

Supporting Information
for

**Highly selective hydrosilylation of olefins and acetylenes by platinum(0)
complexes bearing bulky *N*-heterocyclic carbene ligands**

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1. Synthesis of platinum complexes

A 25mL high-pressure Schlenk vessel equipped with a magnetic stirring bar and connected to gas and vacuum line was charged with imidazolium salt (2.10×10^{-4} mol, 1 equiv), potassium bis(trimethylsilyl)amide (46.3 mg, 2.32×10^{-4} mol, 1.1 equiv) and dry toluene (0.5 M). The reaction mixture was stirred at room temperature for 1 h. Then the Karstedt's catalyst (2.18 mL, 2.10×10^{-4} mol, 2.1-2.4% of Pt in xylene, 1 equiv) was added and the reaction mixture was stirred for 24 h at room temperature. After this time, the reaction mixture was filtered on a pad of Celite and eluted with dichloromethane. The solvents were evaporated under vacuum and cold methanol was added to the remaining content to form a white precipitate. The precipitate was filtered off and the product was dried under vacuum.

2. Analytical data of platinum complexes

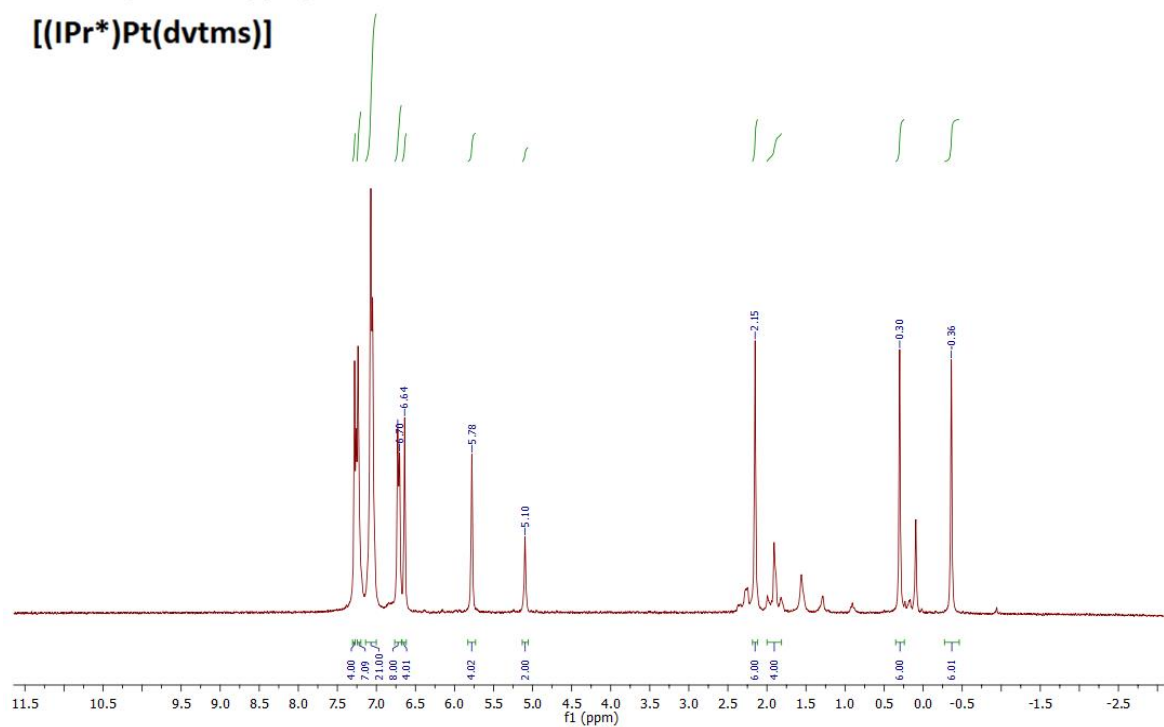
[Pt(IPr*) (dvtms)] (1). White solid, isolated yield: 85%, 232 mg; ^1H NMR (CDCl_3 , δ , ppm): -0.36 (s, 6H, $\text{SiCH}_{3\text{ax}}$), 0.30 (s, 6H, $\text{SiCH}_{3\text{eq}}$), 1.80 – 2.01 (m, 4H, $=\text{CH}_2$ + Si-CH=), 2.15 (s, 6H, CH_3), 2.24 - 2.38 (m, 2H, $=\text{CH}_2$), 5.10 (s, 2H, $\text{CH}^{4.5}\text{Im}$), 5.78 (s, 4H, CHPh_2), 6.64 (s, 4H, CH_{Ar}), 6.72 (d, 8H, $J_{\text{HH}} = 6.7$ Hz, CH_{Ar}), 7.01 – 7.30 (m, 32H, CH_{Ar}); ^{13}C NMR (CDCl_3 , δ , ppm): -1.93 ($\text{SiCH}_{3\text{ax}}$), 2.45 ($\text{SiCH}_{3\text{eq}}$), 21.63 (CH_3), 37.41 ($=\text{CH}_2$), 43.43 (Si-CH=), 51.08 (CHPh_2), 122.52, 126.10, 126.27, 128.13 (d, $J = 2.9$ Hz), 129.15, 129.93, 130.05, 136.30, 137.97, 141.04, 143.71, 144.02, 181.51 (Pt-C_{car}); ^{29}Si NMR (CDCl_3 , δ , ppm): 3.25; ^{195}Pt NMR (CDCl_3 , δ , ppm): -5321; IR (film, cm^{-1}): 3148 (s), 3027 (m), 2954 (br s), 1599 (d), 1494 (s), 1447 (d), 1397 (s), 1302 (s), 1248 (s), 1181 (d), 1078 (s), 940 (m), 782 (m), 698 (s); HRMS (ES+): calcd. for $\text{C}_{77}\text{H}_{74}\text{N}_2\text{ONaSi}_2\text{Pt}$: 1316.4885; found: 1316.4856

[Pt(IPr*^{OMe}) (dvtms)] (2). White solid, isolated yield: 78%, 210.8 mg; ^1H NMR (CDCl_3 , δ , ppm): -0.34 (s, 6H, $\text{SiCH}_{3\text{ax}}$), 0.31 (s, 6H, $\text{SiCH}_{3\text{eq}}$), 1.83 – 2.04 (m, 4H, $=\text{CH}_2$ + Si-CH=), 2.23 - 2.40 (m, 2H, $=\text{CH}_2$), 3.49 (s, 6H, OCH_3), 5.07 (s, 2H, $\text{CH}^{4.5}\text{Im}$), 5.78 (s, 4H, CHPh_2), 6.37 (s, 4H, CH_{Ar}), 6.74 (d, 8H, $J_{\text{HH}} = 6.7$ Hz, CH_{Ar}), 7.01 – 7.31 (m, 32H, CH_{Ar}); ^{13}C NMR (CDCl_3 , δ , ppm): -1.74 ($\text{SiCH}_{3\text{ax}}$), 2.48 ($\text{SiCH}_{3\text{eq}}$), 37.40 ($=\text{CH}_2$), 43.42 (Si-CH=), 51.34 (CHPh_2), 54.98 (OCH_3), 114.79, 122.67, 126.22, 126.47, 128.22 (d, $J = 7.5$ Hz), 129.12, 130.01, 132.00, 142.92, 143.54, 143.75, 158.65, 182.34 (Pt-C_{car}); ^{29}Si NMR (CDCl_3 , δ , ppm): 3.26; ^{195}Pt NMR (CDCl_3 , δ , ppm): -5322; IR (film, cm^{-1}): 3150 (s), 3027 (m), 2959 (m), 1597 (d), 1494 (s), 1464 (d), 1306 (s), 1244 (s), 1181 (m), 1145 (m), 1088 (s), 984 (m), 835 (s), 784 (d), 697 (s); HRMS (ES+) calcd. for $\text{C}_{77}\text{H}_{74}\text{N}_2\text{O}_3\text{NaSi}_2\text{Pt}$: 1348.4783; found: 1348.7460

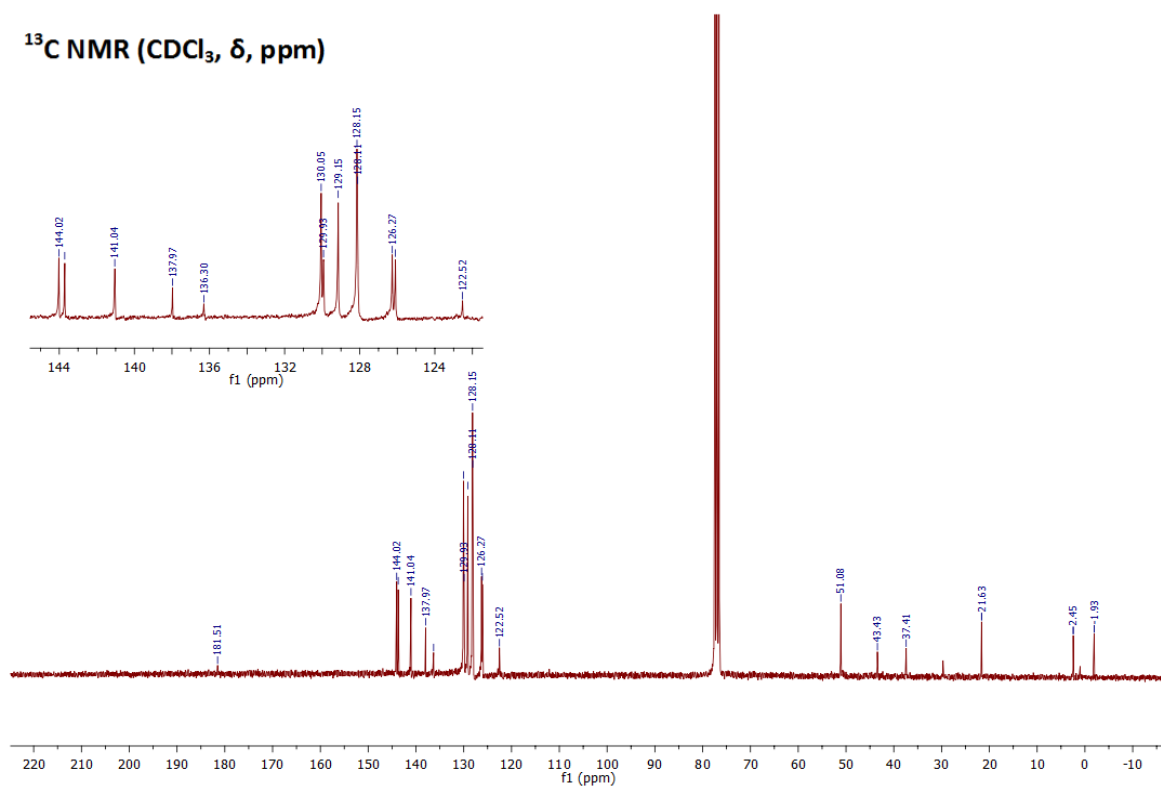
3. NMR spectra of platinum complexes

^1H NMR (CDCl_3 , δ , ppm)

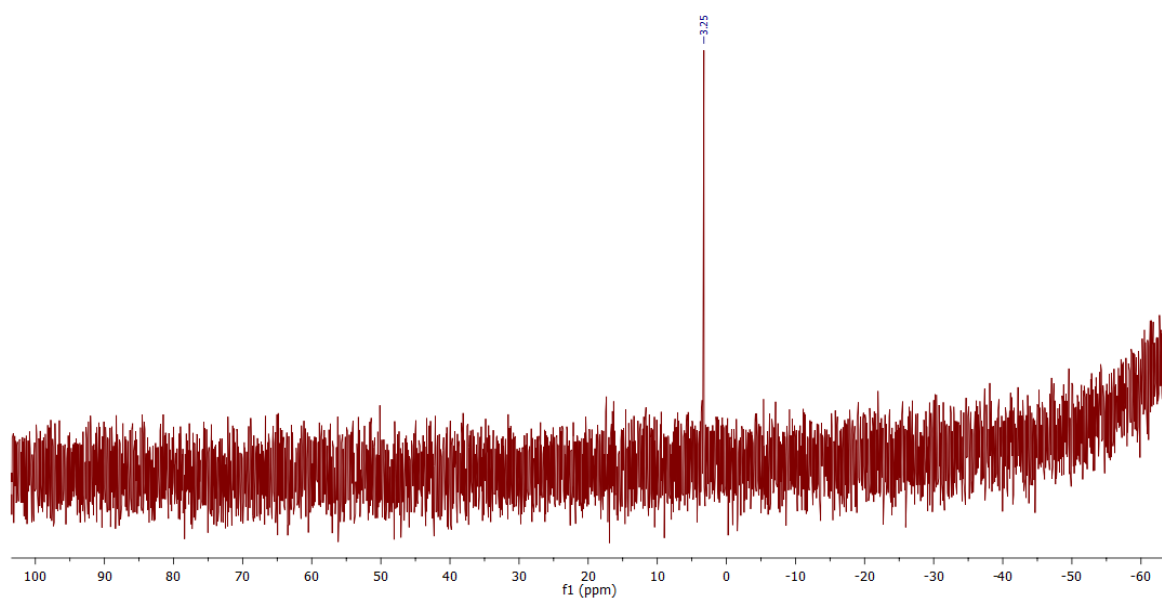
$[(\text{IPr}^*)\text{Pt}(\text{dvtms})]$



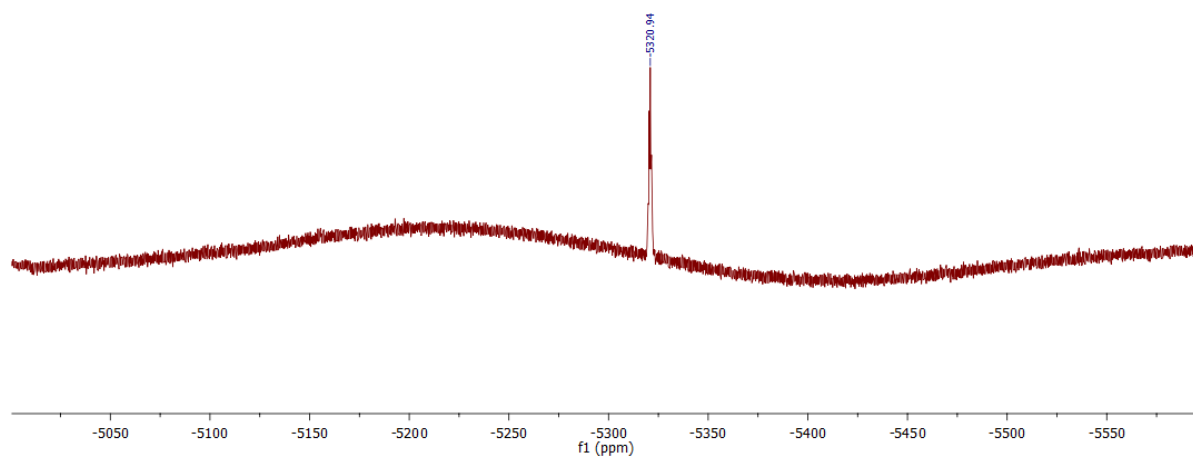
^{13}C NMR (CDCl_3 , δ , ppm)



^{29}Si NMR (CDCl_3 , δ , ppm)

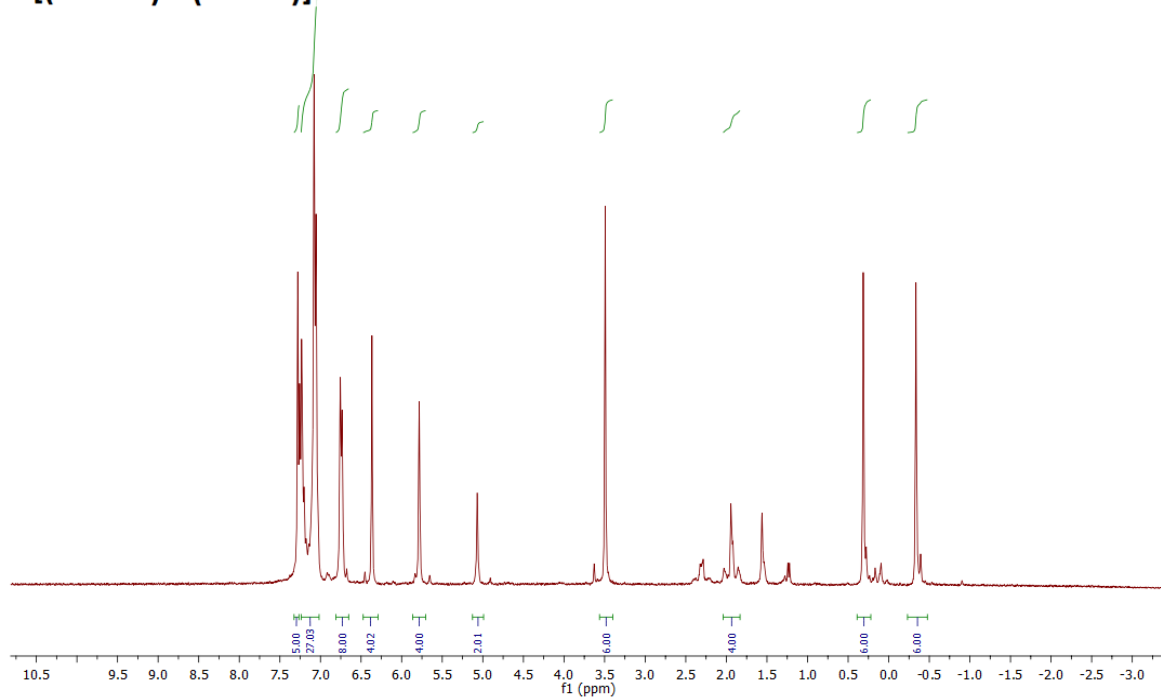


^{195}Pt NMR (CDCl_3 , δ , ppm)

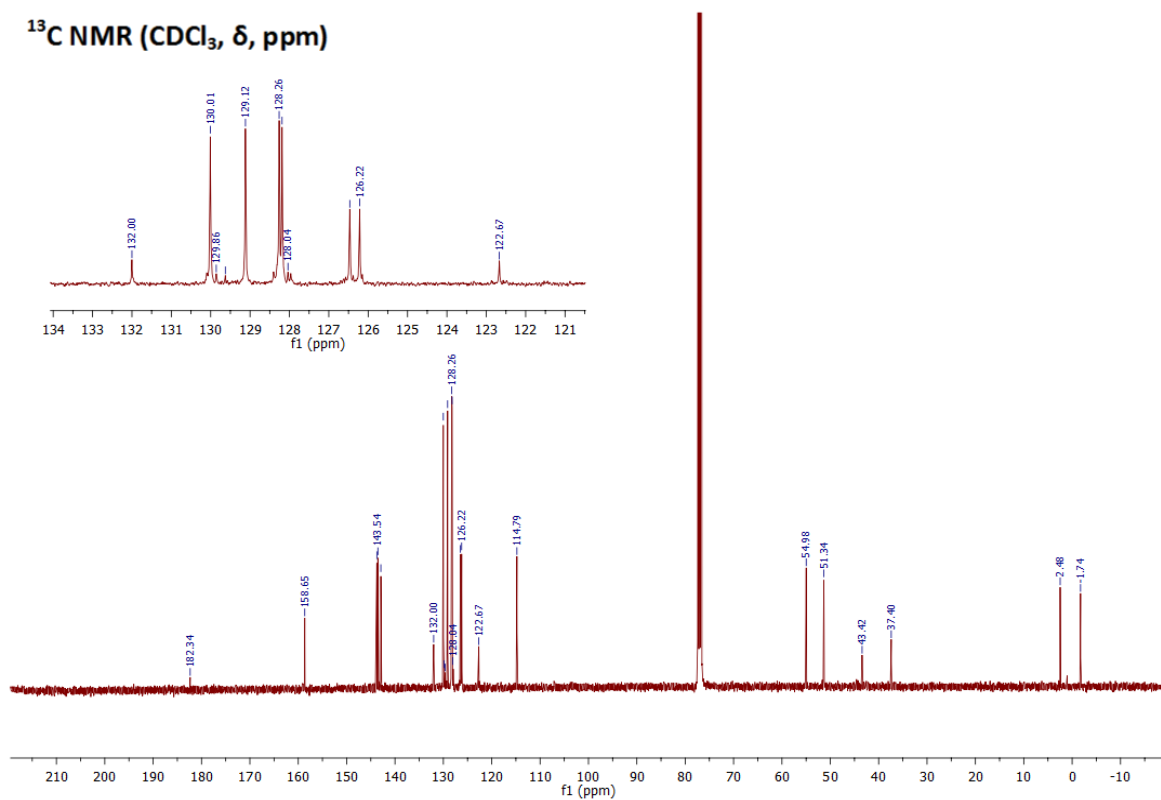


^1H NMR (CDCl_3 , δ , ppm)

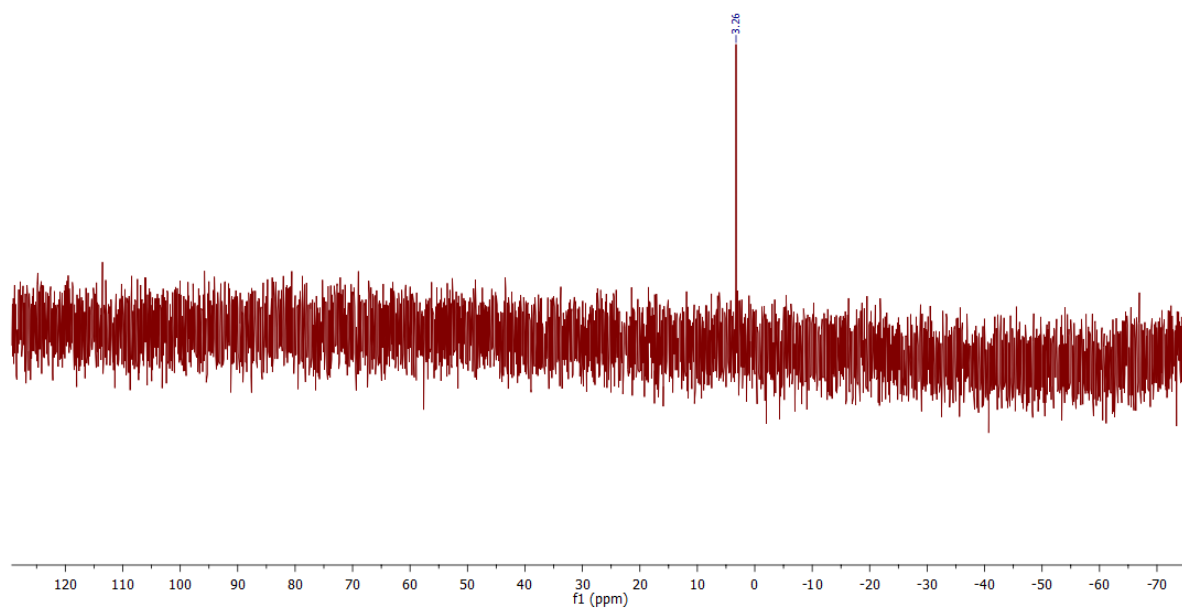
$[(\text{IPr}^*-\text{OMe})\text{Pt}(\text{dvtms})]$



