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Transition-Metal- and Solvent-Free Regioselective Hydrosilylation of Alkenes and Allenes Enabled by Catalytic Sodium *tert*-Butoxide

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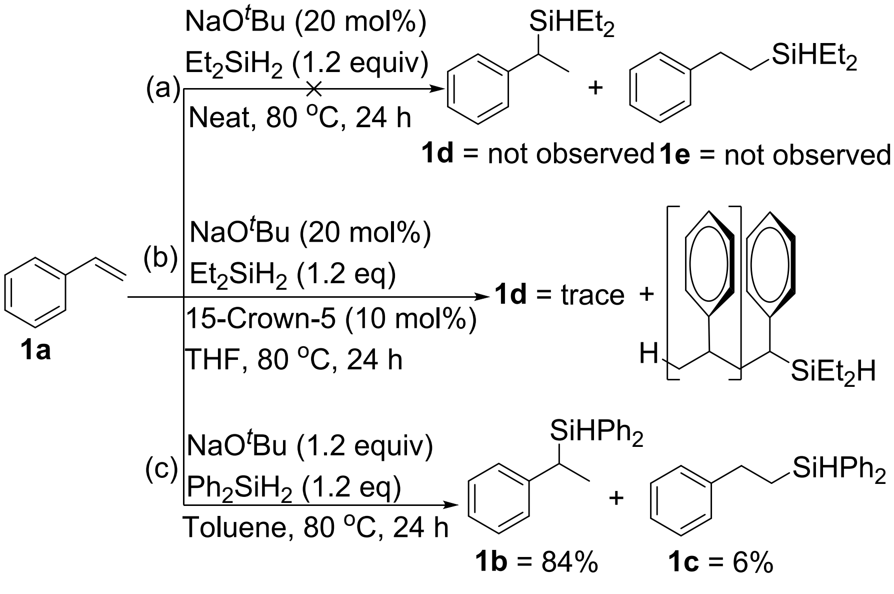
I. General Information

Unless otherwise noted all the reactions are performed in nitrogen filled KIYON glove box or using standard Schlenk technique. All chemicals including all the styrene derivatives are purchased either from Sigma Aldrich, TCI chemicals, BLDpharm, Alfa Aesar, Spectrochem, Avra-chemicals and Combi block and used without further purification unless mentioned. Reagent grade solvents are purchased from SD Fine Chemicals (India), distilled, and deoxygenated by freeze pump thaw cycle (three to four times) before using. Anhydrous toluene was distilled from CaH_2. Anhydrous tetrahydrofuran (THF) was distilled from sodium and benzophenone. Diphenylsilane (97 %) and sodium tert-butoxide (99.9 %) were used throughout all the experiments purchased from Sigma Aldrich. $CDCl_3$ and C_6D_6 were purchased from either Cambridge Isotope Laboratories or Sigma Aldrich and deoxygenated by freeze pump thaw cycle and stored over molecular sieves before use. Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV254 was purchased from MACHEREY-NAGEL GmbH & Co. KG. The removal of solvent was performed on a rotary evaporator in vacuum at a maximum temperature of 45 ºC. All NMR spectra (^1H (400 MHz / 500 MHz), $^{13}C\{^1H\}$ (100 MHz/ 125MHz) and ^{29}Si (80 MHz/ 100MHz) NMR were recorded by a Bruker Avance 400 or 500 MHz NMR spectrometer at an ambient temperature. ^1H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm), whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent (C_6D_6: 128.0 ppm). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment].

GC-MS data were acquired using SHIMADZU GC-MS QP 2010SE system. Infrared (IR) spectra (AT-IR) were recorded from Bruker-ALPHA and OriginPro 9.0 64Bit software was used to plot the data. Absorptions are reported in cm^{-1}. High resolution mass spectrometry was performed on "Micromass Q-TOF Micro instrument. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL, JES-X320.

II. Optimization of the reaction conditions for the alkenes hydrosilylation

We hypothesize that silanes having aromatic rings may provide additional stabilization *via* Na^+–π interaction in hypervalent 'ate' species. To render this hypothesis, styrene (**1a**) was employed as a model substrate; reactions were performed with various silylating reagents at 80 °C for 24 h (Table S6). The reaction of styrene with Et_2SiH_2 and NaO*ᵗ*Bu in neat condition showed no product formation, which is confirmed by GC-MS analysis (Schemes S1a). Reaction in the presence of 15-crown-5 gave polymeric product, indicating the generation of benzyl radical followed by its addition to other styrene molecules (Scheme S1b). Importantly, reaction of **1a** with diphenyl silane (Ph_2SiH_2) gave 84% yield of hydrosilylation product at 80 °C (Scheme S1c). The presence of phenyl ring at the silane reagent (Ph_2SiH_2) is believed to be crucial in this transformation by providing additional stabilization to Na^+ and possibly assisting in the formation of hydrogen atom for the subsequent step (by comparing Schemes S1a and S1c). The ^{1}H NMR of the isolated product showed formation of branched hydrosilylation product **1b**.



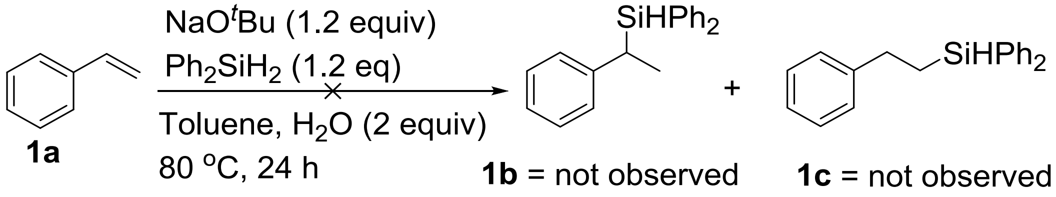
Scheme S1. Screening of silylating reagents for the hydrosilylation of styrene (**1a**).

Experimental Procedures.

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), R_2SiH_2 (R = Et or Ph; 1.2 equiv, 0.3 mmol) and NaO^tBu (28 mg, 1.2 equiv, 0.3 mmol) were added. The reaction mixture was stirred at 80 ºC for 24 h. The crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The product yield was determined from ^1H NMR using nitromethane as an internal standard.

In Scheme S1b, additionally 15-crown-5 (10 mol%) was added to the reaction mixture in THF solvent (1 mL).

In addition, no product was observed when the reaction carried out in the presence of H_2O (10 µL, 2 equiv; 0.5 mmol), probably due to the decomposition of NaO^tBu (Scheme S2). The GC-MS analysis of the reaction mixture shows the presence of ^tBuOH. Therefore, NaO^tBu may reacted with H_2O to form ^tBuOH.

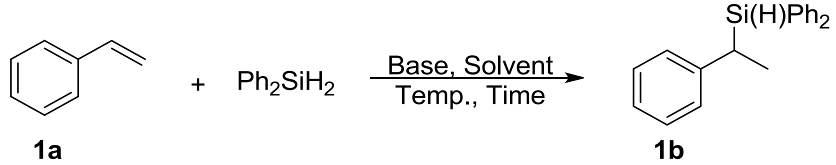


Scheme S2. Hydrosilylation of styrene (**1a**) in the presence of H_2O.

Experimental procedures described in Table 1.

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), Ph_2SiH_2 (0.3 mmol), base (0.3 mmol) and solvent (1 mL) were added. The reaction mixture was stirred for indicated amount of time. The crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of celite. The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ^1H NMR using nitromethane as an internal standard.

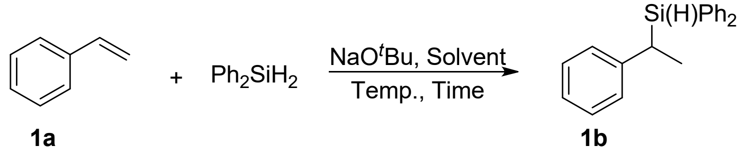
Table S1: Screening of the base for the hydrosilylation of styrene (**1a**).



Entry	Ph_2SiH_2 (equiv)	Base (1.2 equiv)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1	1.2	KOMe	Toluene	80	18	63
2	1.2	NaOMe	Toluene	80	18	0
3[c]	1.2	KO*t*Bu	Toluene	80	18	7
4	**1.2**	**NaO*t*Bu**	**Toluene**	**80**	18	**84**
5	1.2	K_2CO_3	Toluene	80	18	0
6	1.2	NaOEt	Toluene	80	18	0
7	1.2	NaH	Toluene	80	18	7
8	1.2	-	Toluene	80	18	0

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), Base (1.2 equiv, 0.3 mmol), toluene at 80 ºC for 18 h. [b]Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. [c] Styrene hydrosilylation with 1.2 equiv of Ph_2SiH_2 as silane reagent and 0.2 equiv of KO*t*Bu as a base catalyst under neat condition at 80 °C temperature for 24 h yielded 6% of **1b**.

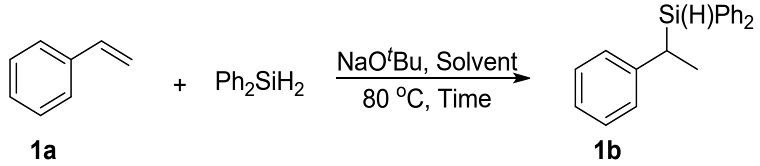
Table S2: Screening of the temperature for the hydrosilylation of styrene (**1a**).[a]



Entry	Ph_2SiH_2 (equiv)	Base (1.2 equiv)	Temp. (˚C)	Solvent	Time (h)	Yield (%)
1	1.2	NaO^{t}Bu	RT	Toluene	18	8
2	1.2	NaO^{t}Bu	50	Toluene	18	51
3	**1.2**	**NaO^{t}Bu**	**80**	**Toluene**	**18**	**84**
4	1.2	NaO^{t}Bu	100	Toluene	18	79

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (1.2 equiv, 0.3 mmol), toluene at given temperature for 18 h. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

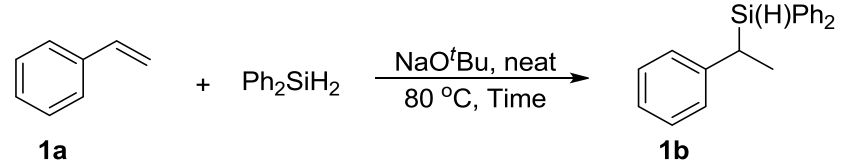
Table S3: Screening of the solvent for the hydrosilylation of styrene (**1a**).[a]



Entry	Ph_2SiH_2 (equiv)	Base (1.2 equiv)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1[c]	1.2	NaO^{t}Bu	DMF	80	18	0
2	1.2	NaO^{t}Bu	Acetonitrile	80	18	0
3	1.2	NaO^{t}Bu	Toluene	80	18	84
4	1.2	NaO^{t}Bu	MTBE	80	18	85
5	1.2	NaO^{t}Bu	Fluorobenzene	80	18	77
6	1.2	NaO^{t}Bu	THF	80	18	85
7	**1.2**	**NaO^{t}Bu**	**Neat**	**80**	**18**	**96**

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (1.2 equiv, 0.3 mmol), solvent at 80 ºC for 18 h. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard. [c]The GC-MS analysis of the reaction mixture showed the presence of dimethylamine, probably due to the reduction of DMF under the reaction conditions. The ^{29}Si NMR of the reaction mixture shows resonance at δ = –44.19 ppm, possibly correspondence to hydrolysis product of diphenylsilane. We assume that trace of moisture present in DMF solvent may responsible for the hydrolysis of diphenylsilane and also decomposition of NaO^{t}Bu.

Table S4: Screening of the time for the hydrosilylation of styrene (**1a**).[a]



Entry	Ph_2SiH_2 (equiv)	Base (1.2 equiv)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1	1.2	NaO^{t}Bu	Neat	80	12	92
2	1.2	NaO^{t}Bu	Neat	80	18	96
3	**1.2**	**NaO^{t}Bu**	**Neat**	**80**	**24**	**100**

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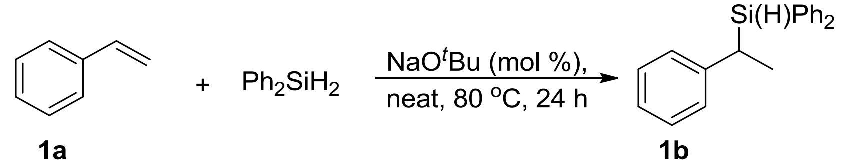
[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (1.2 equiv, 0.3 mmol), neat at 80 ºC for indicated time. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

Table S5: Screening of base loading for the hydrosilylation of styrene (**1a**).[a]



Entry	Ph_2SiH_2 (equiv)	NaO^{t}Bu (equiv)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1	1.2	1.2	Neat	80	24	100
2	1.2	0.05	Neat	80	24	62
3	1.2	0.10	Neat	80	24	80
4	1.2	0.20	Neat	80	24	96

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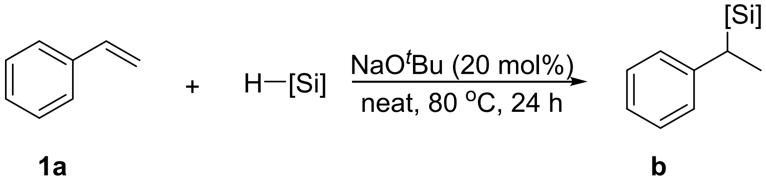
[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (equiv), neat at 80 ºC for 24 h. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

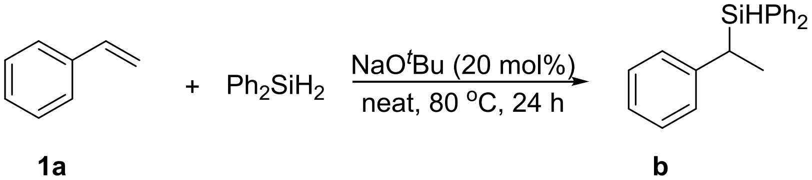
Table S6: Screening of silane reagents for the hydrosilylation of styrene (**1a**).[a]



Entry	H-[Si] (1.2 equiv)	NaO^{t}Bu (mol%)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1	Me_2PhSiH	20	Neat	80	24	3
2	Ph_3SiH	20	Neat	80	24	trace
3	Et_2SiH_2	20	Neat	80	24	0
4	Et_3SiH	20	Neat	80	24	0
5	Ph_2SiH_2	20	Neat	80	24	96
6	$Me(EtO)_2SiH$	20	Neat	80	24	13
7	TMDS	20	Neat	80	24	0

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), [Si]-H (1.2 equiv, 0.3 mmol), NaO^{t}Bu (20 mol %), neat at 80 ºC for 24 h unless otherwise stated. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard. TMDS = Tetramethyldisiloxane.

Table S7: Screening of Ph_2SiH_2 and NaO^{t}Bu obtained from various vendors for the hydrosilylation of styrene (**1a**).[a]



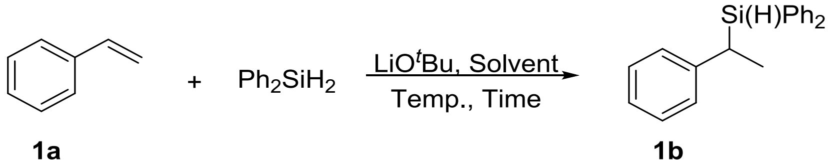
Entry	Ph_2SiH_2 Vendor (1.2 equiv.)	NaO^{t}Bu Vendor (20 mol%)	Time (h)	Yield (%)[b]
1	Sigma-Aldrich (with 97% purity)	Sigma-Aldrich (with 97% purity)	24	96
2	BLD Pharm (with 98% purity)	Sigma-Aldrich (with 97% purity)	24	92
3	Sigma Aldrich (with 97% purity)	Sigma-Aldrich (with 99.9% purity)	24	96
4	Sigma Aldrich (with 97% purity)	Spectrochem (with >97% purity)	24	95

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (20 mol %), neat at 80 ºC for 24 h unless otherwise stated. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard and average of two runs.

Experimental Procedures for Examples Described in Scheme 2.

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), Ph_2SiH_2 (0.3 mmol) and indicated amount of LiO^{t}Bu were added. The reaction mixture was stirred for indicated time and temperature. The crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of celite. The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ^{1}H NMR using nitromethane as an internal standard.

Table S8: Screening of the amount of LiO^{t}Bu for the hydrosilylation of styrene (**1a**).[a]



Entry	Ph_2SiH_2 (equiv)	LiO^{t}Bu (equiv)	Solvent	Temp. (˚C)	Time (h)	Yield (%)[b]
1	1.2	0.20	-	80	24	Trace
2	1.2	0.5	-	120	24	47
3	1.2	0.5	-	120	48	62
4	1.2	1.0	-	120	24	57
5	1.2	1.0	-	120	48	70
6	**1.2**	**1.5**	**-**	**120**	**48**	**79**
7	1.2	1.5	Toluene	120	48	8%

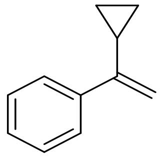
[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), LiO^{t}Bu indicated amount, neat/solvent at given time and temperature. [b]Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

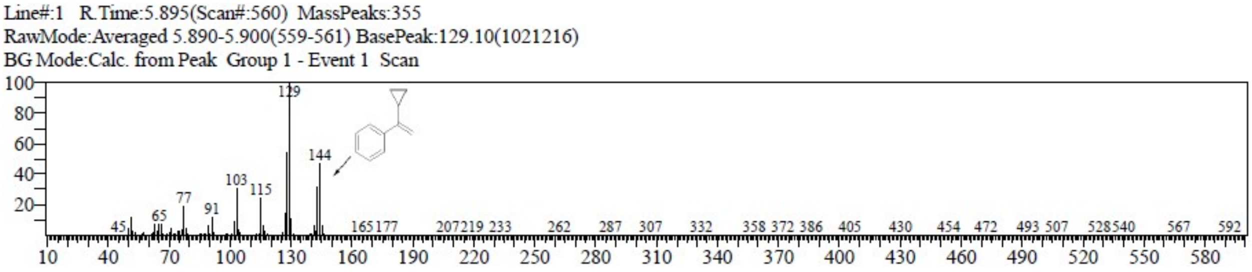
III. Substrate synthesis

*Procedure for the preparation of (1-cyclopropylvinyl)benzene (**26a**)*[1]

Under a nitrogen atmosphere, to an anhydrous THF (13 mL) solution of methyltriphenylphosphonium bromide (2.1 g, 6 mmol) at 0 ºC, n-butyl lithium (2.4 mL, 2.5 M in haxane, 6 mmol) was added dropwise and the mixture was stirred for 1 h. To the above reaction mixture cyclopropyl(phenyl)methanone (730 mg; 5 mmol) was added and stirred at room temperature for another 3 h. After completion of the reaction, the solvent was evaporated and the residue was purified by column chromatography to afford (1-cyclopropylvinyl)benzene (**25a**) as a colorless oil (620 mg, 86% yield).

(1-Cyclopropylvinyl)benzene:



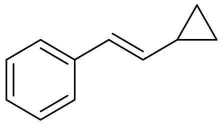


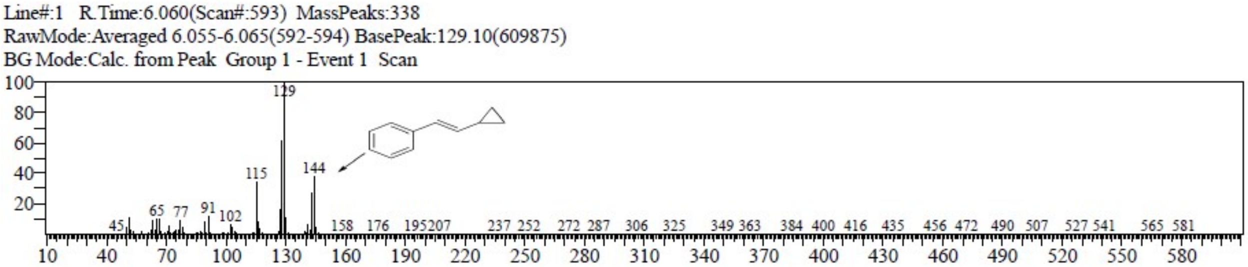
GC-MS analysis of (1-cyclopropylvinyl)benzene (**25a**)

Procedure for the preparation of (2-cyclopropylvinyl)benzene [2]

Under a nitrogen atmosphere, to an anhydrous THF (13 mL) solution of benzyl-triphenyl-phosphonium bromide (5.0 g, 11.5 mmol) at 0 ºC, n-butyl lithium (4.6 mL, 2.5 M in hexane, 11.5 mmol) was added dropwise and the mixture was stirred for 1 h. To the above reaction mixture cyclopropanecarboxaldehyde (0.81 g, 11.5 mmol) was added and stirred at room temperature for another 3 h. After completion of the reaction, the solvent was evaporated and the residue was purified by column chromatography to afford (2-cyclopropylvinyl)benzene (**26a**) as a colorless oil (1.19 g, 72% yield).

(2-Cyclopropylvinyl)benzene:



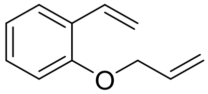


GC-MS Analysis of (E)- and (Z)- 1-(2-Cyclopropylvinyl)benzene

*Procedure for the preparation of 1-(allyloxy)-2-vinylbenzene (**27a**).*[3]

To a vigorously stirred suspension of NaH (0.60 g, 15.0 mmol, 60% in mineral oil) in THF (30 mL), methyltriphenylphosphonium bromide (4.61 g, 12.9 mmol) was added portion wise at 0 ºC. The mixture was allowed to warm to rt and stirred for another 30 min before the addition of 2-(allyloxy)benzaldehyde (1.6 g, 10 mmol) in 10 mL of THF. The reaction mixture was stirred for 2 h, then quenched by H_2O (100 mL). The organic phase was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), and dried over Na_2SO_4. The crude product was purified by column chromatography to afford 1-(allyloxy)-2-vinylbenzene (**27a**) as a colorless oil (1.3 g, 82% yield).

1-(Allyloxy)-2-vinylbenzene (27a):



The spectroscopic data for this product matched the literature data.[3]

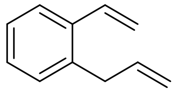
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.27-7.18 (m, 1H), 7.10 (dd, *J* = 17.8, 11.2 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.08 (ddt, *J* = 17.0, 10.4, 5.1 Hz, 1H), 5.75 (dd, *J* = 17.8, 1.3 Hz, 1H), 5.43 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.33-5.23 (m, 2H), 4.56 (d, *J* = 5.1 Hz, 2H).

Procedure for the preparation of 1-(allyl)-2-vinylbenzene (28a).[3]

To a vigorously stirred suspension of NaH (0.60 g, 15.0 mmol, 60% in mineral oil) in THF (30 mL), methyltriphenylphosphonium bromide (4.61 g, 12.9 mmol) was added portion wise at 0 ºC. The mixture was allowed to warm to room temperature and stirred for another 30 min before the addition of 2-(allyl)benzaldehyde (1.4 g, 10 mmol) in 10 mL of THF. The reaction mixture was stirred for 2 h, then quenched by H_2O (100 mL). The organic phase was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), and dried over Na_2SO_4. The crude product was purified by column chromatography to afford 1-(allyl)-2-vinylbenzene (**28a**) as a colorless oil (0.97 g, 68% yield).

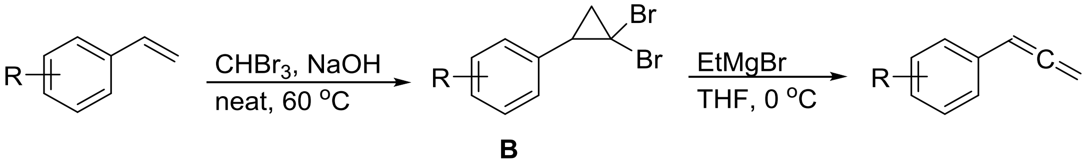
1-Allyl-2-vinylbenzene (28a)

The spectroscopic data for this substrate matches with the literature data.[4]



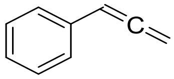
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.09 – 7.05 (m, 1H), 6.88 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.88 (ddt, *J* = 16.4, 10.1, 6.2 Hz, 1H), 5.56 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.21 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.98 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.90 (dd, *J* = 17.1, 1.7 Hz, 1H), 3.37 (d, *J* = 6.2 Hz, 2H).

*General procedure for the preparation of allenes (**23a, 24a and 25a**)*[5]



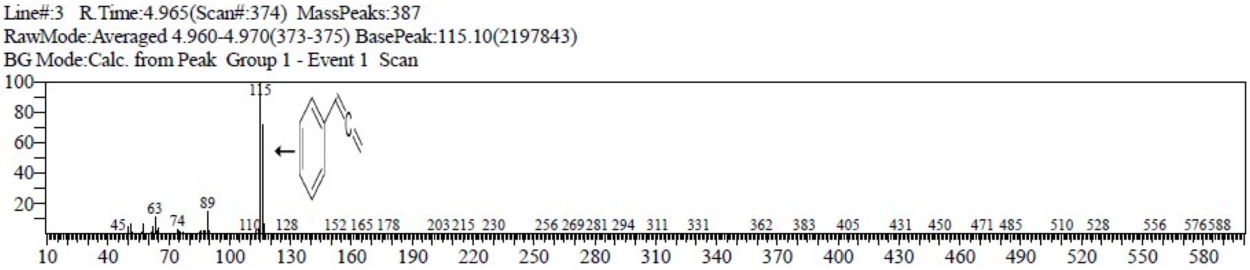
Under a nitrogen atmosphere, to a mixture of styrene (2.08 g, 20 mmol, 1.0 equiv), $CHBr_3$ (8 g, 32 mmol, 1.6 equiv) and triethylbenzylammonium chloride (45.6 mg, 0.2 mmol, 0.01 equiv) was added 50% aq. NaOH (6.4 g, 80 mmol, 4.0 equiv) dropwise over 1 h. The resulting mixture was stirred vigorously at 60 ºC for 24 h and then cooled to room temperature, followed by addition of water (30 mL). The mixture was extracted with ethyl acetate (30 mL x 3), and the combined organic phases were dried over sodium sulfate, and concentrated. The crude product was purified with column chromatography on silica gel to afford **B**. To a stirred THF (6 mL) solution of **B** (6 mmol, 1.0 equiv.) at 0 ºC EtMgBr (4.5 mL, 9 mmol, 2.0 M in THF, 1.5 equiv) was added dropwise under nitrogen atmosphere over 30 min. The resulting mixture was stirred at room temperature for 2 h, quenched with 3 M hydrochloric acid solution and the mixture was diluted with diethyl ether (50 mL). The organic phase was washed with water (50 mL), dried over magnesium sulfate, and concentrated. The crude product was purified with column chromatography on silica gel to afford allenes.

Propa-1,2-dien-1-ylbenzene (23a):



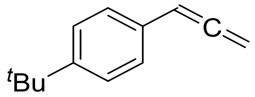
Compound **23a** was prepared following the general procedure for the preparation of allenes. Purification by column chromatography gave **23a** as a colorless oil (584 mg, 84% yield). The spectroscopic data for this substrate matches with the literature data.[5]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27 – 7.17 (m, 4H), 6.82 – 6.76 (m, 1H), 6.22 (d, J = 7.2 Hz, 1H), 5.25 (d, J = 7.6 Hz, 2H).



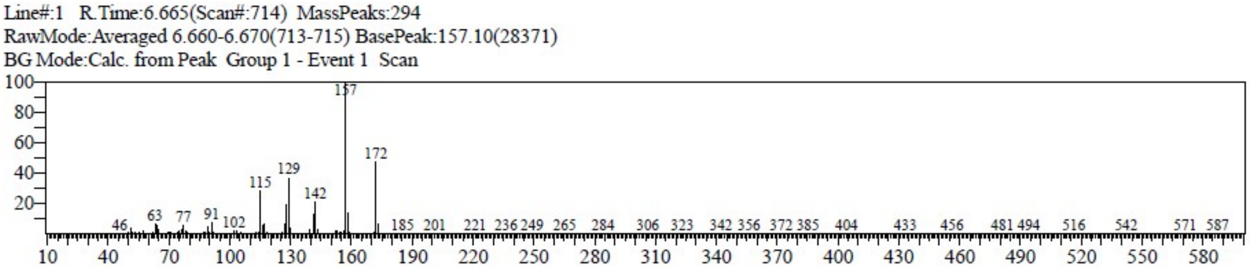
GC-MS analysis of propa-1,2-dien-1-ylbenzene (**23a**)

1-(Tert-butyl)-4-(propa-1,2-dien-1-yl)benzene (24a)



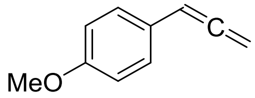
Compound **24a** was prepared following the general procedure for the preparation of allenes. Purification by column chromatography gave **24a** as a colorless oil (680 mg, 66% yield). The spectroscopic data for this substrate matches with the literature data.[5]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 6.08 (t, J = 6.6 Hz, 1H), 5.05 (d, J = 7.7 Hz, 2H), 1.24 (s, 9H).



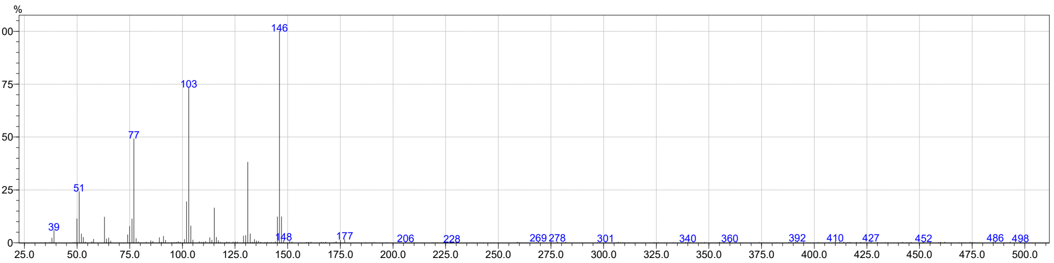
GC-MS analysis of 1-(tert-butyl)-4-(propa-1,2-dien-1-yl)benzene (**24a**).

1-Methoxy-4-(propa-1,2-dien-1-yl)benzene (25a)



Compound **25a** was prepared following the general procedure for the preparation of allenes. Purification by column chromatography gave **25a** as a colorless oil (665 mg, 76% yield). The spectroscopic data for this substrate matches with the literature data.[5]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.07 (t, J = 6.7 Hz, 1H), 5.07 (d, J = 6.7 Hz, 2H), 3.73 (s, 3H).



GC-MS analysis of 1-methoxy-4-(propa-1,2-dien-1-yl)benzene (**25a**).

IV. Substrate scope of Lewis base catalyzed hydrosilylation reaction

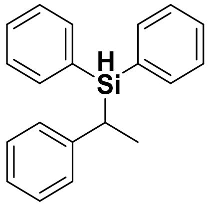
General procedure A (0.25 mmol scale reaction)

In a nitrogen filled glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^tBu (5 mg, 20 mol %), Ph_2SiH_2 (55 mg, 1.2 equiv, 0.3 mmol), and alkene (diene, allene or aldehyde; 0.25 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. After completion, the crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of celite. The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ^1H NMR using nitromethane as an internal standard.

General procedure B (1 mmol scale reaction)

In a nitrogen filled glovebox, to an oven-dried 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^tBu (19 mg, 20 mol %), Ph_2SiH_2 (220 mg, 1.2 equiv, 1.2 mmol), and alkene (diene, allene or aldehyde; 1 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. After completion, the crude reaction mixture was dissolved in Et_2O (20 mL) and passed through a plug of celite. The solvent was removed in vacuo and purified by column chromatography on silica gel to afford desired hydrosilylation product.

Diphenyl(1-phenylethyl)silane (1b)



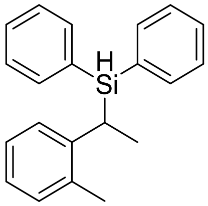
Following general procedure B, colorless oily liquid in 86% (247 mg) yield was obtained from styrene (**1a**, 104 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6b,c,7,8,10]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.52-6.99 (m, 15H), 4.83 (d, *J* = 3.0 Hz, 1H), 2.82 (qd, *J* = 7.5, 3.7 Hz, 1H), 1.46 (d, *J* = 5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 144.39, 135.76, 135.61, 133.08, 129.76, 129.62, 128.21, 127.97, 127.78, 127.76, 124.96, 27.02, 16.55.
^{29}Si NMR (100 MHz, $CDCl_3$): δ (ppm) -8.34.

Diphenyl(1-(o-tolyl)ethyl)silane (2b)

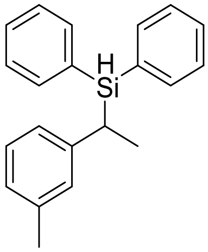


Following general procedure B, colorless oily liquid in 81% (244 mg) yield was obtained from 1-methyl-2-vinylbenzene (**2a**, 118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6b,7,8]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.50 (d, *J* = 8 Hz, 2H), 7.41-7.38 (m, 1H), 7.35-7.26 (m, 5H), 7.21-7.17 (m, 2H), 7.10-7.07 (m, 1H), 7.02-6.97 (m, 3H), 4.77 (d, *J* = 3 Hz, 1H), 2.97 (dq, *J* = 7 Hz, 3.5 Hz, 1H), 2.04 (s, 3H), 1.41 (d, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.89, 135.88, 135.35, 133.40, 132.88, 130.12, 129.82, 129.52, 127.99, 127.75, 126.83, 126.10, 124.79, 22.06, 20.15, 16.64.

Diphenyl(1-(m-tolyl)ethyl)silane (3b)

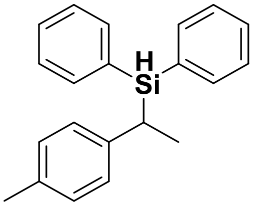


Following general procedure B, colorless oily liquid in 84% (254 mg) yield was obtained from 1-methyl-3-vinylbenzene (**3a**, 118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6b,7,8,10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.38 – 7.28 (m, 6H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.11 – 7.03 (m, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.83 – 6.76 (m, 2H), 4.83 (d, *J* = 3.3 Hz, 1H), 2.77 (qd, *J* = 7.5, 3.3 Hz, 1H), 2.20 (s, 3H), 1.44 (d, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.31, 137.67, 135.88, 135.75, 133.29, 129.82, 129.69, 128.80, 128.19, 128.03, 127.83, 125.83, 124.87, 26.98, 21.56, 16.64.

Diphenyl(1-(p-tolyl)ethyl)silane (4b)

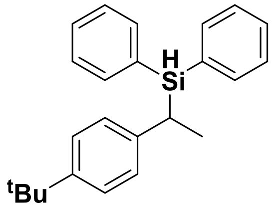


Following general procedure B, colorless oily liquid in 74% (223 mg) yield was obtained from 1-methyl-4-vinylbenzene (**4a**, 118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data. [6b,7,8,10]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43-7.41 (m, 2H), 7.28-7.22 (m, 6H), 7.18-7.15 (m, 2H), 6.90-6.88 (m, 2H), 6.81-6.79 (m, 2H), 4.73 (d, *J* = 3.0 Hz, 2H), 2.69-2.67 (m, 1H), 2.18 (s, 3H), 1.35-1.33 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.26, 135.79, 135.64, 134.48, 134.43, 134.31, 129.71, 129.58, 128.95, 127.95, 127.78, 127.66, 26.43, 21.02, 15.36.

(1-(4-(Tert-butyl)phenyl)ethyl)diphenylsilane (5b)

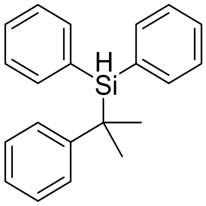


Following general procedure B, colorless oily liquid in 71% (244 mg) yield was obtained from 1-(tert-butyl)-4-vinylbenzene (**5a**, 160 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data. [6b,7,8]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.53-7.51 (m, 2H), 7.42-7.31 (m, 6H), 7.26-7.20 (m, 4H), 6.96-6.94 (d, *J* = 10 Hz, 2H), 4.83 (d, *J* = 5.0 Hz, 1H), 2.82-2.78 (m, 1H), 1.46 (d, *J* = 5 Hz, 3H), 1.29 (s, 9H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 147.73, 141.12, 135.77, 135.61, 133.29, 133.24, 129.67, 129.50, 127.91, 127.67, 127.32, 125.06, 34.30, 31.47, 26.26, 16.52.

Diphenyl(2-phenylpropan-2-yl)silane (6b)

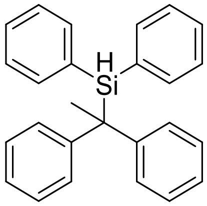


Following general procedure B, colorless oily liquid in 31% (93 mg) yield was obtained from prop-1-en-2-ylbenzene (**6a**, 118 mg, 1.0 mmol).

Chromatography: R$_f$ = 0.6; in hexane/EtOAc in 50:1.

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.24-7.21 (m, 15H), 5.27 (s, 1H), 1.28 (s, 6H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 146.88, 136.38, 135.19, 133.17, 129.54, 129.32, 128.82, 128.06, 127.61, 127.33, 125.52, 39.25, 25.60.
HRMS (ESI) calcd. for $C_{21}H_{21}Si$ [M-H]$^-$: 301.1418; found [M-H]$^-$: 301.1416.

(1,1-Diphenylethyl)diphenylsilane (7b)

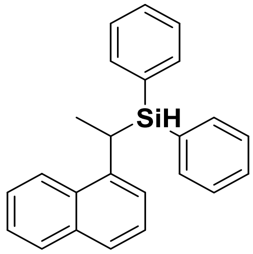


Following general procedure B, colorless oily liquid in 48% (174 mg) yield was obtained from ethene-1,1-diyldibenzene (**7a**, 180 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6c]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.33-7.31 (m, 2H), 7.25-7.14 (m, 18H), 5.27 (s, 1H), 1.88 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 146.88, 136.38, 133.17, 129.54, 128.82, 128.06, 127.61, 125.52, 39.25, 25.60.

