Electronic Supplementary Material (ESI) for ChemComm.

NiH-Catalyzed C(sp^3)−Si Coupling of Alkenes with Vinyl Chlorosilanes

Huanhuan Cui, † Changhao Niu, † Mimi Xing,† and Chun Zhang*,†,‡

† Institute of Molecular Plus, Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Science, Tianjin University, Weijin Rd. 92, Tianjin 300072, China.
‡ State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China.

E-mail: chunzhang@tju.edu.cn.

Supporting Information

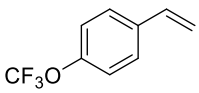
1. General Considerations

All manipulations were conducted with Schlenk tube. ^{1}H NMR spectra were recorded on JNM-ECZ400S/L1, JNM-ECZ600R/S1 and Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. Data were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quar-tet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were obtained by the same NMR and CF_3COOH was employed as external standard for the ^{19}F-NMR measurement. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Waters Ac-quity UPLC Class I/Xevo G2 Q-Tof. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Oil bath was used as the heat source.

2. Synthesis of substrates

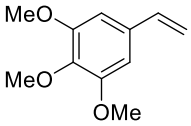
2.1 Synthesis of substrates

Alkenes (**1d, 1f, 1g, 1h, 1i, 1j, 1p, 1r, 1s, 1t, 1u**) are known compounds, and they were prepared according to the corresponding literature reports. Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature. [1-6]



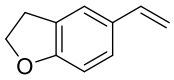
1d

1-(trifluoromethoxy)-4-vinylbenzene[1]



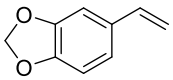
1f

1,2,3-trimethoxy-5-vinylbenzene[2]



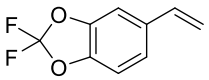
1g

5-vinyl-2,3-dihydrobenzofuran[3]



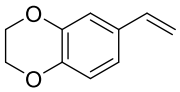
1h

5-vinylbenzo[*d*][1,3]dioxole[4]



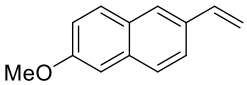
1i

2,2-difluoro-5-vinylbenzo[*d*][1,3]dioxole[5]



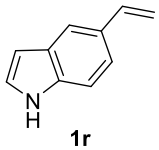
1j

6-vinyl-2,3-dihydrobenzo[*b*][1,4]dioxine[5]



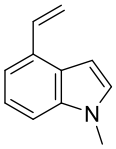
1p

2-methoxy-6-vinylnaphthalene[2]



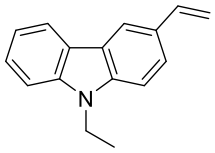
1r

5-vinyl-1*H*-indole[5]



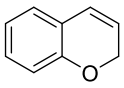
1s

1-methyl-4-vinyl-1*H*-indole[5]



1t

9-ethyl-3-vinyl-9*H*-carbazole[5]

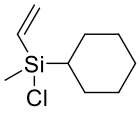


1u

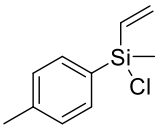
2*H*-chromene[6]

2.2 Synthesis of vinyl chlorosilanes

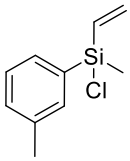
Chlorosilanes (**2a** and **2c**) are commercially available. Chlorosilanes (**2b**, **2d**, **2e**) were synthesized according to the literature procedure.[7] Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature.



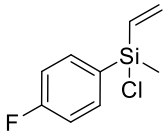
2b: chloro(cyclohexyl)(methyl)(vinyl)silane



2d: chloro(methyl)(*p*-tolyl)(vinyl)silane



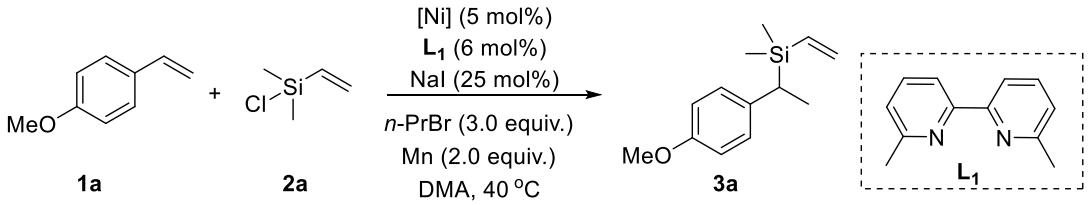
chloro(methyl)(*m*-tolyl)(vinyl)silane



2e: chloro(4-fluorophenyl)(methyl)(vinyl)silane

3. The effect of different reaction conditions

Table S1. The effect of [Ni]-salts [a]

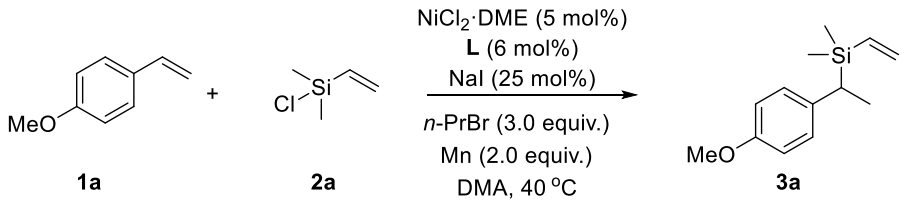


1a 2a 3a

Entry	[Ni]-salts	yield (%)[b]
1	$NiBr_2$·diglyme	52
2	$NiCl_2$·DME	60
3	$NiBr_2$·DME	37
4	$Ni(acac)_2$	46
5	$Ni(OTf)_2$	21
6	NiF_2	22
7	$NiCl_2$	47
8	$NiBr_2$	55
9	NiI_2	29

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), [Ni]-salts (0.01 mmol, 5 mol%), **L_1** (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), NaI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

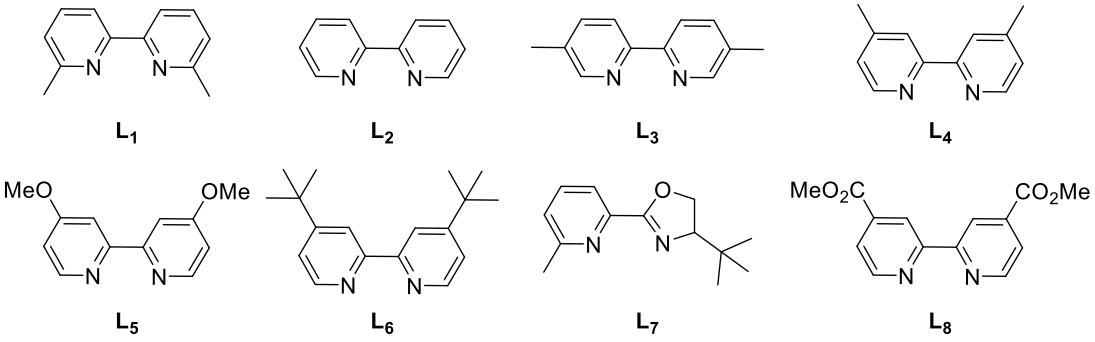
Table S2. The effect of different ligands [a]



1a **2a** **3a**

Entry	L	yield (%)[b]
1	L_1	60
2	L_2	0
3	L_3	0
4	L_4	0
5	L_5	0
6	L_6	0
7	L_7	20
8	L_8	0

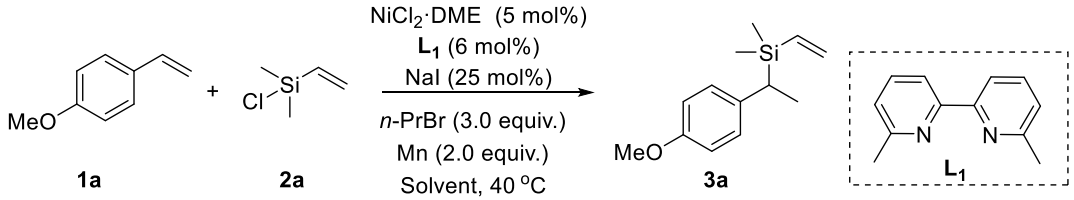
[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), **L** (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), NaI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.



L_1 L_2 L_3 L_4

L_5 L_6 L_7 L_8

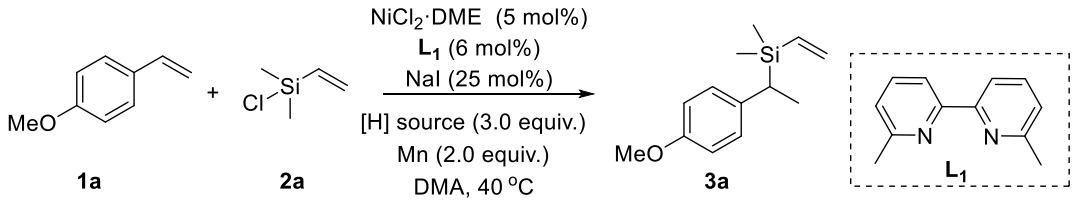
Table S3. The effect of different solvents [a]



Entry	solvent	yield(%)[b]
1	DMA	60
2	DMF	40
3	NMP	37
4	MTBE	46
5	DME	21
6	toluene	22
7	MeCN	47
8	DCM	55
9	THF	29

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), NaI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), Solvent (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

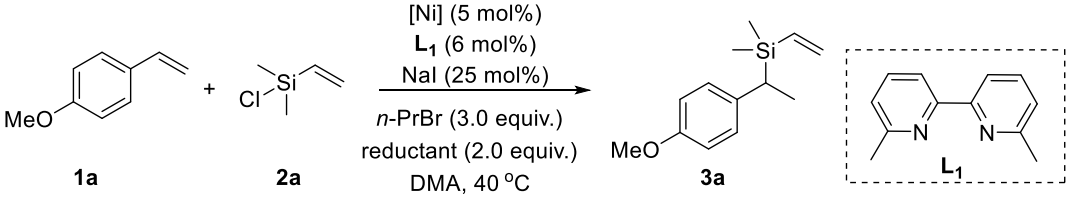
Table S4. The effect of different [H] source [a]



Entry	[H] source	yield(%)[b]
1	$(MeO)_3SiH$	0
2	PMHS	0
3	$PhSiH_3$	0
4	$EtSiH_3$	0
5	HBPin	0

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), [H] source (3.0 equiv.), NaI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

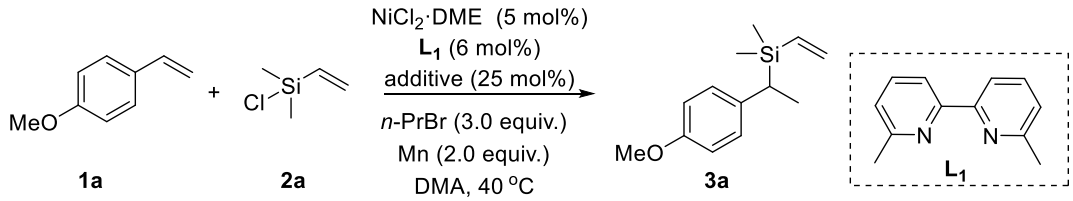
Table S5. The effect of different reductant [a]



Entry	reductant	yield(%)[b]
1	Zn	0
2	Fe	0
3	Cu	0
4	B_2Pin_2/K_3PO_4	0

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), NaI (0.25 equiv.), reductant (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

Table S6. The effect of different additive [a]

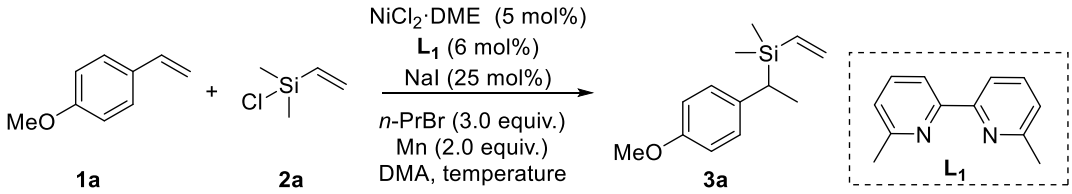


1a **2a** **3a** **L_1**

Entry	additive	yield(%)[b]
1	KI	76
2	CuI	53
3	TBAI	63

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), L_1 (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), additive (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

Table S7. The effect of different temperature [a]

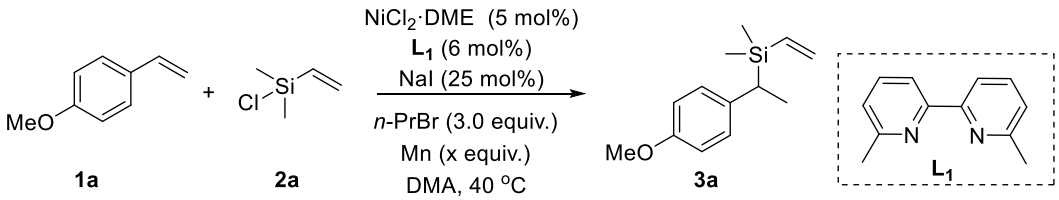


1a **2a** **3a** **L_1**

Entry	temperature	yield(%)[b]
1	0	41
2	10	39
3	25	63
4	60	41
5	80	20

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), **L_1** (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), KI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), temperature, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

Table S8. The effect of reductant equivalent [a]

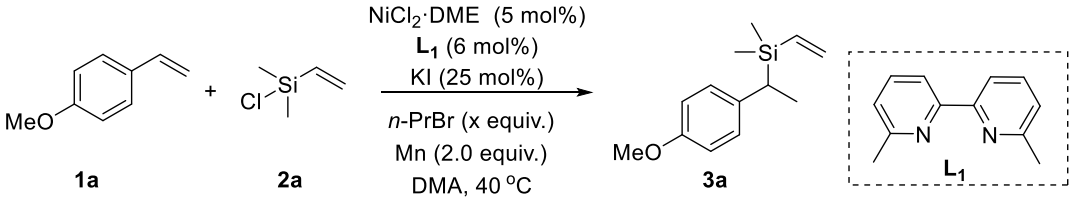


1a **2a** **3a** **L_1**

Entry	x eq.	yield(%)[b]
1	1.0	40
2	1.5	58
3	2.5	72
4	3.0	60

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), **L_1** (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), KI (0.25 equiv.), Mn (x equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard.

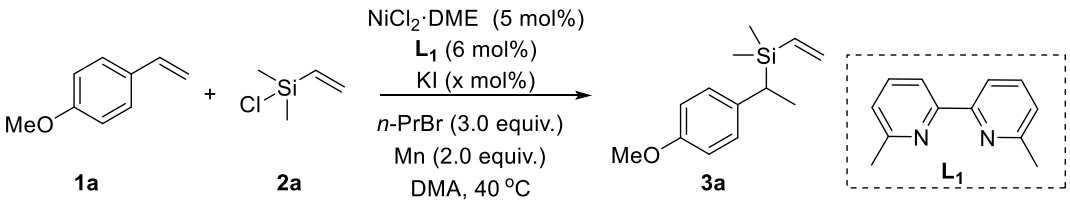
Table S9. The effect of *n*-PrBr equivalent [a]



Entry	x eq.	yield(%)[b]
1	1.0	43
2	2.0	86 (78)[c]
3	4.0	76
4	5.0	56

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), *n*-PrBr (x equiv.), NaI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard. [c]isolated yield.

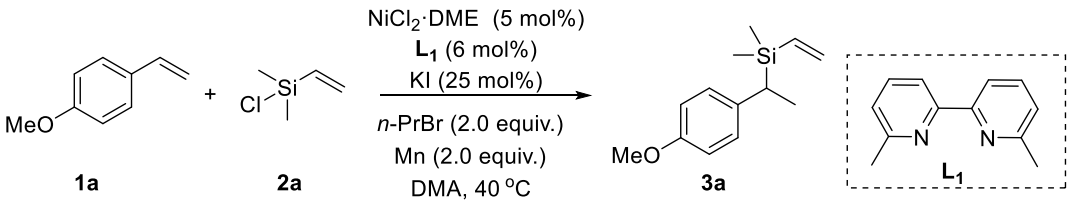
Table S10. The effect of KI equivalent [a]



Entry	x eq.	yield(%)[b]
1	0.1	46
2	0.5	40
3	1.0	20
4	2.0	21

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), *n*-PrBr (3.0 equiv.), KI (x equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard. [c]isolated yield.

Table S11. The effect of **2a** equivalent [a]



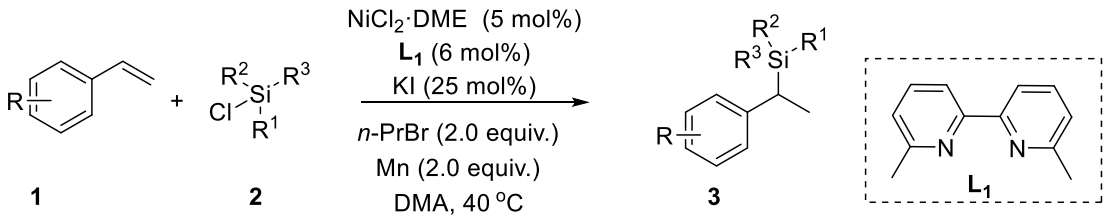
1a **2a** **3a**

Entry	**2a** equiv.	yield(%)[b]
1	1.0	18
2	1.5	27
3	2.5	78
4	3.0	77

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (x equiv.), $NiCl_2$·DME (0.01 mmol, 5 mol%), $\mathbf{L_1}$ (0.012 mmol, 6 mol%), *n*-PrBr (2.0 equiv.), KI (0.25 equiv.), Mn (0.4 mmol, 2.0 equiv.), DMA (1.0 mL), 40 °C, 24 h. [b]NMR yield using CH_2Br_2 as the internal standard. [c]isolated yield.

4. General procedure for the reaction

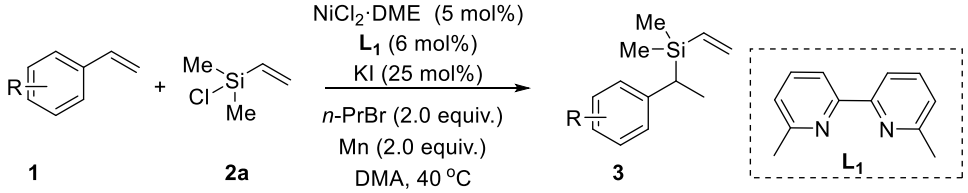
General procedure:

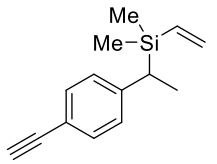


In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05 mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2** (0.4 mmol, 2.0 equiv.) and **1** (0.2 mmol, 1.0 equiv.), *n*-PrBr (0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40^{o}C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3**.

5. Unsuccessful substrate

Table S12. Substrate scope of various alkenes [a]

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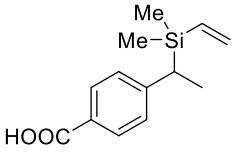
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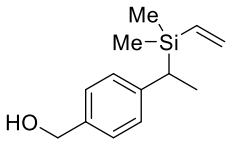
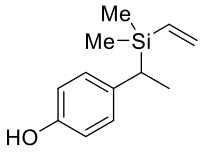
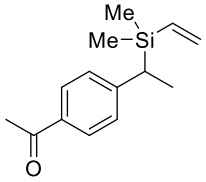
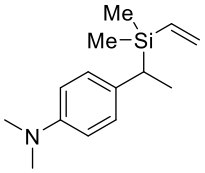

trace

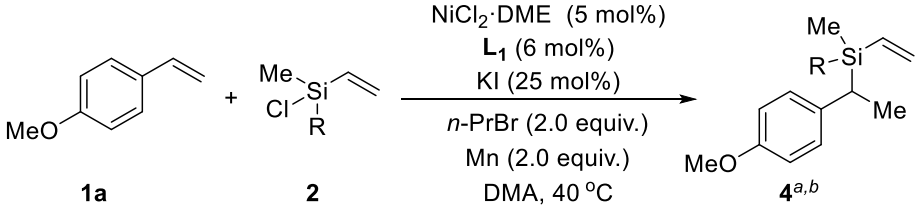

n.d.

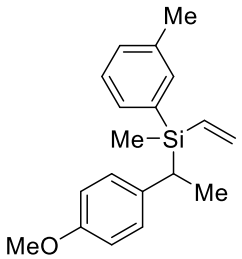

trace

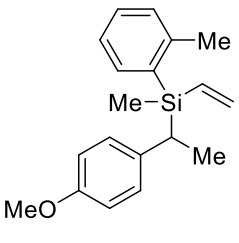

59%[c]

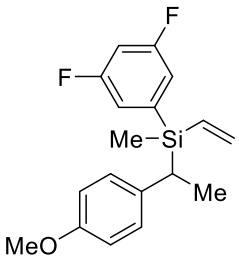
[a] The optimal reaction condition as same as entry 10 of Scheme 2. [b] isolated yield.[c] NMR yield using CH_2Br_2 as internal standard

Table S13. Substrate scope of various chlorosilanes. [a]



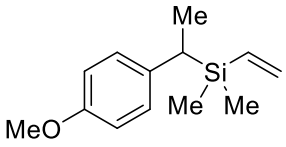

4e: 39%, dr = 1:1


4g: N.R.


4h: trace

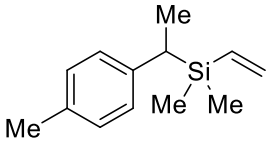
[a] Reaction conditions: The optimal reaction condition as same as entry 10 of Scheme 2. [b] isolated yield.

6. Analytical data for compounds



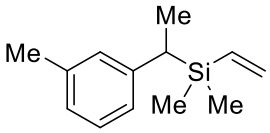
3a

(1-(4-methoxyphenyl)ethyl)dimethyl(vinyl)silane (**3a**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reacton afforded product **3a** as a yellow oil (34.3 mg, 78% yield): Rf = 0.3 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.97 (d, J = 12.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.13-5.95 (m, 2H), 5.67-5.61 (m, 1H), 3.78 (s, 3H), 2.19-2.12 (m, 1H), 1.33 (d, J = 8.0 Hz, 3H), 0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 156.8, 137.5, 137.5, 132.5, 127.9, 113.5, 55.2, 27.9, 15.3, -4.8, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{21}SiO$ $(M + H)^+$: 221.1362, found 221.1360.



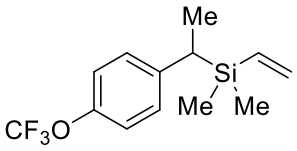
3b

Dimethyl(1-(p-tolyl)ethyl)(vinyl)silane (**3b**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-methyl-4-vinylbenzene (**1b**, 23.6 mg, 0.2 mmol). The above reaction afforded product **3b** as a yellow oil (25.4 mg, 62% yield): Rf = 0.8 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.04 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.09-5.95 (m, 2H), 5.67-5.61 (m, 1H), 2.29 (s, 3H), 2.20-2.14 (m, 1H), 1.33 (d, J = 8.0 Hz, 3H), -0.01 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 142.4, 137.5, 133.7, 132.6, 128.8, 127.2, 28.6, 21.0, 15.2, -4.8, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{21}Si$ $(M + H)^+$: 205.1413, found 205.1414.



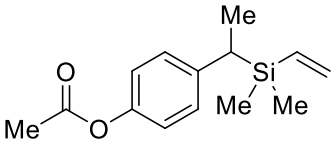
3c

Dimethyl(1-(m-tolyl)ethyl)(vinyl)silane (**3c**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-methyl-3-vinylbenzene (**1c**, 23.6 mg, 0.2 mmol). The above reaction afforded product **3c** as a colorless oil (18.4 mg, 45% yield): Rf = 0.8 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.13-7.10 (m, 1H), 6.91-6.83 (m, 3H), 6.13-5.95 (m, 2H), 5.67-5.61 (m, 1H), 2.31 (s, 3H), 2.21-2.15 (m, 1H), 1.35 (d, J = 4.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 145.5, 137.4, 137.4, 132.5, 128.0, 127.9, 125.2, 124.3, 28.9, 21.6, 15.1, -4.8, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{21}Si$ $(M + H)^+$: 205.1413, found 205.1412.



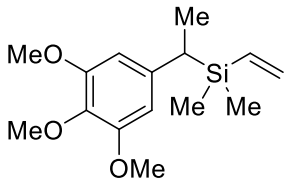
3d

Dimethyl(1-(4-(trifluoromethoxy)phenyl)ethyl)(vinyl)silane (**3d**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-(trifluoromethoxy)-4-vinylbenzene (**1d**, 37.6 mg, 0.2 mmol). The above reaction afforded product **3d** as a colorless oil (29.7 mg, 54% yield): Rf = 0.8 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.08-7.01 (m, 4H), 6.09-5.96 (m, 2H), 5.66-5.60 (m, 1H), 2.26-2.19 (m, 1H), 1.34 (d, J = 8.0 Hz, 3H), 0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 144.4, 136.7, 133.1, 128.1, 120.6, 28.6, 15.0, -5.0, -5.5 ppm; **^{19}F NMR** (376 MHz, Chloroform-d) δ: -58.0 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{18}F_3OSi$ $(M + H)^+$: 275.1079, found 275.1075.



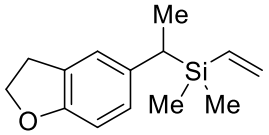
3e

4-(1-(dimethyl(vinyl)silyl)ethyl)phenyl acetate (**3e**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 4-vinylphenyl acetate (**1e**, 32.5 mg, 0.2 mmol). The above reaction afforded product **3e** as a colorless oil (32.7 mg, 66% yield): Rf = 0.4 (petroleum ether : EtOAc = 50:1); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.02 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 12.0 Hz, 2H), 6.11-5.95 (m, 2H), 5.67-5.60 (m, 1H), 2.27 (s, 3H), 2.25-2.19 (m, 1H), 1.34 (d, J = 8.0 Hz, 3H), 0.04 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 169.7, 147.7, 143.0, 137.0, 132.8, 127.8, 120.9, 28.6, 21.2, 15.1, -4.9, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{21}O_2Si$ $(M + H)^+$: 249.1311, found 249.1306.



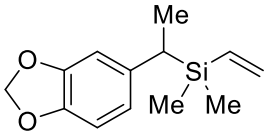
3f

Dimethyl(1-(3,4,5-trimethoxyphenyl)ethyl)(vinyl)silane (**3f**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1,2,3-trimethoxy-5-vinylbenzene (**1f**, 38.8 mg, 0.2 mmol). The above reaction afforded product **3f** as a yellow oil (27.9 mg, 50% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.23 (s, 2H), 6.21-5.95 (m, 2H), 5.67-5.61 (m, 1H), 3.81 (s, 9H), 2.16-2.11 (m, 1H), 1.32 (d, J = 8.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 152.8, 141.3, 137.3, 135.1, 132.7, 104.3, 60.9, 56.0, 29.5, 15.2, -4.8, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{25}O_3Si$ $(M + H)^+$: 281.1573, found 281.1574.



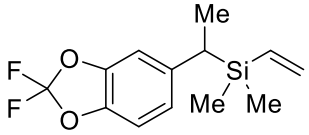
3g

(1-(2,3-dihydrobenzofuran-5-yl)ethyl)dimethyl(vinyl)silane (**3g**): I The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 5-vinyl-2,3-dihydrobenzofuran (**1g**, 29.2 mg, 0.2 mmol). The above reaction afforded product **3g** as a yellow oil (30.8 mg, 66% yield): Rf = 0.3 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.88 (d, J = 4.0 Hz, 1H), 6.76 (d, J = 4.0 Hz, 1H), 6.67 (t, J = 4.0 Hz, 1H), 6.12-5.94 (m, 2H), 5.68-5.60 (m, 1H), 4.55-4.50 (m, 2H), 3.19-3.14 (m, 2H), 2.15-2.10 (m, 1H), 1.31 (d, J = 4.0 Hz, 3H), -0.01 (d, J = 4.0 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 157.3, 137.6, 137.5, 132.6, 126.6, 126.5, 123.6, 108.7, 71.1, 30.1, 28.3, 15.6, -4.7, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{21}OSi$ $(M + H)^+$: 233.1362, found 233.1371.



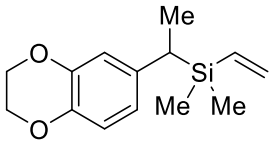
3h

(1-(benzo[d][1,3]dioxol-5-yl)ethyl)dimethyl(vinyl)silane (**3h**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 5-vinylbenzo[*d*][1,3]dioxole (**1h**, 29.6 mg, 0.2 mmol). The above reaction afforded product **3h** as a yellow oil (35.1 mg, 75% yield): Rf = 0.3 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.71-6.67 (m, 1H), 6.56-6.45 (m, 2H), 6.10-5.94 (m, 2H), 5.91-5.87 (m, 2H), 5.67-5.61 (m, 1H), 2.15-2.11 (m, 1H), 1.31 (t, J = 4.0 Hz, 3H), -0.00 (d, J = 8.0 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 147.4, 144.8, 139.6, 137.3, 132.8, 119.8, 108.0, 107.8, 100.7, 28.8, 15.5, -4.8, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{19}O_2Si$ $(M + H)^+$: 235.1154, found 235.1145.



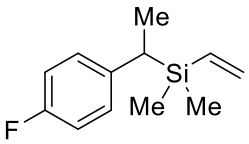
3i

(1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)ethyl)dimethyl(vinyl)silane (**3i**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 2,2-difluoro-5-vinylbenzo[*d*][1,3]dioxole (**1i**, 36.8 mg, 0.2 mmol). The above reaction afforded product **3i** as a yellow oil (41.0 mg, 76% yield): Rf = 0.5 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.92-6.88 (m, 1H), 6.75-6.68 (m, 2H), 6.09-5.98 (m, 2H), 5.68-5.61 (m, 1H), 2.23-2.18 (m, 1H), 1.32 (d, J = 8.0 Hz, 3H), 0.01 (d, J = 4.0 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 143.7, 142.0, 140.9, 136.5, 133.2, 131.6, 121.7, 108.7, 108.1, 29.2, 15.3, -5.0, -5.3 ppm; **^{19}F NMR** (376 MHz, Chloroform-d) δ: -49.9, -49.9 ppm. HRMS (ESI-TOF) m/z calcd for $C_{13}H_{17}F_2O_2Si$ $(M + H)^+$: 271.0966, found 271.0972.



