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SUPPLEMENTARY INFORMATION

Stereoregular cyclic *p*-tolyl-siloxanes with alkyl, O- and N-containing groups as promising reagents for synthesis functionalized organosiloxanes

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S1. **Materials and methods**

All the starting materials were purchased from Acros and Sigma Aldrich company. Solvents were dried and purified according to standard procedures, *n*-butanol was purchased from PanReac and used without further purification. Allyl ethers of ethylene glycols were used freshly distilled, as long storage negatively affected the hydrosililation.

^{1}H, ^{13}C, ^{29}Si, HSQC, HMBC, HSQMBC and ^{1}H DOSY 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). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), m (multiplet).

High-resolution mass spectra were recorded on Bruker maXis QTOF (tandem quadrupole/time-of-flight mass analyzer) mass spectrometer equipped with an ESI source. The m/z scanning range was 100–3000. External calibration of the mass scale was carried out using a low-concentration calibration solution “Tuning mix” (Agilent Technologies). The data were processed using the Bruker Data Analysis 4.0 software.

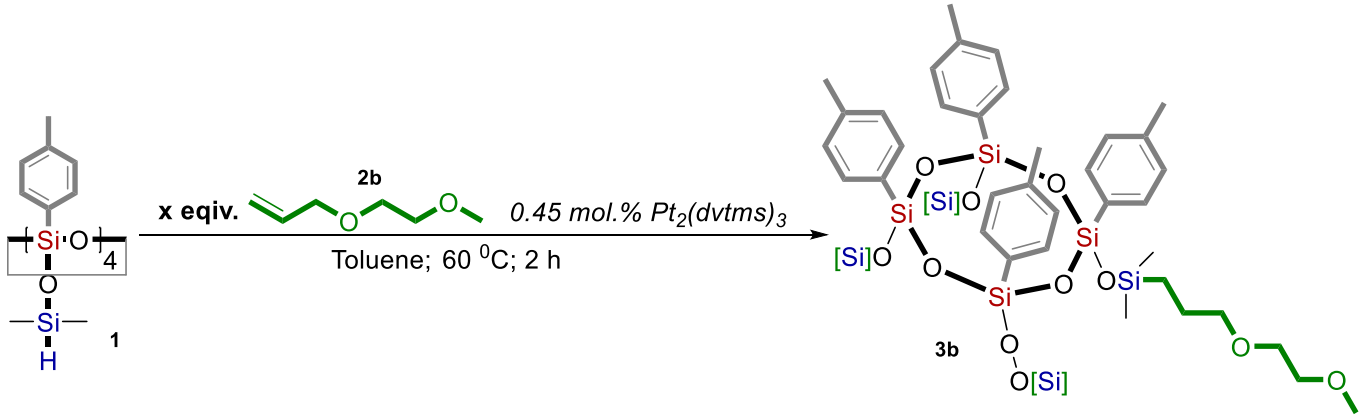
Single crystal X-ray study of compound 1 was carried out in Center for molecule composition studies of INEOS RAS with Bruker APEX-II CCD at 120K.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Shimadzu IRTracer100. Spectra were taken from thin films for liquids or from pills for solids.

GPC analysis was performed on the "Shimadzu" (Japan, Germany), the detector - refractometer RID - 20 Å, the column – Phenogel 5u 500 Å (Size (300 x 7,8 mm)); standart – polystyrene, eluent – THF; temperature – 40°C; speed of flow 1ml/min.
Single crystal X-ray study of compound **3** was carried out in Center for molecule composition studies of INEOS RAS with Bruker APEX-II CCD at 120K.

S2. Screening of reaction conditions for the compound 3b

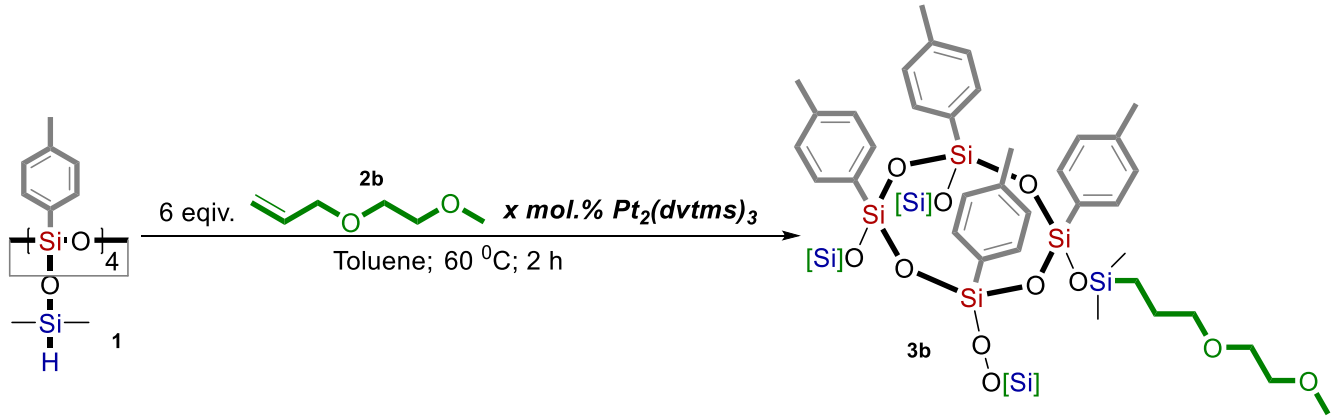
Table S1. The effect of alkene loading [a]



x eqiv., 2b	4	4.4	6	8
Conversion of ***[Si]–H***, %	*98*	*100*	***100***	*100*
Conversion of ***[Si]–H*** - to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups, %	*65*	*72*	***94***	*94*

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2b** (0.12—0.24 mmol, 4—8 eq.), Toluene (0.25 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.45 mol %, 3 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. The conversion of ***[Si]–H*** to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra.

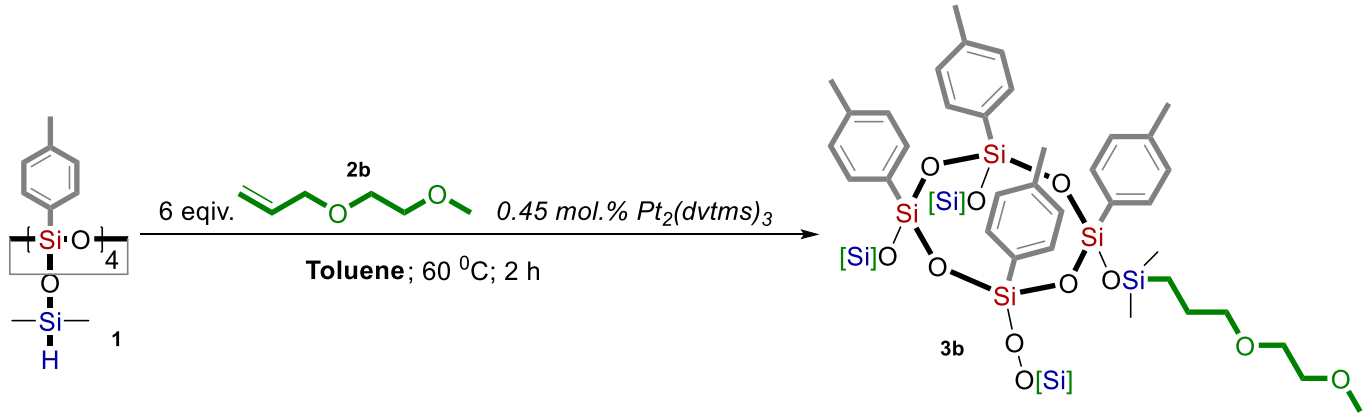
Table S2. The effect of catalyst loading [a]



x mol % $Pt_2(dvtms)_3$	**0.45**	**0.225**	**0.045**
Conversion of ***[Si]–H***, %	***100***	*100*	*100*
Conversion of ***[Si]–H*** - to ***[Si]–CH₂***$CH_2CH_2OC_2H_4OCH_3$ - groups, %	***94[b]***	*93*	*93*

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2b** (0.18 mmol, 6 eq.), Toluene (0.25 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.045—0.45 mol %, 3 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. The conversion of ***[Si]–H*** to ***[Si]–CH₂***$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra. [b] It has been shown that a 10-fold decrease in the catalyst loading - from 0.45 to 0.045 mol% - makes it possible to carry out this process with high efficiency; however, a loading of 0.45 mol% was chosen with a margin for the convenience of loading the catalyst, as well as transferring the reaction conditions to less reactive substrates. Reduced catalyst loading have been used in scaling up the process (see Table S6).

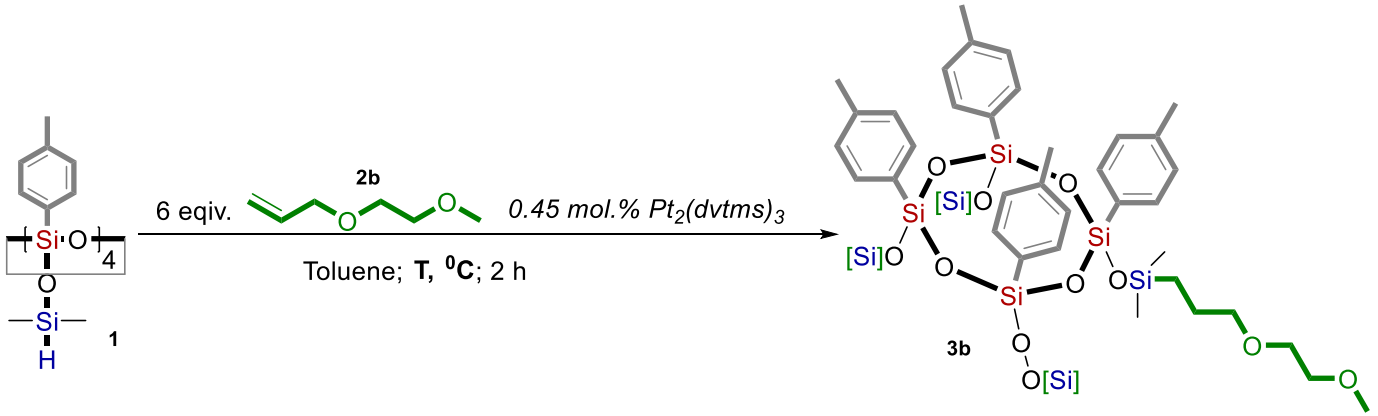
Table S3. The effect of solvent loading [a]



Toluene, mL	**0**	**0.1**	**0.25**	**0.5**	**1**
Conversion of ***[Si]–H***, %	*100*	*100*	***100***	*100*	*100*
Conversion of ***[Si]–H*** - to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups, %	*90*	*90*	***94***	*94*	*94*

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2b** (0.18 mmol, 6 eq.), Toluene (0—1 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.45 mol %, 3 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. The conversion of ***[Si]–H*** to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra.

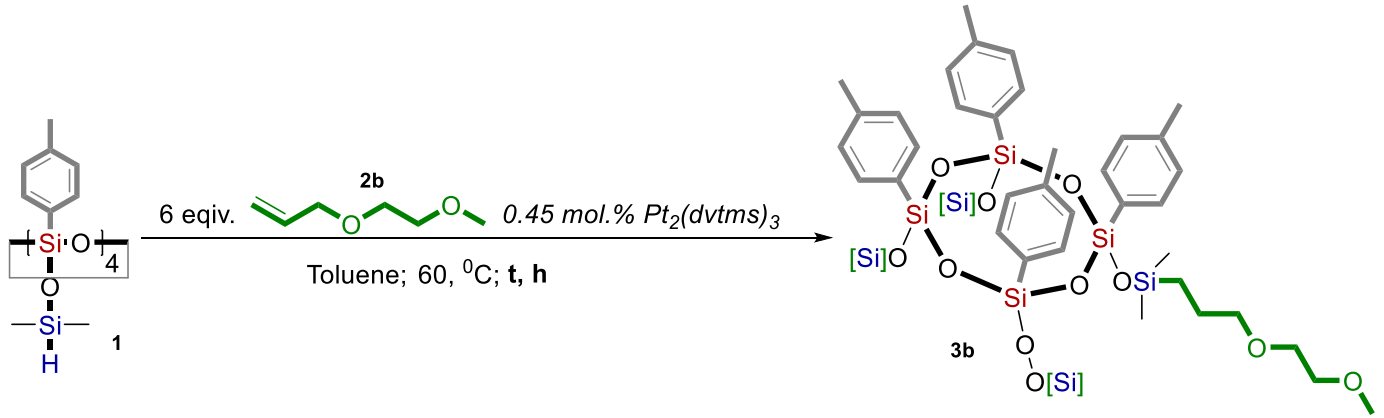
Table S4. The effect of temperature [a]



T, ^{0}C	25	40	60
Conversion of ***[Si]–H***, %	*100*	*100*	***100***
Conversion of ***[Si]–H*** - to ***[Si]–CH$_2$***$CH_2CH_2OC_2H_4OCH_3$ - groups, %	*89*	*91*	***94***

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2a** (0.18 mmol, 6 eq.), Toluene (0.25 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.45 mol %, 3 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 25—60 °C for 2 h. The conversion of ***[Si]–H*** to ***[Si]–CH$_2$***$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra.

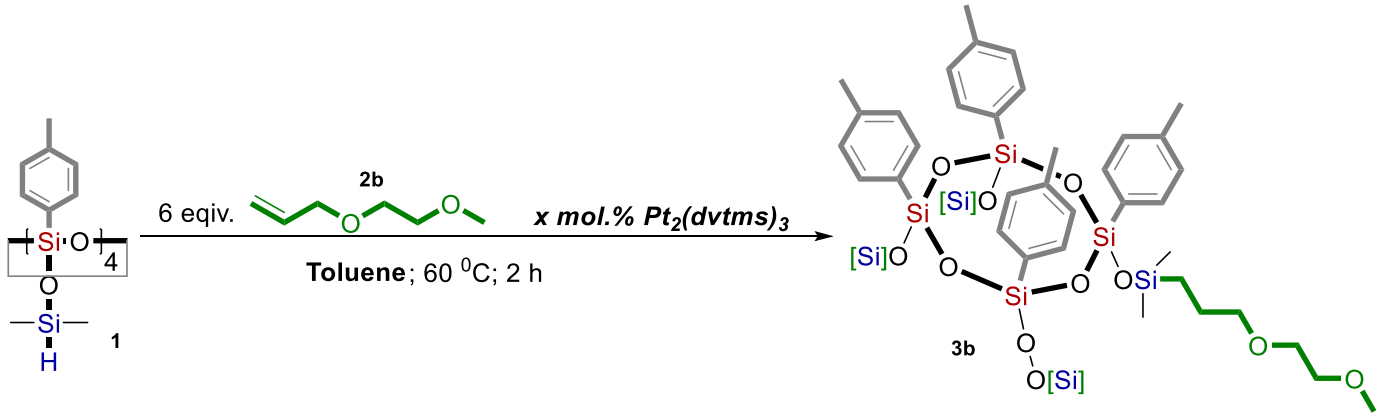
Table S5. The effect of reaction time [a]



t, h	0.5	1	2	6	16[b]
Conversion of ***[Si]–H***, %	*100*	*100*	***100***	*100*	*100*
Conversion of ***[Si]–H*** - to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups, %	*91*	*92*	***94***	*94*	*94*

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2b** (0.18 mmol, 6 eq.), Toluene (0.25 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.45 mol %, 3 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 0.5—6 h. The conversion of ***[Si]–H*** to ***[Si]–CH***$_2$$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra. [b] Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.1 mol %, 0.7 mkL)

Table S6. The effect of scaling [a]



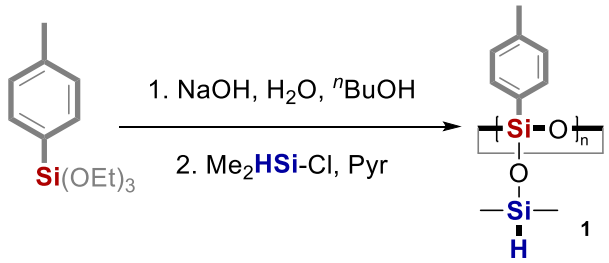
1, g	x mol % $Pt_2(dvtms)_3$	Toluene, ml	Conversion of ***[Si]–H***, %	Conversion of ***[Si]–H*** - to ***[Si]–C***$H_2CH_2CH_2OC_2H_4OCH_3$ - groups, %
0.025	0.45	*0.25*	*100*	*94*
0.1	0.45	*1*	*100*	*94*
0.5	0.225	*2.5*	*100*	*94*
1	0.1125	*2.5*	*100*	*94*

5	0.0225	*2.5*	*100*	*94*

[a] Reaction conditions: **1** (0.03 mmol, 1 eq.), **2b** (0.18 mmol, 6 eq.), Toluene (0.25—2.5 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.0225—0.45 mol %, 3—30 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. The conversion of ***[Si]–H*** to ***[Si]–CH$_2$***$CH_2CH_2OC_2H_4OCH_3$ - groups was determined by ^{1}H NMR spectra.

S3. Methods of synthesis and characterization data for 1 and 3a–g

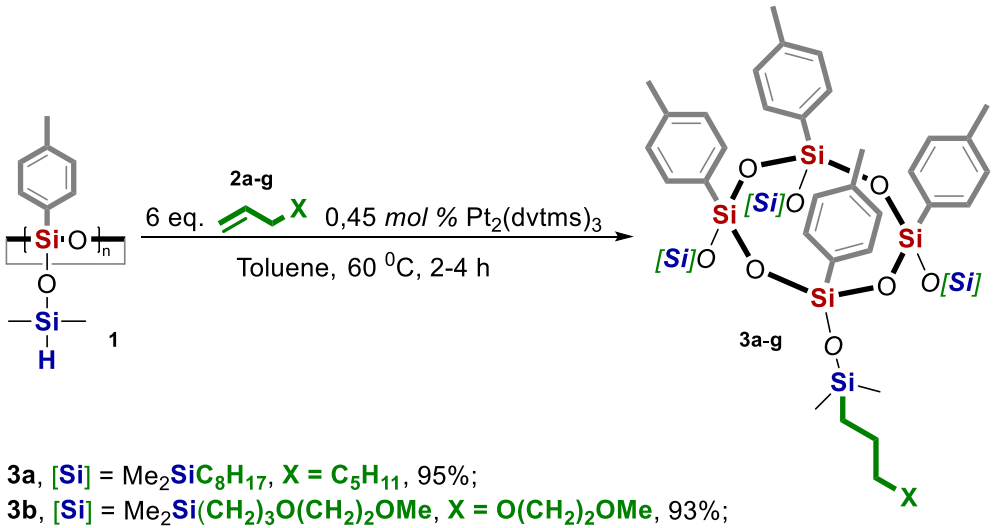
3.1 Synthesis of the compound 1[a]



[a]Reaction conditions:[1] Triethoxy-p-tolylsilane (0.039 mol, 1 eq.), NaOH (0.043 mol, 1.1 eq.), H_2O (0.039 mol, 1 eq.) and ^{n}BuOH (100 mL) were vigorously stirred under reflux until the solution became completely transparent and then for 1 more hour. Within a few hours, crystals were formed and precipitated from the solution. The crystals were separated by filtration through a Schott filter, washed with ^{n}BuOH and dried in vacuo (1 mbar / T_{room} /1 h). Resulting crystalline product was added as a solid to a vigorously stirred mixture of dry toluene (1 L), pyridine (0.168 mol, 16 eq.) and dimethylchlorosilane (DMCS) (0.210 mol, 20 eq.) at room temperature. The mixture was stirred at room temperature for 16 h, then precipitate was filtered and organic layer was washed with water until neutral medium. The organic layer was collected, dried over Na_2SO_4, and filtered, then the solvent was evaporated and the residue was dried under vacuum (1 mbar / T_{room} /1 h). Product **1** was obtained as a colorless oil in 6.2 g (75 %) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 24H); δ = 2.28 (s, 12H); δ = 4.86 (s, 4H); 6.97 (d, 8H); 7.24 (d, 8H); ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -77.44; -3.85; GPC: Mn = 941, Mw = 972, PDI = 1.03.[2]

The oil spontaneously crystalizes at room temperature within a week. The molecular structure of these crystals was analysed using X-Ray analysis.

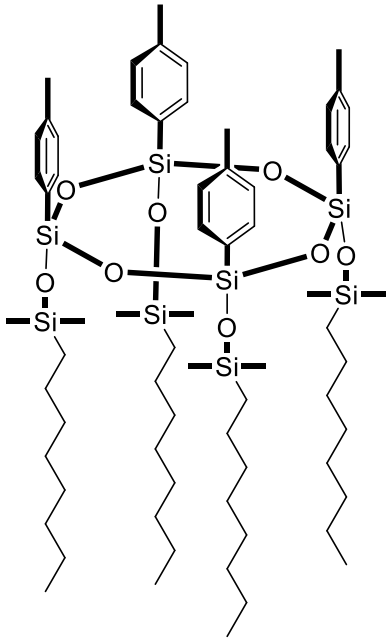
3.2 Synthesis of compounds 3a-g[a]



3a, [Si] = $Me_2SiC_8H_{17}$, X = C_5H_{11}, 95%;
3b, [Si] = $Me_2Si(CH_2)_3O(CH_2)_2OMe$, X = $O(CH_2)_2OMe$, 93%;
3c, [Si] = $Me_2Si(CH_2)_3O[(CH_2)_2O]_2Me$, X = $O[(CH_2)_2O]_2Me$, 92%;
3d, [Si] = $Me_2Si(CH_2)_3O[(CH_2)_2O]_3Me$, X = $O[(CH_2)_2O]_3Me$, 92%;
3e, [Si] = $Me_2Si(CH_2)_3O[(CH_2)_2O]_3H$, X = $O[(CH_2)_2O]_3H$, 60%;
3f, [Si] = $Me_2Si(CH_2)_3NEt_2$, X = NEt_2, 95%; **3g**, [Si] = $Me_2Si(CH_2)_3N(SiMe_3)_2$, X = $N(SiMe_3)_2$, 91%

[a]Reaction conditions: **1** (0.1 g, 0.12 mmol, 1 eq.), **2a—g** (0.081-0.147 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and Karstedt's catalyst ($Pt_2(dvtms)_3$, 0.45 mol %, 12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2—4 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1). The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Products **3a—g** were obtained as colorless oils in 60—95 % yields.

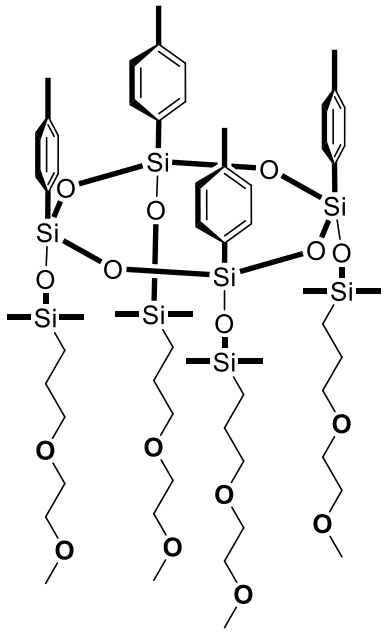
*(2,4,6,8-tetrakis(p-tolyl)-2,4,6,8-tetraoctyl-1,3,5,7,2,4,6,8-tetroxatetrasiloxane, **3a**)*



Method of **3a** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2a** (0.08 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3a** was obtained as colorless oil in 95 % yield (0.147 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 24H); δ = 0.62 (m, 8H); δ = 0.91 (t, 12H); δ = 1.26 (m, 48H); δ = 2.30 (s, 12H); 6.92 (d, 8H); 7.22 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.29, 14.11, 18.17, 21.49, 22.69, 23.19, 29.40, 32.00, 33.54, 127.99, 129.98, 134.11, 139.16; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.32; 10.32; IR (cm^{-1}): 3060, 2920, 1615, 1470, 1250, 1053; HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{68}H_{120}O_8Si_8 + Na]^+$, 1312.7060; found, 1312.7016; $[M + K]^+$: calcd for $[C_{68}H_{120}O_8Si_8 + K]^+$, 1328.6799; found, 1328.6740. GPC: Mn = 1249, Mw = 1295, PDI = 1.04.

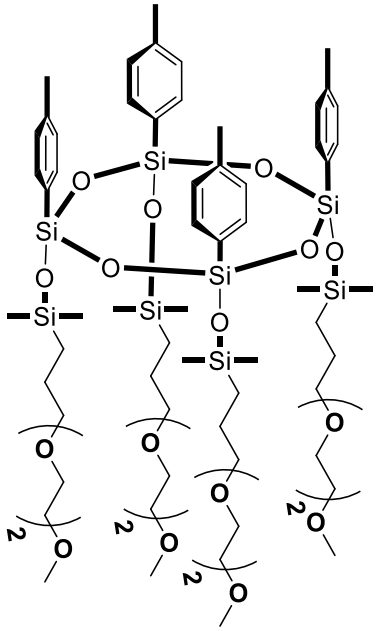
*(2,4,6,8-tetrakis[3-(2-methoxyethoxy)propyl]-2,4,6,8-tetrakis(p-tolyl)-1,3,5,7,2,4,6,8-tetroxatetrasiloxane, **3b**)*



Method of **3b** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2b** (0.083 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3b** was obtained as colorless oil in 93 % yield (purity 97 % according to GPC and ^{1}H NMR spectra, 0.146 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 24H); δ = 0.57 (m, 8H); δ = 1.60 (m, 8H); δ = 2.29 (s, 12H); δ = 3.37 (t, 8H); δ = 3.39 (s, 12H); δ = 3.52 (m, 16H); 6.91 (d, 8H); 7.18 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.18, 13.90, 21.46, 23.19, 58.99, 69.79, 71.96, 74.13, 128.05, 129.58, 134.01, 139.32; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.08; 10.61; IR (cm^{-1}): 3015, 2870, 1605, 1455, 1250, 1053; HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{60}H_{104}O_{16}Si_8 + Na]^+$, 1328.5401; found, 1328.5476; $[M + K]^+$: calcd for $[C_{60}H_{104}O_{16}Si_8 + K]^+$, 1344.5140; found, 1344.5198. GPC: Mn = 1321, Mw = 1373, PDI = 1.04.

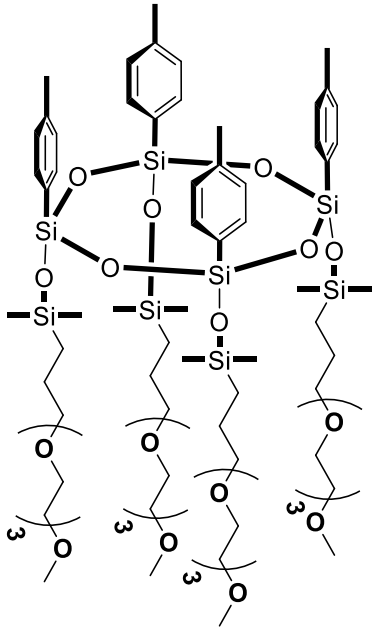
*(2,4,6,8-tetrakis{3-[2-(2-methoxyethoxy)ethoxy]propyl}-2,4,6,8-tetrakis(p-tolyl)-1,3,5,7,2,4,6,8-tetroxatetrasiloxane, **3c**)*



Method of **3c** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2c** (0.114 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3c** was obtained as colorless oil in 92 % yield (purity 95 % according to GPC and ^{1}H NMR spectra, 0.162 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 24H); δ = 0.57 (m, 8H); δ = 1.58 (m, 8H); δ = 2.28 (s, 12H); δ = 3.36 (t, 8H); δ = 3.39 (s, 12H); δ = 3.62 (m, 32H); 6.91 (d, 8H); 7.18 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.19, 13.92, 21.46, 23.21, 58.97, 69.90, 70.50, 71.94, 74.06, 128.06, 129.57, 134.00, 139.33; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.08; 10.59; IR (cm^{-1}): 3040, 2870, 1605, 1455, 1250, 1053; HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{68}H_{120}O_{20}Si_8 + Na]^+$, 1504.6450; found, 1504.6503; $[M + K]^+$: calcd for $[C_{68}H_{120}O_{20}Si_8 + K]^+$, 1520.6189; found, 1520.6242. GPC: Mn = 1465, Mw = 1589, PDI = 1.05.

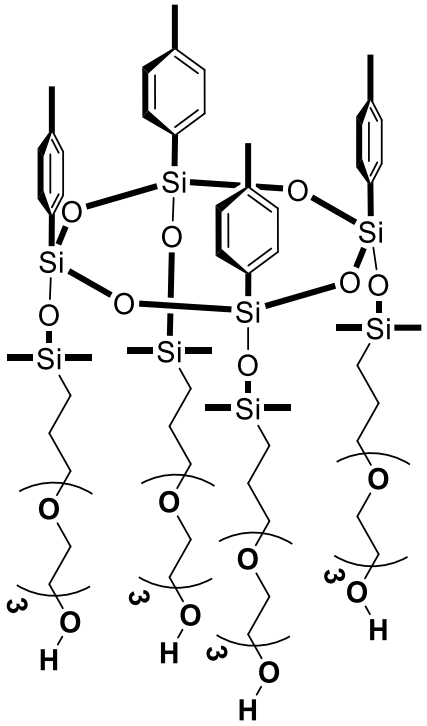
*(2,4,6,8-tetrakis(p-tolyl)-2,4,6,8-tetra-4,7,10,13-tetraoxatetradec-1-yl-1,3,5,7,2,4,6,8-tetroxatetrasiloxane, **3d**)*



Method of **3d** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2d** (0.146 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3d** was obtained as colorless oil in 92 % yield (purity 95 % according to GPC and ^{1}H NMR spectra, 0.181 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 24H); δ = 0.57 (m, 8H); δ = 1.58 (m, 8H); δ = 2.28 (s, 12H); δ = 3.35 (t, 8H); δ = 3.39 (s, 12H); δ = 3.66 (m, 48H); 6.90 (d, 8H); 7.17 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.18, 13.90, 21.45, 23.19, 58.96, 69.86, 70.55, 71.91, 74.05, 128.05, 129.55, 133.99, 139.32; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.08; 10.58; IR (cm^{-1}): 3040, 2870, 1605, 1455, 1250, 1053; HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{76}H_{136}O_{24}Si_8 + Na]^+$, 1680.7499; found, 1680.7533; $[M + K]^+$: calcd for $[C_{76}H_{136}O_{24}Si_8 + K]^+$, 1696.7238; found, 1696.7280. GPC: Mn = 1686, Mw = 1760, PDI = 1.05.

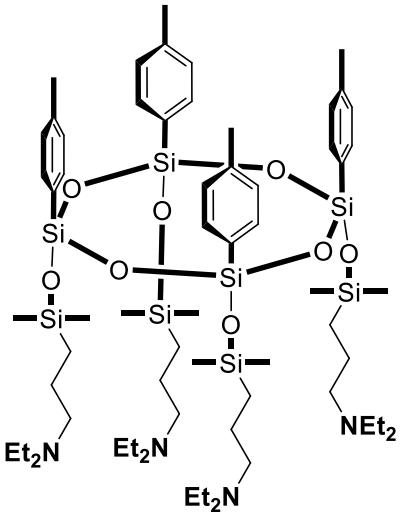
*(2,4,6,8-tetrakis(p-tolyl)-2,4,6,8-tetra-4,7,10,13-tetraoxatetradec-1-yl-1,3,5,7,2,4,6,8-tetroxatetrasiloxane, **3e**)*



Method of **3e** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2e** (0.137 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3e** was obtained as colorless oil in 60 % yield (purity 95 % according ^{1}H NMR spectra, 0.115 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 24H); δ = 0.58 (m, 8H); δ = 1.59 (m, 8H); δ = 2.27 (s, 12H); δ = 3.35 (t, 8H); δ = 3.39 (s, 12H); δ = 3.66 (m, 48H); 6.90 (d, 8H); 7.17 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.10, 13.80, 21.36, 23.07, 61.54, 69.75, 70.24, 70.49, 72.41, 73.94, 127.95, 129.44, 133.88, 139.23; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.07; 10.60; IR (cm^{-1}): 3450, 3040, 2870, 1605, 1455, 1250, 1053; HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{72}H_{128}O_{24}Si_8 + Na]^+$, 1624.6872; found, 1624.6859; HRMS (ESI) m/z $[M + K]^+$: calcd for $[C_{72}H_{128}O_{24}Si_8 + K]^+$, 1640.6612; found, 1640.6591

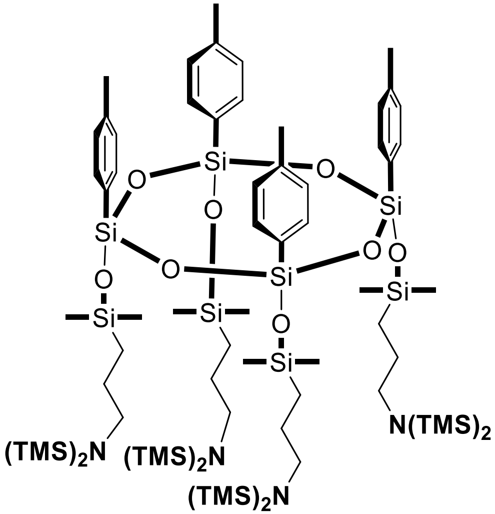
(3,3',3'',3'''-[2,4,6,8-tetrakis(p-tolyl)-1,3,5,7,2,4,6,8-tetroxatetrasilocane-2,4,6,8-tetrayl]tetrakis(N,N-diethylpropan-1-amine) ***3f)***



Method of **3f** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2f** (0.081 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 2 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3f** was obtained as colorless oil in 95 % yield (purity 99 % according to GPC and ^{1}H NMR spectra, 0.148 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 24H); δ = 0.54 (m, 8H); δ = 0.99 (t, 24H); δ = 1.41 (m, 8H); δ = 2.28 (s, 12H); δ = 2.35 (t, 8H); δ = 2.47 (q, 8H); 6.91 (d, 8H); 7.19 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.28, 11.72, 15.81, 20.49, 21.47, 46.80, 56.52, 128.04, 129.69, 134.04, 139.28; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.13; 10.46; IR (cm^{-1}): 3040, 2870, 1610, 1455, 1250, 1053; HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{64}H_{116}O_8N_4Si_8 + H]^+$, 1294.7050; found, 1294.7087; GPC: Mn = 1006, Mw = 1061, PDI = 1.05.