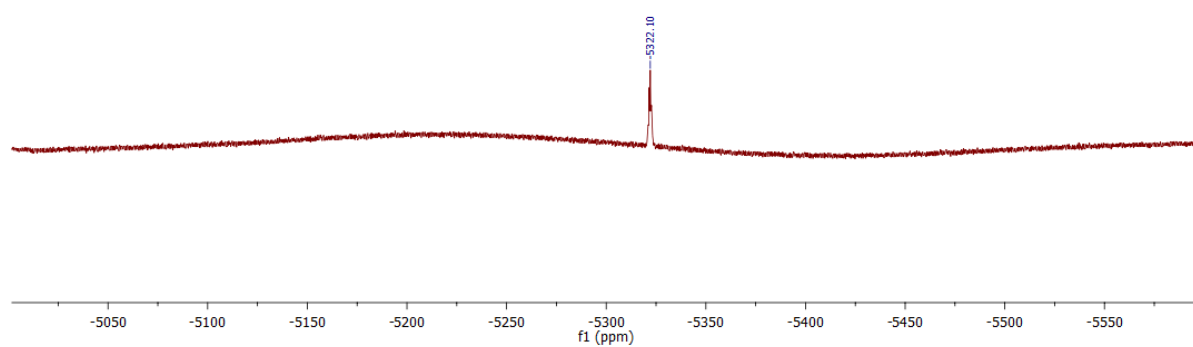
^{13}C NMR (CDCl_3 , δ , ppm)



^{29}Si NMR (CDCl_3 , δ , ppm)



^{195}Pt NMR (CDCl_3 , δ , ppm)



4. The study of catalytic performance of catalyst 2 in hydrosilylation of olefins and acetylenes

Table S1 Hydrosilylation of terminal alkenes in the presence of complex 2

Entry	Olefin	HSiR ₃	2 [mol%]	Time [h]	Yield ^[a] [%]
1	3a	4b	5×10 ⁻³	2	98 ^[b]
2		4c	5×10 ⁻³	7	98
3		4d	5×10 ⁻³	8	96 ^[b]
4		4a	1×10 ⁻⁴	6	98
5		4e	1×10 ⁻¹	24	98
6	3b	4b	1×10 ⁻⁴	9	97 ^[b]
7		4c	5×10 ⁻³	24	98
8		4d	1×10 ⁻³	24	99 ^[b]
9		4a	1×10 ⁻⁵	24	97
10		4e	1×10 ⁻¹	24	93
11	3c	4b	1×10 ⁻³	5	99 ^[b]
12		4c	5×10 ⁻³	3	97
13		4d	1×10 ⁻⁴	8	99 ^[b]
14		4a	1×10 ⁻⁵	3	97
15		4e	1×10 ⁻¹	24	94
16	3d	4b	1×10 ⁻⁴	8	99 ^[b]
17		4c	5×10 ⁻³	24	99
18		4d	1×10 ⁻³	24	97 ^[b]
19		4a	1×10 ⁻⁵	24	99
20		4e	1×10 ⁻¹	24	95
21	3e	4b	5×10 ⁻⁴	4	99 ^[b]
22		4c	5×10 ⁻³	24	91
23		4d	1×10 ⁻⁴	24	88 ^[b]
24		4e	1×10 ⁻¹	24	95
25	3f	4b	5×10 ⁻³	11	98 ^[b]
26		4c	5×10 ⁻³	10	97
27		4d	5×10 ⁻³	24	98 ^[b]
28		4e	1×10 ⁻¹	24	82
29	3g	4a	1×10 ⁻³	24	100
30		4e	1×10 ⁰	24	87
31	3h	4b	5×10 ⁻⁴	9	99 ^[b]
32		4c	5×10 ⁻⁴	10	99
33		4a	1×10 ⁻⁵	8	99
34		4e	1×10 ⁻¹	24	99
35	3i	4b	5×10 ⁻⁴	3	98 ^[b]
36		4c	5×10 ⁻⁴	3	98
37		4d	5×10 ⁻⁴	9	99 ^[b]
38		4e	1×10 ⁻¹	24	96
39	3j	4b	1×10 ⁻³	4	98 ^[b]
40		4c	1×10 ⁻³	4	98
41		4a	2×10 ⁻⁴	8	96
42		4e	1×10 ⁻¹	24	99

Reaction conditions: toluene, 80°C, argon, [olefin]:[silane] = 1:1; ^[a] Determined by GC analysis; ^[b] Reaction performed in closed system

Table S2 Hydrosilylation of terminal arylacetylenes in the presence of complex **2**

Entry	R'C≡CH	HSiR ₃	2 [mol%]	Time [h]	Yield ^[a] [%]	Selectivity ^[b] β-(E):β-(Z):α
1	7a	4a	5×10 ⁻²	3	100	98:2:0
2		4d	5×10 ⁻²	9	98	96:3:1 ^[c]
3		4e	1×10 ⁻¹	24	90	100:0:0
4	7b	4a	5×10 ⁻²	7	98	100:0:0
5		4d	5×10 ⁻²	9	97	98:2:0 ^[c]
6		4e	1×10 ⁻¹	24	100	100:0:0
7	7c	4a	5×10 ⁻²	7	99	99:1:0
8		4d	5×10 ⁻²	8	98	97:2:1 ^[c]
9		4e	1×10 ⁻¹	24	97	100:0:0
10	7d	4a	5×10 ⁻²	7	99	98:1:1
11		4d	5×10 ⁻²	24	90	96:2:2 ^[c]
12		4e	1×10 ⁻¹	24	98	100:0:0
13	7e	4a	5×10 ⁻²	10	98	98:1:1
14		4d	1×10 ⁻²	10	96	96:2:2 ^[c]
15		4e	1×10 ⁻¹	24	96	100:0:0
16	7f	4a	5×10 ⁻²	10	100	100:0:0
17		4b	5×10 ⁻²	12	96	100:0:0 ^[c]
18		4c	1×10 ⁻²	12	93	100:0:0
19		4d	5×10 ⁻²	10	96 ^[c]	100:0:0 ^[c]
20		4e	5×10 ⁻²	24	55	100:0:0
21		4e	1×10 ⁻¹	24	99	100:0:0

Reaction conditions: toluene, 40°, [acetylene]:[silane] = 1:1; ^[a] Determined by GC analysis; ^[b] β-(E):β-(Z):α determined by GC analysis and confirmed by ¹H NMR spectroscopy of the crude reaction mixture; ^[c] Reaction performed in closed system

Table S3 Hydrosilylation of terminal silylacetylenes in the presence of complex **2**

Entry	R ₃ SiC≡CH	HSiR' ₃	Isolated yield [%]
1	7g	4a	89
2	7g	4e	97
3	7h	4a	95
4	7h	4b	93
5	7i	4a	91
6	7i	4b	95
7	7j	4a	93

Reaction conditions: toluene, 40°C, [acetylene]:[silane] = 1:1, cat. **2** (10⁻² mol%), 6-24 h

Table S4 Hydrosilylation of symmetrically substituted internal acetylenes in the presence of complex **2**

Entry	R'C≡CHR'	HSiR ₃	2 [mol%]	Time [h]	Yield ^[a] [%]
1	10a	4a	5×10 ⁻²	7	100
2		4b	5×10 ⁻²	9	99 ^[b]
3		4c	5×10 ⁻²	9	100
4		4d	5×10 ⁻²	10	100 ^[b]
5		4e	1×10 ⁻¹	24	70
6		4e	1	24	100
7	10b	4a	5×10 ⁻²	12	100
8		4b	5×10 ⁻²	18	97 ^[b]
9		4c	5×10 ⁻²	7	96
10		4d	5×10 ⁻²	8	99 ^[b]
11		4e	1×10 ⁻¹	24	100
12	10c	4a	5×10 ⁻²	8	100
13		4b	5×10 ⁻²	6	98 ^[b]
14		4c	5×10 ⁻²	7	97
15		4d	5×10 ⁻²	8	95 ^[b]
16		4e	1×10 ⁻¹	24	94

Reaction conditions: toluene, 90°C, [acetylene]:[silane]= 1:1; ^[a] Determined by GC analysis; ^[b] Reaction performed in closed system

Table S5 Hydrosilylation of 1-aryl-2-trimethylsilylacetylene with trisubstituted silanes in the presence of complex **2**

Entry	ArC≡CSiMe ₃	HSiR ₃	2 [mol%]	Time [h]	Yield ^[a] [%]
1	12a	4a	1×10 ⁻¹	24	99 ^[b]
2		4b	1×10 ⁻¹	24	100
3		4c	1×10 ⁻¹	24	95 ^[b]
4		4d	1×10 ⁻¹	16	97
5		4e	1×10 ⁻¹	24	97
6	12b	4a	5×10 ⁻²	20	99 ^[b]
7		4b	5×10 ⁻²	18	97
8		4c	5×10 ⁻²	12	98 ^[b]
9		4d	5×10 ⁻²	18	100
10		4e	5×10 ⁻²	24	97

Reaction conditions: toluene, 90°C, [acetylene]:[silane] = 1:1; ^[a] Determined by GC analysis; ^[b] Reaction performed in closed system

5. Study of the influence of steric properties of catalysts on the reaction selectivity

Table S6 Hydrosilylation of **12a** with **4c** in the presence of catalyst **15**, **1** and **2**.

Cat	A _H	%V _{bur}	Reaction time [h]	Conversion [%]	Selectivity ^[b] β-(E):β-(Z):α
15	97	- (for SIPr 46.6)	5	99	10:0:1 (ca 91:0:9)
1	201.6	50.9	1	100	100:0:0
2	213.4	52.8	1	100	100:0:0

Reaction conditions taken from reference 13f: reaction performed on 3 mmol scale, solventless, 60°C, [silane]:[acetylene] = 1.1:1; cat. (1 mol%)

Table S7 Hydrosilylation of **7a** with **4c** in the presence of catalyst **15**, **1** and **2**.

Cat	A _H	%V _{bur}	Reaction time [h]	Conversion [%]	Selectivity ^[b] β-(E):β-(Z):α
15	97	- (for SIPr 46.6)	7	95	12:0:1 (ca 92:0:8)
1	201.6	50.9	4	100	99:0:1
2	213.4	52.8	5	100	99:0:1

Reaction conditions taken from reference 13f: reaction performed on 3 mmol scale, solventless, 60°C, [silane]:[acetylene] = 1.1:1; cat. (1 mol%)

6. Mercury poisoning experiment

An oven dried 5 mL glass reactor equipped with a condenser and stirring bar was charged under argon with 1 mL toluene, 26.5 μL phenyl propargyl ether **3j** (1.94×10^{-4} mol), 30 μL, dimethylphenylsilane **4a** (1.94×10^{-4} mol) and 15 μL decane. The reaction mixture was warmed up in an oil bath to 80 °C and platinum complex **1** (0.0025 mg, 1.94×10^{-9} mol) was added to the mixture under argon. The reaction was heated with stirring at 80 °C for 30 minutes. Then the conversion of substrates was measured by using gas chromatography and Hg (1000 equiv. in relation to catalyst) was added. The reaction was carried out at 80 °C upon vigorous stirring for 24 h. Reaction course was monitored by gas chromatography.

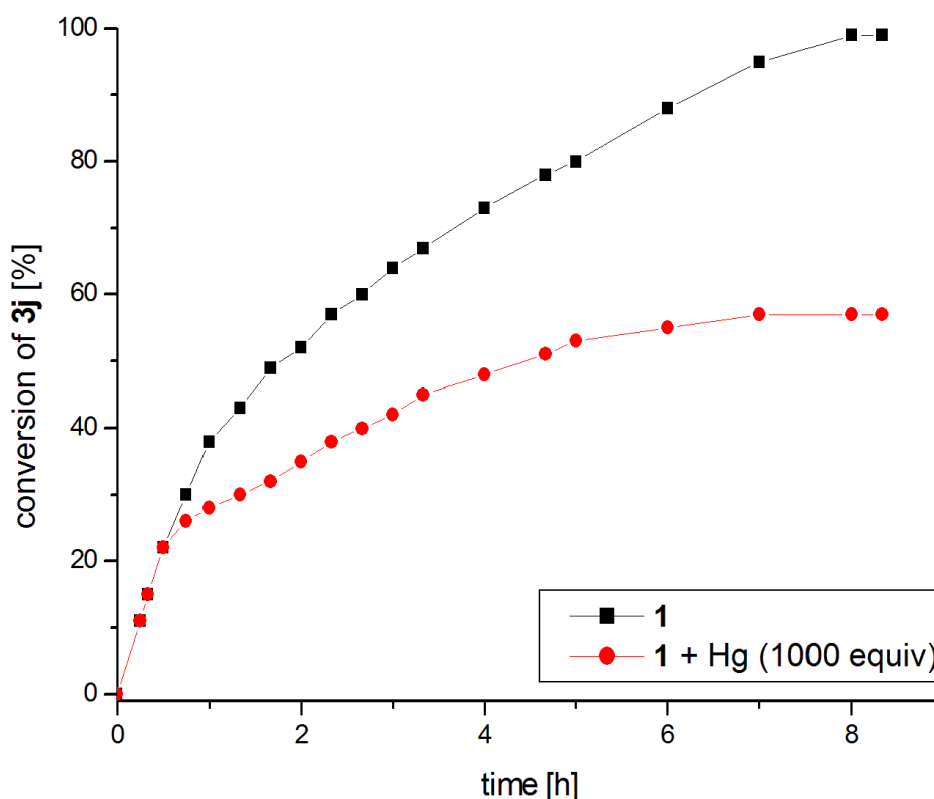


Figure S1 Mercury poisoning experiment. Profiles of the hydrosilylation of phenyl propargyl ether (**3j**) with dimethylphenylsilane (**4a**) performed in the presence of complex **1** with and without addition of mercury excess.

7. Hot filtration test

A 5 mL glass reactor was charged under argon with 1 mL toluene, 26.5 μL phenyl propargyl ether **3j** (1.94×10^{-4} mol), 30 μL dimethylphenylsilane **4a** (1.94×10^{-4} mol) and 15 μL decane. The reaction mixture was warmed up to 80 $^{\circ}\text{C}$ in an oil bath and platinum complex **1** (0.0025 mg, 1.94×10^{-9} mol) was added. The reaction was carried out for 30 minutes. After this time, the hot solution was filtered under argon on the pad of silica gel to a new Schlenk vessel and the reaction was continued. The silica gel from filtration was transferred to a second Schlenk vessel, which was then charged with 1 mL toluene, 26.5 μL phenyl propargyl ether **3j** (1.94×10^{-4} mol), 30 μL dimethylphenylsilane **4a** (1.94×10^{-4} mol) and 15 μL decane. The reaction was carried out in 80 $^{\circ}\text{C}$. Conversion of the substrates in both reactions was observed by gas chromatography.

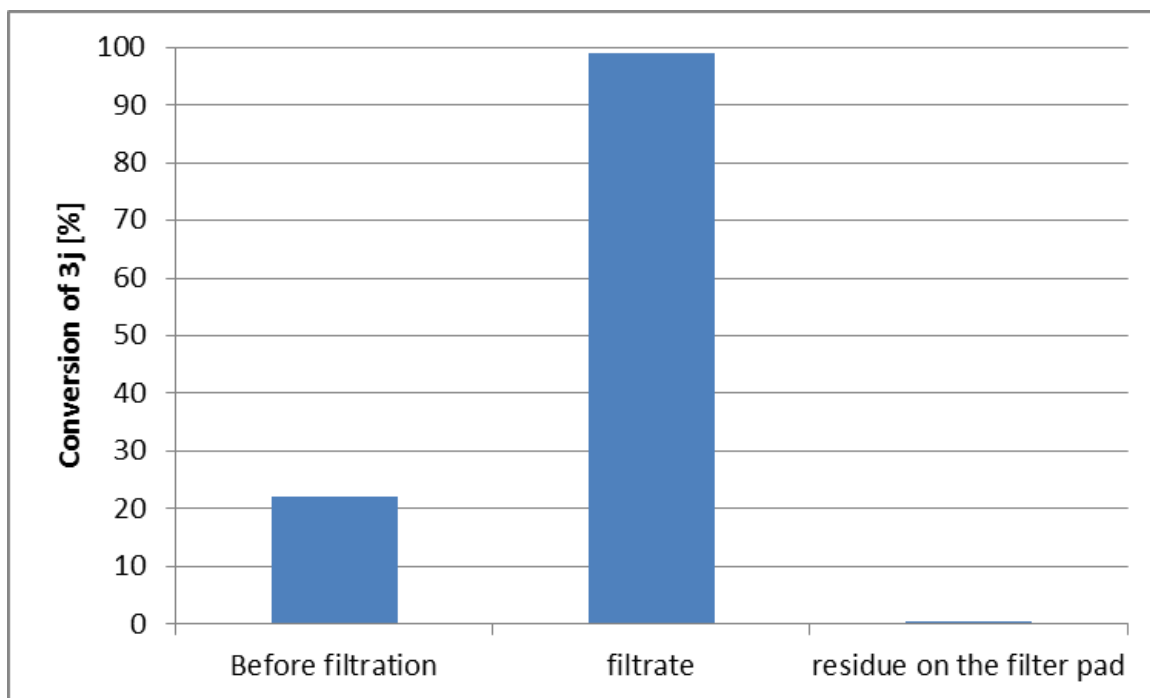


Figure S2 Hot filtration test. hydrosilylation of phenyl propargyl ether (**3j**) with dimethylphenylsilane (**4a**) performed in the presence of complex **1**. Reaction conditions: toluene, 80 °C, **1** (0.001 mol%)

8. The study of the productivity of catalyst **1**

A 10 mL high-pressure Schlenk vessel connected to gas and vacuum line was charged under argon with 30 μL (dimethylphenylsilyl)acetylene **7j** (1.70×10^{-4} mol), 26.3 μL dimethylphenylsilane **4a** (1.70×10^{-4} mol), 15 μL decane and 1 mL toluene. The reaction mixture was warmed up in an oil bath to 40 °C and platinum complex **1** (1.7×10^{-8} mol) was added to the mixture under argon. The progress of the reaction was monitored by gas chromatography (GC) and the reaction mixture was heated until complete conversion of substrates was detected (3 h). Then the next portion of substrates (**7j** and **4a**) was added and the reaction was carried out to achieve a total conversion of substrates again. The above procedure was repeated

9. Analytical data of isolated products

Hydrosilylation of olefins

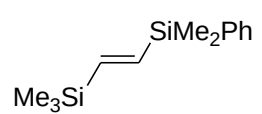

 ^1H NMR (CDCl_3 , δ , ppm): 0.29 (s, 6H, $\text{Si}(\text{CH}_3)_3$), 0.74 – 0.79 (m, 2H, $\text{CH}_2\text{SiMe}_2\text{Ph}$), 1.58 – 1.67 (m, 2H, $\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$), 2.59 (dd, 1H, $J_{\text{HH}} = 5.1$ Hz, 2.7 Hz, $>\text{CH}_2$), 2.79 (dd, 1H, $J_{\text{HH}} = 5.0$ Hz, 4.2 Hz, $>\text{CH}_2$), 3.10 – 3.15 (m, 1H, $>\text{CH}$), 3.36 (dd, 1H, 11.5 Hz, 5.8 Hz,

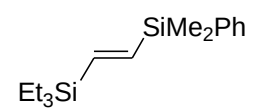
$H_2C-O-CH_2$), 3.39 – 3.50 (m, 2H, $H_2C-O-CH_2$), 3.68 (dd, 1H, 11.5 Hz, 3.1 Hz, $H_2C-O-CH_2$), 7.33 – 7.38 (m, 3H, C_6H_5), 7.50 – 7.54 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, δ , ppm): 0.99 (s, $Si(CH_3)_3$), 11.65, 23.95, 44.29, 50.80, 71.32, 74.24, 127.70, 128.78, 133.49, 139.06.

