Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-free photocatalyzed allylic silylation of allyl acetates and chlorides

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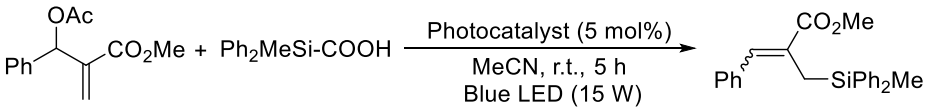
General information

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in glass reaction tubes. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (300-400 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. Precoated silica gel plates F-254 were used for thin-layer analytical chromatography and visualized by UV fluorescence (254 nm) then one of the following: $KMnO_4$, phosphomolybdic acid. NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (*ref: $CHCl_3$ ^1H: 7.26, ^{13}C: 77.16)*. Coupling constants (*J)* were reported in Hz to the nearest 0.1 Hz. Peak multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet) and br (broad). High resolution mass spectrometry (HRMS) was performed on a Waters Micromass (ESI-TOF). Silacarboxylic acids,[1] allyl acetates,[2] and allyl chlorides[3] were synthesized according to reported procedures.

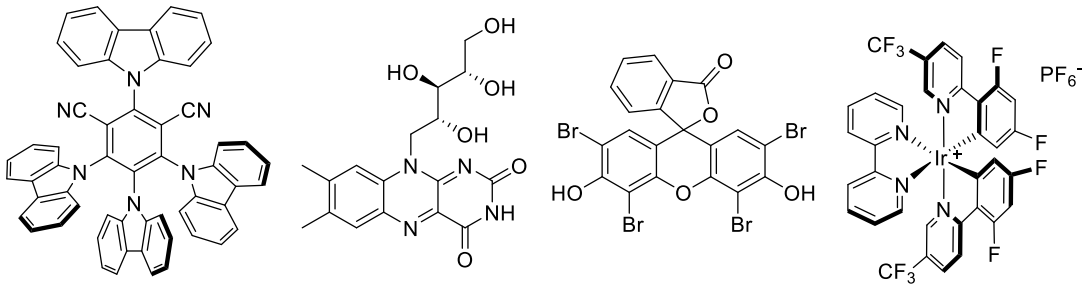
Optimization of reaction conditions

Table S1. Screening of photocatalysts.[a]



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

Entry	Photocatalyst	Yield of **3a** (%)	***Z*:*E***[b]
1	**4CzIPN**	**85**	**1:2**
2	riboflavin	80	1:1.5
3	Eosin Y	52	1:1.6
4[c]	$Ir[dF(CF_3)ppy]_2(bpy)PF_6$	72	1:1



4CzIPN **riboflavin** **Eosin Y** **$Ir[dF(CF_3)ppy]_2(bpy)PF_6$**

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), photocatalyst (5 mol%, 0.01 mmol), MeCN (2 mL) at room temperature under visible light irradiation (blue LED, 460-465 nm, 15 W) under N_2 for 5 h. [b] Determined by ^1H NMR. [c] $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ (2 mol%, 0.004 mmol).

Table S2. Screening of solvents.[a]

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

Entry	Solvent	Yield of **3a** (%)	***Z*:*E*[b]**
1	DMSO	< 5	-
2	NMP	< 5	-
3	DMF	< 5	-
4	DCM	22	1:1.6
5	THF	75	1:1.4
6	**MeCN**	**85**	**1:2**
7	Hexane	17	1:0.9
8	EtOH	70	1:1.2
9	Acetone	78	1:1.8
10	Toluene	45	1:1.2
11	1,4-Dioxane	73	1:1.5
12	H_2O	< 5	1:1
13	MeCN/H_2O (1:1)	85	1:2
14	DCE/H_2O (1:1)	< 5	1:1

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (5 mol%, 0.01 mmol), solvent (2 mL) at room temperature under visible light irradiation (blue LED, 460-465 nm, 15 W) under N_2 for 5 h. [b] Determined by ^{1}H NMR.

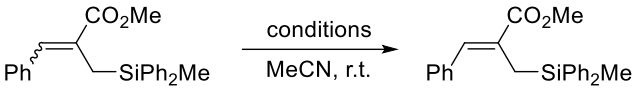
Table S3. Screening of catalyst loading.[a]

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

Entry	x mol%	Yield of **3a** (%)	***Z*:*E*[b]**
1	5	85	1:2
2	**2.5**	**85**	**1:2**
3	1	70	1:2

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (x mol%), MeCN (2 mL) at room temperature under visible light irradiation (blue LED, 460-465 nm, 15 W) under N_2 for 12 h. [b] Determined by ^{1}H NMR.

Table S4. Screening of conditions for isomerization of **3a**.

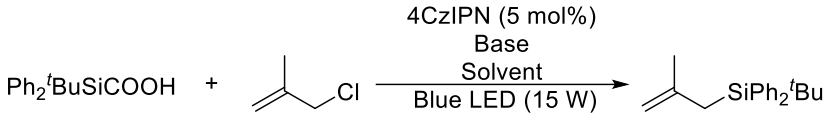


3a **Z-3a**

Entry	conditions	Time (h)	Yield of **3a** (%)	***Z*:*E*** [b]
1	UV irradiation (365 nm)	12	100	1:1.4
2	Ph_2S_2 (100 mol%) (blue LED, 15 W)	1	88	>20:1
3	**Ph_2S_2 (20 mol%) (blue LED, 15 W)**	**1**	**90**	**>20:1**
4	Ph_2S_2 (5 mol%) (blue LED, 15 W)	1	90	15:1

[a] Reaction conditions: **3a** (0.2 mmol, 1.0 equiv.), MeCN (2 mL) at room temperature under N_2. [b] Determined by ^1H NMR.

Table S5. Screening of reaction conditions for the synthesis of **5a**.



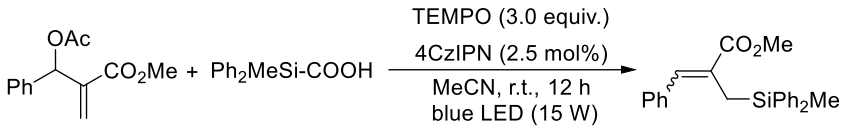
2c **4a** **5a**

Entry	Base	Solvent	Yield of **5a** (%)
1	Et_3N	MeCN	trace
2	Et_3N	THF	trace
3	K_2CO_3	THF	41
4	Na_2CO_3	THF	31
5	$NaHCO_3$	THF	62
6	NaOAc	THF	88
7	K_2HPO_4	THF	54
8	Imidazole	THF	85
9	Pyridine	THF	85
10	Imidazole	EA	88
11	Imidazole	EtOH	77
12	Imidazole	1,4-dioxane	90
13	Imidazole	DMF	64
14	Imidazole	DCM	N.D.
15	Imidazole	DME	92
16	-	DME	13
17	Imidazole	H_2O	N.D.
18[b]	Imidazole	DME	49
19[c]	**Imidazole**	**DME**	**92**

[a] Reaction conditions: **2c** (0.2 mmol, 1.0 equiv.), **4a** (0.4 mmol, 2.0 equiv.), 4CzIPN (5 mol%, 0.01 mmol), base (1.0 equiv.), solvent (2 mL) at room temperature under visible light irradiation (blue LED, 460-465 nm, 15 W) under N_2 for 1 h. [b] 4CzIPN (2.5 mol%). [c] **4a** (0.24 mmol, 1.2 equiv.)

Mechanistic Studies

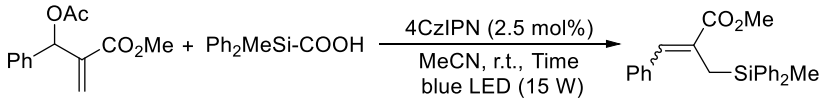
Radical trapping experiments



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

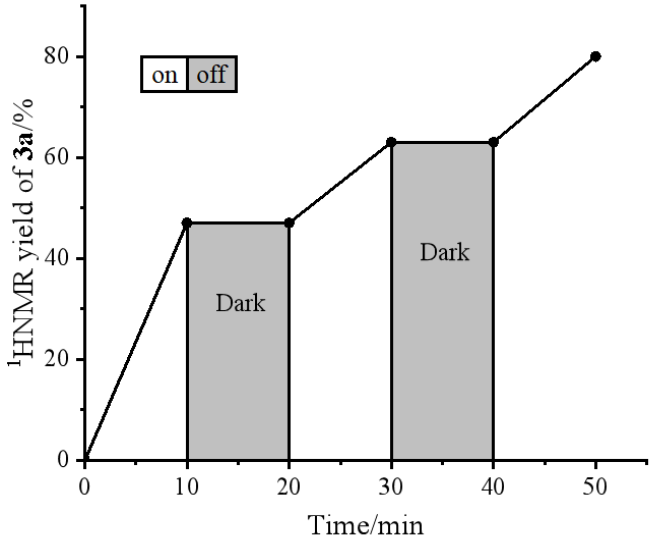
Under nitrogen atmosphere, a 10 mL tube equipped with a magnetic stirrer bar was charged sequentially with allyl acetate **1a** (46.9 mg, 0.2 mmol, 1.0 equiv.), $Ph_2MeSiCOOH$ **2a** (48.5 mg, 0.2 mmol, 1.0 equiv.), TEMPO (93.8 mg, 3.0 equiv.) and 4CzIPN (4.0 mg, 0.005 mmol, 2.5 mol%). Then MeCN (0.1 M, 2 mL) was injected into the reaction tube. The solution was stirred under irradiation with 15 W blue LED at room temperature for 12 h. The reaction mixture was diluted with DCM and detected by GC-MS. The product **3a** was observed in trace amount, indicating the reaction was suppressed by the radical scavenger.

Light/dark experiment



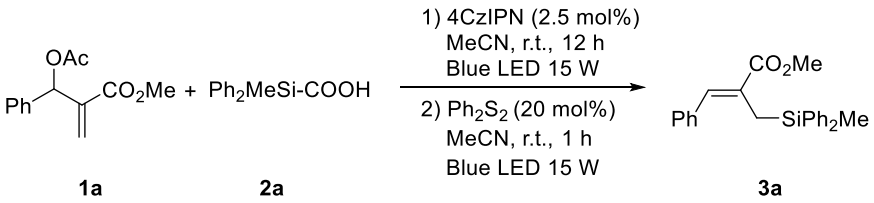
1a **2a** **3a**

Under nitrogen atmosphere, five 10 mL tubes (No. 1-5) equipped with magnetic stirrer bars were charged sequentially with allyl acetate **1a** (46.9 mg, 0.2 mmol, 1.0 equiv.), $Ph_2MeSiCOOH$ **2a** (48.5 mg, 0.2 mmol, 1.0 equiv.), and 4CzIPN (4.0 mg, 0.005 mmol, 2.5 mol%). Then MeCN (0.1 M, 2 mL) was injected into the reaction tube and the reaction mixtures were stirred under irradiation. After 10 min, the Blue LED was turned off, and No.1 vial was removed from the irradiation setup for analysis. The remaining four vials were stirred in the absence of light for an additional 10 min. Then, No.2 vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining three reaction mixtures. After an additional 10 min of irradiation, the Blue LED was turned off, and No. 3 vial was removed for analysis. The remaining two vials were stirred in the absence of light for an additional 10 min. Then, No. 4 vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining last reaction mixture for 10 min, and then it was analyzed. Yields were determined by analysis of the crude ^1H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard.


on
off
Dark
Dark
^{1}HNMR yield of **3a**/%
Time/min
0
20
40
60
80
0
10
20
30
40
50

Synthesis of allylsilanes 3

Typical procedure for the synthesis of 3a



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

Under nitrogen atmosphere, a 10 mL tube equipped with a magnetic stirrer bar was charged sequentially with allyl acetate **1a** (46.9 mg, 0.2 mmol, 1.0 equiv.), $Ph_2MeSiCOOH$ **2a** (48.5 mg, 0.2 mmol, 1.0 equiv.), and 4CzIPN (4.0 mg, 0.005 mmol, 2.5 mol%). Then MeCN (0.1 M, 2 mL) was injected into the reaction tube. The solution was stirred under irradiation with 15 W blue LED at room temperature for 12 h. Upon completion, solvent was removed under vacuum and the residue was purified by a short flash column chromatography to afford the crude product. A solution of the crude product and Ph_2S_2 (8.7 mg, 0.04 mmol, 20 mol%) in MeCN (0.1 M, 2 mL) was stirred under irradiation with 15 W blue LED at room temperature for 1 h. Upon completion, solvent was removed under vacuum and the residue was purified by SiO_2 column chromatography to afford the desired product **3a**.

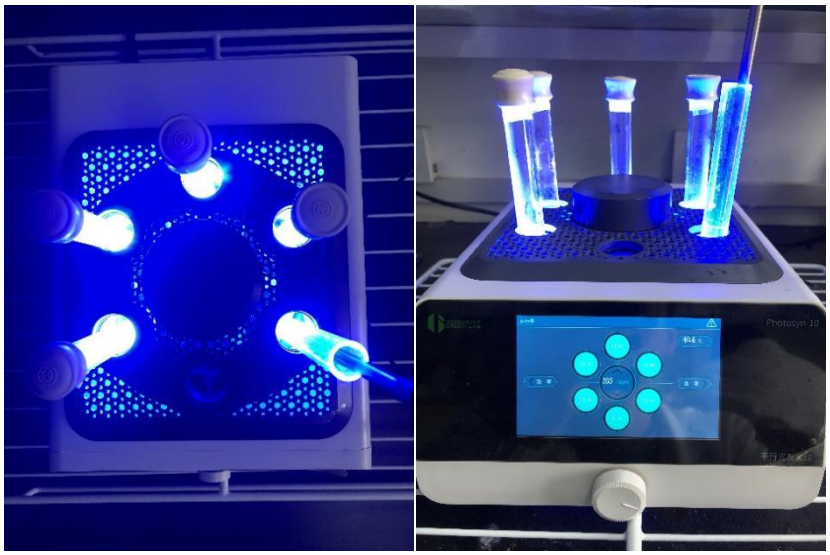
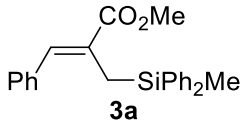


Figure S1. Experimental setup



3a

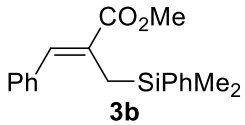
methyl (*Z*)-2-((methyldiphenylsilyl)methyl)-3-phenylacrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 65.4 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.51-7.47 (m, 4H), 7.39-7.31 (m, 6H), 7.26-7.18 (m, 5H), 3.55 (s, 3H), 2.72 (d, J = 0.9 Hz, 1H), 0.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 136.5, 136.4, 136.2, 134.7, 130.6, 129.4, 129.1, 128.4, 127.91, 127.88, 51.9, 16.2, -3.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{24}H_{24}O_2NaSi$, 395.1438; found 395.1444.



3b

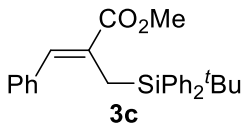
methyl (*Z*)-2-((dimethyl(phenyl)silyl)methyl)-3-phenylacrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 43.5 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.48-7.46 (m, 2H), 7.34-7.33 (m, 3H), 7.30-7.26 (m, 4H), 3.70 (s, 3H), 2.41 (s, 2H), 0.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 138.7, 136.4, 135.8, 133.7, 131.0, 129.20, 129.15, 128.4, 127.9, 127.8, 52.0, 17.6, -2.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{19}H_{22}O_2NaSi$, 333.1281; found 333.1280.



3c

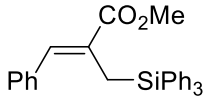
methyl (*Z*)-2-((tert-butyldiphenylsilyl)methyl)-3-phenylacrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 70.5 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 4H), 7.32 (s, 1H), 7.28-7.23 (m, 2H), 7.19-7.15 (m, 7H), 7.12-7.09 (m, 2H), 3.20 (s, 3H), 2.63 (d, J = 1.1 Hz, 2H), 0.94 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 136.54, 136.49, 136.2, 134.1, 131.7, 129.07, 129.03, 128.4, 127.7, 127.3, 51.5, 27.6, 18.7, 11.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{27}H_{30}O_2NaSi$, 437.1907; found 437.1909.



3d

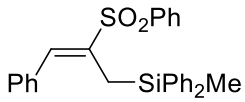
methyl (*Z*)-3-phenyl-2-((triphenylsilyl)methyl)acrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 86.4 mg, 99% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40-7.38 (m, 6H), 7.32-7.21 (m, 9H), 7.11-7.00 (m, 5H), 3.20 (s, 3H), 2.85 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 136.7, 136.1, 134.4, 130.9, 129.6, 129.1, 128.4, 127.9, 51.6, 15.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{29}H_{26}O_2NaSi$, 457.1594; found 457.1599.



3e

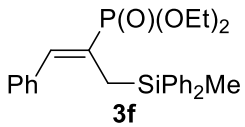
(*E*)-methyldiphenyl(3-phenyl-2-(phenylsulfonyl)allyl)silane

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 72.6 mg, 80% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 8.3, 1.3 Hz, 2H), 7.69 (s, 1H), 7.63-7.55 (m, 2H), 7.48-7.46 (m, 5H), 7.42-7.30 (m, 6H), 7.24-7.11 (m, 5H), 2.53 (s, 2H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.2, 136.6, 135.4, 134.7, 134.07, 133.97, 133.3, 130.0, 129.5, 129.3, 129.2, 129.0, 128.6, 128.4, 128.04, 127.95, 16.1, -3.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{28}H_{26}O_2NaSSi$, 477.1315; found 477.1317.



3f

diethyl (*E*)-(3-(methyldiphenylsilyl)-1-phenylprop-1-en-2-yl)phosphonate

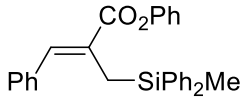
The crude product was purified by column chromatography (SiO_2, PE:EA 5:1 to 2:1). Colorless oil. 49.0 mg, 54% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 4H), 7.41 (s, 1H), 7.37-7.28 (m, 6H), 7.25-7.19 (m, 5H), 3.98-3.94 (m, 4H), 2.67 (dd, J = 21.2, 1.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H), 0.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (d, J = 11.9 Hz), 137.3, 136.1(d, J = 23.9 Hz), 134.6, 129.5, 129.2, 129.1 (d, J = 1.7 Hz), 128.4, 128.0, 127.8, 61.8 (d, J = 6.0 Hz), 16.32 (d, J = 6.3 Hz), 16.30 (d, J = 9.5 Hz), -3.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.06.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{26}H_{31}O_3NaPSi$, 473.1672; found 473.1674.



3g

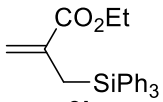
phenyl (*Z*)-2-((methyldiphenylsilyl)methyl)-3-phenylacrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 79.4 mg, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 (dd, J = 7.9, 1.6 Hz, 4H), 7.32-7.22 (m, 9H), 7.15-7.12 (m, 5H), 6.76 (d, J = 7.6 Hz, 2H), 2.74 (s, 2H), 0.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 151.1, 137.9, 136.4, 136.0, 134.9, 130.4, 129.5, 129.4, 129.3, 128.5, 128.3, 128.0, 125.8, 121.8, 16.3, -3.3.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{29}H_{27}O_2Si$, 457.1594; found 457.1594.



3h

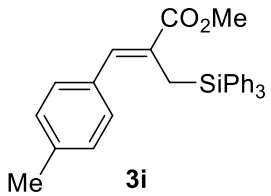
ethyl 2-((triphenylsilyl)methyl)acrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 53.6 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 6H), 7.44-7.35 (m, 9H), 6.01 (s, 1H), 5.30 (s, 1H), 3.72 (q, J = 7.0 Hz, 2H), 2.74 (s, 2H), 1.06 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 167.4, 137.3, 136.0, 134.2, 129.7, 127.9, 123.8, 60.7, 18.4, 14.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{24}H_{24}O_2NaSi$, 395.1438; found 395.1441.



3i

methyl (*Z*)-3-(*p*-tolyl)-2-((triphenylsilyl)methyl)acrylate

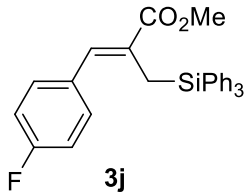
The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 79.9

mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 7H), 7.41-7.39 (m, 3H), 7.36-7.32 (m, 6H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 3.31 (s, 3H), 2.95 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 138.0, 136.8, 136.1, 134.5, 133.2, 130.0, 129.6, 129.2, 129.1, 127.9, 51.6, 21.4, 15.7.

