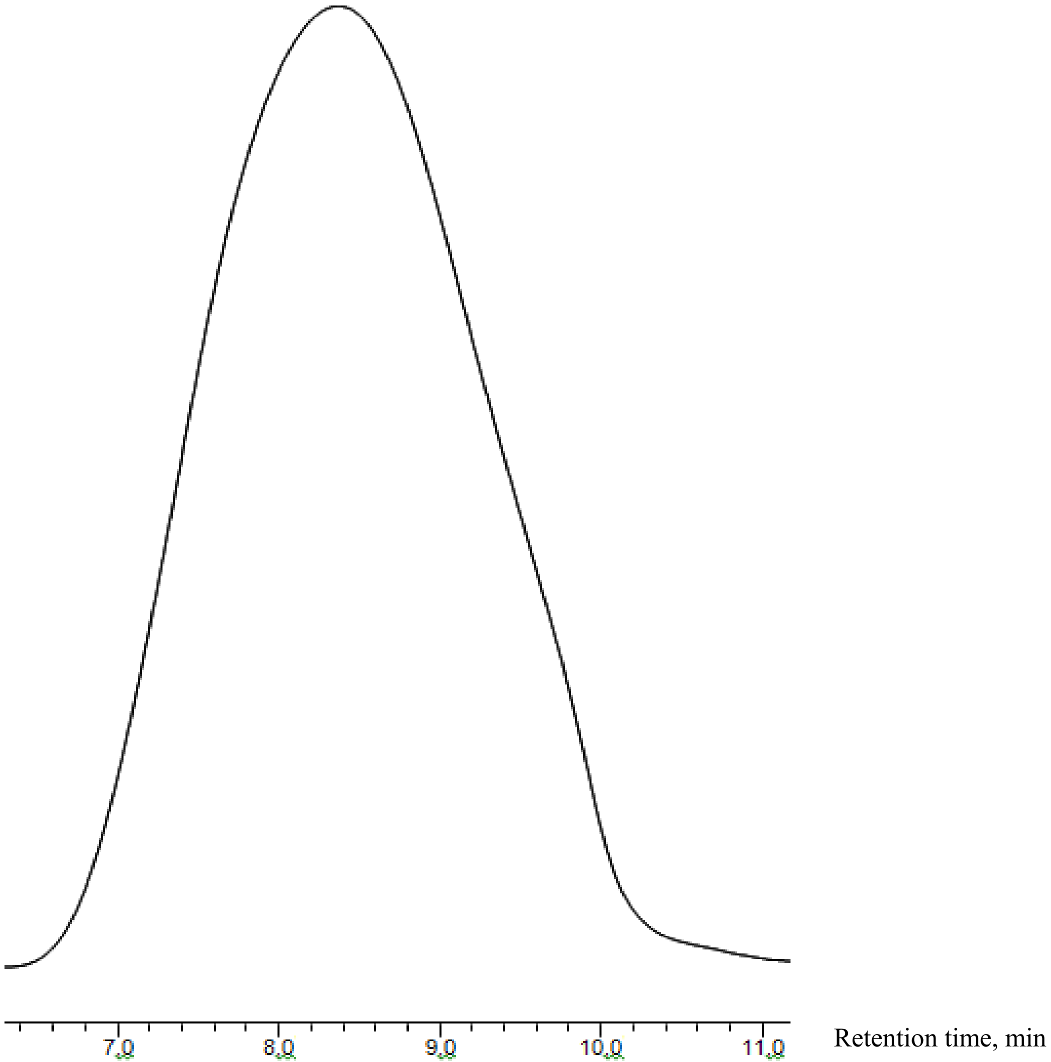


IR spectrum


3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

GPC curve

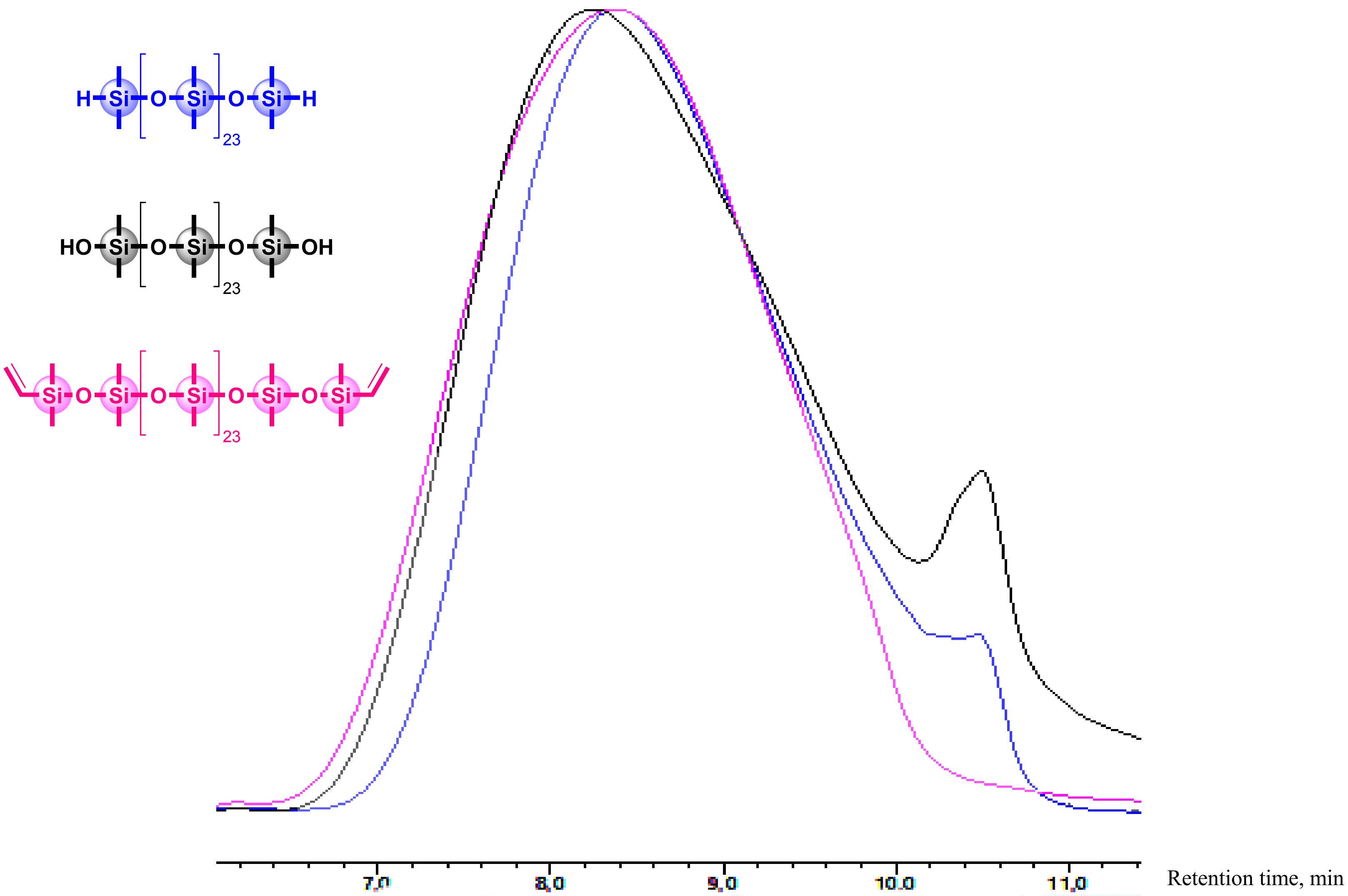
500A



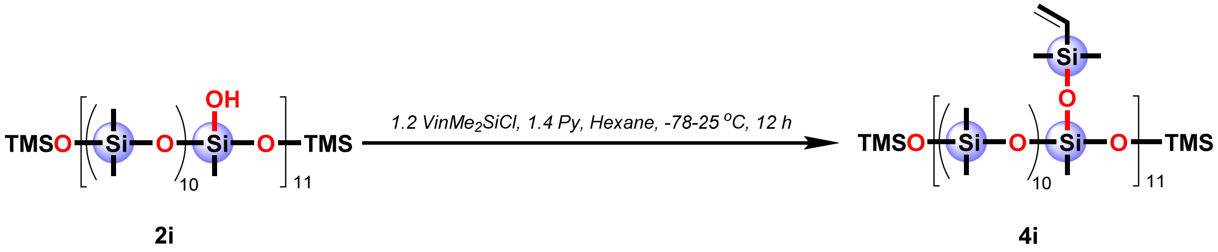
M_w (pss) = 4920;
M_n (pss) = 3076;
PDI (pss) = 1.60.

GPC comparison

500A



13.3. Method for 2i silylation



A solution of **2i** (0.5 g, 0.613 mmol, 1eq.) in hexane (3.5 mL) was dropwise added (up to 5 min) to a solution of pyridine (0.068 g, 0.86 mmol, 1.4 eq) and $VinMe_2SiCl$ (0.089 g, 0.73 mmol, 1.2 eq.) in hexane (1.5 mL) under Ar at -78 °C under stirring. Then the reaction mass was slowly heated to 25°C and stirred for 12 – 15 hours. Next hexane (15 mL) was added and this mixture was washed with water (3×10 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **4i** was obtained as a liquid. The separated yield was 73% (0.405 g).

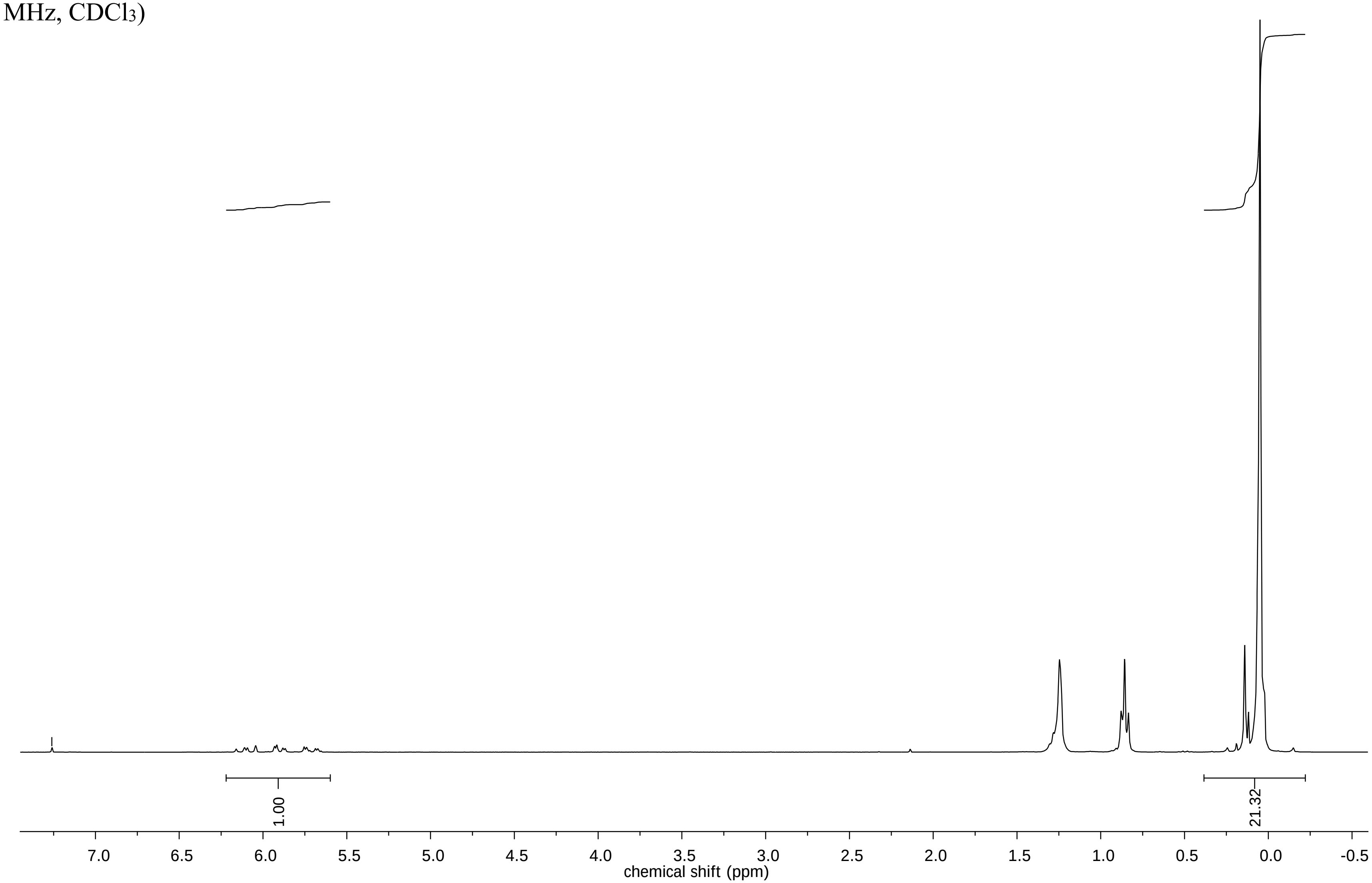
«n» in $[(Me_2SiO)_nMe\textbf{\textit{SiOSiMe}}_{\textbf{\textit{2}}}\textbf{\textit{Vin}}]$-block was determined as a ratio of signal integral intensities of $Me\textbf{\textit{SiOSiMe}}_{\textbf{\textit{2}}}\textbf{\textit{Vin}}$**-** to Me_2Si-groups (^1H NMR).

Characterization data for **4h**:

^1H NMR (400 MHz, $CDCl_3$): δ = 0–0.2 (br, 64H); 5.60–6.20 (m, 3H). ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -66.28; -20 – -22.2 ; -3.83; 7.17 IR (cm^{-1}): 2964; 1261; 1092; 1022. GPC (1000A): M_w (pss) = 14142, M_n (pss) = 4936, PDI = 2.86.

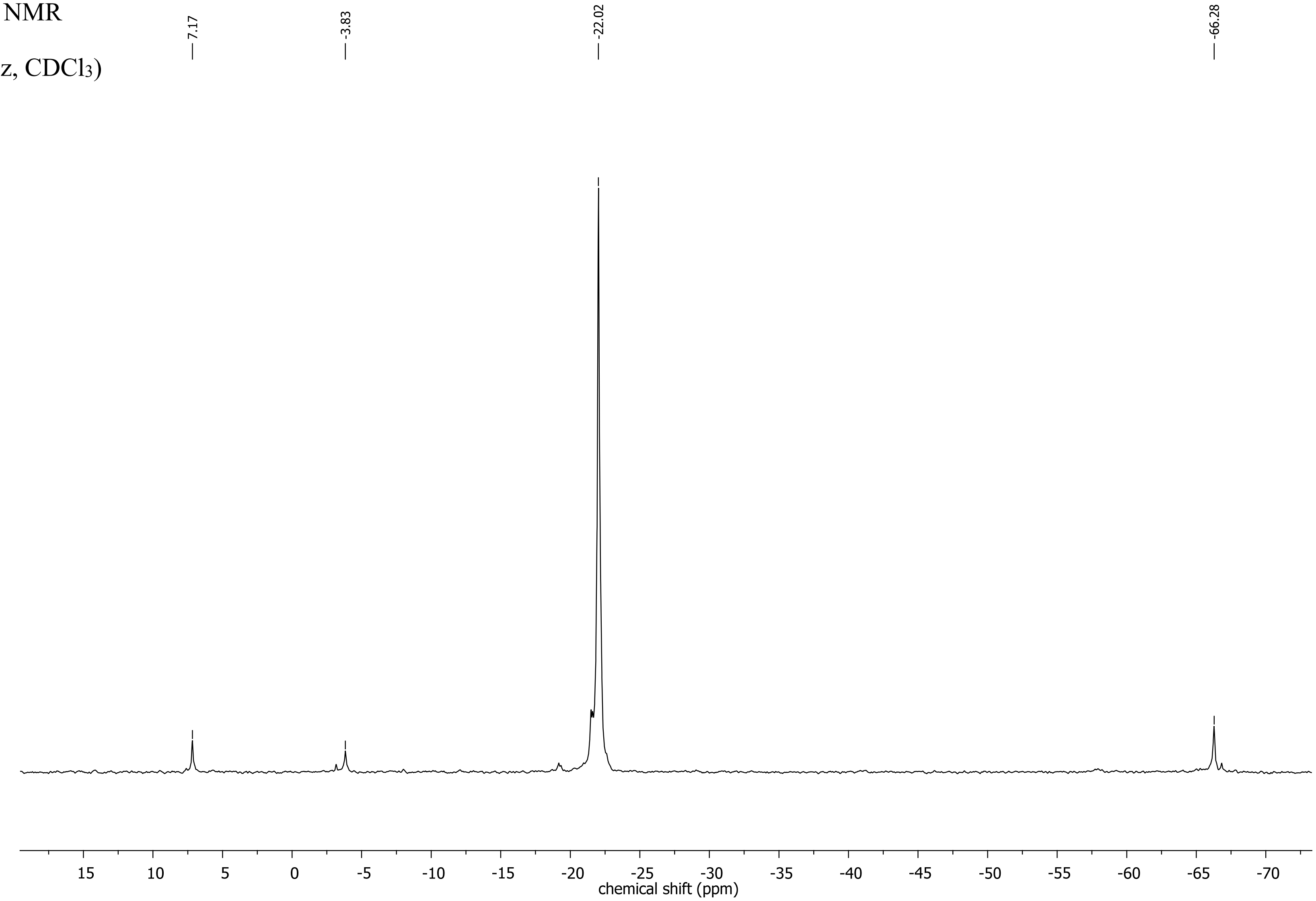
^1H NMR

(400 MHz, $CDCl_3$)



^{29}Si NMR

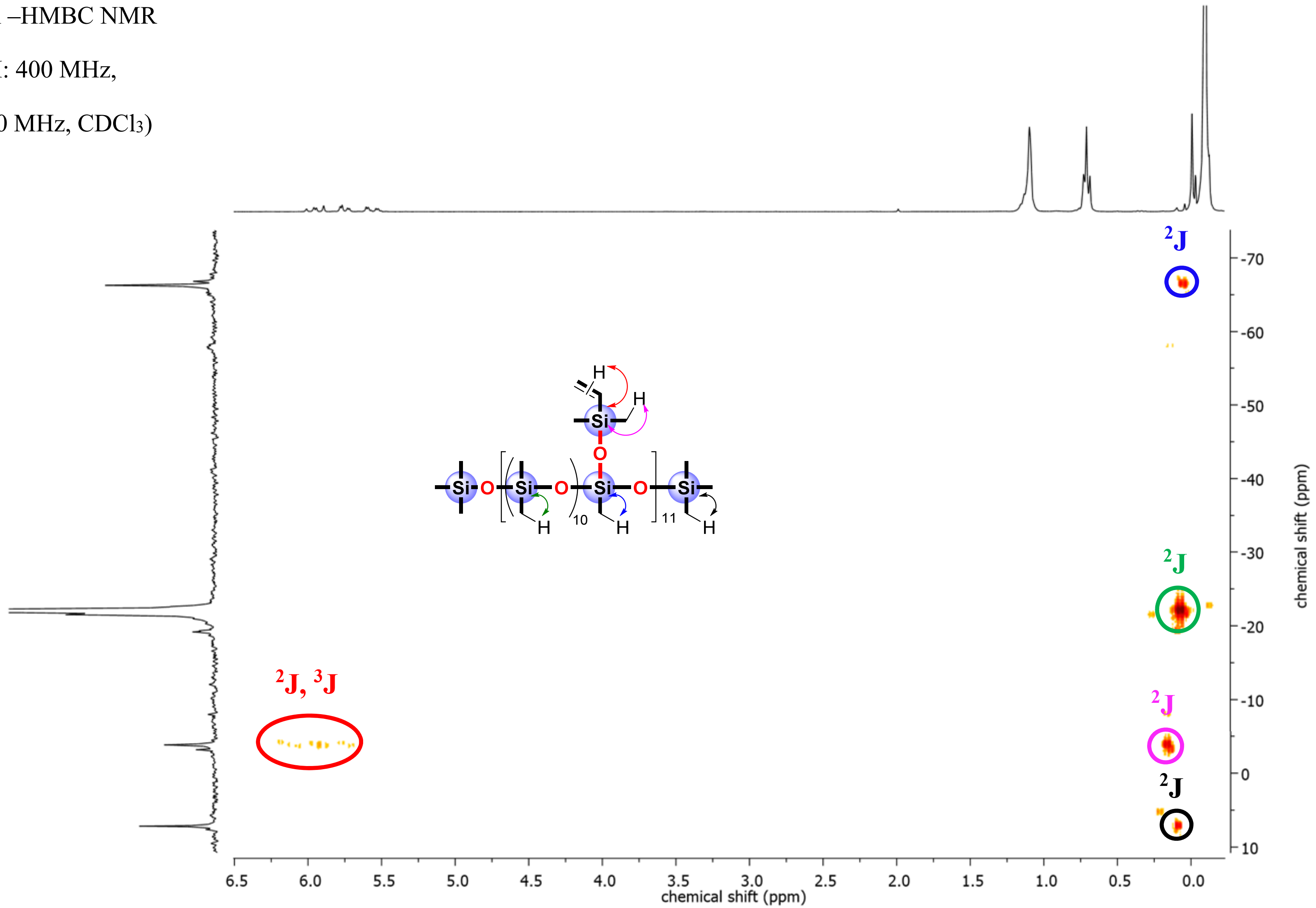
(80 MHz, $CDCl_3$)



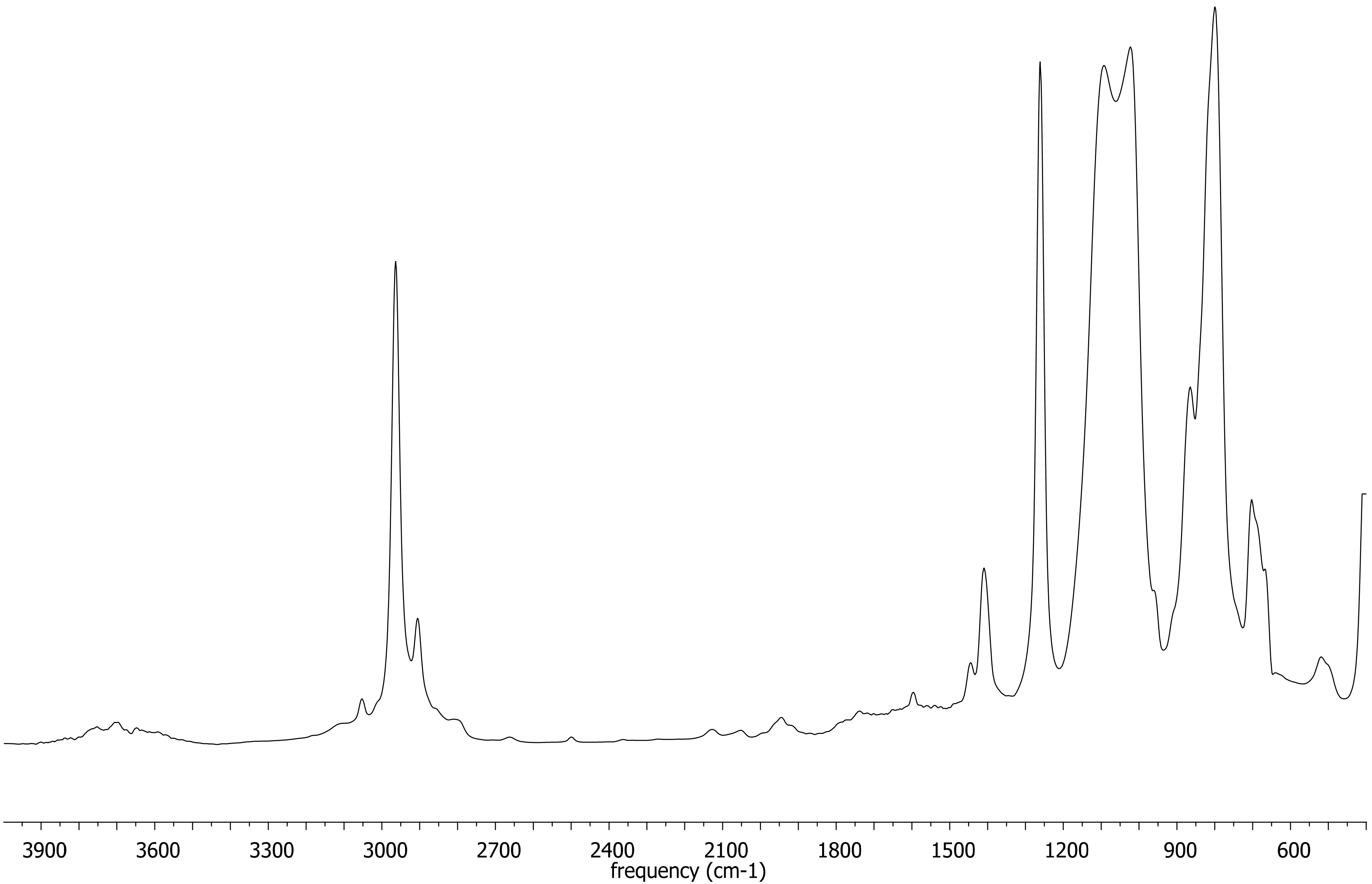
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)

