Synthesis and Characterization of Tetrathiol-substituted Double-Decker or Ladder Silsesquioxane Nano-Cores

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Supporting information

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1. General considerations

All reactions were performed under argon atmosphere using standard Schlenk technique. Diethyl ether was dried using mBRAUN purification system. Toluene was distilled from calcium hydride, stored on 4 Å activated molecular sieves under an argon atmosphere. Potassium thioacetate, thioacetic acid were purchased from TCI, lithium aluminum hydride was purchased from FUJIFILM Wako Pure Chemical Co., azobisisoburyronitrile (AIBN) was purchased from Kushida Chemical Co. and all these reagents were used as received, without further purification. **1**,[1] **4**[2] and **7**[3] were prepared following the previously published protocols. The Fourier transformation nuclear magnetic resonance (NMR) spectra were obtained using a JEOL JNM-ECA 600 (^{1}H at 600.17 MHz, ^{13}C at 150.91 MHz, ^{29}Si at 119.24 MHz) NMR instrument. For ^{1}H NMR, chemical shifts are reported as δ units (ppm) relative to $SiMe_4$ (TMS) and the residual solvents peaks were used as standards. For ^{13}C NMR and ^{29}Si NMR, chemical shifts are reported as δ units (ppm) relative to $SiMe_4$ (TMS), the residual solvents peaks were used as standards and spectra were obtained with complete proton decoupling. MALDI-TOF mass analysis were carried out with a Shimadzu AXIMA Performance instrument using 2,5-dihydroxybenzoic acid (dithranol) as the matrix. All reagents used were of analytical grade. Elemental analyses were performed by the Center for Material Research by Instrumental Analysis (CIA), Gunma University, Japan. IR spectra were measured with a Shimadzu FTIR-8400S. TGA was carried out under a nitrogen flow (250 mL min^{-1}) with a heating rate 10 ˚C min^{-1}. All samples were measured with temperatures ranging from 50 to 1000 ˚C, where they remained for 5 min. The weight loss and heating rate were continuously recorded along the experiment.

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[1] Liu, Y.; Takeda, N.; Ouali, A.; Unno, M. *Inorg. Chem.* **2019**, *58*, 4093-4098.

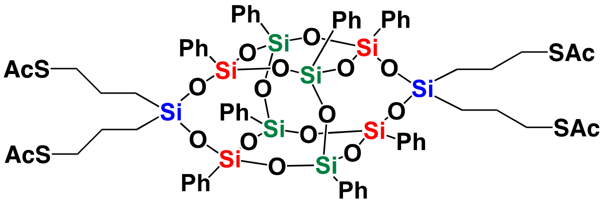
[2] Liu, Y.; Kigure, M.; Koizumi, K.; Takeda, N.; Unno, M.; Ouali, A. *Inorg. Chem.* **2020**, *59*, 15478-15486.

[3] Liu, Y.; Onodera, K.; Takeda, N.; Ouali, A.; Unno, M. *Organometallics* **2019**, *38*, 4373-4376.

2. Experimental procedures and characterization for compounds 2, 3, 5, 6, 8 and 9.

Synthesis of tetrathioacetate-DDSQ 2

After standard cycles of evacuation and backfilling with dry and pure argon, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with DDSQ **1** (0.388 g, 0.3 mmol), AIBN (0.01 g, 0.06 mmol) and distilled toluene (2.2 mL). And then thioacetic acid (127 μL, 1.8 mmol) was added via a syringe at room temperature under argon. The reaction mixture was allowed to heat to 60 ˚C and stir for 16 h at 60 ˚C. The reaction mixture was cooled down to room temperature. The solvent was removed to afford the crude product which was washed with hexane and the desired product was obtained as a white solid **2** (0.439 g, 92 %).



S,S',S'',S'''-((1,3,5,7,11,13,15,17-octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-tetradecaoxa-1,3,5,7,9,11,13,15,17,19-decasilapentacyclo[11.7.1.13,11.15,17.17,15]tetracosane-9,9,19,19-tetrayl)tetrakis(propane-3,1-diyl)) tetraethanethioate (2):

^{1}H NMR (600.17 MHz, CDCl$_3$): δ = 0.75-0.78 (m, 8H), 1.65-1.68 (m, 8H), 2.18 (s, 12H), 2.77 (t, *J* = 7.2 Hz, 8H), 7.20-7.26 (m, 16H), 7.35-7.42 (m, 16H), 7.47-7.49 (m, 8H).

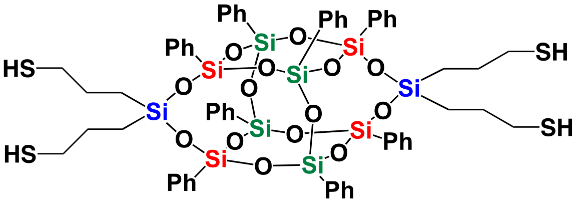
^{13}C{^{1}H} NMR (150.91 MHz, CDCl$_3$): δ = 15.12, 23.14, 30.71, 32.14, 127.91, 128.06, 130.62, 130.66, 131.78, 134.05, 134.25, 195.81 ppm.

^{29}Si{^{1}H} NMR (119.24 MHz, CDCl$_3$): δ = -20.53, -78.56, -79.40 ppm.

MALDI-TOF MS (m/z): 1614.02 ([M+Na]$^+$, calcd 1613.42).

Synthesis of tetrathiol-DDSQ 3

After standard cycles of evacuation and backfilling with dry and pure argon, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with lithium aluminum hydride (0.053 g, 1.4 mmol) and anhydrous diethyl ether (1.9 mL). The mixture was cooled down to 0 ˚C. And then a solution of DDSQ **2** (0.222 g, 0.14 mmol) in anhydrous diethyl ether (0.9 mL), pre-prepared under extremely anhydrous conditions, was added dropwise under argon at 0 ˚C. The resulting mixture was stirred at 0 ˚C for 10 minutes and then hydrochloric acid solution (freshly prepared, 2 M, 1.1 mL) was added dropwise at 0 ˚C. Water and diethyl ether were added and the reaction mixture was transferred into a separation funnel. The aqueous layer was extracted twice with diethyl ether. The gathered organic layer was washed 3 times with water and dried over anhydrous Na_2SO_4. And then the solvent was removed under reduced pressure to afford product which was washed with hexane to give the pure product (0.119 g, 60%) as a white solid. The desired product was further recrystallized in diethyl ether with slow evaporation to give colorless needle crystals.



3,3',3'',3'''-(1,3,5,7,11,13,15,17-octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-tetradecaoxa-1,3,5,7,9,11,13,15,17,19-decasilapentacyclo[11.7.1.13,11.15,17.17,15]tetracosane-9,9,19,19-tetrayl)tetrakis(propane-1-thiol) (3):

^{1}H NMR (600.17 MHz, CDCl$_3$): δ = 0.80-0.83 (m, 8H), 1.06 (t, *J* = 7.9 Hz, 4H), 1.70-1.73 (m, 8H), 2.39-2.43 (m, 8H), 7.20-7.28 (m, 16H), 7.37-7.46 (m, 16H), 7.52-7.53 (m, 8H).

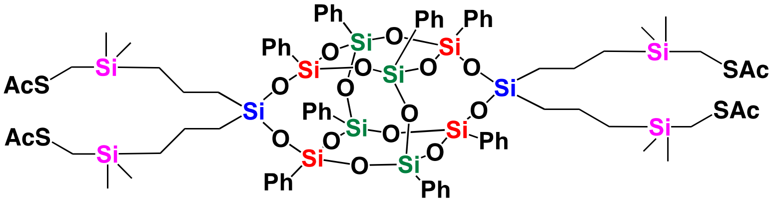
^{13}C{^{1}H} NMR (150.91 MHz, CDCl$_3$): δ = 14.84, 27.67, 27.83, 127.95, 128.10, 130.72, 130.74, 130.88, 131.83, 134.06, 134.27 ppm.

^{29}Si{^{1}H} NMR (119.24 MHz, CDCl$_3$): δ = -20.08, -78.59, -79.44 ppm.

MALDI-TOF MS (m/z): 1446.56 ([M+Na]$^+$, calcd 1445.27).

Synthesis of tetrathioacetate-DDSQ 5

In a vial with a stirring bar, DDSQ **4** (1.3 g, 0.77 mmol) and DMF (13 mL) were introduced at room temperature under air. Potassium thioacetate (0.59 g, 5.1 mmol) was added and the mixture was stirred at room temperature for 16 h. And then the reaction mixture was poured into ice and extracted by chloroform. The organic layer was then washed twice with brine, dried over sodium sulfate and evaporated on the rotavapor (with dichloromethane or diethyl ether several times to remove traces of DMF) to afford the desired product **5** (1.3 g, 91%) as a yellow sticky solid, without any further purification.



***S*,*S*',*S*'',*S*'''-((((1,3,5,7,11,13,15,17-octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-tetradecaoxa-1,3,5,7,9,11,13,15,17,19-decasilapentacyclo[11.7.1.13,11.15,17.17,15]tetracosane-9,9,19,19-tetrayl)tetrakis(propane-3,1-diyl))tetrakis(dimethylsilanediyl))tetrakis(methylene)) tetraethanethioate (5):**

^{1}H NMR (600.17 MHz, CDCl$_3$): δ = -0.22 (s, 24H), 0.50-0.53 (m, 8H), 0.76-0.77 (m, 8H), 1.36-1.37 (m, 8H), 1.87 (s, 8H), 2.20 (s, 12H), 7.13-7.21 (m, 16H), 7.29-7.38 (m, 16H), 7.46-7.48 (m, 8H).

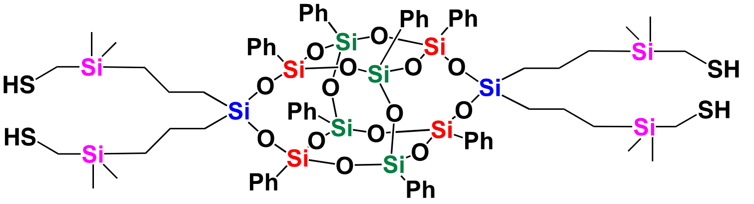
^{13}C{^{1}H} NMR (150.91 MHz, CDCl$_3$): δ = -3.60, 13.08, 17.33, 19.11, 20.15, 30.25, 127.85, 127.98, 130.52, 130.55, 131.16, 132.18, 134.06, 134.19, 197.01 ppm.

^{29}Si{^{1}H} NMR (119.24 MHz, CDCl$_3$): δ = 2.68, -19.29, -78.29, -79.13 ppm.

MALDI-TOF MS (m/z): 1902.09 ([M+Na]$^+$, calcd 1902.15).

Synthesis of tetrathiol-DDSQ 6

After standard cycles of evacuation and backfilling with dry and pure argon, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with lithium aluminum hydride (0.076 g, 2.0 mmol) and anhydrous diethyl ether (2.7 mL). The mixture was cooled down to 0 ˚C. And then a solution of DDSQ **5** (0.376 g, 0.2 mmol) in anhydrous diethyl ether (1.3 mL), pre-prepared under extremely anhydrous conditions, was added dropwise under argon at 0 ˚C. The resulting mixture was stirred at 0 ˚C for 10 minutes and then Hydrochloric acid solution (freshly prepared, 2 M, 1.6 mL) was added dropwise at 0 ˚C. The organic layer was washed with water, dried over sodium sulfate and evaporated on the rotavapor to afford the desired product **6** (0.294 g, 86%) as a white solid, without any further purification.



