

Supporting Information for

Tricky but repeatable synthetic approach to branched, multifunctional silsesquioxane dendrimer derivatives

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1. General Considerations

The chemicals were purchased from the following sources: Sigma-Aldrich for toluene, tetrahydrofuran (THF), *n*-hexane, acetonitrile, methanol, dichloromethane, chloroform, chloroform-*d*, sodium bis(2-methoxyethoxy)aluminum hydride solution, dichloromethylsilane, dichloromethylvinylsilane, allyl glycidyl ether, 1-octene, Karstedt's catalyst – 2% xylene solution; TCI for chlorodimethylsilane; ABCR for trichlorosilane and lithium aluminium hydride; UNISIL for octavinylspherosilicate; Fluka Honeywell for celite. Following silsesquioxanes: iBuT₈-OSiVi, iBuT₈-OSiH, iBuT₈-Vi, PhT₈-Vi, DDSQ-2SiVi, DDSQ-4OSiVi, were prepared according to the literature procedure.¹⁻⁴ All solvents were dried over CaH₂ prior to use and stored under argon over 4Å molecular sieves. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All syntheses were conducted under an argon atmosphere using standard Schlenk-line and vacuum techniques.

2. Measurements

Nuclear Magnetic Resonance (NMR)

¹H, ¹³C, DEPT-135 and ²⁹Si Nuclear Magnetic Resonance (NMR) were performed on Bruker Ultra Shield 600, 400 and 300 spectrometers using CDCl₃ as a solvent. Chemical shifts are reported in ppm with reference to the residual solvent (CHCl₃) peaks for ¹H and ¹³C and to TMS for ²⁹Si NMR.

FT-IR spectroscopy

Fourier Transform-Infrared (FT-IR) spectra were recorded on a Nicolet iS5 (Thermo Scientific) spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm⁻¹ were collected, to record the spectra in a range of 4000-650 cm⁻¹.

Real-time FT-IR spectroscopy

In-situ FT-IR measurements were performed on a Mettler Toledo ReactIR 15 equipped with a DS 6.3 mm AgX DiComp Fiber Probe with a diamond sensor, and a Hg-Cd telluride detector. For all the spectra 256 scans were recorded with the resolution of 1 cm⁻¹ in 1 min intervals.⁵

Gel permeation chromatography (GPC)

Gel permeation chromatography analyses were performed using a Waters Alliance 2695 system equipped with a Waters 2412 RI detector and a set of three serially connected 7.8x300 mm columns (Water Styragel HR1, HR2 and HR4). THF was used as a mobile phase in a flow rate of 0.60 mL/min; the column oven temperature was 35°C and detector temperature 40°C. Molecular weight (M_n, M_w) and polydispersity index (PDI) values were calculated based on calibration curve using polystyrene standards (Shodex) in a range from 1.31 x 10³ to 3.64 x 10⁶ Da.

Elemental analyses (EA)

Elemental analyses (EA) were performed using a Vario EL III instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany).

X-ray crystallography

Diffraction data were collected by the ω -scan technique, for **G0-4D-4H** at 120(1) K, on a Rigaku SuperNova four-circle diffractometer with Atlas CCD detector, equipped with mirror-monochromatized CuK _{α} radiation source ($\lambda = 1.54178 \text{ \AA}$), and for **G1-2D-4H** at 100(1) K, on Rigaku XCalibur four-circle diffractometer with Eos CCD detector, equipped with graphite-monochromatized MoK _{α} radiation source ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz-polarization as well as for absorption effects.⁶ The structures were solved with SHELXT⁷ and refined with the full-matrix least-squares procedure on F² by SHELXL-2013.⁸ All non-hydrogen atoms were refined anisotropically, hydrogen

atoms were placed in idealized positions and refined as ‘riding model’ with isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times U_{eq} of appropriate carrier atoms. In the structure **G0-4D-4H** one of the -O-SiMe₂-CH₂-CH₂-SiHMe₂ groups is disordered over two alternative positions, the site occupation factors refined at 0.75(9)/0.25(9). Weak restraints have been applied to both positional and thermal parameters. The relevant crystallographic data together with the details of structure refinement are listed in **Table S1**.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-2184824 (**G0-4D-4H**), CCDC-2184825 (**G1-2D-4H**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk.

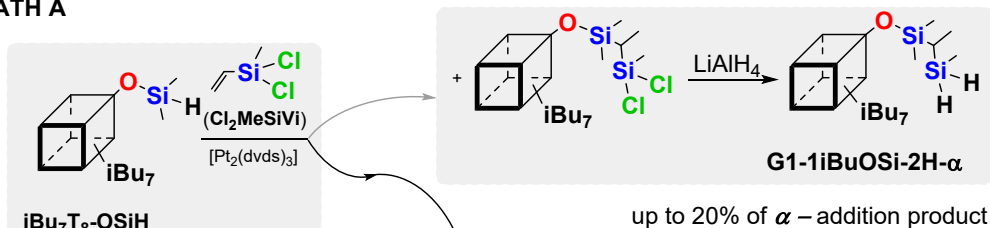
Table S1. Crystal data, data collection and structure refinement

Compound	G0-4D-4H	G1-2D-4H
Formula	C ₇₂ H ₁₀₈ O ₁₄ Si ₁₆	C ₅₆ H ₆₄ O ₁₄ Si ₁₂
Formula weight	1647.02	1298.15
Crystal system	triclinic	orthorhombic
Space group	P-1	Pbca
a (Å)	14.3705(4)	10.1660(3)
b (Å)	14.5795(4)	26.3663(7)
c (Å)	24.7232(5)	24.1387(7)
α (°)	91.0701(18)	90
β (°)	94.006(2)	90
γ (°)	119.020(3)	90
V(Å ³)	4510.3(2)	6470.1(3)
Z	2	4
D _x (g cm ⁻³)	1.213	1.333
F(000)	1752	2720
μ(mm ⁻¹)	2.586	0.300
Reflections:		
collected	40198	16025
unique (R _{int})	16071 (0.0651)	6519 (0.0298)
with I>2σ(I)	14238	5289
R(F) [I>2σ(I)]	0.0915	0.0949
wR(F ²) [I>2σ(I)]	0.2053	0.2372
R(F) [all data]	0.0983	0.1125
wR(F ²) [all data]	0.2088	0.2470
Goodness of fit	1.056	1.040
max/min Δρ (e·Å ⁻³)	1.97/-1.00	1.03/-0.67
CCDC number	2184824	2184825

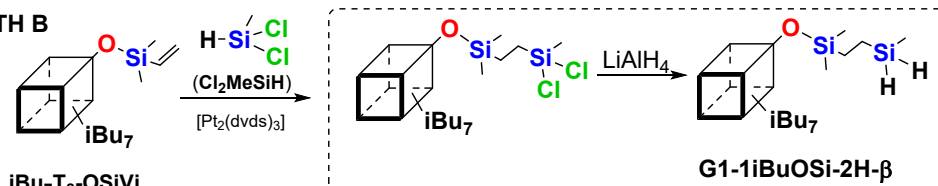
3. Synthetic procedures

The verification of the location of the Si-H bond in the appropriate substrate

PATH A



PATH B



To a two-necked round-bottom flask equipped with a condenser and magnetic stirrer, $\text{iBu}_7\text{T}_8\text{-OSiH}$ (METHOD A)/ $\text{iBu}_7\text{T}_8\text{-OSiVi}$ (METHOD B) (0.100 g, 0.12 mmol/ 0.102 g, 0.11 mmol), anhydrous toluene (3 mL) and dichlorovinylmethylsilane (Cl_2MeSiVi : 0.033 mL, 0.22 mmol) (METHOD A)/ dichloromethylsilane (Cl_2MeSiH : 0.023 mL, 0.22 mmol) (METHOD B) were placed in an argon atmosphere. The reaction was heated to 40°C and $[\text{Pt}_2(\text{dvds})_3]$ (0.13 μL , 1.12×10^{-5} mmol / 0.12 μL , 1.11×10^{-5} mmol) was added. The reaction mixture was kept at 95°C for 24 hours. After cooling it to room temperature, the excess of silane and solvent was evaporated under a vacuum for 5 hours. After that, the compound was dissolved in anhydrous THF (2 mL) and lithium aluminium hydride (0.010 g, 0.27 mmol/0.010 g, 0.26 mmol) was added to the reaction mixture. The reaction was carried out at room temperature for 24 hours. Then, the solvent was evaporated under reduced pressure. *N*-hexane was added to the crude product and the mixture was filtered by a syringe filter (0.2 μm) and washed with *n*-hexane (5 mL). The solvent was evaporated under a vacuum and isolated as a white solid.

Selectivity of $\text{G1-1iBuOSi-2H-}\beta$: $\text{G1-1iBuOSi-2H-}\alpha$ products for PATH A was 80 : 20 and for PATH B was 100 : 0.

General procedure for the one-pot synthesis of dendritic systems with mono- T_8 and double-decker silsesquioxane core through hydrosilylation followed by reduction reaction:

- LiAlH_4 as a reduction agent

The synthetic procedure was described for G0-1iBu-1H as an example. To a two-necked round-bottom flask equipped with a condenser and magnetic stirrer, $\text{iBu}_7\text{T}_8\text{-Vi}$ (0.106 g, 0.13 mmol), anhydrous toluene (3 mL) and chlorodimethylsilane (0.03 mL, 0.25 mmol) were placed in an argon atmosphere. The reaction was heated to 40°C and $[\text{Pt}_2(\text{dvds})_3]$ (0.14 μL , 1.25×10^{-5} mmol) was added. The reaction mixture was kept at 95°C for 24 hours. After cooling it to room temperature, the excess of silane and solvent was evaporated under a vacuum for 5 hours. After that, the compound was dissolved in anhydrous THF (2 mL) and lithium aluminium hydride (0.006 g, 0.15 mmol) was added to the reaction mixture. The reaction was carried out at room temperature for 24 hours. Then, the solvent was evaporated under reduced pressure. *N*-hexane was added to the crude product and the mixture was filtered by a syringe filter (0.2 μm) and washed with *n*-hexane (5 mL). The solvent was evaporated under a vacuum and isolated as a white solid, in a total yield of 90%.

- **Red-Al[®] as a reduction agent**

The procedure for the synthesis of **G0-2D-2H** is described as an example. To a two-neck round-bottom flask equipped with a condenser and magnetic stirrer, **DDSQ-2SiVi** (0.200 g, 0.17 mmol) was placed in argon atmosphere along with anhydrous toluene (6.0 mL), and 4 equivalent of silane-chlorodimethylsilane (0.071 mL, 0.66 mmol) and 10⁻⁴ equiv. of [Pt₂(dvds)₃] (0.38 μL 3.32×10⁻⁵ mmol). The reaction mixture was kept at 95°C for 24 hours. After cooling it to room temperature, the excess of silane and solvent was evaporated under a vacuum for 8 hours. After that anhydrous toluene (8.0 mL), sodium bis(2-methoxyethoxy) aluminium hydride solution (0.65 g, 3.20 mmol) (Red-Al[®]) were added. The reaction mixture was kept at room temperature for 20 hours.

Isolation:

- **Method I:** The post-reaction mixture was evaporated under reduced pressure. The crude product was dissolved in DCM and precipitated in MeCN. After decantation, the remains of MeCN were evaporated. The crude, white powder was washed with DCM several times (3 x 10 mL) and the decant was evaporated under a vacuum and isolated as a white solid, in a total yield of 64%.
- **Method II:** The reaction mixture was added dropwise to the mixture of 10% acetic acid water solution (10 mL) and toluene (5 mL). The white solid was precipitated. After the agitation was turned off, the phases separated. The water layer was extracted by toluene (10 mL). The organic layer was combined and toluene was evaporated under a vacuum. The white solid was isolated in a total yield of 90%.

General procedure for the one-pot synthesis of G1 dendritic systems with octa-T₈ silsesquioxane core through hydrosilylation followed by reduction reaction:

Procedure for the one-pot synthesis of G1-8T-24H:

The reaction was carried out in an oven-dried Schlenk-type reactor under an argon atmosphere. Octavinyl spherosilicate (**octaT₈-OSiVi**) (1.00 g, 0.82 mmol) was placed along with anhydrous toluene (10.0 mL) and trichlorosilane (0.73 mL, 7.23 mmol) was added. To the prepared mixture of reagents Karstedt's complex was added (7.5 μL, 10⁻⁴ mol Pt/ mol SiVi), the reaction vessel was closed and heated at 95°C with stirring. The reaction was monitored with FT-IR and ¹H NMR spectroscopy, by following the band originating from SiVi units (FT-IR 1596 cm⁻¹). After the complete conversion of vinyl units, the reaction was cooled down, and then the toluene and an excess of chlorosilane were evaporated under reduced pressure. The obtained oil was dissolved in 20 mL of anhydrous toluene, and then 4.1 mL of Red-Al[®] sodium bis(2-methoxyethoxy) aluminium hydride solution was added dropwise and the reaction was stirred for 18 hours at room temperature. The resulting mixture was added to 2-propanol and stirred for 1 hour. After that, the solvents and volatile liquids were evaporated under reduced pressure. The product was extracted from the resulting mixture with *n*-hexane and then filtered through a cellite/silica gel column. Evaporation of *n*-hexane led to the formation of transparent oil in a total yield of 85%. NMR analysis showed the formation of only the β isomer. Caution: before the addition of Red-Al[®], the excess of trichlorosilane must be removed from the vessel. The presence of HSiCl₃ during the addition of Red-Al[®] leads to the formation of pyrophoric SiH₄.

Procedure for the one-pot synthesis of G1-8T-16H:

The reaction was carried out in an oven-dried Schlenk-type reactor under an argon atmosphere. Octavinyl spherosilicate (**octaT₈-OSiVi**) (5.00 g, 4,1 mmol, 32.68 mmol of vinyl groups) was placed along with anhydrous toluene (25 mL) and then 3.85 mL (36.98 mmol) dichloromethylsilane was added. To the prepared mixture of reagents Karstedt's complex was added (37.5 μL, 10⁻⁴ mol Pt/ mol SiVi), the reaction vessel was closed and heated at 95°C with stirring. The reaction was monitored with FT-IR

and ^1H NMR spectroscopy, by following the band originating from SiVi units (FT-IR 1596 cm^{-1}). After the complete conversion of vinyl units, the reaction was cooled down, and then the toluene and an excess of chlorosilane were evaporated under reduced pressure. The resulting oil was dissolved in 25 mL of anhydrous toluene and then 13.2 mL Red-Al[®] sodium bis(2-methoxyethoxy) aluminium hydride solution was added dropwise. Then the reaction mixture was stirred overnight at room temperature. After that, the mixture was added to 2-propanol and stirred for one hour. Then the solvents and the volatiles were removed under reduced pressure. The product was extracted from the resulting mixture with *n*-hexane and then filtered through a cellite/silica gel column. Evaporation of *n*-hexane led to the formation of transparent oil in a total yield of 85%. NMR analysis showed the formation of only the β isomer.

General procedure for the one-pot synthesis of G2 dendritic systems with octa-T₈ silsesquioxane core through hydrosilylation followed by reduction reaction:

To a mixture prepared from 2 g of **G1-8T-16H** (1.253 mmol, 20.06 mmol SiH) and 15 mL of anhydrous toluene, dichloromethylvinylsilane was added (3.18 g/2.95 mL, 22.56 mmol). To a resulting mixture, Karstedt's catalyst was added (2×10^{-4} mol Pt/SiH) and the reaction vessel was closed and heated to 100°C. The reaction was monitored with infrared spectroscopy. After the complete conversion of H-Si units mixture was cooled down and the solvent and chlorosilane excess were evaporated under reduced pressure. The obtained oil was dissolved in 20 mL of anhydrous THF and then 0.76 g (20 mmol) of LiAlH₄ was added and the reaction was stirred at room temperature overnight. The resulting mixture was filtered through a cannula. The resulting solution was filtrated through cellite/silica gel column and washed with THF, toluene and diethyl ether. Evaporation of the solvent gave 2.68 g (Yield 77%) of very viscous transparent oil.

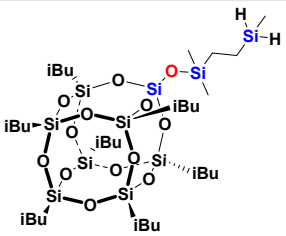
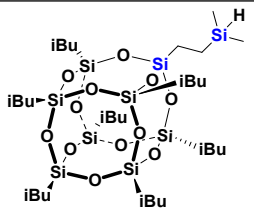
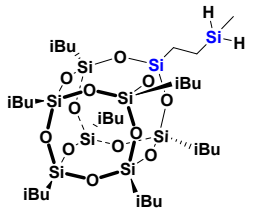
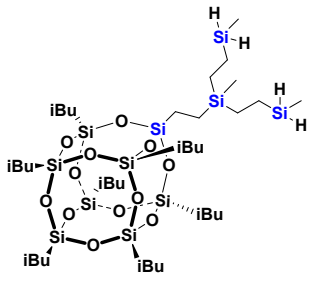
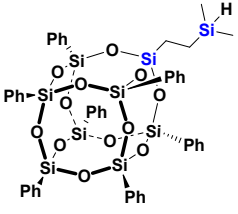
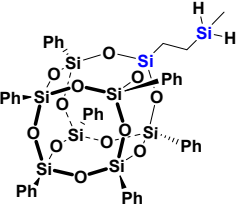
General procedure for the functionalization of G1-4D-8H through hydrosilylation:

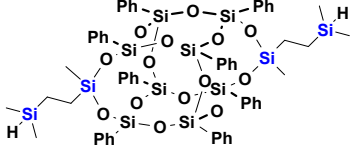
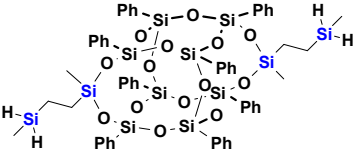
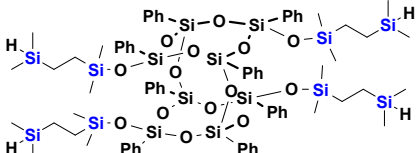
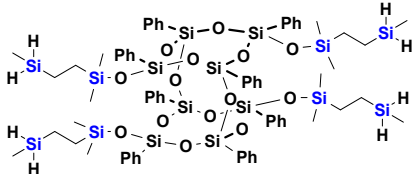
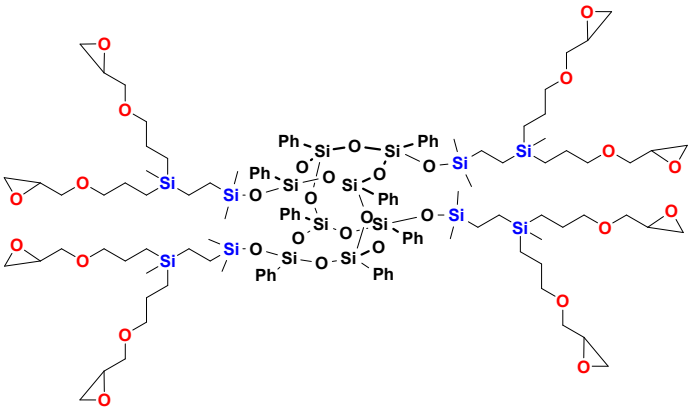
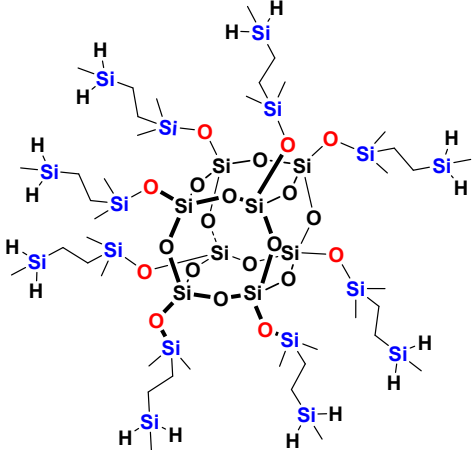
The synthetic protocol is presented for **G1-8D-8epoxy** as an example. To a two-necked round-bottom flask equipped with a condenser and magnetic stirrer, **G1-4D-8H** (0.108 g, 0.07 mmol), toluene (3 mL) and allyl glycidyl ether (0.07 mL, 0.61 mmol) were placed in an argon atmosphere. The reaction was heated to 40°C and [Pt₂(dvds)₃] (0.62 μL , 2.34×10^{-5} mmol) was added. The reaction mixture was kept at 95°C for 24 hours. After cooling it to room temperature, the reaction mixture was transferred to a flask and toluene and unreacted allyl glycidyl ether were evaporated under reduced pressure. The pure product was obtained in a total yield of 85%.

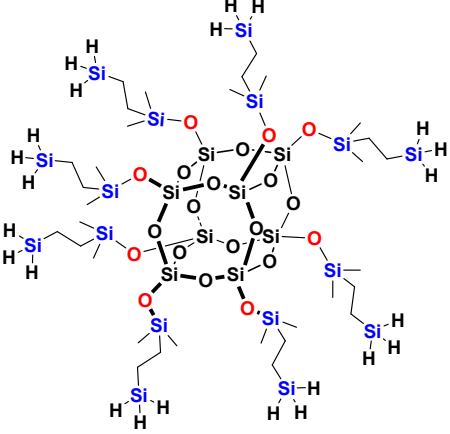
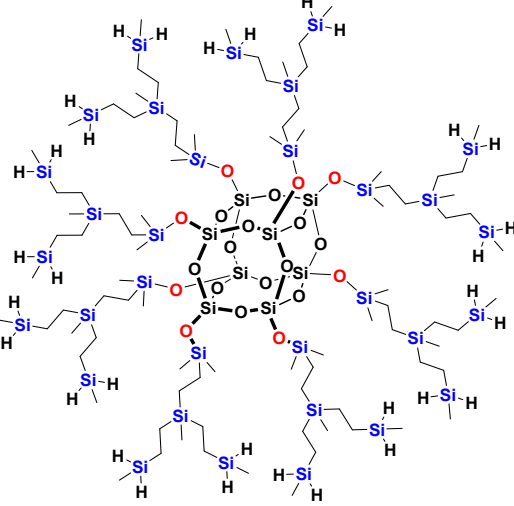
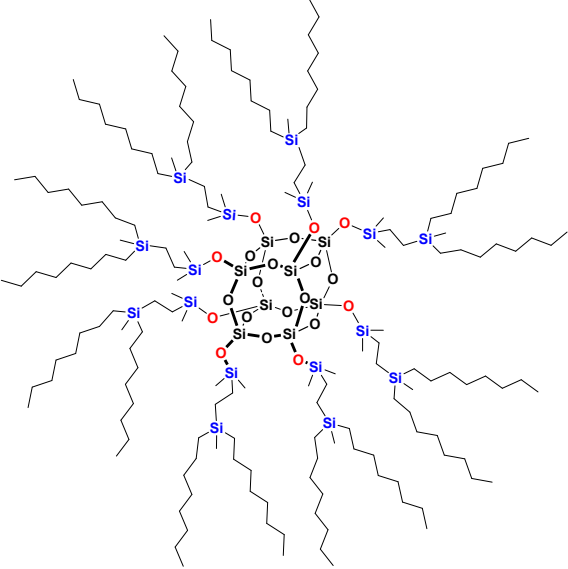
General procedure for the functionalization of G1-16T-16H through hydrosilylation:

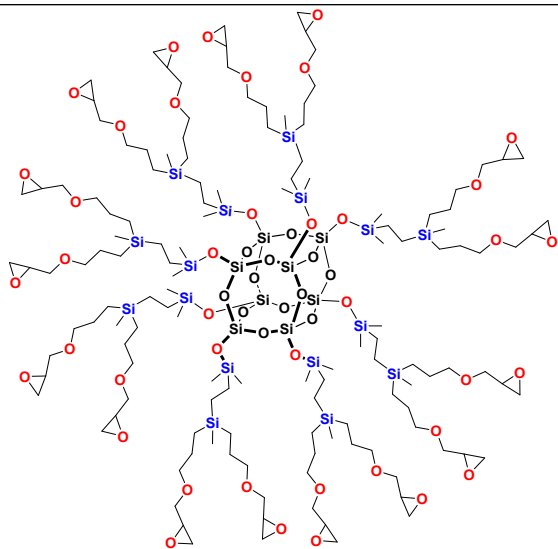
0.5g (0.313mmol, 5.01 mmol SiH) of **G1-8T-16H**, 5.64 mmol of alkene and 2.5 mL of toluene were placed in a 10 mL Schlenk-glass reactor. The prepared mixture was heated to 95°C and Karstedt's complex was added (2×10^{-4} Pt/mol SiH). The reaction was monitored by FT-IR spectroscopy by following the band assigned to SiH units at *ca.* 2124 cm^{-1} . After the disappearance of the H-Si band in the FT-IR spectrum, the mixture was cooled down to room temperature and then filtered through a silica gel/cellite column and washed with toluene. Evaporation of toluene gave viscous oils. Yields: 91% and 88% for 1-octene and allyl-glycidyl ether, respectively.

4. Table of isolated compounds:

Structure	Compound Abbrev.	Isolation Yield[%]	NMR spectra page:
	G1-1iBuOSi-2H-β	89	S-11-
	G0-1iBu-1H	90	S-13-
	G1-1iBu-2H	89	S-15-
 + (α -products)	G2-2iBu-4H	94	S-17-
	G0-1Ph-1H	53	S-20-
	G1-1Ph-2H	72	S-22-

	G0-2D-2H	91	S-24-
	G1-2D-4H	85	S-26-
	G0-4D-4H	94	S-28-
	G1-4D-8H	91	S-30-
	G1-8D-8epoxy	85	S-32-
	G1-8T-16H	85	S-34-

	<p>G1-8T-24H</p>	<p>85</p>	<p>S-36-</p>
	<p>G2-16T-32H</p>	<p>77</p>	<p>S-38-</p>
 <p>+ (α products)</p>	<p>G1-16T-16octyl</p>	<p>91</p>	<p>S-40-</p>



+ (α
products)

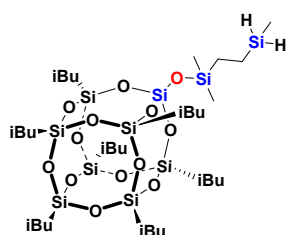
G1-16T-16epoxy

88

S-42-

5. Characterization data of the obtained products (^1H , ^{13}C , ^{29}Si NMR spectra and IR spectroscopy)

G1-1iBuOSi-2H- β



White solid. Isolated Yield 89%

^1H NMR (300 MHz, CDCl_3 , ppm): δ = 0.11 (s, 6H, $-\text{CH}_3$), 0.12-0.15 (t, 3H, $-\text{CH}_3$), 0.59-0.62 (m, 18H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$, CH_2-CH_2), 0.96 (dd, $J_{\text{H-H}}=6.6, 2.1$ Hz, 42H, $-\text{CH}_3$), 1.80-1.91 (m, 7H, $-\text{CH}(\text{CH}_3)_2$), 3.70-3.74 (m, 2H, Si-H).

^{13}C NMR (75.50 MHz, CDCl_3 , ppm): δ = -8.56 (Si- CH_3), -0.73 (Si- CH_3); 2.36 (Si- CH_2 -), 11.79 (Si- CH_2 -), 22.59-22.68 ($-\text{CH}_2\text{CH}(\text{CH}_3)_2$), 24.01-24.04 ($-\text{CH}(\text{CH}_3)_2$), 25.87 ($\text{CH}(\text{CH}_3)_2$).

^{29}Si NMR (79.50 MHz, CDCl_3 , ppm): δ = 11.44 ($-\text{Si}-\text{CH}_3$); -29.08 ($-\text{Si}-\text{H}$), -67.07, -67.10, -67.87, -67.90 ($-\text{Si}-\text{iBu}$), -109.64 (SiO_4).

IR (ATR, cm^{-1}): 2952.30, 2924.49, 2905.56, 2868.00 (C-H), 2127.19 (Si-H), 1464.32 (C-H), 1228.77 (Si-C), 1168.48, 1075.60 (Si-O-Si), 901.41 (Si-H).

EA: Anal. calcd for $\text{C}_{33}\text{H}_{78}\text{O}_{13}\text{Si}_{10}$ (%): C, 41.12, H, 8.16; found: C, 41.28; H, 8.19.

GPC: M_w = 1165; M_n = 955; D = 1.22.

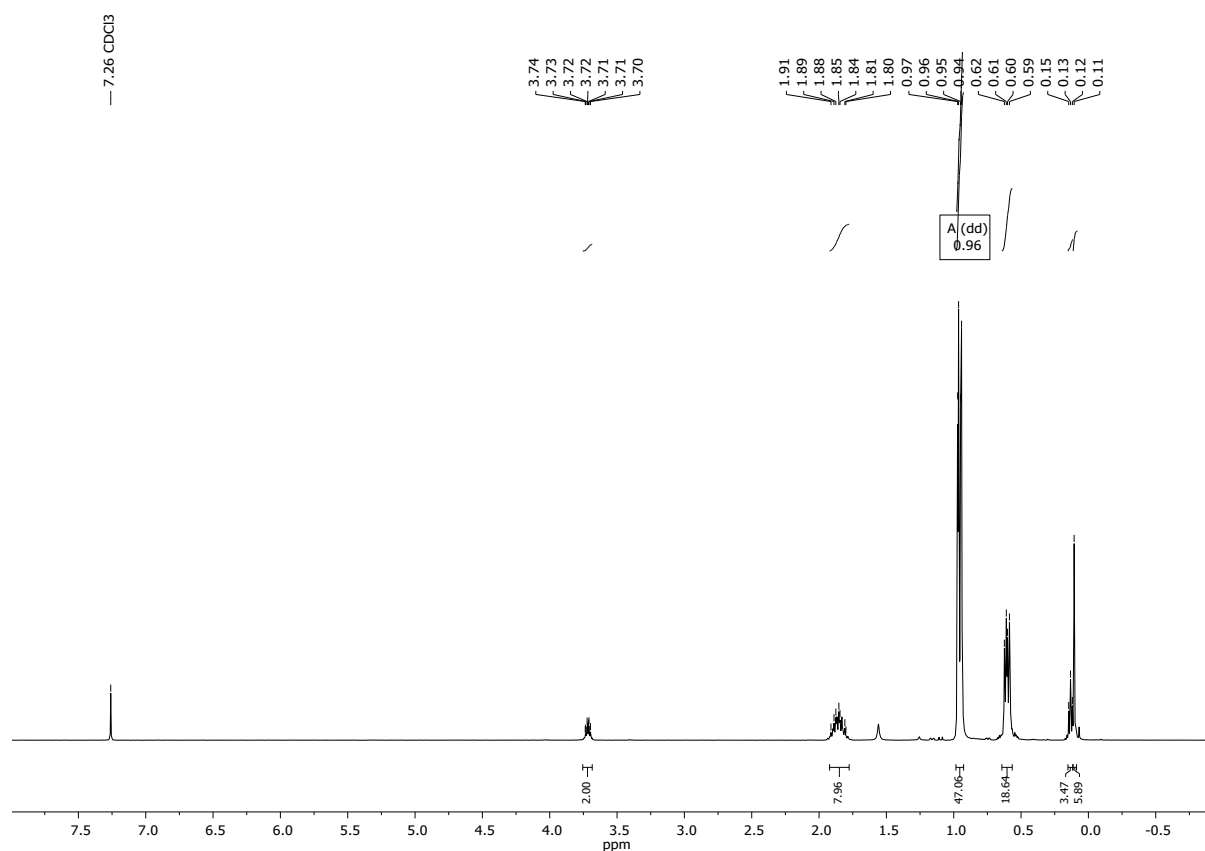


Figure S1 ^1H NMR (300 MHz, CDCl_3) spectrum of G1-1iBuOSi-2H- β .

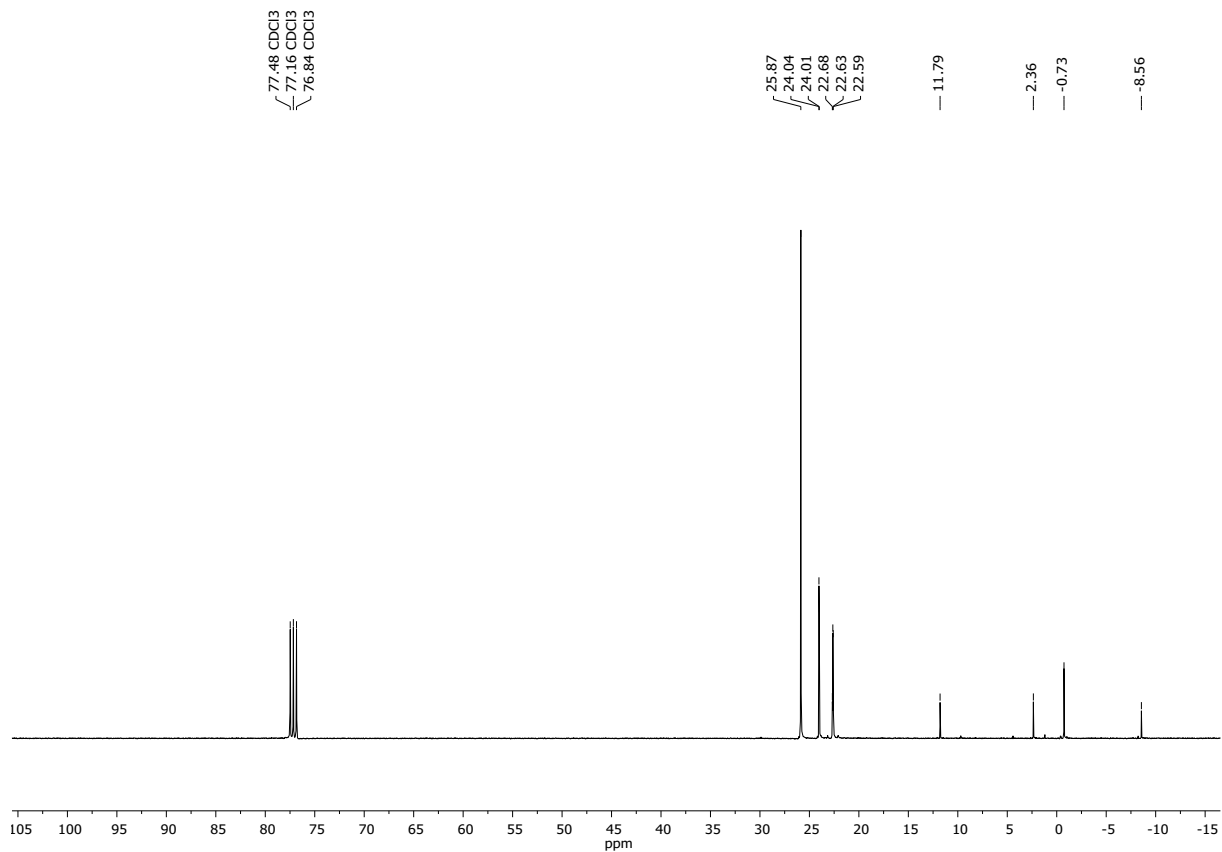


Figure S2 ^{13}C NMR (75.50 MHz, CDCl_3) spectrum of **G1-1iBuOSi-2H- β** .

