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Nickel-Catalyzed Insertions of Vinylidenes into Si–H Bonds

Sourish Biswas, Sudipta Pal and Christopher Uyeda*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

Correspondence: cuyeda@purdue.edu

Supporting Information

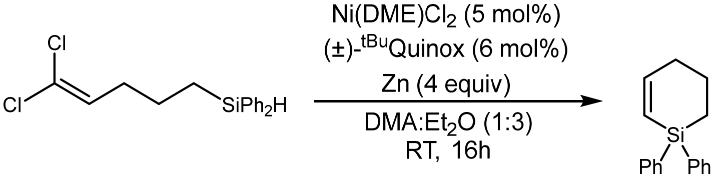
1. General Information

General considerations. Solvents were degassed and stored over activated 3 Å molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over activated 3 Å molecular sieves. Zn powder (325 mesh, 99.9%) was purchased from Strem Chemicals, stored under inert atmosphere, and used without further purification. The ($^{i\text{-pr}}$NDI)$Ni_2(C_6H_6)$ complex was prepared according to a previously reported procedure.[1] The (±)-*t*-Bu-Quinox ligand was prepared according to a previously reported procedure.[2] Unless otherwise noted, all 1,1-dichloroalkenes were prepared according to previously reported procedures.[3] All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted.

Physical methods. ^{1}H, ^{19}F and $^{13}C\{^{1}H\}$ NMR spectra were collected at room temperature on a Varian INOVA 300 MHz, Bruker AV-III-400, or Bruker AV-III-500 NMR spectrometer. ^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer.

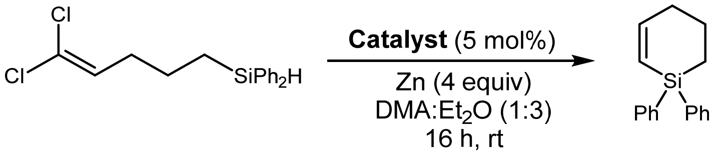
2. Reaction Optimization Studies

General procedure for reaction parameters study. In an N_2-filled glovebox, a 5-mL vial was charged with Ni(DME)Cl_2 (1.1 mg, 0.0050 mmol, 0.050 equiv), (±)-*t*-Bu-Quinox (1.5 mg, 0.0060 mmol, 0.060 equiv), Zn powder (27 mg, 0.40 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and Et_2O (0.2 mL) were added, and the mixture was stirred for 10 min at room temperature. To this mixture was added a solution containing (5,5-dichloropent-4-en-1-yl)diphenylsilane (32.1 mg, 0.100 mmol, 1.0 equiv) and mesitylene (14 µL, 0.10 mmol, 1.0 equiv) dissolved in Et_2O (0.4 mL). The reaction was stirred at room temperature for 16 h. The reaction vial was then removed from the glovebox and opened to ambient atmosphere. Et_2O was removed under a stream of N_2. An aliquot of the crude residue was filtered through a short silica pad, eluting with CH_2Cl_2. The filtrate was then concentrated and analyzed by ^1H NMR.

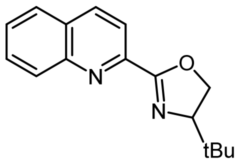


Entry	Deviation from Standard Conditions	Yield
1	none	91%
2	No Zn	0%
3	No Ni(DME)Cl_2	0%
4	No (±)-*t*-Bu-Quinox	0%
5	Mn instead of Zn	85%
6	DMA only instead of Et_2O/DMA	36%
7	Et_2O only instead of Et_2O/DMA	0%

General procedure for ligand effects study. In an N_2-filled glovebox, a 5-mL vial was charged with Ni(DME)Cl_2 (1.1 mg, 0.0050 mmol, 0.050 equiv), Ligand (0.06 equiv), Zn powder (27 mg, 0.40 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and Et_2O (0.2 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing the (5,5-dichloropent-4-en-1-yl)diphenylsilane (32.1 mg, 0.100 mmol, 1.0 equiv) and mesitylene (13.9 µL, 0.100 mmol, 1.0 equiv) dissolved in Et_2O (0.4 mL). The reaction was stirred at room temperature for 16 h. The reaction vial was then removed from the glovebox and opened to ambient atmosphere. Et_2O was removed under a stream of N_2. An aliquot of the crude residue was filtered through a short silica pad, eluting with CH_2Cl_2. The filtrate was then concentrated and analyzed by ^1H NMR.



Entry	Ligand	Yield
1	**3**	91%
2	**4**	50%
3	**5**	17%
4	**6**	83%
5	**7**	45%
6	**8**	43%
7	**S1**	71%
8	**S2**	89%
9	**S3**	18%
10	**S4**	<2%
11	**S5**	23%
12	**S6**	34%



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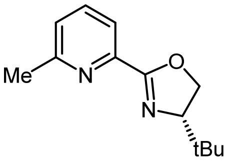

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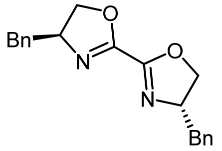

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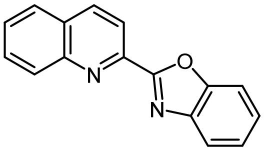

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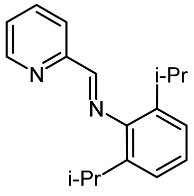

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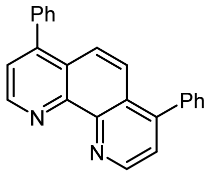

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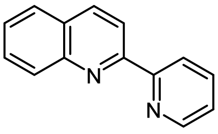
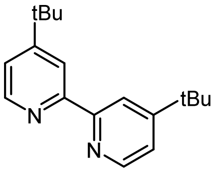


S1



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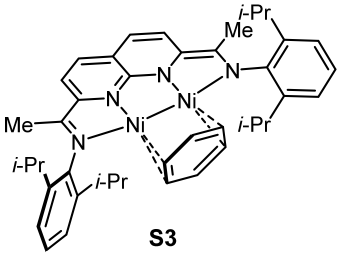

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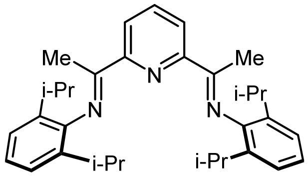

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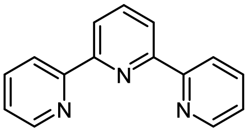

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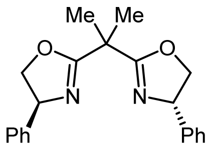
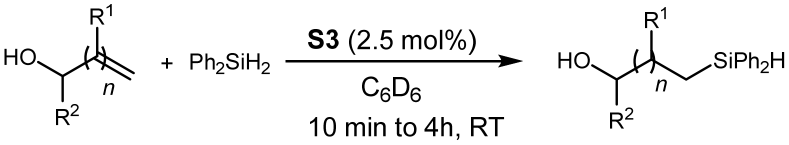
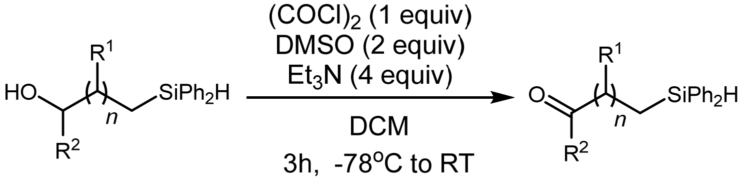


S6

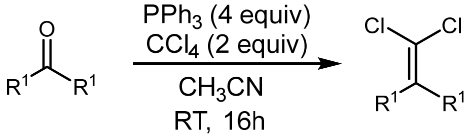
3. Synthesis and Characterization of 1,1-Dichloroalkene Substrates



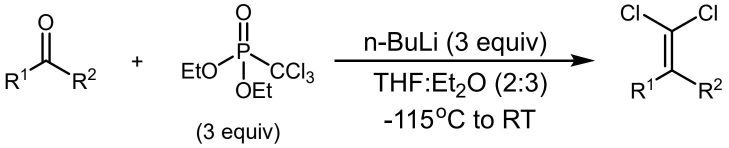
General procedure A: Synthesis of Silyl Alcohols. According to a previously reported procedure:[4] In a N_2 filled glovebox, a 20-dram vial is charged with **S3** (0.025 equiv) dissolved in C_6D_6. To this mixture, a solution containing the unsaturated alcohol (1.0 equiv) and diphenylsilane (1.1 equiv) dissolved in C_6D_6 (0.6 M) was added. The reaction mixture was stirred at room temperature and was monitored by ^{1}H NMR. After full conversion of the unsaturated alcohol, the reaction vial was then removed from the glovebox and opened to ambient temperature. The crude mixture was loaded directly onto a SiO_2 column for purification. Note: the purification must be done as quickly as possible, because the product is susceptible to cyclization.



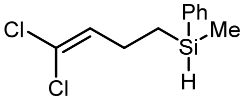
General procedure B: Alcohol Oxidations. In an oven dried round bottom flask, oxalyl chloride (1.0 equiv) was dissolved in CH_2Cl_2 (0.07 M). The solution was then cooled to −78 °C. To this solution, DMSO (2.0 equiv) was added dropwise. The reaction mixture was stirred for 15 min at −78 °C. To the reaction mixture, the silyl alcohol (1.0 equiv) dissolved in CH_2Cl_2 (2 M) was added dropwise. The reaction mixture was allowed to stir for 30 min at −78 °C. Et_3N (4.0 equiv) was added, and the reaction mixture was warmed to room temperature. After 1 h, the reaction was quenched with a saturated solution of NH_4Cl (aq), and the aqueous mixture was extracted with 3 x 10 mL/mmol with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was carried forward to the next step without purification unless otherwise noted.



General Procedure C: Dichlorination of Aldehyde and symmetric ketones. Under N_2 atmosphere, an oven dried 100-mL round bottom flask equipped with a magnetic stir bar was charged with Ph_3P (4.0 equiv) and MeCN (5 mL/mmol). With stirring, a solution containing the aldehyde/ketone (1.0 equiv) and CCl_4 (2.0 equiv) dissolved in MeCN (2 mL/mmol) was added dropwise. Following the addition, the reaction mixture was stirred overnight. The reaction mixture was then quenched with H_2O (15 mL/mmol). The product was extracted with Et_2O (3 x 10 mL/mmol). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography.



General Procedure D. Dichlorination of unsymmetric ketones. According to a previously reported procedure:[5] Under a N_2 atmosphere, an oven dried round bottom flask was charged with diethyl trichloromethylphosphonate (3.0 equiv) dissolved in anhydrous THF (1.7 M) and Et_2O (1.7 M). The solution was cooled to −115 °C (EtOH and liquid N_2 bath). To the solution, 2.5 M *n*-BuLi in hexanes (3.0 equiv) was added dropwise. After 30 min, a solution of the ketone (1.0 equiv) in Et_2O (1.1 M) was added dropwise. The reaction mixture was stirred for additional 1 h at −115 °C before warming to room temperature. After stirring overnight, the reaction mixture was then quenched using saturated NH_4Cl (aq) and extracted with Et_2O. The combined organic phases were dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography.



3-(methyl(phenyl)silyl)propan-1-ol (S7): The reaction was conducted according to the general procedure A without modification using prop-2-en-1-ol (350 mg, 6.03 mmol, 1.0 equiv), methylphenylsilane (0.91 mL, 6.6 mmol, 1.1 equiv), and **S3** (110 mg, 0.151 mmol, 0.025 equiv) in C_6D_6 (4 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R*f* = 0.4) to provide 3-(methyl(phenyl)silyl)propan-1-ol (544 mg, 50% yield) as a pale yellow liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H), 7.42 – 7.32 (m, 3H), 4.38 (h, *J* = 3.6 Hz, 1H), 3.61 (t, *J* = 6.7 Hz, 2H), 1.72 – 1.57 (m, 2H), 1.35 (br s, 1H), 0.92 – 0.79 (m, 2H), 0.39 – 0.34 (m, 3H).

3-(methyl(phenyl)silyl)propanal (*S8*): The reaction was conducted according to the general procedure B without modification using **S7** (544 mg, 3.02 mmol, 1.0 equiv), oxalyl chloride (0.26 mL, 3.0 mmol, 1.0 equiv), dimethylsulfoxide (0.43 mL, 6.0 mmol, 2.0 equiv), and triethylamine (1.7 mL, 12 mmol, 4.0 equiv) in CH_2Cl_2 (40 mL). The crude product was carried forward without purification.

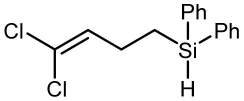
^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.41 – 7.33 (m, 3H), 4.40 (sxt, *J* = 3.6 Hz, 1H), 2.50 – 2.43 (m, 2H), 1.10 (tdd, *J* = 8.2, 3.4, 1.2 Hz, 2H), 0.38 (d, *J* = 3.7 Hz, 3H).

(4,4-dichlorobut-3-en-1-yl)(methyl)(phenyl)silane (*S9*): The reaction was conducted according to the general procedure C without modification using **S8** (178 mg, 1.00 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R*f* = 0.9) to provide (4,4-dichlorobut-3-en-1-yl)(methyl)(phenyl)silane (98 mg, 38% overall yield over two steps) as a colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.43 (m, 2H), 7.42 – 7.29(m, 3H), 5.86 (t, *J* = 7.5 Hz, 1H), 4.40 (h, *J* = 3.6 Hz, 1H), 2.28 (q, *J* = 8.1 Hz, 2H), 1.00 (dtt, *J* = 11.7, 8.2, 3.8 Hz, 2H), 0.43 (d, *J* = 4.0 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.5, 134.3, 131.7, 129.5, 128.0, 119.4, 24.6, 12.4, -5.8.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{11}H_{13}Cl_2Si$: 243.0158; found: 243.0159.



3-(diphenylsilyl)propan-1-ol (S10): The reaction was conducted according to the general procedure A without modification using prop-2-en-1-ol (100 mg, 1.72 mmol, 1.0 equiv), diphenylsilane (0.35 mL, 1.9 mmol, 1.1 equiv) and **S3** (31 mg, 0.043 mmol, 0.025 equiv) in C_6D_6 (3 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f= 0.4) to provide 3-(diphenylsilyl)propan-1-ol (153 mg, 37% yield) as a pale yellow viscous liquid.

^{1}H NMR (300 MHz, C_6D_6) δ 7.55 – 7.51 (m, 4H), 7.21 – 7.27 (m, 6H), 5.08 (t, J = 3.7 Hz, 1H), 3.32 (t, J = 6.5 Hz, 2H), 1.65 – 1.50 (m, 2H), 1.11 – 0.98 (m, 2H).

3-(diphenylsilyl)propanal (S11): The reaction was conducted according to the general procedure B without modification using **S10** (153 mg, 0.631 mmol, 1.0 equiv), oxalyl chloride (0.064 mL, 0.63 mmol, 1.0 equiv), dimethylsulfoxide (0.089 mL, 1.3 mmol, 2.0 equiv) and triethylamine (0.35 mL, 2.5 mmol, 4.0 equiv) in CH_2Cl_2 (10 mL). The crude product was carried forward without purification.

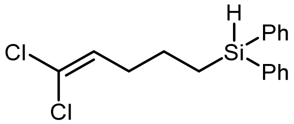
^{1}H NMR (300 MHz, C_6D_6) δ 9.18 (s, 1H), 7.45 – 7.42(m, 4H), 7.16 – 7.14 (m, 6H), 4.96 (t, J = 3.8 Hz, 1H), 2.09 – 1.91 (m, 2H), 1.21 – 1.16 (m, 2H).

(4,4-dichlorobut-3-en-1-yl)diphenylsilane (S12): The reaction was conducted according to the general procedure C without modification using **S11** (240 mg, 1.00 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f = 0.9) to provide ((4,4-dichlorobut-3-en-1-yl)diphenylsilane (166 mg, 49% overall yield over two steps) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.46 – 7.33 (m, 6H), 5.88 (t, J = 7.4 Hz, 1H), 4.89 (t, J = 3.7 Hz, 1H), 2.36 – 2.26 (m, 2H), 1.31 – 1.24 (m, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.2, 133.7, 131.6, 130.0, 128.3, 119.8, 24.7, 11.3.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{16}H_{15}Cl_2Si$: 305.0315; found: 305.0317.



4-(diphenylsilyl)butan-1-ol (S13): The reaction was conducted according to the general procedure A without modification using but-3-en-1-ol (110 mg, 1.52 mmol, 1.0 equiv), diphenylsilane (0.31 mL, 1.7 mmol, 1.1 equiv) and **S3** (50 mg, 0.038 mmol, 0.025 equiv) in C_6D_6 (3 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R*f* = 0.4) to provide 4-(diphenylsilyl)butan-1-ol (257 mg, 66% yield) as a pale yellow viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.50 (m, 4H), 7.48 – 7.31 (m, 6H), 4.88 (t, *J* = 3.6 Hz, 1H), 3.63 (q, *J* = 6.0 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.60 – 1.48 (m, 2H), 1.23 – 1.13 (m, 2H).

4-(diphenylsilyl)butanal (S14): The reaction was conducted according to the general procedure B without modification using **S13** (256 mg, 0.995 mmol, 1.0 equiv), oxalyl chloride (0.080 mL, 1.0 mmol, 1.0 equiv), dimethylsulfoxide (0.1 mL, 2.0 mmol, 2.0 equiv) and triethylamine (0.5 mL, 4.0 mmol, 4.0 equiv) in CH_2Cl_2 (15 mL). The crude product was carried forward without purification.

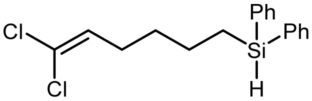
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 1.7 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.43 – 7.33 (m, 6H), 4.88 (t, *J* = 3.7 Hz, 1H), 2.50 (td, *J* = 7.2, 1.7 Hz, 2H), 1.86 – 1.73 (m, 2H), 1.23 – 1.13 (m, 2H).

(5,5-dichloropent-4-en-1-yl)diphenylsilane (S15): The reaction was conducted according to the general procedure C without modification using **S14** (254 mg, 1.00 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R*f* = 0.9) to provide (5,5-dichloropent-4-en-1-yl)diphenylsilane (275 mg , 85% overall yield over two steps) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.46 – 7.35 (m, 6H), 5.84 (t, *J* = 7.4, 1H), 4.89 (td, *J* = 3.7, 1.3 Hz, 1H), 2.25 (qd, *J* = 7.4, 1.1 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.24 – 1.15 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.2, 134.2, 129.8, 129.6, 128.2, 120.4, 33.0, 23.4, 12.0.

HRMS (APCI) (m/z): [M - H]$^+$ Calcd for $C_{17}H_{17}Cl_2Si$: 319.0471; found: 319.0476.



5-(diphenylsilyl)pentan-1-ol (S16): The reaction was conducted according to the general procedure A without modification using pent-4-en-1-ol (120 mg, 1.39 mmol, 1.0 equiv), diphenylsilane (0.28 mL, 1.5 mmol, 1.1 equiv) and **S3** (23 mg, 0.034 mmol, 0.025 equiv) in C_6D_6 (2 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.4) to provide 5-(diphenylsilyl)pentan-1-ol (260 mg, 69% yield) as a pale yellow viscous liquid.

^1H NMR (300 MHz, C_6D_6) δ 7.58 – 7.54 (m, 4H), 7.20 – 7.16 (m, 6H), 5.12 (t, J = 3.7 Hz, 1H), 3.38 – 3.34 (m, 2H), 1.50 – 1.45 (m, 2H), 1.33 – 1.26 (m, 4H), 1.14 – 1.05 (m, 2H).

5-(diphenylsilyl)pentanal (S17): The reaction was conducted according to the general procedure B without modification using **S16** (260 mg, 0.961 mmol, 1.0 equiv), oxalyl chloride (0.080 mL, 1.0 mmol, 1.0 equiv), dimethylsulfoxide (0.14 mL, 1.9 mmol, 2.0 equiv) and triethylamine (0.53 mL, 3.8 mmol, 4.0 equiv) in CH_2Cl_2 (10 mL). The crude product was carried forward without purification.

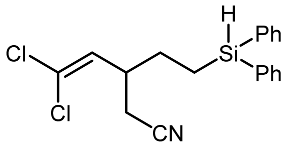
^1H NMR (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 1.8 Hz, 1H), 7.57 – 7.55 (m, 4H), 7.42 – 7.32 (m, 6H), 4.87 (t, *J* = 3.6 Hz, 1H), 2.41 (td, *J* = 7.3, 1.9 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.56 – 1.45 (m, 2H), 1.21 – 1.14 (m, 2H).

(6,6-dichlorohex-5-en-1-yl)diphenylsilane (S18): The reaction was conducted according to the general procedure C without modification using **S17** (268 mg, 1.00 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f = 0.9) to provide (6,6-dichlorohex-5-en-1-yl)diphenylsilane (107 mg, 30% overall yield over two steps) as a colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.44 – 7.34 (m, 6H), 5.80 (t, *J* = 7.4 Hz, 1H), 4.87 (t, *J* = 3.7 Hz, 1H), 2.21 – 2.12 (m, 2H), 1.52 – 1.44 (m, 4H), 1.20 – 1.11 (m, 2H).

^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 135.3, 134.5, 130.0, 129.7, 128.2, 120.0, 31.6, 29.3, 24.1, 12.0.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{18}H_{19}Cl_2Si$: 333.0628; found: 333.0631.



5-(diphenylsilyl)-3-(hydroxymethyl)pentanenitrile (S19): The reaction was conducted according to the general procedure A without modification using 3-(hydroxymethyl)pent-4-enenitrile[6] (238 mg, 2.14 mmol, 1.0 equiv), diphenylsilane (0.44 mL, 2.3 mmol, 1.1 equiv) and **S3** (39 mg, 0.053 mmol, 0.025 equiv) in C_6D_6 (5 mL). The product was purified by column chromatography (SiO_2, 10% EtOAc in CH_2Cl_2, R_f = 0.3) to provide 5-(diphenylsilyl)-3-(hydroxymethyl)pentanenitrile (410 mg, 67% yield) as a deep yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.43 – 7.35 (m, 6H), 4.89 (t, *J* = 3.6 Hz, 1H), 3.71 (dt, *J* = 10.8, 4.2 Hz, 1H), 3.56 (ddd, *J* = 11.0, 6.9, 4.4 Hz, 1H), 2.47 (d, *J* = 6.0 Hz, 2H), 1.93 – 1.82 (m, 2H), 1.59 (ddddd, *J* = 17.2, 13.1, 10.8, 8.9, 6.1 Hz, 2H), 1.20 – 1.10 (m, 2H).

5-(diphenylsilyl)-3-formylpentanenitrile (S20): The reaction was conducted according to the general procedure B without modification using **S19** (410 mg, 1.39 mmol, 1.0 equiv), oxalyl chloride (0.12 mL, 1.4 mmol, 1.0 equiv), dimethylsulfoxide (0.20 mL, 2.8 mmol, 2.0 equiv) and triethylamine (0.77 mL, 5.5 mmol, 4.0 equiv) in CH_2Cl_2 (20 mL). The crude product was carried forward without purification.

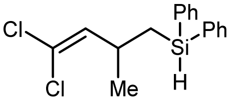
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.59 – 7.52 (m, 4H), 7.46 – 7.34 (m, 6H), 4.90 (t, *J* = 3.6 Hz, 1H), 2.76 (p, *J* = 6.4 Hz, 1H), 2.69 – 2.45 (m, 2H), 2.08 – 1.80 (m, 2H), 1.28 – 1.06 (m, 2H).

5,5-dichloro-3-(2-(diphenylsilyl)ethyl)pent-4-enenitrile (S21): The reaction was conducted according to the general procedure C without modification using **S20** (384 mg, 1.31 mmol, 1.0 equiv), PPh_3 (1.4 g, 5.2 mmol, 4.0 equiv) and CCl_4 (0.20 mL, 3.0 mmol, 2.0 equiv) in MeCN (15 mL). Isolated yields were determined following column chromatography (SiO_2, 10% EtOAc in hexanes, R_f= 0.3) to provide 5,5-dichloro-3-(2-(diphenylsilyl)ethyl)pent-4-enenitrile (250 mg, 50% overall yield over two steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.8, 1.5 Hz, 4H), 7.47 – 7.34 (m, 6H), 5.72 (d, *J* = 9.7 Hz, 1H), 4.87 (t, *J* = 3.7 Hz, 1H), 2.92 – 2.76 (m, 1H), 2.42 (d, *J* = 5.8 Hz, 2H), 1.80 – 1.56 (m, 3H), 1.21 – 1.07 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.1, 133.4, 130.0, 129.8, 128.3, 123.9, 117.5, 39.5, 28.7, 21.9, 9.7.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{19}H_{18}Cl_2NSi$: 358.0580; found: 358.0578 .



3-(diphenylsilyl)-2-methylpropan-1-ol (S22): The reaction was conducted according to the general procedure A without modification using 2-methylprop-2-en-1-ol (110 mg, 1.52 mmol, 1.00 equiv), diphenylsilane (0.31 mL, 1.7 mmol, 1.1 equiv) and **S3** (28 mg, 0.038 mmol, 0.025 equiv) in C_6D_6 (3 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, $R_f = 0.4$) to provide 3-(diphenylsilyl)-2-methylpropan-1-ol (300 mg, 70% yield) as a yellow liquid.

^{1}H NMR (300 MHz, C_6D_6) δ 7.95 – 7.33 (m, 4H), 7.25 – 7.16 (m, 6H), 5.17 (t, J = 4.1 Hz, 1H), 3.26 – 3.16 (m, 2H), 1.35 – 1.27 (m, 1H), 1.00 – 0.94 (m, 5H).

3-(diphenylsilyl)-2-methylpropanal (S23): The reaction was conducted according to the general procedure B without modification using **S22** (300 mg, 1.17 mmol, 1.0 equiv), oxalyl chloride (0.1 mL, 1 mmol, 1 equiv), dimethylsulfoxide (0.17 mL, 2.3 mmol, 2.0 equiv) and triethylamine (0.65 mL, 4.7 mmol, 4.0 equiv) in CH_2Cl_2 (10 mL). The crude product was carried forward without purification.

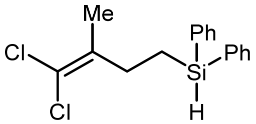
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 1.3 Hz, 1H), 7.59 – 7.56 (m, 4H), 7.48 – 7.29 (m, 6H), 4.99 – 4.97 (m, 1H), 2.52 – 2.43 (m, 1H), 1.66 – 1.57 (m, 2H), 1.16 (d, *J* = 7.1 Hz, 3H).

(4,4-dichloro-2-methylbut-3-en-1-yl)diphenylsilane (S24): The reaction was conducted according to the general procedure C without modification using **S23** (254 mg, 1.00 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, $R_f = 0.9$) to provide (4,4-dichloro-2-methylbut-3-en-1-yl)diphenylsilane (119 mg, 35% overall yield over two steps) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.45 – 7.33 (m, 6H), 5.69 (d, *J* = 9.6 Hz, 1H), 4.92 (t, *J* = 4.0 Hz, 1H), 2.86 – 2.73 (m, 1H),1.30 (ddq, *J* = 11.3, 7.5, 3.6 Hz, 2H), 1.10 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 136.8, 135.2, 134.3, 134.0, 129.8 , 129.8, , 128.2, 128.2, 118.7, 31.7, 22.8, 20.6.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{17}H_{17}Cl_2Si$: 319.0471; found: 319.0470.



4-(diphenylsilyl)butan-2-ol (S25): The reaction was conducted according to the general procedure A without modification using but-3-en-2-ol (500 mg, 6.93 mmol, 1.0 equiv), diphenylsilane (1.4 mL, 7.6 mmol, 1.1 equiv) and **S3** (126 mg, 0.173 mmol, 0.025 equiv) in C_6D_6 (10 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, $R_f = 0.4$) to provide 4-(diphenylsilyl)butan-2-ol (900 mg, 51% yield) as a pale yellow viscous liquid.

^{1}H NMR (300 MHz, C_6D_6) δ 7.61 – 7.51 (m, 4H), 7.22 – 7.21 (m, 6H), 5.11 (t, *J* = 3.5 Hz, 1H), 3.61 – 3.48 (m, 1H), 1.61 – 1.53 (m, 2H), 1.39 – 1.29 (m, 2H), 1.04 (d, J = 6.1 Hz, 3H).

4-(diphenylsilyl)butan-2-one (S26): The reaction was conducted according to the general procedure B without modification using **S25** (900 mg, 3.51 mmol, 1.0 equiv), oxalyl chloride (0.30 mL, 3.5 mmol, 1.0 equiv), dimethylsulfoxide (0.50 mL, 7.0 mmol, 2.0 equiv) and triethylamine (2.0 mL, 14 mmol, 4.0 equiv) in CH_2Cl_2 (30 mL). The crude product was carried forward without purification.

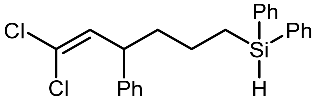
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.44 – 7.34 (m, 6H), 4.91 (t, *J* = 3.5 Hz, 1H), 2.47 – 2.36 (m, 2H), 1.90 (s, 3H), 1.42 – 1.30 (m, 2H).

(4,4-dichloro-3-methylbut-3-en-1-yl)diphenylsilane (S27): The reaction was conducted according to the general procedure C without modification using **S26** (3.2 g, 13 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, $R_f = 0.9$) to provide (4,4-dichloro-3-methylbut-3-en-1-yl)diphenylsilane (1.42 g, 32% overall yield over two steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.4 – 7.39 (m, 6H), 4.95 (t, *J* = 3.7 Hz, 1H), 2.47 – 2.36 (m, 2H), 1.89 (s, 3H), 1.39 – 1.30 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.8, 135.2, 133.8, 129.9, 128.2, 114.1, 30.5, 19.6, 10.0.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{17}H_{17}Cl_2Si$: 319.0471; found: 319.0479.



5-(diphenylsilyl)-2-phenylpentan-1-ol (*S*28): The reaction was conducted according to the general procedure A without modification using 2-phenylpent-4-en-1-ol[7] (500 mg, 3.08 mmol, 1.0 equiv), diphenylsilane (0.63 mL, 3.4 mmol, 1.1 equiv) and **S3** (56 mg, 0.078 mmol, 0.025 equiv) in C_6D_6 (5 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, $R_f = 0.4$) to provide 5-(diphenylsilyl)-2-phenylpentan-1-ol (730 mg, 68% yield) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 7.7, 2.1 Hz, 4H), 7.43 – 7.24 (m, 9H), 7.19 – 7.10 (m, 2H), 4.80 (t, *J* = 3.7 Hz, 1H), 3.80 – 3.57 (m, 2H), 2.88 – 2.69 (m, 1H), 1.83 – 1.61 (m, 2H), 1.41 (p, *J* = 7.9 Hz, 2H), 1.30 – 1.03 (m, 2H).

5-(diphenylsilyl)-2-phenylpentanal (S29): The reaction was conducted according to the general procedure B without modification using **S28** (730 mg, 2.10 mmol, 1.0 equiv), oxalyl chloride (0.18 mL, 2.1 mmol, 1.0 equiv), dimethylsulfoxide (0.30 mL, 4.2 mmol, 2.0 equiv) and triethylamine (1.8 ml, 8.4 mmol, 4.0 equiv) in CH_2Cl_2 (30 mL). The crude product was carried forward without purification.

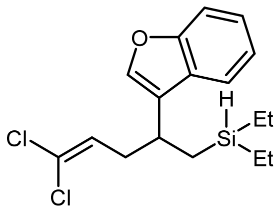
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 – 9.60 (m, 1H), 7.50 – 7.44 (m, 4H), 7.40 – 7.29 (m, 9H), 7.19 – 6.99 (m, 2H), 4.82 (t, *J* = 3.8 Hz, 1H), 3.18 – 2.95 (m, 1H), 2.19 – 2.09 (m, 2H), 1.86 – 1.77 (m, 2H), 1.20 – 1.10 (m, 2H).

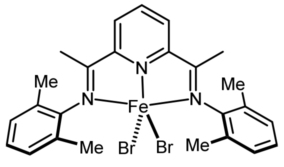
(6,6-dichloro-4-phenylhex-5-en-1-yl)diphenylsilane (S30): The reaction was conducted according to the general procedure C without modification using **S29** (684 mg, 1.98 mmol, 1.0 equiv), PPh_3 (2.1 g, 8.0 mmol, 4.0 equiv) and CCl_4 (0.4 mL, 4.0 mmol, 2.0 equiv) in MeCN (20 mL). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, $R_f = 0.9$) to provide (6,6-dichloro-4-phenylhex-5-en-1-yl)diphenylsilane (506 mg, 59% overall yield over two steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 4H), 7.44 – 7.21 (m, 9H), 7.15 (d, *J* = 7.5 Hz, 2H), 5.93 (d, *J* = 9.8 Hz, 1H), 4.84 (t, *J* = 3.7 Hz, 1H), 3.73 – 3.61 (m, 1H), 1.80 (qt, *J* = 10.1, 6.0 Hz, 2H), 1.56 – 1.41 (m, 2H), 1.17 (qq, *J* = 11.4, 7.6, 5.7 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.5, 135.2, 134.4, 133.4, 129.7, 128.8, 128.1, 127.4, 126.8, 120.4, 45.8, 38.9, 22.2, 12.0.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{24}H_{23}Cl_2Si$: 409.0941; found: 409.0940.





[^{Me}PDI]FeBr$_2$

(2-(benzofuran-3-yl)-4-(benzyloxy)butyl)diethylsilane (S31): According to a previously reported procedure:[8] In a N_2 filled glovebox, a 20-dram vial was charged with [^{Me}PDI]FeBr$_2$[9] (151 mg, 0.260 mmol, 0.060 equiv), toluene (10 mL), and a magnetic stir bar. To this slurry, diethylsilane (1.1 mL, 8.6 mmol, 2.0 equiv) was added followed by dropwise addition of Sodium triethylborohydride in 1 M THF (0.52 mL, 0.52 mmol, 0.12 equiv). The slurry was converted to a homogenous solution, and bubbling was observed. To the solution, 3-(4-(benzyloxy)but-1-en-2-yl)benzofuran[10] (1.2 g, 4.3 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 22 h. The crude reaction mixture was then removed from the glovebox and poured into hexanes (40 mL). To this solution, Sodium hydrogen sulfate (15 g) was added, and the resulting mixture was filtered through celite. The filtrate was concentrated, and the crude product was purified using column chromatography (SiO_2, 20% CH_2Cl_2 in hexanes, R_f = 0.4) to provide (2-(benzofuran-3-yl)-4-(benzyloxy)butyl)diethylsilane (1.1 g, 70% Yield) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.23 (m, 6H), 7.25 – 7.09 (m, 1H), 6.34 (s, 1H), 4.45 (d, *J* = 3.3 Hz, 2H), 3.60 (sept, *J* = 2.9 Hz, 1H), 3.52 – 3.33 (m, 2H), 3.19 (tt, *J* = 8.6, 6.3 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.22 – 1.02 (m, 2H), 0.94 – 0.83 (m, 6H), 0.55 – 0.41 (m, 4H).

3-(benzofuran-3-yl)-4-(diethylsilyl)butan-1-ol (S32): According to a previously reported procedure:[11] In an oven dried 100 mL round bottom flask, lithium (265 mg, 38.2 mmol, 14.0 equiv) and naphthalene (28 mg, 0.22 mmol, 0.080 equiv) were combined with anhydrous THF (20 mL). The mixture was sonicated until the solution turned deep green. The reaction mixture was then taken out from the sonicator bath and stirred at –78 °C for 5 min. To this reaction mixture, a solution containing **S31** (1.0 g, 2.7 mmol, 1.0 equiv) dissolved in THF (6 mL) was added dropwise. The resulting reaction mixture was stirred at –78 °C for 5 h. The crude mixture was quenched using saturated solution of NH_4Cl at –78 °C. The solution was then warmed to room temperature and extracted with ether (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.3) to provide 3-(benzofuran-3-yl)-4-(diethylsilyl)butan-1-ol (241 mg, 32% Yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 1H), 7.44 – 7.39 (m, 1H), 7.24 – 7.15 (m, 2H), 6.42 (s, 1H), 3.69 – 3.62 (m, 2H) 3.61 – 3.53 (m, 1H), 3.24 – 3.11 (m, 1H), 2.08 – 1.96 (m, 2H), 1.84 (br s, 1H), 1.26 – 1.05 (m, 2H), 0.97 – 0.86 (m, 6H), 0.57 – 0.41 (m, 4H).

3-(benzofuran-3-yl)-4-(diethylsilyl)butanal (S33): The reaction was conducted according to the general procedure B without modification using **S32** (237 mg, 0.850 mmol, 1.0 equiv), oxalyl chloride (0.070 mL, 0.90 mmol, 1.0 equiv), dimethylsulfoxide (0.12 mL, 1.7 mmol, 2.0 equiv) and triethylamine (0.50 mL, 3.4 mmol, 4.0 equiv) in CH_2Cl_2 (10 mL). The crude product was carried forward without purification.

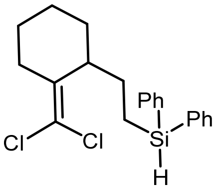
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.76 (t, *J* = 1.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 7.24 – 7.15 (m, 1H), 6.43 (s, 1H), 3.67 – 3.54 (m, 2H), 2.98 – 2.75 (m, 2H), 1.28 – 1.04 (m, 2H), 0.97 – 0.88 (m, 6H), 0.59 – 0.45 (m, 4H).

(2-(benzofuran-3-yl)-5,5-dichloropent-4-en-1-yl)diethylsilane (*S*34): The reaction was conducted according to the general procedure C without modification using **S33** (200 mg, 0.730 mmol, 1.0 equiv), PPh$_3$ (765 mg, 2.90 mmol, 4.0 equiv) and CCl$_4$ (0.14 mL, 1.5 mmol, 2.0 equiv) in MeCN (5 mL). Isolated yields were determined following column chromatography (SiO$_2$, 100% hexanes, R$_f$ = 0.7) to provide (2-(benzofuran-3-yl)-5,5-dichloropent-4-en-1-yl)diethylsilane (156 mg, 54% overall yield over two steps) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 (dd, *J* = 40.0, 10.1 Hz, 2H), 7.25 – 7.20 (m, 2H), 6.43 (s, 1H), 5.82 (t, *J* = 10.2 Hz, 1H), 3.66 (quint, *J* = 3.2 Hz, 1H), 3.11 (quint, *J* = 6.7 Hz, 1H), 2.66 – 2.63 (m, 2H), 1.25 – 1.20 (m, 1H), 1.09 – 1.05 (m, 1H), 0.95 (q, *J* = 8.1 Hz, 6H), 0.57 – 0.50 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 161.3, 154.7, 128.6, 127.5, 123.6, 122.7, 121.4, 120.7, 111.0, 102.3, 36.9, 35.3, 15.8, 8.2, 8.2, 2.9, 2.8.

HRMS (APCI) (m/z): [M + H]$^+$ Calcd for $C_{17}H_{23}Cl_2OSi$: 341.0890; found: 341.0896.



2-(2-(diphenylsilyl)ethyl)cyclohexan-1-ol (S35): The reaction was conducted according to the general procedure A without modification using 2-vinylcyclohexan-1-ol[12] (423 mg, 3.35 mmol, 1.0 equiv), diphenylsilane (0.68 mL, 3.7 mmol, 1.1 equiv) and **S3** (61 mg, 0.084 mmol, 0.025 equiv) in C_6D_6 (5 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.4) to provide 2-(2-(diphenylsilyl)ethyl)cyclohexan-1-ol (700 mg, 67% yield) as a deep yellow viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 7.7, 1.8 Hz, 4H), 7.42 – 7.32 (m, 6H), 4.86 (t, *J* = 3.6 Hz, 1H), 3.21 (tt, *J* = 9.5, 4.6 Hz, 1H), 2.00 – 1.85 (m, 3H), 1.76 – 1.62 (m, 2H), 1.35 – 1.10 (m, 8H), 1.04 (ddt, *J* = 14.8, 12.1, 3.8 Hz, 1H), 0.97 – 0.82 (m, 1H).

2-(2-(diphenylsilyl)ethyl)cyclohexan-1-one (S36): The reaction was conducted according to the general procedure B without modification using **S35** (700 mg, 2.25 mmol, 1.0 equiv), oxalyl chloride (0.19 mL, 2.2 mmol, 1.0 equiv), dimethylsulfoxide (0.32 mL, 4.5 mmol, 2.0 equiv) and triethylamine (1.2 mL, 9.0 mmol, 4.0 equiv) in CH_2Cl_2 (30 mL). The product was purified by column chromatography (SiO_2, 30% CH_2Cl_2 in hexanes, R_f = 0.2) to provide 2-((diphenylsilyl)methyl)cyclohexan-1-one (314 mg, 81% yield) as a white solid.

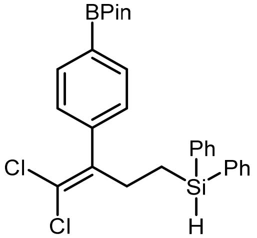
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.42 – 7.32 (m, 6H), 4.86 (t, *J* = 3.6 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.28 – 2.19 (m, 2H), 2.14 – 2.06 (m, 1H), 2.04 – 1.88 (m, 2H), 1.82 (dtd, *J* = 10.7, 4.0, 3.5, 1.8 Hz, 1H), 1.69 – 1.54 (m, 2H), 1.46 – 1.30 (m, 2H), 1.15 (ddt, *J* = 10.1, 6.2, 3.6 Hz, 2H).

(2-(2-(dichloromethylene)cyclohexyl)ethyl)diphenylsilane (S37): The reaction was conducted according to the general procedure D without modification using **S36** (420 mg, 1.36 mmol, 1.0 equiv). Diethyl trichloromethylphosphonate (0.77 mL, 4.1 mmol, 3.0 equiv) and 2.5 M *n*-BuLi in hexanes (1.6 mL, 4.0 mmol, 3.0 equiv) in THF (2 mL) and Et_2O (4 mL). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f = 0.9) to provide (2-(2-(dichloromethylene)cyclohexyl)ethyl)diphenylsilane (332 mg, 65% Yield) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.44 – 7.35 (m, 6H), 4.86 (t, *J* = 3.7 Hz, 1H), 3.04 (dt, *J* = 10.6, 5.7 Hz, 1H), 2.81 – 2.71 (m, 1H), 1.85 (td, *J* = 13.8, 4.5 Hz, 1H), 1.80 – 1.66 (m, 3H), 1.63 – 1.37 (m, 4H), 1.34 – 1.12 (m, 2H), 1.11 – 1.00 (m, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.4, 135.2, 134.4, 134.3, 129.8, 128.2, 112.2, 42.0, 30.3, 27.7, 26.8, 26.3, 20.4, 9.7.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{21}H_{23}Cl_2Si$: 373.0941; found: 373.0945.



3-(diphenylsilyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol (S38): The reaction was conducted according to the general procedure A without modification using 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-ol[3] (624 mg, 2.40 mmol, 1.0 equiv), diphenylsilane (0.49 mL, 2.6 mmol, 1.1 equiv) and **S3** (44 mg, 0.060 mmol, 0.025 equiv) in C_6D_6 (4 mL). The product was purified by column chromatography (SiO_2, 10% EtOAc in CH_2Cl_2, R_f = 0.5) to provide 3-(diphenylsilyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol (595 mg, 56% yield) as a deep yellow liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 2H), 7.54 – 7.47 (m, 3H), 7.45 – 7.28 (m, 9H), 4.84 (t, *J* = 3.7 Hz, 1H), 4.72 – 4.62 (m, 1H), 1.96 – 1.79 (m, 2H), 1.34 (s, 12H), 1.18 – 0.98 (m, 2H).

3-(diphenylsilyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one (S39): The reaction was conducted according to the general procedure B without modification using **S38** (595 mg, 1.34 mmol, 1.0 equiv), oxalyl chloride (0.11 mL, 1.3 mmol, 1.0 equiv), dimethylsulfoxide (0.20 mL, 2.7 mmol, 2.0 equiv) and triethylamine (0.74 mL, 5.3 mmol, 4.0 equiv) in CH_2Cl_2 (20 mL). The crude product was carried forward without purification.

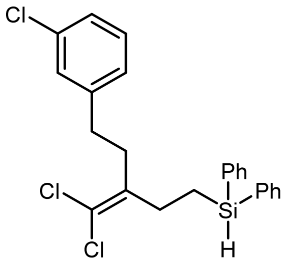
^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 4H), 7.63 – 7.56 (m, 4H), 7.42 – 7.34 (m, 6H), 4.94 (t, *J* = 3.7 Hz, 1H), 3.11 – 3.03 (m, 2H), 1.58 – 1.54 (m, 2H), 1.35 (s, 12H).

