SUPPLEMENTARY INFORMATION

Synthesis of Aromatic Functionalized Cage-Rearranged Silsesquioxanes (T_8, T_{10}, and T_{12}) *via* Nucleophilic Substitution Reactions

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EXPERIMENTAL SECTION

Materials. 3-Chloropropyltrimethoxysilane (purity; >95.0 %) was purchased from Tokyo Chemical Industry Co., Ltd. and used without additional purification for preparing a starting material: octakis(3-chloropropyl)octasilsesquioxane (**1**).[1] 4-Nitrophenol sodium salt hydrate, 4-hydroxybenzaldehyde, and 4-bromophenol were purchased from Sigma Aldrich, while anhydrous *N*,*N*-dimethylformamide (DMF) was bought from Honeywell B&J. Precoated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc.

Physical Measurement and 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, and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer and

elemental analyses were performed on a Perkin Elmer 2400 CHN. Melting points were obtained by using a Gallenkamp Sanyo melting detector. DSC measurements were carried out using a DSC Q200 (TA Instruments). Approximately, 15 mg of the samples were capsulated in aluminum pans and each experiment was performed under nitrogen atmosphere. For MALDI-TOF MS (Bruker Daltonics-Autoflex II) analysis, the matrix 2,5-dihydroxybenzoic acid (DHBA) was dissolved in THF (10 mg/mL), and mixed with sample solution (0.5~1.0 mg/mL in THF) in 1:1 v/v ratio. The samples were spotted onto the target and dried in air. C/H/N elemental analyses of resulting products were carried out by using an elemental analyzer (EA) (CHNS/O Analyzer) Perkin Elmer, PE2400 Series II, while their X-ray powder diffraction patterns were characterized by Bruker model D_8 diffractometer with CuK_α radiation at λ = 0.154 nm. Applied voltage and current were used at 40 kV and 30 mA, respectively. The mode of recorded system was operated with $2\theta = 2.00\text{-}29.99^\circ$ (scan rate = $0.003^\circ\ s^{-1}$).

General procedure to prepare sodium *para*-oxybenzaldehyde and *para*-bromophenoxide salts.

Phenol derivatives were dissolved in sodium hydroxide solution (1 N) at molar ratio of 1:1 and further stirred until turning into a clear solution. The clear solution was stirred at room temperature for 30 minutes. Then the complete reaction was evaporated to obtain phenoxide salts. These solid salts were further dried under vacuum and heated at 60^{o}C to complete a dryness.

Synthesis of *para*-Nitrobenzene-Functionalized Cage-Rearranged Silsesquioxanes. Octakis(3-proproxy-*para*-nitrobenzene)octasilsesquioxane (**2**), decakis(3-proproxy-*para*-nitrobenzene)decasilsesquioxane (**3**), and dodecakis(3-proproxy-*para*-nitrobenzene)dodecasilsesquioxane (**4**). Firstly, a certain amount of sodium *p*-nitrophenol salt hydrate was dried under vacuum at 60°C until the yellow crystals of the salt hydrate turned into an orange powder. Dried *para*-nitrophenol sodium salt (6.34 g; 39.4 mmol) and octakis(3-chloropropyl)octasilsesquioxane (3.00 g; 2.90 mmol) were introduced into a two-neck flask equipped with a condenser and further dried under vacuum at room temperature for an hour. 20 mL of anhydrous DMF was added. After heating at 70°C for 3 days, the solution was cooled in an ice bath, cold CH_2Cl_2 (100 mL) and cold deionized water (40 mL) were added while the solution was stirred for 10 minutes. To the organic layer, 50 ml of water was added and the organic solution was further extracted. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layer was concentrated to *ca.* 100 mL, after which it was washed with saturated $NaHCO_3$ and further washed by a mixture of water and methanol to completely eliminate an excessive starting material of *p*-nitrophenol or until the solution turned to light yellow color. The solution was then dried with anhydrous sodium sulfate. Evaporation of the organic solvent gave a pale yellow, fluffy crude product (3.20 g), which was analyzed by thin-layer chromatography using an eluent of 1.5% ethyl acetate in CH_2Cl_2. TLC analysis showed three separate spots at R_f = 0.45, 0.30 and 0.18 with a broad baseline (R_f = 0–0.15). A partial amount of the crude product (2.74 g) was purified by a gradient column chromatography (a gradient system: 0%, 1%, 1.5%, 2%, and 10% ethyl acetate in CH_2Cl_2) to afford the pure compound **2**

(0.49 g, 0.26 mmol, 11% yield as a white powder, further recrystallized in hot dichloromethane; R_f = 0.45; m.p. 164.3–165.5°C; ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C): δ = 0.79 (t, ^{3}J(H,H) = 8.0 Hz, 16H), 1.91 (quintet, ^{3}J(H,H) = 8.0 Hz, 16H), 3.98 (t, ^{3}J(H,H) = 6.8 Hz, 16H), 6.92 (d, ^{3}J(H,H) = 9.2 Hz, 16H), 8.14 (t, ^{3}J(H,H) = 9.2 Hz, 16H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25°C): δ = 8.64, 23.1, 70.9, 114.9, 126.4, 142.1, 164.6 ppm; ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, 25°C, TMS): δ = -66.7 ppm; HRMS (ESI): m/z calcd for $C_{72}H_{80}N_8O_{36}Si_8$+$K^+$: 1896.2500 [M+$K^+$]; found: 1896.2209.; Anal. Calcd for $C_{72}H_{80}N_8O_{36}Si_8$: %C = 46.54, %H = 4.34, %N = 6.03; found %C = 46.44, %H = 4.56, %N = 6.06. Compound **3** (0.81 g, 0.35 mmol, 18% yield as a pale yellow fluffy solid); R_f = 0.30,^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 0.71 (t, ^{3}J(H,H) = 8.0 Hz, 20H), 1.75 (quintet, ^{3}J(H,H) = 7.6 Hz, 20H), 3.97 (t, ^{3}J(H,H) = 6.8 Hz, 20H), 7.00 (d, ^{3}J(H,H) = 9.2 Hz, 20H), 8.08 (d, ^{3}J(H,H) = 9.2 Hz, 20H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25°C): δ = 7.95, 22.1, 69.9, 114.7, 125.7, 140.6, 163.7 ppm; ^{29}Si{^{1}H} NMR (79 MHz, DMSO-d_6, 25°C, TMS): δ = -68.1 ppm; HRMS (ESI): m/z calcd for $C_{90}H_{100}N_{10}O_{45}Si_{10}$+$K^+$: 2361.3142 [M+$K^+$]; found: 2361.2932.; Anal. Calcd for $C_{90}H_{100}N_{10}O_{45}Si_{10}$: %C = 46.54, %H = 4.34, %N = 6.03; found %C = 46.70, %H = 4.41, %N = 6.10. Compound **4** (0.41 g, 0.15 mmol, 9% yield as a pale yellow fluffy solid); R_f = 0.18; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 0.72 (m, 24H), 1.76 (m, 24H), 3.96 (m, 24 H), 6.98 (d, ^{3}J(H,H) = 9.2 Hz, 24H), 8.05 (d, ^{3}J(H,H) = 9.2 Hz, 24H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6, 25°C): δ = 7.82, 8.41, 22.2, 69.9, 114.6, 125.6, 140.6, and 163.6 ppm; ^{29}Si{^{1}H}NMR (79 MHz, DMSO-d_6, 25°C, TMS): δ = -67.8 and -70.3 ppm; HRMS (ESI): m/z calcd for $C_{108}H_{120}N_{12}O_{54}Si_{12}$+$K^+$: 2825.3910 [M+$K^+$**]**; found**:** 2825.3566.; Anal. Calcd for $C_{108}H_{120}N_{12}O_{54}Si_{12}$: %C = 46.54, %H = 4.34, %N = 6.03; found %C = 46.79, %H = 4.47, %N = 5.74.

Synthesis of *para*-Benzaldehyde-Functionalized Cage-Rearranged Silsesquioxanes. Octakis(3-proproxy-*para*-benzaldehyde)octasilsesquioxane (**5**), decakis(3-proproxy-*para*-benzaldehyde)decasilsesquioxane (**6**), and dodecakis(3-proproxy-*para*-benzaldehyde)dodecasilsesquioxane (**7**). Firstly, a certain amount of sodium *p*-oxybenzaldehyde salt hydrate was dried under vacuum at 60°C until the white powder of the salt hydrate turned into an pale yellow powder. Dried *p*-oxybenzaldehyde salt (4.45 g; 30.9 mmol) and octakis(3-chloropropyl)octasilsesquioxane (2.00 g; 1.93 mmol) were introduced into a two-neck flask equipped with a condenser and further dried under vacuum at room temperature for an hour. 30 mL of anhydrous DMF was added. After heating at 70°C for 1 day, the solution was cooled in an ice bath, cold CH_2Cl_2 (100 mL) and cold deionized water (40 mL) were added while the solution was stirred for 10 minutes. To the organic layer, 50 ml of water was added and the organic solution was further extracted. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layer was concentrated to *ca.* 100 mL, after which it was washed with saturated $NaHCO_3$ followed by water. The solution was then dried with anhydrous sodium sulfate. Evaporation of the organic solvent gave a pale yellow, fluffy crude product (2.45 g), which was analyzed by thin-layer chromatography using an eluent of 30% ethyl acetate in CH_2Cl_2. TLC analysis showed three separate spots at R_f = 0.46, 0.37 and 0.28 with a broad baseline (R_f

= 0–0.20). A partial amount of the crude product (1.24 g) was purified by a gradient column chromatography (a gradient system: 20%, 21% and 22% ethyl acetate in CH_2Cl_2) to afford the pure compound **5** (0.10 g, 0.06 mmol, 6.02 % yield as a white solid, further recrystallized in tetrahydrofuran and hexane (1:1) ; R_f = 0.46; m.p. 104.9–105.5^oC; ^1H NMR (400 MHz, $CDCl_3$, 25^oC): δ = 0.78 (t, $^3J(H,H)$ = 8.4 Hz, 16H), 1.89 (quintet, $^3J(H,H)$ = 7.6 Hz, 16H), 3.94 (t, $^3J(H,H)$ = 6.4 Hz, 16H), 6.94 (d, $^3J(H,H)$ = 8.8 Hz, 16H), 7.78 (d, $^3J(H,H)$ = 8.8 Hz, 16H), 9.81 (s, 8 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25^oC): δ = 8.64, 23.1, 70.9, 114.9, 126.4, 142.1, 164.6 ppm; $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 25^oC, TMS): δ = -66.762 ppm; HRMS (ESI): m/z calcd for $C_{80}H_{88}O_{28}Si_8$+Na^+: 1744.3547 [M+Na^+]; found: 1744.3316.; Anal. Calcd for $C_{80}H_{88}O_{28}Si_8$: %C = 55.79, %H = 5.15; found %C = 56.10, %H = 5.64. Compound **6** (0.25 g, 0.12 mmol, 14.76 % yield as a pale yellow viscous liquid); R_f = 0.37,^1H NMR (400 MHz, $CDCl_3$, 25^oC): δ = 0.78 (t, $^3J(H,H)$ = 8.4 Hz, 20H), 1.89 (quintet, $^3J(H,H)$ = 8.0 Hz, 20H), 3.93 (t, $^3J(H,H)$ = 6.0 Hz, 20H), 6.92 (d, $^3J(H,H)$ = 8.8 Hz, 20H), 7.76 (d, $^3J(H,H)$ = 8.8 Hz, 20H), 9.81 (s, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25^oC): δ = 7.95, 22.1, 69.9, 114.7, 125.7, 140.6, 163.7 ppm; $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 25^oC, TMS): δ = -68.620 ppm; HRMS (ESI): m/z calcd for $C_{100}H_{110}O_{35}Si_{10}$+$Na^+$: 2174.4452 [M+$Na^+$]; found: 2174.4067.; Anal. Calcd for $C_{100}H_{110}O_{35}Si_{10}$: %C = 55.79, %H = 5.15; found %C = 55.55, %H = 5.15. Compound **7** (0.06 g, 0.02 mmol, 3.61% yield as a pale yellow viscous liquid); R_f = 0.28; ^1H NMR (400 MHz, $CDCl_3$, 25^oC): δ = 0.80 (m, 24H), 1.90 (m, 24H), 3.94 (m, 24 H), 6.91 (d, $^3J(H,H)$ = 8.4 Hz, 24H), 7.74 (d, $^3J(H,H)$ = 8.4 Hz, 24H), 9.79 (s, 12H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$, 25^oC): δ = 8.7, 9.3, 22.8, 22.9, 69.8, 114.6, 130.0, 131.9, 163.7, and 190.5 ppm; $^{29}Si\{^1H\}$NMR (79 MHz, $CDCl_3$, 25^oC, TMS): δ = -68.302 and -71.032 ppm; HRMS (ESI): m/z calcd for $C_{120}H_{132}O_{42}Si_{12}$+$Na^+$: 2605.5389 [M+$Na^+$]; found: 2605.5347.; Anal. Calcd for $C_{120}H_{132}O_{42}Si_{12}$: %C = 55.79, %H = 5.15; found %C = 55.45, %H = 5.34.

Synthesis of *para*-Bromobenzene-Functionalized Cage-Rearranged Silsesquioxanes. Octakis(3-proproxy-*para*-bromobenzene)octasilsesquioxane (**8**), decakis(3-proproxy-*para*-bromobenzene)decasilsesquioxane (**9**), and dodecakis(3-proproxy-*para*-nitrobenzene)dodecasilsesquioxane (**10**). Firstly, a certain amount of sodium *p*-bromophenoxide salt hydrate was dried under vacuum at 60°C until the yellow-white crystals of the salt hydrate turned into a white powder. Dried *para*-bromopheoxide sodium salt (4.51 g; 23.1 mmol) and octakis(3-chloropropyl)octasilsesquioxane (2.00 g; 1.93 mmol) were introduced into a round bottom flask covered with a septum and further dried under vacuum at 60°C for 2 hours. 15 mL of anhydrous DMF was added. After heating at 55°C for 12 hours, the solution was cooled in an ice bath, cold CH_2Cl_2 (100 mL) and cold deionized water (40 mL) were added while the solution was stirred for 10 minutes. To the organic layer, 50 ml of water was added and the organic solution was further extracted. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layer was concentrated to *ca.* 100 mL, after which it was washed with saturated $NaHCO_3$ and further washed by a mixture of water and methanol until the solution turned to clear or completely eliminate an excessive starting material of *p*-bromophenol. The

solution was then dried with anhydrous sodium sulfate. Evaporation of the organic solvent gave a clear white, viscous crude product (3.24 g), which was analyzed by thin-layer chromatography using an eluent of 45% CH_2Cl_2 in hexane. TLC analysis showed three separate spots at R_f = 0.45, 0.40, and 0.37 with a broad baseline (R_f = 0–0.15). A partial amount of the crude product (3.12 g) was purified by a gradient column chromatography (an isolated system: 35% CH_2Cl_2 in hexane) to afford the pure compound **8** (0.27 g, 0.13 mmol, 6.57 % yield as a white solid, further recrystallized in system of dichloromethane and hexane); R_f = 0.45; m.p. 134.2-134.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25^{o}C): δ = 0.72 (t, ^{3}J(H,H) = 8.0 Hz, 16H), 1.82 (quintet, ^{3}J(H,H) = 8.0 Hz, 16H), 3.81 (t, ^{3}J(H,H) = 6.4 Hz, 16H), 6.74 (d, ^{3}J(H,H) = 9.2 Hz, 16H), 7.34 (d, ^{3}J(H,H) = 8.8 Hz, 16H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25^{o}C): δ = 8.1, 22.6, 69.5, 112.7, 116.2, 132.2, 158.0 ppm; ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25^{o}C, TMS): δ = -66.765 ppm; MALDI-TOF MS: m/z calcd for $C_{72}H_{80}Br_8O_{20}Si_8$+$H^+$: 2128.69 [M+$H^+$]; found: 2128.390.; Anal. Calcd for $C_{72}H_{80}Br_8O_{20}Si_8$: %C = 40.61, %H = 3.79; found %C = 41.03, %H = 3.97. Compound **9** (0.60 g, 0.23 mmol, 14.59 % yield as a viscous clear liquid); R_f = 0.40,^{1}H NMR (400 MHz, $CDCl_3$, 25^{o}C): δ = 0.72 (t, ^{3}J(H,H) = 8.0 Hz, 20H), 1.81 (quintet, ^{3}J(H,H) = 8.0 Hz, 20H), 3.81 (t, ^{3}J(H,H) = 6.4 Hz, 20H), 6.73 (d, ^{3}J(H,H) = 8.8 Hz, 20H), 7.32 (d, ^{3}J(H,H) = 8.8 Hz, 20H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25^{o}C): δ = 8.7, 22.8, 69.5, 112.8, 116.2, 132.3, 158.0 ppm; ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25^{o}C, TMS): δ = -68.6 ppm; MALDI-TOF MS: m/z calcd for $C_{90}H_{100}Br_{10}O_{25}Si_{10}$+$H^+$: 2658.61 [M+$H^+$]; found: 2658.578.; Anal. Calcd for $C_{90}H_{100}Br_{10}O_{25}Si_{10}$: %C = 40.61, %H = 3.79; found %C =40.96, %H = 3.84. Compound **10** (0.25 g, 0.08 mmol, 6.19 % yield as a white solid); R_f = 0.37; m.p. 126.3-127.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25^{o}C): δ = 0.72 (m, 24H), 1.82 (m, 24H), 3.80 (m, 24 H), 6.71 (d, ^{3}J(H,H) = 8.8 Hz, 24H), 7.30 (d, ^{3}J(H,H) = 6.8 Hz, 24H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25^{o}C): δ = 8.7, 9.3, 22.9, 23.1, 69.7, 112.8, 116.2, 132.3, and 158.0 ppm; ^{29}Si{^{1}H}NMR (79 MHz, $CDCl_3$, 25^{o}C, TMS): δ = -68.300 and -70.973 ppm; MALDI-TOF MS: m/z calcd for $C_{108}H_{120}Br_{12}O_{30}Si_{12}$+$Na^+$: 3217.51 [M+$Na^+$**]**; found**:** 3217.486.; Anal. Calcd for $C_{108}H_{120}Br_{12}O_{30}Si_{12}$: %C = 40.61, %H = 3.79; found %C = 40.66, %H = 3.84.