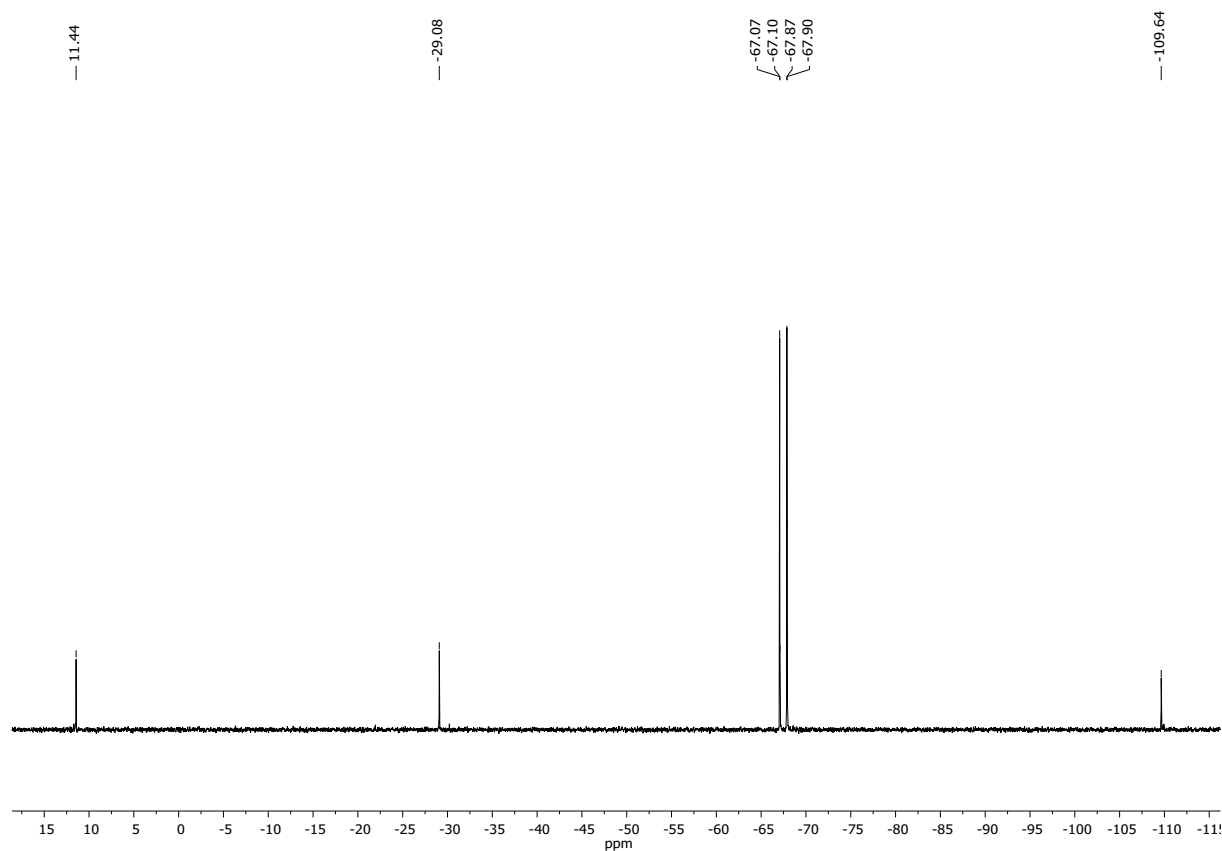
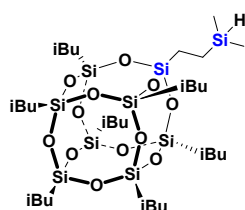


Figure S3 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-1iBuOSi-2H- β** .

G0-iBu-1H



White solid. Isolated Yield 90%

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.06 (d, $J_{\text{H-H}}=3.6$ Hz, 6H, -CH₃), 0.56-0.62 (m, 18H, CH₂CH(CH₃)₂, CH₂-CH₂), 0.96 (d, $J_{\text{H-H}}=6.6$ Hz, 42H, -CH₃), 1.79-1.92 (m, 7H, -CH(CH₃)₂), 3.81-3.85 (m, 1H, Si-H).

¹³C NMR (75.50 MHz, CDCl₃, ppm): δ = -4.75 (Si-CH₃), 5.19 (Si-CH₂-), 5.57 (Si-CH₂-), 22.63-22.68 (-CH₂CH(CH₃)₂), 24.03 (-CH(CH₃)₂), 25.58-26.10 (CH(CH₃)₂).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = -10.12 (-Si-H), -67.29 (-Si-CH₂), -67.62, -67.86, -67.91 (-Si-iBu).

IR (ATR, cm⁻¹): 2951.88, 2924.19, 2904.99, 2868.24 (C-H), 2111.44 (Si-H), 1463.89 (C-H), 1228.51 (Si-C), 1168.00, 1081.27, 1037.66 (Si-O-Si), 885.15 (Si-H).

EA: Anal. calcd for C₃₂H₇₄O₁₂Si₉ (%): C, 42.53, H, 8.25; found: C, 42.70; H, 8.28.

GPC: $M_w = 1007$; $M_n = 865$; $D = 1.16$.

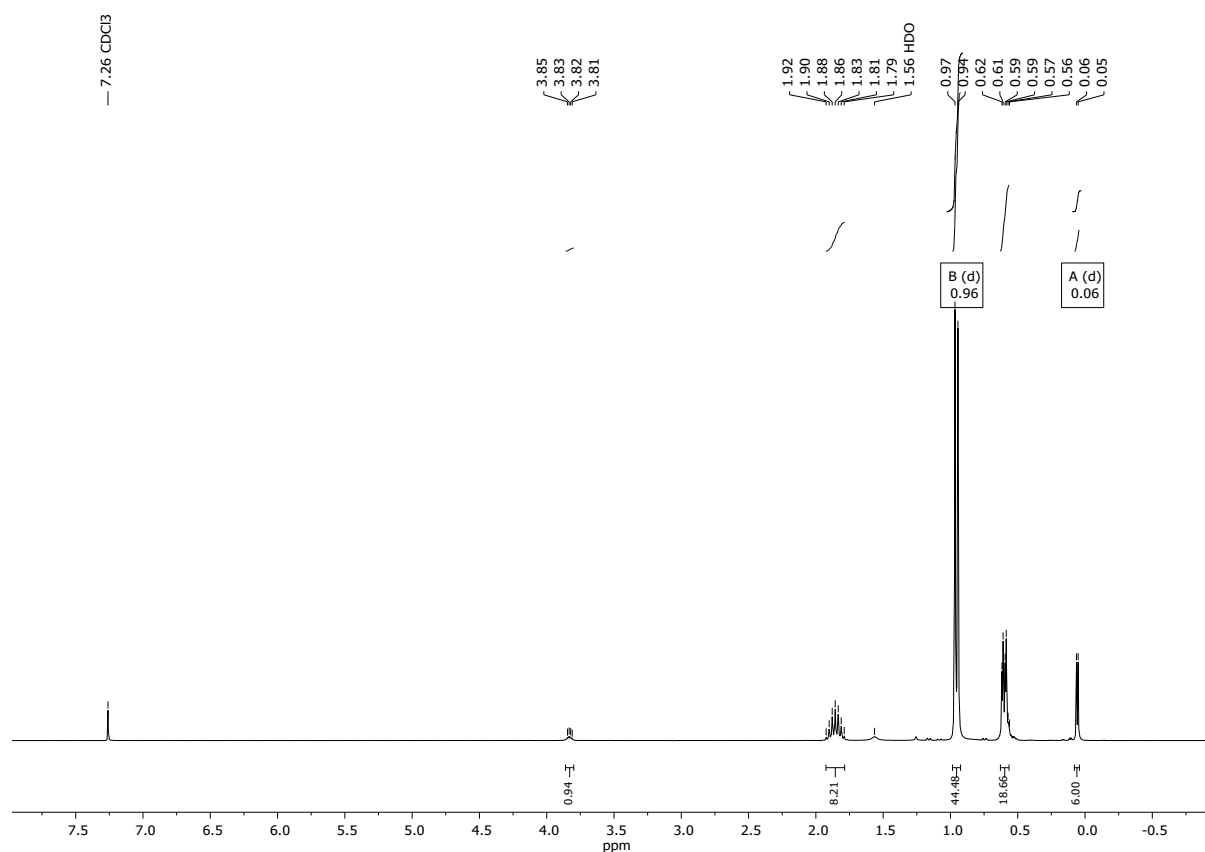


Figure S4 ¹H NMR (300 MHz, CDCl₃) spectrum of G0-iBu-1H.

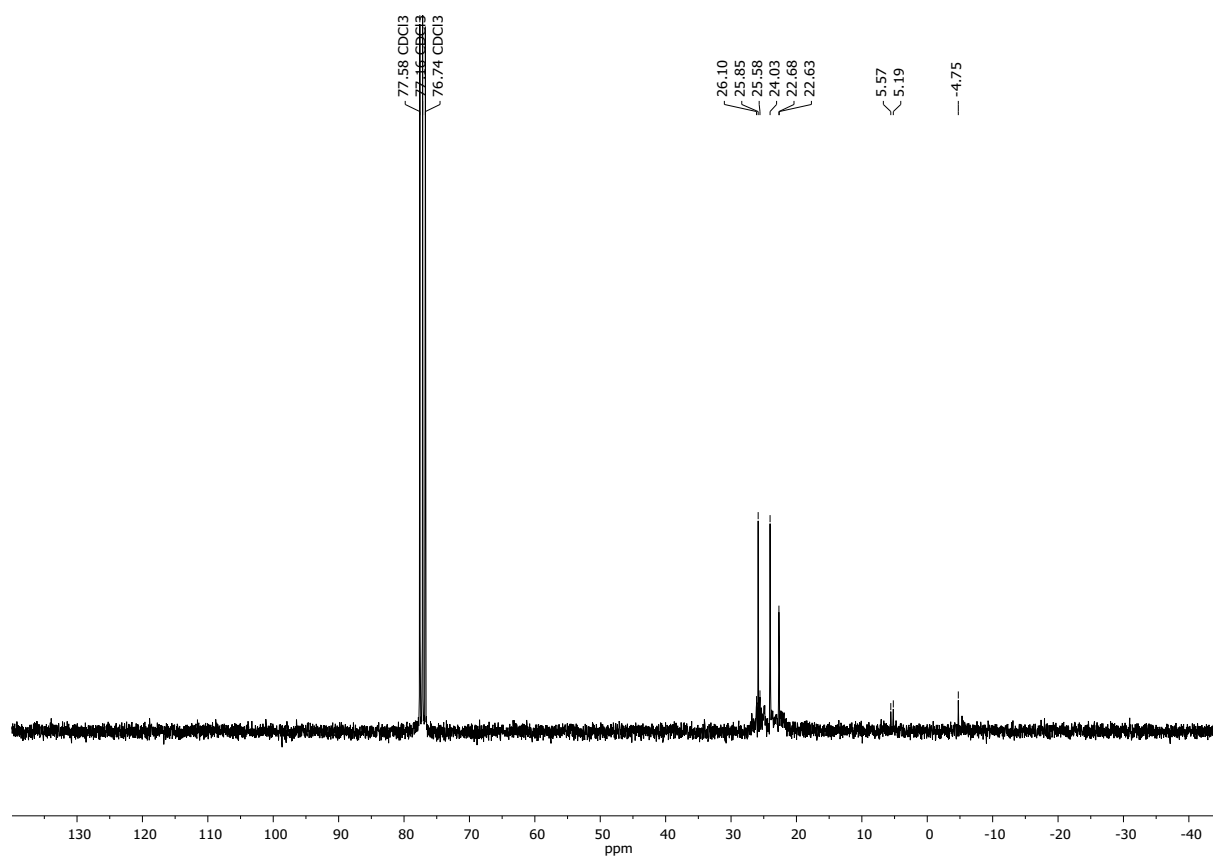


Figure S5 ¹³C NMR (75.50 MHz, CDCl₃) spectrum of G0-1iBu-1H.

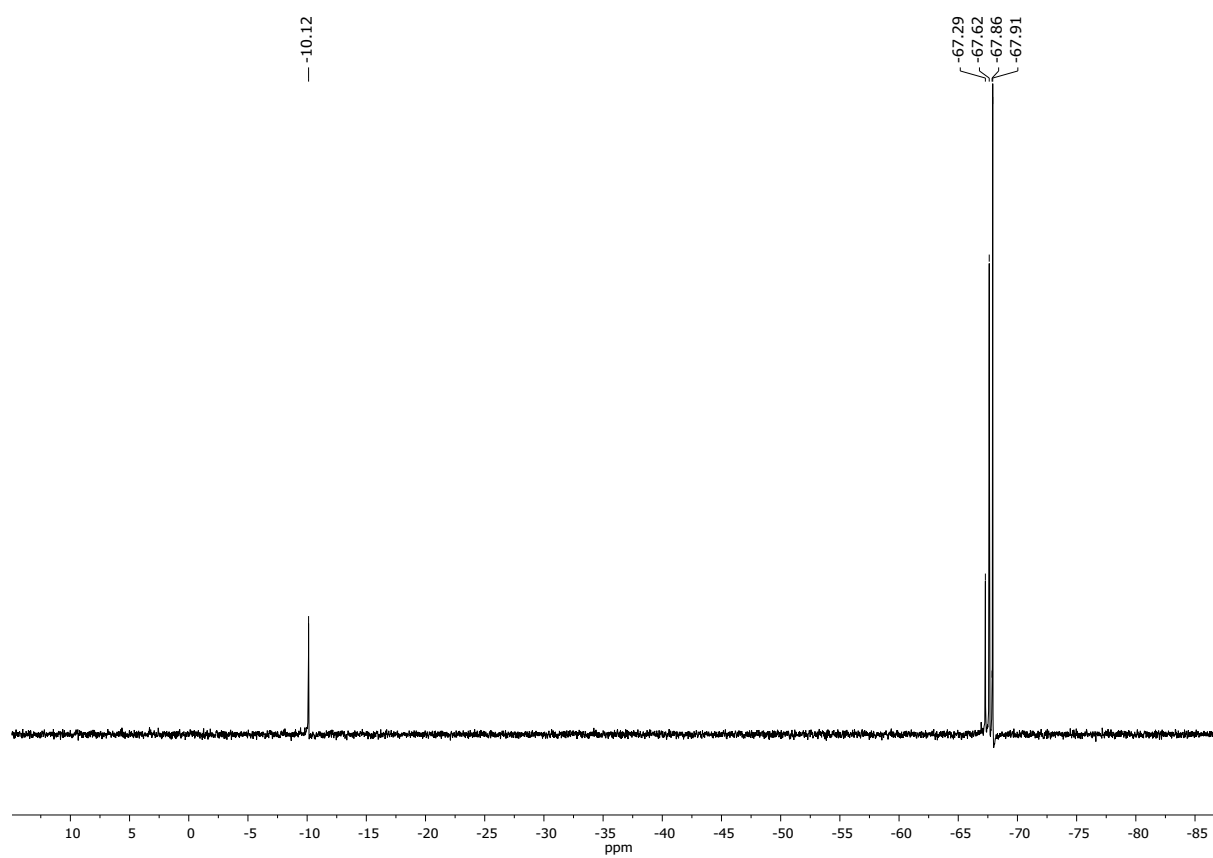
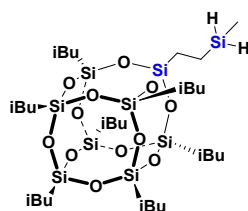


Figure S6 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of G0-1iBu-1H.

G1-iBu-2H



White solid. Isolated Yield 89%

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.13 (t, $J_{\text{H-H}} = 4.1$ Hz, 3H, -CH₃), 0.59-0.64 (m, 18H, CH₂CH(CH₃)₂, CH₂-CH₂), 0.95 (d, $J_{\text{H-H}} = 6.6$ Hz, 42H, -CH₃), 1.86 (dt, 1.86 (dt, $J_{\text{H-H}} = 13.4, 6.7$ Hz, 8H, -CH(CH₃)₂), 3.69-3.73 (m, 2H, Si-H).

¹³C NMR (75.50 MHz, CDCl₃, ppm): δ = -8.60 (Si-CH₃), 2.34 (Si-CH₂-), 6.35 (Si-CH₂-), 22.64-22.68 (-CH₂CH(CH₃)₂), 24.03-24.05 (-CH(CH₃)₂), 25.84-25.86 (CH(CH₃)₂).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = -29.46 (-Si-H), -67.53, -67.59 (-Si-CH₂), -67.72, -67.77, -67.84, -67.90 (-Si-iBu).

IR (ATR, cm⁻¹): 2954.49, 2925.40, 2907.24, 2868.70 (C-H), 2127.43 (Si-H), 1464.85 (C-H), 1264.10 (Si-C), 1167.93, 1095.75, 1037.37 (Si-O-Si), 900.83 (Si-H).

EA: Anal. calcd for C₃₁H₇₂O₁₂Si₉ (%): C, 41.85, H, 8.16; found: C, 42.02; H, 8.19.

GPC: M_w = 971; M_n = 822; \bar{D} = 1.18.

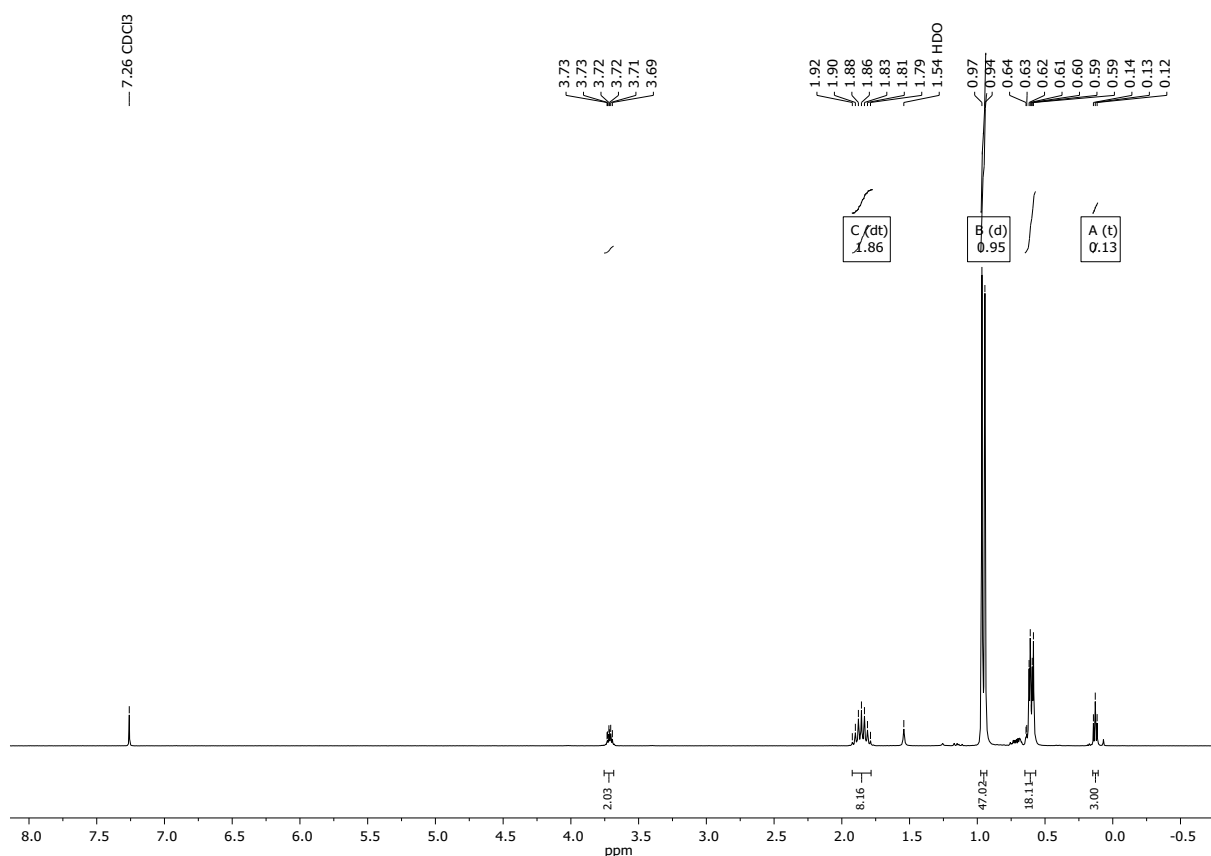


Figure S7 ¹H NMR (300 MHz, CDCl₃) spectrum of G1-iBu-2H.

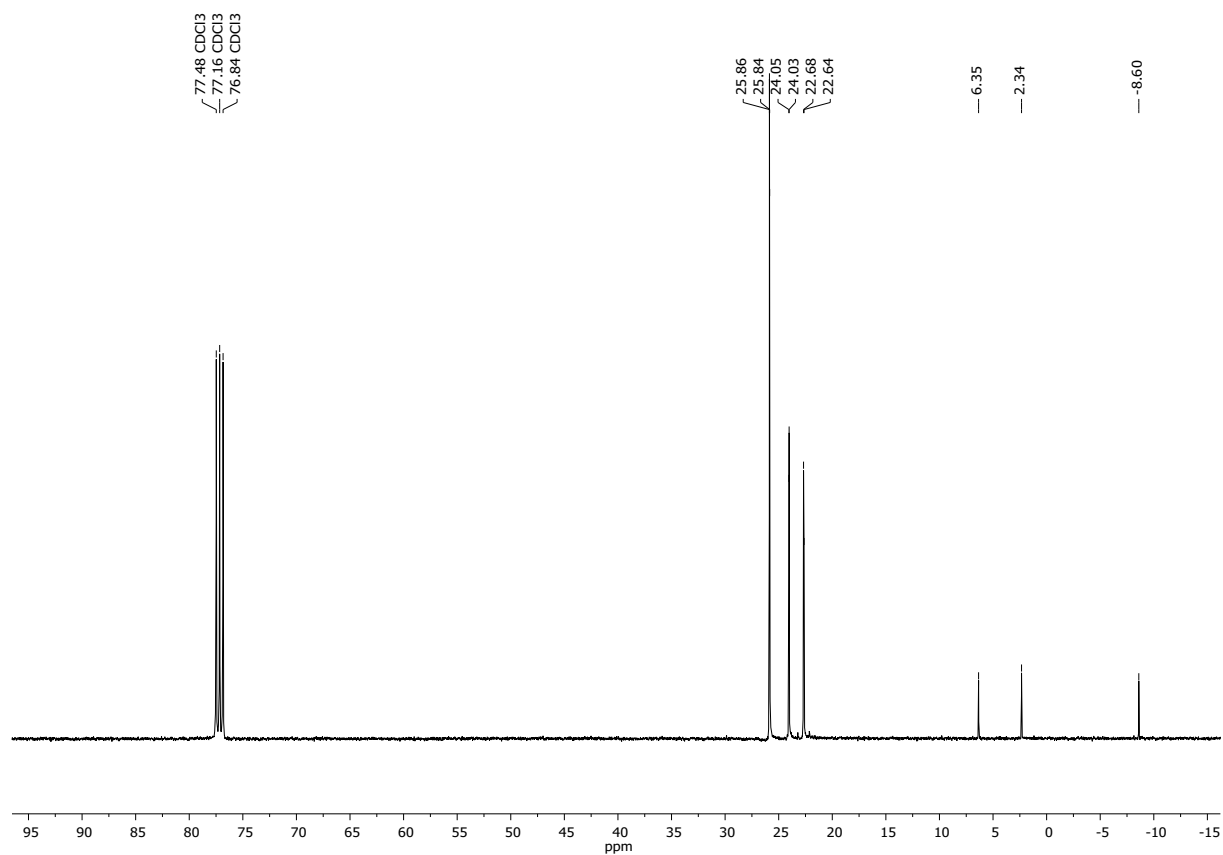


Figure S8 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-iBu-2H**.

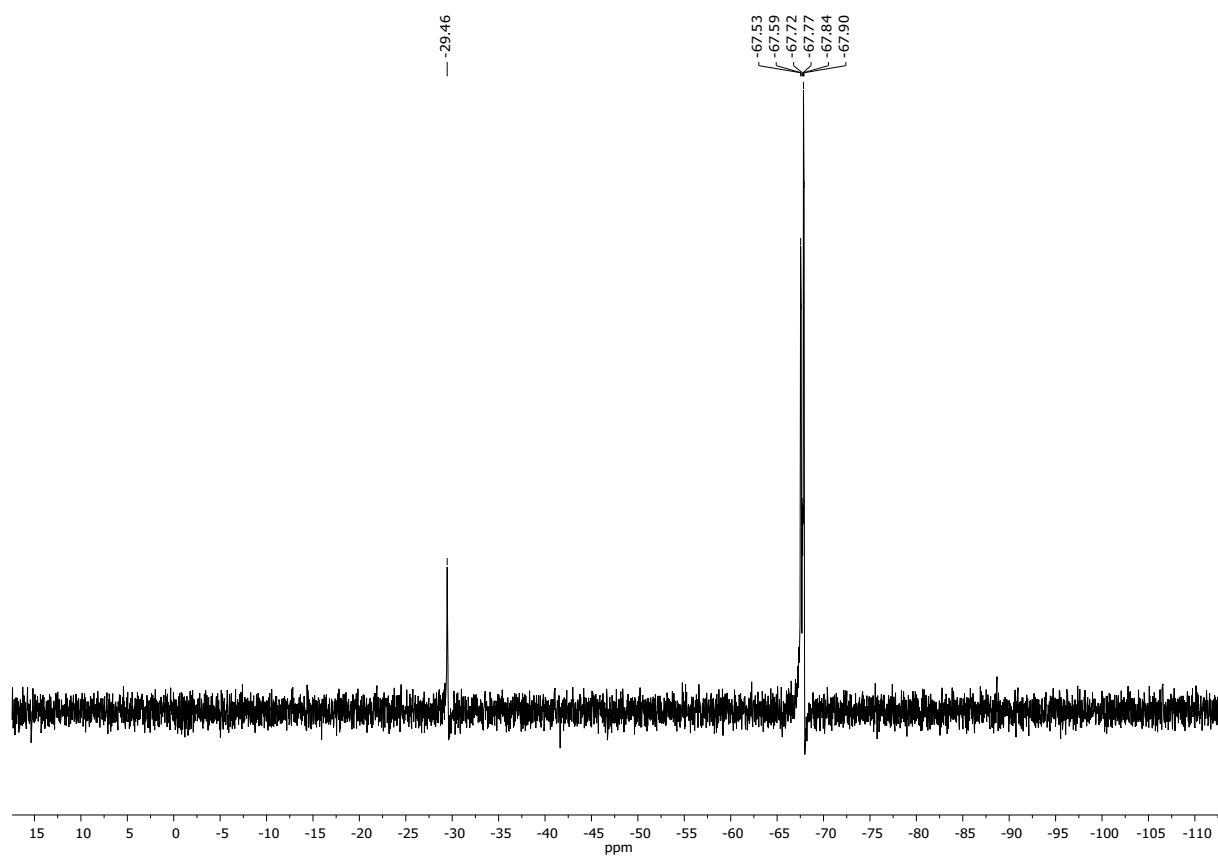
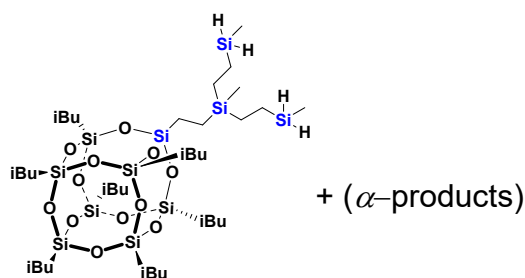


Figure S9 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-iBu-2H**.

G2-2iBu-4H



White solid. Isolated Yield 94% for a mixture of hydrosilylation besides products.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ = 0.05-0.08 (m, 3H, SiCH_3), 0.14-0.16 (m, 3H, SiCH_3), 0.59-0.62 (m, 18H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$, SiCH_2), 0.95 (d, $J_{\text{H-H}}=6.6$ Hz, 42H), 1.79-1.92 (m, 7H, $\text{CH}(\text{CH}_3)_2$), 3.70-3.74 (m, 1H, Si-H), 3.77-3.80 (m, 1H, Si-H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3 , ppm): δ = -8.52, -8.41, -7.38, -6.86, -6.82, -1.53, -1.21, 1.19, 2.35, 3.20 (SiCH_3 , CH-CH_3), 3.63, 3.76, 3.90, 3.99, 5.31, 5.46, 5.57, 6.37, 6.54, 6.88 (Si-CH_2 -), 10.75, 11.13 ($-\text{CH-}$), 22.67-22.71 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$), 24.04-24.07 ($\text{CH}(\text{CH}_3)_2$), 25.87 ($\text{CH}(\text{CH}_3)_2$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): δ = -2.60, -3.31, -4.30 ($-\text{Si-CH}_3$), -29.19, -29.27, -29.63, -29.66 ($-\text{Si-H}$), -67.42, -67.47, -67.60, -67.91 ($-\text{Si-iBu}$).

IR (ATR, cm^{-1}): 2953.05, 2925.10, 2906.08, 2868.54 (C-H), 2123.99 (Si-H) 1464.48 (C-H), 1228.06 (Si-C), 1167.92, 1088.24, 1036.91 (Si-O-Si), 905.95 (Si-H).

GPC: $M_w = 1164$; $M_n = 1072$; $D = 1.09$.

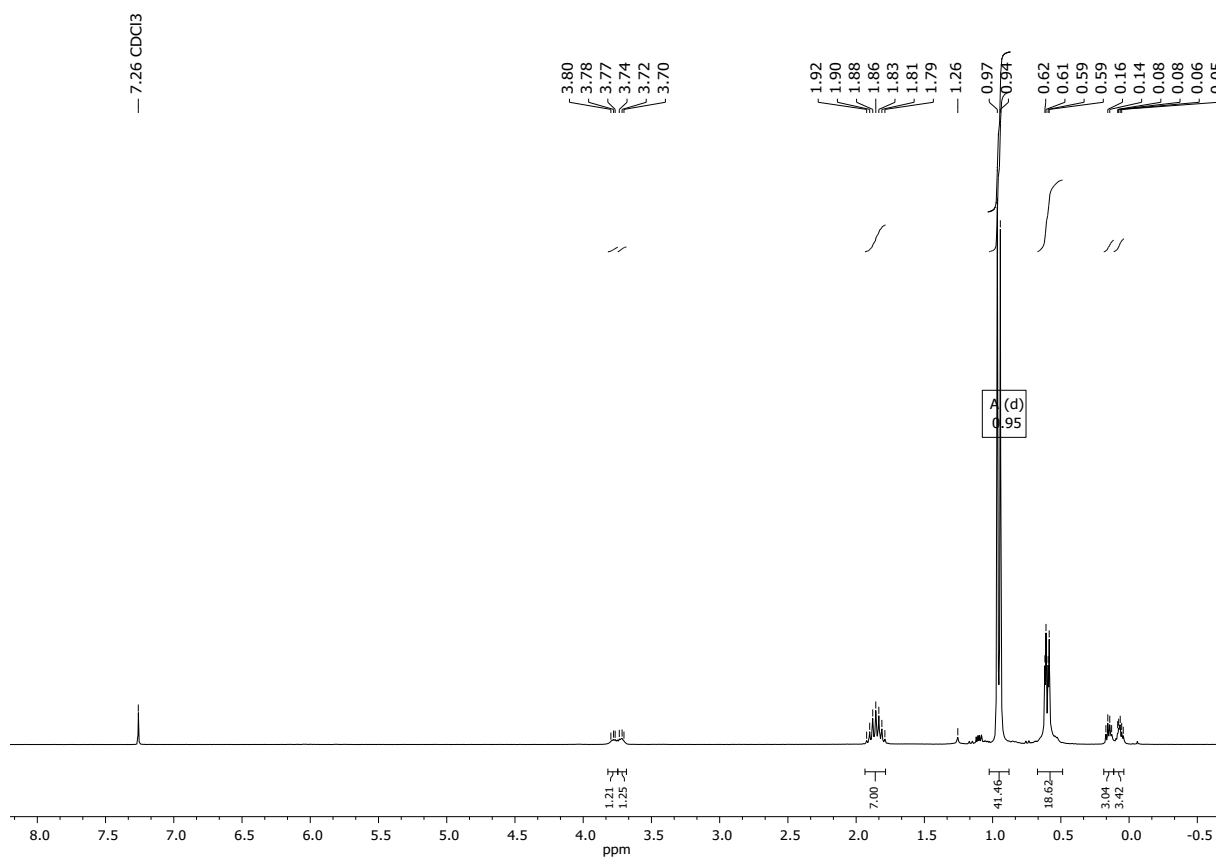


Figure S10 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of G2-2iBu-4H.