(4,4-dichloro-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl) diphenylsilane (S40): The reaction was conducted according to the general procedure D without modification using **S39** (211 mg, 0.550 mmol, 1.0 equiv). diethyl trichloromethylphosphonate (0.31 mL, 1.6 mmol, 3.0 equiv) and 2.5 M *n*-BuLi in hexanes (0.70 mL, 1.6 mmol, 3.0 equiv) in THF (1 mL) and Et_2O (1.5 mL). Isolated yields were determined following column chromatography (SiO_2, 15% Et_2O in hexanes, R_f = 0.5) to provide (4,4-dichloro-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)diphenylsilane (165 mg, 59% overall yield over two steps) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.45 (m, 4H), 7.35 (dddd, *J* = 14.1, 8.4, 5.9, 2.3 Hz, 8H), 7.20 – 7.15 (m, 2H), 4.83 (t, *J* = 3.7 Hz, 1H), 2.76 – 2.63 (m, 2H), 1.35 (s, 12H), 1.22 – 1.16 (m, 4H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.0, 141.6, 135.7, 135.2, 134.9, 133.6, 129.9, 128.2, 128.1, 127.8, 84.0, 31.5, 29.9 25.0, 10.1.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{28}H_{30}BCl_2O_2Si$: 506.1516; found: 506.1513.



1-(3-chlorophenyl)-5-(diphenylsilyl)pentan-3-ol (S41): The reaction was conducted according to the general procedure A without modification using 5-(3-chlorophenyl)pent-1-en-3-ol[13] (1.24 g, 6.30 mmol, 1.0 equiv), diphenylsilane (1.3 mL, 6.9 mmol, 1.1 equiv) and **S3** (115 mg, 0.160 mmol, 0.025 equiv) in C_6D_6 (10 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.4) to provide 1-(3-chlorophenyl)-5-(diphenylsilyl)pentan-3-ol (1.3 g, 55% yield) as a deep yellow viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 4H), 7.45 – 7.32 (m, 6H), 7.21 – 7.12 (m, 3H), 7.04 (dt, *J* = 6.9, 1.8 Hz, 1H), 4.87 (t, *J* = 3.6 Hz, 1H), 3.61 – 3.53 (m, 1H), 2.84 – 2.52 (m, 2H), 1.76 – 1.59 (m, 4H), 1.44 – 0.98 (m, 3H).

1-(3-chlorophenyl)-5-(diphenylsilyl)pentan-3-one (S42): The reaction was conducted according to the general procedure B without modification using **S41** (1.30 g, 3.41 mmol, 1.0 equiv), oxalyl chloride (0.29 mL, 3.0 mmol, 1.0 equiv), dimethylsulfoxide (0.48 mL, 6.8 mmol, 2.0 equiv) and triethylamine (1.9 mL, 14 mmol, 4.0 equiv) in CH_2Cl_2 (50 mL). The product was purified by column chromatography (20% Et_2O in hexanes, R_f = 0.2) to provide 1-(3-chlorophenyl)-5-(diphenylsilyl)pentan-3-one (1.12 g, 87% yield) as a colorless liquid.

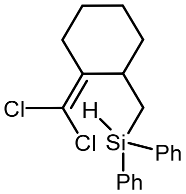
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 4H), 7.46 – 7.33 (m, 6H), 7.22 – 7.10 (m, 3H), 7.01 (dt, *J* = 6.8, 1.8 Hz, 1H), 4.85 (t, *J* = 3.8 Hz, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.67 – 2.58 (m, 2H), 2.52 – 2.43 (m, 2H), 1.44 – 1.33 (m, 2H).

(5-(3-chlorophenyl)-3-(dichloromethylene)pentyl)diphenylsilane (S43): The reaction was conducted according to the general procedure D without modification using **S42** (500 mg, 1.32 mmol, 1.0 equiv), diethyl trichloromethylphosphonate (0.74 mL, 4.0 mmol, 3.0 equiv) and 2.5 M *n*-BuLi in hexanes (1.6 mL, 4.0 mmol, 3.0 equiv) in THF (2 mL) and Et_2O (4 mL) . Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f = 0.9) to provide (5-(3-chlorophenyl)-3-(dichloromethylene)pentyl)diphenylsilane (394 mg, 67% Yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.47 – 7.33 (m, 7H), 7.23 – 7.14 (m, 2H), 7.12 – 7.11 (m, 1H), 7.03 – 6.96 (m, 1H), 4.89 (t, *J* = 3.7 Hz, 1H), 2.68 – 2.58 (m, 2H), 2.54 – 2.43 (m, 2H), 2.38 – 2.27 (m, 2H), 1.36 – 1.21 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.1, 139.9, 135.7, 135.2, 134.3, 133.6, 130.0, 129.8, 128.6, 128.3, 126.6, 126.5, 35.1, 33.1, 28.7, 10.2.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{24}H_{22}Cl_3Si$: 443.0551; found: 443.0542.



2-((diphenylsilyl)methyl)cyclohexan-1-ol (S44): The reaction was conducted according to the general procedure A without modification using 2-methylenecyclohexan-1-ol[14] (198 mg, 1.76 mmol, 1.0 equiv), diphenylsilane (0.36 mL, 1.9 mmol, 1.1 equiv) and **S3** (32 mg, 0.040 mmol, 0.025 equiv) in C_6D_6 (3 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.4) to provide 2-((diphenylsilyl)methyl)cyclohexan-1-ol (392 mg, 75% yield) as a deep yellow viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 4H), 7.43 – 7.29 (m, 6H), 4.98 – 4.93 (m, 1H), 3.18 (dt, *J* = 9.7, 5.3 Hz, 1H), 1.99 – 1.82 (m, 2H), 1.80 – 1.65 (m, 2H), 1.39 – 0.84 (m, 8H)

2-((diphenylsilyl)methyl)cyclohexan-1-one (S45): The reaction was conducted according to the general procedure B without modification using **S44** (390 mg, 1.32 mmol, 1.0 equiv), oxalyl chloride (0.11 mL, 1.3 mmol, 1.0 equiv), dimethylsulfoxide (0.19 mL, 2.6 mmol, 2.0 equiv) and triethylamine (0.73 mL, 5.3 mmol, 4.0 equiv) in CH_2Cl_2 (20 mL). The crude product was carried forward without purification.

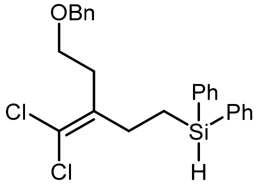
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.48 – 7.31 (m, 6H), 4.85 (t, *J* = 3.7 Hz, 1H), 2.41 – 1.08 (m, 11H).

((2-(dichloromethylene)cyclohexyl)methyl)diphenylsilane (S46): The reaction was conducted according to the general procedure D without modification using **S45** (330 mg, 1.12 mmol, 1.0 equiv), diethyl trichloromethylphosphonate (0.63 mL, 3.4 mmol, 3.0 equiv) and 2.5 M *n*-BuLi in hexanes (1.3 mL, 3.4 mmol, 3.0 equiv) in THF (2 mL) and Et_2O (3 mL) . Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9) to provide ((2-(dichloromethylene)cyclohexyl)methyl)diphenylsilane (328 mg, 55% overall yield over two steps) as a pale yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (ddt, *J* = 7.4, 5.4, 1.6 Hz, 4H), 7.43 – 7.32 (m, 6H), 4.91 (ddd, *J* = 4.9, 3.3, 1.6 Hz, 1H), 3.31 (dd, *J* = 8.8, 4.9 Hz, 1H), 2.68 (dtt, *J* = 14.3, 3.0, 1.4 Hz, 1H), 2.01 (td, *J* = 14.0, 4.6 Hz, 1H), 1.83 – 1.68 (m, 2H), 1.61 (tt, *J* = 14.2, 3.9 Hz, 1H), 1.55 – 1.34 (m, 5H), 1.25 (ttd, *J* = 13.2, 9.2, 8.2, 3.8 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.6, 135.2, 135.2, 134.6, 134.1, 129.8, 129.8,, 128.1, 111.4, 35.3, 32.3, 27.3, 26.7, 19.9, 15.6.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{20}H_{23}Cl_2Si$: 359.0784; found: 359.0779.



1-(benzyloxy)-5-(diphenylsilyl)pentan-3-ol (S47): The reaction was conducted according to the general procedure A without modification using 5-(benzyloxy)pent-1-en-3-ol[15] (837 mg, 4.35 mmol, 1.0 equiv), diphenylsilane (0.89 mL, 4.8 mmol, 1.1 equiv) and **S3** (79 mg, 0.11 mmol, 0.025 equiv) in C_6D_6 (7 mL). The product was purified by column chromatography (SiO_2, 100% CH_2Cl_2, R_f = 0.3) to provide 1-(benzyloxy)-5-(diphenylsilyl)pentan-3-ol (1.1 g, 67% yield) as a yellow viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.40 – 7.28 (m, 11H), 4.87 (t, *J* = 3.7 Hz, 1H), 4.50 (s, 2H), 3.83 – 3.74 (m, 1H), 3.72 – 3.57 (m, 2H), 1.79 – 1.70 (m, 2H), 1.65 – 1.53 (m, 2H), 1.37 – 1.28 (m, 2H), 1.18 – 1.06 (m, 1H).

1-(benzyloxy)-5-(diphenylsilyl)pentan-3-one (S48): The reaction was conducted according to the general procedure B without modification using **S47** (1.1 g, 2.9 mmol, 1.0 equiv), oxalyl chloride (0.25 mL, 2.9 mmol, 1.0 equiv), dimethylsulfoxide (0.40 mL, 5.8 mmol, 2.0 equiv) and triethylamine (1.6 mL, 11 mmol, 4.0 equiv) in CH_2Cl_2 (40 mL). The crude product was carried forward without purification.

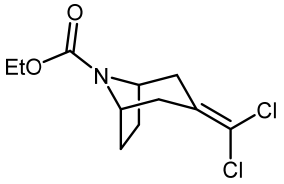
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.43 – 7.27 (m, 11H), 4.86 (t, *J* = 3.8 Hz, 1H), 4.47 (s, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 6.3 Hz, 2H), 2.58 – 2.50 (m, 2H), 1.47 – 1.33 (m, 2H).

(5-(benzyloxy)-3-(dichloromethylene)pentyl)diphenylsilane (S49): The reaction was conducted according to the general procedure D without modification using **S48** (650 mg, 1.73 mmol, 1.0 equiv). diethyl trichloromethylphosphonate (1.0 mL, 5.2 mmol, 3.0 equiv) and 2.5 M *n*-BuLi in hexanes (2.1 mL, 5.2 mmol, 3.0 equiv) in THF (3 mL) and Et_2O (5 mL). Isolated yields were determined following column chromatography (SiO_2, 5% Et_2O in hexanes, R_f = 0.3) to provide (5-(benzyloxy)-3-(dichloromethylene)pentyl)diphenylsilane (233 mg, 23% overall yield over two steps) as a colorless viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.44 – 7.26 (m, 11H), 4.87 (t, *J* = 3.7 Hz, 1H), 4.46 (s, 2H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.43 – 2.32 (m, 2H), 1.30 (dq, *J* = 13.2, 4.3 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.6, 138.3, 138.2, 135.2, 133.8, 129.9, 128.5, 128.2, 127.8, 127.7, 73.0, 67.6, 33.6, 29.1, 10.1.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{25}H_{25}Cl_2OSi$: 439.1046; found: 439.1042.

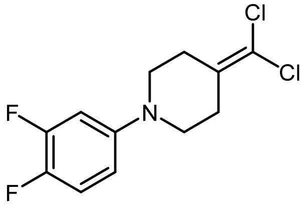


ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (S50): The reaction was conducted according to the general procedure A without modification using ethyl 3-oxo-8-azabicyclo[3.2.1]octane-8-carboxylate (1.0 g, 5.1 mmol, 1.0 equiv), PPh_3 (5.3 g, 20 mmol, 4.0 equiv) and CCl_4 (1.0 mL, 10 mmol, 2.0 equiv) in MeCN (60 mL). Isolated yields were determined following column chromatography (SiO_2, 10% Et_2O in hexanes, R_f = 0.2) to provide ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (1.3 g, 98% Yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (s, 2H), 4.16 (qd, *J* = 7.1, 2.6 Hz, 2H), 2.69 (d, *J* = 16.1 Hz, 2H), 1.94 (s, 2H), 1.69 – 1.48 (m, 3H), 1.27 (td, *J* = 7.1, 2.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.0, 131.3, 116.7, 61.2, 53.1, 37.8, 37.3, 28.8, 28.7, 28.2, 28.0, 14.9.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{11}H_{16}Cl_2NO_2$: 264.0553; found: 264.0555.



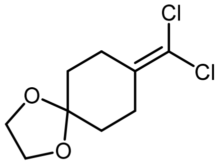
4-(dichloromethylene)-1-(3,4-difluorophenyl)piperidine (S51): The reaction was conducted according to the general procedure A without modification using 1-(3,4-difluorophenyl)piperidin-4-one (500 mg, 2.37 mmol, 1.0 equiv). PPh_3 (2.5 g, 9.5 mmol, 4.0 equiv) and CCl_4 (0.5 mL, 4.7 mmol, 2.0 equiv) in MeCN (25 mL). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.1) to provide 4-(dichloromethylene)-1-(3,4-difluorophenyl)piperidine (546 mg, 82% Yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 6.98 (m, 1H), 6.70 (ddd, *J* = 13.2, 6.8, 2.9 Hz, 1H), 6.58 (dtd, *J* = 9.0, 3.2, 1.5 Hz, 1H), 3.19 (t, *J* = 5.8 Hz, 4H), 2.62 (t, *J* = 5.8 Hz, 4H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.8, 147.9, 147.8, 133.6, 117.5 (d, $^2J_{CF}$ = 17.0 Hz), 113.7, 112.0, 105.8 (d, $^2J_{CF}$ = 20.0 Hz), 49.7, 30.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -138.0 (ddd, *J* = 22.0, 13.3, 9.0 Hz), -151.0 – -151.2 (m).

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{12}H_{12}Cl_2F_2N$: 278.0309; found: 278.0311.



8-(dichloromethylene)-1,4-dioxaspiro[4.5]decane (S52): The reaction was conducted according to the general procedure A without modification using 1,4-dioxaspiro[4.5]decan-8-one

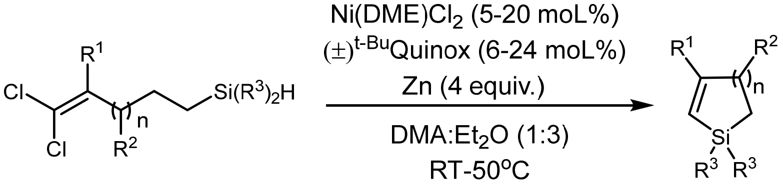
(500 mg, 3.20 mmol, 1.0 equiv). PPh_3 (3.4 g, 13 mmol, 4.0 equiv) and CCl_4 (0.62 mL, 6.4 mmol, 2.0 equiv) in MeCN (35 mL). Isolated yields were determined following column chromatography (SiO_2, 5% Et_2O in hexanes, R_f = 0.2) to provide 8-(dichloromethylene)-1,4-dioxaspiro[4.5]decane (635 mg, 89% Yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 4H), 2.60 – 2.45 (m, 4H), 1.75 – 1.65 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.7, 108.1, 64.6, 34.5, 28.7.

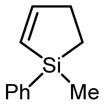
HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_9H_{13}Cl_2O_2$: 223.0287; found: 223.0284.

4. Substrate Scope Studies and Characterization Data for Si–H insertion Products



General Procedure A for the Intramolecular Si–H insertion reaction. In an N_2-filled glovebox, a 5-mL vial was charged with $Ni(DME)Cl_2$ (2.2 mg, 0.010 mmol, 0.050 equiv), (±)-*t*-Bu-Quinox (3.1 mg, 0.012 mmol, 0.060 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.4 mL) and Et_2O (0.4 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing the substrate (0.20 mmol, 1.0 equiv) dissolved in Et_2O (0.8 mL). The reaction was stirred at room temperature. After 16 h, the reaction vial was removed from the glovebox and opened to ambient atmosphere. Et_2O was removed under N_2 stream, and the crude residue was loaded directly onto a SiO_2 column for purification.

General Procedure B for the Intramolecular Si–H insertion reaction. In an N_2-filled glovebox, a 10-mL microwave vial was charged with $Ni(DME)Cl_2$ (8.8 mg, 0.040 mmol, 0.20 equiv), (±)-*t*-Bu-Quinox (12 mg, 0.048 mmol, 0.24 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.4 mL) and Et_2O (0.4 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing the substrate (0.20 mmol, 1.0 equiv) dissolved in Et_2O (0.8 mL). The Schlenk tube was sealed inside the glovebox, removed then heated in an oil bath set to 50 °C. After 48 h, the Schlenk tube was opened to ambient atmosphere. Et_2O was removed under N_2 stream, and the crude residue was loaded directly onto a SiO_2 column for purification.



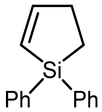
1-methyl-1-phenyl-2,3-dihydro-1H-silole (9): The reaction was conducted according to the general procedure A without modification using (4,4-dichlorobut-3-en-1-yl)(methyl)(phenyl)silane (49 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

24 mg isolated (68% yield), colorless oil

^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.40 – 7.33 (m, 3H), 7.00 (dt, *J* = 10.1, 2.7 Hz, 1H), 6.07 (dt, *J* = 10.1, 2.2 Hz, 1H), 2.62 (tt, *J* = 7.9, 2.4 Hz, 2H), 1.06 – 0.84 (m, 2H), 0.49 (s, 3H).

^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 155.2, 138.9, 134.0, 129.2, 128.8, 127.9, 32.4, 8.8, -3.0.

HRMS (APCI) (m/z): $[M + H – CH_3]^+$ Calcd for $C_{10}H_{12}Si$: 161.0937; found: 161.1325.



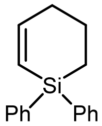
1,1-diphenyl-2,3-dihydro-1H-silole (10): The reaction was conducted according to the general procedure without A modification using (4,4-dichlorobut-3-en-1-yl)diphenylsilane (69 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

44 mg isolated (93% yield), colorless oil

^1H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 4H), 7.43 – 7.34 (m, 6H), 7.12 (dt, *J* = 10.1, 2.7 Hz, 1H), 6.28 (dt, *J* = 10.1, 2.2 Hz, 1H), 2.70 (ddt, *J* = 9.4, 5.0, 2.5 Hz, 2H), 1.27 – 1.19 (m, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.5, 136.6, 135.0, 129.5, 128.0, 127.2, 32.5, 8.1.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{16}H_{17}Si$: 237.1094; found:237.1095.



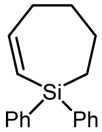
1,1-diphenyl-1,2,3,4-tetrahydrosiline (2): The reaction was conducted according to the general procedure A without modification using (5,5-dichloropent-4-en-1-yl)diphenylsilane (64 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

44 mg isolated (87% yield), colorless oil

^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H), 7.43 – 7.32 (m, 6H), 7.04 (dt, *J* = 14.1, 4.0 Hz, 1H), 6.08 (dt, *J* = 14.1, 2.1 Hz, 1H), 2.29 (tdd, *J* = 6.0, 4.0, 2.0 Hz, 2H), 1.97 – 1.86 (m, 2H), 1.25 – 1.16 (m, 2H).

$^{13}C\ \{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 152.0, 136.9, 135.0, 129.4, 128.0, 122.6, 31.1, 21.0, 10.3.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{17}H_{19}Si$: 251.1251; found:251.1258.



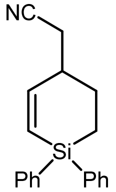
1,1-diphenyl-2,3,4,5-tetrahydro-1*H*-silepine (11): The reaction was conducted according to the general procedure A without modification using (6,6-dichlorohex-5-en-1-yl)diphenylsilane (67 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

15 mg isolated (29% yield), colorless oil

^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 4H), 7.37 – 7.35 (m, 6H), 7.01 – 6.88 (m, 1H), 6.06 (d, J = 14.2 Hz, 1H), 2.34 – 2.29 (m, 2H), 1.89 – 1.77 (m, 2H), 1.67 – 1.61 (m, 2H), 1.27 – 1.24 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.9, 137.4, 134.8, 129.2, 128.0, 126.7, 31.4, 27.8, 23.1, 12.1.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{18}H_{21}Si$: 265.1407; found: 265.1405.



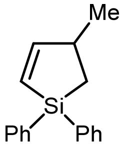
2-(1,1-diphenyl-1,2,3,4-tetrahydrosilin-4-yl)acetonitrile (12): The reaction was conducted according to the general procedure A with the following modification using 5,5-dichloro-3-(2-(diphenylsilyl)ethyl)pent-4-enenitrile (72.1 mg, 0.200 mmol, 1.0 equiv), $Ni(DME)Cl_2$ (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52.3 mg, 0.800 mmol, 4.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 10% EtOAc in hexanes, R_f= 0.4).

34 mg isolated (58% yield), pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.45 – 7.32 (m, 6H), 6.85 (ddd, J = 14.1, 2.6, 1.0 Hz, 1H), 6.27 (ddd, J = 14.0, 2.4, 1.2 Hz, 1H), 2.71 – 2.73 (m, 1H), 2.46 – 2.43 (m, 2H), 2.23 – 2.16 (m, 1H), 1.81 – 1.69 (m, 1H), 1.42 – 1.46 (m, 1H), 1.21 – 1.13 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.3, 135.0, 134.9, 129.8, 128.2, 128.2, 126.5, 118.6, 37.5, 26.9, 24.1, 8.3.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{19}H_{20}NSi$: 290.1359; found: 290.1362.



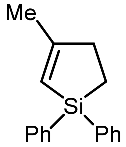
4-methyl-1,1-diphenyl-2,3-dihydro-1*H*-silole (13): The reaction was conducted according to the general procedure A without modification using (4,4-dichloro-3-methylbut-3-en-1-yl)diphenylsilane (64 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

43 mg isolated (86% yield), colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.48 (m, 5H), 7.45 – 7.31 (m, 7H), 5.83 (s, 1H), 2.65 – 2.53 (m, 2H), 1.99 (s, 3H), 1.35 – 1.29 (m, 2H).

^{13}C $\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.2, 136.8, 135.0, 135.0, 129.5, 128.0, 126.1, 39.8, 24.1, 17.9.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{17}H_{19}Si$: 251.1251; found:251.1256.



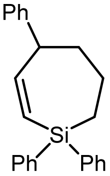
3-methyl-1,1-diphenyl-2,3-dihydro-1H-silole (14): The reaction was conducted according to the general procedure A without modification using 4,4-dichloro-2-methylbut-3-en-1-yl)diphenylsilane (64 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

46 mg isolated (92% yield), colorless oil

^1H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 4H), 7.33 – 7.14(m, 6H), 6.87 (dd, *J* = 9.9, 2.5 Hz, 1H), 6.24 (dd, *J* = 9.7, 2.2 Hz, 1H), 2.85 (dqt, *J* = 9.6, 7.0, 3.6 Hz, 1H), 1.55 (dd, *J* = 15.1, 8.1 Hz, -1H), 1.14 (d, *J* = 7.2 Hz, 3H), 0.85 (dd, *J* = 15.1, 4.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.8, 137.2, 135.0, 129.4, 128.0, 121.2, 36.7, 23.5, 9.8.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{17}H_{19}Si$: 251.1251; found:251.1247.



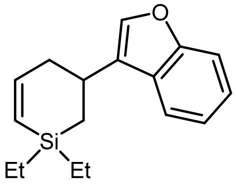
1,1,5-triphenyl-2,3,4,5-tetrahydro-1*H*-silepine (15): The reaction was conducted according to the general procedure A with the following modification using (6,6-dichloro-4-phenylhex-5-en-1-yl)diphenylsilane (82 mg, 0.20 mmol, 1.0 equiv), $Ni(DME)Cl_2$ (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

27 mg isolated (40% yield), colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.53 (m, 4H), 7.43 – 7.36 (m, 6H), 7.32 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 6.84 (dd, J = 14.1, 5.5 Hz, 1H), 6.11 (dd, J = 14.1, 1.9 Hz, 1H), 3.69 – 3.62 (m, 1H), 2.03 – 1.81 (m, 4H), 1.45 – 1.38 (m, 1H), 1.30 – 1.15 (m, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 134.9, 134.7, 129.4, 129.3, 128.7, 128.1, 128.1, 127.6, 126.3, 125.7, 48.8, 35.9, 21.9, 11.7.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{24}H_{25}Si$: 341.1720; found: 341.1721.



3-(benzofuran-3-yl)-1,1-diethyl-1,2,3,4-tetrahydrosiline (16): The reaction was conducted according to the general procedure A without modification using (2-(benzofuran-3-yl)-5,5-

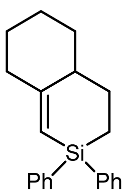
dichloropent-4-en-1-yl)diethylsilane (68 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 5% Et_2O in hexanes, R_f= 0.9).

41 mg isolated (75% yield), yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 36.5, 7.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.88 (ddd, *J* = 14.6, 5.4, 1.9 Hz, 1H), 6.41 (s, 1H), 5.86 – 5.78 (m, 1H), 3.21 – 3.14 (m, 1H), 2.73 – 2.68 (m, 1H), 2.30 – 2.23 (m, 1H), 1.29 – 1.27 (m, 1H), 1.06 – 0.90 (m, 7H), 0.71 – 0.58 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.4, 154.7, 148.3, 129.0, 124.9, 123.3, 122.5, 120.5, 110.9, 99.9, 35.6, 33.5, 13.7, 7.8, 7.4, 5.5, 4.9.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{17}H_{23}OSi$: 271.1513; found:271.1518.



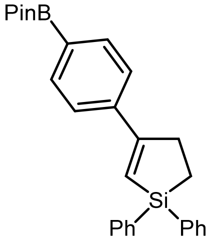
2,2-diphenyl-2,3,4,4a,5,6,7,8-octahydrobenzo*[c]*siline (17): The reaction was conducted according to the general procedure B without modification using (2-(2-(dichloromethylene)cyclohexyl)ethyl)diphenylsilane (75 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

32 mg isolated (52% yield), pale yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 4H), 7.43 – 7.32 (m, 6H), 5.69 (s, 1H), 2.48 – 2.43 (m, 1H), 2.29 – 2.16 (m, 2H), 2.07 – 1.99 (m, 1H), 1.91 – 1.77 (m, 3H), 1.66 – 1.34 (m, 2H), 1.29 – 1.18 (m, 3H), 1.02 (ddd, *J* = 14.4, 12.3, 3.3 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.1, 137.3, 137.2, 135.2, 135.0, 129.3, 129.2, 127.9, 114.4, 42.8, 41.8, 36.1, 28.7, 28.3, 26.8, 7.5.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{21}H_{25}Si$: 305.1720; found: 305.1723.



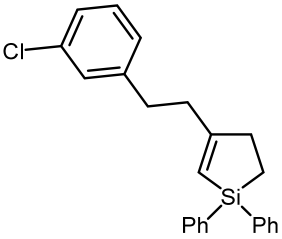
1,1-diphenyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3-dihydro-1*H*-silole (18): The reaction was conducted according to the general procedure B without modification using (4,4-dichloro-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)diphenylsilane (102 mg, 0.200 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 15% Et_2O in hexanes, R_f= 0.5).

33 mg isolated (38% yield), white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 2H), 7.65 – 7.53 (m, 6H), 7.44 – 7.34 (m, 7H), 6.71 (t, *J* = 1.8 Hz, 1H), 3.18 – 3.06 (m, 2H), 1.51 – 1.41 (m, 2H), 1.36 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.7, 142.2, 136.4, 135.1, 134.9, 134.7, 129.6, 128.1, 125.5, 123.9, 83.9, 33.1, 25.0, 9.3.

HRMS (APCI) (m/z): Calcd for $C_{28}H_{31}{}^{10}BO_2Si$: 437.2217; found: 437.2216.



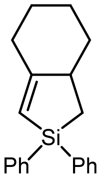
4-(3-chlorophenethyl)-1,1-diphenyl-2,3-dihydro-1*H*-silole (19): The reaction was conducted according to the general procedure B without modification using (5-(3-chlorophenyl)-3 (dichloromethylene)pentyl)diphenylsilane (89 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

24 mg isolated (32% yield), yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 4H), 7.45 – 7.32 (m, 6H), 7.25 – 7.16 (m, 3H), 7.09 (ddd, *J* = 6.7, 3.2, 1.7 Hz, 1H), 5.89 (p, *J* = 1.7 Hz, 1H), 2.88 (dd, *J* = 8.9, 6.9 Hz, 2H), 2.66 – 2.60 (m, 2H), 2.60 – 2.53 (m, 2H), 1.37 – 1.22 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 144.2, 136.8, 135.0, 134.2, 129.7, 129.4, 128.6, 128.0, 126.8, 126.2, 120.6, 38.2, 35.4, 33.9, 9.4.

HRMS (APCI) (m/z): [M + H]$^+$ Calcd for $C_{24}H_{24}ClSi$: 375.1330; found: 375.1335.



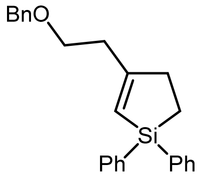
2,2-diphenyl-2,4,5,6,7,7a-hexahydro-1*H*-benzo*[c]*silole (20): The reaction was conducted according to the general procedure B without modification using ((2 (dichloromethylene)cyclohexyl)methyl)diphenylsilane (72 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 100% hexanes, R_f= 0.9).

42 mg isolated (73% yield), pale yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 4H), 7.42 – 7.32 (m, 6H), 5.73 (d, *J* = 1.9 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.18 (tdt, *J* = 13.3, 5.2, 1.4 Hz, 1H), 2.10 (ddt, *J* = 12.8, 4.9, 2.5 Hz, 1H), 1.90 – 1.76 (m, 2H), 1.58 (dd, *J* = 15.5, 8.7 Hz, 1H), 1.47 (qt, *J* = 13.0, 3.4 Hz, 1H), 1.40 – 1.29 (m, 1H), 1.24 – 1.08 (m, 1H), 0.83 (dd, *J* = 15.5, 4.7 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.9, 137.5, 137.4, 135.1, 135.0, 129.3, 127.9, 118.1, 45.7, 39.3, 36.3, 28.0, 27.0, 17.6.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{20}H_{23}Si$: 291.1563; found: 291.1553.



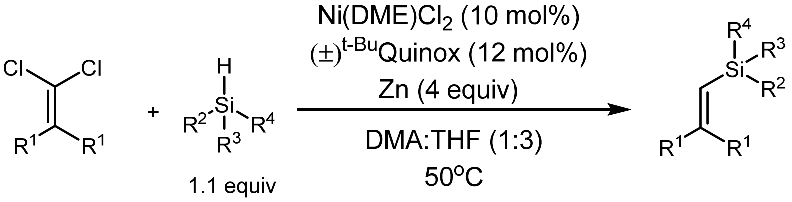
4-(2-(benzyloxy)ethyl)-1,1-diphenyl-2,3-dihydro-1*H*-silole (21): The reaction was conducted according to the general procedure B without modification using (5-(benzyloxy)-3-(dichloromethylene)pentyl)diphenylsilane (88 mg, 0.20 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 10% Et_2O in hexanes, R_f = 0.5).

49 mg isolated (66% yield), yellow oil

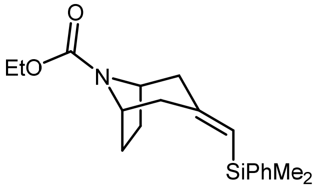
^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.45 – 7.29 (m, 11H), 5.95 (p, J = 1.6 Hz, 1H), 4.57 (s, 2H), 3.75 (t, J = 6.9 Hz, 2H), 2.71 – 2.58 (m, 4H), 1.38 – 1.26 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 138.6, 136.9, 135.0, 129.4, 128.5, 128.0, 127.8, 127.7, 121.2, 73.1, 68.9, 37.1, 35.6, 9.2.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{25}H_{27}OSi$: 371.1826; found: 371.1823.



General Procedure for the Intermolecular Si–H insertion reaction. In an N_2-filled glovebox, a 5-mL vial was charged with $Ni(DME)Cl_2$ (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and THF (0.2 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing the 1,1-dichloroalkene (0.20 mmol, 1.0 equiv) and the silane (0.22 mmol, 1.1 equiv) dissolved in THF (0.4 mL). The reaction was stirred at 50 °C. After 16 h, the reaction vial was cooled to room temperature before removing from the glovebox. It was then opened to ambient atmosphere and THF was removed under a stream of N_2. The crude residue was loaded directly onto a SiO_2 column for purification.



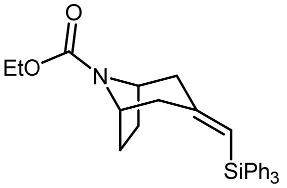
ethyl 3-((dimethyl(phenyl)silyl)methylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (22): The reaction was conducted according to the general procedure without modification using ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (53 mg, 0.20 mmol, 1.0 equiv) and dimethylphenylsilane (33.7 μL, 0.220 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 10% Et_2O in hexanes, R_f= 0.2).

48 mg isolated (75% yield), colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.34 (td, *J* = 4.1, 3.5, 2.0 Hz, 3H), 5.54 (s, 1H), 4.40 – 4.07 (m, 5H), 2.77 – 2.52 (m, 1H), 2.21 (d, *J* = 12.5 Hz, 1H), 2.13 (dd, *J* = 14.0, 2.4 Hz, 1H), 1.95 – 1.67 (m, 3H), 1.59 (q, *J* = 7.7, 6.4 Hz, 1H), 1.46 – 1.30 (m, 1H), 1.30 – 1.17 (m, 4H), 0.36 (d, *J* = 2.5 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 153.2, 139.8, 133.8, 129.0, 127.9, 126.4, 61.0, 54.3, 54.0, 28.5, 27.8, 14.9.

HRMS (APCI) (m/z): [M + H]$^+$ Calcd for $C_{19}H_{28}NO_2Si$: 330.1884; found: 330.1886.



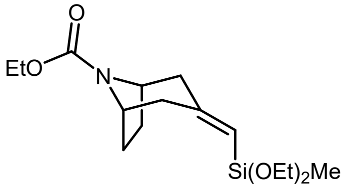
ethyl 3-((triphenylsilyl)methylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (23): The reaction was conducted according to the general procedure without modification using ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (53 mg, 0.20 mmol, 1.0 equiv) and triphenylsilane (57 mg, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 10% Et_2O in hexanes R_f = 0.2).

55 mg isolated (61% yield), white solid

^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 6.4, 1.7 Hz, 6H), 7.46 – 7.32 (m, 9H), 5.98 (s, 1H), 4.33 (d, *J* = 21.6 Hz, 1H), 4.21 – 3.93 (m, 3H), 2.78 (d, *J* = 21.4 Hz, 1H), 2.31 (dd, *J* = 14.3, 2.4 Hz, 1H), 2.16 (t, *J* = 5.6 Hz, 1H), 1.87 (s, 1H), 1.70 – 1.52 (m, 2H), 1.35 – 1.11 (m, 5H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.0, 135.8, 135.6, 129.6, 128.1, 123.0, 61.0, 54.0, 54.0, 14.9.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{29}H_{32}NO_2Si$: 454.2197; found: 454.2195.



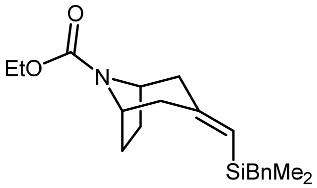
ethyl 3-((diethoxy(methyl)silyl)methylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (24): The reaction was conducted according to the general procedure without modification using ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (53 mg, 0.20 mmol, 1.0 equiv) and diethoxymethylsilane (35 μL, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 15% Et_2O in hexanes R_f = 0.3).

39 mg isolated (59% yield), white solid

^1H NMR (400 MHz, $CDCl_3$) δ 5.28 (t, *J* = 2.1 Hz, 1H), 4.33 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.57 (d, *J* = 14.2 Hz, 2H), 2.42 (d, *J* = 43.2 Hz, 1H), 2.09 (dt, *J* = 14.2, 1.6 Hz, 1H), 1.88 (t, *J* = 6.4 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.29 – 1.18 (m, 10H), 0.18 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.7, 154.1, 123.1, 61.0, 58.2, 54.3, 54.1, 28.7, 18.5, 14.9, -2.6.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{16}H_{30}NO_4Si$: 328.1939; found: 328.1936.



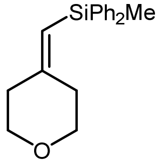
ethyl 3-((benzyldimethylsilyl)methylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (25): The reaction was conducted according to the general procedure without modification using ethyl 3-(dichloromethylene)-8-azabicyclo[3.2.1]octane-8-carboxylate (53 mg, 0.20 mmol, 1.0 equiv) and Benzyldimethylsilane (35 μL, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 10% Et_2O in hexanes, R_f = 0.2).

49 mg isolated (72% yield), yellow oil

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.17 (m, 2H), 7.10 – 7.03 (m, 1H), 7.03 – 6.96 (m, 2H), 5.35 (d, *J* = 2.0 Hz, 1H), 4.29 (d, *J* = 22.8 Hz, 2H), 4.20 – 4.12 (m, 2H), 2.72 – 2.35 (m, 1H), 2.26 (d, *J* = 12.9 Hz, 1H), 2.15 (s, 2H), 2.12 – 2.04 (m, 1H), 1.94 – 1.80 (m, 2H), 1.64 – 1.42 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 4H), 0.08 (d, *J* = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 154.1, 140.1, 128.3, 128.3, 126.5, 124.1, 61.0, 54.4, 54.0, 28.7, 27.9, 26.8, 14.9, -1.5, -1.6.

HRMS (APCI) (m/z): [M + H]$^+$ Calcd for $C_{20}H_{30}NO_2Si$: 344.2040; found: 344.2038.



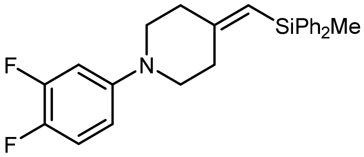
methyldiphenyl((tetrahydro-4*H*-pyran-4-ylidene)methyl)silane (26): The reaction was conducted according to the general procedure without modification **33** (33 mg, 0.20 mmol, 1.0 equiv) and methyldiphenylsilane (44 µL, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 10% Et$_2$O in hexanes, R$_f$= 0.3).

43 mg isolated (73% yield), colorless oil

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.47 (m, 4H), 7.40 – 7.29 (m, 6H), 5.57 (t, *J* = 1.1 Hz, 1H), 3.79 – 3.72 (m, 2H), 3.55 – 3.48 (m, 2H), 2.41 (t, *J* = 4.9 Hz, 2H), 0.64 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 157.4, 137.8, 134.7, 129.3, 128.0, 118.8, 69.8, 68.9, 40.7, 35.7, -1.7.

HRMS (APCI) (m/z): [M + H]$^+$ Calcd for $C_{19}H_{23}OSi$: 295.1513; found: 295.1508.



1-(3,4-difluorophenyl)-4-((methyldiphenylsilyl)methylene)piperidine (27): The reaction was conducted according to the general procedure with following modification 4-(dichloromethylene)-1-(3,4-difluorophenyl)piperidine (56 mg, 0.20 mmol, 1.0 equiv), Methyldiphenylsilane (44 µL, 0.22 mmol, 1.1 equiv), Ni(DME)Cl$_2$ (8.8 mg, 0.040 mmol, 0.20 equiv), (±)-*t*-Bu-Quinox (12 mg, 0.048 mmol, 0.24 equiv) and Zn powder (52 mg, 0.80 mmol, 4.0 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 100% hexanes, R$_f$= 0.2).

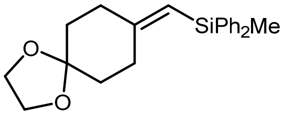
40 mg isolated (49% yield), colorless oil**.**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.52 (m, 4H), 7.42 – 7.32 (m, 6H), 7.05 – 6.94 (m, 1H), 6.66 (ddd, J = 13.5, 6.8, 3.0 Hz, 1H), 6.54 (dtd, J = 8.4, 3.3, 1.5 Hz, 1H), 5.63 (s, 1H), 3.28 – 3.21 (m, 2H), 3.03 – 2.97 (m, 2H), 2.54 – 2.47 (m, 2H), 2.27 (t, J = 5.9 Hz, 2H), 0.66 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.0, 137.7, 134.7, 129.3, 128.0, 119.3, 119.1, 117.4, 117.3 (d, $^2J_{CF}$ = 18.2 Hz), 111.8, 105.6 (d, $^2J_{CF}$ = 20.2 Hz), 51.9, 51.1, 39.1, 33.8, -1.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ -138.3 (dt, J = 22.0, 12.2 Hz), -151.7 – -152.0 (m).

HRMS (APCI) (m/z): [M + H]+ Calcd for $C_{25}H_{26}F_2NSi$: 406.1797; found: 406.1794.



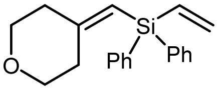
((1,4-dioxaspiro[4.5]decan-8-ylidene)methyl)(methyl)diphenylsilane (28): The reaction was conducted according to the general procedure with following modification 8-(dichloromethylene)-1,4-dioxaspiro[4.5]decane (45 mg, 0.20 mmol, 1.0 equiv), Methyldiphenylsilane (44 µL, 0.22 mmol, 1.1 equiv), Ni(DME)Cl_2 (8.8 mg, 0.040 mmol, 0.20 equiv), (±)-*t*-Bu-Quinox (12 mg, 0.048 mmol, 0.24 equiv) and Zn powder (52 mg, 0.80 mmol, 4.0 equiv). Isolated yields were determined following column chromatography (SiO_2, 5% Et_2O in hexanes, R_f = 0.2).

29 mg isolated (41% yield), colorless oil**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.38 – 7.31 (m, 6H), 5.55 (s, 1H), 3.97 – 3.91 (m, 4H), 2.51 – 2.42 (m, 2H), 2.27 – 2.19 (m, 2H), 1.82 – 1.75 (m, 2H), 1.56 – 1.47 (m, 2H), 0.64 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 137.7, 134.5, 128.9, 127.7, 118.3, 108.2, 64.2, 37.1, 36.2, 35.1, 31.4, -1.9.

HRMS (APCI) (m/z): [M + H]+ Calcd for $C_{22}H_{27}O_2Si$: 351.1775; found: 351.1778.



diphenyl((tetrahydro-4*H*-pyran-4-ylidene)methyl)(vinyl)silane (29): The reaction was conducted according to the general procedure without modification **33** (33 mg, 0.20 mmol, 1.0 equiv) and diphenyl(vinyl)silane[16] (46 mg, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 5% Et_2O in hexanes, R_f= 0.4).

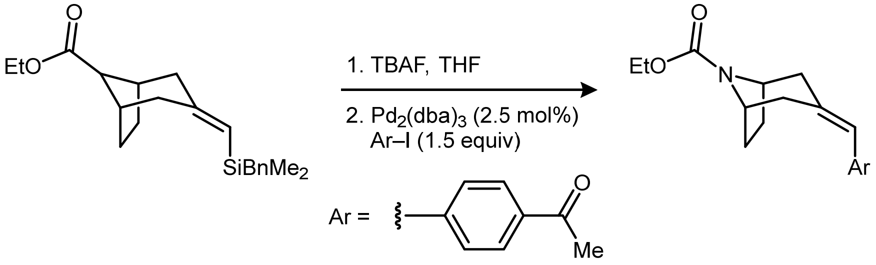
21 mg isolated (34% yield), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.42 – 7.31 (m, 6H), 6.57 – 6.48 (m, 1H), 6.22 (dd, J = 14.5, 3.7 Hz, 1H), 5.82 (dd, J = 20.1, 3.7 Hz, 1H), 5.59 (s, 1H), 3.80 – 3.73 (m, 2H), 3.54 (t, J = 5.5 Hz, 2H), 2.44 (t, J = 6.1 Hz, 2H), 2.22 (t, J = 5.1 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.5, 135.8, 135.6, 135.4, 129.5, 128.0, 121.9, 116.6, 69.8, 68.9, 40.8, 36.1.

HRMS (APCI) (m/z): [M + H]+ Calcd for $C_{20}H_{23}OSi$: 307.1513; found: 307.1509.

5. Hiyama Cross-Coupling Product



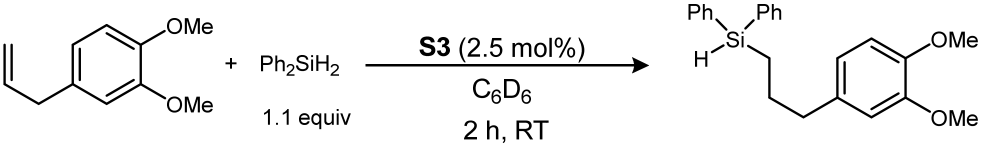
ethyl 3-(4-acetylbenzylidene)-8-azabicyclo[3.2.1]octane-8-carboxylate (30): According to a previously reported procedure:[17] Under an N_2 atmosphere, an oven dried 25-mL round bottom flask was charged with 4-iodoacetophenone (74 mg, 0.30 mmol, 1.5 equiv). A solution containing **25** (69 mg, 0.20 mmol, 1.0 equiv) dissolved in anhydrous THF (1 mL) was added to the flask and stirred at 0 °C. To this reaction mixture, TBAF in 1 M THF (0.40 mL, 0.40 mmol, 2,0 equiv) was added dropwise. The mixture turned deep orange gradually over 10 min. After 15 min of stirring at 0 °C, solid $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 0.025 equiv) was added, and the reaction was warmed to room temperature. The reaction mixture was stirred for 4 h at ambient temperature. The reaction mixture was diluted with Et_2O (20 mL) and then was filtered through a silica pad. The filtrate was concentrated, and the crude product was purified by column chromatography (SiO_2, 10% EtOAc in hexanes, R_f = 0.15) to yield ethyl 3-(4-acetylbenzylidene)-8-azabicyclo[3.2.1]octane-8-carboxylate as a white solid (34 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.45 (s, 1H), 4.32 (d, J = 36.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.73 (s, 1H), 2.57 (s, 5H), 2.23 – 2.15 (m, 1H), 1.98 – 1.76 (m, 2H), 1.74 – 1.61 (m, 1H), 1.49 – 1.36 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.6, 154.1, 142.4, 138.1, 135.1, 129.1, 128.4, 128.0, 61.0, 54.4, 43.1, 28.6, 28.1, 26.6, 14.9.

HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{19}H_{24}NO_3$: 314.1751; found: 314.1753.

6. Sequential Hydrosilylation and Vinylidene Si–H Insertion Product

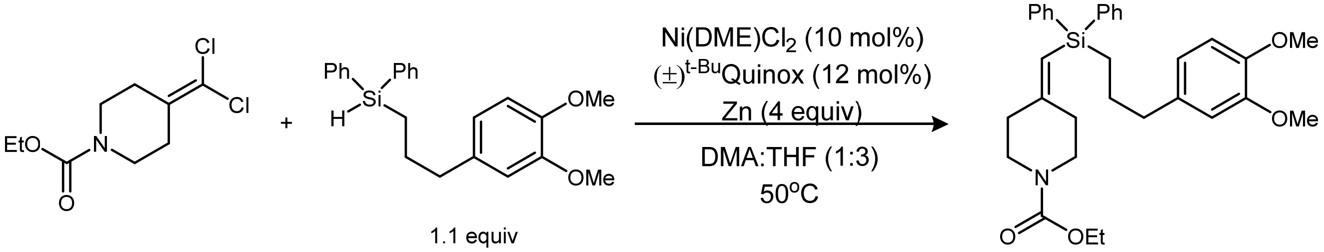


(3-(3,4-dimethoxyphenyl)propyl)diphenylsilane (S53): According to a previously reported procedure:[4] In a N_2 filled glovebox, a 20-dram vial is charged with **S3** (31 mg, 0.042 mmol, 0.025 equiv) dissolved in C_6D_6 (2 mL). To this mixture, a solution containing **31** (0.30 mL, 2.0 mmol, 1.0 equiv) and diphenylsilane (0.30 mL, 2.0 mmol, 1.0 equiv) dissolved in C_6D_6 (1 mL) was added. The reaction mixture was stirred for 2 h at room temperature. After full conversion of the unsaturated alcohol, the reaction vial was then removed from the glovebox and opened to ambient temperature. The crude mixture was loaded directly onto a SiO_2 column (SiO_2, 100% CH_2Cl_2, R_f = 0.3) to provide (3-(3,4-dimethoxyphenyl)propyl)diphenylsilane (432 mg, 71% yield) as a yellow viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.48 (m, 3H), 7.46 – 7.30 (m, 6H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.72 – 6.59 (m, 2H), 4.87 (t, *J* = 3.6 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.9 Hz, 2H), 1.36 – 1.07 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.9, 147.2, 135.3, 134.9, 134.5, 129.7, 128.1, 120.5, 111.9, 111.2, 56.0, 55.9, 38.8, 26.5, 11.8.

HRMS (APCI) (m/z): $[M - H]^+$ Calcd for $C_{23}H_{25}O_2Si$: 361.1618; found: 361.1619.



ethyl 4-(((3-(3,4-dimethoxyphenyl)propyl)diphenylsilyl)methylene)piperidine-1-carboxylate (32): The reaction was conducted according to the general procedure for the intermolecular Si–H insertion reaction without modification using ethyl 4-(dichloromethylene)piperidine-1-carboxylate (48 mg, 0.20 mmol, 1.0 equiv) and (3-(3,4-dimethoxyphenyl)propyl)diphenylsilane (80 mg, 0.22 mmol, 1.1 equiv). Isolated yields were determined following column chromatography (SiO_2, 20% Et_2O in hexanes, R_f = 0.4).

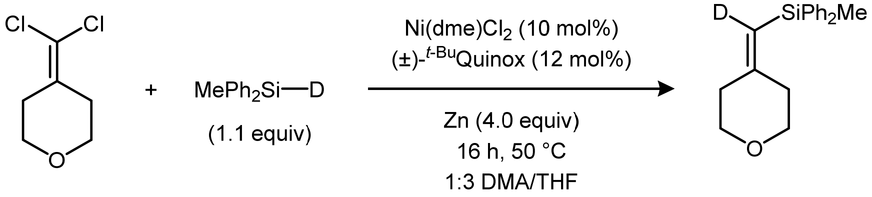
60 mg isolated (57% yield), yellow viscous oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 4H), 7.45 – 7.28 (m, 6H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.72 – 6.54 (m, 2H), 5.64 (s, 1H), 4.13 (dq, *J* = 14.2, 7.1 Hz, 2H), 3.85 (d, *J* = 7.9 Hz, 7H), 3.53 (t, *J* = 5.9 Hz, 2H), 3.22 (t, *J* = 5.8 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.37 (t, *J* = 5.9 Hz, 2H), 2.06 (t, *J* = 5.8 Hz, 2H), 1.73 (dq, *J* = 12.1, 8.2, 7.5 Hz, 2H), 1.39 – 1.08 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.2, 155.5, 151.1, 148.9, 147.2, 136.6, 135.0, 129.3, 128.0, 120.5, 118.6, 111.9, 111.2, 61.4, 56.0, 55.9, 45.7, 44.8, 39.6, 39.3, 26.2, 14.8, 14.5.

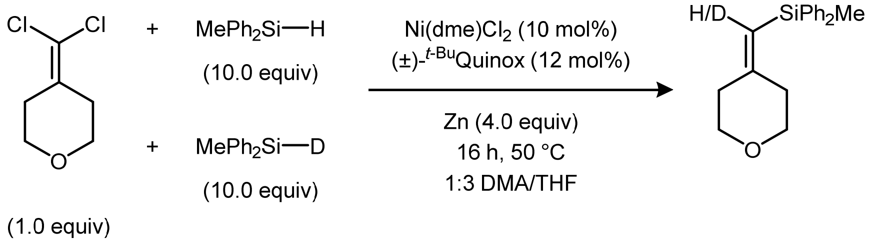
HRMS (APCI) (m/z): $[M + H]^+$ Calcd for $C_{32}H_{30}NO_4Si$: 530.2721; found: 530.2729.

7. Deuterium Isotope Experiments



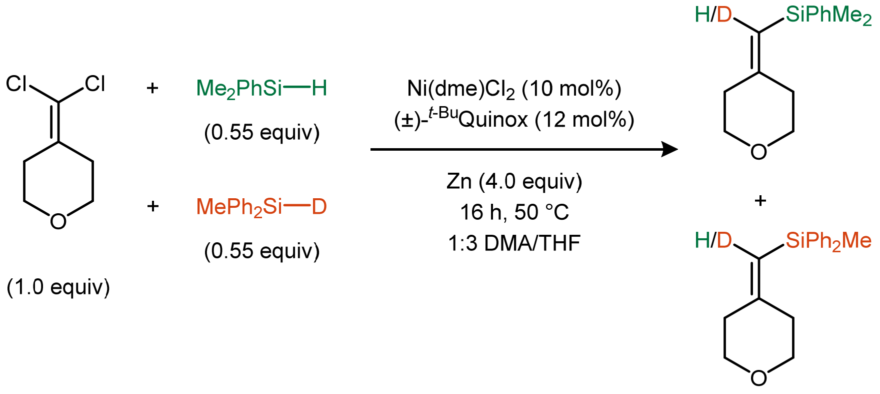
methyldiphenyl((tetrahydro-4H-pyran-4-ylidene)methyl-*d*)silane (26-*d*₁): In an N_2-filled glovebox, a 5-mL vial was charged with Ni(DME)Cl_2 (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and THF (0.2 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing **33** (33 mg, 0.20 mmol, 1.0 equiv) and methyldiphenylsilane-*d*[18] (44 mg, 0.22 mmol, 1.1 equiv) dissolved in THF (0.4 mL). The reaction was stirred at 50 °C. After 16 h, the crude reaction mixture was cooled to room temperature before removing from the reaction vial from the glovebox. It was then opened to ambient atmosphere, THF was removed under an N_2 stream, and the crude residue was loaded directly onto a SiO_2 column for purification (SiO_2, 10% Et_2O in hexanes, R_f = 0.2) to provide methyldiphenyl((tetrahydro-4H-pyran-4-ylidene)methyl-d)silane as a colorless liquid (46 mg, 77% yield, >99% deuterium incorporation).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.49 (m, 4H), 7.45 – 7.29 (m, 6H), 3.76 (t, *J* = 5.5 Hz, 2H), 3.53 (t, *J* = 5.5 Hz, 2H), 2.46 – 2.37 (m, 2H), 2.23 – 2.14 (m, 2H), 0.65 (s, 3H).



Kinetic Isotope Effect Experiment: In an N_2-filled glovebox, a 5-mL vial was charged with Ni(DME)Cl_2 (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and THF (0.2 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing **33** (33 mg, 0.20 mmol, 1.0 equiv), methyldiphenylsilane-*d*[18] (399 mg, 2.00 mmol, 10.0 equiv) and methyldiphenylsilane (399 mg, 2.00 mmol, 10.0 equiv) dissolved in THF (0.4 mL). The reaction was stirred at 50 °C. After 16 h, the crude reaction mixture was cooled to room temperature before removing the reaction vial from the glovebox. It was then opened to ambient atmosphere, THF was removed under an N_2 stream, and the crude residue was loaded directly onto a SiO_2 column for purification (SiO_2, 10% Et_2O in hexanes, R_f = 0.2) to provide the mixture of methyldiphenyl((tetrahydro-4H-pyran-4-ylidene)methyl-*d*)silane and methyldiphenyl((tetrahydro-4H-pyran-4-ylidene)methyl)silane as a colorless liquid (92 mg, 78% overall yield, KIE = 1.0 from ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H), 7.43 – 7.32 (m, 6H), 5.59 (s, 0.52H), 3.82 – 3.71 (m, 2H), 3.60 – 3.47 (m, 2H), 2.42 (t, *J* = 5.5 Hz, 2H), 2.25 – 2.14 (m, 2H), 0.66 (s, 3H).



Scrambling Experiment with 33: In an N_2-filled glovebox, a 5-mL vial was charged with $Ni(DME)Cl_2$ (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and THF (0.2 mL) were added, and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution containing **33** (33 mg, 0.20 mmol, 1.0 equiv), methyldiphenylsilane-*d*[18] (22 mg, 0.11 mmol, 0.55 equiv) and dimethylphenylsilane (17 µL 0.11 mmol, 0.55 equiv) dissolved in THF (0.4 mL). The reaction was stirred at 50 °C. After 16 h, the crude reaction mixture was cooled to room temperature before removing from the glovebox. It was then opened to ambient atmosphere, THF was removed under an N_2 stream. The crude residue was then loaded directly onto a SiO_2 column for purification (SiO_2, 100% hexanes, R_f = 1.0) to provide the mixture of unreacted silanes as a colorless liquid and then (SiO_2, 10% Et_2O in hexanes, R_f= 0.2) to provide the mixture of **26** and **34** as a colorless liquid.

Mixture of unreacted silanes: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 9H), 7.46 – 7.32 (m, 14H), 4.97 (q, *J* = 3.8 Hz, 1H), 0.65 (d, *J* = 3.9 Hz, 7H); *Mixture of **26** and **34***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.48 (m, 5H), 7.46 – 7.31 (m, 10H), 5.40 (s, 1H), 3.81 – 3.64 (m, 5H), 3.63 – 3.55 (m, 2H), 3.56 – 3.49 (m, 2H), 2.54 – 2.49 (m, 1H), 2.41 (t, *J* = 5.5 Hz, 2H), 2.35 (t, *J* = 5.5 Hz, 2H), 2.25 (t, *J* = 5.5 Hz, 2H), 2.22 – 2.15 (m, 2H), 0.64 (s, 3H), 0.37 (s, 7H).

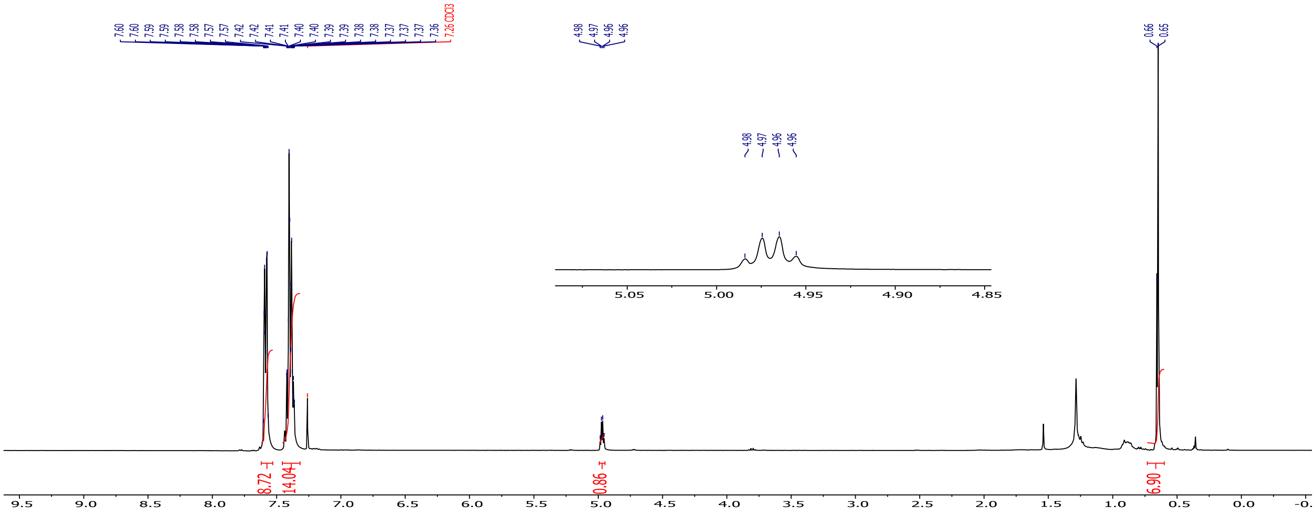


Figure S1 ^{1}H NMR of mixture of unreacted silanes recovered by column chromatography (400 MHz, $CDCl_3$, 295 K)

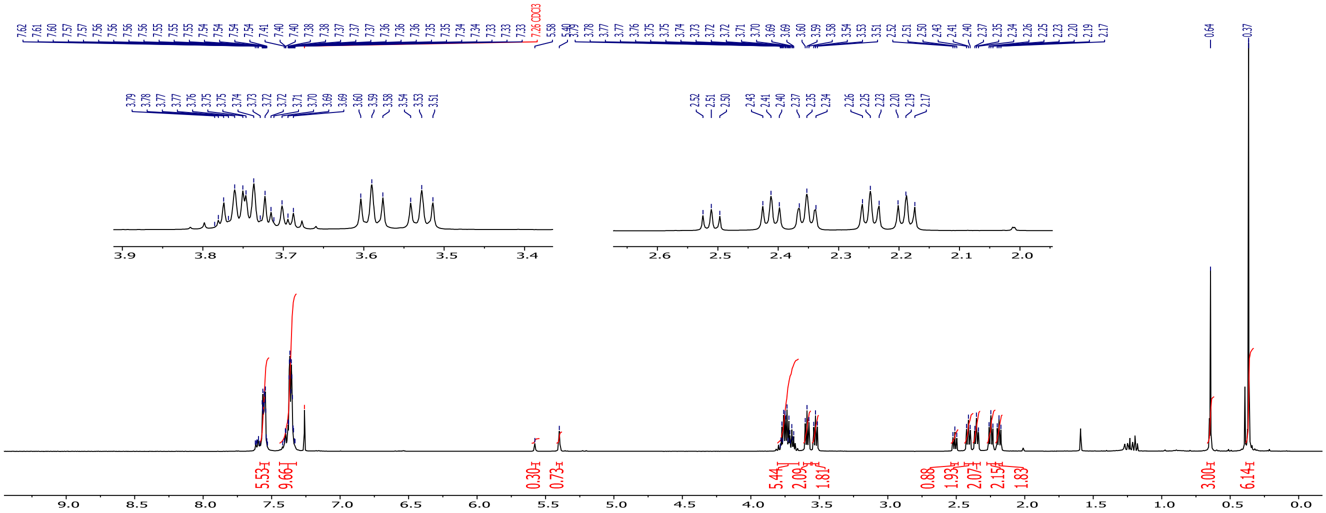


Figure S2 ^{1}H NMR of mixture of **26** and **34** (400 MHz, $CDCl_3$, 295 K)

$$\mathrm{MePh_2Si{-}D} + \mathrm{Me_2PhSi{-}H} \xrightarrow[\substack{\text{Zn (4.0 equiv)}\\ \text{16 h, 50 °C}\\ \text{1:3 DMA/THF}}]{\substack{\mathrm{Ni(dme)Cl_2}\text{ (10 mol\%)}\\ (\pm)\text{-}^{t\text{-Bu}}\text{Quinox (12 mol\%)}}} \mathrm{MePh_2Si{-}D/H} + \mathrm{Me_2PhSi{-}H/D}$$

Scrambling Experiment without 33: In an N_2-filled glovebox, a 5-mL vial was charged with $Ni(DME)Cl_2$ (4.4 mg, 0.020 mmol, 0.10 equiv), (±)-*t*-Bu-Quinox (6.1 mg, 0.024 mmol, 0.12 equiv), Zn powder (52 mg, 0.80 mmol, 4.0 equiv), and a magnetic stir bar. DMA (0.2 mL) and THF (0.2 mL) were added and the mixture was stirred for 10 min in ambient temperature. To this mixture was added a solution of the methyldiphenylsilane-*d*[18] (20 mg, 0.10 mmol, 1.0 equiv) and dimethylphenylsilane (15 µL, 0.10 mmol, 1.0 equiv) dissolved in THF (0.4 mL). The reaction was stirred at 50 °C. After 1 h, the crude reaction mixture was cooled to room temperature and run through a short silica pad inside the glovebox before checking ^1H NMR.

^1H NMR (400 MHz, C_6D_6) δ 5.09 (s, 0.43H), 4,58 (s, 0.45H), 0.46 (d, *J* = 3.9 Hz, 3H), 0.21 (d, *J* = 3.9 Hz, 6H).

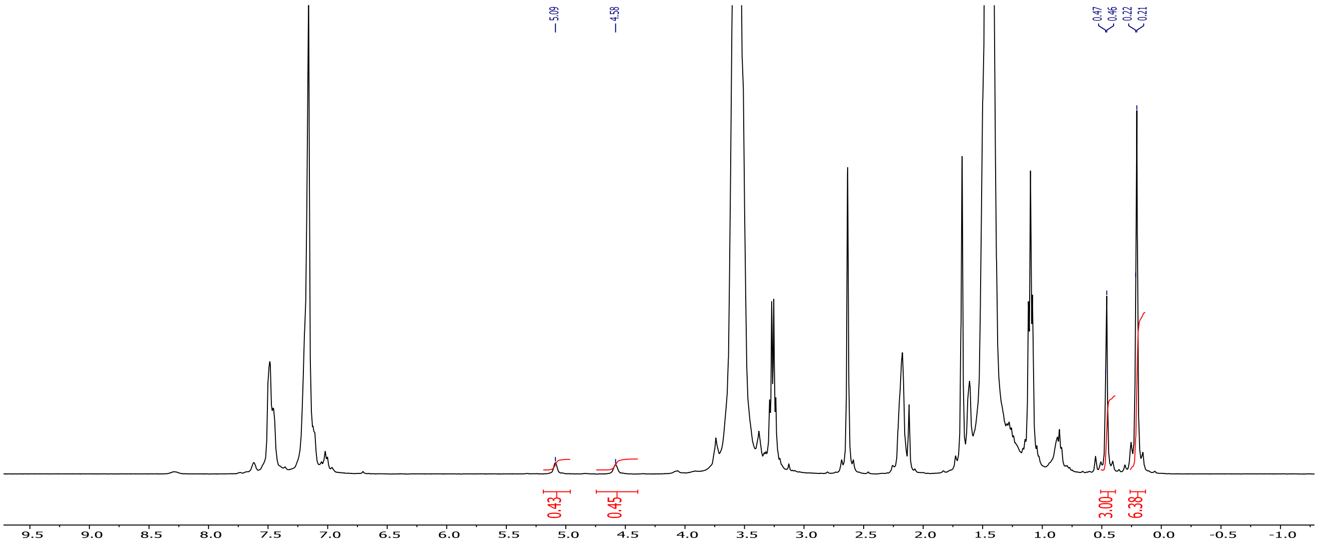
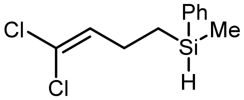


Figure S3 ^1H NMR of crude mixture of scrambled silanes (400 MHz, C_6D_6, 295 K)

8. NMR Data for the 1,1-Dichloroalkene Substrates



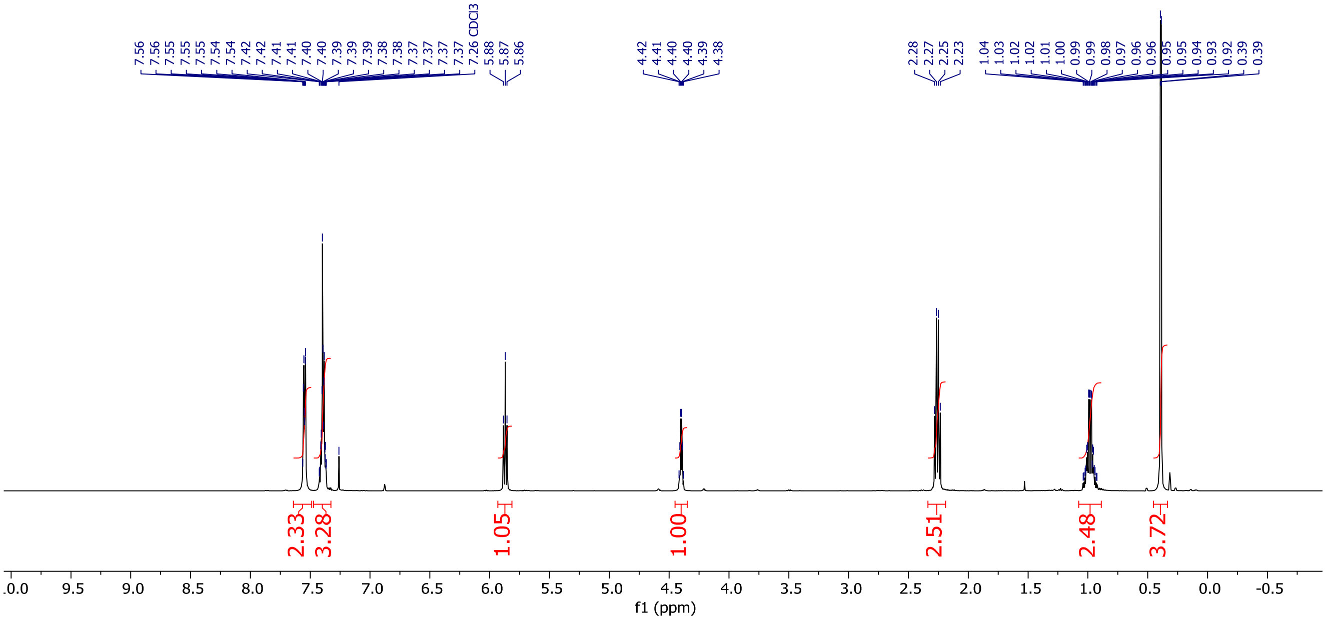


Figure S4 ^{1}H NMR of **S9** (500 MHz, $CDCl_3$, 295K)

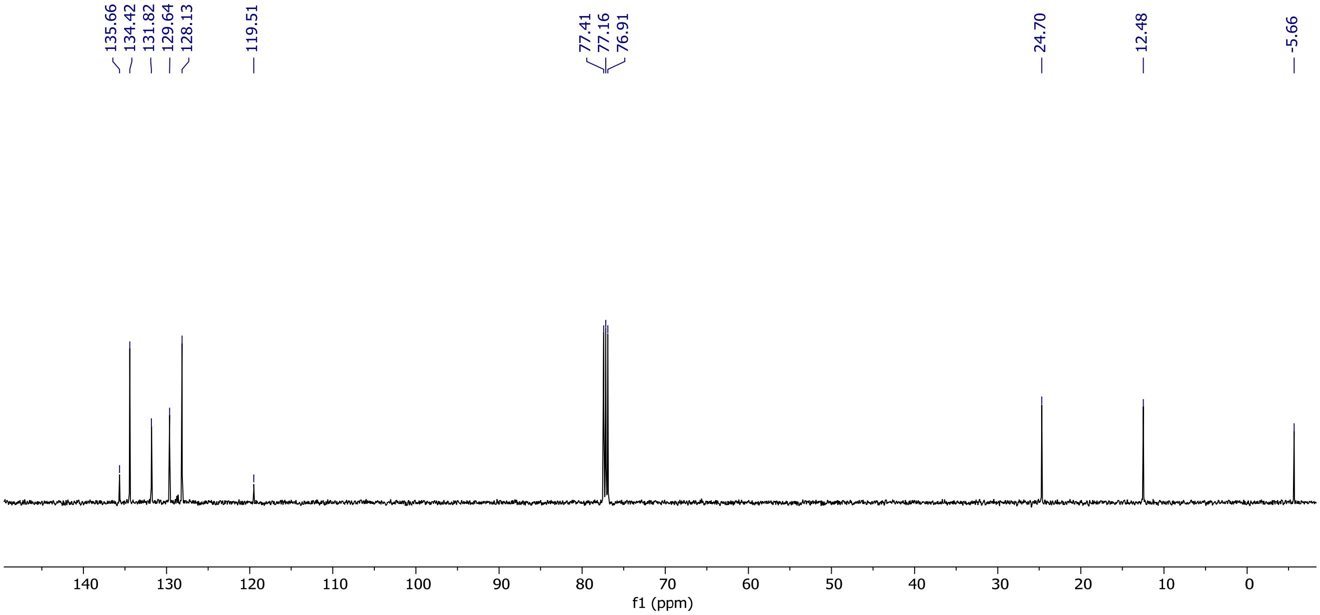


Figure S5 ^{13}C NMR of **S9** (126 MHz, $CDCl_3$, 295K)

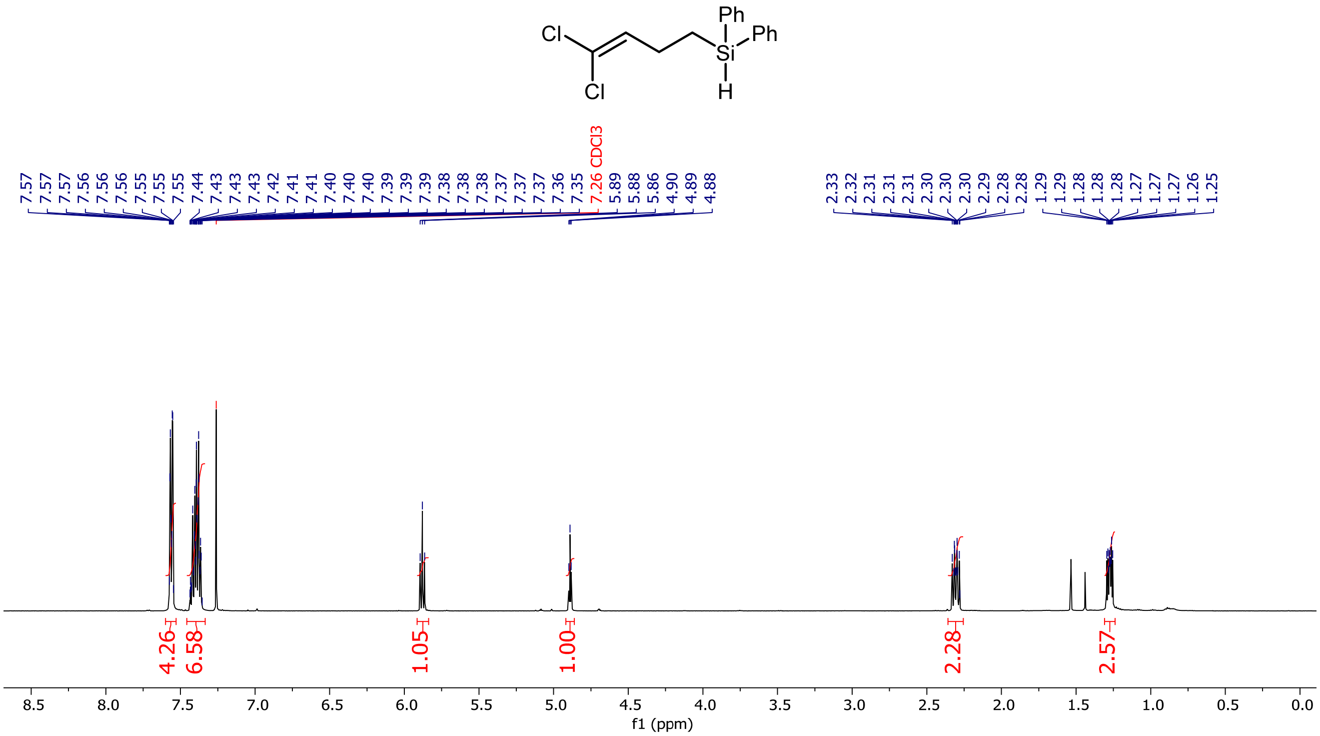


Figure S6 ^{1}H NMR of **S12** (500 MHz, $CDCl_3$, 295K)

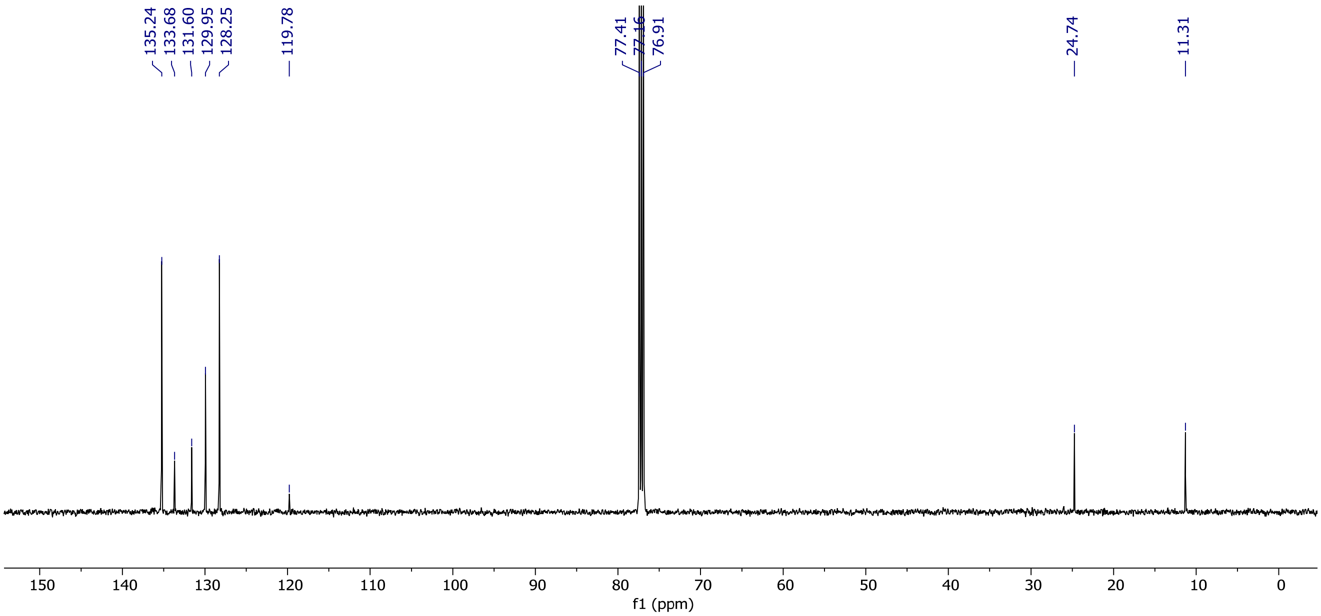


Figure S7 ^{13}C NMR of **S12** (126 MHz, $CDCl_3$, 295K)

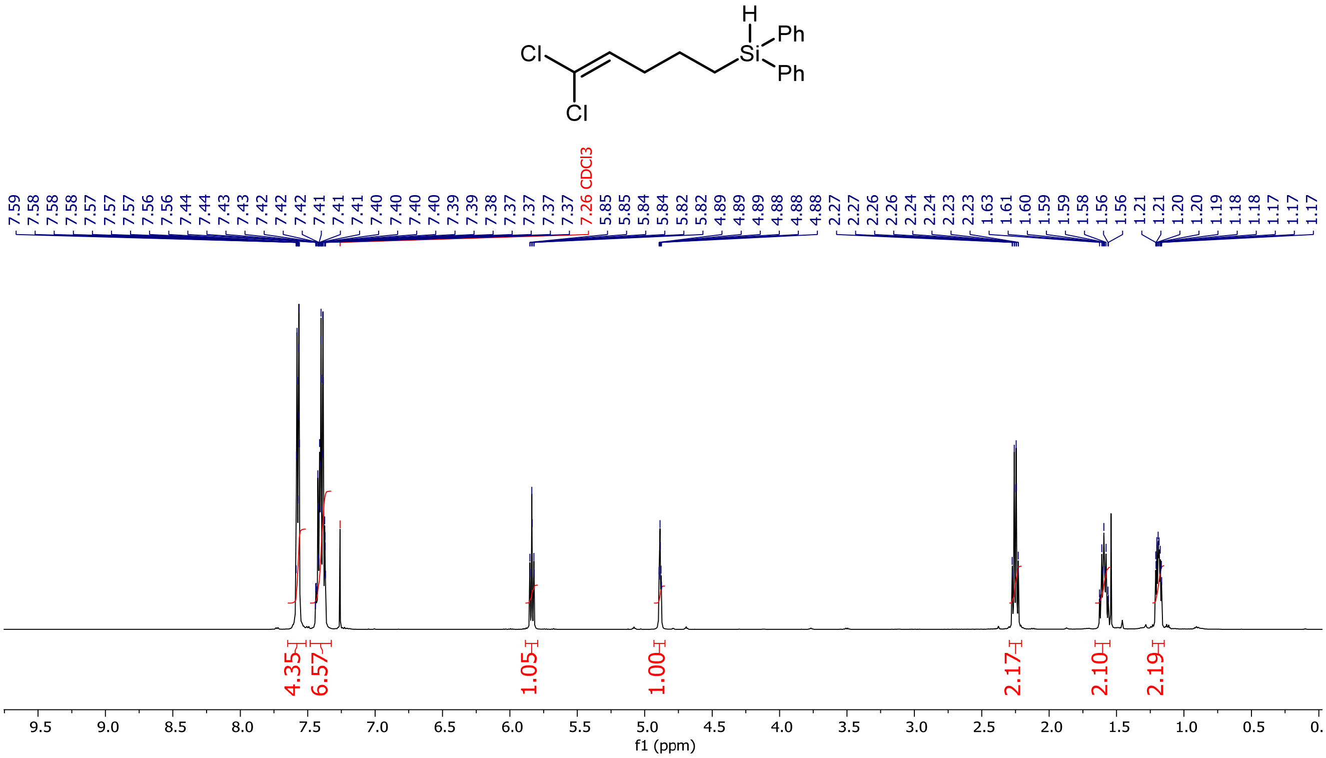


Figure S8 ^{1}H NMR of **S15** (500 MHz, $CDCl_3$, 295K)

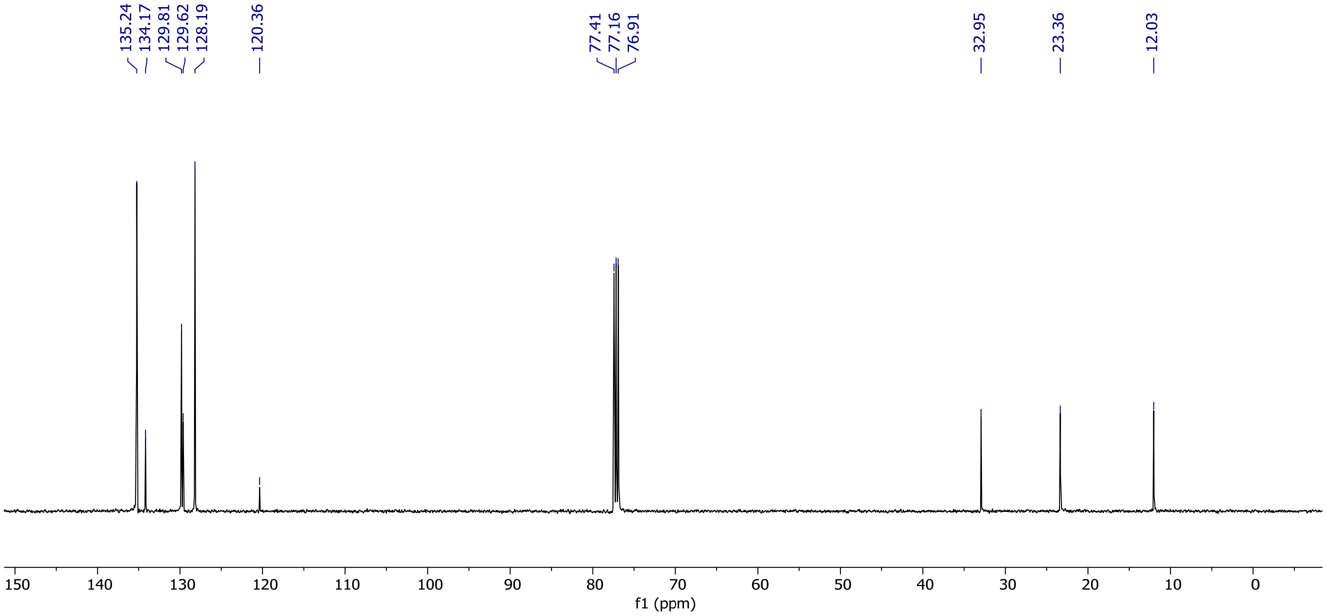
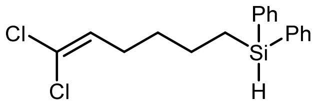


Figure S9 ^{13}C NMR of **S15** (126 MHz, $CDCl_3$, 295K)



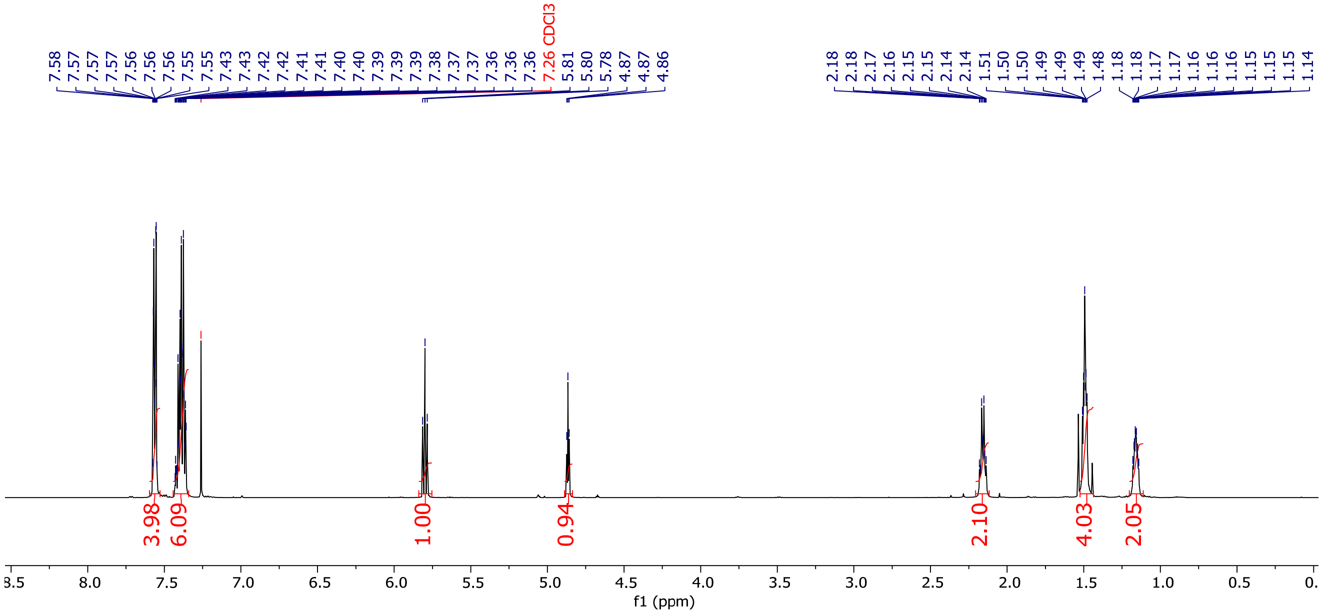


Figure S10 ^1H NMR of **S18** (500 MHz, $CDCl_3$, 295K)

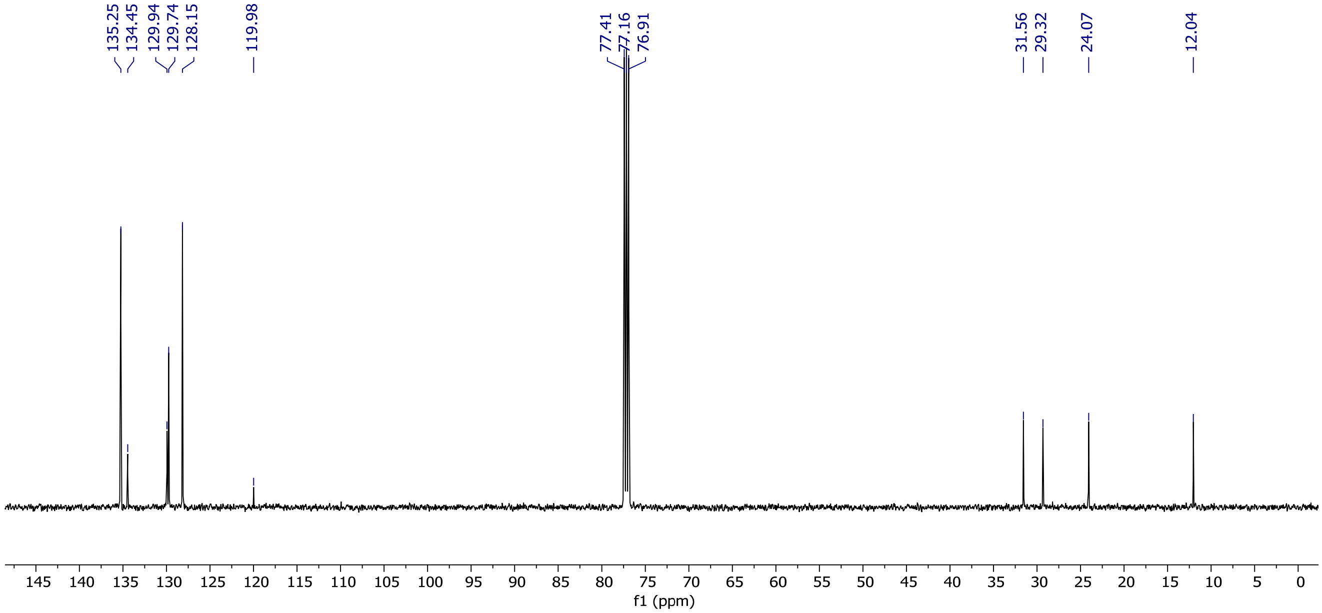
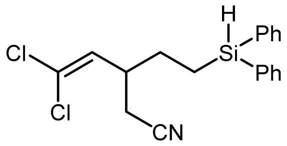


Figure S11 ^{13}C NMR of **S18** (126 MHz, $CDCl_3$, 295K)



