

Supporting Information

Synthesis and Characterization of Highly Pure Azido-functionalized Polyhedral Oligomeric Silsesquioxanes (POSS)

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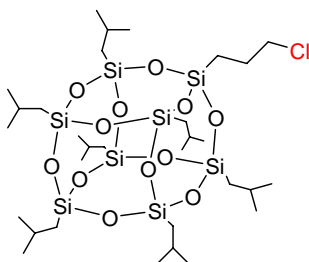
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Characterization and reagents

^1H (300 MHz), ^1H (500 MHz), ^{13}C (125 MHz), and ^{29}Si (99 MHz) NMR spectra were obtained in CDCl_3 on a Varian 300 MHz and 500MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm relative to CHCl_3 (δ 7.26, ^1H), CDCl_3 (δ 77.0, ^{13}C) and tetramethylsilane (δ 0.00, ^{29}Si). Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) was performed using a Voyager-DE RP (Applied Biosystems) in linear and reflectron modes. The matrix 2,5-dihydroxybenzoic acid (DHBA) was dissolved in THF (10 mg/mL), and mixed with the sample solution (0.5~1 mg/mL in THF) in 1:1 v/v ratio. The samples were spotted onto the target and dried in air. Elemental analyses were performed by CHNOS Elemental Analyzer, Vario EL III. Column chromatography (CC): SiO_2 60 (230~400 mesh, 40~63 μm) from E. Merck. TLC glass plates coated with SiO_2 60 F₂₅₄ from E. Merck, visualization by UV light.

Reagents and solvents were purchased and used without further purification, except for THF, which was distilled in the presence of CaH_2 . All reactions were performed in standard glassware.

Experiment



Synthesis of (3-chloropropyl)hepta(i-butyl)octasilsesquioxane (2)

Under a dry nitrogen atmosphere, 3-chloropropyltrichlorosilane (1.79 mL, 2.43 g, 11.5 mmol) was added drop wise over ten minutes period to a solution mixture of **1** (9.08 g, 11.47 mmol), triethylamine (36 mmol, 5.049 mL), and 90 mL of dry THF at room temperature. The reaction solution was kept stirring for overnight. After the encapping reaction completed, the suspension solution was filtered to remove a white salt of triethylamine hydrochloride. Evaporation of the mother liquid gave a crude product, which was further dissolved with 50 mL of THF. Some insoluble remaining was filtered out to obtain the clear solution. The solution was added with the same amount of methanol to fully precipitate the product, filtered, several washed with methanol, and dried over vacuum to obtain a white solid. The product was further purified by recrystallization in THF and methanol to yield colorless crystals (7.47 g, 8.37 mmol, 73%yield).

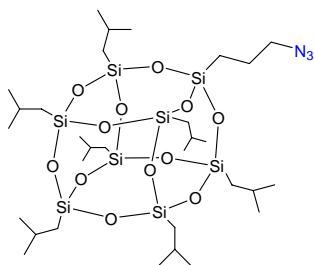
^1H NMR (500 MHz, CDCl_3): δ = 3.53 (t, 2H), 1.88 (m, 7H), 1.82 (overlapped, 2H), 0.96 (d, 42H), 0.75 (m, 2H), 0.62 (m, 14H).

^{13}C NMR (125 MHz, CDCl_3): δ = 47.27, 26.45, 25.69, 25.66, 23.88, 23.84, 22.47, 22.41, 9.76.

^{29}Si NMR (99 MHz, CDCl_3): δ = -67.57, -67.87, -68.10 (relative intensity ratio 3:4:1).

MALDI-TOF MS [$\text{C}_{31}\text{H}_{69}\text{ClO}_{12}\text{Si}_8 + \text{Na}$] $^+$: Calcd. 915.25, found 915.71.

Elemental analyses ($\text{C}_{31}\text{H}_{69}\text{ClO}_{12}\text{Si}_8$): Calcd. C 41.65, H 7.78; Found C 41.48, H 7.92.



Synthesis of (3-azidopropyl)hepta(i-butyl)octasilsesquioxane (3)

Under a dry nitrogen atmosphere, a solution mixture of dry DMF (70 ml), dry THF (20 ml), and **2** (2.0 g, 2.24 mmol) was added with 3 equivalent of sodium azide (6.71 mmol, 0.436 g). The solution mixture was kept stirring at 70°C for 24 hours and reaction was cooled down at room temperature. The reaction solution was quenched by pouring in 80 g of ice to fully precipitate a product. The product was filtered, dried over vacuum, and further recrystallized in THF and methanol mixture solvent to obtain a colorless product (1.88 g, 2.09 mmol, 93%yield).

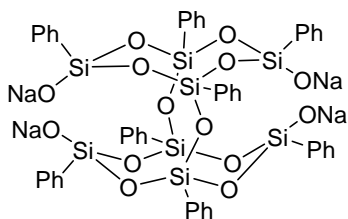
^1H NMR (300 MHz, CDCl_3): δ = 3.27 (t, 2H), 1.89 (m, 7H), 1.74 (quin, 2H), 0.97 (d, 42H), 0.69 (overlapped, 2H), 0.62 (m, 14H).

^{13}C NMR (125 MHz, CDCl_3): δ = 53.62, 25.68, 25.65, 23.89, 23.84, 22.46, 22.41, 9.29.

^{29}Si NMR (99 MHz, CDCl_3): δ = -67.57, -67.86, -68.12 (relative intensity ratio 3:4:1).

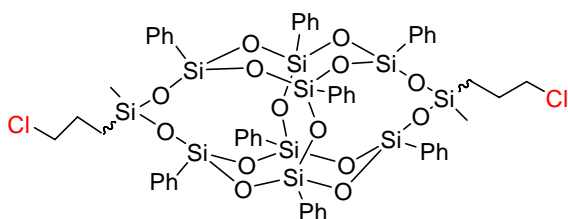
MALDI-TOF MS [$\text{C}_{31}\text{H}_{69}\text{N}_3\text{O}_{12}\text{Si}_8 + \text{Na}$] $^+$: Calcd. 922.29, found 922.96.

Elemental analyses ($\text{C}_{31}\text{H}_{69}\text{ClO}_{12}\text{Si}_8$): Calcd. C 41.34, H 7.72, N 4.67; Found C 41.23, H 7.83, N 4.47.



Synthesis of double-decker silsesquioxane (DDQ) (4)

According to synthetic literature of **4**,^{2m} phenyltrimethoxysilane (44.9 mL, 47.6 g, 0.24 mol) was added dropwise to a solution mixture of 2-propanol (240 mL), deionized water (5 mL, 0.28 mol), and sodium hydroxide (6.40 g, 0.16 mol) at room temperature for 15 minutes. The reaction mixture was refluxed for 4 hours to obtain a white precipitate. The suspension solution was cooled down at room temperature for overnight. The product was filtered, washed with 2-propanol, and dried over 60°C for 5 hours to obtain a white powder of **4** (21.5 g, 18.57 mmol, 62%yield).



Synthesis of 3,13-di(3-chloropropyl)-3,13-dimethyl-1,5,7,9,11,15,17,19-octaphenylhexacyclo[15.3.1(1,13).1(3,11).1(5,17).1(9,15)]decasiloxane (5)

Under a dry nitrogen atmosphere, 3-chloropropylmethylchlorosilane (10.18 g, 8.45 mL, 53.1 mmol) was added dropwise to solution mixture of a 180 mL THF, **4** (20.5 g, 17.71 mmol), and triethylamine (10 mL, 61.7 mmol) at room temperature for 10 minutes. After stirring overnight, the reaction was filtered to remove an insoluble salt of triethylamine hydrochloride (HNEt₃Cl). Evaporation of the solution gave a dryness of crude. 100 mL of THF was added into the crude, which was further refiltered to remove some remaining insoluble. Equivalent volume of hexane was added into the mother liquid and kept standing at room temperature for two days to obtain a white crystalline as the isomeric mixture of **5** (2.82 g, 2.16 mmol, 12.2%yield).

Cis and *trans*-**5** (in the presence of isomeric mixture of 1:1 ratio):

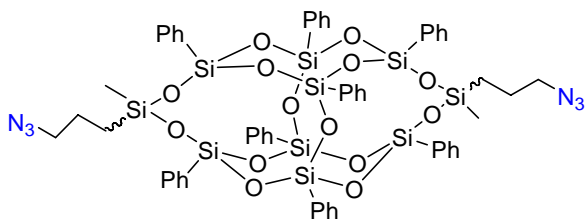
^1H NMR (500 MHz, CDCl_3): $\delta = 7.54\text{--}7.18$ (m, 40H), 3.42 (t, 4H), 1.89 (m, 4H), 0.87 (m, 4H), 0.315–0.312 (s, 6H; indicated isomeric mixture).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 134.03, 134.01, 133.99, 133.86, 131.76, 130.88, 130.78, 130.71, 130.45, 130.43, 130.39, 127.84, 127.69, 47.44, 26.34, 14.34, -0.917, -0.925$.

^{29}Si NMR (99 MHz, CDCl_3): $\delta = -18.35, -78.46, -79.46$ (*trans*-**5**; relative intensity ratio 1:2:2); $\delta = -18.35, -78.51, -79.40, -79.49$ (*cis*-**5**; relative intensity ratio 1:2:1:1)

MALDI-TOF MS [$\text{C}_{56}\text{H}_{58}\text{Cl}_2\text{O}_{14}\text{Si}_{10} + \text{Na}$] $^+$: Calcd. 1329.08, found 1328.21.

Elemental analyses ($\text{C}_{56}\text{H}_{58}\text{Cl}_2\text{O}_{14}\text{Si}_{10}$): Calcd. C 51.47, H 4.47; Found C 51.34, H 4.48.