(((1,3,5,7,11,13,15,17-octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-tetradecaoxa-1,3,5,7,9,11,13,15,17,19-decasilapentacyclo[11.7.1.13,11.15,17.17,15]tetracosane-9,9,19,19-tetrayl)tetrakis(propane-3,1-diyl))tetrakis(dimethylsilanediyl))tetramethanethiol (6):

^{1}H NMR (600.17 MHz, CDCl$_3$): δ = -0.14 (s, 24H), 0.58-0.60 (m, 8H), 0.80-0.83 (m, 8H), 0.94 (t, J = 6.9 Hz, 4H), 1.41 (d, J = 6.9 Hz, 8H), 1.74 (s, 8H), 7.20-7.27 (m, 16H), 7.37-7.45 (m, 16H), 7.52-7.54 (m, 8H).

$^{13}C\{^1H\}$ NMR (150.91 MHz, $CDCl_3$): δ = -4.17, 6.97, 17.36, 18.59, 20.25, 127.89, 127.99, 130.54, 130.58, 131.19, 132.23, 134.09, 134.23 ppm.

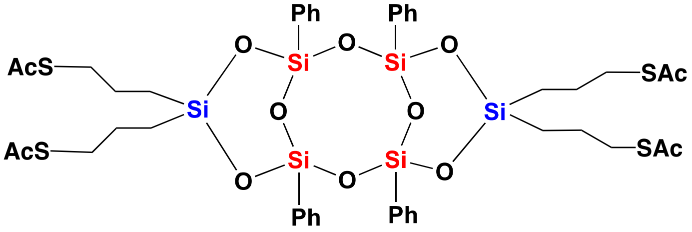
$^{29}Si\{^1H\}$ NMR (119.24 MHz, $CDCl_3$): δ = 3.87, -19.27, -78.34, -79.15 ppm.

MALDI-TOF MS (m/z): 1733.79 ($[M+Na]^+$, calcd 1734.00).

Elemental analysis: Calcd for $C_{72}H_{100}O_{14}S_4Si_{14}$ • H_2O: C, 50.02; H, 5.95; S, 7.42. Found: C, 49.80; H, 5.74; S, 7.32.

Synthesis of tetrathioacetate Laddersiloxane 8

After standard cycles of evacuation and backfilling with dry and pure argon, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with Laddersiloxane **7** (0.385 g, 0.5 mmol), AIBN (0.017 g, 0.1 mmol) and distilled toluene (3.6 mL). And then thioacetic acid (210 μL, 2.96 mmol) was added via a syringe at room temperature under argon. The reaction mixture was allowed to heat to 60 °C and stir for 16 h at 60 °C. The reaction mixture was cooled down to room temperature. The solvent was removed to afford the crude product which was washed with cold hexane and the desired product was obtained as a yellow oil **8** (0.510 g, 91 %).



_S,S',S'',S'''_-((1,3,7,9-tetraphenyl-2,4,6,8,10,12,13,14-octaoxa-1,3,5,7,9,11-hexasilatricyclo[7.3.1.13,7]tetradecane-5,5,11,11-tetrayl)tetrakis(propane-3,1-diyl)) tetraethanethioate (8):

^1H NMR (600.17 MHz, $CDCl_3$): δ = 0.80-0.84 (m, 4H), 0.96-1.01 (m, 4H), 1.53-1.61 (m, 4H), 1.75-1.83 (m, 4H), 2.28 (s, 6H), 2.34 (s, 6H), 2.75 (t, *J* = 7.33 Hz, 4H), 2.97 (t, *J* = 7.3 Hz, 4H), 7.33-7.37 (m, 8H), 7.43-7.47 (m, 4H), 7.62-7.65 (m, 8H).

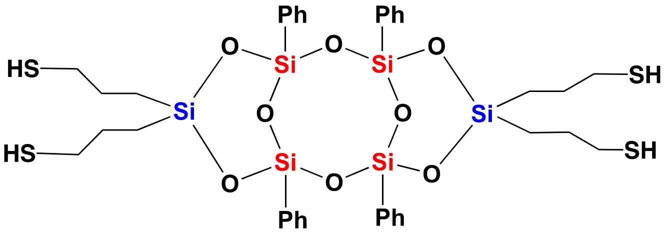
$^{13}C\{^1H\}$ NMR (150.91 MHz, $CDCl_3$): δ = 15.10, 15.45, 22.97, 23.06, 30.79, 30.88, 32.06, 32.13, 128.13, 129.97, 131.18, 134.25, 195.67, 195.79 ppm.

$^{29}Si\{^1H\}$ NMR (119.24 MHz, $CDCl_3$): δ = -6.67, -67.11 ppm.

MALDI-TOF MS (m/z): 1095.40 ($[M+Na]^+$, calcd 1095.12).

Synthesis of tetrathiol-Laddersiloxane 9

After standard cycles of evacuation and backfilling with dry and pure argon, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with lithium aluminum hydride (0.065 g, 1.72 mmol) and anhydrous diethyl ether (2.8 mL). The mixture was cooled down to 0 ˚C. And then a solution of Laddersiloxane **8** (0.460 g, 0.428 mmol) in anhydrous diethyl ether (2.8 mL), pre-prepared under extremely anhydrous conditions, was added dropwise under argon at 0 ˚C. The resulting mixture was stirred at 0 ˚C for 10 minutes and then hydrochloric acid solution (freshly prepared, 2 M, 3.5 mL) was added dropwise at 0 ˚C. Water and dichloromethane were added and the reaction mixture was transferred into a separation funnel. The aqueous layer was extracted twice with dichloromethane. The gathered organic layer was washed 3 times with water and dried over anhydrous Na_2SO_4. And then the solvents were removed under reduced pressure. The residue was passed through a column chromatography (eluent: dichloromethane 100%) to afford the pure product as a white solid (0.145 g, 38%).



3,3',3'',3'''-(1,3,7,9-tetraphenyl-2,4,6,8,10,12,13,14-octaoxa-1,3,5,7,9,11-hexasilatricyclo[7.3.1.13,7]tetradecane-5,5,11,11-tetrayl)tetrakis(propane-1-thiol) (9):

^{1}H NMR (600.17 MHz, CDCl$_3$): δ = 0.83-0.87 (m, 4H), 1.00-1.05 (m, 4H), 1.11 (t, *J* = 8.0 Hz, 2H), 1.45 (t, *J* = 8.01 Hz, 2H), 1.56-1.64 (m, 4H), 1.81-1.88 (m, 4H), 2.36-2.42 (m, 4H), 2.61-2.66 (m, 4H), 7.34-7.38 (m, 8H), 7.44-7.48 (m, 4H), 7.65-7.67 (m, 8H).

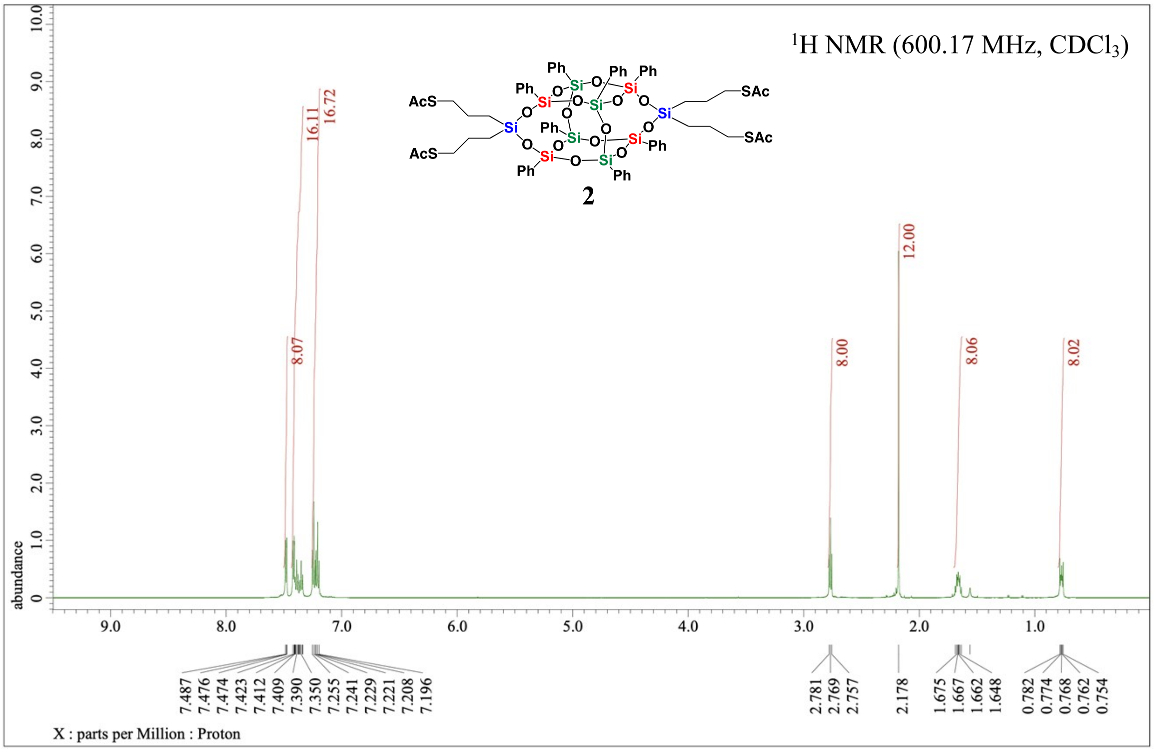
^{13}C{^{1}H} NMR (150.91 MHz, CDCl$_3$): δ = 14.66, 15.18, 27.28, 27.43, 27.78, 27.84, 128.17, 129.99, 131.27, 134.25 ppm.

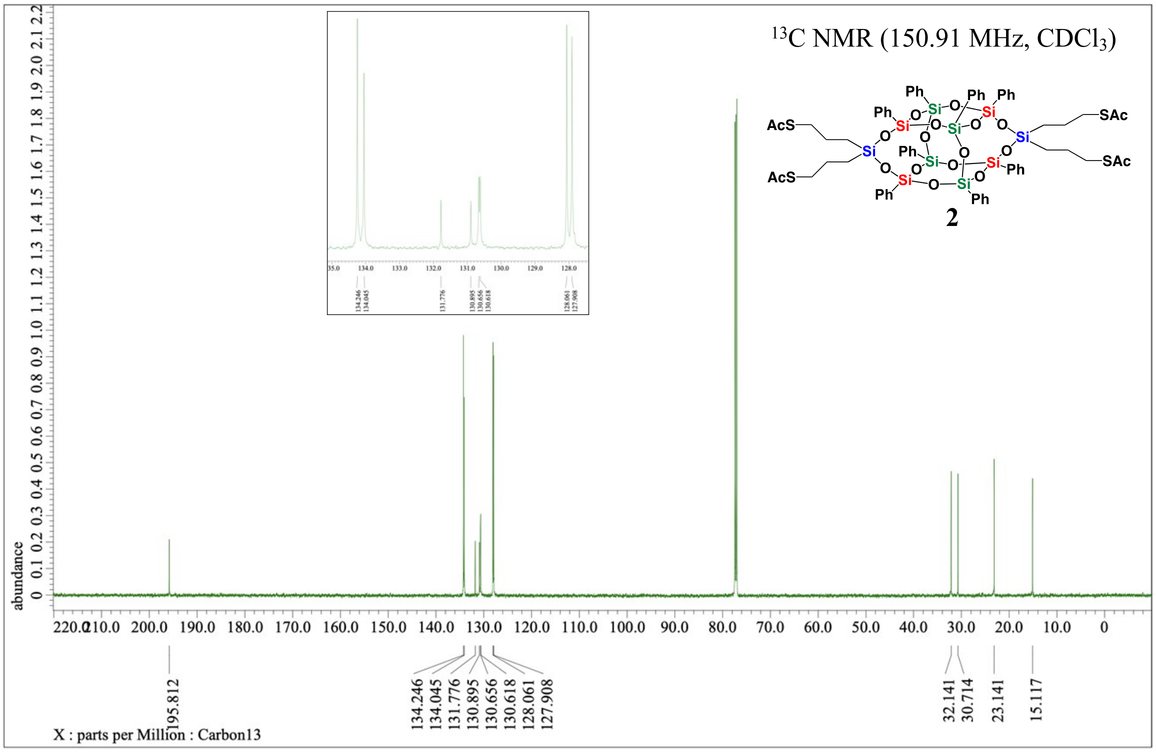
^{29}Si{^{1}H} NMR (119.24 MHz, CDCl$_3$): δ = -6.67, -67.49 ppm.