(N,N',N'',N'''-[[2,4,6,8-tetrakis(p-tolyl)-1,3,5,7,2,4,6,8-tetroxatetrasiloxane-2,4,6,8-tetrayl]tetrakis(propane-3,1-diyl)]tetrakis[1,1,1-trimethyl-N-(trimethylsilyl)silanamine], ***3g****)*



Method of **3g** synthesis: **1** (0.1 g, 0.12 mmol, 1 eq.), **2g** (0.144 g, 0.72 mmol, 6 eq.), Toluene (1 mL) and (0.45 mol.% $Pt_2(dvtms)_3$) Karstedt's catalyst (12 mkL) were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) at 60 °C for 4 h. Then all volatiles were evaporated (40 ^{0}C / 1 mbar). Reaction mass was filtered through a short pad (4 cm) of silica gel (V = 10 mL) by eluent: Hexane / EtOAc – 1 / 1. The solvent was evaporated and the residue was dried under vacuum (40 ^{0}C / 1 mbar). Product **3g** was obtained as colorless oil in 91 % yield (purity 98 % according to GPC and ^{1}H NMR spectra, 0.18 g).

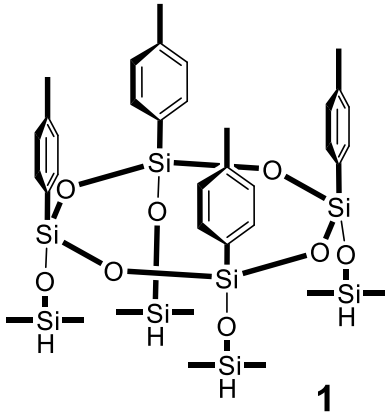
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 72H); δ = 0.21 (s, 24H); δ = 0.49 (m, 8H); δ = 1.31 (m, 8H); δ = 2.29 (s, 12H); δ = 2.69 (m, 8H); 6.91 (d, 8H); 7.20 (d, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.26, 2.09, 15.44, 21.49, 28.88, 49.13, 128.07, 129.69, 134.07, 139.25; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = -79.13; 5.07; 10.10; IR (cm^{-1}): 3040, 2870, 1610, 1455, 1250, 1053; GPC: Mn = 1820, Mw = 1890, PDI = 1.04.

S4. ^{1}H, ^{13}C and ^{29}Si, HSQC and HMBC NMR, GPC, IR, ESI

MS spectra of 1 and 3a-g

^{1}H NMR

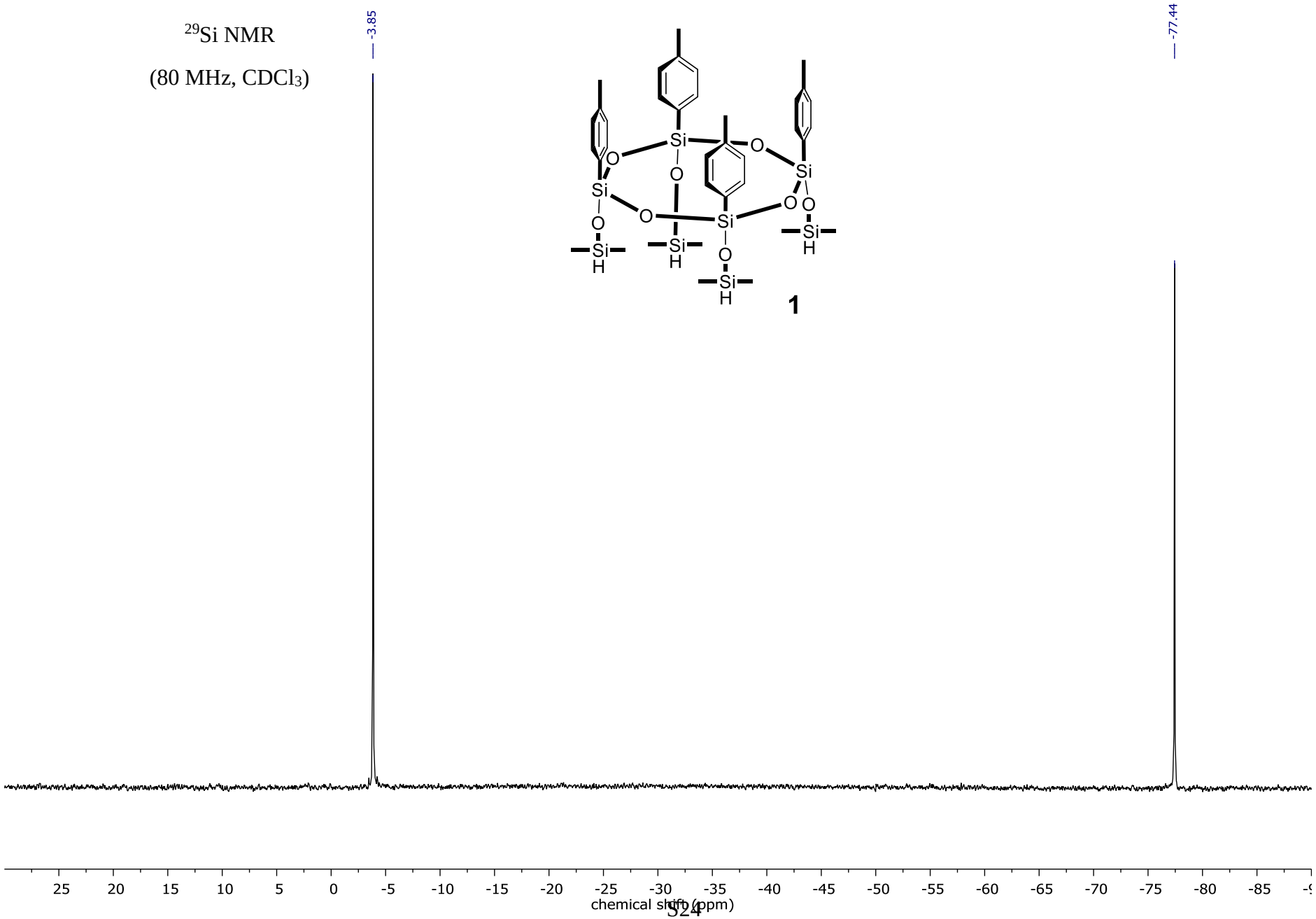
(400 MHz, $CDCl_3$)



1

^{29}Si NMR

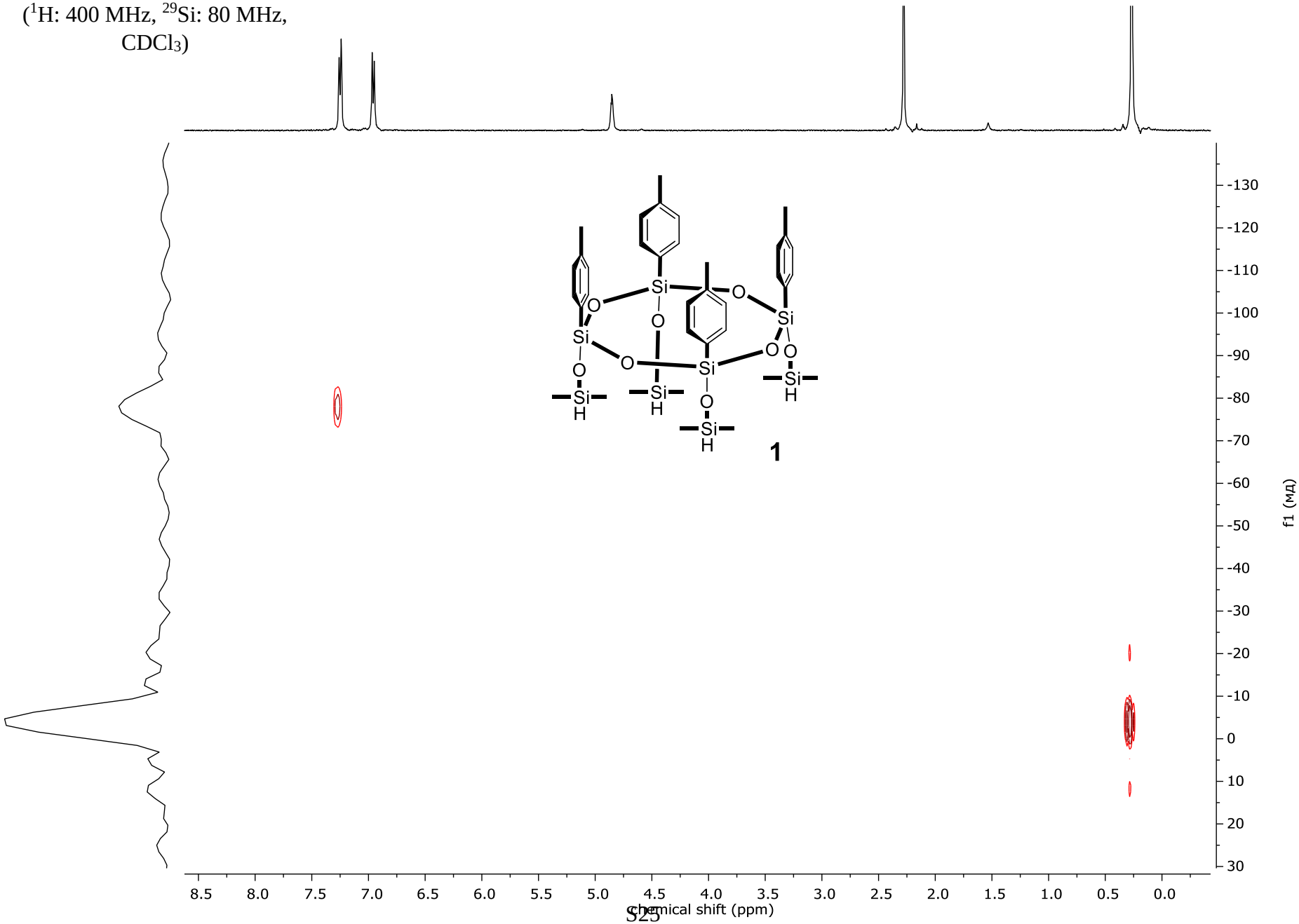
(80 MHz, $CDCl_3$)



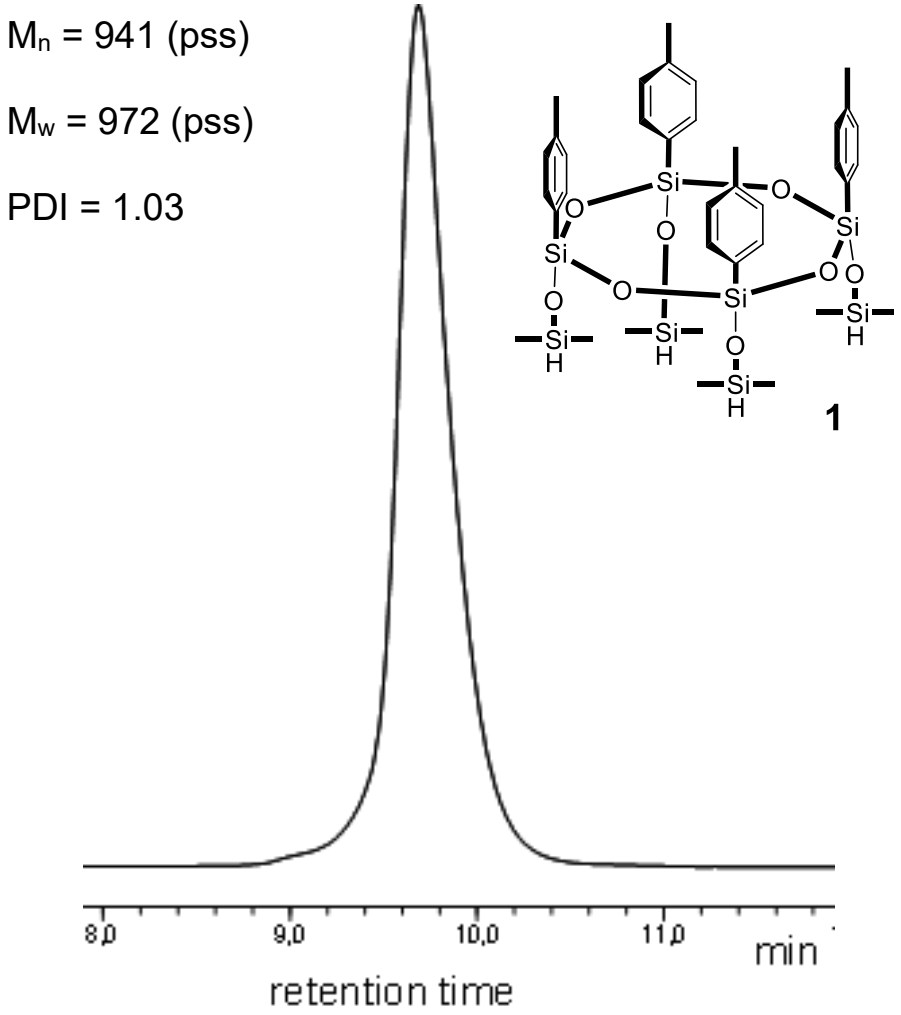
1

^{1}H,^{29}Si–HMBC NMR

(^{1}H: 400 MHz, ^{29}Si: 80 MHz, $CDCl_3$)



GPC



X-ray dataset for compound **1** were measured with Bruker APEX DUO (Mo radiation) diffractometer in Centre for Molecular composition studies of INEOS RAS. Experimental and crystallographic data are summarized in Table S7. Structures were solved

by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C–H bond lengths and equivalent displacement parameters (Ueq(H) = 1.2Ueq(X), X – central atom of XH_2 group; Ueq(H) = 1.5Ueq(Y), Y – central atom of YH_3 group. All structures were solved with the ShelXT program and refined with the ShelXL program. Molecular graphics was drawn using OLEX2 program.[3-5] CCDC **2069758** contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

Compound **1** forms colorless crystals with an orthorhombic unit cell (spacegroup $P2_12_12_1$) with two molecule per asymmetric unit. Some $SiH(CH_3)_2$ groups are disordered. The molecules form layers, where molecules interact by weak C–H…O contacts. Molecules from different "layers" interact by C–H…H–C and C–H…π contacts. So, tolyl fragments do not form any stacking interactions.

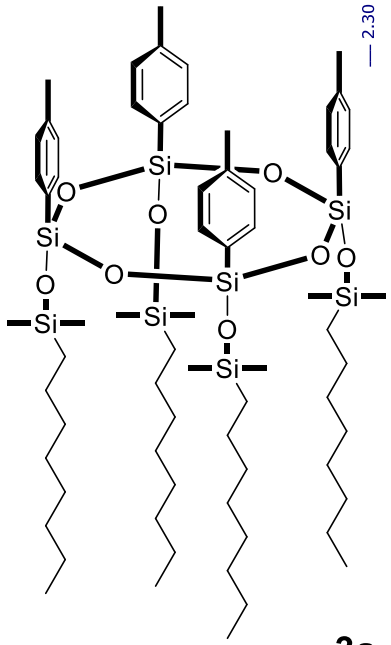
Table S7 Crystal data and structure refinement for yr516.

Identification code	1
Empirical formula	$C_{36}H_{56}O_8Si_8$
Formula weight	841.52
Temperature/K	120
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.2751(14)
b/Å	22.028(2)
c/Å	41.384(7)

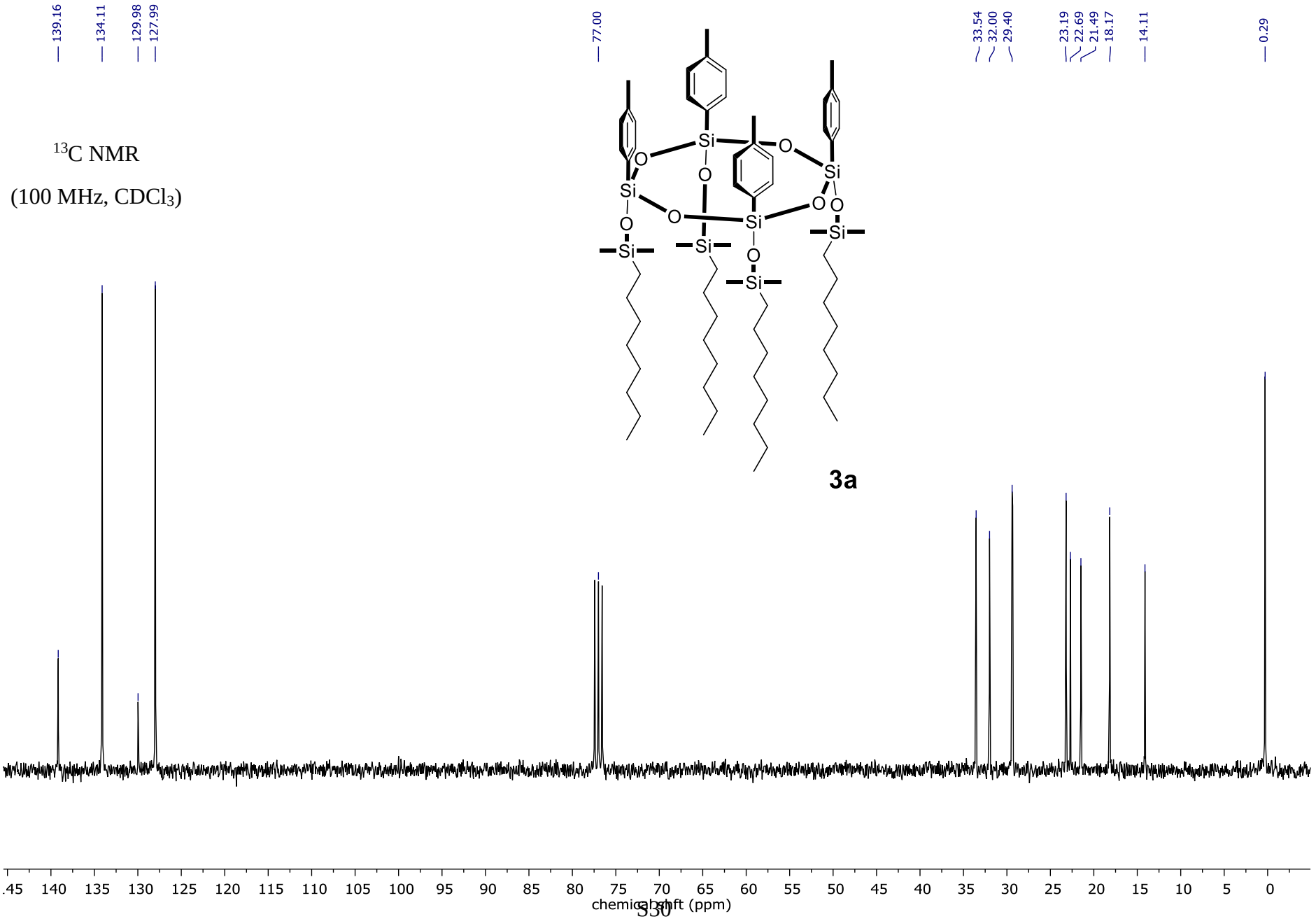
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9367(2)
Z	8
ρ_{calc}g/cm^3	1.194
μ/mm^{-1}	0.272
Crystal size/mm^3	0.21 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.968 to 61.344
Index ranges	-14 ≤ h ≤ 14, -31 ≤ k ≤ 31, -59 ≤ l ≤ 59
Reflections collected	109594
Independent reflections	28693 [R_{int} = 0.1182, R_{sigma} = 0.1250]
Data/restraints/parameters	28693/13/991
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0831, wR_2 = 0.1735
Final R indexes [all data]	R_1 = 0.1305, wR_2 = 0.1938
Largest diff. peak/hole / e Å^{-3}	0.72/-0.58
Flack parameter	0.03(5)

^{1}H NMR

(400 MHz, $CDCl_3$)

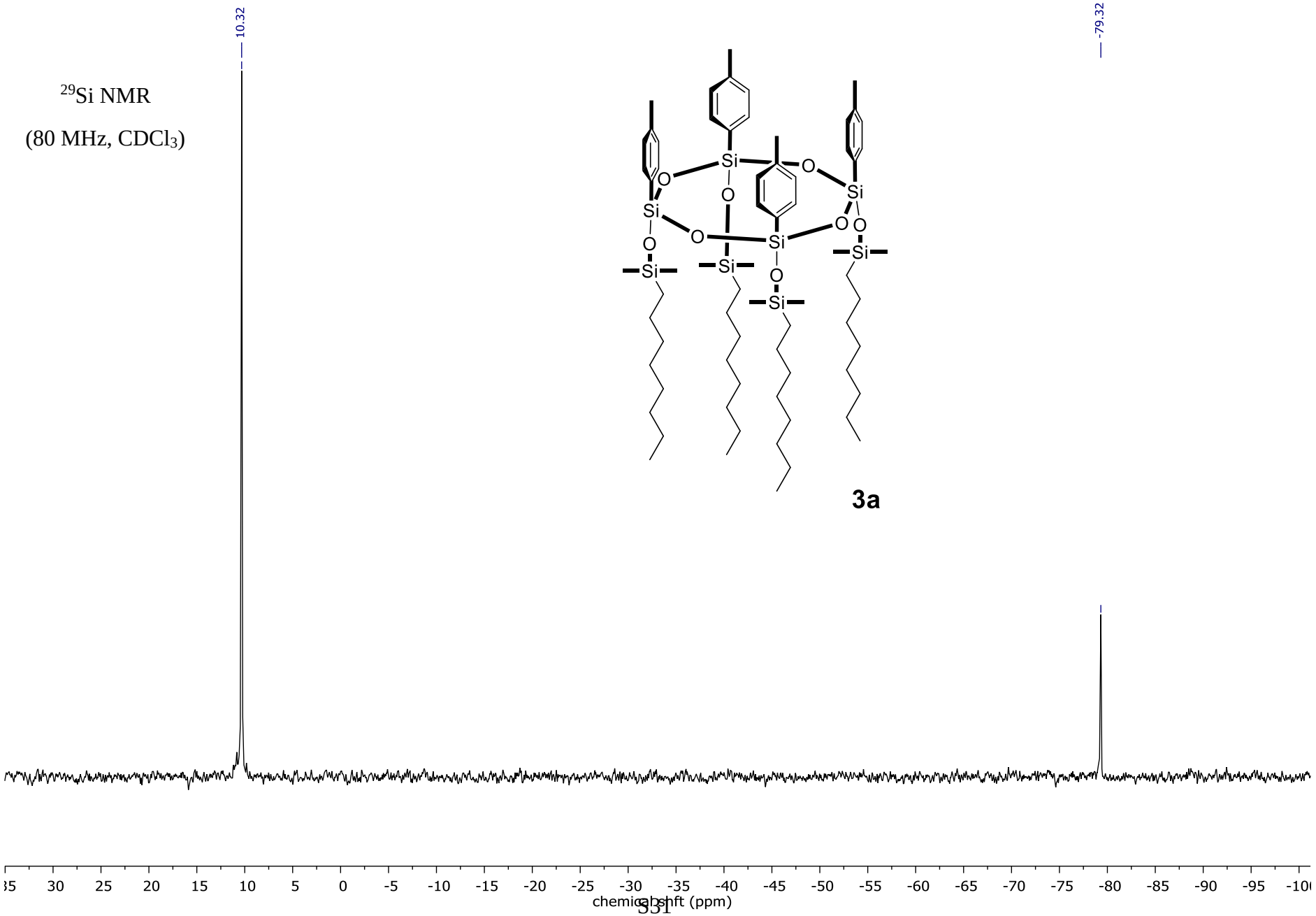


3a


139.16
134.11
129.98
127.99
77.00
33.54
32.00
29.40
23.19
22.69
21.49
18.17
14.11
0.29
^{13}C NMR
(100 MHz, $CDCl_3$)
3a
chemical shift (ppm)

^{29}Si NMR

(80 MHz, $CDCl_3$)

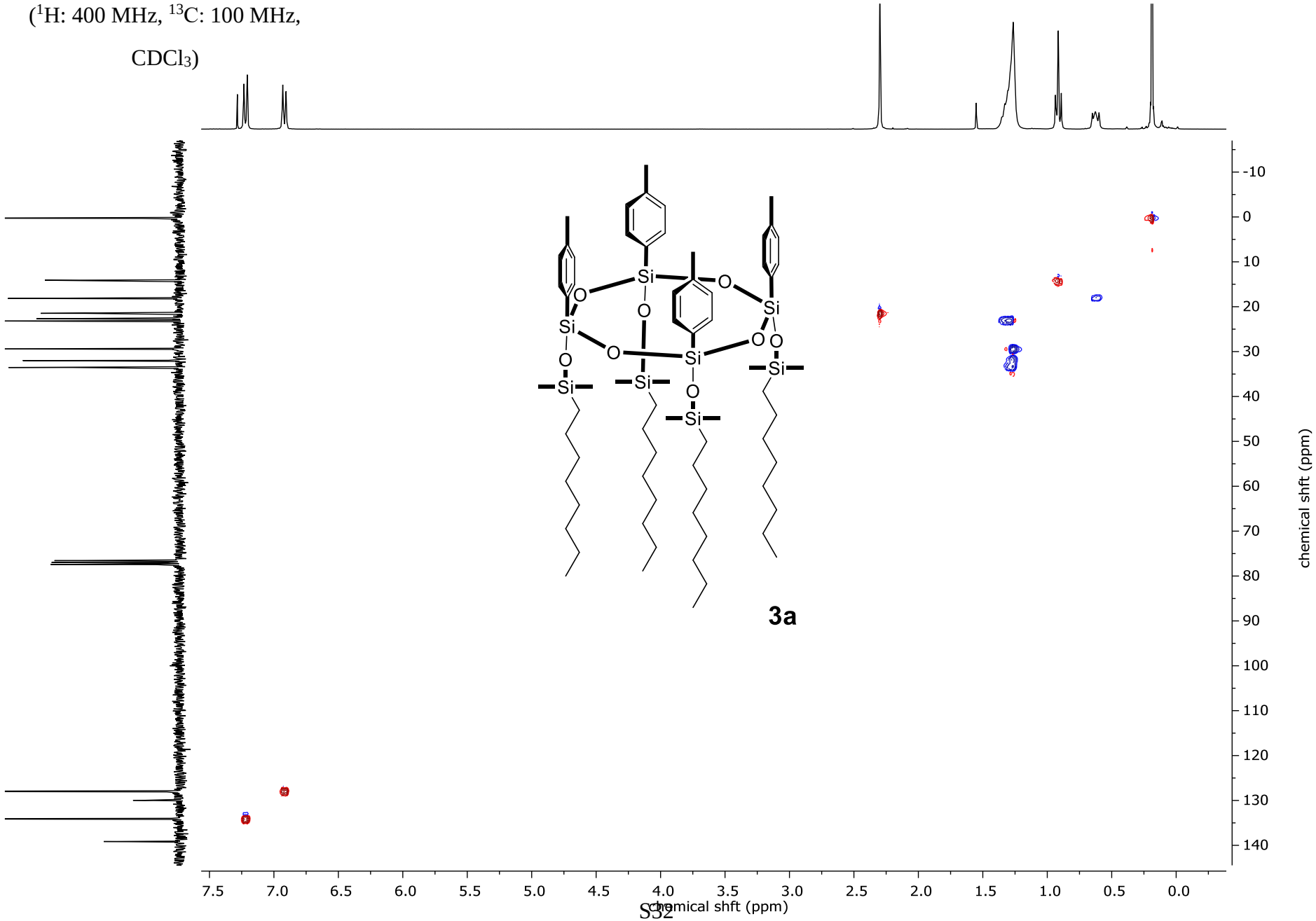


3a

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

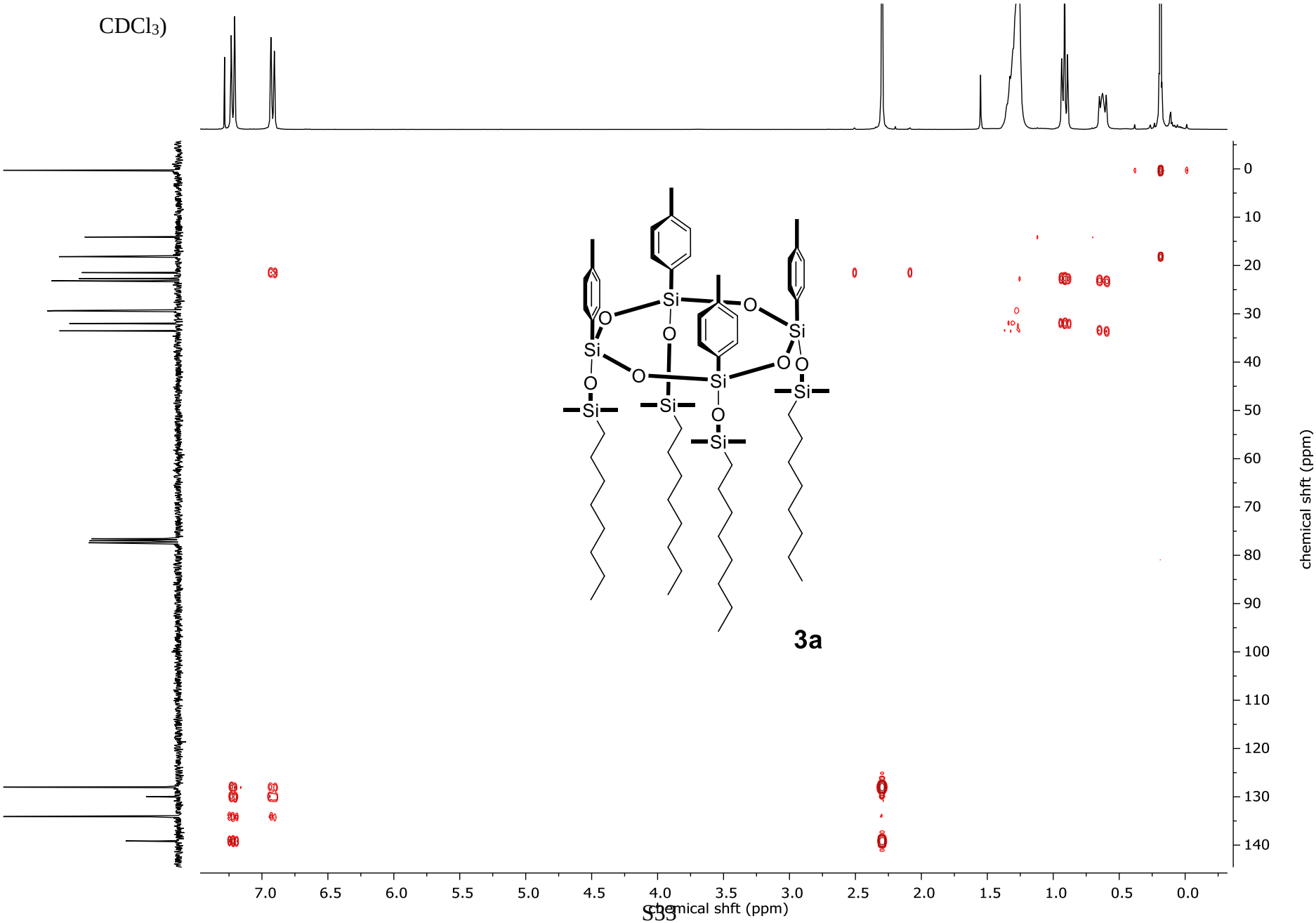
$CDCl_3$)



