

**Bis(imino)pyridine Iron Complexes for Aldehyde and Ketone
Hydrosilylation.**

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Supporting Information

Table of Contents

Experimental	S3
References	S26

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.¹ Hydrogen and deuterium gas were passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Benzene-*d*₆ and toluene-*d*₈ were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves or titanocene, respectively. **1-(N₂)₂**,² and **1-(CH₂SiMe₃)₂**³ were prepared according to literature procedures. All aldehydes and ketones were purchased from commercial sources and were vacuum distilled from CaH₂ before use.

¹H NMR spectra were recorded on Varian Mercury 300, Inova 400 and 500 spectrometers operating at 299.76, 399.78 and 500.62 MHz, respectively. ²H NMR spectra were recorded at 20 °C on Inova 400 and 500 spectrometers operating at 61.37 and 76.85 MHz, respectively. ¹³C NMR spectra were recorded on the same spectrometers operating at 101.535 or 125.893 MHz, respectively. All ¹H and ¹³C NMR chemical shifts are reported relative to SiMe₄ using ¹H (residual) and ¹³C chemical shifts of the solvent as a secondary standard. Solution magnetic moments were determined by Evans method⁴ using a ferrocene standard and are the average value of at least two independent measurements. ¹H NMR multiplicity and coupling constants are reported where applicable. Peak width at half height is given for paramagnetically broadened resonances.

Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073 \text{ \AA}$). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

General Procedure for Catalytic Hydrosilylation. A scintillation vial was charged with 1 mL of a solution of $4 \times 10^{-4} \text{ M}$ catalyst precursor in toluene, followed by the addition of $4 \times 10^{-4} \text{ M}$ moles of the substrate. To the stirring solution was added $8 \times 10^{-4} \text{ M}$ moles of PhSiH_2 (or appropriate silane). The reaction was stirred for the allotted time, typically one or three hours, after which time the vial was removed from the drybox and the reaction was quenched by the addition of an ether-water mixture. The reaction mixture was then passed through silica to remove the iron residue. Excess silane was removed in vacuo. Many reactions were run in pentane to facilitate solvent removal and characterization of the silyl ethers by ^1H NMR spectroscopy. Conversions to the corresponding silyl ether were monitored by GC. If the corresponding alcohol was desired, the reaction mixtures were stirred with an equal volume of 1 M HCl or 10

%NaOH overnight. The organic layer was separated the aqueous layer extracted twice with diethyl ether and the organic layers were combined, passed through silica and dried over MgSO₄. Conversions were determined by GC.

Preparation of (^{Cy}APDI)Fe(CH₂SiMe₃)₂ (2-(CH₂SiMe₃)₂). A 20 mL scintillation vial was charged with 0.443 g (1.00 mmol) of (py)₄FeCl₂ and approximately 3-5 mL pentane were added. The resulting slurry was cooled to -35 °C for approximately 30 minutes after which time a pentane solution of LiCH₂SiMe₃ (0.188 g, 2.00 mmol) was added dropwise. The yellow slurry turned dark purple as it was warmed. The reaction mixture was stirred for 1-2 hours at ambient temperature. After this time, the reaction mixture was filtered through Celite and the filtrate was transferred to a fresh scintillation vial. A pentane slurry of ^{Cy}APDI ligand (0.326 g, 1.00 mmol) was added dropwise to the stirring solution. The purple solution immediately turned dark violet. This mixture was stirred for 1-2 hours at ambient temperature. The mixture was then cooled to -35 °C and filtered to afford 0.460 g (83 %) of 2-(CH₂SiMe₃)₂ as a dark purple crystalline solid. Crystals suitable for X-ray diffraction were grown from a solution of pentane at -35 °C. The compound is indefinitely stable at 23 °C in an inert atmosphere and slowly decomposes upon heating to 45 °C in benzene-*d*₆ solution. Analysis for C₂₉H₅₃N₃FeSi₂: Calcd C, 62.67; H, 9.54; N, 7.56. Found: C, 62.43; H, 9.26; N, 7.83. Magnetic susceptibility: μ_{eff} = 4.7 μ_B (benzene-*d*₆, 23 °C). ¹H NMR (benzene-*d*₆), δ = 212.90 (1192 Hz, 1H, *p*-pyr), 47.89 (64 Hz, 1H imine-cyclohexyl ipso CH), 39.79 (147 Hz, 2H, *m*-pyr), 9.05 (295 Hz), 2.48-0.79 (cyclohexyl CH's), -81.83 (100 Hz, imine-cyclohexyl ipso CH), -133.16 (737 Hz, 6H, C(CH₃)).

Characterization of Hydrosilylation Products by Gas Chromatography. Gas chromatography for the diphenyl silyl ethers was performed on a Shimadzu GC-2010 gas chromatograph. GC analyses were performed using a Restek 15 m x 0.25 mm RTX-5 5% diphenyl-95% dimethyl polysiloxane column with a film thickness 0.25 μm . The following temperature program was used: 30 $^{\circ}\text{C}$, 3 min; 10 $^{\circ}\text{C}/\text{min}$ to 80 $^{\circ}\text{C}$; and 15 $^{\circ}\text{C}/\text{min}$ to 245 $^{\circ}\text{C}$, 5 min. The corresponding alcohols were analyzed on a Supelco 30 m x 0.25 mm BETA DEX 120 capillary column. Temperature programs for the various alcohols are as follows:

1-Phenylethanol. 60 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 100 $^{\circ}\text{C}$; and 15 $^{\circ}\text{C}/\text{min}$ to 150 $^{\circ}\text{C}$, 5 min.
Enantiomer retention times: 13.8 min (R), 13.97 min

1-(4-*tert*-butylphenyl)ethanol. 80 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, 5 min; and 15 $^{\circ}\text{C}/\text{min}$ to 170 $^{\circ}\text{C}$, 10 min. Enantiomer retention times: 14.54 min, 15.11 min.

(1-(4-methoxyphenyl)ethanol. 80 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, 5 min; and 15 $^{\circ}\text{C}/\text{min}$ to 170 $^{\circ}\text{C}$, 10 min. Enantiomer retention times: 21.40 min, 21.59 min

(1-(2,4-dimethoxyphenyl)ethanol. 80 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, 10 min; and 15 $^{\circ}\text{C}/\text{min}$ to 170 $^{\circ}\text{C}$, 10 min. Enantiomer retention times: 33.18 min, 33.46 min.

(1-(4-(trifluoromethyl)phenyl)ethanol. 80 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, 5 min; and 15 $^{\circ}\text{C}/\text{min}$ to 170 $^{\circ}\text{C}$, 10 min. Enantiomer retention times: 14.54 min, 15.11 min.

(1-(4-(trifluoromethyl)phenyl)ethanol. 80 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, 5 min; and 15 $^{\circ}\text{C}/\text{min}$ to 170 $^{\circ}\text{C}$, 10 min. Enantiomer retention times: 14.54 min, 15.11 min.

(1-(3,5-(bistrifluoromethyl)phenyl)ethanol. 80 °C; 5 °C/min to 100 °C, 5 min; 5 °C/min to 100 °C, 5 min; and 15 °C/min to 170 °C, 8 min. Enantiomer retention times: 14.19 min, 14.88 min.

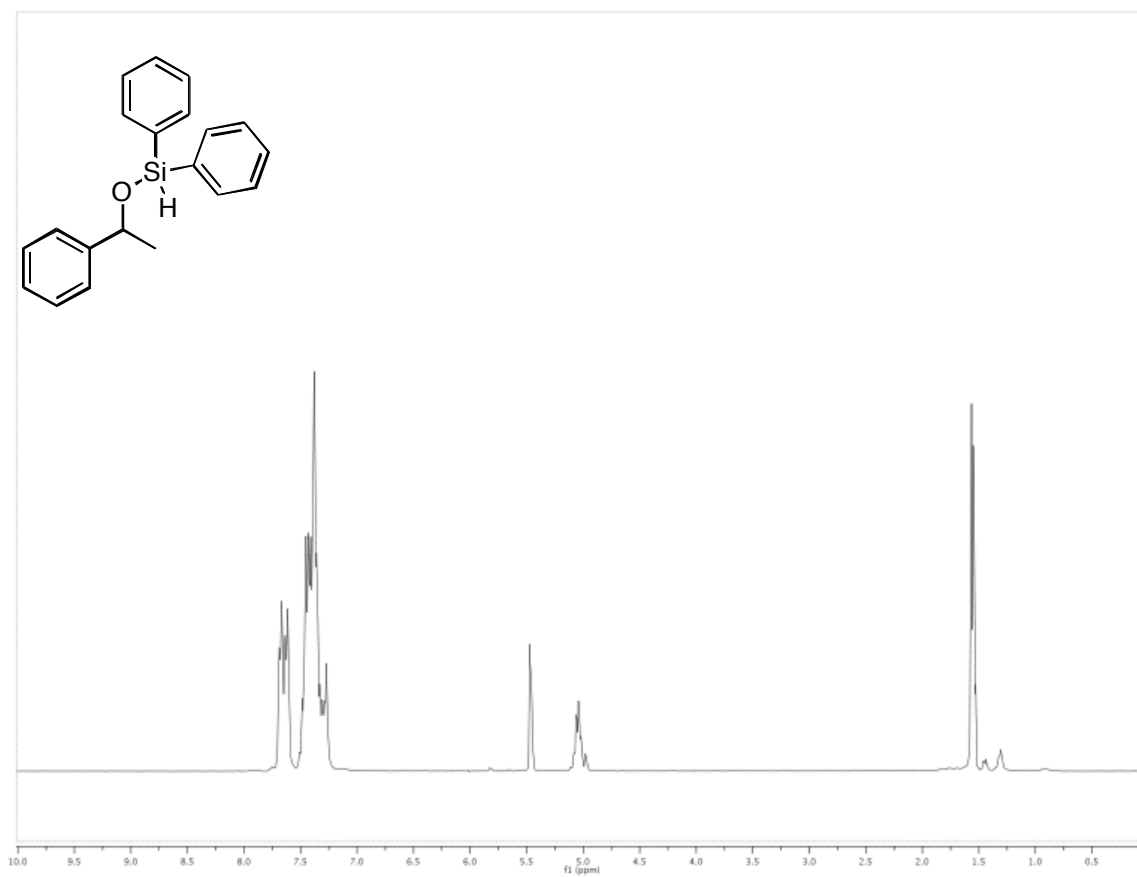
1-(4-(dimethylamino)phenyl)ethanol. 80 °C; 5 °C/min to 140 °C, 15 min; and 15 °C/min to 170 °C, 20 min. Alcohol retention time: 48.3 min.