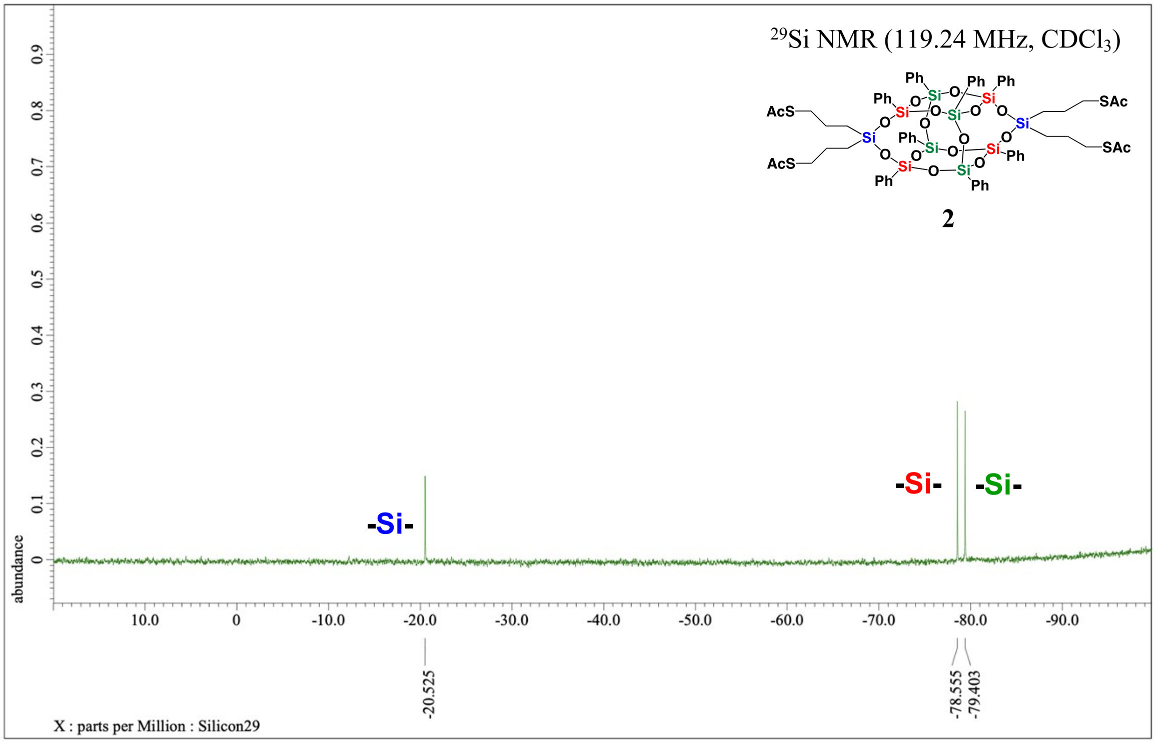
MALDI-TOF MS (m/z): 928.55 ([M+Na]$^+$, calcd 928.51).

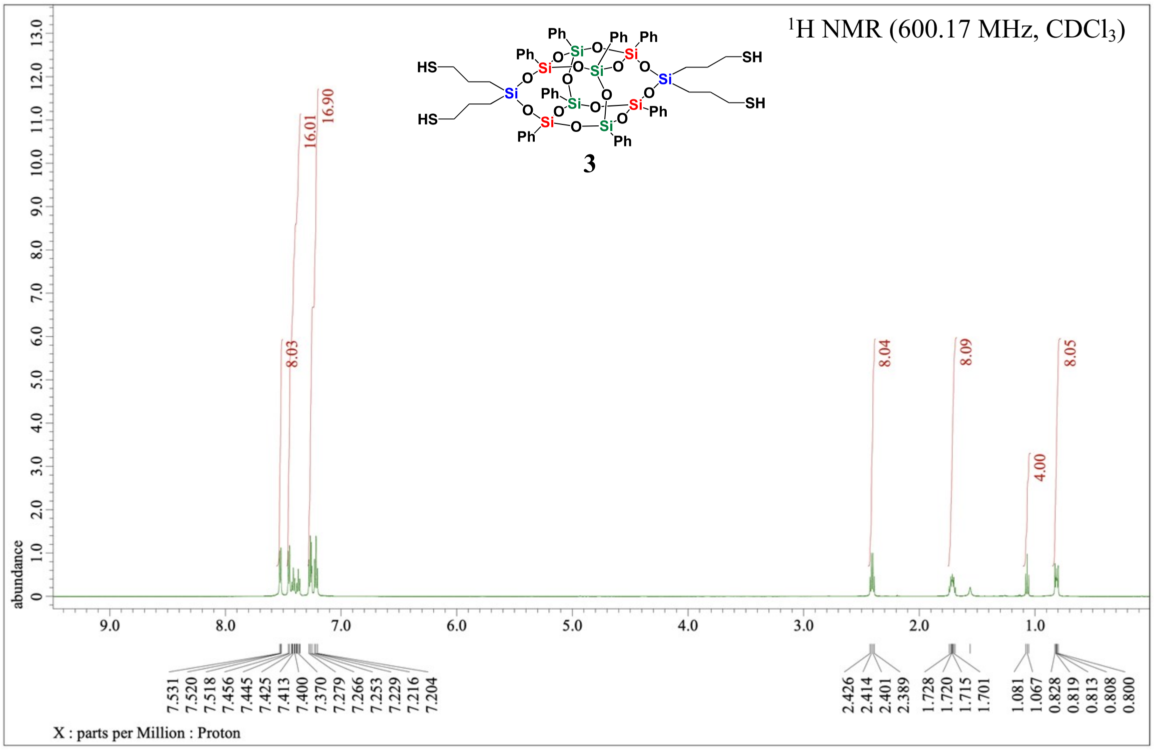
Elemental analysis: Calcd for $C_{36}H_{48}O_8S_4Si_6 \cdot 2H_2O$: C, 45.92; H, 5.57; S, 13.62. Found: C, 45.66; H, 5.29; S, 13.90.

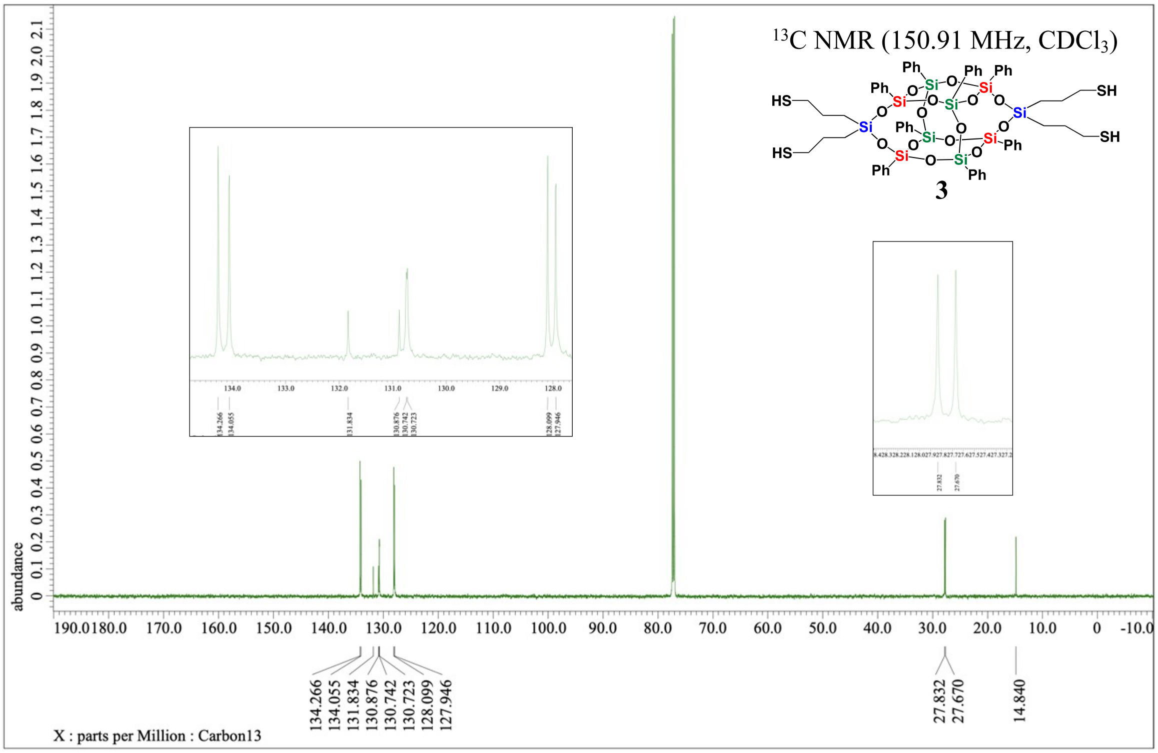
3. ^{1}H, ^{13}C and ^{29}Si-NMR Spectra for compounds 2, 3, 5, 6, 8 and 9