Synthesis of 3,13-di(3-azidopropyl)-3,13-dimethyl-1,5,7,9,11,15,17,19-octaphenylhexacyclo[15.3.1(1,13).1(3,11).1(5,17).1(9,15)]decasiloxane (6)

Under a dry nitrogen atmosphere, a solution mixture of 50 mL of dry DMF, 20 mL of dry THF, sodium azide (0.269 g, 4.14 mmol), and **5** (0.90 g, 0.689 mmol) was heated at 60°C for 24 hours. The solution was cooling down at room temperature, slowly poured into 50 mL of dichloromethane, and kept stirring for 10 minutes. 100 g of ice added into a solution, kept stirring for 30 minutes to separate two layers. The dichloromethane layer was separated, further washed with water (100 mL), dried over saturated sodium chloride solution, and sodium sulfate. Evaporation of solvent gave a crude product, which were further purified by column chromatography in hexane 1: dichloromethane 1.2 ($R_f = 0.35$). The isomeric mixture of product was obtained in white solid (0.80 g, 0.602 mmol, 87.4%yield). Isomeric mixture of *trans* and *cis*-**6** was separated by recrystallization in the

different solvent mixture. Firstly, the isomeric mixture was thoroughly dissolved in 10 mL of THF, then 10 mL of methanol was added upon a turning clear solution. The solution was stand at room temperature for three days to completely form a crystalline *trans*-**6**, filtered, and dried over air. Evaporation of mother liquid gave the residue of cis isomer. 5 mL of THF was added to dissolve a residue, followed by adding 25 mL of hexane. The solution was also turning a clear solution and standing at room temperature for three days to fully crystallize a *cis*-**6**.

Trans-**6**:

¹H NMR (500 MHz, CDCl₃): δ = 7.526-7.189 (m, 40H), 3.118-3.090 (t, 4H), 1.675-1.535 (m, 4H), 0.767-0.743 (m, 4H), 0.309 (s, 6H).

¹³C NMR (125 MHz, CDCl₃): δ = 133.99, 133.84, 131.74, 130.81, 130.46, 127.86, 127.70, 53.844, 22.525, 13.854, -0.963.

²⁹Si NMR (99 MHz, CDCl₃): δ = -18.292, -78.490, -79.478 (relative intensity ratio 1:2:2).

MALDI-TOF MS [C₅₆H₅₈N₆O₁₄Si₁₀ + Na]⁺: Calcd. 1342.16, found 1341.59.

Elemental analyses (C₅₆H₅₈N₆O₁₄Si₁₀): Calcd. C 50.96, H 4.43, N 6.37; Found C 50.80, H 4.44, N 6.44.

Cis-**6**:

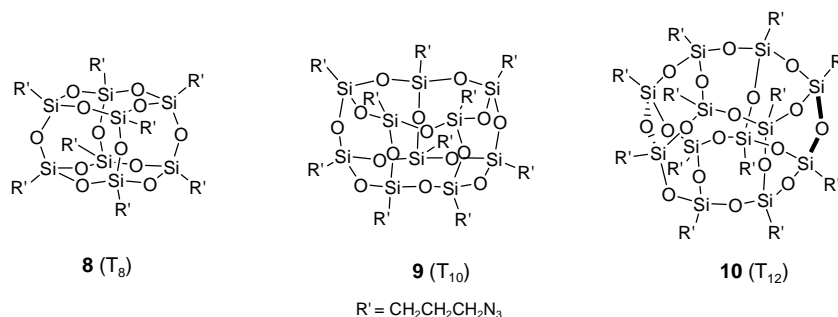
¹H NMR (500 MHz, CDCl₃): δ = 7.528-7.181 (m, 40H), 3.121-3.091 (m, 4H), 1.677-1.644 (m, 4H), 0.778-0.746 (m, 4H), 0.308 (s, 6H).

¹³C NMR (125 MHz, CDCl₃): δ = 133.98, 133.84, 131.74, 130.85, 130.80, 130.75, 130.46, 130.40, 127.86, 127.72, 127.70, 127.68, 53.840, 22.517, 13.846, -0.974.

²⁹Si NMR (99 MHz, CDCl₃): δ = -18.274, -78.490, -79.478 (relative intensity ratio 1:1:1).

MALDI-TOF MS [C₅₆H₅₈N₆O₁₄Si₁₀ + Na]⁺: Calcd. 1342.16, found 1342.13.

Elemental analyses (C₅₆H₅₈N₆O₁₄Si₁₀): Calcd. C 50.96, H 4.43, N 6.37; Found C 50.80, H 4.46, N 6.42.



Synthesis of multi-azido-functionalized polyhedral oligomeric silsesquioxanes

A mixture of $T_8\text{-Cl}_8$ (**7**) (1.0 g, 0.964 mmol), sodium azide (0.81 g, 12.45 mmol) and dry DMF (100 mL) was heated at 60 °C under nitrogen and mechanical stirring for 16 h. The reaction mixture was filtered to remove salt partially, and then product was poured into 100 mL $\text{CHCl}_3/100$ mL H_2O . The aqueous phase was extracted three times with 150 mL CHCl_3 . The combined organic solvent was evaporated until about 150 mL left, and then washed with 100 mL water for three times, dried over Na_2SO_4 and evaporated. A yellowish viscous liquid was obtained (crude product, 0.9 g). The resulting crude product was purified by column chromatography, however for the better efficiency, 1 gram of sample/ 80 grams of silica gel was introduced (ethyl acetate/hexane = 2: 5) to yield octakis(3-azidopropyl)silsesquioxane (**8**) (abbr. as $T_8\text{-(N}_3)_8$, $R_f = 0.60$, 0.25 g, 0.230 mmol) and a mixture of **9** and **10** ($R_f = 0.55$). The second column chromatography (ethyl acetate/hexane = 2: 9) was used to separate deca(3-azidopropyl)silsesquioxane (**9**) (abbr. as $T_{10}\text{-(N}_3)_{10}$, $R_f = 0.35$, 0.45 g, 0.331 mmol) and dodeca(3-azidopropyl)silsesquioxane (**10**) (abbr. as $T_{12}\text{-(N}_3)_{12}$, $R_f = 0.30$, 0.18 g, 0.110 mmol).

$T_8\text{-(N}_3)_8$:

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.71\text{-}0.74$ (t, 16H, SiCH_2), 1.66-1.73 (quin, 16H, CH_2), 3.25-3.28 (t, 16H, CH_2N_3).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): $\delta = 8.95$ (SiCH_2 -), 22.42 ($-\text{CH}_2$), 53.36 ($-\text{CH}_2\text{N}_3$).

$^{29}\text{Si NMR}$ (CDCl_3 , 99 MHz): $\delta = -67.04$.

MALDI-TOF MS [$\text{C}_{24}\text{H}_{48}\text{N}_{24}\text{O}_{12}\text{Si}_8 + \text{H}$] $^+$: Calcd. 1089.21, found 1063.20.

Elemental analyses ($\text{C}_{24}\text{H}_{48}\text{N}_{24}\text{O}_{12}\text{Si}_8$): Calcd. C 26.46, H 4.44, N 30.86; Found C 26.47, H 4.471, N 30.84.

T₁₀-(N₃)₁₀:

¹H NMR (CDCl₃, 500 MHz): δ = 0.70-0.73 (t, 20H, SiCH₂), 1.65-1.71 (quin, 20H, CH₂), 3.26-3.29 (t, 20H, CH₂N₃).

¹³C NMR (CDCl₃, 125 MHz): δ = 9.56 (SiCH₂-), 22.60 (-CH₂), 53.42 (-CH₂N₃).

²⁹Si NMR (CDCl₃, 99 MHz): δ = -68.94.

MALDI-TOF MS [C₃₀H₆₀N₃₀O₁₅Si₁₀ + H]⁺: Calcd. 1361.26, found 1335.30.

Elemental analyses (C₃₀H₆₀N₃₀O₁₅Si₁₀): Calcd. C 26.46, H 4.44, N 30.86; Found C 26.46, H 4.472, N 30.80.

T₁₂-(N₃)₁₂:

¹H NMR (CDCl₃, 500 MHz): δ = 0.66-0.72 (SiCH₂), 1.63-1.70 (CH₂), 3.26-3.29 (CH₂N₃).

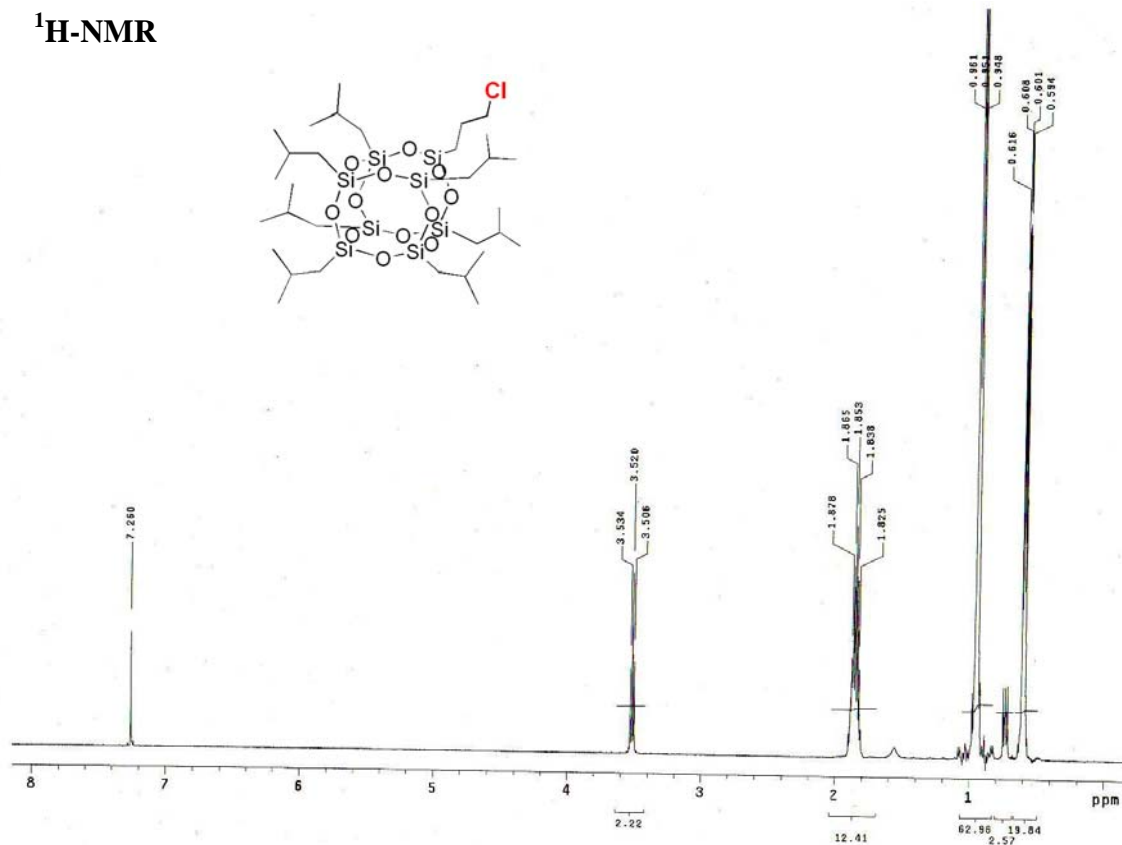
¹³C NMR (CDCl₃, 125 MHz): δ = 9.59, 10.10 (SiCH₂-); 22.63, 22.77 (-CH₂); 53.45, 53.49 (-CH₂N₃).