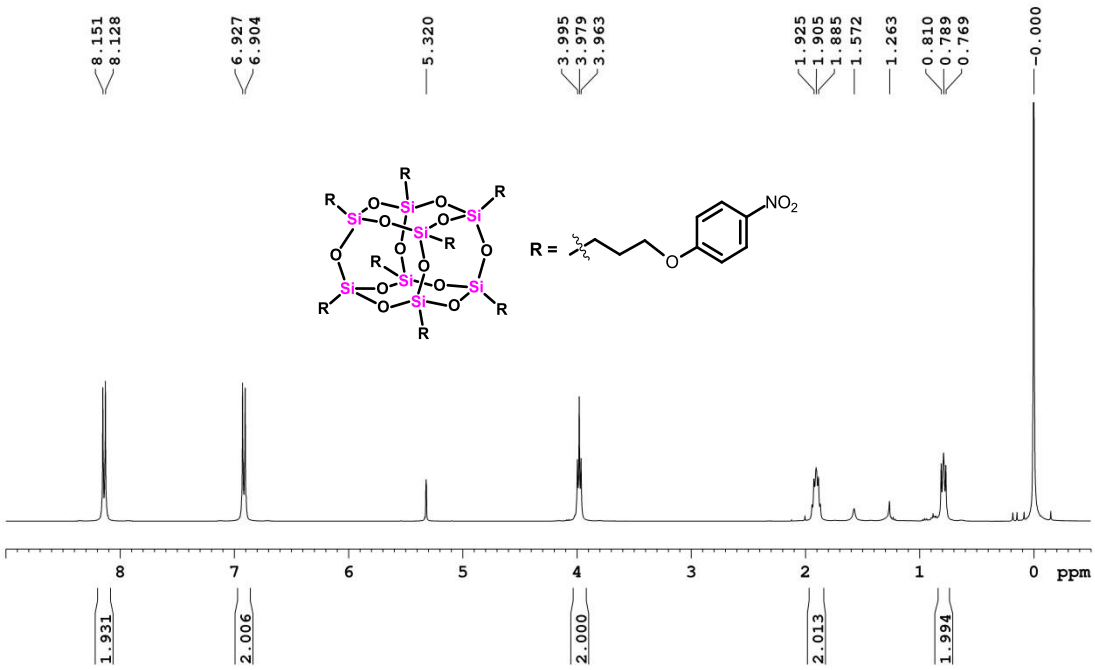

Figure S1: ^{1}H NMR (400 MHz) of compound **2** in CD_2Cl_2

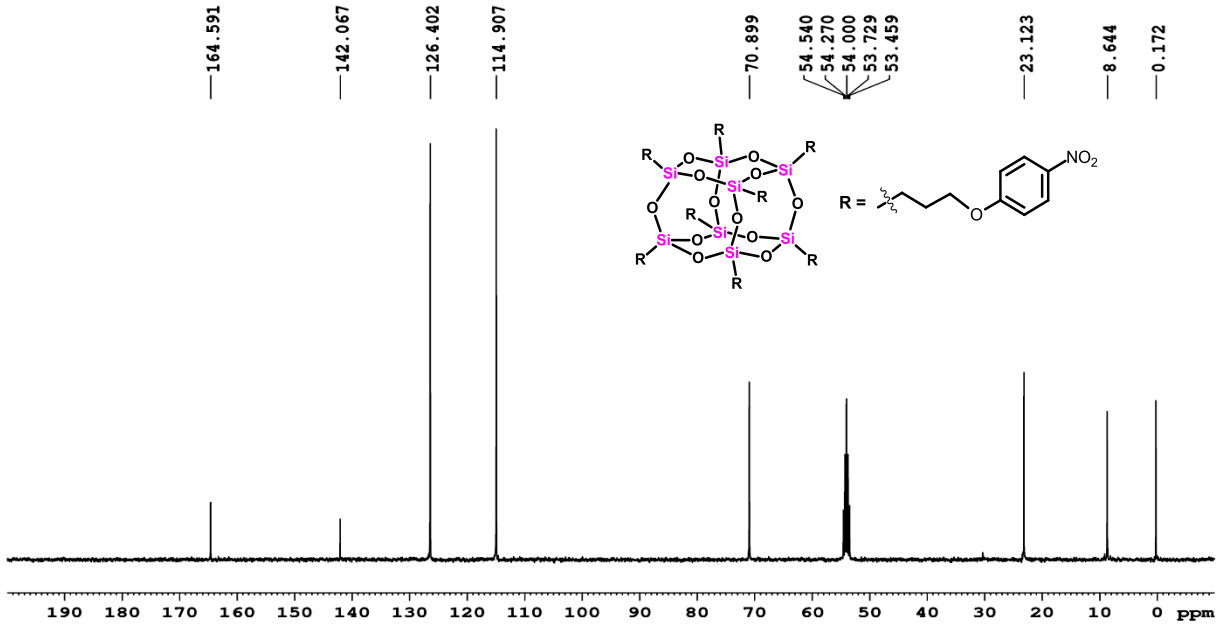

Figure S2: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **2** in CD_2Cl_2

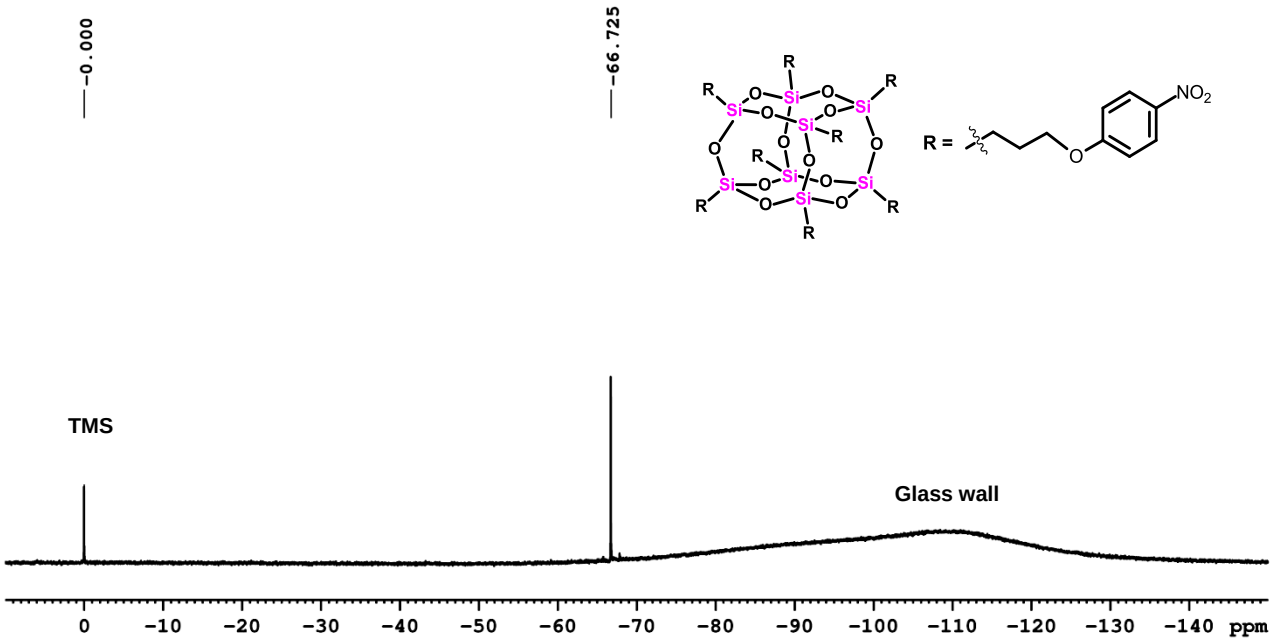

Figure S3: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of compound **2** in CD_2Cl_2

Mass Spectrum List Report

Analysis Info

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	T8-NO2		

Acquisition Parameter

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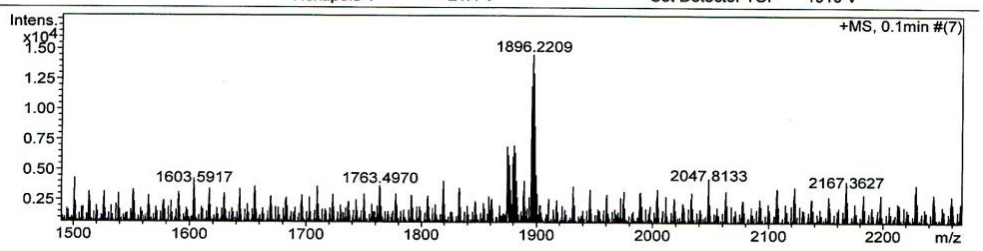
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	51.3694	4523	31.1	4.0	0.0098	5222
2	53.7003	5693	39.1	5.1	0.0081	6631
3	56.1399	4077	28.0	3.5	0.0316	1776
4	63.6702	4136	28.4	3.6	0.0126	5066
5	66.3081	4145	28.5	3.6	0.0087	7646
6	77.2718	4226	29.0	3.7	0.0146	5289
7	89.2337	4015	27.6	3.4	0.0272	3277
8	105.2455	3993	27.4	3.4	0.0152	6940
9	133.5407	4016	27.6	3.5	0.0139	9590
10	145.1805	4840	33.2	4.3	0.0176	8253
11	297.8333	5151	35.4	5.2	0.0451	6602
12	504.7354	4574	31.4	4.7	0.0270	18728
13	765.8210	5704	39.2	6.0	0.0375	20431
14	1081.2926	5063	34.8	5.2	0.0536	20171
15	1450.9314	5806	39.9	6.1	0.1221	11887
16	1874.2990	5670	38.9	5.8	0.3198	5861
17	1874.8189	4643	31.9	4.7	0.0972	19288
18	1875.2681	6206	42.6	6.4	0.2923	6417
19	1876.2863	5423	37.2	5.6	0.2317	8099
20	1879.2574	6117	42.0	6.3	0.2683	7004
21	1880.2454	7011	48.2	7.3	0.2532	7426
22	1881.2551	6409	44.0	6.7	0.2435	7726
23	1882.2464	4117	28.3	4.1	0.2982	6311
24	1895.2300	11920	81.9	12.8	0.2539	7465
25	1896.2209	14560	100.0	15.8	0.2806	6758
26	1897.2275	13004	89.3	14.0	0.2783	6818
27	1898.2237	8569	58.9	9.1	0.2855	6649
28	1899.2265	4597	31.6	4.6	0.2724	6973
29	2352.8494	6656	45.7	6.9	0.0591	39813
30	2885.3235	4636	31.8	4.7	0.0729	39602

Figure S4: HRMS (ESI) of compound **2**

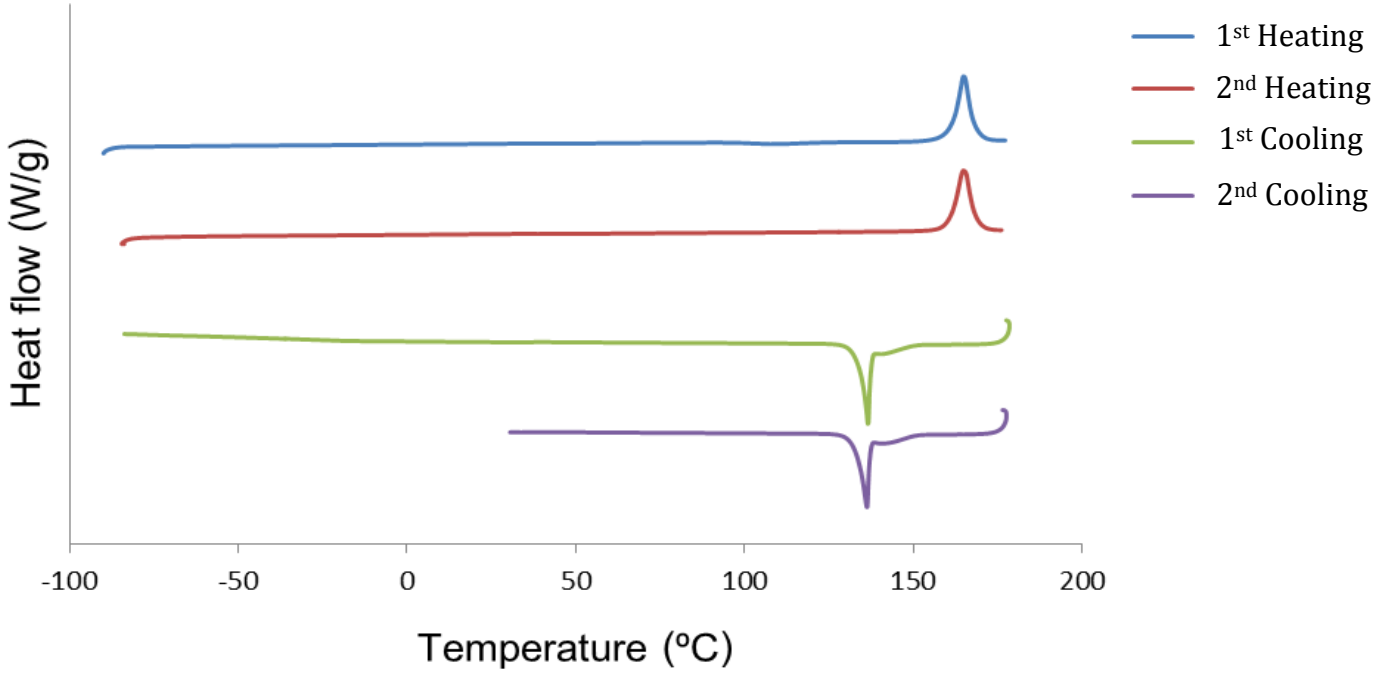


Figure S5: DSC thermograms of compound **2** over the temperature range from -90 to 180°C at heating and cooling rates of 20°C/min under nitrogen atmosphere.