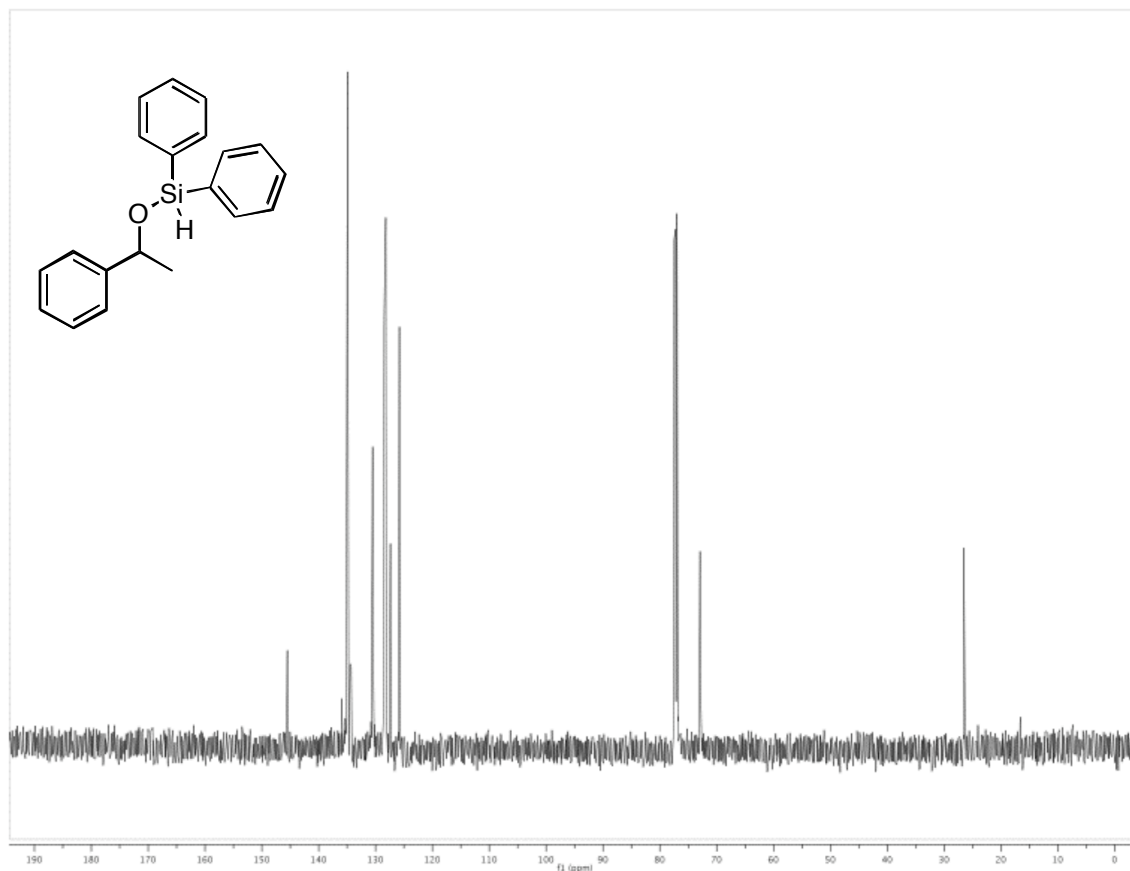
1,2,3,4-tetrahydronaphthalen-1-ol. 80 °C, 10 min; 5 °C/min to 110 °C, 8 min; and 15 °C/min to 160 °C, 11 min. Enantiomer retention times: 28.29 min, 28.53 min.

2-Hexanol. 60 °C, 10 min; 2 °C/min to 70 °C, 5 min; and 15 °C/min to 160 °C, 5 min. Enantiomer retention times: 16.22 min, 16.53 min.

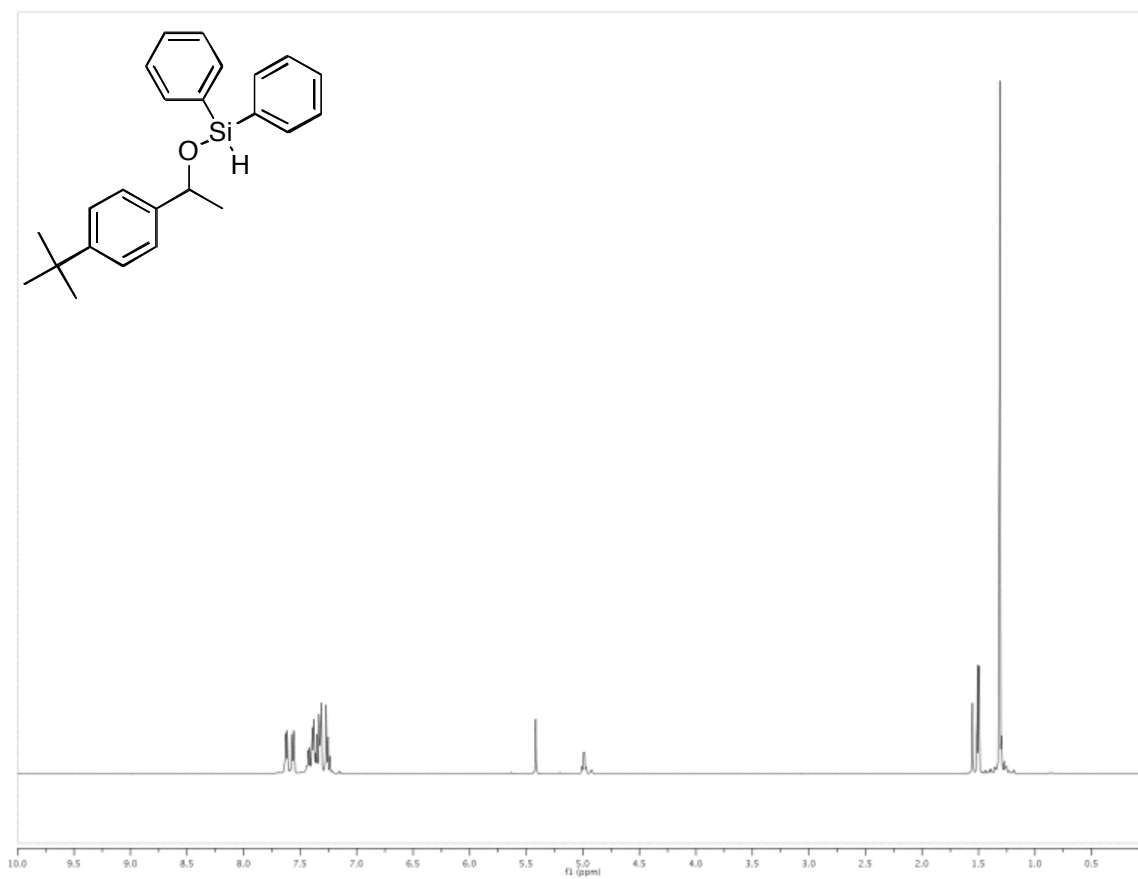
Characterization of Hydrosilylation Products.