²⁹Si NMR (CDCl₃, 99 MHz): δ = -68.69, -71.36 (relative intensity ratio 1:2).

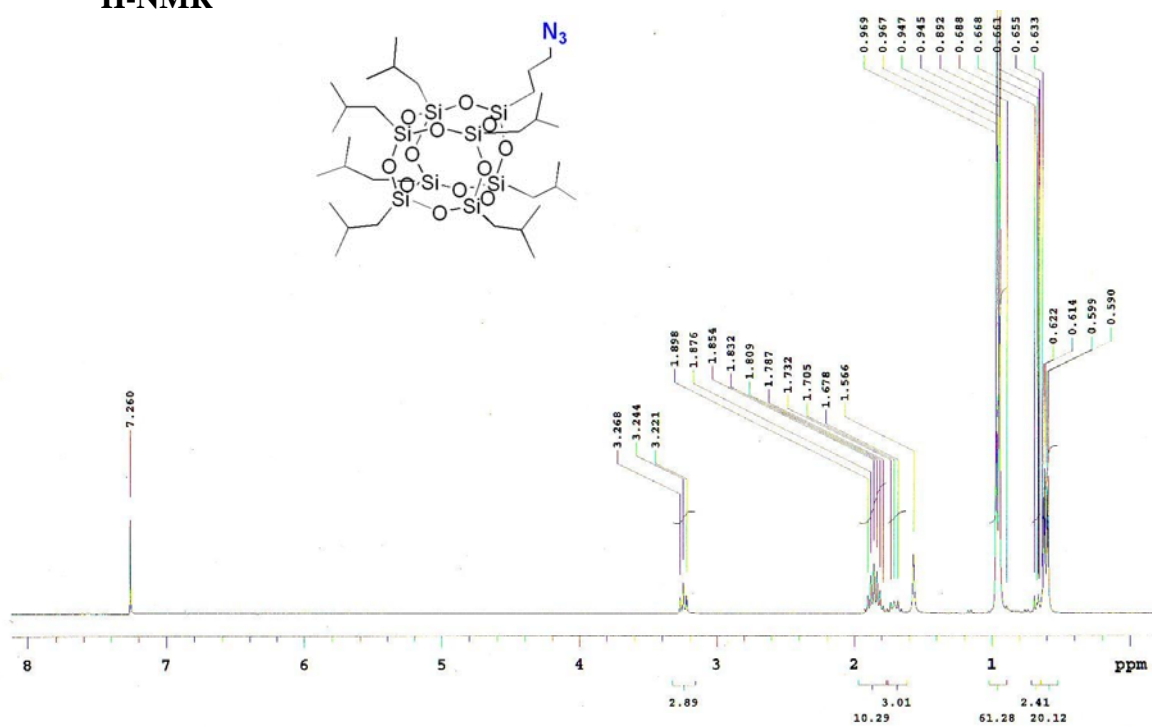
MALDI-TOF MS [C₃₆H₇₂N₃₆O₁₈Si₁₂ + H]⁺: Calcd. 1634.32, found 1608.45.

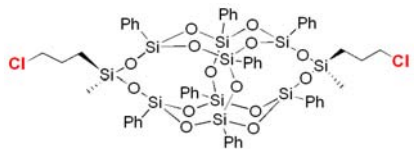
Elemental analyses (C₃₆H₇₂N₃₆O₁₈Si₁₂): Calcd. C 26.46, H 4.44, N 30.86; Found C 26.45, H 4.452, N 30.83.