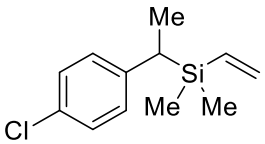
3j

(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethyl)dimethyl(vinyl)silane (**3j**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 6-vinyl-2,3-dihydrobenzo[*b*][1,4]dioxine (**1j**, 32.4 mg, 0.2 mmol). The above reaction afforded product **3j** as a yellow oil (25.1 mg, 51% yield): Rf = 0.6 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.73 (d, J = 8.0 Hz, 1H), 6.55-6.49 (m, 2H), 6.13-5.95 (m, 2H), 5.67-5.61 (m, 1H), 4.22 (s, 4H), 2.12-2.07 (m, 1H), 1.29 (d, J = 8.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 143.1, 140.6, 138.9, 137.4, 132.5, 120.3, 116.6, 115.5, 64.5, 64.3, 28.2, 15.3, -4.8, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{19}O_2Si$ $(M - H)^-$: 247.1154, found 247.1151.



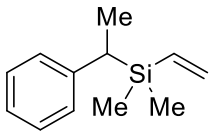
3k

(1-(4-fluorophenyl)ethyl)dimethyl(vinyl)silane (**3k**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-fluoro-4-vinylbenzene (**1k**, 24.6 mg, 0.2 mmol). The above reaction afforded product **3k** as a colorless oil (58.6 mg, 70% yield): Rf = 0.7 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.04-6.94 (m, 4H), 6.15-6.00 (m, 2H), 5.71-5.65 (m, 1H), 2.27-2.21 (m, 1H), 1.38 (d, J = 8.0 Hz, 3H), 0.04 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 137.0, 132.8, 128.2, 128.2, 114.8, 114.6, 28.3, 15.2, -5.0, -5.5 ppm; **^{19}F NMR** (376 MHz, Chloroform-d) δ: -119.7 ppm. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{18}FSi$ $(M + H)^+$: 209.1162, found 209.1158.



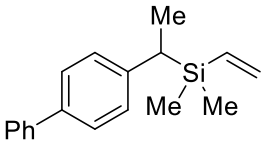
3l

(1-(4-chlorophenyl)ethyl)dimethyl(vinyl)silane (**3l**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-chloro-4-vinylbenzene (**1l**, 27.7 mg, 0.2 mmol). The above reaction afforded product **3l** as a colorless oil (69.8 mg, 78% yield): Rf = 0.7 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.19 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 12.0 Hz, 2H), 6.09-5.95 (m, 2H), 5.66-5.60 (m, 1H), 2.22-2.17 (m, 1H), 1.33 (d, J = 8.0 Hz, 3H), -0.01 (d, J = 4.0 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 144.1, 136.8, 133.0, 129.9, 128.4, 128.0, 28.7, 15.0, -5.0, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{18}ClSi$ $(M + H)^+$: 225.0866, found 225.0861.



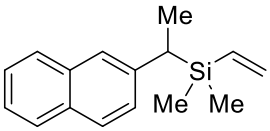
3m

Dimethyl(1-phenylethyl)(vinyl)silane (**3m**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), styrene (**1m**, 20.8 mg, 0.2 mmol). The above reaction afforded product **3m** as a colorless oil (43.4 mg, 57% yield): Rf = 0.8 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.25-7.21 (m, 2H), 7.10-7.00 (m, 3H), 6.12-5.95 (m, 2H), 5.67-5.61 (m, 1H), 2.25-2.19 (m, 1H), 1.36 (d, J = 8.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 145.6, 137.4, 132.7, 128.1, 127.3, 124.5, 29.1, 15.1, -4.8, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{19}Si$ $(M + H)^+$: 191.1256, found 191.1250.



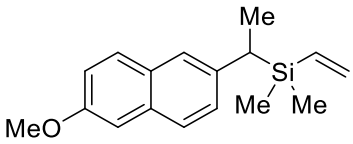
3n

(1-([1,1'-biphenyl]-4-yl)ethyl)dimethyl(vinyl)silane (**3n**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 4-vinyl-1,1'-biphenyl (**1n**, 36.0 mg, 0.2 mmol). The above reaction afforded product **3n** as a colorless oil (34.0 mg, 64% yield): Rf = 0.5 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.60 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 6.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.17-5.99 (m, 2H), 5.71-5.65 (m, 1H), 2.31-2.26 (m, 1H), 1.40 (d, J = 8.0 Hz, 3H), 0.05 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 144.9, 141.3, 137.3, 137.3, 132.9, 128.8, 127.7, 126.9, 126.9, 126.8, 28.9, 15.1, -4.7, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{23}Si$ $(M + H)^+$: 267.1569, found 267.1579.



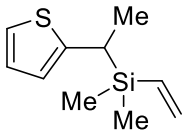
3o

Dimethyl(1-(naphthalen-2-yl)ethyl)(vinyl)silane (**3o**): I The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 2-vinylnaphthalene (**1o**, 30.8 mg, 0.2 mmol). The above reaction afforded product **3o** as a yellow oil (33.2 mg, 69% yield): Rf = 0.5 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.75-7.67 (m, 3H), 7.43-7.32 (m, 3H), 7.21-7.16 (m, 1H), 6.12-5.93 (m, 2H), 5.65-5.59 (m, 1H), 2.39-2.34 (m, 1H), 1.43 (d, J = 8.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 143.3, 137.2, 133.7, 132.7, 131.4, 127.5, 127.3, 127.2, 127.2, 125.7, 124.5, 124.3, 29.4, 15.1, -4.8, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{21}Si$ $(M + H)^+$: 241.1413, found 241.1408.



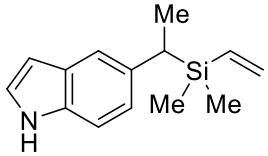
3p

(1-(6-methoxynaphthalen-2-yl)ethyl)dimethyl(vinyl)silane (**3p**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 2-methoxy-6-vinylnaphthalene (**1p**, 36.8 mg, 0.2 mmol). The above reaction afforded product **3p** as a colorless oil (24.8 mg, 46% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.63-7.58 (m, 2H), 7.36 (s, 1H), 7.17-7.14 (m, 1H), 7.09-7.07 (m, 2H), 6.13-5.93 (m, 2H), 5.65-5.59 (m, 1H), 3.88 (s, 3H), 2.35-2.30 (m, 1H), 1.42 (d, J = 8.0 Hz, 3H), -0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 156.8, 140.9, 137.4, 132.6, 132.3, 129.3, 128.8, 127.6, 126.2, 124.3, 118.5, 105.7, 55.3, 29.0, 15.2, -4.8, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{23}OSi$ $(M + H)^+$: 271.1518, found 271.1512.



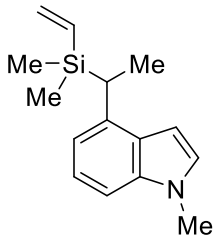
3q

Dimethyl(1-(thiophen-2-yl)ethyl)(vinyl)silane (**3q**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 2-vinylthiophene (**1q**, 22.0 mg, 0.2 mmol). The above reaction afforded product **3q** as a yellow oil (22.0 mg, 56% yield): Rf = 0.6 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.01 (d, J = 4Hz, 1H), 6.91-6.89 (m, 1H), 6.63-6.60 (m, 1H), 6.13-5.99 (m, 2H), 5.70-5.66 (m, 1H), 2.53-2.50 (m, 1H), 1.39 (d, J = 4.0 Hz, 3H), 0.06 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 136.9, 133.0, 126.6, 121.7, 120.9, 24.6, 16.9, -4.9, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{10}H_{17}SSi$ $(M + H)^+$: 197.0820, found 197.0822.



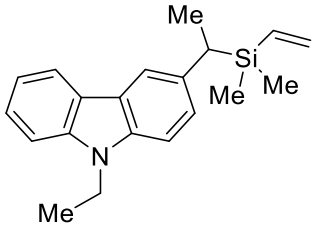
3r

5-(1-(dimethyl(vinyl)silyl)ethyl)-1H-indole (**3r**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 5-vinyl-1H-indole (**1r**, 28.6 mg, 0.2 mmol). The above reaction afforded product **3r** as a brown oil (27.2 mg, 59% yield): Rf = 0.3 (EtOAc : petroleum ether = 1 : 10); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.96 (s, 1H), 7.29-7.23 (m, 2H), 7.14-7.11 (m, 1H), 6.91-6.88 (m, 1H), 6.45 (s, 1H), 6.16-5.93 (m, 2H), 5.67-5.62 (m, 1H), 2.31-2.25 (m, 1H), 1.40 (d, J = 8.0 Hz, 3H), 0.00 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 138.0, 136.9, 133.8, 132.3, 128.1, 124.1, 122.6, 118.2, 110.4, 102.2, 28.7, 15.8, -4.6, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{20}NSi$ $(M + H)^+$: 230.1365, found 230.1374.



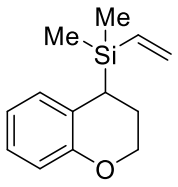
3s

4-(1-(dimethyl(vinyl)silyl)ethyl)-1-methyl-1H-indole (**3s**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 1-methyl-4-vinyl-1H-indole (**1s**, 31.4 mg, 0.2 mmol). The above reaction afforded product **3s** as a yellow oil (31.3 mg, 64% yield): Rf = 0.3 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.19-6.98 (m, 3H), 6.85-6.80 (m, 1H), 6.46 (d, J = 8.0 Hz, 1H), 6.20-6.09 (m, 1H), 6.00-5.93 (m, 1H), 5.72-5.64 (m, 1H), 3.78 (s, 3H), 2.73-2.68 (m, 1H), 1.47 (d, J = 8.0 Hz, 3H), 0.01 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 138.7, 138.1, 136.5, 132.2, 127.8, 127.6, 121.8, 116.5, 105.5, 100.2, 33.0, 25.4, 15.5, -4.1, -5.0 ppm; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{22}NSi$ $(M + H)^+$: 244.1521, found 244.1531.



3t

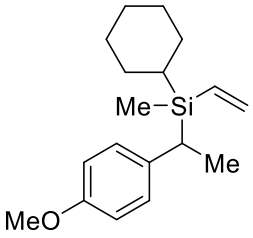
3-(1-(dimethyl(vinyl)silyl)ethyl)-9-ethyl-9H-carbazole (**3t**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 9-ethyl-3-vinyl-9H-carbazole (**1t**, 44.2 mg, 0.2 mmol). The above reaction afforded product **3t** as a grey oil (45.0 mg, 73% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 8.11 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.48-7.39 (m, 2H), 7.32-7.19 (m, 3H), 6.23-6.00 (m, 2H), 5.73-5.67 (m, 1H), 4.36 (s, 2H), 2.46-2.40 (m, 1H), 1.51 (d, J = 8.0 Hz, 3H), 1.45 (d, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 3H), 0.07 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 140.2, 138.0, 137.9, 136.0, 132.6, 125.8, 125.4, 123.0, 122.9, 120.4, 118.4, 118.3, 108.5, 108.0, 37.7, 28.8, 16.0, 14.0, -4.5, -5.2 ppm; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{26}NSi$ $(M + H)^+$: 308.1834, found 308.1848.



3u

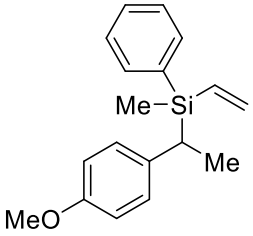
chroman-4-yldimethyl(vinyl)silane (**3u**): The general procedure was followed using chlorodimethyl(vinyl)silane (**2a**, 48.3 mg, 0.4 mmol), 2H-chromene (**1u**, 26.4 mg, 0.2 mmol). The above reaction afforded product **3u** as a yellow oil (20.4 mg, 47% yield): Rf = 0.4 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.06-7.00 (m, 2H), 6.84-6.80 (m, 2H), 6.23-6.00 (m, 2H), 5.75-5.69 (m, 1H), 4.24-4.11 (m, 2H), 2.45-2.39 (m, 1H), 2.24-2.15 (m, 1H), 2.06-2.01 (m,

1H), 0.16 (d, *J* = 4.0 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) *δ*: 154.3, 137.7, 133.0, 129.0, 125.9, 124.6, 119.9, 116.8, 65.5, 29.7, 24.4, 24.3, -3.6, -3.9 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{19}OSi$ $(M + H)^+$: 219.1205, found 219.1201.



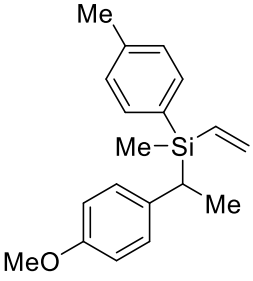
4b

cyclohexyl(1-(4-methoxyphenyl)ethyl)(methyl)(vinyl)silane (**4b**): The general procedure was followed using chloro(cyclohexyl)(methyl)(vinyl)silane (**2b**, 75.0 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reaction afforded product **4b** as a yellow oil (38.8 mg, 67% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) *δ*: 6.97 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.17-5.96 (m, 2H), 5.65-5.52 (m, 1H), 3.78 (s, 3H), 2.29-2.23 (m, 1H), 1.32 (d, *J* = 8.0 Hz, 4H), 1.18-1.04 (m, 6H), 0.90-0.83 (m, 4H), -0.06 (d, *J* = 48.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) *δ*: 156.7, 137.8, 135.2, 133.5, 133.4, 128.2, 113.5, 113.4, 55.2, 31.9, 29.7, 29.4, 28.1, 27.7, 27.6, 27.0, 25.5, 25.3, 23.1, 22.7, 15.9, 14.1, -9.5, -9.6 ppm; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{29}OSi$ $(M + H)^+$: 289.1988, found 289.1997.



4c

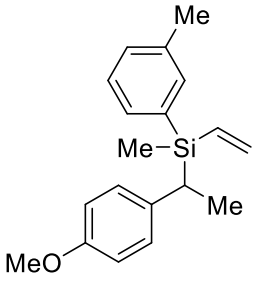
(1-(4-methoxyphenyl)ethyl)(methyl)(phenyl)(vinyl)silane (**4c**): The general procedure was followed using chloro(methyl)(phenyl)(vinyl)silane (**2c**, 72.3 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reaction afforded product **4c** as a yellow oil (30.7 mg, 54% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.49-7.46 (m, 2H), 7.43-7.36 (m, 3H), 6.96-6.93 (m, 2H), 6.84-6.81 (m, 2H), 6.47-6.12 (m, 2H), 5.84-5.74 (m, 2H), 3.83 (s, 3H), 2.55-2.48 (m, 1H), 1.45-1.39 (m, 3H), 0.35 (d, *J* = 20.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) *δ*: 156.9, 136.8, 136.3, 135.8, 135.3, 134.8, 134.7, 134.7, 134.2, 129.2, 129.1, 128.4, 128.3, 127.6, 113.4, 55.2, 27.5, 27.4, 15.8, 15.7, -6.5, -6.9 ppm; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{23}OSi$ $(M + H)^+$: 283.1518, found 283.1515.



4d

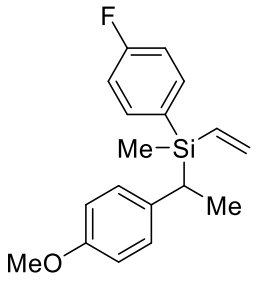
(1-(4-methoxyphenyl)ethyl)(methyl)(p-tolyl)(vinyl)silane (**4d**): The general procedure was

followed using chloro(methyl)(p-tolyl)(vinyl)silane (**2d**, 78.4 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reaction afforded product **4d** as a yellow oil (41.3 mg, 70% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.10 (d, J = 8.0 Hz, 2H), 6.96-6.93 (m, 2H), 6.70-6.54 (m, 4H), 6.18-5.83 (m, 2H), 5.55-5.44 (m, 1H), 3.57 (s, 3H), 2.25-2.21 (m, 1H), 2.15 (s, 3H), 1.17-1.11 (m, 3H), 0.05 (d, J = 20.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 156.9, 139.0, 138.9, 137.0, 135.6, 134.9, 134.8, 134.7, 134.4, 134.0, 132.5, 132.0, 128.5, 128.4, 128.3, 113.4, 55.2, 27.6, 27.5, 21.5, 15.9, 15.8, -6.3, -6.8 ppm; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{25}OSi$ $(M + H)^+$: 297.1675, found 297.1679.



4e

(1-(4-methoxyphenyl)ethyl)(methyl)(m-tolyl)(vinyl)silane (**4e**): The general procedure was followed using chloro(methyl)(m-tolyl)(vinyl)silane (**2e**, 78.4 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reaction afforded product **4e** as a yellow oil (23.3 mg, 39% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.21-7.16 (m, 4H), 6.89-6.86 (m, 2H), 6.76-6.73 (m, 2H), 6.39-6.03 (m, 2H), 5.75-5.64 (m, 1H), 3.76 (s, 3H), 2.45-2.39 (m, 1H), 2.31 (s, 3H), 1.36-1.30 (m, 3H), 0.25 (d, J = 24.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 156.9, 136.9, 136.0, 135.5, 135.4, 135.3, 134.8, 134.6, 134.1, 131.8, 131.7, 130.0, 129.9, 128.4, 127.5, 113.4, 55.2, 27.5, 27.4, 21.5, 15.8, 15.7, -6.4, -7.0 ppm; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{25}OSi$ $(M + H)^+$: 297.1675, found 297.1668.

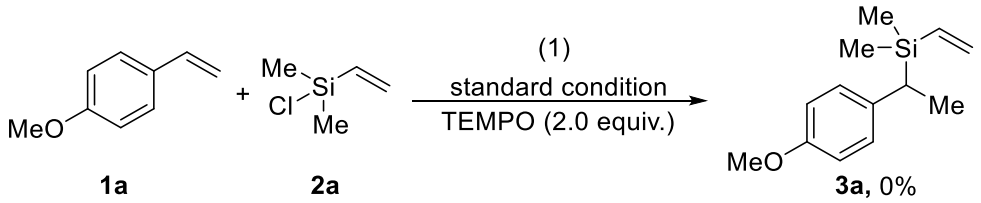


4g

(4-fluorophenyl)(1-(4-methoxyphenyl)ethyl)(methyl)(vinyl)silane (**4g**): The general procedure was followed using chloro(4-fluorophenyl)(methyl)(vinyl)silane (**2g**, 80.0 mg, 0.4 mmol), 1-methoxy-4-vinylbenzene (**1a**, 26.8 mg, 0.2 mmol). The above reaction afforded product **4g** as a yellow oil (21.6 mg, 36% yield): Rf = 0.2 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-d) δ: 7.28-7.23 (m, 2H), 6.96-6.90 (m, 2H), 6.78-6.75 (m, 2H), 6.68-6.65 (m, 2H), 6.29-5.98 (m, 2H), 5.69-5.58 (m, 1H), 3.69 (s, 3H), 2.35-2.30 (m, 1H), 1.28-1.23 (m, 3H), 0.19 (d, J = 8.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ: 157.0, 136.7, 136.6, 136.5, 135.0, 134.8, 134.6, 134.4, 128.3, 114.9, 114.7, 114.7, 113.4, 55.2, 27.5, 15.7, 15.6, -6.5 -6.6 ppm; **^{19}F NMR** (376 MHz, Chloroform-d) δ: -111.79 (d, J = 3.8 Hz), -111.86 (d, J = 3.8 Hz) ppm; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{22}FOSi$ $(M + H)^+$: 301.1424, found 301.1420.

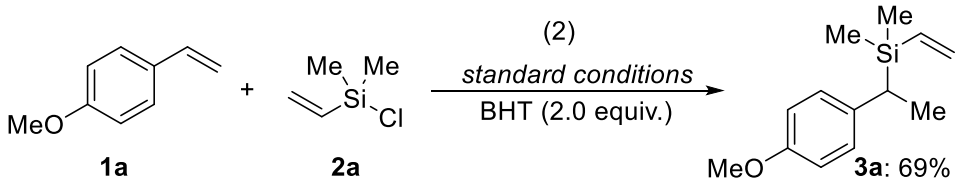
7. discussion on mechanism

7.1 Radical traping experiments



1a **2a** **3a,** 0%

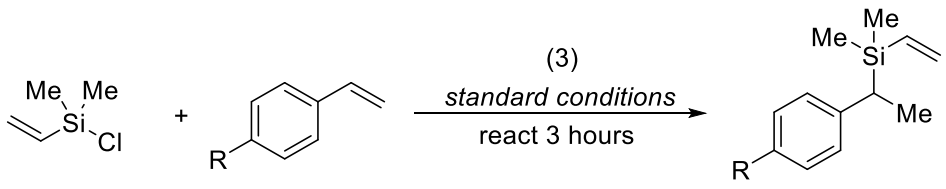
In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$ ĐME (2.2 mg, 0.01 mmol, 5 mol%), $\mathbf{L_1}$ (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%), TEMPO (62.5 mg, 0.4 mmol). The bottle was evacuated and back-filled under a N2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) and **1a** (26.8 mg, 0.2 mmol, 1.0 equiv.), *n*-PrBr (49.2 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 ^oC for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL× 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. In this reaction system, no target product was detected.



1a **2a** **3a**: 69%

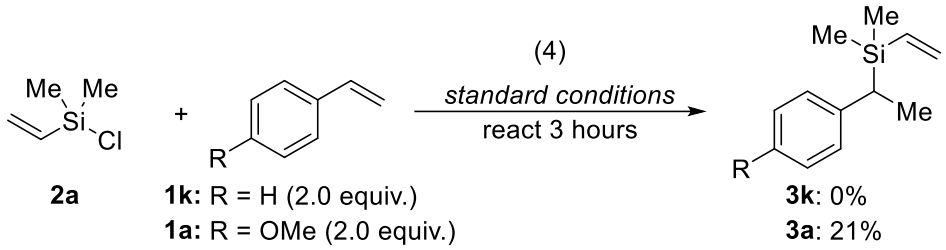
In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$ ĐME (2.2 mg, 0.01 mmol, 5 mol%), $\mathbf{L_1}$ (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%), 2,6-di-tert-butyl-4-methylphenol (88.0 mg, 0.4 mmol). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) and **1a** (26.8 mg, 0.2 mmol, 1.0 equiv.), *n*-PrBr (49.2 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 ^oC for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Product **3a** (29.4 mg, 69%) was obtained as a yellow oil.

7.2 Competition experiments



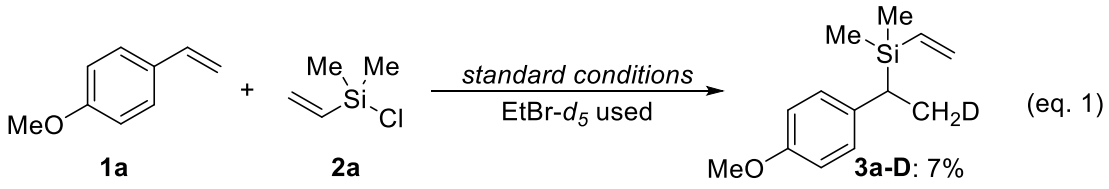
2a **1k:** R = H (2.0 equiv.) **3k**: 25%
1i: R = F (2.0 equiv.) **3i**: 0%

In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$ ĐME (1.6 mg, 0.0075, 5 mol%), **L_1** (1.7 mg, 0.009 mmol, 6 mol%), Mn (16.5 mg, 0.3 mmol, 2.0 equiv.), KI (6.2 mg, 0.0375 mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (18.1 mg, 0.15 mmol, 1.0 equiv.), **1k** (31.2 mg, 0.3 mmol, 2.0 equiv.) and **1i** (36.6 mg, 0.3 mmol, 2.0 equiv.), *n*-PrBr (36.9 mg, 0.3 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40°C for 3 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The above system afforded **3k** with 25 % yield HNMR and without **3i**.



In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$ ĐME (1.6 mg, 0.0075, 5 mol%), **L1** (1.7 mg, 0.009 mmol, 6 mol%), Mn (16.5 mg, 0.3 mmol, 2.0 equiv.), KI (6.2 mg, 0.0375 mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (18.1 mg, 0.15 mmol, 1.0 equiv), **1k** (31.2 mg, 0.3 mmol, 2.0 equiv) and **1a** (40.3 mg, 0.3 mmol, 2.0 equiv), n-PrBr (36.9 mg, 0.3 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40°C for 3 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The above system afforded **3a** with 21 % yield HNMR and without **3k**.

Sheme S1. Isotopic labelling



In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$ ĐME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) and **1a** (26.8 mg, 0.2 mmol, 1.0 equiv.), EtBr-d5 (45.6 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 °C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL ×

3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Product **3a-D** (3.1 mg, 7%) was obtained as a yellow oil.

3a-D: **^{1}H NMR** (400 MHz, Chloroform-d) δ: 6.97 (d, J = 12.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.15-5.94 (m, 2H), 5.69-5.57 (m, 1H), 3.77 (s, 3H), 2.19-2.13 (m, 1H), 1.33 (d, J = 8.0 Hz, 2.25H), 0.00 (s, 6H).

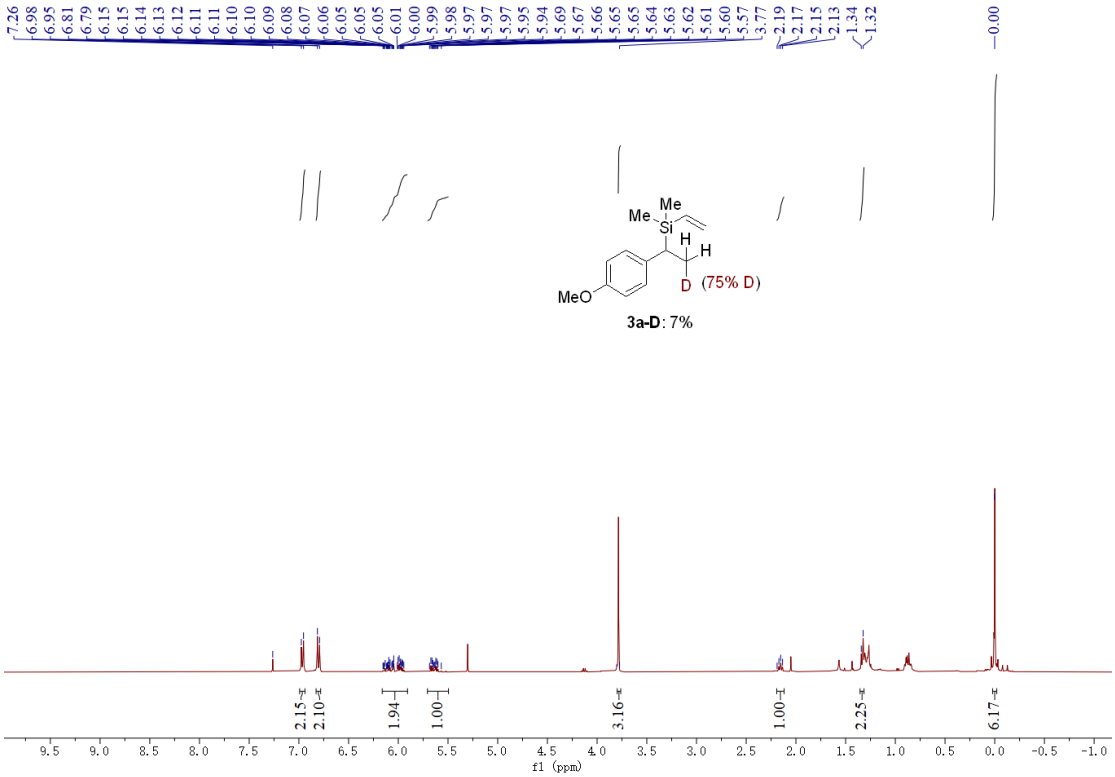
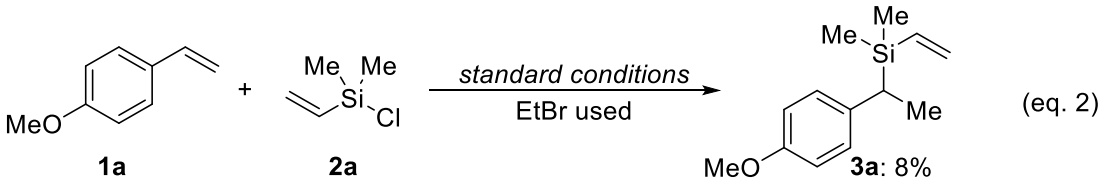
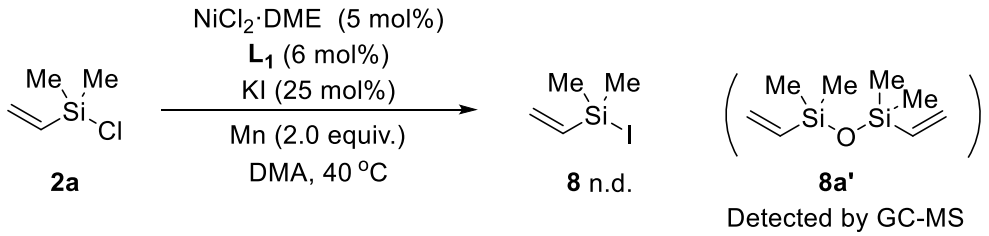


Figure S1. ^{1}H NMR analysis of 3a-D

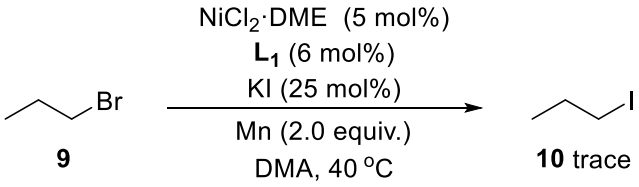


In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) and **1a** (26.8 mg, 0.2 mmol, 1.0 equiv.), EtBr (43.6 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 ^{o}C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Product **3a** (3.5 mg, 8%) was obtained as a yellow oil.