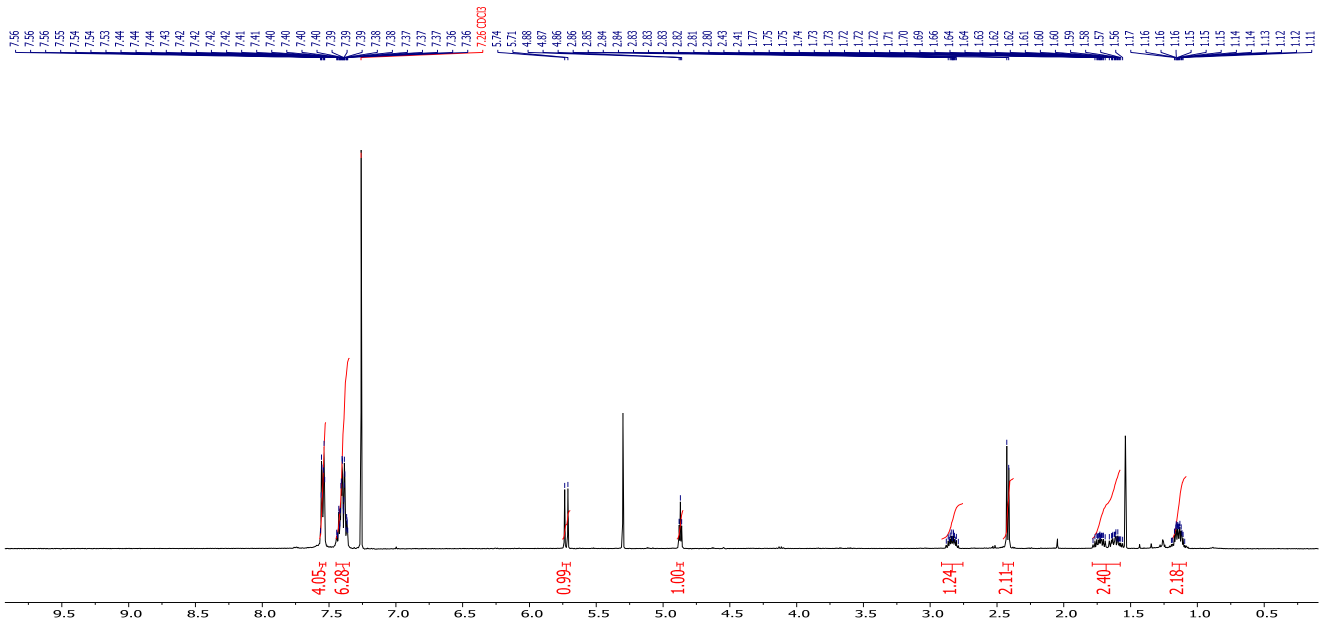


Figure S12 ^{1}H NMR of **S21** (400 MHz, $CDCl_3$, 295K)

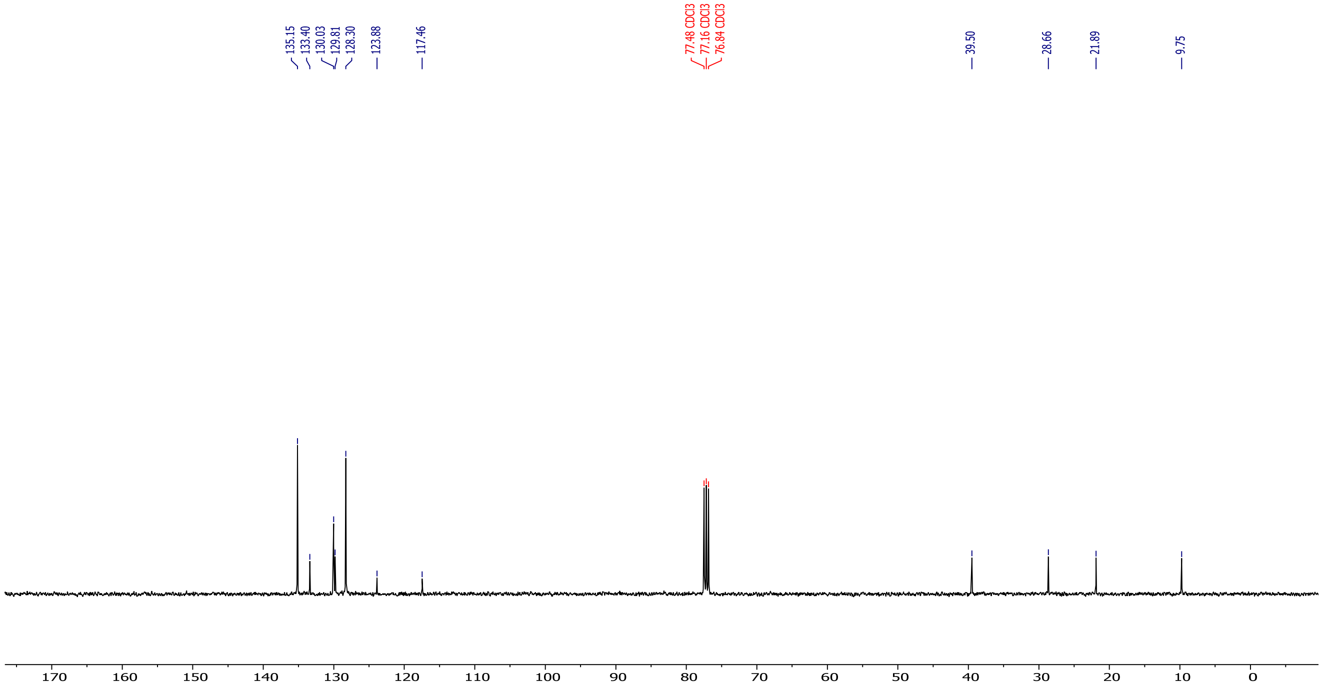


Figure S13 ^{13}C NMR of **S21** (126 MHz, $CDCl_3$, 295K)

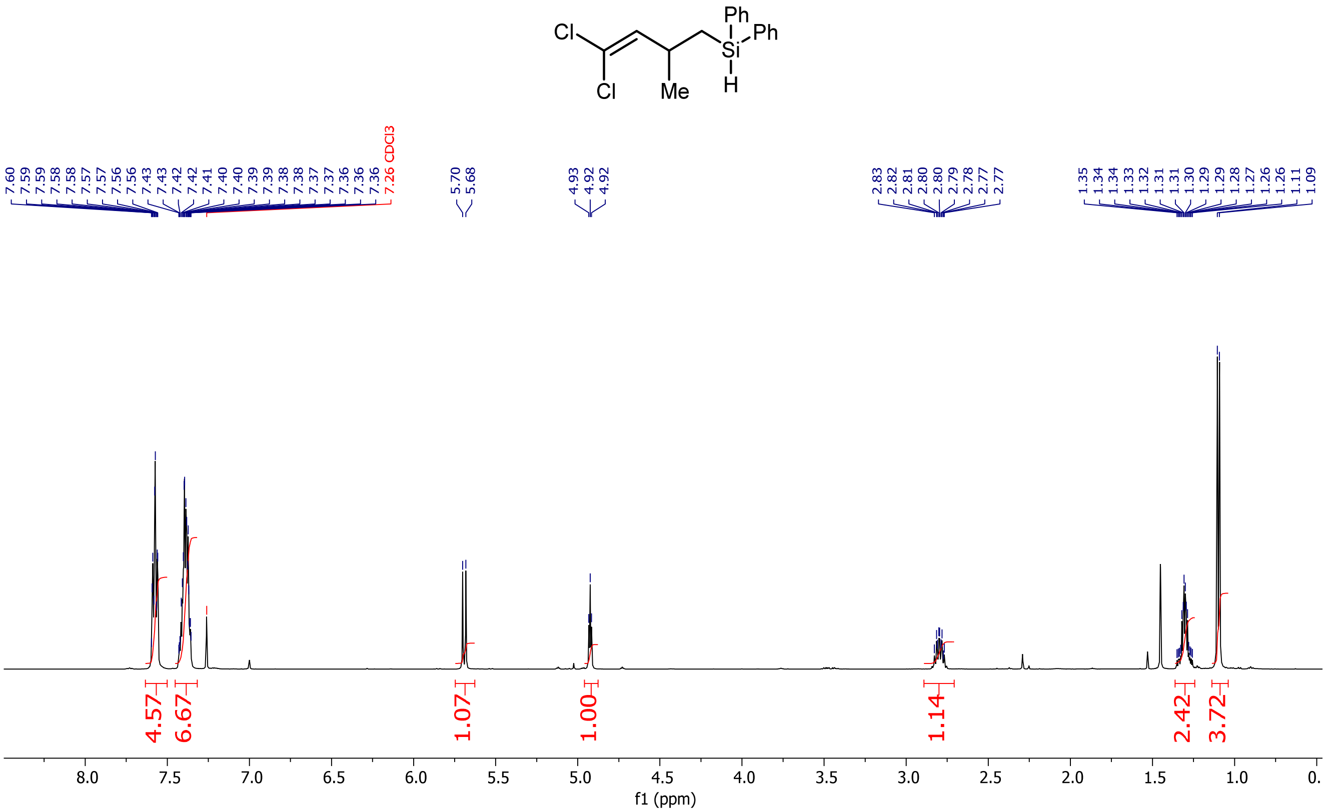


Figure S14 ^{1}H NMR of **S24** (500 MHz, $CDCl_3$, 295K)

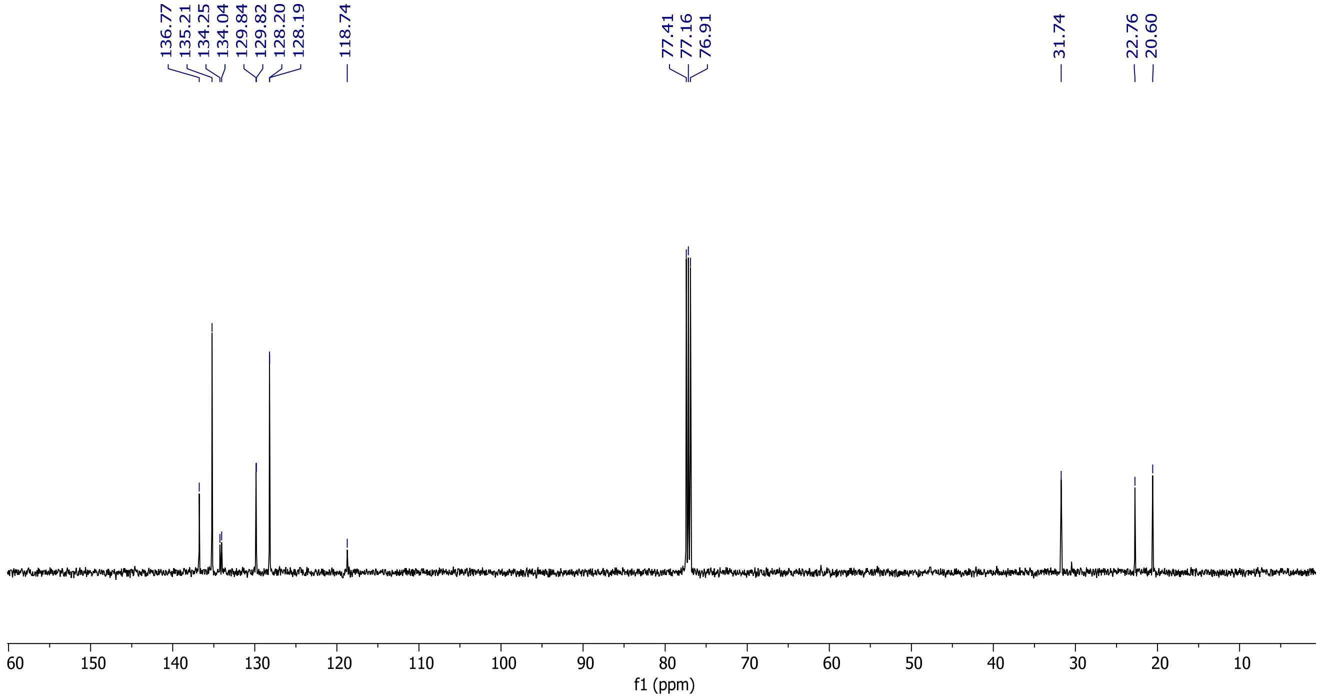


Figure S15 ^{13}C NMR of **S24** (126 MHz, $CDCl_3$, 295K)

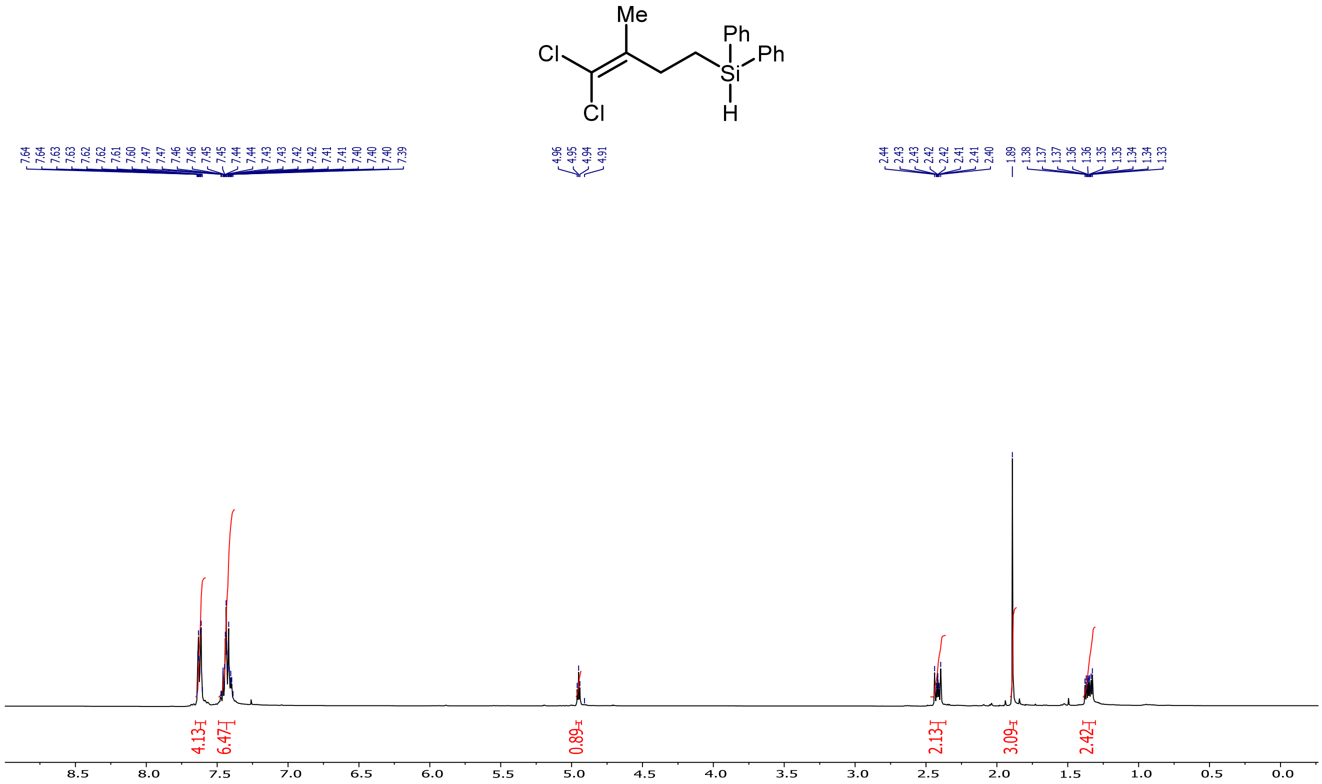


Figure S16 ^{1}H NMR of **S27** (500 MHz, $CDCl_3$, 295K)

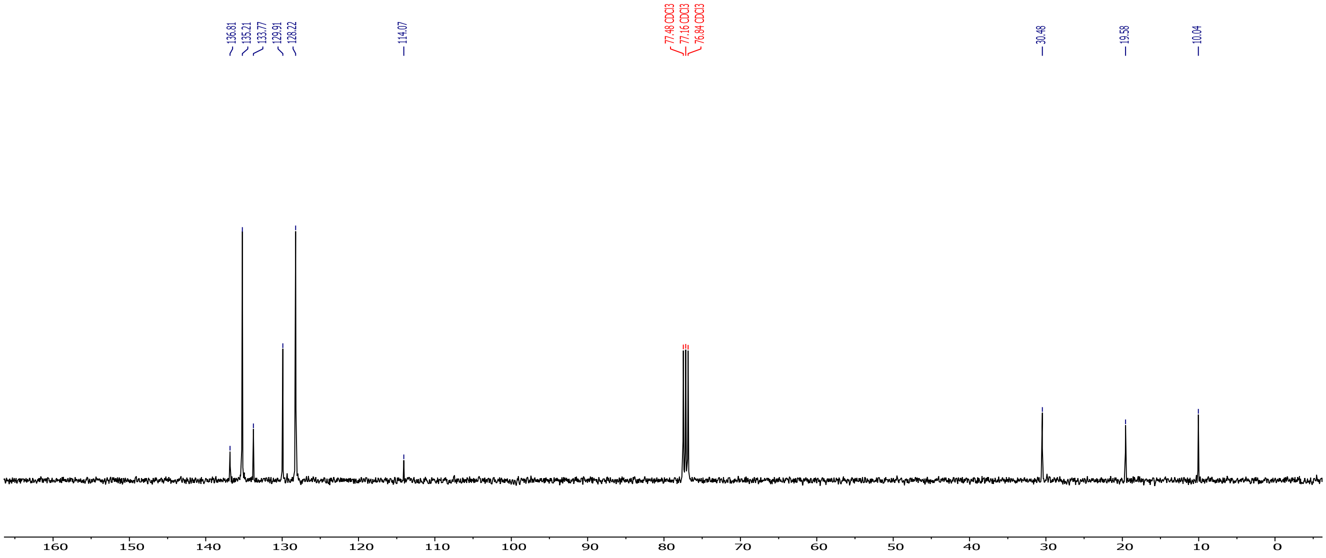
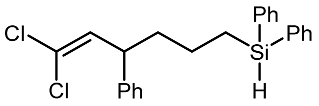


Figure S17 ^{13}C NMR of **S27** (126 MHz, $CDCl_3$, 295K)



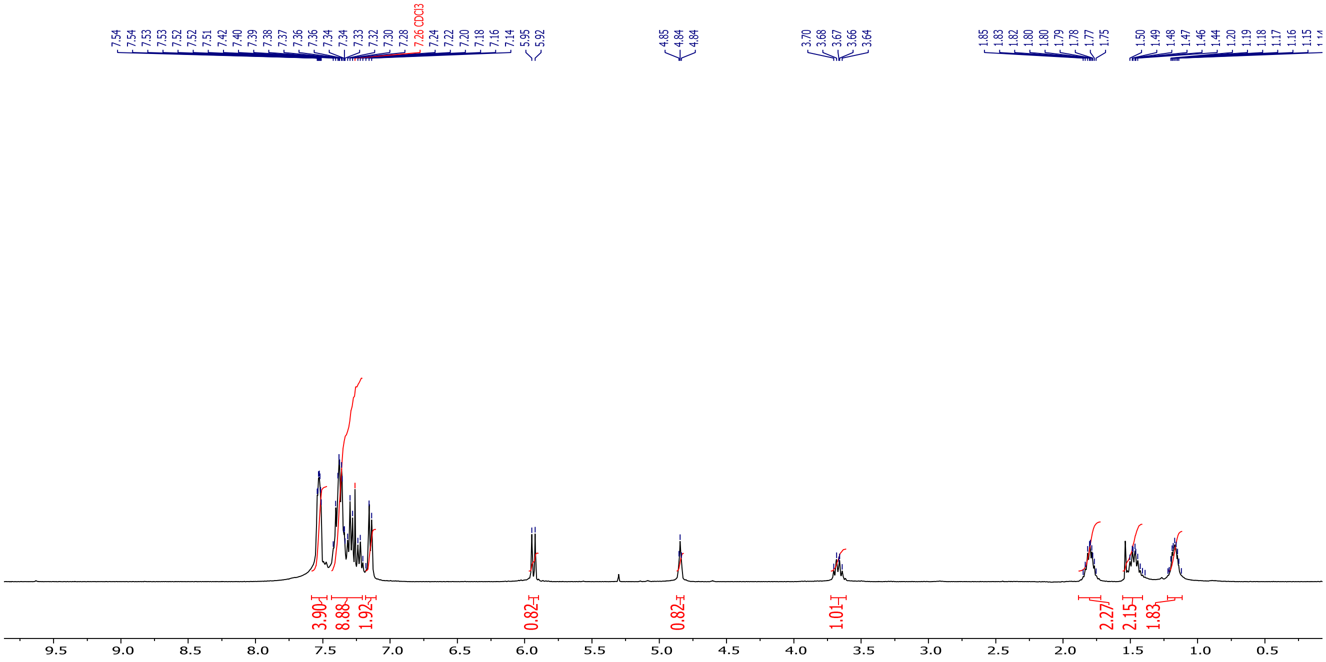


Figure S18 ^{1}H NMR of **S30** (400 MHz, $CDCl_3$, 295K)

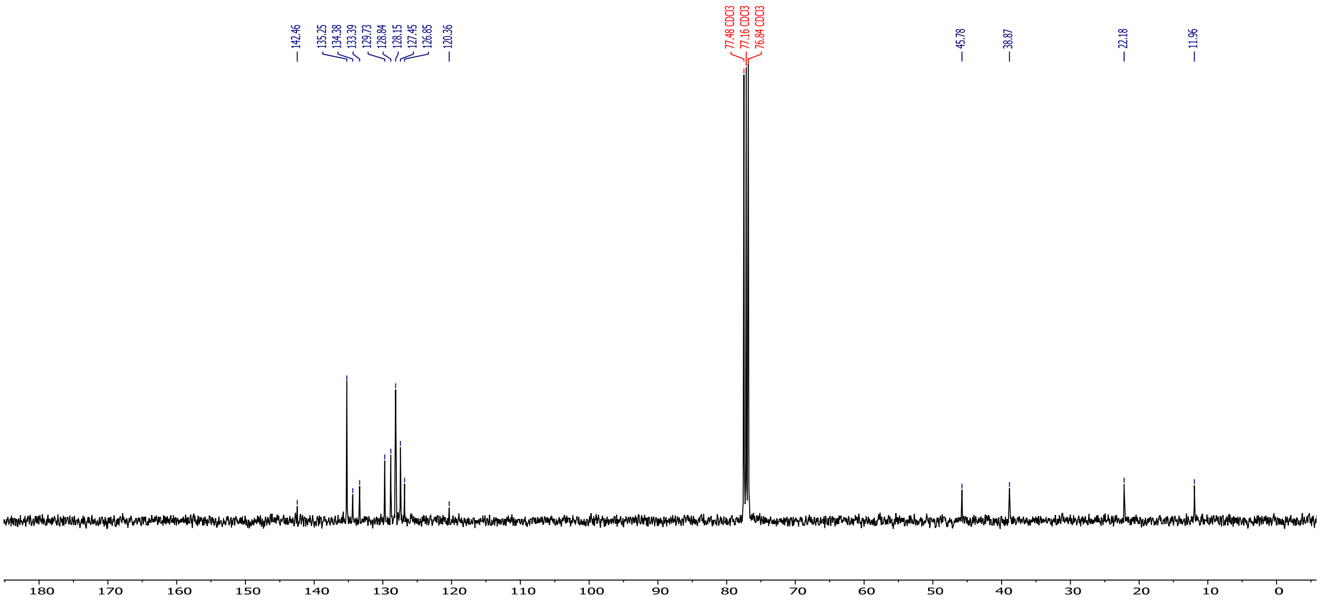


Figure S19 ^{13}C NMR of **S30** (101 MHz, $CDCl_3$, 295K)

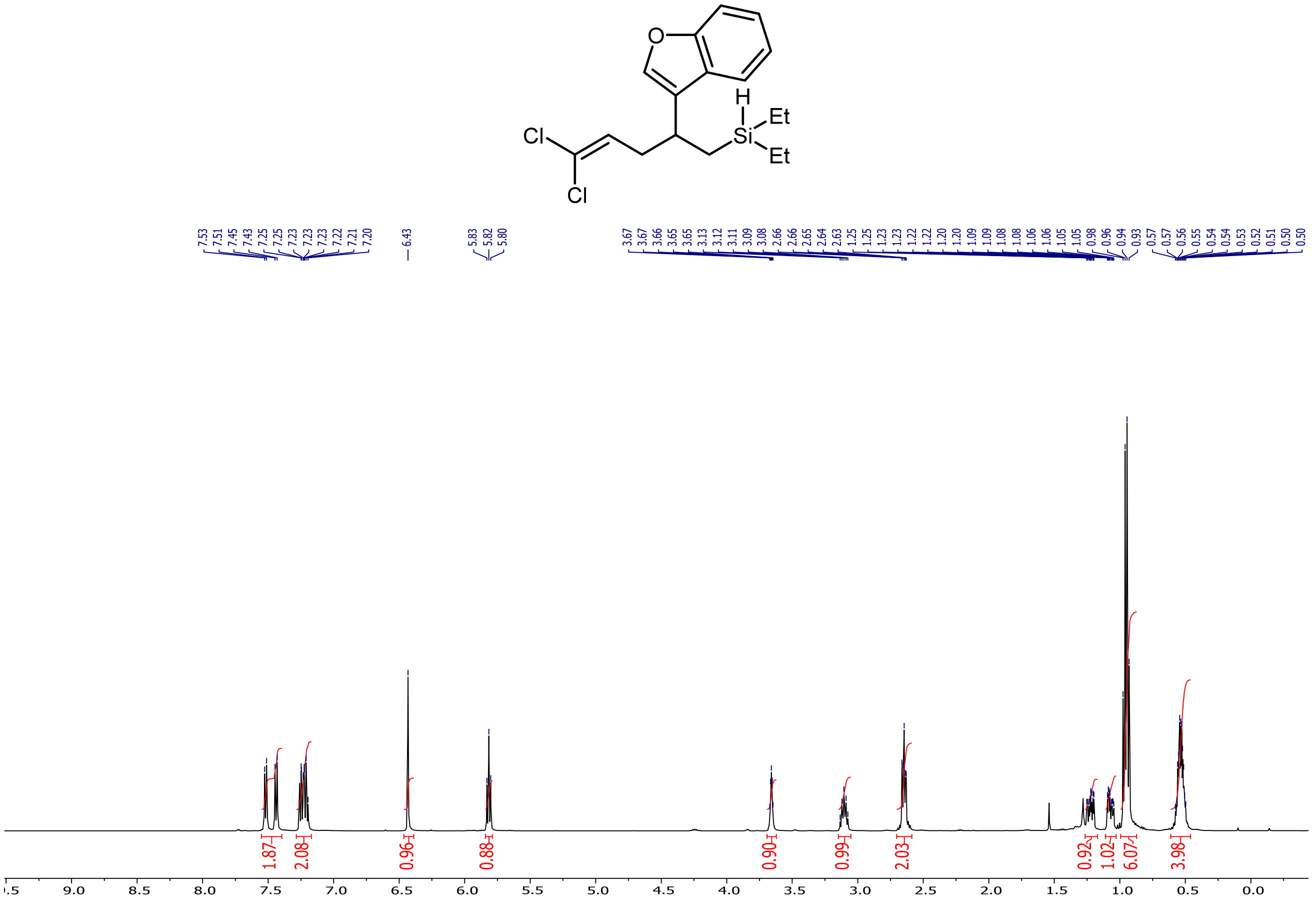


Figure S20 ^{1}H NMR of **S34** (500 MHz, CDCl$_3$, 295K)

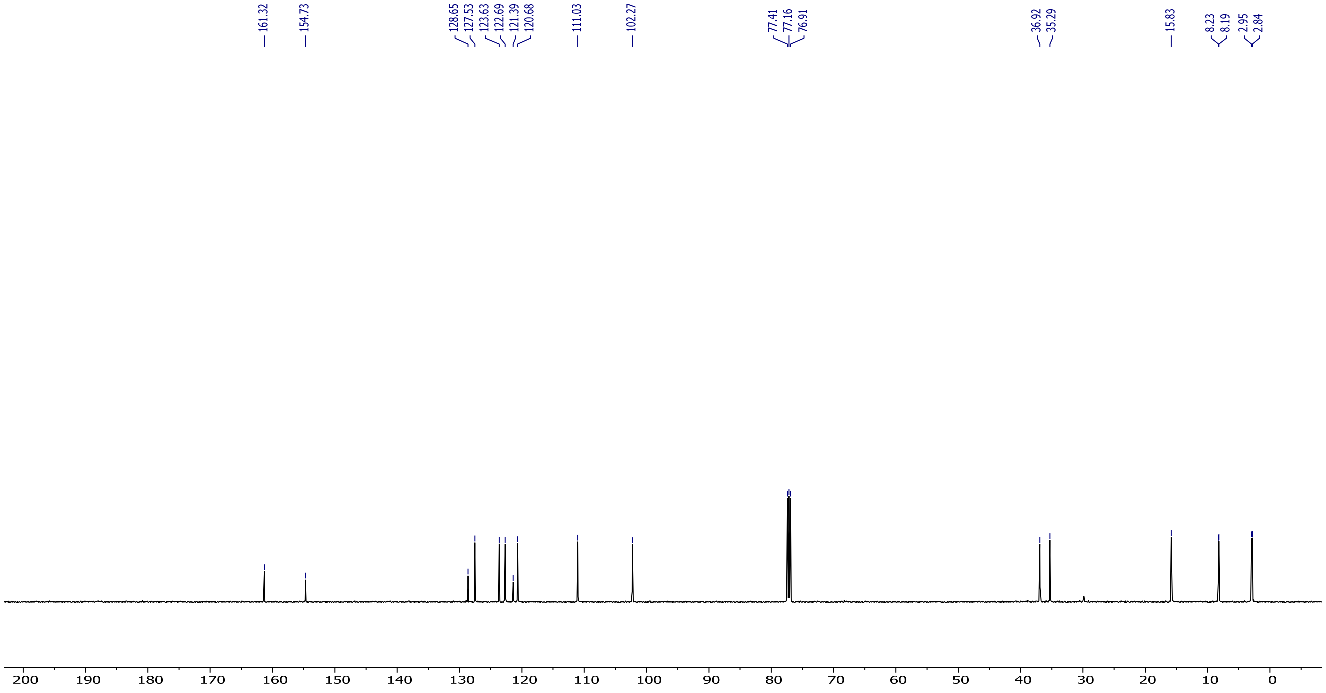
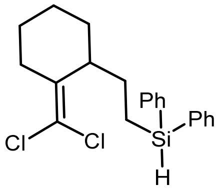


Figure S21 ^{13}C NMR of **S34** (126 MHz, CDCl$_3$, 295K)



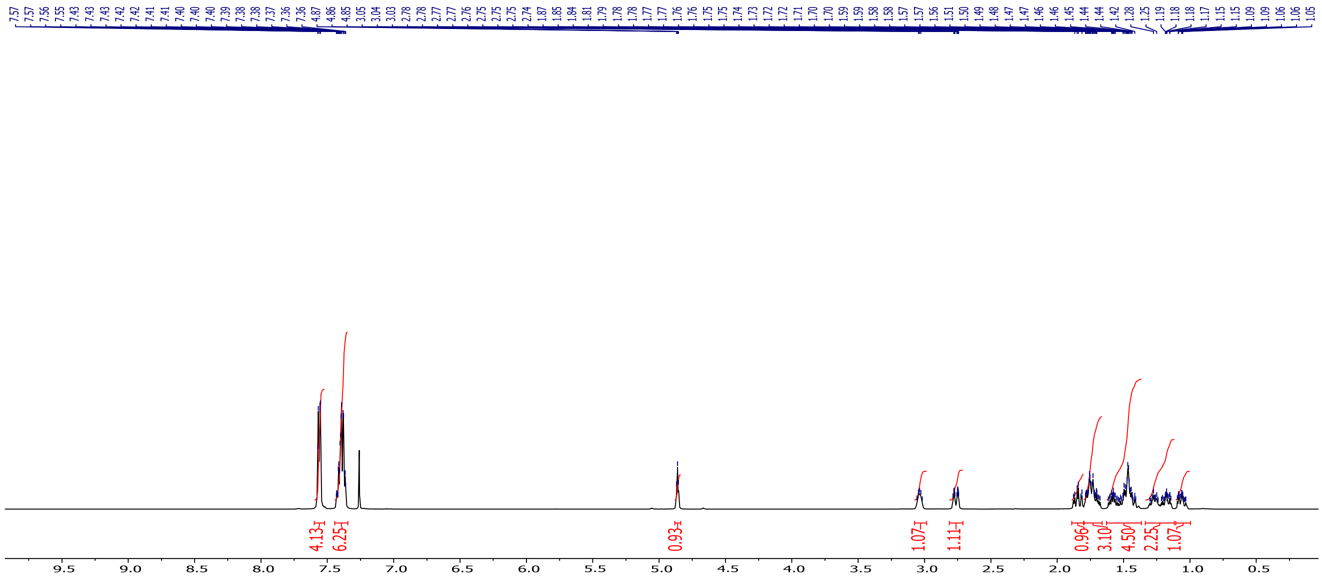


Figure S22 ^{1}H NMR of **S37** (500 MHz, $CDCl_3$, 295K)

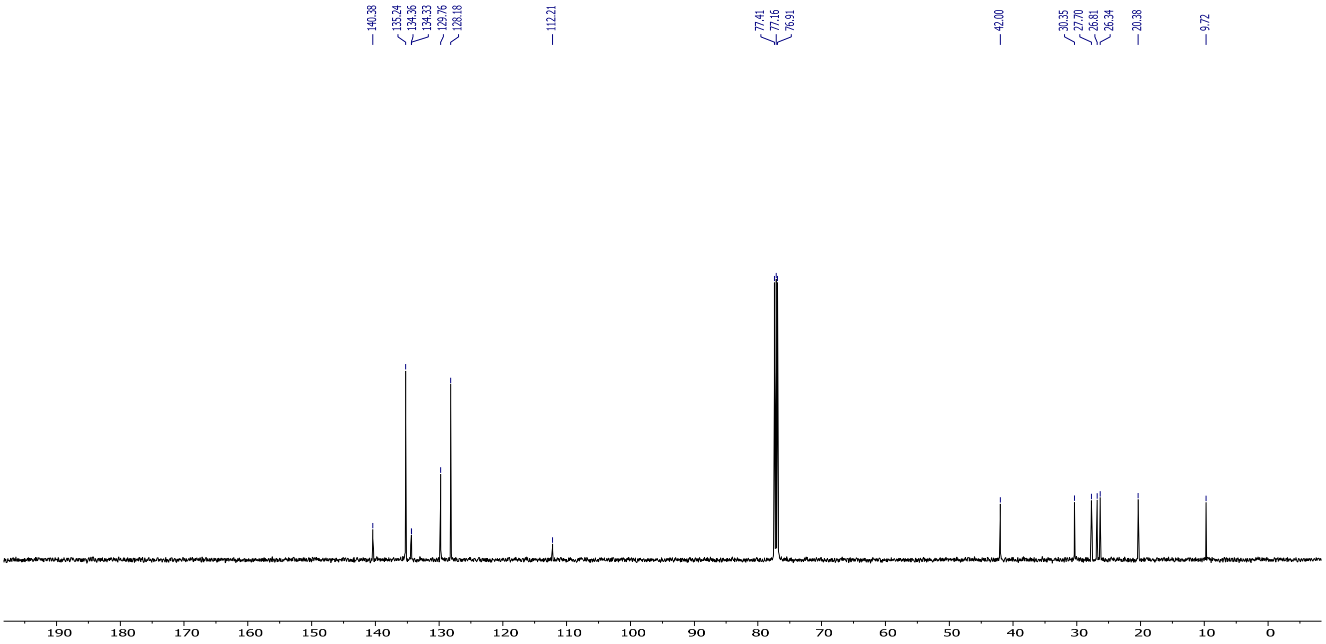
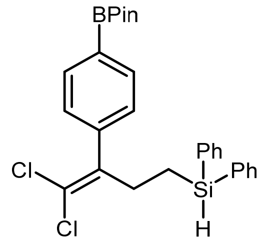


Figure S23 ^{13}C NMR of **S37** (126 MHz, $CDCl_3$, 295K)



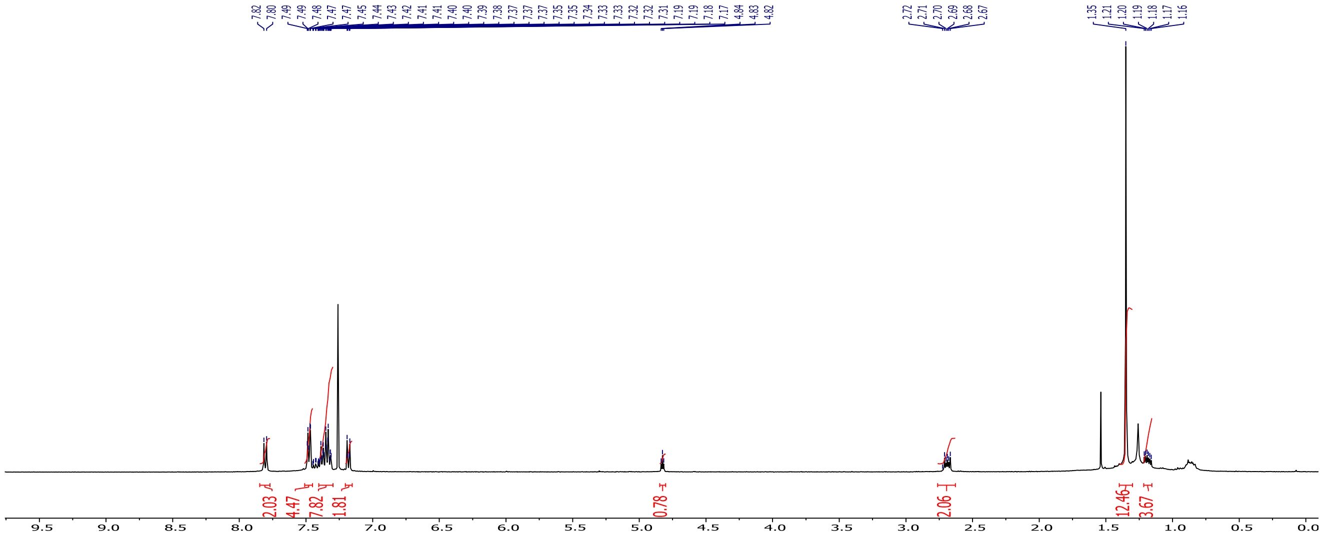


Figure S24 ^{1}H NMR of **S40** (400 MHz, $CDCl_3$, 295K)

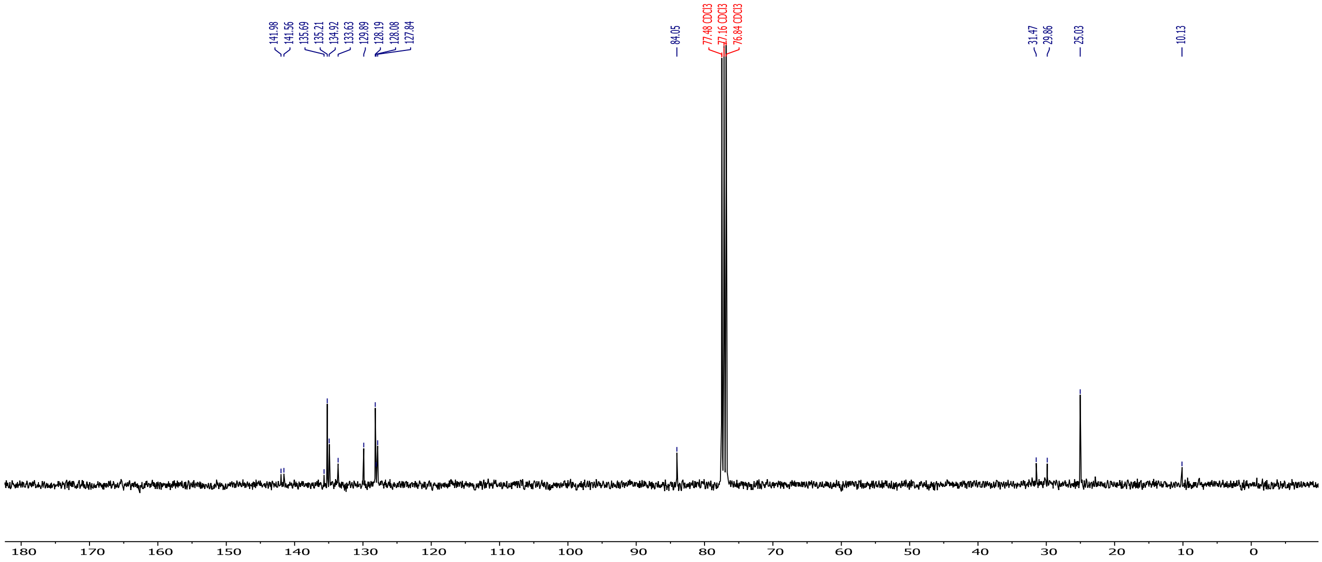
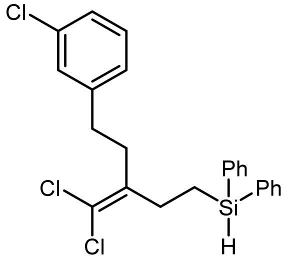


Figure S25 ^{1}H NMR of **S40** (101 MHz, $CDCl_3$, 295K)



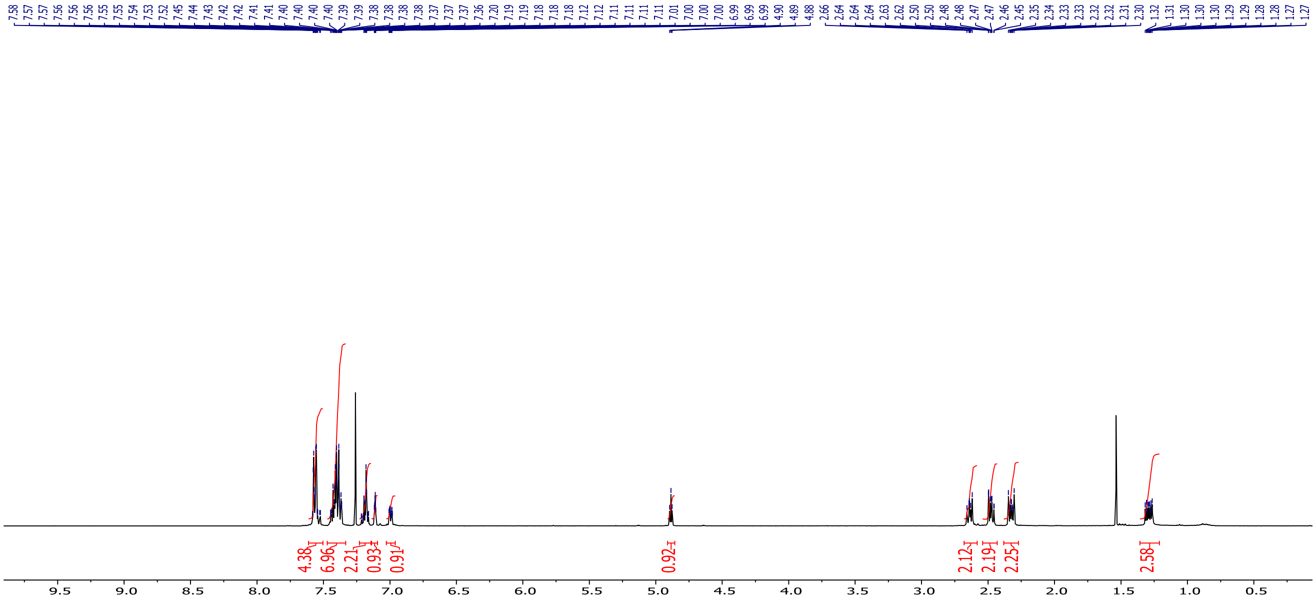


Figure S26 ^{1}H NMR of **S43** (400 MHz, CDCl$_3$, 295K)

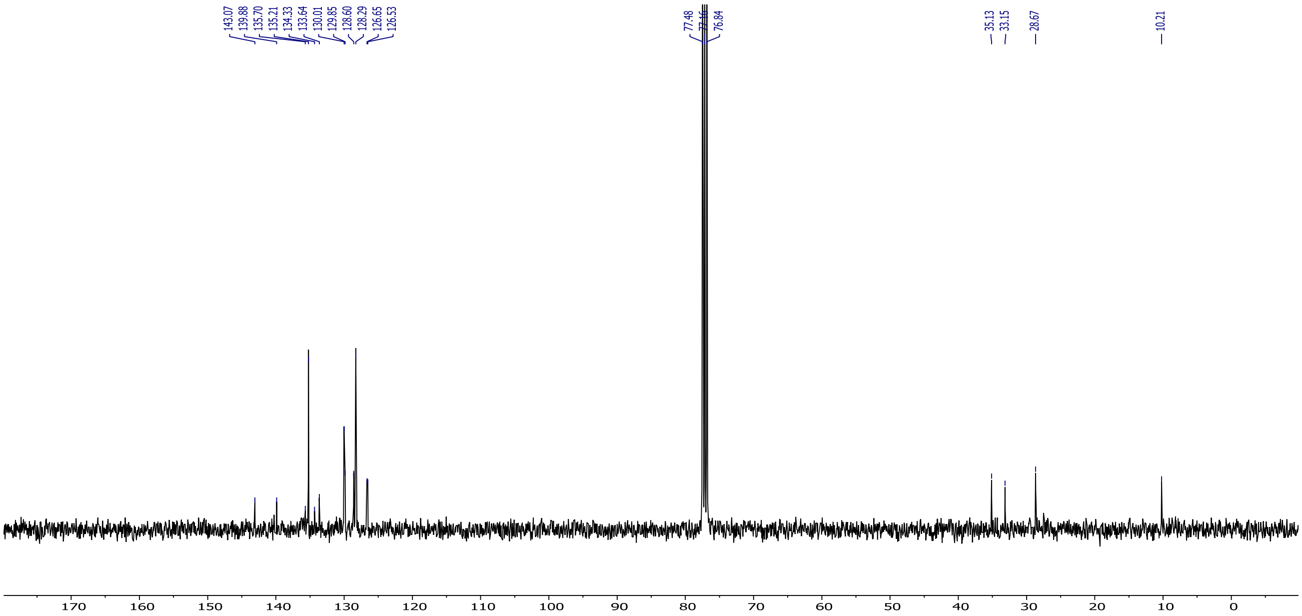
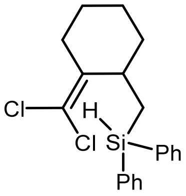