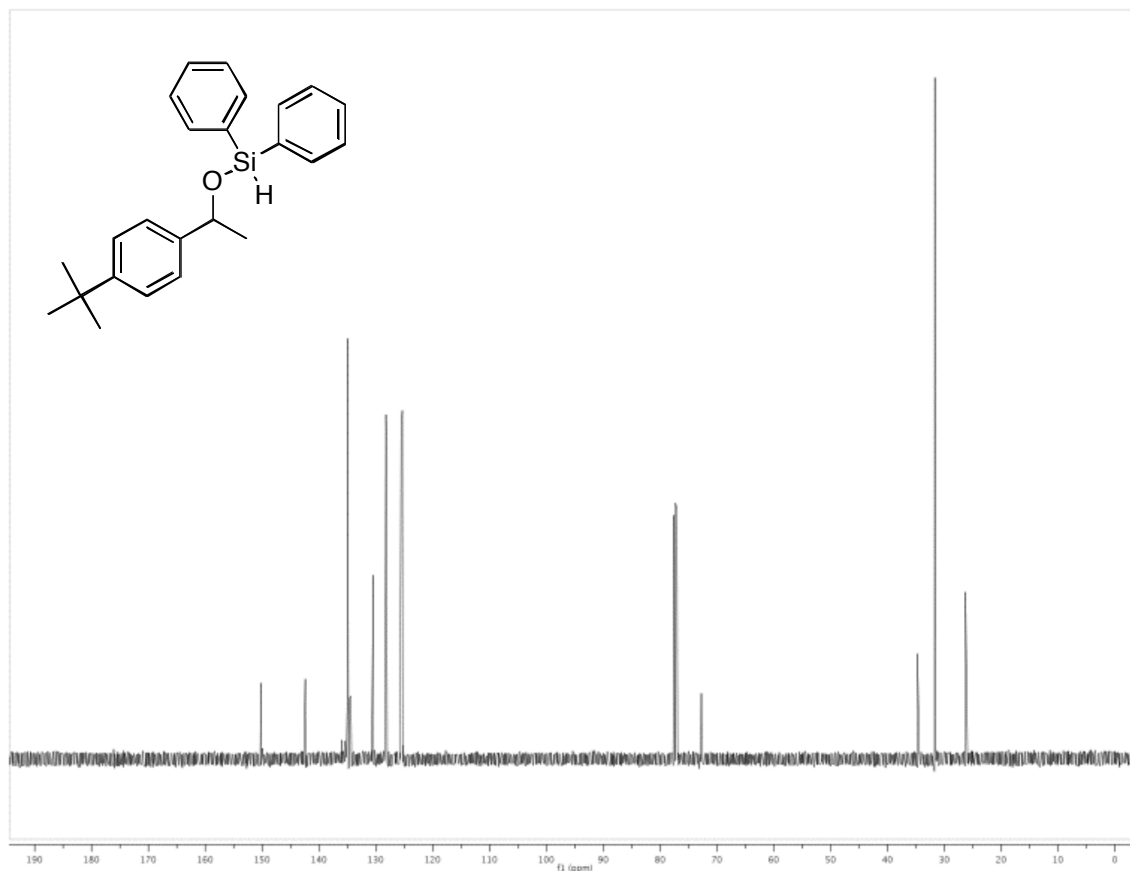
Preparation of Diphenyl(1-phenylethoxy)silane. A general hydrosilylation in pentane was performed. The solvent was removed and the product exhibited an ^1H NMR spectrum that matched the literature values. The retention time on the Restek RTX-5 column with the indicated temperature profile is 19.06 min. . ^1H NMR (chloroform-*d*). δ = 7.72-7.52 (dd, J = 7, 28 Hz, 4H, SiArH), 7.36-7.27 (m, 10H), 5.45 (s, 1H, SiH), 4.99 (q, 6Hz, 1H, CH), 1.49 (d, 6 Hz, 3H, CH_3), 1.33, (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 150.13, 142.34, 134.92, 134.90, 134.54, 134.33, 130.46, 130.39, 128.16, 128.10, 125.48, 125.28, 72.68, 34.67, 31.61, 26.23. ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 145.52, 134.97, 134.93, 134.50, 134.30, 130.59, 130.53, 128.49, 128.27, 128.20, 127.39, 125.81, 72.93, 26.52.



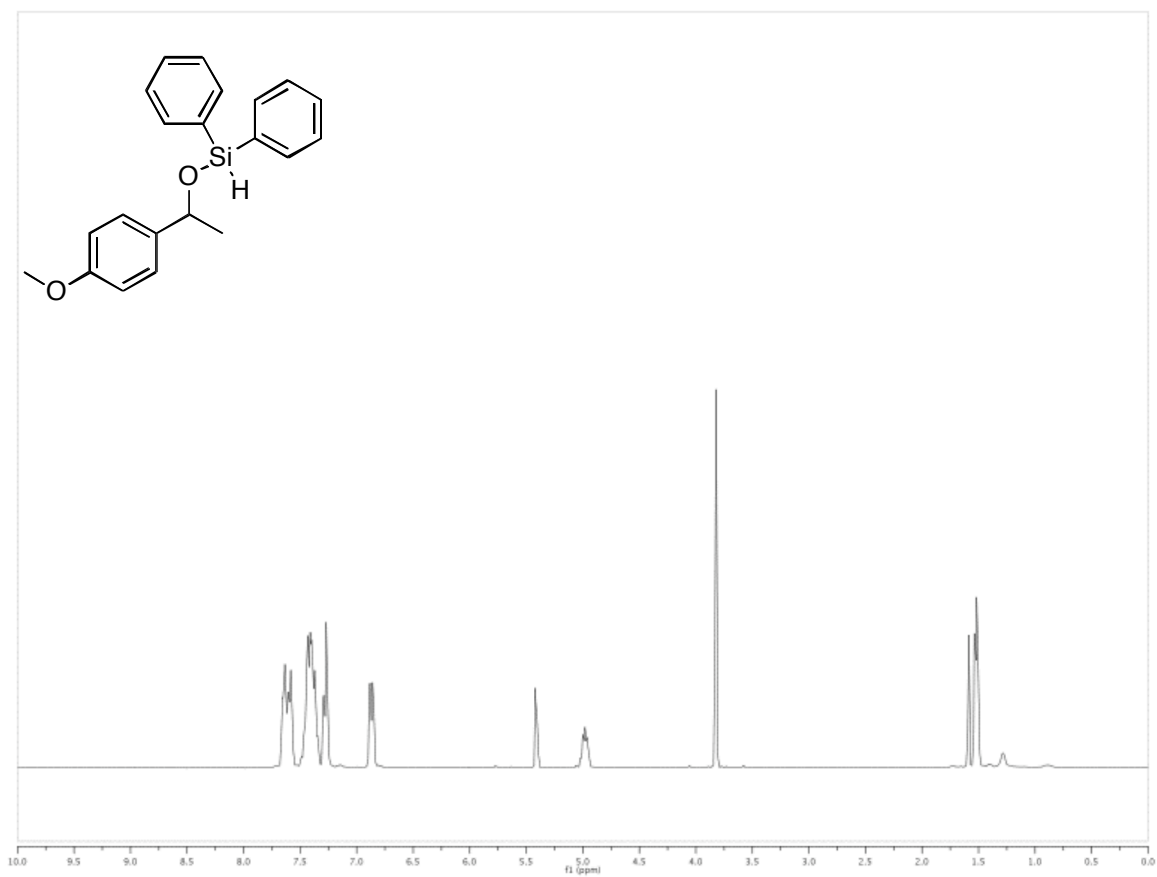


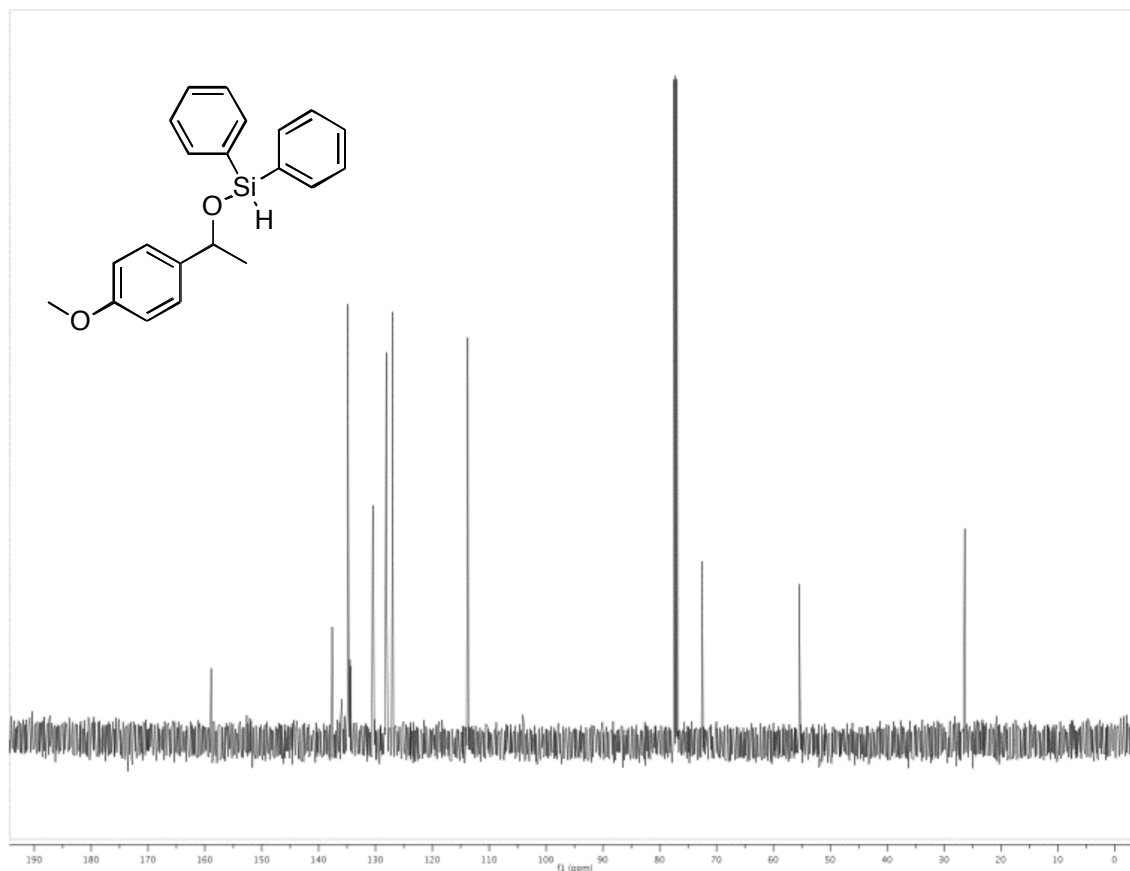
Preparation of (1-(4-*tert*-butylphenyl)ethoxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by GC and ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 21.36 min. ^1H NMR (chloroform-*d*). δ = 7.72-7.52 (dd, J = 7, 28 Hz, 4H, SiArH), 7.36-7.27 (m, 10H), 5.45 (s, 1H, SiH), 4.99 (q, 6Hz, 1H, CH), 1.49 (d, 6 Hz, 3H, CH_3), 1.33, (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 150.13, 142.34, 134.92, 134.90, 134.54, 134.33, 130.46, 130.39, 128.16, 128.10, 125.48, 125.28, 72.68, 34.67, 31.61, 26.23. MS (%) m/z 360 (M^+ , 3), 344 (16), 225 (23), 199 (100), 183 (64)



