Electronic Supplementary Information

Borane-Catalyzed Selective Dihyrosilylation of Terminal Alkynes: Reaction Development and Mechanistic Insight

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1. General Information

Unless otherwise noted, all reactions were carried out with standard Schlenk techniques under argon or in an argon-filled glove-box. $B(C_6F_5)_3$ was purchased from TCI and used without purification. Other commercial chemicals were purchased from Acros, Sigma-Aldrich, J&K, and Alfa Aesar Chemical Companies and used as received. Anhydrous CH_2Cl_2 was purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on aluminum oxide (200–300 mesh, neutral, Shanghai Wusi Chemical Co., Ltd) or silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd).

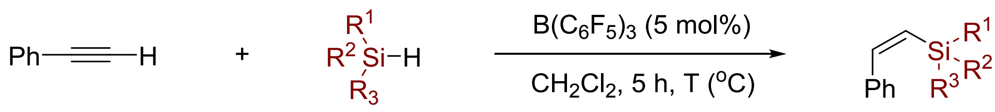
^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR, and 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an APCI or ESI ionization source and a TOF detector mass spectrometer.

2. Experimental Details for the Monohydrosilylation of Terminal Alkyne

2.1 Optimization Studies

General procedure. In an argon-filled glovebox, $B(C_6F_5)_3$ (10 mg, 0.02 mmol, 5 mol%), hydrosilane (0.48 mmol, 1.2 equiv), 1,2,3,4,5,6-hexamethylbenzene (32 mg, 0.2 mmol, 0.5 equiv, as an internal standard) and dichloromethane (1.0 mL) were added to an oven-dried reaction vial. The reaction vial was capped, removed from the glovebox, and stirred at varied temperatures. Phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv) was then added to the reaction solution over a period of 5 min. After indicated time, an aliquot (approximately 50 μL) of the reaction solution was then directly transferred to an NMR tube and $CDCl_3$ (0.4 mL) was added. The conversion was determined by ^{1}H NMR by the integration of the remaining phenylacetylene and internal standard. The results are tabulated in Table S1.

Table S1. Optimization of Reaction Conditions.[a]

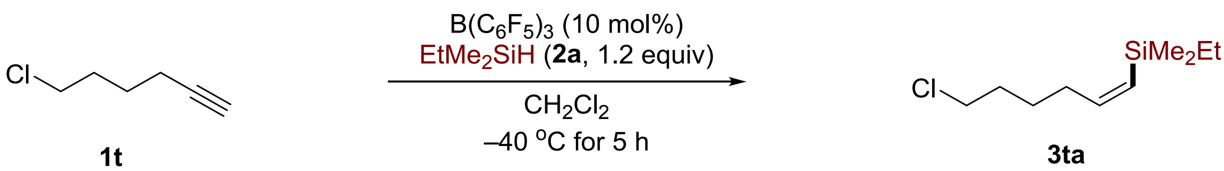


entry	hydrosilanes	T (°C)	conversion (%)[b]	yield (%)[b]
1	$EtMe_2SiH$	r.t	69%	31%
2	$EtMe_2SiH$	5 °C	84%	58%
3	$EtMe_2SiH$	–20 °C	93%	81%
4[c]	$EtMe_2SiH$	–40 °C	>95%	81%
5	**$EtMe_2SiH$**	**–40 °C**	**>95%**	**84% (81%)[d]**
6	Et_3SiH	–40 °C	37%	<5%
7	$PhMe_2SiH$	–40 °C	86%	46%
8	$PhMeSiH_2$	–40 °C	60%	20%
9	Et_2SiH_2	–40 °C	>95%	55%
10	Ph_2SiH_2	–40 °C	50%	ND
11	$PhSiH_3$	–40 °C	48%	ND

[a]Reaction conditions: **1a** (0.4 mmol, 1.0 equiv), hydrosilane (0.48 mmol, 1.2 equiv), $B(C_6F_5)_3$ (0.02 mmol), in dichloromethane (1.0 mL). [b]Conversions and yields were determined by NMR analysis with 1,2,3,4,5,6-hexamethylbenzene as an internal standard. [c]For 16 h. [d]Isolated yield of analytically pure material after flash chromatography on silica gel. ND = Not detected.

2.2 Monohydrosilylation of aliphatic terminal alkyne **1t**

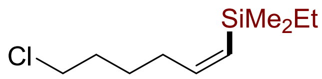
2.2.1 Synthetic Procedure



A reaction vial was charged with $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 10 mol%), CH_2Cl_2 (1 mL), ethyl dimethylsilane (42 mg, 0.48 mmol, 1.2 equiv) in a argon filled-glove box. The solution was cooled to –40

°C and then 6-chlorohex-1-yne **1w** (47 mg, 0.4 mmol, 1.0 equiv) was added *via* syringe over a period of 5 min. The reaction mixture was stirred at –40 °C for 5 hours. After which, diethyl ether (4 mL) and water (1 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with diethyl ether (2×2 mL). The organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel (petroleum ether 40–60 °C) to afford the desired product **3wa** (43.2 mg, 53%).

2.2.2 Characterization Data of (Z)-(6-Chlorohex-1-en-1-yl)(ethyl)dimethylsilane (**3ta**)

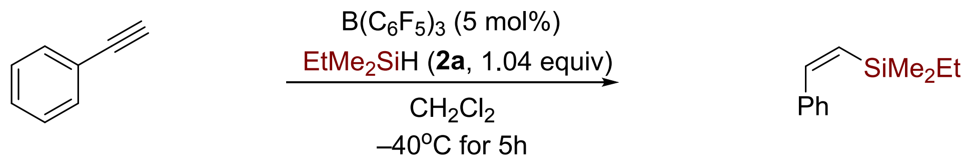


3ta
$C_{10}H_{21}ClSi$
M = 204.81 g/mol

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.30 (dt, *J* = 14.4, 7.3 Hz, 1H), 5.49 (dt, *J* = 14.0, 1.3 Hz, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.15 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.83–1.75 (m, 2H), 1.57–1.50 (m, 2H), 0.94 (t, *J* = 7.9 Hz, 3H), 0.57 (q, *J* = 8.0 Hz, 2H), 0.09 (s, 6H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.6, 128.7, 45.1, 32.9, 32.4, 27.1, 8.5, 7.6, –1.9. **IR (film)**: 2965, 2843, 1054, 1032, 1012, 913, 743 cm^{-1}. **HRMS (ESI)** calculated for $C_{10}H_{21}ClSi^+$ $[M+H]^+$ 205.1179; Found: 205.1183.

2.3 Gram-Scale Synthesis of Vinylsilane with Phenylacetylene

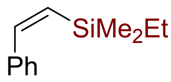
2.3.1 Synthetic Procedure



1a, 5 mmol — **3aa**, 81% (0.77 g)

A reaction vial was charged with $B(C_6F_5)_3$ (128 mg, 0.25 mmol, 5.0 mol%), CH_2Cl_2 (1 mL), $EtMe_2SiH$ (457 mg, 5.2 mmol, 1.04 equiv) in an argon-filled glove box. The solution was cooled to –40 °C and then phenylacetylene (510 mg, 5 mmol, 1.0 equiv) was slowly added via syringe over a period of 20 min. The reaction mixture was stirred at –40 °C for 5 hours. Diethyl ether (4 mL) and water (1 mL) was slowly added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted twice with diethyl ether (3×3 mL). Then, the organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel (petroleum ether 40–60 °C) to afford **3aa** (0.77 g, 81%).

2.3.2 Characterization Data of (*Z*)-Ethyldimethyl(styryl)silane (**3aa**)

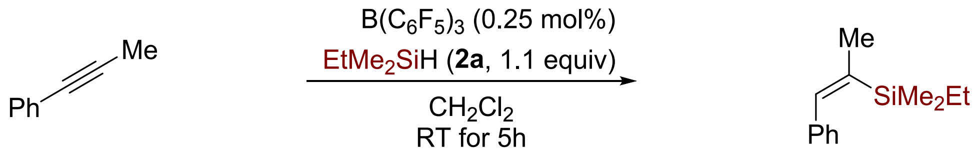


3aa
$C_{12}H_{18}Si$
M = 190.36 g/mol

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, *J* = 15.2 Hz, 1H), 7.36–7.24 (m, 5H), 5.83 (d, *J* = 15.2 Hz, 1H), 0.90 (t, *J* = 7.9 Hz, 3H), 0.55 (q, *J* = 7.9 Hz, 2H), 0.02 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 147.2, 140.4, 131.9, 128.2, 120.0, 127.4, 8.6, 7.5, –1.9 ppm. **IR** (film): 3058, 3024, 2955, 2910, 2874, 1682, 1592, 1492, 1457, 1377, 779, 699, 662 cm^{-1}. **HRMS** (ESI): calculated for $C_{12}H_{19}Si^+$ [M+H]$^+$ 191.1256; found 191.1250.

2.4 Gram-Scale Synthesis of Vinylsilane with 1-Phenylpropyne

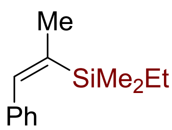
2.4.1 Synthetic Procedure



1x, 8 mmol   **3xa**, 89% (1.45 g)

A reaction vial was charged with $B(C_6F_5)_3$ (10.2 mg, 0.25 mol%), CH_2Cl_2 (1 mL), ethyl dimethylsilane (0.774 g, 8.8 mmol) in a argon filled-glove box. Then 1-phenylpropyne **1x** (0.928 g, 8 mmol) was added *via* syringe, and the reaction mixture was stirred at room temperature for 24 hours. After which, diethyl ether (4 mL) and water (1 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with diethyl ether (3×3 mL). The organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel (petroleum ether 40–60 ^{o}C) to afford the desired product **3xa** (1.45 g, 89%).

2.4.2 Characterization Data of (Z)-Ethyldimethyl(1-phenylprop-1-en-2-yl)silane (**3ua**)

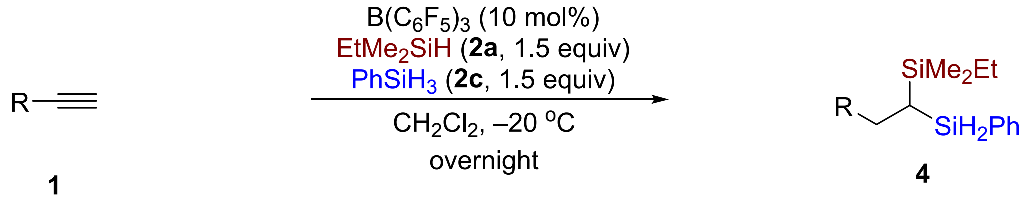


3ua
$C_{13}H_{20}Si$
M = 204.38 g/mol

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.16 (m, 6H), 1.97 (d, *J* = 1.7 Hz, 3H), 0.86 (t, *J* = 7.9 Hz, 3H), 0.47 (q, *J* = 7.7 Hz, 2H), –0.09 (s, 6H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ142.1, 140.9, 139.5, 128.7, 127.8, 126.7, 25.6, 8.1, 7.6, –2.4. **IR (film)**: 3058, 3022, 2952, 2911, 2874, 1593, 1490, 1441, 816, 775, 698, 638 cm^{-1}. **HRMS (ESI)** calculated for $C_{13}H_{21}Si^+$ $[M+H]^+$ 205.1413; Found: 205.1411.

3. Experimental Details for the Synthesis of Geminal Bis(silanes) 4

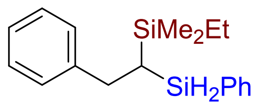
3.1 General Procedure for the Borane-Catalyzed Dihyrosilylation of Terminal Alkynes



A reaction vial was charged with 10 mol% of $B(C_6F_5)_3$ (unless otherwise noted), CH_2Cl_2 (1 mL), $EtMe_2SiH$ (53 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (65 mg, 0.6 mmol, 1.5 equiv) in an argon-filled glove box. The solution was cooled to –20 °C and then the corresponding alkyne **1** was slowly added *via* syringe over a period of 5 min. After stirring at –20 °C overnight, the reaction mixture was quenched by saturated sodium bicarbonate solution (1 mL) under –20 °C, and then diluted by diethyl ether (4 mL). The organic phase was separated, and the aqueous layer was extracted twice with diethyl ether (4 mL). Then, the organic layers were combined, and dried over anhydrous sodium sulfate, and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford the desired product **4**.

3.2 Characterization Data of Geminal Bis(silanes) 4

3.2.1 Ethyldimethyl(2-phenyl-1-(phenylsilyl)ethyl)silane (**4aac**)

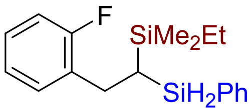


4aac
$C_{18}H_{26}Si_2$
M = 298.58 g/mol

Prepared from phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4aac** as a colorless oil (109 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H), 7.33–7.30 (m, 1H), 7.28–7.25 (m, 2H), 7.23–7.18 (m, 2H), 7.15–7.12 (m, 3H), 4.36 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.27 (dd, *J* = 5.6, 3.9 Hz, 1H), 2.95 (dd, *J* = 14.3, 5.9 Hz, 1H), 2.74 (dd, *J* = 14.2, 9.2 Hz, 1H), 0.90 (t, *J* = 7.9 Hz, 3H), 0.74–0.68 (m, 1H), 0.52 (qd, *J* = 7.9, 1.7 Hz, 2H), -0.01 (s, 3H), -0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.5, 135.5, 133.3, 129.4, 128.7, 128.3, 127.9, 125.9, 32.9, 10.7, 7.5, 7.1, –3.4, –3.6 ppm. **IR** (film):

3066, 3026, 2910, 2874, 2131, 1507, 1454, 1249, 1134, 1115, 1035, 970, 938, 984, 859, 833, 777, 698 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{27}Si_2^+$ $[M+H]^+$: 299.1646; found 299.1650.

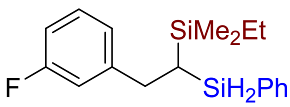
3.2.2 Ethyl(2-(2-fluorophenyl)-1-(phenylsilyl)ethyl)dimethylsilane (**4bac**)



4bac
$C_{18}H_{25}FSi_2$
M = 316.57 g/mol

Prepared from 1-ethynyl-2-fluorobenzene **1b** (48 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4bac** as a colorless oil (114 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39–7.23 (m, 5H), 7.16–7.06 (m, 2H), 6.96 (t, *J* = 7.1 Hz, 1H), 6.95–6.86 (m, 1H), 4.36 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.28–4.24 (m, 1H), 2.99 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.76 (dd, *J* = 14.2, 9.8 Hz, 1H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.84–0.78 (m, 1H), 0.57–0.50 (m, 2H), 0.01 (s, 3H), –0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.3 (d, *J* = 244.6 Hz), 135.4, 133.1, 130.9 (d, *J* = 4.9 Hz), 130.3 (d, *J* = 15.3 Hz), 129.4, 127.9, 127.7 (d, *J* = 8.1 Hz), 123.8 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 22.3 Hz), 26.4, 9.2, 7.5, 7.00, –3.6, –3.7 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ –117.6 ppm. **IR** (film): 3068, 3050, 2953, 2910, 2874, 2132, 1584, 1489, 1455, 1428, 1250, 1226, 1115, 1039, 855, 736 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{24}FSi_2^{\bullet+}$ $[M–H]^{\bullet+}$: 315.1395; found 315.1396.

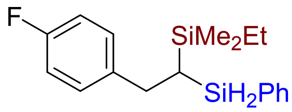
3.2.3 Ethyl(2-(3-fluorophenyl)-1-(phenylsilyl)ethyl)dimethylsilane (**4cac**)



4cac
$C_{18}H_{25}FSi_2$
M = 316.57 g/mol

Prepared from 1-ethynyl-3-fluorobenzene **1c** (48 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4cac** as a colorless oil (102 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41–7.27 (m, 5H), 7.18–7.12 (m, 1H), 6.9 (d, *J* = 7.8 Hz, 1H), 6.86–6.80 (m, 2H), 4.30–4.26 (m, 1H), 4.28 (dd, *J* = 5.4, 4.2 Hz, 1H), 2.95 (dd, *J* = 14.3, 5.5 Hz, 1H), 2.77–2.70 (m, 1H), 0.93 (t, *J* = 8.0 Hz, 3H), 0.76–0.66 (m, 1H), 0.59–0.51 (m, 2H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 245.4 Hz), 146.1 (d, *J* = 6.9 Hz), 135.4, 133.0, 129.7 (d, *J* = 8.3 Hz), 129. 5, 127.9, 124.3, 115.6 (d, *J* = 20.9 Hz), 112.8 (d, *J* = 21.1 Hz), 32.8, 10.6, 7.5, 7.1, –3.5, –3.6 ppm. **$^{19}F\{^1H\}$ NMR** (376 MHz, $CDCl_3$): δ –113.9 ppm. **IR** (film): 3068, 2954, 2910, 2874, 2132, 1614, 1588, 1487, 1449, 1251, 1115, 1035, 857, 779, 716 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{24}FSi_2^{\bullet+}$ $[M–H]^{\bullet+}$: 315.1395; found 315.1399.

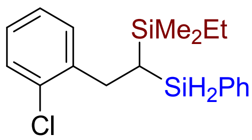
3.2.4 Ethyl(2-(4-fluorophenyl)-1-(phenylsilyl)ethyl)dimethylsilane (**4dac**)



4dac
$C_{18}H_{25}FSi_2$
M = 316.57 g/mol

Prepared from 1-ethynyl-4-fluorobenzene **1d** (48 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4dac** as a colorless oil (99 mg, 79% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 3H), 7.29–7.24 (m, 2H), 7.05 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.86 (t, *J* = 8.7 Hz, 2H), 4.36 (dd, *J* = 5.5, 2.6 Hz, 1H), 4.25 (dd, *J* = 5.5, 4.2 Hz, 1H), 2.93 (dd, *J* = 14.3, 5.8 Hz, 1H), 2.70 (dd, *J* = 14.3, 9.4 Hz, 1H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.70–0.64 (m, 1H), 0.53 (q, *J* = 7.8 Hz, 2H), 0.01 (s, 3H), 0.00 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz,$CDCl_3$): δ 161.4 (d, *J* = 243.2 Hz), 139.1 (d, *J* = 2.7 Hz), 135.4, 133.1, 129.9 (d, *J* = 7.8 Hz), 129.5, 127.9, 114.9 (d, *J* = 21.1 Hz), 32.3, 11.0, 7.5, 7.1, –3.5, –3.6 ppm. **$^{19}F\{^1H\}$ NMR** (376 MHz, $CDCl_3$): δ –117.8 ppm. **IR** (film): 3068, 2953, 2910, 2874, 2131, 1600, 1508, 1428, 1249, 1156, 1115, 1035, 861, 824 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{24}FSi_2^{\bullet+}$ $[M–H]^{\bullet+}$: 315.1395; found 315.1398.

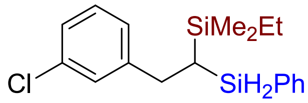
3.2.5 (2-(2-Chlorophenyl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4eac**)



4eac
$C_{18}H_{25}ClSi_2$
M = 333.02 g/mol

Prepared from 1-chloro-2-ethynylbenzene **1e** (54 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4eac** as a colorless oil (56 mg, 42% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ 7.34–7.27 (m, 3H), 7.24–7.16 (m, 4H), 7.08–7.02 (m, 2H), 4.38 (dd, J = 5.3, 2.4 Hz, 1H), 4.28–4.24 (m, 1H), 3.11 (dd, J = 14.1, 5.9 Hz, 1H), 2.82 (dd, J = 14.1, 10.3 Hz, 1H), 1.05–0.97 (m, 1H), 0.92 (t, J = 7.9 Hz, 3H), 0.59–0.52 (m, 2H), 0.02 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 140.6, 135.3, 134.1, 133.1, 131.0, 129.7, 129.3, 127.8, 127.5, 126.5, 31.2, 8.2, 7.5, 7.0, –3.5, –3.7 ppm. **IR** (film): 3067, 3000, 2953, 2873, 2131, 1570, 1471, 1443, 1250, 1114, 1051, 856, 749 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{26}ClSi_2^+$ $[M+H]^+$: 333.1256; found 333.1253.

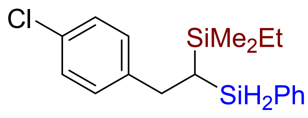
3.2.6 (2-(3-Chlorophenyl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4fac**)



4fac
$C_{18}H_{25}ClSi_2$
M = 333.02 g/mol

Prepared from 1-chloro-3-ethynylbenzene **1f** (54 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4fac** as a colorless oil (104 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38–7.25 (m, 5H), 7.13–7.08 (m, 3H), 6.98 (dt, J = 5.9 Hz, 1H), 4.36 (dd, J = 5.6, 2.6 Hz, 1H), 4.28–4.25 (m, 1H), 2.93 (dd, J = 14.3, 5.8 Hz, 1H), 2.70 (dd, J = 14.3, 9.5 Hz, 1H), 0.93 (t, J = 7.9 Hz, 3H), 0.72-0.67 (m, 1H), 0.55 (q, J = 8.0 Hz, 2H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 145.5, 135.4, 134.1, 132.9, 129.5, 128.8, 127.9, 126.8, 126.1, 32.8, 10.6, 7.5, 7.0, –3.5, –3.6 ppm (two *Ar-C* resonances are overlapped). **IR** (film): 3068, 3000, 2953, 2910, 2873, 2131, 1596, 1456, 1446, 1250, 1115, 1025, 858, 831, 719 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{26}ClSi_2^+$ $[M+H]^+$: 333.1256; found 333.1247.

3.2.7 (2-(4-Chlorophenyl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4gac**)

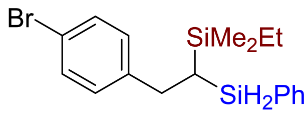


4gac
$C_{18}H_{25}ClSi_2$
M = 333.02 g/mol

Prepared from 1-chloro-4-ethynylbenzene **1g** (54 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4gac** as a colorless oil (106 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (t, J = 6.1 Hz, 3H), 7.28–7.24

(m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 4.36 (dd, *J* = 5.6, 2.6 Hz, 1H), 4.27–4.24 (m, 1H), 2.92 (dd, *J* = 14.3, 5.8 Hz, 1H), 2.69 (dd, *J* = 14.3, 9.5 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 3H), 0.70–0.64 (m, 1H), 0.54 (q, *J* = 7.7 Hz, 2H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 141.9, 135.4, 133.0, 131.6, 130.0, 129.5, 128.4, 127.9, 32.4, 10.8, 7.5, 7.1, –3.5, –3.6 ppm. **IR** (film): 3068, 3000, 2953, 2910, 2873, 2131, 1489, 1428, 1249, 1115, 1025, 816 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{26}ClSi_2^+$ $[M+H]^+$: 333.1256; found 333.1259.

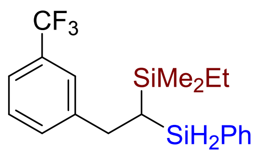
3.2.8 (2-(4-Bromophenyl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4hac**)



4hac
$C_{18}H_{25}BrSi_2$
M = 377.47 g/mol

Prepared from 1-bromo-4-ethynylbenzene **1h** (72 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4hac** as a colorless oil (98 mg, 67% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 3H), 7.28–7.23 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.35 (dd, *J* = 5.5, 2.6 Hz, 1H), 4.26–4.21 (m, 1H), 2.89 (dd, *J* = 14.3, 5.7 Hz, 1H), 2.66 (dd, *J* = 14.3, 9.5 Hz, 1H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.70–0.62 (m, 1H), 0.58–0.48 (m, 2H), 0.00 (s, 3H), –0.01 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 142.4, 135.4, 132.9, 131.3, 130.4, 129.5, 127.9, 119.6, 32.5, 10.8, 7.5, 7.0, –3.5, –3.6 ppm. **IR** (film): 3067, 2999, 2952, 2909, 2873, 2131, 1589, 1486, 1456, 1428, 1249, 1115, 1094, 1025, 816 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{26}BrSi_2^+$ $[M+H]^+$: 377.0751; found 377.0752.

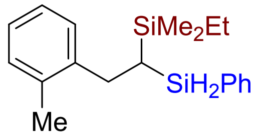
3.2.9 Ethyldimethyl(1-(phenylsilyl)-2-(3-(trifluoromethyl)phenyl)ethyl)silane (**4iac**)



4iac
$C_{19}H_{25}F_3Si_2$
M = 366.57 g/mol

Prepared from 1-ethynyl-3-(trifluoromethyl)benzene **1i** (68 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4iac** as a colorless oil (76 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37–7.21 (m, 9H), 4.37 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.27–4.24 (m, 1H), 3.01 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.77 (dd, *J* = 14.4, 9.7 Hz, 1H), 0.93 (t, *J* = 7.9 Hz, 3H), 0.76 – 0.69 (m, 1H), 0.55 (q, *J* = 7.9 Hz, 2H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 144.3, 135.3, 132.8, 132.1, 130.6 (q, *J* = 3.7 Hz), 129.5, 128.7, 127.9, 125.4 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.3 Hz) 122.8 (q, *J* = 3.9 Hz), 32.9, 10.6, 7.5, 7.0, –3.5, –3.6 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ –62.60 ppm. **IR** (film): 3069, 2954, 2911, 2875, 2133, 1595, 1449, 1332, 1251, 1165, 1089, 831, 718 cm^{-1}. **HRMS** (APCI): calculated for $C_{19}H_{24}F_3Si_2^{\bullet+}$ $[M–H]^{\bullet+}$: 365.1363; found 365.1371.

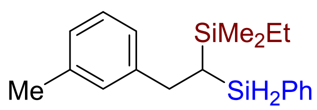
3.2.10 Ethyldimethyl(1-(phenylsilyl)-2-(o-tolyl)ethyl)silane (**4jac**)



4jac
$C_{19}H_{28}Si_2$
M = 312.60 g/mol

Prepared from 1-ethynyl-2-methylbenzene **1j** (46 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4jac** as a colorless oil (110 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 3H), 7.25–7.20 (m, 2H), 7.16–7.13 (m, 1H), 7.06–7.04 (m, 3H), 4.36 (dd, *J* = 5.6, 2.7 Hz, 1H), 4.25–4.27 (m, 1H), 2.97 (dd, *J* = 14.5, 5.9 Hz, 1H), 2.74 (dd, *J* = 14.5, 10.1 Hz, 1H), 2.23 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 3H), 0.80–0.75 (m, 1H), 0.60–0.52 (m, 2H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 141.2, 136.0, 135.3, 133.4, 130.4, 129.4, 129.3, 127.8, 126.2, 125.8, 30.5, 19.6, 8.7, 7.6, 7.1, –3.5, –3.6 ppm. **IR** (film): 3067, 3050, 2952, 2911, 2873, 2131, 1607, 1486, 1428, 1249, 1115, 1036, 857, 832, 716 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{29}Si_2^+$ $[M+H]^+$: 313.1802; found 313.1799.

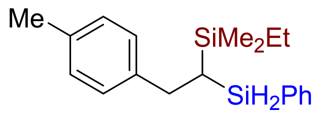
3.2.11 Ethyldimethyl(1-(phenylsilyl)-2-(m-tolyl)ethyl)silane (**4kac**)



4kac
$C_{19}H_{28}Si_2$
M = 312.60 g/mol

Prepared from 1-ethynyl-3-methylbenzene **1k** (46 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4kac** as a colorless oil (101 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 3H), 7.28–7.23 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 1H), 4.36 (dd, *J* = 5.6, 2.6 Hz, 1H), 4.26 (dd, *J* = 5.6, 4.0 Hz, 1H), 2.92 (dd, *J* = 14.2, 5.7 Hz, 1H), 2.70 (dd, *J* = 14.2, 9.4 Hz, 1H), 2.25 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.72–0.68 (m, 1H), 0.56–0.50 (m, 2H), 0.01 (s, 3H), –0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.3, 137.8, 135.5, 133.5, 129.5, 129.4 128.2, 127.8, 126.6, 125.7, 32.9, 21.5, 10.6, 7.5, –3.5, –3.6 ppm. **IR** (film): 3067, 3050, 2952, 2911, 2873, 2131, 1607, 1486, 1428, 1249, 1115, 1036, 857, 832, 716 cm^{-1}. **HRMS** (APCI): calculated for $C_{19}H_{29}Si_2^+$ [M+H]$^+$: 313.1802; found 313.1792.

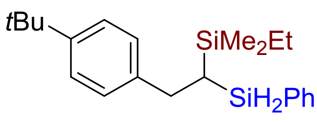
3.2.12 Ethyldimethyl(1-(phenylsilyl)-2-(p-tolyl)ethyl)silane (**4lac**)



4lac
$C_{19}H_{28}Si_2$
M = 312.60 g/mol

Prepared from 1-ethynyl-4-methylbenzene **1l** (46 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4lac** as a colorless oil (101 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 7.05–7.01 (m, 4H), 4.37 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.30–4.26 (m, 1H), 2.94 (dd, *J* = 14.1, 5.9 Hz, 1H), 2.72 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.31 (s, 3H), 0.92 (t, *J* = 7.7 Hz, 3H), 0.76–0.67 (m, 1H), 0.57–0.51 (m, 2H), 0.01 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 140.4, 135. 5, 135.3, 133.4, 129.3, 128.9, 128.6, 127.8, 32.5, 21.1, 10.8, 7.6, 7.1, –3.4, –3.6 ppm. **IR** (film): 3087, 3048, 2952, 2911, 2873, 2131, 1514, 1484, 1428, 1377, 1249, 1115, 1036, 859 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{29}Si_2^+$ [M+H]$^+$: 313.1802; found 313.1800.

3.2.13 (2-(4-(Tert-butyl)phenyl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4mac**)

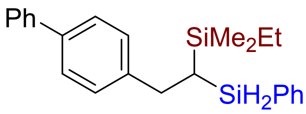


4mac
$C_{22}H_{34}Si_2$
M = 354.68 g/mol

Prepared from 1-(tert-butyl)-4-ethynylbenzene **1m** (63 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$

(41 mg, 0.08 mmol, 0.2 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4mac** as a colorless oil (100 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.27 (m, 3H), 7.25–7.19 (m, 4H), 7.06 (d, *J* = 8.2 Hz, 2H), 4.37 (dd, *J* = 5.5, 2.4 Hz, 1H), 4.28 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.95 (dd, *J* = 14.2, 5.4 Hz, 1H), 2.70 (dd, *J* = 14.2, 9.7 Hz, 1H), 1.30 (s, 9H), 0.92 (t, *J* = 7.9 Hz, 3H), 0.75–0.65 (m, 1H), 0.55 (qd, *J* = 7.8, 2.5 Hz, 2H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.8, 140.4, 135.4, 133.5, 129.3, 128.4, 127.8, 125.2, 34.5, 32.5, 31.6, 10.9, 7.6, 7.0, –3.5, –3.7 ppm. **IR** (film): 3067, 3051, 2956, 2907, 2873, 2130, 1514, 1428, 1267, 1249, 1114, 1035, 821, 778, 698 cm^{-1}. **HRMS** (APCI): calculated for $C_{22}H_{35}Si_2^+$ [M+H]$^+$: 355.2272; found 355.2267.

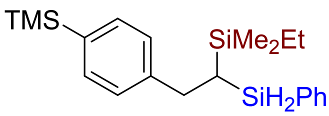
3.2.14 (2-([1,1'-Biphenyl]-4-yl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4nac**)



4nac
$C_{24}H_{30}Si_2$
M = 374.67 g/mol

Prepared from 4-ethynyl-1,1'-biphenyl **1n** (71 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4nac** as a colorless oil (91 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62–7.58 (m, 2H), 7.49–7.43 (m, 4H), 7.40–7.32 (m, 4H), 7.30–7.25 (m, 2H), 7.23–7.20 (m, 2H), 4.44 (td, *J* = 5.8, 2.4 Hz, 1H), 4.37–4.32 (m, 1H), 3.05 (dt, *J* = 14.1, 5.2 Hz, 1H), 2.81 (ddd, *J* = 14.5, 9.5, 5.1 Hz, 1H), 0.97 (td, *J* = 7.9, 5.5 Hz, 3H), 0.85–0.74 (m, 1H), 0.65–0.59 (m, 2H), 0.08 (s, 3H), 0.07 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 142.6, 141.3, 138.9, 135.4, 133.3, 129.3, 129.1, 128.8, 127.9, 127.1, 127.0, 32.7, 10.9, 7.6, 7.1, -3.4, -3.6 ppm (two *Ar-C* resonances are overlapped). **IR** (film): 3066, 3052, 3026, 2999, 2952, 2909, 2872, 2130, 1601, 1487, 1428, 1285, 1249, 1115, 1035, 860, 825 cm^{-1}. **HRMS** (ESI): calculated for $C_{24}H_{31}Si_2^+$ [M+H]$^+$: 375.1959; found 375.1961.

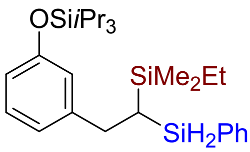
3.2.15 Ethyldimethyl(1-(phenylsilyl)-2-(4-(trimethylsilyl)phenyl)ethyl)silane (**4oac**)



4oac
$C_{21}H_{34}Si_3$
M = 370.76 g/mol

Prepared from (4-ethynylphenyl)trimethylsilane **1o** (70 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4oac** as a colorless oil (115 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.30–7.25 (m, 3H), 7.24–7.19 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.36 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.27 (dd, *J* = 5.6, 4.0 Hz, 1H), 2.96 (d, *J* = 14.2, 5.4 Hz, 1H), 2.71 (d, *J* = 14.2, 9.7 Hz, 1H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.73–0.67 (m, 1H), 0.55 (qd, *J* = 7.8, 2.4 Hz, 2H), 0.24 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 145.1, 138.5, 136.4, 134.4, 130.3, 129.2, 128.8, 33.9, 11.7, 8.6, 8.0, 0.12, –2.5, –2.6 ppm (two *Ar-C* resonances are overlapped). **IR** (film): 3067, 3052, 2954, 2910, 2874, 2131, 1599, 1428, 1248, 1108, 1035, 839 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{35}Si_3^+$ [M+H]$^+$: 371.2041; found 371.2043.

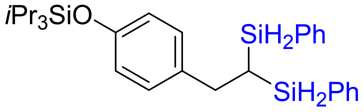
3.2.16 Ethyldimethyl(1-(phenylsilyl)-2-(3-((triisopropylsilyl)oxy)phenyl)ethyl)silane (**4pac**)



4pac
$C_{27}H_{46}OSi_3$
M = 470.92 g/mol

Prepared from (3-ethynylphenoxy)triisopropylsilane **1p** (110mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4pac** as a colorless oil (138 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 6.5 Hz, 2H), 7.36–7.25 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.72–6.66 (m, 3H), 4.35 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.28 (dd, *J* = 5.6, 3.7 Hz, 1H), 2.87 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.69 (dd, *J* = 14.2, 8.9 Hz, 1H), 1.28–1.19 (m, 3H), 1.10 (s, 12H), 1.09 (s, 6H),0.89 (t, *J* = 7.9 Hz,3H), 0.70–0.65 (m, 1H), 0.54–0.45 (m, 2H), -0.02 (s, 3H), -0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.1, 145.1, 135.5, 133.3, 129.5, 129.2, 127.9, 121.4, 120.2, 117.4, 32.8, 18.1, 12.8, 10.5, 7.5, 7.1, -3.4, -3.6 ppm. **IR** (film): 2945, 2866, 2129, 1599, 1583, 1484, 1275, 1157, 854 cm^{-1}. **HRMS** (ESI): calculated for $C_{27}H_{46}OSi_3Na^+$ [M+Na]$^+$: 493.2749; found 493.2739.

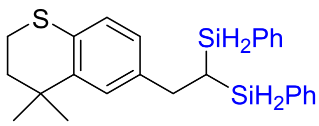
3.2.17 (2-(4-((triisopropylsilyl)oxy)phenyl)ethane-1,1-diyl)bis(phenylsilane) (**4qcc**)



4qcc
$C_{29}H_{42}OSi_3$
M = 490.91 g/mol

Prepared from (4-ethynylphenoxy)triisopropylsilane **1q** (110mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4qcc** as a colorless oil (53 mg, 27% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.9, 1.4 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 4H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.35 (dd, *J* = 6.2, 3.4 Hz, 2H), 4.32 (dd, *J* = 6.2, 3.5 Hz, 2H), 2.82 (d, *J* = 7.8 Hz, 2H), 1.27–1.18 (m, 3H), 1.04–0.98, 1.10 (s, 12H), 1.08 (s, 8H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.4, 135.7, 134.7, 132.0, 129.8, 129.6, 128.0, 119.8, 32.9, 18.1, 12.8, 7.1 ppm. **IR** (film): 2944, 2866, 2107, 1601, 1503, 1263, 1013, 906, 837 cm^{-1}. **HRMS** (ESI): calculated for $C_{29}H_{42}OSi_3Na^+$ $[M+Na]^+$: 513.2436; found 513.2435.

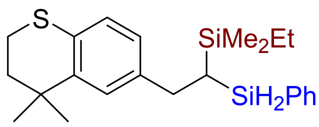
3.2.18 (2-(4,4-Dimethylthiochroman-6-yl)ethane-1,1-diyl)bis(phenylsilane) (**4rcc**)



4rcc
$C_{25}H_{30}SSi_2$
M = 418.16 g/mol

Prepared from (4-ethynylphenyl)trimethylsilane **1r** (81 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4rcc** as a colorless oil (25 mg, 15% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44–7.21 (m, 4H), 7.40–7.35 (m, 2H), 7.31 (t, *J* = 7.1 Hz, 4H), 7.06 (d, *J* = 1.9 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0, 1.9 Hz, 1H), 4.40 (dd, *J* = 6.1, 3.2 Hz, 2H), 4.36 (dd, *J* = 6.1, 3.7 Hz, 2H), 3.01–2.98 (m, 2H), 1.93–1.89 (m, 2H), 1.05–0.99 (m, 1H), 1.23 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 141.9, 138.1, 135.6, 131.9, 129.8, 129.1, 128.0, 126.9, 126.7, 126.5, 37.9, 33.7, 33.0, 30.3, 23.2, 7.1 ppm. **IR** (film): 3067, 2952, 2873, 2130, 1589, 1505, 1488, 1240, 870, 831, 691 cm^{-1}. **HRMS** (ESI): calculated for $C_{25}H_{31}SSi_2^+$ $[M+H]^+$: 419.1680; found 419.1680.

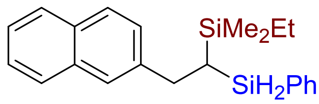
3.2.19 (2-(4,4-Dimethylthiochroman-6-yl)-1-(phenylsilyl)ethyl)(ethyl)dimethylsilane (**4rac**)



4rac
$C_{23}H_{34}SSi_2$
M = 398.75 g/mol

Prepared from (4-ethynylphenyl)trimethylsilane **1r** (81 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) by *adding the $PhSiH_3$ in 5 hours' delay after the initial $EtMe_2SiH$ addition.* Purification by flash column chromatography on silica gel using petroleum ether (40–60 °C) to afford bis(silane) **4rac** as a colorless oil (68 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34–7.29 (m, 3H), 7.26–7.23 (m, 2H), 7.09 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0, 1.8 Hz, 1H), 4.35 (dd, *J* = 5.5, 2.4 Hz, 1H), 4.26 (dd, *J* = 5.4, 4.1 Hz, 1H), 3.01–2.98 (m, 2H), 2.88 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.65 (dd, *J* = 14.2, 9.5 Hz, 1H), 1.99–1.85 (m, 2H), 1.24 (s, 3H), 1.23 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.67–0.62 (m, 1H), 0.53 (dd, *J* = 7.8, 2.5 Hz, 2H), 0.0 (s, 3H), –0.1 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 141.7, 139.2, 135.4, 133.3, 129.3, 128.7, 127.9, 126.9, 126.6, 126.5, 38.1, 33.0, 32.9, 30.4, 23.2, 10.9, 7.6, 7.1, –3.4, –3.6 ppm. **IR** (film): 3068, 2952, 2873, 2131, 1589, 1505, 1488, 1240, 859, 831, 691 cm^{-1}. **HRMS** (ESI): calculated for $C_{23}H_{34}NaSSi_2^+$ $[M+Na]^+$: 421.1812; found 421.1816.

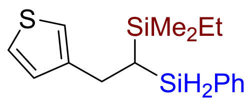
3.2.20 Ethyldimethyl(2-(naphthalen-2-yl)-1-(phenylsilyl)ethyl)silane (**4sac**)



4sac
$C_{22}H_{28}Si_2$
M = 348.64 g/mol

Prepared from 2-ethynylnaphthalene **1s** (61 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4sac** as a colorless oil (88 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85–7.77 (m, 1H), 7.74 (t, *J* = 7.4 Hz, 2H), 7.58 (s, 1H), 7.50–7.45 (m, 2H), 7.41–7.36 (m, 2H), 7.33–7.28 (m, 2H), 7.24–7.19 (m, 2H), 4.45 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.37 (dd, *J* = 5.8, 3.9 Hz, 1H), 3.18 (dd, *J* = 14.3, 5.5 Hz, 1H), 2.96 (dd, *J* = 14.3, 9.4 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 3H), 0.95–0.83 (m, 1H), 0.67–0.58 (m, 2H), 0.10 (s, 3H), 0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 140.9, 135.5, 133.6, 133.2, 132.2, 129.4, 127.9, 127.8, 127.7, 127.6, 127.4, 126.8, 125.9, 125.2, 33.2, 10.6, 7.6, 7.1, –3.4, –3.5 ppm. **IR** (film): 3051, 2952, 2909, 2872, 2131, 1599, 1507, 1428, 1248, 1116, 1035, 937, 878, 742, 698 cm^{-1}. **HRMS** (APCI): calculated for $C_{22}H_{29}Si_2^+$ $[M+H]^+$: 349.1802; found 349.1802.

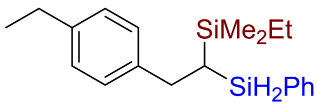
3.2.21 Ethyldimethyl(1-(phenylsilyl)-2-(thiophen-3-yl)ethyl)silane (**4tac**)



4tac
$C_{16}H_{24}SSi_2$
M = 304.59 g/mol

Prepared from 3-ethynylthiophene **1t** (43 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4tac** as a colorless oil (26 mg, 21% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.38–7.33 (m, 1H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.16 (dd, *J* = 4.7, 3.2 Hz, 1H), 6.87–6.84 (m, 2H), 4.38 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.28 (dd, *J* = 5.7, 4.0 Hz, 1H), 2.95 (dd, *J* = 14.7, 5.8 Hz, 1H), 2.80 (dd, *J* = 14.7, 9.1 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 3H), 0.73–0.63 (m, 1H), 0.54 (qd, *J* = 7.9, 1.7 Hz, 2H), 0.01 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.9, 135.5, 133.3, 129.5, 128.4, 127.9, 125.5, 120.6, 27.5, 10.2, 7.6, 7.0, –3.5, –3.7 ppm. **IR** (film): 3067, 2952, 2909, 2873, 2131, 1456, 1428, 1249, 1115, 1035, 857, 832, 719 cm^{-1}. **HRMS** (APCI): calculated for $C_{16}H_{25}SSi_2^+$ $[M+H]^+$: 305.1210; found 305.1218.

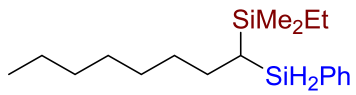
3.2.22 Ethyl(2-(4-ethylphenyl)-1-(phenylsilyl)ethyl)dimethylsilane (**4uac**)



4uac
$C_{20}H_{30}Si_2$
M = 326.63 g/mol

Prepared from *1-(4-ethynylphenyl)ethanone* **1u** (29 mg, 0.2 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 53 mg, 0.6 mmol, 3 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 3 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (10.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash column chromatography on silica gel using petroleum ether (40–60 °C) to afford bis(silane) **4uac** as a colorless oil (35 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 3H), 7.26–7.22 (m, 2H), 7.06–7.01 (m, 4H), 4.35 (dd, *J* = 5.6, 2.6 Hz, 1H), 4.27 (dd, *J* = 5.6, 3.9 Hz, 1H), 2.93 (dd, *J* = 14.2, 5.7 Hz, 1H), 2.71 (dd, *J* = 14.2, 9.4 Hz, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.72–0.66 (m, 1H), 0.53 (ddd, *J* = 10.8, 7.9, 2.4 Hz, 2H), -0.00 (s, 3H), -0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 141.9, 140.6, 135.5, 133.5, 129.3, 128.6, 127.8, 127.8, 32.6, 28.6, 15.9, 10.8, 7.5, 7.1, –3.5, –3.6 ppm. **IR** (film): 2955, 2873, 2128, 1512, 1248, 1008, 857, 816, 732 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{30}NaSi_2^+$ $[M+Na]^+$: 349.1778; found 349.1778.

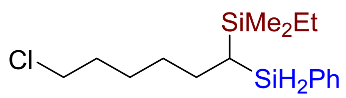
3.2.23 Ethyldimethyl(1-(phenylsilyl)octyl)silane (**4vac**)



4vac
$C_{18}H_{34}Si_2$
M = 306.64 g/mol

Prepared from oct-1-yne **1v** (44 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) by performing the reaction at –40 °C for 5 h, and then stirring at room temperature for 24 h. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4vac** as a colorless oil (100 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.40–7.32 (m, 3H), 4.39 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.28 (dd, *J* = 5.2, 4.2 Hz, 1H), 1.62–1.41 (m, 2H), 1.31–1.17 (m, 10H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.54 (qd, *J* = 7.8, 3.1 Hz, 2H), 0.31–0.21 (m, 1H), 0.01 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 135.5, 134.1, 129.5, 128.0, 32.3, 31.9, 29.8, 29.2, 26.9, 22.8, 14.3, 8.1, 7.6, 7.2, –3.3, –3.5 ppm. **IR** (film): 3068, 2955, 2873, 2129, 1506, 1485, 1428, 1249, 1115, 858, 715, 698 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{35}Si_2^+$ $[M+H]^+$: 307.2272; found 307.2270.

3.2.24 (6-Chloro-1-(phenylsilyl)hexyl)(ethyl)dimethylsilane (**4wac**)



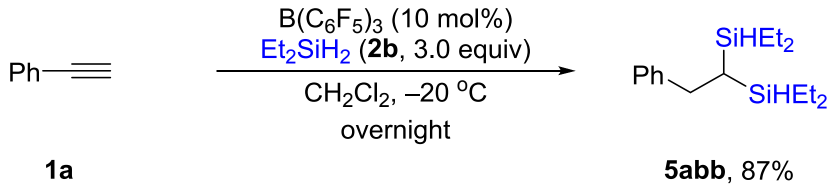
4wac
$C_{16}H_{29}ClSi_2$
M = 313.02 g/mol

Prepared from 6-chlorohex-1-yne **1w** (46 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ (**2a**, 54 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ (**2c**, 64 mg, 0.6 mmol, 1.5 equiv) in the presence of 20 mol% $B(C_6F_5)_3$ (41 mg, 0.08 mmol, 0.2 equiv) by performing the reaction at –40 °C for 5 h, and then stirring at room temperature for 24 h. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4wac** as a colorless oil (64 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.39–7.32 (m, 3H), 4.39 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.28 (dd, *J* = 5.6, 4.3 Hz, 1H), 3.45 (t, *J* = 6.7 Hz, 2H), 1.71–1.57 (m, 3H), 1.52–1.46 (m, 1H), 1.41–1.29 (m, 4H), 0.91 (t, *J* = 7.9 Hz, 3H), 0.54 (qd, J = 7.9, 2.2 Hz, 2H), 0.26 (ddd, *J* = 8.3, 4.5, 3.0 Hz, 1H), –0.01 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.5, 133.9, 129.6, 128.1, 45.2, 32.5, 31.5, 27.0, 26.9, 8.1, 7.6, 7.2, –3.4, –3.5 ppm. **IR** (film): 3 3068, 2953, 2873, 2128, 1519, 1428, 1248, 1115, 941, 858, 778, 717 cm^{-1}. **HRMS** (ESI): calculated for $C_{16}H_{30}ClSi_2^+$ $[M+H]^+$: 313.1569; found 313.1572.

4. Experimental Details for the Reactivities of Other Hydrosilanes

4.1 Dihydrosilylation of Phenylacetylene with Et_2SiH_2

4.1.1 Synthetic procedure



Prepared from phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv), Et_2SiH_2 **2b** (106 mg, 1.2 mmol, 3 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **5abb** as a colorless oil (97 mg, 87% yield).

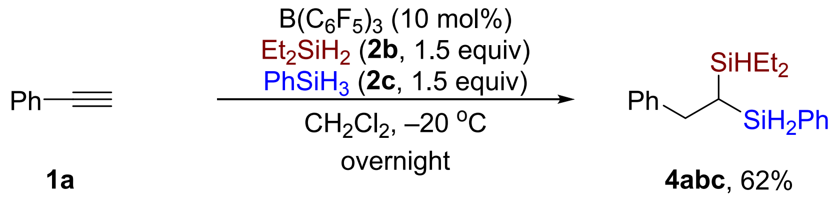
4.1.2 Characterization data of (2-Phenylethane-1,1-diyl)bis(diethylsilane) (**5abb**)

5abb
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.23 (m, 2H), 7.21–7.15 (m, 3H), 3.70 (h, *J* = 3.5 Hz, 2H), 2.81 (d, *J* = 7.7 Hz, 2H), 0.99–0.92 (m, 12H), 0.65–0.45 (m, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.9, 128.5, 128.3, 125.9, 32.7, 8.8, 8.7, 7.7, 3.6, 3.1 ppm. **IR** (film): 3084, 3026, 2954, 2911, 2874, 2100, 1603, 1494, 1455, 1414, 1238, 1135, 1010, 811, 746, 697 cm^{-1}. **HRMS** (APCI): calculated for $C_{16}H_{31}Si_2^+$ $[M+H]^+$: 279.1959; found 279.1955.

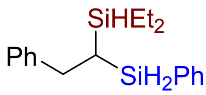
4.2 Selective Dihydrosilylation of Phenylacetylene with Et_2SiH_2/$PhSiH_3$ Combination

4.2.1 Synthetic procedure



Prepared from phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv), Et_2SiH_2 **2b** (53 mg, 0.6 mmol, 1.5 equiv) and $PhSiH_3$ **2c** (64 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4abc** as a colorless oil (74 mg, 62% yield).

4.2.2 Characterization data of diethyl(2-phenyl-1-(phenylsilyl)ethyl)silane (**4abc**)

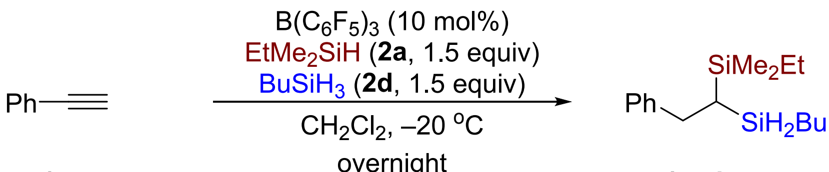


4abc
$C_{18}H_{26}Si_2$
M = 298.58 g/mol

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 3H), 4.38 (dd, *J* = 5.8, 3.0 Hz, 1H), 4.33 (dd, *J* = 5.8, 4.0 Hz, 1H), 3.77 (h, *J* = 3.2 Hz, 1H), 2.92 (dd, *J* = 14.2, 7.3 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.1 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 6H), 0.85 (tq, *J* = 7.1, 3.6 Hz, 1H), 0.59 (pd, *J* = 7.9, 3.4 Hz, 4H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.1, 135.6, 132.8, 129.6, 128.7, 128.4, 127.9, 125.1, 33.5, 8.7, 7.6, 3.2, 2.8 ppm. **IR** (film): 3084, 3025, 2953, 2932, 2889, 2872, 2130, 1494, 1454, 1428, 1115, 1036, 935, 857, 767, 697 cm^{-1}. **HRMS** (APCI): calculated for $C_{18}H_{27}Si_2^+$ [M+H]$^+$: 299.1646; found 299.1645.

4.3 Selective Dihydrosilylation of Phenylacetylene with $EtMe_2SiH_2$/$BuSiH_3$ Combination

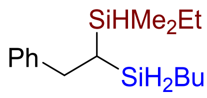
4.3.1 Synthetic procedure



Prepared from phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ **2a** (53 mg, 0.6 mmol, 1.5 equiv) and $BuSiH_3$ **2d** (53 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv) according to the general procedure. Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4add** as a colorless oil (97 mg, 81% yield for **4add**).

Note: in the case of $EtMe_2SiH_2$/$BuSiH_3$ Combination, A slightly amount symmetric dihydrosilylation product was detected, the yield of **4add** was estimated based on the ratio of unsymmetric and symmetric in ^{1}H NMR spectrum.

