Supplementary Materials

Photoredox/nickel dual-catalyzed reductive C(sp^2)–Si cross-coupling

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1 General Information

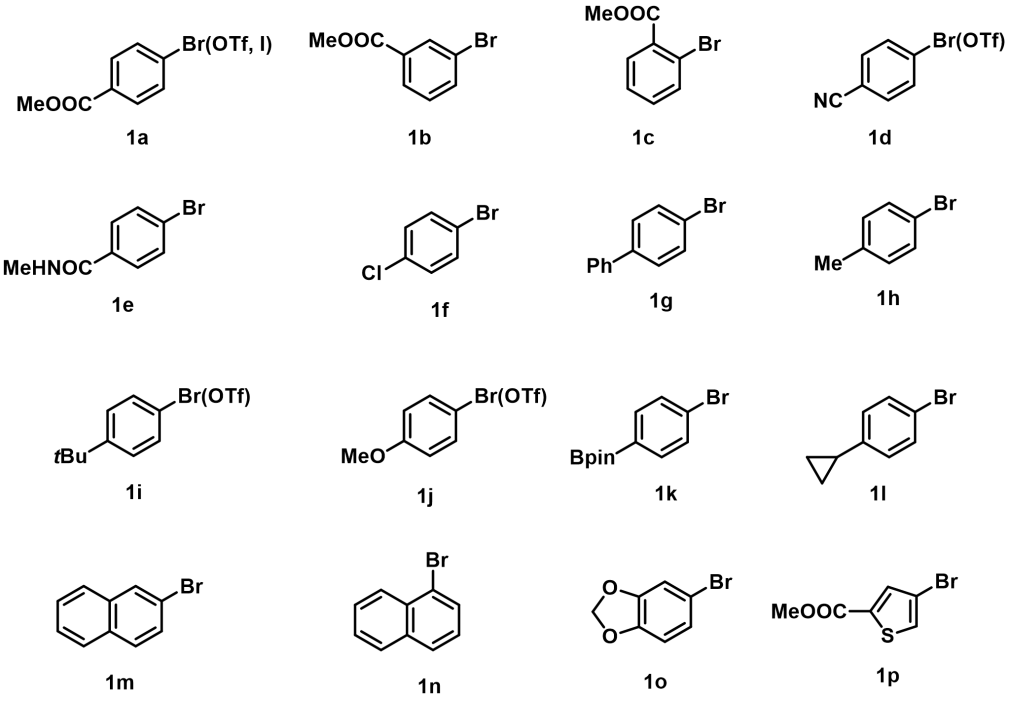
Reactions were performed in flame-dried glassware under a static pressure of nitrogen unless otherwise stated. All the materials were purchased from Bidepharm, Energy Chemical, Adamas-beta® *etc*. and used as received unless otherwise noted. Anhydrous DMSO, DMF, DMAc, Dioxane, CH_3CN (99.8%, extra dry) were purchased from Energy Chemical and stored in a glovebox. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gels using the indicated solvents. The High Resolution MS analyses were performed on BRUKER FT-ICR-MS SolariX 7T with ESI mode. GC analyses were performed on Shimadzu GC 2010 Pro instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a *Bruker* AV600 and *Bruker* AV400 instrument, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signals were used as references for ^1H (TMS: δ_H = 0.00 ppm) and ^{13}C NMR spectra ($CDCl_3$: δ_C = 77.16 ppm, middle line). *n*-Tridecane was used as an internal standard to calculate GC yields. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constants (Hz), and integration.

The photoreactor is homemade and each vial was illuminated by one lamp bead (parameters: 1.5 W blue LED, λ_{max} = 455 nm, Cree xpe2 royal blue). Unless otherwise photoredox reactions were set-up in 10 mL vial and stirred (800 rpm) at a distance of 1.0 cm from the irradiating plate. In addition, fan (rear part) was used to maintain a temperature of 20−35 °C.

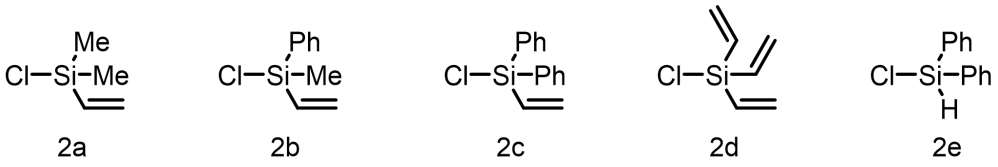
2 Catalysts and Starting Materials

The photocatalysts 4-CzIPN, $Ir[dFppy]_2(dtbbpy)PF_6$, $Ir(ppy)_2(dtbbpy)PF_6$, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, $Ir(ppy)_2bpyPF_6$ and $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ were prepared according to the reported procedures[1]-[2]. The photocatalysts $Ru(bpy)_3Cl_2$, $Ru(bpy)_3PF_6$, and $Ir(ppy)_3$ were purchased from Energy Chemical.

2.1 The following aryl electrophiles were used in this study

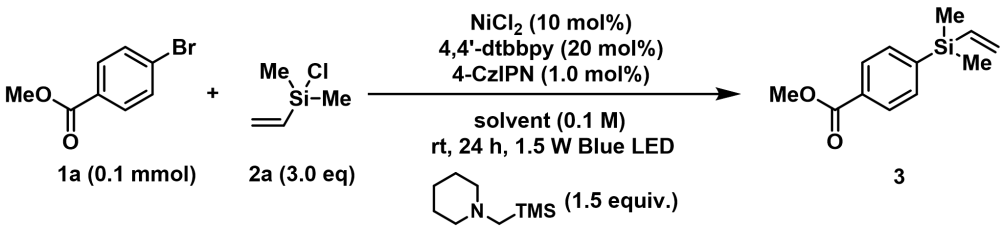


2.2 The following chlorosilanes were used in this study



3 Optimization of the Reaction Conditions

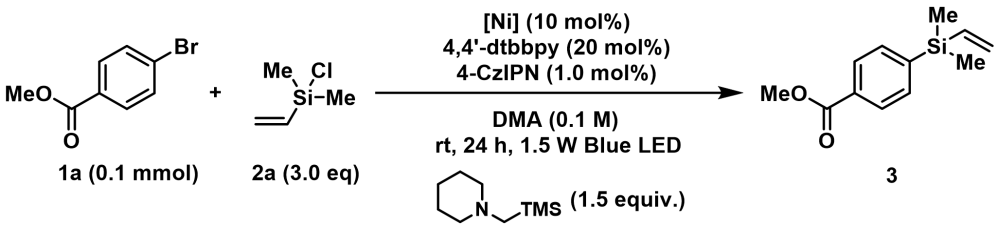
3.1 Supplementary Table 1. The effect of solvents



Entry	Solvent	Yield of **3** (%)[a]
1	DMF	4
2	DMA	15
3	MeCN	0
4	PhMe	0
5	NMP	8
6	DMSO	0
7	THF	0

[a] GC yield, with tridecane as internal standard.

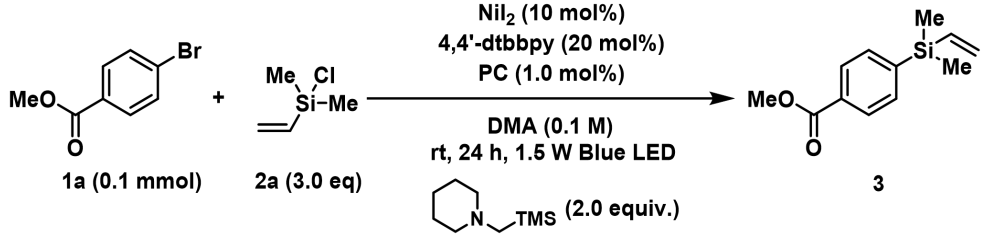
3.2 Supplementary Table 2. The effect of Ni-catalysts

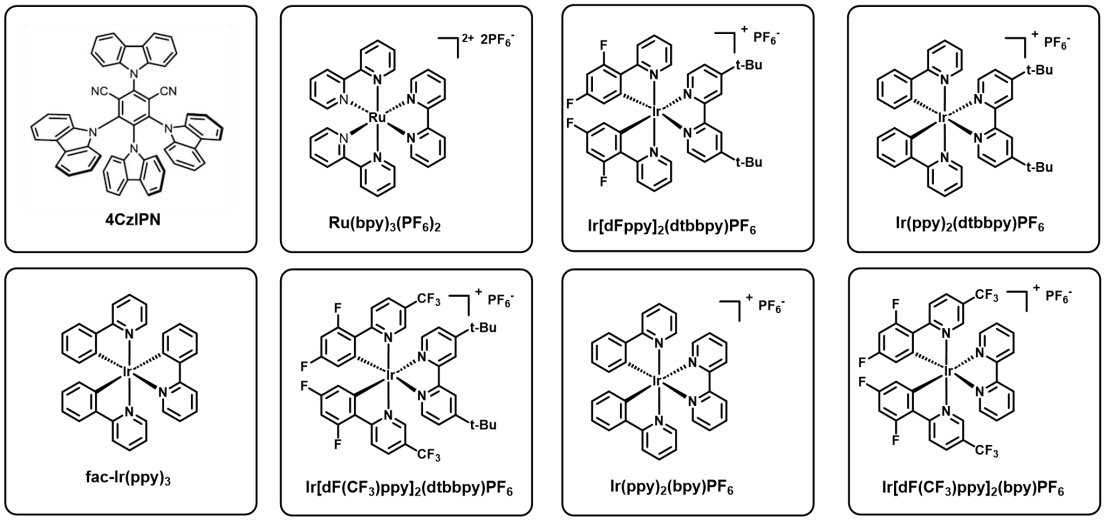


Entry	Ni-catalyst	Yield of **3** (%)[a]
1	$NiCl_2$	15
2	$NiBr_2$	4
3	NiI_2	22 (39)[b]
4	$NiBr_2$•glyme	0
5	$NiCl_2$•glyme	0
6	$[Ni(acac)_2]_3$	11
7	$Ni(PPh_3)_2Br_2$	trace
8	$NiCl_2$•$6H_2O$	0

[a] GC yield, with tridecane as internal standard. [b] 2.0 equiv. of reductant was added.

3.3 Supplementary Table 3. The effect of photocatalysts

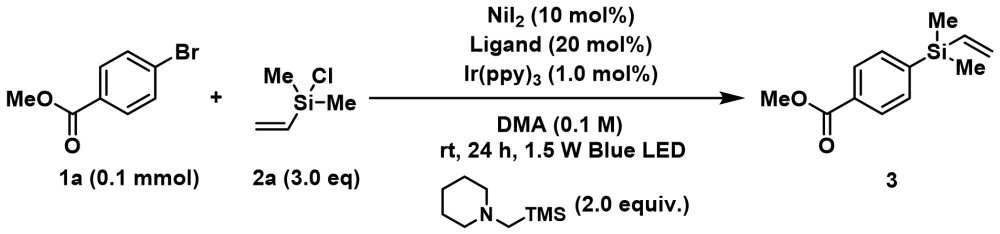


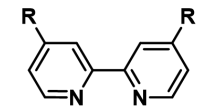


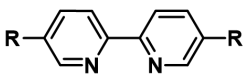
Entry	Photocatalyst	Yield of **3** (%)[a]
1	4-CzIPN	39
2	$Ru(bpy)_3Cl_2$	0
3	$Ru(bpy)_3(PF_6)_2$	0
4	$Ir(dF(CF_3)ppy)_2dtbbpyPF_6$	29
5	$Ir(ppy)_2dtbbpyPF_6$	26
6	*fac*-$Ir(ppy)_3$	50
7	$Ir(ppy)_2bpyPF_6$	22
8	$Ir(dF(CF_3)ppy)_2bpyPF_6$	28
9	$Ir(dFppy)_2dtbbpyPF_6$	23
10	10-phenylphenothiazine	17
11	10-methylphenothiazine	10

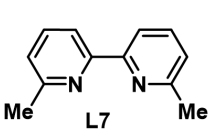
[a] GC yield, with tridecane as internal standard.

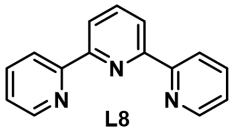
3. Supplementary Table 4. The effect of ligands

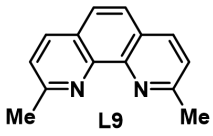


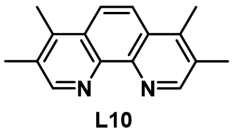








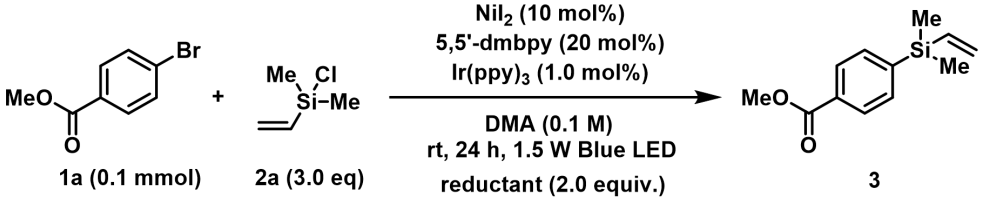


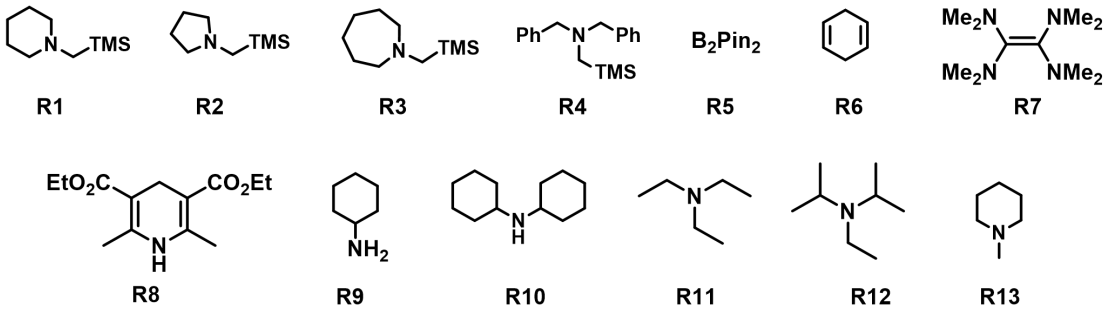


Entry	Ligand	Yield of **3** (%)[a]
1	L1	50
2	L2	11
3	L3	0
4	L4	64
5	L5	21
6	L6	0
7	L7	6
8	L8	22
9	L9	0
10	L10	0

[a] GC yield, with tridecane as internal standard.

3.5 Supplementary Table 5. The effect of reductants

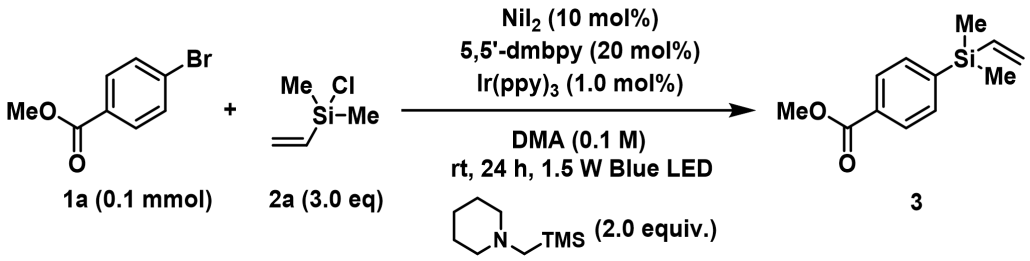




Entry	Reductant	Yield of **3** (%)[a]
1	R1	64
2	R2	21
3	R3	14
4	R4	0
5	R5	0
6	R6	0
7	R7	0
8	R8	0
9	R9	0
10	R10	0
11	R11	0
12	R12	0
13	R13	0
14	R12 + TMSCl	0

[a] GC yield, with tridecane as internal standard.

3.6 Supplementary Table 6. Control experiments



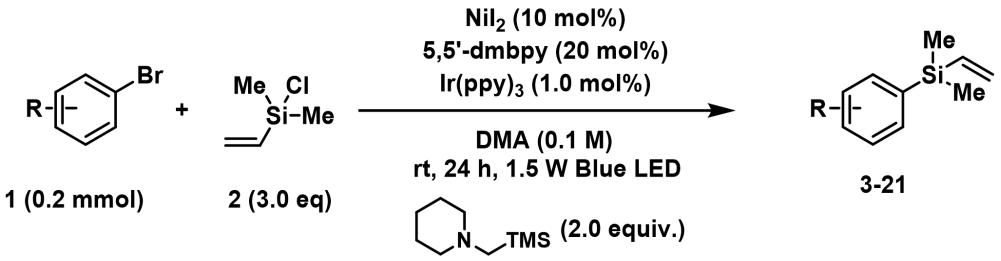
1a (0.1 mmol) 2a (3.0 eq) 3

Entry	Deviation	Yield of **3** (%)[a]
1	none	64
2	no Ni	0
3	no Ligand	0
4	no PC	0
5	no Light	0
6	using $Ni(cod)_2$	49

[a] GC yield, with tridecane as internal standard.

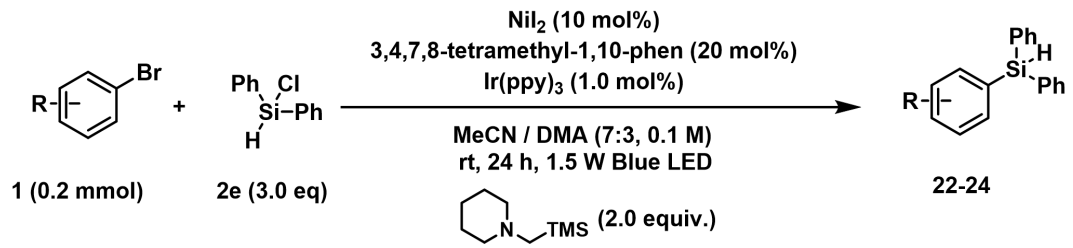
4 General procedure for reductive carbonyl-aryl coupling

4.1 General Procedure A for the coupling of vinyl chlorosilanes



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added aryl bromide **1** (0.20 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 40 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.). Then, DMA (0.10 M, 2.0 mL), reductant **R1** (69 mg, 0.40 mmol, 2.0 equiv.) and chlorosilane **2** (0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the residue was purified by flash chromatography to give the corresponding product.

4.2 General Procedure B for the coupling of chlorohydrosilanes

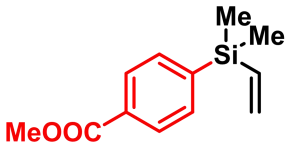


The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 3,4,7,8-tetramethyl-1,10-phenanthroline (9.5 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.), aryl bromide **1** (0.20 mmol, 1.0 equiv.), chlorohydrosilane **2e** (0.60 mmol, 3.0 equiv.). Then, MeCN / DMA (7:3, 0.10 M, 2.0 mL), reductant **R1** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the

glovebox, then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the residue was purified by flash chromatography to give the corresponding product.

5 Spectroscopic data of the products

Methyl 4-(dimethyl(vinyl)silyl)benzoate (3)

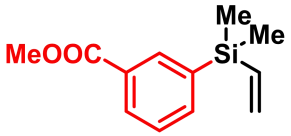


Chemical Formula: $C_{12}H_{16}O_2Si$
Exact Mass: 220.0920

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R1** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (27.3 mg, 62% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.61 – 7.59 (m, 2H), 6.32 – 6.23 (m, 1H), 6.10 – 6.06 (m, 1H), 5.79 – 5.73 (m, 1H), 3.92 (s, 3H), 0.37 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.41, 144.96, 137.25, 133.94, 133.59, 130.59, 128.65, 52.23, -2.96 ppm. **HRMS** (ESI) for $C_{12}H_{17}O_2Si^+$ [$(M+H)^+$]: calculated 221.0992, found 221.0983.

Methyl 3-(dimethyl(vinyl)silyl)benzoate (4)



Chemical Formula: $C_{12}H_{16}O_2Si$
Exact Mass: 220.0920

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (23.8 mg, 54% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 8.01 (m, 1H), 7.71 – 7.70 (m, 1H), 7.51 – 7.49 (m,

1H), 7.45 – 7.42 (m, 1H), 6.46 – 6.40 (m, 1H), 6.03 – 6.02(m, 1H), 5.75 – 5.72 (m, 1H), 3.89 (s, 3H), 0.41 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.76, 141.01, 139.81, 136.19, 135.83, 131.62, 131.58, 130.16, 129.16, 52.07, -1.47 ppm. **HRMS** (ESI) for $C_{12}H_{17}O_2Si^+$ [$(M+Na)^+$]: calculated 221.0992, found 221.0982.

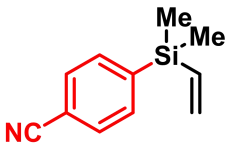
Methyl 2-(dimethyl(vinyl)silyl)benzoate (5)

Chemical Formula: $C_{12}H_{16}O_2Si$
Exact Mass: 220.0920

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (25.5 mg, 58% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 – 8.18 (m, 1H), 8.03 – 8.01 (m, 1H), 7.71 – 7.70 (m, 1H), 7.44 – 7.41 (m, 1H), 6.33 – 6.24 (m, 1H), 6.10 – 6.06 (m, 1H), 5.80 – 5.74 (m, 1H), 3.92 (s, 3H), 0.38 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.52, 139.20, 138.48, 137.47, 134.98, 133.52, 130.30, 129.62, 127.93, 52.21, -2.85 ppm. **HRMS** (ESI) for $C_{12}H_{16}O_2SiNa^+$ [$(M+Na)^+$]: calculated 243.0812, found 243.0809.

4-(Dimethyl(vinyl)silyl)benzonitrile (6)



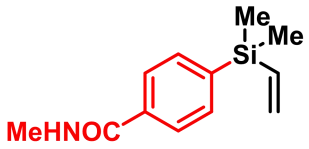
Chemical Formula: $C_{11}H_{13}NSi$
Exact Mass: 187.0817

Prepared according to the general procedure A using **1a** (36.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash

column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (17.3 mg, 46% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.61 (m, 4H), 6.27 – 6.21 (m, 1H), 6.12 – 6.09 (m, 1H), 5.79 – 5.76 (m, 1H), 0.37 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.54, 136.51, 134.42 , 134.16, 131.11, 119.12, 112.72, -3.12 ppm. **HRMS** (ESI) for $C_{11}H_{13}NSiNa^+$ [$(M+Na)^+$]: calculated 210.0709, found 210.0709.

4-(Dimethyl(vinyl)silyl)-N-methylbenzamide (7)

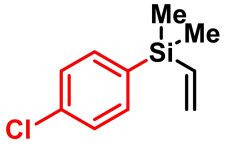


Chemical Formula: $C_{12}H_{17}NOSi$
Exact Mass: 219.1079

Prepared according to the general procedure A using **1a** (42.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (25.8 mg, 59% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 4H), 7.33 (s, 1H), 6.29 – 6.23 (m, 1H), 6.05 – 6.03 (m, 1H), 5.75 – 5.72 (m, 1H), 2.17 (s, 3H), 0.32 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.43, 138.73, 138.10, 134.81, 134.04, 132.97, 119.26, 24.79, -2.74 ppm. **HRMS** (ESI) for $C_{12}H_{18}NSi^+$ [$(M+H)^+$]: calculated 220.1152, found 220.1150.

(4-Chlorophenyl)dimethyl(vinyl)silane (8)



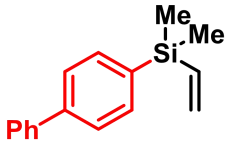
Chemical Formula: $C_{10}H_{13}ClSi$
Exact Mass: 196.0475

Prepared according to the general procedure A using **1a** (38.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$

(1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (16.9 mg, 43% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.34 – 7.33 (m, 2H), 6.29 – 6.23 (m, 1H), 6.08 – 6.06 (m, 1H), 5.77 – 5.73 (m, 1H), 0.35 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.58, 136.85, 135.49, 135.34, 133.39, 128.15, -2.81 ppm. **HRMS** (ESI) for $C_{10}H_{14}ClSi^+$ [$(M+H)^+$]: calculated 197.0548, found 197.0530.

[1,1'-Biphenyl]-4-yldimethyl(vinyl)silane (9)

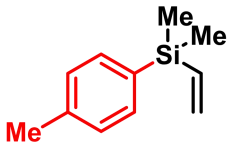


Chemical Formula: $C_{16}H_{18}Si$
Exact Mass: 238.1178

Prepared according to the general procedure A using **1a** (46.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (28.1 mg, 59% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.60 (m, 6H), 7.46 – 7.44 (m, 2H), 7.37 – 7.34 (m, 1H), 6.36 – 6.30 (m, 1H), 6.10 – 6.08 (m, 1H), 5.82 – 5.78 (m, 1H), 0.40 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.96, 141.27, 138.07, 137.31, 134.48, 133.08, 128.90, 127.51, 127.32, 126.70, -2.74 ppm. **HRMS** (ESI) for $C_{16}H_{19}Si^+$ [$(M+H)^+$]: calculated 239.1251, found 239.1250.

Dimethyl(p-tolyl)(vinyl)silane (10)

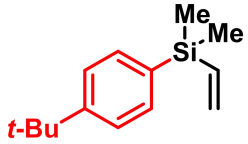


Chemical Formula: $C_{11}H_{16}Si$
Exact Mass: 176.1021

Prepared according to the general procedure A using **1a** (34.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (13.7 mg, 39% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 2H), 7.19 – 7.18 (m, 2H), 6.31 – 6.26 (m, 1H), 6.06 – 6.03 (m, 1H), 5.77 – 5.73 (m, 1H), 2.35 (s, 3H), 0.34 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.02, 138.37, 134.87, 134.03, 132.77, 127.51, 128.78, 21.60, -2.71 ppm. **HRMS** (ESI) for $C_{11}H_{16}NaSi^+$ [$(M+Na)^+$]: calculated 199.0913, found 199.0910.

(4-(*tert*-Butyl)phenyl)dimethyl(vinyl)silane (11)



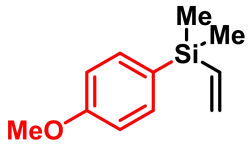
Chemical Formula: $C_{14}H_{22}Si$
Exact Mass: 218.1491

Prepared according to the general procedure A using **1a** (42.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (22.7 mg, 52% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.52 (m, 2H), 7.45 – 7.44 (m, 2H), 6.37 – 6.31 (m, 1H), 6.11 – 6.09 (m, 1H), 5.83 – 5.79 (m, 1H), 1.37 (s, 9H), 0.39 (s, 6H) ppm. **^{13}C NMR**

(151 MHz, $CDCl_3$) δ 152.09, 138.40, 134.98, 133.89, 132.75, 124.92, 34.78, 31.41, -2.71 ppm. **HRMS** (ESI) for $C_{14}H_{23}Si^+$ [$(M+H)^+$]: calculated 219.1564, found 219.1573.

(4-Methoxyphenyl)dimethyl(vinyl)silane (12)

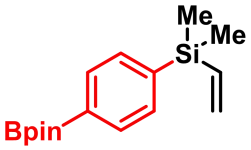


Chemical Formula: $C_{11}H_{16}OSi$
Exact Mass: 192.0970

Prepared according to the general procedure A using **1a** (36.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (28.10 mg, 43% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 6.95 – 6.94 (m, 2H), 6.34 – 6.28 (m, 1H), 6.08 – 6.05 (m, 1H), 5.78 – 5.75 (m, 1H), 3.84 (s, 3H), 0.36 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.39, 144.95, 137.25, 133.94, 133.58, 128.65, 52.21, -2.79 ppm. **HRMS** (ESI) for $C_{11}H_{17}OSi^+$ [$(M+H)^+$]: calculated 193.1043, found 193.1033.

Dimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(vinyl)silane (13)

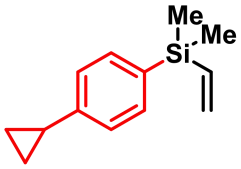


Chemical Formula: $C_{16}H_{25}BO_2Si$
Exact Mass: 288.1717

Prepared according to the general procedure A using **1a** (56.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (32.3 mg, 56% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.80 (m, 2H), 7.55 – 7.54 (m, 2H), 6.32 – 6.26 (m, 1H), 6.08 – 6.05 (m, 1H), 5.78 – 5.74 (m, 1H), 1.35 (s, 12H), 0.36 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.37, 137.88, 134.03, 133.26, 133.10, 24.98, -2.87 ppm. **HRMS** (ESI) for $C_{16}H_{25}BO_2NaSi^+$ [$(M+Na)^+$]: calculated 311.1609, found 311.1607.

(4-Cyclopropylphenyl)dimethyl(vinyl)silane (14)

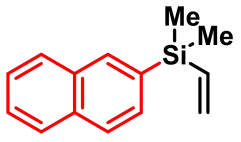


Chemical Formula: $C_{13}H_{18}Si$
Exact Mass: 202.1178

Prepared according to the general procedure A using **1a** (39.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (17.0 mg, 42% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 2H), 7.08 – 7.07 (m, 2H), 6.31 – 6.25 (m, 1H), 6.06 – 6.04 (m, 1H), 5.77 – 5.73 (m, 1H), 1.90 – 1.88 (m, 1H), 0.98 – 0.97 (m, 2H), 0.73 – 0.72 (m, 1H), 0.34 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.21, 138.37, 134.88, 134.02, 132.76, 125.28, 15.52, 9.51, -2.71 ppm. **HRMS** (ESI) for $C_{13}H_{18}NaSi^+$ [$(M+Na)^+$]: calculated 225.1070, found 225.1065.

Dimethyl(naphthalen-2-yl)(vinyl)silane (15)



Chemical Formula: $C_{14}H_{16}Si$
Exact Mass: 212.1021

Prepared according to the general procedure A using **1a** (41.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4

mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (19.1 mg, 45% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 8.03 (m, 1H), 7.84 – 7.83 (m, 3H), 7.62 – 7.60 (m, 1H), 7.50 – 7.49 (m, 2H), 6.40 – 6.34 (m, 1H), 6.12 – 6.10 (m, 1H), 5.83 – 5.80 (m, 1H), 0.44 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.07, 135.98, 134.61, 133.86, 133.17, 133.08, 130.26, 128.19, 127.84, 127.11, 126.46, 126.03, -2.71 ppm. **HRMS** (ESI) for $C_{14}H_{17}Si^+$ [$(M+H)^+$]: calculated 213.1094, found 213.1096.

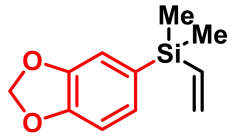
Dimethyl(naphthalen-1-yl)(vinyl)silane (16)

Chemical Formula: $C_{14}H_{16}Si$
Exact Mass: 212.1021

Prepared according to the general procedure A using **1a** (41.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (22.1 mg, 52% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.14 (m, 1H), 7.90 – 7.88 (m, 2H), 7.75 – 7.74 (m, 1H), 7.51 – 7.48 (m, 3H), 6.52 – 6.48 (m, 1H), 6.14 – 6.11 (m, 1H), 5.88 – 5.85 (m, 1H), 0.56 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.97, 137.11, 136.37, 134.06, 133.53, 132.93, 130.15, 129.16, 128.53, 125.74, 125.51,125.25, -1.48 ppm. **HRMS** (ESI) for $C_{14}H_{17}Si^+$ [$(M+H)^+$]: calculated 213.1094, found 213.1096.

Benzo[d][1,3]dioxol-5-yldimethyl(vinyl)silane (17)

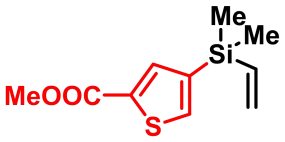


Chemical Formula: $C_{11}H_{14}O_2Si$
Exact Mass: 206.0763

Prepared according to the general procedure A using **1a** (40.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (18.5 mg, 45% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.99 (m, 2H), 6.87 – 6.85 (m, 1H), 6.30 – 6.24 (m, 1H), 6.07 – 6.05 (m, 1H), 5.94 (s, 2H), 5.77 – 5.74 (m, 1H), 0.56 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.54, 147.51, 138.18, 132.94, 131.49, 127.95, 113.32, 108.72, 100.65, -2.58 ppm. **HRMS** (ESI) for $C_{11}H_{15}O_2Si^+$ [$(M+H)^+$]: calculated 207.0836, found 207.0789.

Methyl 4-(dimethyl(vinyl)silyl)thiophene-2-carboxylate (18)



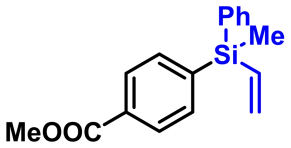
Chemical Formula: $C_{10}H_{14}O_2SSi$
Exact Mass: 226.0484

Prepared according to the general procedure A using **1a** (44.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (72.4 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (18.5 mg, 41% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 6.78 (m, 1H), 7.55 – 7.55 (m, 1H), 6.21 – 6.12 (m, 1H), 6.00 – 5.97 (m, 1H), 5.96 (s, 2H), 5.70 – 5.64 (m, 1H), 3.81 (s, 3H), 0.27 (s, 6H)

ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.98, 141.01, 139.03, 138.55, 137.25, 134.54, 133.48, 52.25, -2.40 ppm. **HRMS** (ESI) for $C_{10}H_{14}O_2SNaSi^+$ [$(M+Na)^+$]: calculated 249.0376, found 249.0372.

Methyl 4-(methyl(phenyl)(vinyl)silyl)benzoate (19)

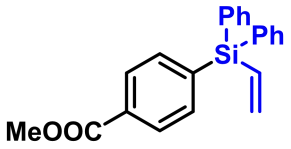


Chemical Formula: $C_{17}H_{18}O_2Si$
Exact Mass: 282.1076

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (109.6 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (31.0 mg, 55% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.62 – 7.60 (m, 1H), 7.62 – 7.60 (m, 2H), 7.39 – 7.37 (m, 3H), 6.52 – 6.43 (m, H), 6.25 – 6.20 (m, 1H), 5.83 – 5.77 (m, 1H), 3.92 (s, 3H), 0.66 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.35, 142.85, 135.64, 135.54, 135.20, 134.95, 133.75, 130.96, 129.71, 128.71, 128.12, 52.24, -4.15 ppm. **HRMS** (ESI) for $C_{17}H_{19}O_2Si^+$ [$(M+H)^+$]: calculated 283.1149, found 283.1149.

Methyl 4-(diphenyl(vinyl)silyl)benzoate (20)



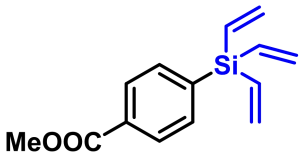
Chemical Formula: $C_{22}H_{20}O_2Si$
Exact Mass: 344.1233

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (146.9 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified

by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (29.6 mg, 43% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.63 – 7.61 (m, 2H), 7.52 – 7.51 (m, 4H), 7.44 – 7.38 (m, 6H), 6.74 – 6.65 (m, H), 6.37 – 6.33 (m, 1H), 5.84 – 5.78 (m, 1H), 3.92 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.34, 140.88, 137.53, 136.06, 133.55, 133.31, 131.21, 129.97, 128.72, 128.16, 52.28 ppm. **HRMS** (ESI) for $C_{22}H_{20}O_2NaSi^+$ [$(M+Na)^+$]: calculated 367.1125, found 367.1125.

Methyl 4-(trivinylsilyl)benzoate (21)

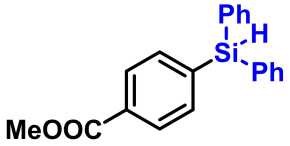


Chemical Formula: $C_{14}H_{16}O_2Si$
Exact Mass: 244.0920

Prepared according to the general procedure A using **1a** (43.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (86.8 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.4 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in DMA (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (32.7 mg, 67% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.64 – 7.62 (m, 2H), 6.36 – 6.20 (m, 6H), 5.86 – 5.80 (m, 3H), 3.92 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.33, 141.02, 136.64, 135.16, 133.15, 130.99, 128.67, 52.25 ppm. **HRMS** (ESI) for $C_{14}H_{16}O_2NaSi^+$ [$(M+Na)^+$]: calculated 267.0812, found 267.0812.

Methyl 4-(diphenylsilyl)benzoate (22)



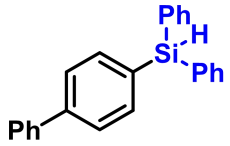
Chemical Formula: $C_{20}H_{18}O_2Si$
Exact Mass: 318.1076

Prepared according to the general procedure B using **1a** (43.0 mg, 0.2 mmol, 1.0

equiv.), **2a** (131.2 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 3,4,7,8-tetramethyl-1,10-phenanthroline (9.5 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in MeCN / DMAc (7 : 3, 0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (33.1 mg, 52% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.04 (m, 2H), 7.69 – 7.68 (m, 2H), 7.59 – 7.58 (m, 4H), 7.47 – 7.45 (m, 2H), 7.42 – 7.39 (m, 4H), 5.52 (s, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.23, 139.86, 135.91(2 C), 132.59, 131.38, 128.89, 128.33, 52.30 ppm. **HRMS** (ESI) for $C_{20}H_{19}O_2Si^+$ [$(M+H)^+$]: calculated 319.1149, found 319.1157.

[1,1'-Biphenyl]-4-yldiphenylsilane (23)

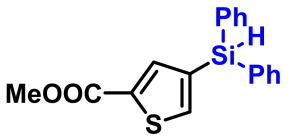


Chemical Formula: $C_{24}H_{20}Si$
Exact Mass: 336.1334

Prepared according to the general procedure B using **1a** (46.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (131.2 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 3,4,7,8-tetramethyl-1,10-phenanthroline (9.5 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in MeCN / DMAc (7 : 3, 0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (30.2 mg, 45% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.70 (m, 2H), 7.67 – 7.64 (m, 7H), 7.49 – 7.39 (m, 10H), 5.52 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.70, 141.02, 136.44, 135.97, 133.46, 132.18, 130.01, 128.95, 128.24, 127.69, 127.32, 126.93 ppm. **HRMS** (ESI) for $C_{24}H_{20}NaSi^+$ [$(M+Na)^+$]: calculated 359.1226, found 359.1232.

Methyl 4-(diphenylsilyl)thiophene-2-carboxylate (24)



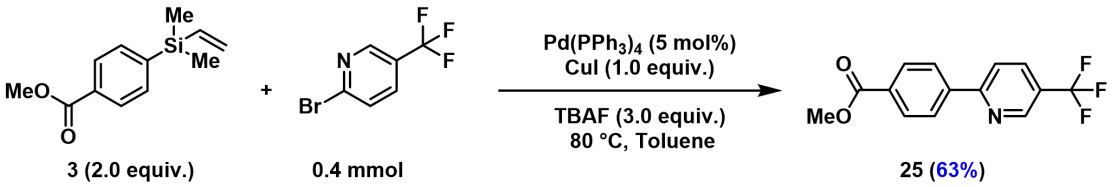
Chemical Formula: $C_{18}H_{16}O_2SSi$
Exact Mass: 324.0640

Prepared according to the general procedure B using **1a** (44.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (131.2 mg, 0.6 mmol, 3.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 3,4,7,8-tetramethyl-1,10-phenanthroline (9.5 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.) in MeCN / DMAc (7 : 3, 0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (27.2 mg, 42% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.93 (m, H), 7.74 – 7.74 (m, 1H), 7.59 – 7.58 (m, 4H), 7.47 – 7.39 (m, 6H), 5.52 (s, 1H), 3.88 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.79, 141.95, 139.36, 135.65, 135.60, 135.20, 132.65, 130.30, 128.37, 52.32 ppm. **HRMS** (ESI) for $C_{18}H_{17}O_2SSi^+$ [$(M+H)^+$]: calculated 325.0713, found 325.0714.

6 Synthetic Application and Mechanistic Studies

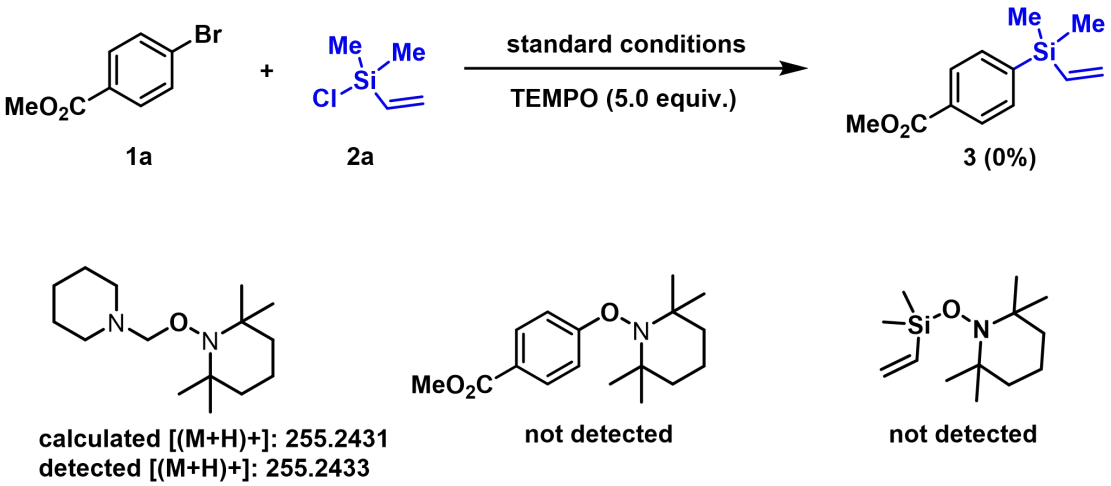
6.1 Synthetic application



An oven-dried vial equipped with a stir-bar was added $Pd(PPh_3)_4$ (23.2 mg, 0.02 mmol), CuI (76.2 mg, 0.4 mmol), and $TBAF{\cdot}3H_2O$ (378.6 mg, 1.2 mmol). A solution of arylsilanes 3 (0.8 mmol) and aryl bromides (0.4 mmol) in PhOMe (2.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the residue was purified by flash chromatography to give the corresponding product.

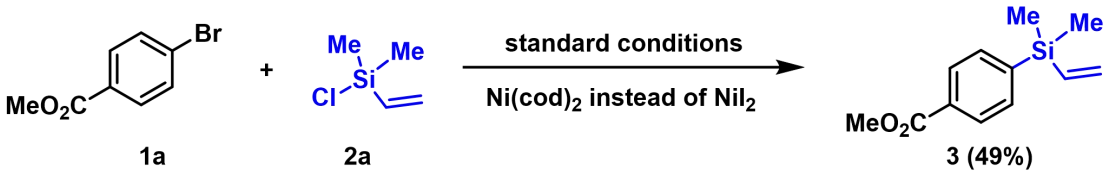
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 – 9.00 (m, H), 8.21 – 8.19 (m, 2H), 8.15 – 8.14 (m, 2H), 8.05 – 8.04 (m, 1H), 7.93 – 7.92 (m, 1H), 3.99 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.79, 159.58, 146.94 (q, $J_{C\text{-}F}$ = 4.0 Hz), 142.05, 134.28 (q, $J_{C\text{-}F}$ = 3.5 Hz), 131.52, 130.34, 127.38, 125.69 (q, $J_{C\text{-}F}$ = 33.2 Hz), 123.73 (q, $J_{C\text{-}F}$ = 271.8 Hz), 120.59, 52.45 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.32 ppm.

6.2 Radical trapping experiment



An oven-dried vial equipped with a stir-bar was added **1a** (43.0 mg, 0.20 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.2 mg, 20 μmol, 0.20 equiv.), NiI_2 (6.4 mg, 20 μmol, 0.10 equiv.), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 156.7 mg, 1.0 mmol, 5.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R1** (69.0 mg, 0.40 mmol, 2.0 equiv.) and **2a** (72.4 mg, 0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The desired product **3** was not detected in this experiment.

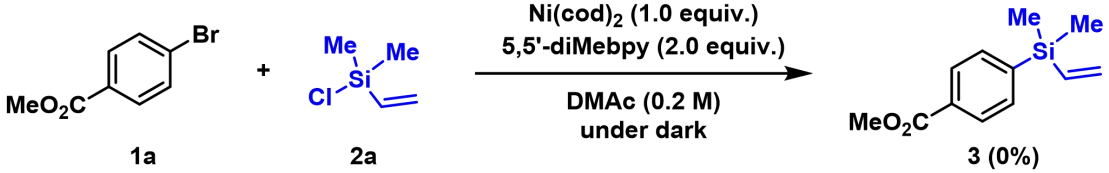
6.3 Control experiment with cat. $Ni(cod)_2$



An oven-dried vial equipped with a stir-bar was added **1a** (43.0 mg, 0.20 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.2 mg, 20 μmol, 0.20 equiv.), $Ni(cod)_2$ (5.4 mg, 20 μmol, 0.10 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R1** (69.0 mg, 0.40 mmol, 2.0 equiv.) and **2a** (72.4 mg, 0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with

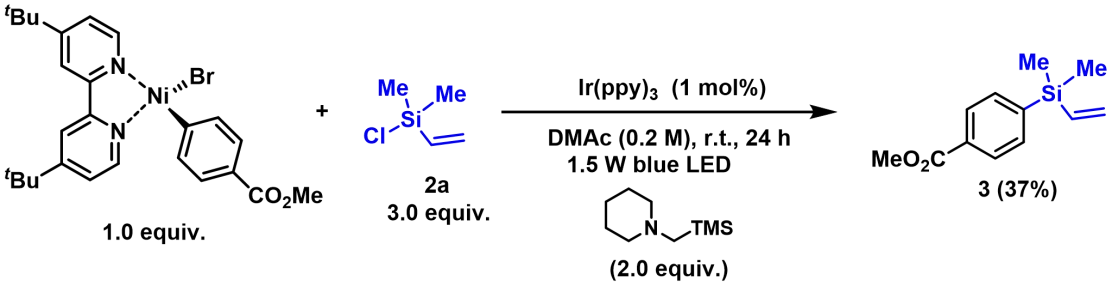
cooling from a fan for 24 h. The desired product **3** was detected in 49% yield.

6.4 Control experiment with stoichio. $Ni(cod)_2$ under dark



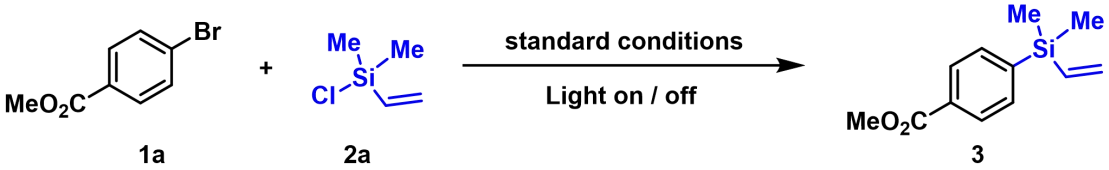
An oven-dried vial equipped with a stir-bar was added **1a** (43.0 mg, 0.20 mmol, 1.0 equiv.), 5,5'-dmbpy (72 mg, 0.40 mmol, 2.0 equiv.), $Ni(cod)_2$ (6.4 mg, 0.20 mmol, 1.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), and **2a** (72.4 mg, 0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox then stirred for 24 h under dark. The desired product **3** was not detected in this experiment.

6.5 Control experiment with $ArNi^{II}$ complex



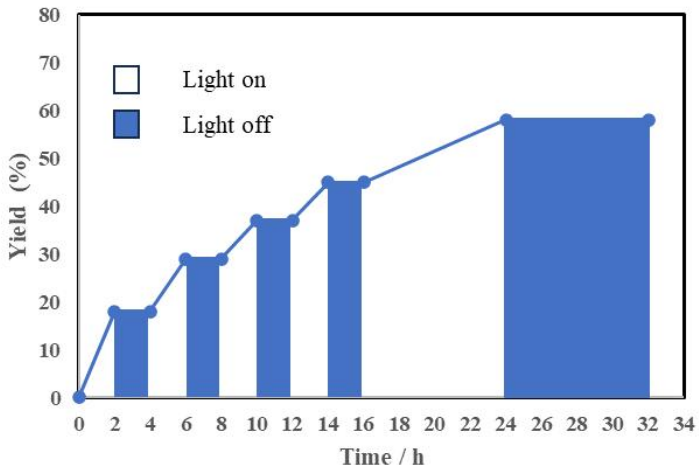
An oven-dried vial equipped with a stir-bar was added $ArNi^{II}$ complex (108 mg, 0.20 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R1** (69.0 mg, 0.40 mmol, 2.0 equiv.) and **2a** (72.4 mg, 0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The desired product **3** was detected in 37% yield.

6.6 Light on-off experiment



An oven-dried vial equipped with a stir-bar was added **1a** (43.0 mg, 0.20 mmol, 1.0

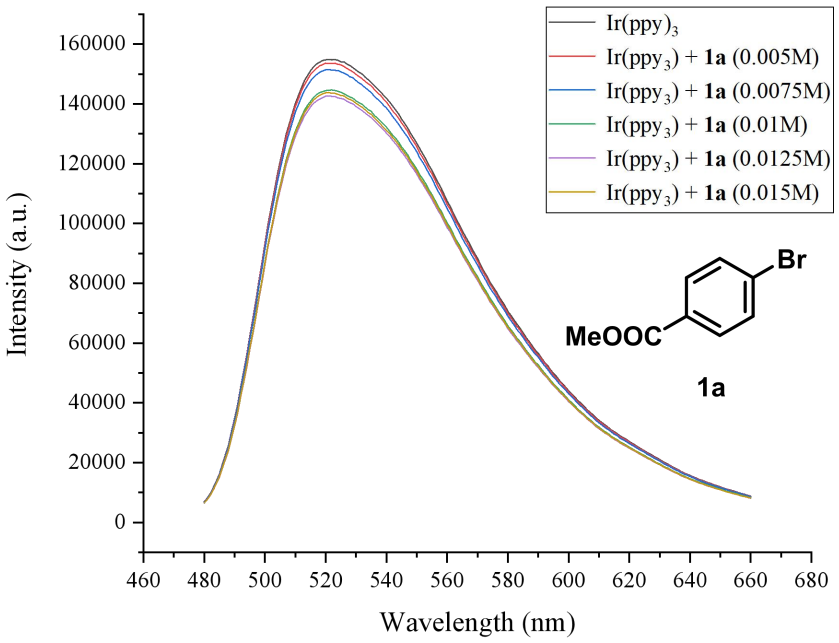
equiv.), $Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-dmbpy (7.2 mg, 20 μmol, 0.20 equiv.), NiI_2 (5.4 mg, 20 μmol, 0.10 equiv.), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 156.7 mg, 1.0 mmol, 5.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R1** (69.0 mg, 0.40 mmol, 2.0 equiv.) and **2a** (72.4 mg, 0.60 mmol, 3.0 equiv.) were added. The resulting mixture was irradiated with a 1.5 W blue LED lamp and stirred at room temperature for 2 h. 50 μL of the reaction mixture was taken from the reaction tube and was analyzed by GC. The tube was then covered with aluminum foil and the reaction mixture was stirred in the dark for 2 h. Another 50 μL of the reaction mixture was taken and analyzed by GC. This procedure was repeated. In the fifth run, the reaction was allowed to perform for 8 h under the irradiation of the blue LED. The time profile is shown in the following figure.



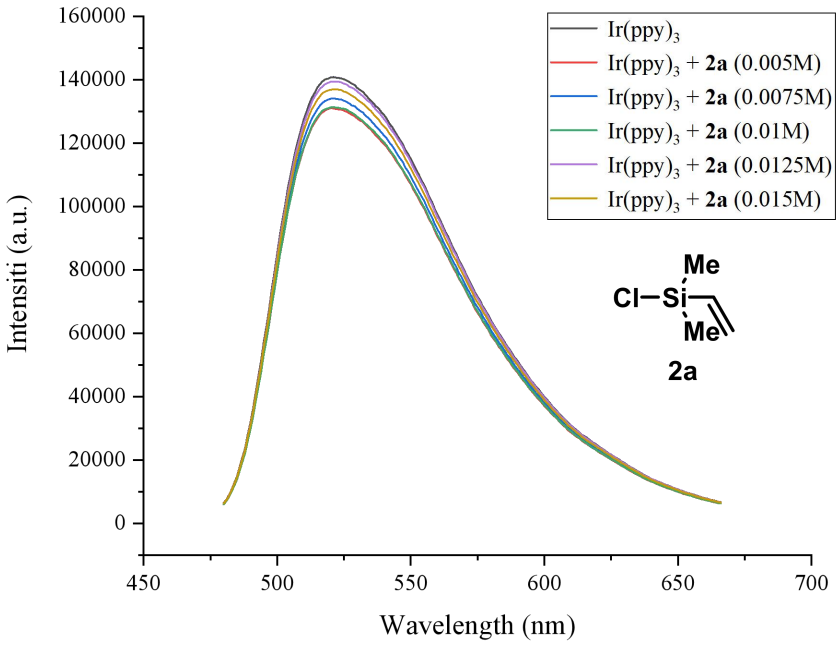
Supplementary Figure 1. Time profile of the trifluoromethylation/cyclization with and without light.

6.7 Fluorescence quenching (Stern-Volmer) studies

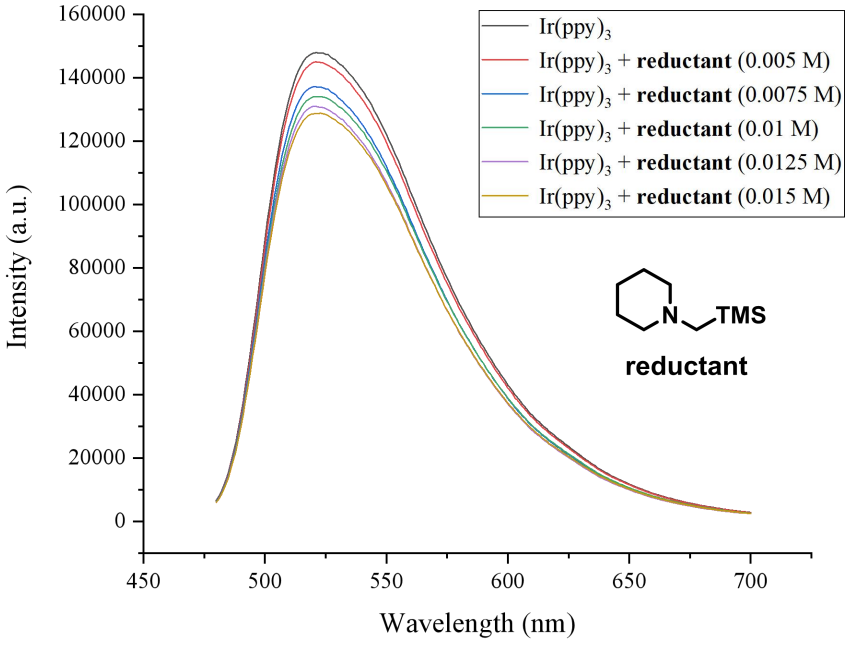
Emission intensities were recorded using Agilent Technologies of Cary Eclipse Fluorescence spectrophotometer. All $Ir(ppy)_3$ solutions were excited at 460 nm and the emission intensity was collected at 480-660 nm. In a typical experiment, to a 1 x 10^{-4} M solution of $Ir(ppy)_3$ in DMAc was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette (we used the relative concentrations of this reaction under standard conditions to compare different components as quenchers). The emission of the sample was collected. The linear slope suggests that NiI_2 is the most efficient quencher of photocatalyst.