$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

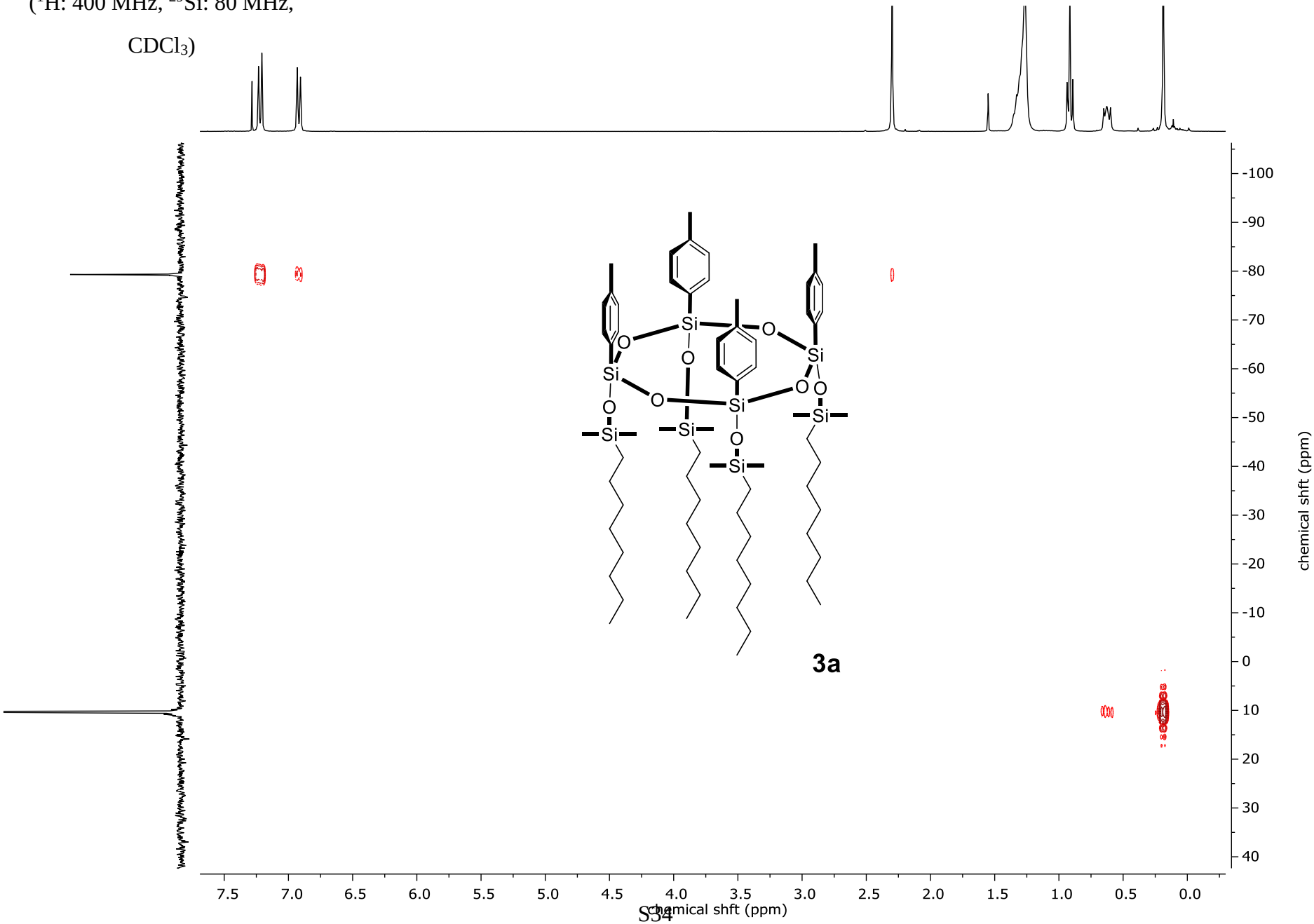
$CDCl_3$)



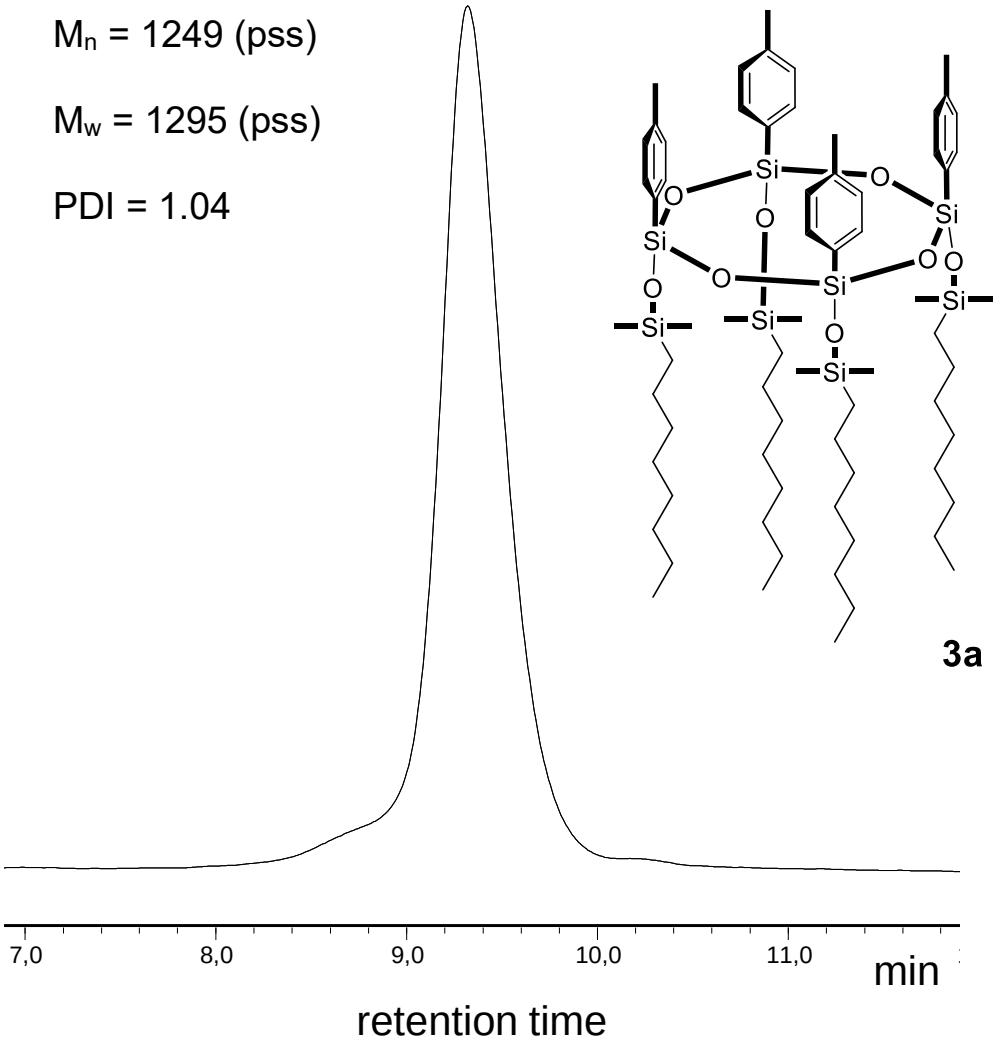
$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

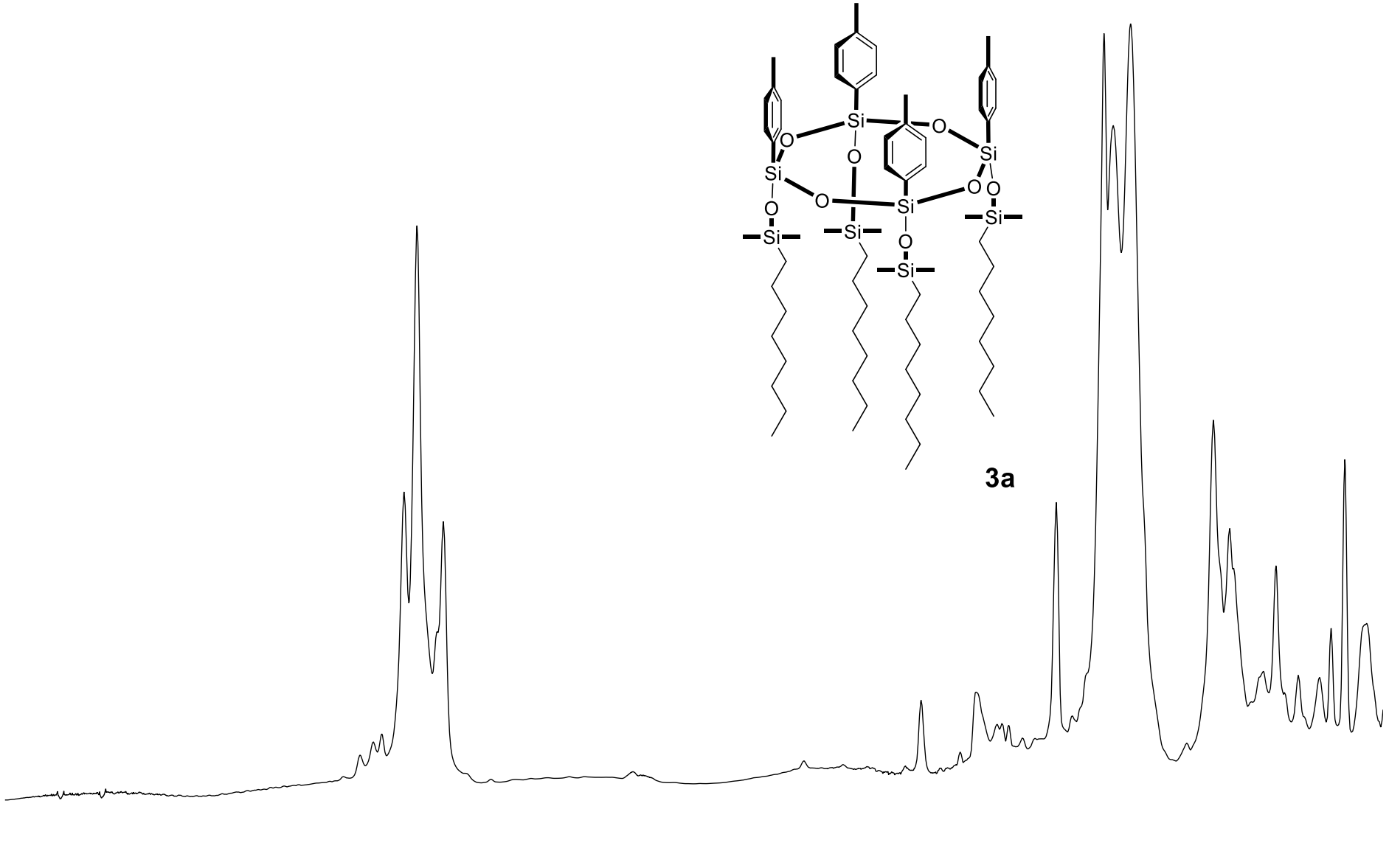
$CDCl_3$)



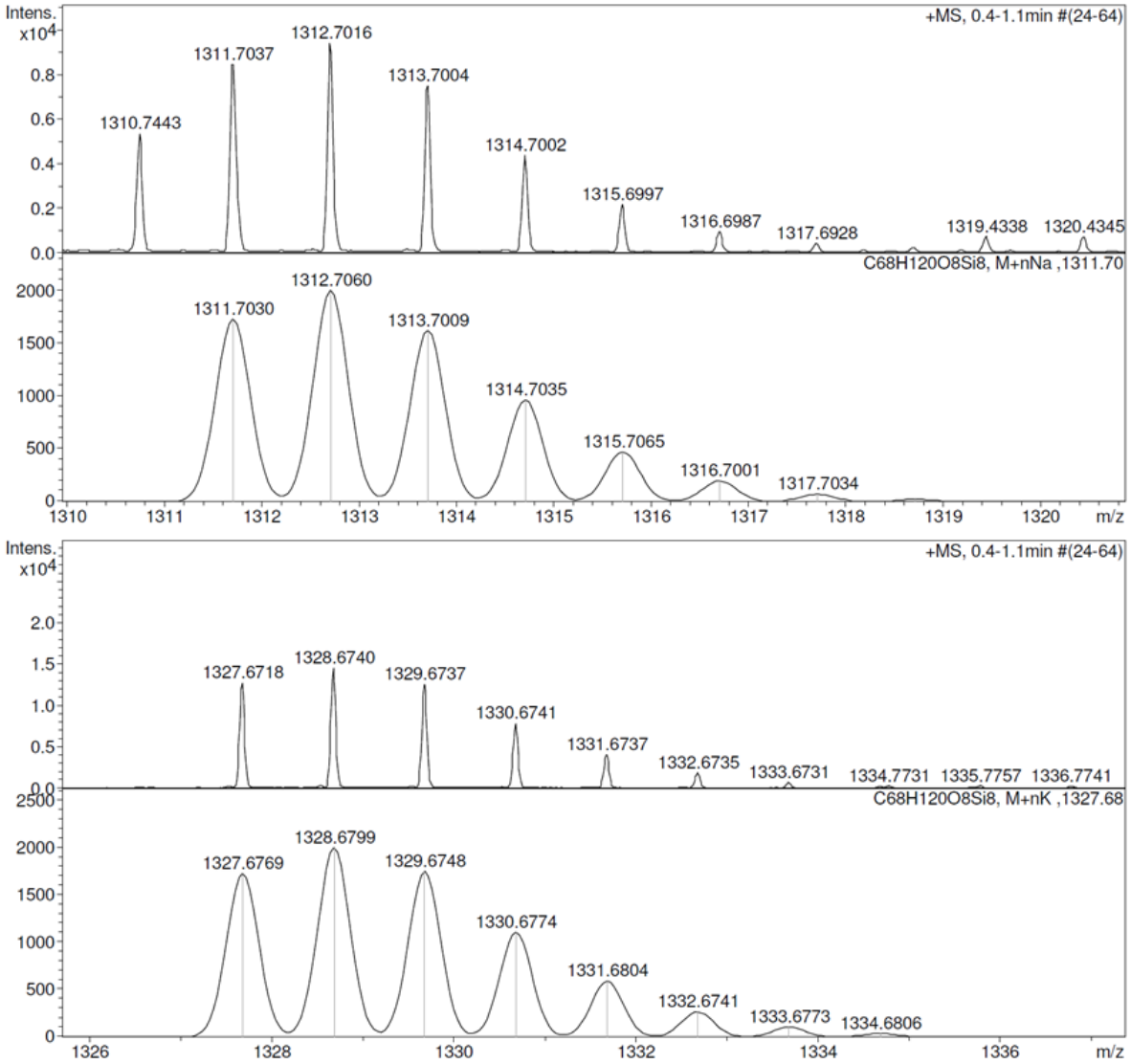
GPC

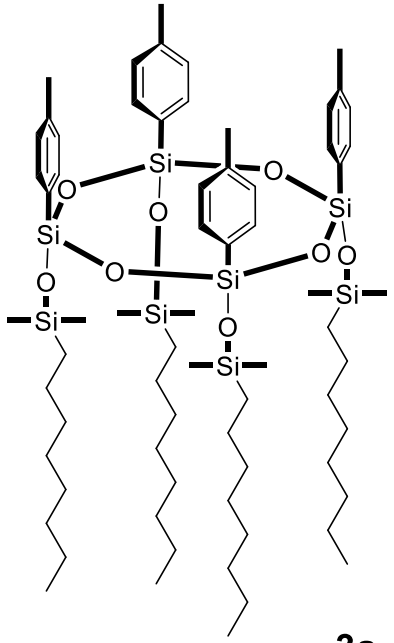

M_n = 1249 (pss)
M_w = 1295 (pss)
PDI = 1.04
3a
7,0
8,0
9,0
10,0
11,0
min
retention time

IR-spectrum

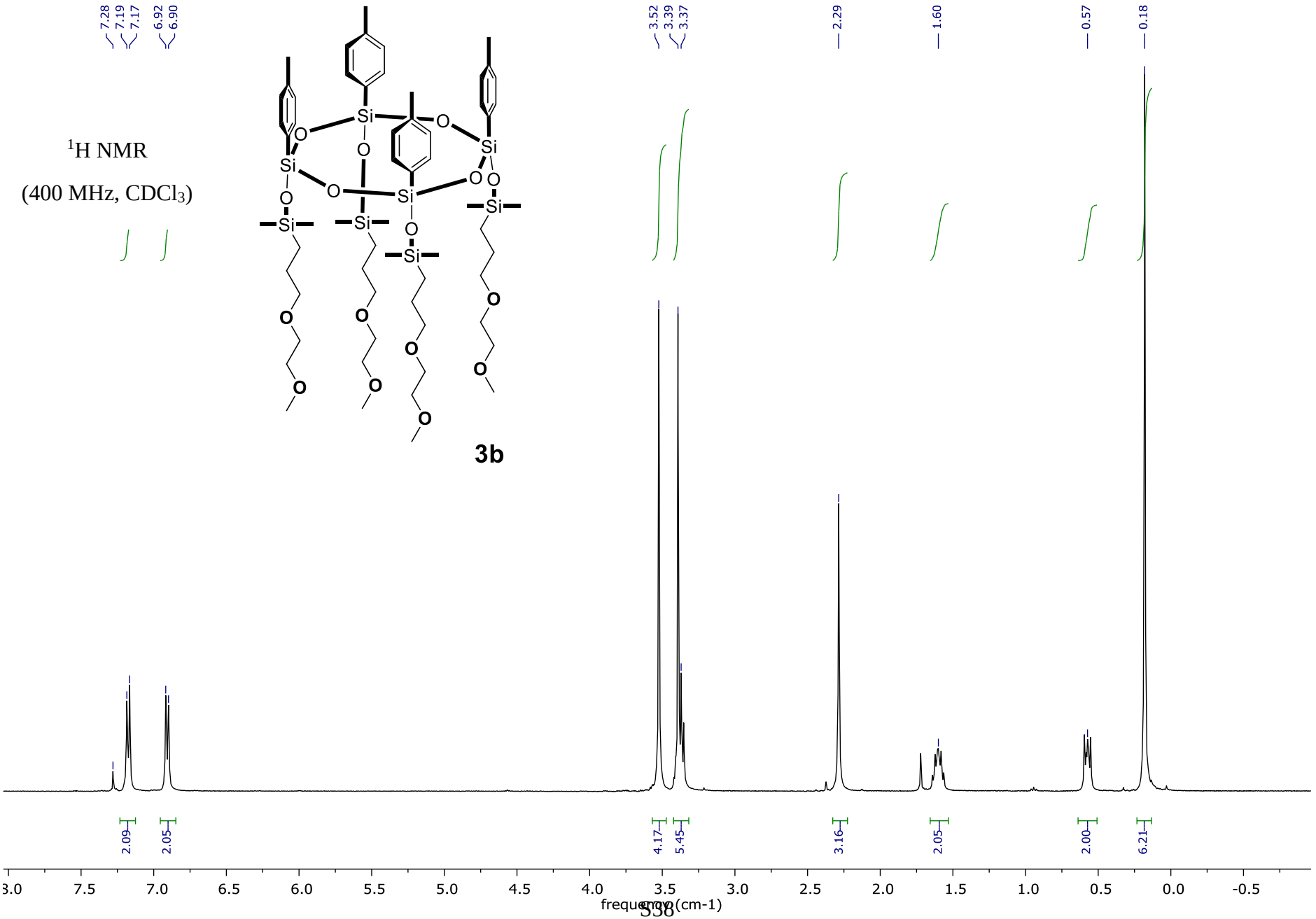

3a
3900
3700
3500
3300
3100
2900
2700
2500
2300
2100
1900
1700
1500
1300
1100
900
700
500
frequency (cm-1)

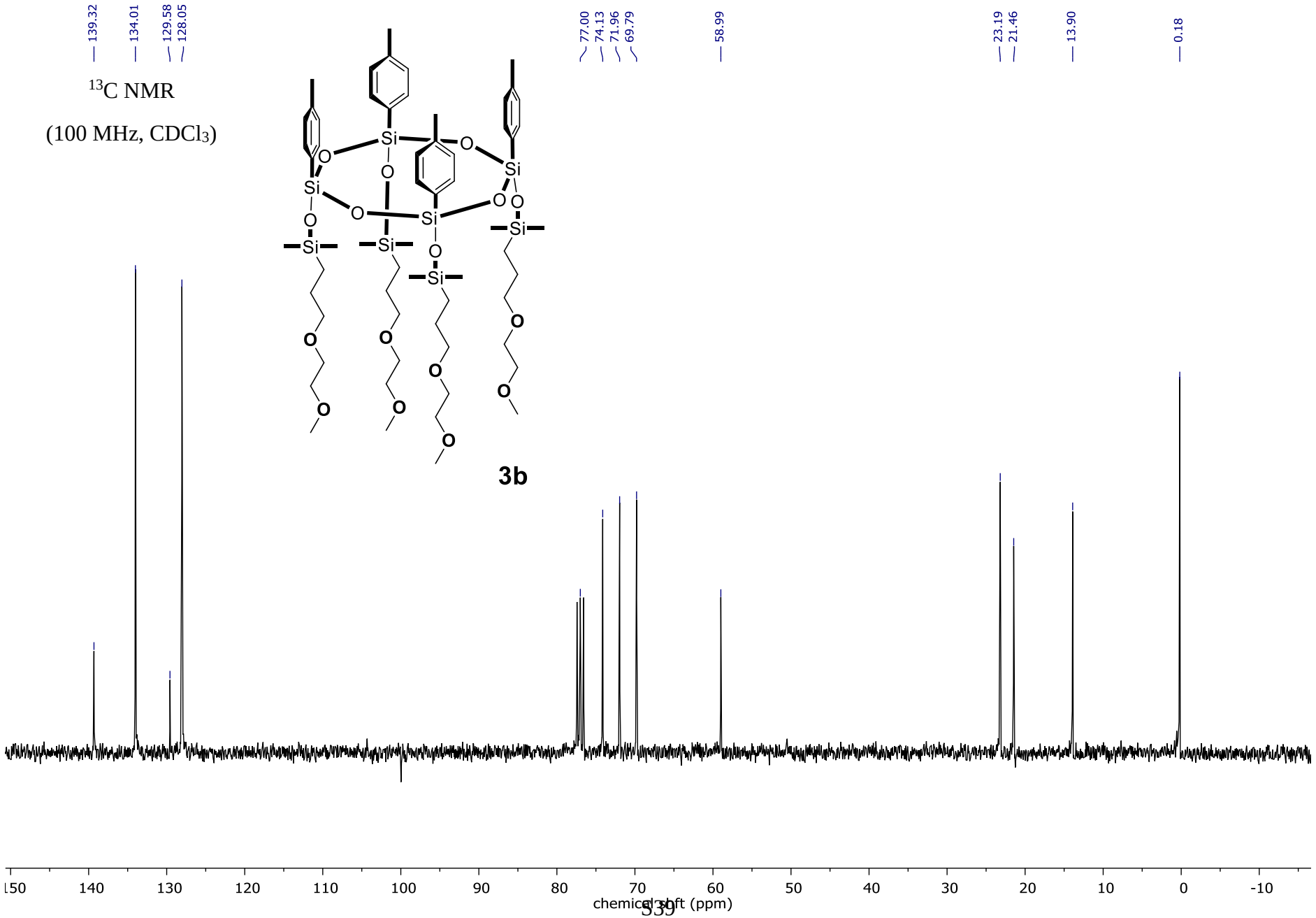
HRMS (ESI)


Intens.
x10^4
+MS, 0.4-1.1min #(24-64)
1310.7443
1311.7037
1312.7016
1313.7004
1314.7002
1315.6997
1316.6987
1317.6928
1319.4338
1320.4345
C68H120O8Si8, M+nNa ,1311.70
1311.7030
1312.7060
1313.7009
1314.7035
1315.7065
1316.7001
1317.7034
m/z
Intens.
x10^4
+MS, 0.4-1.1min #(24-64)
1327.6718
1328.6740
1329.6737
1330.6741
1331.6737
1332.6735
1333.6731
1334.7731
1335.7757
1336.7741
C68H120O8Si8, M+nK ,1327.68
1327.6769
1328.6799
1329.6748
1330.6774
1331.6804
1332.6741
1333.6773
1334.6806
m/z



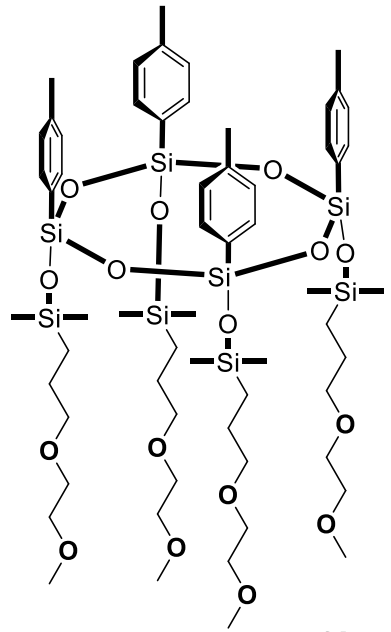
3a


7.28
7.19
7.17
6.92
6.90
3.52
3.39
3.37
2.29
1.60
0.57
0.18
^{1}H NMR
(400 MHz, $CDCl_3$)
3b
2.09
2.05
4.17
5.45
3.16
2.05
2.00
6.21
frequency (cm-1)


139.32
134.01
129.58
128.05
77.00
74.13
71.96
69.79
58.99
23.19
21.46
13.90
0.18
^{13}C NMR
(100 MHz, $CDCl_3$)
3b
chemical shift (ppm)

^{29}Si NMR

(80 MHz, $CDCl_3$)

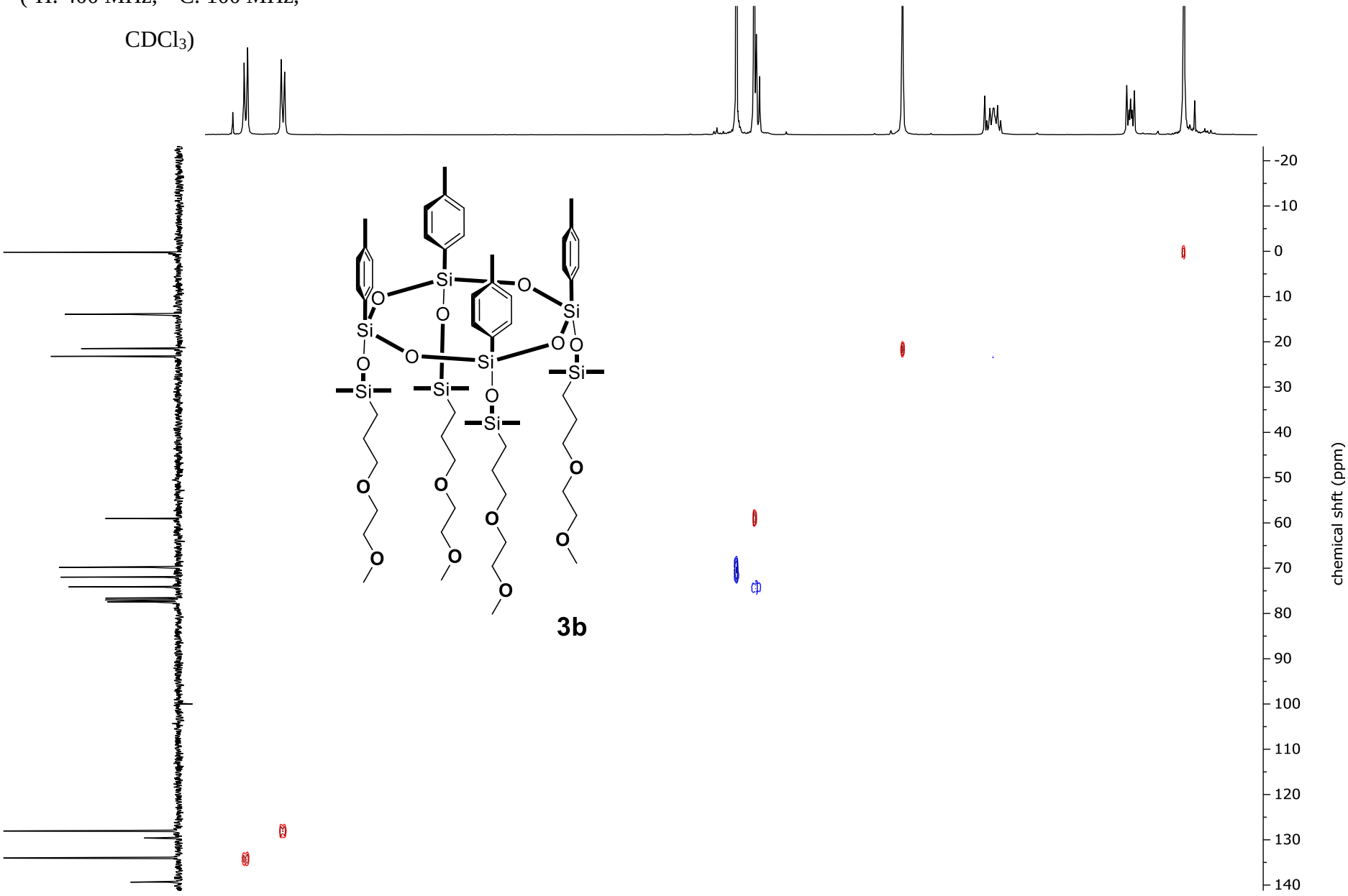


3b

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

$CDCl_3$)

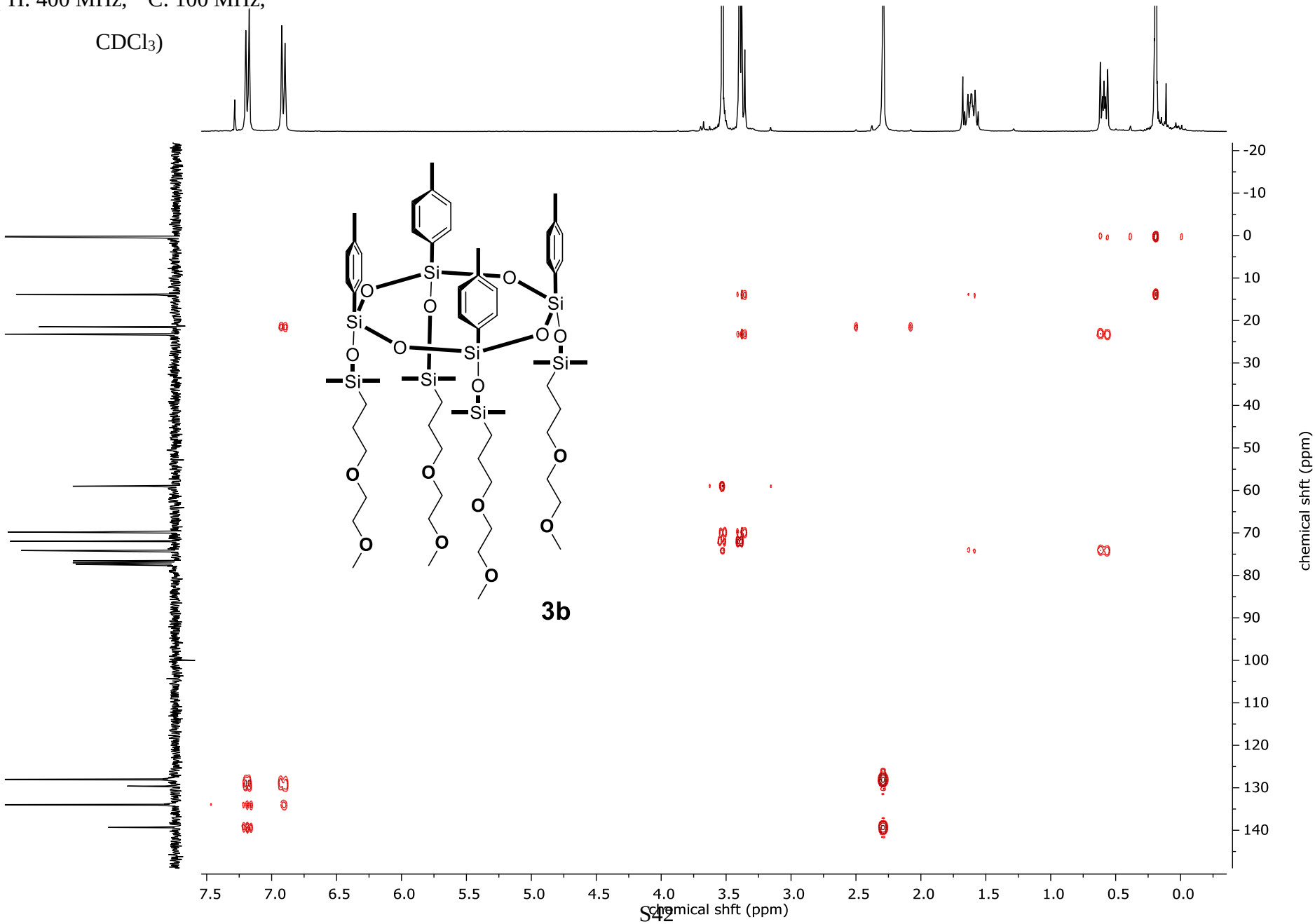


3b

$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

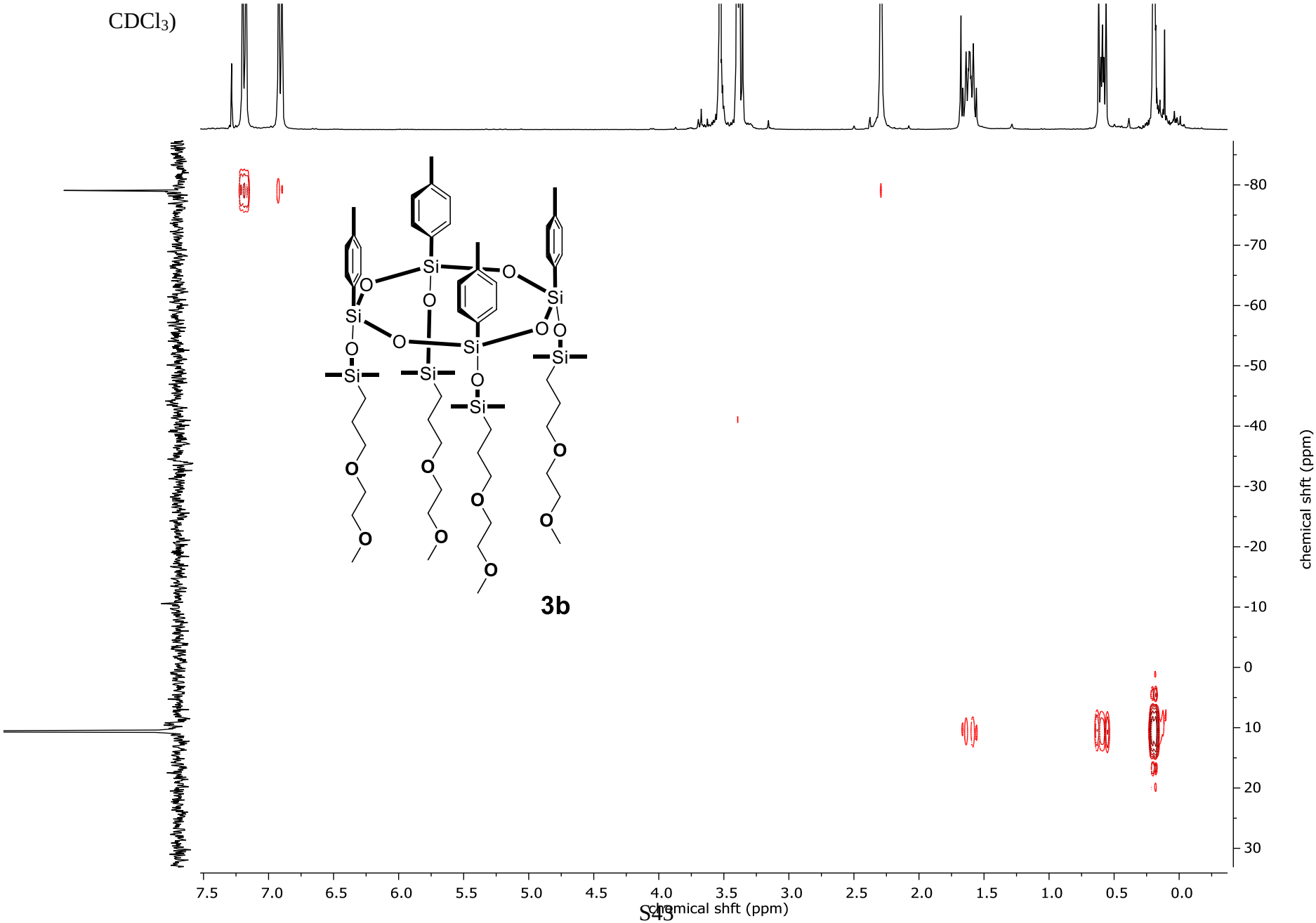
$CDCl_3$)