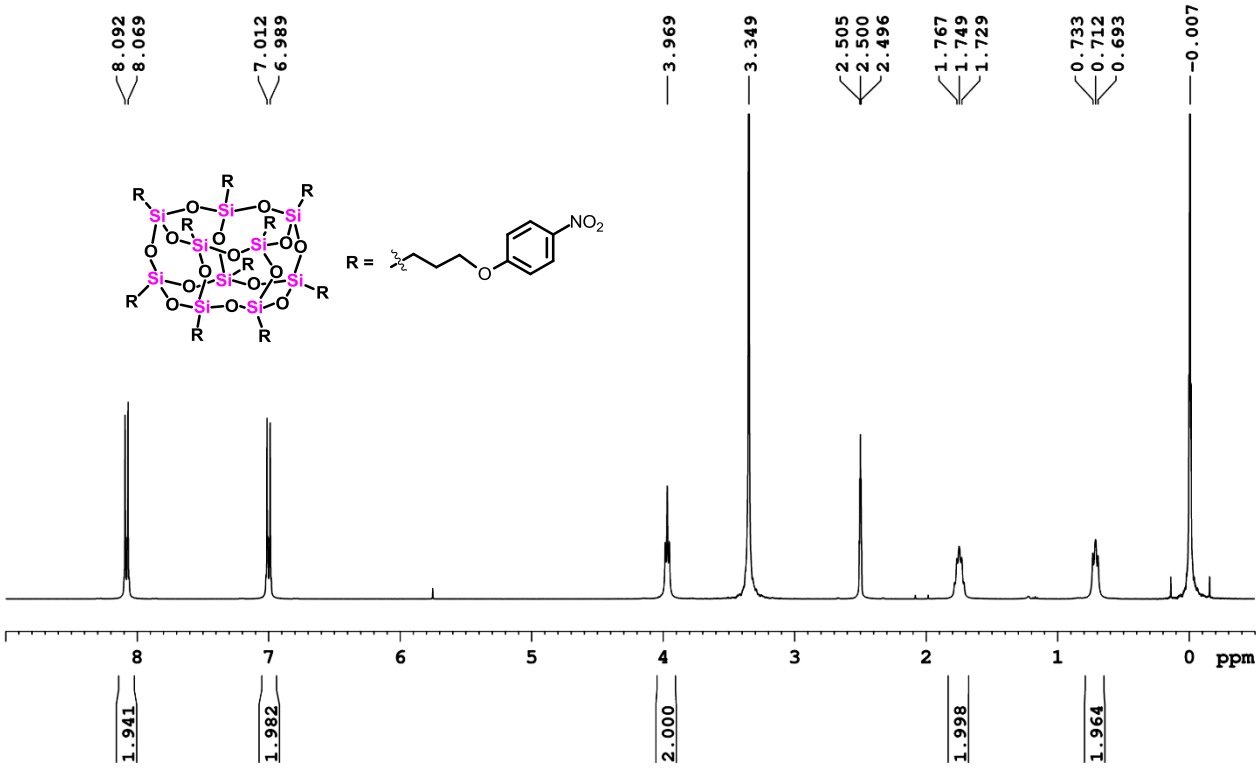


Figure S6: ^{1}H NMR (400 MHz) of compound **3** in DMSO-d_6

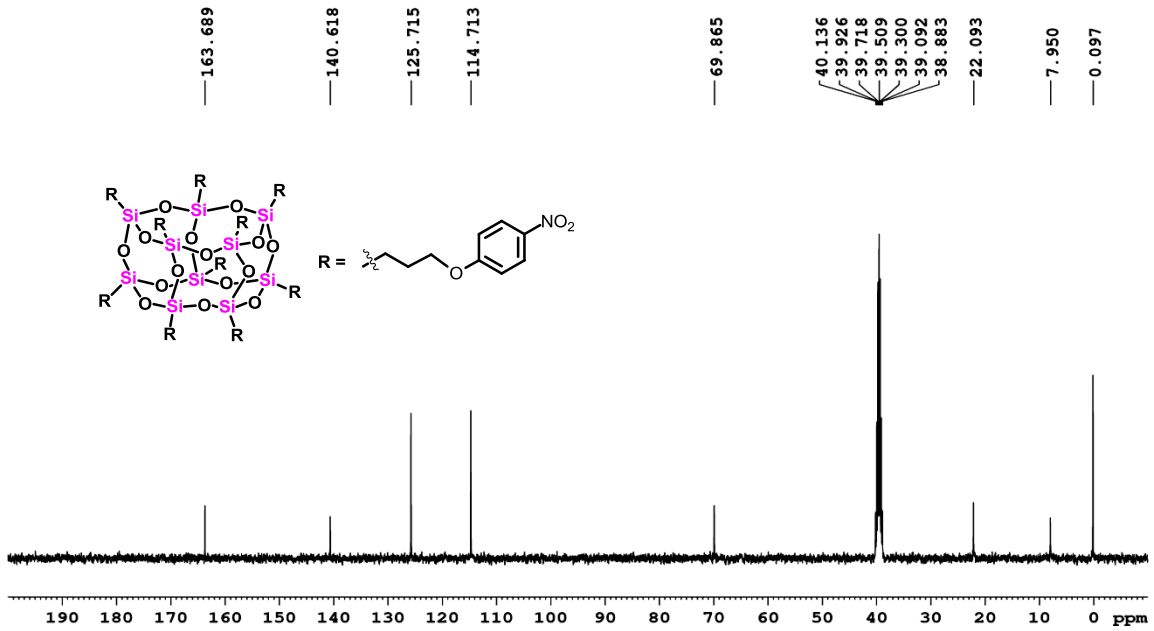


Figure S7: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **3** in DMSO-d_6

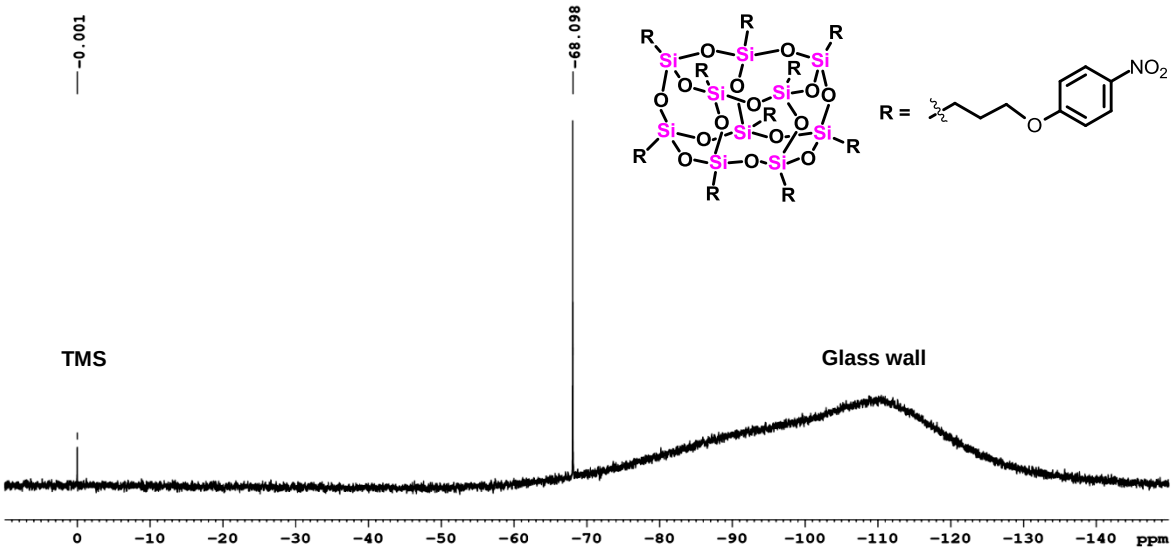


Figure S8: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of compound **3** in DMSO-d_6

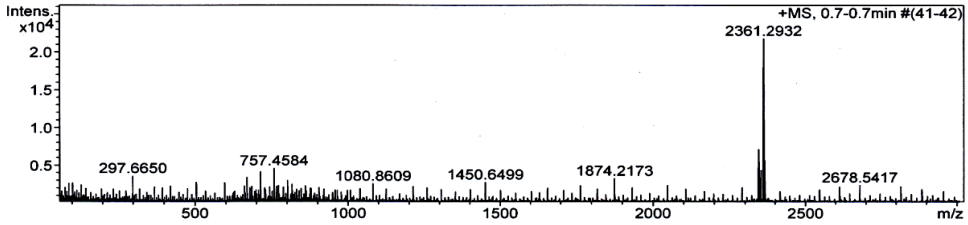
Mass Spectrum List Report

Analysis Info

Analysis Name	VESCH561003003.d	Acquisition Date	10/3/2013 2:35:00 PM
Method	Natee20130403.m	Operator	Administrator
Sample Name	T10-Nitro	Instrument	micrOTOF 72
	T10-Nitro		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	75 V
Scan Range	n/a	Capillary Exit	280.0 V	Set Pulsar Pull	398 V
Scan Begin	50 m/z	Hexapole RF	600.0 V	Set Pulsar Push	380 V
Scan End	3000 m/z	Skimmer 1	54.4 V	Set Reflector	1300 V
		Hexapole 1	21.4 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	89.1348	2642	12.1	13.2	0.0067	13231
2	101.8472	2665	12.3	13.3	0.0077	13162
3	297.6650	3583	16.5	20.2	0.0131	22768
4	297.7350	2755	12.7	15.4	0.0183	16242
5	297.7628	2802	12.9	15.7	0.0193	15429
6	504.4881	2770	12.7	15.6	0.0170	29710
7	504.6238	2573	11.8	14.5	0.0281	17981
8	596.1225	2715	12.5	14.2	0.0178	33443
9	669.4121	3400	15.6	16.5	0.0824	8125
10	713.4376	4176	19.2	19.5	0.0918	7775
11	757.4584	4594	21.1	21.2	0.0914	8289
12	801.4865	3029	13.9	13.9	0.1129	7102
13	815.5010	2511	11.5	11.5	0.1177	6928
14	1080.8609	2556	11.8	13.6	0.0232	46579
15	1450.6499	2743	12.6	15.6	0.0679	21358
16	1874.2173	3244	14.9	18.3	0.0316	59248
17	2343.3198	4683	21.5	23.6	0.2930	7999
18	2344.3186	7139	32.8	36.2	0.2982	7862
19	2345.3126	7027	32.3	35.7	0.3145	7458
20	2346.3190	5430	25.0	27.5	0.3107	7553
21	2347.3172	3458	15.9	17.3	0.3283	7150
22	2352.2213	4389	20.2	22.2	0.0344	68429
23	2352.4265	3215	14.8	16.2	0.0606	38830
24	2359.3000	11915	54.8	61.4	0.2909	8110
25	2360.2986	19012	87.4	98.4	0.3118	7570
26	2361.2932	21746	100.0	112.7	0.2929	8060
27	2362.2953	15896	73.1	82.3	0.3155	7487
28	2363.2945	10919	50.2	56.4	0.3145	7514
29	2364.2959	5662	26.0	29.1	0.3083	7669
30	2365.2870	2941	13.5	14.9	0.3114	7596

Figure S9: HRMS (ESI) of compound **3**

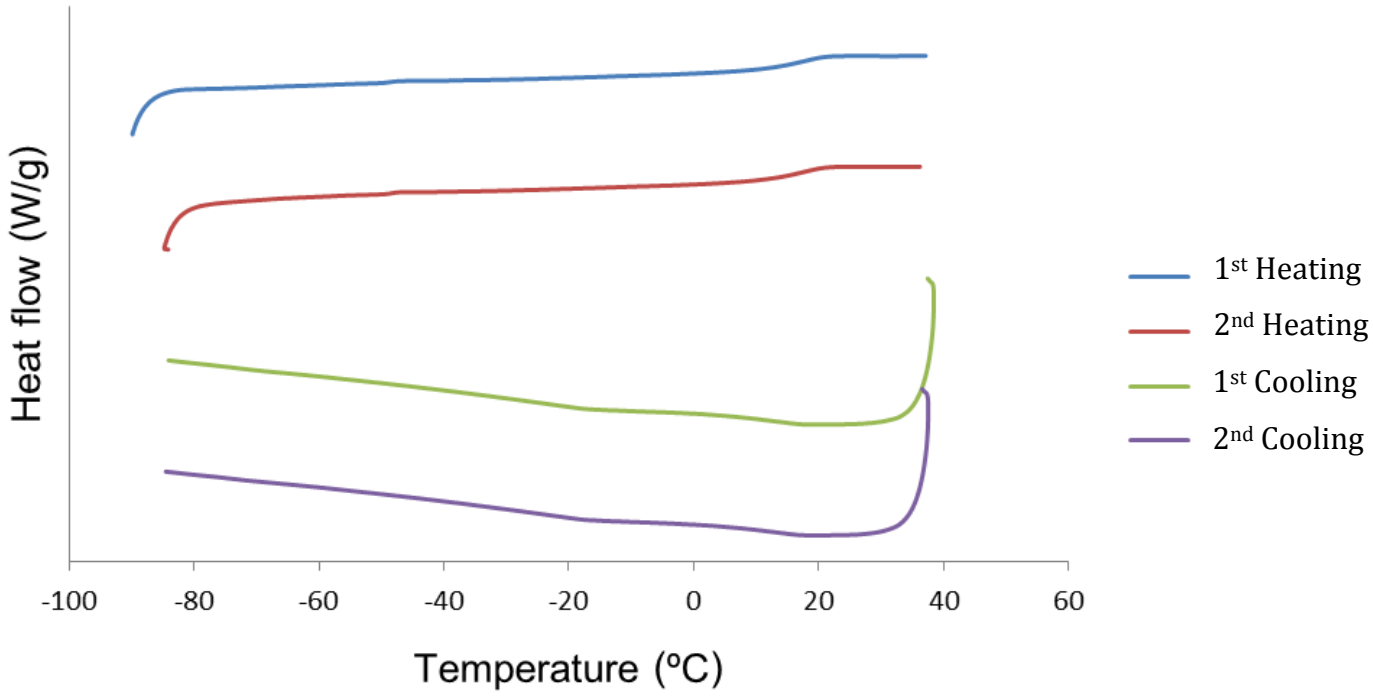


Figure S10: DSC thermograms of compound **3** over the temperature range from -90 to 40°C at a heating and cooling rate of 20°C/min under nitrogen atmosphere.