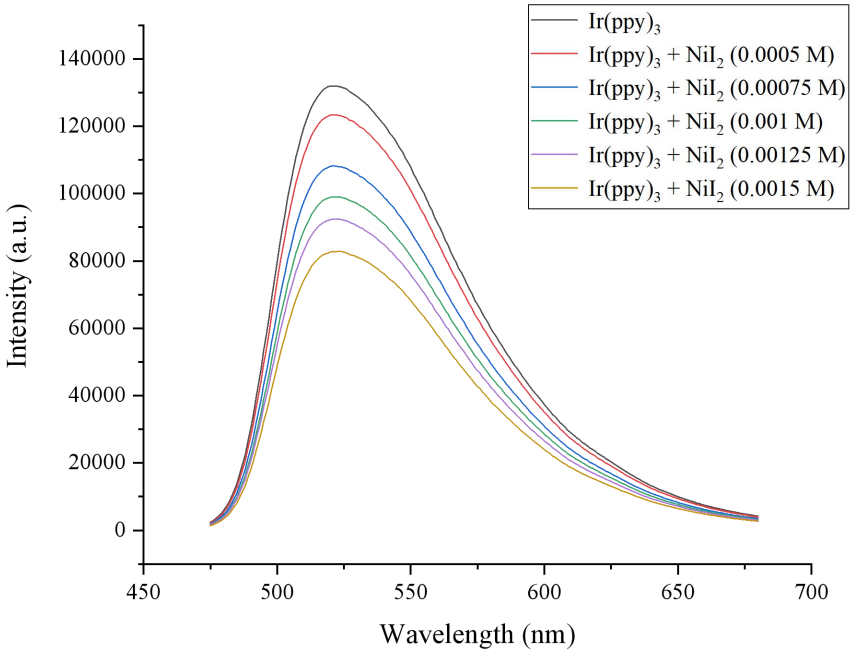
Supplementary Figure 2. Quenching with variable amounts of **1a**



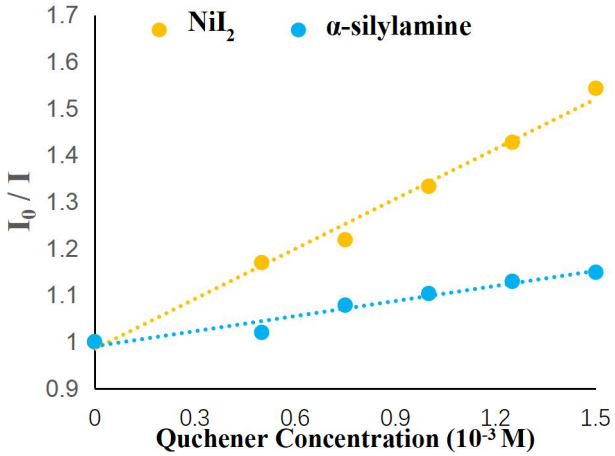
Supplementary Figure 3. Quenching with variable amounts of **2a**



Supplementary Figure 4. Quenching with variable amounts of **reductant**



Supplementary Figure 5. Quenching with variable amounts of **NiI_2**



Supplementary Figure 6. Fluorescence quenching (Stern-Volmer) curve of **NiI_2 and reductant**

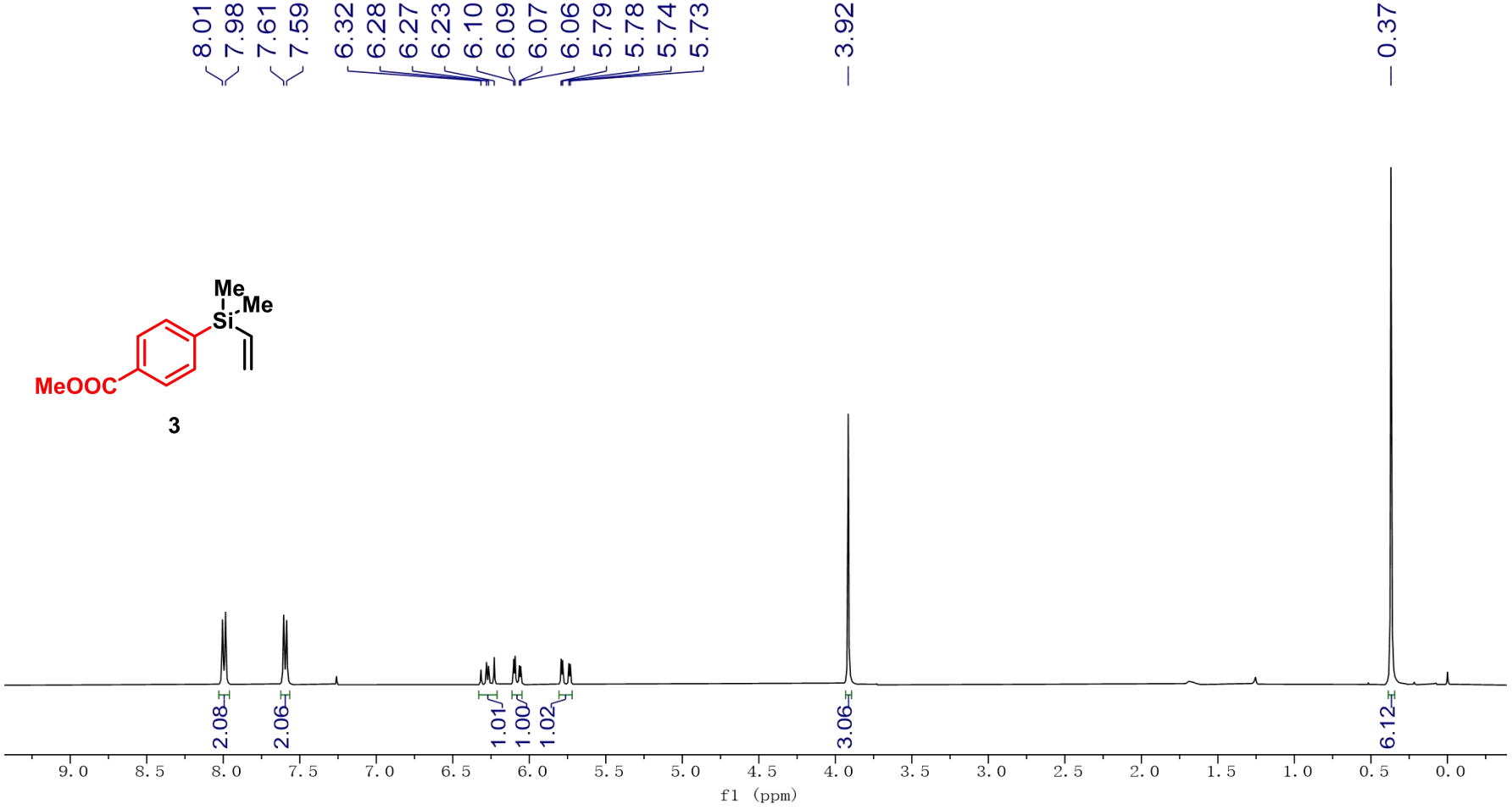
7 References

1. Luo J, Zhang J. Donor–Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic $C(sp^3)-C(sp^2)$ Cross-Coupling. *ACS Catal* 2016;6:873−7. [DOI: 10.1021/acscatal.5b02204]

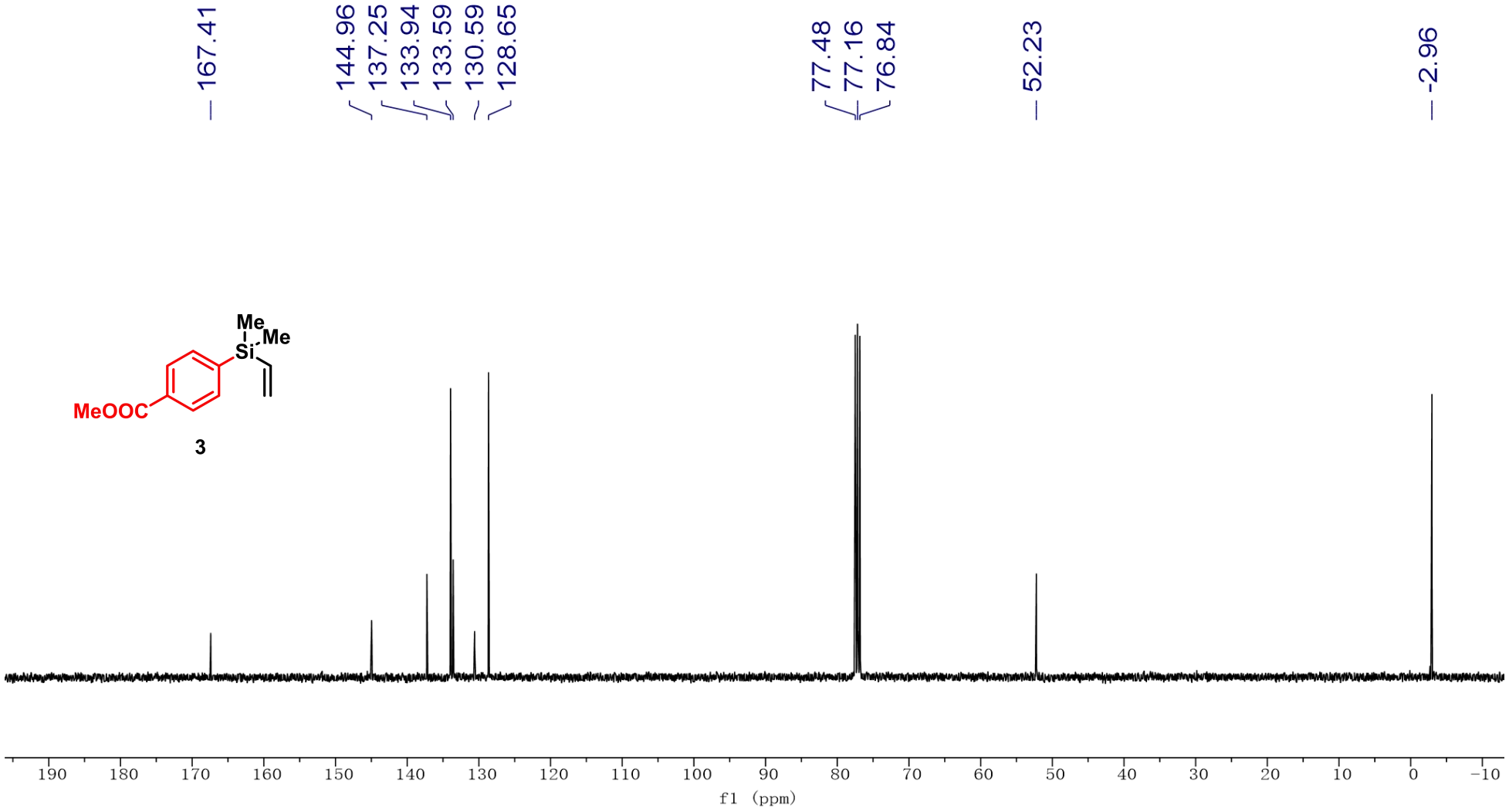
2. Singh A, Teegardin K, Kelly M, Prasad KS, Krishnan S, Weaver JD. Facile synthesis and complete characterization of homoleptic and heteroleptic cyclometalated Iridium(III) complexes for photocatalysis. *J Organomet Chem* 2015;776:51–9. [DOI: 10.1016/j.jorganchem.2014.10.037]

8 NMR Spectra

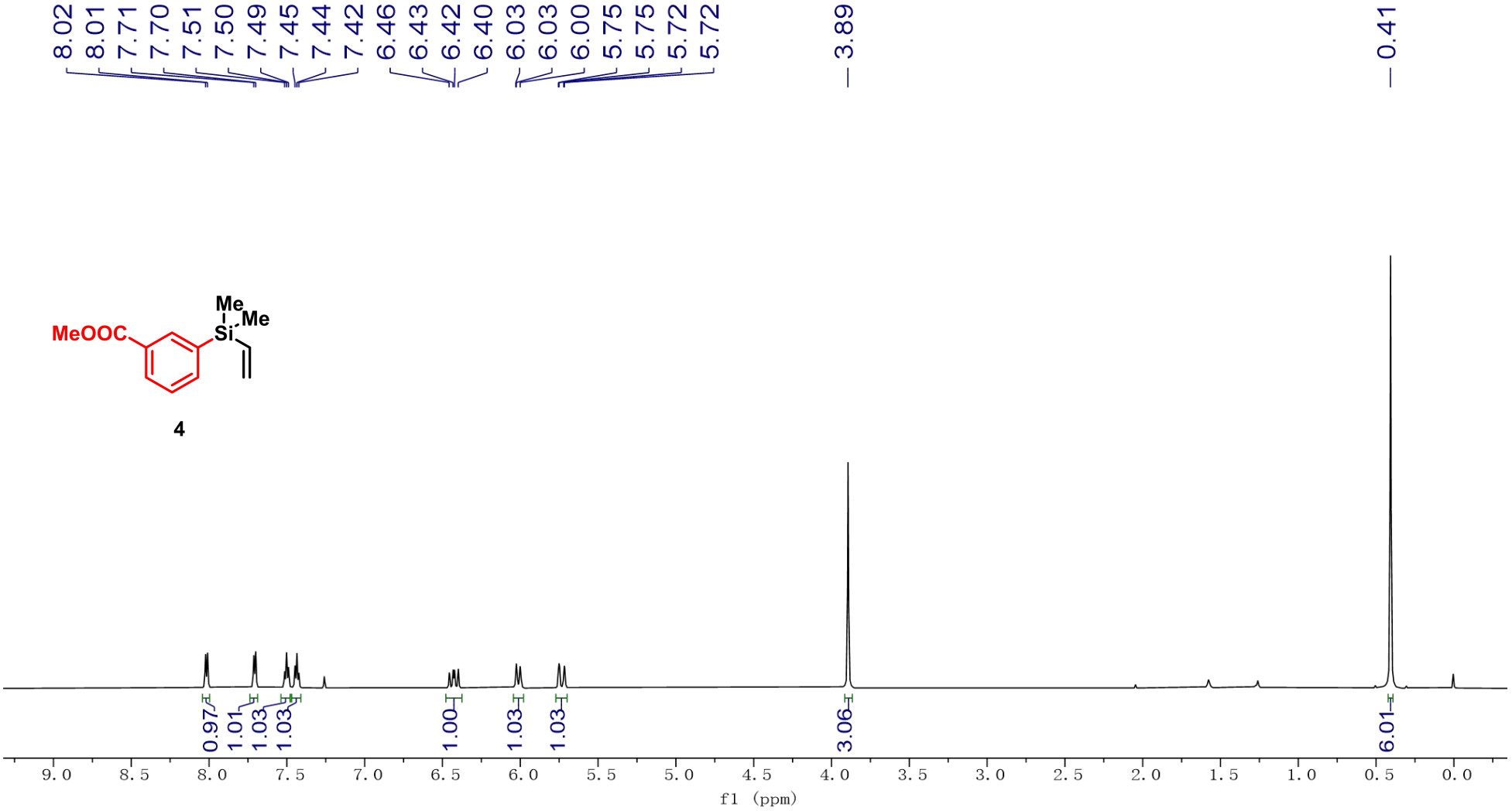
^{1}H NMR of 3 (600 MHz, $CDCl_3$)



^{13}C NMR of 3 (151 MHz, $CDCl_3$)

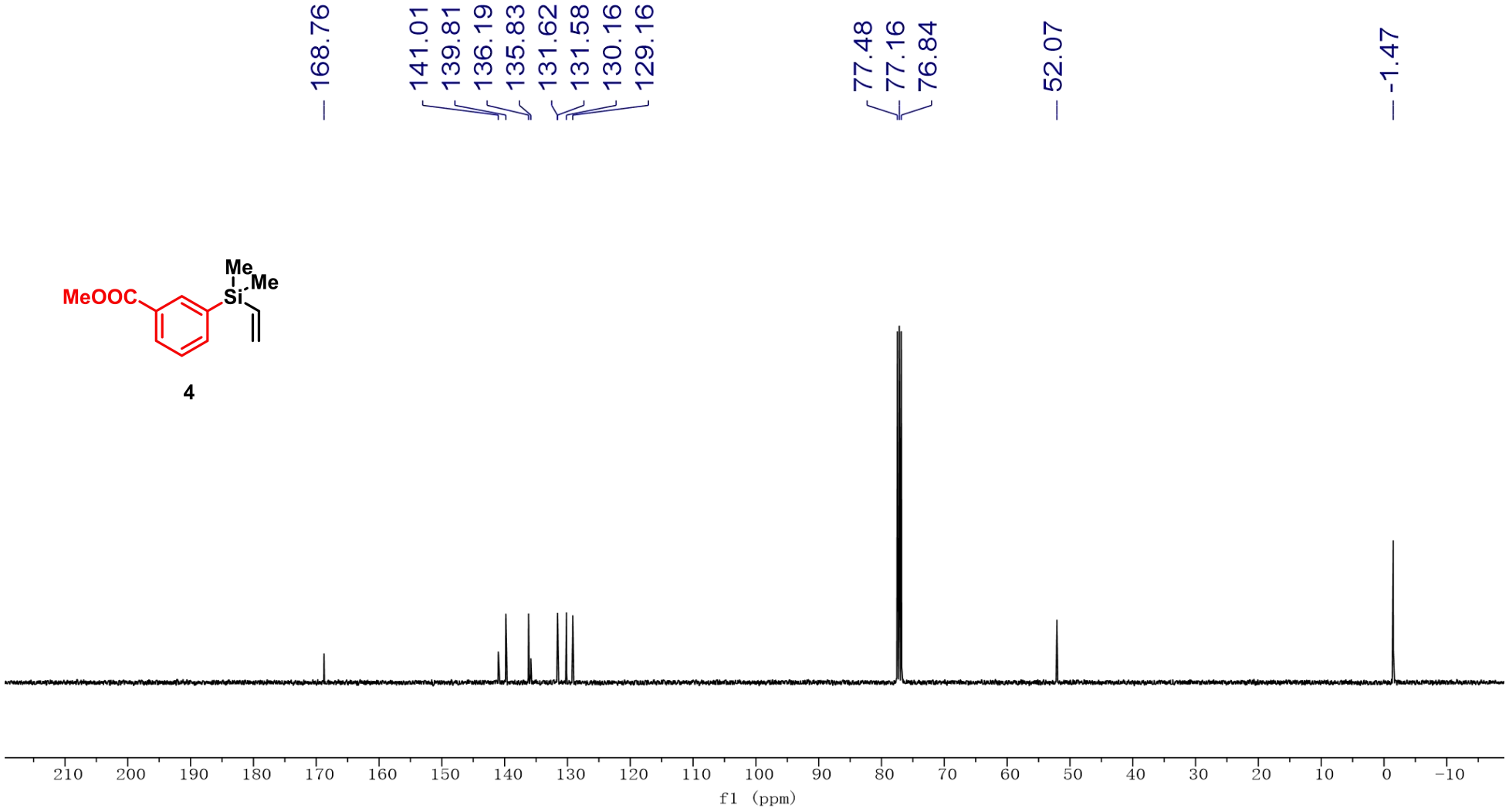


^{1}H NMR of 4 (600 MHz, $CDCl_3$)

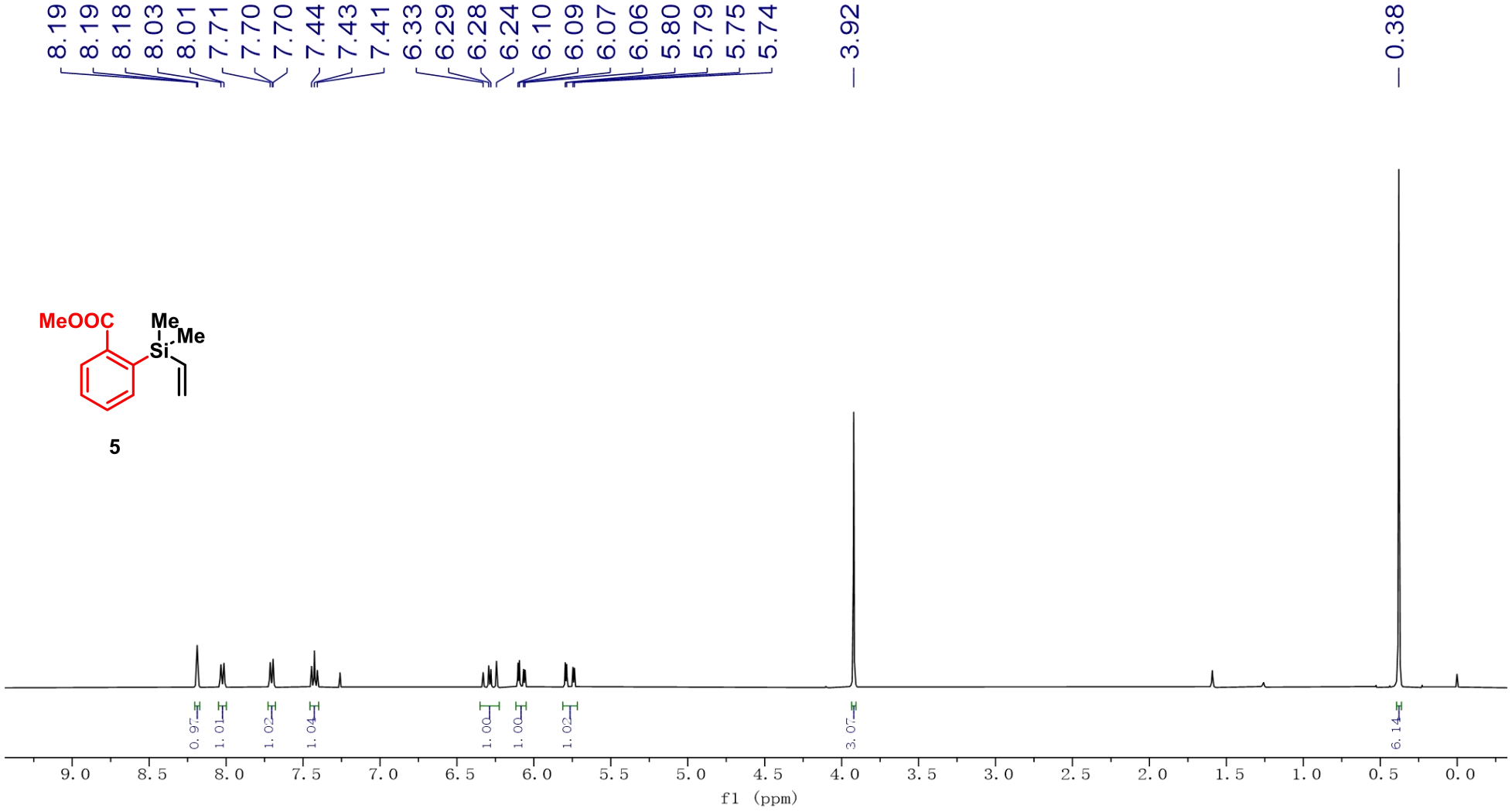


4

^{13}C NMR of 4 (151 MHz, $CDCl_3$)

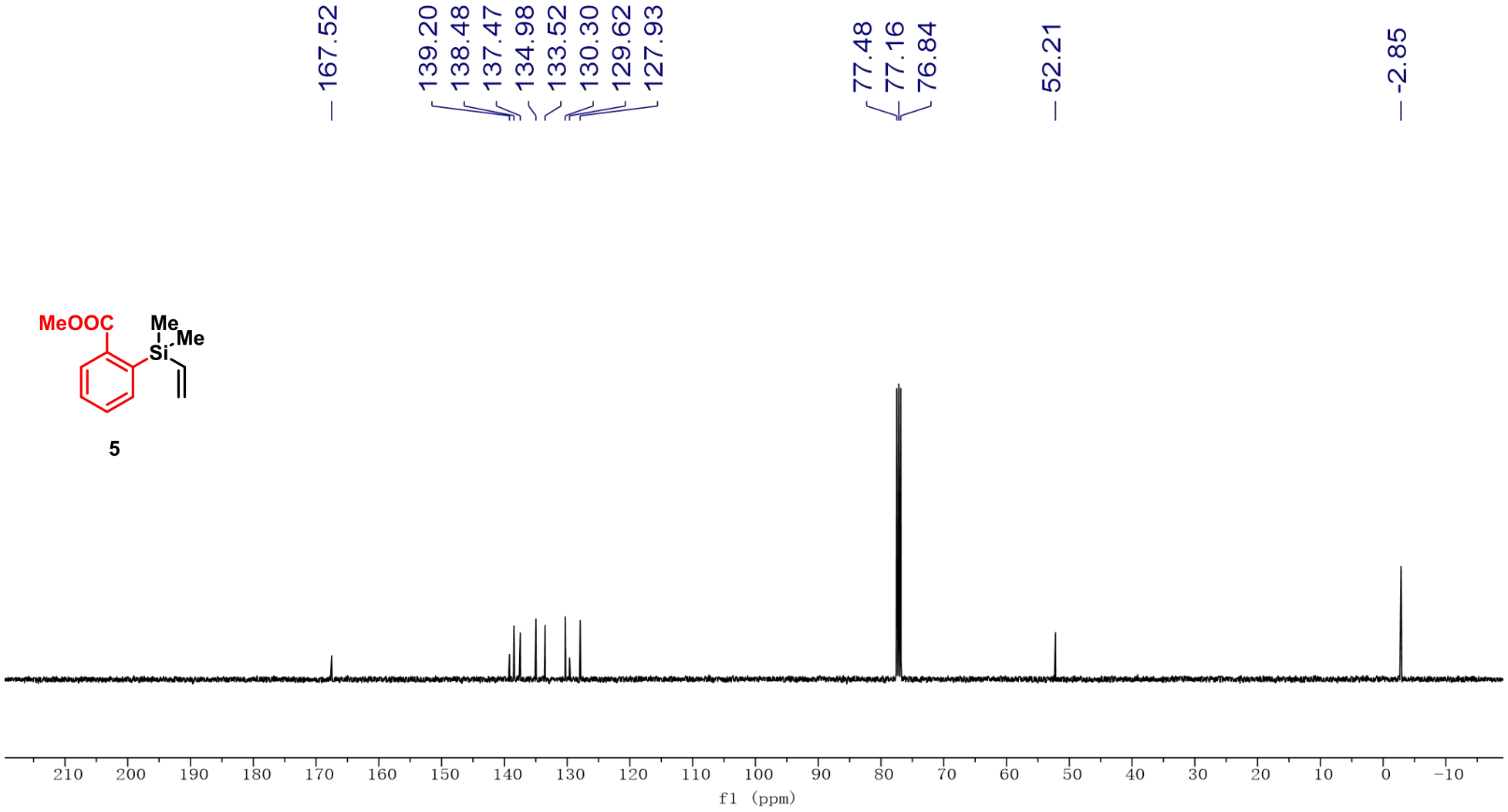


^{1}H NMR of 5 (600 MHz, $CDCl_3$)