4.3.2 Characterization data of diethyl(2-phenyl-1-(phenylsilyl)ethyl)silane (**4aad**)

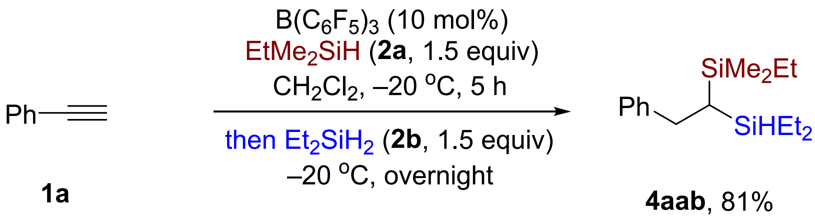


4aad
$C_{16}H_{31}Si_2$
M = 279.59 g/mol

¹H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.24 (m, 2H), 7.19–7.15 (m, 3H), 3.69–3.60 (m, 2H), 2.96 (dd, *J* = 14.1, 5.3 Hz, 1H), *2.84 (d, J = 8.0 Hz, 0.08H, characteristic peak for the symmetric hydrosilylation product with* $BuSiH_3$ *or* $EtMe_2SiH_2$ *was detected in the ¹H NMR spectrum*), 2.61 (dd, *J* = 14.1, 10.3 Hz, 1H), 1.26–1.15 (m, 4H), 0.94 (t, *J* = 7.9 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.55 (ddd, *J* = 9.9, 7.9, 1.4 Hz, 2H), 0.46–0.43 (m, 1H), 0.39–0.30 (m, 2H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. **¹³C{¹H} NMR** (100 MHz, $CDCl_3$): 143.9, 128.6, 128.4, 125.9, 33.3, 27.9, 25.9, 13.8, 9.7, 9.0, 7.6, 6.9, –3.6, –3.7 ppm. **IR** (film): 2954, 2922, 2854, 2116, 1494, 1454, 1248, 1031, 986, 897 cm^{-1}. **HRMS** (APCI): calculated for $C_{16}H_{31}NaSi_2^+$ $[M+Na]^+$: 301.1778; found 301.1782.

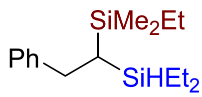
4.4 Selective Dihydrosilylation of Phenylacetylene with $EtMe_2SiH$/Et_2SiH_2 Combination

4.4.1 Synthetic procedure



Prepared from phenylacetylene **1a** (41 mg, 0.4 mmol, 1.0 equiv), $EtMe_2SiH$ **2a** (54 mg, 0.6 mmol, 1.5 equiv) and Et_2SiH_2 **2b** (53 mg, 0.6 mmol, 1.5 equiv) in the presence of 10 mol% $B(C_6F_5)_3$ (21 mg, 0.04 mmol, 0.1 equiv). *Note: the* Et_2SiH_2 *was added in 5 hours' delay after the initial* $EtMe_2SiH$ *addition.* Purification by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford bis(silane) **4aab** as a colorless oil (90 mg, 81% yield).

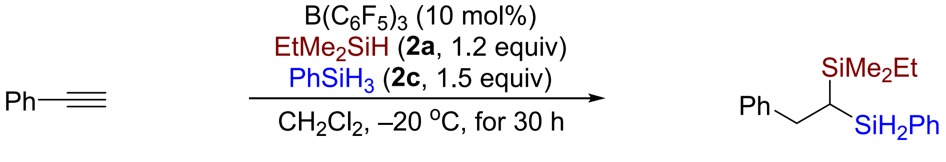
4.4.2 Characterization data of (1-(diethylsilyl)-2-phenylethyl)(ethyl)dimethylsilane (**4aab**)



4aab
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

¹H NMR (400 MHz, $CDCl_3$): δ 7.27–7.16 (m, 5H), 3.71–3.66 (m, 1H), 2.86 (dd, *J* = 14.1, 6.1 Hz, 1H), 2.70 (dd, *J* = 14.1, 8.9 Hz, 1H), 0.96 (t, *J* = 7.9 Hz, 3H), 0.91–0.86 (m, 6H), 0.63–0.29 (m, 7H), 0.01 (s, 3H), –0.01 (s, 3H) ppm. **¹³C{¹H} NMR** (100 MHz, $CDCl_3$): δ 144.4, 128.5, 128.3, 125.8, 32.1, 10.6, 9.1, 8.8, 7.6, 7.5, 4.1, 3.5, –2.9, –3.1 ppm. **IR** (film): 3026, 2952, 2873, 2098, 1516, 1454, 1422, 1248, 1009, 831, 771, 697 cm^{-1}. **HRMS** (APCI): calculated for $C_{16}H_{31}Si_2^+$ [M+H]$^+$: 279.1959; found 279.1959.

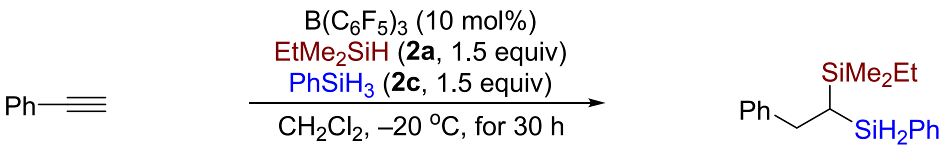
5. Gram-Scale Synthesis of Geminal Bis(silane) 4aac



1a **4aac**, 90% (2.7 g scale)

Synthetic procedure: In an argon-filled glovebox, a 25 mL Schlenk tube was charged with $B(C_6F_5)_3$ (511 mg, 1.0 mmol, 10 mol%), CH_2Cl_2 (5 mL), $EtMe_2SiH$ (1.10 g, 12.5 mmol, 1.25 equiv) and $PhSiH_3$ (1.62 g, 15.0 mmol, 1.5 equiv). The solution was cooled to –20 °C, and then phenylacetylene **1a** (1.02 g, 10 mmol, 1.0 equiv) diluted with 1 mL CH_2Cl_2 was slowly added *via* syringe over a period of 10 min. After stirring at –20 °C for 30 h, the reaction mixture was quenched by saturated sodium bicarbonate solution (5 mL) under –20 °C, and then diluted by diethyl ether (5 mL). The organic phase was separated, and the aqueous layer was extracted with diethyl ether (10 mL x 2). Then, the organic layers were combined, and dried over anhydrous sodium sulfate, and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford the desired product **4aac** (2.7 g, 90% yield).

6. Robustness test: Glove-Box-free Synthesis



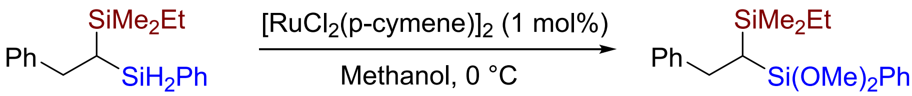
1a ***1 mmol scale*** **4aac**, 90%

Synthetic procedure: In a 5 mL Schlenk tube was charged with $B(C_6F_5)_3$ (52 mg, 0.1 mmol, 10 mol%), CH_2Cl_2 (1 mL), $EtMe_2SiH$ (0.132 g, 1.5 mmol, 1.5 equiv) and $PhSiH_3$ (0.162 g, 1.5 mmol, 1.5 equiv). All the chemicals were added in the open atmosphere without the exclusion of air or moisture, The solution was cooled to –20 °C, and then phenylacetylene **1a** (0.102 g, 1.0 mmol, 1.0 equiv) was slowly added *via* syringe over a period of 10 min. After stirring at –20 °C for 20 h, the reaction mixture was quenched by saturated sodium bicarbonate solution (5 mL) under –20 °C, and then diluted by diethyl ether (2 mL). The organic phase was separated, and the aqueous layer was extracted with diethyl ether (3 mL x 2). Then, the organic layers were combined, and dried over anhydrous sodium sulfate, and filtered. After removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on neutral aluminum oxide using petroleum ether (40–60 °C) to afford the desired product **4aac** (0.274 g, 90% yield).

7. Product Transformation

7.1 Synthesis of Unsymmetrical Geminal Bis(silane) **6**

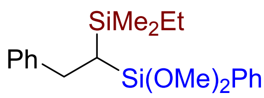
7.1.1 Synthetic procedure



4aac **6**, 87%

To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.01 mmol, 2 mol %) in MeOH (0.5 mL), 1,1-bis(silane) **4aac** (2.0 mmol, 596.0 mg) was added at 0 °C (ice bath) under argon atmosphere. The reaction mixture was stirred at 0 °C for 3h. Then, the mixture was diluted with hexane (5.0 mL), filtered, and washed with hexane (2 × 5 mL). The combined filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (PE/EA = 100:1 to 20:1, v/v) afforded the desired product **6** (624.0 mg, 87% yield) as a colorless oil.

7.1.2 Characterization data of (1-(dimethoxy(phenyl)silyl)-2-phenylethyl)(ethyl)dimethylsilane **6**

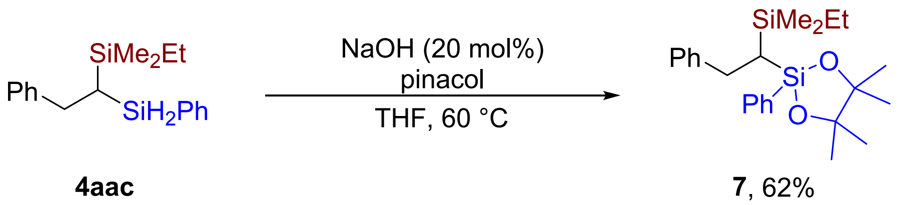


6
$C_{20}H_{30}O_2Si_2$
M = 358.63 g/mol

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.59 (m, 2H), 7.51–7.39 (m, 3H), 7.34–7.26 (m, 2H), 7.25–7.16 (m, 3H), 3.63 (s, 3H), 3.55 (s, 3H), 3.03 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.81 (dd, *J* = 14.5, 6.6 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 3H), 0.82 (t, *J* = 6.8 Hz, 1H), 0.52 (qd, *J* = 7.8, 2.3 Hz, 2H), 0.04 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 144.4, 134.7, 133.9, 129.9, 128.6, 128.1, 127.9, 125.6, 50.9, 50.7, 30.5, 14.0, 7.6, 7.5, –2.8, –2.9 ppm. **HRMS** (ESI): calculated for $C_{24}H_{37}O_2Si_2^+$ $[M+H]^+$: 359.1857; found 359.1859.

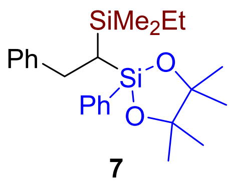
7.2 Synthesis of Unsymmetrical Geminal Bis(silane) **7**

7.2.1 Synthetic Procedure



In an argon-filled glovebox, a Schlenk tube was charged with NaOH (4 mg, 0.1 mmol, 20 mol%), THF (2.0 mL), pinacol (65 mg, 0.55 mmol, 1.1 equiv) and **4aac** (149 mg, 0.5 mmol, 1.0 equiv). The mixture was stirred at 60 °C for 24 h. After the reaction mixture was cooled to room temperature, saturated aqueous NH_4Cl solution (10.0 mL) was added. The mixture was extracted with diethyl ether (10.0 mL x 3). The combined organic layer was washed with water and dried over by sodium sulfate. After removal of diethyl ether, the residue was purified by preparative TLC (Petroleum ether/EtOAc = 20:1 v/v) to afford **7** as a colorless oil (127 mg, 62% yield).

7.2.2 Characterization data of 2-(1-(ethyldimethylsilyl)-2-phenylethyl)-4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxasilolane 7



7

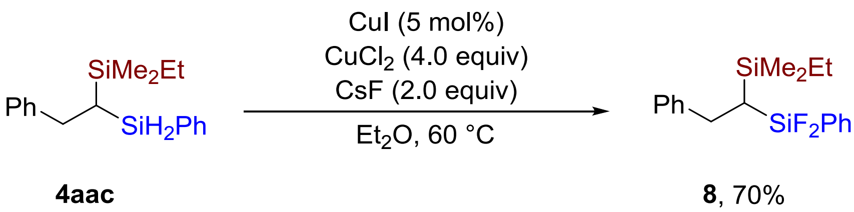
$C_{24}H_{36}O_2Si_2$

M = 412.72 g/mol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.38–7.16 (m, 8H), 3.21 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.74 (dd, *J* = 14.2, 6.6 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 1.12 (s, 3H), 0.79–0.74 (m, 4H), 0.47–0.36 (m, 2H), –0.07 (s, 3H), –0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 144.5, 137.4, 133.9, 129.7, 128.6, 128.3, 127.7, 125.8, 81.7, 81.5, 30.8, 26.2, 25.9, 17.6, 7.7, 7.4, –2.7, –2.9 ppm. **IR** (film): 3067, 2977, 2952, 2873, 1495, 1428, 1375, 1143, 1117, 966, 831, 738, 699 cm^{-1}. **HRMS** (ESI): calculated for $C_{24}H_{37}O_2Si_2^+$ $[M+H]^+$: 413.2327; found 413.2328.

7.3 Synthesis of Unsymmetrical Geminal Bis(silane) 8

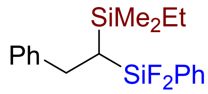
7.3.1 Synthetic procedure



To a 10 mL Schlenk tube, CuI (4.8 mg, 0.025 mmol, 5 mol%), $CuCl_2$ (269 mg, 2.0 mmol, 4.0 equiv), CsF (152 mg, 1.0 mmol, 2.0 equiv) and dry Et_2O (2.0 mL), **4aac** (149 mg, 0.5 mmol, 1.0 equiv) was added.

The mixture was stirred at 60 °C for 36 h, and then diluted with hexane (10 mL) and filtered. The desired product **4aac** was obtained in 70% yield (117.3 mg) as a colorless oil by removing the solvent under vacuum.

7.3.2 Characterization data of (1-(difluoro(phenyl)silyl)-2-phenylethyl)(ethyl)dimethylsilane (**8**)



8

$C_{18}H_{24}F_2Si_2$

M = 334.56 g/mol

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.35 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.20–7.10 (m, 5H), 2.91 (d, *J* = 7.2 Hz, 2H), 0.97–0.88 (m, 4H), 0.63–0.55 (m, 2H), 0.08 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 142.8, 133.7 (t, *J* = 2.2 Hz), 131.4, 130.4 (t, *J* = 19.5 Hz), 128.5, 128.4, 128.1, 126.2, 29.8, 14.7 (t, *J* = 14.3 Hz), 7.3, 7.2, 0.1, –3.1 (d, *J* = 18.2 Hz) ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ –133.6 (d, *J* = 19.6 Hz, 1 F), –138.1 (d, *J* = 19.6 Hz, 1 F) ppm. **IR** (film): 3067, 3025, 2952, 2873, 1495, 1428, 1428, 1249, 1116, 1036, 982, 835, cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{24}F_2Si_2^+$ [M+H]$^+$: 335.1457; found 335.1459.

8. Control Experiments and KIE Studies

8.1 Control experiments

Phenyl acetylene (0.2 mmol, 20.4 mg) was added to a solution at –20 °C of $B(C_6F_5)_3$ (0.04 mmol, 21 mg, 20 mol%) and hydrosilane (0.3 mmol, 1.5 equiv.) in 0.40 mL of CD_2Cl_2 in an NMR tube. All of the NMR samples were placed at –20 °C for 5 hours, and then the NMR spectra were recorded at room temperature.

As shown in Figure S1a, with $PhSiH_3$ as the silane source, we detected only a trace amount of the characteristic peak of geminal bis(silane) (i.e., a doublet at δ = 2.82 ppm). ^{19}F NMR spectrum of the reaction mixture of $PhSiH_3$, **1a** and 20 mol% of $B(C_6F_5)_3$ confirms the significant deterioration of $B(C_6F_5)_3$ in the case of $PhSiH_3$ (Figure S2a). The crude ^{1}H NMR spectra clearly shown the formation of hydrosilylation or dihydrosilylation product with $EtMe_2SiH$ or Et_2SiH_2 (Figure S1b and S1c). ^{19}F NMR spectra of the reaction mixture of phenylacetylene **1a** with $EtMe_2SiH$ or Et_2SiH_2 indicated that most of $B(C_6F_5)_3$ was untouched (Figure S2b and S2c).

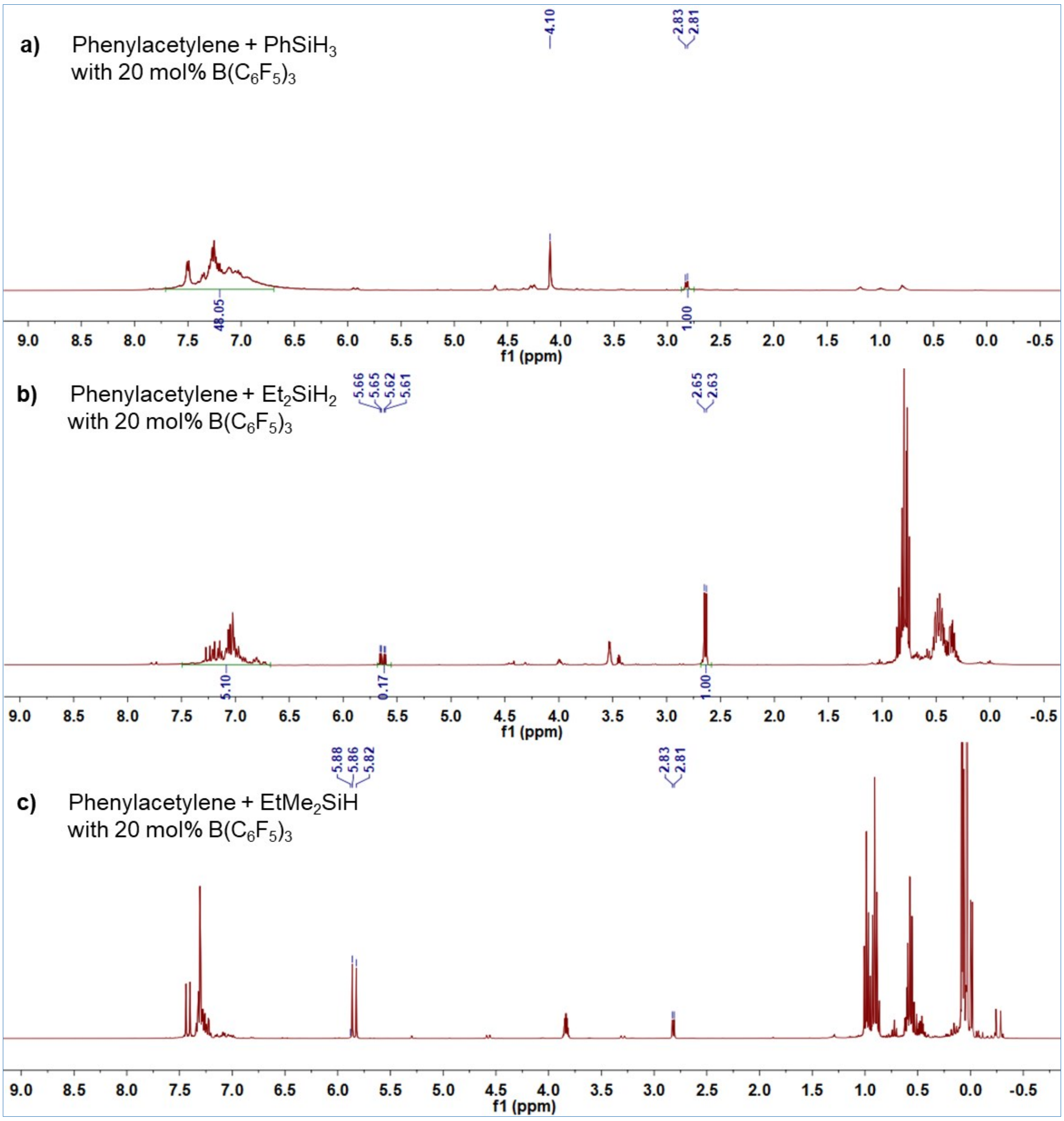


Figure S1. ^{1}**H NMR** spectra (400 MHz MHz, CD_2Cl_2) for the hydrosilylation reaction of phenylacetylene with different hydrosilanes a) with $PhSiH_3$; b) with Et_2SiH_2; c) with $EtMe_2SiH$.

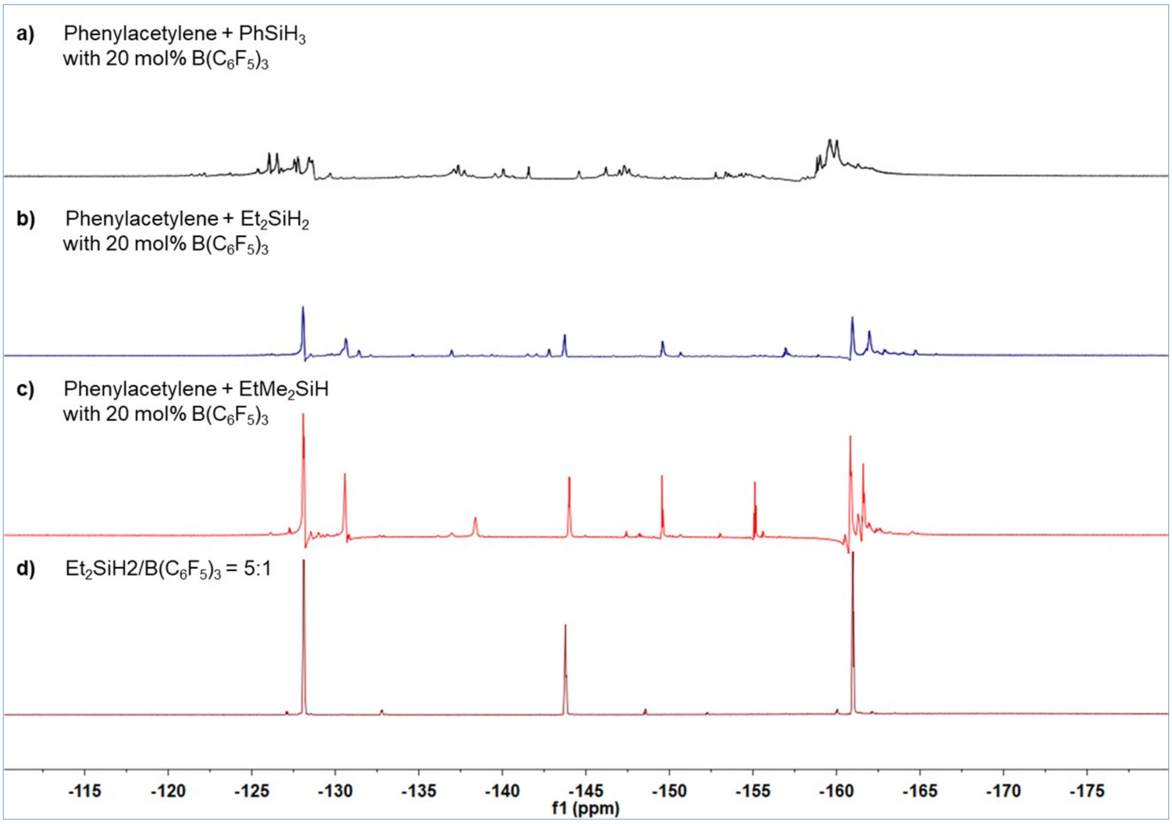
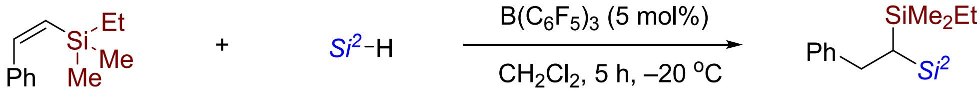


Figure S2. **$^{19}F\{^{1}H\}$ NMR** spectrum (376 MHz MHz, CD_2Cl_2) for the hydrosilylation reaction of phenylacetylene with different hydrosilanes a) with $PhSiH_3$; b) with Et_2SiH_2; c) with $EtMe_2SiH$; a 5:1 mixture of Et_2SiH_2 and $B(C_6F_5)_3$.

8.2 Effect of hydrosilanes on the hydrosilylation of vinylsilane

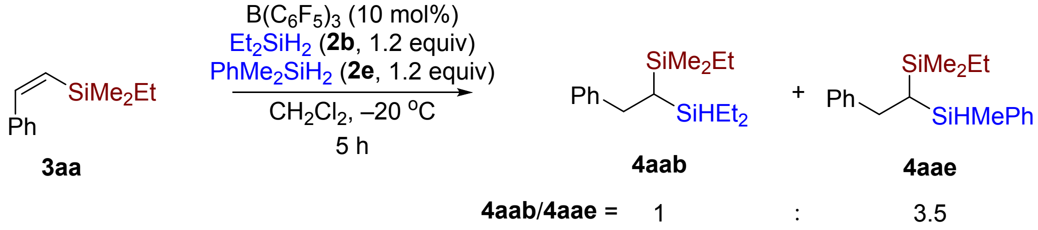
General procedure A: In an argon-filled glovebox, $B(C_6F_5)_3$ (5.1 mg, 0.02 mmol, 5 mol%), hydrosilane (0.24 mmol, 1.2 equiv), 1,2,3,4,5,6-hexamethylbenzene (16 mg, 0.1 mmol, 0.5 equiv, as an internal standard) and dichloromethane (1.0 mL) were added to an oven-dried reaction vial. The reaction vial was capped, removed from the glovebox, and stirred at varied temperatures. Vinylsilane **3aa** (38 mg, 0.2 mmol, 1.0 equiv) was then added to the reaction solution. After 5 hours, an aliquot (approximately 50 µL) of the reaction solution was then directly transferred to an NMR tube and $CDCl_3$ (0.4 mL) was added. The yield of was determined by ^{1}H NMR by the integration of the corresponding geminal bis(silanes) and internal standard. The results are tabulated in Scheme S1.

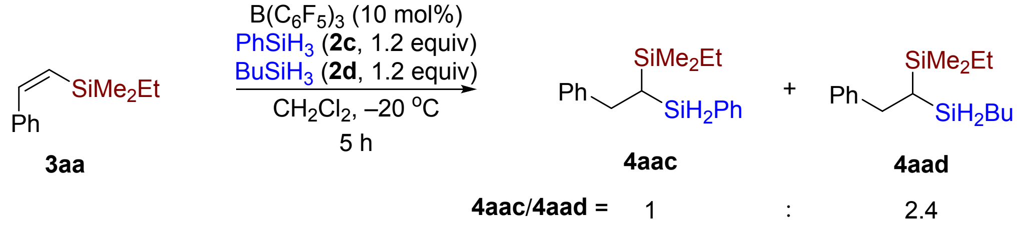


3aa **2** **4**

Si^2-H	
$EtMe_2SiH$	< 5%
$PhMe_2SiH$	< 5%
$PhMeSiH_2$	83%
Et_2SiH_2	43%

Scheme S1. Comparison of the reactivity of different hydrosilanes for hydrosilylation of vinylsilane **3aa**. Yields were determined by ^{1}H NMR analysis with 1,2,3,4,5,6-hexamethylbenzene as an internal standard.





Scheme S2. Competition experiments: reactions were performed in 0.2 mmol scale, and the crude material was purified by flash column chromatography on neutral aluminum oxide using *n*-hexane. Ratios were determined by ^{1}H NMR analysis.

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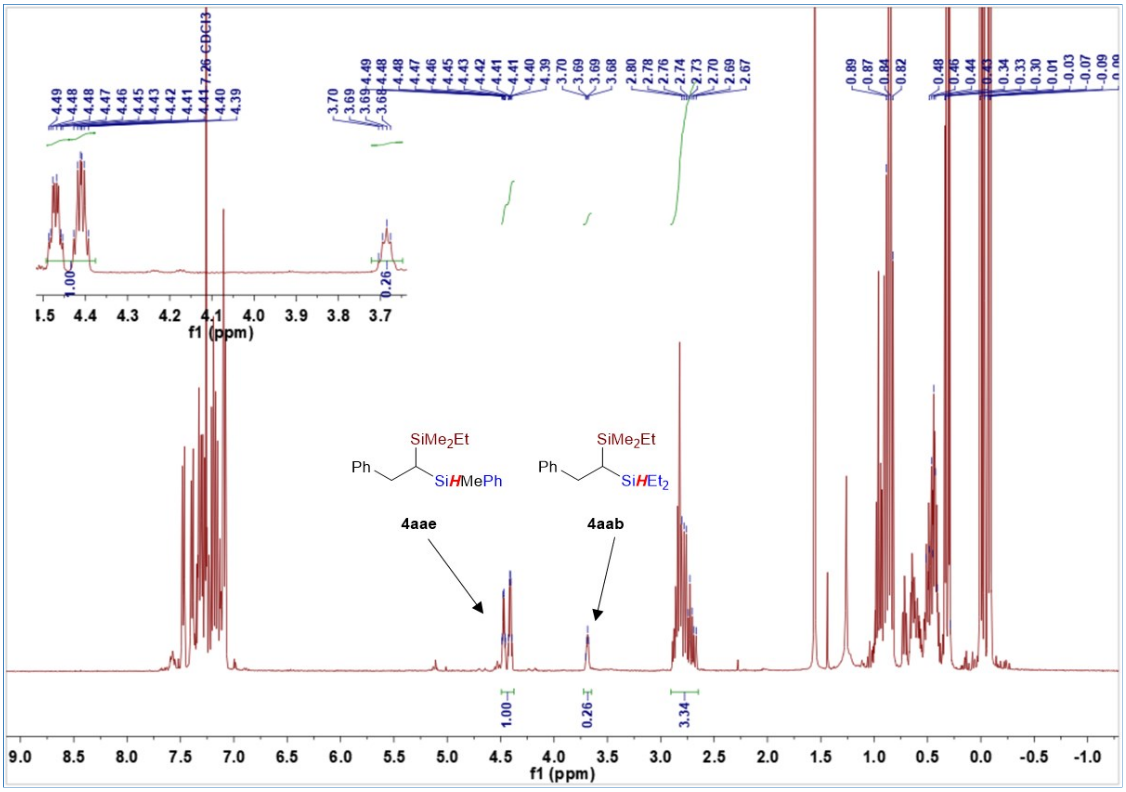


Figure S3. **^{1}H NMR** spectrum (400 MHz MHz, $CDCl_3$) for the hydrosilylation reaction of vinylsilane **3aa** in the presence of Et_2SiH_2 (**2b**) and $PhMeSiH_2$ (**2e**).

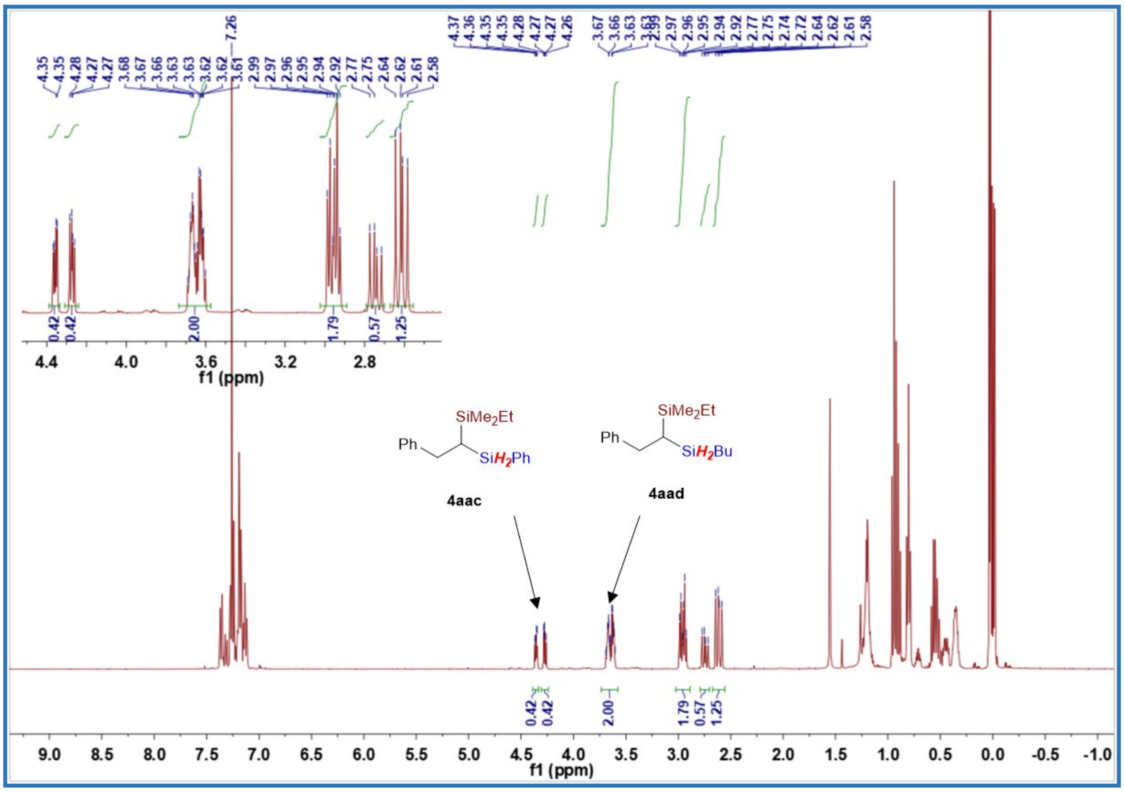


Figure S4. ^{1}**H NMR** spectrum (400 MHz MHz, $CDCl_3$) for the hydrosilylation reaction of vinylsilane **3aa** in the presence of $PhSiH_3$ (**2c**) and $BuSiH_3$ (**2d**).

8.3 KIE Studies

General procedure

A 5 mL reaction vial was charged with indicated concentration of $B(C_6F_5)_3$, $PhSiH_3$ (or $PhSiD_3$), 1,2,3,4,5,6-hexamethylbenzene (16 mg, 0.1 mmol, 0.5 equiv., as an internal standard), and CH_2Cl_2 (1 mL) in an argon-filled glove box. Then the solution was vigorously stirred at –20 °C and the vinylsilane **3aa** was added *via* a syringe. At 40, 80, 120, 160, 200, 240 seconds, under Ar atmosphere, 30 μL of the reaction mixture was carefully taken out by micro-syringe into an NMR tube and quenched with $CDCl_3$ (0.4 mL) immediately. The reaction mixture was analyzed by ^{1}H NMR, and the molar concentration of **4aac** was determined by the integration of the characteristic peak of which at 2.95 (dd, J = 14.3, 5.9 Hz, 1H) ppm against the internal standard. These reactions were all performed two times at the same conditions and the average value was taken for each time point. The concentration of geminal bis(silane) **4aac** (only the data < 25% yield was used) was plotted against the reaction time and the slope of the linear portion of the curve was used to determine the initial rates (k_{in}) of the reaction.

Kinetic isotope effect (KIE) determination for the hydrosilylation of vinylsilane ***3aa***

The KIE was measured by parallel intermolecular competition experiments: two reactions were set at the same time using vinylsilane **3aa** (38 mg, 0.2 mmol, 1.0 equiv.), 0.0045 M of $B(C_6F_5)_3$ (0.0045 mmol, 2.25 mol%) in the presence of $PhSiH_3$ (32 mg, 0.3 mmol, 1.50 equiv.) and $PhSiD_3$ (32 mg, 0.3 mmol, 1.50

equiv.), respectively. The concentration of geminal bis(silane) **4aac** and [D_3]-**4aac** at different reaction times was measured using ^{1}H NMR analysis with 1,2,3,4,5,6-hexamethylbenzene (0.1 M) as the internal standard. Initial reaction rates were determined and a KIE value of 0.81 was found.

Table S2. Concentration of **4aac** and [D_3]-**4aac** at different time interval

Time (s)	[**4aac**]	[[D3]-**4aac**]
40	0.008	0.0105
80	0.0155	0.0210
120	0.024	0.0320
160	0.0315	0.0385
200	0.038	0.0475
240	0.045	--

Table S3. The k_{in} value of [**4aac**] and [[D_3]-**4aac**] with $PhSiH_3$ and $PhSiD_3$

	k_{in} (mol L^{-1} s^{-1})
[**4aac**]	1.86E-04
[[D3]-**4aac**]	2.29E-04

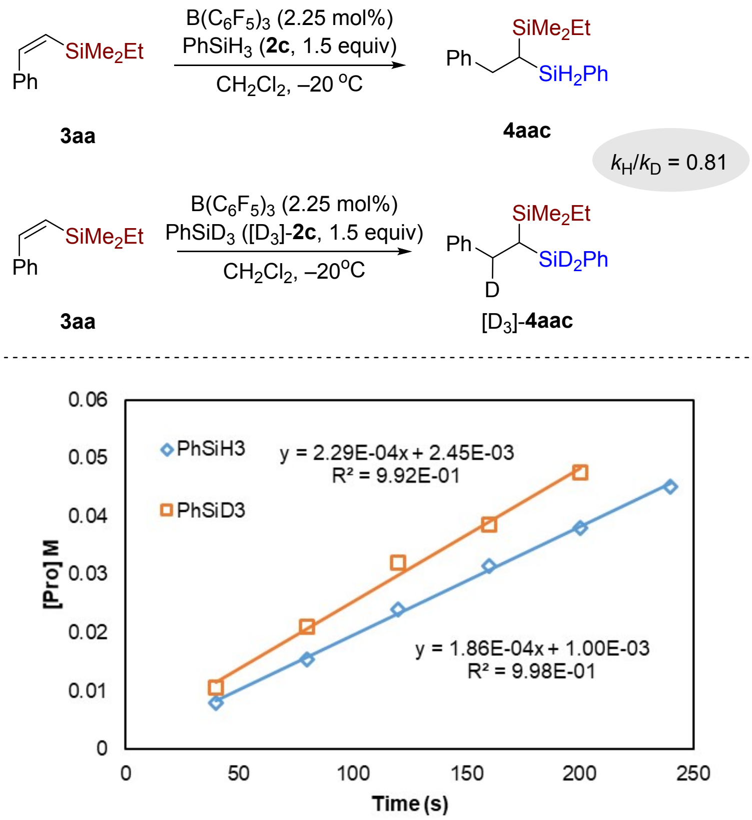


Figure S5. Up: parallel intermolecular competition experiments. Bottom: Plot of the change in geminal bis(silane) **4aac** and [D_3]-**4aac** with time for the reaction of vinylsilane **3aa** (0.2 M), $B(C_6F_5)_3$ (0.0045 M), with 0.3 M of $PhSiH_3$ and $PhSiD_3$ at –20 °C, respetively. The curve depicts the results of an unweighted least-square fit to y = a*x + b ($PhSiH_3$: a = 1.86 x 10^{-4}, b = 1.0 x 10^{-3}, R^2 = 0.998; $PhSiD_3$: a = 2.29 x 10^{-4}, b = 2.45 x 10^{-3}, R^2 = 0.992).

9. Computational Investigations

9.1 Computational Details

All calculations were performed with the Gaussian 16 package.[S1] The 3D structures of the optimized species were generated using CYLview.[S2] Geometry optimizations were performed at M06-2X[S3]/6-311G(d,p) level of theory in conjugation with the polarizable continuum model (PCM)[S4] solvation model for dichloromethane. To get more accurate energies, single-point energy calculations were done with the same functional and solvation model using the cc-pVTZ basis set. For the monohydrosilylation of phenylacetylene with $PhSiH_3$, the related S_N2@Si transition state could not be located with M06-2X functional. We therefore performed a relax scan with the B3LYP functional,[S5] augmented with Grimme's D3 dispersion correction.[S6] However, the energy increases monotonically at the decreasing distance of the Si-C bond. Our further calculations show that the resulting ion-pair intermediate doesn't exist as a minimum structure on the potential energy surface. (see Figure S10 for details).

Activation free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it along the reaction pathways.

9.2 $B(C_6F_5)_3$-catalyzed dihydrosilylation of phenylacetylene with Me_3SiH and $PhSiH_3$

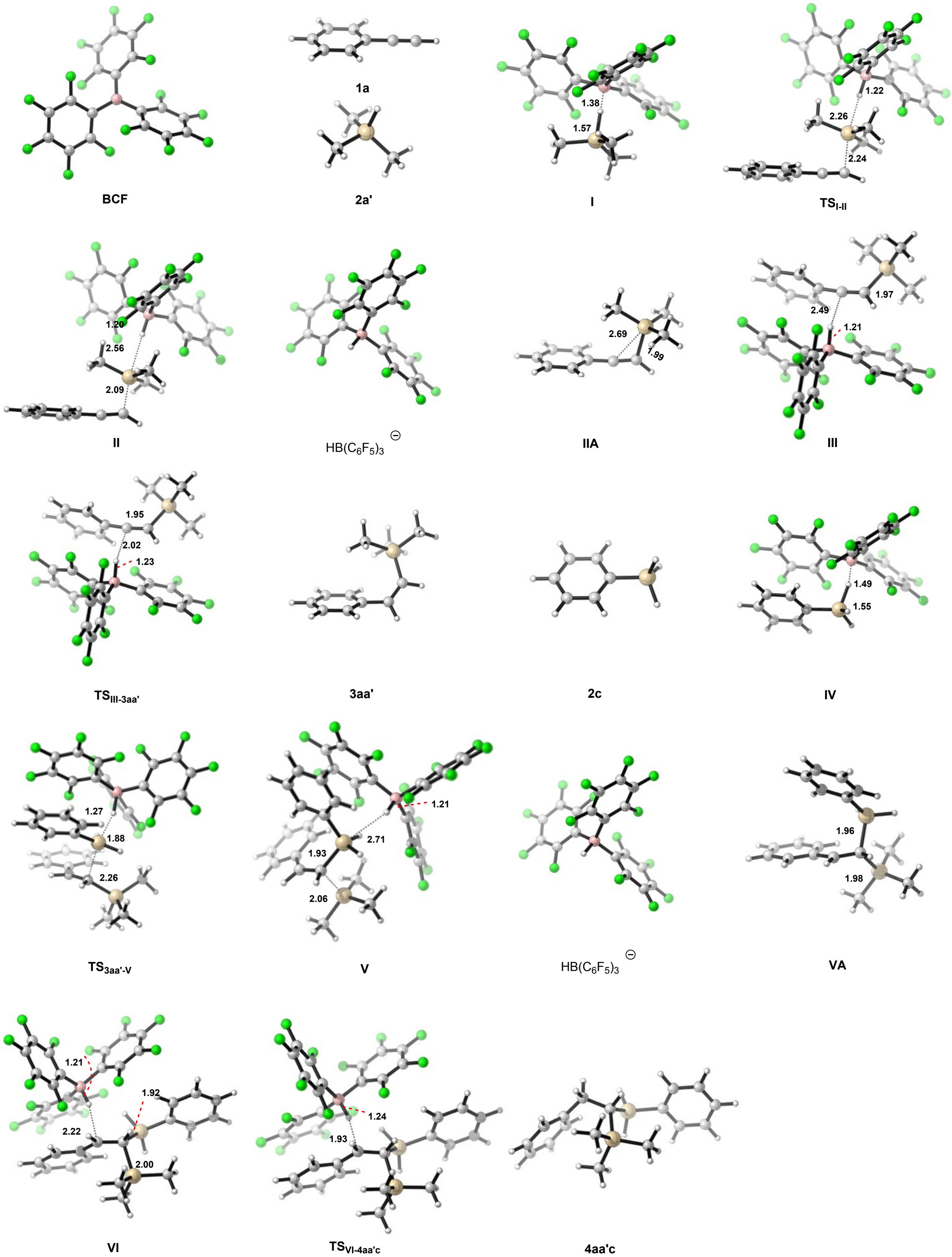


Figure S6. 3D structures involved in $B(C_6F_5)_3$-catalyzed dihydrosilylation of phenylacetylene with Me_3SiH **2a'** and $PhSiH_3$ **2c** (distance are given in Å). Color code: H, white; C, gray; B, pink; F, green; Si, brown.

9.3 *cis*-Hydrosilylation pathway of phenylacetylene

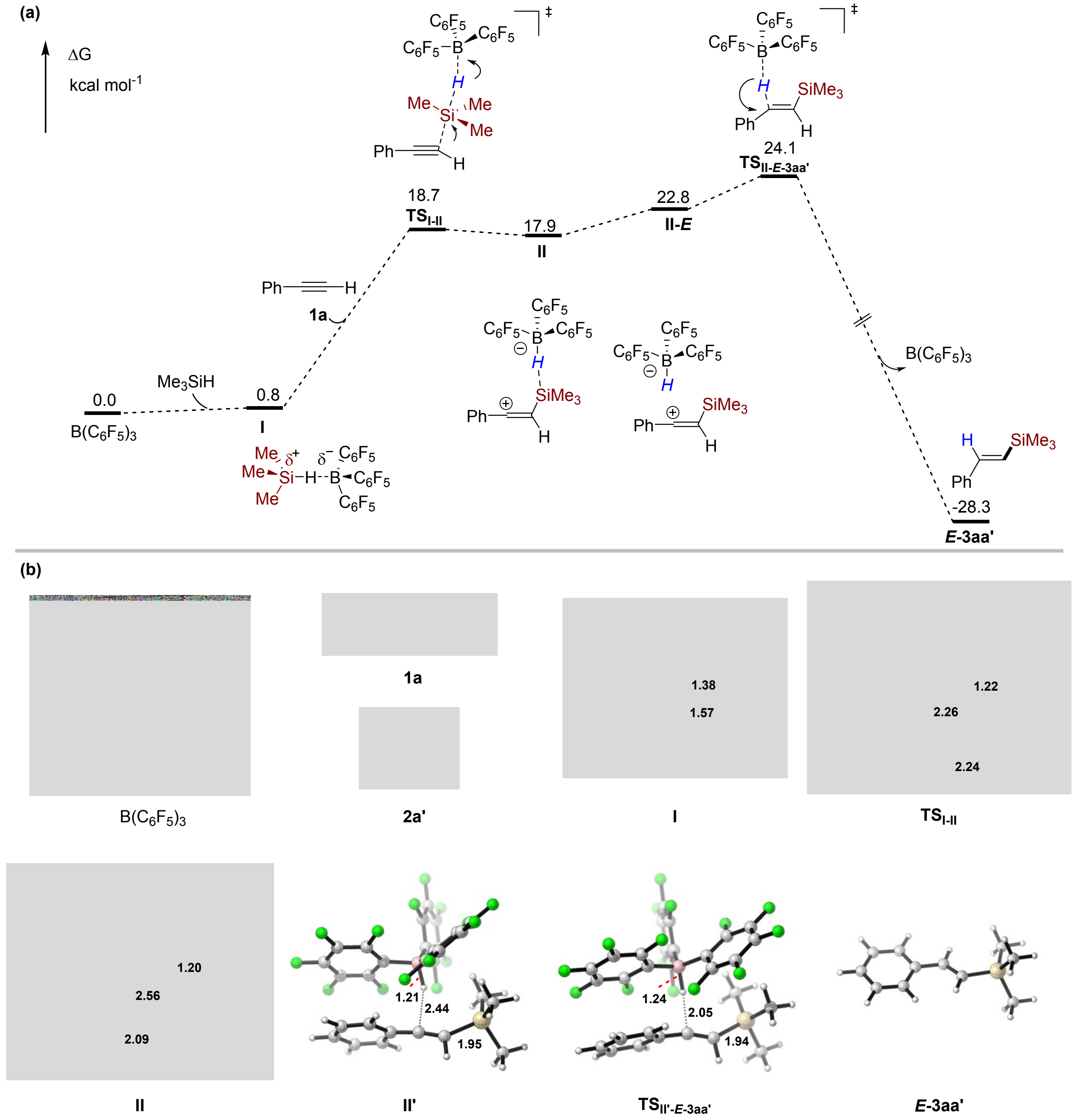


Figure S7. Free energy profile of $B(C_6F_5)_3$-catalyzed *cis*-hydrosilylation reaction of phenylacetylene **1a** with Me_3SiH **2a'**. Color code: H, white; C, gray; B, pink; F, green; Si, brown.

For the monohydrosilylation of terminal alkyne, hydride transfer from borohydride $[HB(C_6F_5)_3]^-$ to the vinyl cation at the same side of the silyl group (*via* $\mathbf{TS_{II'\text{-}\mathit{E}\text{-}3aa'}}$) generates the *cis*-hydrosilylation product (Figure S7). However, this pathway requires an activation barrier of 24.1 kcal mol^{-1} in the hydride transfer step ($\mathbf{TS_{II'\text{-}\mathit{E}\text{-}3aa'}}$), being much higher than that of *trans*-hydrosilylation pathway ($\Delta G^{\neq}$ = 18.2 kcal mol^{-1}). The large activation barrier difference between these two pathways can account for the observed stereoselectivity in the monohydrosilylation step.

9.4 1,1-Carboboration reaction of phenylacetylene with $B(C_6F_5)_3$

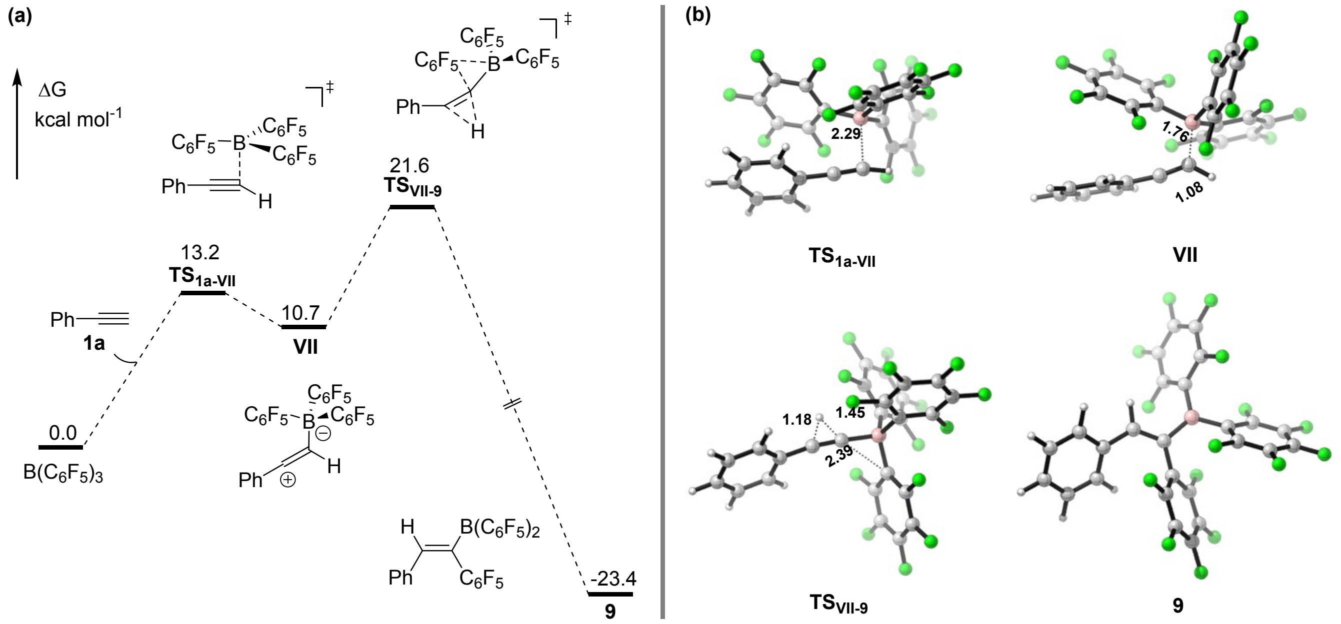
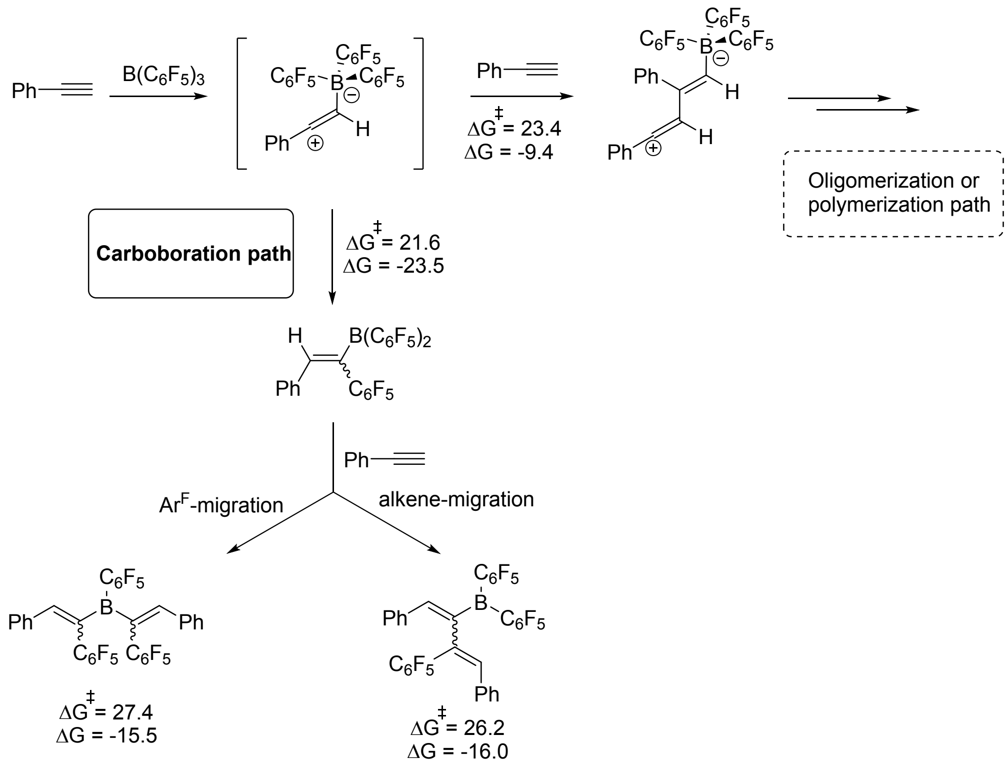


Figure S8. (a) Free energy profile of 1,1-carboboration reaction between $B(C_6F_5)_3$ and phenylacetylene **1a** (in kcal mol^{-1}). (b) Key transition states and intermediates. Color code: H, white; C, gray; B, pink; F, green; Si, brown.