HRMS (ESI-TOF) m/z: $[M + K]^+$ calculated for $C_{30}H_{28}O_2KSi$, 487.1490; found 487.1487.



3j

methyl (*Z*)-3-(4-fluorophenyl)-2-((triphenylsilyl)methyl)acrylate

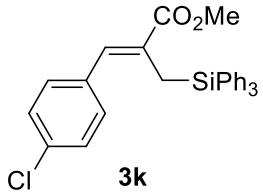
The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 68.9 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.49 (m, 7H), 7.44-7.40 (m, 3H), 7.37-7.33 (m, 6H), 7.07 (dd, *J* = 8.4, 5.5 Hz, 2H), 6.83 (dd, $J_1 = J_2$ = 8.5 Hz, 2H), 3.31 (s, 3H), 2.91 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 163.3 (d, *J* = 247.8 Hz), 136.1, 135.5, 134.2, 132.1 (d, *J* = 3.2 Hz), 130.9 (d, *J* = 8.3 Hz), 130.8, 129.7, 127.9, 115.4 (d, *J* = 21.4 Hz), 51.7, 15.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{29}H_{25}O_2FNaSi$, 475.1500; found 475.1513.



3k

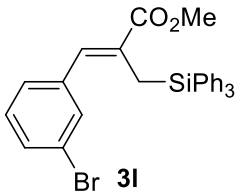
methyl (*Z*)-3-(4-chlorophenyl)-2-((triphenylsilyl)methyl)acrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 69.0 mg, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 7H), 7.44-7.40 (m, 3H), 7.39-7.32 (m, 6H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.32 (s, 3H), 2.92 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 136.0, 135.3, 134.5, 134.1, 133.7, 131.5, 130.4, 129.8, 128.6, 128.0, 51.7, 15.9.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{29}H_{25}ClO_2NaSi$, 491.1205; found 491.1201.



3l

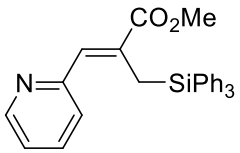
methyl (*Z*)-3-(3-bromophenyl)-2-((triphenylsilyl)methyl)acrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 60.7 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.38 (m, 10H), 7.35-7.31 (m, 7H), 7.22 (s, 1H), 7.01-6.99 (m, 2H), 3.31 (s, 3H), 2.92 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.3, 136.0, 135.0, 134.0, 132.3, 131.6, 130.8, 129.9, 129.7, 128.0, 127.5, 122.6, 51.8, 15.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{29}H_{25}BrO_2NaSi$, 535.0699; found 535.0701.



3m

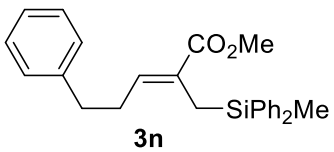
methyl (*Z*)-2-((dimethyl(phenyl)silyl)methyl)-3-(pyridin-2-yl)acrylate

The crude product was purified by column chromatography (SiO_2, PE:EA 40:1 to 20:1). White solid, mp 96-98 °C (PE:EA). 77.5 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 5.4, 2.0 Hz, 1H), 7.47-7.36 (m, 7H), 7.29-7.22 (m, 4H), 7.22-7.16 (m, 6H), 6.94-6.92 (m, 2H), 3.59 (s, 3H), 3.32 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 155.4, 148.9, 136.1, 136.0, 134.9, 134.6, 133.4, 129.3, 127.5, 126.1, 122.1, 51.8, 16.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{28}H_{25}NO_2Si$, 436.1727; found 436.1725.



3n

methyl (*Z*)-2-((methyldiphenylsilyl)methyl)-5-phenylpent-2-enoate

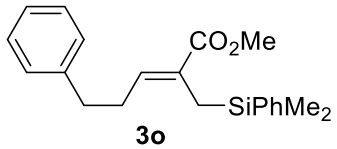
The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 51.0 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 4H), 7.48-7.42 (m, 7H), 7.37-7.33 (m, 2H), 7.19-7.16 (m, 1H), 7.12 (d, J = 7.6 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 3.61 (s, 3H), 2.62 (t, J = 7.8 Hz, 2H),

2.45 (s, 2H), 2.23 (td, J = 7.8, 7.7 Hz, 2H), 0.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 141.4, 139.1, 136.6, 134.8, 129.5, 129.4, 128.5, 128.4, 127.9, 126.1, 51.6, 34.8, 30.8, 15.8, -4.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{26}H_{28}O_2NaSi$, 423.1751; found 423.1751.



3o

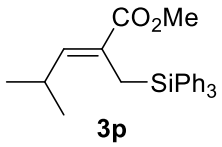
methyl (*Z*)-2-((dimethyl(phenyl)silyl)methyl)-5-phenylpent-2-enoate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 44.0 mg, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.36-7.34 (m, 3H), 7.30-7.28 (m, 2H), 7.22-7.20 (m, 1H), 7.11-7.09 (m, 2H), 6.65 (t, J = 7.2 Hz, 1H), 3.62 (s, 3H), 2.61 (t, J = 7.9 Hz, 2H), 2.23 (td, J = 7.9, 7.2 Hz, 2H), 2.01 (s, 2H), 0.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.5, 138.8, 138.4, 133.7, 129.9, 129.2, 128.5, 128.4, 127.9, 126.1, 51.7, 34.9, 30.9, 17.3, -2.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{21}H_{26}O_2NaSi$, 361.1594; found 361.1591.



3p

methyl (Z)-4-methyl-2-((triphenylsilyl)methyl)pent-2-enoate

The crude product was purified by column chromatography (SiO_2, PE:EA 20:1). Colorless oil. 54.0 mg, 67% yield.

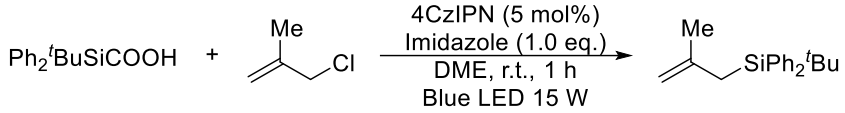
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 6H), 7.25-7.34 (m, 9H), 6.31 (d, J = 10.2 Hz, 1H), 3.16 (s, 3H), 2.57 (s, 2H), 2.29-2.22 (m, 1H), 0.62 (d, J = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 147.0, 136.1, 134.4, 129.6, 127.8, 126.5, 51.3, 28.5, 21.8, 14.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{26}H_{28}O_2NaSi$, 423.1751; found 423.1755.

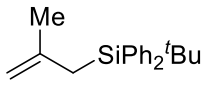
Synthesis of allylsilanes 5

Typical procedure for the synthesis of 5a



2c **4a** **5a**

A 10 mL tube equipped with a magnetic stirrer bar was charged sequentially with $Ph_2{}^tBuSiCOOH$ (0.2 mmol, 1.0 equiv.), imidazole (0.2 mmol, 1.0 equiv.) and 4CzIPN (7.9 mg, 5 mol%), evacuated and refilled with N_2. DME (2 mL) and allyl chloride (0.24 mmol, 1.2 equiv.) were sequentially added and the solution was stirred under irradiation with 15 W blue LED at room temperature for 1 h. Upon completion, solvent was removed under vacuum and the residue was purified by SiO_2 column chromatography to afford the desired product **5a**.



5a

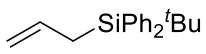
***tert*-butyl(2-methylallyl)diphenylsilane**

The crude product was purified by column chromatography (SiO_2, PE). Colorless oil. 54.2 mg, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 4H), 7.44-7.35 (m, 6H), 4.61 (s, 1H), 4.59 (s, 1H), 2.25 (s, 2H), 1.42 (s, 3H), 1.11 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.3, 135.0, 129.2, 127.5, 110.9, 27.9, 25.6, 22.3, 18.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{20}H_{26}NaSi$, 317.1696; found 317.1696.



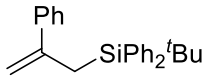
5b

allyl(*tert*-butyl)diphenylsilane

The crude product was purified by column chromatography (SiO_2, PE). Colorless oil. 44.8 mg, 80% yield. The spectra were in accordance with the reported literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 4H), 7.43-7.34 (m, 6H), 5.82-5.75 (m, 1H), 4.92 (ddt, J = 16.6, 3.5, 1.7 Hz, 1H), 4.82 (ddt, J = 10.0 Hz, 3.3, 1.1 Hz, 1H), 2.21 (dt, J = 7.9, 1.4 Hz, 2H), 1.08 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 134.8, 134.5, 129.2, 127.7, 114.6, 28.0, 18.9, 18.6.



5c

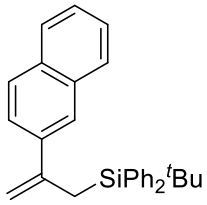
***tert*-butyldiphenyl(2-phenylallyl)silane**

The crude product was purified by column chromatography (SiO_2, PE). Colorless oil. 53.4 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.39-7.35 (m, 2H), 7.31-7.29 (m, 4H), 7.22-7.15 (m, 5H), 5.04 (d, J = 1.4 Hz, 1H), 4.83 (td, $J_1 = J_2$ = 1.4 Hz, 1H), 2.67 (d, J = 1.4 Hz, 2H), 1.08 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 143.5, 136.4, 134.4, 129.0, 128.0, 127.4, 127.0, 126.5, 113.5, 28.0, 19.1, 18.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{25}H_{29}Si$, 357.2033; found 357.2027.



5d

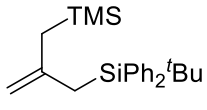
***tert*-butyl(2-(naphthalen-2-yl)allyl)diphenylsilane**

The crude product was purified by column chromatography (SiO_2, PE to PE:EA = 100:1). Colorless oil. 49.8 mg, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 1H), 7.68-7.54 (m, 7H), 7.45-7.22 (m, 9H), 5.20 (s, 1H), 4.97 (s, 1H), 2.79 (s, 2H), 1.09 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 140.5, 136.4, 134.4, 133.2, 132.6, 129.0, 128.3, 127.42, 127.35, 125.8, 125.6, 125.3, 125.1, 113.9, 28.0, 19.3, 18.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{29}H_{31}Si$, 407.2190; found 407.2175.



5e

***tert*-butyldiphenyl(2-((trimethylsilyl)methyl)allyl)silane**

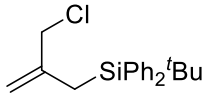
The crude product was purified by column chromatography (SiO_2, PE). Colorless oil. 70.5 mg, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 4H), 7.39-7.32 (m, 6H), 4.47 (s, 1H), 4.34 (s, 1H), 2.14

(s, 2H), 1.16 (s 2H), 1.08 (s, 9H), 0.08 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.2, 129.1, 127.5, 114.0, 108.1, 29.2, 27.9, 23.0, 18.7, -1.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{23}H_{34}NaSi_2$, 389.2091; found 389.2092.



5f

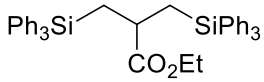
***tert*-butyl(2-(chloromethyl)allyl)diphenylsilane**

The crude product was purified by column chromatography (SiO_2, PE). Colorless oil. 43.6 mg, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4H), 7.42-7.35 (m, 6H), 4.93 (d, J = 1.2 Hz, 1H), 4.77 (d, J = 1.2 Hz, 1H), 3.55 (d, J = 0.9 Hz, 2H), 2.35 (d, J = 1.1 Hz, 2H), 1.09 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.3, 134.0, 129.5, 127.7, 115.4, 50.4, 27.9, 18.6, 16.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{20}H_{26}ClSi$, 330.1565; found 330.1558.



6

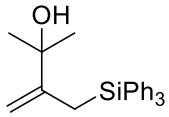
ethyl 3-(triphenylsilyl)-2-((triphenylsilyl)methyl)propanoate

Under nitrogen atmosphere, a 10 mL tube equipped with a magnetic stirrer bar was charged sequentially with ethyl 2-(acetoxymethyl)acrylate (31.6 mg, 0.2 mmol, 1.0 equiv.), $Ph_3SiCOOH$ (152.2 mg, 0.5 mmol, 2.5 equiv.), and 4CzIPN (8.0 mg, 0.01 mmol, 5 mol%). Then MeCN (0.1 M, 2 mL) was injected into the reaction tube. The solution was stirred under irradiation with 15 W blue LED at room temperature for 12 h. Upon completion, solvent was removed under vacuum and the residue was purified by column chromatography to afford the desired product **3a** (SiO_2, PE:EA 40:1 to 20:1). White solid, (PE:EA) mp 158-160 °C. 66.9 mg, 53% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 18H), 7.31-7.28 (m, 12H), 3.16 (q, J = 7.2 Hz, 2H), 3.04-3.00 (m, 1H), 1.85 (dd, J = 14.8, 8.8 Hz, 2H), 1.69 (dd, J = 14.8, 5.6 Hz, 2H), 0.80 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 135.9, 134.5, 129.5, 127.9, 60.1, 36.8, 21.0, 13.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{42}H_{40}O_2NaSi_2$, 655.2459; found 655.2454.



7

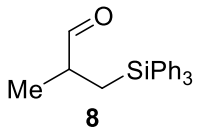
2-methyl-3-((triphenylsilyl)methyl)but-3-en-2-ol

To a solution of **3h** (0.2 mmol, 74.5 mg) in THF (2 mL) was added MeMgBr (2.5 mL, 1.0 M in THF) at 0 °C, and the mixture was stirred at room temperature for 12 h. The reaction was quenched by saturated aqueous NH_4Cl (5 mL) and extracted with EtOAc (5 mL x 2). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and evaporated. The crude product was purified by column chromatography (SiO_2, PE:EA 40:1 to 20:1). Colorless oil, 65.4 mg, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 6H), 7.45-7.31 (m, 9H), 4.91 (s, 1H), 4.70 (s, 1H), 2.51 (s, 2H), 1.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 136.4, 135.1, 129.8, 128.0, 109.3, 73.5, 28.9, 17.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{24}H_{26}ONaSi$, 381.1645; found 381.1641.



8

2-methyl-3-(triphenylsilyl)propanal

To a solution of $LiAlH_4$ (0.24 mmol, 7.6 mg) in THF (2 mL) was added **3h** (0.2 mmol, 74.5 mg) at 0 °C, and the mixture was stirred at room temperature for 12 h. H_2O (5 mL) and EtOAc (5 mL) were added and the organic layer was separated, dried ($MgSO_4$), filtered and evaporated. The crude product was purified by column chromatography (SiO_2, PE:EA 40:1 to 20:1). White solid, mp 55-57 °C (PE:EA). 55.4 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) 9.51 (d, J = 1.4 Hz, 1H), 7.77-7.49 (m, 6H), 7.46-7.31 (m, 9H), 2.57-2.52 (m, 1H), 1.95 (dd, J = 15.1, 4.9 Hz, 1H), 1.30 (dd, J = 15.0, 8.8 Hz, 1H), 1.02 (d, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 135.8, 134.5, 129.9, 128.2, 42.3, 16.7, 13.9.

HRMS (ESI-TOF) m/z: $[M + K]^+$ calculated for $C_{22}H_{22}OKSi$, 369.1072; found 369.1087.

Reference

(1) (a) S. D. Friis, R. H. Taaning, A. T. Lindhardt and T. Skrydstrup, Silacarboxylic Acids as Efficient Carbon Monoxide Releasing Molecules: Synthesis and Application in Palladium-Catalyzed Carbonylation Reactions, *J. Am. Chem. Soc*., 2011, **133**, 18114−18117; (b) N.-X. Xu, B.-X. Li, C. Wang and M. Uchiyama, Sila- and Germacarboxylic Acids: Precursors for the Corresponding Silyl and Germyl Radicals, *Angew. Chem., Int. Ed.,* 2020, **59**, 10639−10644.

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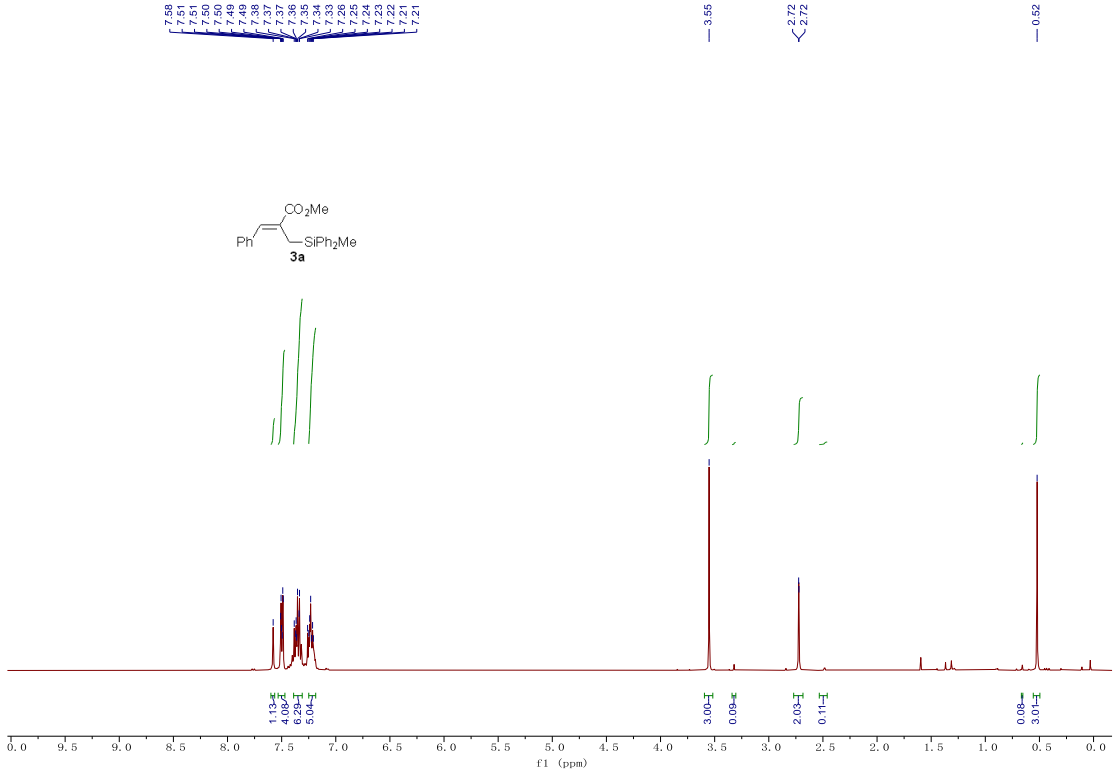
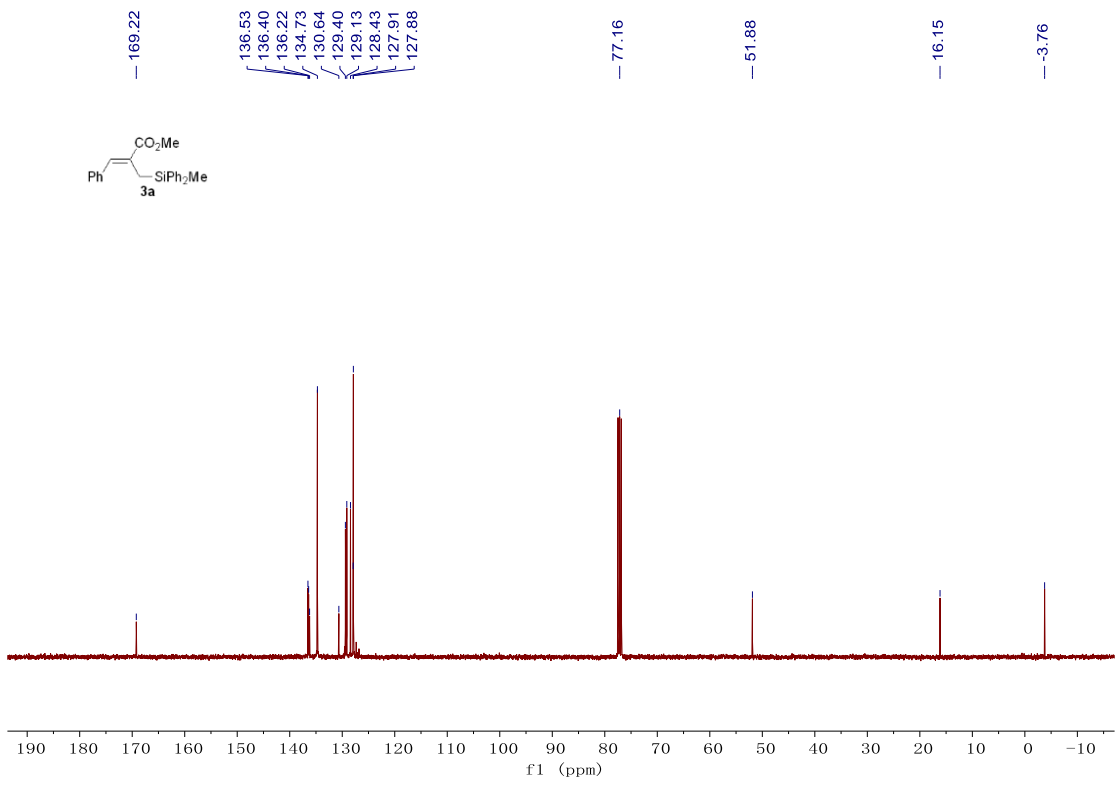
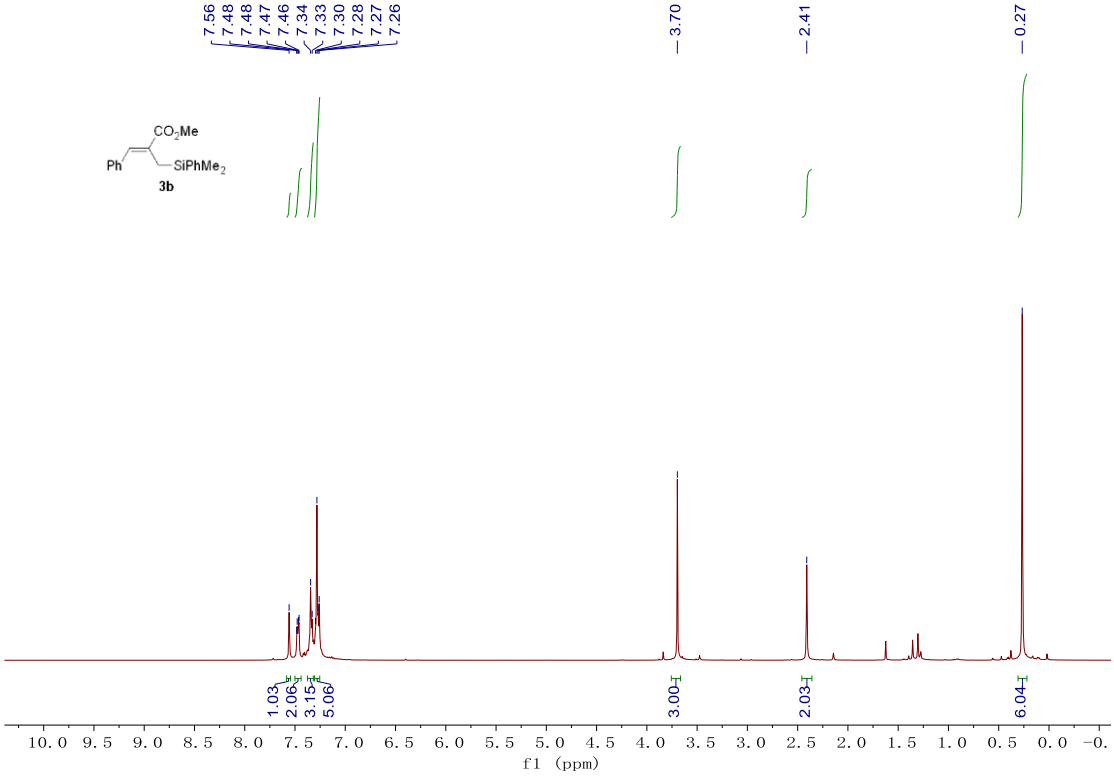
NMR Spectra of all Compounds