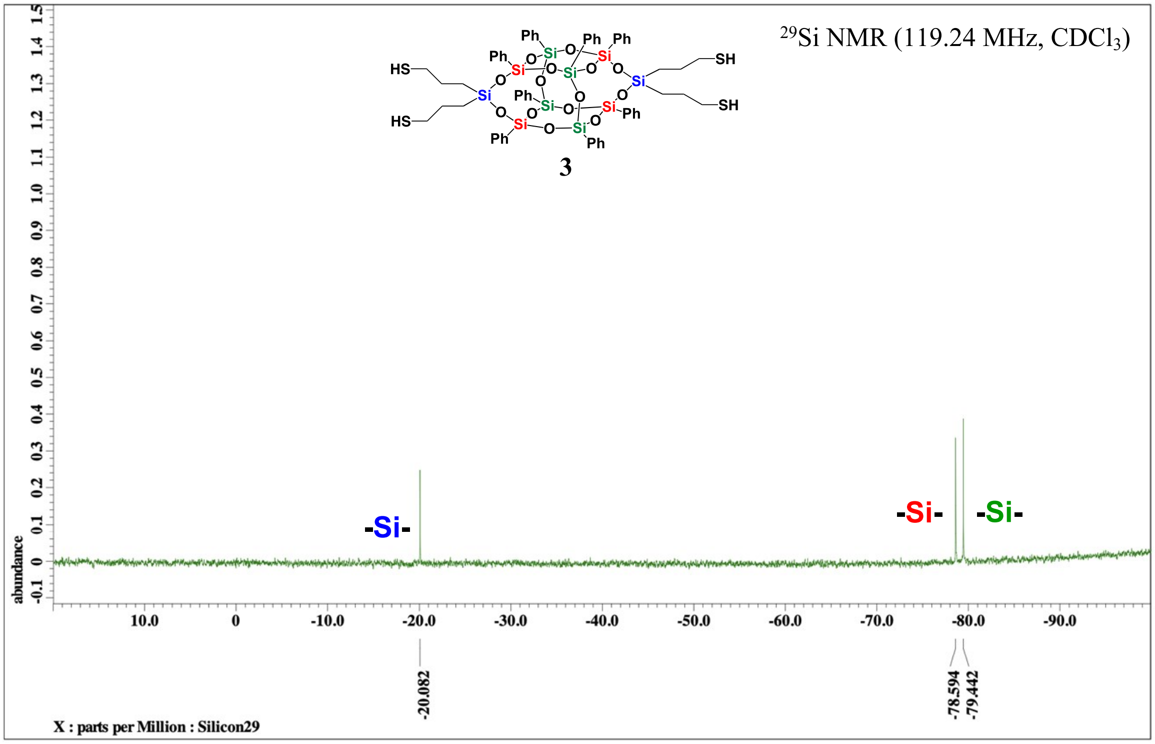


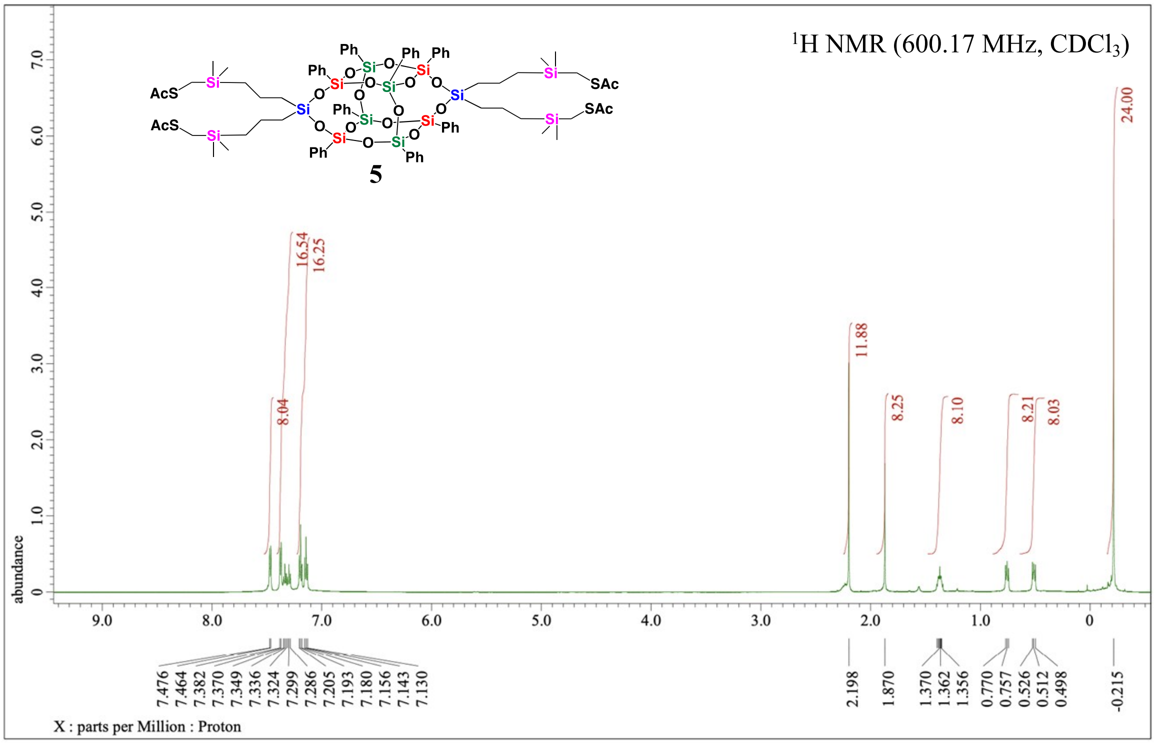



^{29}Si NMR (119.24 MHz, CDCl$_3$)
2
-Si-
-Si-
-Si-
-20.525
-78.555
-79.403
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
X : parts per Million : Silicon29
AcS
SAc
Ph
Si
O

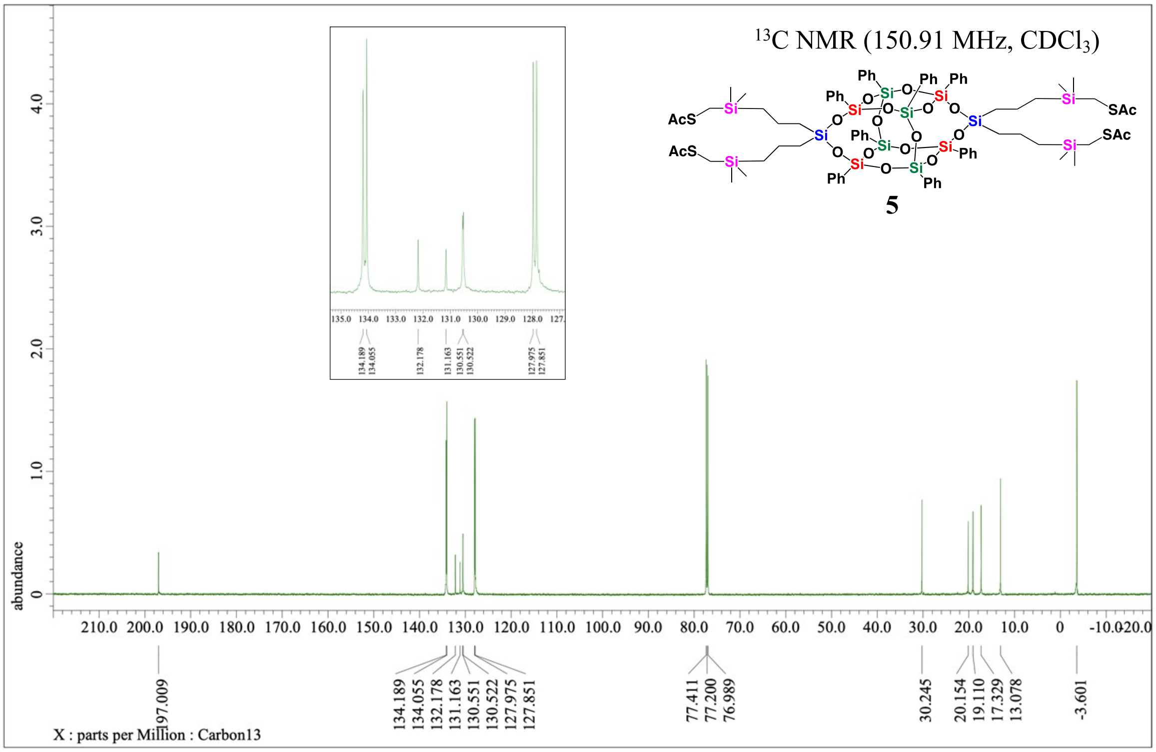

^{1}H NMR (600.17 MHz, CDCl$_3$)
3
8.03
16.01
16.90
8.04
8.09
4.00
8.05
7.531
7.520
7.518
7.456
7.445
7.425
7.413
7.400
7.370
7.279
7.266
7.253
7.229
7.216
7.204
2.426
2.414
2.401
2.389
1.728
1.720
1.715
1.701
1.081
1.067
0.828
0.819
0.813
0.808
0.800
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton
HS
SH
Ph
Si
O


^{13}C NMR (150.91 MHz, CDCl$_3$)
3
HS
SH
Ph
Si
O
abundance
134.266
134.055
131.834
130.876
130.742
130.723
128.099
127.946
27.832
27.670
14.840
X : parts per Million : Carbon13

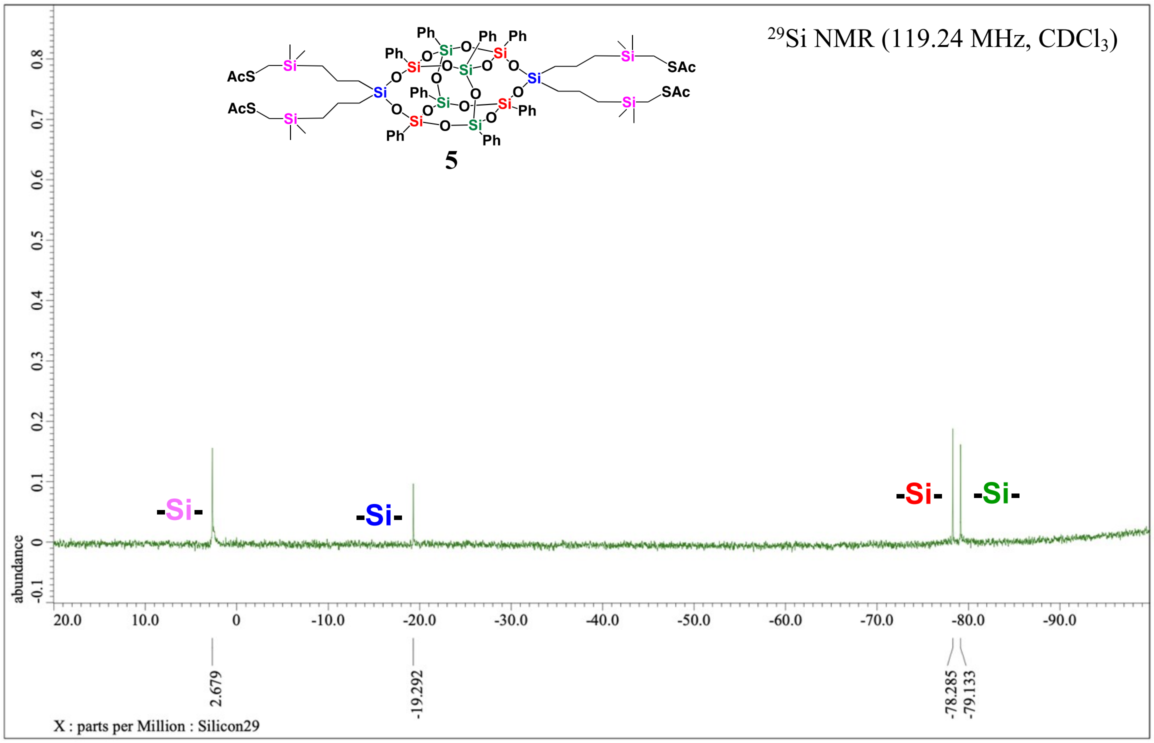

^{29}Si NMR (119.24 MHz, CDCl$_3$)
3
HS
SH
Ph
Si
O
-Si-
-Si-
-Si-
abundance
-20.082
-78.594
-79.442
X : parts per Million : Silicon29