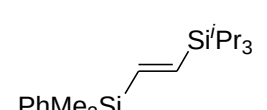
$PhMe_2Si(CH_2)_3CH_2OH$ 1H NMR ($CDCl_3$, δ , ppm): 0.3 (s, 6H, $Si(CH_3)_3$), 0.75 – 0.82 (m, 2H, CH_2SiMe_2Ph), 1.32 – 1.41 (m, 6H, $(CH_2)_3CH_2OH$), 1.52 – 1.60 (m, 2H, $CH_2CH_2SiMe_2Ph$), 1.98 (s, 1H, OH), 3.62 (t, 2H, $J_{HH} = 6.7$ Hz, CH_2OH), 7.36 – 7.4 (m, 3H, Ph), 7.53 – 7.57 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, δ , ppm): -3.11 (s, $Si(CH_3)_3$), 15.56, 23.73, 25.28, 32.54, 33.22, 68.78 (CH_2OH), 127.60, 128.65, 133.43, 139.51

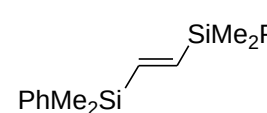
$Me-Si(CH_2)_{11}CH_3$ with $OSiMe_3$ groups at both ends
 1H NMR ($CDCl_3$, δ , ppm): 0.01 (s, 3H, $SiCH_3$), 0.09 (s, 18H, $Si(CH_3)_3$), 0.43 – 0.5 (m, 2H, $SiCH_2-$), 0.89 (t, 3H, $J_{HH} = 6.9$ Hz, $-CH_2CH_3$), 1.21 – 1.35 (m, 20H, $-(CH_2)_9CH_3$); ^{13}C NMR ($CDCl_3$, δ , ppm): -0.25 ($SiCH_3$), 1.04, 1.86, 14.12, 17.66, 22.72, 23.11, 29.40, 29.42, 29.64, 29.70, 29.75, 31.97, 33.28

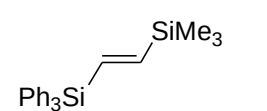
Hydrosilylation of terminal acetylenes

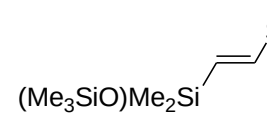

¹H NMR (CDCl₃, δ, ppm): 0.14 (s, 9H, Si(CH₃)₃), 0.40 (s, 6H, Si(CH₃)₂Ph), 6.77 (s, 2H, =CH₂), 7.38 – 7.43 (m, 3H, Ph), 7.55 – 7.60 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ, ppm): -2.87 (Si(CH₃)₂Ph), -1.58 (Si(CH₃)₃), 127.75, 128.89, 133.89, 138.79, 148.03, 153.03


¹H NMR (CDCl₃, δ, ppm): 0.38 (s, 6H, Si(CH₃)₂Ph), 0.64 (q, 6H, J_{HH} = 7.5 Hz, SiCH₂CH₃), 0.98 (t, 9H, J_{HH} = 7.9 Hz, SiCH₂CH₃), 6.69 (d, 1H, J_{HH} = 22.7 Hz, =CH₂), 6.80 (d, 1H, J_{HH} = 22.7 Hz, =CH₂), 7.36 – 7.41 (m, 3H, Ph), 7.53 – 7.58 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ, ppm): -2.83 (Si(CH₃)₂Ph), 3.19 (SiCH₂CH₃), 7.36 (SiCH₂CH₃), 127.71, 128.83, 133.86, 138.89, 149.53, 149.91

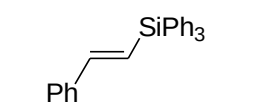

¹H NMR (CDCl₃, δ, ppm): 0.37 (s, 6H, Si(CH₃)₂), 1.05 – 1.1 (m, 18H, iPr), 1.11 – 1.2 (m, 3H, SiCH<), 6.66 (d, 1H, J_{HH} = 22.9 Hz, =CH), 6.82 (d, 1H, J_{HH} = 22.9 Hz, =CH), 7.35 – 7.40 (m, 3H, Ph), 7.52 – 7.57 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ, ppm): -2.77 (Si(CH₃)₂Ph), 10.68, 18.64, 127.70, 128.82, 133.86, 138.93, 147.60, 150.97

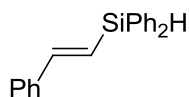

¹H NMR (CDCl₃, δ, ppm): 0.37 (s, 12H, Si(CH₃)₂Ph), 6.84 (s, 2H, =CH₂), 7.36 – 7.39 (m, 6H, Ph), 7.52 – 7.55 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ, ppm): -2.93 (Si(CH₃)₂Ph), 127.74, 128.92, 133.87, 138.55, 150.32


¹H NMR (CDCl₃, δ, ppm): 0.16 (s, 9H, Si(CH₃)₃), 6.87 (d, 1H, J_{HH} = 22.4 Hz, =CH), 7.14 (d, 1H, J_{HH} = 22.4 Hz, =CH), 7.37 – 7.47 (m, 9H, Ph), 7.52 – 7.59 (m, 6H, Ph); ¹³C NMR (CDCl₃, δ, ppm): 1.58 (Si(CH₃)₃), 127.85, 129.49, 134.52, 136.03, 143.36, 157.81


¹H NMR (CDCl₃, δ, ppm): 0.09 (overlapping s, 15H, Si(CH₃)₂(OSi(CH₃)₃), 0.58 (q, 6H, J_{HH} = 7.6 Hz, SiCH₂CH₃), 0.94 (t, 9H, J_{HH} = 7.9 Hz, SiCH₂CH₃), 6.43 (d, 1H, J_{HH} = 22.9 Hz, =CH), 6.63 (d, 1H, J_{HH} = 22.9 Hz, =CH); ¹³C NMR (CDCl₃, δ, ppm): -0.75, 1.84, 3.07 (SiCH₂CH₃), 7.31 (SiCH₂CH₃), 148.67, 149.49

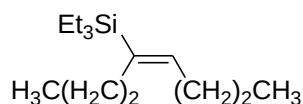

¹H NMR (CDCl₃, δ, ppm): 0.10 (overlapping s, 18H, Si(CH₃)₂(OSi(CH₃)₃) and SiCH<), 0.98 – 1.19 (m, 18H, iPr), 6.47 (d, 1H, J_{HH} = 23.1 Hz, =CH), 6.61 (d, 1H, J_{HH} = 23.1 Hz, =CH); ¹³C NMR (CDCl₃, δ, ppm): -0.64, 1.87, 10.67, 18.58, 146.62, 150.81


¹H NMR (CDCl₃, δ, ppm): 6.90 (s, 2H, =CH), 7.17 – 7.24 (m, 2H, Ph), 7.27 – 7.44 (m, 12H, Ph); ¹³C NMR (CDCl₃, δ, ppm): 122.93, 126.78, 127.93, 128.53, 128.57, 129.62, 134.47, 136.04, 138.03, 148.88

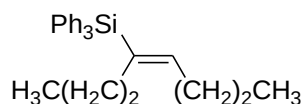


^1H NMR (CDCl_3 , δ , ppm): 5.16 (d, 1H, $J_{\text{HH}} = 3.1\text{ Hz}$, SiH), 6.61 (dd, 1H, $J_{\text{HH}} = 19.0, 3.2\text{ Hz}$, $=\text{CHSi}$), 6.99 (d, $J_{\text{HH}} = 19.0\text{ Hz}$, $=\text{CH}$), 7.12 – 7.27 (m, 7H, Ph), 7.31 – 7.37 (m, 3H, Ph), 7.45 – 7.55 (m, 5H, Ph); ^{13}C NMR (CDCl_3 , δ , ppm): 121.62, 126.85, 128.19, 128.69, 129.90, 133.70, 135.65, 137.93, 149.25

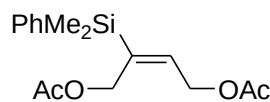
Hydrosilylation of internal acetylenes



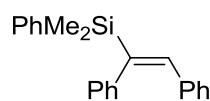
^1H NMR (CDCl_3 , δ , ppm): 0.57 (q, 6H, $J_{\text{HH}} = 7.6\text{ Hz}$, SiCH_2CH_3), 0.87 – 0.94 (m, 15H, CH_3), 1.24 – 1.45 (m, 4H, $(\text{CH}_2)_2\text{CH}_3$), 2.00 – 2.14 (m, 4H, $(\text{CH}_2)_2\text{CH}_3$), 5.67 (t, 1H, $J_{\text{HH}} = 6.9\text{ Hz}$, $=\text{CH}$); ^{13}C NMR (CDCl_3 , δ , ppm): 3.16 (SiCH_2CH_3), 7.44 (SiCH_2CH_3), 13.85 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 14.56 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.81 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 23.41 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 30.47 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 32.27 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 137.37 ($=\text{CH}$), 141.87



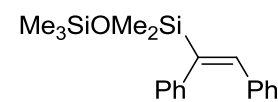
^1H NMR (CDCl_3 , δ , ppm): 0.86 (t, 3H, $J_{\text{HH}} = 7.3\text{ Hz}$, $(\text{CH}_2)_2\text{CH}_3$), 1.07 (t, 3H, $J_{\text{HH}} = 7.3\text{ Hz}$, $(\text{CH}_2)_2\text{CH}_3$), 1.22 – 1.33 (m, 2H, $(\text{CH}_2)_2\text{CH}_3$), 1.51 – 1.61 (m, 2H, $(\text{CH}_2)_2\text{CH}_3$), 2.33 – 2.40 (m, 4H, $(\text{CH}_2)_2\text{CH}_3$), 6.14 (t, 1H, $J_{\text{HH}} = 7.0\text{ Hz}$, $=\text{CH}$), 7.44 – 7.54 (m, 9H, C_6H_5), 7.69 – 7.73 (m, 6H, C_6H_5); ^{13}C NMR (CDCl_3 , δ , ppm): 13.99 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 14.37 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.66 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 23.38 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 31.07 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 32.51 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 127.61, 129.20, 135.00, 135.19, 136.32 ($=\text{CH}$), 147.33



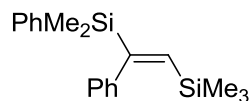
^1H NMR (CDCl_3 , δ , ppm): 0.41 (s, 6H, $\text{SiPh}(\text{CH}_3)_2$), 1.83 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 4.72 – 4.77 (m, 4H, $-\text{CH}_2\text{O}-$), 6.01 (tt, 1H, $J_{\text{HH}} = 5.8\text{ Hz}, 1.4\text{ Hz}$, $=\text{CH}$), 7.32 – 7.38 (m, 3H, $-\text{C}_6\text{H}_5$), 7.46 – 7.51 (m, 2H, $-\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , δ , ppm): -2.84 ($\text{SiPh}(\text{CH}_3)_2$), 1.0 ($\text{SiPh}(\text{CH}_3)_2$), 20.62 (CH_3), 29.91 (CH_3), 61.40 ($-\text{CH}_2\text{O}-$), 62.70 ($-\text{CH}_2\text{O}-$), 127.79, 129.16, 132.95, 133.81, 137.26, 138.36, 138.69, 170.25 ($\text{C}=\text{O}$), 170.75 ($\text{C}=\text{O}$)



^1H NMR (CDCl_3 , δ , ppm): 0.51 (s, 6H, $\text{SiPh}(\text{CH}_3)_2$), 6.95 (s, 1H, $=\text{CH}$), 7.0 – 7.07 (m, 4H, Ph), 7.15 – 7.18 (m, 3H, Ph), 7.27 – 7.36 (m, 3H, Ph), 7.44 – 7.48 (m, 3H, Ph), 7.64 – 7.68 (m, 2H, Ph); ^{13}C NMR (CDCl_3 , δ , ppm): -3.08 ($\text{SiPh}(\text{CH}_3)_2$), 125.69, 127.14, 127.61, 127.72, 127.86, 128.5, 129.07, 129.51, 134.24, 137.18, 137.64, 139.17, 142.26, 144.96.

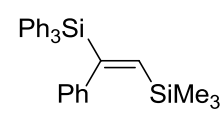


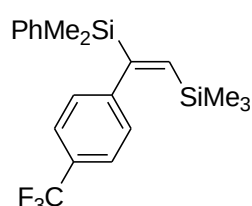
^1H NMR (CDCl_3 , δ , ppm): 0.1 (s, 9H, $\text{OSi}(\text{CH}_3)_3$), 0.19 (s, 6H, SiCH_3), 6.91 (s, 1H, $=\text{CH}$), 6.98 – 7.02 (m, 2H, Ph), 7.04 – 7.06 (m, 2H, Ph), 7.09 – 7.13 (m, 3H, Ph), 7.19 – 7.24 (m, 1H, Ph), 7.28 – 7.33 (m, 2H, Ph); ^{13}C NMR (CDCl_3 , δ , ppm): 0.15 ($\text{OSi}(\text{CH}_3)_3$), 1.92 (CH_3), 125.66, 127.08, 127.64, 127.86, 128.52, 129.53, 137.22, 137.62, 141.96, 146.39



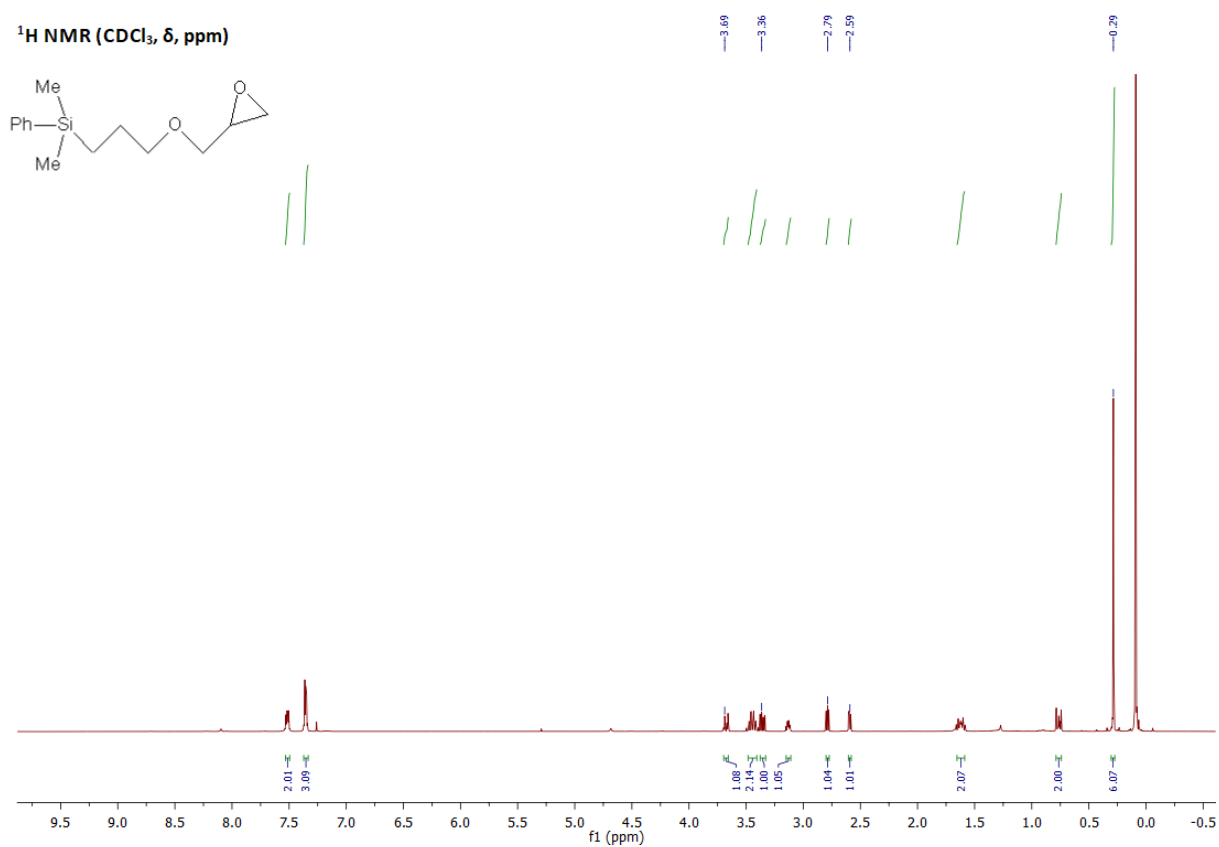
^1H NMR (CDCl_3 , δ , ppm): -0.21 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.31 (s, 6H, $\text{SiPh}(\text{CH}_3)_2$), 6.39 (s, 1H, $=\text{CH}$), 6.84 – 6.80 (m, 2H, $-\text{C}_6\text{H}_5$), 7.11 – 7.20 (m, 3H, $-\text{C}_6\text{H}_5$), 7.29 – 7.33 (m, 3H, $-\text{C}_6\text{H}_5$), 7.43 – 7.47 (m, 2H,

-C₆H₅); ¹³C NMR (CDCl₃, δ, ppm): -3.06 (SiPh(CH₃)₂), 0.01 (Si(CH₃)₃), 125.66, 127.47 (d, *J* = 2.0 Hz), 127.60, 128.89, 134.13, 137.88, 144.99, 146.13, 164.11.

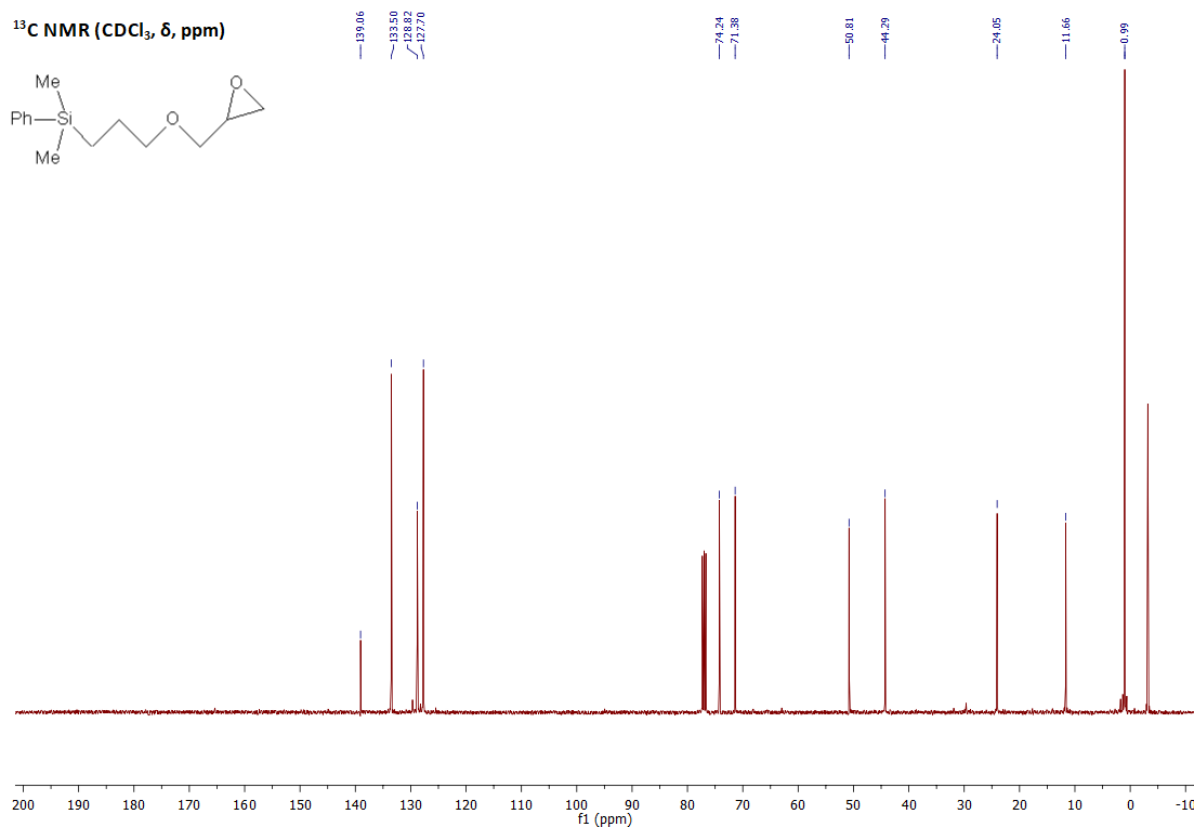
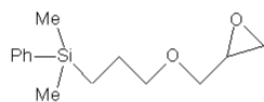
 ¹H NMR (CDCl₃, δ, ppm): -0.17 (s, 3H, CH₃), 6.62 (s, 1H, =CH), 6.81 – 6.86 (m, 2H, C₆H₅), 7.09 – 7.13 (m, 2H, C₆H₅), 7.28 – 7.33 (m, 6H, C₆H₅), 7.37 – 7.42 (m, 10H, C₆H₅); ¹³C NMR (CDCl₃, δ, ppm): -0.04 (CH₃), 125.88, 127.42, 127.58, 128.11, 129.35, 133.94, 136.46, 144.56, 151.42, 159.46.

 ¹H NMR (CDCl₃, δ, ppm): -0.15 (s, 9H, Si(CH₃)₃), 0.38 (s, 6H, SiPh(CH₃)₂), 6.51 (s, 1H, =CH), 6.97 (dd, *J*_{HH} = 8.6 Hz, 0.7 Hz, 2H, C₆H₄-CF₃), 7.34 – 7.43 (m, 4H, C₆H₄-CF₃ and C₆H₅), 7.46 – 7.51 (m, 3H, C₆H₅); ¹³C NMR (CDCl₃, δ, ppm): -3.28 (SiPh(CH₃)₂), -0.04 (Si(CH₃)₃), 124.47 (q, *J* = 3.8 Hz, CF₃), 127.72, 127.76, 129.16, 134.07, 137.14, 147.06, 148.89, 148.90, 155.25, 162.95

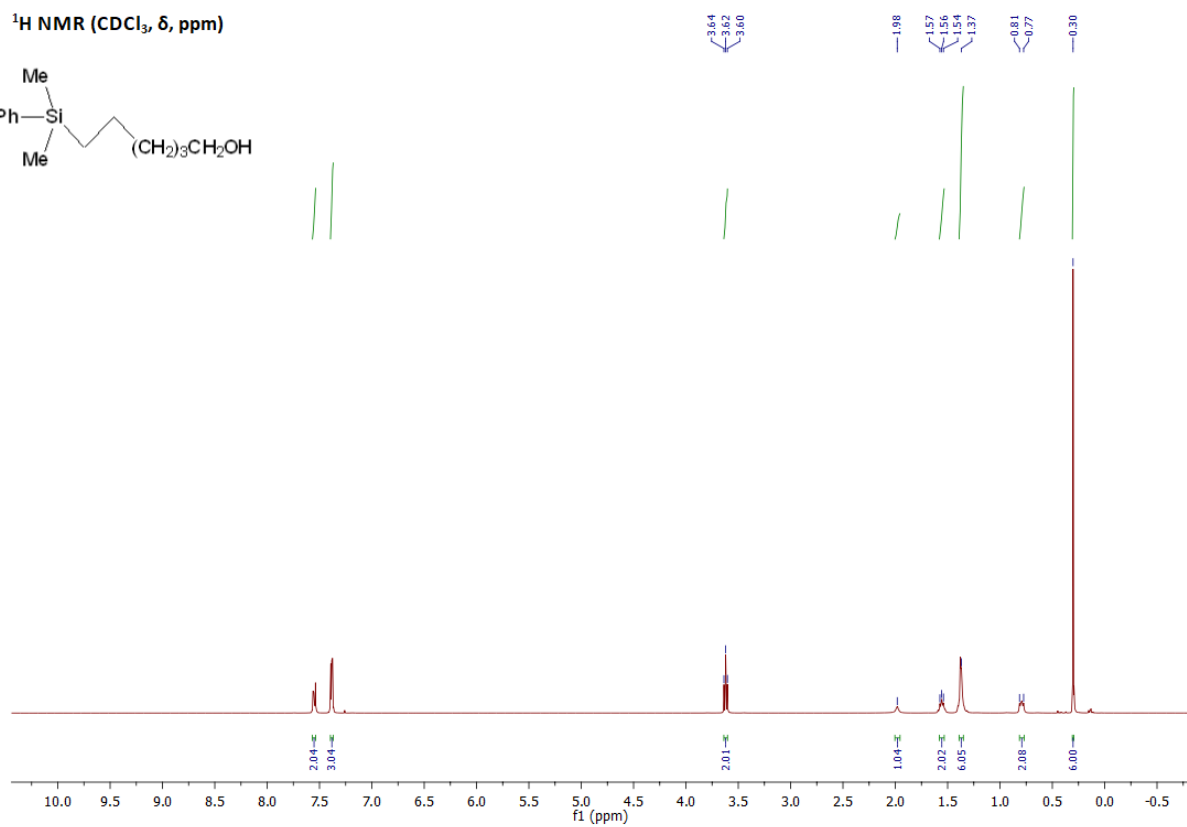
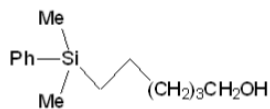
10. NMR spectra of isolated products