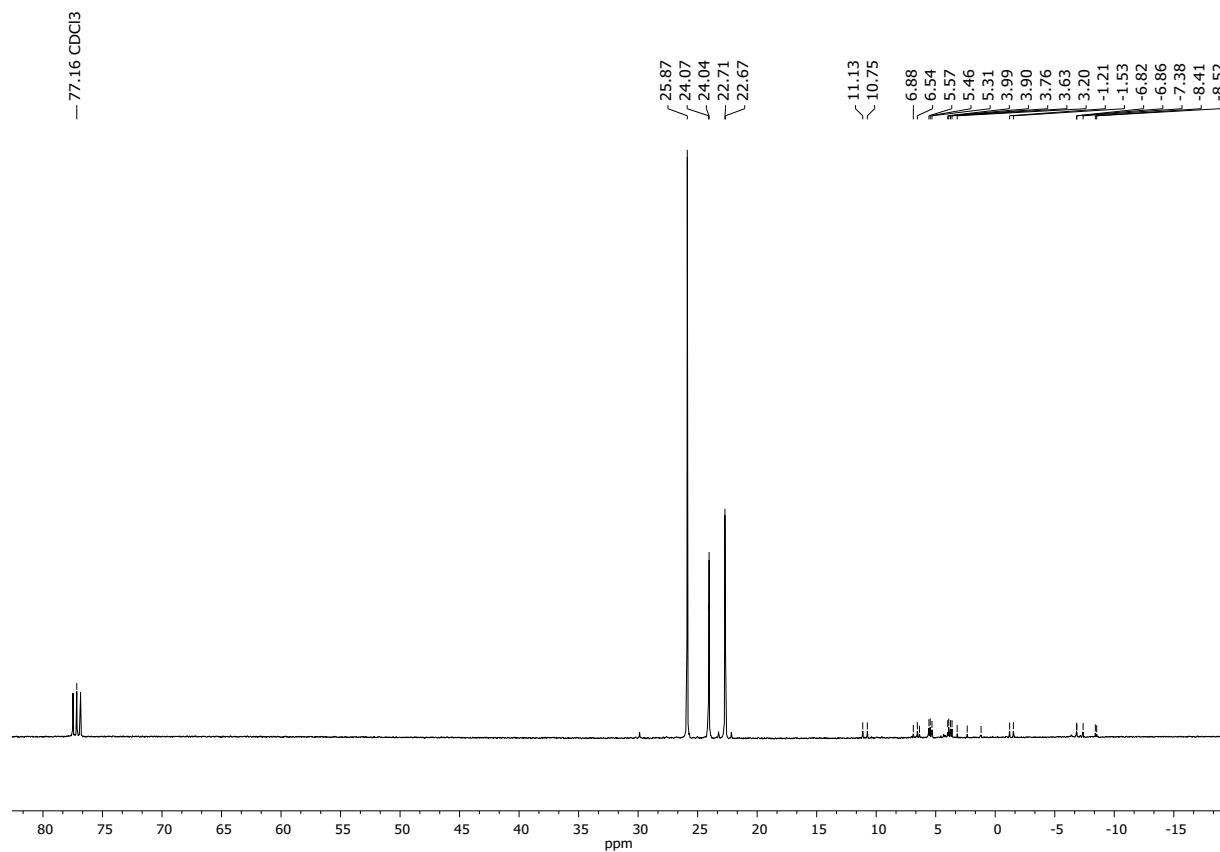


Figure S11 ¹³C NMR (101 MHz, CDCl₃) spectrum of G2-2iBu-4H.

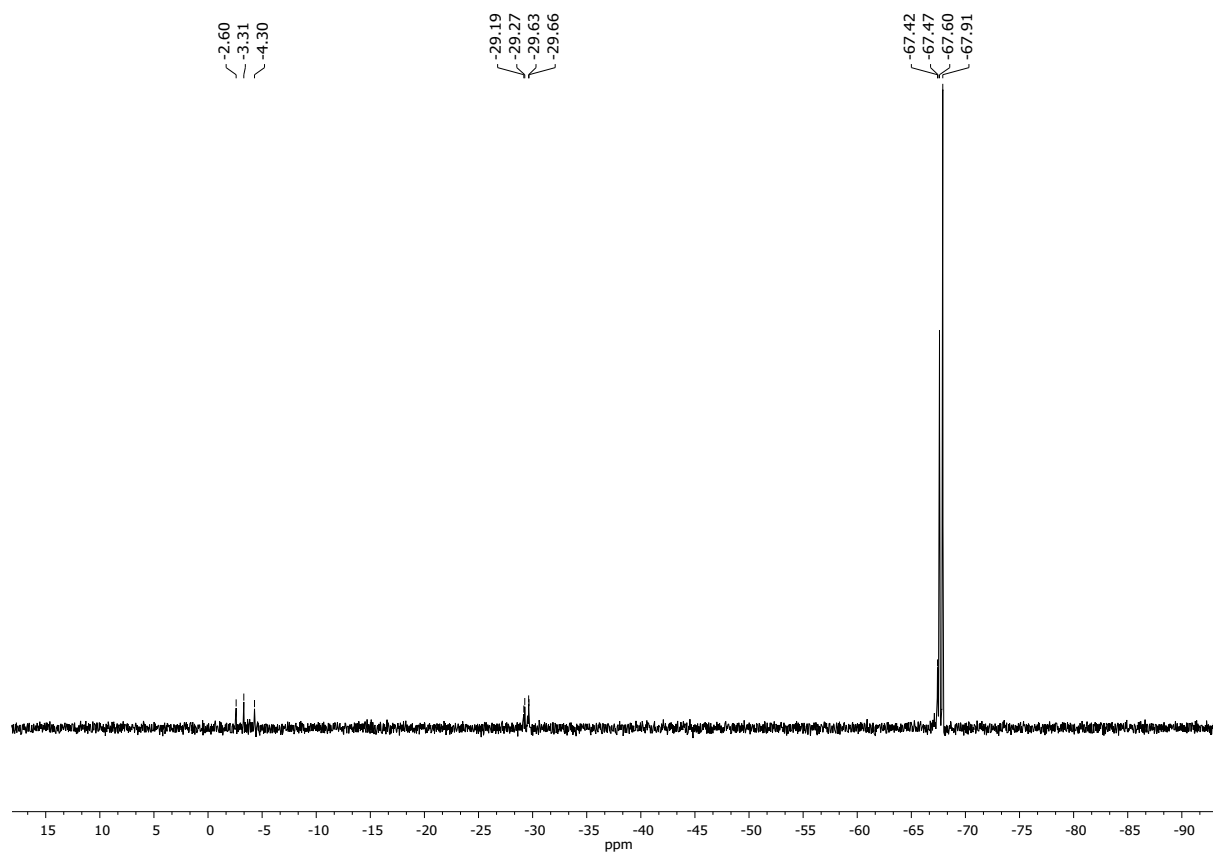


Figure S12 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of G2-2iBu-4H.

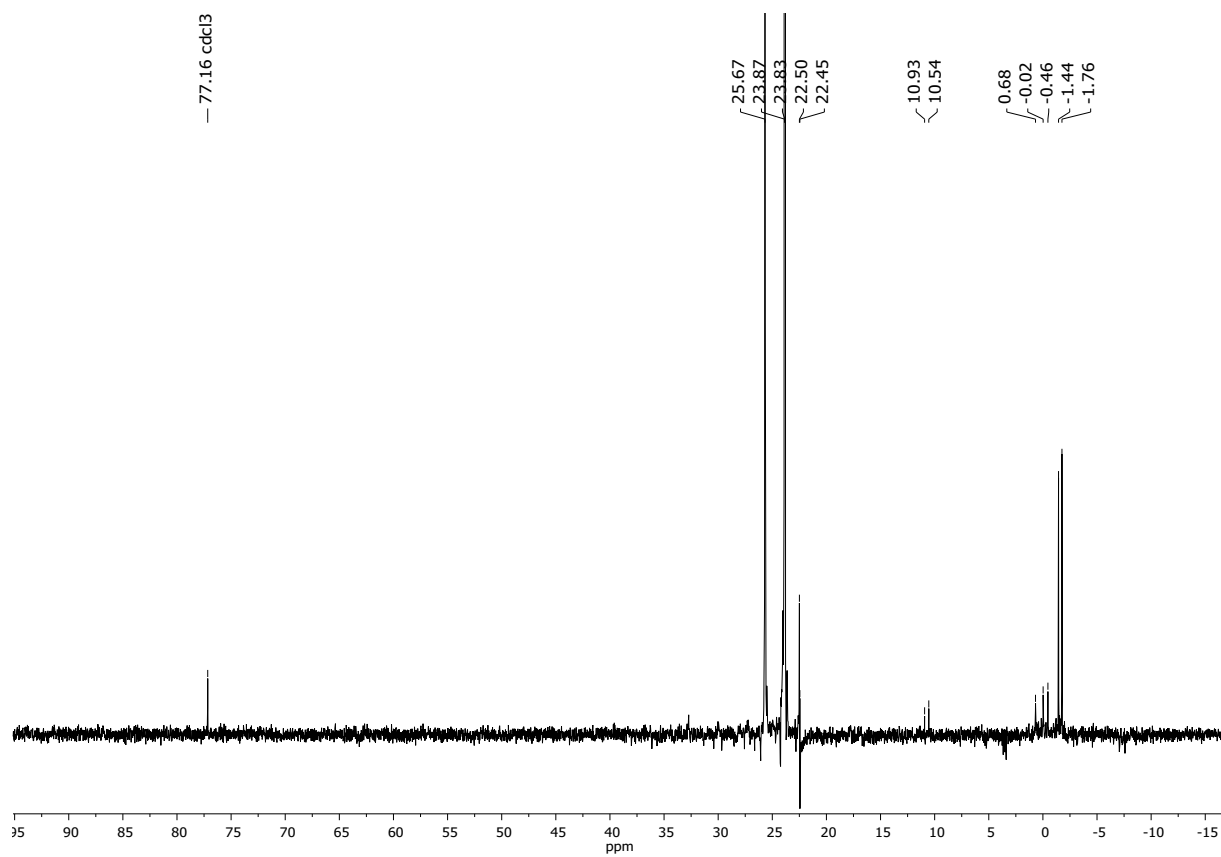
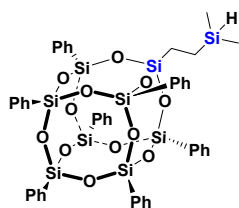


Figure S13 DEPT-135 (101 MHz, CDCl₃) spectrum of G2-2iBu-4H.

G0-1Ph-1H



White solid. Isolated Yield 53%

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.03 (d, *J*_{H-H} = 3.6 Hz, 6H, -CH₃), 0.69-0.85 (m, 4H, Si-CH₂-), 3.81-3.88 (m, 2H, -Si-H), 7.33-7.49 (m, 23H, -Ph), 7.73-7.78 (m, 15H, -Ph).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -4.77 (Si-CH₃), 5.07 (Si-CH₂-), 5.62 (Si-CH₂-) 128.00, 130.38-130.43, 130.65, 130.88, 134.33-134.35 (-Ph).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = -9.96 (-Si-H), -64.91 (-Si-CH₂-), -78.31, -78.65, -78.79 (-Si-Ph).

IR (ATR, cm⁻¹): 3072.92, 3051.03, 3027.73 (C-H phenyl), 2957.13, 2918.07 (C-H), 2103.87 (Si-H), 1593.94, 1430.53 (C=C phenyl), 1191.12, 1132.34, 1082.74, 1027.83 (Si-O-Si), 996.63 (C-H phenyl), 883.73 (Si-H).

EA: Anal. calcd for C₄₆H₄₆O₁₂Si₉ (%): C, 52.94, H, 4.44; found: C, 53.15; H, 4.46.

GPC: *M*_w = 825; *M*_n = 666; *D* = 1.24.

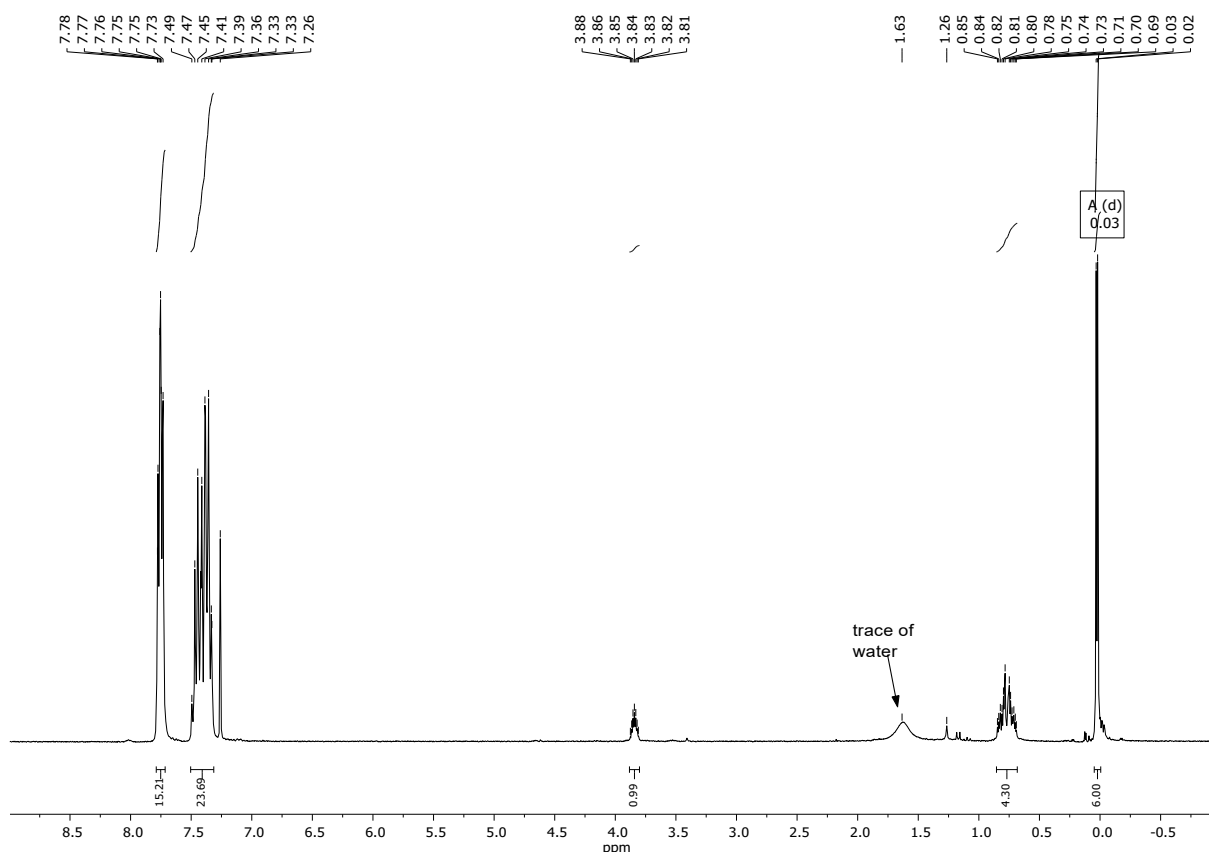


Figure S14 ¹H NMR (300 MHz, CDCl₃) spectrum of G0-1Ph-1H.

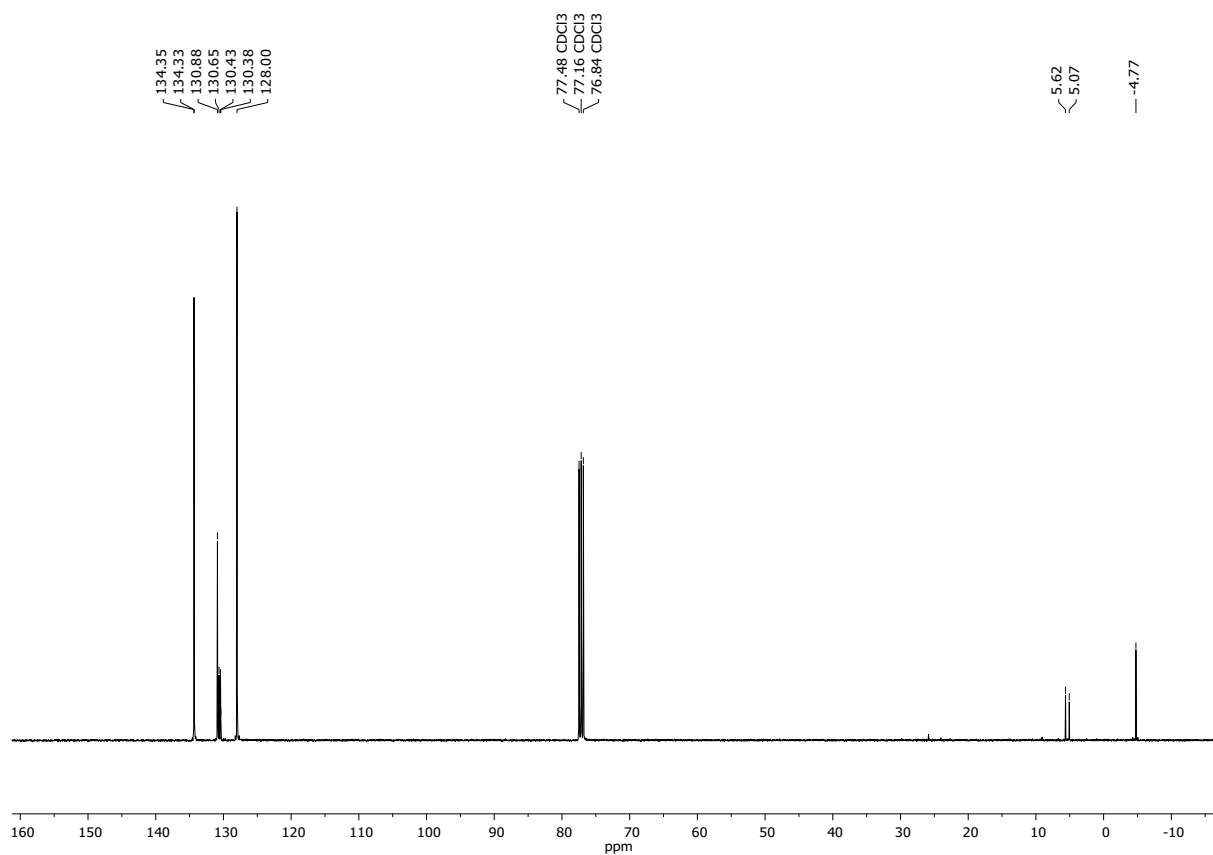


Figure S15 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G0-1Ph-1H**.

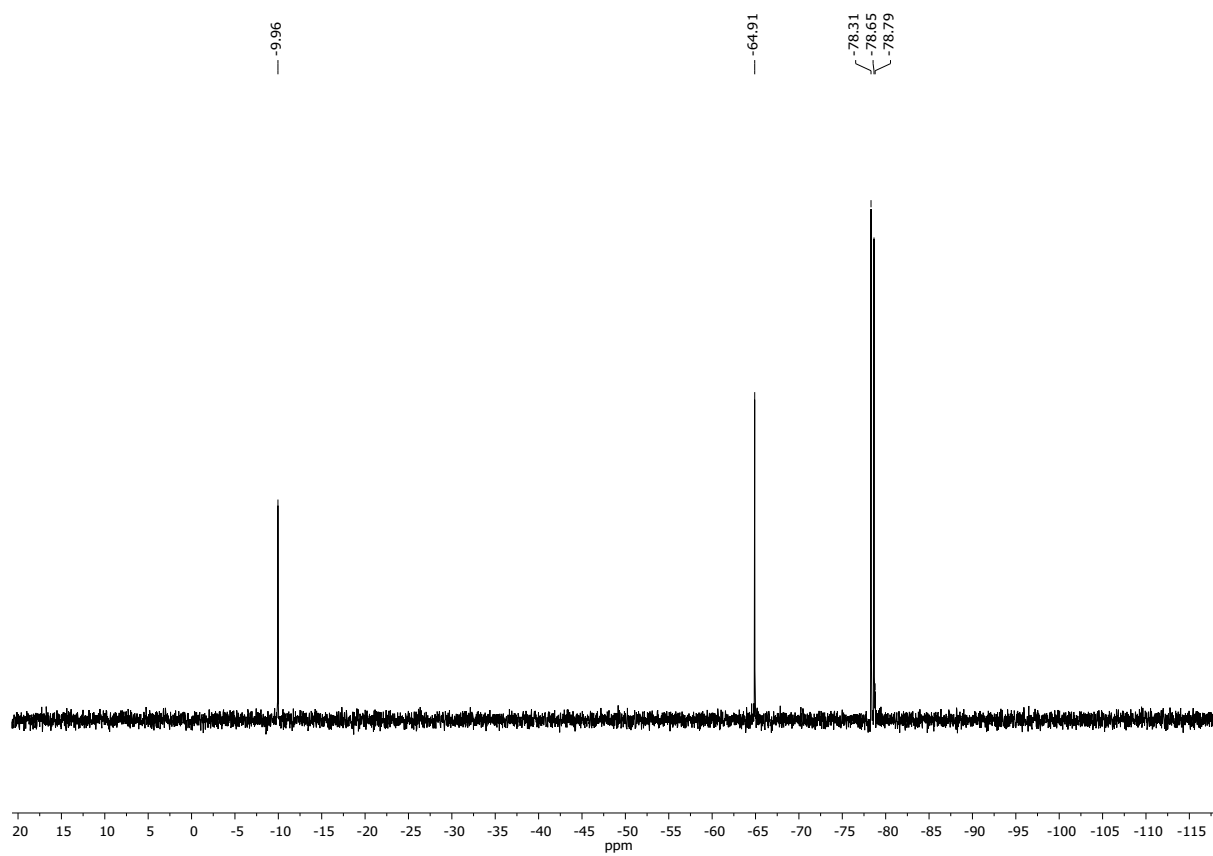
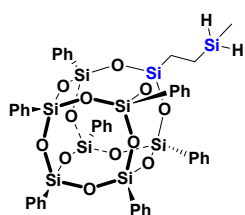


Figure S16 ^1H NMR (79.50 MHz, CDCl_3) spectrum of **G0-1Ph-1H**.

G1-1Ph-2H



White solid. Isolated Yield 72%

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ = 0.08 (t, $J_{\text{H-H}} = 4.1$ Hz, 3H, $-\text{CH}_3$), 0.80-0.90 (m, 4H, $-\text{Si-CH}_2-$), 3.69-3.73 (m, 2H, $-\text{Si-H}$), 7.34-7.50 (m, 22H, $-\text{Ph}$), 7.73-7.78 (m, 14H, $-\text{Ph}$).

$^{13}\text{C NMR}$ (75.50 MHz, CDCl_3 , ppm): δ = -8.68 ($-\text{Si-CH}_3$), 2.39 ($-\text{Si-CH}_2-$), 6.19 ($-\text{Si-CH}_2-$), 128.00-128.02, 130.36-130.41, 130.59, 130.90, 134.32-134.34 ($-\text{Ph}$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): δ = -29.32 ($-\text{Si-H}$), -65.43 ($-\text{Si-CH}_2-$), -78.33, -78.66 ($-\text{Si-Ph}$).

IR (ATR, cm^{-1}): 3073.06, 3051.25, 3028.00 (C-H phenyl), 2921.19 (C-H), 2126.47 (Si-H), 1593.96, 1430.56 (C=C phenyl), 1191.09, 1132.78, 1085.13, 1028.00, (Si-O-Si), 996.83 (C-H phenyl), 897.46 (Si-H).

EA: Anal. calcd for $\text{C}_{45}\text{H}_{44}\text{O}_{12}\text{Si}_9$ (%): C, 52.50, H, 4.31; found: C, 52.71; H, 4.33.

GPC: $M_w = 785$; $M_n = 643$; $D = 1.22$.

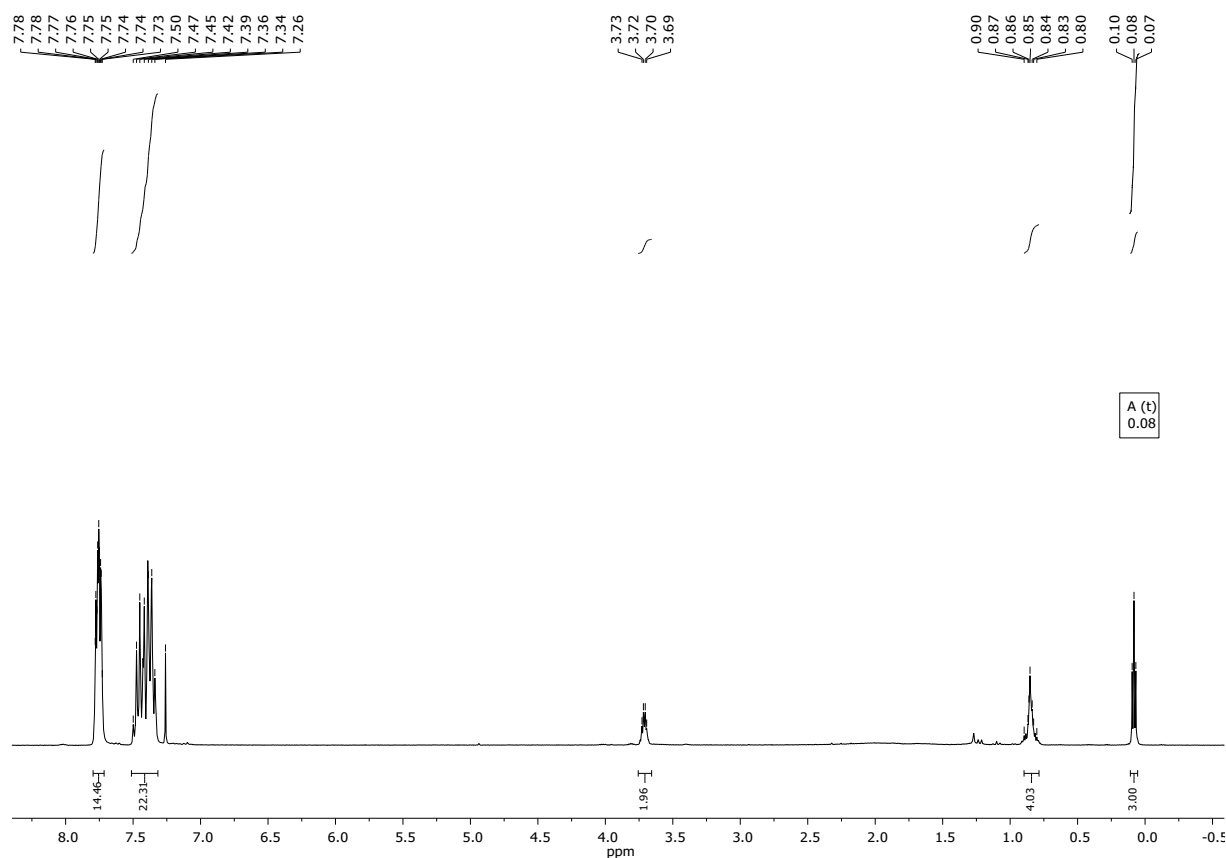


Figure S17 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of **G1-1Ph-2H**.

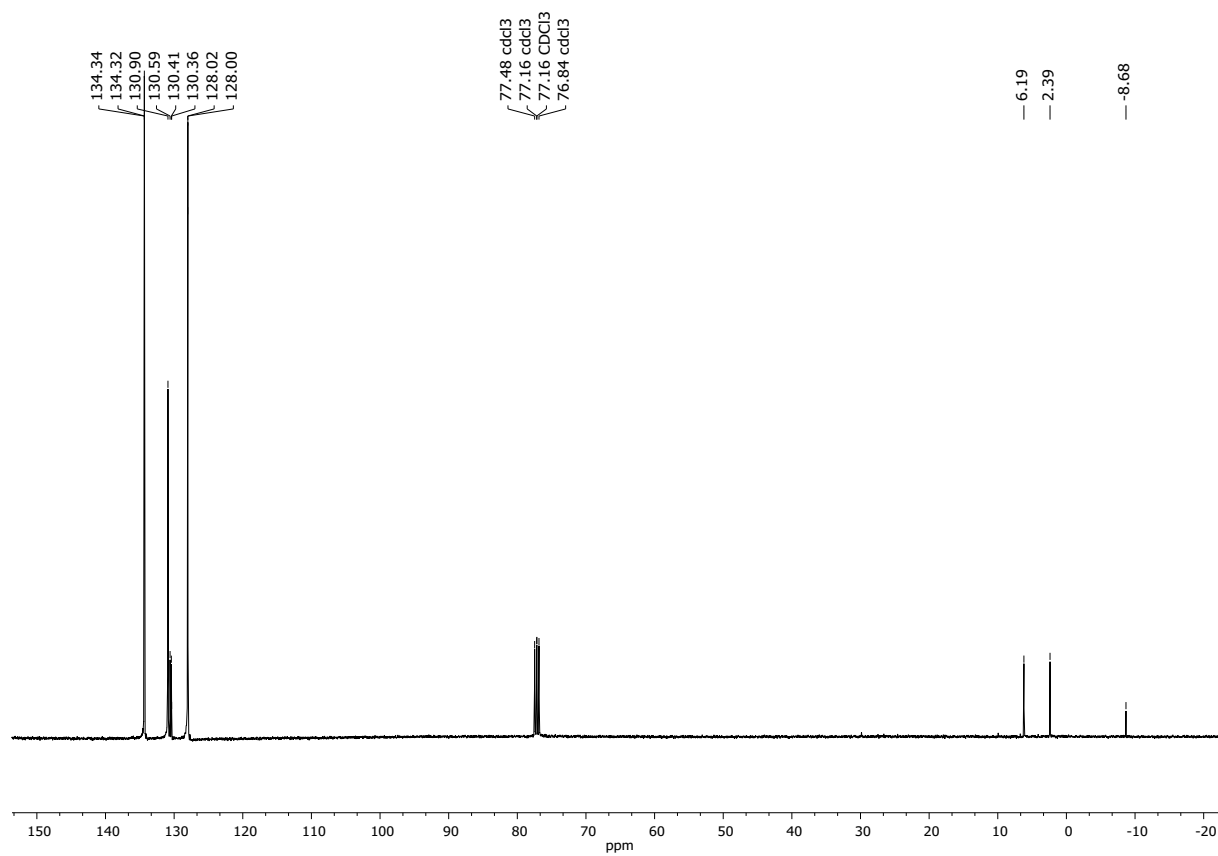


Figure S18 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-1Ph-2H**.

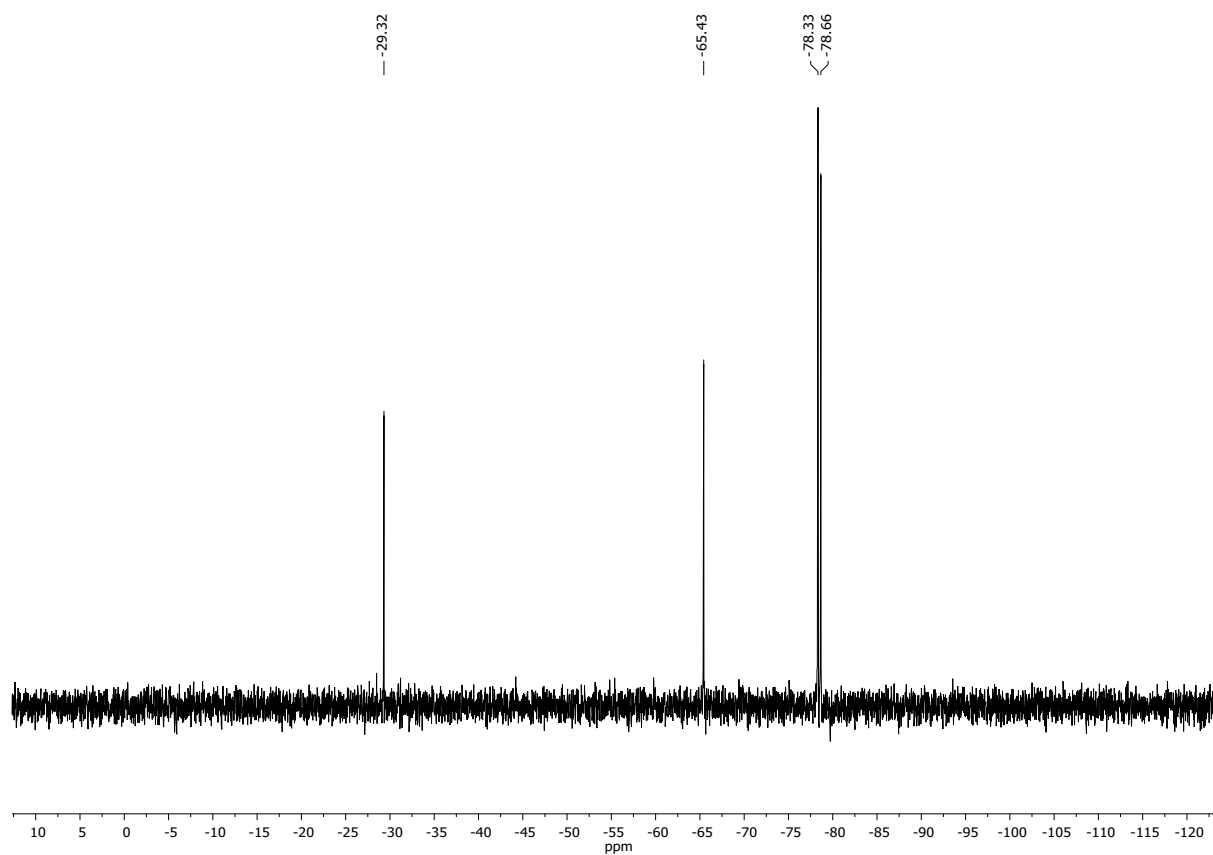
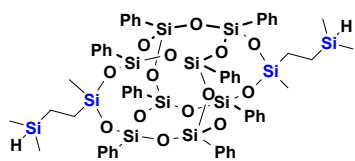


Figure S19 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-1Ph-2H**.

G0-2D-2H



White solid. Isolated Yield 91%

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = -0.09$ (d, $J_{\text{H-H}}=6.6$ Hz, 12H, $-\text{CH}_3$), 0.28 (s, 6H, $-\text{CH}_3$), 0.55-0.68 (m, 8H, Si-CH_2), 3.74 (dt, $J_{\text{H-H}}=6.8, 3.4$ Hz, 2H, $-\text{Si-H}$), 7.16-7.55 (m, 40H, $-\text{Ph}$).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3 , ppm): $\delta = -4.86$ (Si-CH_3), -1.42 (Si-CH_3), 5.37 (Si-CH_2), 9.74 (Si-CH_2), 127.76, 127.90, 130.44, 131.24, 132.31, 134.09, 134.21 ($-\text{Ph}$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): $\delta = -9.76$ ($-\text{Si-H}$), -17.50 ($-\text{Si}(\text{CH}_3)-$), -78.68 , -79.65 ($-\text{Si-Ph}$).