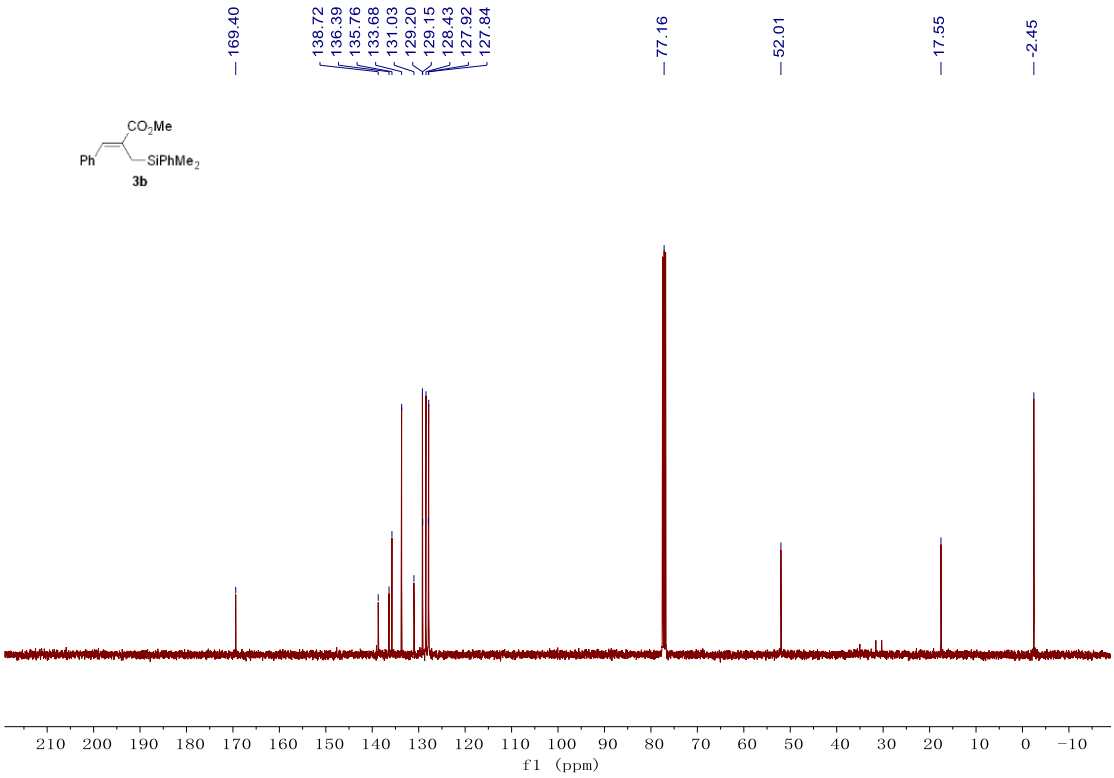
3a; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



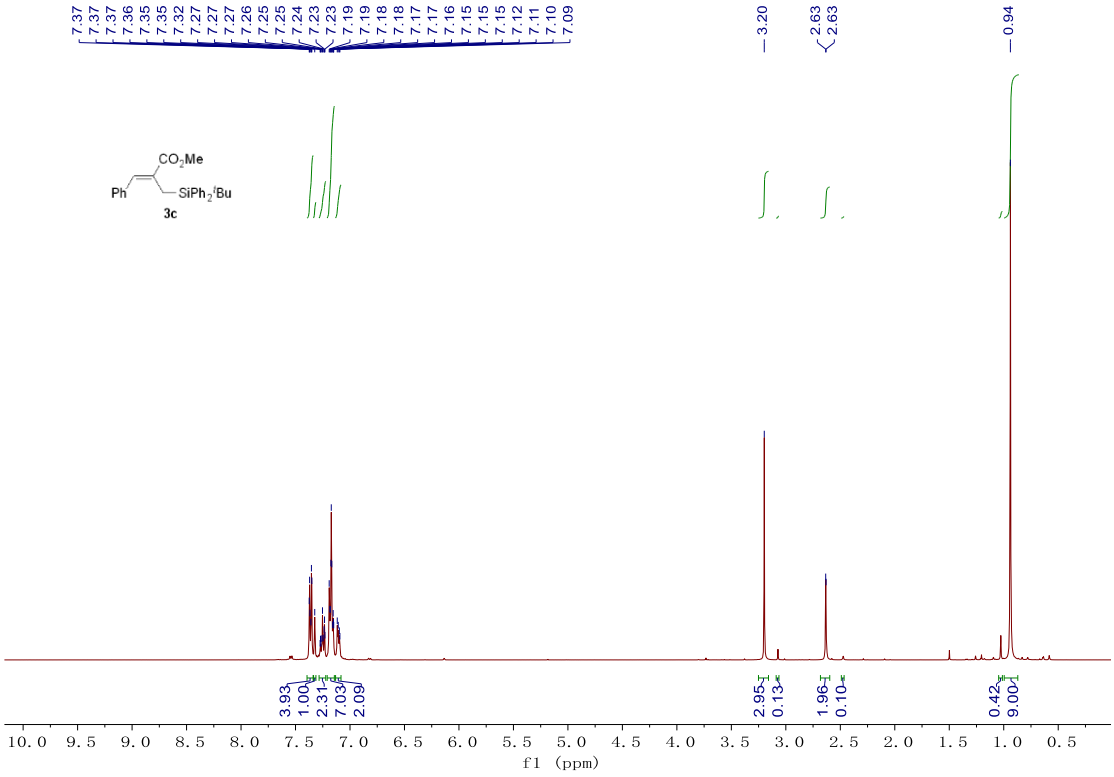


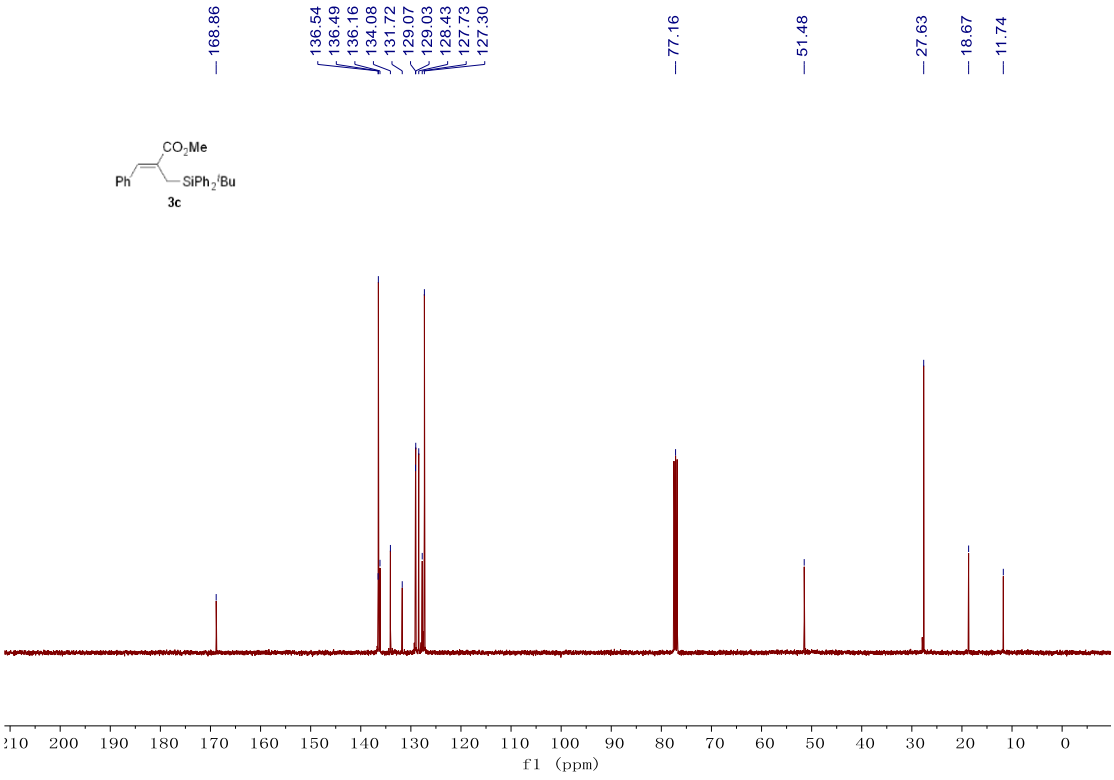
3b; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



