Electronic Supplementary Information (ESI)

Synthesis and isolation of non-chromophore cage-rearranged silsesquioxanes from base-catalyzed reactions

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EXPERIMENTAL SECTION

Materials

Octakis(3-chloropropyl)octasilsesquioxane (**1**) was prepared according to a literature report.[5d] 2-nitrophenol (purity; 98%), 3-nitrophenol (purity; 99%), and anhydrous N, N-dimethyl formamide were purchased from Sigma Aldrich, used without additional purification, while the commercial grade of hexane, ethyl acetate, and methylene chloride was further distilled. Precoated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc.

Instrumentation

Fourier transform nuclear magnetic resonance spectra were obtained by using a Bruker-Ascend^{TM} 400 high-resolution magnetic resonance spectrometer for ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz) and $^{29}Si\{^{1}H\}$ (79 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane (TMS) and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer.

General procedure to prepare sodium *o*-nitrophenolate and *m*-nitrophenolate salts.

Either 2-nitrophenol or 3-nitrophenol was dissolved in a sodium hydroxide solution (1 M) at a molar ratio of 1:1. Then, the solution mixture was stirred at room temperature for 1 hour until becoming a clear solution. Evaporation of water gave derivatives of nitrophenolate sodium salts. Then, the solid salts were further dried under a vacuum for an overnight, while being heated at 70°C to complete a perfect dryness.

Synthesis of octakis(3-propyl-*o*-oxynitrobenzene)octasilsesquioxane (2), decakis(3-propyl-*o*-oxynitrobenzene)decasilsesquioxane (3), and dodecakis(3-propyl-*o*-oxynitrobenzene)dodecasilsesquioxane (4).

In a 50 ml of dried round bottom flask, sodium *o*-nitrophenolate salt (4.23 g, 26.2 mmol) was further dried for 5 hours under vacuum while being heated at 70°C. Then, dried compound **1** (2.00 g, 1.93 mmol) was added, followed by the addition of dried DMF (15 mL) into the solid mixture. Then, the reaction solution was heated to 100°C for 1 day. The reaction was then stopped by cooling down in an ice bath. In order to remove soluble inorganic salts, 150 ml of cold CH_2Cl_2 and 50 ml of cold deionized water were added into the reaction mixture, becoming a two-phase solution between organic and aqueous layers. The aqueous layer was extracted by 50 mL of CH_2Cl_2 for three times. After that, combined organic layers were washed with 50 ml of cold deionized water and saturated $NaHCO_3$ solution for three times. Then, it was further washed with cold deionized water until the organic phase changed color from orange to light yellow in order to completely remove an excess of 2-nitrophenol. Anhydrous sodium sulfate was added into the organic solution resulting in a clear yellow solution, followed by a filtration. Evaporation of organic solvent gave a yellow sticky crude product (3.48 g). Finally, the crude product was purified by silica gel column chromatography (100% CH_2Cl_2 to obtain three major products at R_f at 0.38, 0.30 and 0.24, identified as T_8, T_{10}, and T_{12} products, respectively. Compound **2** (T_8, 0.2993 g, 0.1612 mmol, 5% yield),^{1}H NMR ($CDCl_3$): δ 0.82 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, $J_{(H-H)}$ = 6.28 Hz), 6.94 (m, 1H), 7.07 (d, 1H, $J_{(H-H)}$ = 8.04 Hz), 7.46 (m, 1H), 7.77 (dd, 1H, $J_{(H-H)}$ = 3.24 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.46, 139.86, 134.10, 125.46, 119.94, 114.52, 71.05, 22.61, 7.92 ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ -66.70 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{72}H_{80}N_8O_{36}Si_8Na]^+$, *m/z* 1879.2727; found, *m/z* 1879.2657. Compound **3** (T_{10}, 0.6422 g, 0.2768 mmol, 18% yield),^{1}H NMR ($CDCl_3$): δ 0.82 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, $J_{(H-H)}$ = 6.28 Hz), 6.94 (m, 1H), 7.07 (d, 1H, $J_{(H-H)}$ = 8.08 Hz), 7.46 (m, 1H), 7.77 (dd, 1H, $J_{(H-H)}$ = 3.24 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.83, 140.11, 134.43, 125.71, 120.17, 114.93, 71.48, 23.14, 8.90 ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ -68.41 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{90}H_{100}N_{10}O_{45}Si_{10}Na]^+$, *m/z* 2343.3434; found, *m/z* 2343.3255. Compound **4** (T_{12}, 0.1285 g, 0.04616 mmol, 4% yield) ^{1}H NMR ($CDCl_3$): δ 0.84 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, $J_{(H-H)}$ = 6.10 Hz), 6.99 (t, 1H, $J_{(H-H)}$ = 7.70Hz), 7.08 (d, 1H, $J_{(H-H)}$ = 8.40 Hz), 7.45 (m, 1H), 7.74 (dd, 1H, $J_{(H-H)}$ = 3.11 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.90, 140.03, 134.46, 125.68, 120.09, 115.02, 71.61, 23.34, 9.52, 8.94 ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ

-67.98, -70.75 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{108}H_{120}N_{12}O_{54}Si_{12}Na]^+$, *m/z* 2808.4175; found, *m/z* 2808.4170.

Synthesis of octakis(3-propyl-*m*-oxynitrobenzene)octasilsesquioxane (5), decakis(3-propyl-*m*-oxynitrobenzene)decasilsesquioxane (6), and dodecakis(3-propyl-*m*-oxynitrobenzene)dodecasilsesquioxane (7).

To complete a perfect dryness of sodium salt, *m*-nitrophenolate sodium salt was further dried under a vacuum at 70 °C for 5 hours until the orange solids of the salt hydrate to dried red powder. Then, dried compound **1** (2.00 g; 1.93 mmol) and sodium *m*-nitrophenol salt (3.73 g, 23.1 mmol) were added into 50 mL of dried round bottom flask, dried under vacuum at room temperature for an additional hour. Anhydrous N,N-dimethyl formamide (DMF) (15 mL) was added into the solid mixture. After heating at 70℃ for 24 hours, the reaction mixture was cooled down in an ice-bath, followed by the addition of cold CH_2Cl_2 (150 mL) and deionized water (50 mL) to extract products in organic layer out from aqueous layer. The aqueous layer was further extracted by 50 mL of CH_2Cl_2 (3 times). The combined organic layers were further washed with saturated $NaHCO_3$ and washed with water in the final. The organic solution was dried by anhydrous sodium sulfate. Then, evaporation of organic layer gave the yellow sticky crude product (3.07g), and analyzed by thin-layer chromatography (TLC) with 10% of hexane in CH_2Cl_2. The result showed three separate spots at R_f = 0.35, 0.25 and 0.14, identified as T_8, T_{10}, and T_{12} products, respectively. Compound **5** (T_8, 0.11 g, 0.0592mmol, 3%yield), ^{1}H NMR ($CDCl_3$): δ 0.82 (t, 2H, $J_{(H-H)}$ = 3.09 Hz), 1.92 (m, 2H), 3.96 (t, 2H, $J_{(H-H)}$ = 6.44 Hz), 7.16 (dd, 1H, $J_{(H-H)}$ = 3.37 Hz), 7.37 (t, 1H, $J_{(H-H)}$ = 8.22 Hz), 7.63 (t, 1H, $J_{(H-H)}$ = 2.14 Hz), 7.74 (dd, 1H, $J_{(H-H)}$ = 3.09 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.38, 149.14, 129.97, 121.61, 115.70, 108.39, 70.01, 22.54, 8.09 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -66.70 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{72}H_{80}N_8O_{36}Si_8Na]^+$, *m/z* 1879.2727; found, *m/z* 1879.2875. Compound **6** (T_{10}, 0.42 g, 0.1808 mmol, 12% yield), ^{1}H NMR ($CDCl_3$): δ 0.82 (t, 2H, $J_{(H-H)}$ = 8.20 Hz), 1.92 (m, 2H), 3.95 (t, 2H, $J_{(H-H)}$ = 6.42 Hz), 7.15 (dd, 1H, $J_{(H-H)}$ = 3.39 Hz), 7.36 (t, 1H, $J_{(H-H)}$ = 8.22 Hz), 7.62 (t, 1H, $J_{(H-H)}$ = 2.22 Hz), 7.74 (dd, 1H, $J_{(H-H)}$ = 3.15 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.60, 149.32, 130.20, 121.78, 115.86, 108.68, 70.36, 22.99, 8.96 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -68.53 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{90}H_{100}N_{10}O_{45}Si_{10}Na]^+$, *m/z* 2343.3434; found, *m/z* 2343.3512. Compound **9** (T_{12}, 0.26 g, 0.0933 mmol, 7% yield), ^{1}H

NMR ($CDCl_3$): δ 0.86 (t, 2H, $J_{(H-H)}$ = 8.24 Hz), 1.95 (m, 2H), 3.95 (t, 2H, $J_{(H-H)}$ = 4.18 Hz), 7.13 (dd, 1H, $J_{(H-H)}$ = 8.24 Hz), 7.31 (t, 1H, $J_{(H-H)}$ = 8.16 Hz), 7.58 (t, 1H, $J_{(H-H)}$ = 2.06 Hz), 7.68 (dd, 1H, $J_{(H-H)}$ = 3.12 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.60, 149.38, 130.29, 121.74, 116.00, 108.74, 70.47, 23.26, 9.58, 9.01 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -68.21, -70.90 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{108}H_{120}N_{12}O_{54}Si_{12}Na]^+$, *m/z* 2808.4175; found, *m/z* 2808.4812

General procedure to prepare cage-rearranged silsesquioxanes (T_8, T_{10}, and T_{12}) under base-catalyzed reaction at different reaction times.

In each reaction cycle, compound **1**, 1.00 g, 0.96 mmol) and K_2CO_3 (0.0625 g, 0.45 mmol) were added into dried two-neck round bottom flask equipped with condenser and magnetic stirring bar. The solid mixture was dried under vacuum for 1 hour. Then, anhydrous DMF (10 ml) was added to the solid mixture. Then, the reaction mixture was heated at 60°C under dried nitrogen to vary reaction times for 15 mins, 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, and 24 hrs. Isolated yields of each product were determined using conventional liquid chromatography as shown in Figure S1. To work up, the solution mixture was then extracted using CH_2Cl_2 (3 x 50 mL). The organic phase was collected and extracted further using H_2O (3 x 100 mL). The organic layer was dried by anhydrous sodium sulfate and evaporated to obtain pale white viscous liquid. The crude product was purified by silica gel column chromatography (30% CH_2Cl_2/Hexane) to obtain three major products at R_f at 0.41, 0.35 and 0.28, identified as octakis(3-chloropropyl)octasilsesquioxane (**1**), decakis(3-chloropropyl)decasilsesquioxane (**8**) and dodecakis(3-chloropropyl)dodecasilsesquioxane (**9**), respectively. Compound **1**, ^1H NMR ($CDCl_3$): δ 0.79 (m, 2H), 1.86 (m, 2H), 3.53 (t, 2H, $J_{(H-H)}$ = 6.58 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.34, 26.25, 47.02 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -67.07 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{24}H_{48}Cl_8NaO_{12}Si_8]^+$, *m/z* 1058.8647; found, *m/z* 1058.8539. Compound **8**, ^1H NMR ($CDCl_3$): δ 0.79 (m, 2H), 1.86 (m, 2H), 3.53 (t, 2H, $J_{(H-H)}$ = 6.52 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.34, 26.25, 47.02 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -68.94 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{31}H_{62}Cl_{10}NaO_{14}Si_{10}]^+$, *m/z* 1316.8527; found, *m/z* 1316.8177. Compound **9**, ^1H NMR ($CDCl_3$): δ 0.77 (m, 2H), 1.85 (m, 2H), 3.54 (t, 2H, $J_{(H-H)}$ = 6.58 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.00, 10.49, 26.50, 26.60, 47.15, 47.21 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -68.68, -71.34 ppm. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{36}H_{72}Cl_{12}NaO_{18}Si_{12}]^+$, *m/z* 1576.8021; found, *m/z* 1576.8498.

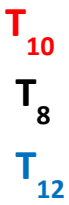


Figure S1: Weight percentages of compounds **1** (T_8), **8** (T_{10}), and **9** (T_{12}) with time for base-catalyzed reactions. Isolated yields determined using conventional liquid chromatography.