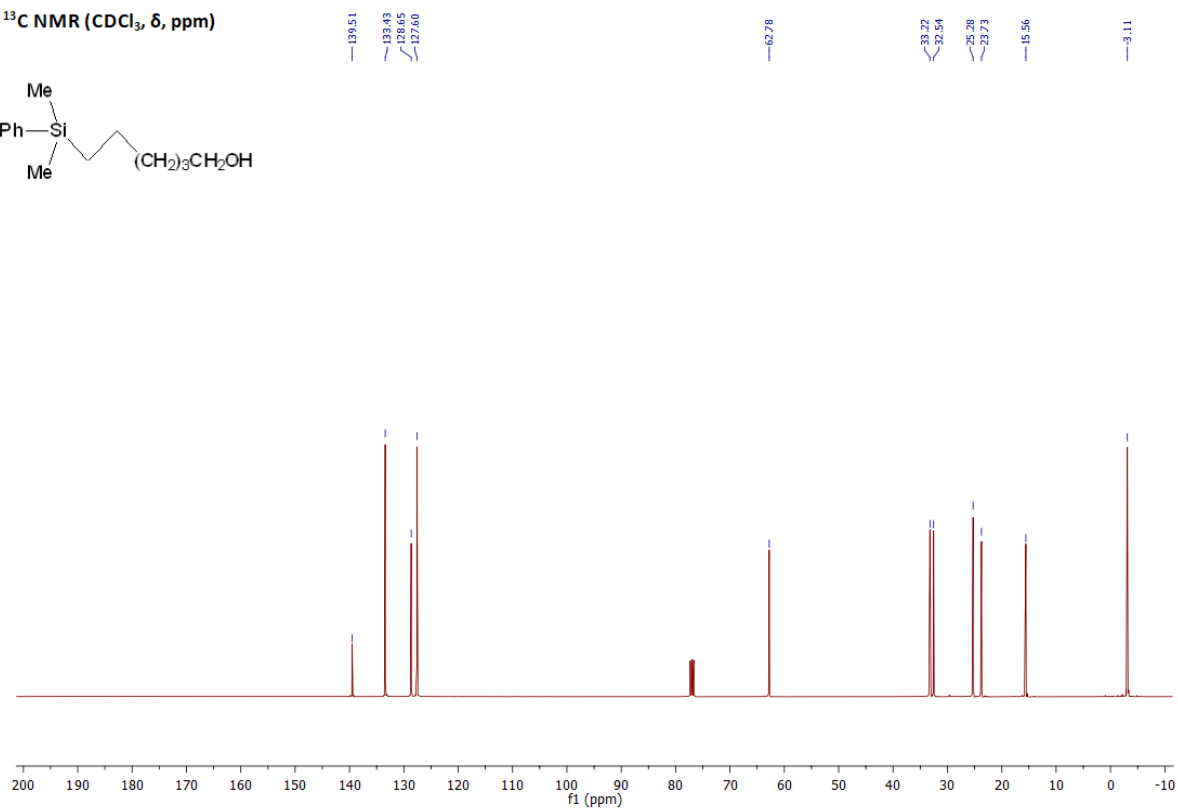
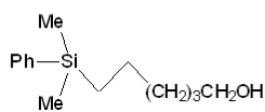
¹³C NMR (CDCl₃, δ, ppm)



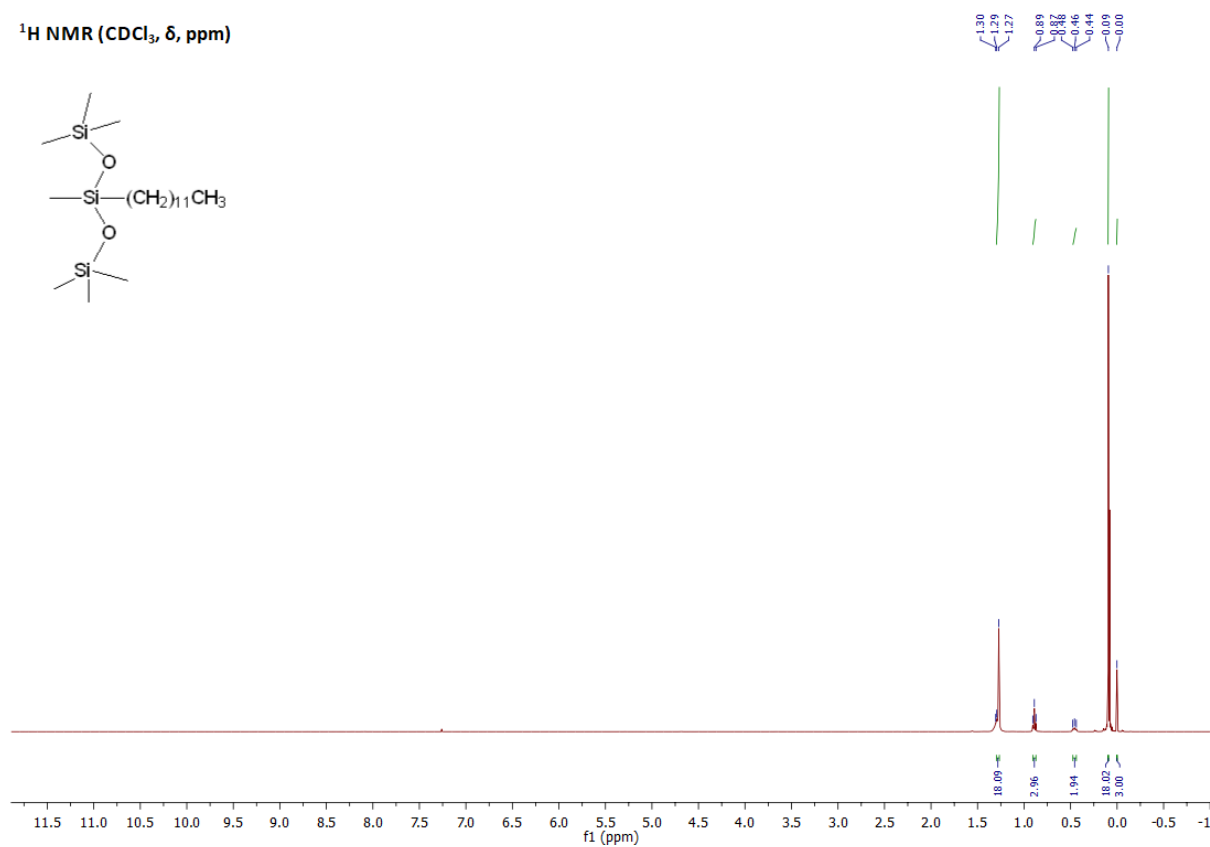
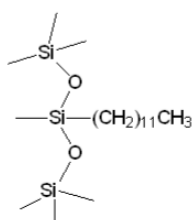
¹H NMR (CDCl₃, δ, ppm)



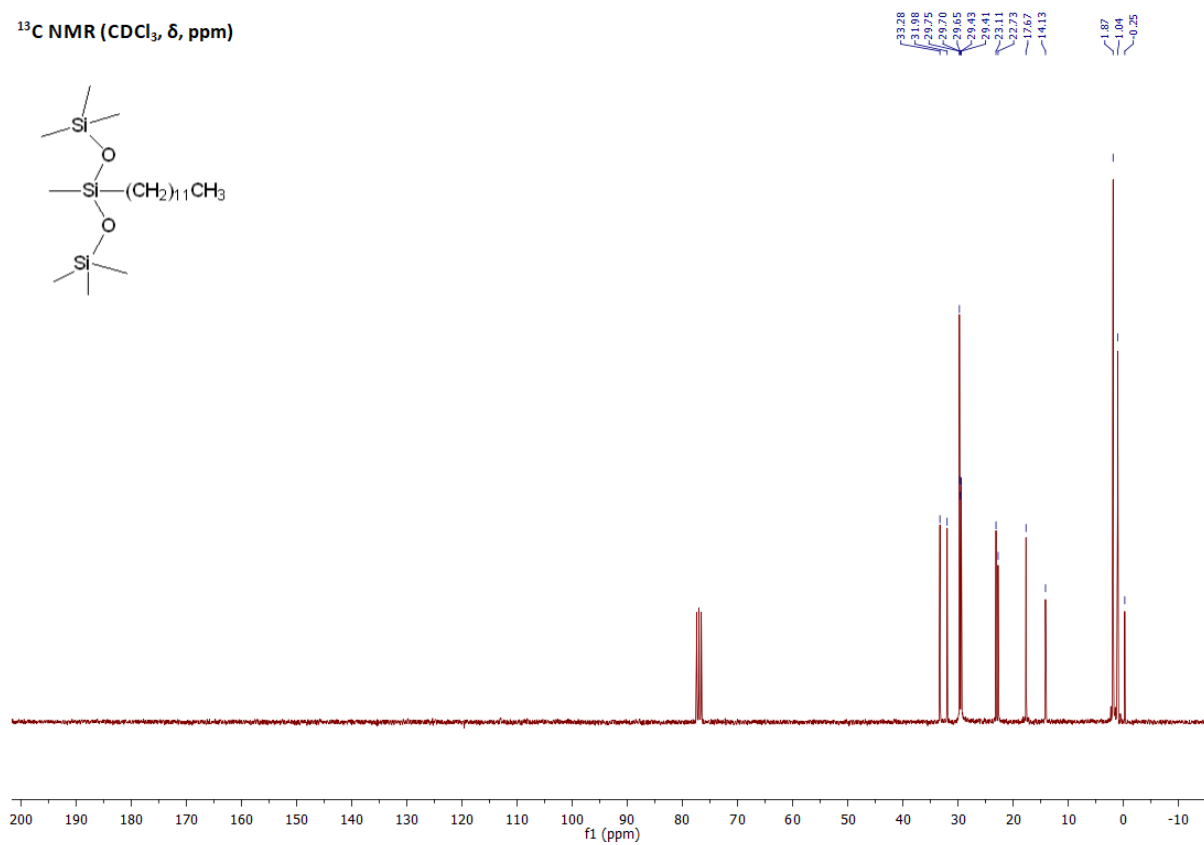
¹³C NMR (CDCl₃, δ, ppm)



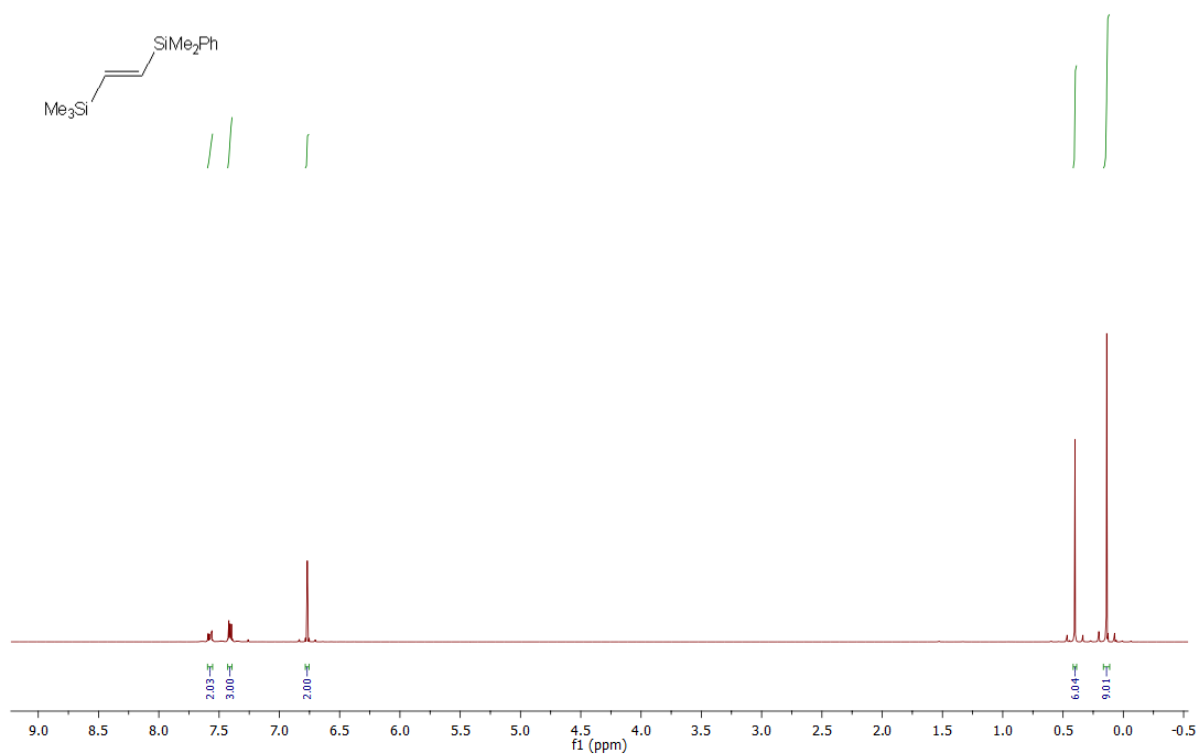
¹H NMR (CDCl₃, δ, ppm)



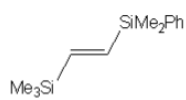
^{13}C NMR (CDCl_3 , δ , ppm)



^1H NMR (CDCl_3 , δ , ppm)



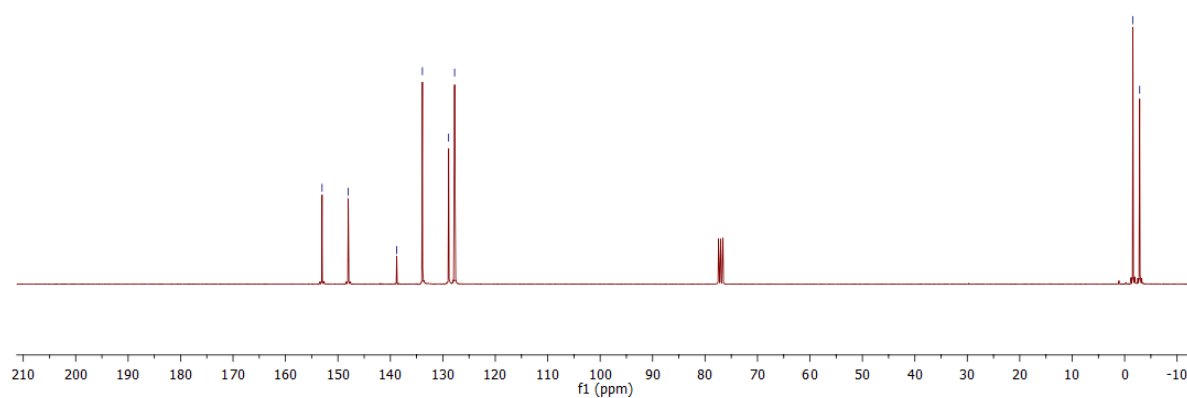
¹³C NMR (CDCl₃, δ, ppm)



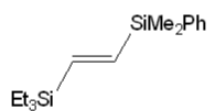
153.03
148.03

138.79
138.89
128.89
127.75

-1.98
-2.87

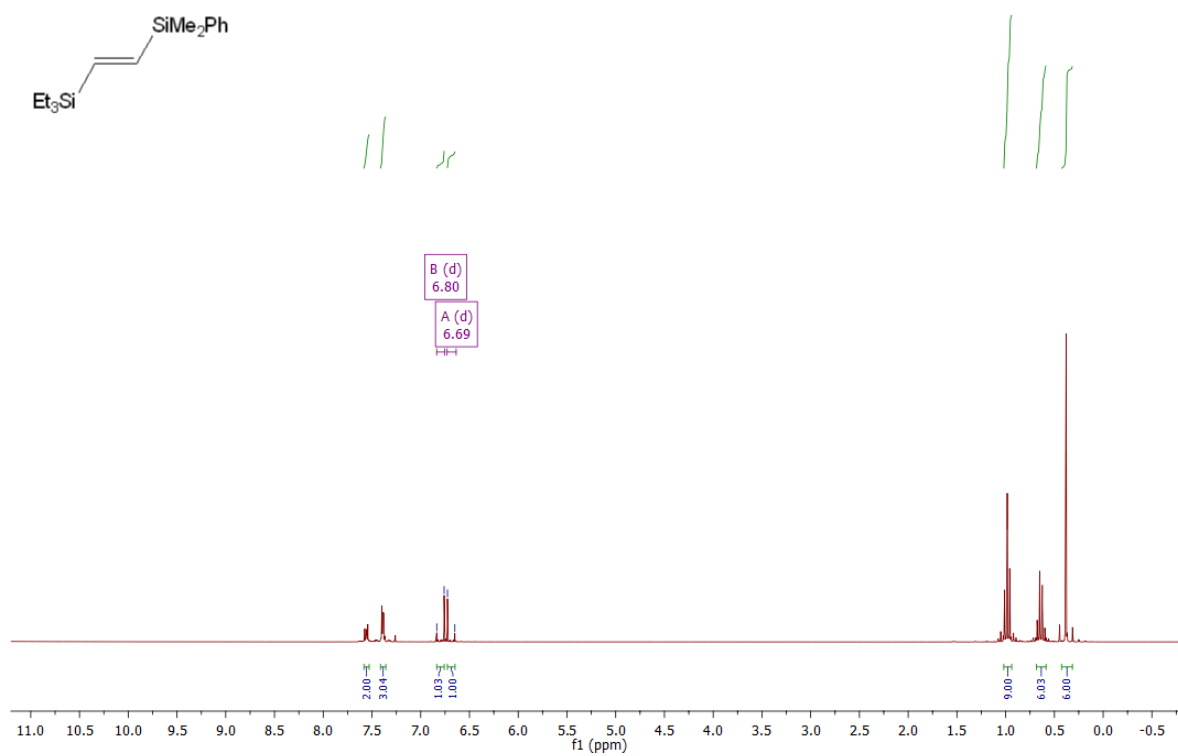


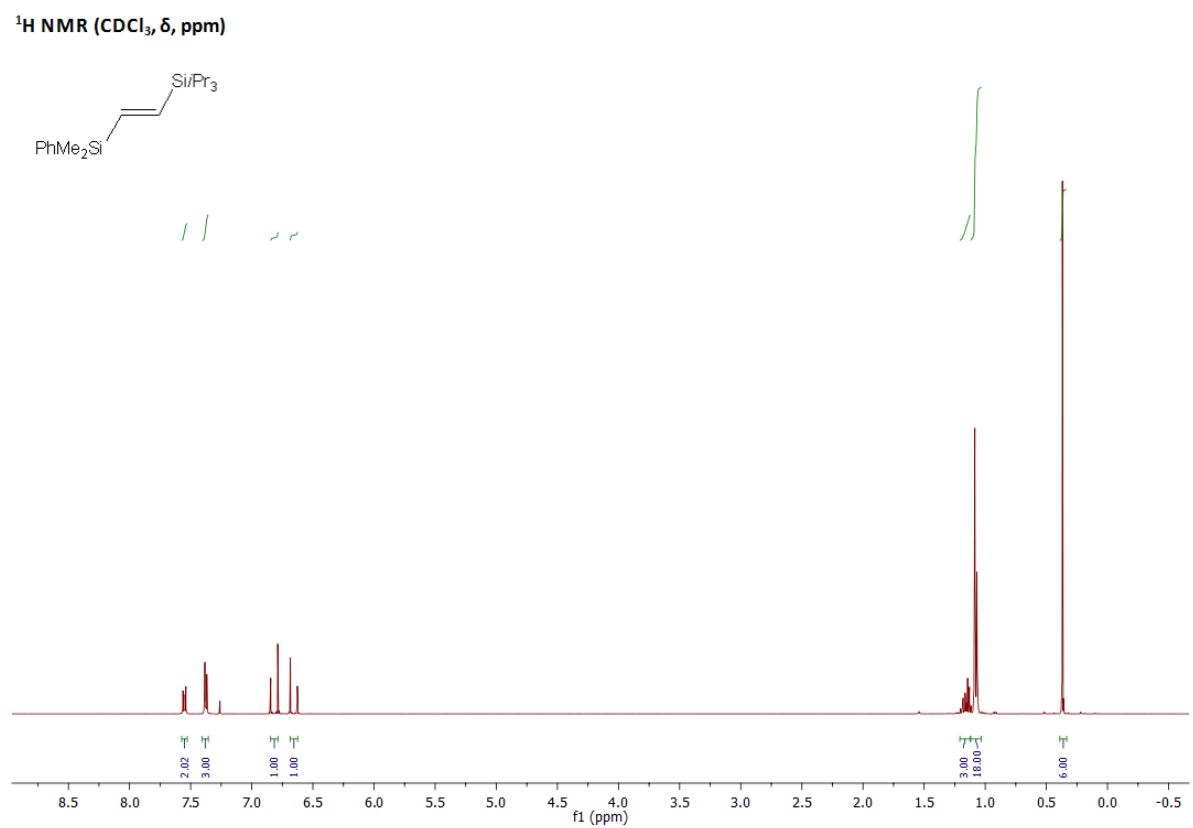
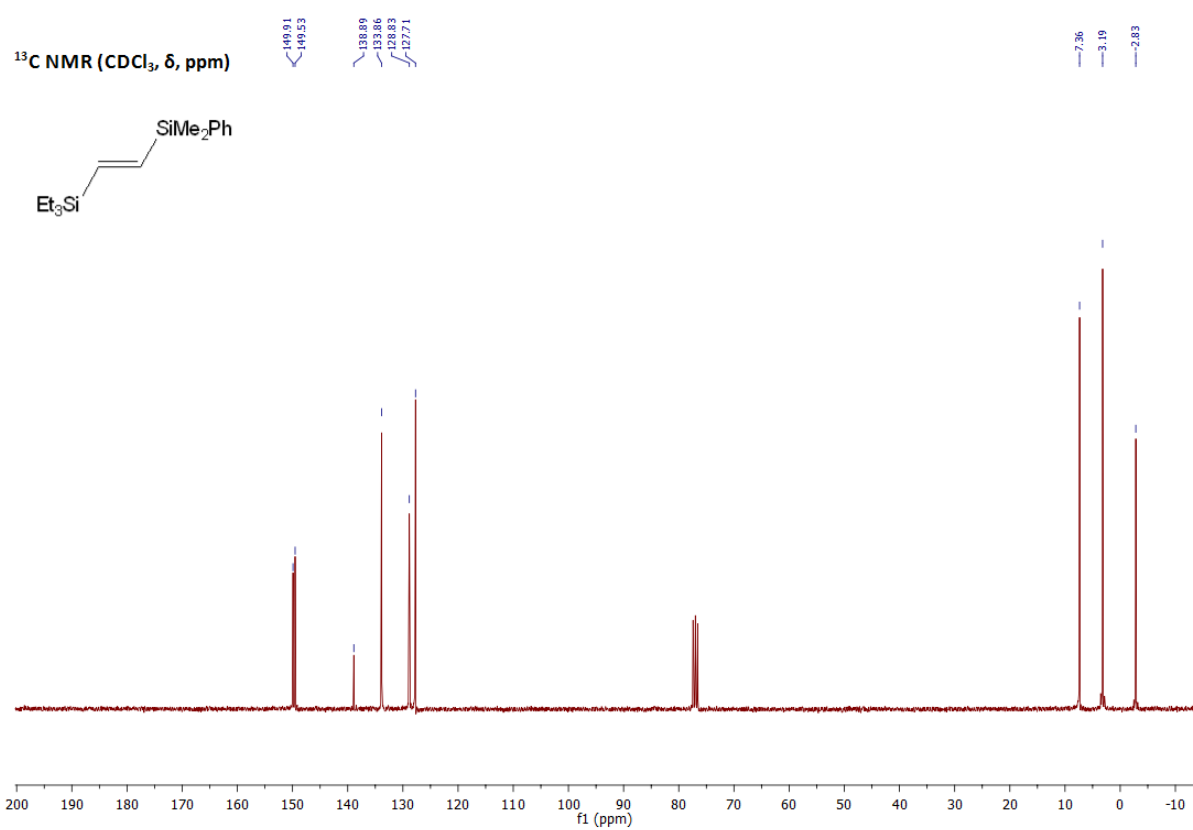
¹H NMR (CDCl₃, δ, ppm)