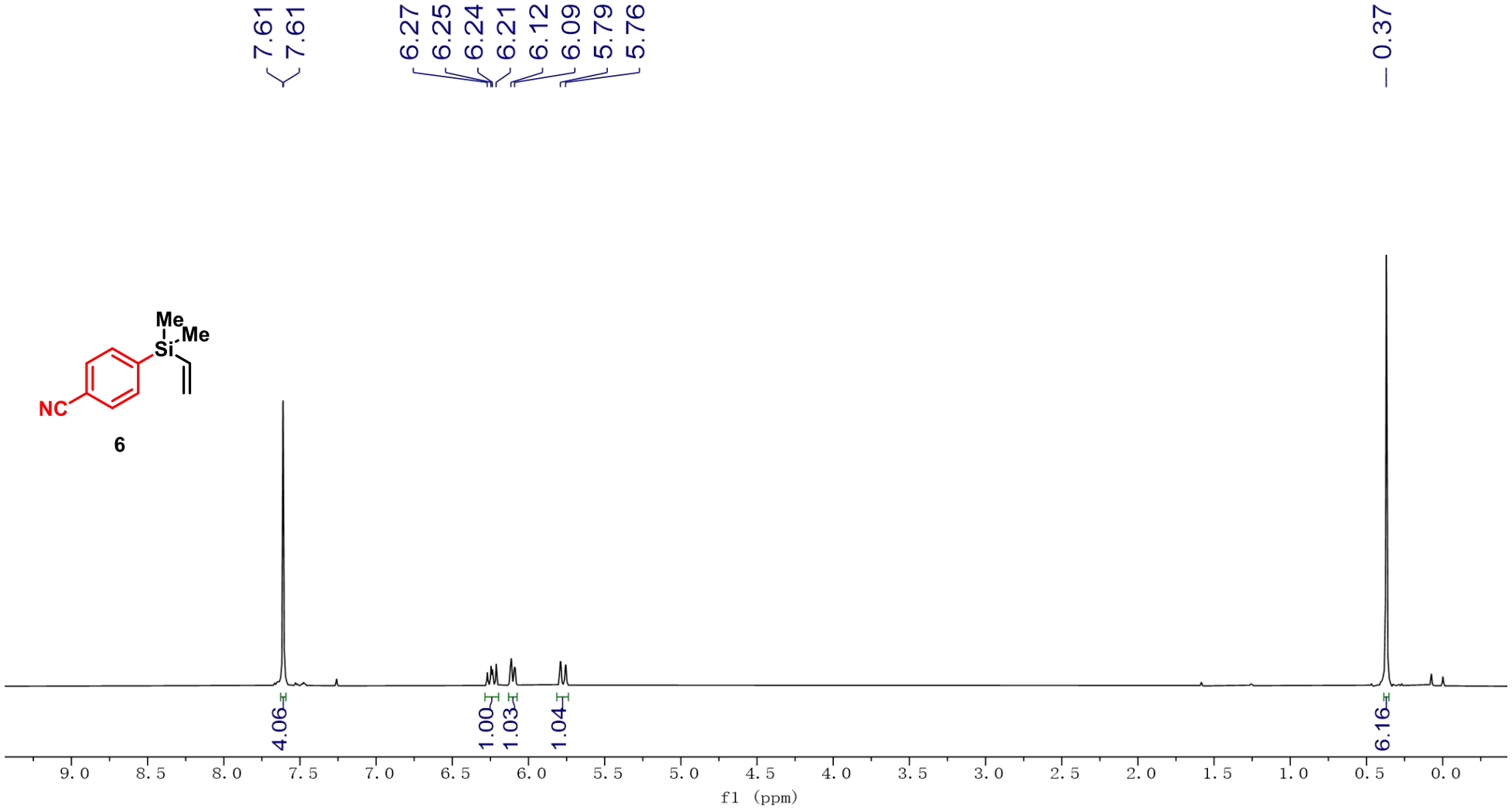


5

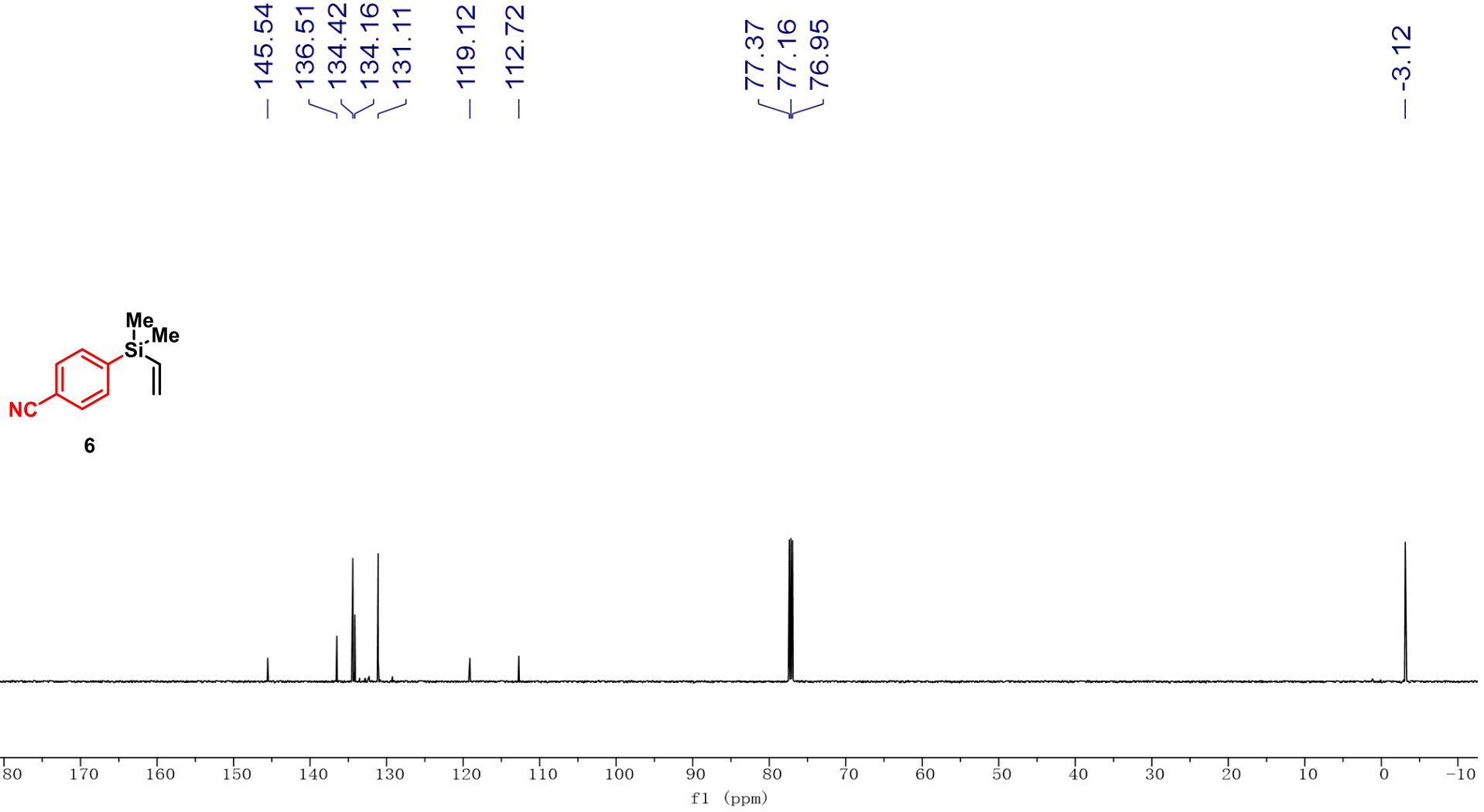
^{13}C NMR of 5 (151 MHz, $CDCl_3$)



^{1}H NMR of 6 (400 MHz, $CDCl_3$)

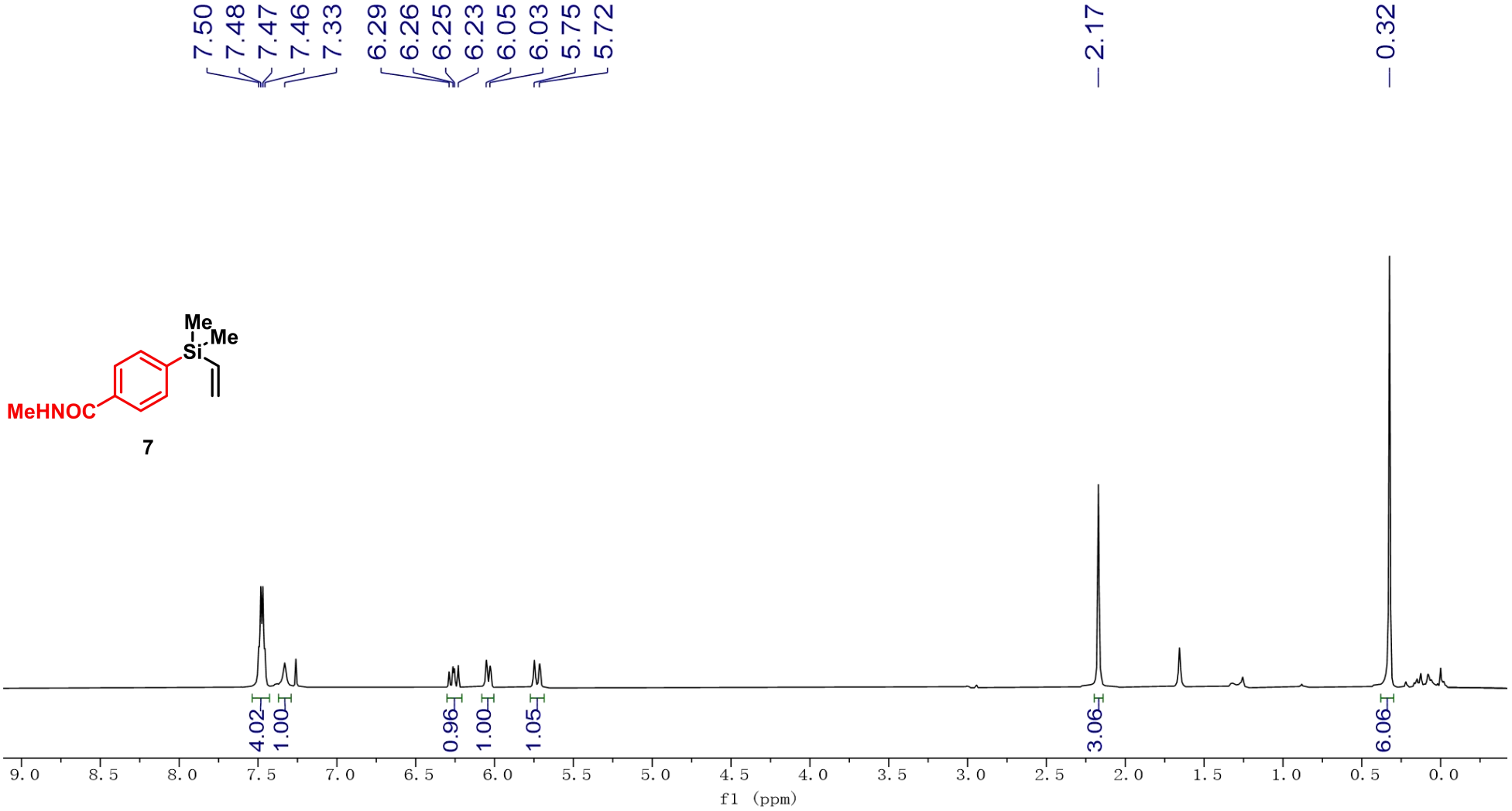


^{13}C NMR of 6 (101 MHz, $CDCl_3$)

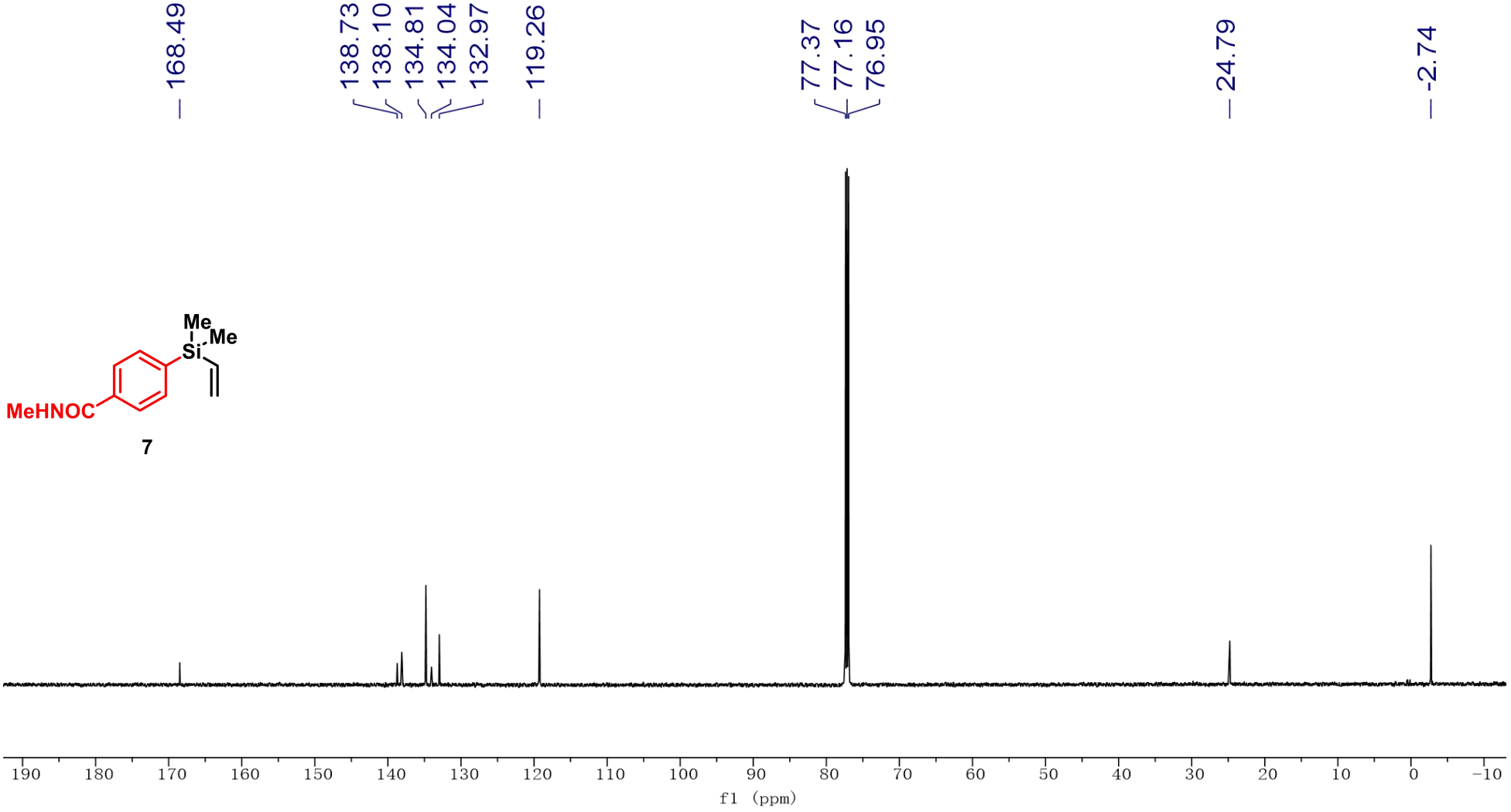


6

^{1}H NMR of 7 (400 MHz, $CDCl_3$)

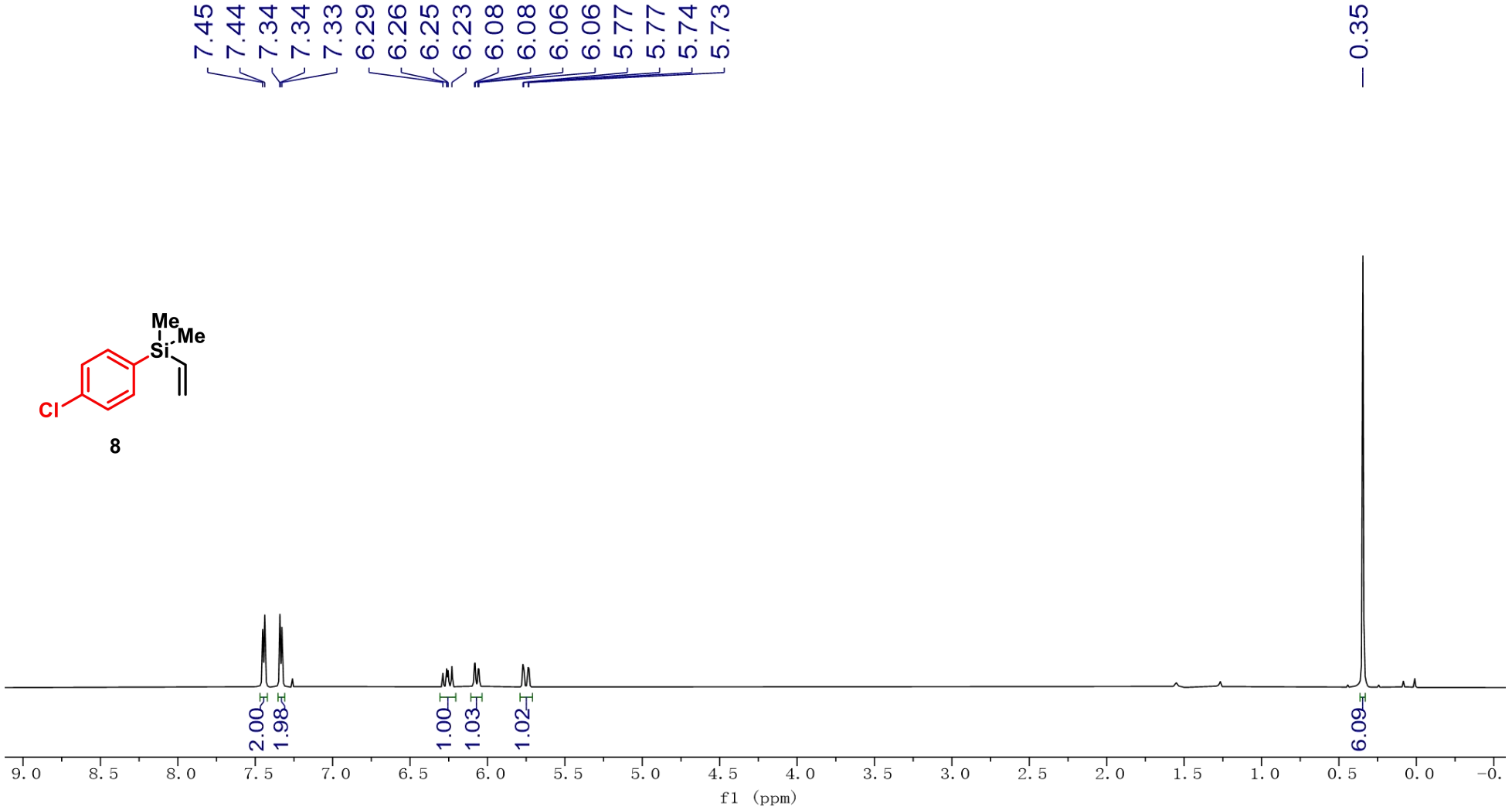


^{13}C NMR of 7 (101 MHz, $CDCl_3$)



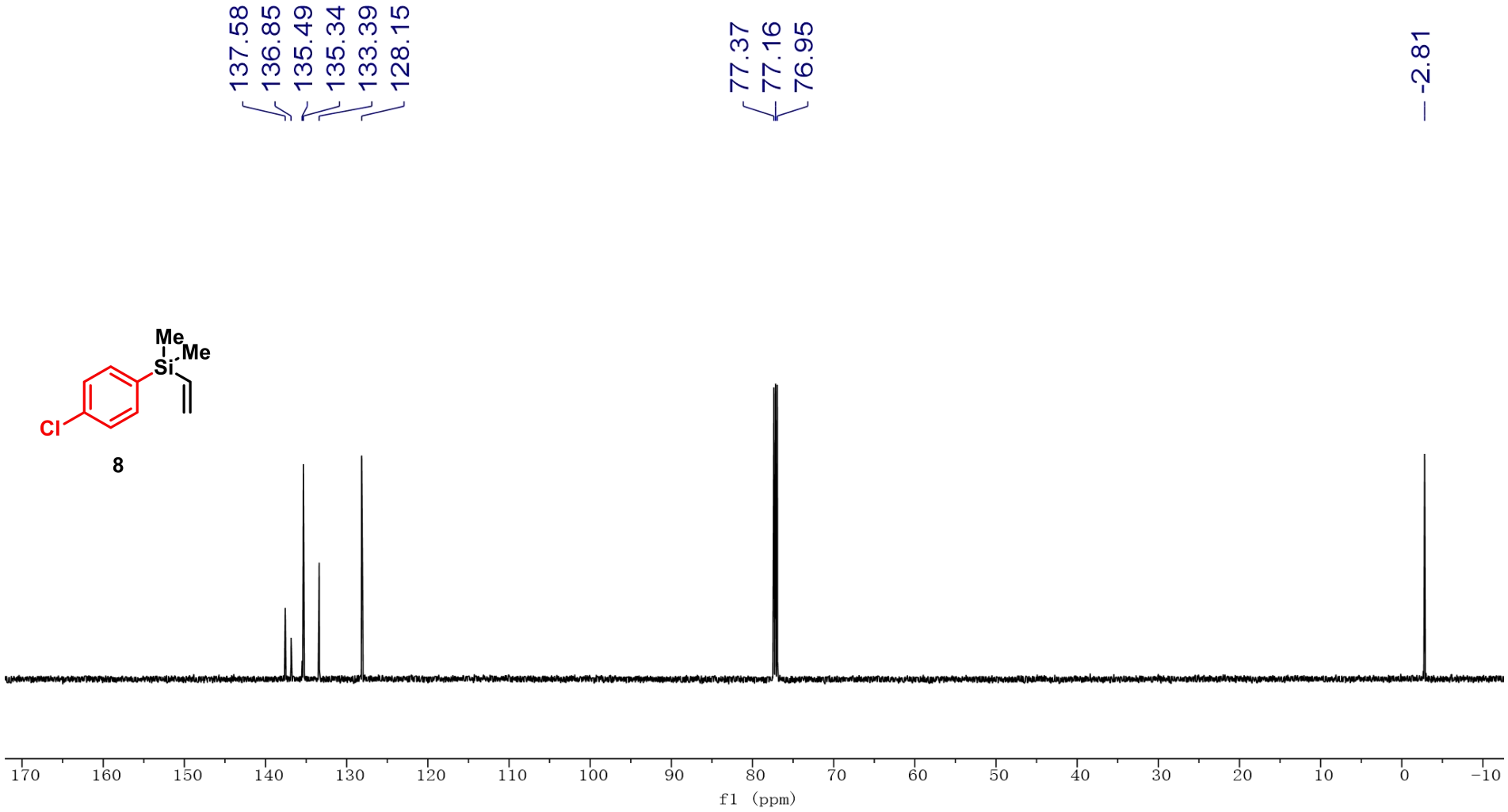
7

^{1}H NMR of 8 (600 MHz, $CDCl_3$)

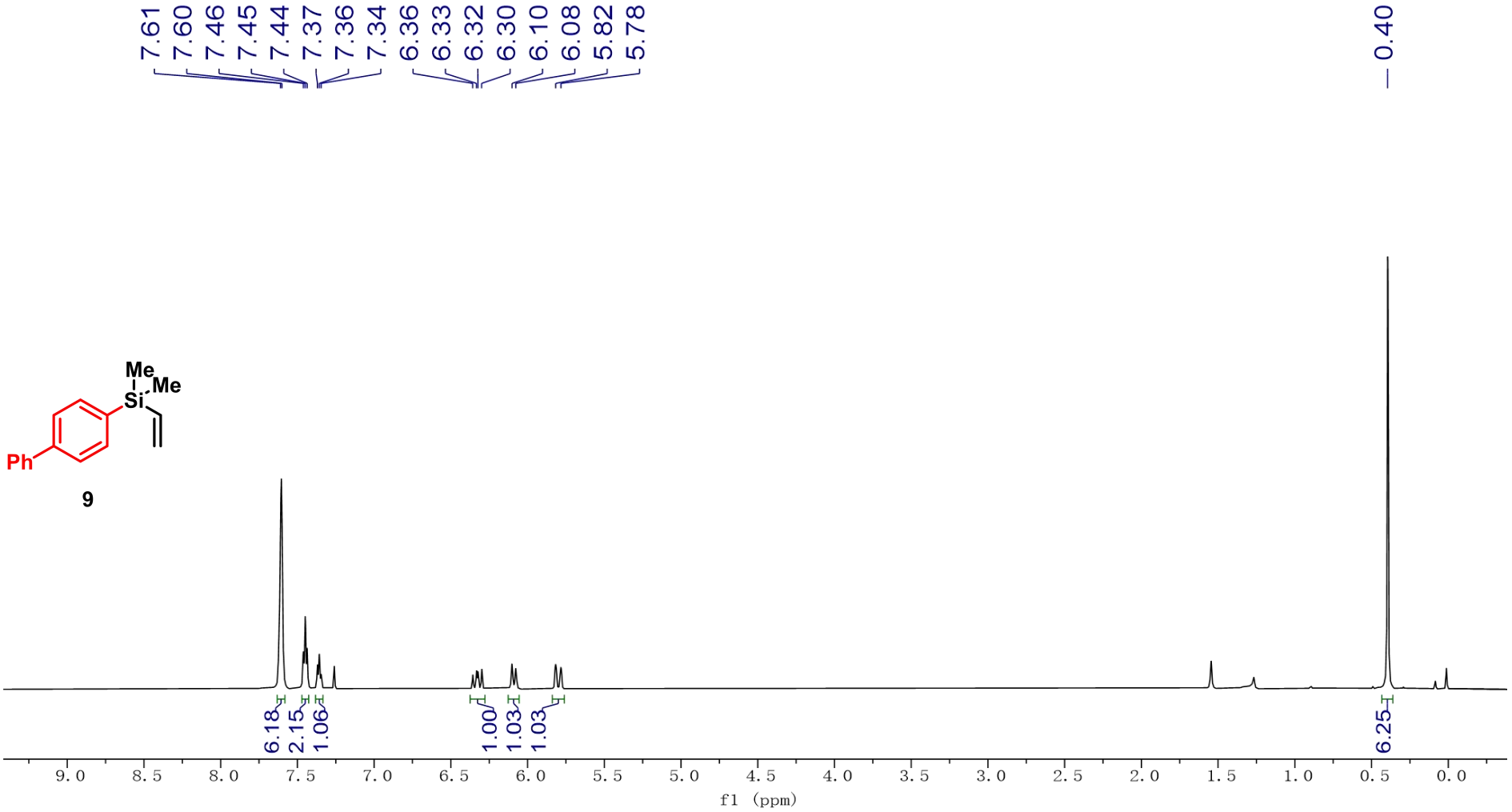


8

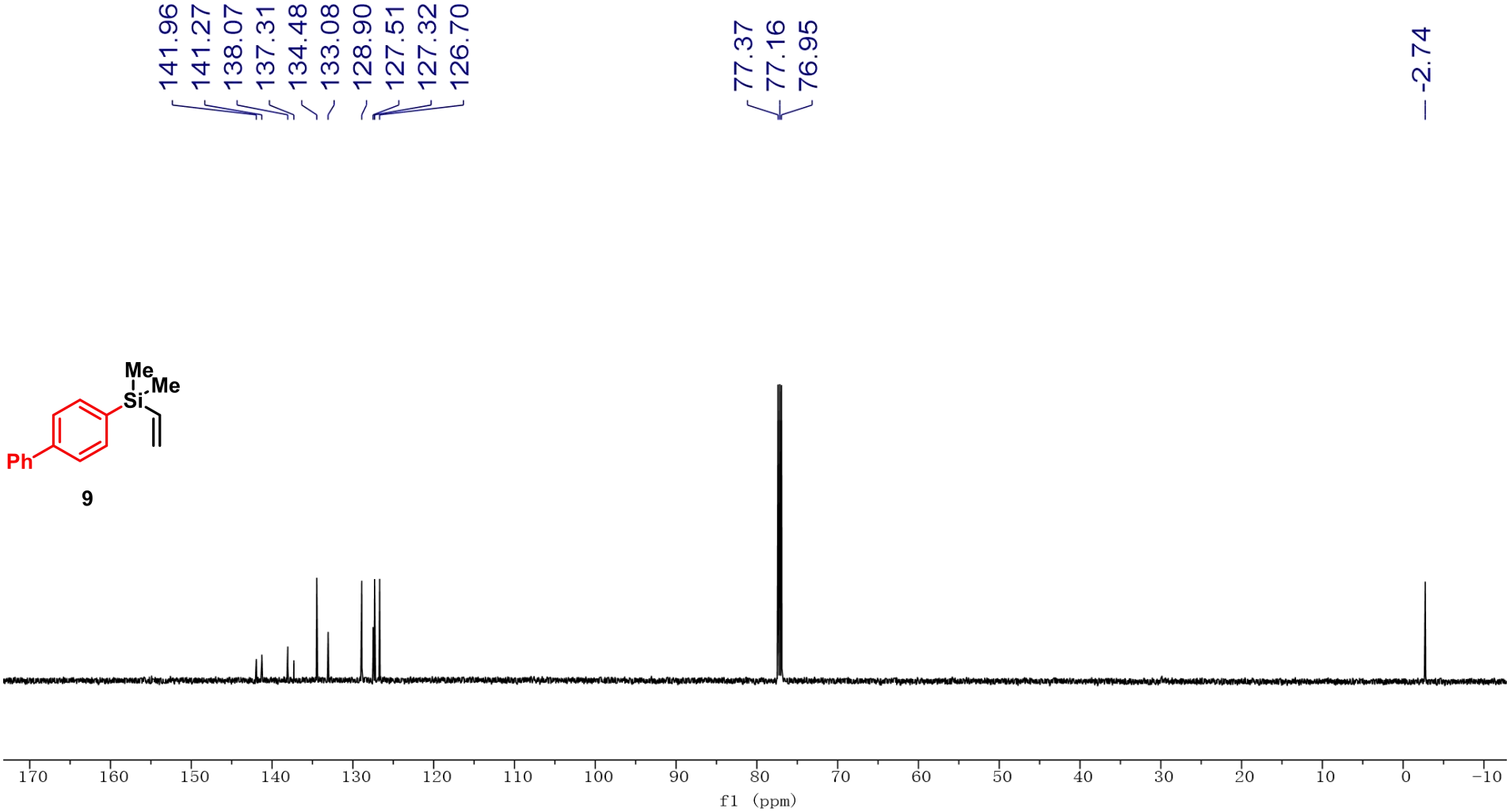
^{13}C NMR of 8 (151 MHz, $CDCl_3$)