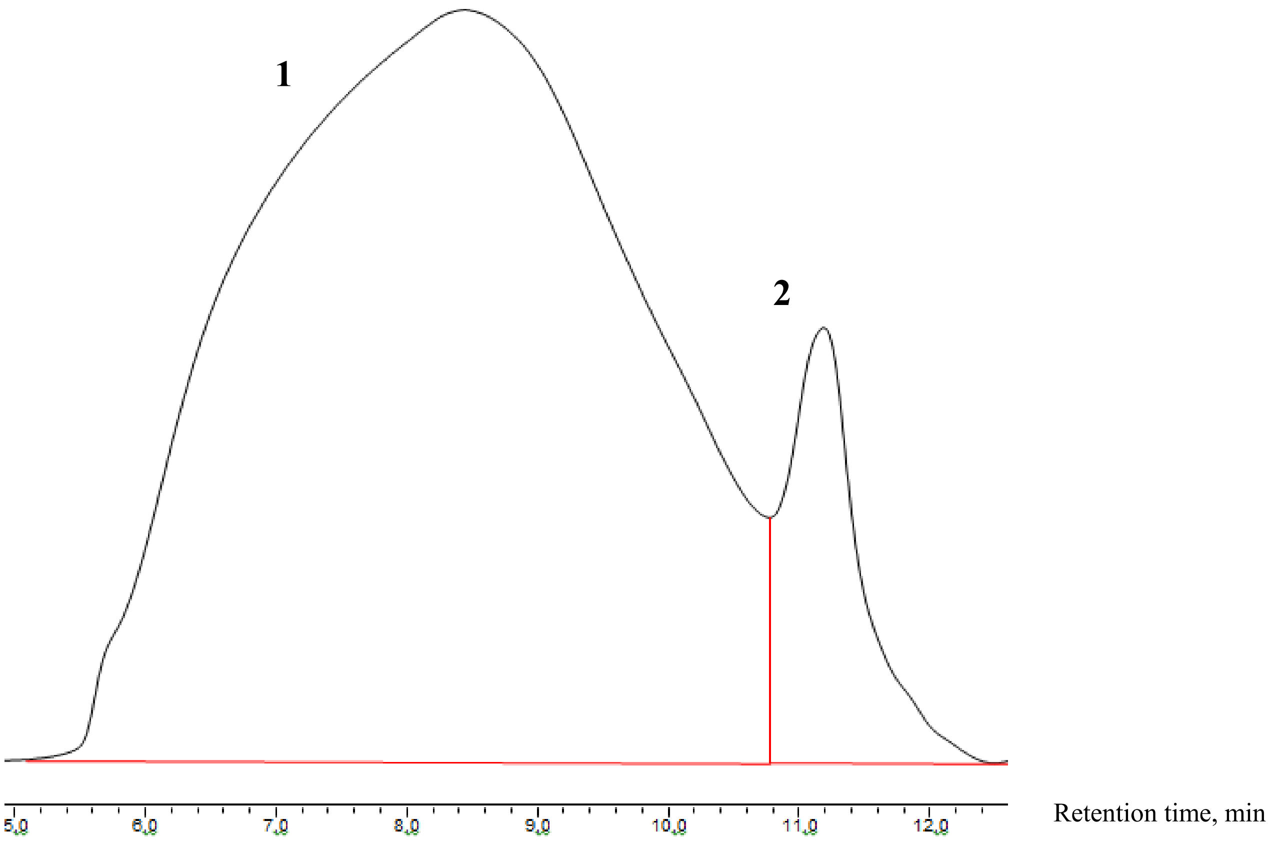


IR spectrum


3900
3600
3300
3000
2700
2400
2100
1800
1500
1200
900
600
frequency (cm-1)

GPC curve

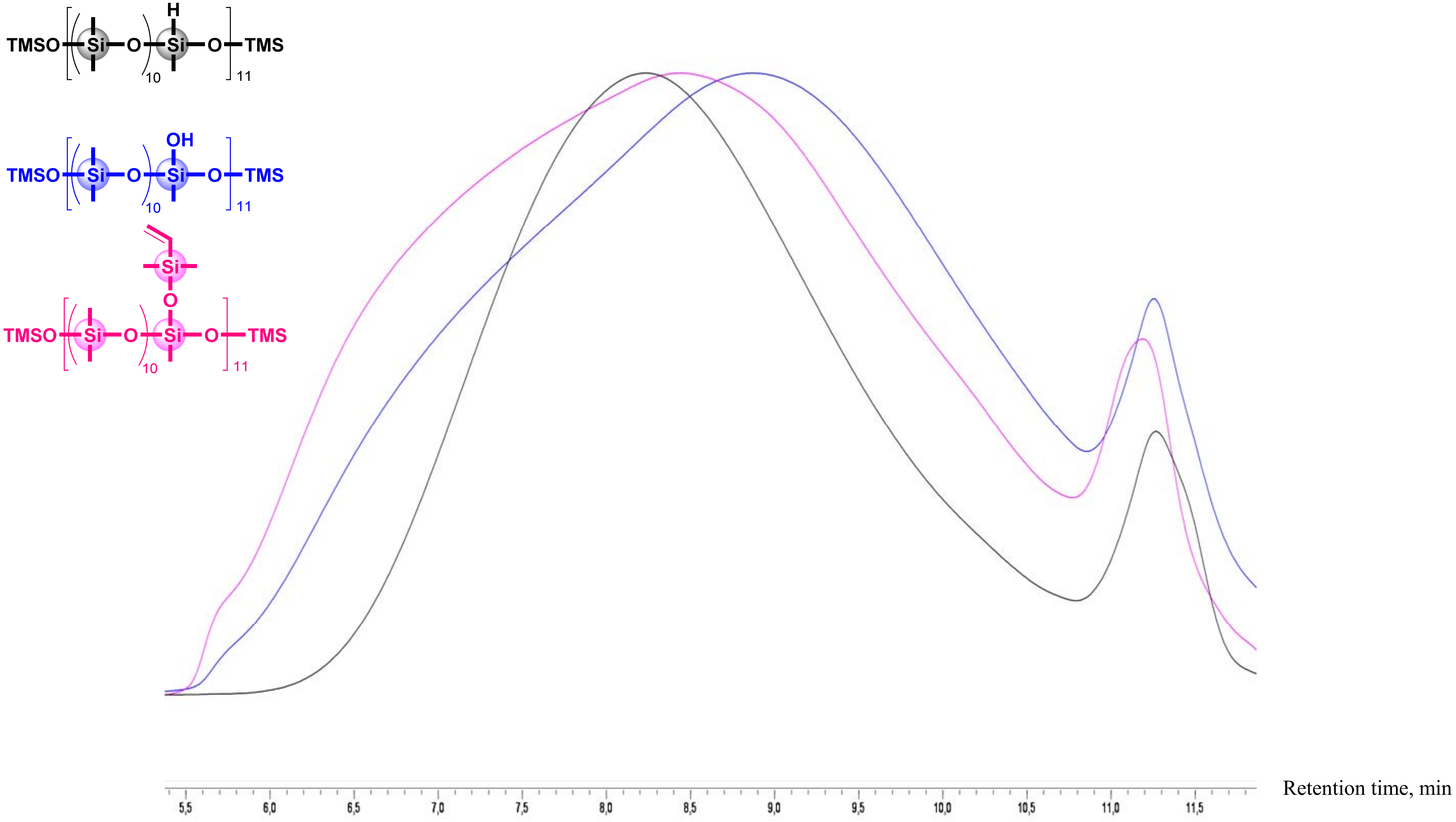
1000A



Peak 1. M_w (pss)= 14142,
M_n (pss) = 4936,
PDI = 2.86

GPC comparison

1000A



13.4. Method for 2j silylation

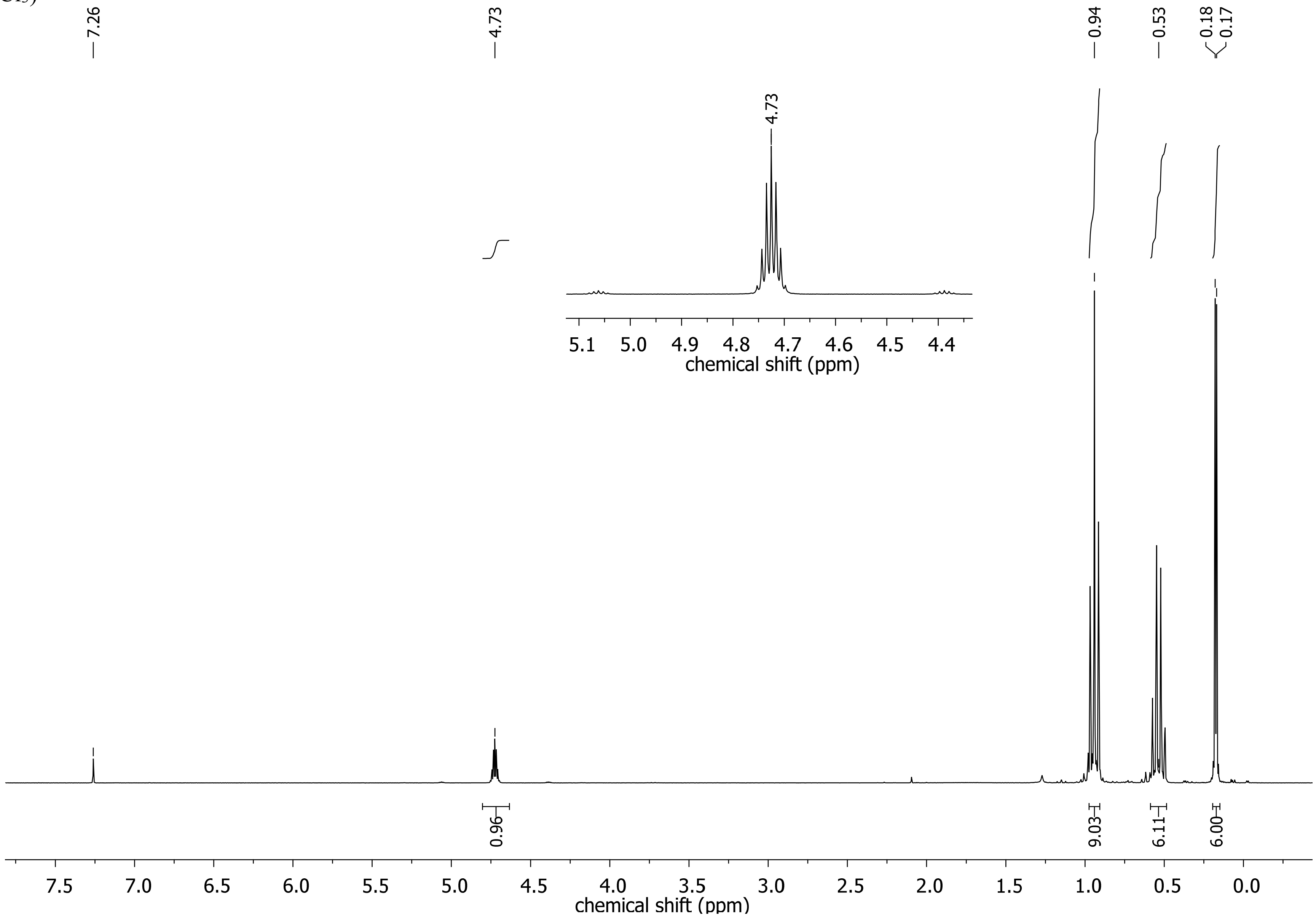
Step 1. **1j** (9.44 g, 81.2 mmol, 1 eq.), NHPI (2.65 g, 16.24 mmol, 0.2 eq.), $Co(OAc)_2 \times 4H_2O$ (0.20 g, 0.81 µmol, 0.01 eq.) and MeCN (180 mL) were stirred in a 2000 mL round bottomed flask at 25 °C for 8 h under the oxygen static atmosphere. Then MeCN was evaporated (190-200 mbar, T_{bath} = 40 °C). The yield of **2j** was 87 – 90% (determined by GLC).
Step 2. Hexane (80 mL) was added to reaction mixture. A solution of pyridine (8.99 g, 113.68 mmol, 1.4 eq.) in hexane (15 mL) and a solution of Me_2SiHCl (11.76 g, 97.44 mmol, 1.2 eq.) in hexane (15 mL) were synchronously dropwise added (up to 5 min) under Ar at -78 °C under stirring. Then it was slowly heated to 25^{o}C and stirred for 12 – 15 hours. Next hexane (300 mL) was added and this mixture was washed with water (3×200 mL). The organic fraction was dried over Na_2SO_4 and filtered. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **1b** was obtained as a liquid. The separated yield was 35% (5.44 g).

Characterization data for 1,1,1-triethyl-3,3-dimethyldisiloxane (**1b**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (d, J = 4.0 Hz, 6H); 0.53 (q, J = 10.8 Hz, 6H); 0.94 (t, J = 10.8 Hz, 9H); 4.73 (m, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.94; 6.11; 6.65. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -7.06; 11.81. IR (cm^{-1}): 2957; 2118; 1252; 1069.

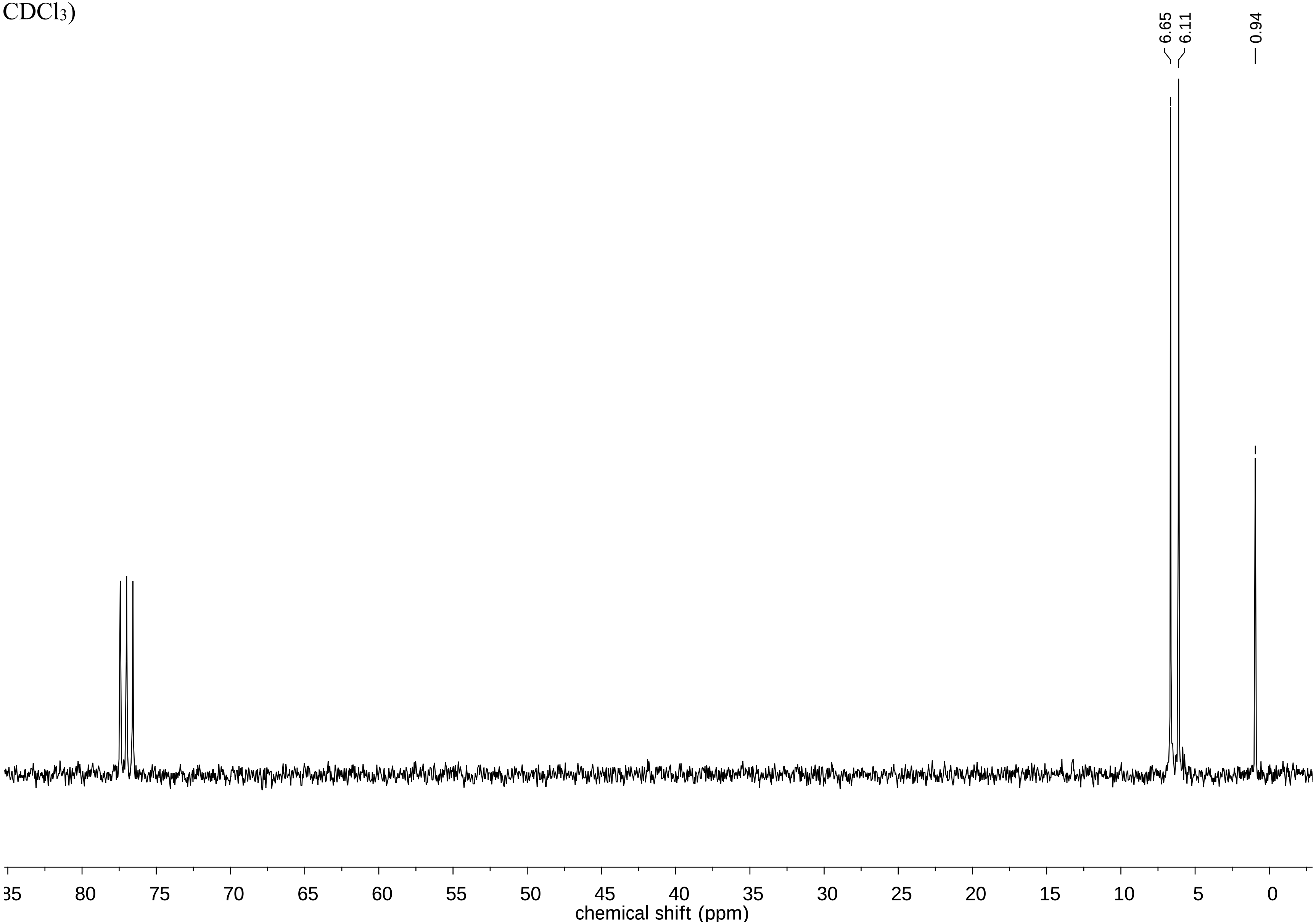
^{1}H NMR

(400 MHz, $CDCl_3$)



^{13}C NMR

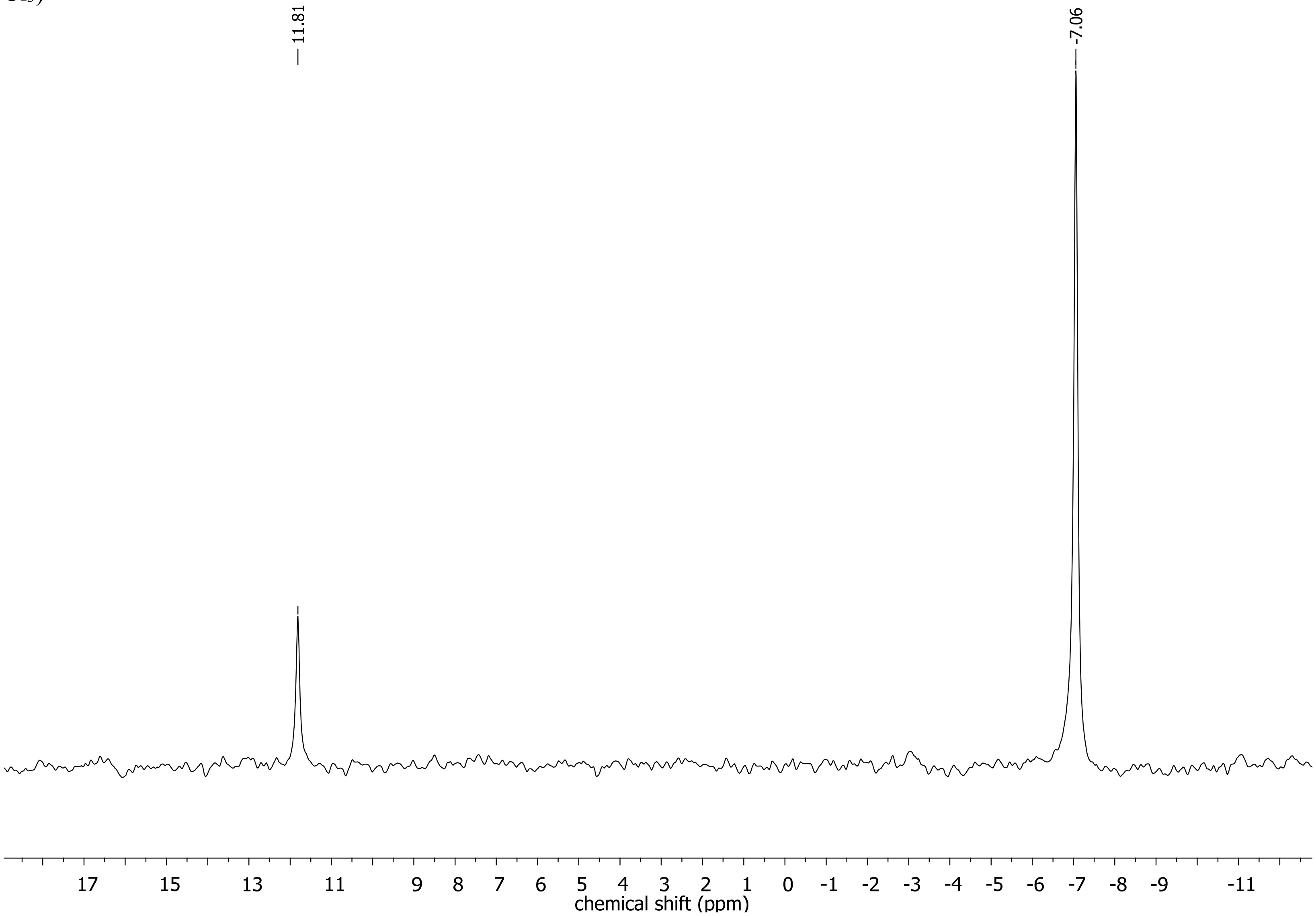
(100 MHz, $CDCl_3$)



^{29}Si NMR

(80 MHz, $CDCl_3$)

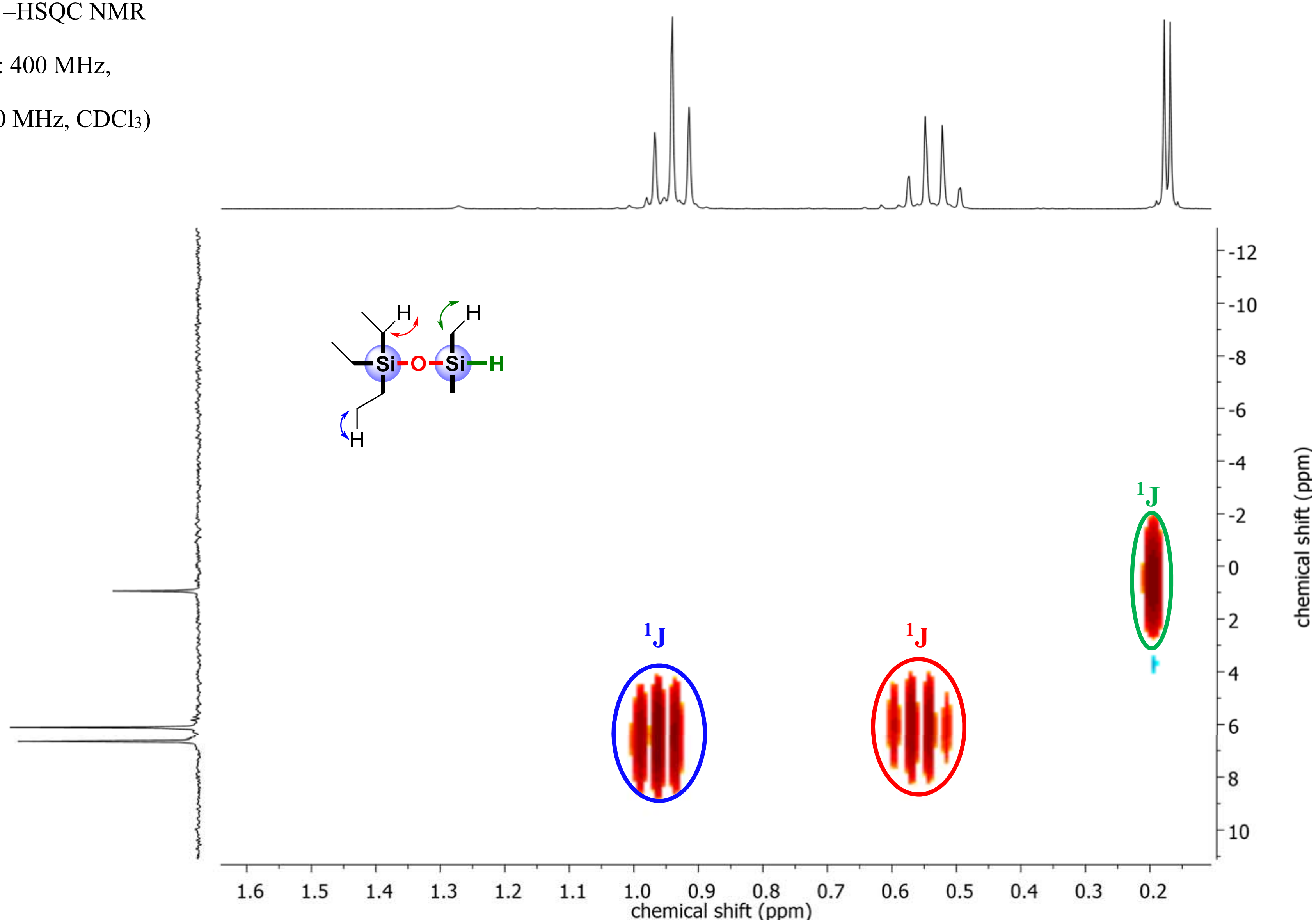
131



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

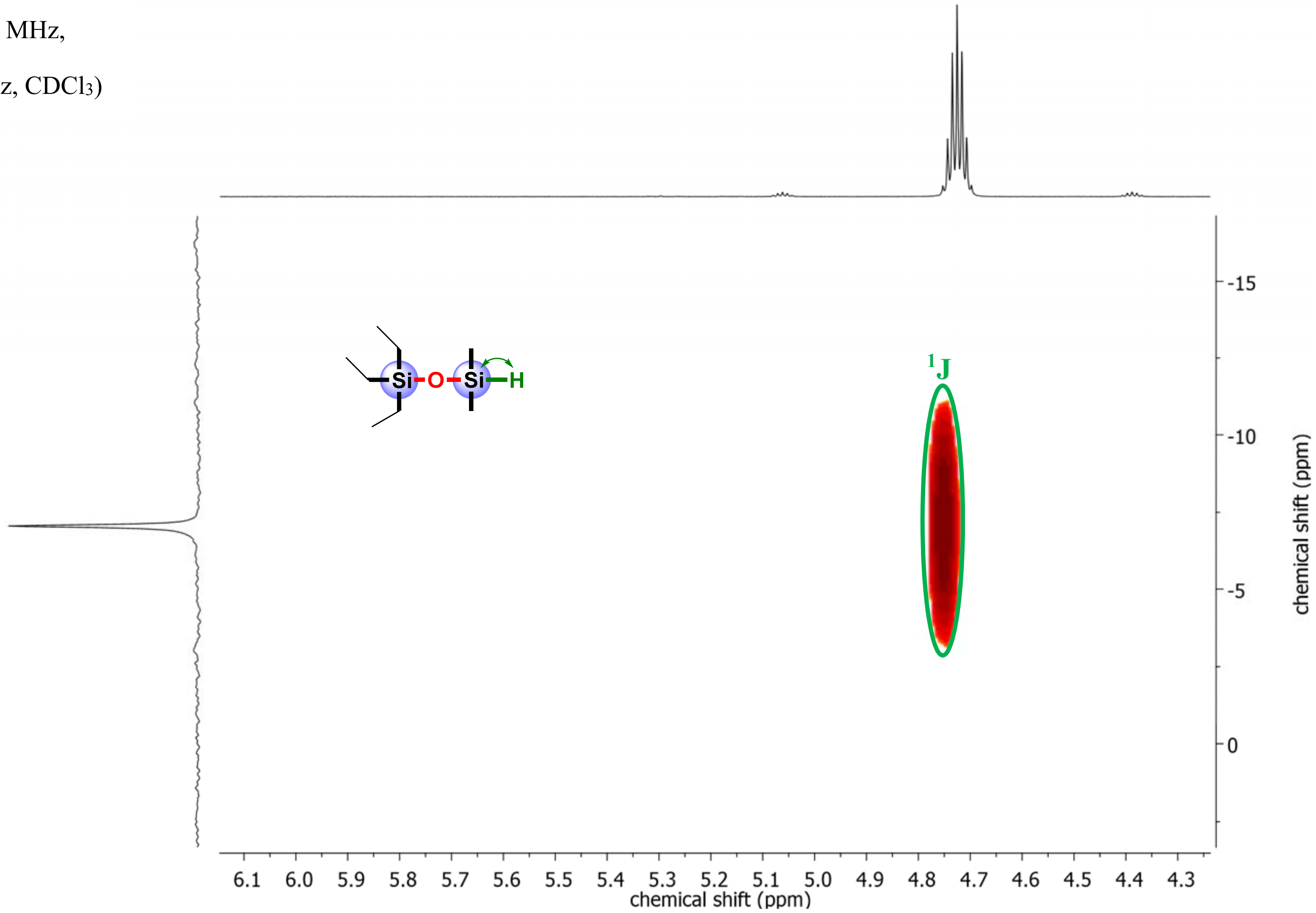
^{13}C: 100 MHz, CDCl$_3$)