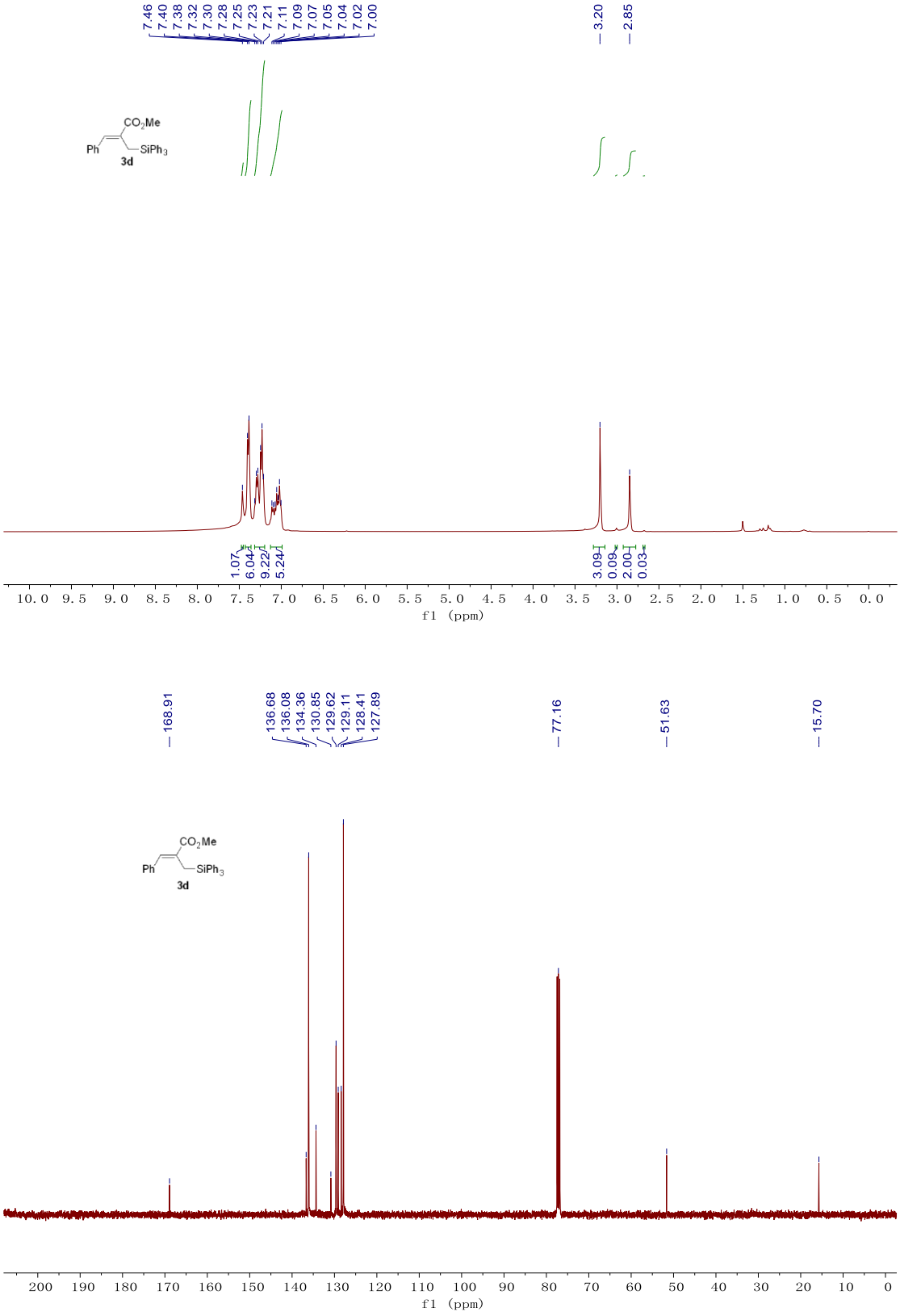


3c; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

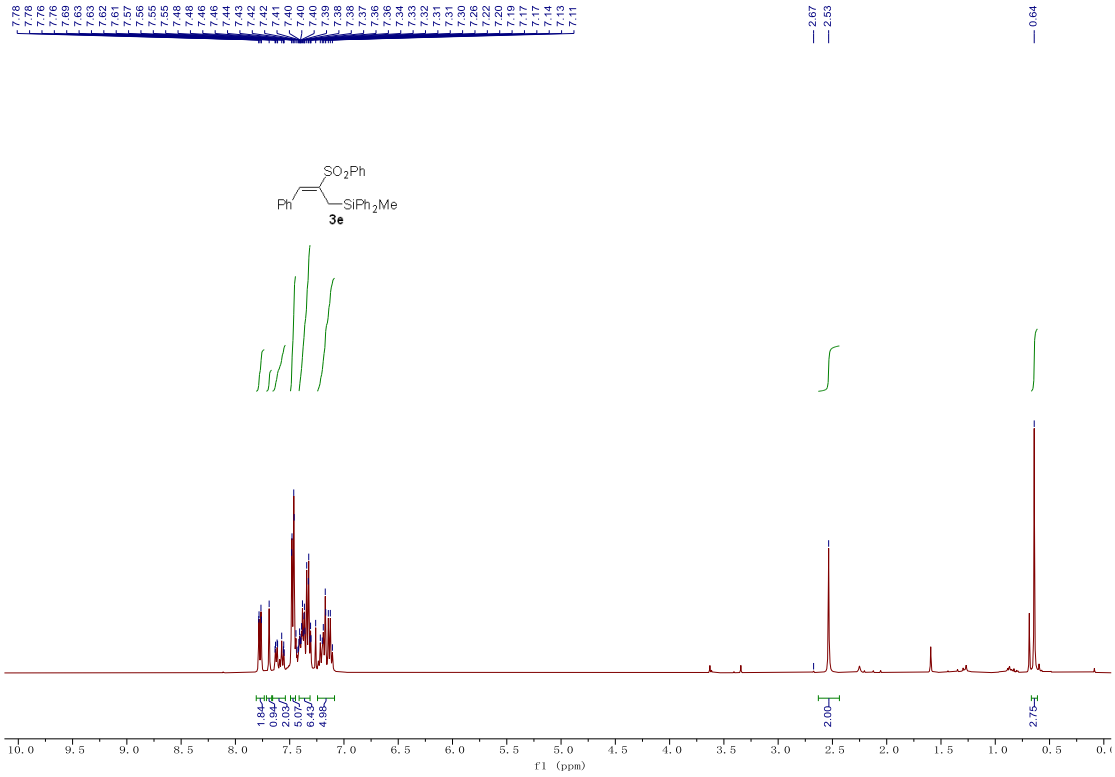


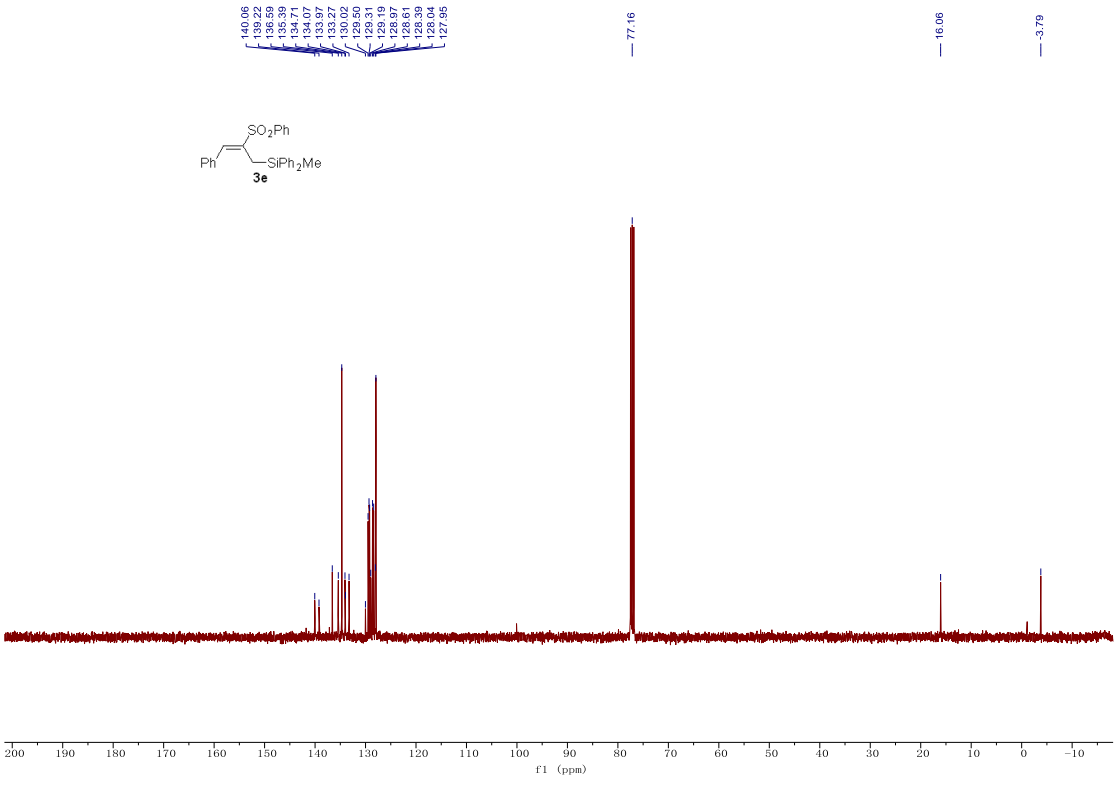


3d; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

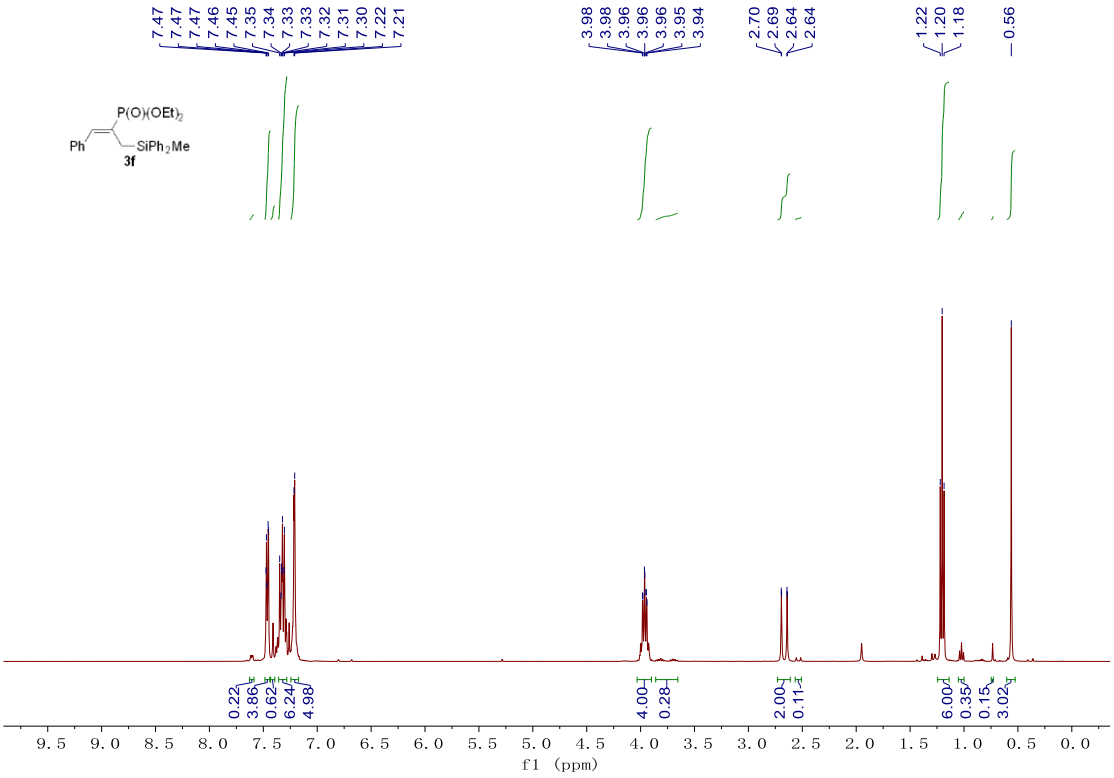


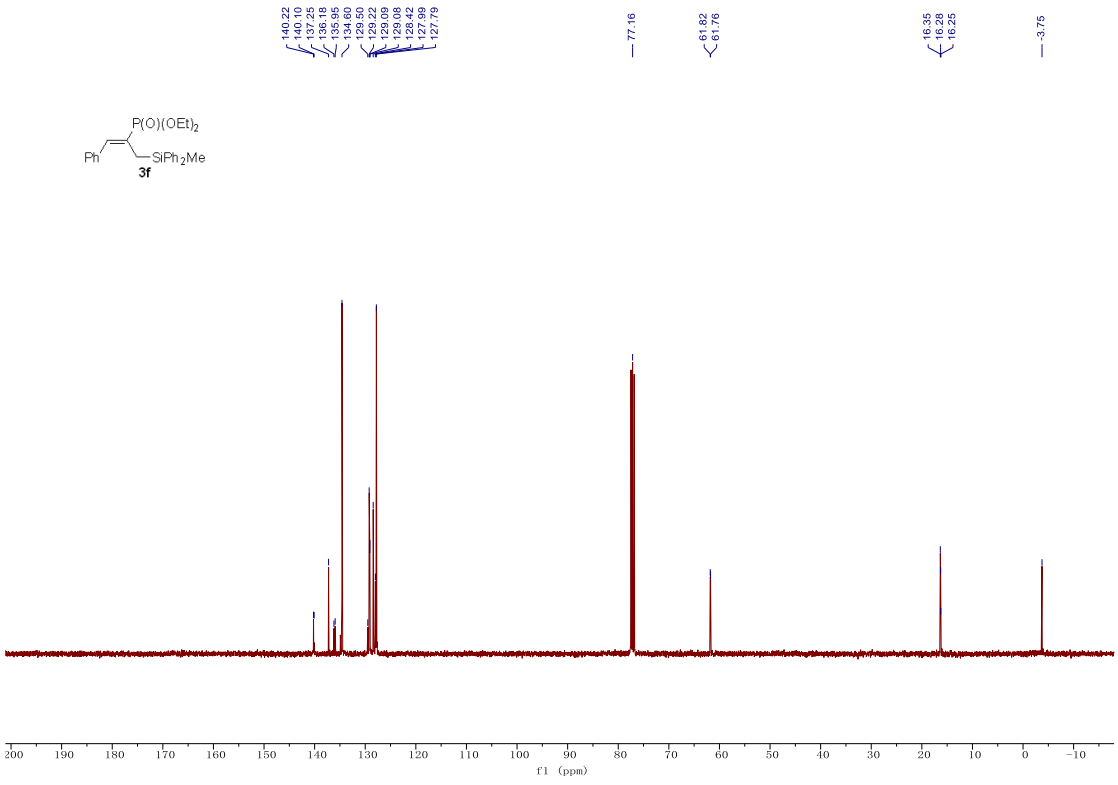
3e; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

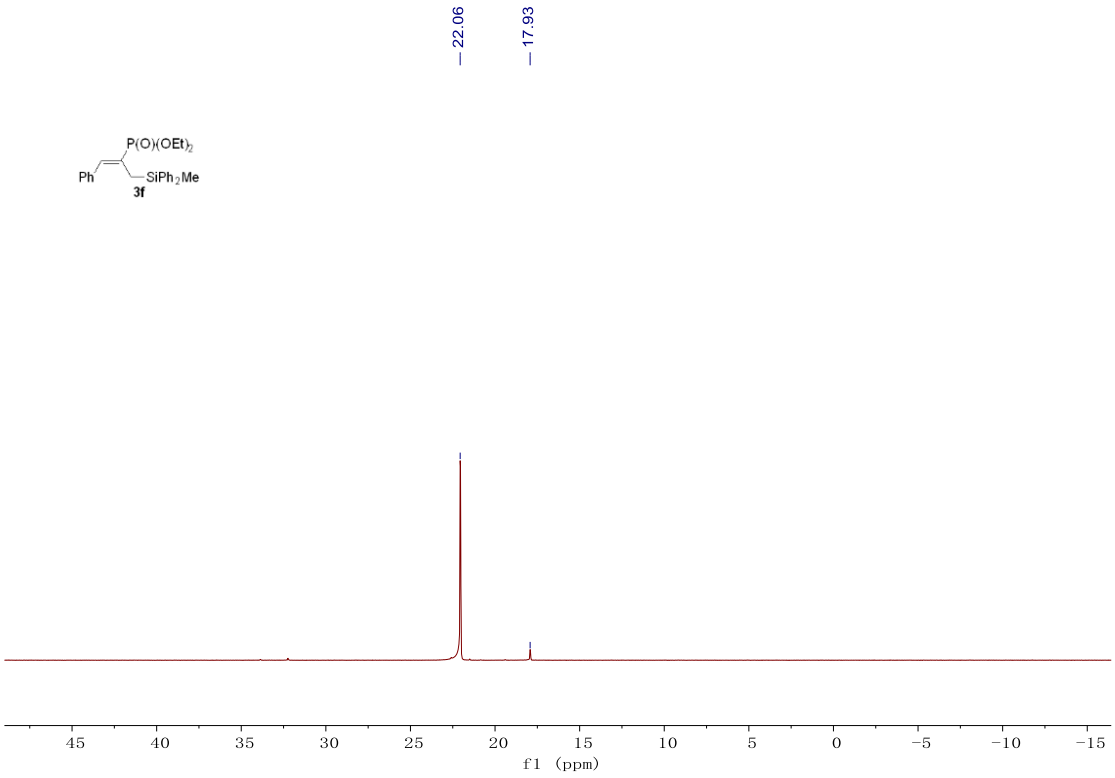




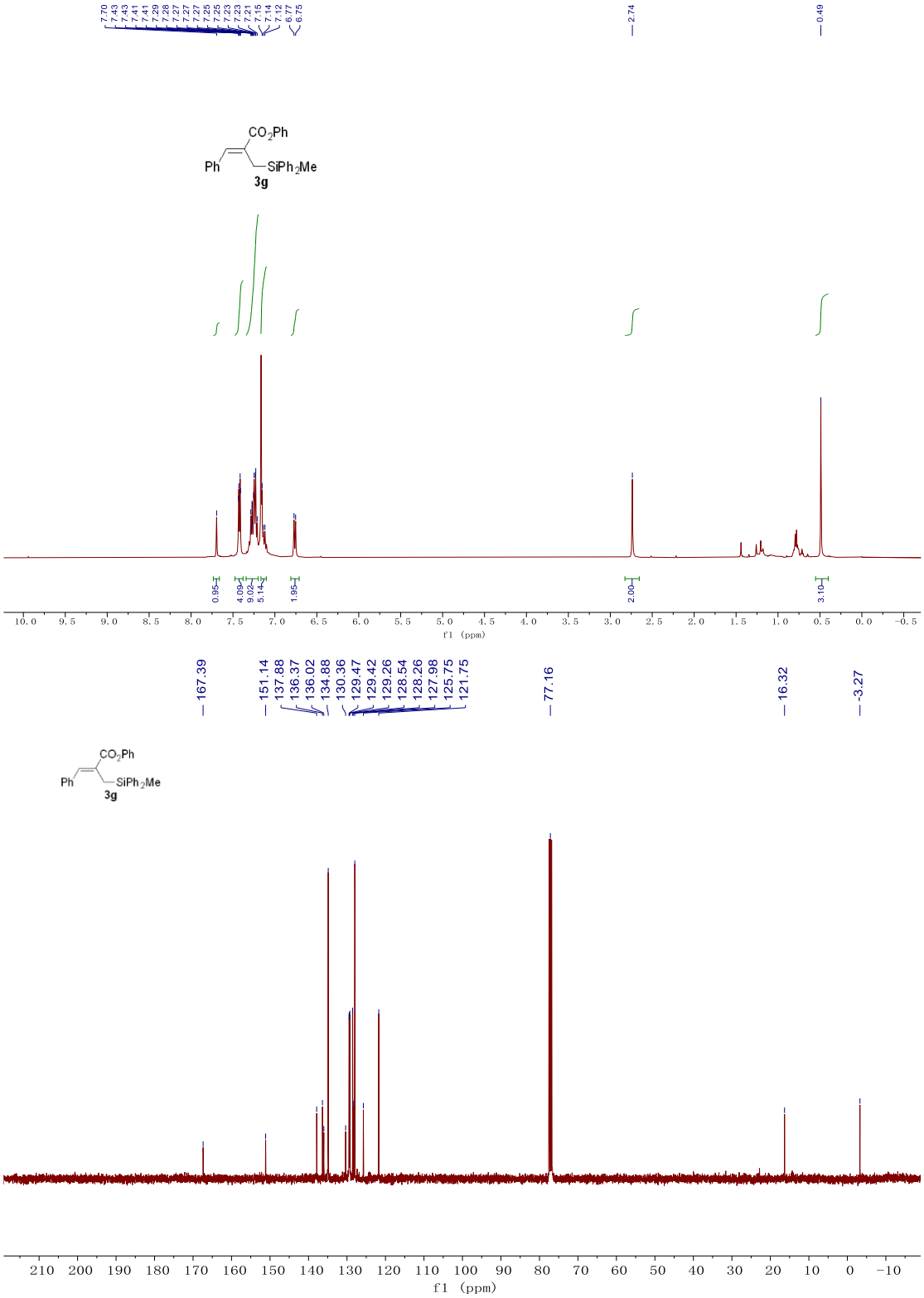
3f; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$); ^{31}P NMR (162 MHz, $CDCl_3$)



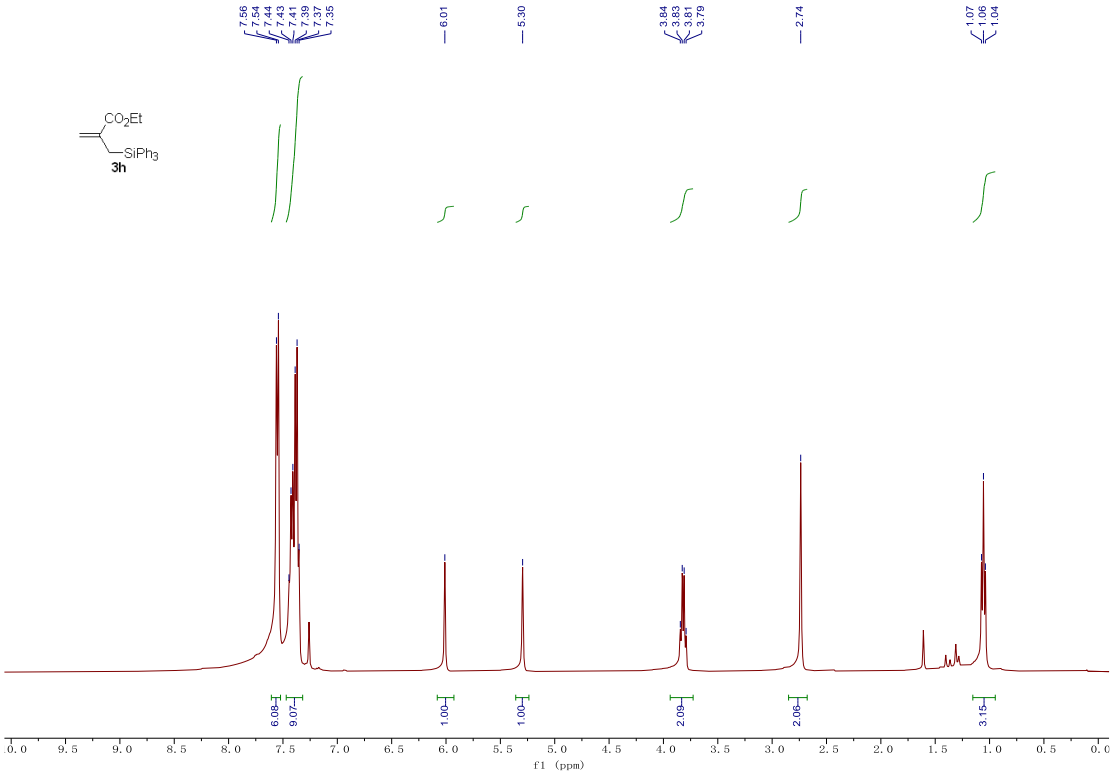


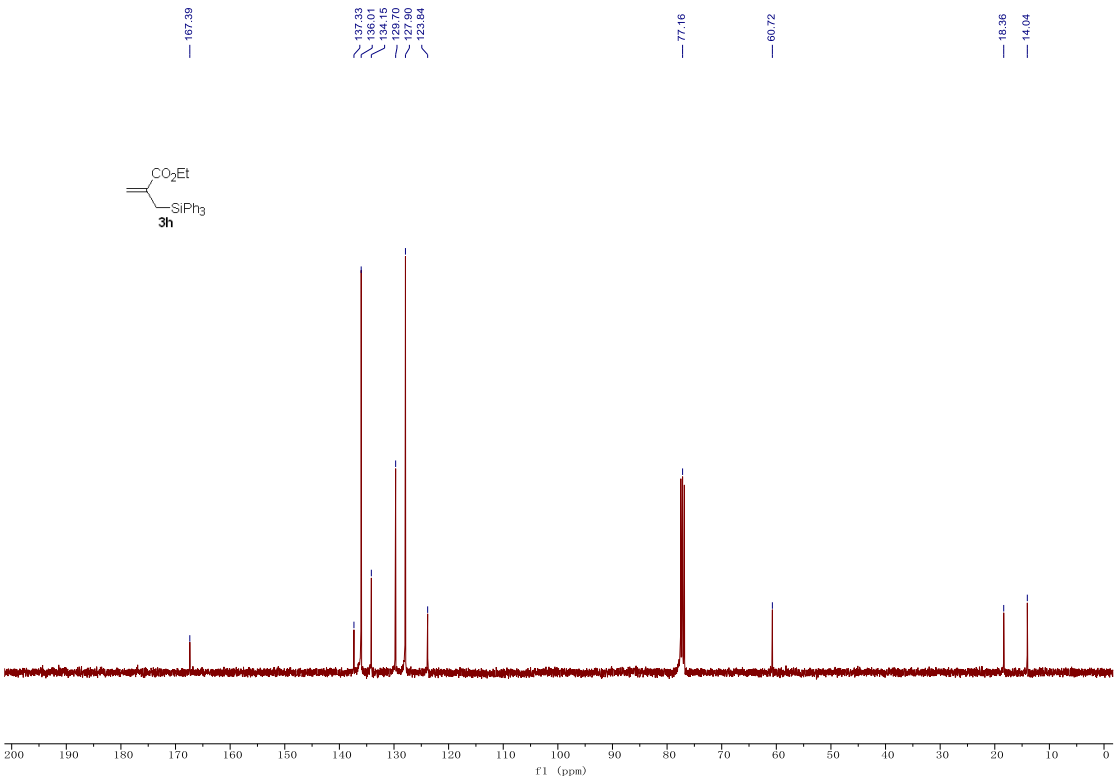

22.06
17.93
P(O)(OEt)2
Ph
SiPh2Me
3f
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
f1 (ppm)