Figure S27 ^{13}C NMR of **S43** (101 MHz, CDCl$_3$, 295K)



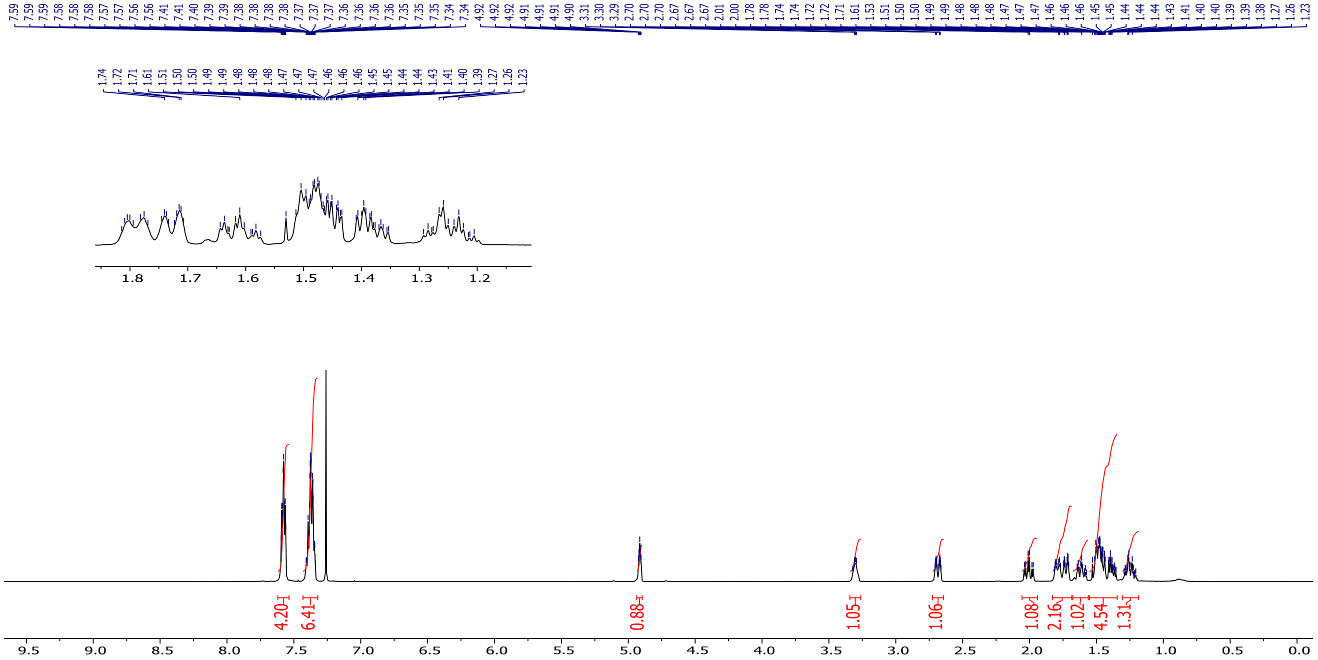


Figure S28 ^{1}H NMR of **S46** (500 MHz, $CDCl_3$, 295K)

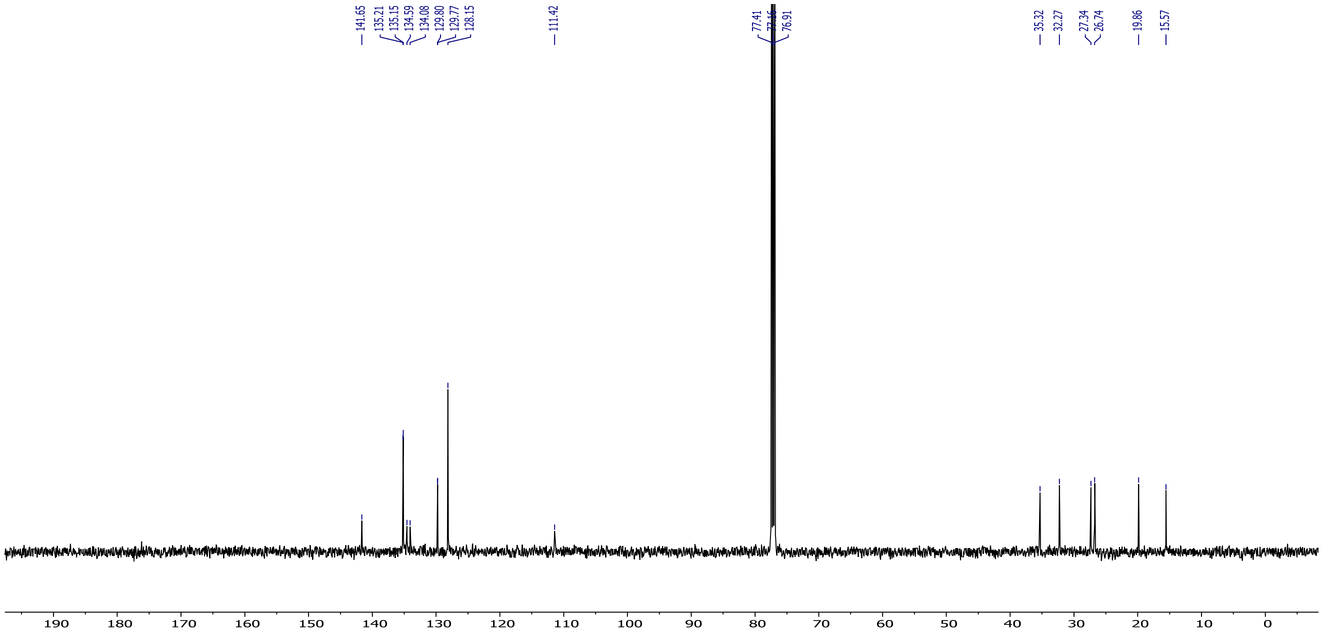
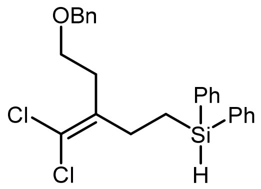


Figure S29 ^{13}C NMR of **S46** (125 MHz, $CDCl_3$, 295K)



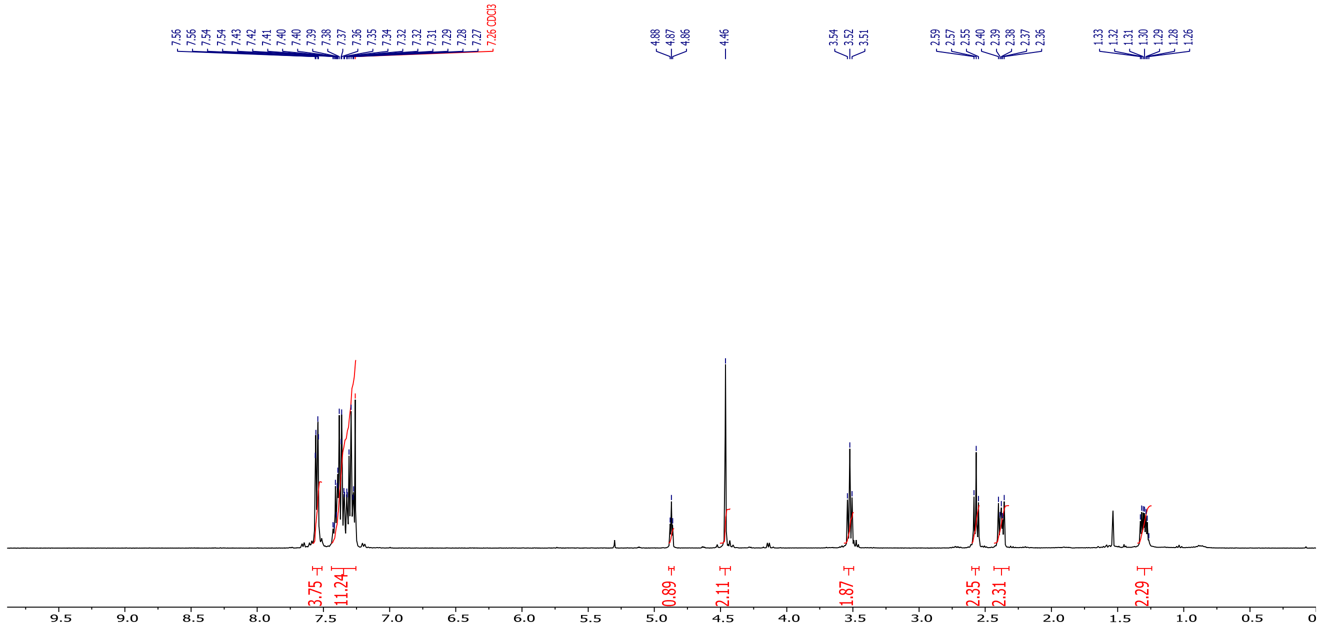


Figure S30 ^{1}H NMR of **S49** (400 MHz, $CDCl_3$, 295K)

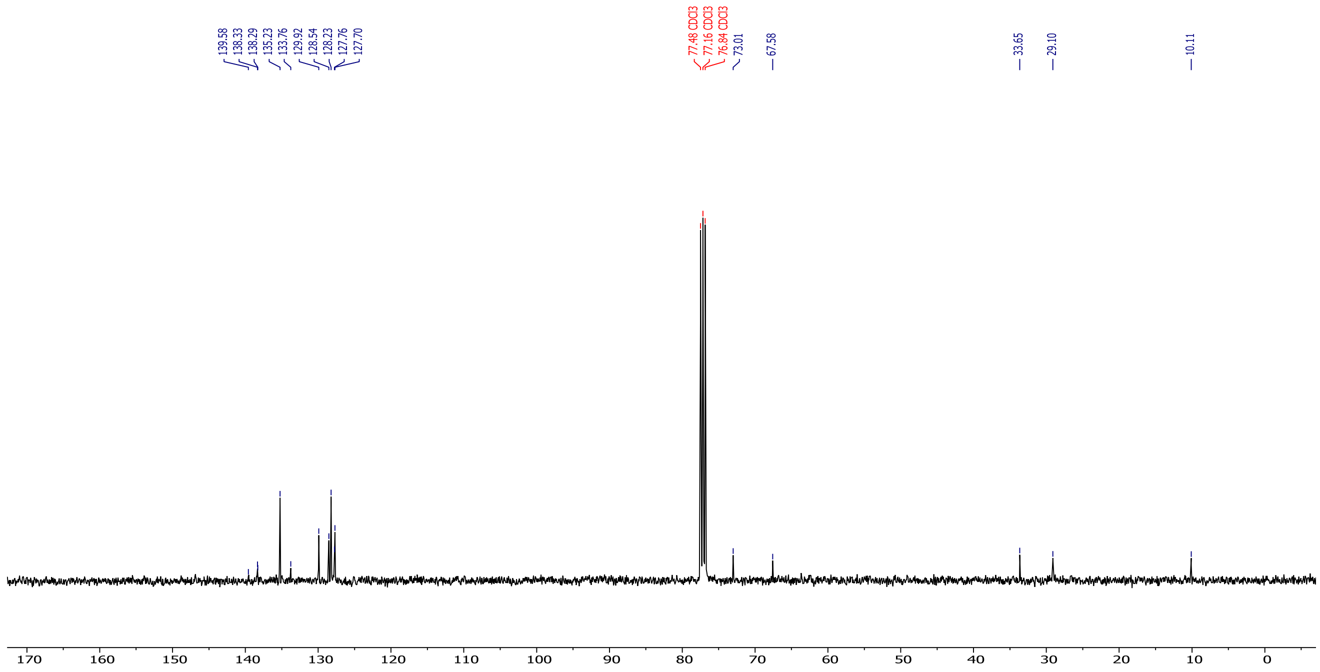
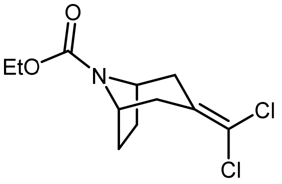


Figure S31 ^{13}C NMR of **S49** (101 MHz, $CDCl_3$, 295K)



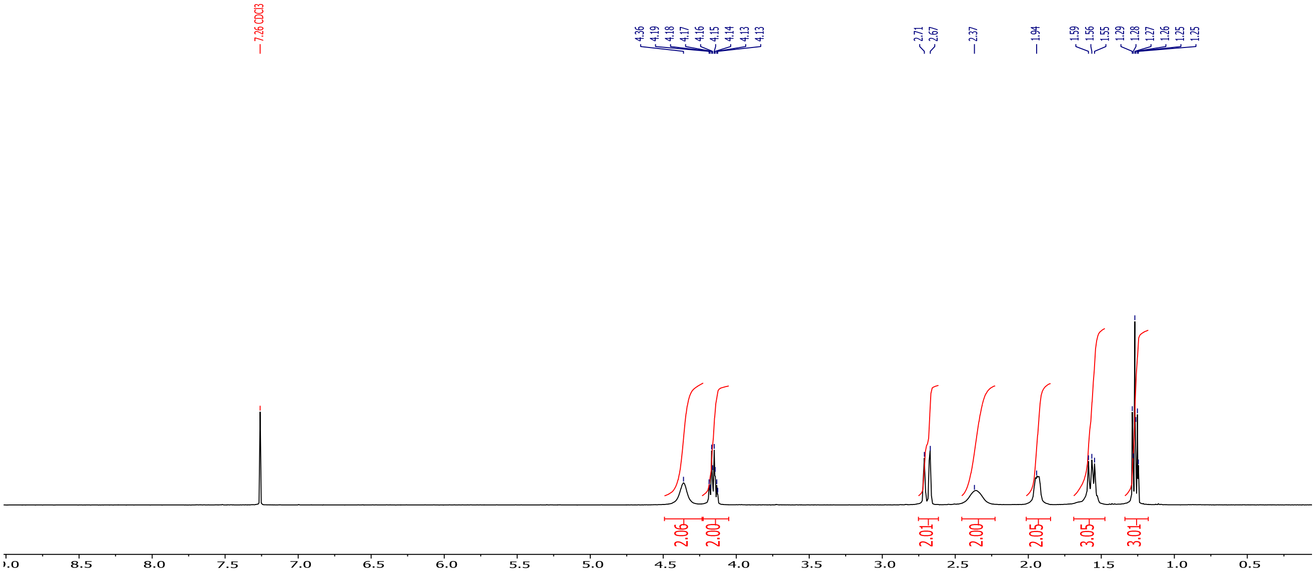


Figure S32 ^{1}H NMR of **S50** (400 MHz, $CDCl_3$, 295K)

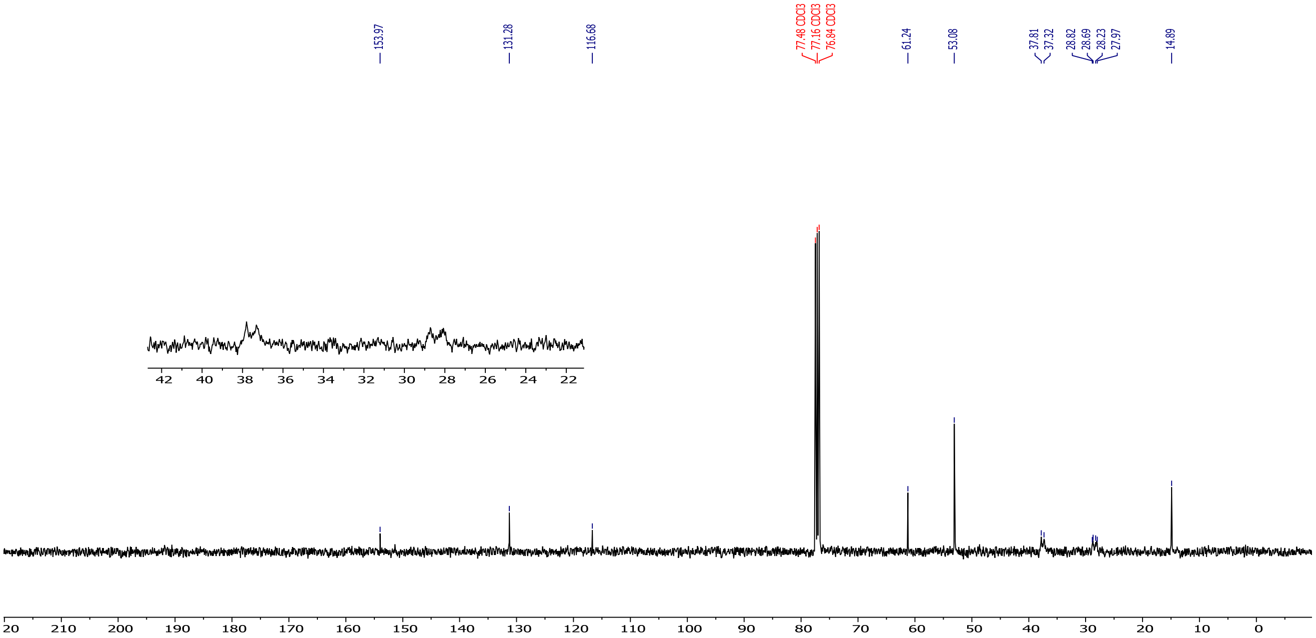


Figure S33 ^{13}C NMR of **S50** (101 MHz, $CDCl_3$, 295K)

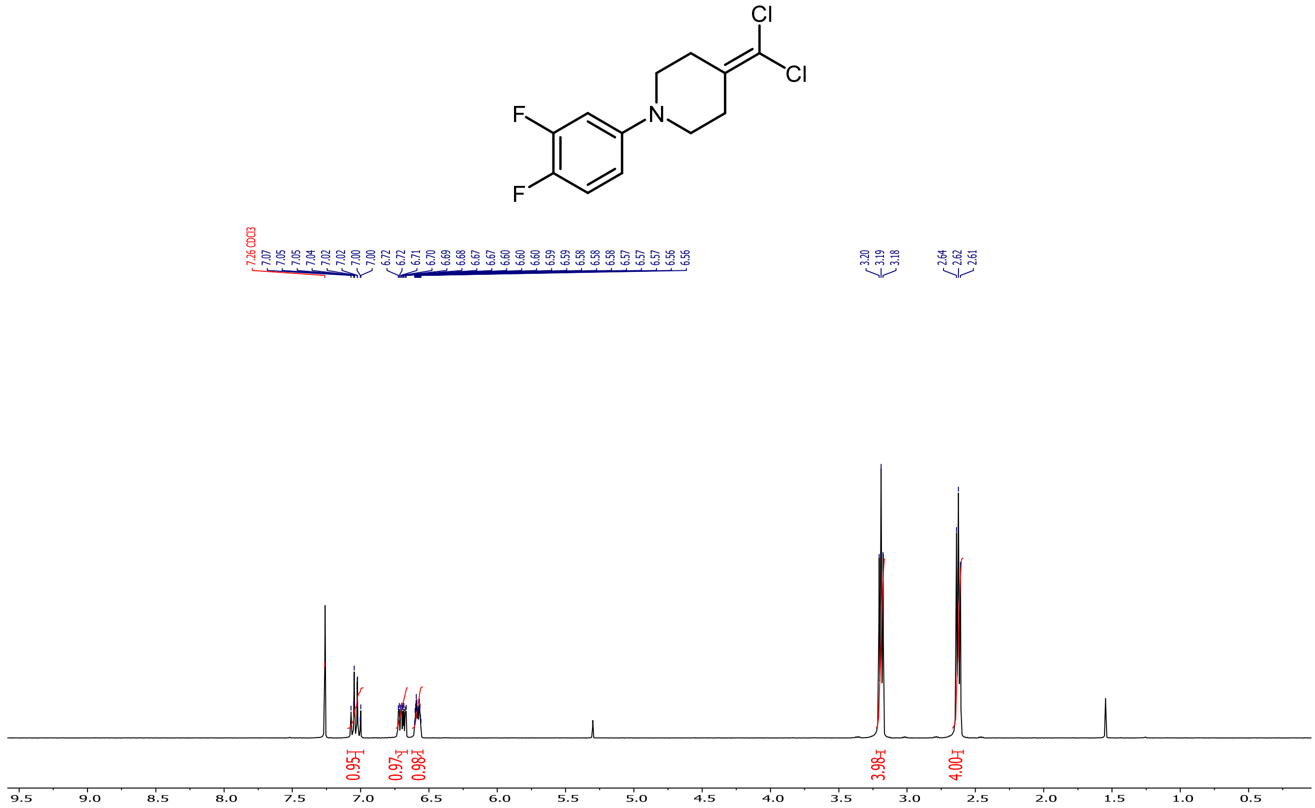


Figure S34 ^{1}H NMR of **S51** (400 MHz, $CDCl_3$, 295K)

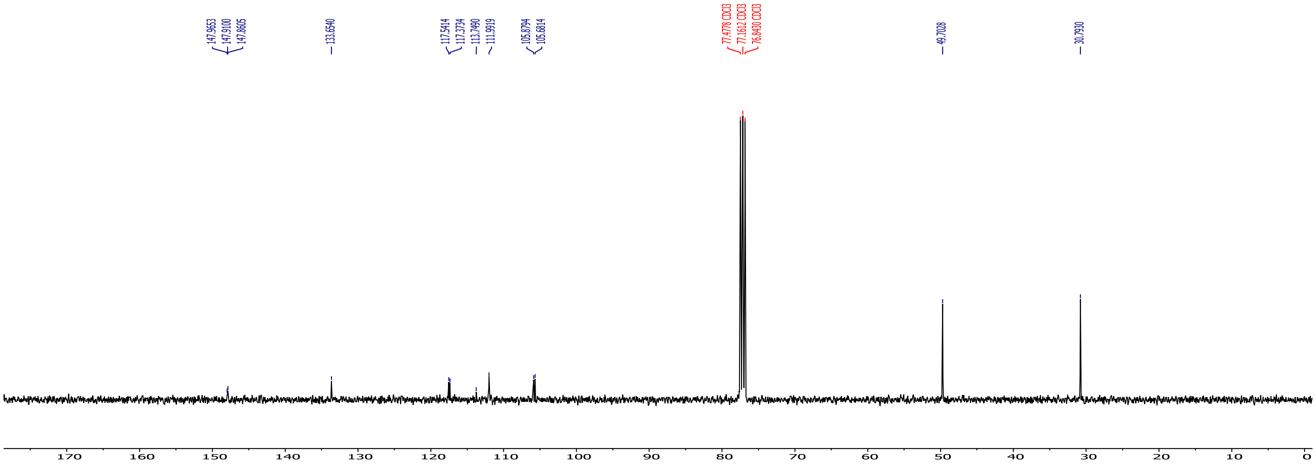


Figure S35 ^{13}C NMR of **S51** (101 MHz, $CDCl_3$, 295K)

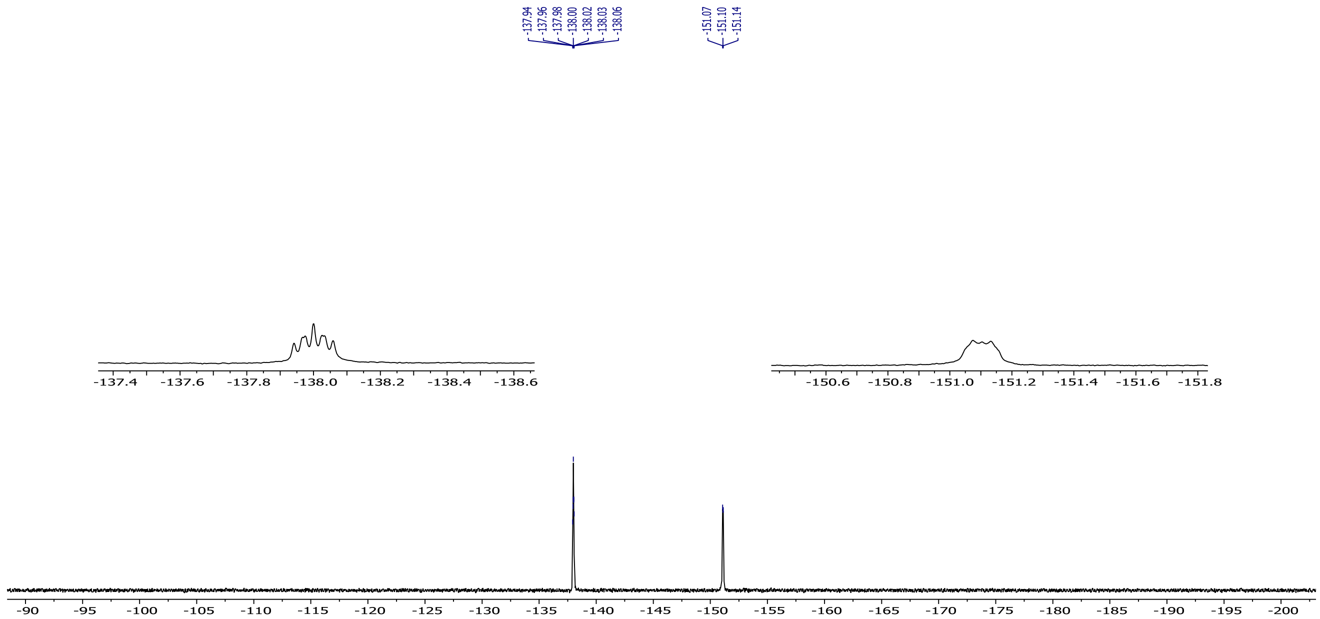
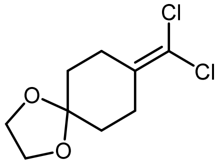


Figure S36 ^{19}F NMR of **S51** (376 MHz, $CDCl_3$, 295K)



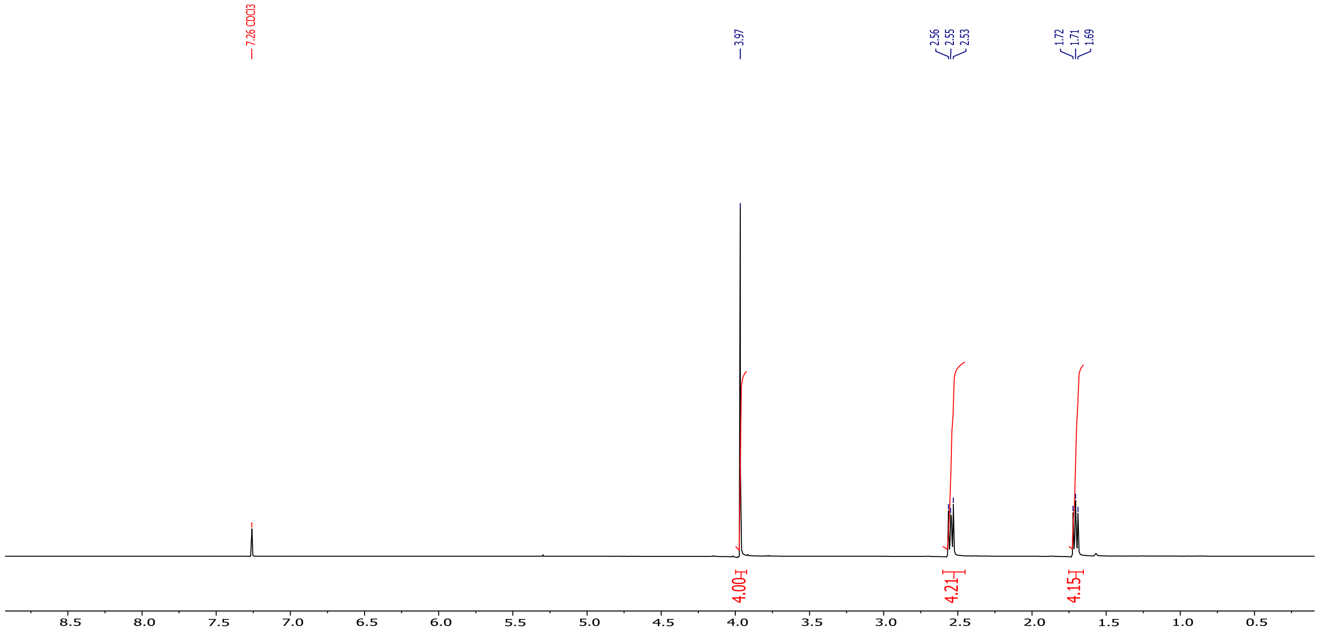


Figure S37 ^{1}H NMR of **S52** (400 MHz, $CDCl_3$, 295K)

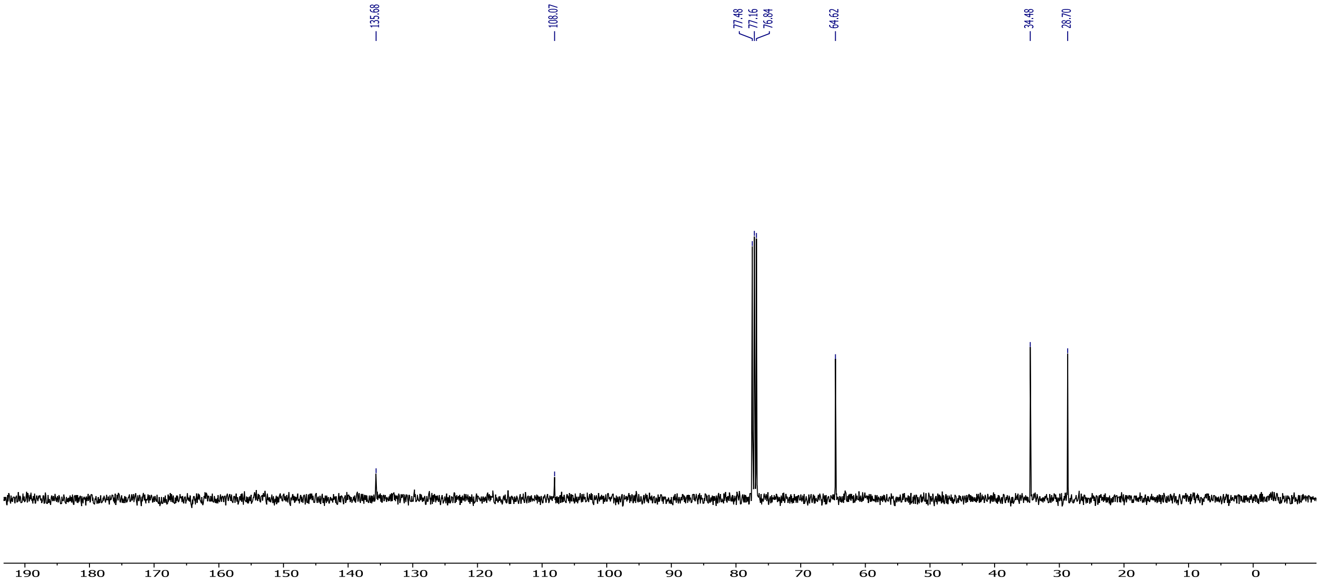
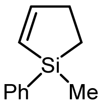


Figure S38 ^{13}C NMR of **S52** (101 MHz, $CDCl_3$, 295K)

9. NMR Data for the Si–H insertion Products



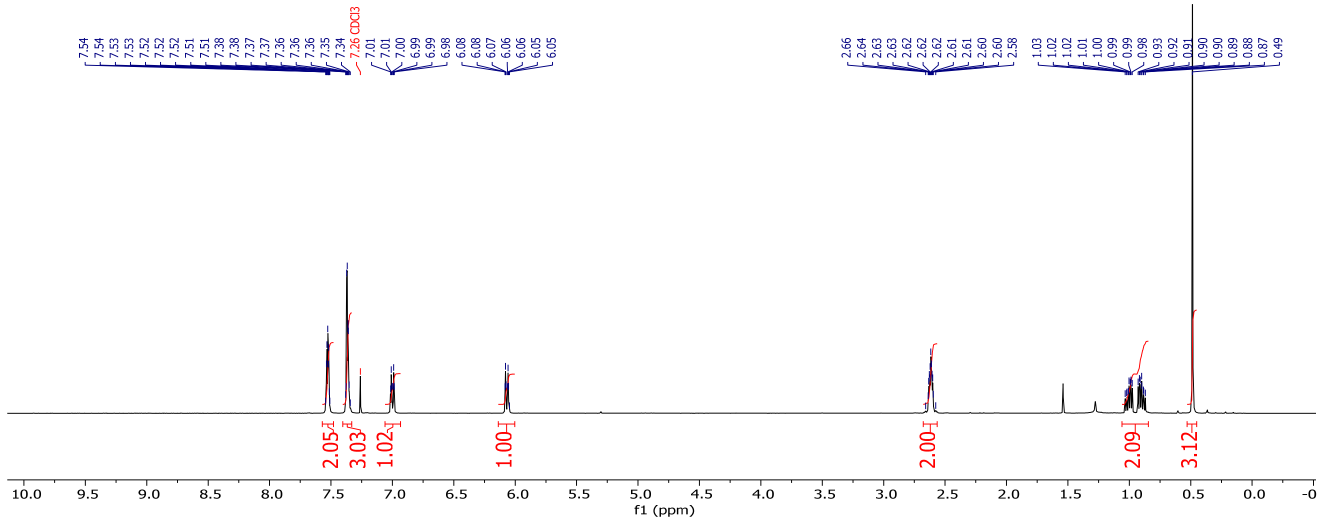


Figure S39 ^{1}H NMR of **9** (500 MHz, CDCl$_3$, 295K)

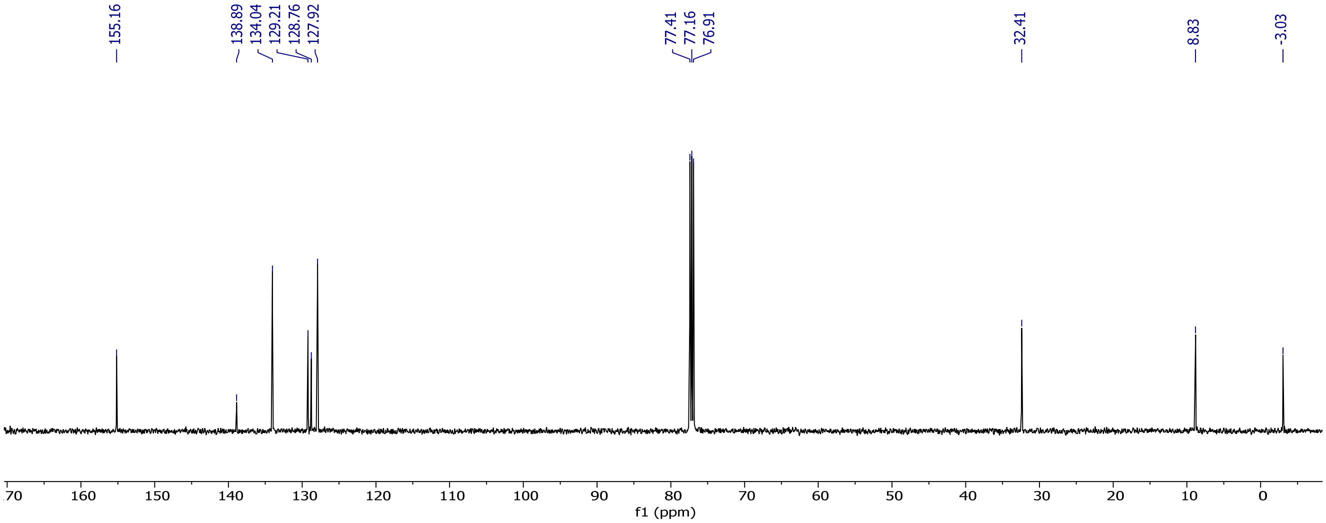
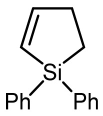


Figure S40 ^{13}C NMR of **9** (126 MHz, CDCl$_3$, 295K)



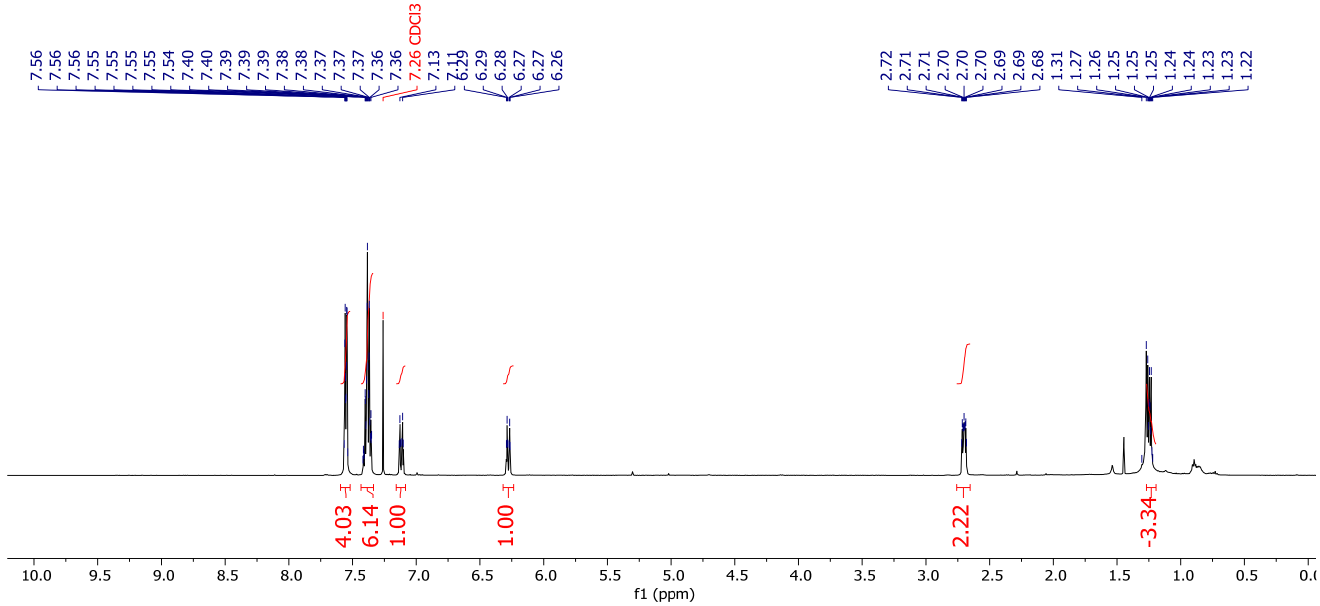


Figure S41 ^{1}H NMR of **10** (500 MHz, $CDCl_3$, 295K)

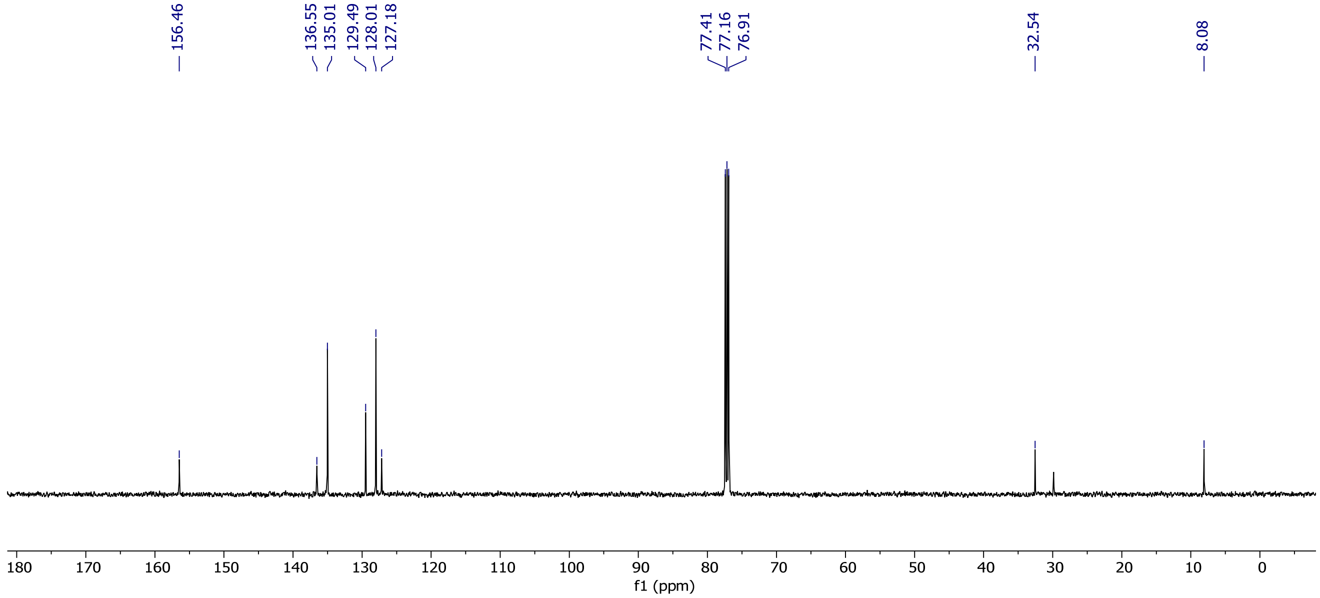


Figure S42 ^{13}C NMR of **10** (126 MHz, $CDCl_3$, 295K)

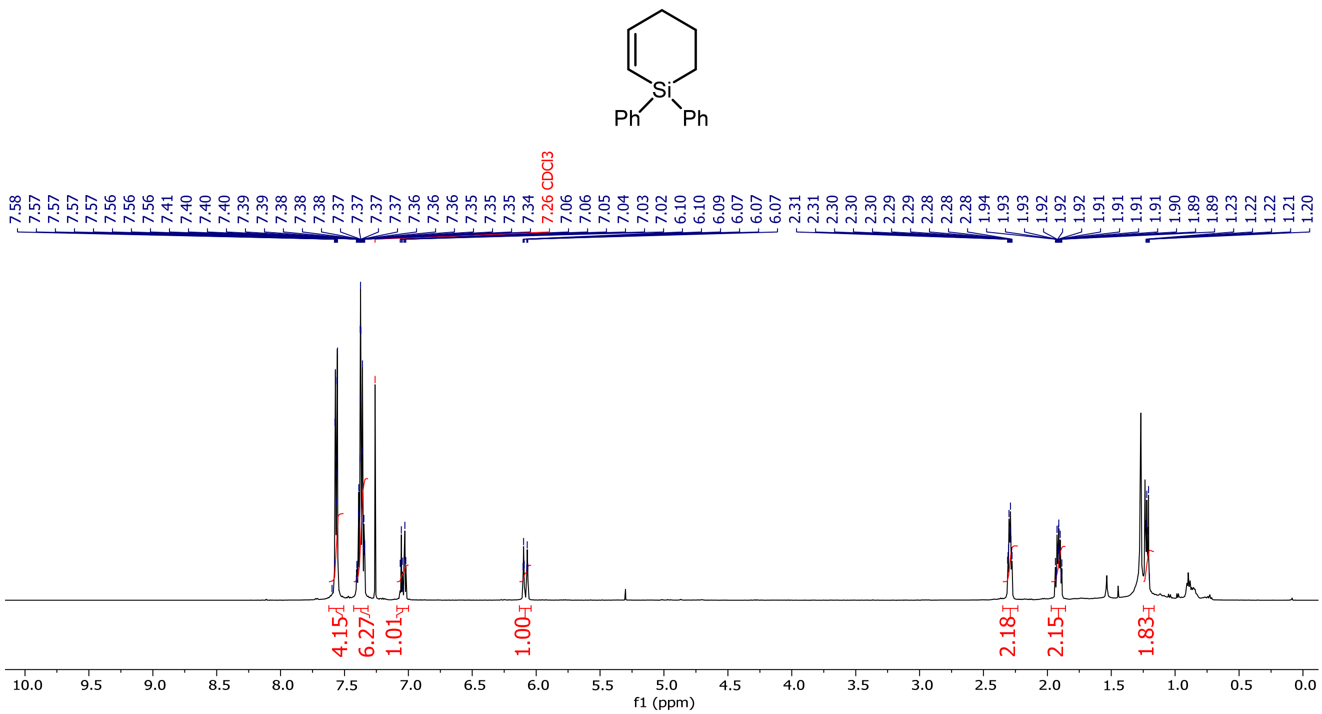


Figure S43 ^{1}H NMR of **2** (500 MHz, $CDCl_3$, 295K)