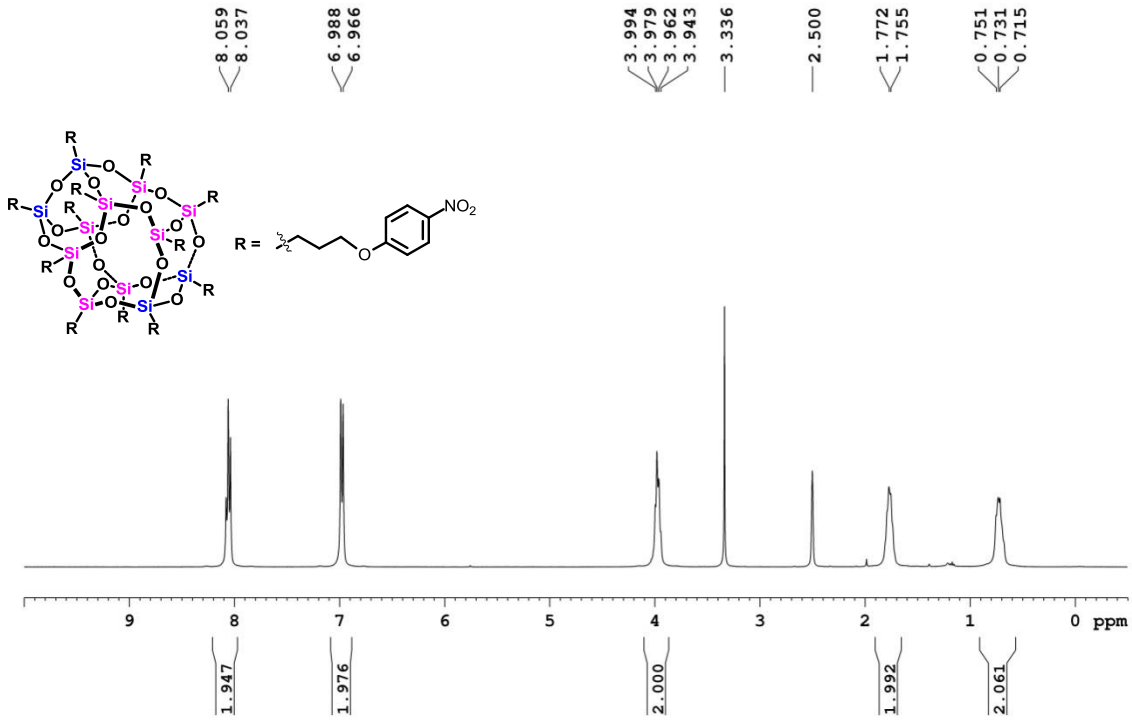


Figure S11: ^{1}H NMR (400 MHz) of compound **4** in DMSO-d_6

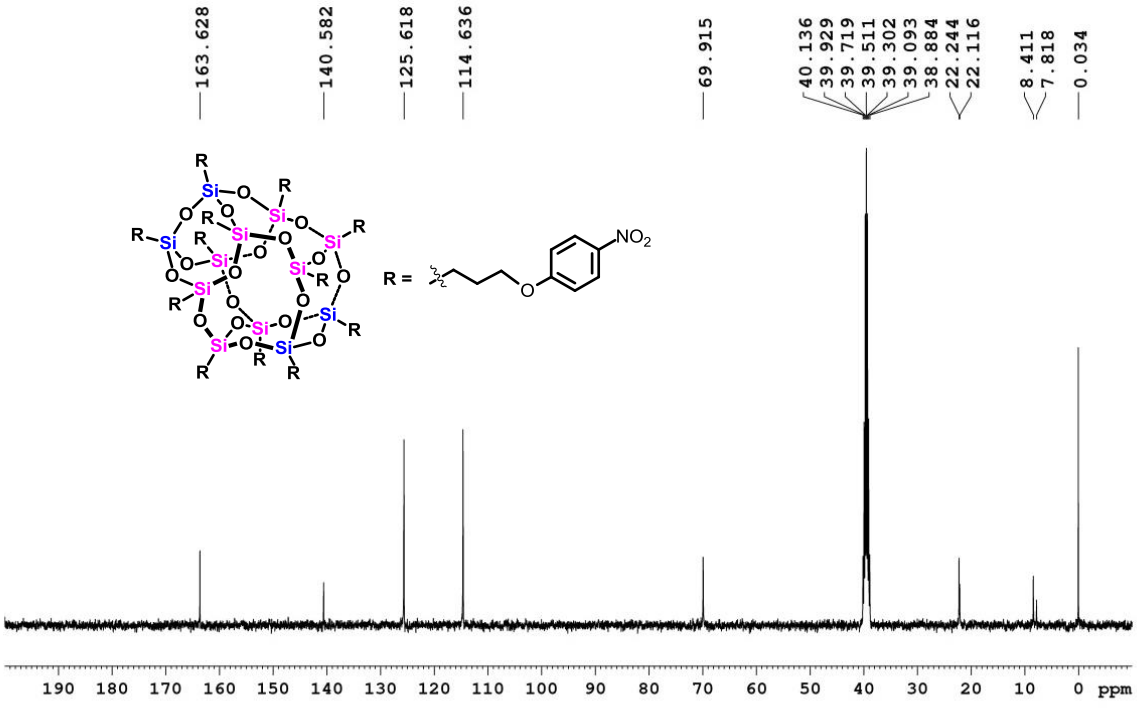


Figure S12: ^{13}C{^{1}H} NMR (100 MHz) of compound **4** in DMSO-d_6

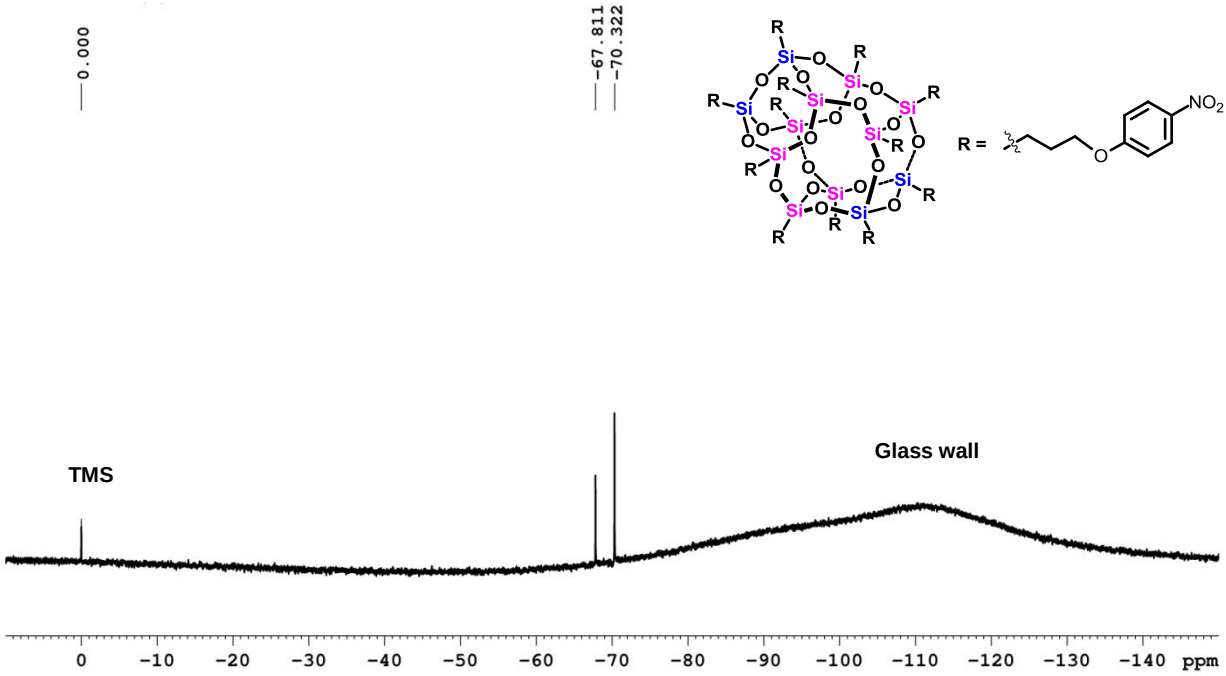


Figure S13: $^{29}Si\{^{1}H\}$ NMR (79MHz) of compound **4** in DMSO-d_6

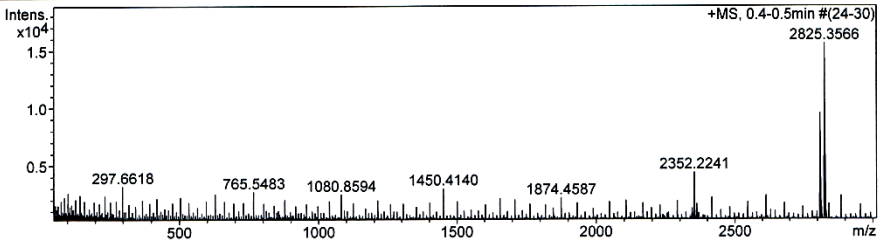
Mass Spectrum List Report

Analysis Info

Analysis Name	VESCH5610030021.d	Acquisition Date	10/3/2013 2:39:54 PM
Method	Natee20130403.m	Operator	Administrator
Sample Name	T12-Nitro	Instrument	micrOTOF 72
	T12-Nitro		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	75 V
Scan Range	n/a	Capillary Exit	400.0 V	Set Pulsar Pull	398 V
Scan Begin	50 m/z	Hexapole RF	800.0 V	Set Pulsar Push	380 V
Scan End	3000 m/z	Skimmer 1	54.4 V	Set Reflector	1300 V
		Hexapole 1	21.4 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	89.1344	2267	14.6	12.2	0.0069	13009
2	101.8467	2648	17.0	14.4	0.0075	13558
3	101.8914	2301	14.8	12.4	0.0077	13188
4	145.1505	2439	15.7	13.2	0.0101	14374
5	234.0787	2359	15.2	13.8	0.0110	21355
6	234.1524	2248	14.4	13.2	0.0116	20213
7	297.6618	3200	20.6	20.1	0.0133	22311
8	297.7618	2827	18.2	17.7	0.0157	18921
9	504.6242	2226	14.3	14.2	0.0215	23512
10	765.5483	2678	17.2	16.5	0.0211	36362
11	1080.8594	2457	15.8	15.0	0.0237	45595
12	1450.4140	2958	19.0	19.0	0.0286	50766
13	1450.6257	2812	18.1	18.0	0.0375	38704
14	2352.2241	4373	28.1	26.7	0.0337	69727
15	2352.4329	3208	20.6	19.4	0.0596	39440
16	2611.5760	2348	15.1	14.7	0.0356	73356
17	2807.3876	4084	26.2	25.2	0.3716	7555
18	2808.3857	7781	50.0	48.5	0.3631	7735
19	2809.3902	9486	60.9	59.2	0.3719	7555
20	2810.3893	7889	50.7	49.1	0.3645	7711
21	2811.3948	5437	34.9	33.7	0.3862	7280
22	2812.3949	3850	24.7	23.7	0.3303	8515
23	2823.3585	5708	36.7	35.3	0.3820	7392
24	2824.3611	12436	79.9	77.5	0.3861	7315
25	2825.3566	15570	100.0	97.2	0.3618	7810
26	2826.3574	14126	90.7	88.1	0.3489	8100
27	2827.3650	10269	66.0	63.9	0.3534	8000
28	2828.3626	5807	37.3	35.9	0.3884	7281
29	2829.3518	3363	21.6	20.6	0.3950	7162
30	2884.8419	2326	14.9	14.0	0.0414	69614

Figure S14: HRMS (ESI) of compound **4**

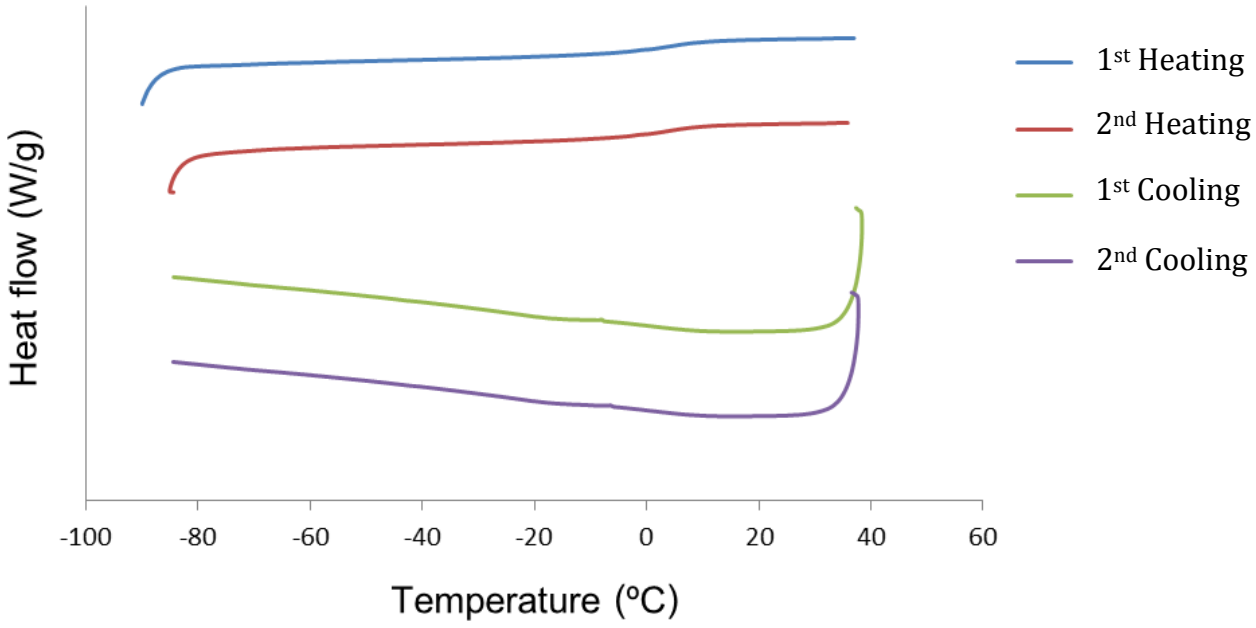


Figure S15: DSC thermograms of compound **4** over the temperature range from -90 to 40°C at a heating and cooling rate of 20°C/min under nitrogen atmosphere.

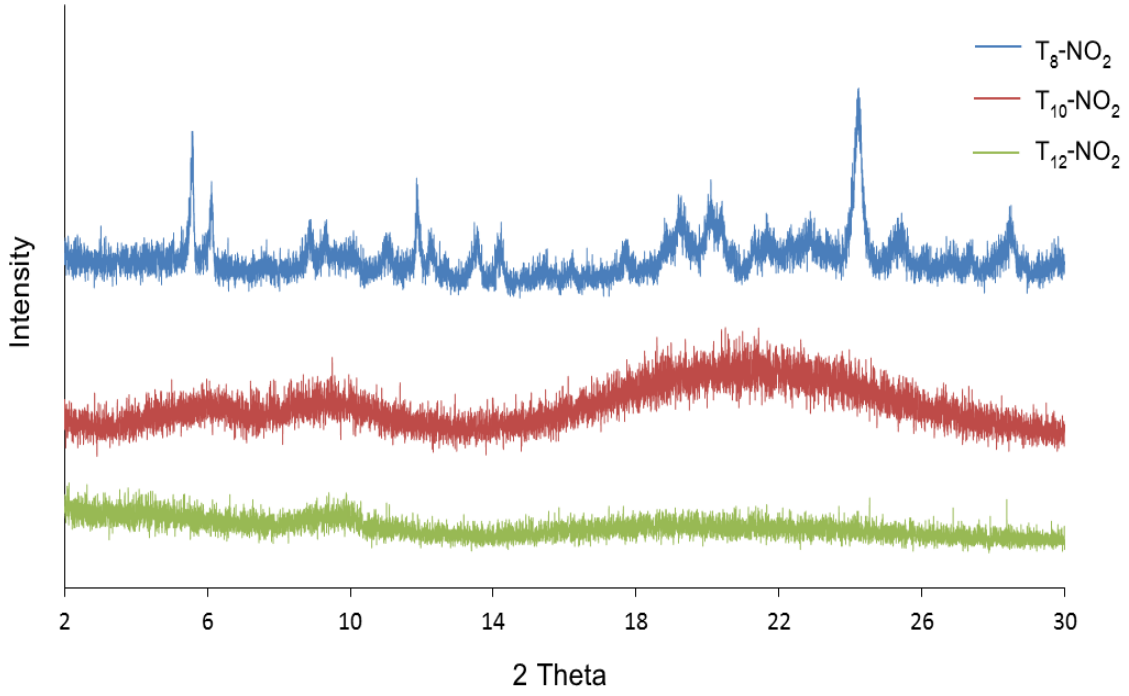


Figure S16: X-ray powder diffractograms of compounds **2**, **3** and **4**.

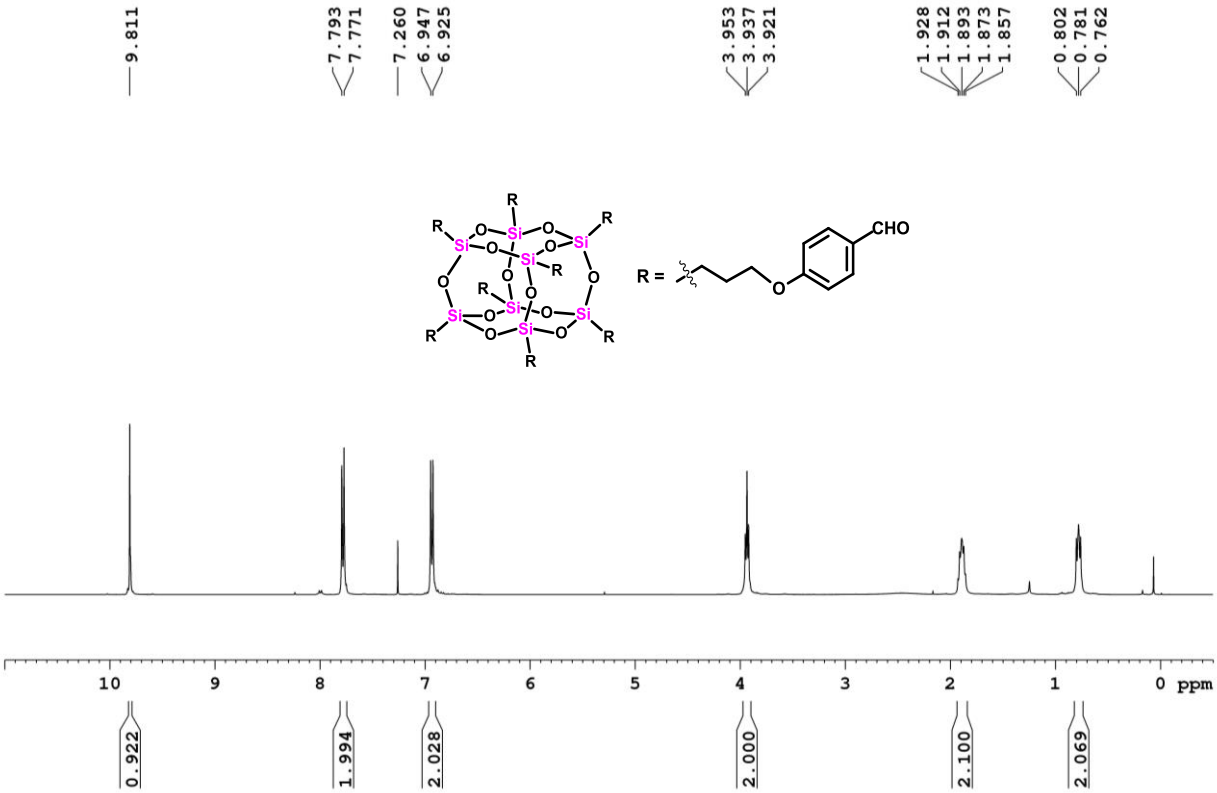


Figure S17: ^{1}H NMR (400 MHz) of compound **5** in $CDCl_3$

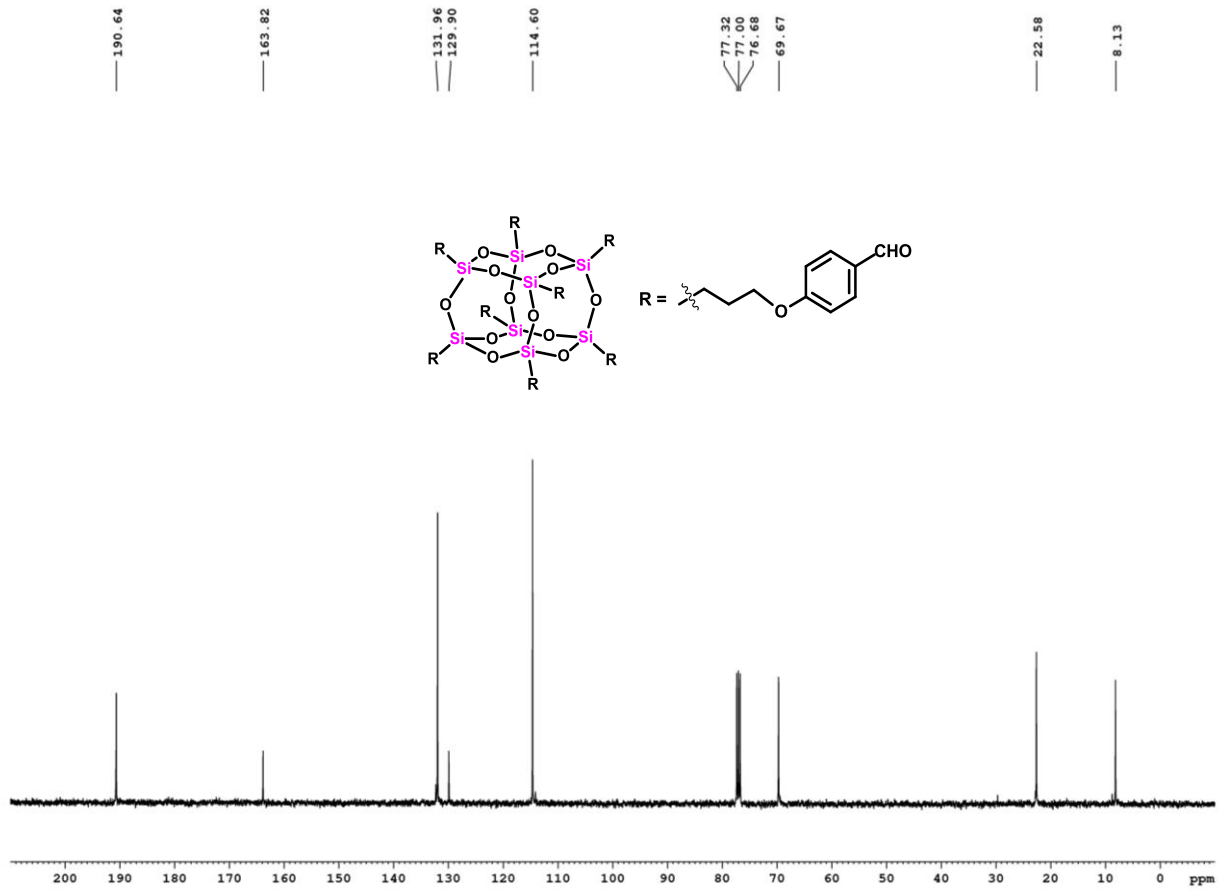


Figure S18: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **5** in $CDCl_3$