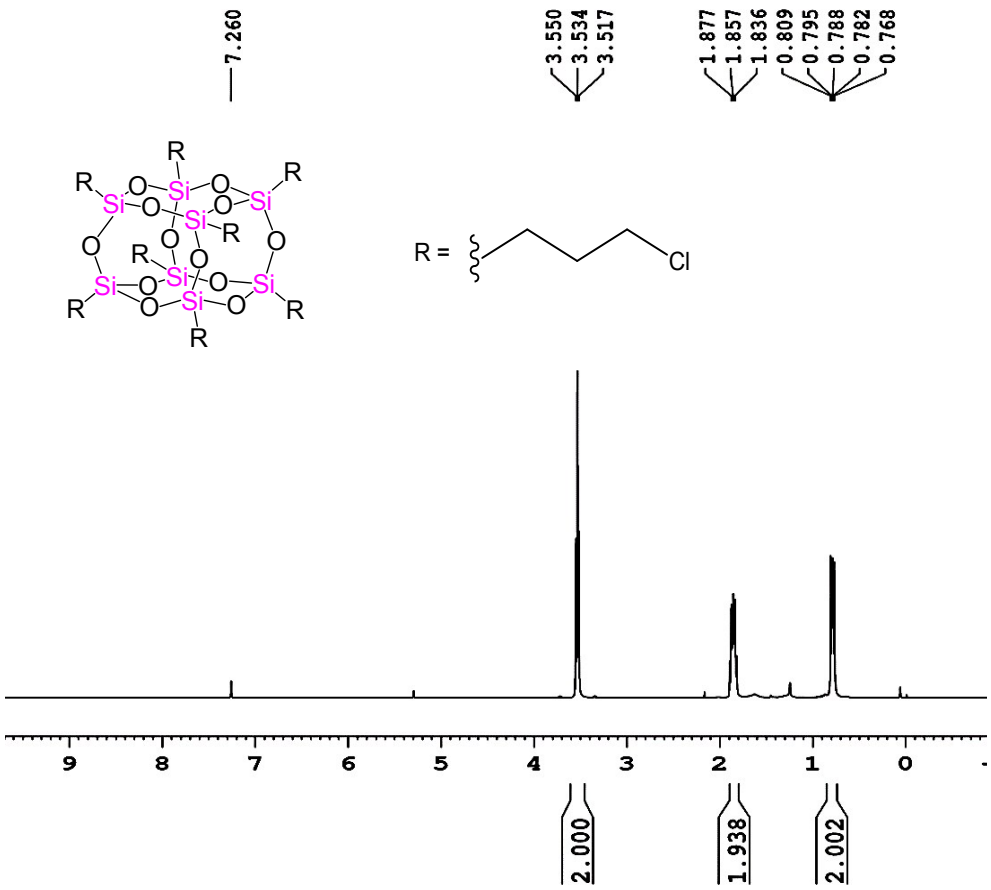


Figure S2: ^{1}H-NMR (400 MHz) of octakis(3-chloropropyl)octasilsesquioxane (**1**) in $CDCl_3$

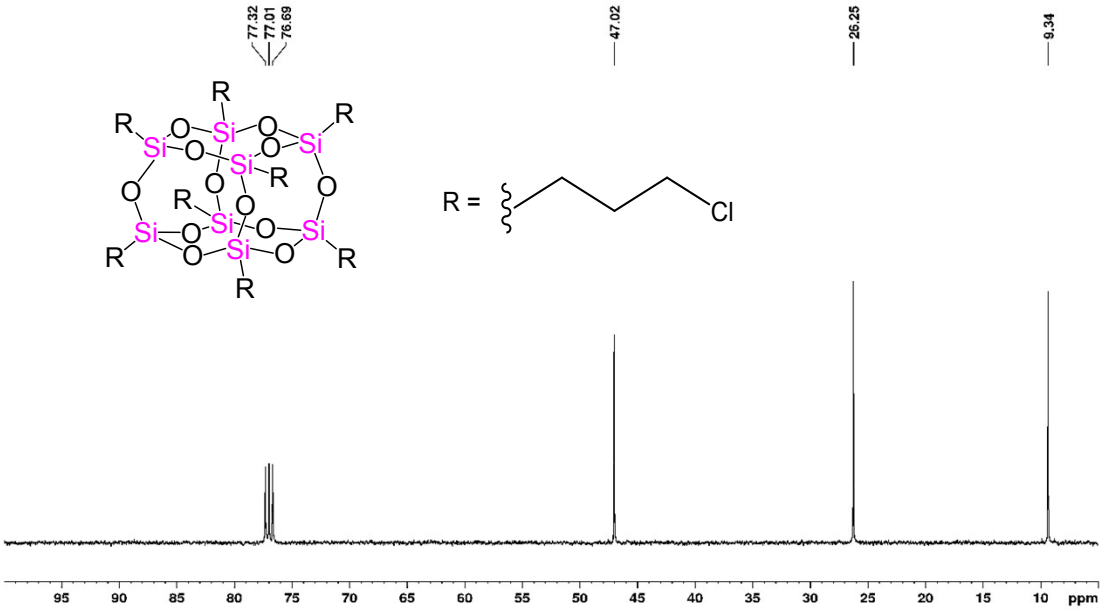


Figure S3: ^{13}C{^{1}H} NMR (100 MHz) of octakis(3-chloropropyl)octasilsesquioxane (**1**) in $CDCl_3$

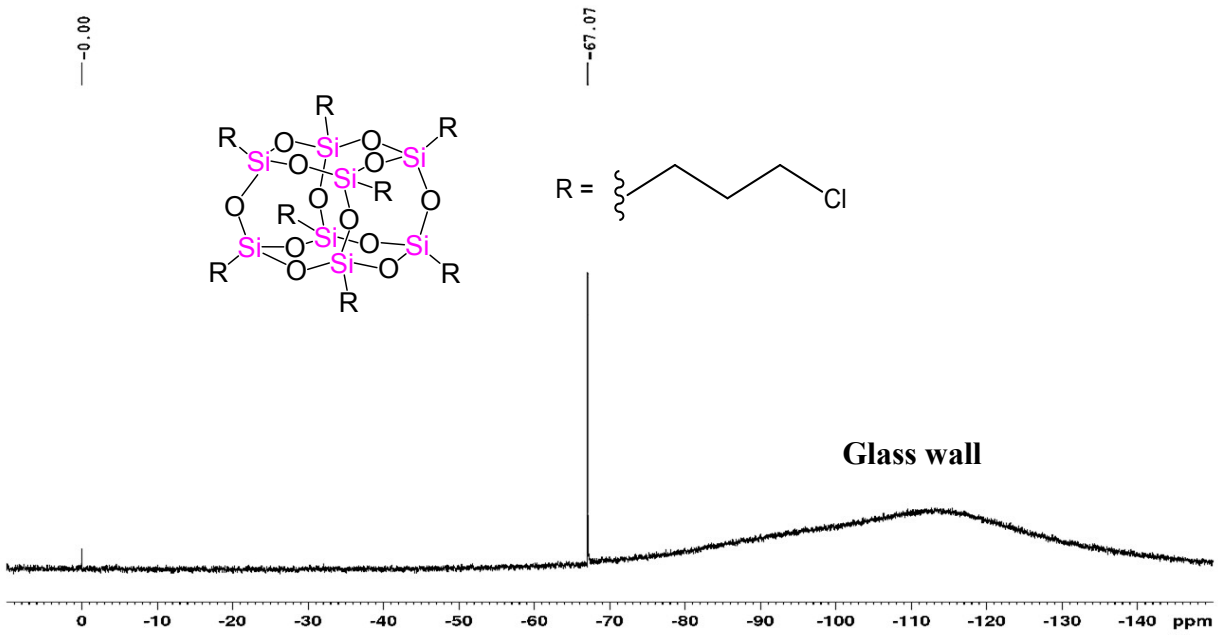
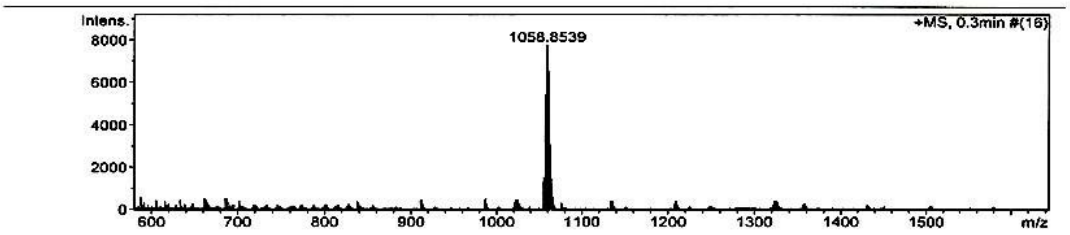


Figure S4: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of octakis(3-chloropropyl)octasilsesquioxane (**1**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	413.2748	33938	100.0	3500.7	0.0558	7406
2	414.2780	8080	23.8	830.7	0.0552	7502
3	415.2801	1142	3.4	116.8	0.0552	7517
4	441.3049	2393	7.1	227.1	0.0573	7703
5	442.3106	704	2.1	66.4	0.0591	7488
6	661.5338	618	1.8	42.6	0.0867	7628
7	685.4359	6653	19.6	459.7	0.0781	8774
8	686.4361	2738	8.1	188.5	0.0791	8678
9	687.4465	667	2.0	45.4	0.0799	8606
10	1054.8594	1542	4.5	122.7	0.1213	8695
11	1055.8595	989	2.9	78.4	0.1105	9556
12	1056.8577	5395	15.9	430.1	0.1108	9537
13	1057.8592	3119	9.2	248.2	0.1109	9539
14	1058.8539	7753	22.8	617.4	0.1191	8893
15	1059.8524	4484	13.2	356.5	0.1025	10339
16	1060.8523	6516	19.2	517.9	0.1143	9281
17	1061.8530	3122	9.2	247.6	0.1177	9024
18	1062.8502	3069	9.0	243.2	0.1199	8862
19	1063.8494	1488	4.4	117.5	0.1175	9055
20	1064.8487	1179	3.5	92.9	0.1157	9205
21	1278.8590	633	1.9	47.8	0.1224	10449
22	1280.8601	2128	6.3	162.1	0.1423	9002
23	1281.8601	1720	5.1	130.9	0.1320	9711
24	1282.8568	4363	12.9	333.0	0.1245	10300
25	1283.8569	2878	8.5	219.5	0.1199	10709
26	1284.8562	4326	12.7	330.2	0.1199	10719
27	1285.8553	2502	7.4	190.7	0.1364	9429
28	1286.8564	2638	7.8	201.2	0.1274	10097
29	1287.8529	1387	4.1	105.5	0.1437	8960
30	1288.8502	1142	3.4	86.8	0.1397	9223

Figure S5: HRMS (ESI) of octakis(3-chloropropyl)octasilsesquioxane (**1**)

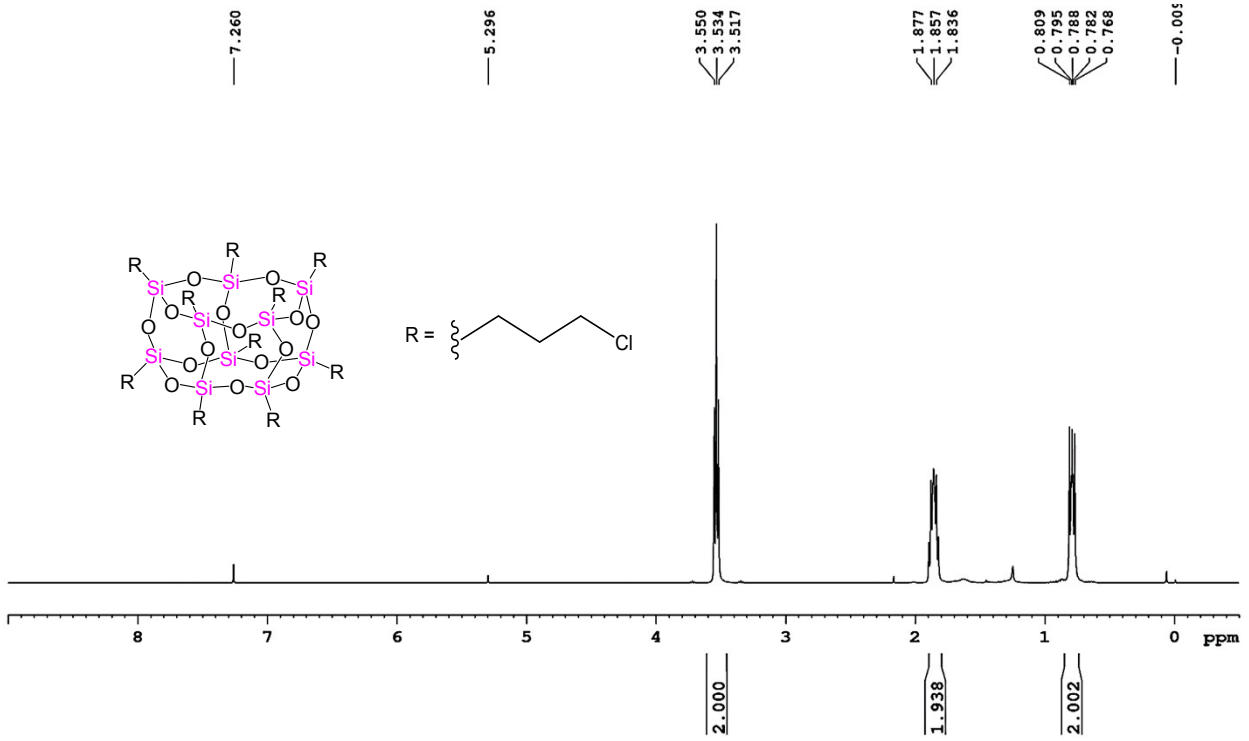


Figure S6: ^{1}H NMR (400 MHz) of decakis(3-chloropropyl)decasilsesquioxane (**8**) in $CDCl_3$