^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

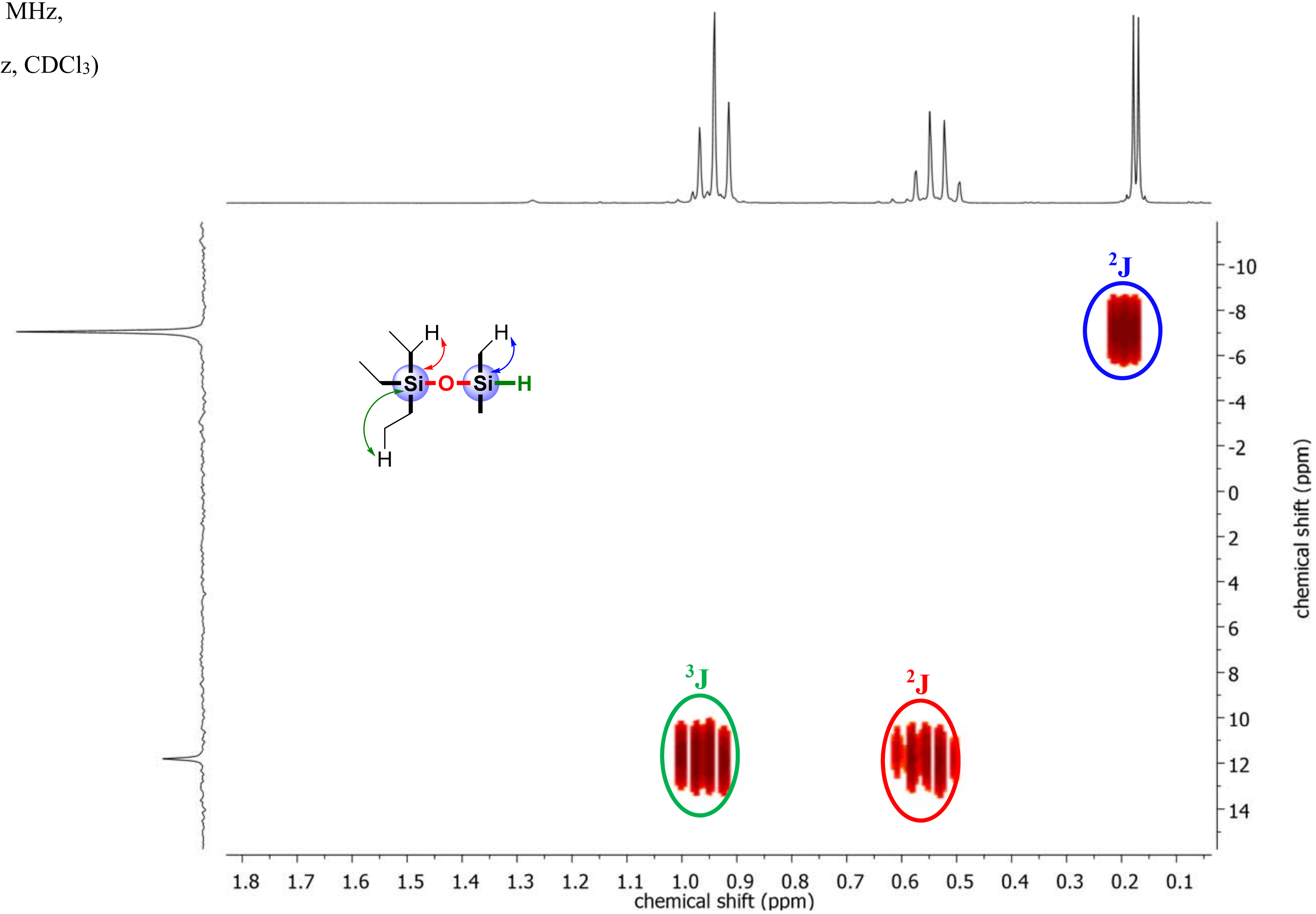
^{29}Si: 80 MHz, CDCl$_3$)



^{1}H, ^{29}Si –HMBC NMR

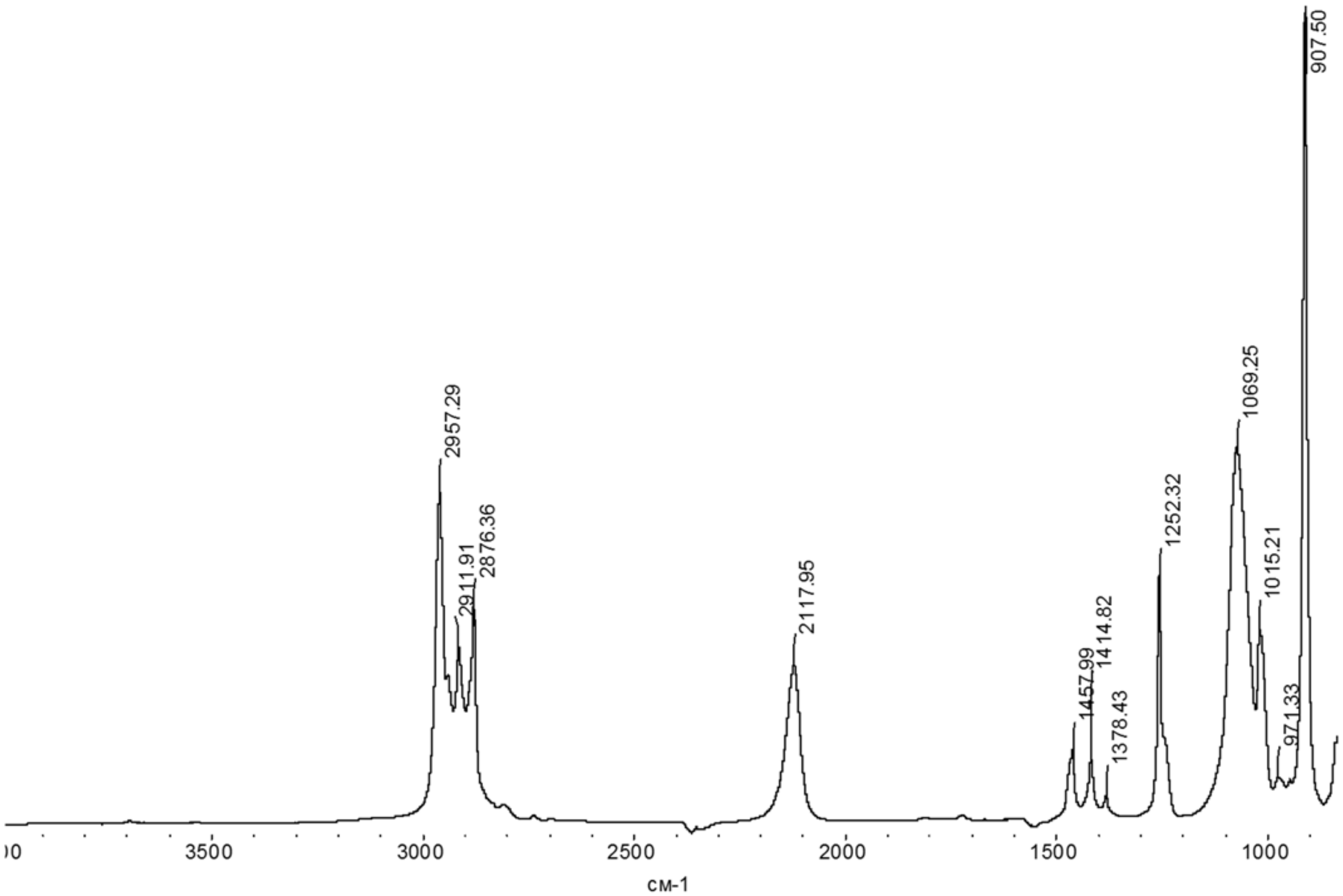
(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)



IR-spectrum

(CCl$_4$ solution)



14. Methods of synthesis and characterization data for 1d-i

14.1. Method of 1b synthesis

1b was obtained using optimized conditions by **1j** *in situ* silylation (see **13.4**).

14.2. Method of 1d synthesis

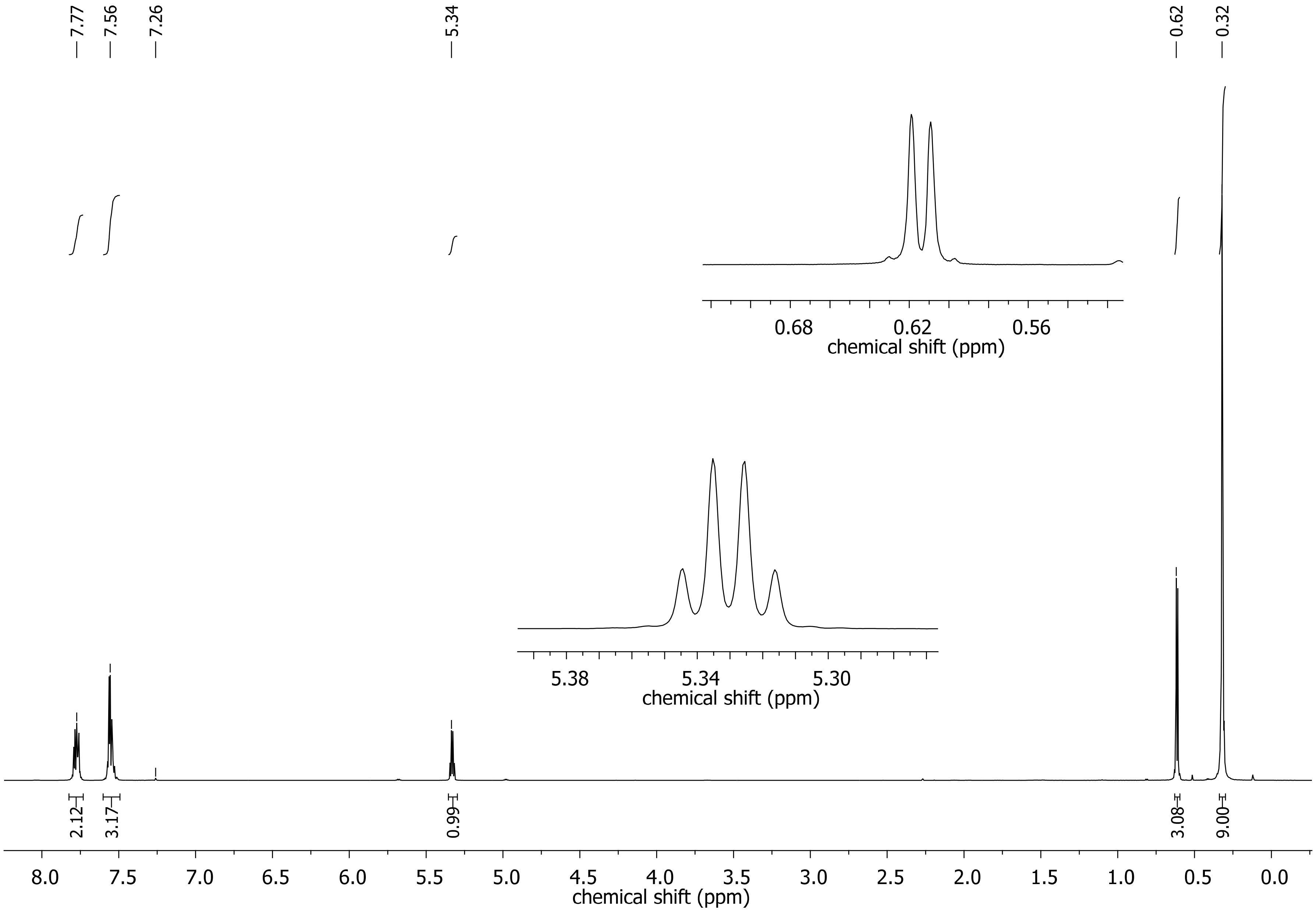
Chloro(methyl)phenylsilane (PhSiH(Me)Cl) (28.6 g, 0.18 mol, 1eq) was dropwise added to a solution of trimethylsilanol (21.0 g, 0.23 mol, 1.27 eq) and pyridine (17.3 g, 0.22 mol, 1.22 eq) in 200 ml of hexane at -70 ^{o}C. Then the mixture was slowly heated to 25 ^{o}C and stirred for 12 more hours. Then it it was filtered and washed with water to get rid of pyridine hydrochloride, and the solution was dried over Na_2SO_4. Then hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **1d** was obtained as colorless oil by distillation under reduced pressure (BP = 69-70 ^{0}C / 25 mbar). The separated yield was 74% (28.03 g).

Characterization data for 1,1,1,3-tetramethyl-3-phenyldisiloxane (**1d**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.32 (s, 9H); 0.62 (d, J = 4.0 Hz, 3H); 5.34 (q, J = 4.0 Hz, 1H); 7.56 (m, 3H); 7.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =-0.14; 1.81; 128.01; 129.87; 133.48; 138.08. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -14.66; 11.00. IR (cm^{-1}): 2959; 2124; 1255; 1056.

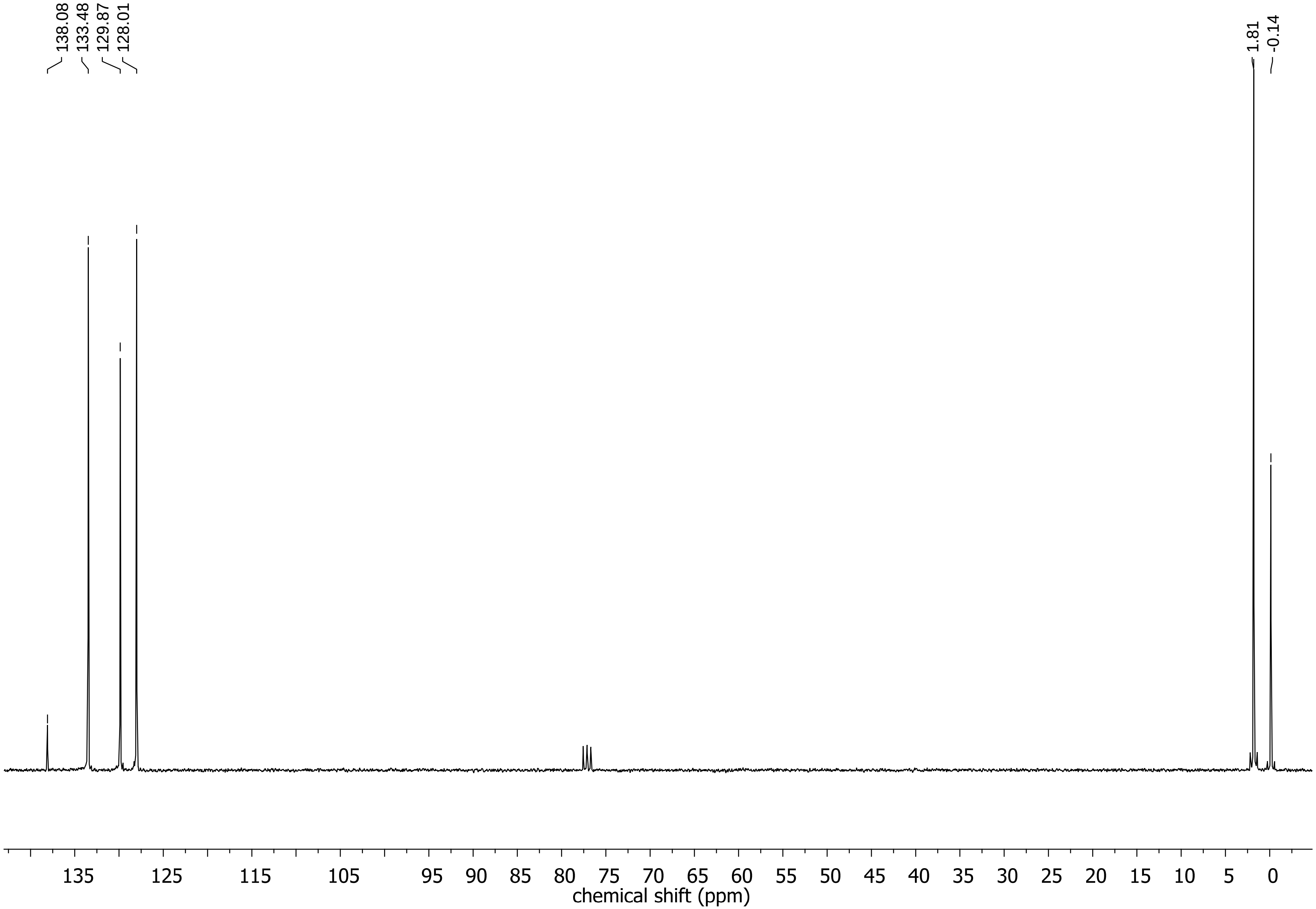
^{1}H NMR

(400 MHz, $CDCl_3$)



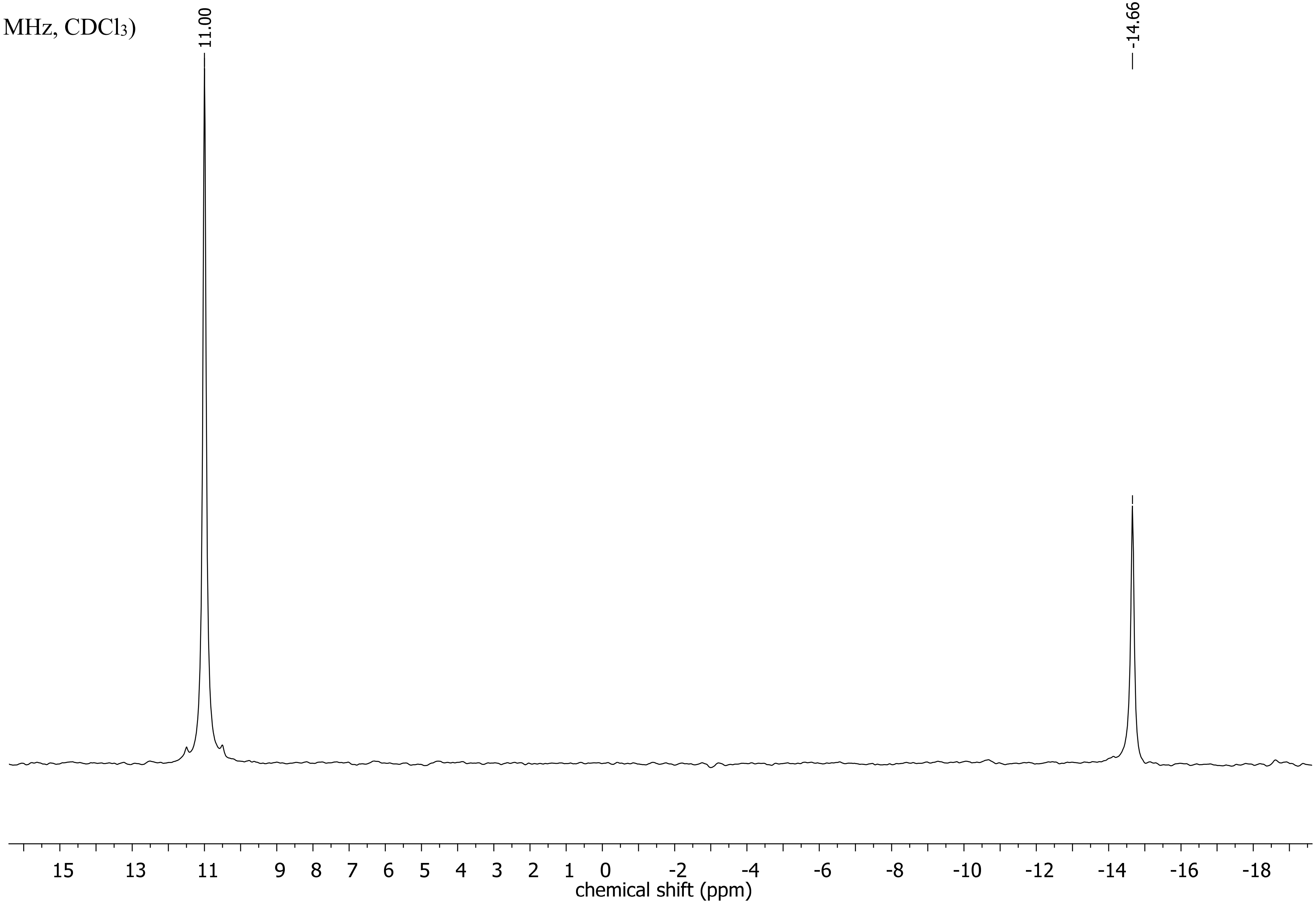
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

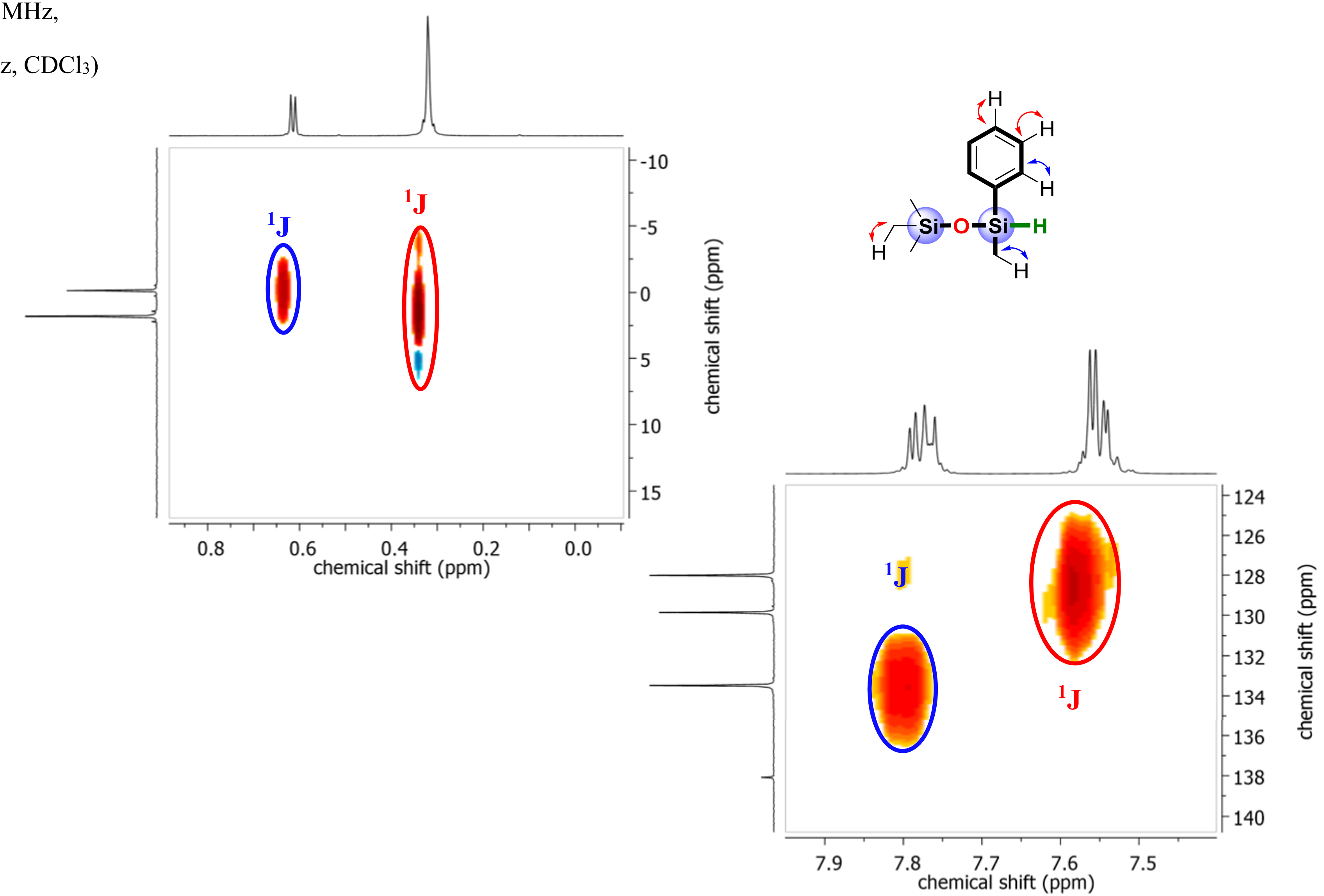
(80 MHz, $CDCl_3$)



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

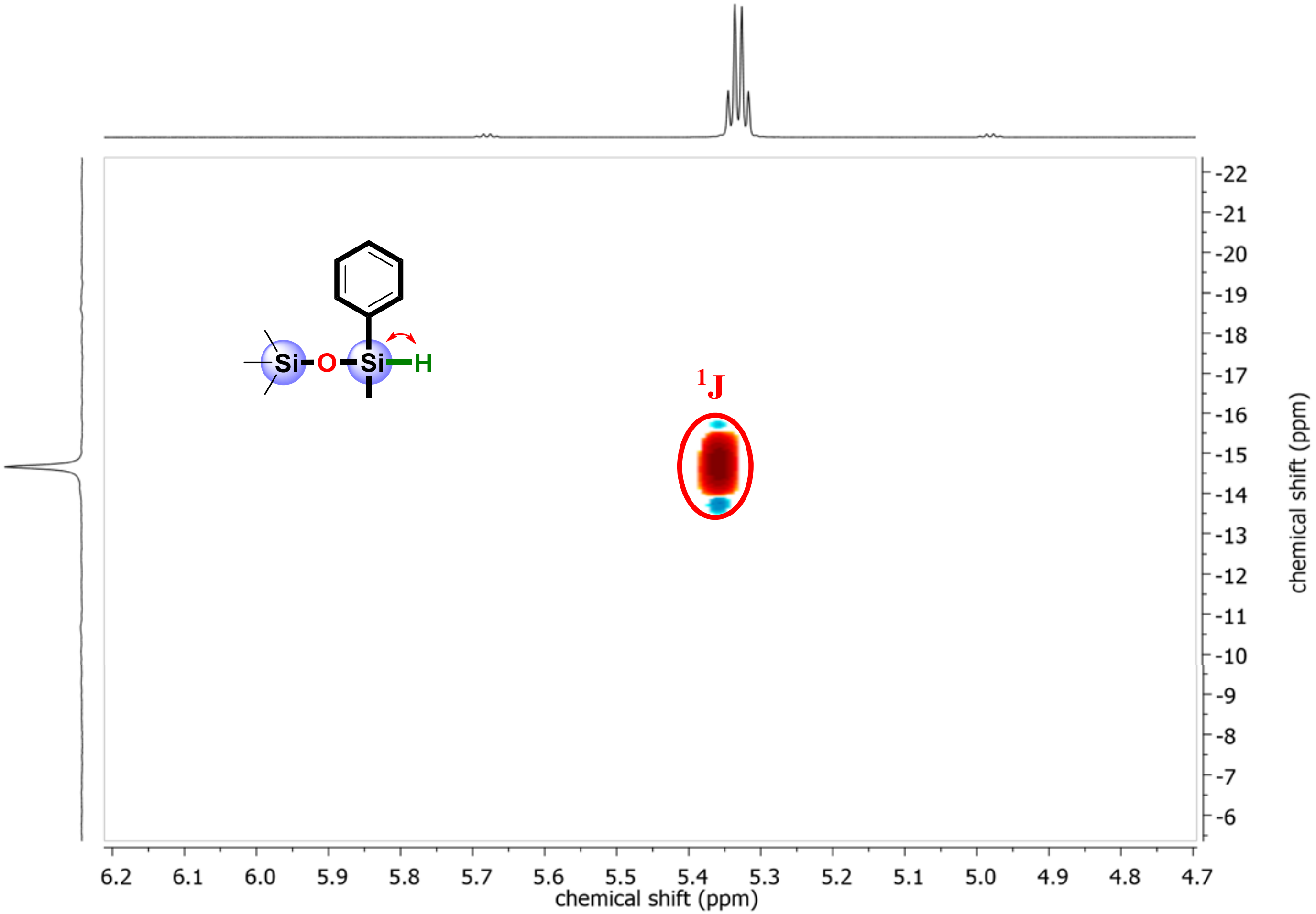
^{13}C: 100 MHz, CDCl$_3$)