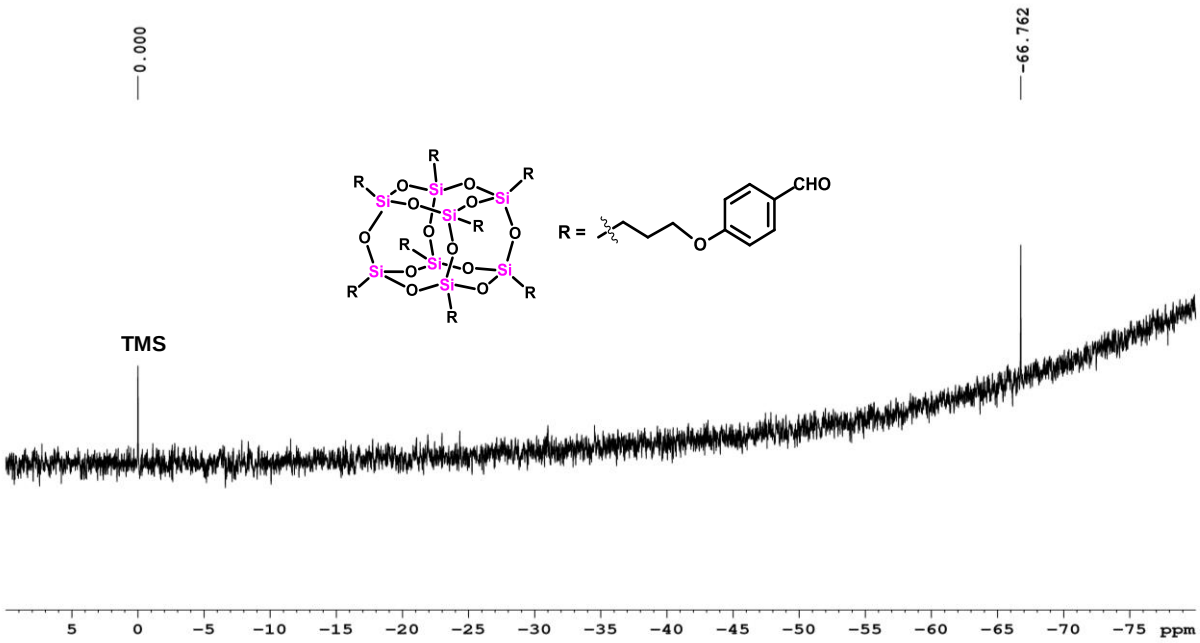


Figure S19: $^{29}Si\{^{1}H\}$ NMR (79MHz) of compound **5** in $CDCl_3$

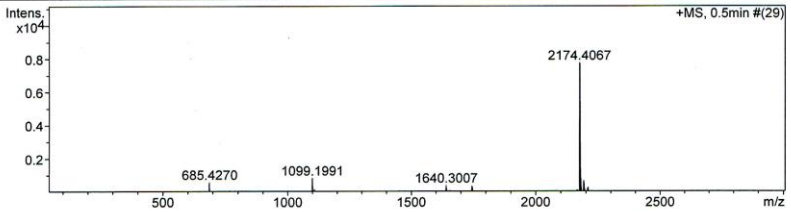
Mass Spectrum List Report

Analysis Info

Analysis Name	VERK570701003.d	Acquisition Date	7/1/2014 12:25:32 PM
Method	Natee20130403.m	Operator	Administrator
Sample Name	Para-ben S2.2	Instrument	micrOTOF 72
	Para-ben S2.2		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	350.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	388 V
Scan End	3000 m/z	Skimmer 1	54.4 V	Set Reflector	1300 V
		Hexapole 1	21.4 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	685.4270	600	7.7	112.2	0.0725	9458
2	686.4325	248	3.2	45.9	0.0707	9706
3	1098.1987	452	5.8	75.3	0.1048	10476
4	1098.7008	706	9.1	118.0	0.0981	11203
5	1099.1991	841	10.9	140.6	0.0912	12050
6	1099.7008	637	8.2	106.3	0.0887	12393
7	1100.2049	368	4.8	61.1	0.0974	11294
8	1639.3006	301	3.9	51.6	0.1621	10114
9	1640.3007	403	5.2	69.2	0.1646	9964
10	1641.3055	309	4.0	52.8	0.1815	9042
11	1743.3270	250	3.2	40.5	0.1773	9833
12	1744.3219	353	4.6	57.5	0.1744	10003
13	1745.3328	314	4.1	51.1	0.1667	10471
14	2173.4042	4276	55.2	490.1	0.1990	10922
15	2174.4067	7744	100.0	890.8	0.1859	11695
16	2175.4031	7676	99.1	885.7	0.2152	10108
17	2176.4085	5386	69.6	623.2	0.2166	10048
18	2177.4060	2959	38.2	343.2	0.1985	10972
19	2178.3998	1429	18.5	166.0	0.2051	10622
20	2179.3964	803	10.4	93.3	0.2077	10494
21	2180.3895	435	5.6	50.5	0.2127	10252
22	2181.3795	283	3.7	32.7	0.1714	12728
23	2189.3830	361	4.7	43.0	0.1998	10958
24	2190.3838	633	8.2	76.1	0.2380	9204
25	2191.3848	672	8.7	81.1	0.2011	10895
26	2192.3951	533	6.9	64.4	0.2139	10249
27	2193.3961	300	3.9	36.1	0.2372	9248
28	2206.4143	239	3.1	30.0	0.2419	9120
29	2207.4187	287	3.7	36.2	0.2225	9922
30	2208.4045	258	3.3	32.6	0.1558	14173

Figure S20: HRMS (ESI) of compound **5**

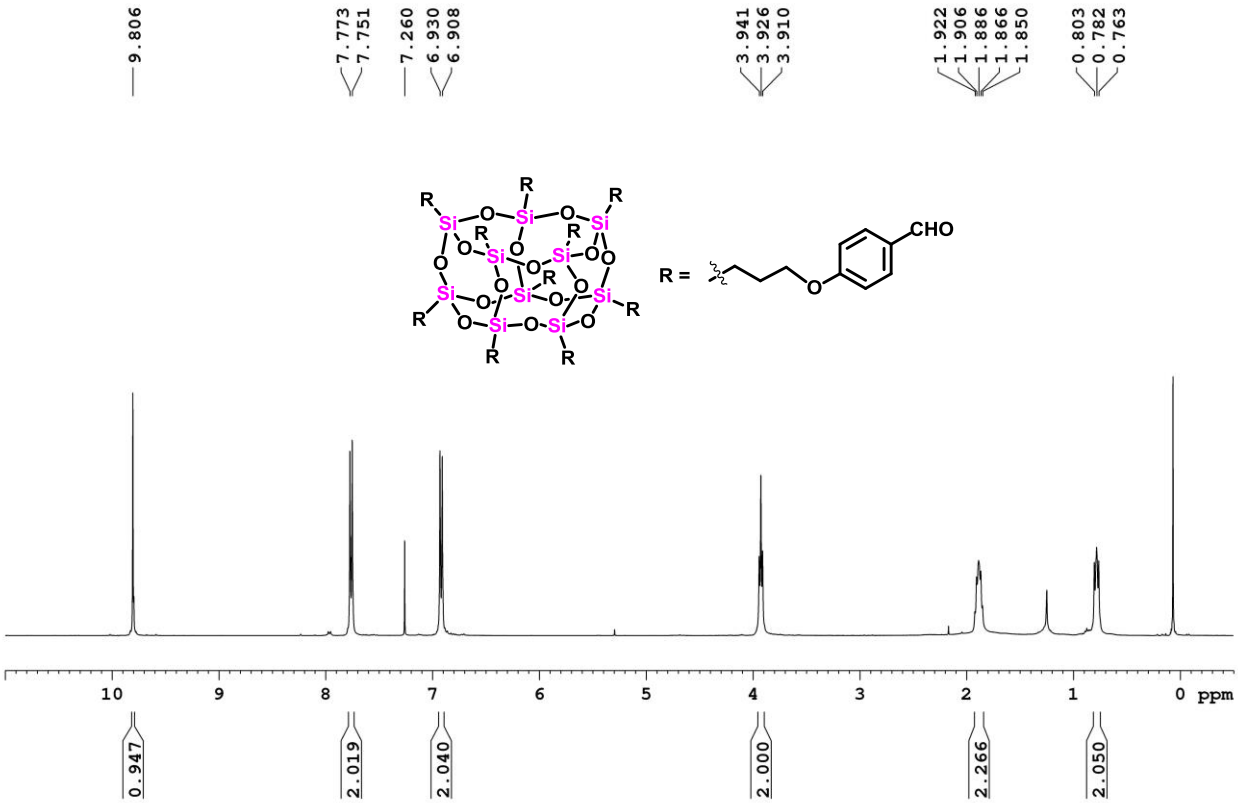


Figure S21: ^{1}H NMR (400 MHz) of compound **6** in $CDCl_3$

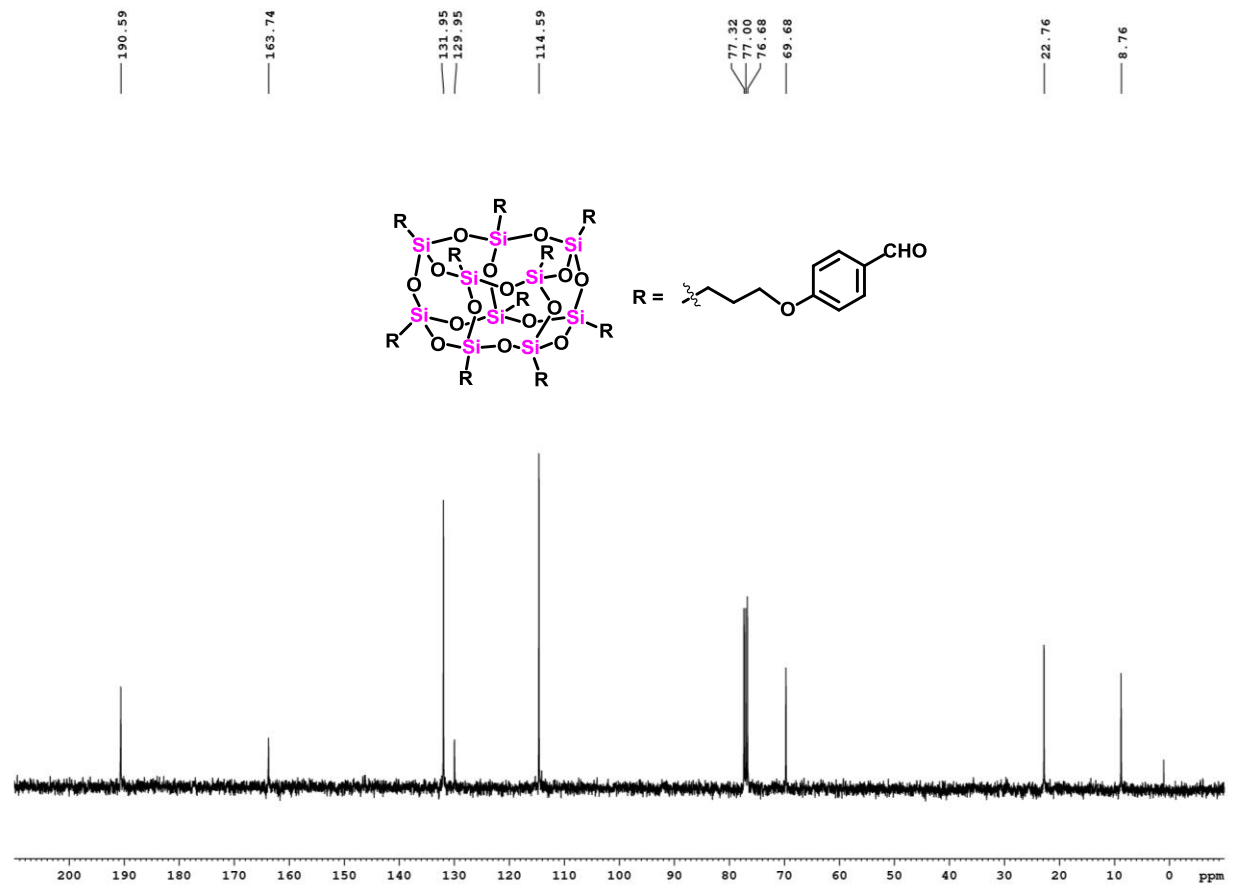


Figure S22: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **6** in $CDCl_3$

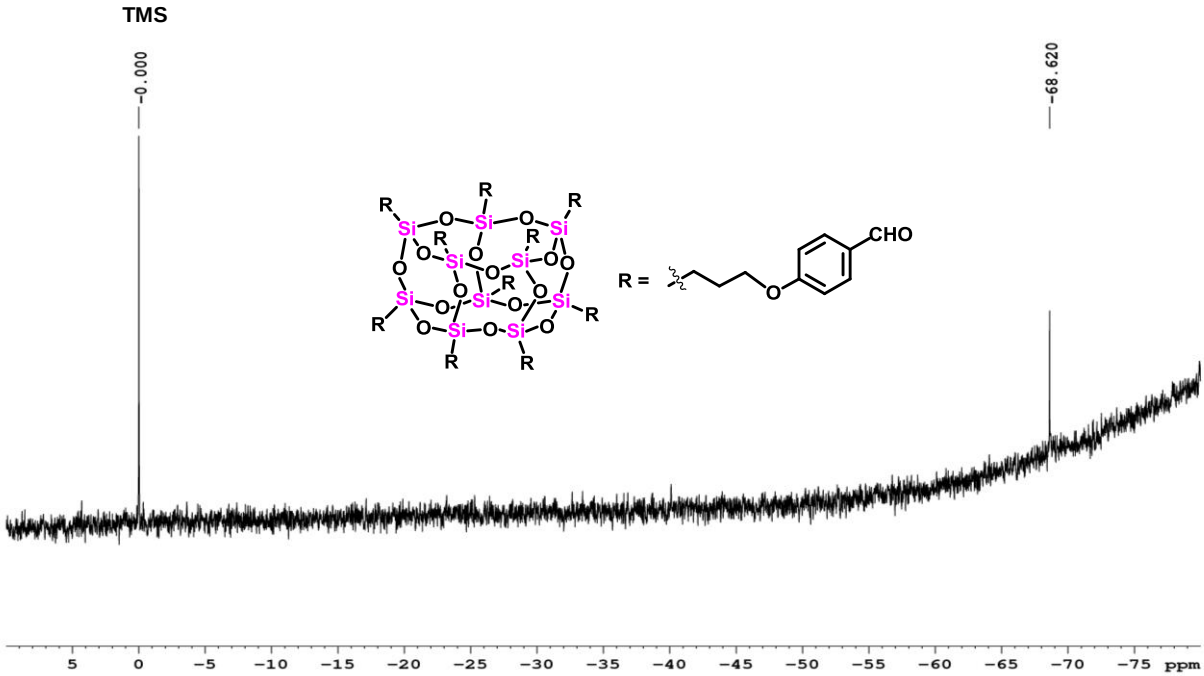


Figure S23: $^{29}Si\{^{1}H\}$ NMR (79MHz) of compound **6** in $CDCl_3$

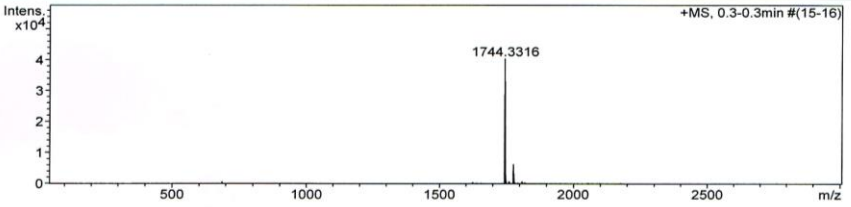
Mass Spectrum List Report

Analysis Info

Analysis Name	VERK570701001.d	Acquisition Date	7/1/2014 12:18:21 PM
Method	Natee20130403.m	Operator	Administrator
Sample Name	1DN-1	Instrument	micrOTOF 72
	Para-ben S1		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	350.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	388 V
Scan End	3000 m/z	Skimmer 1	54.4 V	Set Reflector	1300 V
		Hexapole 1	21.4 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	685.4272	570	1.4	125.1	0.0669	10240
2	1623.3055	307	0.8	23,3	0.1523	10657
3	1624.3066	401	1.0	30.5	0.1458	11140
4	1625.3091	287	0.7	21.5	0.1753	9273
5	1743.3308	28686	71.2	1560.3	0.1593	10947
6	1744.3316	40315	100.0	2201.6	0.1662	10498
7	1745.3339	32817	81.4	1799.1	0.1721	10144
8	1746.3322	18498	45.9	1017.8	0.1677	10411
9	1747.3310	7819	19.4	431.7	0.1612	10838
10	1748.3291	2821	7.0	156.0	0.1668	10481
11	1749.3287	1015	2.5	56.0	0.1845	9479
12	1750.3239	416	1.0	22.8	0.1667	10502
13	1759.3205	570	1.4	32.6	0.1748	10066
14	1760.3181	673	1.7	38.7	0.1876	9381
15	1761.3246	604	1.5	34.8	0.1758	10018
16	1762.3151	436	1.1	25.1	0.1655	10647
17	1763.3209	265	0.7	15.2	0.1380	12780
18	1775.3531	4350	10.8	269.7	0.1807	9825
19	1776.3527	6275	15.6	391.0	0.1729	10275
20	1777.3525	5624	14.0	352.0	0.1662	10693
21	1778.3536	3252	8.1	204.2	0.1636	10868
22	1779.3524	1628	4.0	102.4	0.1535	11589
23	1780.3554	602	1.5	37.7	0.1868	9532
24	1781.3323	330	0.8	20.5	0.1916	9296
25	1807.3685	538	1.3	38.4	0.1794	10076
26	1808.3735	667	1.7	48.0	0.1695	10669
27	1809.3669	613	1.5	44.3	0.1676	10798
28	1810.3750	418	1.0	30.2	0.1670	10838
29	1818.3445	256	0.6	19.1	0.1780	10217
30	1819.3390	267	0.7	20.1	0.1916	9493