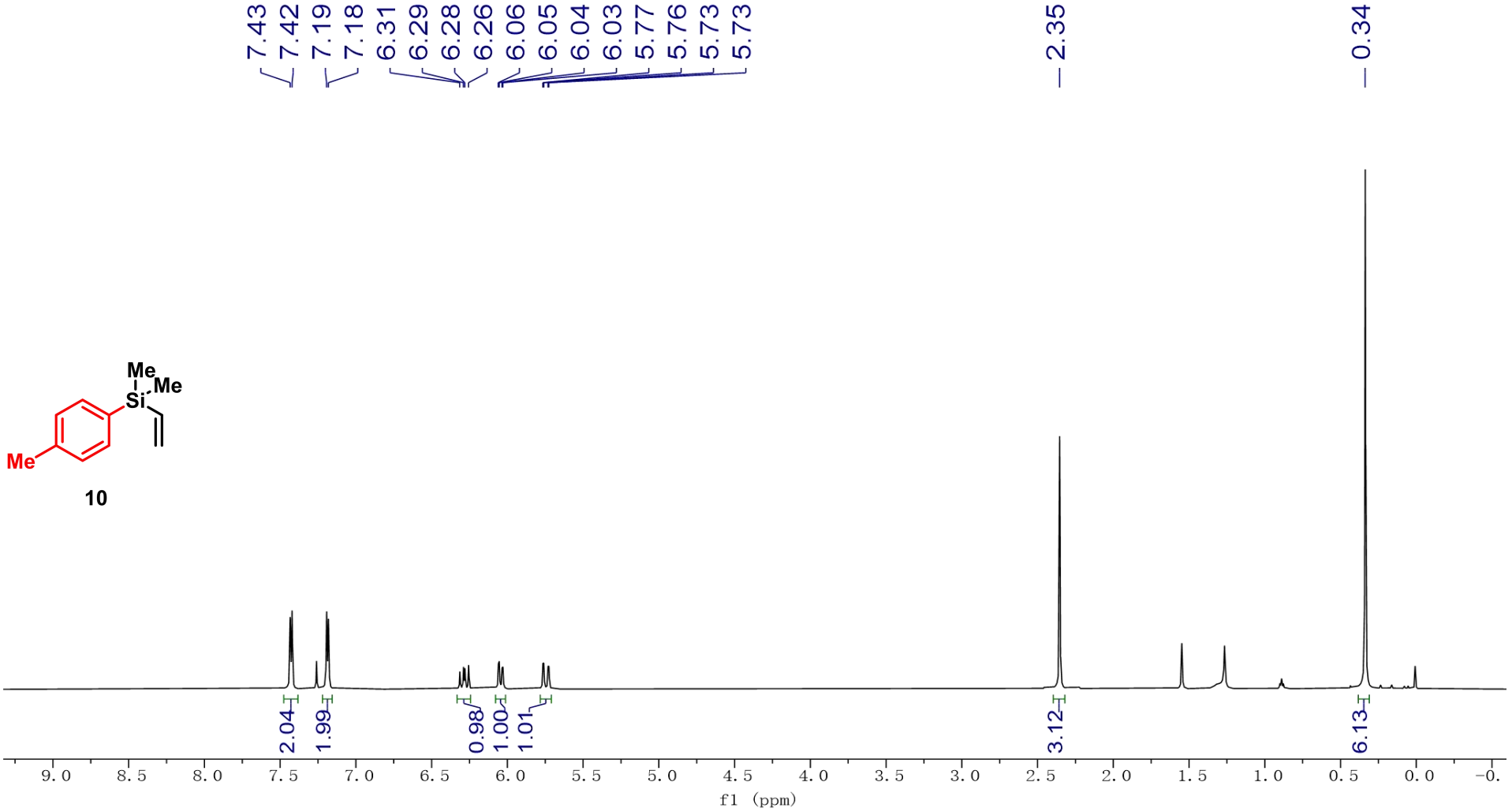
^{1}H NMR of 9 (600 MHz, $CDCl_3$)



^{13}C NMR of 9 (151 MHz, $CDCl_3$)

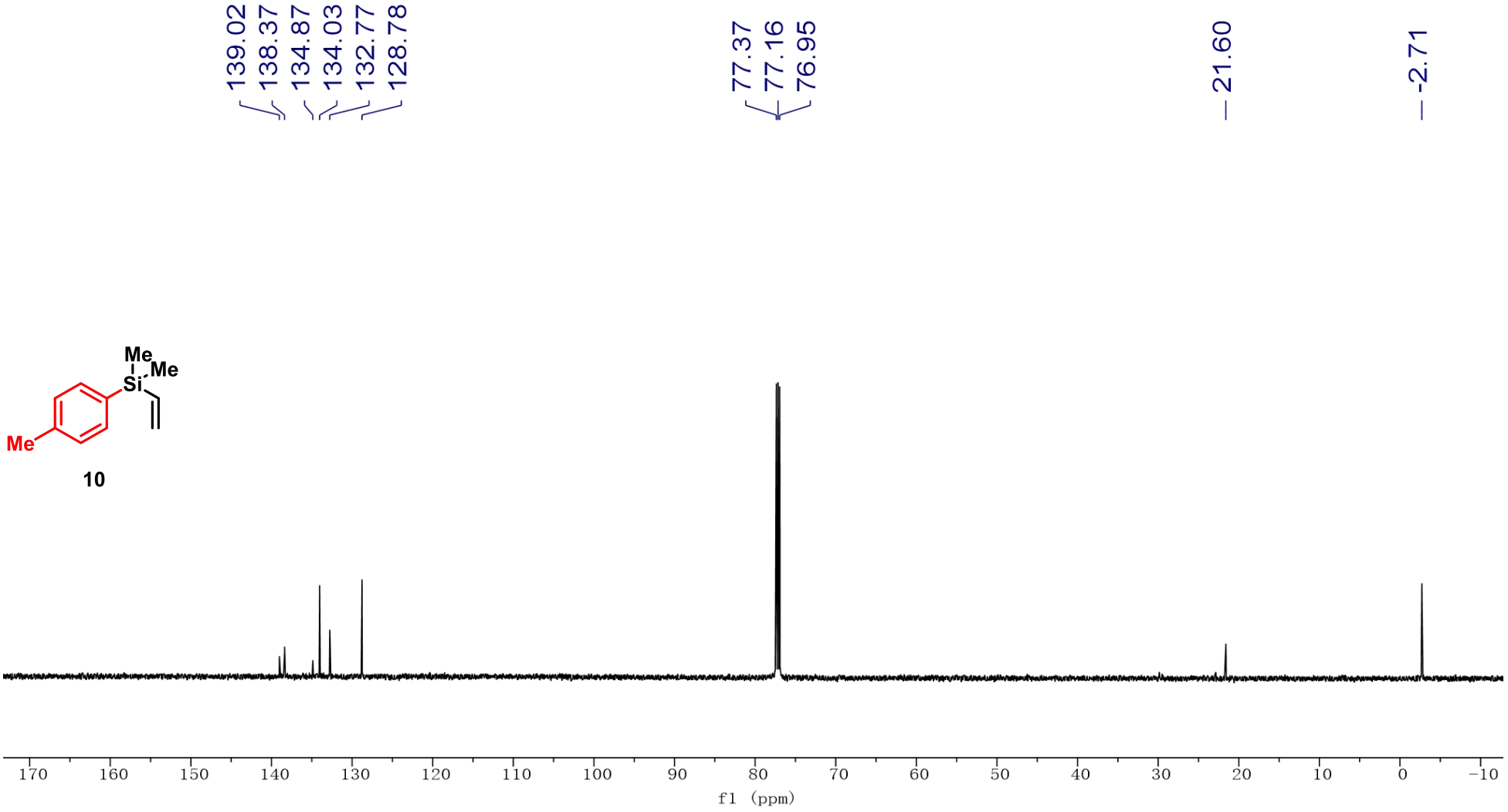


^{1}H NMR of 10 (600 MHz, $CDCl_3$)

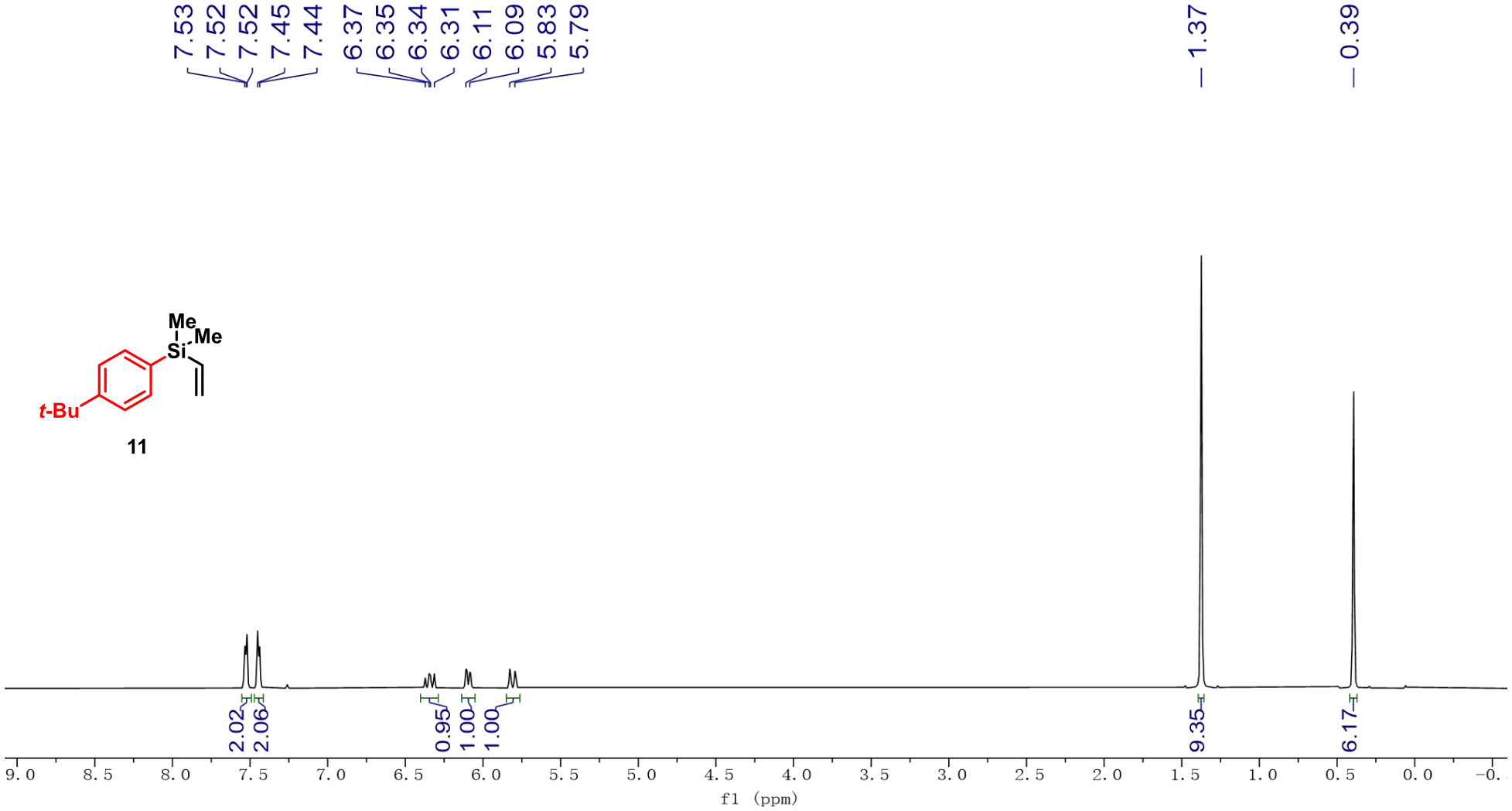


10

^{13}C NMR of 10 (151 MHz, $CDCl_3$)

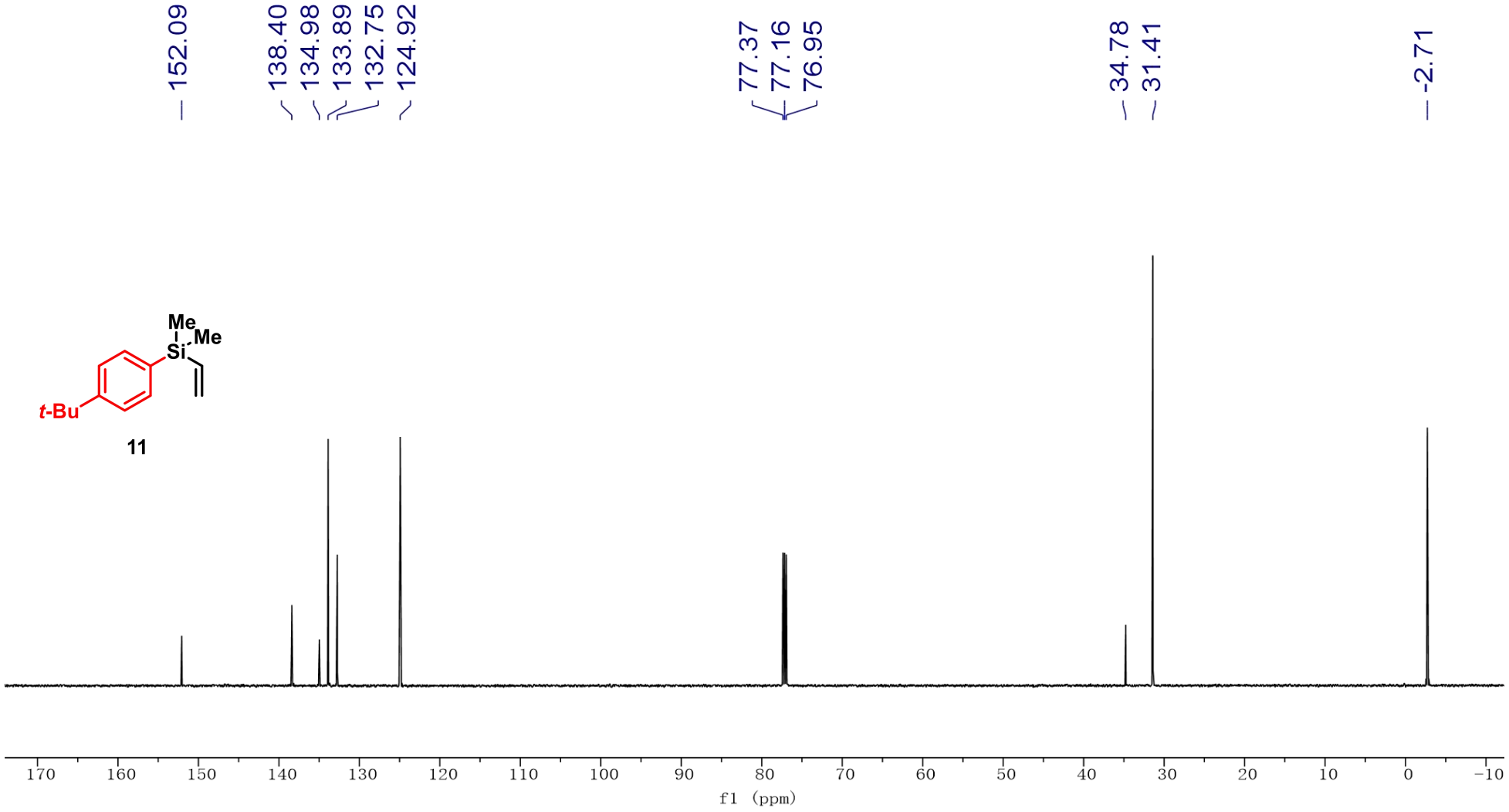


^{1}H NMR of 11 (400 MHz, $CDCl_3$)

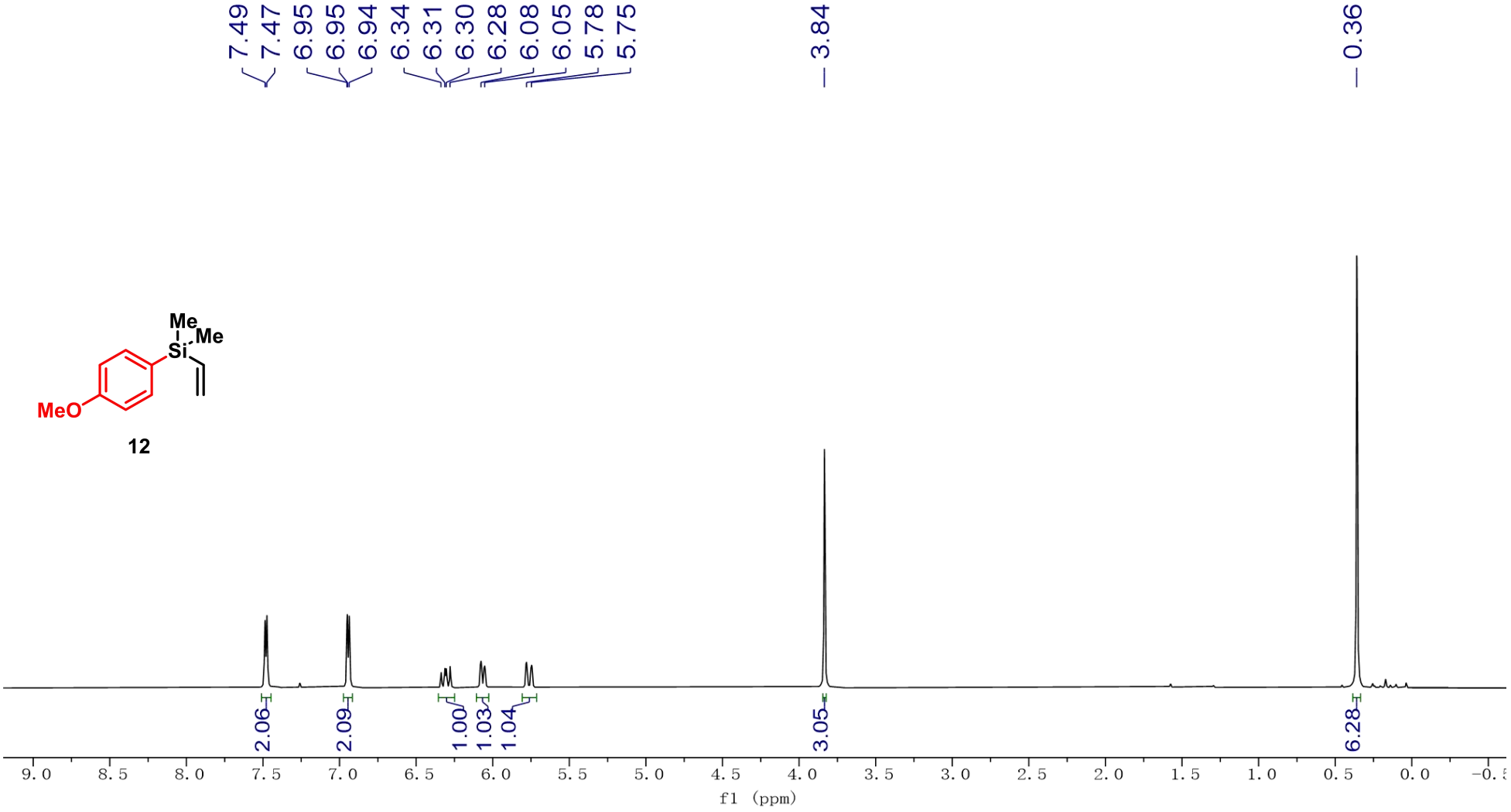


11

^{13}C NMR of 11 (151 MHz, $CDCl_3$)

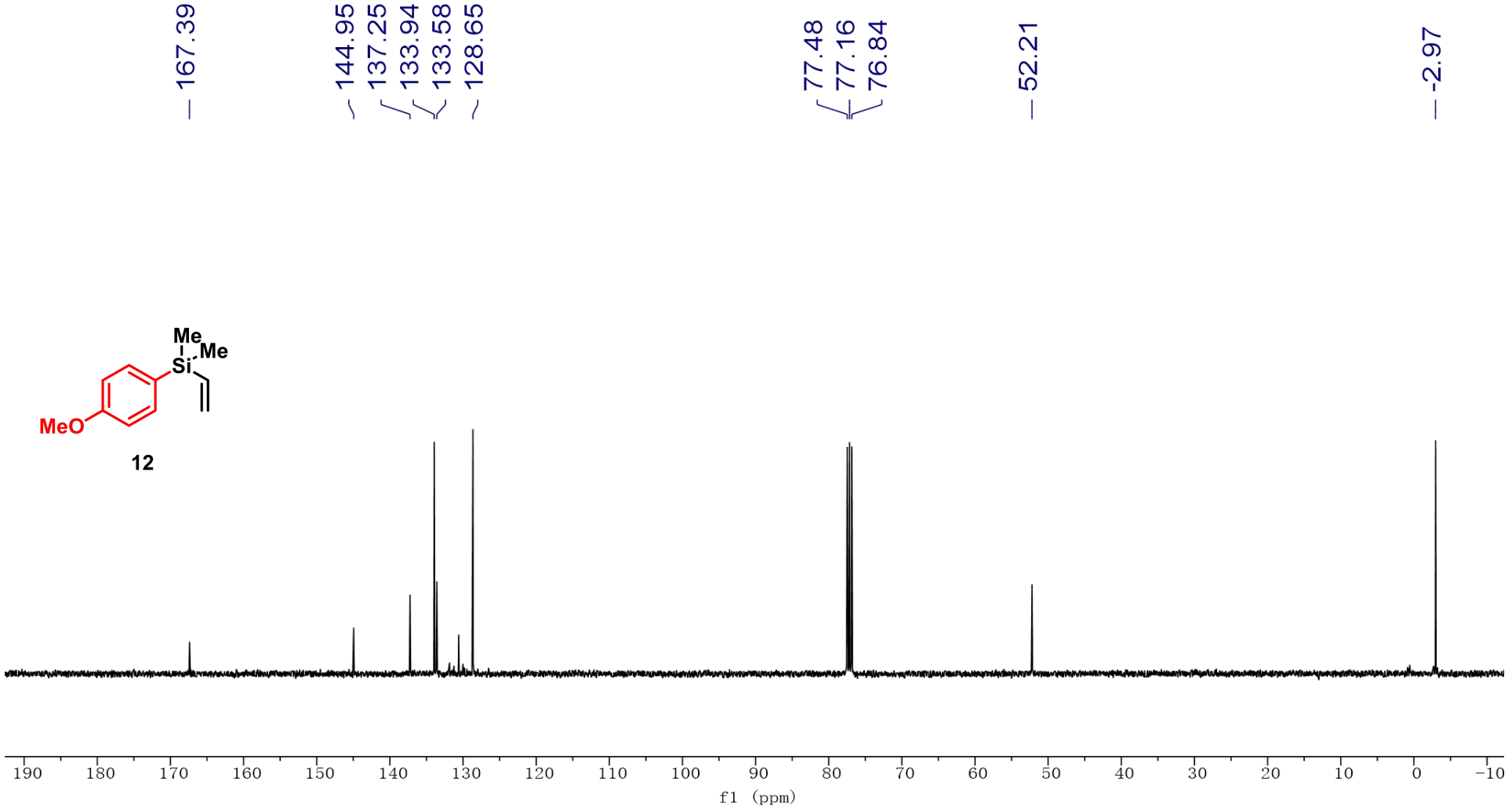


^{1}H NMR of 12 (600 MHz, $CDCl_3$)

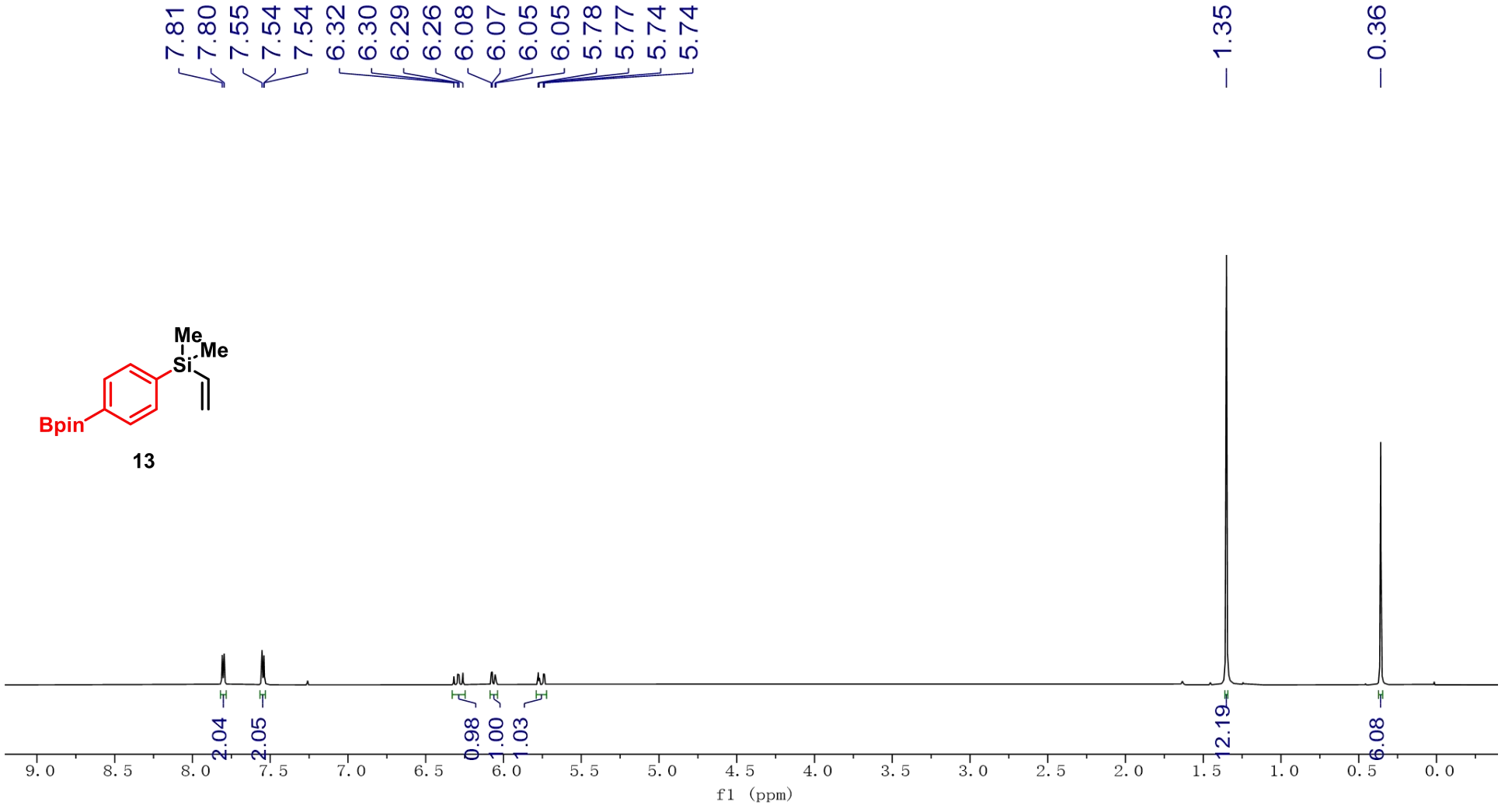


12

^{13}C NMR of 12 (151 MHz, $CDCl_3$)