^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

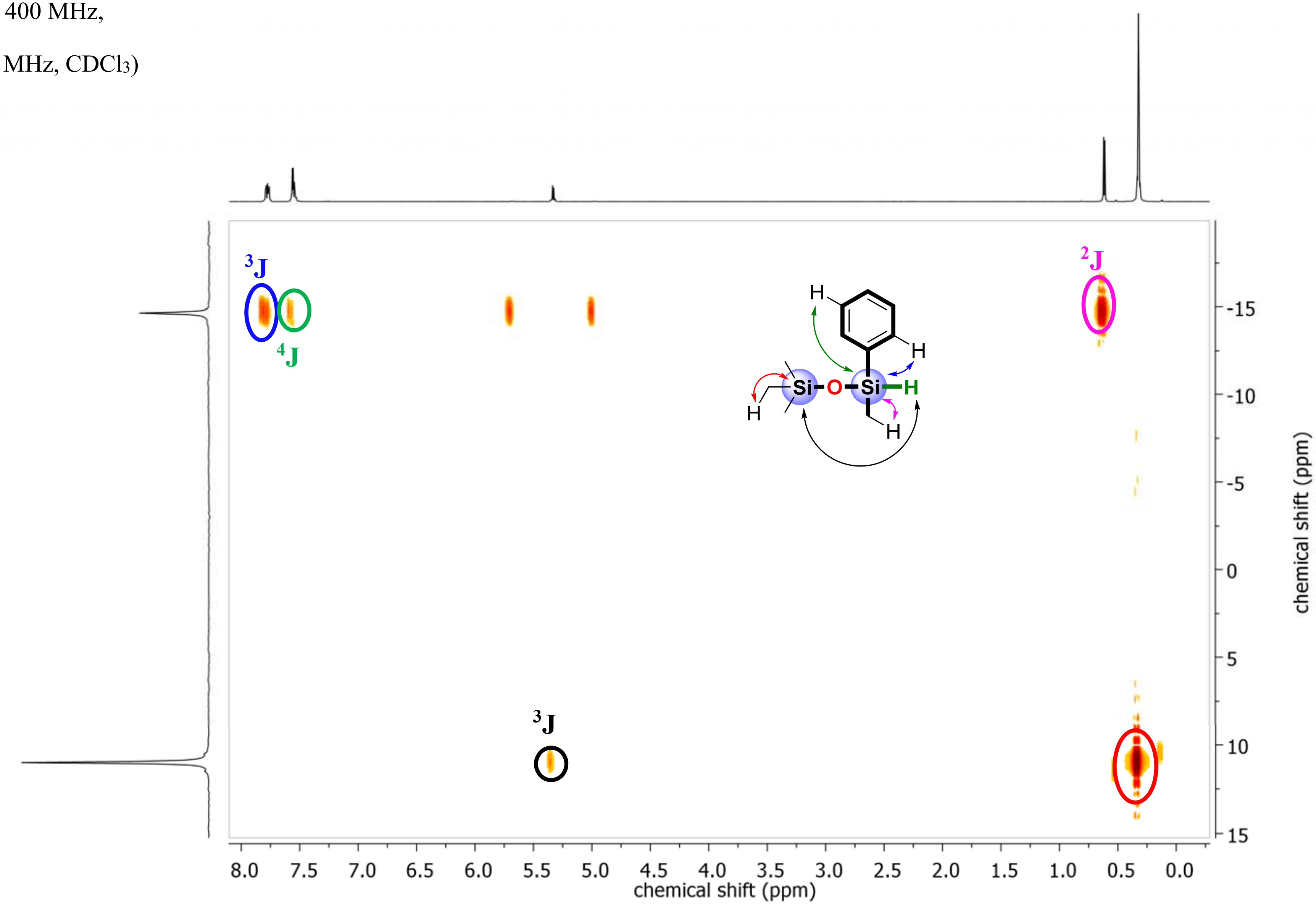
^{29}Si: 80 MHz, CDCl$_3$)



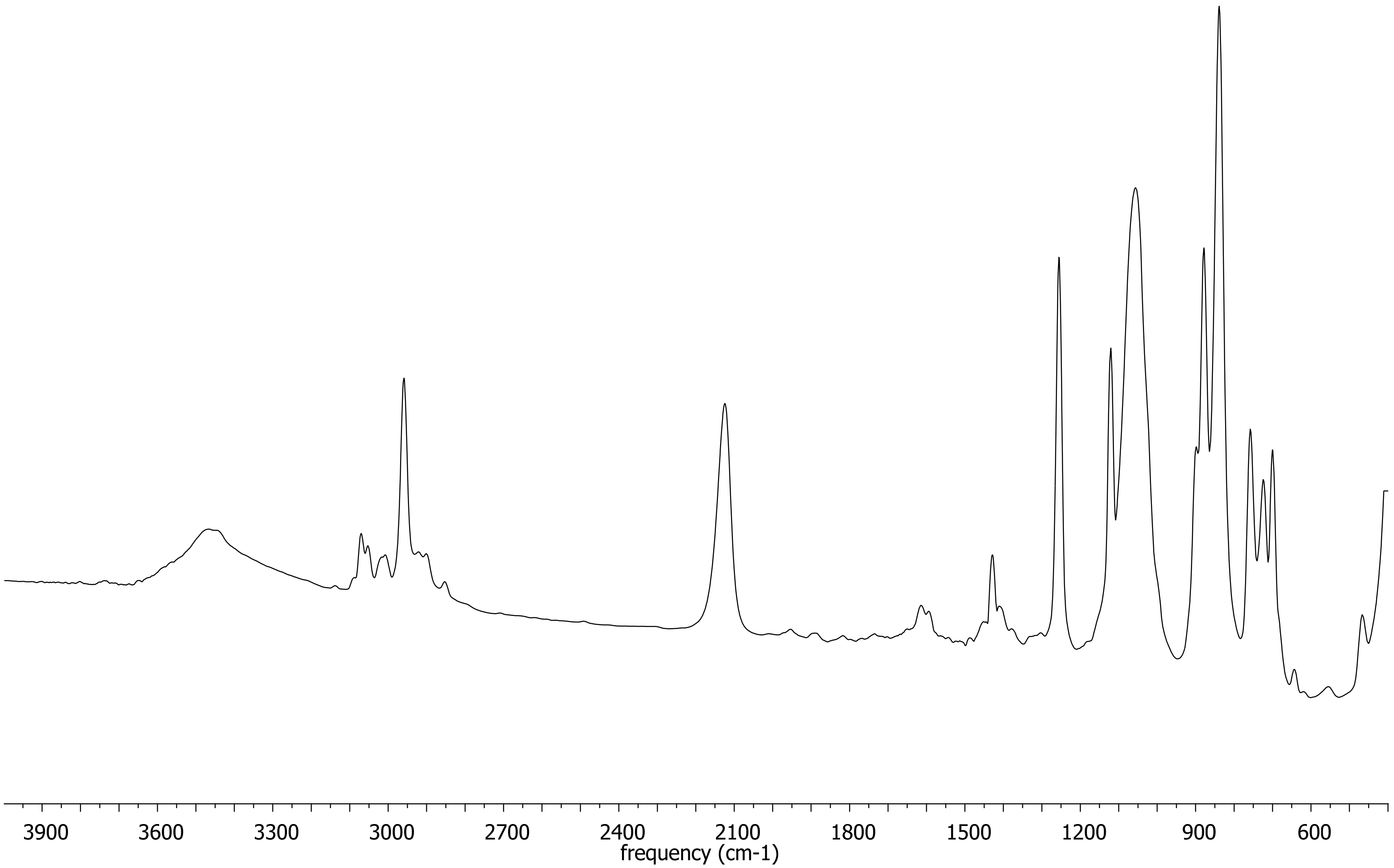
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)



IR spectrum


3900
3600
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frequency (cm-1)

14.3. Method of 1e synthesis

Step 1. A solution of phenyl chloride (29.5 g, 0.26 mol, 1 eq) in THF (200 mL) was added to magnesium (6.24 g, 0.26 mol, 1 eq) at reflux. The obtained solution of phenyl magnesium chloride was added to a solution of methyltrichlorosilane (57.4 g, 0.39 mol, 1.5 eq) in TolH (200 ml) under Ar at -30 ^{o}C. Then the reaction mixture was brought to room temperature and reacted continuously for 8 h under stirring. Then, THF and excess of methyltrichlorosilane were distilled and resulting mixture was filtered, precipitate was washed with TolH (3 times, 100 ml). Toluene fractions were collected and TolH was evaporated (90 - 100 mbar, T_{bath} = 50 °C).

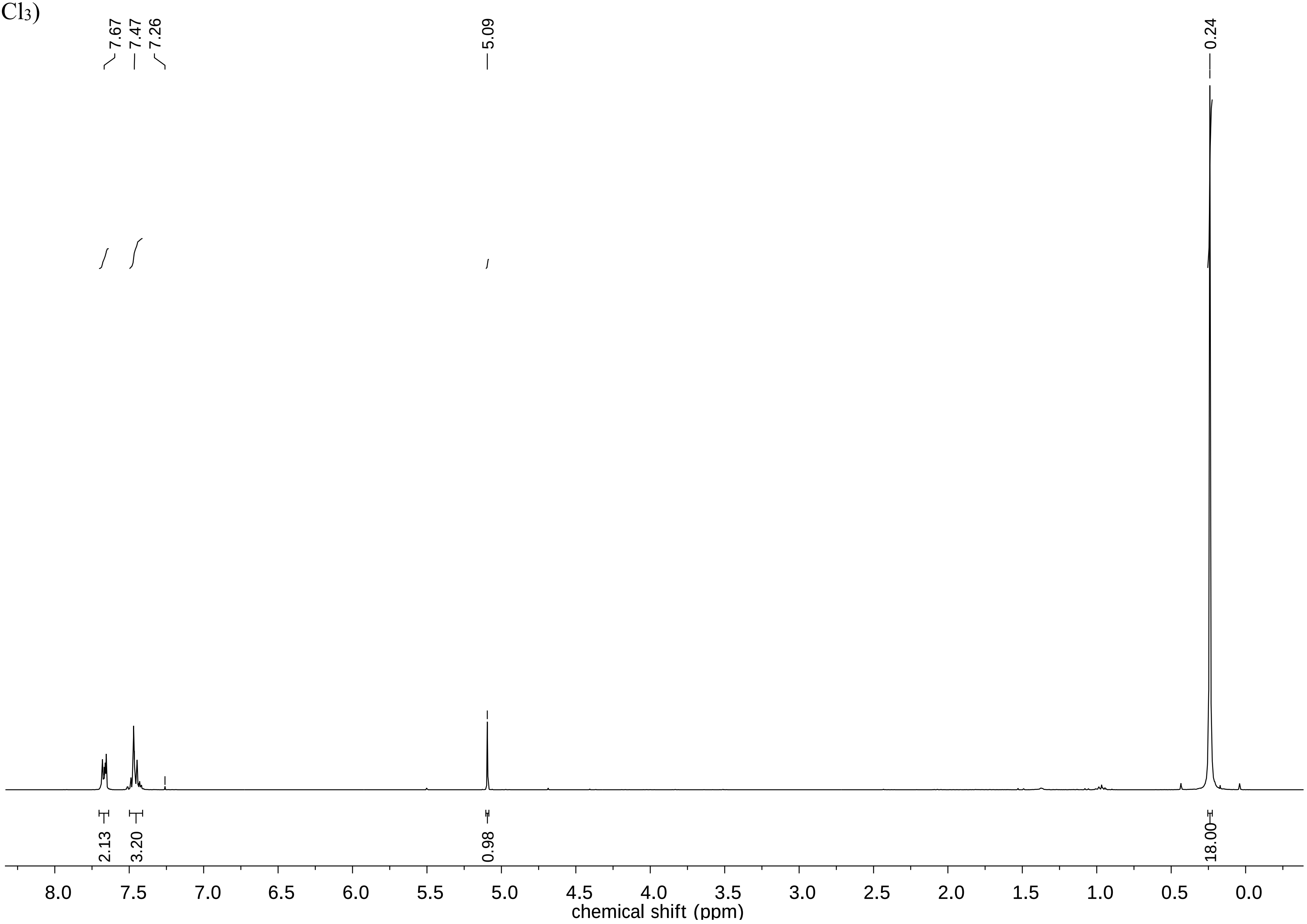
Step 2. A concentrated solution from the first step was added dropwise to a solution of trimethylsilanol (68 g, 0.76 mol, 2.9 eq) and pyridine (60 g, 0.76 mol, 2.9 eq) in TolH (300 mL) at of -70 °C under Ar. Then the reaction mixture was brought to room temperature and reacted continuously overnight under stirring. Then the solution was washed with water (3 times, 150 mL) and dried over Na_2SO_4. TolH was evaporated (90 - 100 mbar, T_{bath} = 50 °C). Product **1e** was obtained as colorless oil by distillation under reduced pressure (BP = 169-170 ^{0}C/ 150 mbar). Separated yield was 20% (15 g).

Characterization data for 1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**1e**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 18H); 5.09 (s, 1H); 7.47 (m, 3H); 7.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.73; 127.81; 130.04; 133.14; 137.1;. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -49.26; 10.67. IR (cm^{-1}): 2959; 2154; 1256; 1062.

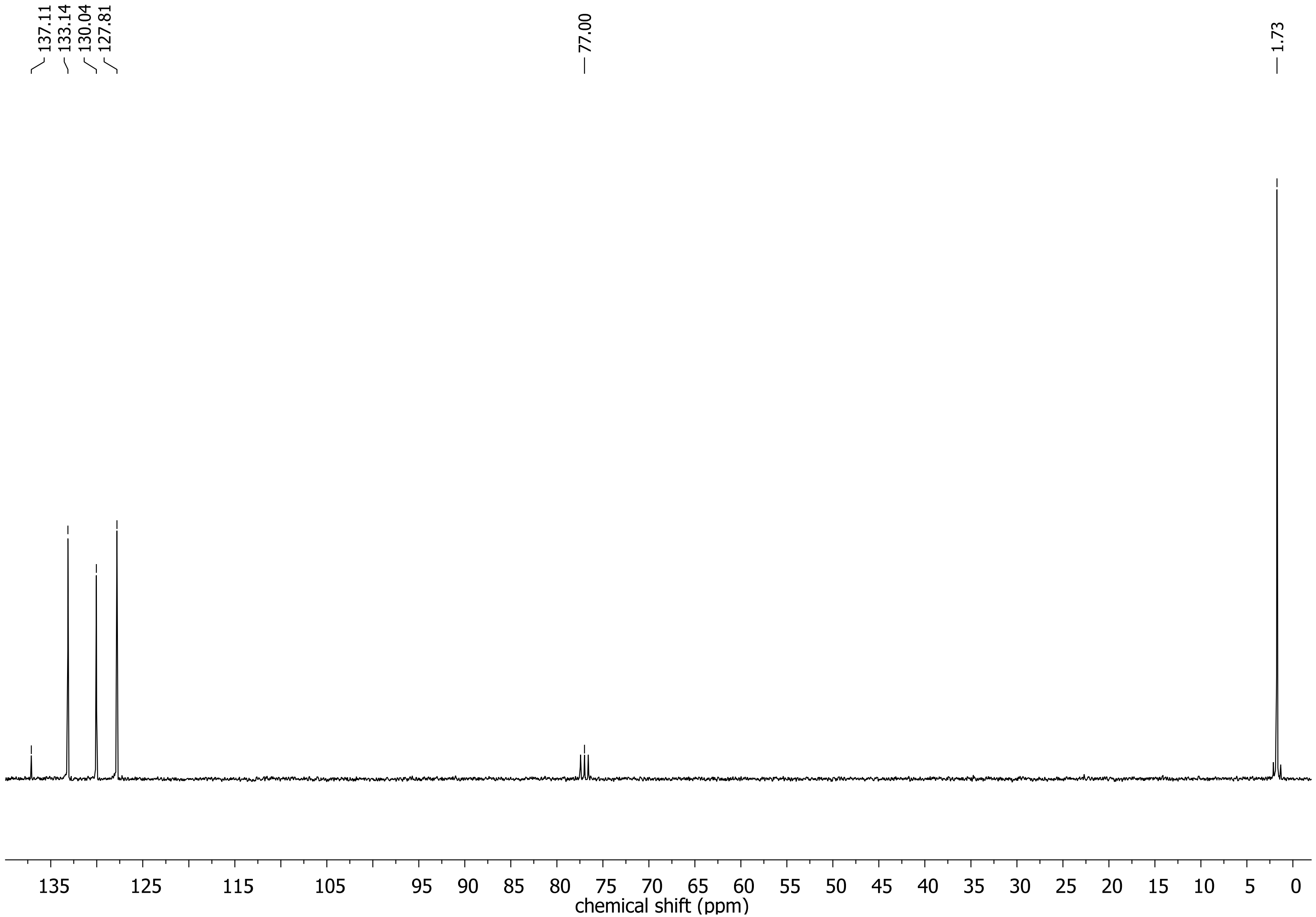
^{1}H NMR

(400 MHz, CDCl$_3$)



^{13}C NMR

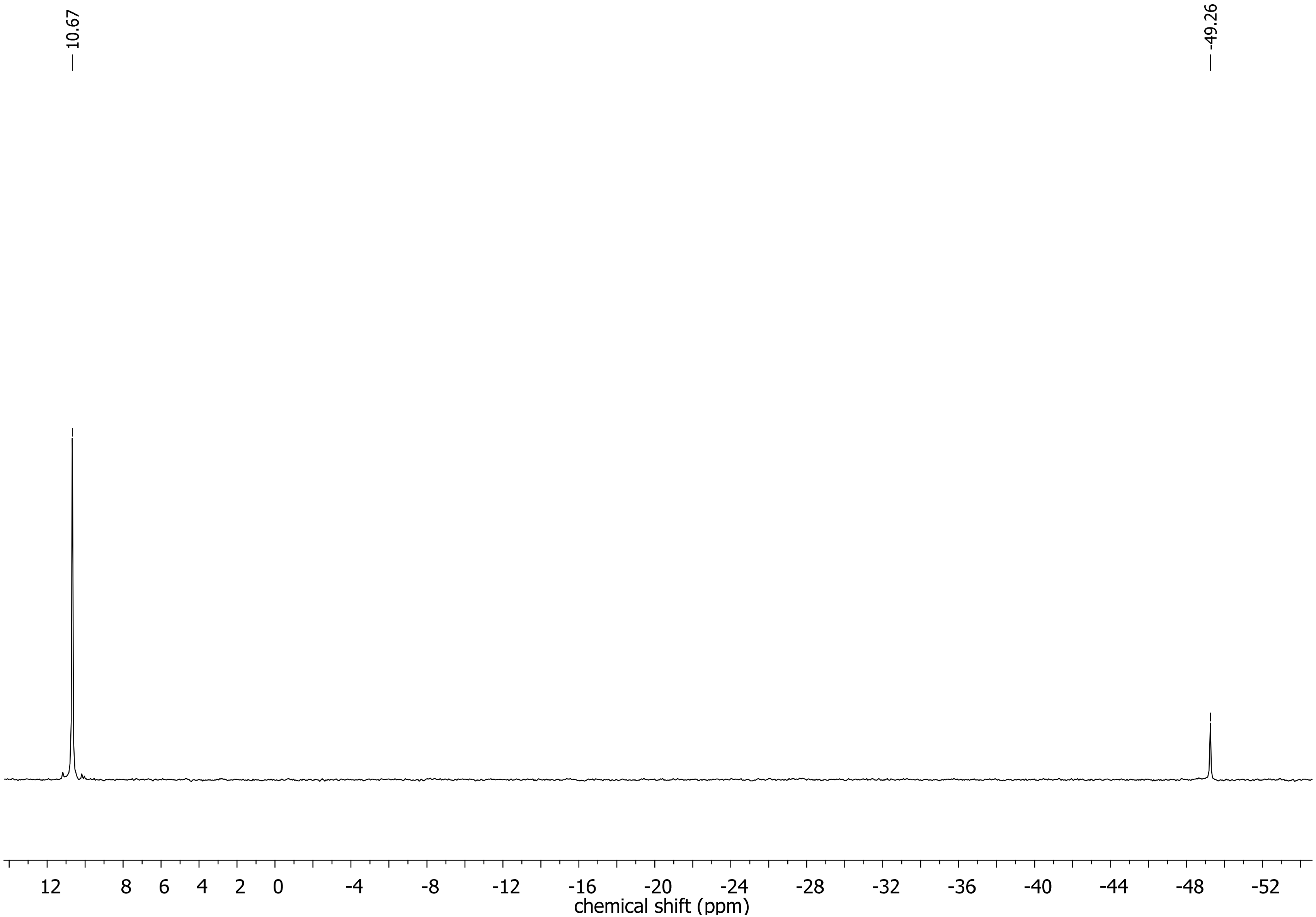
(100 MHz, $CDCl_3$)



^{29}Si NMR

(80 MHz, $CDCl_3$)

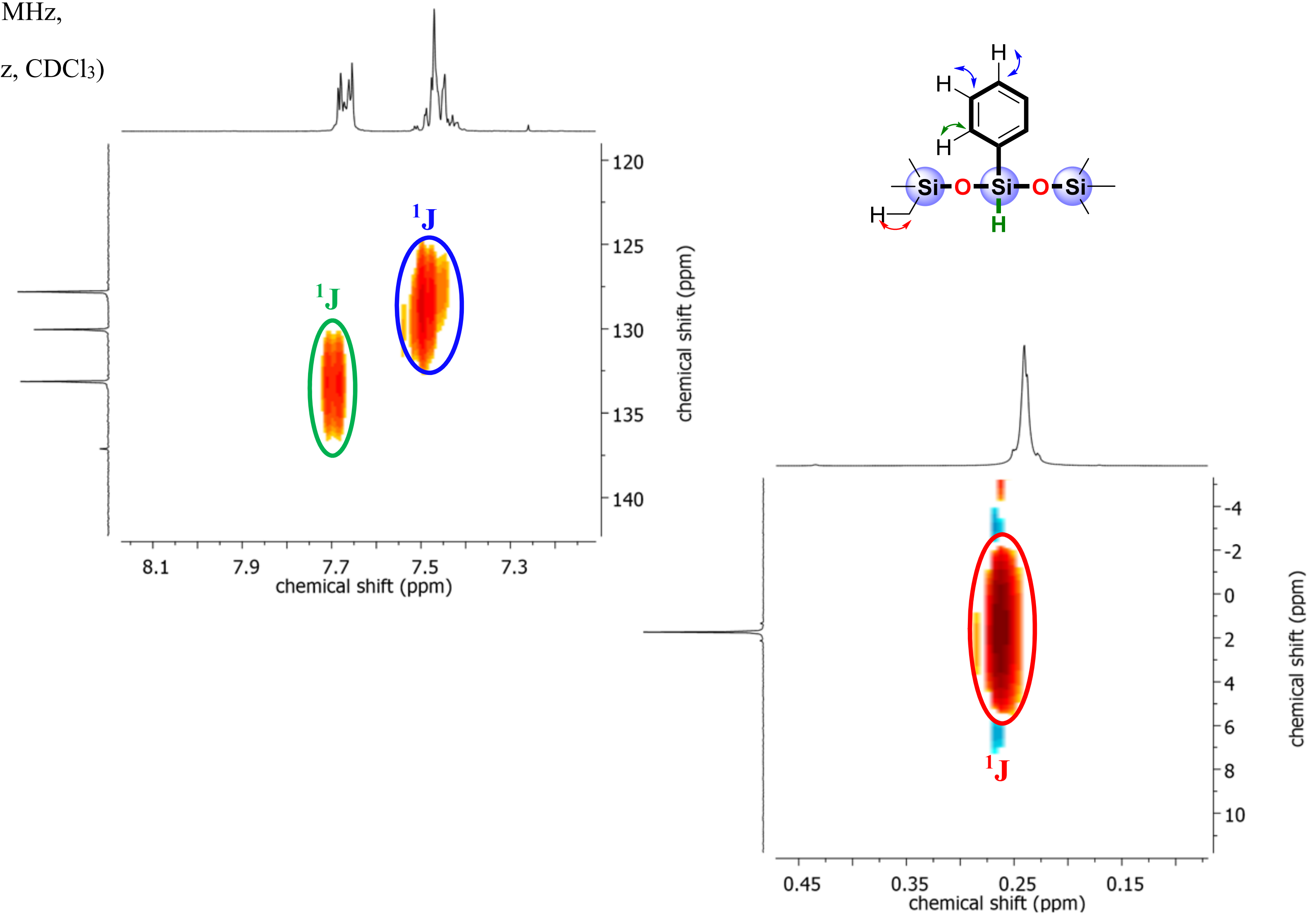
148



^{1}H, ^{13}C –HSQC NMR

(^{1}H: 400 MHz,

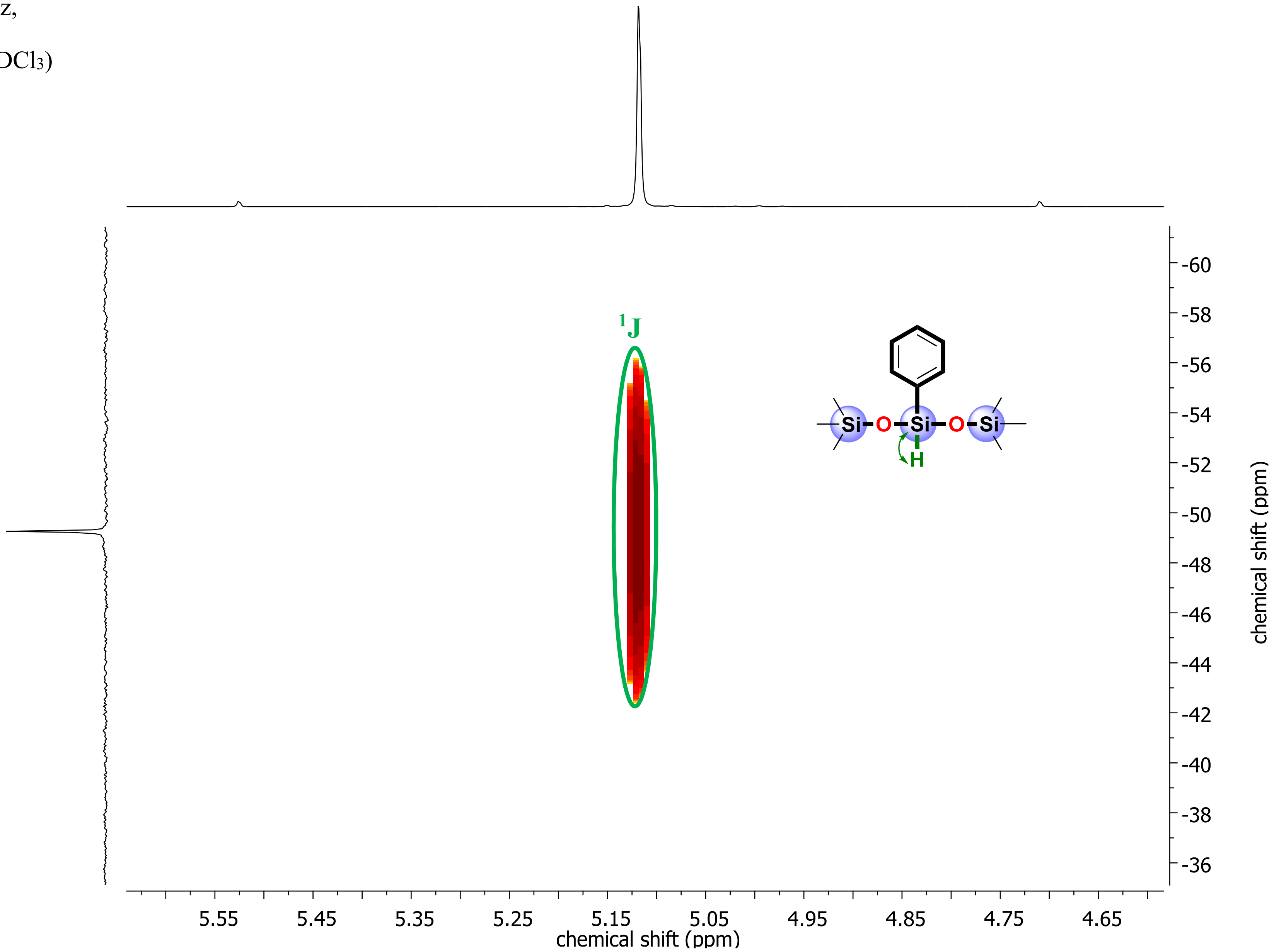
^{13}C: 100 MHz, CDCl$_3$)