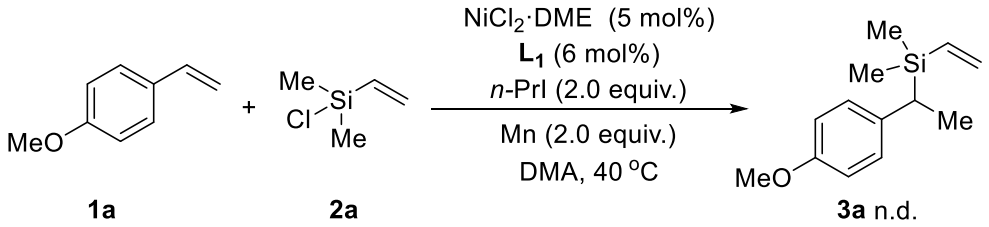
7.4 Control experiments



In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 °C for 24 h. The resulting mixture was filtered. The reaction system was monitored by GC-MS. In the above reaction system, **8a'** was detected without any relative signal about **8a**.



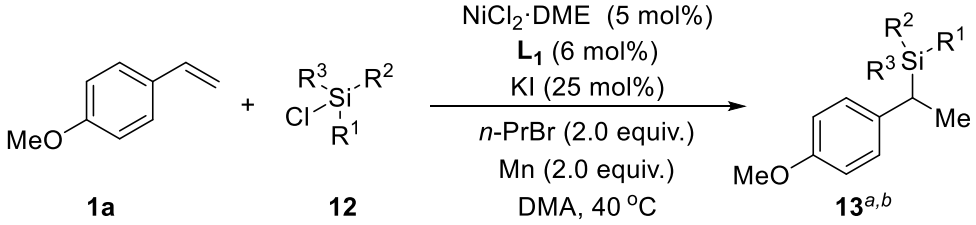
In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.), KI (8.3 mg, 0.05mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **9** (49.2 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 °C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4. The reaction system was monitored by GC-MS, and trace **10** was detected.



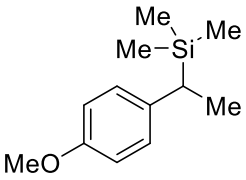
In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (2.2 mg, 0.01 mmol, 5 mol%), **L_1** (2.2 mg, 0.012 mmol, 6 mol%), Mn (22 mg, 0.4 mmol, 2.0 equiv.). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. After above, **2a** (48.3 mg, 0.4 mmol, 2.0 equiv.) and **1a** (26.8 mg, 0.2 mmol, 1.0 equiv.), *n*-PrBr (68.0 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40 °C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and

quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. In this reaction system, no target product was detected by GC-MS.

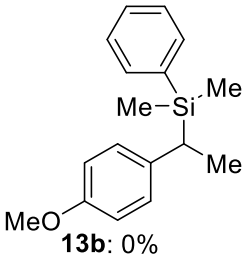
Table S14. The effect of olefins on Si



1a **12** **13**[a,b]



13a: 0%

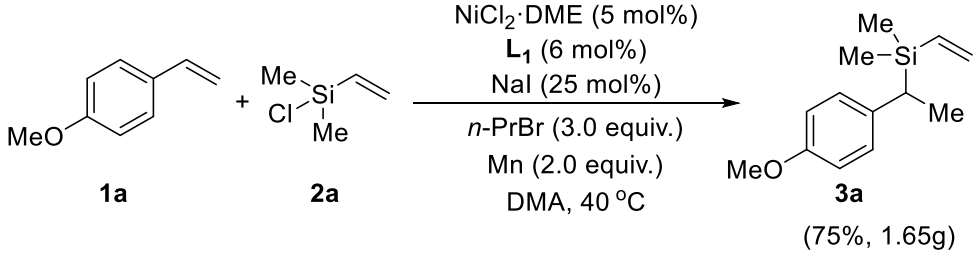


13b: 0%

[a] Reaction conditions: The optimal reaction condition as same as entry 10 of Scheme 2.
[b] isolated yield.

8. Further transformations for the product

8.1 Gram scale reaction



1a **2a** **3a**

(75%, 1.65g)

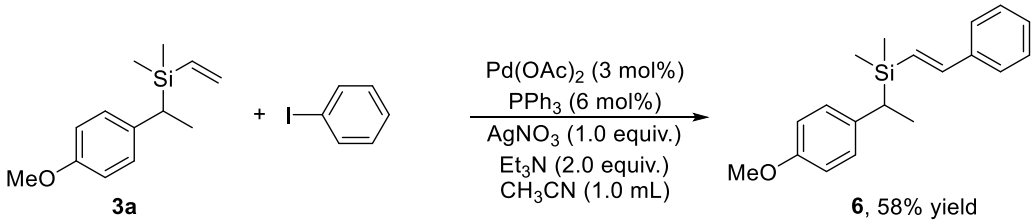
In an oven dried glass bottle, which contained a stirring bar, was charged with $NiCl_2$·DME (110.0 mg, 0.5 mmol, 5 mol%), **L1** (110.4 mg, 0.6 mmol, 6 mol%), Mn (1.1 g, 20 mmol, 2.0 equiv.), KI (415 mg, 2.5mmol, 25 mol%). The bottle was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (50 mL) was added under N_2. After above, **2a** (20.0 mmol, 2.4 g, 2.0 equiv.) and **1a** (10.0 mmol, 1.3 g, 1.0 equiv.), *n*-PrBr (20 mmol, 2.5 g, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 40°C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H_2O (2 mL), then it was extracted with EtOAc (10 mL × 3), the organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product 75% **3a**.

8.2 Procedure for synthesis of 5[8]

3a **5**

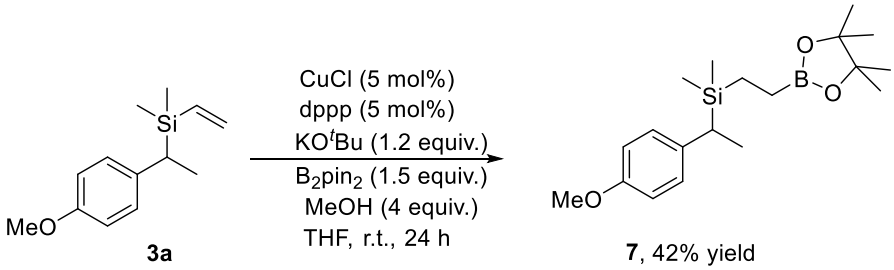
A solution of *m*-chloroperbenzoic acid (41.4 mg, 0.24 mmol, 1.2 equiv.) in 0.2 mL of CH_2C1_2 was added at room temperature to a mixture containing **3a** (44.0 mg, 0.2 mmol, 1.0 equiv.) and anhydrous Na_2HPO_4 (34.1 mg, 2.4 mmol, 1.2 equiv.) in 0.2 mL of CH_2Cl_2. The mixture was stirred 12 h. Saturated $NaHSO_3$ solution (20 mL) was added, and the mixture was stirred for 30 min. Saturated $NaHCO_3$ solution (4 mL) was next added carefully, and stirring was continued for another 30 min. The organic layer was separated, washed with saturated $NaHSO_3$ solution and brine, dried, and concentrated. The combined organic layers were dried ($MgSO_4$), and the crude product obtained was then purified by column chromatography (silica gel/pentane) to give the corresponding product **5** as a colorless oil (30.3 mg, 64% yield): Rf = 0.2 (EtOAc:petroleum ether = 1:100); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ: 7.03-7.00 (m, 2H), 6.84-6.80 (m, 2H), 3.78 (s, 3H), 2.89-2.83 (m, 1H), 2.50-2.44 (m, 1H), 2.33-2.28 (m, 1H), 2.20-2.14 (m, 1H), 1.41 (t, *J* = 8.0 Hz, 3H), -0.02 (d, *J* = 12.0 Hz, 3H), -0.10 (d, *J* = 12.0 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ: 157.0, 157.0, 136.7, 136.7, 127.9, 127.9, 113.7, 113.7, 55.23, 44.4, 44.4, 42.6, 42.6, 26.9, 26.7, 15.3, 15.1, -6.9, -7.4, -7.7, -7.8; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{21}O_2Si$ $(M + H)^+$: 237.1311, found 237.1315.

8.3 Procedure for synthesis of 6[9]



A mixture consisting of palladium(II) acetate (1.4 mg, 0.06mmol), triphenylphosphine (3.1mg, 0.012 mmol), silver nitrate (34.0 mg, 0.2 mmol), iodobenzene (40.8 mg, 0.2 mmol), (1-(4-methoxyphenyl)ethyl)dimethyl(vinyl)silane (44.0 mg, 0.2 mmol), triethylamine (40.0 mg, 2.0 mmol), and 1 mL of acetonitrile was placed in 25 mL Schlenk tube, The suspension was heated in an oil bath at 60 ℃ for 24 h. After being cooled to room temperature, the reaction mixture was added to water (5 mL) and extracted twice with 30 mL of EtOAc. The combined organic layers were dried ($MgSO_4$), and the crude product obtained was then purified by column chromatography (silica gel / pentane) to give the corresponding product **6** as a yellow oil (34.3 mg, 58% yield): Rf = 0.4 (petroleum ether); **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ*: 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.95-6.90 (m, 3H), 6.50 (d, *J* = 20.0 Hz, 1H), 3.86 (s, 3H), 2.36-2.30 (m, 1H), 1.47 (d, *J* = 8.0 Hz, 3H), 0.19 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) *δ*: 156.9, 145.1, 138.4, 137.5, 128.6, 128.1, 128.1, 126.7, 126.5, 113.6, 55.3, 28.4, 15.5, -4.4, -4.9; **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{25}OSi$ $(M + H)^+$: 297.1675, found 297.1673.

8.4 Procedure for synthesis of 7[10]



In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with **3a** (44.0 mg, 0.2 mmol), CuCl (1.0 mg, 0.01 mmol), dppp (4.0 mg, 0.01 mmol), and KO^{t}Bu (27.0 mg, 0.24 mmol), the tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Anhydrous THF (2.0 mL), MeOH (26.0 mg, 0.8 mmol) and B_2pin_2 (77.0 mg, 0.3 mmol) was added subsequently under N_2, the resulting mixture was allowed to stir at r.t. for 24 hours. The reaction mixture diluted with EtOAc (5.0 mL) and H_2O (5.0 mL). Then it was extracted with EtOAc (5.0 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **7** (29.2 mg, 42% yield) as a colorless oil: Rf = 0.5 (EtOAc:petroleum ether = 1:10); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ: 6.98 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.19-2.14 (m, 1H), 1.34 (d, *J* = 8.0 Hz, 3H), 1.26 (s, 12H), 0.74-0.70 (m, 2H), 0.58-0.54 (m, 2H), -0.09 (d, *J* = 20.0 Hz, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ: 156.6, 138.1, 127.8, 113.5, 82.9, 55.2, 27.4, 24.8, 15.3, 6.2, -5.4, -5.7; **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{34}BO_3Si$ $(M + H)^+$: 348.2407, found 348.2404.

9. References

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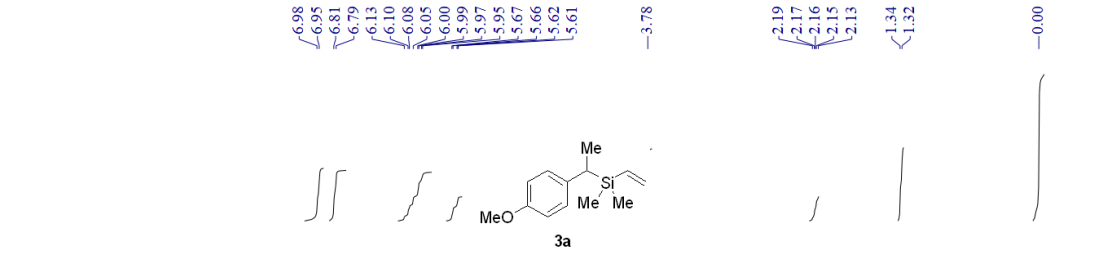
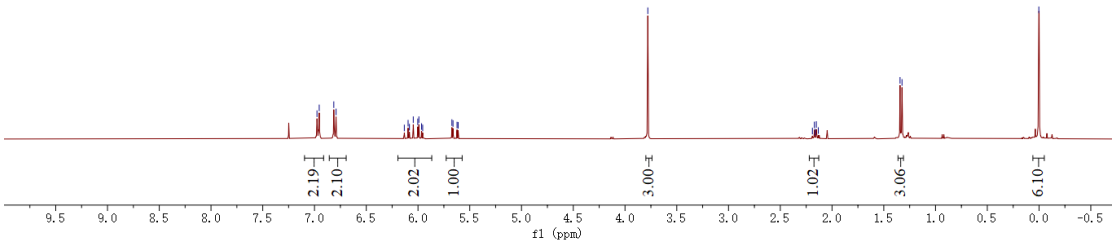
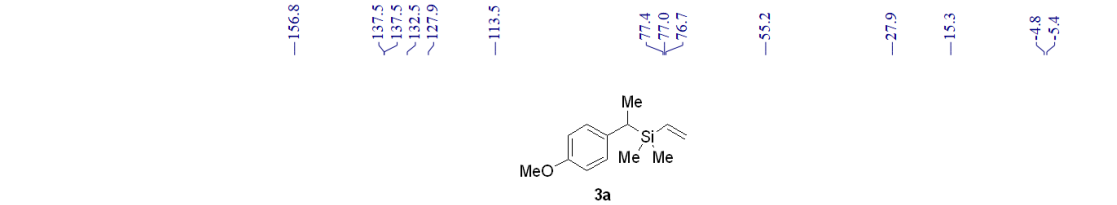
10. NMR spectra of products

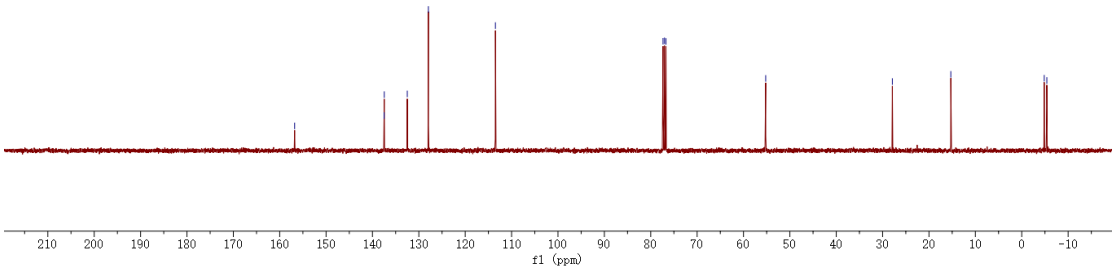


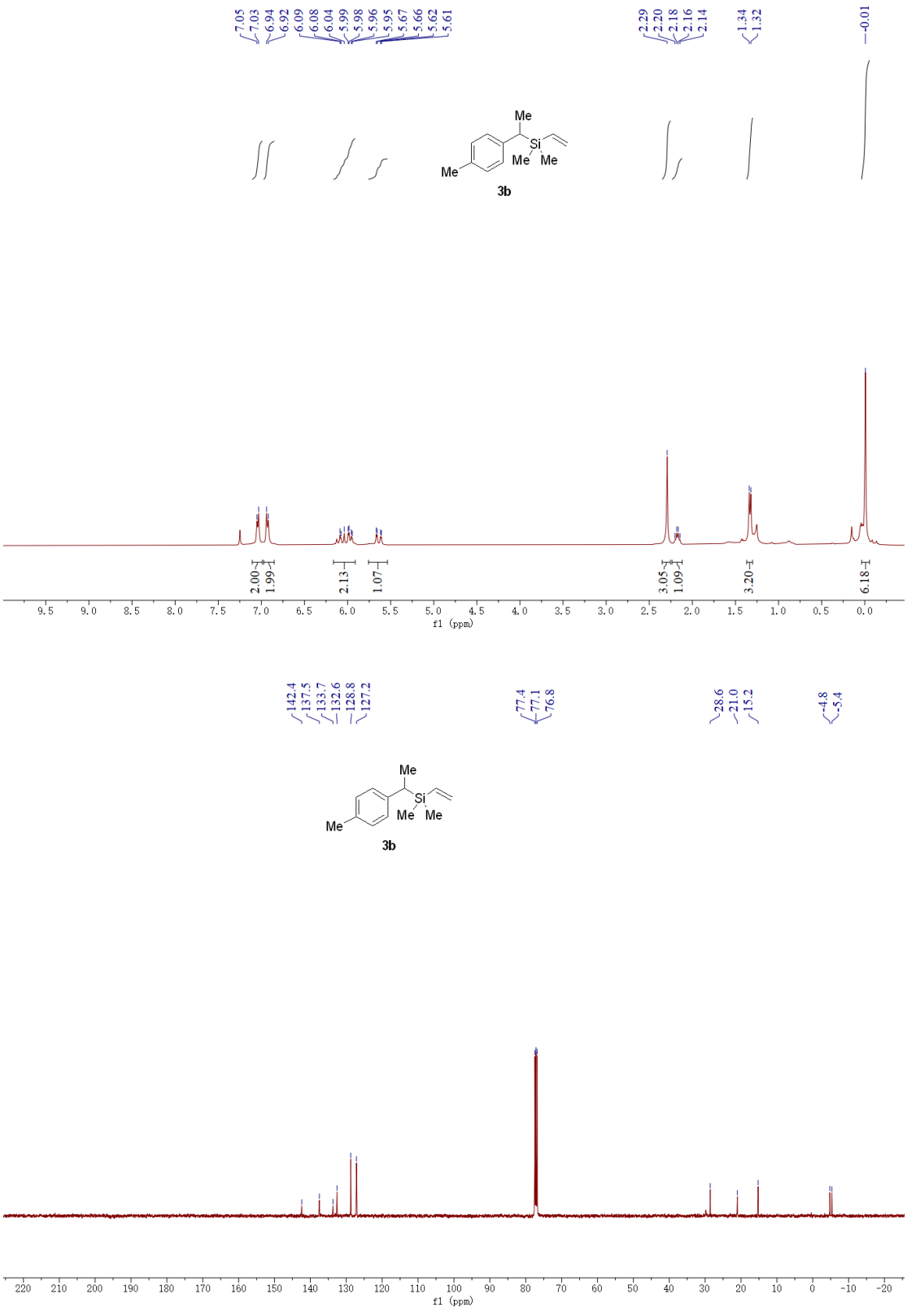
3a





3a

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3b
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1.07
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1.09
3.20
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f1 (ppm)
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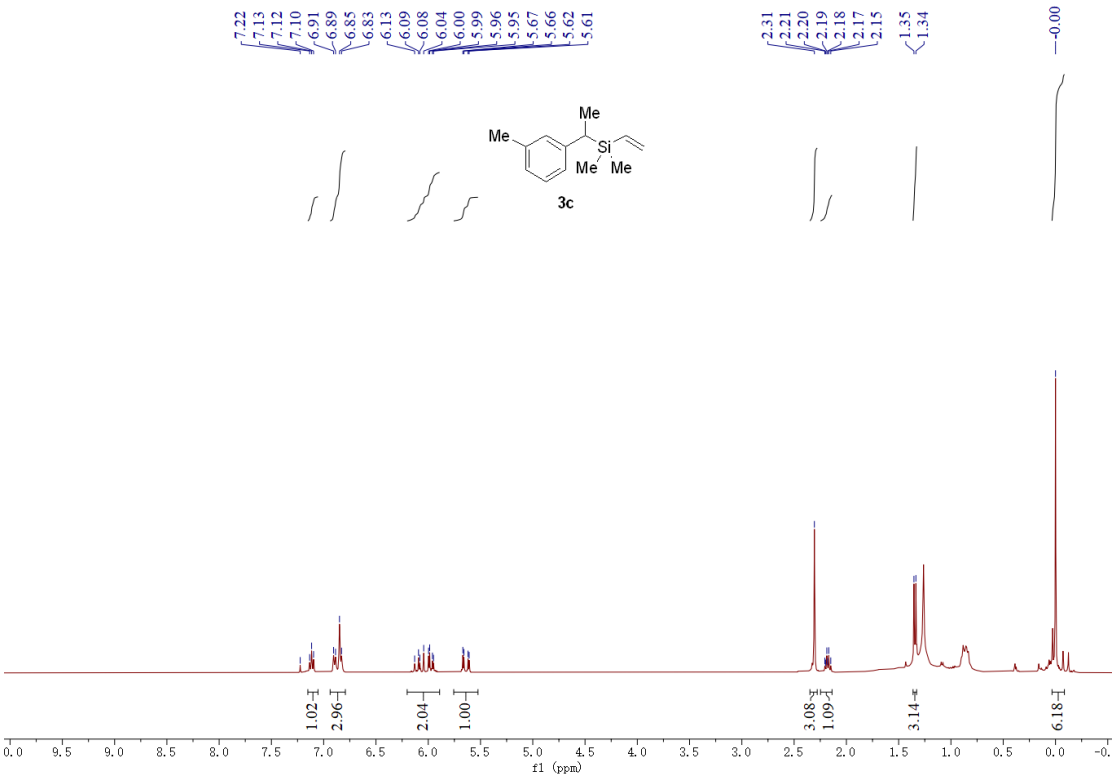
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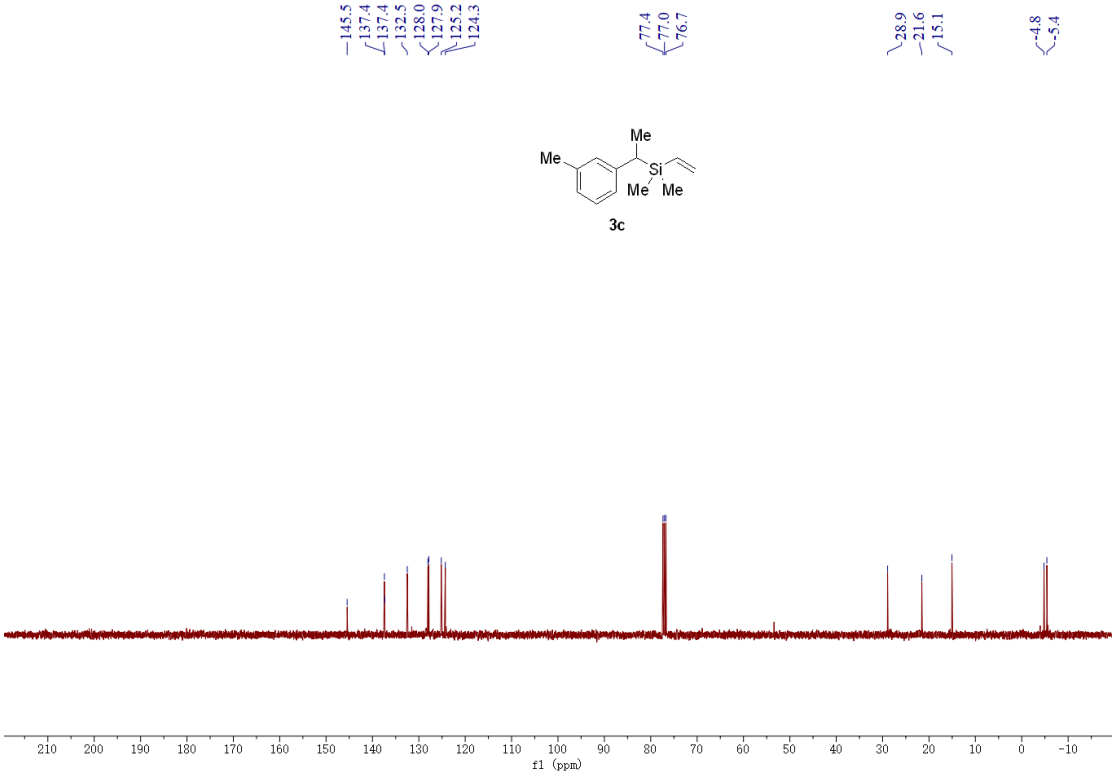
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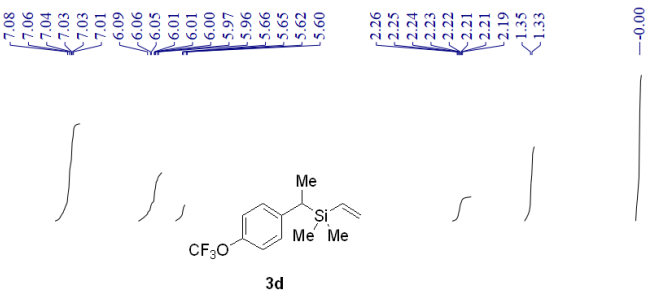
f1 (ppm)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7.06
7.04
7.03
7.03
7.01
6.09
6.06
6.05
6.01
6.01
6.00
5.97
5.96
5.66
5.65
5.62
5.60
2.26
2.25
2.24
2.23
2.22
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2.21
2.19
1.35
1.33
0.00
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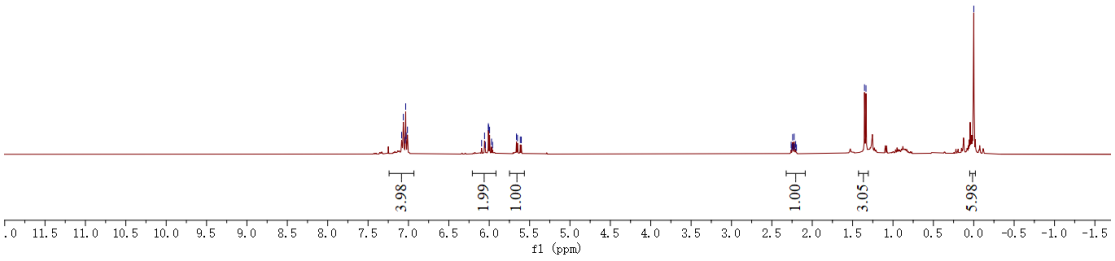
Si
Me
Me
CF3O

3d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3.05
5.98
f1 (ppm)


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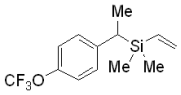
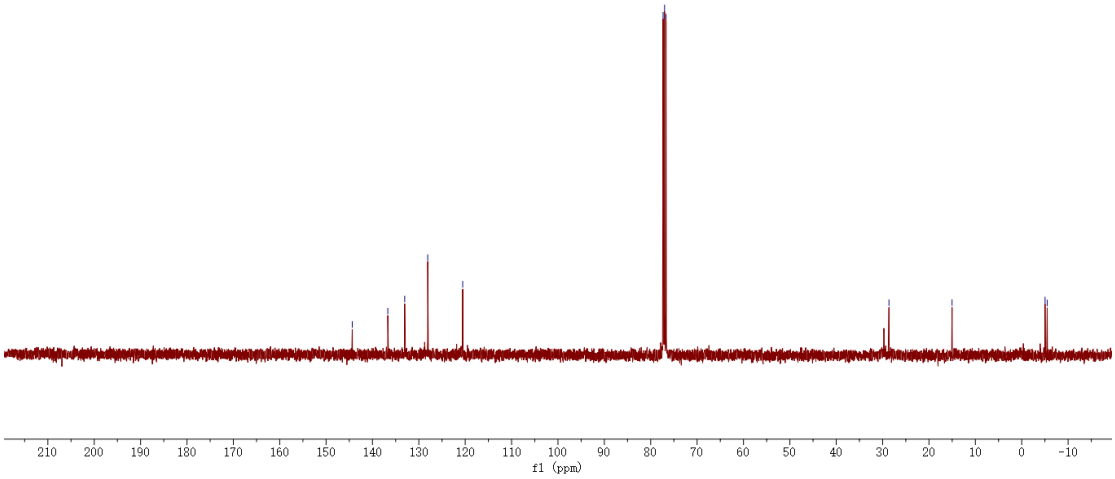
120.55
77.34
77.02
76.70
28.63
15.02
-5.03
-5.49