¹H-NMR

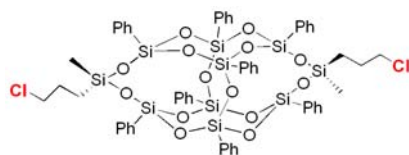


¹H-NMR



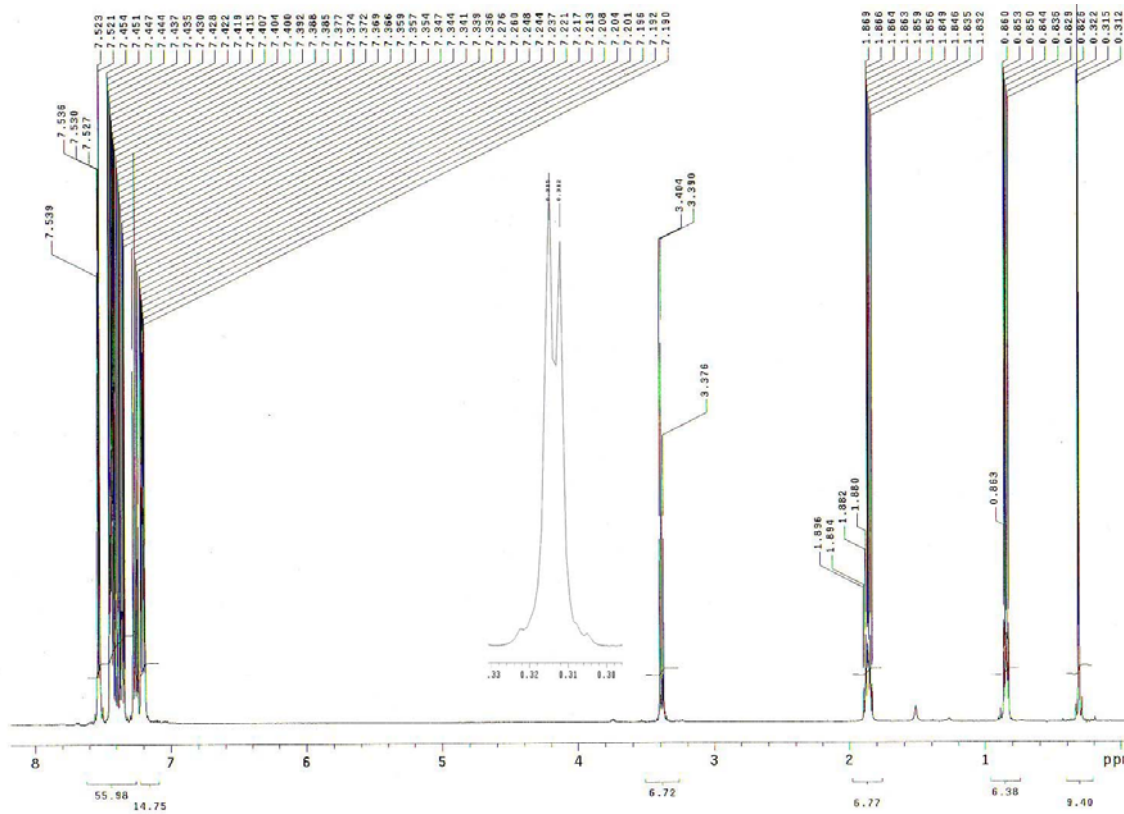


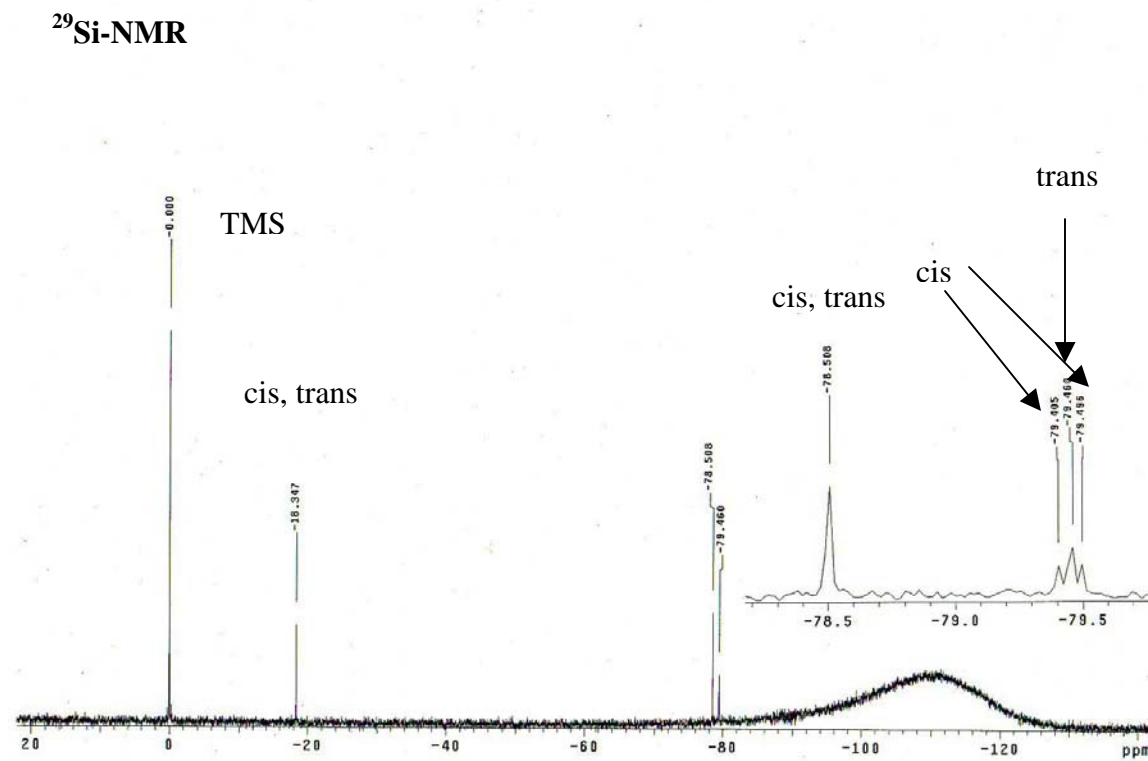
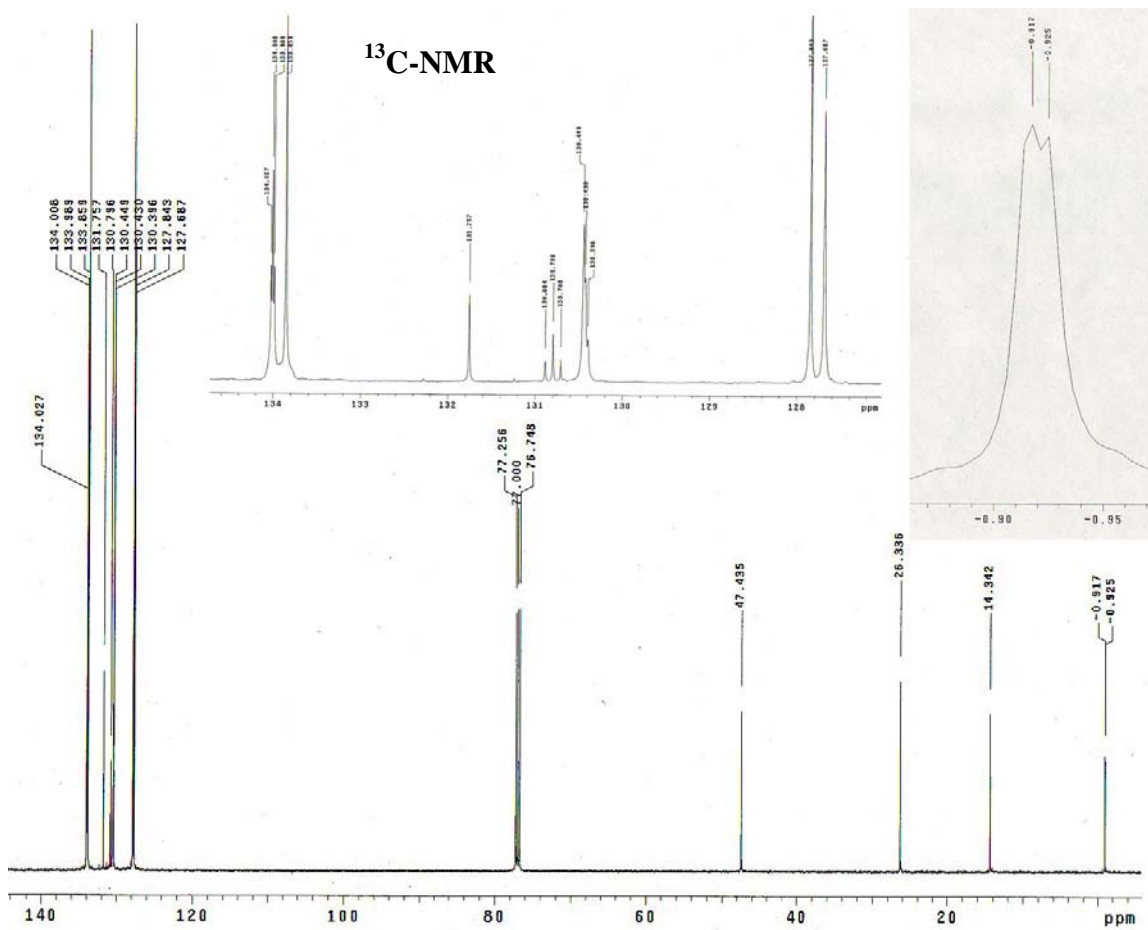
cis