^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

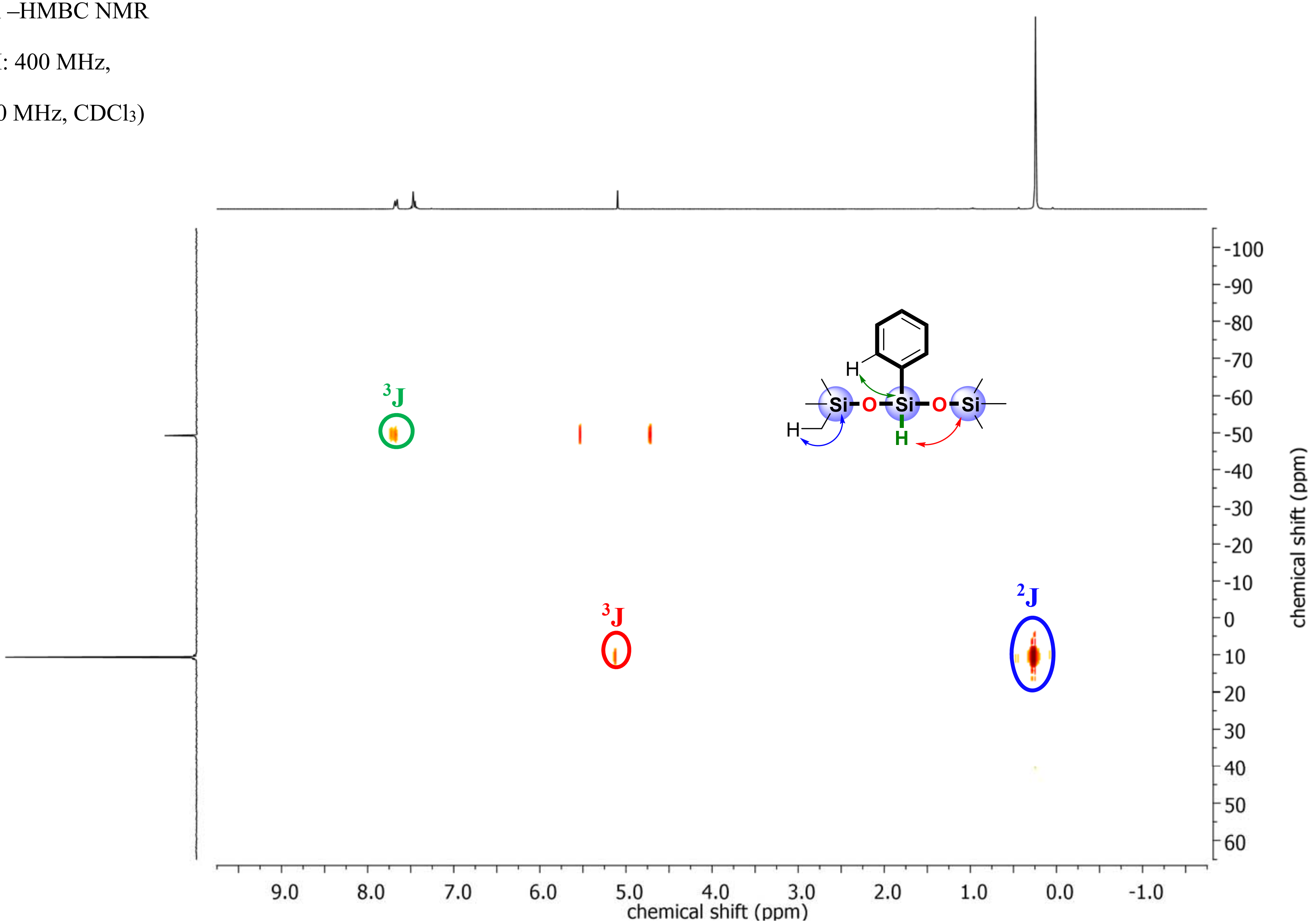
^{29}Si: 80 MHz, CDCl$_3$)



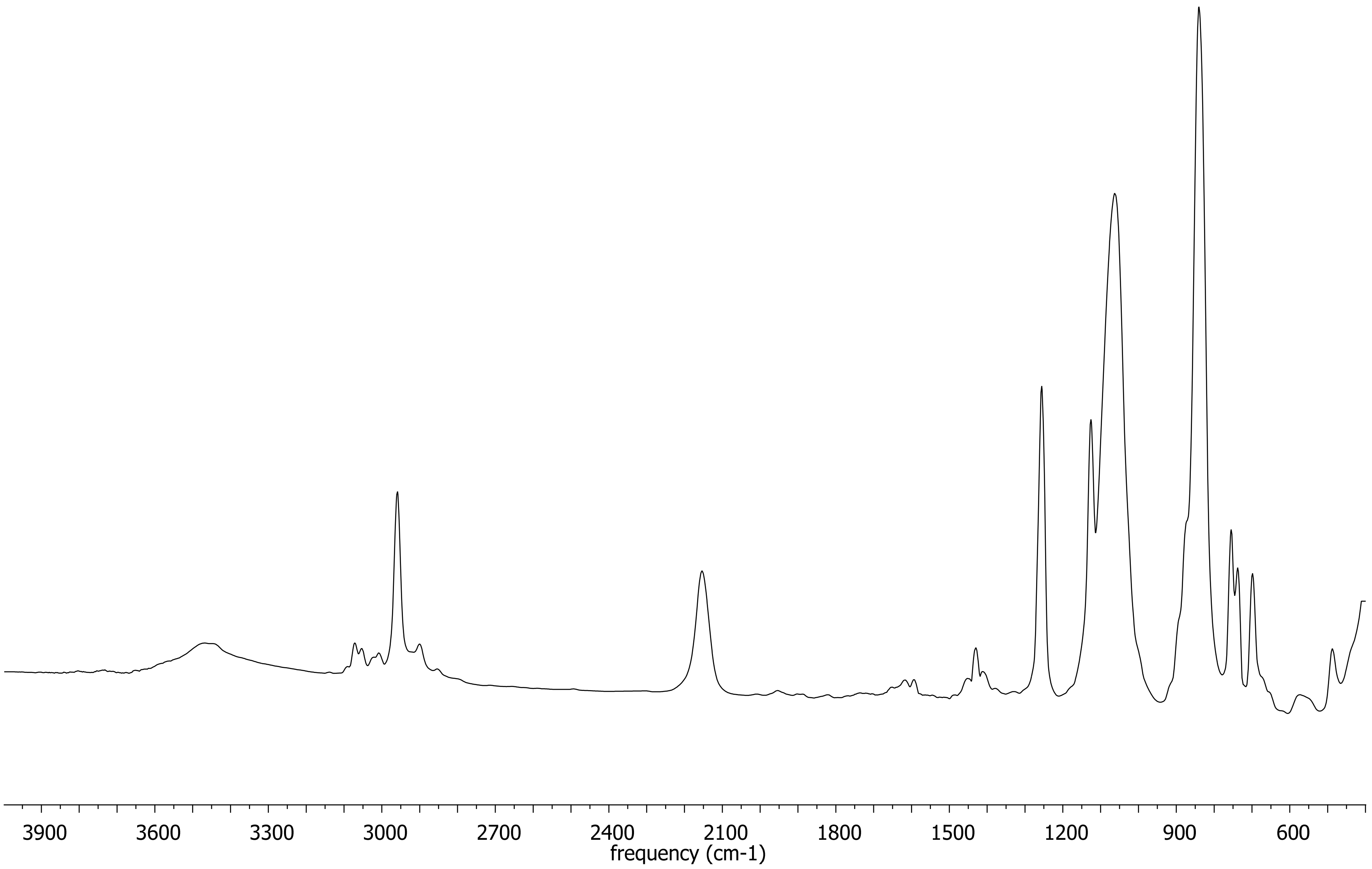
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)



IR spectrum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900
600
frequency (cm-1)

14.4. Method of 1f synthesis

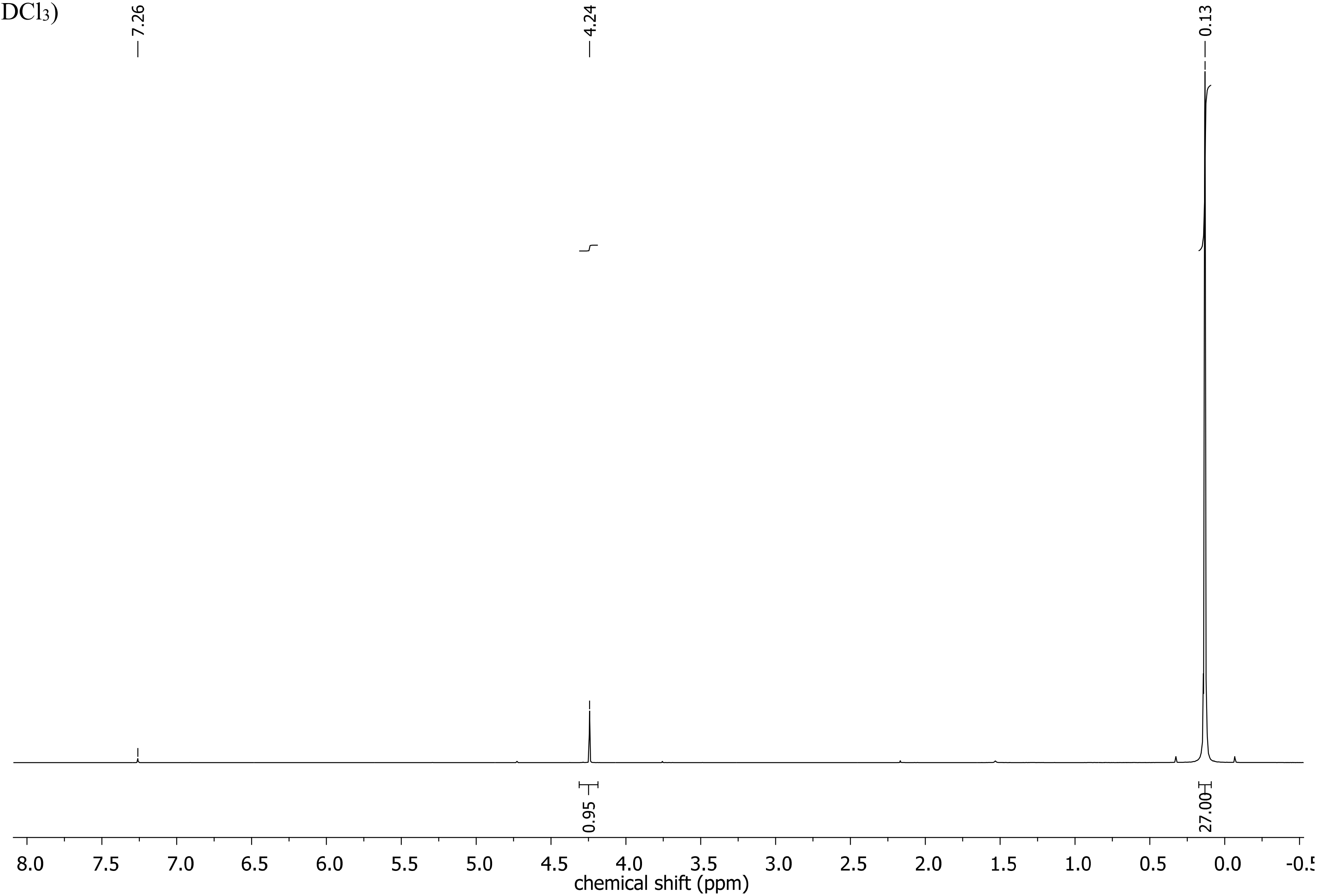
A solution of trichlorosilane ($HSiCl_3$) (10.0 g, 0.074 mol, 1 eq) in hexane (10mL) was dropwise added to a solution of trimethylsilanol (22.0 g, 0.28 mol, 3.78 eq) and pyridine (22.0 g, 0.28 mol, 3.78 eq) in hexane (60 mL) at -70 ^{o}C. Then the mixture was slowly heated to 25 ^{o}C and stirred for 12 more hours. Then it was filtered and washed with water to get rid of pyridine hydrochloride, and the solution was dried over Na_2SO_4. Hexane was evaporated (290 – 300 mbar, T_{bath} = 40 °C). Product **1f** was obtained as colorless oil by distillation under atmospheric pressure (BP = 187-189 ^{0}C). Separated yield was 53%.

Characterization data for 1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (**1f**):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 27H); 4.24 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.63. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -82.79; 9.34. IR (cm^{-1}): 2960; 2204; 1256; 1065.

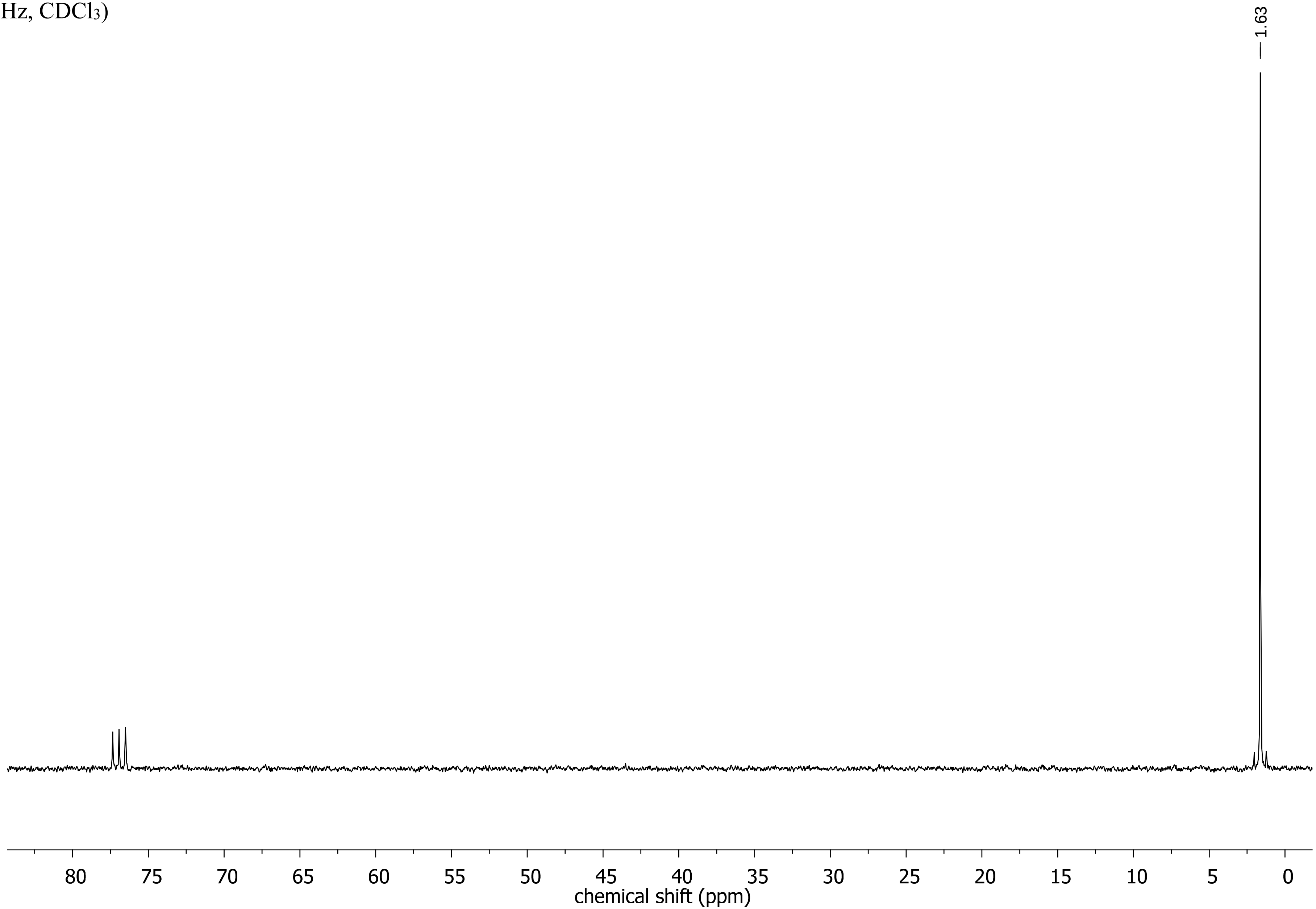
^{1}H NMR

(400 MHz, CDCl$_3$)



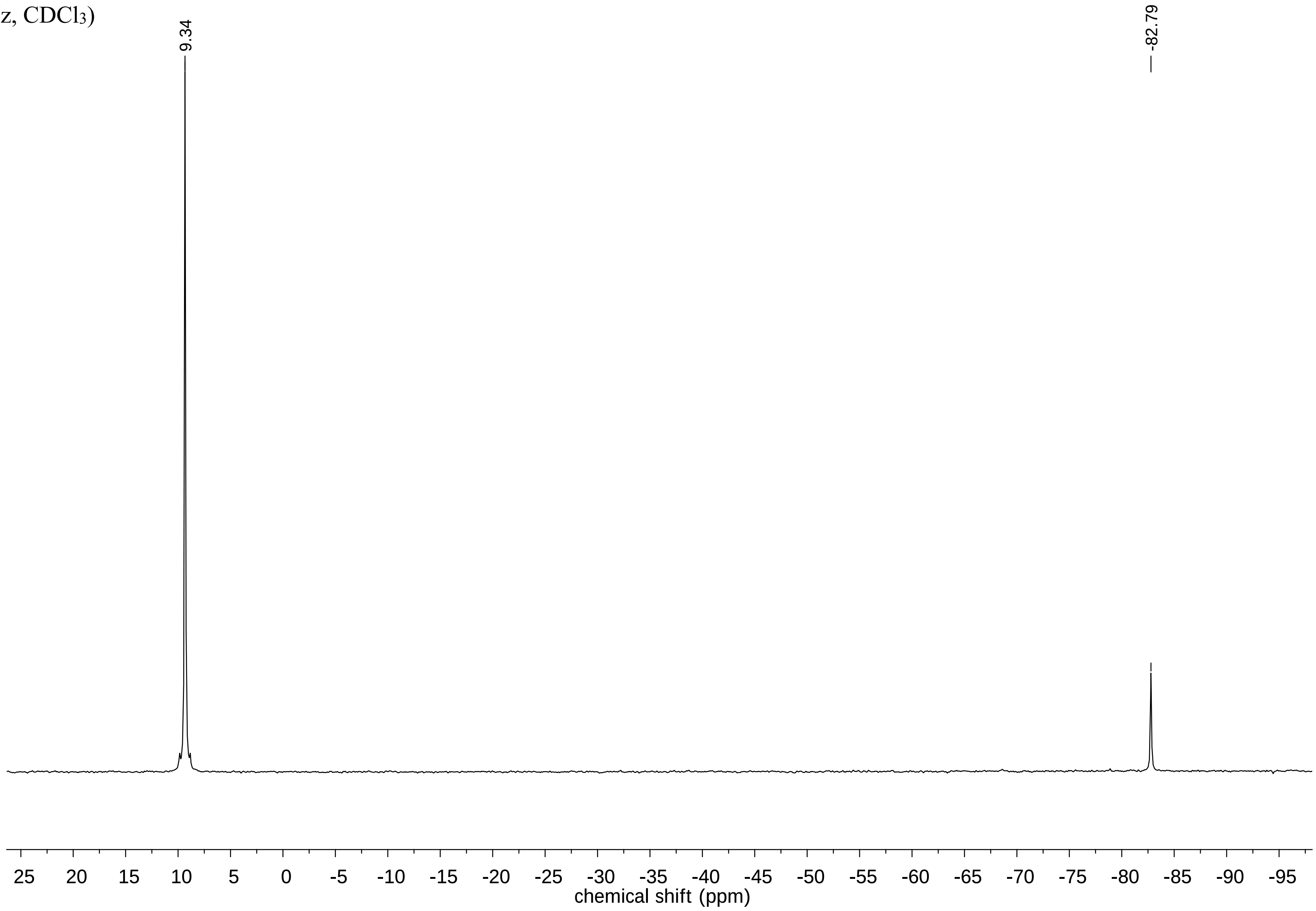
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

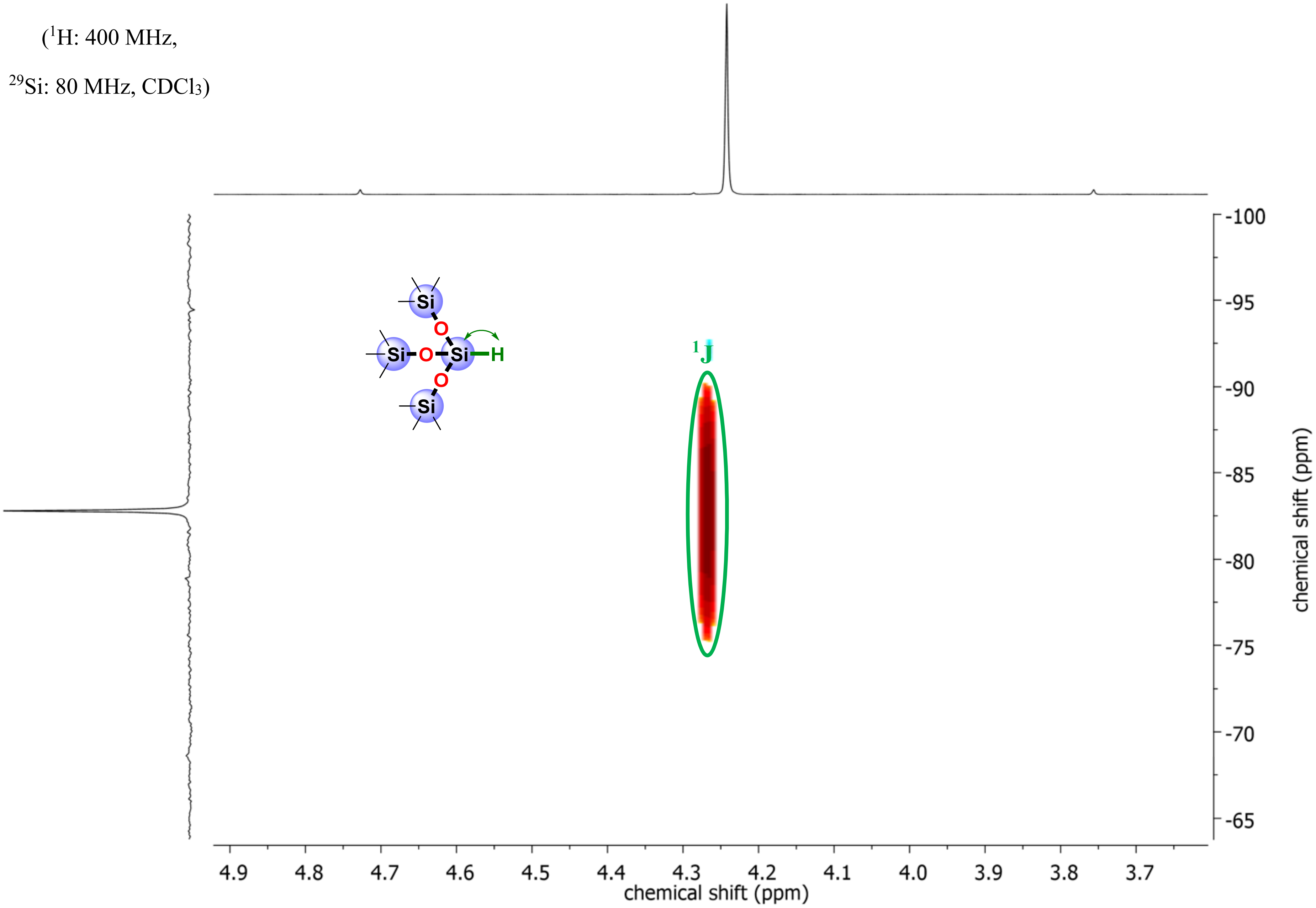
(80 MHz, $CDCl_3$)