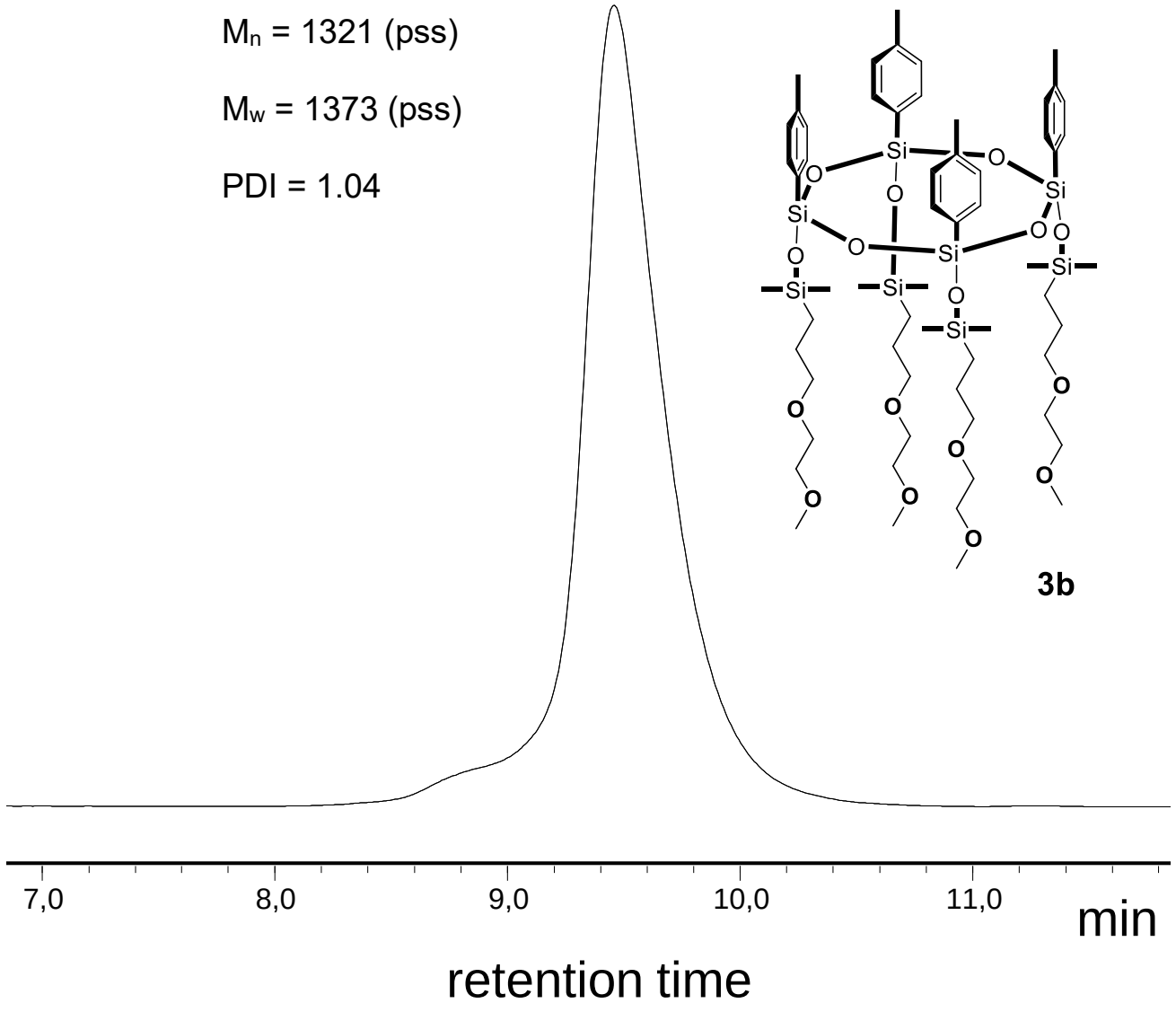
$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

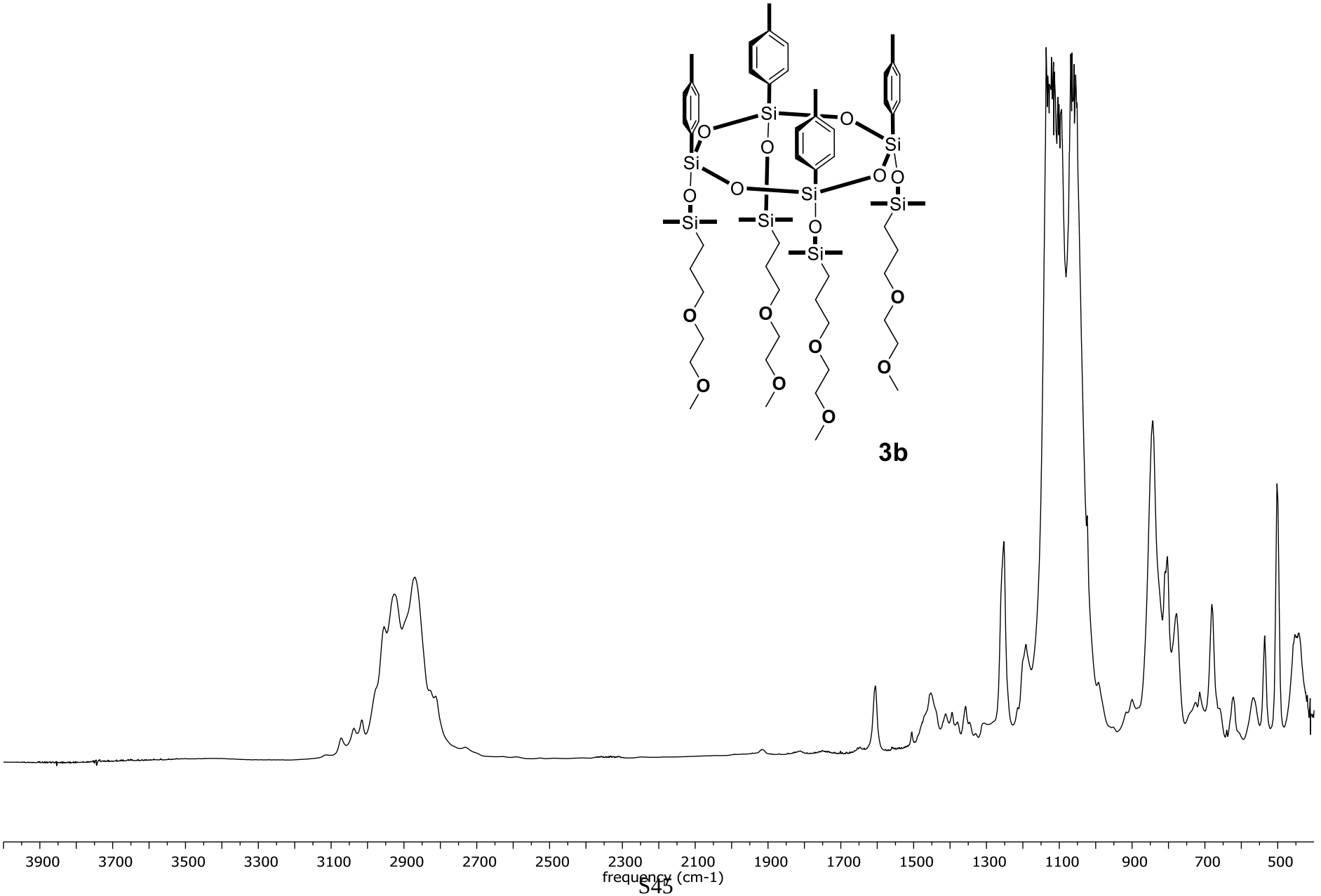
$CDCl_3$)



GPC

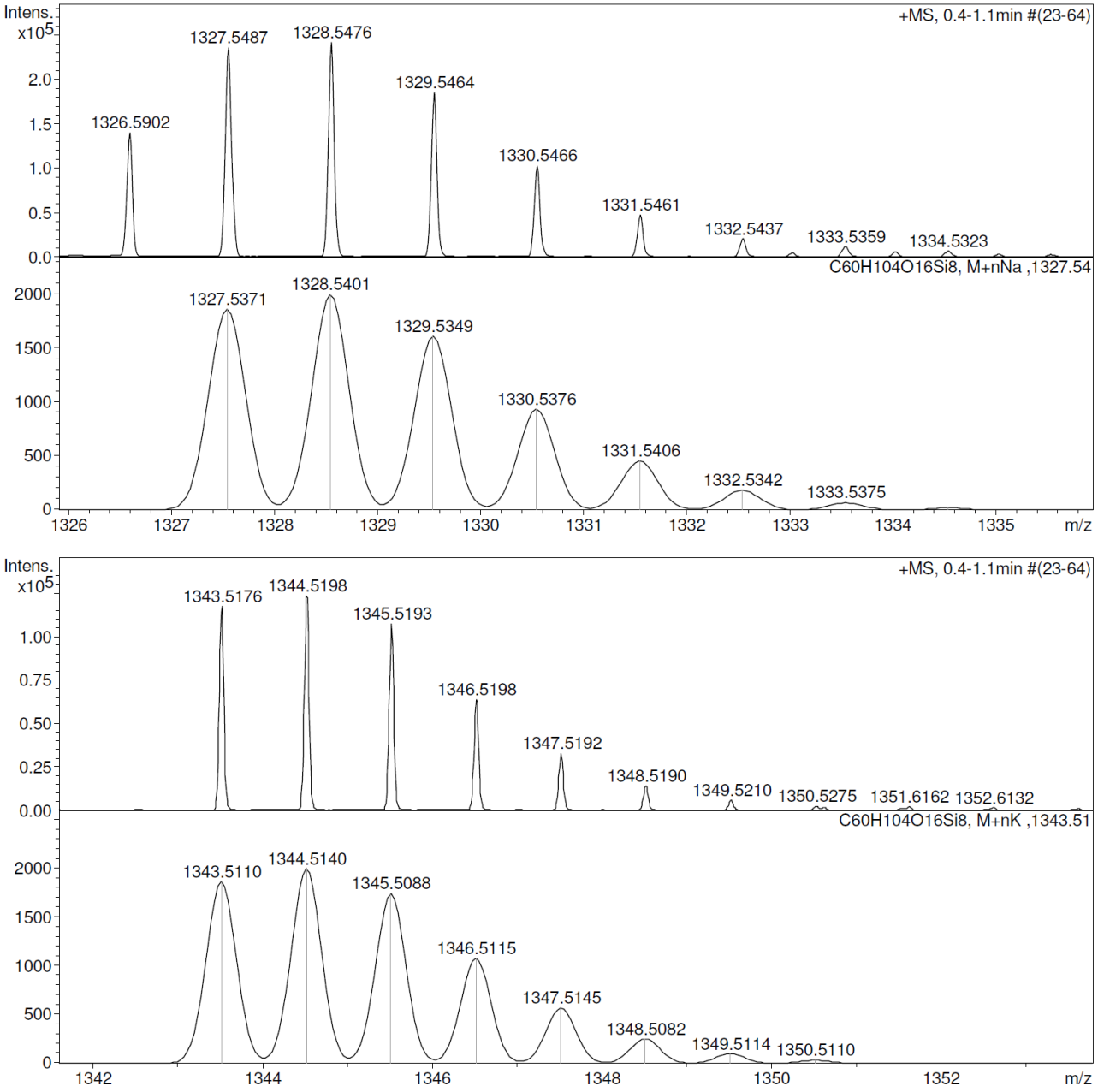

Mn = 1321 (pss)
Mw = 1373 (pss)
PDI = 1.04
3b
7,0
8,0
9,0
10,0
11,0
min
retention time

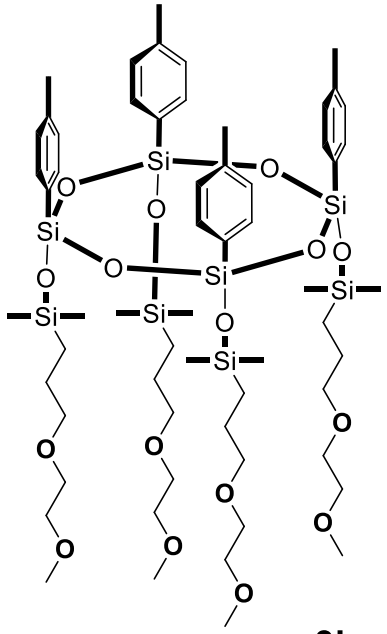
IR-spectrum



3b

HRMS (ESI)

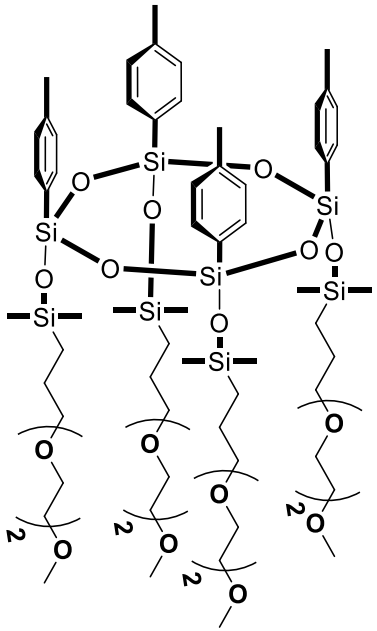

Intens.
x10^5
+MS, 0.4-1.1min #(23-64)
1327.5487
1328.5476
1329.5464
1326.5902
1330.5466
1331.5461
1332.5437
1333.5359
1334.5323
C60H104O16Si8, M+nNa ,1327.54
1327.5371
1328.5401
1329.5349
1330.5376
1331.5406
1332.5342
1333.5375
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
m/z
Intens.
x10^5
+MS, 0.4-1.1min #(23-64)
1343.5176
1344.5198
1345.5193
1346.5198
1347.5192
1348.5190
1349.5210
1350.5275
1351.6162
1352.6132
C60H104O16Si8, M+nK ,1343.51
1343.5110
1344.5140
1345.5088
1346.5115
1347.5145
1348.5082
1349.5114
1350.5110
1342
1344
1346
1348
1350
1352
m/z



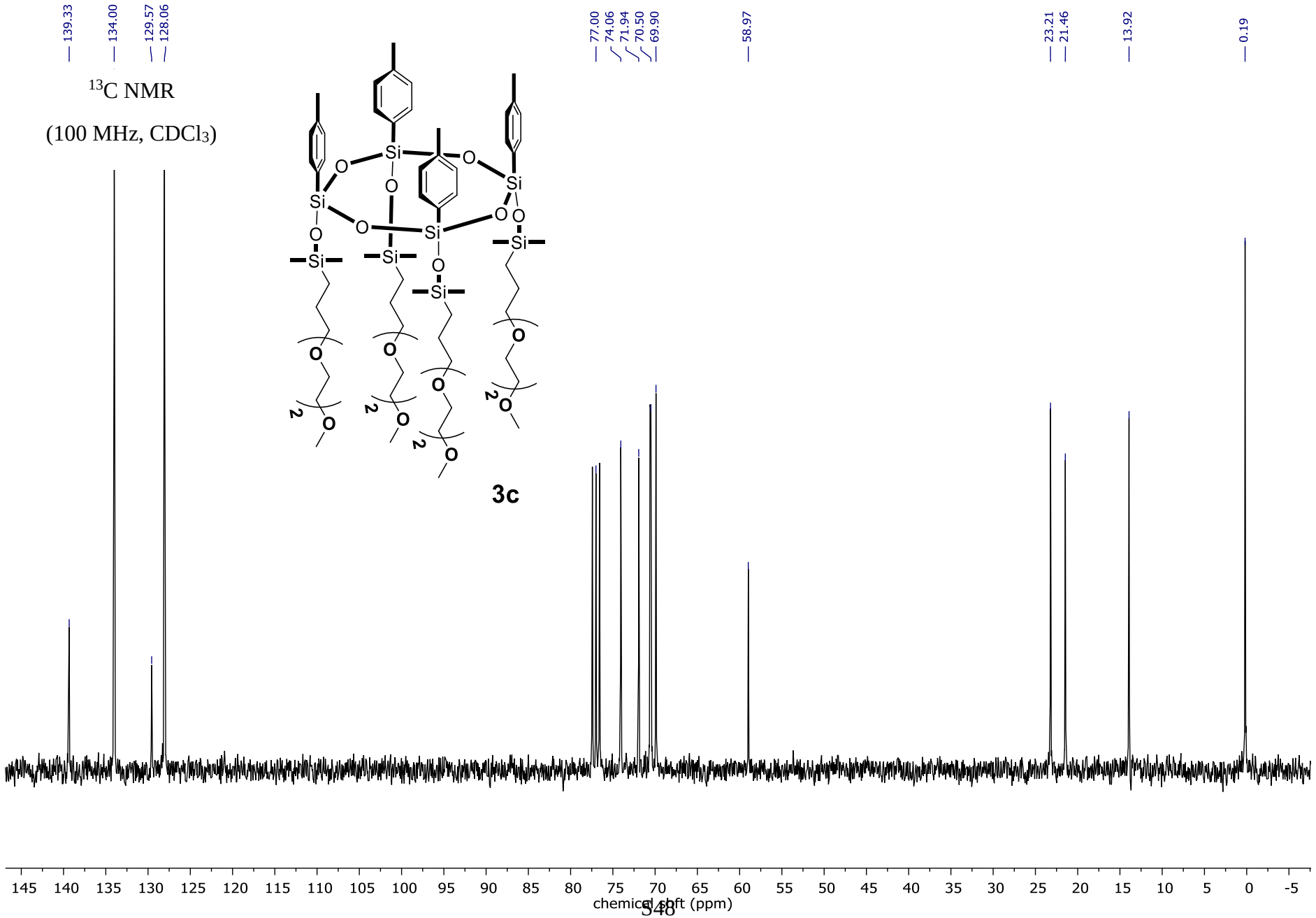
3b

^{1}H NMR

(400 MHz, $CDCl_3$)

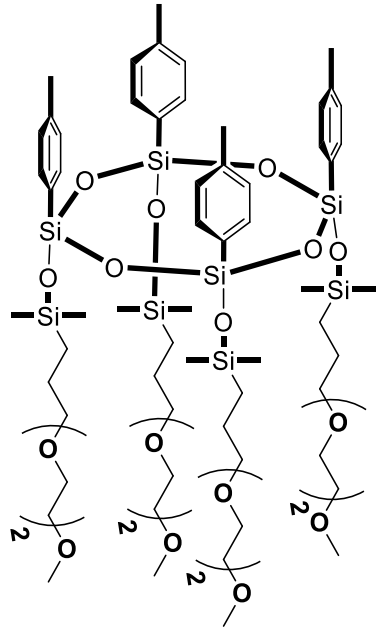


3c


139.33
134.00
129.57
128.06
77.00
74.06
71.94
70.50
69.90
58.97
23.21
21.46
13.92
0.19
^{13}C NMR
(100 MHz, $CDCl_3$)
3c
145 140 135 130 125 120 115 110 105 100 95 90 85 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, $CDCl_3$)

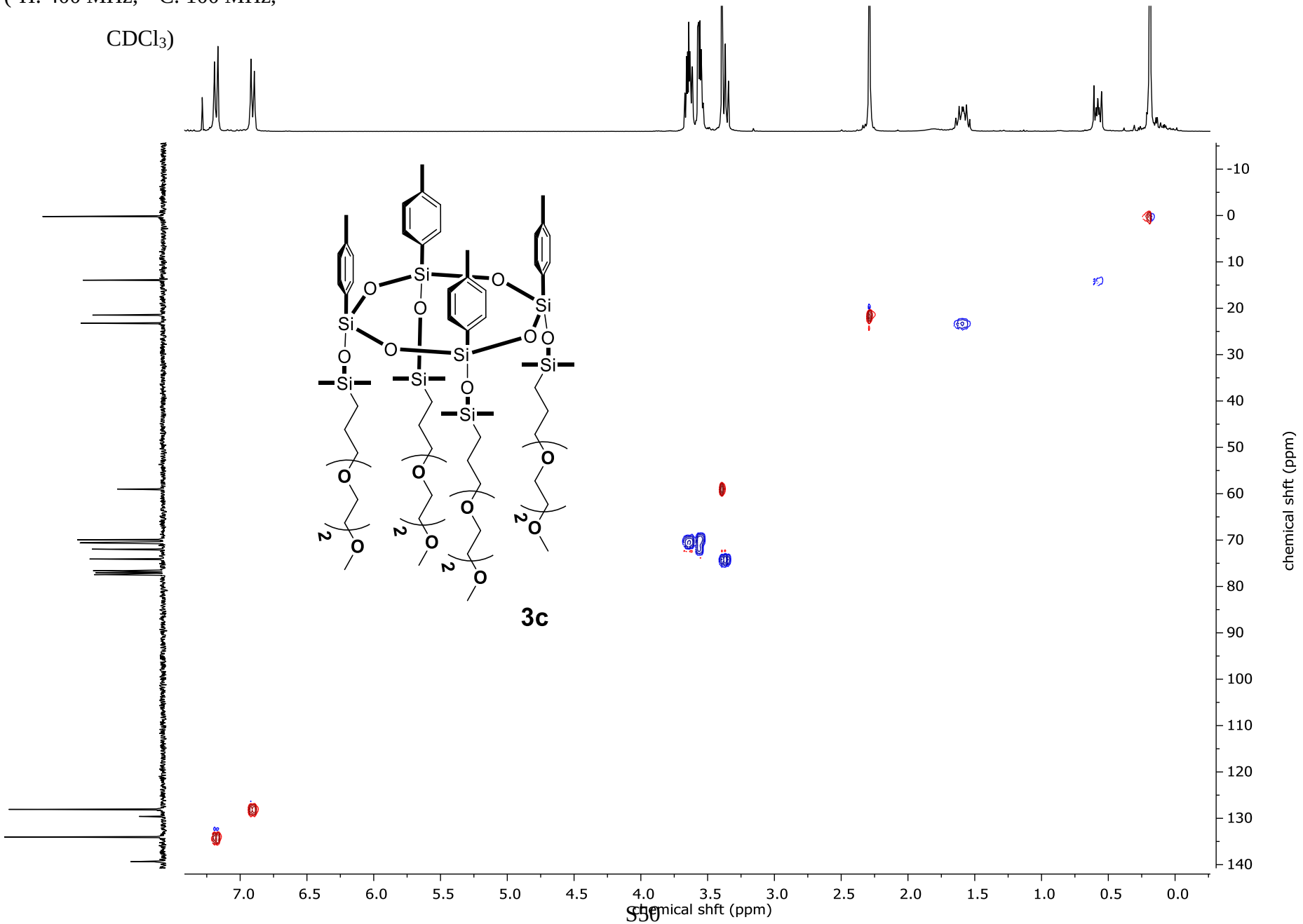


3c

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

$CDCl_3$)

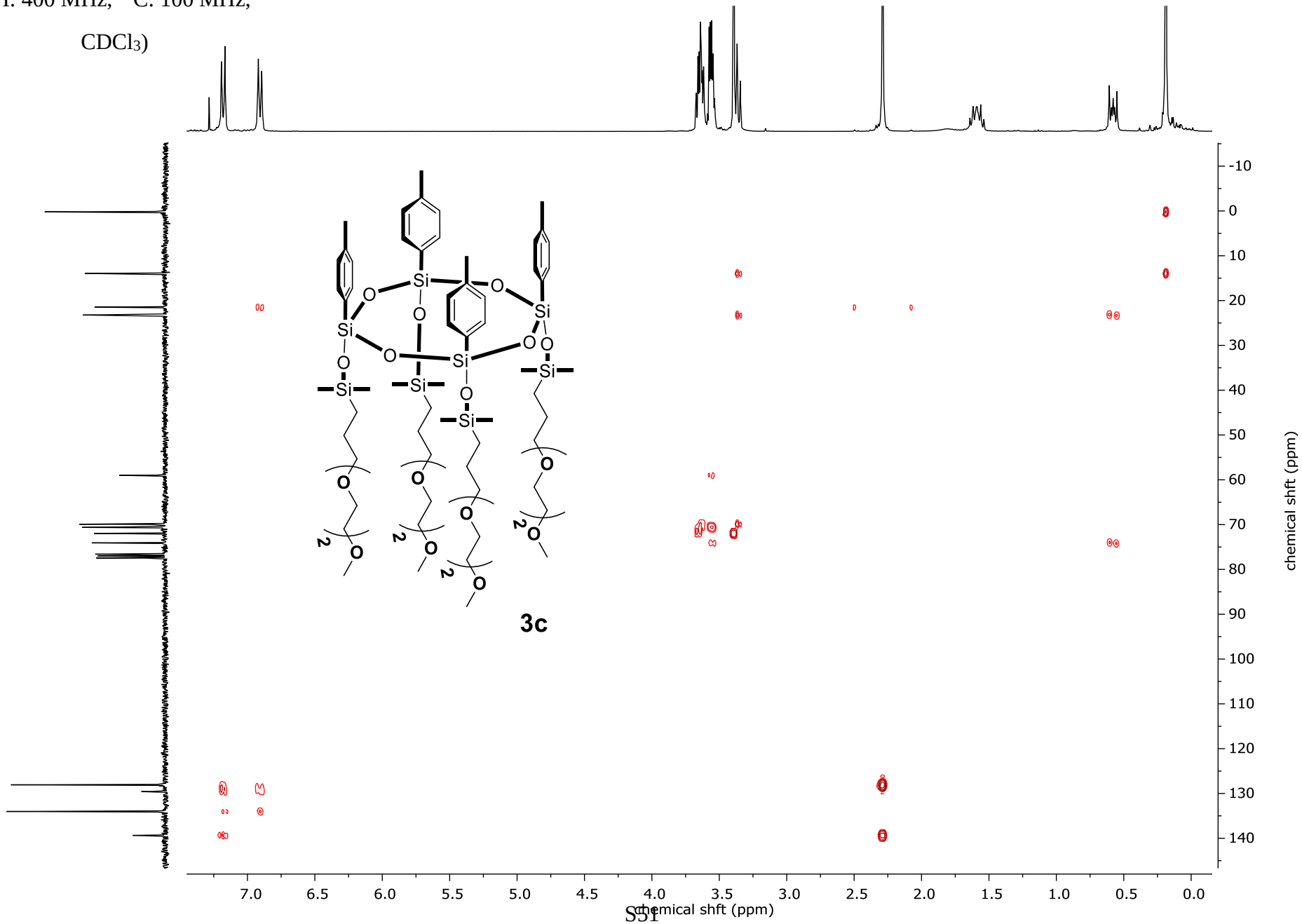


3c

$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

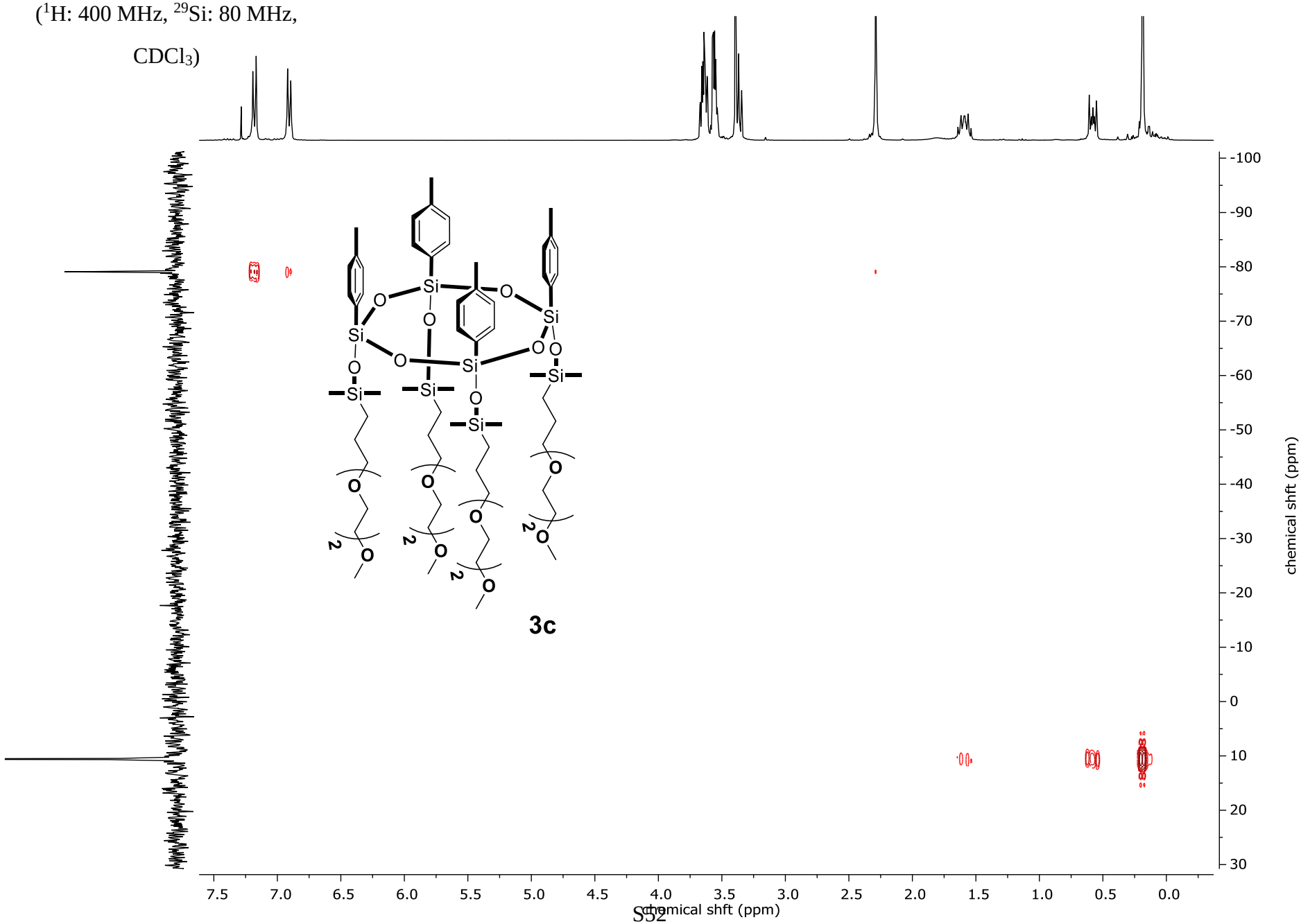
$CDCl_3$)



