

SUPPORTING INFORMATION

Cobalt-Catalyzed Selective Synthesis of Disiloxanes and Hydrodisiloxanes

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General Experimental: All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBRAUN glove box. Chemicals were purchased from sigma-Aldrich, across, Alfa-aesar, Himedia chemicals and used without further purification. ^1H and ^{13}C NMR are recorded at Bruker AV-400 (^1H : 400 MHz ^{13}C : 100.6 MHz ^{29}Si : 79 MHz) machine. ^1H and ^{13}C { ^1H } NMR chemical shifts were reported in ppm down field from tetramethylsilane. Multiplicity abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; se-Pt, Septet; m, multiplet; Assignment of ^{13}C NMR signals was done based on one dimensional (dept-135) NMR technique.

Safety warning: Although we have not come across any problem during this work, all the reactions that involve libaration of molecular hydrogen should be carried out with due care and inside the ventilated fumehood.

Synthesis of Catalyst **1:** To a 100 mL round-bottom flask suspension of CoBr_2 (218 mg, 1 mmol) in ethanol was placed and the ligand N,N' -(pyridine-2,6-diylbis(methylene))bis(2-methylpropan-2-amine)¹ (249 mg, 1 mmol) was added to the reaction mixture. Then, the reaction mixture was allowed to stir at room temperature for 14 h. Upon completion of reaction, the solvent was removed under vacuum. The resultant residue was washed with

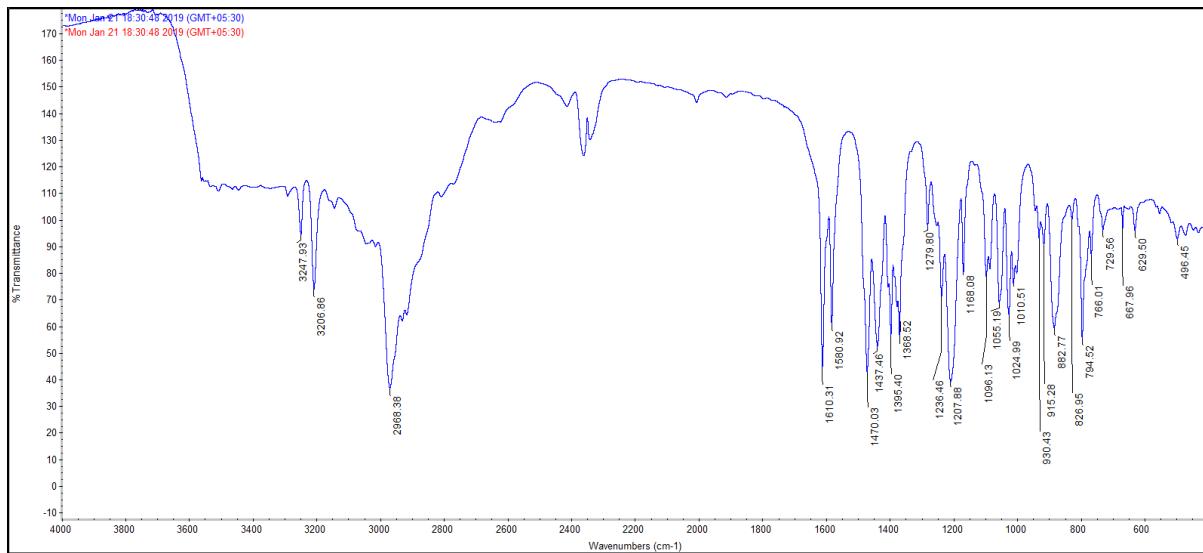
hexane (3×2 mL) and dried under reduced pressure to obtain complex **1** as a blue solid (400 mg, 85 %).

Spectral Data of Catalyst 1: Blue solid. Yield 400 mg (85%). IR (DCM): 3434, 1631, 1443, 1403, 1382, 1275, 750, 668 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 9.53 (brs, 2H, NH), 7.33-7.28 (d, 3H, $J = 20$ Hz, pyridine- CH), 4.44 (s, 4H, CH_2), 1.72 (s, 18H, CH_3).

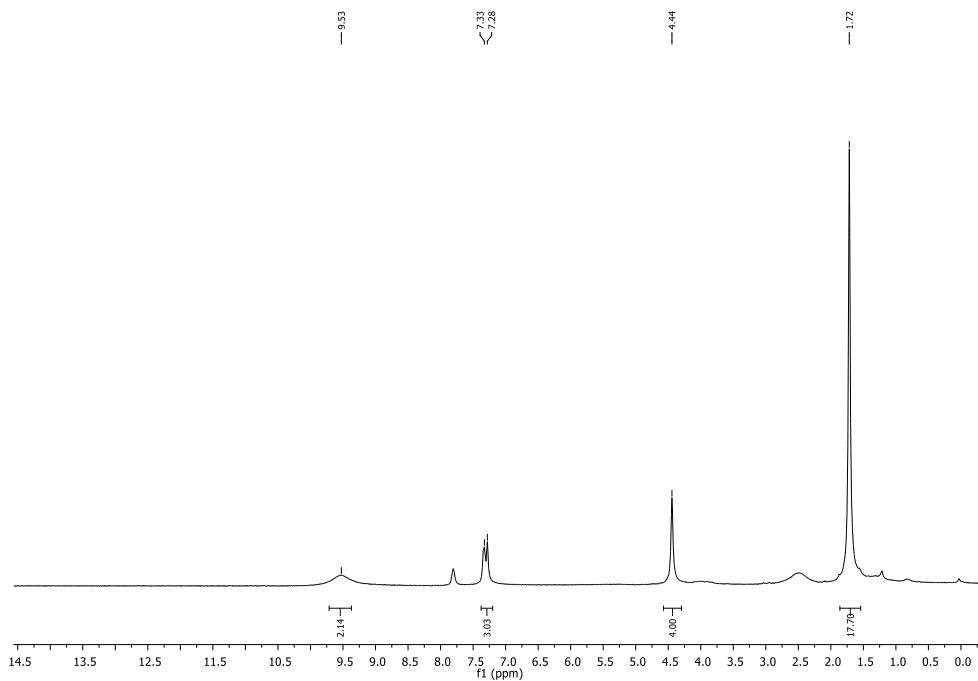
X-ray Analyses and Crystal Data of 1: Crystals suitable for single crystal x-ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEXCCD detector and with an Incoatecmicrosource (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073$ \AA , multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT² and corrected for absorption with SADABS.³ The structure was solved by direct methods and refined on F^2 with SHELXL-97.⁴

Crystal Data of Catalyst 1 : $[(\text{N,N,N}^{\text{HtBu}})\text{CoBr}_2]$ (1): $\text{C}_{15}\text{H}_{27}\text{Br}_2\text{CoN}_3$, blue block, crystal dimension : $0.2 \times 0.14 \times 0.14$ mm $^{-1}$, $M = 468.14$, monoclinic with space group $\text{P}121/\text{C}1$, $a = 10.8842$ (4) \AA , $b = 11.4192(4)$ \AA , $c = 15.8101(6)$ \AA , $\alpha = 90^\circ$, $\beta = 104.557^\circ$, $\gamma = 90^\circ$, $V = 1901(4)$ \AA^3 , $Z = 4$, $F(000) = 940$, $\mu\text{-(MoK}_\alpha\text{)} = 5.102$ mm $^{-1}$, $2\theta\text{max} = 59.318$, $\rho_{\text{calcd}} = 1.635$ Mg/m^3 , $T = 298(2)$ K, min/max transmission factors = 0.4280/0.7460, 22165 Reflections collected 5539 unique ($R1 = 0.1085$), $WR2 = 0.1499$ (all data). Residual electron density max/min = 1.612/-0.868 e. \AA^{-3} . The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 1875074**.

IR Spectrum of Catalyst **1**:



¹H NMR Spectrum of Catalyst **1** in CDCl₃:

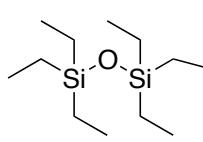


General Procedure for Synthesis of Symmetrical Siloxanes: To an oven dried sealed tube, silane (1 mmol), catalyst **1** (2 mol %), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. Degassed water (2 mmol) was added and the reaction mixture was allowed to stir at 60 °C in a preheated oil bath for two hours. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum. The reaction

mixture was subjected to GC analysis and column chromatography on silica gel (100-200 mesh, petroleum ether/EtOAc=100:1) provided the pure products.

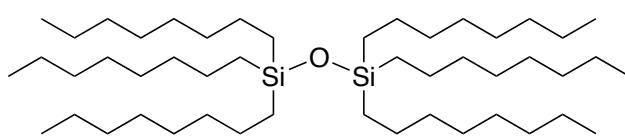
Spectral Data of Symmetrical Siloxanes:

1,1,1,3,3,3-Hexaethylsiloxane (2a):⁵ Colourless liquid. Yield: (116 mg, 94%). IR (DCM):



2815, 2803, 2721, 1681, 1643, 1553, 1123, 1078, 987, 768 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.98-0.94 (t, 18H, *J* = 8 Hz, CH₃), 0.57-0.52 (q, 12H, *J* = 4 Hz, CH₂-Si). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 6.79 (CH₃), 6.43 (CH₂-Si).

1,1,1,3,3,3-Hexaoctylsiloxane (2b):⁶ Colourless liquid. Yield: (322 mg, 86%). IR (DCM):



2957, 2854, 2922, 1638, 1460, 1409, 1378, 1176, 1108, 1015, 916, 845, 813 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ

1.23-1.19 (m, 72H, CH₂), 0.82-0.79 (t, 18H, *J* = 8 Hz, CH₃), 0.51-0.48 (m, 12H, CH₂).

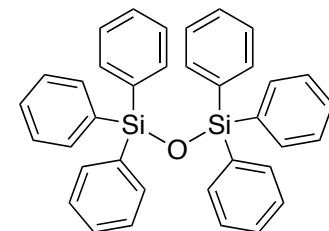
¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 33.58 (CH₂), 32.13 (CH₂), 29.50 (CH₂), 29.45 (CH₂), 24.87 (CH₂), 22.87 (CH₂), 14.28 (CH₂), 11.49 (CH₃).

1,1,3,3-Tetramethyl-1,3-diphenylsiloxane (2c):⁵ Colourless liquid. Yield: (143 mg, 99%).

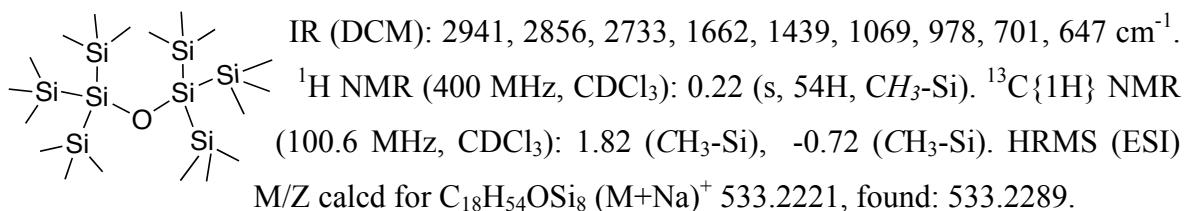
IR (DCM): 2957, 2898, 1560, 1542, 1509, 1427, 1254, 1120, 1061, 1027, 998, 831, 795, 745 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.66 (m, 4H, ArCH), 7.48-7.46 (m, 6H, ArCH), 0.46 (s, 12 H, CH₃-Si). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 139.84 (ArCH), 133.04 (ArCH), 129.30 (ArCH), 127.75 (ArCH), 0.86 (CH₃-Si).

1,1,1,3,3,3-Hexaphenyldisiloxane (2d):⁵ White colour solid. Yield: (240 mg, 89%). IR (DCM): 2360, 2340, 2065, 1868, 1844, 1733, 1716, 1636, 1260, 1118, 712 cm⁻¹. ¹H NMR

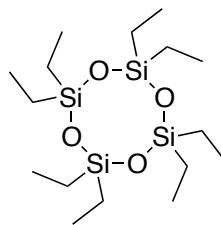
(400 MHz, CDCl₃): δ 7.51-7.50 (m, 12H, ArCH), 7.41-7.39 (m, 6H, ArCH), 7.30-7.28 (m, 12H, ArCH). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 135.47 (ArCH), 135.21 (ArCH), 129.81 (ArCH), 127.71 (ArCH).



1,1,1,3,3,3-Hexakis(trimethylsilyl)disiloxane (2e): Colourless liquid. Yield: (234 mg, 92%).

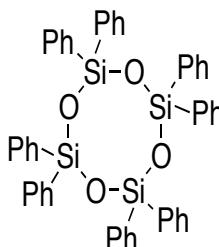


2,2,4,4,6,6,8,8-Octaethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilicone (3a): Colourless liquid.



Yield: (99 mg, 97%). IR (DCM): 2959, 2914, 2879, 2073, 1634, 1461, 1413, 1275.30, 1242, 1087, 1005 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.03-0.99 (t, 24H, $J = 8$ Hz, CH_3), 0.65-0.60 (q, 16H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 7.40 (CH_3), 6.25 ($\text{CH}_2\text{-Si}$). HRMS (ESI) M/Z calcd for $\text{C}_{16}\text{H}_{40}\text{O}_4\text{Si}_4$ ($\text{M}+\text{H}^+$) 409.2076, found: 409.2099.

2,2,4,4,6,6,8,8-Octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilicone (3b):⁵ White colour solid.



Yield: (192 mg, 96%). IR (DCM): 2852, 2286, 1428, 1118, 1089, 997, 771 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.55 (d, 16H, $J = 8$ Hz, ArCH), 7.44-7.40 (t, 8H, $J = 8$ Hz, ArCH), 7.28-7.24 (t, 16H, $J = 8$ Hz, ArCH). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 134.44 (ArCH), 130.10 (ArCH), 127.69 (ArCH).

General Procedure for Synthesis of Macroyclic Siloxane Cage 4: To an oven dried Schlenk tube, catalyst **1** (2 mol %), $\text{KO}^\text{t}\text{Bu}$ (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere and allowed to stir for 10 minutes at room temperature. After that phenylsilane (1 mmol) was added to the reaction mixture. Degassed water (3 mmol) was added and the reaction mixture was allowed to stir at 60 °C in a preheated oil bath for two hours. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and pure product was isolated by column chromatography on silica gel (100-200 mesh, petroleum ether/EtOAC=100:10) provided the pure product **4**. Further, the product was dried under vacuum overnight and crystallized by using DCM.

Spectral Data of Macroyclic Siloxane Cage 4: White color solid. Yield: (90 mg, 69%). IR (DCM): 3019, 2924, 2820, 1638, 1594, 1364, 1132, 852 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ

7.72-7.02 (m, 60H, ArCH). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 134.20 (ArCH), 134.12 (ArCH), 130.57 (ArCH), 127.92 (ArCH), 127.74 (ArCH).

General Procedure for Synthesis of Unsymmetrical Siloxane: To a screw cap scintillation vial, silanol (0.5 mmol), silane (0.5 mmol), catalyst **1** (2 mol %), and KO^tBu (4 mol%) were added under nitrogen atmosphere inside a glove box [notably, silanol added to trihydrosilanes in 2:1 ratio and for dihydrosilanes in 1:1 ratio]. Then, the reaction vial was sealed and allowed to stir at room temperature for 1 h. After completion of reaction, the solvent was removed under vacuum and the resultant residue was subjected to GC analysis and pure product was isolated by column chromatography.

Spectral Data of Unsymmetrical Siloxanes:

1,1,1-Triethyl-3,3-diphenyldisiloxane (5a):⁸ Colourless liquid. Yield: (130 mg, 82%). IR $\text{Ph}_3\text{Si}(\text{O})\text{SiEt}_3$ (DCM): 2955, 2876, 2124, 1639, 1429, 1238, 1115, 1065, 1008, 848, 822 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.62 (m, 4H, ArCH), 7.45-7.39 (m, 6H, ArCH), 5.55 (s, 1H, Si-H), 0.97-0.93 (t, 9H, $J = 8$ Hz, CH_3), 0.64-0.58 (q, 6H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 136.27 (ArCH), 134.16 (ArCH), 129.98 (ArCH), 127.88 (ArCH), 6.72 (CH_3), 6.14 ($\text{CH}_2\text{-Si}$).

1,1,1-Triethyl-3-methyl-3-phenyldisiloxane (5b):⁷ Colourless liquid. Yield: (111 mg, 88%). IR (DCM): 2909, 2955, 2855, 2126, 1508, 1458, 1414, 1252, 1068, 1010, 892, 869, 758 cm^{-1} . $\text{Me}_3\text{Si}(\text{O})\text{SiEt}_3$ ^1H NMR (400 MHz, CDCl_3): δ 7.618-7.595 (m, 2H, ArCH), 7.433-7.381 (m, 3H, ArCH), 5.152-5.131 (q, 1H, $J = 4$ Hz, Si-H), 0.973-0.934 (t, 9H, $J = 8$ Hz, CH_3), 0.611-0.551 (q, 6H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$), 0.445-0.438 (d, 3H, $J = 2.8$ Hz, $\text{CH}_3\text{-Si}$). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 138.15 (ArCH), 133.30 (ArCH), 129.67 (ArCH), 127.83 (ArCH), 6.72 (CH_3), 6.12 ($\text{CH}_2\text{-Si}$), -0.10 ($\text{CH}_3\text{-Si}$).

3,3-Diphenyl-1,1,1-tripropylsiloxane (5c):⁷ Colourless liquid. Yield: (139 mg, 78%). IR (DCM): 2953, 2924, 2867, 1560, 1542, 1511, 1420, 1102, 1057, 750 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.52-7.50 (m, 4H, ArCH), 7.35-7.28 (m, 6H, ArCH), 5.42 (s, 1H, Si-H), 1.29-1.23 (m, 6H, CH_2), 0.84-0.81 (t, 12H, $J = 8$ Hz, CH_3), 0.51-0.47 (t, 6H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$). $^{13}\text{C}\{1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 136.26 (ArCH), 134.16 (ArCH), 129.94 (ArCH), 127.84 (ArCH), 18.30 (CH_2), 18.15 (CH_3), 16.68 ($\text{CH}_2\text{-Si}$).

3-Methyl-3-phenyl-1,1,1-tripropylsilyl disiloxane (5d):⁷ Colourless liquid. Yield: (123 mg, 83

%). IR (DCM): 2955, 2925, 2868, 1667, 1655, 1258, 1204, 1123, 1045, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.489-7.437 (m, 2H, ArCH), 7.316-7.203 (m, 3H, ArCH), 5.024-5.017 (d, 1H, *J* = 2.8 Hz, Si-H), 1.267-1.188 (m, 6H, CH₂), 0.828-0.810 (m, 9H, CH₃), 0.449-0.407 (m, 6H, CH₂-Si), 0.237-0.196 (m, 3H, CH₃-Si). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 138.10 (ArCH), 133.28 (ArCH), 129.36 (ArCH), 127.46 (ArCH), 18.35 (CH₂), 18.24 (CH₃), 16.69 (CH₂-Si), -0.14 (CH₃-Si).

1,1,1-Triisopropyl-3,3-diphenylsilyl disiloxane (5e): Colourless liquid. Yield: (143 mg, 84%).

IR (DCM): 2942, 2866, 2351, 2125, 1640, 1462, 1428, 1115, 1084, 1027, 882, 844, 732 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.62 (m, 4H, ArCH), 7.44-7.29 (m, 6H, ArCH), 5.62 (s, 1H, Si-H), 1.05-1.03 (d, 21H, *J* = 8 Hz, CH₃, CH). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 136.45 (ArCH), 135.71 (ArCH), 134.23 (ArCH), 129.95 (ArCH), 127.86 (ArCH), 17.84 (CH₃), 12.81 (CH-Si). HRMS (ESI) M/Z calcd for C₂₁H₃₂OSi₂ (M+Na)⁺ 379.1884, found: 379.1881.

1,1,1-Triisobutyl-3,3-diphenylsilyl disiloxane (5f): Colourless liquid. Yield: (169 mg, 84%).

IR (DCM): 3070, 3051, 2952, 2925, 2894, 2125, 1590, 1463, 1380, 1328, 1220, 1066, 998, 853, 780, 764 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.60 (m, 4H, ArCH), 7.44-7.37 (m, 6H, ArCH), 5.54 (s, 1H, Si-H), 1.86-1.79 (m, 3H, CH), 0.92-0.91 (d, 18H, *J* = 4 Hz, CH₃), 0.64-0.63 (d, 6H, *J* = 4 Hz, CH₂). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 136.29 (ArCH), 134.34 (ArCH), 129.95 (ArCH), 127.85 (ArCH), 27.41 (CH), 26.50 (CH₃), 24.28 (CH₂-Si). ²⁹Si NMR (79MHz, CDCl₃): δ 8.99, 13.44-15.07 (Si-H). HRMS (ESI) M/Z calcd for C₂₄H₃₈OSi₂ (M+Na)⁺ 421.2353, found: 421.2356.

1,1,1-Triisobutyl-3-methyl-3-phenylsilyl disiloxane (5g): Colourless liquid. Yield: (148 mg, 88%). IR (DCM): 2953, 2894, 2714, 2619, 2124, 1633, 1465, 1364, 1252, 1163, 1071, 949,

870, 761 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.512-7.495 (m, 2H, ArCH), 7.328-7.278 (m, 3H, ArCH), 5.052-5.045 (d, 1H, *J* = 2.8 Hz, Si-H), 1.785-1.685 (m, 3H, CH), 0.857-0.840 (d, 18H, *J* = 8 Hz, CH₃), 0.521-0.504 (d, 6H, *J* = 8 Hz, CH₂), 0.345-0.338 (d, 3H, *J* = 2.8 Hz, CH₃-Si). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 138.07 (ArCH), 134.85 (ArCH), 133.43 (ArCH), 129.63 (ArCH), 127.77 (ArCH), 27.36 (CH), 26.44 (CH₃), 24.28 (CH₂-Si), -0.05 (CH₃-Si). HRMS (ESI) M/Z calcd for C₁₉H₃₆OSi₂ (M+Na)⁺ 359.2197, found: 359.2200.

3,3-Diphenyl-1,1,1-tris(trimethylsilyl)disiloxane (5h): Colourless liquid. Yield: (191 mg, 85%). IR (DCM): 2956, 2130, 1638, 1251, 1054, 839, 732 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.54 (m, 4H, ArCH), 7.37-7.28 (m, 6H, ArCH), 5.46-5.43 (m, 1H, Si-H), 0.02-0.05 (m, 27H, $\text{CH}_3\text{-Si}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 135.87 (ArCH), 134.31 (ArCH), 129.97 (ArCH), 127.80 (ArCH), 1.90 ($\text{CH}_3\text{-Si}$), 1.48 ($\text{CH}_3\text{-Si}$), -2.26 ($\text{CH}_3\text{-Si}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CDCl_3): δ 10.52, -13.44, -22.73 (Si-H). HRMS (ESI) M/Z calcd for $\text{C}_{21}\text{H}_{38}\text{OSi}_5$ ($\text{M}+\text{Na}$) $^+$ 469.1661, found: 469.1668.

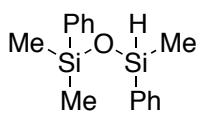
1,1-Dimethyl-1-octadecyl-3,3-diphenyldisiloxane (5i): Colourless liquid. Yield: (202 mg, 83%). IR (DCM): 3070, 2923, 2852, 2127, 1638, 1466, 1429, 1376, 1252, 1125, 1058, 1026, 937, 822 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.65-7.63 (m, 4H, ArCH), 7.47-7.40 (m, 6H, ArCH), 5.54 (s, 1H, Si-H), 1.32 (s, 32H, CH_2), 0.95-0.92 (t, 3H, $J = 8$ Hz, CH_3), 0.64-0.60 (t, 2H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$), 0.15 (s, 6H, $\text{CH}_3\text{-Si}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 136.14 (ArCH), 135.72 (ArCH), 134.20 (ArCH), 130.00 (ArCH), 127.90 (ArCH), 33.41 (CH_2), 31.98 (CH_2), 29.76 (CH_2), 29.61 (CH_2), 29.42 (CH_2), 23.17 (CH_2), 22.74 (CH_2), 18.15 (CH_2), 14.16 (CH_3), -0.14 ($\text{CH}_3\text{-Si}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CDCl_3): δ 11.82, -14.44 (Si-H). NMR HRMS (ESI) M/Z calcd for $\text{C}_{32}\text{H}_{54}\text{OSi}_2$ ($\text{M}+\text{H}$) $^+$ 511.3786, found: 511.3769.

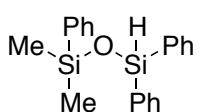
1,1,3-Trimethyl-1-octadecyl-3-phenyldisiloxane (5j): Colourless liquid. Yield: (189 mg, 87%). IR (DCM): 2956, 2911, 2836, 2103, 1590, 1441, 1377, 1344, 1109, 1067, 966, 872 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.60-7.58 (m, 2H, ArCH), 7.43-7.40 (m, 3H, ArCH), 5.11-5.10 (m, 1H, Si-H), 1.29 (s, 32H, CH_2), 0.93-0.89 (t, 3H, $J = 8$ Hz, CH_3), 0.59-0.57 (t, 2H, $J = 8$ Hz, $\text{CH}_2\text{-Si}$), 0.44-0.43 (d, 3H, $J = 4$ Hz, $\text{CH}_3\text{-Si}$), 0.10 (s, 6H, $\text{CH}_3\text{-Si}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 138.03 (ArCH), 133.36 (ArCH), 129.70 (ArCH), 127.84 (ArCH), 33.45 (CH_2), 32.00 (CH_2), 29.78 (CH_2), 29.44 (CH_2), 24.43 (CH_2), 23.22 (CH_2), 22.76 (CH_2), 18.18 (CH_2), 14.16 (CH_2), 0.12 (CH_3), -0.21 ($\text{CH}_3\text{-Si}$), -4.39 ($\text{CH}_3\text{-Si}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CDCl_3): δ 11.83, -14.43 (Si-H). HRMS (ESI) M/Z calcd for $\text{C}_{27}\text{H}_{52}\text{OSi}_2$ ($\text{M}+\text{H}$) $^+$ 449.3629, found: 449.3614.