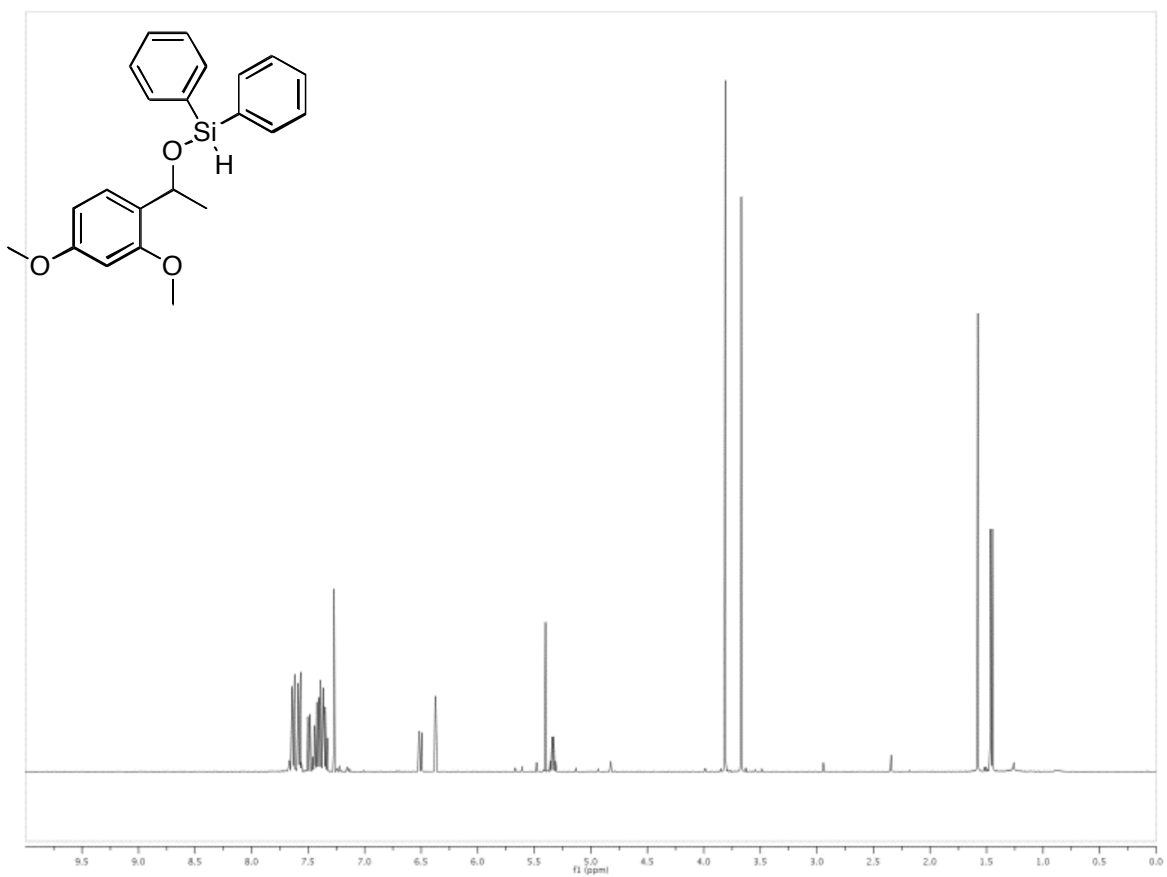


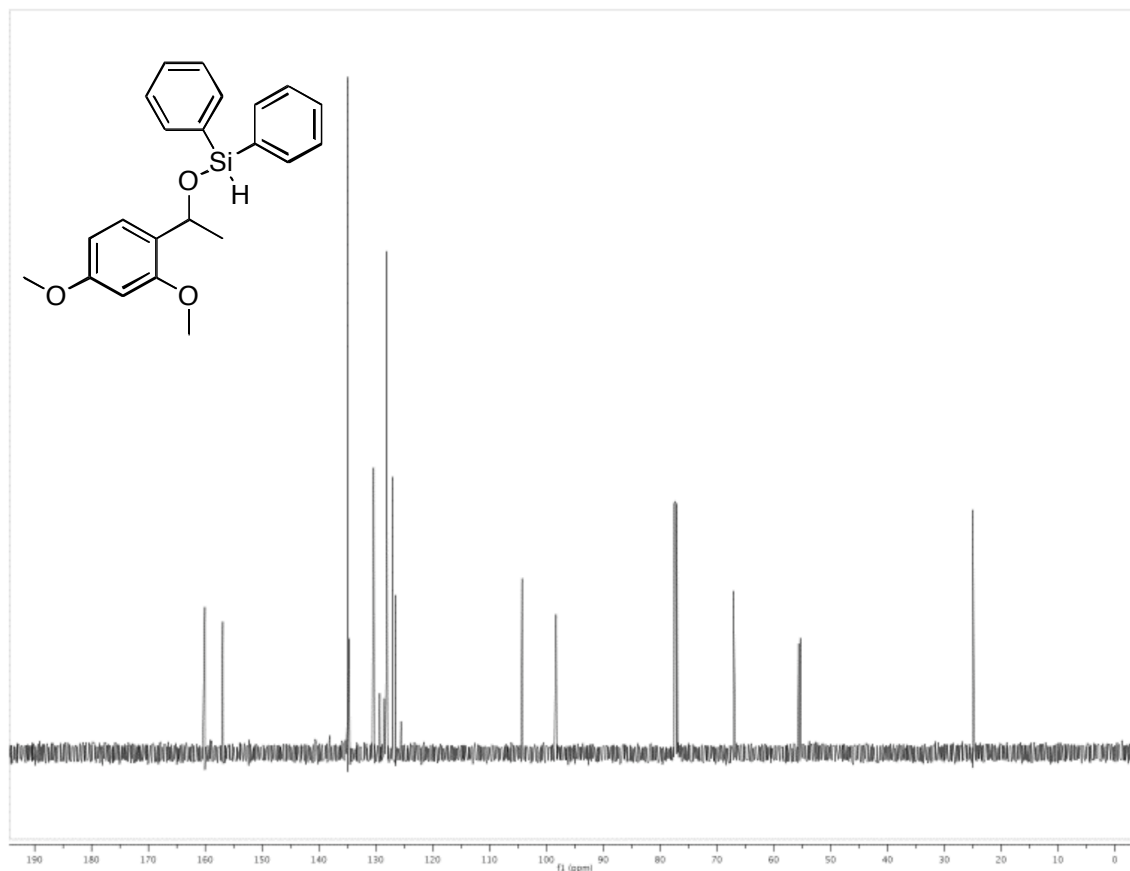
Preparation of (1-(4-methoxyphenyl)ethoxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by GC and ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 21.07 min. ^1H NMR (chloroform-*d*). δ = 7.62-7.56 (dd, 7, 26 Hz, 4H, SiArH), 7.38-7.14 (m, 8H), 6.81 (d, 2H, Ar), 5.41(s, 1H, SiH), 4.95 (q, 6, Hz, 1H, CH), 3.70 (s, 3H, OCH₃), 1.48 (d, 6 Hz, 3H, CH₃). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 158.91, 137.62, 134.89, 134.85, 134.49, 134.32, 130.47, 130.39, 128.17, 128.10, 127.02, 113.75, 72.53, 55.45, 26.34.