IR (ATR, cm^{-1}): 3072.06, 3050.62 (C-H phenyl), 2955.52, 2915.23 (C-H), 2109.39 (Si-H), 1593.53, 1429.33 (C=C phenyl), 1247.32 (Si-C), 1081.98, 1028.47 (Si-O-Si), 997.37 (C-H phenyl), 884.62 (Si-H).

EA: Anal. calcd for $\text{C}_{58}\text{H}_{68}\text{O}_{14}\text{Si}_{12}$ (%): C, 52.53, H, 5.17; found: C, 52.74; H, 5.19.

GPC: $M_w = 1106$; $M_n = 954$; $D = 1.16$.

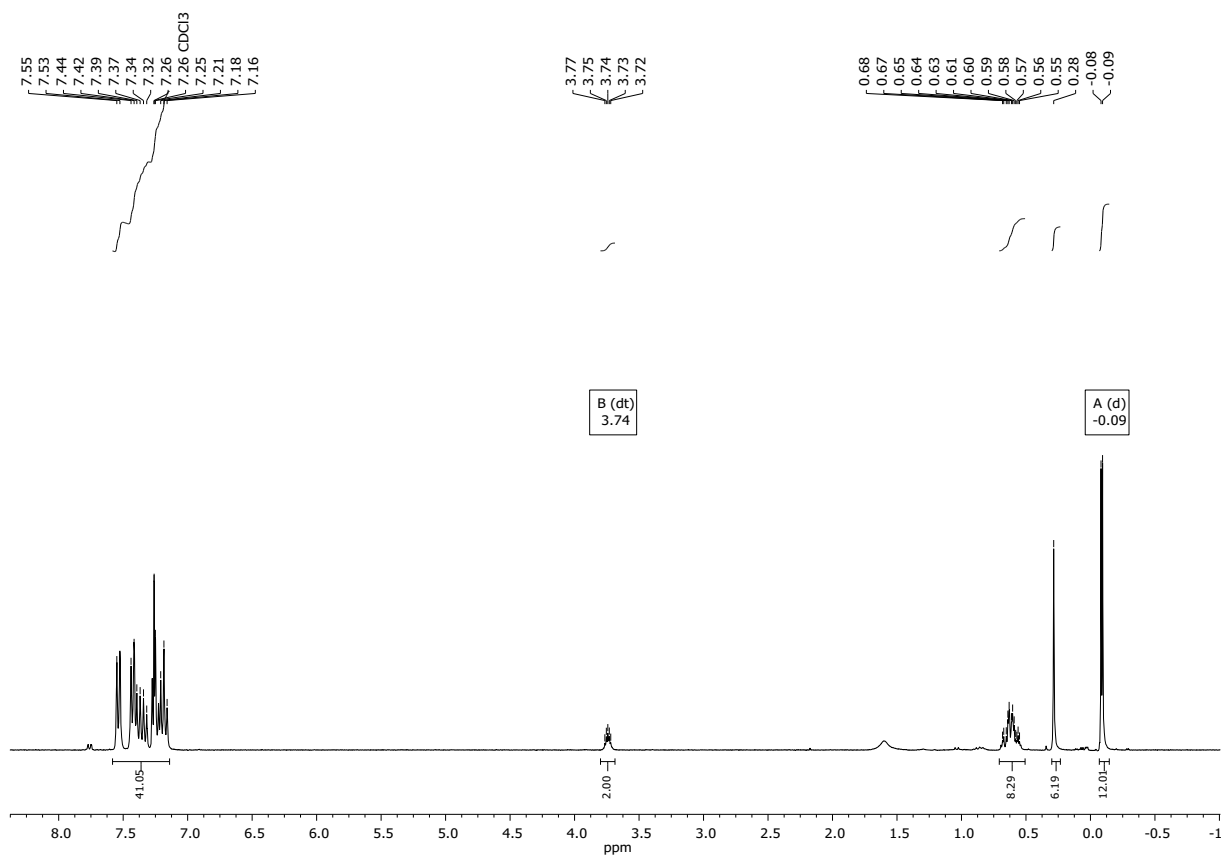


Figure S20 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of G0-2D-2H.

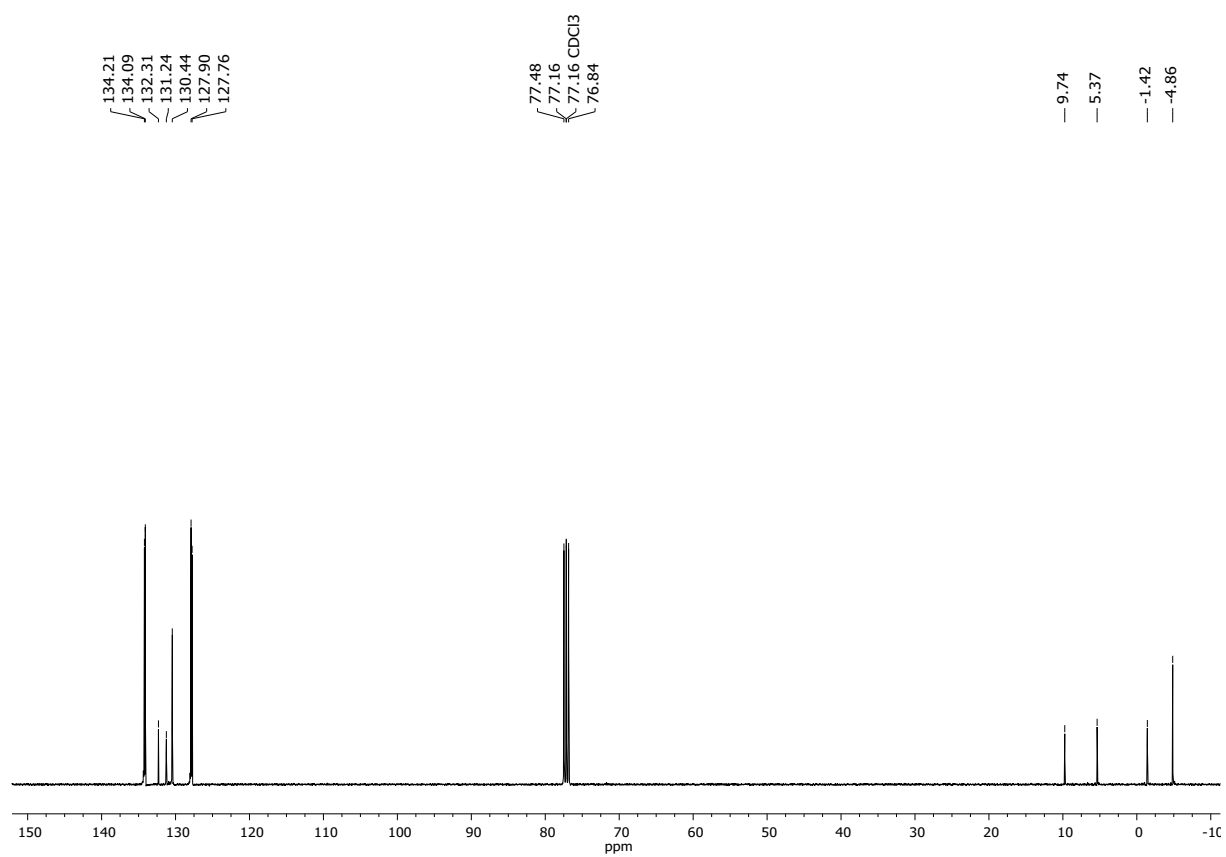


Figure S21 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G0-2D-2H**.

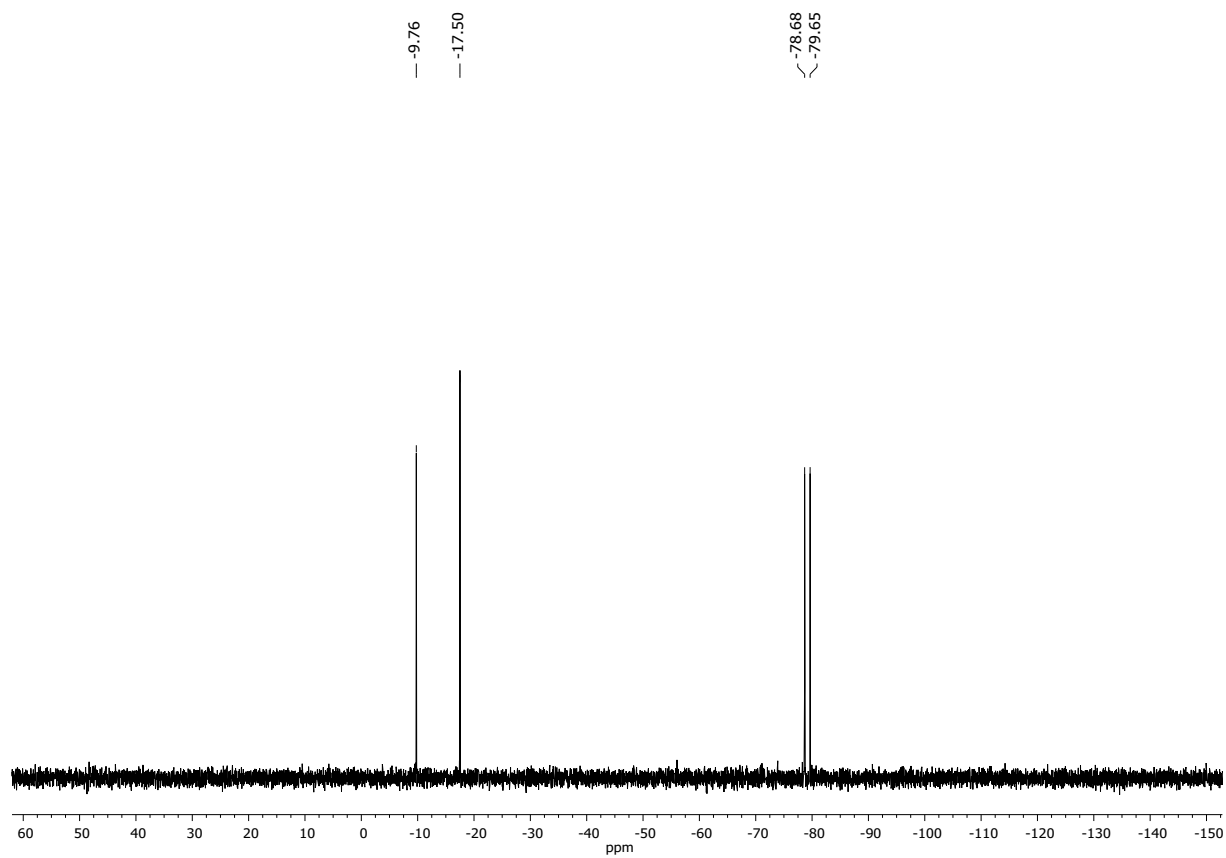
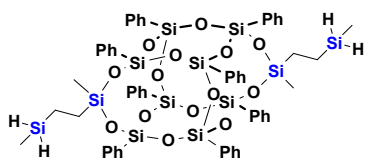


Figure S22 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G0-2D-2H**.

G1-2D-4H



White solid. Isolated Yield 85%

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = -0.03$ (t, $J_{\text{H-H}}=4.0$ Hz, 6H, $-\text{CH}_3$), 0.30 (s, 6H, $-\text{CH}_3$), 0.71 (s, 8H, Si-CH_2-), 3.63 (q, $J_{\text{H-H}}= 3.6$ Hz, 4H, $-\text{Si-H}$), 7.17-7.55 (m, 40H, $-\text{Ph}$).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3 , ppm): $\delta = -8.73$ (Si-CH_3), -1.39 (Si-CH_3), 2.16 (Si-CH_2-), 10.89 (Si-CH_2-) 127.78, 127.93, 130.47, 131.18, 132.23, 134.07, 134.20 ($-\text{Ph}$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): $\delta = -17.97$ ($-\text{Si}(\text{CH}_3)-$), -29.03 ($-\text{Si-H}$), -78.64 , -79.61 ($-\text{Si-Ph}$).

IR (ATR, cm^{-1}): 3071.80, 3050.96 (C-H phenyl), 2954.83, 2921.75, 2852.53 (C-H), 2126.30 (Si-H), 1593.50, 1429.26 (C=C phenyl), 1264.13 (Si-C), 1085.31, 1028.99 (Si-O-Si), 997.36 (C-H phenyl), 893.18 (Si-H).

EA: Anal. calcd for $\text{C}_{56}\text{H}_{64}\text{O}_{14}\text{Si}_{12}$ (%): C, 51.81, H, 4.97; found: C, 52.02; H, 4.99.

GPC: $M_w = 1033$; $M_n = 878$; $D = 1.18$.

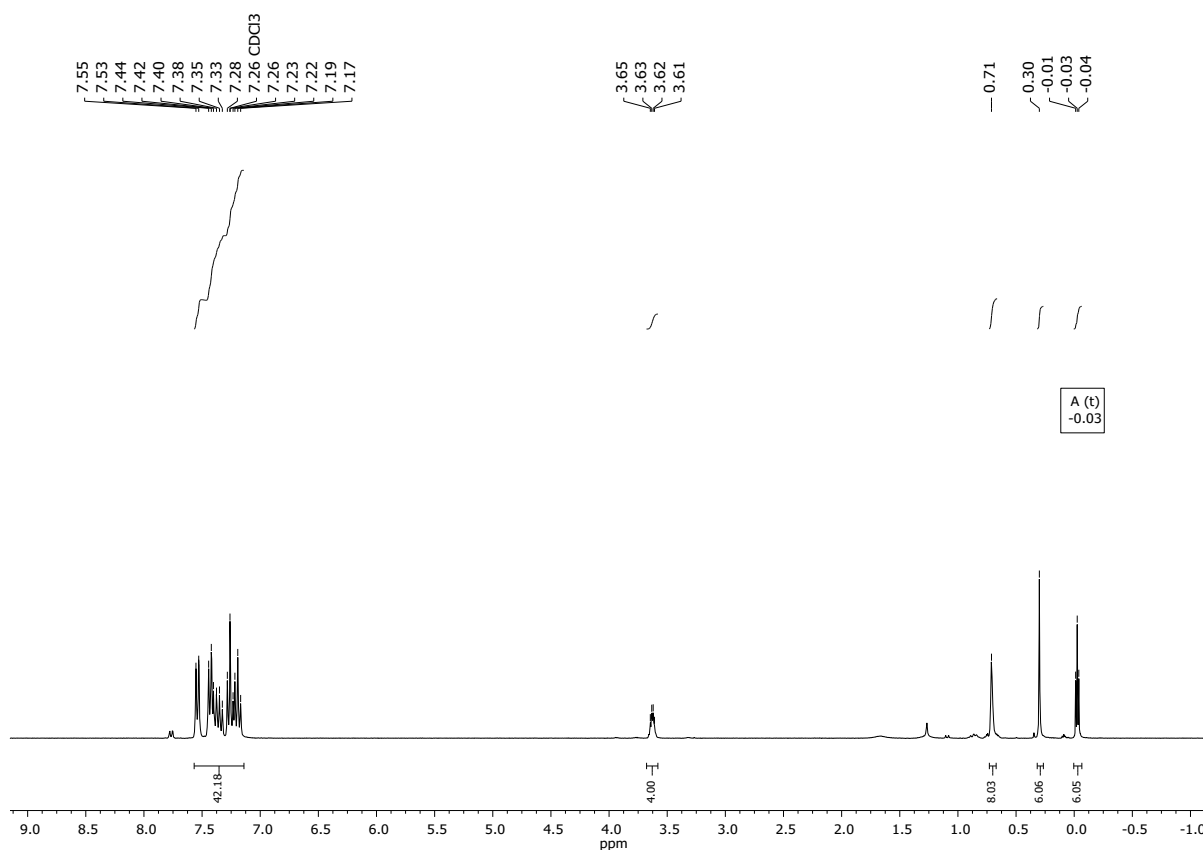


Figure S23 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of G1-2D-4H.

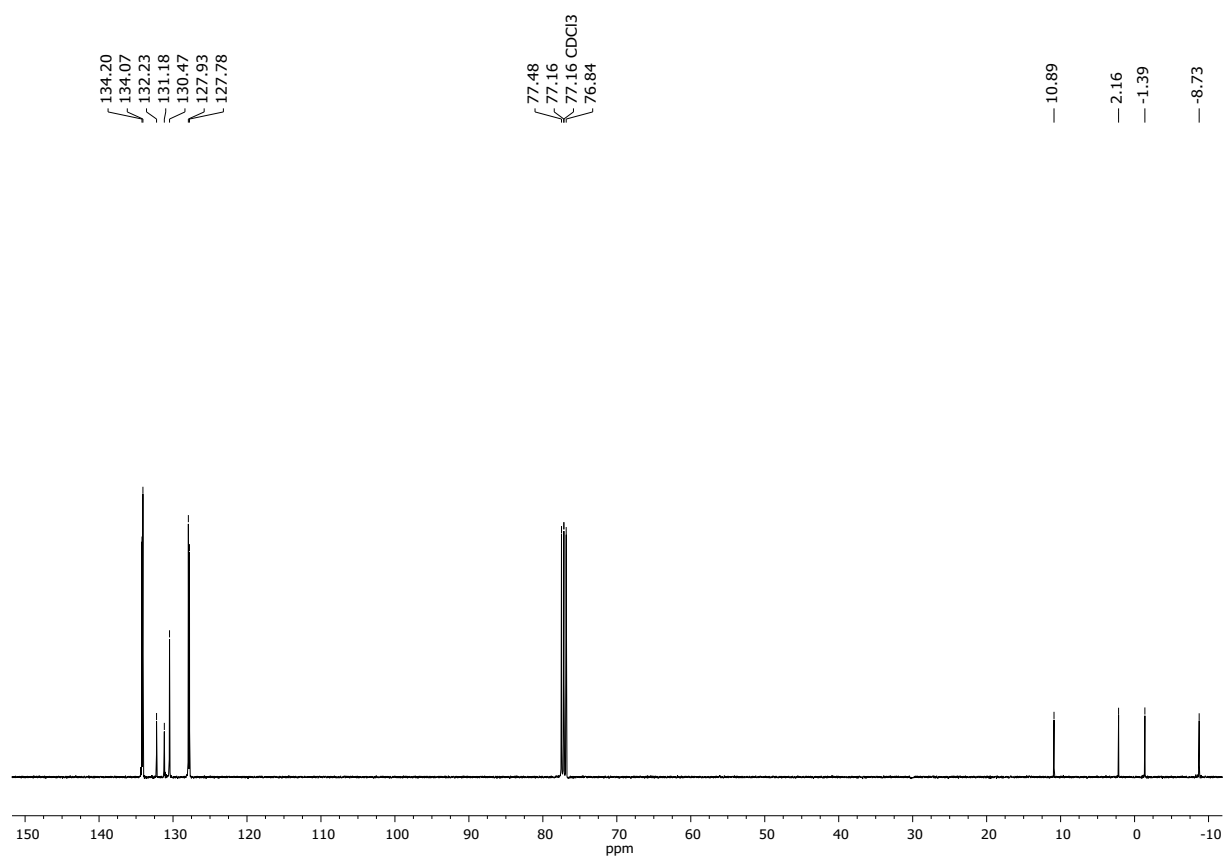


Figure S24 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-2D-4H**.

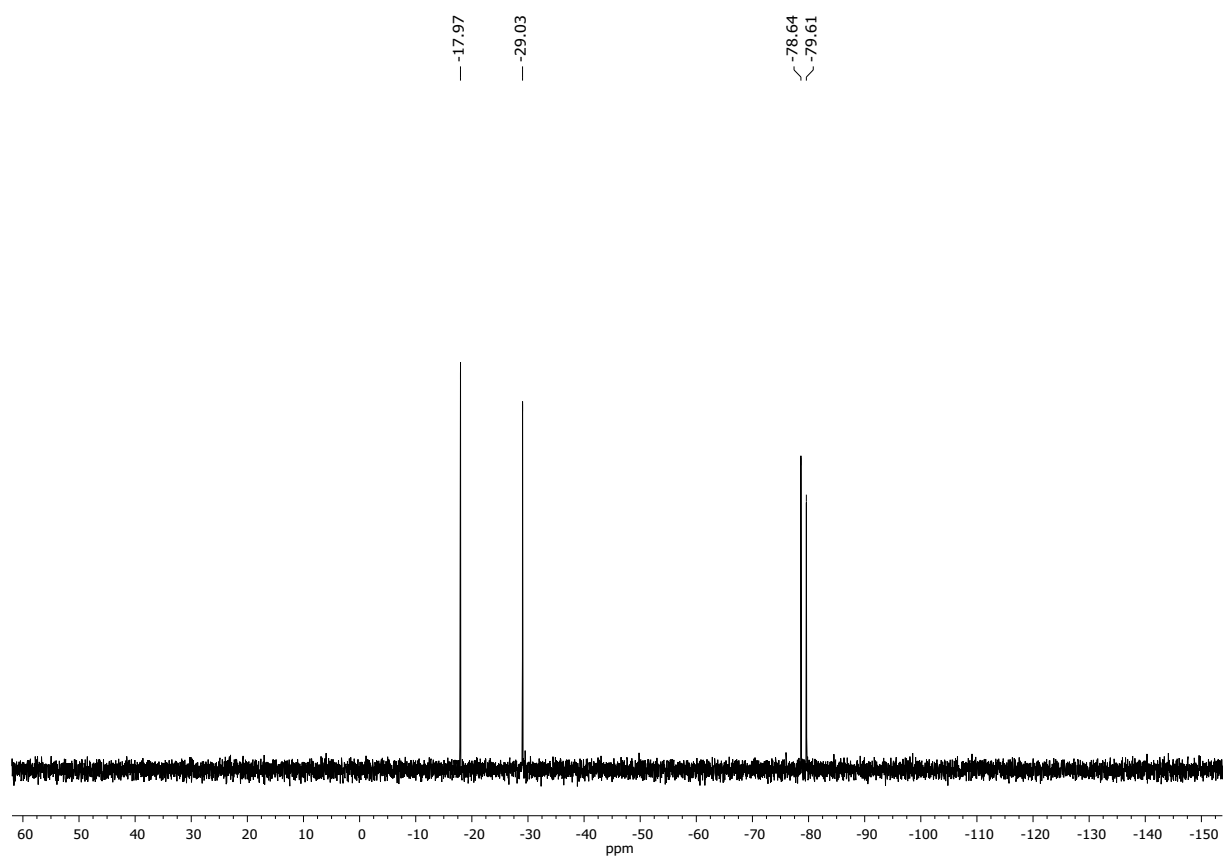
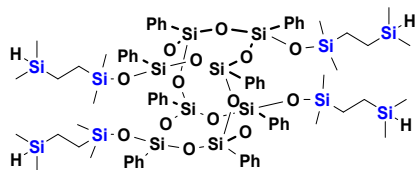


Figure S25 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-2D-4H**.

G0-4D-4H



White solid. Isolated Yield 94%

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = -0.21$ (d, $J_{\text{H-H}}=3.6$ Hz, 24H, $-\text{CH}_3$), 0.00 (s, 24H, $-\text{CH}_3$), 0.18-0.23 (m, 8H, Si-CH_2-), 0.33-0.39 (m, 8H, Si-CH_2-), 3.57 (dt, $J_{\text{H-H}}= 6.8, 3.4$ Hz, 4H, $-\text{Si-H}$), 7.08-7.45 (m, 40H, $-\text{Ph}$).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3 , ppm): $\delta = -4.93$ (Si-CH_3), 0.40 (Si-CH_3), 5.68 (Si-CH_2-), 10.80 (Si-CH_2-) 127.56, 127.60, 129.85, 130.22, 131.87, 133.71, 134.41, 134.47 ($-\text{Ph}$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): $\delta = 11.45$ ($-\text{Si}-(\text{CH}_3)_2$), -10.14 ($-\text{Si-H}$), -78.64 , -79.61 ($-\text{Si-Ph}$).

IR (ATR, cm^{-1}): 3072.24, 3050.84 (C-H phenyl), 2954.49, 2906.60 (C-H), 2104.74 (Si-H), 1593.67, 1429.56 (C=C phenyl), 1248.53 (Si-C), 1126.83, 1100.37, 1045.14 (Si-O-Si), 998.28 (C-H phenyl), 885.41 (Si-H).

EA: Anal. calcd for $\text{C}_{72}\text{H}_{108}\text{O}_{14}\text{Si}_{16}$ (%): C, 52.51, H, 6.61; found: C, 52.72; H, 6.64.

GPC: $M_w = 1519$; $M_n = 1343$; $D = 1.13$.

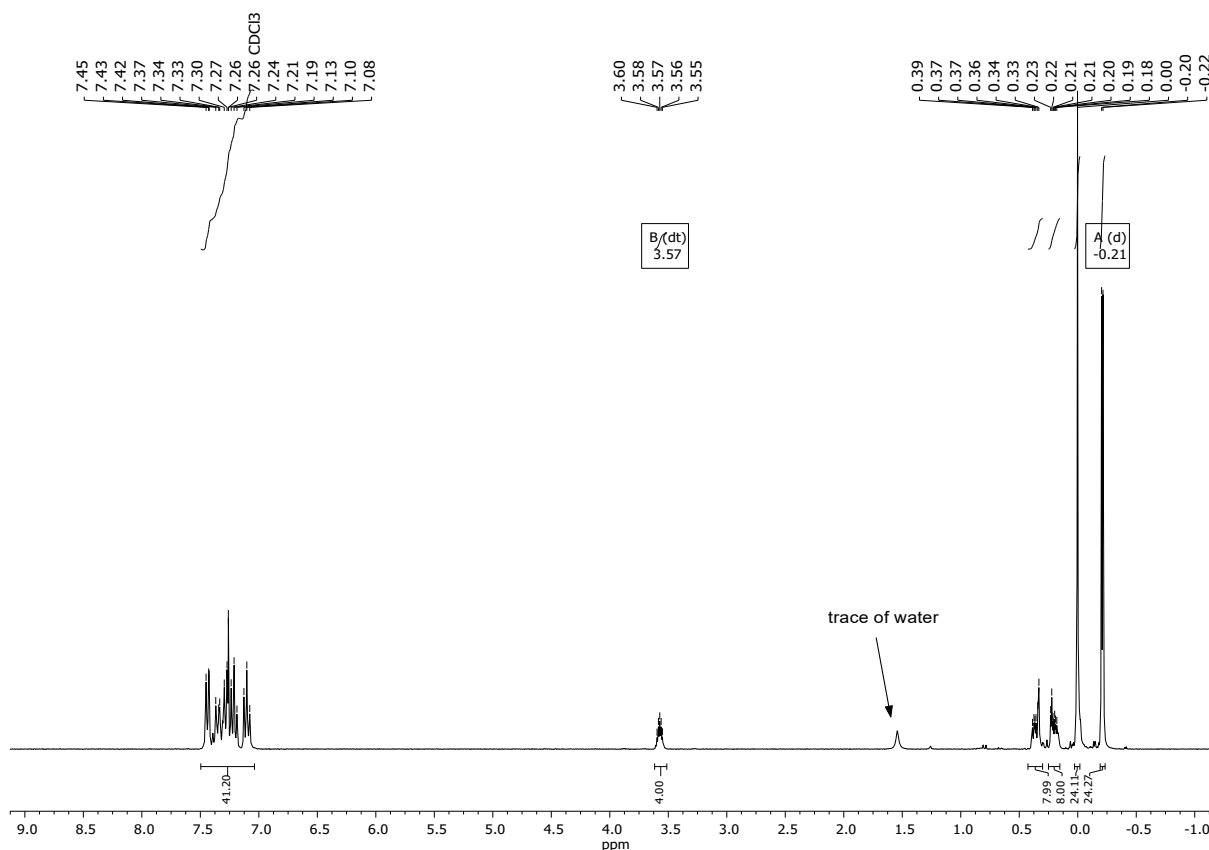


Figure S26 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of G0-4D-4H.

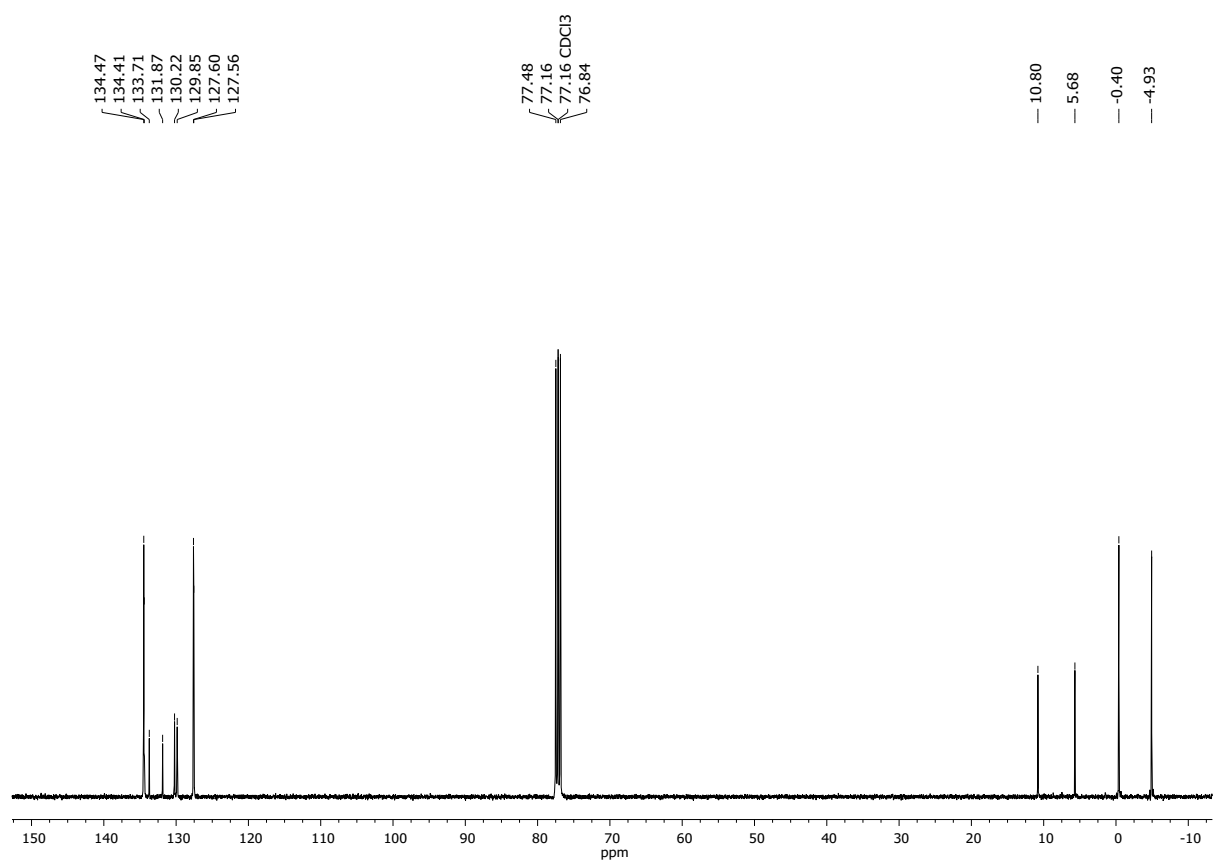


Figure S27 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G0-4D-4H**.

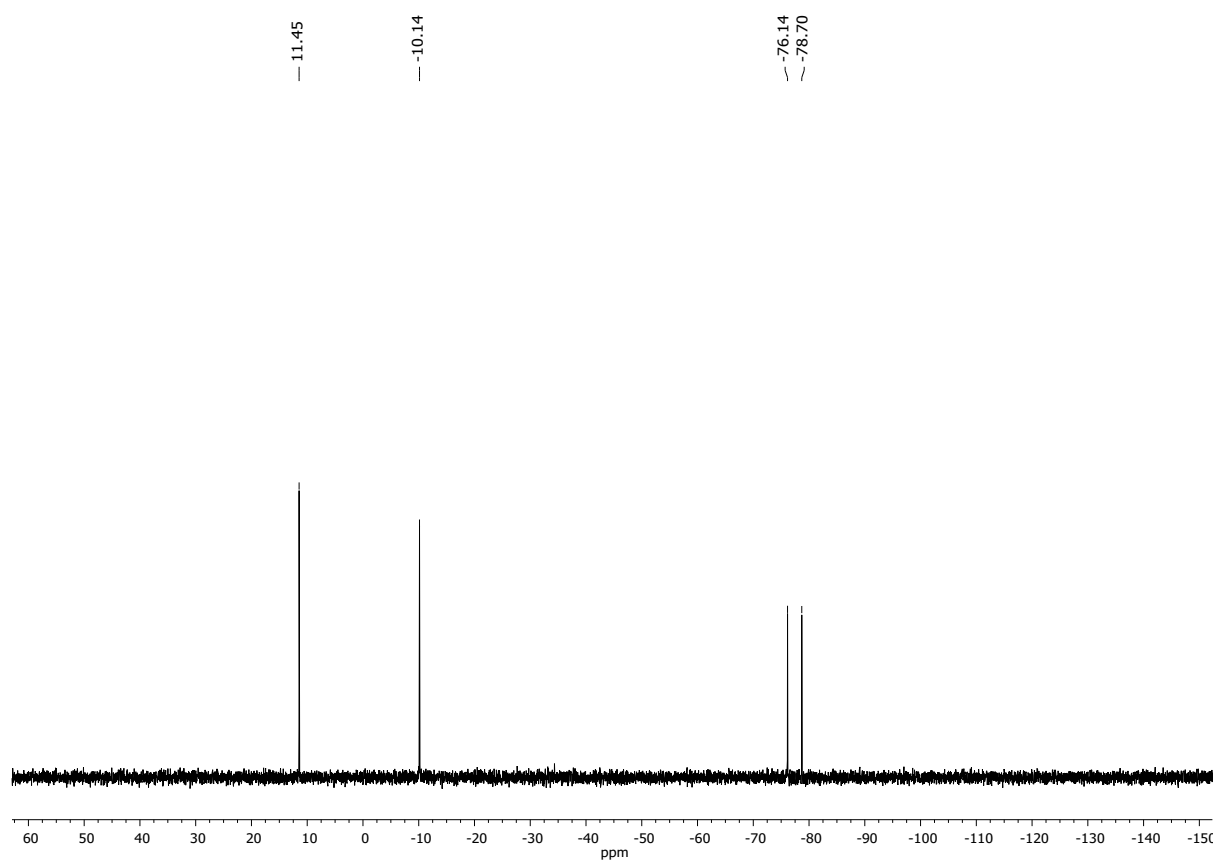
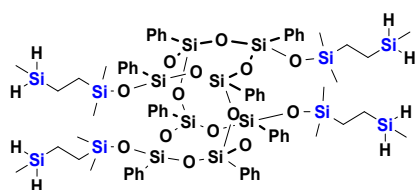


Figure S28 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G0-4D-4H**.