(1-(Naphthalen-1-yl)ethyl)diphenylsilane (8b)

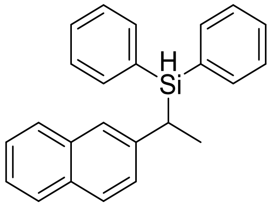


Following general procedure B, colorless oily liquid in 79% (267 mg) yield was obtained from 1-vinylnaphthalene (**8a**, 154 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[7,8]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.55-6.92 (m, 17H), 4.85 (d, J = 3.2Hz, 1H), 2.81 (qd, J = 7.4Hz, 3.2Hz, 1H), 1.46 (d, J = 7.2Hz, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 141.51, 136.44, 135.86, 134.40, 133.72, 133.31, 131.96, 130.24, 130.09, 129.32, 128.35, 128.29, 126.03, 125.82, 125.73, 124.59, 124.07, 123.68, 21.70, 17.35.

(1-(Naphthalen-2-yl)ethyl)diphenylsilane (9b)

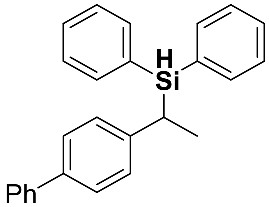


Following general procedure B, colorless oily liquid in 88% (297 mg) yield was obtained from 2-vinylnaphthalene (**9a**, 154 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[7,8,10]

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.81 (d, *J* = 8.4 Hz, 1H), 7.72-7.69 (m, 2H), 7.60-7.58 (m, 2H), 7.46-7.38 (m, 9H), 7.32-7.28 (m, 2H), 7.22-7.20 (m, 1H), 4.98 (d, *J* = 3.2 Hz, 1H), 3.06 (dq, *J* = 7.2 Hz, 3.2 Hz, 1H), 1.6 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 142.58, 136.24, 136.10, 135.90, 134.88, 134.20, 133.47, 132.07, 130.25, 130.25, 130.13, 128.44, 128.27, 128.10, 128.04, 128.00, 127.83, 127.75, 126.23, 125.79, 125.25, 27.74, 17.09.

(1-([1,1'-Biphenyl]-4-yl)ethyl)diphenylsilane (10b)

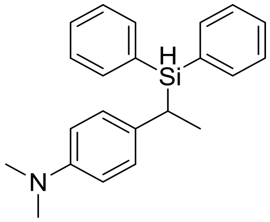


Following general procedure B, colorless oily liquid in 85% (309 mg) yield was obtained from 4-vinyl-1,1'-biphenyl (**10a**, 180 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[7,8,10]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.57-7.52 (m, 4H), 7.42-7.24 (m, 13H), 7.6 (d, *J* = 3 Hz, 2H), 4.86 (d, *J* = 3.0 Hz, 1H), 2.86 (qd, *J* = 7.5, 3.5 Hz, 1H), 1.49 (d, *J* = 5 Hz, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 143.62, 141.12, 137.73, 135.78, 135.64, 132.99, 129.81, 129.68, 128.74, 128.13, 128.00, 127.82, 126.90, 126.85, 126.75, 26.75, 16.51.

4-(1-(Diphenylsilyl)ethyl)-N,N-dimethylaniline (11b)



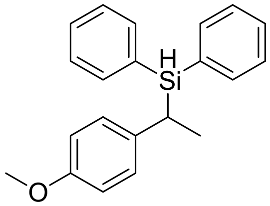
Following general procedure B, light yellow oily liquid in 52% (172 mg) yield was obtained from N,N-dimethyl-4-vinylaniline (**11a**, 147 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[7]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.52 (d, *J* = 7 Hz, 2H), 7.35-7.32 (m, 5H), 7.27-7.24 (m, 3H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.82 (d, *J* = 3 Hz, 1H), 2.88 (s, 6H), 2.74-2.69 (m, 1H), 1.41 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 148.48, 135.77, 135.66, 133.64, 133.57, 132.49, 129.54, 129.42, 128.34, 127.85, 127.69, 127.61, 113.15, 40.99, 25.47, 16.94.

(1-(4-Methoxyphenyl)ethyl)diphenylsilane (12b)



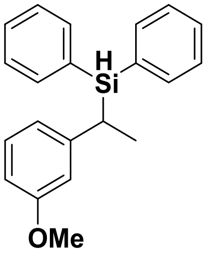
Following general procedure B, colorless oily liquid in 86% (273 mg) yield was obtained from 1-methoxy-4-vinylbenzene (**12a**, 134 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6b,7,8,10]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.66-7.63 (m, 2H), 7.89-7.35 (m, 4H), 7.26-7.21 (m, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 9 Hz, 2H), 4.82 (d, *J* = 3.5 Hz, 1H), 3.72 (s, 3H), 2.75 (dq, *J* = 7.5 Hz, 3 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 157.21, 136.38, 135.79, 135.67, 134.73, 134.51, 134.45, 130.10, 129.74, 129.62, 128.63, 127.99, 127.86, 127.81, 127.69, 113.75, 55.28, 25.90, 16.95.

(1-(3-Methoxyphenyl)ethyl)diphenylsilane (13b)

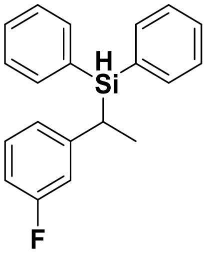


Following general procedure B, colorless oily liquid in 83% (263 mg) yield was obtained from 1-methoxy-3-vinylbenzene (**13a**, 134 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6a]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.53-7.51 (m, 2H), 7.39-7.32 (m, 6H), 7.27-7.07 (m, 4H), 6.64-6.61 (m, 2H), 4.83 (d, *J* = 3.5 Hz, 1H), 3.61 (s, 3H), 2.81 (qd, *J* = 7.5, 3.2 Hz, 1H), 1.45 (d, *J* = 10 Hz, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 159.44, 146.02, 135.75, 135.63, 134.40, 133.11, 133.06, 129.76, 129.64, 129.10, 127.97, 127.78, 127.64, 120.16, 113.12, 110.87, 54.99, 27.18, 16.46.

(1-(3-Fluorophenyl)ethyl)diphenylsilane (14b)

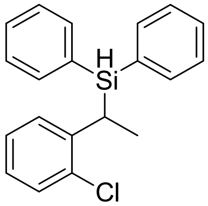


Following general procedure B, light yellow oily liquid in 81% (247 mg) yield was obtained from 1-fluoro-3-vinylbenzene (**14a**, 122 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[6b,7,8]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.51-7.49 (m, 2H), 7.41-7.33 (m, 6H), 7.27-7.24 (m, 2H), 7.11-7.07 (m, 1H), 6.77-6.74 (m, 2H), 6.69-6.66 (m, 1H), 4.81 (d, *J* = 3.5 Hz, 1H), 2.84-2.80 (m, 1H), 1.43 (d, *J* = 10 Hz, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 163.87, 161.93, 147.27 (d), 135.68 (d), 132.59 (d), 129.92 (d), 129.47 (d), 128.70 (d), 128.05 (d), 123.43 (d), 114.46 (d), 111.82 (d), 27.11, 16.31.

(1-(2-Chlorophenyl)ethyl)diphenylsilane (15b)

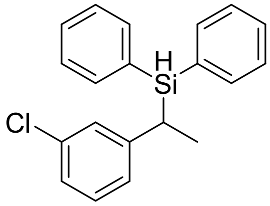


Following general procedure B, light yellow oily liquid in 84% (270 mg) yield was obtained from 1-chloro-2-vinylbenzene (**15a**, 138 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[8]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.58-7.53 (m, 3H), 7.42-7.39 (m, 3H), 7.36-7.32 (m, 4H), 7.26-7.23 (m, 2H), 7.04-6.98 (m, 2H), 4.83 (d, *J* = 3 Hz, 1H), 3.44 (dq, *J* = 7.5 Hz, 3 Hz, 1H), 1.41 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 142.46, 135.96, 135.92, 135.40, 133.44, 133.36, 132.95, 132.49, 129.95, 129.92, 129.74, 129.40, 128.31, 128.16, 128.06, 127.86, 126.83, 126.06, 22.87, 16.14.

(1-(3-Chlorophenyl)ethyl)diphenylsilane (16b)

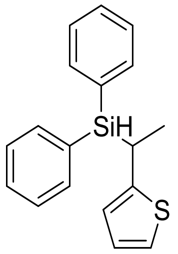


Following general procedure B, light yellow oily liquid in 70% (225 mg) yield was obtained from 1-chloro-3-vinylbenzene (**16a**, 138 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[7,8,10]

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.56-7.49 (m, 2H), 7.39-7.33 (m, 6H), 7.27-7.25 (m, 2H), 7.07-7.04 (m, 2H), 6.83-6.82 (m, 1H), 4.80-4.78 (m, 1H), 2.80-2.76 (m, 1H), 1.41 (d, *J* = 7 Hz, 3H.
^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 146.64, 135.86, 135.69, 135.54, 134.00, 132.50, 132.48, 129.94, 129.83, 129.31, 128.06, 127.88, 127.73, 125.91, 125.07, 27.05, 16.26.

Diphenyl(1-(thiophen-2-yl)ethyl)silane (17b)

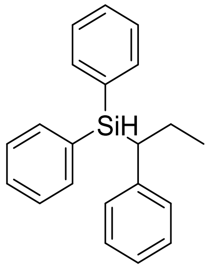


Following general procedure B, light yellow oily liquid in 82% (294 mg) yield was obtained from 2-vinylthiophene (**17a**, 110 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.47 – 7.45 (m, 2H), 7.35 – 7.20 (m, 8H), 6.91 (dd, J = 5.1, 1.0 Hz, 1H), 6.76 (dd, J = 5.1, 3.5 Hz, 1H), 6.50 (d, J = 3.4 Hz, 1H), 4.83 (d, J = 3.2 Hz, 1H), 3.04 (qd, J = 7.4, 3.2 Hz, 1H), 1.42 (d, J = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.19, 135.70, 135.60, 132.77, 132.66, 129.89, 129.82, 128.02, 127.88, 126.74, 122.85, 121.83, 22.31, 18.10.

Diphenyl(1-phenylpropyl)silane (18b)



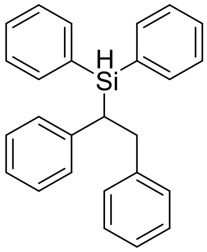
Following general procedure B, colorless oily liquid in 41% (123 mg) yield was obtained from (E)-prop-1-en-1-ylbenzene (**18a**, 118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.43-7.39 (m, 1H), 7.38 – 7.30 (m, 5H), 7.27 – 7.22 (m, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.1 Hz, 2H), 4.87 (d, *J* = 3.5 Hz, 1H), 2.57 (dt, *J* = 11.3, 3.8 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 142.22, 135.76, 135.57, 133.37, 133.22, 129.70, 129.49, 128.59, 128.19, 127.95, 127.70, 124.96, 36.04, 24.34, 13.98.

(1,2-Diphenylethyl)diphenylsilane (19b)



Following general procedure B, colorless oily liquid in 17% (61 mg) yield was obtained from (E)-1,2-diphenylethene (**19a**, 180 mg, 1.0 mmol).

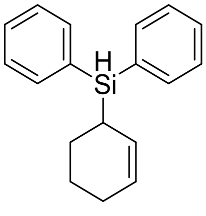
Chromatography: R$_f$ = 0.6; in hexane/EtOAc in 50:1.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 – 7.55 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.34 - 7.32 (m, 2H), 7.26 – 7.22 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 4H), 7.06 – 7.02 (m, 2H), 6.96 – 6.94 (m, 4H), 4.94 (d, *J* = 3.2 Hz, 1H), 3.21 (dd, *J* = 14.1, 3.4 Hz, 1H), 3.10 (t, *J* = 15 Hz, 1H), 3.03 – 3.00 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 141.47 (d, *J* = 6.1 Hz), 135.64 (d, *J* = 19.7 Hz), 134.33, 132.93, 132.73, 129.98, 129.82, 129.59, 128.60 (d, *J* = 25.0 Hz), 128.15 – 127.92 (m), 127.65 (d, *J* = 19.3 Hz), 125.68, 125.05, 37.22, 35.84.

HRMS (ESI) calcd. for $C_{23}H_{24}OSiNa$ [M+Na]$^+$: 387.1545; found [M+Na]$^+$: 387.1548.

Cyclohex-2-en-1-yldiphenylsilane (20b)



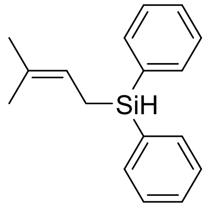
Following general procedure B, colorless oily liquid in 80% (211 mg) yield was obtained from cyclohexa-1,3-diene (**20a**, 80 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[9]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62-7.61 (m, 2H), 7.57-7.55 (m, 2H), 7.39-7.34 (m, 6H), 5.72-5.66 (m, 2H), 4.77 (d, *J* = 4 Hz, 1H), 1.53 (s, 1H), 1.42 (s, 2H), 1.26 (s, 4 H).

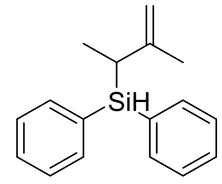
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 135.61, 135.36, 133.75, 133.52, 129.61, 129.56, 127.96, 127.13, 126.63, 25.30, 24.44, 23.33, 22.11.

(3-Methylbut-2-en-1-yl)diphenylsilane (21b-c)



+

21b



21c

21b : **21c** = 76 : 24

21b

The spectroscopic data is consistent with literature data.[12,13]

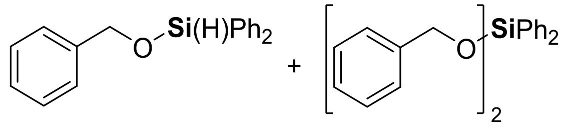
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.65 – 7.63 (m, 5H), 7.45 – 7.39 (m, 9H), 5.21 – 5.17 (m, 1H), 4.97 (t, *J* = 5 Hz, 1H), 2.10 (d, *J* = 5 Hz, 2H), 1.69 (t, *J* = 5 Hz, 3H), 1.44 – 1.42 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 135.15, 134.38, 132.13, 129.60, 127.88, 117.73, 25.69, 18.63, 13.64.

21c

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.65 – 7.63 (m, 5H), 7.45 – 7.39 (m, 9H), 4.88 (d, J = 3.2 Hz, 1H), 4.80 – 4.76 (m, 1H), 4.66 – 4.60 (m, 1H), 2.33 – 2.27 (m, 1H), 1.73 (s, 3H), 1.28 (d, J = 7.4 Hz, 3H).

Mixture of mono and bis(Benzyloxy)diphenylsilane (22b-c)

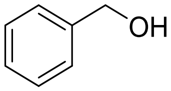


^{1}H NMR spectrum of the catalytic hydrosilylation reaction of benzaldehyde with Ph_2SiH_2 catalyzed by NaO^tBu. Unassigned peaks in the spectrum corresponds to the internal standard nitromethane.

The spectroscopic data is consistent with literature data.[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 4H), 7.74 (s, 5H), 7.62-7.47 (m, 21H), 7.38-7.31 (m, 5H), 5.82-5.66 (m, 1H), 5.09-4.92 (m, 4H), 4.77 (s, 1H).

Phenylmethanol (22d)



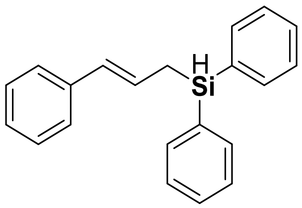
In a nitrogen filled glovebox, to an oven-dried 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (19 mg, 20 mol%), Ph_2SiH_2 (110 mg, 0.5 equiv, 0.5 mmol), and benzaldehyde (**22a**; 106 mg, 1 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. After completion, the crude reaction mixture was hydrolyzed in MeOH/SiO_2 (7 mL) at 60 ºC for 30 h. Crude product was dissolved in distilled water and extracted with copious amount of DCM (30 mL). The solvent was removed in vacuo and purified by column chromatography on silica gel to afford desired benzyl alcohol (**22d**) product in 89% yield (96 mg).

The spectroscopic data is consistent with literature data.[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.29-7.21 (m, 5H), 4.49 (s, 2H), 3.41 (br, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 141.00, 128.54, 127.55, 127.09, 64.87.

Diphenyl(1-phenylallyl)silane (23b)



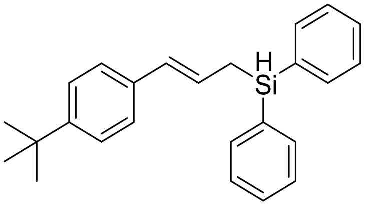
Following general procedure B, colorless oily liquid in 67% (201 mg) yield was obtained from propa-1,2-dien-1-ylbenzene (**23a**, 116 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.58 (dd, J = 9.8, 8.7 Hz, 6H), 7.46 (d, J = 6.7 Hz, 4H), 7.21 (d, J = 2.9 Hz, 5H), 6.33-6.20 (m, 2H), 4.92 (t, J = 2.8 Hz, 1H), 2.27 (dd, J = 7.0, 3.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 138.04, 135.21, 134.33, 129.98, 129.76, 128.40, 128.01, 126.47, 125.95, 125.64, 19.13.

(*E*)-(3-(4-(tert-butyl)phenyl)allyl)diphenylsilane (24b)



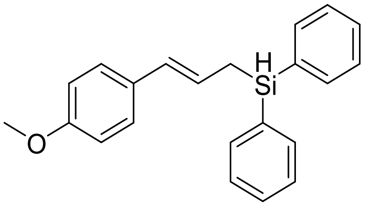
Following general procedure B, colorless oily liquid in 78% (277 mg) yield was obtained from 1-(tert-butyl)-4-(propa-1,2-dien-1-yl)benzene (**24a**, 172 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[5]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58-7.57 (m, 4H), 7.37-7.34 (m, 6H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 11.4 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.6, 7.7 Hz, 1H), 4.92 (t, *J* = 3.4 Hz, 1H), 2.27 (dd, *J* = 7.6, 3.4 Hz, 2H), 1.28 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 149.44, 136.22, 134.84, 133.59, 129.89, 129.73, 128.00, 125.37, 125.30, 125.09, 34.42, 31.31, 19.06.

(*E*)-(3-(4-Methoxyphenyl)allyl)diphenylsilane (25b)



Following general procedure B, colorless oily liquid in 82% (246 mg) yield was obtained from 1-methoxy-4-(propa-1,2-dien-1-yl)benzene (**25a**, 146 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.[5]

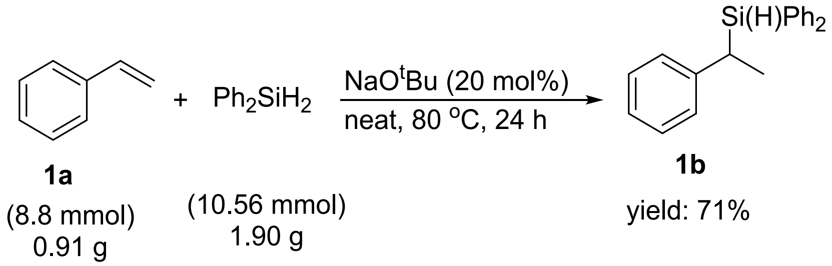
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, J = 7.3 Hz, 4H), 7.38 (d, J = 7.6 Hz, 1H), 7.34 – 7.21 (m, 6H), 7.12 – 7.04 (m, 3H), 6.70 (d, J = 8.5 Hz, 2H), 6.17 (d, J = 15.7 Hz, 1H), 6.01 (dt, J = 15.7, 7.9 Hz, 1H), 4.83 (t, J = 3.4 Hz, 1H), 3.67 (s, 3H), 2.17 (dd, J = 7.9, 3.4 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 158.51, 135.32, 134.43, 133.74, 131.04, 130.09, 129.82, 129.63, 128.09, 127.67, 126.80, 123.73, 113.94, 55.32, 19.00.

V. Gram scale reaction

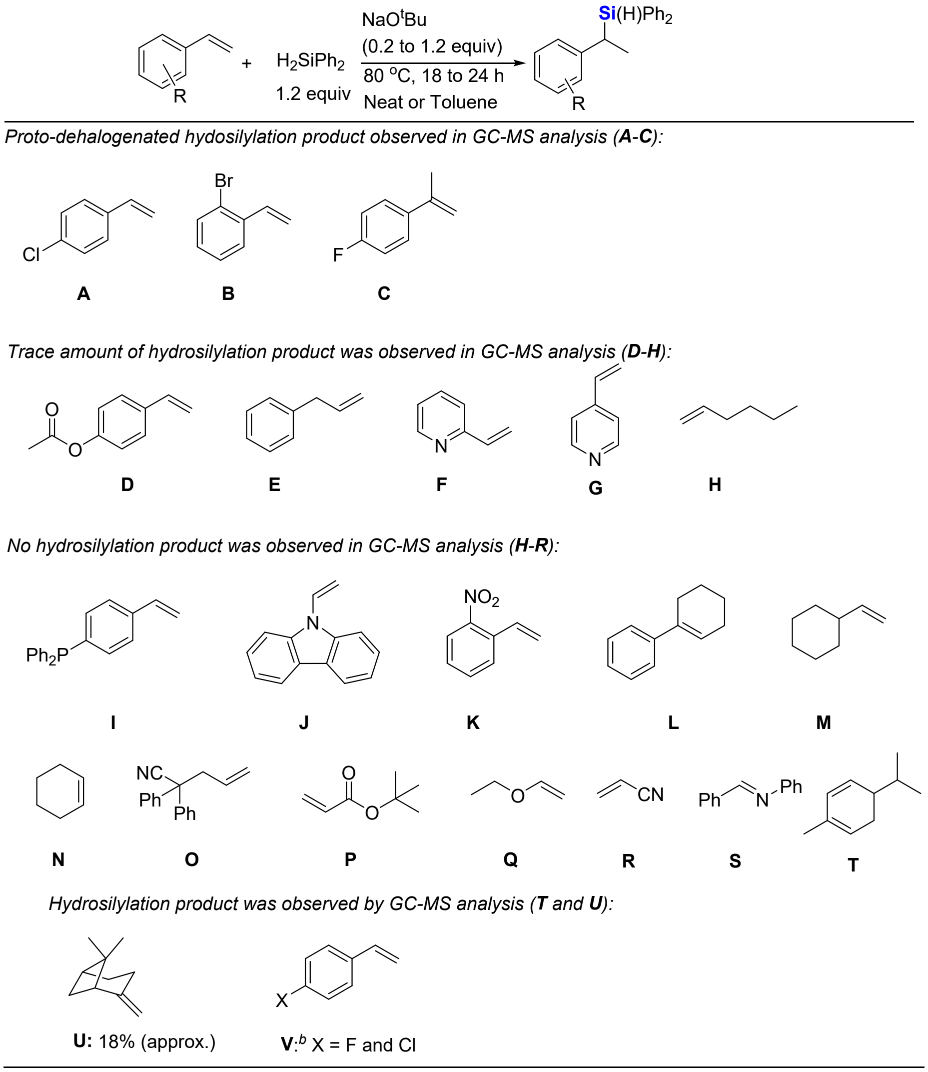
Experimental Procedure.

In a glovebox, to an oven-dried 100 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (169 mg, 20 mol %), H_2SiPh_2 (1.9 g, 1.2 equiv, 10.56 mmol), and styrene (**1a**; 0.9 g, 8.8 mmol) were added and the reaction mixture was stirred vigorously at 80 ºC for 24 h. The volatiles were removed in vacuo to afford the crude reaction mixture which was purified by column chromatography to give diphenyl(1-phenylethyl)silane (**1b**; 1.81 g, 71%) as a colourless oil.



VI. List of unsuccessful substrates

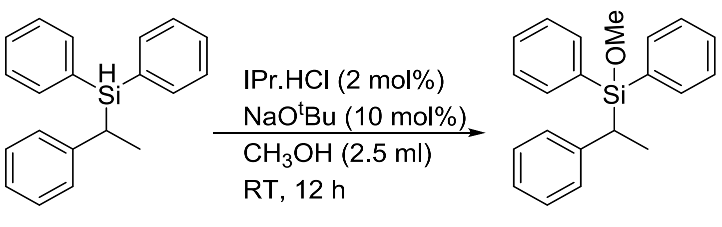
In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (4.8 mg, 20 mol %), H_2SiPh_2 (55 mg, 1.2 equiv, 0.3 mmol), and alkene (0.25 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. The volatiles were removed in vacuo to afford the reaction mixture, which was analyzed by GC-MS.



[a]Reaction conditions: Alkene (1.0 mmol, 1equiv), Ph_2SiH_2 (1.2 equiv), NaO^{t}Bu (20 mol%), Neat, 24 h at 80 ºC. [b]**1b** was obtained in 86% yield after the hydrodehalogenation of *p*-chlorostyrene and 76% yield of **1b** was obtained after the hydrodehalogenation of *p*-fluorostyrene.

VII. Synthetic application

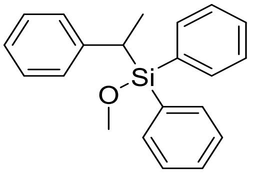
Synthesis of siloxane from ***1b****.*



1b **1b-OMe:** 98% (90%)

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stir bar IPr·HCl (2.1 mg, 0.005 mmol, 2 mol%), NaO^{t}Bu (2.4 mg, 0.01 mmol), CH$_3$OH (2.5 mL) and **1b** (72 mg, 0.25 mmol) were added. The tube was then sealed, and the resulting mixture was stirred at room temperature for 12 h, after which the reaction mixture was filtered through a celite column with Et$_2$O (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography afforded **1b-OMe** as a colorless oil (71 mg, 90% yield).

Methoxydiphenyl(1-phenylethyl)silane (1b-OMe)



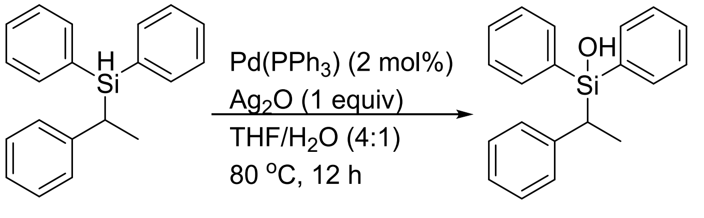
Chromatography: R_f = 0.4; in hexane/EtOAc 50:1.

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.52-7.51 (m, 2H), 7.43-7.30 (m, 8H), 7.20-7.06 (m, 3H), 6.98-6.97 (m, 2H), 3.47 (s, 3H), 2.87-2.84 (m, 1H), 1.46-1.43 (m, 3H).

^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 143.70, 135.54, 135.40, 133.06, 133.92, 129.97, 129.94, 128.31, 127.99, 127.78, 127.70, 124.89, 51.89, 28.33, 15.73.

HRMS (ESI) calcd. for $C_{21}H_{22}OSiNa$ [M+Na]$^+$: 341.1338; found [M+Na]$^+$: 341.1338.

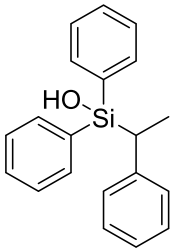
Synthesis of silanol from 1b:



1b **1b-OH:** 95% (83%)

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stir bar $Pd(PPh_3)_4$ (5.79 mg, 0.005 mmol, 2 mol%), Ag_2O (57.9 mg, 0.25 mmol), THF (1.0 mL), H_2O (0.25 mL), and **1b** (72 mg, 0.25 mmol) were added. The tube was then sealed, and the resulting mixture was stirred at 80 ºC for 12 h, after which the reaction mixture was filtered through a celite column using Et_2O (30 mL). The organic phase was concentrated under reduced pressure. The crude reaction mixture was purified with column chromatography to give **1b-OH** as a colorless oil (63 mg, 83% yield).

Diphenyl(1-phenylethyl)silanol (1b-OH)

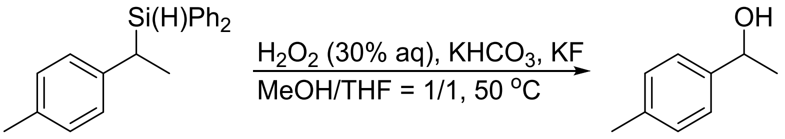


The spectroscopic data is consistent with literature data.[10a]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.53-7.52 (m, 2H), 7.43-7.26 (m, 8H), 7.15-7.12 (m, 2H), 7.07-7.04 (m, 1H), 6.99-6.97 (m, 2H), 2.82-2.77 (m, 1H), 2.50-2.40 (m, 1H), 1.43 (d, J = 10Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.63, 134.84, 134.46, 130.02, 129.99, 128.29, 128.06, 127.86, 127.81, 125.09, 29.19, 15.48.

Synthesis of 1-(*p*-tolyl)ethan-1-ol (4c)



4b **4c**

To a solution of **4b** (151 mg, 0.5 mmol, 1.0 equiv) in MeOH and THF (4 mL, MeOH/THF in 1:1 ratio), KF (232 mg, 4.0 mmol, 8.0 equiv), $KHCO_3$ (250 mg, 2.5 mmol, 5 equiv) and H_2O_2 (1.2 ml, 30% aqueous solution) were added. Then the mixture was stirred at 50 ºC. After 20 h, the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $NaSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1 followed by hexane/EtOAc = 6/1) affording 54 mg (80% yield) of **4c** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.16 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.74 (q, *J* = 6.4 Hz, 1H), 2.25 (s, 3H), 1.97 (s, 1H), 1.38 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.93, 137.08, 129.15, 125.38, 70.19, 25.06, 21.07.

VIII. Mechanistic investigations

Procedure of AT-IR measurement:

In a glovebox, in oven-dried 4 mL glass vials, four different samples were prepared prior to AT-IR analysis.

In sample vial (a) only NaO^{t}Bu was charged and sealed with plastic cap, and then the IR spectrum was recorded (Figure S1a).

In sample vial (b) only Ph_2SiH_2 was charged and sealed with plastic cap, and then the IR spectrum was recorded. The Si–H stretch was observed at 2137 cm^{-1} (Figure S1b).

In sample vial (c) mixture of NaO^{t}Bu and Ph_2SiH_2 were charged and sealed with plastic cap (at room temperature), and then the IR spectrum was recorded (Figure S1c).

In sample vial (d) mixture of NaO^{t}Bu and Ph_2SiH_2 were charged and sealed with plastic cap and stirred at 80 ºC for 10 min and then the IR spectrum was recorded (Figure S1d).

The AT-IR analysis of (c) and (d) demonstrated that observed Si–H stretch (2137 cm^{-1}) was diminished and a new peak appeared at 2036 cm^{-1}, implied formation of pentacoordinated species. The frequency difference of pentacoordinated species from Ph_2SiH_2 was observed about $\Delta v = 101$ cm^{-1}.

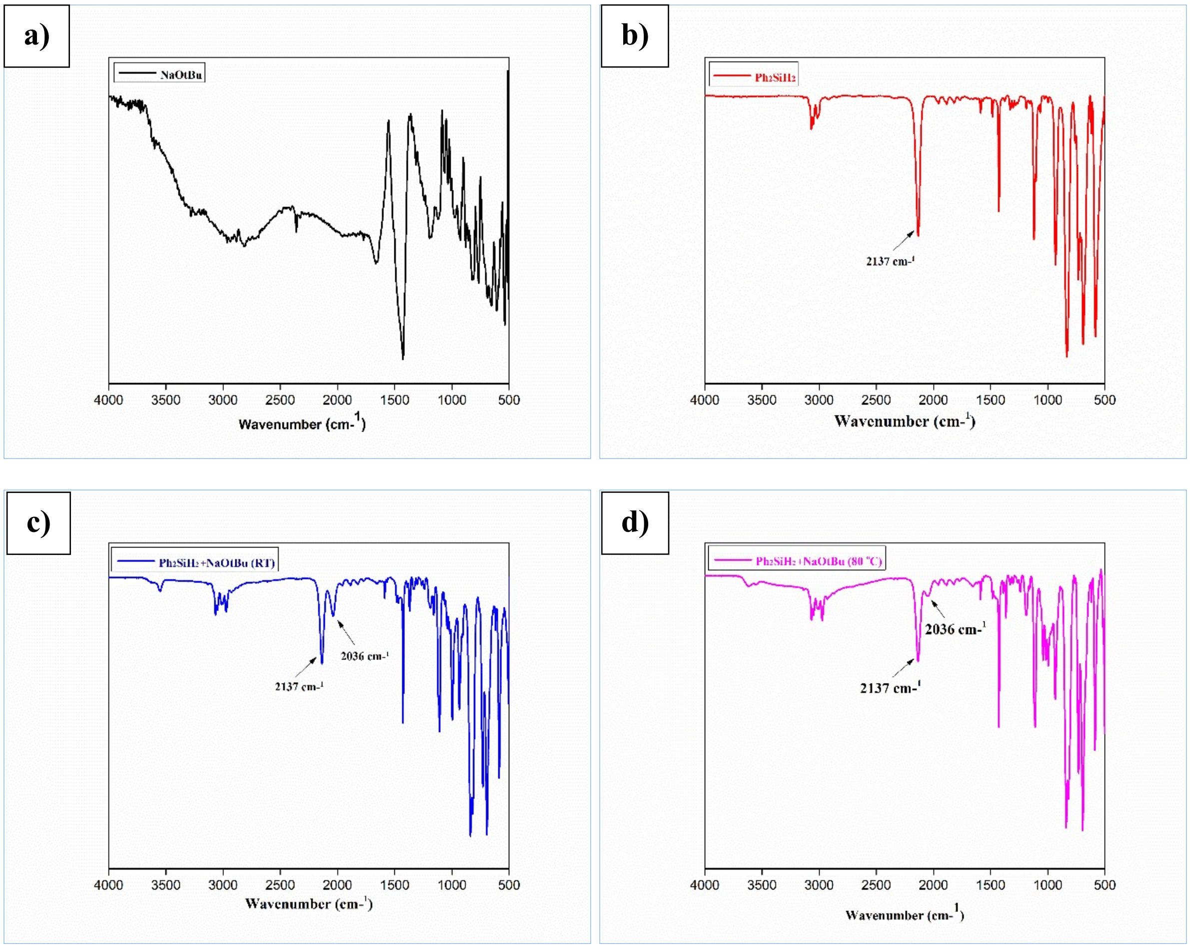
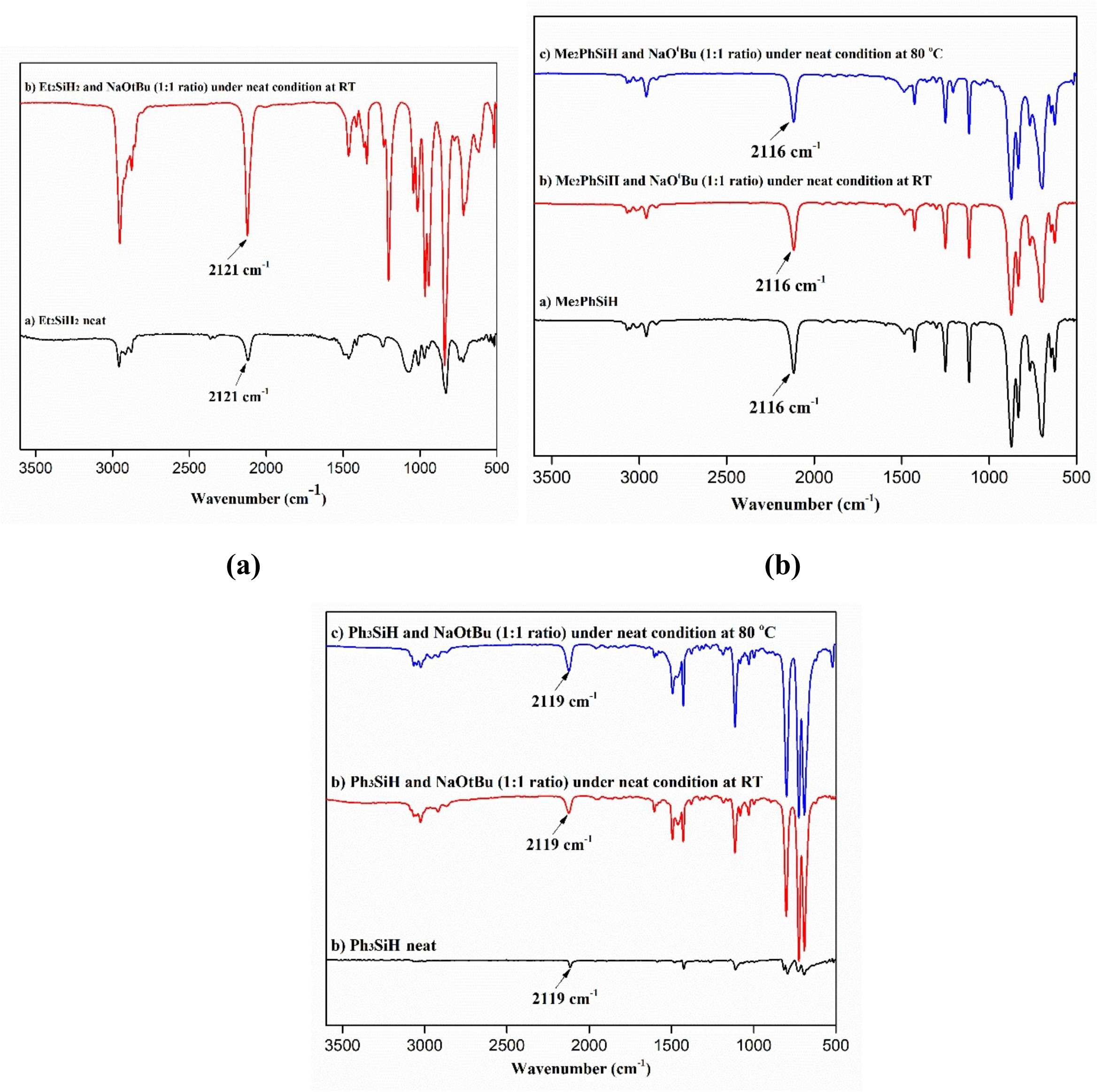


Figure S1: AT-IR Spectra of: (a) NaO^{t}Bu, (b) Ph_2SiH_2, (c) Reaction mixture of NaO^{t}Bu and Ph_2SiH_2 at RT, and (d) Reaction mixture of NaO^{t}Bu and Ph_2SiH_2 at 80 ºC for 10 min.