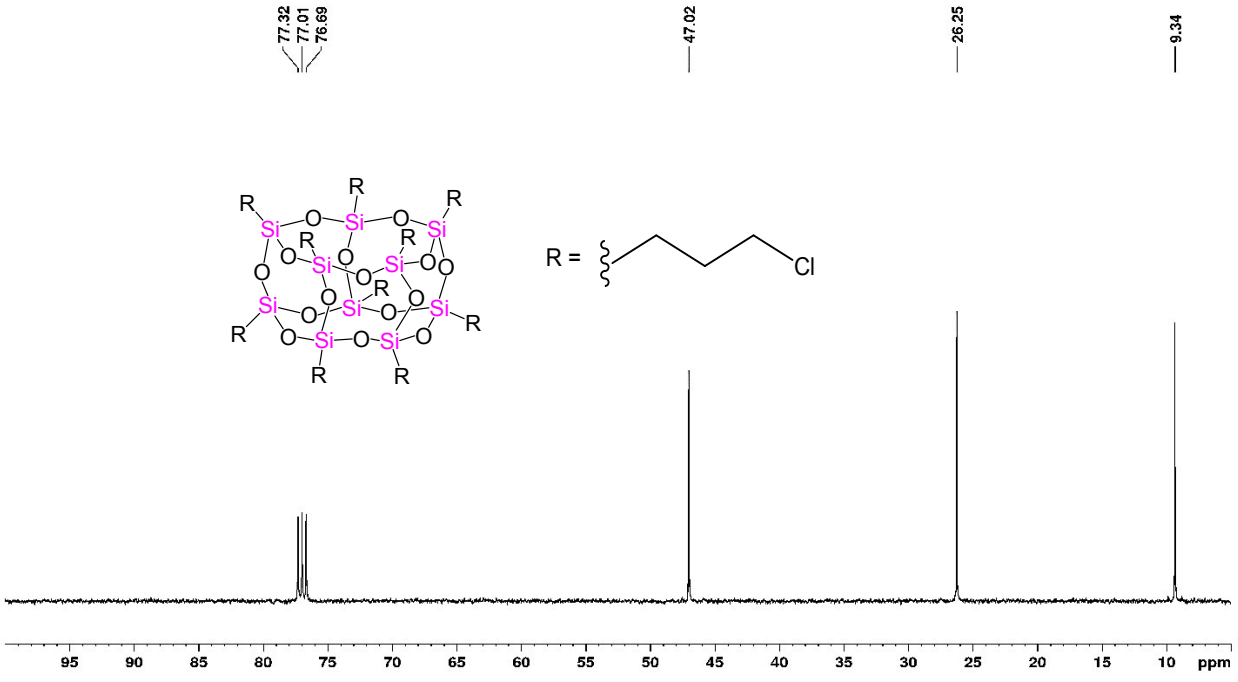


Figure S7: $^{13}C\{^{1}H\}$ NMR (100 MHz) of decakis(3-chloropropyl)decasilsesquioxane (**8**) in $CDCl_3$

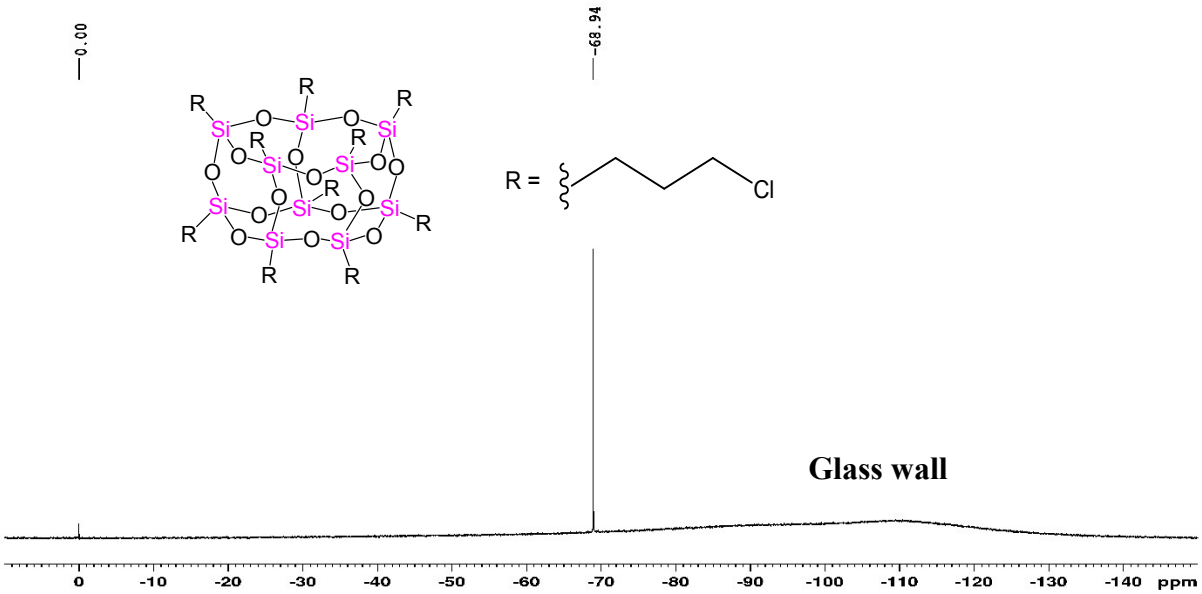
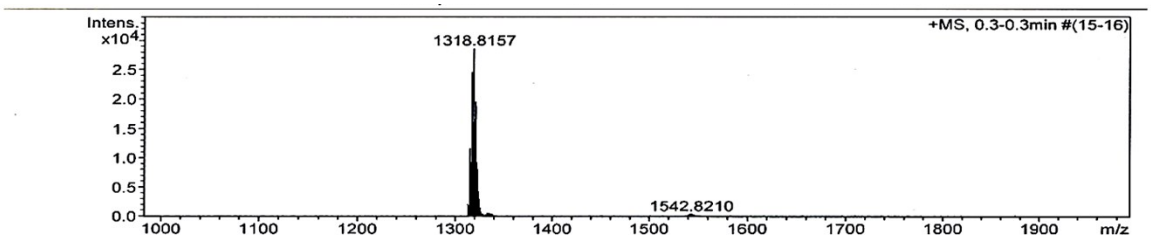


Figure S8: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of decakis(3-chloropropyl)decasilsesquioxane (**8**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	400.3854	1000	3.5	78.2	0.0539	7434
2	413.2744	27845	97.4	2080.7	0.0556	7438
3	414.2775	6752	23.6	502.1	0.0550	7527
4	415.2788	1036	3.6	76.2	0.0555	7476
5	441.3044	3426	12.0	230.0	0.0573	7697
6	442.3100	935	3.3	62.0	0.0601	7360
7	493.3524	1350	4.7	75.9	0.0570	8650
8	521.3817	2309	8.1	120.2	0.0698	7474
9	549.4136	1961	6.9	97.0	0.0708	7761
10	577.4533	885	3.1	42.9	0.0932	6199
11	605.4672	800	2.8	38.4	0.1172	5165
12	633.5007	784	2.7	37.3	0.0987	6418
13	638.6033	1006	3.5	48.1	0.0703	9086
14	661.5360	885	3.1	42.0	0.0936	7069
15	685.4350	5299	18.5	255.2	0.0815	8408
16	686.4371	2334	8.2	111.8	0.0812	8458
17	1312.8225	2167	7.6	124.3	0.1409	9317
18	1313.8198	1874	6.6	107.1	0.1316	9985
19	1314.8204	11588	40.5	664.8	0.1265	10395
20	1315.8199	9207	32.2	526.8	0.1191	11047
21	1316.8177	24538	85.9	1401.9	0.1315	10011
22	1317.8188	16058	56.2	914.9	0.1432	9206
23	1318.8157	28581	100.0	1625.1	0.1301	10135
24	1319.8153	16578	58.0	940.0	0.1264	10442
25	1320.8138	19558	68.4	1106.5	0.1275	10362
26	1321.8126	9280	32.5	523.3	0.1473	8972
27	1322.8099	8085	28.3	454.8	0.1421	9309
28	1323.8090	4219	14.8	236.3	0.1334	9924
29	1324.8096	2976	10.4	166.1	0.1383	9576
30	1325.8087	1462	5.1	81.0	0.1350	9824

Figure S9: HRMS (ESI) of decakis(3-chloropropyl)decasilsesquioxane (**8**)

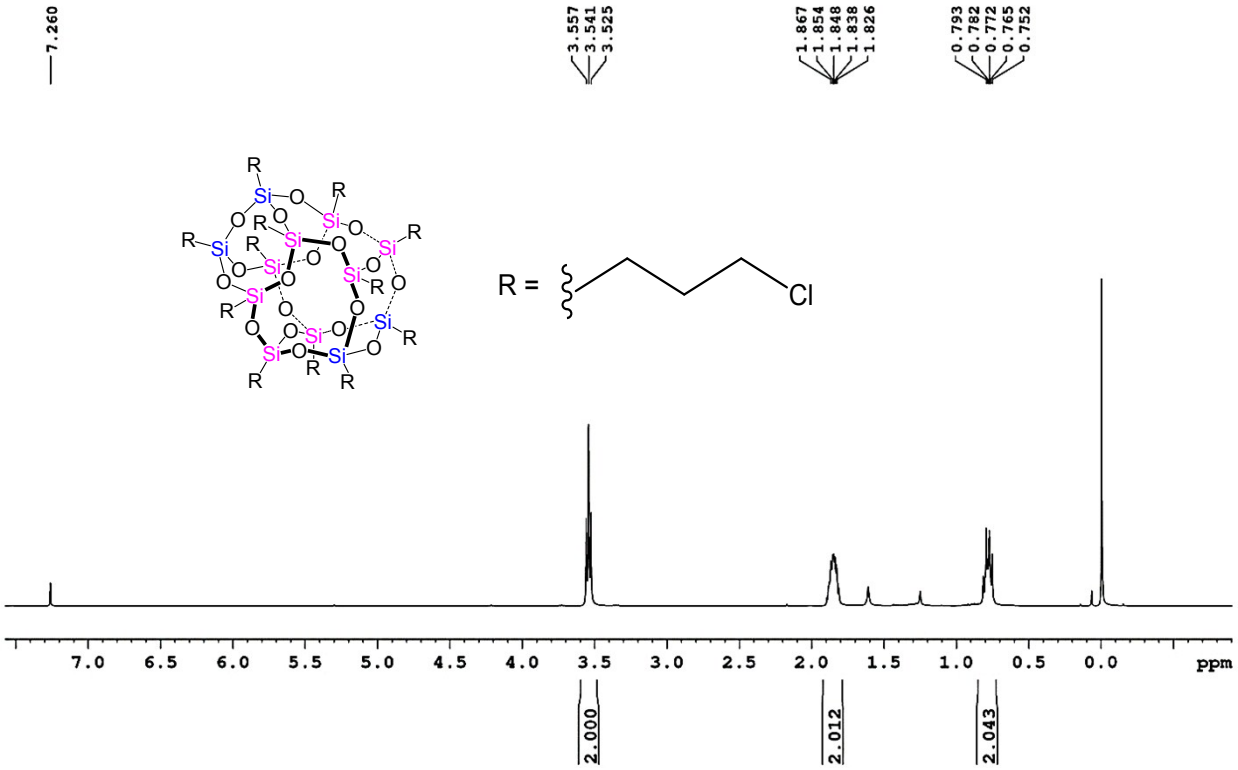


Figure S10: ^{1}H NMR (400 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane (**9**) in $CDCl_3$

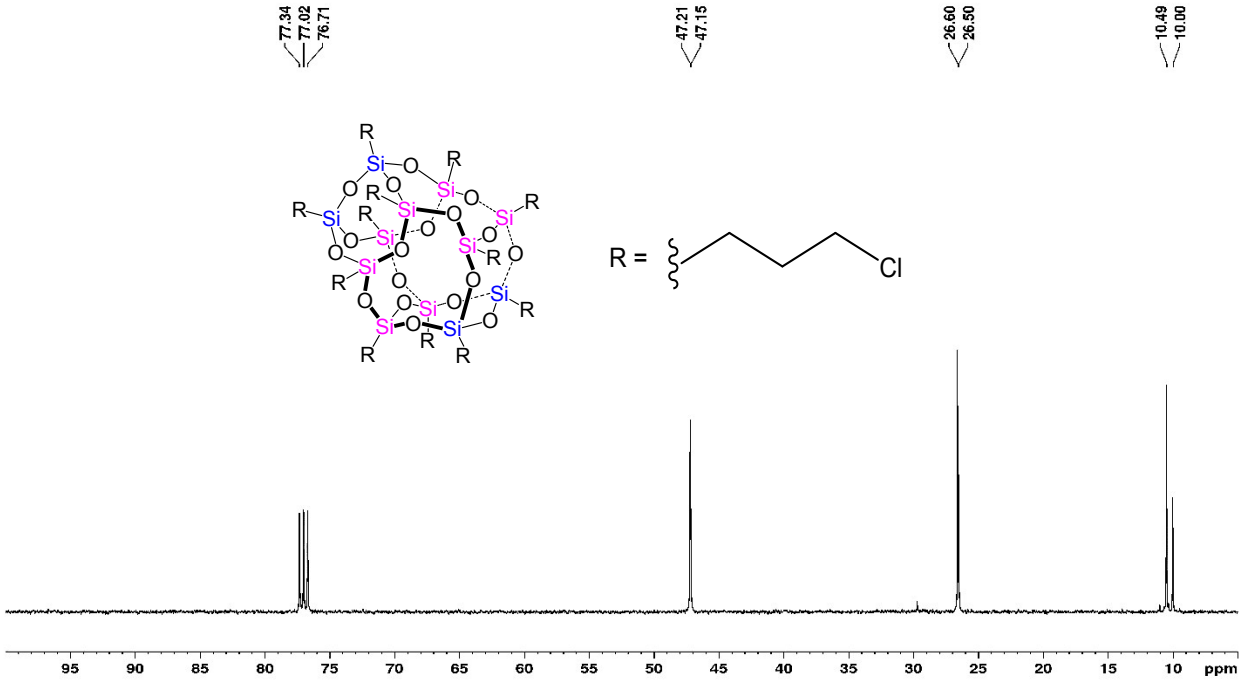


Figure S11: $^{13}C\{^{1}H\}$ NMR (100 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane (**9**) in $CDCl_3$