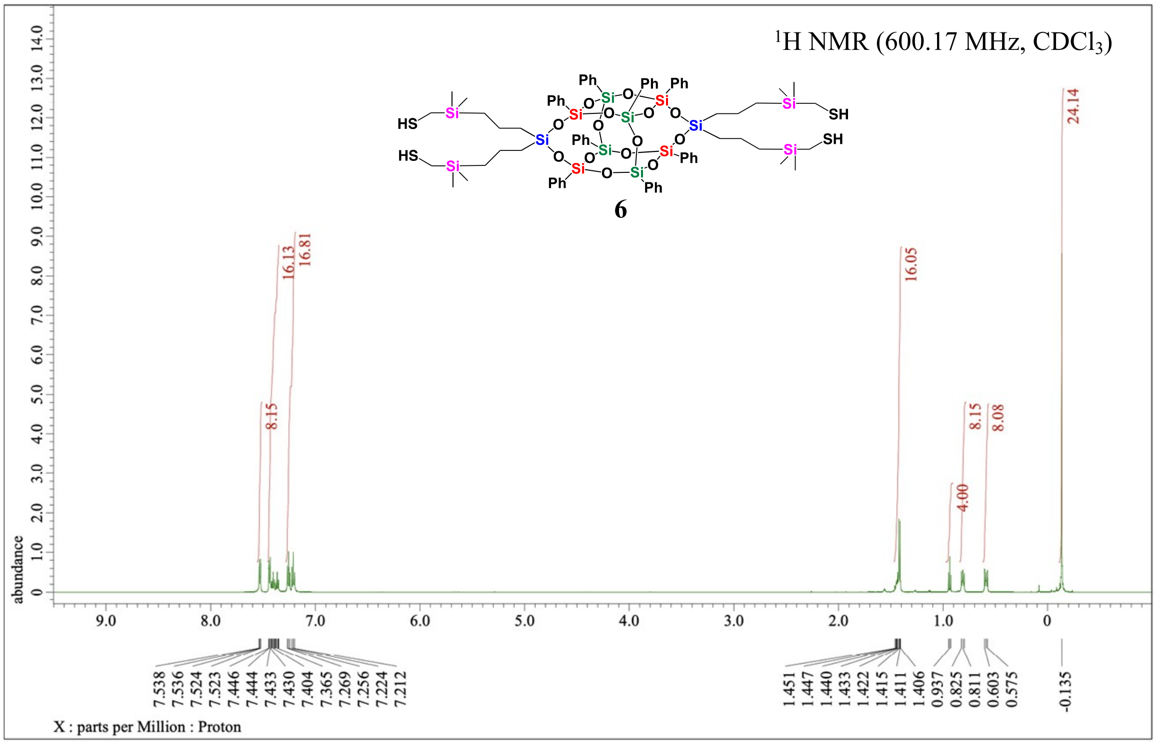


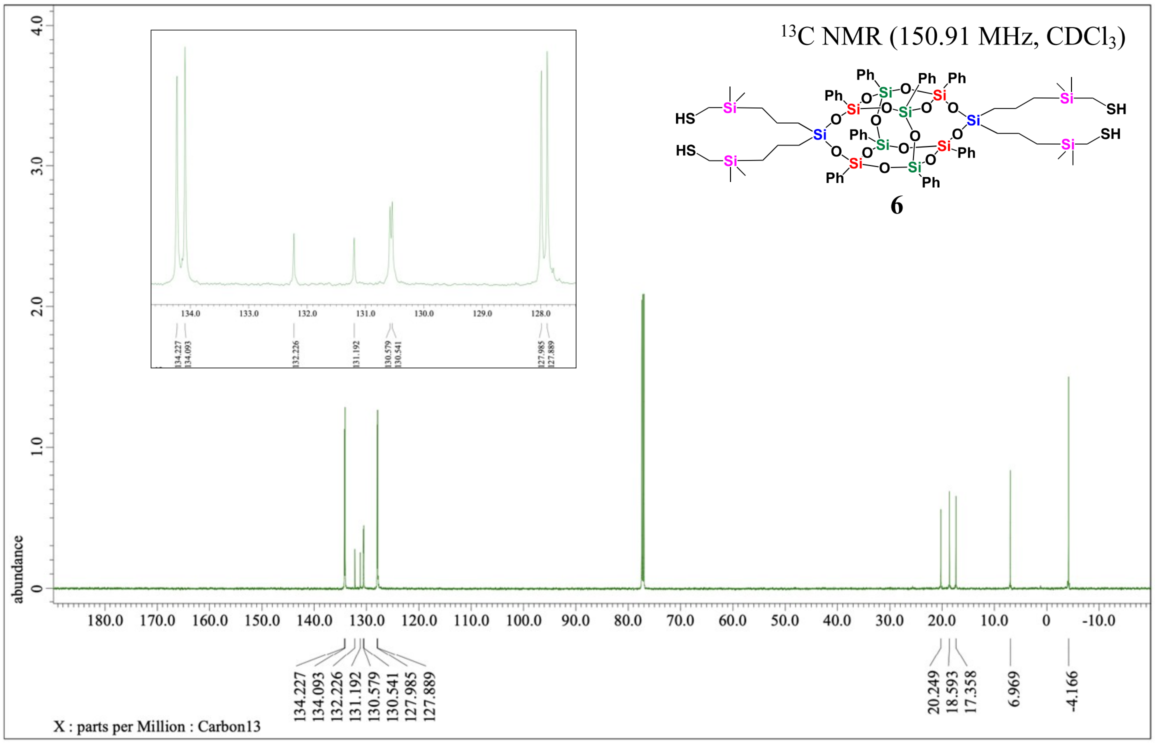
1H NMR (600.17 MHz, CDCl3)
5
AcS
SAc
Si
Ph
O
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.04
16.54
16.25
11.88
8.25
8.10
8.21
8.03
24.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.476
7.464
7.382
7.370
7.349
7.336
7.324
7.299
7.286
7.205
7.193
7.180
7.156
7.143
7.130
2.198
1.870
1.370
1.362
1.356
0.770
0.757
0.526
0.512
0.498
-0.215
X : parts per Million : Proton

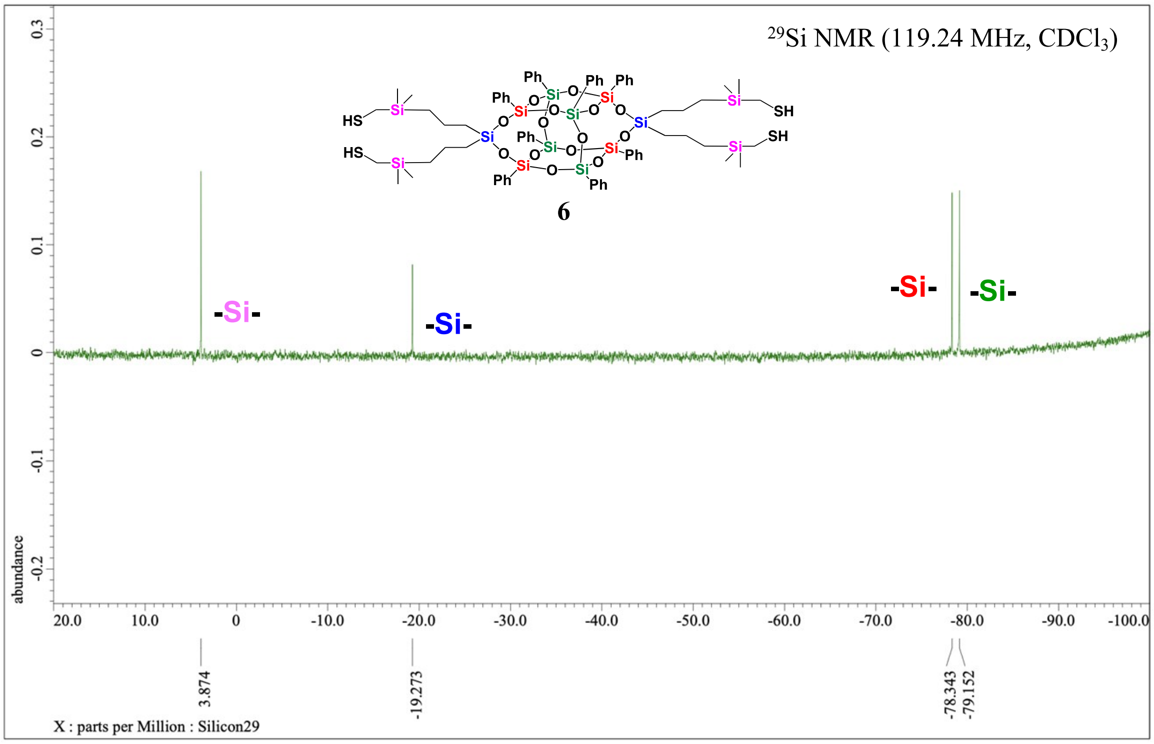


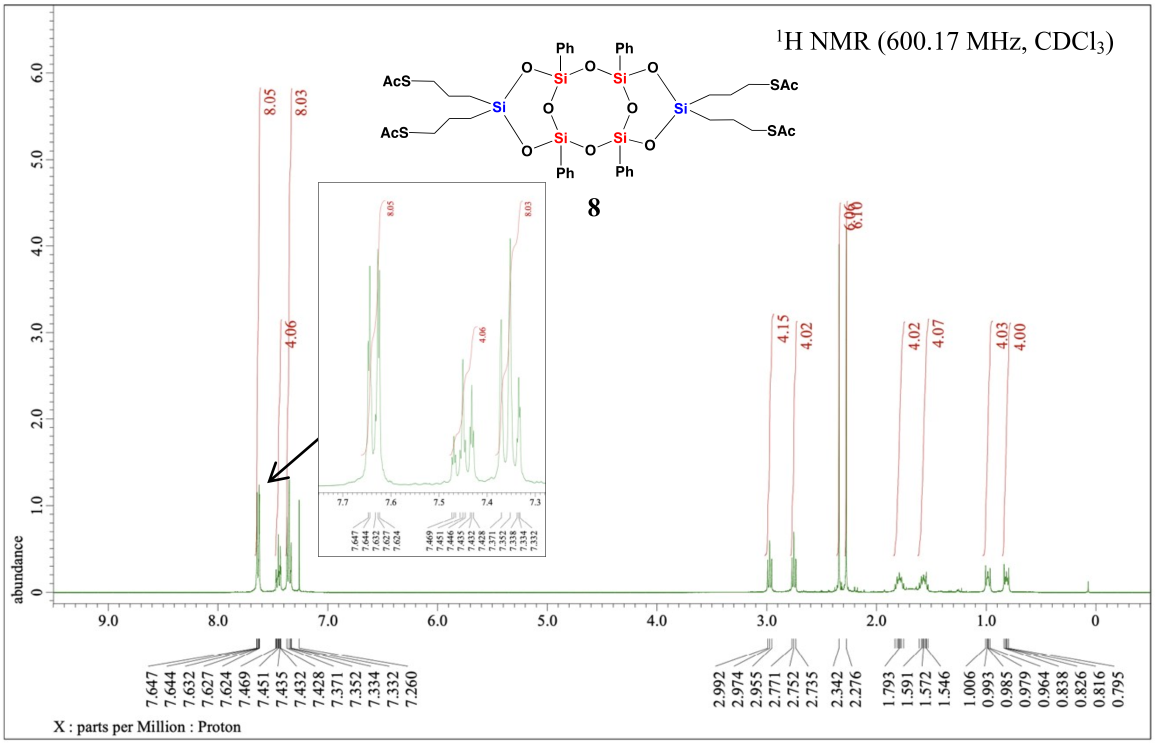
13C NMR (150.91 MHz, CDCl3)
5
AcS
SAc
Si
Ph
O
abundance
4.0
3.0
2.0
1.0
0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.
134.189
134.055
132.178
131.163
130.551
130.522
127.975
127.851
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
197.009
134.189
134.055
132.178
131.163
130.551
130.522
127.975
127.851
77.411
77.200
76.989
30.245
20.154
19.110
17.329
13.078
-3.601
X : parts per Million : Carbon13


^{29}Si NMR (119.24 MHz, CDCl$_3$)
AcS
SAc
Si
O
Ph
5
-Si-
-Si-
-Si-
-Si-
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
20.0
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
2.679
-19.292
-78.285
-79.133
X : parts per Million : Silicon29