Reactions using different silane reagents (Et_2SiH_2, Me_2PhSiH and Ph_3SiH) with NaO^{t}Bu.

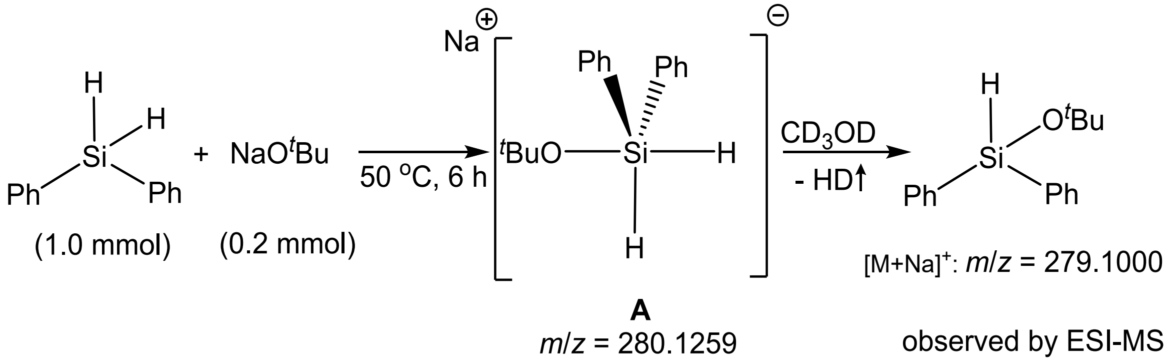


(a) **(b)**

(c)

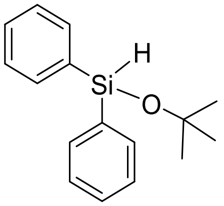
Figure S2: AT-IR Spectra of: (a) Reaction mixture of NaO^{t}Bu and Et_2SiH_2 at RT, (b) Reaction mixture of NaO^{t}Bu and Me_2PhSiH at RT and 80 °C, (c) Reaction mixture of NaO^{t}Bu and Ph_3SiH at RT and 80 °C.

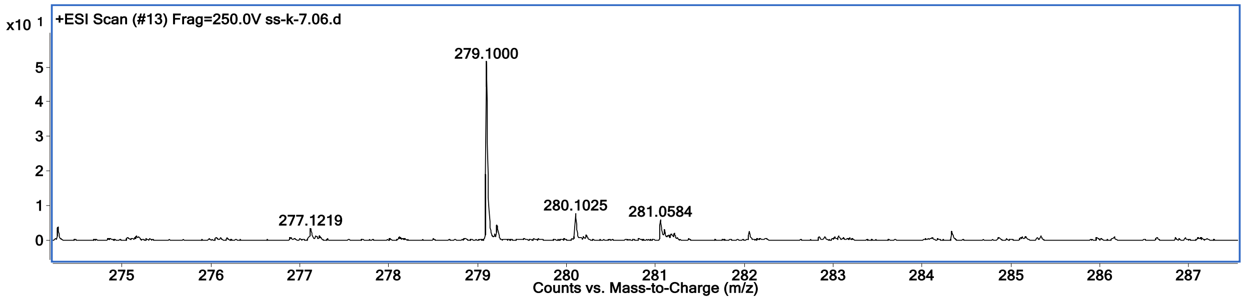
ESI-MS studies of intermediate (A):



Scheme S3. Reaction of Ph_2SiH_2 with NaO^{t}Bu in CD_3OD.

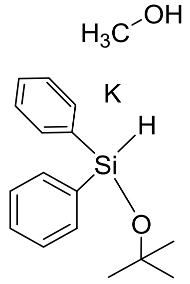
In a glovebox, to an oven-dried Y-NMR tube, NaO^{t}Bu (20 mg, 0.2 mmol) and Ph_2SiH_2 (184.0 mg, 5 equiv, 1.0 mmol) were added and the reaction mixture was stirred at 50 °C for 6 h. Mass sample was prepared in glove box using freshly distilled and degassed MeOH. When reactant Ph_2SiH_2 and NaO^{t}Bu were mixed in methanol, vigorous effervescence observed. Immediate ESI-MS were performed after samples preparation (Scheme S3).



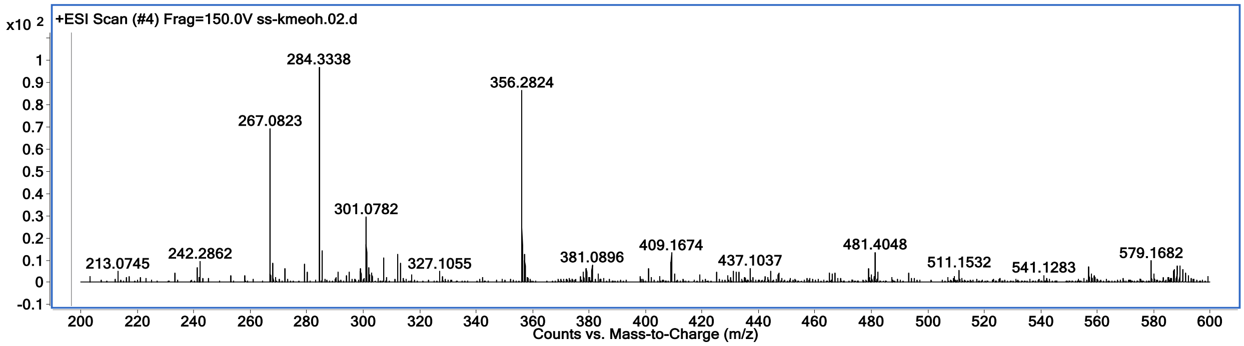


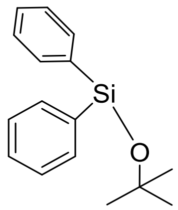
HRMS (ESI) calcd. for $C_{16}H_{20}OSiNa$ [M+Na]$^+$: 279.1181; found [M+Na]$^+$: 279.1000.

Other relevant peaks observed in (+ESI) HRMS:



Exact mass: 327.1183
Observed: 327.1055

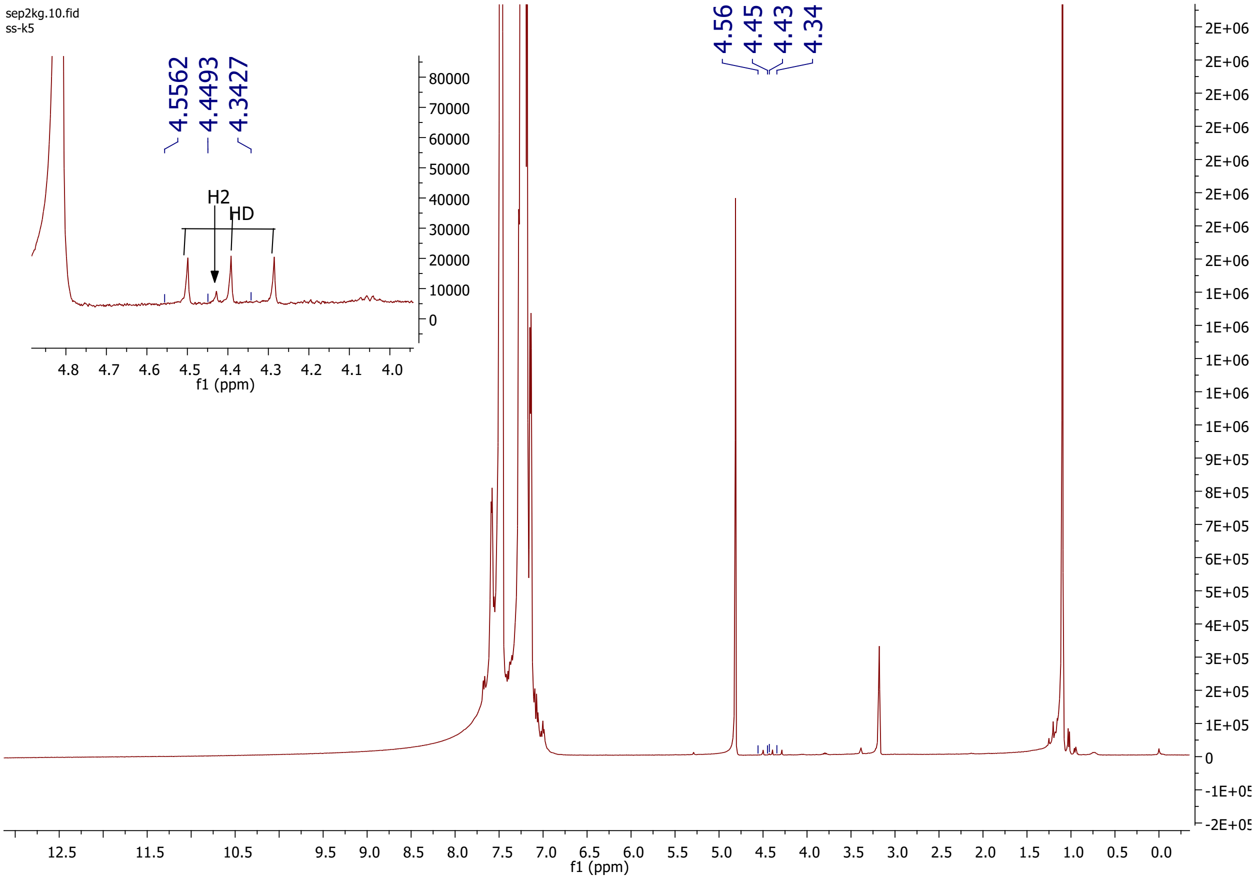




Exact Mass $[M+H]^+$: 256.1283
Observed [M+H]+: 256.0897

HRMS data obtained after irreversible hydrogen evolution of intermediate (A)

To validate the irreversible hydrogen evolution during ESI-MS analysis due to MeOH, isotope labelling experiment was performed using CD_3OD. The sample was taken near 400 MHz NMR spectrometer and CD_3OD (400 uL) was added. Intense liberation of gas was observed. The NMR tube was capped immediately and secured with parafilm. The ^1H NMR was recorded within 5 minute of sample preparation. Vigorous effervescence were continues observed inside the sealed NMR tube even after 15 minutes of data acquisition.

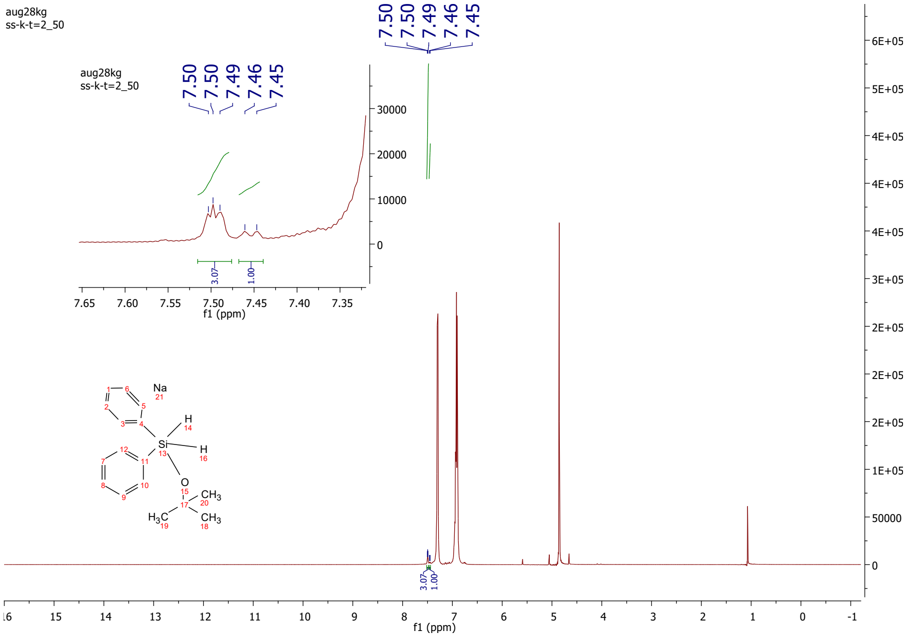


^{1}H NMR of [(A)+CD_3OD] (400 MHz, C_6D_6)

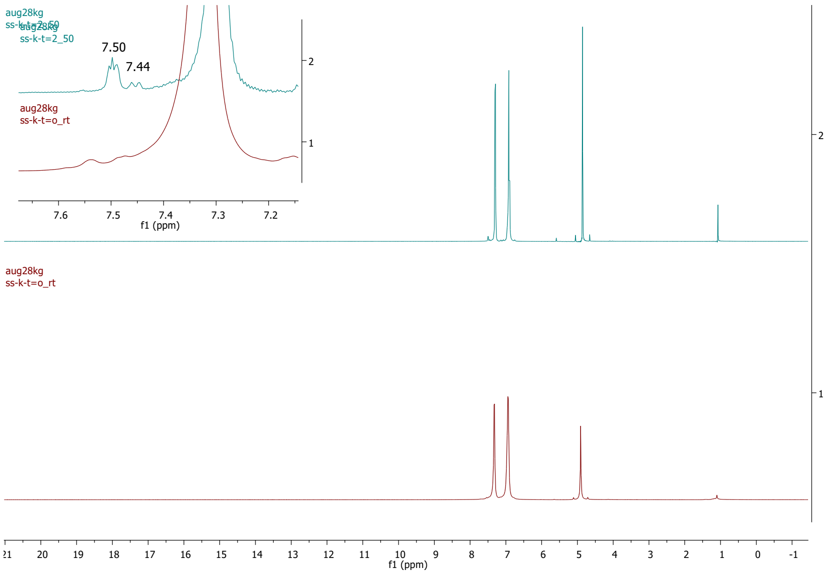
Variable temperature NMR study

In a glovebox, to an oven-dried Y-NMR tube, NaO^{t}Bu (26 mg, 0.27 mmol) and Ph_2SiH_2 (249.0 mg, 5 equiv, 1.35 mmol) were added and the reaction mixture was monitor by ^{1}H NMR spectroscopy.

The ^{1}H NMR was recorded at room temperature and 50 °C. The ^{1}H NMR recorded at 50 °C showed de-shielded proton signals.



^{1}H NMR (500 MHz, C_6D_6) spectrum at 50 °C.

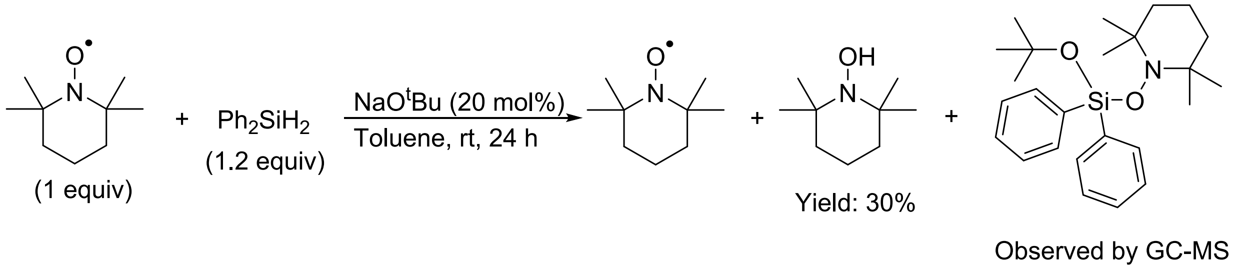


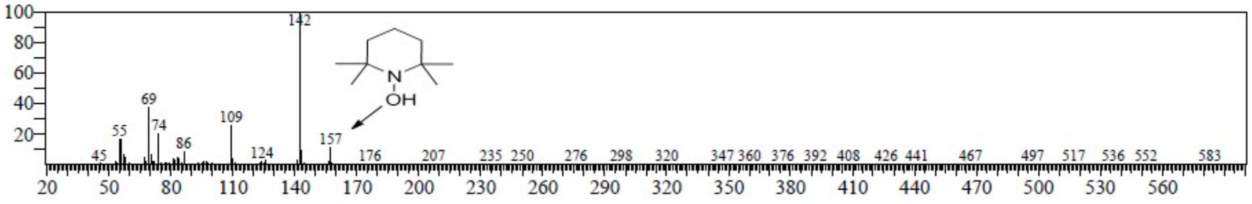
^{1}H NMR (500 MHz, C_6D_6) spectrum at room temperature and at 50 °C.

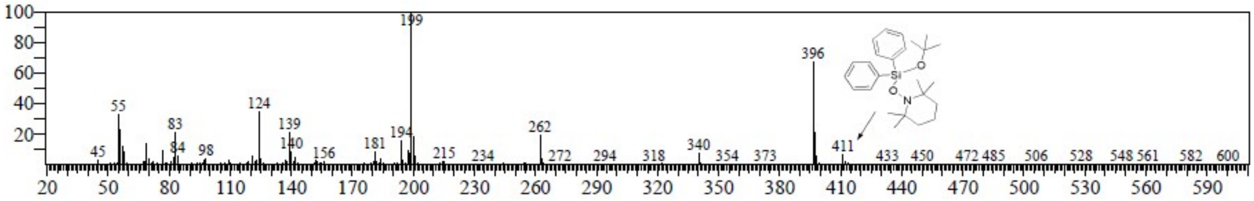
Preliminary studies on catalytic reaction mechanism.

Experimental Procedures for Examples Described in Scheme 6: Reaction in the presence of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl)

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^tBu (4.8 mg, 20 mol %), Ph_2SiH_2 (55 mg, 1.2 equiv, 0.3 mmol), TEMPO (39 mg, 0.25 mmol) and toluene (1 mL) were added and the reaction mixture was stirred at room temperature for 24 h. The volatiles were removed in vacuo and rude reaction mixture was analyzed by GC-MS.







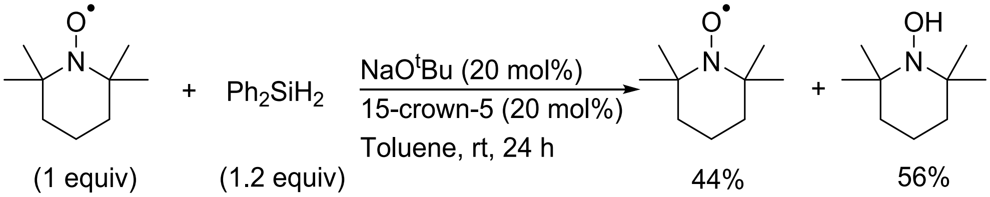
The GC-MS analysis of the reaction mixture showed the formation of reduced TEMPO product. Careful analysis of the reaction mixture showed a signal correspond to TEMPO-$SiPh_2(O^tBu)$ adduct (m/z = 411), formed from the trapping of the silyl radical by TEMPO.

GC-MS: m/z 411 (M^+), 396 (M^+-CH_3)

Further, addition of styrene (**1a**) or crown ether (15-crown-5) to the above reaction mixture also gave reduce TEMPO radical product.

Reaction in the presence of 15-crown-5 and TEMPO

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (5 mg, 20 mol %), Ph_2SiH_2 (55 mg, 1.2 equiv, 0.3 mmol), TEMPO (39 mg, 0.25 mmol), 15-crown-5 (11 mg, 20 mol %) and toluene (1 mL) were added to reaction vial and the reaction mixture was stirred at room temperature for 24 h. The volatiles were removed in vacuo, and crude reaction mixture was analyzed by GC-MS.

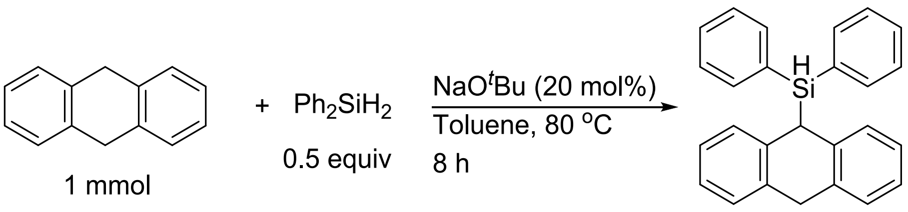


Experimental Procedures for Examples Described in Scheme 7.

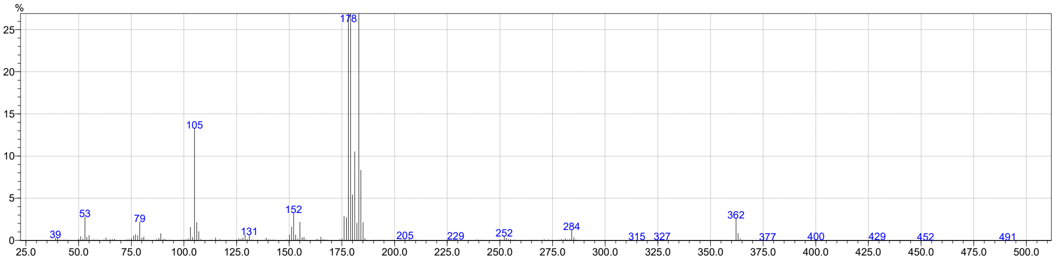
In a nitrogen filled glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (5 mg, 20 mol %), Ph_2SiH_2 (55 mg, 0.3 equiv, 0.3 mmol), and alkene (cyclohexene or 1-hexene; 0.25 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. After completion, the crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of celite. The solvent was removed in vacuo, and crude reaction mixture was analyzed by GC-MS analysis.

Stoichiometric reaction of DHA with Ph_2SiH_2 in the absence of 1a.

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar rapped by Al foil, 9,10-dihydroanthracene (1 equiv), NaO^tBu (19.2 mg, 20 mol %) and toluene (1 mL) were added and stirred until clear solution obtained. To this, Ph_2SiH_2 (92 mg, 0.5 equiv) was added and the reaction mixture was stirred at 80 ºC for 8 h and analyzed by GC-MS. Result shows the formation of DHA-$SiHPh_2$ adduct at m/z = 284 (M^+-Ph).



DHA–$SiPh_2H$ adduct
Observed by GC-MS
m/*z*: 362, 284 (M^+-Ph)

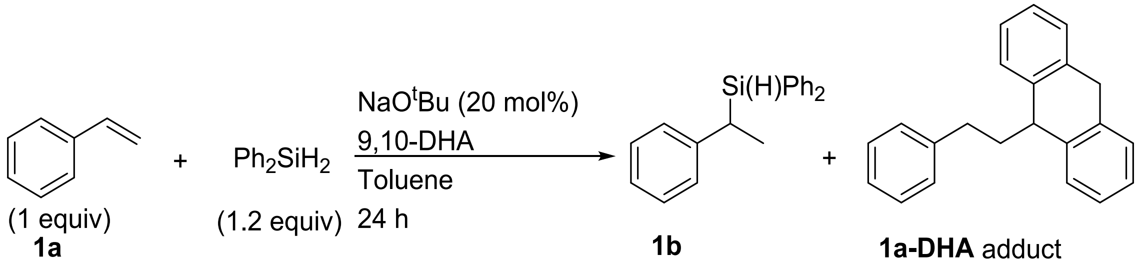


GC-MS of DHA–$SiPh_2H$ adduct

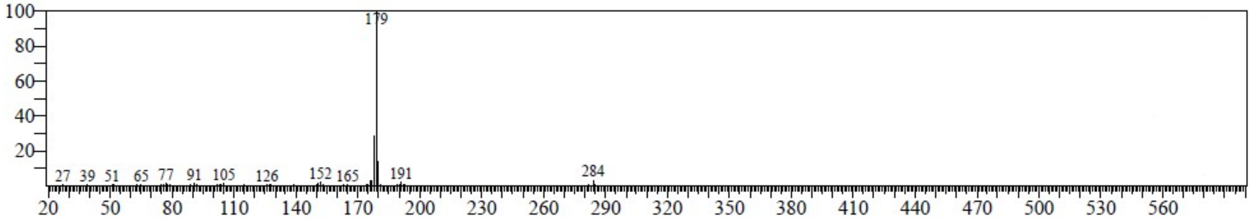
Radical Scavenger Experiments: Experimental Procedures for Examples Described in Scheme 8.

Using 9,10-Dihydroanthracene (Scheme 8a).

In a glovebox, to an oven-dried 15 mL thick-walled reaction tube equipped with a magnetic stirring bar rapped by Al foil, 9,10-dihydroanthracene (1.2-10 equiv) and toluene (8-10 mL) were added and stirred until clear solution obtained. To this, NaO^{t}Bu (19.2 mg, 20 mol %), Ph_2SiH_2 (220 mg, 1.2 equiv, 1.2 mmol) and styrene (**1a**; 104 mg, 1 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. The volatiles were removed in vacuo and analyzed by GC-MS and ^{1}H NMR spectroscopy.

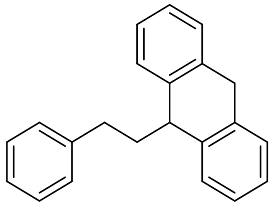


Styrene (**1a**) (mmol)	Ph_2SiH_2 (equiv)	NaO^{t}Bu (20 mol%)	9,10-DHA (equiv)	Temp. (ºC)	Time (h)	**1b** (%)	9,10-DHA Adduct (%)
0.25	1.2	5 mg	1.2	40	24	33	0
0.25	1.2	5 mg	2	80	24	75	11
0.1	1.2	2 mg	5	80	24	54	46
0.1	**1.2**	2 mg	**10**	**80**	**24**	**26**	**74**



GC-MS of **1a-DHA** adduct

9-Phenethyl-9,10-dihydroanthracene (1a-DHA)



Chromatography: R_f = 0.7; in hexane.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.4 Hz, 4H), 7.24 – 7.19 (m, 6H), 7.15 – 7.10 (m, 3H), 4.14 (d, J = 18.3 Hz, 1H), 3.95 (t, J = 7.2 Hz, 1H), 3.86 (d, J = 18.4 Hz, 1H), 2.60 (t, J = 10 Hz, 2H), 1.98 – 1.92 (m, 2H).

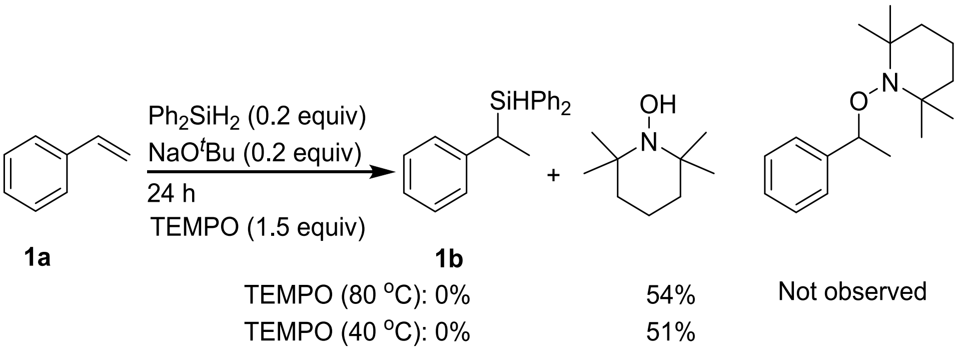
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.02, 140.44, 136.17, 128.37, 128.35, 128.03, 127.89, 126.20, 126.14, 125.79, 47.04, 38.84, 35.37, 33.63.

DEPT – 135: 135.44, 135.21, 128.73, 128.37, 128.35, 128.03, 127.89, 126.20, 126.14, 125.79, 47.04, 38.84, 35.38, 33.63.

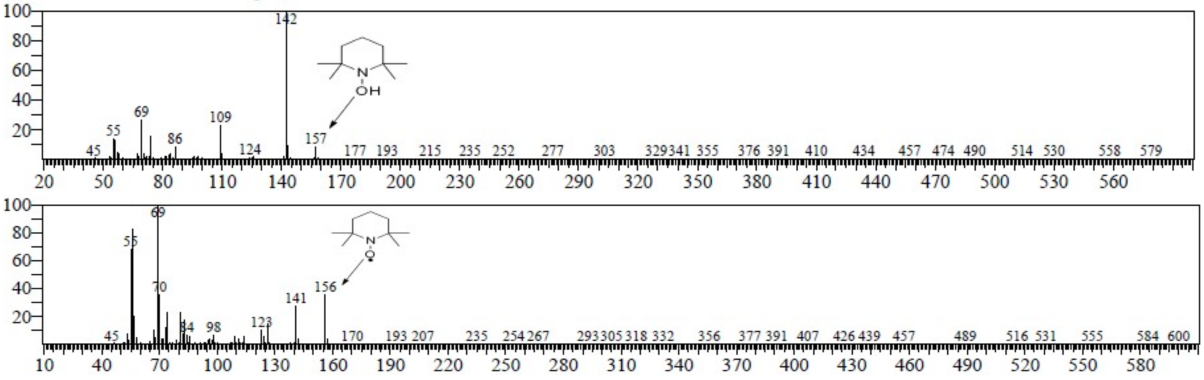
HRMS (ESI) calcd. for $C_{23}H_{24}OSiNa$ $[M+H]^+$: 285.1643; found $[M+H]^+$: 285.1643.

Using TEMPO (Scheme 8b).

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (4.8 mg, 20 mol %), Ph_2SiH_2 (55 mg, 1.2 equiv, 0.3 mmol), styrene (**1a**; 26 mg, 0.25 mmol), TEMPO and toluene (1 mL) were added and the reaction mixture was stirred at given temperature for 24 h. The volatiles were removed in vacuo and analysed by GC-MS.

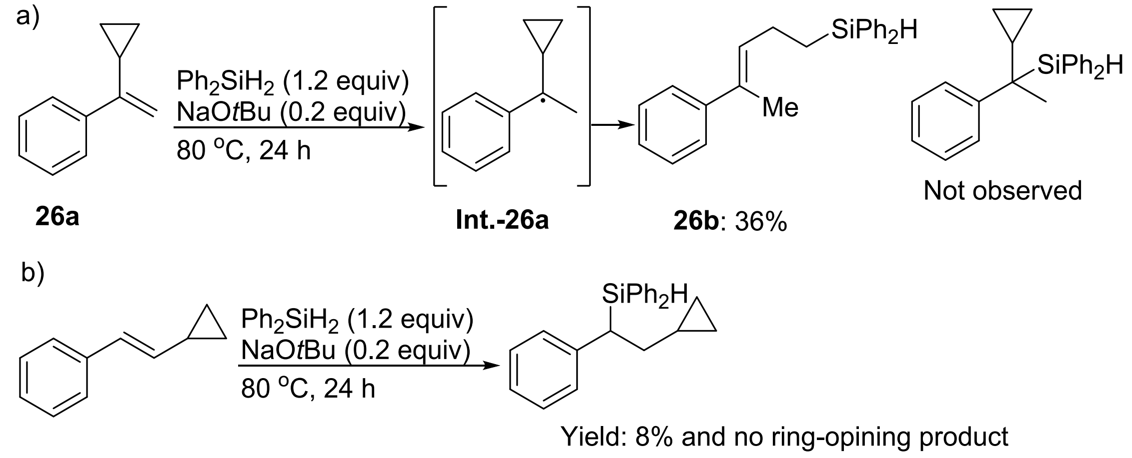


Styrene (**1a**) (mmol)	Ph_2SiH_2 (equiv)	NaO^{t}Bu (20 mol%)	TEMPO (equiv)	Temp. (ºC)	Time (h)	TEMPO (%)	Reduced TEMPO (%)
0.25	1.2	5 mg	1.5	80	24	46	54
0.25	1.2	5 mg	1.5	40	24	49	51
0.25	1.2	5 mg	1	40	24	83	17



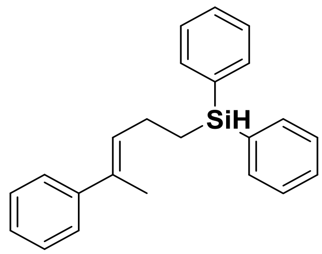
GC-MS of TEMPO added reaction mixture

Radical Clock Experiments. Experimental Procedures for Examples Described in Scheme 9.



In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (19.2 mg, 20 mol %), Ph_2SiH_2 (220 mg, 1.2 equiv, 1.2 mmol), and alkene (α-cyclopropyl-substituted styrene (**26a**) or β-cyclopropyl styrene; 1 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. The volatiles were removed in vacuo to afford the hydrosilylation product, which were purified by column chromatography. Experiment with β-cyclopropyl styrene gave only 8% of hydrosilylated product, however, no ring-opened product was observed by GC-MS analysis.

Diphenyl(4-phenylpent-3-en-1-yl)silane (26b)



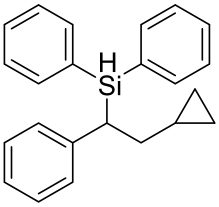
Chromatography: R_f = 0.6; in hexane/EtOAc 50:1.

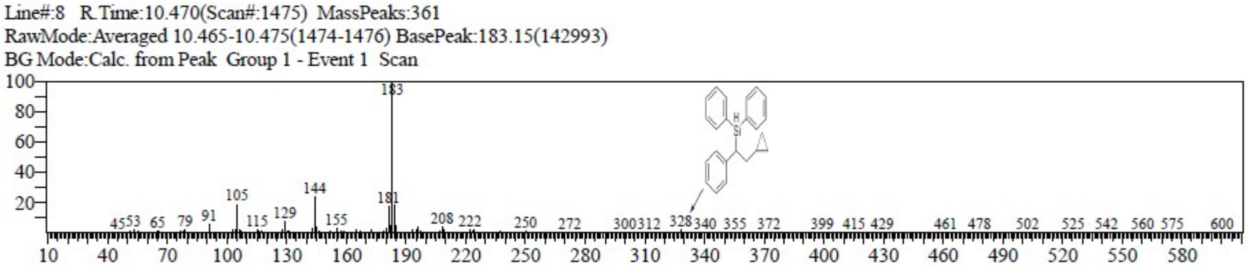
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.50 (d, J = 10 Hz, 4H), 7.33-7.26 (m, 6H), 7.22-7.17 (m, 4H), 7.14-7.10 (m, 1H), 5.72 (t, J = 10 Hz, 1H), 4.85 (t, J = 1 H), 2.28 (dd, J = 15 Hz, 10 Hz, 2H), 1.84 (s, 3H), 0.80-0.77 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.91, 135.20, 134.39, 134.09, 130.34, 129.62, 128.14, 128.07, 126.50, 125.65, 23.60, 15.71, 12.46.

HRMS (ESI) calcd. for $C_{23}H_{24}OSiNa$ [M+H]$^+$: 329.1726; found [M+H]$^+$: 329.1727.

(2-Cyclopropyl-1-phenylethyl)diphenylsilane

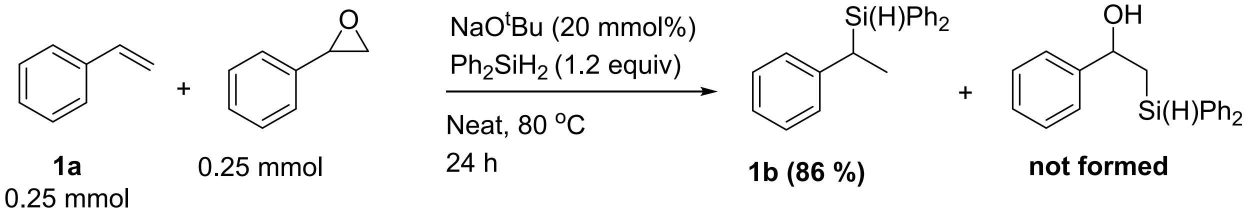




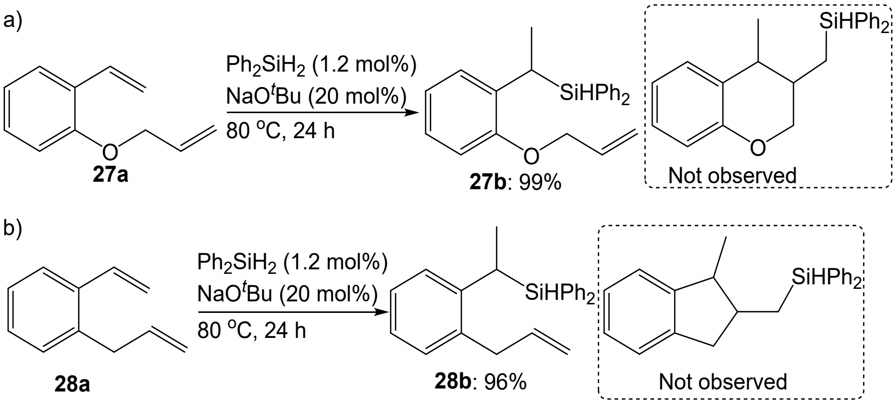
GC-MS of reaction mixture of β-cyclopropyl styrene

Additional Control Experiment

To investigate the possibility of silyl anions formation, a mixture of styrene **1a** and 2-phenyloxirane was exposed to H_2SiPh_2 and NaO^{t}Bu. However, no desired products were observed, excluding the formation of nucleophilic benzyl or silyl anions species.

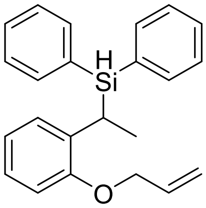


Experimental Procedure for Example Described in Scheme 10.



In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, NaO^{t}Bu (19.2 mg, 20 mol %), Ph_2SiH_2 (220 mg, 1.2 equiv, 1.2 mmol), and 1-(allyloxy)-2-vinylbenzene (**27a** or **28a**; 1 mmol) were added and the reaction mixture was stirred at 80 ºC for 24 h. The volatiles were removed in vacuo to afford the hydrosilylation product, which were purified by column chromatography.