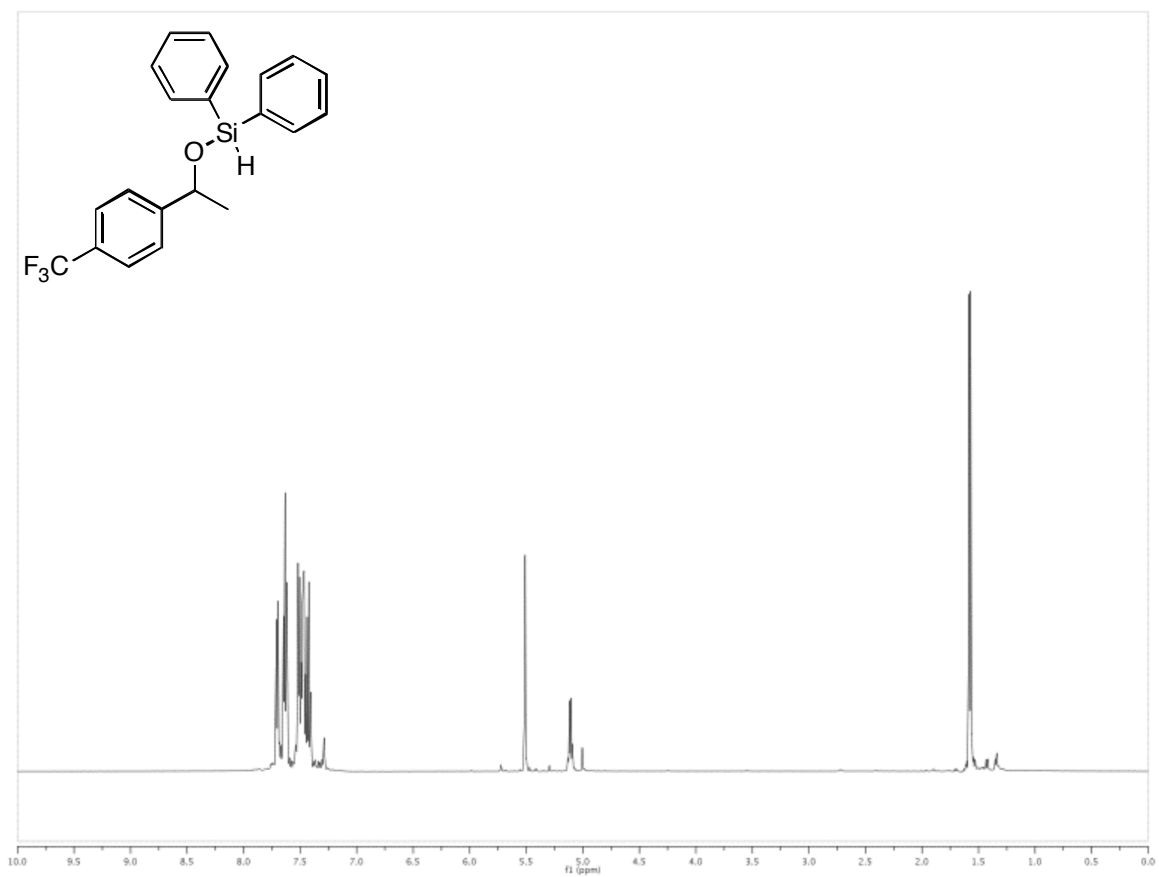


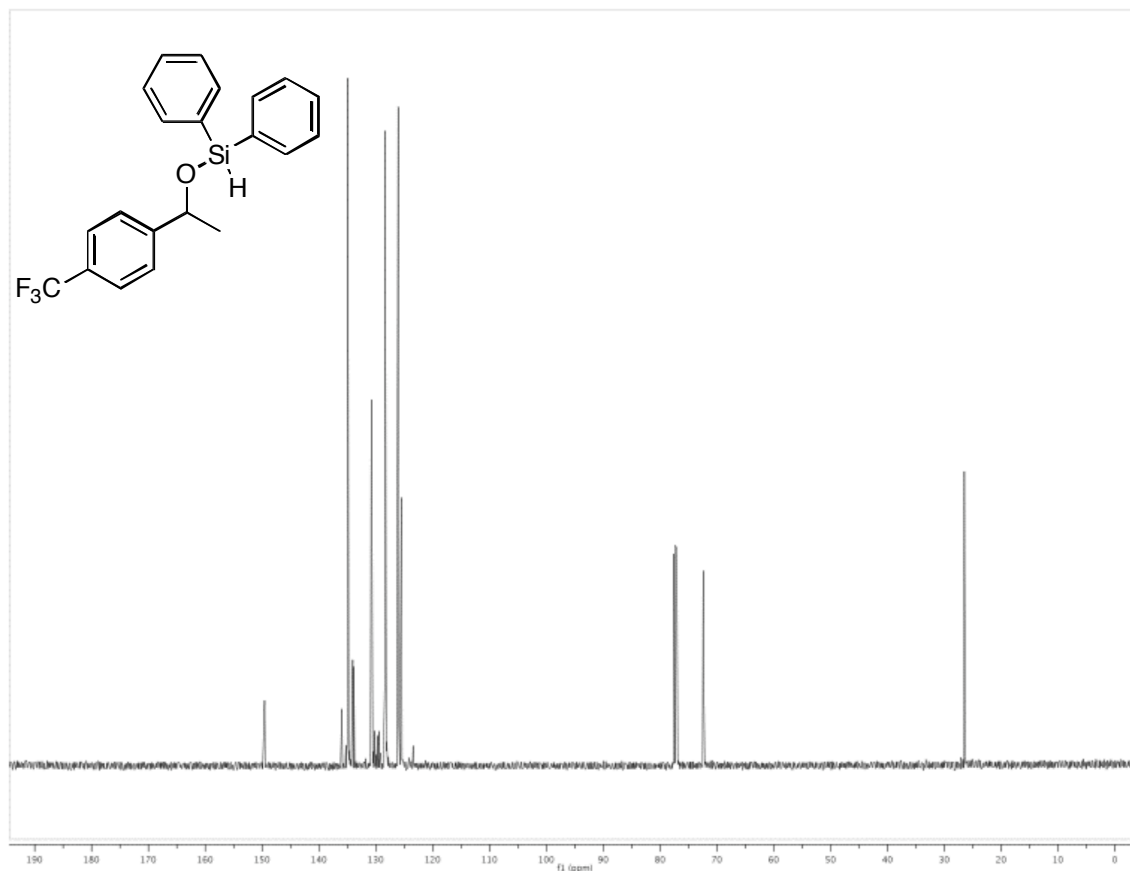
Preparation of (1-(2,4-dimethoxyphenyl)ethoxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by GC and ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 22.66 min. ^1H NMR (chloroform-*d*). δ = 7.70-7.55 (dd, 7, 26 Hz, 4H, SiArH), 7.49 (d, 7 Hz, 1H, Ar), 7.48-7.30 (m, 6H), 6.47 (dd, 2, 8 Hz, 1H, Ar), 6.34 (d, 2 Hz, 1H, Ar), 5.42 (s, 1H, SiH), 5.35 (q, 6 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 1.46 (d, 6 Hz, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 160.00, 156.85, 134.88, 134.83, 134.65, 130.32, 130.25, 129.24, 128.44, 128.08, 128.01, 126.97, 126.43, 125.50, 67.03, 55.53, 55.26, 24.92. MS (%) m/z 364 (M^+ , 22), 349 (100), 271 (22), 227 (18), 199 (30), 183 (57), 165 (55), 151 (100).