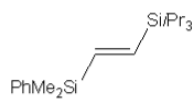
6.84
6.76
6.73
6.65

B (d)
6.80
A (d)
6.69





¹³C NMR (CDCl₃, δ, ppm)



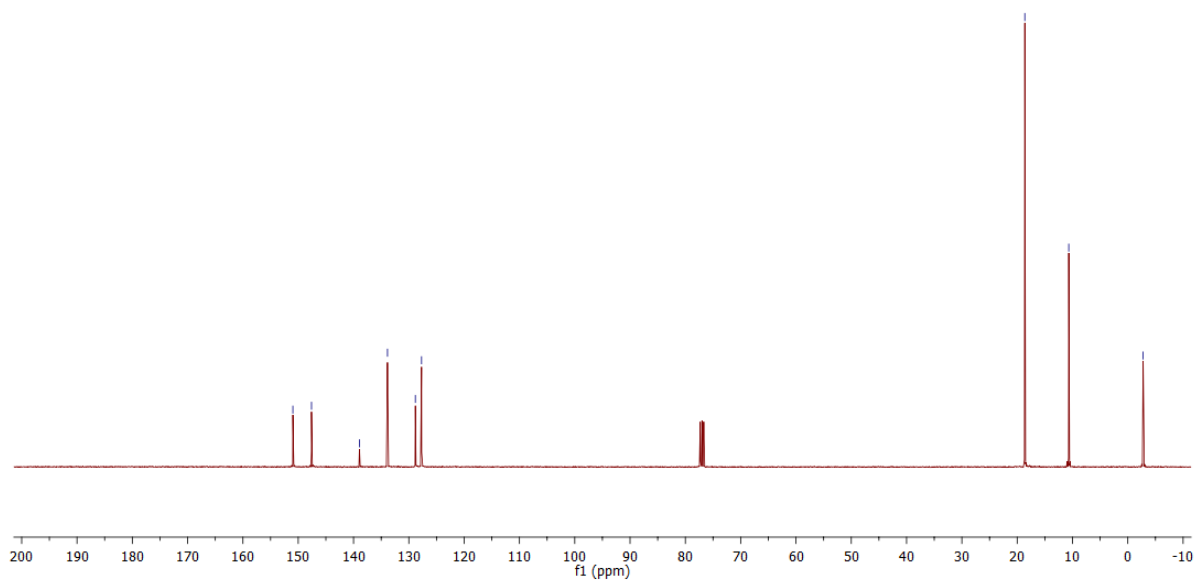
150.97
147.60

138.93
133.86
128.82
127.70

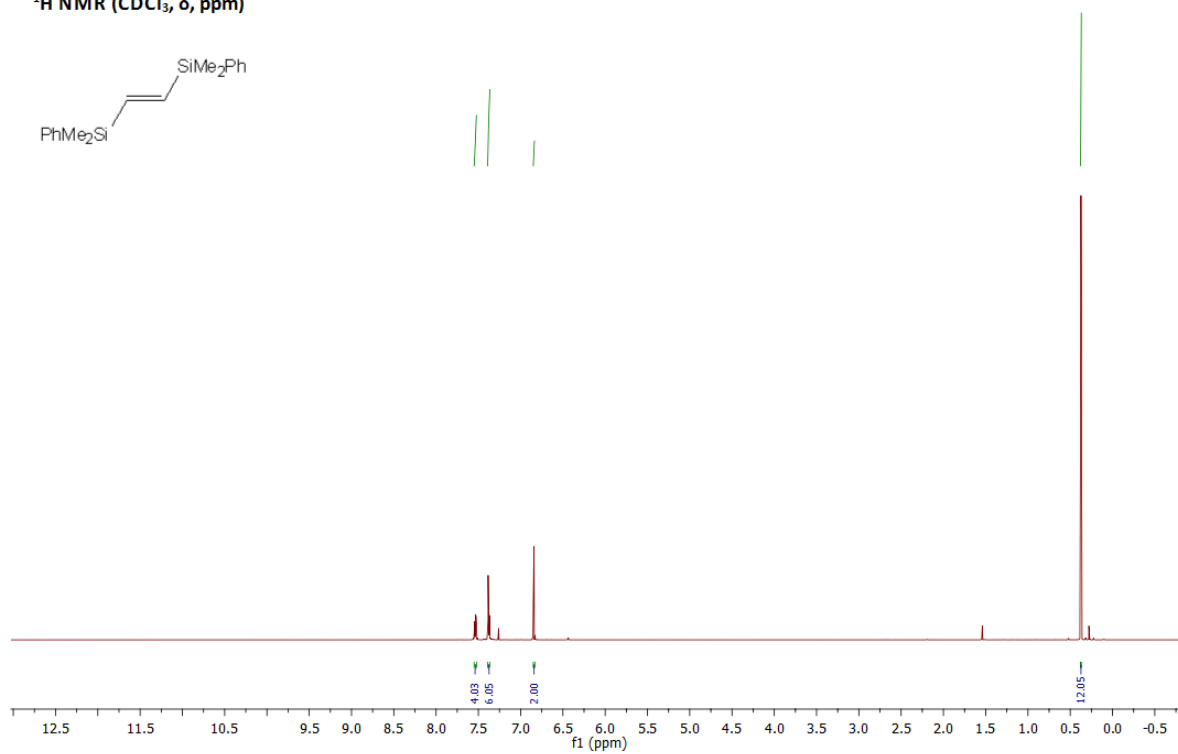
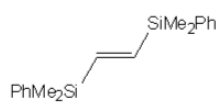
18.62

10.68

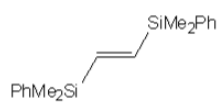
2.77



¹H NMR (CDCl₃, δ, ppm)



¹³C NMR (CDCl₃, δ, ppm)



150.32

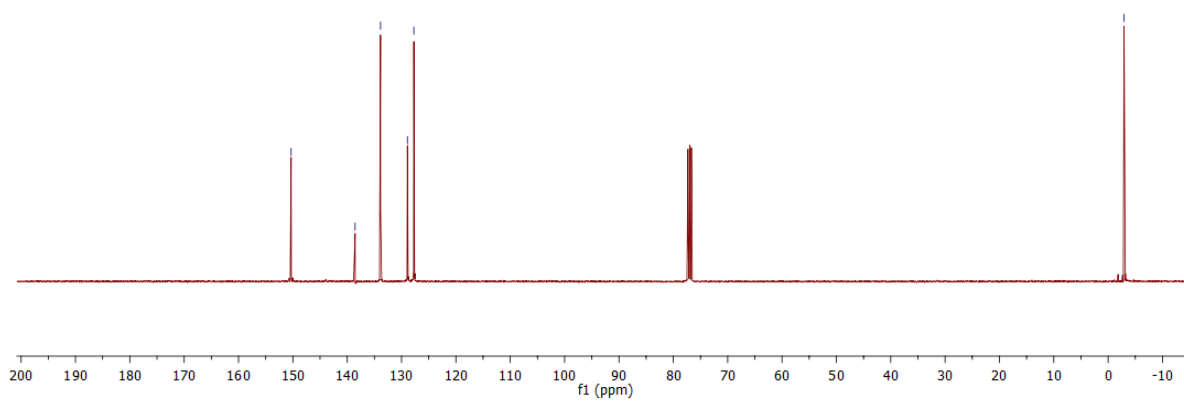
138.55

133.87

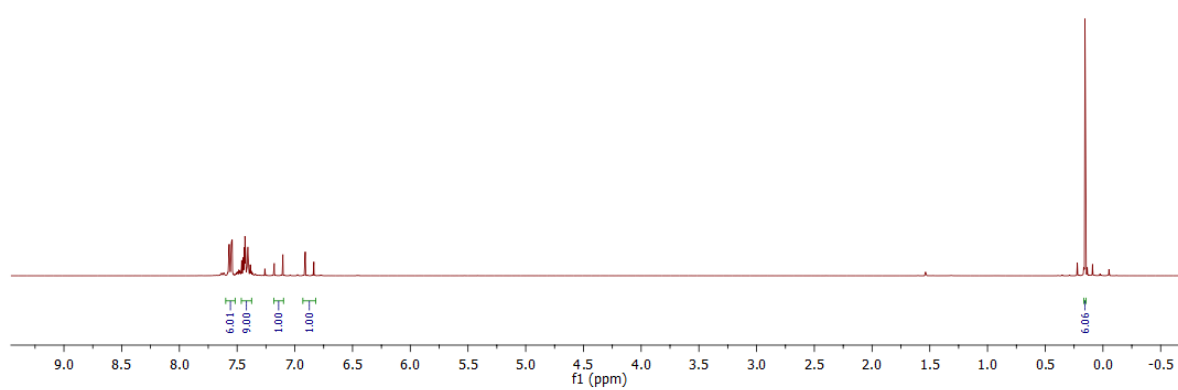
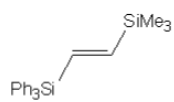
128.92

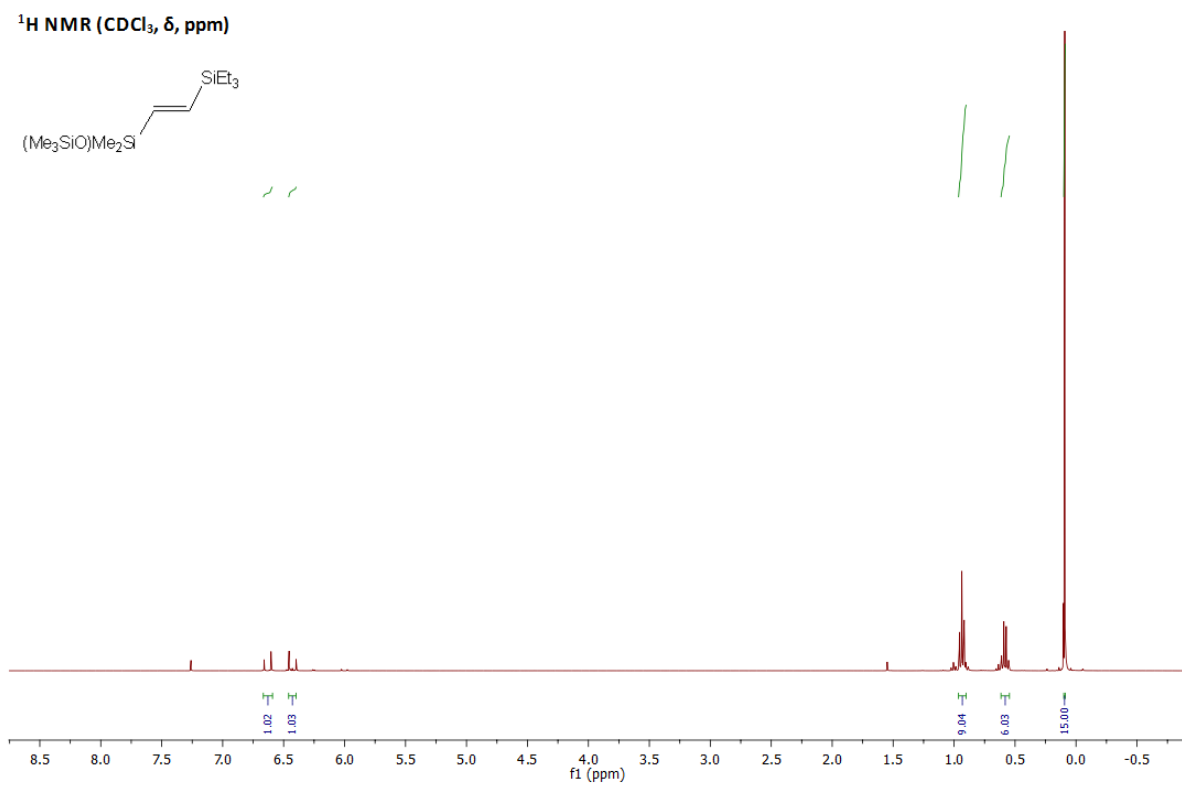
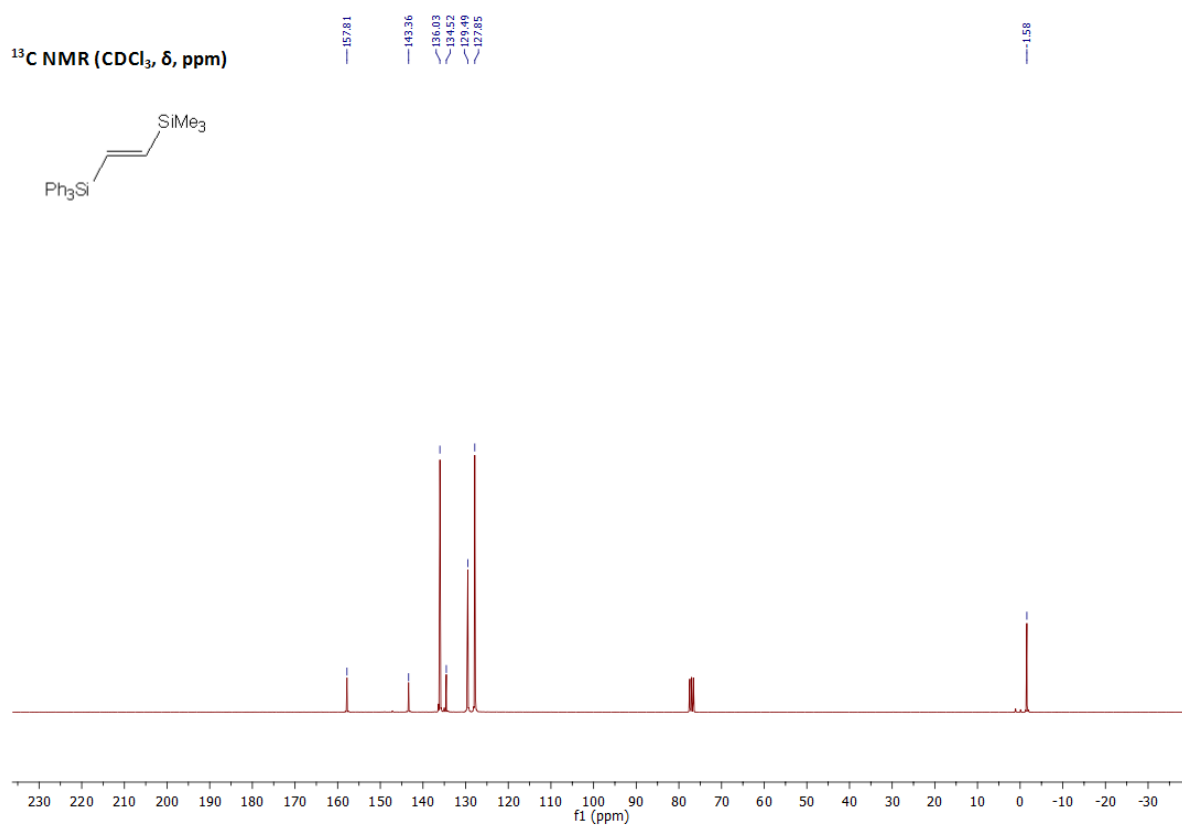
127.74

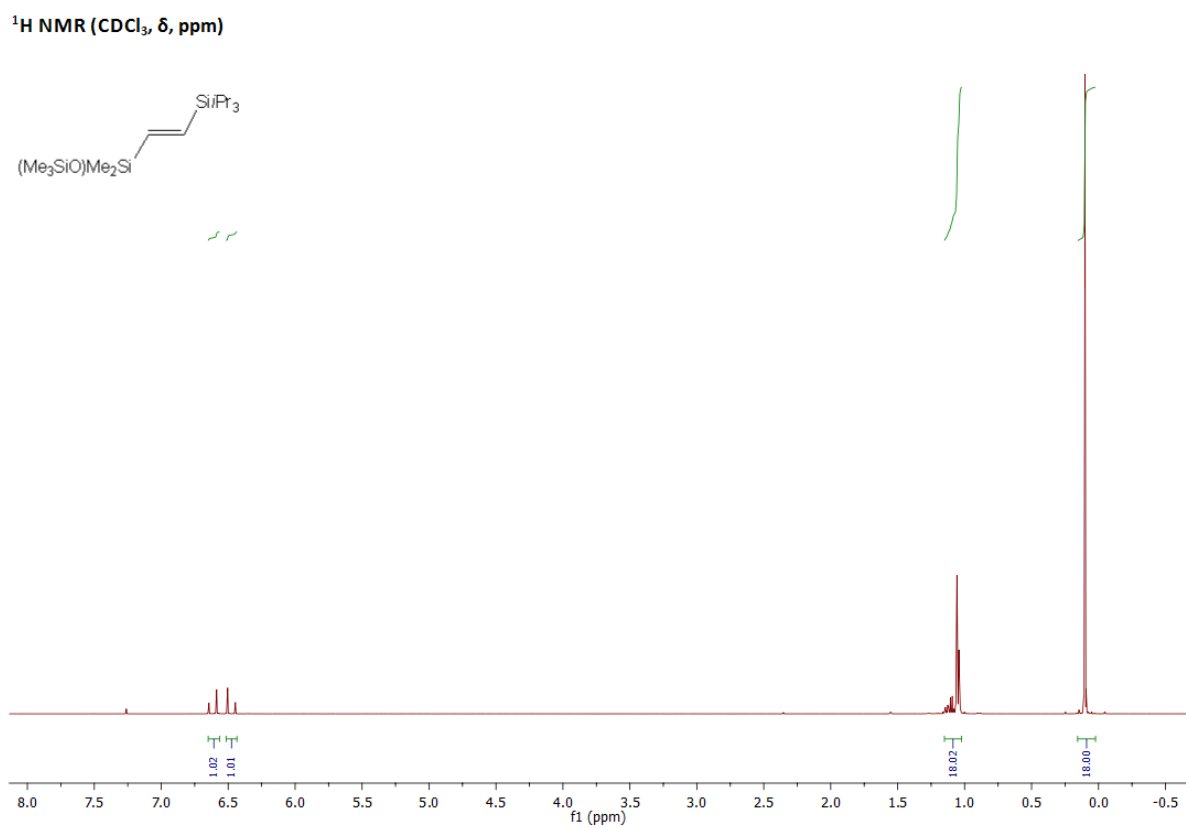
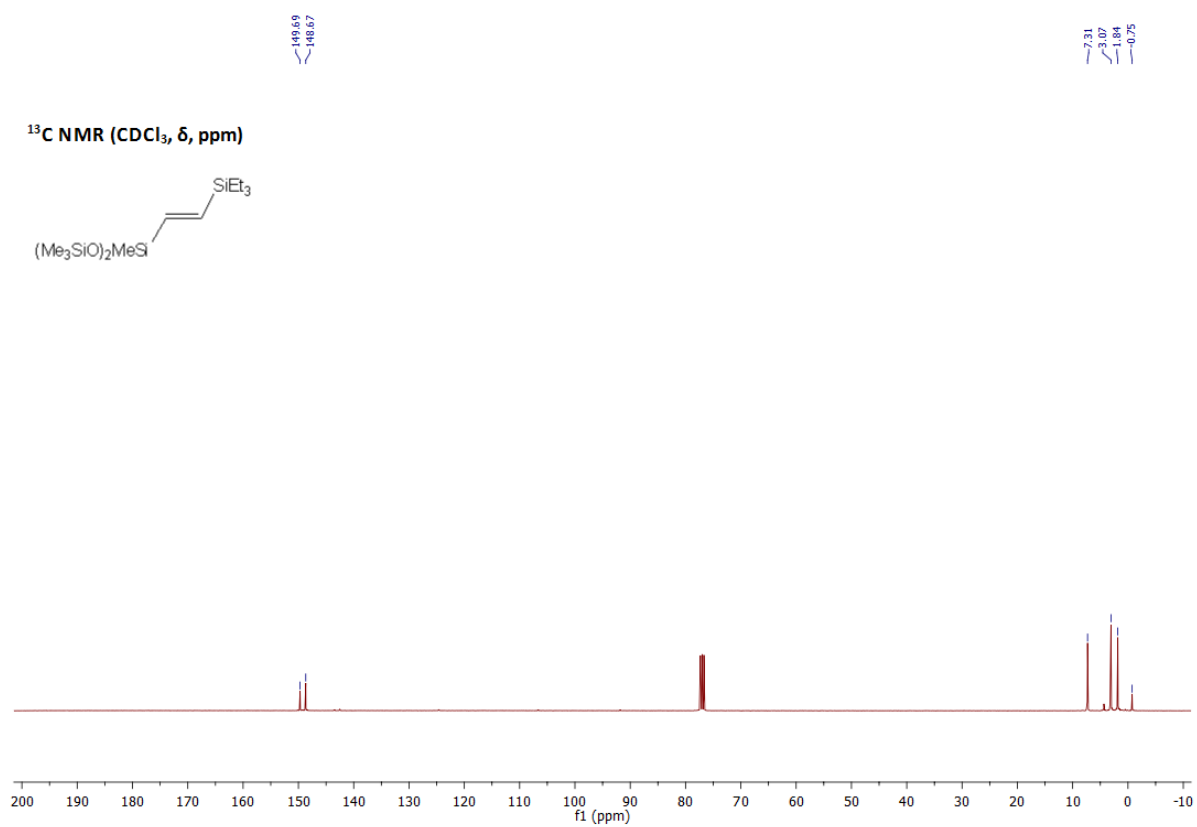
-2.93