3g; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

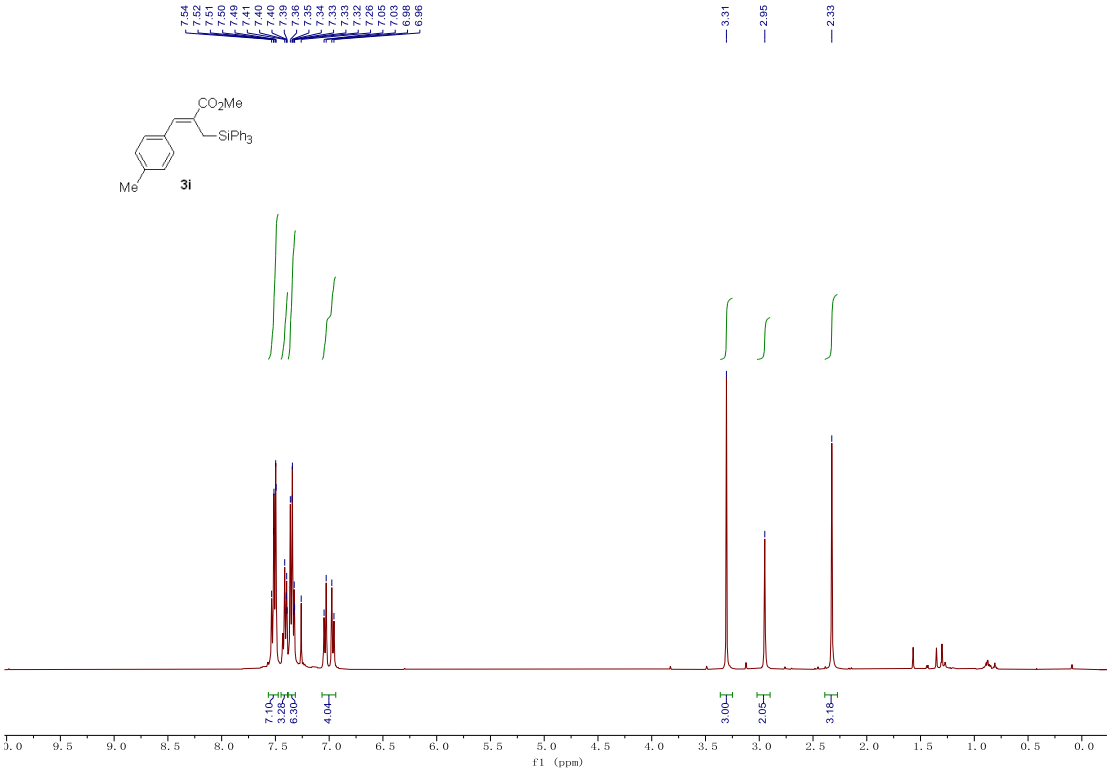


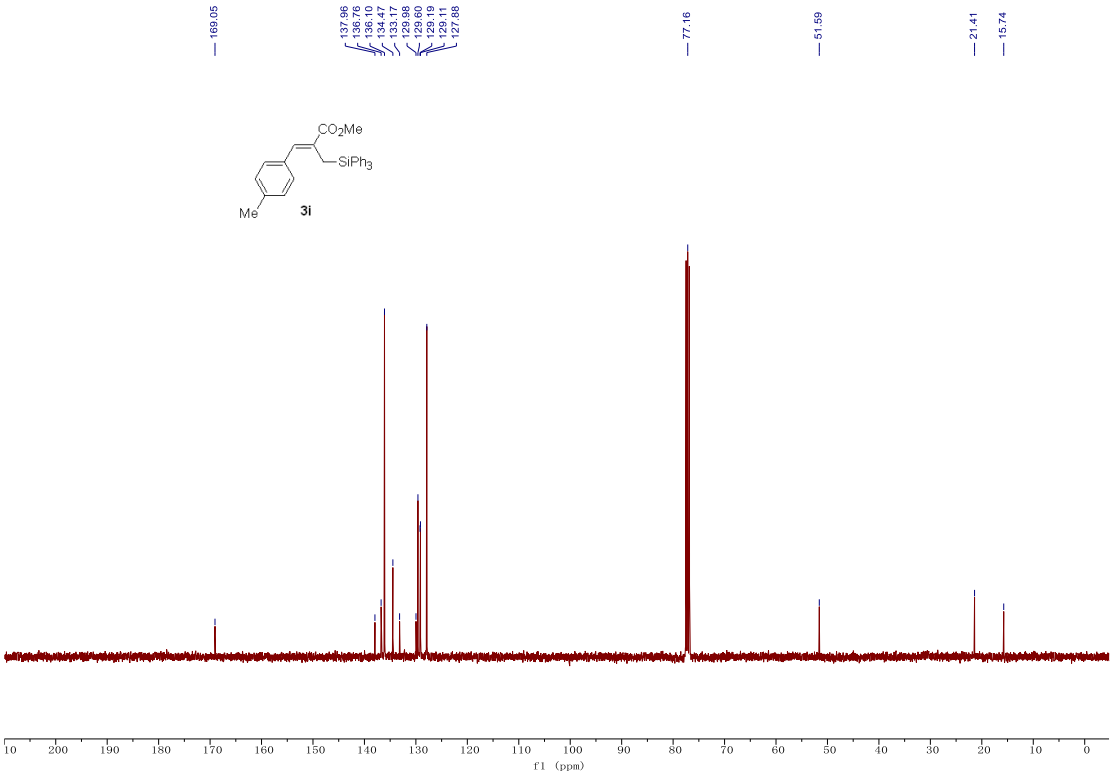
3h; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



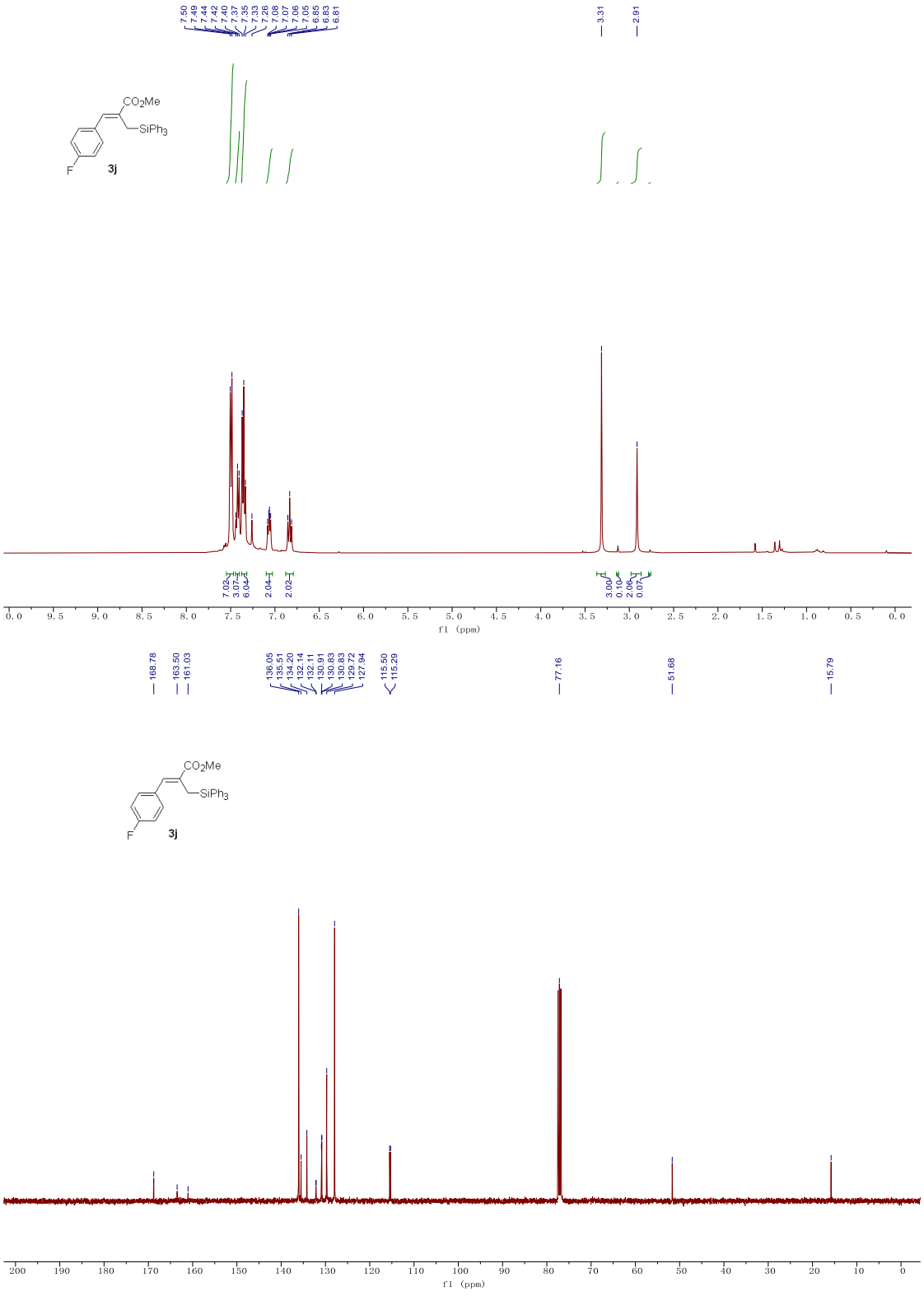


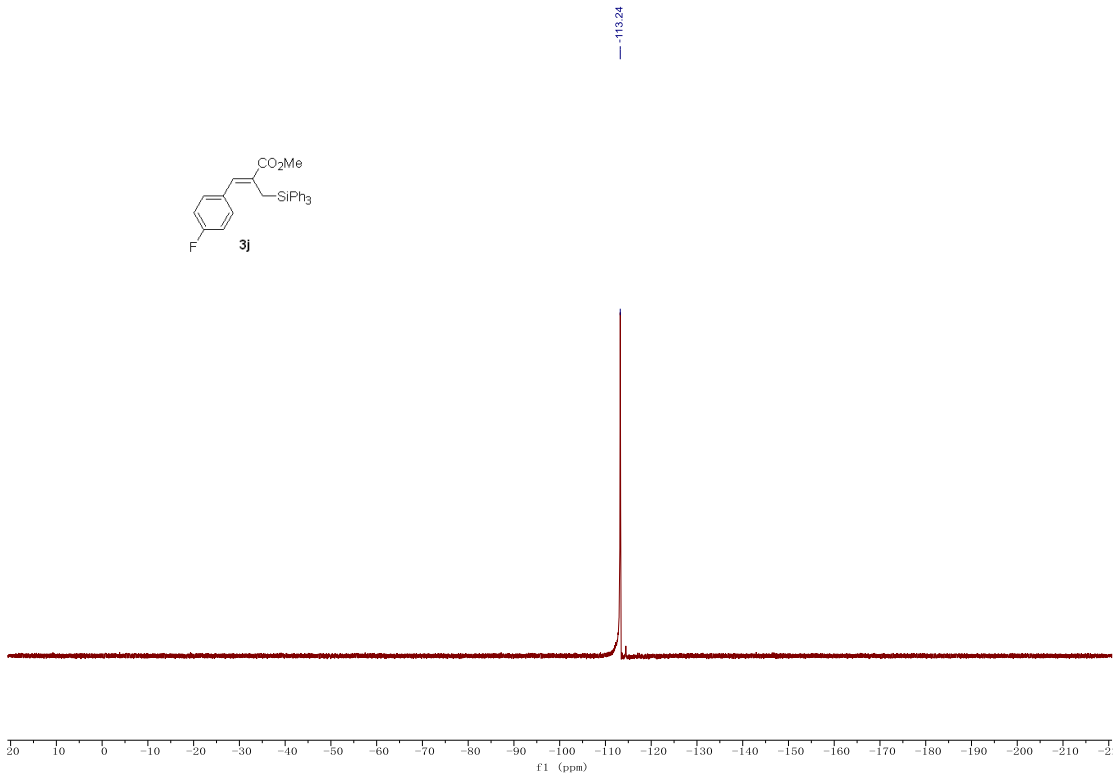
3i; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)





3j; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$); ^{19}F NMR (471 MHz, $CDCl_3$)

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F
3j
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-30
-40
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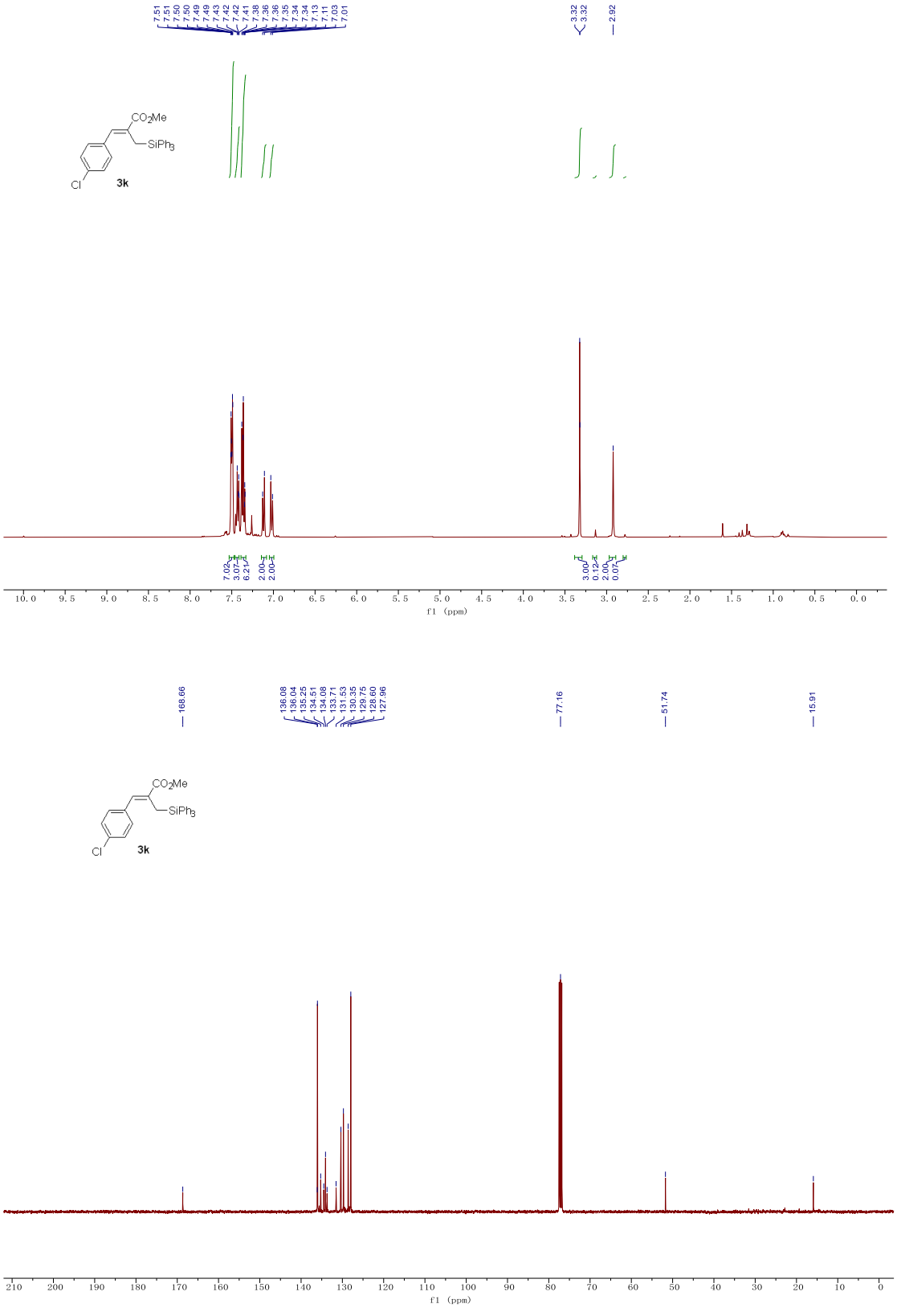
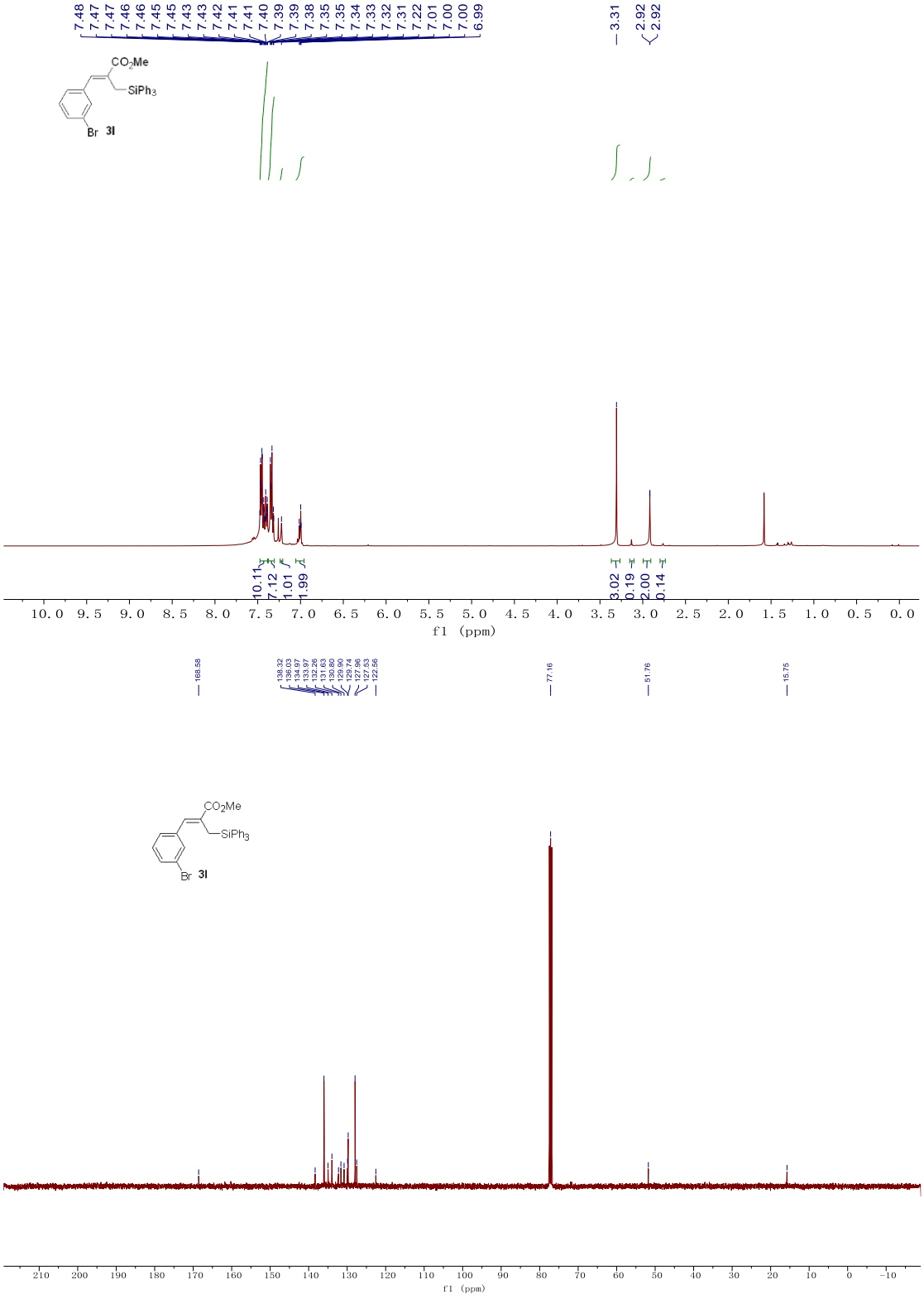
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

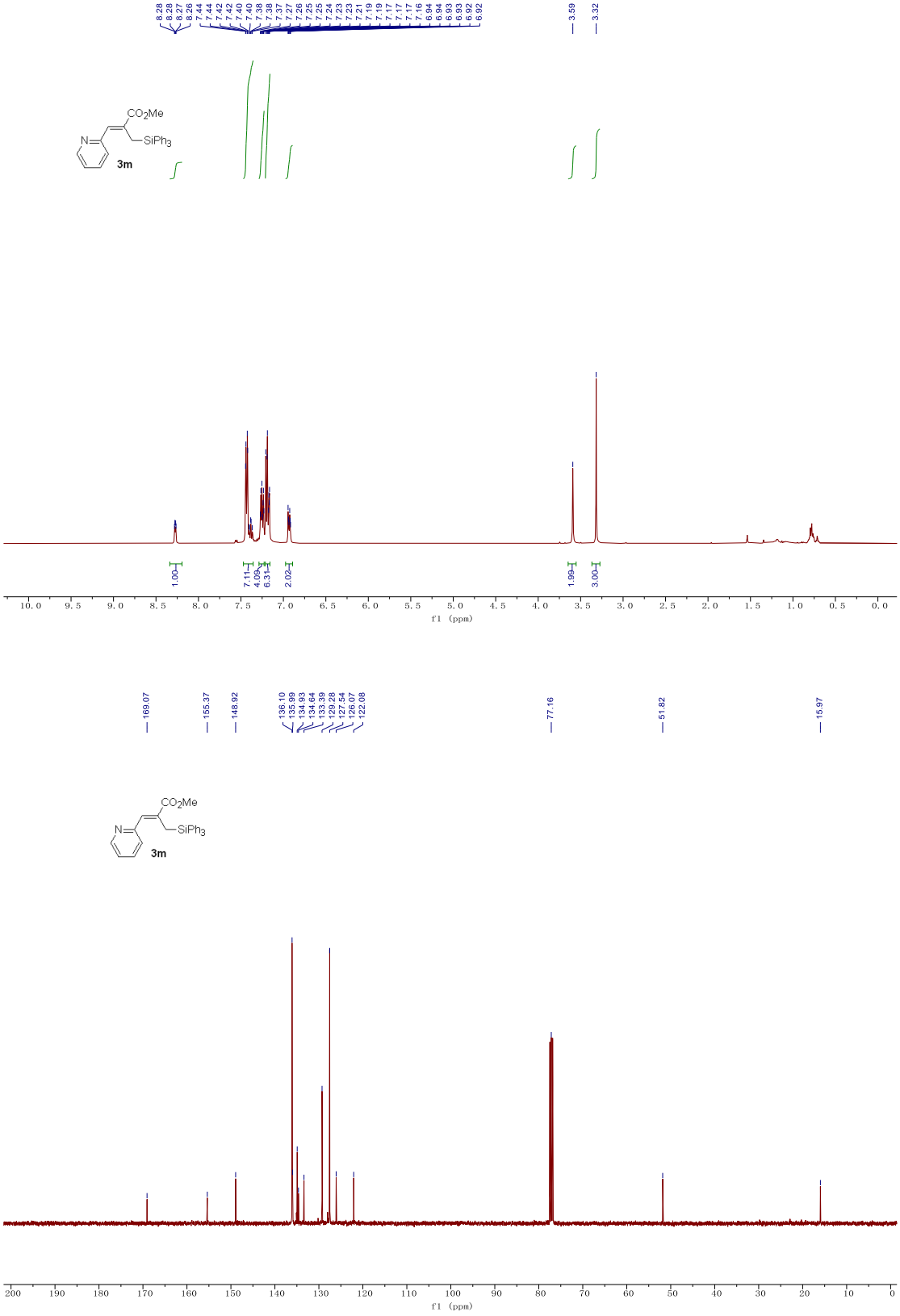
3k; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