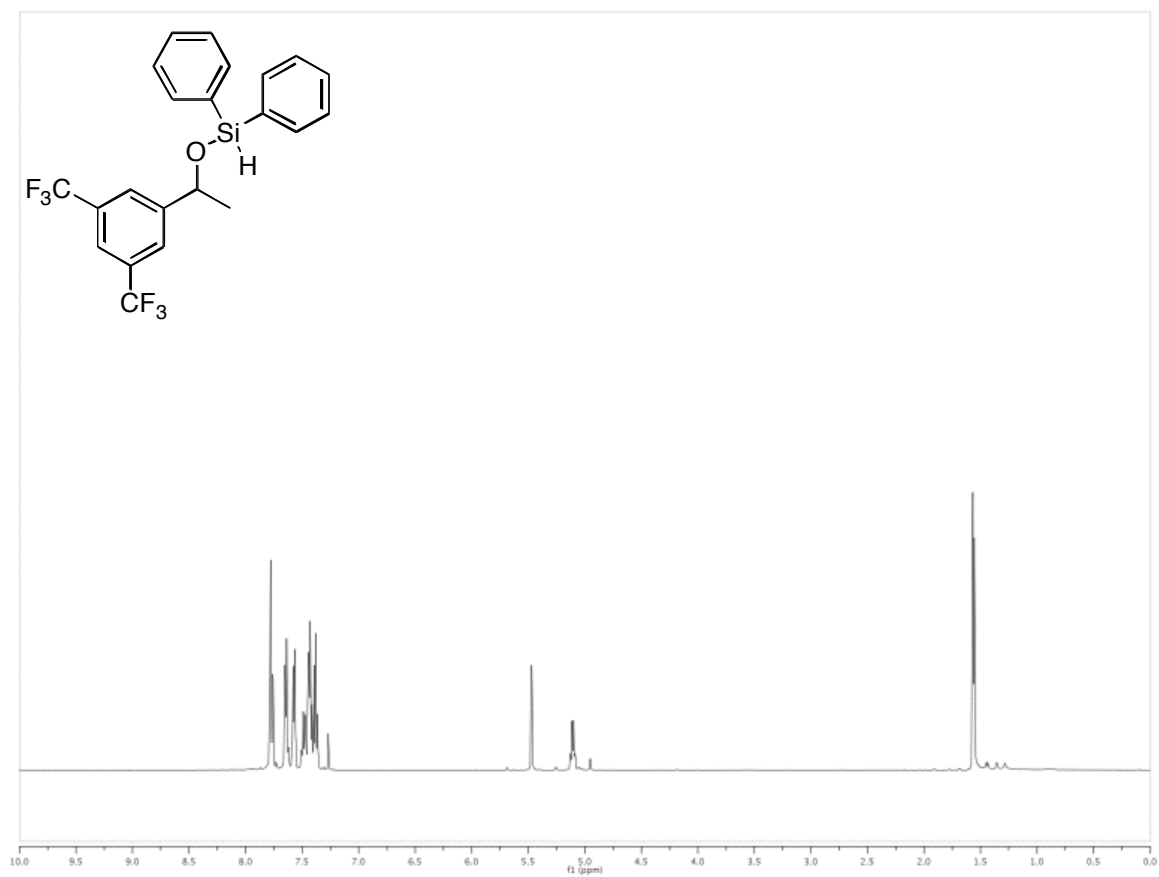


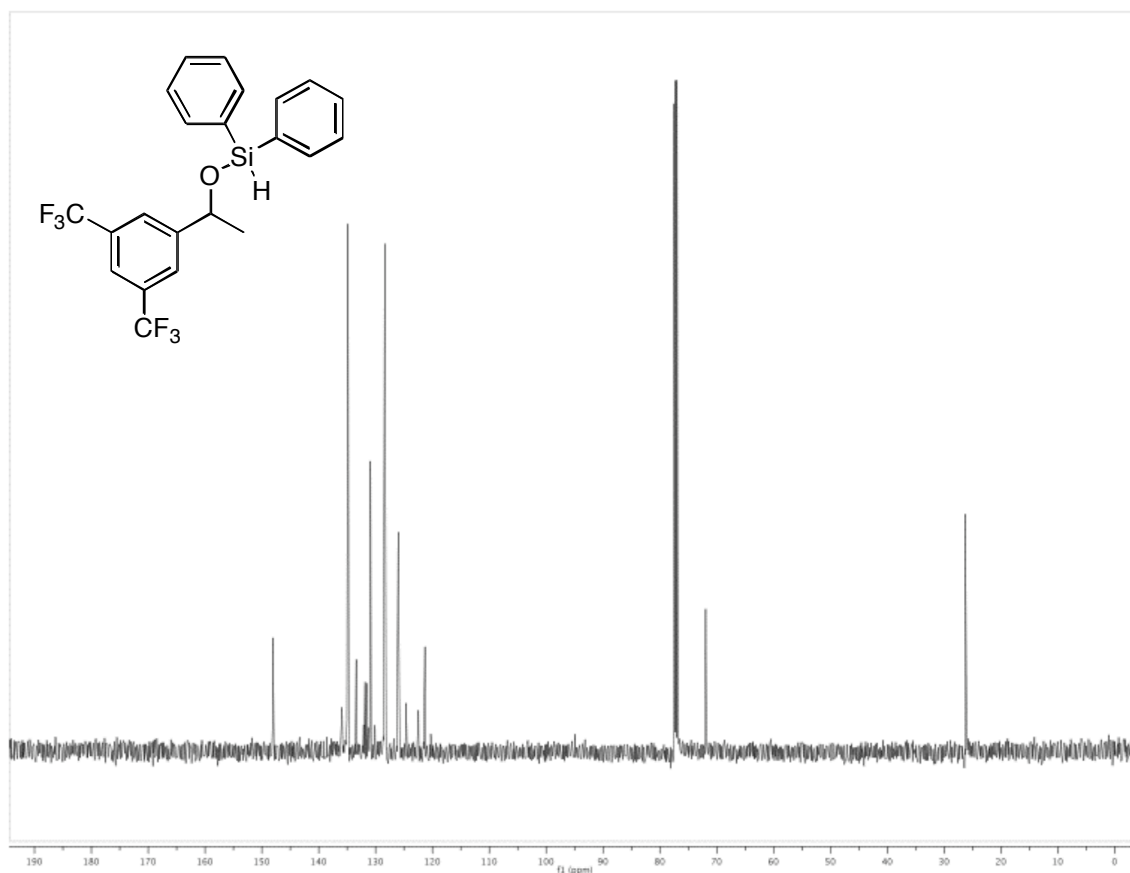
Preparation of (1-(4-(trifluoromethyl)phenyl)ethoxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by GC and ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 18.81 min. ^1H NMR (chloroform-*d*). δ = 7.71-7.66 (d, 8Hz, 2H), 7.64-7.59 (m, 4H, Ar), 7.52-7.38 (m, 8H), 5.49 (s, 1H, SiH), 5.09 (q, 6 Hz, 1H, CH), 1.56 (d, 6 Hz, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 149.55, 135.97, 134.90, 134.48, 134.05, 133.88, 130.79, 130.74, 128.38, 128.32, 126.07, 125.52 (q, J_{CF} 4 Hz), 123.45, 72.39, 26.46. MS (%) m/z 372 (M^+ , 4), 357 (38), 294 (61), 279 (84), 235 (38), 225 (61), 216 (22), 199 (100), 183 (95).