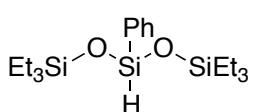
1,1,3-Trimethyl-1,3-diphenyldisiloxane (5k):⁷ Colourless liquid. Yield: (109 mg, 80%). IR (DCM): 2966, 2869, 2144, 1853, 1821, 1609, 1603, 1588, 1561, 1118, 707 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.54 (m, 4H, ArCH), 7.40-7.29 (m, 6H, ArCH), 0.35-0.32 (m,

9H, CH_3 -Si). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 139.48 (ArCH),

 137.90 (ArCH), 133.29 (ArCH), 133.08 (ArCH), 129.58 (Ar-CH),
 129.31 (ArCH), 127.71 (ArCH), 127.67 (ArCH), 0.75 (CH_3 -Si), 0.72
 (CH_3 -Si), 0.03 (CH_3 -Si). HRMS (ESI) M/Z calcd for $C_{15}H_{20}OSi_2$ ($M+Na$)⁺ 295.0950, found: 295.2133.

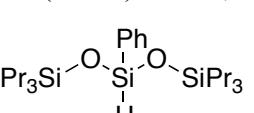
1,1-Dimethyl-1,3,3-triphenylsiloxyane (5l):⁷ Colourless liquid. Yield: (136 mg, 82%). IR (DCM): 2983, 2821, 1834, 1809, 1653, 1641, 1575, 1553, 1270, 1188, 987, 847 cm^{-1} . 1H NMR


 (400 MHz, $CDCl_3$): δ 7.66-7.61 (m, 6H, ArCH), 7.48-7.40 (m, 9H, ArCH), 5.62 (s, 1H, Si-H), 0.44 (s, 6H, Si- CH_3). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 139.11 (ArCH), 135.74 (ArCH), 134.30 (ArCH), 133.13 (ArCH), 130.14 (ArCH), 129.49 (ArCH), 127.98 (ArCH), 127.82 (ArCH), 0.62 (CH_3 -Si).

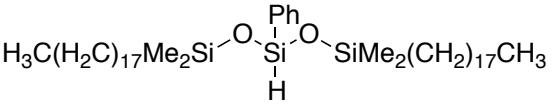
1,1,1,5,5,5-Hexaethyl-3-phenyltrisiloxane (5m):⁷ Colourless liquid. Yield: (161 mg, 87%). IR (DCM): 2955, 2912, 2877, 2146, 1369, 1459, 1429, 1238, 1124, 1067, 1004, 873, 853 cm^{-1} .


 1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H, ArCH), 7.43-7.37 (m, 3H, ArCH), 5.07 (s, 1H, Si-H), 0.98-0.94 (t, 18H, J = 8 Hz, CH_3), 0.63-0.57 (q, 12H, J = 8 Hz, CH_2 -Si). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 137.45 (Ar-CH), 133.03 (Ar-CH), 129.92 (Ar-CH), 127.71 (Ar-CH), 6.69 (CH_3), 6.12 (CH_2 -Si).

3-Phenyl-1,1,1,5,5,5-hexapropyltrisiloxane (5n):⁷ Colourless liquid. Yield: (190 mg, 82%).

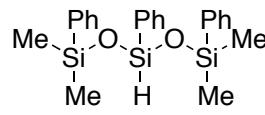
IR (DCM): 2955, 2926, 1518, 1462, 1408, 1102, 1055, 706 cm^{-1} . 1H NMR (400 MHz, 
 $CDCl_3$): δ 7.585-7.566 (m, 2H, ArCH), 7.431-7.377 (m, 3H, ArCH), 5.018-5.015 (d, 1H, J = 12 Hz, Si-H), 1.400-1.343 (m, 12H, CH_2), 0.954-0.951 (m, 18H, CH_3), 0.608-0.563 (m, 12H, CH_2 -Si). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 137.46 (ArCH), 133.01 (ArCH), 129.85 (ArCH), 127.66 (ArCH), 18.32 (CH_2), 18.19 (CH_3), 16.67 (CH_2 -Si).

1,1,5,5-Tetramethyl-1,5-dioctadecyl-3-phenyltrisiloxane (5o): Colourless liquid. Yield: (330 mg, 75%). IR (DCM): 2955, 2929, 2852, 2154, 2111, 1638, 1466, 1430, 1377, 1251,


 $1125, 1061, 886 \text{ } cm^{-1}$. 1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 2H, ArCH), 7.43-7.37 (m, 3H, ArCH), 4.99 (s, 1H, Si-H), 1.28 (s, 64H, CH_2), 0.92-0.89 (t, 6H, J = 8 Hz, CH_3), 0.60-0.57 (m, 4H, CH_2 -Si), 0.12-0.08 (m, 12H,

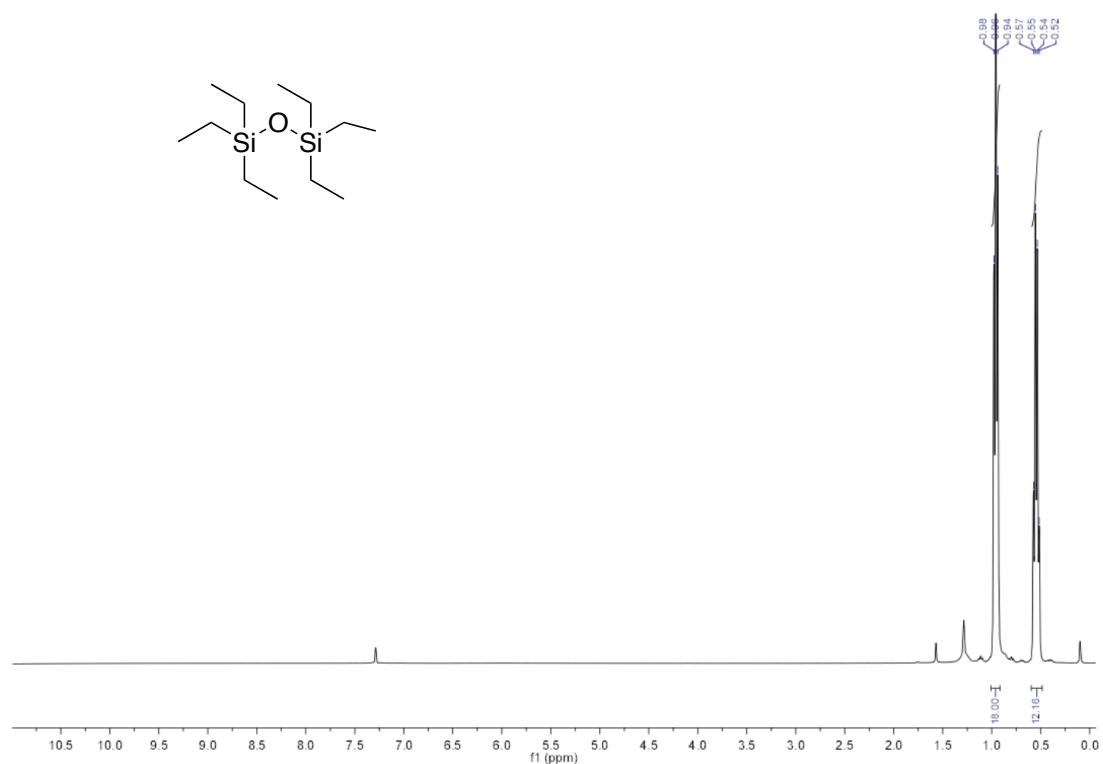
CH_3 -Si). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 137.21 (ArCH), 133.12 (ArCH), 129.95 (ArCH), 127.73 (ArCH), 33.48 (CH_2), 33.27 (CH_2), 31.98 (CH_2), 29.77 (CH_2), 29.66 (CH_2), 29.43 (CH_2), 24.42 (CH_2), 23.18 (CH_2), 22.74 (CH_2), 18.22 (CH_2), 14.14 (CH_3), 0.16 (CH_2 -Si), -4.41 (CH_3 -Si). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$): δ 11.47, -49.00 (Si-*H*). HRMS (ESI) M/Z calcd for $C_{46}H_{92}O_2Si_3$ ($M+H$) $^+$ 761.6483, found: 761.6489.

1,1,5,5-Tetramethyl-1,3,5-triphenyltrisiloxane (5p): Colourless liquid. Yield: (199 mg, 84%). IR (DCM): 3070, 2959, 2152, 1638, 1428, 1302, 1190, 1121, 1075, 998, 883, 998, 861 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.56 (m, 6H, ArCH), 7.44-7.34 (m, 9H, ArCH), 5.14 (s, 1H, Si-*H*), 0.38 (s, 12H, CH_3 -Si). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 139.05 (ArCH), 136.44 (ArCH), 133.07 (ArCH), 130.17 (ArCH), 129.42 (ArCH), 127.82 (ArCH), 127.76 (ArCH), 0.59 (CH_3 -Si), 0.57 (CH_3 -Si). HRMS (ESI) M/Z calcd for $C_{22}H_{28}OSi_3$ ($M+Na$) $^+$ 431.1289, found: 431.1305.

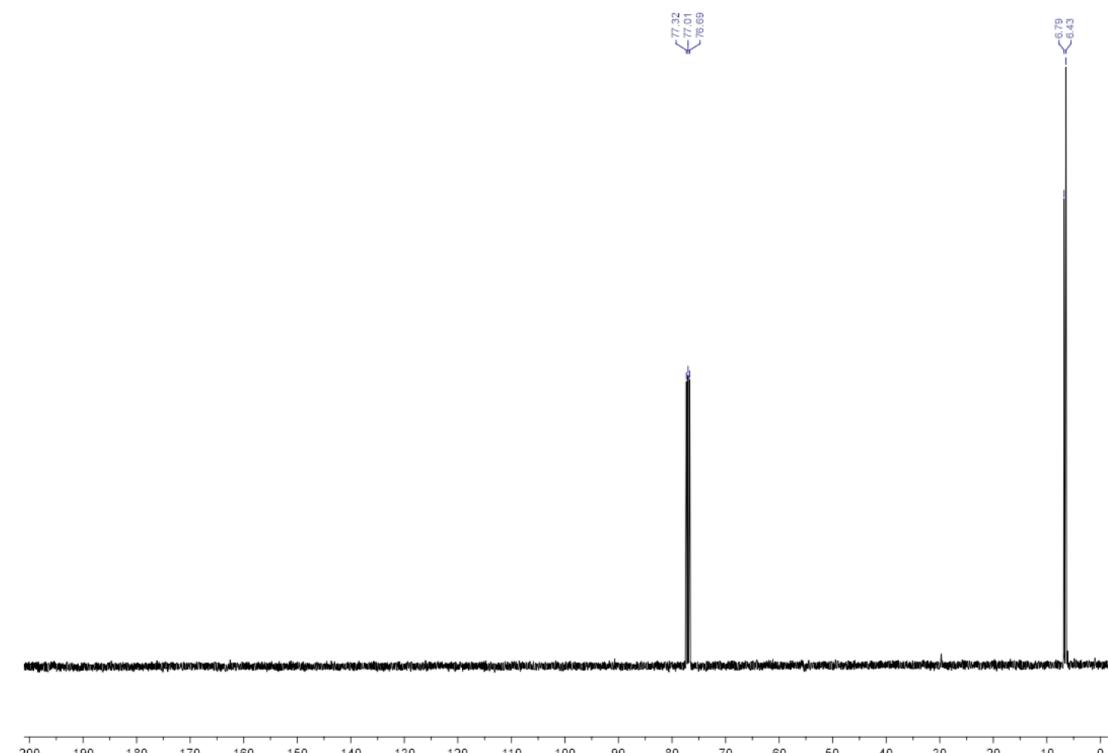


NMR Spectra for Symmetrical Siloxane :

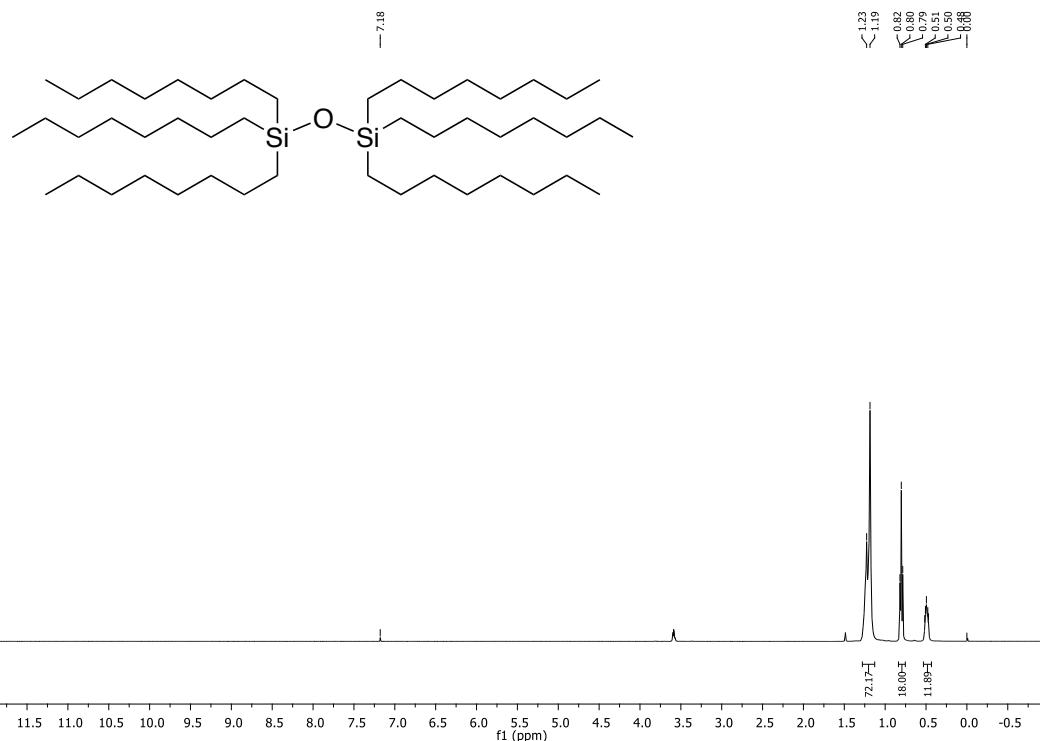
^1H NMR spectrum of 1,1,1,3,3,3-hexaethyldisiloxane (400 MHz, CDCl_3)



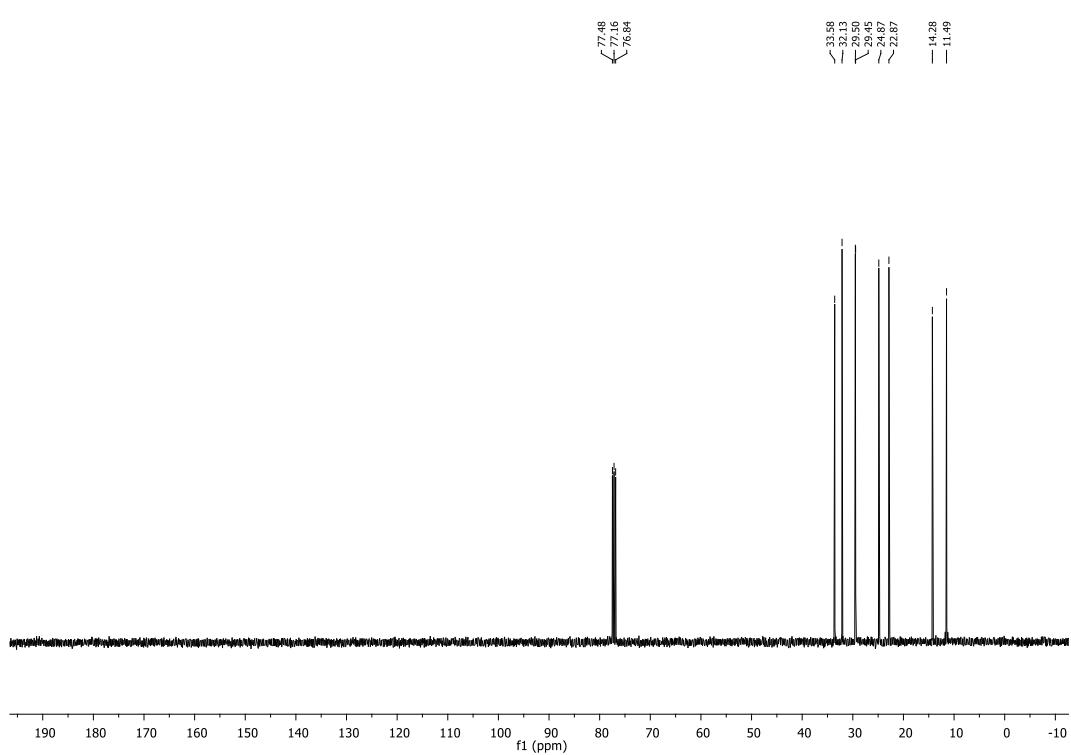
^{13}C NMR spectrum of 1,1,1,3,3,3-hexaethyldisiloxane (100.6 MHz, CDCl_3)



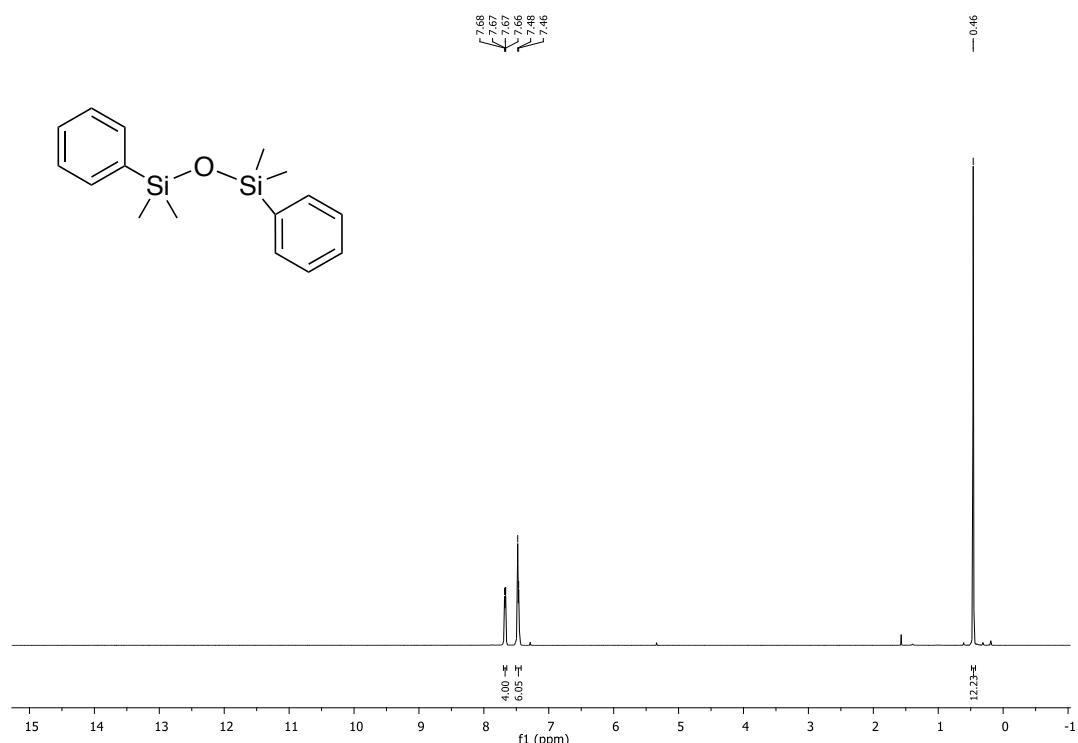
¹H NMR spectrum of 1,1,1,3,3,3-hexaoctyldisiloxane (400 MHz, CDCl₃)



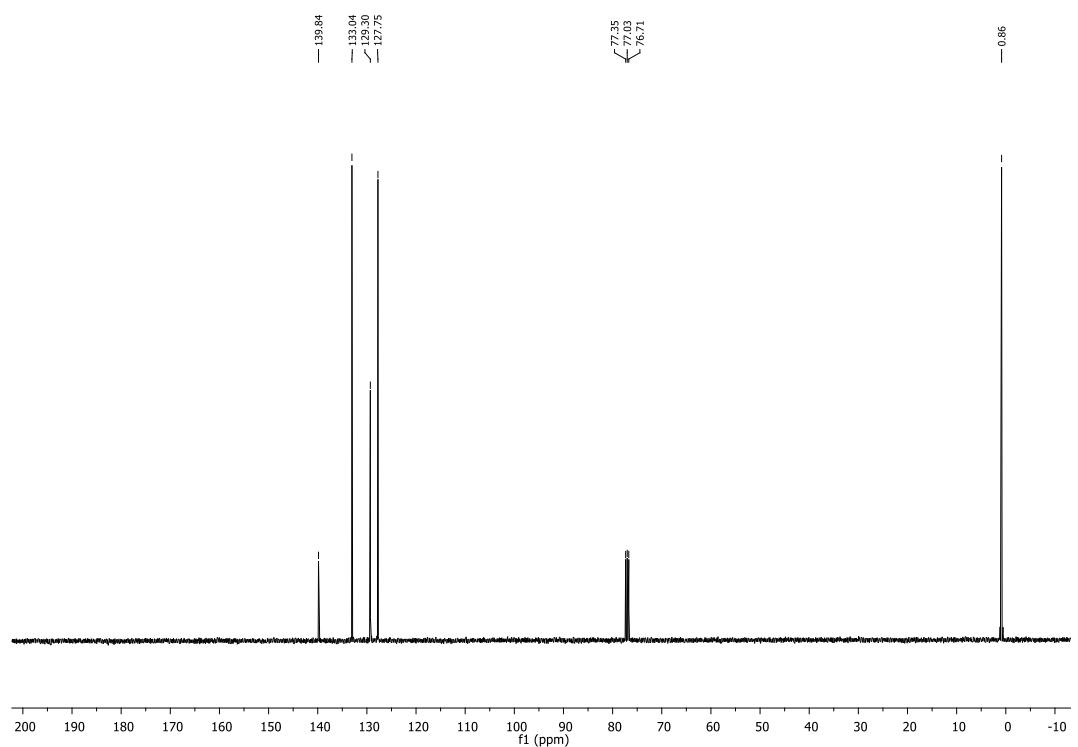
¹³C NMR spectrum of 1,1,1,3,3,3-hexaoctyldisiloxane (100.6 MHz, CDCl₃)



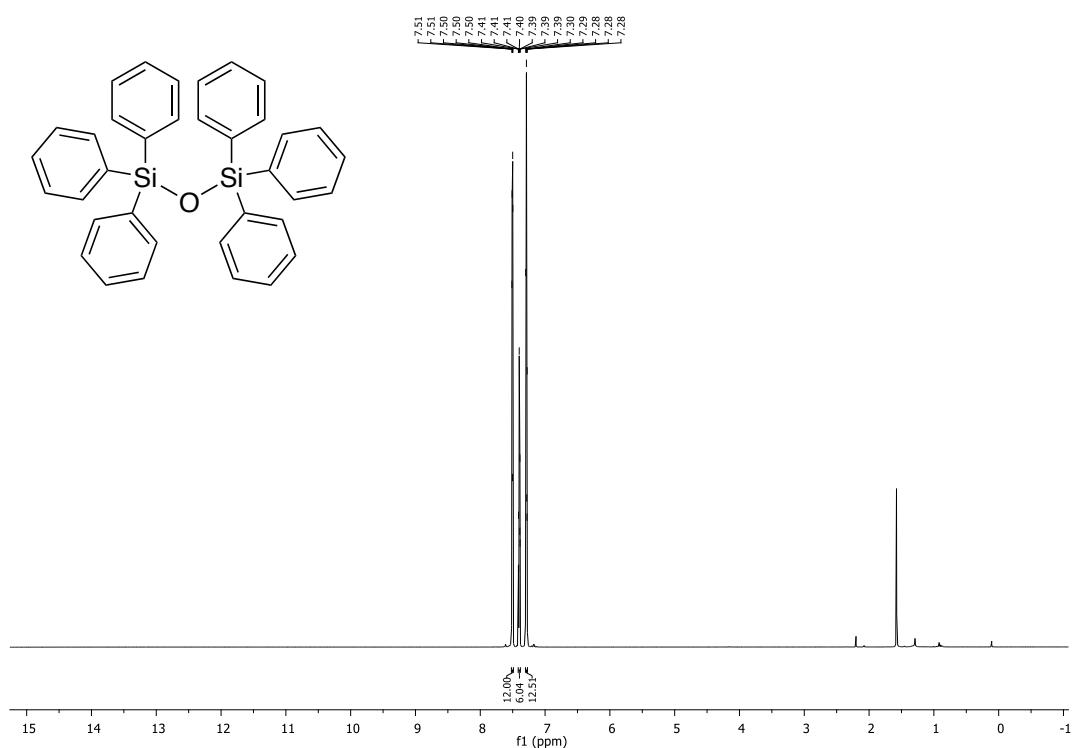
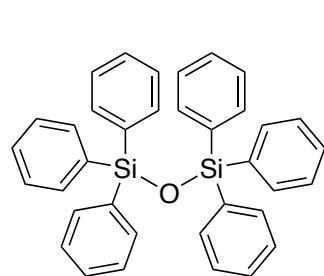
^1H NMR spectrum of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (400 MHz, CDCl_3)



