

***Preparation of tri(alkenyl)functional open-cage silsesquioxanes
as specific polymer modifiers***

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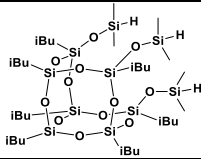
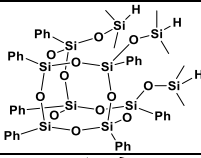
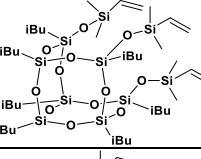
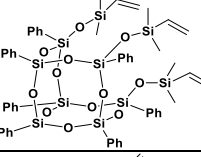
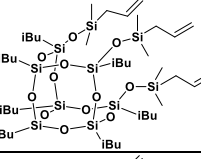
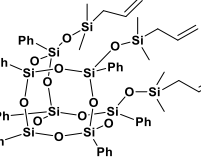
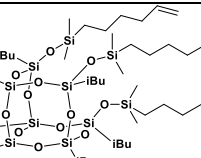
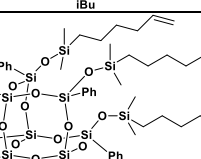
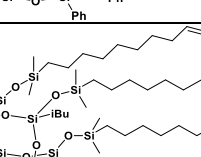
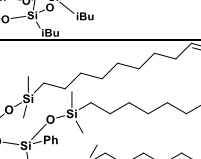
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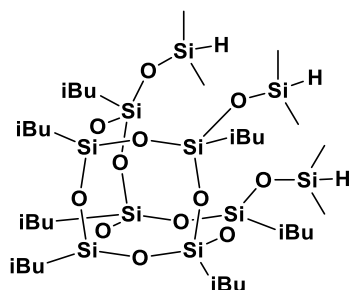
1. Table of obtained products

Prod. Abbreviation	Structure	Page
SQ-iBu-SiH		S 3
SQ-Ph-SiH		S 5
SQ-iBu-Vi		S 7
SQ-Ph-Vi		S 9
SQ-iBu-All		S 11
SQ-Ph-All		S 13
SQ-iBu-Hex		S 15
SQ-Ph-Hex		S 17
SQ-iBu-Dec		S 19
SQ-Ph-Dec		S 21

1.1 Spectroscopic analysis of obtained products along with the copies of ^1H , ^{13}C , ^{29}Si NMR spectra

SQ-iBu-SiH

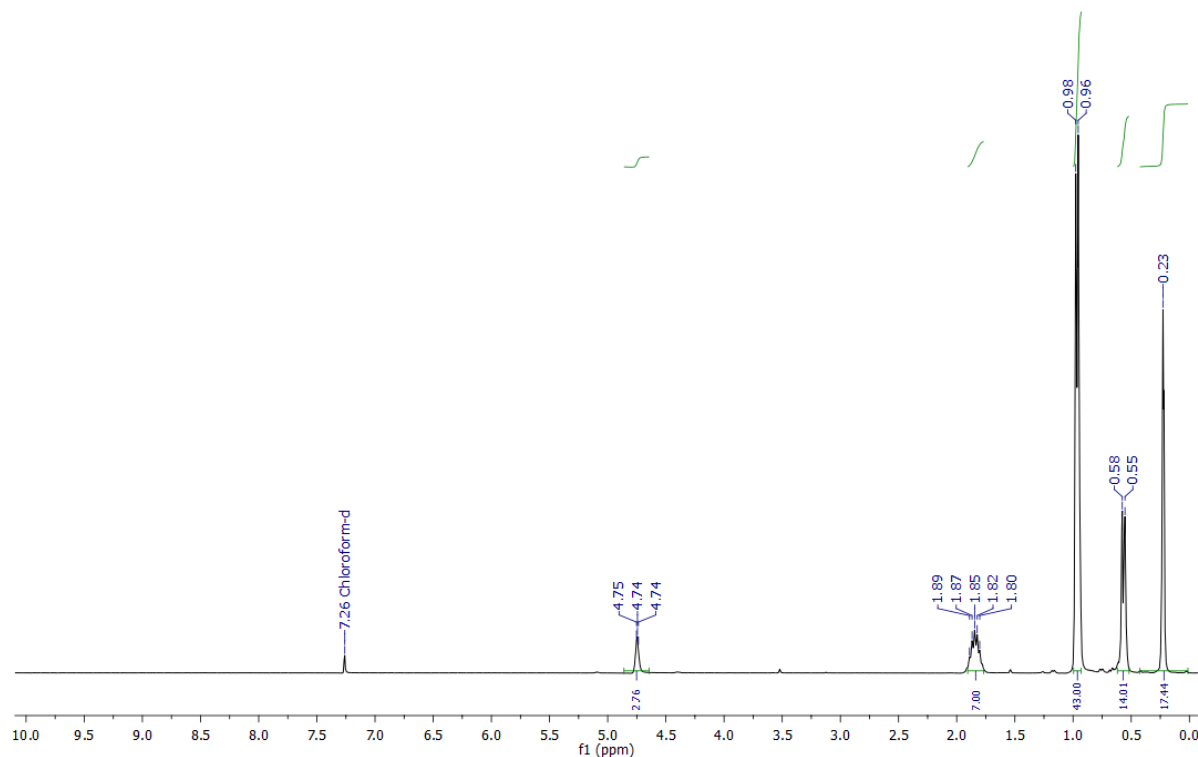
3,7,14-tris[(hydro)dimethylsiloxy]-1,3,5,7,9,11,14-hepta(isobutyl)tricyclo[7.3.3^{15,11}]heptasiloxane



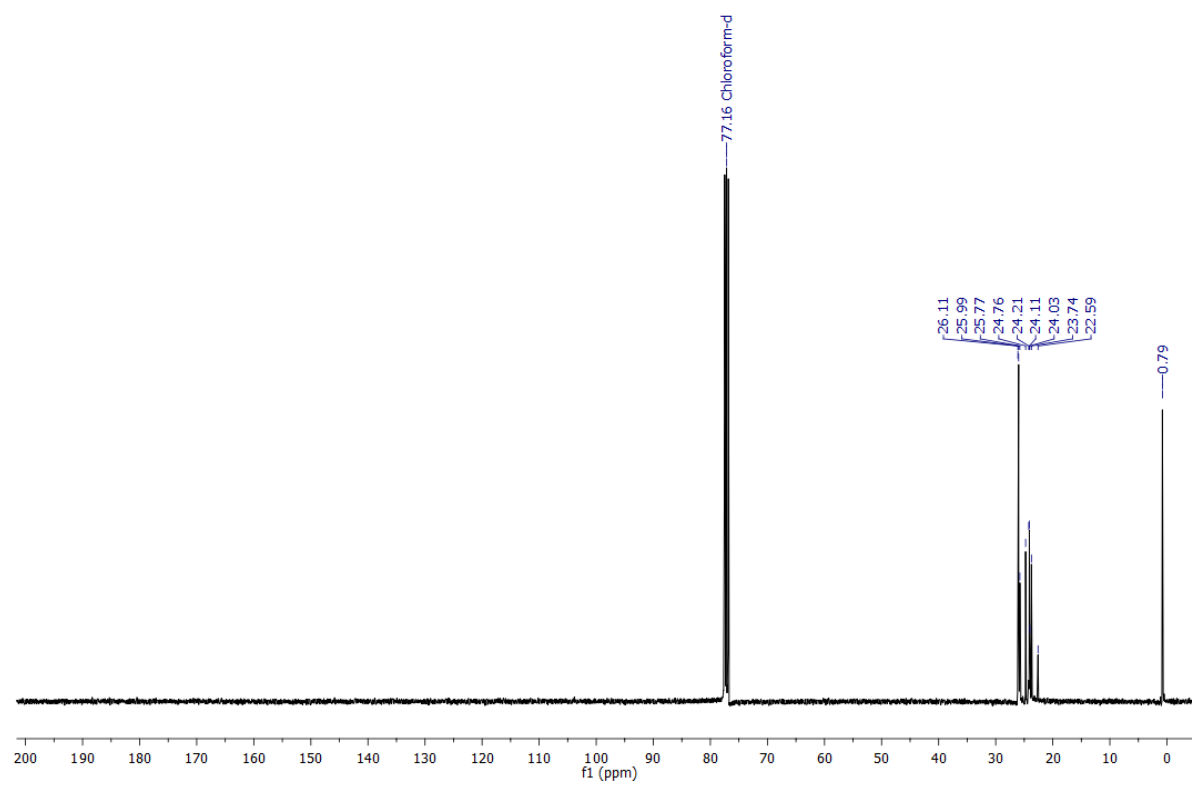
Colorless waxy solid, isolated yield **78%**.

^1H NMR (300.2 MHz, CDCl_3 , δ , ppm): 0.23 (s, 18H, $-\text{SiCH}_3$), 0.55-0.58 (m, 14H, $-\text{CH}_2-$ (iBu)), 0.96-0.98 (m, 42H, $-\text{CH}_3$ (iBu)), 1.80-1.89 (m, 7H, $-\text{CH}-$ (iBu)), 4.74-4.75 (m, 3H, Si-H). **^{13}C NMR** (100.6 MHz, CDCl_3 , δ , ppm): -0.79 ($-\text{SiCH}_3$), 22.59, 23.74, 24.03-24.21, 24.76, 25.77, 25.99-26.11 (iBu). **^{29}Si NMR** (79.5 MHz, CDCl_3 , δ , ppm): -5.48 (Si-H), -67.12, -67.68, -68.01. **FT-IR** (cm^{-1}): 2953.62, 2902.15, 2869.31 ($-\text{C}-\text{H}$), 2138.98 (Si-H), 1465.75 ($-\text{C}-\text{H}$), 1252.58, 1227.70 (Si-C), 1050.99 (Si-O). The assignments are consistent with literature[1].

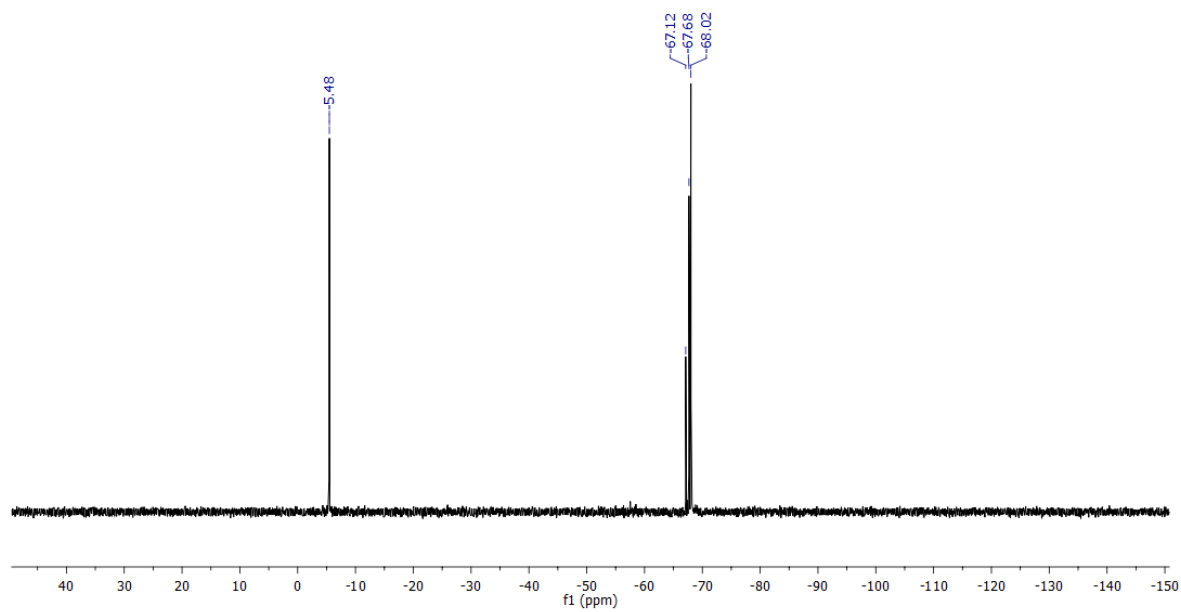
^1H NMR



^{13}C NMR

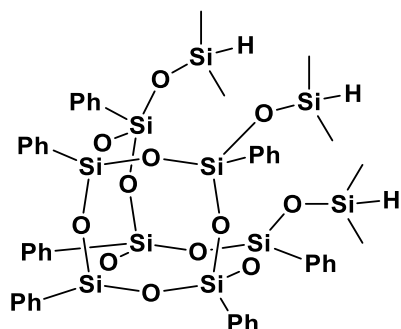


^{29}Si NMR



SQ-Ph-SiH

3,7,14-tris[(hydro)dimethylsiloxy]-1,3,5,7,9,11,14-hepta(phenyl)tricyclo[7.3.3^{15,11}]heptasiloxane

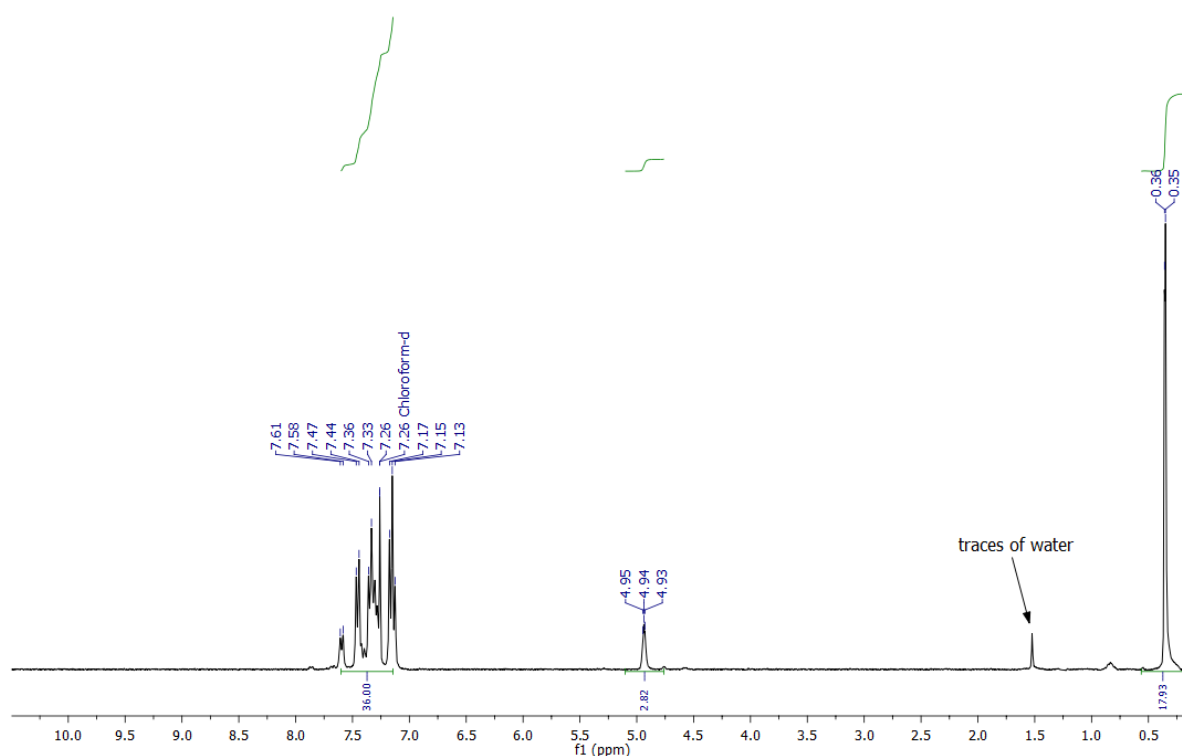


White solid, isolated yield **94%**.