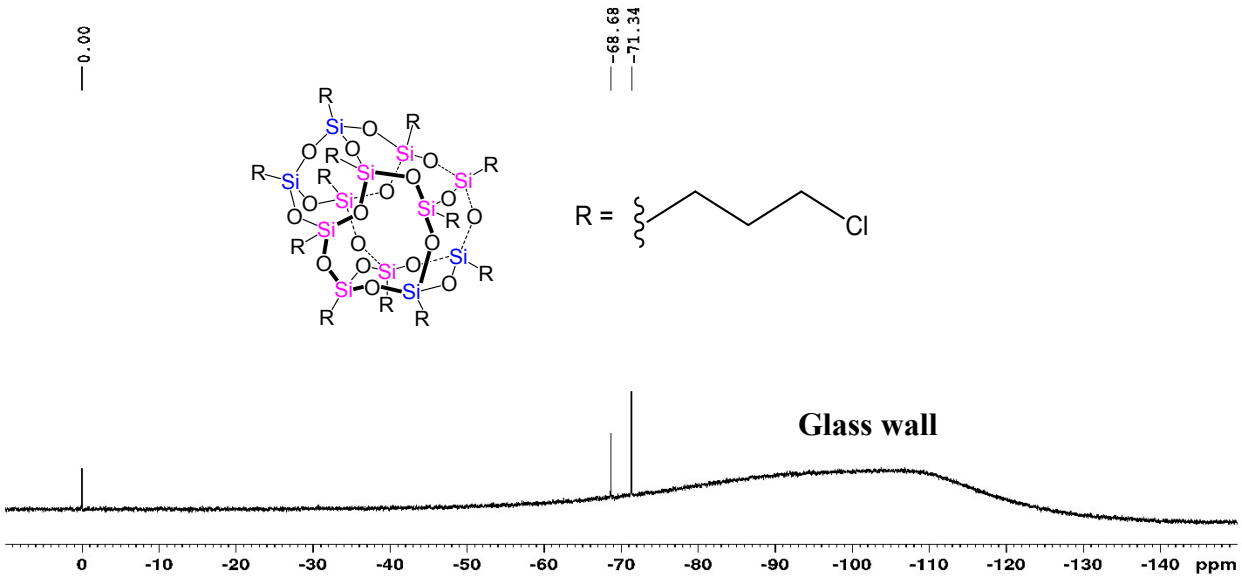
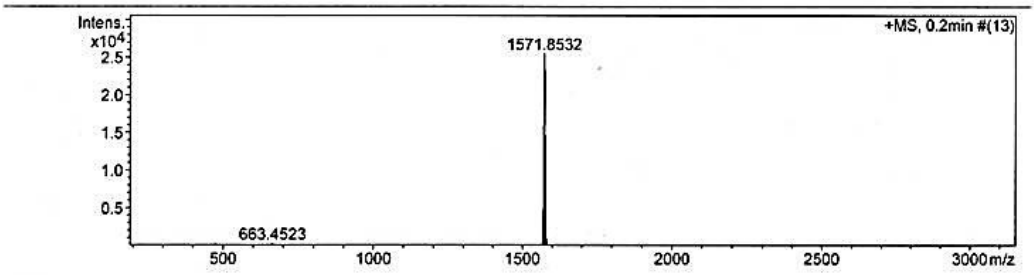


Figure S12: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane (**9**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	56.1211	211	0.8	21.3	0.0055	10276
2	77.3381	203	0.8	20.5	0.0061	12632
3	101.9294	130	0.5	13.0	0.0069	14875
4	112.0079	154	0.6	15.5	0.0070	15934
5	234.1929	126	0.5	14.3	0.0097	24257
6	473.3994	263	1.0	31.4	0.0619	7644
7	596.1552	138	0.5	15.6	0.0163	36540
8	663.4523	315	1.2	37.1	0.0759	8744
9	922.0147	132	0.5	16.6	0.0884	10425
10	1038.5471	134	0.5	16.8	0.0211	49171
11	1450.5085	125	0.5	9.1	0.0247	58616
12	1565.8566	443	1.7	30.9	0.1698	9224
13	1566.8513	404	1.6	28.2	0.1517	10328
14	1567.8559	4864	19.1	345.4	0.1502	10436
15	1568.8587	4365	17.1	310.8	0.1625	9654
16	1569.8576	15857	62.2	1133.4	0.1850	8486
17	1570.8547	13453	52.7	964.3	0.1724	9110
18	1571.8532	25508	100.0	1834.2	0.1811	8681
19	1572.8540	17771	69.7	1281.5	0.1817	8658
20	1573.8514	23313	91.4	1686.3	0.1885	8350
21	1574.8518	14409	56.5	1045.2	0.1815	8675
22	1575.8494	14607	57.3	1062.7	0.1666	9458
23	1576.8498	8284	32.5	604.3	0.1449	10881
24	1577.8438	5569	21.8	407.3	0.1388	11368
25	1578.8417	2271	8.9	166.4	0.1651	9566
26	1579.8465	939	3.7	68.8	0.1760	8977
27	1580.8428	376	1.5	27.4	0.2071	7633
28	1581.8516	201	0.8	14.5	0.1373	11519
29	1583.4562	130	0.5	9.3	0.0263	60295
30	1916.8031	128	0.5	16.4	0.0295	64923

Figure S13: HRMS (ESI) of dodecakis(3-chloropropyl)dodecasilsesquioxane (**9**)

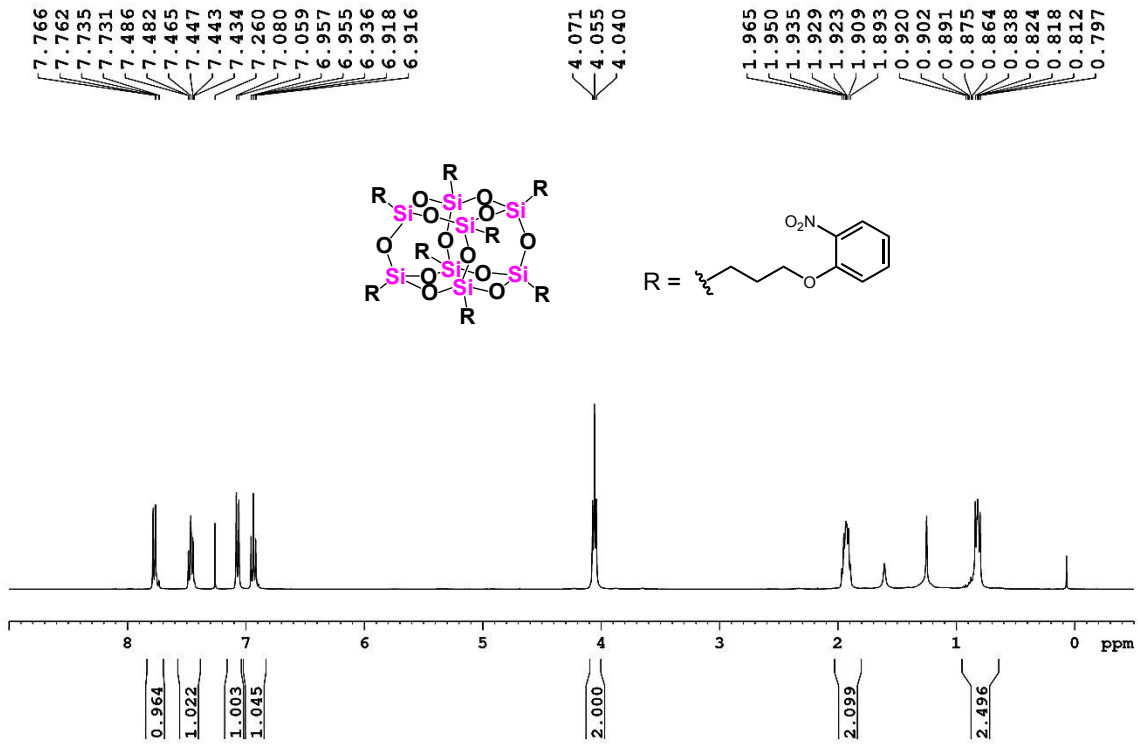


Figure S14: ^{1}H NMR (400 MHz) of octakis(3-propyl-*o*-oxynitrobenzene)octasilsesquioxane (**2**) in $CDCl_3$

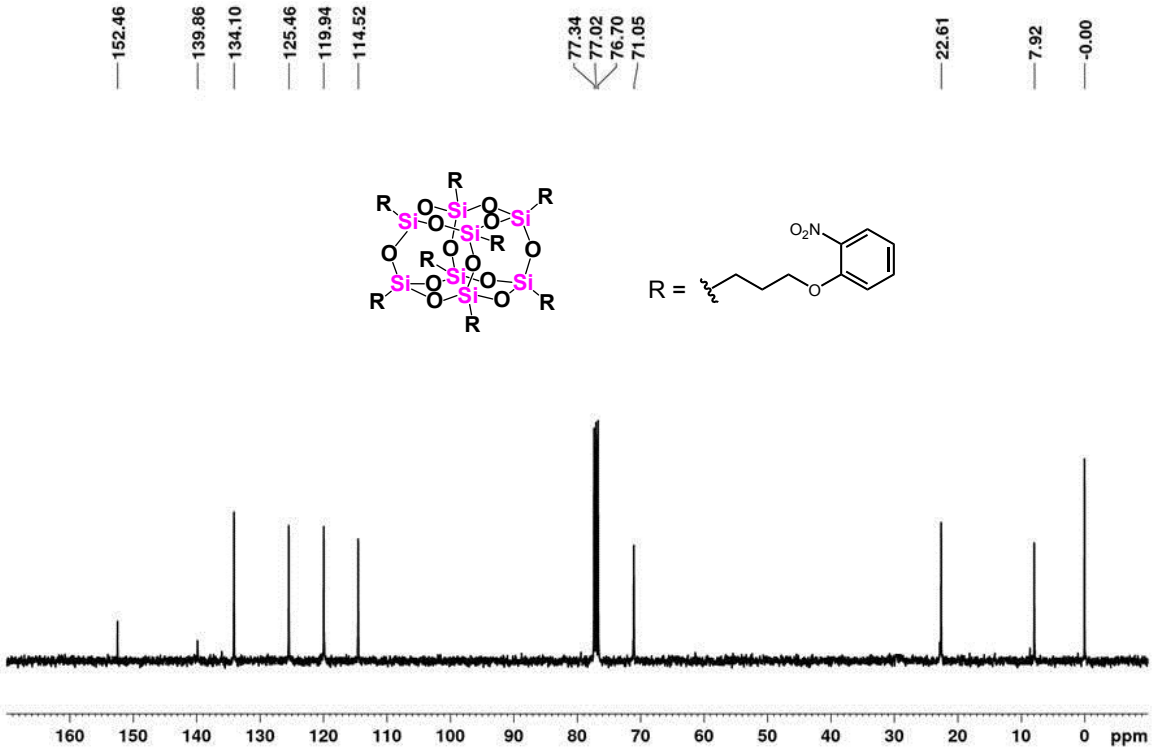


Figure S15: $^{13}C\{^{1}H\}$ NMR (100 MHz) of octakis(3-propyl-*o*-oxynitrobenzene)octasilsesquioxane (**2**) in $CDCl_3$

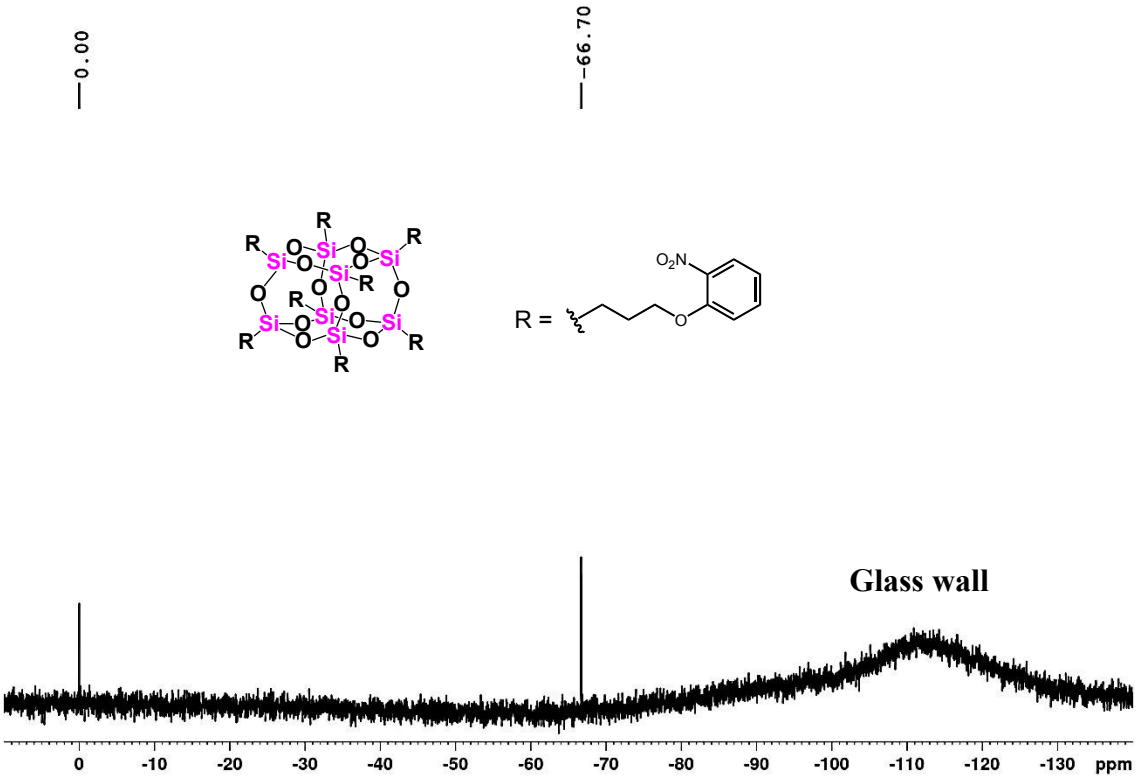
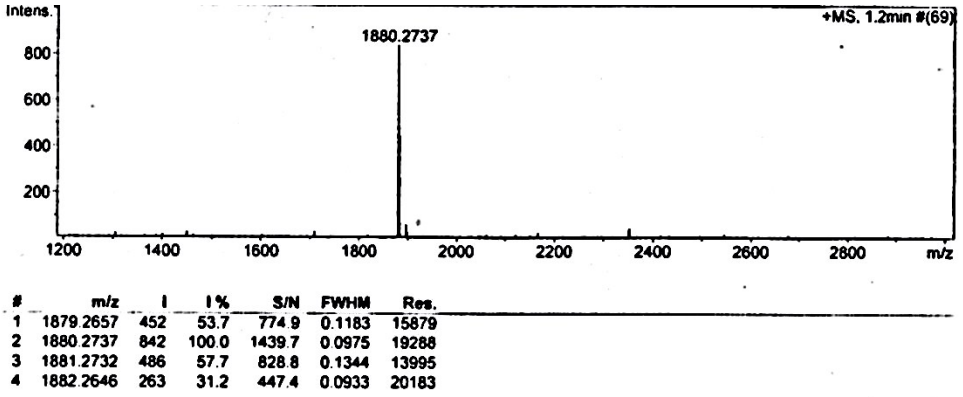