^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

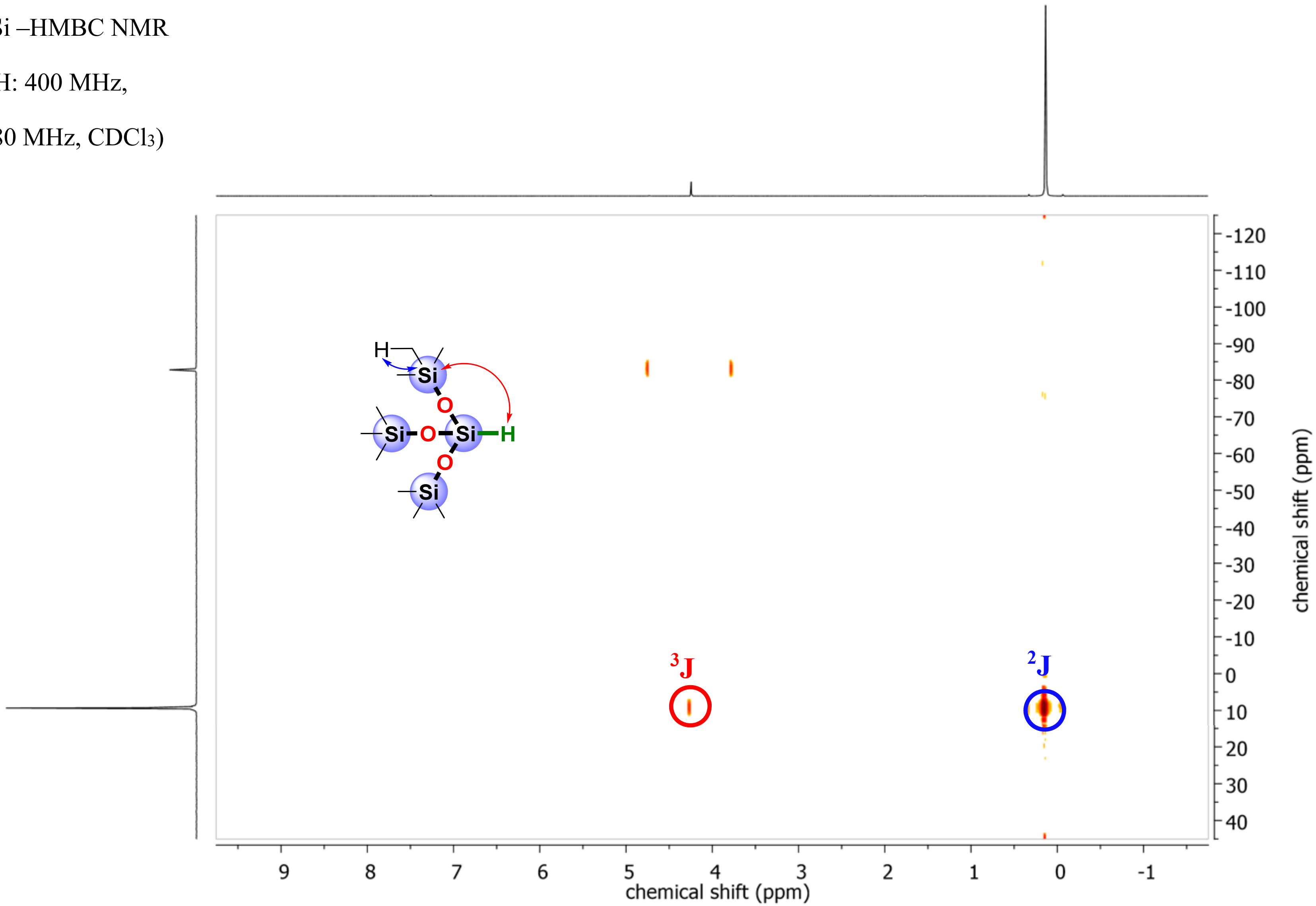
^{29}Si: 80 MHz, CDCl$_3$)



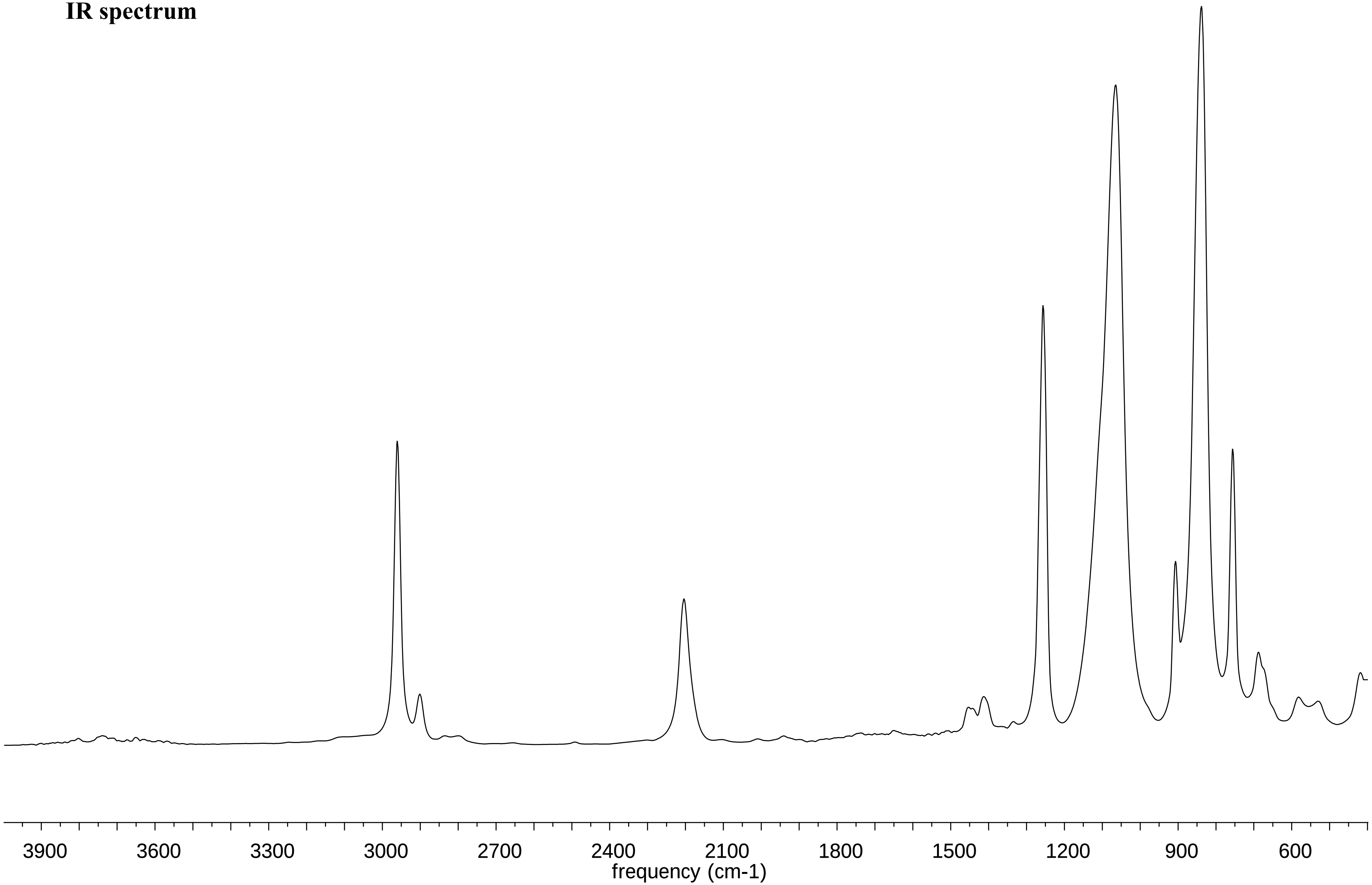
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, CDCl$_3$)



IR spectrum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2400
2100
1800
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1200
900
600
frequency (cm-1)

14.5. Method of 1g synthesis

1g was obtained using optimized conditions by **1a** *in situ* silylation (see **13.1**).

14.6. Method of 1h synthesis

Octamethylcyclotetrasiloxane (15 g, 50.57 mmol, 1eq), tetramethyldisiloxane (2.71 g, 20.23 mmol, 0.4 eq) and sulfonic cation resin (purolite, 0.89 g, 5% mass) were stirred in a round bottomed flask at 80 °C for 24 hours. Then the reaction mixture was diluted with hexane (10 mL) and filtered, the catalyst was washed with hexane. Hexane fractions were collected, then the solvent was evaporated (300 – 350 mbar, T_{bath} = 40 °C), and the product was additionally dried under vacuum (1 mbar, 80 °C, 3 hours). Product **1h** was obtained as colorless liquid with 88% yield (15.52 g).

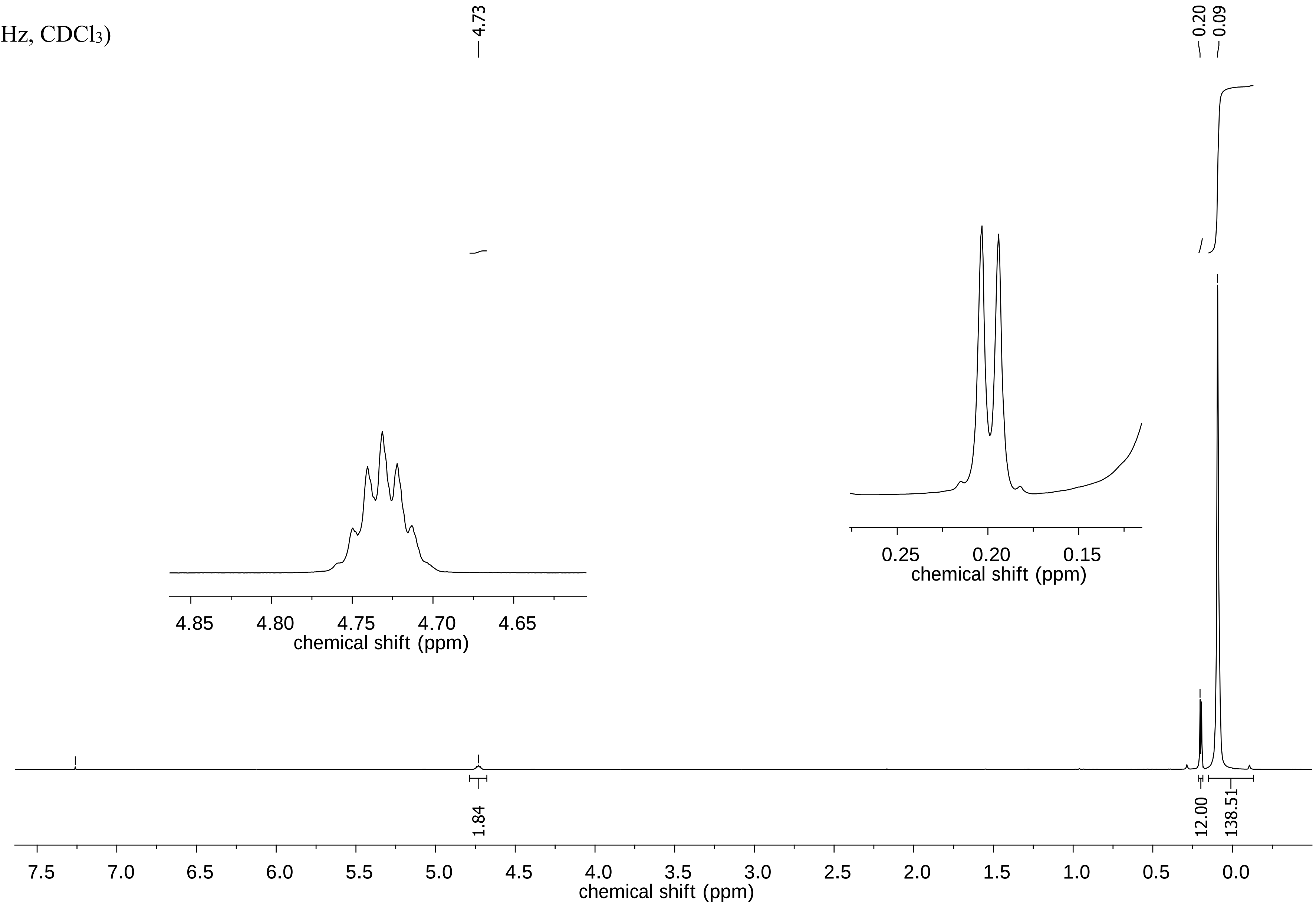
The length (a degree of polymerization) of the macromolecule was calculated as ratio of signal integral intensities of terminal to internal CH_3-groups for **1h** (^1H NMR).

Characterization data for **1h**:

^1H NMR (400 MHz, $CDCl_3$): δ = 0.09 (br, 138H); 0.20 (d, J = 3.6 Hz, 12H); 4.73 (m, J = 3.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.98. ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -7.00; -19.98; -21.5 – -22.5. IR (cm^{-1}): 2964; 2128; 1261; 1091; 1023. GPC (500A): M_w (pss) = 4145; M_n (pss) = 2796; PDI = 1.48.

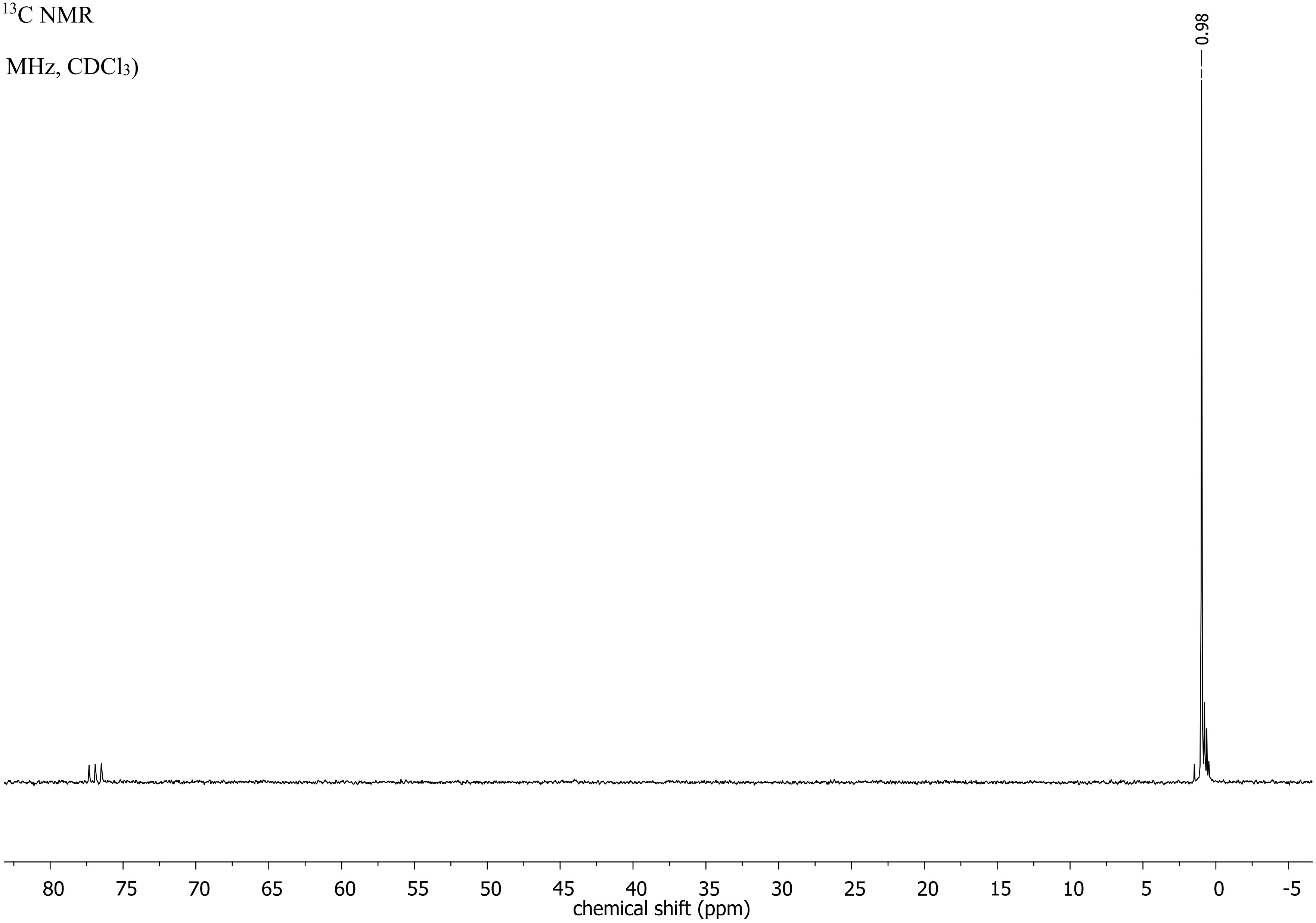
^{1}H NMR

(400 MHz, $CDCl_3$)



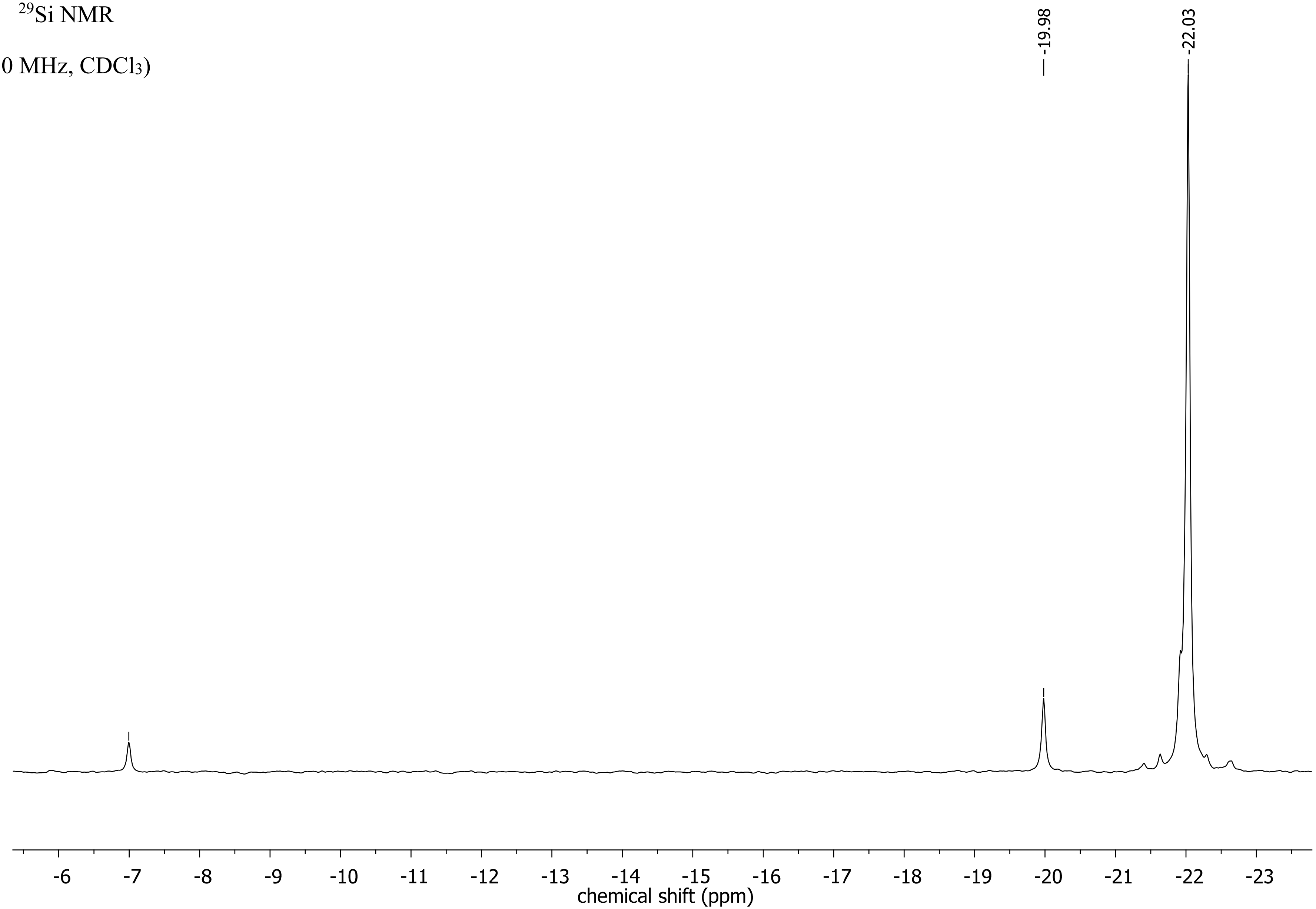
^{13}C NMR

(100 MHz, $CDCl_3$)



^{29}Si NMR

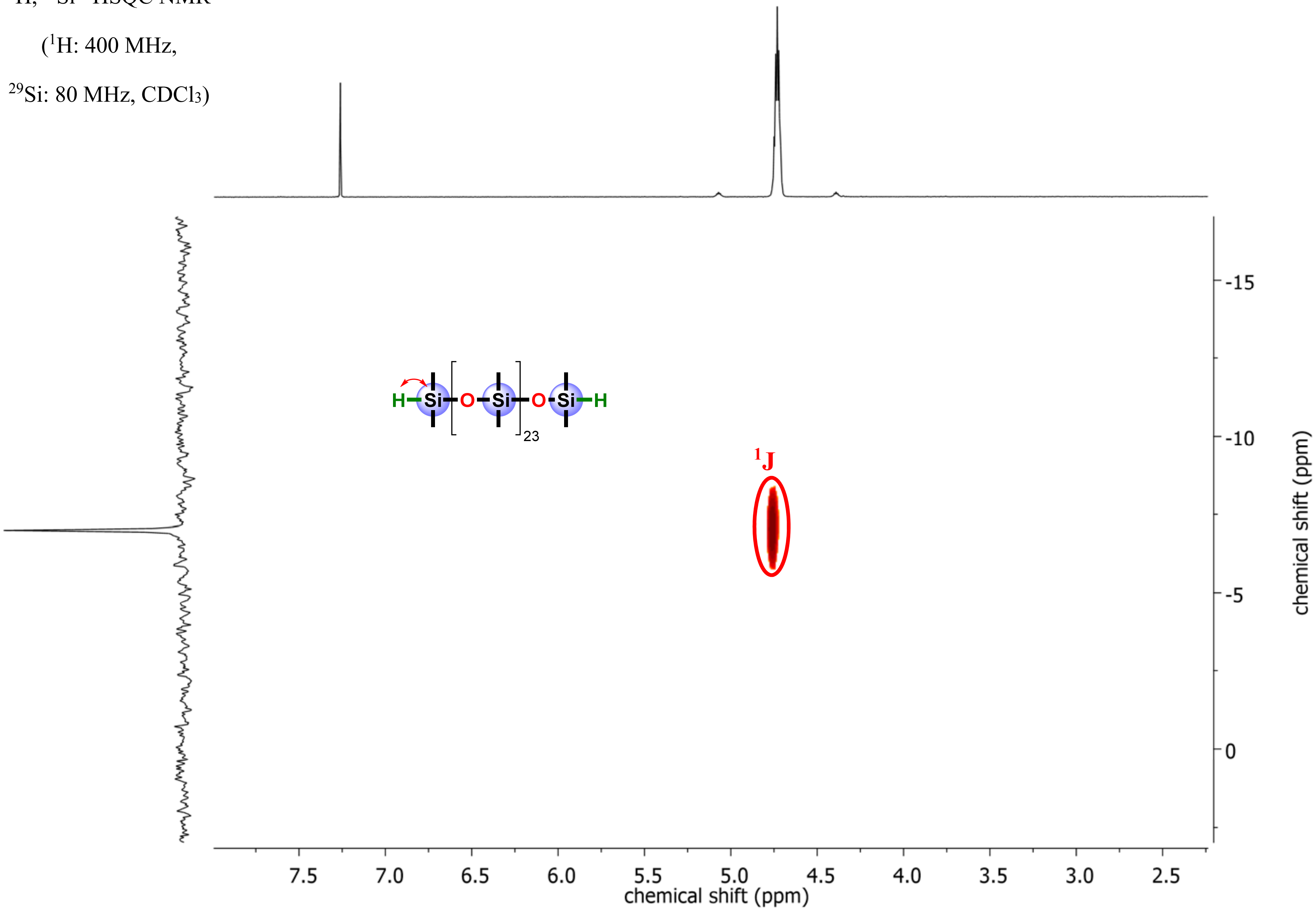
(80 MHz, $CDCl_3$)



^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

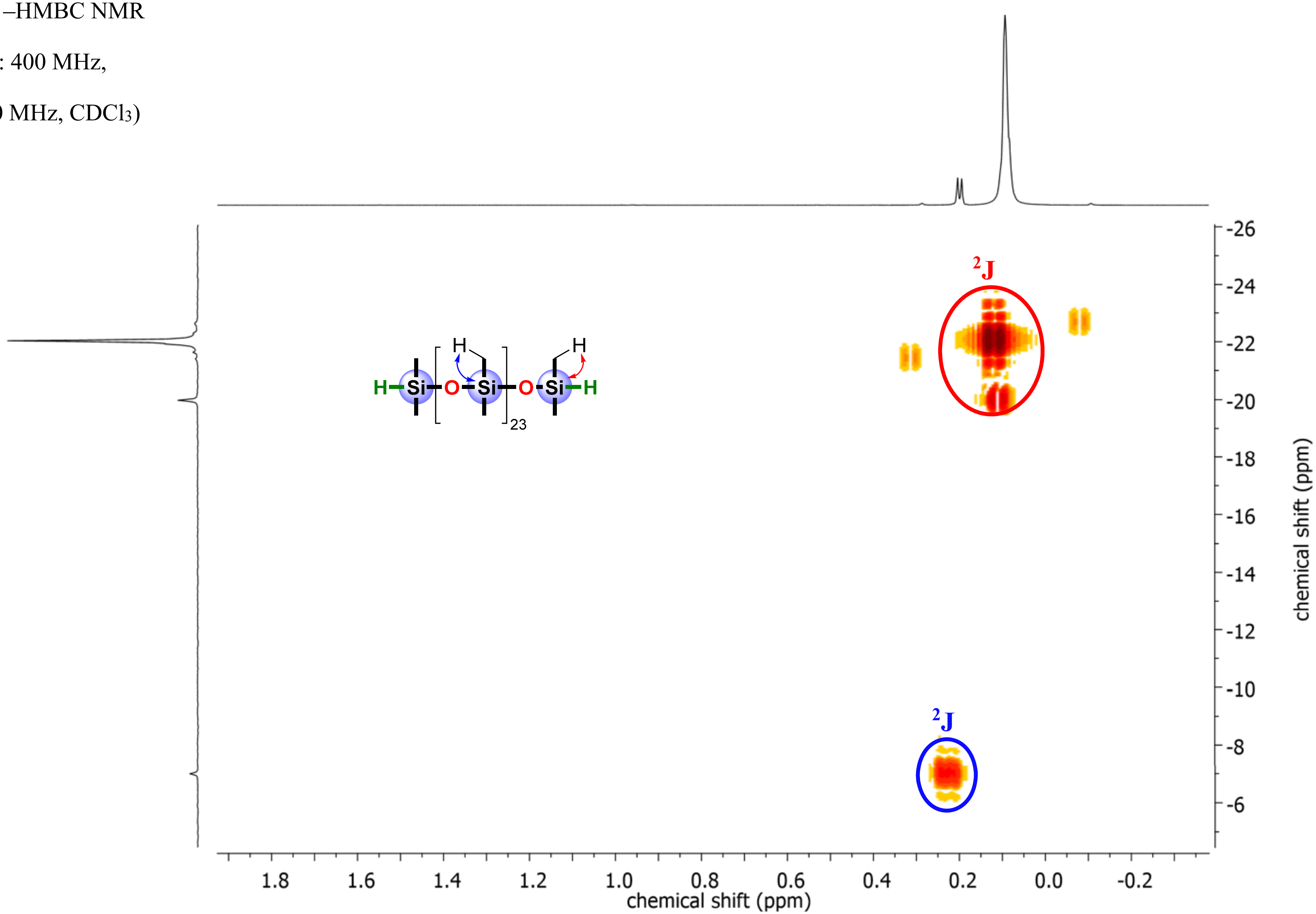
^{29}Si: 80 MHz, $CDCl_3$)