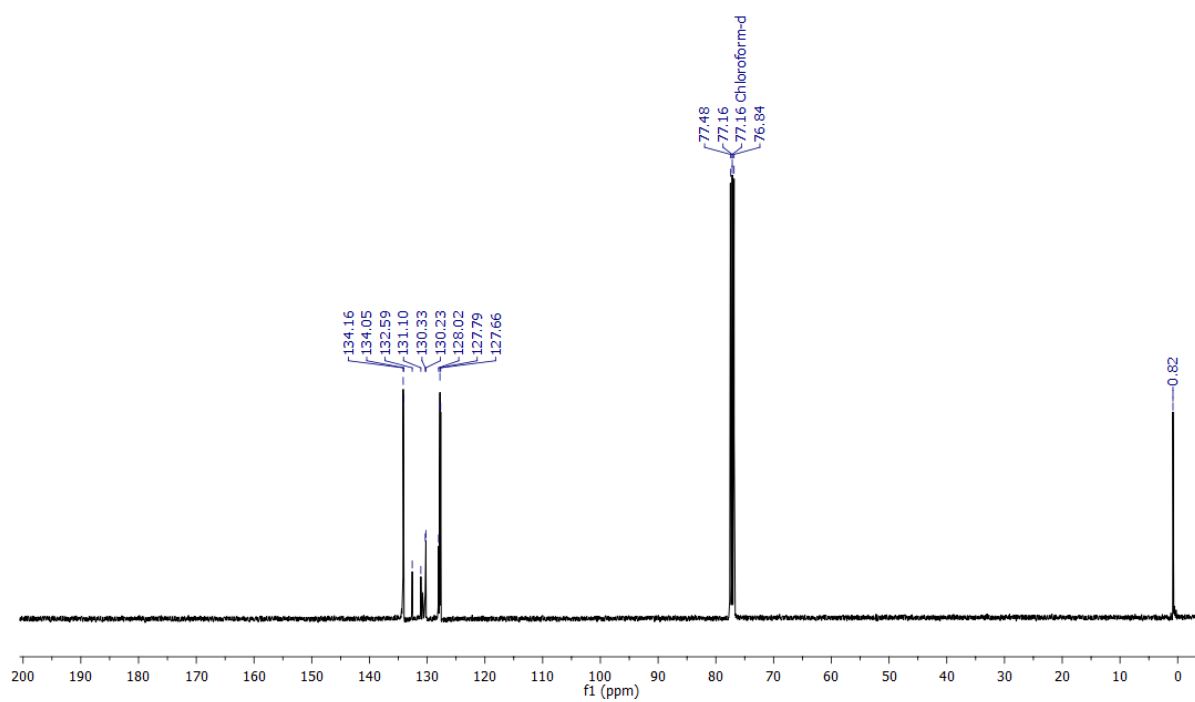
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.35-0.36 (m, 18H, -SiCH₃), 4.93-4.95 (m, 3H, Si-H), 7.13-7.61 (m, 35H, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.82 (-SiCH₃), 127.66-128.02, 130.23-130.33, 131.10, 132.59, 134.05-134.16 (Ph). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -2.83 (Si-H), -77.27, -77.61, -78.24.

FT-IR (cm⁻¹): 3074.58, 3054.01 (C-H phenyl), 2961.89 (-C-H), 2135.55 (Si-H), 1594.72 (C=C phenyl), 1490.37 (-C-H), 1430.27 (C=C phenyl), 1253.96 (Si-C), 1057.80, 1029.00 (Si-O), 998.45 (C-H phenyl). The assignments are consistent with the literature[2].

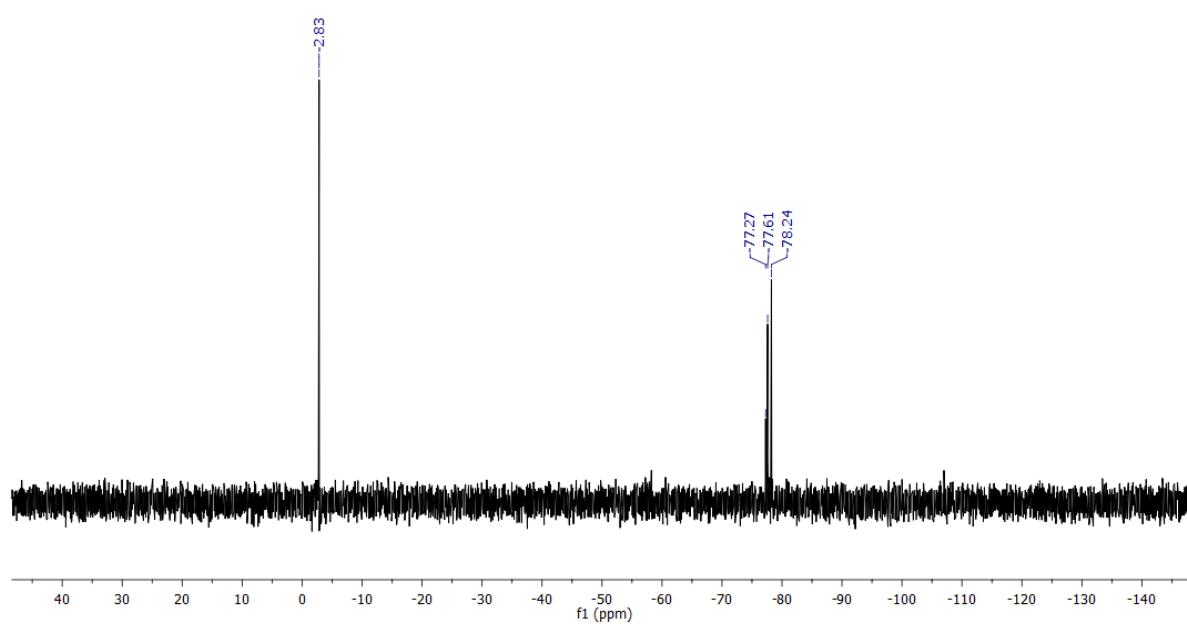
¹H NMR



^{13}C NMR

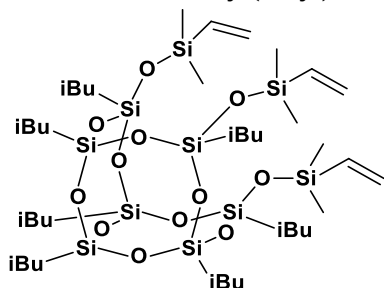


^{29}Si NMR



SQ-iBu-Vi

3,7,14-tris[dimethyl(vinyl)siloxy]-1,3,5,7,9,11,14-hepta(isobutyl)tricyclo[7.3.3^{15,11}]heptasiloxane



Colorless waxy solid, isolated yield **96%**

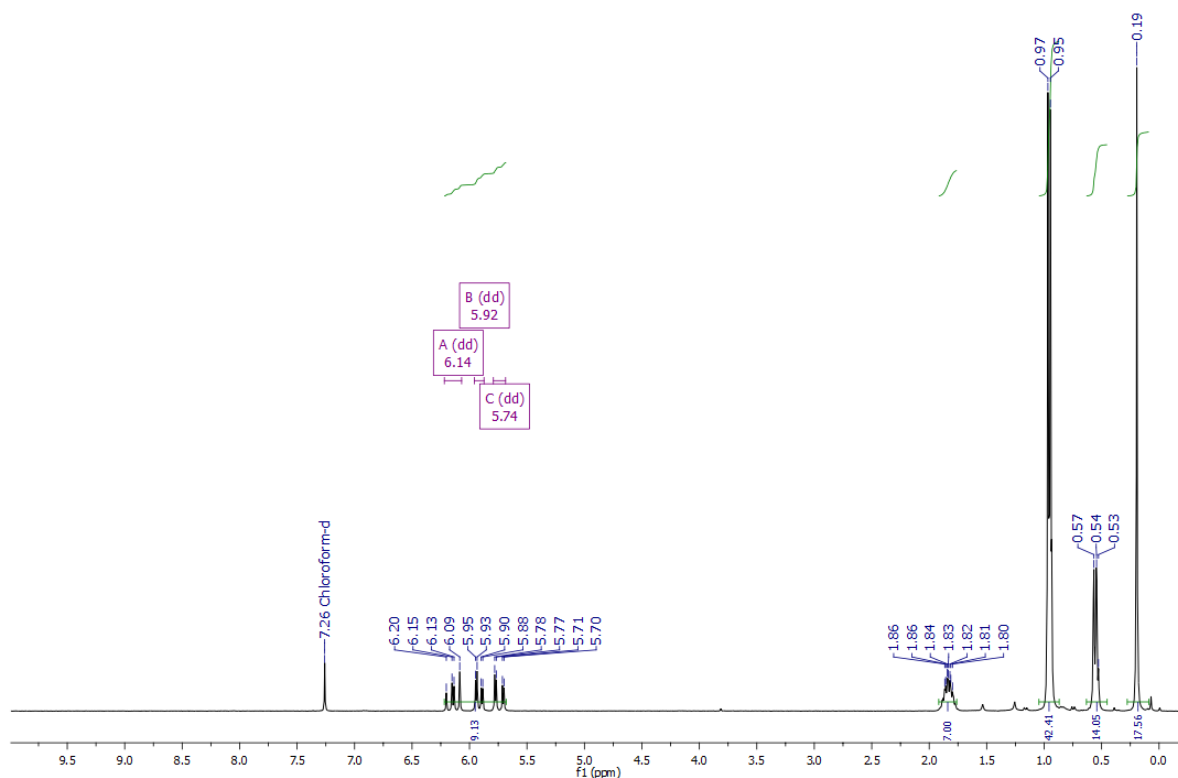
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.19 (s, 18H, -SiCH₃), 0.53-0.57 (m, 14H, -CH₂- (iBu)), 0.95-0.97 (m, 42H, -CH₃ (iBu)), 1.80-1.86 (m, 7H, -CH- (iBu)), 5.74 (dd, *J*_{H,H} = 20.2 Hz, 4.1 Hz, 3H, H₂C=CH), 5.92 (dd, *J*_{H,H} = 14.9 Hz, 4.1 Hz, 3H, H₂C=CH-), 6.14 (dd, *J*_{H,H} = 20.2 Hz, 14.9 Hz, 3H, H₂C=CH-). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.53 (-SiCH₃), 22.62, 23.89, 24.10-24.21, 25.13, 25.79, 26.02-26.18 (iBu), 131.90 (H₂C=CH-), 139.30 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -2.68 (-OSi(CH₃)₂-), -67.29, -67.81, -68.04.

FT-IR (cm⁻¹): 3050.94 (=C-H), 2953.09, 2868.69 (-C-H), 1595.49 (C=C), 1465.73 (-C-H), 1252.59 (Si-C), 1045.58 (Si-O).

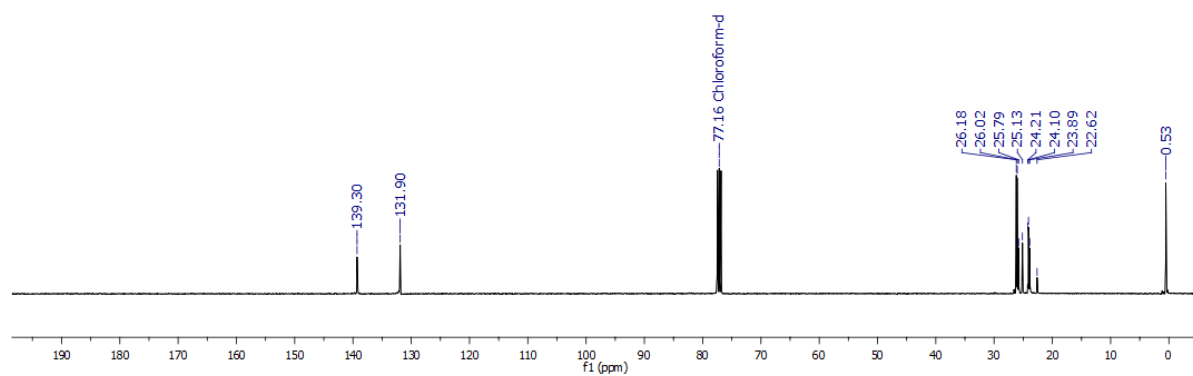
The assignments are consistent with those in the literature[2,3].

Chemical formula: C₄₀H₉₀O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₄₀H₉₀NaO₁₂Si₁₀: *m/z* 1065.4023, found: 1065.4026.