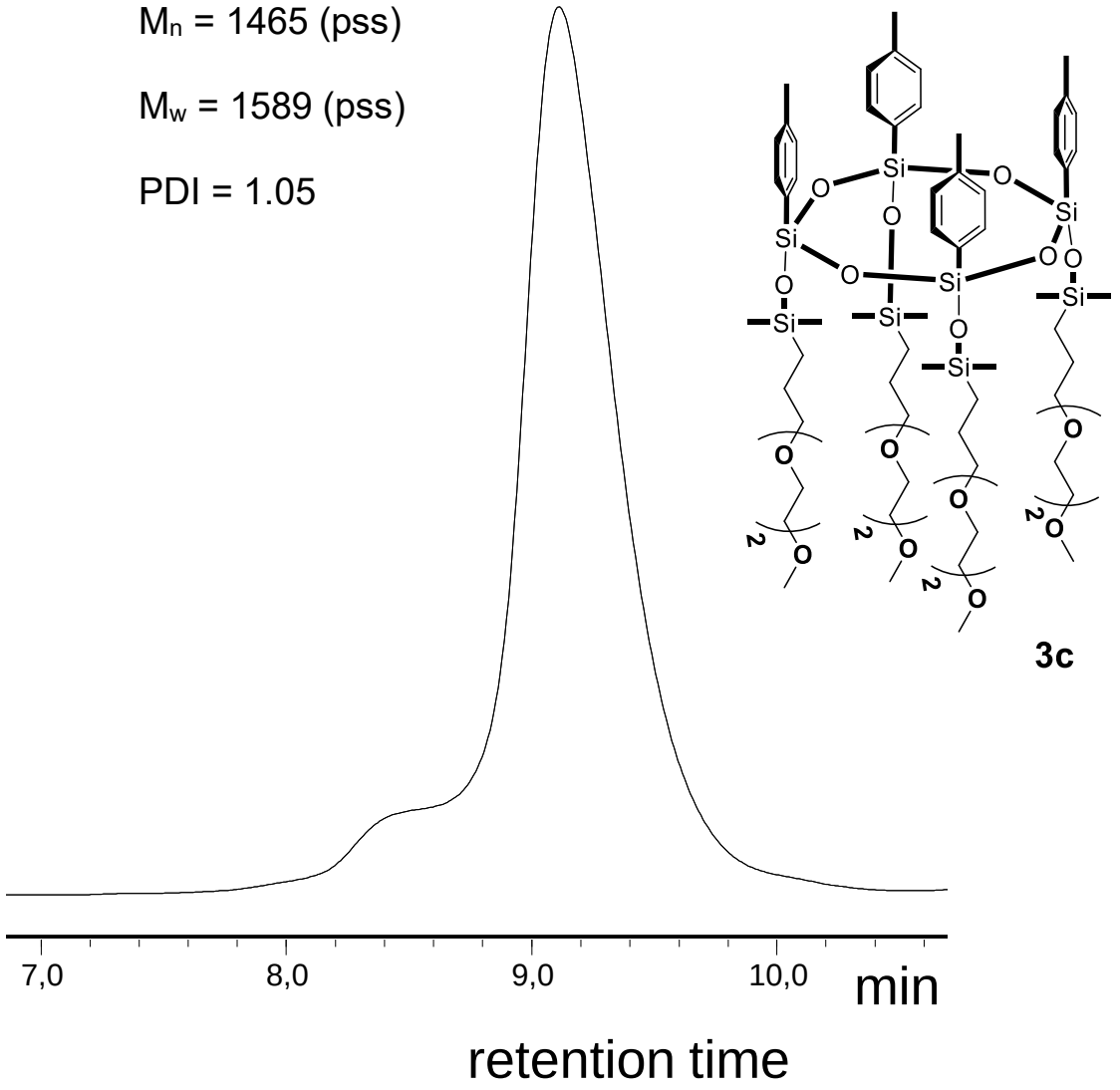
$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

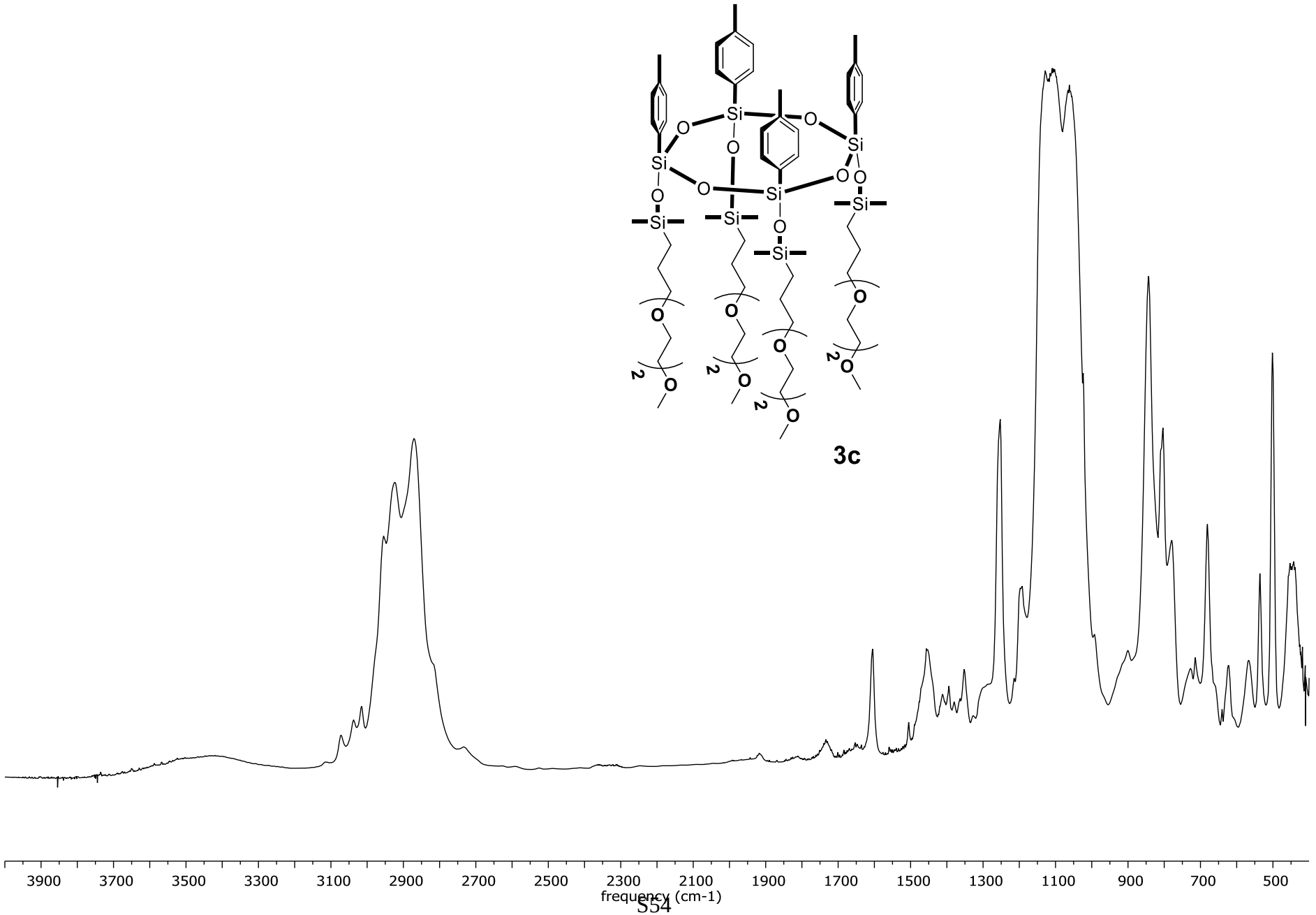
$CDCl_3$)



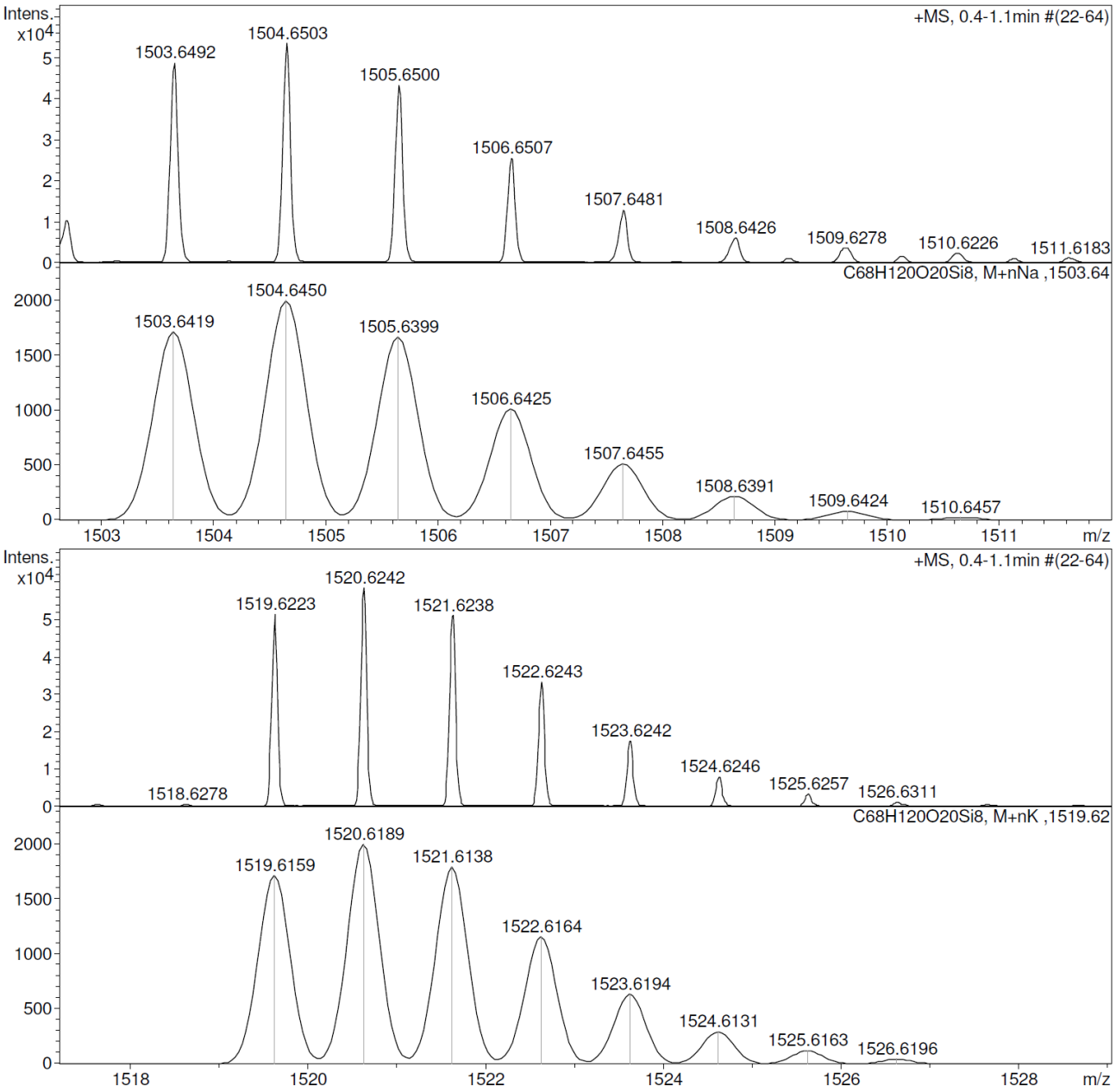
GPC


Mn = 1465 (pss)
Mw = 1589 (pss)
PDI = 1.05
3c
7,0
8,0
9,0
10,0
min
retention time

IR-spectrum


3c
3900
3700
3500
3300
3100
2900
2700
2500
2300
2100
1900
1700
1500
1300
1100
900
700
500
frequency (cm-1)

HRMS (ESI)


Intens.
x10^4
+MS, 0.4-1.1min #(22-64)
1503.6492
1504.6503
1505.6500
1506.6507
1507.6481
1508.6426
1509.6278
1510.6226
1511.6183
C68H120O20Si8, M+nNa ,1503.64
1503.6419
1504.6450
1505.6399
1506.6425
1507.6455
1508.6391
1509.6424
1510.6457
m/z
Intens.
x10^4
+MS, 0.4-1.1min #(22-64)
1518.6278
1519.6223
1520.6242
1521.6238
1522.6243
1523.6242
1524.6246
1525.6257
1526.6311
C68H120O20Si8, M+nK ,1519.62
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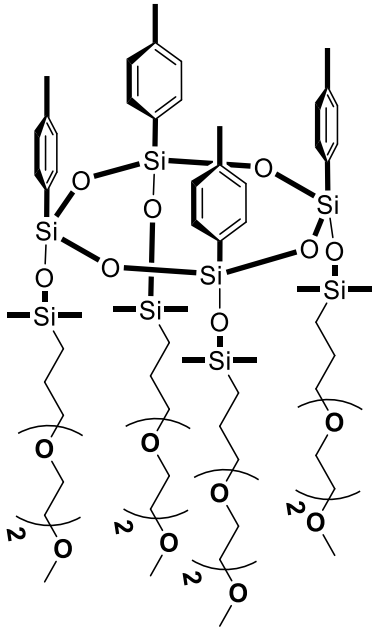
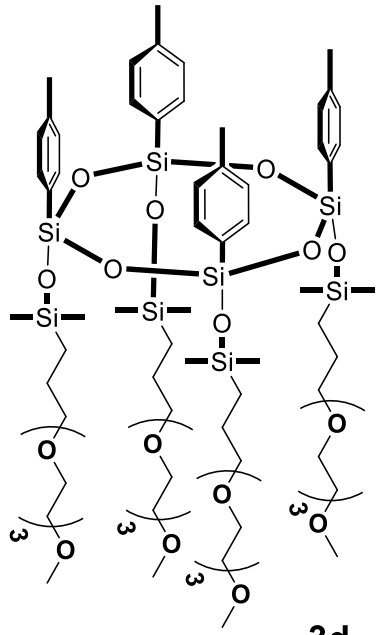
1523.6194
1524.6131
1525.6163
1526.6196
m/z



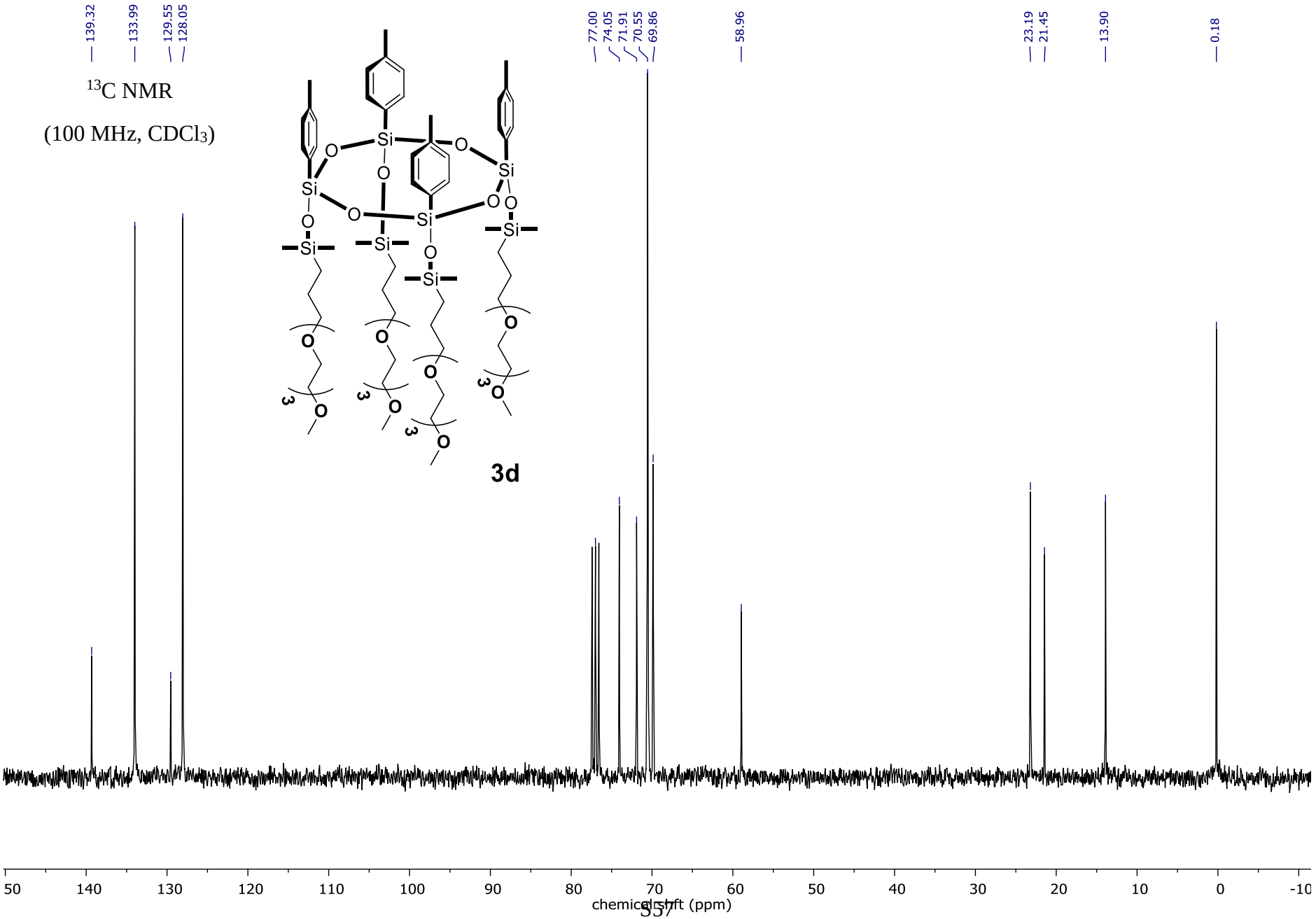
3c

^{1}H NMR

(400 MHz, $CDCl_3$)

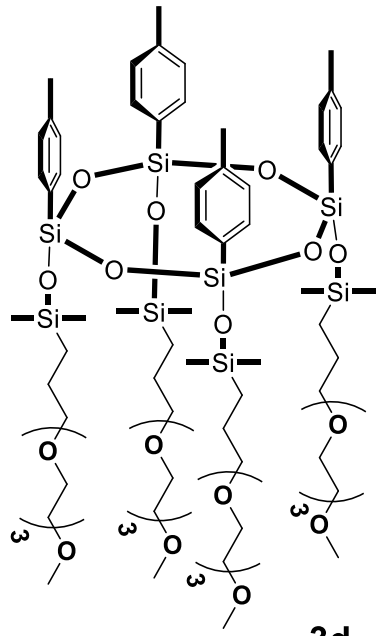


3d


139.32
133.99
129.55
128.05
77.00
74.05
71.91
70.55
69.86
58.96
23.19
21.45
13.90
0.18
^{13}C NMR
(100 MHz, $CDCl_3$)
3d
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
chemical shift (ppm)

^{29}Si NMR

(80 MHz, $CDCl_3$)

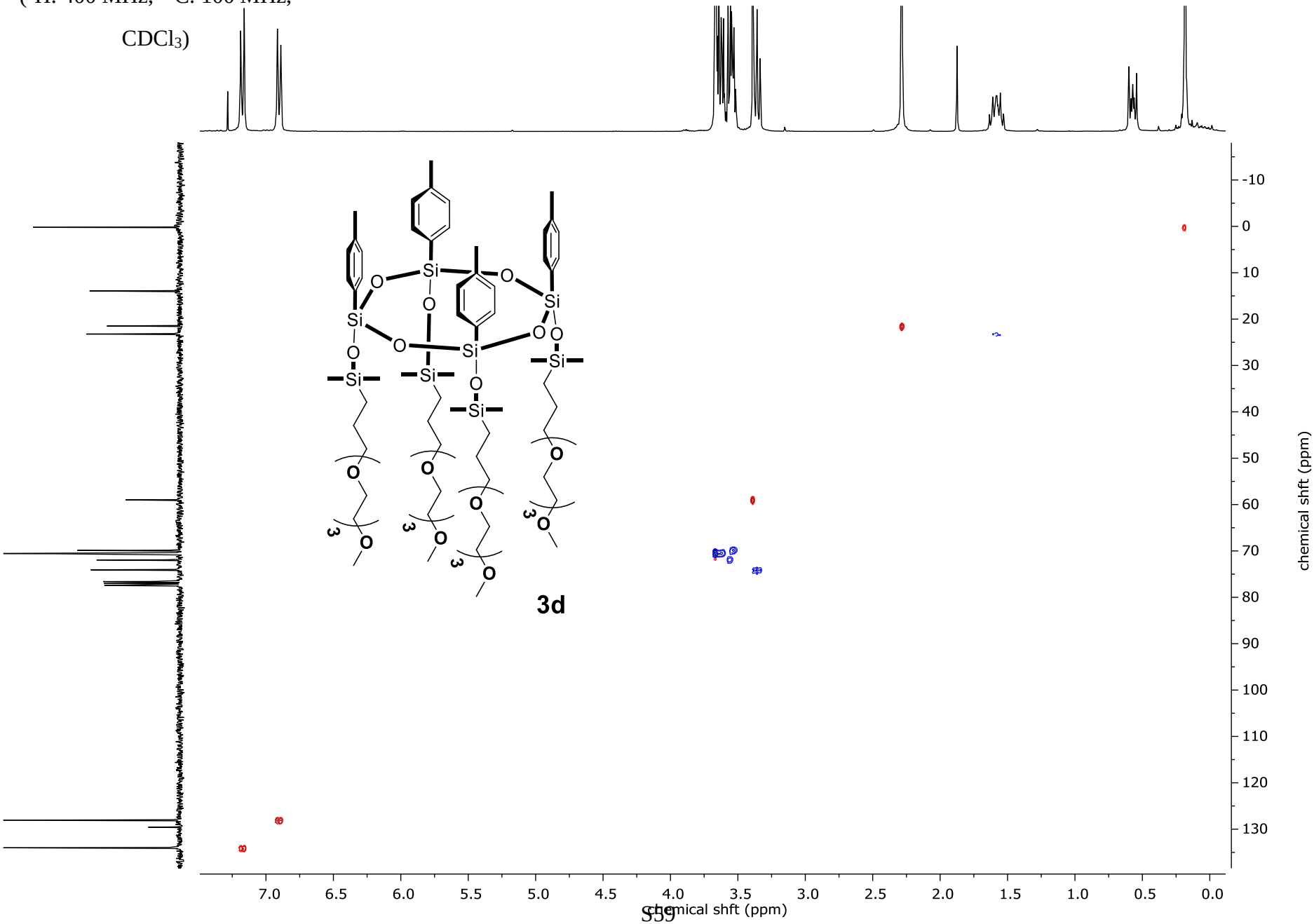


3d

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

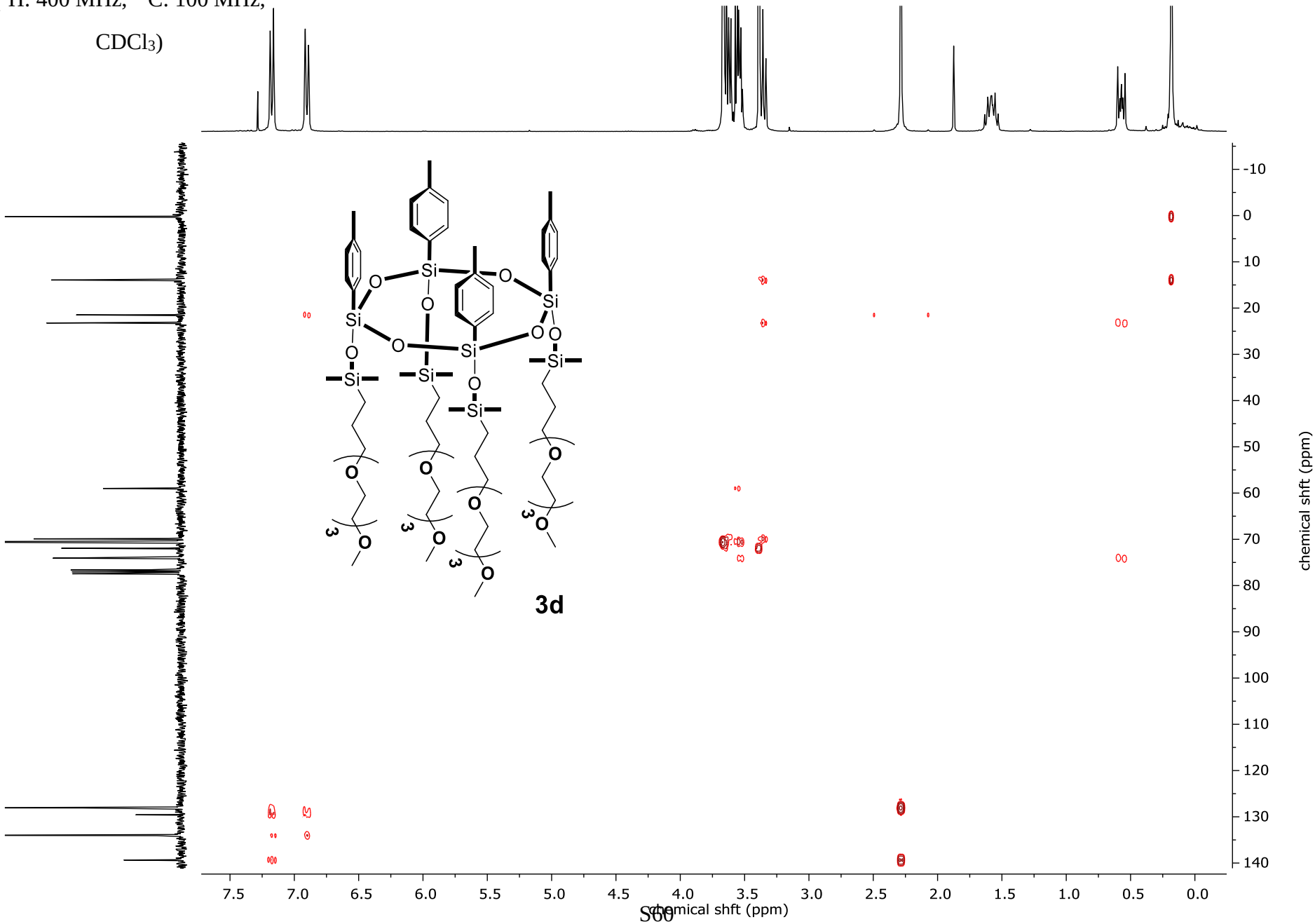
$CDCl_3$)



$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

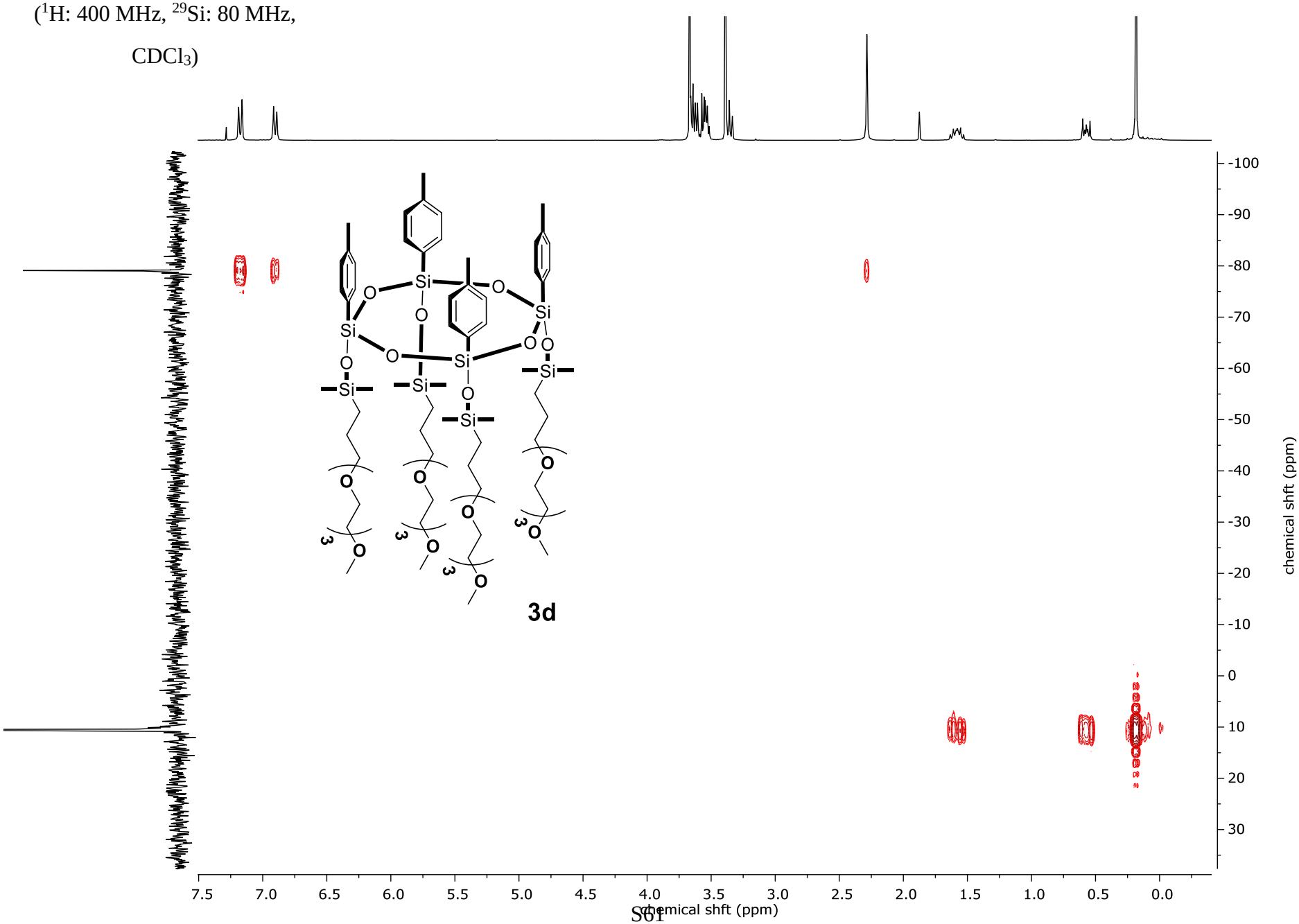
$CDCl_3$)



$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

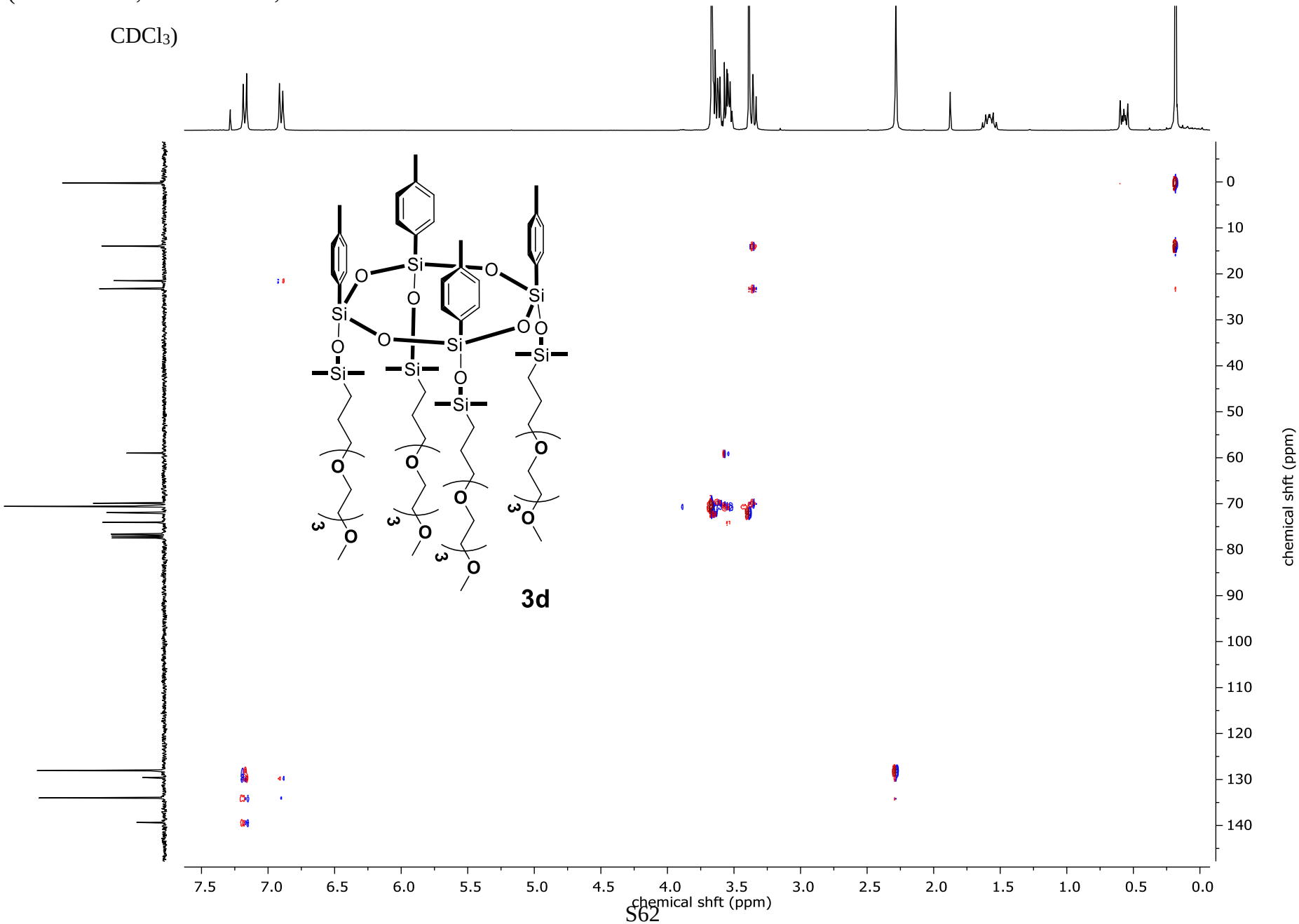
$CDCl_3$)