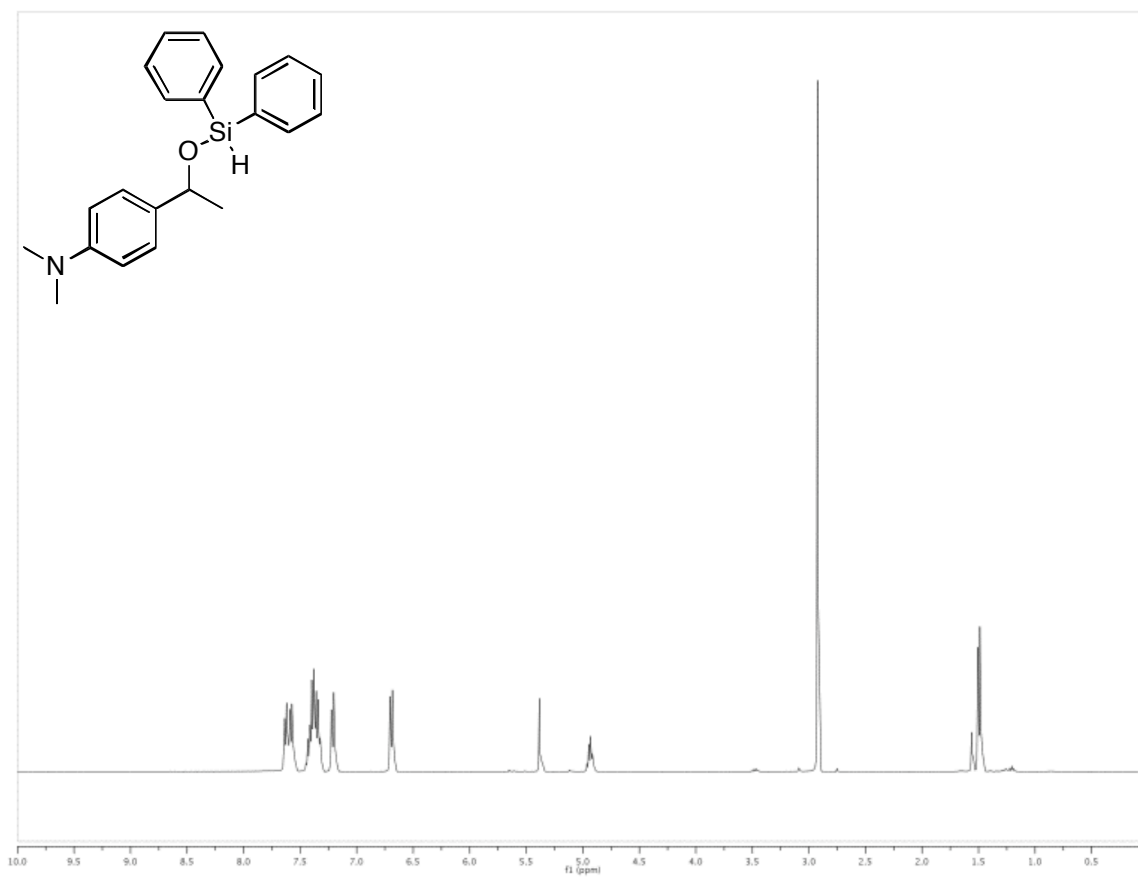


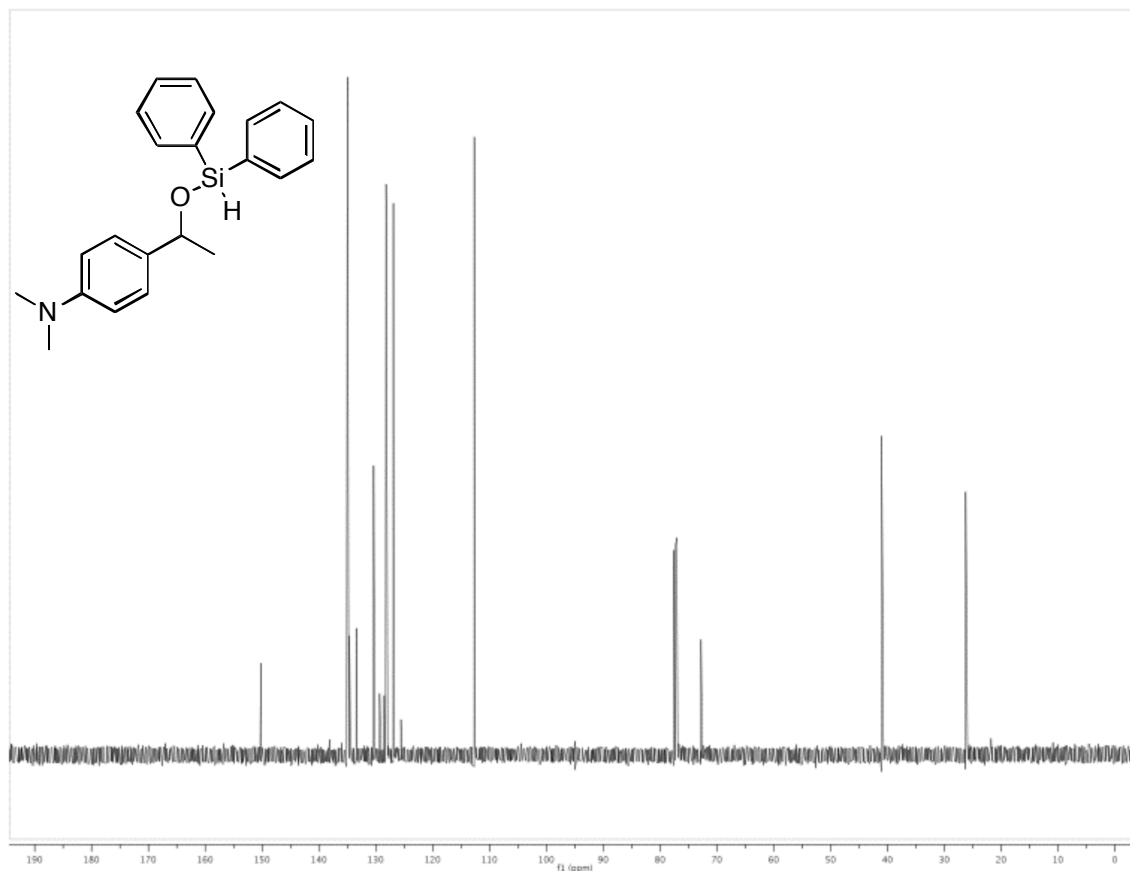
Preparation of (1-(3,5-bis-trifluoromethyl)ethoxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by GC and ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 17.31 min. ^1H NMR (chloroform-*d*). δ = 7.78 (s, 2H, Ar), 7.76 (s, 1H, Ar), 7.65 (d, 7 Hz, 2H), 7.57 (d, 7 Hz, 2H), 7.52-7.34 (m, 6H, Ar), 5.47 (s, 1H, SiH), 5.11 (q, 6 Hz, 1H, CH), 1.56 (d, 6H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 148.08, 135.90, 134.87, 134.81, 133.42, 133.35, 130.89, 130.86, 128.38, 128.34, 126.02, 124.64, 122.47, 121.32 (q, J_{CF} 3 Hz), 71.95, 26.30. MS (%) m/z 439 (M^+ , 3), 421 (11), 362 (90), 240 (12), 222 (79), 199 (100), 183 (90).



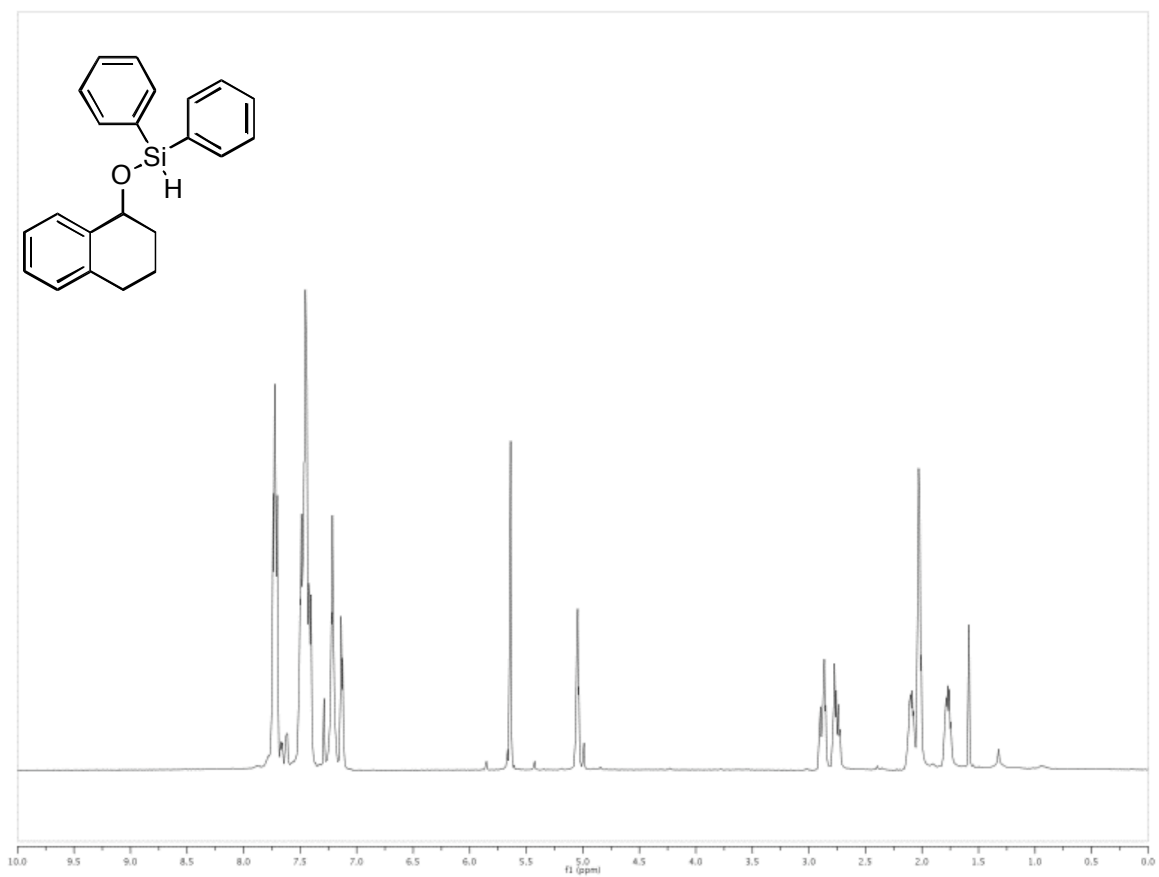


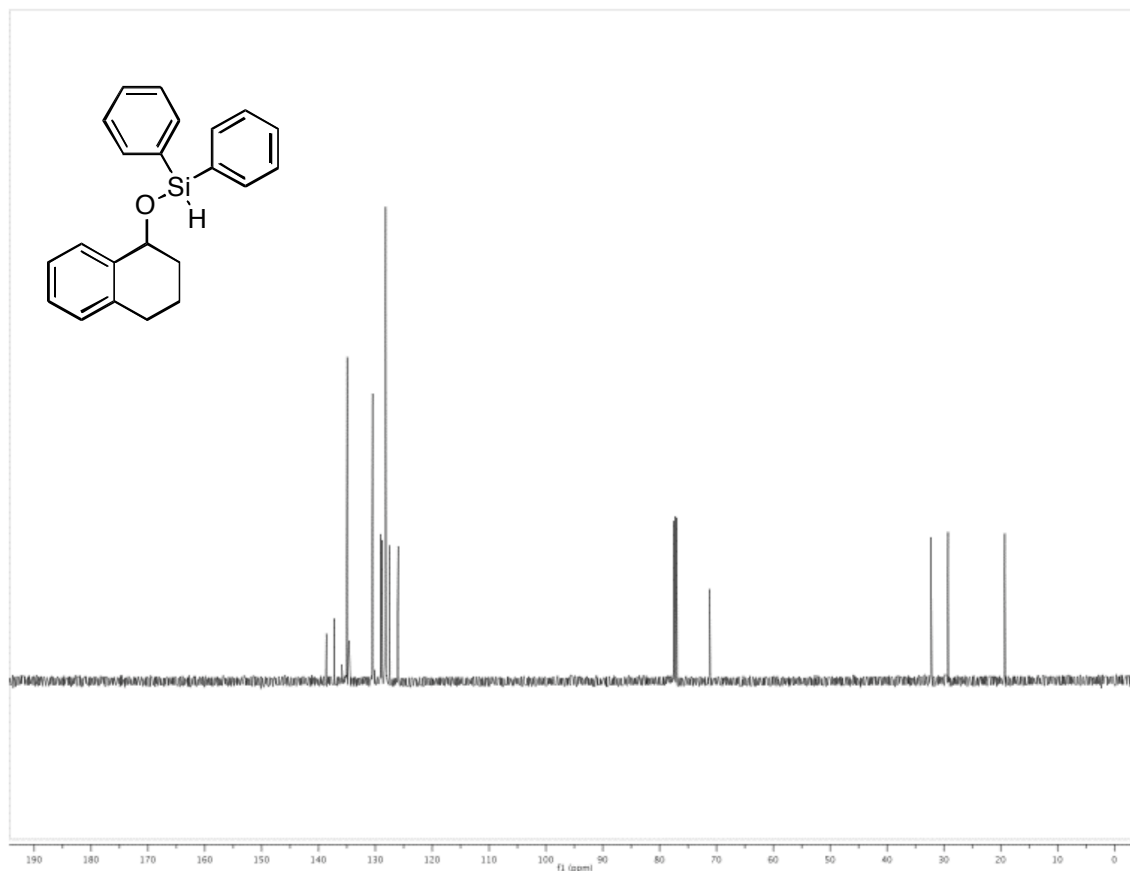
Preparation of 4-(1-(diphenylsiloxy)ethyl)-N,N-dimethylbenzenamine. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by ¹H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 23.21 min. ¹H NMR (chloroform-*d*). δ = 7.73-7.58 (m, 4H, SiArH), 7.52-7.36 (m, 6H), 7.28-7.25 (dd, 1, 9 Hz, 2H), 6.78-6.71 (dd, 1, 9 Hz, 2H), 5.44 (d, 1 Hz, 1H, SiH), 5.03-4.96 (q, 6Hz, 1H, CH), 2.99 (s, 6H, NMe₂) 1.56 (d, 6 Hz, 3H, CH₃). ¹³C {¹H} NMR (chloroform-*d*). δ = 150.13, 142.35, 134.92, 134.90, 134.54, 134.33, 130.46, 130.39, 128.16, 128.10, 125.28, 72.68, 34.67, 31.61, 26.23