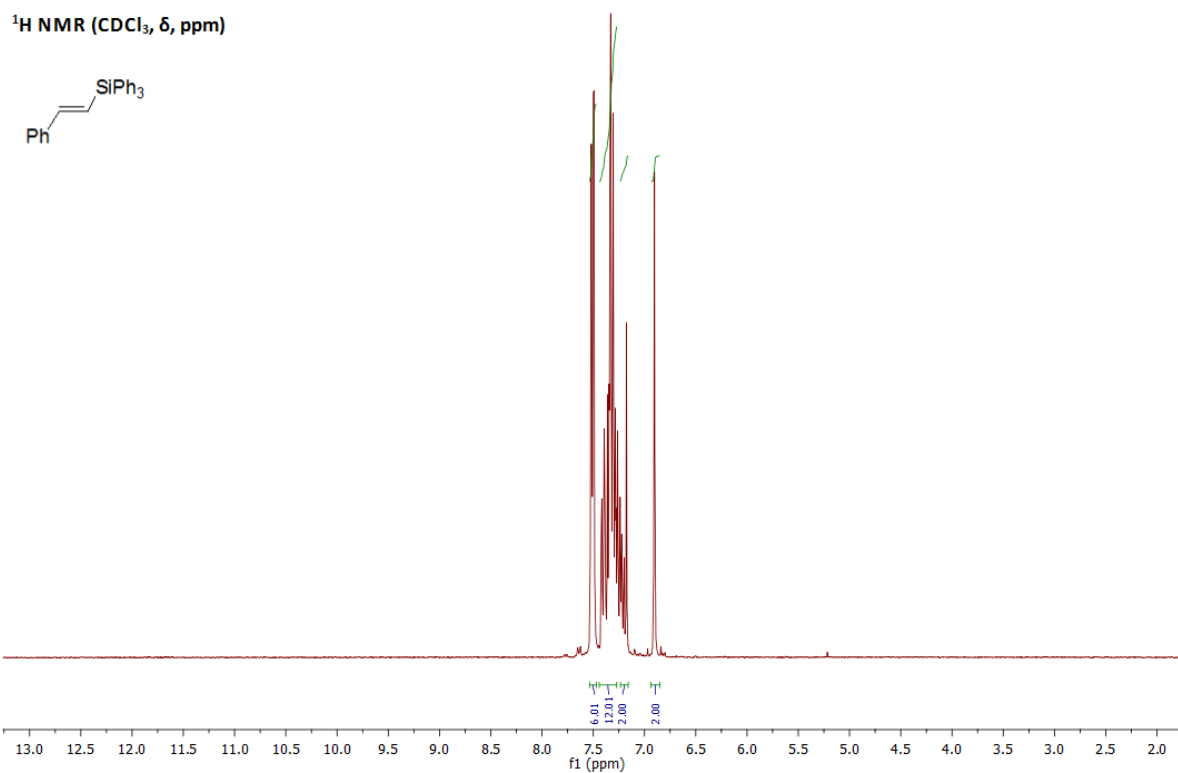
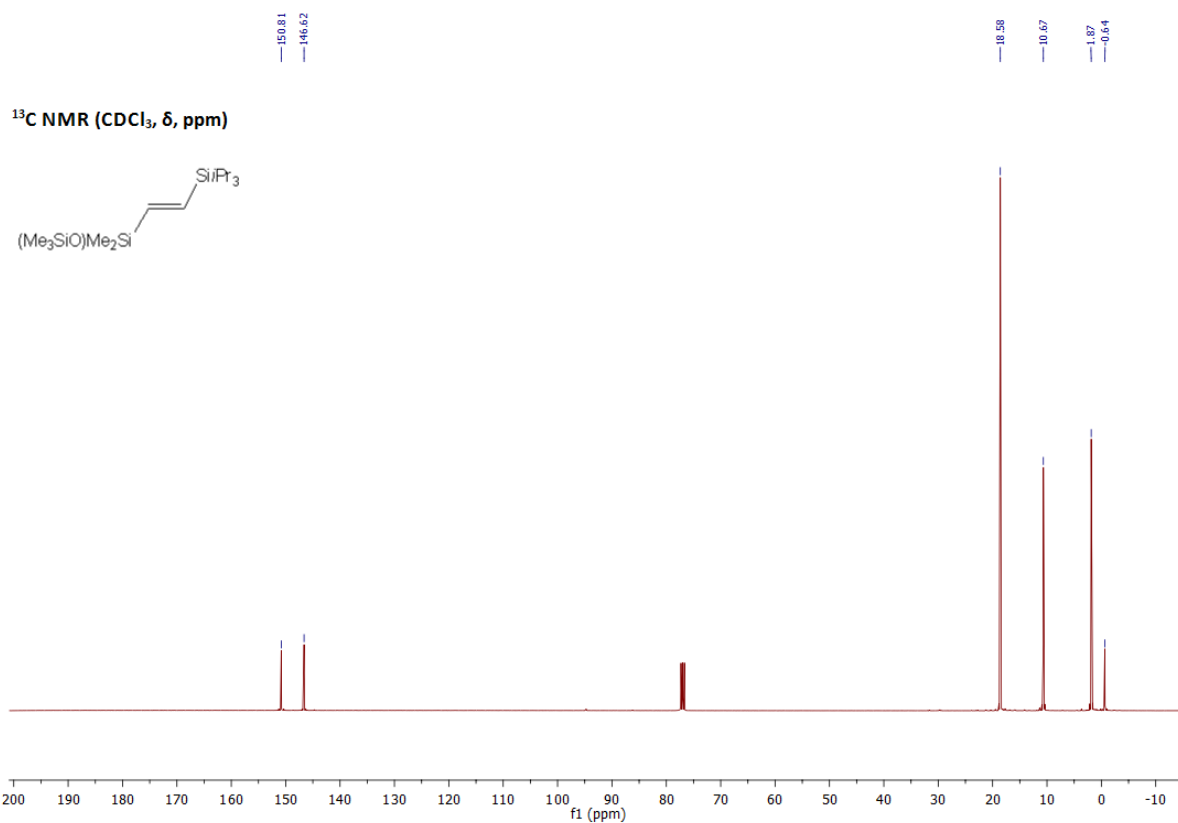


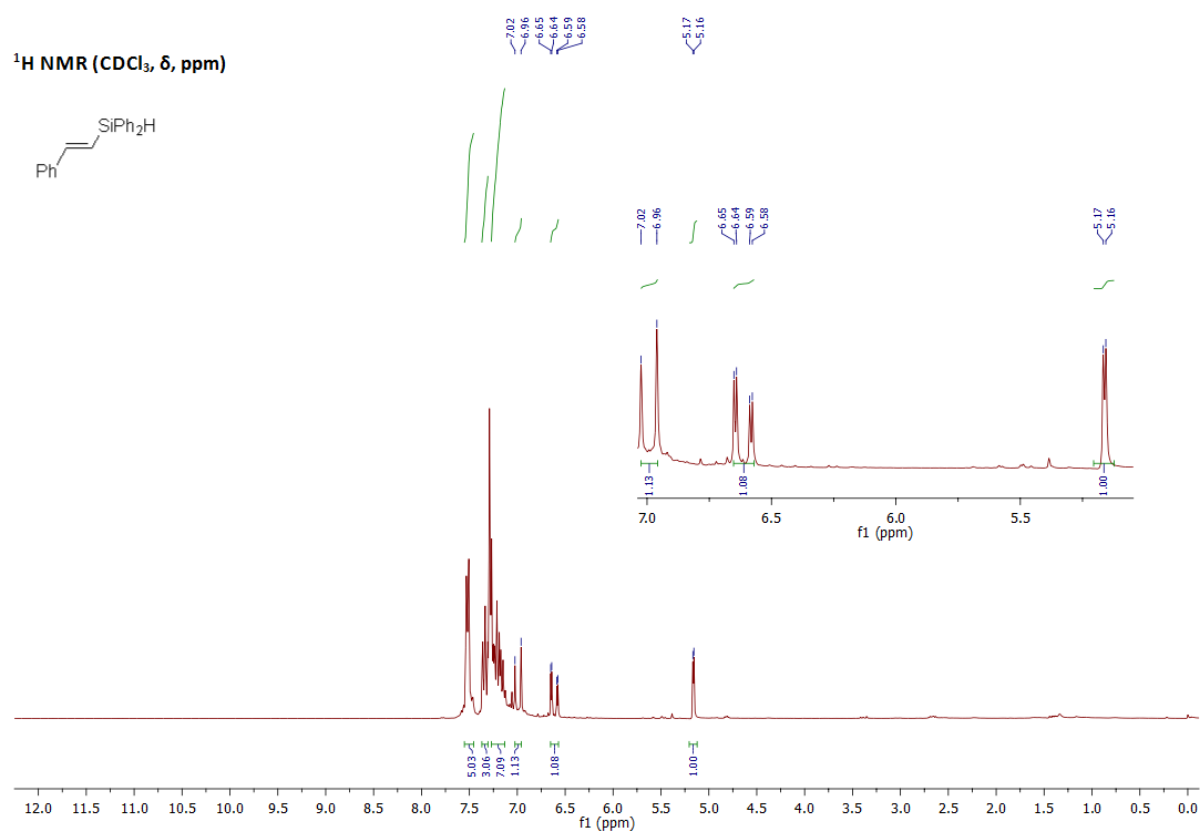
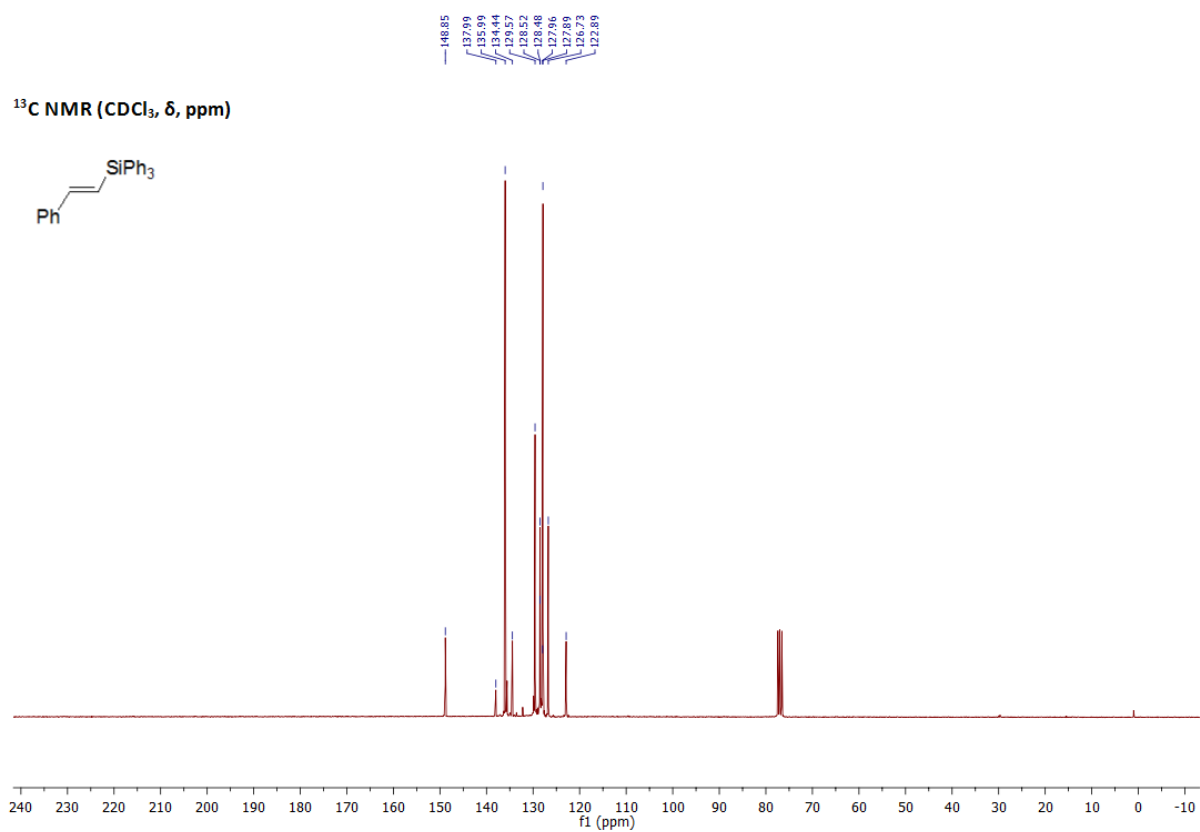
¹H NMR (CDCl₃, δ, ppm)



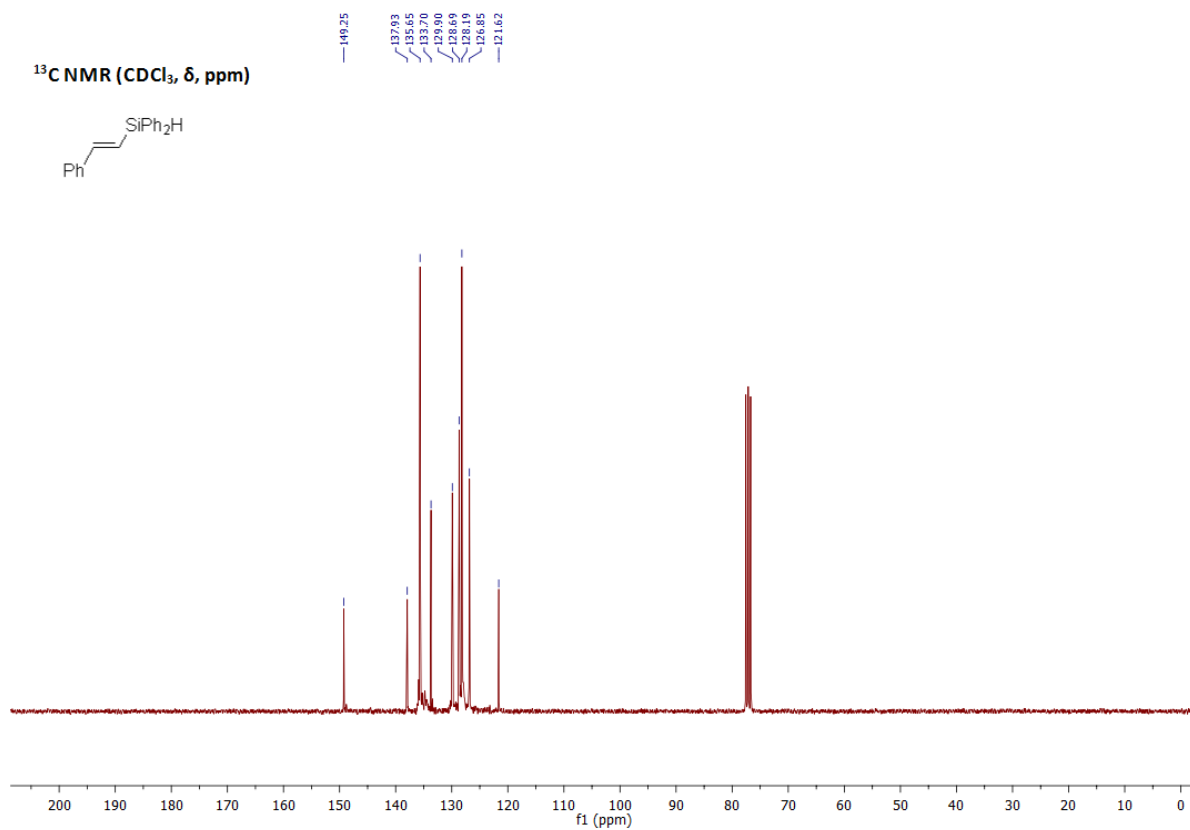
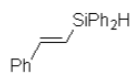




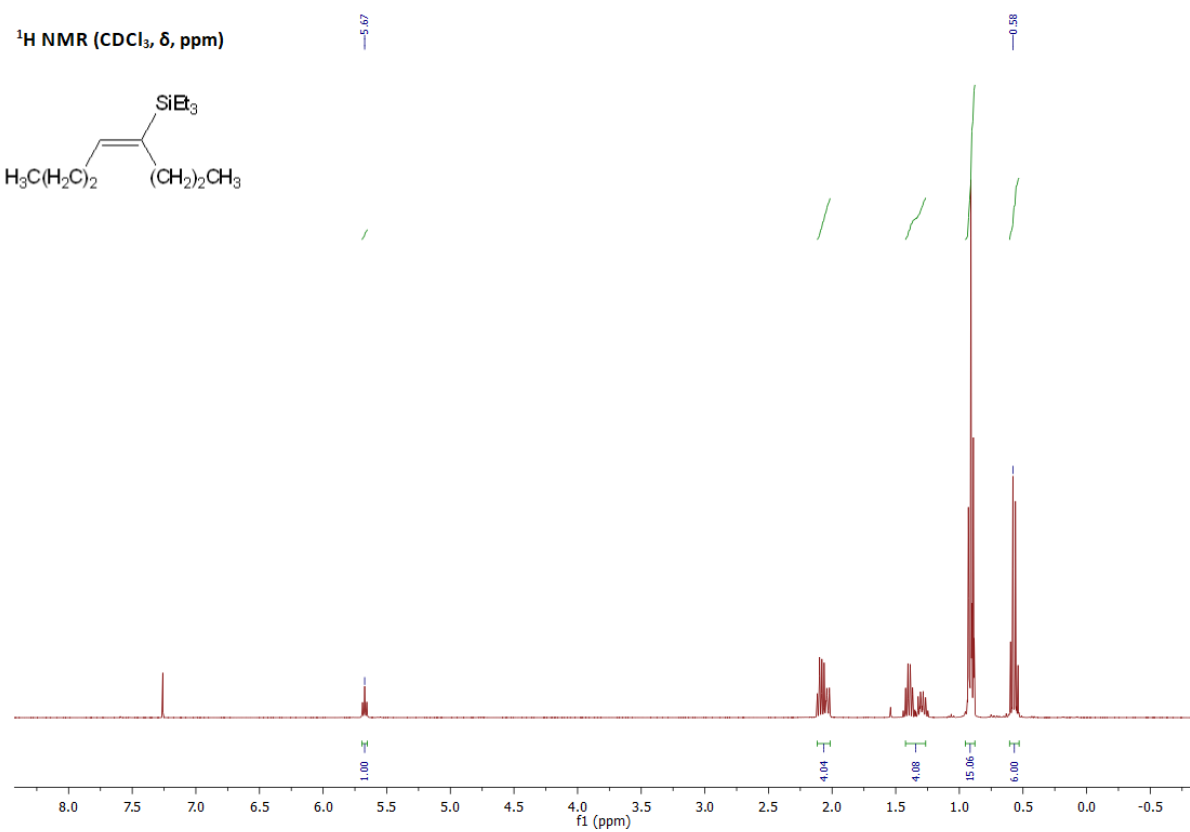
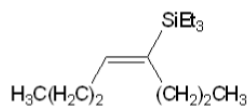




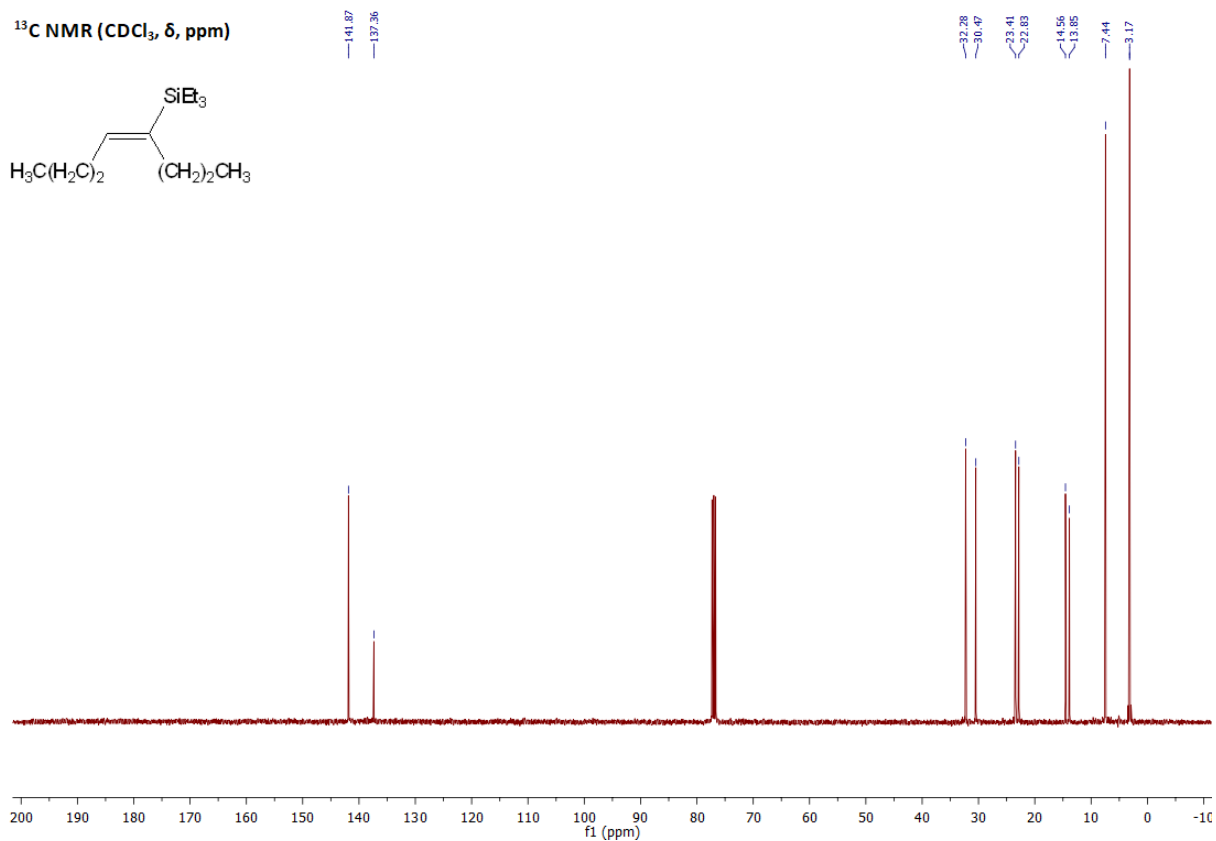
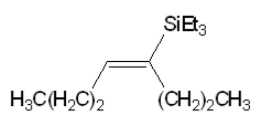
¹³C NMR (CDCl₃, δ, ppm)