^{1}H,^{13}C–HSQMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

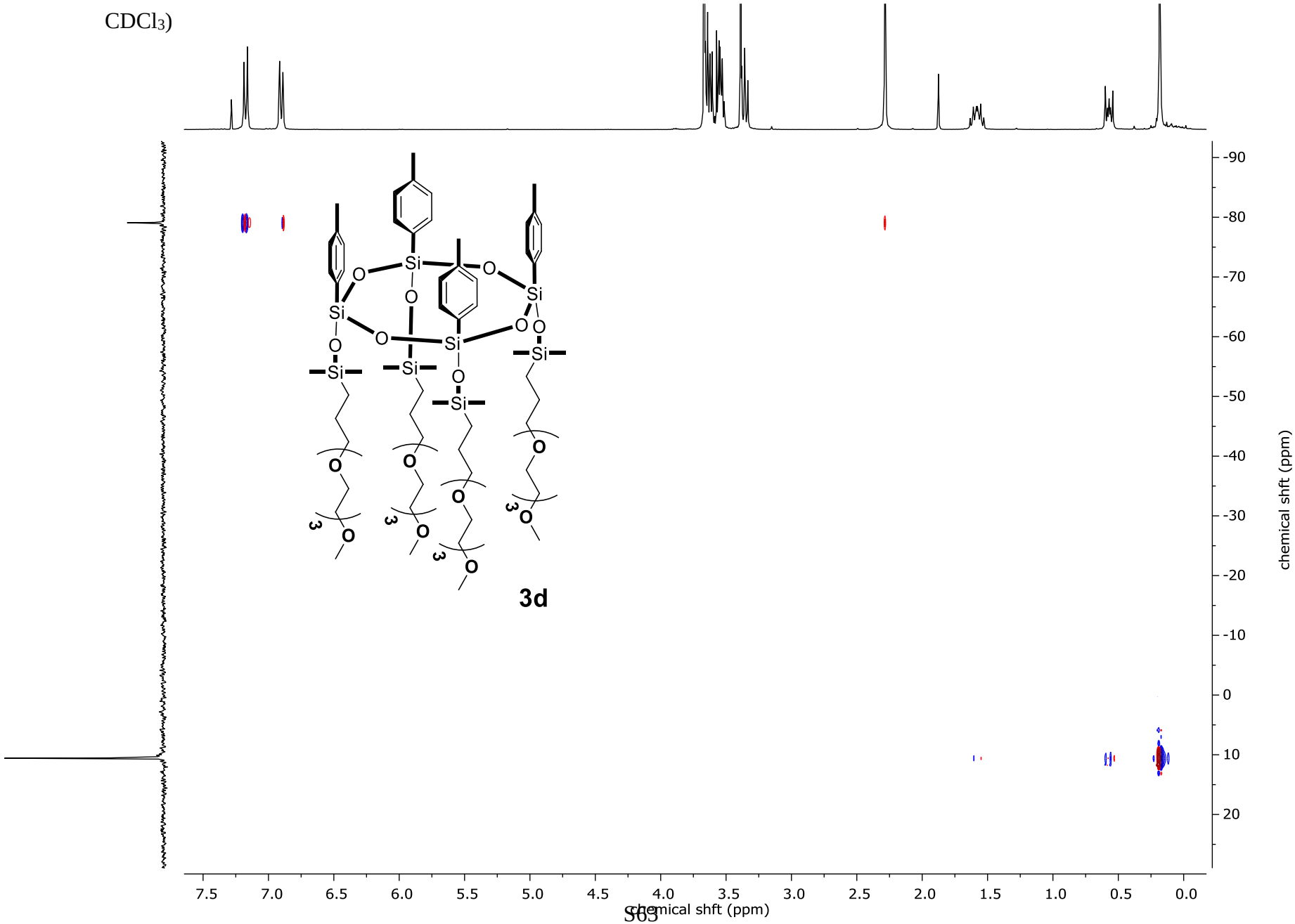
$CDCl_3$)

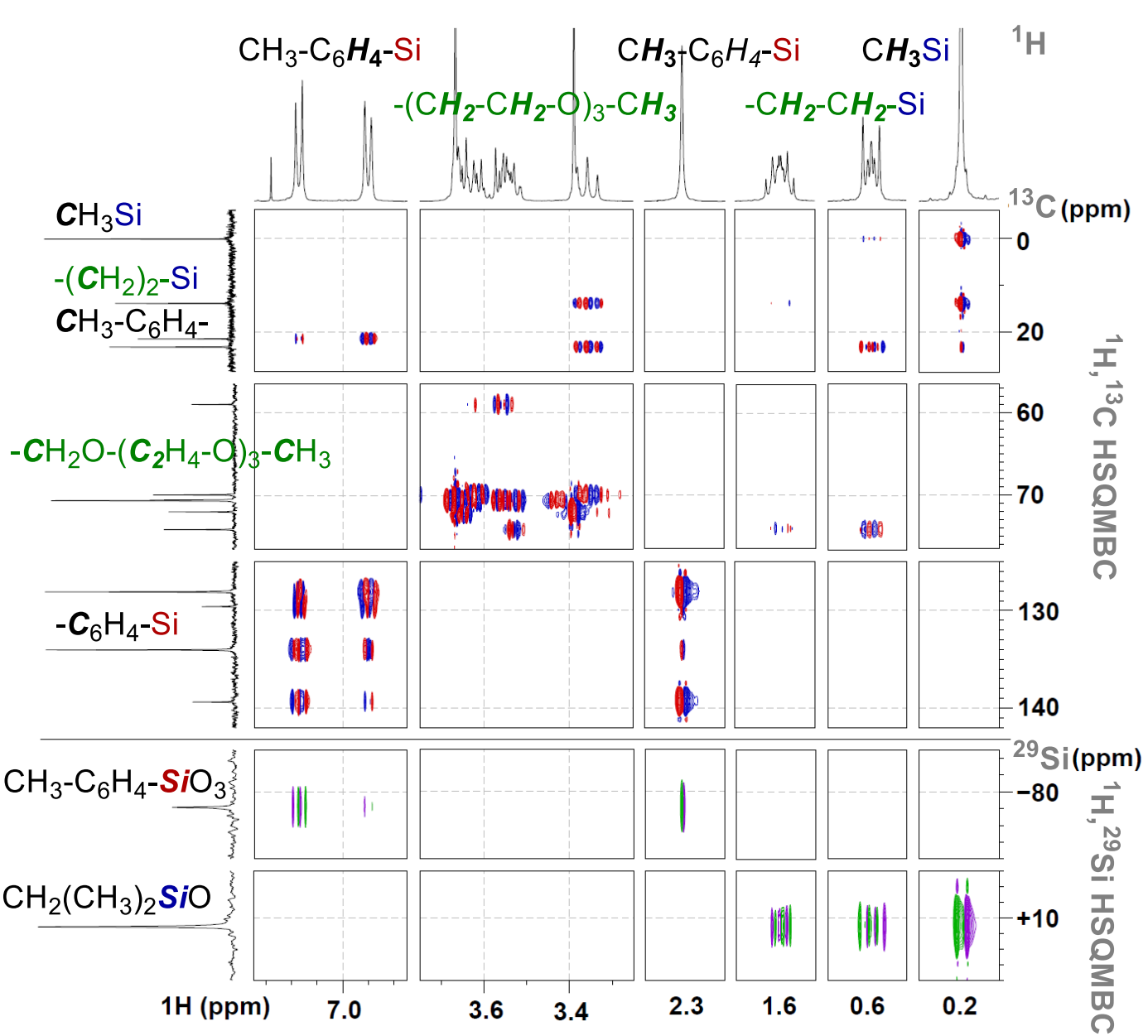


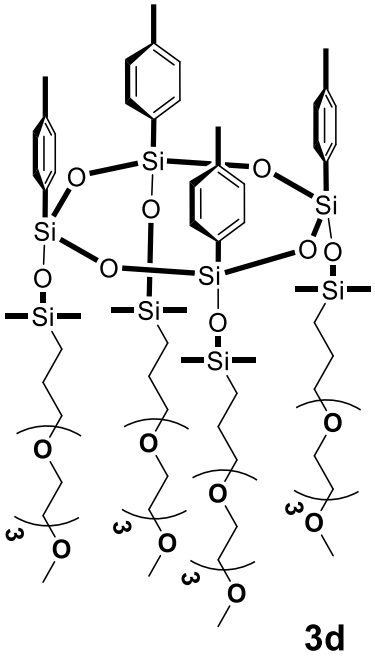
$^{1}H,^{29}Si$–HSQMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

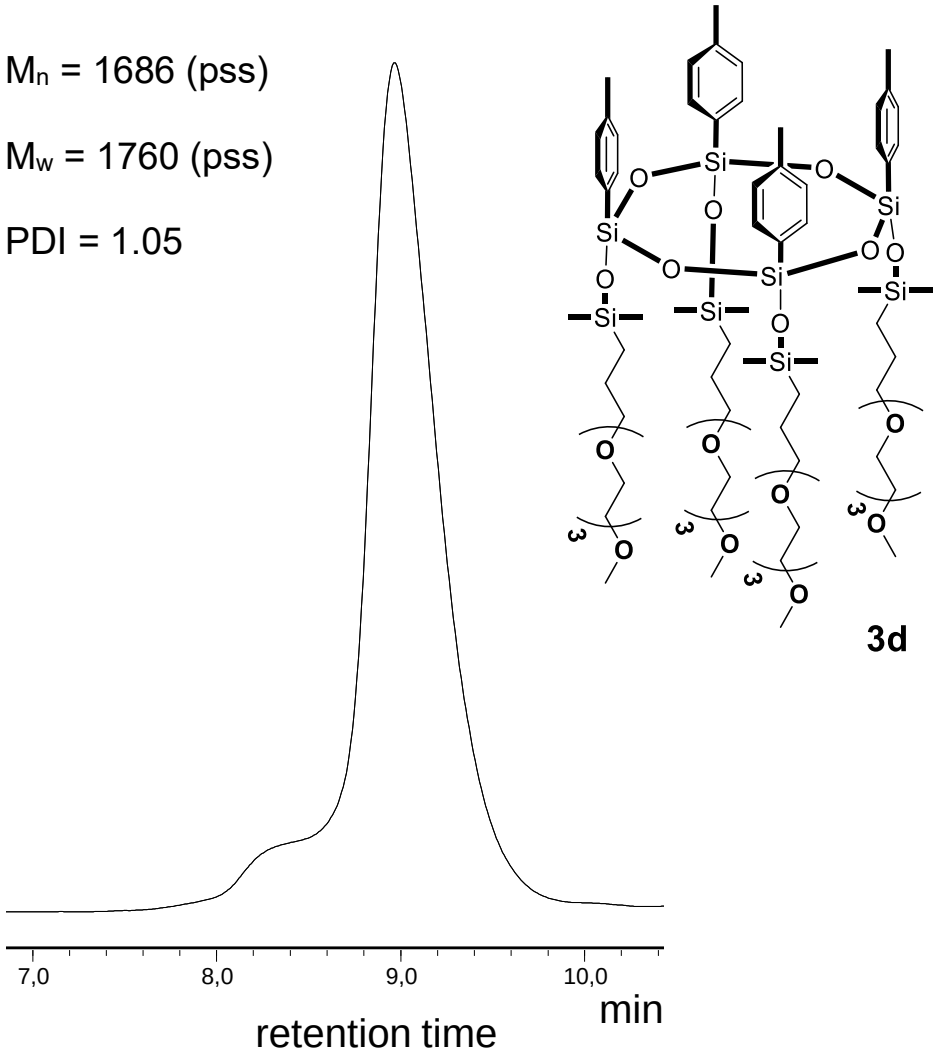
$CDCl_3$)



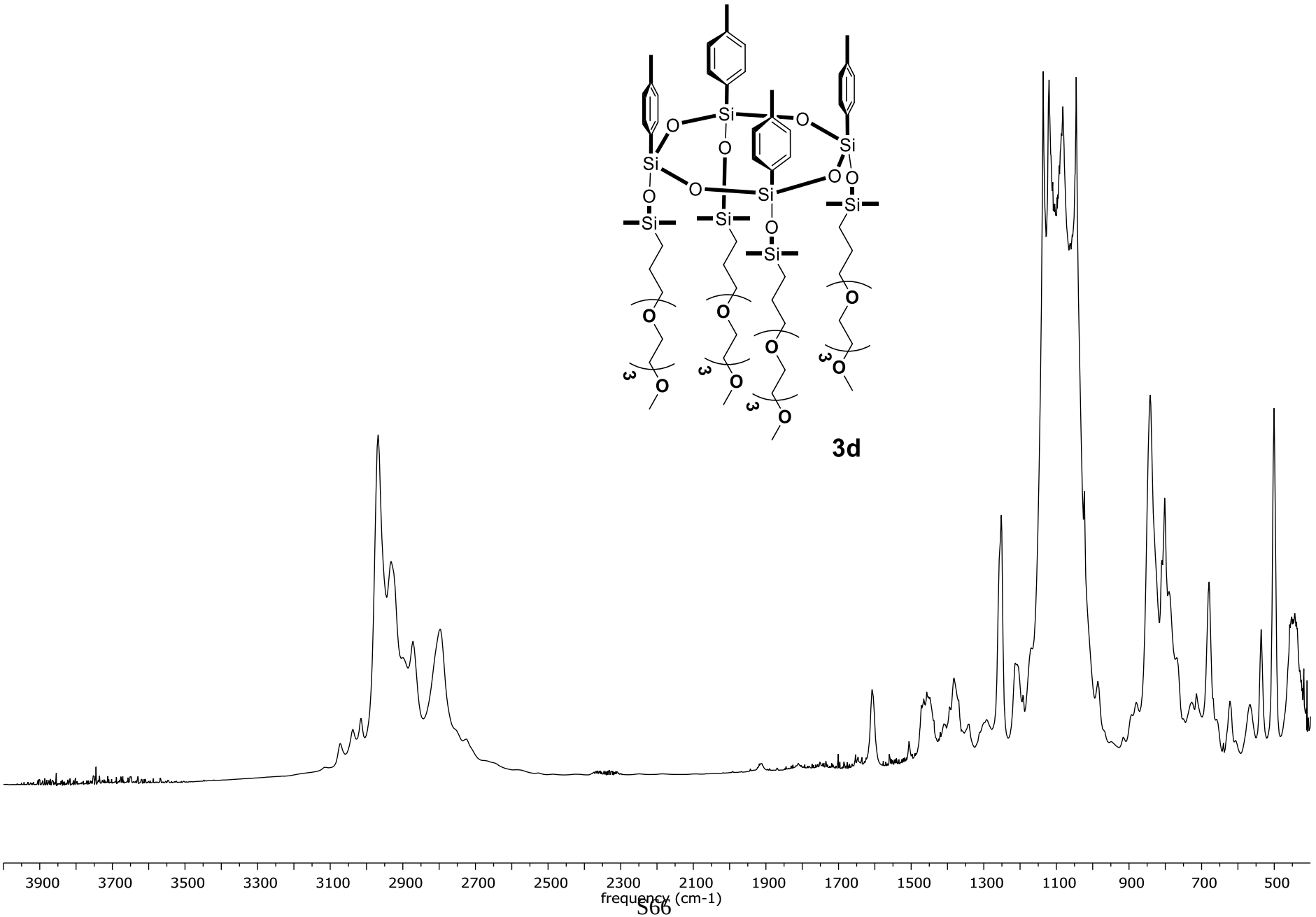

CH3-C6H4-Si
CH3-C6H4-Si
CH3Si
1H
-(CH2-CH2-O)3-CH3
-CH2-CH2-Si
13C (ppm)
CH3Si
-(CH2)2-Si
CH3-C6H4-
-CH2O-(C2H4-O)3-CH3
-C6H4-Si
0
20
60
70
130
140
1H, 13C HSQMBC
29Si (ppm)
CH3-C6H4-SiO3
CH2(CH3)2SiO
-80
+10
1H, 29Si HSQMBC
1H (ppm)
7.0
3.6
3.4
2.3
1.6
0.6
0.2


3d

GPC

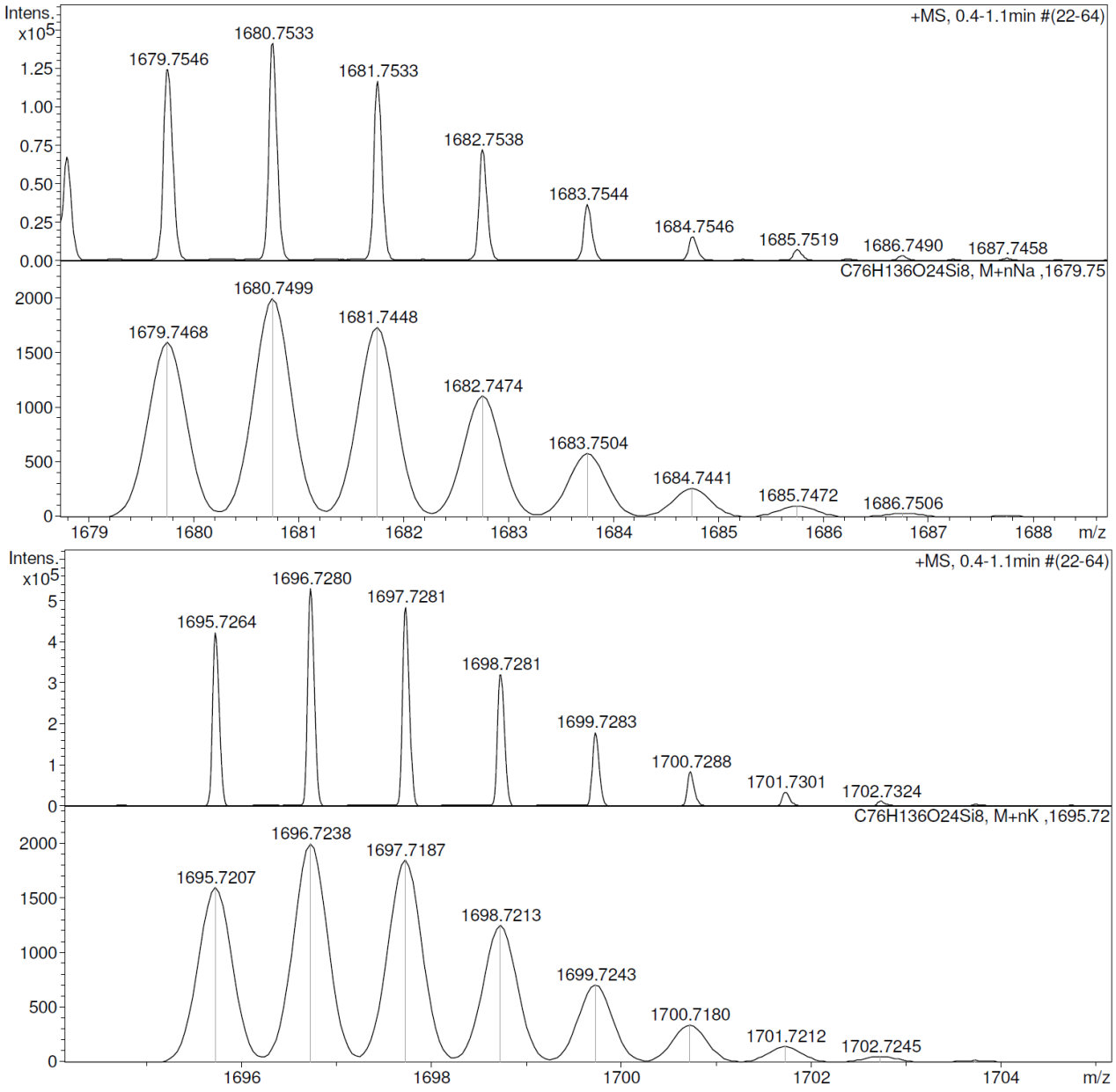

Mn = 1686 (pss)
Mw = 1760 (pss)
PDI = 1.05
7,0
8,0
9,0
10,0
min
retention time
3d

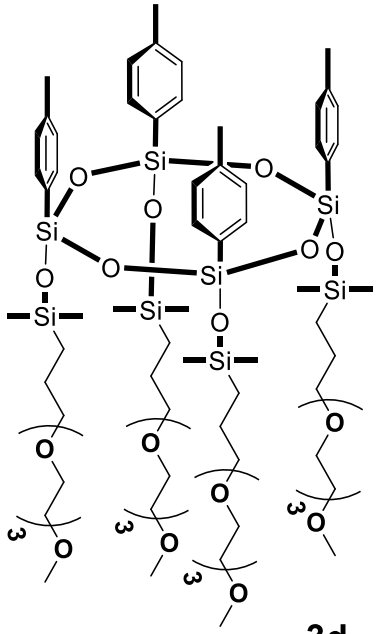
IR-spectrum



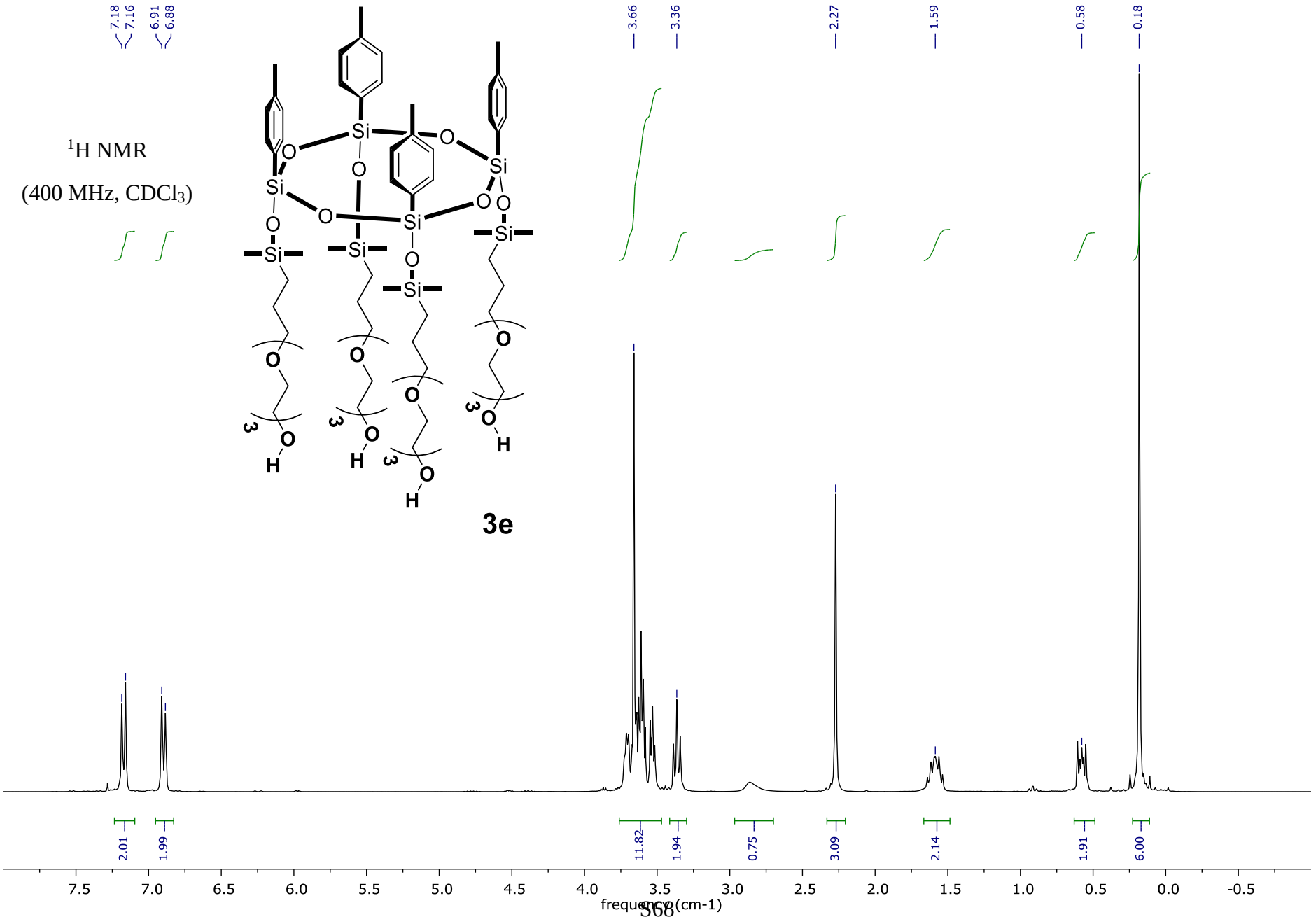
3d

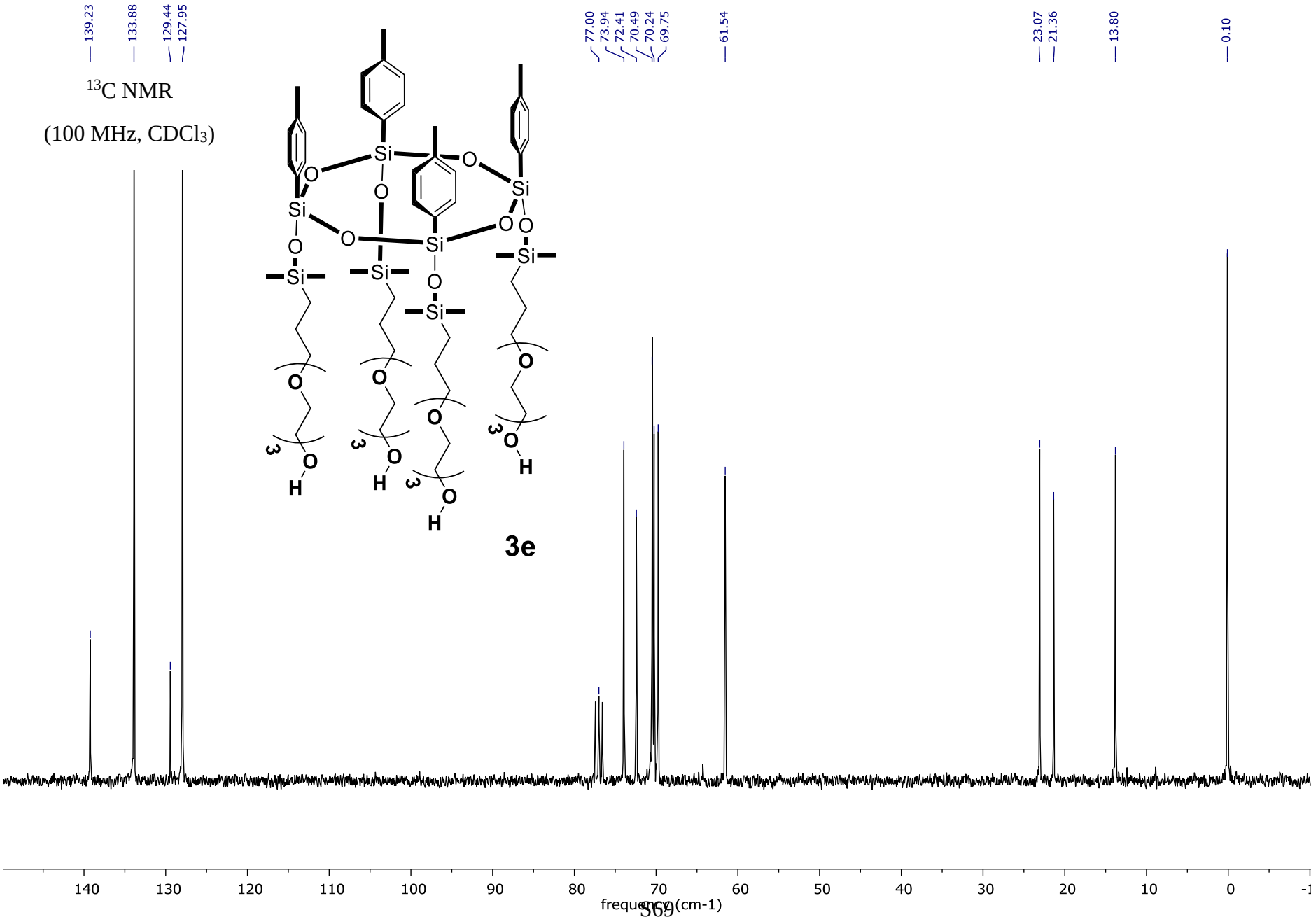
HRMS (ESI)


+MS, 0.4-1.1min #(22-64)
Intens.
x10^5
1679.7546
1680.7533
1681.7533
1682.7538
1683.7544
1684.7546
1685.7519
1686.7490
1687.7458
C76H136O24Si8, M+nNa ,1679.75
1679.7468
1680.7499
1681.7448
1682.7474
1683.7504
1684.7441
1685.7472
1686.7506
m/z
+MS, 0.4-1.1min #(22-64)
1695.7264
1696.7280
1697.7281
1698.7281
1699.7283
1700.7288
1701.7301
1702.7324
C76H136O24Si8, M+nK ,1695.72
1695.7207
1696.7238
1697.7187
1698.7213
1699.7243
1700.7180
1701.7212
1702.7245



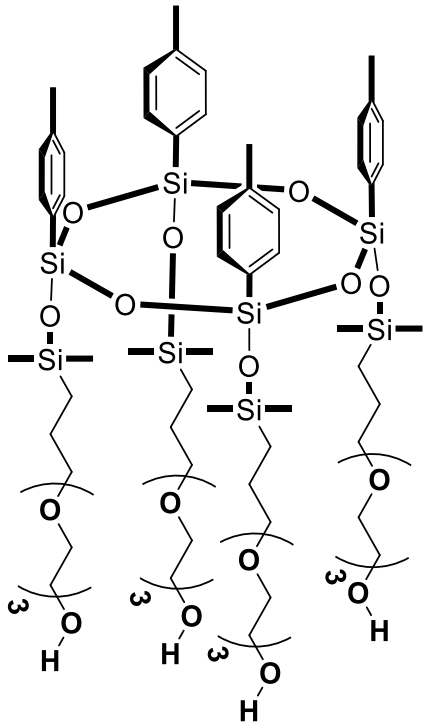
3d


7.18
7.16
6.91
6.88
3.66
3.36
2.27
1.59
0.58
0.18
^{1}H NMR
(400 MHz, $CDCl_3$)
3e
2.01
1.99
11.82
1.94
0.75
3.09
2.14
1.91
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
frequency (cm-1)


139.23
133.88
129.44
127.95
77.00
73.94
72.41
70.49
70.24
69.75
61.54
23.07
21.36
13.80
0.10
^{13}C NMR
(100 MHz, $CDCl_3$)
3e
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
frequency (cm-1)

^{29}Si NMR

(80 MHz, $CDCl_3$)