Figure S24: HRMS (ESI) of compound **6**

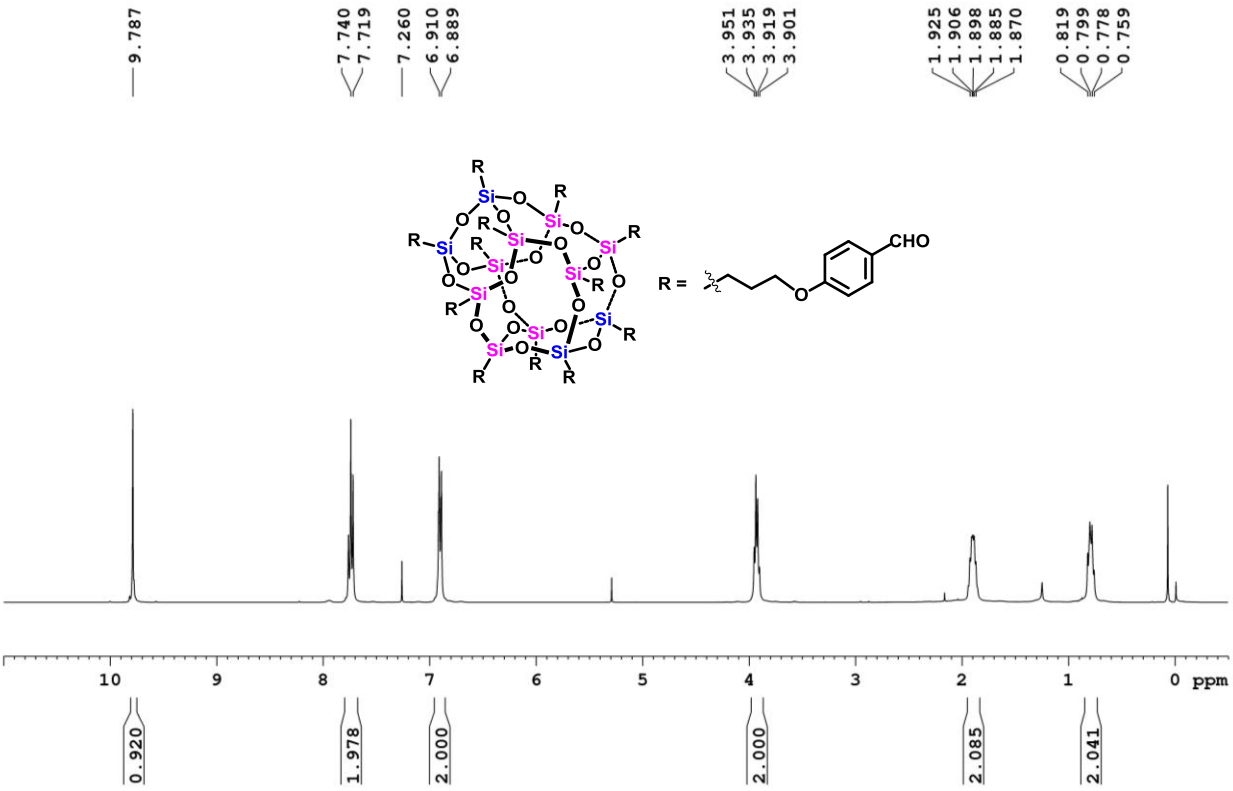


Figure S25: ^{1}H NMR (400 MHz) of compound **7** in $CDCl_3$

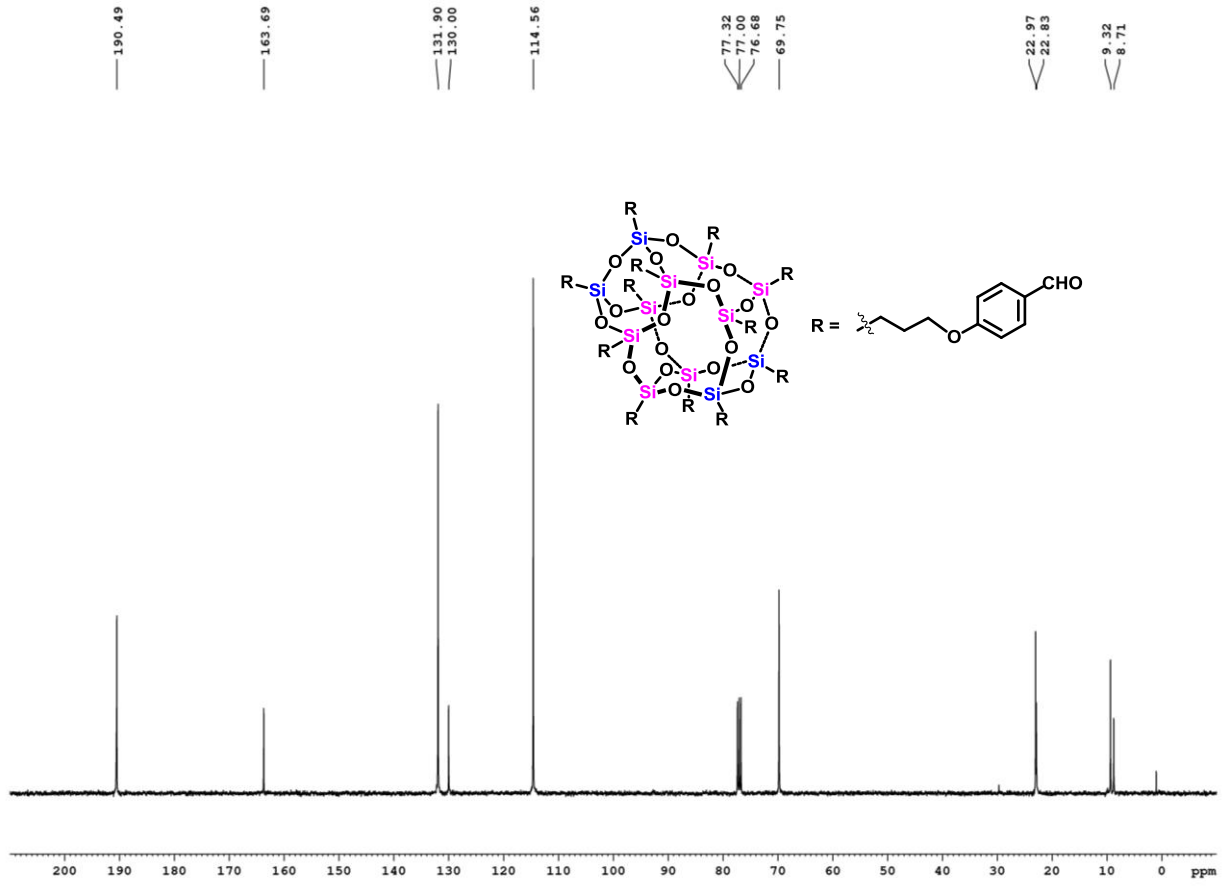


Figure S26: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **7** in $CDCl_3$

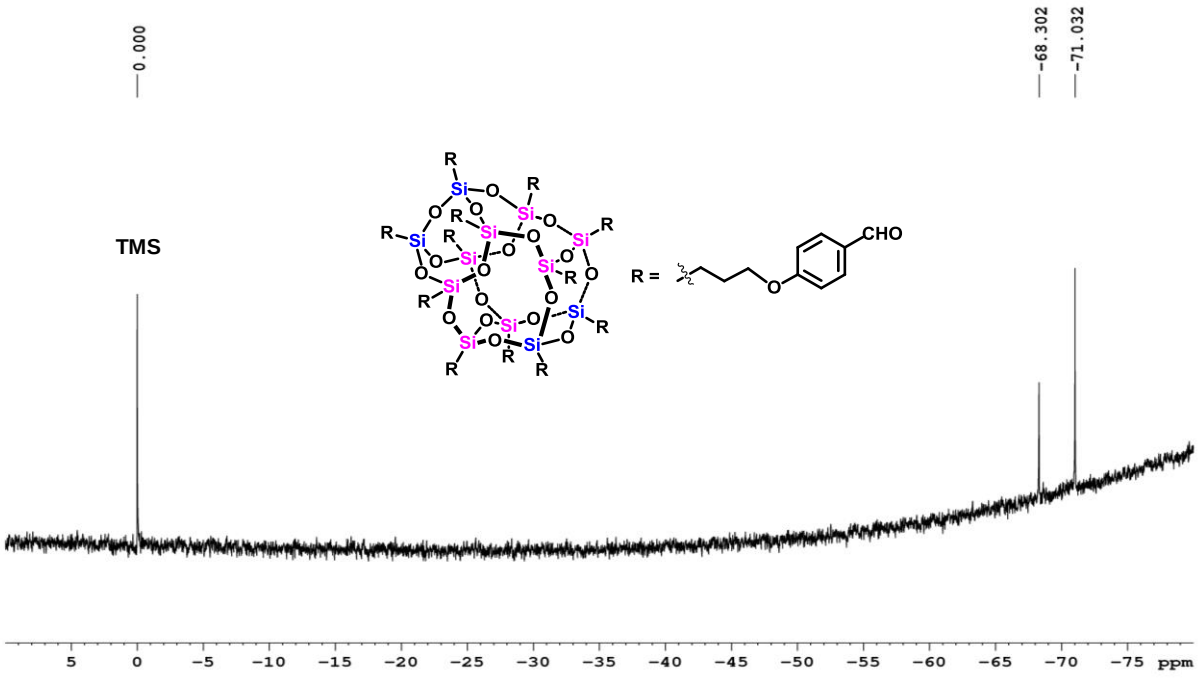


Figure S27: $^{29}Si\{^{1}H\}$ NMR (79MHz) of compound **7** in $CDCl_3$

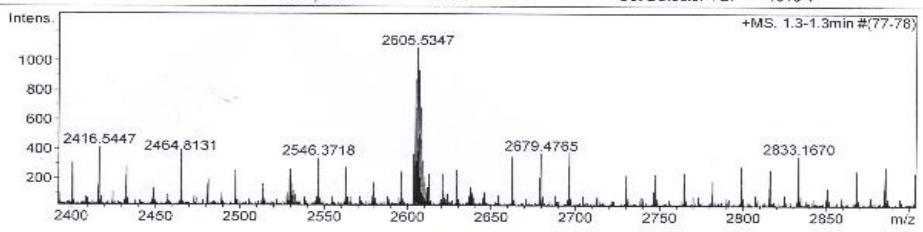
Mass Spectrum List Report

Analysis Info

Analysis Name	VERC571029005.d	Acquisition Date	10/29/2014 4:01:14 PM
Method	Natee20130403.m	Operator	Administrator
Sample Name	T12-p-benzaaldehyde-1	Instrument	micrOTOF 72
	T12-p-benzaaldehyde-1		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	400.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	386 V
Scan End	3000 m/z	Skimmer 1	54.4 V	Set Reflector	1300 V
		Hexapole 1	21.4 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	2416.5447	289	26.8	11.3	0.0328	73644
2	2416.5447	288	26.8	11.3	0.0328	73643
3	2432.6836	268	24.9	10.5	0.0334	72929
4	2448.7817	121	11.2	4.7	0.0403	60762
5	2464.8131	371	34.4	14.4	0.0317	77787
6	2529.8686	181	16.8	7.0	0.0121	209253
7	2546.3718	326	30.3	12.8	0.0346	73544
8	2562.7205	265	24.6	10.4	0.0331	77418
9	2579.1801	158	14.7	6.3	0.0340	75855
10	2595.7911	184	17.0	7.3	0.0343	75597
11	2604.5235	863	80.1	34.3	0.2366	11008
12	2605.5347	1077	100.0	42.9	0.2511	10377
13	2606.5414	923	85.7	36.7	0.2542	10254
14	2607.5578	673	62.5	26.8	0.2053	12703
15	2608.5631	293	27.2	11.7	0.2913	8955
16	2610.5493	118	11.0	4.7	0.1976	13209
17	2611.5436	129	12.0	5.2	0.0488	53563
18	2612.5128	217	20.1	8.6	0.0400	65393
19	2629.1667	245	22.7	9.8	0.0344	76322
20	2637.5468	134	12.4	5.4	0.0969	27224
21	2662.5487	340	31.5	13.8	0.0358	74390
22	2679.4765	362	33.6	14.7	0.0345	77665
23	2730.1675	214	19.9	8.9	0.0345	79234
24	2764.2784	227	21.0	9.5	0.0344	80383
25	2798.7311	274	25.4	11.7	0.0356	78559
26	2833.1670	346	32.1	15.0	0.0352	80510
27	2885.3990	151	14.1	6.7	0.0385	75038
28	2938.1817	237	22.0	10.6	0.0355	82814
29	2955.8509	392	36.4	17.6	0.0360	82083
30	2973.5651	271	25.2	12.1	0.0355	83682