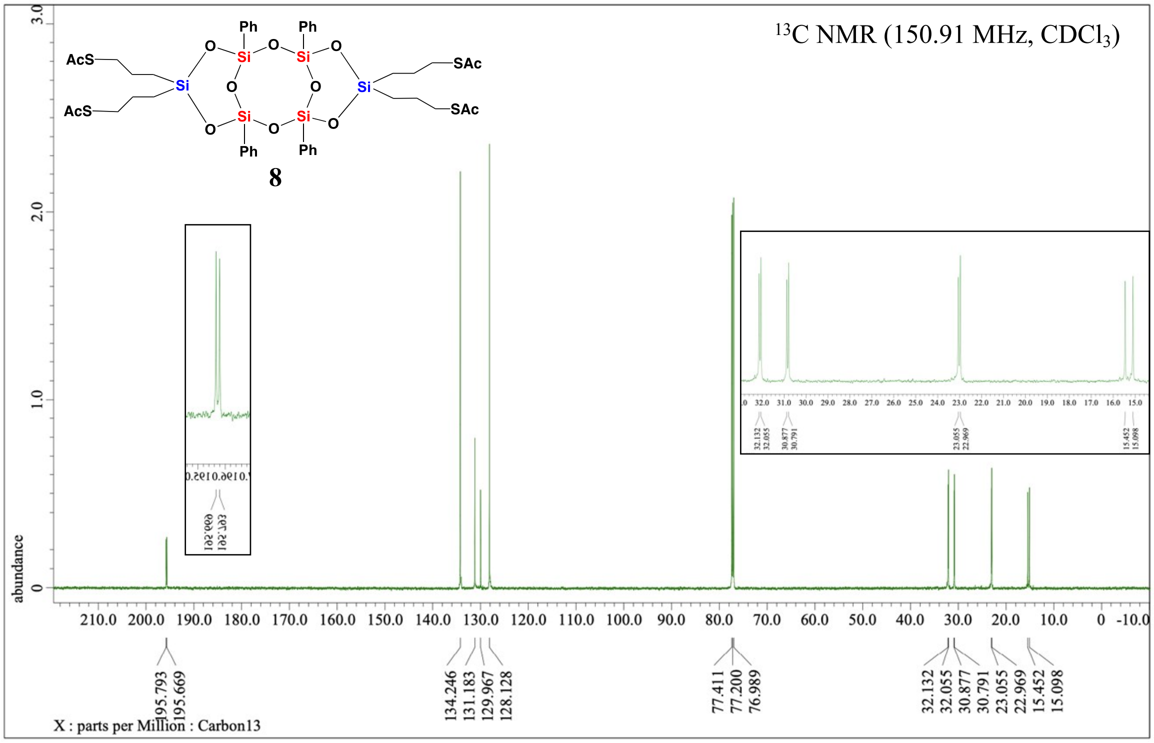

^{1}H NMR (600.17 MHz, CDCl$_3$)
HS
SH
Si
O
Ph
6
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.15
16.13
16.81
16.05
4.00
8.15
8.08
24.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.538
7.536
7.524
7.523
7.446
7.444
7.433
7.430
7.404
7.365
7.269
7.256
7.224
7.212
1.451
1.447
1.440
1.433
1.422
1.415
1.411
1.406
0.937
0.825
0.811
0.603
0.575
-0.135
X : parts per Million : Proton


^{13}C NMR (150.91 MHz, CDCl$_3$)
6
HS
SH
Ph
Si
O
abundance
4.0
3.0
2.0
1.0
0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
134.227
134.093
132.226
131.192
130.579
130.541
127.985
127.889
20.249
18.593
17.358
6.969
-4.166
134.0 133.0 132.0 131.0 130.0 129.0 128.0
X : parts per Million : Carbon13

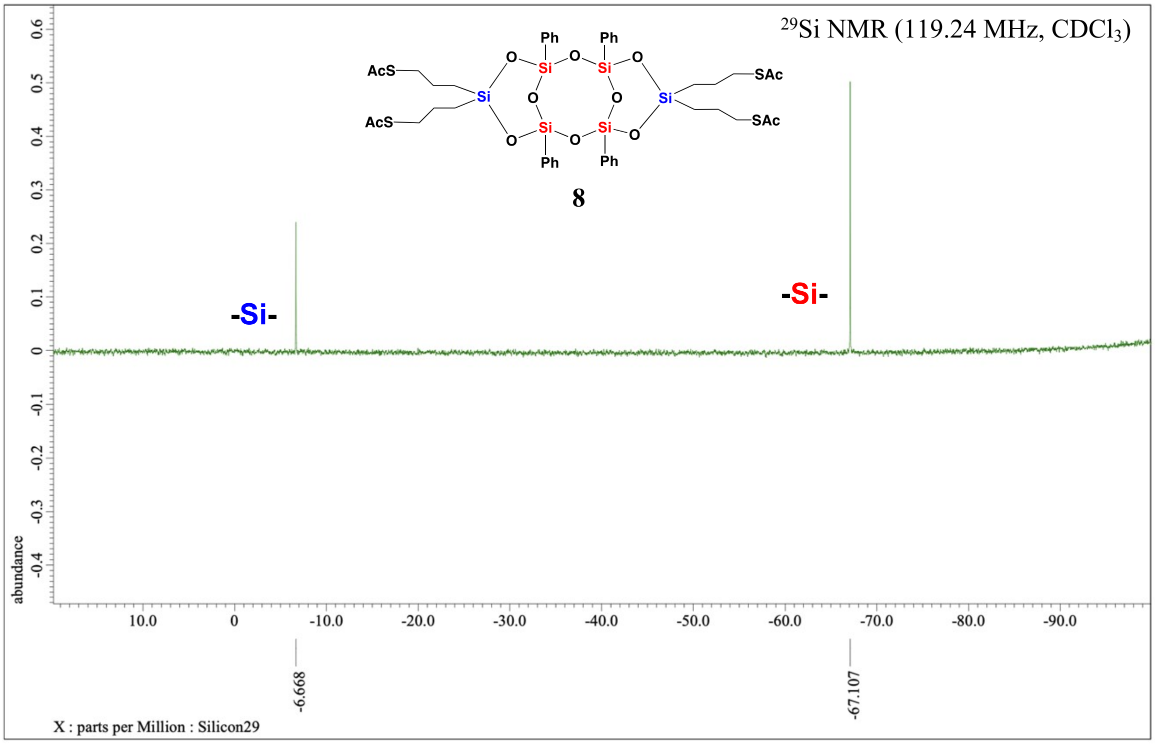

^{29}Si NMR (119.24 MHz, CDCl$_3$)
6
HS
SH
Ph
Si
O
-Si-
-Si-
-Si-
-Si-
abundance
0.3
0.2
0.1
0
-0.1
-0.2
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0
3.874
-19.273
-78.343
-79.152
X : parts per Million : Silicon29

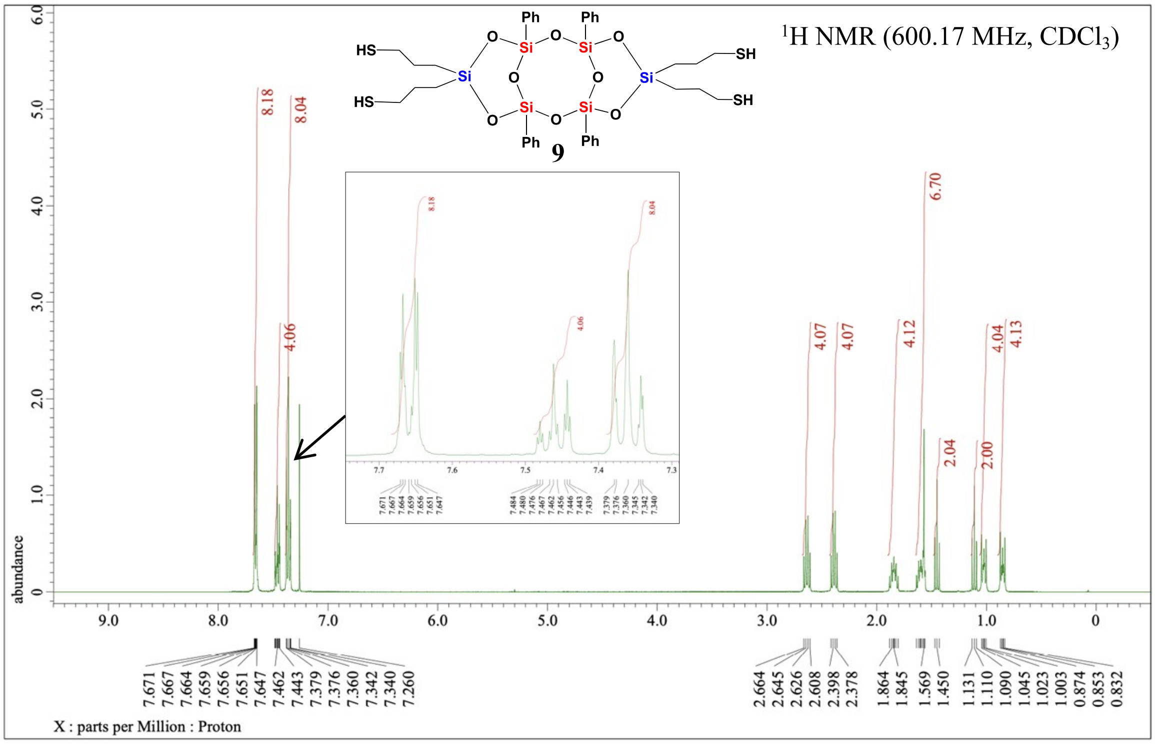


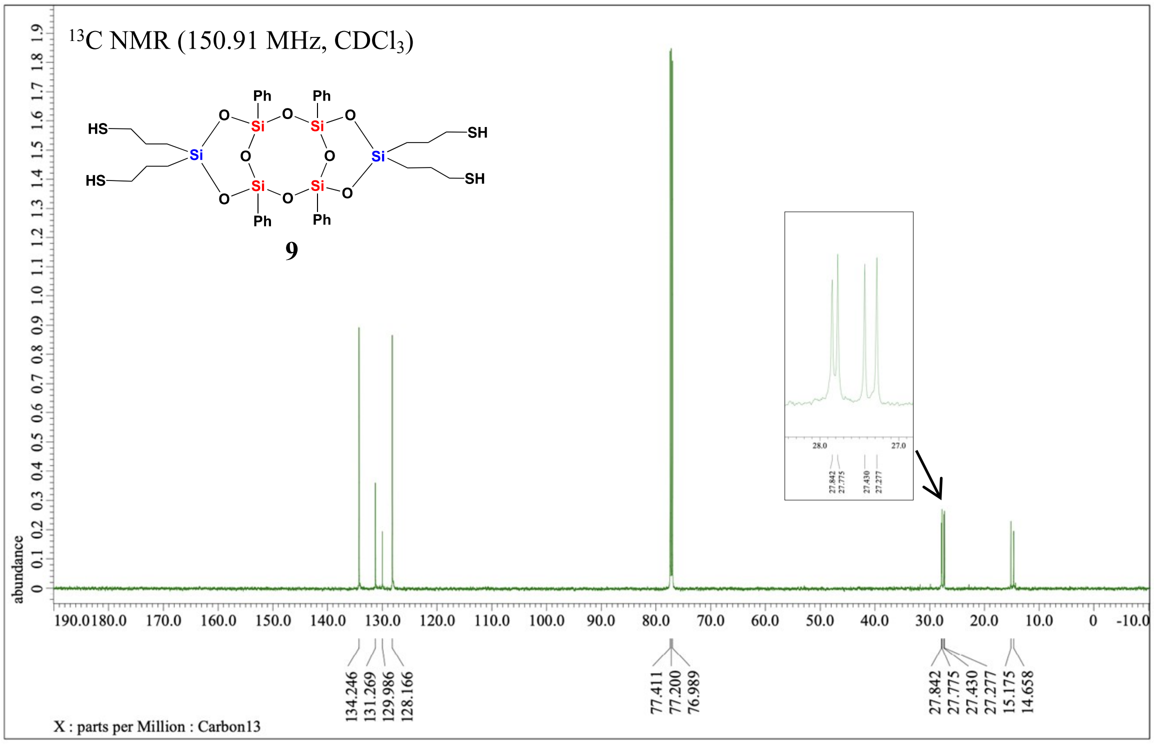
^{1}H NMR (600.17 MHz, CDCl$_3$)
8
AcS
SAc
Si
O
Ph
8.05
8.03
4.06
6.06
6.10
4.15
4.02
4.02
4.07
4.03
4.00
7.647 7.644 7.632 7.627 7.624 7.469 7.451 7.446 7.435 7.432 7.428 7.371 7.352 7.338 7.334 7.332 7.260
2.992 2.974 2.955 2.771 2.752 2.735 2.342 2.276 1.793 1.591 1.572 1.546 1.006 0.993 0.985 0.979 0.964 0.838 0.826 0.816 0.795
abundance
X : parts per Million : Proton