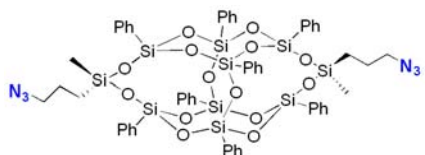


trans

¹H-NMR

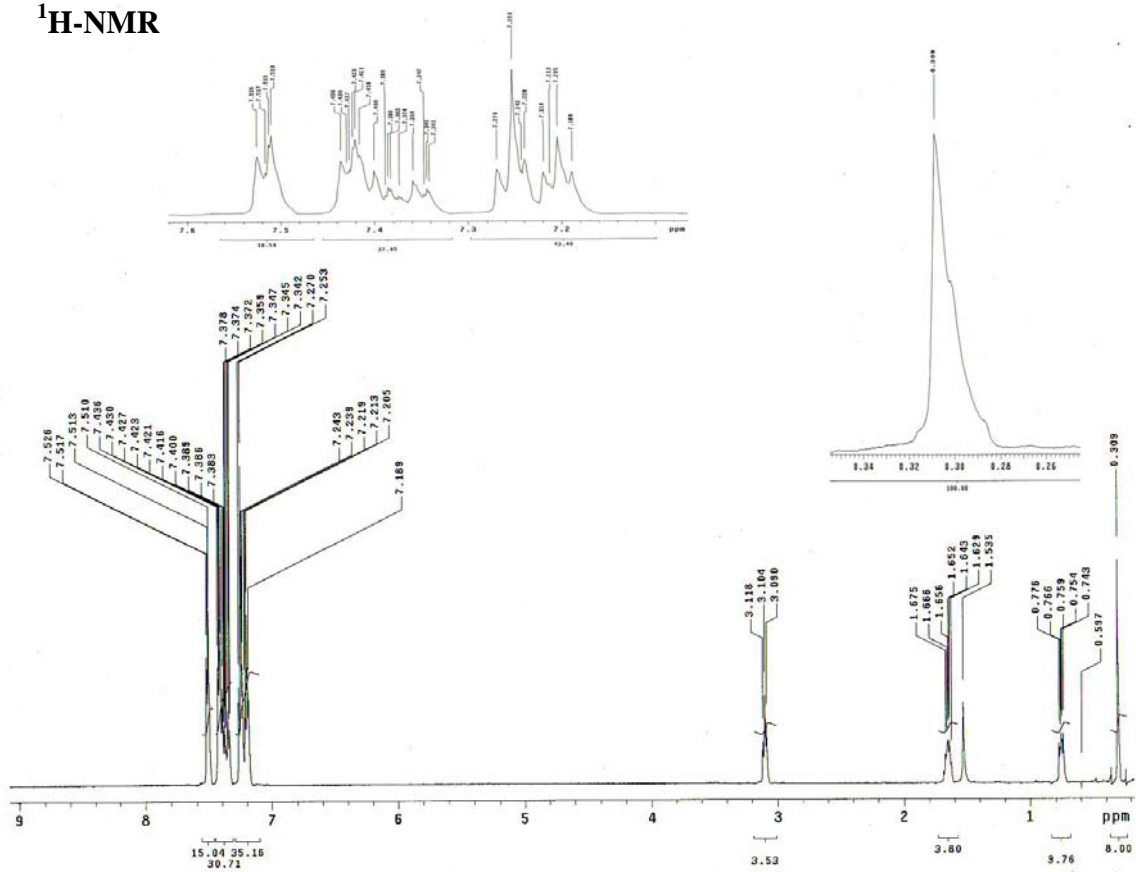




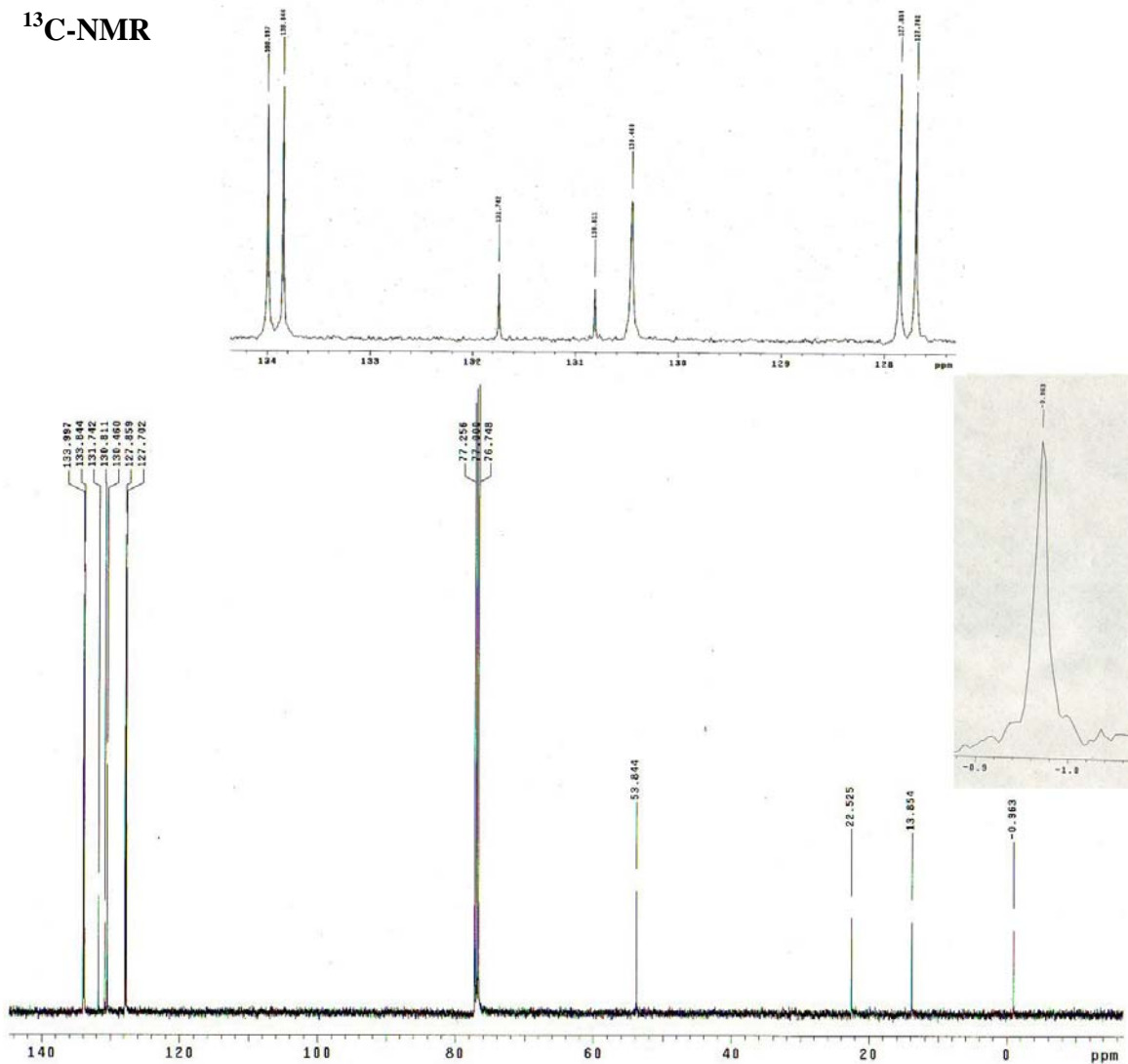


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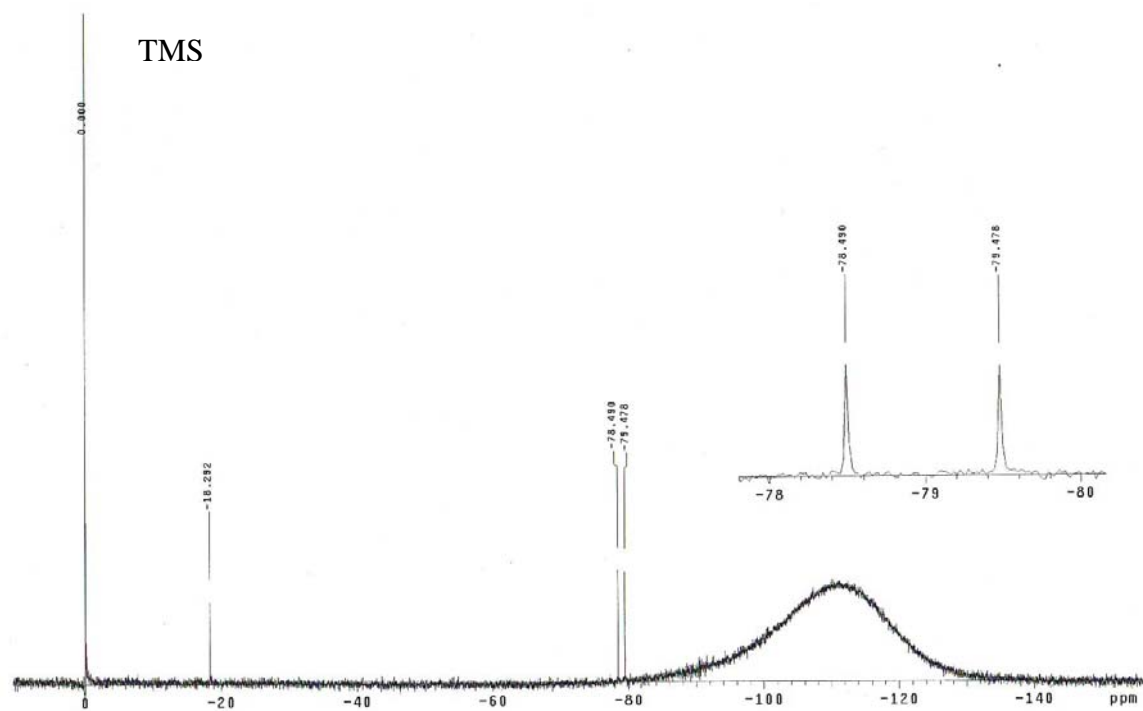
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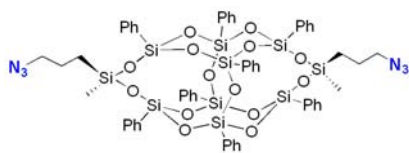