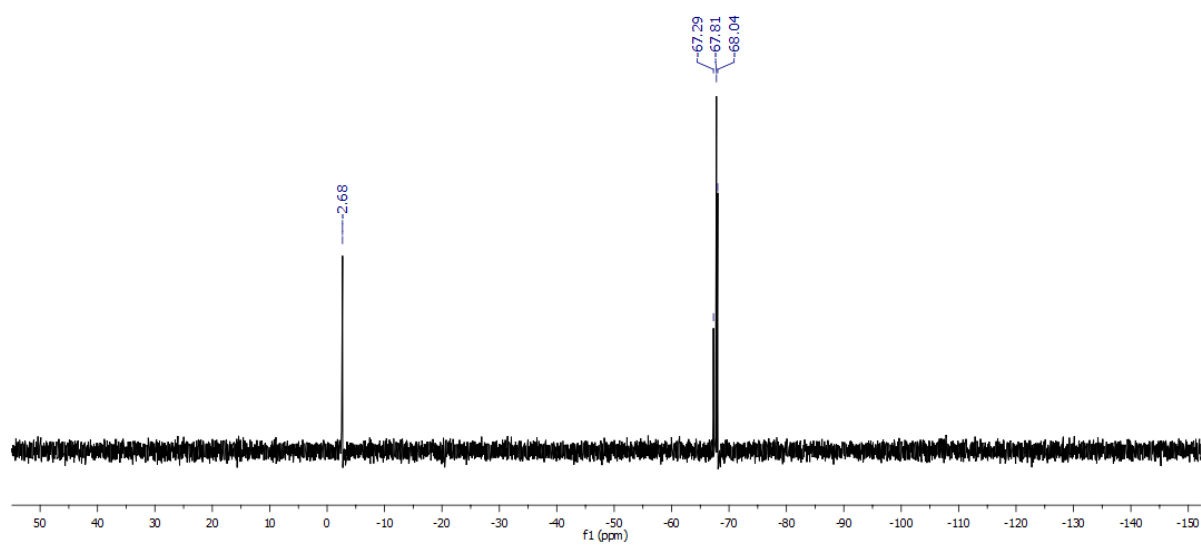
¹H NMR



¹³C NMR

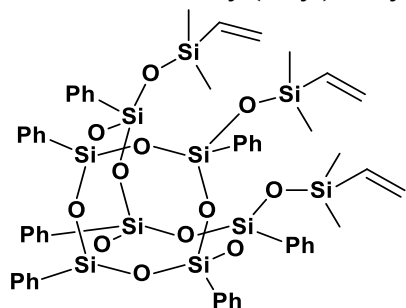


²⁹Si NMR



SQ-Ph-Vi

3,7,14-tris[dimethyl(vinyl)siloxy]-1,3,5,7,9,11,14-hepta(phenyl)tricyclo[7.3.3^{15,11}]heptasiloxane



White solid, isolated yield **95%**

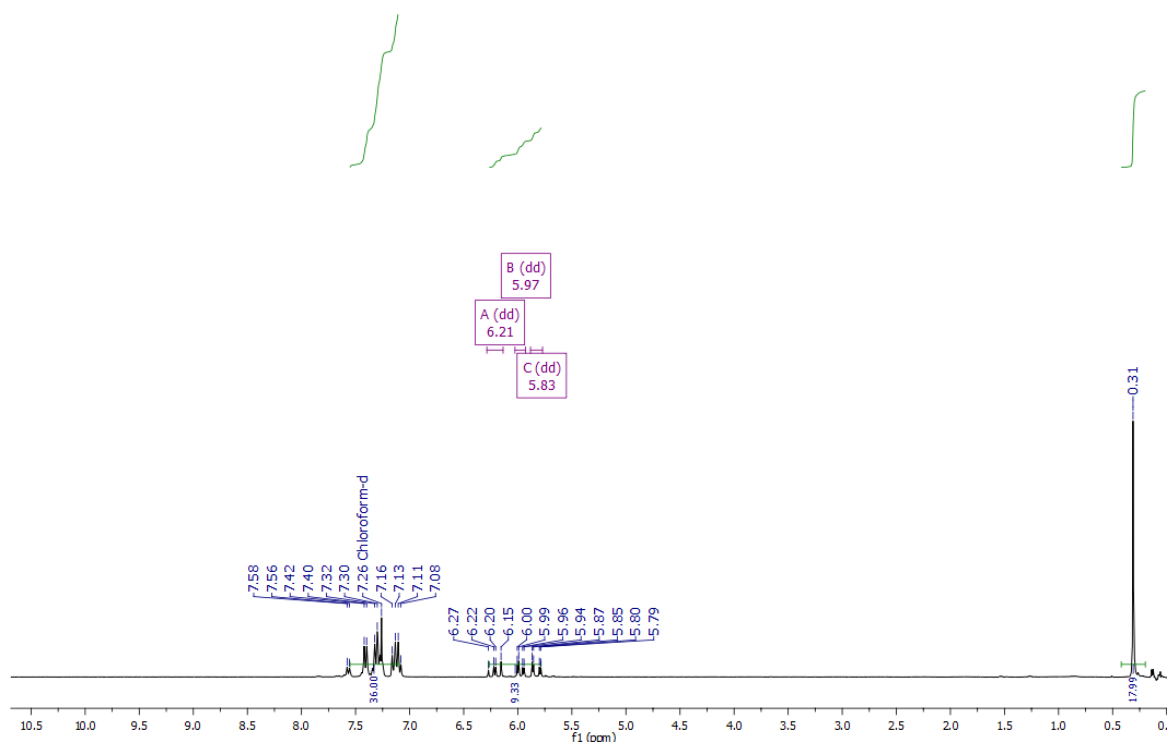
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.31 (s, 18H, -SiCH₃), 5.83 (dd, *J*_{H,H} = 20.2 Hz, 4.0 Hz, 3H, H₂C=CH-), 5.97 (dd, *J*_{H,H} = 14.9 Hz, 4.0 Hz, 3H, H₂C=CH-), 6.21 (dd, *J*_{H,H} = 20.2 Hz, 14.9 Hz, 3H, H₂C=CH-), 7.08-7.58 (m, 35H, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.54 (-SiCH₃), 127.60-128.67, 128.01, 130.08-130.23, 131.27 (Ph), 132.55 (H₂C=CH-), 132.88, 134.13-134.17 (Ph), 138.75 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -0.17 (-OSi(CH₃)₂-), -77.41, -77.80, -78.16.

FT-IR (cm⁻¹): 3073.49, 3051.43 (C-H phenyl), 2960.76, 2853.27 (-C-H), 1593.97 (C=C phenyl), 1489.99 (-C-H), 1430.09 (C=C phenyl), 1264.25 (Si-C), 1129.68, 1049.14 (Si-O), 997.91 (C-H phenyl).

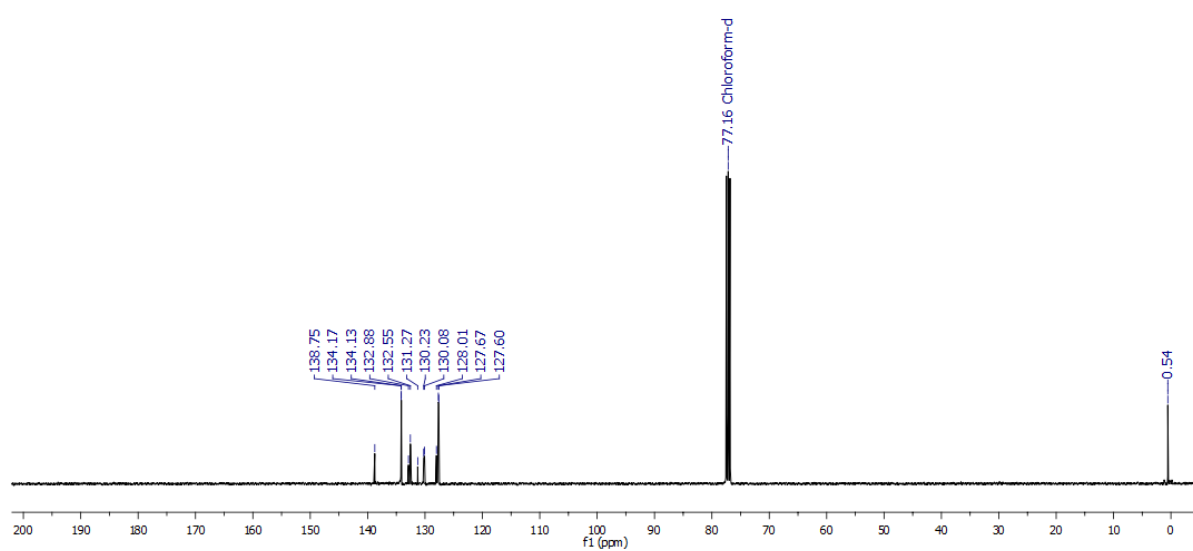
The assignments are consistent with those in the literature[2].

Chemical formula: C₅₄H₆₂O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₅₄H₆₂HN⁺a⁺O₁₂Si₁₀: *m/z* 1206.1904, found: 1206.1906.

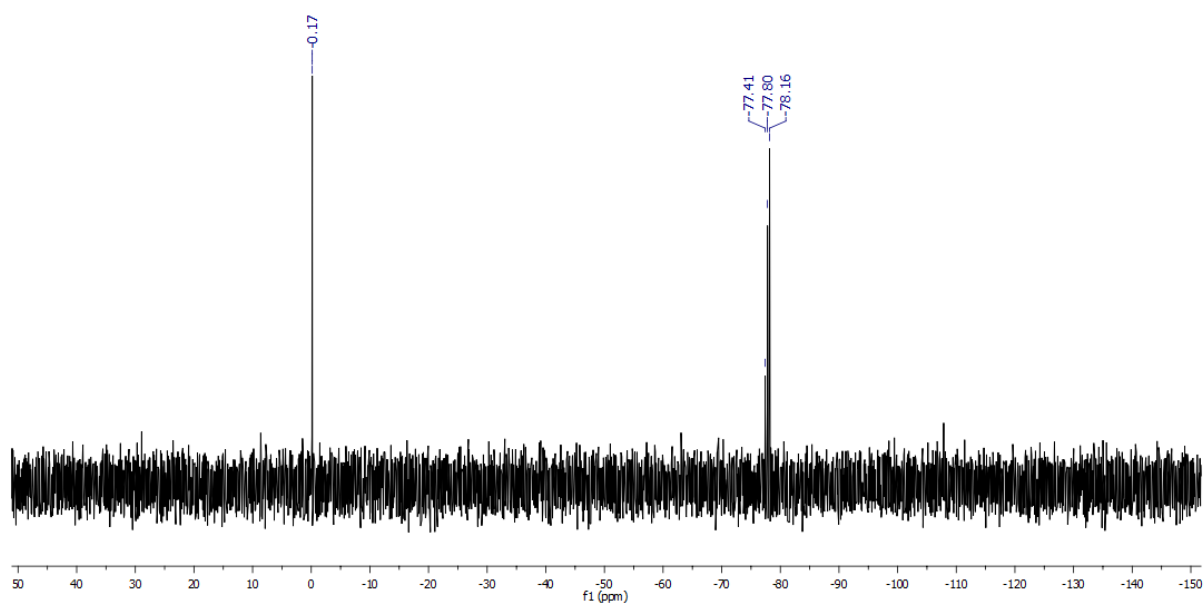
¹H NMR



^{13}C NMR

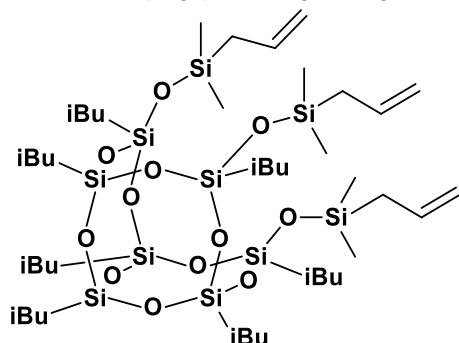


^{29}Si NMR



SQ-iBu-All

3,7,14-tris[(allyl)dimethylsiloxy]-1,3,5,7,9,11,14-hepta(isobutyl)tricyclo[7.3.3^{15,11}]heptasiloxane



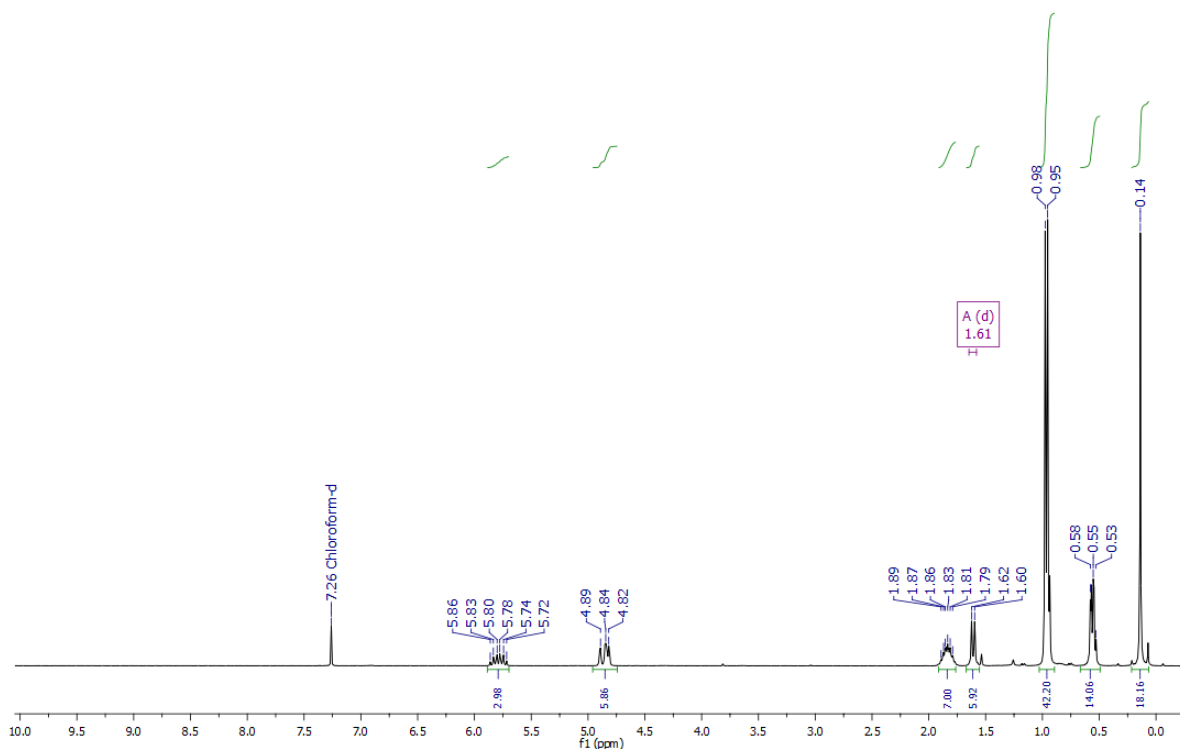
Colorless waxy, isolated yield **94%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.14 (s, 18H, -SiCH₃), 0.53-0.58 (m, 14H, -CH₂- (iBu)), 0.95-0.98 (m, 42H, -CH₃ (iBu)), 1.61 (dd, *J*_{H,H} = 8.1 Hz, 6H, H₂C=CH-CH₂-), 1.79-1.89 (m, 7H, -CH- (iBu)), 4.82-4.89 (m, 6H, H₂C=CH-), 5.72-5.86 (m, 3H, H₂C=CH-). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.09 (-SiCH₃), 22.59, 23.90, 24.14-24.23, 25.12, 25.78, 26.01-26.18 (iBu), 26.27 (H₂C=CH-CH₂-), 113.49 (H₂C=CH-), 134.53 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 5.92 (-OSi(CH₃)₂-), -67.30, -67.63, -68.02.