(1-(2-(Allyloxy)phenyl)ethyl)diphenylsilane (27b)



Chromatography: R_f = 0.6; in hexane/EtOAc 50:1.

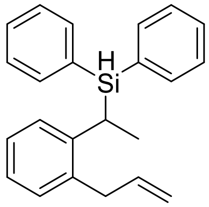
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.56 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 – 7.24 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.10 – 7.01 (m, 1H), 6.87 (td, *J* = 7.4, 0.8 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 5.86 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.28 (ddd, *J* = 17.3, 3.2, 1.6 Hz, 1H), 5.22 – 5.12 (m, 1H), 4.76 (d, *J* = 3.5 Hz, 1H), 4.29 (ddt, *J* = 12.8, 5.2, 1.4 Hz, 1H), 4.03 (ddt, *J* = 12.8, 4.9, 1.5 Hz, 1H), 3.38 (dq, *J* = 11.5, 3.8 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 155.25, 135.79, 135.41, 133.97, 133.80, 133.78, 133.43, 129.63, 129.31, 127.93, 127.53, 127.44, 125.64, 120.75, 116.90, 111.16, 68.59, 18.76, 15.79.

^{29}Si NMR (100 MHz, $CDCl_3$) δ (ppm) -7.98.

HRMS (ESI) calcd. for $C_{23}H_{24}OSiNa$ $[M+Na]^+$: 367.1494; found $[M+Na]^+$: 367.1492.

(1-(2-Allylphenyl)ethyl)diphenylsilane (28b)



Chromatography: R_f = 0.6; in hexane/EtOAc 50:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.28 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 6.7 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.07 – 7.04 (m, 1H), 7.00 – 6.95 (m, 3H), 5.70 (ddt, J = 16.5, 10.1, 6.3 Hz, 1H), 4.89 (dd, J = 10.1, 1.3 Hz, 1H), 4.83 – 4.72 (m, 2H), 3.16 (dd, J = 16.1, 6.4 Hz, 1H), 2.94 (ddd, J = 12.2, 11.1, 4.8 Hz, 2H), 1.34 (d, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.97, 137.17, 136.91, 135.89, 135.39, 133.39, 132.94, 129.85, 129.56 (d, J = 2.8 Hz), 128.04, 127.73, 127.46, 126.56, 125.06, 115.72, 37.60, 21.66, 17.14.

HRMS (ESI) calcd. for $C_{23}H_{24}OSiNa$ $[M+Na]^+$: 351.1545; found $[M+Na]^+$: 351.1549.

EPR Experiments:

EPR spectroscopy was utilized to detect radical intermediates in these hydrosilylation reactions. However, due to the very short lifetime and insufficient concentrations of radial species at ambient temperature it is quite tough for EPR detection and characterization.

First, in a nitrogen-filled glove box, 1-methyl-4-vinylbenzene (Figure S3a), NaO^{t}Bu (Figure S3b), and Ph_2SiH_2 (Figure S3c) were added separately to an oven-dried 10 mL thick-walled reaction tubes and then transferred into an EPR tubes, which were fitted with a plastic cap, taped with parafilm, and then removed from the glove box. EPR spectra was acquired at room temperature. However, no EPR signal were observed. Also, EPR measurement was carried out for toluene solvent to exclude the presence of any radical species in it.

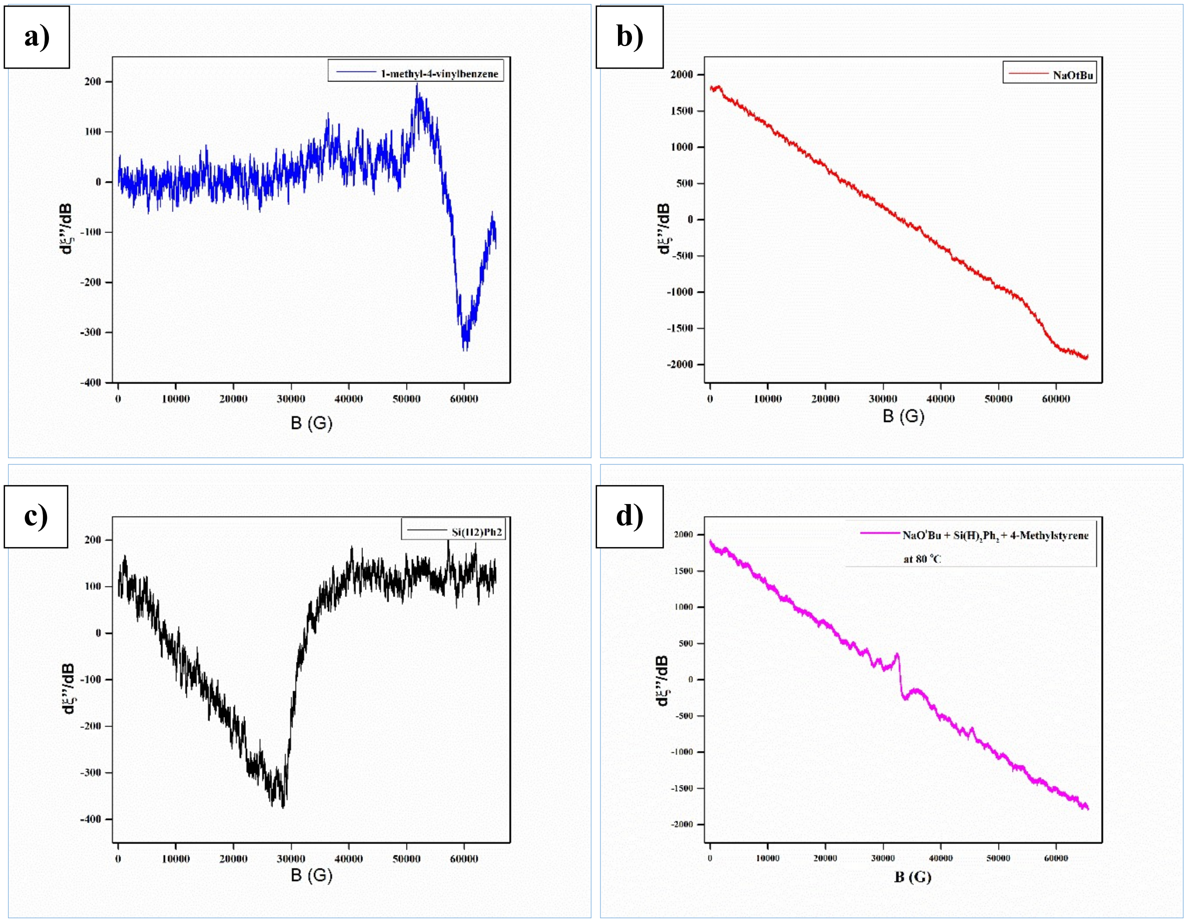


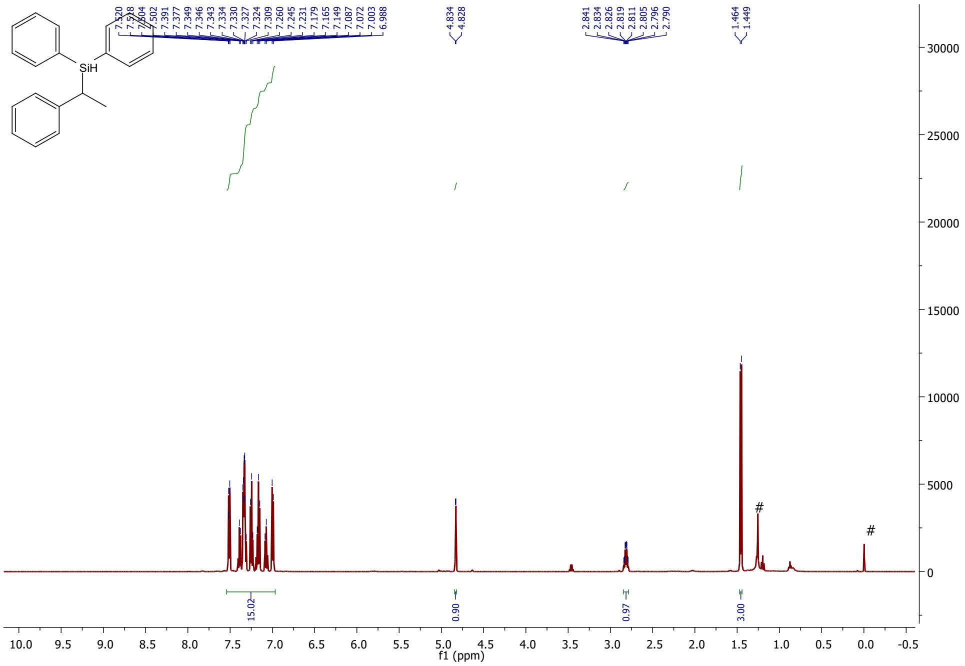
Figure S3: EPR Spectra of: (a) 1-methyl-4-vinylbenzene, (b) NaO^{t}Bu, (c) Diphenylsilane, and (d) Reaction Mixture of NaO^{t}Bu, Diphenylsilane and 1-Methyl-4-vinylbenzene in Toluene Solvent After 5 min at 80 ºC.

In the next experiment (Figure S3d), 1-methyl-4-vinylbenzene (11.8 mg, 0.1 mmol), NaO^{t}Bu (1.9 mg, 20 mol%), Ph_2SiH_2 (21.96 mg, 1.2 equiv, 0.12 mmol) and toluene (0.1 mL) were added to an oven-dried 10 mL thick-walled reaction tube and stirred at 80 ºC for 5 min. Then transferred the reaction mixture into an EPR tube, which was fitted with a plastic cap, taped with parafilm. EPR spectra was acquired at room temperature. A signal at approximately g = 1.3501 was observed.

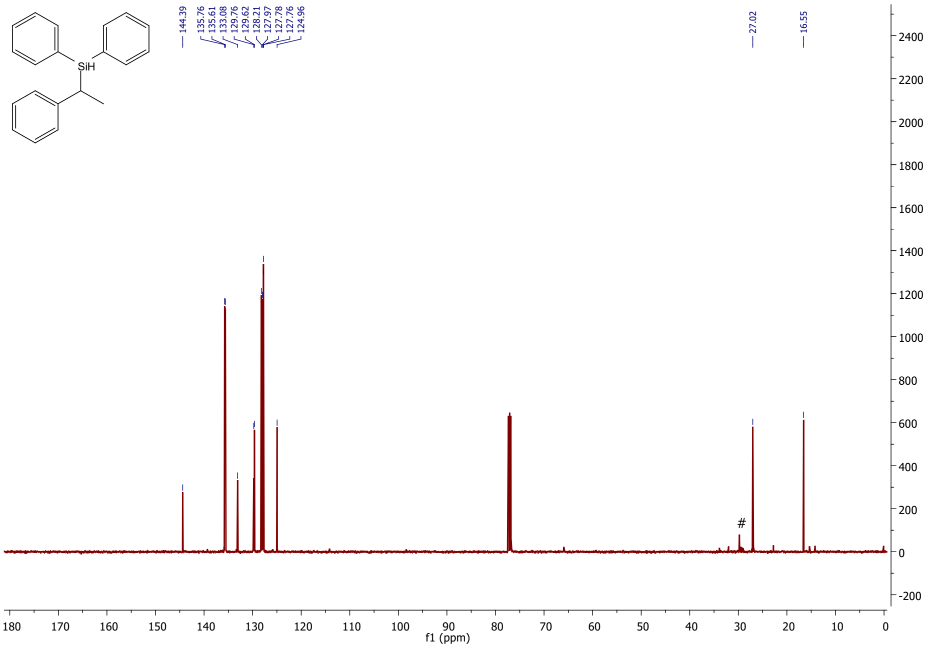
IX. Spectroscopic Data of Hydrosilylation products

Note: Resonances denoted by (#) corresponds to solvent/grease/impurities.

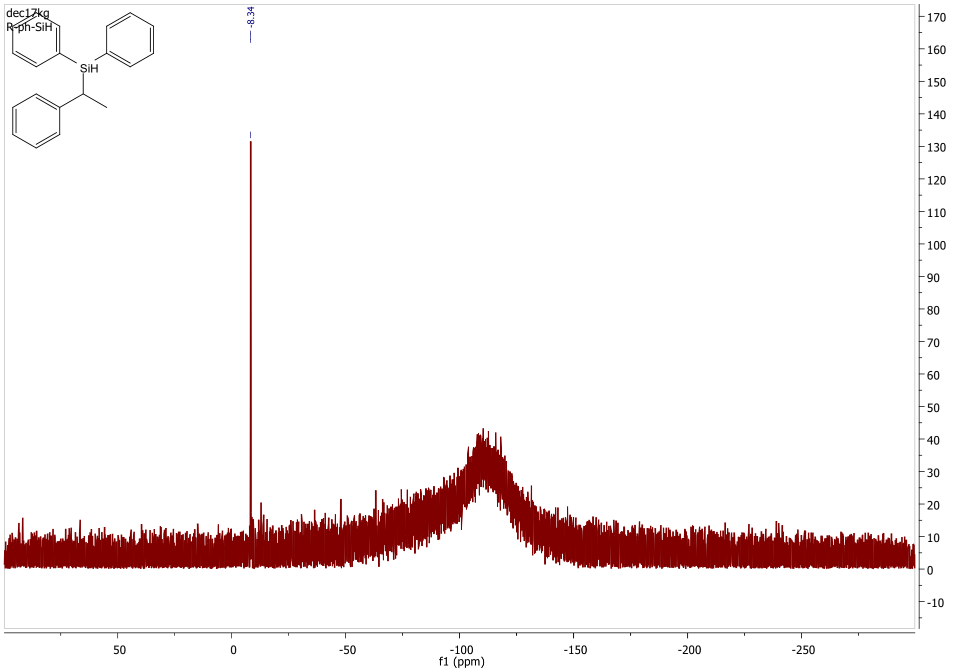
Diphenyl(1-phenylethyl)silane (1b)



^{1}H NMR of 1b (500 MHz, CDCl$_3$)

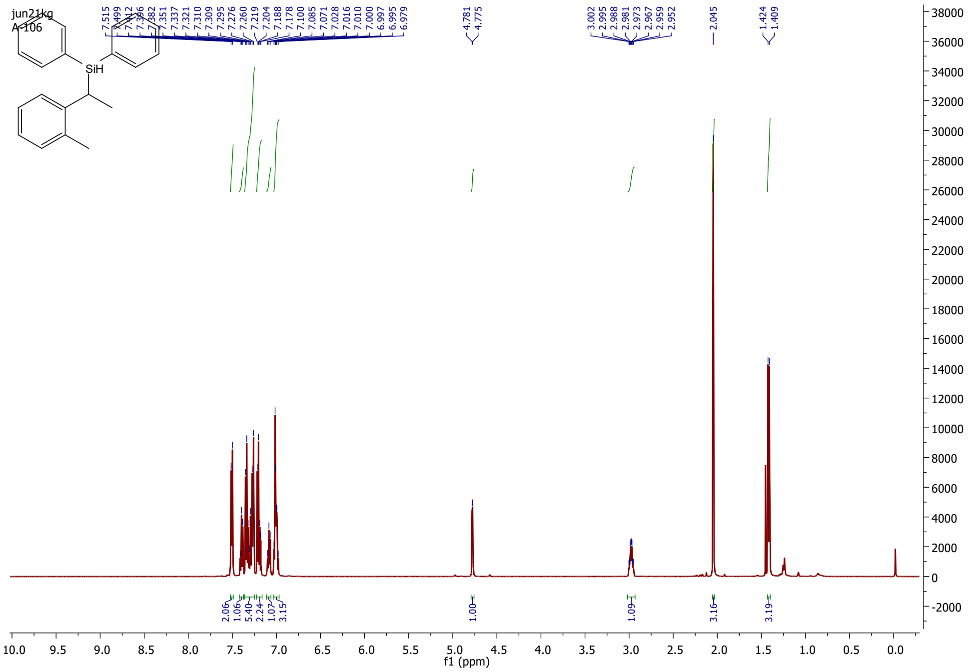


^{13}C NMR of 1b (125 MHz, CDCl$_3$)

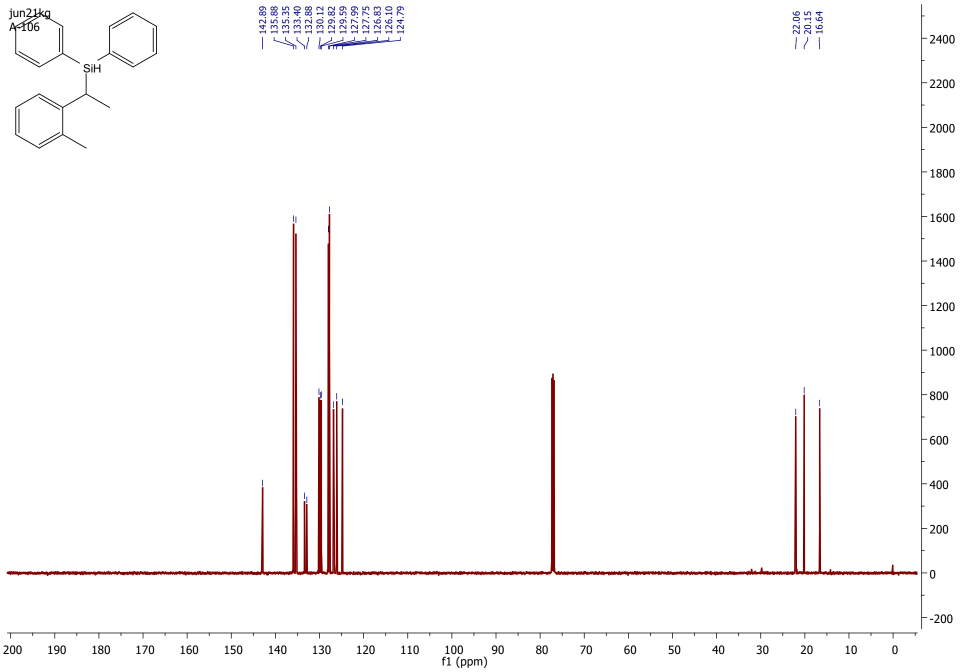


^{29}Si NMR of 1b (100 MHz, CDCl$_3$)

Diphenyl(1-(o-tolyl)ethyl)silane (2b)

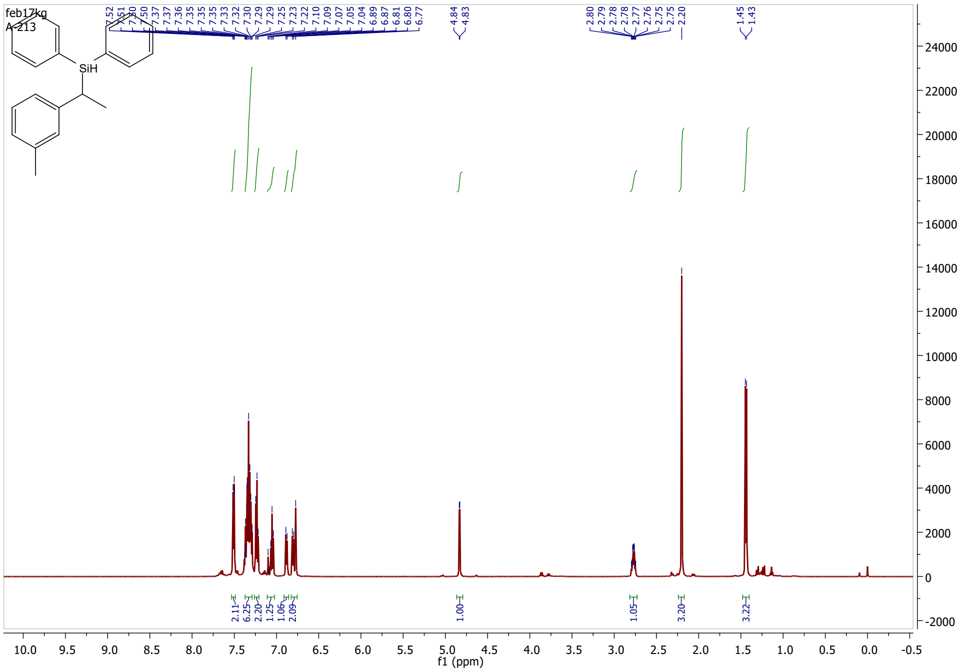


^{1}H NMR of 2b (500 MHz, CDCl$_3$)

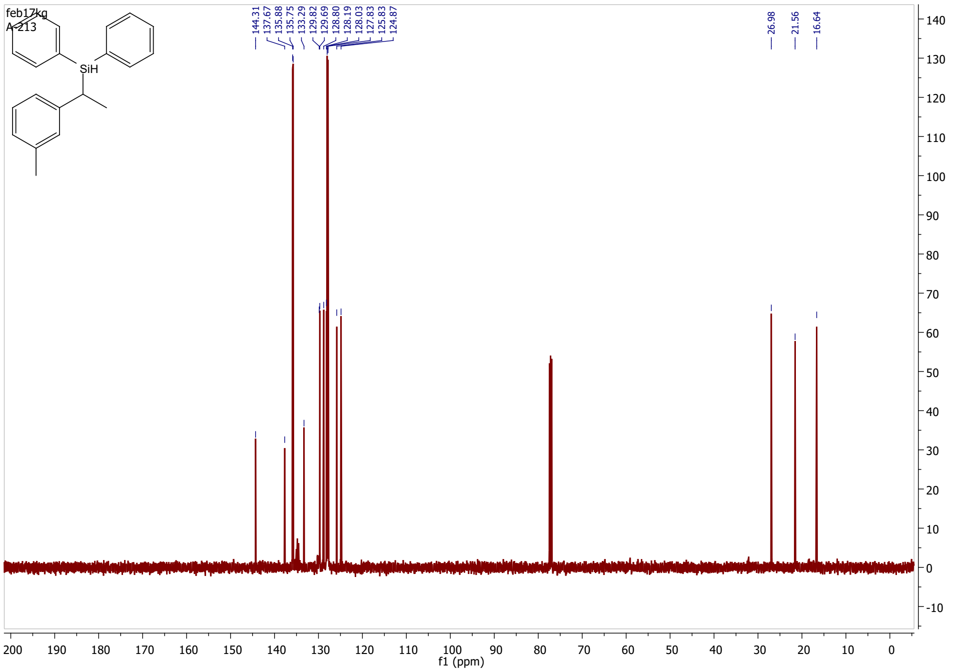


^{13}C NMR of 2b (125 MHz, CDCl$_3$)

Diphenyl(1-(m-tolyl)ethyl)silane (3b)

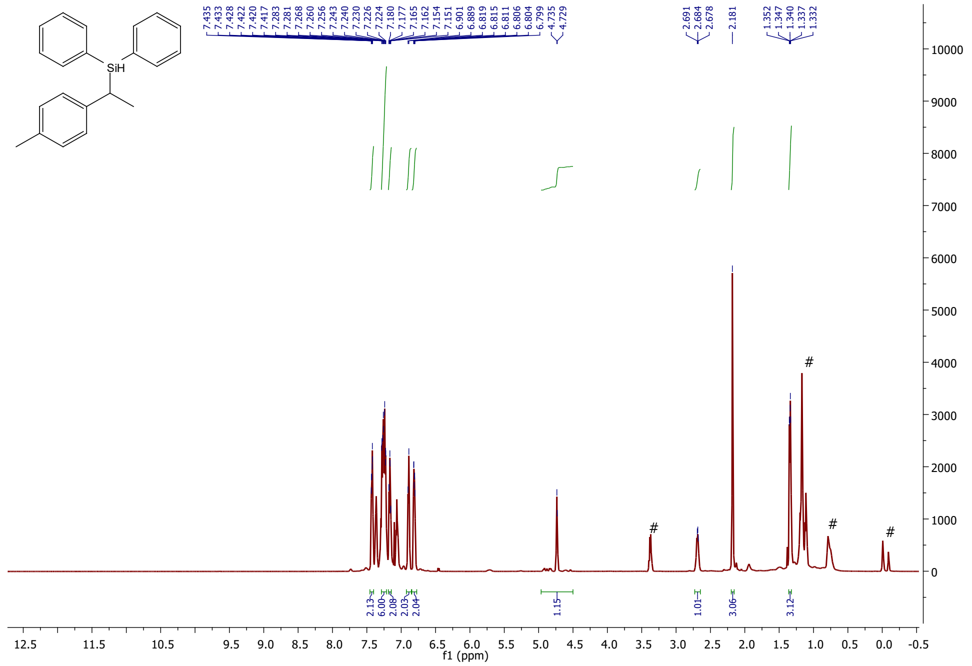


^{1}H NMR of 3b (500 MHz, CDCl$_3$)

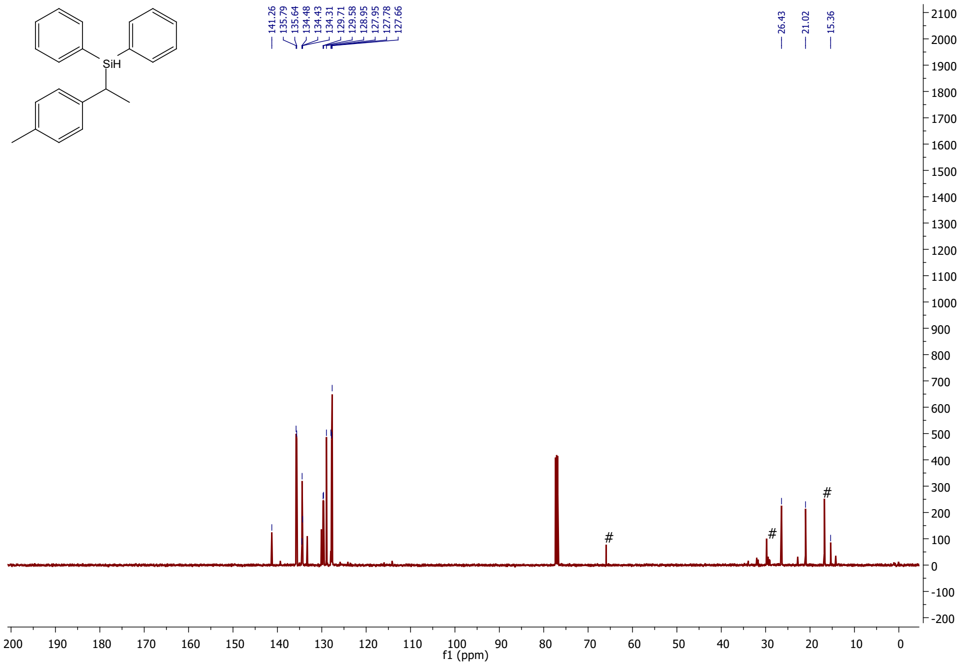


^{13}C NMR of 3b (125 MHz, CDCl$_3$)

Diphenyl(1-(p-tolyl)ethyl)silane (4b)

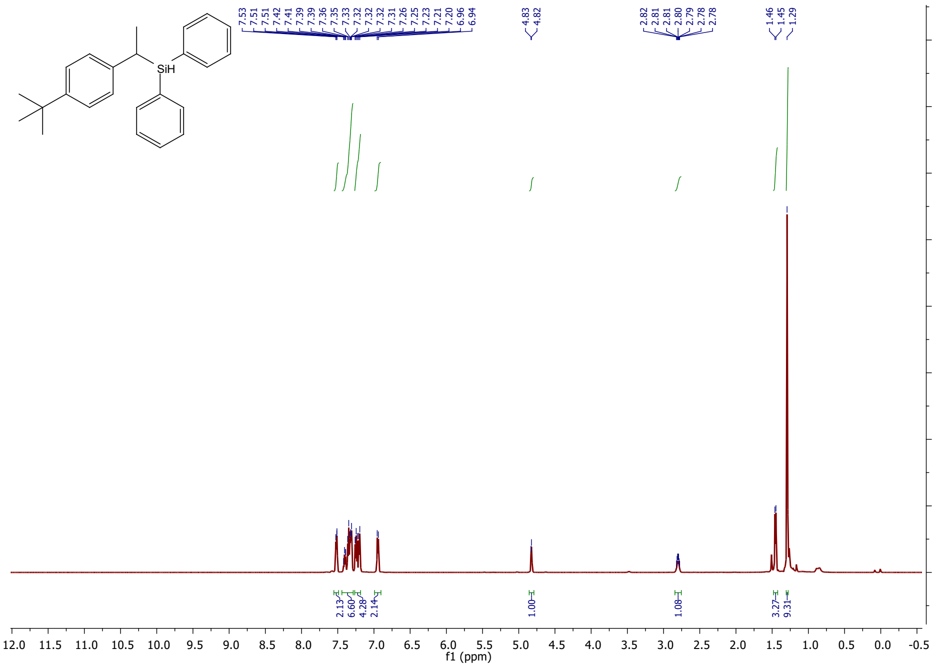


^{1}H NMR of 4b (500 MHz, CDCl$_3$)

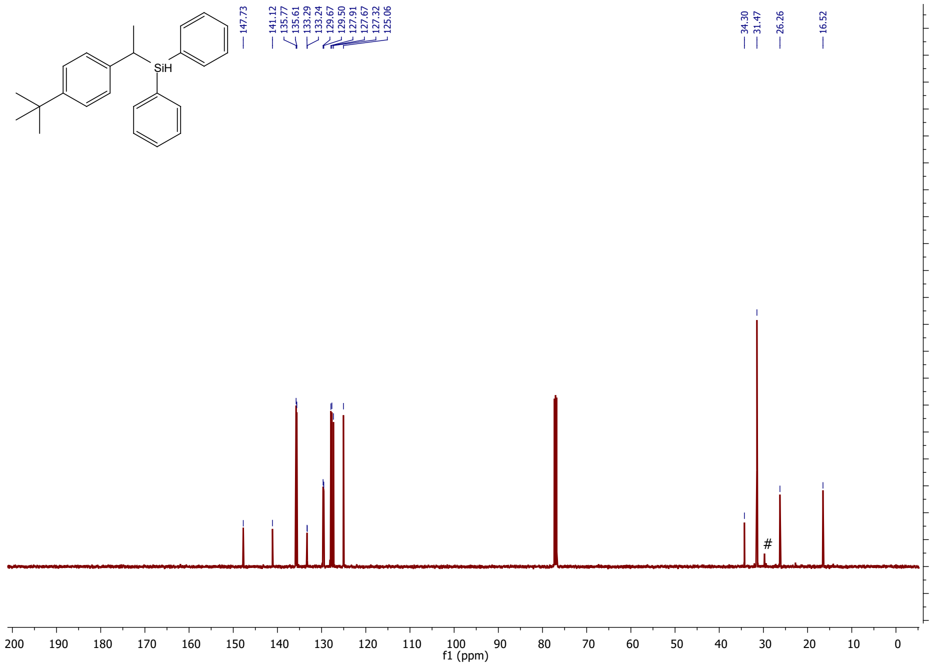


^{13}C NMR of 4b (125 MHz, CDCl$_3$)

(1-(4-(Tert-butyl)phenyl)ethyl)diphenylsilane (5b)

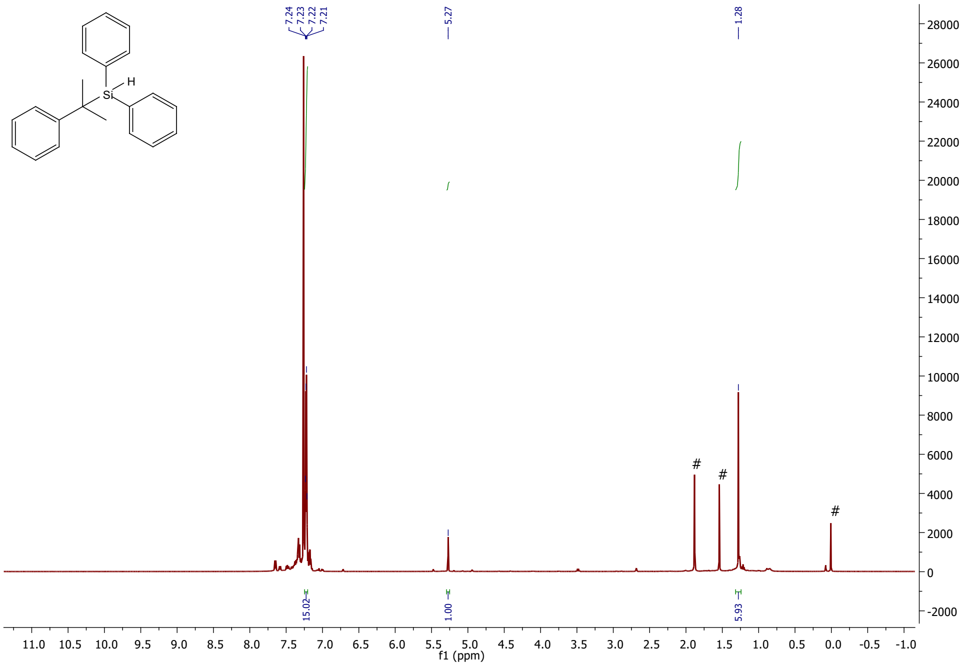


^{1}H NMR of 5b (500 MHz, CDCl$_3$)

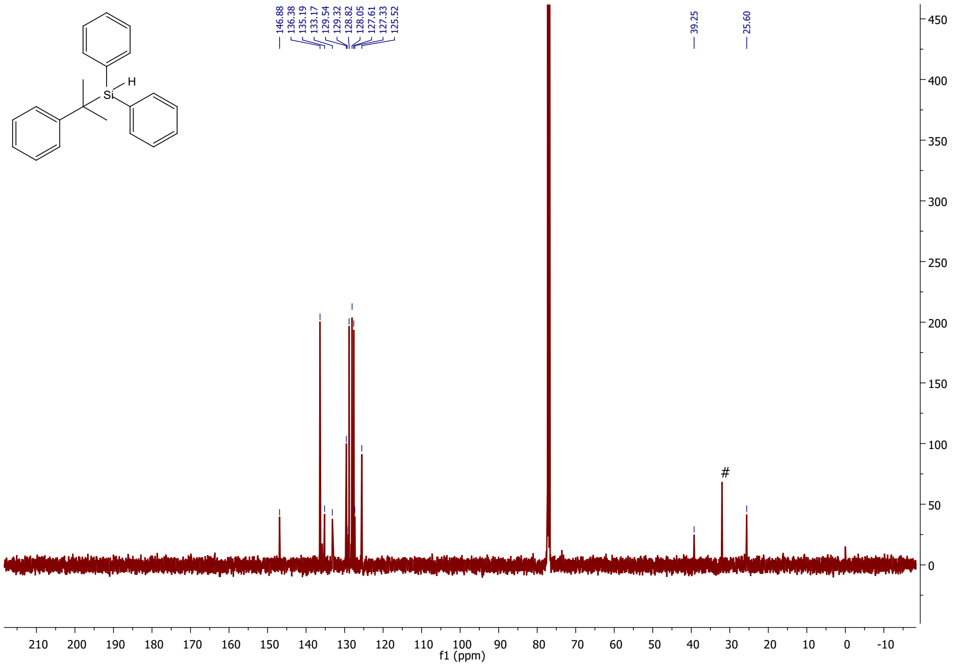


^{13}C NMR of 5b (125 MHz, CDCl$_3$)

Diphenyl(2-phenylpropan-2-yl)silane (6b)

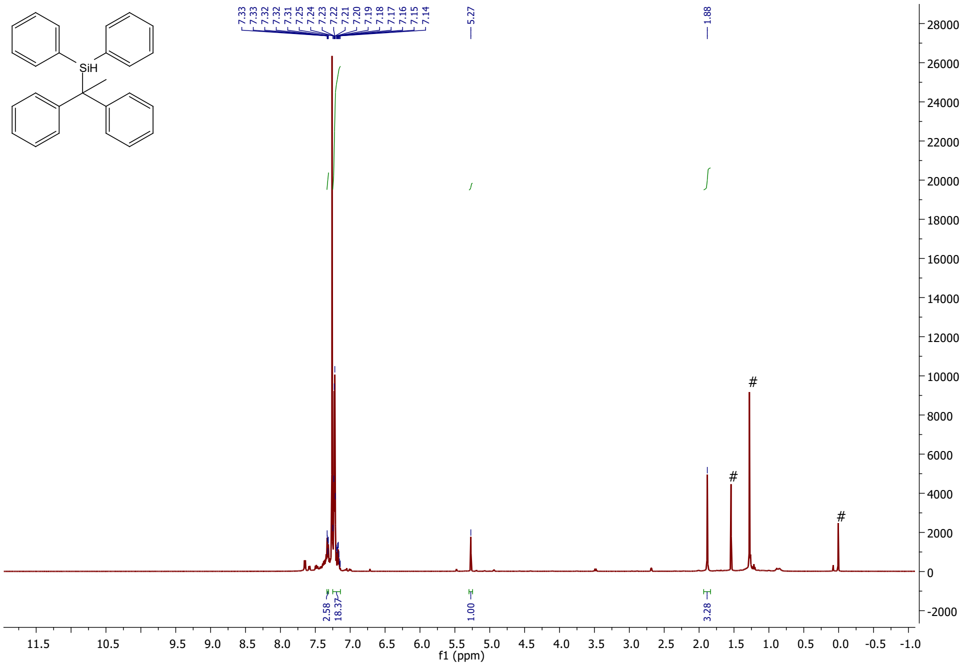


^{1}H NMR of 6b (500 MHz, CDCl$_3$)