As shown in Figure S8, the carboboration reaction between $B(C_6F_5)_3$ and phenylacetylene proceeds sequentially through the electrophilic association of $B(C_6F_5)_3$ and **1a** leading to a Lewis acid-alkyne σ-complex **VII**, a concerted intramolecular Ar^F/hydrogen shift generating alkenylborane **9**. The formation of alkenylborane **9** is exothermic by 23.4 kcal mol^{-1} with an activation barrier of 21.6 kcal mol^{-1} in the rate-determining step (*via* $\mathbf{TS_{VII\text{-}9}}$). This result suggests that the deterioration of $B(C_6F_5)_3$ through 1,1-carboboration reaction is possible. These computational results are consistent with previous experimental studies by Erker *et al* (*carboboration reaction finished in short reaction time at room temperature*).[S7] The relative lower barrier suggests that conducting the reaction at a lower temperature and slow addition of the terminal alkyne to the reaction mixture are necessary to achieve high yields of vinylsilanes and 1,1-bis(silanes).



Scheme S3. Computational analysis on other possible pathways for the reaction between $B(C_6F_5)_3$ and phenylacetylene. Activation barriers and energies are in kcal mol^{-1}.

9.5 Theoretical investigation on the effect of hydrosilanes

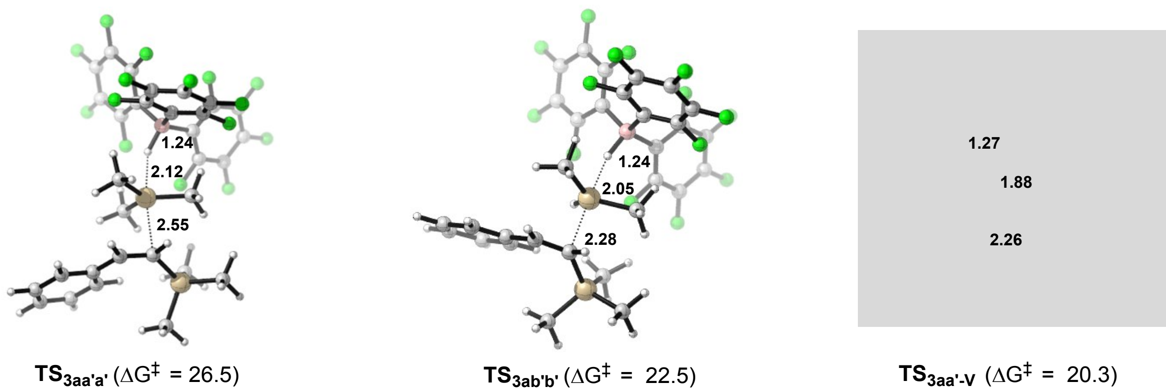


Figure S9. Optimized geometries of vinylsilane hydrosilylation transition states (**TS$_{3aa'a'}$**, with Me_3SiH; **TS$_{3ab'b'}$**, with Me_2SiH_2; and **TS$_{3aa'-V}$**, with $PhSiH_3$). The barriers listed in parenthesis are obtained at the level M06-2X/cc-pVTZ//M06-2X/6-311G(d,p), in kcal mol^{-1}. Color code: H, white; C, gray; B, pink; F, green; Si, brown.

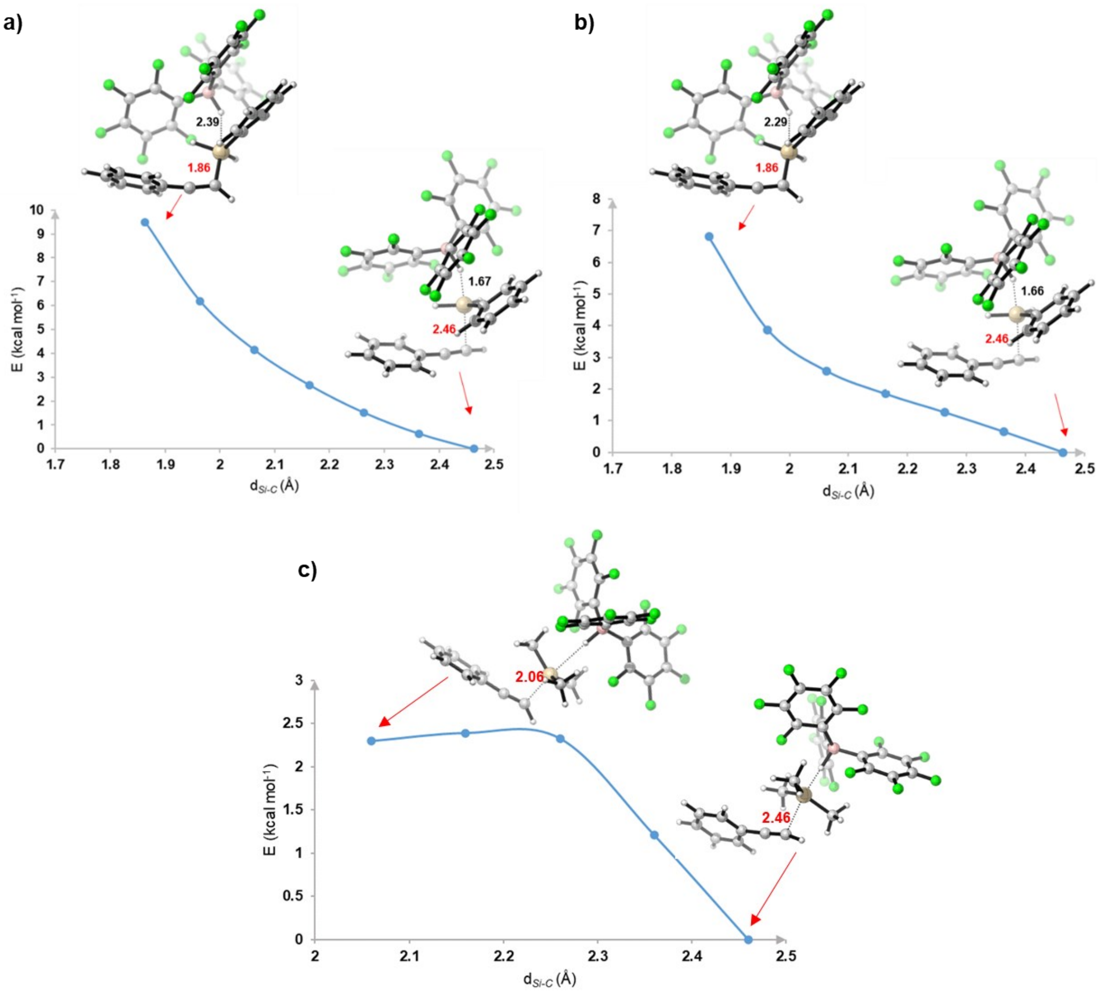


Figure S10. Relaxed scans for the Si-H bond cleavage of with phenylacetylene (**1aa**): a) $PhSiH_3$, at the M06-2X/6-31G(d,p)/(PCM, solvent = CH_2Cl_2) level of theory; b) $PhSiH_3$ at B3LYP-D3/6-31G(d,p)/(PCM, solvent = CH_2Cl_2) level of theory; c) Me_3SiH, at the M06-2X/6-31G(d,p)/(PCM, solvent = CH_2Cl_2) level of theory. Color code: H, white; C, gray; B, pink; F, green; Si, brown.

We also computed the reaction of alkyne **1a** with $PhSiH_3$ instead of Me_3SiH. However, the related S_N2@Si transition state could not be located after extensive endeavors. For the monohydrosilylation of phenylacetylene (**1a**) with $PhSiH_3$ (**2c**), no S_N2@Si transition state could be located with the M06-2X functional. We performed relaxed scans by fixing the Si-C bond distance from 2.46 Å to 1.86 Å with M06-2X and B3LYP-D3 functional (see Figure S10). The energy increases monotonically at the decreasing distance of the Si-C bond. Our further calculations show that the resulting ion-pair intermediate doesn’t exist as a minimum structure on the potential energy surface. These results are consistent with the experimental observation that only a trace amount of related product was detected for the hydrosilylation of phenylacetylene with $PhSiH_3$ as the silane.

9.6 Kinetic isotope effect calculations

The kinetic isotope effect calculations for the hydrosilylation of vinylsilane step were conducted with two different methods and the quantum tunneling correction, as discussed below:

Bigeleisen-Mayer method: According to Bigeleisen and Mayer's theory,[S8] the kinetic isotope effect can be expressed as a ratio of partition functions of the ground state and the transition state. For a non-linear structure with N atoms at a critical point on the potential energy surface, a frequency calculation gives $(3N - 6)$ frequencies ($\upsilon_0, \upsilon_1, \ldots, \upsilon_{3N-7}$). All the frequencies should be real if it is a ground state (GS) structure. For a transition state (TS) structure, which is a first-order saddle point on the potential energy surface, there should be exactly one imaginary frequency. We assume that the real frequencies υ_i are sorted from low to high, and if there exists an imaginary frequency, we denote it as υ_0. The equation to obtain the KIE is given by Bigeleisen and Mayer's theory as follows:

$$KIE = \frac{k_H}{k_D}$$
$$= \frac{u_{0,H}^{TS}}{u_{0,D}^{TS}} \times \prod_{i=0}^{3N-7}\left[\frac{u_{i,D}^{GS}}{u_{i,H}^{GS}} \cdot \frac{\exp\left(-u_{i,D}^{GS}/2\right)}{\exp\left(-u_{i,H}^{GS}/2\right)} \cdot \frac{1 - \exp\left(-u_{i,H}^{GS}\right)}{1 - \exp\left(-u_{i,D}^{GS}\right)}\right] \times \prod_{i=1}^{3N-7}\left[\frac{u_{i,H}^{TS}}{u_{i,D}^{TS}} \cdot \frac{\exp\left(-u_{i,H}^{TS}/2\right)}{\exp\left(-u_{i,D}^{TS}/2\right)} \cdot \frac{1 - \exp\left(-u_{i,D}^{TS}\right)}{1 - \exp\left(-u_{i,H}^{TS}\right)}\right]$$

where u represents frequencies scaled by h/k_BT, leading to: $u_i = h\upsilon_i/(k_BT)$, similarly hereinafter. The ground state and transition state frequencies are denoted by superscript *GS* and *TS*, while the subscript *H* and *D* represent the frequencies from hydrogen and deuterium isotopomers.

Rigid-rotor harmonic oscillator (Δ*H*Δ*S*) method: According to the methodologies developed by the O'Leary laboratory,[S9] the kinetic isotope effect is given by the following equation:

$$KIE = \frac{k_H}{k_D} = \exp\left(\frac{\Delta G_D - \Delta G_H}{k_BT}\right)$$

where Δ*G* represents the Gibbs free energy change from GS to TS. It is given by the sum of the electronic energy difference and the Gibbs thermal correction difference:

$$\Delta G = \Delta EE + \Delta G_{corr} = \Delta EE + \Delta H_{corr} - T\Delta S_{corr}$$

where $\Delta EE = EE^{TS} - EE^{GS}$ denotes the electronic energy difference between TS and GS. It is similar with the enthalpy thermal correction Δ*Hcorr* and the entropy thermal correction ΔS_{corr}. Those are $\Delta H_{corr} = H_{corr}^{TS} - H_{corr}^{GS}$ and $\Delta S_{corr} = S_{corr}^{TS} - S_{corr}^{GS}$.

According to our knowledge of statistical thermodynamics, H_{corr} is given by:

$$H_{corr} = ZPE + H_{vib} + E_{rot} + E_{trans} + k_BT$$

The last term k_BT is the same in both H_{corr}^{TS} and H_{corr}^{GS}, so it does not contribute ΔH_{corr}. E_{rot} and E_{trans} cancel each other in TS and GS in the same way, because $E_{trans} = (3/2)k_BT$, and for nonlinear molecules, $E_{rot} = (3/2)k_BT$.

Thus, only the first two terms of H_{corr} should be calculated. The zero-point vibrational energy (*ZPE*) is calculated as:

$$ZPE^{GS} = \frac{1}{2}\sum_{i=0}^{3N-7} h\nu_i^{GS}$$

$$ZPE^{TS} = \frac{1}{2}\sum_{i=0}^{3N-7} h\nu_i^{TS}$$

while the vibrational contribution to the enthalpy H_{vib} is:

$$H_{vib}^{GS} = k_B T \sum_{i=0}^{3N-7} u_i^{GS} \frac{exp(-u_i^{GS})}{1 - exp(-u_i^{GS})}$$

$$H_{vib}^{TS} = k_B T \sum_{i=0}^{3N-7} u_i^{TS} \frac{exp(-u_i^{TS})}{1 - exp(-u_i^{TS})}$$

Then we consider the entropy thermal correction Δ_{Scorr}. It is given by:

$$S_{coor} = S_{vib} + S_{rot} + S_{trans}$$

The translation contribution S_{trans} can be described as:

$$S_{trans} = k_B\left\{\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{k_B T}{p}\right] + \frac{5}{2}\right\}$$

where *m* denotes the mass of the structure and *p* denotes the pressure. From GS to TS, the mass and pressure of a structure do not change. Thus, S_{trans} does not contribute to ΔS_{corr}. The rotation contribution S_{rot} for a non-linear structure is given by:

$$S_{rot} = k_B\left\{\ln\left[\frac{8\pi^2}{\sigma h^3}(2\pi k_B T)^{3/2}(I_A I_B I_C)^{1/2}\right] + \frac{3}{2}\right\}$$

where I_A, I_B and I_C are three components of the moment of inertia for the structure. For the hydrosilylation of vinylsilane step, both GS and TS belong to the *C*1 group, leading to the rotational symmetry number σ = 1. As a result, the contribution of S_{rot} to ΔS_{corr} is:

$$\Delta S_{rot} = \frac{1}{2}k_B \ln\left[\frac{(I_A I_B I_C)^{TS}}{(I_A I_B I_C)^{GS}}\right]$$

Finally, the vibrational contribution S_{vib} is given by:

$$S_{vib}^{GS} = k_B \sum_{i=0}^{3N-7} \left\{ u_i^{GS} \frac{exp\left(-u_i^{GS}\right)}{1 - exp\left(-u_i^{GS}\right)} - \ln\left[1 - exp\left(-u_i^{GS}\right)\right] \right\}$$

$$S_{vib}^{TS} = k_B \sum_{i=0}^{3N-7} \left\{ u_i^{TS} \frac{exp\left(-u_i^{TS}\right)}{1 - exp\left(-u_i^{TS}\right)} - \ln\left[1 - exp\left(-u_i^{TS}\right)\right] \right\}$$

Quantum tunneling correction: Finally we applied a quantum tunneling (*QT*) correction with the Northrop and Bell's one-dimensional parabolic approximation:[S10]

$$QT = \frac{QT_H}{QT_D}$$

where

$$QT_H = \frac{\left|u_{0,H}^{TS}\right|/2}{\sin\left(\left|u_{0,H}^{TS}\right|/2\right)}$$

and

$$QT_D = \frac{\left|u_{0,D}^{TS}\right|/2}{\sin\left(\left|u_{0,D}^{TS}\right|/2\right)}$$

The final KIEs reported in the manuscript and this supplementary information for both the Bigeleisen-Mayer and rigid-rotor harmonic oscillator methods are as follows:

$$KIE = (KIE) \cdot (QT)$$

Constants: In all above equations, we take Avogadro constant as N_A = 6.02214076 × 1023 mol^{-1}, Boltzmann constant as k_B = 1.3806488 × 10^{-23} J · K^{-1}, Plank constant as h = 6.62607015 × 10^{-34} J · s, the speed of light as c = 2.99792458 × 108 m · s^{-1}, and the reaction temperature as T in Kelvin.

Kinetic isotope effects are calculated with a python-based program Gaussian_KIE developed by ourselves. The results of the calculated kinetic isotope effects are listed in Table S4.

Table S4. Computed KIE values with the Bigeleisen-Mayer (BM) and rigid-rotor harmonic oscillator (Δ*H*Δ*S*) methods for the hydrosilylation of vinylsilane step.

GS→ TS	KIE_{comp}(BM)	KIE_{comp}(Δ*H*Δ*S*)
3aa' → **TS$_{3aa'-V}$**	0.7471	0.7702
VI → **TS$_{VI-4aa'c}$**	1.396	1.444

10. NMR Spectra

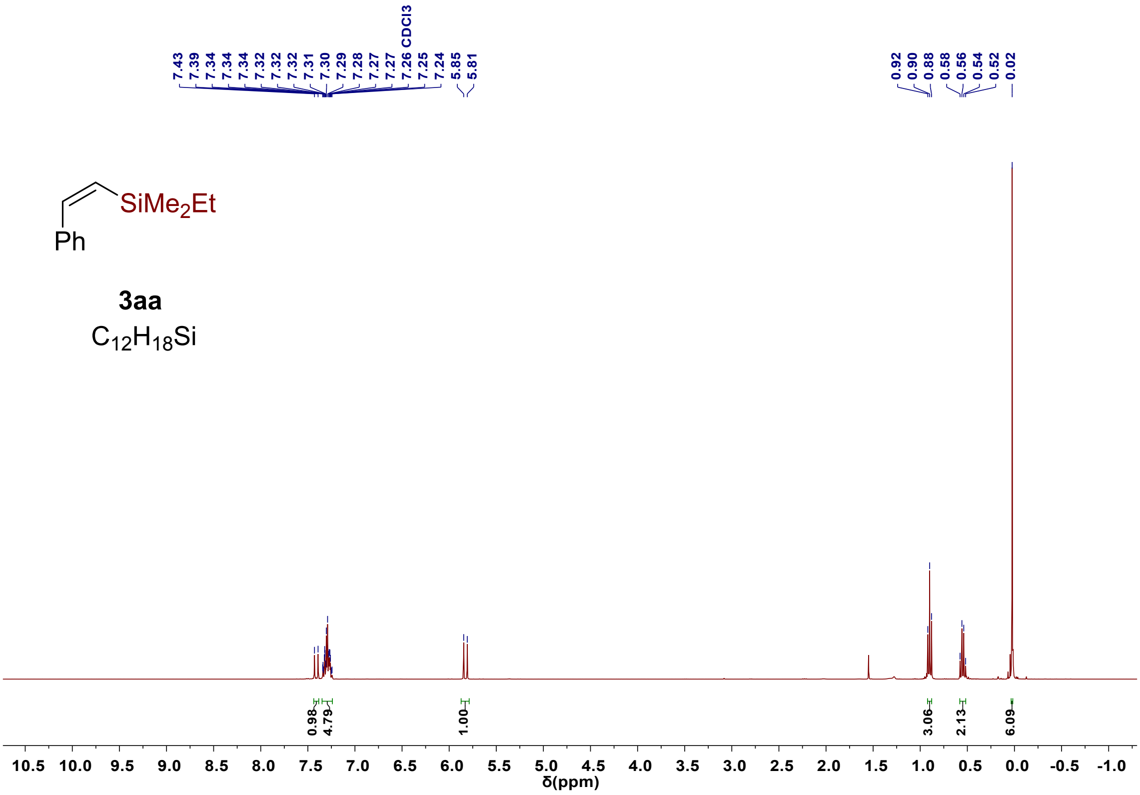


Figure S11. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **3aa**.

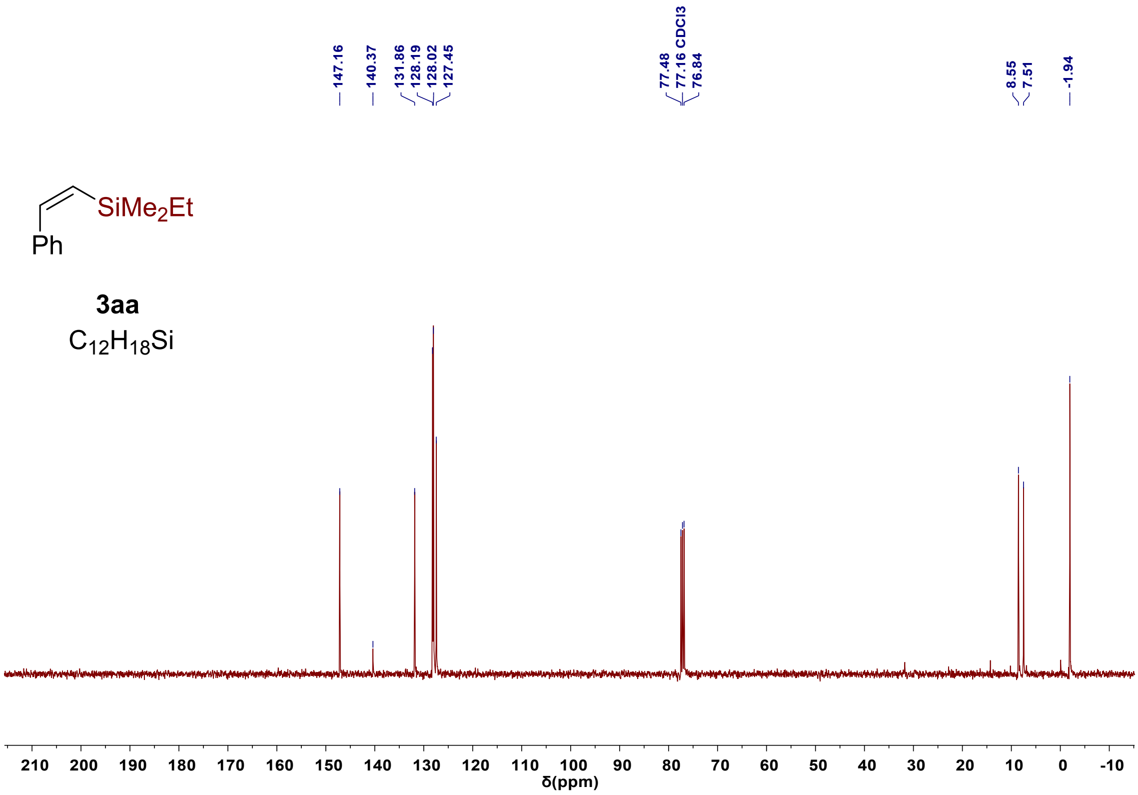


Figure S12. **^{13}C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **3aa**.

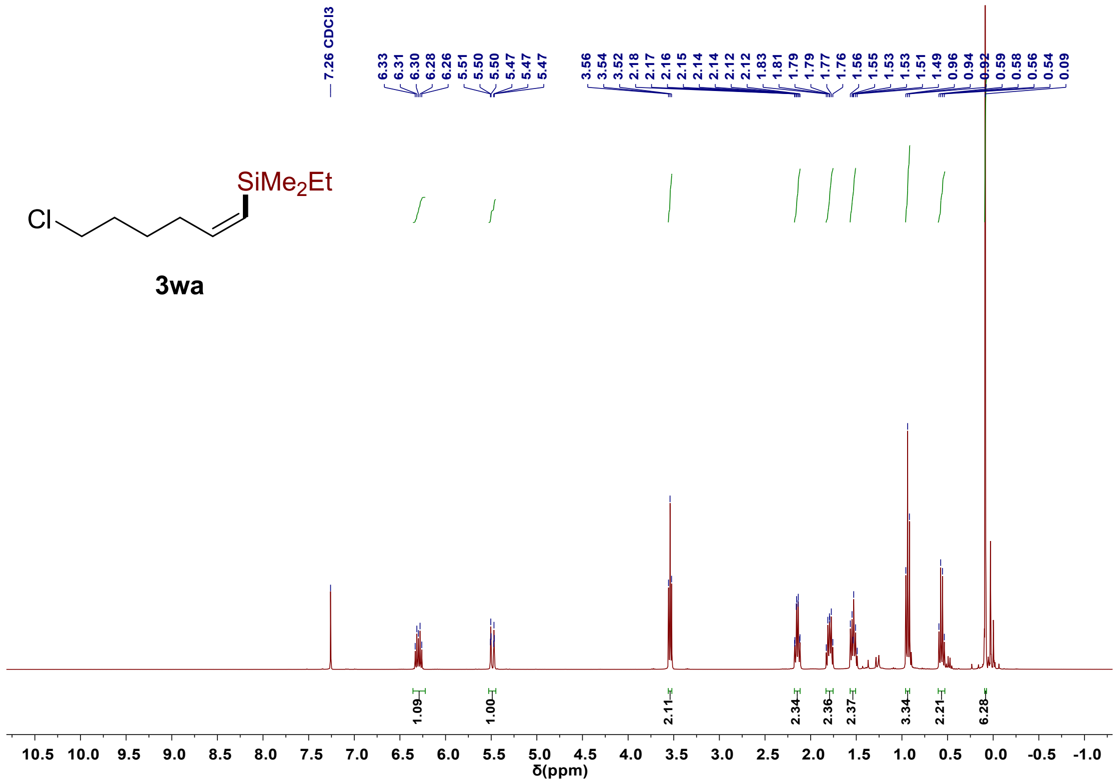


Figure S13. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **3wa**.

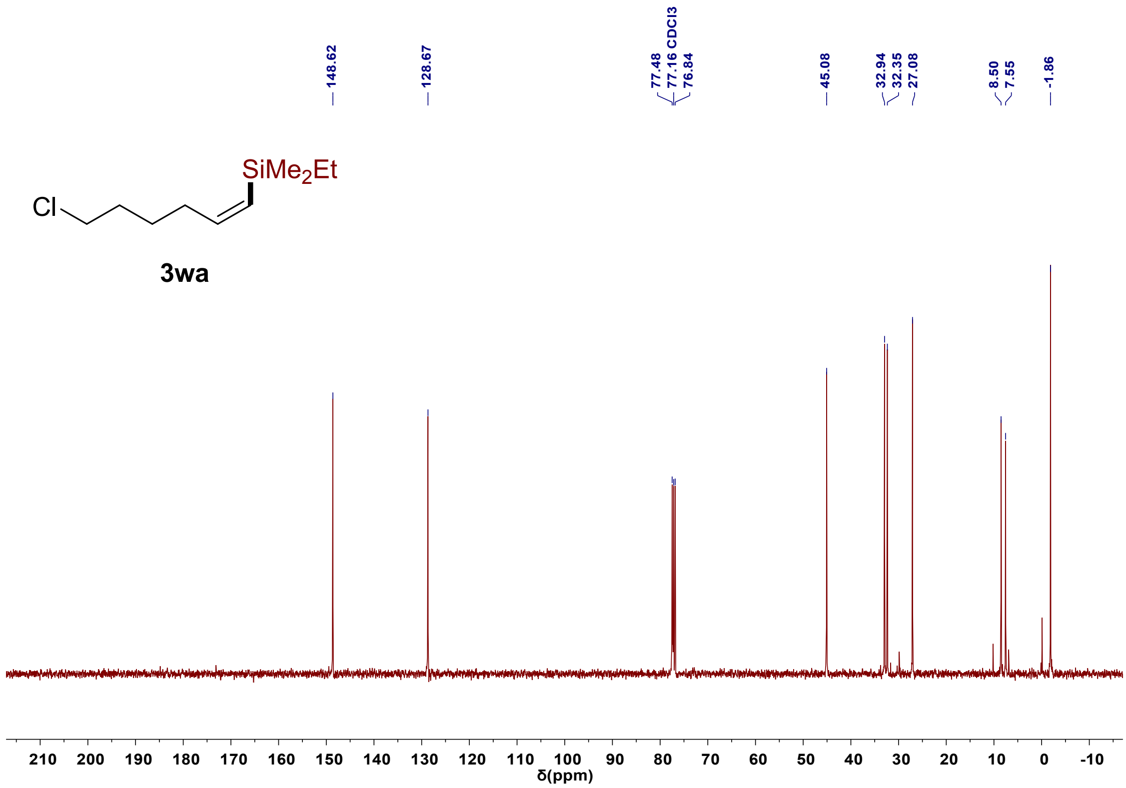


Figure S14. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **3wa**.

3xa

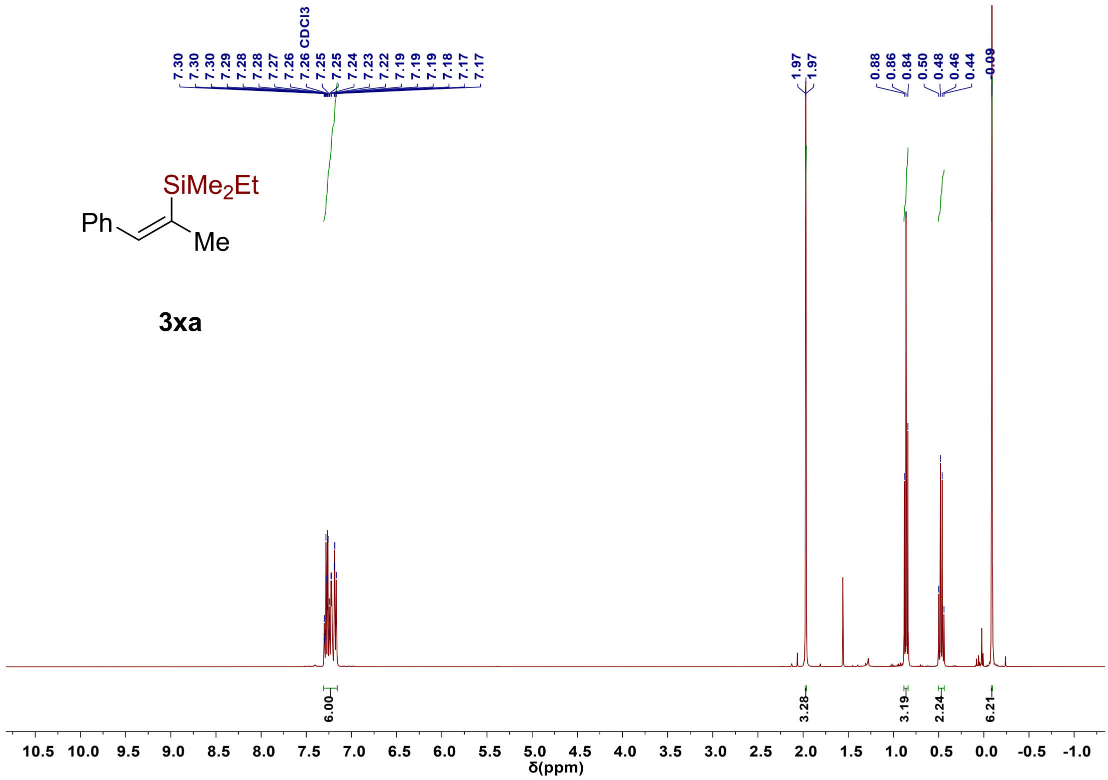


Figure S15. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of the compound **3xa**.

3xa

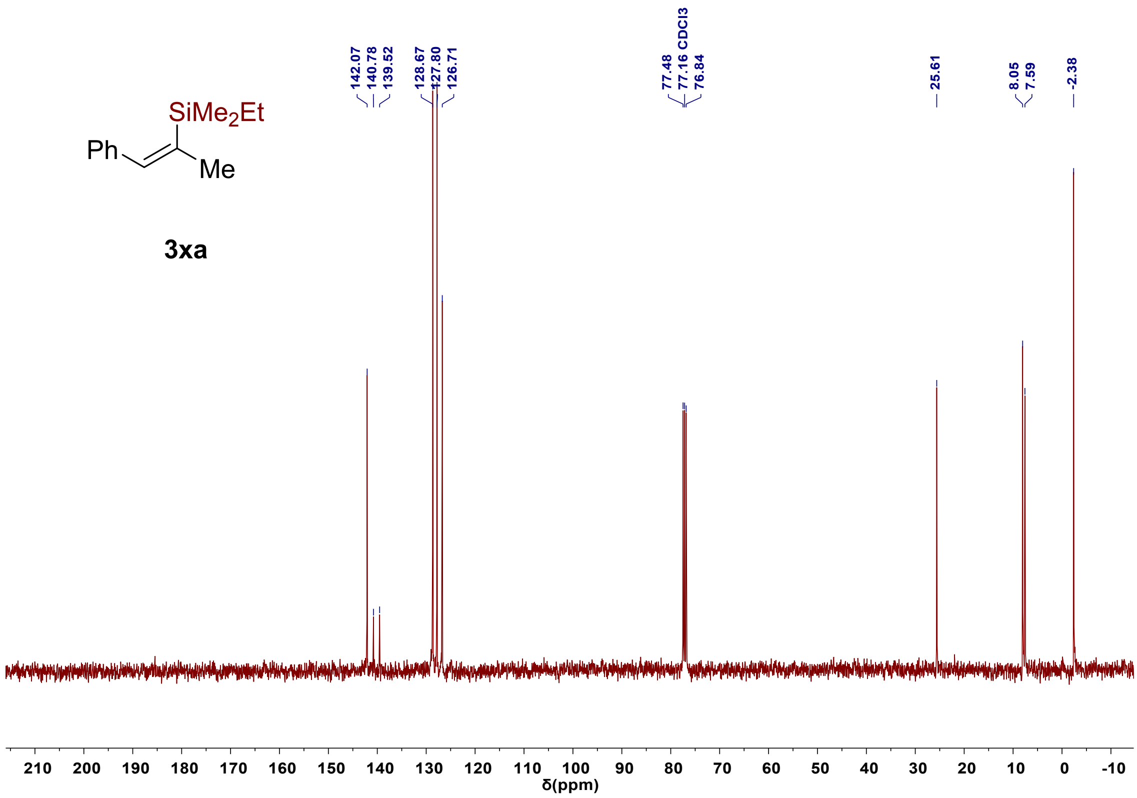


Figure S16. **$^{13}C\{^{1}H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **3xa**.

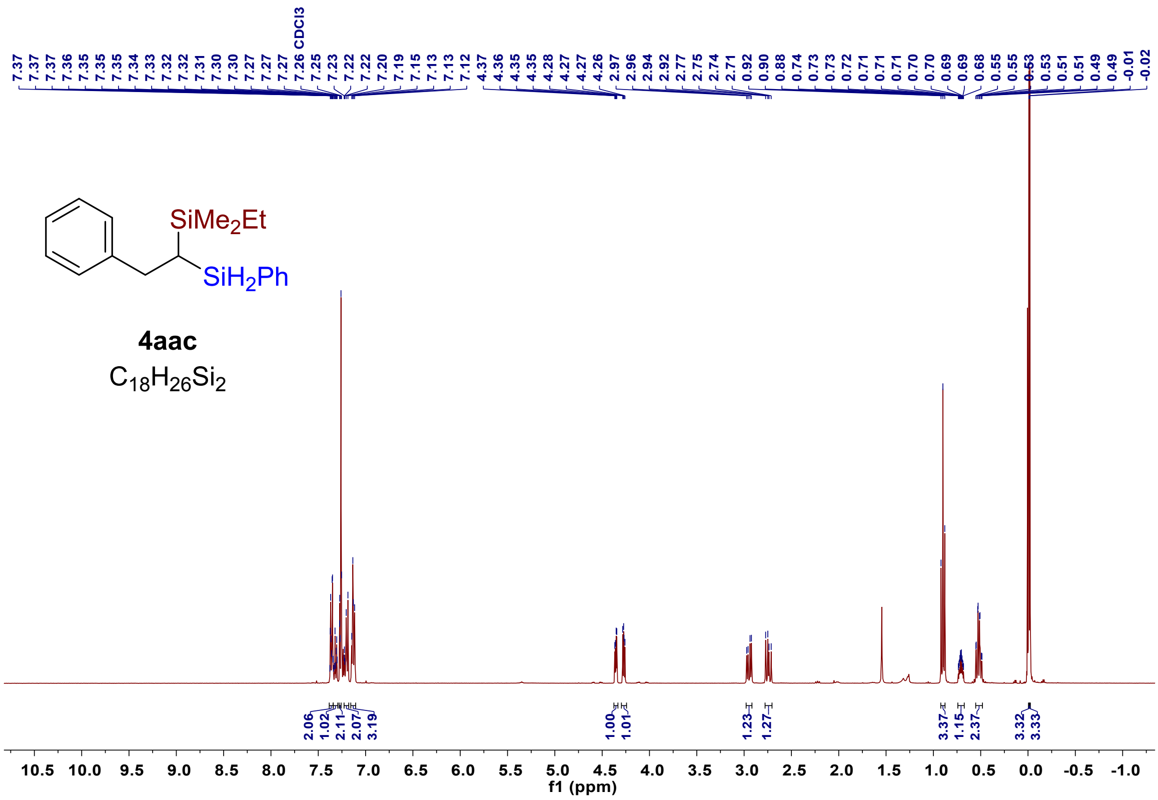


Figure S17. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4aac**.

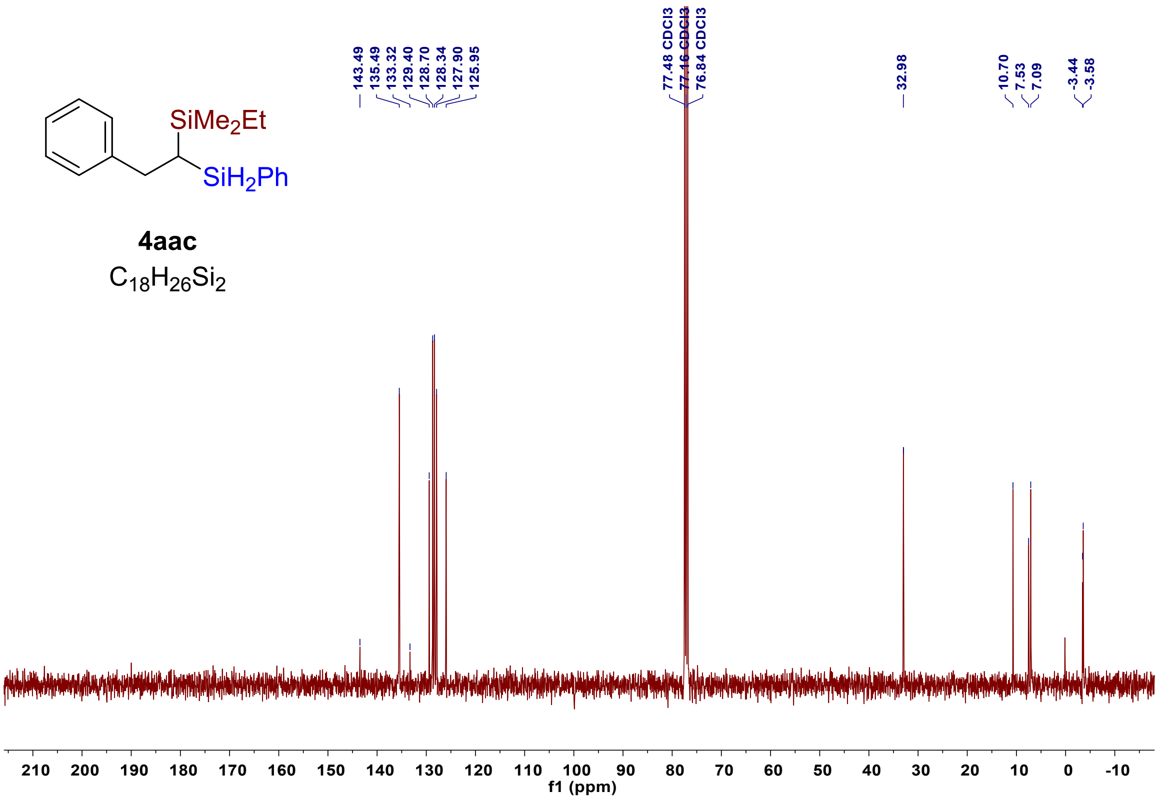


Figure S18. **$^{13}C\{^1H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **4aac**.

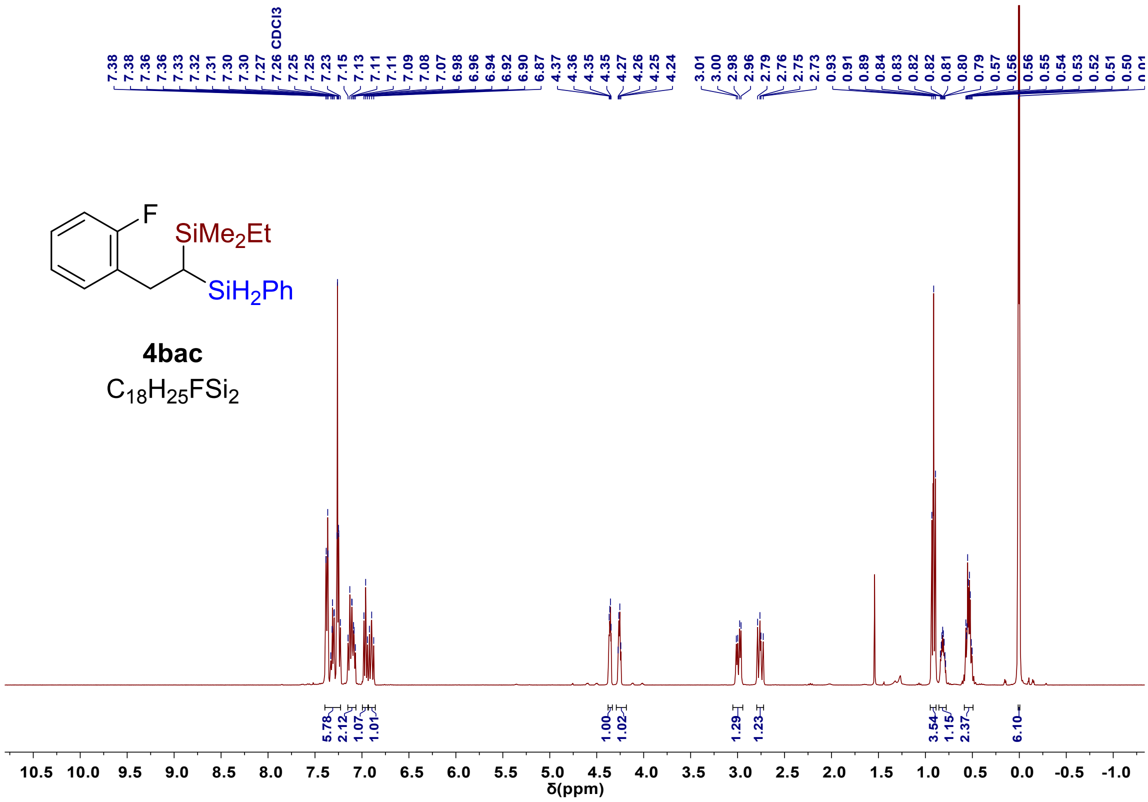


Figure S19. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of the compound **4bac**.

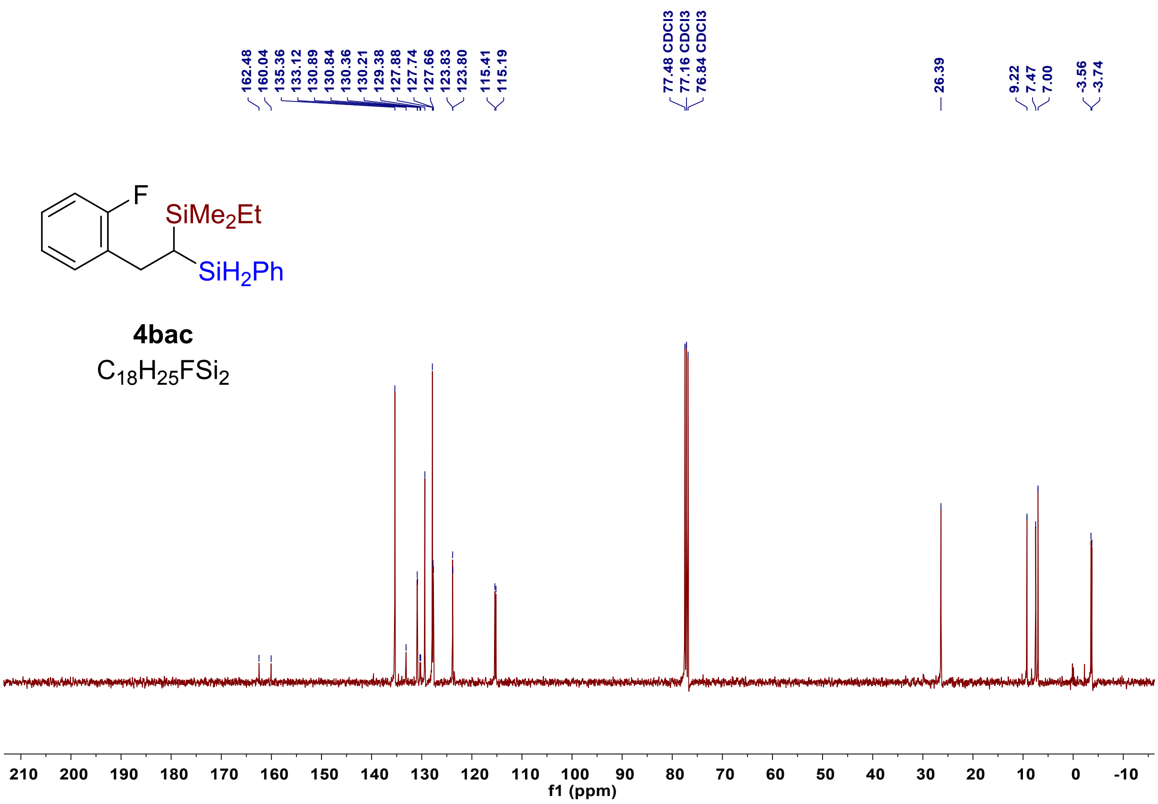


Figure S20. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4bac**.

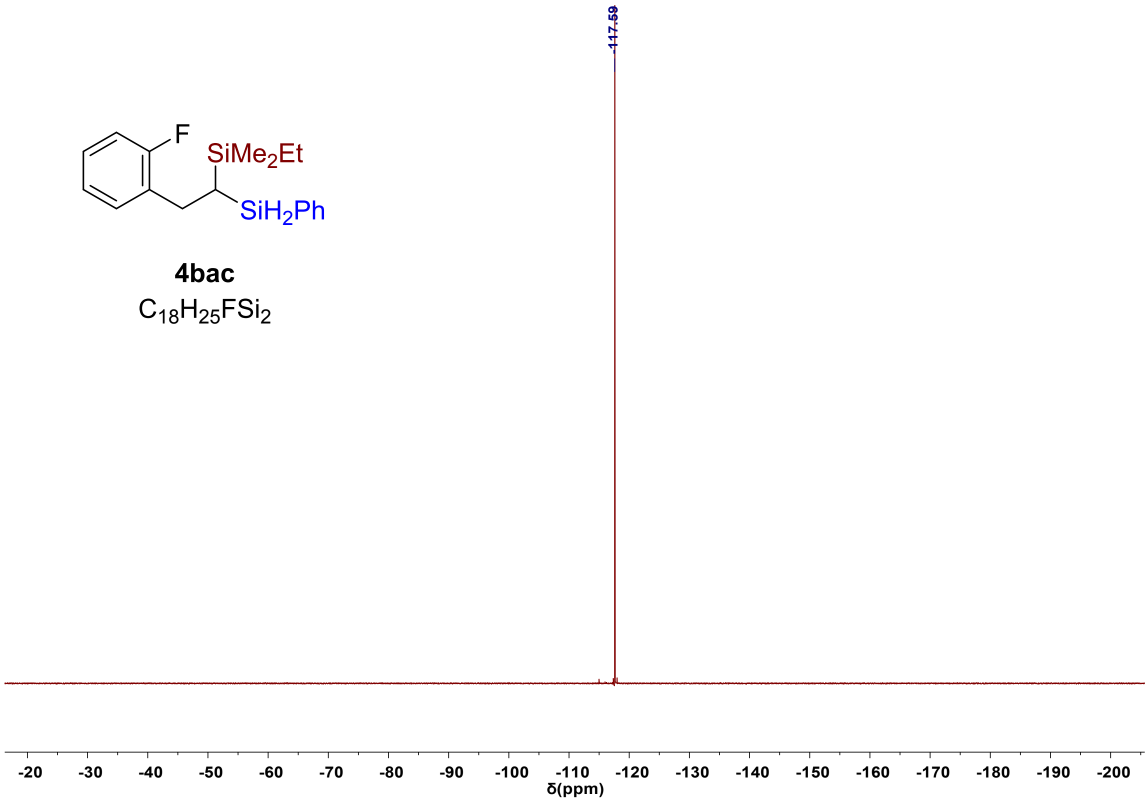


Figure S21. **$^{19}F\{^1H\}$ NMR** spectrum (376 MHz MHz, $CDCl_3$) of compound **4bac**.

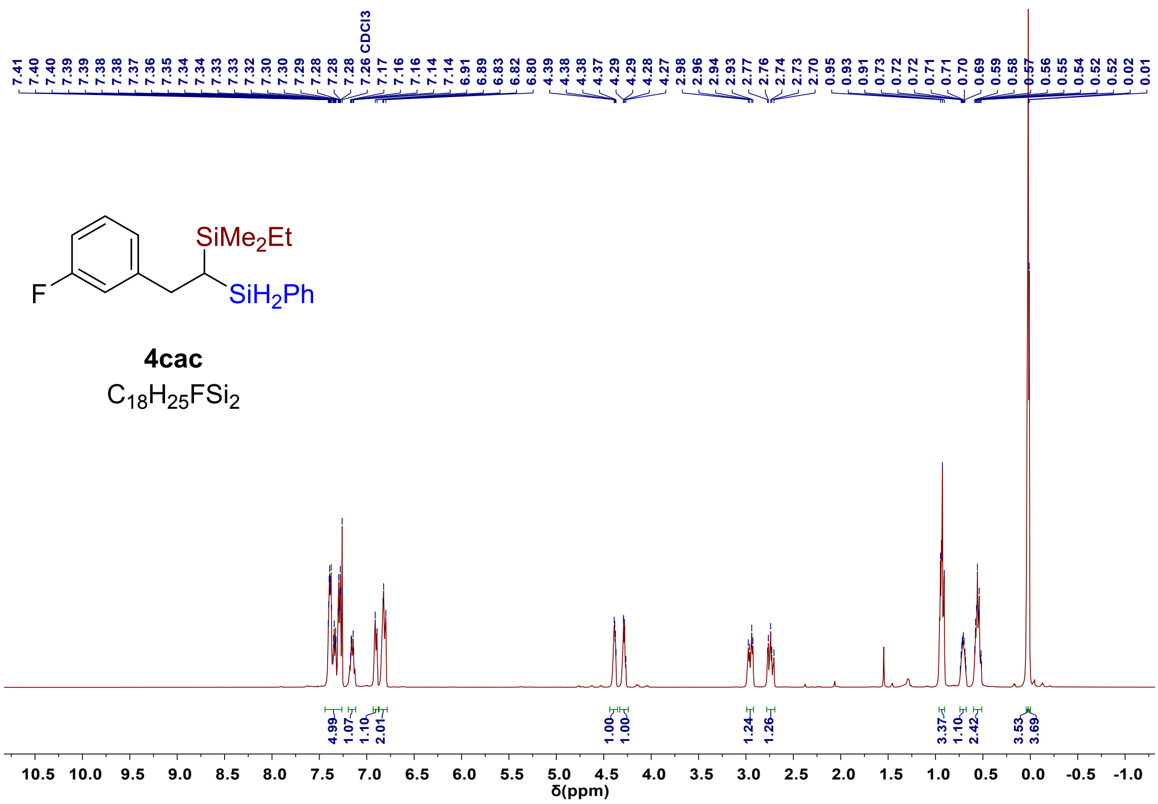


Figure S22. **^1H NMR** spectrum (400 MHz, $CDCl_3$) of the compound **4cac**.