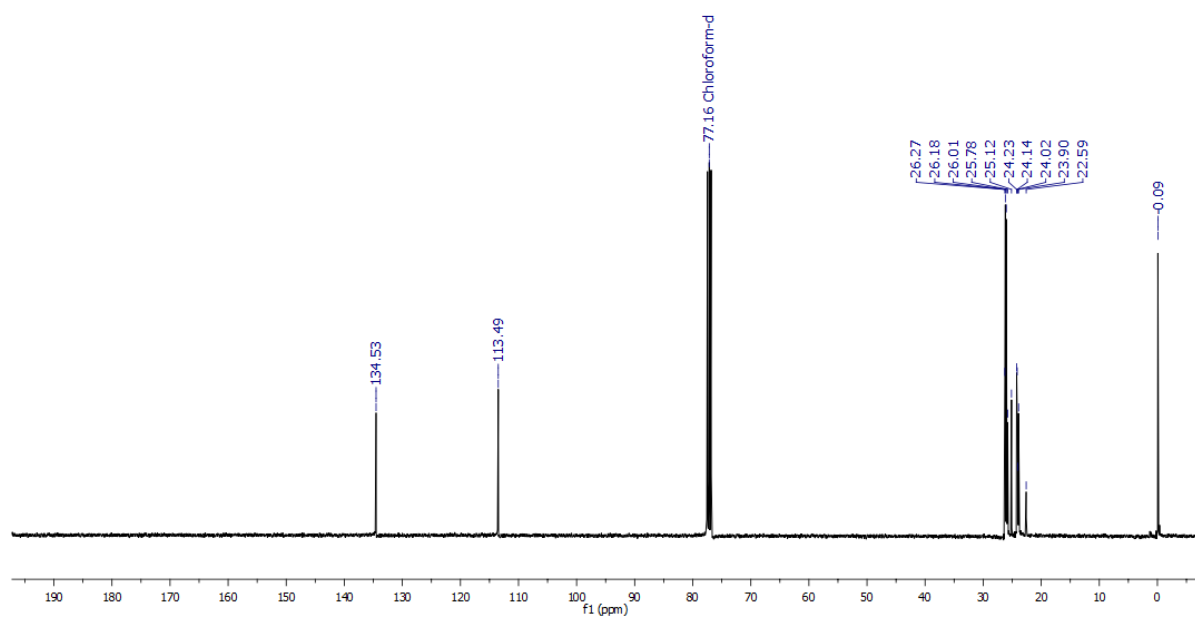
FT-IR (cm⁻¹): 3078.71 (=C-H), 2953.89, 2870.35 (-C-H), 1631.41 (C=C), 1465.62 (-C-H), 1253.53 (Si-C), 1075.85, 1047.24 (Si-O).

Chemical formula: C₄₃H₉₆O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₄₃H₉₆H⁺Na⁺O₁₂Si₁₀: *m/z* 1108.4559, found: 1108.4549.

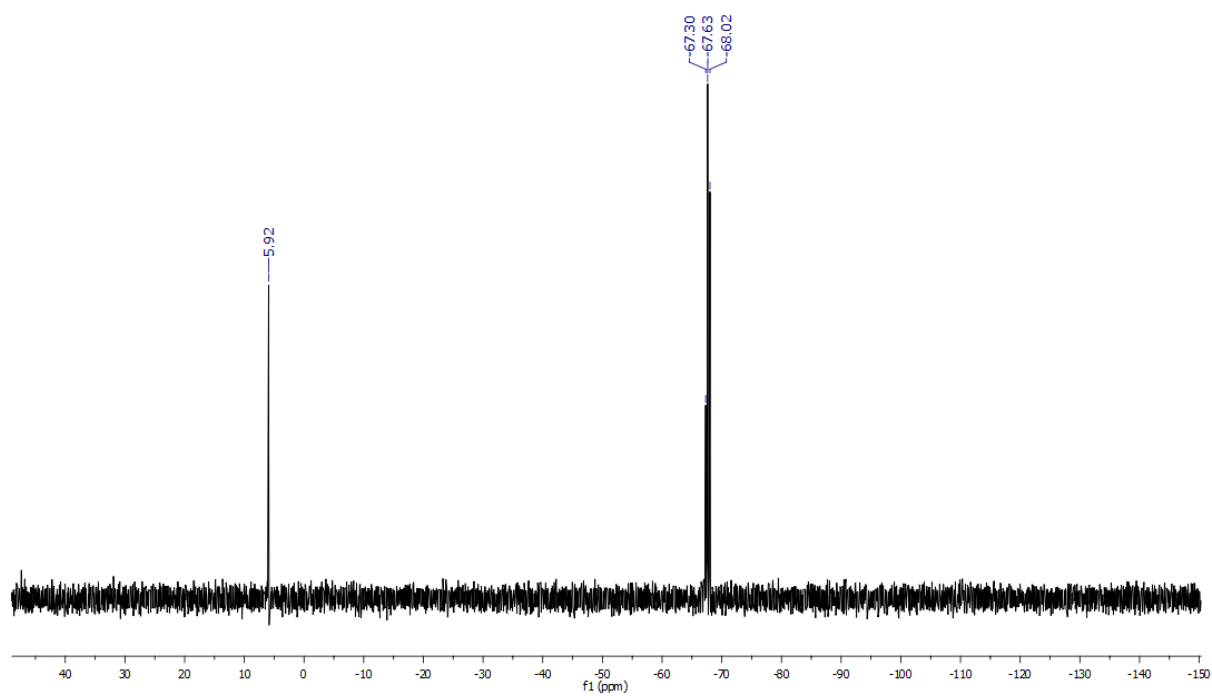
¹H NMR



^{13}C NMR

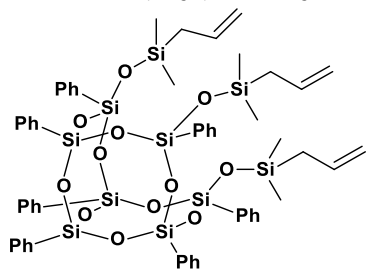


^{29}Si NMR



SQ-Ph-All

3,7,14-tris[(allyl)dimethylsiloxy]-1,3,5,7,9,11,14-hepta(phenyl)tricyclo[7.3.3^{15,11}]heptasiloxane



White solid, isolated yield **92%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.26 (s, 18H, -SiCH₃), 1.70 (dd, *J*_{H,H} = 7.9 Hz, 6H, H₂C=CH-CH₂-), 4.83-4.91 (m, 6H, H₂C=CH-), 5.74-5.88 (m, 3H, H₂C=CH-), 7.08-7.57 (m, 35H, Ph).

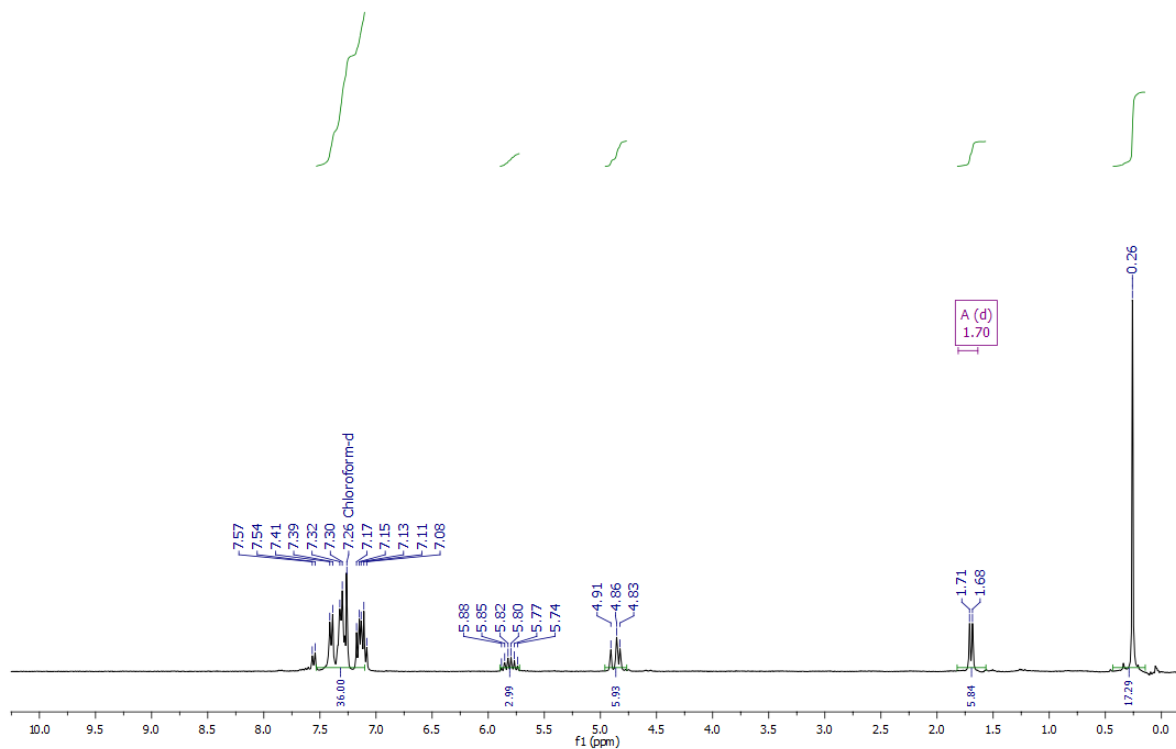
¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): -0.06 (-SiCH₃), 26.15 (H₂C=CH-CH₂-), 113.91 (H₂C=CH-), 127.64-127.71, 128.02, 130.14-130.28, 131.21, 132.80 (Ph), 134.09 (H₂C=CH-), 134.14-134.16 (Ph).

²⁹Si NMR (79.5 MHz, CDCl₃, δ, ppm): 8.53 (-OSi(CH₃)₂-), -77.41, -77.81, -78.04.

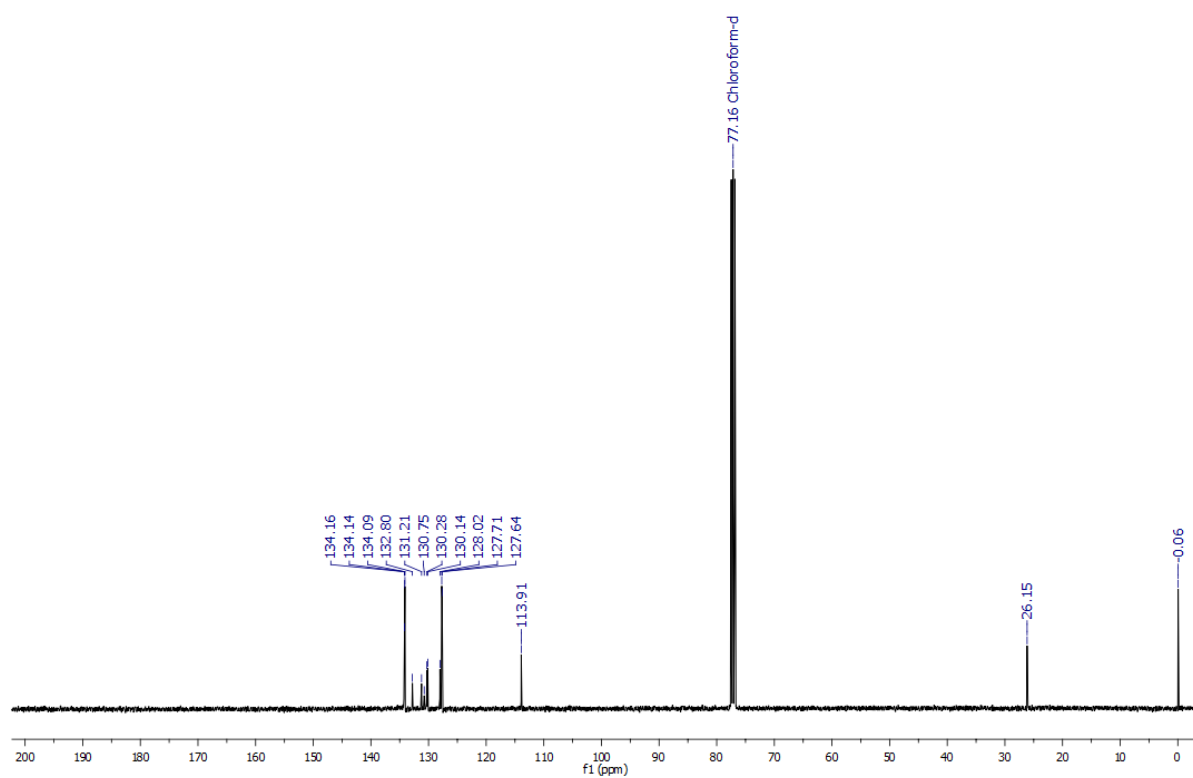
FT-IR (cm⁻¹): 3073.09, 3027.62 (C-H phenyl), 2958.51, 2916.05 (-C-H), 1630.24 (C=C), 1594.32 (C=C phenyl), 1489.96 (-C-H), 1430.03 (C=C phenyl), 1255.44 (Si-C), 1129.05, 1047.24 (Si-O), 997.89 (C-H phenyl).

Chemical formula: C₅₇H₆₈O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₅₇H₆₈HNaO₁₂Si₁₀: *m/z* 1248.2379, found: 1248.2390.