¹³C-NMR



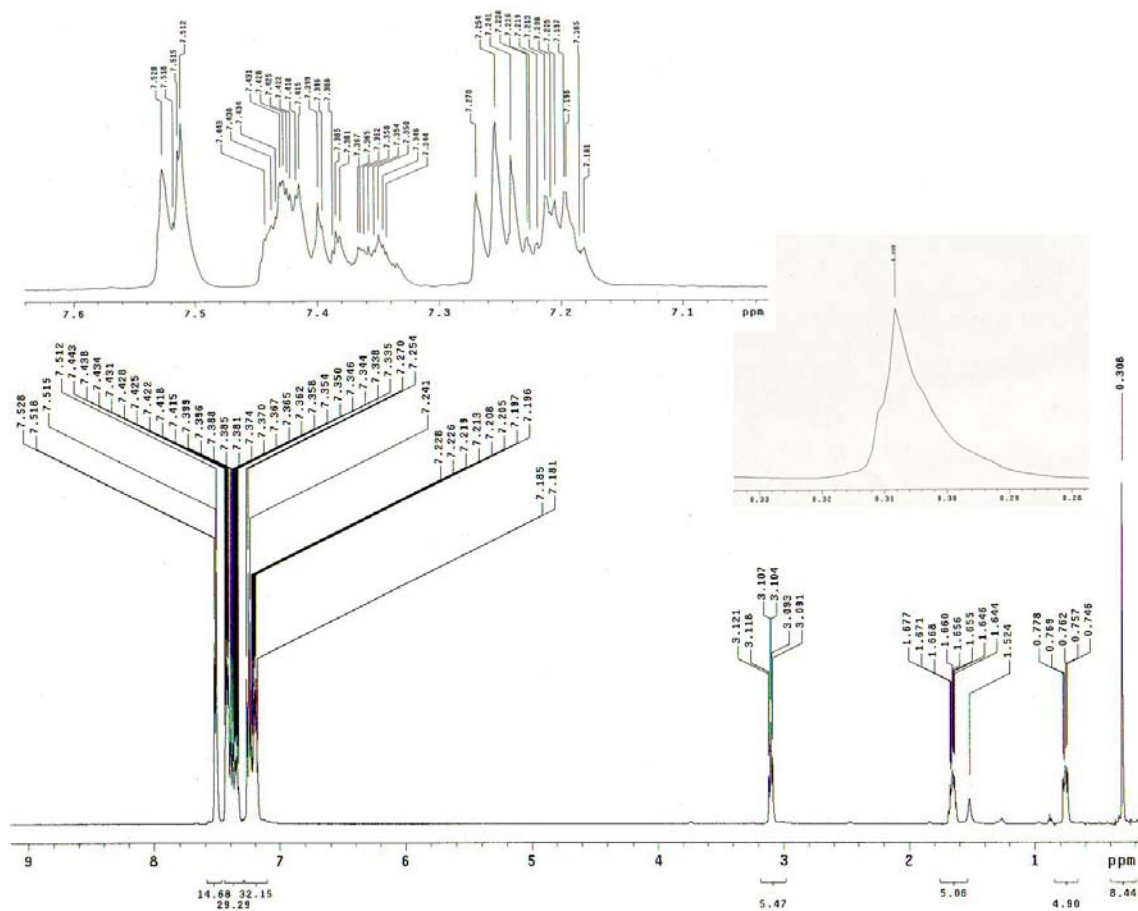
$^{29}\text{Si-NMR}$

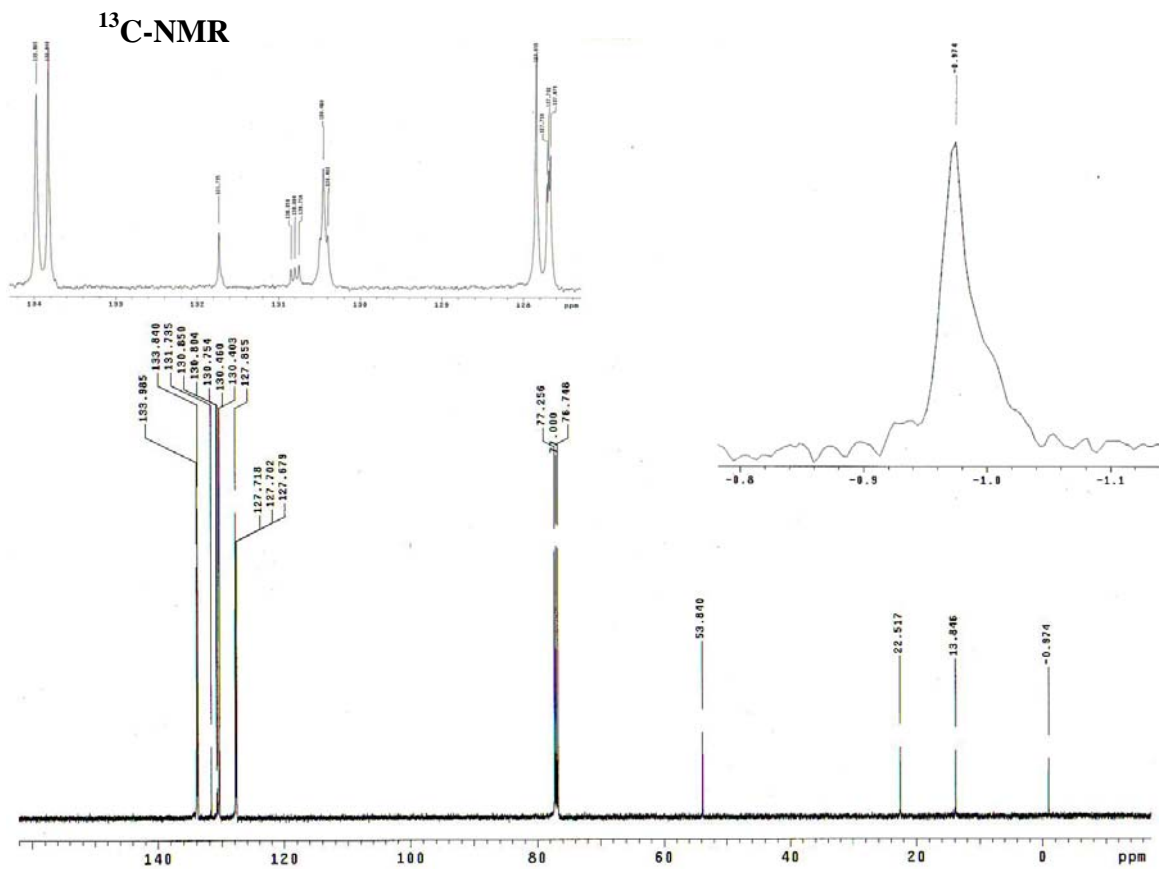




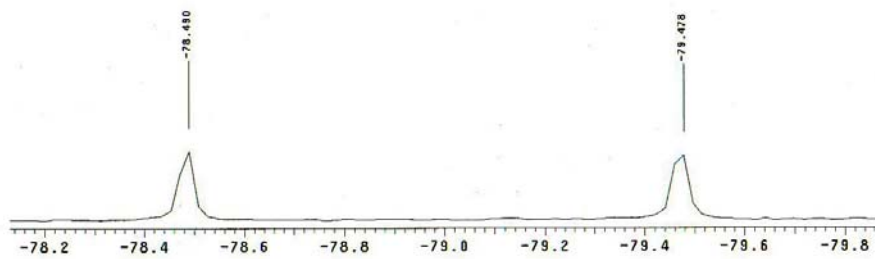
cis

¹H-NMR

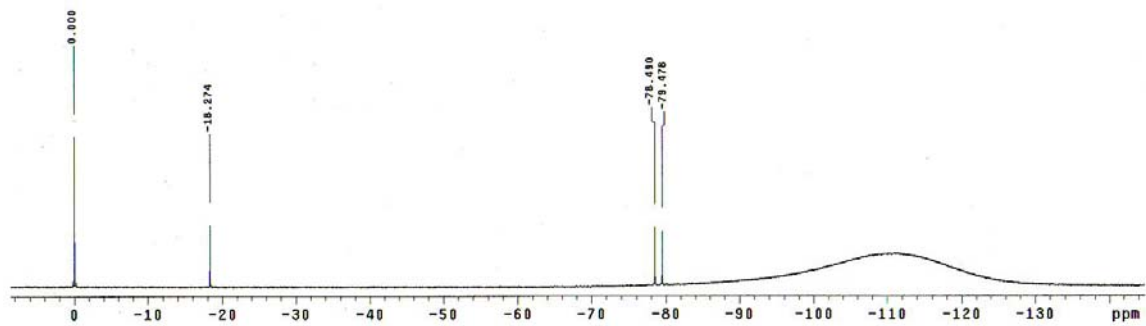




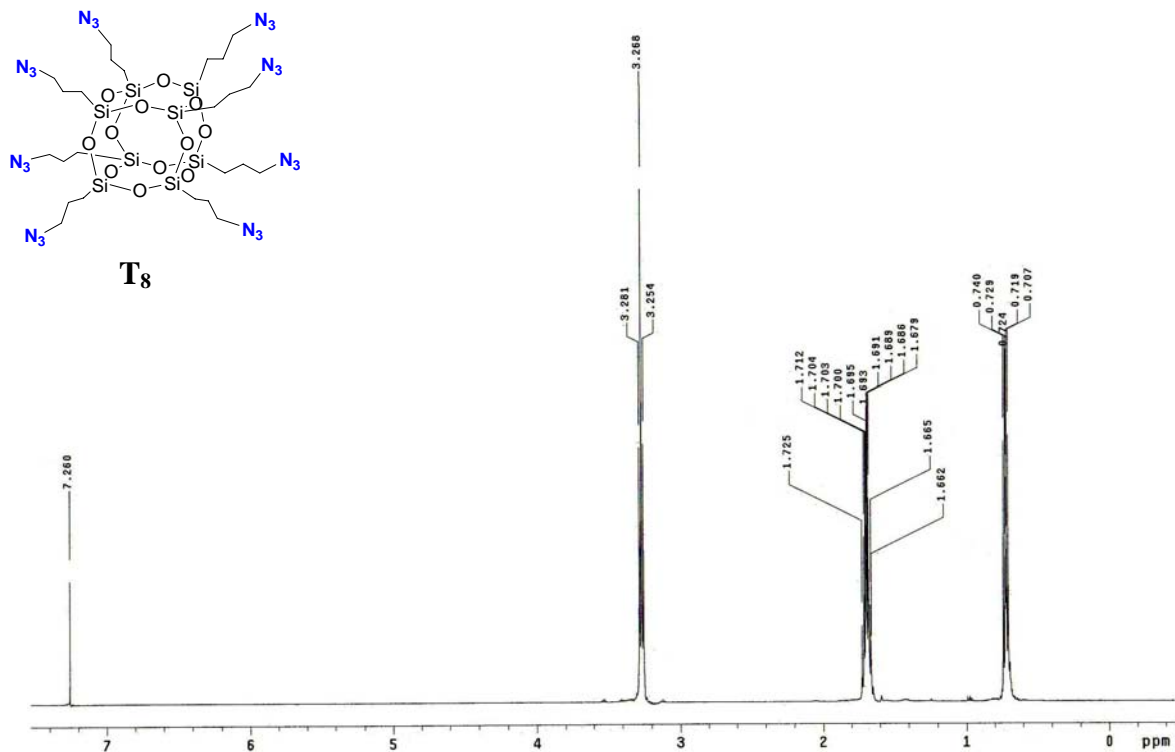
^{29}Si -NMR



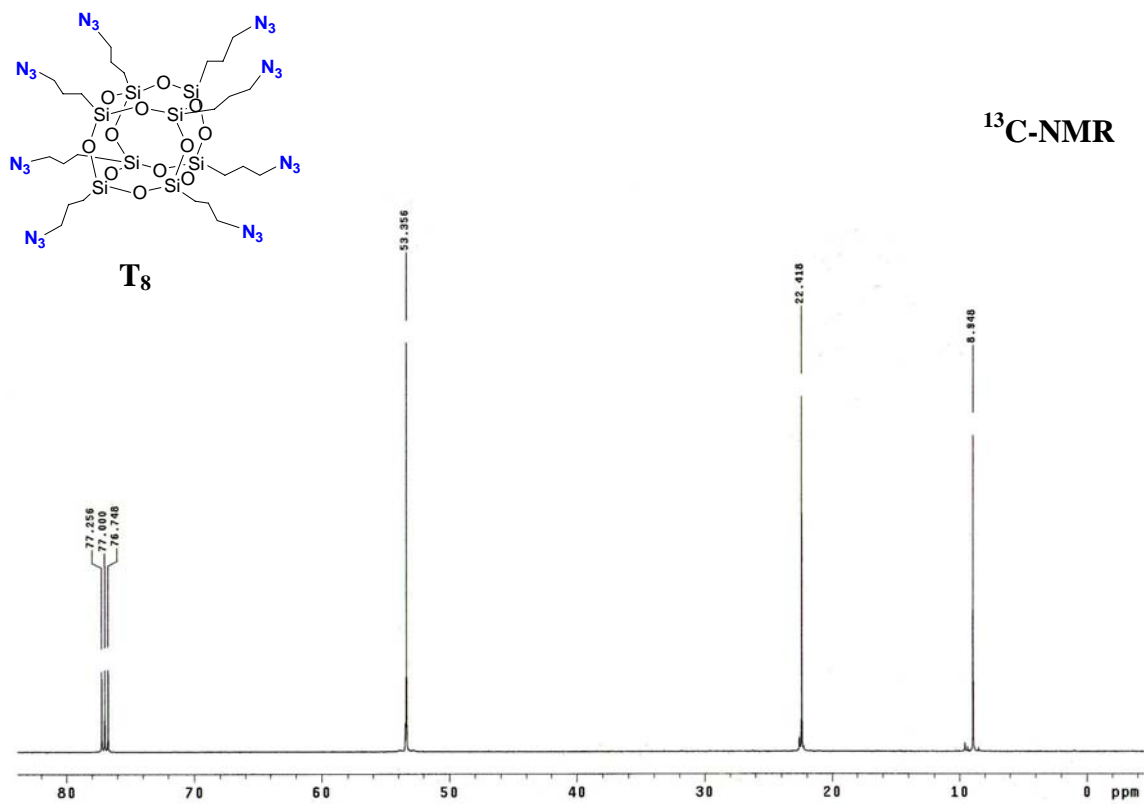