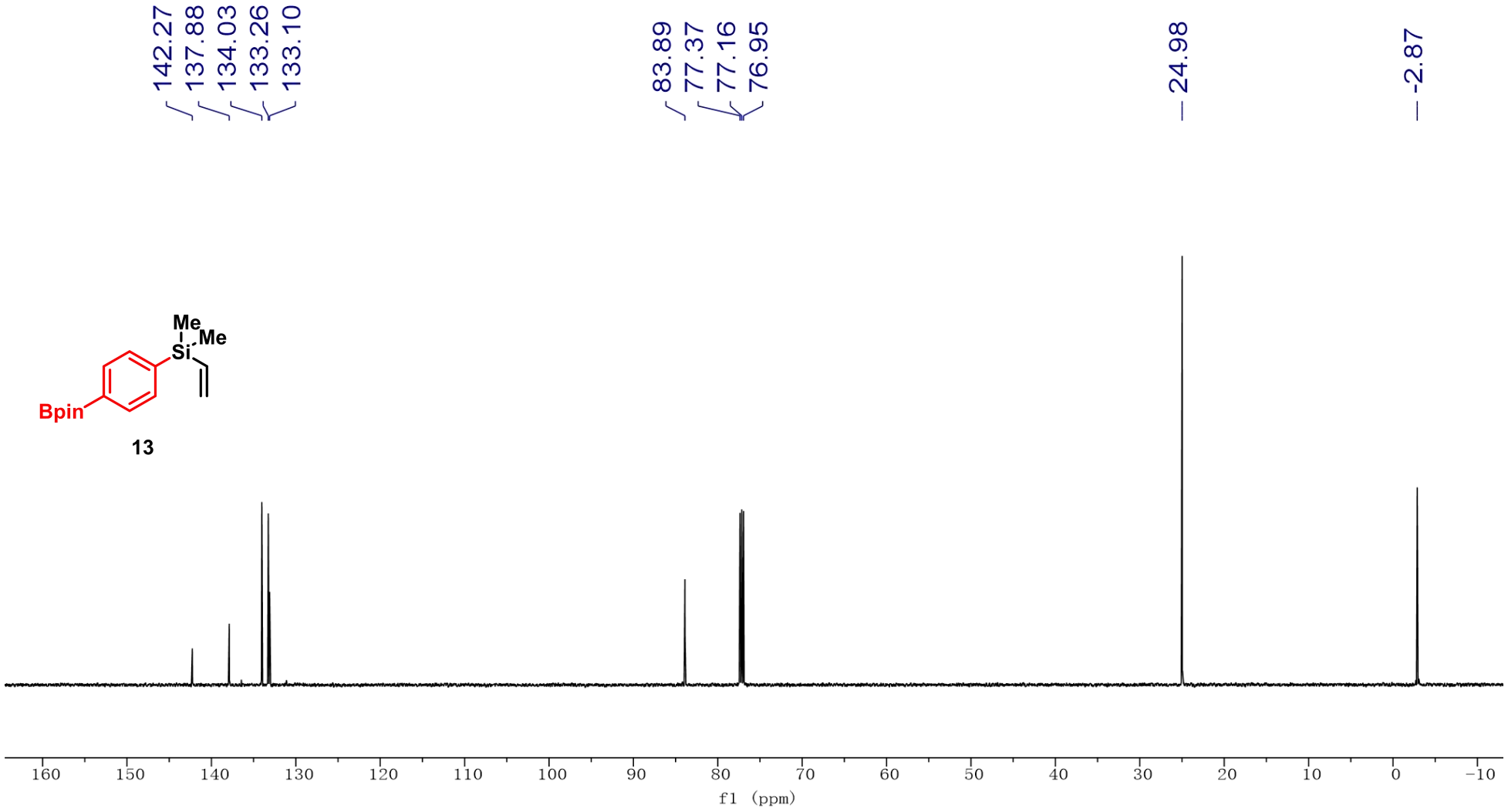


^{1}H NMR of 13 (600 MHz, $CDCl_3$)



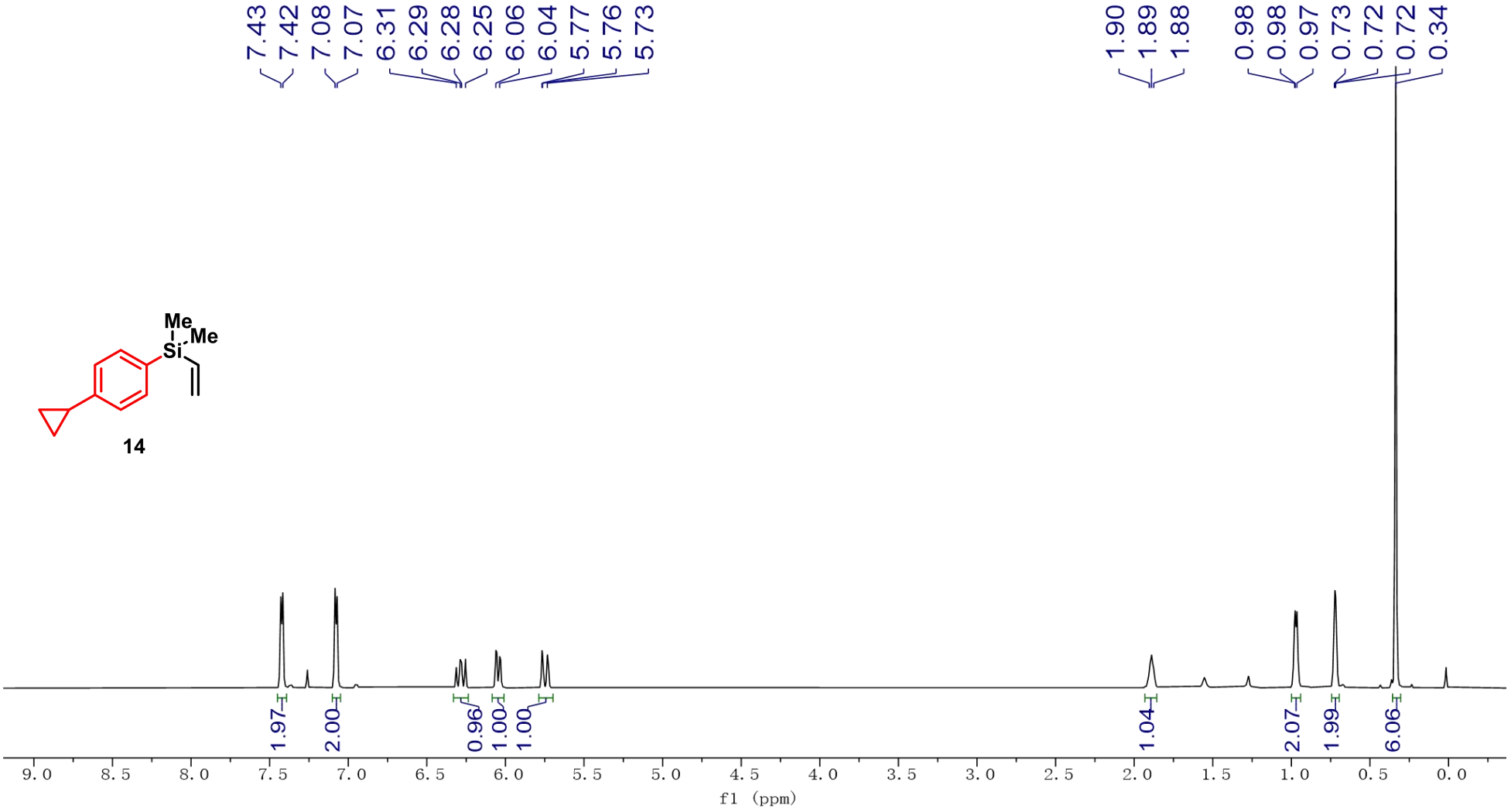
13

^{13}C NMR of 13 (151 MHz, $CDCl_3$)

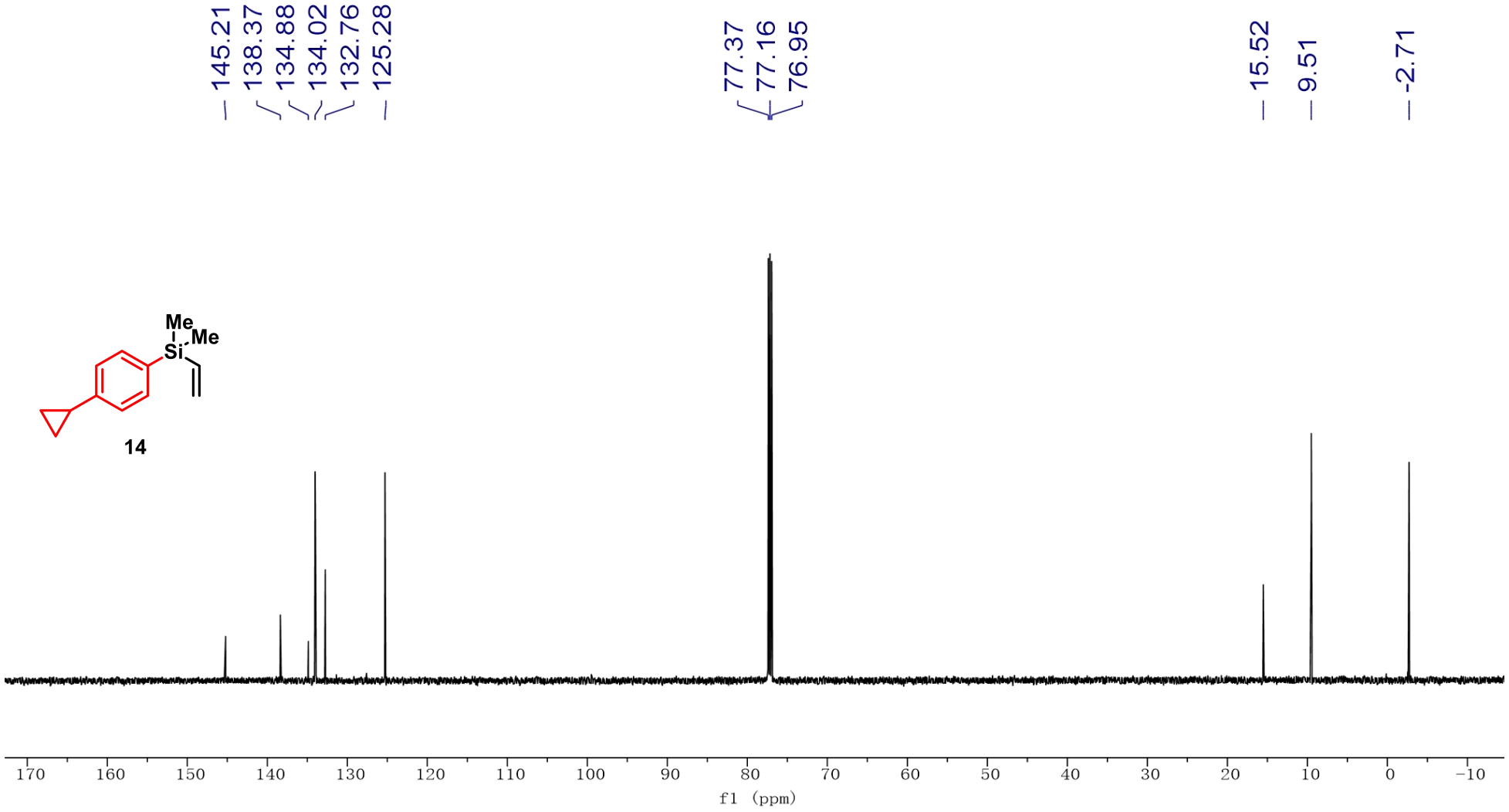


13

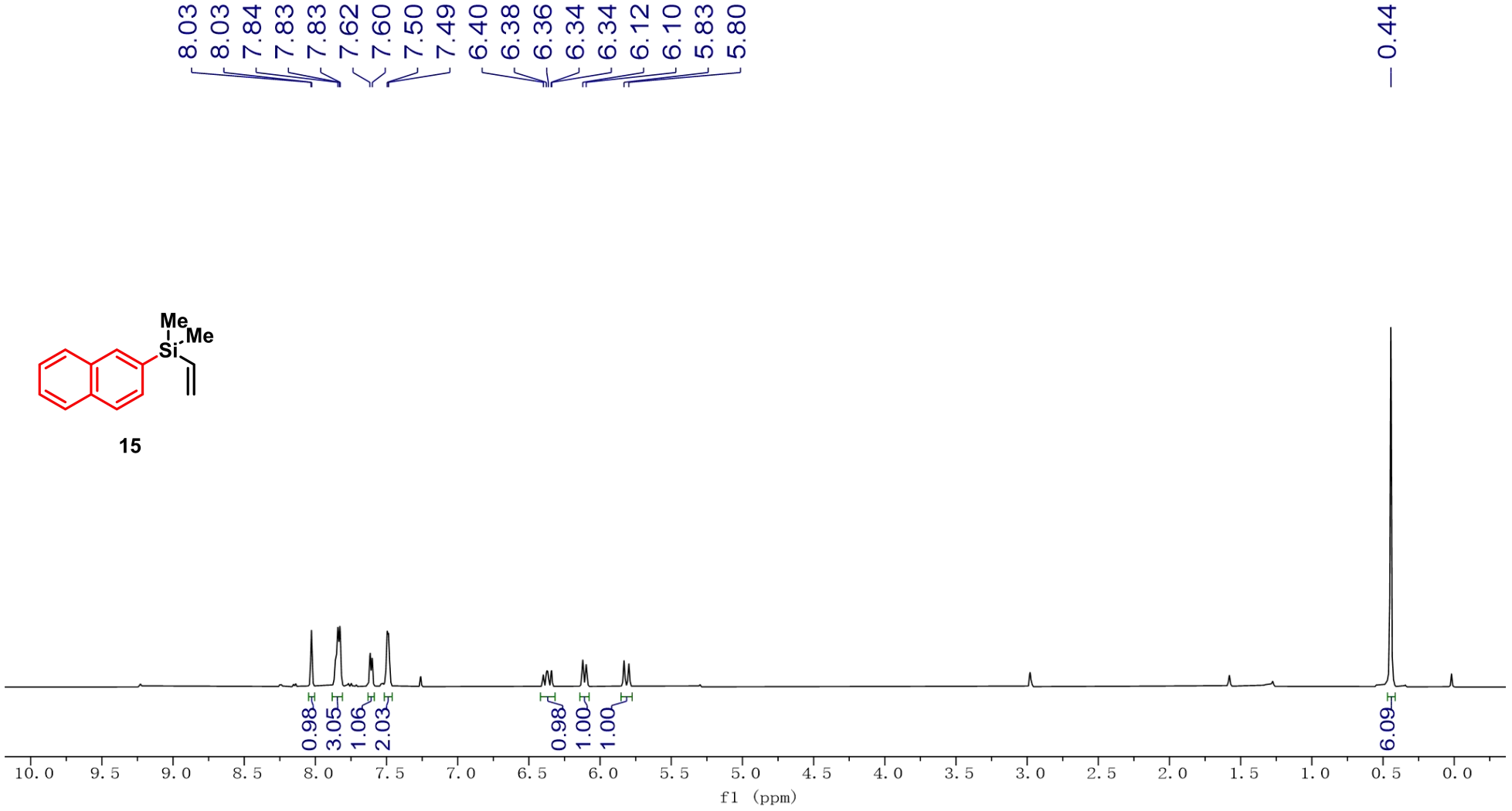
^{1}H NMR of 14 (600 MHz, $CDCl_3$



^{13}C NMR of 14 (151 MHz, $CDCl_3$)

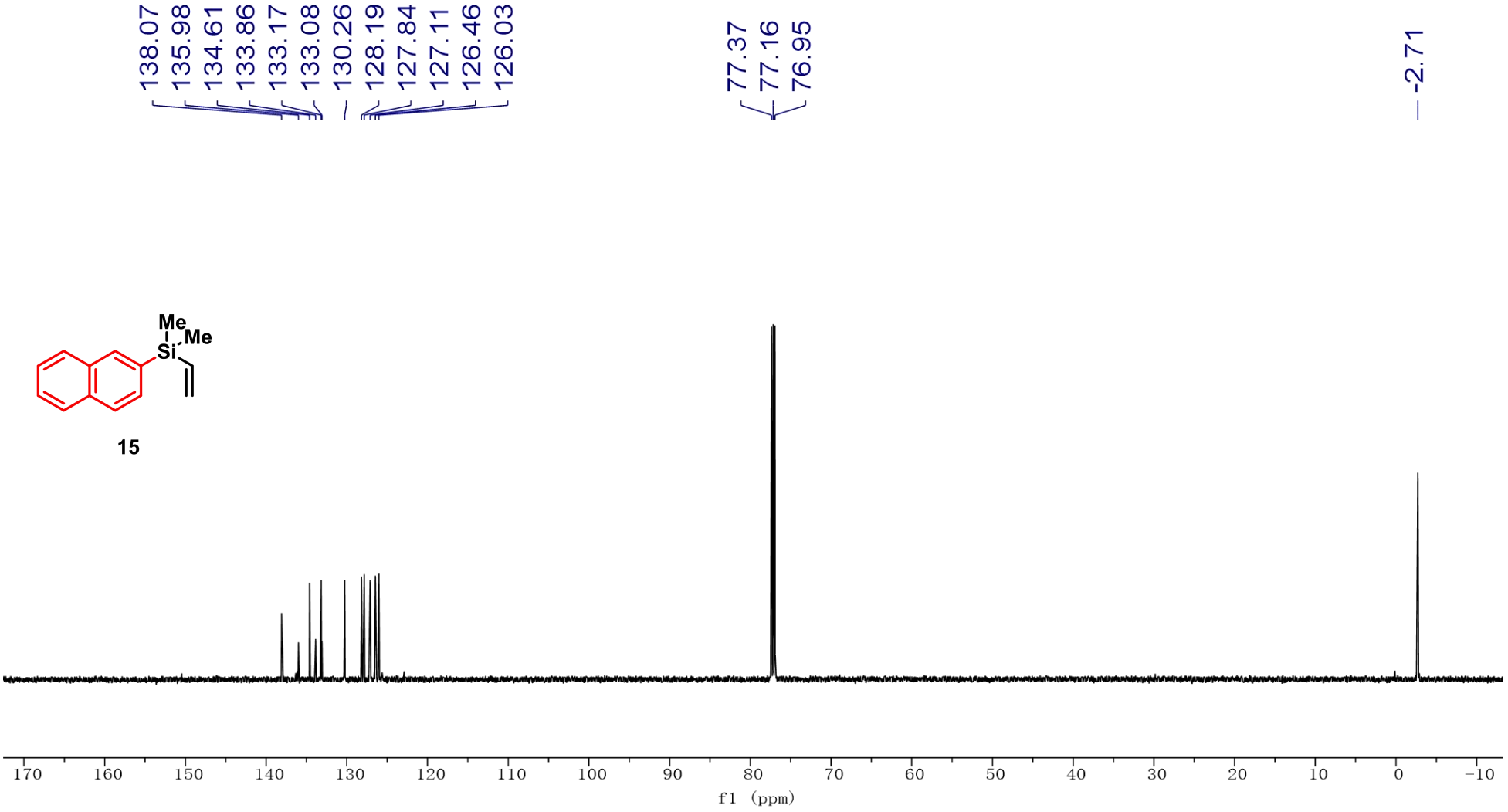


^{1}H NMR of 15 (400 MHz, $CDCl_3$)

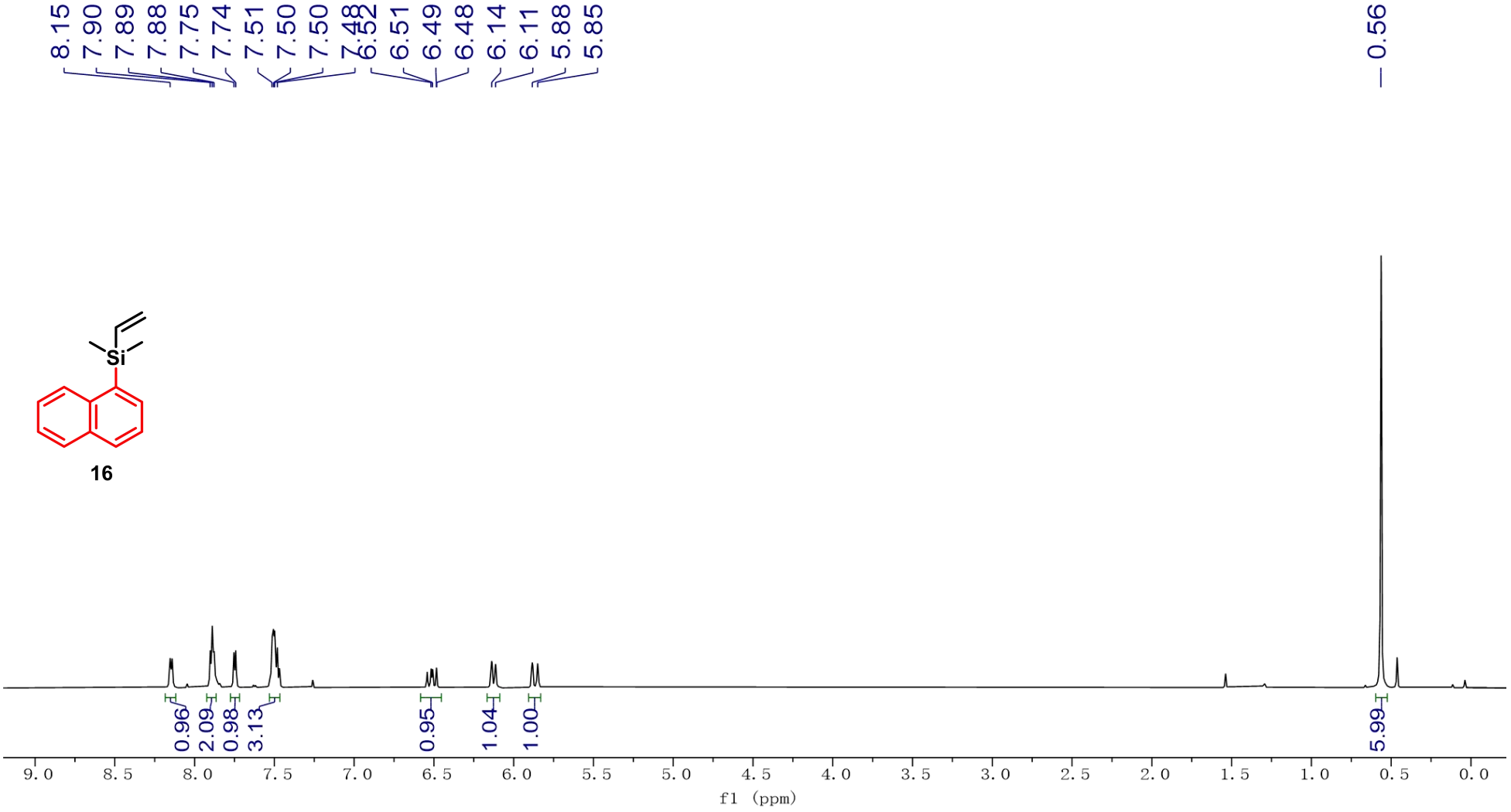


15

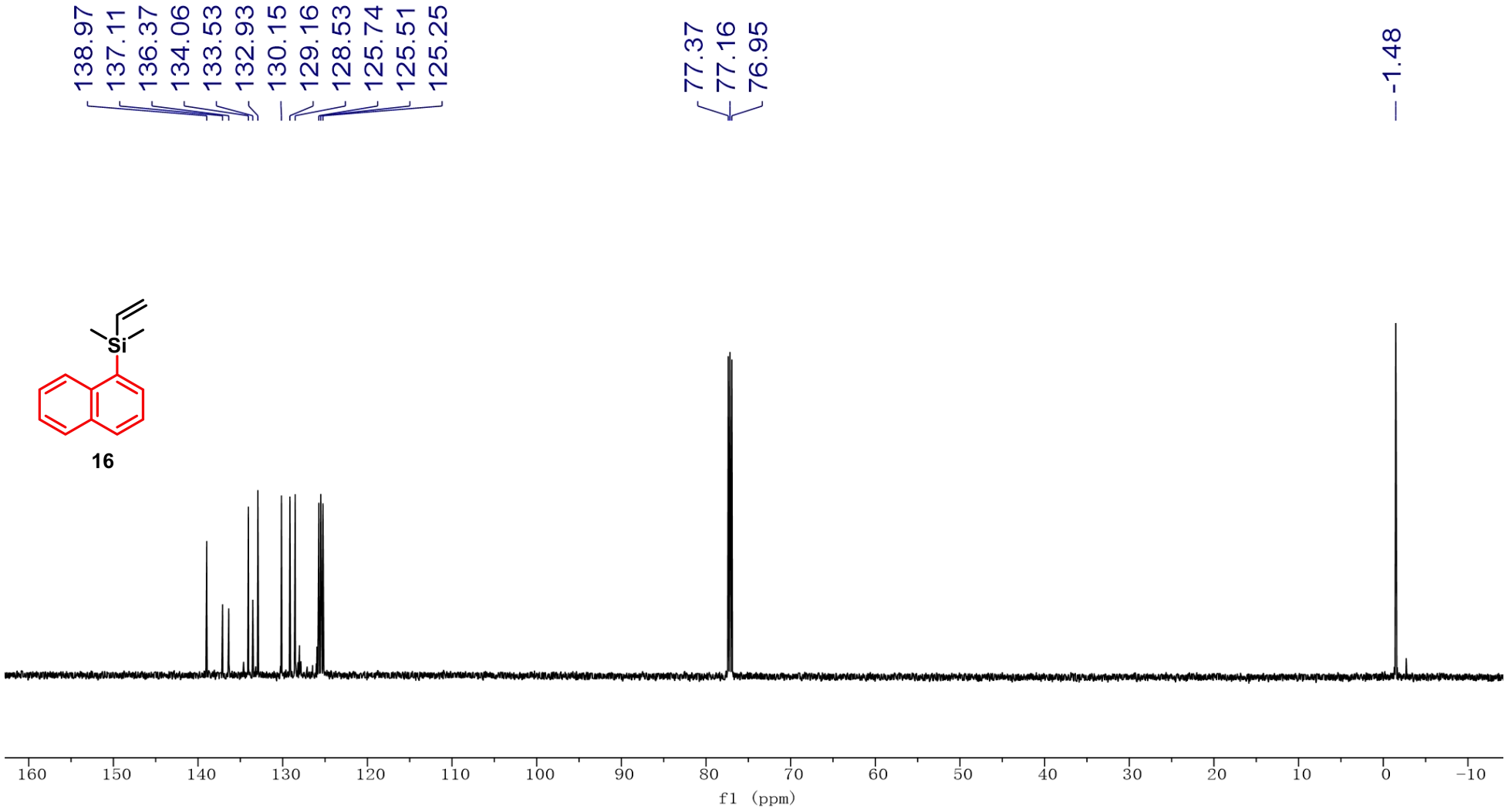
^{13}C NMR of 15 (101 MHz, $CDCl_3$)



^{1}H NMR of 16 (400 MHz, $CDCl_3$)