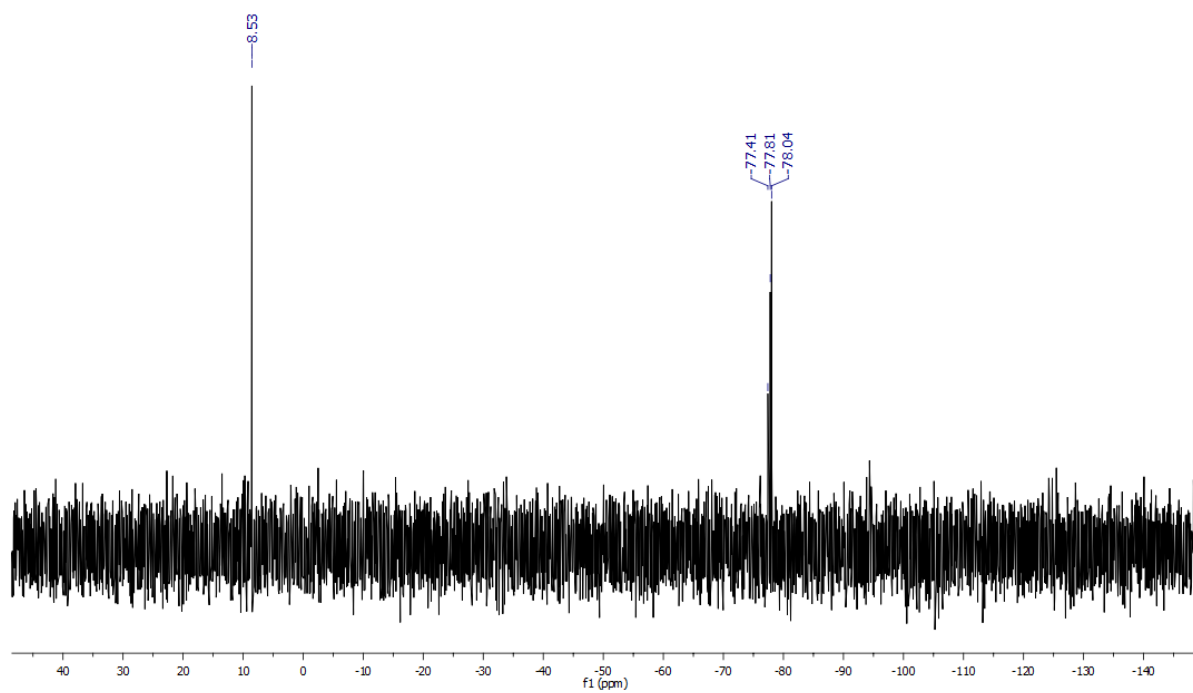
¹H NMR



^{13}C NMR

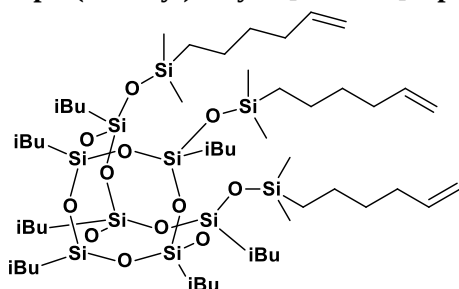


^{29}Si NMR



SQ-iBu-Hex

3,7,14-tris[dimethyl(hex-5-enyl)siloxy]-1,3,5,7,9,11,14-hepta(isobutyl)tricyclo[7.3.3^{15,11}]heptasiloxane



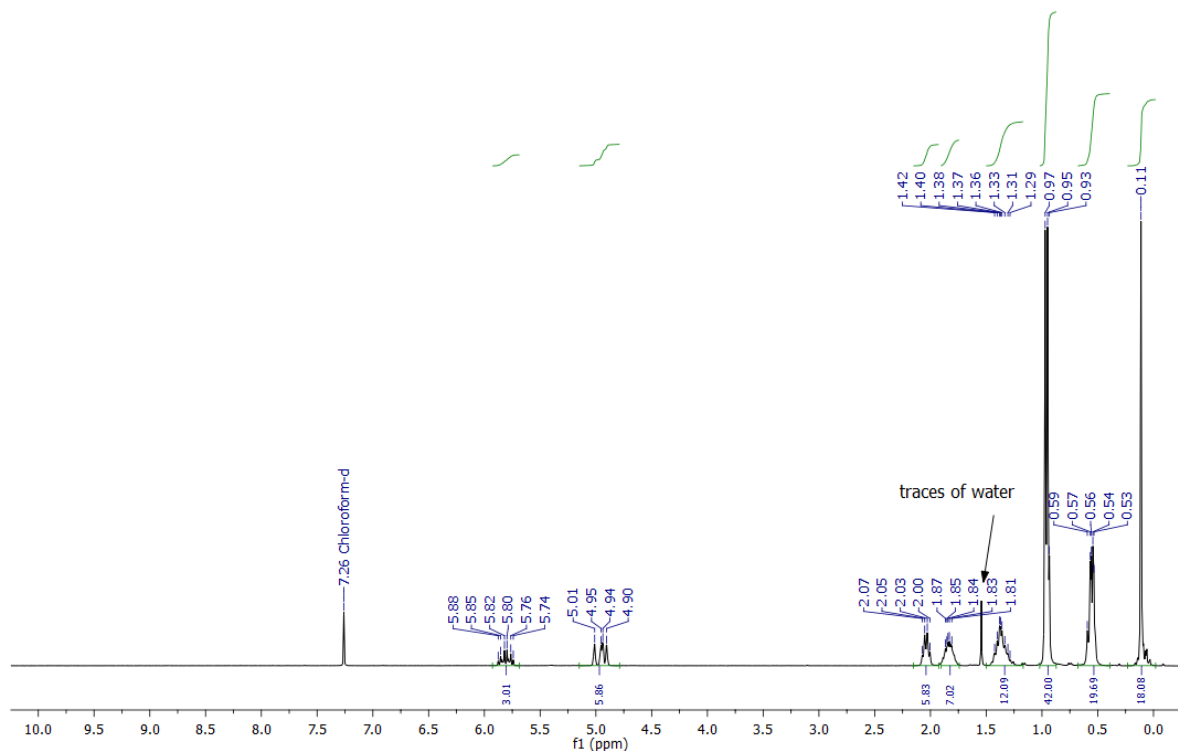
Colorless oil, isolated yield **90%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.11 (s, 18H, -SiCH₃), 0.53-0.59 (m, 20H, -CH₂- (iBu, hexenyl)), 0.93-0.97 (m, 42H, -CH₃ (iBu)), 1.29-1.42 (m, 12H, -CH₂- (hexenyl)), 1.81-1.87 (m, 7H, -CH- (iBu)), 2.00-2.07 (m, 6H, -CH₂- (hexenyl)), 4.90-5.01 (m, 6H, H₂C=CH-), 5.74-5.88 (m, 3H, H₂C=CH-). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.47 (-SiCH₃), 18.14 (-CH₂- (hexenyl)), 22.62 (iBu), 22.62 (-CH₂- (hexenyl)), 23.94, 24.02, 24.14, 24.25, 25.21, 25.79, 26.02, 26.19 (iBu), 114.19 (H₂C=CH-), 139.33 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 9.02 (-OSi(CH₃)₂-), -67.35, -67.78, -68.23.

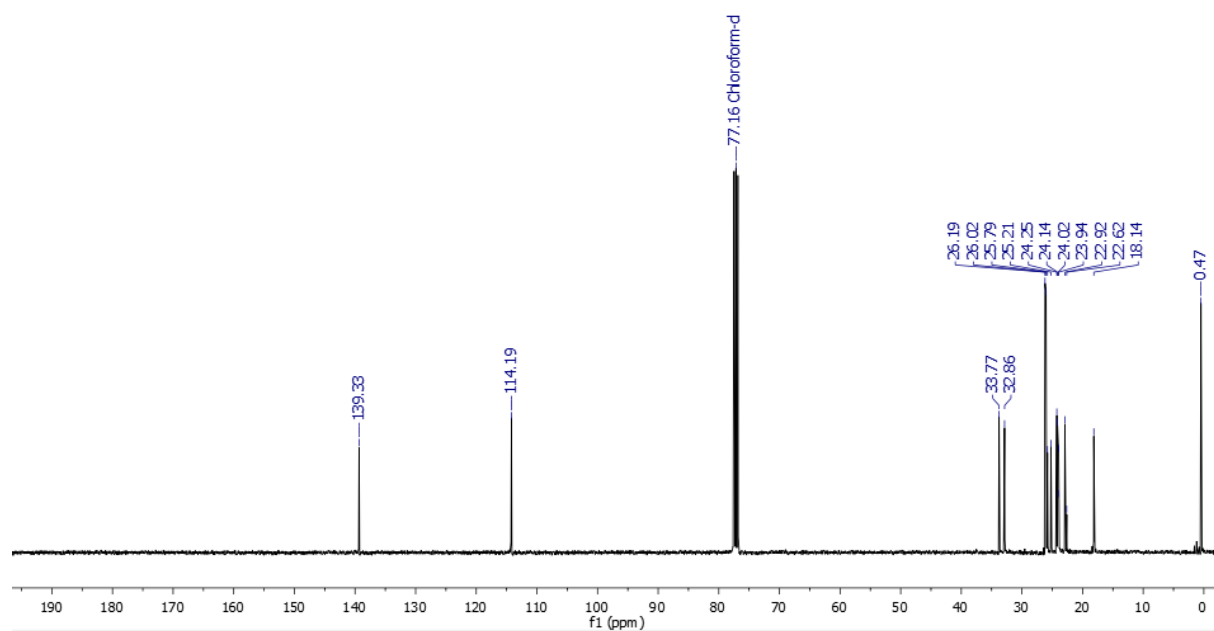
FT-IR (cm⁻¹): 3076.41 (=C-H), 2952.88, 2868.19 (-C-H), 1641.18 (C=C), 1465.38 (-C-H), 1251.92 (Si-C), 1079.28, 1049.03 (Si-O).

Chemical formula: C₅₂H₁₁₄O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₅₂H₁₁₄ H⁺Na⁺O₁₂Si₁₀: *m/z* 1234.5968, found:1234.5964.

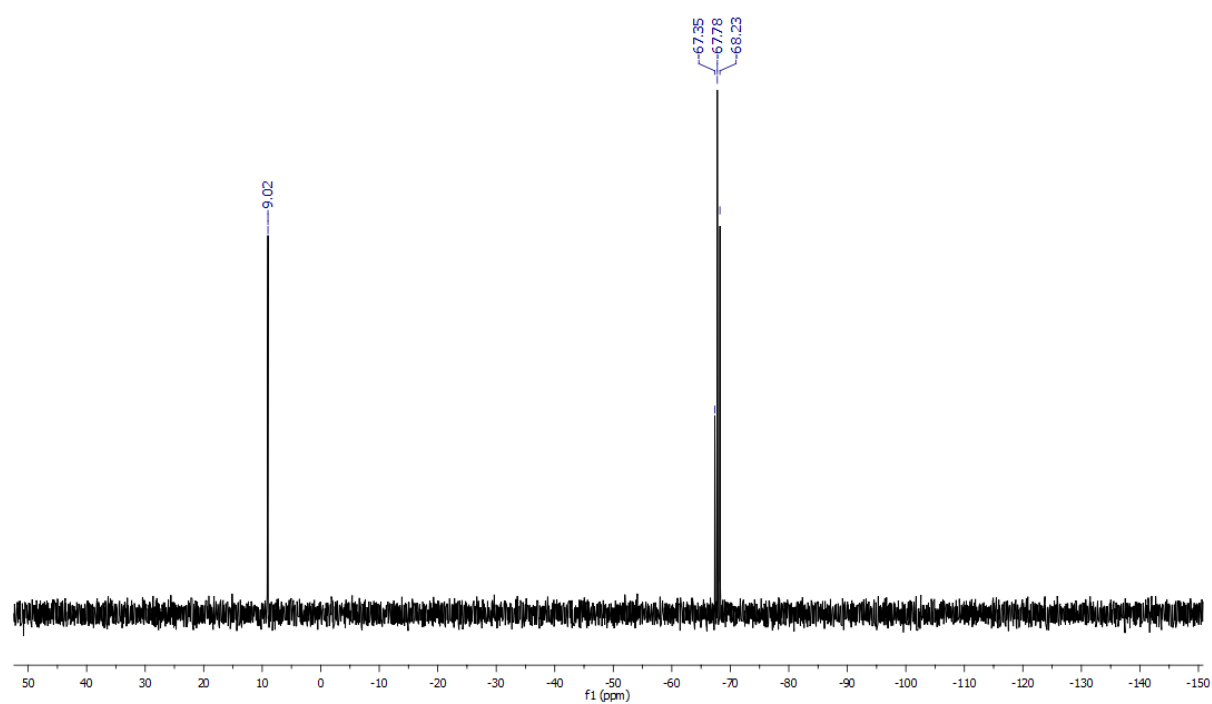
¹H NMR



¹³C NMR

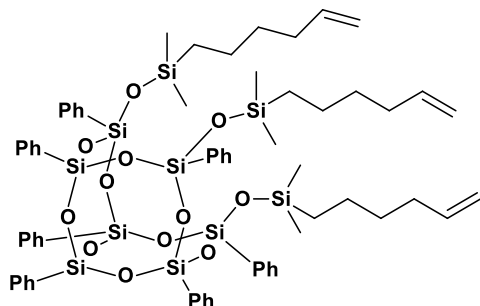


²⁹Si NMR



SQ-Ph-Hex

3,7,14-tris[dimethyl(hex-5-enyl)siloxy]-1,3,5,7,9,11,14-hepta(phenyl)tricyclo[7.3.3^{15,11}]heptasiloxane