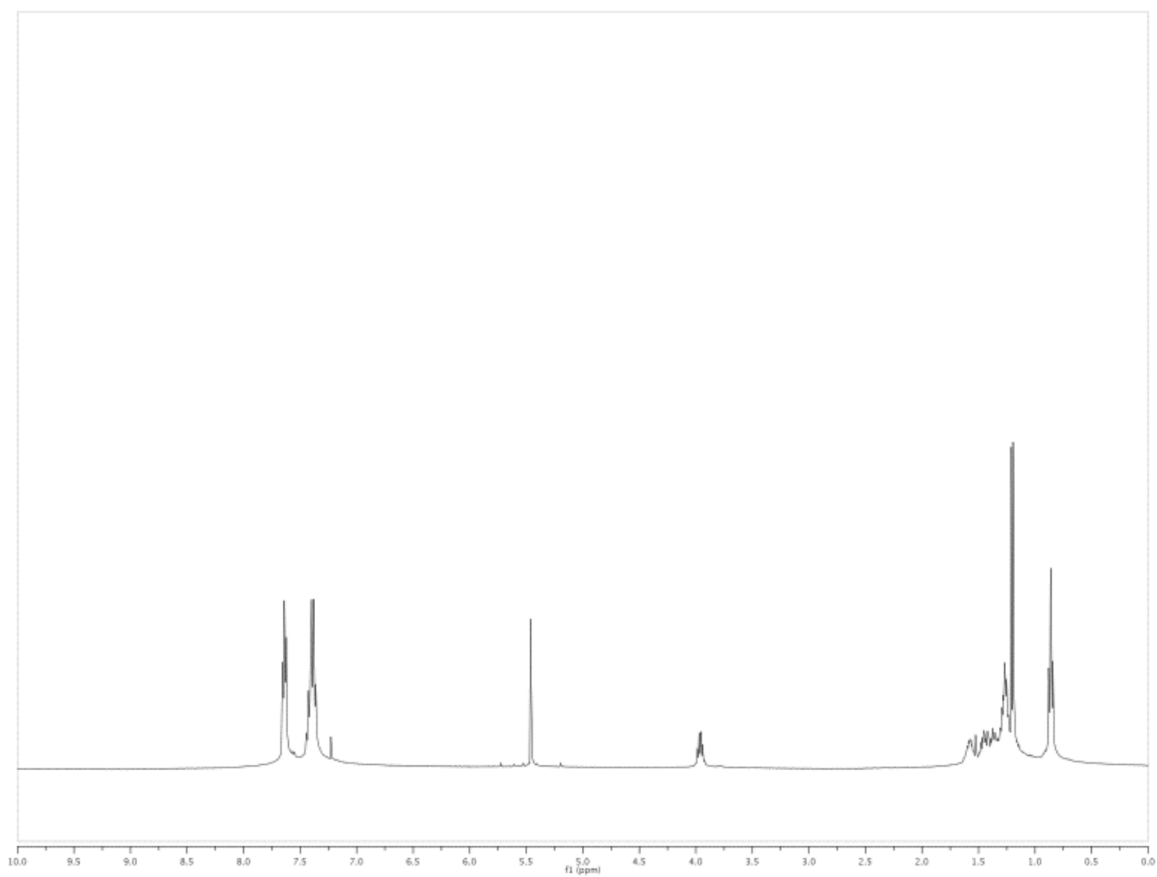


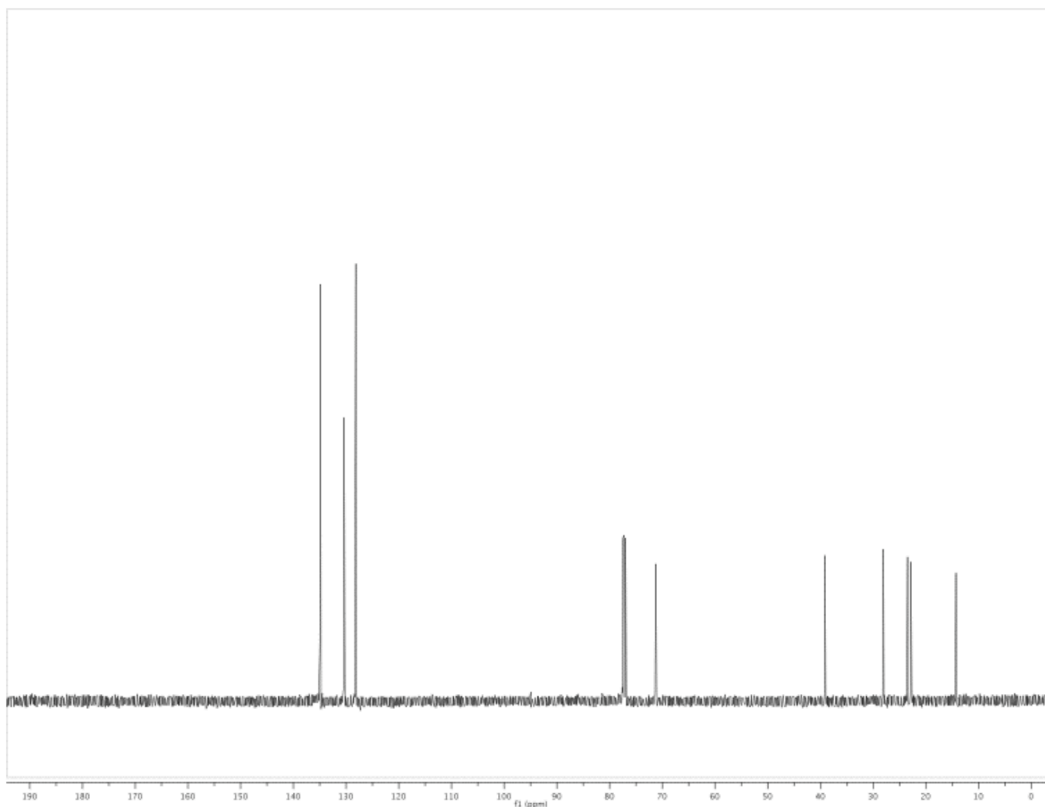
Preparation of Diphenyl(1,2,3,4-tetrahydronaphthalen-1-yloxy)silane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 22.14 min. ^1H NMR (chloroform-*d*). δ = 7.67-7.55 (m), 7.13-7.03 (m), 5.59 (s, 1H, SiH), 4.97 (t, 5 Hz, 1H, CH), 2.70 (m, 2H, CH_2), 2.00-1.93 (m, 4H), 1.66-1.64 (m, 2H). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 138.62, 137.25, 134.96, 134.96, 134.71, 134.59, 130.48, 129.03, 128.83, 128.19, 127.51, 126.00, 71.17, 32.28, 29.26, 19.28. MS (%) m/z 330 (M^+ , 5), 301 (11), 287 (22), 252 (41), 224 (31), 199 (100), 183 (31)





Preparation of (Hexan-2-yloxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 17.29 min. ^1H NMR (chloroform-*d*). δ = 7.72-7.65 (m, 4H), 7.50-7.38(m, 6H), 5.47 (s, 1H, SiH), 3.96 (m, 1H, CH), 1.57-1.20 (m, 9H). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 134.88, 134.86, 130.38, 128.14, 71.22, 39.14, 28.06, 23.47, 22.82, 14.28. MS (%) m/z 283 (M^+ , 7), 269 (10), 227 (95), 206 (76), 199 (70), 183 (100)





Preparation of (Hex-5-en-2-yloxy)diphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is 17.29 min. ^1H NMR (chloroform-*d*). δ = 7.74-7.60 (m, 4H), 7.51-7.32 (m, 6H), 5.87-5.73 (m, 1H), 5.49 (s, 1H, SiH), 5.04-4.91(dd, 21, 7 Hz, 2H), 4.02 (m, 1H, CH), 2.28-2.04 (m, 2H). 1.76-1.64 (m, 2H), 1.23(d, 8 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (chloroform-*d*). δ = 138.80, 135.95, 134.93, 130.49, 128.22, 114.76, 70.66, 38.64, 30.20, 23.49. MS (%) m/z 281 (M^+ , 2), 227 (26), 204 (40), 199 (23), 183 (100)

Preparation of 4-methylbenzyloxydiphenylsilane. A general hydrosilylation in pentane was performed. The solvent was removed and the product was characterized by ^1H NMR. The retention time on the Restek RTX-5 column with the indicated temperature profile is

20.05 min. ¹H NMR (chloroform-*d*). δ = 7.79-7.60 (dd, 4H), 7.50-7.30 (m, 6H), 7.26-7.09 (m, 4H), 4.83 (s, 1H, SiH), 4.80 (s, 2H, CH₂), 2.35 (s, 3H, CH₃). MS (%) *m/z* 304 (M⁺, 4), 225 (8), 211 (23), 199 (100), 183 (11)

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