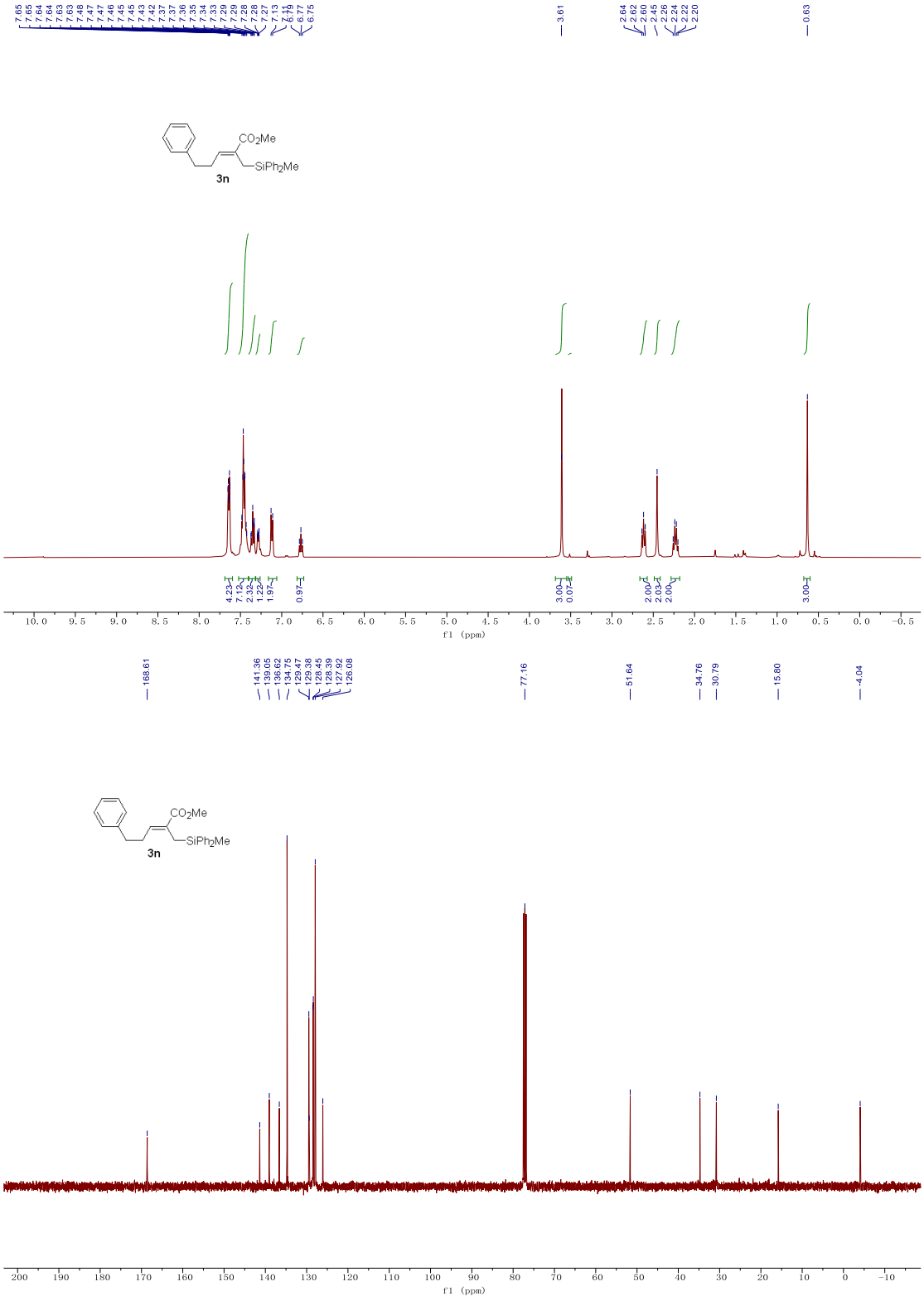
3l; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



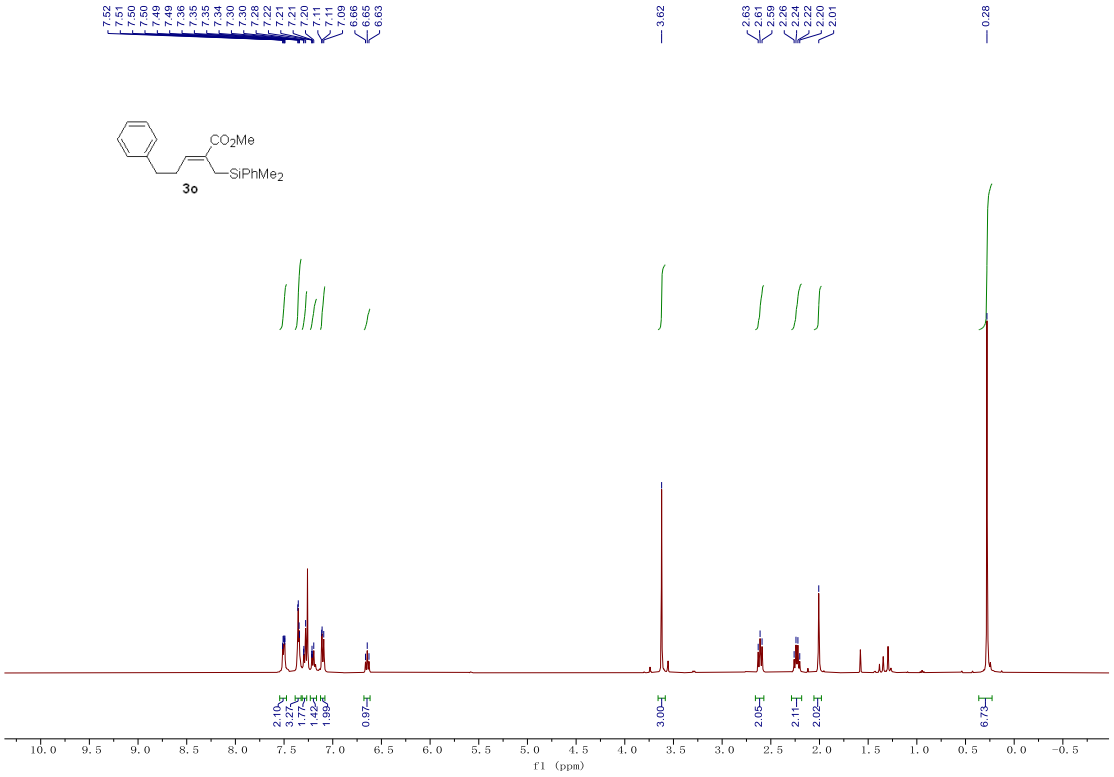
3m; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