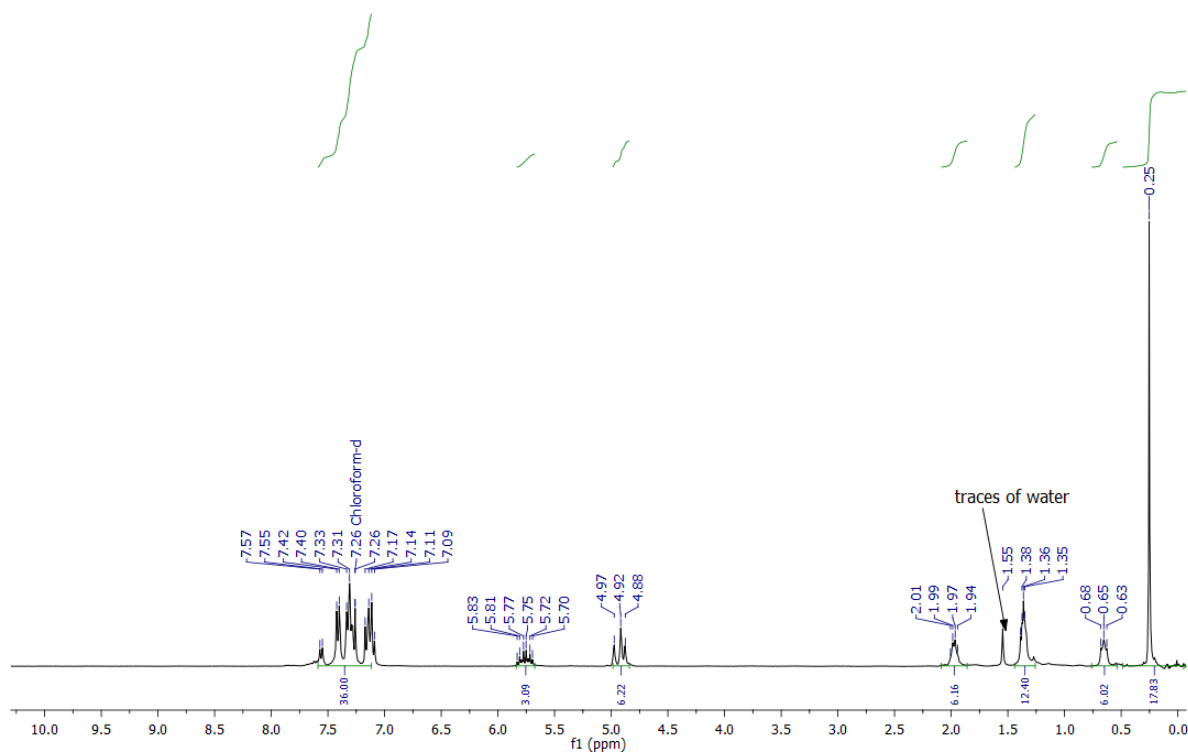
White solid, isolated yield **84%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.25 (s, 18H, -SiCH₃), 0.63-0.68 (m, 6H, -CH₂- (hexenyl)), 1.35-1.38 (m, 12H, -CH₂- (hexenyl)), 1.94-2.01 (m, 6H, -CH₂- (hexenyl)), 4.88-4.97 (m, 6H, H₂C=CH-), 5.70-5.83 (m, 3H, H₂C=CH-), 7.09-7.57 (m, 35H, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.52 (-SiCH₃), 18.13, 22.87, 32.83, 33.68 (-CH₂- (hexenyl)), 114.20 (H₂C=CH-), 127.61-127.68, 127.99, 130.04-130.23, 130.70, 131.38, 133.10, 134.10-134.17 (Ph), 139.26 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.78 (-OSi(CH₃)₂-), -77.38, -77.90, -78.12.

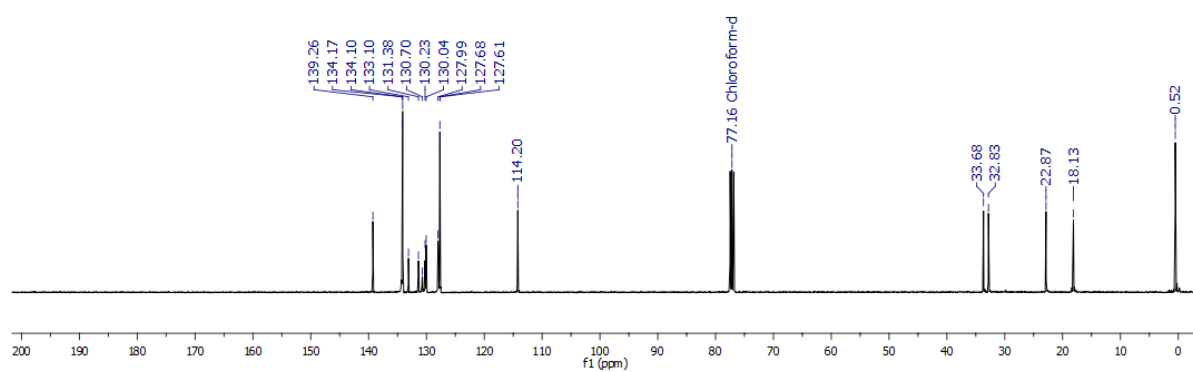
FT-IR (cm⁻¹): 3072.75, 3051.80 (C-H phenyl), 2955.76, 2853.79 (-C-H), 1640.29 (C=C), 1593.88 (C=C phenyl), 1489.77 (-C-H), 1429.86 (C=C phenyl), 1251.59 (Si-C), 1045.76 (Si-O), 997.84 (C-H phenyl).

Chemical formula: C₆₆H₈₆O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₆₆H₈₆HN⁺O₁₂Si₁₀: *m/z* 1374.3782, found: 1374.3783.

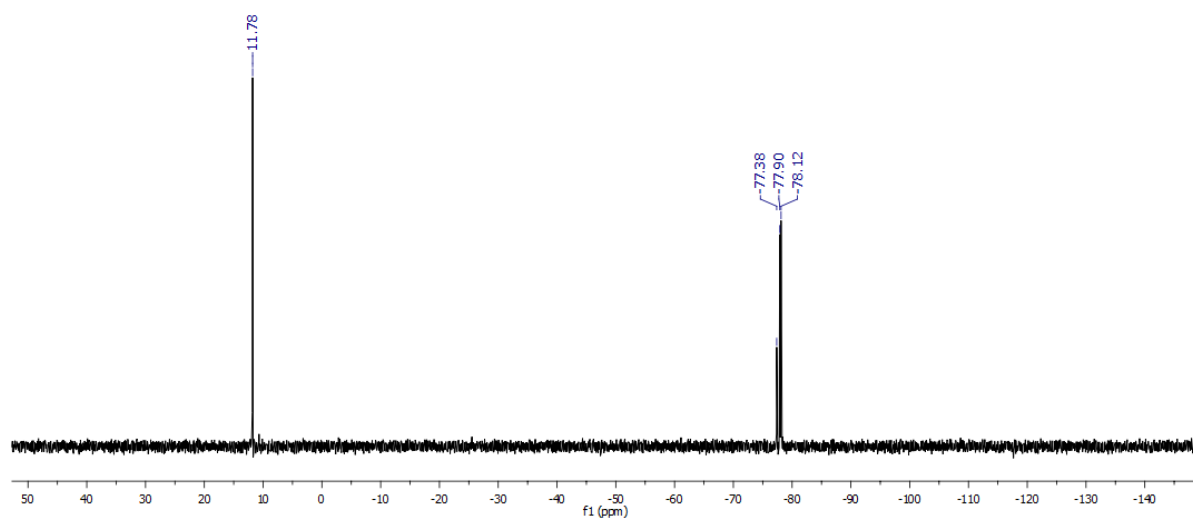
¹H NMR



^{13}C NMR

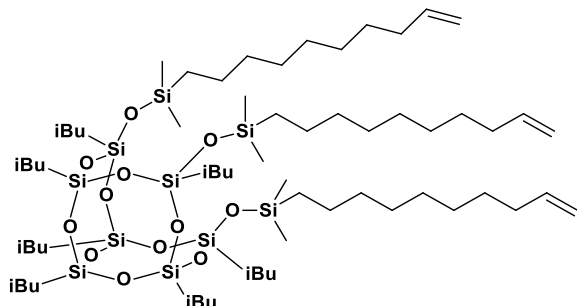


^{29}Si NMR



SQ-iBu-Dec

3,7,14-tris[dimethyl(dec-9-enyl)siloxy]-1,3,5,7,9,11,14-hepta(isobutyl)tricyclo[7.3.3^{15,11}]heptasiloxane



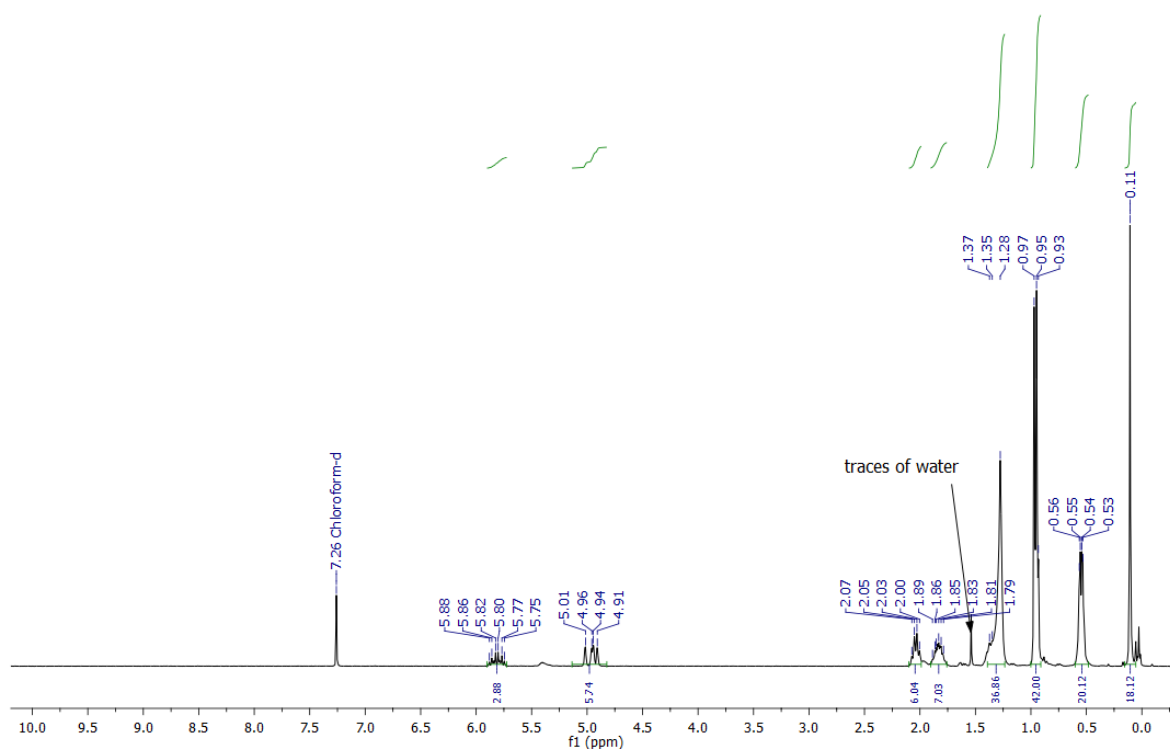
Colorless oil, isolated yield **89%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.11 (s, 18H, -SiCH₃), 0.53-0.56 (m, 20H, -CH₂- (iBu, decenyl)), 0.93-0.97 (m, 42H, -CH₃ (iBu)), 1.28-1.37 (m, 36H, -CH₂- (decenyl)), 1.79-1.89 (m, 7H, -CH- (iBu)), 2.00-2.07 (m, 6H, -CH₂- (decenyl)), 4.91-5.01 (m, 6H, H₂C=CH-), 5.75-5.88 (m, 3H, H₂C=CH-). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.48 (-SiCH₃), 18.31, 23.38 (-CH₂- (decenyl)), 23.94-24.25, 25.21, 25.78, 26.03, 26.19 (iBu), 29.14, 29.41, 29.59, 29.68, 33.69, 34.00 (-CH₂- (decenyl)), 114.23 (H₂C=CH-), 139.42 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 9.09 (-OSi(CH₃)₂-), -67.35, -67.82, -68.30.

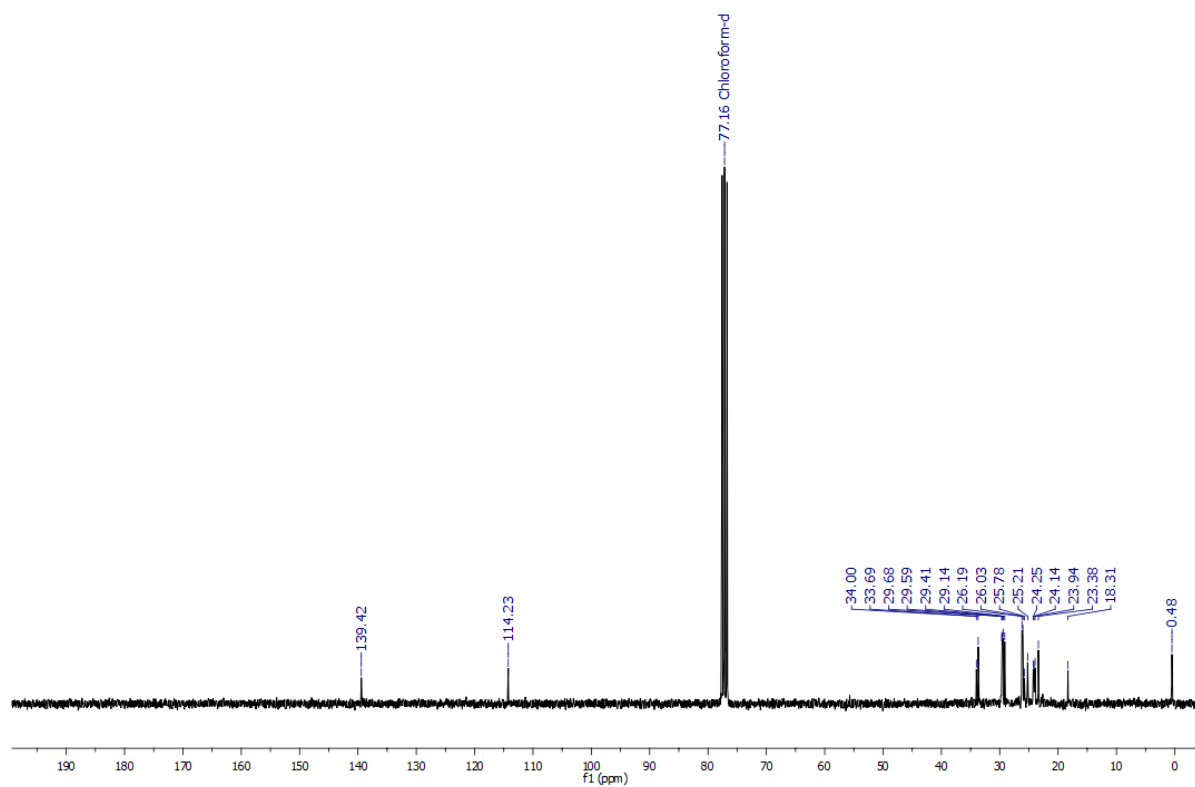
FT-IR (cm⁻¹): 3076.99 (=C-H), 2952.57, 2853.82 (-C-H), 1641.10 (C=C), 1465.20 (-C-H), 1251.13 (Si-C), 1074.40 (Si-O).