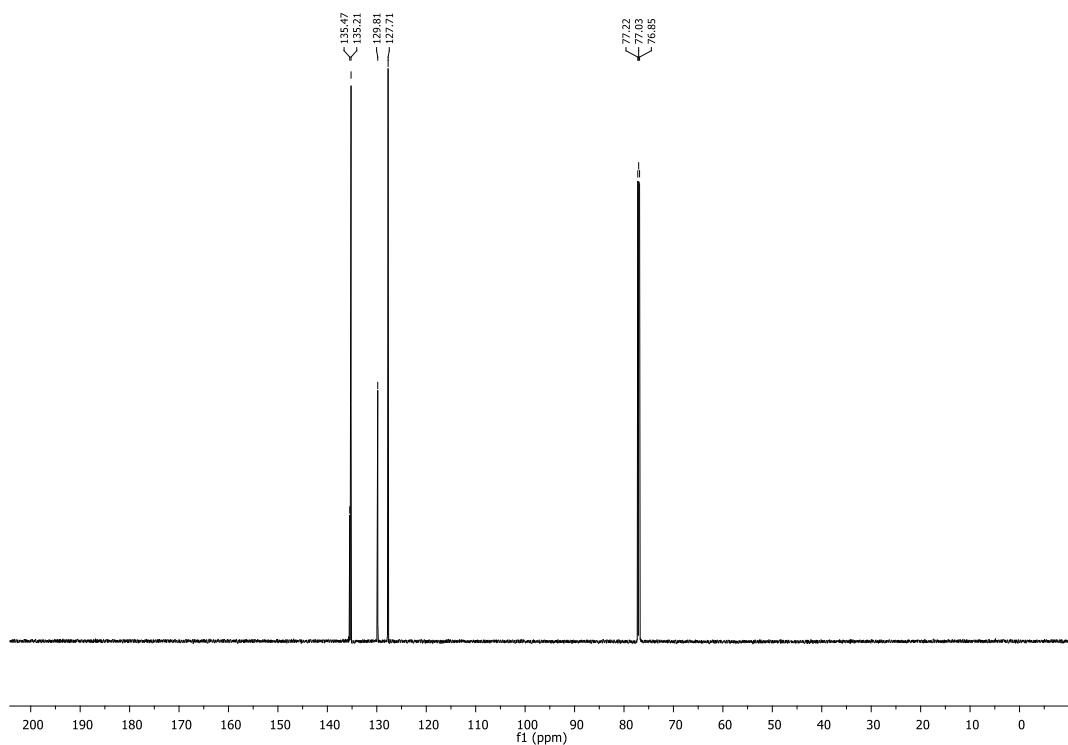
^{13}C NMR spectrum of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (100.6 MHz, CDCl_3)



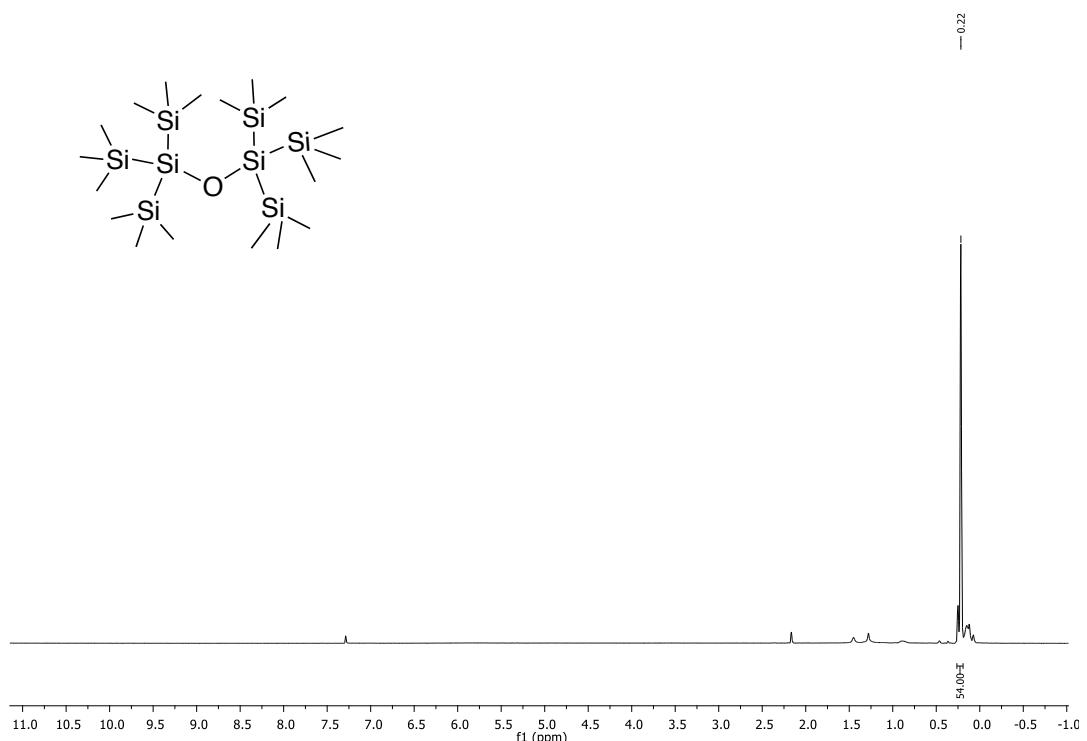
¹H NMR spectrum of 1,1,1,3,3,3-hexaphenyldisiloxane (400 MHz, CDCl₃)



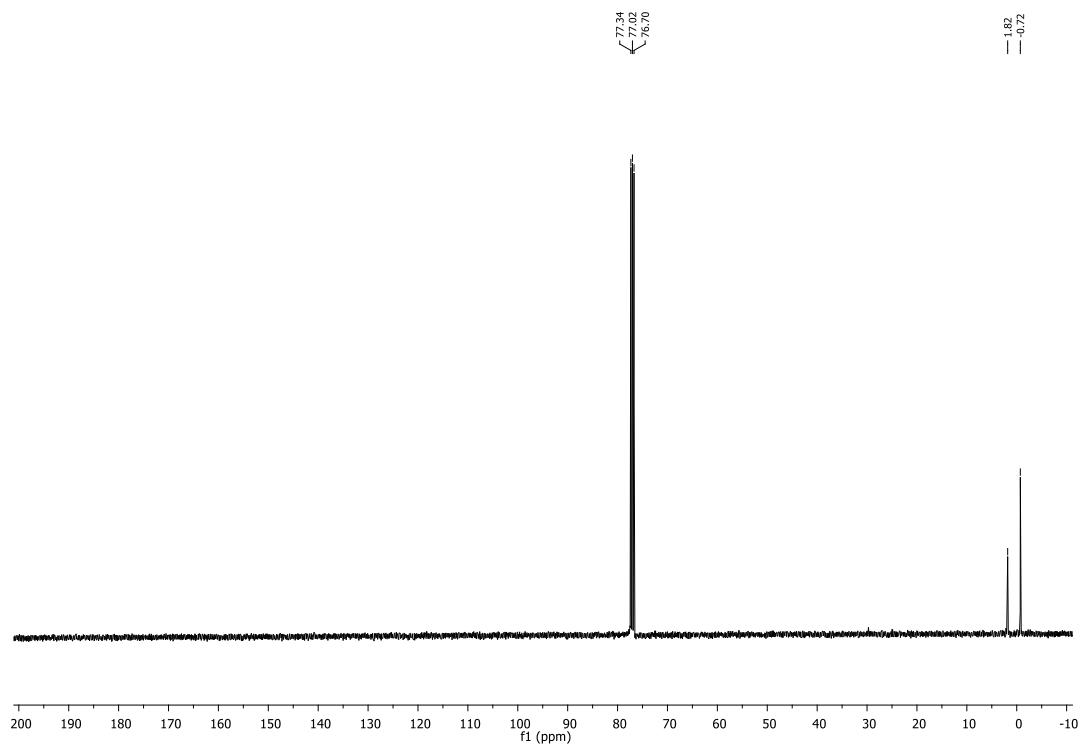
¹³C NMR spectrum of 1,1,1,3,3,3-hexaphenyldisiloxane (100.6 MHz, CDCl₃)



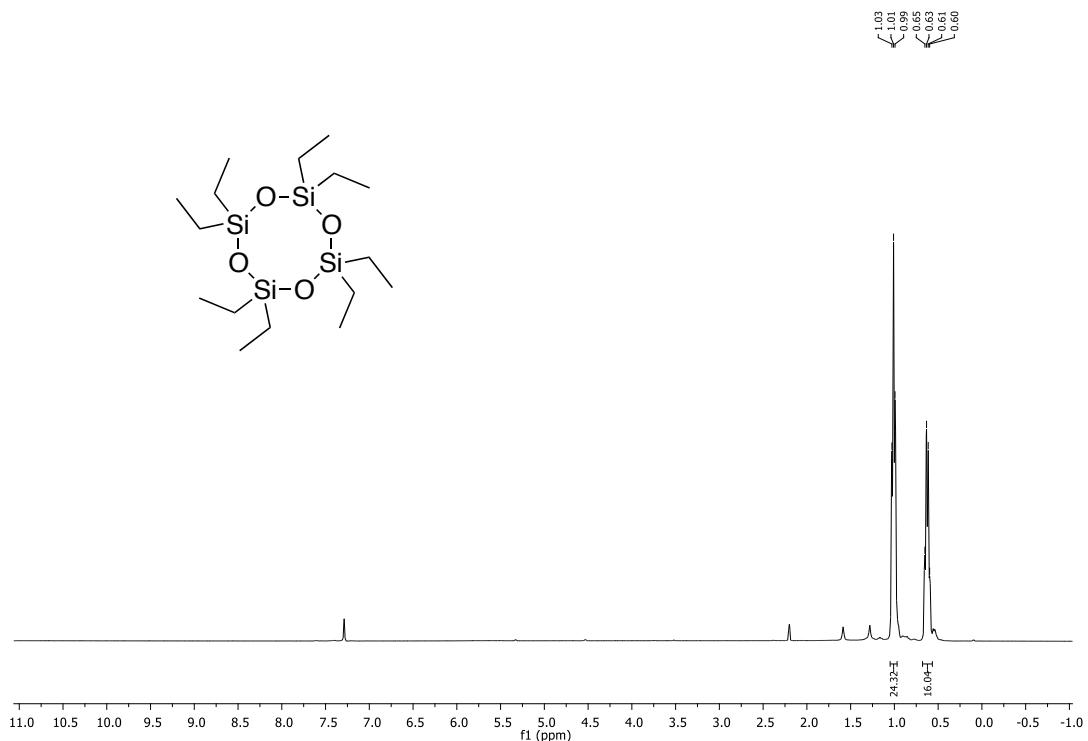
^1H NMR spectrum of 1,1,1,3,3,3- hexakis(trimethylsilyl) disiloxane (400 MHz, CDCl_3)



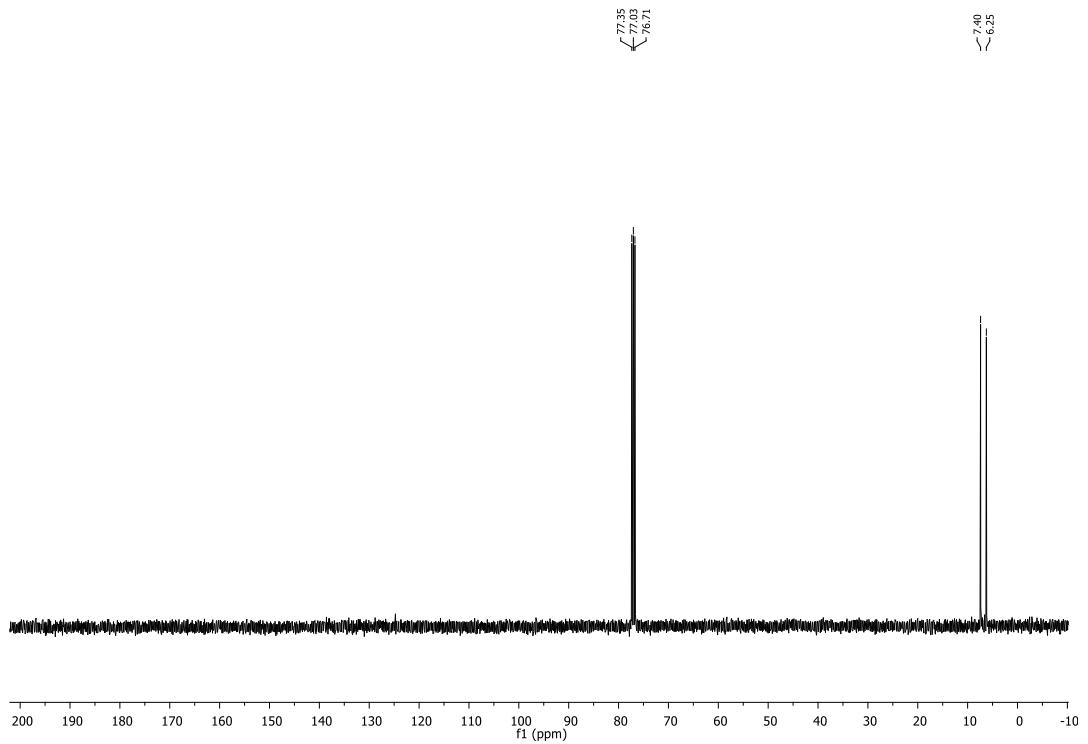
^{13}C NMR spectrum of 1,1,1,3,3,3- hexakis(trimethylsilyl) disiloxane (100.6 MHz, CDCl_3)



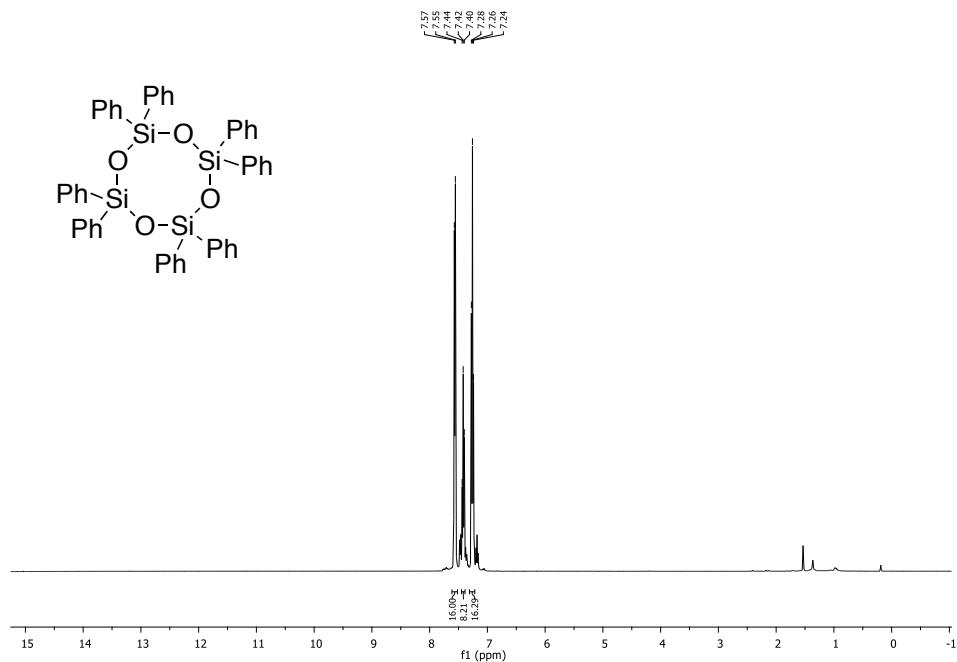
^1H NMR spectrum of 2,2,4,4,6,6,8,8-octaethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilicone: (400 MHz, CDCl_3)



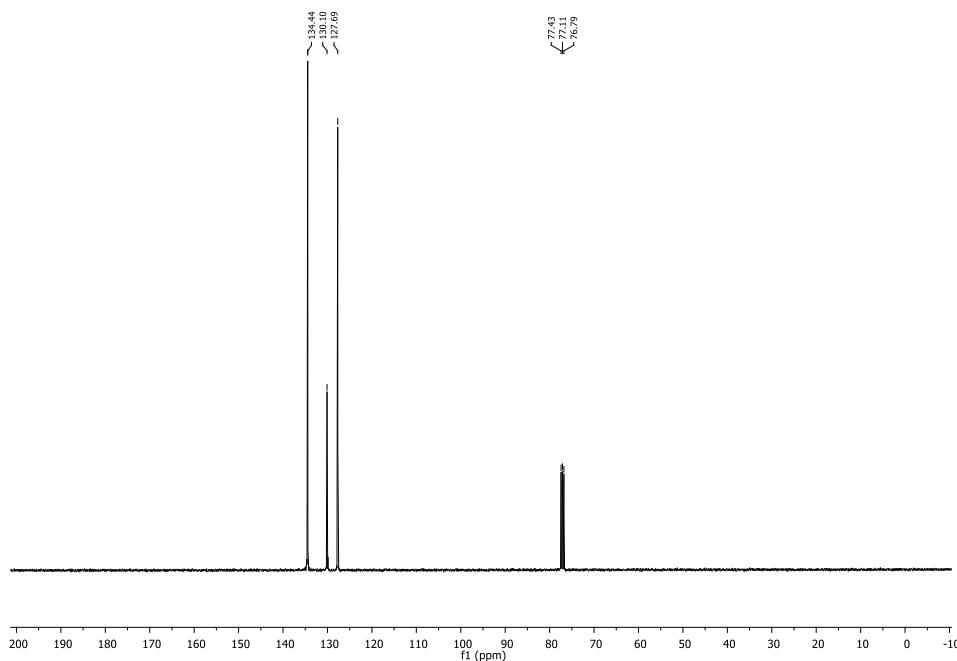
^{13}C NMR spectrum of 2,2,4,4,6,6,8,8-octaethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilicone: (100.6 MHz CDCl_3)



¹H NMR spectrum of 2,2,4,4,6,6,8,8-octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (400 MHz, CDCl₃)

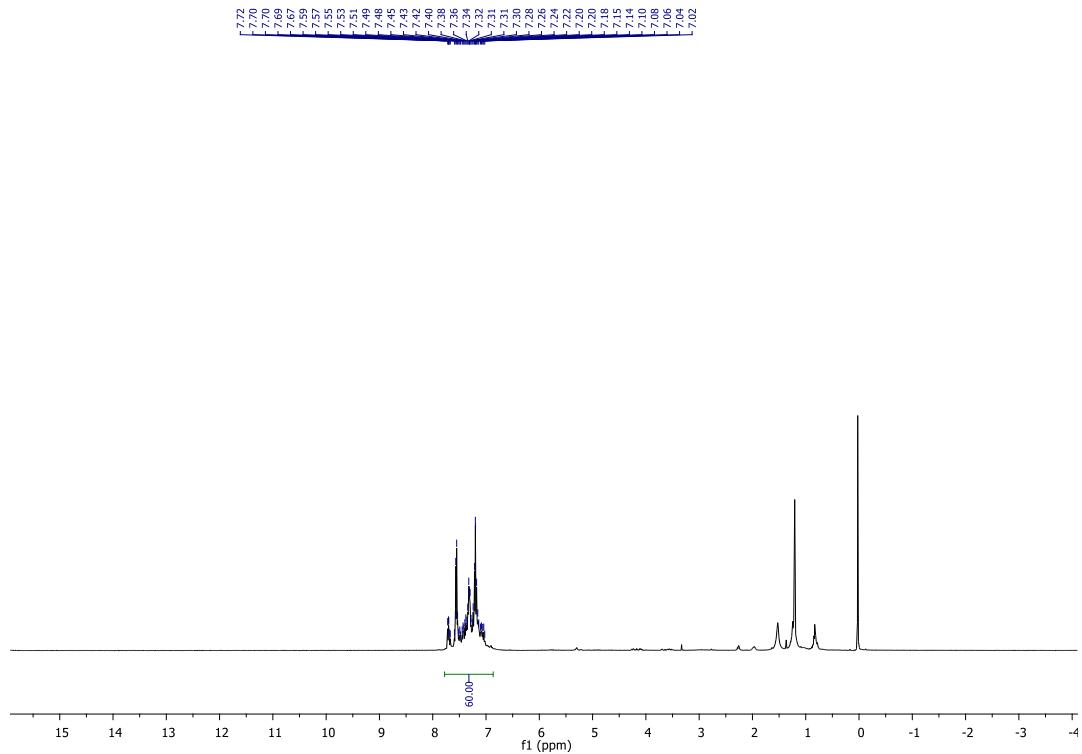


¹³C NMR spectrum of 2,2,4,4,6,6,8,8-octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (100.6 MHz, CDCl₃)

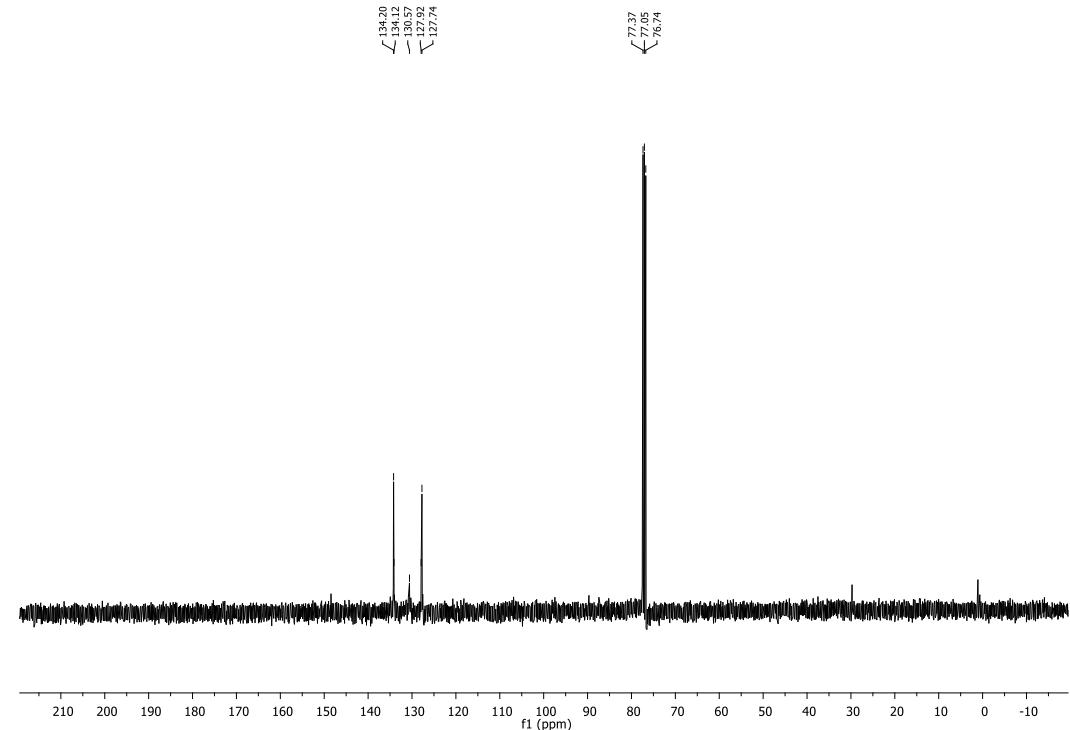


NMR Spectra for Macroyclic Siloxane Cage 4:

^1H NMR spectrum of macrocyclic siloxane cage 4 (400 MHz, CDCl_3)

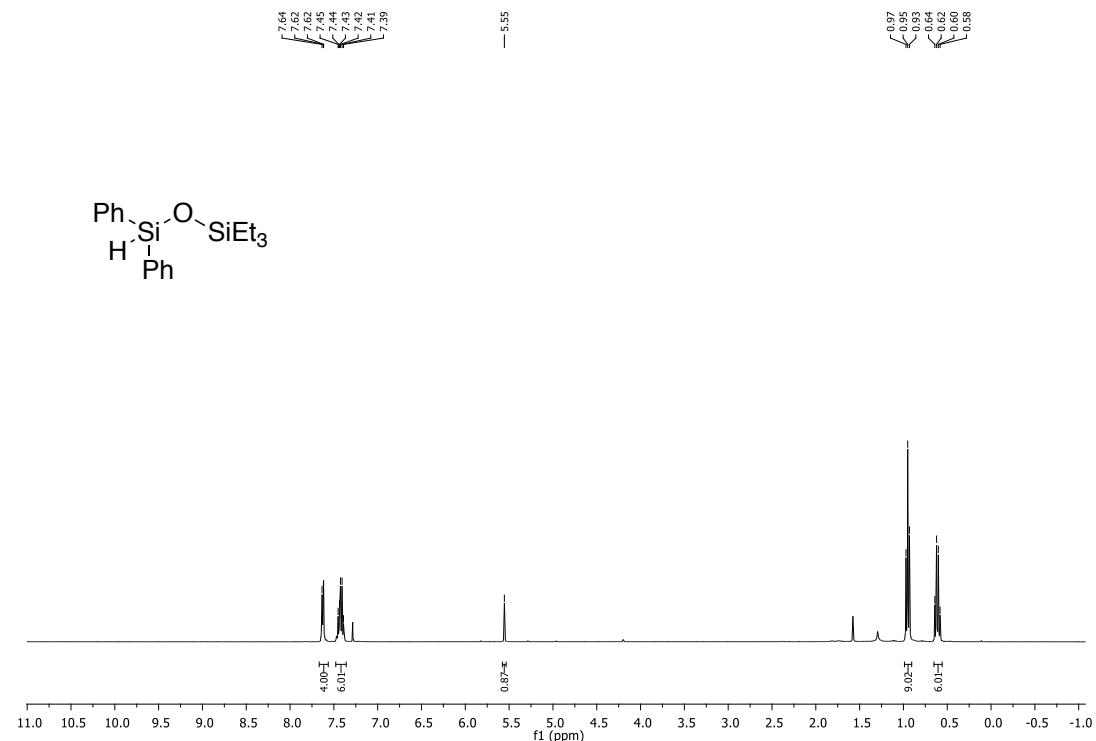


^{13}C NMR spectrum of macrocyclic siloxane cage 4 (100.6 MHz, CDCl_3)