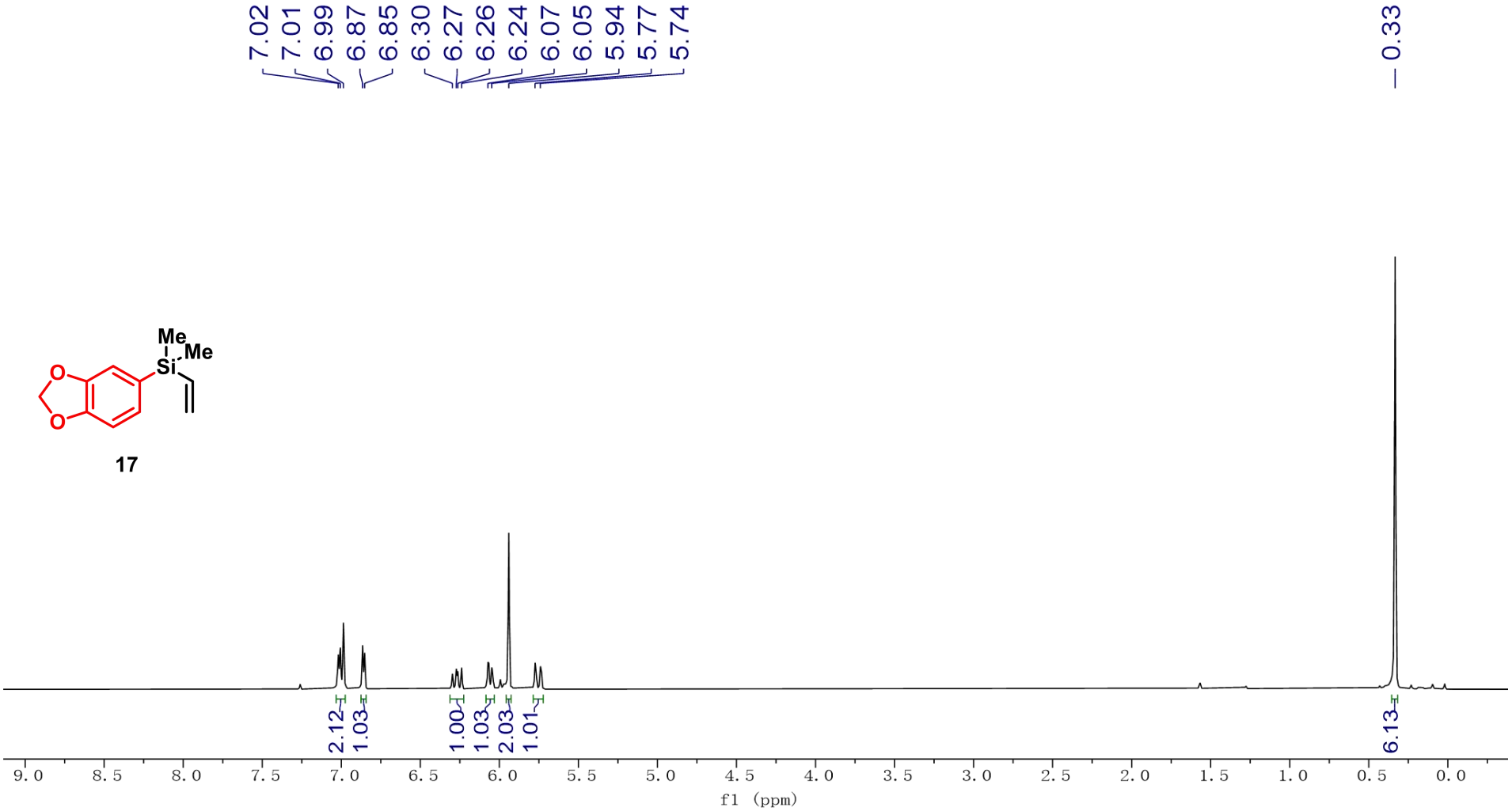


^{13}C NMR of 16 (101 MHz, $CDCl_3$)

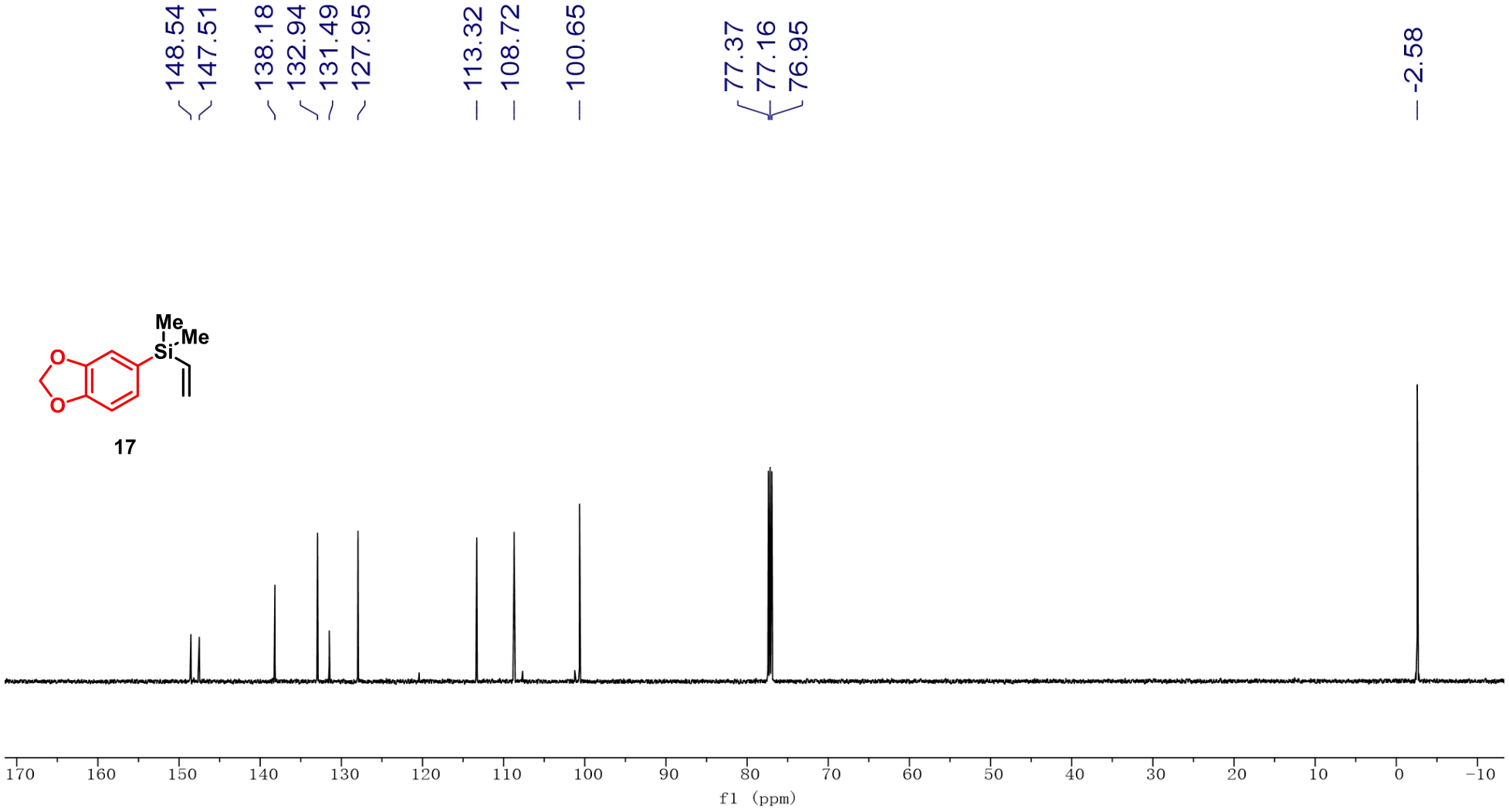


16

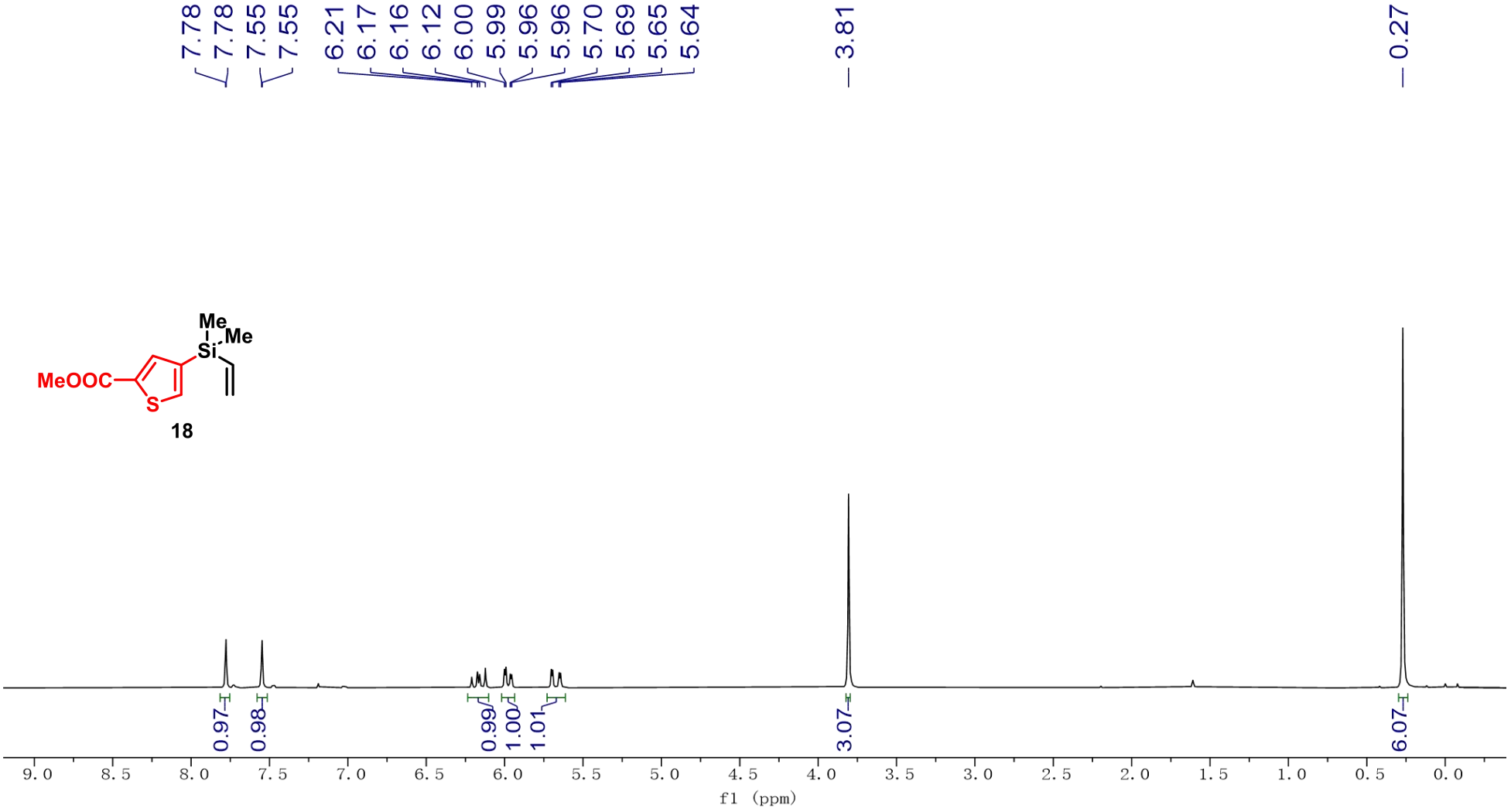
^{1}H NMR of 17 (400 MHz, $CDCl_3$)



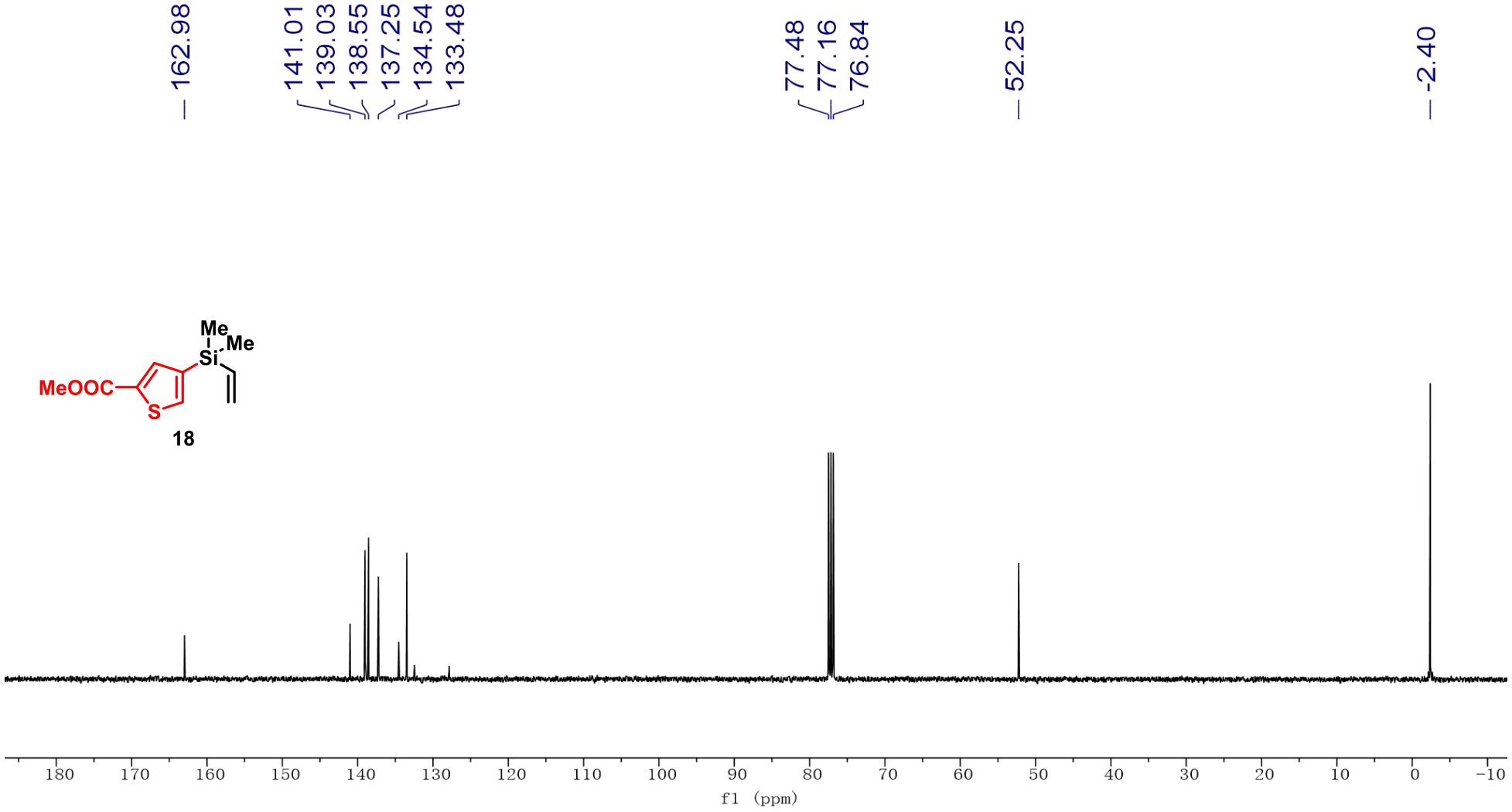
^{13}C NMR of 17 (101 MHz, $CDCl_3$)



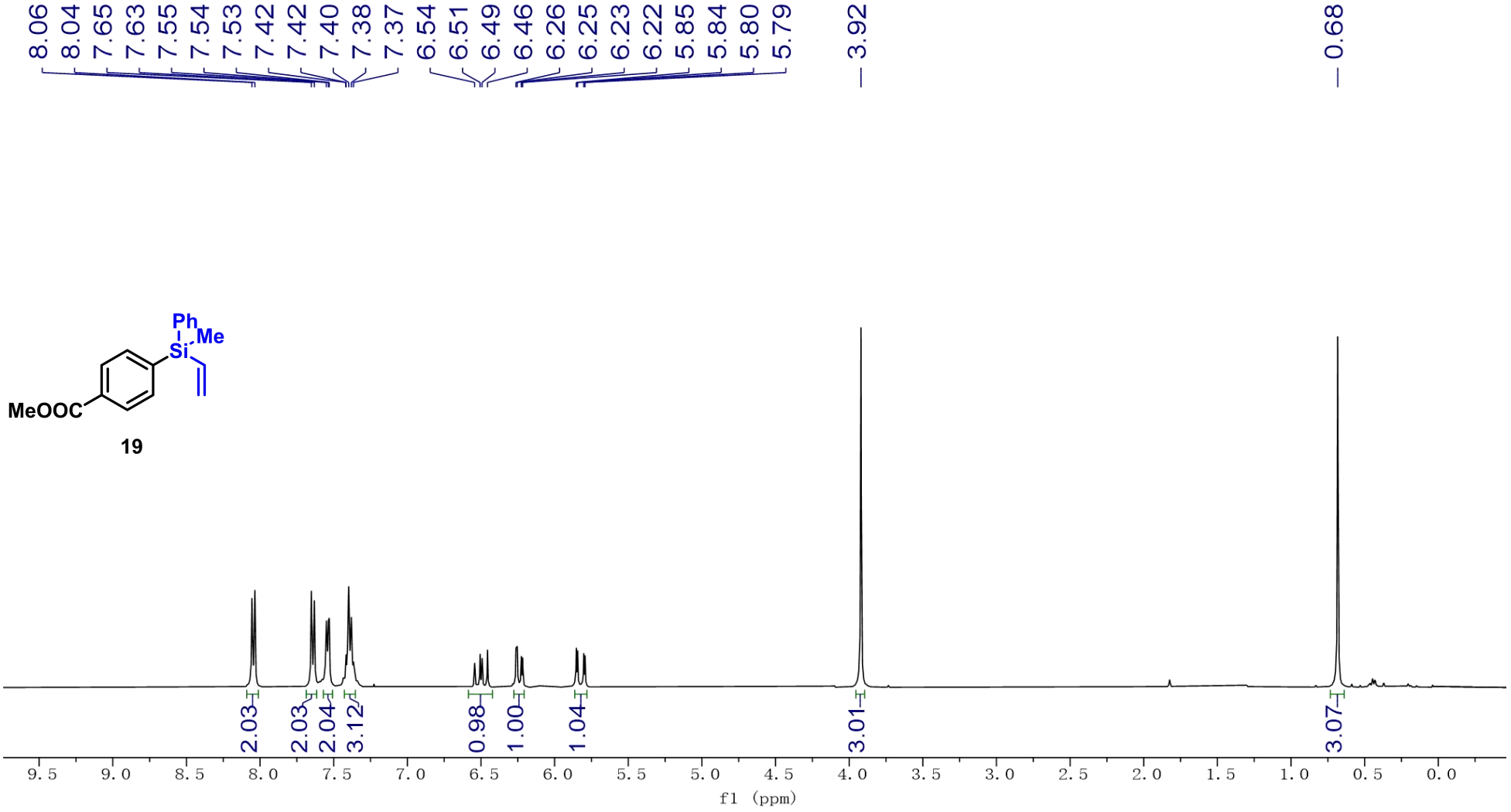
^{1}H NMR of 18 (600 MHz, $CDCl_3$)



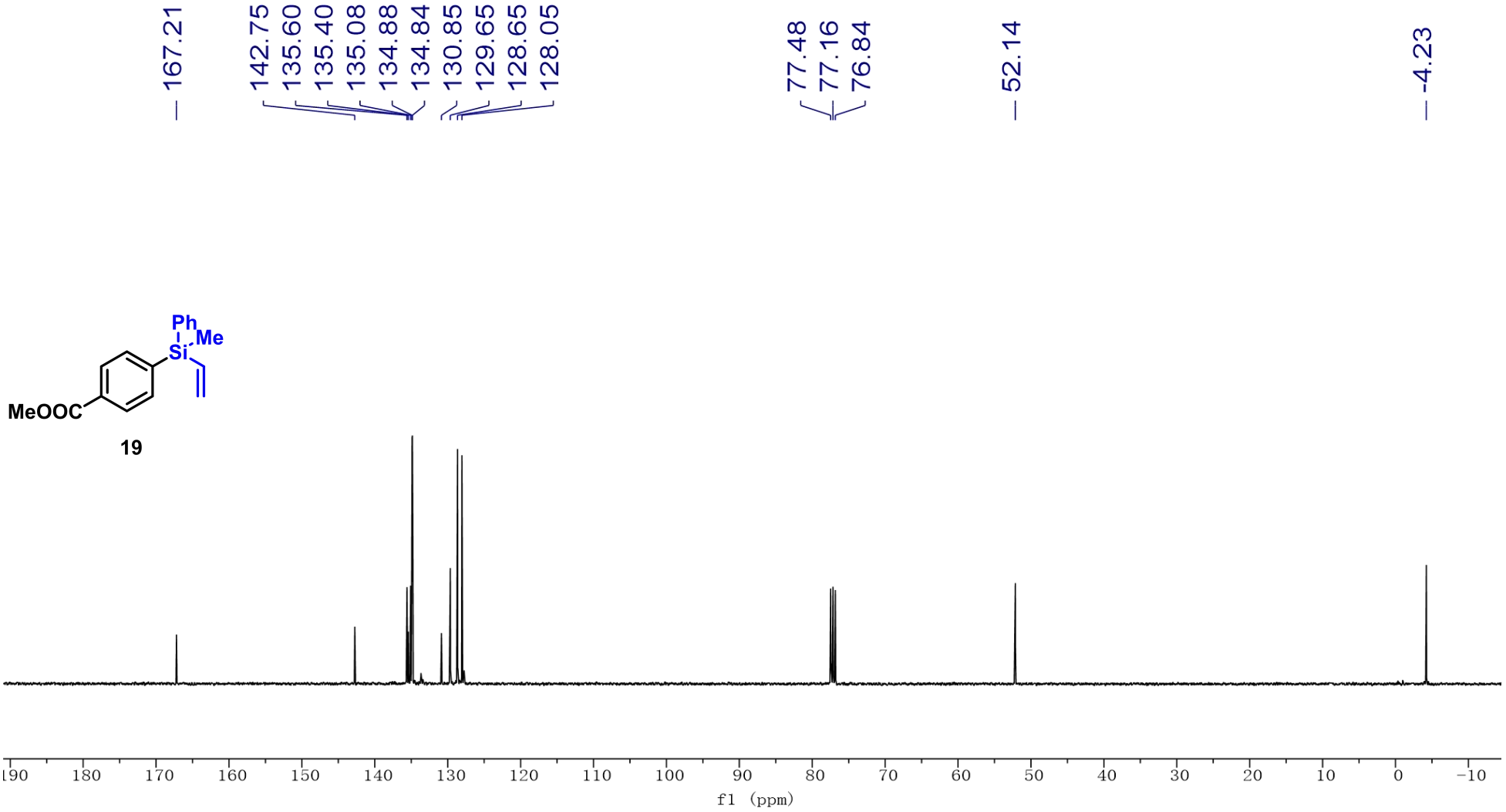
^{13}C NMR of 18 (151 MHz, $CDCl_3$)



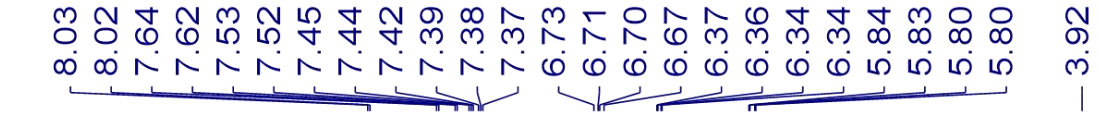
^{1}H NMR of 19 (600 MHz, $CDCl_3$)

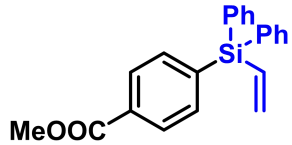


^{13}C NMR of 19 (151 MHz, $CDCl_3$)

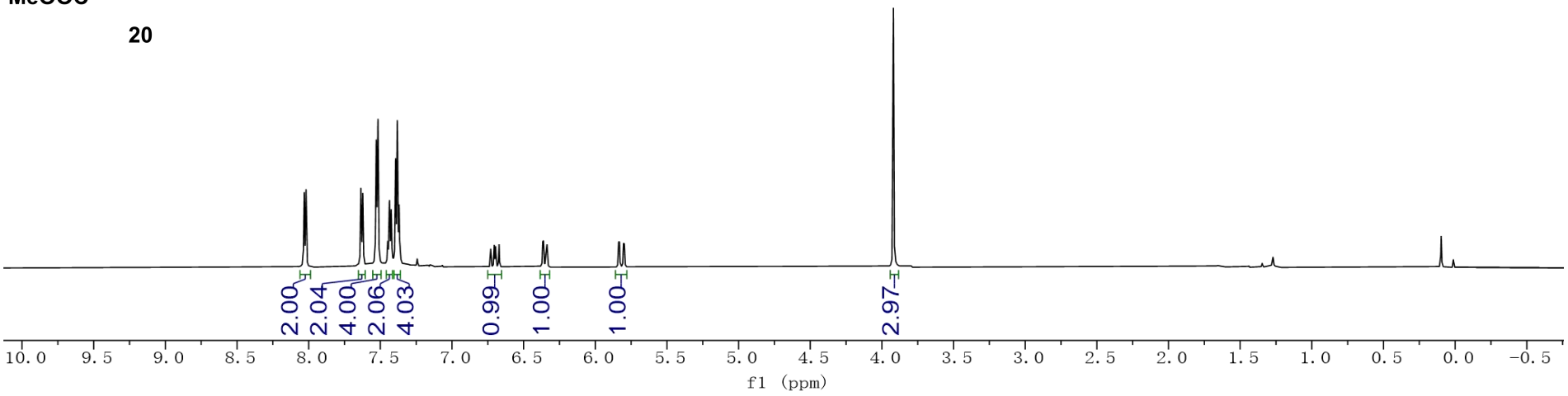


^{1}H NMR of 20 (400 MHz, $CDCl_3$)