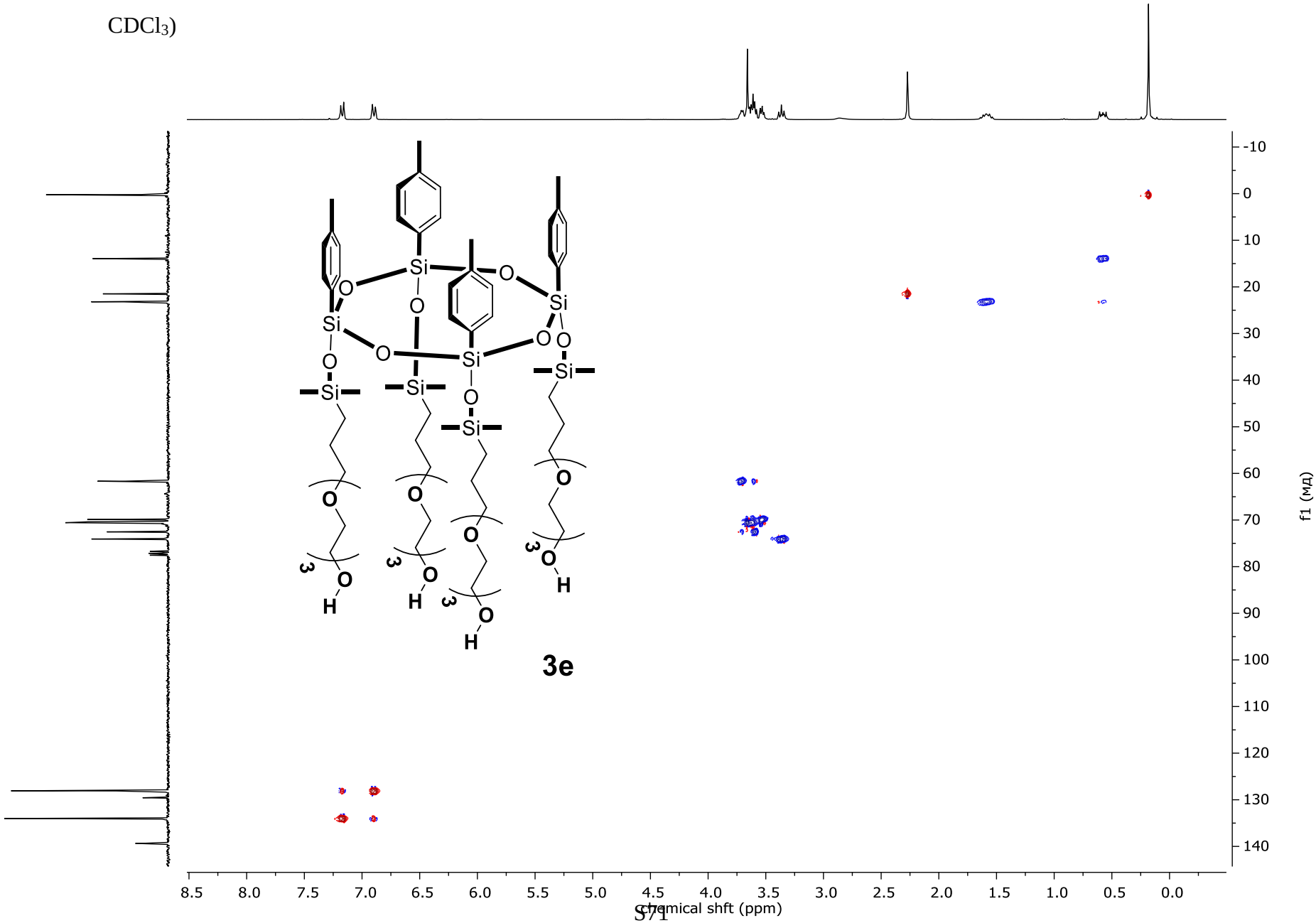


3e

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

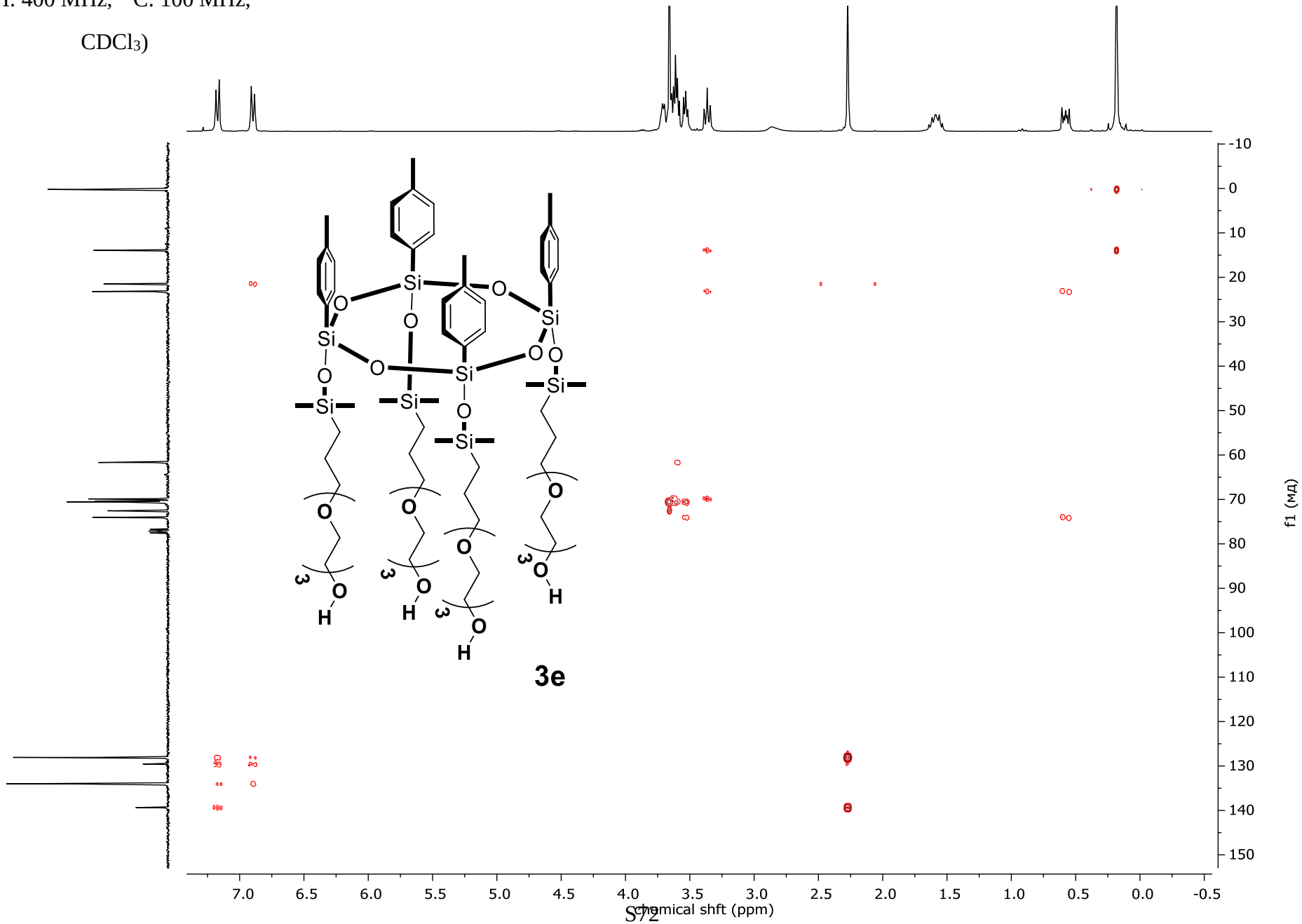
$CDCl_3$)



$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

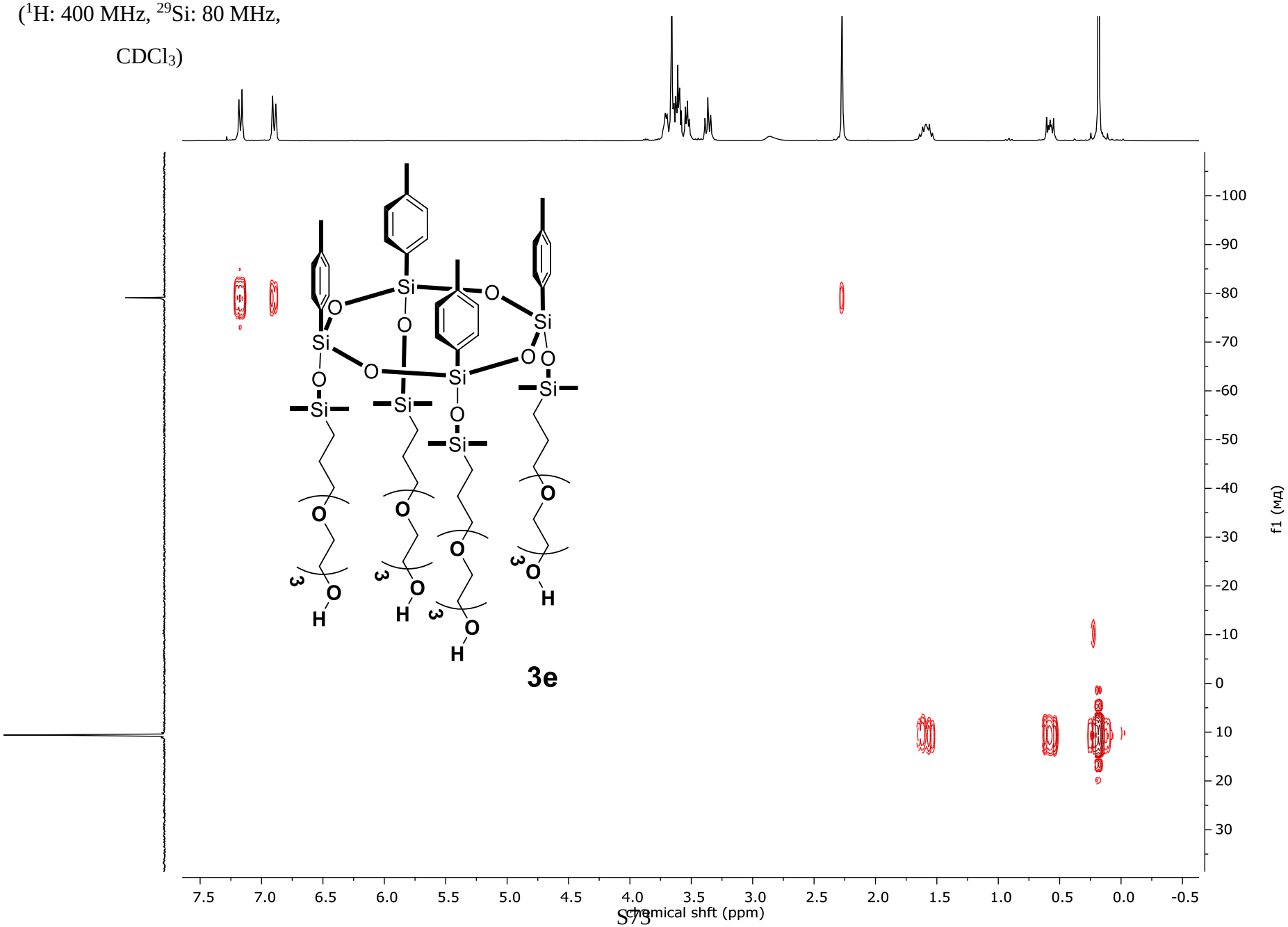
$CDCl_3$)



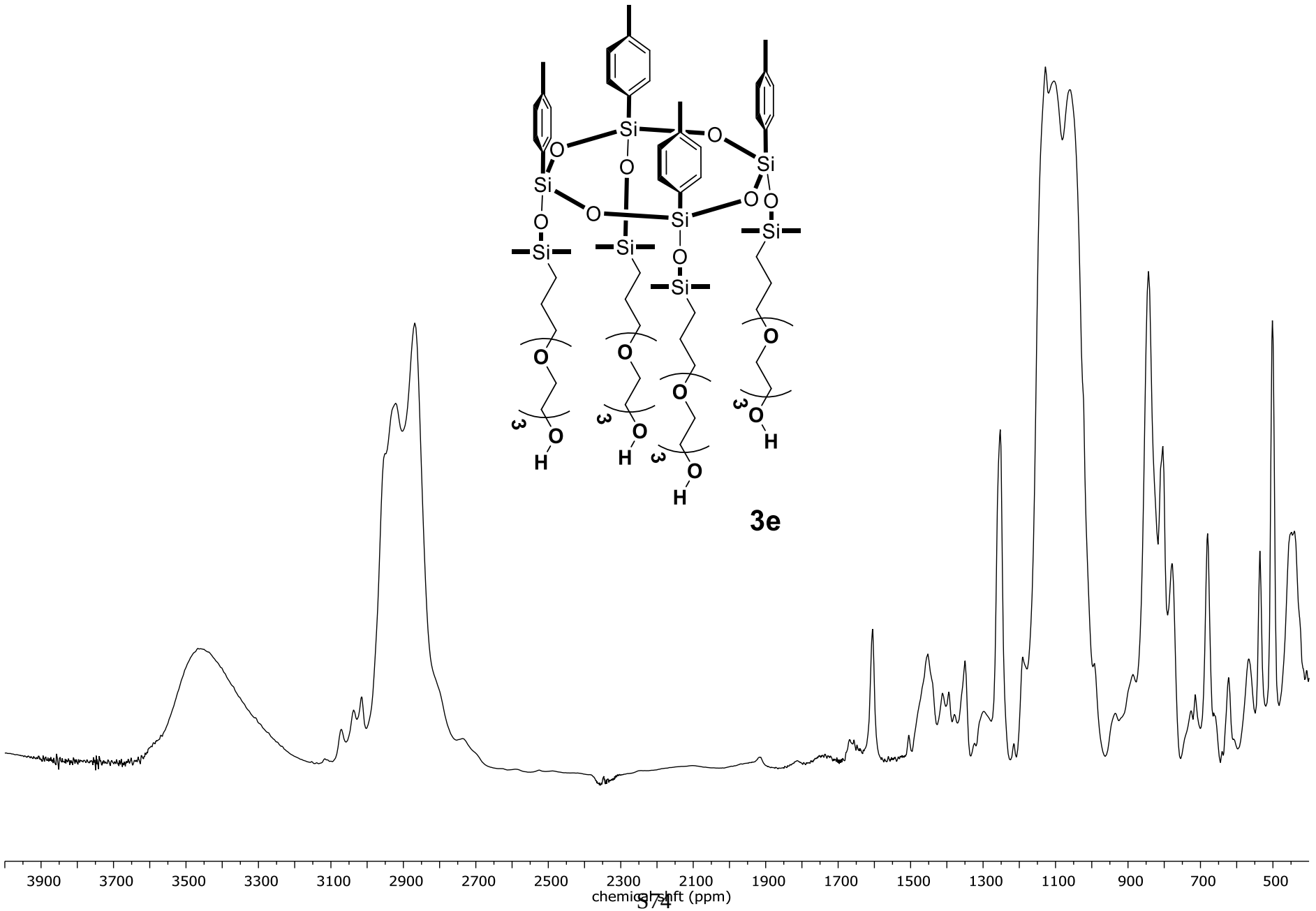
^{1}H,^{29}Si–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

$CDCl_3$)

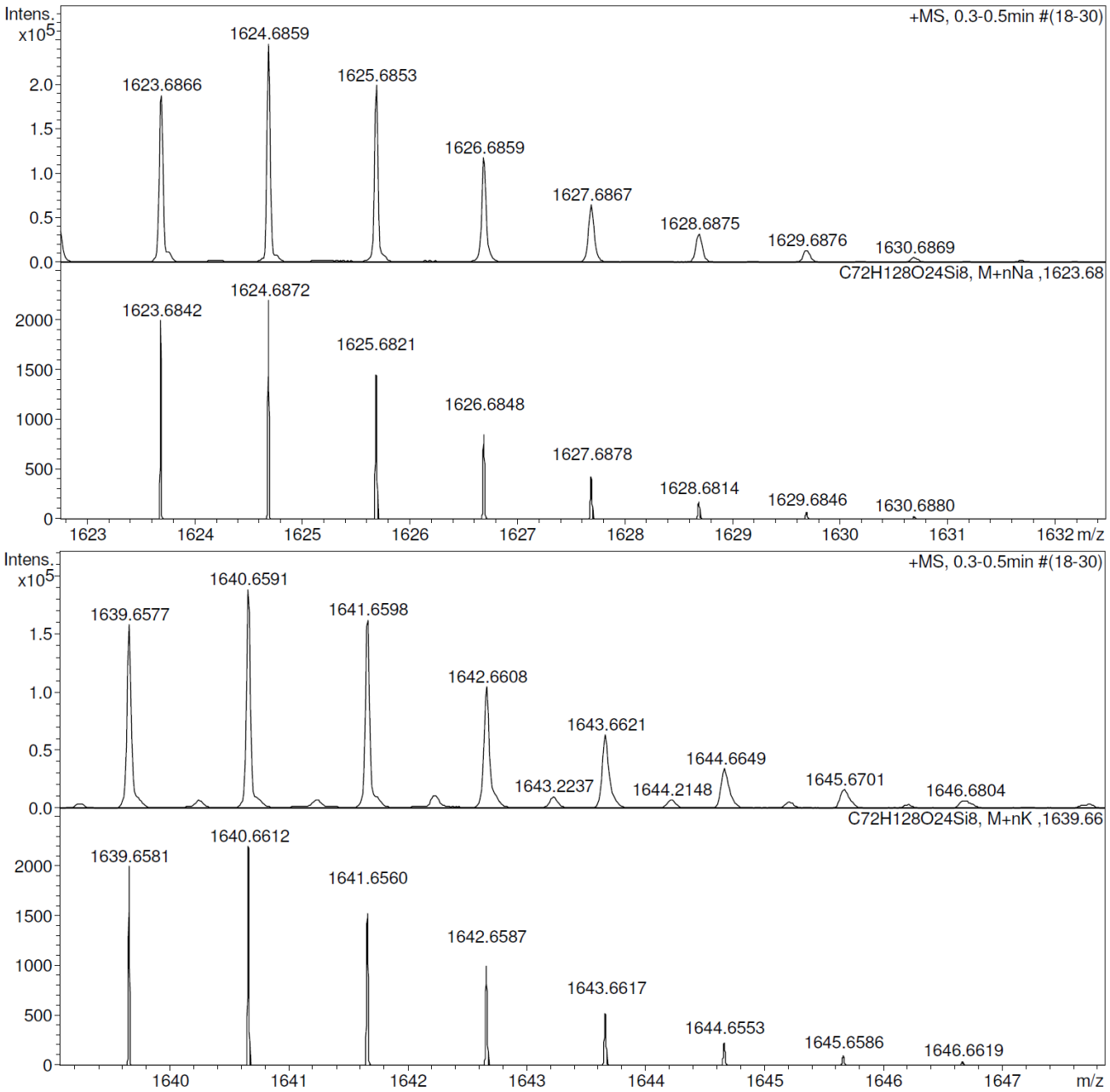


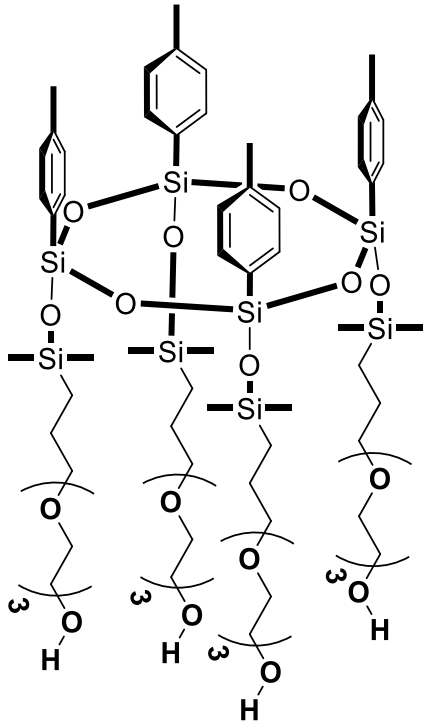
IR-spectrum



3e

HRMS (ESI)

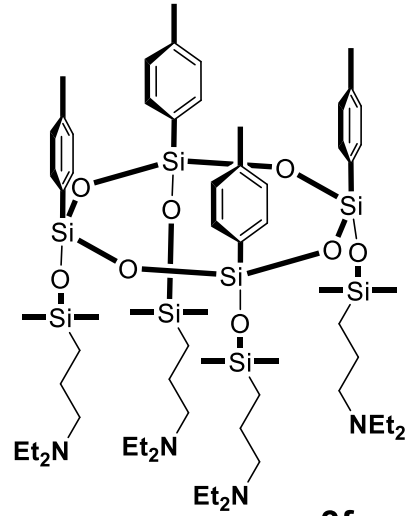

Intens.
x10^5
+MS, 0.3-0.5min #(18-30)
1624.6859
1623.6866
1625.6853
1626.6859
1627.6867
1628.6875
1629.6876
1630.6869
C72H128O24Si8, M+nNa ,1623.68
1624.6872
1623.6842
1625.6821
1626.6848
1627.6878
1628.6814
1629.6846
1630.6880
m/z
+MS, 0.3-0.5min #(18-30)
1640.6591
1639.6577
1641.6598
1642.6608
1643.6621
1644.6649
1643.2237
1644.2148
1645.6701
1646.6804
C72H128O24Si8, M+nK ,1639.66
1640.6612
1639.6581
1641.6560
1642.6587
1643.6617
1644.6553
1645.6586
1646.6619
m/z



3e

^{1}H NMR

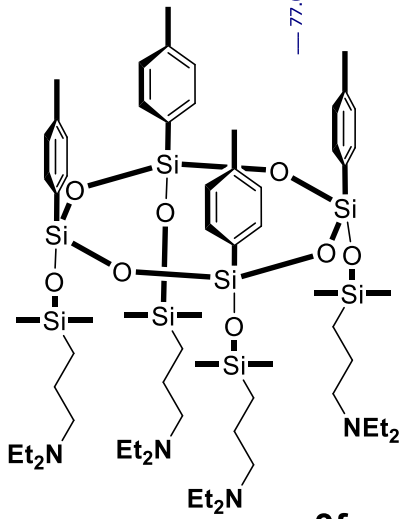
(400 MHz, $CDCl_3$)



3f

^{13}C NMR

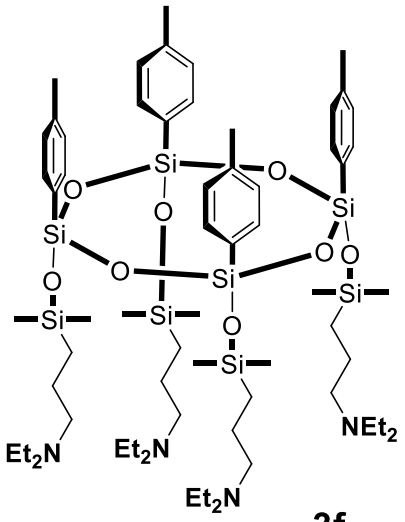
(100 MHz, $CDCl_3$)



3f

^{29}Si NMR

(80 MHz, $CDCl_3$)

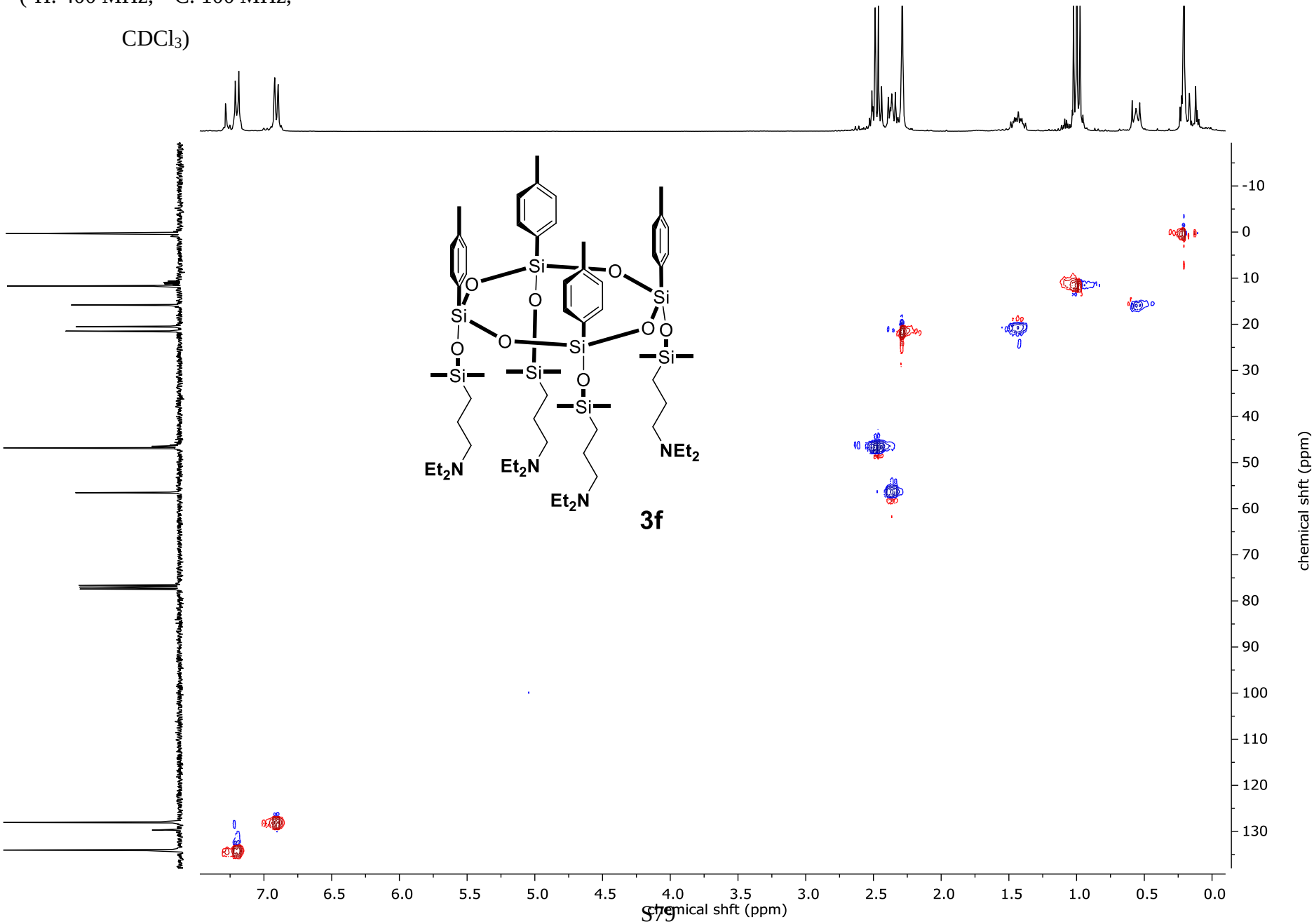


3f

^{1}H,^{13}C edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

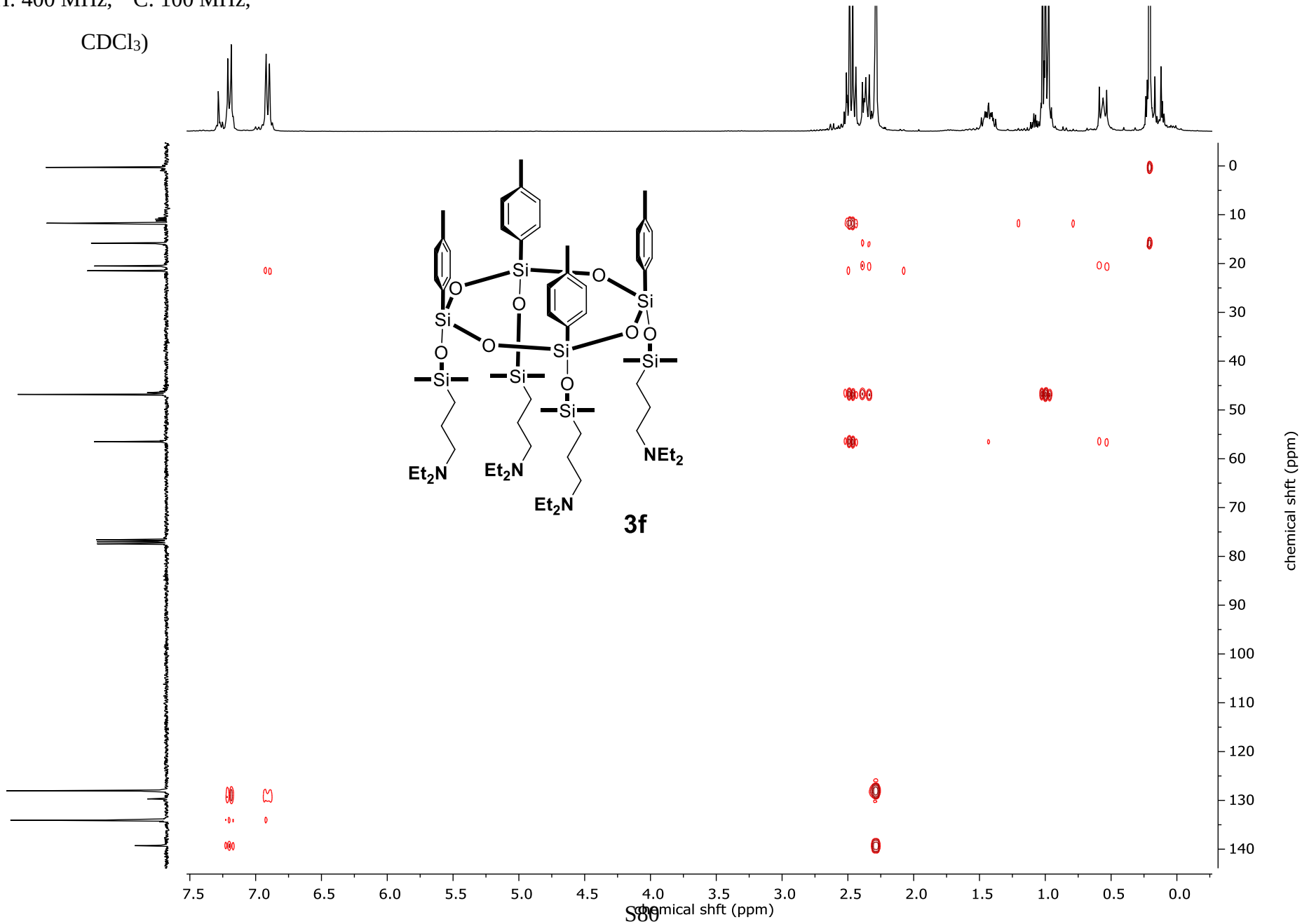
$CDCl_3$)



$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

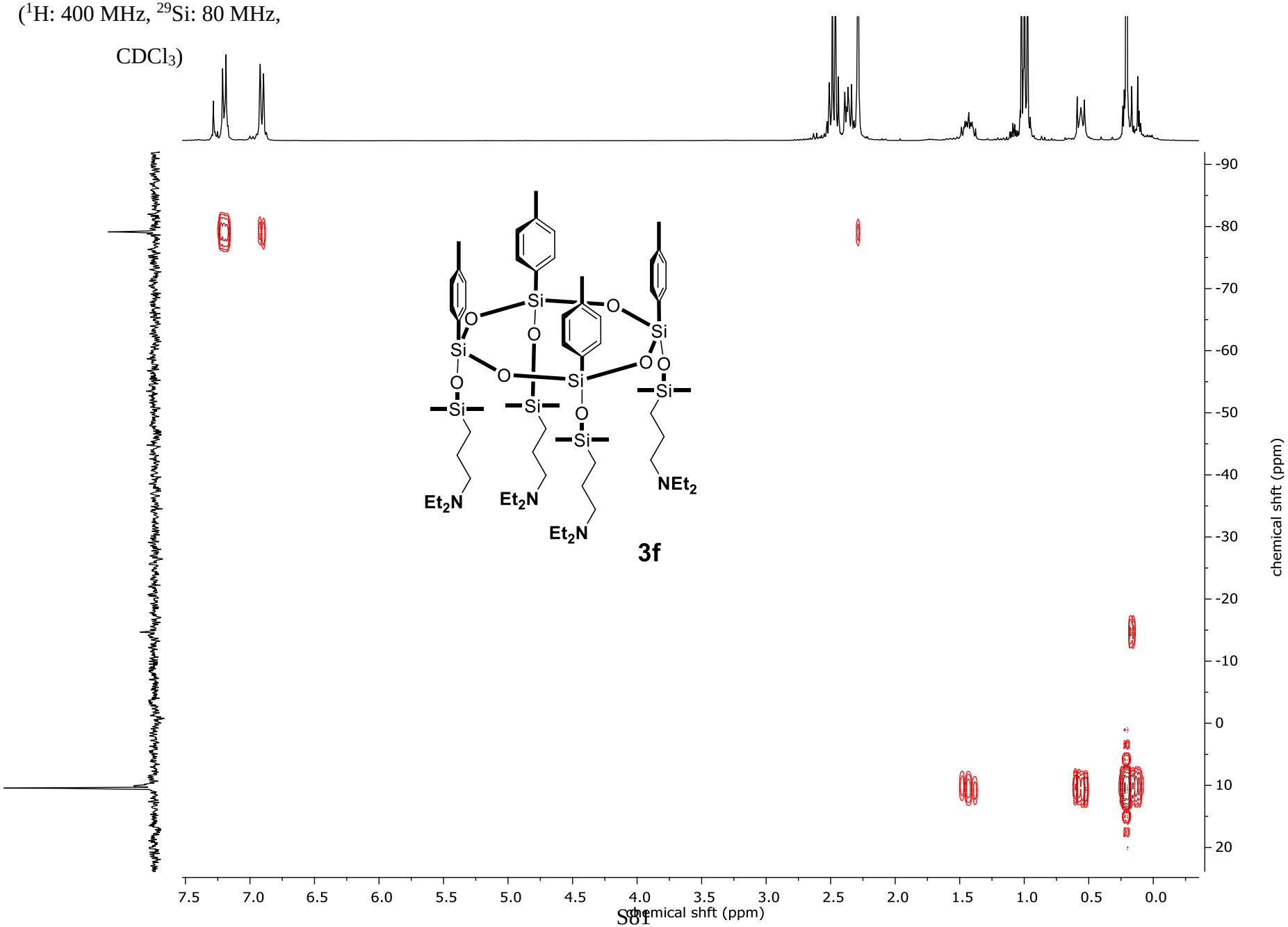
$CDCl_3$)