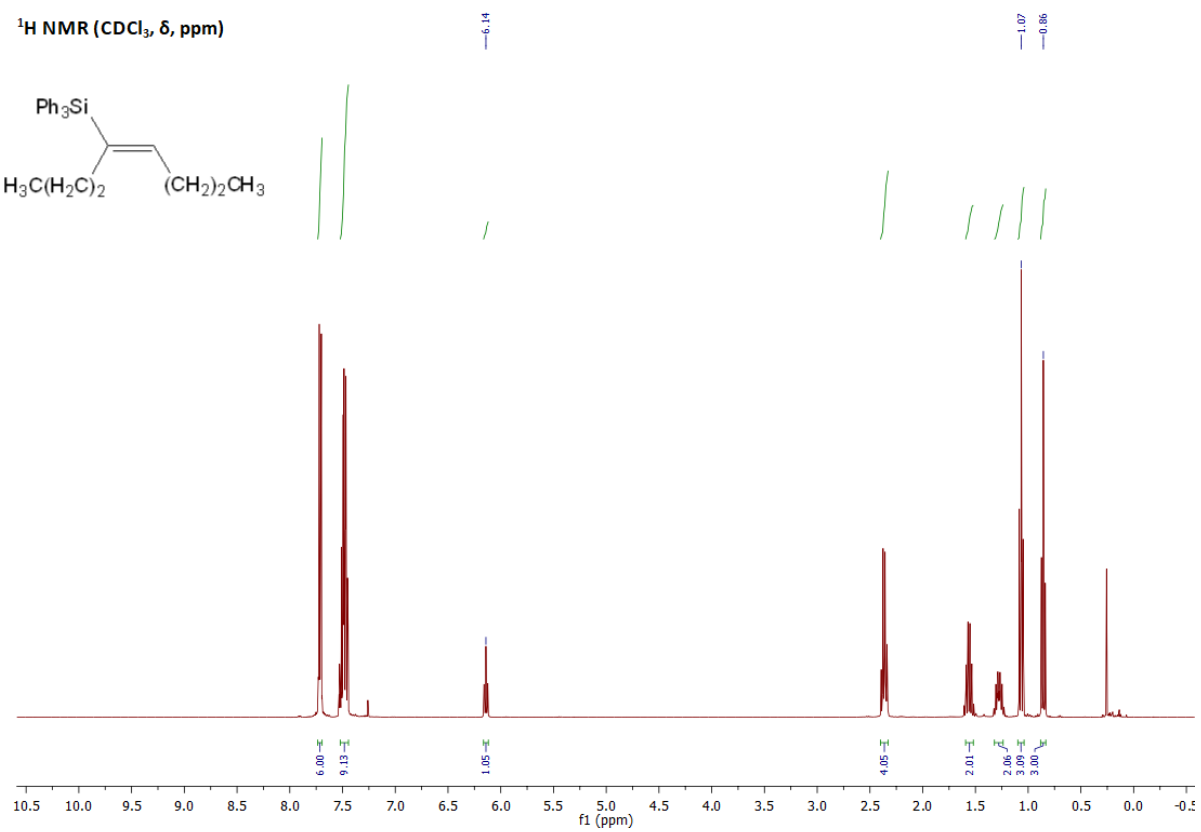
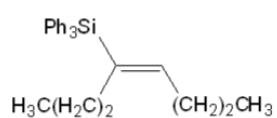
¹H NMR (CDCl₃, δ, ppm)

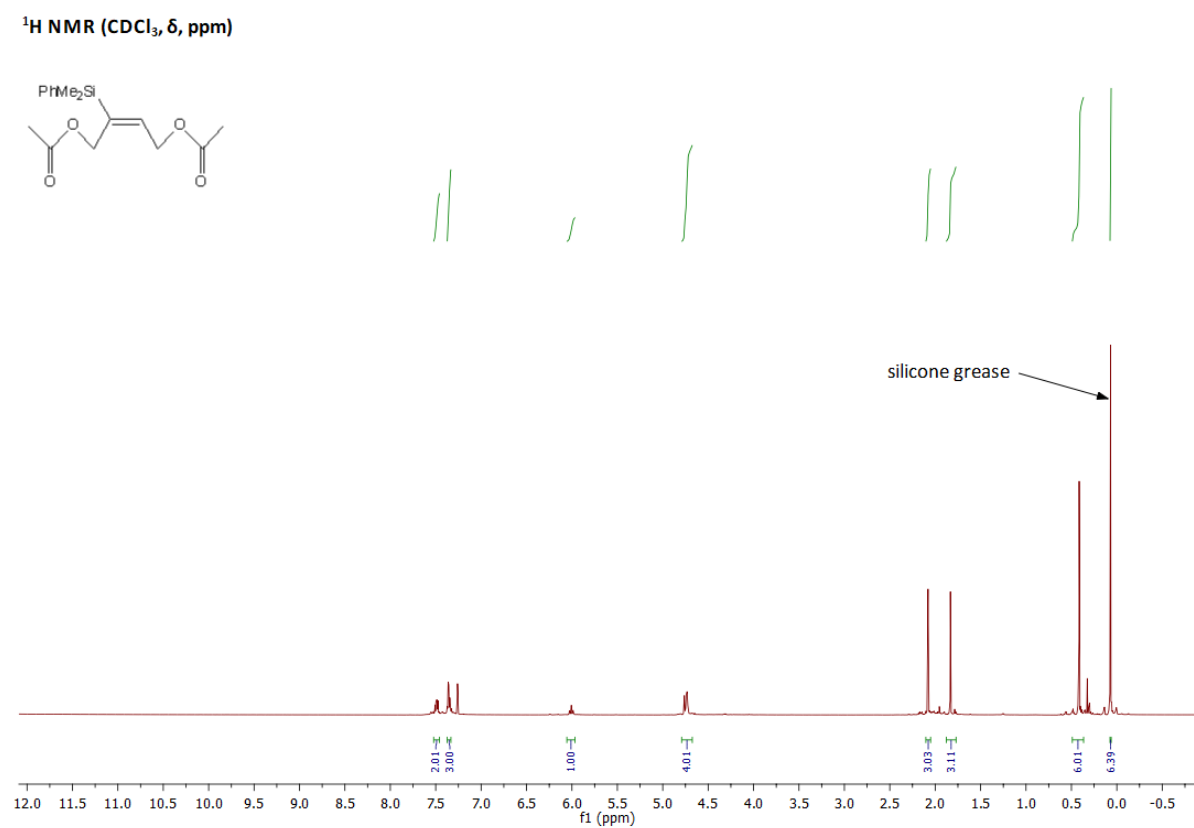
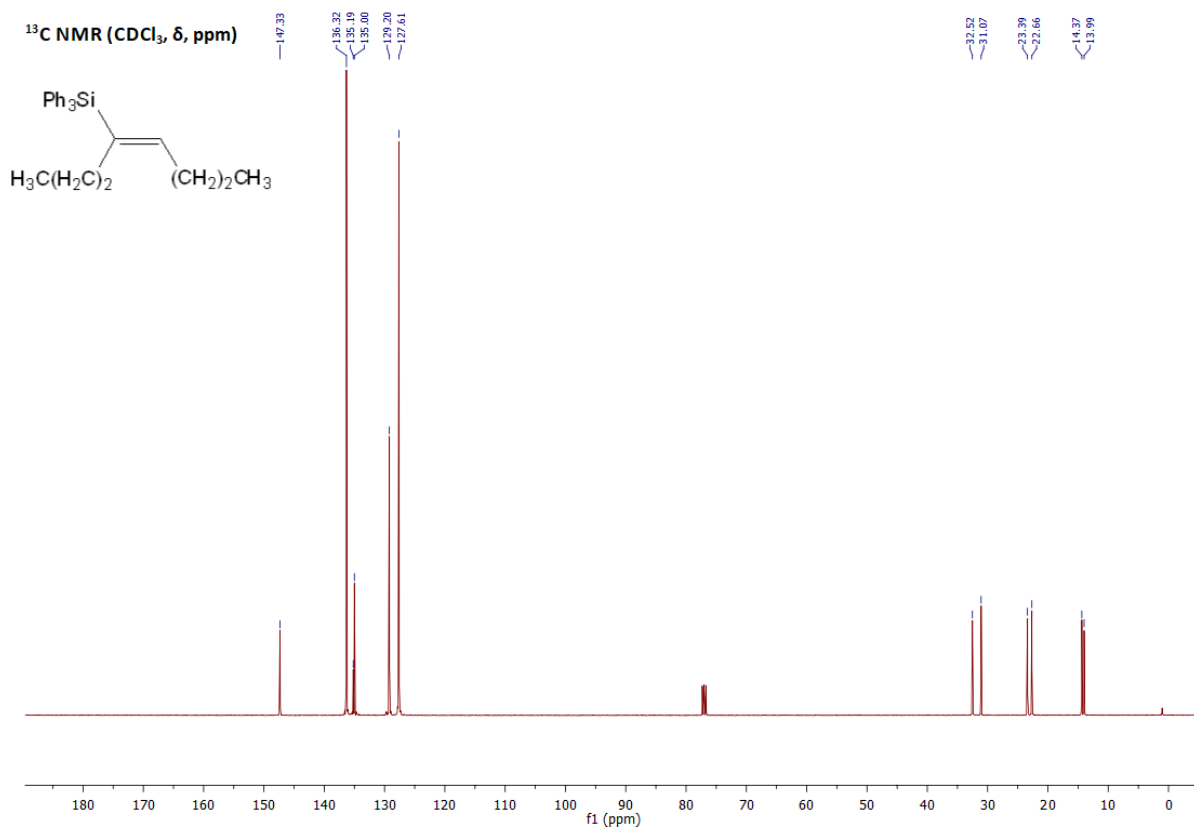


^{13}C NMR (CDCl_3 , δ , ppm)

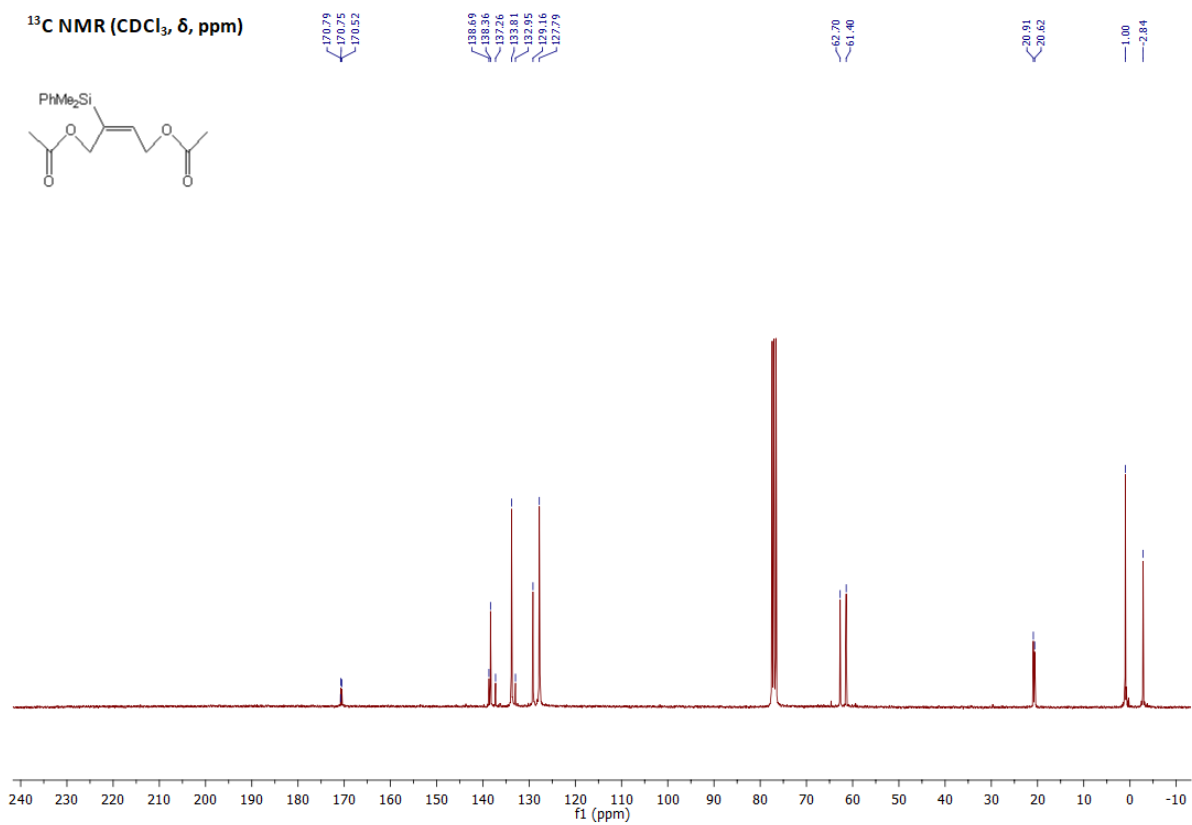
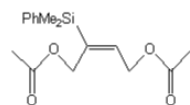


^1H NMR (CDCl_3 , δ , ppm)

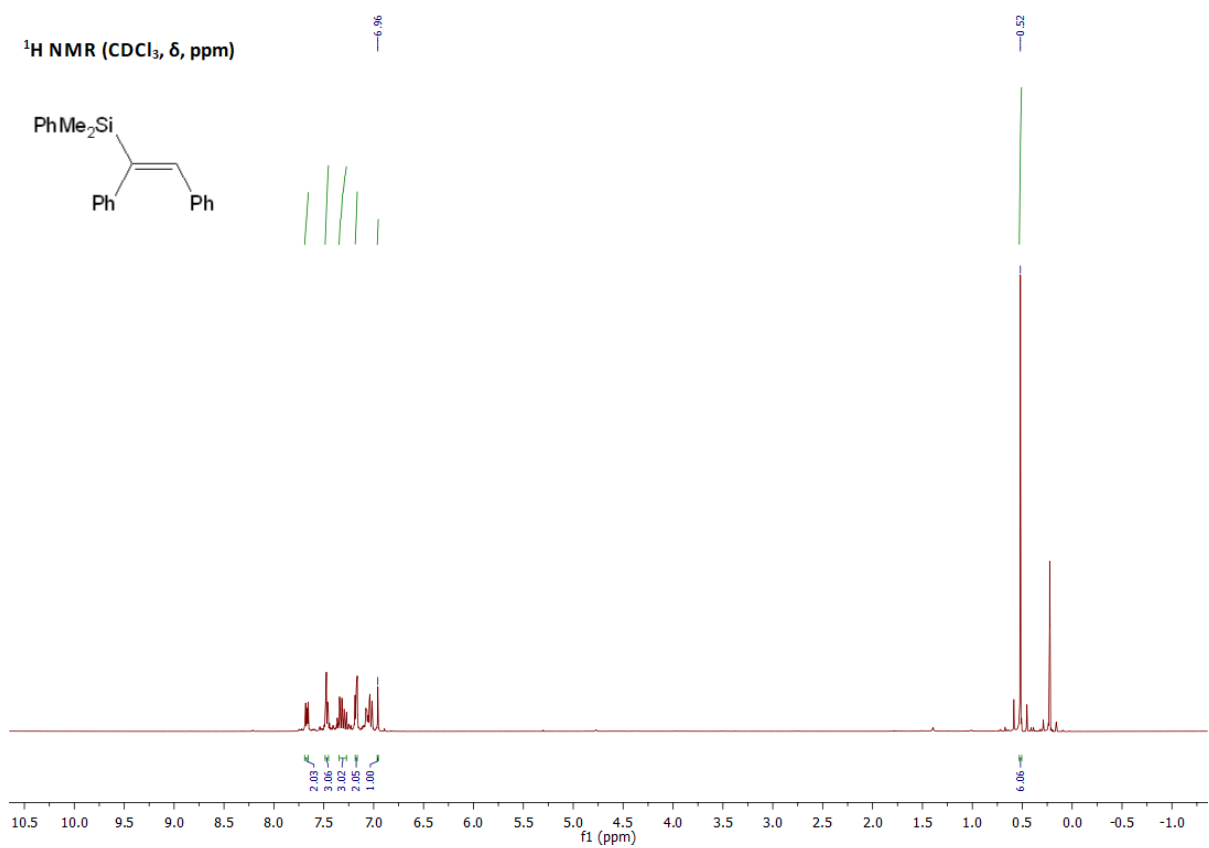
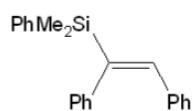




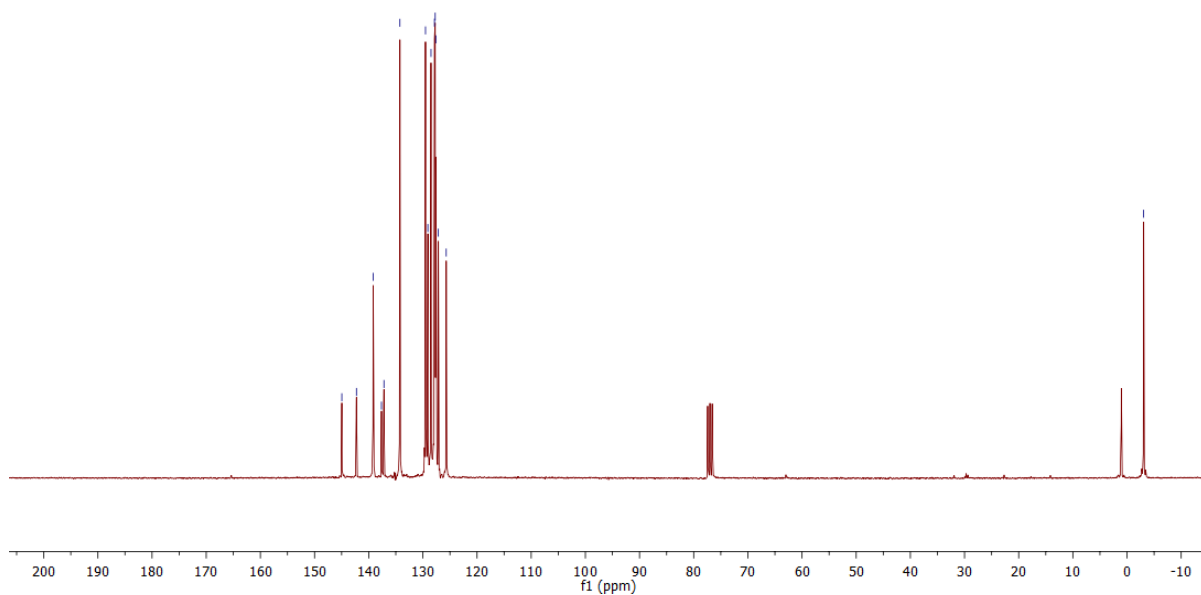
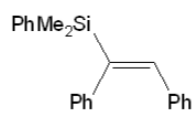
¹³C NMR (CDCl₃, δ, ppm)



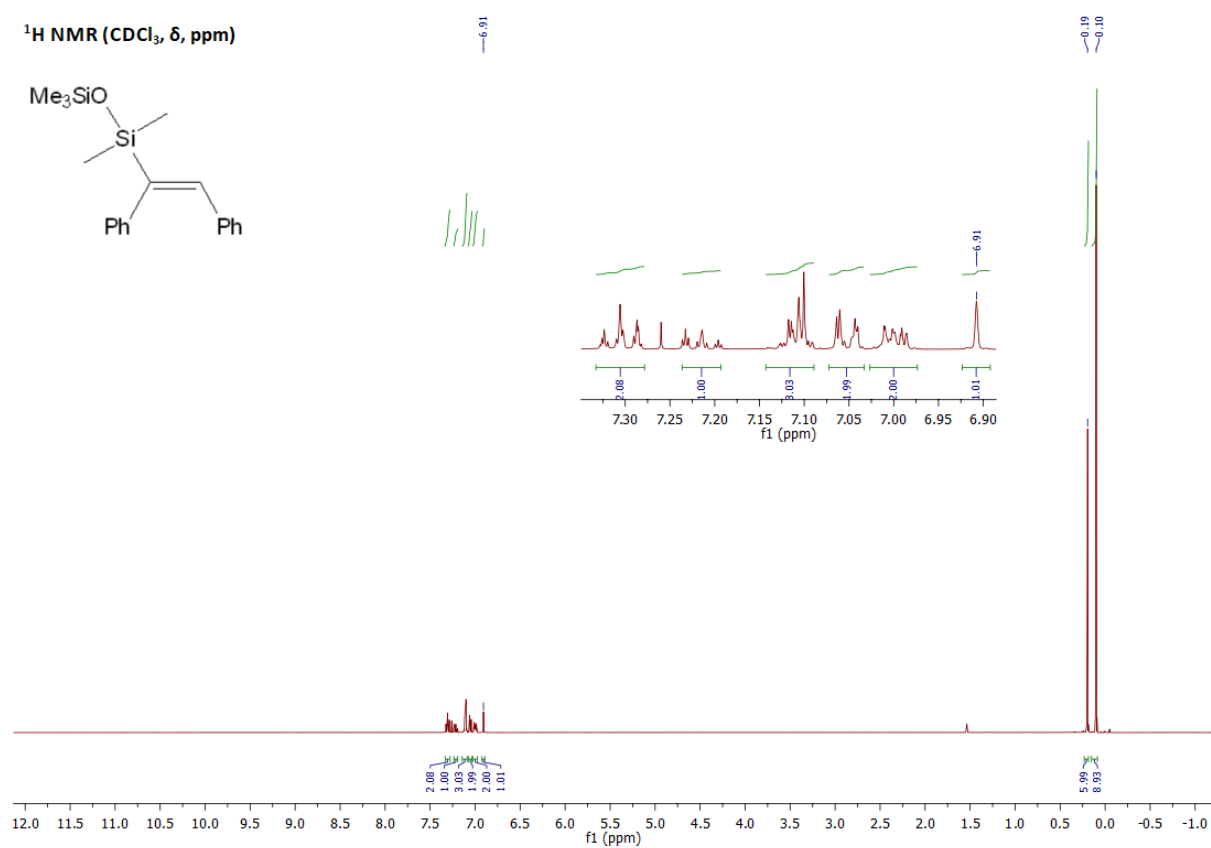
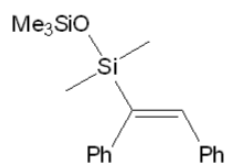
¹H NMR (CDCl₃, δ, ppm)



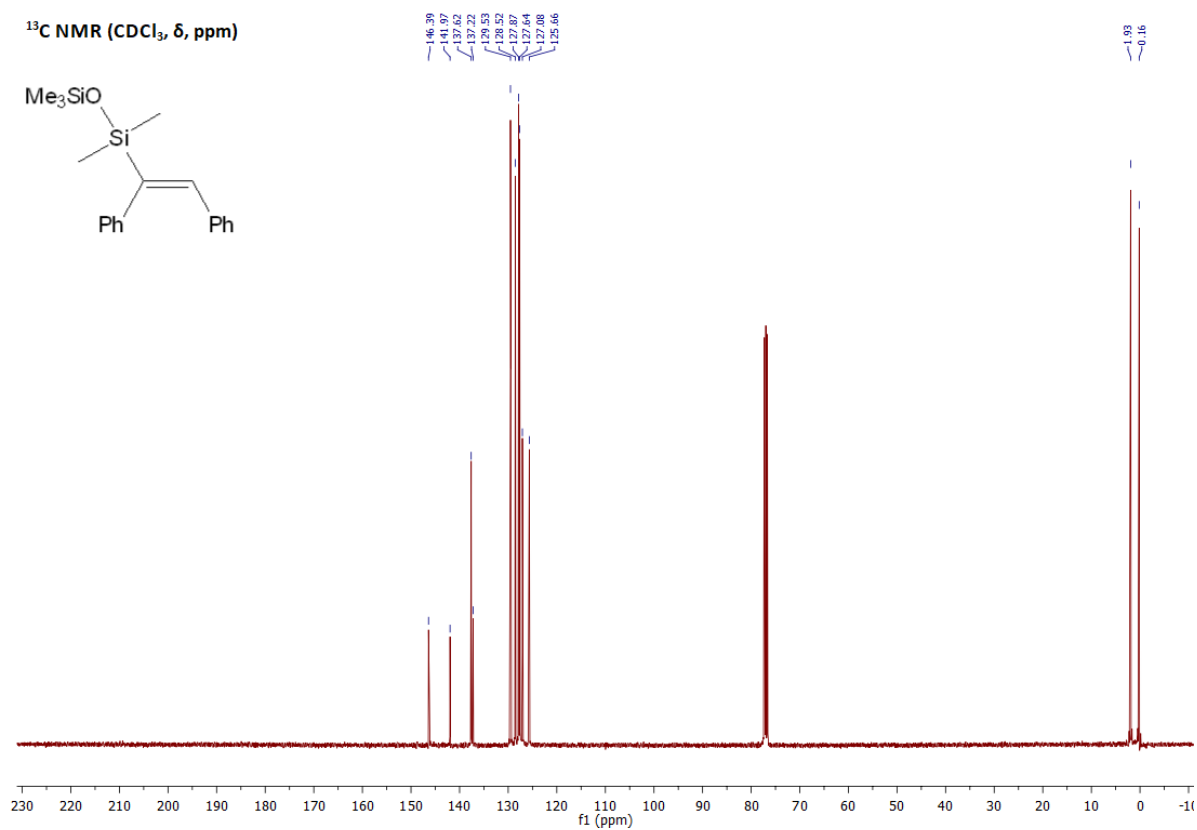
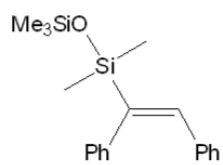
144.96
142.26
139.17
137.64
137.18
134.24
129.51
129.08
128.50
127.86
127.72
127.61
127.14
125.69