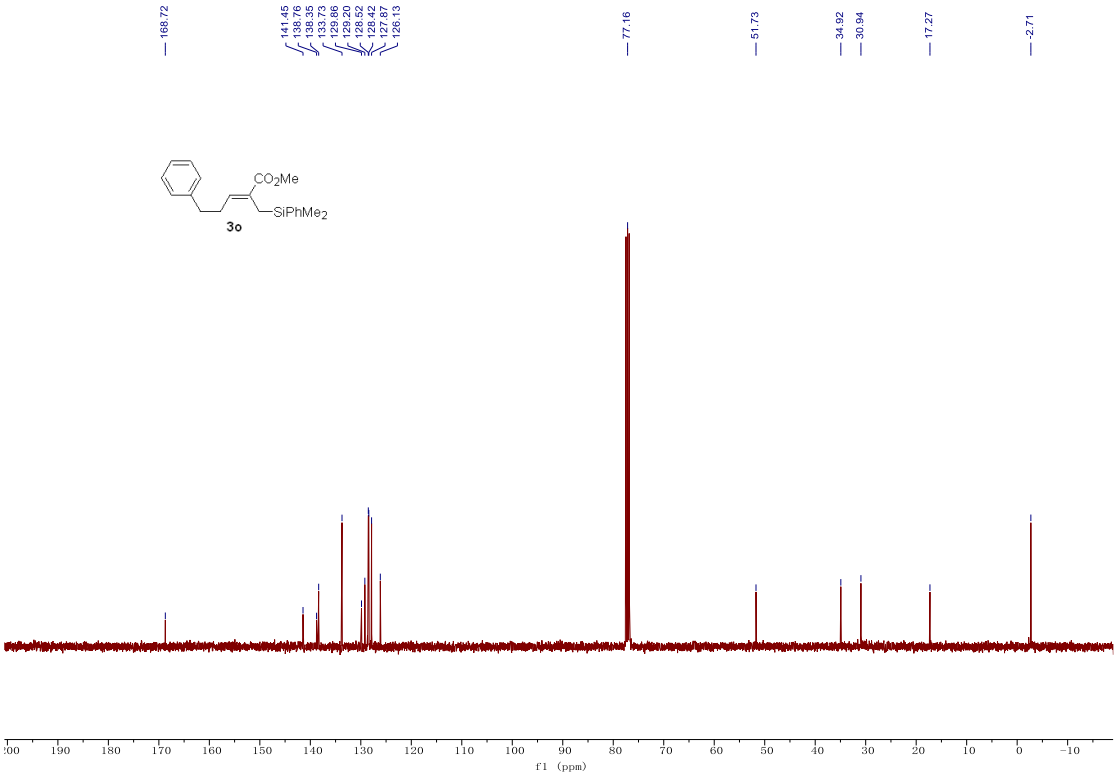


3n; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

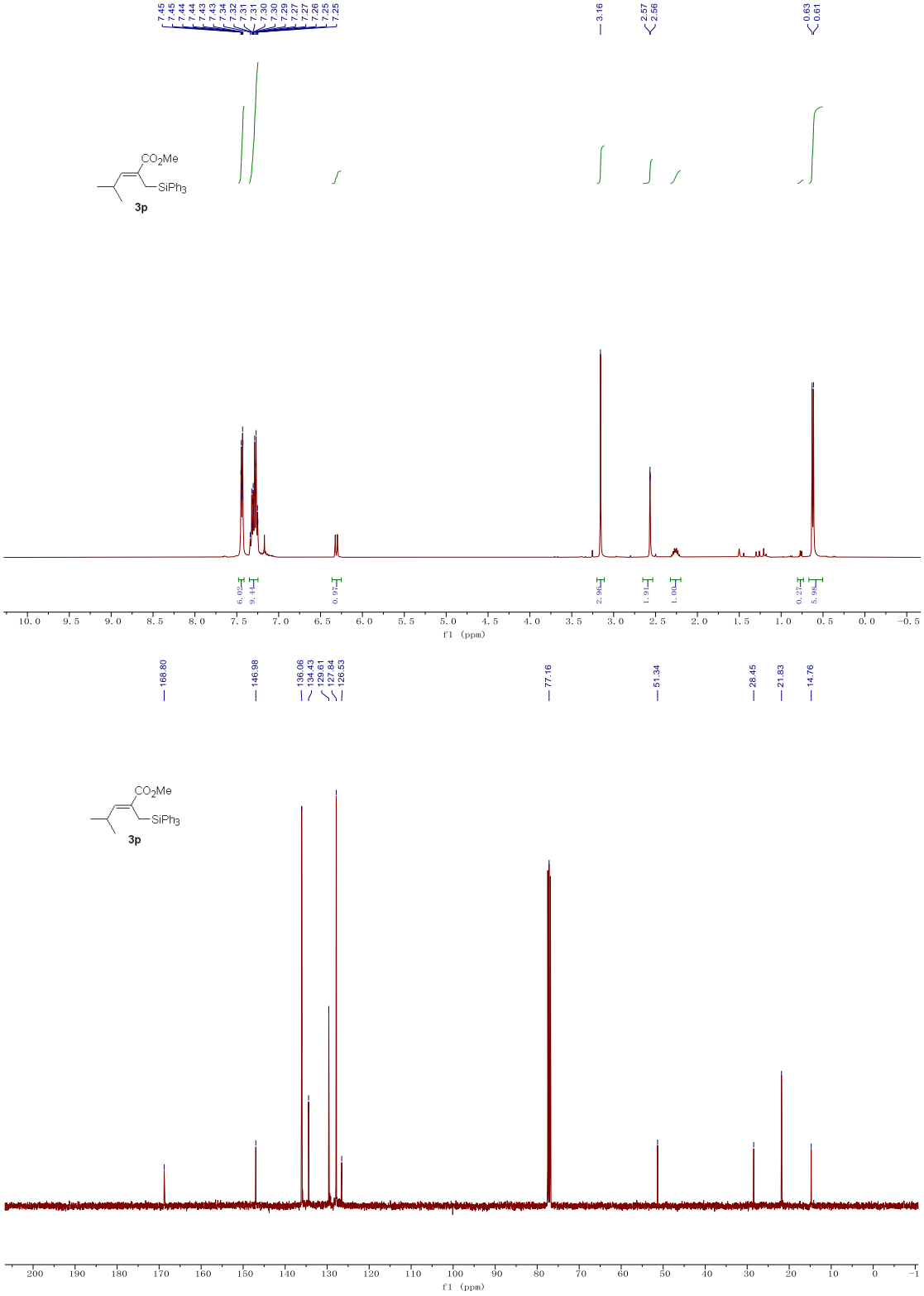


3o; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

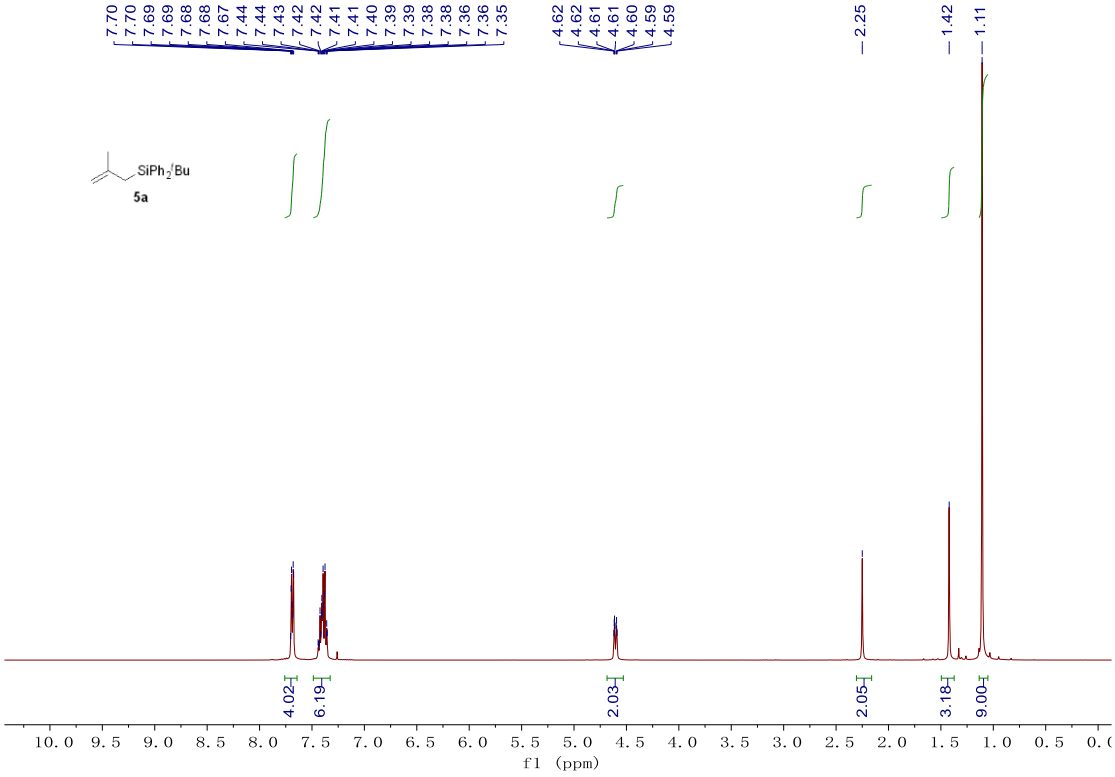


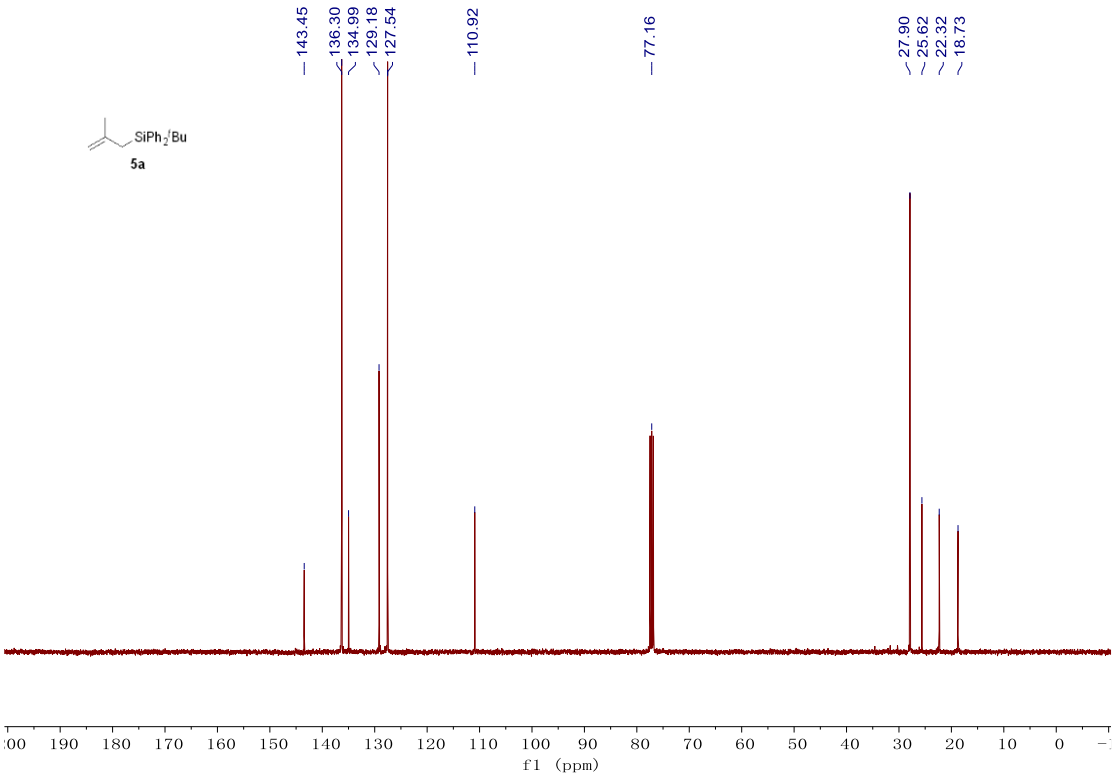


3p; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

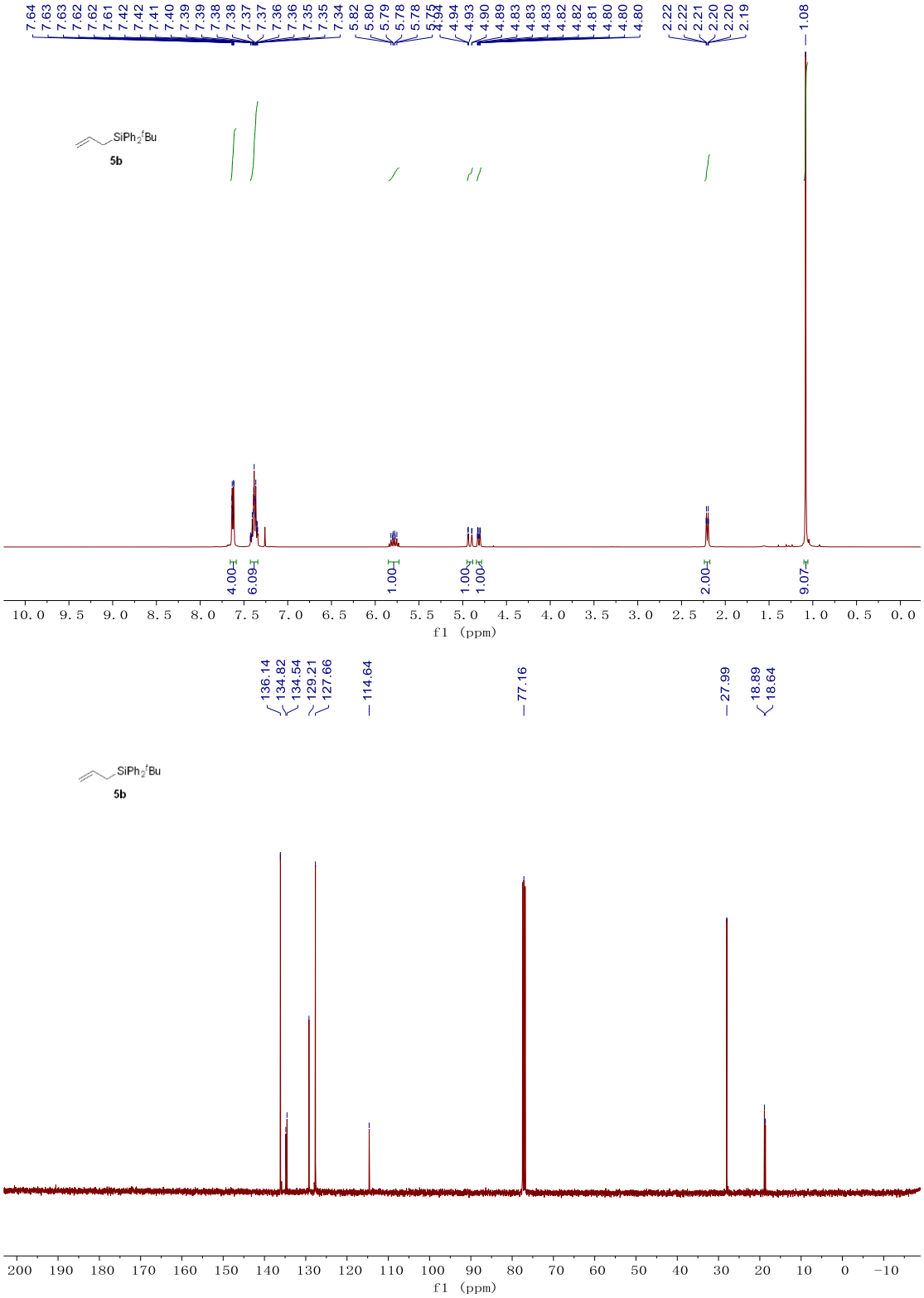


5a; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

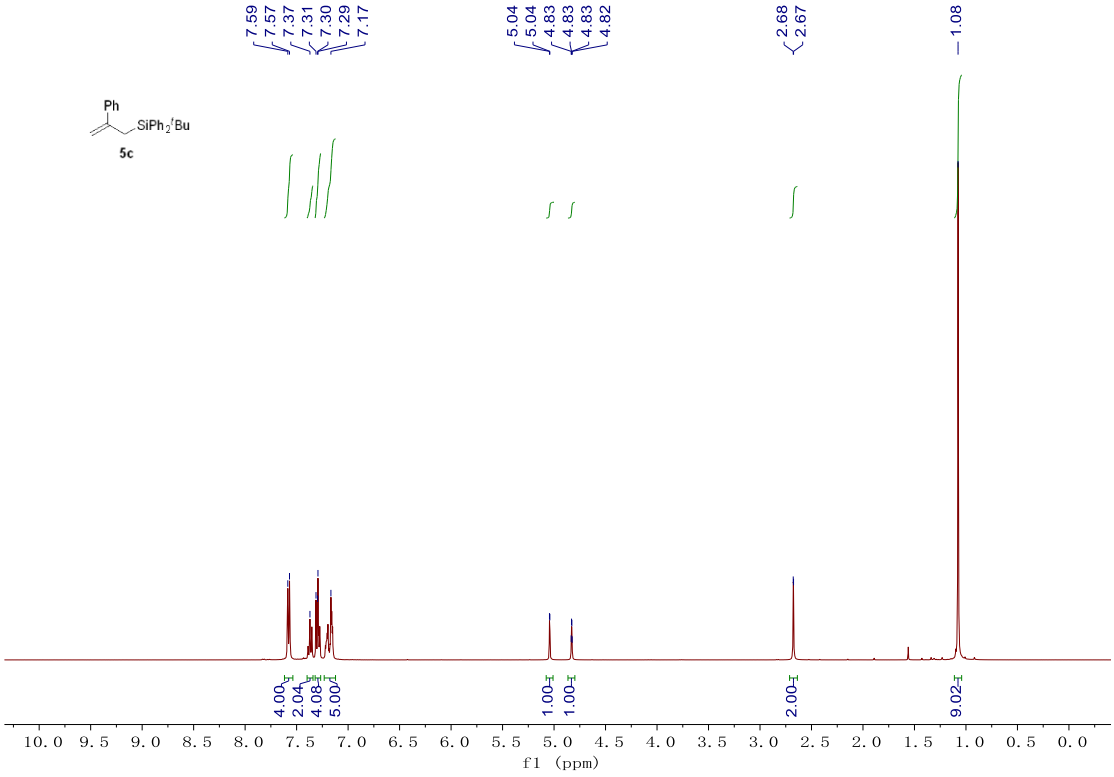


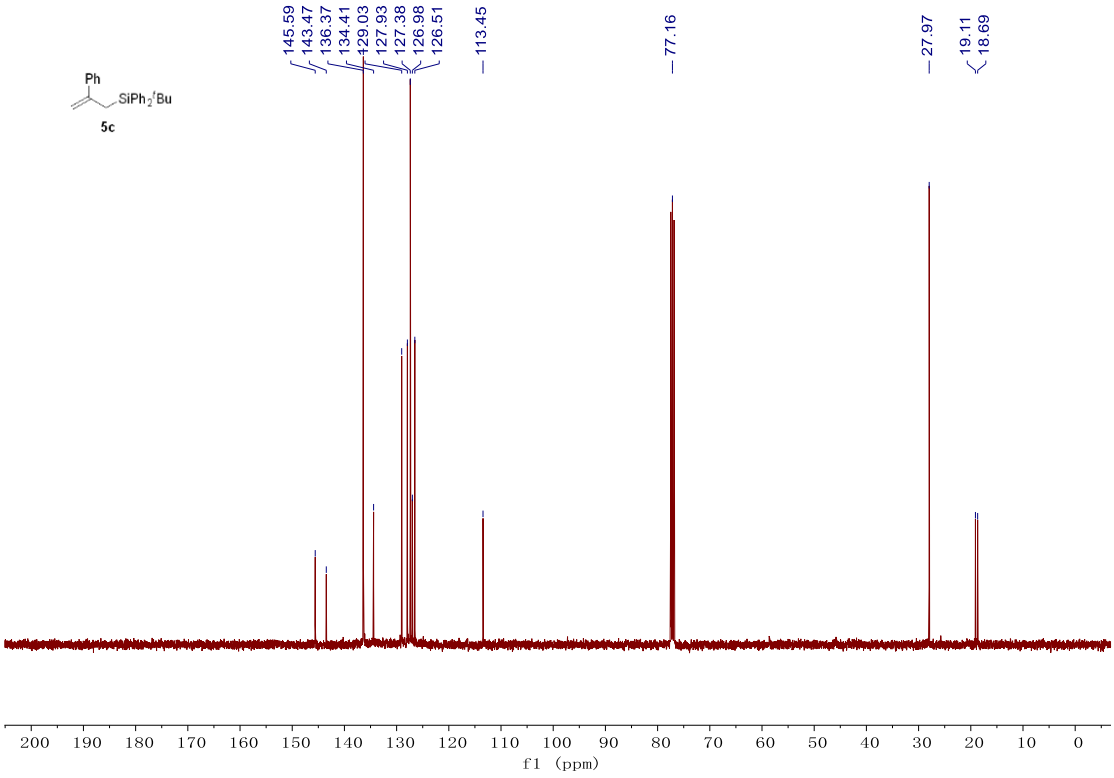


5b; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

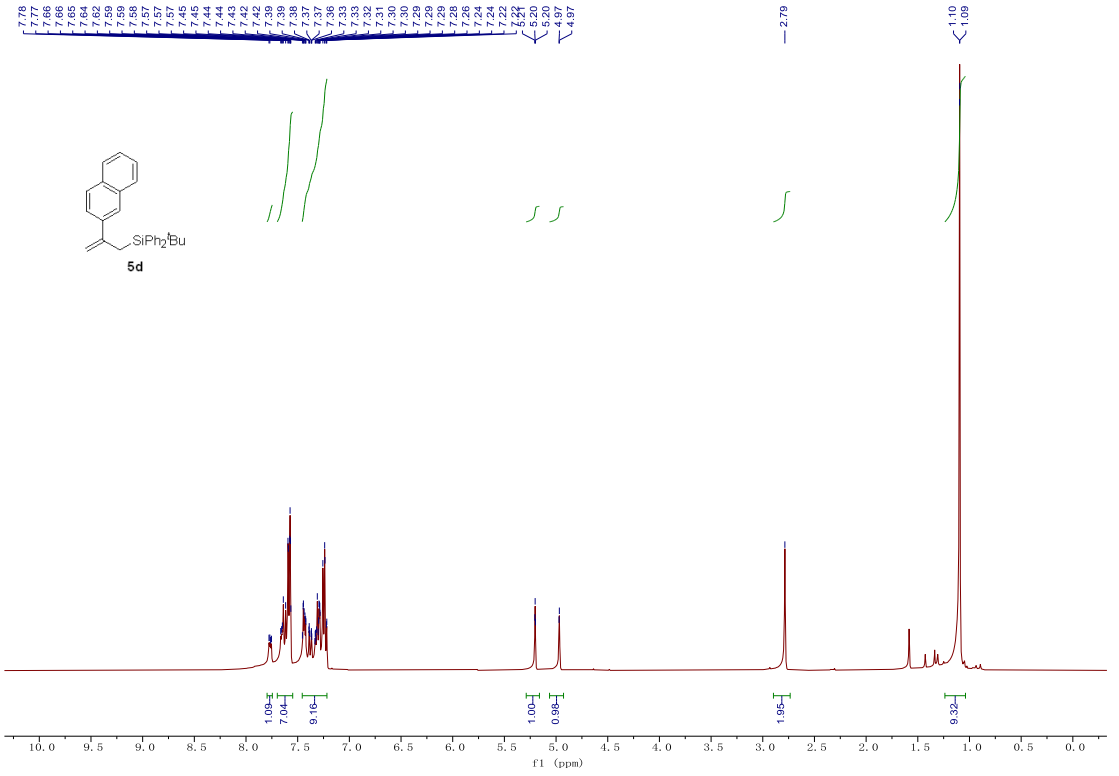


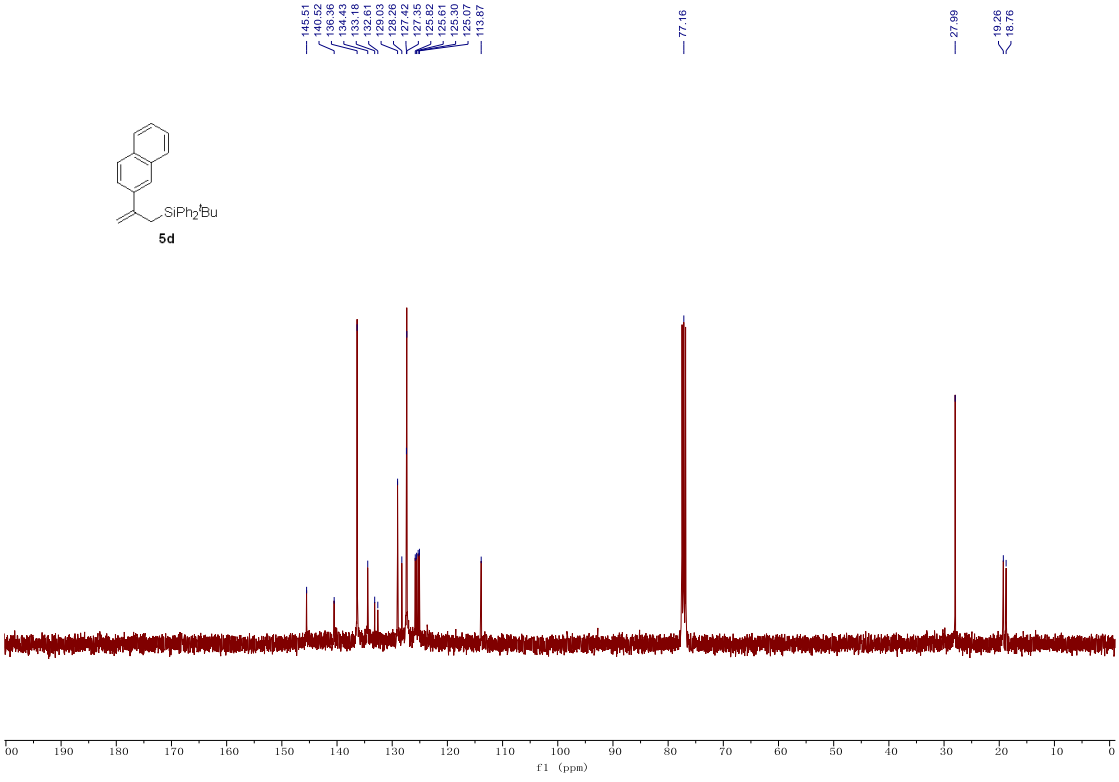
5c; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



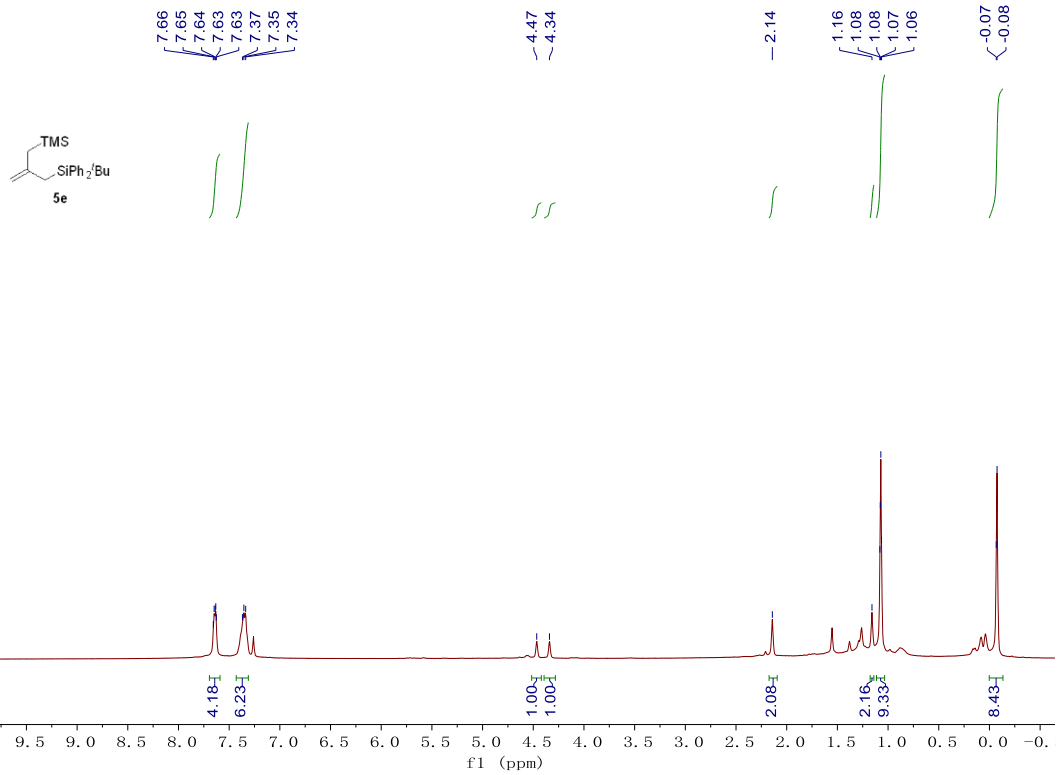


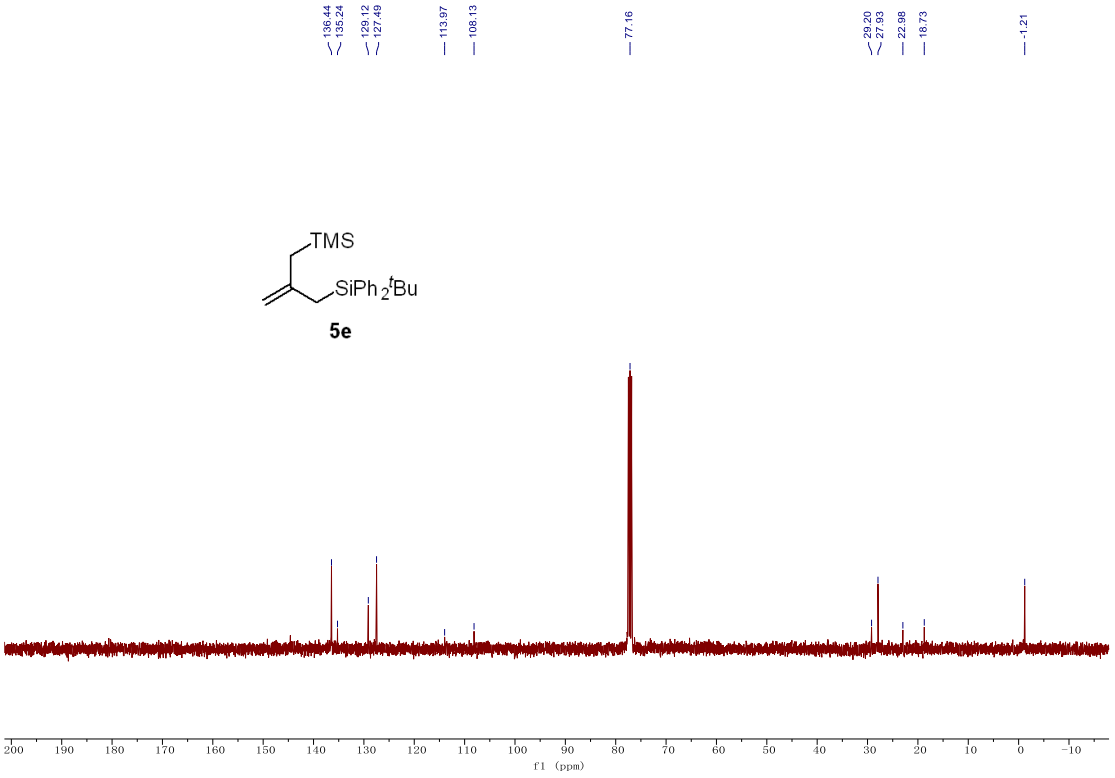
5d; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