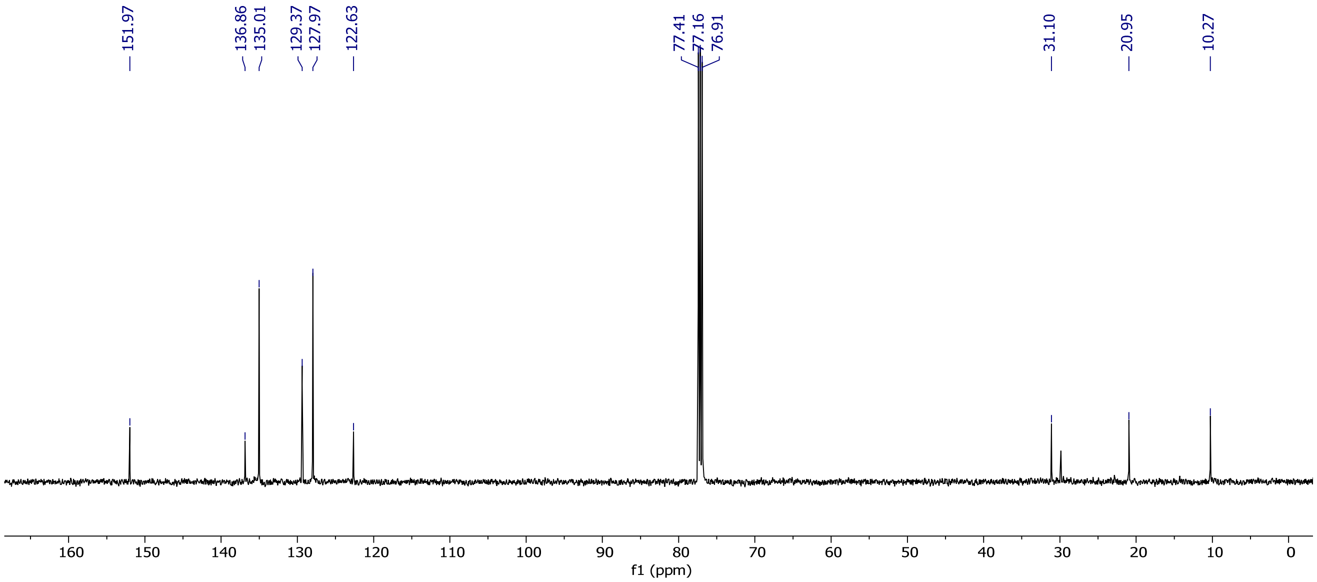
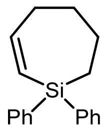


Figure S44 ^{13}C NMR of **2** (126 MHz, $CDCl_3$, 295K)



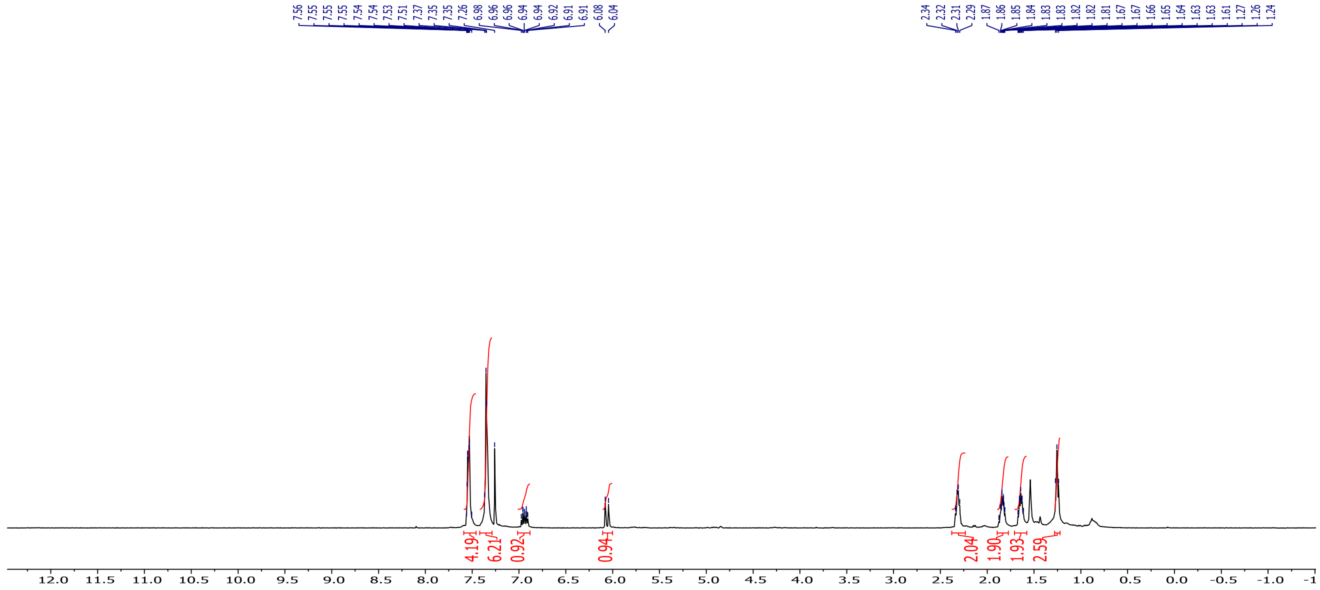


Figure S45 ^{1}H NMR of **11** (400 MHz, CDCl$_3$, 295K)

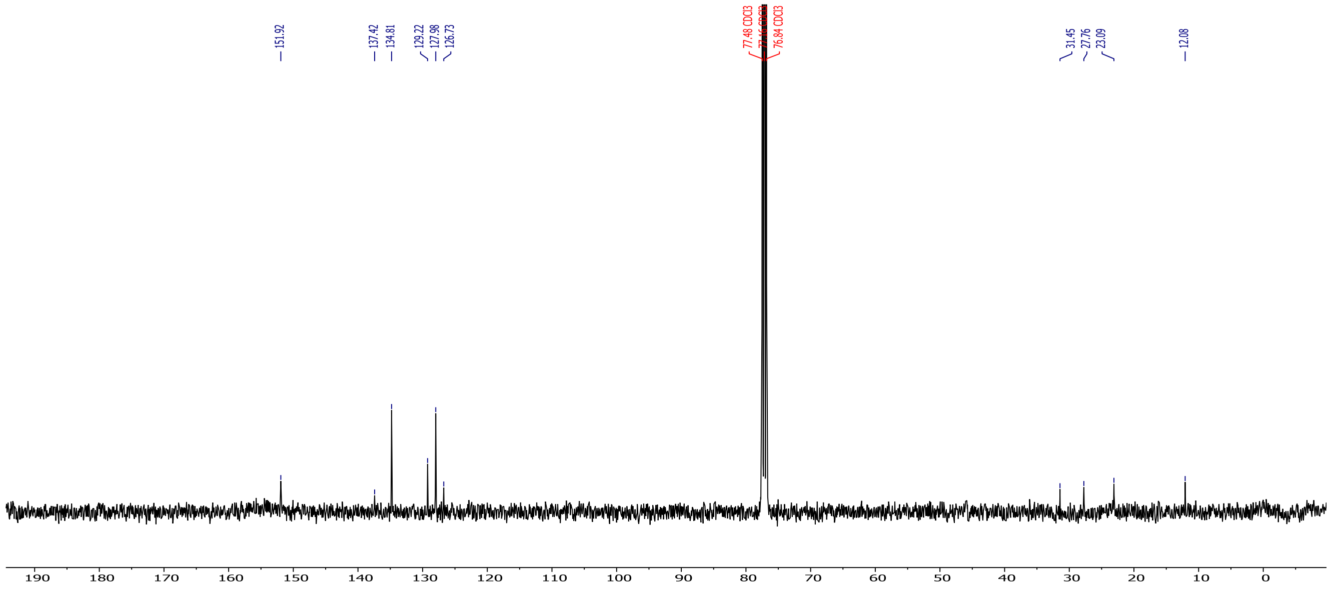
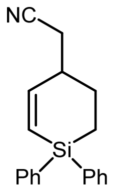


Figure S46 ^{13}C NMR of **11** (126 MHz, CDCl$_3$, 295K)



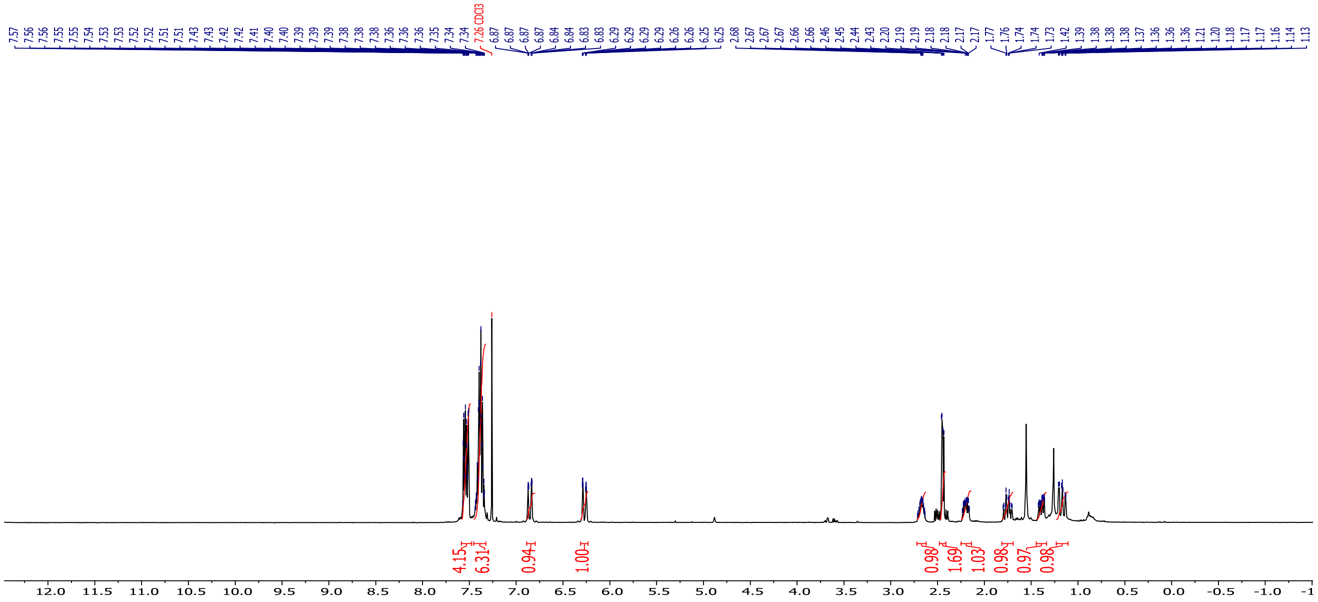


Figure S47 ^{1}H NMR of **12** (400 MHz, CDCl$_3$, 295K)

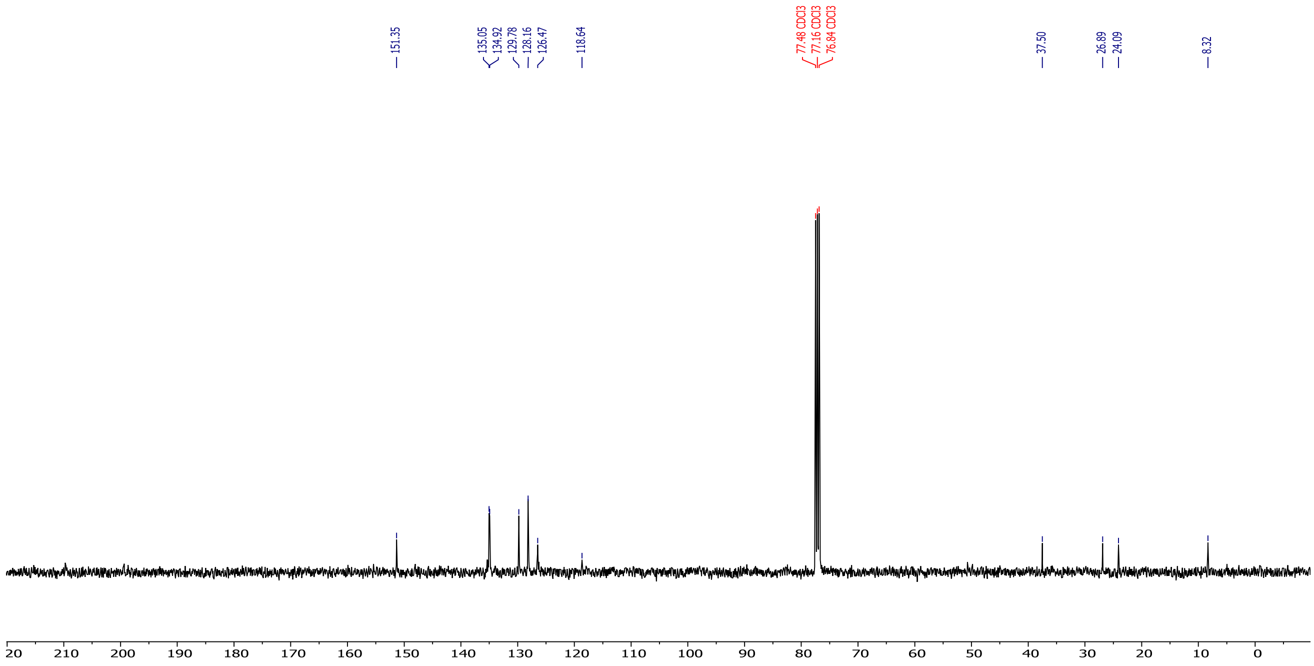
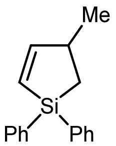


Figure S48 ^{13}C NMR of **12** (101 MHz, CDCl$_3$, 295K)



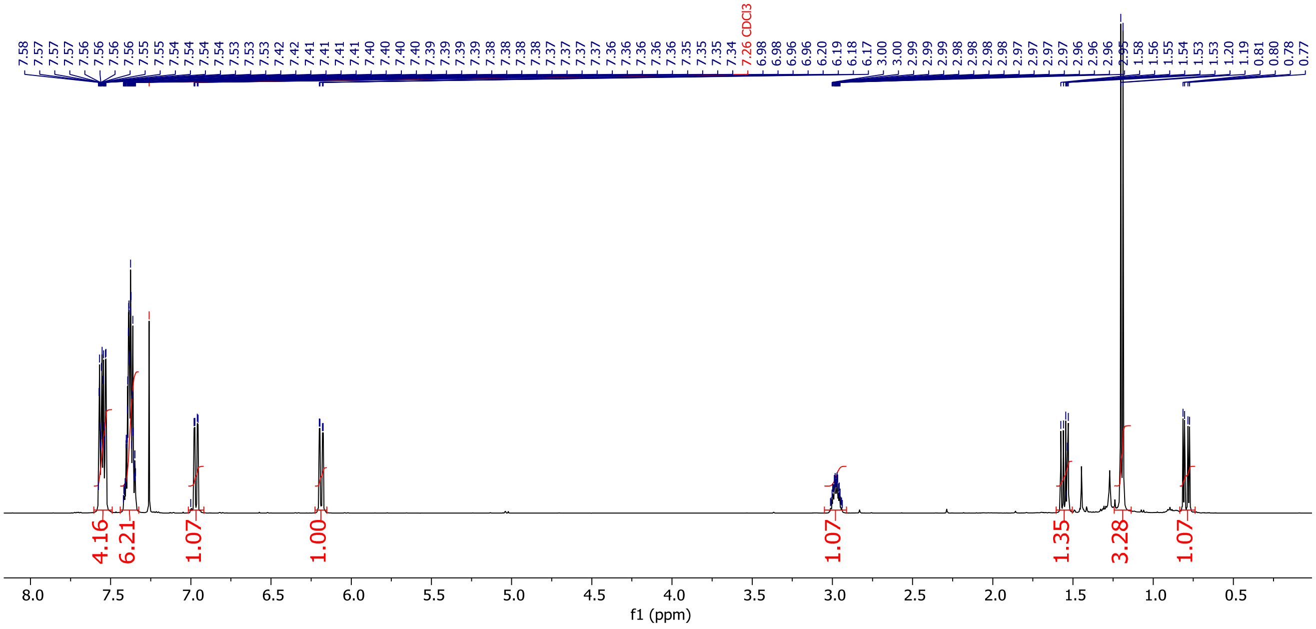


Figure S49 ^{1}H NMR of **13** (500 MHz, CDCl$_3$, 295K)

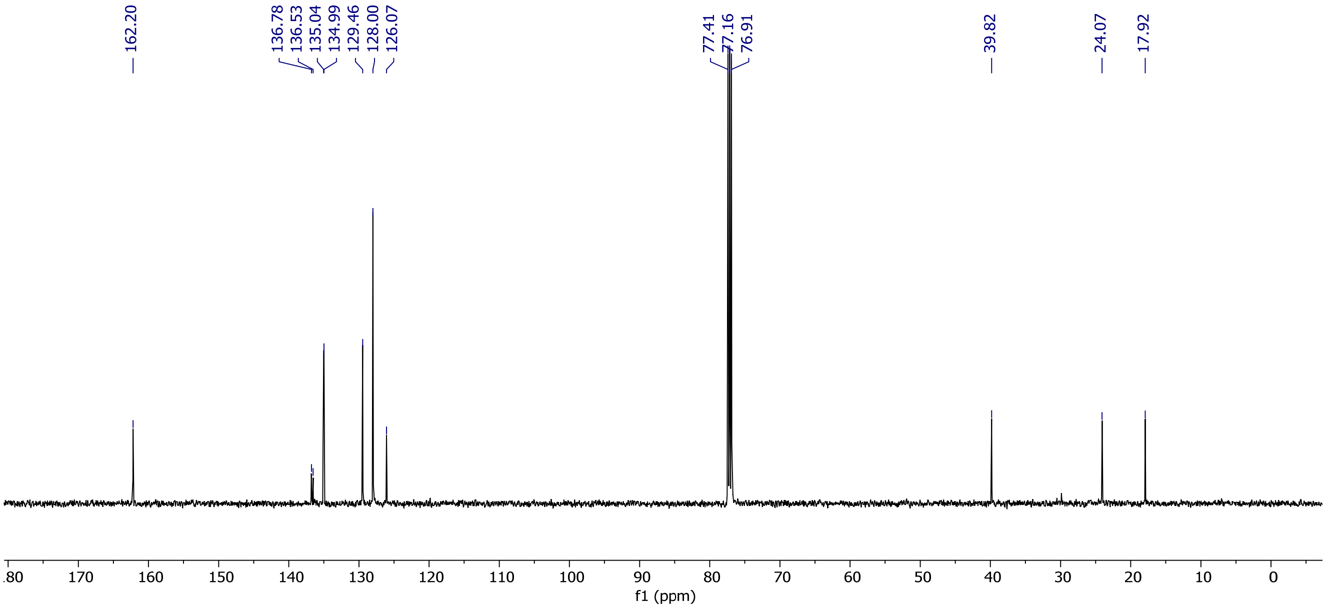


Figure S50 ^{13}C NMR of **13** (101 MHz, CDCl$_3$, 295K)

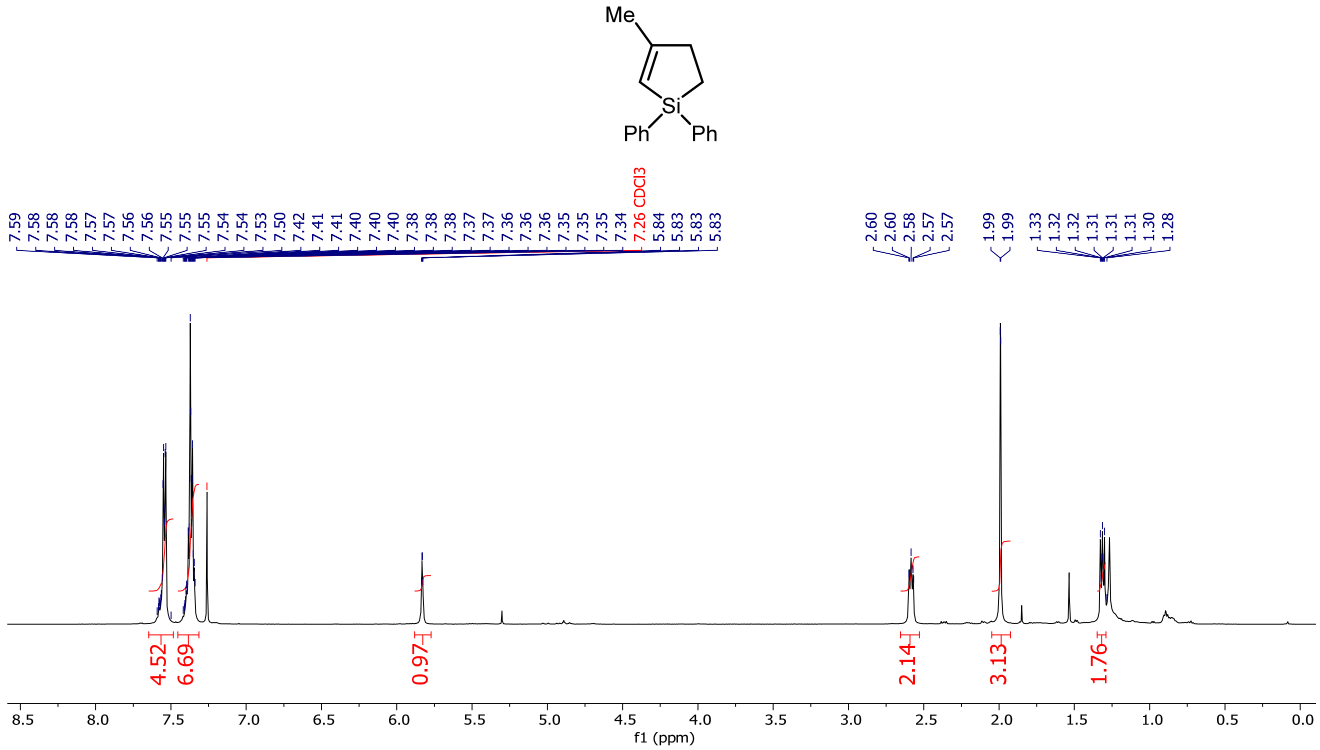


Figure S51 ^{1}H NMR of **14** (500 MHz, CDCl$_3$, 295K)

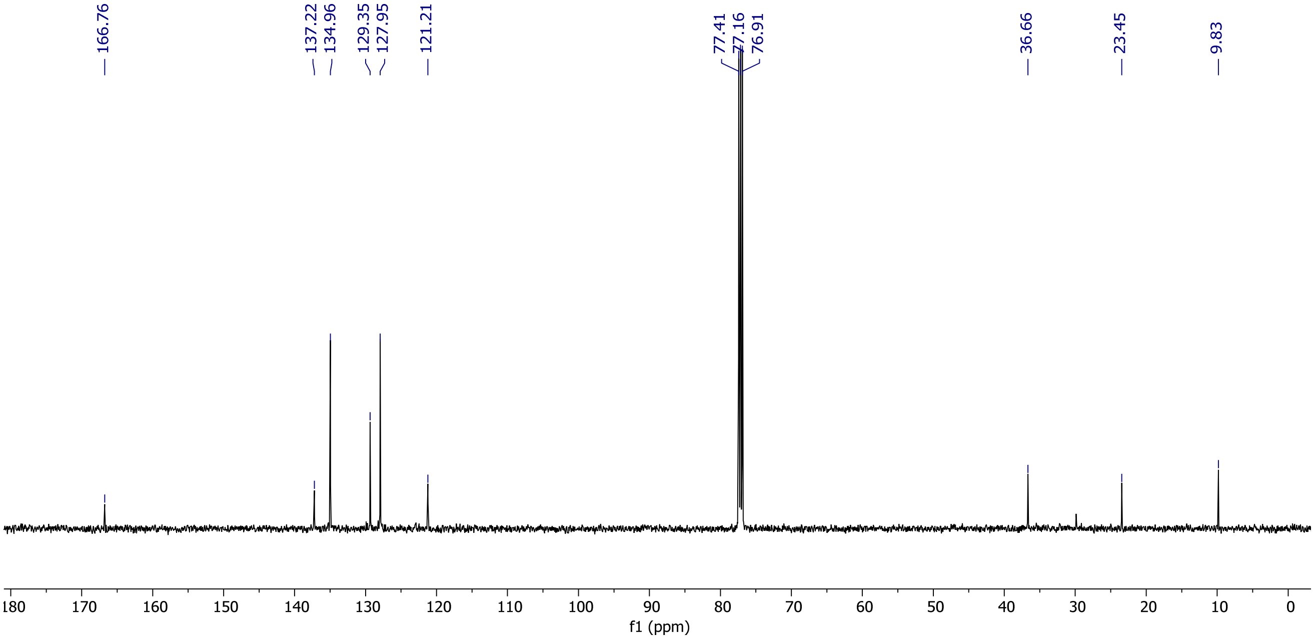


Figure S52 ^{13}C NMR of **14** (126 MHz, CDCl$_3$, 295K)

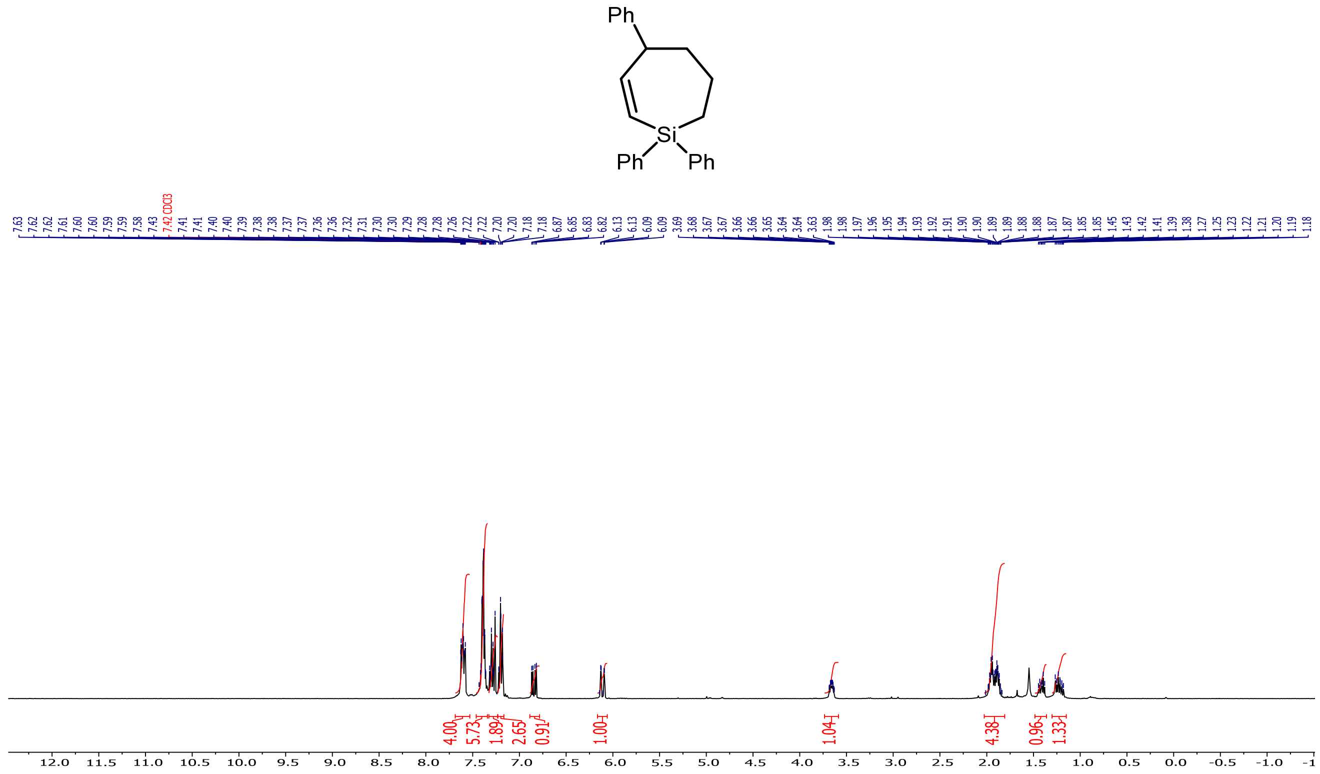


Figure S53 ^{1}H NMR of **15** (400 MHz, CDCl$_3$, 295K)

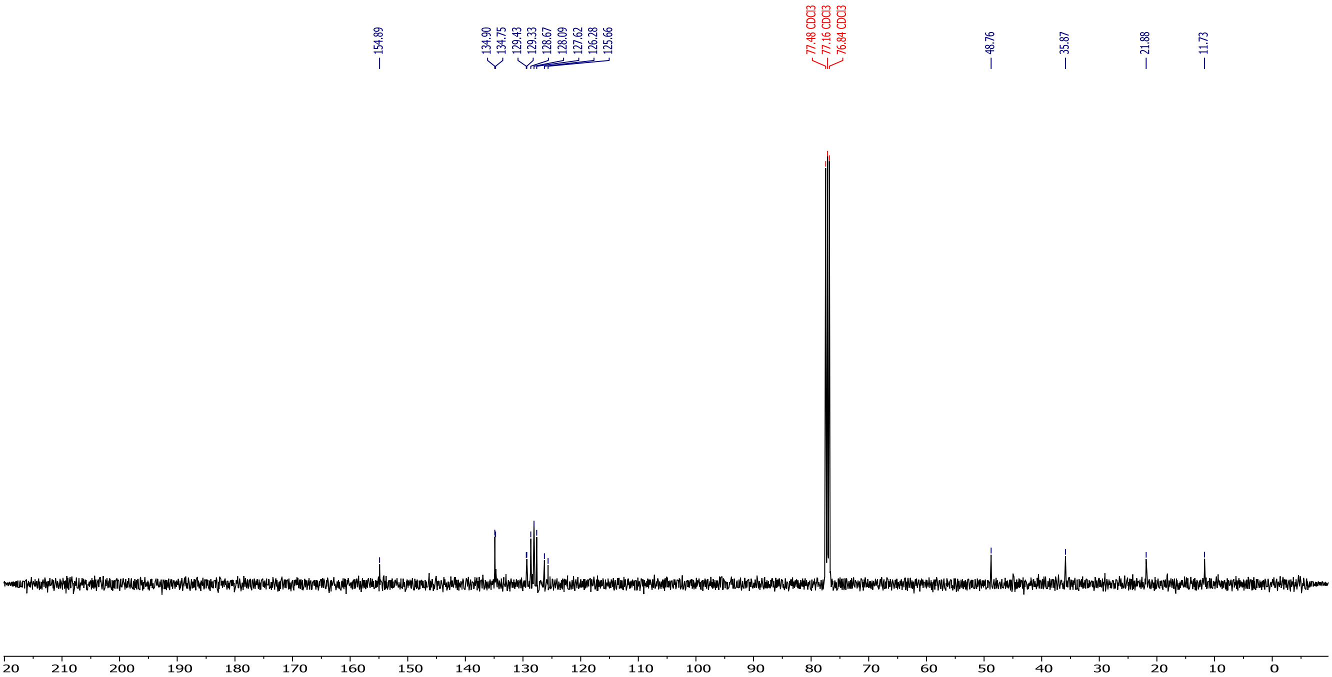


Figure S54 ^{13}C NMR of **15** (101 MHz, CDCl$_3$, 295K)

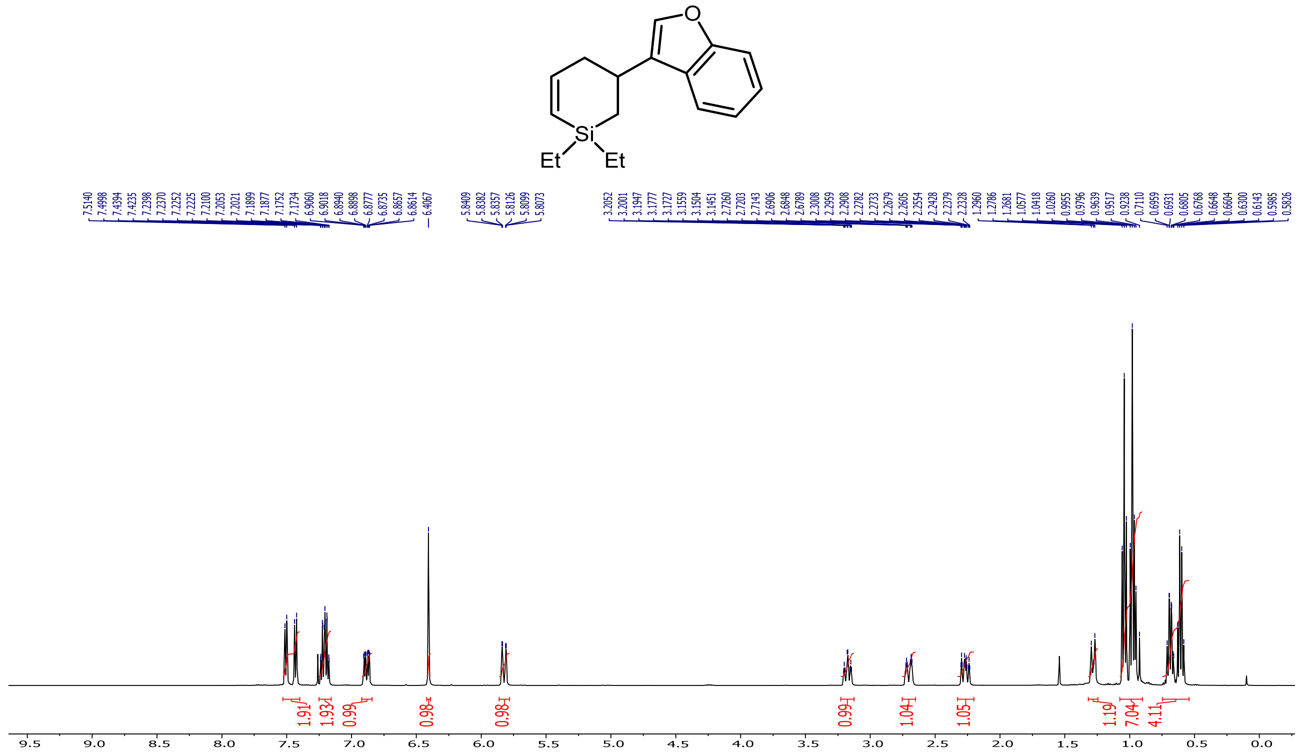


Figure S55 ^{1}H NMR of **16** (500 MHz, $CDCl_3$, 295K)

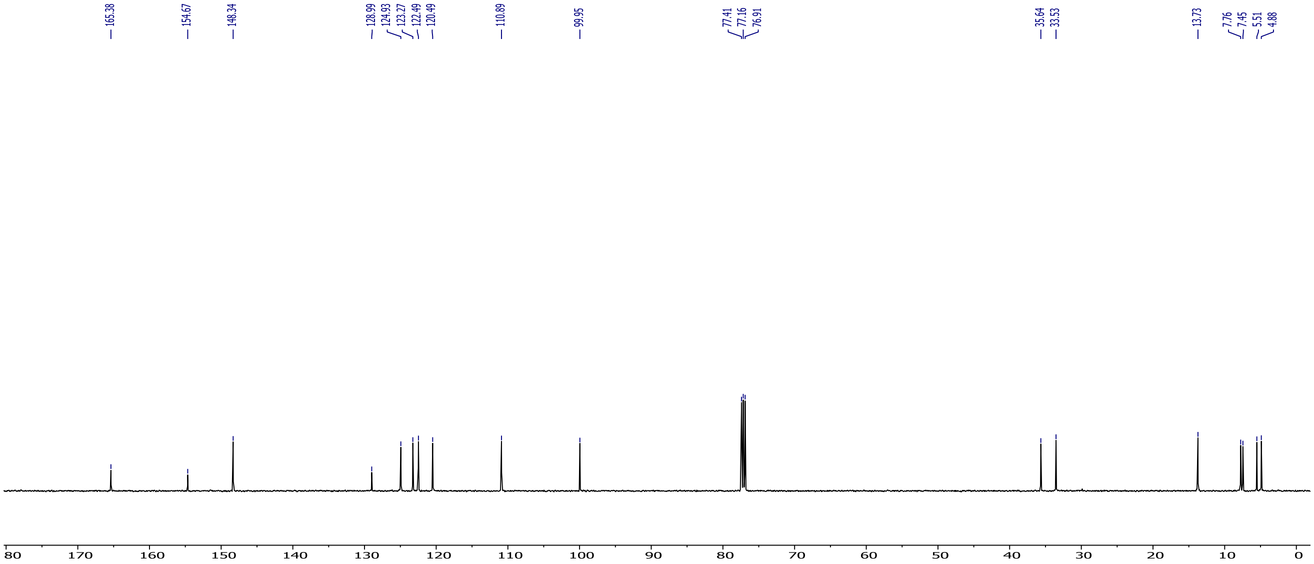


Figure S56 ^{13}C NMR of **16** (126 MHz, $CDCl_3$, 295K)

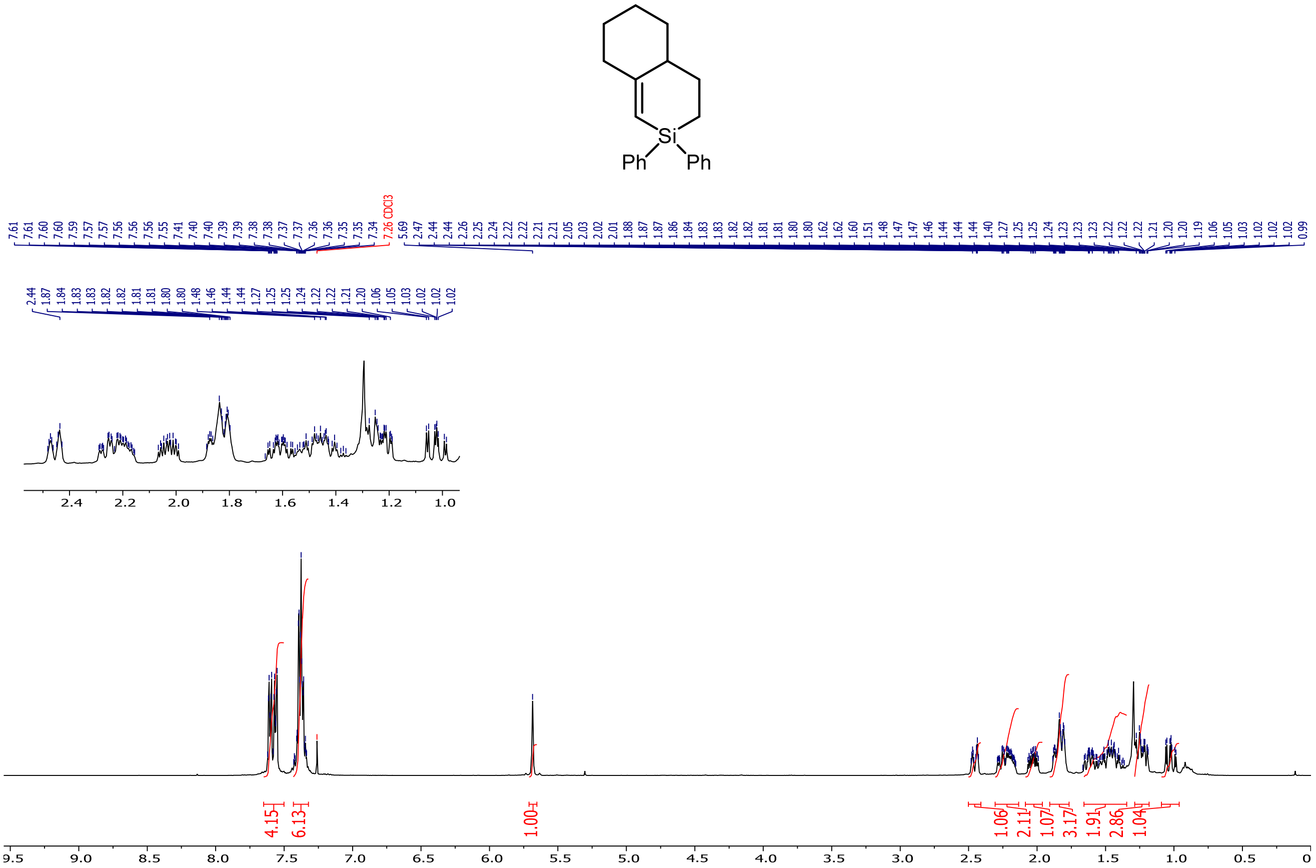


Figure S57 ^{1}H NMR of **17** (400 MHz, CDCl$_3$, 295K)

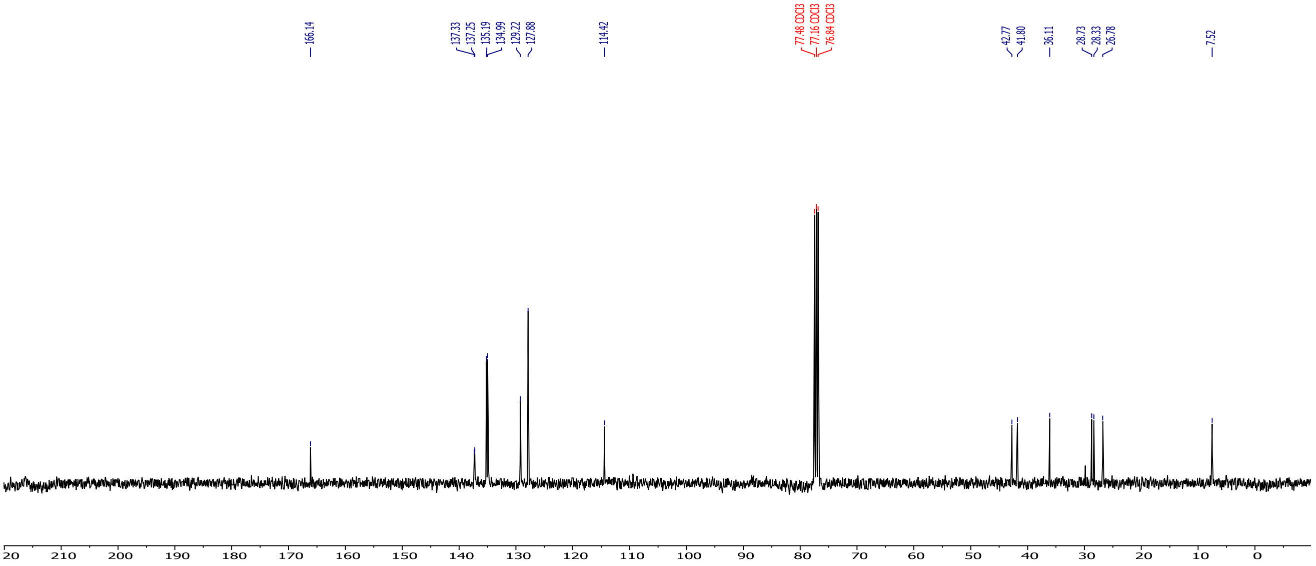


Figure S58 ^{13}C NMR of **17** (101 MHz, CDCl$_3$, 295K)

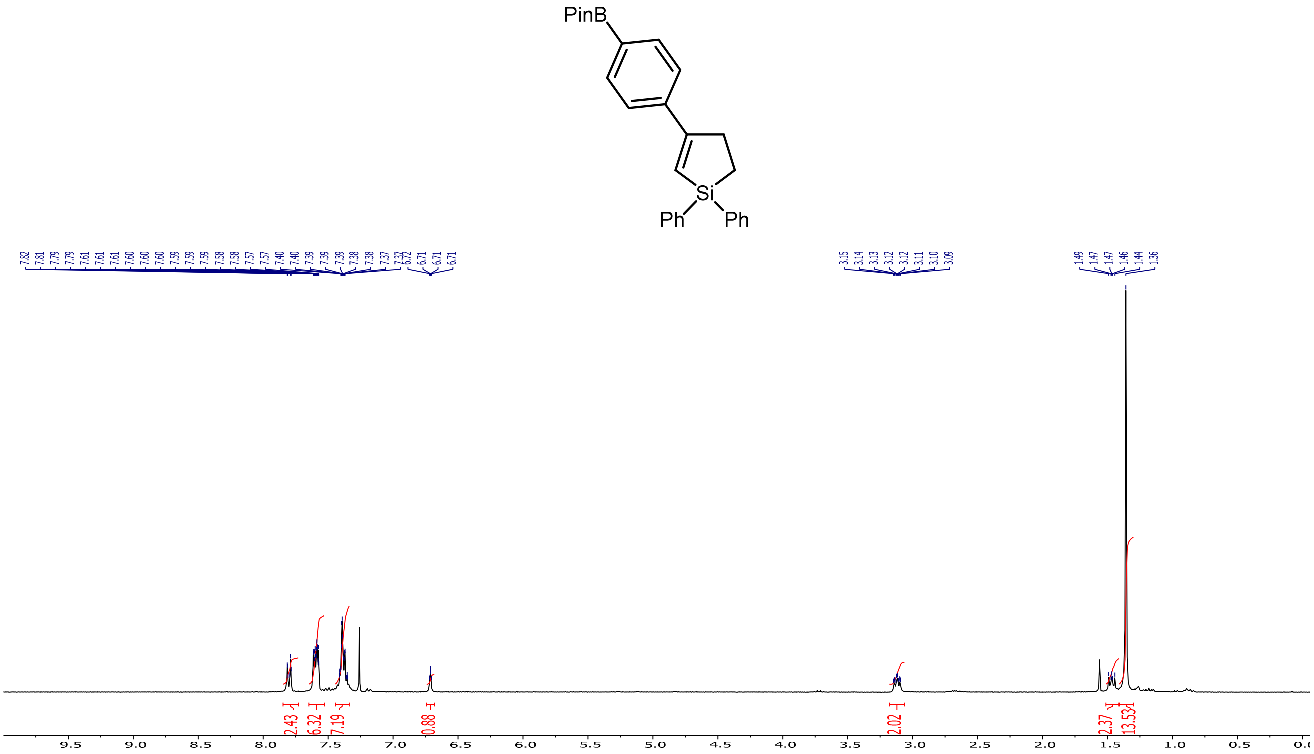


Figure S59 ^{1}H NMR of **18** (400 MHz, $CDCl_3$, 295K)