Me
Si
Me
Me
CF3O

3d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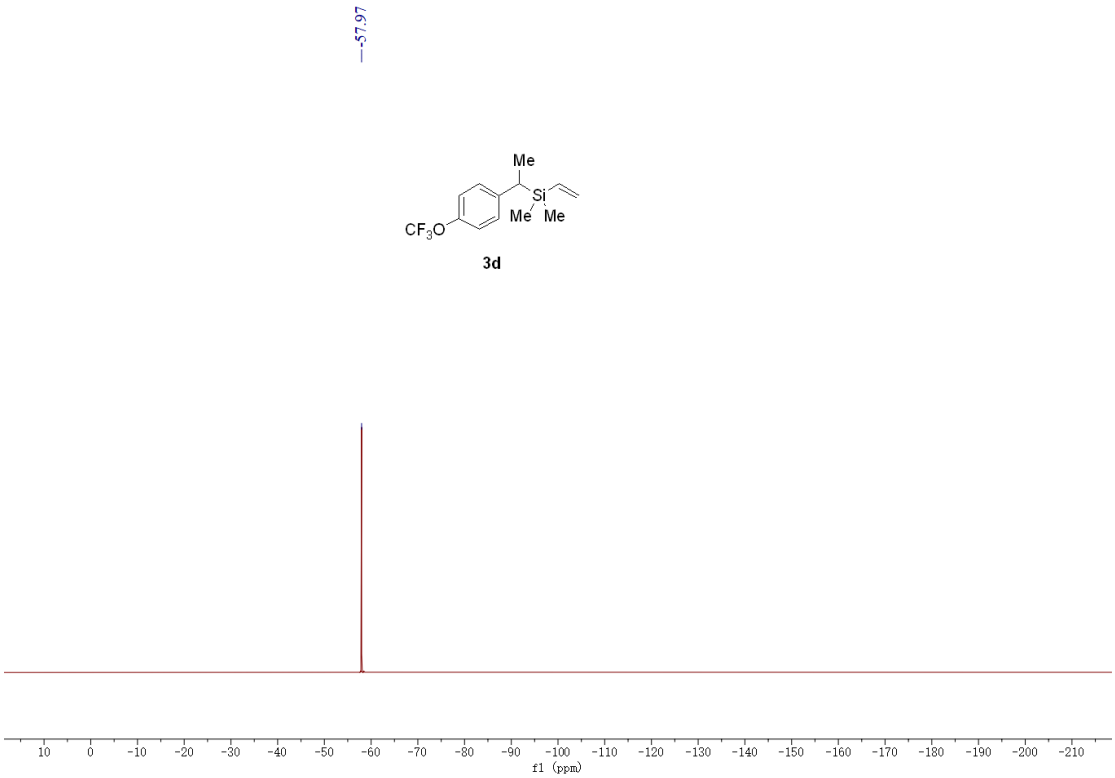
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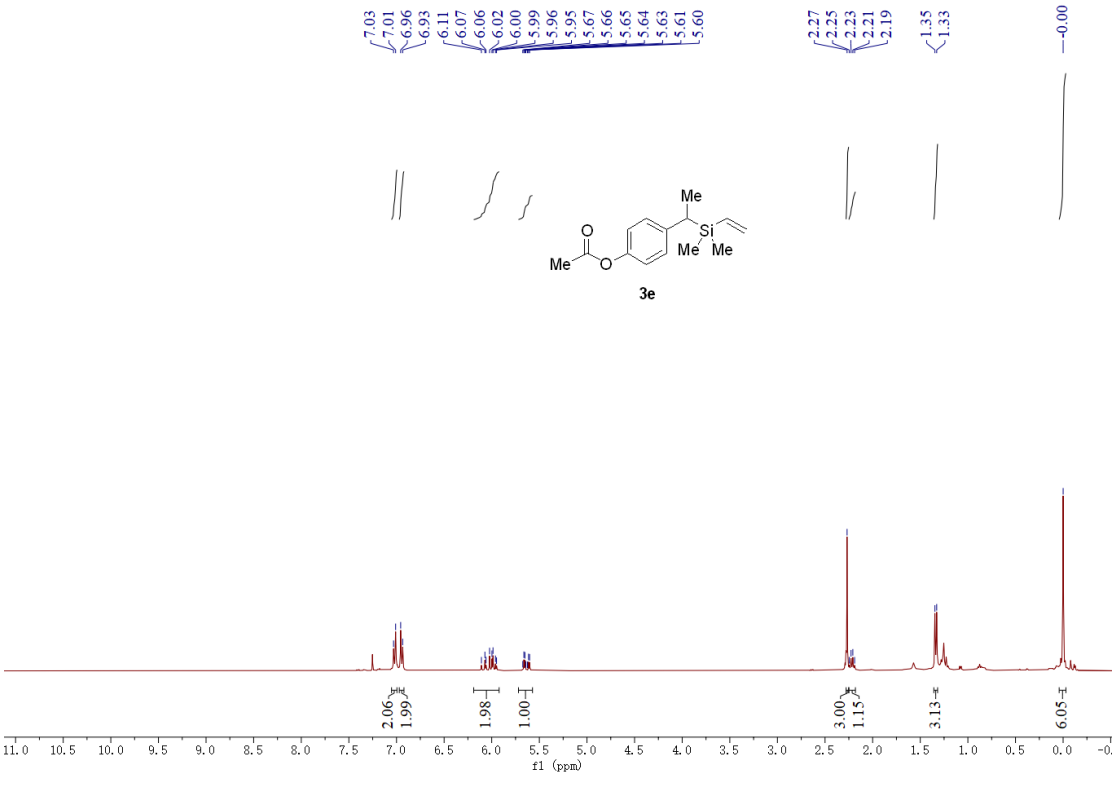
Me
Si
Me
Me
CF3O
3d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.01
6.96
6.93
6.11
6.07
6.06
6.02
6.00
5.99
5.96
5.95
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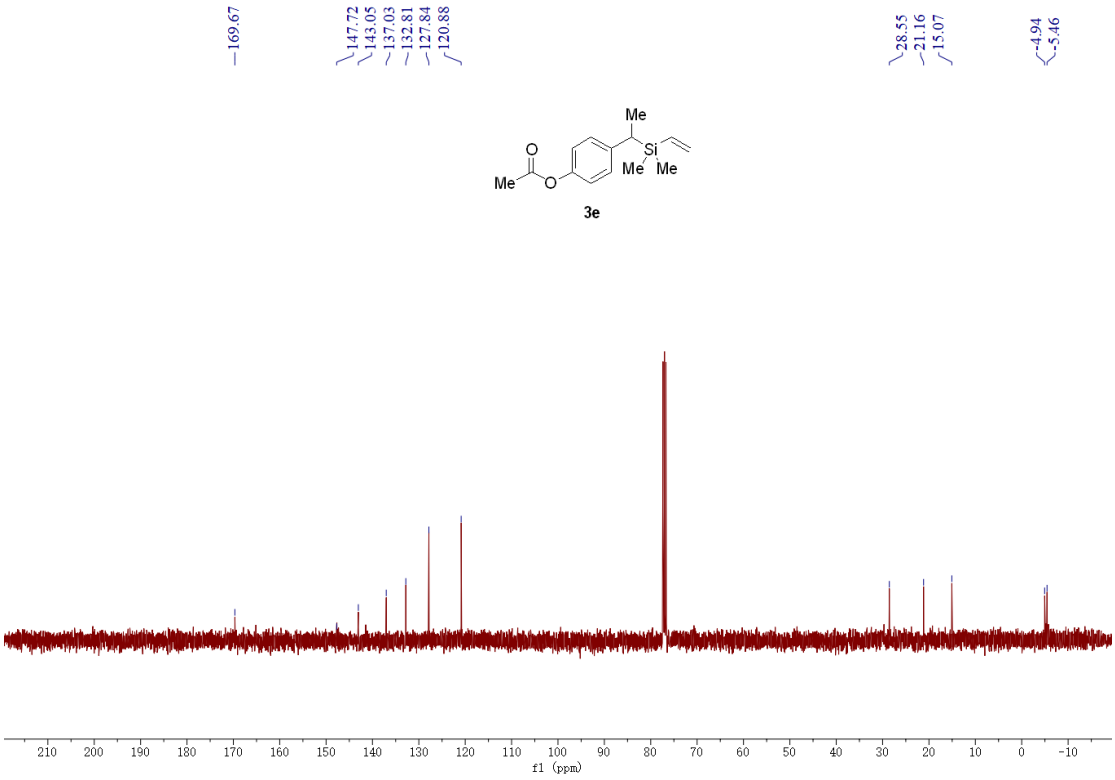
5.66
5.65
5.64
5.63
5.61
5.60
2.27
2.25
2.23
2.21
2.19
1.35
1.33
0.00
Me
Si
Me
Me
O
Me
O
3e
2.06
1.99
1.98
1.00
3.00
1.15
3.13
6.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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147.72
143.05
137.03
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127.84
120.88
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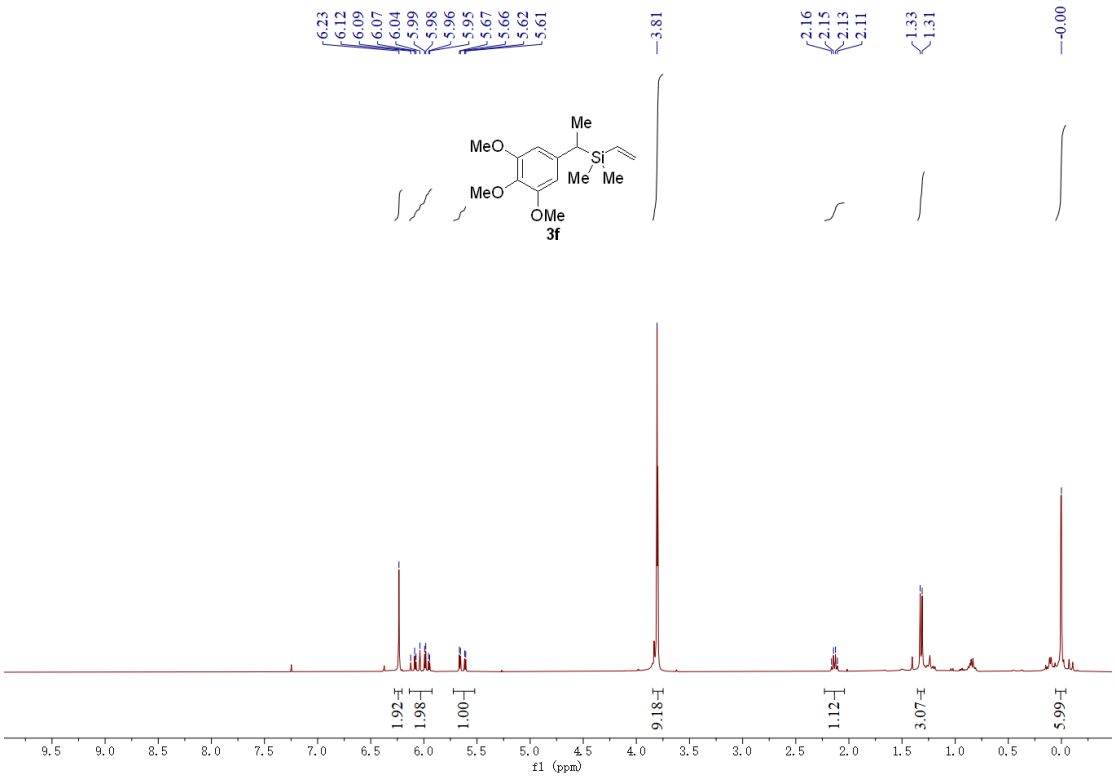
21.16
15.07
-4.94
-5.46
Me
O
Si
Me
Me
Me
O
3e
f1 (ppm)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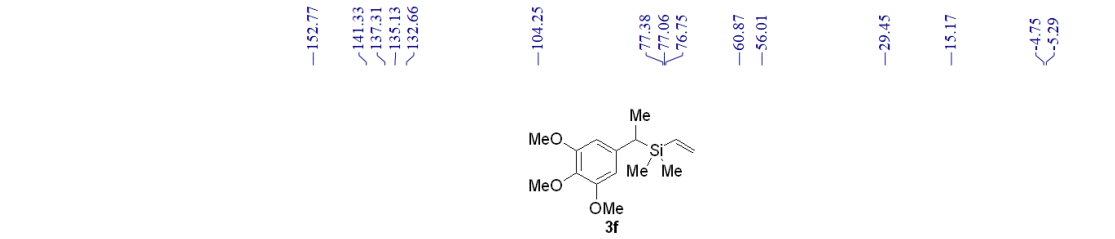
6.12
6.09
6.07
6.04
5.99
5.98
5.96
5.95
5.67
5.66
5.62
5.61
3.81
2.16
2.15
2.13
2.11
1.33
1.31
0.00
Me
MeO
Si
Me
Me
MeO
OMe
3f
1.92
1.98
1.00
9.18
1.12
3.07
5.99
f1 (ppm)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141.33
137.31
135.13
132.66
104.25
77.38
77.06
76.75
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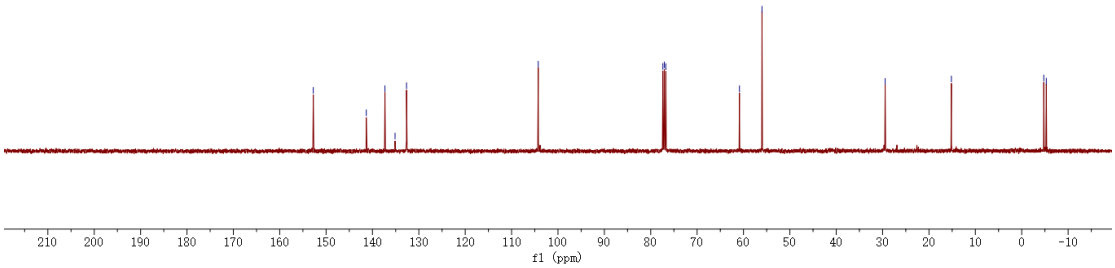
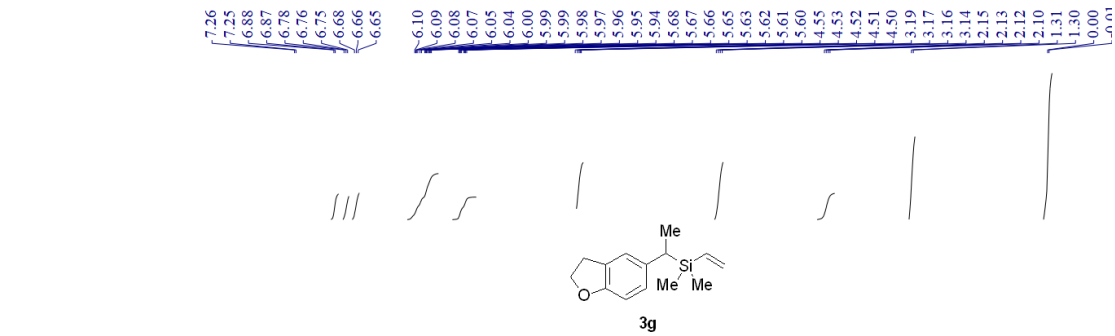
56.01
29.45
15.17
-4.75
-5.29
Me
MeO
Si
Me
Me
MeO
OMe
3f


f1 (ppm)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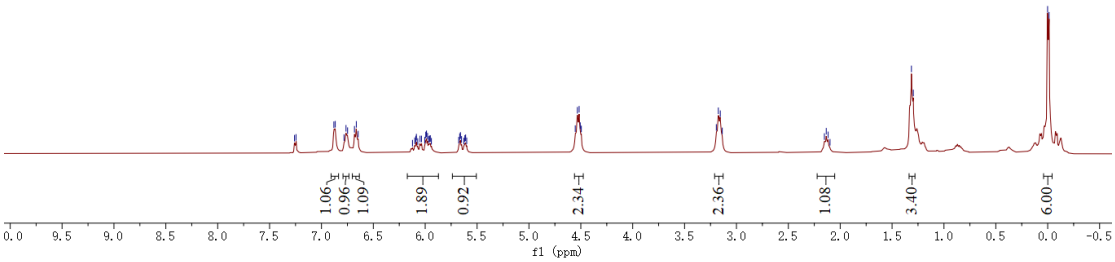
6.78
6.76
6.75
6.68
6.66
6.65
6.10
6.09
6.08
6.07
6.05
6.04
6.00
5.99
5.99
5.98
5.97
5.96
5.95
5.94
5.68
5.67
5.66
5.65
5.63
5.62
5.61
5.60
4.55
4.53
4.52
4.51
4.50
3.19
3.17
3.16
3.14
2.15
2.13
2.12
2.10
1.31
1.30
0.00
Me
Si
Me
Me
O
3g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1.09
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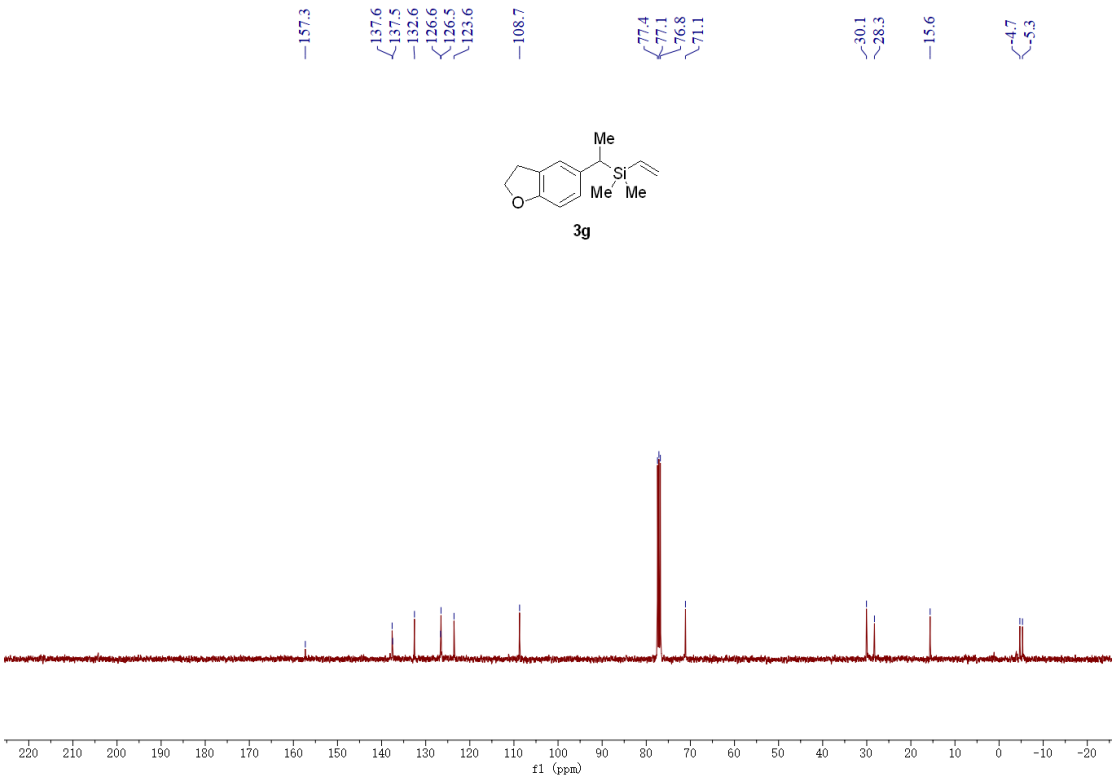
0.92
2.34
2.36
1.08
3.40
6.00
f1 (ppm)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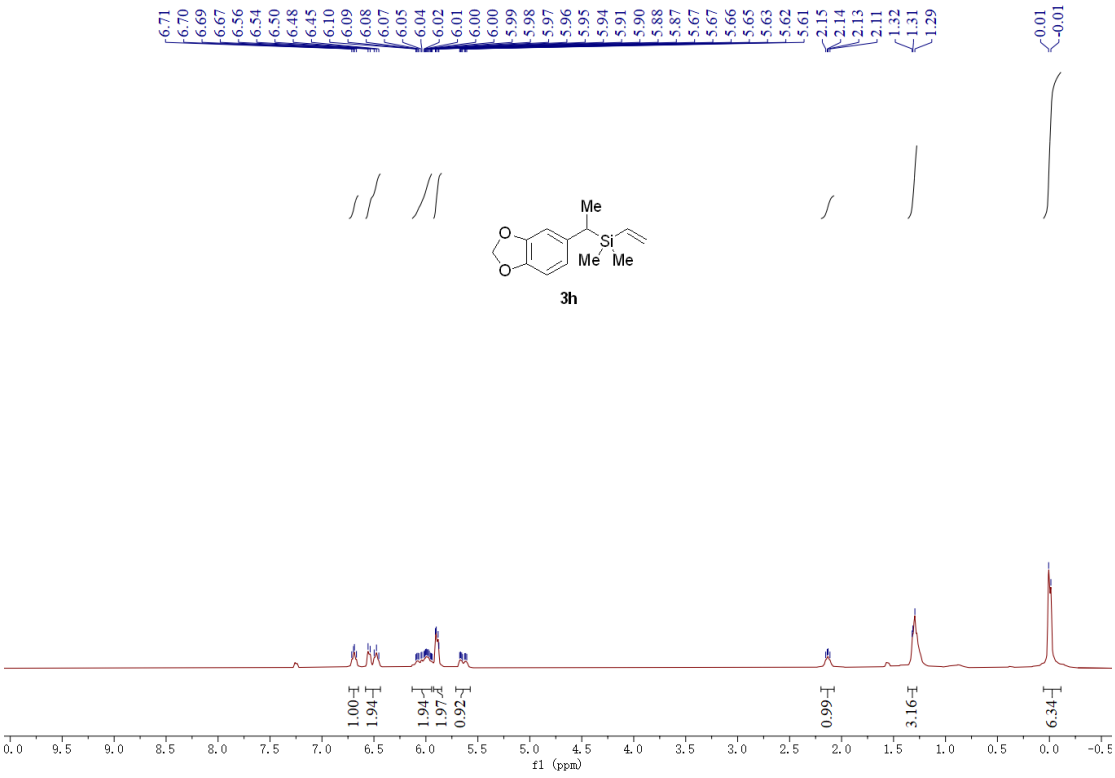
137.6
137.5
132.6
126.6
126.5
123.6
108.7
77.4
77.1
76.8
71.1
30.1
28.3
15.6
4.7
-5.3
Me
Si
Me
Me
O
3g
f1 (ppm)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6.70
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6.56
6.54
6.50
6.48
6.45
6.10
6.09
6.08
6.07
6.05
6.04
6.02
6.01
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5.97
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5.94
5.91
5.90
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5.87
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5.67
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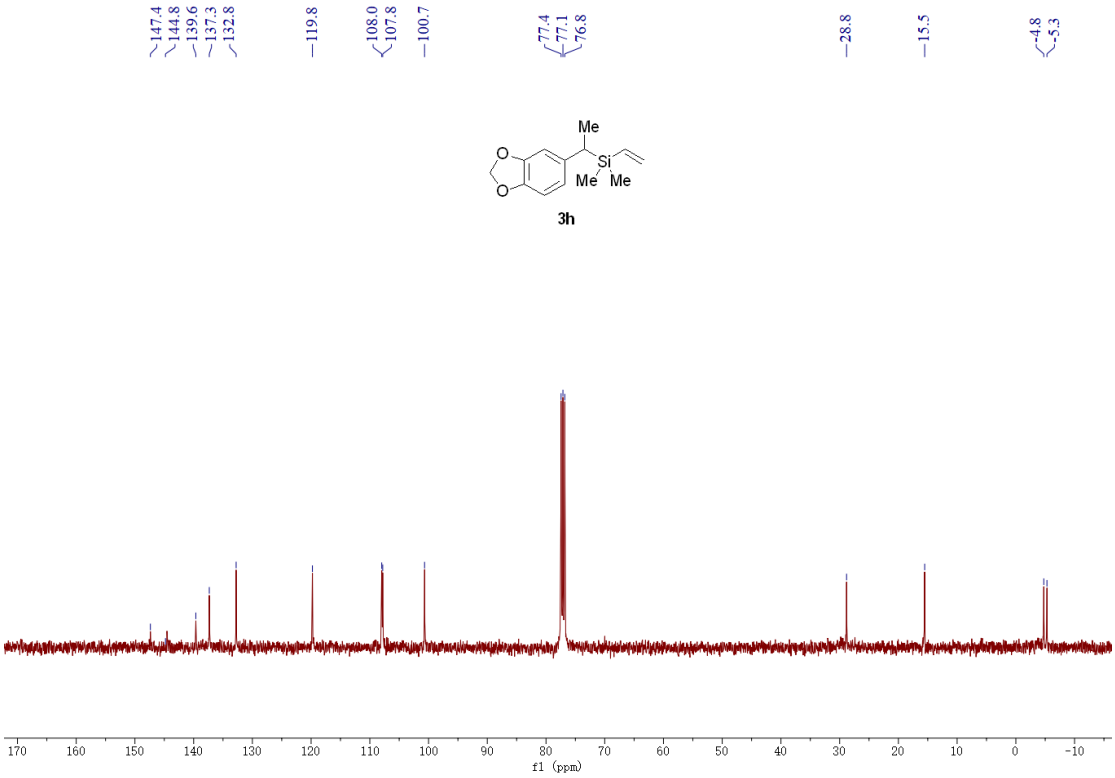
5.65
5.63
5.62
5.61
2.15
2.14
2.13
2.11
1.32
1.31
1.29
0.01
-0.01
Me
Si
Me
Me
O
O
3h
1.00
1.94
1.94
1.97
0.92
0.99
3.16
6.34
f1 (ppm)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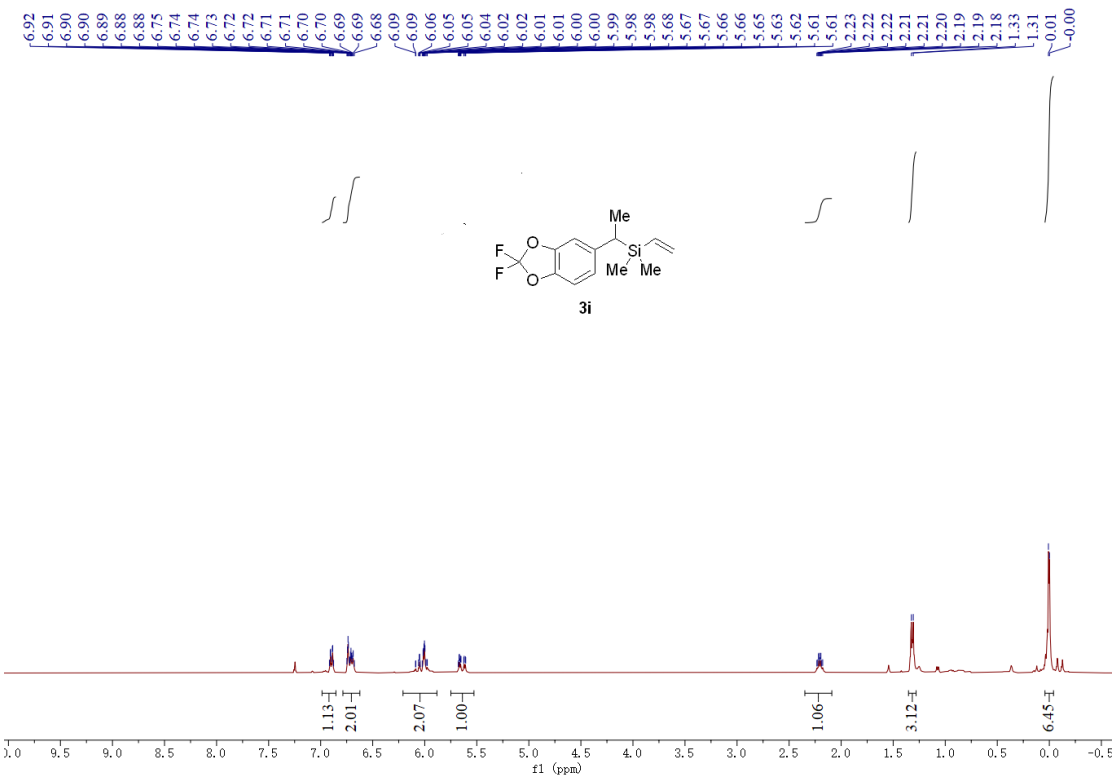
137.3
132.8
119.8
108.0
107.8
100.7
77.4
77.1
76.8
28.8
15.5
-4.8
-5.3
Me
O
O
Si
Me
Me
3h
f1 (ppm)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6.88
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6.74
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6.71
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6.70
6.70
6.69
6.69
6.68
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6.04
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5.98
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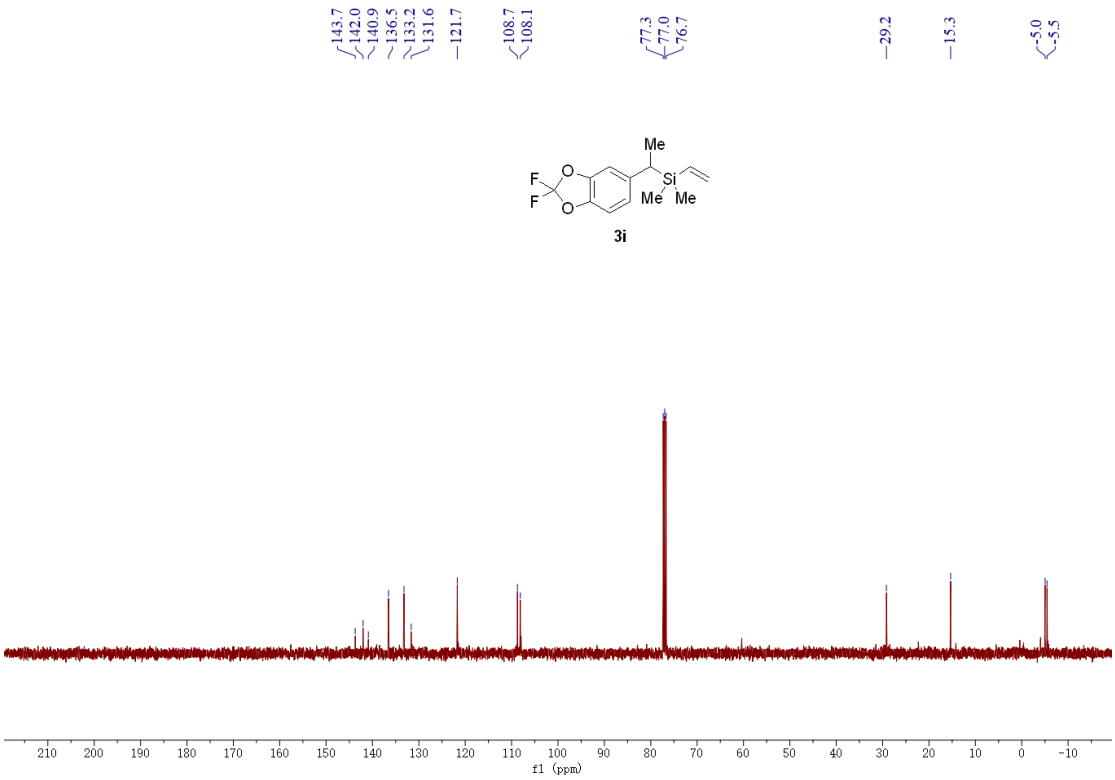
5.66
5.66
5.65
5.63
5.62
5.61
5.61
2.23
2.22
2.22
2.21
2.21
2.20
2.19
2.19
2.18
1.33
1.31
0.01
-0.00
Me
F
F
O
O
Si
Me
Me
3i
1.13
2.01
2.07
1.00
1.06
3.12
6.45
f1 (ppm)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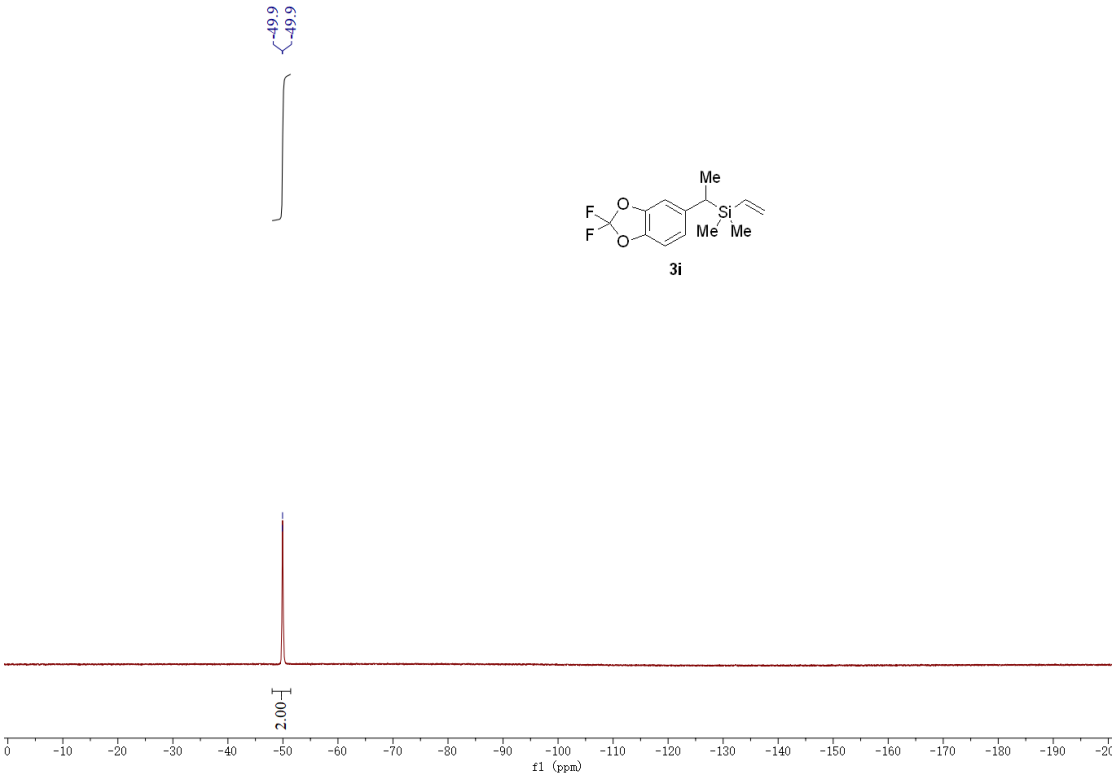
136.5
133.2
131.6
121.7
108.7
108.1
77.3
77.0
76.7
29.2
15.3
-5.0
-5.5
Me
F
F
O
O
Si
Me
Me
3i
f1 (ppm)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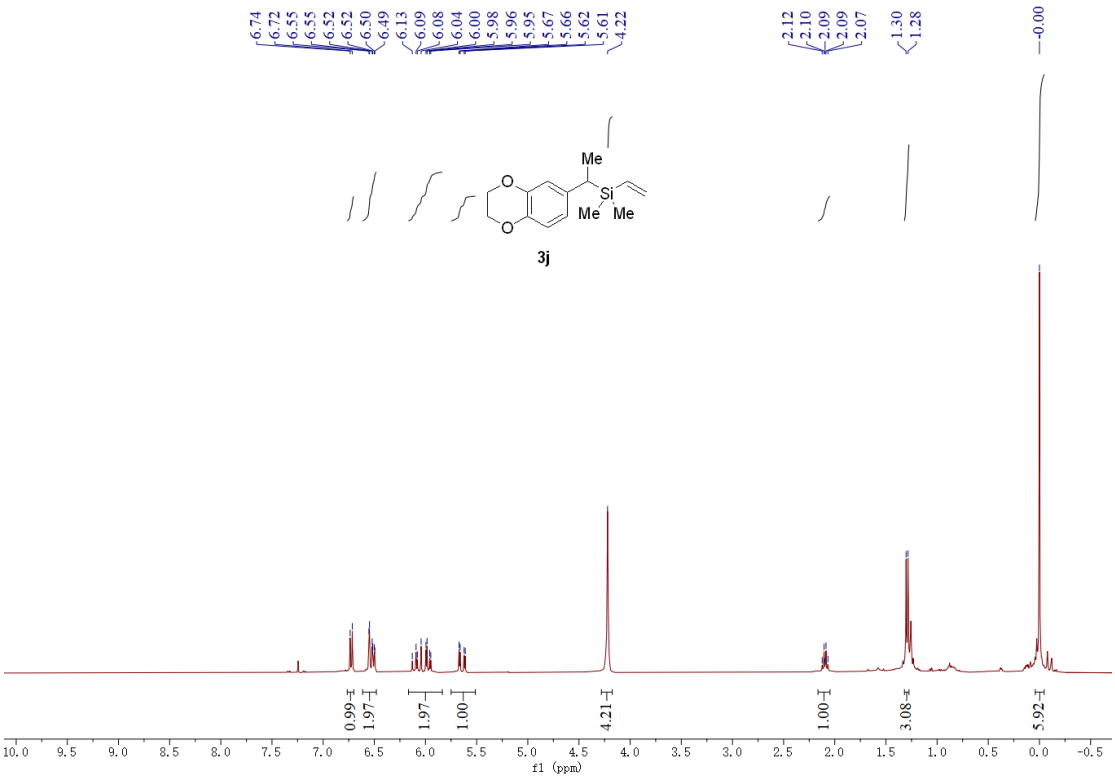
-49.9
Me
F
F
O
O
Si
Me
Me
3i
2.00
f1 (ppm)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6.50
6.49
6.13
6.09
6.08
6.04
6.00
5.98
5.96
5.95
5.67
5.66
5.62
5.61
4.22
2.12
2.10
2.09
2.09
2.07
1.30
1.28
0.00
Me
O
Si
Me
Me
O
0.99
1.97
1.97
1.00
4.21
1.00
3.08
5.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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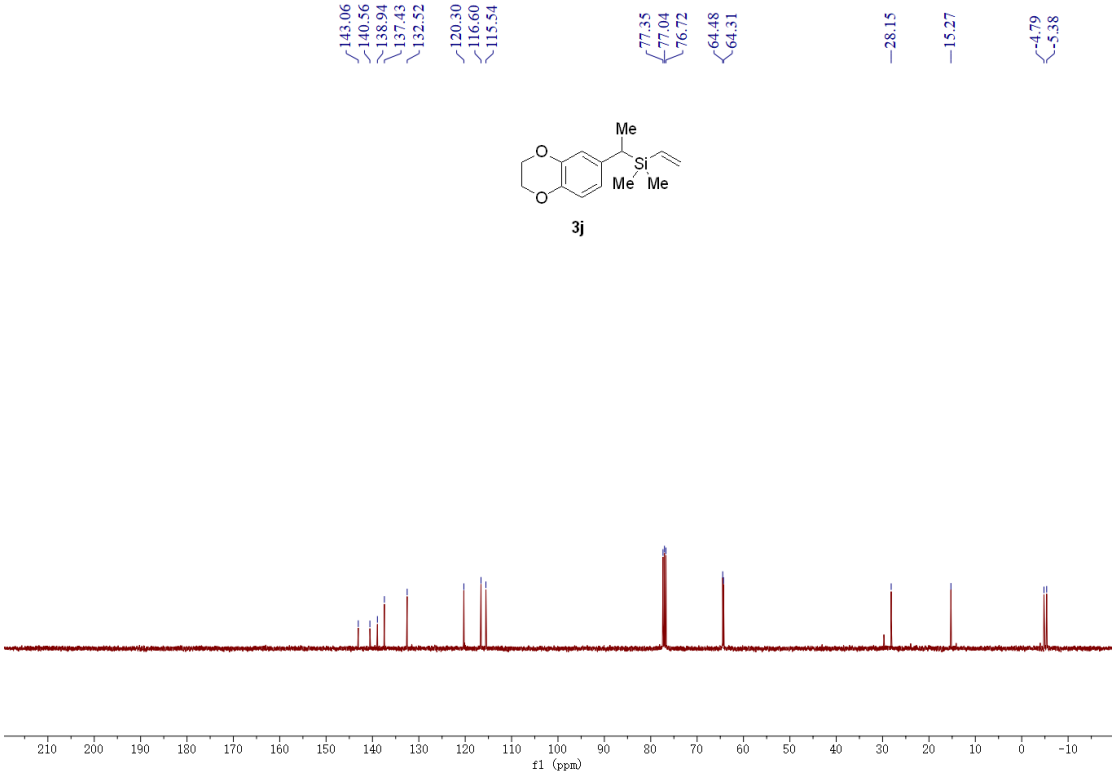
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3j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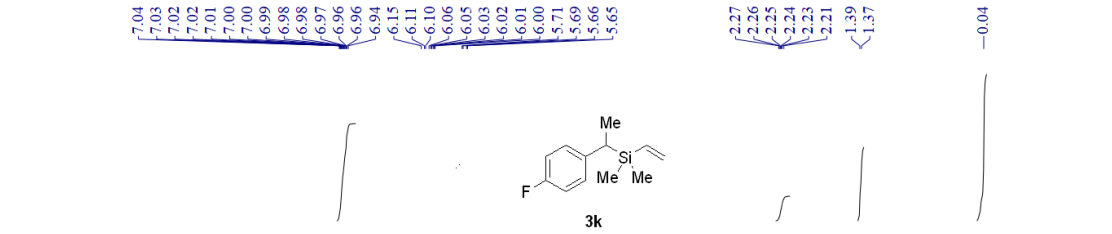
132.52
120.30
116.60
115.54
77.35
77.04
76.72
64.48
64.31
28.15
15.27
4.79
5.38
Me
O
Si
Me
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3j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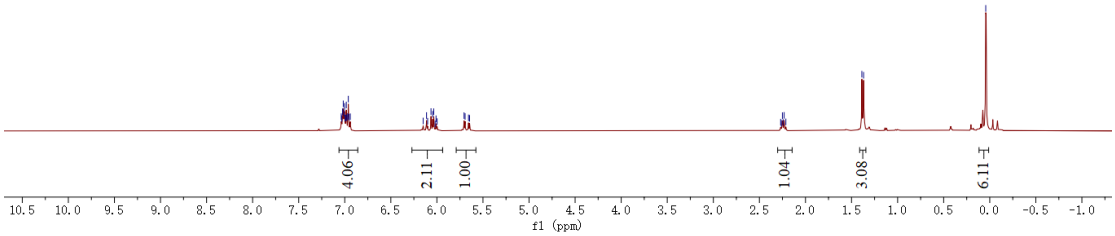
7.03
7.02
7.02
7.01
7.00
7.00
6.99
6.98
6.98
6.97
6.96
6.96
6.94
6.15
6.11
6.10
6.06
6.05
6.03
6.02
6.01
6.00
5.71
5.69
5.66
5.65
2.27
2.26
2.25
2.24
2.23
2.21
1.39
1.37
0.04
Me
Si
Me
Me
F