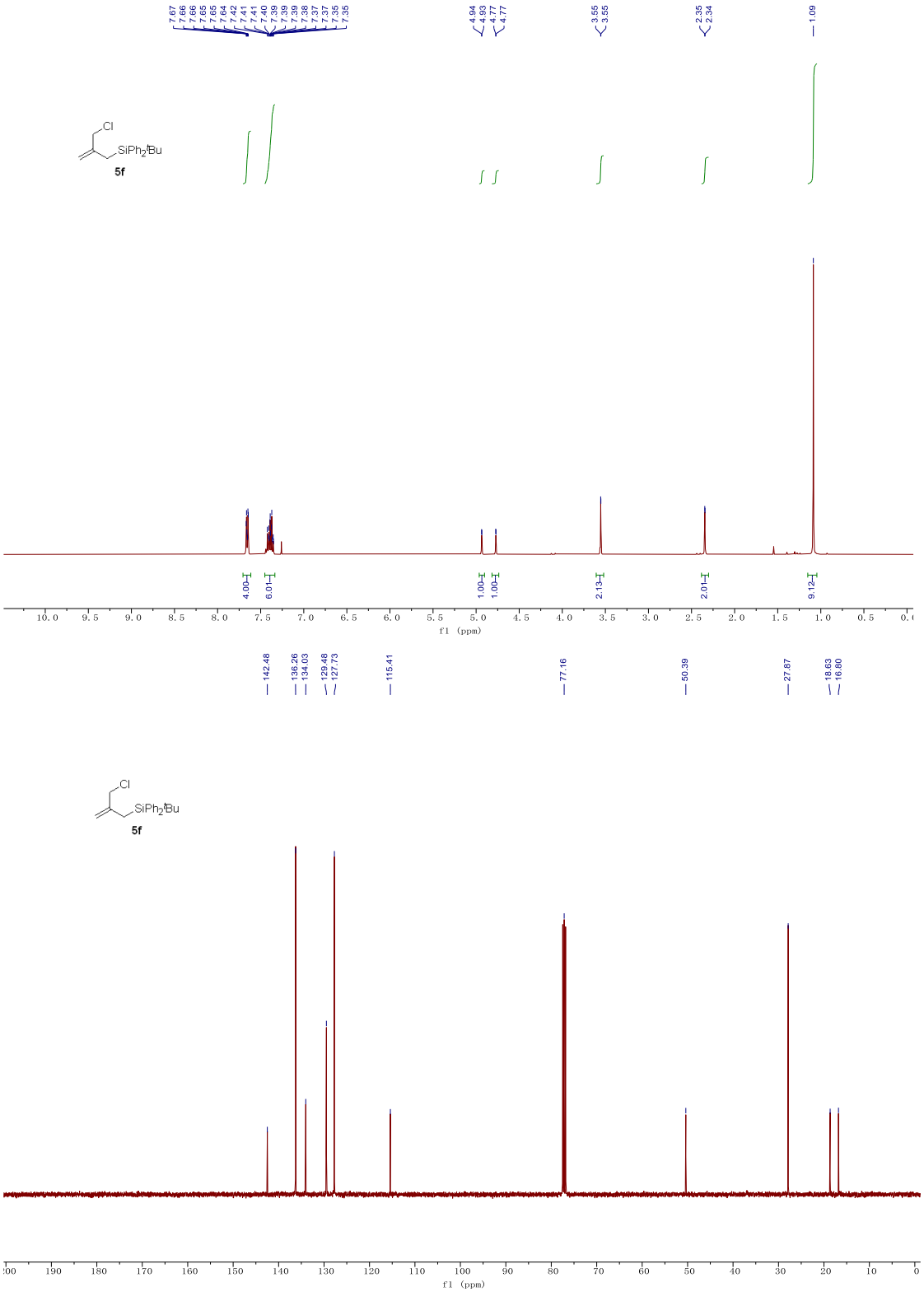


5e; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

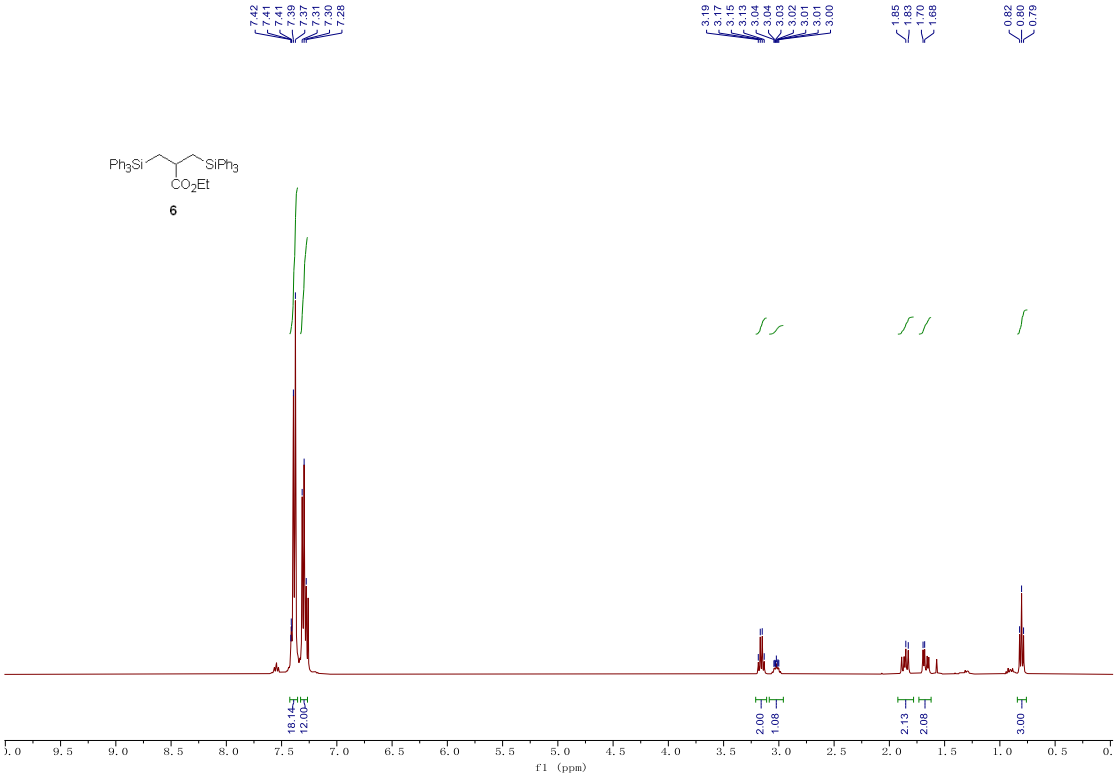


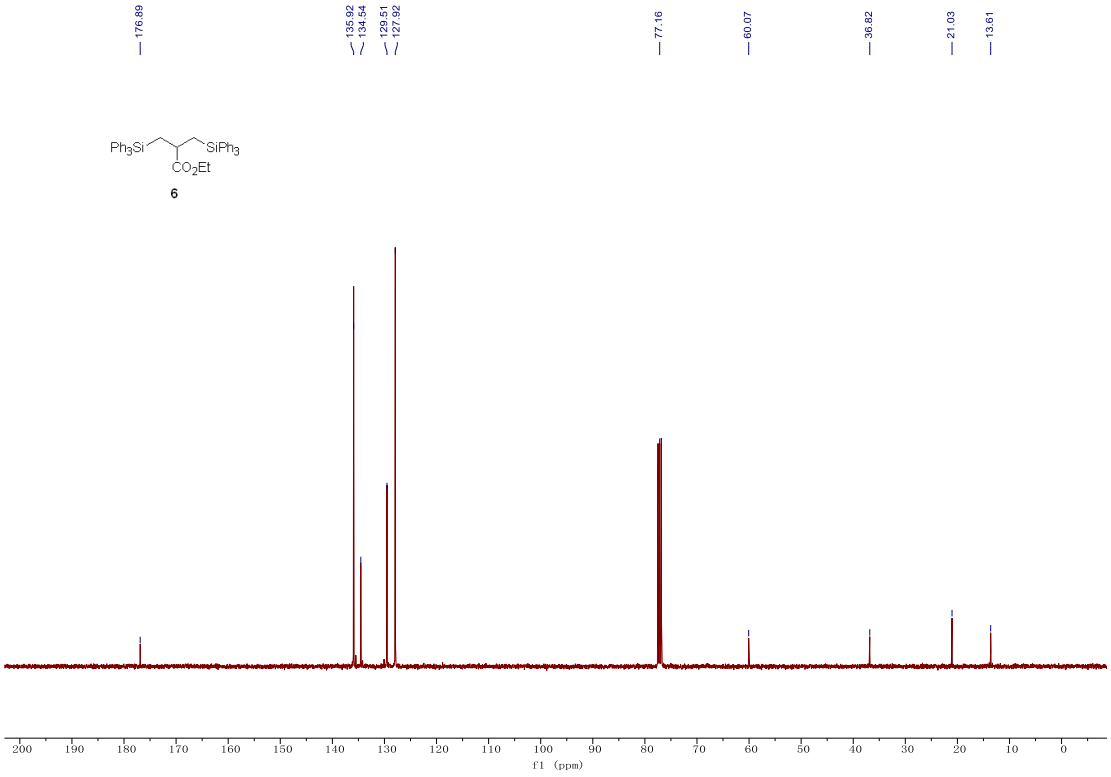


5f; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

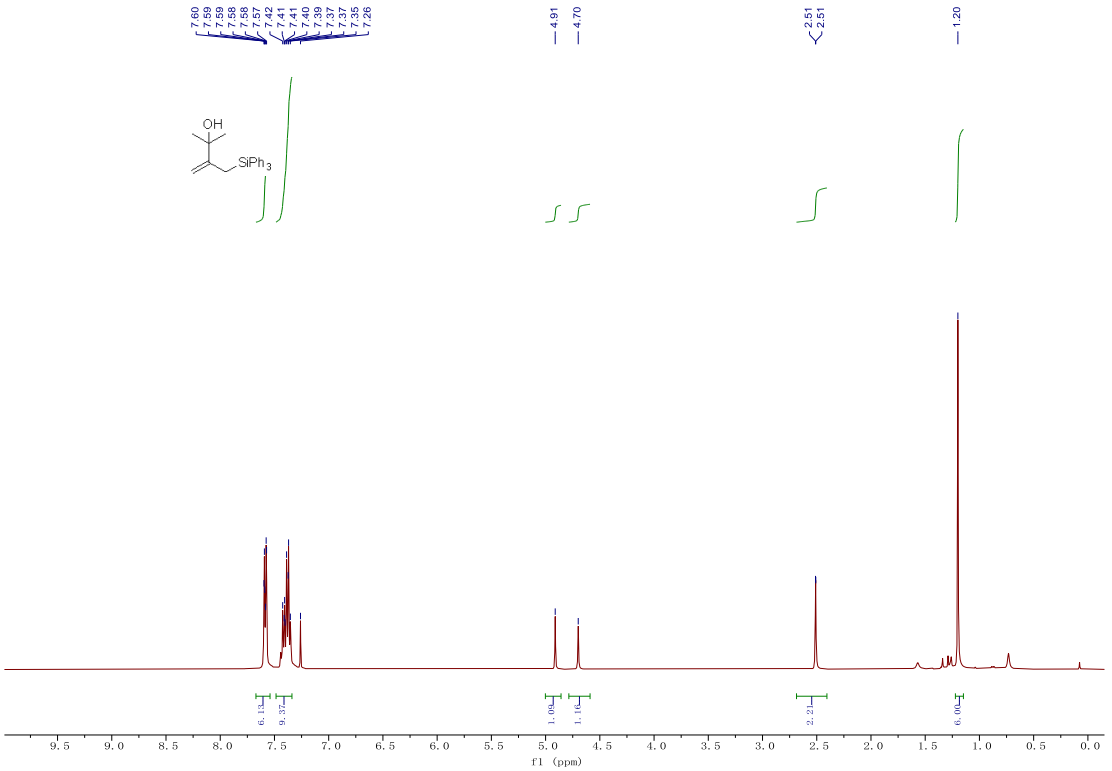


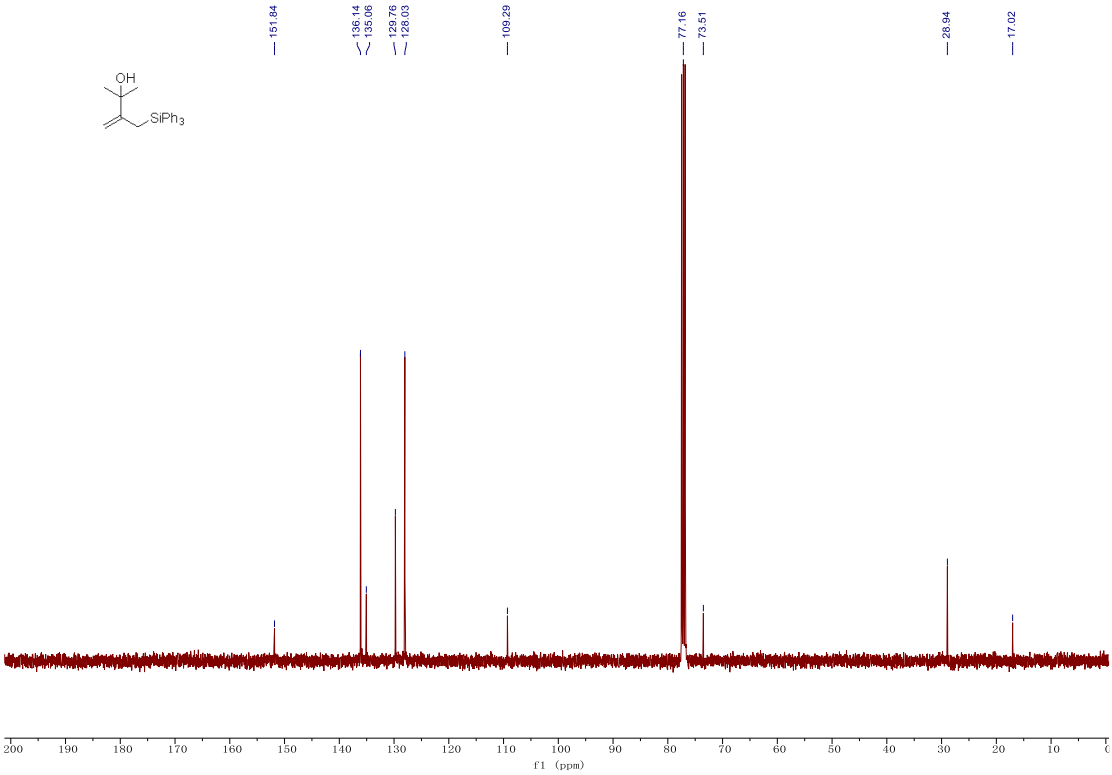
6; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



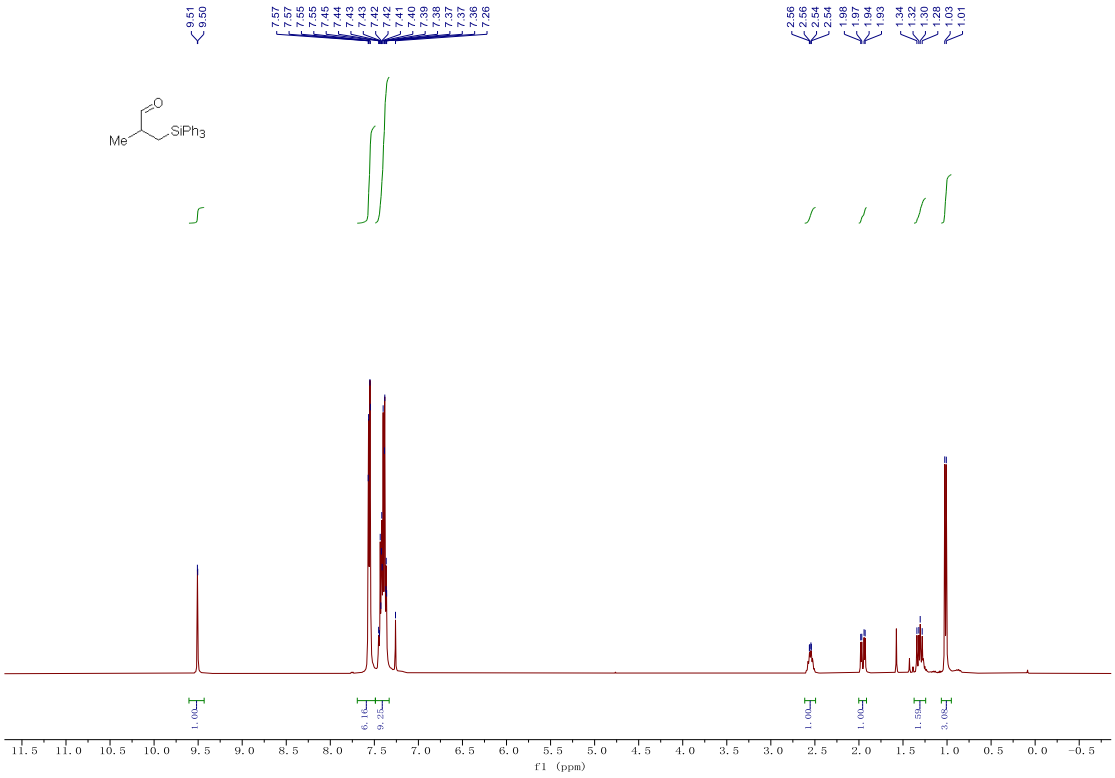


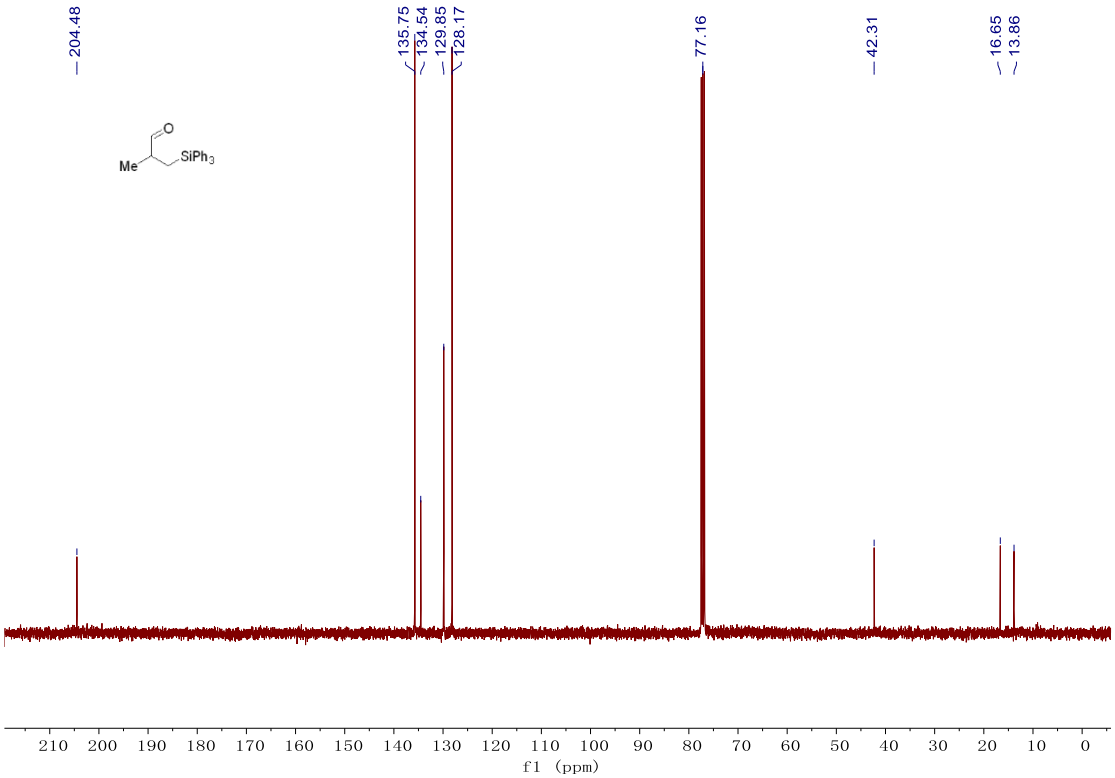
7; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)





8; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)





Crystal data of **3m**

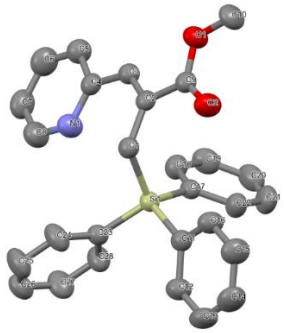


Table 1 Crystal data and structure refinement for mo230226a.

Identification code	mo230226a
Empirical formula	$C_{28}H_{25}NO_2Si$
Formula weight	435.58
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	8.2953(17)
b/Å	11.112(2)
c/Å	13.432(3)
α/°	75.647(4)
β/°	76.178(4)
γ/°	86.139(4)
Volume/Å^3	1164.7(4)
Z	2
ρ_{calc}g/cm^3	1.242
μ/mm^{-1}	0.126
F(000)	460.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.216 to 61.05
Index ranges	-9 ≤ h ≤ 11, -15 ≤ k ≤ 15, -18 ≤ l ≤ 19
Reflections collected	24067
Independent reflections	6555 [R_{int} = 0.0293, R_{sigma} = 0.0313]
Data/restraints/parameters	6555/0/290
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1062
Final R indexes [all data]	R_1 = 0.0715, wR_2 = 0.1203
Largest diff. peak/hole / e Å^{-3}	0.25/-0.22