Chemical formula: C₆₄H₁₃₈O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₆₄H₁₃₈NaO₁₂Si₁₀: *m/z* 1401.7779, found: 1401.7794.

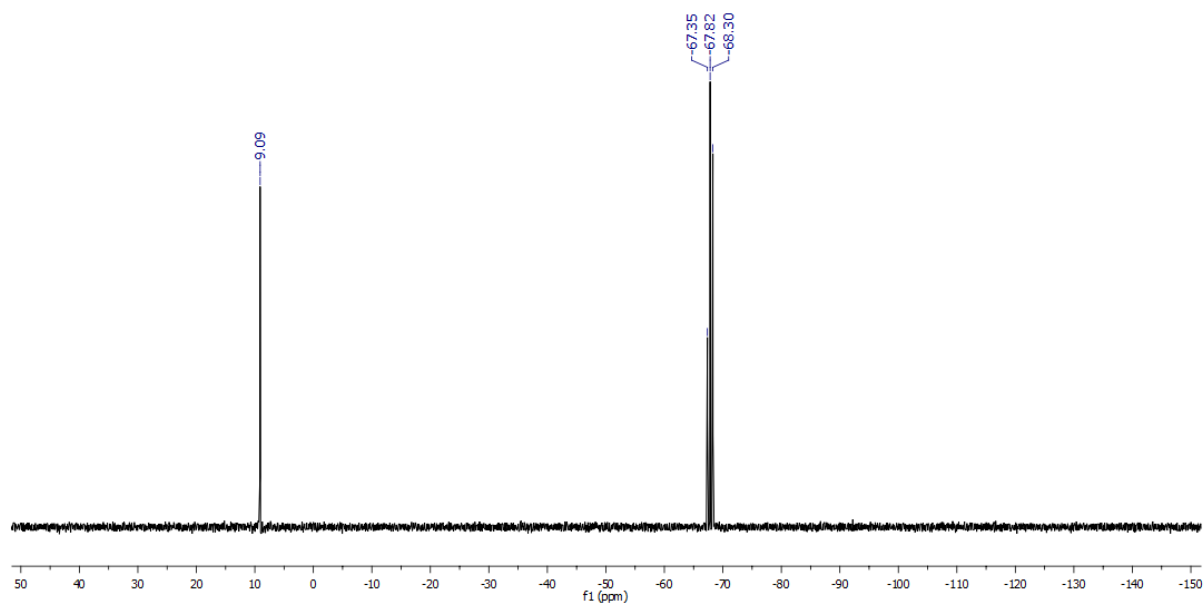
¹H NMR



^{13}C NMR

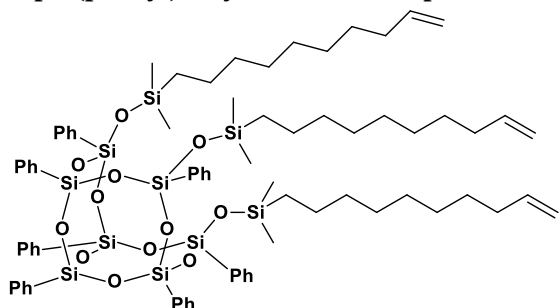


^{29}Si NMR



SQ-Ph-Dec

3,7,14-tris[dimethyl(dec-9-enyl)siloxy]-1,3,5,7,9,11,14-hepta(phenyl)tricyclo[7.3.3^{15,11}]heptasiloxane



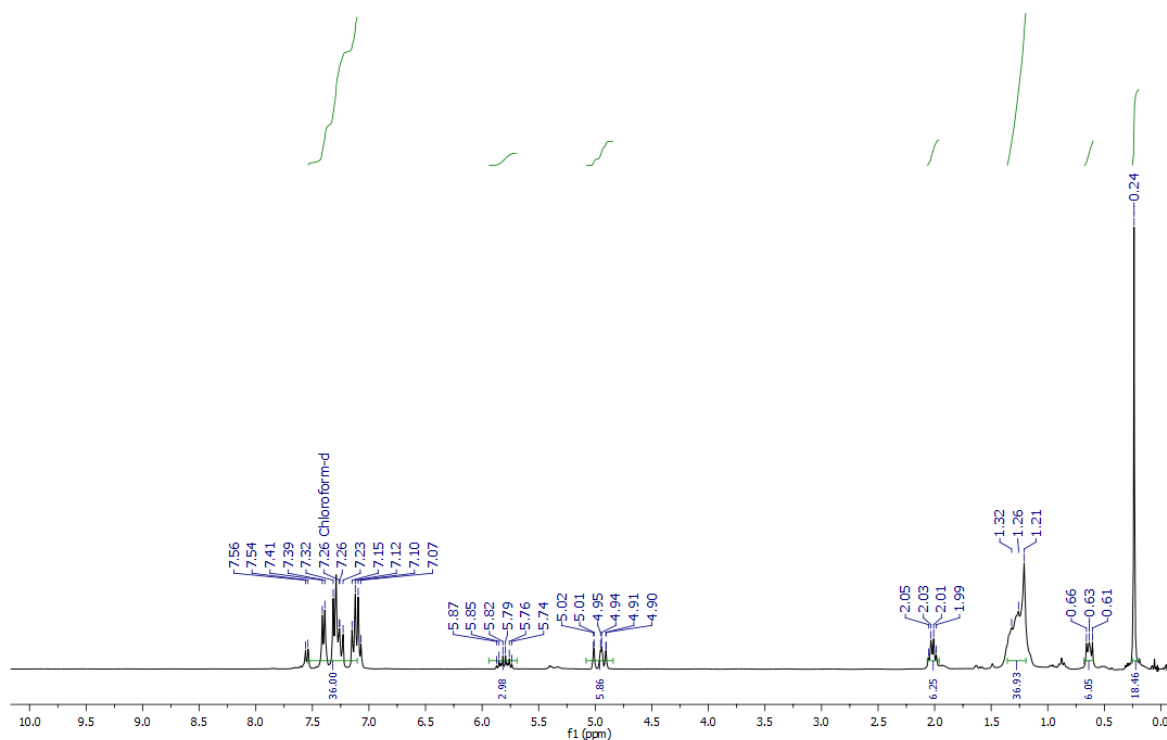
White solid, isolated yield **85%**

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.24 (s, 18H, -SiCH₃), 0.61-0.66 (m, 6H, -CH₂- (decenyl)), 1.21-1.32 (m, 36H, -CH₂- (decenyl)), 1.99-2.05 (m, 6H, -CH₂- (decenyl)), 4.90-5.02 (m, 6H, H₂C=CH-), 5.74-5.87 (m, 3H, H₂C=CH-), 7.07-7.56 (m, 35H, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.55 (-SiCH₃), 18.32, 23.36, 29.14, 29.40, 29.54, 29.67, 33.69, 34.02 (-CH₂- (decenyl)), 114.26 (H₂C=CH-), 127.60-127.67, 128.00, 130.02-130.20, 130.70, 131.43, 133.18, 134.12-134.19 (Ph), 139.37 (H₂C=CH-). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.88 (-OSi(CH₃)₂-), -77.35, -77.94, -78.12.

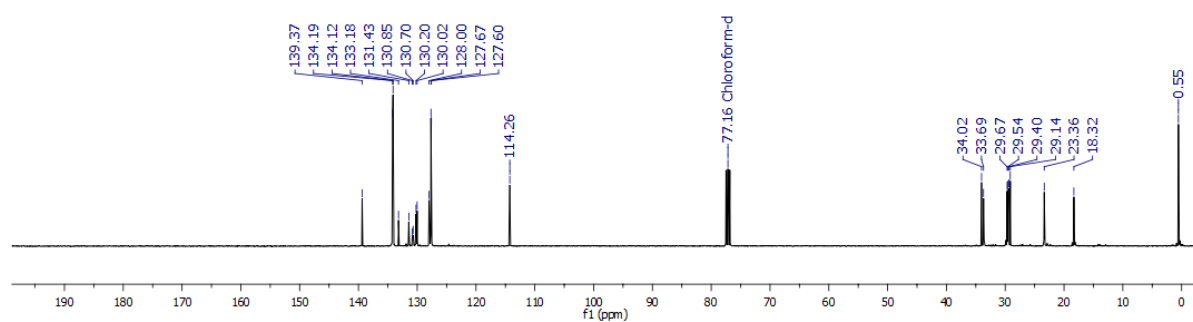
FT-IR (cm⁻¹): 3072.82, 3005.99 (C-H phenyl), 2922.05, 2852.58 (-C-H), 1640.29 (C=C), 1594.23 (C=C phenyl), 1489.92 (-C-H), 1429.92 (C=C phenyl), 1251.05 (Si-C), 1129.45, 1048.09 (Si-O), 997.84 (C-H phenyl).

Chemical formula: C₇₈H₁₁₀O₁₂Si₁₀. **MALDI-ToF MS**: Calcd. for C₇₈H₁₁₀ HNa⁺O₁₂Si₁₀: *m/z* 1541.5488, found: 1541.5588.

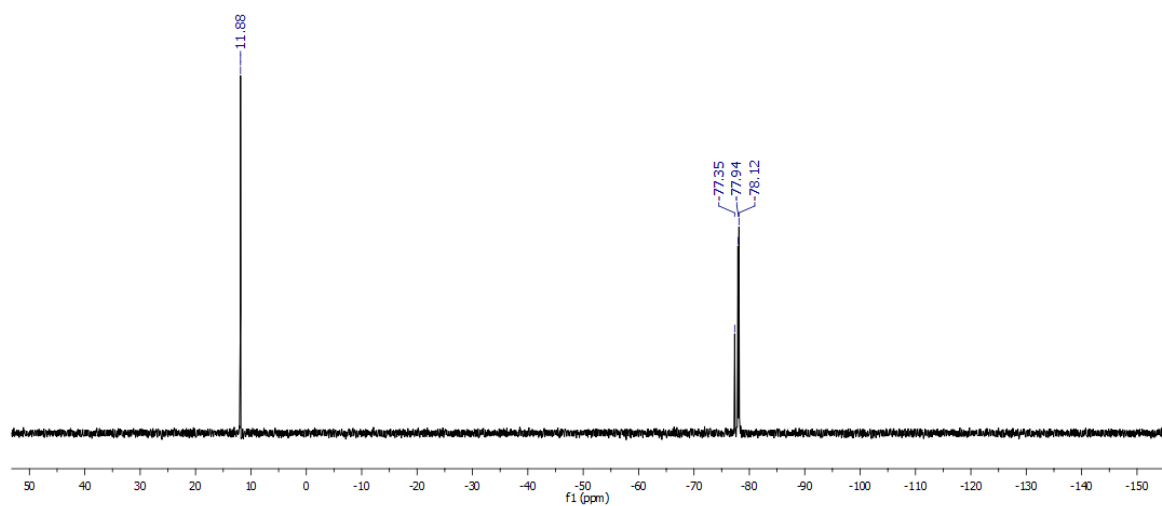
¹H NMR



¹³C NMR



²⁹Si NMR



2. Additional NMR spectra

2.1 Product SQ-iBu-Hex obtained in a different conditions of condensation reaction

a) in a concentrated THF solution (0.63M) – a complete conversion of **SQ-iBu-OH** is observed.

b) diluted THF solution (0.13M) – an incomplete condensation of **SQ-iBu-OH** and presence of Si-OH moiety at -58 ppm is noted.

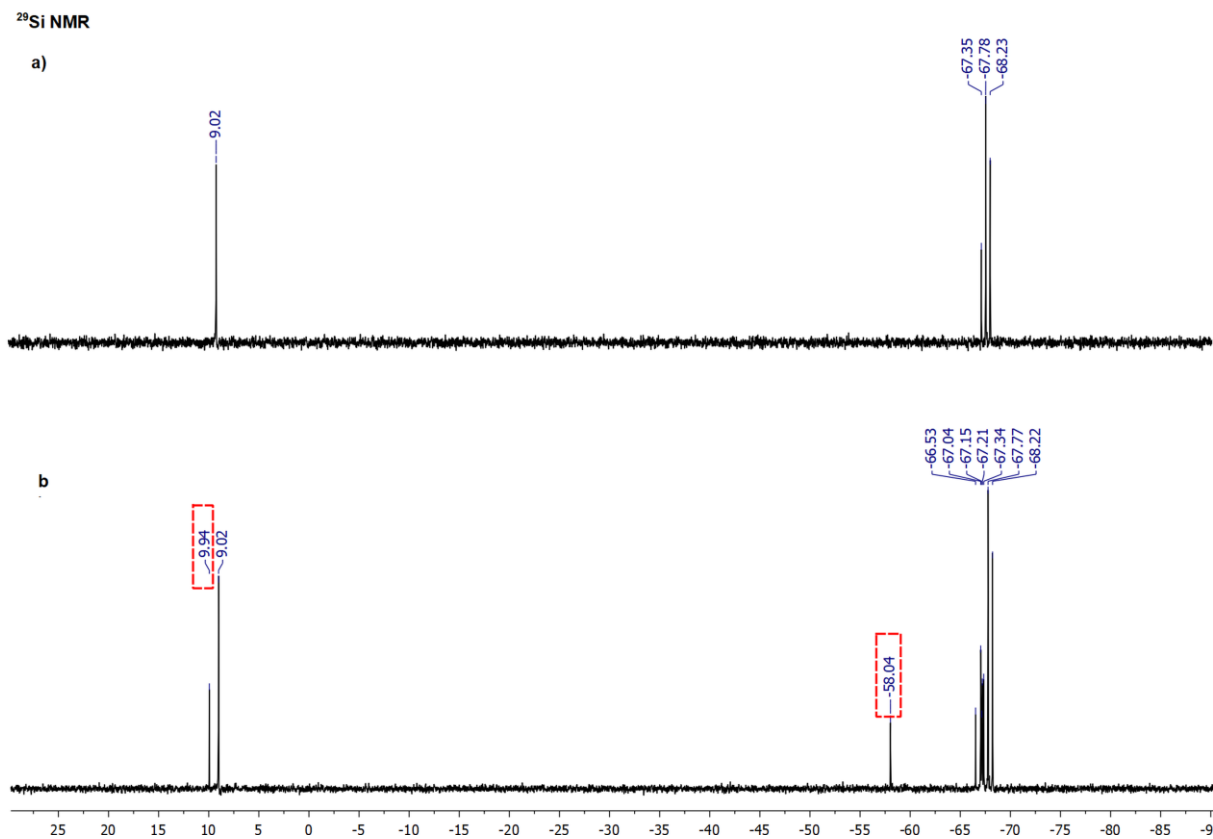


Figure S1. ²⁹Si NMR spectra of isolated **SQ-iBu-Hex** obtained *via* condensation reaction performed a) in a concentrated THF solution (0.63M); b) diluted THF solution (0.13M)