3k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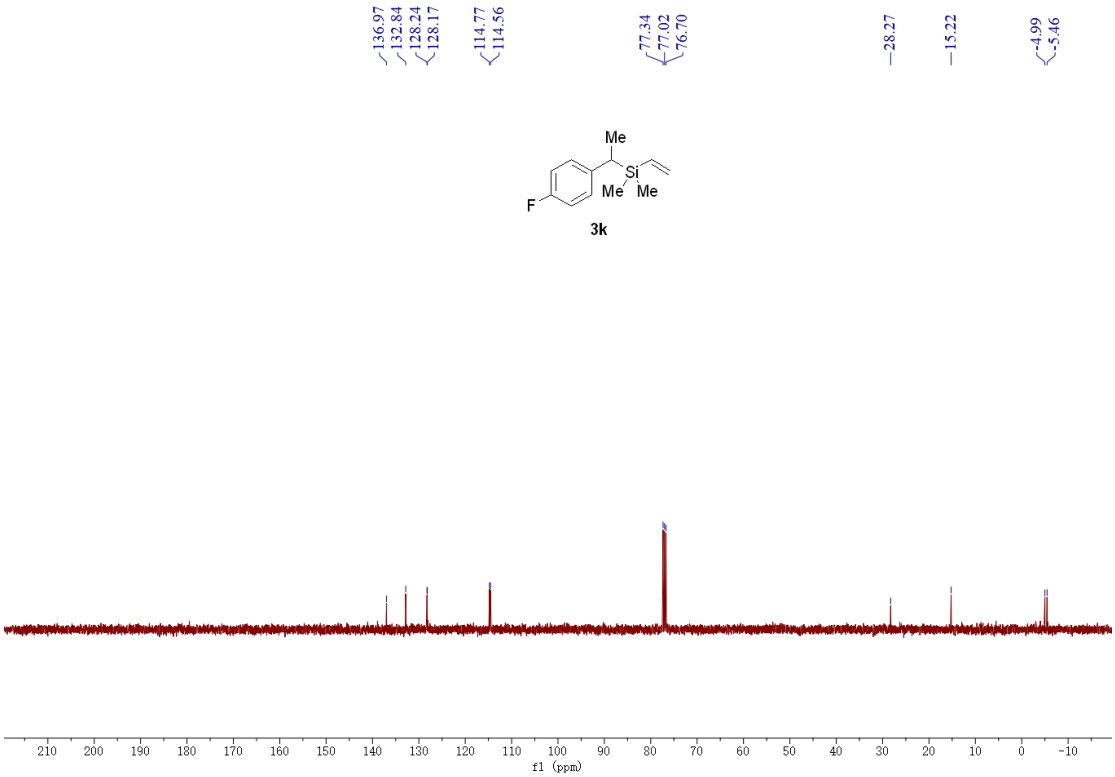
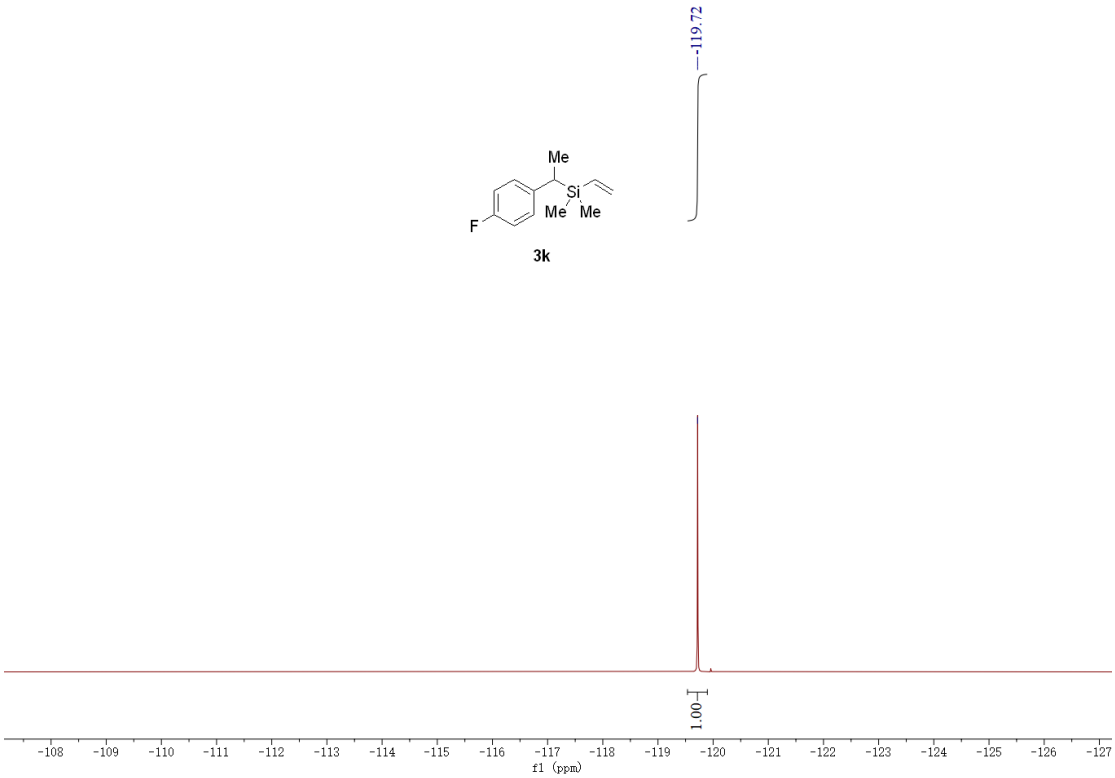
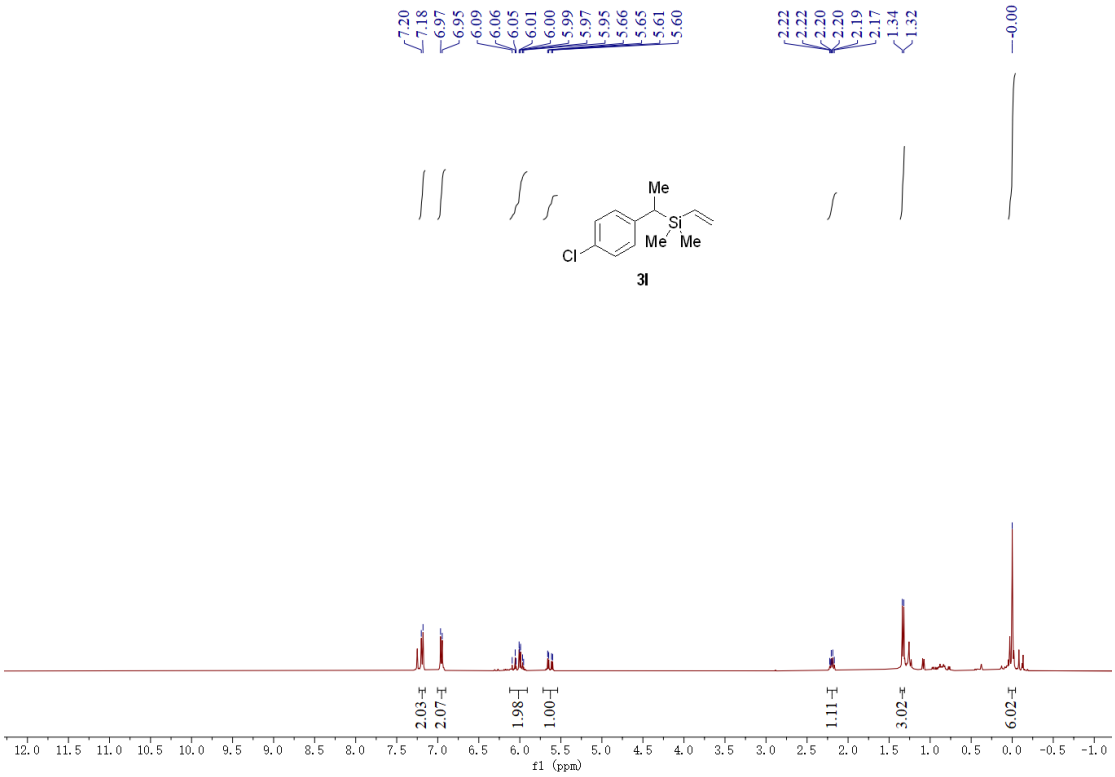
2.11
1.00
1.04
3.08
6.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


136.97
132.84
128.24
128.17
114.77
114.56
77.34
77.02
76.70
28.27
15.22
4.99
5.46
Me
Si
Me
Me
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3k