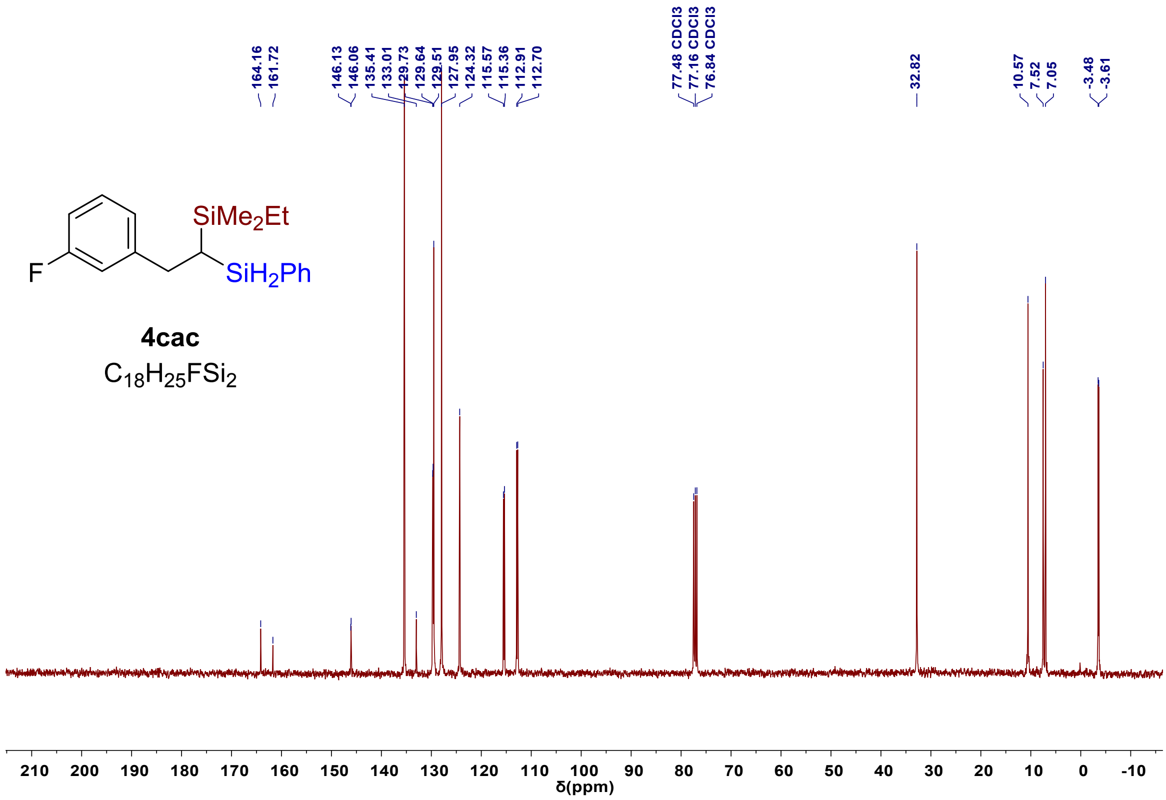


Figure S23. **$^{13}C\{^1H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **4cac**.

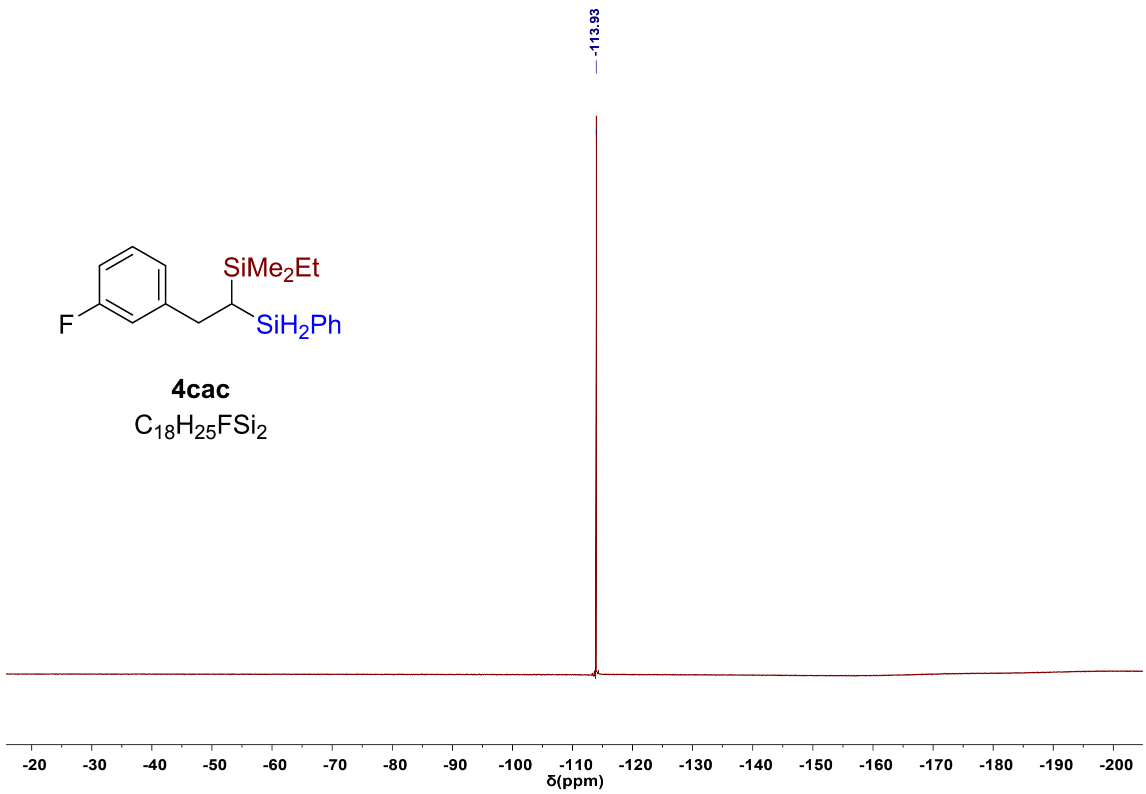


Figure S24. **$^{19}F\{^1H\}$ NMR** spectrum (376 MHz MHz, $CDCl_3$) of compound **4cac**.

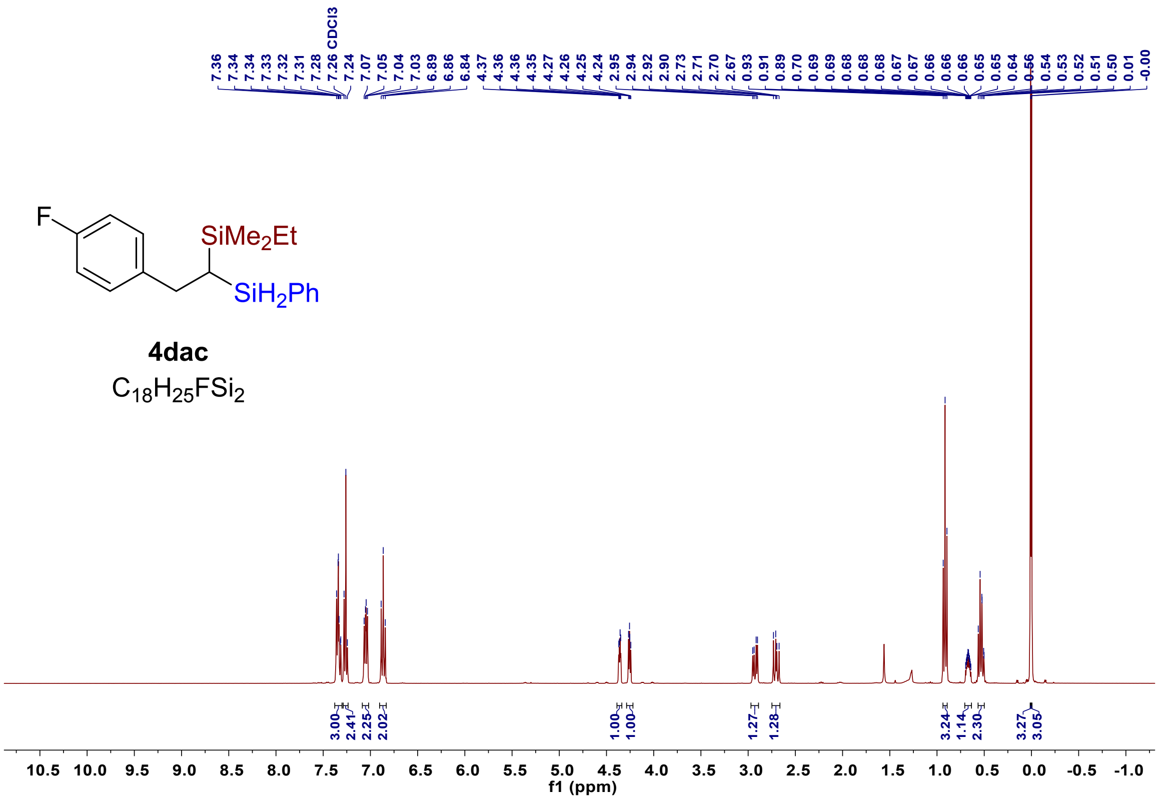


Figure S25. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4dac**.

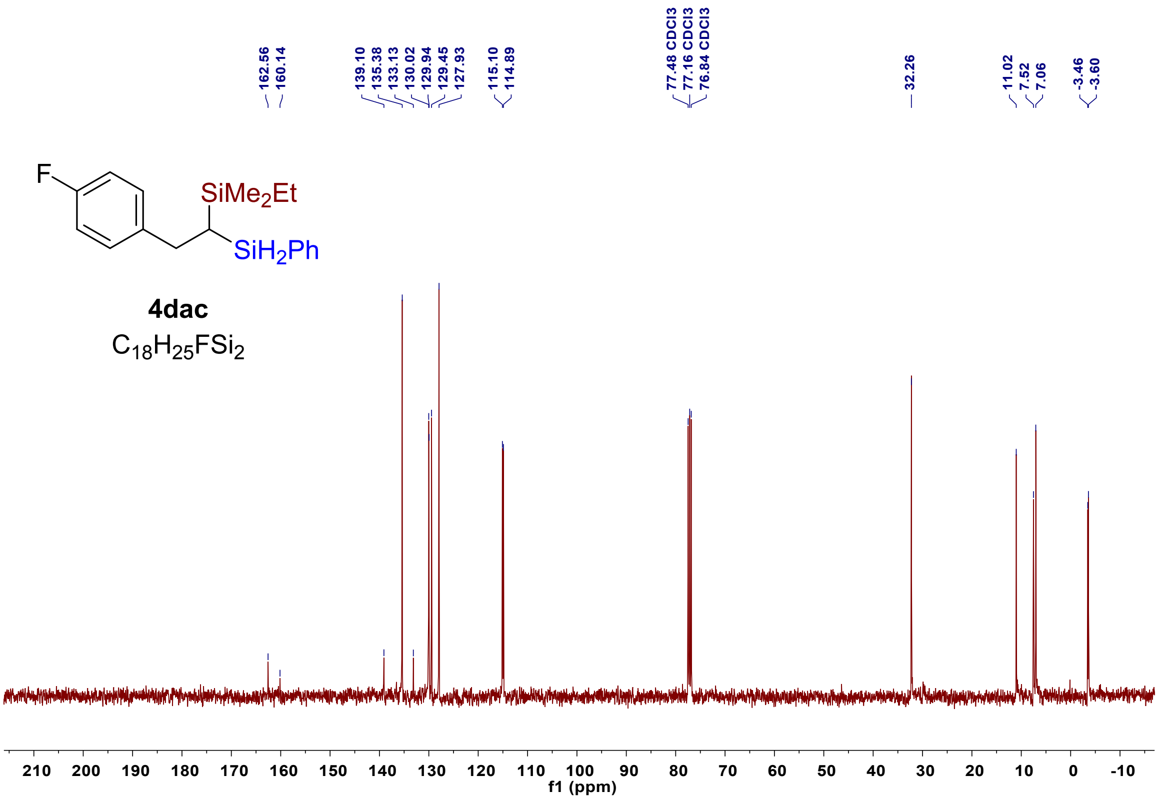


Figure S26. **^{13}C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4dac**.

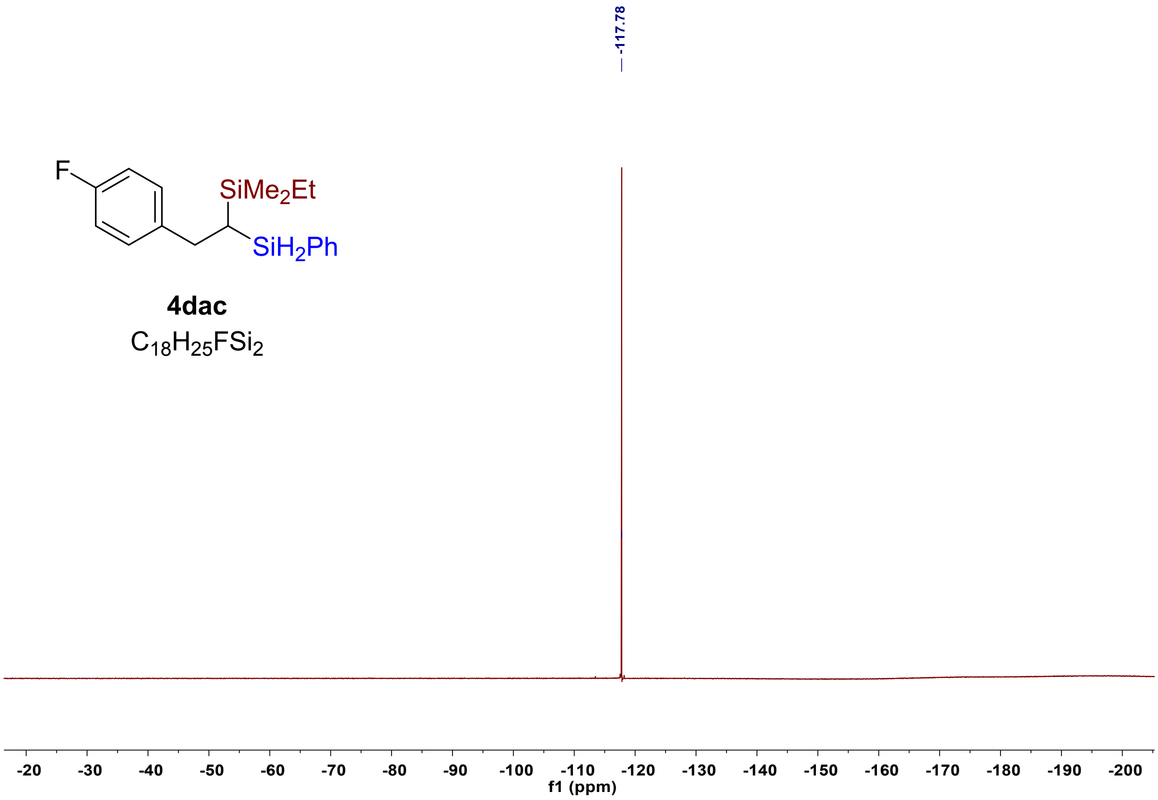


Figure S27. **$^{19}F\{^{1}H\}$ NMR** spectrum (376 MHz MHz, $CDCl_3$) of compound **4dac**.

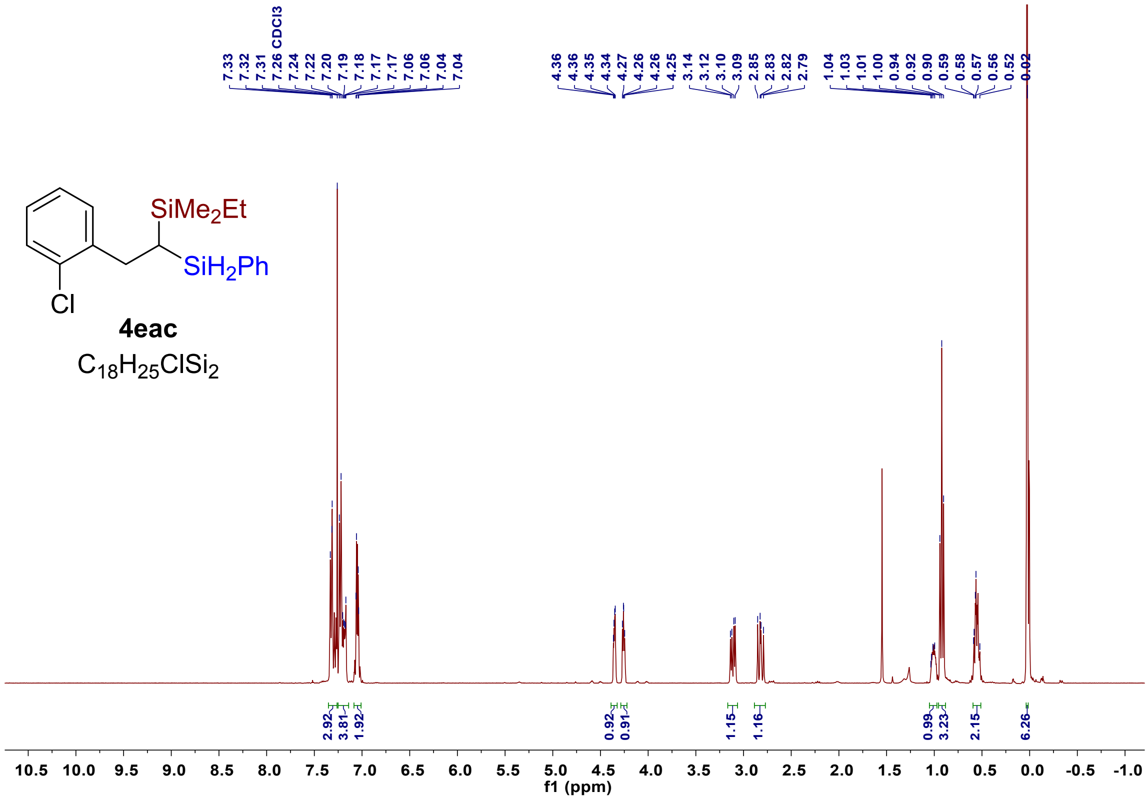


Figure S28. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4eac**.

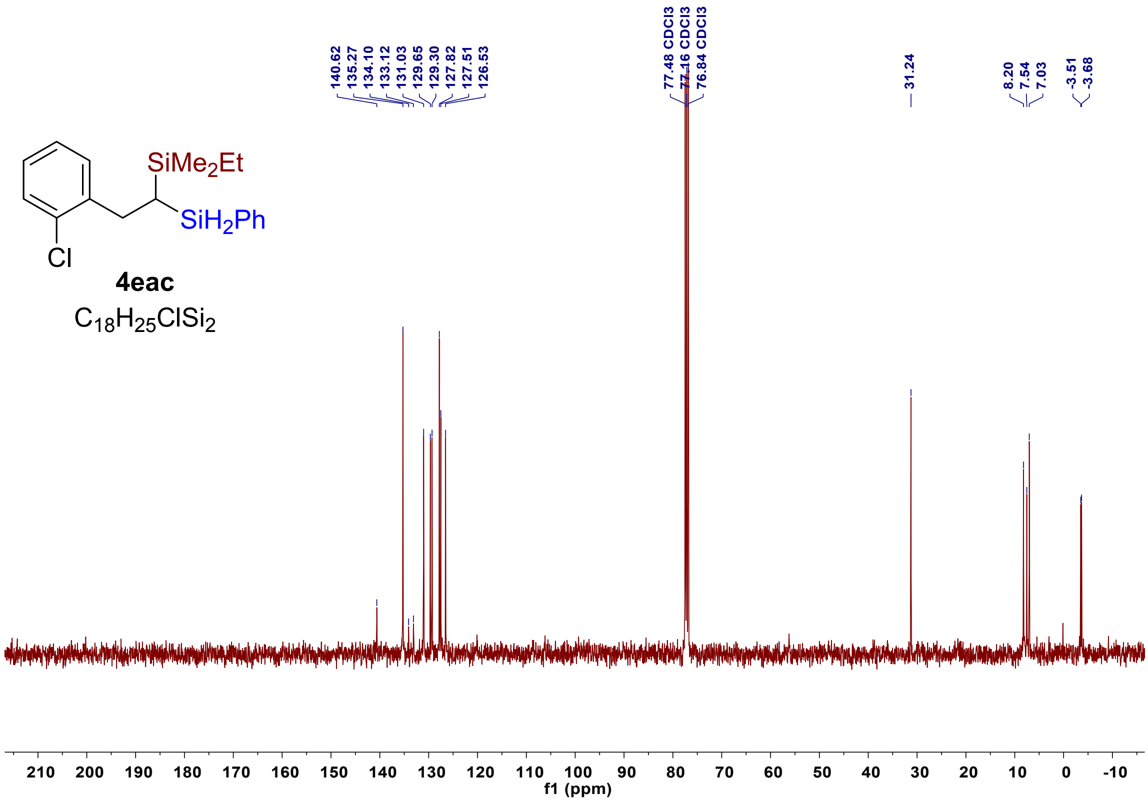


Figure S29. $^{13}C\{^{1}H\}$ **NMR** spectrum (100 MHz, $CDCl_3$) of compound **4eac**.

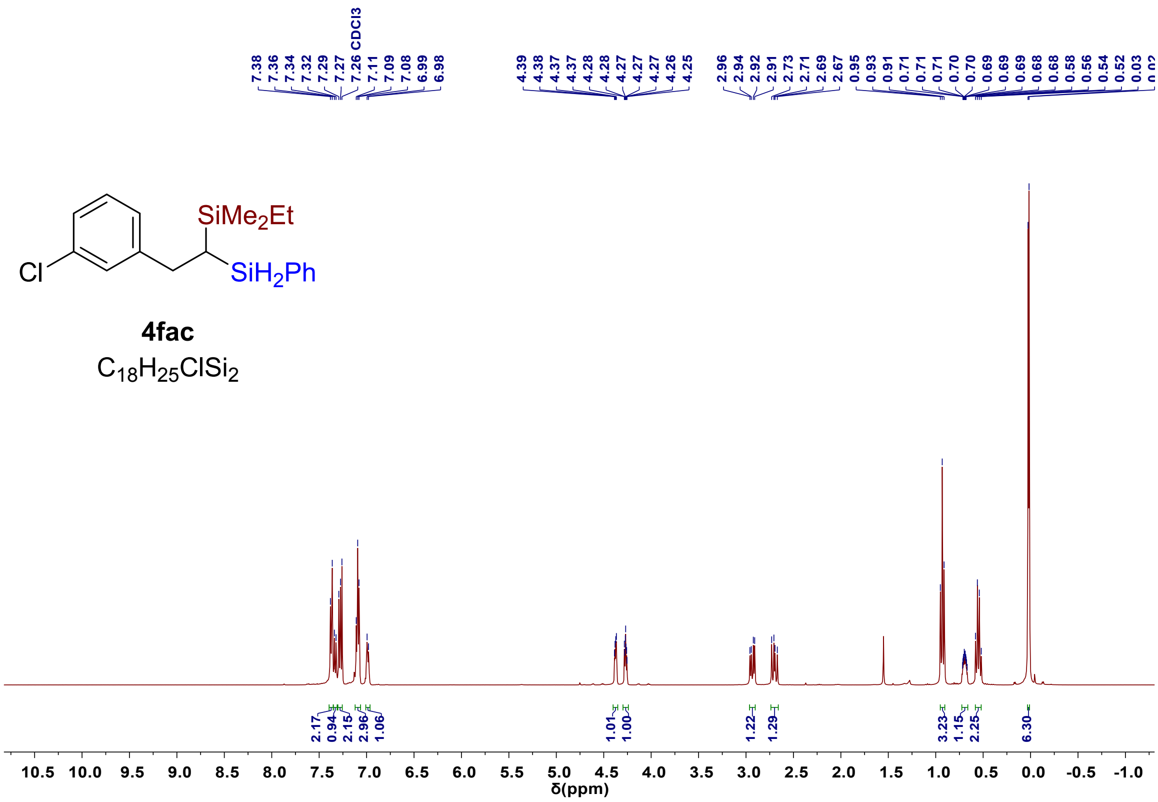


Figure S30. ^{1}H **NMR** spectrum (400 MHz, $CDCl_3$) of compound **4fac**.

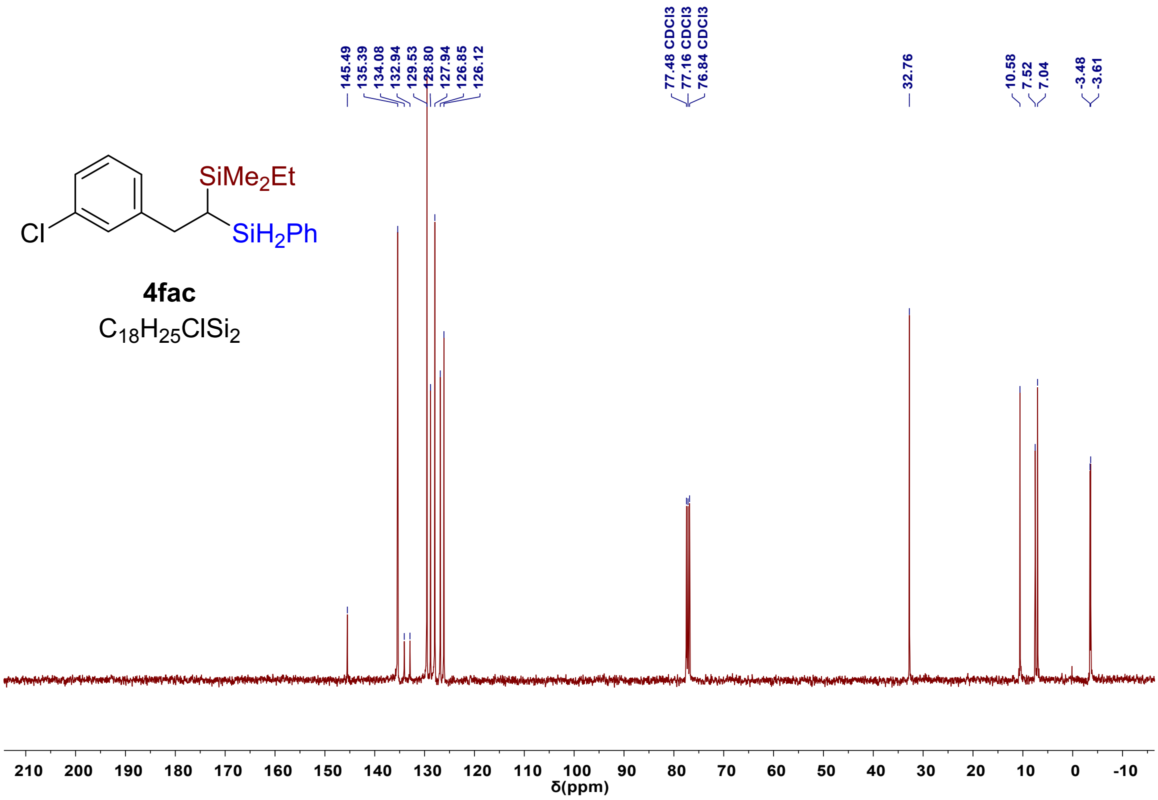


Figure S31. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4fac**.

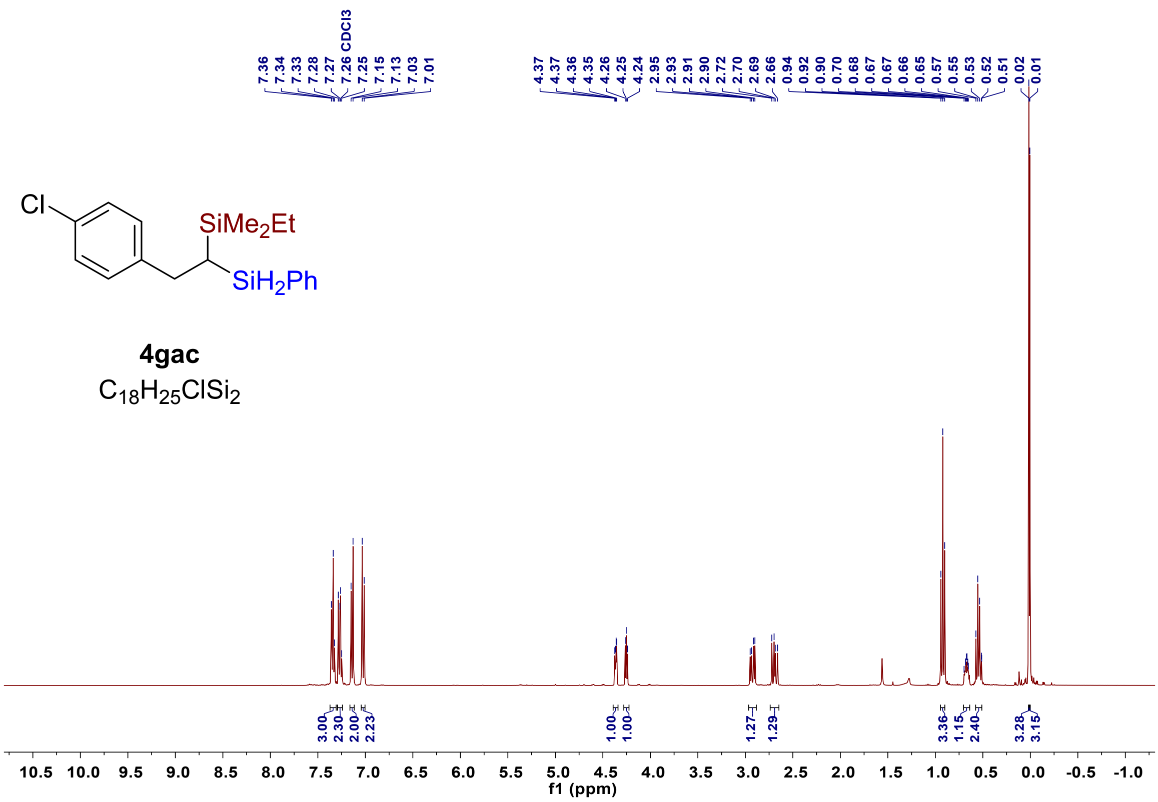


Figure S32. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4gac**.

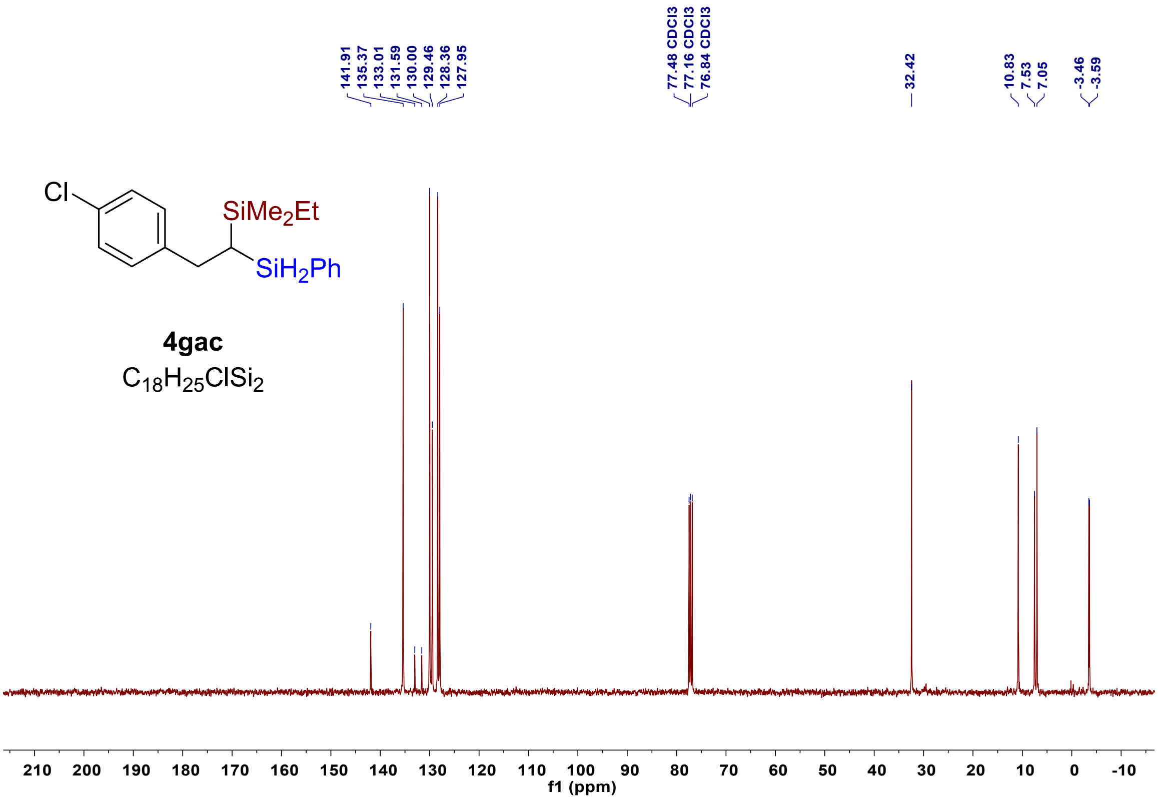


Figure S33. **$^{13}C\{^1H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **4gac**.

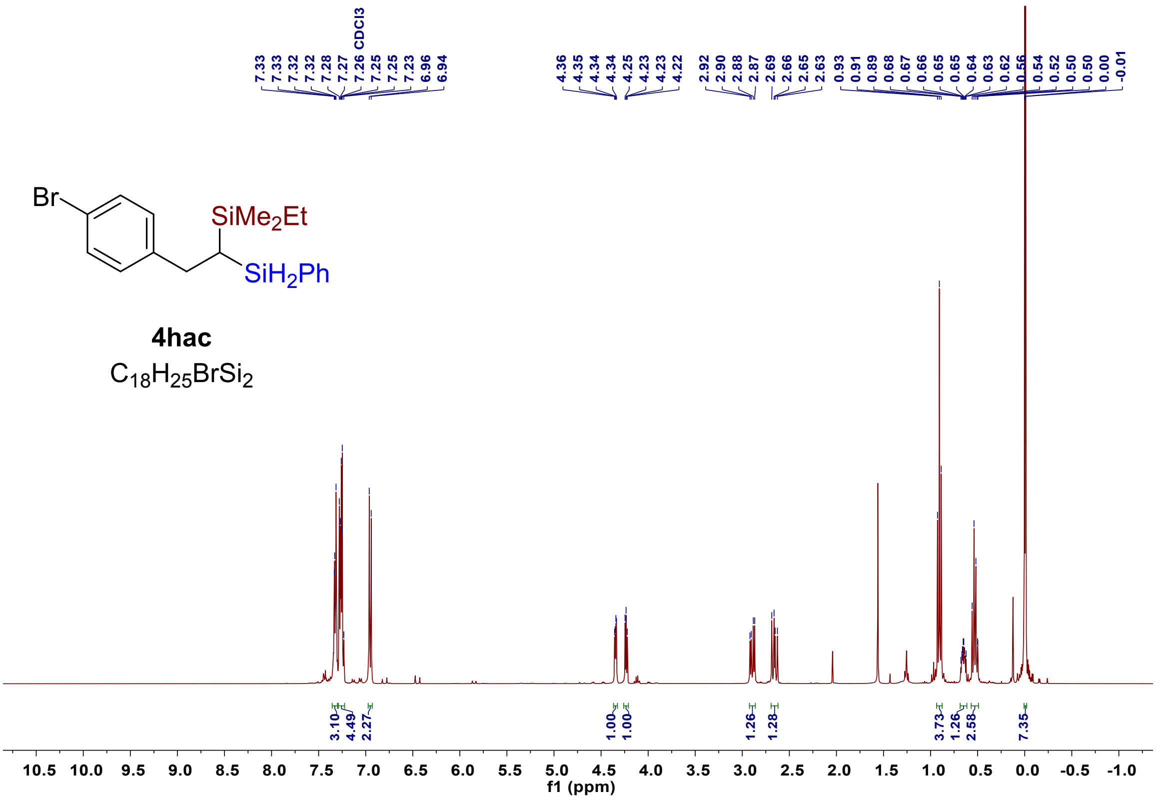


Figure S34. **^1H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4hac**.

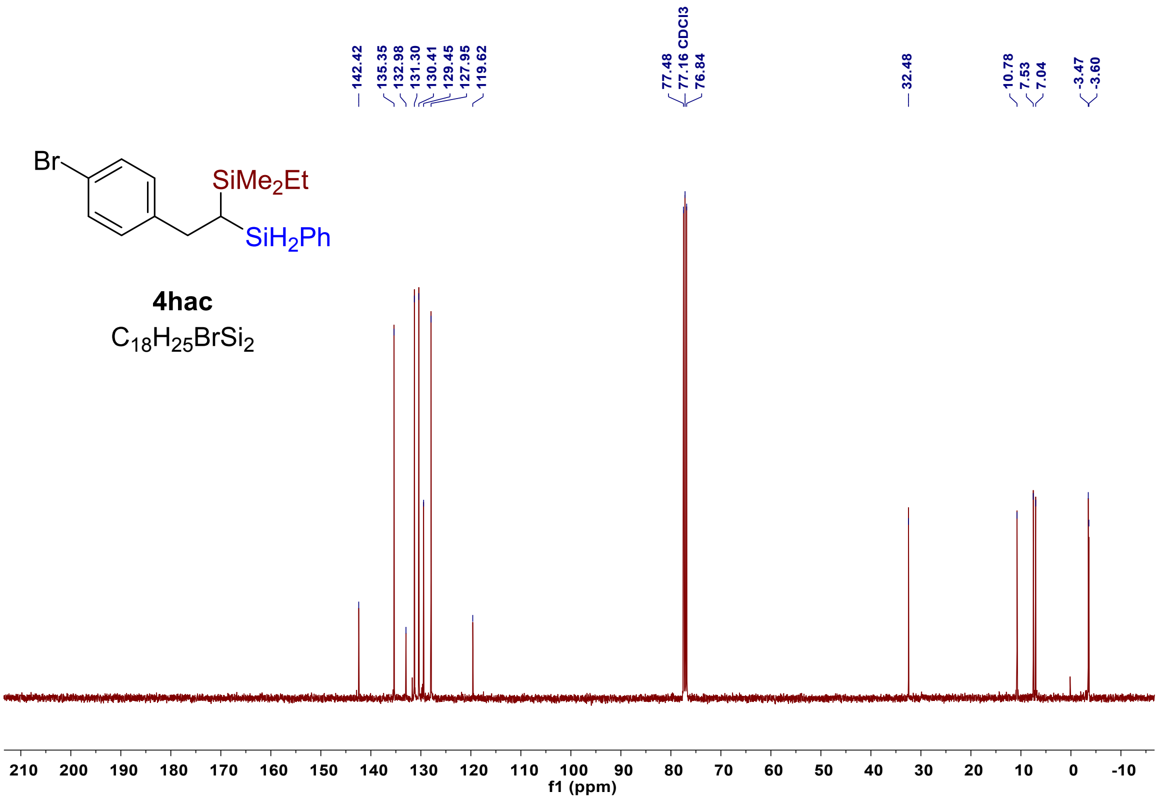


Figure S35. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4hac**.

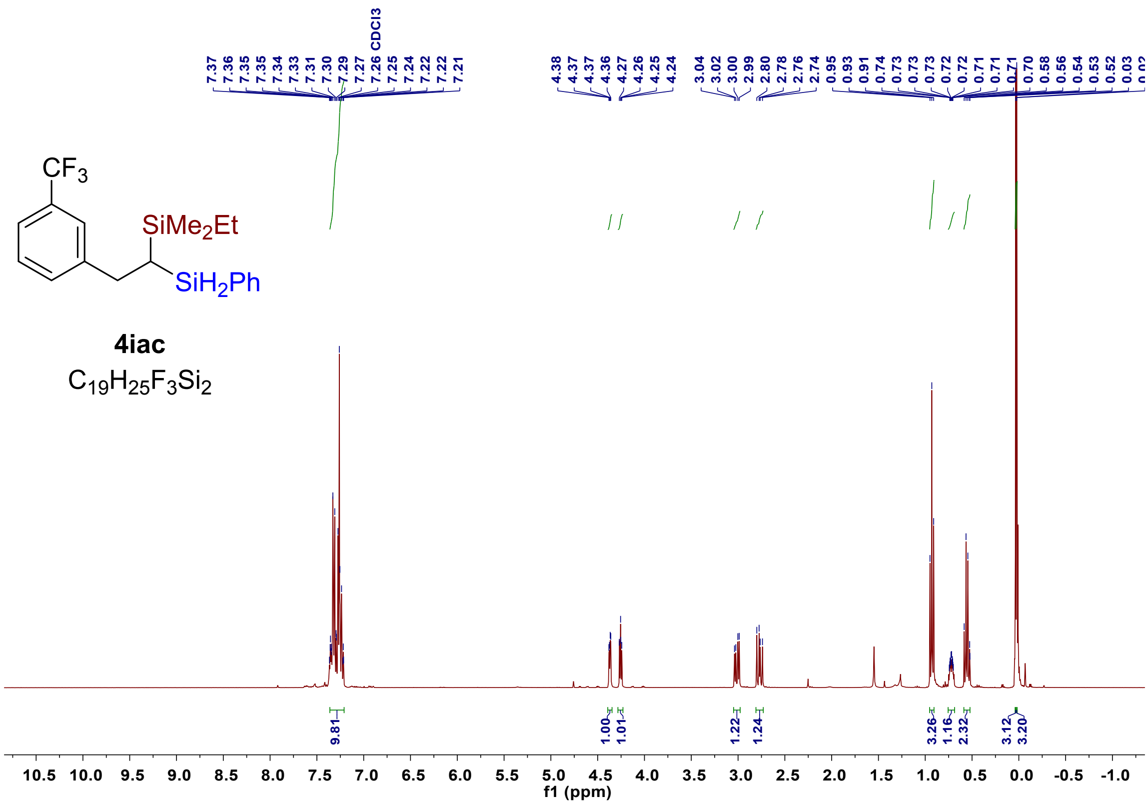


Figure S36. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4iac**.

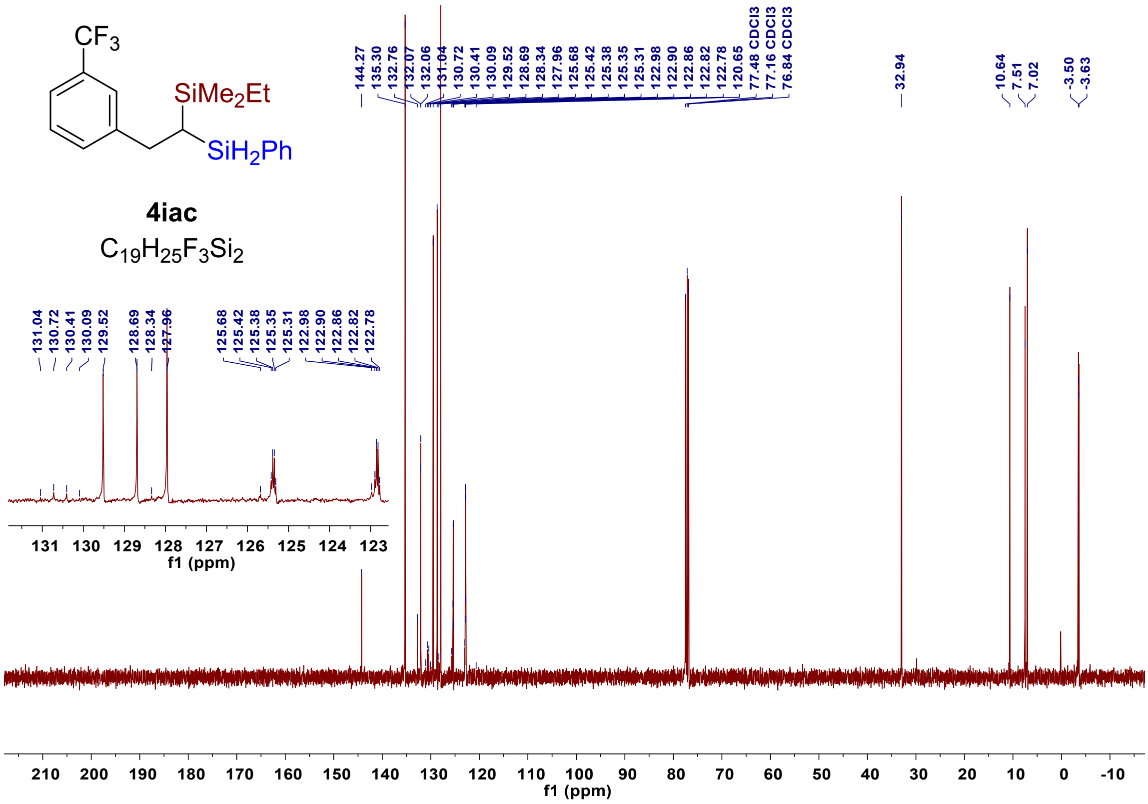


Figure S37. $^{13}C\ \{^{1}H\}$ **NMR** spectrum (100 MHz, $CDCl_3$) of compound **4iac**.

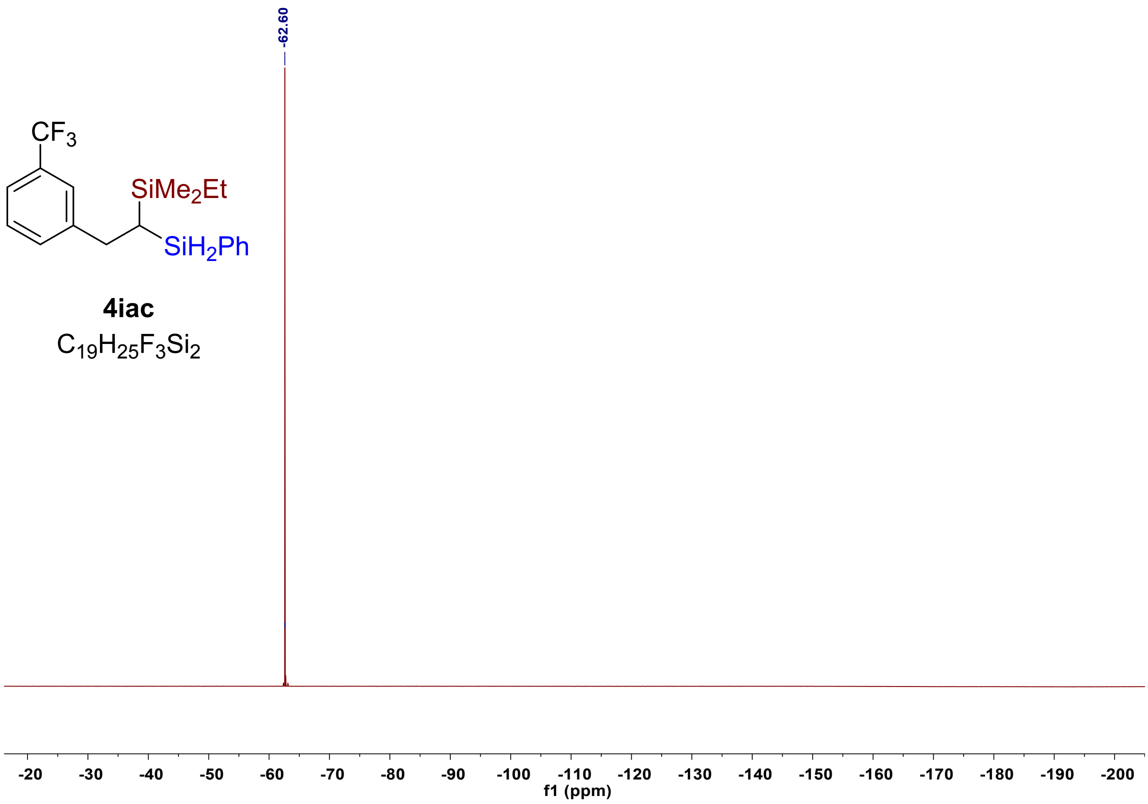


Figure S38. $^{19}F\{^{1}H\}$ **NMR** spectrum (376 MHz MHz, $CDCl_3$) of compound **4iac**.

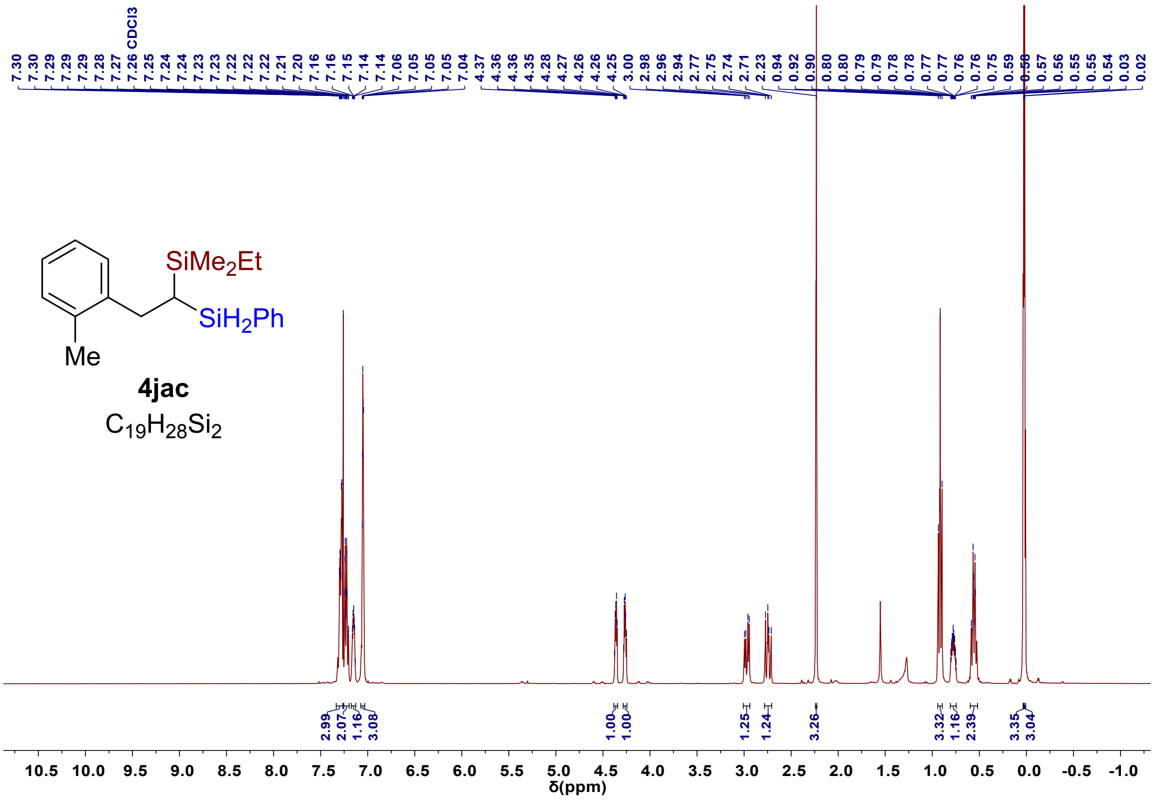


Figure S39. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4jac**.

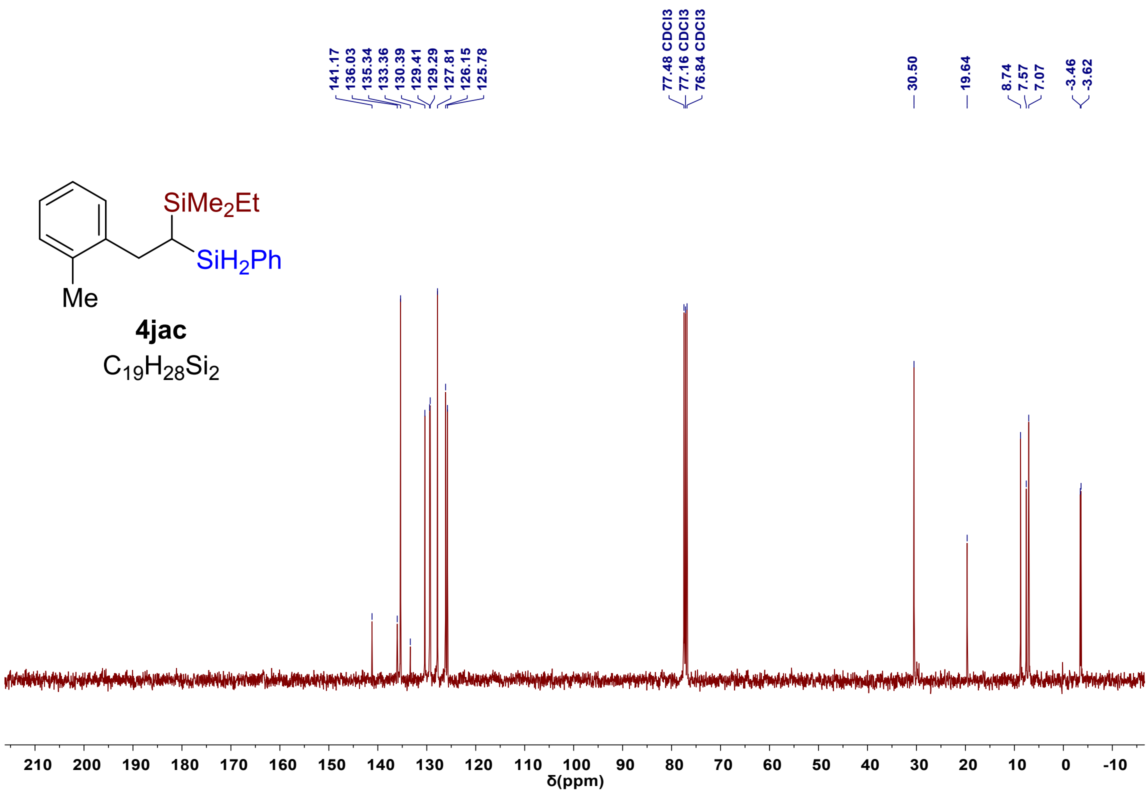


Figure S40. [13]**C{**[1]**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4jac**.