2.2 Thermal cross-condensation of SQ-iBu-Vi

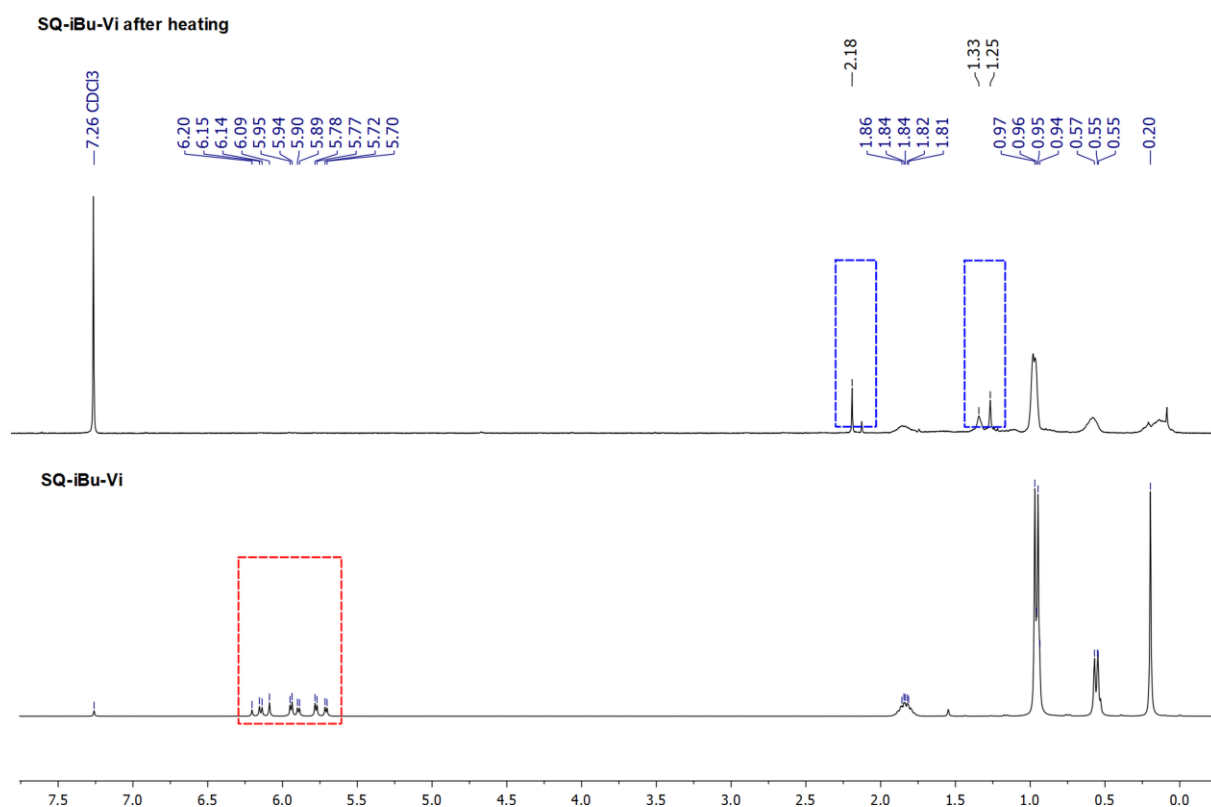
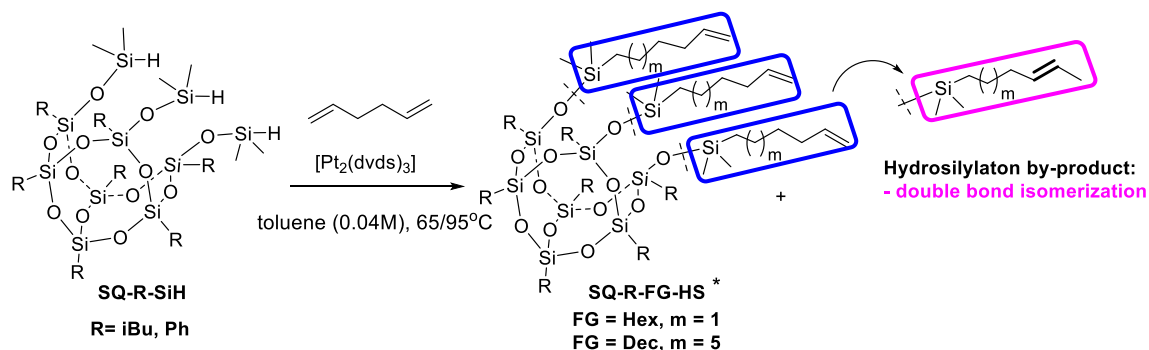


Figure S2. ¹H NMR spectra of isolated **SQ-iBu-Vi** and material abbreviated as **SQ-iBu-Vi after heating**, obtained as a result of 30 min heating of neat **SQ-iBu-Vi** at 200°C at steel plate.

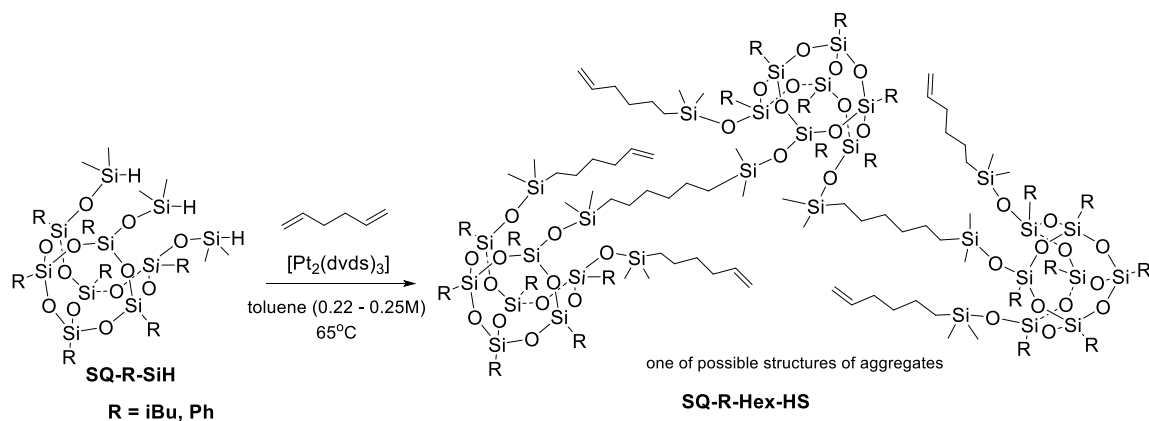
3. Products of hydrosilylation of dienes by SQ-R-SiH conducted in different conditions

a) Hydrosilylation of 1,5-hexadiene/1,9-decadiene by SQ-R-SiH in a diluted toluene solution (0.04M)



* accompanied by compounds of alkenyl chains with isomerized C=C group

b) Hydrosilylation of 1,5-hexadiene by SQ-R-SiH in a concentrated toluene solution (0.22-0.25M) and one of possible structures of an aggregate



4. GPC chromatograms

Hydrosilylation of 1,5-hexadiene by SQ-R-SiH in a concentrated toluene solution (R=iBu, 0.22M; R=Ph, 0.25M) resulting in **SQ-R-Hex-HS**.

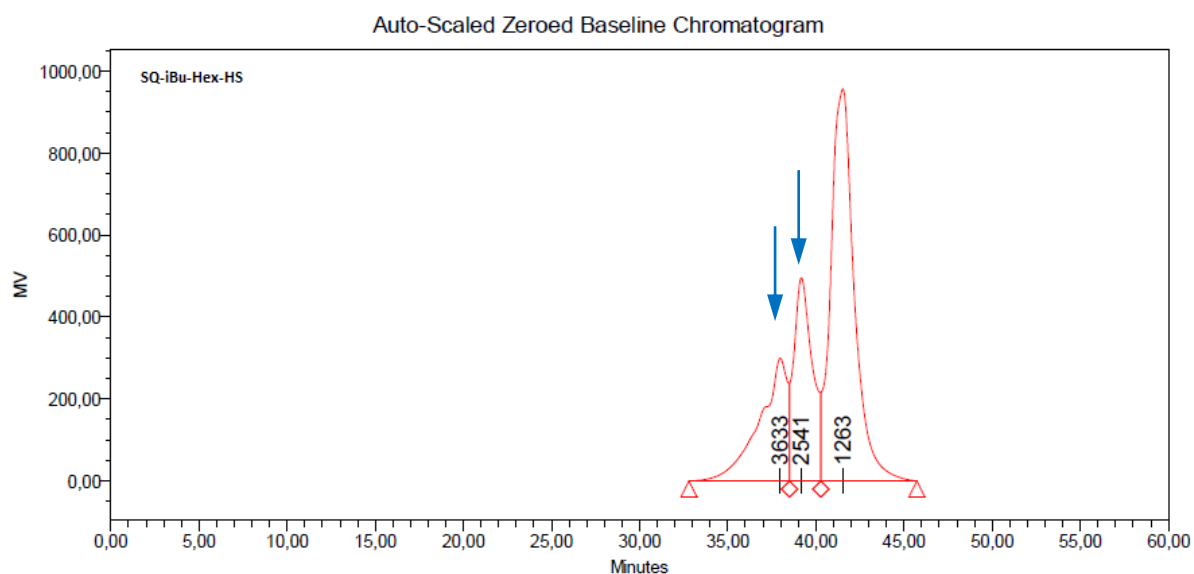


Figure S3. GPC analysis of crude **SQ-iBu-Hex-HS**, obtained *via* hydrosilylation of 1,5-hexadiene by **SQ-iBu-SiH** at 0.22M concentration of **SQ-iBu-SiH** in toluene. The marked peaks correspond with the higher M_w of compounds resulting from intermolecular hydrosilylation of 1,5-hexadiene by two or three **SQ-iBu-SiH** molecules.

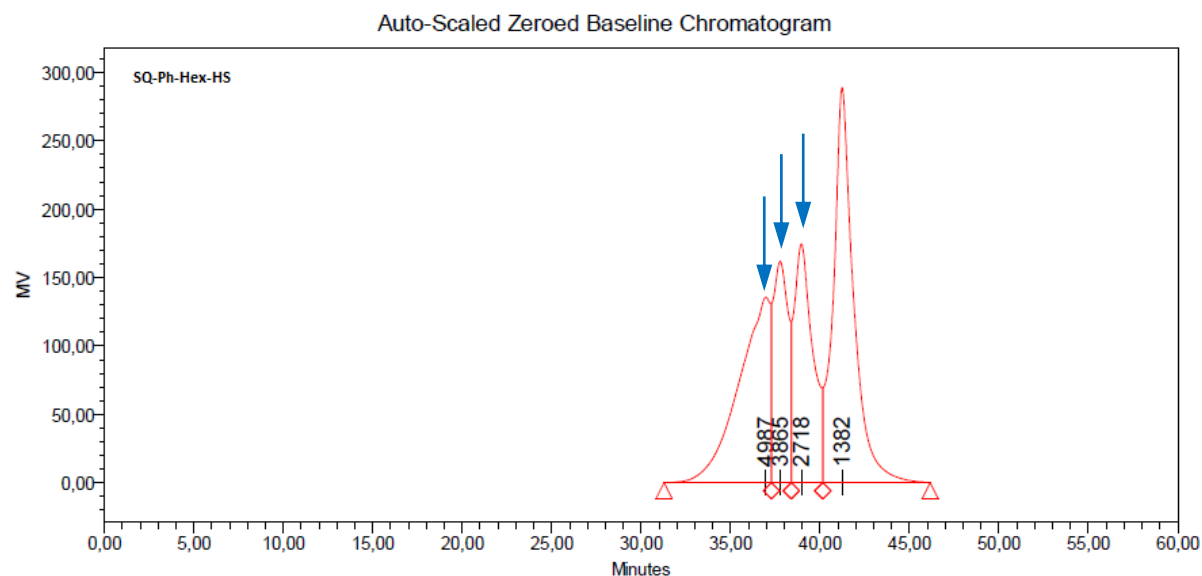


Figure S4. GPC analysis of crude **SQ-Ph-Hex-HS**, obtained *via* hydrosilylation of 1,5-hexadiene by **SQ-Ph-SiH** at 0.22M concentration of **SQ-Ph-SiH** in toluene. The marked peaks correspond with the higher M_w of compounds resulting from intermolecular hydrosilylation of 1,5-hexadiene by two or three **SQ-Ph-SiH** molecules.

5. References

1. Dutkiewicz, M.; Karasiewicz, J.; Rojewska, M.; Skrzypiec, M.; Dopierała, K.; Prochaska, K.; Maciejewski, H. Synthesis of an Open-Cage Structure POSS Containing Various Functional Groups and Their Effect on the Formation and Properties of Langmuir Monolayers. *Chem. - A Eur. J.* **2016**, *22*, 13275–13286.
2. Yuasa, S.; Sato, Y.; Imoto, H.; Naka, K. Fabrication of composite films with poly(methyl methacrylate) and incompletely condensed cage-silsesquioxane fillers. *J. Appl. Polym. Sci.* **2018**, *135*, 46033.
3. Kaźmierczak, J.; Kuciński, K.; Hreczycho, G. Highly Efficient Catalytic Route for the Synthesis of Functionalized Silsesquioxanes. *Inorg. Chem.* **2017**, *56*, 9337–9342.