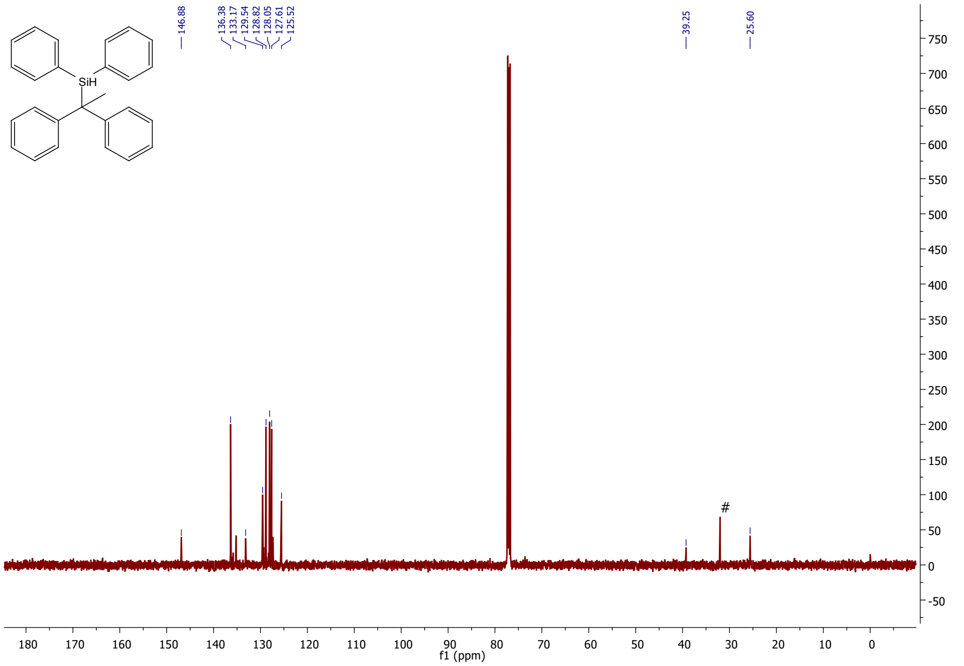


^{13}C NMR of 6b (125 MHz, CDCl$_3$)

(1,1-Diphenylethyl)diphenylsilane (7b)

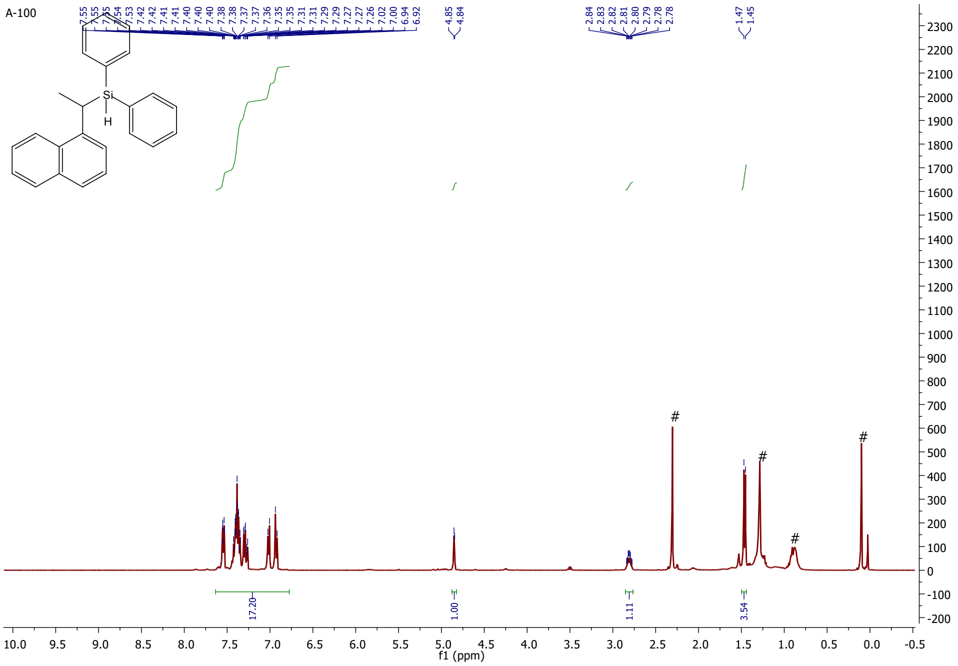


^{1}H NMR of 7b (500 MHz, CDCl$_3$)

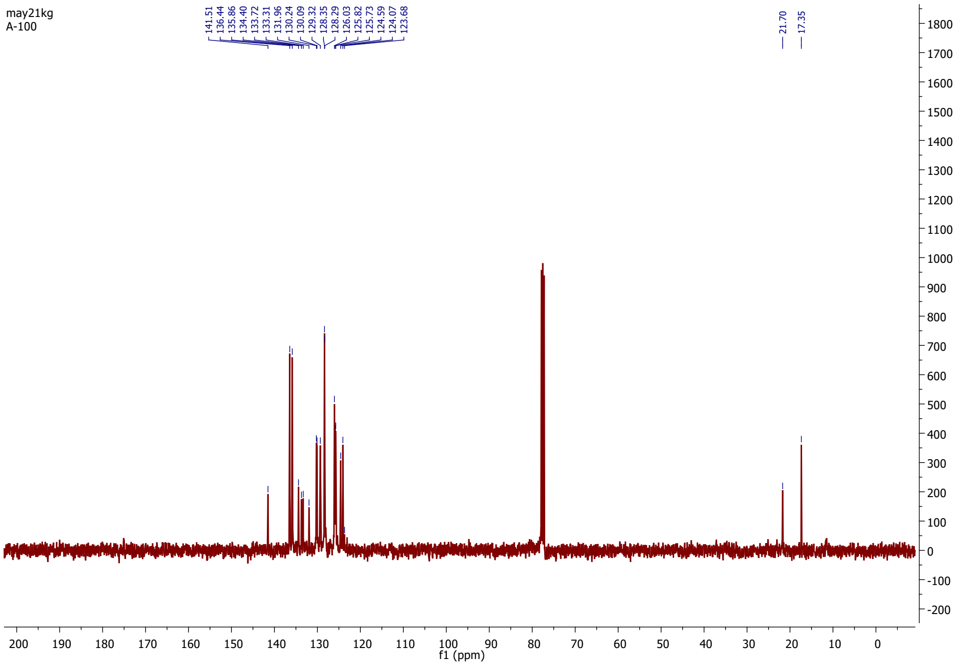


^{13}C NMR of 7b (125 MHz, CDCl$_3$)

(1-(Naphthalen-1-yl)ethyl)diphenylsilane (8b)

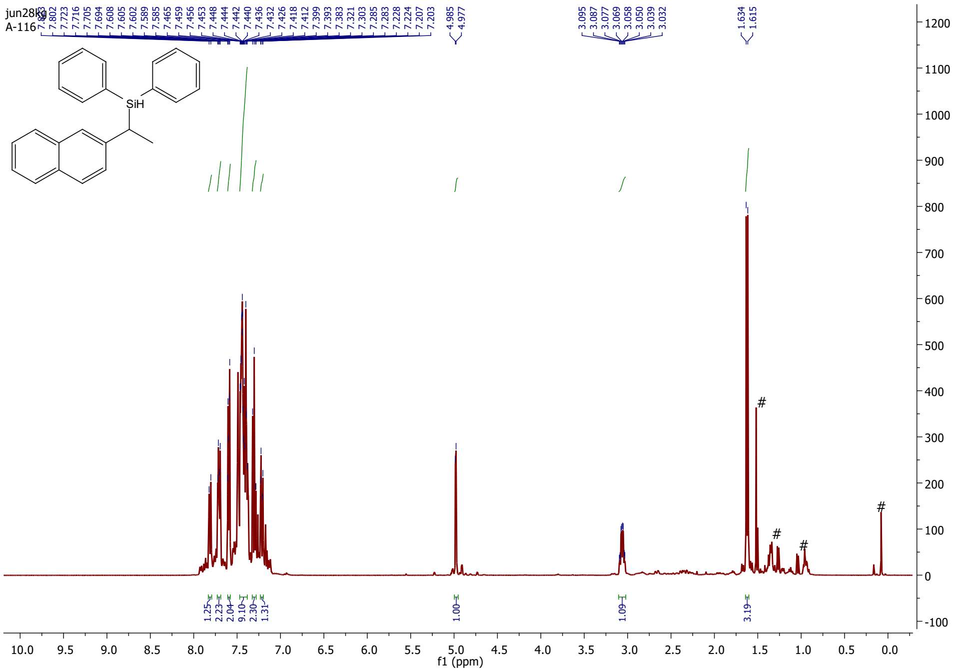


^{1}H NMR of 8b (500 MHz, CDCl$_3$)

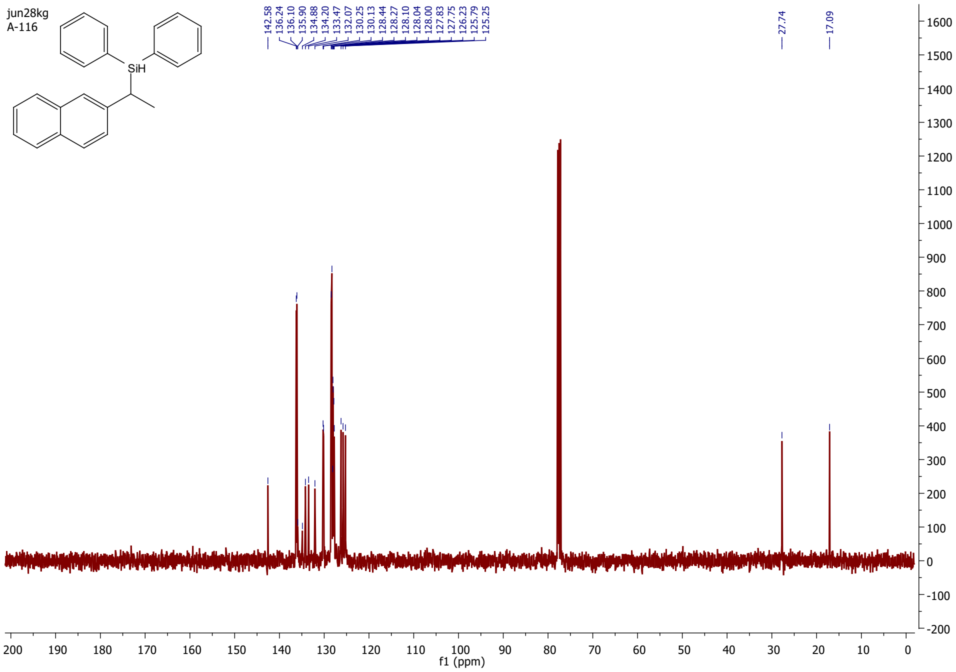


^{13}C NMR of 8b (125 MHz, CDCl$_3$)

(1-(Naphthalen-2-yl)ethyl)diphenylsilane (9b)

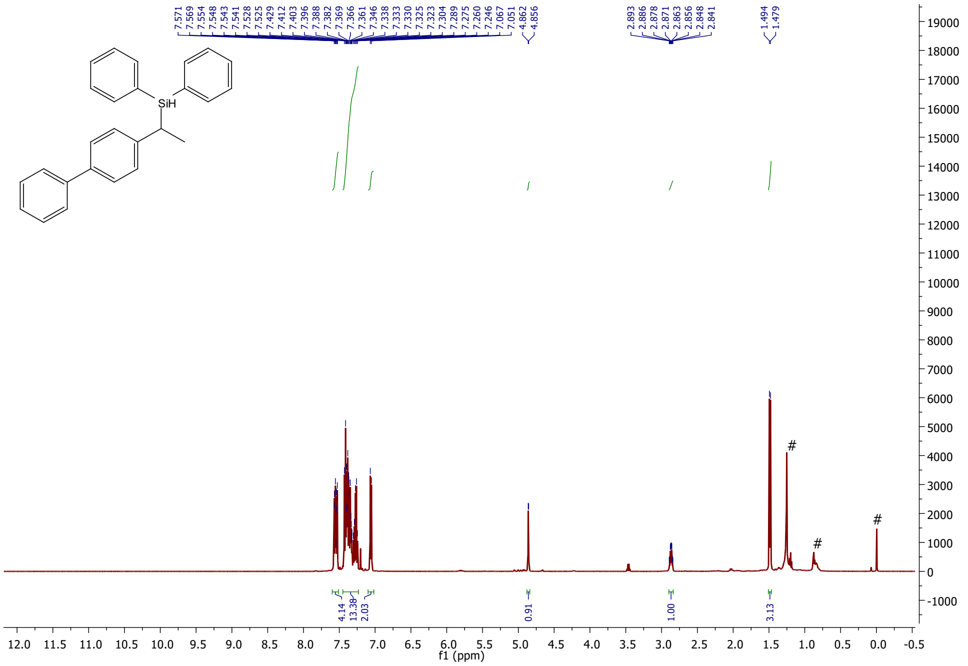


^{1}H NMR of 9b (400 MHz, CDCl$_3$)

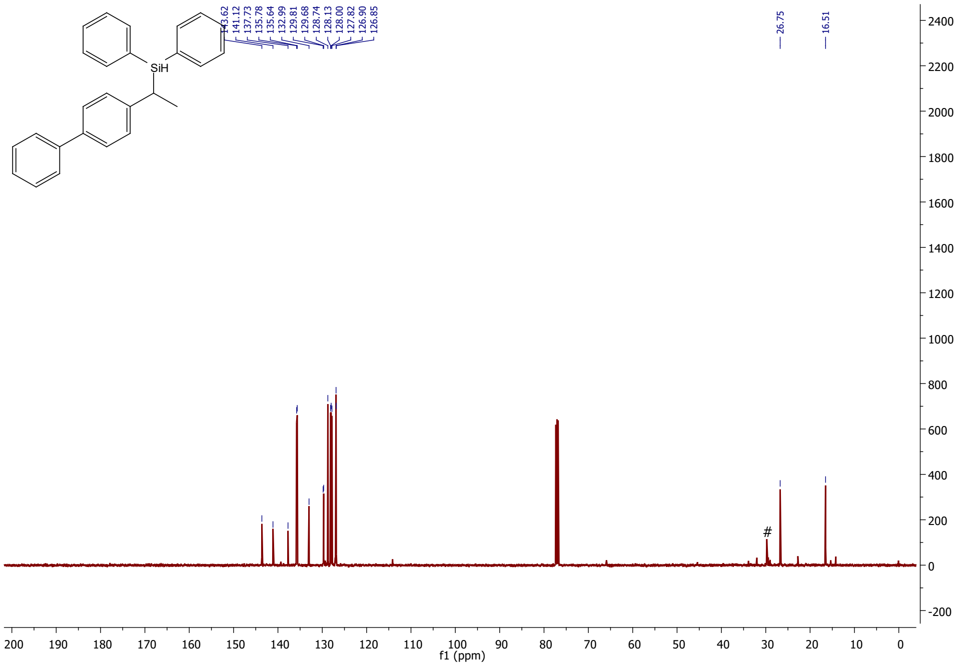


^{13}C NMR of 9b (100 MHz, CDCl$_3$)

(1-([1,1'-Biphenyl]-4-yl)ethyl)diphenylsilane (10b)

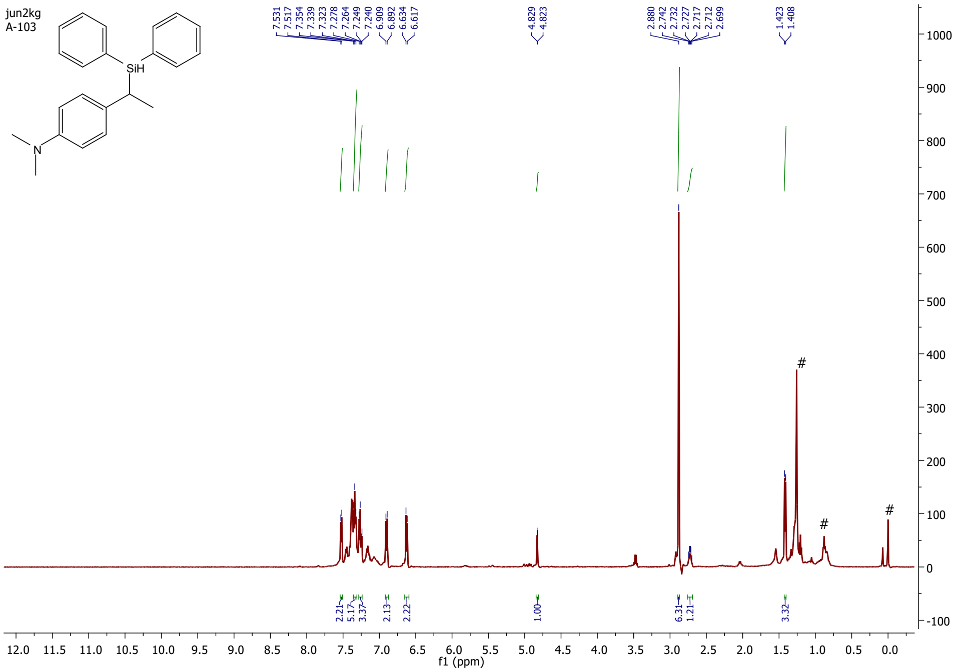


^{1}H NMR of 10b (500 MHz, CDCl$_3$)

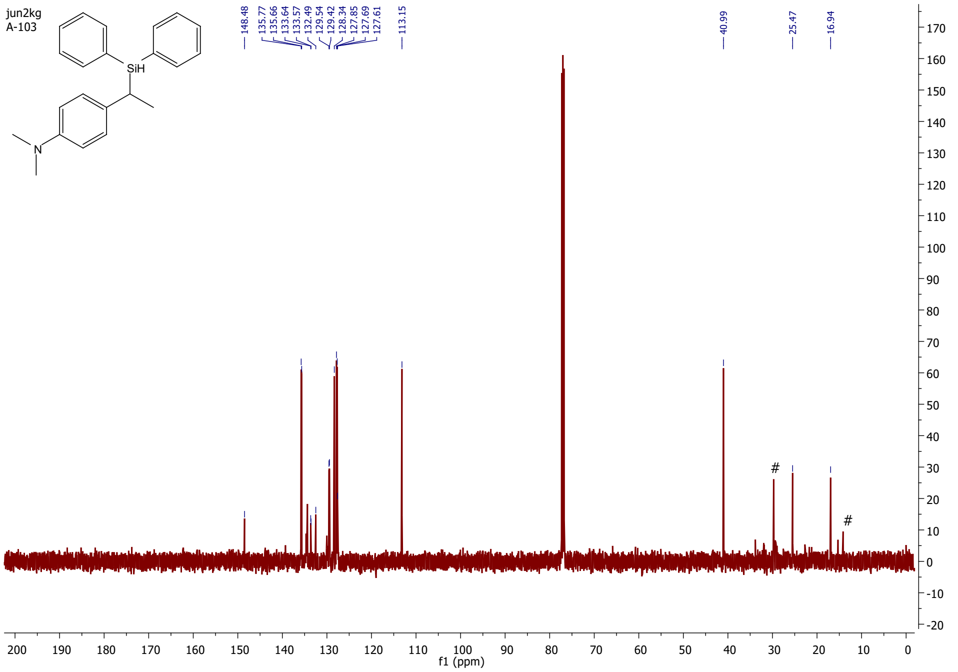


^{13}C NMR of 10b (125 MHz, CDCl$_3$)

4-(1-(Diphenylsilyl)ethyl)-N,N-dimethylaniline (11b)

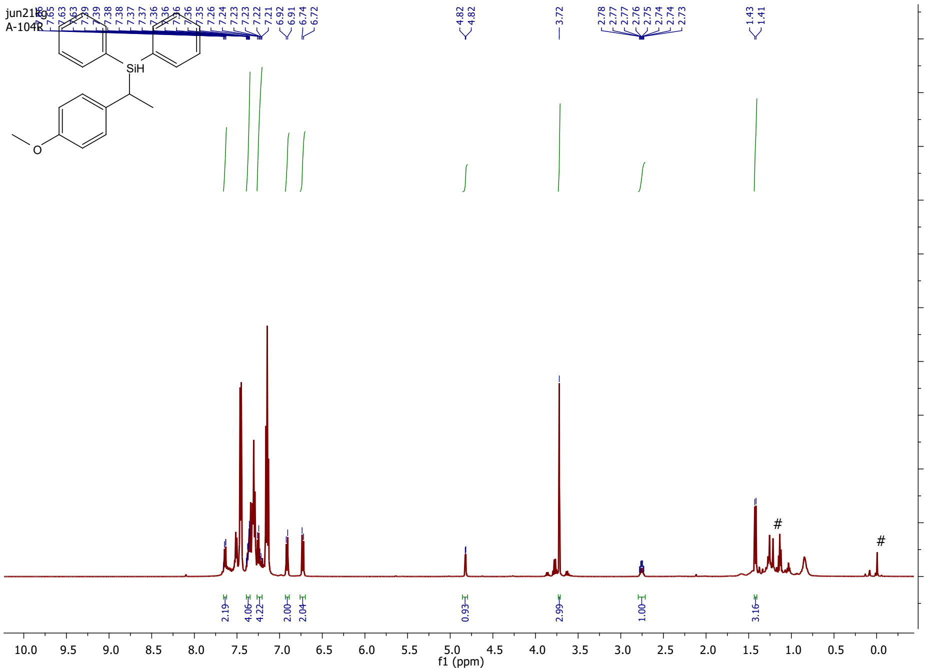


^{1}H NMR of 11b (500 MHz, CDCl$_3$)

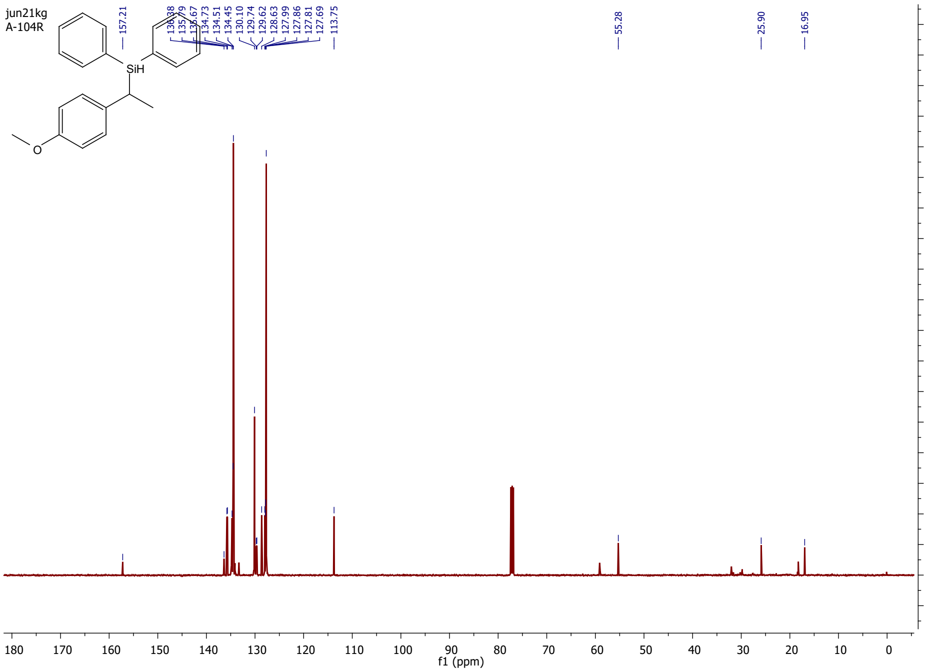


^{13}C NMR of 11b (125 MHz, CDCl$_3$)

(1-(4-Methoxyphenyl)ethyl)diphenylsilane (12b)

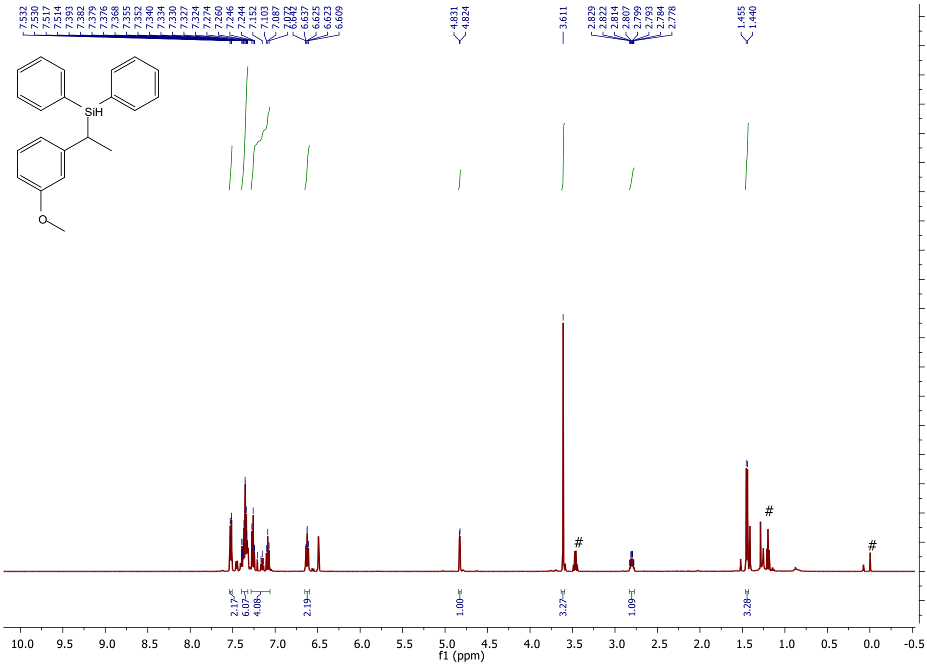


^{1}H NMR of 12b (500 MHz, CDCl$_3$)

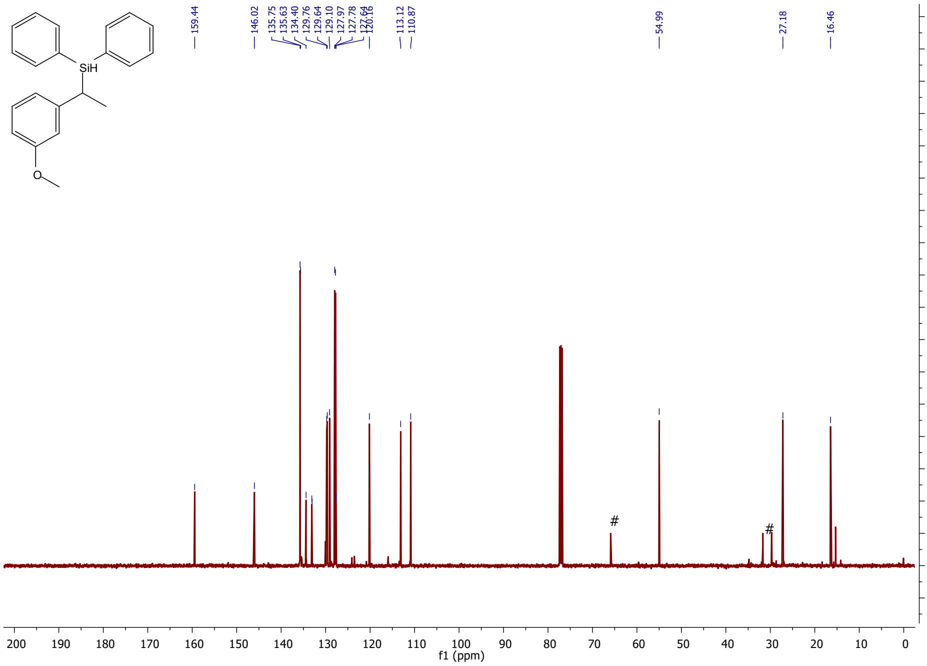


^{13}C NMR of 12b (125 MHz, CDCl$_3$)

(1-(3-Methoxyphenyl)ethyl)diphenylsilane (13b)

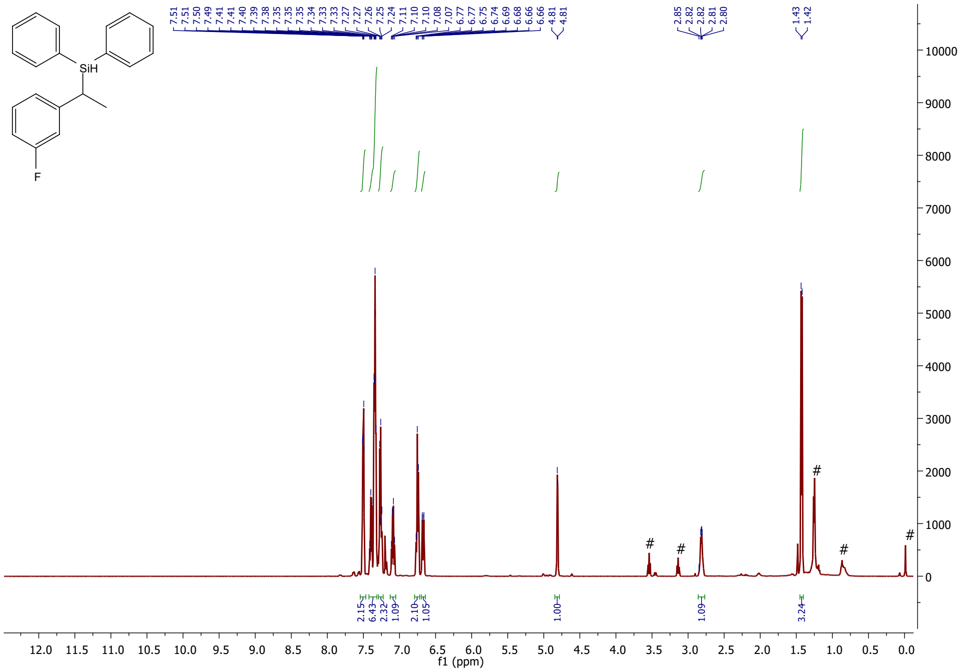


^{1}H NMR of 13b (500 MHz, CDCl$_3$)

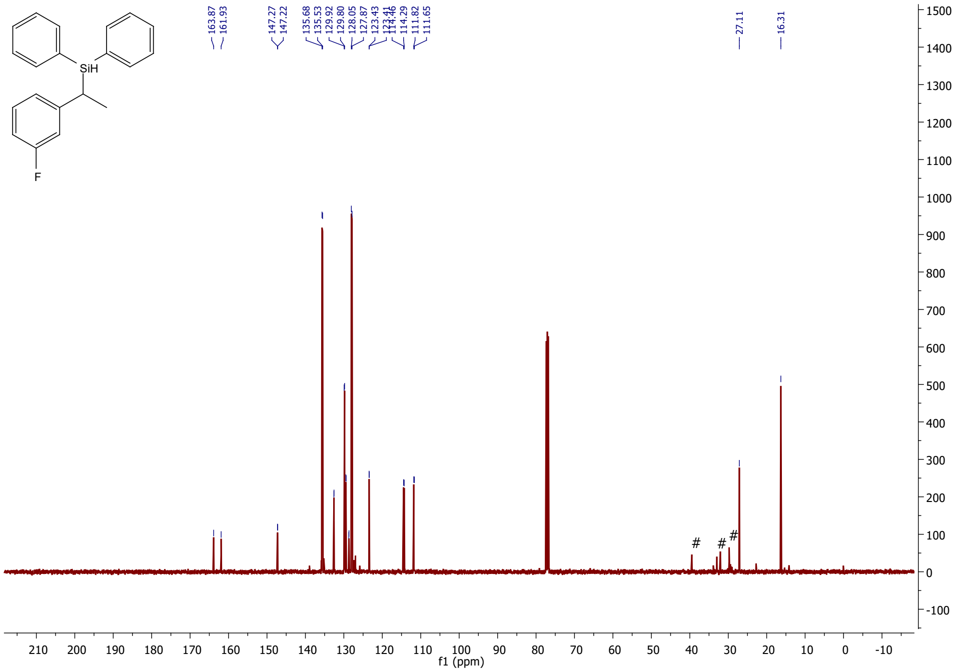


^{13}C NMR of 13b (125 MHz, CDCl$_3$)

(1-(3-Fluorophenyl)ethyl)diphenylsilane (14b)

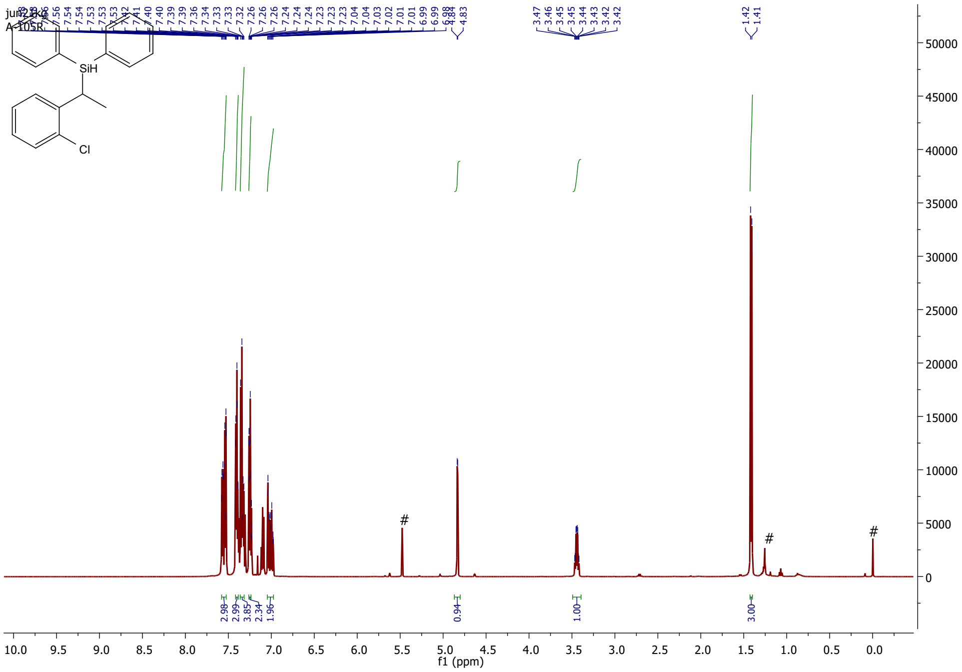


^{1}H NMR of 14b (500 MHz, CDCl$_3$)

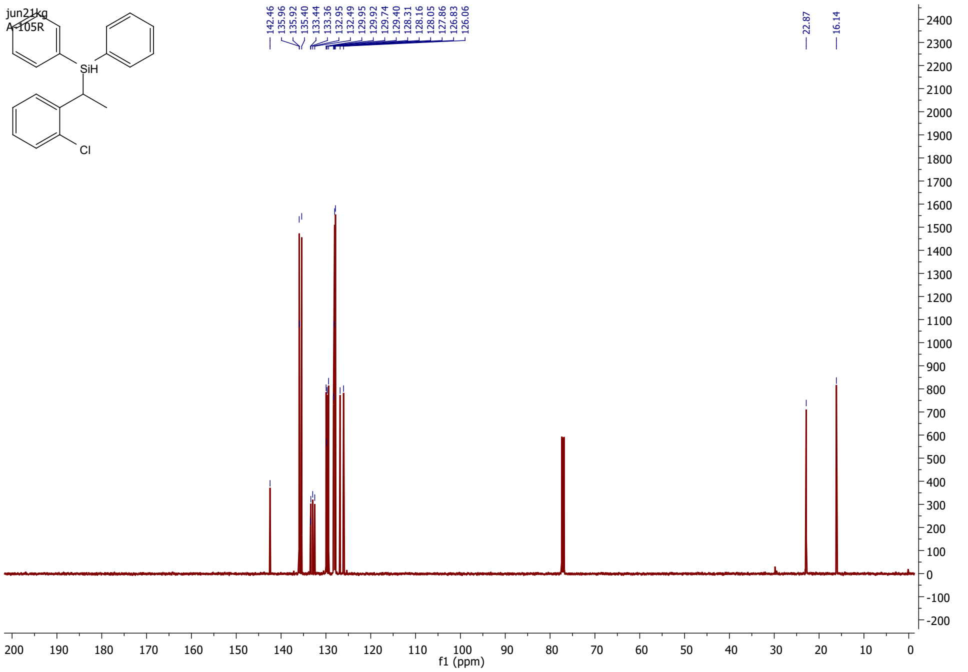


^{13}C NMR of 14b (125 MHz, CDCl$_3$)

(1-(2-Chlorophenyl)ethyl)diphenylsilane (15b)

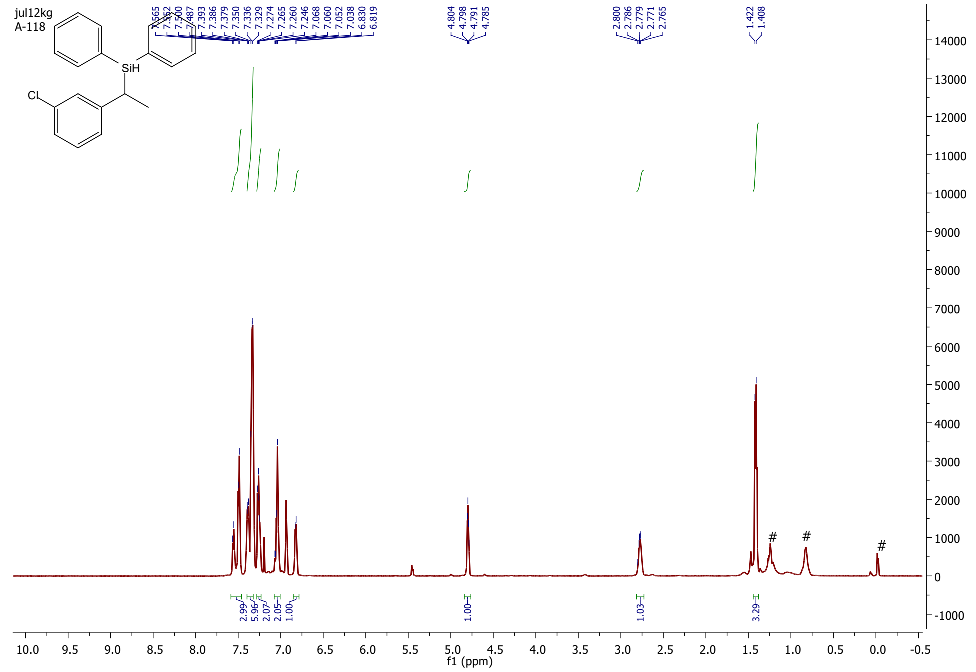


^{1}H NMR of 15b (500 MHz, CDCl$_3$)