Figure S28: HRMS (ESI) of compound **7**

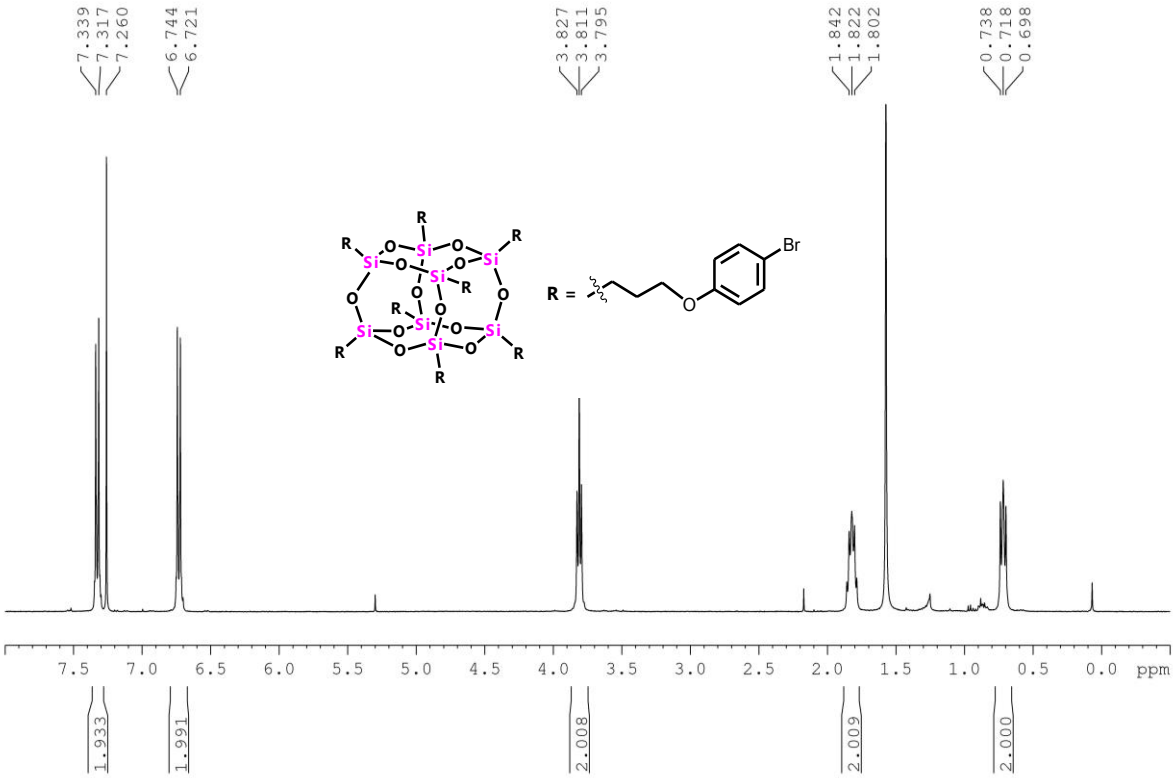


Figure S29: ^{1}H NMR (400 MHz) of compound **8** in $CDCl_3$

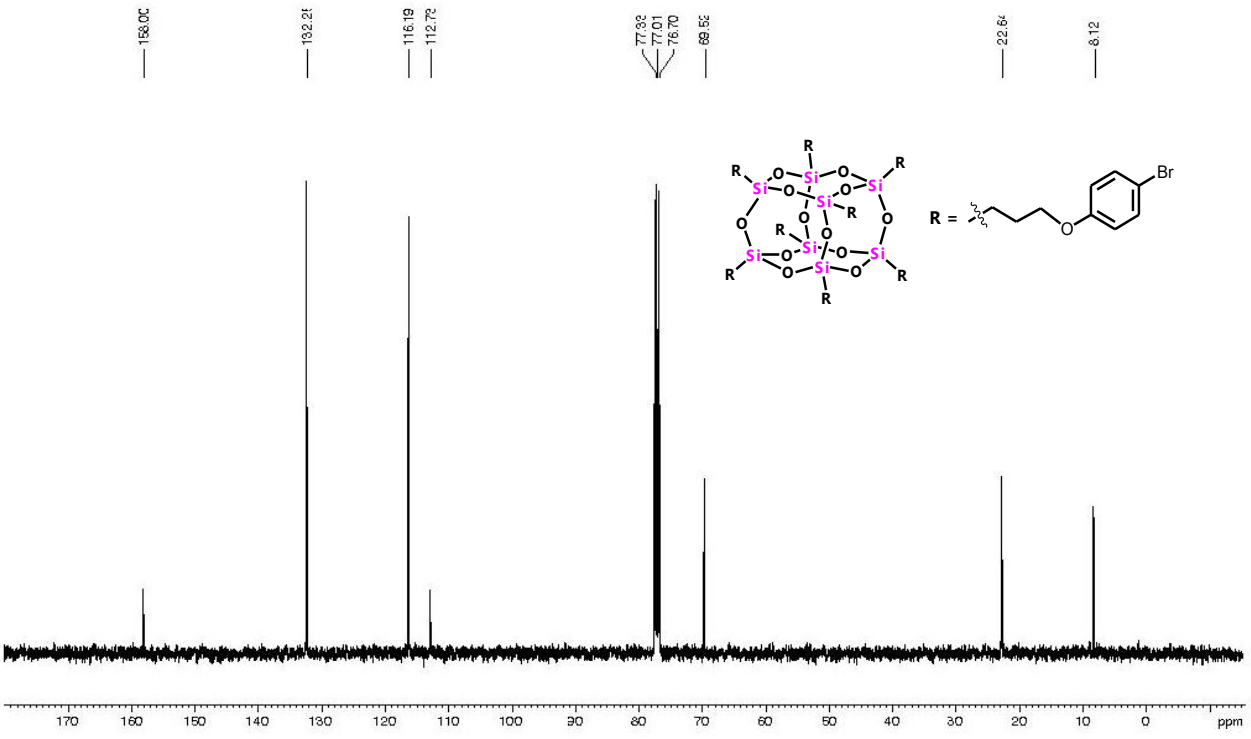


Figure S30: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **8** in $CDCl_3$

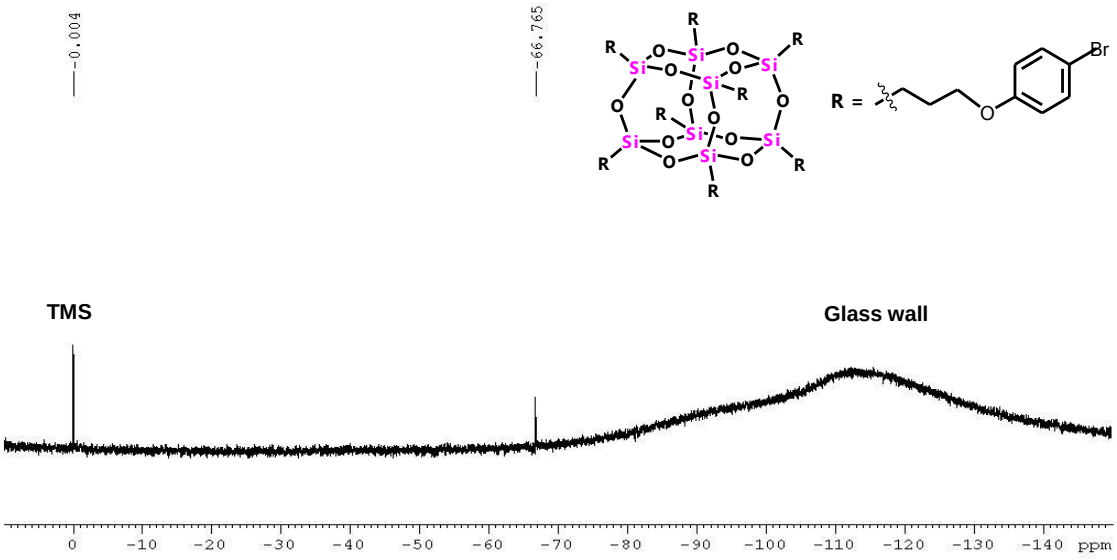
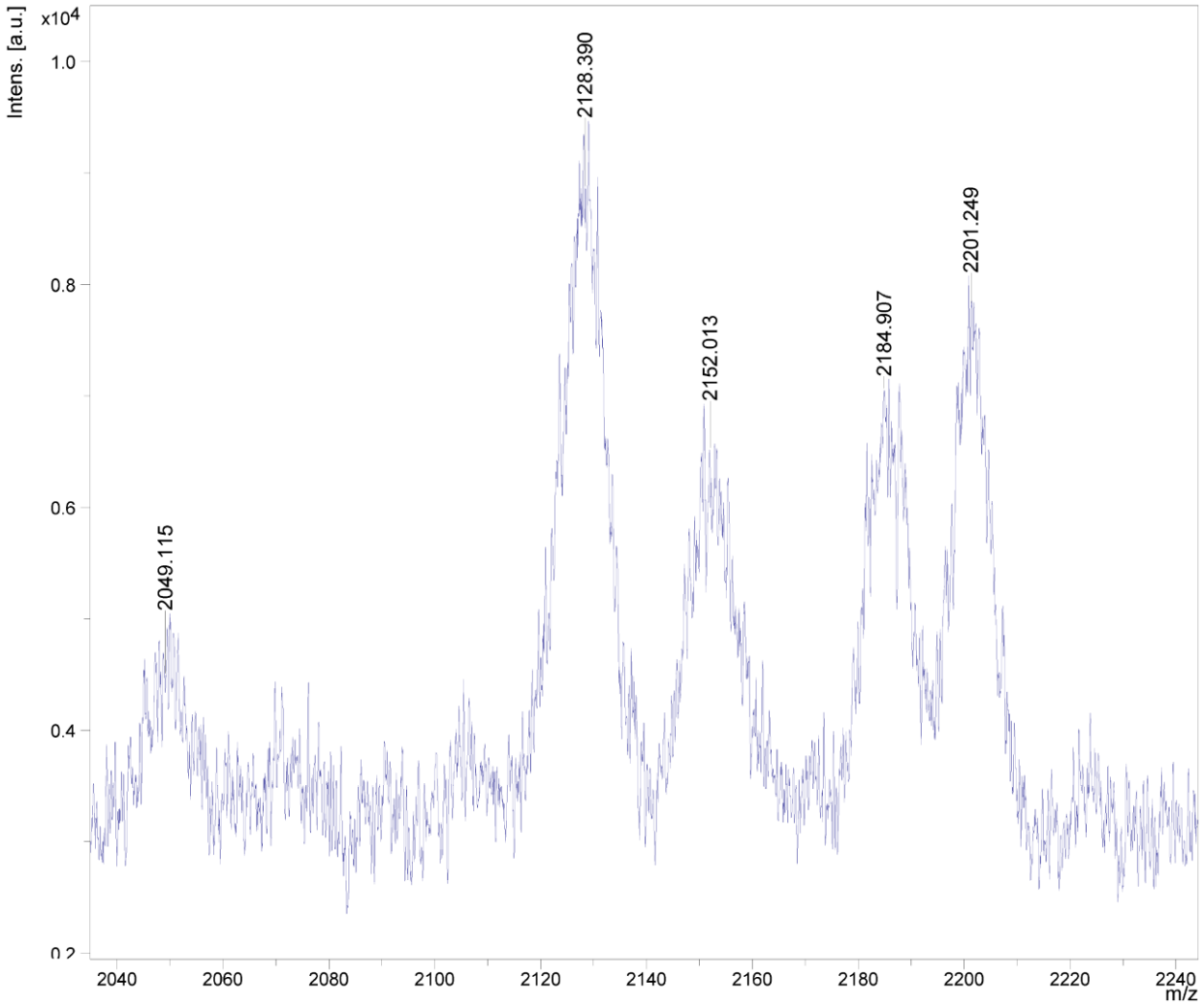


Figure S31: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of compound **8** in $CDCl_3$

D:\DATA\Pat\20140910\T8Gate1000-2

Comment 1

Comment 2



Acquisition Parameter

Date of acquisition	2014-09-10 13:30:19
Acquisition method name	D:\Methods\flexControlMethods\LP_pepmix_jj.par
Aquisition operation mode	Linear
Voltage polarity	POS
Number of shots	380
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

User	Pat
Instrument	FLEX-PC
Instrument type	autoflexTOF/TOF

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Figure S32: MALDI-TOF MS of compound **8**

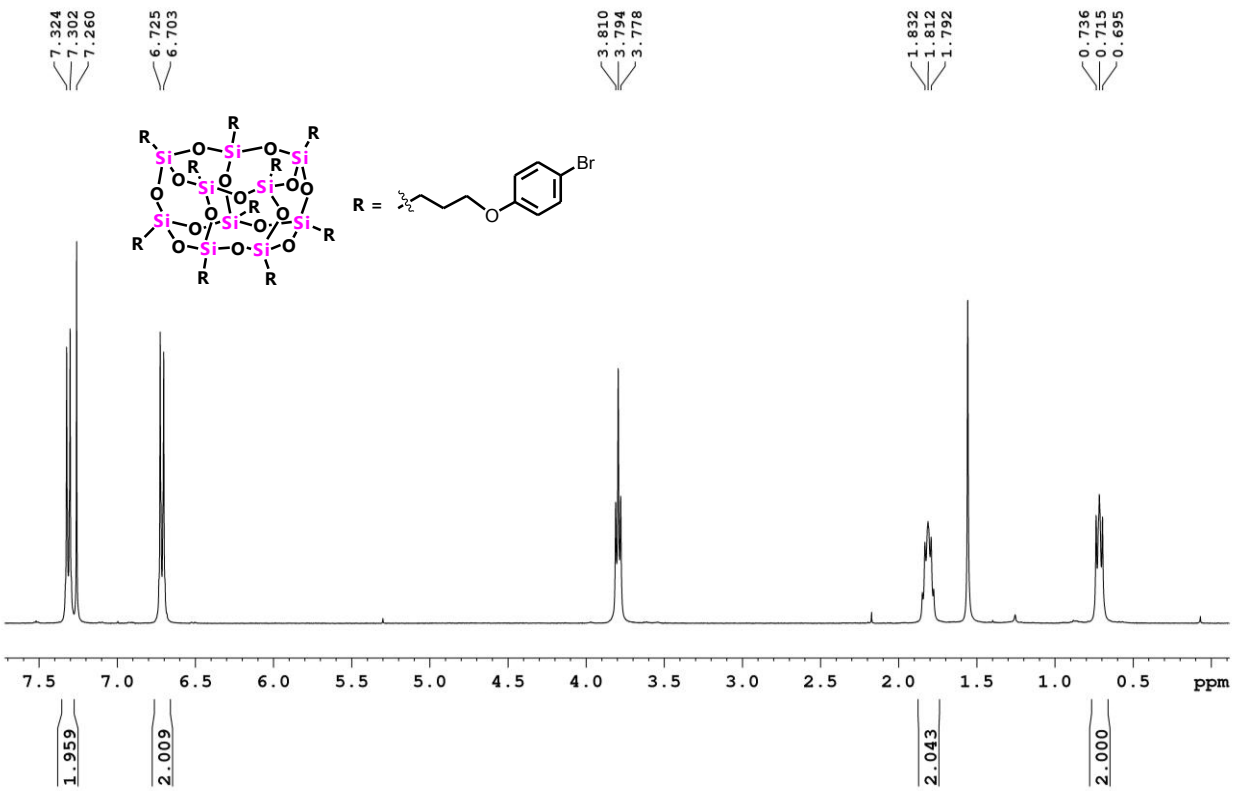


Figure S33: ^{1}H NMR (400 MHz) of compound **9** in $CDCl_3$

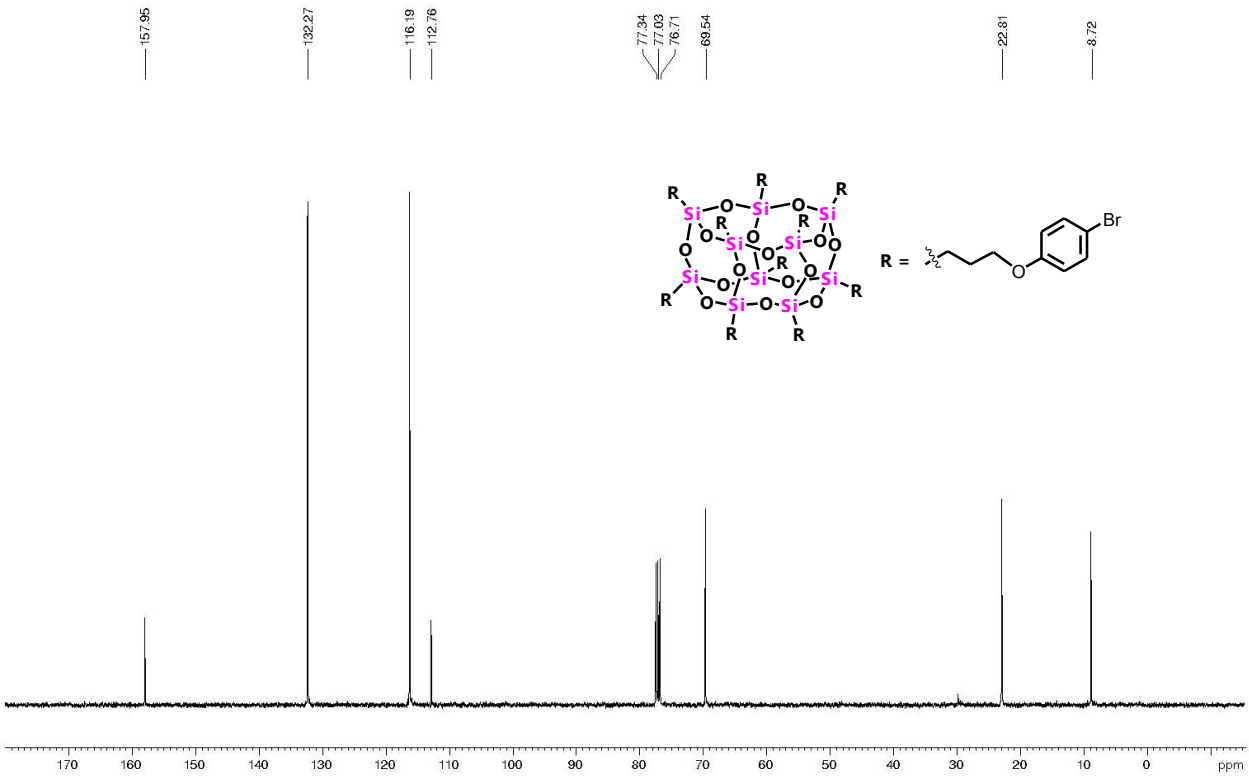


Figure S34: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **9** in $CDCl_3$