G1-4D-8H



White solid. Isolated Yield 91%

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ = -0.13 (t, $J_{\text{H-H}}=4.1$ Hz, 12H, $-\text{CH}_3$), 0.03 (s, 24H, $-\text{CH}_3$), 0.30-0.38 (m, 8H, Si- CH_2 -), 0.42-0.49 (m, 8H, Si- CH_2 -), 3.47 (h, $J_{\text{H-H}}= 3.6$ Hz, 4H, $-\text{Si-H}$), 7.11-7.47 (m, 40H, $-\text{Ph}$).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3 , ppm): δ = -8.82 (Si- CH_3), -0.36 (Si- CH_3), 2.38 (Si- CH_2 -), 12.00 (Si- CH_2 -) 127.61, 129.91, 130.27, 131.76, 133.59, 134.39, 134.46 ($-\text{Ph}$).

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): δ = 11.18 ($-\text{Si}-(\text{CH}_3)_2$), -29.37 ($-\text{Si-H}$), -76.07, -78.69 ($-\text{Si-Ph}$).

IR (ATR, cm^{-1}): 3072.10, 3050.82 (C-H phenyl), 2957.14, 2915.36 (C-H), 2124.73 (Si-H), 1593.63, 1429.65 (C=C phenyl), 1251.08 (Si-C), 1128.24, 1104.83, 1052.57 (Si-O-Si), 998.39 (C-H phenyl), 900.99 (Si-H).

EA: Anal. calcd for $\text{C}_{68}\text{H}_{100}\text{O}_{14}\text{Si}_{16}$ (%): C, 51.34, H, 6.34; found: C, 51.55; H, 6.37.

GPC: $M_w = 1387$; $M_n = 1232$; $D = 1.13$.

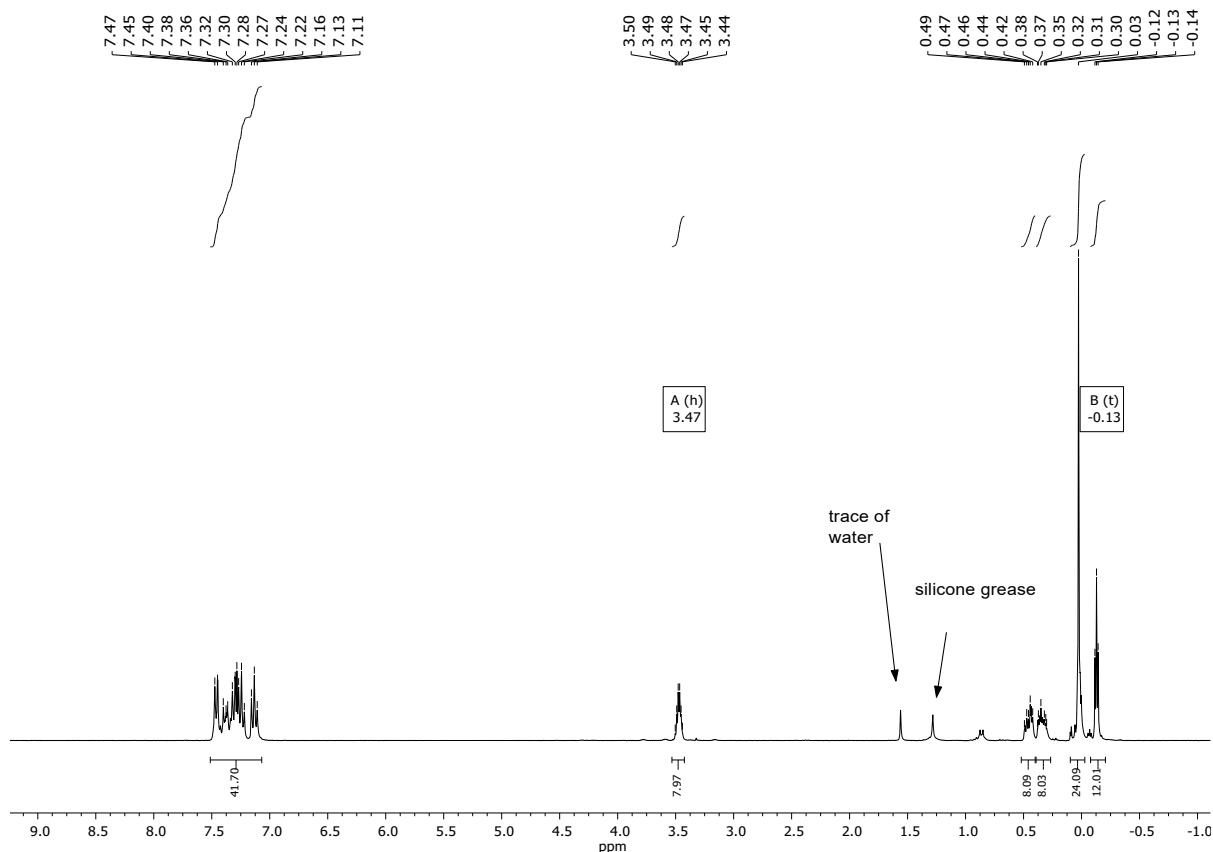


Figure S29 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of G1-4D-8H.

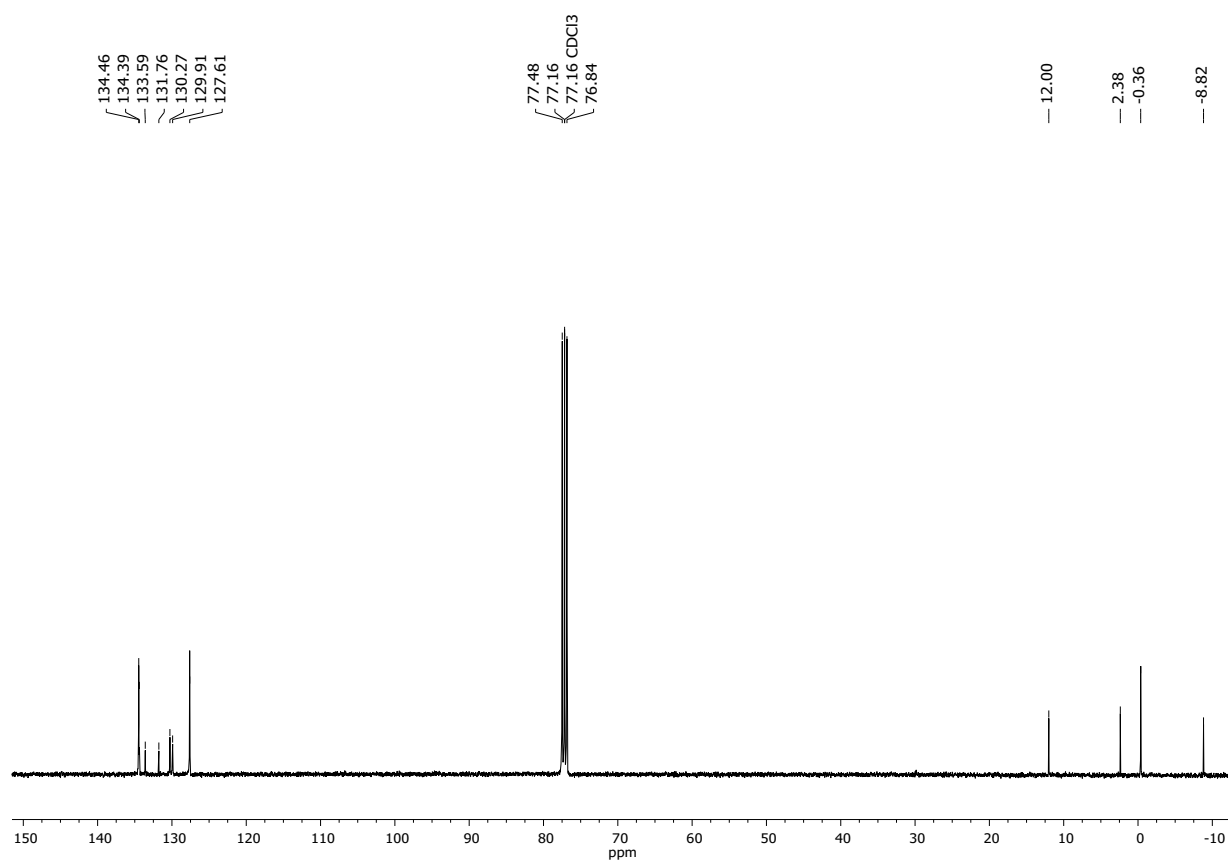


Figure S30 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-4D-8H**.

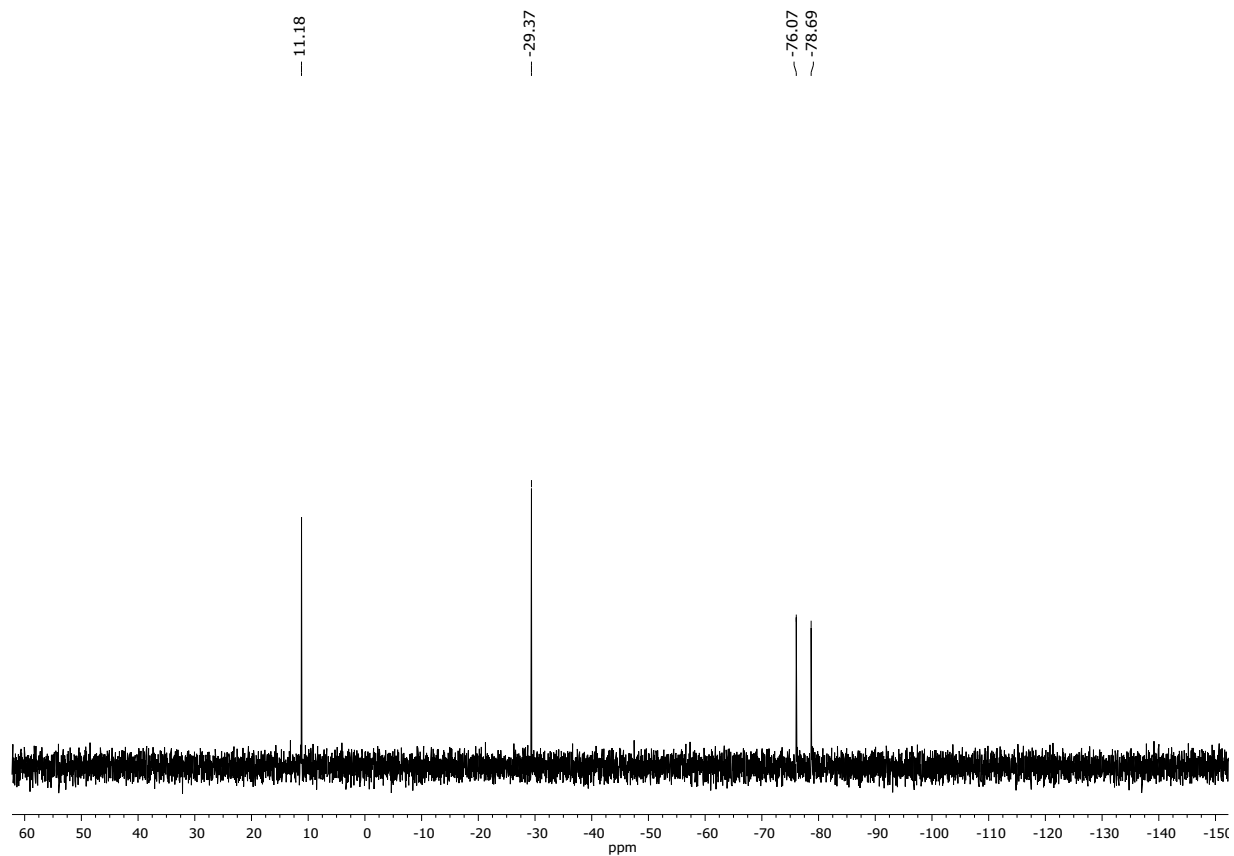
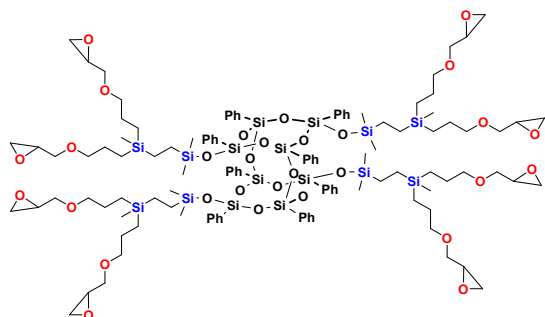


Figure S31 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-4D-8H**.

G1-8D-8epoxy



White waxy solid. Isolated Yield 85%

¹H NMR (300 MHz, CDCl₃, ppm): δ = -0.34 (s, 12H, -CH₃), 0.01 (s, 24H, -CH₃), 0.10-0.26 (m, 32H, Si-CH₂-), 1.36 (dt, *J*_{H-H} = 14.4, 7.1 Hz, 16H, -CH₂-), 2.58 (dd, *J*_{H-H} = 4.9, 2.6 Hz, 8H, CH₂-O), 2.77 (t, *J*_{H-H} = 4.5 Hz, 8H, CH₂-O), 3.11 (dt, *J*_{H-H} = 8.5, 4.9 Hz, 8H, CH-O), 3.27-3.36 (m, 24H, CH₂-O), 3.64 (dd, *J*_{H-H} = 11.4, 3.0 Hz, 8H, CH₂-O), 7.07-7.44 (m, 40H, -Ph).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -6.12 (Si-CH₃), -0.45 (Si-CH₃), 4.90 (Si-CH₂-), 8.90 (Si-CH₂-), 10.30 (-Si-CH₂-), 24.02 (-CH₂-), 44.45 (CHO), 50.95 (CHO), 71.51 (OCH₂), 74.61 (CH₂O), 127.55, 127.59, 129.87, 130.27, 131.80, 133.61, 134.31, 134.37 (-Ph).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = 11.59 (-Si-(CH₃)₂), 5.48 (-Si-CH₃), -76.13, -78.68 (-Si-Ph).

IR (ATR, cm⁻¹): 3071.54, 3049.24, 3002.88 (C-H phenyl), 2950.25, 2923.28, 2868.39 (C-H), 1593.28, 1429.79 (C=C phenyl), 1249.94 (Si-C), 1127.10, 1096.83, 1042.86 (Si-O-Si), 997.90 (C-H phenyl).

EA: Anal. calcd for C₁₁₆H₁₈₀O₃₀Si₁₆ (%): C, 55.64, H, 7.25; found: C, 55.86; H, 7.28.

GPC: M_w = 2096; M_n = 1819; Đ = 1.15.

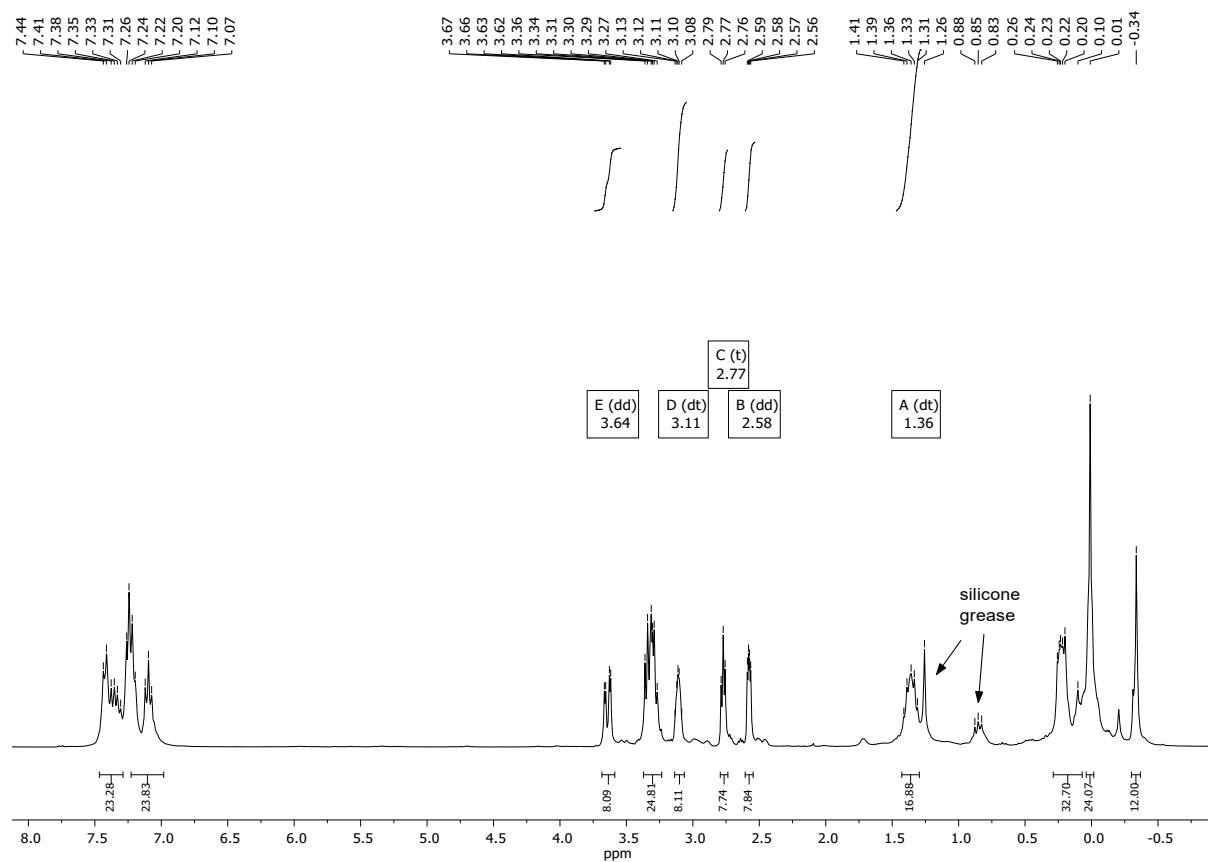


Figure S32 ¹H NMR (300 MHz, CDCl₃) spectrum of G1-8D-8epoxy.

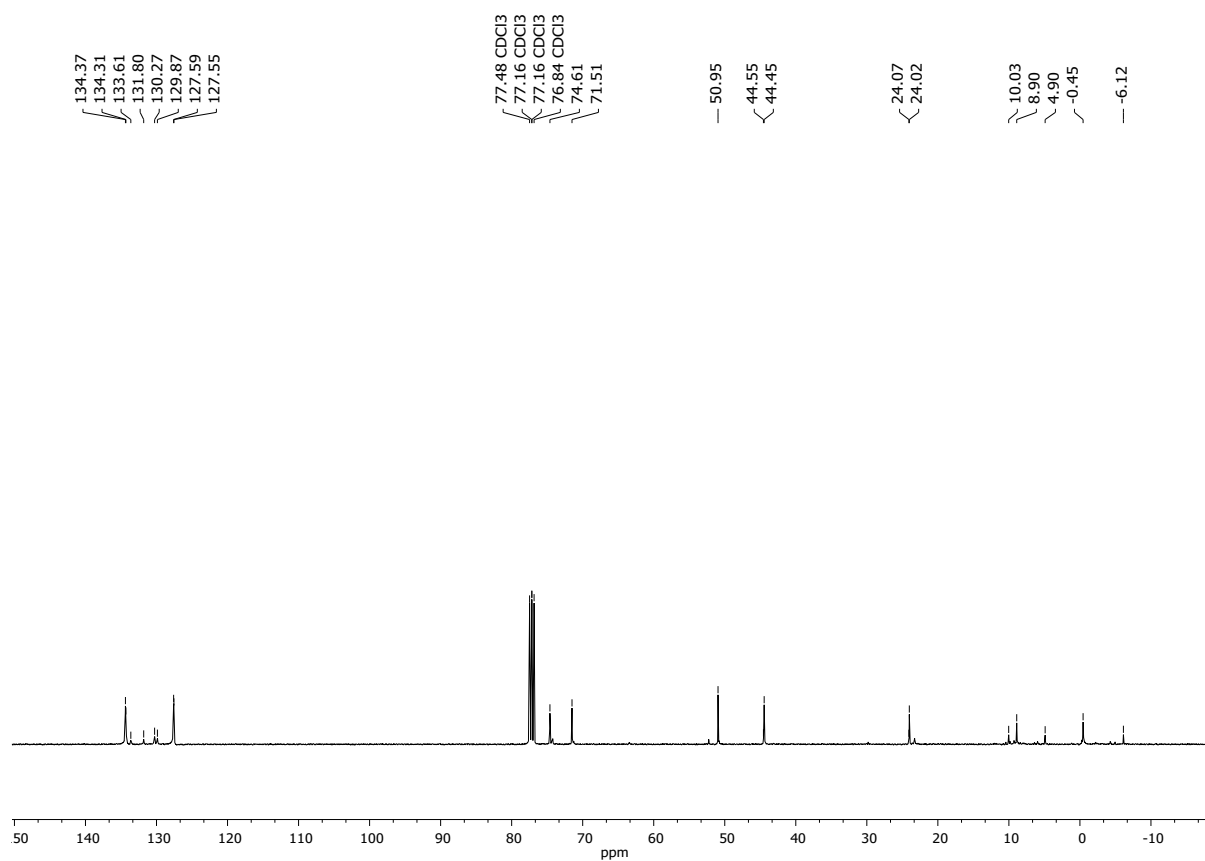


Figure S33 ¹³C NMR (101 MHz, CDCl₃) spectrum of **G1-8D-8epoxy**.

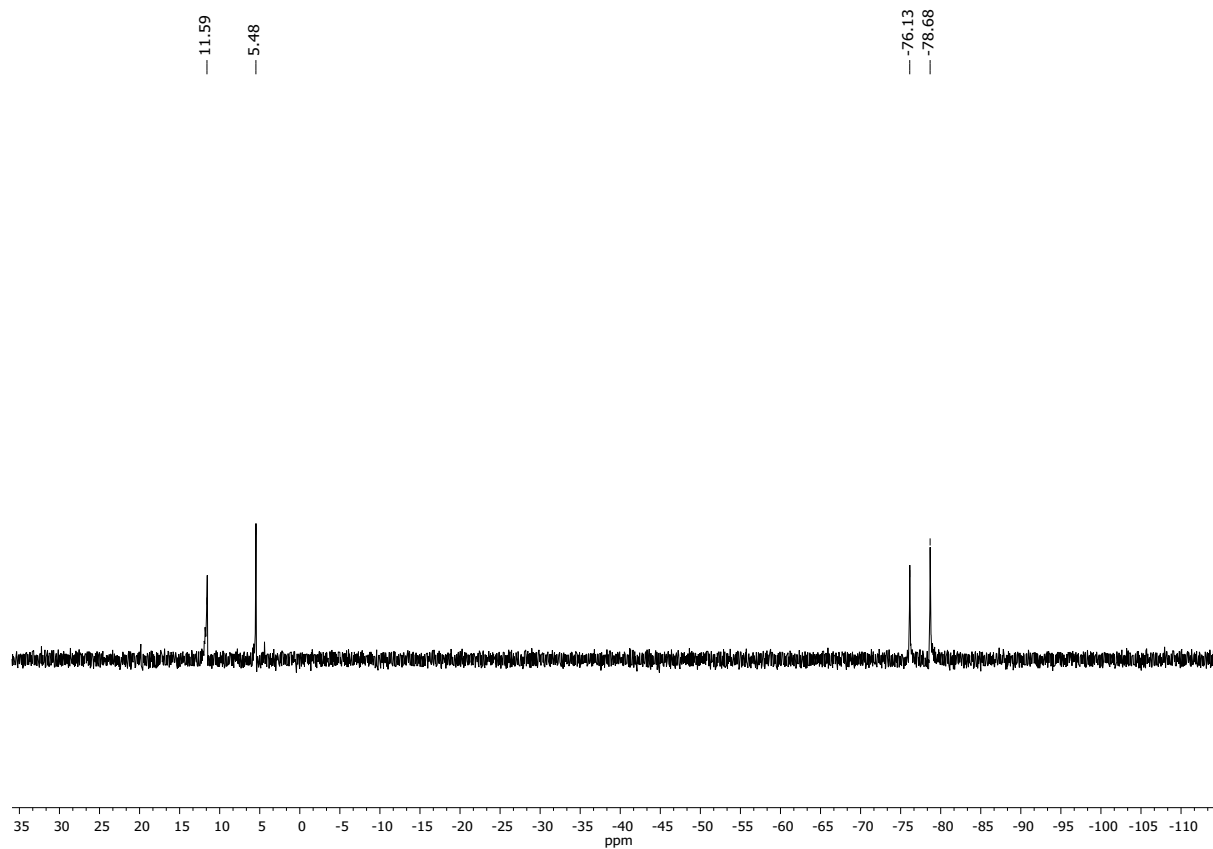
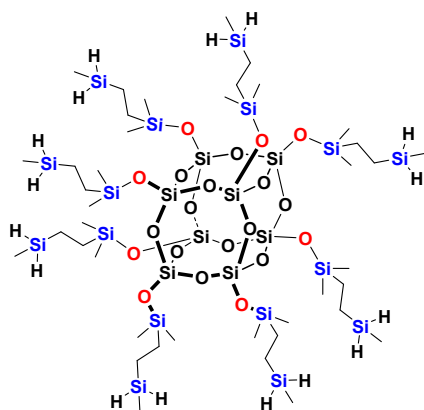


Figure S34 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of **G1-8D-8epoxy**.

G1-8T-16H



Viscous oils. Isolated Yield 85%

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.14 (s, 72H, -CH₃), 0.58 (m, 32H, Si-CH₂-), 3.73 (m, 16H, -Si-H).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -8.55 (H₂Si-CH₃), -0.74 (Si-CH₃), 2.25 (Si-CH₂-), 11.63 (CH₂-Si).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = 12.75 (-Si-CH₃), -29.14 (H₂Si-CH₂), -108.92 (-SiO₄, cage).

IR (ATR, cm⁻¹): 2959.91, 2913.95 (C-H), 2124.87 (Si-H), 1251.80 (Si-C), 1137.51, 1072.97, 1053.98 (Si-O-Si), 944.71 (Si-H).

EA: Anal. calcd for C₁₁₆H₁₈₀O₃₀Si₁₆ (%): C, 30.11, H, 7.58; found: C, 30.23; H, 7.61.

GPC: M_w = 1920; M_n = 1817; D = 1.057.

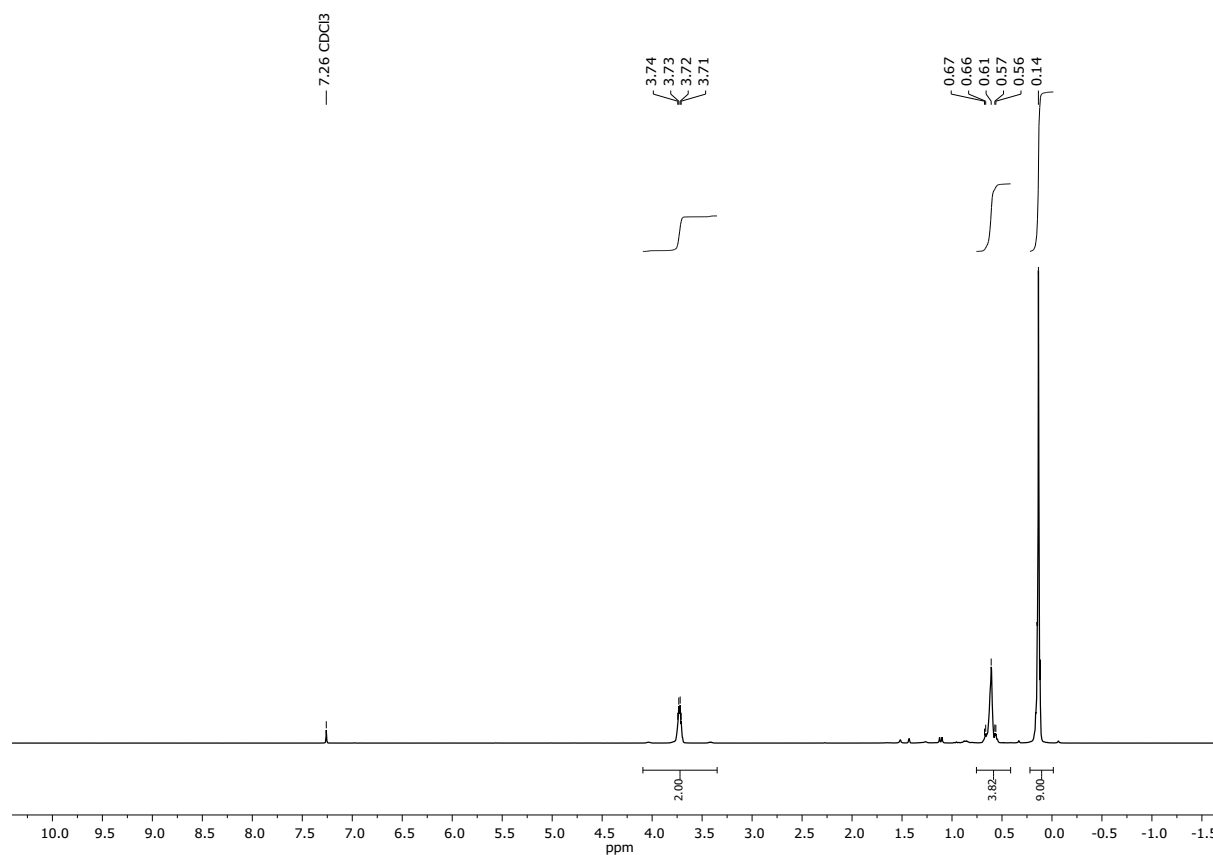


Figure S35 ¹H NMR (300 MHz, CDCl₃) spectrum of G1-8T-16H.

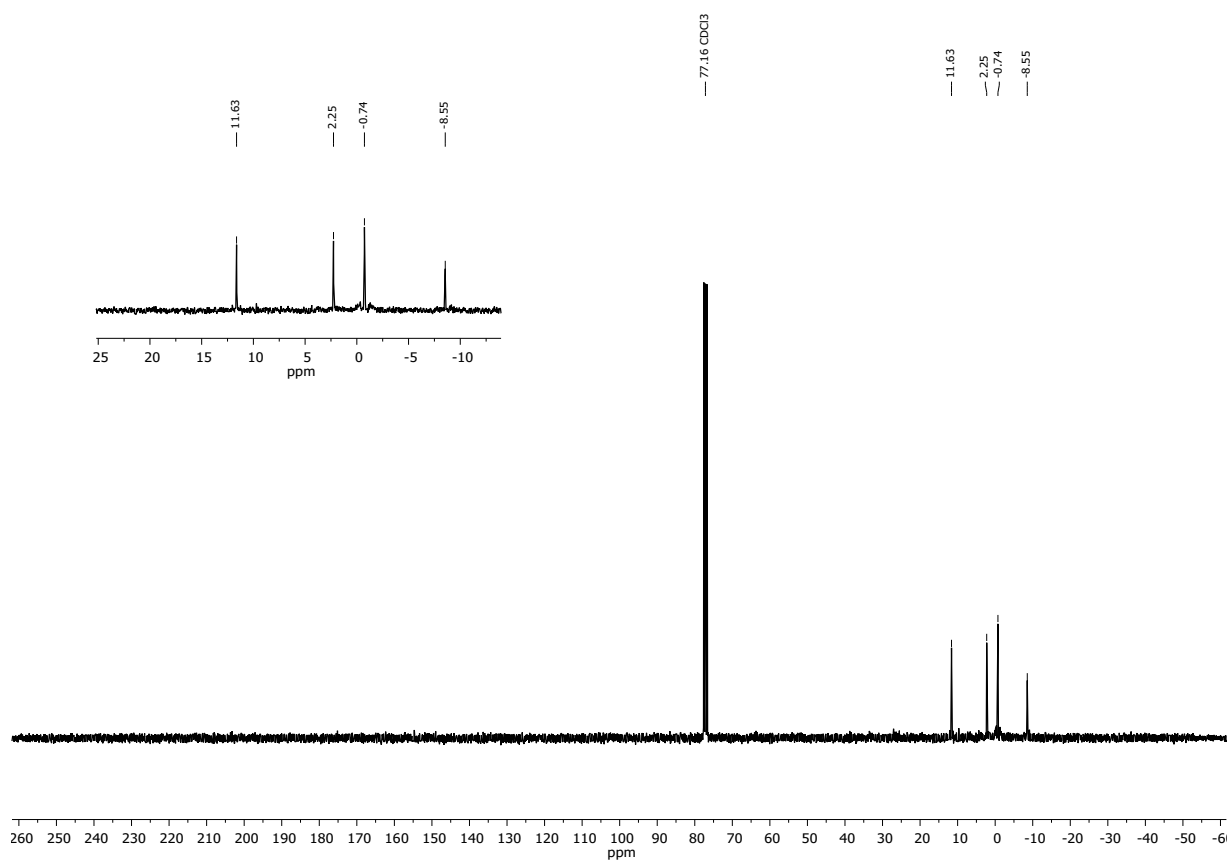


Figure S36 ^{13}C NMR (75.50 MHz, CDCl_3) spectrum of G1-8T-16H.