-119.72
Me
Si
Me
Me
F
3k
1.00
-108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127
f1 (ppm)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5.95
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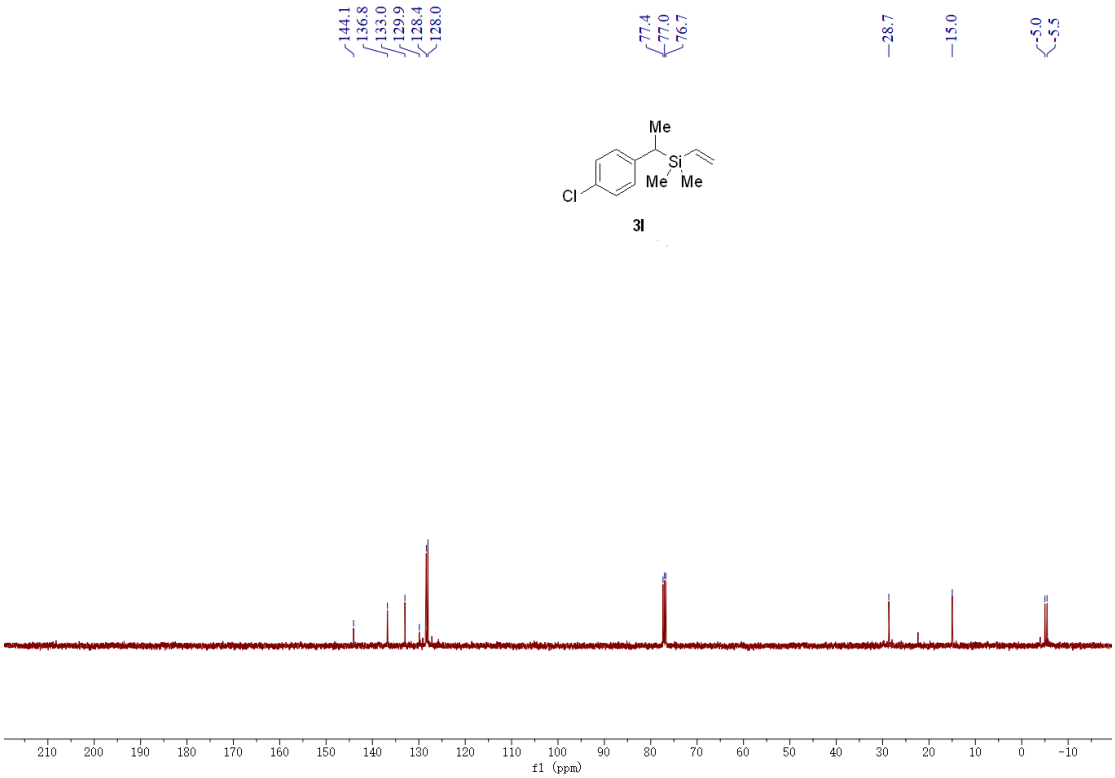
5.65
5.61
5.60
2.22
2.22
2.20
2.20
2.19
2.17
1.34
1.32
0.00
Me
Si
Me
Me
Cl
3l
2.03
2.07
1.98
1.00
1.11
3.02
6.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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136.8
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128.4
128.0
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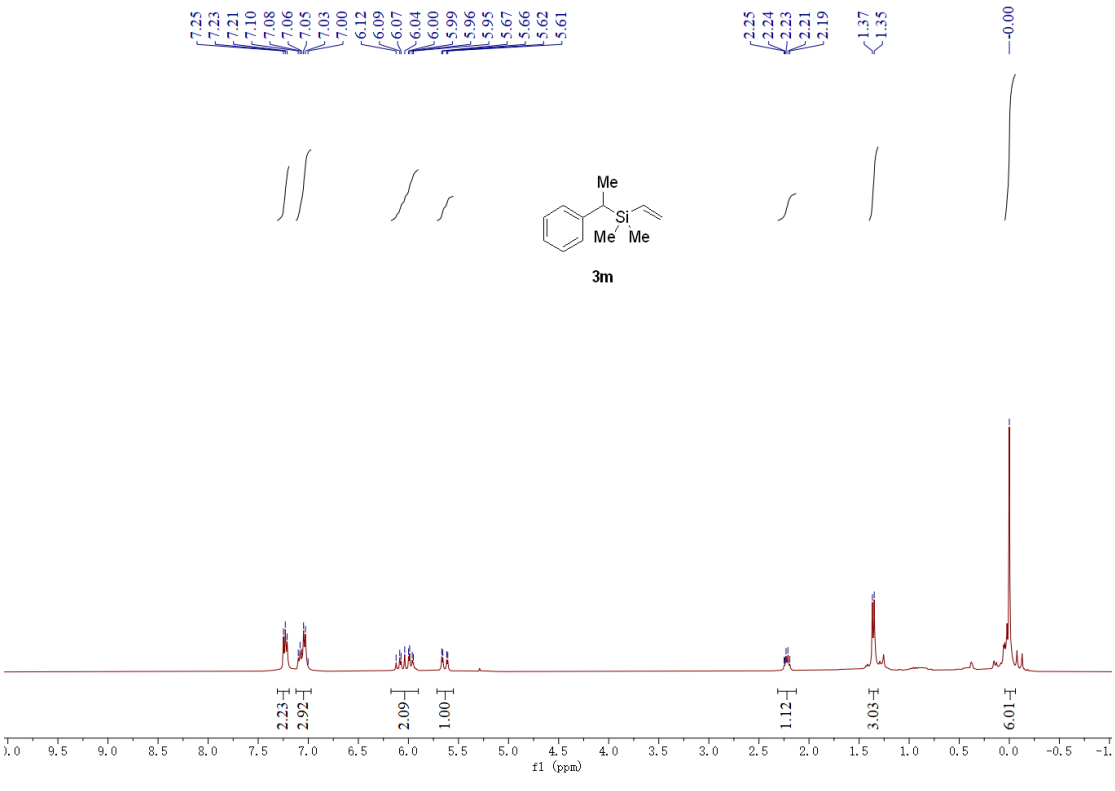
77.0
76.7
28.7
15.0
-5.0
-5.5
Me
Si
Me
Me
Cl
3l
f1 (ppm)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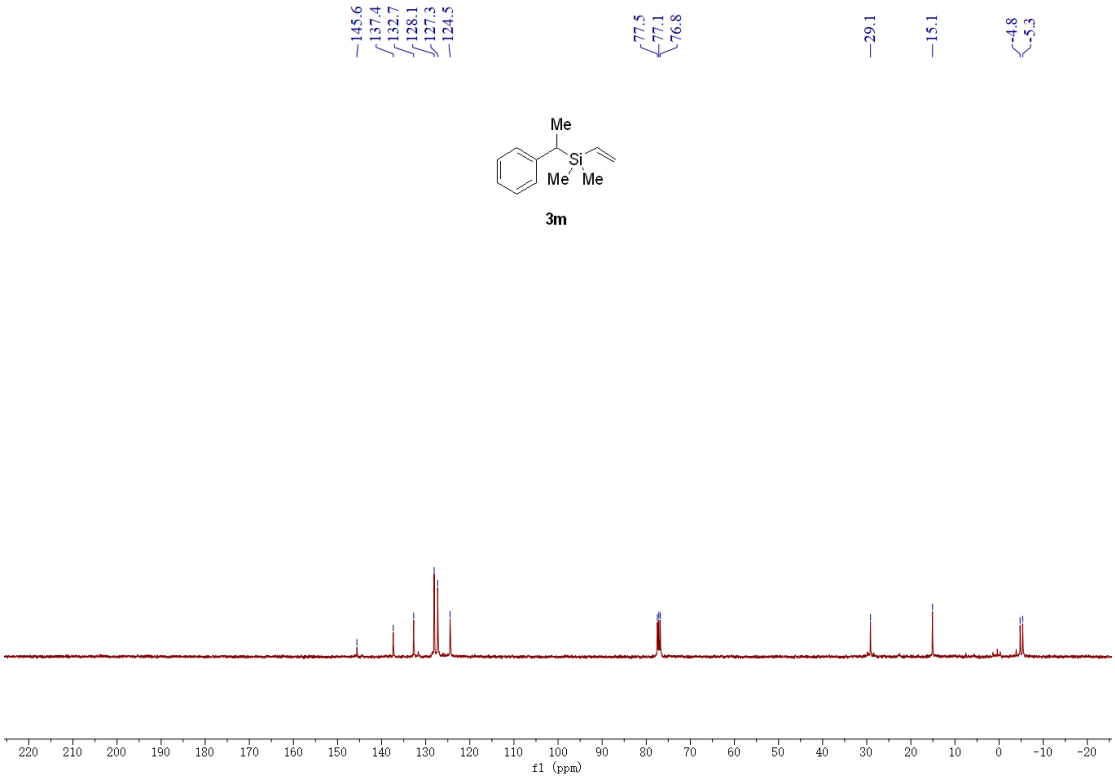
7.08
7.06
7.05
7.03
7.00
6.12
6.09
6.07
6.04
6.00
5.99
5.96
5.95
5.67
5.66
5.62
5.61
2.25
2.24
2.23
2.21
2.19
1.37
1.35
0.00
Me
Si
Me
Me
3m
2.23
2.92
2.09
1.00
1.12
3.03
6.01
f1 (ppm)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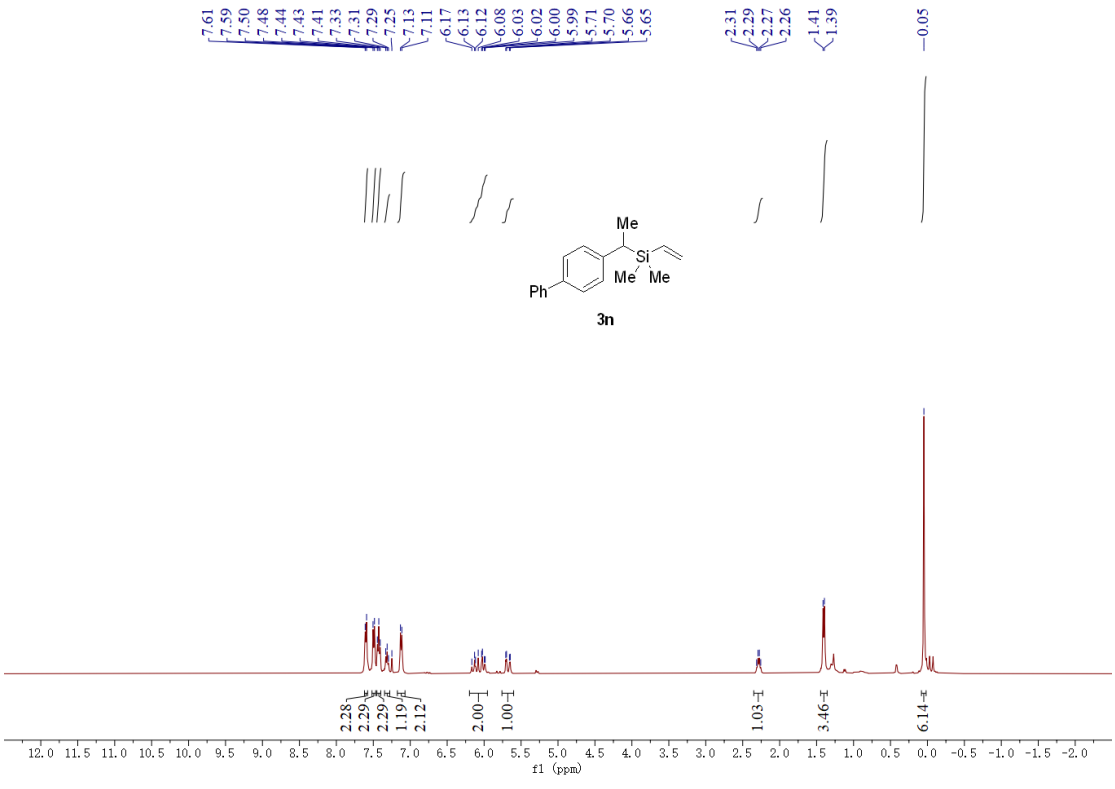
132.7
128.1
127.3
124.5
77.5
77.1
76.8
29.1
15.1
-4.8
-5.3
Me
Si
Me
Me
3m
f1 (ppm)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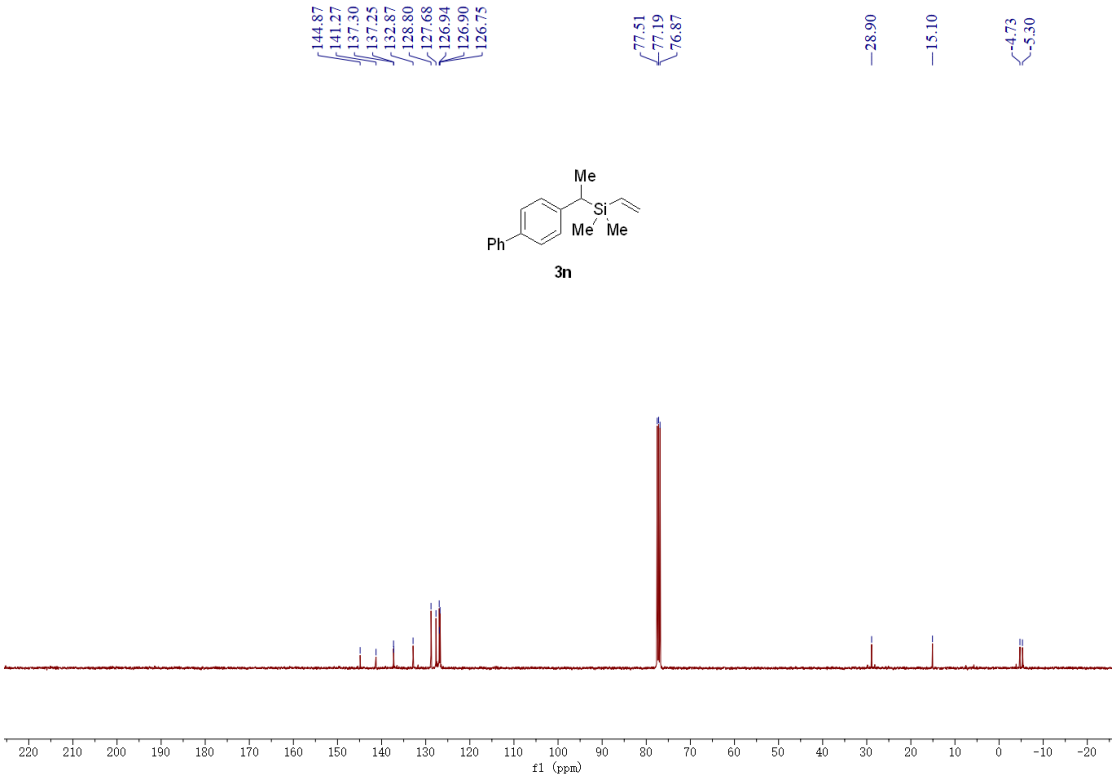
7.41
7.33
7.31
7.29
7.25
7.13
7.11
6.17
6.13
6.12
6.08
6.03
6.02
6.00
5.99
5.71
5.70
5.66
5.65
2.31
2.29
2.27
2.26
1.41
1.39
0.05
Me
Si
Me
Me
Ph
3n
2.28
2.29
2.29
1.19
2.12
2.00
1.00
1.03
3.46
6.14
f1 (ppm)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126.94
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126.75
77.51
77.19
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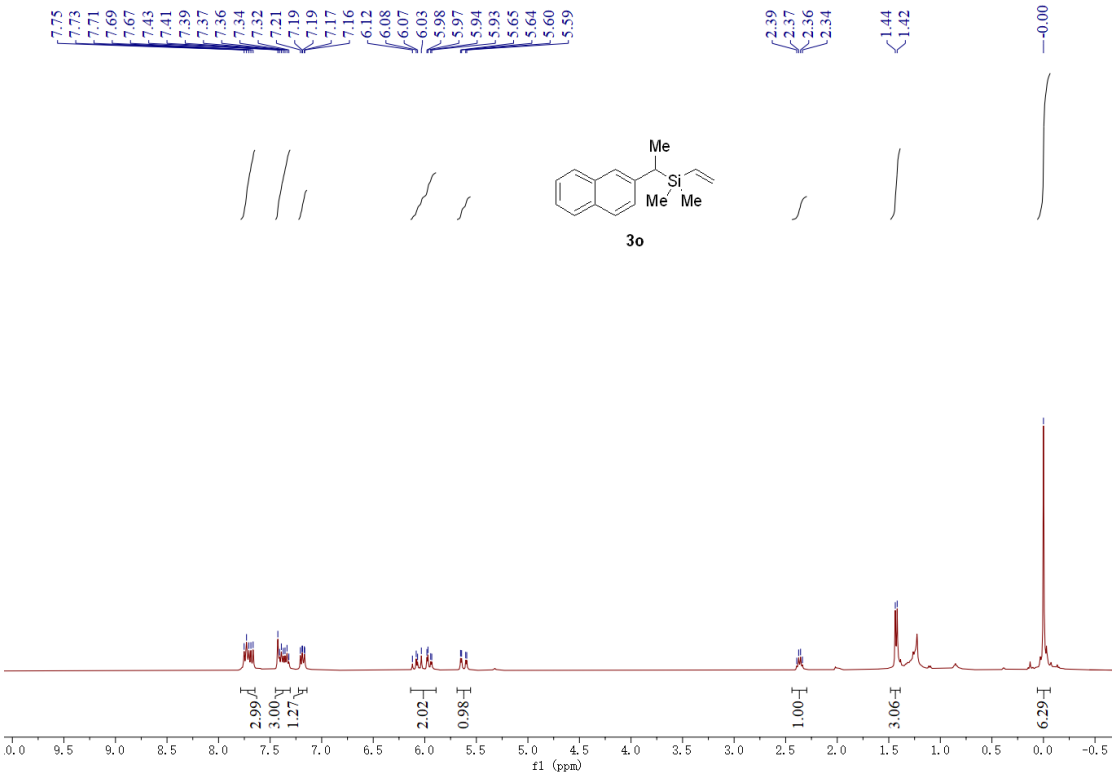
28.90
15.10
4.73
-5.30
Me
Si
Me
Me
Ph
3n
f1 (ppm)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7.73
7.71
7.69
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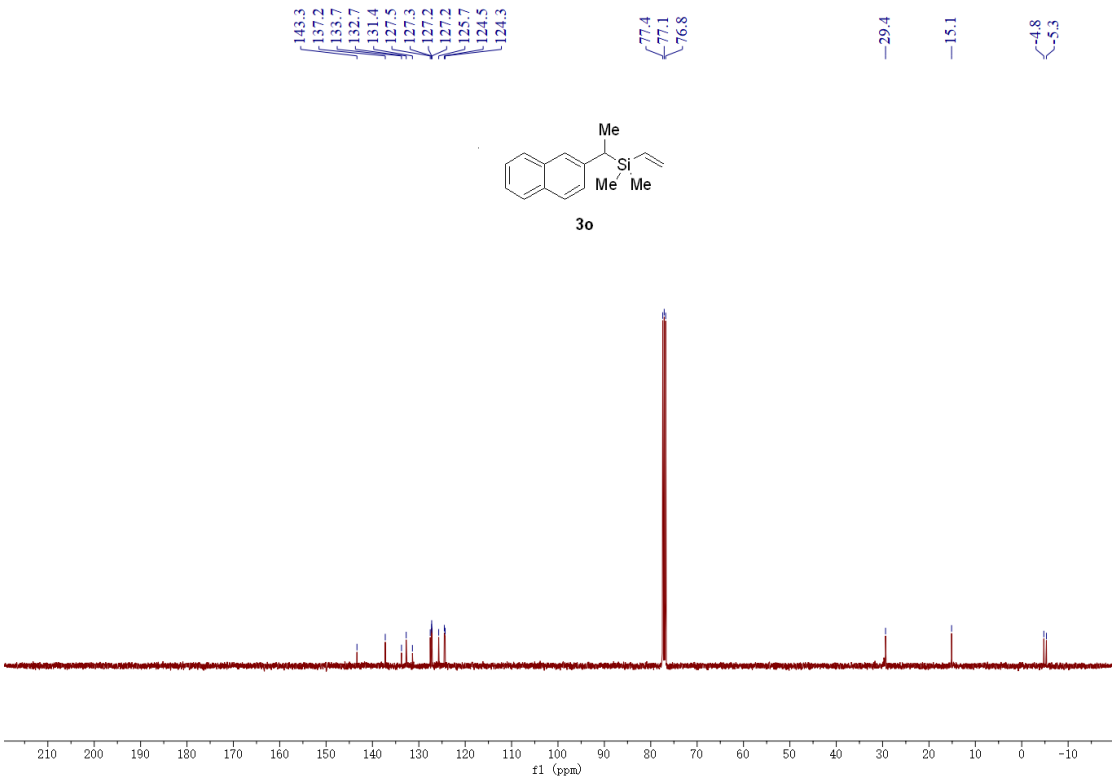
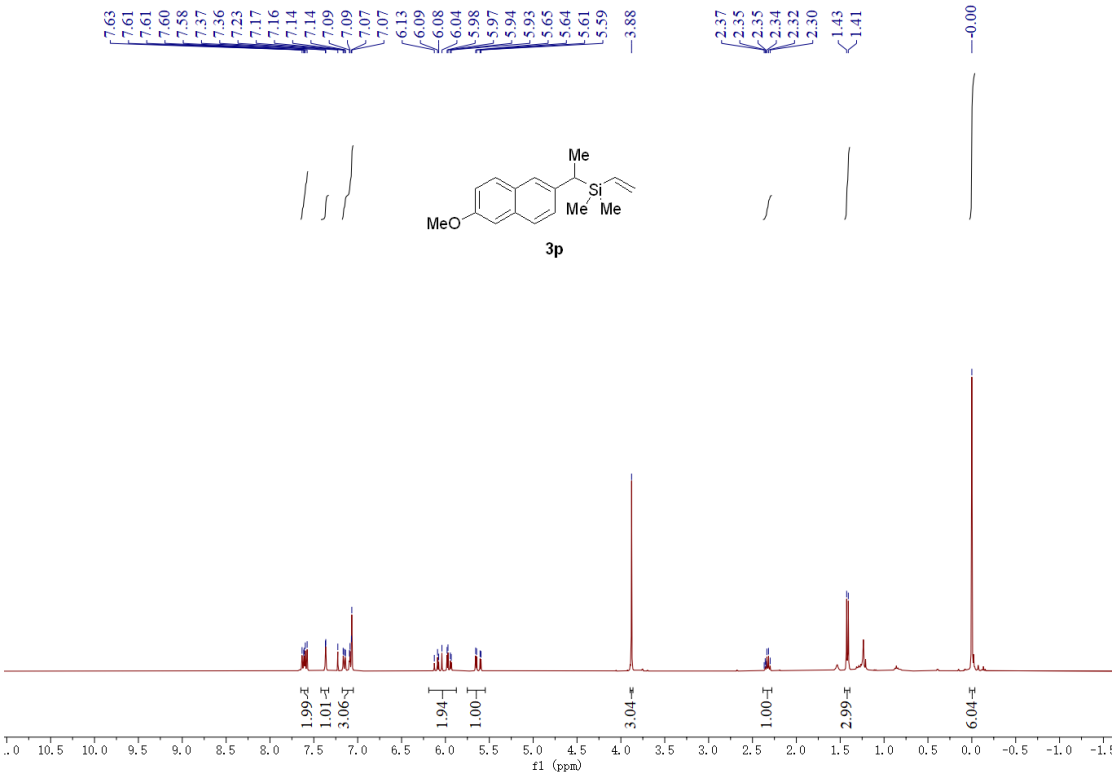
7.43
7.41
7.39
7.37
7.36
7.34
7.32
7.21
7.19
7.19
7.17
7.16
6.12
6.08
6.07
6.03
5.98
5.97
5.94
5.93
5.65
5.64
5.60
5.59
2.39
2.37
2.36
2.34
1.44
1.42
0.00
Me
Si
Me
Me
3o
2.99
3.00
1.27
2.02
0.98
1.00
3.06
6.29
f1 (ppm)


143.3
137.2
133.7
132.7
131.4
127.5
127.3
127.2
127.2
125.7
124.5
124.3
77.4
77.1
76.8
29.4
15.1
-4.8
-5.3
Me
Si
Me
Me
3o
f1 (ppm)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7.60
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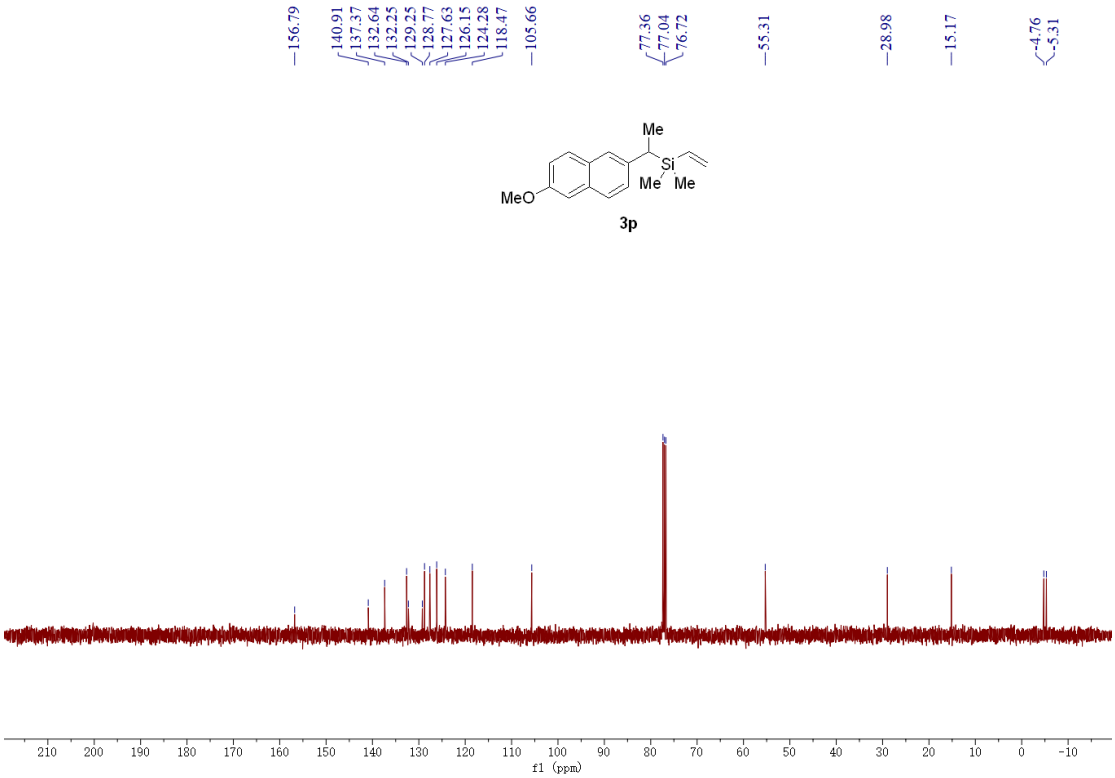
7.37
7.36
7.23
7.17
7.16
7.14
7.14
7.09
7.09
7.07
7.07
6.13
6.09
6.08
6.04
5.98
5.97
5.94
5.93
5.65
5.64
5.61
5.59
3.88
2.37
2.35
2.35
2.34
2.32
2.30
1.43
1.41
0.00
Me
Si
Me
Me
MeO
3p
1.99
1.01
3.06
1.94
1.00
3.04
1.00
2.99
6.04
f1 (ppm)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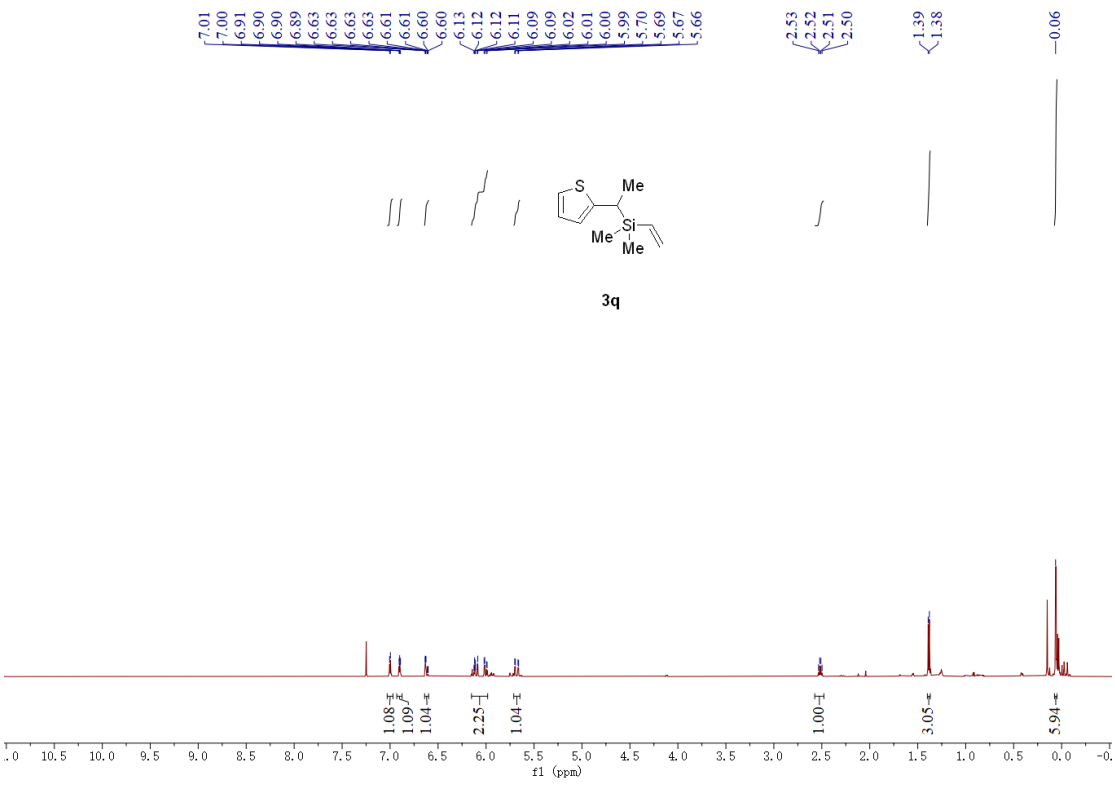
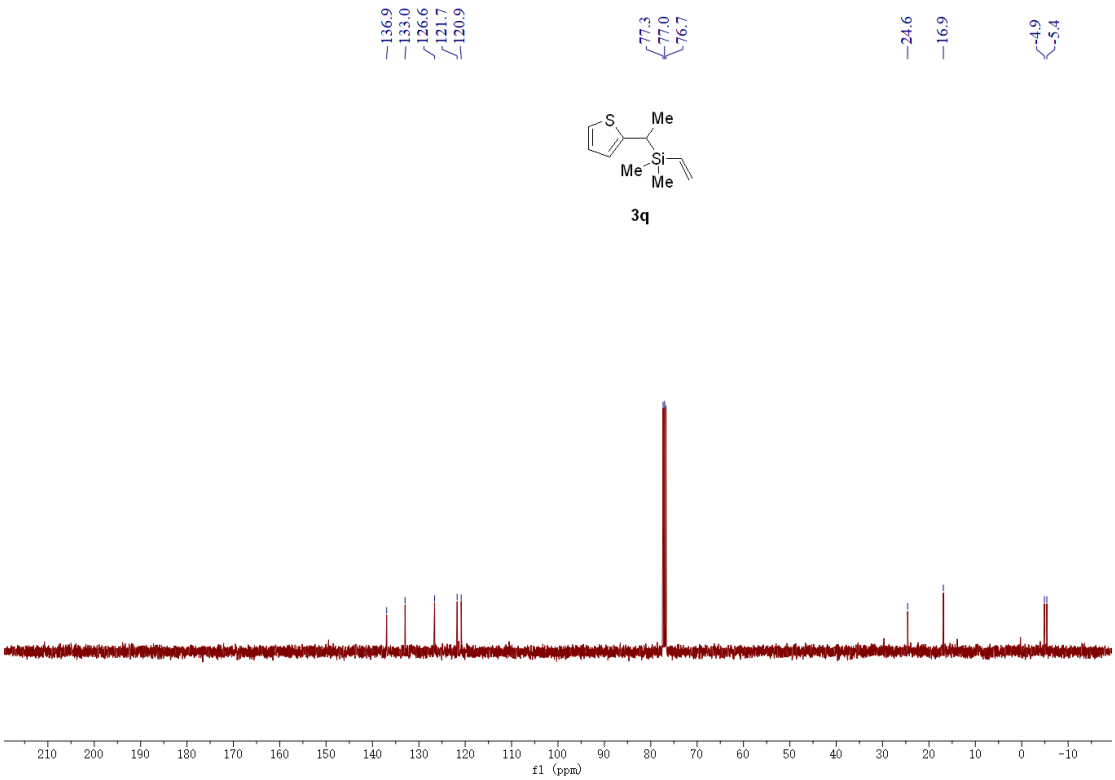
140.91
137.37
132.64
132.25
129.25
128.77
127.63
126.15
124.28
118.47
105.66
77.36
77.04
76.72
55.31
28.98
15.17
-4.76
-5.31
Me
Si
Me
Me
MeO
f1 (ppm)

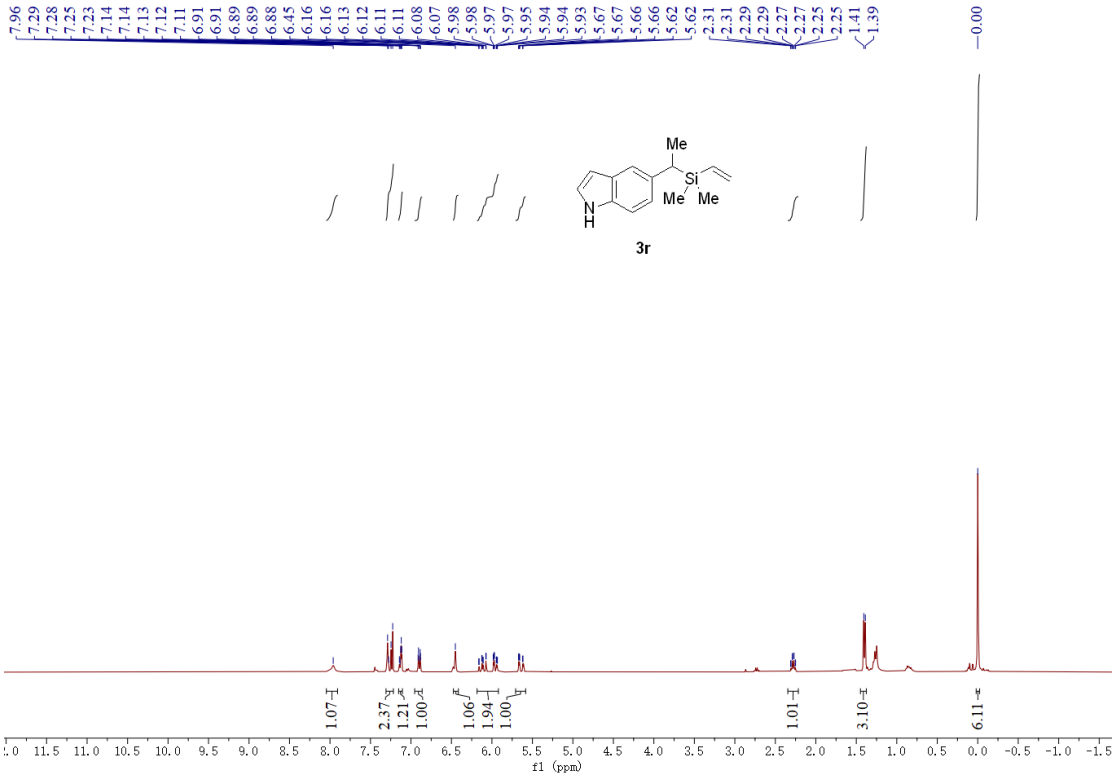
3p


7.01
7.00
6.91
6.90
6.90
6.89
6.63
6.63
6.63
6.63
6.61
6.61
6.60
6.60
6.13
6.12
6.12
6.11
6.09
6.09
6.02
6.01
6.00
5.99
5.70
5.69
5.67
5.66
2.53
2.52
2.51
2.50
1.39
1.38
0.06
S
Me
Me
Si
Me
1.08
1.09
1.04
2.25
1.04
1.00
3.05
5.94
f1 (ppm)

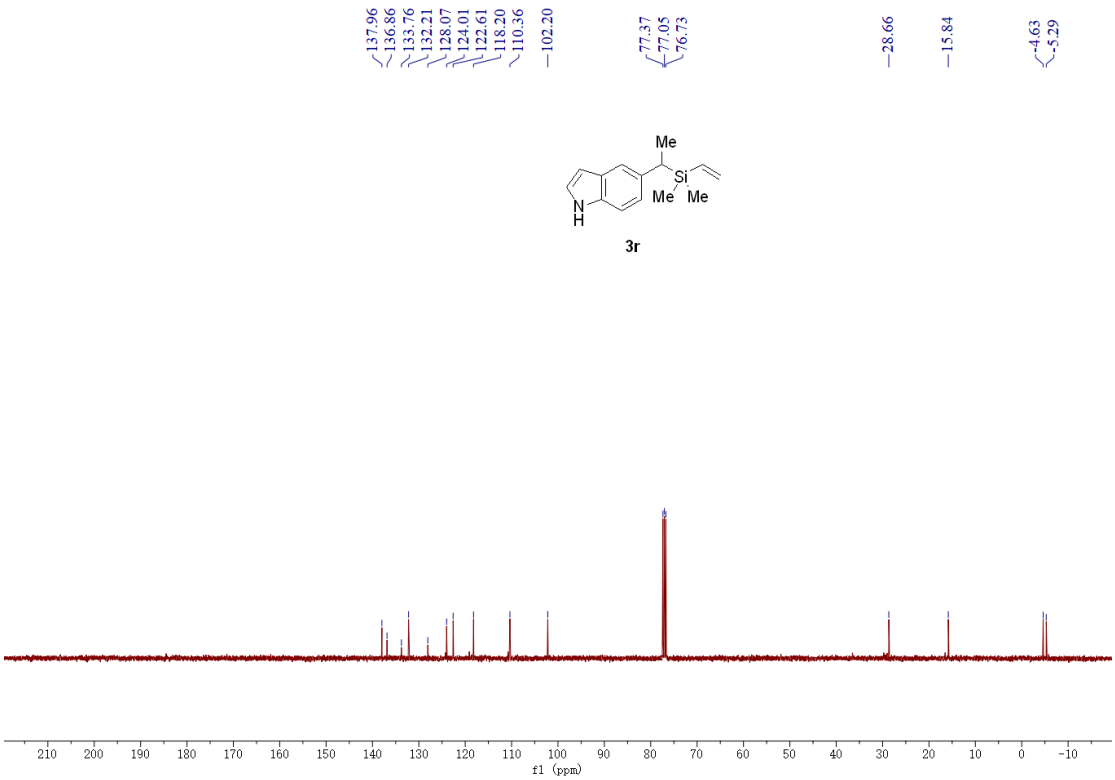
3q


136.9
133.0
126.6
121.7
120.9
77.3
77.0
76.7
24.6
16.9
-4.9
-5.4
S
Me
Si
Me
Me
f1 (ppm)