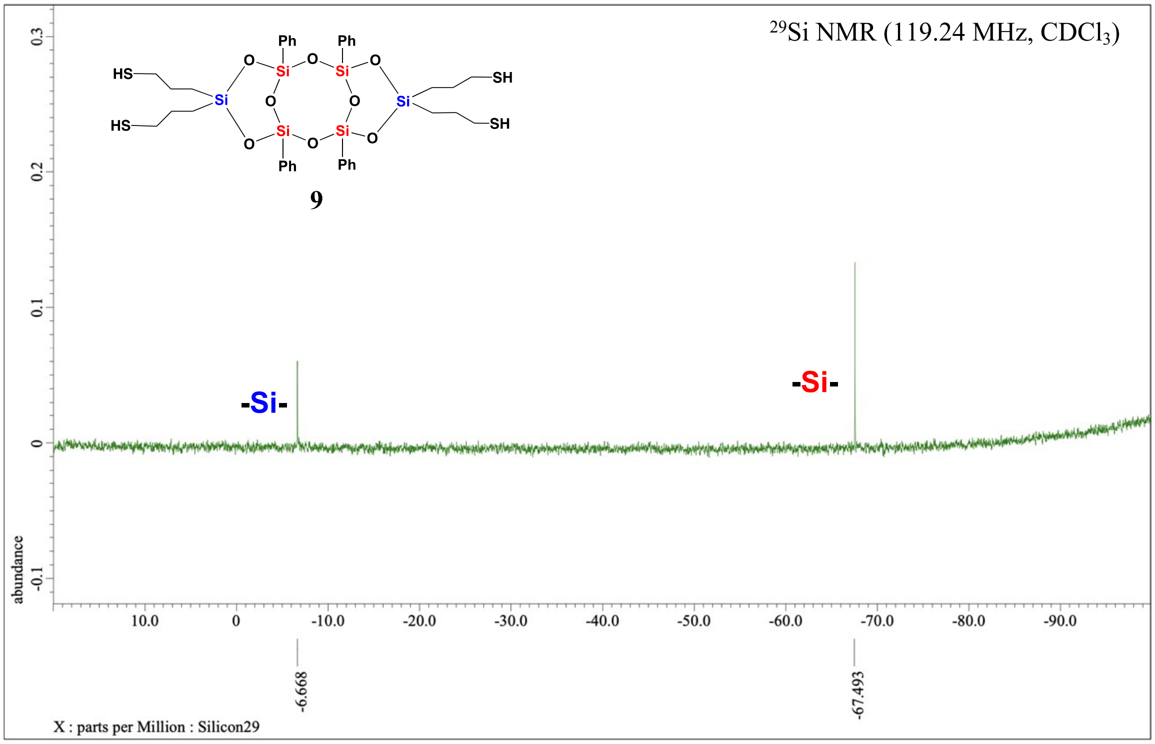


^{13}C NMR (150.91 MHz, CDCl$_3$)
8
AcS
SAc
Si
O
Ph
195.793 195.669
134.246 131.183 129.967 128.128
77.411 77.200 76.989
32.132 32.055 30.877 30.791 23.055 22.969 15.452 15.098
abundance
X : parts per Million : Carbon13


^{29}Si NMR (119.24 MHz, CDCl$_3$)
AcS
AcS
SAc
SAc
Si
O
Ph
8
-Si-
-Si-
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-6.668
-67.107
X : parts per Million : Silicon29


^{1}H NMR (600.17 MHz, CDCl$_3$)
HS
HS
SH
SH
Si
O
Ph
9
8.18
8.04
4.06
4.07
4.07
4.12
6.70
2.04
2.00
4.04
4.13
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.7
7.6
7.5
7.4
7.3
7.671
7.667
7.664
7.659
7.656
7.651
7.647
7.484
7.480
7.476
7.467
7.462
7.456
7.446
7.443
7.439
7.379
7.376
7.360
7.345
7.342
7.340
7.462
7.443
7.260
2.664
2.645
2.626
2.608
2.398
2.378
1.864
1.845
1.569
1.450
1.131
1.110
1.090
1.045
1.023
1.003
0.874
0.853
0.832
X : parts per Million : Proton


^{13}C NMR (150.91 MHz, CDCl$_3$)
9
abundance
X : parts per Million : Carbon13
190.0180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
134.246
131.269
129.986
128.166
77.411
77.200
76.989
27.842
27.775
27.430
27.277
15.175
14.658
28.0
27.0


^{29}Si NMR (119.24 MHz, CDCl$_3$)
9
-Si-
-Si-
abundance
X : parts per Million : Silicon29
10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0
-6.668
-67.493

4. Infrared spectra for compounds 2, 3, 5, 6, 8 and 9

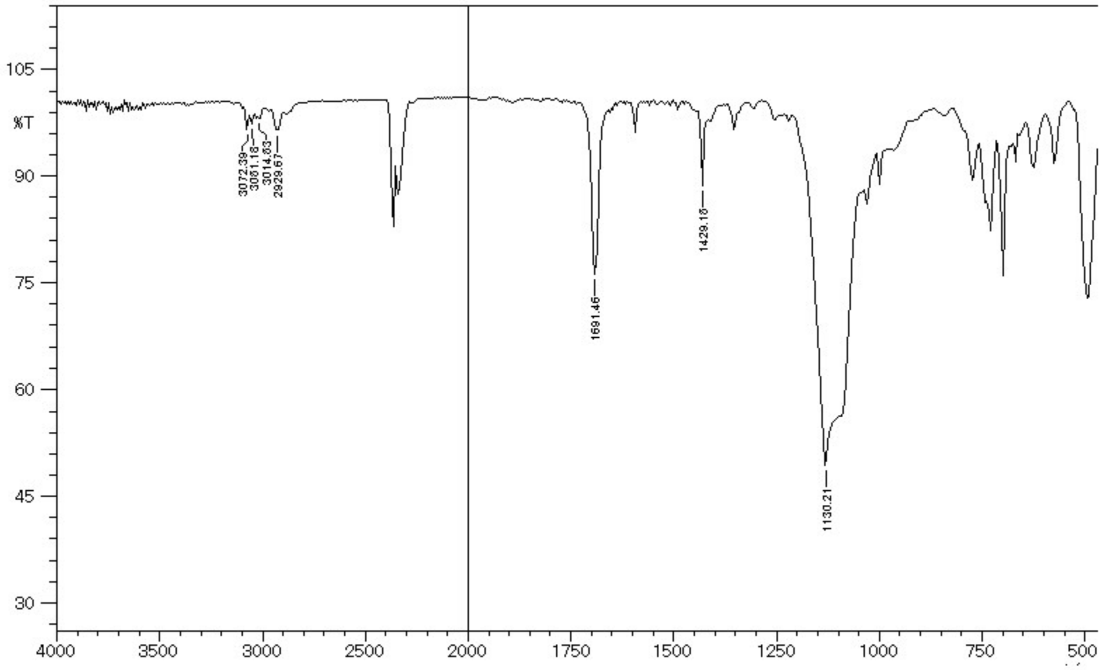


Figure S1: Infrared spectrum for **2**.

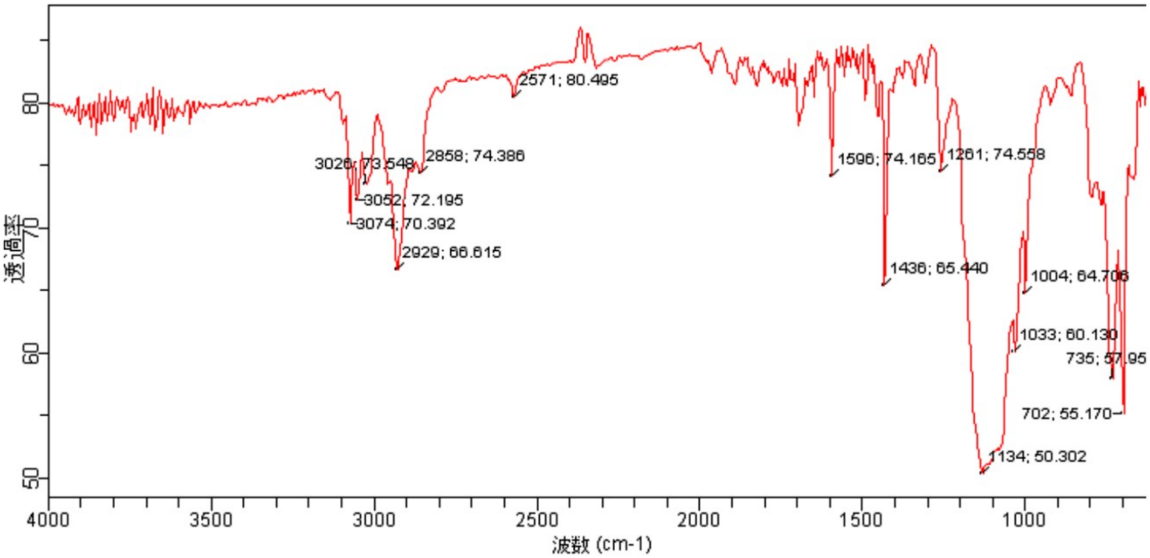


Figure S2: Infrared spectrum for **3**.

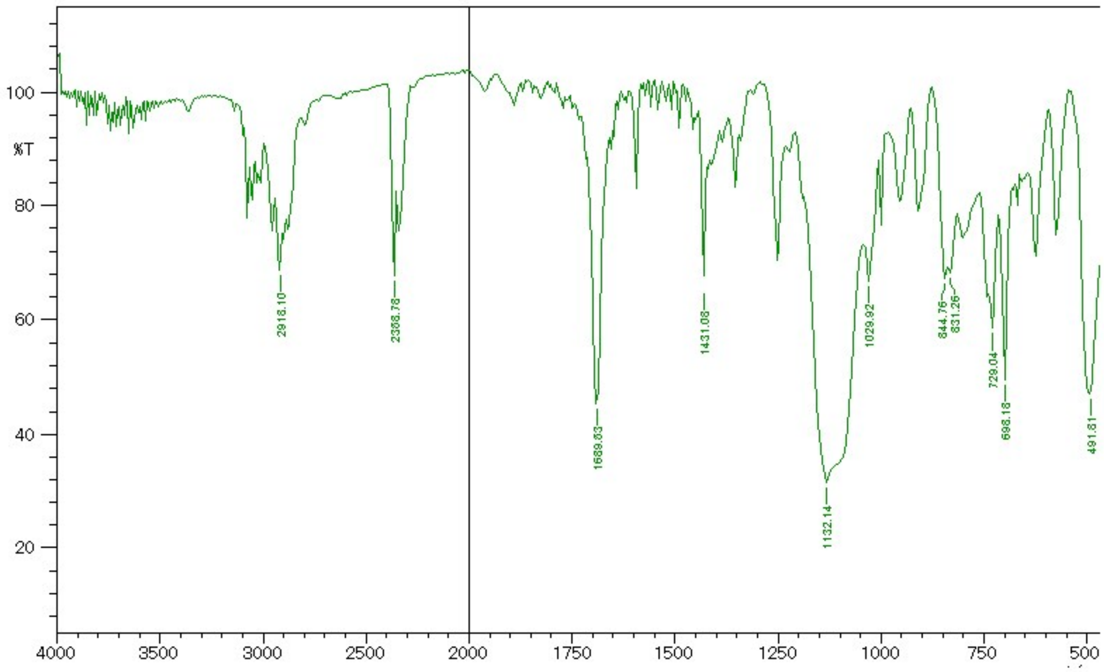


Figure S3: Infrared spectrum for **5**.