Figure S16: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of octakis(3-propyl-*o*-oxynitrobenzene)octasilsesquioxane (**2**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	1879.2657	452	53.7	774.9	0.1183	15879
2	1880.2737	842	100.0	1439.7	0.0975	19288
3	1881.2732	486	57.7	828.8	0.1344	13995
4	1882.2646	263	31.2	447.4	0.0933	20183

Figure S17: HRMS (ESI) of octakis(3-propyl-*o*-oxynitrobenzene)octasilsesquioxane (**2**)

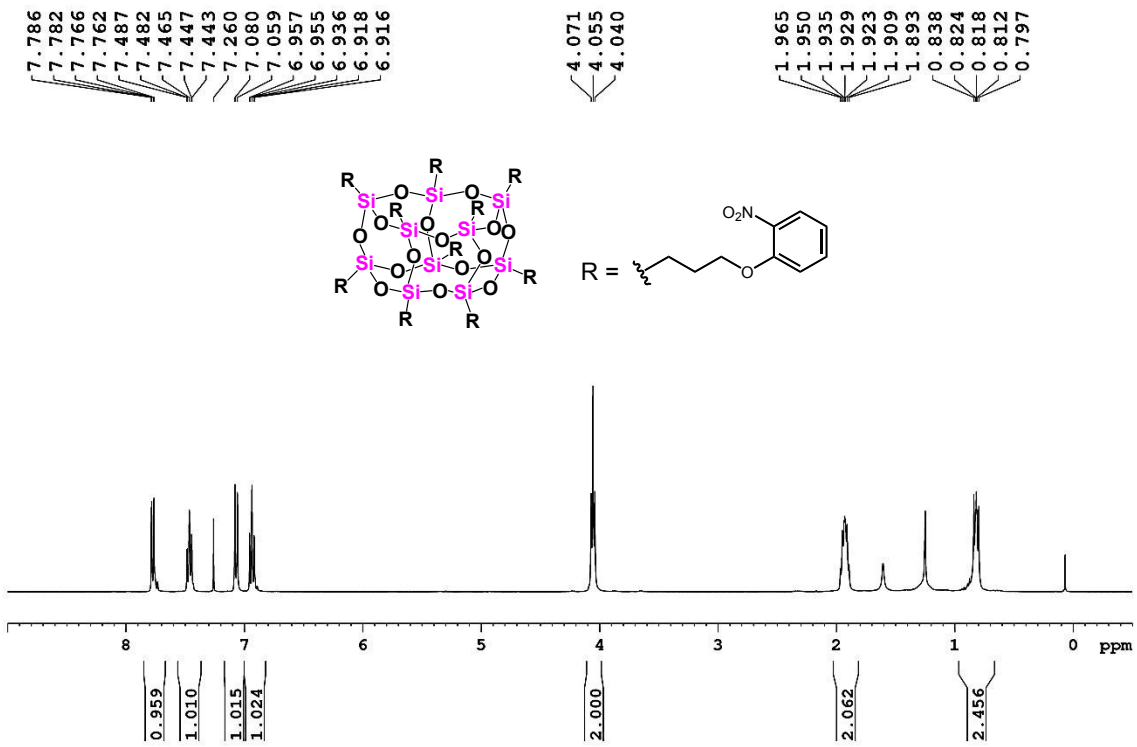


Figure S18: ^{1}H NMR (400 MHz) of decakis(3-propyl-*o*-oxynitrobenzene)decasilsesquioxane (**3**) in $CDCl_3$

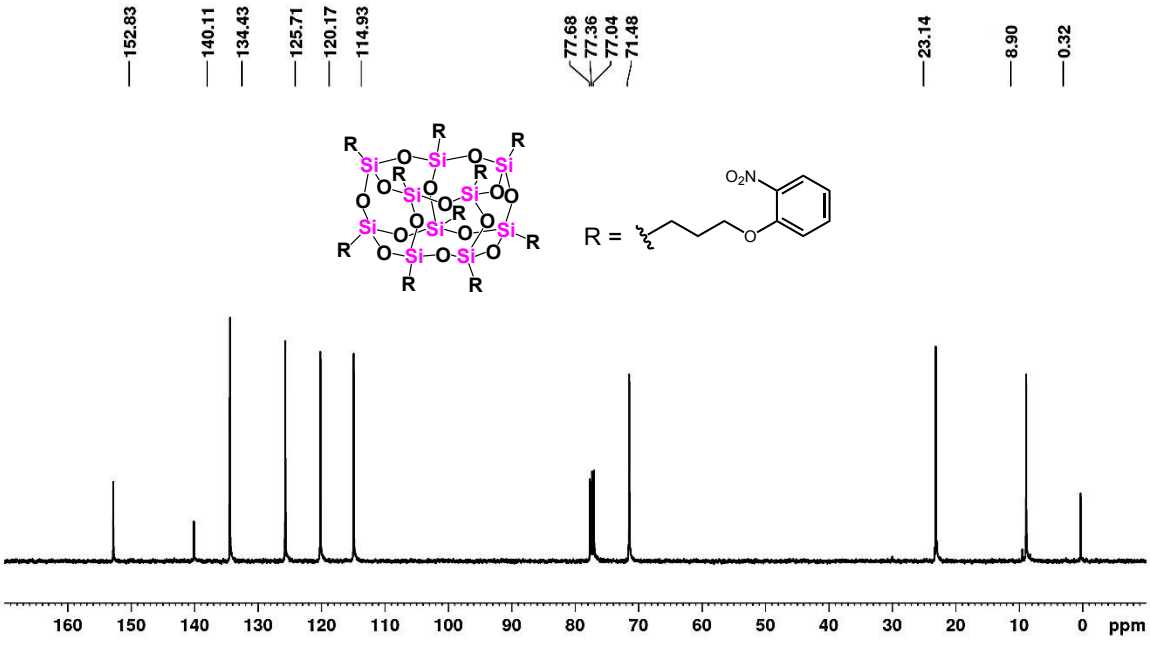


Figure S19: $^{13}C\{^{1}H\}$ NMR (100 MHz) of decakis(3-propyl-*o*-oxynitrobenzene)decasilsesquioxane (**3**) in $CDCl_3$

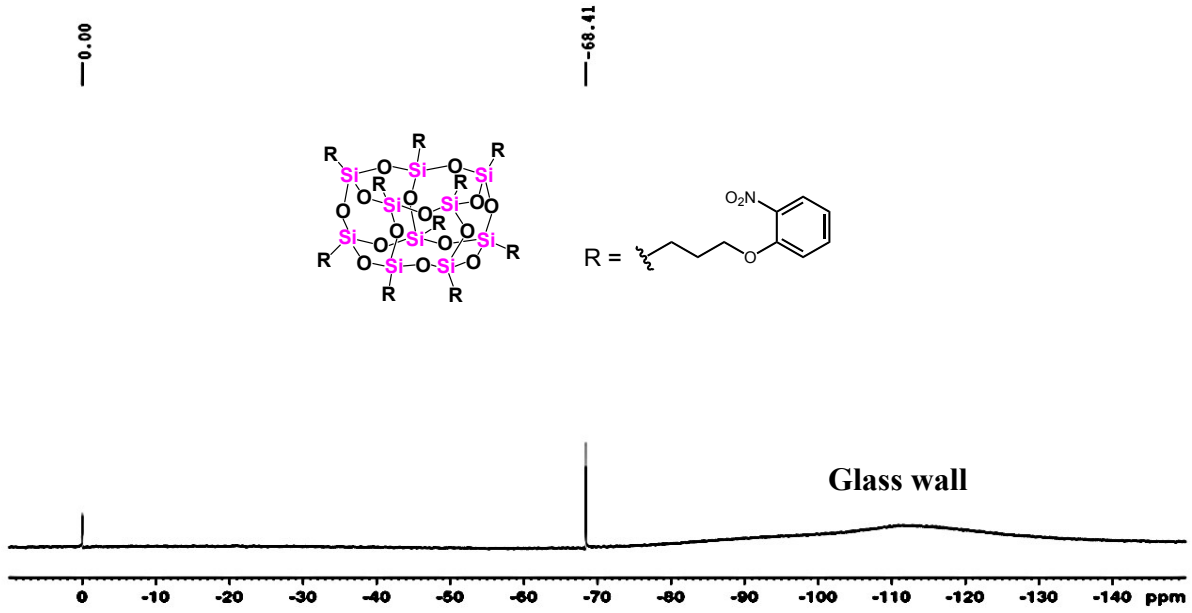
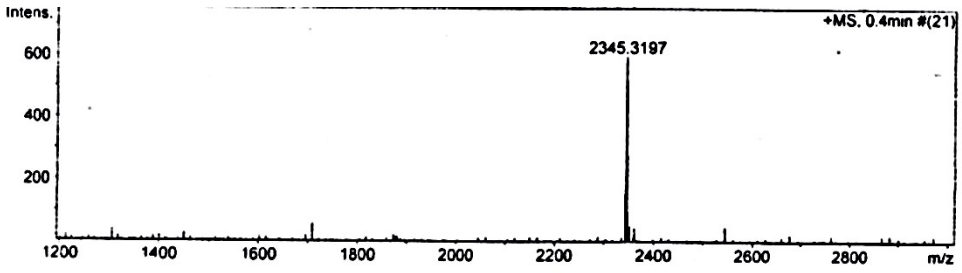


Figure S20: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of decakis(3-propyl-*o*-oxynitrobenzene)decasilsesquioxane (**3**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	595.3859	131	16.5	62.6	0.0402	14821
2	639.4112	766	96.5	334.9	0.0493	12969
3	640.4142	174	21.9	75.8	0.0486	13190
4	683.4356	794	100.0	319.6	0.0461	14820
5	684.4420	131	16.5	52.4	0.0611	11197
6	699.4144	111	14.0	43.2	0.0486	14384
7	727.4611	479	60.3	178.5	0.0515	14116
8	728.4669	104	13.1	38.4	0.0576	12637
9	771.4868	190	23.9	71.6	0.0529	14593
10	1183.1579	273	34.4	132.1	0.0784	15091
11	1183.6592	418	52.6	202.3	0.0809	14622
12	1184.1607	464	58.4	224.7	0.0856	13833
13	1184.6645	337	42.4	163.3	0.0882	13433
14	1185.1603	162	20.4	78.5	0.0929	12759
15	2343.3255	155	19.5	93.9	0.1488	15750
16	2344.3200	506	63.7	307.0	0.1323	17716
17	2345.3197	599	75.4	363.8	0.1129	20780
18	2346.3175	280	35.3	170.3	0.1183	19831

Figure S21: HRMS (ESI) of decakis(3-propyl-*o*-oxynitrobenzene)decasilsesquioxane (**3**)

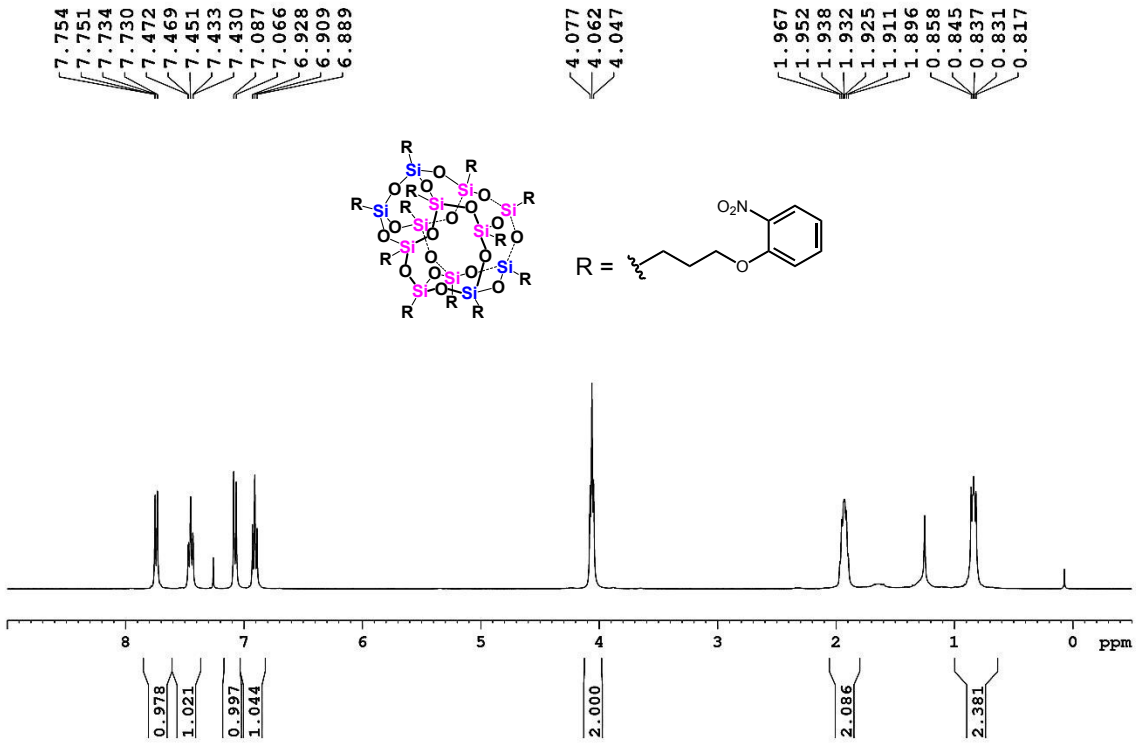


Figure S22: ^{1}H NMR (400 MHz) of dodecakis(3-propyl-*o*-oxynitrobenzene)dodecasilsesquioxane (**4**) in $CDCl_3$