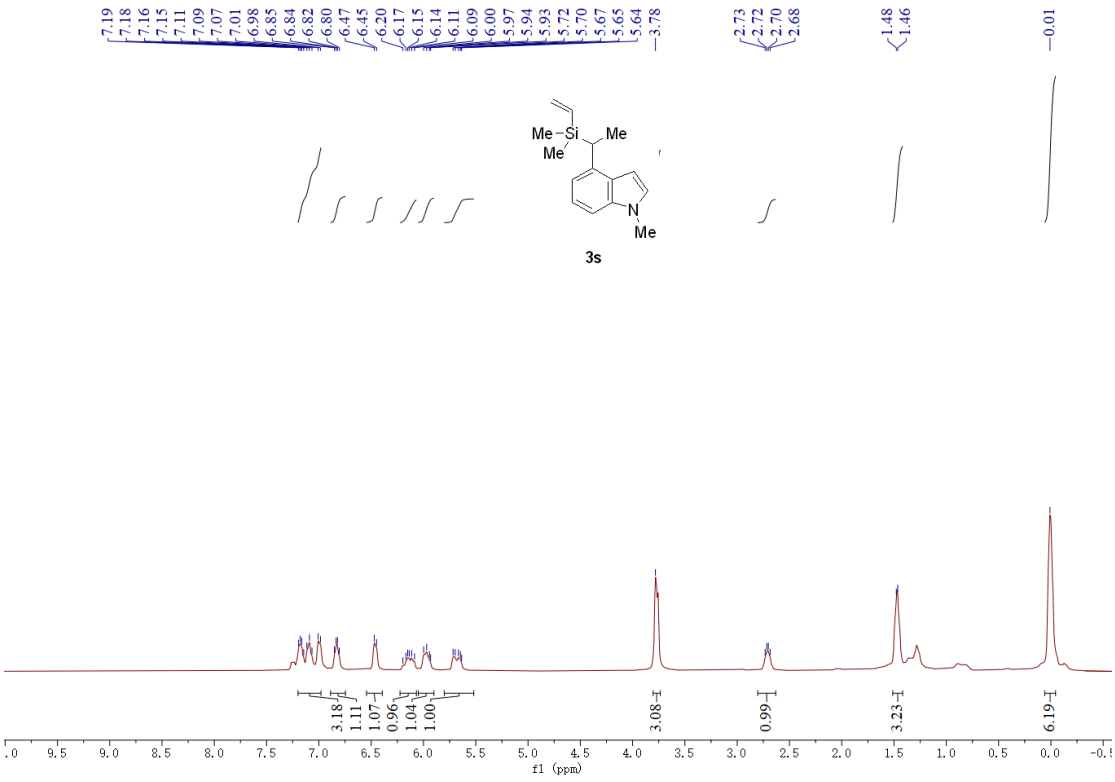
3q


7.96
7.29
7.28
7.25
7.23
7.14
7.14
7.13
7.12
7.11
6.91
6.91
6.89
6.89
6.88
6.45
6.16
6.16
6.13
6.12
6.11
6.11
6.08
6.07
5.98
5.98
5.97
5.97
5.95
5.94
5.94
5.93
5.67
5.67
5.66
5.66
5.62
5.62
2.31
2.31
2.29
2.29
2.27
2.27
2.25
2.25
1.41
1.39
0.00
Me
Si
Me
Me
N
H
1.07
2.37
1.21
1.00
1.06
1.94
1.00
1.01
3.10
6.11
f1 (ppm)

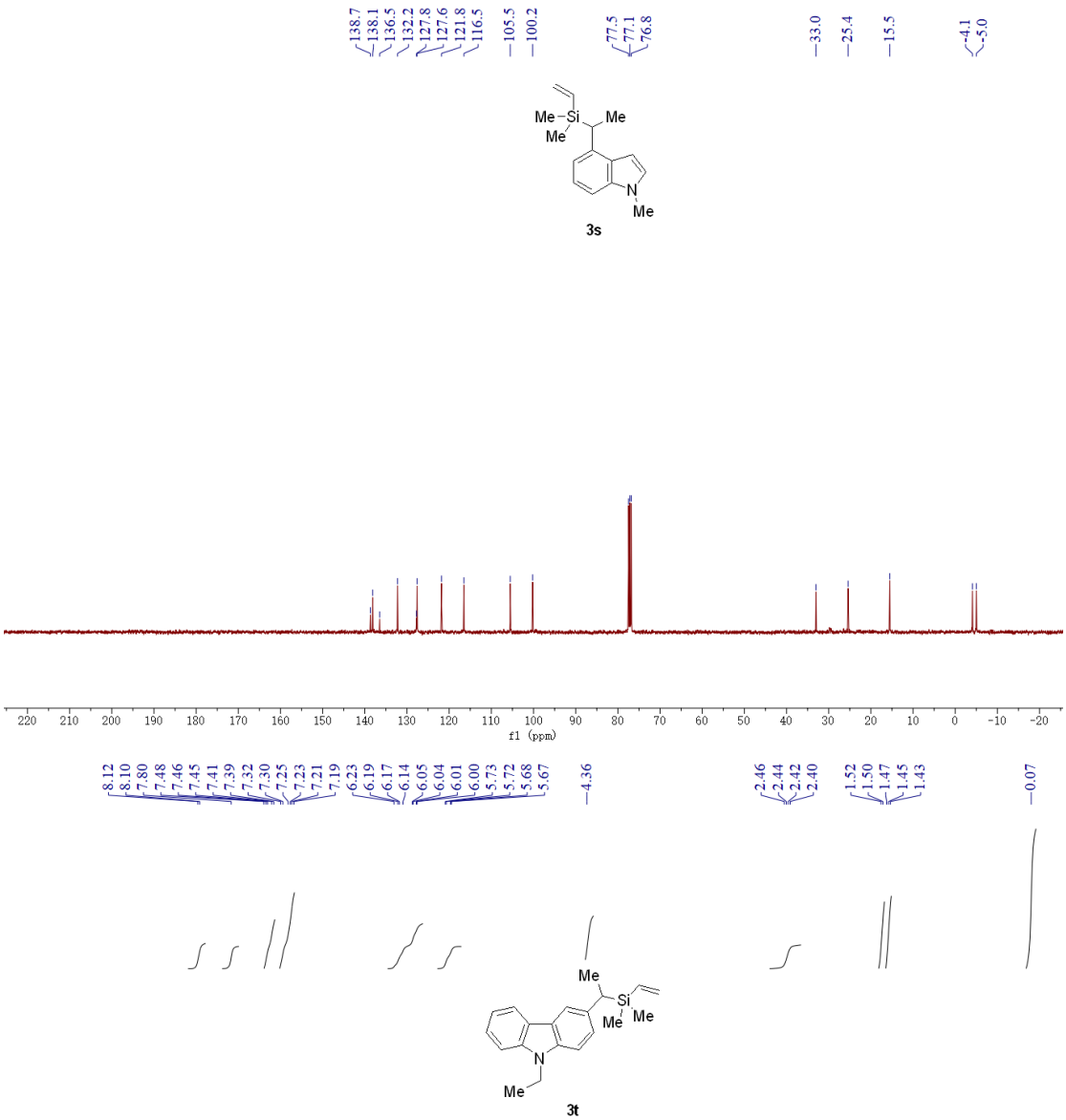
3r

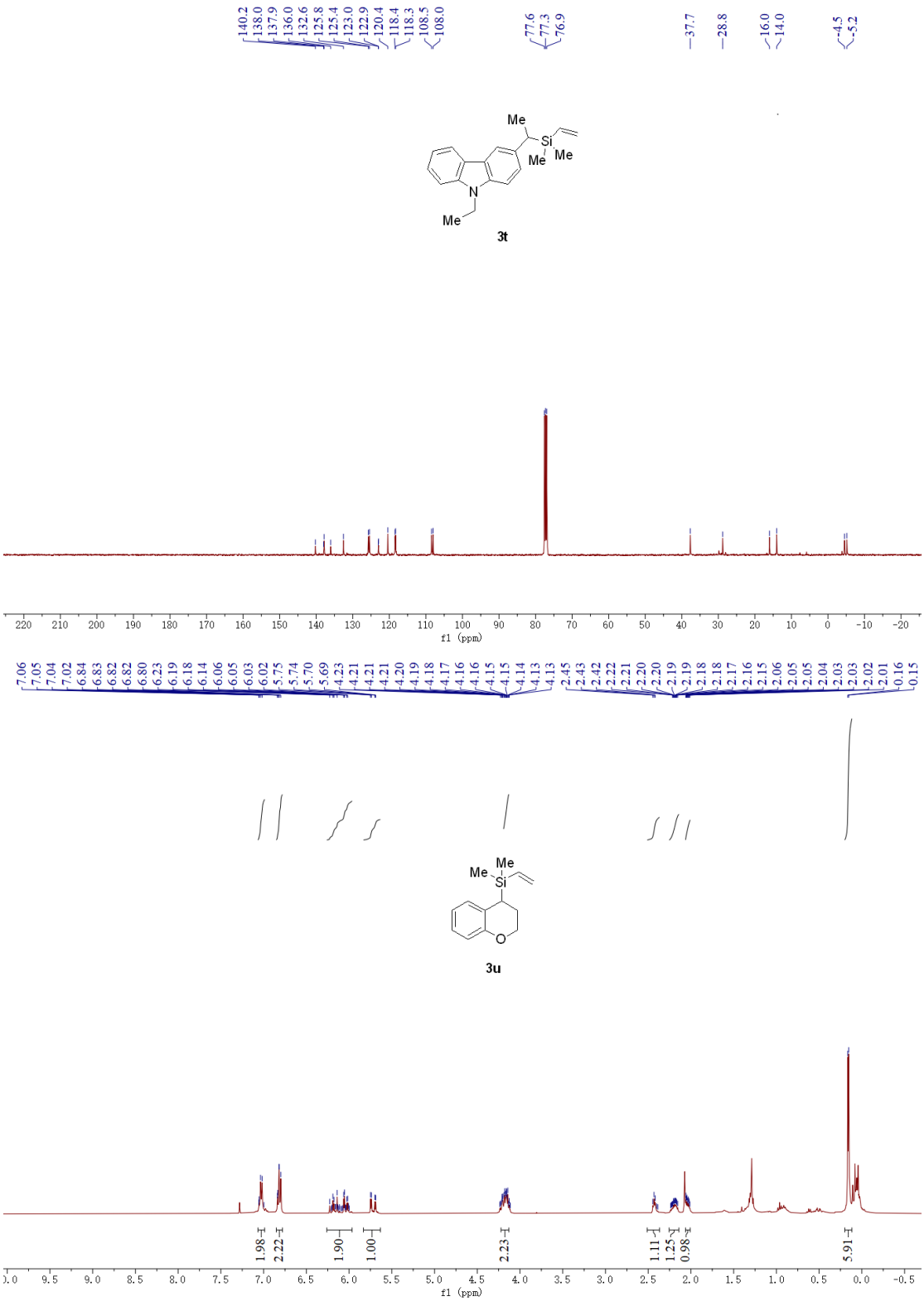

137.96
136.86
133.76
132.21
128.07
124.01
122.61
118.20
110.36
102.20
77.37
77.05
76.73
28.66
15.84
-4.63
-5.29
Me
Si
Me
Me
N
H
f1 (ppm)

3r


7.19
7.18
7.16
7.15
7.11
7.09
7.07
7.01
6.98
6.85
6.84
6.82
6.80
6.47
6.45
6.20
6.17
6.15
6.14
6.11
6.09
6.00
5.97
5.94
5.93
5.72
5.70
5.67
5.65
5.64
3.78
2.73
2.72
2.70
2.68
1.48
1.46
0.01
Me
Si
Me
Me
Me
N
Me
3.18
1.11
1.07
0.96
1.04
1.00
3.08
0.99
3.23
6.19
f1 (ppm)

3s


138.7
138.1
136.5
132.2
127.8
127.6
121.8
116.5
105.5
100.2
77.5
77.1
76.8
33.0
25.4
15.5
4.1
-5.0
Me
Si
Me
Me
N
Me
3s
f1 (ppm)
8.12
8.10
7.80
7.48
7.46
7.45
7.41
7.39
7.32
7.30
7.25
7.23
7.21
7.19
6.23
6.19
6.17
6.14
6.05
6.04
6.01
6.00
5.73
5.72
5.68
5.67
4.36
2.46
2.44
2.42
2.40
1.52
1.50
1.47
1.45
1.43
0.07
Me
Si
Me
Me
N
Me
3t
1.14
1.01
2.23
3.45
2.04
1.00
2.39
1.07
3.03
3.29
6.33
f1 (ppm)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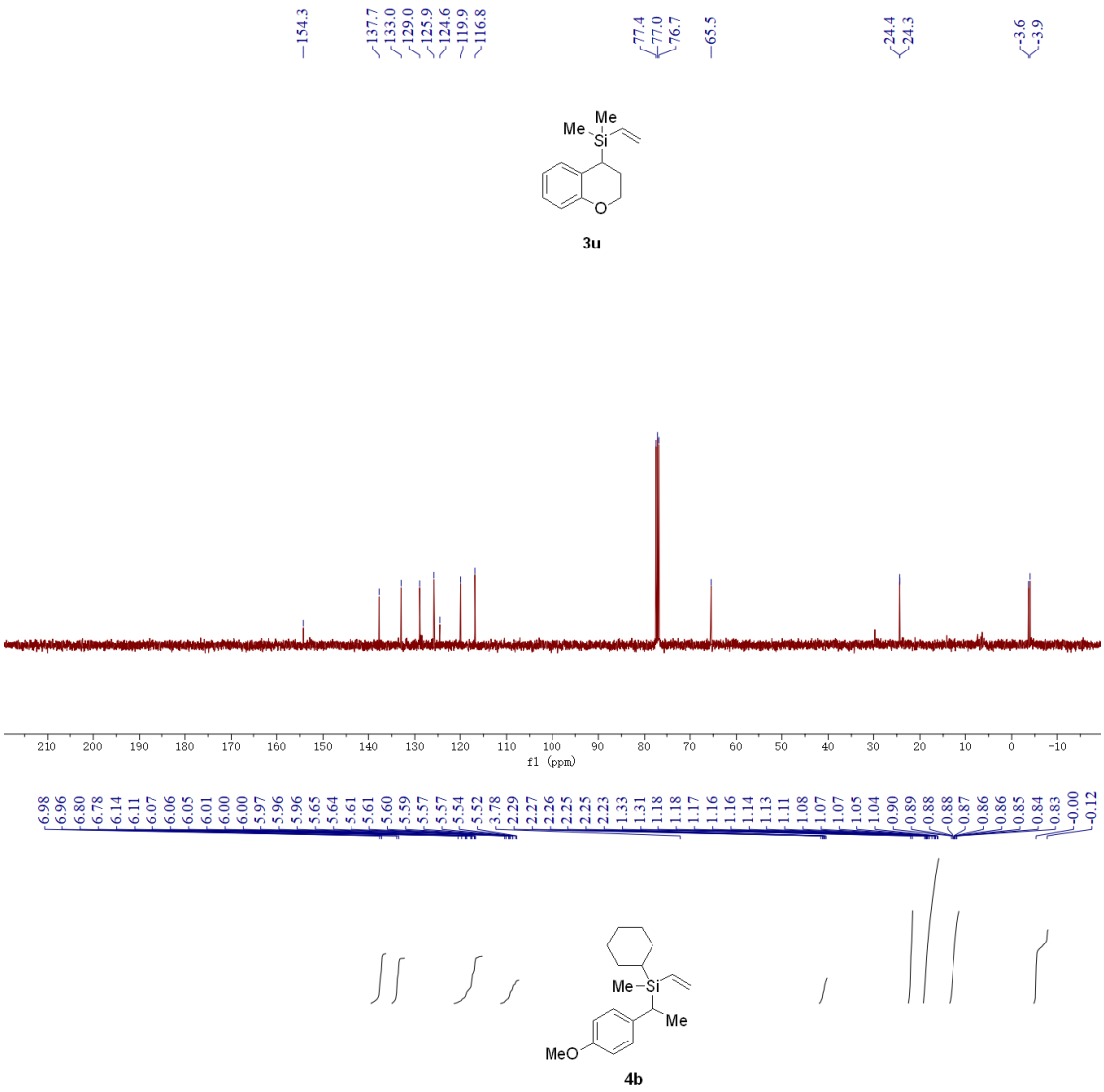
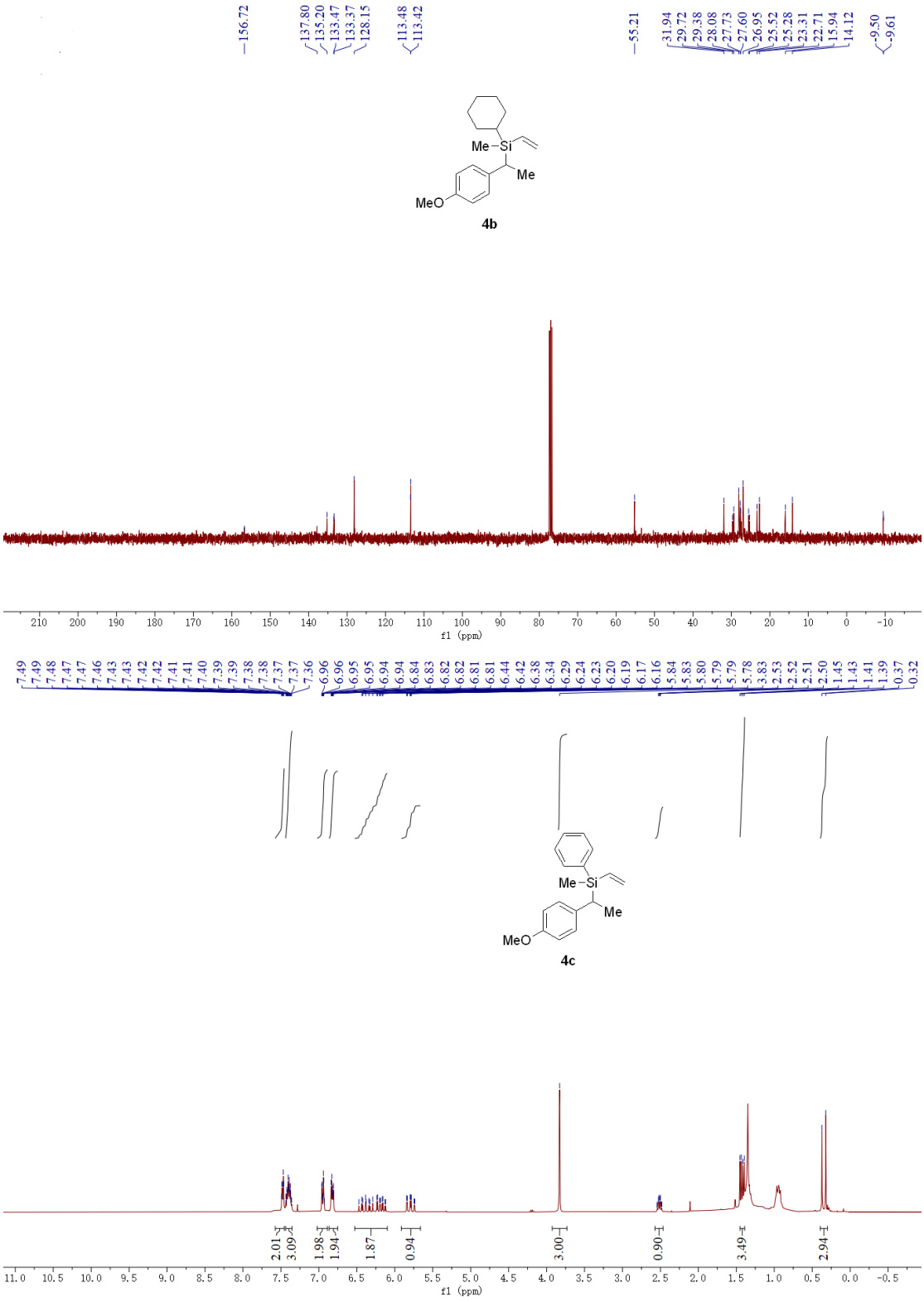
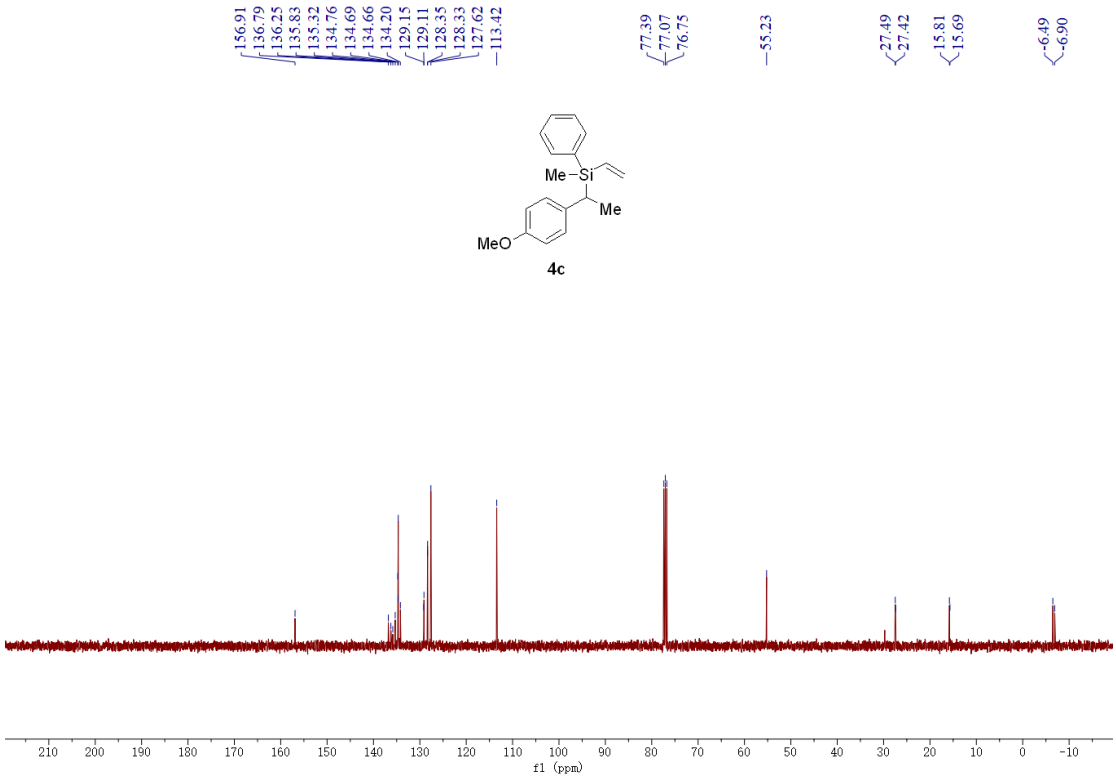
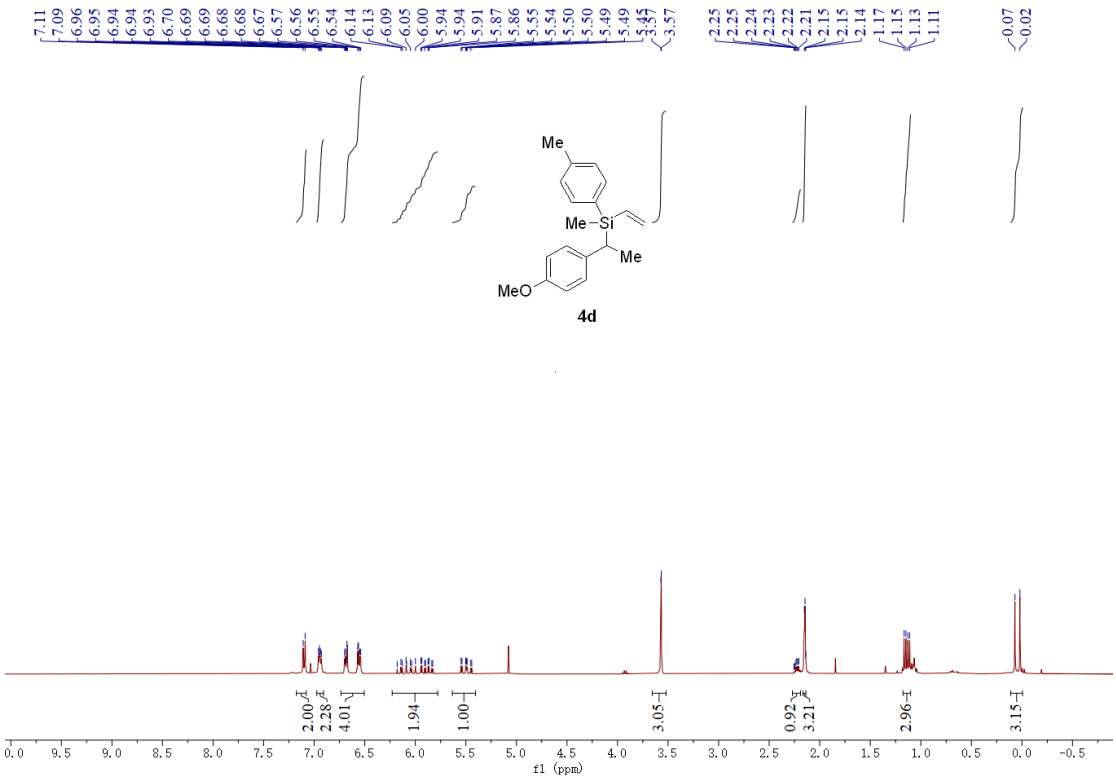
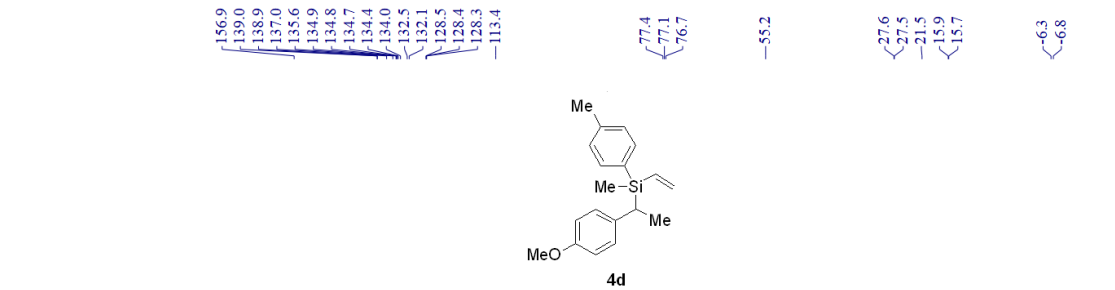
138.0
137.9
136.0
132.6
125.8
125.4
123.0
122.9
120.4
118.4
118.3
108.5
108.0
77.6
77.3
76.9
37.7
28.8
16.0
14.0
-4.5
-5.2
Me
Si
Me
Me
N
Me
3t
f1 (ppm)
7.06
7.05
7.04
7.02
6.84
6.83
6.82
6.82
6.80
6.23
6.19
6.18
6.14
6.06
6.05
6.03
6.02
5.75
5.74
5.70
5.69
4.23
4.21
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.16
4.15
4.15
4.14
4.13
2.45
2.43
2.42
2.22
2.21
2.20
2.20
2.19
2.19
2.18
2.18
2.17
2.16
2.15
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.01
0.16
0.15
Me
Me
Si
O
3u
1.98
2.22
1.90
1.00
2.23
1.11
1.25
0.98
5.91
f1 (ppm)


154.3
137.7
133.0
129.0
125.9
124.6
119.9
116.8
77.4
77.0
76.7
65.5
24.4
24.3
-3.6
-3.9
Me
Me
Si
O
3u
f1 (ppm)
6.98
6.96
6.80
6.78
6.14
6.11
6.07
6.06
6.05
6.01
6.00
6.00
5.97
5.96
5.96
5.65
5.64
5.61
5.61
5.60
5.59
5.57
5.57
5.54
5.52
3.78
2.29
2.27
2.26
2.25
2.25
2.23
1.33
1.31
1.18
1.18
1.17
1.16
1.16
1.14
1.13
1.11
1.08
1.07
1.07
1.05
1.04
0.90
0.89
0.88
0.88
0.87
0.86
0.86
0.85
0.84
0.83
-0.00
-0.12
Me
Si
Me
MeO
4b
2.13
1.93
2.01
1.00
3.08
1.10
4.00
6.22
3.97
3.18
f1 (ppm)

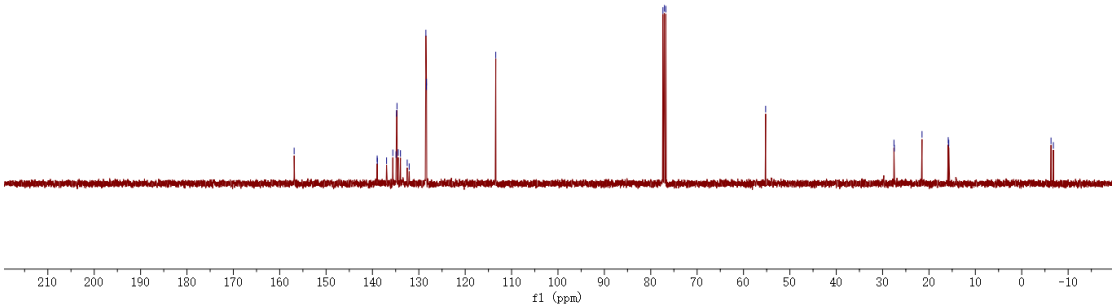

156.72
137.80
135.20
133.47
133.37
128.15
113.48
113.42
55.21
31.94
29.72
29.38
28.08
27.73
27.60
26.95
25.52
25.28
23.31
22.71
15.94
14.12
-9.50
-9.61
Me
Si
Me
MeO
4b
f1 (ppm)
7.49
7.49
7.48
7.47
7.47
7.46
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
6.96
6.96
6.95
6.95
6.94
6.94
6.84
6.83
6.82
6.82
6.81
6.81
6.44
6.42
6.38
6.34
6.29
6.24
6.23
6.20
6.19
6.17
6.16
5.84
5.83
5.80
5.79
5.79
5.78
3.83
2.53
2.52
2.51
2.50
1.45
1.43
1.41
1.39
0.37
0.32
Me
Si
Me
MeO
4c
2.01
3.09
1.98
1.94
1.87
0.94
3.00
0.90
3.49
2.94
f1 (ppm)