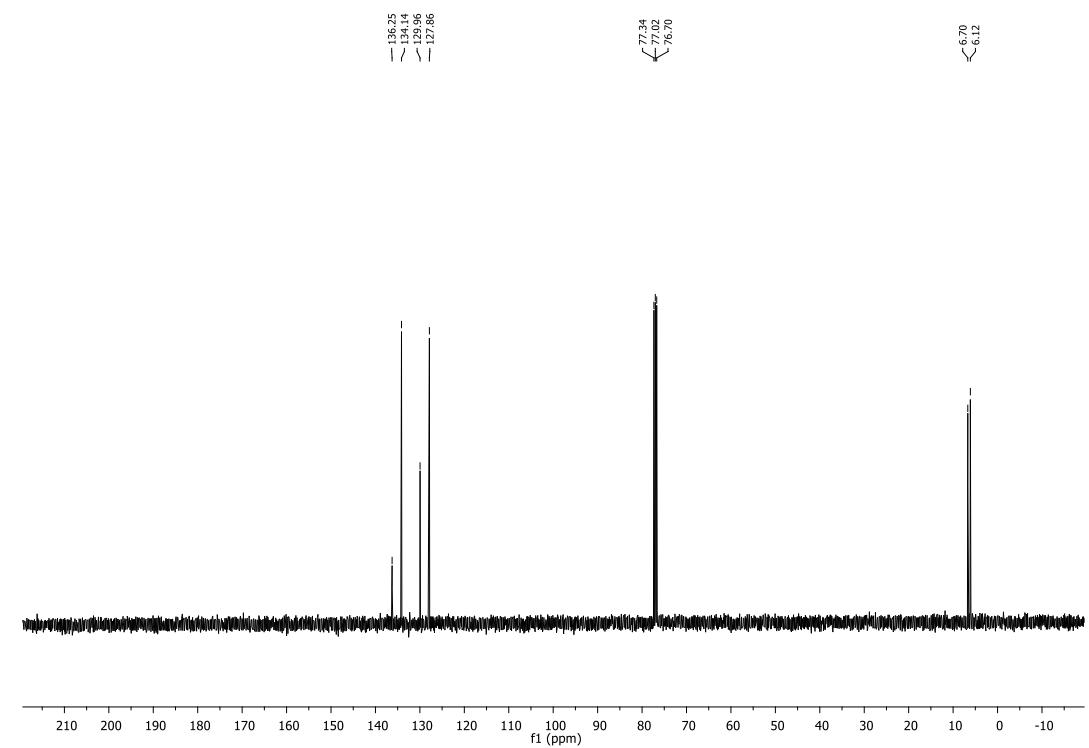


NMR Spectra for Unsymmetrical Siloxanes:

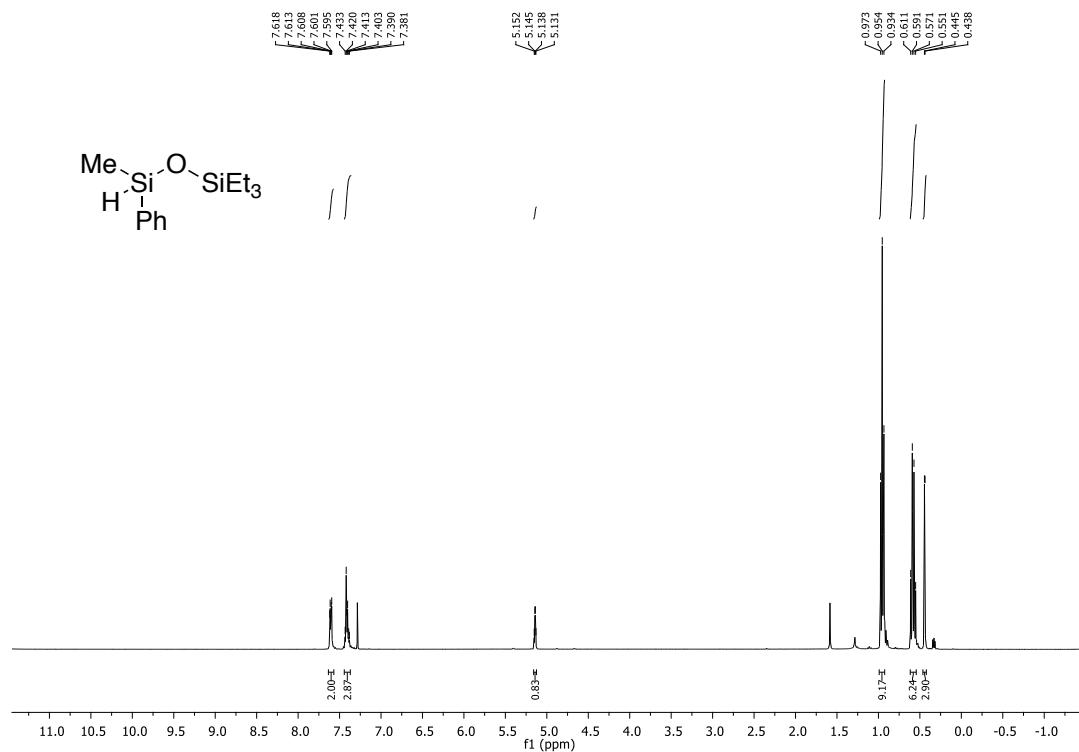
^1H NMR spectrum of 1,1,1-triethyl-3,3-diphenyldisiloxane (400 MHz, CDCl_3)



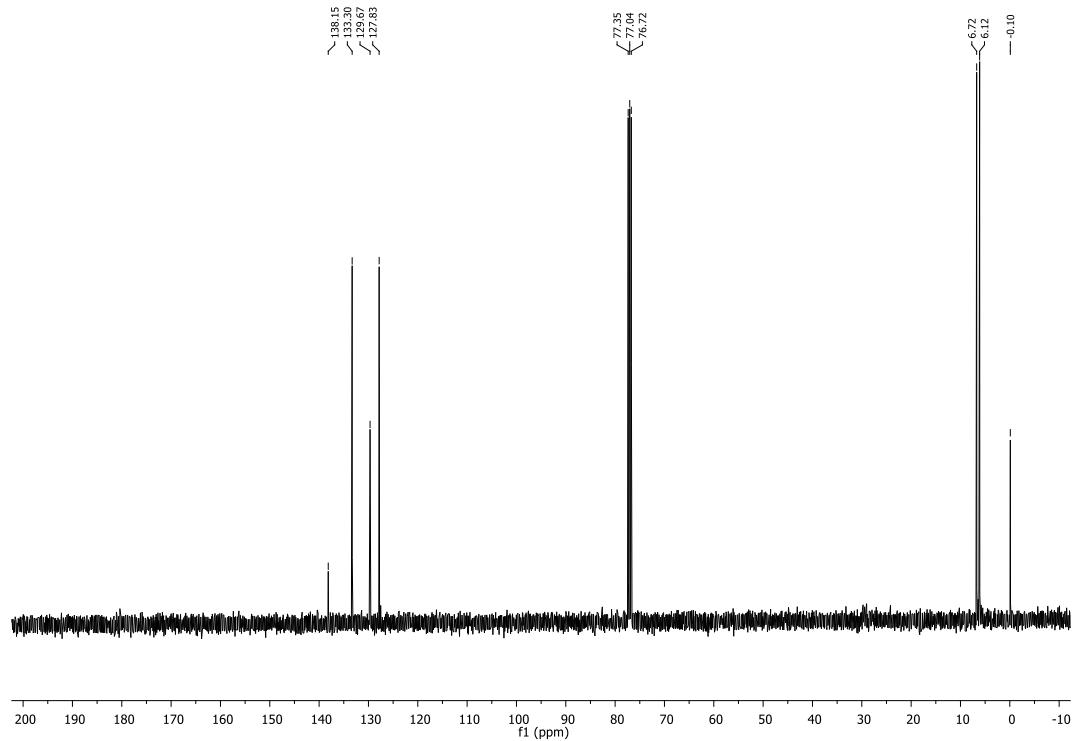
^{13}C NMR spectrum of 1,1,1-triethyl-3,3-diphenyldisiloxane (100.6 MHz, CDCl_3)



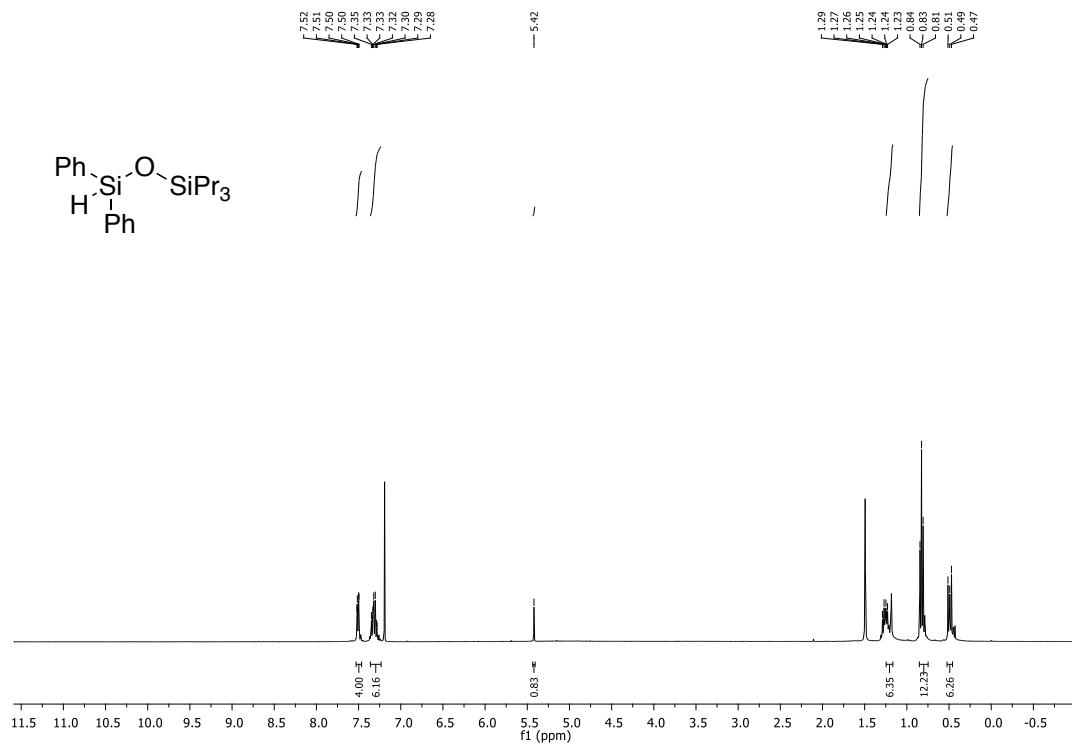
¹H NMR spectrum of 1,1,1-triethyl-3-methyl-3-phenyldisiloxane (400 MHz, CDCl₃)



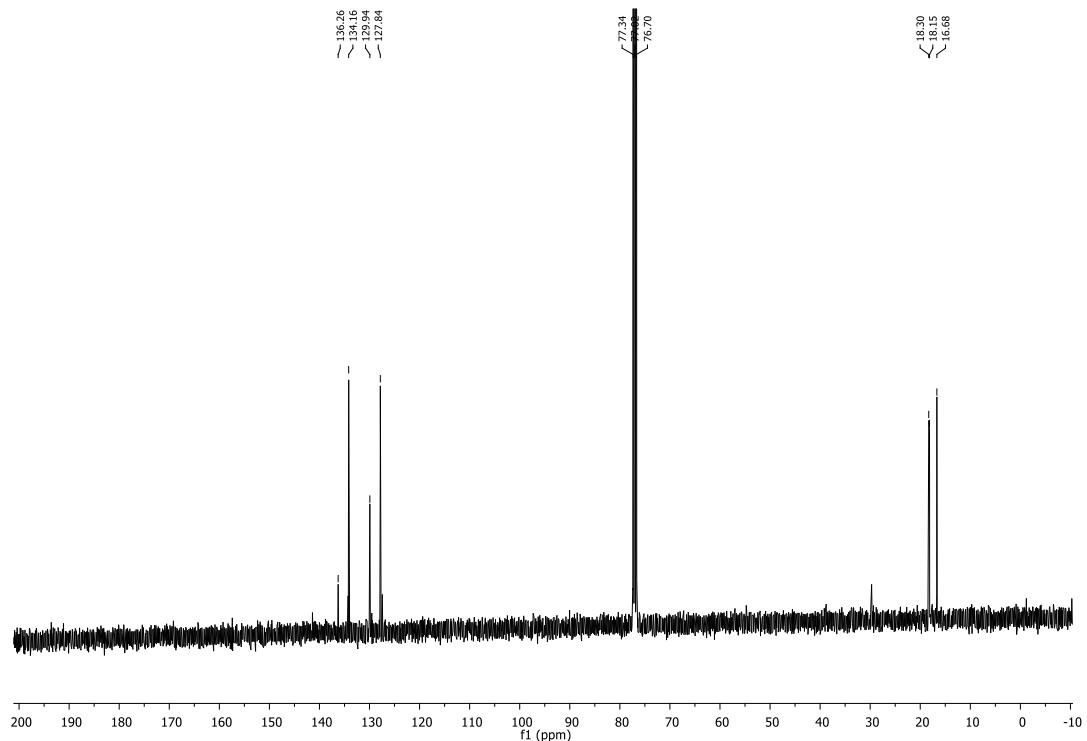
¹³C NMR spectrum of 1,1,1-triethyl-3-methyl-3-phenyldisiloxane (100.6 MHz, CDCl₃)



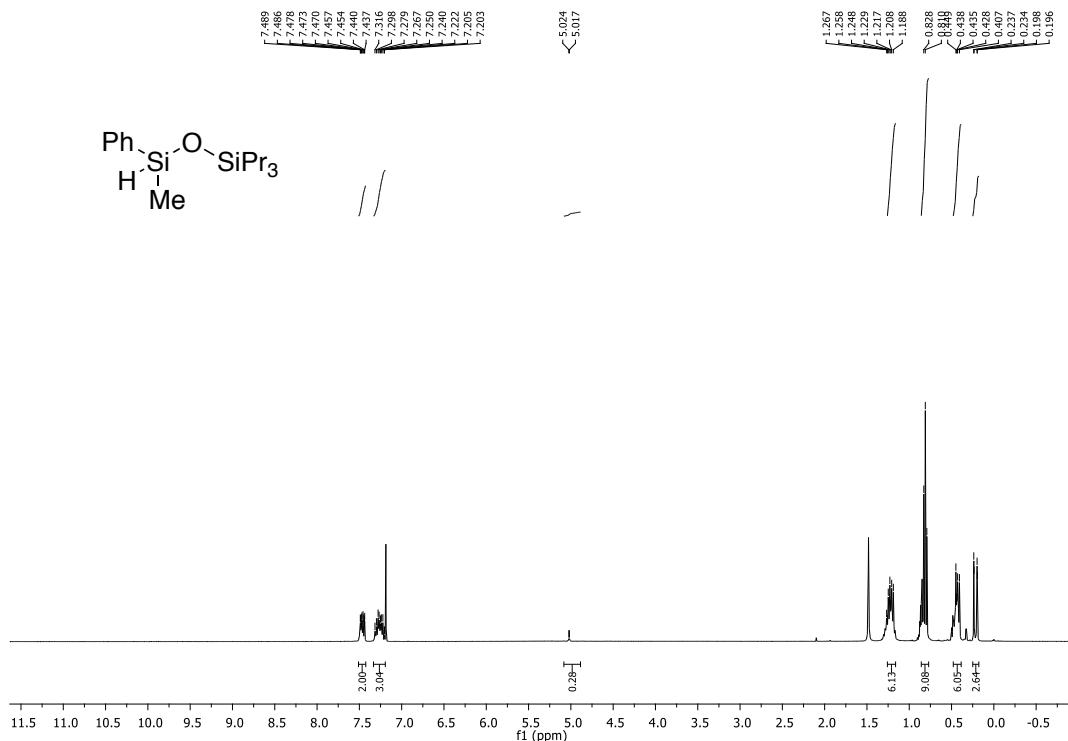
^1H NMR spectrum of 3,3-diphenyl-1,1,1-tripropylsiloxyane (400 MHz, CDCl_3)



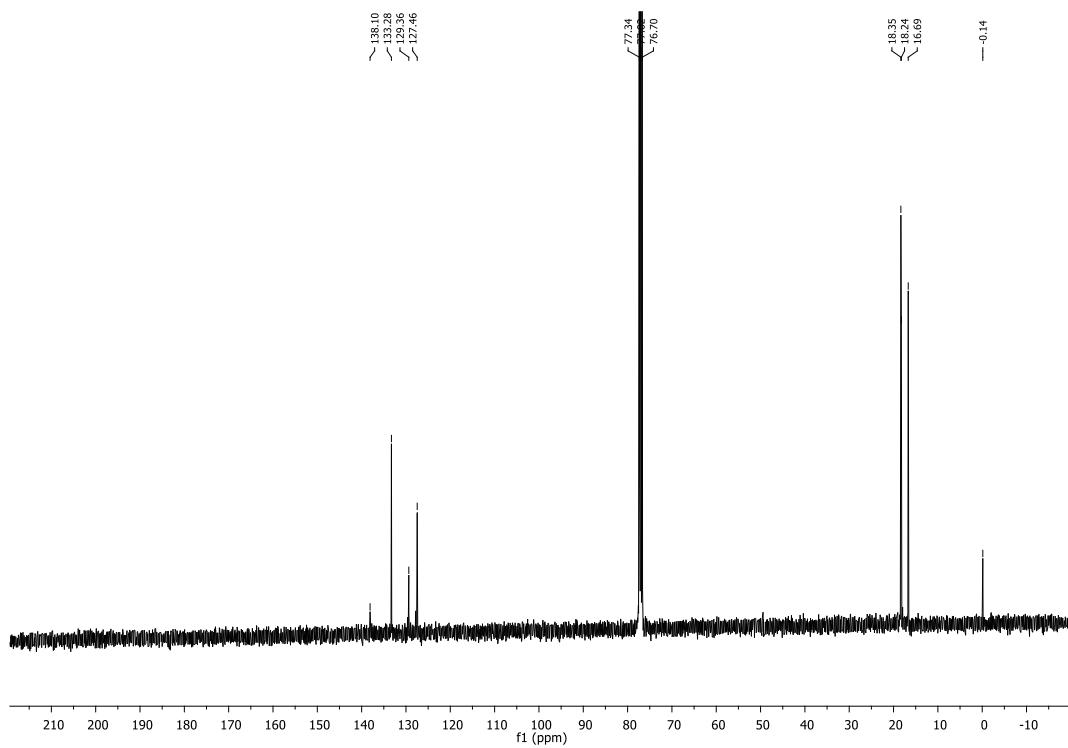
^{13}C NMR spectrum of 3,3-diphenyl-1,1,1-tripropylsiloxyane (100.6 MHz, CDCl_3)



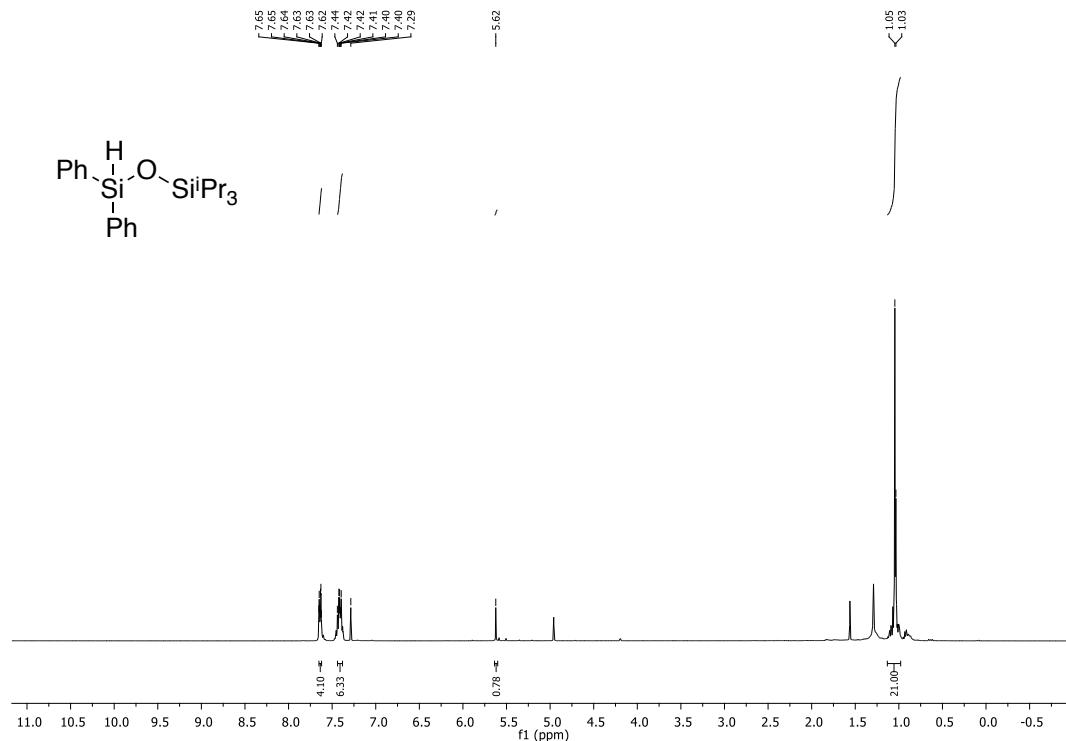
^1H NMR spectrum of 3-methyl-3-phenyl-1,1,1-tripropylsiloxane (400 MHz, CDCl_3)



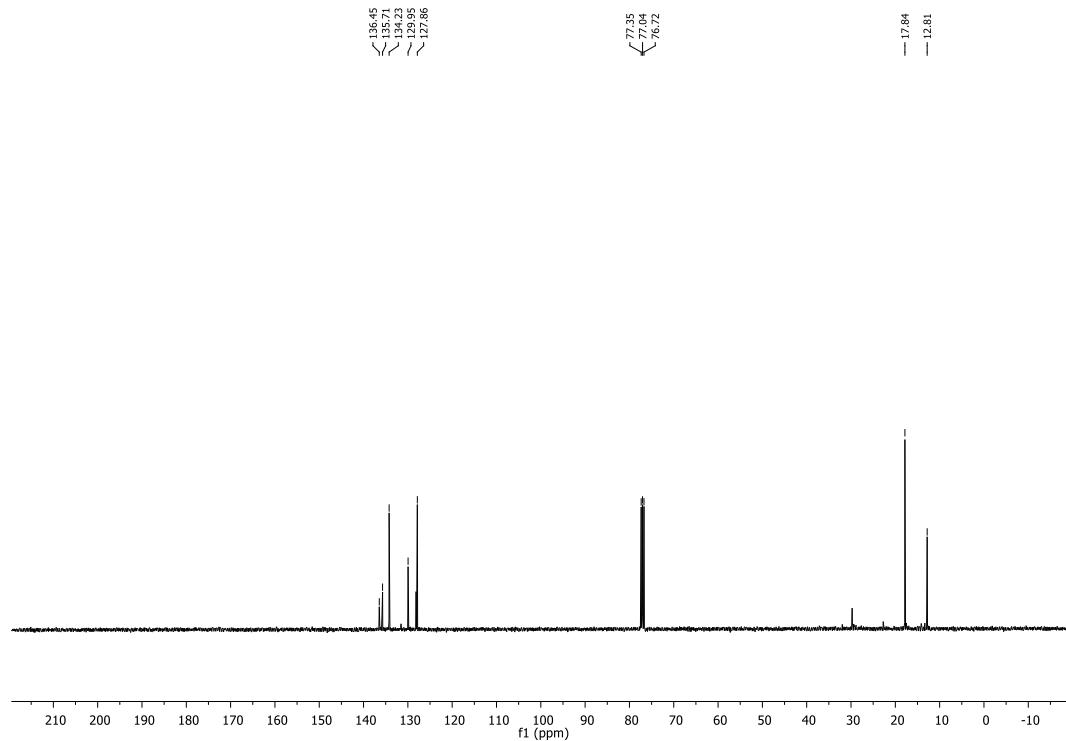
^{13}C NMR spectrum of 3-methyl-3-phenyl-1,1,1-tripropylsiloxane (100.6 MHz, CDCl_3)