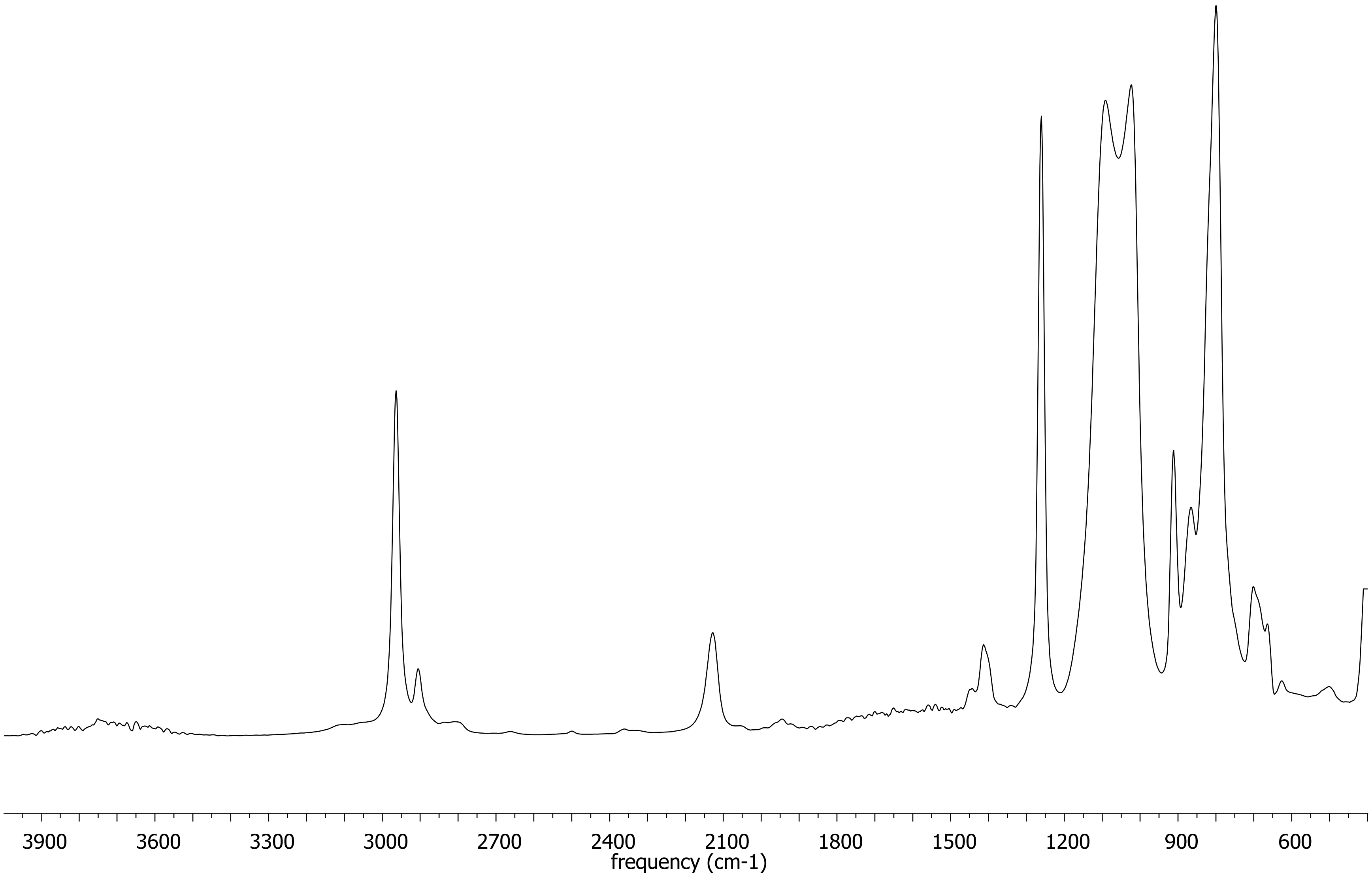
^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)



IR spectrum


3900
3600
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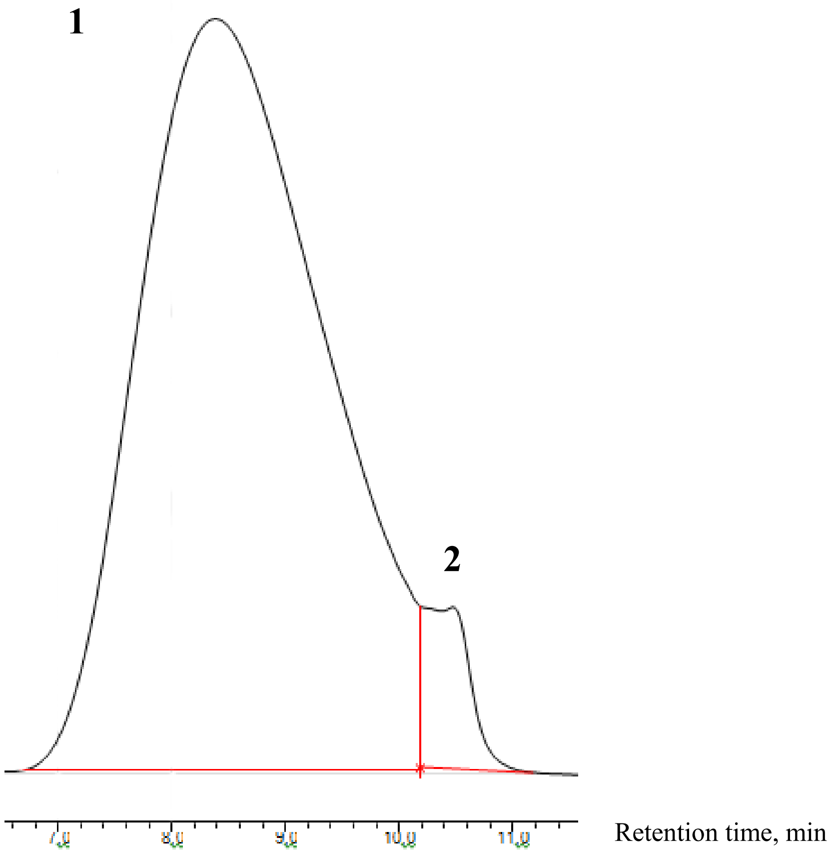
1200
900
600
frequency (cm-1)

GPC curve

(500A)



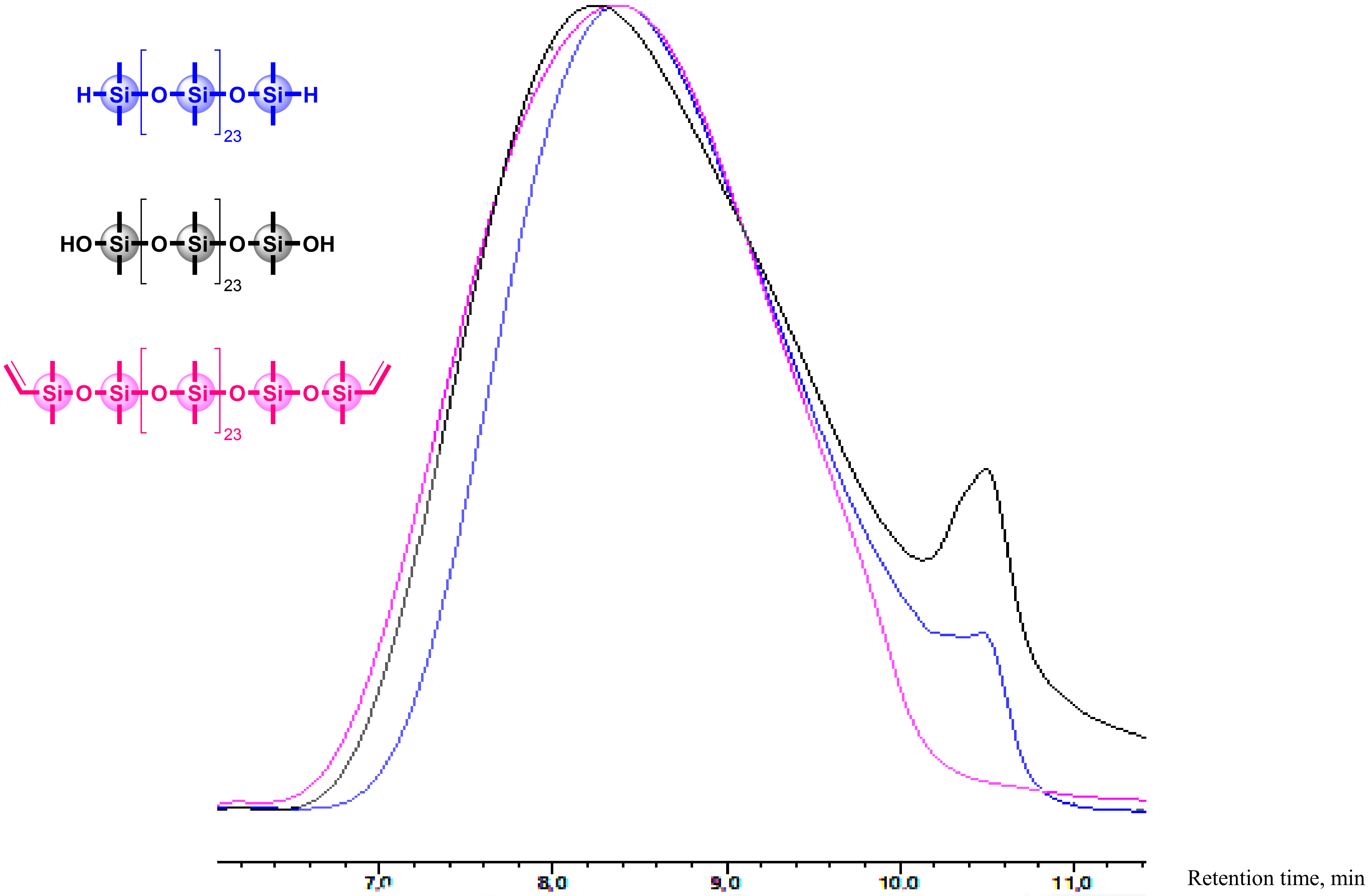
Peak 1. M_w (pss)= 4145;

M_n (pss) = 2796;

PDI = 1.48.

GPC comparison

500A



14.7. Method of 1i synthesis

Octamethylcyclotetrasiloxane (20 g, 67.55 mmol, 1eq), polymethylhydrosiloxane (1.88 g, 0.0004697 mmol, 0.0007 eq), hexamethyldisiloxane (0.87 g, 0.0054 mmol, 0.08 eq) and sulfonic cation resin (purolite, 0.68 g, 3% mass) were stirred in a round bottomed flask at 80 ºC for 24 hours. Then the reaction mixture was diluted with hexane (10 mL) and filtered, the catalyst was washed with hexane. Hexane fractions were collected and then the solvent was evaporated (300 – 350 mbar, T_{bath} = 40 °C), and the product was additionally dried under vacuum (1 mbar, 80 ºC, 3 hours). Product **1i** was obtained as colorless liquid with 94% yield (21.43 g).

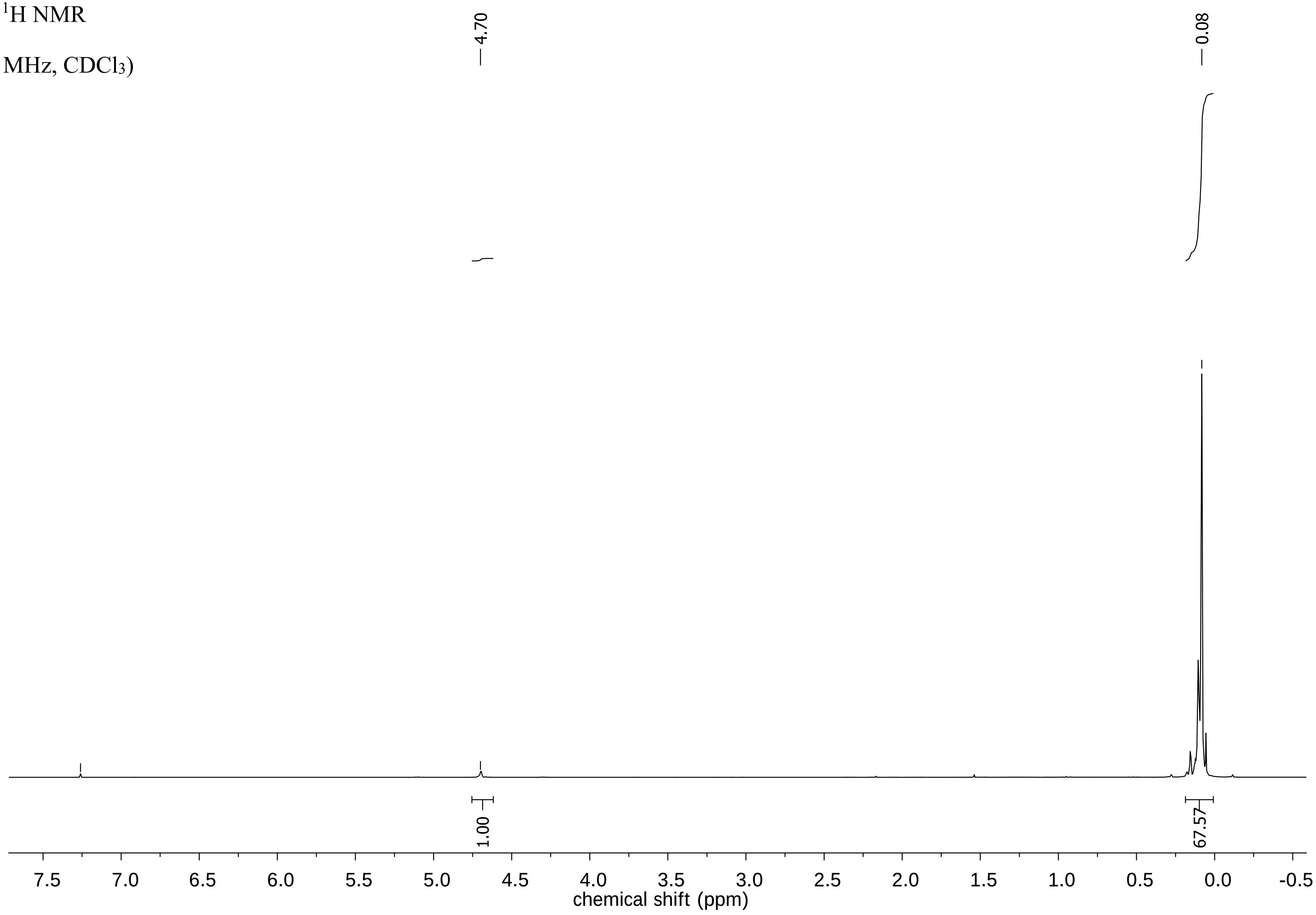
«n» in [$(Me_2SiO)_n$Me***SiH***]-block was determined as a ratio of signal integral intensities of Me***SiH***- to Me_2Si-groups (^{1}H NMR). Length of the macromolecule («m» in TMSO[$(Me_2SiO)_{10}$Me***SiH***$]_m$OTMS block) was calculated using GPC data.

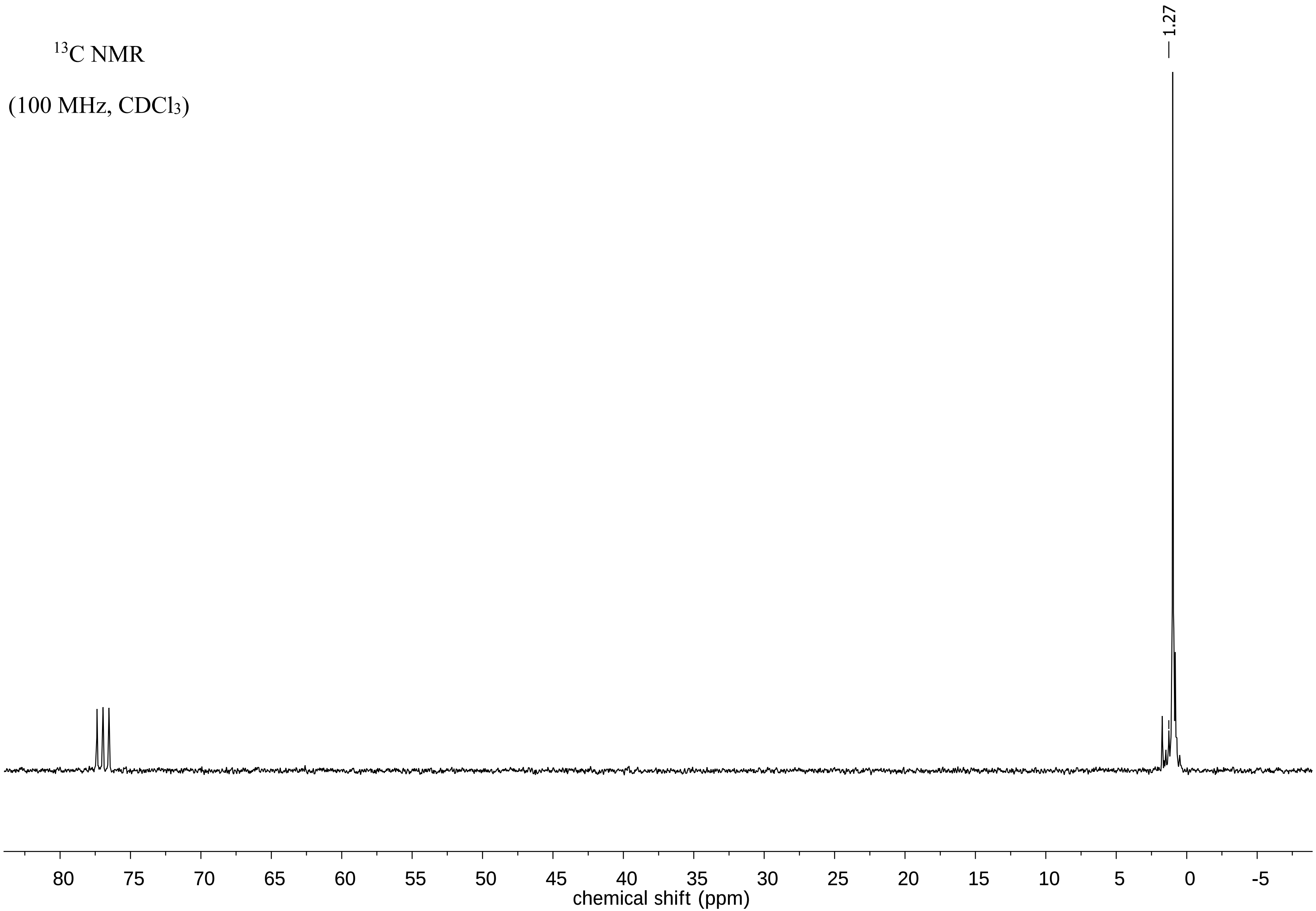
Characterization data for **1i**:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04-0.18 (br, 68H); 0.20 (d, J = 3.6 Hz, 12H); 4.70 (m, J = 3.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.27. ^{29}Si NMR (80 MHz, $CDCl_3$): δ =-37.62; -22.01– -20.62; 7.18. IR (cm^{-1}): 2963; 2157; 1261; 1090; 1022. GPC (1000A): M_w (pss) = 9678, M_n (pss) = 4978, PDI = 1.94.

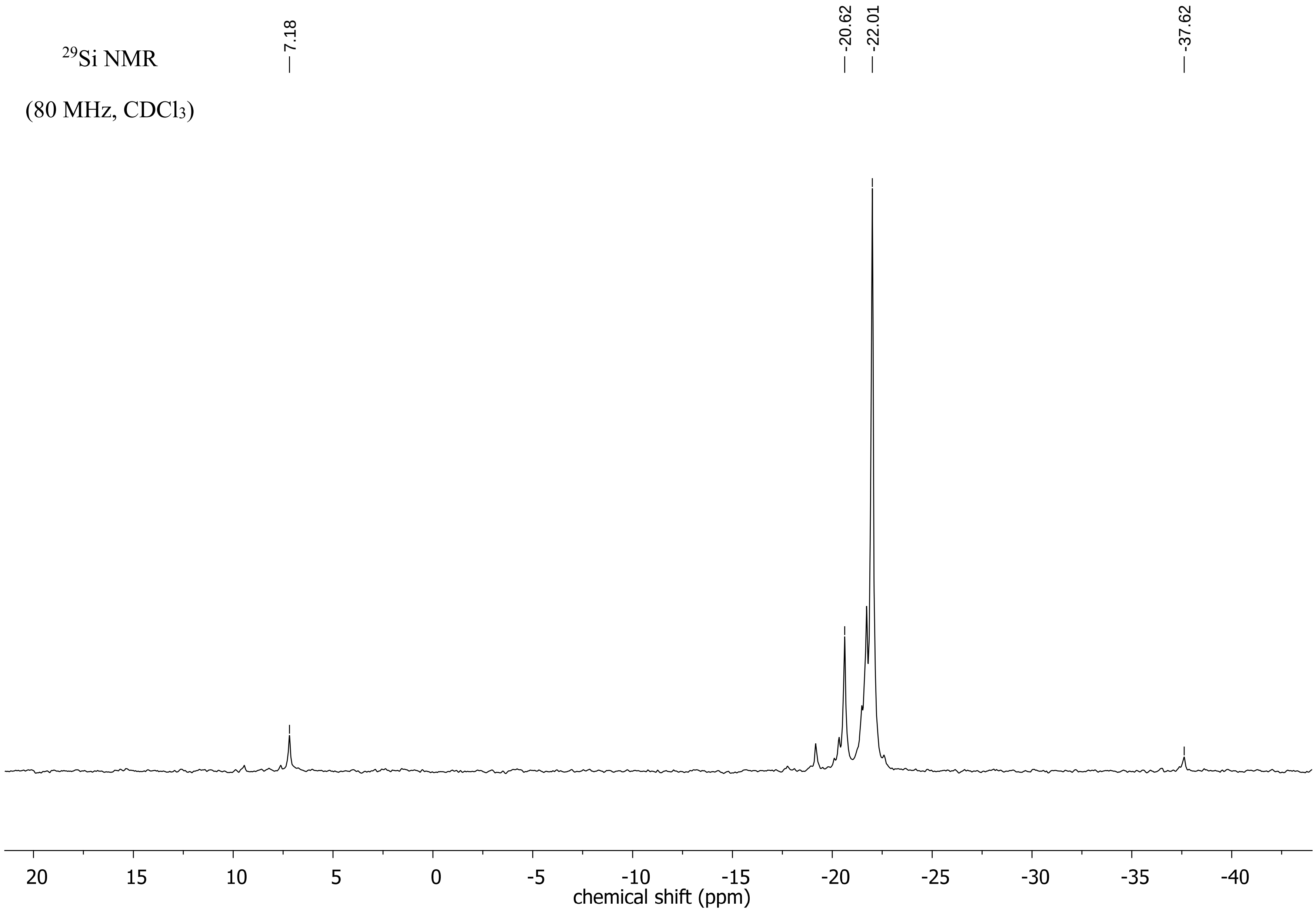
^{1}H NMR

(400 MHz, $CDCl_3$)





^{13}C NMR
(100 MHz, $CDCl_3$)
1.27
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
chemical shift (ppm)