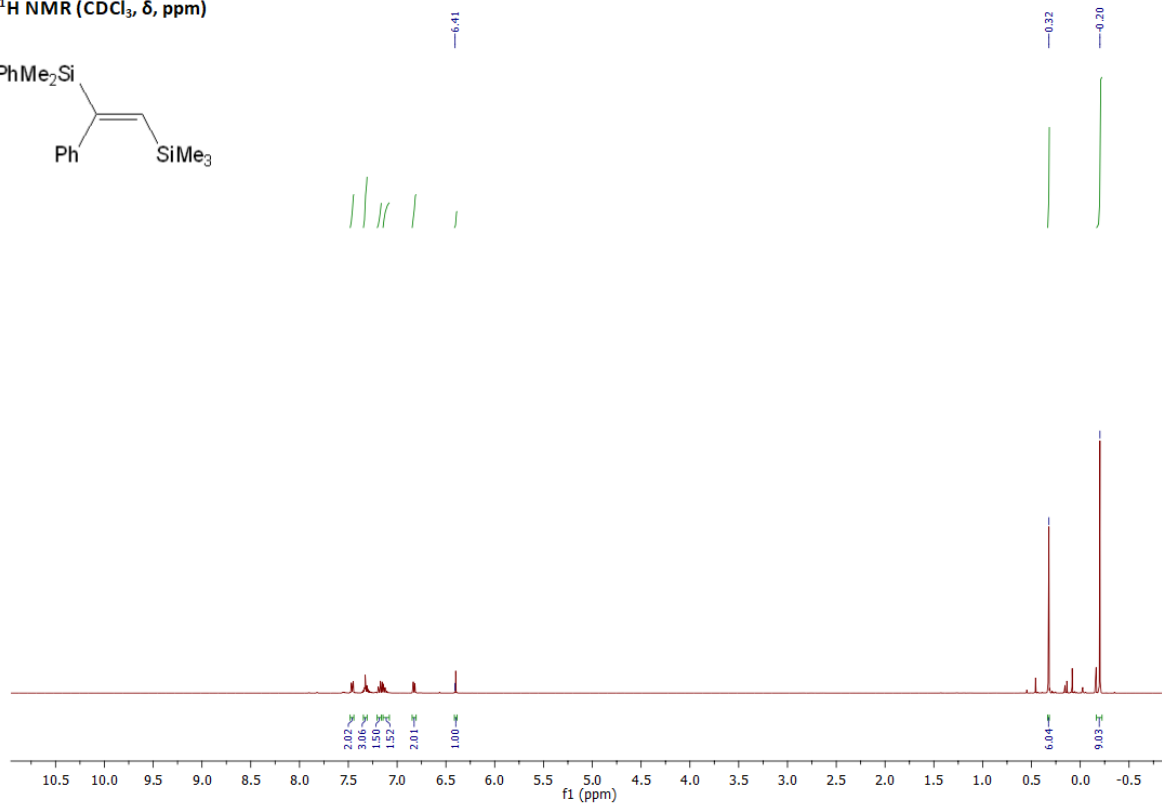
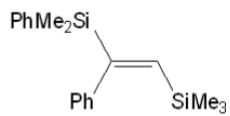
-6.91



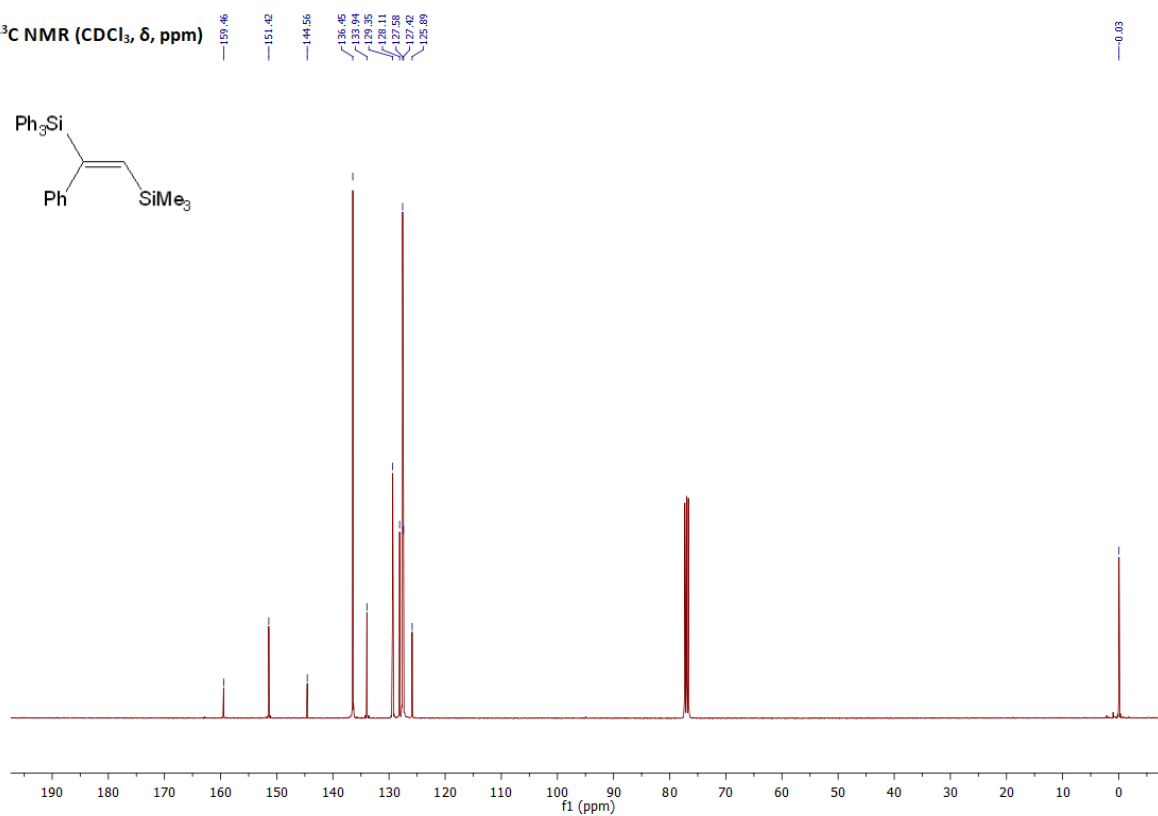
¹³C NMR (CDCl₃, δ, ppm)



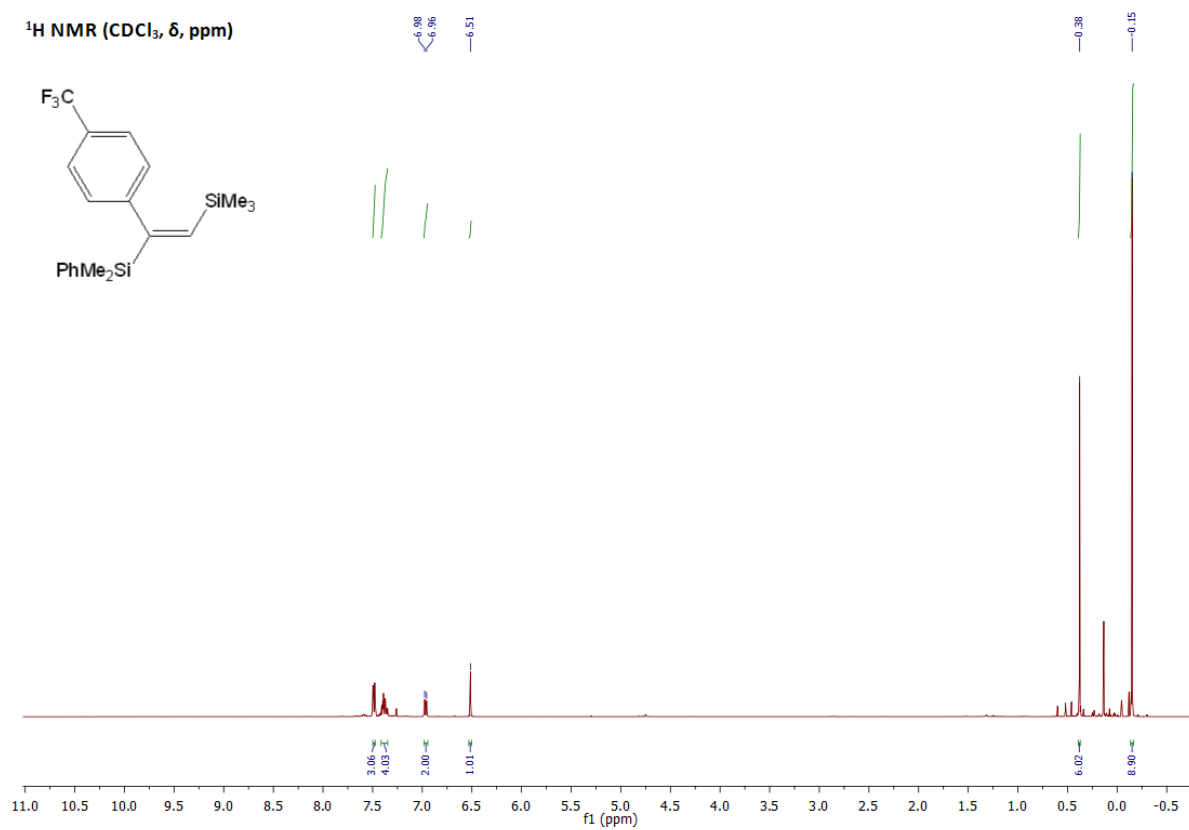
¹H NMR (CDCl₃, δ, ppm)

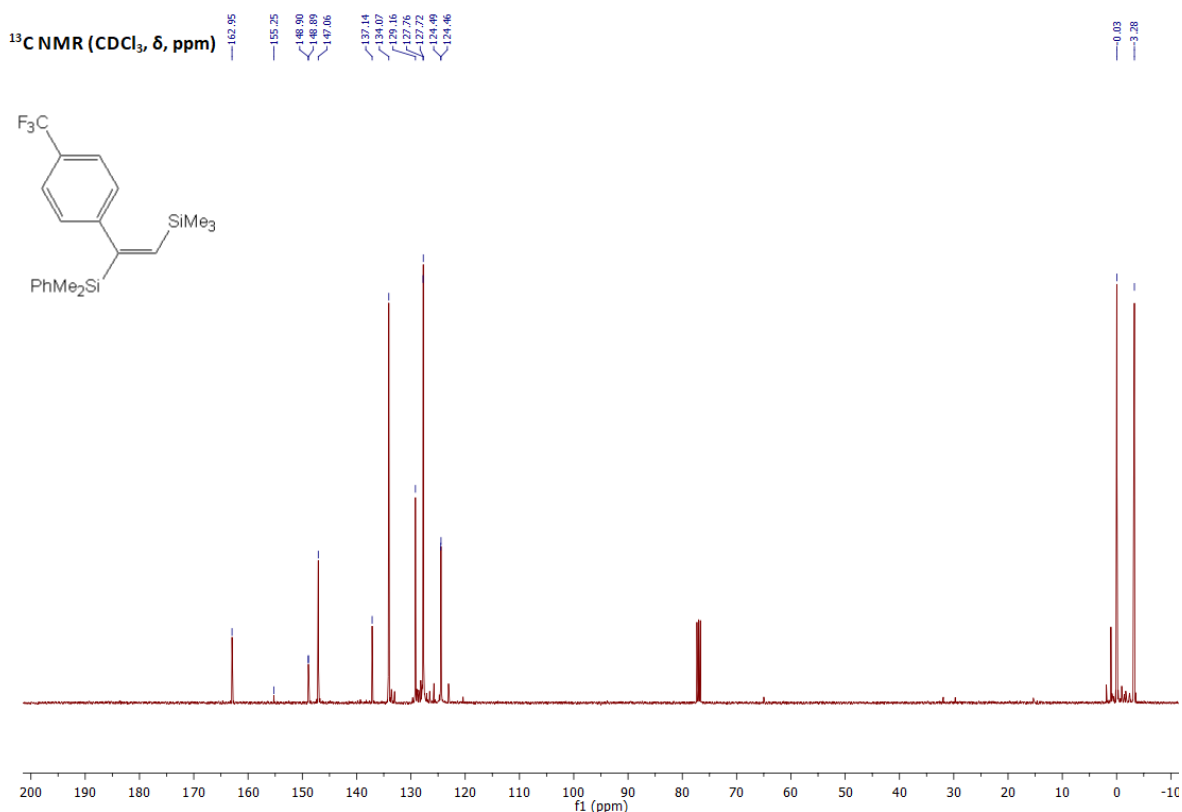


¹³C NMR (CDCl₃, δ, ppm)



¹H NMR (CDCl₃, δ, ppm)





11. X-ray analysis

Diffraction data were collected at room temperature by the ω -scan technique on Rigaku four-circle diffractometers: for *E*-**8ae** and *E*-**9ge** on Xcalibur with Eos CCD detector and graphite-monochromated MoK α radiation ($\lambda=0.71069$ Å), for **13ae** and *E*-**9ja** on SuperNova with Atlas detector and mirror-monochromatized CuK α radiation ($\lambda=1.541878$ Å). The data were corrected for Lorentz-polarization as well as for absorption effects [1]. Precise unit-cell parameters were determined by a least-squares fit of 1463 (*E*-**8ae**), 15164 (**13ae**) 13160 (*E*-**9ge**) and 2997 (*E*-**9ja**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT-2013 [2] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013 [2]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times U_{eq} of appropriate carrier atoms. Structure of *E*-**8ae** was previously reported. [3]

Table S8 lists the relevant experimental data and refinement details. Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-1573576 (*E*-**8ae**), CCDC-1573577 (**13ae**), CCDC-1576102 (*E*-**9ge**), and CCDC-1576645 (*E*-**9ja**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

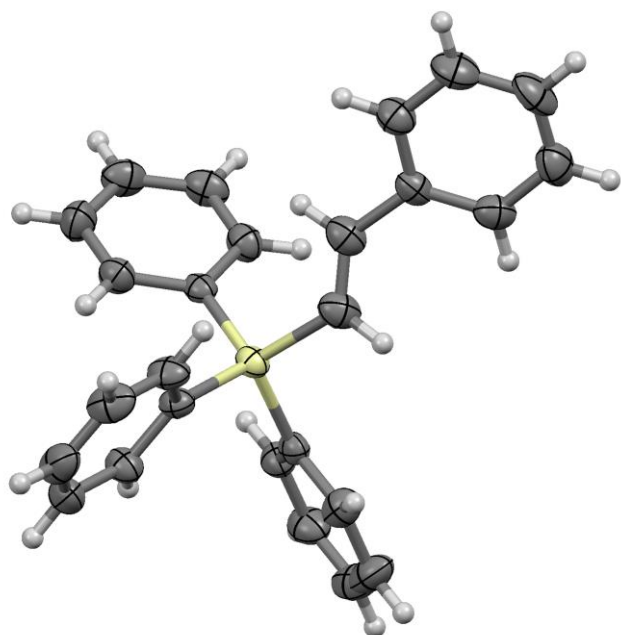


Figure S3. A perspective view of the molecule *E*-**8ae**. Ellipsoids are drawn at the 33% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

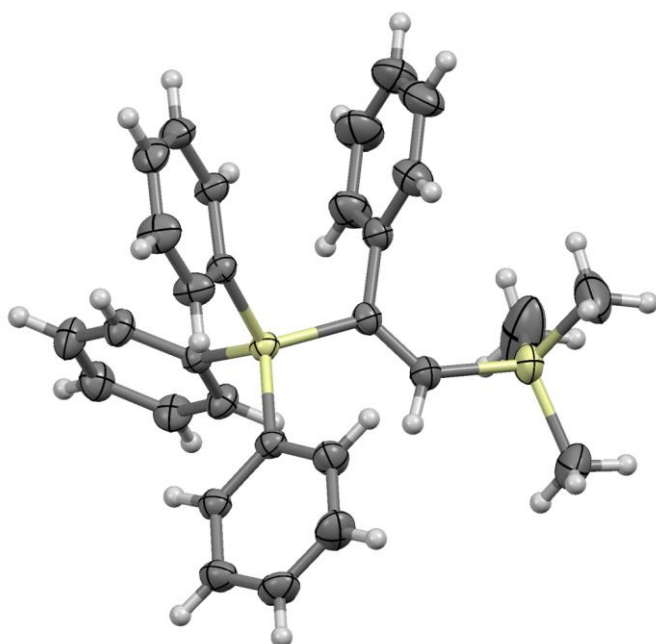


Figure S4. A perspective view of the molecule **13ae**. Ellipsoids are drawn at the 30% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

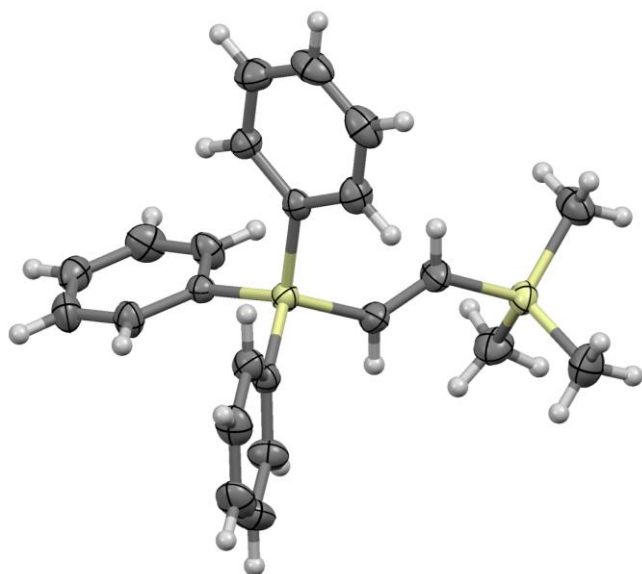


Figure S5. A perspective view of the molecule *E-9ge*. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

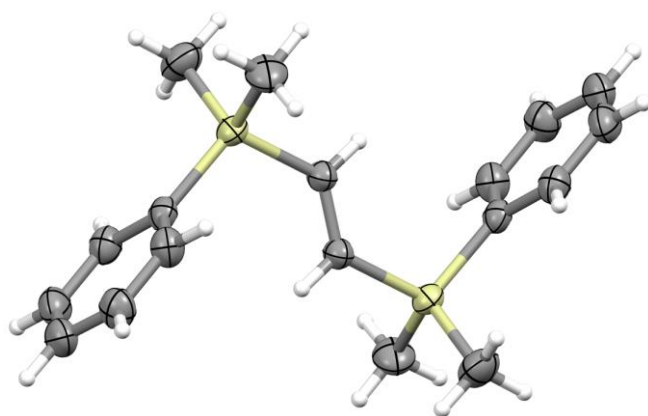


Figure S6. A perspective view of the molecule *E-9ja*. Ellipsoids are drawn at the 33% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

Table S8. Crystal data, data collection and structure refinement

Compound	<i>E-8ae</i>	<i>13ae</i>	<i>E-9ge</i>	<i>E-9ja</i>
Formula	C ₂₆ H ₂₂ Si	C ₂₉ H ₃₀ Si ₂	C ₂₃ H ₂₆ Si ₂	C ₁₈ H ₂₄ Si ₂
Formula weight	362.52	434.71	358.62	296.55
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2 ₁	P-1	P2 ₁ /c	P2 ₁ /c
a(Å)	7.3950(3)	8.4538(3)	7.73575(15)	6.64183(12)
b(Å)	11.3284(6)	9.4718(2)	11.6019(2)	7.04562(13)
c(Å)	12.5905(9)	18.2391(5)	23.8408(4)	19.7073(3)
α(°)	90	96.590(2)	90	90
β(°)	99.449(6)	94.901(2)	90.0063(17)	96.4325(16)
γ(°)	90	112.805(2)	90	90
V(Å ³)	1040.44(10)	1323.87(7)	2139.70(7)	916.41(3)
Z	2	2	4	2
D _x (g cm ⁻³)	1.16	1.09	1.11	1.08
F(000)	384	464	768	320
μ(mm ⁻¹)	0.120	1.294	0.168	1.653
Θ range (°)	3.28 – 28.35	2.46 – 75.59	3.10 – 25.00	4.53 – 76.34
Reflections:				
collected	4208	20109	37587	3560
unique (R _{int})	2903 (0.013)	5383 (0.020)	3755 (0.021)	1850 (0.014)
with I>2σ(I)	2471	5111	3265	1734
R(F) [I>2σ(I)]	0.041	0.040	0.035	0.036
wR(F ²) [I>2σ(I)]	0.095	0.111	0.099	0.101
R(F) [all data]	0.052	0.041	0.041	0.037
wR(F ²) [all data]	0.102	0.113	0.102	0.104
Goodness of fit	1.03	1.06	1.05	1.05
max/min Δρ (e Å ⁻³)	0.39/-0.18	0.27/-0.23	0.25/-0.20	0.23/-0.22

12. References

- [1] CrysAlisPro 1.171.38.46 (Rigaku Oxford Diffraction, **2015**)
- [2] G. M. Sheldrick, *Acta Crystallogr.*, **2015**, C71, 3-8.
- [3] L.N. Lewis, K.G. Sy, G.L. Bryant Junior, P.E. Donahue, *Organometallics*, **1991**, 10, 3750.