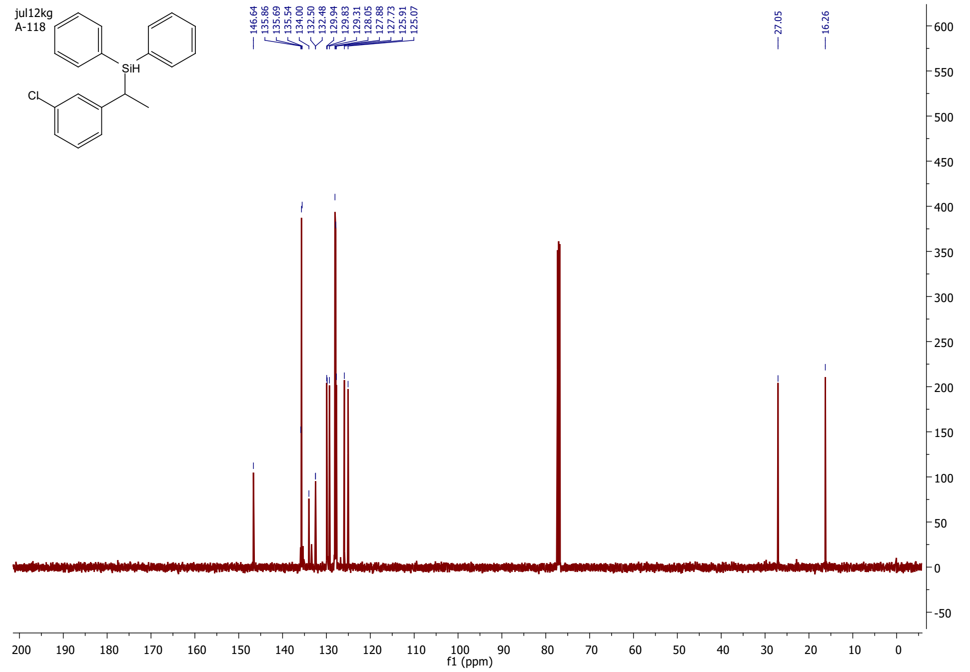


^{13}C NMR of 15b (125 MHz, CDCl$_3$)

(1-(3-Chlorophenyl)ethyl)diphenylsilane (16b)

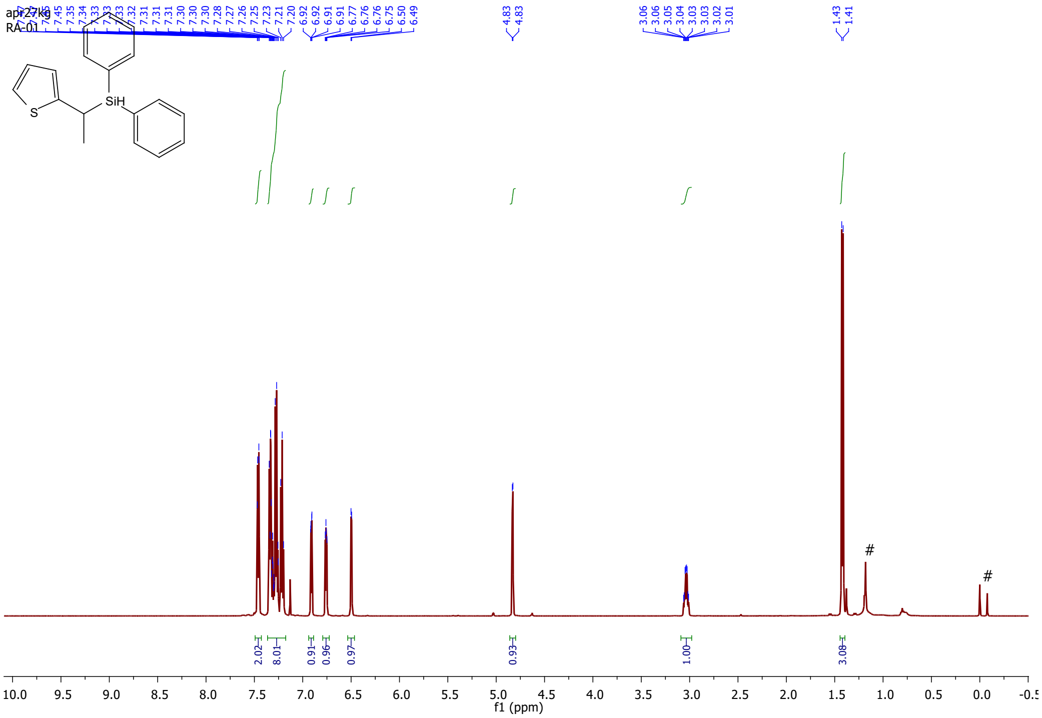


^{1}H NMR of 16b (500 MHz, CDCl$_3$)

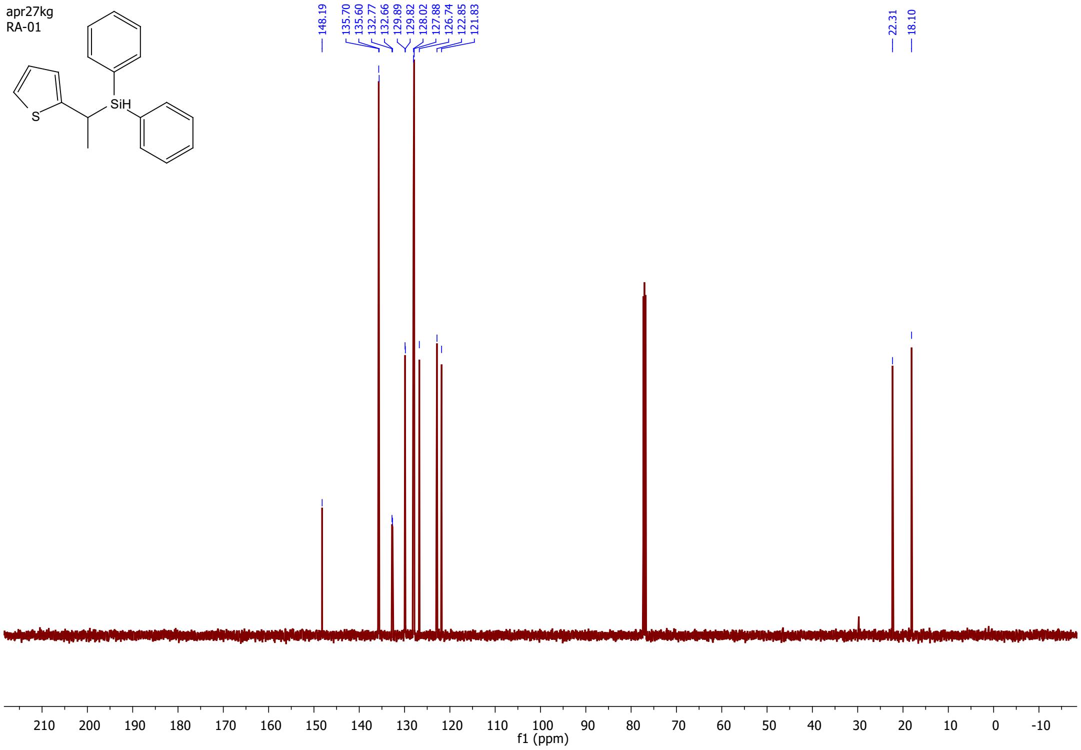


^{13}C NMR of 16b (125 MHz, CDCl$_3$)

Diphenyl(1-(thiophen-2-yl)ethyl)silane (17b)

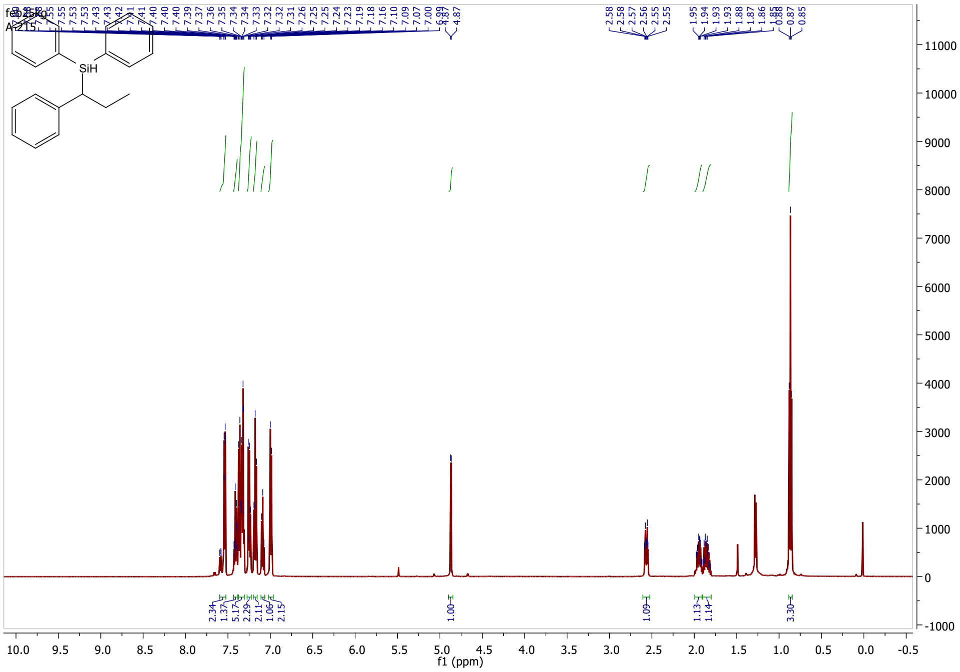


^{1}H NMR of 17b (500 MHz, CDCl$_3$)

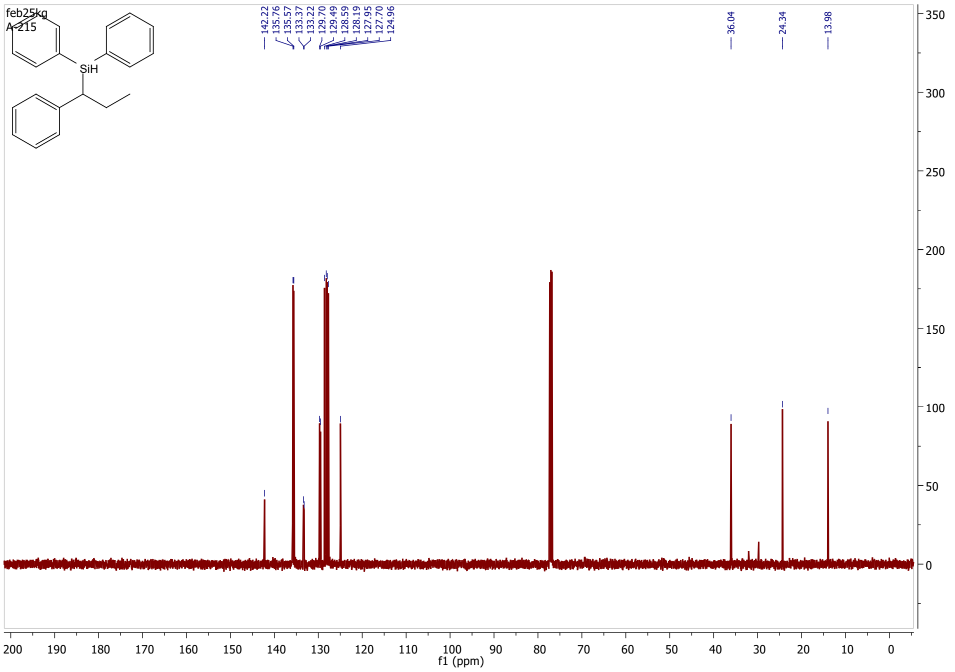


^{13}C NMR of 17b (125 MHz, CDCl$_3$)

Diphenyl(1-phenylpropyl)silane (18b)

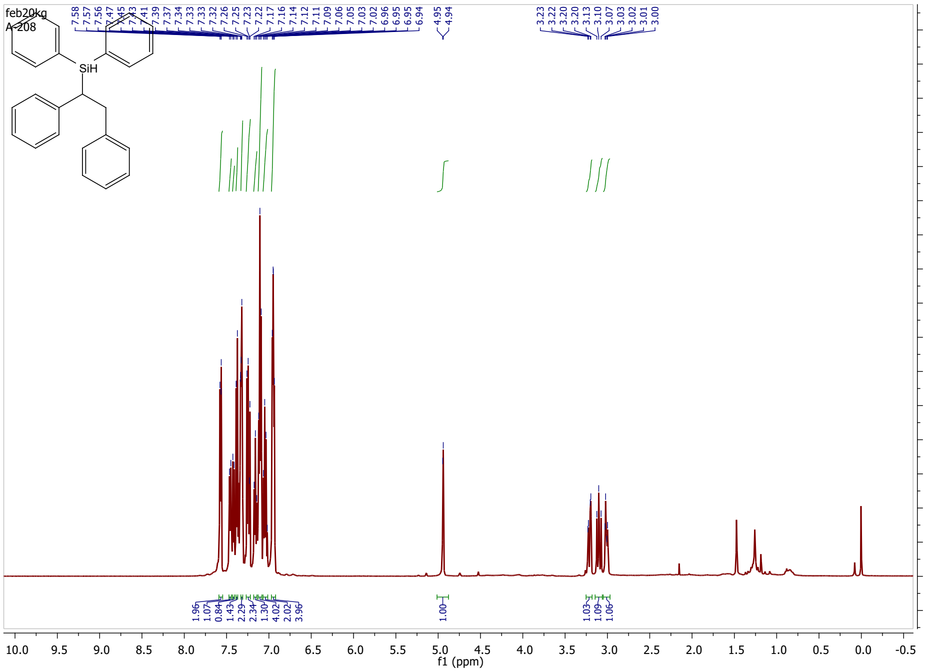


^{1}H NMR of 18b (500 MHz, CDCl$_3$)

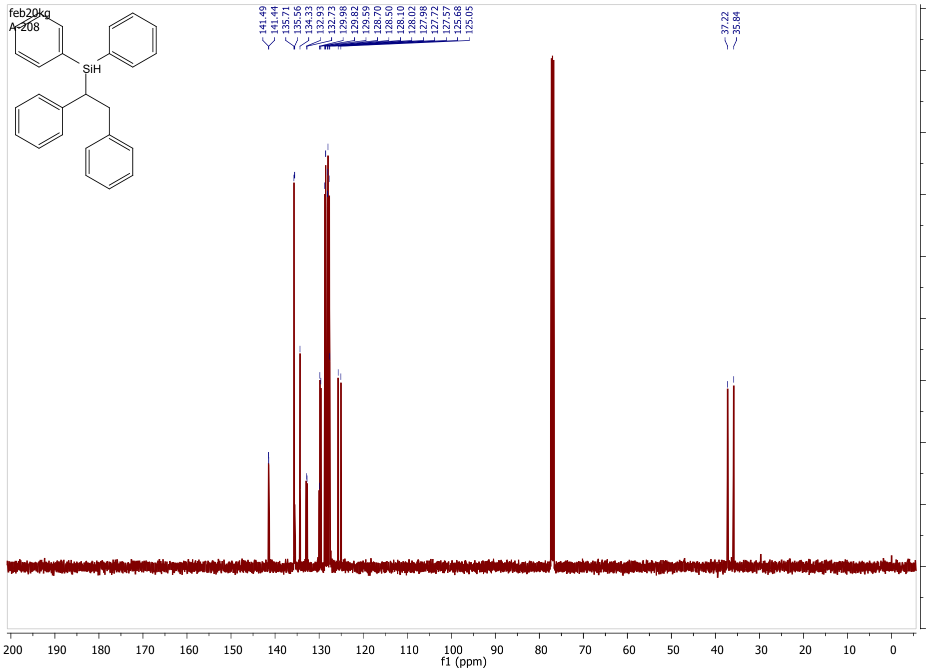


^{13}C NMR of 18b (125 MHz, CDCl$_3$)

(1,2-Diphenylethyl)diphenylsilane (19b)

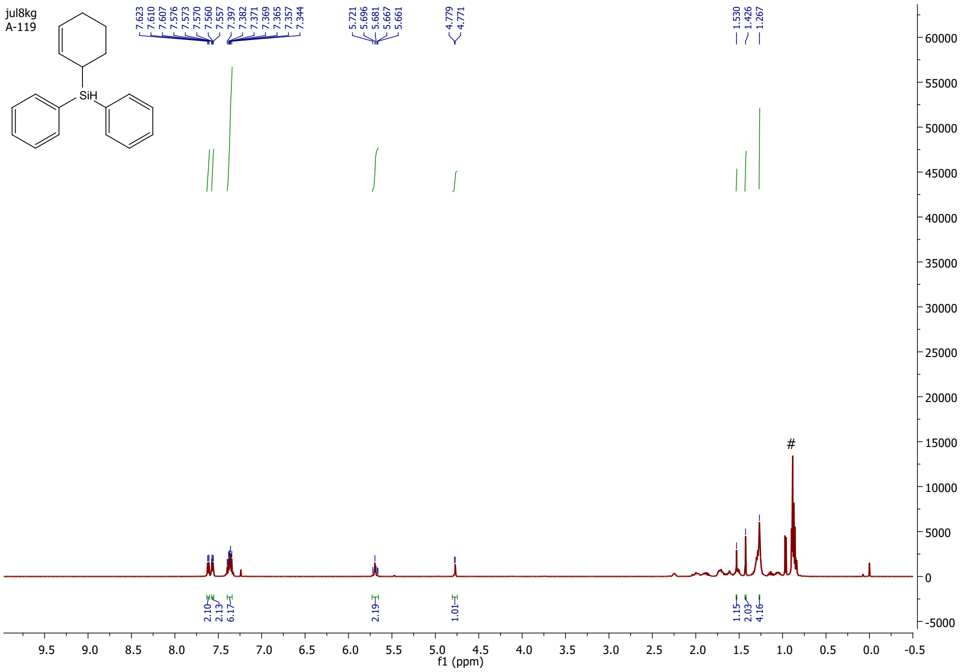


^{1}H NMR of 19b (500 MHz, CDCl$_3$)

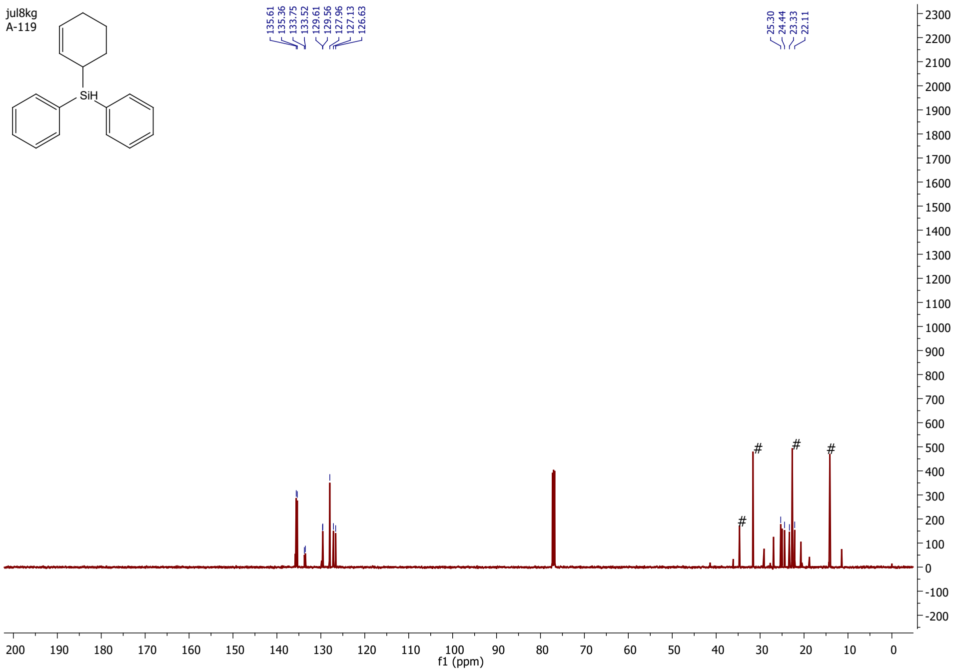


^{13}C NMR of 19b (125 MHz, CDCl$_3$)

Cyclohex-2-en-1-yldiphenylsilane (20b)

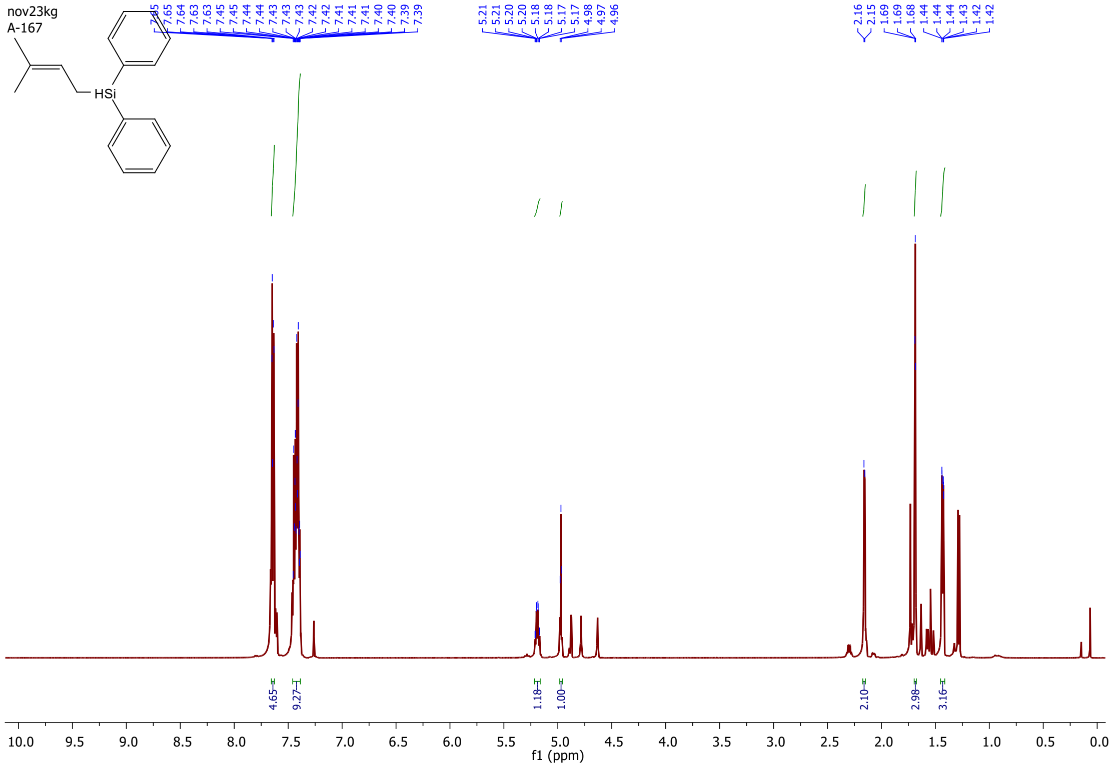


^{1}H NMR of 20b (500 MHz, CDCl$_3$)

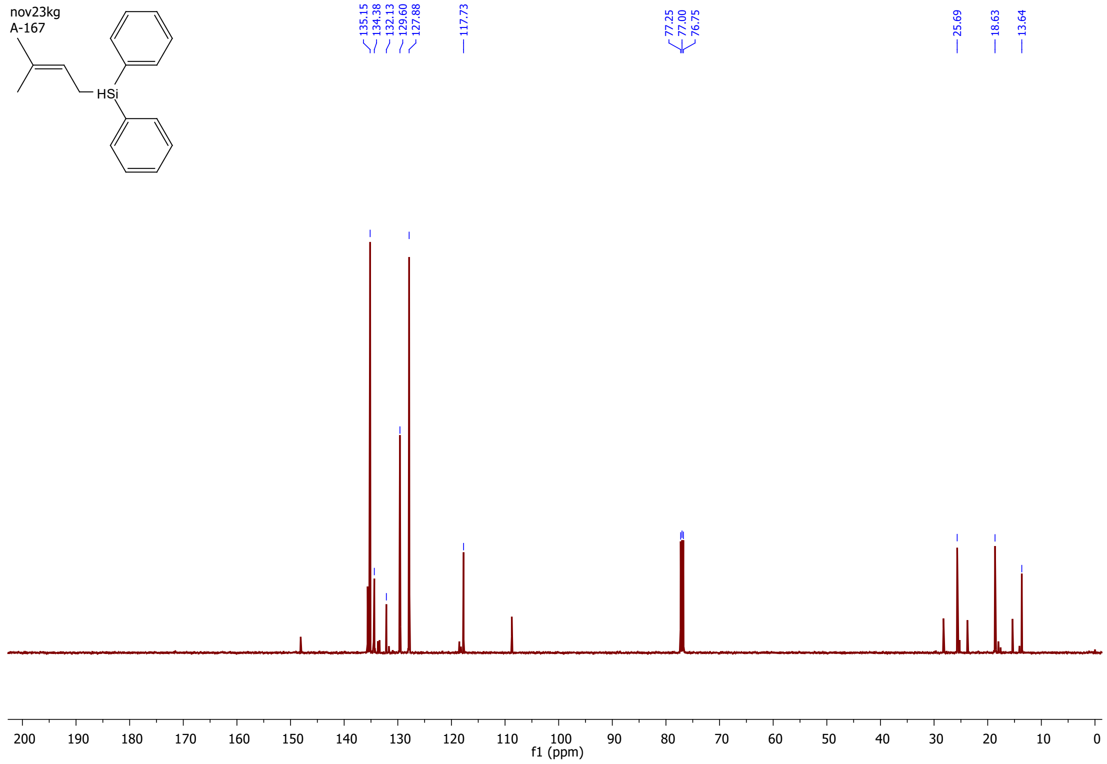


^{13}C NMR of 20b (125 MHz, CDCl$_3$)

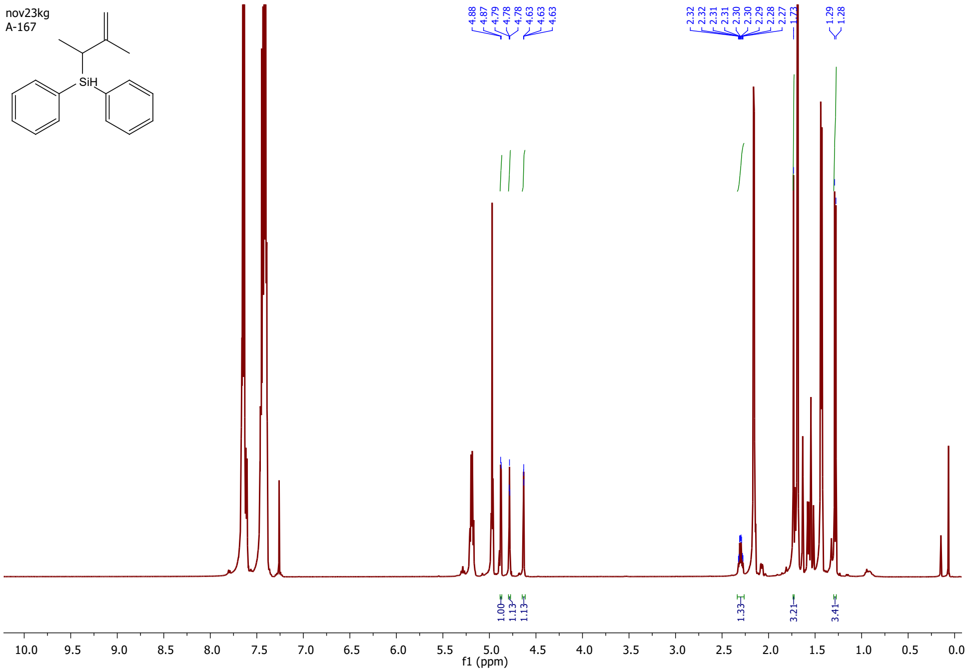
(3-Methylbut-2-en-1-yl)diphenylsilane (21b and 21c)



^{1}H NMR of 21b (500 MHz, CDCl$_3$)

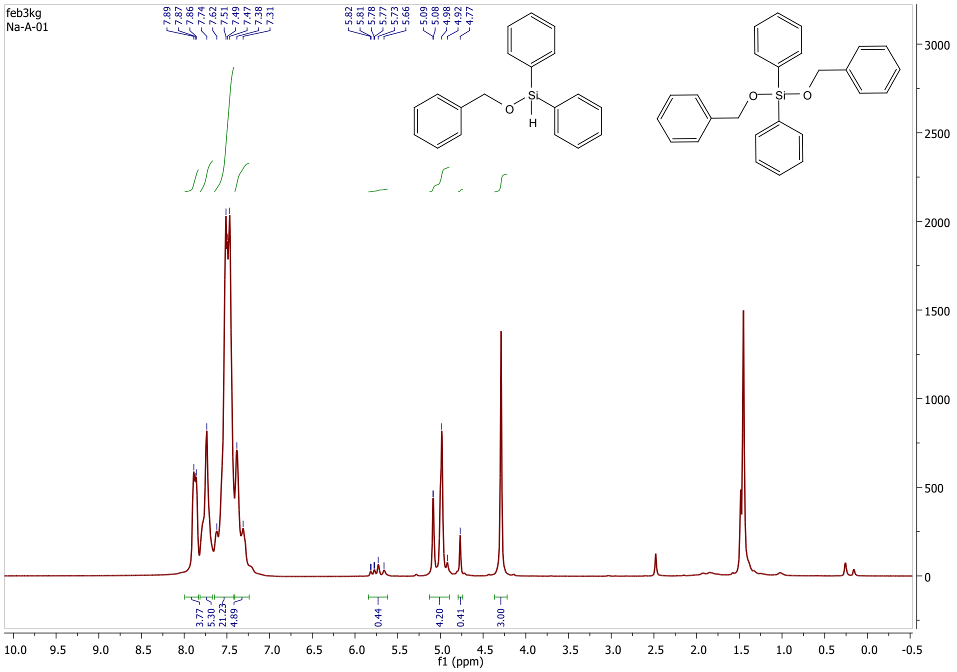


^{13}C NMR of 21b (125 MHz, CDCl$_3$)



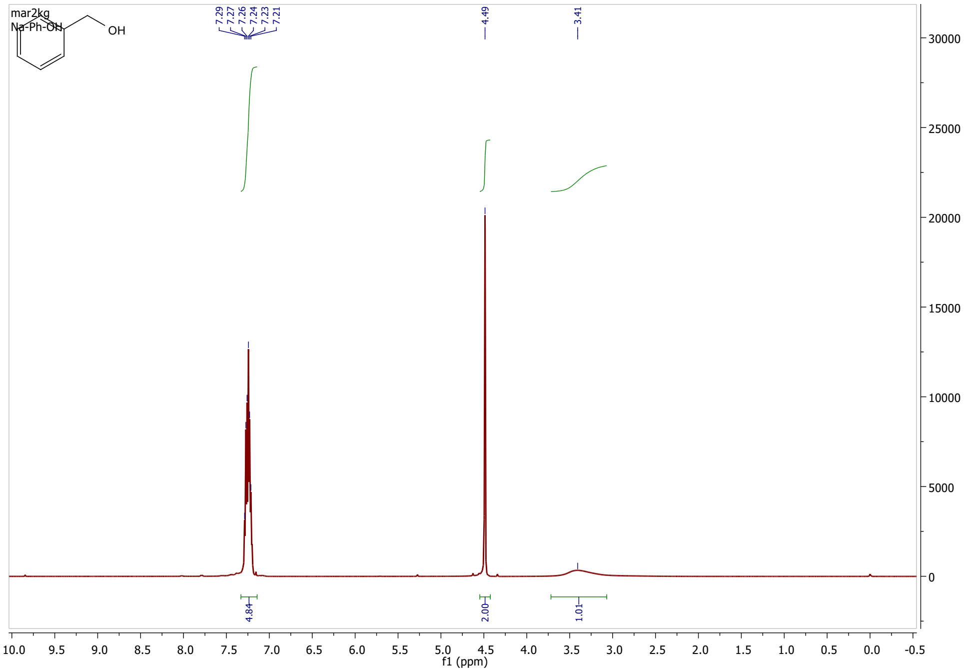
^{1}H NMR of 21c (500 MHz, CDCl$_3$)

Mono and bis(Benzyloxy)diphenylsilane (22b-c)

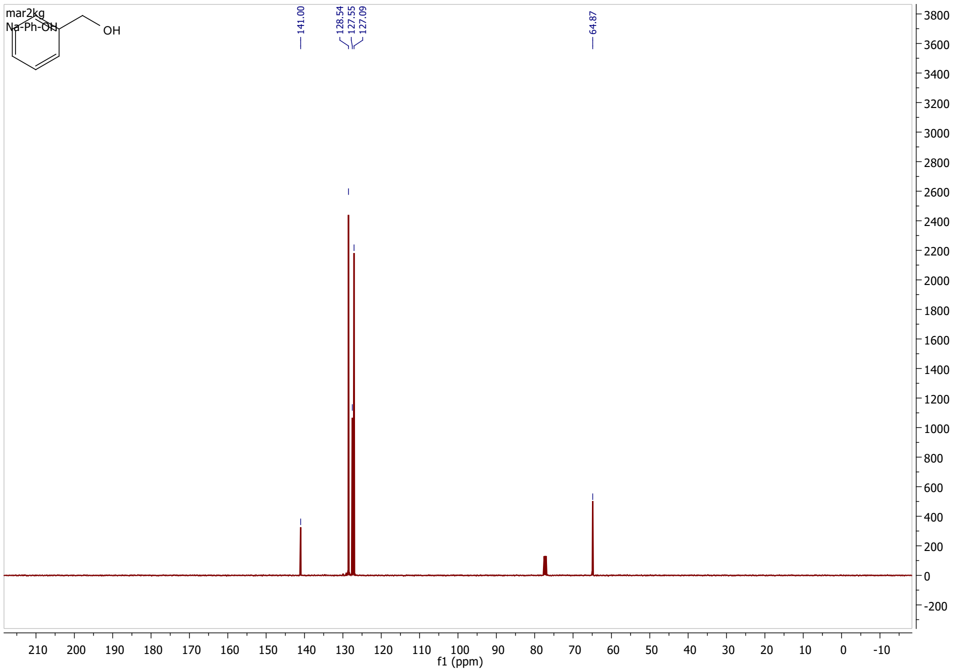


^{1}H NMR of 22b and 22c (500 MHz, CDCl$_3$)

Phenylmethanol (22d)

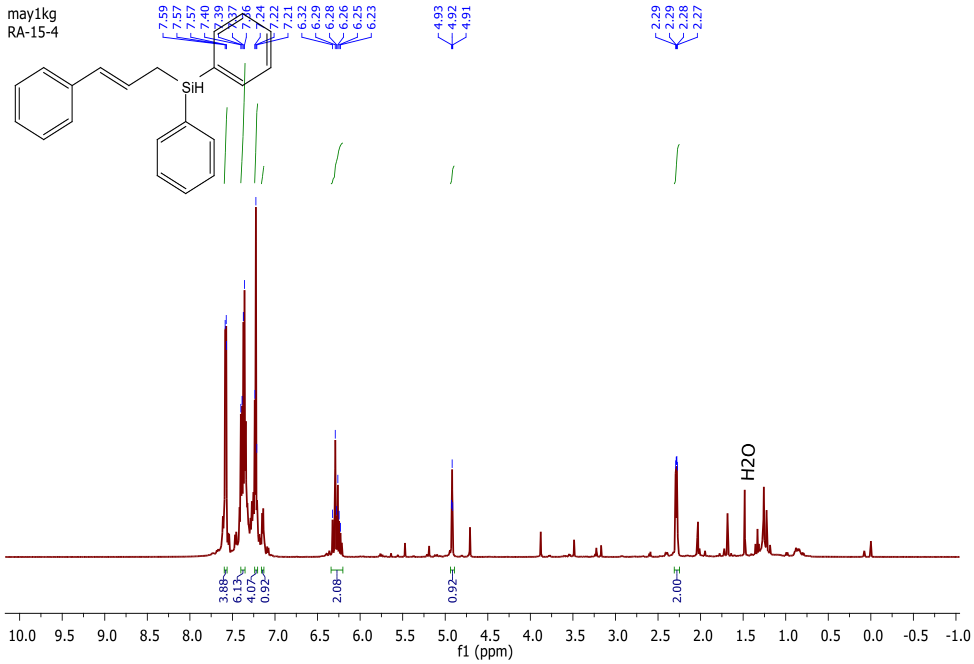


^{1}H NMR of 22d (500 MHz, CDCl$_3$)