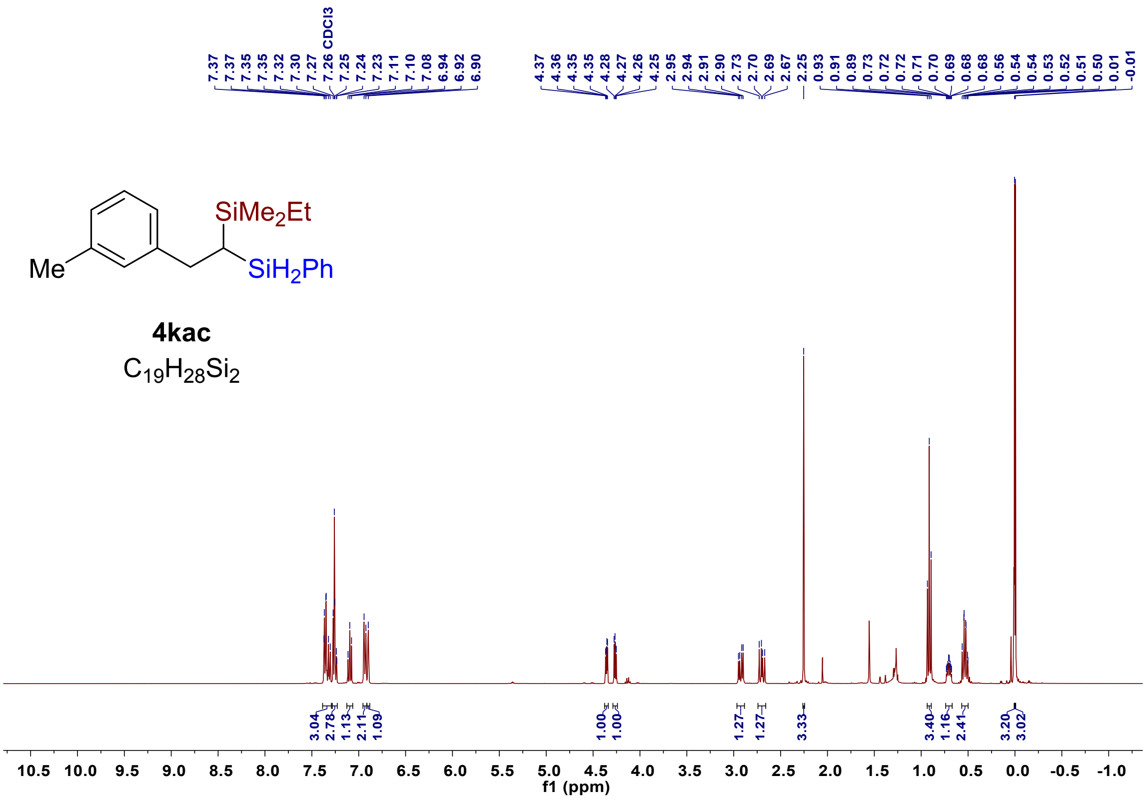


Figure S41. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4kac**.

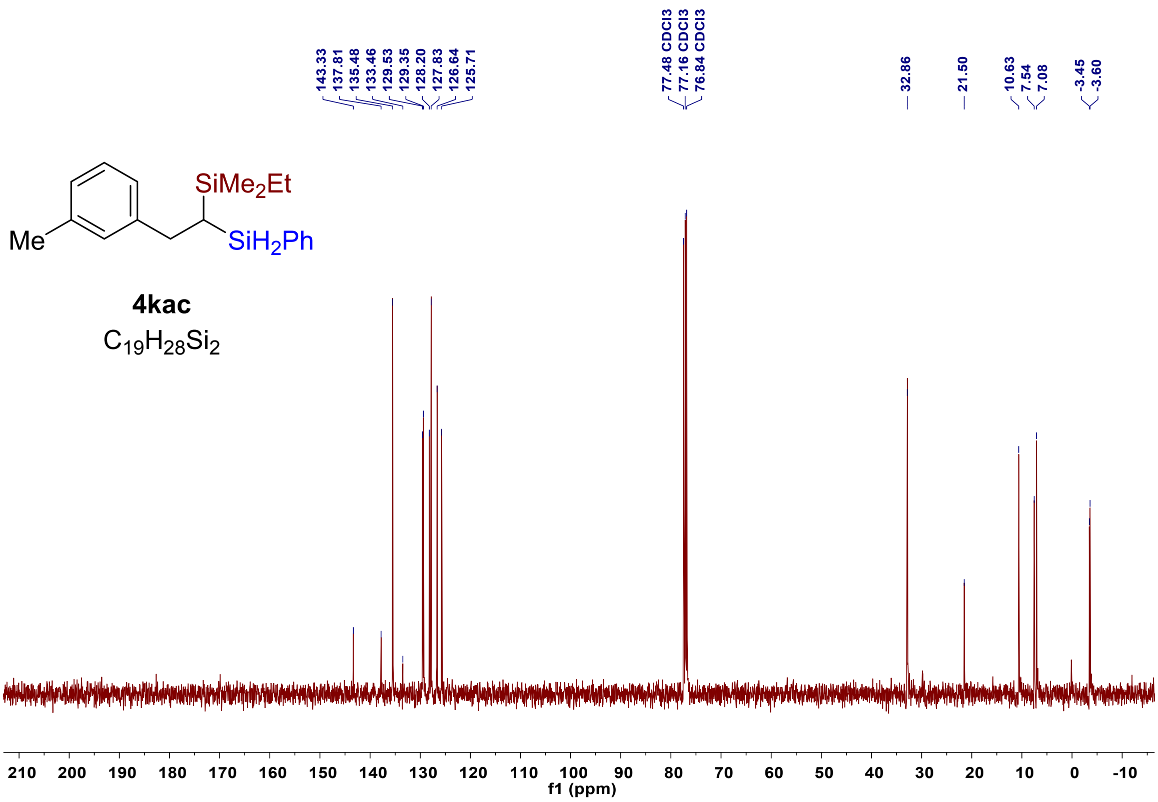


Figure S42. [13]**C{**[1]**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4kac**.

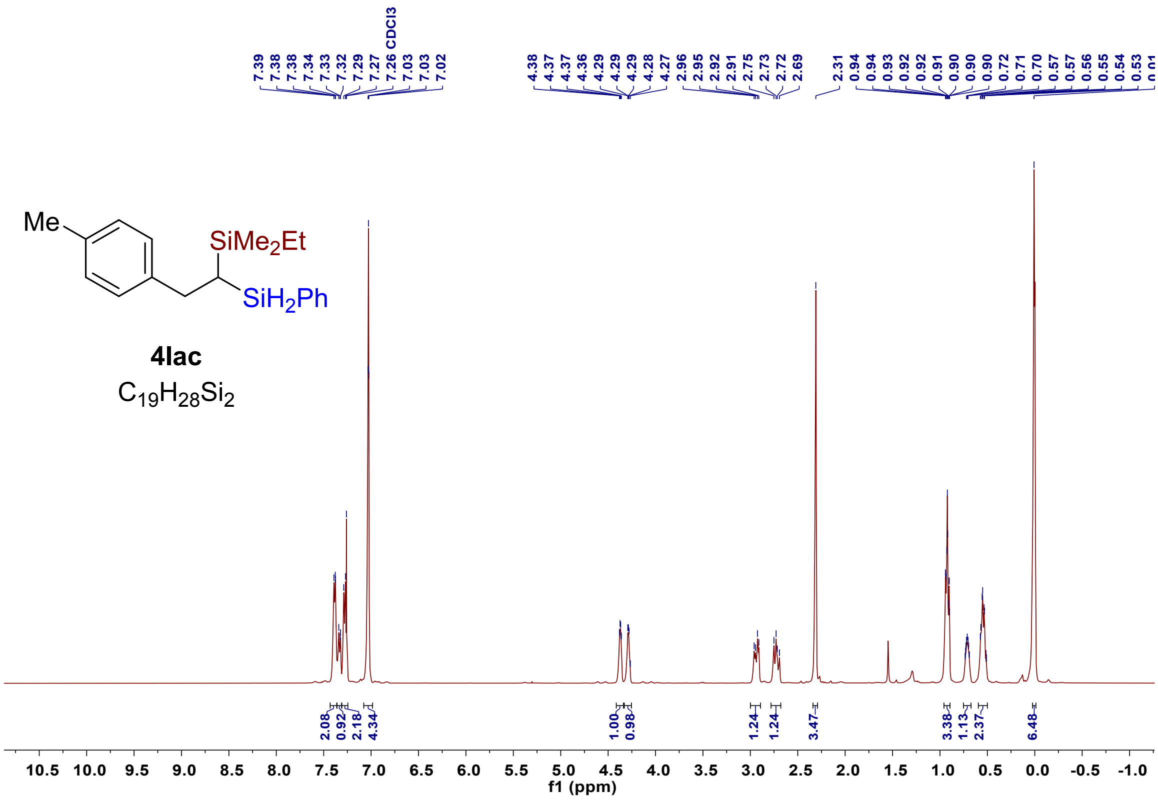


Figure S43. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4lac**.

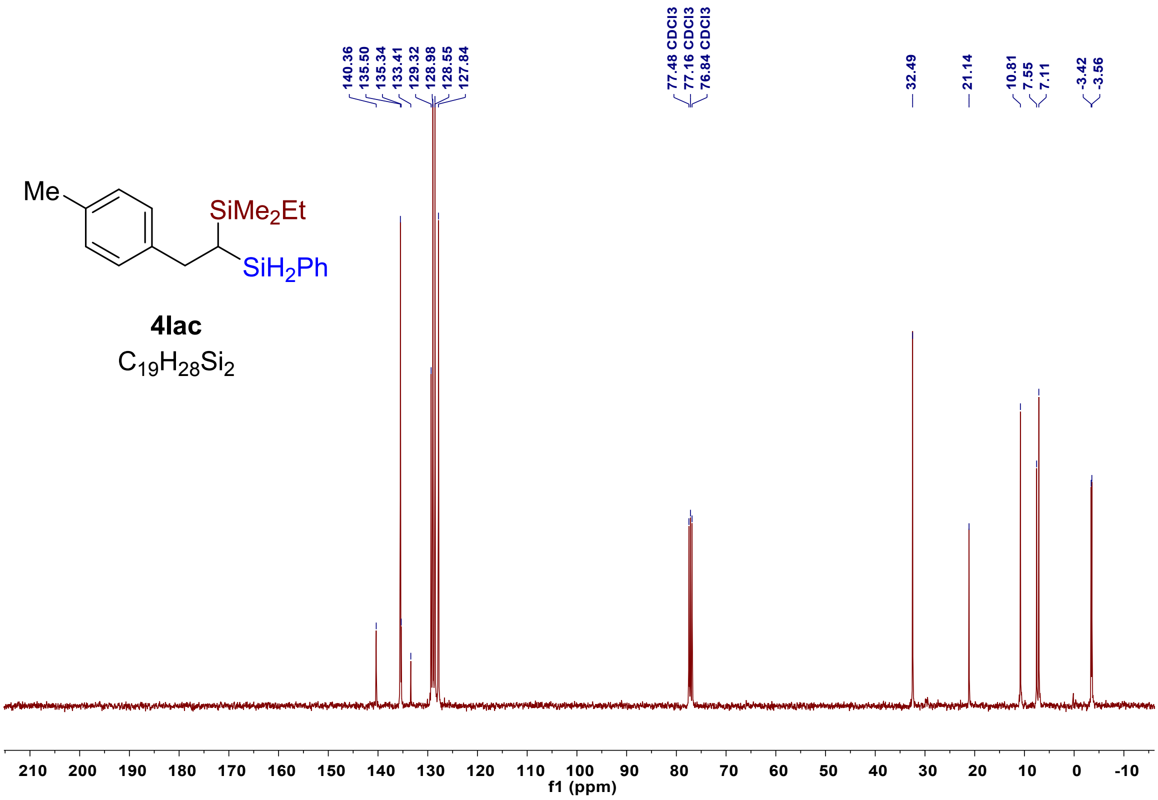


Figure S44. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4lac**.

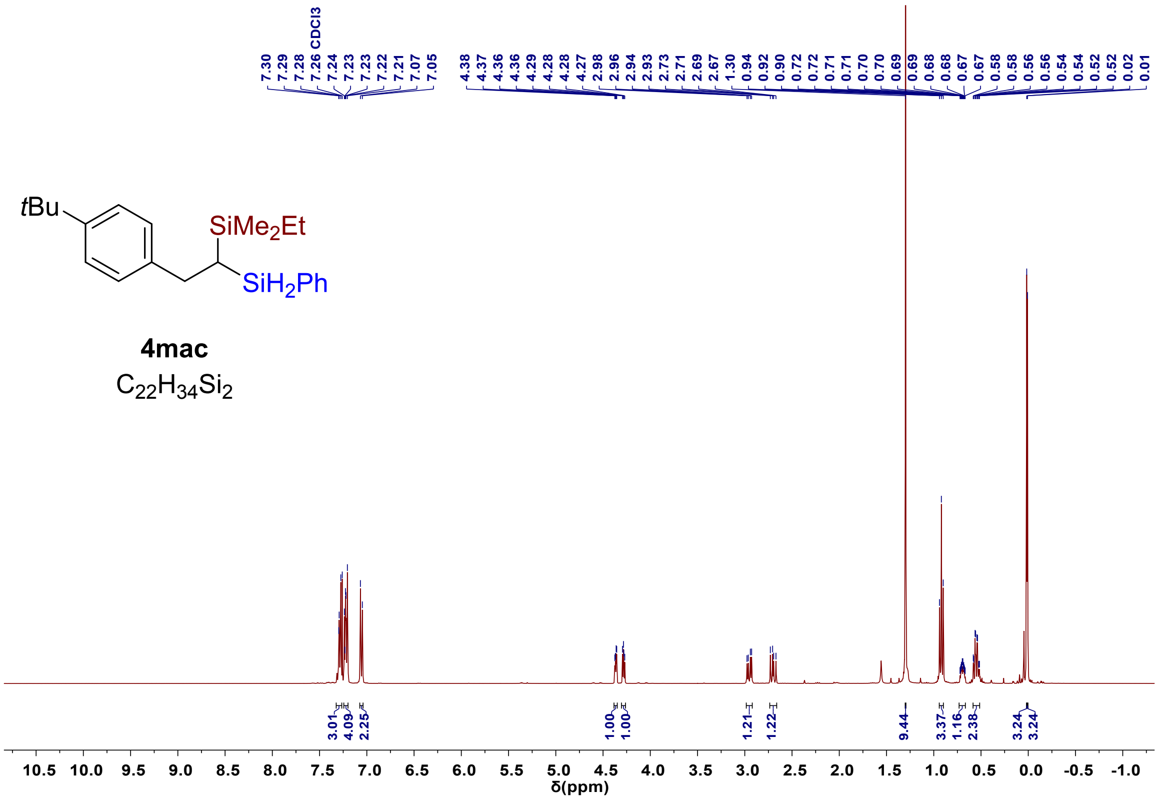


Figure S45. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4mac**.

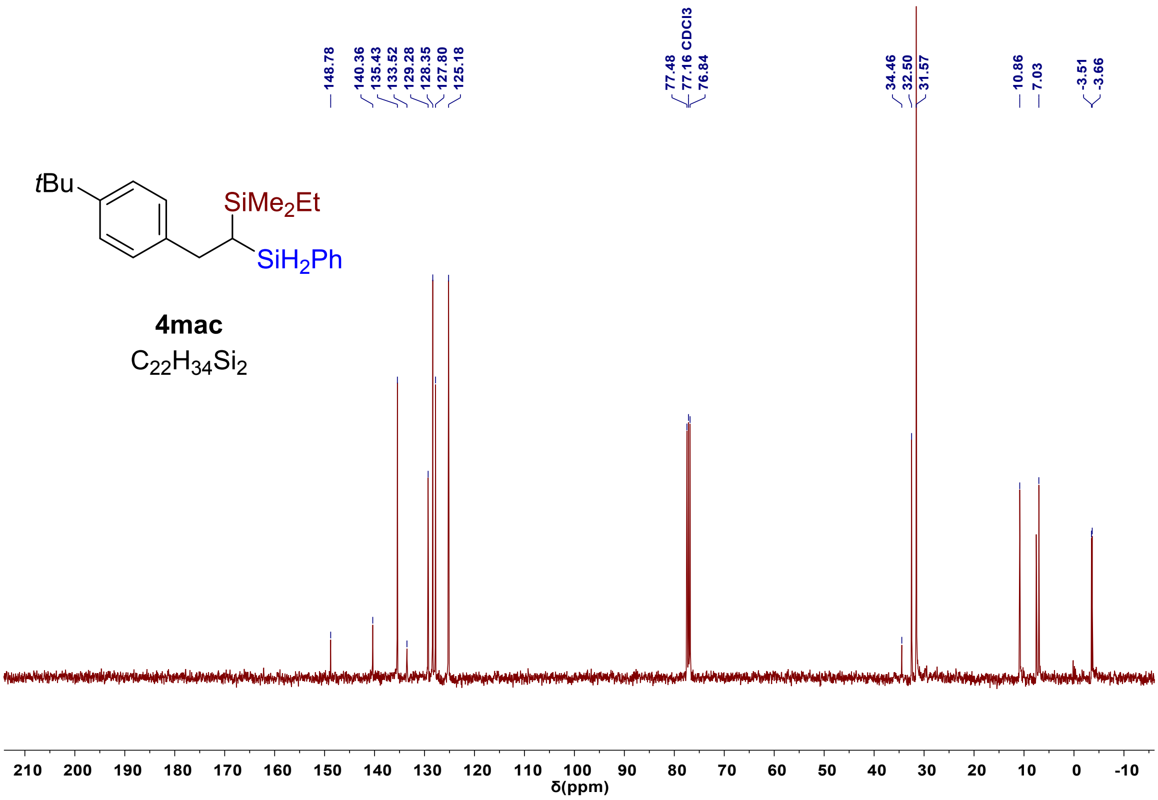


Figure S46. [13]**C{**[1]**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4mac**.

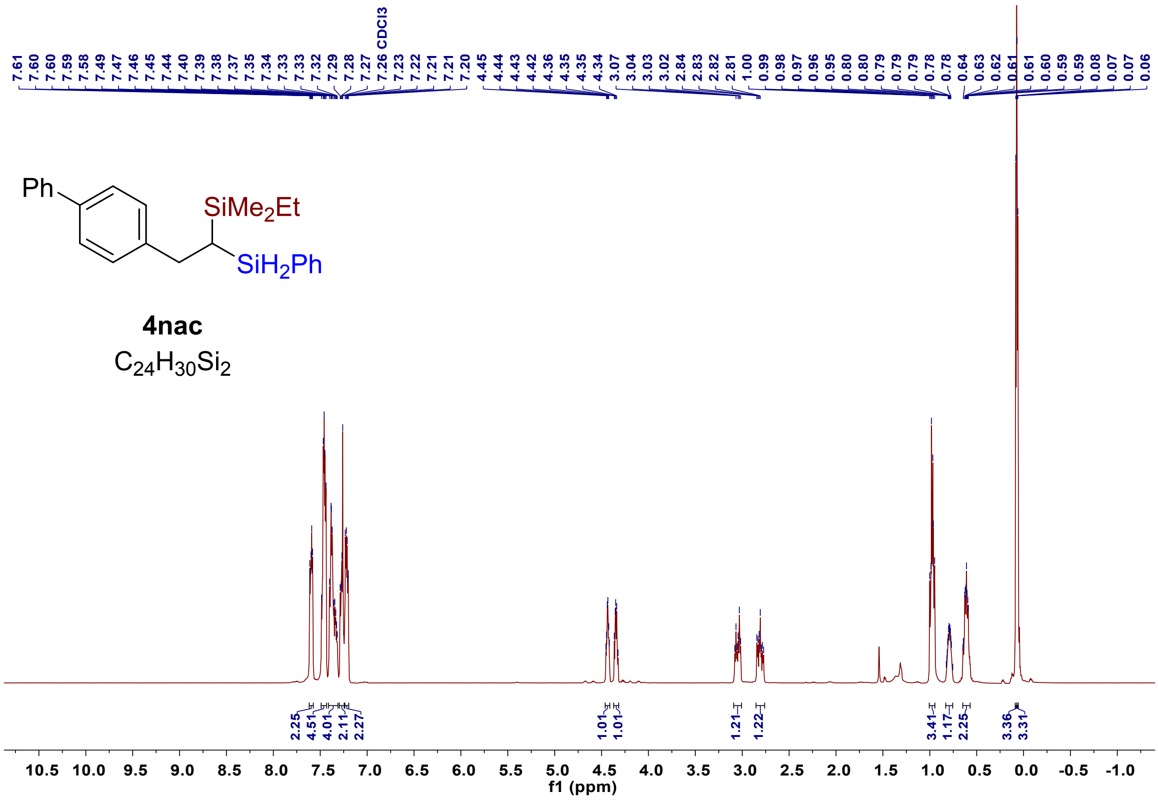


Figure S47. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4nac**.

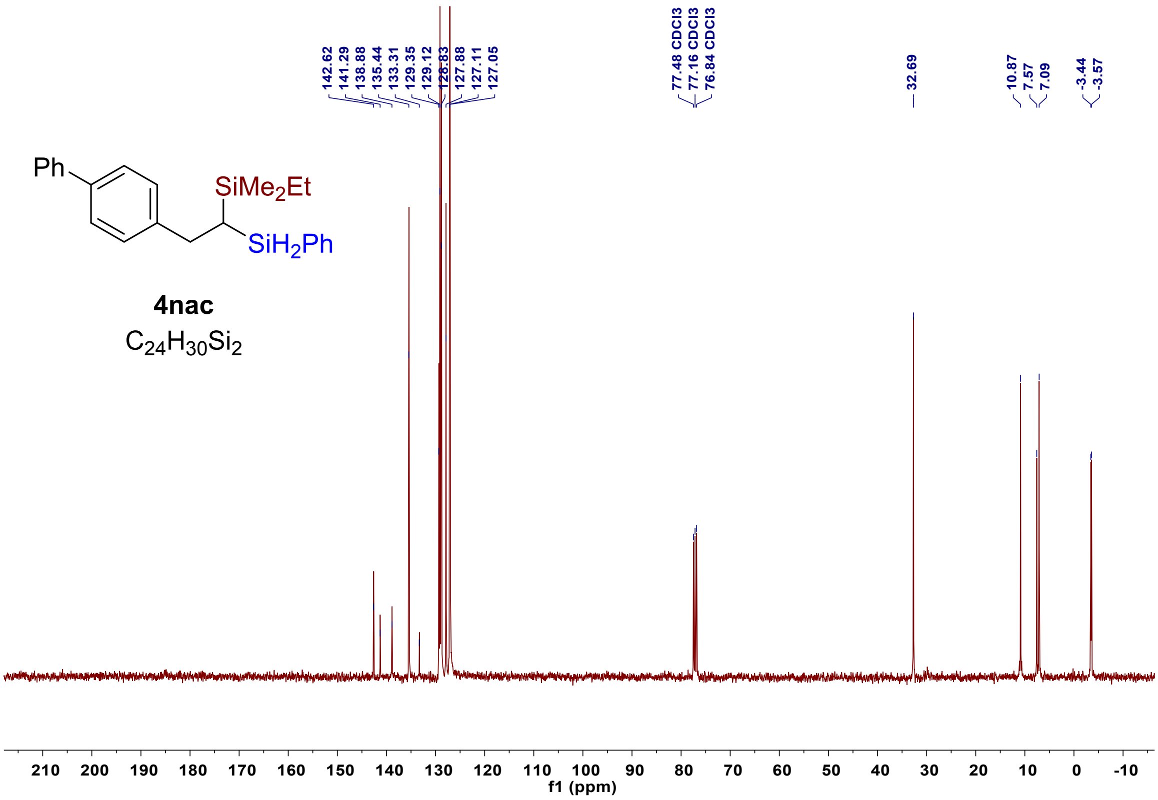


Figure S48. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4nac**.

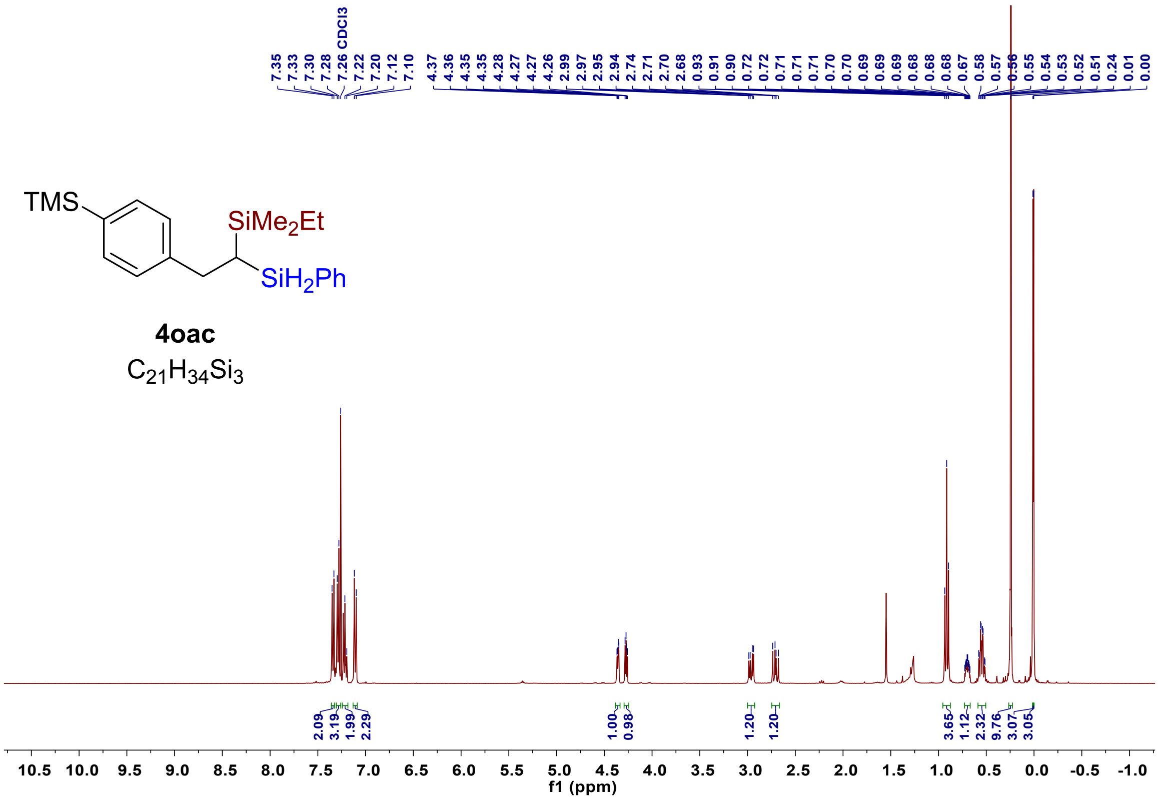


Figure S49. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4oac**.

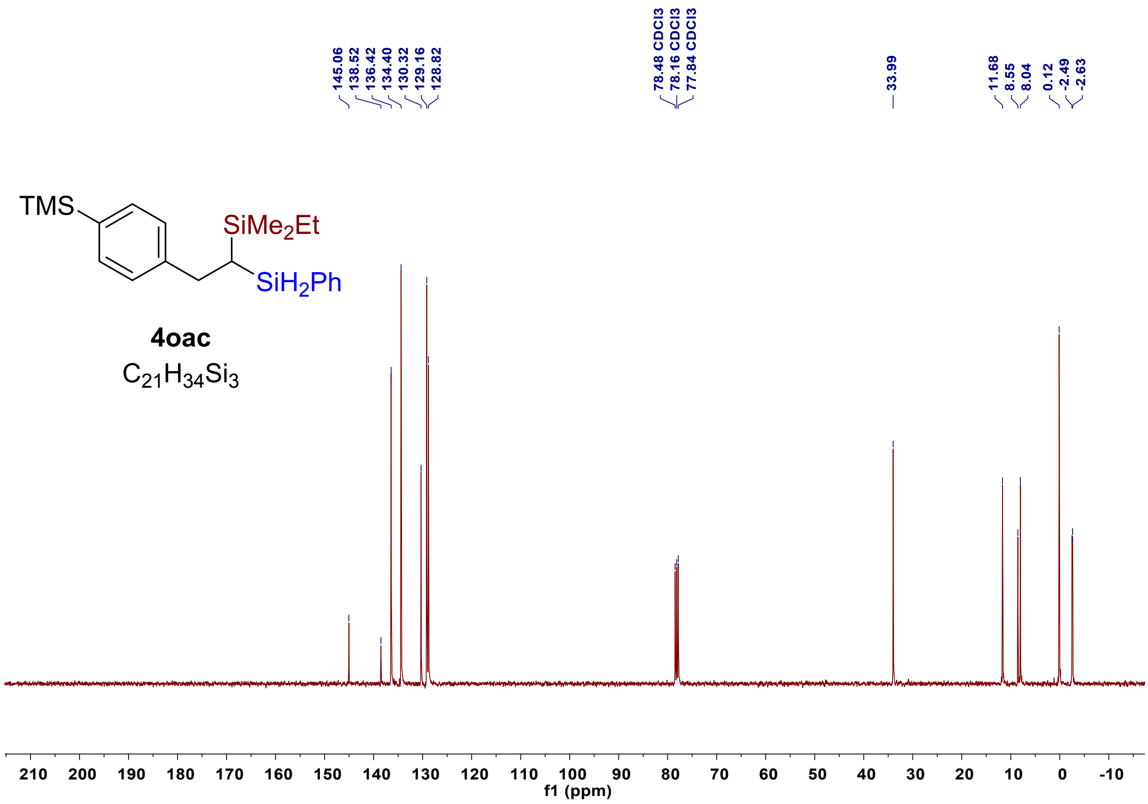


Figure S50. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4oac**.

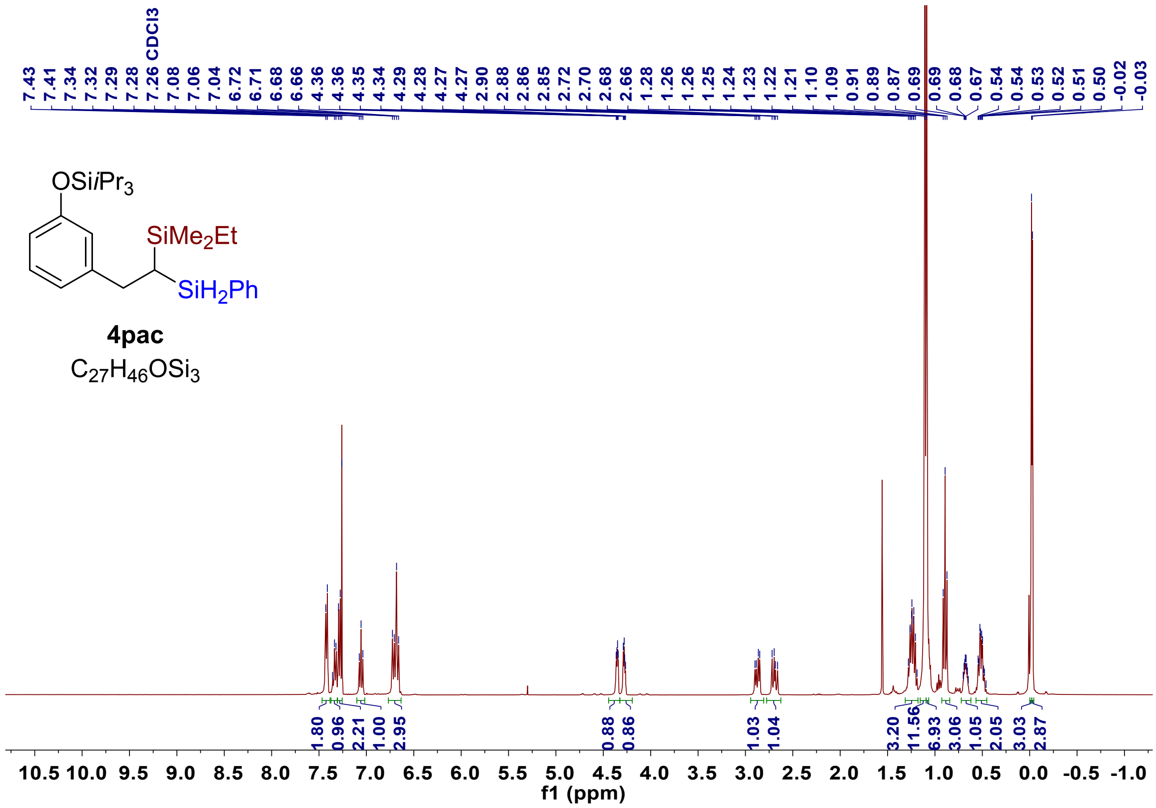


Figure S51. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4pac**.

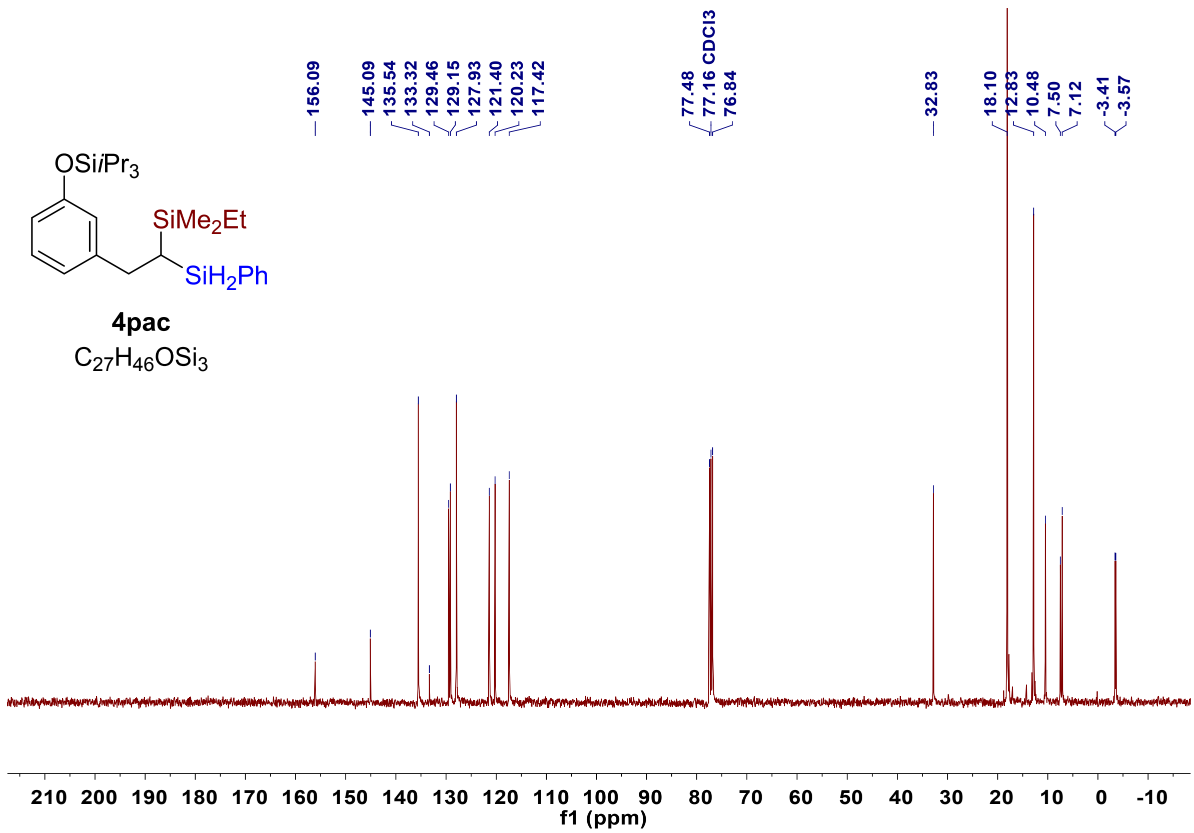


Figure S52. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4pac**.

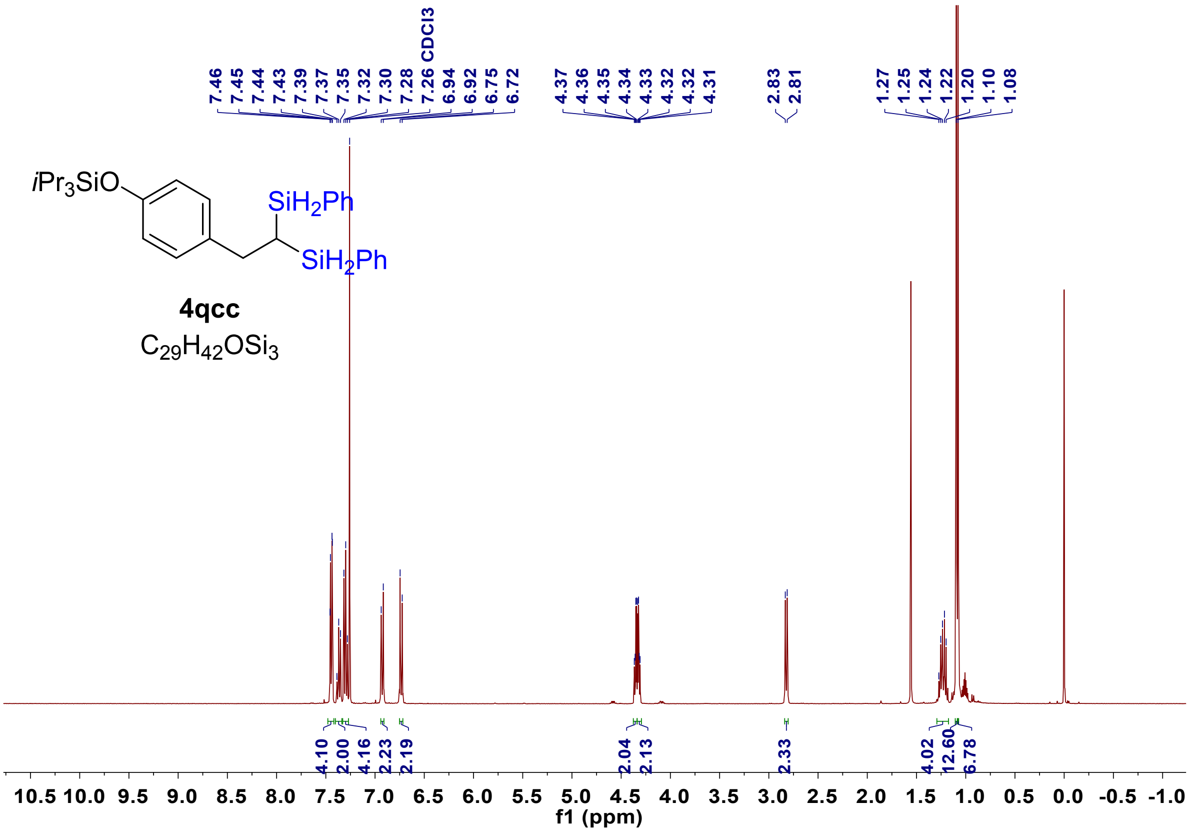


Figure S53. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4qcc**.

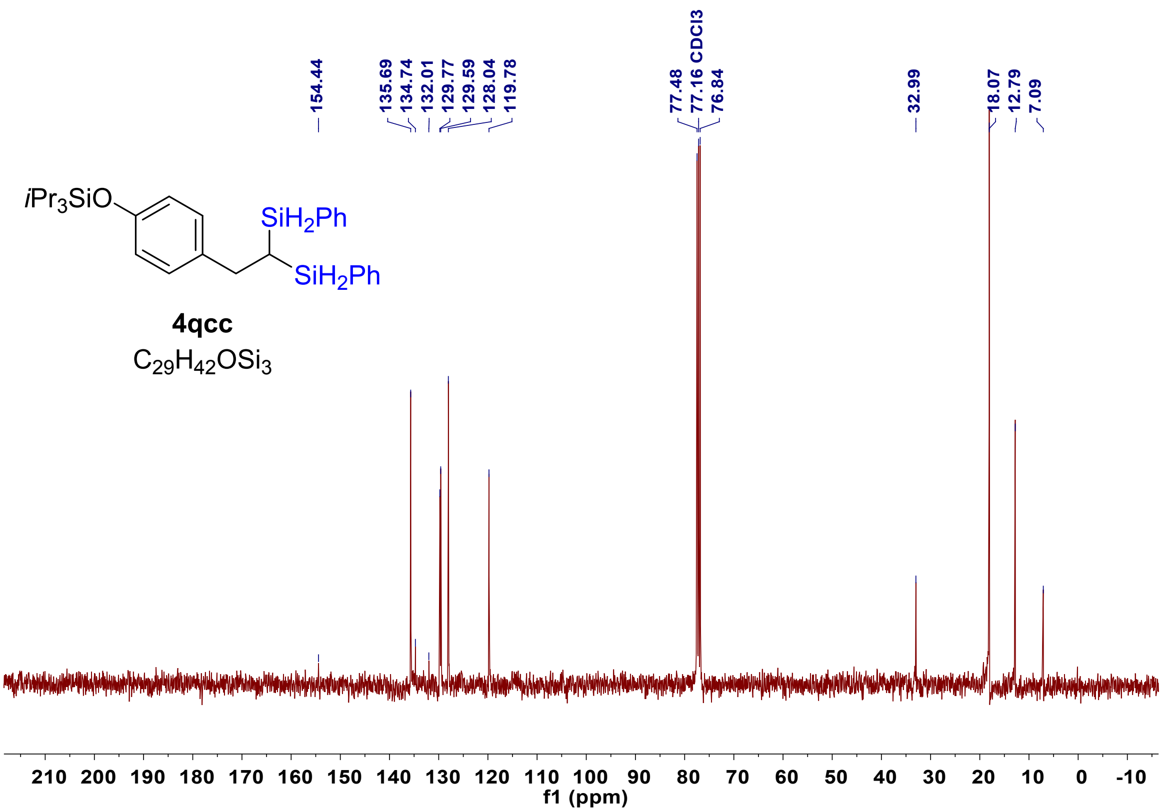


Figure S54. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4qcc.**

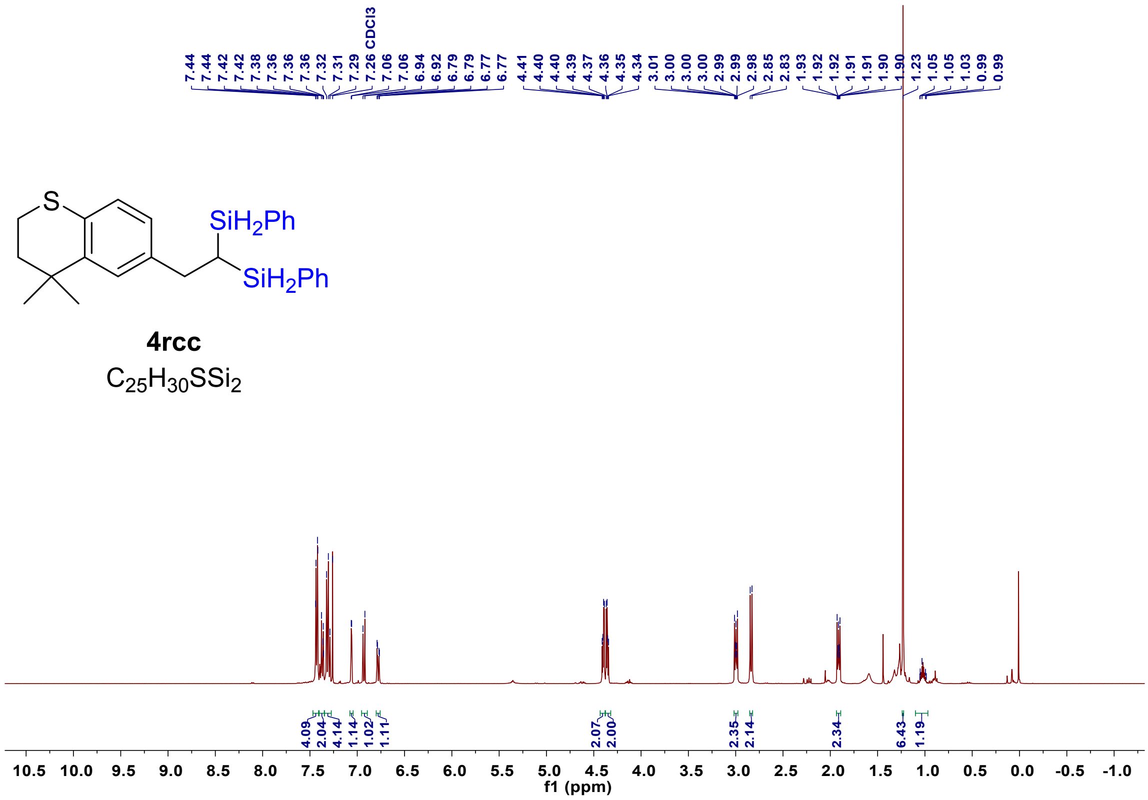


Figure S55. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4rcc**.

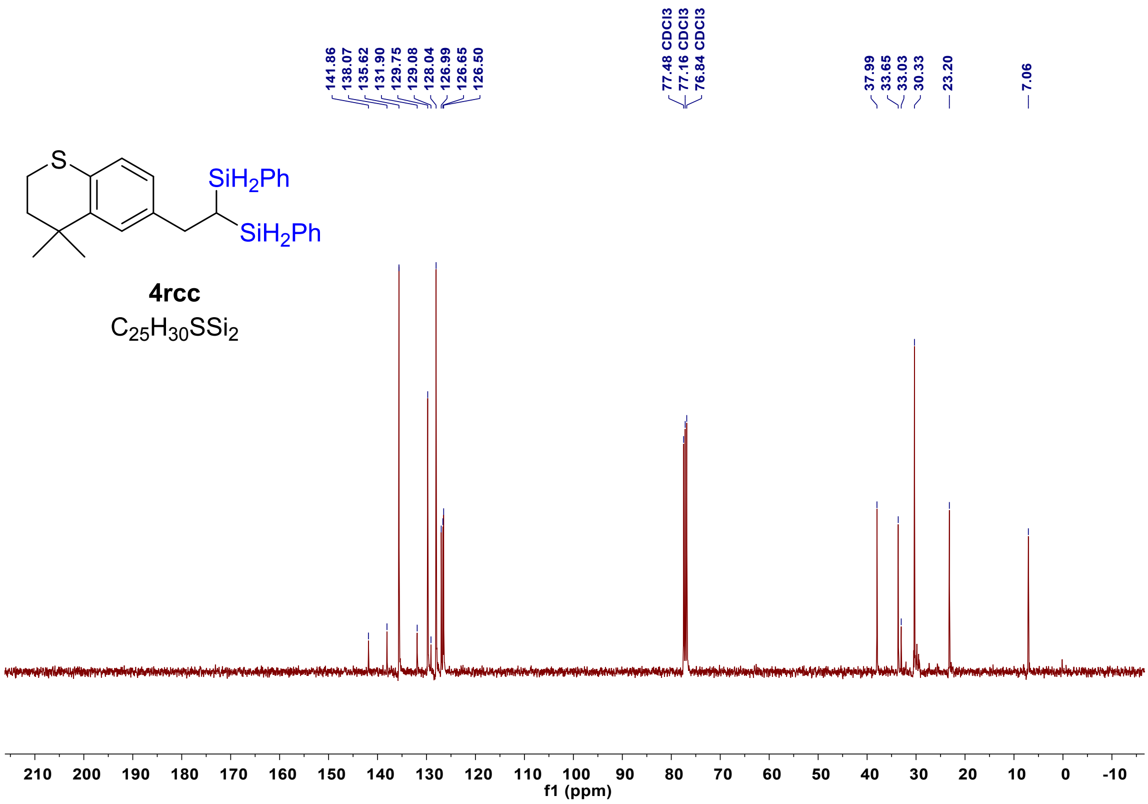


Figure S56. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4rcc**.

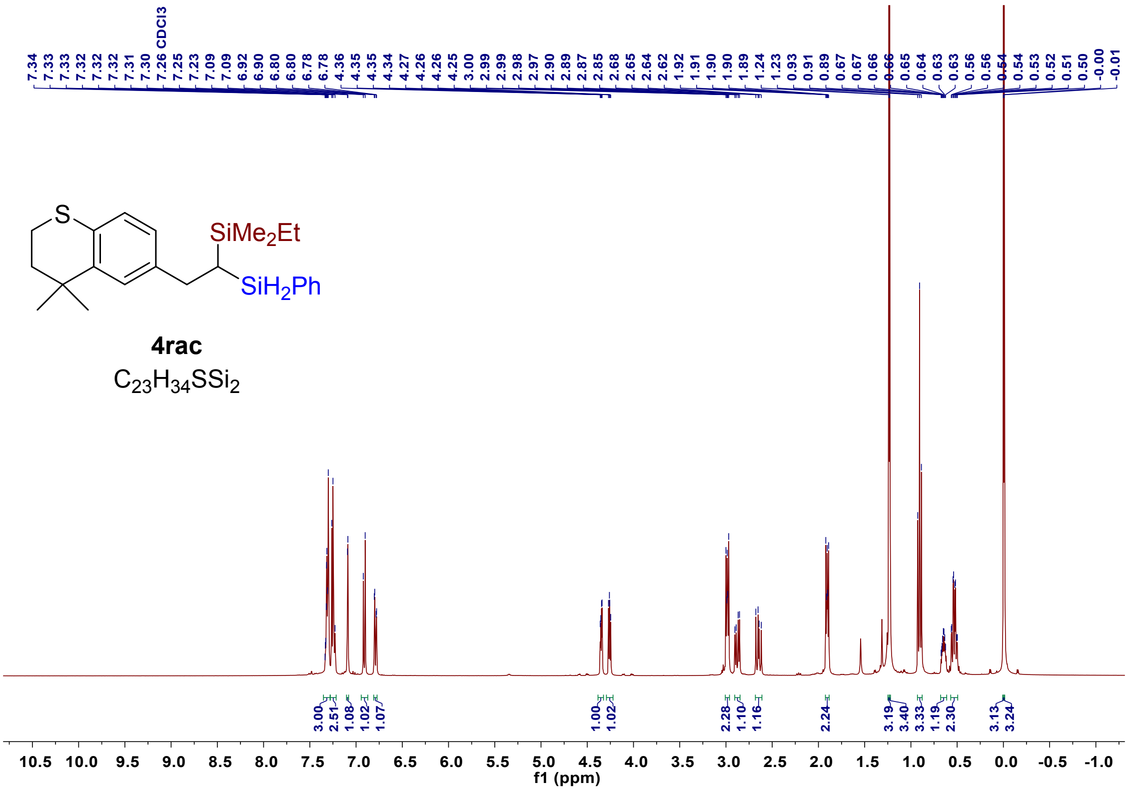


Figure S57. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4rac**.

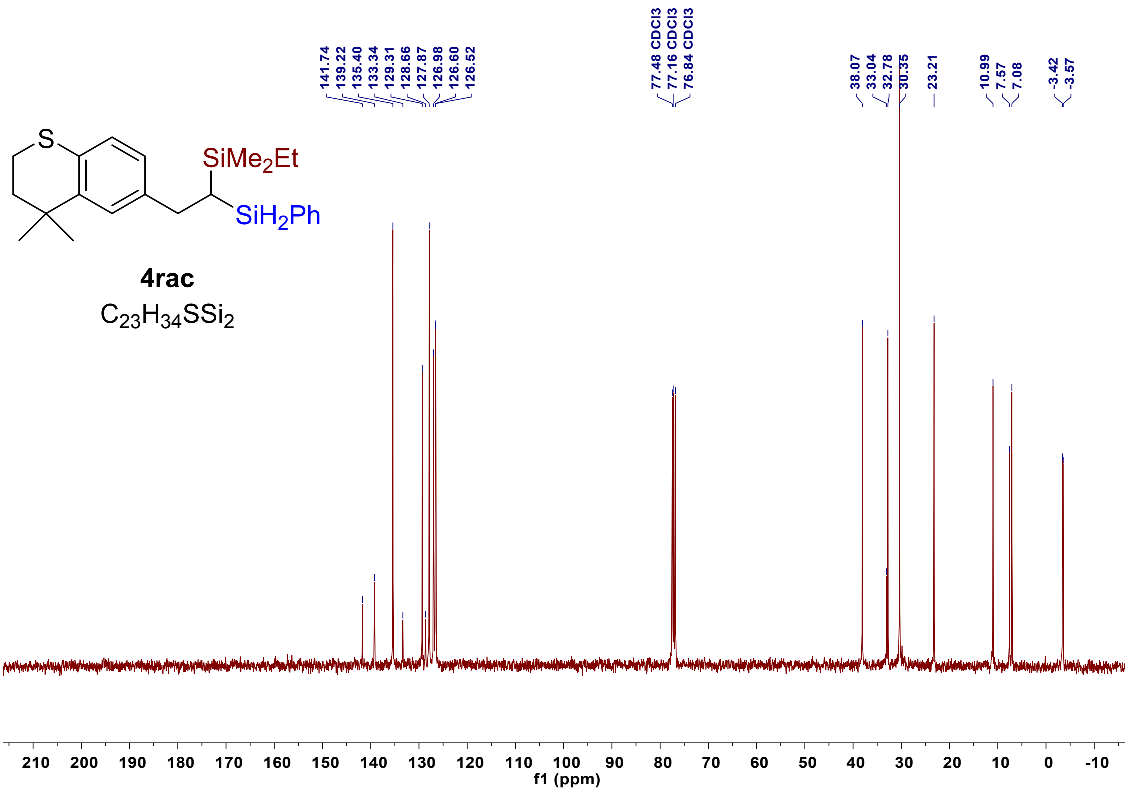


Figure S58. ^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4rac**.