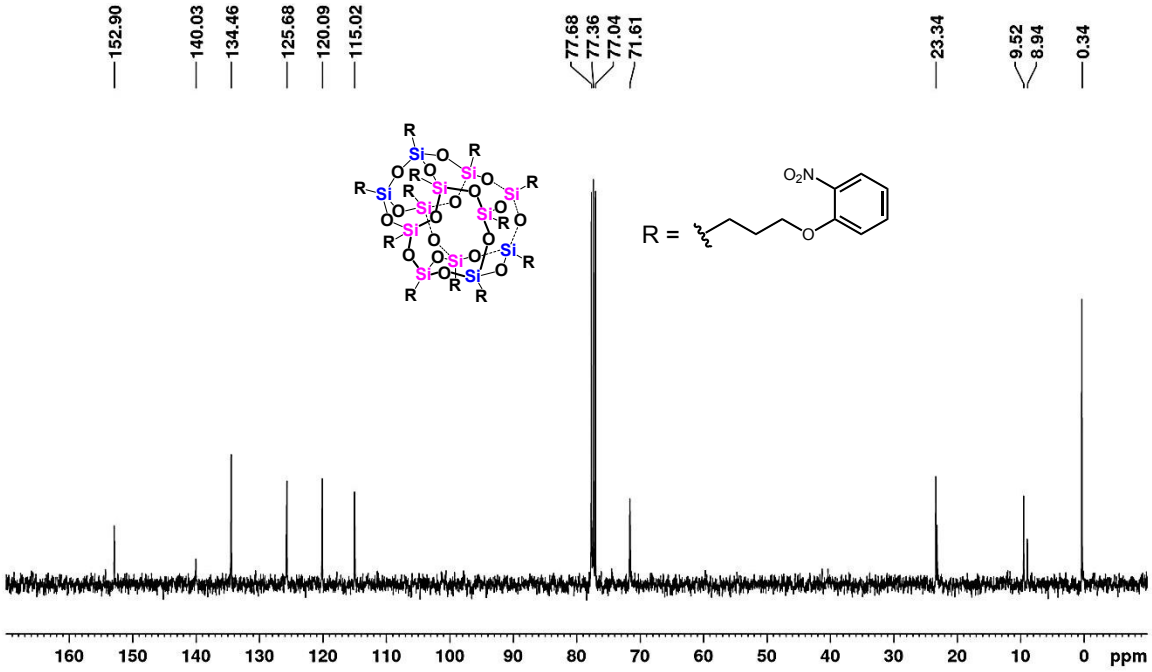


Figure S23: $^{13}C\{^{1}H\}$ NMR (100 MHz) of dodecakis(3-propyl-*o*-oxynitrobenzene)dodecasilsesquioxane (**4**) in $CDCl_3$

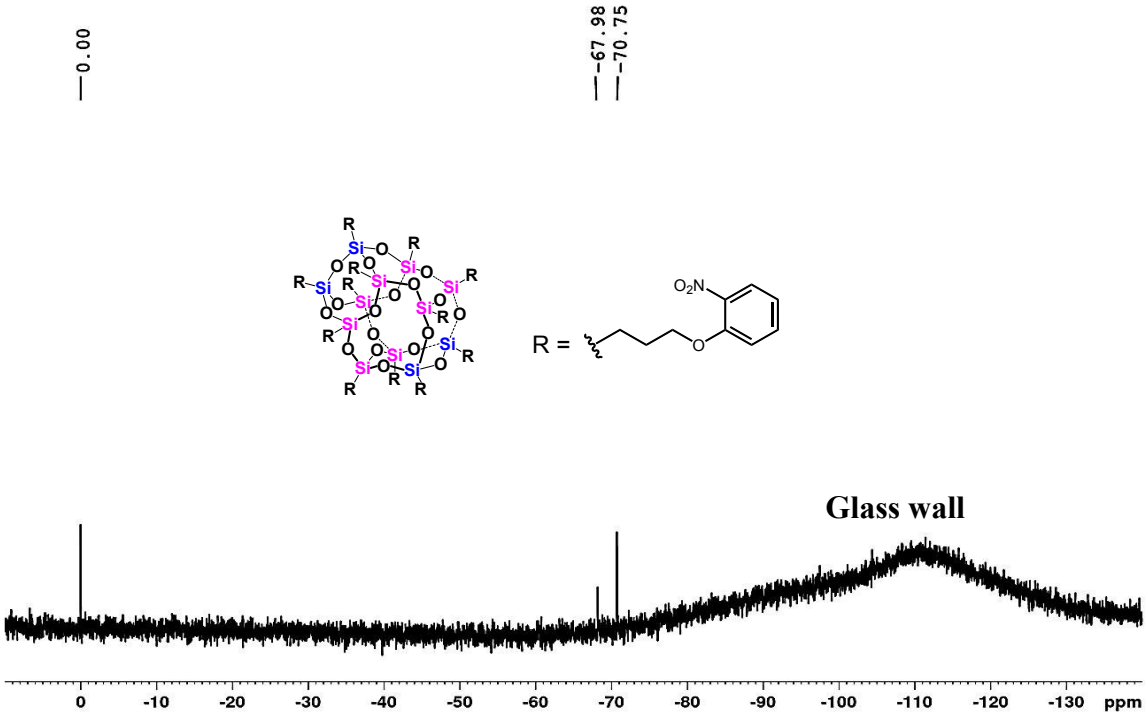
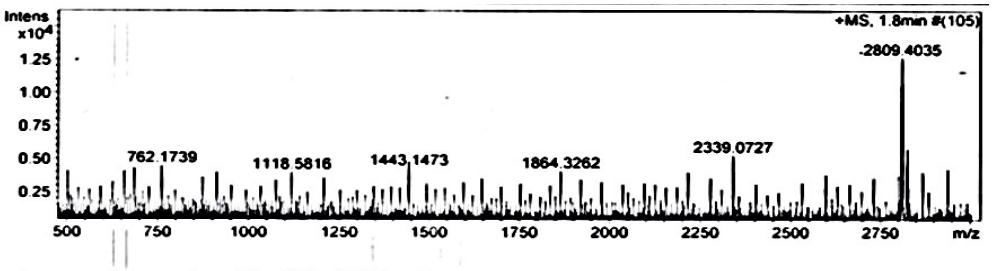


Figure S24: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of dodecakis(3-propyl-*o*-oxynitrobenzene)dodecasilsesquioxane (**4**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	144.9766	3901	30.8	6.5	0.0099	14684
2	145.0537	3957	31.2	6.6	0.0138	10478
3	214.1874	3923	31.0	7.0	0.0100	21394
4	296.8567	4528	35.8	8.9	0.0124	23951
5	296.9630	3931	31.0	7.7	0.0346	8571
6	473.9412	4012	31.7	8.3	0.0161	29475
7	502.6029	4127	32.6	8.6	0.0165	30488
8	658.5221	3942	31.1	7.9	0.0184	35851
9	685.4353	4313	34.1	8.6	0.1089	6295
10	762.1739	4487	35.4	8.9	0.0205	37097
11	912.1720	3992	31.5	7.8	0.0205	44601
12	1118.5816	4016	31.7	8.0	0.0229	48746
13	1443.1473	4303	34.0	8.7	0.0347	41627
14	1864.0689	3981	31.4	7.9	0.0303	61428
15	1864.3262	4102	32.4	8.2	0.0410	45451
16	2215.2641	3983	31.4	7.6	0.0326	68046
17	2339.0727	5293	41.8	10.5	0.0332	70556
18	2339.2598	4619	36.5	9.1	0.0609	38427
19	2807.4203	6783	53.6	14.2	0.4925	5700
20	2808.4170	10499	82.9	22.2	0.4962	5659
21	2809.4035	12665	100.0	26.9	0.5346	5256
22	2810.4032	10651	84.1	22.6	0.5131	5477
23	2811.3926	7671	60.6	16.1	0.5204	5403
24	2812.4056	4692	37.0	9.7	0.5559	5059
25	2824.3580	4631	36.6	9.6	0.5021	5625
26	2825.3764	5560	43.9	11.6	0.5122	5516
27	2826.3724	5052	39.9	10.5	0.5037	5611
28	2827.3720	4039	31.9	8.3	0.4549	6216
29	2937.8228	4240	33.5	8.7	0.0387	75894
30	2938.0295	3985	31.5	8.2	0.0418	70213

Figure S25: HRMS (ESI) of dodecakis(3-propyl-*o*-oxynitrobenzene)dodecasilsesquioxane (**4**)

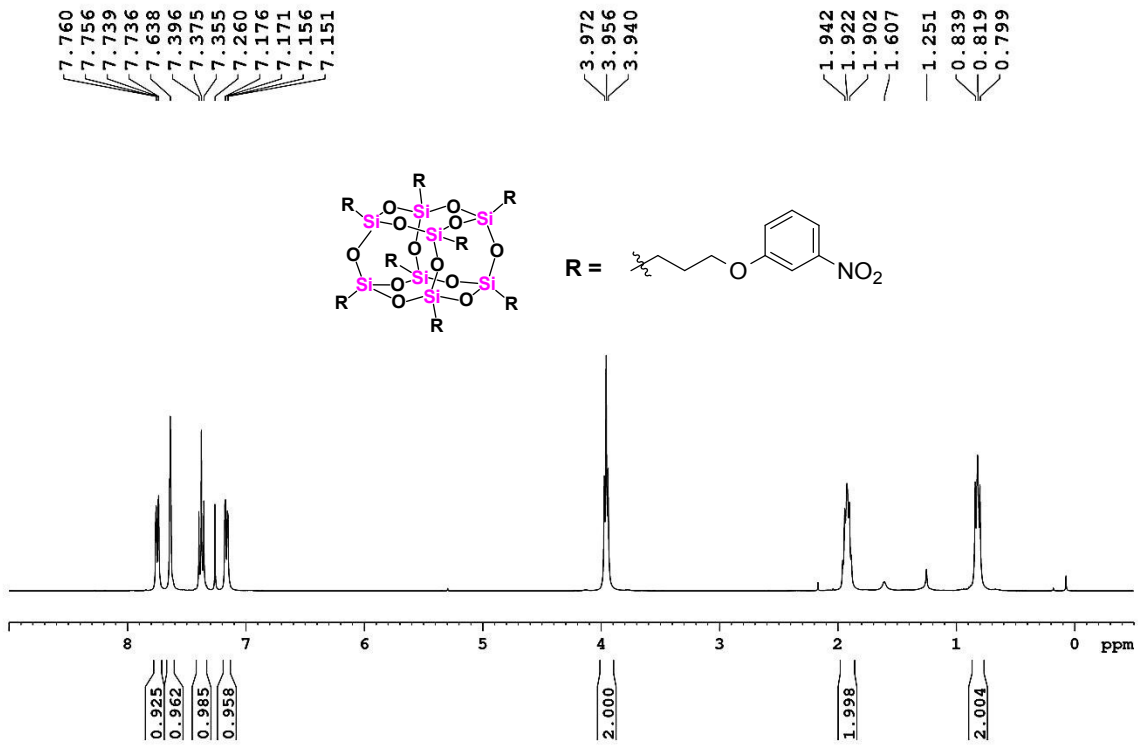


Figure S26: ^{1}H-NMR (400 MHz) of octakis(3-propyl-*m*-oxynitrobenzene)octasilsesquioxane (**5**) in $CDCl_3$

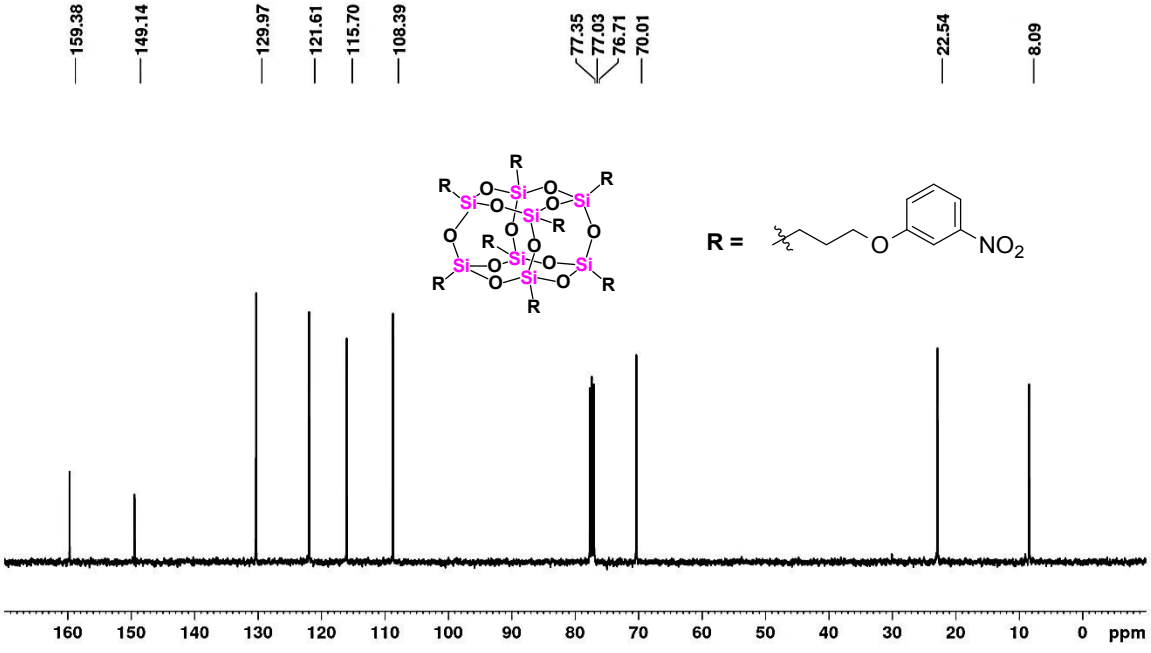


Figure S27: ^{13}C{^{1}H} NMR (100 MHz) of octakis(3-propyl-*m*-oxynitrobenzene)octasilsesquioxane (**5**) in $CDCl_3$