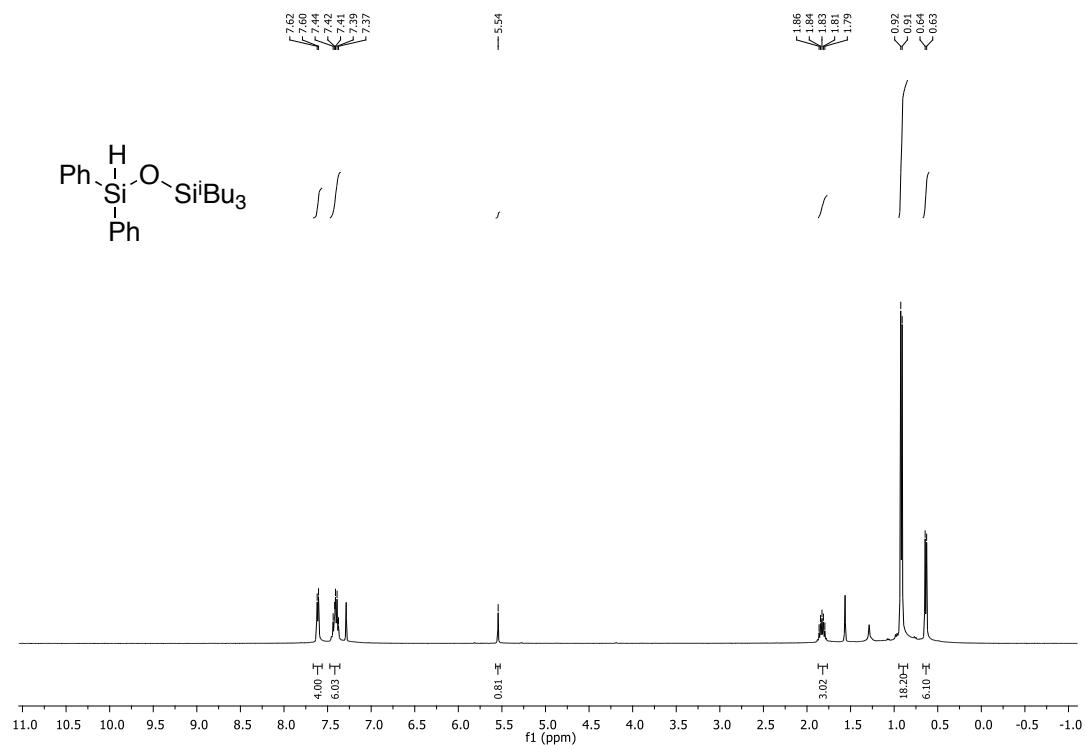
¹H NMR spectrum of 1,1,1-triisopropyl-3,3-diphenylsiloxyane (400 MHz, CDCl₃)



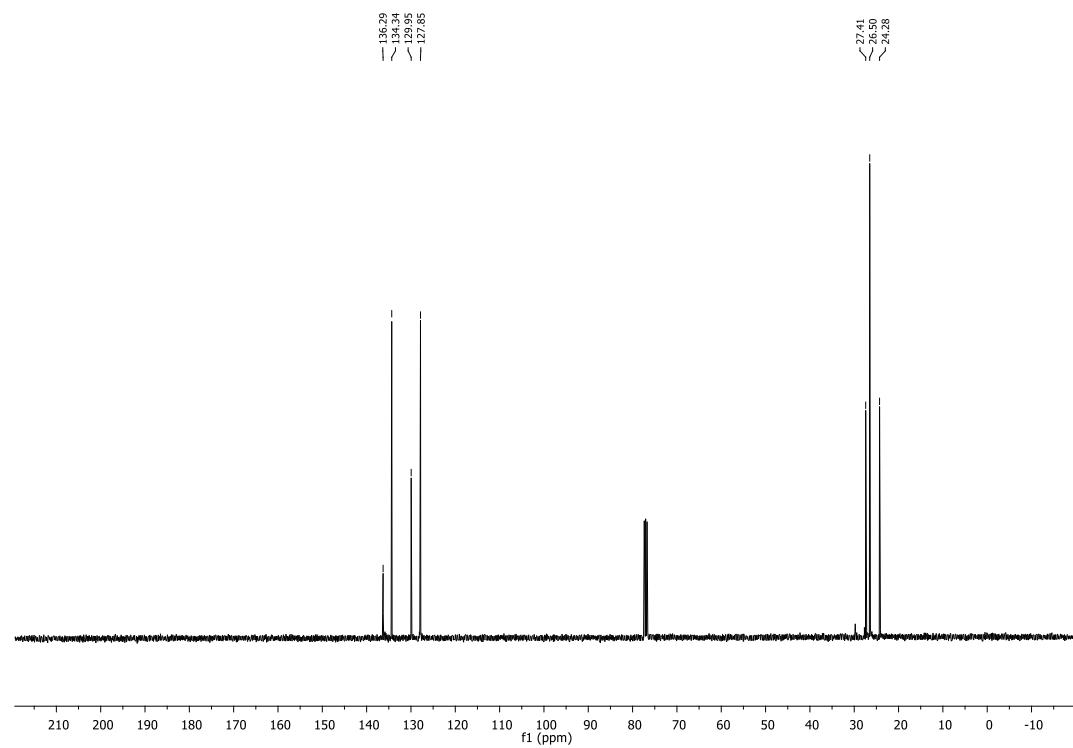
¹³C NMR spectrum of 1,1,1-triisopropyl-3,3-diphenylsiloxyane (100.6 MHz, CDCl₃)



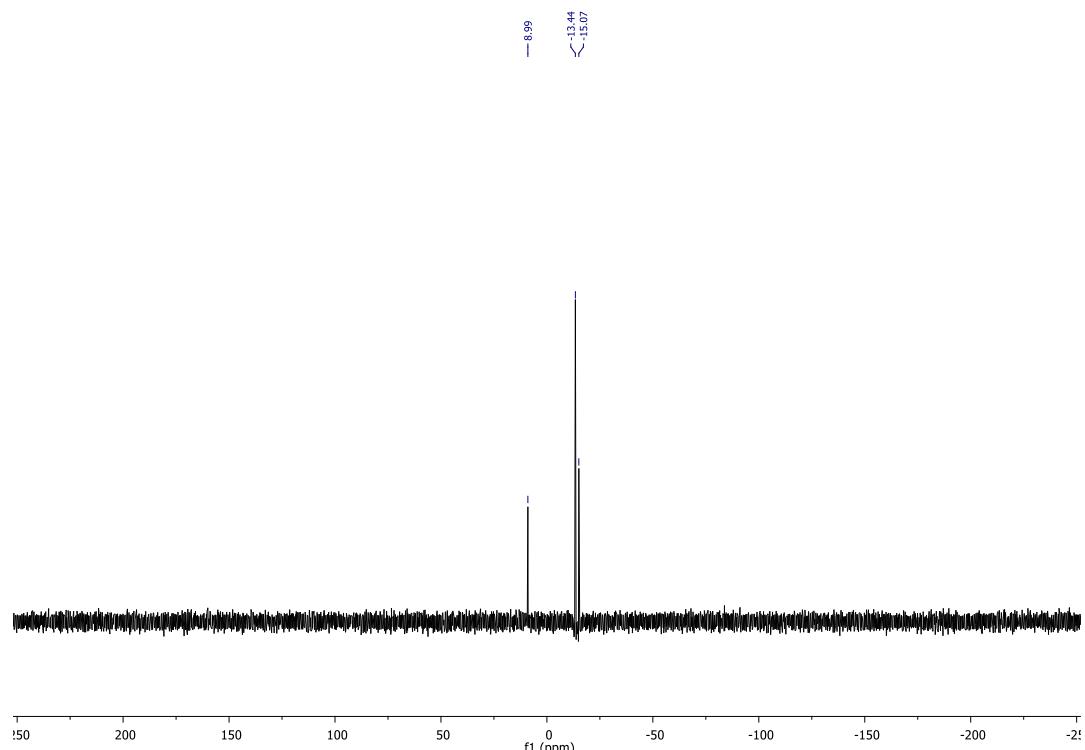
¹H NMR spectrum of 1,1,1-triisobutyl-3,3-diphenylsiloxyne (400 MHz, CDCl₃)



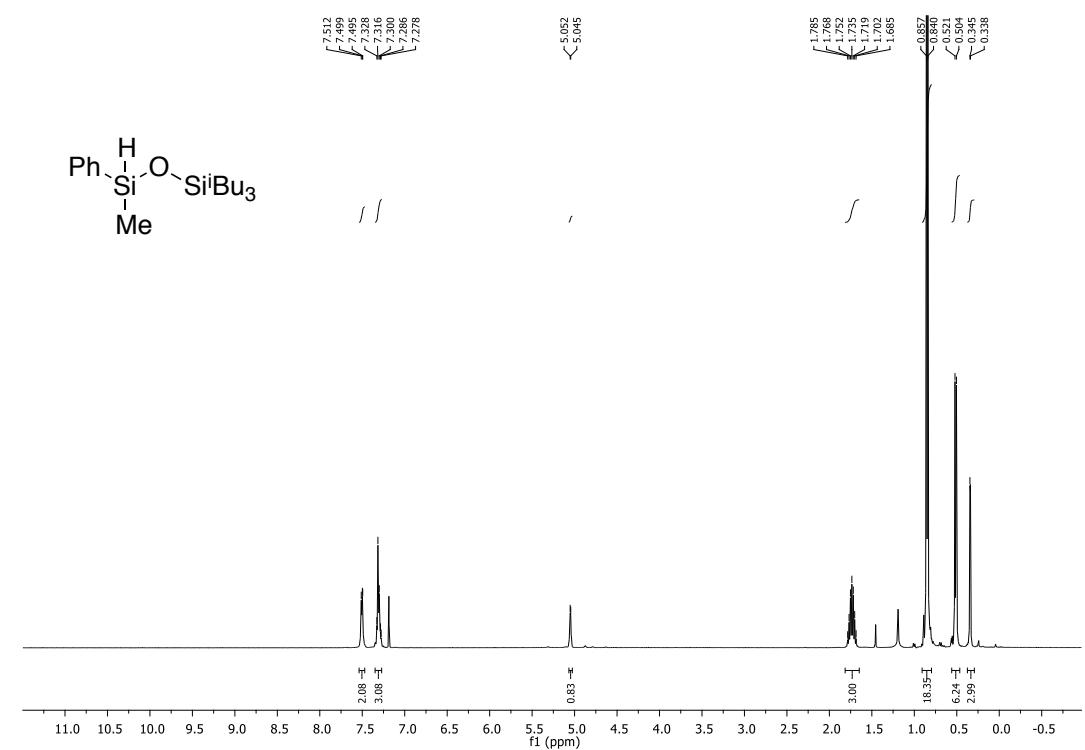
¹³C NMR spectrum of 1,1,1-triisobutyl-3,3-diphenylsiloxyne (100.6 MHz, CDCl₃)



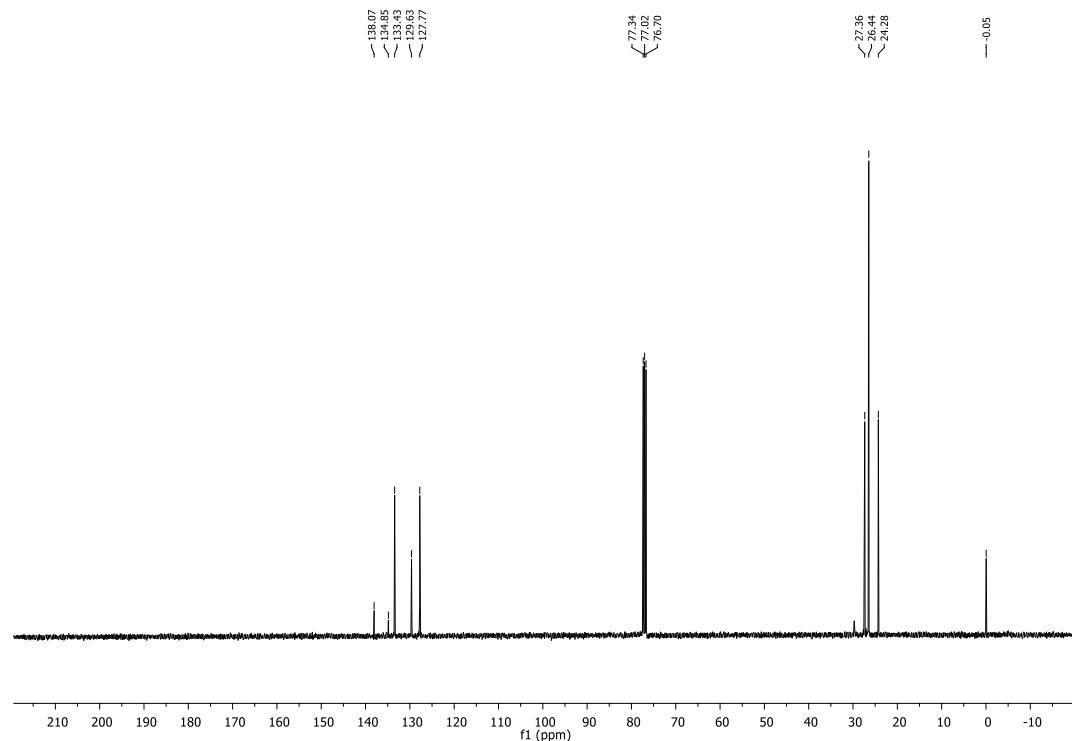
²⁹Si NMR spectrum of 1,1,1-triisobutyl-3,3-diphenylsiloxane (79 MHz, CDCl₃)



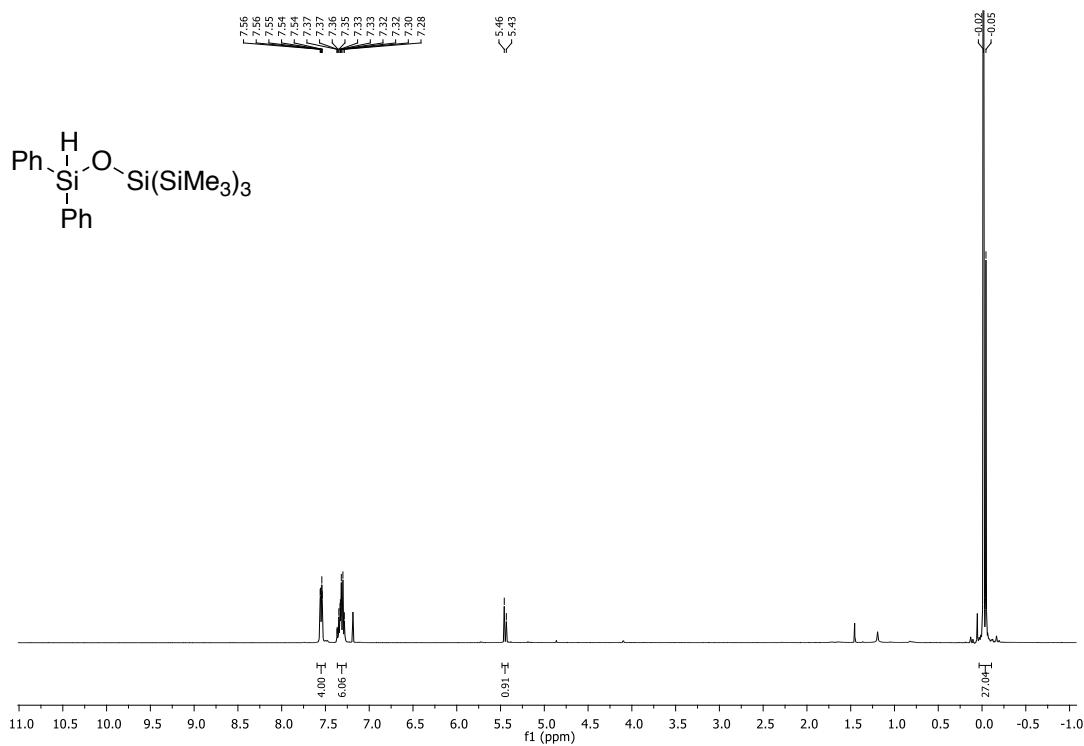
¹H NMR spectrum of 1,1,1-triisobutyl-3-methyl-3-phenyldisiloxane (400 MHz, CDCl₃)



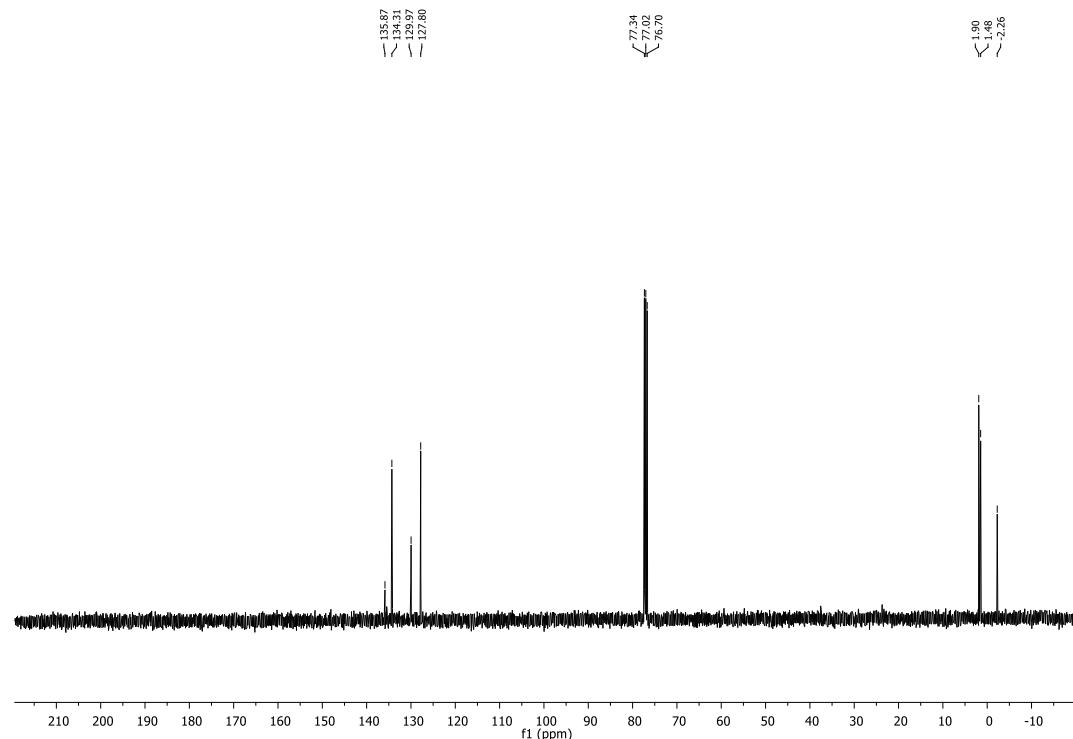
^{13}C NMR spectrum of 1,1,1-triisobutyl-3-methyl-3-phenyldisiloxane (100.6 MHz, CDCl_3)



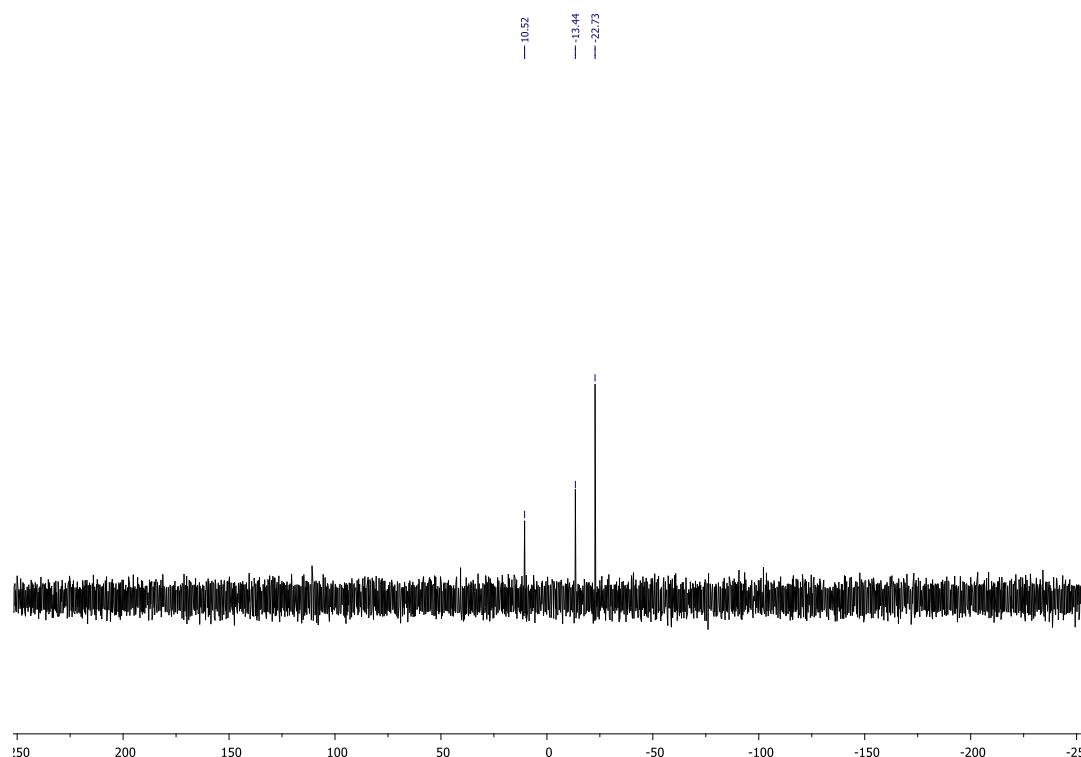
^1H NMR spectrum of 3,3-diphenyl-1,1,1-tris(trimethylsilyl)disiloxane (400 MHz, CDCl_3)



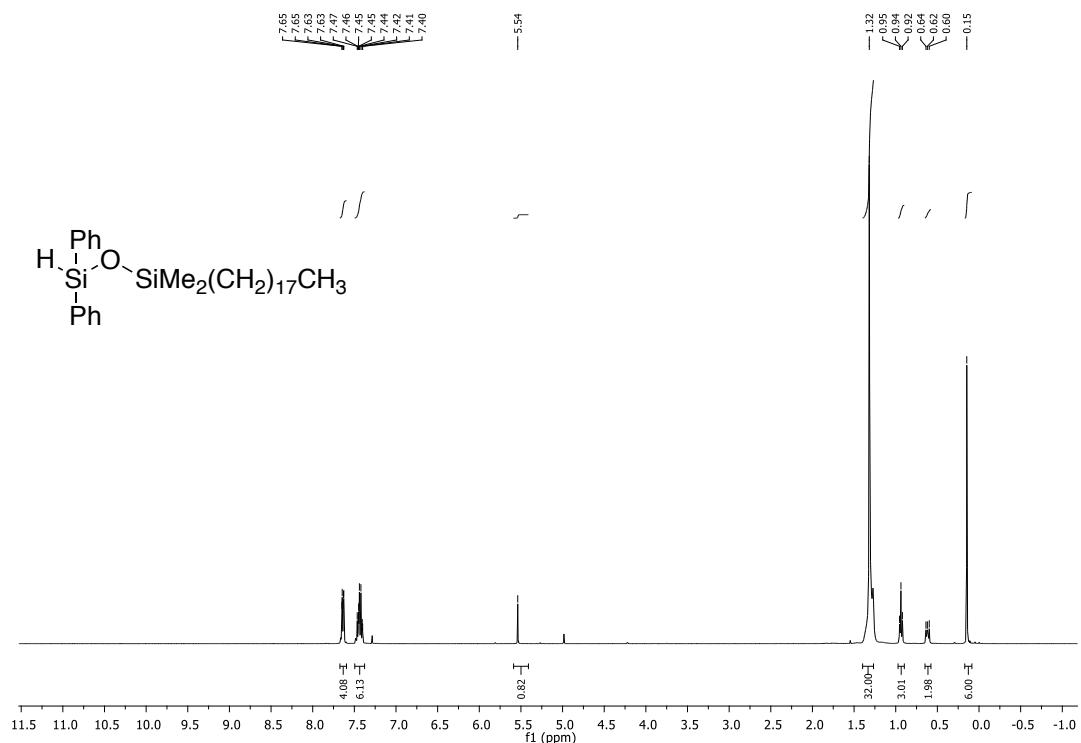
^{13}C NMR spectrum of 3,3-diphenyl-1,1,1-tris(trimethylsilyl)disiloxane (100.6 MHz, CDCl_3)



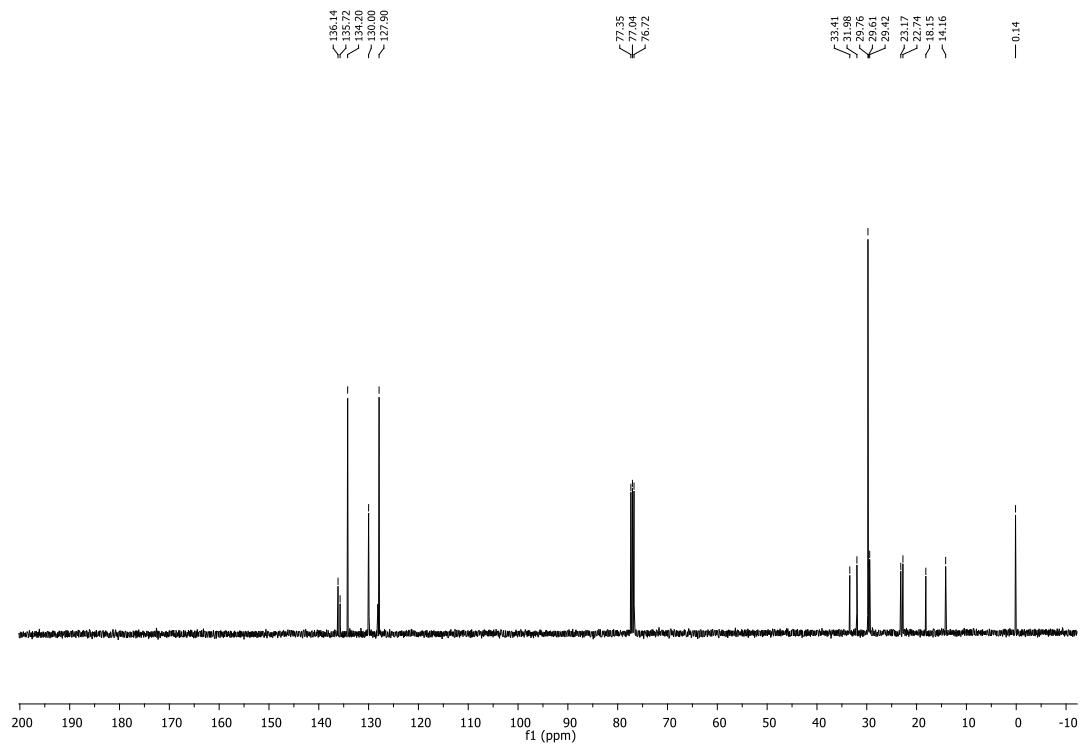
^{29}Si NMR spectrum of 3,3-diphenyl-1,1,1-tris(trimethylsilyl)disiloxane (79 MHz, CDCl_3)