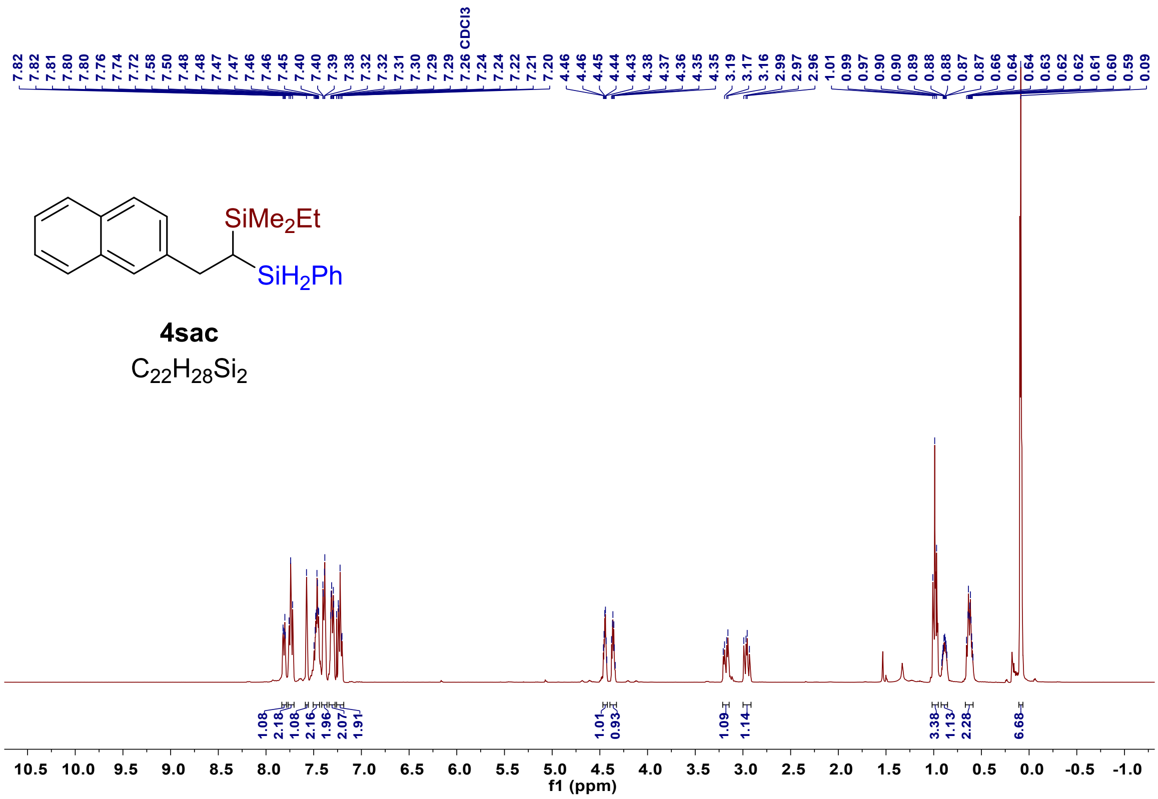


Figure S59. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4sac**.

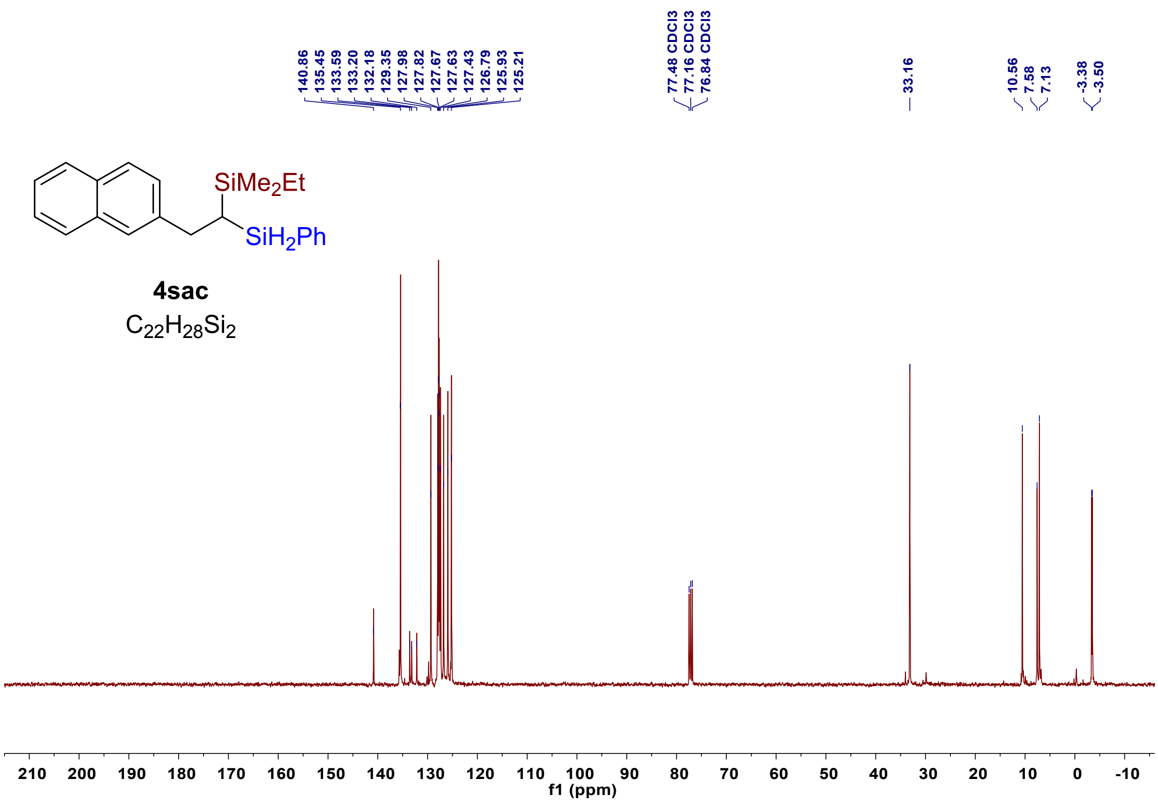


Figure S60. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4sac**.

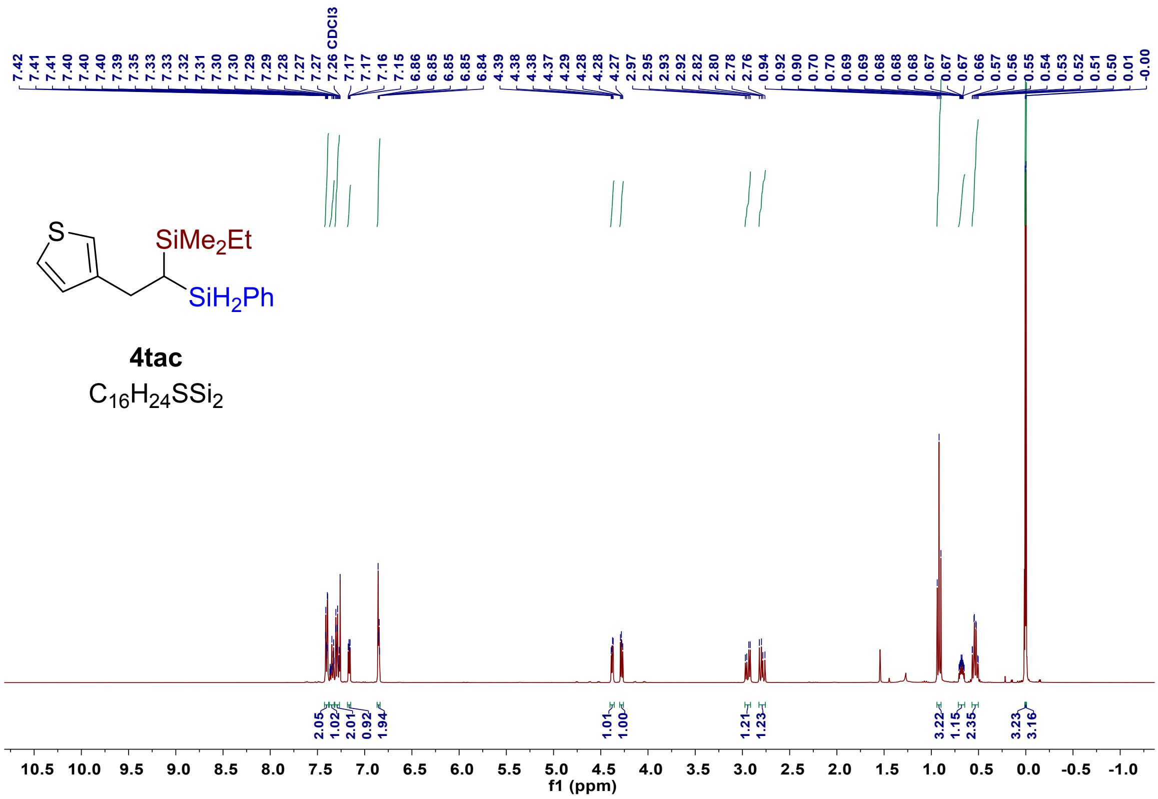


Figure S61. **[1]H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4tac**.

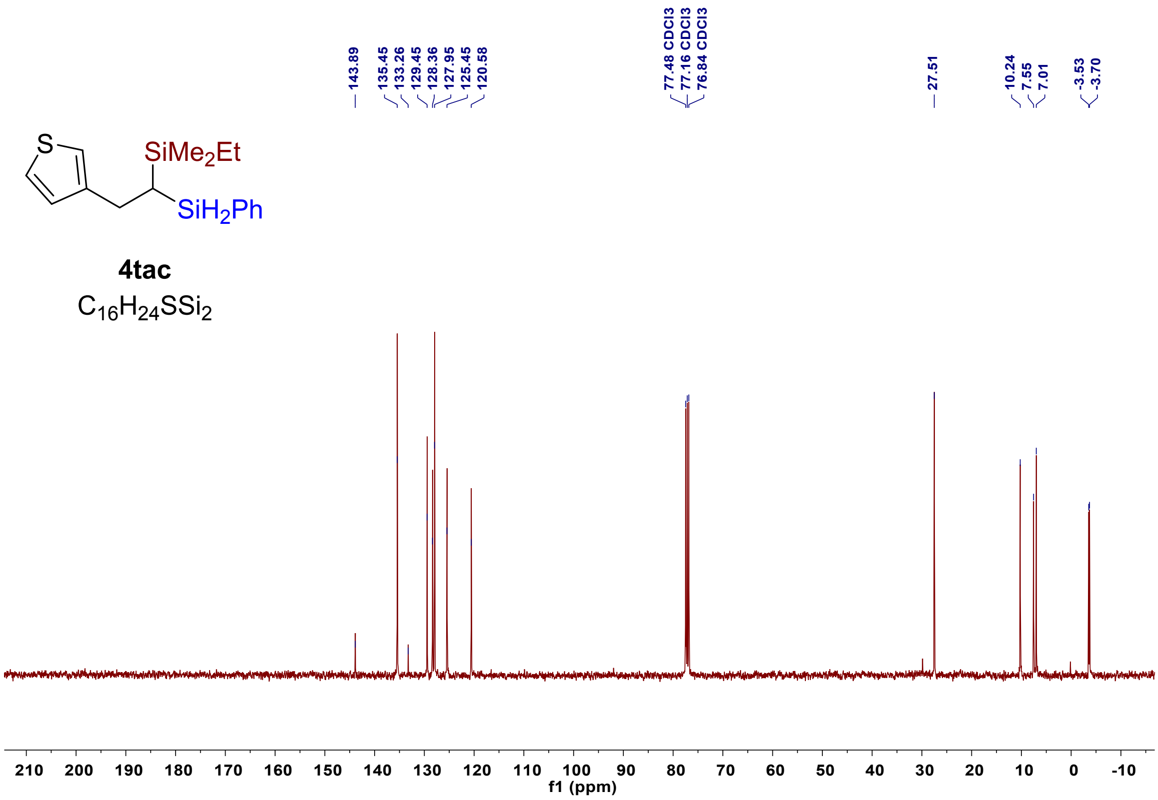


Figure S62. **[13]C{[1]H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4tac**.

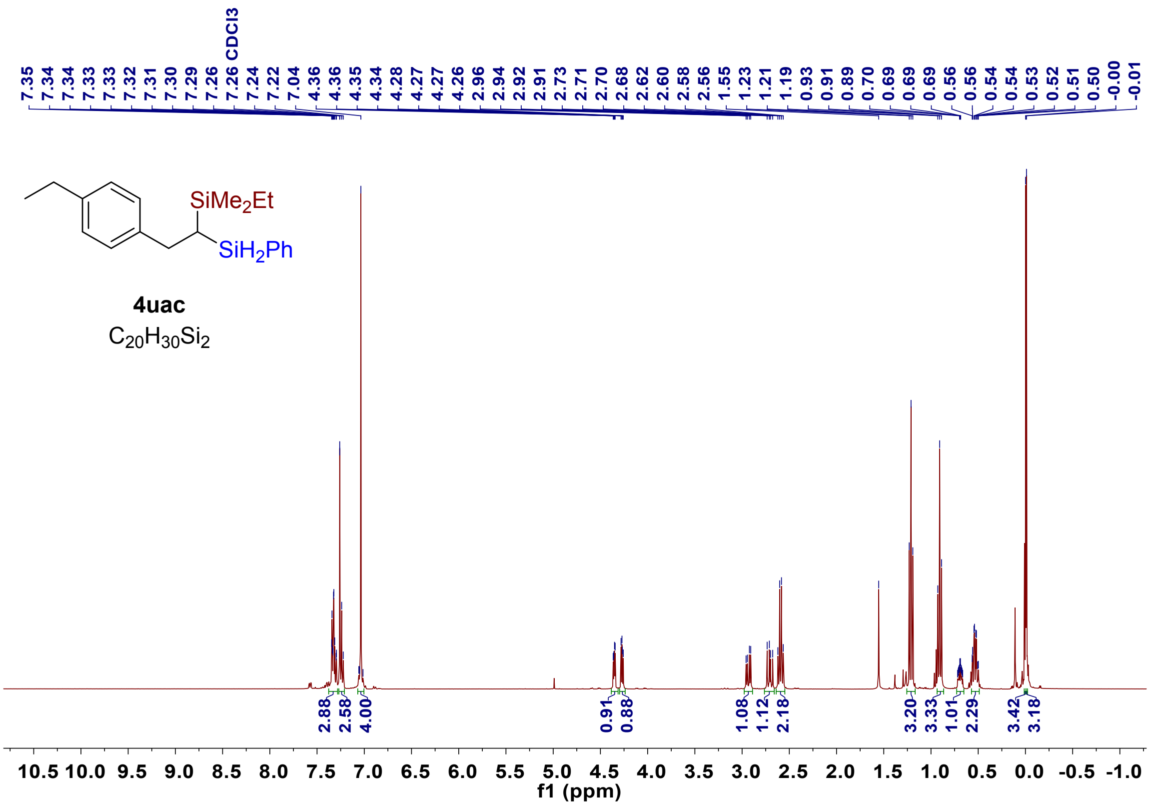


Figure S63. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4uac**.

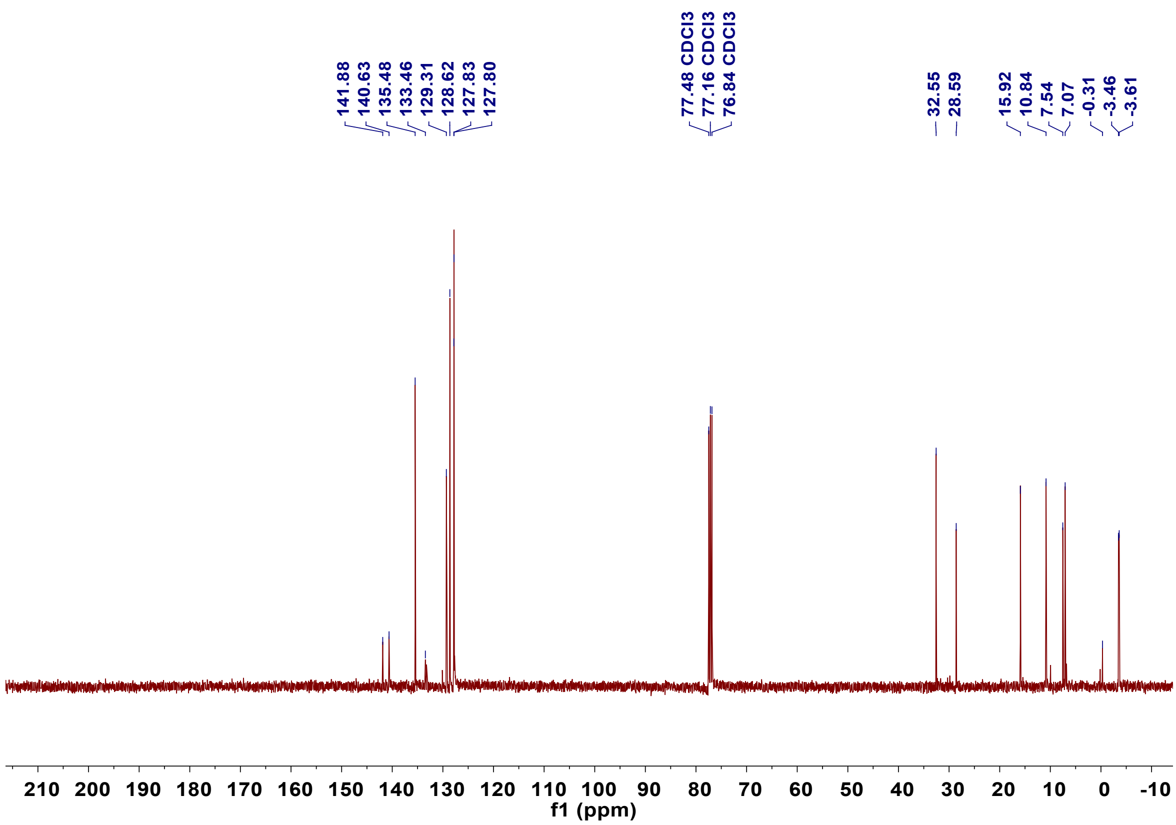


Figure S64. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4uac**.

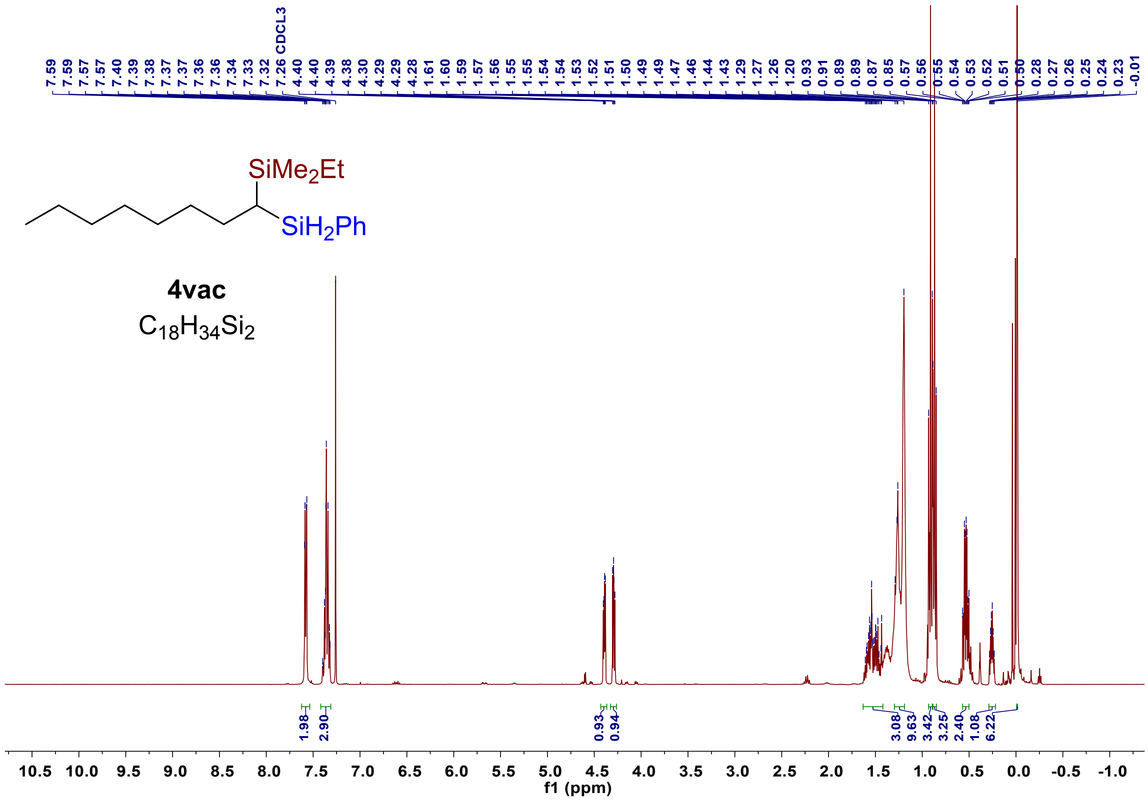


Figure S65. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4vac**.

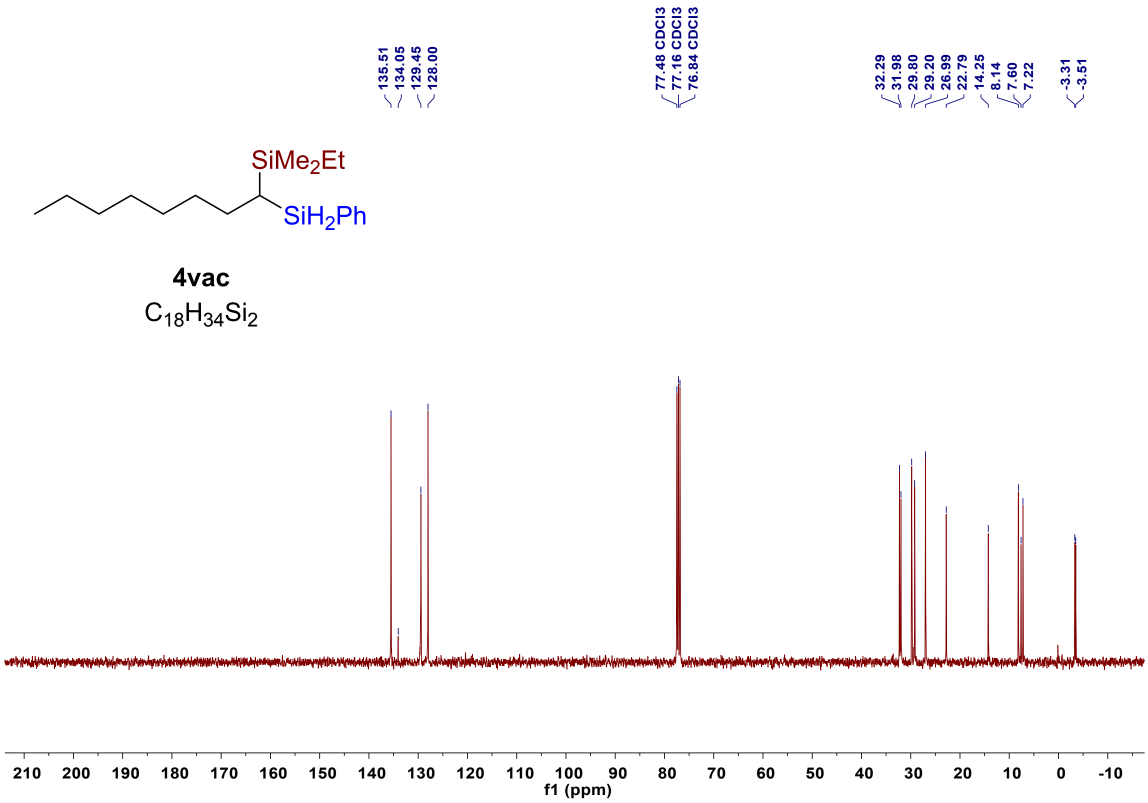


Figure S66. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4vac**.

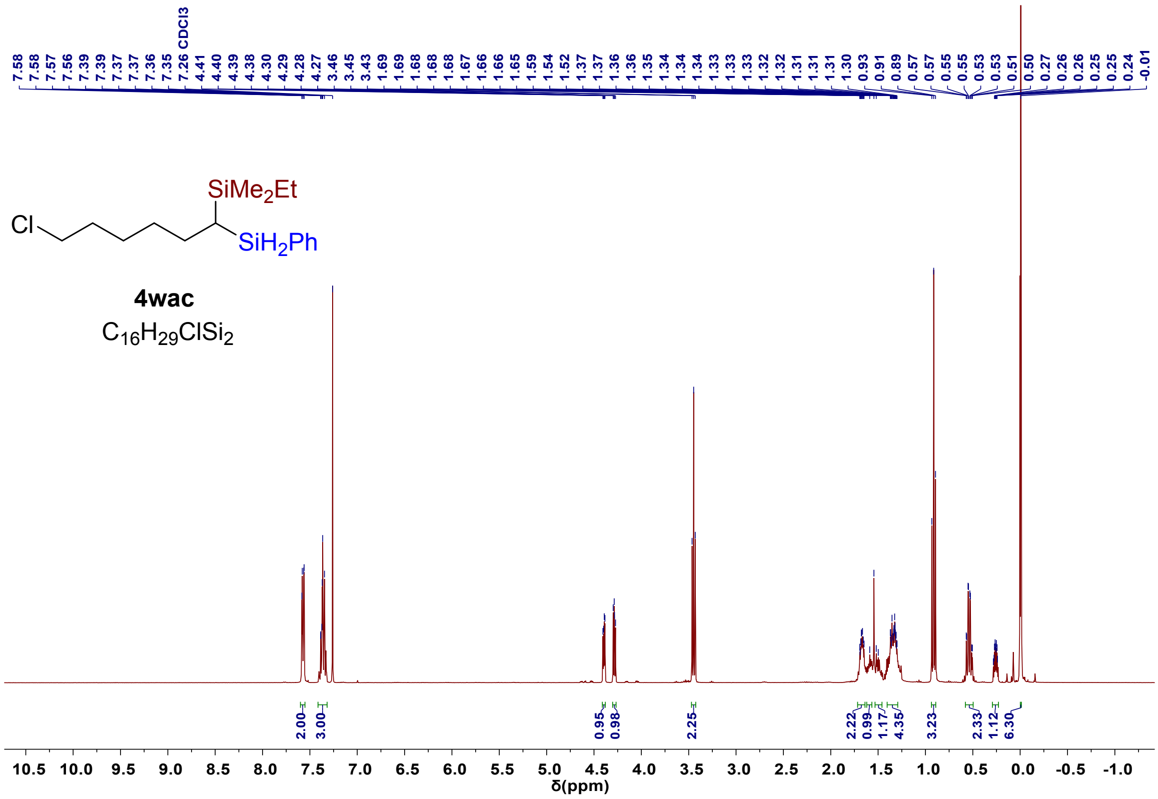


Figure S67. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4wac**.

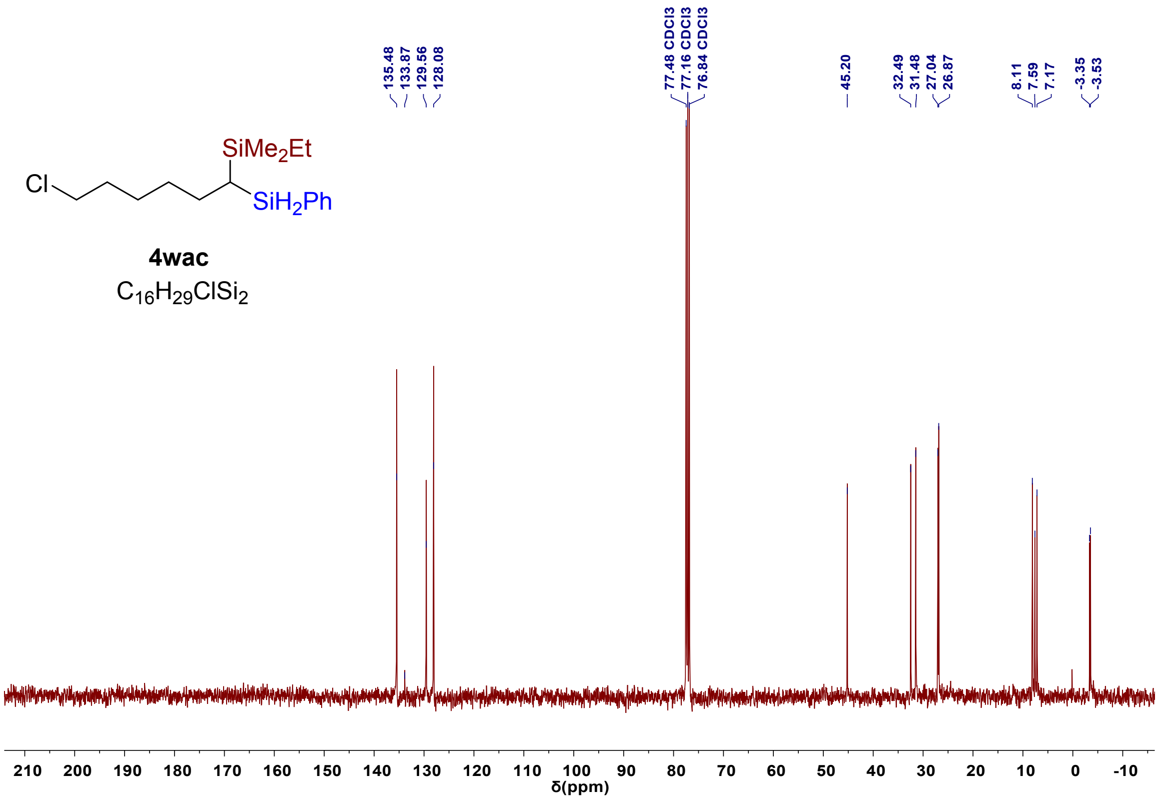


Figure S68. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4wac**.

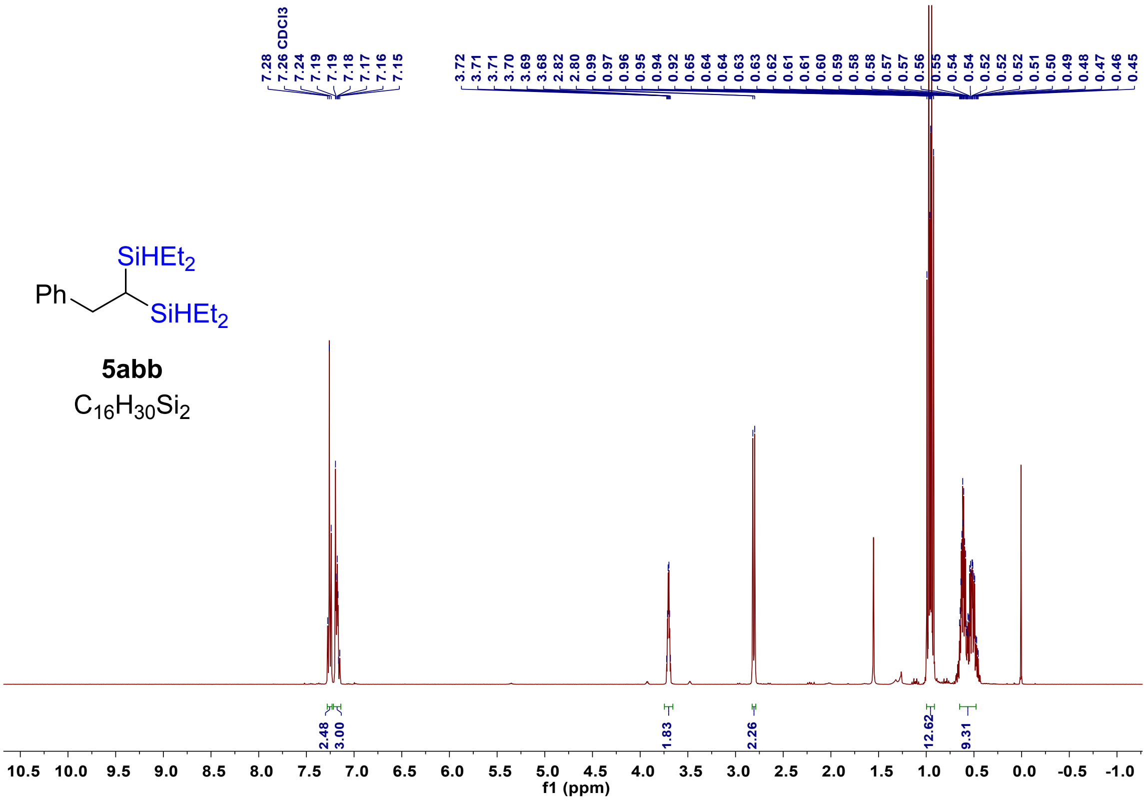


Figure S69. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **5abb**.

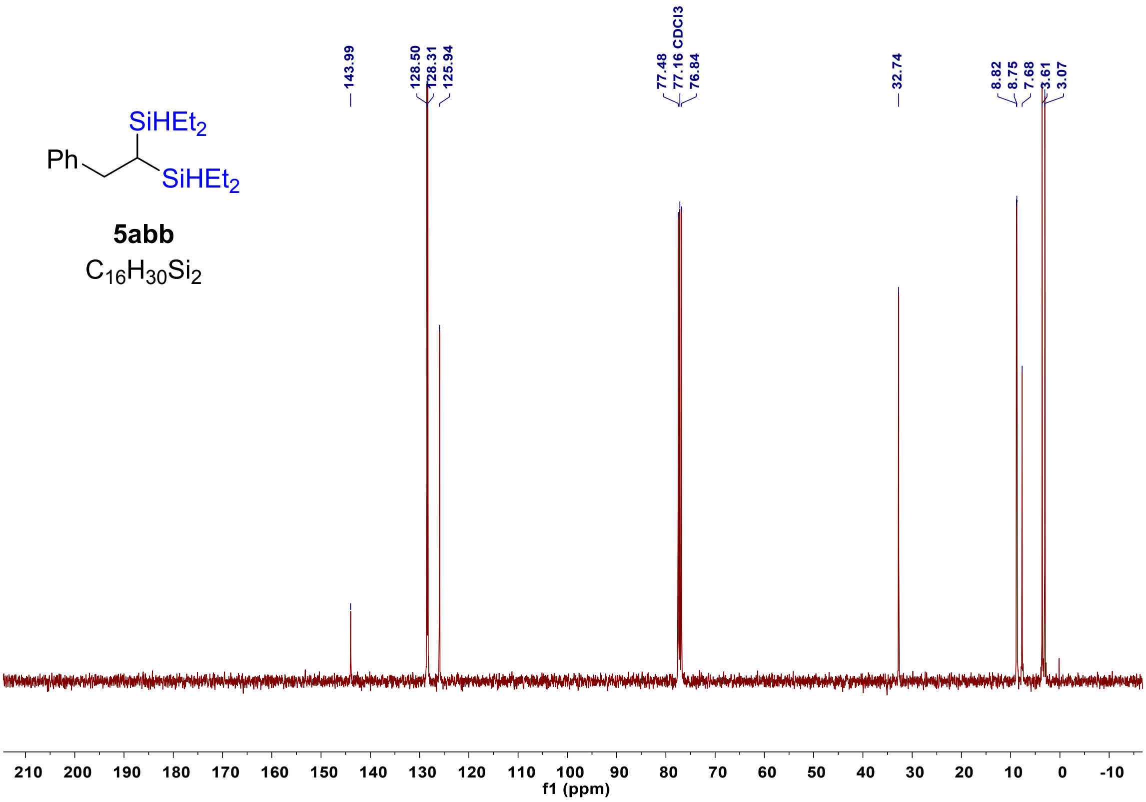


Figure S70. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **5abb**.

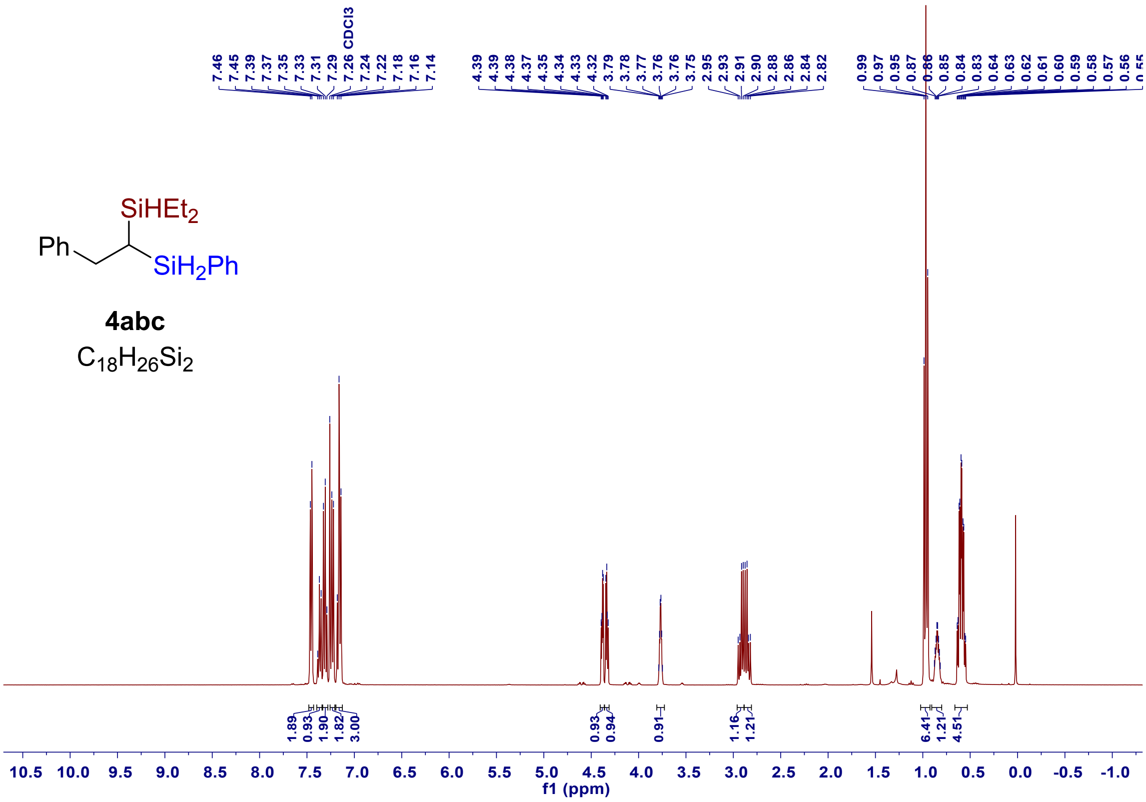


Figure S71. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4abc**.

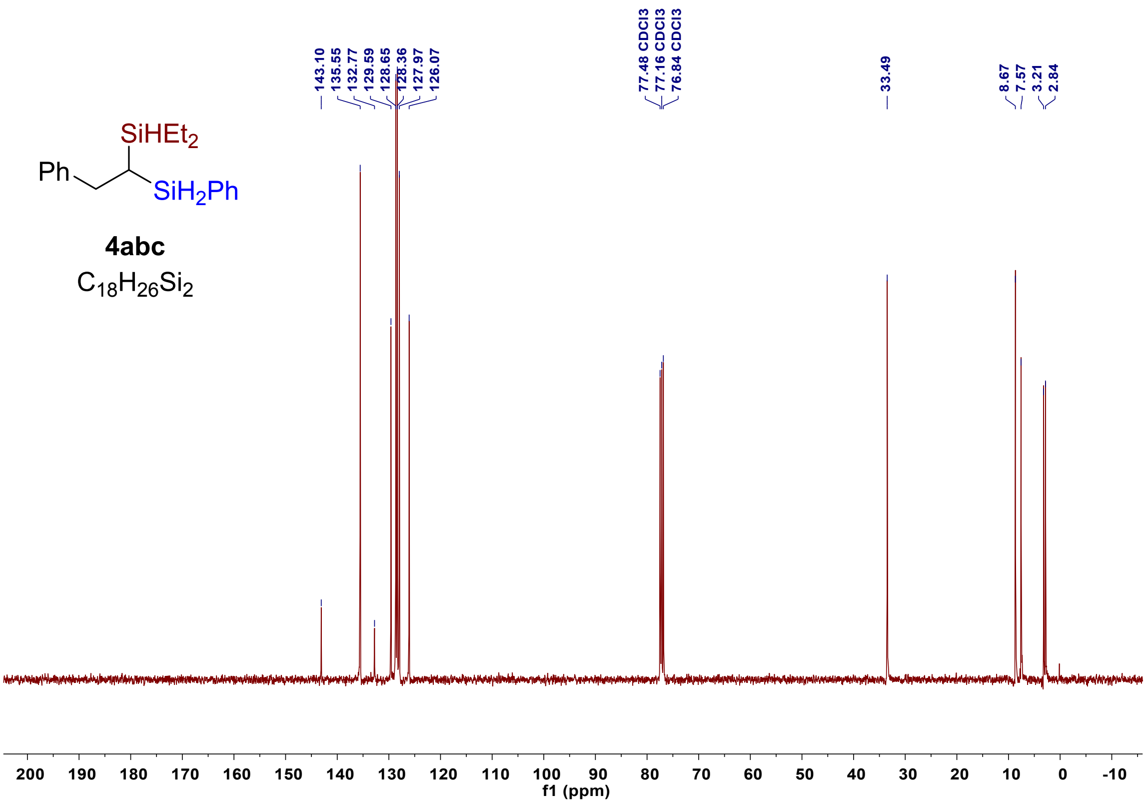


Figure S72. ^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4abc**.

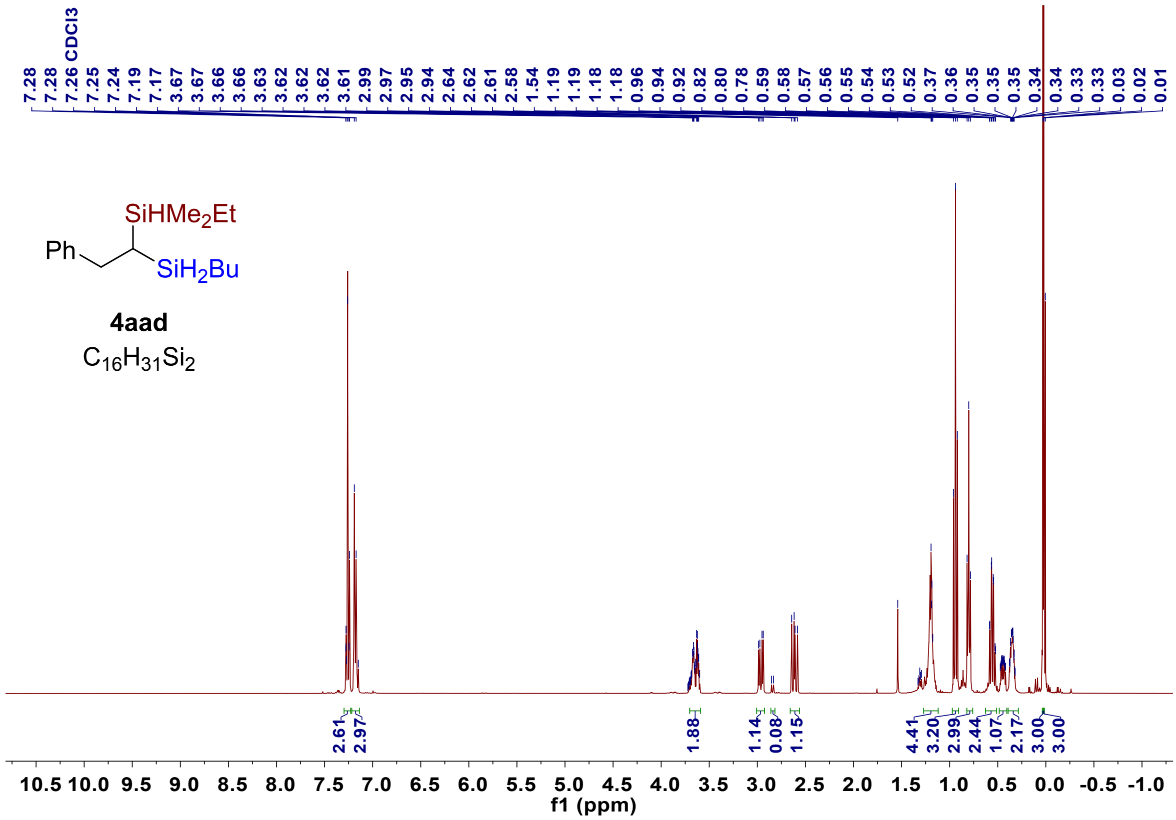


Figure S73. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4aad**.

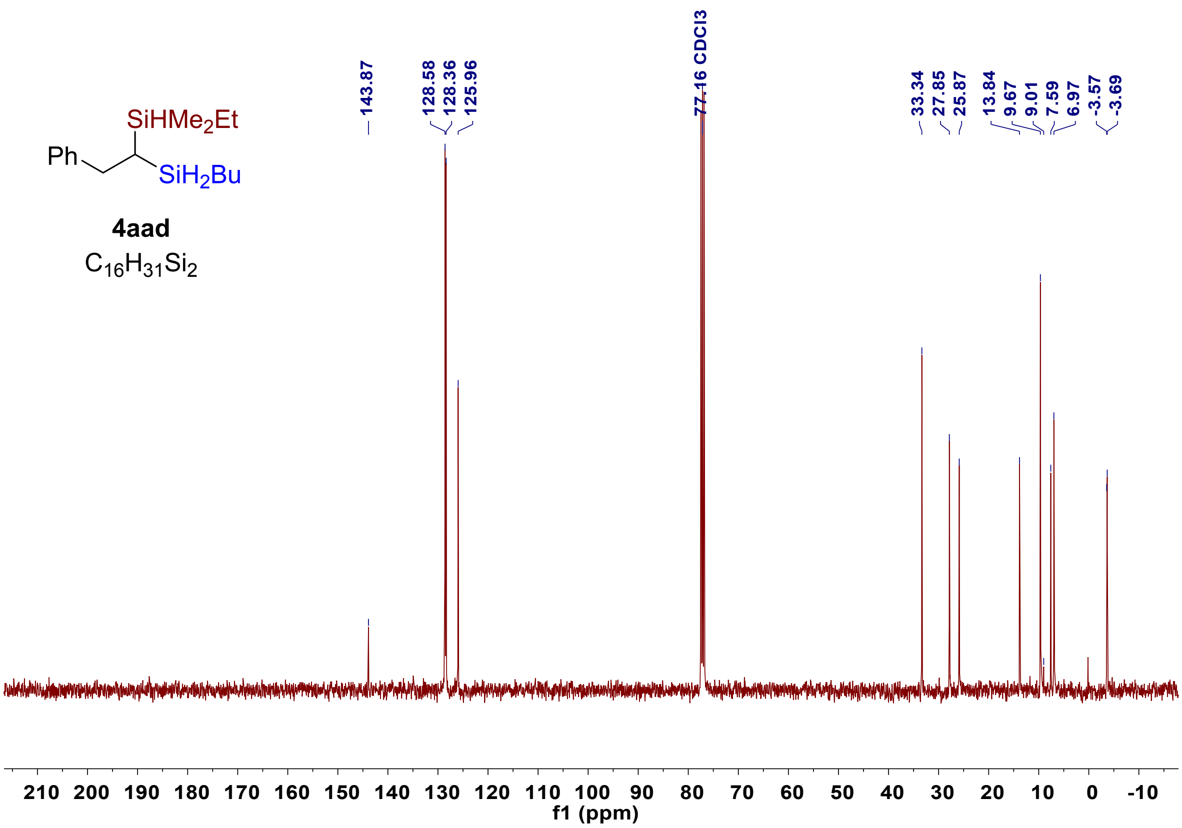


Figure S74. **$^{13}C\{^1H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **4aad**.

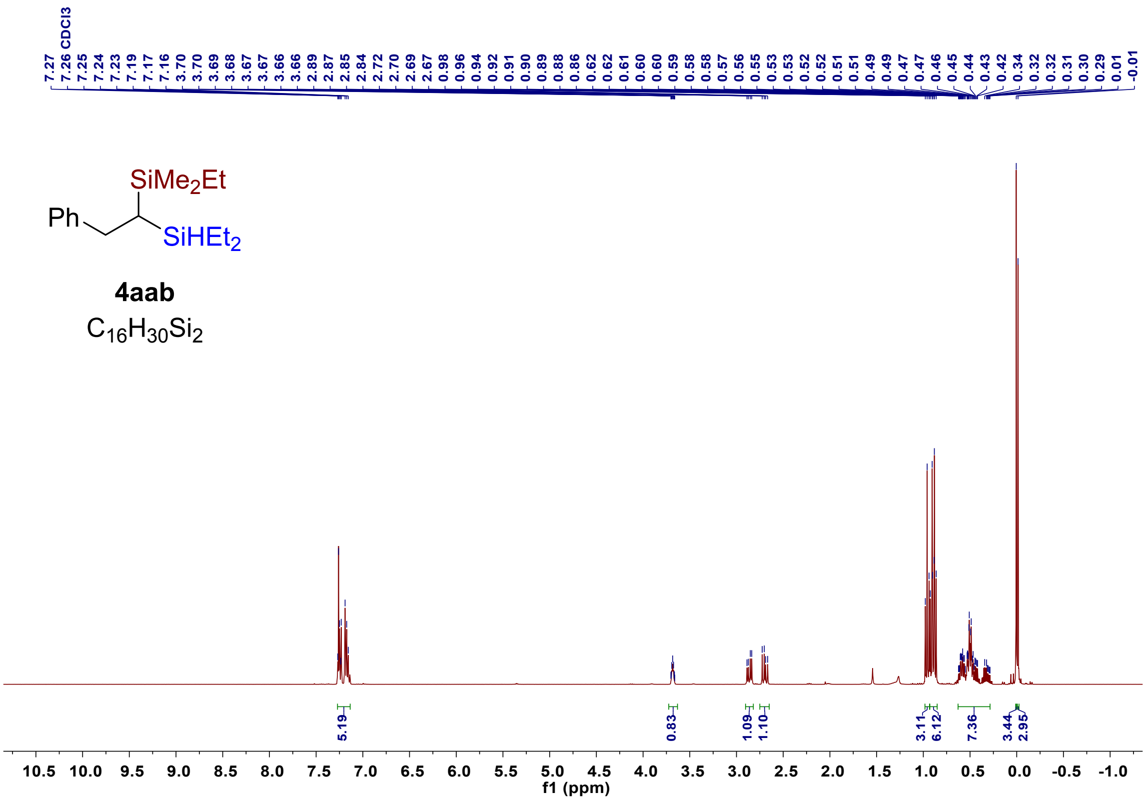


Figure S75. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4aab**.