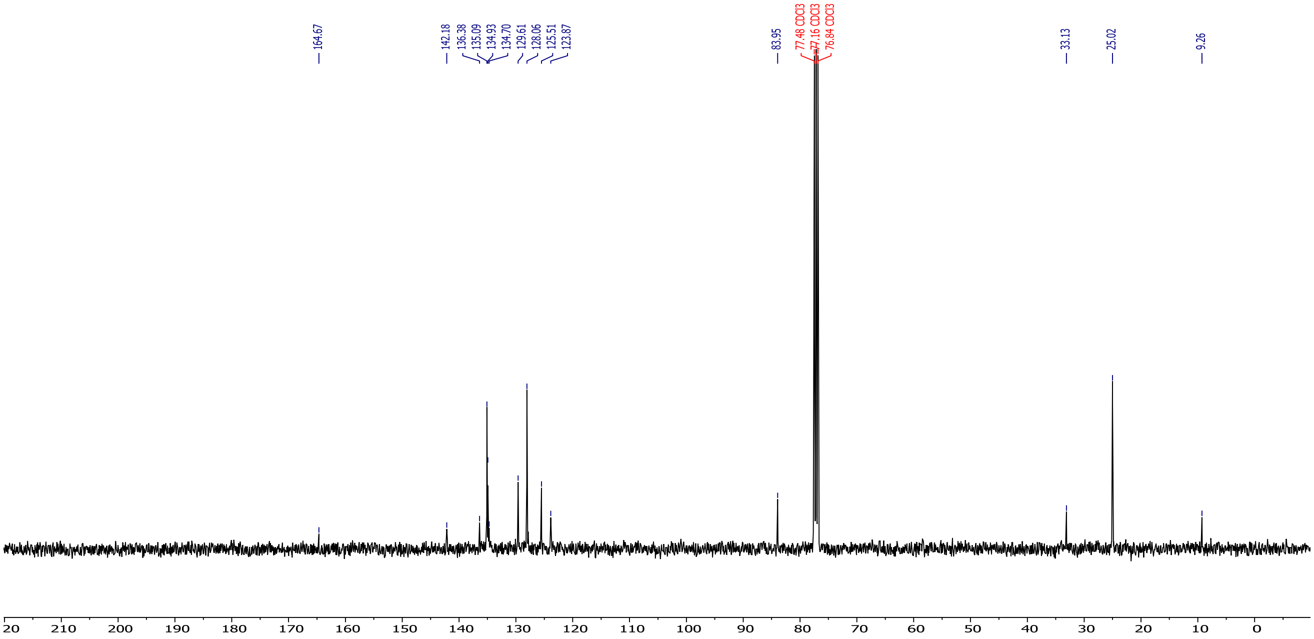
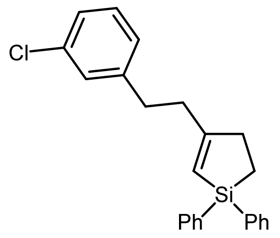


Figure S60 ^{13}C NMR of **18** (126 MHz, $CDCl_3$, 295K)



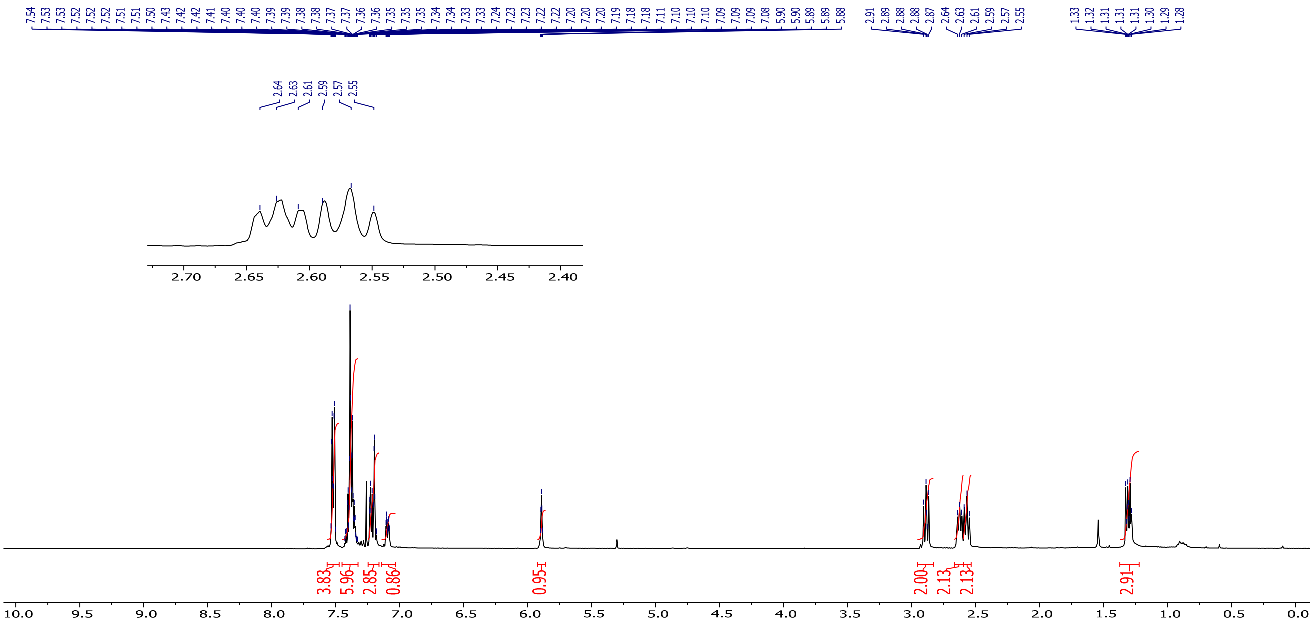


Figure S61 ^{1}H NMR of **19** (400 MHz, $CDCl_3$, 295K)

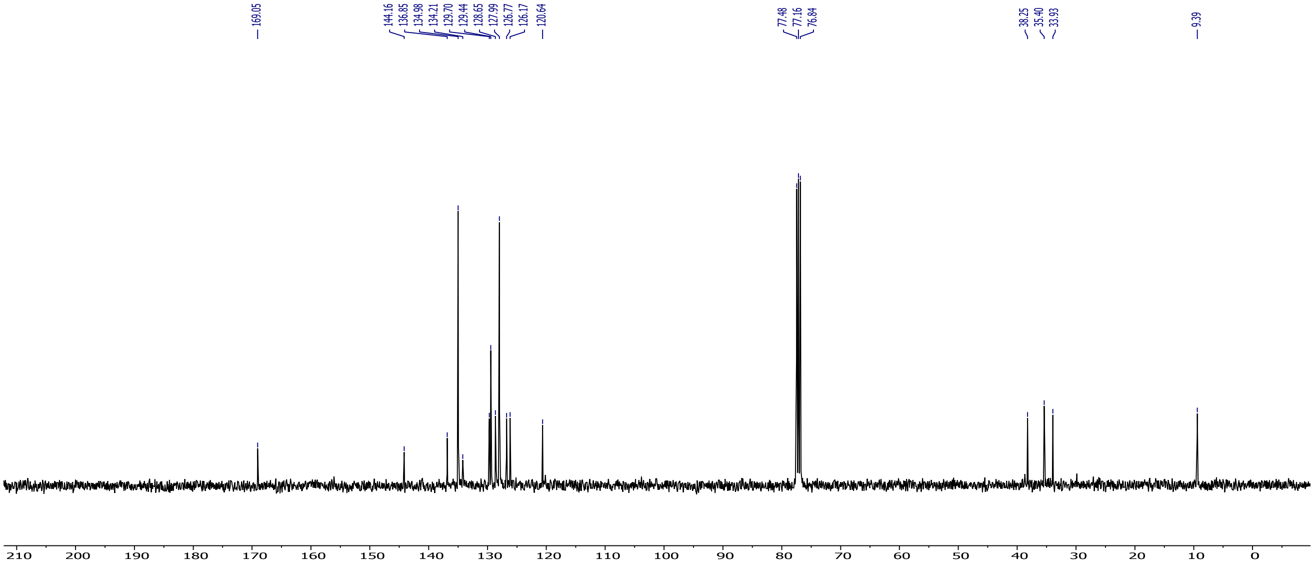


Figure S62 ^{13}C NMR of **19** (126 MHz, $CDCl_3$, 295K)

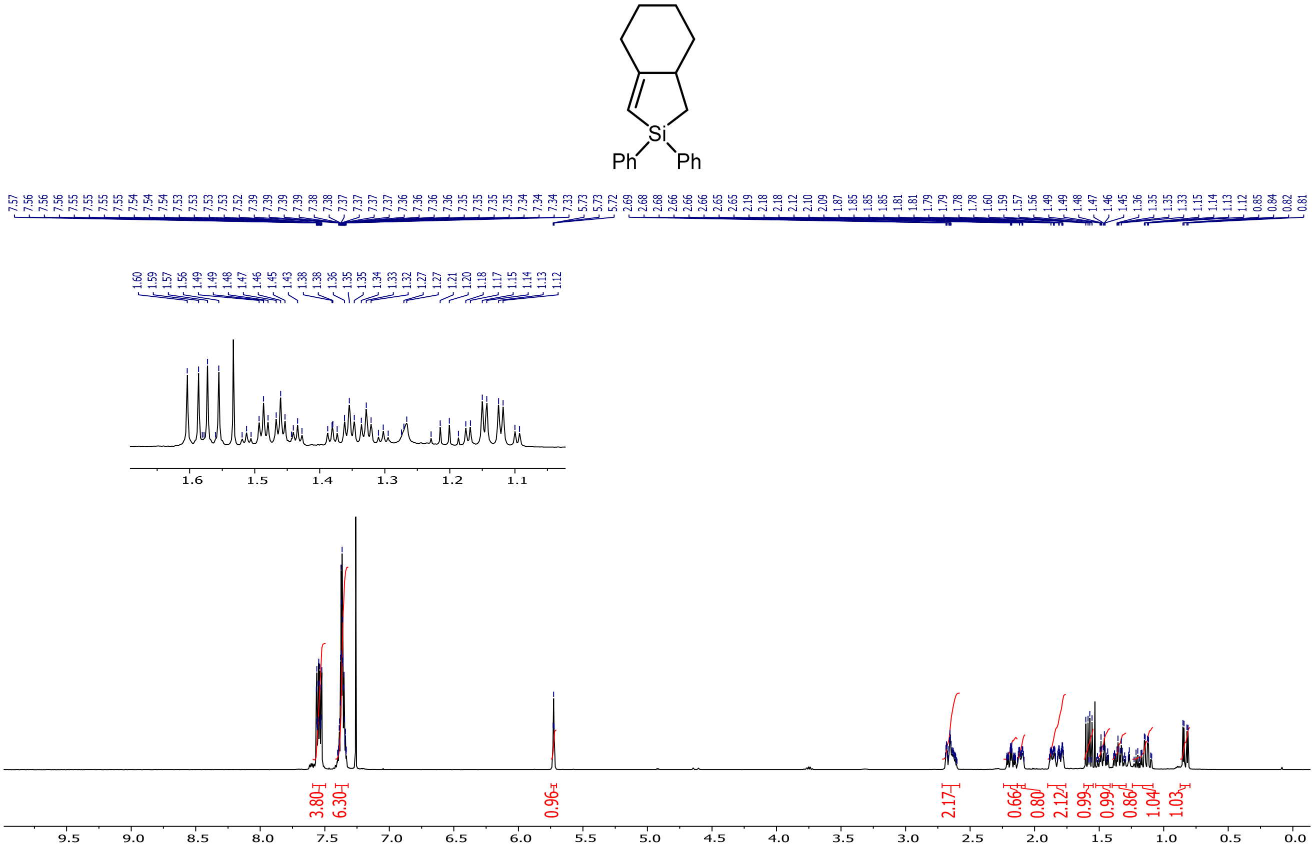


Figure S63 ^{1}H NMR of **20** (500 MHz, CDCl$_3$, 295K)

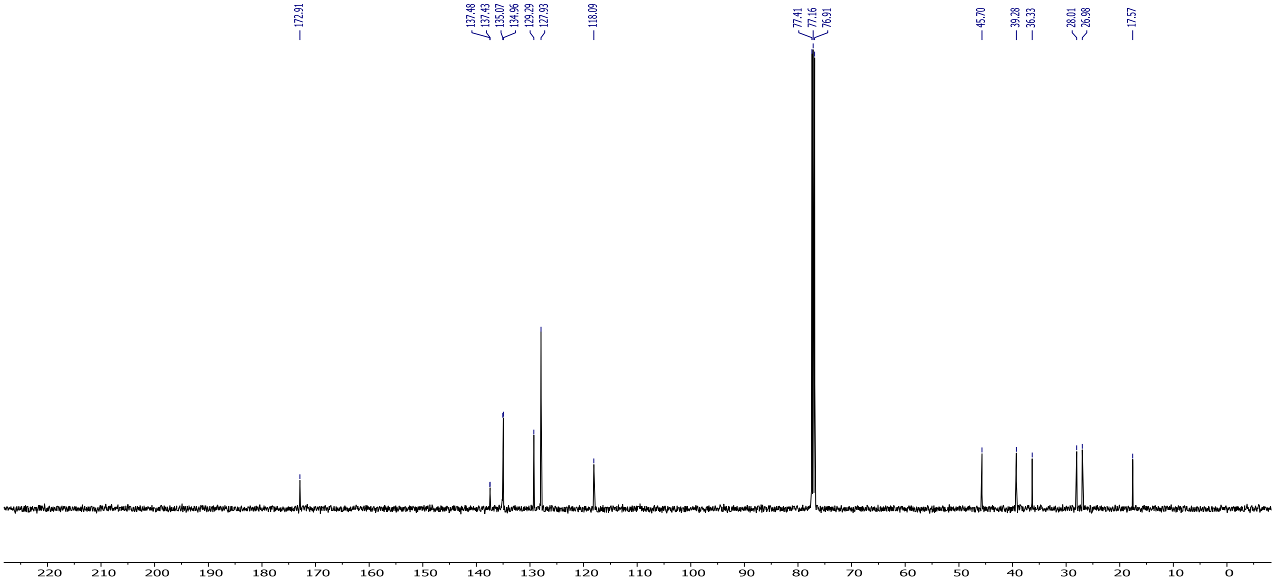
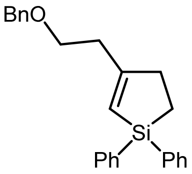


Figure S64 ^{13}C NMR of **20** (126 MHz, CDCl$_3$, 295K)



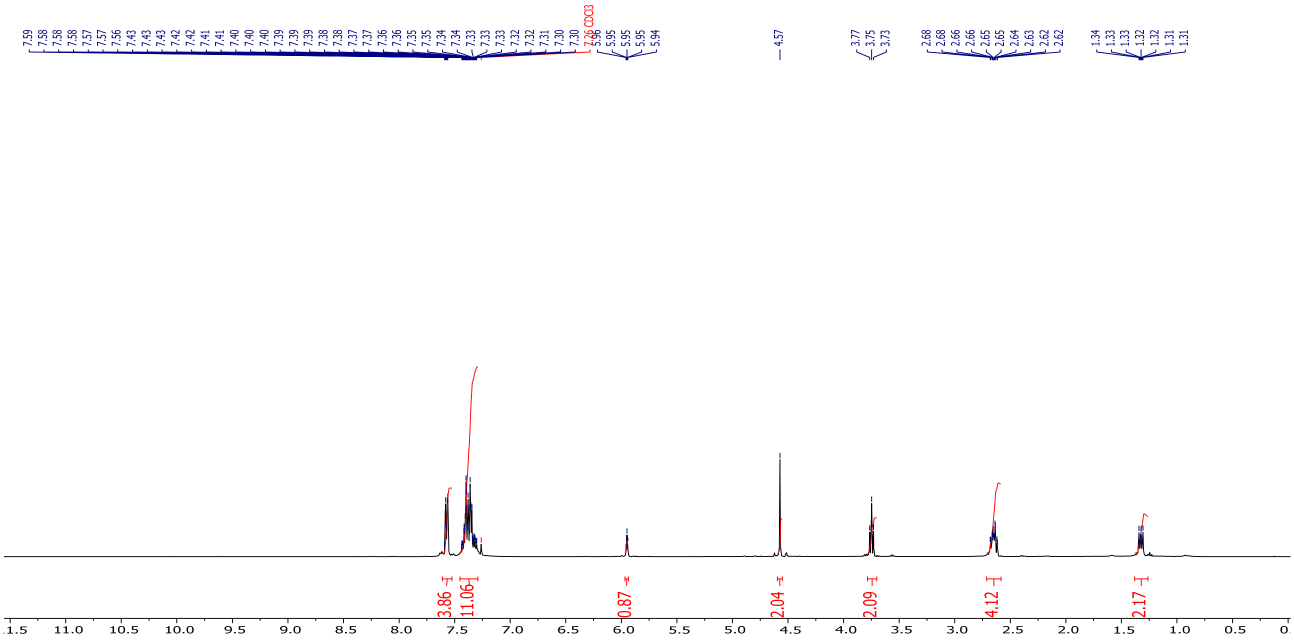


Figure S65 ^{1}H NMR of **21** (300 MHz, $CDCl_3$, 295K)

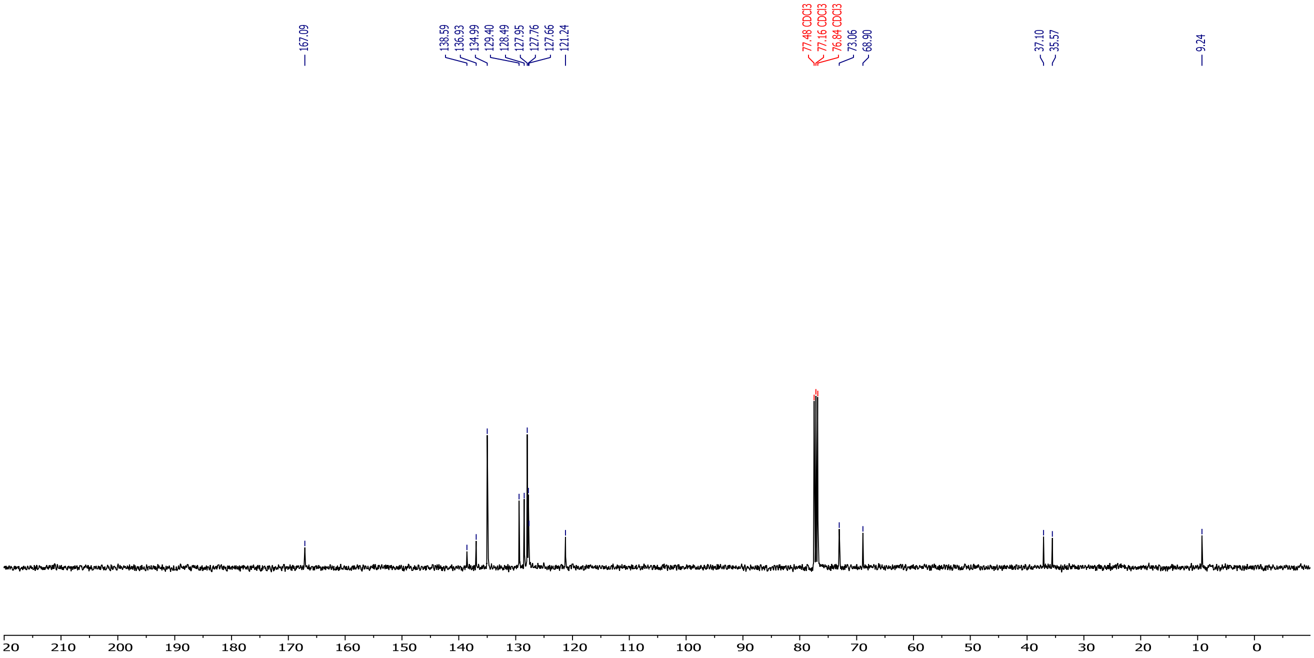
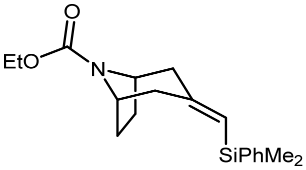


Figure S66 ^{13}C NMR of **21** (126 MHz, $CDCl_3$, 295K)



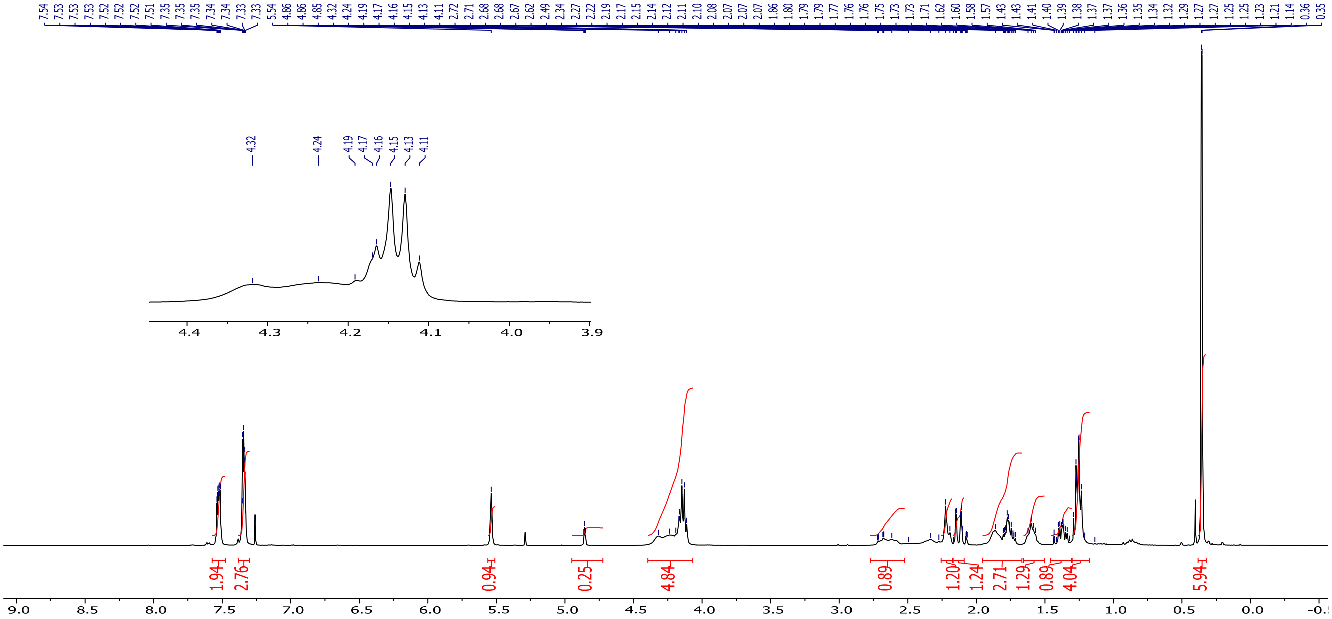


Figure S67 ^{1}H NMR of **22** (400 MHz, CDCl$_3$, 295K)

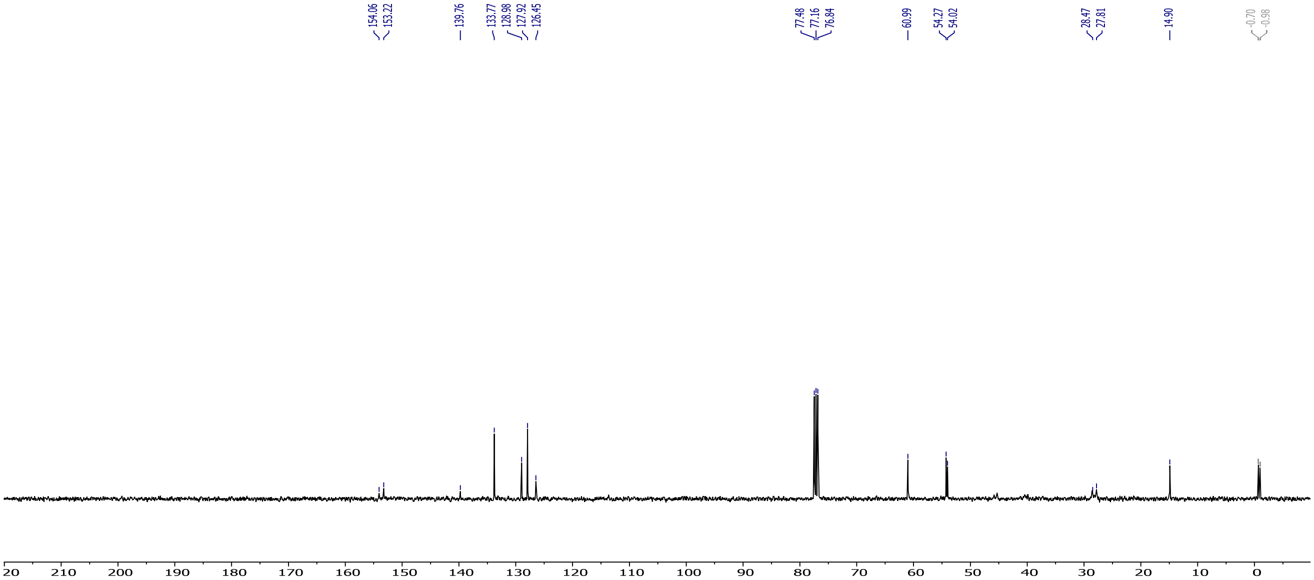
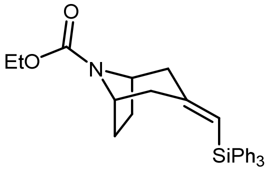


Figure S ^{13}C NMR of **22** (101 MHz, CDCl$_3$, 295K)



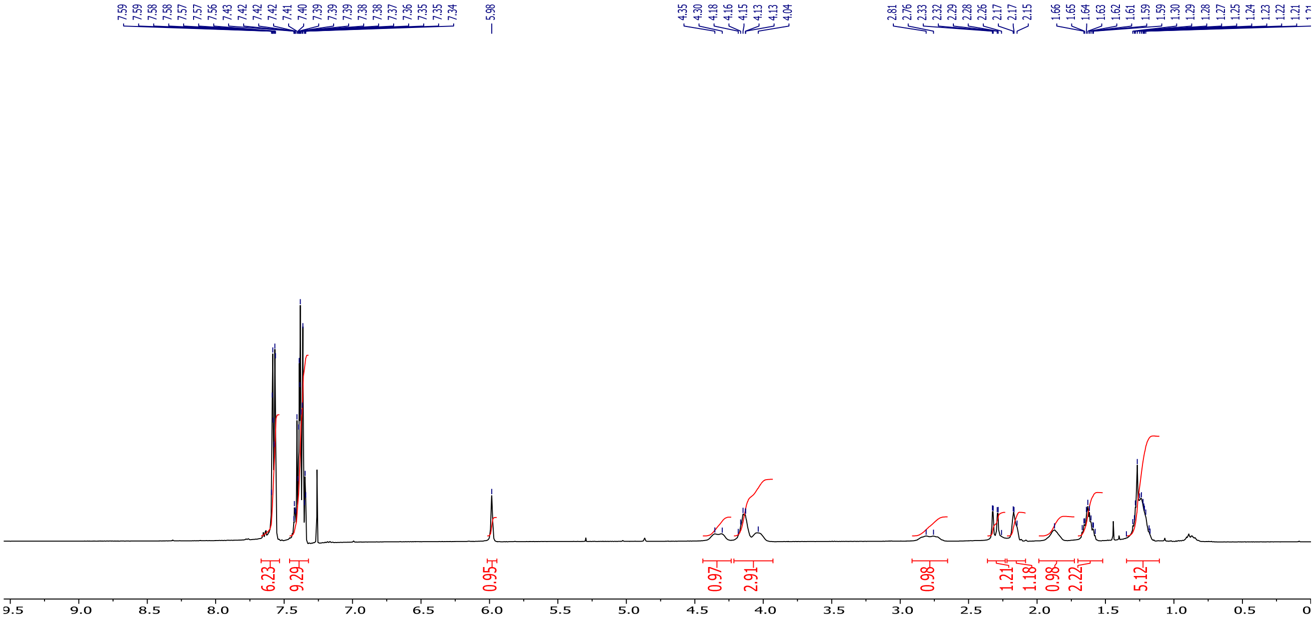


Figure S68 ^{1}H NMR of **23** (400 MHz, CDCl$_3$, 295K)

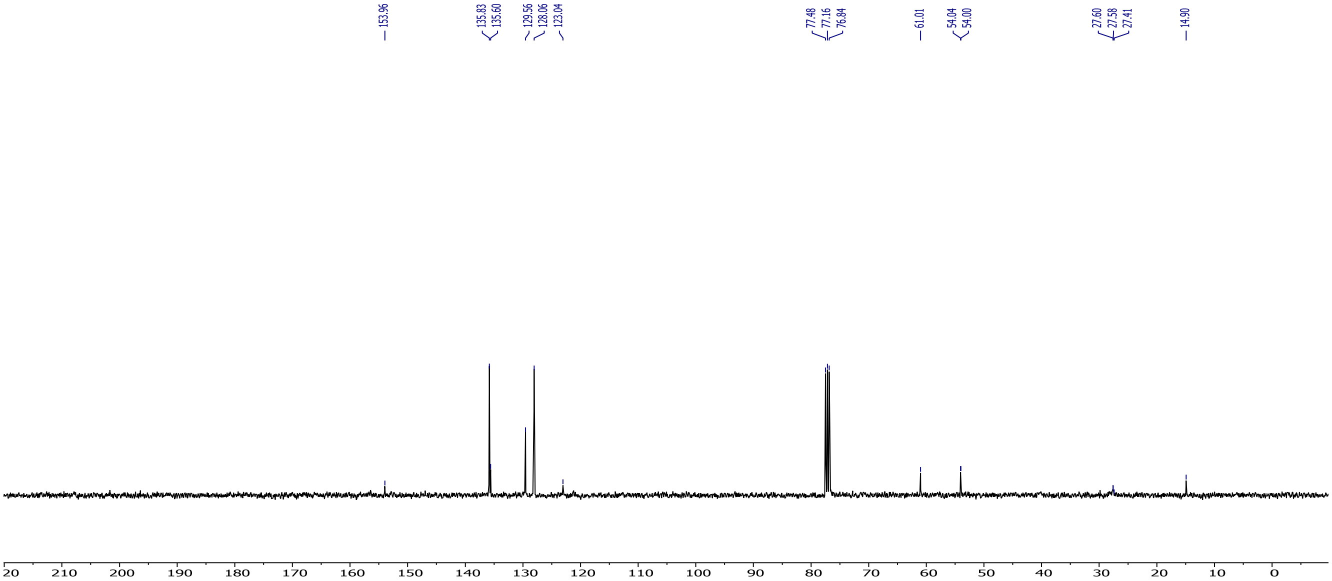
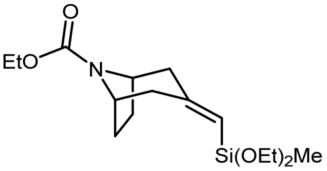


Figure S69 ^{13}C NMR of **23** (101 MHz, CDCl$_3$, 295K)



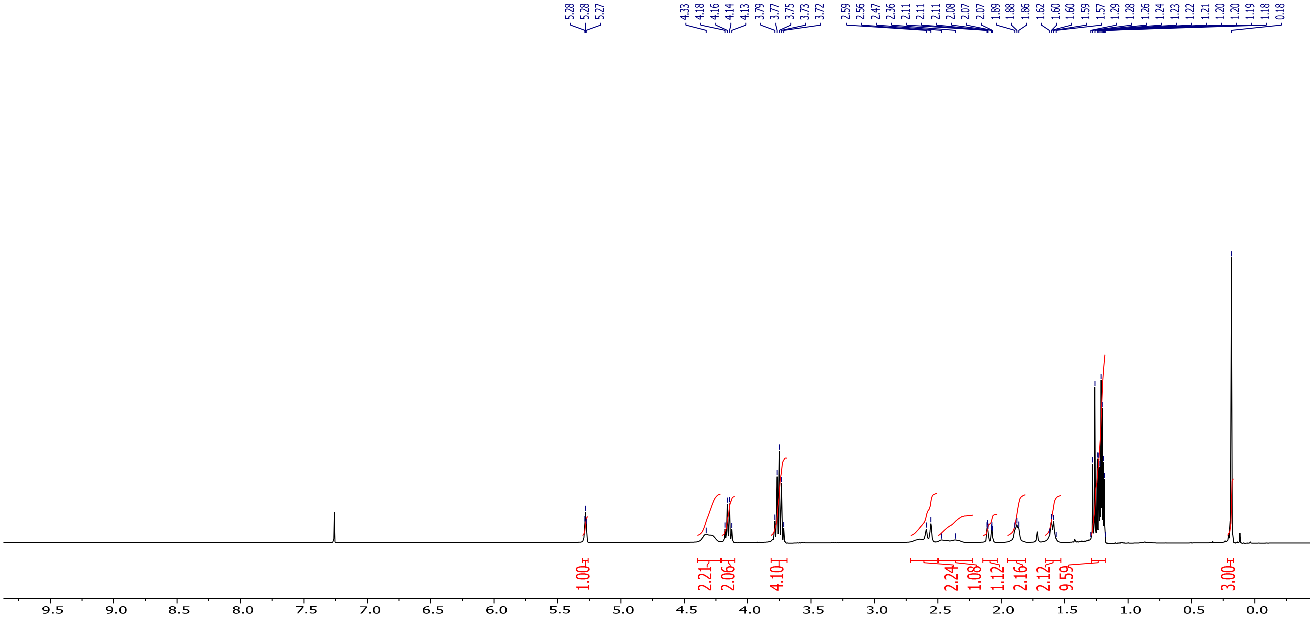


Figure S70 ^{1}H NMR of **24** (400 MHz, $CDCl_3$, 295K)

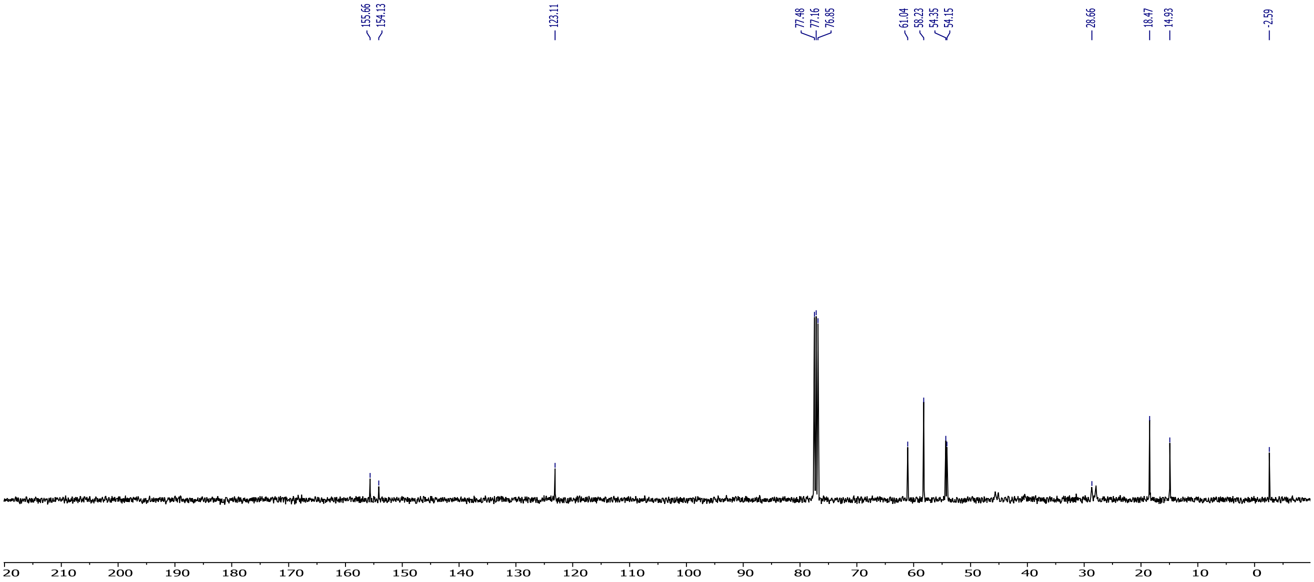


Figure S71 ^{13}C NMR of **24** (101 MHz, $CDCl_3$, 295K)

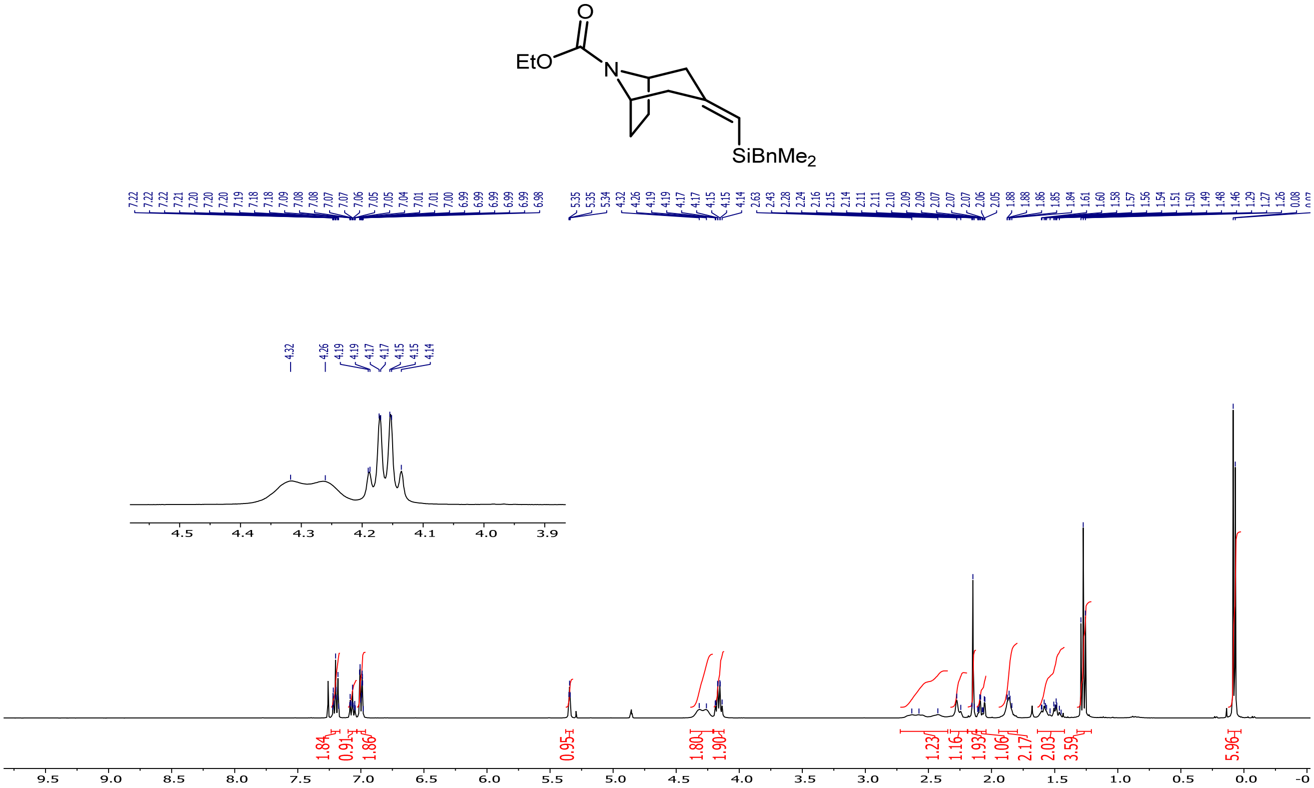


Figure S72 ^{1}H NMR of **25** (400 MHz, $CDCl_3$, 295K)

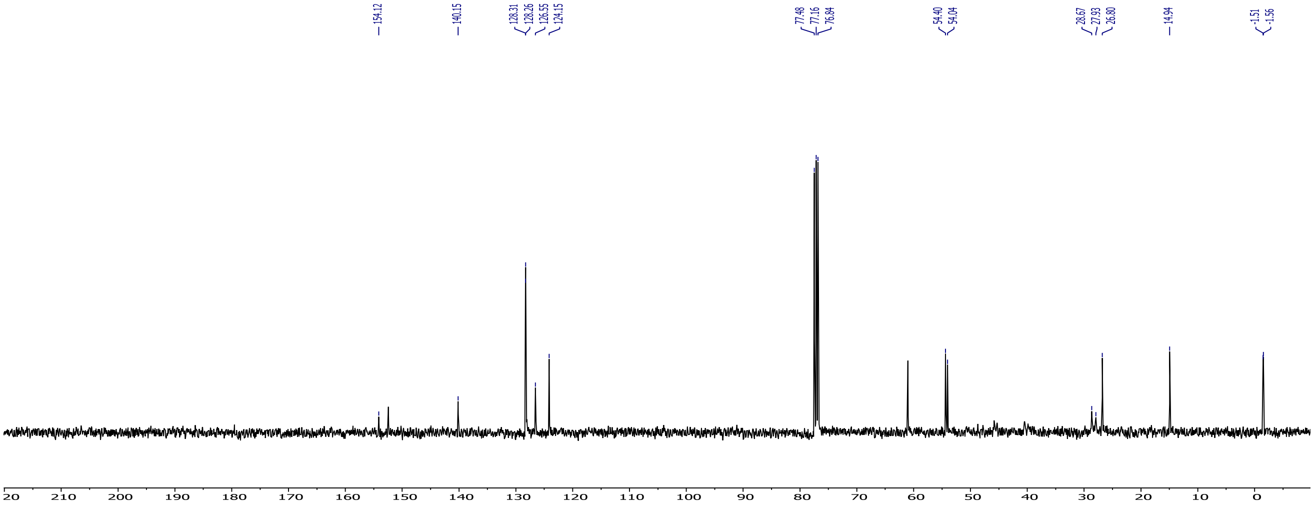


Figure S73 ^{13}C NMR of **25** (101 MHz, $CDCl_3$, 295K)

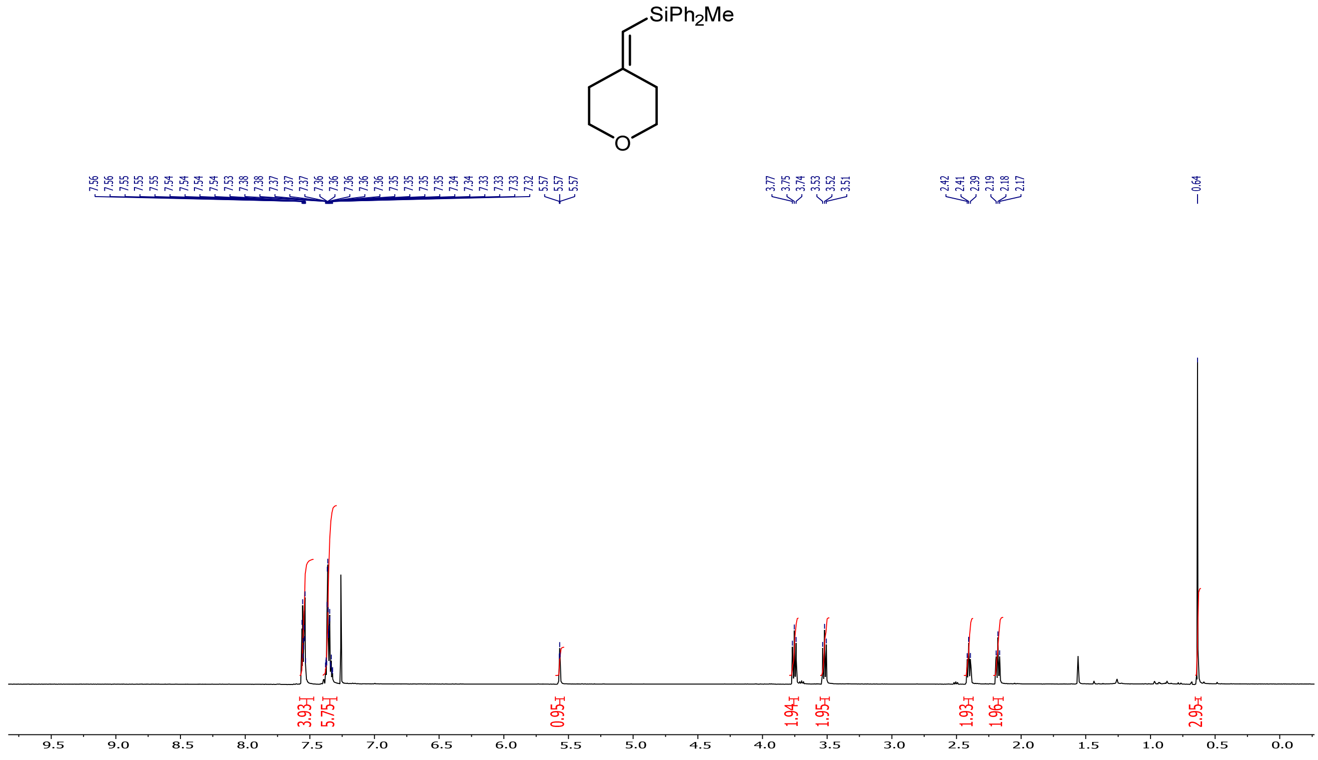


Figure S74 ^{1}H NMR of **26** (400 MHz, CDCl$_3$, 295K)