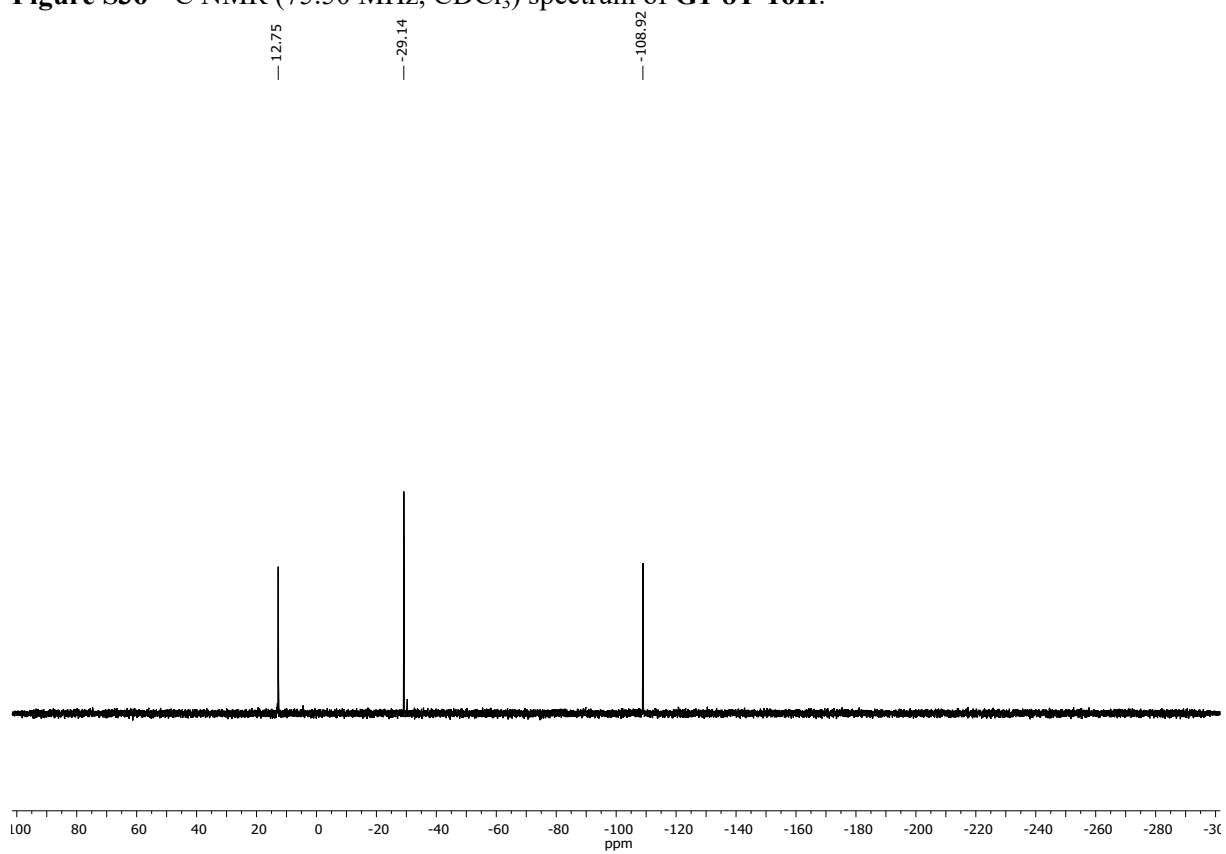
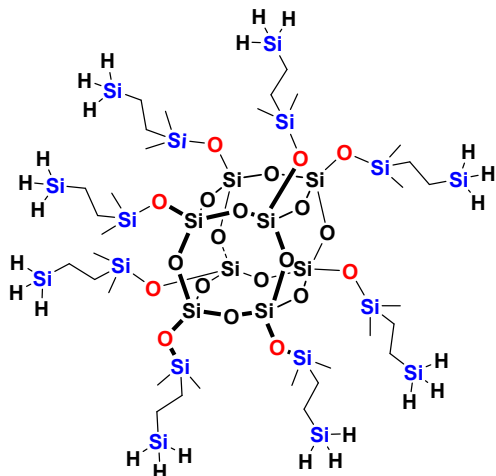


Figure S37 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of G1-8T-16H.

G1-8T-24H



Viscous oils. Isolated Yield 85%

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.14 (s, 48H, -CH₃), 0.68 (m, 32H, Si-CH₂-), 3.55 (t, *J*_{H-H} = 3.6 Hz, 24H, -Si-H).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -1.85 (H₃Si-CH₂), -0.69 (Si-CH₃), 13.41 (Si-CH₂-).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = 12.52 (-Si-CH₂), -53.75 (H₃Si-CH₂), -108.99 (-SiO₄, cage).

IR (ATR, cm⁻¹): 2958.98, 2920.74, 2894.91 (C-H), 2143.97 (Si-H), 1253.39 (Si-C), 1139.52, 1072.63, 1055.82 (Si-O-Si), 922.13 (Si-H).

EA: Anal. calcd for C₁₁₆H₁₈₀O₃₀Si₁₆ (%): C, 25.91, H, 7.07; found: C, 26.01; H, 7.07.

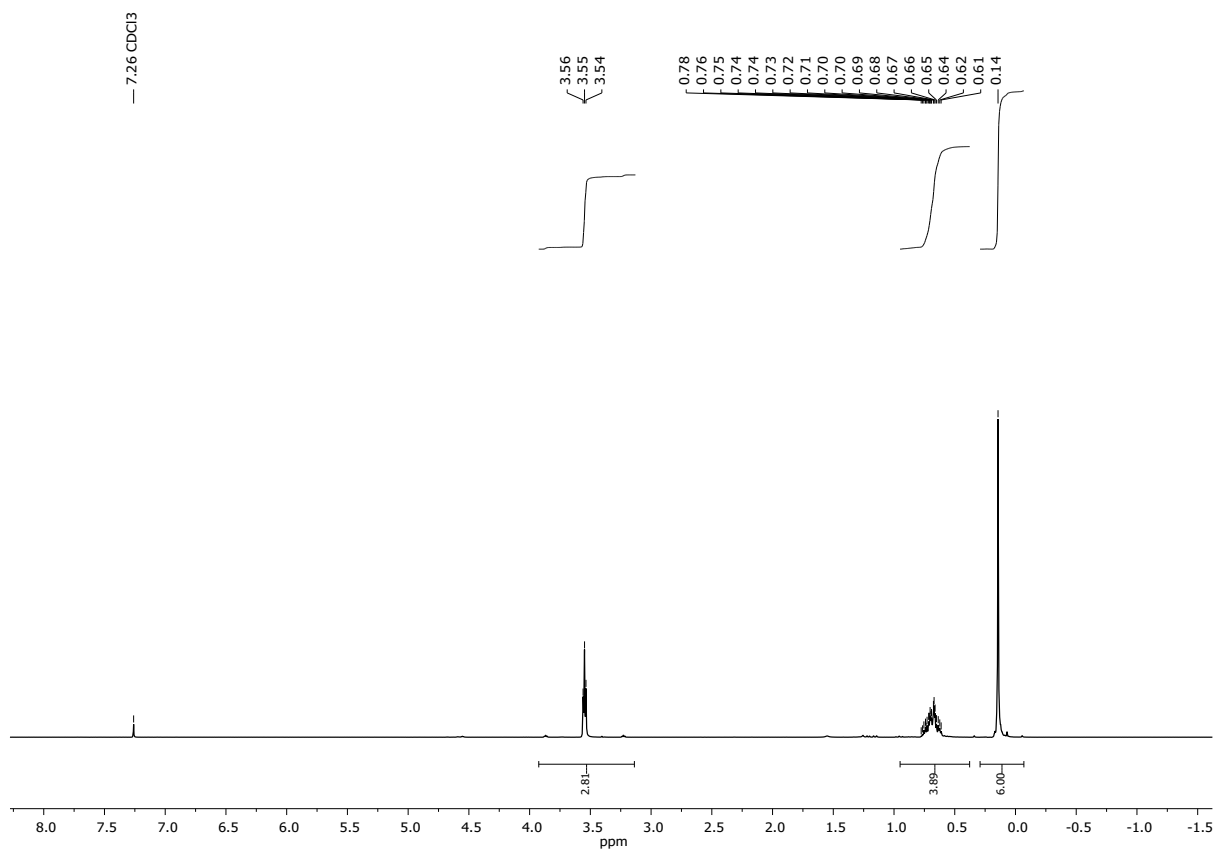


Figure S38 ¹H NMR (300 MHz, CDCl₃) spectrum of G1-8T-24H.

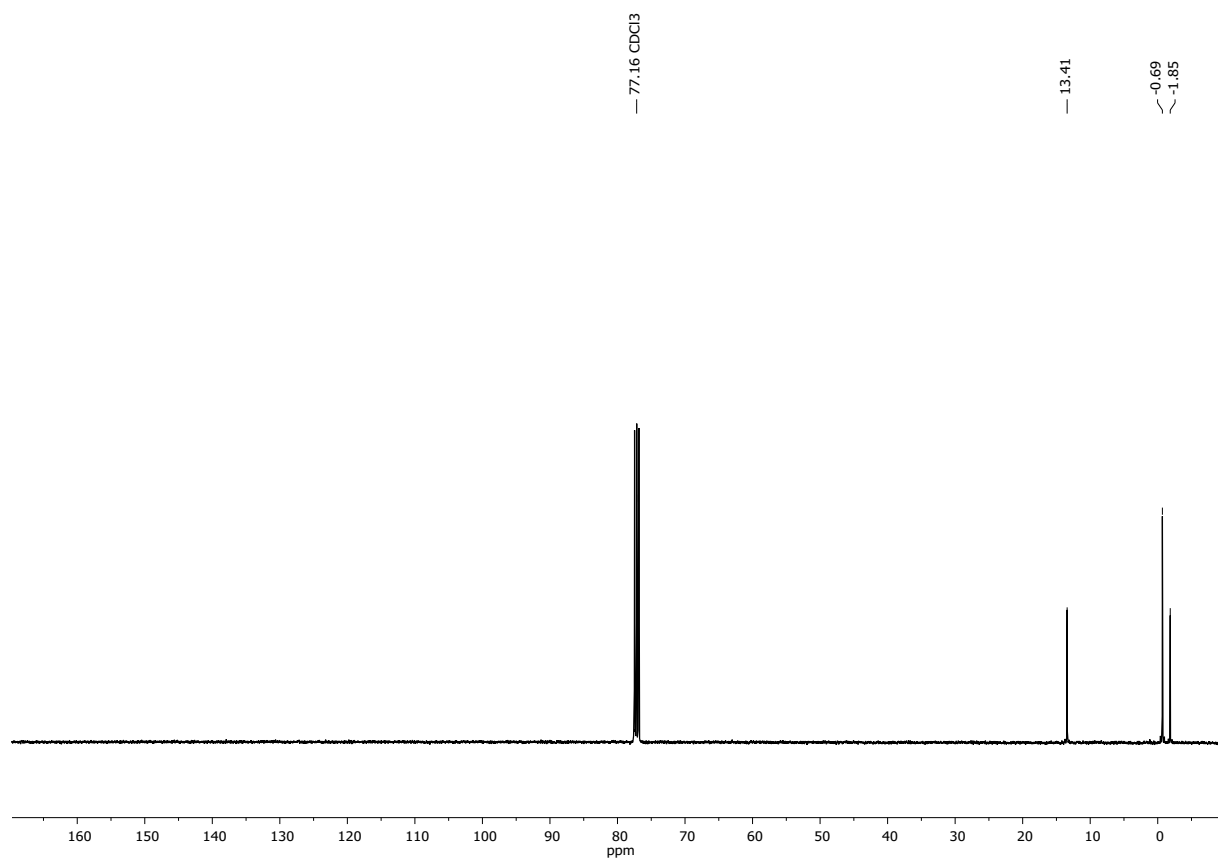


Figure S39 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-8T-24H**.

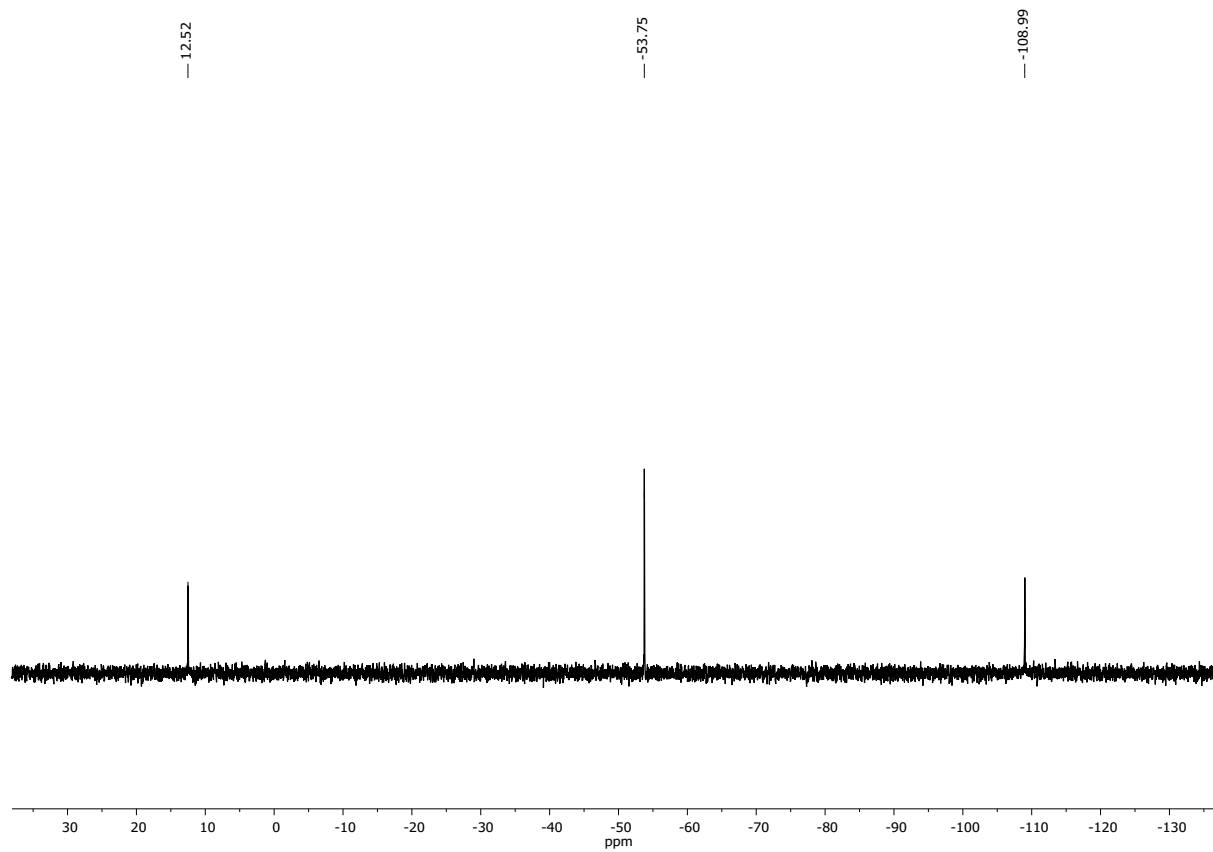
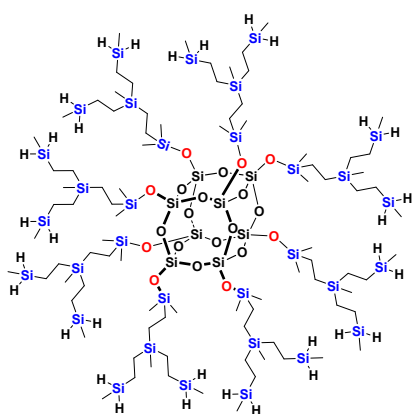


Figure S40 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-8T-24H**.

G2-16T-32H



Viscous oils. Isolated Yield 77% for mixture of hydrosilylation besides products.

¹H NMR (300 MHz, CDCl₃, ppm): δ = 0.13-0.06 (SiCH₃), 1.26-0.43 (SiCH₂CH₂Si, SiCH(CH₃)Si), 3.74 (m, SiH₂).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -8.52, -8.42, -8.37, -7.37, -7.17, -7.10, -6.84, -6.81, -6.77, -6.66, -6.33, -6.23, -6.15, -1.63, -1.26, -0.88, -0.82, -0.75, -0.29, 0.13, 0.18, 0.89, 3.24, 3.60, 3.68, 3.81, 3.88, 4.05, 4.14, 4.16, 4.23, 4.31, 5.50, 5.59, 6.52, 6.57, 6.62, 6.85, 7.00, 9.51, 9.68, 9.89, 10.03, 10.54, 10.56, 10.59, 10.74, 10.81, 11.28.

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = 12.84 (SiCH₃)₂, 7.88 (Si-O-Si), -2.49, -3.26, -3.53, -3.67, -3.88, -4.19, -4.39, -4.42, -4.83 (SiCH₂, SiCH(CH₃), SiCH₃), -29.24, -29.68 (RSiH₂), -108.84 (SiO₄ cage).

IR (ATR, cm⁻¹): 2957.31, 2907.82, 2882.15 (C-H), 2123.32 (Si-H), 1250.59 (Si-C), 1174.87, 1135.11, 1078.02, 1053.84 (Si-O-Si), 944.71 (Si-H).

GPC: M_w = 2801; M_n = 2678; *D* = 1.046.

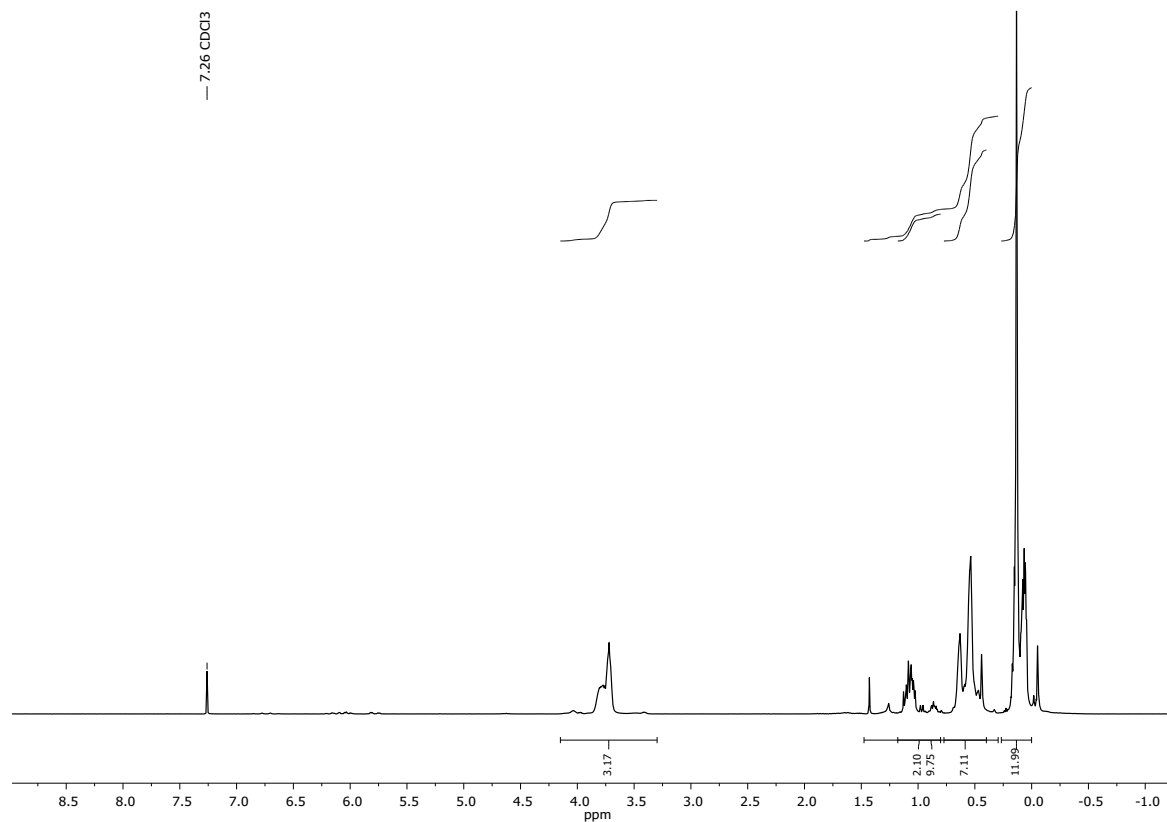


Figure S41 ¹H NMR (300 MHz, CDCl₃) spectrum of G2-16T-32H.

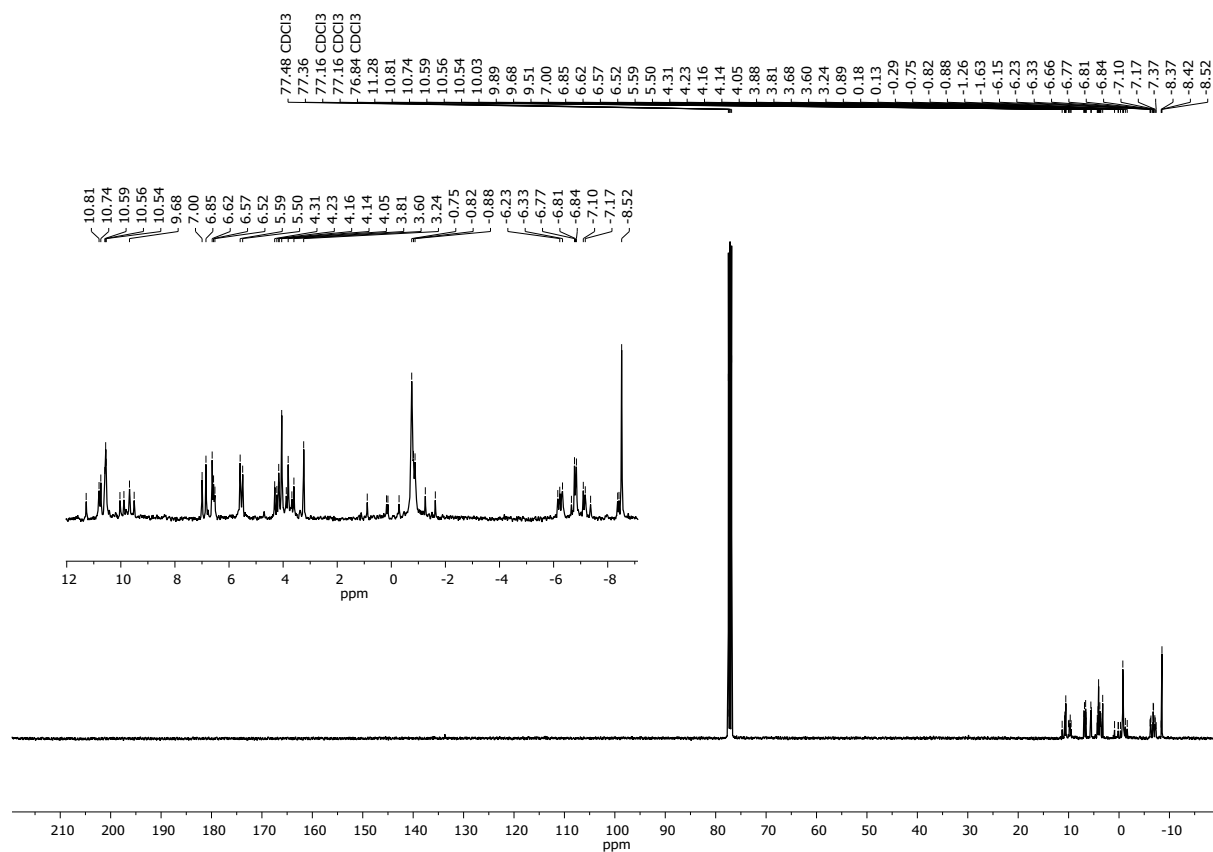


Figure S 42 ¹³C NMR (101 MHz, CDCl₃) spectrum of G2-16T-32H.

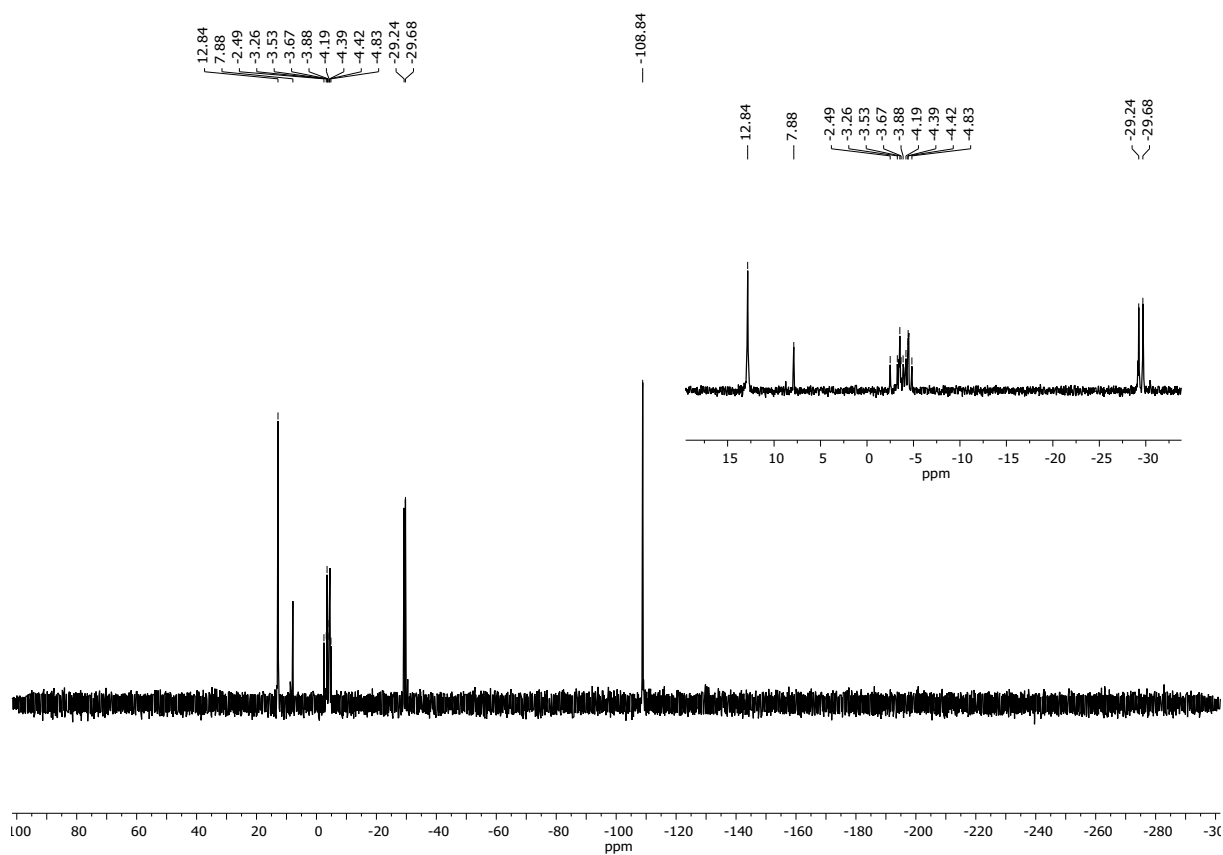
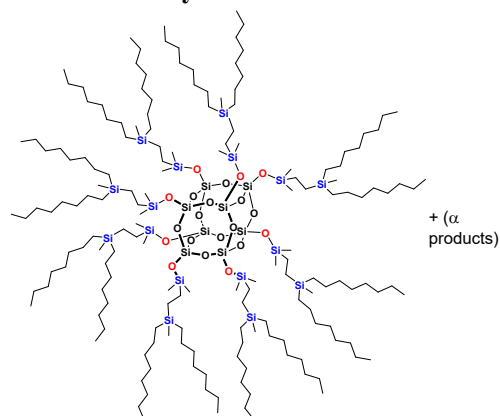


Figure S43 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of G2-16T-32H.

G1-16T-16octyl



Viscous oils. Isolated Yield 91% for mixture of hydrosilylation besides products (13% of the α -isomer - based on methyl integration at the SiCH₃ group)

¹H NMR (300 MHz, CDCl₃, ppm): δ = -0.08 (s, -SiCH₃, β isomer), -0.05 (s, -SiCH₃, α isomer), 0.13 (s, Si(CH₃)₂), 0.36-0.50 (m, Si-CH₂-), 0.88 (t, -CH₃), 1.27 (s, CH₂₀octyl).

¹³C NMR (101 MHz, CDCl₃, ppm): δ = -3.71, 6.47 (α isomer), -5.47 (Si-CH₃), -0.09 (Si-CH₃), 5.01 (Si-CH₂-), 9.76 (Si-CH₂-), 13.49, 14.28, 22.88, 24.09, 29.51, 32.15, 34.05 (CH₂).

²⁹Si NMR (79.50 MHz, CDCl₃, ppm): δ = 12.95 (-Si(CH₃)₂), 4.75 (SiCH₃, β isomer), 4.15 (SiCH₃, α isomer), -108.72 (SiO₄ cage).

IR (ATR, cm⁻¹): 2955.68, 2919.98, 2872.36, 2852.40 (C-H), 1250.69 (Si-C), 1134.43, 1077.66, 1051.30 (Si-O-Si).

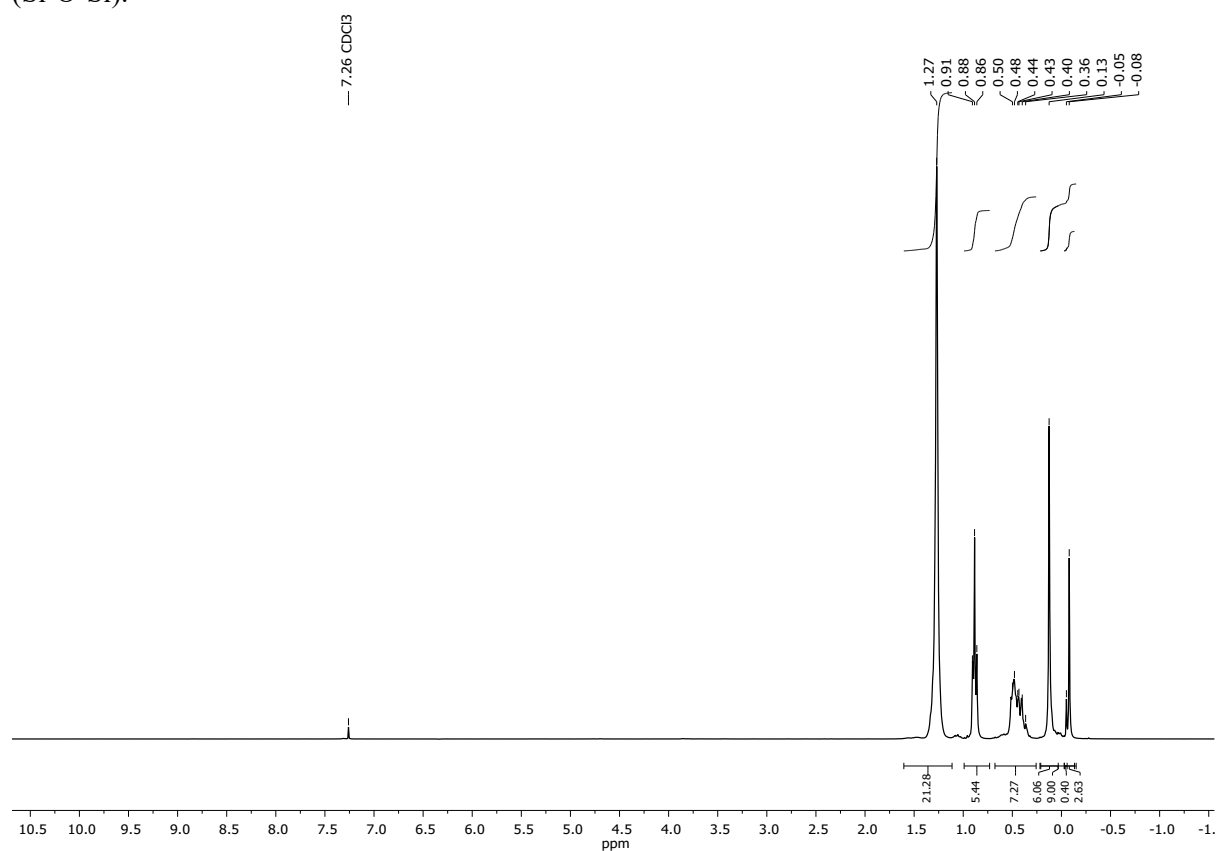


Figure S44 ¹H NMR (300 MHz, CDCl₃) spectrum of G1-16T-16octyl.