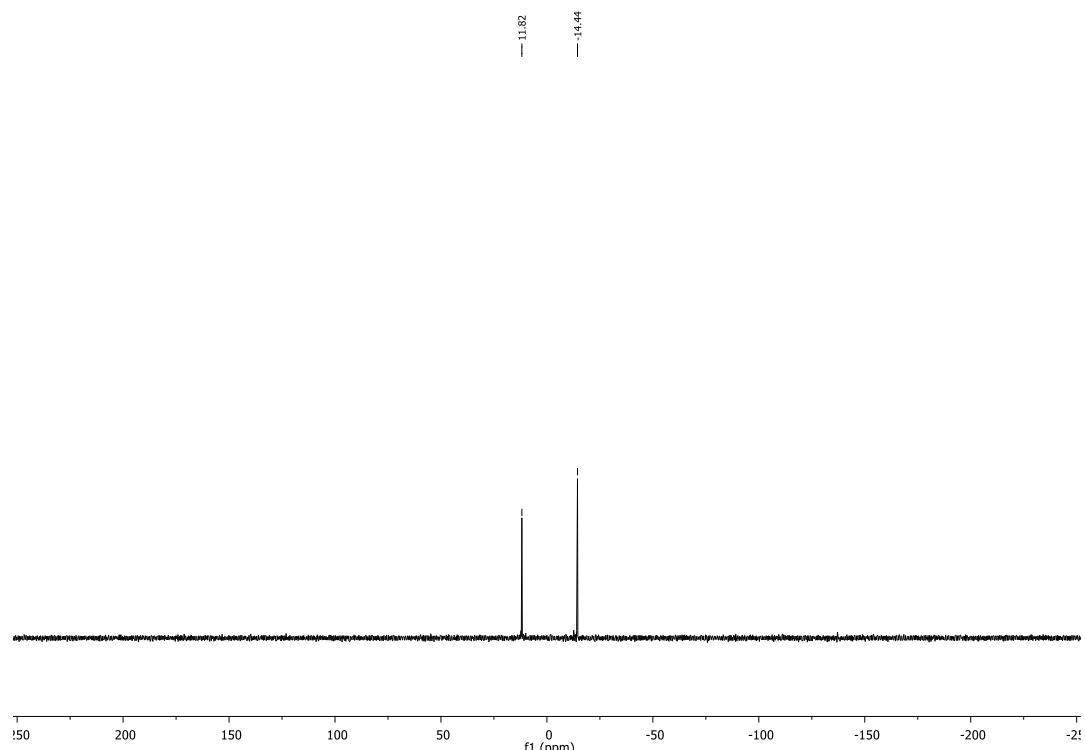
¹H NMR spectrum of 1,1-dimethyl-1-octadecyl-3,3-diphenyldisiloxane (400 MHz, CDCl₃)



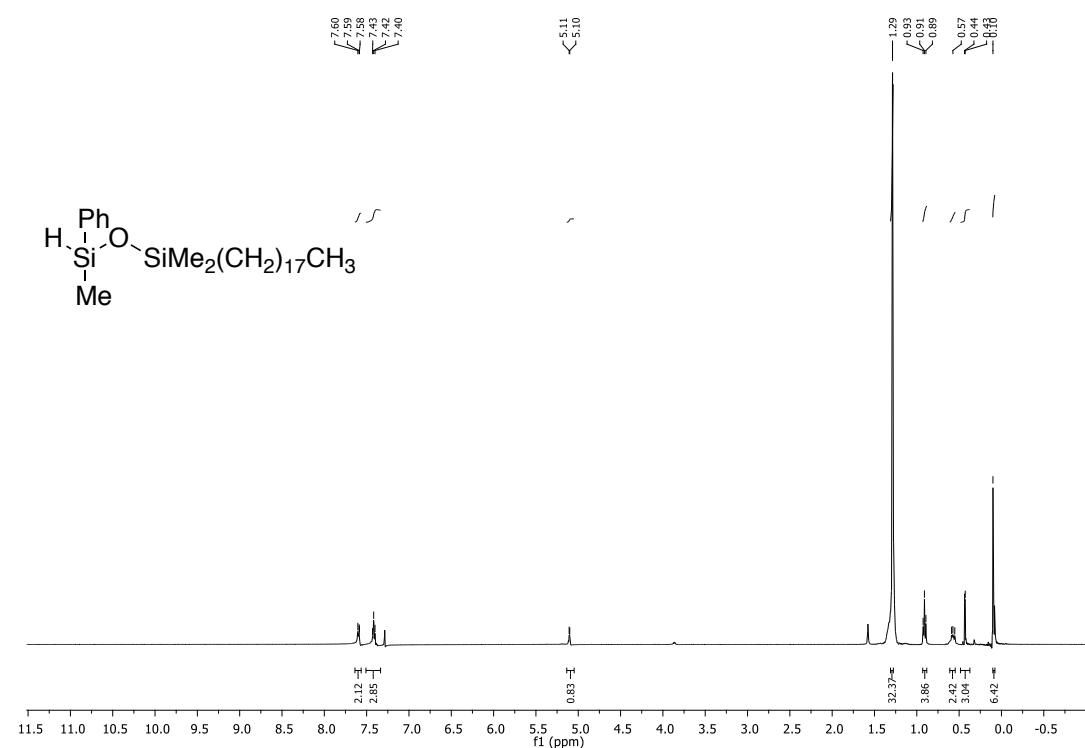
¹³C NMR spectrum of 1,1-dimethyl-1-octadecyl-3,3-diphenyldisiloxane (100.6 MHz, CDCl₃)



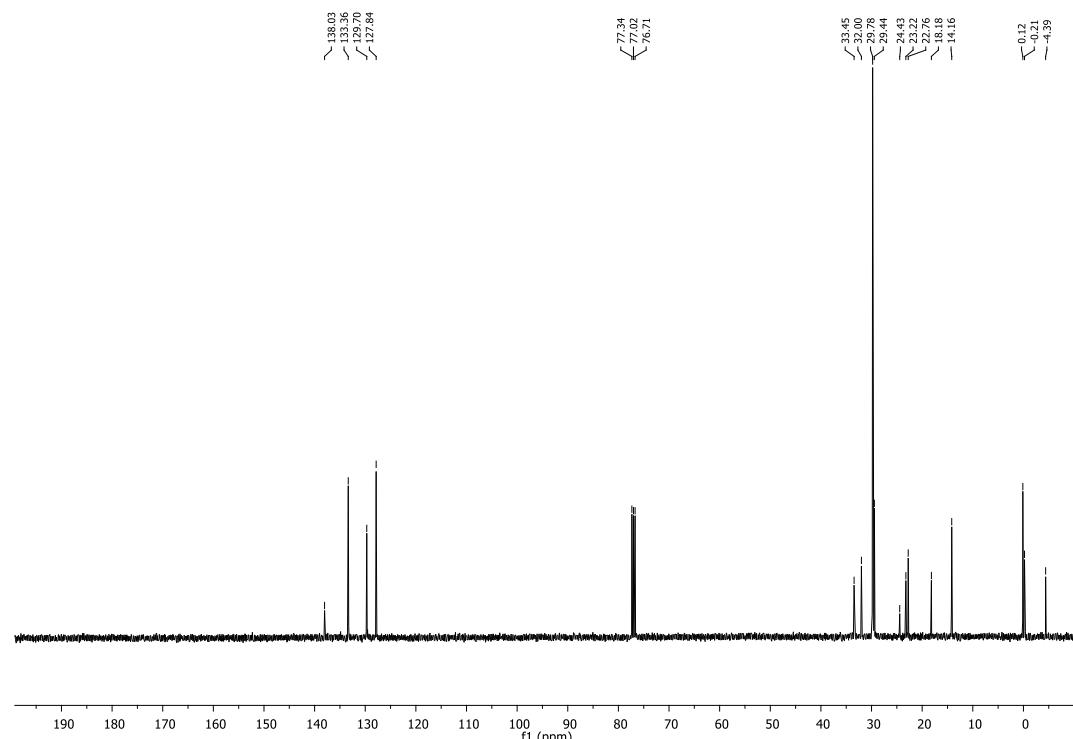
²⁹Si NMR spectrum of 1,1-dimethyl-1-octadecyl-3,3-diphenyldisiloxane (79 MHz, CDCl₃)



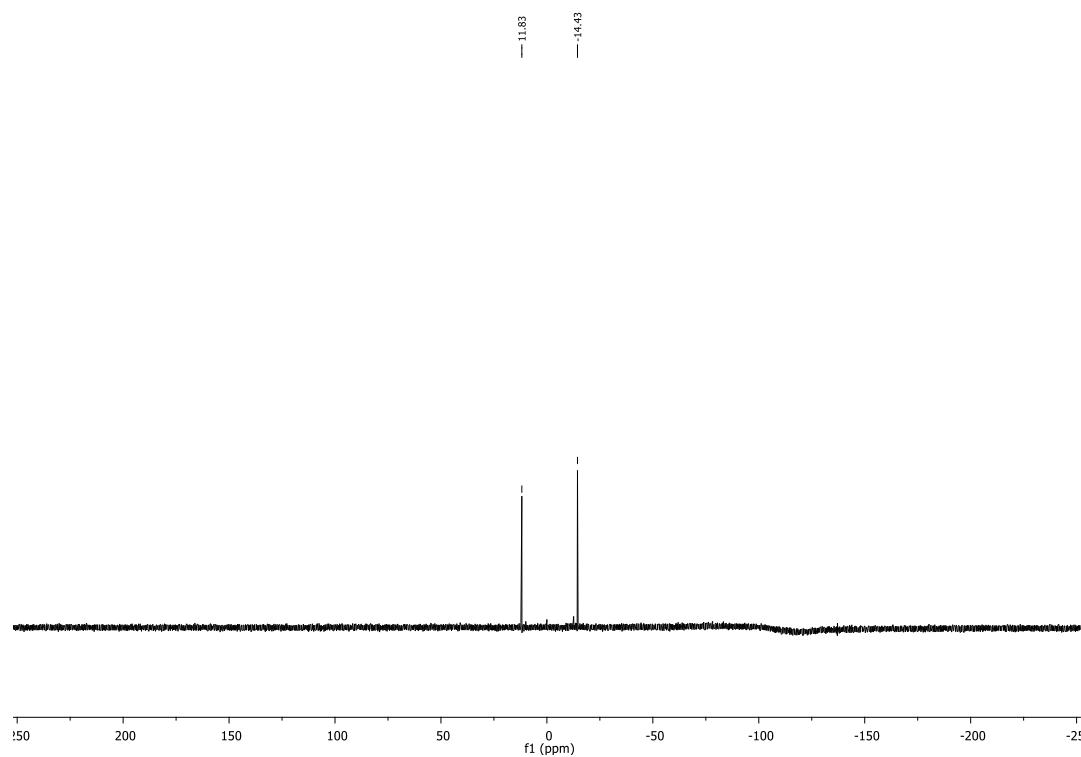
¹H NMR spectrum of 1,1,3-trimethyl-1-octadecyl-3-phenyldisiloxane (400 MHz, CDCl₃)



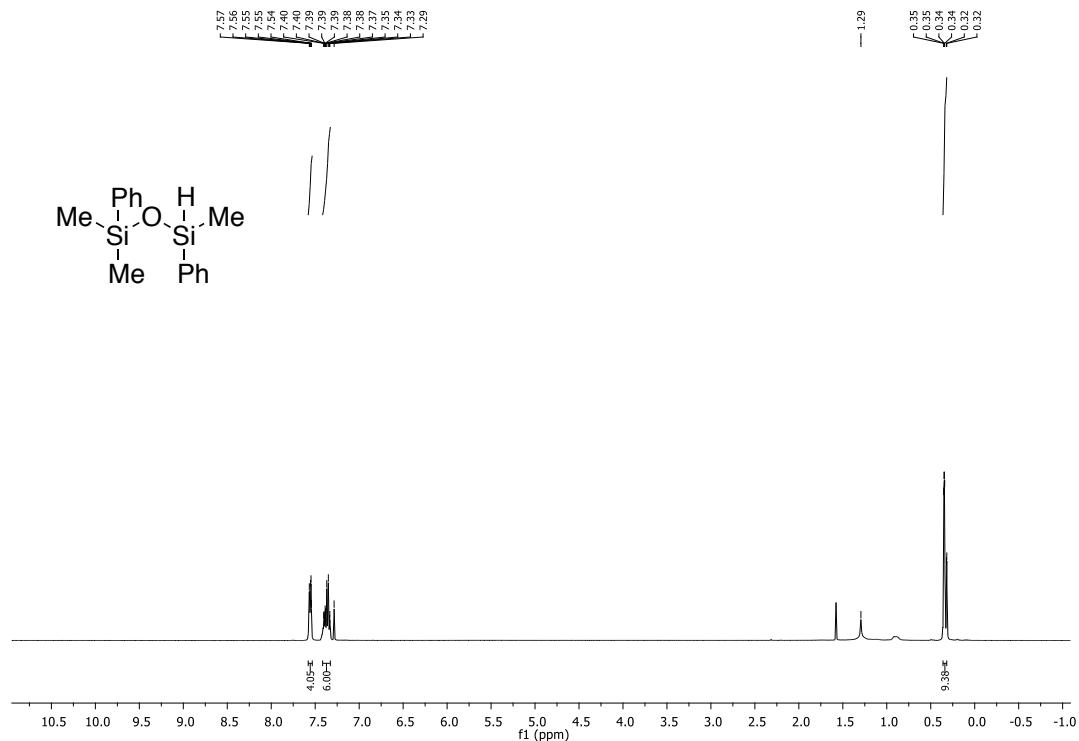
^{13}C NMR spectrum of 1,1,3-trimethyl-1-octadecyl-3-phenyldisiloxane (100.6 MHz, CDCl_3)



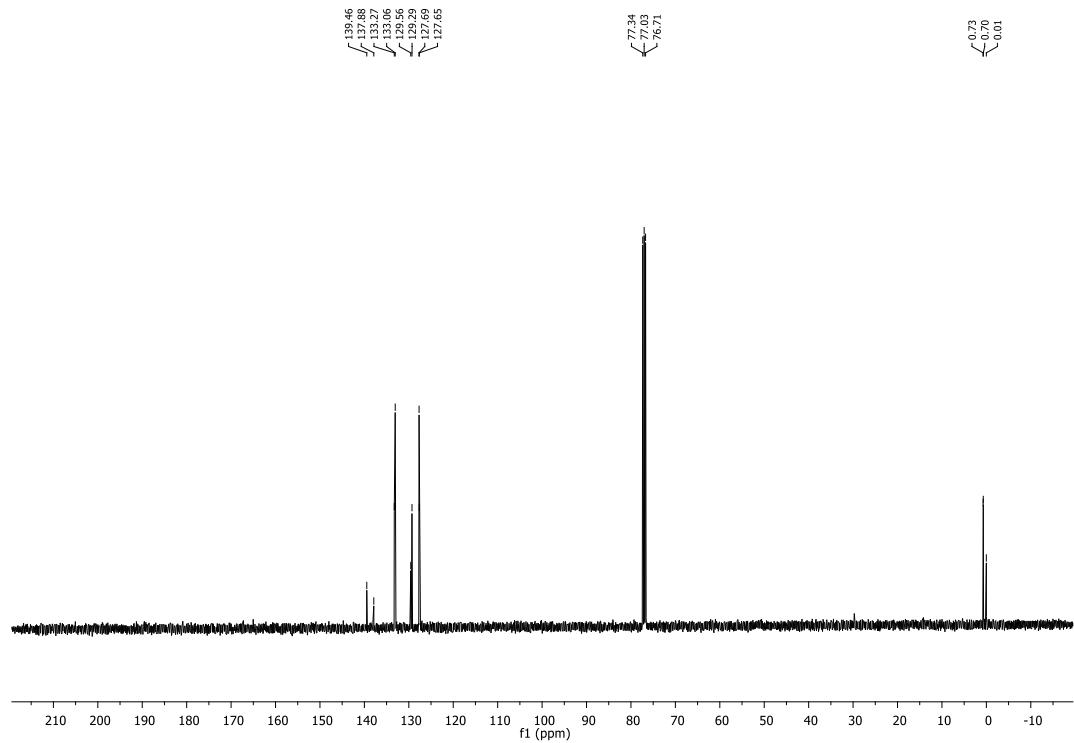
^{29}Si NMR spectrum of 1,1,3-trimethyl-1-octadecyl-3-phenyldisiloxane (79 MHz, CDCl_3)



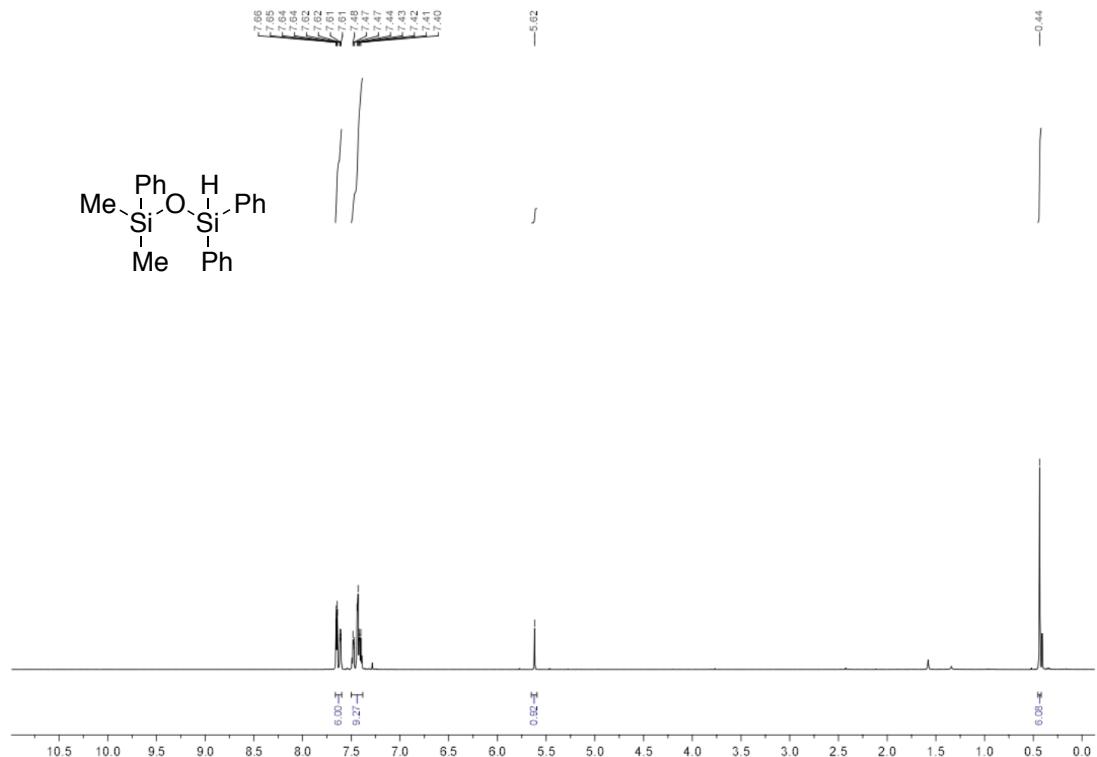
¹H NMR spectrum of 1,1,3-trimethyl-1,3-diphenyldisiloxane (400 MHz, CDCl₃)



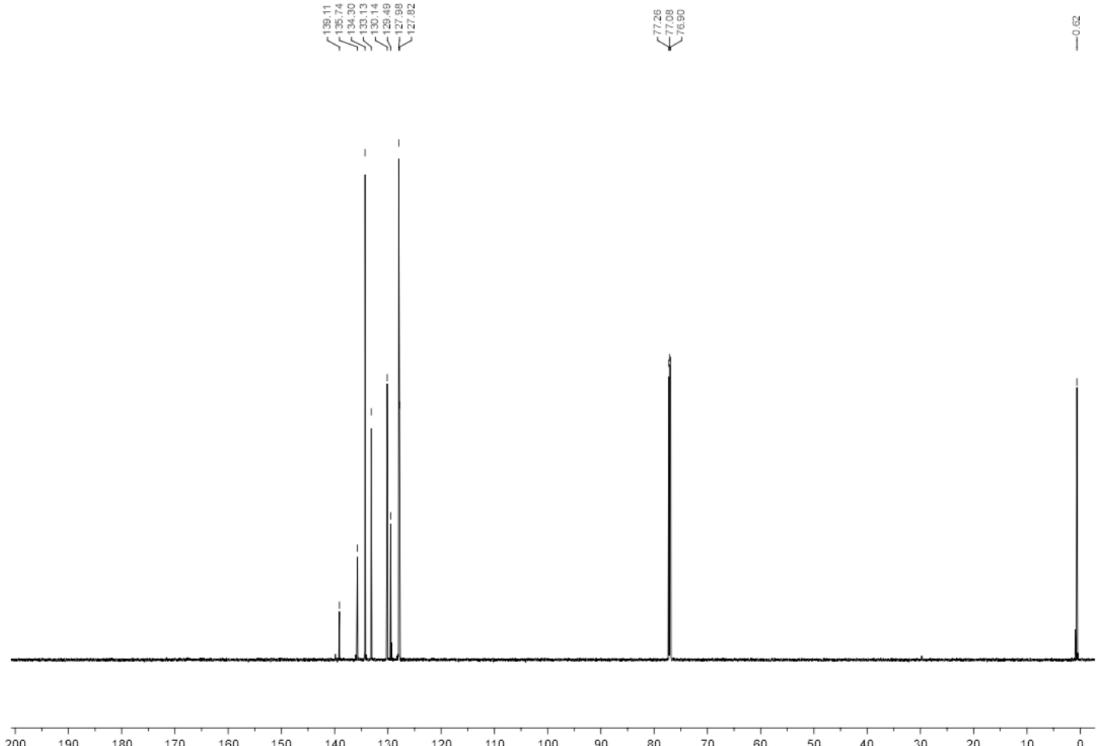
¹³C NMR spectrum of 1,1,3-trimethyl-1,3-diphenyldisiloxane (100.6 MHz, CDCl₃)



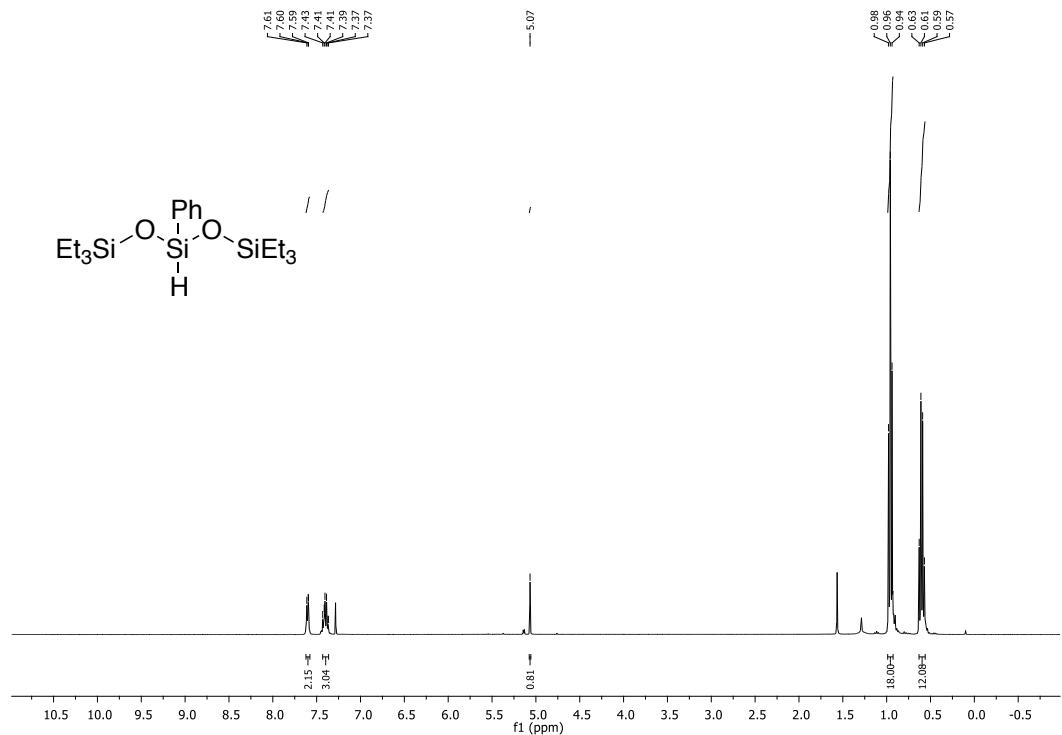
¹H NMR spectrum of 1,1-dimethyl-1,3,3-triphenylsilsiloxane (400 MHz, CDCl₃)