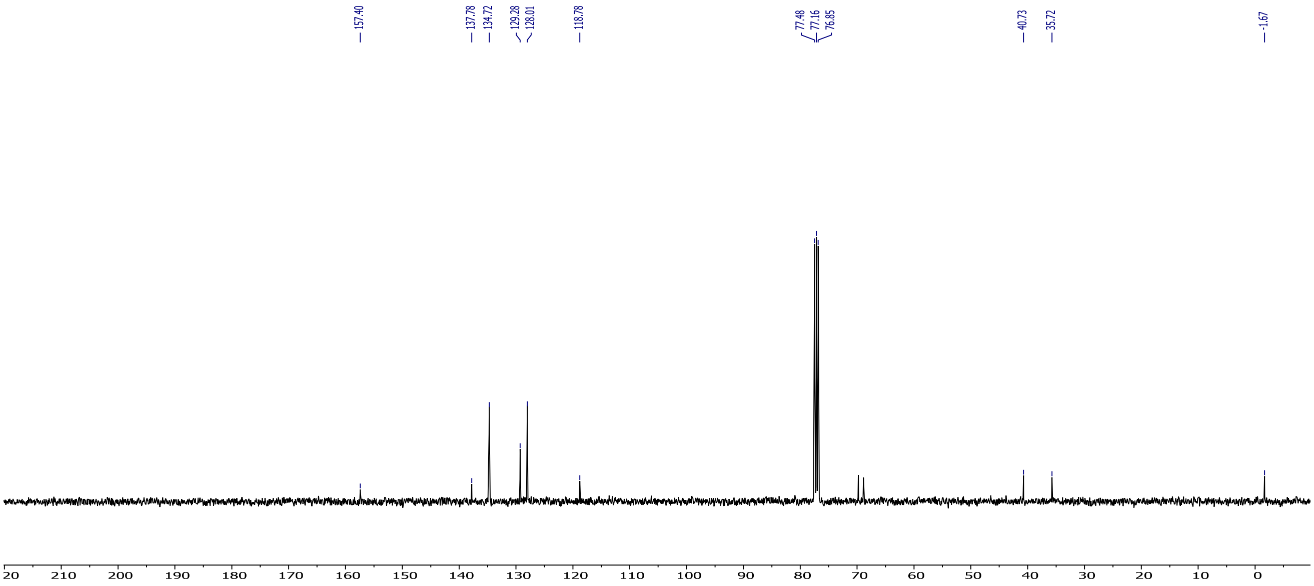
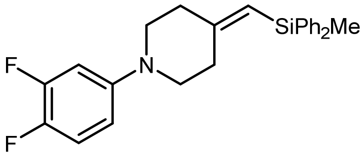


Figure S75 ^{13}C NMR of **26** (101 MHz, CDCl$_3$, 295K)



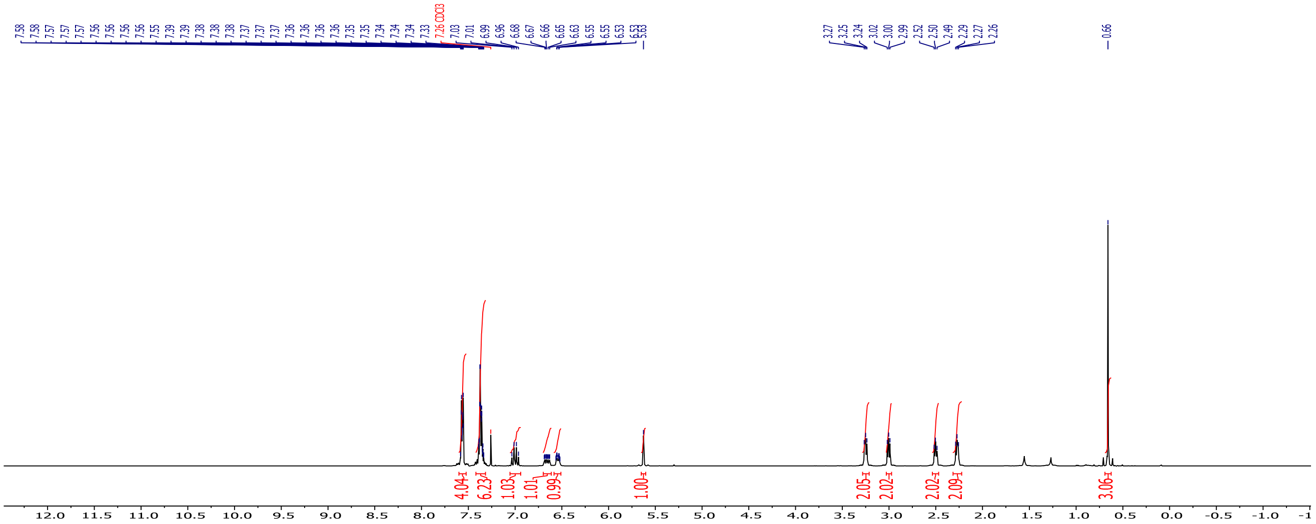


Figure S76 ^{1}H NMR of **27** (400 MHz, CDCl$_3$, 295K)

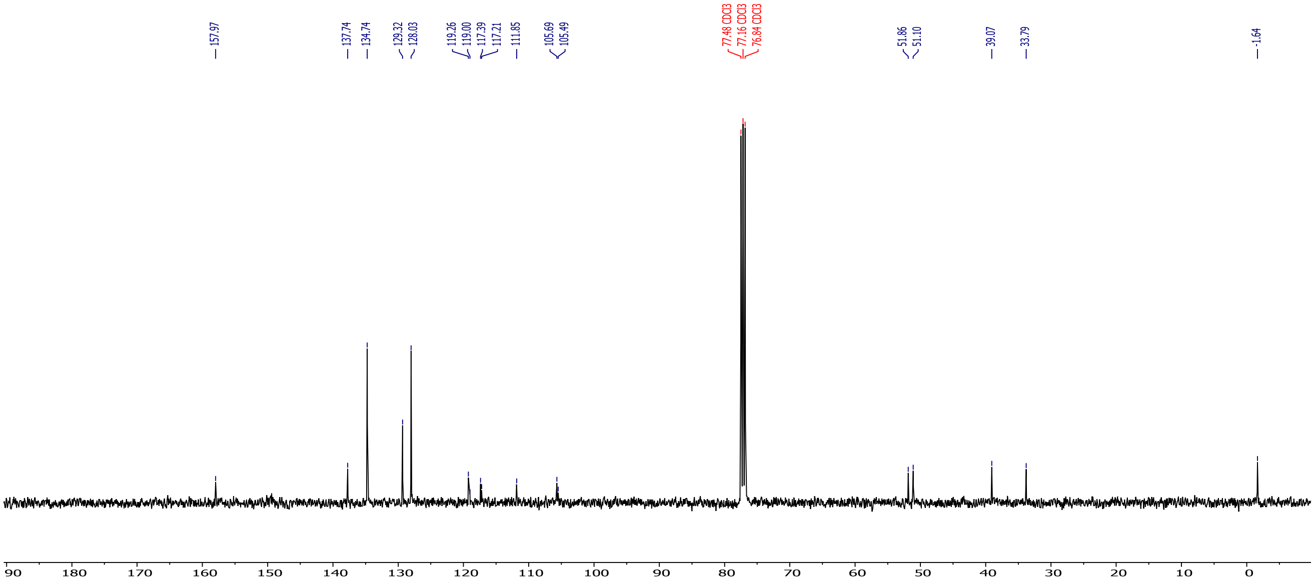


Figure S77 ^{13}C NMR of **27** (101 MHz, CDCl$_3$, 295K)

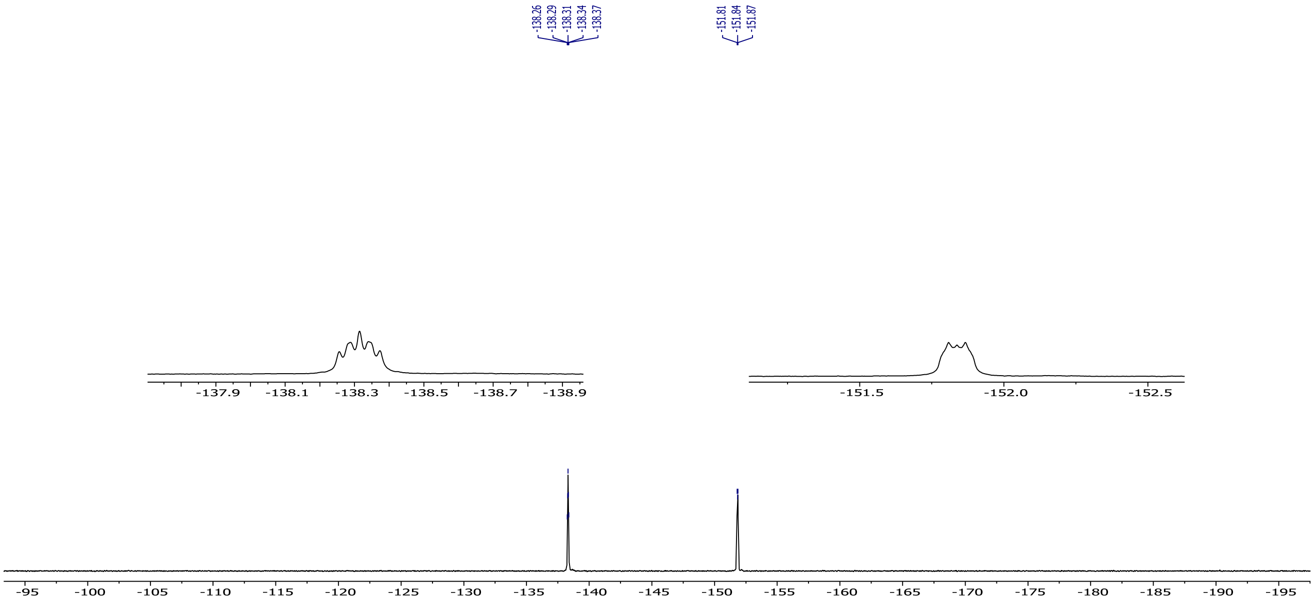
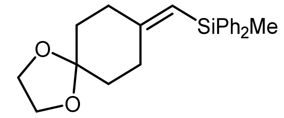


Figure S78 ^{19}F NMR of **27** (376 MHz, $CDCl_3$, 295K)



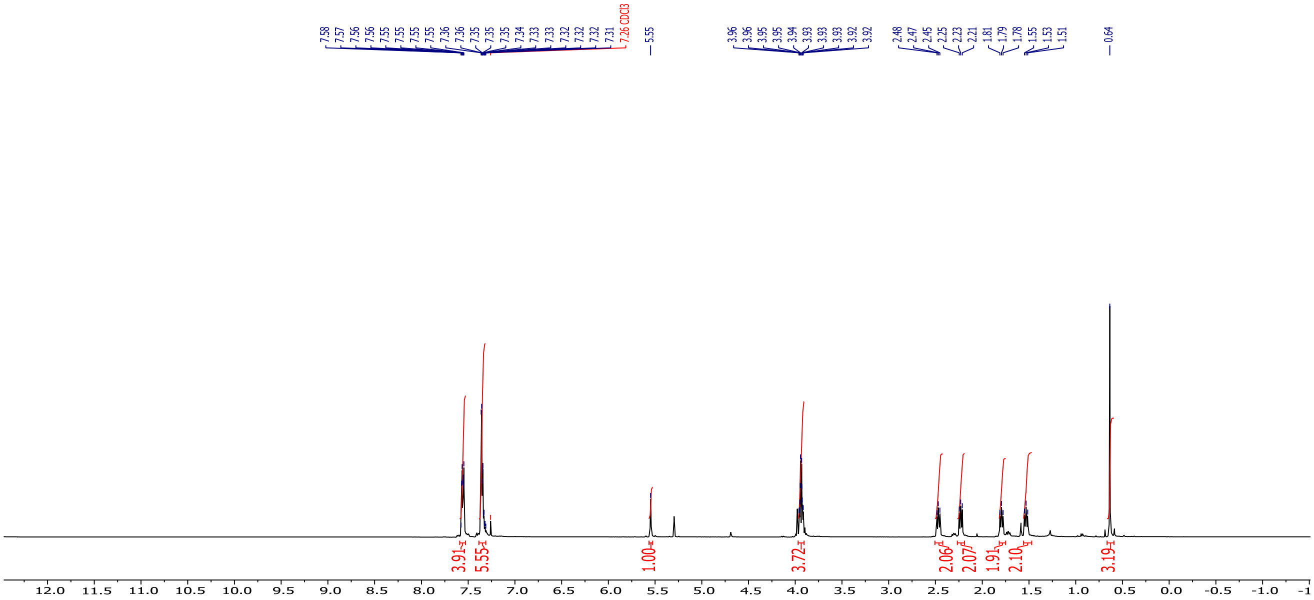


Figure S79 ^{1}H NMR of **28** (400 MHz, $CDCl_3$, 295K)

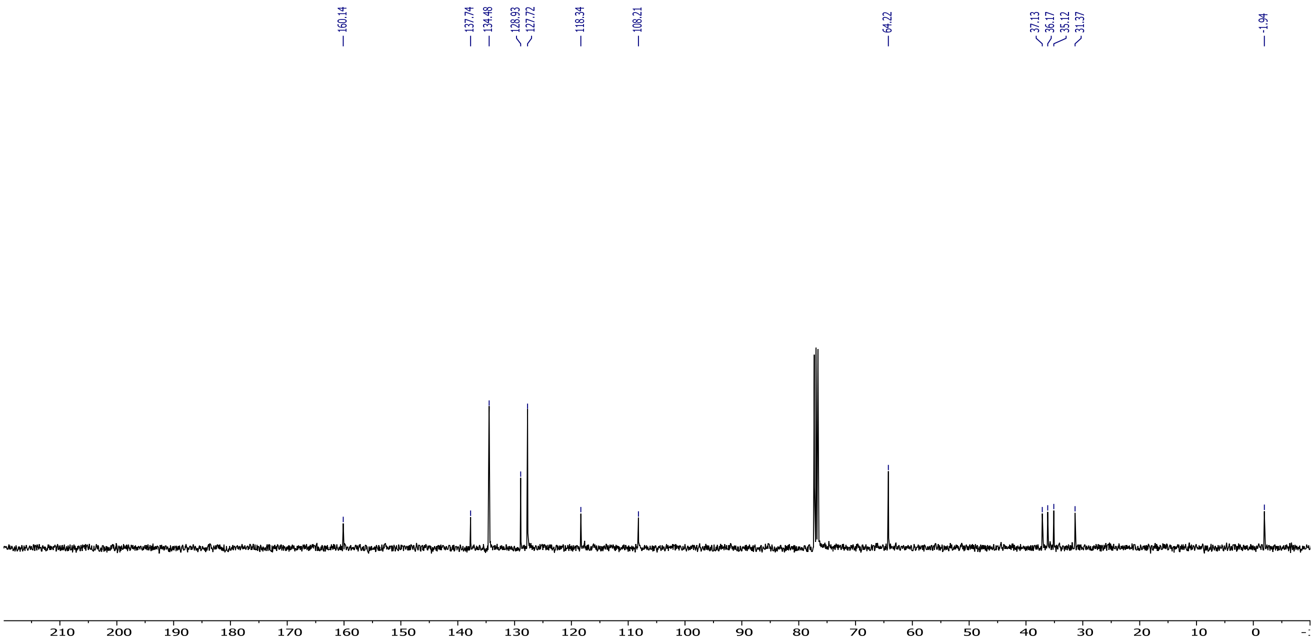
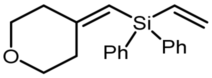


Figure S80 ^{13}C NMR of **28** (101 MHz, $CDCl_3$, 295K)



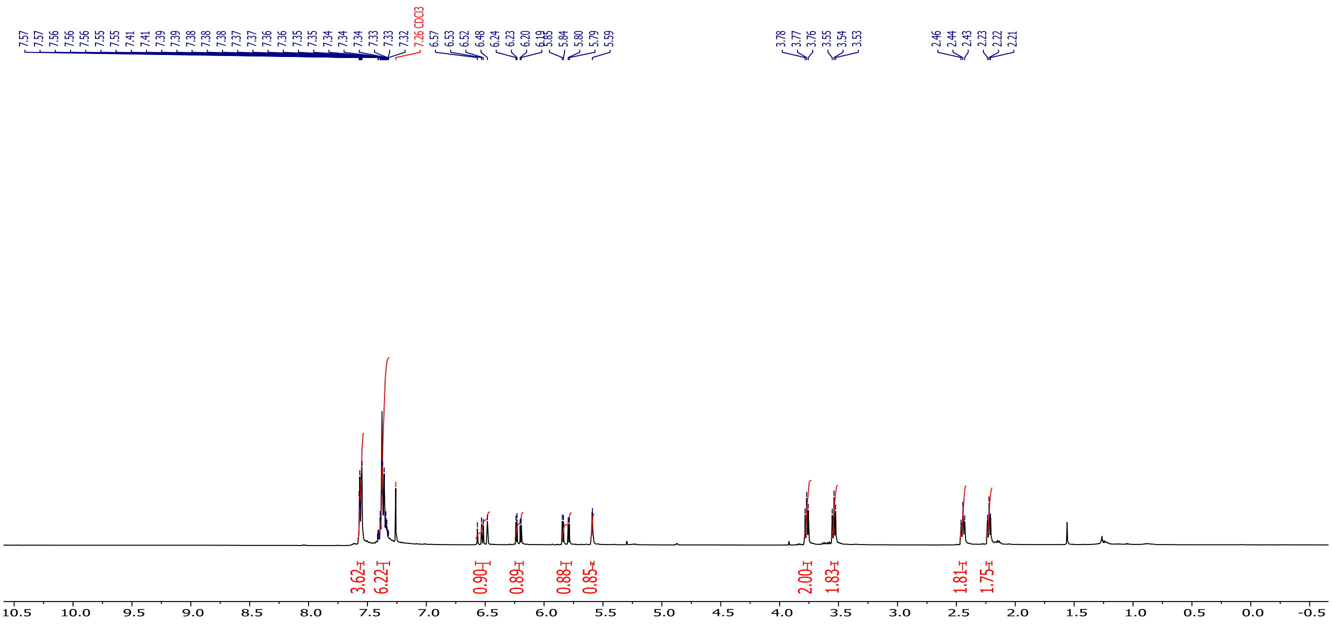


Figure S81 ^{1}H NMR of **29** (400 MHz, CDCl$_3$, 295K)

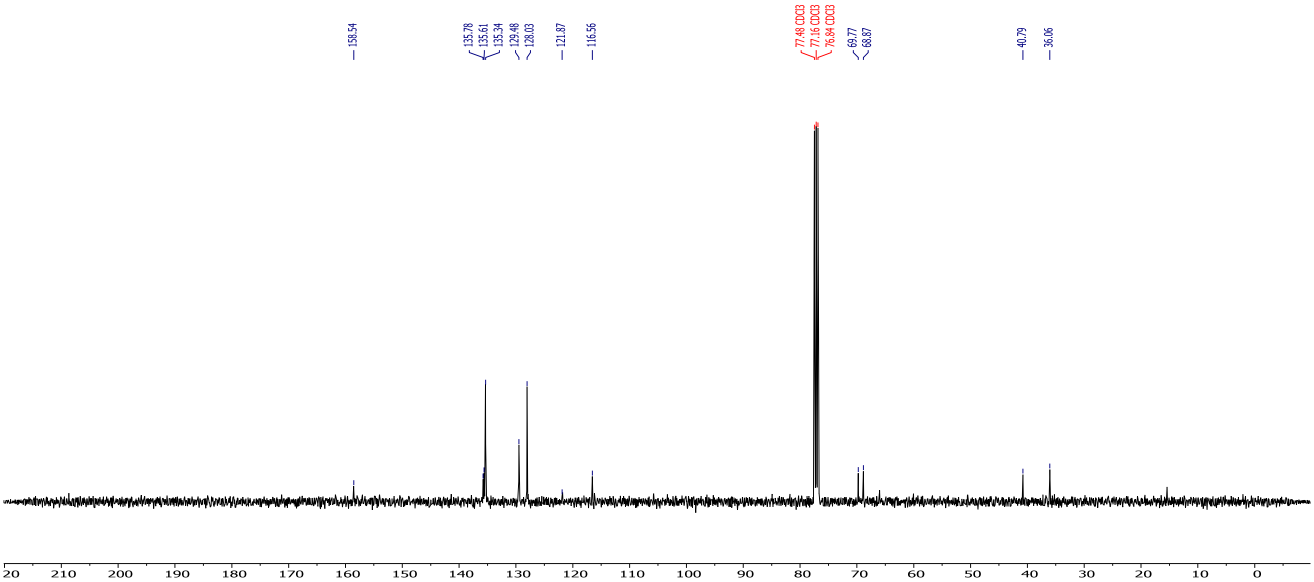
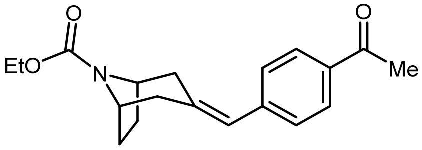


Figure S82 ^{13}C NMR of **29** (101 MHz, CDCl$_3$, 295K)

10. NMR Data for the Hiyama Coupling Product



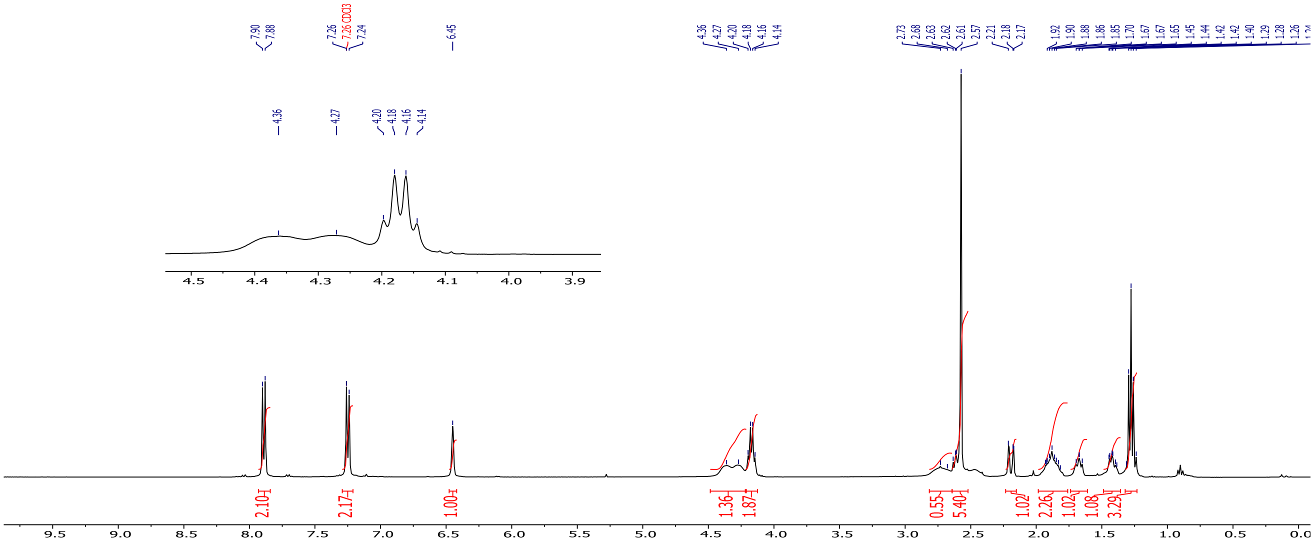


Figure S83 ^{1}H NMR of **30** (400 MHz, $CDCl_3$, 295K)

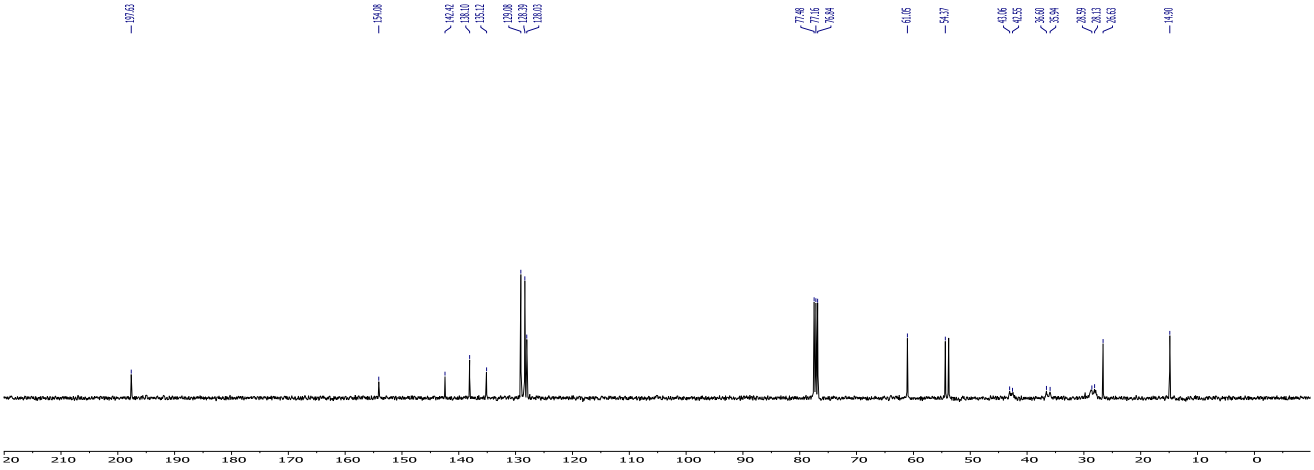
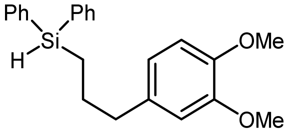


Figure S84 ^{13}C NMR of **30** (101 MHz, $CDCl_3$, 295K)

11. NMR Data for the Sequential Hydrosilylation and Vinylidene Si–H Insertion Product



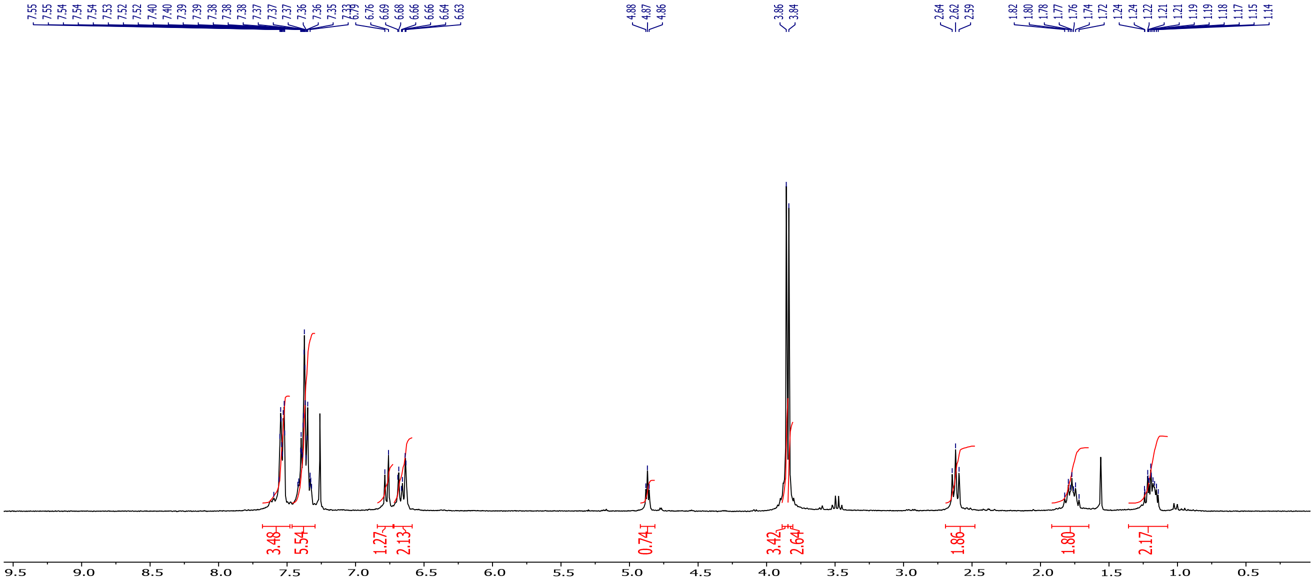


Figure S85 ^{1}H NMR of **S53** (300 MHz, CDCl$_3$, 295K)

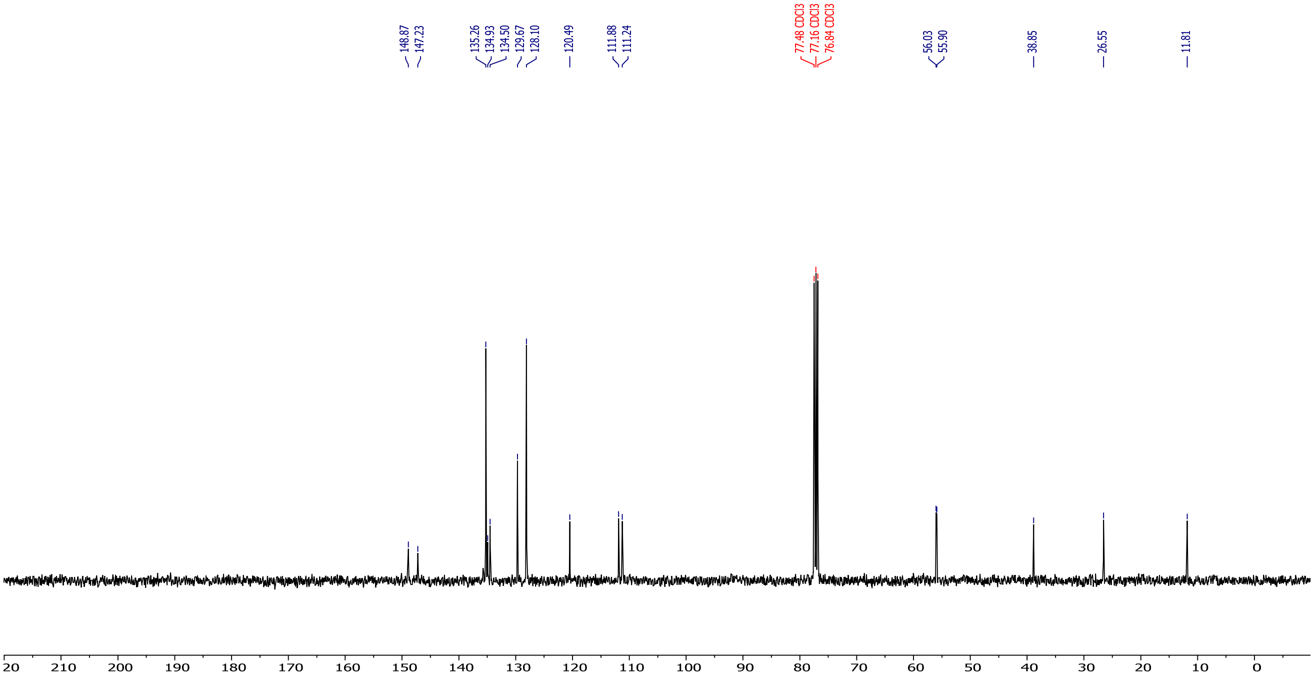
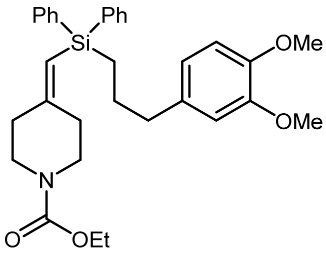


Figure S86 ^{13}C NMR of **S53** (101 MHz, CDCl$_3$, 295K)



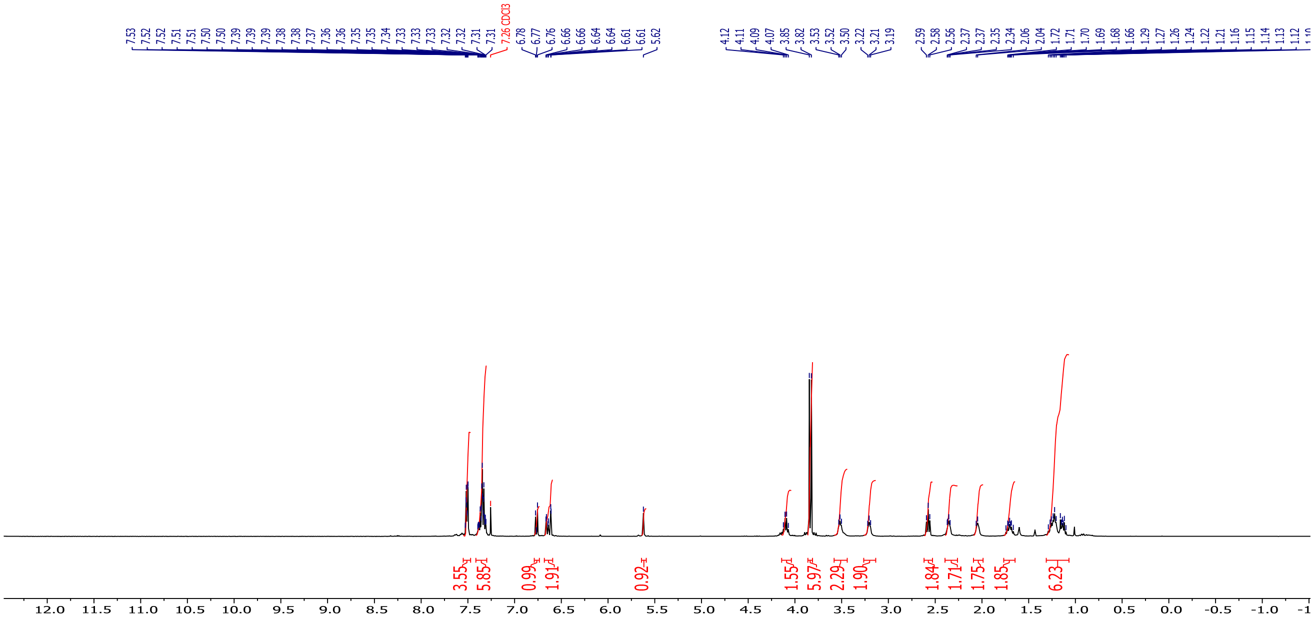


Figure S87 ^{1}H NMR of **32** (400 MHz, CDCl$_3$, 295K)

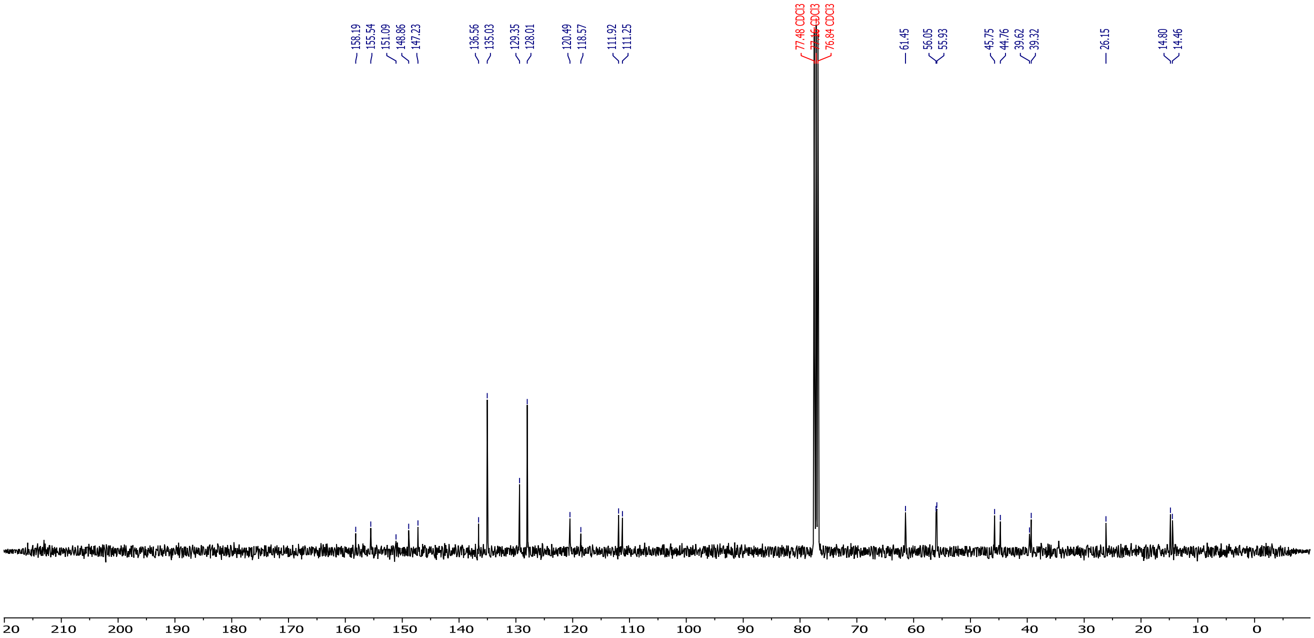


Figure S88 ^{13}C NMR of **32** (101 MHz, CDCl$_3$, 295K)

12. NMR Data for Deuterium Isotope Experiments

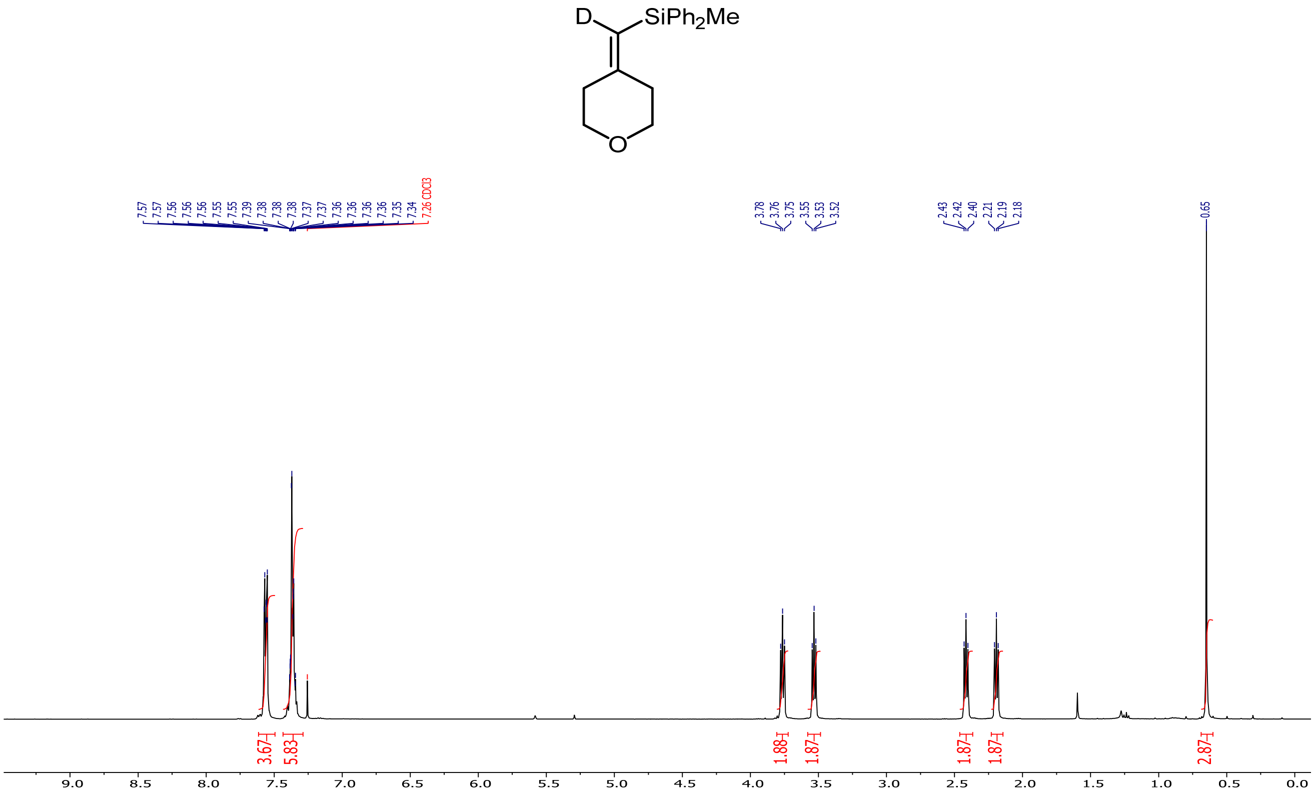


Figure S89 ^{1}H NMR of **26-*d*$_1$** (400 MHz, $CDCl_3$, 295K)

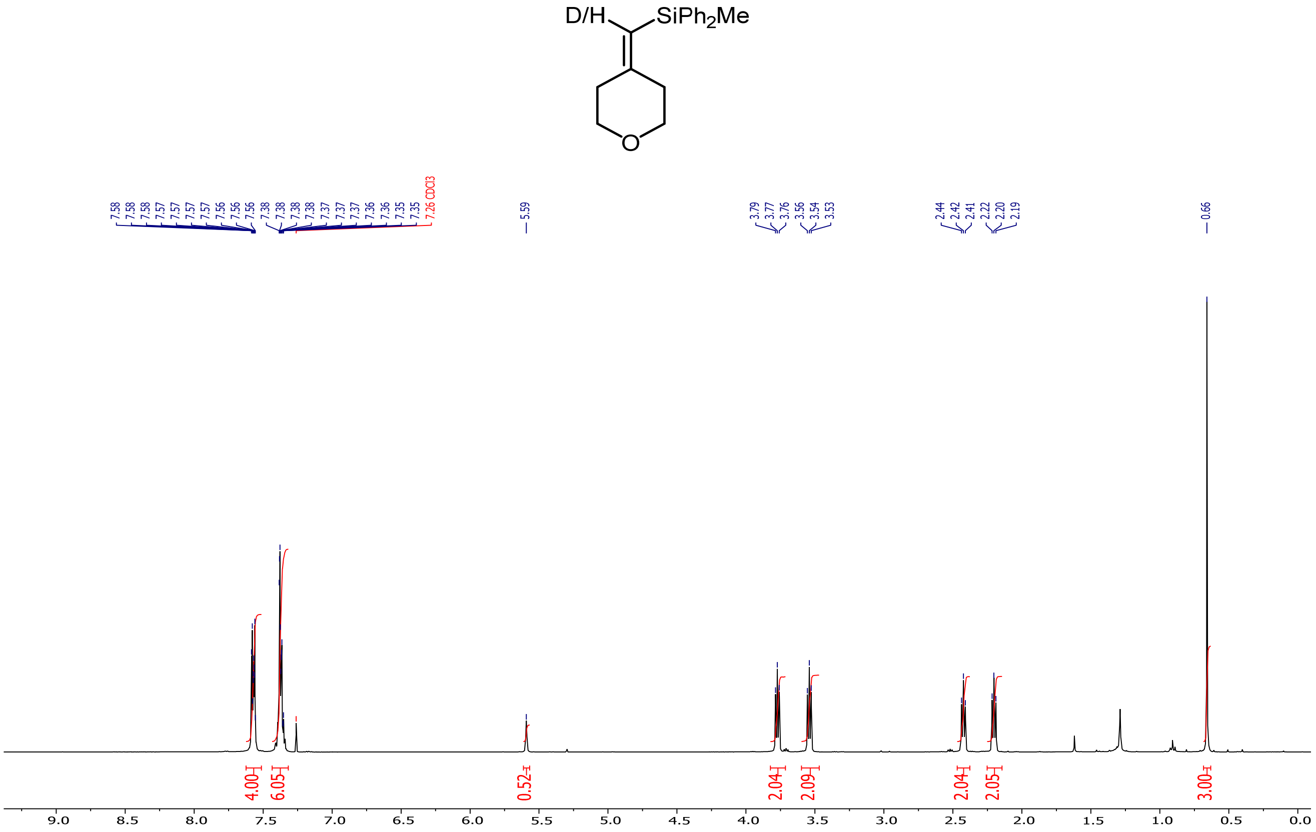


Figure S90 ^{1}H NMR of **26** (400 MHz, $CDCl_3$, 295K)

13. References

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