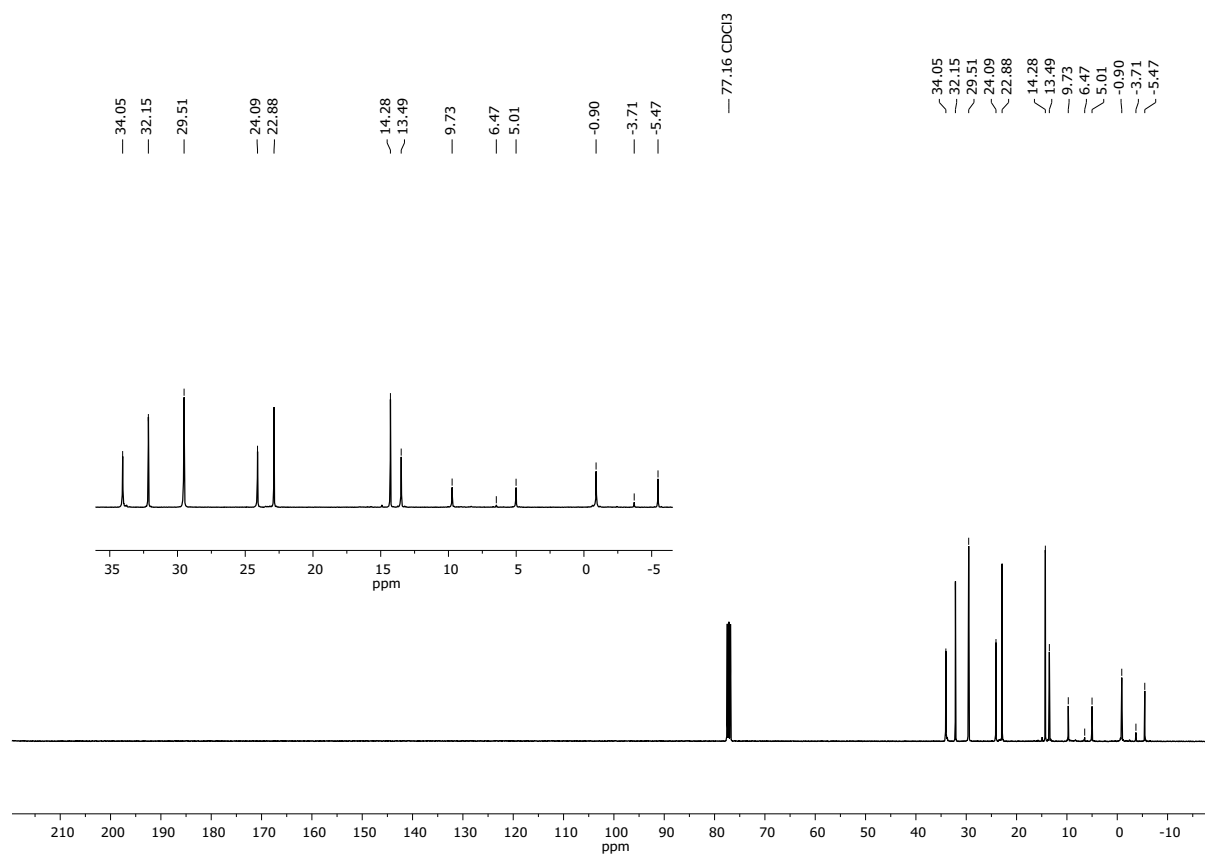


Figure S45 ¹³C NMR (101 MHz, CDCl₃) spectrum of **G1-16T-16octyl**.

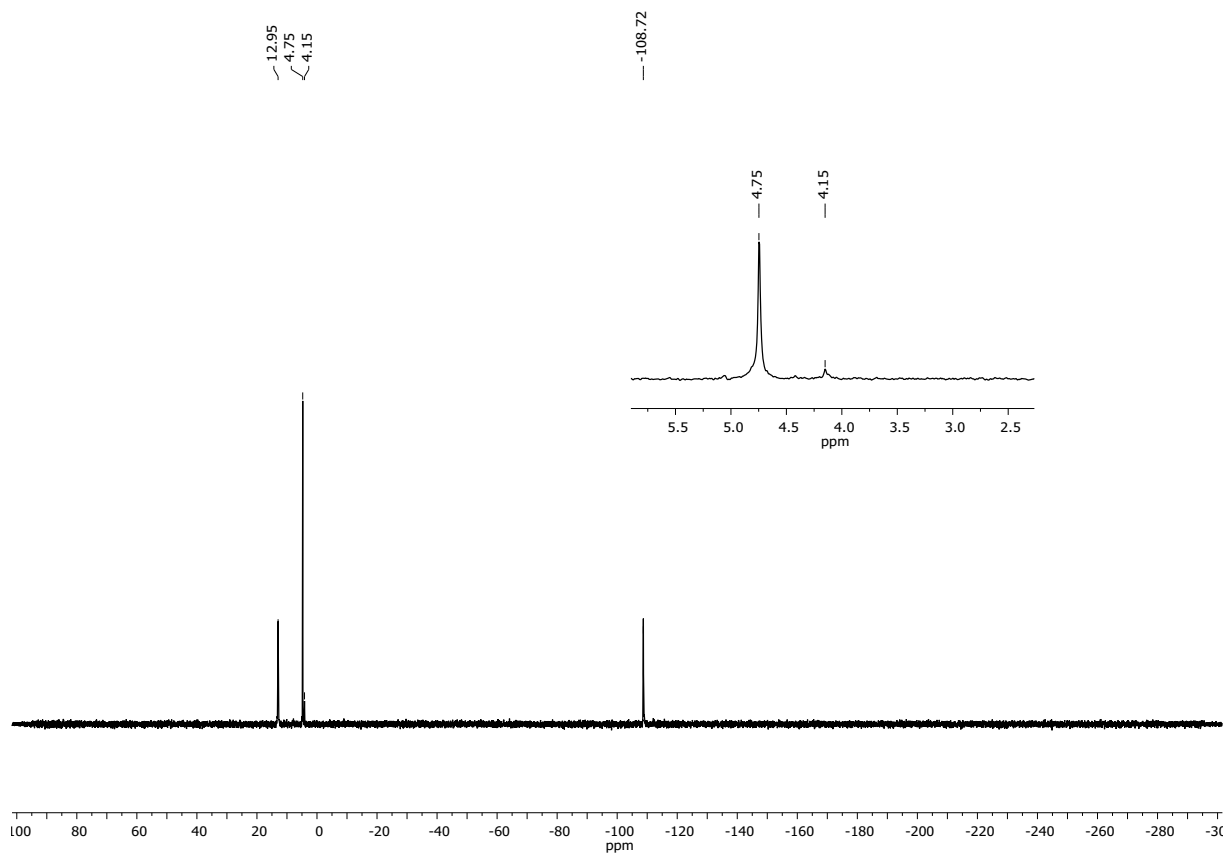
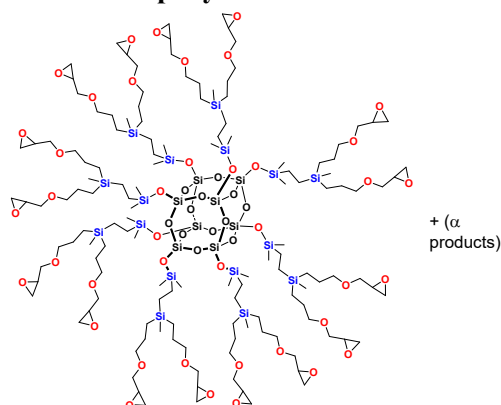


Figure S46 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of G1-16T-16octyl.

G1-16T-16epoxy



Viscous oils. Isolated Yield 88% for mixture of hydrosilylation besides products.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = -0.06$ (s, $-\text{SiCH}_3$), 0.10 (s, $-\text{Si}(\text{CH}_3)_2$), 0.38-0.55 (m, SiCH_2), 1.44-1.63 (m, Si-CH_2-), 2.58 (m, $\text{CH}_{\text{oxirane}}$), 2.77 (m, $\text{CH}_{\text{oxirane}}$), 3.06-3.18 (m, $\text{CH}_{\text{oxirane}}$), 3.30-3.51 (m, $\text{CH}_2\text{-O}$), 3.68 (dd, $J_{\text{H-H}} = 11.5, 3.0$ Hz, O-CH_2).

$^{13}\text{C NMR}$ (75.50 MHz, CDCl_3 , ppm): $\delta = -5.73, -0.96, 4.77, 9.09, 9.15, 9.55, 23.54, 24.14, 44.36, 50.87, 50.93, 71.53, 74.58$.

$^{29}\text{Si NMR}$ (79.50 MHz, CDCl_3 , ppm): $\delta = 13.06$ ($-\text{Si}(\text{CH}_3)_2$), 5.87 (SiCH_3CH_2 , β isomer), 4.77 (SiCH_3CH , α isomer), -108.81 (SiO_4 cage).

IR (ATR, cm^{-1}): 2996.17, 2953.34, 2953.14, 2870.45 (C-H), 1251.01 (Si-C), 1134.17, 1074.61, 1049.68 (Si-O-Si).

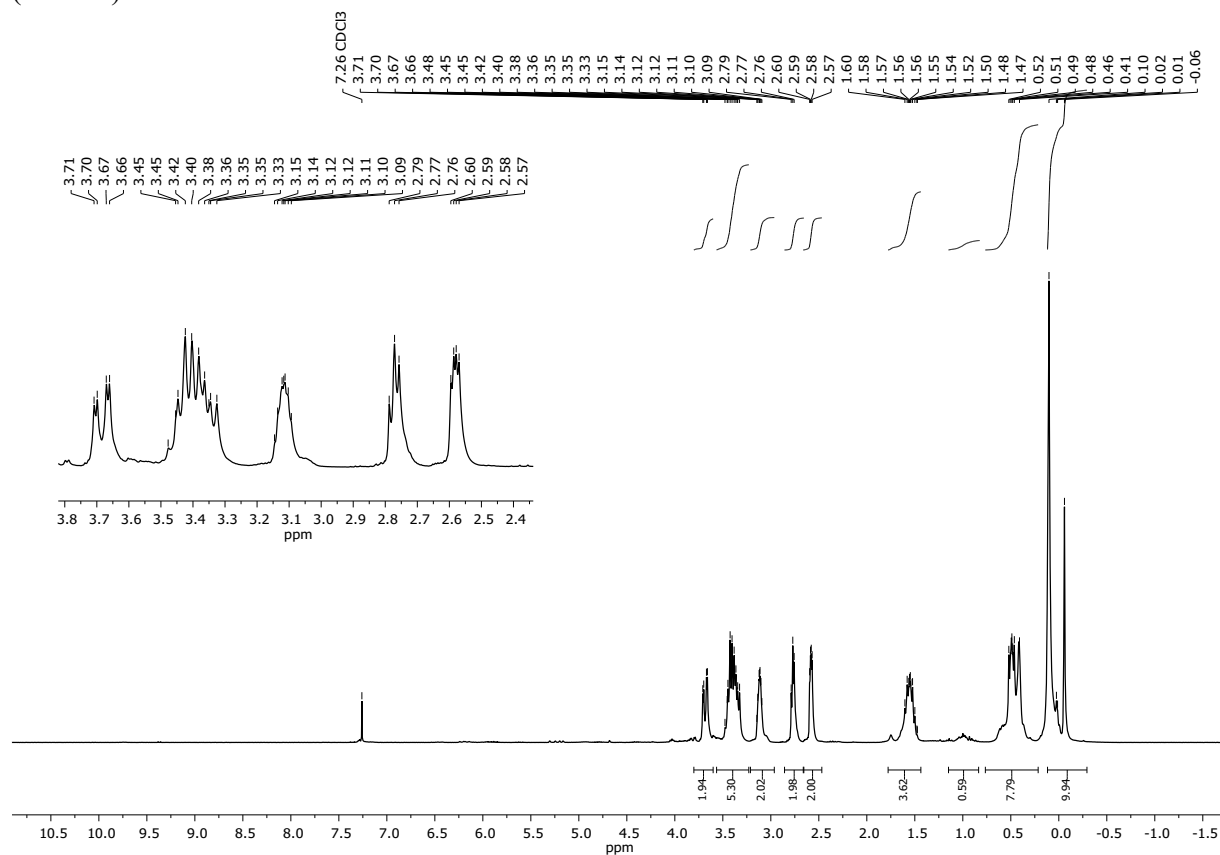


Figure S47 $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of **G1-16T-16epoxy**.

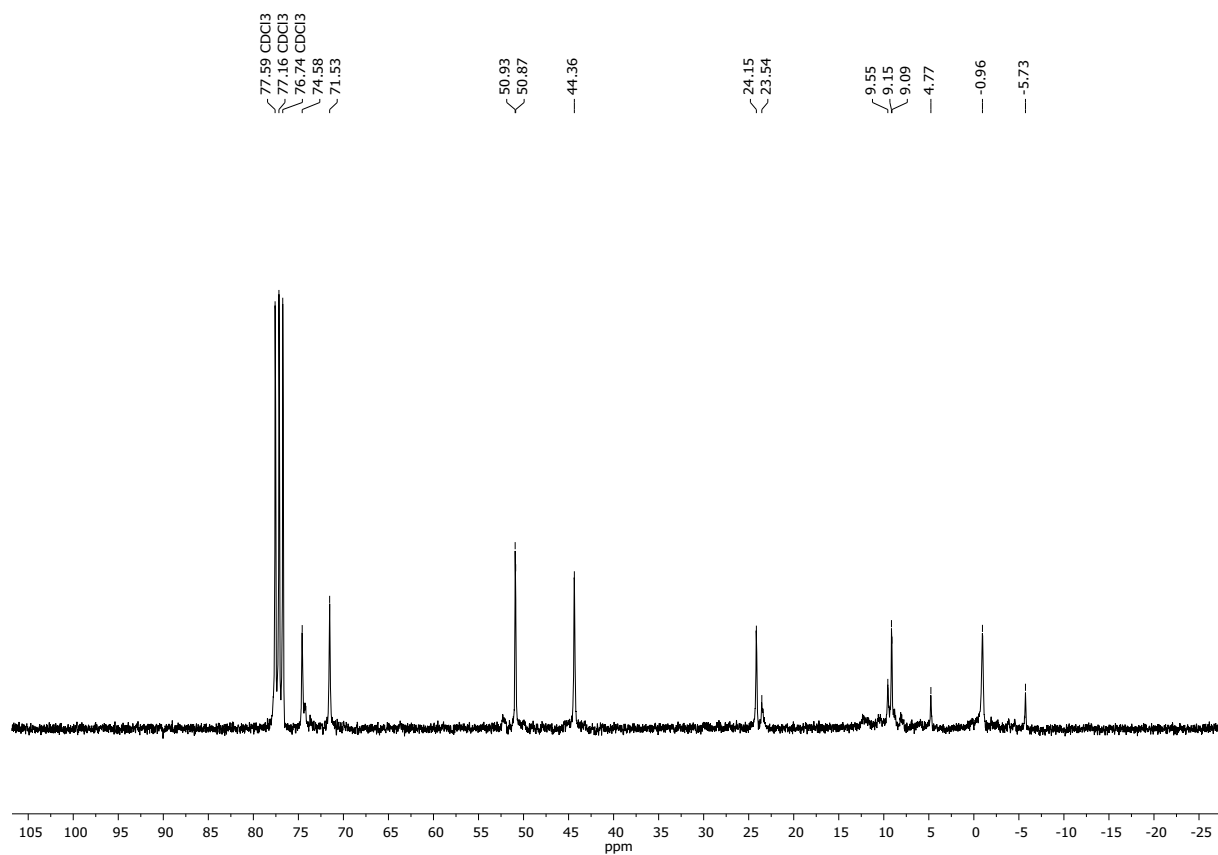


Figure S48 ¹³C NMR (75.50 MHz, CDCl₃) spectrum of G1-16T-16epoxy.

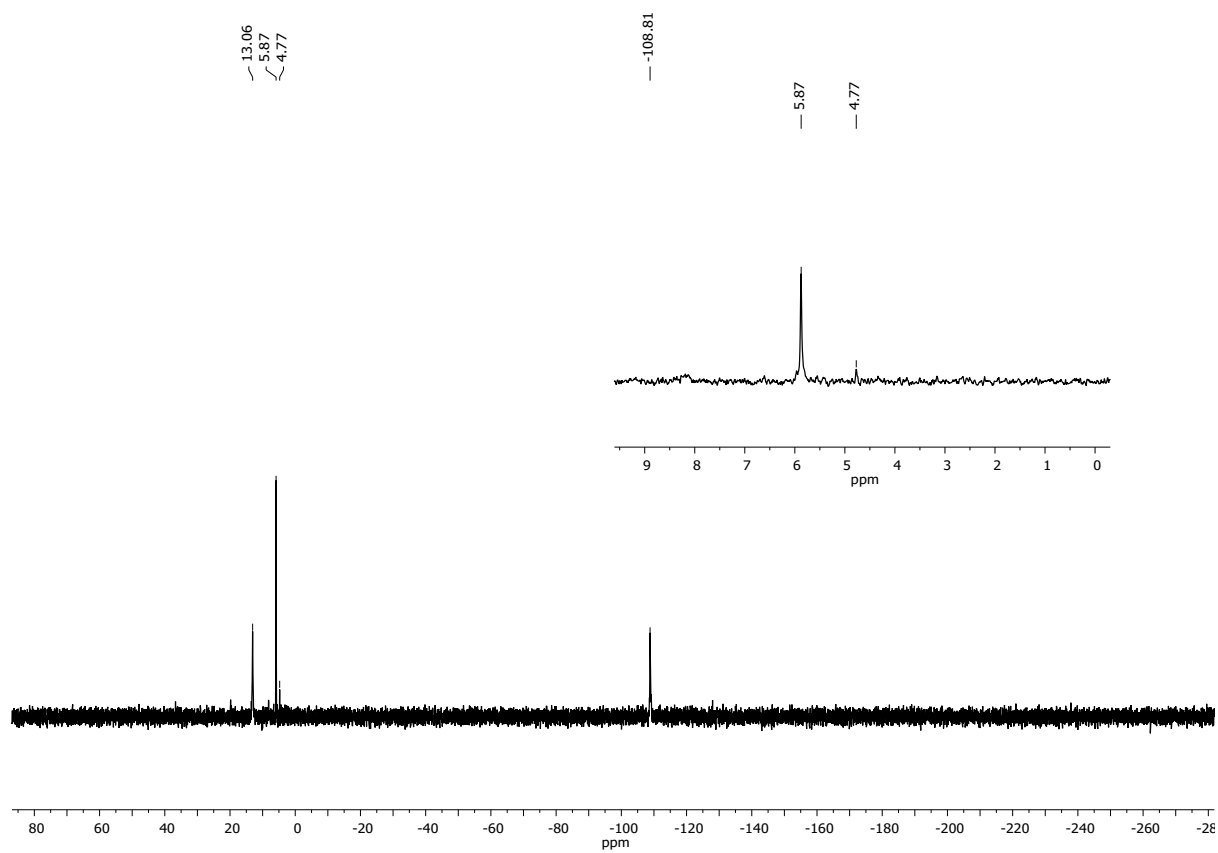


Figure S49 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of G1-16T-16epoxy.

6. Additional information and NMR spectra

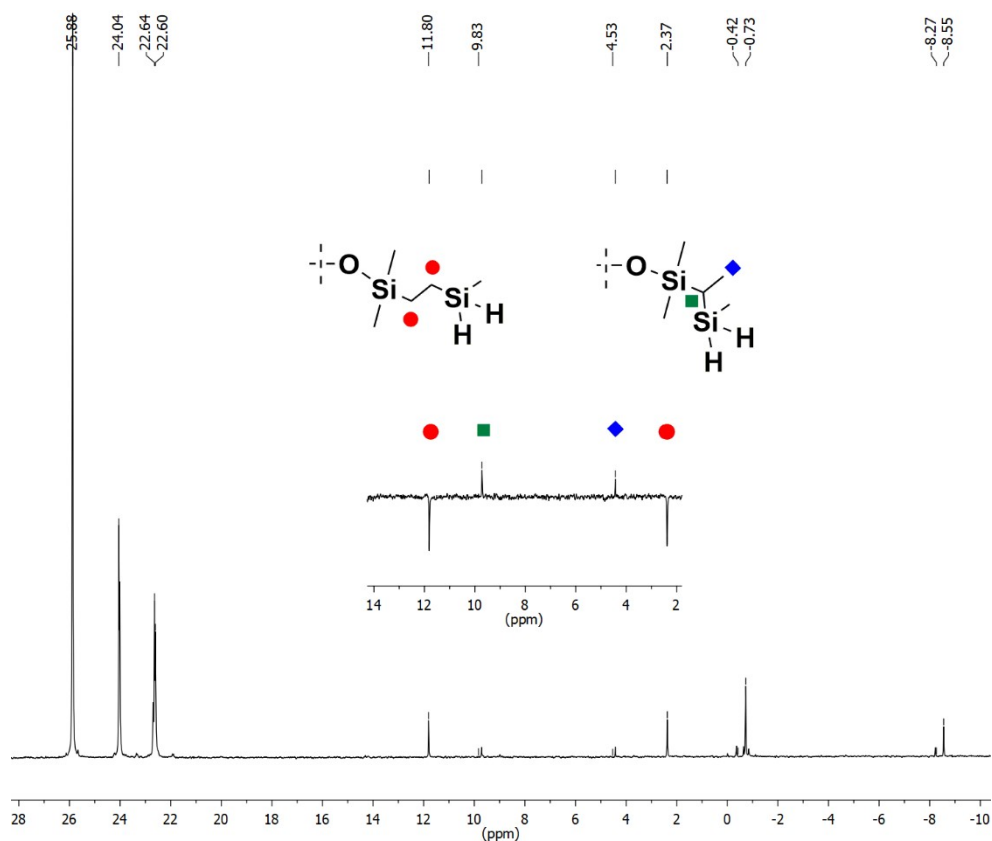


Figure S50 ^{13}C NMR (75.50 MHz, CDCl_3) spectrum of mixture of two products: **G1-1iBuOSi-2H- β** and **G1-1iBuOSi-2H- α** . Inset: DEPT-135 (101 MHz, CDCl_3) spectrum.

Procedure for the one-pot synthesis of dendritic systems with octa- T_8 silsesquioxane core through hydrosilylation followed by reduction reaction with using octakis(dimethylsiloxy)silsesquioxane and trichlorovinylsilane

The reaction was carried out in an oven-dried Schlenk-type reactor under argon atmosphere. To a mixture prepared from 1g (0.982 mmol) of octakis(dimethylsiloxy)silsesquioxane and 10 mL of anhydrous toluene, 1.15 mL (9.04 mmol) of trichlorovinylsilane was added at room temperature. To the prepared mixture of reagents Karstedt's complex was added (9 μL , 10^{-4} mol Pt/ mol SiH), reaction vessel was closed and heated at 95°C with stirring. The reaction was monitored with FT-IR spectroscopy, by following the band originating from SiH units (2141 cm^{-1}). After the complete conversion of hydrosilyl units, the reaction was cooled down, then the toluene and an excess of chlorosilane were evaporated under reduced pressure. Obtained oil was dissolved in 20 mL of anhydrous toluene, and then 5.3 mL of Red-Al[®] sodium bis(2-methoxyethoxy)aluminum hydride solution was added dropwise and the reaction was stirred overnight at room temperature. The resulting mixture was added to 2-propanol and stirred for 30 minutes. After that, the solvents and volatile liquids were evaporated under reduced pressure. The product was extracted from the resulting mixture with *n*-hexane and then filtered through a celite/silica gel column. Evaporation of *n*-hexane led to the formation of transparent oil. Yield 84%. NMR analysis revealed the existence of two isomers: $\beta : \alpha = 64 : 36$ – on the basis on ^1H NMR integrals.

^1H NMR (300 MHz, CDCl_3 , ppm): $\delta = 0.14, 0.17$ ($-\text{SiCH}_3$), 0.69 (m, β isomer $\text{SiCH}_2\text{CH}_2\text{Si}$ and α isomer $\text{SiCH}(\text{CH}_3)\text{Si}$), 1.15 (d, $J_{\text{H-H}} = 7.5\text{ Hz}$, 1H, α isomer $\text{SiCH}(\text{CH}_3)\text{Si}$), 3.55 (m, SiH_3).

^{13}C NMR (101 MHz, CDCl_3 , ppm): $\delta = -1.85$ ($\text{SiCH}_2\text{CH}_2\text{SiH}_3$), -1.25 ($\text{SiCH}(\text{CH}_3)\text{SiH}_3$), -0.71 (SiCH_3), 0.58 (SiCH_3), 11.05 ($\text{SiCH}(\text{CH}_3)\text{Si}$), 13.42 (SiCH_2).

^{29}Si NMR (79.50 MHz, CDCl_3 , ppm): $\delta = 12.99$ - 12.42 (OSiCH_2 , $\text{OSiCH}(\text{CH}_3)$), -53.74 ($\text{CH}_2\text{CH}_2\text{SiH}_3$), -54.64 ($\text{OSiCH}(\text{CH}_3)\text{SiH}_3$), -108.96 - 109.25 (SiO_4 cage).

IR (ATR, cm^{-1}): 2961.33, 2893.98 (C-H), 1256.70 (Si-C), 1144.13, 1077.20, 1057.72 1004.77 (Si-O-Si).

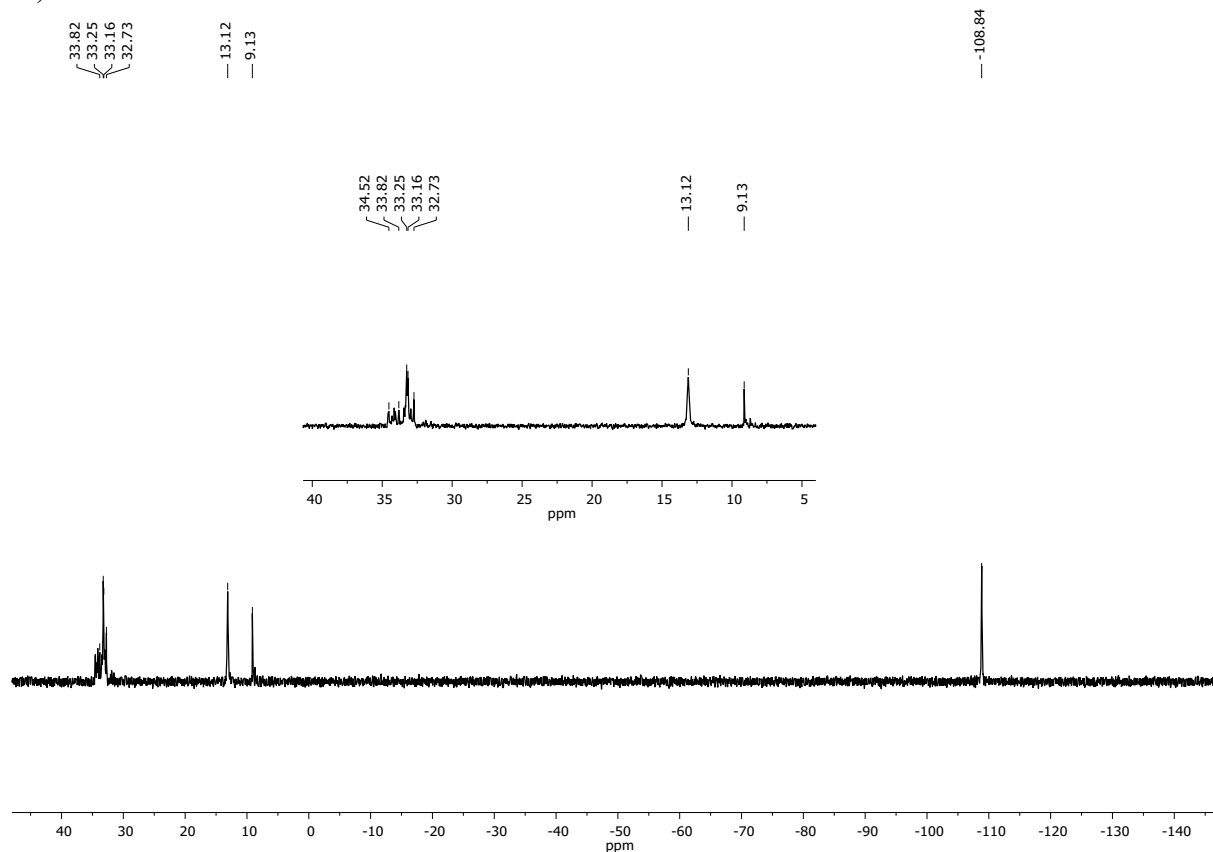


Figure S51 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of mixture of chlorinated products (**G1-8T-24Cl-mix**) obtained by the reaction of octakis(dimethylsiloxy)silsesquioxane with trichlorovinylsilane *via* hydrosilylation reaction.

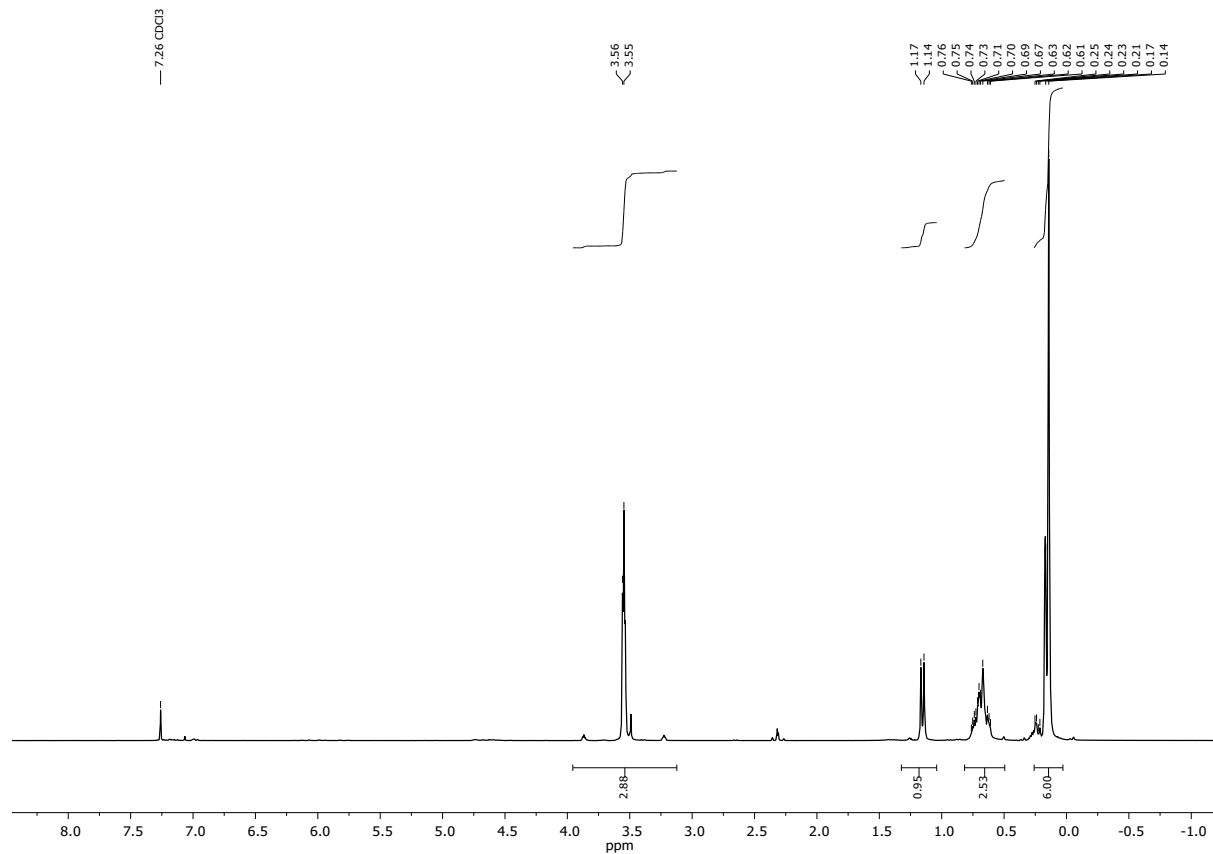


Figure S52 ¹H NMR (300 MHz, CDCl₃) spectrum of mixture of hydrogen derivative products (**G1-8T-24H-mix**) obtained by the reduction.

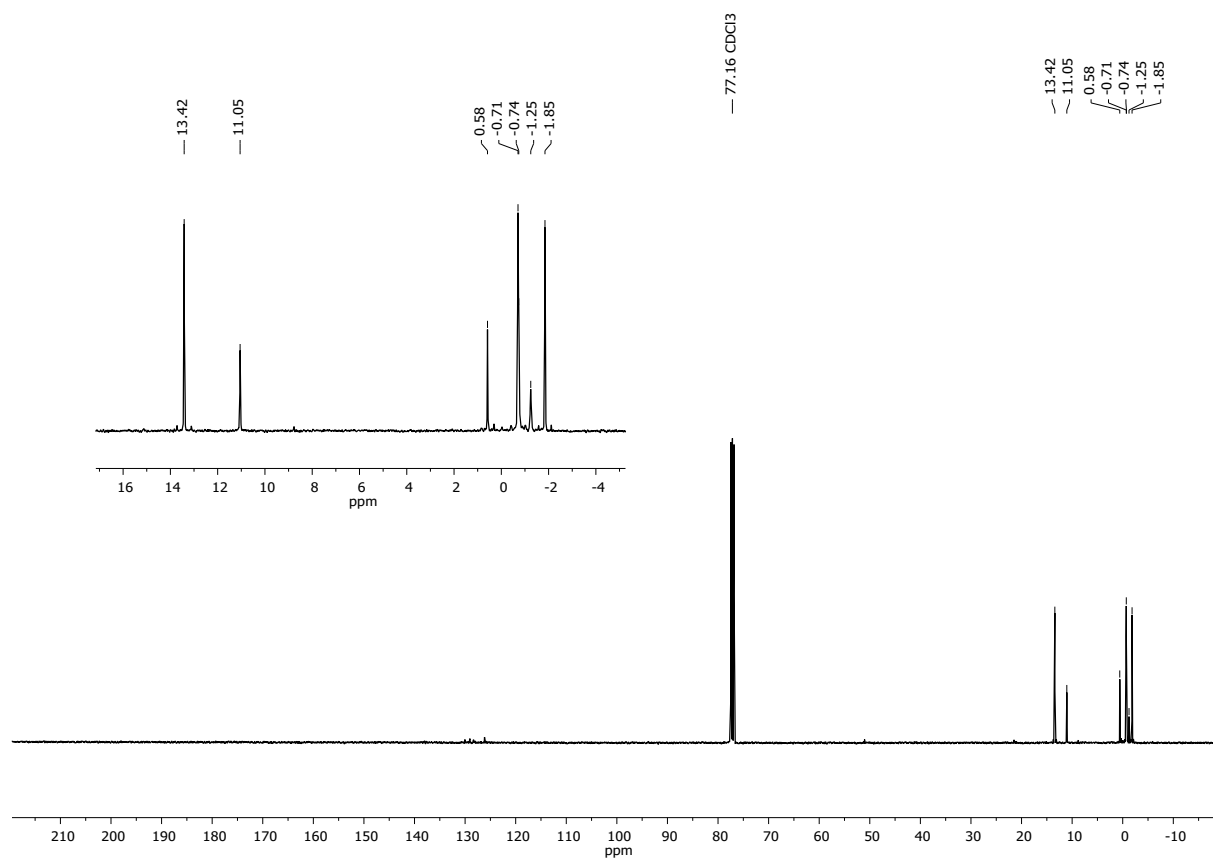


Figure S53 ^{13}C NMR (101 MHz, CDCl_3) spectrum of mixture of hydrogen derivative products (G1-8T-24H-mix) obtained by the reduction.