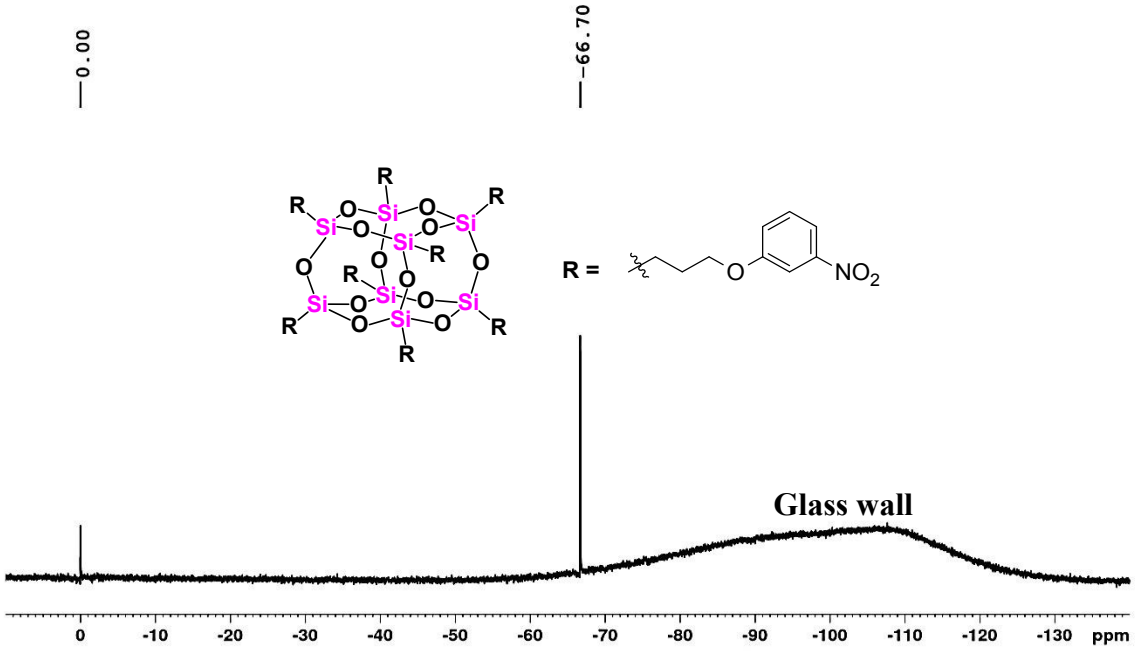
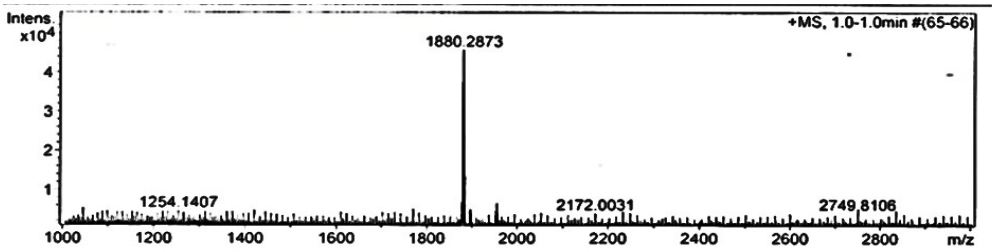


Figure S28: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of octakis(3-propyl-*m*-oxynitrobenzene)octasilsesquioxane (**5**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	1087.8915	4273	9.3	4.1	0.0492	22131
2	1098.4913	4642	10.2	4.5	0.0292	37669
3	1120.1109	4328	9.5	4.0	0.0299	37482
4	1163.9252	4311	9.4	3.8	0.0345	33705
5	1220.0630	4631	10.1	4.0	0.0644	18950
6	1254.1407	4674	10.2	4.0	0.0304	41281
7	1324.0157	4183	9.2	3.5	0.0316	41963
8	1609.4781	4268	9.3	4.3	0.0784	20534
9	1701.6929	4267	9.3	4.4	0.0382	44513
10	1769.3980	4446	9.7	4.7	0.1251	14147
11	1782.9072	4151	9.1	4.4	0.0403	44281
12	1877.2798	6067	13.3	6.8	0.2961	6340
13	1877.7607	6932	15.2	7.9	0.2646	7096
14	1878.2807	5843	12.8	6.6	0.2758	6810
15	1878.7858	4864	10.6	5.3	0.2899	6481
16	1879.2875	37468	82.0	46.4	0.3004	6257
17	1880.2873	45716	100.0	56.7	0.2977	6316
18	1881.2874	39683	86.8	49.2	0.2960	6356
19	1882.2901	24358	53.3	29.9	0.3054	6163
20	1883.2956	13914	30.4	16.7	0.2880	6539
21	1884.2912	6362	13.9	7.2	0.3079	6120
22	1894.1816	4477	9.8	4.9	0.0368	51454
23	1895.2763	4787	10.5	5.2	0.2878	6586
24	1896.2634	5186	11.3	5.7	0.3015	6289
25	1897.2519	4898	10.7	5.4	0.3400	5580
26	1953.3150	4511	9.9	5.0	0.3321	5882
27	1954.3124	6027	13.2	6.9	0.3081	6343
28	1955.3070	6491	14.2	7.5	0.2788	7013
29	1956.3165	4138	9.1	4.5	0.3041	6432
30	2749.8106	4188	9.2	4.6	0.0498	55201

Figure S29: HRMS (ESI) of octakis(3-propyl-*m*-oxynitrobenzene)octasilsesquioxane (**5**)

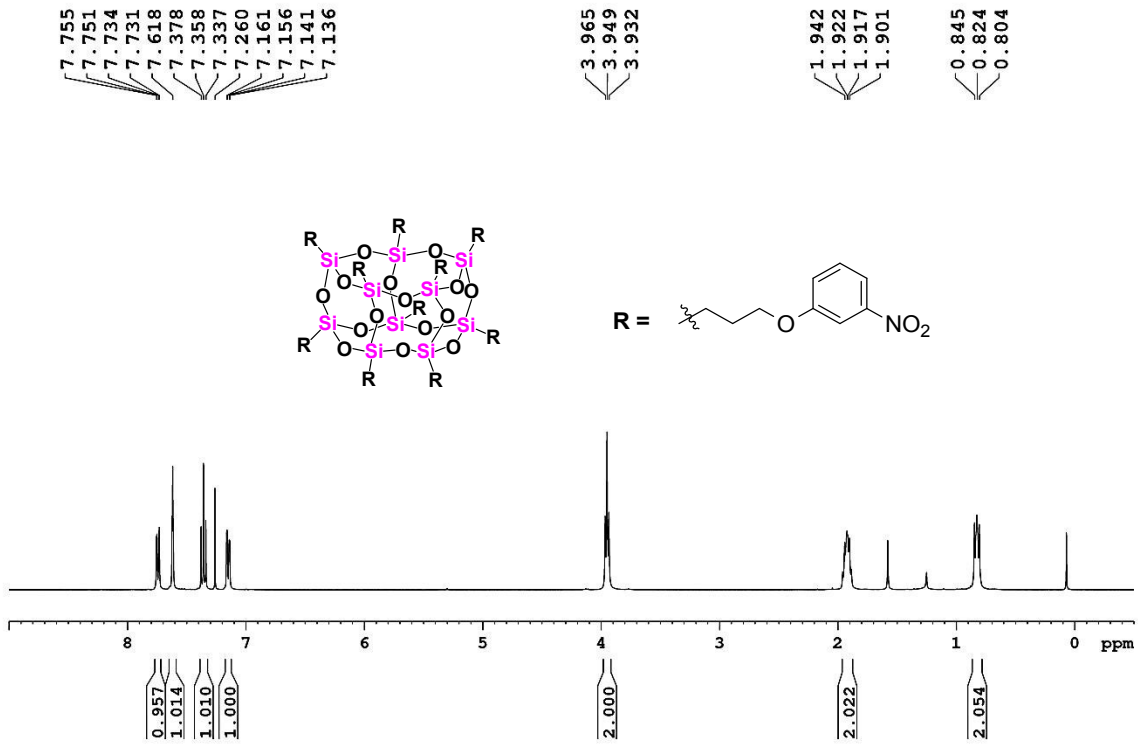


Figure S30: ^{1}H NMR (400 MHz) of decakis(3-propyl-*m*-oxynitrobenzene)decasilsesquioxane (**6**) in $CDCl_3$

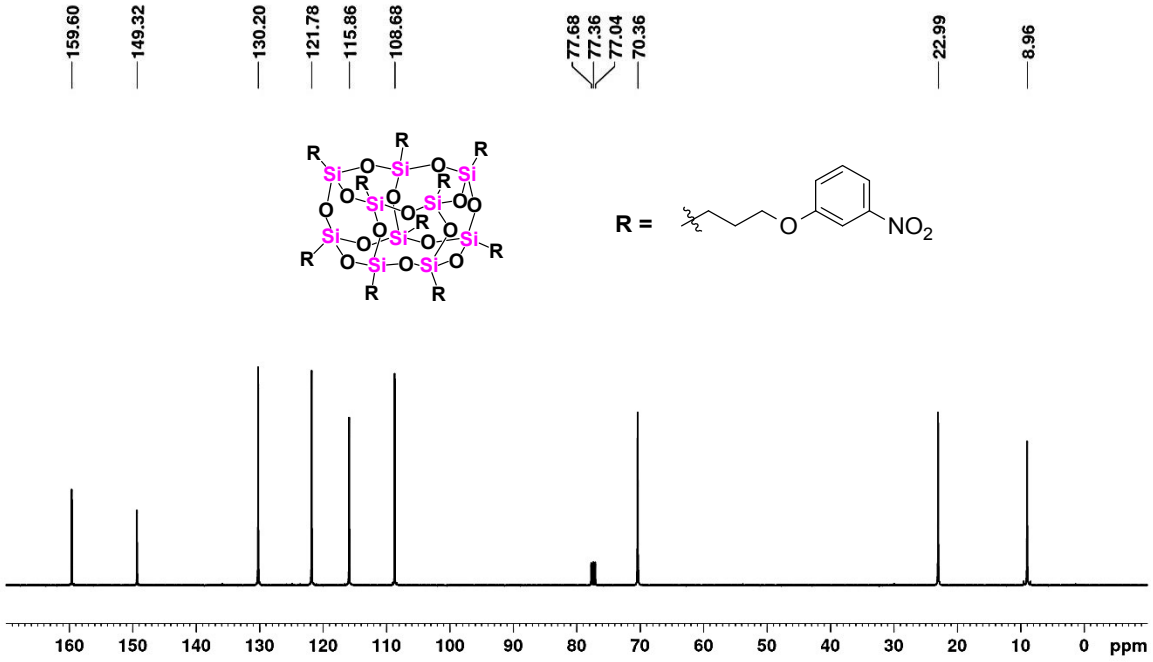


Figure S31: $^{13}C\{^{1}H\}$ NMR (100 MHz) of decakis(3-propyl-*m*-oxynitrobenzene)decasilsesquioxane (**6**) in $CDCl_3$