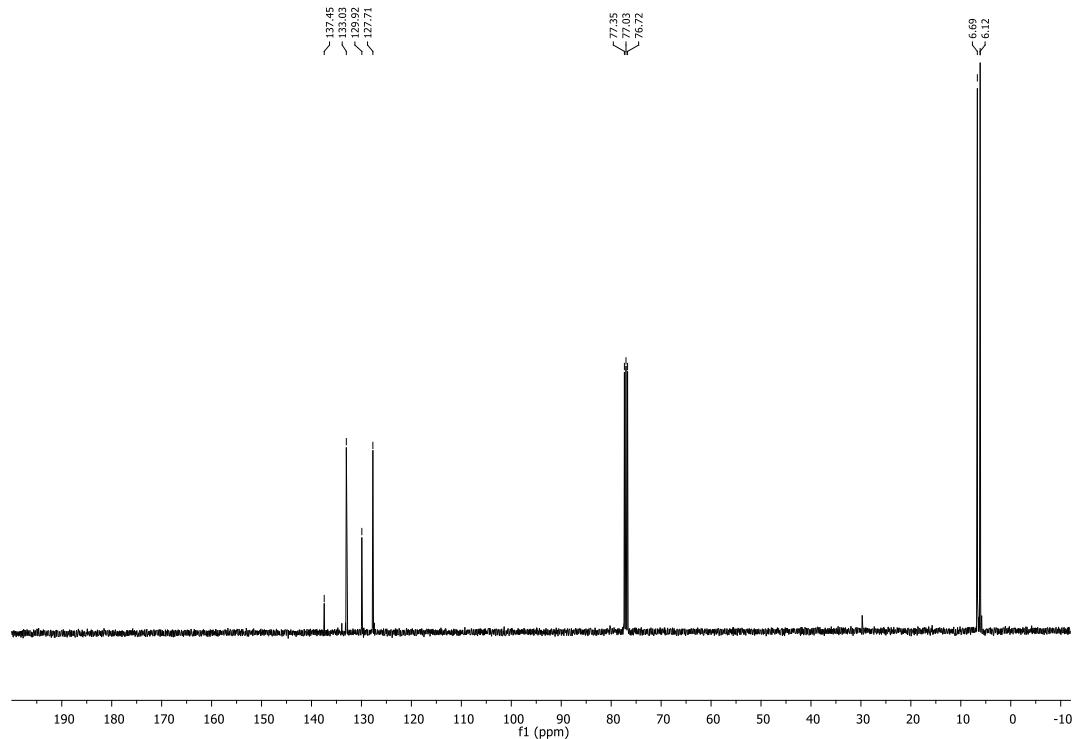
¹³C NMR spectrum of 1,1-dimethyl-1,3,3-triphenylsilsiloxane (100.6 MHz, CDCl₃)



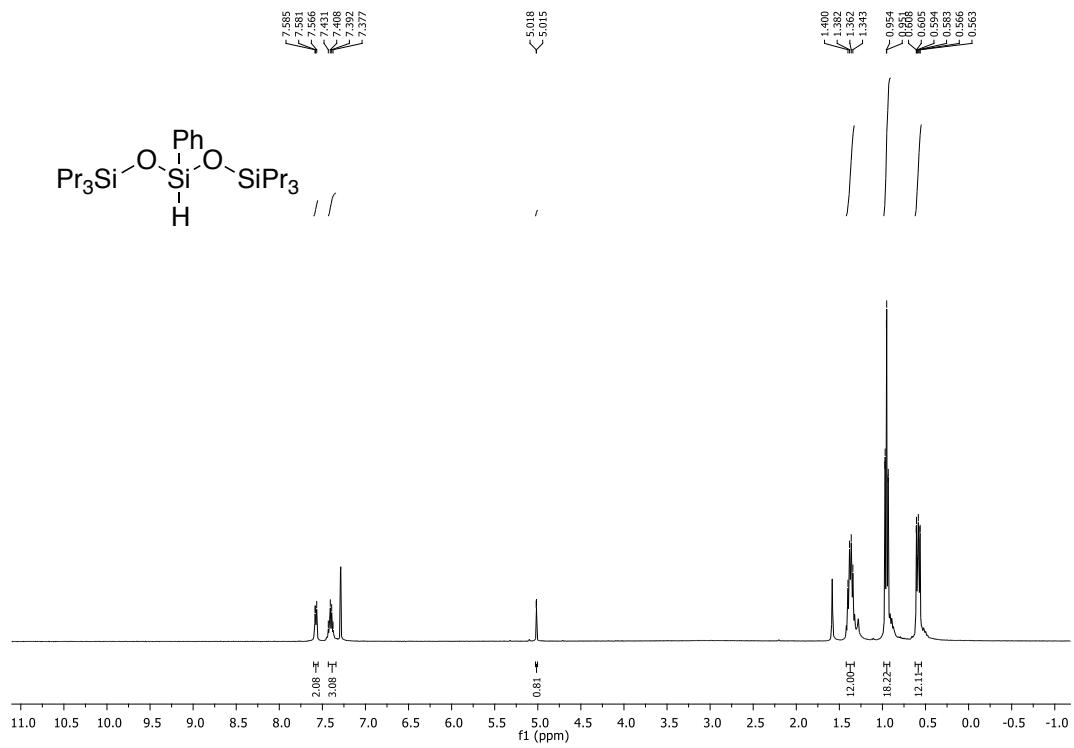
¹H NMR spectrum of 1,1,1,5,5-hexaethyl-3-phenyltrisiloxane (400 MHz, CDCl₃)



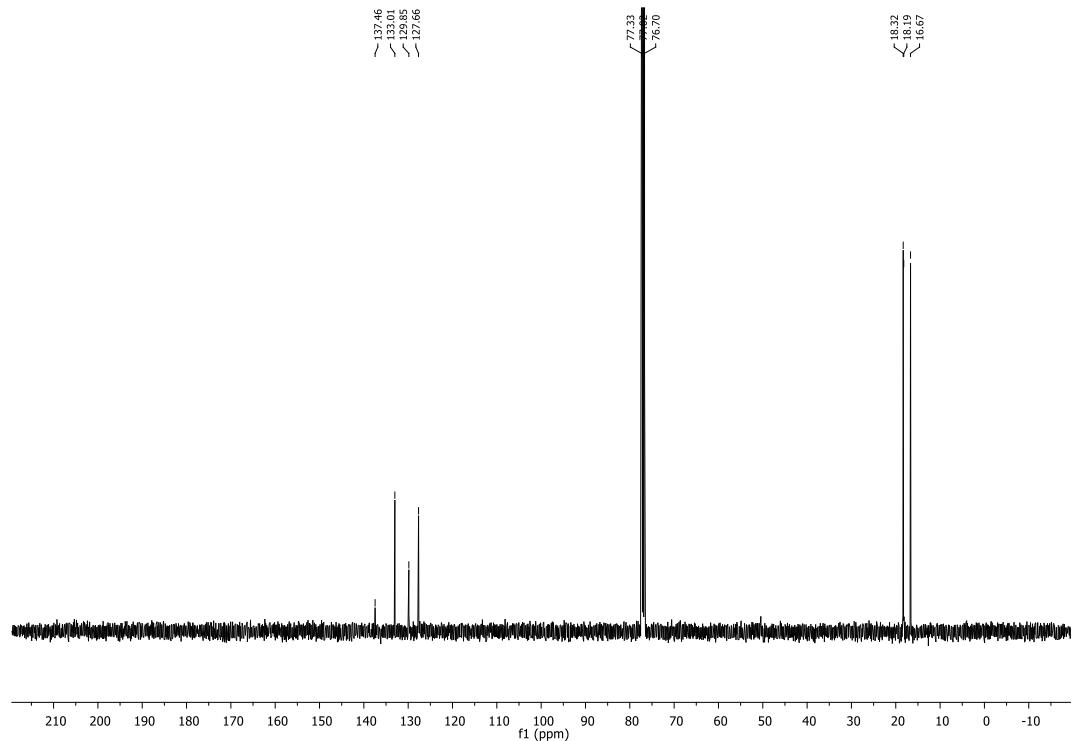
¹³C NMR spectrum of 1,1,1,5,5-hexaethyl-3-phenyltrisiloxane (100.6 MHz, CDCl₃)



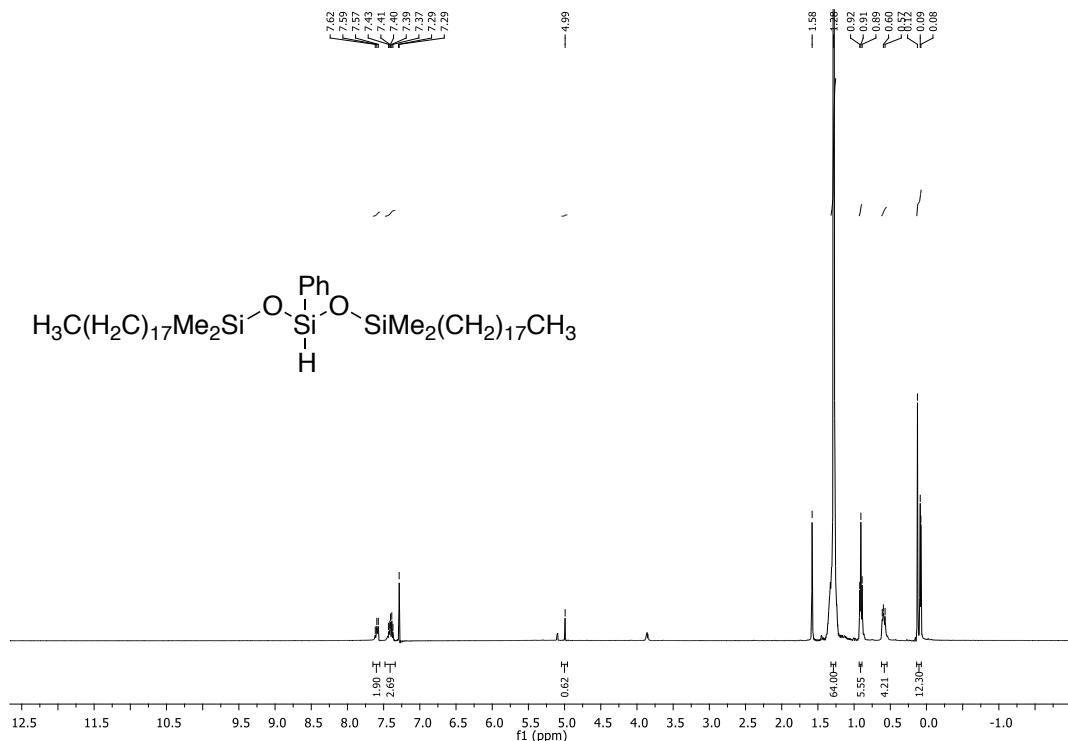
^1H NMR spectrum of 3-phenyl-1,1,5,5-hexapropyltrisiloxane (400 MHz, CDCl_3)



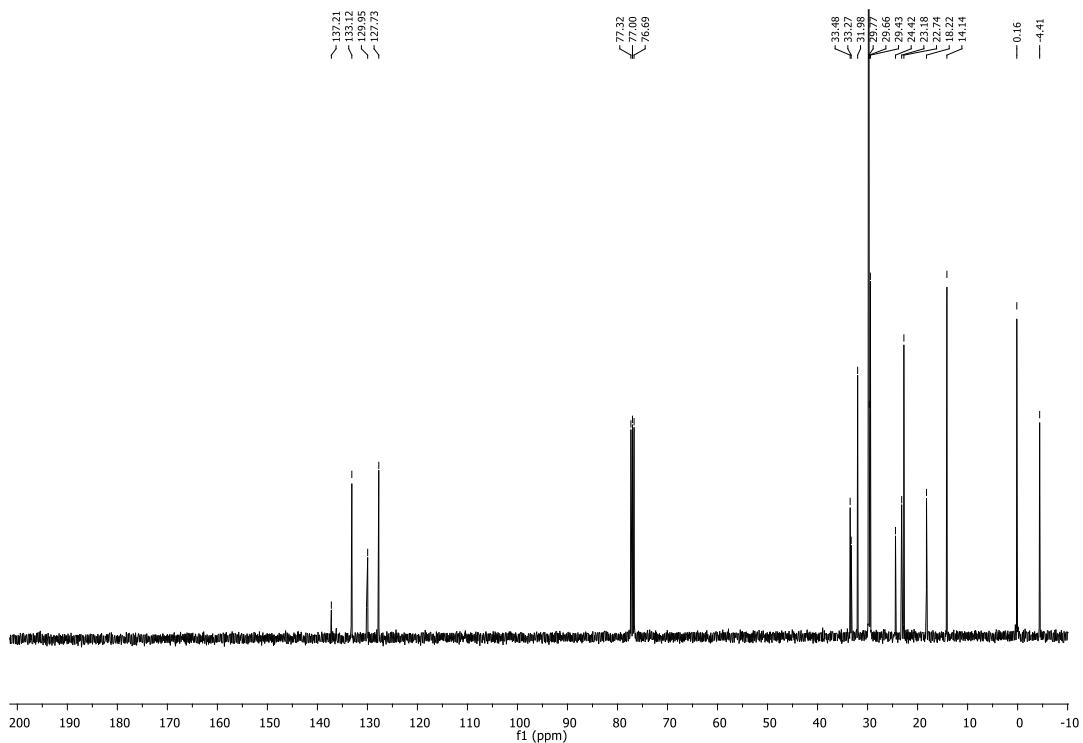
^{13}C NMR spectrum of 3-phenyl-1,1,5,5-hexapropyltrisiloxane (100.6 MHz, CDCl_3)



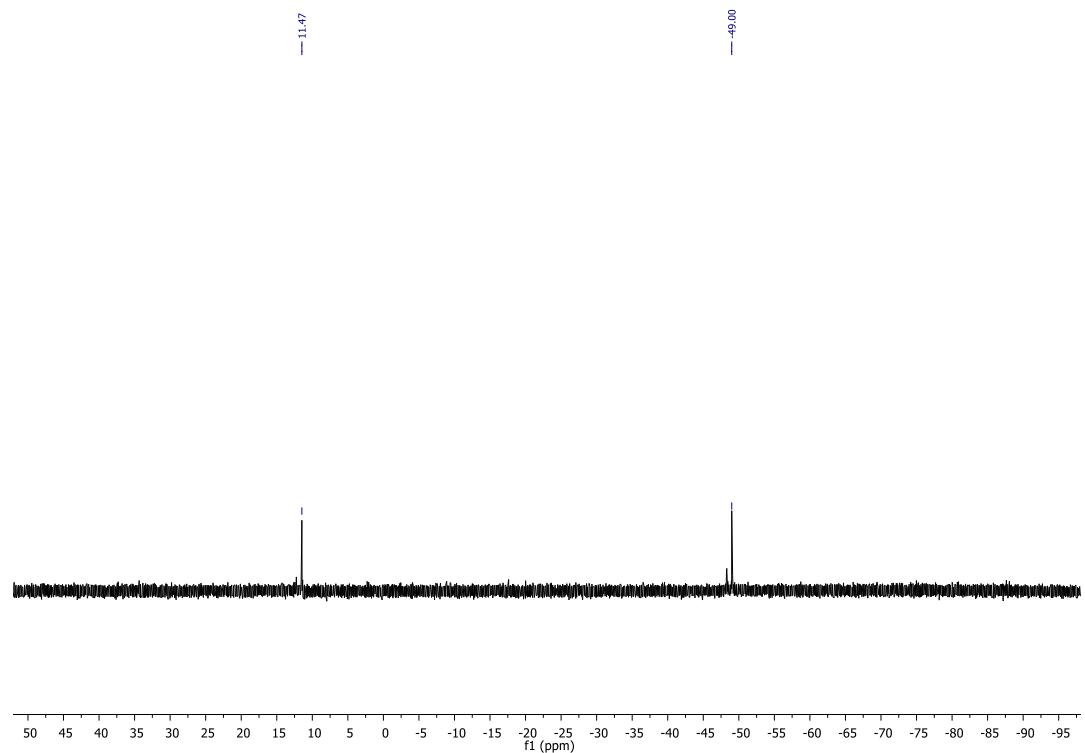
¹H NMR spectrum of 1,1,5,5-tetramethyl-1,5-dioctadecyl-3-phenyltrisiloxane (400 MHz, CDCl₃)



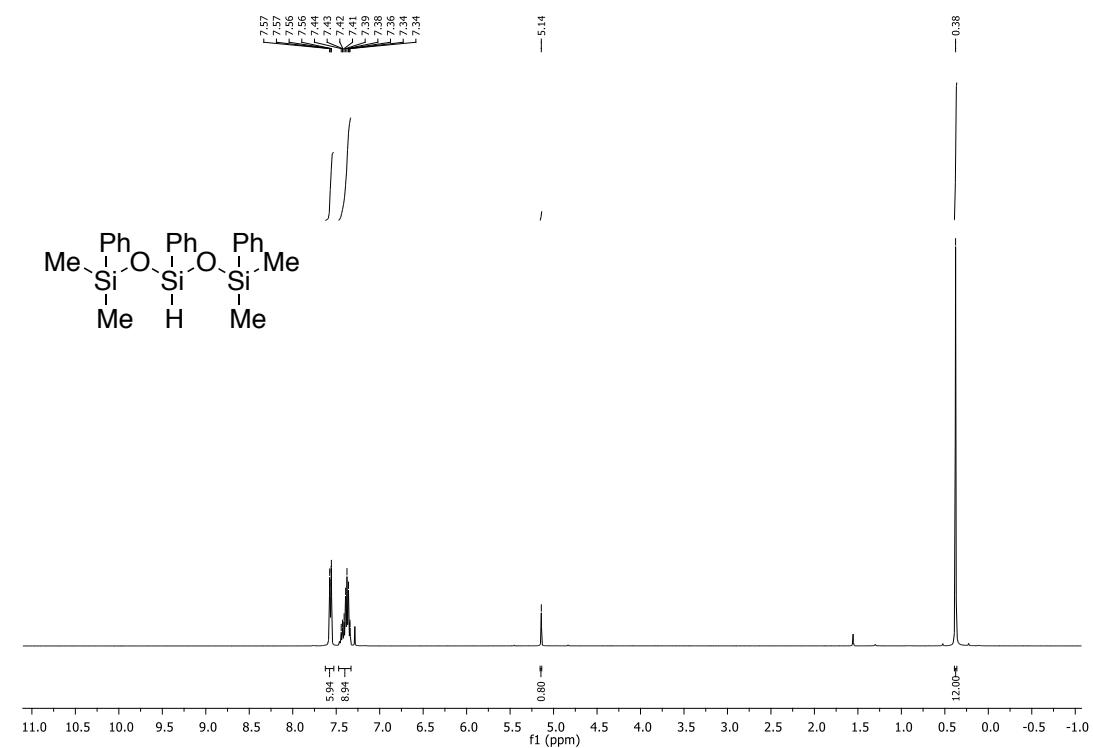
¹³C NMR spectrum of 1,1,5,5-tetramethyl-1,5-dioctadecyl-3-phenyltrisiloxane (100.6 MHz, CDCl₃)



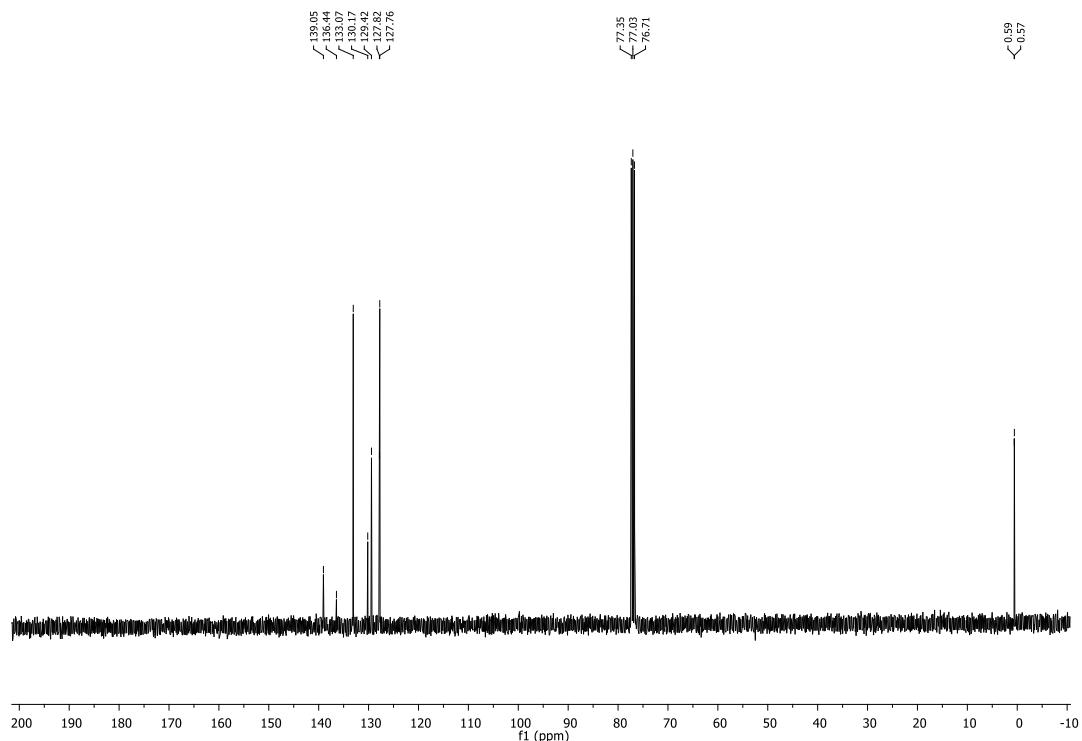
^{29}Si NMR spectrum of 1,1,5,5-tetramethyl-1,5-dioctadecyl-3-phenyltrisiloxane (79 MHz, CDCl_3)



^1H NMR spectrum of 1,1,5,5-tetramethyl-1,3,5-triphenyltrisiloxane (400 MHz, CDCl_3)



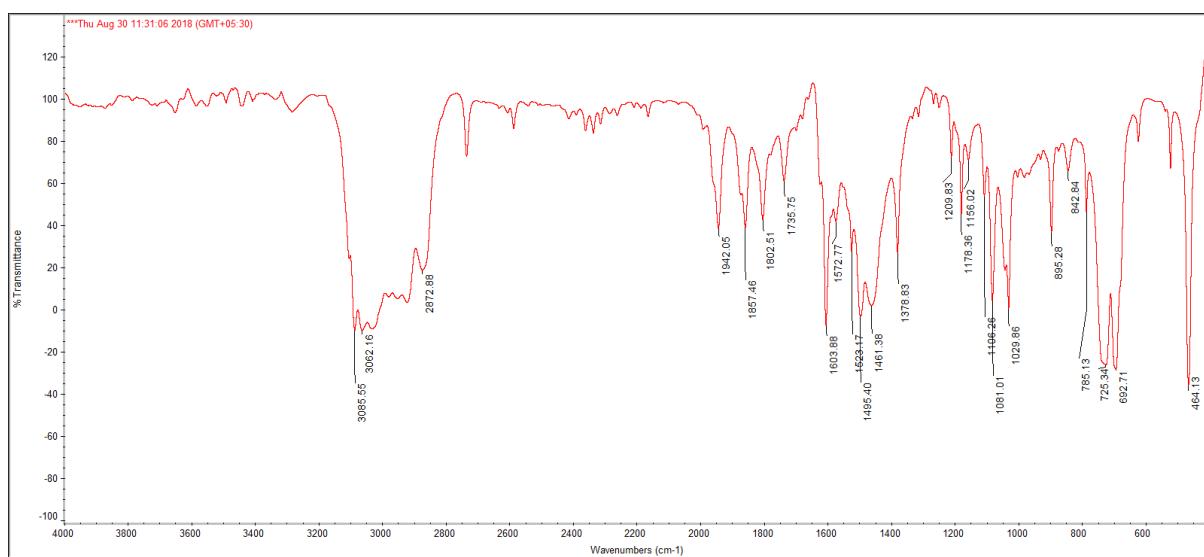
^{13}C NMR spectrum of 1,1,5,5-tetramethyl-1,3,5-triphenyltrisiloxane (100.6 MHz, CDCl_3)



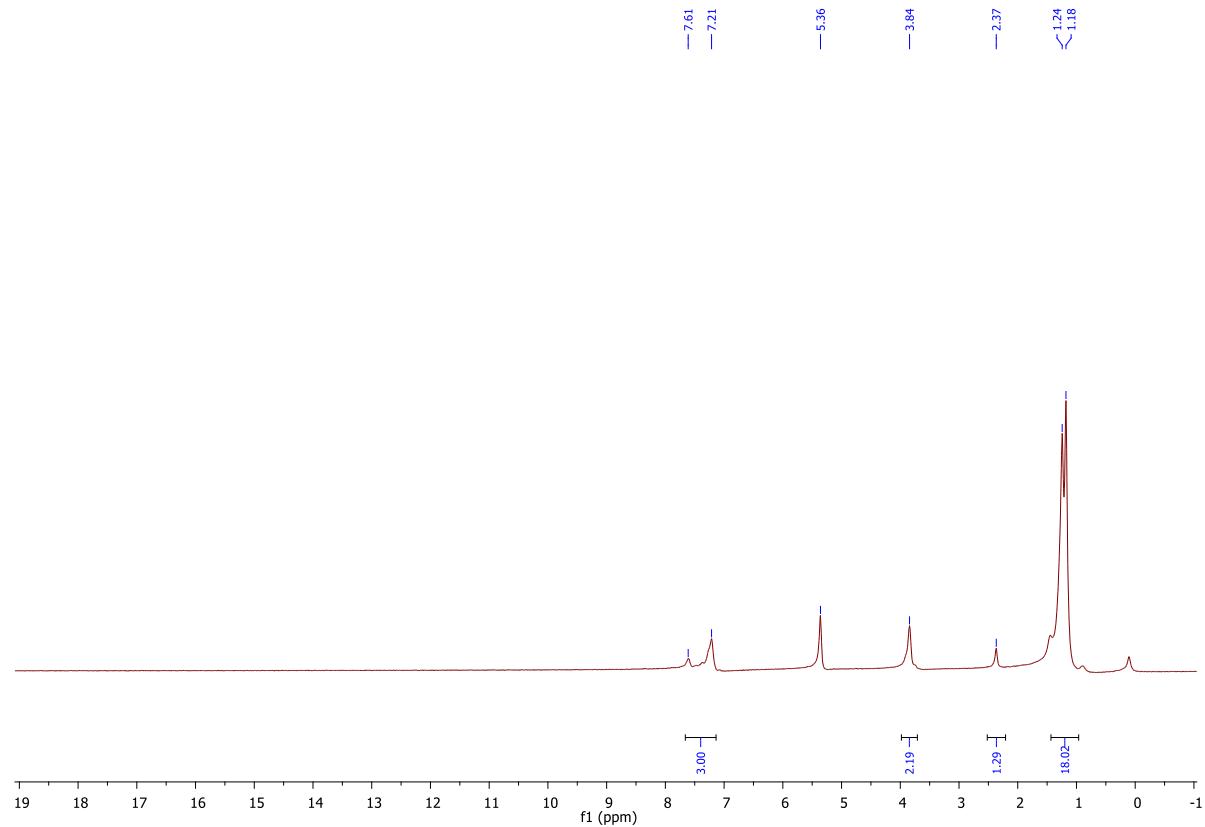
Mercury Poisoning Experiment : To an oven dried Schlenk tube, silane (1 mmol), catalyst **1** (2 mol %), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. Degassed water (2 mmol) and Hg (10 mmol) were added to the reaction mixture. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath for 2 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and cyclotetrasiloxane **3b** was isolated by column chromatography using silica gel (100-200 mesh, petroleum ether/EtOAC=100:1)

Synthesis of Intermediate **6 from Catalyst **1**:** To a screw cap scintillation vial, catalyst **1** (1 equiv., 0.056 g) and KO^tBu (2 equiv, 0.026 g) in dioxane (2 mL) were added under nitrogen atmosphere and the reaction mixture allowed to stir at room-temperature for 30 min. After completion of the reaction, solvent was evaporated under vacuum. The resultant residue was dissolved in DCM and the solution was filtered through a pad of celite. The solvent was evaporated under reduced pressure and yield of complex **6** was found to be 89 % (0.032 g). IR spectrum of **6** indicated the absence of amine signal at 3206.9 cm^{-1} found in **1** and ^1H NMR spectrum of **6** also showed the disappearance of amine protons (NH singnal appeared at δ 9.53 ppm for catalyst **1** disappeared in **6**).