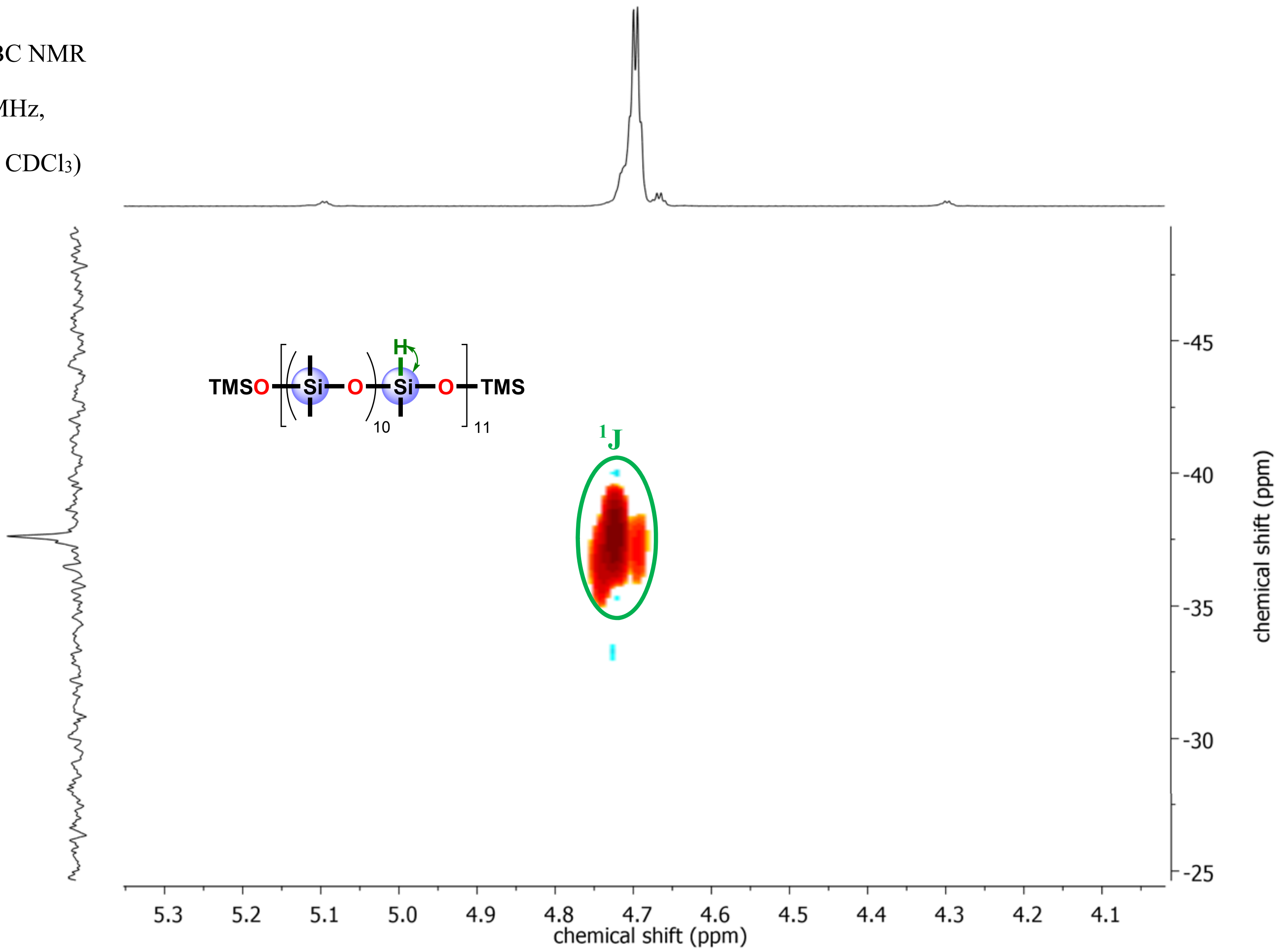
^{29}Si NMR

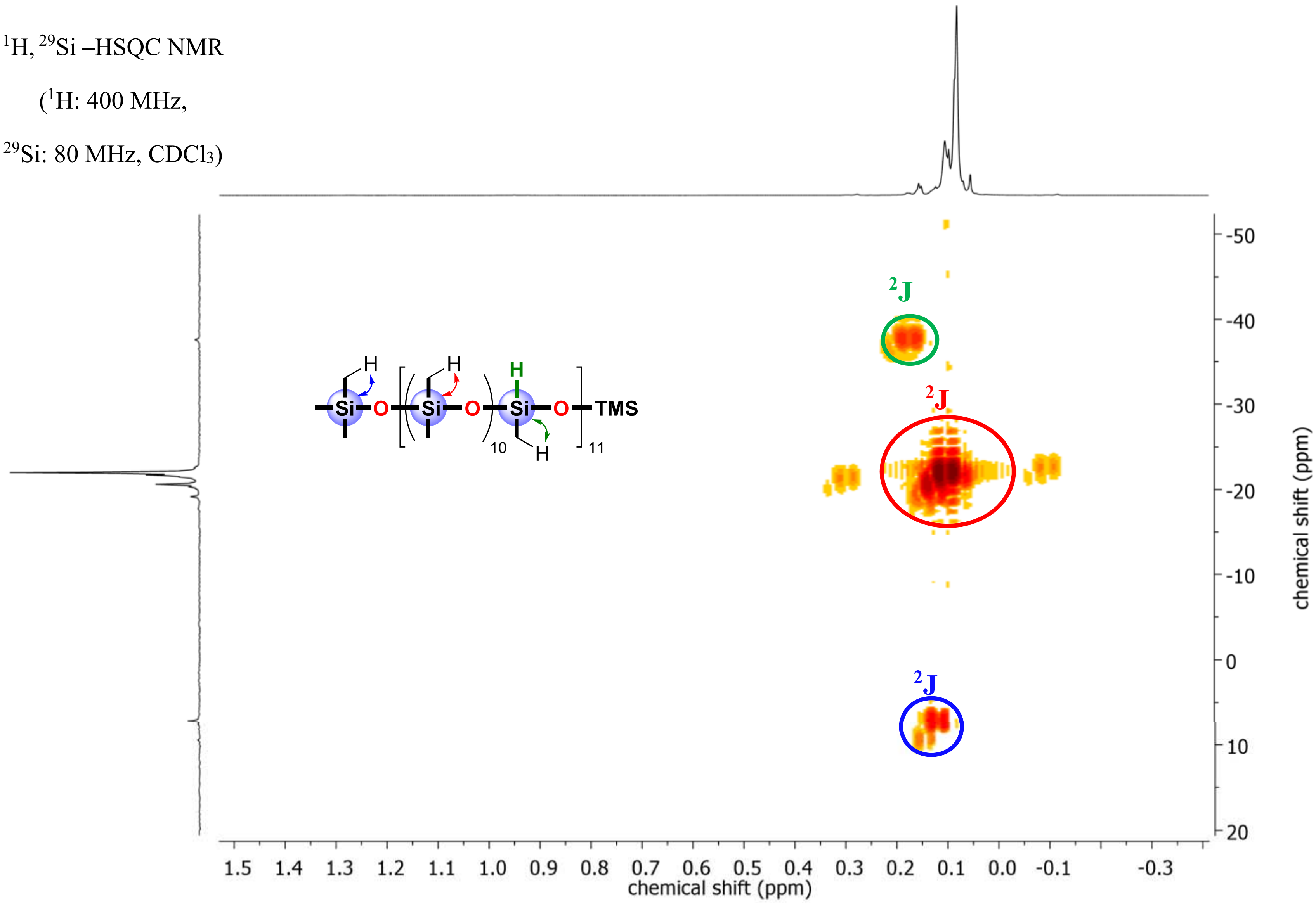
(80 MHz, $CDCl_3$)

^{1}H, ^{29}Si –HMBC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)



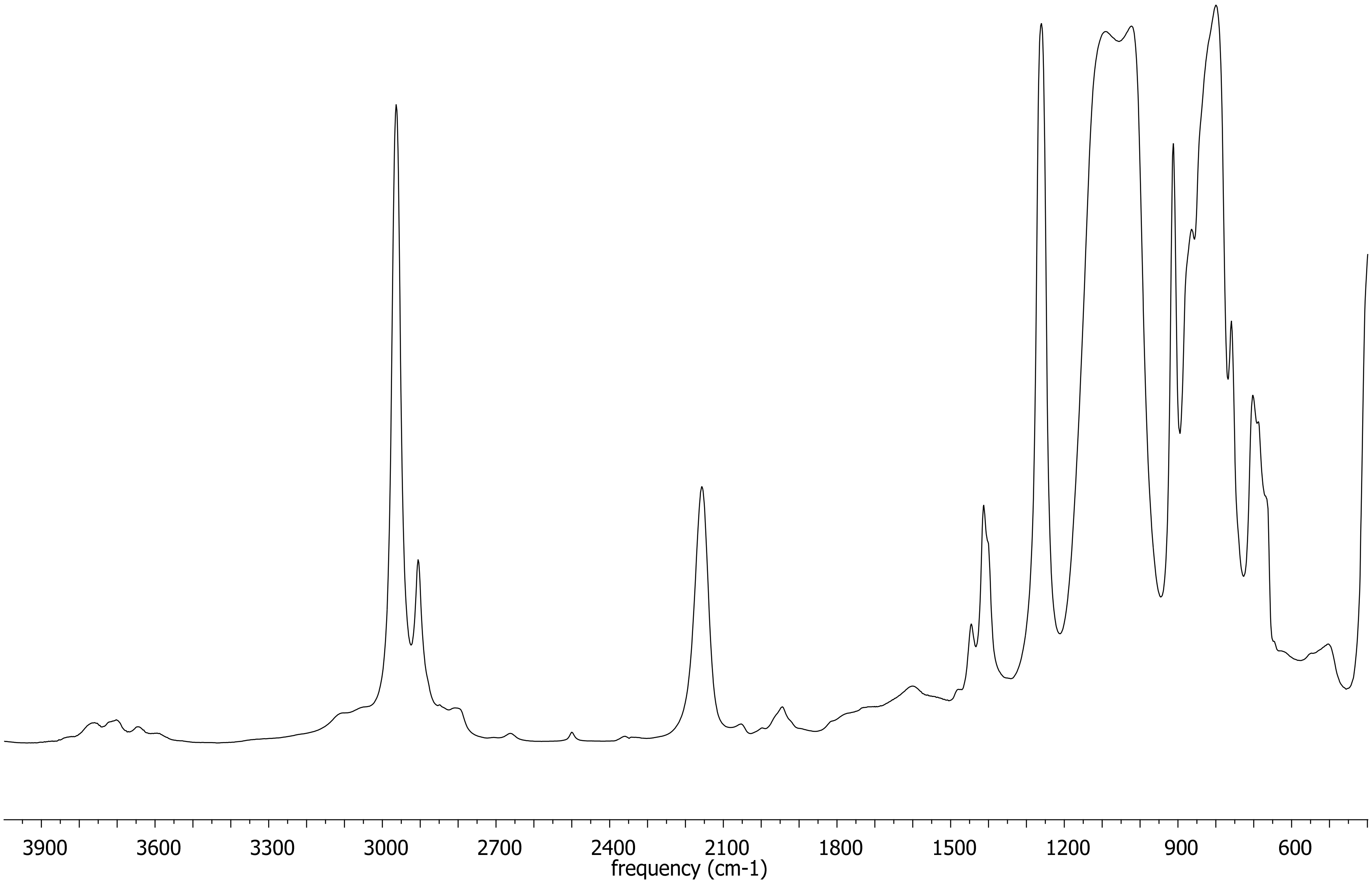


^{1}H, ^{29}Si –HSQC NMR

(^{1}H: 400 MHz,

^{29}Si: 80 MHz, $CDCl_3$)

IR spectrum


3900
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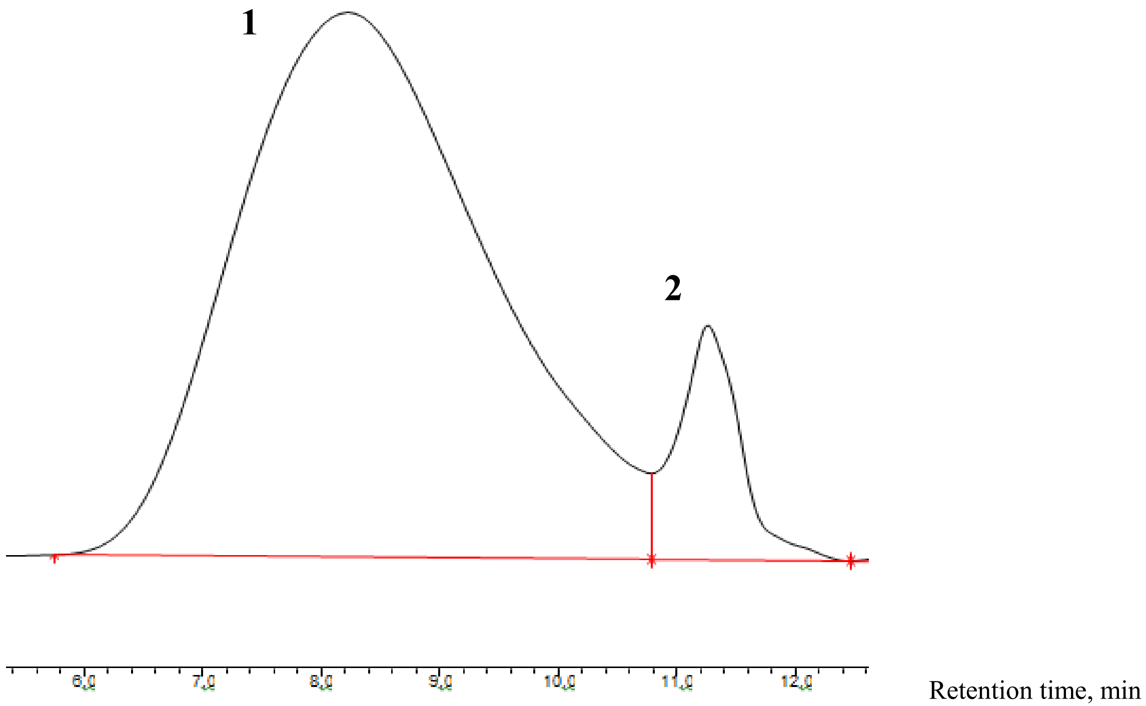
frequency (cm-1)

GPC curve

(1000A)



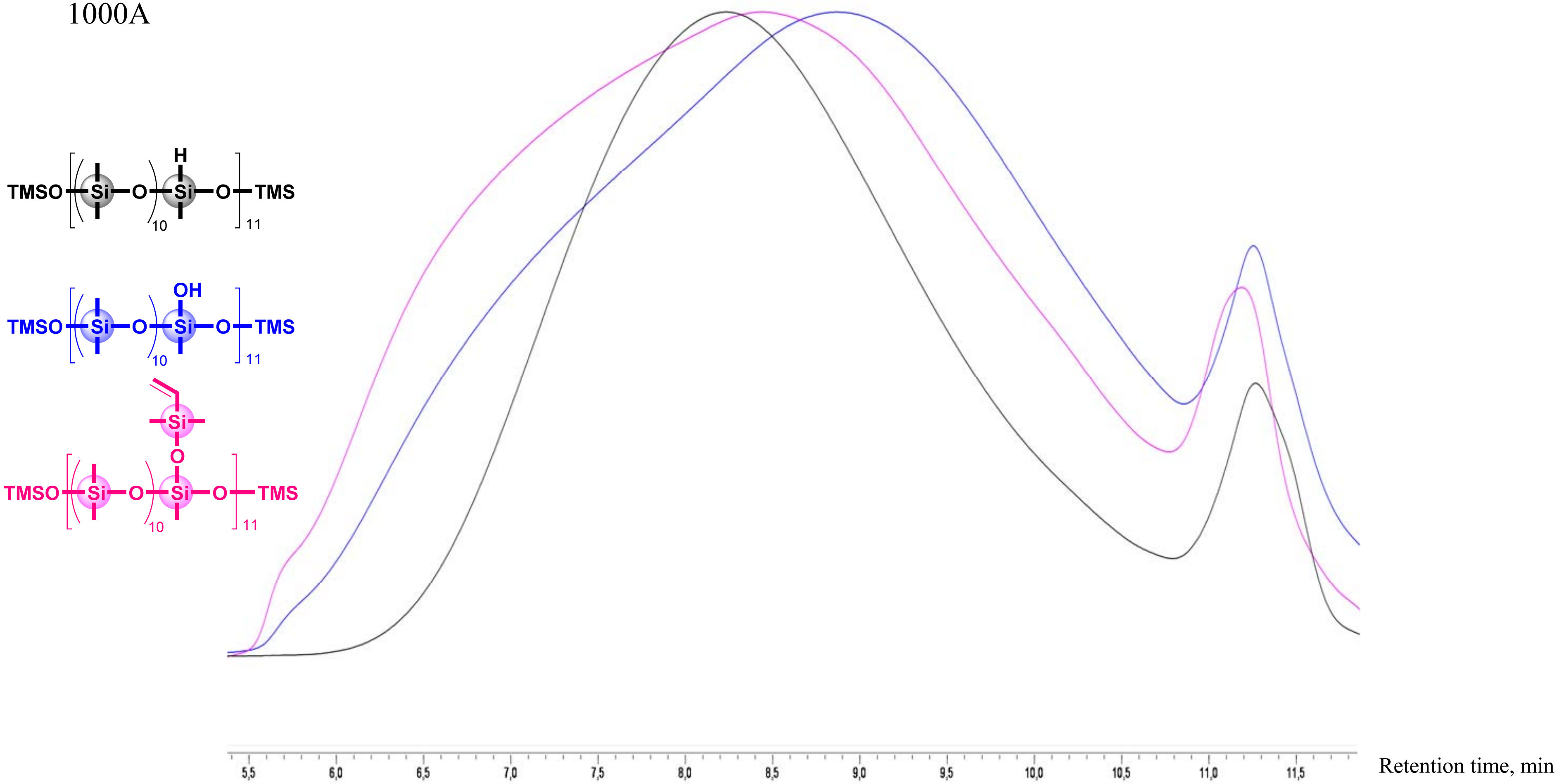
Peak 1. M_n (pss) = 4978

M_w (pss) = 9678

PDI = 1.94

GPC comparison

1000A



15. X-Ray data

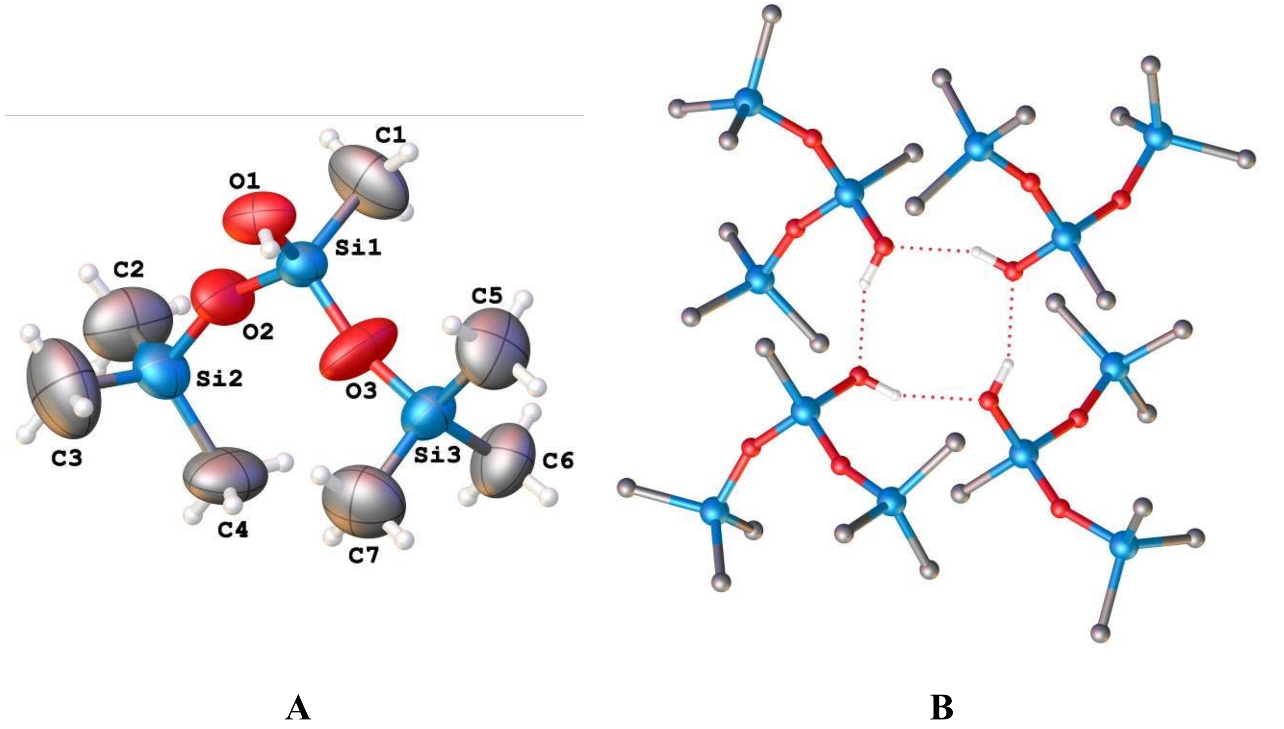


Figure 1. Molecular structure of 2a presented in thermal ellipsoids (50% probability) (A). Tetramers formed in crystal structure 2a via O-H…O bonds (B).

According to X-ray study at 230K compound **2a** crystallized in primitive tetragonal lattice. The lengths of Si1-O2 and Si1-O3 bonds (1.592(3) and 1.580(4) Å) differ by 0.01 Å than can be attributed to the anomeric effect hydroxyl group (e.g. the donation of electron density from the lone pair of O1 atom to the lowest unoccupied orbital of the Si-O3 bond). The Si1-O1 bond is noticeably longer than other Si-O ones in **2a**, possibly due to its participation in O-H…O bonds with the nearest molecules in crystal. Indeed, the molecules of **2a** form O-H…O bonded tetramers around -4 axis (Figure 1B).

At room temperature compound **2a** is viscous liquid. Thus, to measure the X-ray diffraction we crystallized **2a** *in situ* in thin glass capillary near the melting point. Upon cooling there was the phase transition because the changes in the diffraction pattern were clearly visible. Unfortunately, it was impossible to establish the structure at lower temperatures due to changes in crystal mosaicity than can be an indicative for the destruction of the single crystal. Most probably, crystals of **2a** at temperatures of 150 – 100 K retained the tetragonal lattice but changed the space group. Thus, we report crystallographic data measured at 230 K. The tables of bond lengths and angles can be found below. All crystallographic data was submitted to CSD (submission number **CCDC 1819095**) and can be obtained free of charge upon request.

Crystal Data for $C_7H_{22}O_3Si_3$ (M =238.51 g/mol): tetragonal, space group P-42$_1$c (no. 114), a = 17.5199(18) Å, c = 10.0567(14) Å, V = 3086.9(8) Å^3, Z = 8, μ(MoKα) = 0.291 mm^{-1}, d_{calc} = 1.026 g/cm^3, 30200 reflections measured (3.288° ≤ 2θ ≤ 62.112°), 4918 unique (R_{int} = 0.0730, R_{sigma} = 0.0686) which were used in all calculations. The final R_1 was 0.0500 (I > 2σ(I)) and wR_2 was 0.1359 (all data).

Table 1 Crystal data and structure refinement for 2a.

Identification code	exp230
Empirical formula	$C_7H_{22}O_3Si_3$
Formula weight	238.51
Temperature/K	230
Crystal system	tetragonal

Space group	P-4$2_1$c
a/Å	17.5199(18)
b/Å	17.5199(18)
c/Å	10.0567(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3086.9(8)
Z	8
ρ_{calc}g/cm^3	1.026
μ/mm^{-1}	0.291
F(000)	1040.0
Crystal size/mm^3	0.2 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.288 to 62.112
Index ranges	$-25 \le h \le 20$, $-15 \le k \le 23$, $-14 \le l \le 14$
Reflections collected	30200
Independent reflections	4918 [R_{int} = 0.0730, R_{sigma} = 0.0686]
Data/restraints/parameters	4918/0/125
Goodness-of-fit on F^2	0.945
Final R indexes [I>=2σ (I)]	R_1 = 0.0500, wR_2 = 0.1118
Final R indexes [all data]	R_1 = 0.1323, wR_2 = 0.1359
Largest diff. peak/hole / e Å^{-3}	0.17/-0.22
Flack parameter	-0.04(8)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si1	5406.3(5)	6758.2(5)	8770.7(10)	56.2(3)
Si2	5380.9(7)	8322.2(6)	10232.9(12)	74.8(3)
Si3	3968.4(7)	6832.2(6)	6913.8(12)	70.8(3)
O2	5575.1(19)	7496.2(15)	9646(3)	101.2(10)
O3	4681(2)	6934(2)	7886(4)	125.8(14)
O1	5233.1(14)	6048.9(15)	9745(3)	84.4(8)
C7	3116(4)	7111(4)	7841(7)	140(2)
C5	3901(4)	5830(3)	6378(7)	131(2)
C6	4114(4)	7470(3)	5490(5)	114.3(17)
C1	6244(4)	6539(3)	7787(6)	125(2)
C2	6303(4)	8816(3)	10460(7)	139(2)
C4	4765(4)	8859(3)	9067(7)	132(2)
C3	4907(6)	8181(5)	11819(6)	174(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Si1	59.5(6)	45.7(5)	63.4(5)	1.2(4)	-3.5(5)	2.6(4)
Si2	91.3(8)	48.2(5)	85.0(7)	-8.1(5)	2.2(7)	-1.9(5)
Si3	75.9(7)	65.2(6)	71.4(6)	5.8(5)	-17.0(5)	-4.1(6)
O2	121(2)	66.5(17)	116(2)	-28.9(17)	-33(2)	20.2(16)
O3	137(3)	93(2)	148(3)	14(2)	-86(3)	5(2)
O1	65.6(15)	74.4(17)	113(2)	34.0(16)	8.3(16)	-1.5(13)
C7	119(5)	144(5)	158(5)	12(5)	30(5)	4(4)

C5	173(6)	78(3)	143(5)	-13(3)	-14(5)	-28(4)
C6	147(5)	107(4)	89(3)	25(3)	-7(3)	-11(3)
C1	129(5)	102(4)	144(5)	11(3)	75(4)	-2(3)
C2	118(4)	102(4)	197(7)	3(4)	-30(5)	-28(3)
C4	138(5)	77(3)	180(6)	-3(4)	-30(5)	30(3)
C3	226(8)	168(7)	129(5)	-11(5)	64(6)	-28(6)

Table 4 Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	O2	1.592(3)	Si2	C4	1.850(6)
Si1	O3	1.581(3)	Si2	C3	1.816(6)
Si1	O1	1.612(3)	Si3	O3	1.596(3)
Si1	C1	1.811(5)	Si3	C7	1.828(6)
Si2	O2	1.600(3)	Si3	C5	1.840(5)
Si2	C2	1.846(6)	Si3	C6	1.834(5)

Table 5 Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Si1	O1	108.97(19)	C3	Si2	C2	110.8(4)
O2	Si1	C1	108.9(2)	C3	Si2	C4	111.0(4)
O3	Si1	O2	107.59(17)	O3	Si3	C7	107.3(3)
O3	Si1	O1	109.95(19)	O3	Si3	C5	109.7(3)
O3	Si1	C1	112.6(3)	O3	Si3	C6	107.5(2)
O1	Si1	C1	108.8(2)	C7	Si3	C5	110.6(3)
O2	Si2	C2	106.5(2)	C7	Si3	C6	110.4(3)
O2	Si2	C4	110.5(2)	C6	Si3	C5	111.2(3)
O2	Si2	C3	107.4(3)	Si1	O2	Si2	154.1(2)

C2	Si2	C4	110.5(3)	Si1	O3	Si3	162.1(3)

Table 6 Hydrogen Bonds for 2a.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O1	H1	O1[1]	0.83	1.98	2.711(4)	147.3

[1] 1-Y,+X,2-Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	***x***	***y***	***z***	**U(eq)**
H1	4779	5922	9672	127
H7A	3151	7646	8081	210
H7B	3077	6804	8642	210
H7C	2667	7030	7294	210
H5A	3817	5507	7147	197
H5B	4372	5682	5941	197
H5C	3478	5774	5762	197
H6A	4118	7996	5795	171
H6B	3703	7400	4856	171
H6C	4597	7353	5068	171
H1A	6297	6914	7082	188
H1B	6191	6035	7401	188
H1C	6693	6553	8351	188
H2A	6593	8562	11152	209
H2B	6211	9342	10714	209
H2C	6588	8803	9633	209
H4A	4254	8647	9083	197
H4B	4972	8821	8175	197

H4C	4746	9391	9333	197
H3A	4450	7878	11689	261
H3B	4769	8673	12193	261
H3C	5248	7918	12424	261

Experimental

Single crystal of $C_7H_{22}O_3Si_3$ were grown in glass capillary mounted on goniometer head at **'Bruker APEX-II CCD'** diffractometer. The crystal was kept at 230 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.5 times of:

All C(H,H,H) groups, All O(H) groups

2.a Tetrahedral OH refined with riding coordinates:

O1(H1)

2.b Idealised Me refined as rotating group:

C7(H7A,H7B,H7C), C5(H5A,H5B,H5C), C6(H6A,H6B,H6C), C1(H1A,H1B,H1C), C2(H2A,

H2B,H2C), C4(H4A,H4B,H4C), C3(H3A,H3B,H3C)

This report has been created with Olex2, compiled on 2017.08.10 svn.r3458 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.