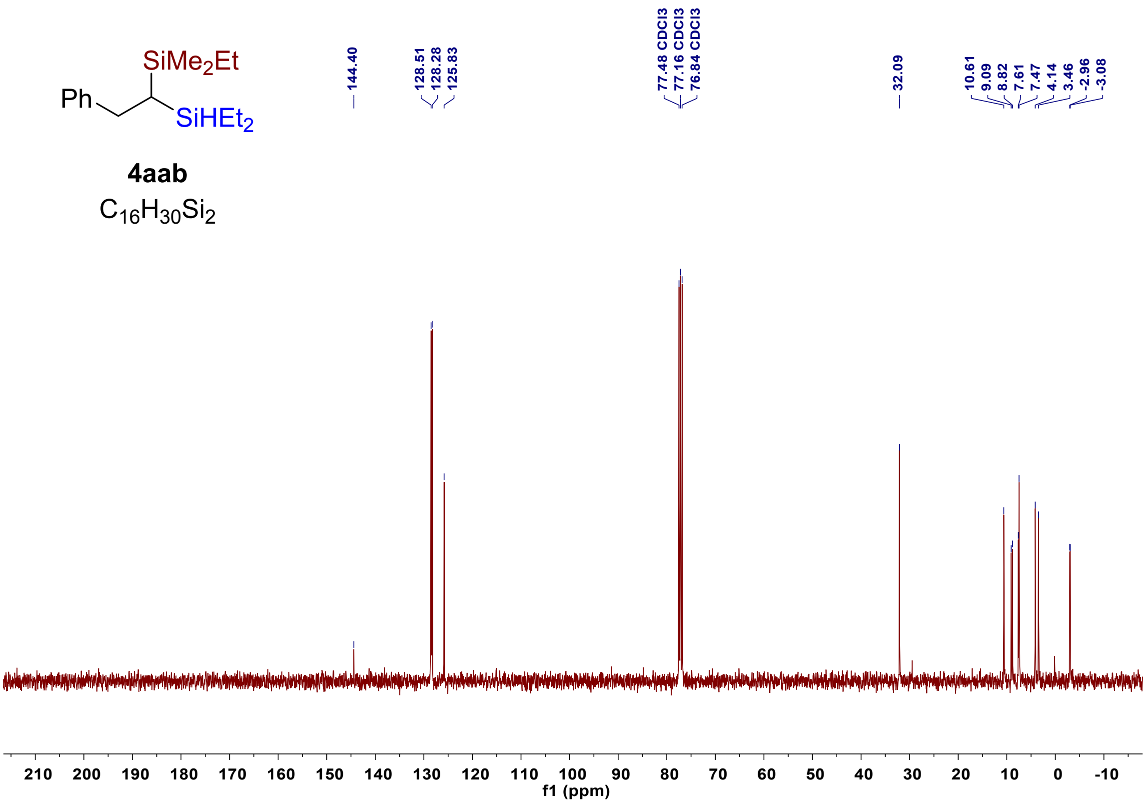


Figure S76. [13]**C{**[1]**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4aab**.

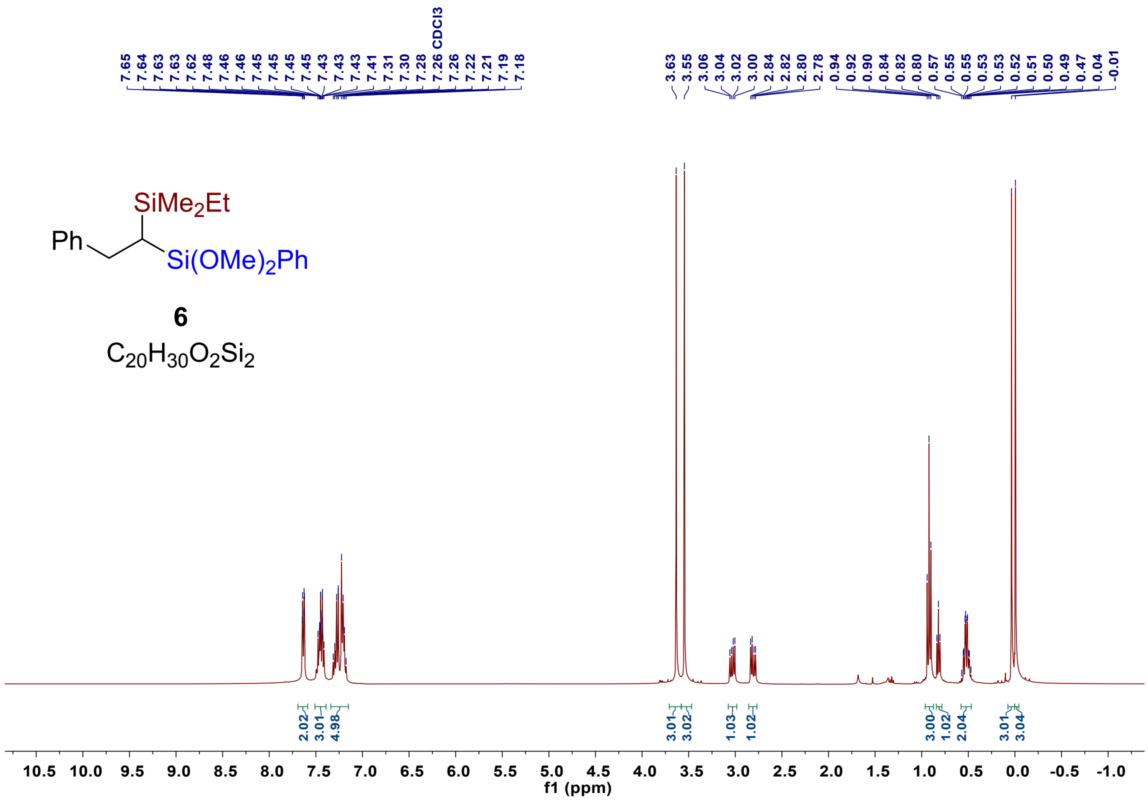


Figure S77. [1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **6**.

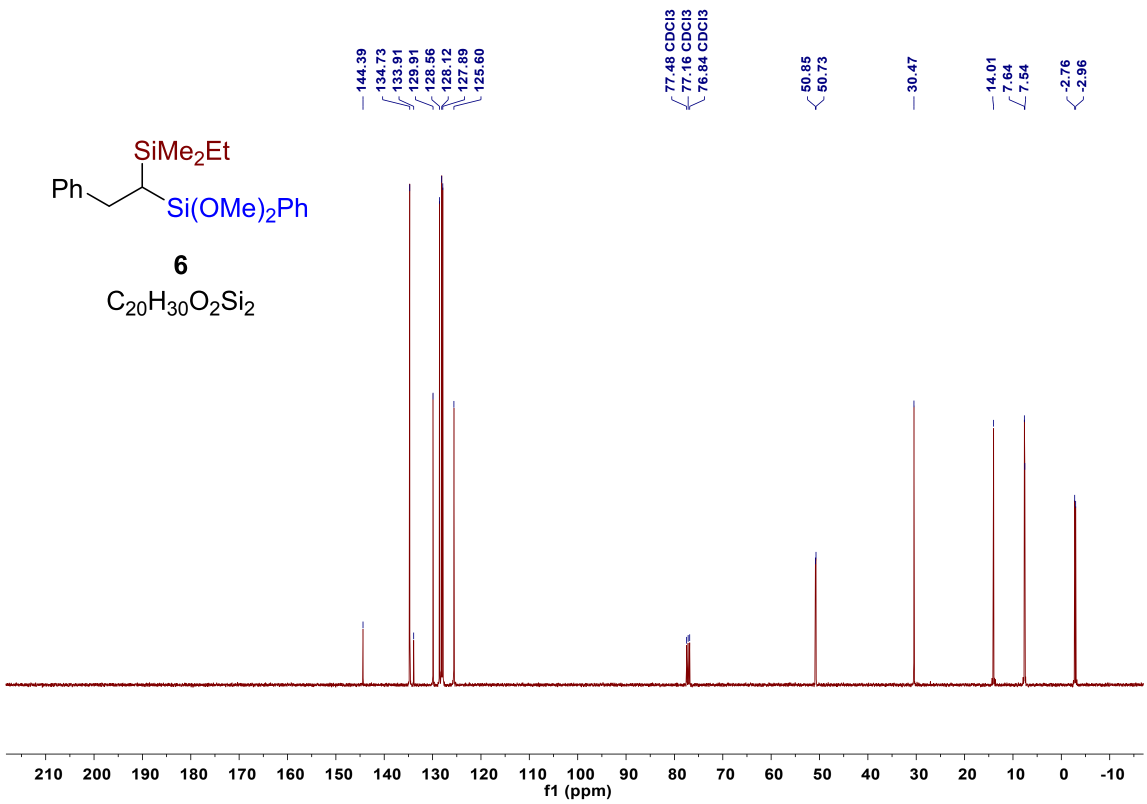


Figure S78. [13]**C{**[1]**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **6**.

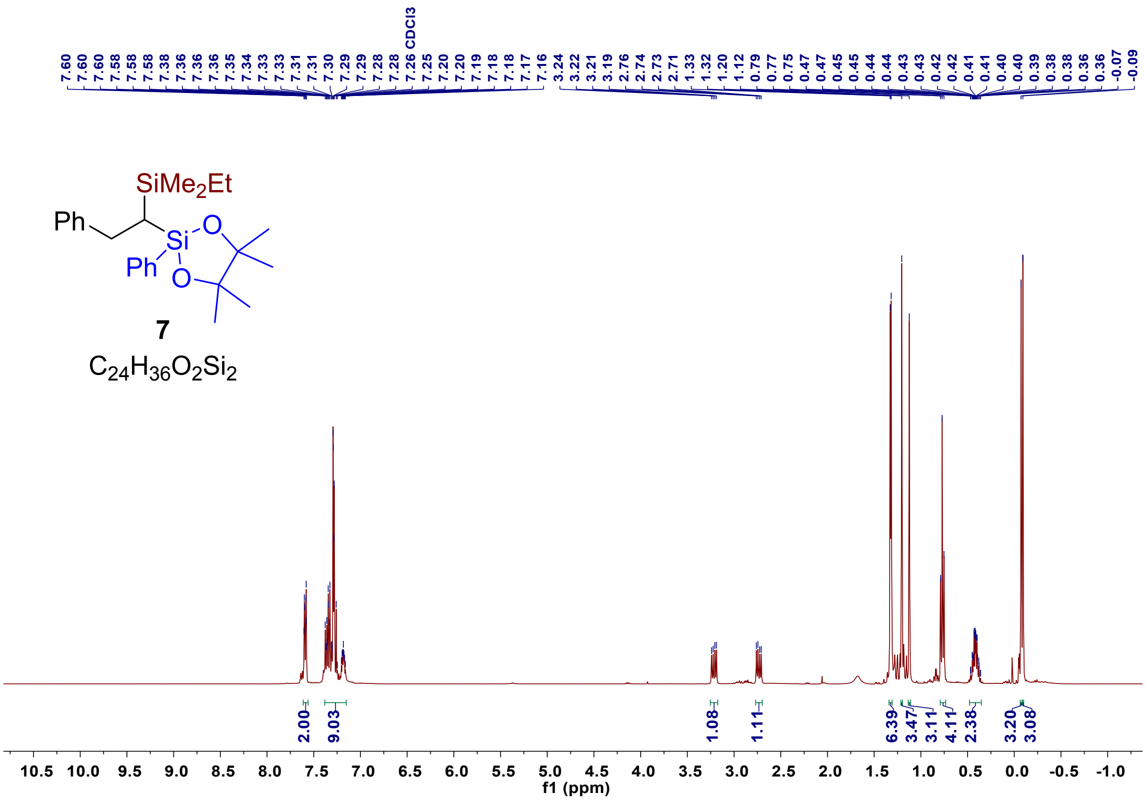


Figure S79. ^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **7**.

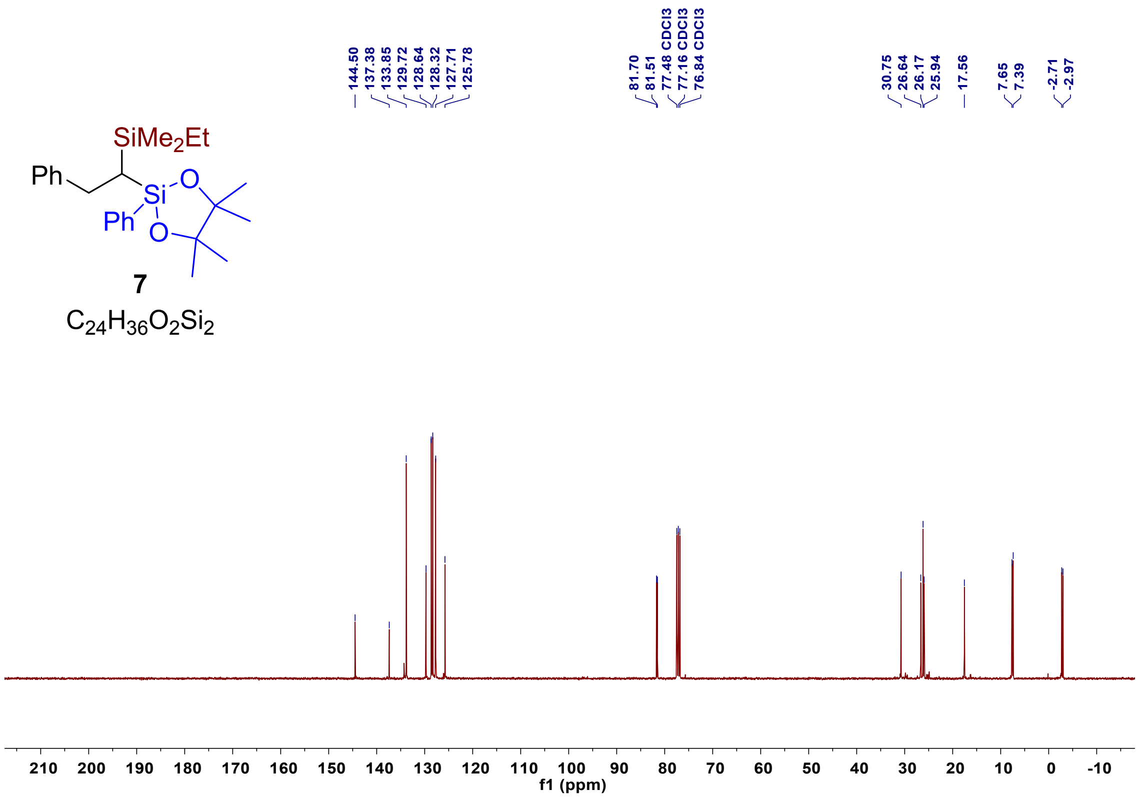


Figure S80. ^{13}**C{**^{1}**H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **7**.

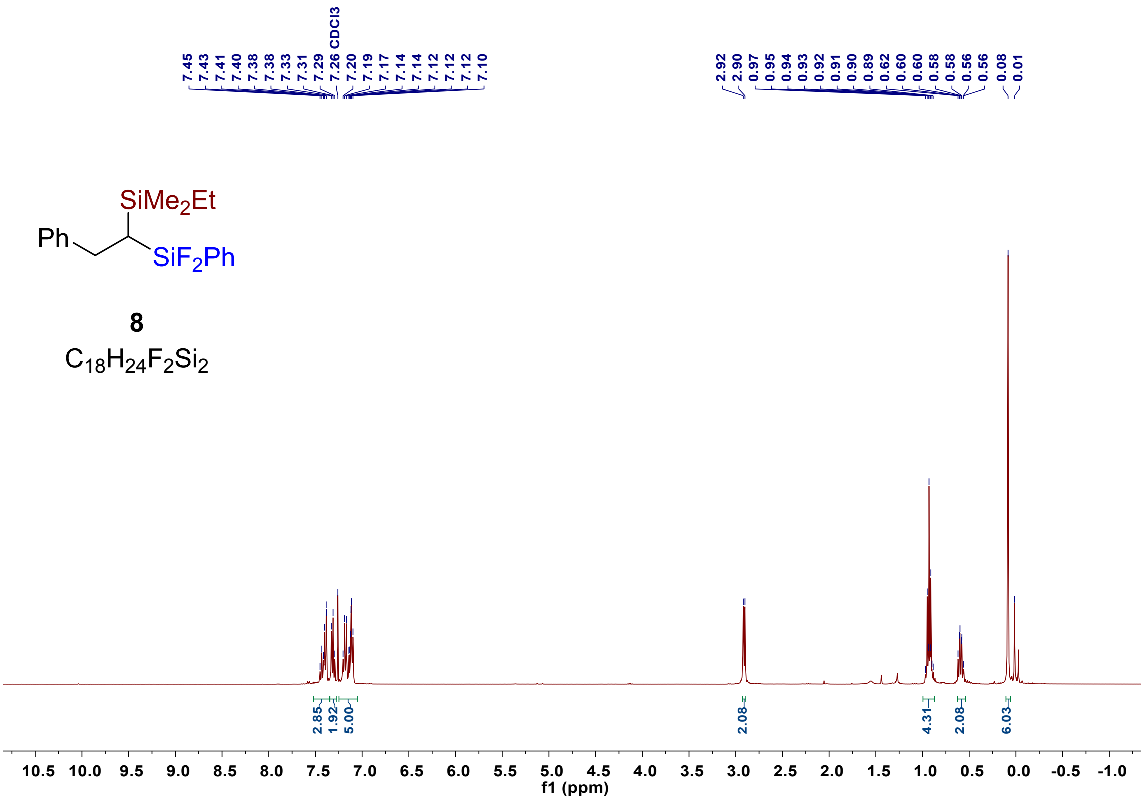


Figure S81. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **8**.

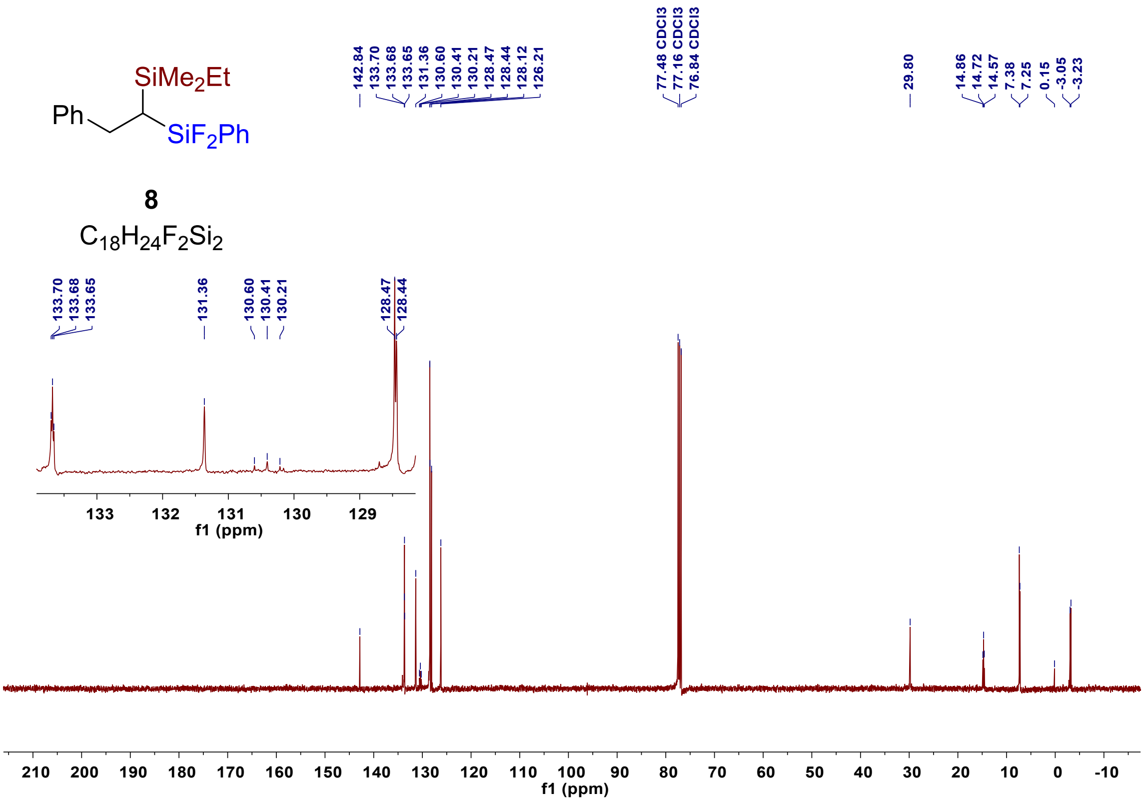
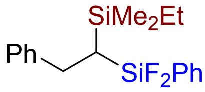


Figure S82. **$^{13}C\{^{1}H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **8**.



8
$C_{18}H_{24}F_2Si_2$

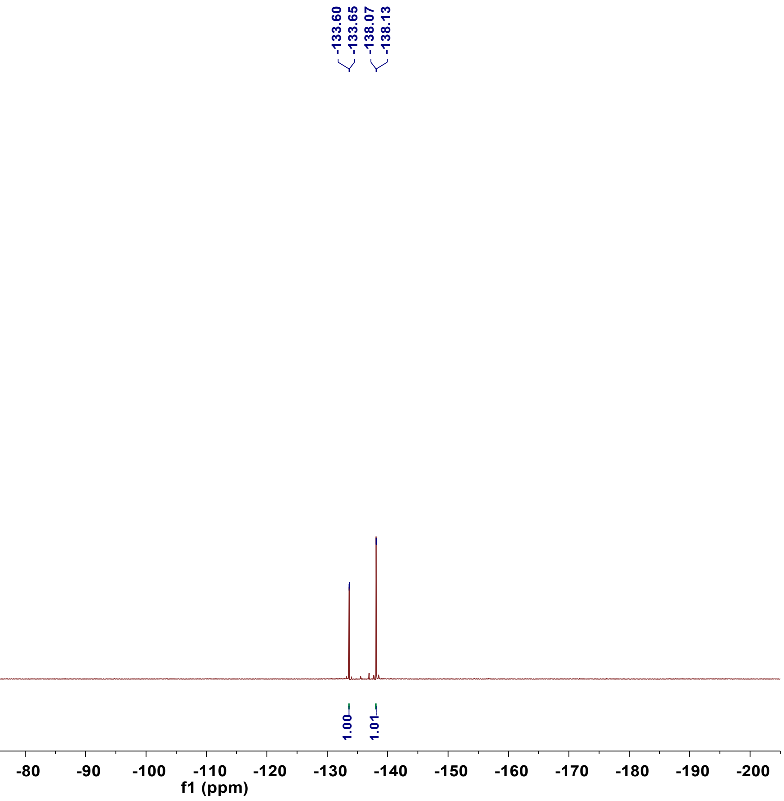


Figure S83. **$^{19}F\{^1H\}$ NMR** spectrum (376 MHz MHz, $CDCl_3$) of compound **8**.

11. Energies and Cartesian Coordinates of the Optimized Structures

$B(C_6F_5)_3$

M06-2X/6-311G(d,p) free energy: -2208.064745
M06-2X/6-311G(d,p) SCF energy: -2208.1626693
M06-2X/cc-PVTZ SCF energy: -2208.422318

B	0.00082500	-0.00122300	0.00175600
C	-1.28311700	-0.89883300	0.00261800
C	-1.32850200	-2.13160200	-0.64952000
C	-2.45633900	-0.51545500	0.65336500
C	-2.45680200	-2.92980800	-0.66910200
C	-3.59589900	-1.29750300	0.67001100
C	-3.59489500	-2.50972500	-0.00035800
C	-0.13565800	1.55955700	0.00121100
C	-1.18420500	2.21313900	-0.64741500
C	0.78341500	2.38636400	0.64839700
C	-1.31437200	3.58913900	-0.66706900
C	0.67358700	3.76417100	0.66408800
C	-0.38054800	4.36698400	-0.00250700
C	1.42033200	-0.66389600	0.00036400
C	2.51148500	-0.08213900	-0.64632000
C	1.67583100	-1.87406300	0.64668300
C	3.76830200	-0.65709800	-0.66400700
C	2.92416400	-2.46742100	0.66442100
C	3.97424900	-1.85515000	0.00021100
F	-4.67977900	-3.26561800	-0.00174400
F	-2.45999100	-4.09038400	-1.31509700
F	-0.26279400	-2.58689000	-1.30871800
F	-4.68672200	-0.89961400	1.31492900
F	-2.51579000	0.64146700	1.31331900
F	-2.11258500	1.51637700	-1.30321700
F	-2.32124100	4.16960700	-1.31009300
F	-0.49521300	5.68421200	-0.00434800
F	1.56492700	4.51214900	1.30457800
F	1.81796800	1.86226500	1.30598100
F	2.37324100	1.07075300	-1.30136200
F	4.77564300	-0.07469300	-1.30455400
F	5.17248000	-2.41411800	-0.00042200
F	3.12508800	-3.61368400	1.30463000
F	0.70362300	-2.50892300	1.30176200

Me_3SiH

M06-2X/6-311G(d,p) free energy: -409.719058
M06-2X/6-311G(d,p) SCF energy: -409.8078127
M06-2X/cc-PVTZ SCF energy: -409.8269317

Si	-0.00021700	-0.00004500	0.38354600
C	0.68201700	1.64122900	-0.22458500
H	1.70524100	1.79735700	0.12486000
H	0.69145800	1.66692400	-1.31756900
H	-0.00036500	-0.00031900	1.87250800
C	-1.76254600	-0.23015500	-0.22477800
H	-2.40980500	0.57715600	0.12561800
H	-1.78966800	-0.23378500	-1.31775000
C	1.08078900	-1.41100400	-0.22462800
H	0.70606000	-2.37542400	0.12598500
H	1.09741000	-1.43288700	-1.31760300
H	-2.18090700	-1.17648400	0.12578100
H	0.07251600	2.47697900	0.12682300
H	2.10953200	-1.29930000	0.12565300

I

M06-2X/6-311G(d,p) free energy: -2617.786655
M06-2X/6-311G(d,p) SCF energy: -2617.9959024
M06-2X/cc-PVTZ SCF energy: -2618.2704664

Si	-0.00791800	-0.00437500	2.84889400
C	-0.00219700	1.80894200	3.25831600
H	0.72568400	2.34098800	2.64199300
H	-0.98727800	2.25555400	3.11577800
H	0.28444500	1.93592200	4.30591800
C	-1.58212200	-0.90676000	3.25378400
H	-1.83114600	-0.73276100	4.30429300
H	-2.40857600	-0.53480800	2.64441100
H	-1.47824400	-1.98183500	3.09990900
C	1.55827700	-0.91501300	3.26559800

H	1.64556100	-1.82585900	2.66955200
H	2.43907100	-0.29248900	3.10123100
H	1.53303000	-1.20186300	4.32060700
B	0.00185800	-0.00154700	-0.10734100
C	1.47809200	-0.57240400	-0.35912500
C	1.78101700	-1.68311200	-1.13322300
C	2.56258500	0.03898900	0.25725400
C	3.07428900	-2.16327800	-1.28097600
C	3.86260300	-0.41330000	0.14841400
C	4.11885300	-1.52748500	-0.63483600
C	-1.23103900	-0.99271700	-0.36516900
C	-2.34411400	-0.69495000	-1.13784400
C	-1.24652800	-2.23897100	0.24847400
C	-3.40984100	-1.57095200	-1.28525300
C	-2.29134300	-3.13493500	0.13979800
C	-3.38462100	-2.79442100	-0.64088800
C	-0.24052100	1.56261800	-0.35947200
C	-1.31325100	2.19683300	0.25443300
C	0.57179600	2.37969800	-1.13230600
C	-1.57005100	3.54914500	0.14582100
C	0.34217000	3.73994100	-1.28054400
C	-0.73123800	4.32738200	-0.63600900
F	-0.20505900	-2.60309200	1.01603000
F	-2.26188600	-4.30401400	0.77386700
F	-4.40124400	-3.63759300	-0.76800900
F	-4.45681200	-1.24317800	-2.03808000
F	-2.43831800	0.47054100	-1.78618300
F	2.35377700	1.12149500	1.02597900
F	4.85746000	0.19926300	0.78454800
F	5.35914100	-1.98134500	-0.76279600
F	3.31775700	-3.23135100	-2.03613100
F	0.82142300	-2.34900800	-1.78391200
F	1.62912400	1.88084500	-1.78104400
F	1.14661100	4.48415100	-2.03507900
F	-0.95704700	5.62860400	-0.76434000
F	-2.59833900	4.10548300	0.78045800
F	-2.14844500	1.47488200	1.02089500
H	-0.00116400	-0.00651200	1.27517800

phenylacetylene

M06-2X/6-311G(d,p) free energy: -308.258757
M06-2X/6-311G(d,p) SCF energy: -308.3386706
M06-2X/cc-PVTZ SCF energy: -308.3736187

C	-1.50733500	1.20542000	0.00000600
C	-0.11905500	1.20964000	-0.00000500
C	0.58588200	0.00001100	-0.00003500
C	-0.11904500	-1.20963000	-0.00000600
C	-1.50732600	-1.20542900	0.00000000
C	-2.20404700	-0.00000800	0.00001200
H	-2.04598800	2.14514100	0.00001500
H	0.42876500	2.14406700	-0.00002300
H	0.42879500	-2.14404600	-0.00000500
H	-2.04596700	-2.14515600	0.00001900
H	-3.28722900	-0.00001000	0.00004300
C	2.02060700	-0.00000300	-0.00001000
C	3.22266400	-0.00000200	0.00002000
H	4.28755400	0.00001000	0.00007000

$TS_{I\text{-}II}$

M06-2X/6-311G(d,p) free energy: -2926.016392
M06-2X/6-311G(d,p) SCF energy: -2926.3257806
M06-2X/cc-PVTZ SCF energy: -2926.6358541

C	2.24412200	1.14945100	-0.26626500
C	2.53524800	0.82071900	-1.40588800
Si	3.27072700	-0.50918400	0.83766000
C	3.97672100	-1.65012700	-0.44764400
H	4.53161500	-2.44277500	0.05425200
H	3.18667000	-2.10220100	-1.05054700
H	4.67130800	-1.12168500	-1.10324400
C	4.41576800	0.70564500	1.66081100
H	3.85045300	1.54117700	2.07757300
H	4.95522900	0.22285500	2.47588900
H	5.13367200	1.08881600	0.93246700
C	1.66095600	-0.98324000	1.64434400
H	1.27727200	-0.15954200	2.24898000
H	0.92581300	-1.23677400	0.87752900
H	1.80536700	-1.85443500	2.28391300
C	2.93048600	0.37356000	-2.69068600
C	4.12935700	0.84607200	-3.24676100
C	2.12760400	-0.54168700	-3.38831000

C	4.51998200	0.39713700	-4.49764800
H	4.73492400	1.55209200	-2.69200000
C	2.53142200	-0.98231500	-4.63805000
H	1.20613600	-0.89456100	-2.94185500
C	3.72365700	-0.51471900	-5.18847400
H	5.44332700	0.75398000	-4.93519400
H	1.92109600	-1.68997500	-5.18395200
H	4.03522800	-0.86465500	-6.16509900
B	4.64009300	-2.77566000	3.09654600
C	3.59732600	-2.80480700	4.34467900
C	3.26171400	-3.93143500	5.08166200
C	2.95979600	-1.63722200	4.73896300
C	2.34030300	-3.91565700	6.11711600
C	2.02830700	-1.57405500	5.76179000
C	1.71522800	-2.72845700	6.45686300
C	4.74441800	-4.20022900	2.31594300
C	5.78064600	-5.11218600	2.46014400
C	3.74919200	-4.58406200	1.42855800
C	5.84749300	-6.30538100	1.75820400
C	3.77477300	-5.76335200	0.70242400
C	4.83819500	-6.63193900	0.86925600
C	6.09376500	-2.15789100	3.48777100
C	6.87354900	-1.55305400	2.51225100
C	6.65593300	-2.17664100	4.75628300
C	8.10724600	-0.97402000	2.75908900
C	7.88843500	-1.61451400	5.04994700
C	8.61814500	-1.00513200	4.04426500
F	2.67988900	-3.78880300	1.23452400
F	2.79257000	-6.06924600	-0.14729600
F	4.88713000	-7.77396300	0.18658800
F	6.86725300	-7.14716300	1.93441000
F	6.77413700	-4.88156000	3.33130600
F	3.23652800	-0.47841000	4.11118300
F	1.43595000	-0.42222000	6.08257800
F	0.82599100	-2.69680500	7.44736000
F	2.05388900	-5.02803000	6.79547300
F	3.85257400	-5.10948900	4.83160100
F	6.02310300	-2.78054300	5.77311400
F	8.38425100	-1.66062700	6.28753100
F	9.80286400	-0.45893400	4.31037000
F	8.80275300	-0.39231500	1.78023200
F	6.43345400	-1.50124200	1.24067400
H	4.15962000	-1.99547500	2.29385900
H	1.79346500	1.75888700	0.49214300

II

M06-2X/6-311G(d,p) free energy: -2926.017732

M06-2X/6-311G(d,p) SCF energy: -2926.3263322

M06-2X/cc-PVTZ SCF energy: -2926.63636

C	3.97788300	-0.09745800	-2.99149800
C	4.93825100	-0.08399000	-2.21438900
Si	2.29232400	-0.04485400	-1.75843200
C	2.88191300	-0.18185800	0.00023400
H	2.01718900	-0.10155200	0.65999600
H	3.37171300	-1.14081800	0.18353200
H	3.57055300	0.62696000	0.25412900
C	1.66364900	1.62625900	-2.28495700
H	1.61575700	1.69553400	-3.37358300
H	0.65823200	1.77714100	-1.88863700
H	2.31782300	2.41371300	-1.90463700
C	1.47586700	-1.55545400	-2.47956800
H	1.20867500	-1.38391500	-3.52426800
H	2.14848600	-2.41357600	-2.41692600
H	0.57053500	-1.78439800	-1.91543400
C	5.92163400	-0.05352900	-1.21568600
C	6.42527900	1.18657800	-0.77788500
C	6.37955700	-1.25950000	-0.65122600
C	7.37994700	1.21153200	0.22205800
H	6.05739100	2.10090700	-1.22629400
C	7.33387300	-1.21618500	0.34844600
H	5.97599900	-2.20076300	-1.00293700
C	7.82886600	0.01453900	0.78127900
H	7.77517800	2.15648900	0.57067100
H	7.69342600	-2.13393200	0.79466600
H	8.57466400	0.04140200	1.56650500
B	-1.00526900	0.00463500	0.06312000
C	-2.04349200	-0.75676900	-0.93526600
C	-3.08643500	-1.57843700	-0.53265000
C	-1.90258700	-0.62392600	-2.30951300
C	-3.91485600	-2.24840600	-1.41907500
C	-2.70241000	-1.27719200	-3.23319500
C	-3.71803800	-2.10007300	-2.78108300

C	-0.77686000	-0.78910000	1.46864600
C	-1.38173300	-0.46804900	2.67574200
C	0.09166700	-1.87025400	1.52210000
C	-1.12804300	-1.14291600	3.85936800
C	0.37886800	-2.57267800	2.68141500
C	-0.23693800	-2.20195500	3.86294400
C	-1.36409900	1.57957600	0.27604300
C	-0.35026100	2.49122500	0.53468500
C	-2.63727200	2.12673900	0.20661000
C	-0.55784400	3.85312800	0.68363200
C	-2.89383200	3.48079300	0.35253000
C	-1.84440700	4.35173700	0.58923500
F	0.71054900	-2.29489100	0.40391000
F	1.23554900	-3.59680900	2.67119500
F	0.01936200	-2.86189700	4.99153100
F	-1.73706400	-0.79124400	4.99385700
F	-2.28253300	0.52421800	2.74185600
F	-0.94485500	0.17656200	-2.81450100
F	-2.50621300	-1.12206000	-4.54478400
F	-4.50362900	-2.73822900	-3.64747500
F	-4.90380400	-3.02872800	-0.97781500
F	-3.35623300	-1.74337300	0.77138700
F	-3.70548500	1.33836400	0.01266500
F	-4.13894100	3.95568300	0.27640000
F	-2.07275900	5.65662300	0.73102300
F	0.46146600	4.68338700	0.91727500
F	0.92258300	2.06797900	0.65430600
H	0.05906300	-0.01320400	-0.50141100
H	3.70833300	-0.13174900	-4.03424400

IIA

M06-2X/6-311G(d,p) free energy: -717.202526
M06-2X/6-311G(d,p) SCF energy: -717.3850549
M06-2X/cc-PVTZ SCF energy: -717.4389511

C	-3.27507600	-1.21601700	0.20541800
C	-2.00072600	-1.23266700	-0.32372600
C	-1.35208300	-0.00532300	-0.59134700
C	-1.99181300	1.22778700	-0.32819200
C	-3.26602100	1.22277800	0.20143300
C	-3.89994500	0.00619600	0.46555600
H	-3.78802200	-2.14420300	0.41871000
H	-1.48858700	-2.16266400	-0.53598200
H	-1.47357000	2.15362700	-0.54394000
H	-3.77178500	2.15562500	0.41161600
H	-4.89995300	0.01028200	0.88249500
C	-0.06496000	-0.00836000	-1.10898900
C	1.14102500	-0.00416300	-1.43466900
Si	2.28299500	0.00123700	0.20630200
C	1.17374400	-0.07370400	1.69760000
H	0.56793400	-0.98260700	1.70845700
H	1.80232400	-0.08144300	2.59213500
H	0.51132100	0.79222100	1.76368900
C	3.32243100	-1.52401000	-0.02259500
H	3.90285600	-1.46941100	-0.94540000
H	4.01869600	-1.60871500	0.81639600
H	2.70442900	-2.42321700	-0.04646200
C	3.21909900	1.60141400	0.05216100
H	2.54316200	2.45809400	0.06841000
H	3.90690400	1.69217400	0.89756000
H	3.80417000	1.63107900	-0.86889200
H	1.66414900	-0.00175800	-2.38292800

$HB(C_6F_5)_3^-$

M06-2X/6-311G(d,p) free energy: -2208.813514
M06-2X/6-311G(d,p) SCF energy: -2208.9174947
M06-2X/cc-PVTZ SCF energy: -2209.176408

B	-0.00003700	-0.00602300	0.87603200
C	-1.39712500	-0.71330000	0.40351600
C	-2.07623100	-0.42832800	-0.77338300
C	-2.00454600	-1.66845200	1.20748600
C	-3.27724500	-1.02058400	-1.12876500
C	-3.20396600	-2.28907300	0.89109600
C	-3.84815100	-1.95815000	-0.28648700
C	0.08289000	1.55716300	0.40117600
C	0.69027200	2.00822100	-0.76293800
C	-0.47203300	2.55551100	1.19059000
C	0.76726600	3.34502600	-1.11935400
C	-0.42116000	3.90449900	0.87264900
C	0.20834600	4.30277700	-0.29200200
C	1.31517300	-0.85860800	0.40824500

C	2.45756900	-0.86051800	1.19750000
C	1.40675600	-1.62332400	-0.74670800
C	3.60469000	-1.57607900	0.88863700
C	2.53032500	-2.35646000	-1.09382700
C	3.63890400	-2.33492000	-0.26639100
F	-1.10933600	2.24519400	2.33100800
F	-0.97098300	4.82191000	1.67433200
F	0.26947100	5.59454900	-0.61869300
F	1.36470100	3.72112500	-2.25436500
F	1.22689400	1.13817300	-1.63282800
F	-1.43395700	-2.04862700	2.36205700
F	-3.74437200	-3.19956000	1.70706100
F	-5.00291100	-2.54133300	-0.61130400
F	-3.88681800	-0.70647000	-2.27614500
F	-1.56905500	0.44549300	-1.65693100
F	0.38597000	-1.66790400	-1.61740000
F	2.56206300	-3.07578900	-2.22000900
F	4.73086500	-3.03184700	-0.58421900
F	4.67400300	-1.54240900	1.68997400
F	2.50257500	-0.13900800	2.32913400
H	-0.00223700	-0.00377900	2.07854800

III

M06-2X/6-311G(d,p) free energy: -2926.021341
M06-2X/6-311G(d,p) SCF energy: -2926.3325779
M06-2X/cc-PVTZ SCF energy: -2926.639059

C	1.57844400	4.08307000	1.84749800
C	1.75174500	2.73622100	2.09586600
C	2.17456800	1.89016500	1.04539400
C	2.43135000	2.41039500	-0.24592700
C	2.27848800	3.76429000	-0.46587700
C	1.84602000	4.59129400	0.57444800
H	1.23380600	4.74148200	2.63340200
H	1.55019500	2.31117400	3.07083700
H	2.74909500	1.74361400	-1.03531700
H	2.47533200	4.18169200	-1.44498400
H	1.70628900	5.64939000	0.38667000
C	2.33245900	0.53410100	1.28996700
C	2.63731800	-0.66065000	1.52706300
Si	4.57537200	-0.95038500	1.70981700
C	4.78740100	-1.68440100	3.40748400
H	4.47354000	-0.98023100	4.18028200
H	4.20920200	-2.60385500	3.51521000
H	5.84252900	-1.92178600	3.56827500
C	4.91645900	-2.13603100	0.31316900
H	4.64736700	-1.69385100	-0.64826100
H	5.98121700	-2.38319600	0.29150900
H	4.35272600	-3.06375300	0.43711900
C	5.43251800	0.69110700	1.51201000
H	5.26319300	1.12056000	0.52201000
H	5.10552700	1.41053600	2.26640600
H	6.50896300	0.54526500	1.63324100
B	-0.71249500	-0.31820500	0.20617000
C	-0.74339700	1.09934700	-0.60819400
C	-0.61908200	1.29866600	-1.97505200
C	-0.96836600	2.25691900	0.13068600
C	-0.64828600	2.55392700	-2.56773400
C	-1.02227600	3.52496400	-0.42016700
C	-0.84545100	3.67593100	-1.78426900
C	0.00789900	-1.57461500	-0.55712700
C	-0.41085700	-2.89622900	-0.44640300
C	1.19517600	-1.42246300	-1.26614800
C	0.27145500	-3.97253400	-0.99903200
C	1.90837000	-2.46182900	-1.83643100
C	1.44271800	-3.75743000	-1.69889600
C	-2.25461200	-0.61324700	0.64198100
C	-2.69735300	-0.61840200	1.95376000
C	-3.23502500	-0.82062300	-0.31689800
C	-4.02561800	-0.82242500	2.30214100
C	-4.56842200	-1.03259100	-0.01679700
C	-4.96588100	-1.03141500	1.31039900
F	1.73698000	-0.19830700	-1.41621500
F	3.04270400	-2.23040700	-2.50304000
F	2.11479200	-4.77717500	-2.22864500
F	-0.19039500	-5.21542800	-0.85167100
F	-1.52190300	-3.21672900	0.23525400
F	-1.13930800	2.17710900	1.46164000
F	-1.20507400	4.60453800	0.34643000
F	-0.85530600	4.89098100	-2.33245400
F	-0.49455400	2.68992100	-3.88715200
F	-0.45923800	0.26085400	-2.80927100
F	-2.89006400	-0.83724400	-1.61545100

F	-5.47222800	-1.23691200	-0.97824800
F	-6.24521300	-1.23071500	1.62759500
F	-4.40690600	-0.82028100	3.58260200
F	-1.84112700	-0.43112300	2.97033700
H	-0.07190000	-0.11924100	1.21549300
H	1.99517500	-1.53620700	1.54292500

TS$_{III-3aa'}$

M06-2X/6-311G(d,p) free energy: -2926.020711
M06-2X/6-311G(d,p) SCF energy: -2926.3314396
M06-2X/cc-PVTZ SCF energy: -2926.638051

C	0.90070100	4.09674400	1.98277900
C	1.11832000	2.75010300	2.20193600
C	1.71807000	1.97451600	1.18834100
C	2.10035300	2.56210900	-0.03803900
C	1.89717800	3.91577800	-0.22964000
C	1.29054300	4.67453100	0.77296700
H	0.42371300	4.70017800	2.74342700
H	0.81441300	2.27328700	3.12535400
H	2.55470400	1.94918700	-0.80370700
H	2.19215000	4.38159300	-1.16115200
H	1.11266600	5.73038500	0.60702600
C	1.93724500	0.61054000	1.40094300
C	2.44234000	-0.52210000	1.64592100
Si	4.36653700	-0.52500700	1.97864600
C	4.58387800	-1.36176600	3.62925200
H	4.11430600	-0.78211100	4.42626700
H	4.14995400	-2.36347700	3.62369700
H	5.65001800	-1.45147400	3.85397500
C	4.99619600	-1.52401100	0.53428100
H	4.72170200	-1.05156500	-0.41172000
H	6.08577400	-1.60078300	0.57680200
H	4.58156300	-2.53502200	0.54677300
C	4.98024500	1.23416300	1.97346100
H	4.85336300	1.70515700	0.99617000
H	4.46772200	1.84239300	2.72260600
H	6.04724500	1.23704100	2.21104800
B	-0.62709600	-0.35460300	0.01207500
C	-0.81158100	1.02302000	-0.83496300
C	-0.58601400	1.23285300	-2.18678000
C	-1.22545100	2.14995500	-0.12970900
C	-0.69986800	2.47738600	-2.79157100
C	-1.36267200	3.40521400	-0.69327400
C	-1.08366100	3.57239200	-2.03881100
C	0.19551600	-1.56468900	-0.70617100
C	-0.15336900	-2.91029600	-0.66370900
C	1.42243400	-1.32156100	-1.31792400
C	0.63701600	-3.92728300	-1.18512900
C	2.24161100	-2.29880900	-1.85155400
C	1.84548700	-3.62338200	-1.78035400
C	-2.08122200	-0.77236500	0.60172100
C	-2.40773300	-0.73856100	1.94589900
C	-3.11131400	-1.12845800	-0.25533400
C	-3.67497600	-1.04498600	2.42224000
C	-4.38683800	-1.44564200	0.17360900
C	-4.66908300	-1.40059700	1.52971000
F	1.88582000	-0.06102300	-1.40379800
F	3.40755700	-1.98286100	-2.41917000
F	2.61751200	-4.58584000	-2.27749200
F	0.24032800	-5.19805400	-1.10846400
F	-1.29770100	-3.31708800	-0.09512700
F	-1.49598600	2.04943800	1.18321200
F	-1.72648700	4.45725300	0.04427800
F	-1.18568900	4.77526800	-2.60159800
F	-0.45111700	2.62745700	-4.09403600
F	-0.24148600	0.21692600	-2.99121000
F	-2.86967600	-1.19877900	-1.57449400
F	-5.34308300	-1.79352500	-0.69019700
F	-5.89068100	-1.70002200	1.96955000
F	-3.94588400	-0.99845200	3.72917300
F	-1.49181200	-0.39890400	2.86678800
H	0.06069700	-0.01992800	0.97518500
H	1.94933700	-1.48669500	1.56951000

3aa'

M06-2X/6-311G(d,p) free energy: -718.019669
M06-2X/6-311G(d,p) SCF energy: -718.2138151
M06-2X/cc-PVTZ SCF energy: -718.2653908

C	3.33560000	0.45646900	0.73445100
C	2.29560300	1.26825600	0.29801100

C	1.27050000	0.74594400	-0.49727600
C	1.33823000	-0.59439600	-0.88592100
C	2.38484800	-1.40567600	-0.45991500
C	3.38099900	-0.88456200	0.35990700
H	4.11384800	0.86985000	1.36503900
H	2.26303700	2.31270600	0.58953100
H	0.57094200	-0.99219200	-1.54055800
H	2.42472800	-2.44269000	-0.77199800
H	4.19529700	-1.51543200	0.69556000
C	0.14275600	1.60498100	-0.92427500
C	-1.15418200	1.29697300	-0.80012000
Si	-1.96422700	-0.12601500	0.13885600
C	-3.60971000	0.56611800	0.73379900
H	-3.45952700	1.42768300	1.38955200
H	-4.22733400	0.88778300	-0.10910100
H	-4.16853400	-0.18987800	1.29161700
C	-2.31878500	-1.60924300	-0.96344800
H	-1.40773400	-2.13573900	-1.25498300
H	-2.95865200	-2.31839000	-0.43048300
H	-2.84188100	-1.30403300	-1.87319000
C	-0.95256800	-0.64380800	1.63693300
H	-0.06432100	-1.21697700	1.36669000
H	-0.62846800	0.23437400	2.20189400
H	-1.57102700	-1.26001300	2.29600100
H	0.43032100	2.56185700	-1.35974400
H	-1.85125900	2.03896200	-1.19268400

$PhSiH_3$

M06-2X/6-311G(d,p) free energy: -2730.847655
M06-2X/6-311G(d,p) SCF energy: -2731.053001
M06-2X/cc-PVTZ SCF energy: -2731.338855

Si	5.93189500	0.30164300	-4.56030100
H	6.89116600	-0.48023600	-3.74731900
H	6.54307000	0.55955000	-5.88551100
H	5.65579800	1.60185600	-3.90795500
C	4.32740700	-0.65666100	-4.73396300
C	4.32793800	-2.05586800	-4.80055500
C	3.09843400	0.00926500	-4.82040700
C	3.14189600	-2.76649900	-4.95594200
H	5.26360900	-2.60149900	-4.72665600
C	1.90948600	-0.69721300	-4.97603400
H	3.06442700	1.09267200	-4.76209900
C	1.93056600	-2.08675600	-5.04482300
H	3.16195800	-3.84893800	-5.00421500
H	0.96795800	-0.16445200	-5.04009000
H	1.00564100	-2.63876700	-5.16358200

IV

M06-2X/6-311G(d,p) free energy: -2730.847655
M06-2X/6-311G(d,p) SCF energy: -2731.053001
M06-2X/cc-PVTZ SCF energy: -2731.338855

Si	7.08749100	2.59788600	-4.73457600
B	8.69952300	4.86687000	-5.89566000
C	10.01829400	4.39200300	-5.14046100
C	11.15424000	3.88893400	-5.76523800
C	10.04534200	4.36760700	-3.74779600
C	12.23452900	3.37923400	-5.06106000
C	11.10498200	3.87778000	-3.01060900
C	12.20580800	3.36795600	-3.67848300
C	8.54619200	4.60072900	-7.46389600
C	8.28037200	5.60472300	-8.38629100
C	8.65956900	3.32036300	-7.98950700
C	8.13151600	5.35356200	-9.74234400
C	8.50749300	3.02505400	-9.32921100
C	8.24106300	4.05831700	-10.21415300
C	7.88191700	6.11443100	-5.32676600
C	6.50930300	6.20035400	-5.52134000
C	8.46775700	7.18459700	-4.66610100
C	5.74659300	7.26731200	-5.08363800
C	7.74086300	8.27676400	-4.22186800
C	6.37326600	8.31662600	-4.43206400
F	8.93240700	2.29793700	-7.16220700
F	8.61844100	1.77805100	-9.77606300
F	8.09678200	3.80499700	-11.50769800
F	7.88568700	6.34710300	-10.59139100
F	8.17443500	6.88046600	-8.00269000
F	8.97516200	4.79045200	-3.06138800
F	11.07224600	3.87084500	-1.68166700
F	13.21964300	2.85762300	-2.99331600
F	13.29308000	2.89212800	-5.70372300

F	11.25736000	3.86936700	-7.09721500
F	9.78482000	7.20180000	-4.43831900
F	8.34232100	9.28552900	-3.59718600
F	5.66458800	9.35558000	-4.00944500
F	4.43240800	7.29976000	-5.28477500
F	5.86807600	5.20513000	-6.15342200
H	7.77334400	3.80386700	-5.41572300
H	6.51634500	1.87393700	-5.88120200
C	8.40794100	1.72492700	-3.76908100
C	8.43076300	1.86053100	-2.37342700
C	9.43596100	1.00365600	-4.39468200
C	9.45869000	1.29981200	-1.62334800
H	7.64971900	2.41879900	-1.86840200
C	10.46919400	0.45475500	-3.64440100
H	9.43837400	0.87431300	-5.47015500
C	10.48456300	0.60823000	-2.25983300
H	9.46829800	1.41799400	-0.54685500
H	11.26572300	-0.08802200	-4.13965000
H	11.29648600	0.18816400	-1.67811800
H	6.08785200	3.23648000	-3.86107500

TS$_{3aa'\text{-}V}$

M06-2X/6-311G(d,p) free energy: -3448.845797

M06-2X/6-311G(d,p) SCF energy: -3449.2736839

M06-2X/cc-PVTZ SCF energy: -3449.6089149

C	-0.18093400	-5.87553000	2.04804500
C	0.60218000	-4.73063900	2.05310200
C	1.79076600	-4.67738500	2.79880100
C	2.18416800	-5.81496800	3.52612800
C	1.40658800	-6.96107000	3.51279100
C	0.22268800	-6.99130900	2.77533400
H	-1.09660900	-5.90299400	1.47139000
H	0.29943600	-3.86329200	1.47651600
H	3.11034200	-5.81386500	4.08653000
H	1.72227900	-7.83441600	4.07047600
H	-0.37986900	-7.89143000	2.76378000
C	2.57900100	-3.45927000	2.72471900
C	3.74337600	-3.13237100	3.37486100
Si	4.23075100	-3.51006200	5.20524500
C	5.23764800	-1.99890600	5.66182100
H	6.12739100	-1.91650700	5.03187000
H	4.65198200	-1.08382100	5.54743800
H	5.56663600	-2.06571200	6.70183800
C	2.63450000	-3.56972000	6.18551000
H	2.02382200	-4.44189300	5.94409900
H	2.87021600	-3.61010300	7.25257400
H	2.03863000	-2.67269700	6.00138700
C	5.26352900	-5.03590000	5.55395400
H	4.80457500	-5.98920600	5.28956400
H	6.24523200	-4.99361900	5.07929700
H	5.42249400	-5.04428900	6.63735600
H	2.18811400	-2.73617700	2.00922200
H	4.08290800	-2.12763100	3.10991200
Si	5.16484100	-4.29022800	2.04854300
H	6.26184400	-4.01216300	2.98362000
H	4.33364200	-5.49108700	2.12764600
C	5.20016400	-3.24965200	0.50676400
C	6.44935500	-2.80910300	0.04945200
C	4.06628700	-2.97460100	-0.26579700
C	6.56109700	-2.11412200	-1.14997500
H	7.34555900	-3.03348400	0.62143300
C	4.17438700	-2.26930300	-1.45923100
H	3.09198800	-3.34202400	0.03839700
C	5.42264100	-1.84249800	-1.90375200
H	7.53488600	-1.79139400	-1.49866800
H	3.28966000	-2.07241300	-2.05204400
H	5.50925200	-1.30718700	-2.84205600
B	6.73116500	-6.49608200	0.63897300
C	6.61560100	-6.02394900	-0.90454600
C	7.68620000	-5.74119900	-1.74087300
C	5.36837300	-5.70731800	-1.43169200
C	7.53849400	-5.17575500	-3.00067700
C	5.17447700	-5.14444500	-2.67742000
C	6.27651700	-4.86780800	-3.46880200
C	8.21442000	-6.89372000	1.14595500
C	8.79787300	-8.06471100	0.68480900
C	8.96341600	-6.17046800	2.05630900
C	10.04582900	-8.50312700	1.08639100
C	10.21828900	-6.57334000	2.49079700
C	10.76087200	-7.74720800	2.00201900
C	5.67151500	-7.62311200	1.13555700
C	5.40848500	-7.71185200	2.49527700