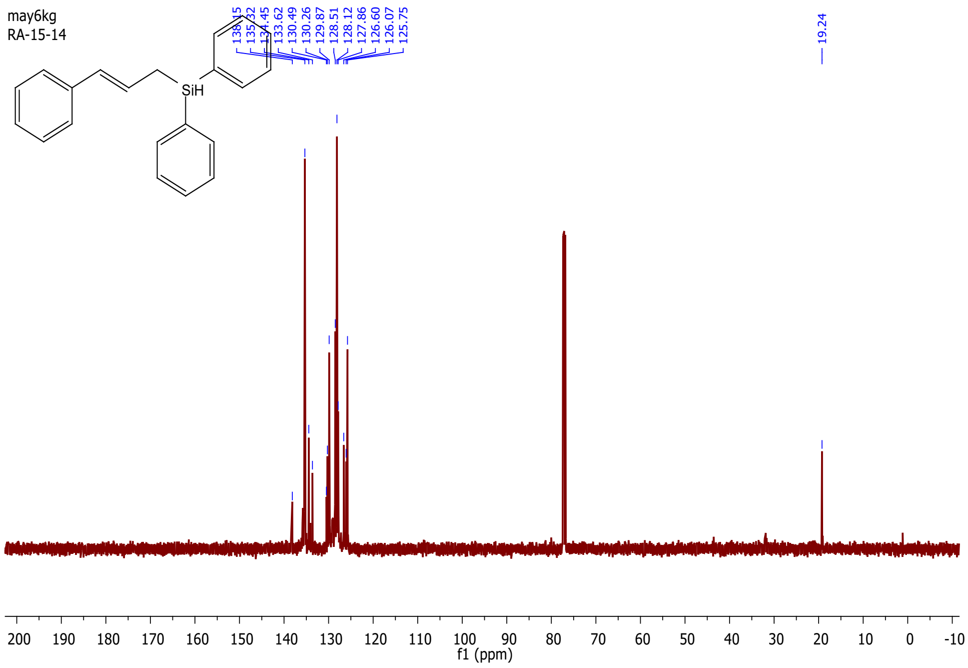


^{13}C NMR of 22d (125 MHz, CDCl$_3$)

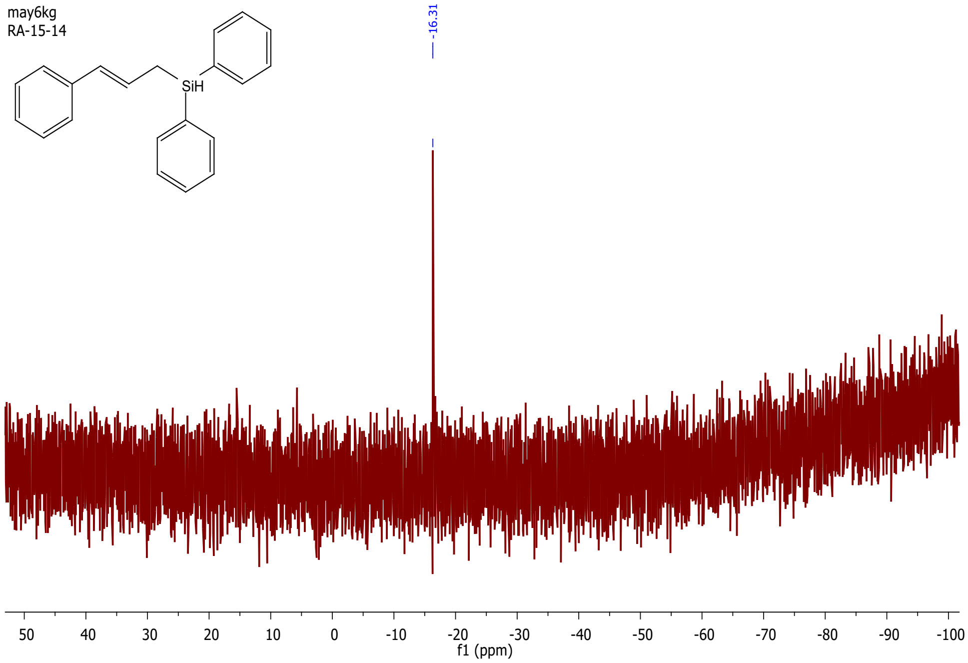
Diphenyl(1-phenylallyl)silane (23b)



^{1}H NMR of 23b (500 MHz, CDCl$_3$)

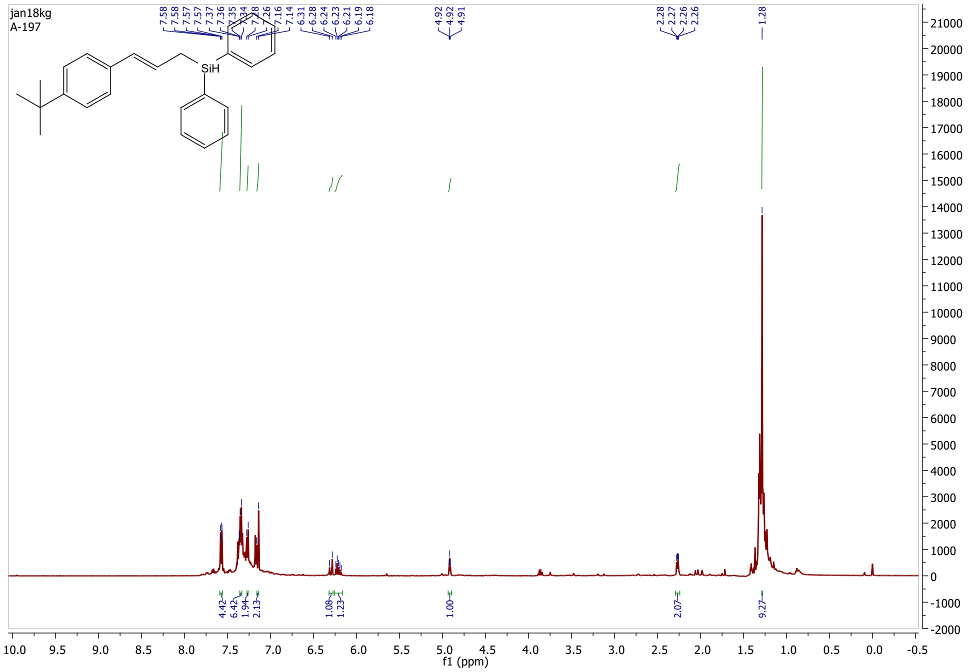


^{13}C NMR of 23b (125 MHz, CDCl$_3$)

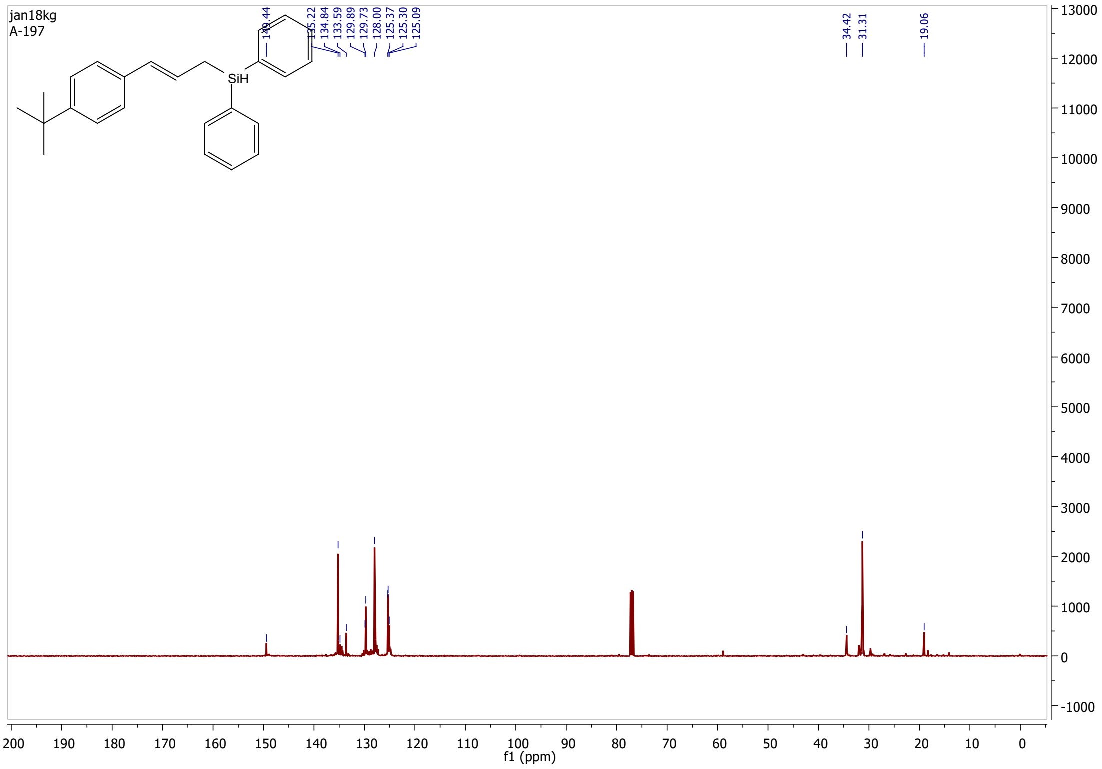


^{29}**Si NMR of 23b (100 MHz, CDCl$_3$)**

(*E*)-(3-(4-(tert-Butyl)phenyl)allyl)diphenylsilane (24b)

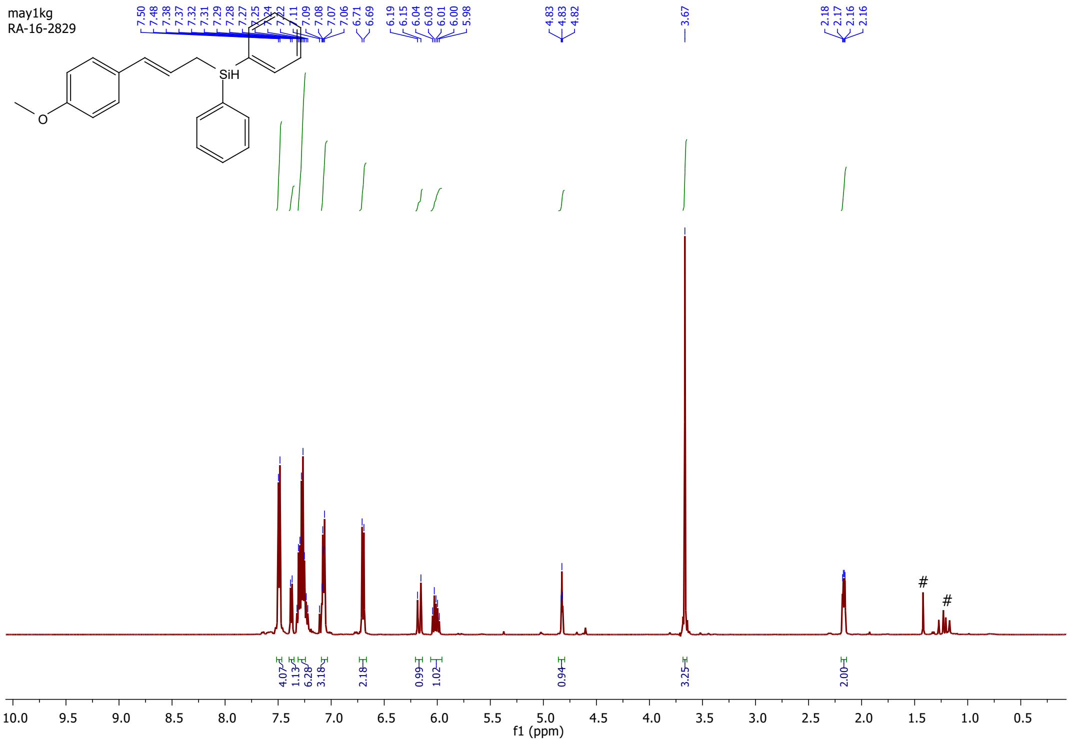


^{1}H NMR of 24b (500 MHz, CDCl$_3$)

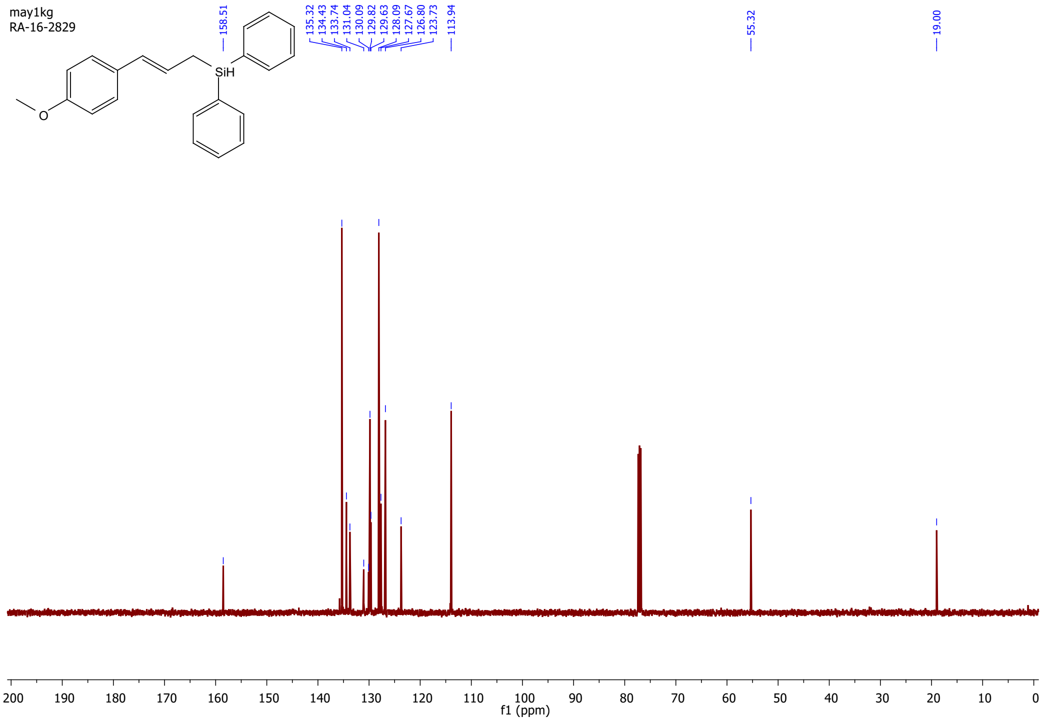


^{13}C NMR of 24b (125 MHz, CDCl$_3$)

(*E*)-(3-(4-Methoxyphenyl)allyl)diphenylsilane (25b)

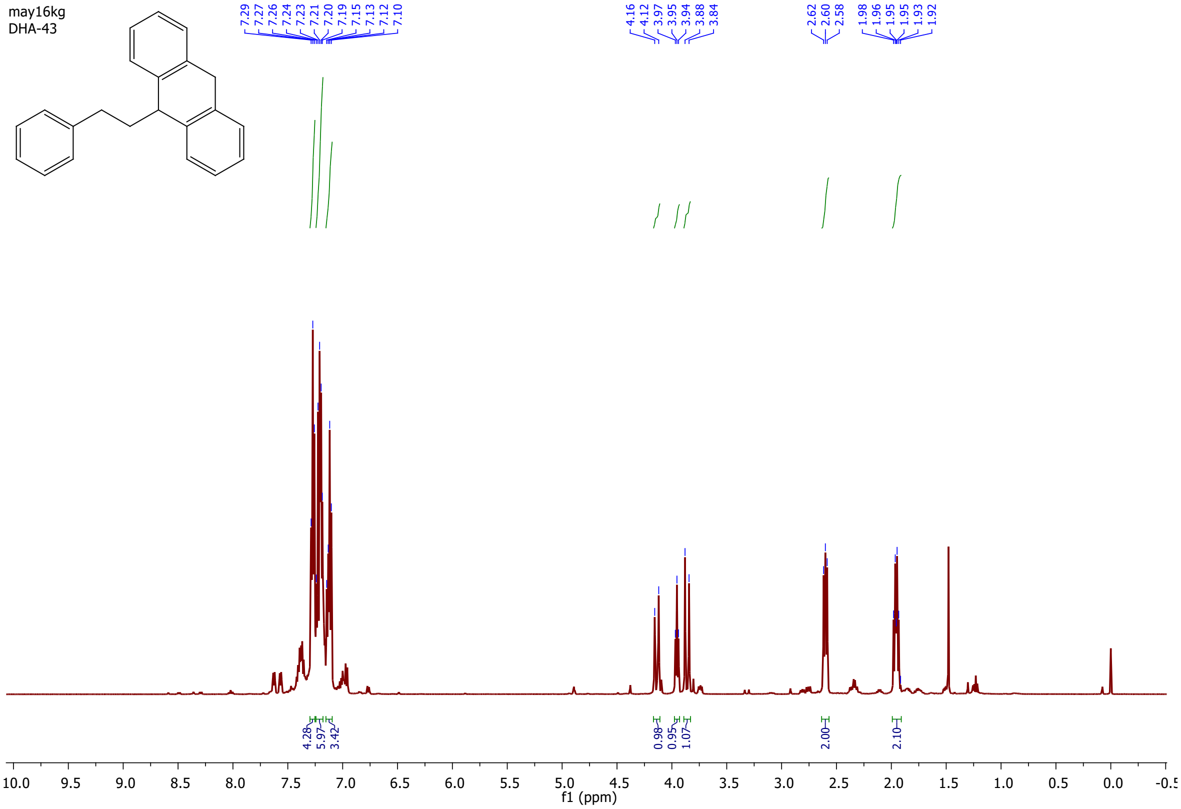


^{1}H NMR of 25b (500 MHz, CDCl$_3$)

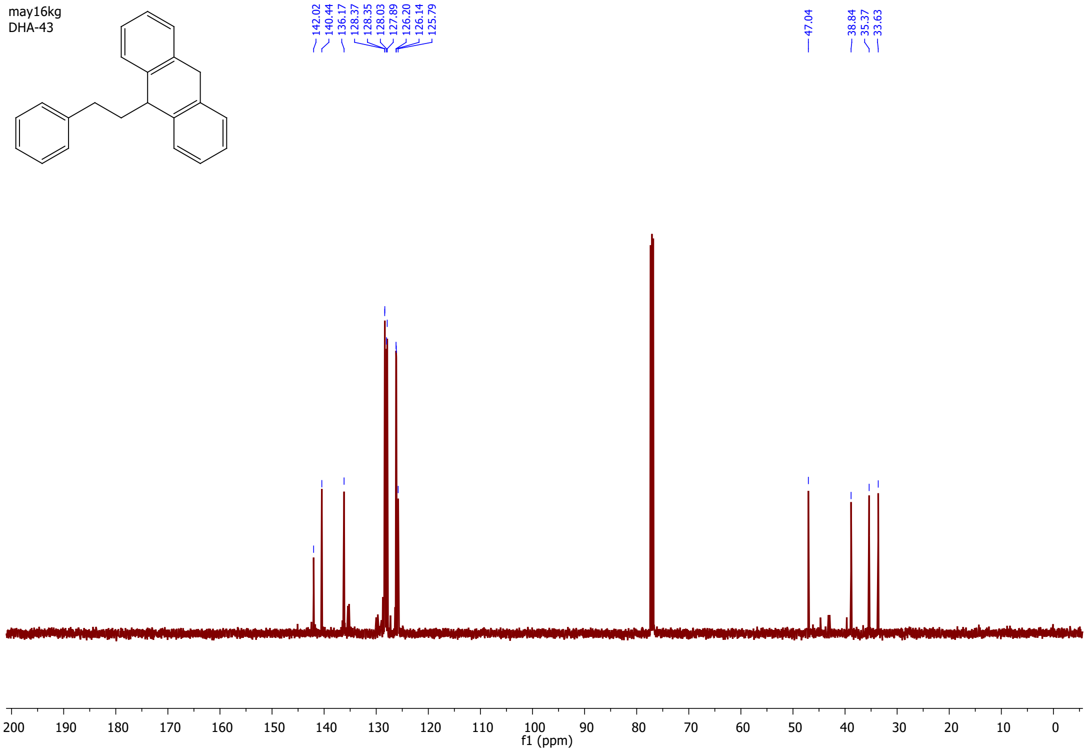


^{13}C NMR of 25b (125 MHz, CDCl$_3$)

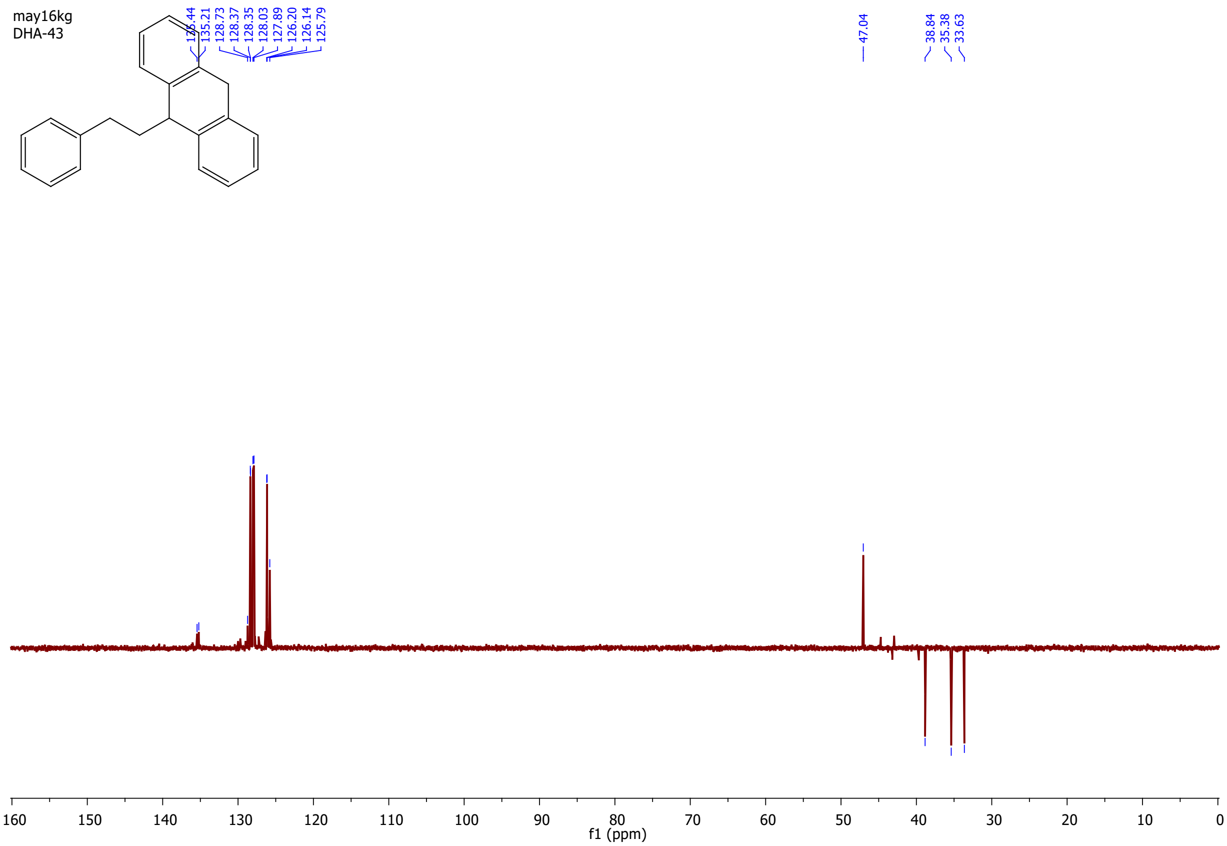
9-Phenethyl-9,10-dihydroanthracene (1a-DHA)



^{1}H NMR of 1a-DHA (500 MHz, CDCl$_3$)

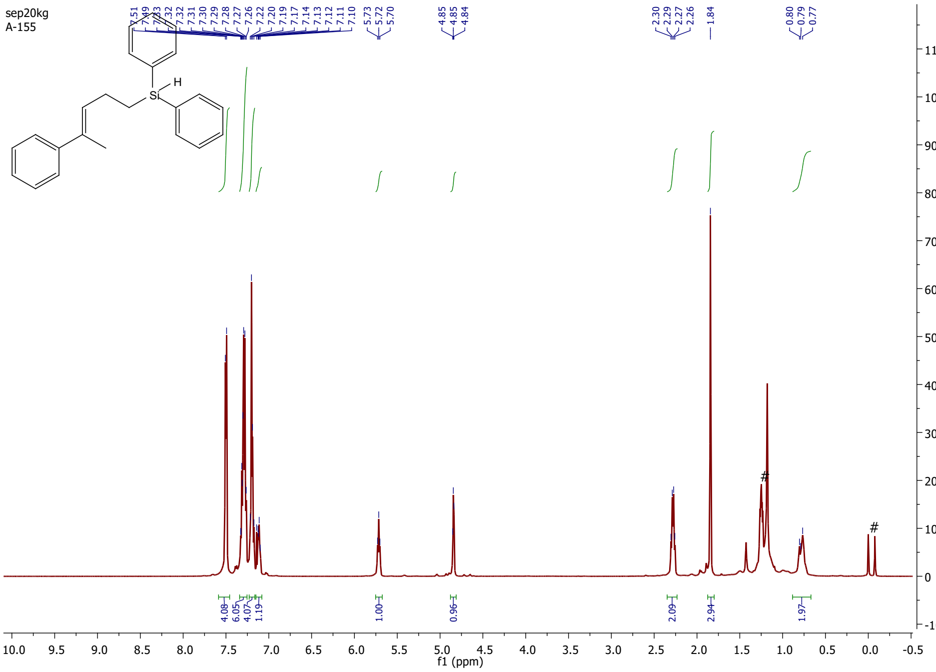


^{13}C NMR of 1a-DHA (125 MHz, CDCl$_3$)

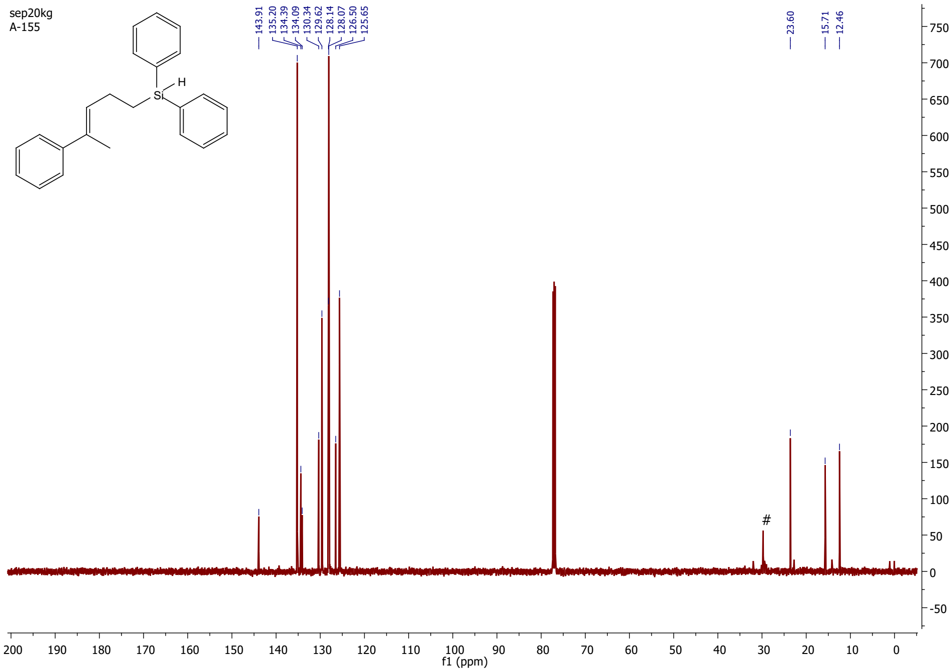


DEPT-135 of 1a-DHA (125 MHz, CDCl$_3$)

Diphenyl(4-phenylpent-3-en-1-yl)silane (26b)

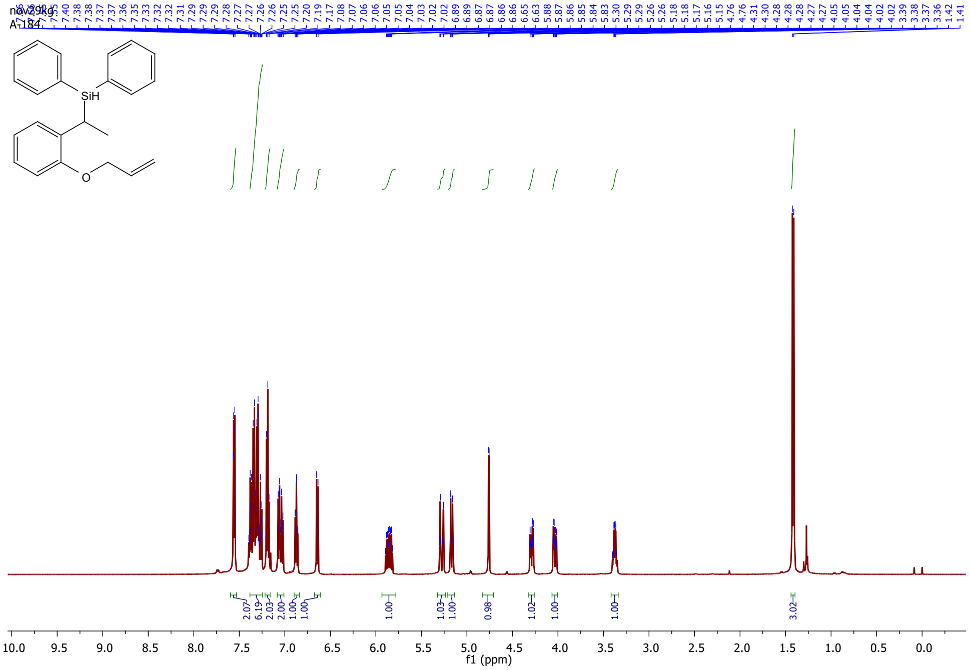


^{1}H NMR of 26b (500 MHz, CDCl$_3$)

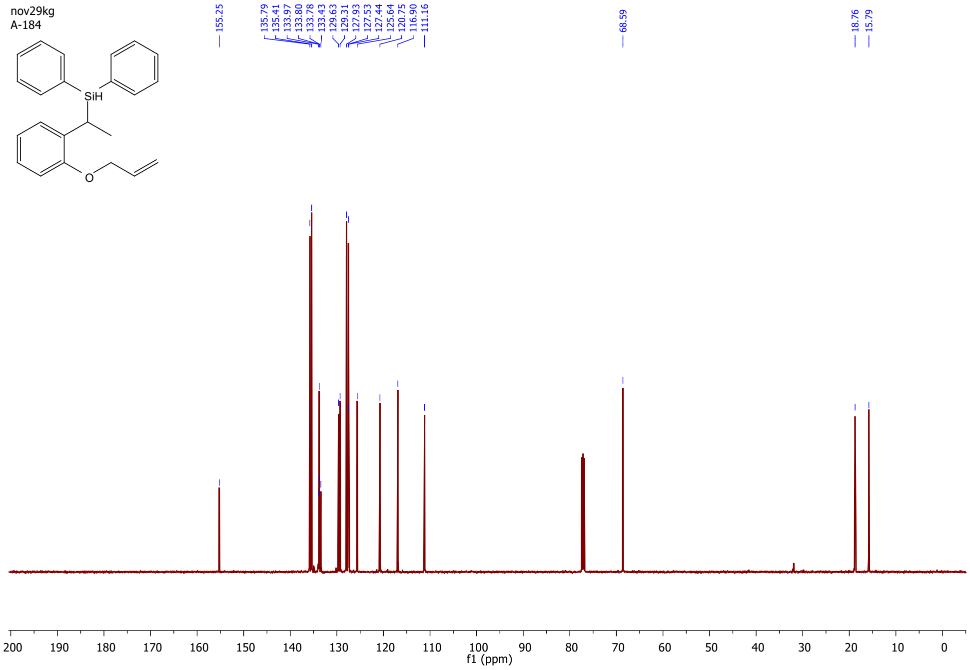


^{13}C NMR of 26b (126 MHz, CDCl$_3$)

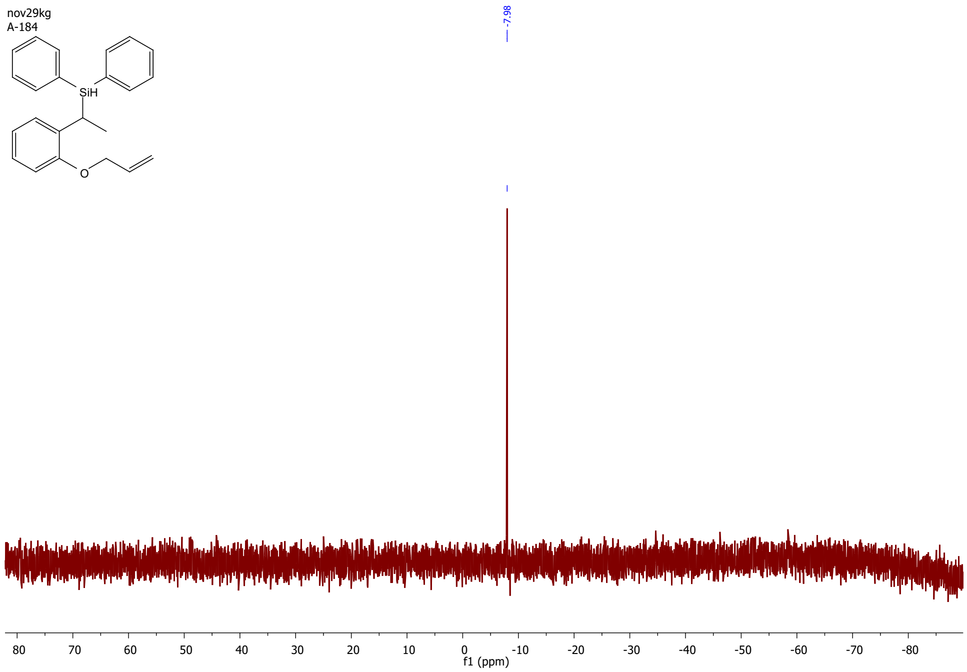
(1-(2-(Allyloxy)phenyl)ethyl)diphenylsilane (27b)



^{1}H NMR of 27b (500 MHz, CDCl$_3$)

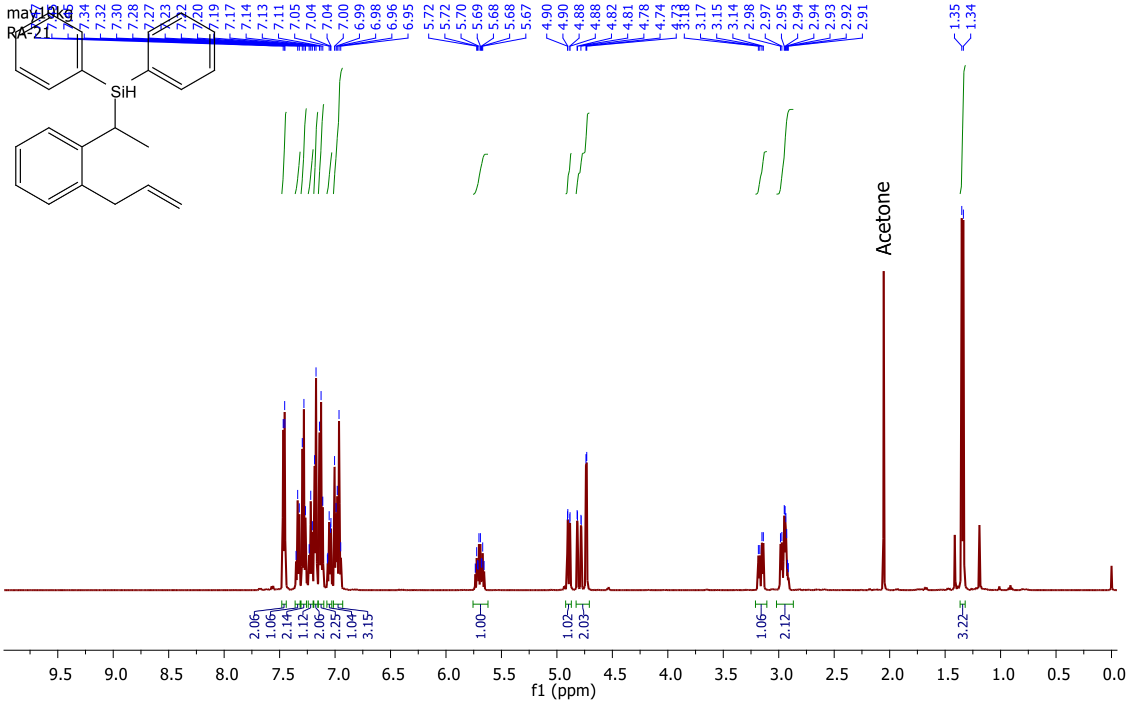


^{13}C NMR of 27b (125 MHz, CDCl$_3$)

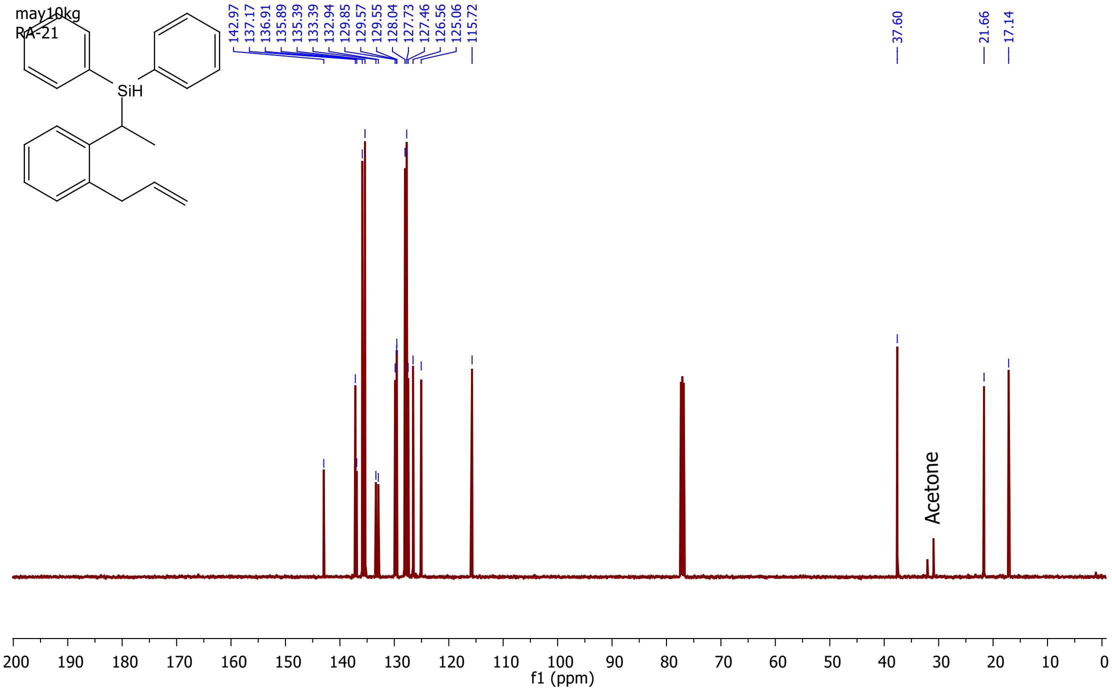


^{29}Si NMR of 27b (100 MHz, $CDCl_3$)