IR spectrum of intermediate **6** in DCM



¹H NMR spectrum of intermediate **6** in CD₂Cl₂:



Catalysis by Intermediate 6: Synthesis of 2a. To an oven dried sealed tube, triethylsilane (1 mmol), isolated **6** (2 mol%) and dioxane (2 ml) were added under nitrogen atmosphere. Degassed water (2 mmol) was added to the reaction mixture. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath for 2 h. After cooling the reaction mixture to

room temperature, the solvent was evaporated under vacuum and the compound **2a** was isolated using column chromatography.

Catalysis by Intermediate 6: Synthesis of 2d. To an oven dried sealed tube, triphenylsilane (1 mmol), isolated **6** (2 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. Degassed water (2 mmol) was added to the reaction mixture. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath for 2 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and the compound **2d** was isolated using column chromatography.

Experiments to Verify Involvement of Intermediate Silanol in Reaction: To an oven dried sealed tube, diphenylsilanediol (1 mmol), catalyst **1** (2 mol%), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and cyclotetrasiloxane **3b** was isolated by column chromatography with quantitative yield.

However, performing the similar reaction at room temperature (instead of 60 °C), formation of **3b** was observed in only 21% yield.

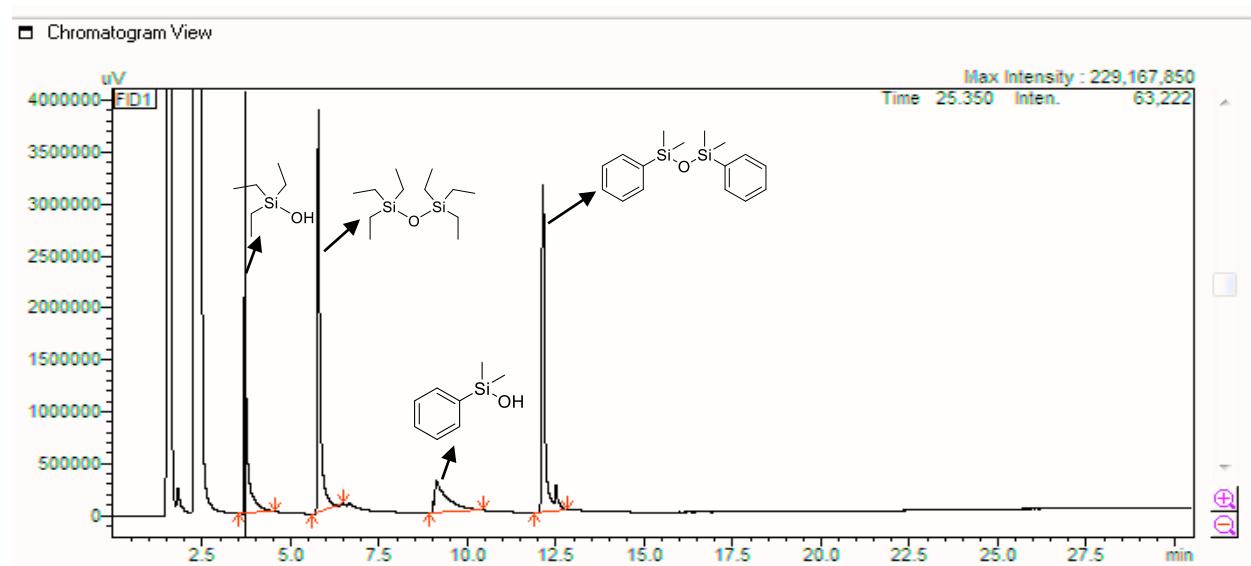
Experiments to Verify Involvement Dehydrative Condensastion Pathway in Reaction: To an oven dried sealed tube, triethylsilanol (1 mmol), triethylsilane (1 mmol), catalyst **1** (2 mol%), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath. After completion, reaction mixture was analyzed by GC, which confirmed that triethylsilane remains unreacted. Self coupling of triethylsilanol was observed to provide the corresponding siloxanes **2a**. When similar reaction was carried out at room-temperature only trace amount of **2a** was formed.

Attempted Interruption of Catalytic Cycle: To an oven dried sealed tube, triethylsilanol (1 mmol), triethylsilane (1 mmol), catalyst **1** (2 mol%), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. The reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath. Further, after 10 minute, styrene, arylhalides (bromobenzene and benzylbromide) and alcohols (methanol and benzyl alcohol) were added independently to the reaction mixture to interrupt the catalytic cycle. However these attempts were failed to interrupt the cycle and **2a** was formed in quantitative yield.

Detection of Dehydrogenative Coupling Pathway for Unsymmetrical

Monohydrosiloxane Synthesis: To a screw cap scintillation vial, triethylsilanol (1 mmol) and dimethylphenylsilanol (1 mmol), catalyst **1** (2 mol %), KO^tBu (4 mol%) and THF (2 mL) were added under nitrogen atmosphere. The reaction mixture was allowed to stir at room-temperature for one hour. After completion, reaction mixture was analyzed by GC and both silanols were found to remain unreacted. When the similar reaction was carried out at 60 $^{\circ}\text{C}$, the corresponding siloxanes **2a** and **2c** from triethylsilanol and dimethylphenylsilanol were observed, respectively (GC analyses). Notably, no cross-coupling product between the different silanols was formed.

GC Spectrum of Reaction Mixture for Scheme 5i:

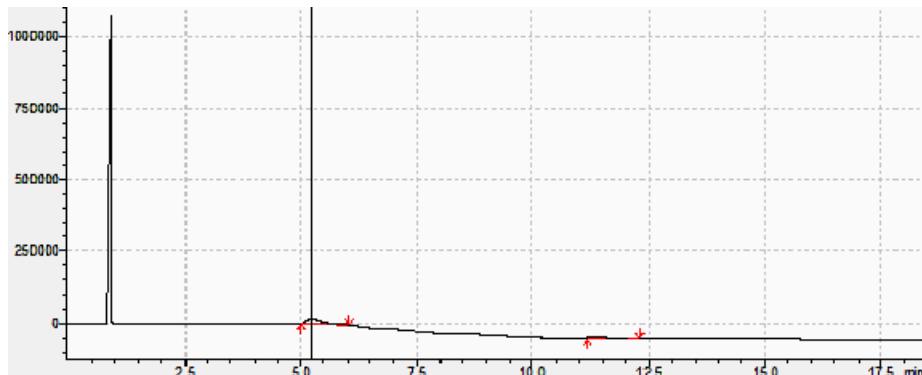


Experiment to Confirm Necessity of Catalyst for Unsymmetrical Siloxane Synthesis : To an oven dried Schlenk tube, triethylsilanol (1 mmol) and dimethylphenylsilanol (1 mmol) and toluene (2ml) were added under nitrogen atmosphere. The reaction mixture was allowed to stir at 120 $^{\circ}\text{C}$ in a pre-heated oil bath for 2 h. Upon completion, the reaction mixture was subjected to GC analysis: both the silanols found unreacted.

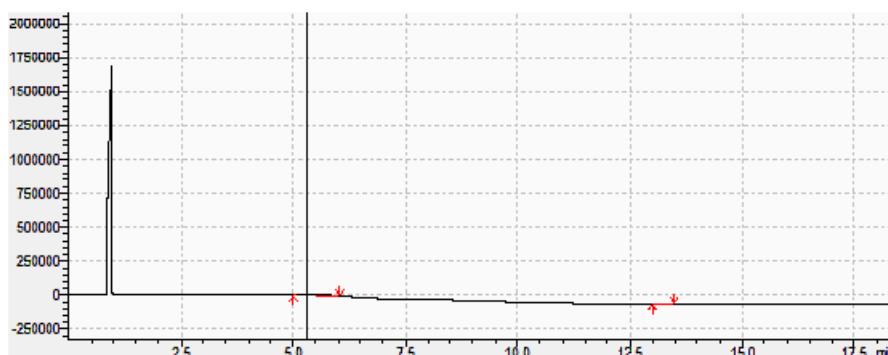
Detection of Molecular Hydrogen by Gas Chromatography : To an oven dried Schlenk tube, triethylsilanol (1 mmol), diphenylsilane (1 mmol), catalyst **1** (2 mol %), and KO^tBu (4 mol%) were added under nitrogen atmosphere inside glove box. The reaction mixture was allowed to stir at room temperature for one hour. After completion of reaction, the internal gas phase (2ml) was syringed out and subjected to Gas Chromatography [Shimadzu, HP-

Molesieve (TCD) 30 meter from Agilent] analysis, which clearly confirmed the formation of molecular hydrogen from the reaction.

GC Spectrum of H₂ (standard):



GC Spectrum of Reaction Mixture:



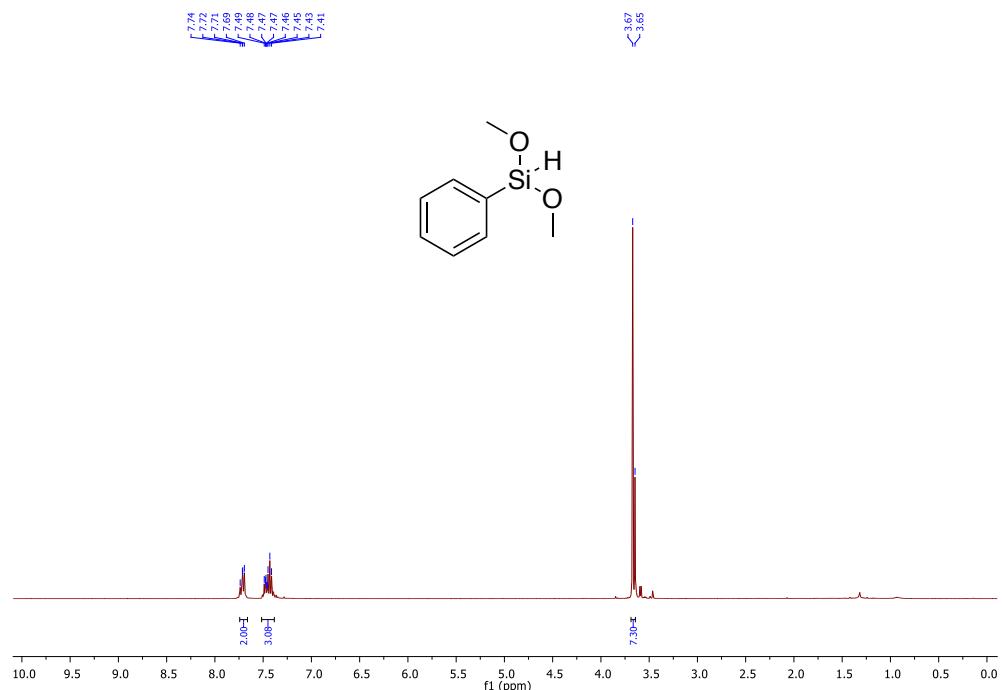
Interuption of Catalytic Cycle by Alcohol: To an oven dried Schlenk tube, triethylsilanol (2 mmol), phenylsilane (1 mmol), catalyst **1** (2 mol %), and base KO^tBu (4 mol%) and THF (2 mL) were added under nitrogen atmosphere inside the glove box and the reaction was allowed to stir at room- temperature. After 10 minute methanol (2 mmol) was added to reaction mixture and stirring was continued for one hour. After completion, reaction mixture was analyzed by GC and the higher alkoxy silane **7** was found in 13% while monohydrosiloxane **5m** found 71% (GC analyses).

However, performing the similar reaction by adding styrene or arylhalide instead of adding alcohol failed to interupt the catalytic cycle.

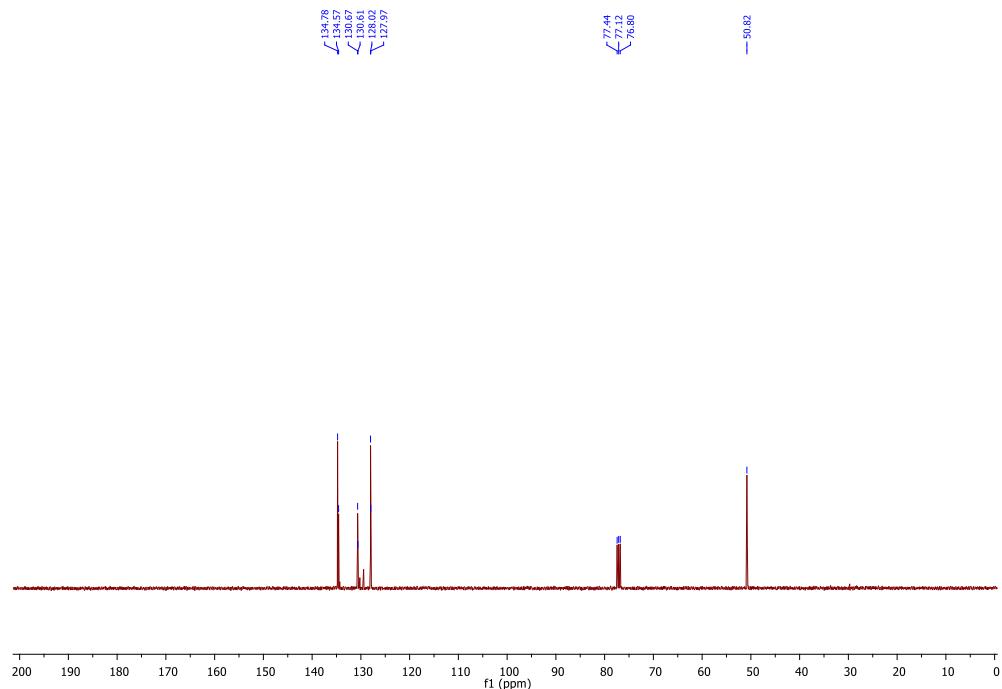
Dehydrogenative Coupling of Alcohol and Silane: To an oven dried Schlenk tube, methanol (2 mmol), phenylsilane (1 mmol), catalyst **1** (2 mol %), and KO^tBu (4 mol%) and THF (2 mL) were added under nitrogen atmosphere inside the glove box and the reaction was allowed to stir at room temperature for one hour. After completion of reaction the solvent

was removed under vacuum and the compound **7** was isolated by column chromatography in quantitative yield.

¹H NMR spectrum of Dimethoxy(phenyl)silane (400 MHz, CDCl₃):



¹³C NMR spectrum of Dimethoxy(phenyl)silane (400 MHz, CDCl₃)



Competition Reaction Between Phenylsilane and Diphenylsilane: To an oven dried Schlenk tube, phenylsilane (1 mmol), diphenylsilane (1 mmol), triethylsilanol (2 mmol), catalyst **1** (2

mol %), and KO^tBu (4 mol%) and THF (2 mL) were added under nitrogen atmosphere inside the glove box and the reaction was allowed to stir at room temperature for one hour. After completion, reaction mixture was analyzed by GC and the monohydrodisiloxane **5m** was found in 76% while monohydrosiloxane **5a** was found in 11% (GC analyses).

Volumetric Estimation of Hydrogen Gas Liberated During Catalysis (3b): To an oven dried Schlenk tube, silane (0.5 mmol), catalyst **1** (2 mol %), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. Degassed water (2 mmol) was added and the reaction mixture allowed to stir at 60 °C in a pre-heated oil bath with Schlenk side arm connected to a gas burette via cold trap (to remove solvent vapors). The reaction was repeated thrice to get consistent reading and the number of moles of hydrogen evolved was calculated by taking the vapour pressure of water at 298K = 23.7695 Torr. Volume of water displaced = 24 mL, Atmospheric pressure = 758.3124 Torr, $R = 62.3635 \text{ L Torr K}^{-1} \text{ mol}^{-1}$.

$$n_{\text{H}_2} = [(P_{\text{atm}} - P_{\text{water}}) * V] / RT = 0.00094 \text{ moles. Expected value} = 0.001 \text{ mole or 1 mmol.}$$

Volumetric Estimation of Hydrogen Gas Liberated from Synthesis of 4: To an oven dried Schlenk tube, silane (0.5 mmol), catalyst **1** (2 mol %), KO^tBu (4 mol%) and dioxane (2 mL) were added under nitrogen atmosphere. Degassed water (2 mmol) was added and the reaction mixture was allowed to stir at 60 °C in a pre-heated oil bath with Schlenk side arm connected to a gas burette via cold trap (to remove solvent vapors). The reaction was repeated thrice to get consistent reading and the number of moles of hydrogen evolved was calculated by taking the vapour pressure of water at 298K = 23.7695 Torr. volume of water displaced = 37.3 mL, Atmospheric pressure = 758.3124 Torr, $R = 62.3635 \text{ L Torr K}^{-1} \text{ mol}^{-1}$. $n_{\text{H}_2} = [(P_{\text{atm}} - P_{\text{water}}) * V] / RT = 0.00147 \text{ moles. Expected value} = 0.0015 \text{ mole or 1.5 mmol.}$

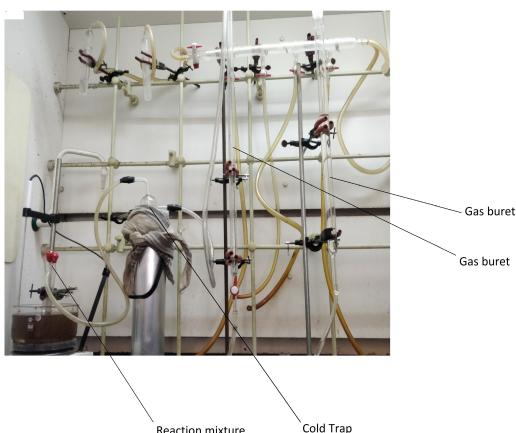
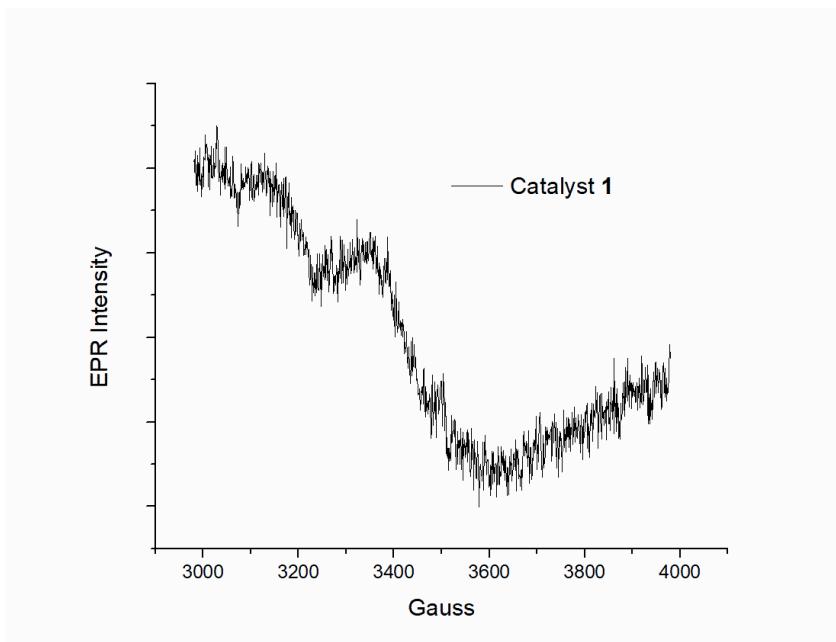
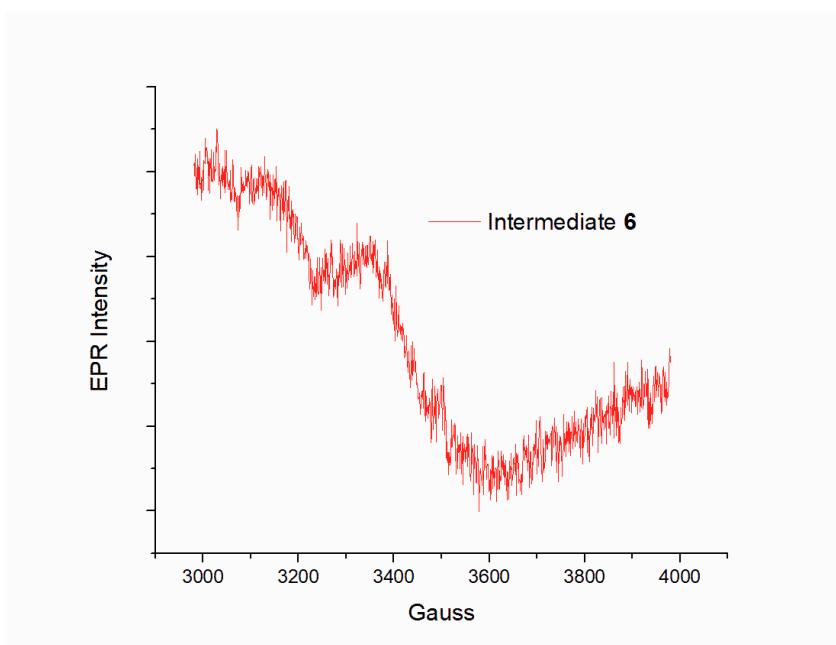


Figure S1 :-Experimental Set-up for Estimstion of Hydrogen Gas Evolution.

EPR Spectra of Catalyst 1 and Intermediate 6 :



Catalyst 1

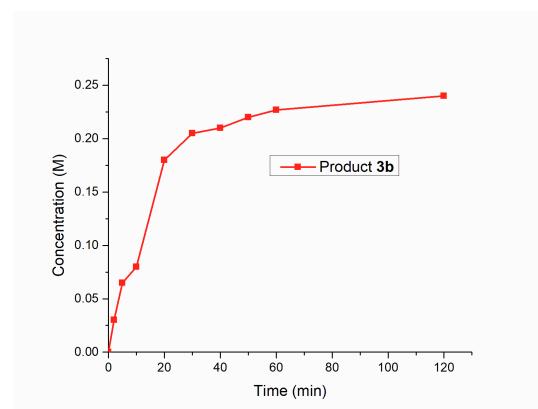
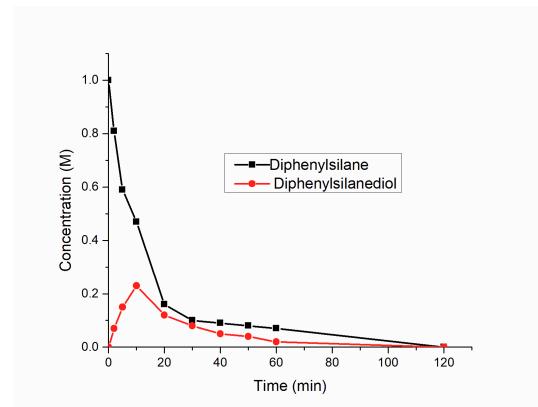


Intermediate 6

Figure S2 :-EPR Spectra of Catalyst 1 and Intermediate 6

Monitoring of Reaction Progress by GC: Re-run Experiments Tested for Reproducibility of the reaction

a)



b) Formation of unsymmetrical siloxane product **5a**

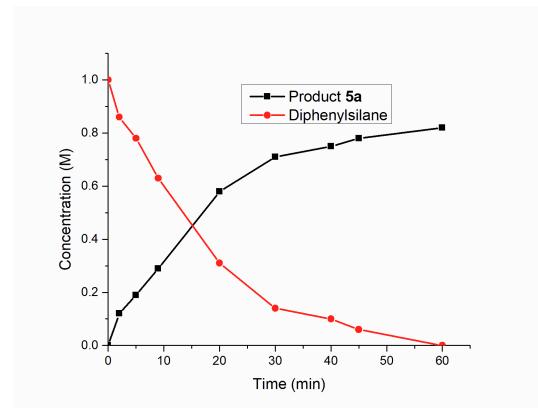


Figure S3 :- Re-run Experiments Tested for Reproducibility of the reaction. Monitoring the reaction progress of symmetrical cyclotetrasiloxane **3b**. a) Conversion of diphenylsilane and formation of diphenylsilanediol intermediate. Formation of product **3b**. b) Formation of unsymmetrical siloxane product **5a**.

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