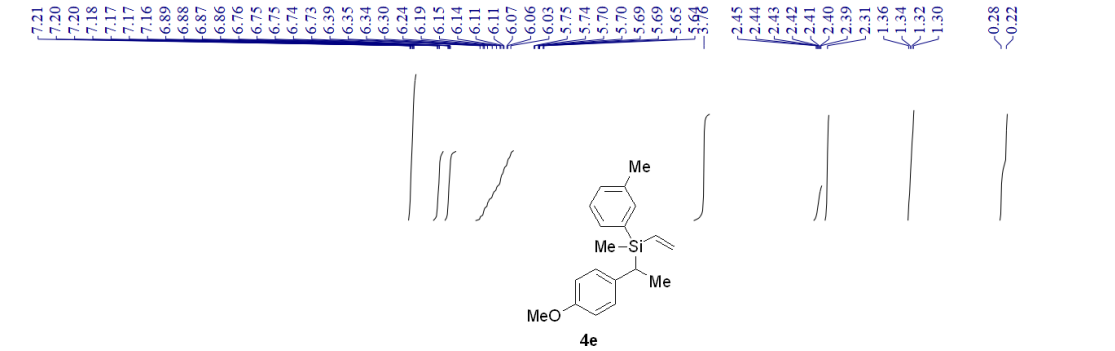

156.91
136.79
136.25
135.83
135.32
134.76
134.69
134.66
134.20
129.15
129.11
128.35
128.33
127.62
113.42
77.39
77.07
76.75
55.23
27.49
27.42
15.81
15.69
6.49
6.90
Me
Si
Me
MeO
4c
f1 (ppm)


7.11
7.09
6.96
6.95
6.94
6.94
6.93
6.70
6.69
6.69
6.68
6.68
6.67
6.57
6.56
6.55
6.54
6.14
6.13
6.09
6.05
6.00
5.94
5.94
5.91
5.87
5.86
5.55
5.54
5.50
5.50
5.49
5.49
3.57
3.57
2.25
2.25
2.24
2.23
2.22
2.21
2.15
2.15
2.14
1.17
1.15
1.13
1.11
0.07
0.02
Me
Me
Si
Me
MeO
4d
2.00
2.28
4.01
1.94
1.00
3.05
0.92
3.21
2.96
3.15
f1 (ppm)

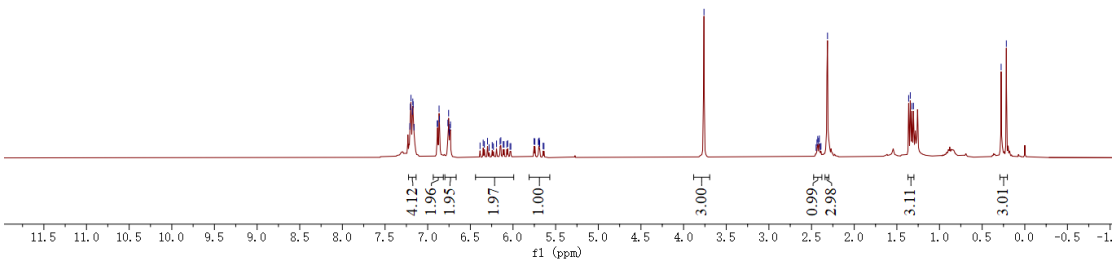

156.9
139.0
138.9
137.0
135.6
134.9
134.8
134.7
134.4
134.0
132.5
132.1
128.5
128.4
128.3
113.4
77.4
77.1
76.7
55.2
27.6
27.5
21.5
15.9
15.7
-6.3
-6.8
Me
Me–Si
Me
MeO

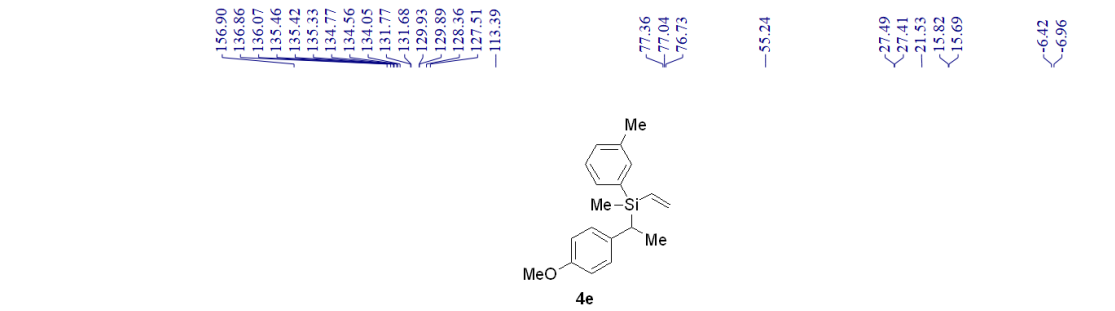
4d


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

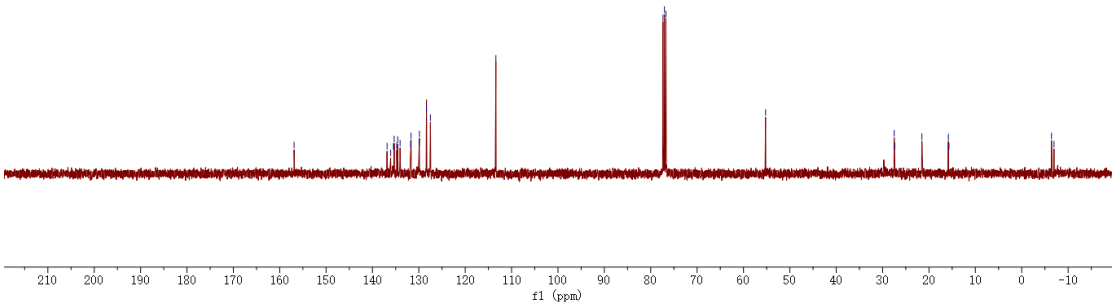

7.21
7.20
7.20
7.18
7.17
7.17
7.16
6.89
6.88
6.87
6.86
6.76
6.75
6.75
6.74
6.73
6.39
6.35
6.34
6.30
6.24
6.19
6.15
6.14
6.11
6.11
6.07
6.06
6.03
5.75
5.74
5.70
5.70
5.69
5.69
5.65
5.64
3.78
2.45
2.44
2.43
2.42
2.41
2.40
2.39
2.31
1.36
1.34
1.32
1.30
0.28
0.22
Me
Me–Si
Me
MeO

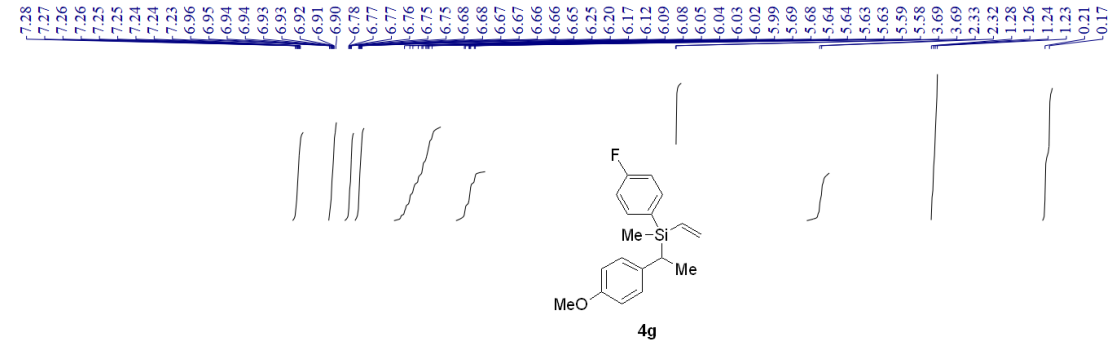
4e


4.12
1.96
1.95
1.97
1.00
3.00
0.99
2.98
3.11
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

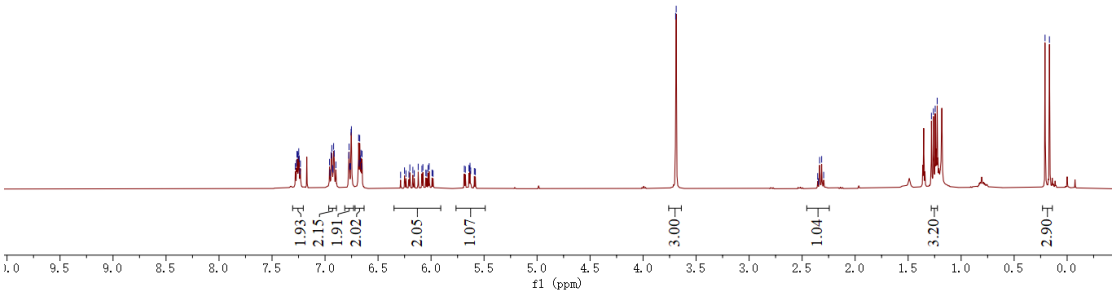

156.90
136.86
136.07
135.46
135.42
135.33
134.77
134.56
134.05
131.77
131.68
129.93
129.89
128.36
127.51
113.39
77.36
77.04
76.73
55.24
27.49
27.41
21.53
15.82
15.69
6.42
6.96
Me
Me–Si
Me
MeO

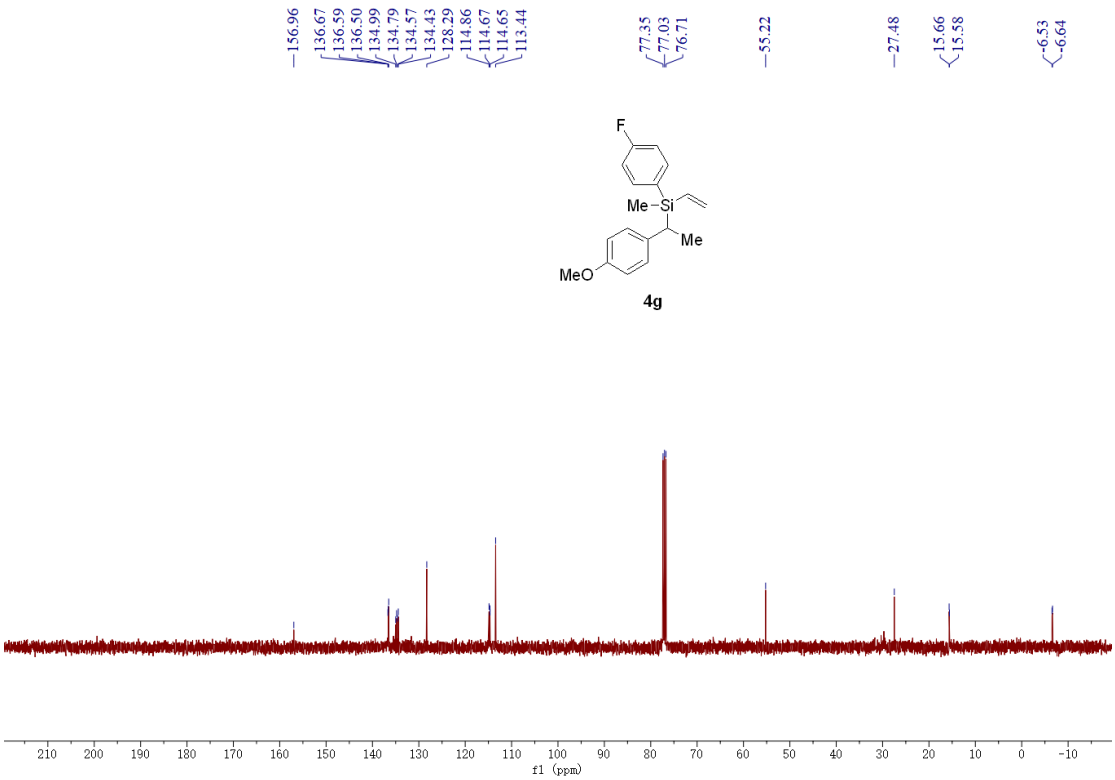
4e

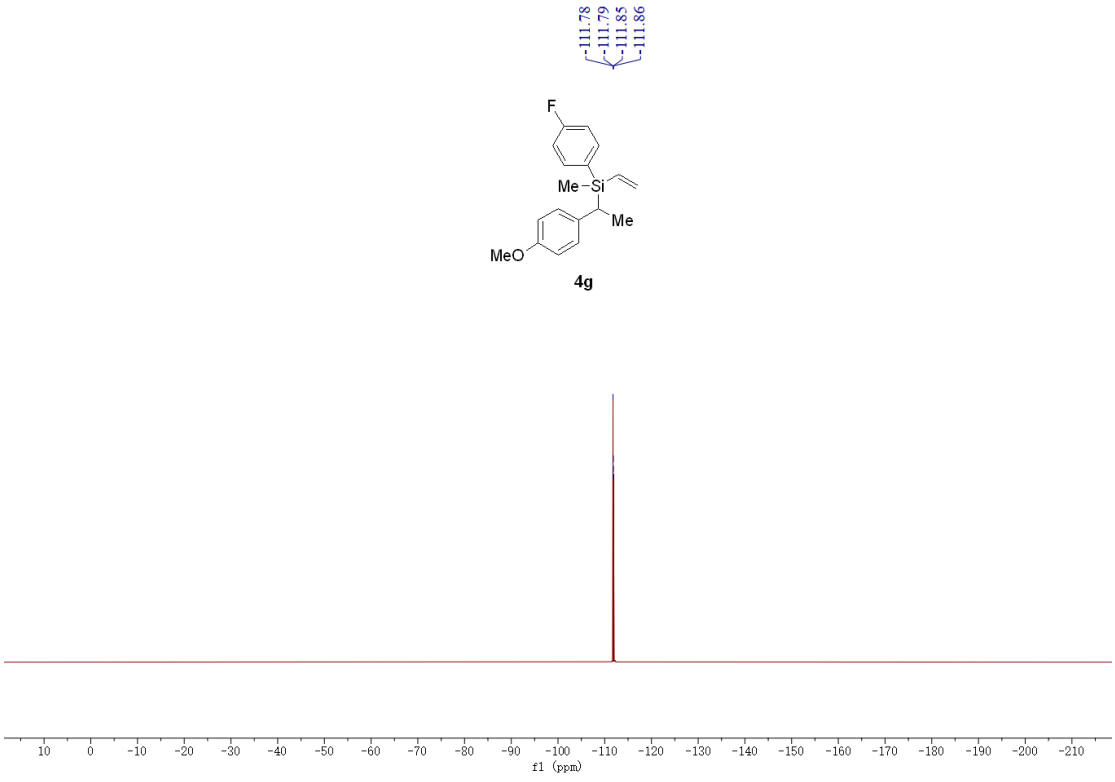

f1 (ppm)

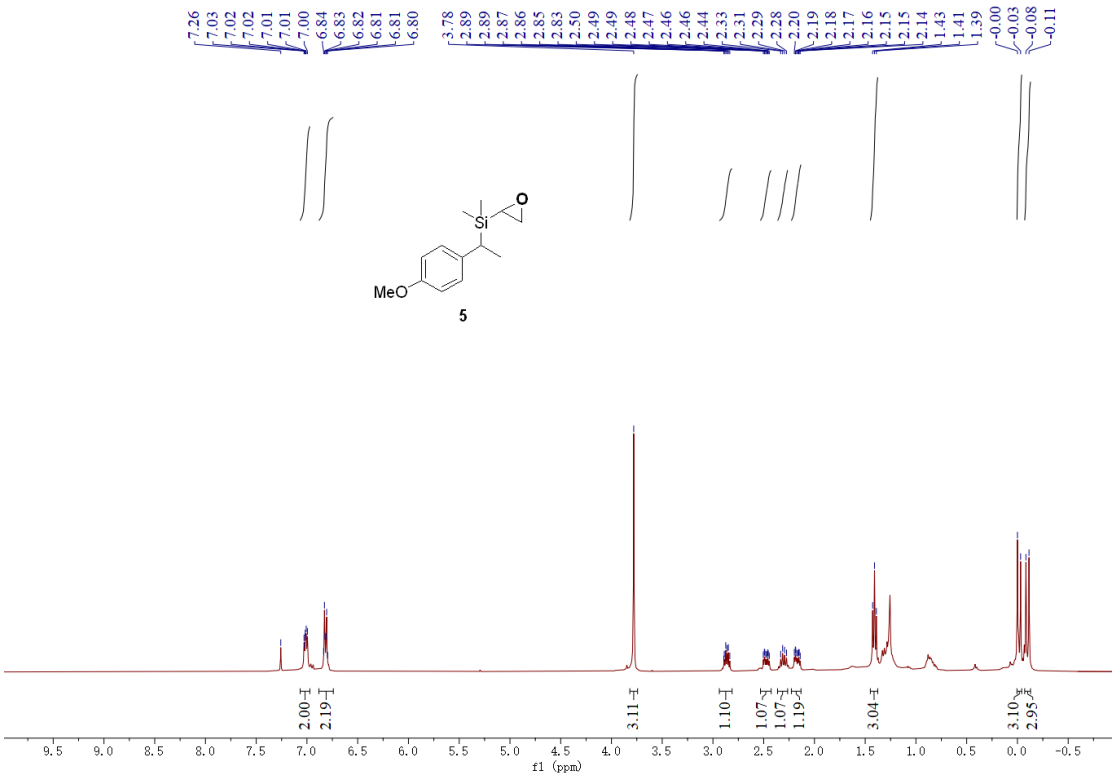

7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
6.96
6.95
6.94
6.94
6.93
6.93
6.92
6.91
6.90
6.78
6.77
6.77
6.76
6.75
6.75
6.68
6.68
6.67
6.67
6.66
6.66
6.65
6.25
6.20
6.17
6.12
6.09
6.08
6.05
6.04
6.03
6.02
5.99
5.69
5.68
5.64
5.64
5.63
5.63
5.59
5.58
3.69
3.69
2.33
2.32
1.28
1.26
1.24
1.23
0.21
0.17
F
Me–Si
Me
MeO

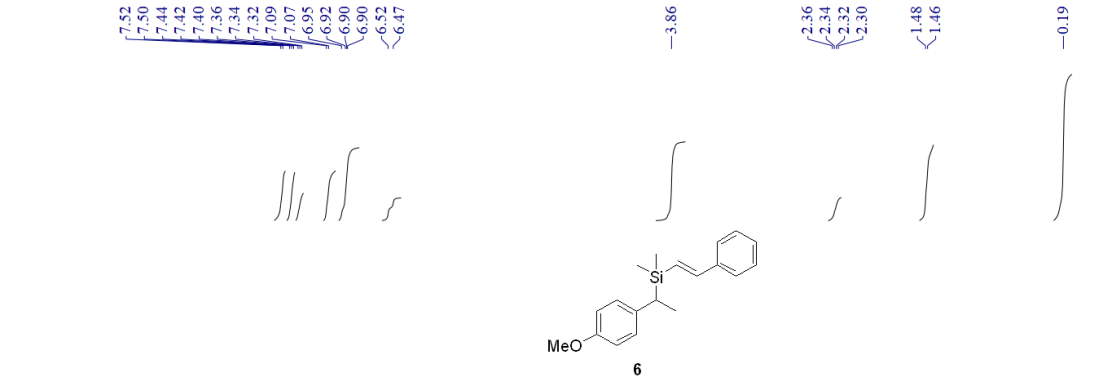
4g


1.93
2.15
1.91
2.02
2.05
1.07
3.00
1.04
3.20
2.90
f1 (ppm)

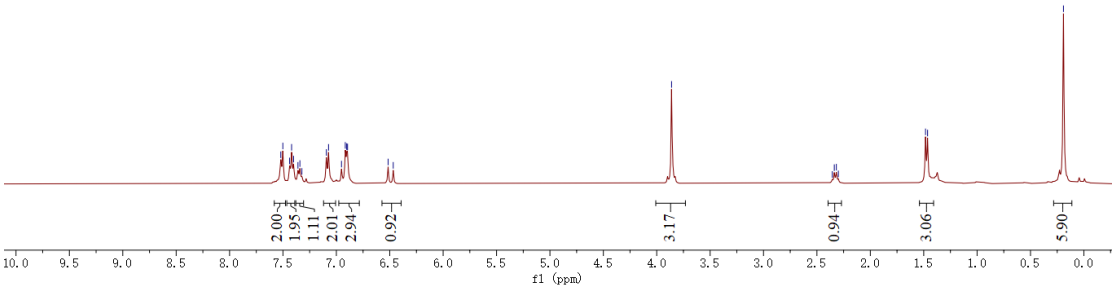

156.96
136.67
136.59
136.50
134.99
134.79
134.57
134.43
128.29
114.86
114.67
114.65
113.44
77.35
77.03
76.71
55.22
27.48
15.66
15.58
6.53
6.64
F
Me
Si
Me
MeO
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


111.78
111.79
111.85
111.86
F
Me
Si
Me
MeO
4g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

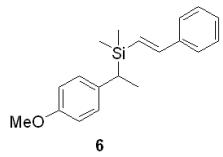

7.26
7.03
7.02
7.02
7.01
7.01
7.00
6.84
6.83
6.82
6.81
6.81
6.80
3.78
2.89
2.89
2.87
2.86
2.85
2.83
2.50
2.49
2.49
2.48
2.47
2.46
2.46
2.44
2.33
2.31
2.29
2.28
2.20
2.19
2.18
2.17
2.16
2.15
2.15
2.14
1.43
1.41
1.39
0.00
-0.03
-0.08
-0.11
Si
O
MeO
5
2.00
2.19
3.11
1.10
1.07
1.07
1.19
3.04
3.10
2.95
f1 (ppm)
157.0
157.0
136.7
136.7
127.9
127.9
113.7
113.7
77.3
77.0
76.7
55.2
44.4
44.4
42.6
42.6
26.9
26.7
15.3
15.1
-6.9
-7.4
-7.7
-7.8
Si
O
MeO
5
f1 (ppm)


7.52
7.50
7.44
7.42
7.40
7.36
7.34
7.32
7.09
7.07
6.95
6.92
6.90
6.90
6.52
6.47
3.86
2.36
2.34
2.32
2.30
1.48
1.46
0.19
Si
MeO

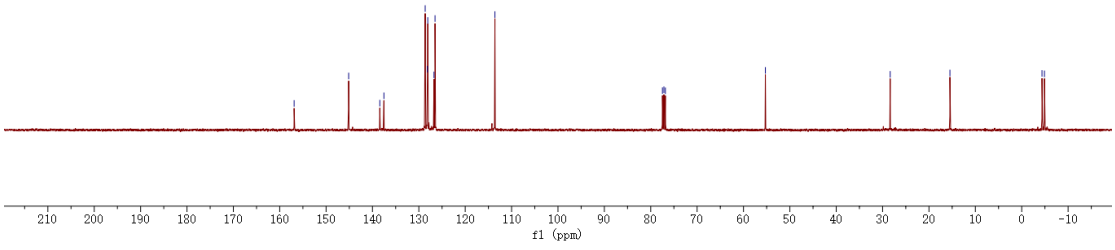
6

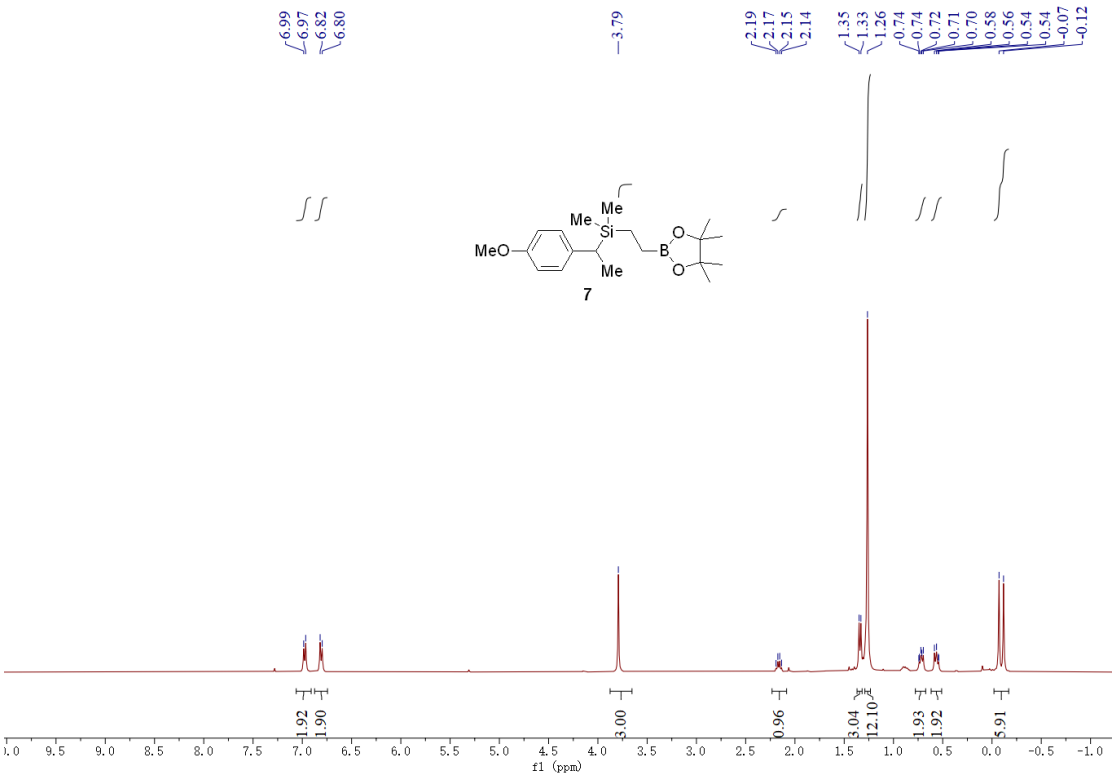

2.00
1.95
1.11
2.01
2.94
0.92
3.17
0.94
3.06
5.90
f1 (ppm)

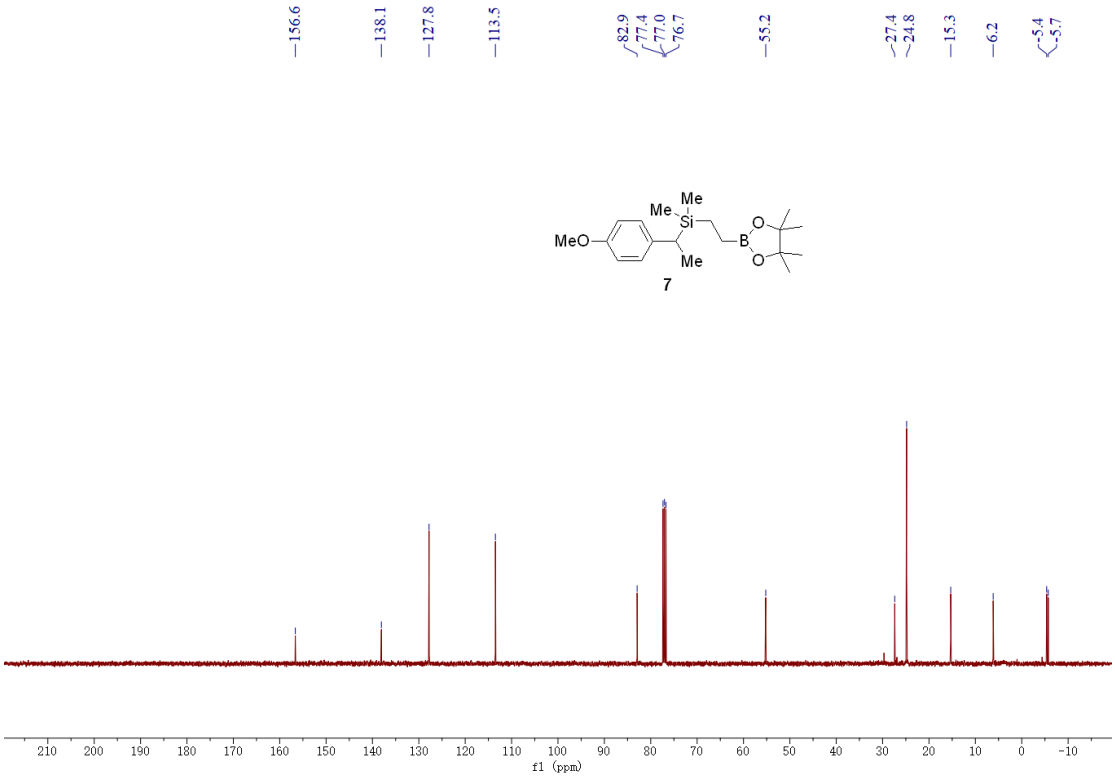

156.9
145.1
138.4
137.5
128.6
128.1
128.1
126.7
126.5
113.6
77.5
77.2
76.8
55.3
28.4
15.5
-4.4
-4.9


Si
MeO

6


f1 (ppm)


6.99
6.97
6.82
6.80
3.79
2.19
2.17
2.15
2.14
1.35
1.33
1.26
0.74
0.72
0.71
0.70
0.58
0.56
0.54
0.54
-0.07
-0.12
Me
Me
Si
MeO
B
O
O
Me
7
1.92
1.90
3.00
0.96
3.04
12.10
1.93
1.92
5.91
f1 (ppm)


156.6
138.1
127.8
113.5
82.9
77.4
77.0
76.7
55.2
27.4
24.8
15.3
6.2
-5.4
-5.7
Me
Me
Si
MeO
B
O
O
Me
7
f1 (ppm)