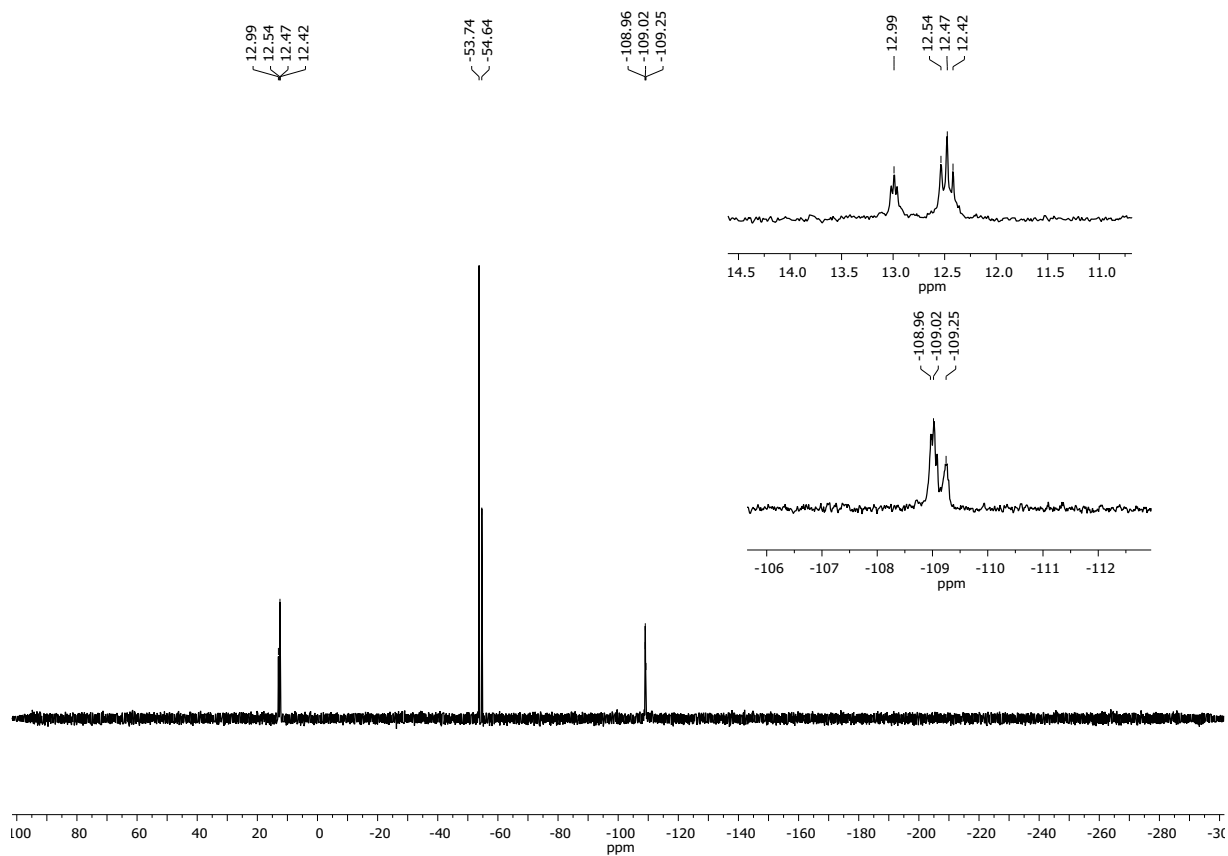


Figure S54 ^1H NMR (79.50 MHz, CDCl_3) spectrum of mixture of hydrogen derivative (**G1-8T-24H-mix**) products obtained by the reduction.

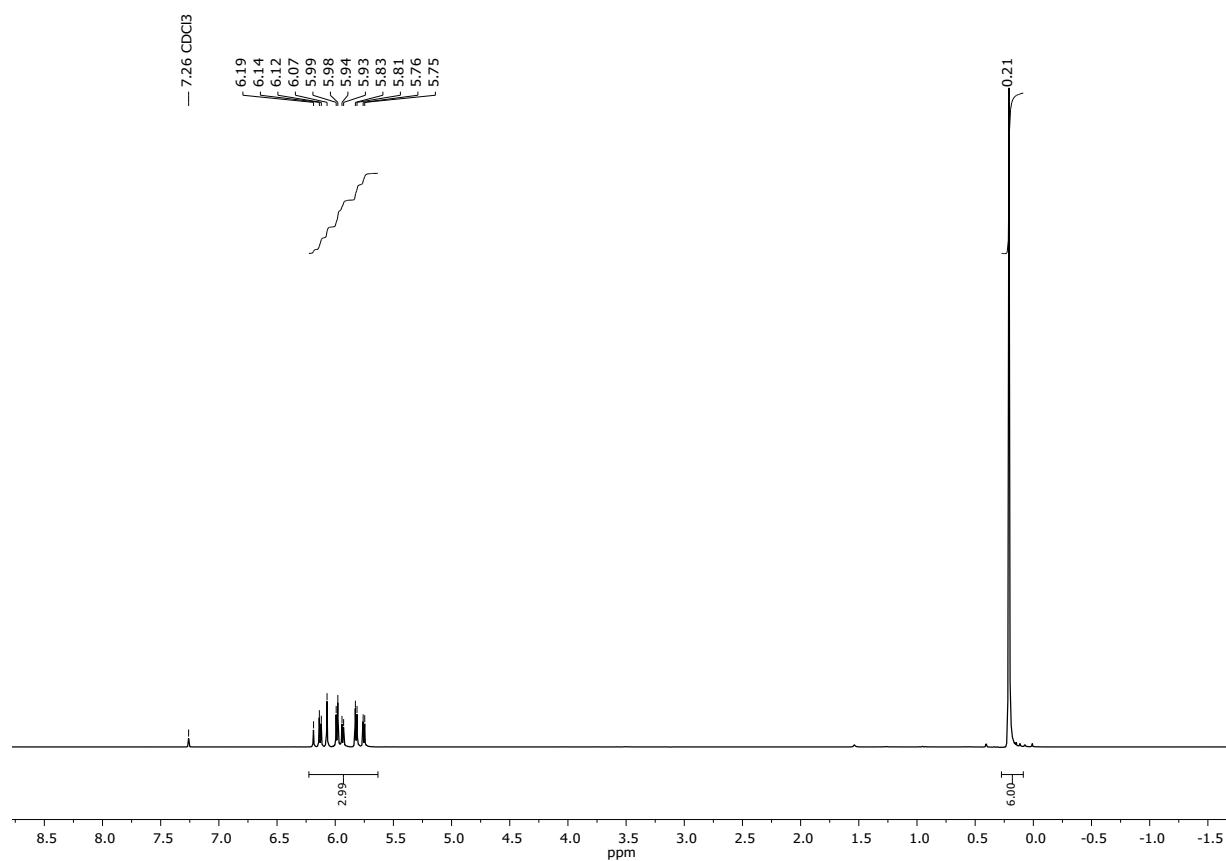


Figure S55 ¹H NMR (300 MHz, CDCl₃) spectrum of octavinyl spherosilicate. (GPC: $M_w = 1359$; $M_n = 1253$; $D = 1.08$)

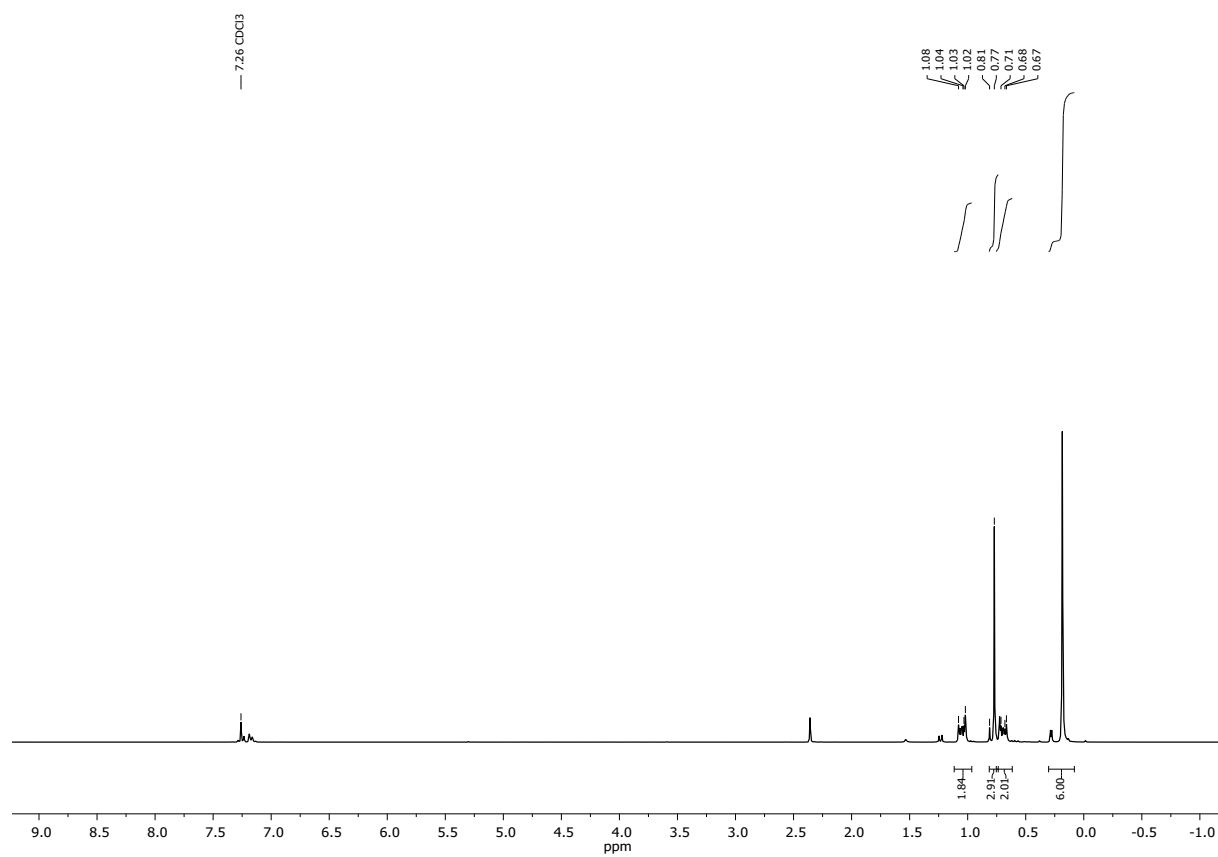


Figure S56 ¹H NMR (300 MHz, CDCl₃) spectrum of **G1-8T-16Cl**.

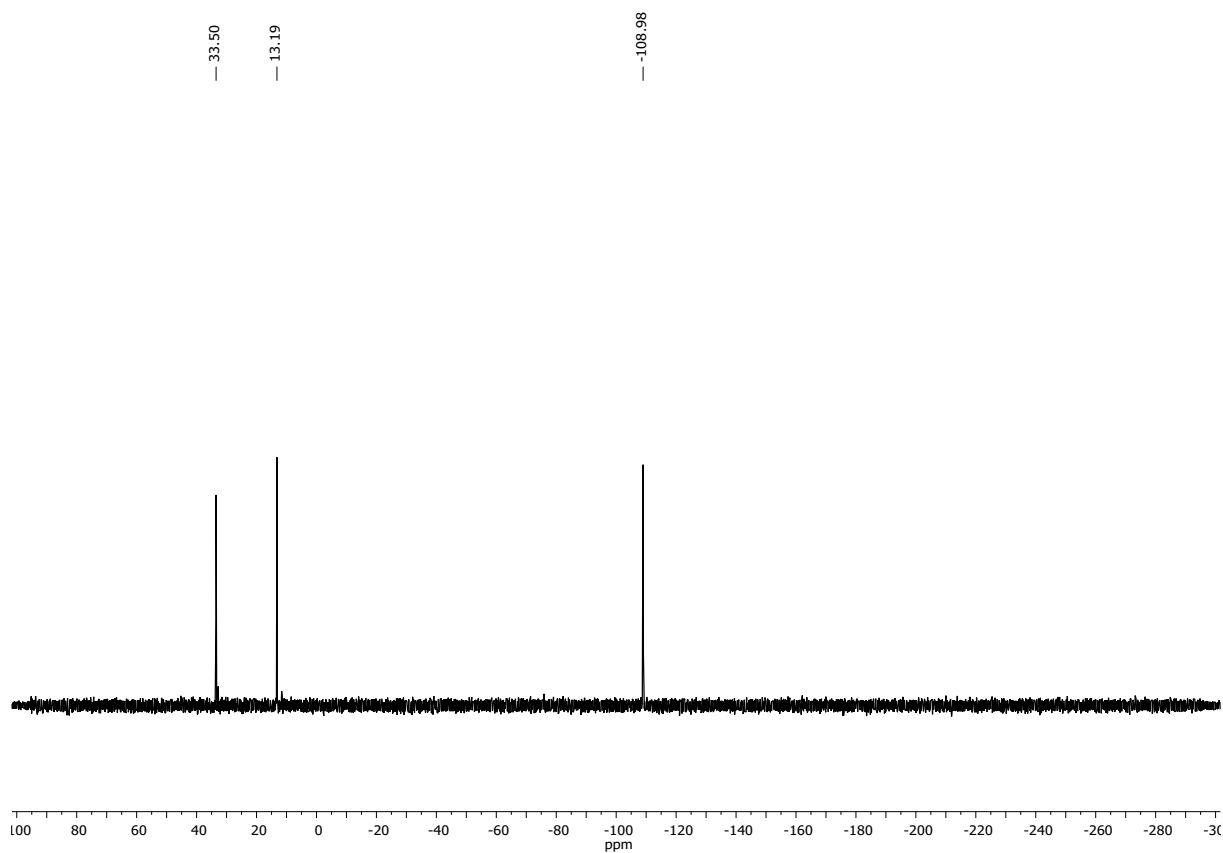


Figure S57 ²⁹Si NMR (79.50 MHz, CDCl₃) spectrum of **G1-8T-16Cl**.

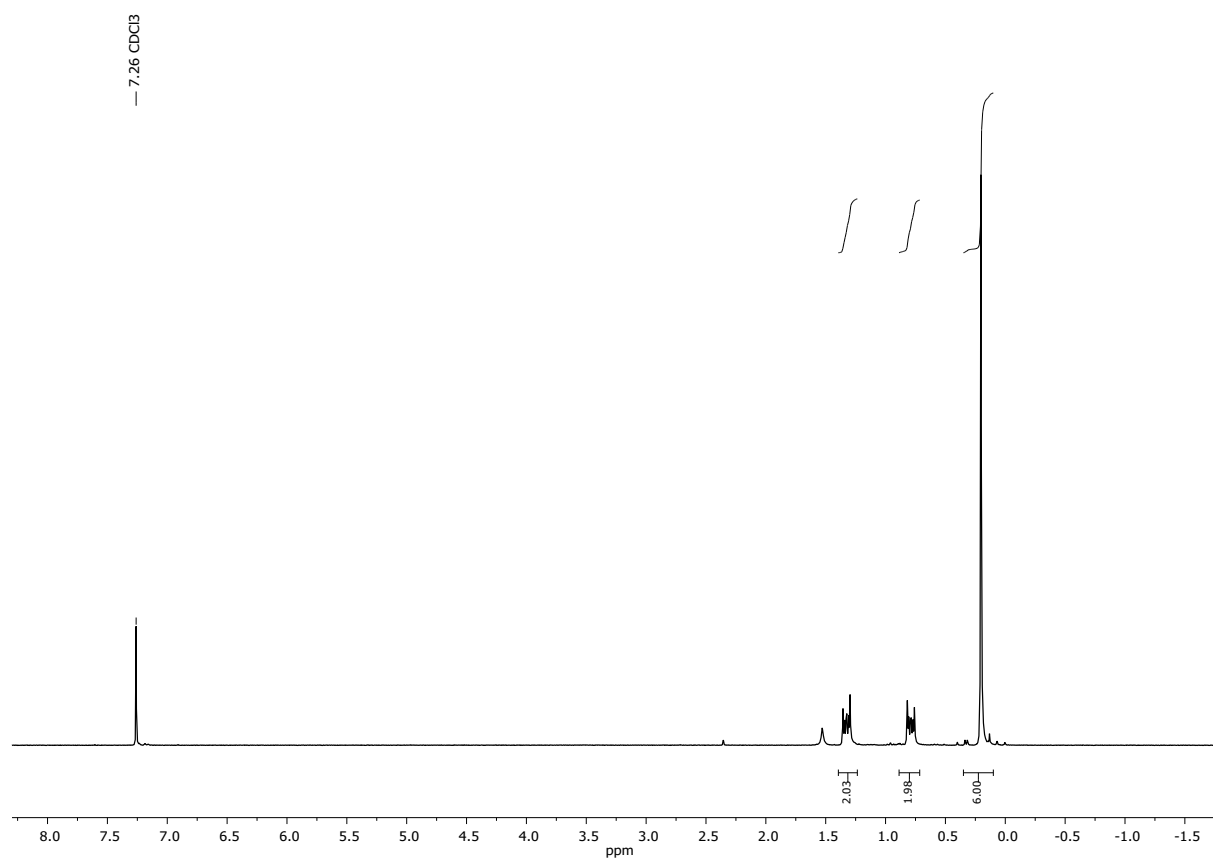


Figure S58 ¹H NMR (300 MHz, CDCl₃) spectrum of **G1-8T-24Cl**.

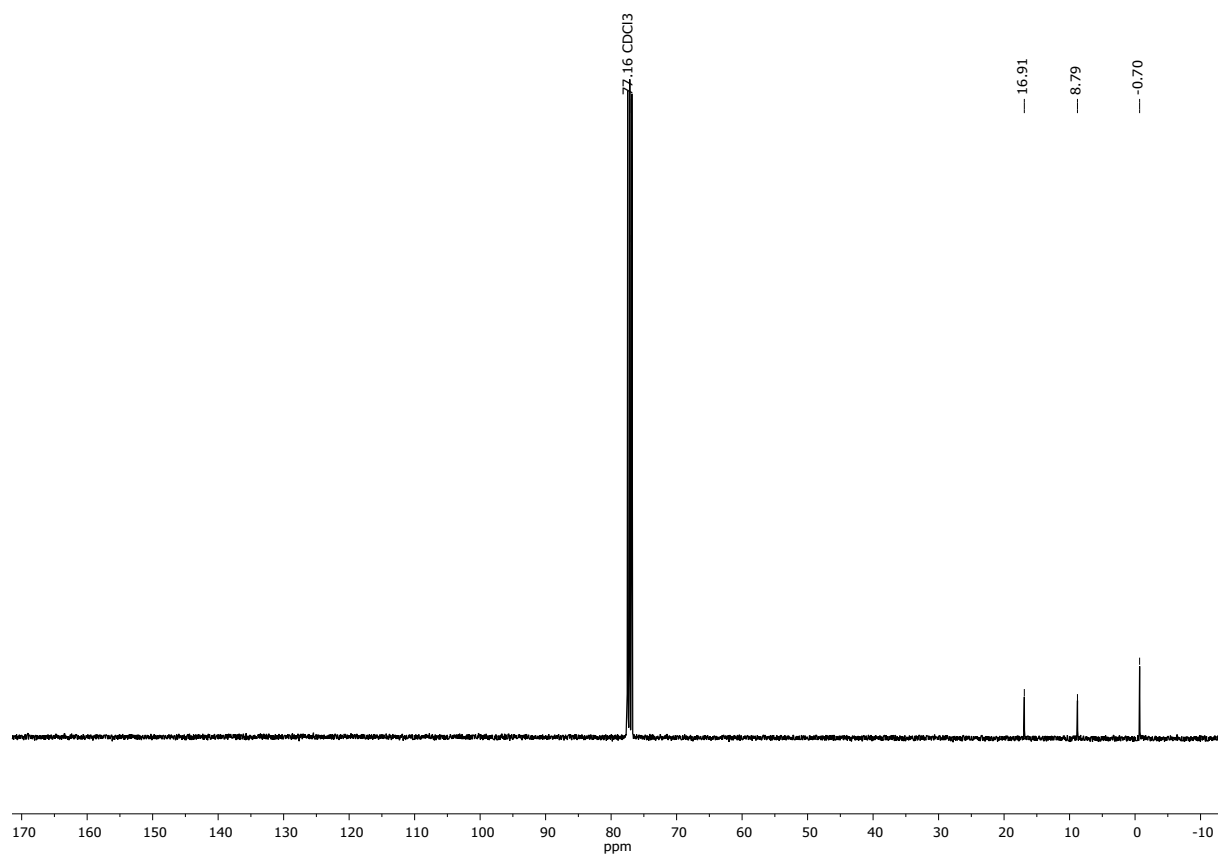


Figure S59 ^{13}C NMR (101 MHz, CDCl_3) spectrum of **G1-8T-24Cl**.

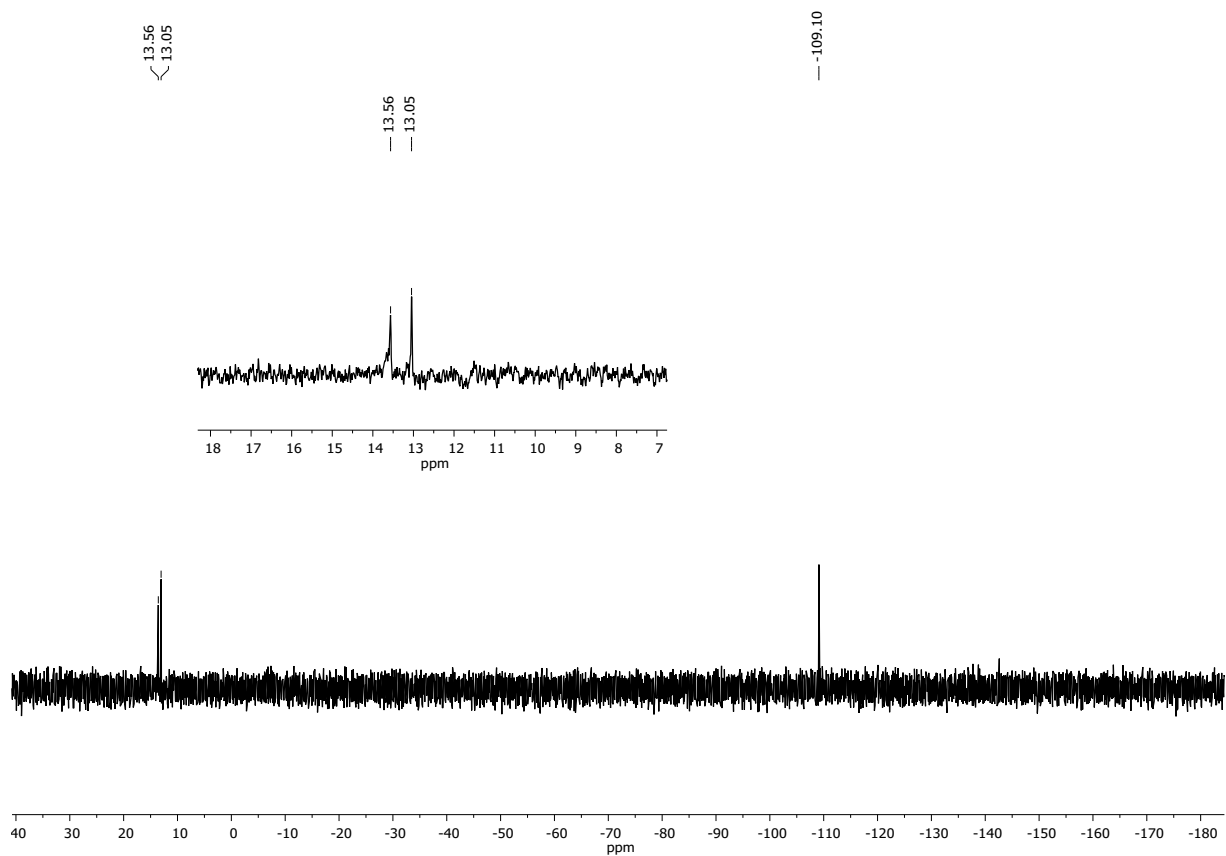


Figure S60 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of **G1-8T-24Cl**.

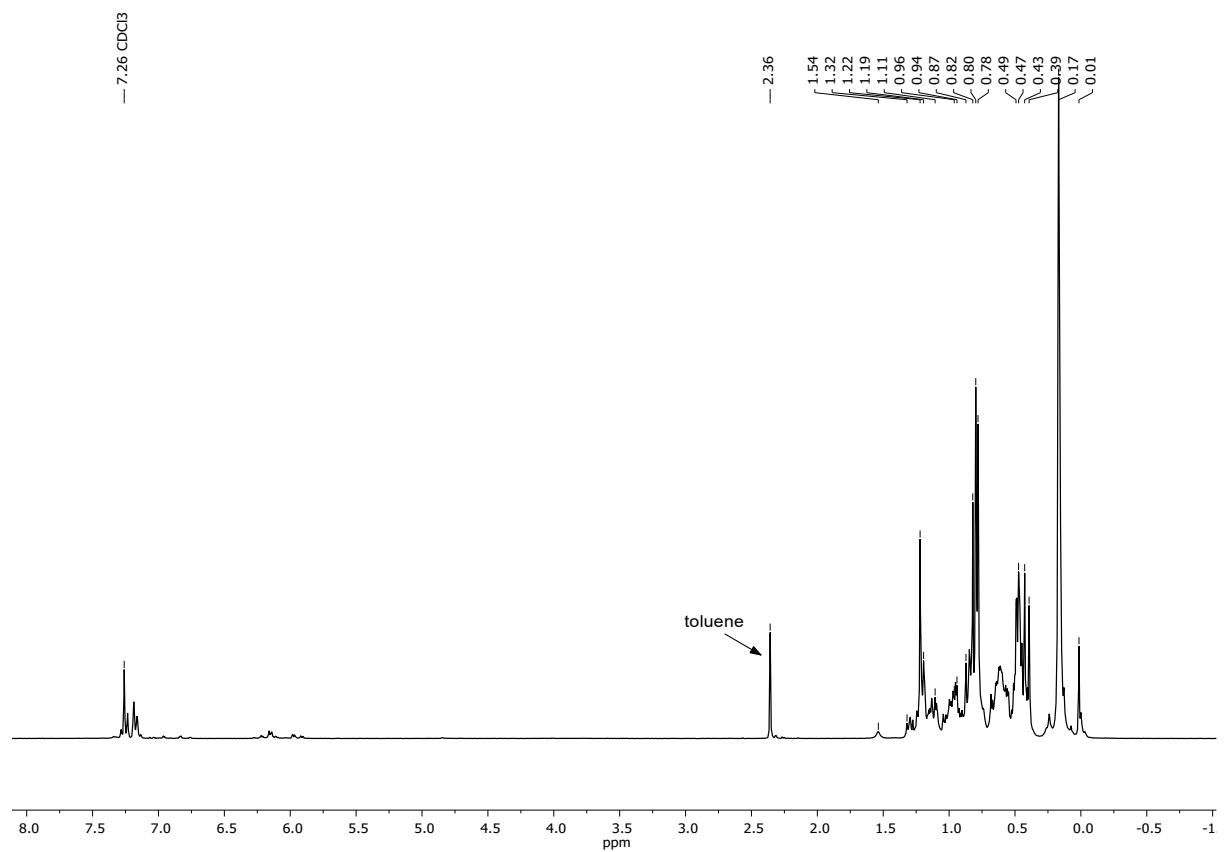


Figure S61 ^1H NMR (300 MHz, CDCl_3) spectrum of reaction mixture of **G2-16T-32Cl**.

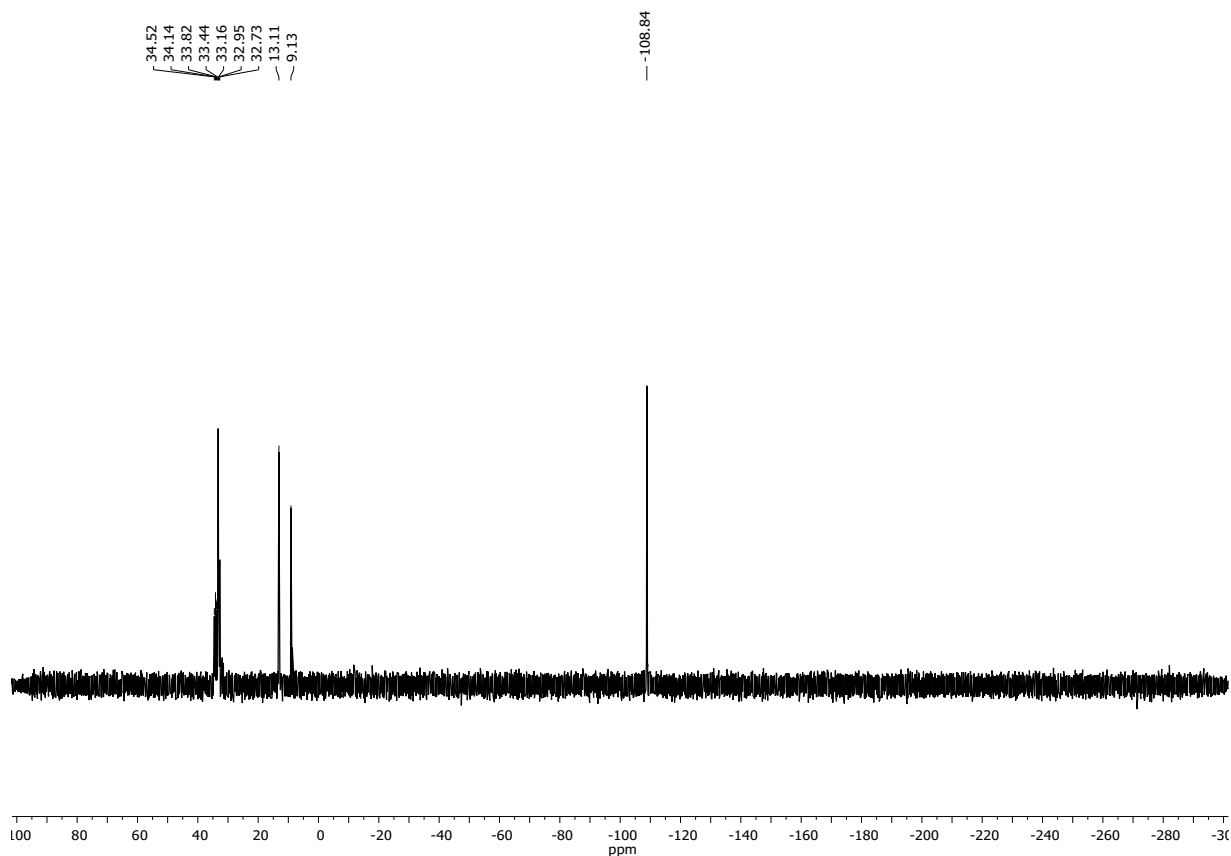


Figure S62 ^{29}Si NMR (79.50 MHz, CDCl_3) spectrum of reaction mixture of G2-16T-32Cl.

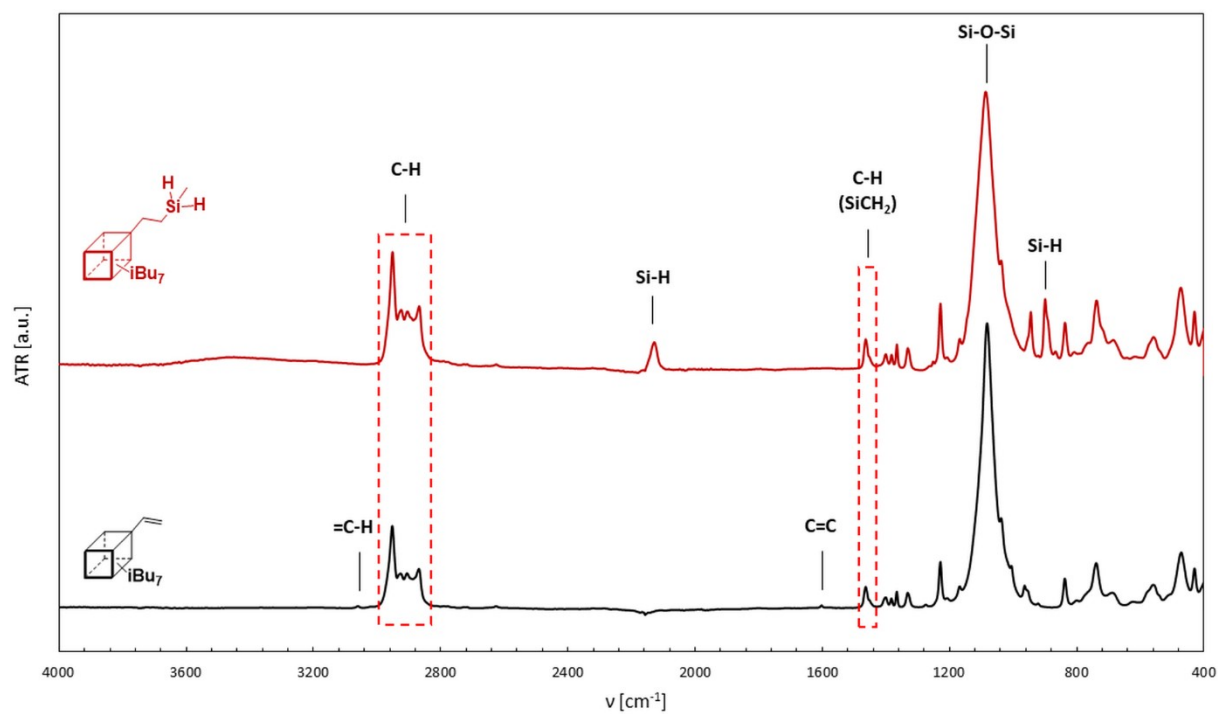


Figure S63 FT-IR stacked spectra of $\text{iBu}_7\text{T}_8\text{-Vi}$ and G1-1iBu-2H for isolated compounds.

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