C	4.92951600	-8.48181200	0.33927500
C	4.42608100	-8.51702500	3.04082400
C	3.94599500	-9.32101100	0.84416000
C	3.68210200	-9.32819400	2.20251200
F	8.49640400	-5.01772400	2.56512100
F	10.90415500	-5.84271500	3.37121100
F	11.96389200	-8.14904600	2.40601900
F	10.56919700	-9.63238700	0.60827200
F	8.14073600	-8.81041100	-0.21658400
F	4.26573900	-5.91311500	-0.68928200
F	3.95170500	-4.83964000	-3.11240300
F	6.11857300	-4.29499200	-4.65959900
F	8.60703900	-4.91032500	-3.75426400
F	8.95006800	-5.98045600	-1.35948200
F	5.11358800	-8.51374300	-0.98575800
F	3.24210100	-10.10992300	0.03257000
F	2.71385800	-10.09430500	2.69979100
F	4.16050100	-8.48623400	4.35108300
F	6.08599400	-6.92176200	3.34753300
H	6.42825500	-5.45097000	1.28637900

V

M06-2X/6-311G(d,p) free energy: -3448.847354

M06-2X/6-311G(d,p) SCF energy: -3449.2762757

M06-2X/cc-PVTZ SCF energy: -3449.6093284

C	-0.04532400	-5.93652000	5.80720400
C	0.40284200	-4.79225400	5.17004500
C	1.58010900	-4.82185200	4.39502500
C	2.27981400	-6.03751000	4.25160500
C	1.82925400	-7.17578500	4.88944700
C	0.67110200	-7.12330300	5.66996500
H	-0.94523200	-5.90876600	6.40743700
H	-0.14189500	-3.86042400	5.27154100
H	3.17667300	-6.09474500	3.64957000
H	2.37183600	-8.10405400	4.77305000
H	0.32321100	-8.01992800	6.16875700
C	2.02053300	-3.58025300	3.82969800
C	3.23617500	-3.23183300	3.23156300
Si	4.37900200	-2.94344600	4.92158600
C	5.90442900	-2.11328900	4.24710000
H	6.55490500	-2.79594400	3.69963700
H	5.65415500	-1.26828800	3.60293000
H	6.46522000	-1.73353200	5.10708000
C	3.39990800	-1.80533700	6.02704800
H	2.52493900	-2.30274400	6.45181500
H	4.03695600	-1.48404800	6.85541600
H	3.07112500	-0.91262300	5.49019800
C	4.74570700	-4.57528500	5.74702800
H	3.89154100	-4.95758100	6.30868500
H	5.09236300	-5.34812500	5.05705900
H	5.55664400	-4.38504300	6.45972200
H	1.31029600	-2.76567500	3.97506300
H	3.18635000	-2.20350000	2.86097500
Si	4.35107400	-4.26143900	2.03703600
H	5.36178000	-3.28860000	1.58651900
H	4.95697800	-5.33973500	2.83100000
C	3.36582800	-4.86134100	0.56290800
C	3.98647600	-4.82083800	-0.69465000
C	2.06200900	-5.36456000	0.64657900
C	3.32250300	-5.26958800	-1.83166700
H	5.00506200	-4.45563100	-0.78595000
C	1.39649200	-5.81427000	-0.49045800
H	1.54920900	-5.41399200	1.60217200
C	2.02581700	-5.76475300	-1.73067000
H	3.82162900	-5.24171400	-2.79283900
H	0.39011500	-6.20705700	-0.40627600
H	1.51039100	-6.12058100	-2.61475500
B	6.76173200	-6.76099400	1.25374600
C	5.41117500	-7.63721800	0.94299700
C	5.03312200	-7.84046300	-0.38194600
C	4.43632700	-8.01370200	1.86039400
C	3.81952800	-8.37645400	-0.77662300
C	3.21038100	-8.56066800	1.51117000
C	2.89317000	-8.74189700	0.18055200
C	8.03400400	-7.10831800	0.28344300
C	8.85007700	-8.21703600	0.44772800
C	8.40338800	-6.26409400	-0.75734900
C	9.95442100	-8.48726400	-0.34638000
C	9.49813700	-6.49344000	-1.57525800
C	10.28195600	-7.61461100	-1.36682200
C	7.24750600	-6.73702200	2.81548600
C	7.68941200	-5.53754900	3.36149600

C	7.23979500	-7.80527900	3.70410400
C	8.04072500	-5.37438900	4.69199800
C	7.59218000	-7.69055300	5.04097300
C	7.98779000	-6.46324800	5.54219400
F	7.68798300	-5.16374900	-1.03844700
F	9.80630200	-5.64903500	-2.56393200
F	11.33886000	-7.85096900	-2.14377800
F	10.70161600	-9.57467100	-0.13752500
F	8.58820700	-9.10551500	1.41807100
F	4.59231900	-7.79978100	3.18694100
F	2.31155300	-8.87472100	2.45111300
F	1.69966200	-9.21462500	-0.17580100
F	3.51488900	-8.49380500	-2.07039800
F	5.82842300	-7.43038300	-1.38339600
F	6.83625200	-9.01994500	3.31188500
F	7.54001500	-8.74783500	5.85487100
F	8.30112200	-6.32657500	6.83021100
F	8.39609700	-4.17656300	5.16873900
F	7.75934000	-4.42933200	2.60047800
H	6.43948800	-5.63170700	0.97120800

VA

M06-2X/6-311G(d,p) free energy: -1240.028888
M06-2X/6-311G(d,p) SCF energy: -1240.325446
M06-2X/cc-PVTZ SCF energy: -1240.407979

C	0.68522200	-0.75438900	1.92254400
C	0.71296000	-1.14156900	0.58338000
C	0.00760700	-0.41488000	-0.36616600
C	-0.74136800	0.72044200	0.06198600
C	-0.73850200	1.11132400	1.42005000
C	-0.04837600	0.35528700	2.34922900
H	1.22998800	-1.34188000	2.65191100
H	1.26496800	-2.02412000	0.28397500
H	-1.10269800	1.42409900	-0.68848900
H	-1.28430100	1.99844000	1.71826000
H	-0.06006900	0.62939200	3.39554600
C	-0.25854800	-0.90597400	-1.77025400
C	-1.78388400	-1.25561000	-1.80598900
Si	-2.17845700	-3.11937400	-1.96384300
C	-3.99676400	-3.32075100	-1.54317400
H	-4.20409800	-3.09360500	-0.49208200
H	-4.61821500	-2.66667600	-2.16074900
H	-4.31765400	-4.35069300	-1.71843400
C	-1.81442700	-3.65569600	-3.71902000
H	-0.77183000	-3.46087400	-3.98303800
H	-1.99514200	-4.72730800	-3.83507300
H	-2.45160300	-3.12450000	-4.42981400
C	-1.10784600	-4.06615800	-0.74737700
H	-0.04857000	-4.01406600	-1.01217100
H	-1.22488300	-3.70063300	0.27637700
H	-1.39317000	-5.12157400	-0.75548600
H	0.38128100	-1.76004800	-1.99856900
H	-2.27512400	-0.76562800	-2.65258700
Si	-2.45273700	-0.56325300	-0.20750800
H	-2.37461900	-1.41719300	0.99191100
C	-3.94265900	0.51897400	-0.20373400
C	-4.69573200	0.64888700	0.97209600
C	-4.34520900	1.21003500	-1.35546300
C	-5.82981900	1.45146000	0.99359600
H	-4.39718200	0.12077600	1.87192300
C	-5.47896300	2.01210600	-1.33052900
H	-3.77546000	1.12586200	-2.27529000
C	-6.21923100	2.13140400	-0.15696700
H	-6.40917100	1.54572800	1.90363600
H	-5.78636000	2.54246900	-2.22324800
H	-7.10373400	2.75677700	-0.13982200
H	-0.03297000	-0.11861400	-2.49130100

VI

M06-2X/6-311G(d,p) free energy: -3448.852463
M06-2X/6-311G(d,p) SCF energy: -3449.280291
M06-2X/cc-PVTZ SCF energy: -3449.6140013

C	1.51998800	-4.31557700	-0.58315900
C	0.80653200	-3.32183700	-1.23163500
C	-0.35628700	-2.77907400	-0.64777200
C	-0.76449800	-3.23277600	0.62393700
C	-0.03832200	-4.21158100	1.27428000
C	1.09679100	-4.75753000	0.66828700
H	2.41163700	-4.72981000	-1.03503800
H	1.13850600	-2.94315000	-2.19158400

H	-1.65118300	-2.83523600	1.09998300
H	-0.34632200	-4.55409900	2.25419100
H	1.66330300	-5.52185700	1.18777200
C	-1.05991800	-1.78821700	-1.40364700
C	-2.34729800	-1.24204500	-1.19696400
Si	-3.62894400	-2.61576300	-1.88611500
C	-5.30213000	-1.80199500	-1.73186800
H	-5.63162100	-1.73627000	-0.69262400
H	-5.31277200	-0.79725500	-2.15999100
H	-6.02522500	-2.41564500	-2.27736400
C	-3.14950300	-2.90895100	-3.66583600
H	-2.17393400	-3.39583000	-3.74124800
H	-3.88700200	-3.55926700	-4.14330800
H	-3.11253800	-1.97139600	-4.22547300
C	-3.52679400	-4.18205400	-0.87871100
H	-2.57163700	-4.69648200	-0.99855100
H	-3.70594900	-4.01148900	0.18482300
H	-4.31332800	-4.85110800	-1.24177100
H	-0.55964200	-1.50726300	-2.32780200
H	-2.51749900	-0.44099500	-1.92486100
Si	-2.94235900	-0.62103100	0.51667400
H	-3.60395000	-1.71214200	1.26982200
H	-1.72490300	-0.17594800	1.22061900
C	-4.19904400	0.73381900	0.24991000
C	-5.38408600	0.72410000	0.99731500
C	-3.98742400	1.78404600	-0.65181300
C	-6.32903800	1.73393900	0.84913600
H	-5.57590200	-0.08083900	1.69999400
C	-4.92919600	2.79746500	-0.79893000
H	-3.08478300	1.82076800	-1.25159200
C	-6.10138400	2.77184600	-0.04956000
H	-7.24119800	1.71075500	1.43338000
H	-4.74295000	3.60678200	-1.49453300
H	-6.83609300	3.55986700	-0.16499200
B	1.09250900	0.42110900	0.02583700
C	1.55680800	-0.58875400	1.21842800
C	2.53408100	-1.55743300	1.00925600
C	0.93012700	-0.68001900	2.45877300
C	2.88493300	-2.51881600	1.94296500
C	1.25052000	-1.62405200	3.42193600
C	2.23888400	-2.55493700	3.16347400
C	2.28901900	0.78173500	-1.02955100
C	3.35240800	1.59715200	-0.67062100
C	2.31569000	0.33819800	-2.34177200
C	4.37264200	1.95759400	-1.53544600
C	3.31261600	0.67159300	-3.24508600
C	4.34958700	1.49141000	-2.83813800
C	0.40977700	1.83163900	0.47899500
C	-0.50986100	2.41564100	-0.38239000
C	0.69033700	2.57420500	1.61788400
C	-1.13957200	3.62553300	-0.14127300
C	0.07794200	3.78513300	1.90505400
C	-0.84653200	4.31427400	1.02184300
F	1.35705800	-0.48642600	-2.81109600
F	3.28654900	0.20968500	-4.49760400
F	5.31804500	1.82473200	-3.69002000
F	5.37207500	2.74428600	-1.13180400
F	3.43109800	2.07086800	0.58198900
F	-0.07054500	0.15311200	2.78793200
F	0.59718700	-1.65893900	4.58555300
F	2.53422000	-3.49772500	4.05719100
F	3.79632100	-3.44965400	1.64869500
F	3.17845100	-1.64229900	-0.16778100
F	1.58118100	2.13911300	2.51872400
F	0.37380000	4.45178200	3.02303400
F	-1.43756000	5.47911500	1.28228100
F	-2.01512300	4.13286600	-1.01420800
F	-0.83340900	1.79907700	-1.53864500
H	0.23776800	-0.18039600	-0.59192800

TS$_{VI\text{-}4aa'c}$

M06-2X/6-311G(d,p) free energy: -3448.851158
M06-2X/6-311G(d,p) SCF energy: -3449.2798879
M06-2X/cc-PVTZ SCF energy: -3449.6131013

C	1.41346000	-4.42308200	-0.56185900
C	0.77136500	-3.35492900	-1.16745900
C	-0.32111800	-2.72924800	-0.53859400
C	-0.72931200	-3.17276600	0.73329300
C	-0.07264800	-4.22673100	1.34252800
C	0.99160200	-4.85623200	0.69289800
H	2.25075700	-4.90271000	-1.05172600
H	1.10763300	-2.98474800	-2.12942700

H	-1.55746700	-2.70395000	1.24906600
H	-0.38085000	-4.56024200	2.32569100
H	1.50371300	-5.67861700	1.17863000
C	-0.96917400	-1.66471900	-1.25985500
C	-2.28203800	-1.14190200	-1.07857000
Si	-3.49188100	-2.51194100	-1.86758500
C	-5.18855700	-1.73270900	-1.79766400
H	-5.57141000	-1.67567300	-0.77626900
H	-5.19552200	-0.72621600	-2.22172000
H	-5.87233000	-2.35674900	-2.38040700
C	-2.91201500	-2.76872100	-3.62469800
H	-1.93350500	-3.25505900	-3.65533300
H	-3.62023300	-3.40887000	-4.15697000
H	-2.84357400	-1.81992900	-4.16208200
C	-3.42858200	-4.10382600	-0.89425900
H	-2.47463400	-4.62206500	-1.00843700
H	-3.62153800	-3.95413400	0.17013600
H	-4.21436600	-4.75823700	-1.28421500
H	-0.48377400	-1.41168800	-2.19800400
H	-2.43245200	-0.31927100	-1.78657400
Si	-2.96390200	-0.57290500	0.61223100
H	-3.62295300	-1.69261300	1.32584700
H	-1.80210400	-0.09759300	1.38746200
C	-4.24462800	0.75464200	0.31300300
C	-5.42943100	0.74788800	1.06038600
C	-4.04961600	1.78302000	-0.61682000
C	-6.38874800	1.74006700	0.88613400
H	-5.61023200	-0.04151500	1.78333300
C	-5.00459800	2.77984200	-0.78975000
H	-3.14988200	1.81532500	-1.22150500
C	-6.17588500	2.75784700	-0.03881400
H	-7.30088400	1.71873700	1.47054400
H	-4.83051000	3.57220500	-1.50777100
H	-6.92163000	3.53219200	-0.17425600
B	1.07010000	0.37043500	0.00470500
C	1.55347900	-0.63035400	1.18838300
C	2.51577800	-1.60884700	0.94815200
C	0.95991300	-0.71856200	2.44557900
C	2.88216500	-2.57667900	1.86807200
C	1.30239500	-1.66621500	3.39769000
C	2.27215100	-2.60677600	3.10761100
C	2.24776800	0.74268700	-1.06669200
C	3.29614800	1.57494000	-0.69934000
C	2.28778400	0.30797300	-2.38106100
C	4.31234500	1.95879600	-1.55857800
C	3.28105400	0.66514300	-3.27913400
C	4.30175700	1.50102000	-2.86428500
C	0.35672400	1.76846300	0.43737800
C	-0.55471500	2.33938000	-0.44163800
C	0.62764900	2.52787900	1.56839400
C	-1.18729600	3.55199900	-0.22386000
C	0.00726000	3.73975700	1.83362800
C	-0.91012400	4.25460000	0.93484800
F	1.34759900	-0.53244800	-2.85760300
F	3.26600300	0.20985900	-4.53337100
F	5.26611900	1.85683200	-3.71044200
F	5.29531400	2.76005700	-1.14560600
F	3.36265700	2.04172500	0.55580900
F	-0.03031300	0.11330000	2.80209900
F	0.68072600	-1.69961600	4.57782700
F	2.58313200	-3.55397100	3.98961000
F	3.77478100	-3.51503200	1.54677600
F	3.12509100	-1.69430100	-0.24631000
F	1.52197600	2.11735300	2.47551000
F	0.29293500	4.42258600	2.94339600
F	-1.50622100	5.42024100	1.17402800
F	-2.04961400	4.04891800	-1.11451300
F	-0.86073600	1.70769300	-1.59463100
H	0.20280200	-0.27172700	-0.60713500

4aa‘c

M06-2X/6-311G(d,p) free energy: -1240.832412
M06-2X/6-311G(d,p) SCF energy: -1241.1396
M06-2X/cc-PVTZ SCF energy: -1241.2198154

C	1.70449300	-4.50598500	-1.25193400
C	1.16313700	-3.28744700	-1.65369000
C	0.46293900	-2.47961900	-0.75687300
C	0.35456200	-2.90585400	0.57010200
C	0.88982600	-4.12243400	0.97689900
C	1.55839800	-4.93353700	0.06306700
H	2.23935700	-5.11974500	-1.96732500
H	1.28535500	-2.95972200	-2.68066100

H	-0.14345100	-2.27638800	1.30066500
H	0.78974000	-4.43628800	2.00935100
H	1.97289800	-5.88359600	0.37823500
C	-0.18788400	-1.19528400	-1.21801900
C	-1.74264500	-1.22810400	-1.20791400
Si	-2.51587600	-2.64668400	-2.21154000
C	-4.35835000	-2.30330700	-2.39640900
H	-4.88955300	-2.41575700	-1.44778600
H	-4.54295900	-1.28787200	-2.75803800
H	-4.79513300	-3.00551000	-3.11240900
C	-1.73822100	-2.67577500	-3.92516500
H	-0.68452300	-2.95999200	-3.89093800
H	-2.25748400	-3.39776600	-4.56153200
H	-1.81045100	-1.69409400	-4.40173000
C	-2.31362300	-4.32597700	-1.38664000
H	-1.26754200	-4.63479600	-1.32579700
H	-2.72318300	-4.31797400	-0.37298300
H	-2.86127700	-5.07913400	-1.96131200
H	0.15356300	-0.98250800	-2.23529000
H	-2.07580200	-0.32600100	-1.74375600
Si	-2.52597300	-1.01625200	0.49471300
H	-2.72250000	-2.29849300	1.21882300
H	-1.63696100	-0.16006300	1.32702000
C	-4.22444600	-0.22487800	0.33064800
C	-5.34478400	-0.79550600	0.94672500
C	-4.41301000	0.93382100	-0.43446600
C	-6.61107000	-0.23606700	0.79832400
H	-5.23132100	-1.69594800	1.54255800
C	-5.67533800	1.49821200	-0.58613600
H	-3.56597400	1.40647900	-0.92366200
C	-6.77784900	0.91077400	0.02884200
H	-7.46633300	-0.69616200	1.27945400
H	-5.80037300	2.39367200	-1.18375100
H	-7.76283200	1.34631200	-0.09159700
H	0.16558000	-0.36882000	-0.59140300

2b‘

M06-2X/6-311G(d,p) free energy: -370.425436
M06-2X/6-311G(d,p) SCF energy: -370.488211
M06-2X/cc-PVTZ SCF energy: -370.5031949

Si	4.89444200	-4.37558500	-0.67644900
H	5.66977800	-3.78557100	-1.79806000
C	3.53416600	-5.47379400	-1.35910200
H	3.94416500	-6.27532400	-1.97659300
H	2.96380300	-5.92893100	-0.54622800
C	4.17794200	-3.00376900	0.38538600
H	3.49823700	-2.38035800	-0.19993900
H	3.61633300	-3.42097300	1.22429600
H	4.96434100	-2.36276700	0.78853700
H	2.84288800	-4.89188000	-1.97289100
H	5.83682100	-5.19171600	0.13167800

TS$_{3aa‘a‘}$

M06-2X/6-311G(d,p) free energy: -3335.766784
M06-2X/6-311G(d,p) SCF energy: -3336.1990542
M06-2X/cc-PVTZ SCF energy: -3336.5239225

C	-0.80864200	-5.18652400	3.05391900
C	0.17090200	-4.25275100	2.74245400
C	1.46392200	-4.36716000	3.27109400
C	1.76063200	-5.46133000	4.09585300
C	0.78640700	-6.39806300	4.40047900
C	-0.50218700	-6.25850700	3.88528200
H	-1.80569300	-5.08120900	2.64508300
H	-0.06354400	-3.41793000	2.09087400
H	2.76427800	-5.59770000	4.47562300
H	1.02964500	-7.24231400	5.03345400
H	-1.26182200	-6.99227900	4.12589800
C	2.43275900	-3.32943000	2.92331600
C	3.66944100	-3.07730400	3.43344300
Si	4.44778500	-3.47971700	5.13584500
C	5.64497800	-2.06333300	5.42159300
H	6.46710600	-2.04894800	4.70333100
H	5.12403400	-1.10430900	5.35886100
H	6.07636100	-2.14471300	6.42273600
C	3.10659000	-3.37998500	6.44476000
H	2.38769400	-4.19882100	6.40150600
H	3.57924400	-3.39840500	7.43100700
H	2.55834400	-2.43913400	6.35242600
C	5.37375600	-5.11091000	5.28936300
H	4.71667900	-5.98210700	5.33885800

H	6.10974200	-5.28352000	4.50089000
H	5.91905300	-5.07127300	6.23751300
H	2.07123200	-2.65529800	2.14777700
H	4.09216500	-2.15626500	3.02721100
Si	4.75592200	-4.28307100	1.46914200
B	6.94721400	-5.19434600	-0.74139600
C	6.96326200	-3.69629600	-1.38879100
C	7.81922100	-2.66393900	-1.02716700
C	6.02367200	-3.34273400	-2.35174400
C	7.75102200	-1.38403600	-1.56023500
C	5.91566700	-2.08327900	-2.91116400
C	6.79360800	-1.09033200	-2.51145200
C	8.26171600	-5.58338400	0.14090600
C	9.52105400	-5.54456100	-0.44394200
C	8.23561100	-6.05991600	1.44013400
C	10.68080900	-5.91947000	0.20776700
C	9.37206300	-6.44413200	2.13784100
C	10.60332500	-6.37551900	1.51477900
C	6.76911000	-6.40686000	-1.82155500
C	6.36706800	-7.65319400	-1.35999400
C	7.07817200	-6.36080800	-3.17420600
C	6.23504900	-8.77214700	-2.16361200
C	6.96314100	-7.45643100	-4.01725000
C	6.53580000	-8.66991600	-3.51039600
F	7.07334500	-6.15637100	2.11319600
F	9.28469700	-6.87835500	3.39609900
F	11.70671200	-6.74141600	2.16251400
F	11.86636800	-5.84985400	-0.39782800
F	9.64134600	-5.10390600	-1.70502100
F	5.13617600	-4.25706000	-2.78264200
F	4.98128500	-1.81626800	-3.82336300
F	6.71154500	0.13075400	-3.03255300
F	8.60107300	-0.43728500	-1.16217900
F	8.77672200	-2.84793800	-0.10178400
F	7.51433900	-5.22946300	-3.74500300
F	7.26509500	-7.35252600	-5.31232800
F	6.42081000	-9.72964400	-4.30755700
F	5.83514400	-9.93964200	-1.65789000
F	6.09686300	-7.81977300	-0.05237200
H	5.95282200	-5.24316100	0.00187800
C	3.74309600	-3.53195600	0.10239300
H	3.83696100	-2.44383800	0.08211400
H	4.06933200	-3.92904800	-0.85777800
H	2.69214200	-3.80017600	0.22275300
C	6.28640300	-3.38028100	2.03342100
H	6.11519600	-2.30261400	2.00270600
H	6.56659600	-3.66872800	3.04602800
H	7.12907800	-3.60756700	1.38287000
C	4.26611000	-5.99485600	1.98327100
H	3.18150400	-6.09384900	1.91675100
H	4.72571500	-6.71416400	1.30661500
H	4.59103100	-6.22982600	2.99610800

$TS_{3ab'b'}$

M06-2X/6-311G(d,p) free energy: -3296.478599
M06-2X/6-311G(d,p) SCF energy: -3296.881782
M06-2X/cc-PVTZ SCF energy: -3297.2034183

C	-0.31560300	-5.72876400	2.49117400
C	0.44479300	-4.56984000	2.45493200
C	1.74833100	-4.55321300	2.97669000
C	2.28432300	-5.73841100	3.50536200
C	1.52822300	-6.89860200	3.52821100
C	0.22652300	-6.89302200	3.02808700
H	-1.32325000	-5.72857400	2.09562700
H	0.03245600	-3.66169000	2.02923000
H	3.29738300	-5.75957700	3.88275500
H	1.95164700	-7.81001500	3.93064300
H	-0.36190300	-7.80224900	3.04983300
C	2.48019700	-3.29885300	2.91592700
C	3.69467100	-2.96401100	3.46046800
Si	4.46948600	-3.54729500	5.12335200
C	5.35803700	-2.01455400	5.73441100
H	6.14254400	-1.69110800	5.04619500
H	4.65664400	-1.18653500	5.86368700
H	5.82294500	-2.21716300	6.70274400
C	3.06384900	-3.94990100	6.29756000
H	2.54481500	-4.87860100	6.05722600
H	3.47213300	-4.04601200	7.30771500
H	2.33039300	-3.13983600	6.30578900
C	5.68723200	-4.97099200	5.02857700
H	5.31999700	-5.86451500	4.52087700
H	6.62453900	-4.68607500	4.54851400

H	5.92080100	-5.25285500	6.06014600
H	1.97811900	-2.54049300	2.31557900
H	3.93788600	-1.91500800	3.27395300
Si	4.82722400	-3.79139800	1.66701200
B	6.85688700	-4.98935700	-0.54403700
C	7.03891600	-3.60366200	-1.38555300
C	8.03661700	-2.66524100	-1.14907700
C	6.14744000	-3.24102700	-2.39030700
C	8.15302500	-1.46976500	-1.84345900
C	6.22233500	-2.06106100	-3.10874600
C	7.24123100	-1.16561700	-2.83553500
C	8.18951700	-5.47129200	0.25929500
C	9.37366700	-5.70903000	-0.42620000
C	8.23214100	-5.75368100	1.61258600
C	10.52958600	-6.16832900	0.17674900
C	9.36803300	-6.21393900	2.26404100
C	10.52514400	-6.42414500	1.53936800
C	6.35392900	-6.27404800	-1.41290400
C	5.69359600	-7.30480300	-0.75708100
C	6.59579500	-6.49680000	-2.76138700
C	5.27124900	-8.46715100	-1.38018300
C	6.19246500	-7.64588100	-3.42458200
C	5.52473600	-8.63802800	-2.72952000
F	7.14421400	-5.57905200	2.38391300
F	9.34994700	-6.45460500	3.57654400
F	11.62640400	-6.86758100	2.14147200
F	11.64322700	-6.36883800	-0.52886400
F	9.42530900	-5.46864400	-1.74477300
F	5.12216100	-4.05226300	-2.70463300
F	5.32640500	-1.77801200	-4.05442700
F	7.33381800	-0.02341300	-3.51124500
F	9.13419100	-0.61255900	-1.56037700
F	8.95933000	-2.86319200	-0.19140300
F	7.23687100	-5.58395800	-3.50447900
F	6.44174500	-7.80595100	-4.72553800
F	5.13129700	-9.74732300	-3.35236500
F	4.63387700	-9.42080900	-0.69829200
F	5.44072600	-7.20399500	0.55896400
H	5.96903800	-4.79416400	0.29240100
C	3.75468300	-3.24218300	0.24443800
H	3.54392600	-2.17270000	0.31630500
H	4.24693000	-3.43502300	-0.70618800
H	2.80838300	-3.78753500	0.24474100
C	6.32276800	-2.74982100	2.06870200
H	6.06478300	-1.69136000	1.99099700
H	6.68512900	-2.95104700	3.07679100
H	7.13489300	-2.96174300	1.37255400
H	4.69570100	-5.17789900	2.12352000

TS$_{3b'b'\text{-}iso}$

M06-2X/6-311G(d,p) free energy: -3296.47513
M06-2X/6-311G(d,p) SCF energy: -3296.88055
M06-2X/cc-PVTZ SCF energy: -3297.20278

C	-0.43428600	-5.59435100	2.32175200
C	0.53863000	-4.64138100	2.05726200
C	1.67404400	-4.53125400	2.87532700
C	1.82036600	-5.41621000	3.95564600
C	0.85381400	-6.37166300	4.21430300
C	-0.27676700	-6.45847700	3.40028900
H	-1.30851600	-5.66669600	1.68759200
H	0.42455800	-3.96831100	1.21503000
H	2.70039800	-5.37205500	4.58121400
H	0.97775800	-7.05385900	5.04570900
H	-1.03171500	-7.20725500	3.60713600
C	2.63769700	-3.49782100	2.54196300
C	3.79736500	-3.11620200	3.17435900
Si	4.28962400	-3.16522300	5.03264500
C	5.47734000	-1.72941600	5.23206400
H	6.43406500	-1.89694900	4.73462800
H	5.04312300	-0.80669400	4.83903600
H	5.67689900	-1.57715900	6.29630400
C	2.74510200	-2.80021100	6.03135800
H	1.97771500	-3.57154800	5.95494200
H	3.01942800	-2.70046900	7.08532200
H	2.30899300	-1.85243400	5.70590800
C	5.12212700	-4.73723800	5.63941000
H	4.44924100	-5.59028800	5.74569800
H	5.96838800	-5.04603400	5.02222500
H	5.51402600	-4.51549000	6.63689700
H	2.38456900	-2.96404900	1.62592200
H	4.20470800	-2.21337800	2.71084100
Si	5.07137900	-4.40647500	1.79810400

B	7.04081100	-5.30449200	-0.52063200
C	6.91988500	-3.76885200	-1.04648100
C	7.83449800	-2.74975400	-0.82223800
C	5.77202000	-3.37182100	-1.72431100
C	7.64428500	-1.44128600	-1.24619500
C	5.53863800	-2.08244400	-2.16526500
C	6.49027400	-1.10524600	-1.92697900
C	8.48179200	-5.72131900	0.11081800
C	9.62479500	-5.66535000	-0.67542000
C	8.66520300	-6.23969400	1.38100100
C	10.87297700	-6.06930700	-0.24147200
C	9.89854700	-6.65865000	1.86165400
C	11.00835100	-6.57364600	1.04305600
C	6.68074900	-6.43901300	-1.63592500
C	6.35680000	-7.71523100	-1.19502700
C	6.72596600	-6.28908700	-3.01401600
C	6.06878600	-8.77303400	-2.03980500
C	6.44579800	-7.32071300	-3.89825800
C	6.11332800	-8.57044300	-3.40833000
F	7.62958800	-6.35302300	2.23368100
F	10.02154800	-7.14340700	3.09852200
F	12.20032100	-6.97089200	1.48343300
F	11.94226600	-5.98369900	-1.03363900
F	9.53409200	-5.18031300	-1.92298200
F	4.80465600	-4.27038800	-1.97109700
F	4.41272600	-1.76896000	-2.80840700
F	6.28919900	0.14427500	-2.33926500
F	8.56237300	-0.50610700	-0.99793000
F	8.97164200	-2.97581700	-0.14293900
F	7.04725900	-5.11074700	-3.56732600
F	6.49584900	-7.12150100	-5.21664900
F	5.84170100	-9.57048500	-4.24473100
F	5.75707100	-9.97685300	-1.55638100
F	6.32261700	-7.97202500	0.12515300
H	6.19326400	-5.44276900	0.35983500
C	6.63620600	-3.54903200	2.35462000
H	6.89769300	-3.82821100	3.37581400
H	7.46634100	-3.83248200	1.70758100
H	6.51563800	-2.46574500	2.30054300
C	4.61908300	-6.12424600	2.34720500
H	4.59861300	-6.20794700	3.43427800
H	3.63626800	-6.39219000	1.95520200
H	5.35221500	-6.83029900	1.96105200
H	4.47333300	-3.90576900	0.55422800

$TS_{1a\text{-}VII}$

M06-2X/6-311G(d,p) free energy: -2516.308365
M06-2X/6-311G(d,p) SCF energy: -2516.5092946
M06-2X/cc-PVTZ SCF energy: -2516.7979731

B	-0.52432000	0.03293700	-0.18981700
C	-1.31178700	-1.36738900	-0.19364800
C	-1.40616900	-2.35339000	-1.16189400
C	-1.92796000	-1.65827400	1.01914800
C	-2.08599800	-3.54495800	-0.94751100
C	-2.61283400	-2.82982700	1.27132500
C	-2.69266200	-3.78452400	0.27045500
C	-1.36735700	1.38508200	-0.21066700
C	-0.74215400	2.62517500	-0.34730700
C	-2.75937300	1.43662300	-0.14750100
C	-1.42065600	3.82635700	-0.40127000
C	-3.47460500	2.62416000	-0.18673500
C	-2.80329000	3.82502300	-0.31552600
C	0.84514800	-0.06139600	0.61445000
C	1.25419500	0.82967300	1.60250100
C	1.71823400	-1.12134900	0.37241400
C	2.47739100	0.72734300	2.24585500
C	2.94896000	-1.25260000	0.98836700
C	3.33523000	-0.31047500	1.92597200
F	-3.49474900	0.32741700	-0.04209500
F	-4.80192100	2.61330900	-0.10880900
F	-3.47505700	4.96571200	-0.35995400
F	-0.76538200	4.97510400	-0.53543300
F	0.58862400	2.69224800	-0.44895500
F	-1.87735400	-0.74436300	2.00057700
F	-3.19254000	-3.04739400	2.44862600
F	-3.34445500	-4.92160100	0.48240900
F	-2.14995600	-4.46339900	-1.90916700
F	-0.83013700	-2.21647600	-2.36001300
F	1.40905200	-2.04145200	-0.54769300
F	3.76317300	-2.25725100	0.67872800
F	4.51692000	-0.40649300	2.51880900
F	2.83069800	1.61323500	3.17342600

F	0.46315100	1.83029900	1.99682400
C	4.61173000	-0.89092400	-2.03890200
C	3.27172300	-0.78587800	-2.37699500
C	2.55696200	0.37342100	-2.03717500
C	3.20249300	1.43336400	-1.38486500
C	4.54200200	1.31199100	-1.04365600
C	5.24241100	0.14993800	-1.35985000
H	5.16079100	-1.79017500	-2.28734800
H	2.75811100	-1.59820100	-2.87530600
H	2.64942100	2.32855400	-1.13851500
H	5.03948400	2.12225600	-0.52536400
H	6.28457300	0.05642600	-1.07959500
C	1.15340100	0.40991400	-2.28446900
C	-0.05290300	0.35086900	-2.40988700
H	-1.04416800	0.35869400	-2.80607800

VII

M06-2X/6-311G(d,p) free energy: -2516.312258
M06-2X/6-311G(d,p) SCF energy: -2516.5123694
M06-2X/cc-PVTZ SCF energy: -2516.801128

B	0.43020900	0.05982800	-0.45048900
C	-0.17623800	0.20472100	-2.09330500
C	1.08925000	1.54027100	-0.30046500
C	0.26469200	2.65933900	-0.23101000
C	0.72549300	3.95987200	-0.16662700
C	2.09087500	4.19025600	-0.17942100
C	2.95579300	3.11633800	-0.26197900
C	2.44897700	1.82576800	-0.33057600
F	-1.06901300	2.49848900	-0.21835100
F	-0.12196000	4.98487500	-0.09448800
F	2.56227800	5.43059100	-0.11785900
F	4.27081000	3.32715600	-0.28392500
F	3.36409600	0.85362700	-0.43441100
C	-1.42315100	0.24925100	-2.15165600
C	-0.76016100	-0.29847100	0.60641800
C	1.47944800	-1.18257600	-0.39837100
C	1.68684900	-2.16217000	-1.35481000
C	2.56044500	-3.22557000	-1.16918100
C	3.25852000	-3.33845500	0.01715500
C	3.07405600	-2.38795200	1.00870800
C	2.19371700	-1.34807600	0.78328700
F	2.04782400	-0.44425900	1.76385500
F	3.74326300	-2.48745400	2.15626900
F	4.09939500	-4.35051800	0.20841500
F	2.72600700	-4.13990900	-2.12487000
F	1.03740900	-2.13679700	-2.52861300
C	-1.06626000	0.39358300	1.77116700
C	-2.10117900	0.02692900	2.62011500
C	-2.87139900	-1.08347500	2.32792400
C	-2.58054100	-1.82888000	1.19885100
C	-1.52701500	-1.43955900	0.39214500
F	-1.27386400	-2.21827700	-0.67412400
F	-3.30878600	-2.90320000	0.89853400
F	-3.87236800	-1.43698500	3.12714200
F	-2.35737600	0.73553600	3.71870800
F	-0.36082400	1.46611600	2.14794800
H	0.59158800	0.29885400	-2.84724300
C	-2.81047700	0.22783500	-2.02620200
C	-3.50177400	-0.99545100	-2.18246300
C	-3.50817900	1.41075800	-1.69828200
C	-4.86934900	-1.02825400	-1.99448300
H	-2.94599600	-1.88910400	-2.43399500
C	-4.87676300	1.35911800	-1.51472300
H	-2.95827300	2.33506500	-1.58427100
C	-5.54950500	0.14442800	-1.65803900
H	-5.41080700	-1.95871700	-2.10262500
H	-5.42454100	2.25574400	-1.25655500
H	-6.62175900	0.11066200	-1.50599200

TS$_{VII\text{-}9}$

M06-2X/6-311G(d,p) free energy: -2516.292189
M06-2X/6-311G(d,p) SCF energy: -2516.4893069
M06-2X/cc-PVTZ SCF energy : -2516.7806825

C	1.01326100	-1.93177500	1.52863900
C	0.70593900	-0.58517400	1.39865800
C	0.97464000	0.19753800	2.51146100
C	1.49880400	-0.32499500	3.68444000
C	1.77826900	-1.67742100	3.76926400
C	1.53512400	-2.49495800	2.67859400
B	0.17240400	-0.05027900	-0.04585500

C	1.43727500	-0.08526000	-1.06125800
C	1.65466400	-1.02680900	-2.05195400
C	2.80609800	-1.05755500	-2.82595500
C	3.79540100	-0.11794700	-2.60805900
C	3.62564800	0.83737100	-1.61750000
C	2.46537300	0.82815900	-0.86801000
F	0.74173300	-1.98007300	-2.30785200
F	2.96599300	-1.98396500	-3.76918200
F	4.90492800	-0.13095900	-3.33915900
F	4.57664400	1.74348000	-1.40171400
F	2.33423100	1.76308300	0.08282400
F	0.73178100	1.51273000	2.50257000
F	1.73596700	0.46302300	4.73111200
F	2.28071400	-2.18798700	4.88832600
F	1.80702600	-3.79615700	2.74637900
F	0.81138000	-2.75452700	0.47965500
C	-1.05138400	-0.94454400	-0.53643100
C	-2.03330300	-1.63410900	-0.87596300
C	-0.66892100	1.35950200	0.00104100
C	-1.63120700	1.56395200	0.98502000
C	-2.39180600	2.71432800	1.08372300
C	-2.21143700	3.72248900	0.15250700
C	-1.28220700	3.55686700	-0.85816400
C	-0.54272900	2.38585800	-0.92751400
F	-1.85862300	0.61112400	1.89942500
F	-3.29589900	2.85545700	2.04999600
F	-2.93158600	4.83484100	0.22332300
F	-1.11223600	4.51820700	-1.76268000
F	0.31394200	2.29488400	-1.94954900
H	-1.09947100	-2.36075700	-0.86388500
C	-3.37383100	-2.07210200	-1.19568900
C	-4.44406000	-1.27761100	-0.77232600
C	-3.59263900	-3.24947800	-1.91299000
C	-5.73876300	-1.66880400	-1.07938500
H	-4.25665500	-0.37427600	-0.20492700
C	-4.89374500	-3.62930600	-2.21108700
H	-2.75436300	-3.85444100	-2.23530100
C	-5.96364600	-2.84120200	-1.79689000
H	-6.57287300	-1.05978200	-0.75498600
H	-5.07144500	-4.54060500	-2.76756900
H	-6.97705700	-3.14228300	-2.03183900

9

M06-2X/6-311G(d,p) free energy: -2516.363780
M06-2X/6-311G(d,p) SCF energy: -2516.565191
M06-2X/cc-PVTZ SCF energy: -2516.8568863

B	0.83322200	-0.04302700	-0.15084400
C	-1.70768400	-0.32867500	0.27176900
C	-2.83622500	-0.37287400	-0.54009000
C	-1.80166300	0.41604800	1.44115900
C	-4.01265900	0.26376800	-0.18650300
C	-2.96442600	1.06606800	1.81621400
C	-4.07712600	0.98349000	0.99648600
C	0.65519300	1.50907500	-0.32533400
C	-0.24775400	2.04916400	-1.23596900
C	1.37625800	2.41771000	0.44155000
C	-0.43527800	3.41198500	-1.38146300
C	1.20477400	3.78624600	0.33240700
C	0.29526800	4.28195700	-0.58777500
C	2.28286500	-0.62965700	-0.02938100
C	3.31349000	-0.18020600	-0.85137500
C	2.62721000	-1.58553200	0.92358200
C	4.60641900	-0.66128700	-0.76042300
C	3.91566200	-2.07511000	1.05259200
C	4.90577700	-1.61275400	0.20169700
F	2.25432600	1.97912900	1.34638600
F	1.89738500	4.62553400	1.09475000
F	0.12572100	5.58963100	-0.71091000
F	-1.29608500	3.89348700	-2.27181500
F	-0.95310100	1.24481600	-2.03641000
F	-0.73281800	0.51944100	2.23825800
F	-3.01996600	1.76371400	2.94616000
F	-5.20169500	1.59944900	1.33794700
F	-5.07860500	0.20286900	-0.97871100
F	-2.80261500	-1.02732800	-1.69766700
F	1.71816700	-2.04341100	1.78511600
F	4.21223600	-2.97687600	1.98232700
F	6.14013600	-2.07937000	0.30800000
F	5.55907000	-0.22417900	-1.57692800
F	3.06649100	0.73566600	-1.79047600
C	-3.32994900	-4.35836200	0.39217800
C	-2.37855400	-3.35041400	0.46180200

C	-1.26891900	-4.27851200	-1.47071800
C	-2.23465200	-5.27281400	-1.55141800
C	-3.26879800	-5.31241400	-0.62120700
H	-4.11864300	-4.40417100	1.13313700
H	-2.41924400	-2.62806200	1.26783800
H	-0.45453600	-4.25304600	-2.18634400
H	-2.17533100	-6.02114300	-2.33207500
H	-4.01801200	-6.09291000	-0.67578100
C	-0.41305700	-0.95502000	-0.09778300
C	-1.34370300	-3.29120500	-0.48120400
C	-0.30435100	-2.25661600	-0.45158600
H	0.67311900	-2.59301500	-0.79203000

II-*E*

M06-2X/6-311G(d,p) free energy: -2926.014407
M06-2X/6-311G(d,p) SCF energy: -2926.3273719
M06-2X/cc-PVTZ SCF energy: -2926.6329178

C	3.15607200	-3.30036800	0.52321500
C	1.80026600	-3.16252600	0.73924700
C	1.35265800	-2.42412200	1.86243300
C	2.28081600	-1.82162100	2.74568100
C	3.63167000	-1.95393700	2.49961600
C	4.06314800	-2.69340200	1.39549100
H	3.51550400	-3.87066200	-0.32343300
H	1.07783700	-3.62753700	0.08498500
H	1.91465600	-1.25418700	3.59182100
H	4.35314300	-1.48433100	3.15451700
H	5.12615300	-2.79183200	1.20714200
C	0.00473100	-2.36743700	2.17362600
C	-1.18840900	-2.45045600	2.58583900
Si	-2.80794200	-1.37180400	2.72988100
C	-3.99064200	-2.03762600	1.45372600
H	-3.71200900	-1.70729500	0.45333400
H	-4.03365000	-3.12842400	1.46503000
H	-4.99135000	-1.65356900	1.67115500
C	-3.35963300	-1.80183300	4.46305800
H	-2.61194900	-1.50838400	5.20318100
H	-4.28609800	-1.26797700	4.68998100
H	-3.55152000	-2.87210000	4.56855500
C	-2.49735700	0.45276400	2.57485600
H	-1.67185400	0.77617000	3.20882100
H	-2.29401900	0.77201600	1.55309800
H	-3.40887000	0.95415500	2.91671600
B	-0.09375000	0.31855900	-0.00887000
C	1.34996700	-0.08301100	-0.67622600
C	1.60297400	-0.61171600	-1.93475500
C	2.49180800	0.16861400	0.07980400
C	2.87666600	-0.92344400	-2.39245500
C	3.77932700	-0.10687200	-0.34330800
C	3.97414900	-0.67403500	-1.59024600
C	-1.40408500	-0.24497100	-0.81743400
C	-2.53696800	0.48055600	-1.16628600
C	-1.46427800	-1.58340800	-1.18609100
C	-3.61148400	-0.05386500	-1.86619000
C	-2.50242900	-2.16175800	-1.89323100
C	-3.59151500	-1.38297700	-2.24425000
C	-0.05289100	1.94056300	0.16799900
C	0.13602000	2.58745100	1.37853200
C	-0.09737400	2.77219500	-0.94262700
C	0.23799100	3.96792200	1.49277400
C	-0.00140600	4.14953700	-0.87792100
C	0.16778600	4.75302500	0.35801800
F	-0.44532700	-2.40166900	-0.86433200
F	-2.47460600	-3.45472100	-2.22105500
F	-4.61413200	-1.91248700	-2.91168800
F	-4.66499500	0.70406700	-2.17338500
F	-2.66675000	1.77330100	-0.82513800
F	2.37408100	0.70706800	1.30537800
F	4.82942200	0.12827800	0.44880900
F	5.20221200	-0.97922200	-2.00669900
F	3.05319600	-1.45171900	-3.60542000
F	0.60586800	-0.84697700	-2.80127400
F	-0.25764400	2.22877800	-2.16077600
F	-0.06576900	4.90209900	-1.97879500
F	0.26587800	6.07895000	0.44923500
F	0.41336700	4.54402200	2.68525300
F	0.24172700	1.89857300	2.52593600
H	-0.11457600	-0.18366100	1.09715100
H	-1.34568500	-3.40443000	3.11217500

TS$_{\mathbf{II\text{-}\mathit{E}\text{-}3aa'}}$

M06-2X/6-311G(d,p) free energy: -2926.012456
M06-2X/6-311G(d,p) SCF energy: -2926.3265659
M06-2X/cc-PVTZ SCF energy: -2926.6319162

C	3.40857200	-2.90928300	1.11255500
C	2.04578400	-2.74256500	1.26754100
C	1.56944000	-1.76476200	2.17006900
C	2.47189100	-0.95926100	2.89918600
C	3.83043900	-1.13311700	2.72207400
C	4.29369100	-2.10292700	1.83075600
H	3.78807300	-3.65870600	0.42998800
H	1.34206800	-3.35867600	0.72775600
H	2.08366100	-0.20619400	3.57321200
H	4.53230900	-0.51366700	3.26420000
H	5.36096300	-2.22822000	1.68984700
C	0.20293200	-1.63260200	2.41846500
C	-0.96573400	-1.73184600	2.90881800
Si	-2.71396300	-0.90073100	2.87810300
C	-3.80409800	-1.97591300	1.81257500
H	-3.64355100	-1.76832200	0.75480300
H	-3.63258500	-3.03935900	1.99101500
H	-4.84950300	-1.75507500	2.04532700
C	-3.21319200	-1.01093500	4.67633700
H	-2.51702600	-0.46407000	5.31616000
H	-4.20602500	-0.57249300	4.80590300
H	-3.25515300	-2.04805700	5.01714700
C	-2.67347500	0.87209400	2.32086100
H	-2.02650700	1.47438600	2.95880500
H	-2.35868700	0.99640400	1.28542900
H	-3.69629000	1.25236300	2.41175100
B	-0.10416200	0.24170400	-0.11918100
C	1.35463400	-0.16178200	-0.73900800
C	1.62833800	-0.93670900	-1.85897400
C	2.48722700	0.32492300	-0.08889300
C	2.91484400	-1.25903800	-2.27045000
C	3.78514500	0.04194100	-0.47258000
C	4.00222200	-0.77302400	-1.56936500
C	-1.38670900	-0.51802400	-0.79067000
C	-2.55154600	0.07189000	-1.26806600
C	-1.37954900	-1.90479000	-0.89012600
C	-3.59535600	-0.64148400	-1.84405700
C	-2.38604000	-2.65935300	-1.46314000
C	-3.50946300	-2.01649800	-1.95392900
C	-0.17983900	1.86733400	-0.11699100
C	-0.04308500	2.64716100	1.01987100
C	-0.27938300	2.56979000	-1.30898500
C	-0.05063300	4.03434000	0.99147600
C	-0.28978000	3.95040200	-1.38636500
C	-0.17636000	4.68908000	-0.21973100
F	-0.32191600	-2.59116000	-0.42221000
F	-2.29589000	-3.98789400	-1.53052600
F	-4.50199100	-2.71423900	-2.49904800
F	-4.68244500	-0.01057000	-2.28805000
F	-2.74802900	1.39702300	-1.18371100
F	2.34998500	1.11052700	0.99232400
F	4.82525400	0.51393500	0.21844000
F	5.24181500	-1.08246400	-1.94283400
F	3.11189100	-2.02606600	-3.34395800
F	0.64131800	-1.41787200	-2.62896000
F	-0.38646000	1.89061600	-2.46212000
F	-0.40435600	4.57741100	-2.55880600
F	-0.18295900	6.02035900	-0.26634200
F	0.07352800	4.74234500	2.11678800
F	0.11948000	2.08304800	2.22744500
H	-0.07346700	-0.12441100	1.06055100
H	-0.95052200	-2.53941600	3.65916800

***E*-3aa‘**

M06-2X/6-311G(d,p) free energy: -718.024512
M06-2X/6-311G(d,p) SCF energy: -718.218194
M06-2X/cc-PVTZ SCF energy: -718.2706572

C	-3.92026900	1.05194600	0.03403400
C	-2.54306200	1.24157600	-0.00045900
C	-1.66451600	0.15328400	-0.02994300
C	-2.20666800	-1.13836200	-0.03569500
C	-3.58062300	-1.32988900	-0.00295500
C	-4.44406600	-0.23596400	0.03385800
H	-4.58253900	1.90913700	0.05933400
H	-2.13680500	2.24769600	-0.00140900
H	-1.55129800	-2.00045700	-0.07409400
H	-3.98263300	-2.33617800	-0.00981800
H	-5.51623200	-0.38940300	0.05857500

C	-0.21095200	0.41420700	-0.05569200
C	0.77913300	-0.48197000	0.05071500
Si	2.59880100	-0.03448700	0.00893500
C	3.40372800	-0.58288900	1.61661800
H	2.95913400	-0.07009700	2.47287000
H	3.28361400	-1.65888900	1.76694200
H	4.47453700	-0.36236000	1.60605700
C	3.41975900	-0.92783800	-1.42698700
H	2.98376900	-0.62088400	-2.38066200
H	4.49040200	-0.70803800	-1.45580600
H	3.30125200	-2.01043000	-1.33352300
C	2.77829100	1.82277400	-0.20140400
H	2.32081600	2.16527000	-1.13309700
H	2.31470300	2.36547000	0.62635900
H	3.83667500	2.09487900	-0.22876900
H	0.04308800	1.46848600	-0.16586600
H	0.51377500	-1.53262500	0.17528100

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