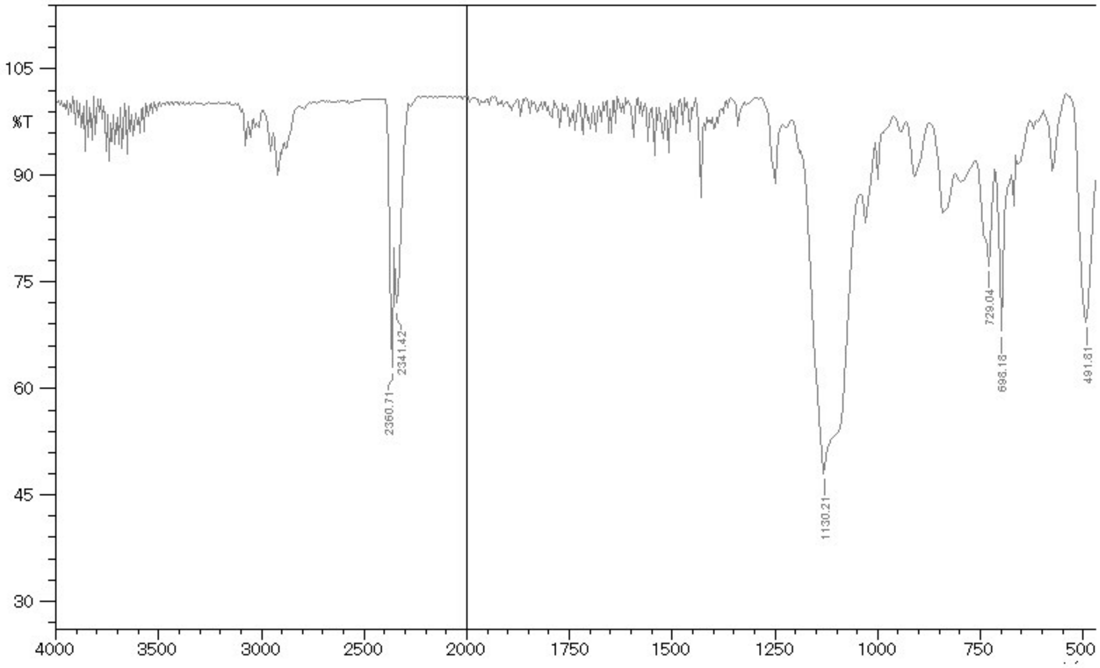


Figure S4: Infrared spectrum for **6**.

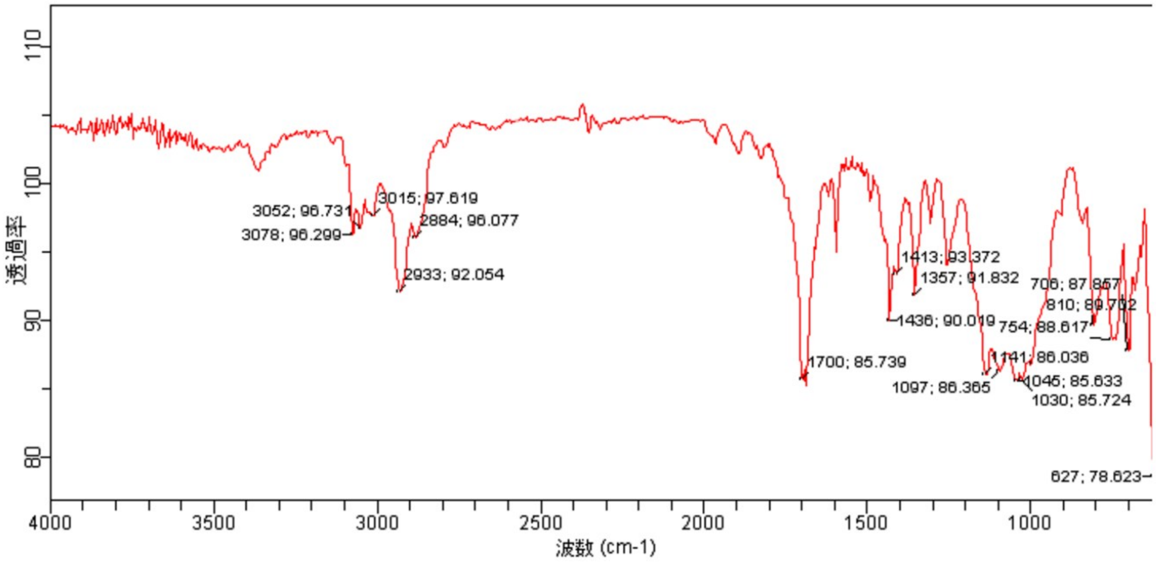


Figure S5: Infrared spectrum for **8**.

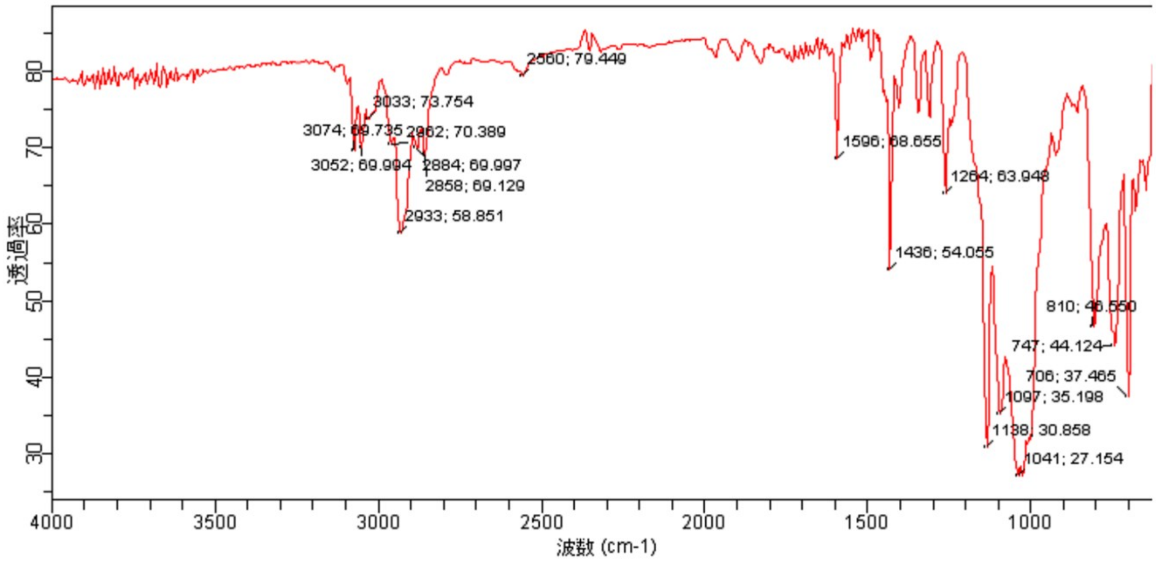


Figure S6: Infrared spectrum for **9**.

5. X-ray diffraction and crystallography for compound 3

Single crystals of **3** suitable for X-ray structural analysis were obtained by slow recrystallization from diethyl ether for **3**. The crystals were immersed in a drop of oil and mounted on a MicroMount. The intensity data were collected on Rigaku VariMax with an XtaLAB P200 diffractometer using multi-layer mirror-monochromated Mo K_α radiation (λ = 0.71075 Å). The structures were solved using SHELXT[4], and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97[5]). All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed using AFIX instructions. The crystal data and refinement details are shown in Table 1. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-2002789 for DDSQ-(CH2)3-SH **3**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal Data and Refinement Details for compound 3

Compounds	**3**
empirical formula	$C_{60}H_{68}O_{14}S_4Si_{10}$
formula weight	1422.28
temperature (K)	130(2)
crystal system	triclinic
space group	*P*-1
a (Å)	13.0930(11)
b (Å)	13.1385(11)
c (Å)	20.1689(18)
α (deg)	89.636(3)
β (deg)	86.119(3)
γ (deg)	89.734(3)
V (Å^3)	3461.4(5)
Z	2
D_{calc} (Mg m^{-3})	1.365
absorp coeff (mm^{-1})	0.371
crystal size (mm)	0.32×0.10×0.03
θ range (°)	2.542-27.500
no. of reflns measd	57655
no. of indep reflns	15743
R_{int}	0.0474
completeness	99.3%

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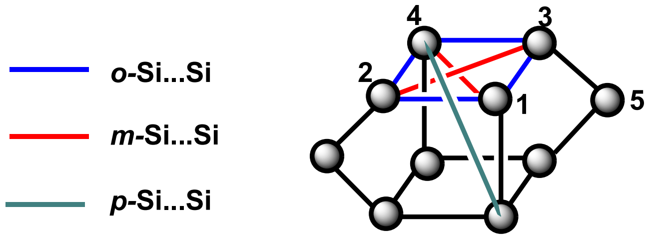
[4] Sheldrick, G. M., *Acta Crystallogr. A*, **2015**, *71*, 3-8.

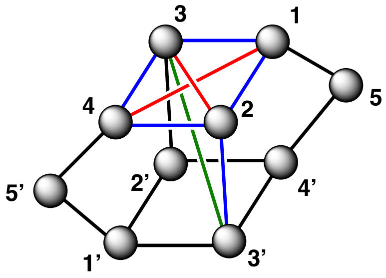
[5] Sheldrick, G. M., *Acta Crystallogr. C*, **2015**, *71*, 3-8.

data/restraints/parameters	15743/0/797
goodness–of–fit on F^2	1.061
final R indices $[I>2\sigma(I)]^a$	$R_1 = 0.0470$ $wR_2 = 0.1300$
R indices (all data)^a	$R_1 = 0.0601$ $wR_2 = 0.1363$
largest diff. peak and hole (e Å^{-3})	1.303 and -1.063

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, w$R_2 = [(\Sigma w\square F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Interatomic Si…Si distances (Å)





Si1	Si2	3.1758(8)
Si2	Si4	3.1126(8)
Si4	Si3	3.1026(8)
Si3	Si1	3.0984(9)
Si2	Si3'	3.2163(8)
Si1	Si4'	4.6241(8)
Si1	Si4	4.3936(8)
Si3	Si2	4.2069(9)
Si1	Si3'	5.2974(8)
Si2	Si4'	4.6236(8)
Si2	Si1'	4.9958(8)
Si4	Si3'	4.9050(8)
Si1	Si1'	6.6830(9)
Si2	Si2'	5.0421(9)
Si3	Si3'	5.5373(9)
Si4	Si4'	6.0587(8)

Table S3. Intermolecular contacts within the sum of van der Waals radii[6]

atom 1	symmetry operator	atom 2	symmetry operator	distance/Å
O4	x, y, z	H3	x, -1+y, z	2.697
C20	-x, 1-y, 1-z	H47	-1+x, y, z	2.863
C20	x, y, z	H2	x, -1+y, z	2.864
H8	x, y, z	C32	-1+x, 1+y, 1+z	2.878
H41	-x, 1-y, 1-z	C28	-1+x, y, z	2.881
H16	-x, 1-y, 1-z	S3	-1+x, 1+y, z	2.929

6. Thermogravimetric analysis of compounds 2, 3, 5, 6, 8 and 9

Table S4. Thermal properties for compounds 2, 3, 5, 6, 8, 9 under N_2

Compounds	**Si+O ratio (%)**	**T_m (°C)**	**Td_5 (°C)**	**Residue at 1000 °C (%)**
2	35.8	134	375	49
5	37.4	-	374	33
3	35.5	134	349	55
6	36.1	102	346	38
8	33.6	-	343	55
9	32.7	129	354	56

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[6] Bondi, A., *J. Phys. Chem.*, **1964**, *68*, 441-451.