TMS

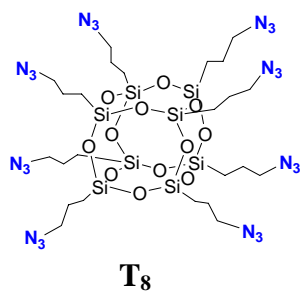


$^1\text{H-NMR}$

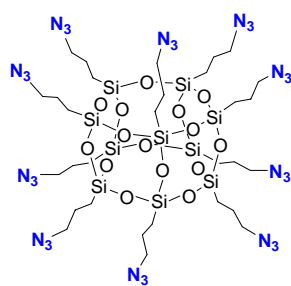
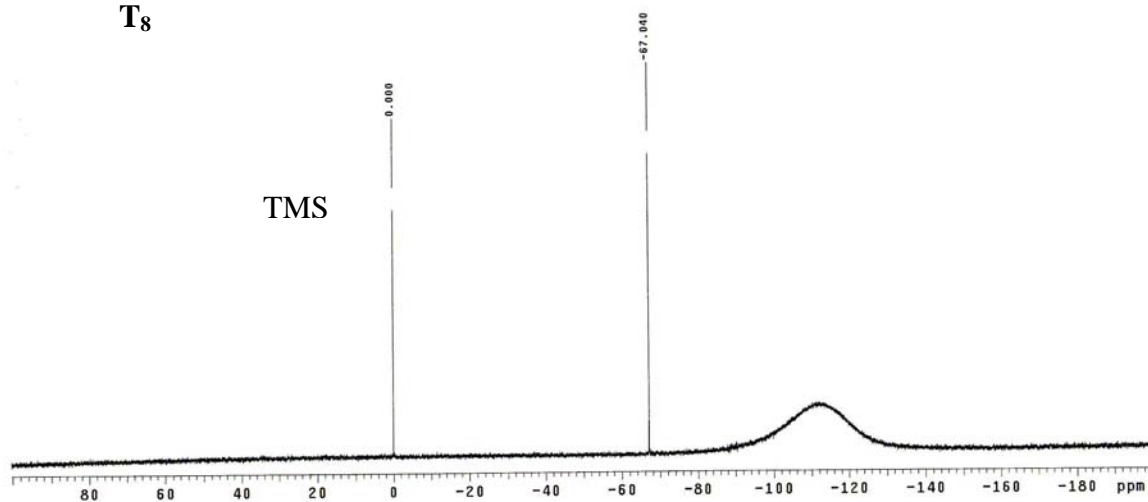


$^{13}\text{C-NMR}$

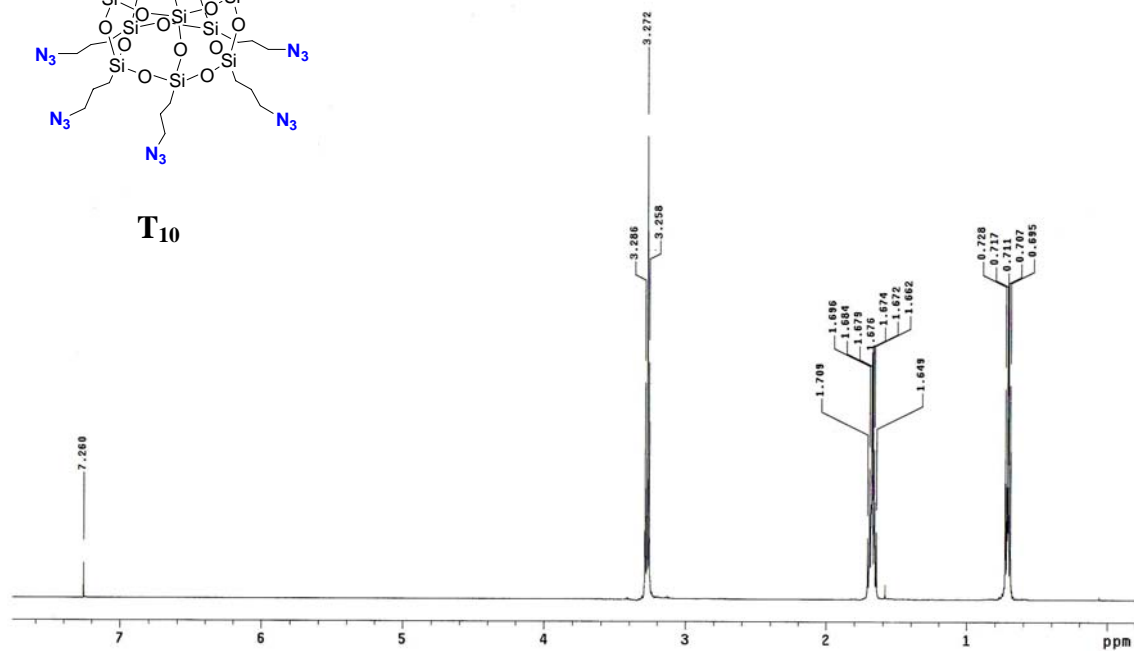


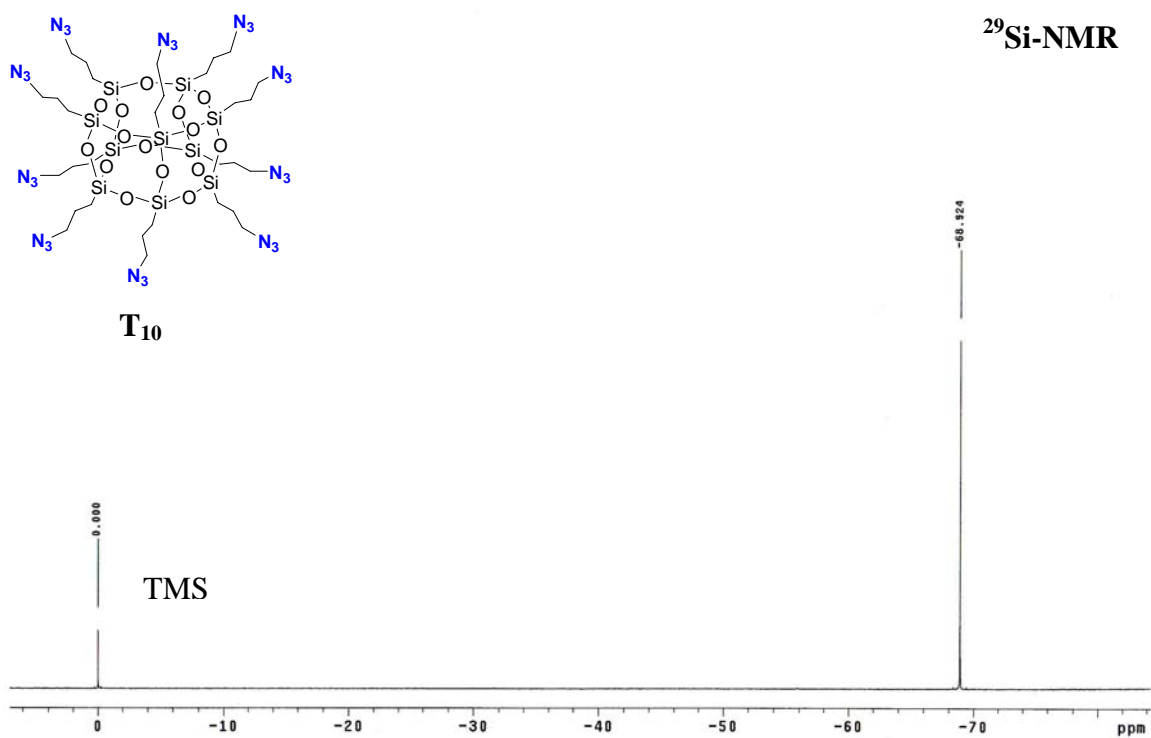
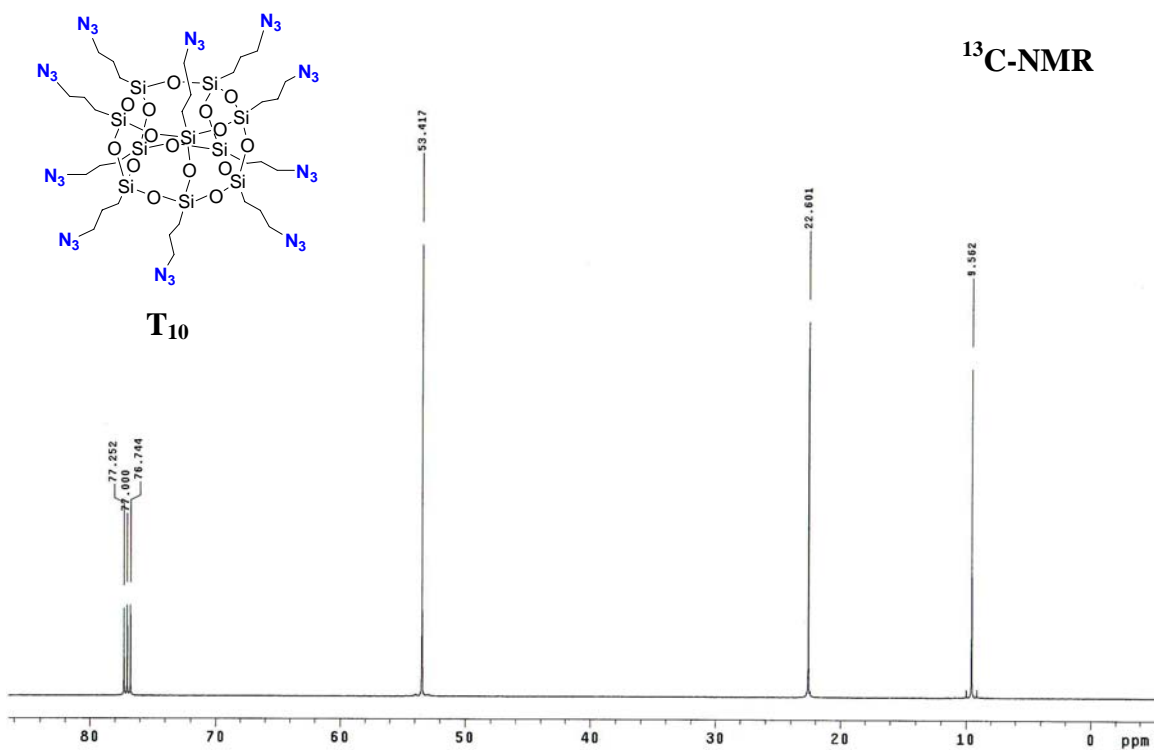