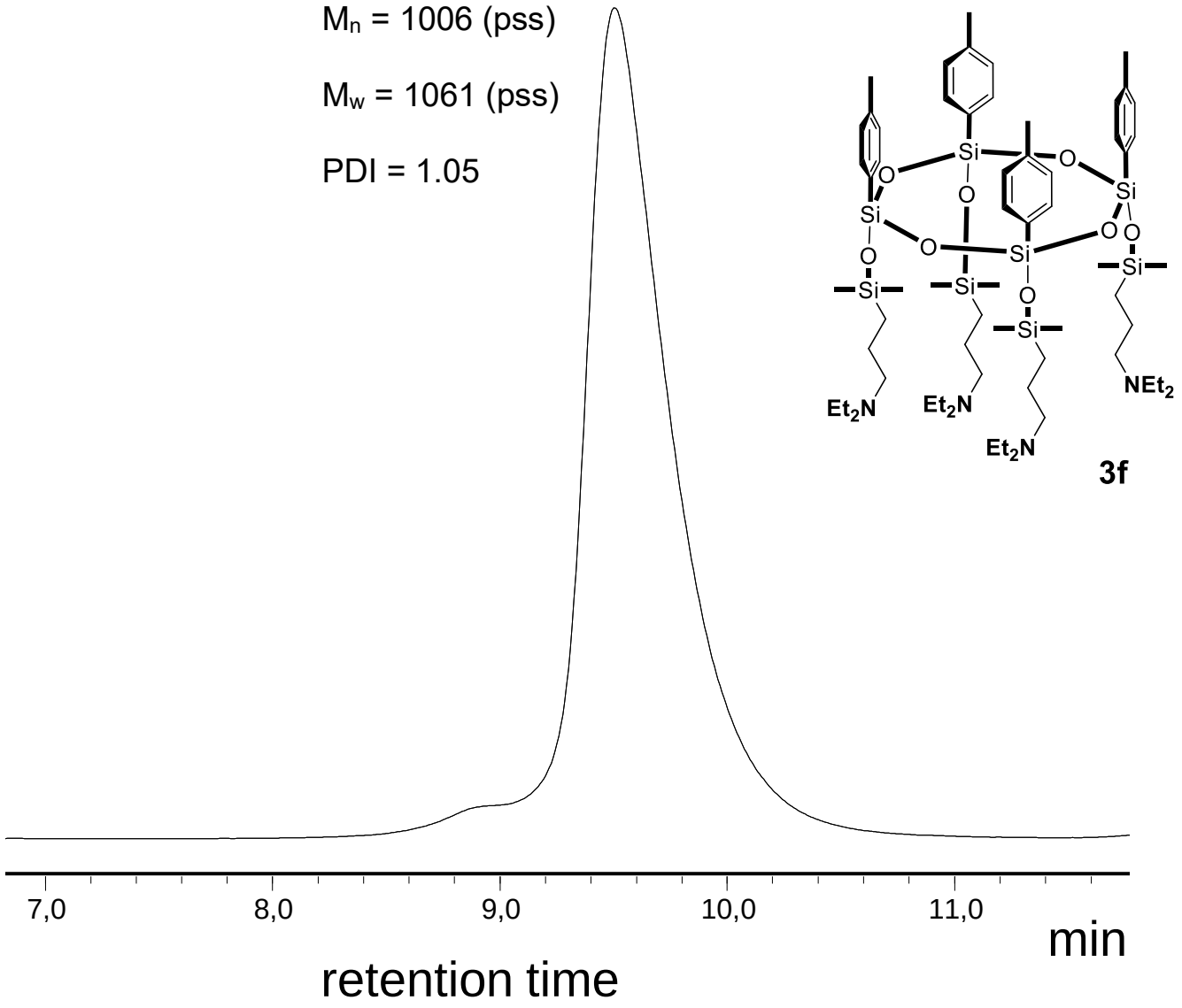
$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

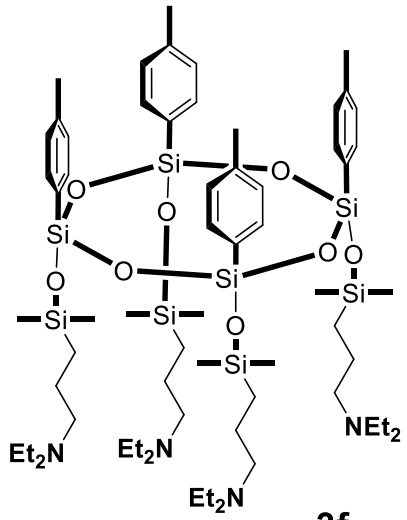
$CDCl_3$)



GPC

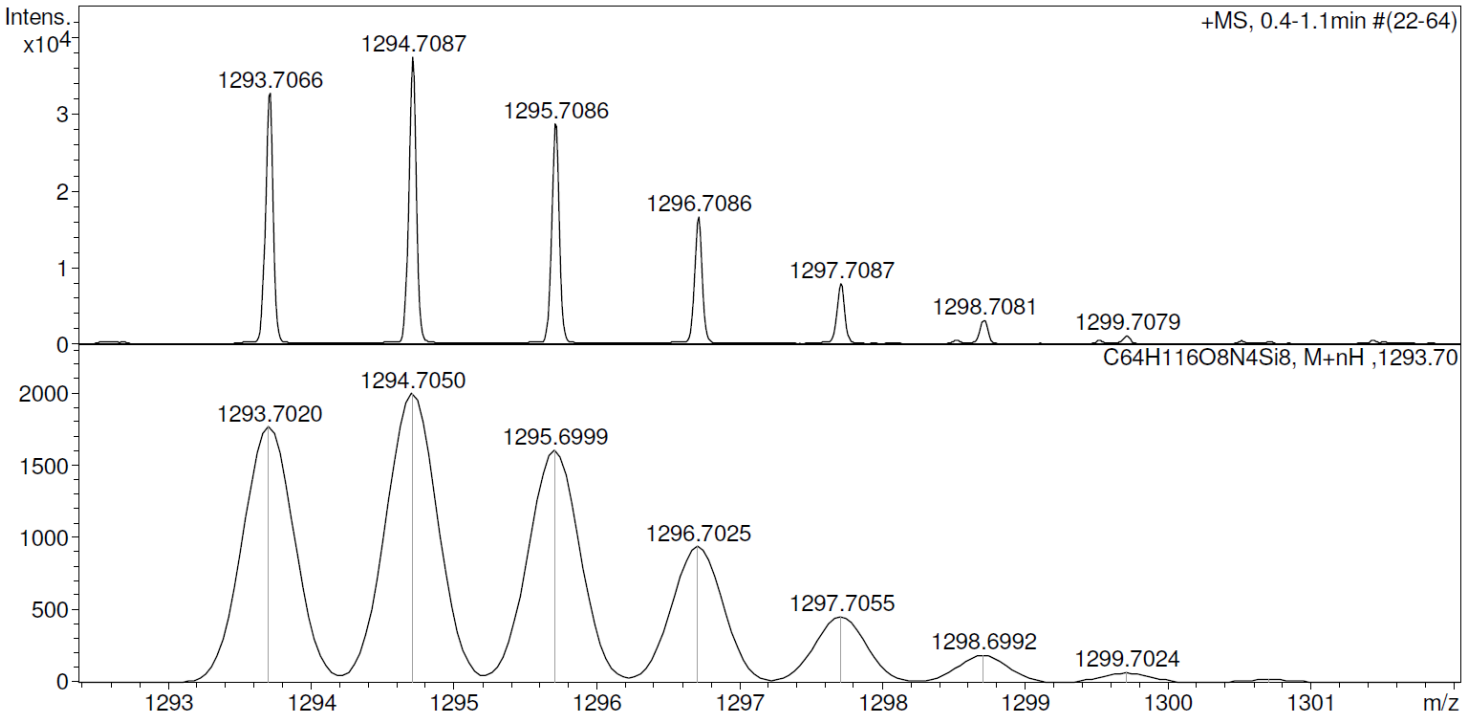

M_n = 1006 (pss)
M_w = 1061 (pss)
PDI = 1.05
Et2N
Et2N
Et2N
NEt2
3f
7,0
8,0
9,0
10,0
11,0
min
retention time

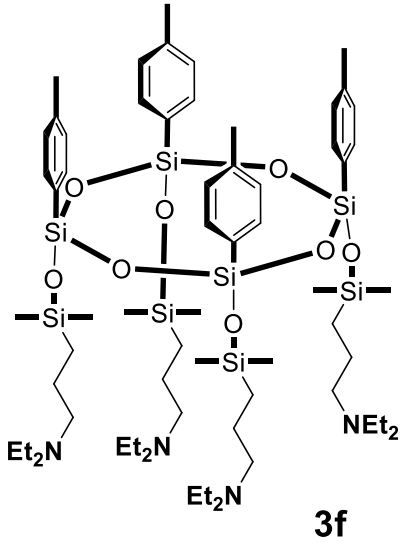
IR-spectrum



3f

HRMS (ESI)

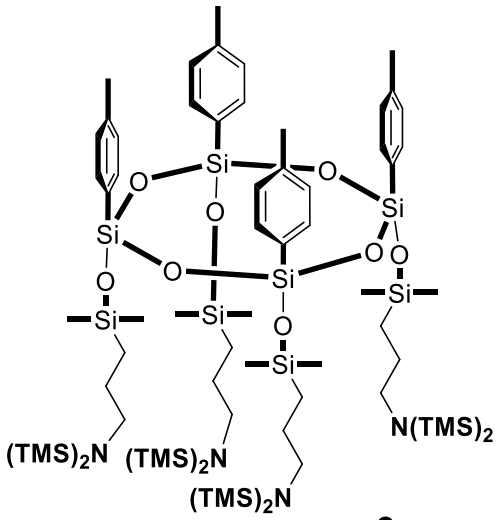

Intens.
x10^4
+MS, 0.4-1.1min #(22-64)
1293.7066
1294.7087
1295.7086
1296.7086
1297.7087
1298.7081
1299.7079
C64H116O8N4Si8, M+nH ,1293.70
1293.7020
1294.7050
1295.6999
1296.7025
1297.7055
1298.6992
1299.7024
m/z


Et2N
Et2N
Et2N
NEt2

3f

^{1}H NMR

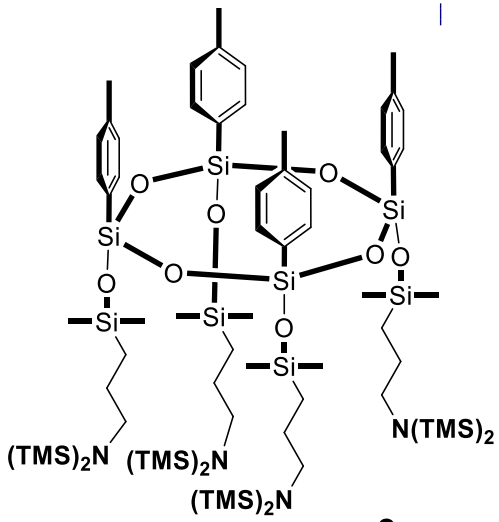
(400 MHz, $CDCl_3$)



3g

^{13}C NMR

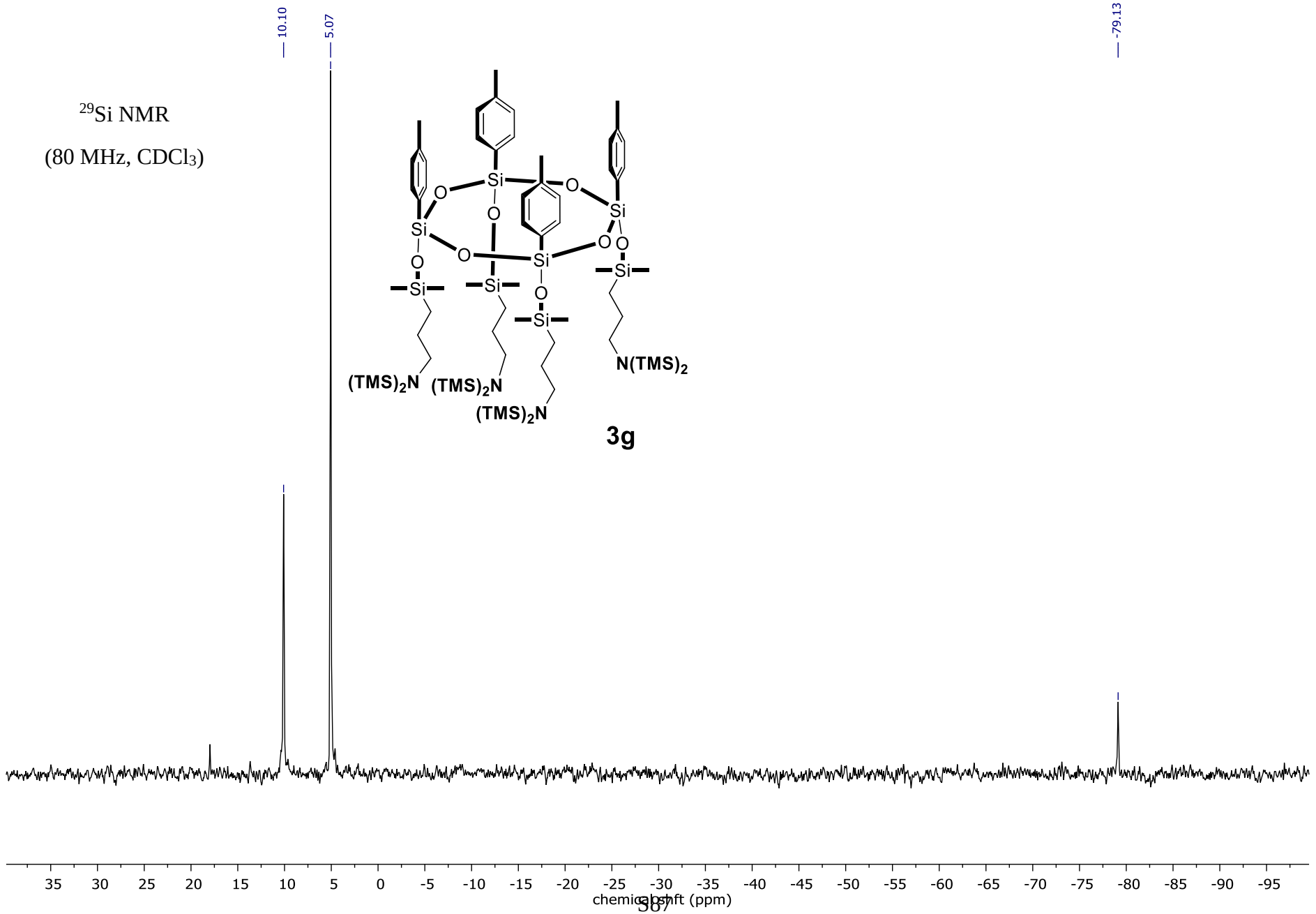
(100 MHz, $CDCl_3$)



3g

^{29}Si NMR

(80 MHz, $CDCl_3$)

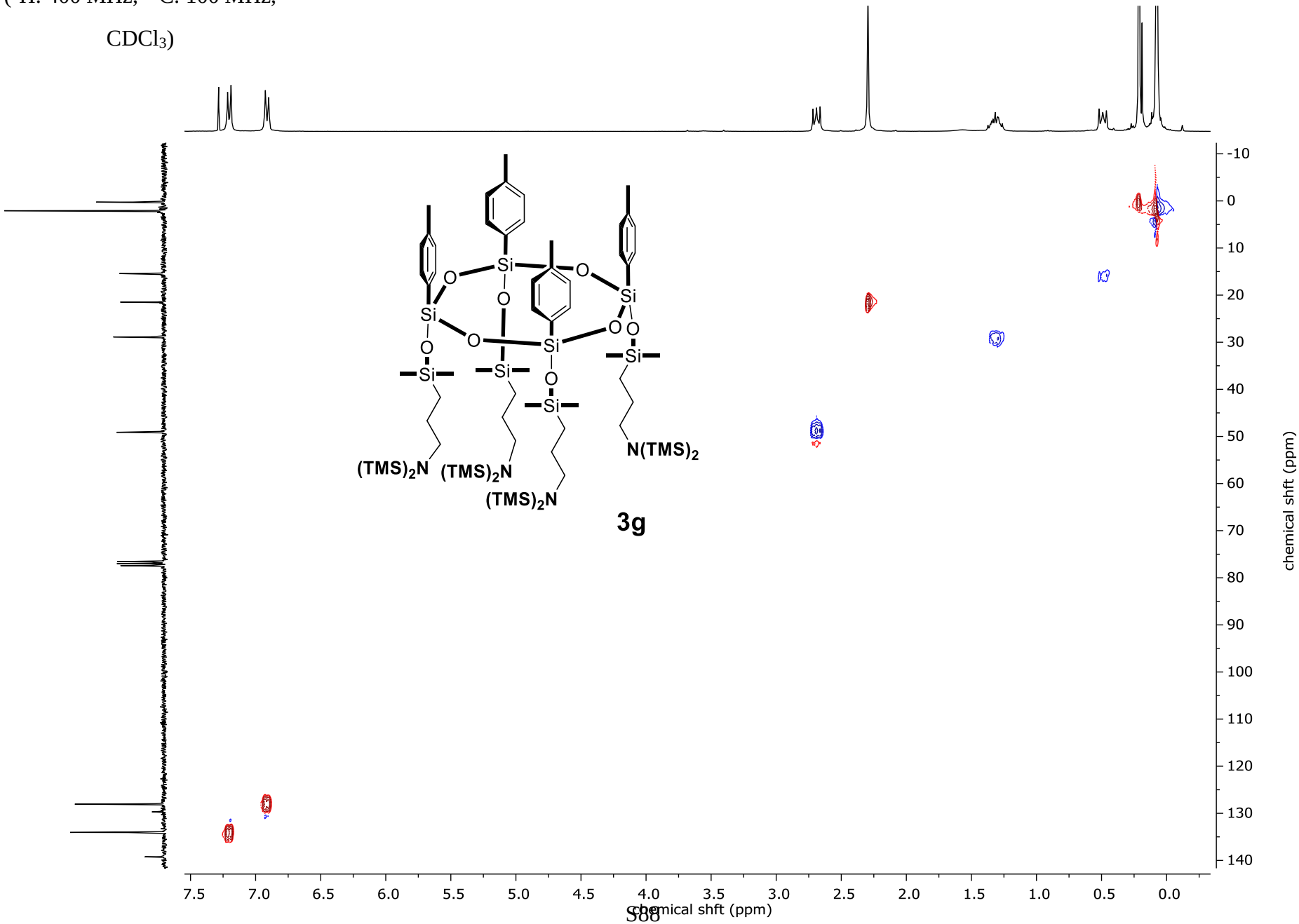


3g

$^{1}H,^{13}C$ edited-HSQC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

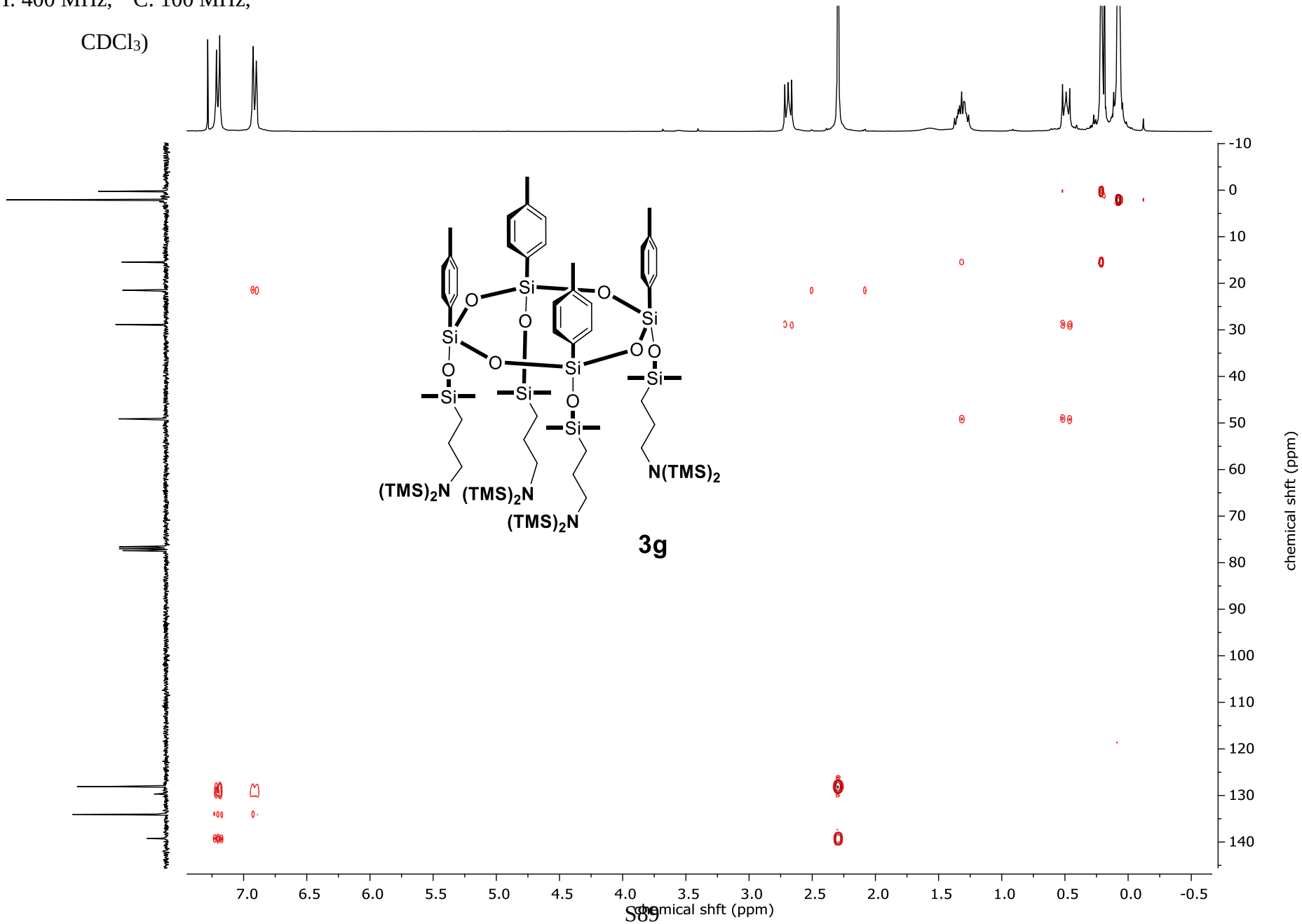
$CDCl_3$)



$^{1}H,^{13}C$–HMBC NMR,

(^{1}H: 400 MHz, ^{13}C: 100 MHz,

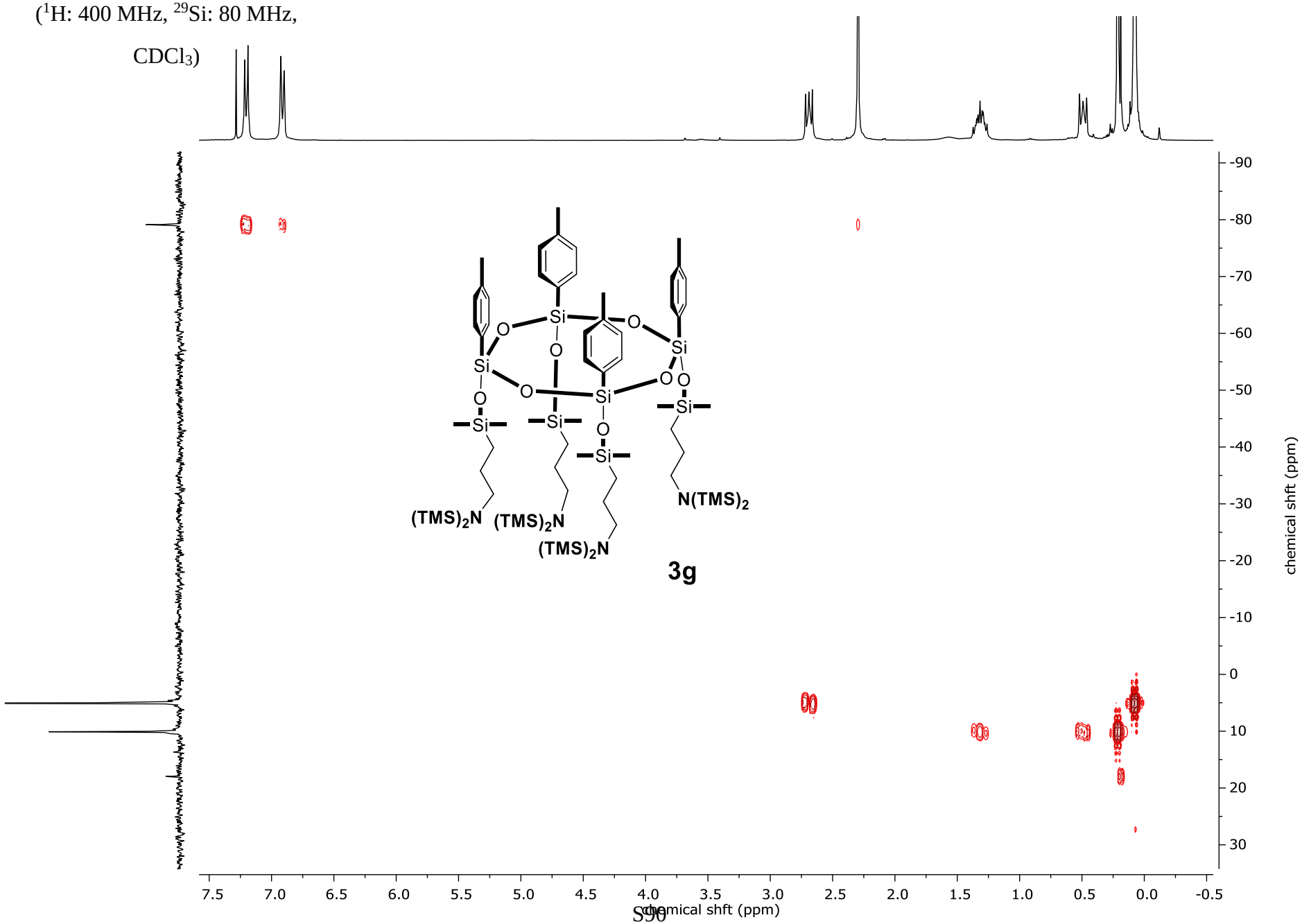
$CDCl_3$)



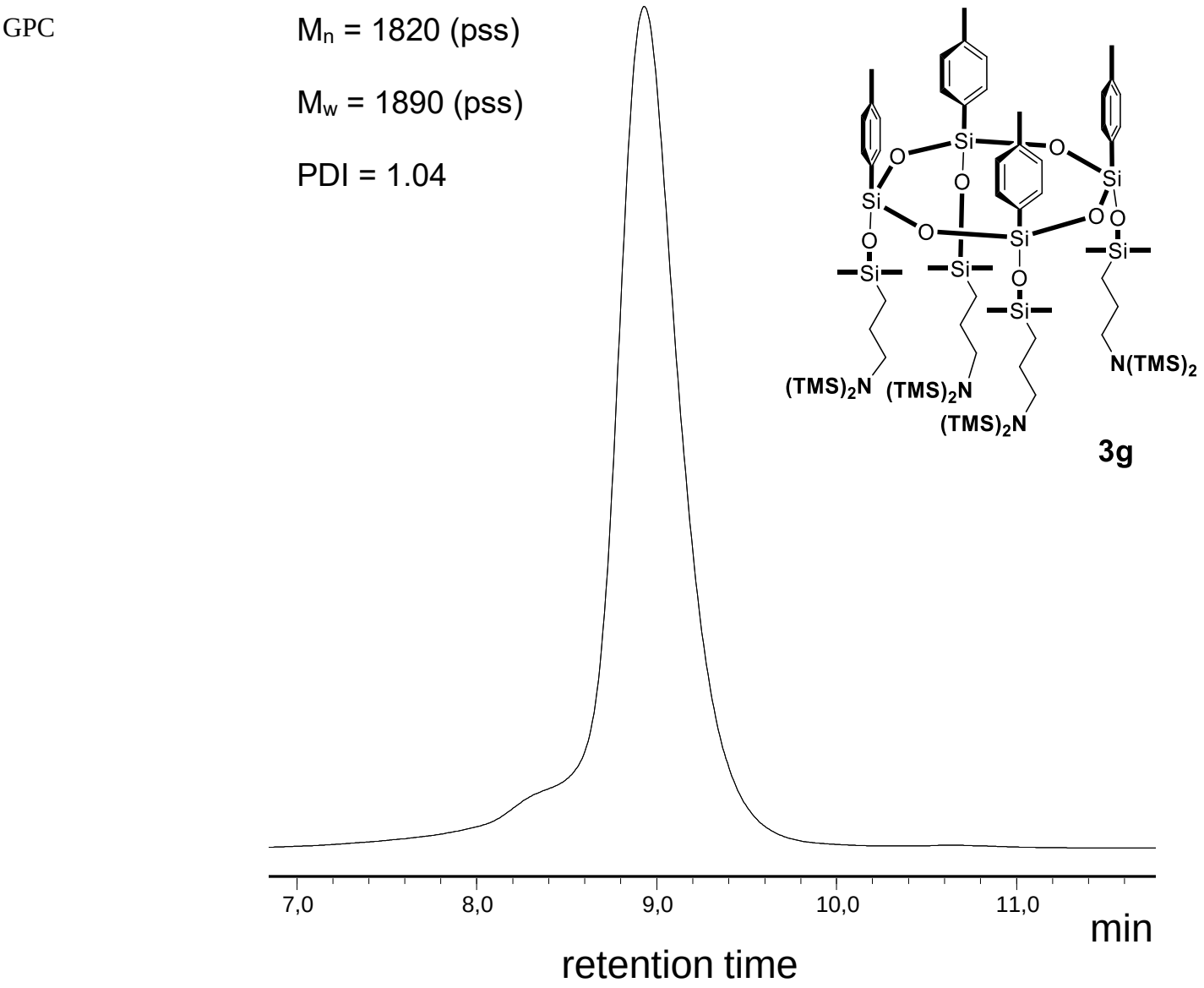
$^{1}H,^{29}Si$–HMBC NMR,

(^{1}H: 400 MHz, ^{29}Si: 80 MHz,

$CDCl_3$)



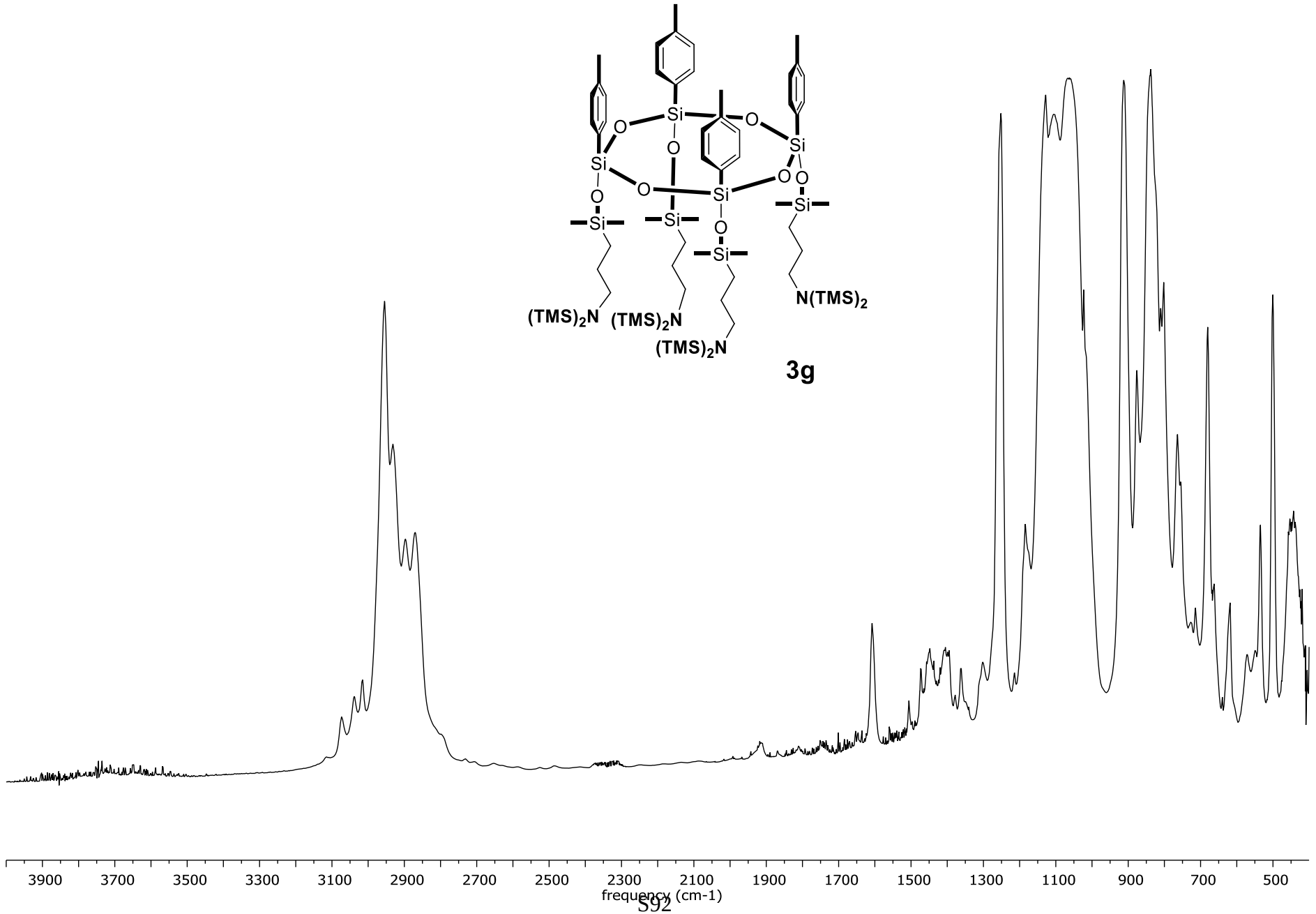
GPC


M_n = 1820 (pss)
M_w = 1890 (pss)
PDI = 1.04
7,0
8,0
9,0
10,0
11,0
min
retention time

(TMS)2N
(TMS)2N
(TMS)2N
N(TMS)2

3g

IR-spectrum



3g

S5. References

1. D. N. Kholodkov, A. A. Anisimov, S. N. Zimovets, A. A. Korlyukov, R. A. Novikov, A. V. Arzumanyan and A. M. Muzafarov, *Journal of Organometallic Chemistry*, 2020, **914**, 121223.
2. Y. S. Vysochinskaya, A. A. Anisimov, S. A. Milenin, A. A. Korlyukov, F. M. Dolgushin, E. G. Kononova, A. S. Peregudov, M. I. Buzin, O. I. Shchegolikhina and A. M. Muzafarov, *Mendeleev Communications*, 2018, **28**, 418-420.
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