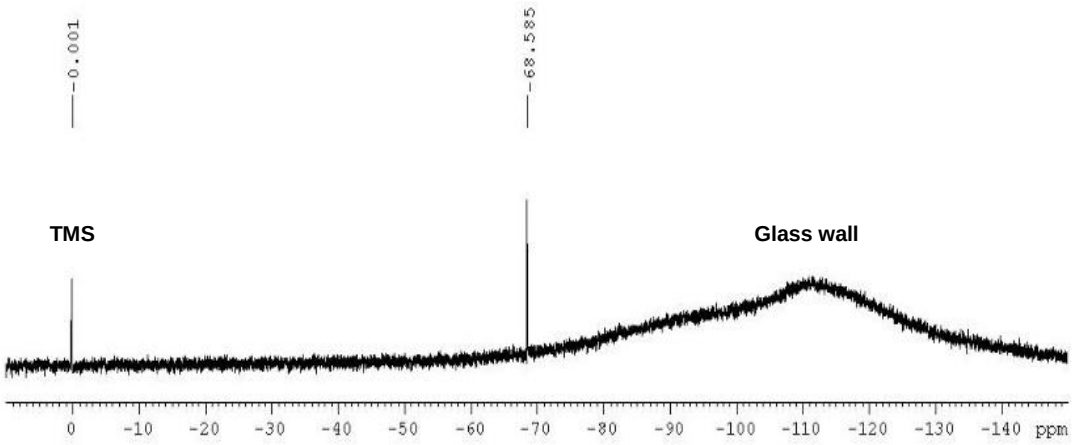
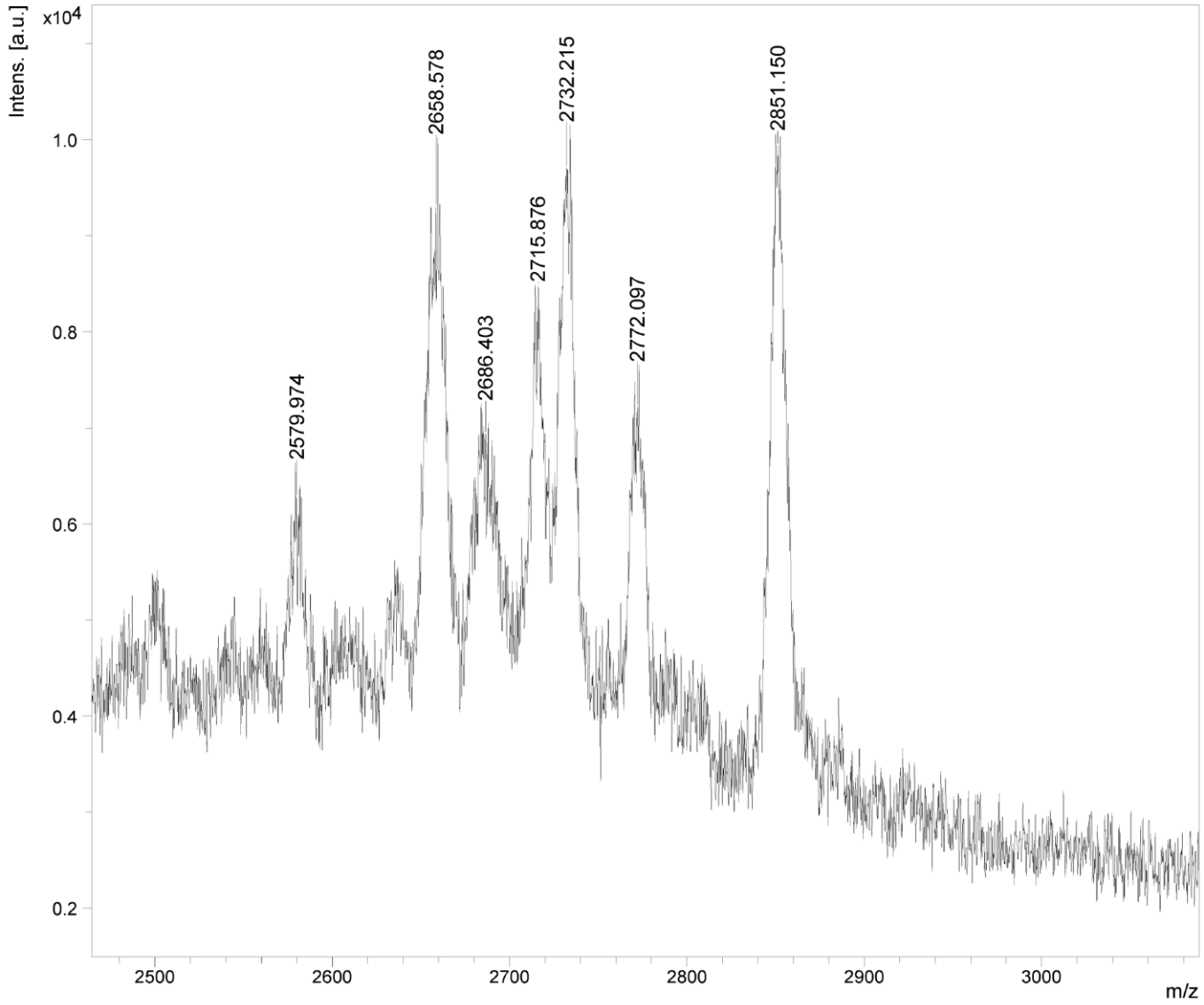


Figure S35: $^{29}Si\{^{1}H\}$ NMR (79 MHz) of compound **9** in $CDCl_3$

D:\DATA\Pat\20140910\T10Gate1000-2

Comment 1

Comment 2



Acquisition Parameter

Date of acquisition	2014-09-10 13:40:03
Acquisition method name	D:\Methods\flexControlMethods\LP_pepmix_jj.par
Aquisition operation mode	Linear
Voltage polarity	POS
Number of shots	590
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

User	Pat
Instrument	FLEX-PC
Instrument type	autoflexTOF/TOF

Bruker Daltonics flexAnalysis printed: 09/13/2014 12:46:55 PM

Figure S36: MALDI-TOF MS of compound **9**

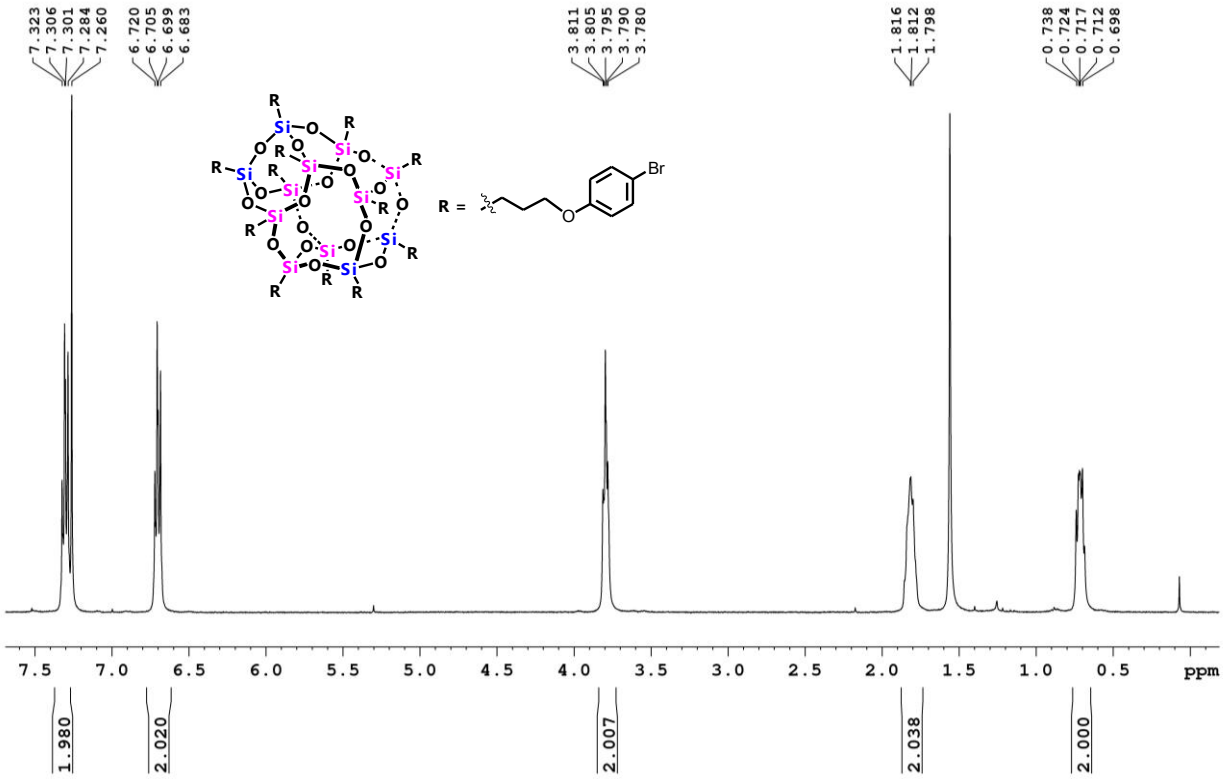


Figure S37: ^{1}H NMR (400 MHz) of compound **10** in $CDCl_3$

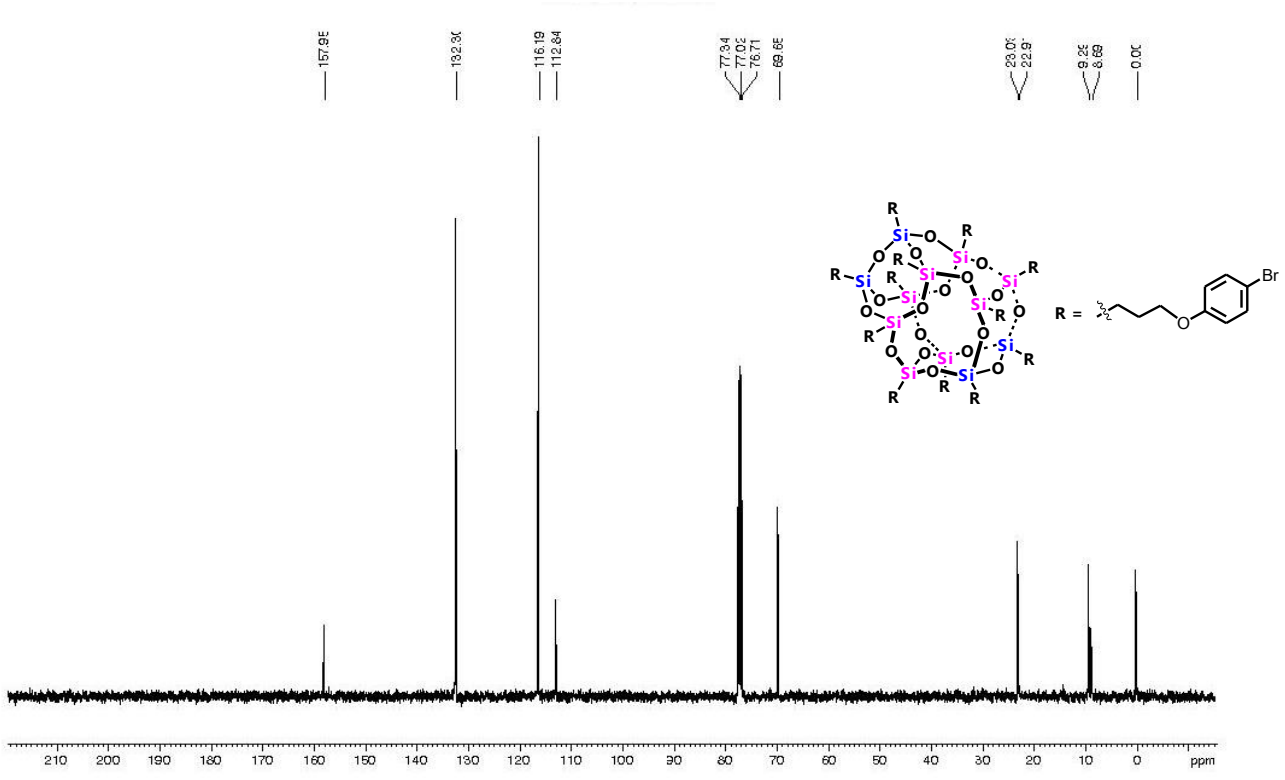


Figure S38: $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **10** in $CDCl_3$

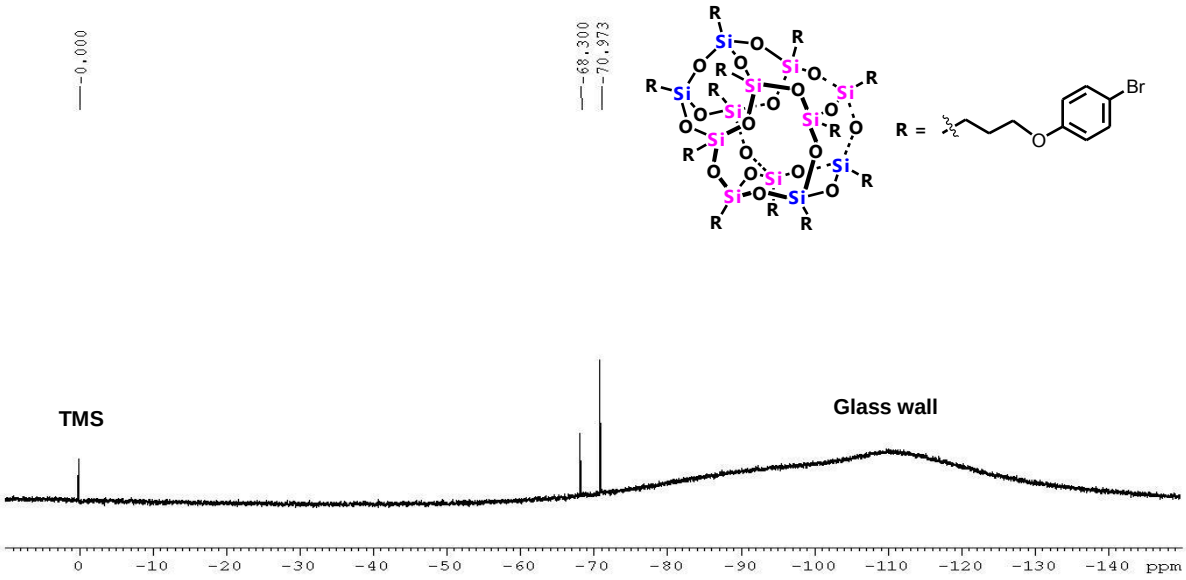
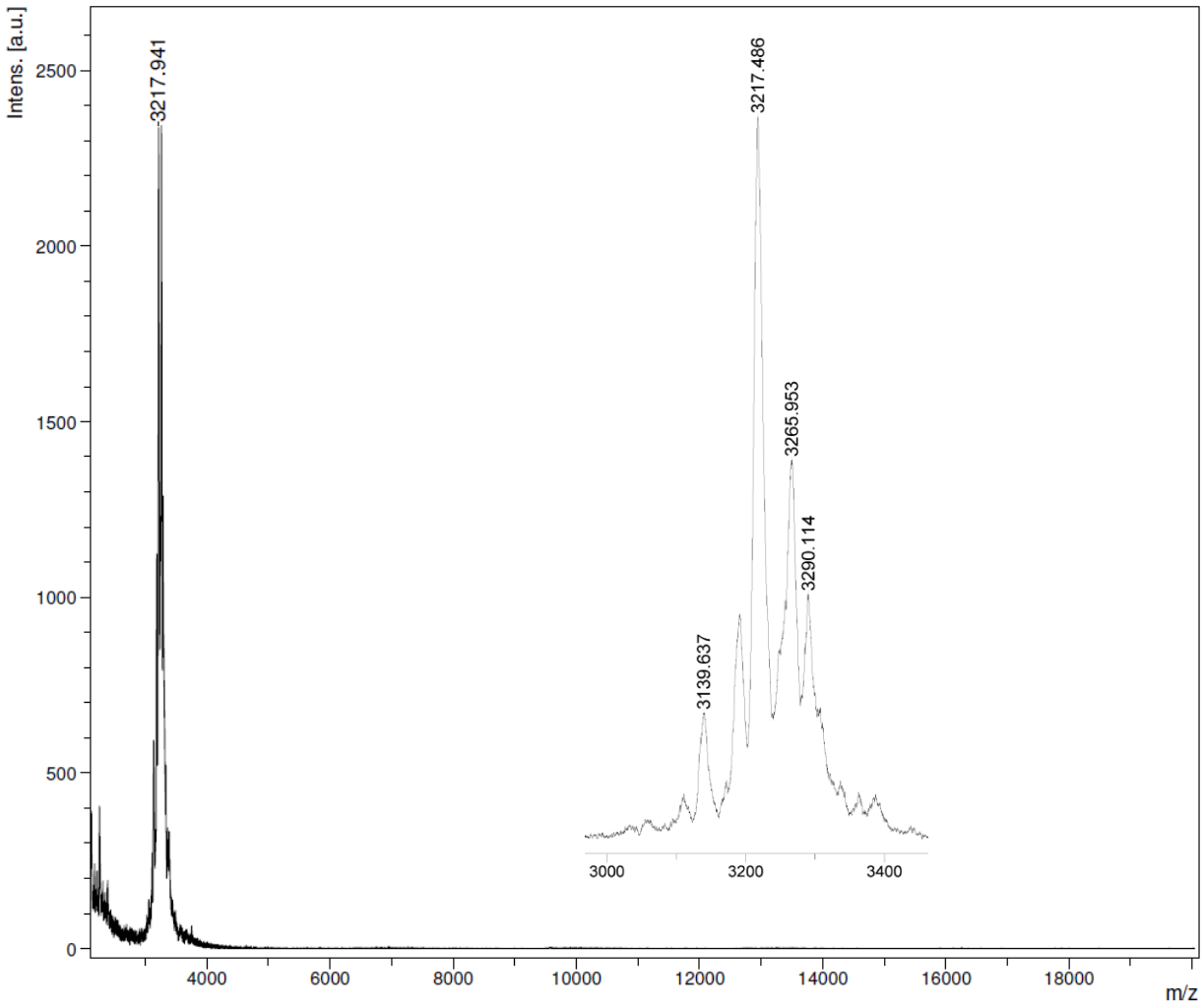


Figure S39: $^{29}Si\{^{1}H\}$ NMR (79MHz) of compound **10** in $CDCl_3$

D:\DATA\Pat\20140826\T12DHB1-10LPpromix

Comment 1
Comment 2



Acquisition Parameter

Date of acquisition	2014-08-26 12:25:29
Acquisition method name	D:\Methods\flexControlMethods\LP_ProtMix.par
Aquisition operation mode	Linear
Voltage polarity	POS
Number of shots	650
Name of spectrum used for calibration	20140826\StdPepmix2
Calibration reference list used	PeptideCalibStandard mono

Instrument Info

User	Pat
Instrument	FLEX-PC
Instrument type	autoflexTOF/TOF

Bruker Daltonics flexAnalysis printed: 08/26/2014 12:39:50 PM

Figure S40: MALDI-TOF MS of compound **10**

Reference

1. B. Marciniec, M. Dutkiewicz, H. Maciejewski, and M. Kubicki, *Organometallics* 2008, **27**, 793-794.