²⁹Si-NMR

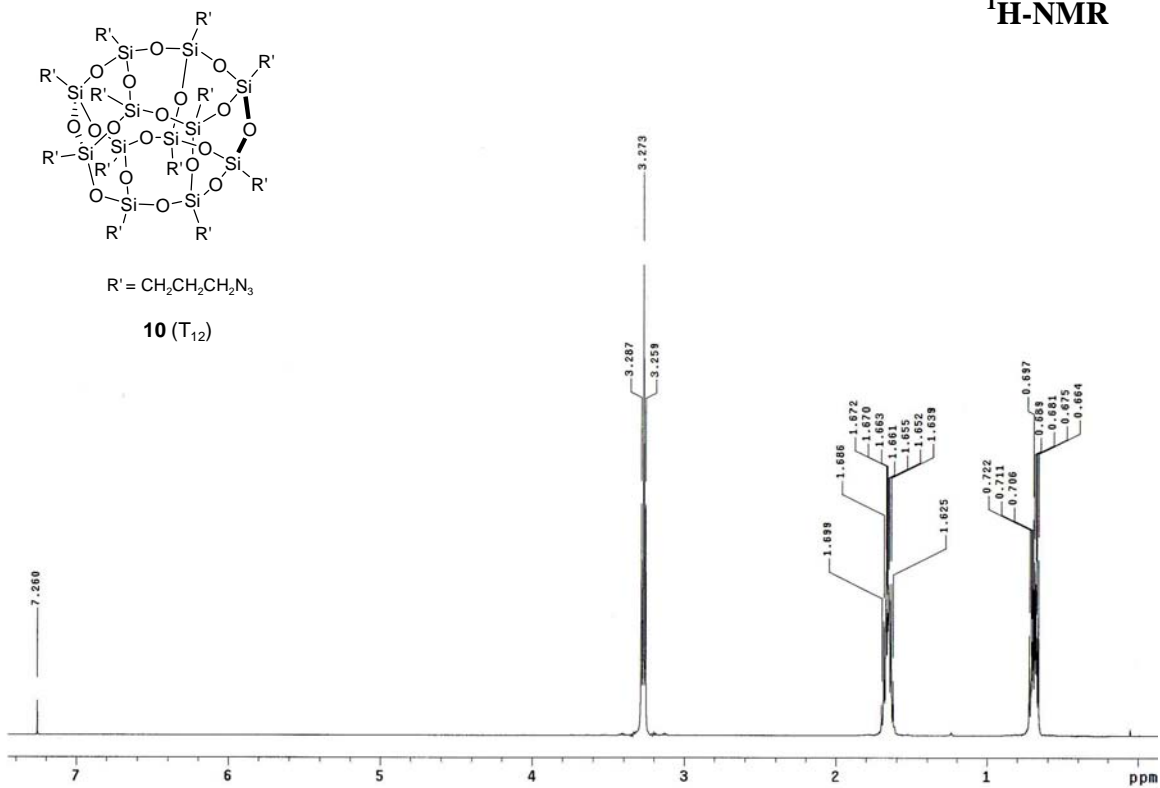


¹H-NMR

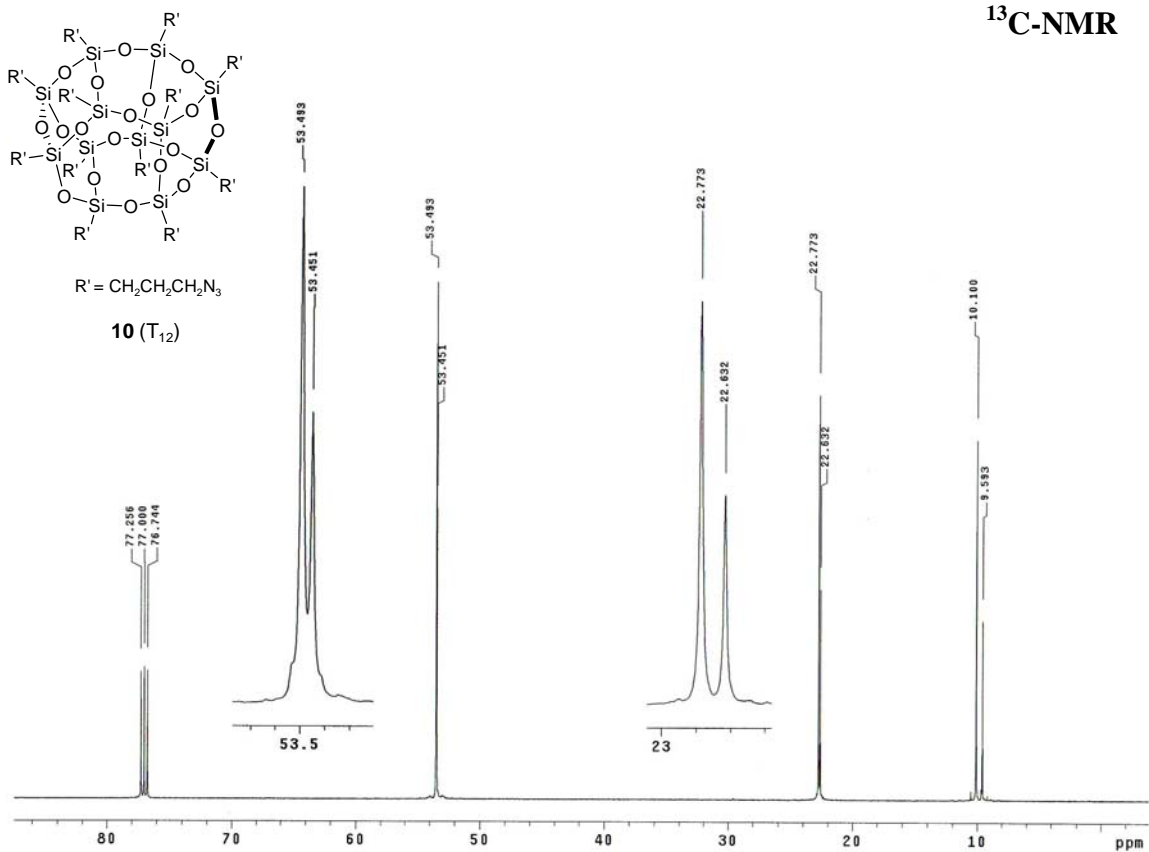


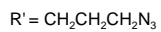
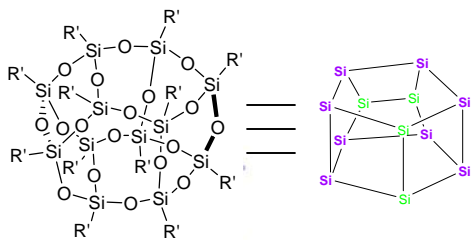


¹H-NMR

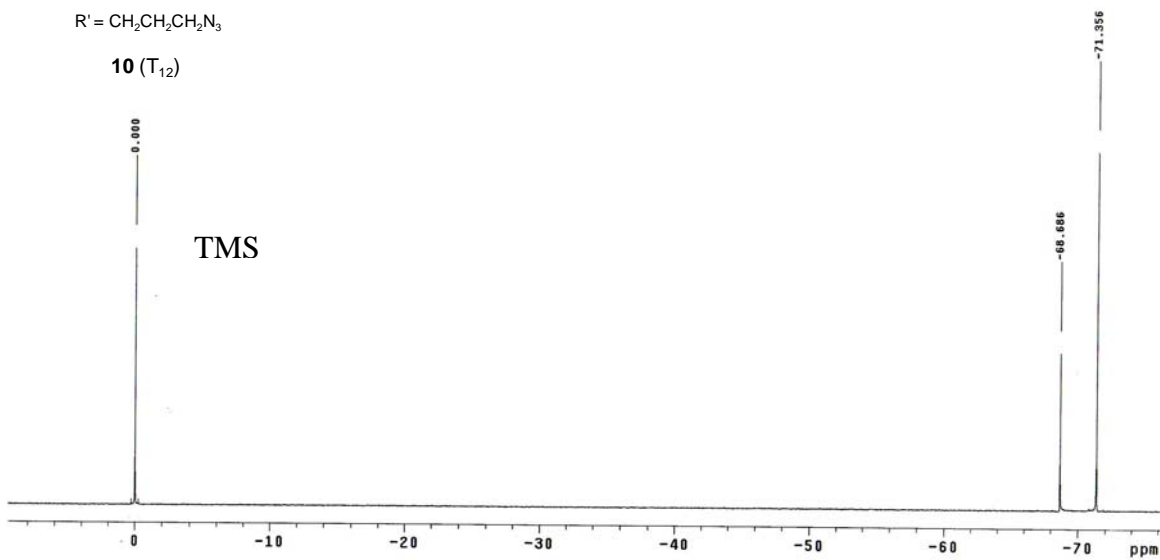


¹³C-NMR





10 (T₁₂)



²⁹Si-NMR