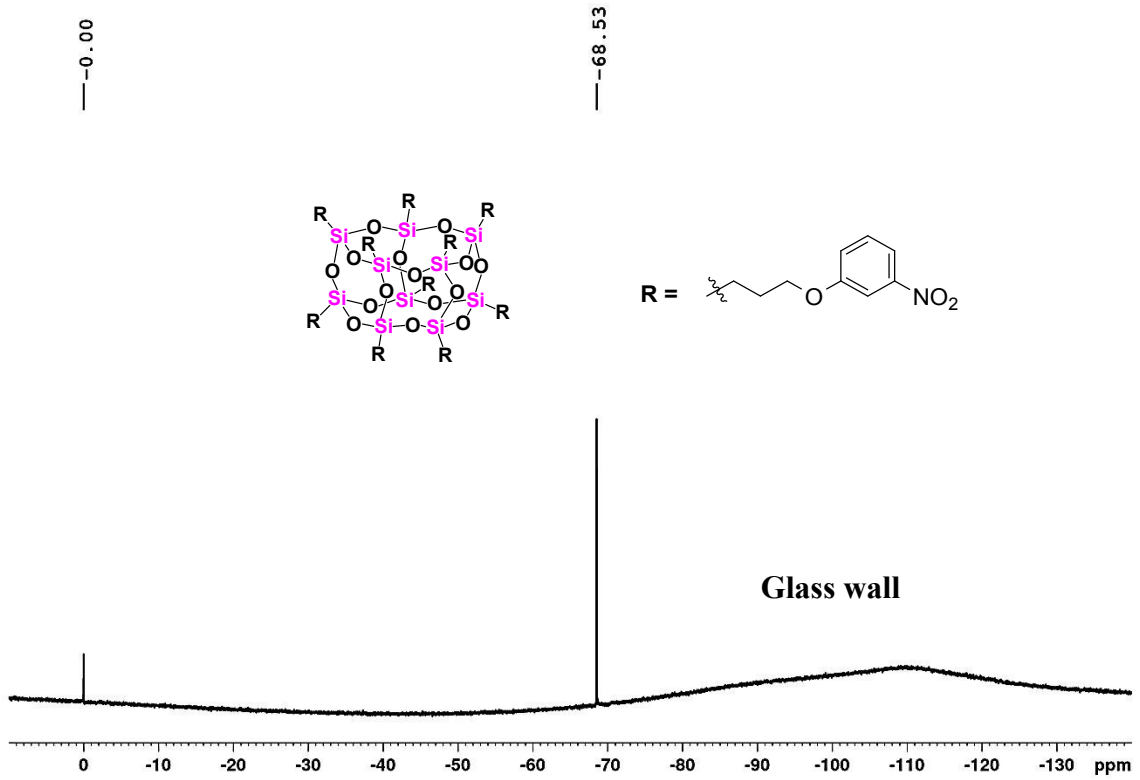
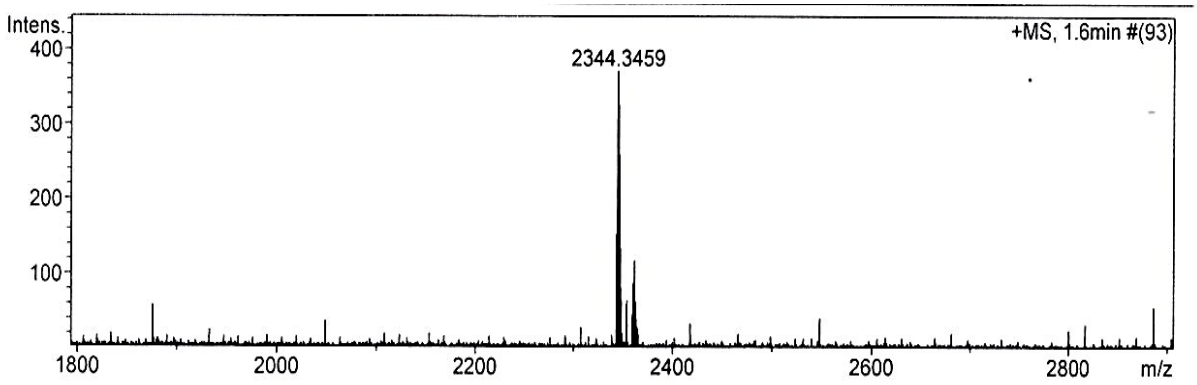


Figure S32: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of decakis(3-propyl-*m*-oxynitrobenzene)decasilsesquioxane (**6**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	2343.3512	145	39.1	29.1	0.2236	10479
2	2344.3459	371	100.0	75.0	0.2093	11201
3	2345.3415	326	87.9	65.9	0.2270	10332
4	2346.3349	258	69.5	52.1	0.1304	17988
5	2347.3369	135	36.4	27.1	0.1246	18844

Figure S33: HRMS (ESI) of decakis(3-propyl-*m*-oxynitrobenzene)decasilsesquioxane (**6**)

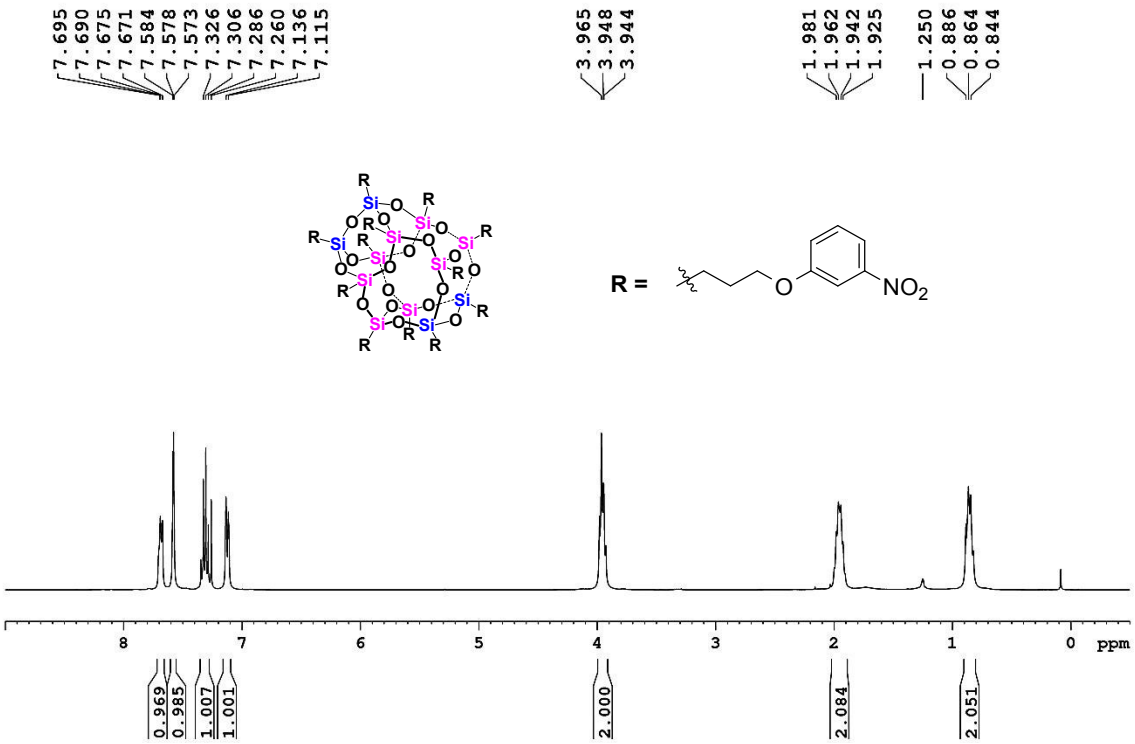


Figure S34: ^{1}H NMR (400 MHz) of dodecakis(3-propyl-*m*-oxynitrobenzene)dodecasilsesquioxane (**7**) in $CDCl_3$

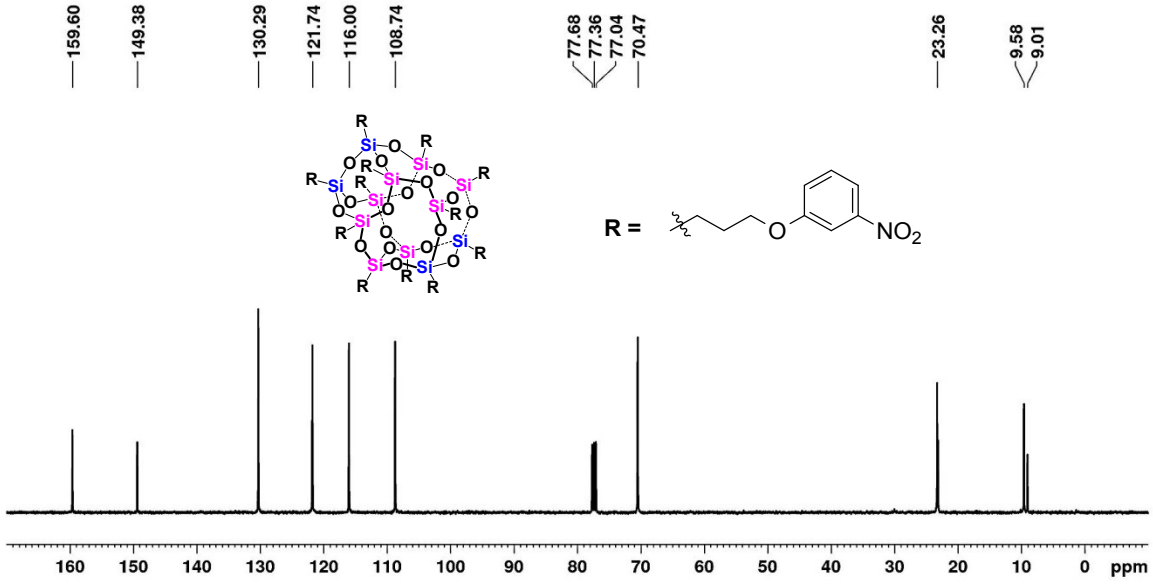


Figure S35: $^{13}C\{^{1}H\}$ NMR (100 MHz) of dodecakis(3-propyl-*m*-oxynitrobenzene)dodecasilsesquioxane (**7**) in $CDCl_3$

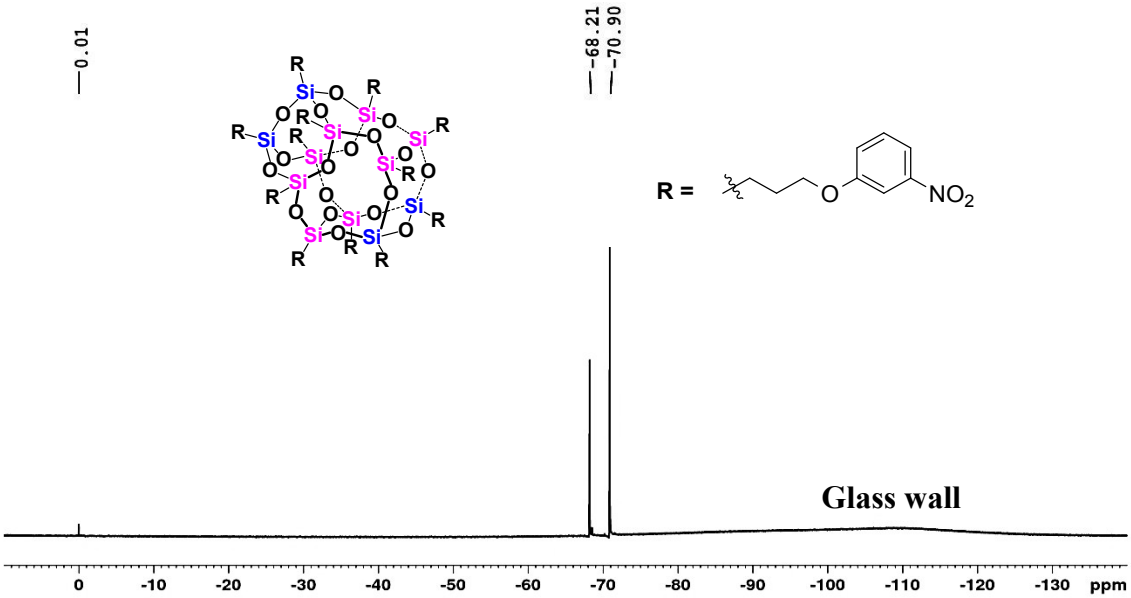
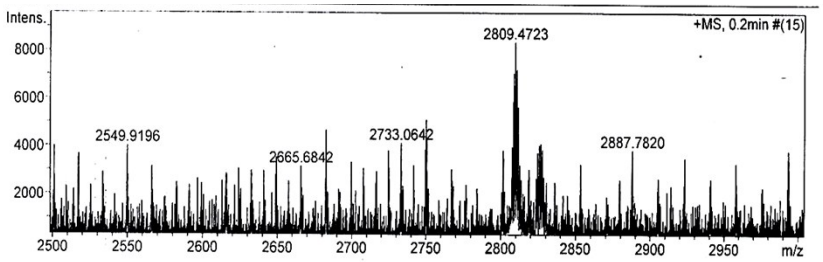


Figure S36: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of dodecakis(3-propyl-*m*-oxynitrobenzene)dodecasilsesquioxane (**7**) in $CDCl_3$



#	m/z	I	I %	S/N	FWHM	Res.
1	1087.9004	3964	47.5	4.0	0.0516	21085
2	1098.4842	4152	49.7	4.2	0.0298	36811
3	1141.9230	4390	52.6	4.2	0.0340	33628
4	1163.9216	4858	58.2	4.6	0.0329	35380
5	1186.1801	4578	54.8	4.2	0.0285	41639
6	1220.0625	4965	59.4	4.5	0.0562	21712
7	1231.2692	5067	60.7	4.6	0.0294	41927
8	1231.4092	4034	48.3	3.5	0.0403	30557
9	1335.8362	4164	49.9	3.6	0.0468	28540
10	1359.6971	4043	48.4	3.6	0.0510	26674
11	1371.6169	5480	65.6	5.1	0.0330	41529
12	1395.7376	3980	47.6	3.7	0.0425	32841
13	1408.0223	4063	48.6	3.8	0.0605	23284
14	1420.1008	4206	50.4	4.1	0.0321	44182
15	1444.6362	4253	50.9	4.2	0.0288	50215
16	1494.3818	3934	47.1	3.9	0.0402	37166
17	1609.4375	4116	49.3	4.1	0.0602	26737
18	1769.3966	5085	60.9	5.7	0.2602	6799
19	1838.1074	3874	46.4	4.3	0.0392	46889
20	2126.7425	4295	51.4	5.0	0.0605	35151
21	2232.8968	4769	57.1	5.5	0.0914	24436
22	2500.8538	3986	47.7	4.4	0.0447	55960
23	2549.9196	3999	47.9	4.4	0.0832	30635
24	2733.0642	4130	49.4	4.6	0.0518	52774
25	2808.4812	6877	82.3	8.2	0.4248	6611
26	2809.4723	8353	100.0	10.1	0.3819	7356
27	2810.4755	7107	85.1	8.5	0.4521	6217
28	2811.4453	5627	67.4	6.6	0.2924	9615
29	2825.4838	4019	48.1	4.5	0.4591	6154
30	2826.4525	4097	49.0	4.6	0.4724	5983

Figure S37: HRMS (ESI) of dodecakis(3-propyl-*m*-oxynitrobenzene)dodecasilsesquioxane (**7**)