(1-(2-Allylphenyl)ethyl)diphenylsilane (28b)

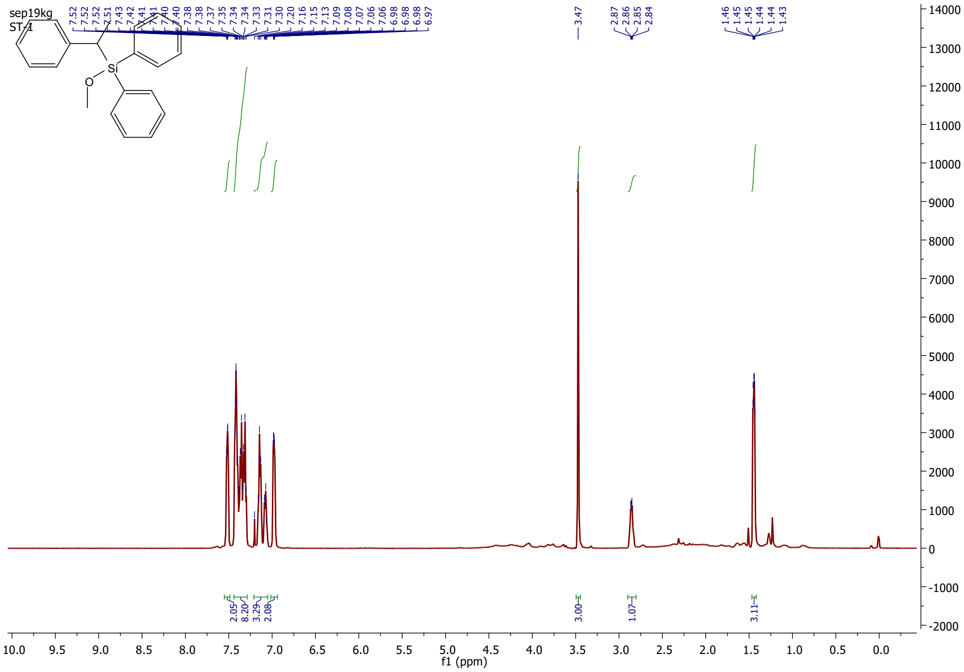


^{1}H NMR of 28b (500 MHz, CDCl$_3$)

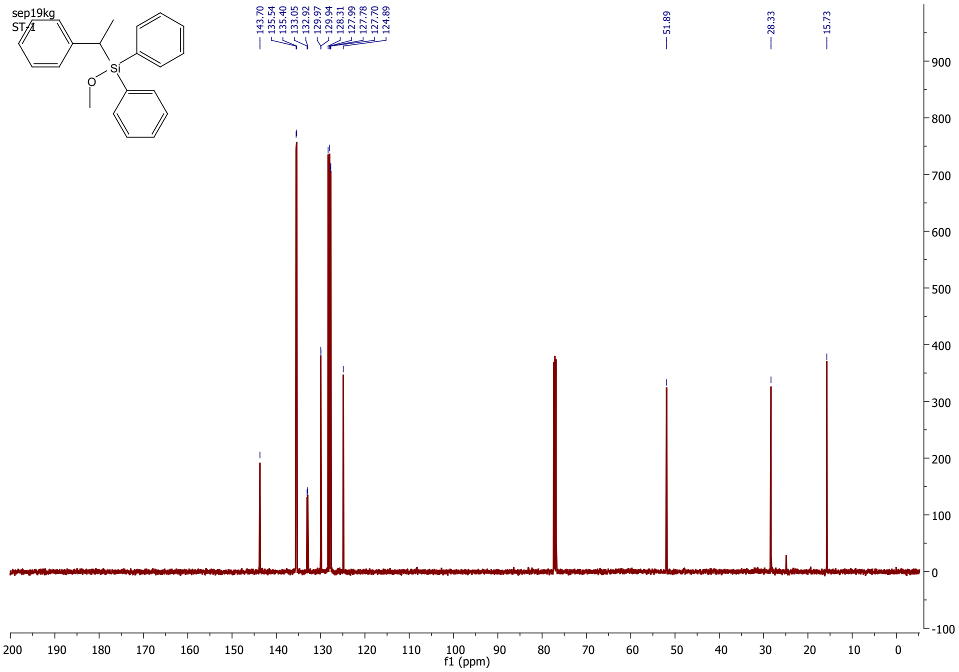


^{13}C NMR of 28b (125 MHz, CDCl$_3$)

Methoxydiphenyl(1-phenylethyl)silane (1b-OMe)

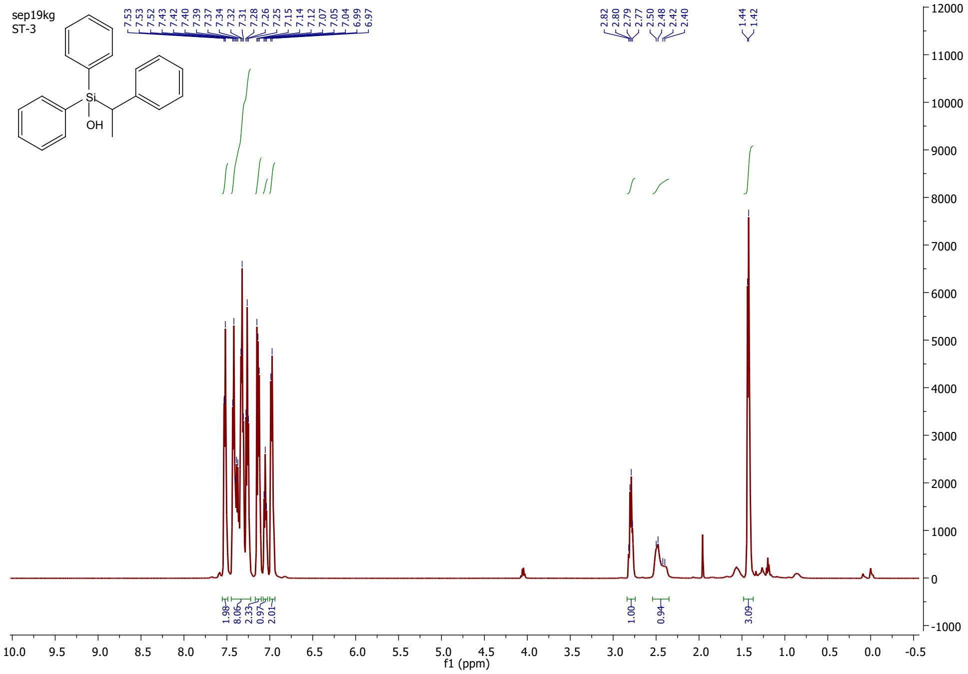


^{1}H NMR of 1b-OMe (500 MHz, CDCl$_3$)

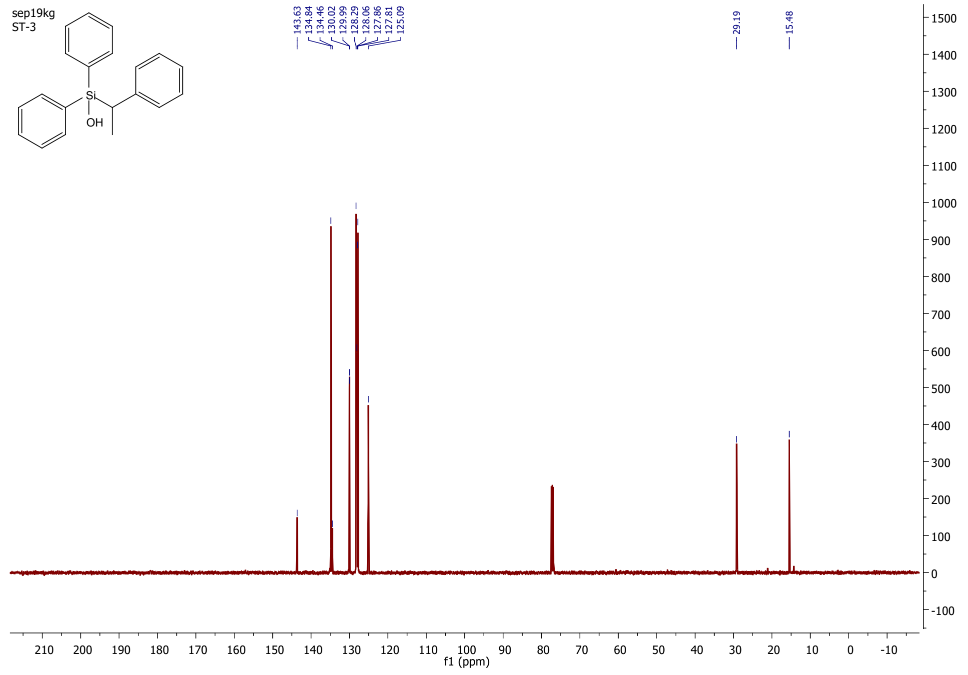


^{13}C NMR of 1b-OMe (126 MHz, CDCl$_3$)

Diphenyl(1-phenylethyl)silanol (1b-OH)

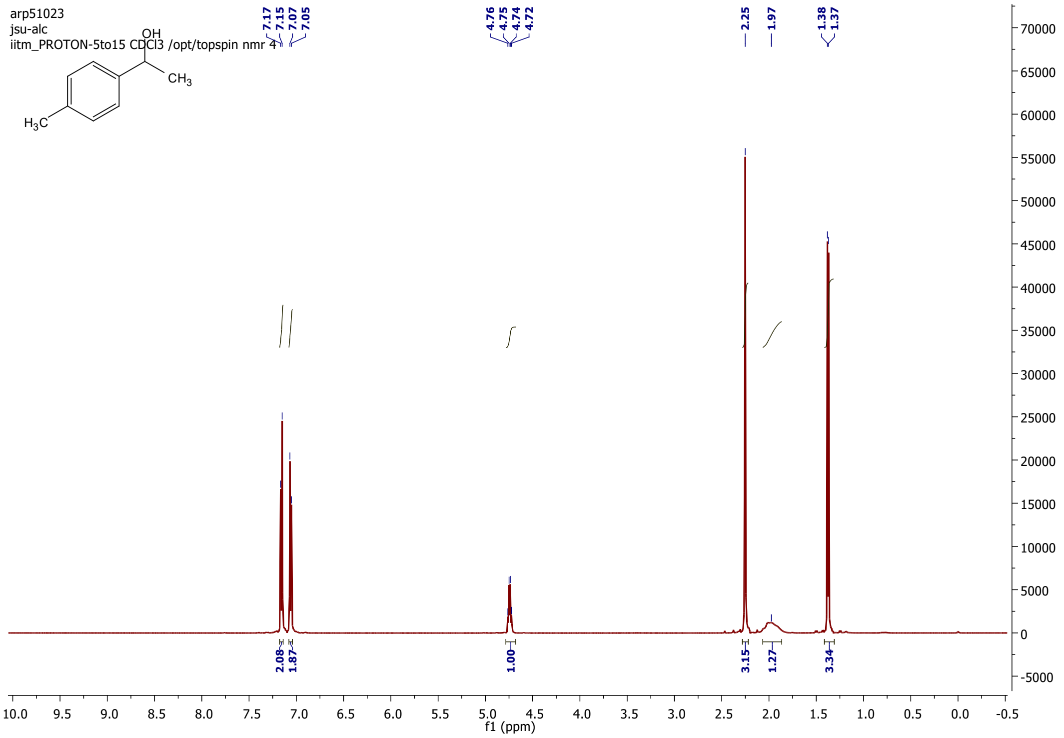


^{1}H NMR of 1b-OH (500 MHz, CDCl$_3$)

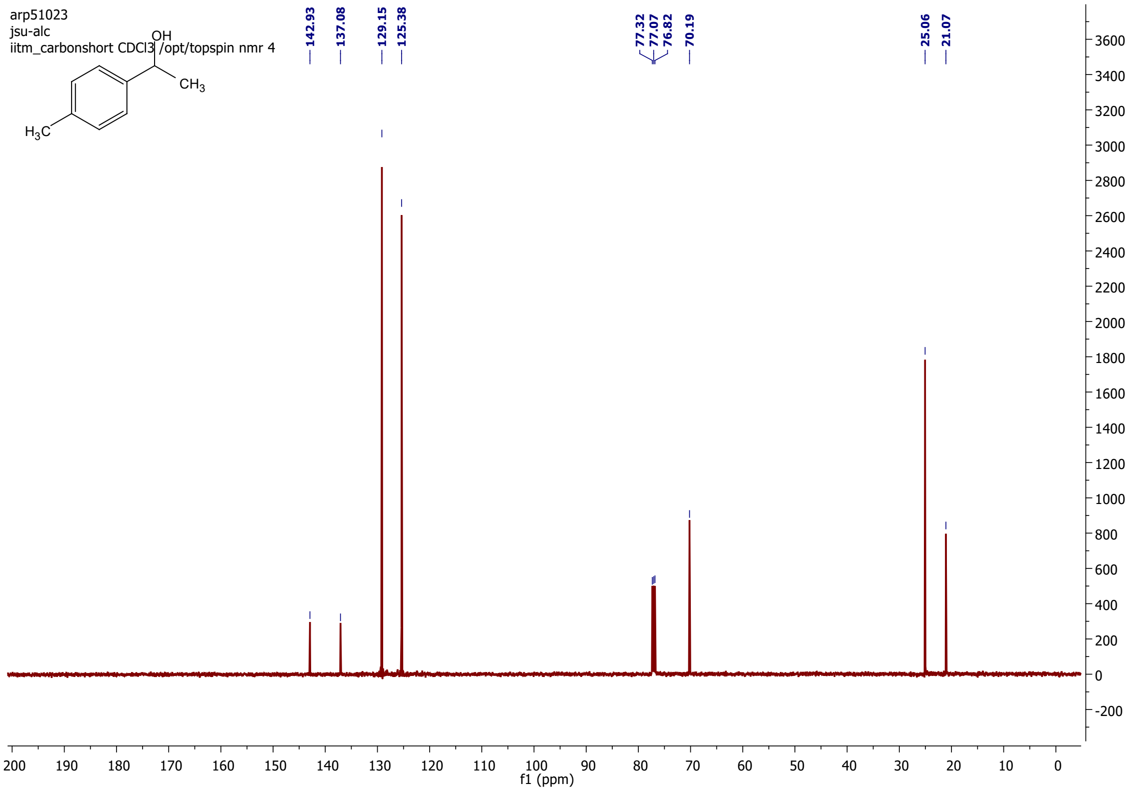


^{13}C NMR of 1b-OH (125 MHz, CDCl$_3$)

1-(p-Tolyl)ethan-1-ol (4c)



^{1}H NMR of 4c (500 MHz, CDCl$_3$)

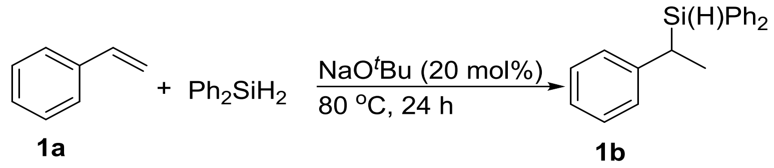


^{13}C NMR of 4c (125 MHz, CDCl$_3$)

X. Inductively Coupled Plasma (ICP) Analysis

Sodium tert-butoxide was purchased from sigma Aldrich with the purity of 95% and 99.9%.

Table S9. *Control Reactions with NaO^{t}Bu of Different Grades.*



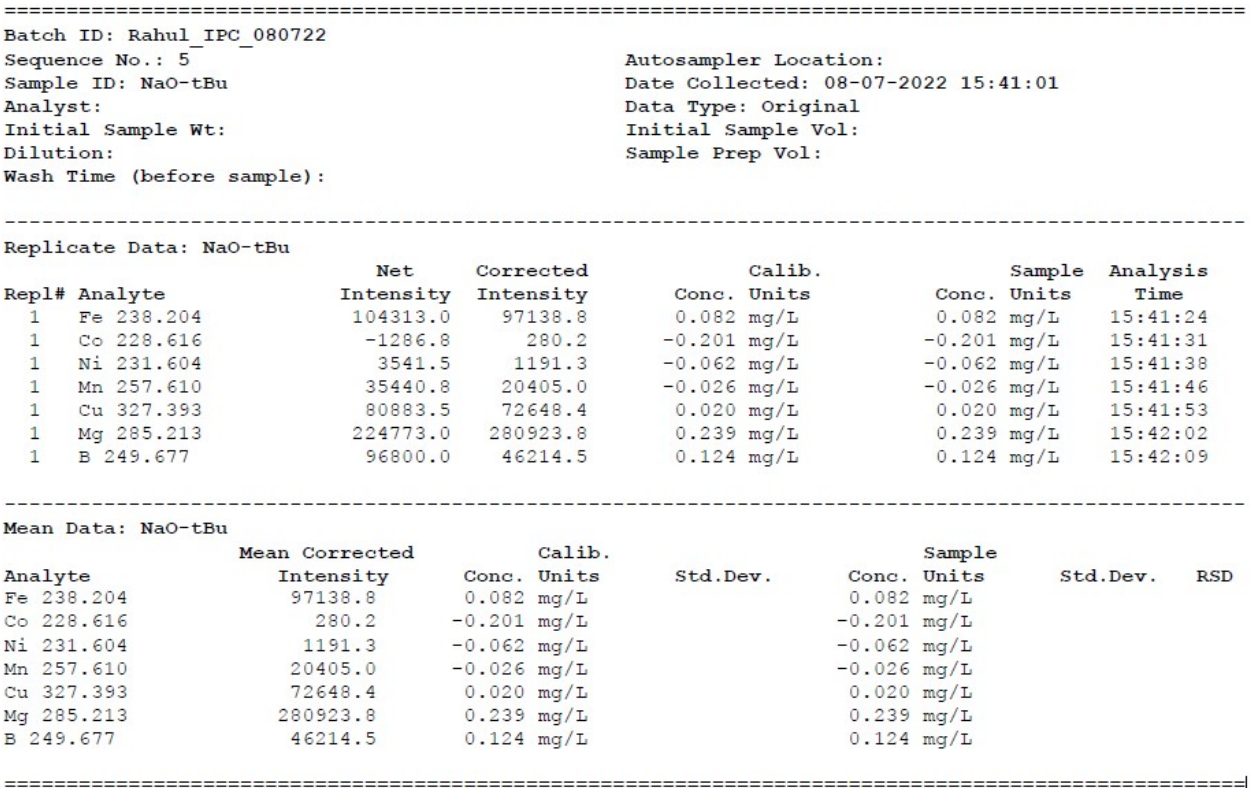
Entry	Ph_2SiH_2 (equiv)	NaO^{t}Bu (mol%)	Vendor	Grade	Time (h)	Yield (%)
1	1.2	20	Aldrich	95%	24	100
2	1.2	20	Aldrich	99.9%	24	100

Reaction conditions: **1a** (0.25 mmol, 1 equiv.), Ph_2SiH_2 (1.2 equiv, 0.3 mmol), NaO^{t}Bu (20 mol%), neat at 80 ºC for 24 h. Yields were determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

In a glovebox, to an oven-dried 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), Ph_2SiH_2 (0.3 mmol), and NaO^{t}Bu (20 mol%) from different grade were added. The reaction mixture was stirred for 24 h. The crude reaction mixture was dissolved in Et_2O (5 mL) and passed through a plug of celite. The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ^{1}H NMR using nitromethane as an internal standard.

Inductively Coupled Plasma (ICP) Analysis

The ICP analysis of NaO^{t}Bu (99.9%) was carried out to check the presence of the trace metals contamination. A snapshot of inductively coupled plasma (ICP) analysis result is shown in Figure S4.



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==================================================================================================
Batch ID: Rahul_IPC_080722
Sequence No.: 5                                   Autosampler Location:
Sample ID: NaO-tBu                                Date Collected: 08-07-2022 15:41:01
Analyst:                                          Data Type: Original
Initial Sample Wt:                                Initial Sample Vol:
Dilution:                                         Sample Prep Vol:
Wash Time (before sample):

--------------------------------------------------------------------------------------------------
Replicate Data: NaO-tBu
                              Net     Corrected             Calib.                Sample  Analysis
Repl# Analyte              Intensity  Intensity        Conc. Units          Conc. Units     Time
  1   Fe 238.204            104313.0    97138.8        0.082 mg/L           0.082 mg/L    15:41:24
  1   Co 228.616             -1286.8      280.2       -0.201 mg/L          -0.201 mg/L    15:41:31
  1   Ni 231.604              3541.5     1191.3       -0.062 mg/L          -0.062 mg/L    15:41:38
  1   Mn 257.610             35440.8    20405.0       -0.026 mg/L          -0.026 mg/L    15:41:46
  1   Cu 327.393             80883.5    72648.4        0.020 mg/L           0.020 mg/L    15:41:53
  1   Mg 285.213            224773.0   280923.8        0.239 mg/L           0.239 mg/L    15:42:02
  1   B 249.677              96800.0    46214.5        0.124 mg/L           0.124 mg/L    15:42:09

--------------------------------------------------------------------------------------------------
Mean Data: NaO-tBu
                   Mean Corrected         Calib.                          Sample
Analyte               Intensity      Conc. Units      Std.Dev.      Conc. Units      Std.Dev.   RSD
Fe 238.204             97138.8       0.082 mg/L                     0.082 mg/L
Co 228.616               280.2      -0.201 mg/L                    -0.201 mg/L
Ni 231.604              1191.3      -0.062 mg/L                    -0.062 mg/L
Mn 257.610             20405.0      -0.026 mg/L                    -0.026 mg/L
Cu 327.393             72648.4       0.020 mg/L                     0.020 mg/L
Mg 285.213            280923.8       0.239 mg/L                     0.239 mg/L
B 249.677              46214.5       0.124 mg/L                     0.124 mg/L

==================================================================================================
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Figure S4. ICP analysis of NaO^{t}Bu (99.9%).

XI. Computational Details

All calculation were performed employing a DFT method implemented in the Gaussian 09 suite of programs.[16] For geometry optimization and frequency analysis, we adopted the unrestricted PBE0 functional.[17] During geometry optimization we used the 6-311++G(2d,2p) basis set. The geometries were optimized without any symmetry constraints. For each transition state, in addition to analyzing the character of the normal mode associated with the imaginary frequency, intrinsic reaction coordinate (IRC) analysis[18] was performed to confirm that it connects the correct reactant and product on the potential energy surface.

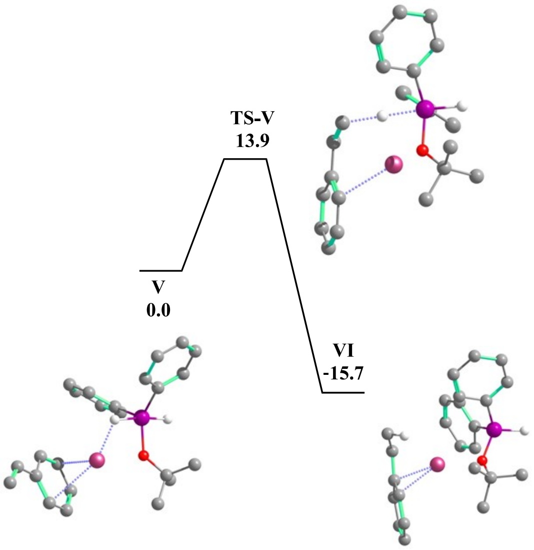

Figure S5. Free energy profile for the reaction of **A** (**I**) with styrene. For the sake of clarity, non-essential hydrogen atoms have been omitted from the illustration. All energies are in kcal/mol.

Figure S5 shows the energy profile for the hydrogen transfer with the presence of sodium cation (Na^+). Based on the calculation, it observed that the Na^+ binds the reactant styrene *via* cation–π complex that forms a salt bridge with the pentacoordinated silicon complex. The transition state barrier associated with this TS_V is 13.9 kcal/mol gives intermediate VI, which is exergonic by around 16 kcal/mol.

Table S10. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at PBE0/6-311++G(2d,2p) basis set level of theory.

I

Na	0.141331000	-2.690409000	-3.014633000
Si	2.282340000	-4.128233000	-1.936678000
O	2.277653000	-2.446718000	-2.548751000
H	3.196990000	-3.763332000	-0.757536000
H	1.355920000	-4.370781000	-3.248021000
C	3.158275000	-1.368044000	-2.223687000
C	0.718027000	-4.395899000	-0.820044000
C	-0.464799000	-4.962598000	-1.316290000
C	0.709882000	-3.977995000	0.516975000
C	-1.602421000	-5.107032000	-0.523833000
C	-0.422795000	-4.103916000	1.315033000
C	-1.584323000	-4.668185000	0.795508000
H	-0.476453000	-5.332933000	-2.342709000
H	1.618146000	-3.550322000	0.934791000
H	-2.496416000	-5.572238000	-0.929968000
H	-0.400885000	-3.766351000	2.347319000
H	-2.467348000	-4.772802000	1.418443000
C	3.355921000	-5.624552000	-2.460807000
C	4.423832000	-6.035369000	-1.655704000
C	3.107866000	-6.352012000	-3.628438000
C	5.204410000	-7.136700000	-1.991122000
C	3.884326000	-7.452048000	-3.977619000
C	4.935169000	-7.847650000	-3.156277000
H	4.640269000	-5.477344000	-0.747209000
H	2.287041000	-6.043273000	-4.272073000
H	6.024901000	-7.440496000	-1.347225000
H	3.673449000	-8.001776000	-4.890649000
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H	3.198147000	-1.681277000	-0.079448000
H	3.551242000	-0.012184000	-0.573306000
C	4.608374000	-1.792508000	-2.441849000
H	4.876275000	-2.608429000	-1.767322000
H	4.748775000	-2.136458000	-3.470561000
H	5.288761000	-0.954517000	-2.260058000
C	2.805013000	-0.243318000	-3.194889000
H	2.918647000	-0.585704000	-4.227443000
H	1.769097000	0.085247000	-3.044929000
H	3.451172000	0.627011000	-3.045115000

II

Na	2.826436000	-5.372958000	0.307352000
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O	3.101373000	-3.307154000	-0.321323000
H	2.274709000	-2.175760000	-2.265700000
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C	0.467151000	-4.001578000	0.617674000
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H	-2.296572000	-5.835071000	1.359715000
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C	5.319085000	-6.405065000	-2.184144000
C	3.562308000	-7.150165000	-3.637572000
C	4.825606000	-7.339426000	-3.086595000
H	4.947750000	-4.568840000	-1.135407000
H	1.832411000	-5.886240000	-3.745121000
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H	5.424861000	-8.199501000	-3.369099000
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H	2.214062000	-0.749041000	-0.547252000
H	2.034253000	-1.288624000	1.130199000
H	3.274216000	-0.095707000	0.714071000
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H	3.745954000	-2.801741000	2.169310000
H	5.201393000	-3.277026000	1.256194000
H	5.010101000	-1.611503000	1.824064000
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H	5.546188000	-2.444129000	-1.100392000
H	4.325791000	-1.419807000	-1.871486000
H	5.325919000	-0.772710000	-0.559783000

III

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Si	-1.098983000	-5.161936000	-0.007499000
O	-2.638977000	-5.148705000	0.702884000
H	-1.014599000	-3.644124000	0.555837000
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H	-4.457803000	-5.242815000	2.535639000

IV

Na	0.233360000	-2.639225000	-2.540036000
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O	3.057291000	-3.793598000	0.141386000
H	2.409101000	-2.504434000	-1.758493000
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H	-0.138107000	-5.512721000	-2.341077000
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C	3.462978000	-5.419542000	-2.025427000
C	4.171647000	-6.208097000	-1.108874000
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C	4.432429000	-6.754751000	-3.816010000
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H	2.728883000	-1.633411000	1.643685000
H	4.277318000	-0.862635000	1.250627000
C	4.680344000	-3.530834000	1.833951000
H	3.892539000	-3.669836000	2.579825000
H	5.122694000	-4.507868000	1.620009000
H	5.456592000	-2.886133000	2.259391000

V

Na	0.896370000	-2.973463000	-3.955111000
Si	2.498826000	-4.157947000	-1.797023000
O	2.673081000	-2.632981000	-2.708367000
H	3.155603000	-3.545467000	-0.547828000
H	1.840443000	-4.664908000	-3.193190000
C	3.468998000	-1.487605000	-2.393712000
C	0.790118000	-4.410439000	-0.934537000
C	-0.137757000	-5.344823000	-1.409904000
C	0.423629000	-3.657052000	0.185916000
C	-1.369380000	-5.534514000	-0.790338000
C	-0.821255000	-3.808195000	0.792906000
C	-1.720386000	-4.753851000	0.308628000
H	0.122426000	-5.942240000	-2.282569000
H	1.135694000	-2.942714000	0.593106000
H	-2.057064000	-6.291344000	-1.158876000
H	-1.084980000	-3.201870000	1.655173000
H	-2.683860000	-4.889796000	0.791063000
C	3.693474000	-5.655543000	-1.852283000
C	4.574062000	-5.890476000	-0.790541000
C	3.718980000	-6.554702000	-2.922357000
C	5.434855000	-6.983217000	-0.787741000
C	4.580128000	-7.647449000	-2.935296000
C	5.440058000	-7.865087000	-1.863878000
H	4.578132000	-5.198835000	0.049188000
H	3.045607000	-6.388030000	-3.760448000
H	6.104997000	-7.147310000	0.051464000
H	4.582750000	-8.330846000	-3.780035000
H	6.114339000	-8.716484000	-1.868706000

C	2.929983000	-0.763020000	-1.160759000
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H	3.030184000	-1.388634000	-0.272416000
H	3.475005000	0.171963000	-0.992876000
C	4.926264000	-1.895830000	-2.192521000
H	5.023398000	-2.563512000	-1.334169000
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H	2.321990000	-0.259492000	-3.768824000
H	3.960802000	0.337944000	-3.474994000
C	-1.246284000	-1.147490000	-3.093796000
C	-0.981862000	-0.704674000	-4.391243000
C	-1.723458000	-2.439212000	-2.893030000
H	-1.071129000	-0.493705000	-2.246445000
C	-1.193423000	-1.542987000	-5.478873000
H	-0.608174000	0.301150000	-4.554638000
C	-1.685835000	-2.846243000	-5.296757000
H	-0.983174000	-1.177849000	-6.478698000
C	-1.941757000	-3.274568000	-3.985919000
C	-1.934292000	-3.772802000	-6.408717000
H	-2.308830000	-4.282622000	-3.817925000
H	-1.904869000	-2.809671000	-1.888941000
C	-1.788930000	-3.520953000	-7.710222000
H	-2.278484000	-4.760599000	-6.108402000
H	-2.005362000	-4.284799000	-8.448232000
H	-1.459374000	-2.559558000	-8.091699000

TS-V

Na	0.155073000	-2.465831000	-2.772511000
Si	2.345234000	-4.115885000	-1.831043000
O	2.406098000	-2.480279000	-2.440133000
H	3.149924000	-3.831373000	-0.564819000
H	1.394906000	-4.317504000	-3.319535000
C	3.395039000	-1.470530000	-2.167741000
C	0.670652000	-4.394974000	-0.940968000
C	-0.274703000	-5.338479000	-1.365663000
C	0.326314000	-3.578634000	0.147633000
C	-1.496896000	-5.482322000	-0.716547000
C	-0.908789000	-3.693867000	0.781218000
C	-1.820836000	-4.652758000	0.352909000
H	-0.041380000	-5.975964000	-2.213695000
H	1.051064000	-2.856947000	0.518934000
H	-2.202077000	-6.238292000	-1.048962000
H	-1.151628000	-3.049386000	1.621077000
H	-2.779105000	-4.755719000	0.852333000
C	3.399604000	-5.595687000	-2.394512000
C	4.079525000	-6.330845000	-1.415913000
C	3.542783000	-5.995486000	-3.726661000
C	4.847371000	-7.441063000	-1.749636000
C	4.333280000	-7.086848000	-4.072755000
C	4.979229000	-7.818357000	-3.082030000
H	4.007885000	-6.021735000	-0.375673000
H	3.034493000	-5.439170000	-4.507703000
H	5.353047000	-8.006209000	-0.972218000
H	4.442083000	-7.370662000	-5.115367000
H	5.588739000	-8.676610000	-3.347944000
C	3.203791000	-0.902026000	-0.763920000
H	2.190545000	-0.502590000	-0.646840000
H	3.364206000	-1.673831000	-0.008462000
H	3.909483000	-0.085582000	-0.580405000
C	4.796395000	-2.050125000	-2.333143000
H	4.982556000	-2.840005000	-1.601552000
H	4.917068000	-2.471570000	-3.335116000
H	5.551443000	-1.270285000	-2.194410000
C	3.161969000	-0.379444000	-3.207663000
H	3.271426000	-0.787413000	-4.216153000
H	2.155364000	0.041678000	-3.112166000
H	3.880440000	0.436427000	-3.083827000
C	-1.960345000	0.046565000	-5.548856000
C	-0.622836000	-0.324394000	-5.636046000
C	-2.900029000	-0.918198000	-5.185682000
H	-2.266614000	1.064929000	-5.760931000
C	-0.224601000	-1.628881000	-5.367927000
H	0.125360000	0.409064000	-5.922401000
C	-1.160698000	-2.626661000	-5.003643000
H	0.826947000	-1.885717000	-5.466555000
C	-2.511618000	-2.218711000	-4.912954000
C	-0.790520000	-3.986820000	-4.681314000
H	-3.259103000	-2.956578000	-4.634371000
H	-3.949936000	-0.650112000	-5.113823000
C	0.495125000	-4.495965000	-4.690946000
H	-1.595954000	-4.629198000	-4.334615000
H	0.625422000	-5.570030000	-4.617821000
H	1.274806000	-3.995576000	-5.259461000

VI

Na	-0.184689000	-2.930831000	-2.989171000
Si	2.145039000	-3.807277000	-0.933542000
O	1.837515000	-2.479457000	-1.914797000
H	2.863437000	-3.399779000	0.306084000
H	1.464622000	-4.393091000	-5.965627000
C	2.752758000	-1.486259000	-2.462465000
C	0.388570000	-4.358848000	-0.552436000
C	-0.029136000	-5.683587000	-0.729680000
C	-0.549902000	-3.426937000	-0.078040000
C	-1.337508000	-6.064333000	-0.449620000
C	-1.860004000	-3.804286000	0.196561000
C	-2.254171000	-5.125708000	0.008916000
H	0.674817000	-6.424118000	-1.098009000
H	-0.251169000	-2.393562000	0.084848000

H	-1.643671000	-7.094743000	-0.598145000
H	-2.571142000	-3.070090000	0.561714000
H	-3.276184000	-5.422388000	0.221438000
C	3.122197000	-5.150174000	-1.783526000
C	4.248814000	-5.708341000	-1.168183000
C	2.737211000	-5.636912000	-3.041641000
C	4.969945000	-6.724672000	-1.786084000
C	3.457902000	-6.649953000	-3.661103000
C	4.573922000	-7.194988000	-3.032810000
H	4.569195000	-5.345398000	-0.194582000
H	1.868583000	-5.223225000	-3.552116000
H	5.841475000	-7.147167000	-1.296212000
H	3.148869000	-7.011454000	-4.636619000
H	5.136980000	-7.986105000	-3.517983000
C	3.873863000	-1.210831000	-1.470656000
H	3.476839000	-0.870425000	-0.510223000
H	4.486681000	-2.102432000	-1.301461000
H	4.531354000	-0.430722000	-1.863478000
C	3.304377000	-2.014354000	-3.779345000
H	3.886021000	-2.927122000	-3.625192000
H	2.492295000	-2.226080000	-4.480945000
H	3.956157000	-1.265674000	-4.239067000
C	1.913705000	-0.236816000	-2.686863000
H	1.118728000	-0.409863000	-3.420191000
H	1.468077000	0.100297000	-1.746600000
H	2.537085000	0.571758000	-3.078343000
C	-1.074594000	0.232605000	-5.468259000
C	-0.034440000	-0.407695000	-6.147544000
C	-1.993482000	-0.572709000	-4.789660000
H	-1.187521000	1.310205000	-5.498939000
C	0.121531000	-1.783285000	-6.124283000
H	0.671296000	0.187097000	-6.723566000
C	-0.769709000	-2.638334000	-5.396741000
H	0.929879000	-2.231707000	-6.694008000
C	-1.859795000	-1.950689000	-4.756435000
C	-0.557249000	-4.025163000	-5.224257000
H	-2.631097000	-2.548093000	-4.267374000
H	-2.846919000	-0.115487000	-4.293680000
C	0.436690000	-4.770663000	-6.072628000
H	-1.437816000	-4.596313000	-4.921604000
H	0.464293000	-5.830897000	-5.797880000
H	0.214815000	-4.731171000	-7.154305000

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