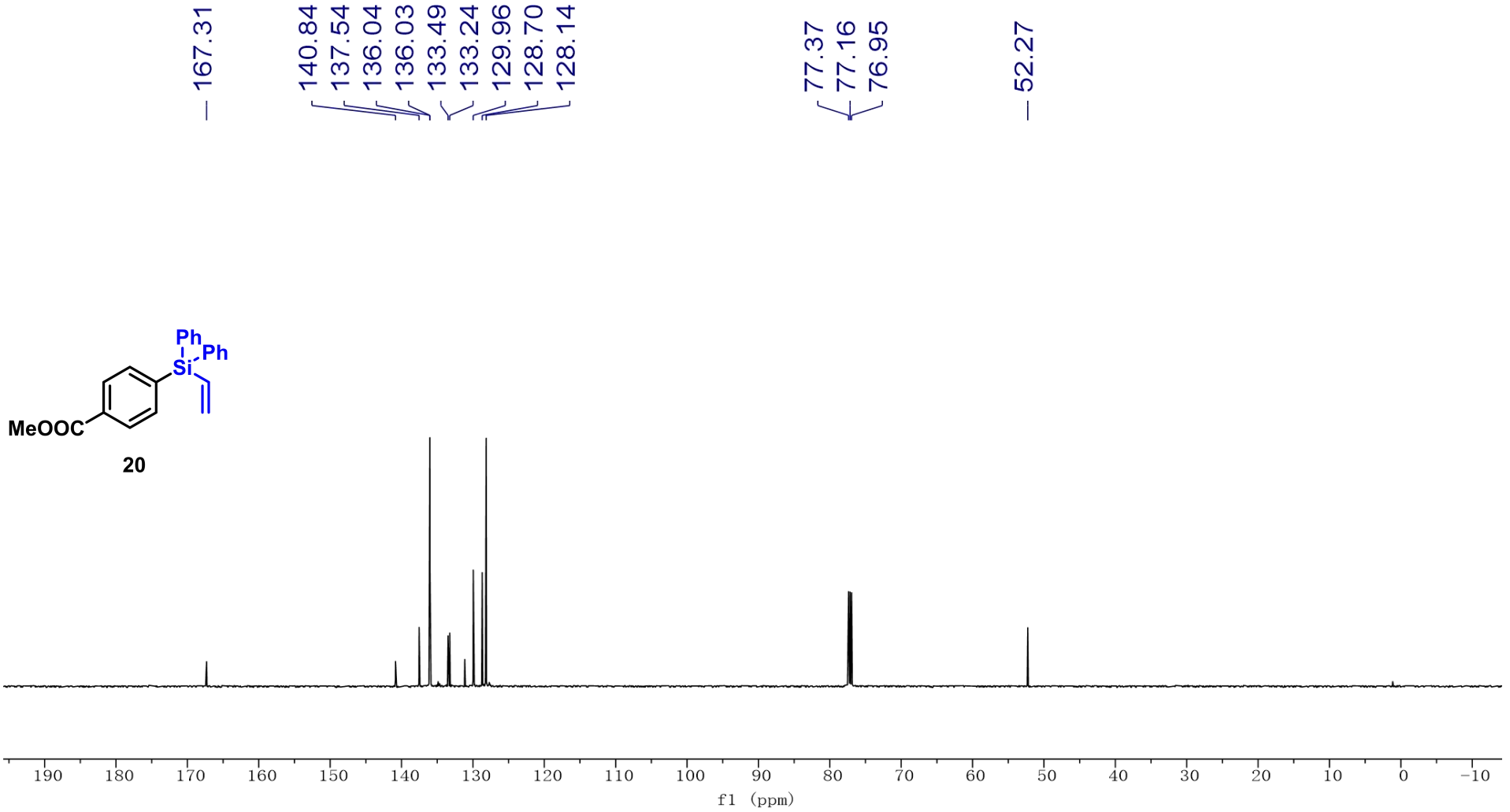




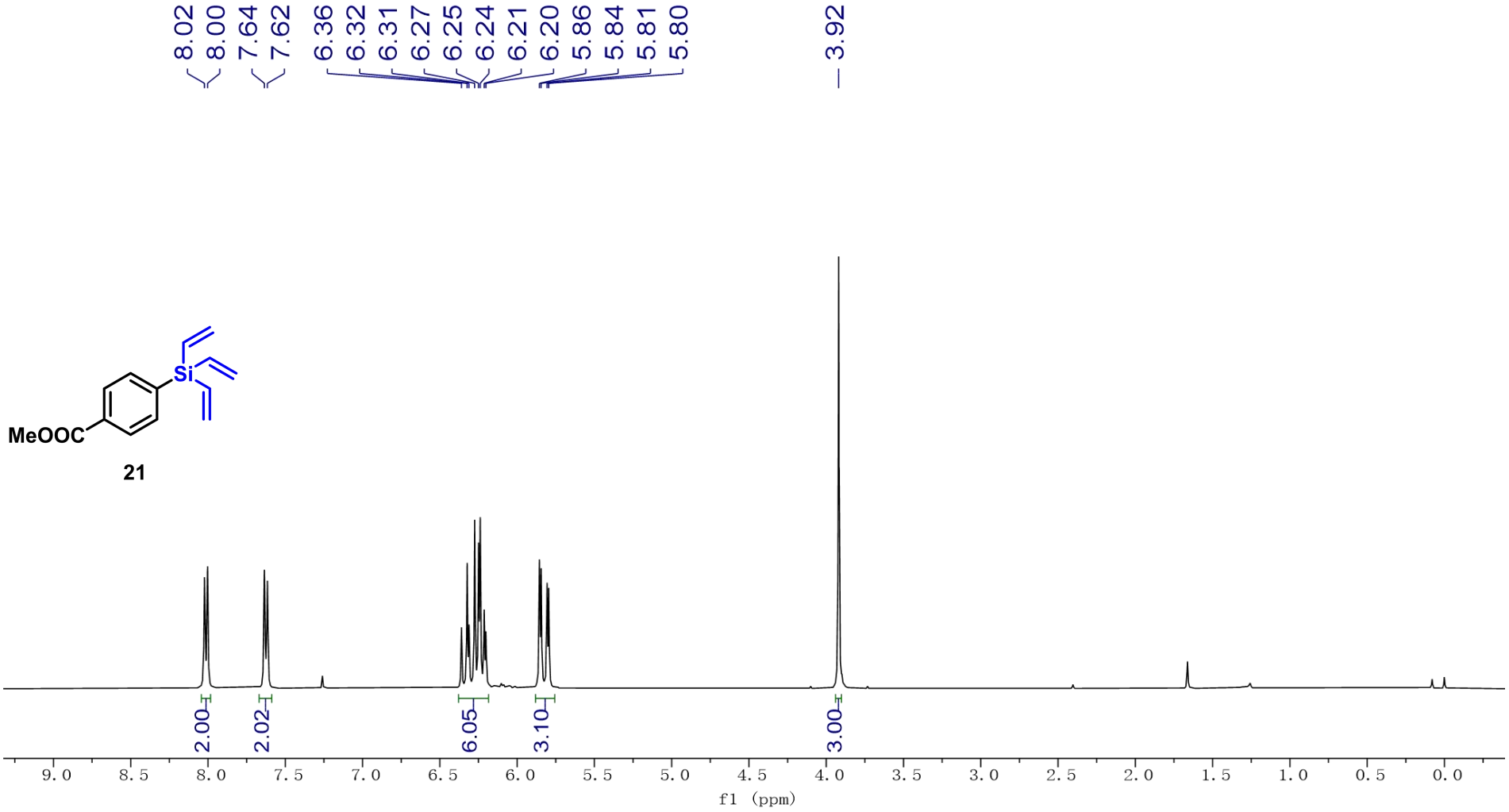
20



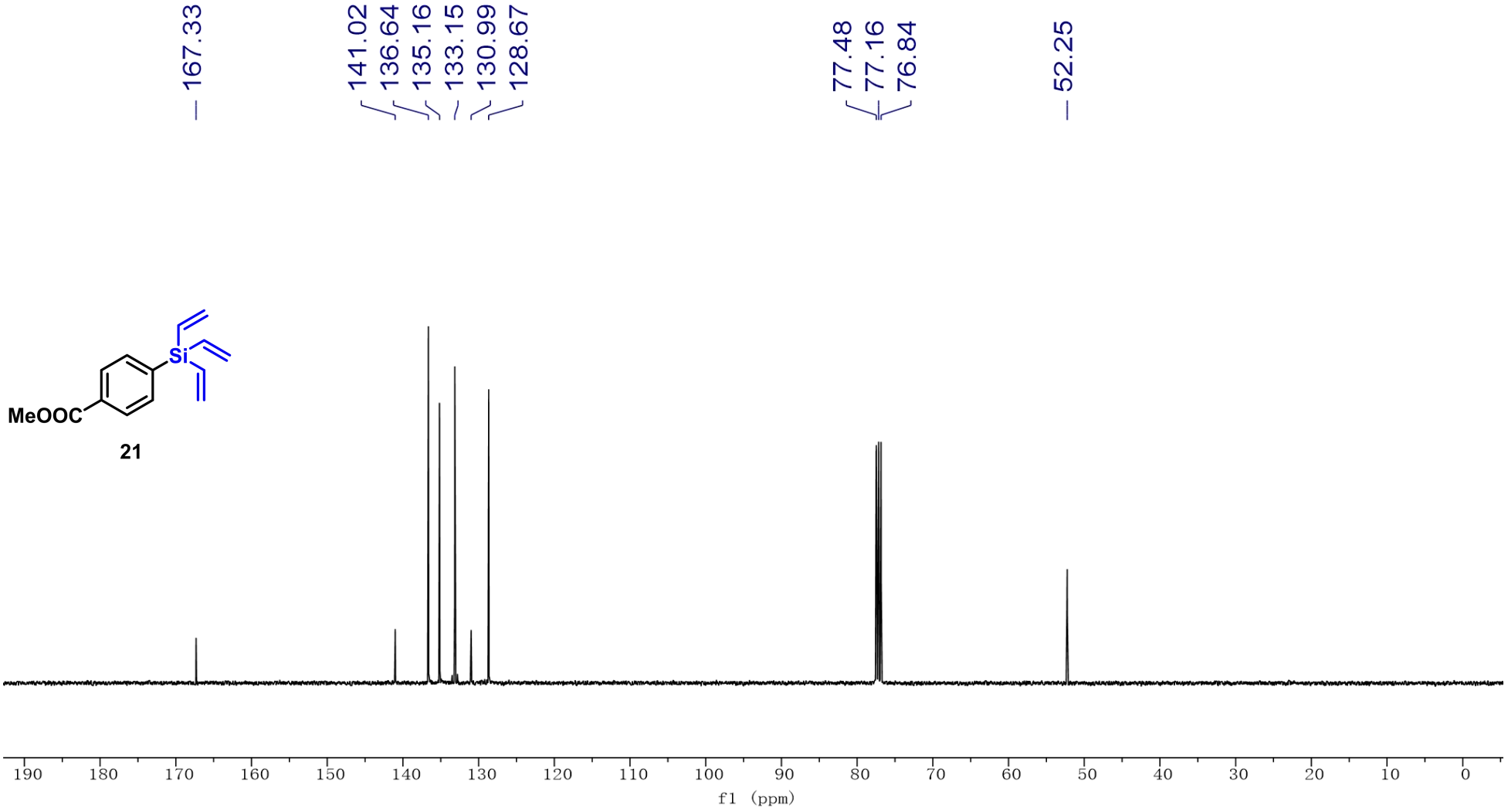
^{13}C NMR of 20 (101 MHz, $CDCl_3$)



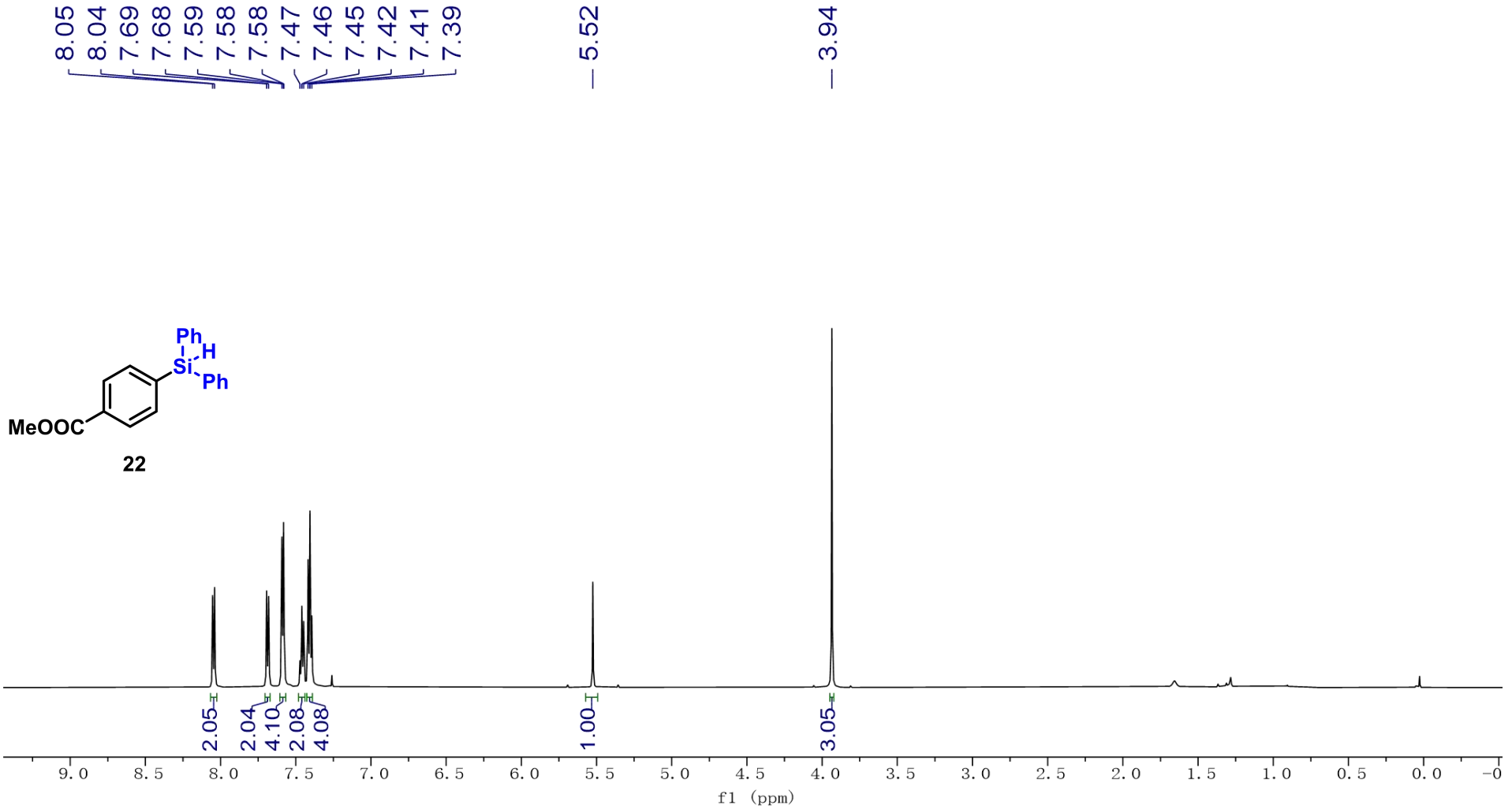
^{1}H NMR of 21 (600 MHz, $CDCl_3$)



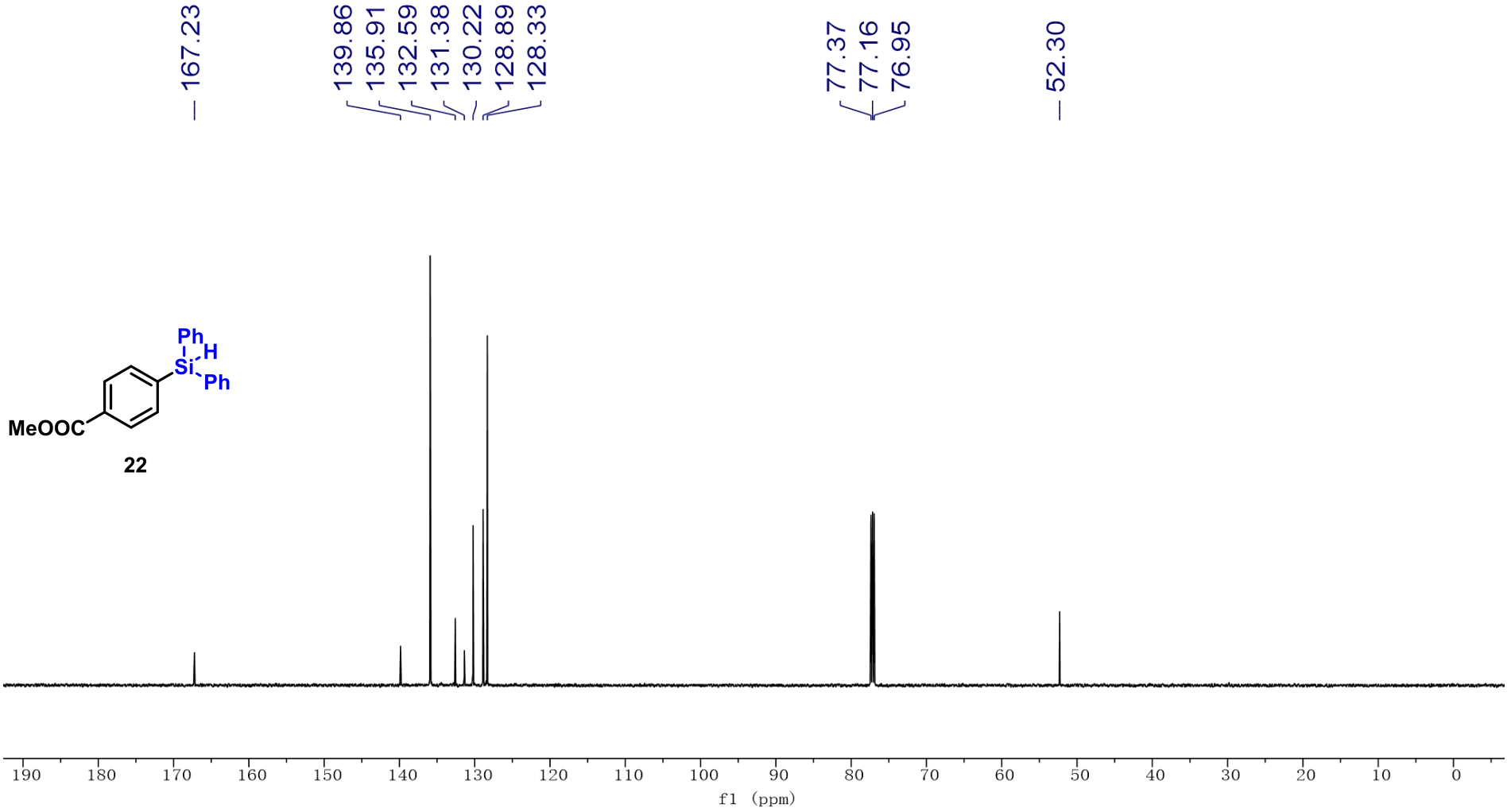
^{13}C NMR of 21 (151 MHz, $CDCl_3$)



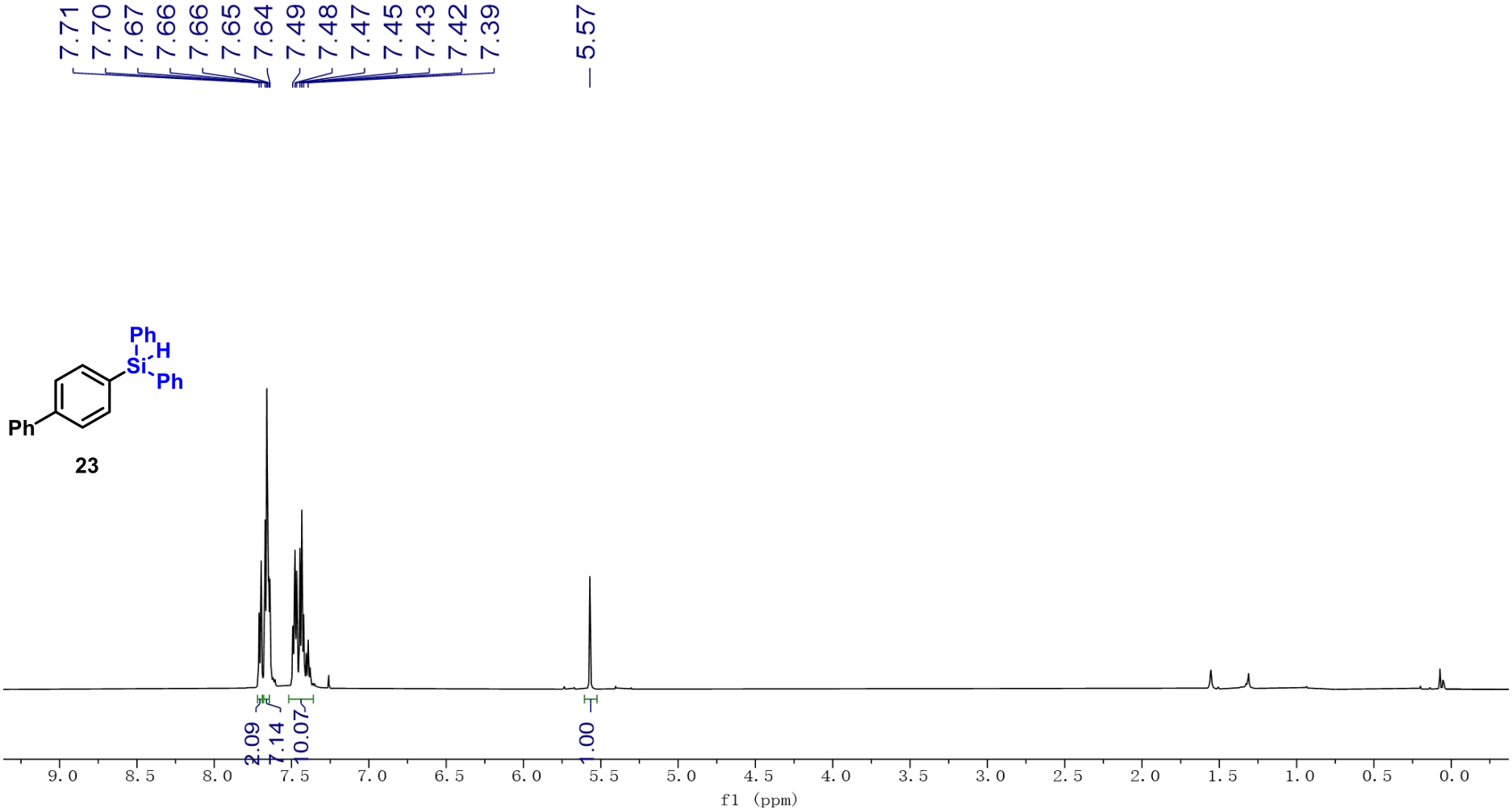
^{1}H NMR of 22 (600 MHz, $CDCl_3$)



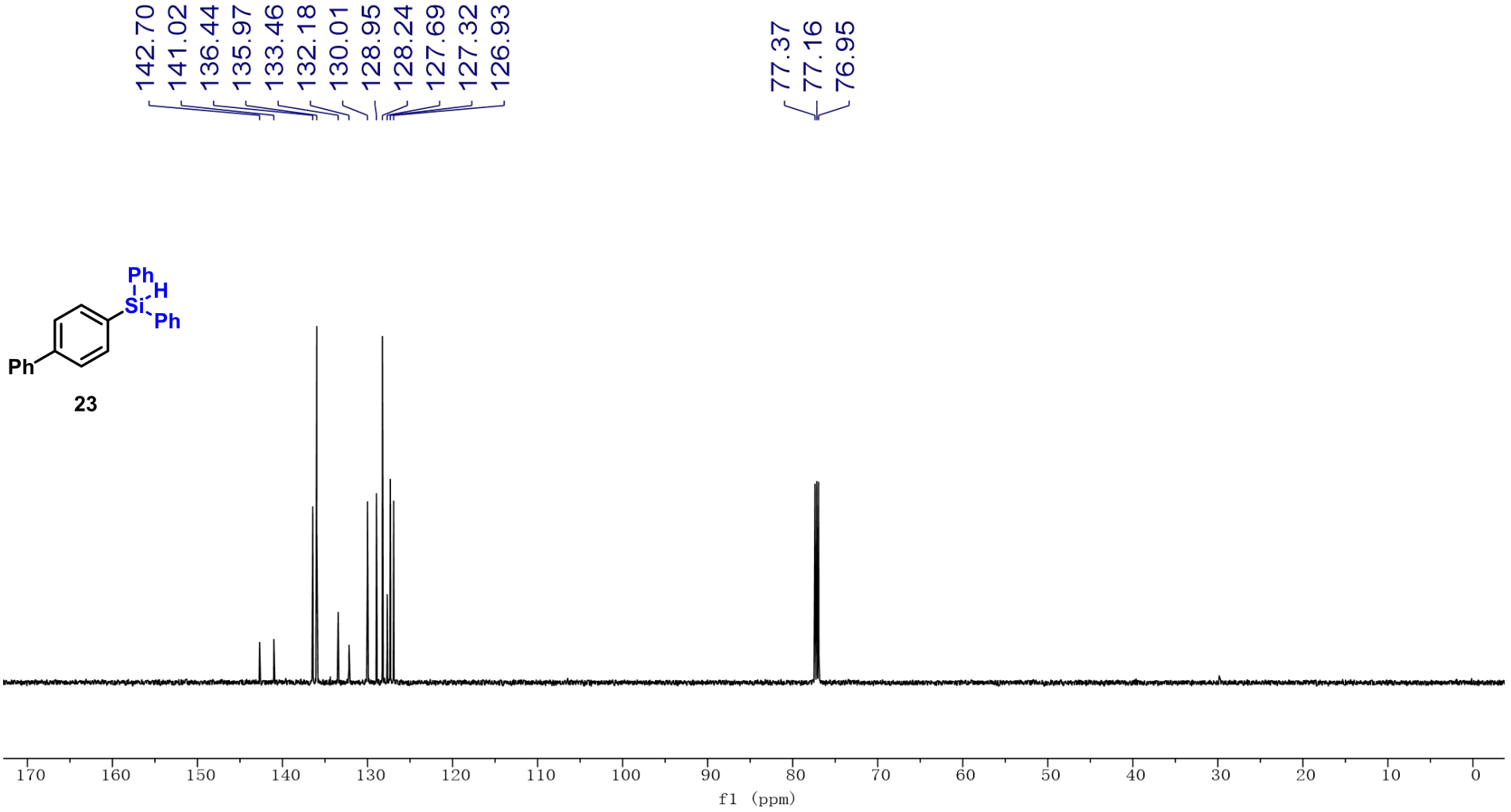
^{13}C NMR of 22 (151 MHz, $CDCl_3$)



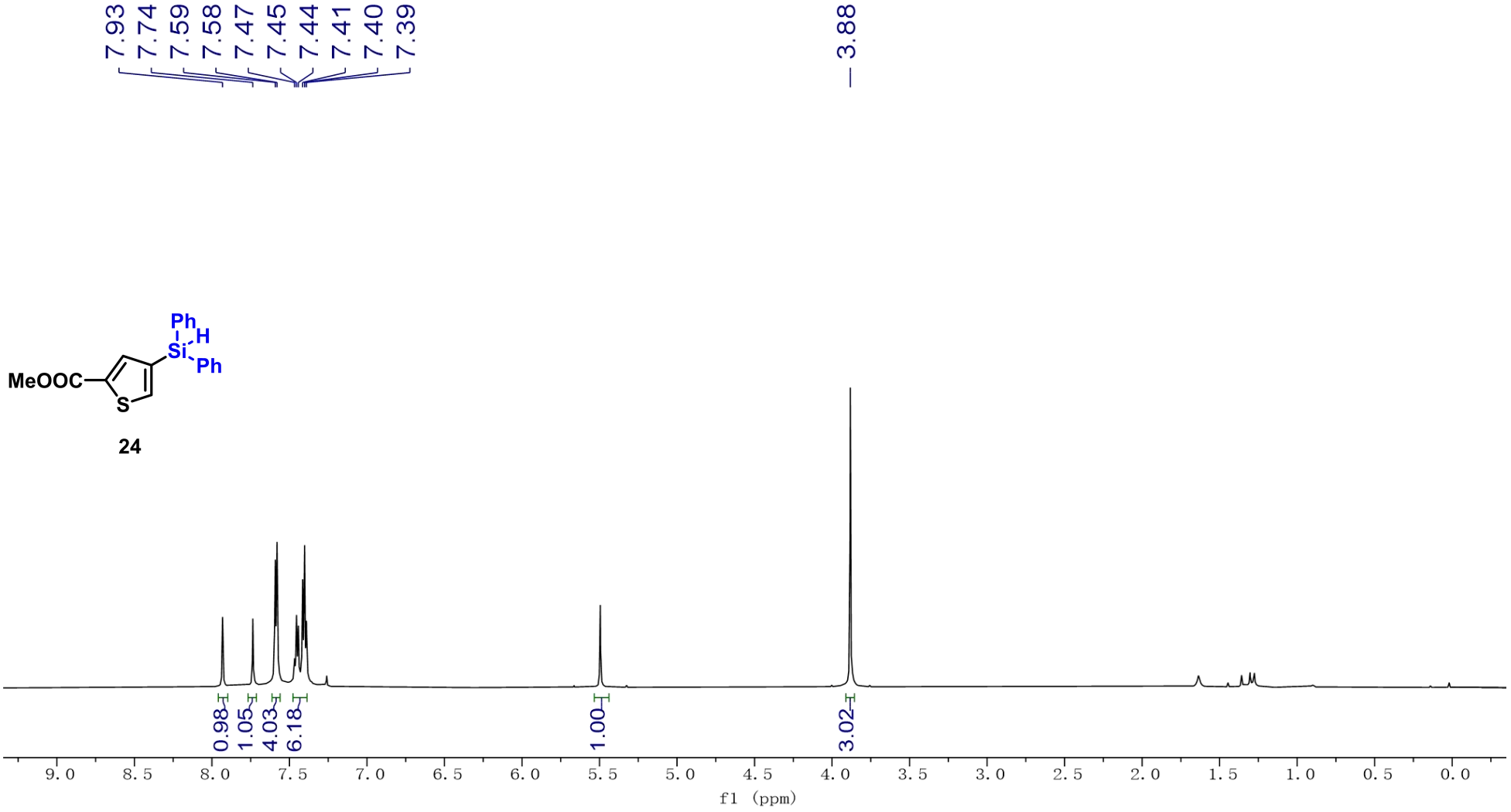
^{1}H NMR of 23 (600 MHz, $CDCl_3$)



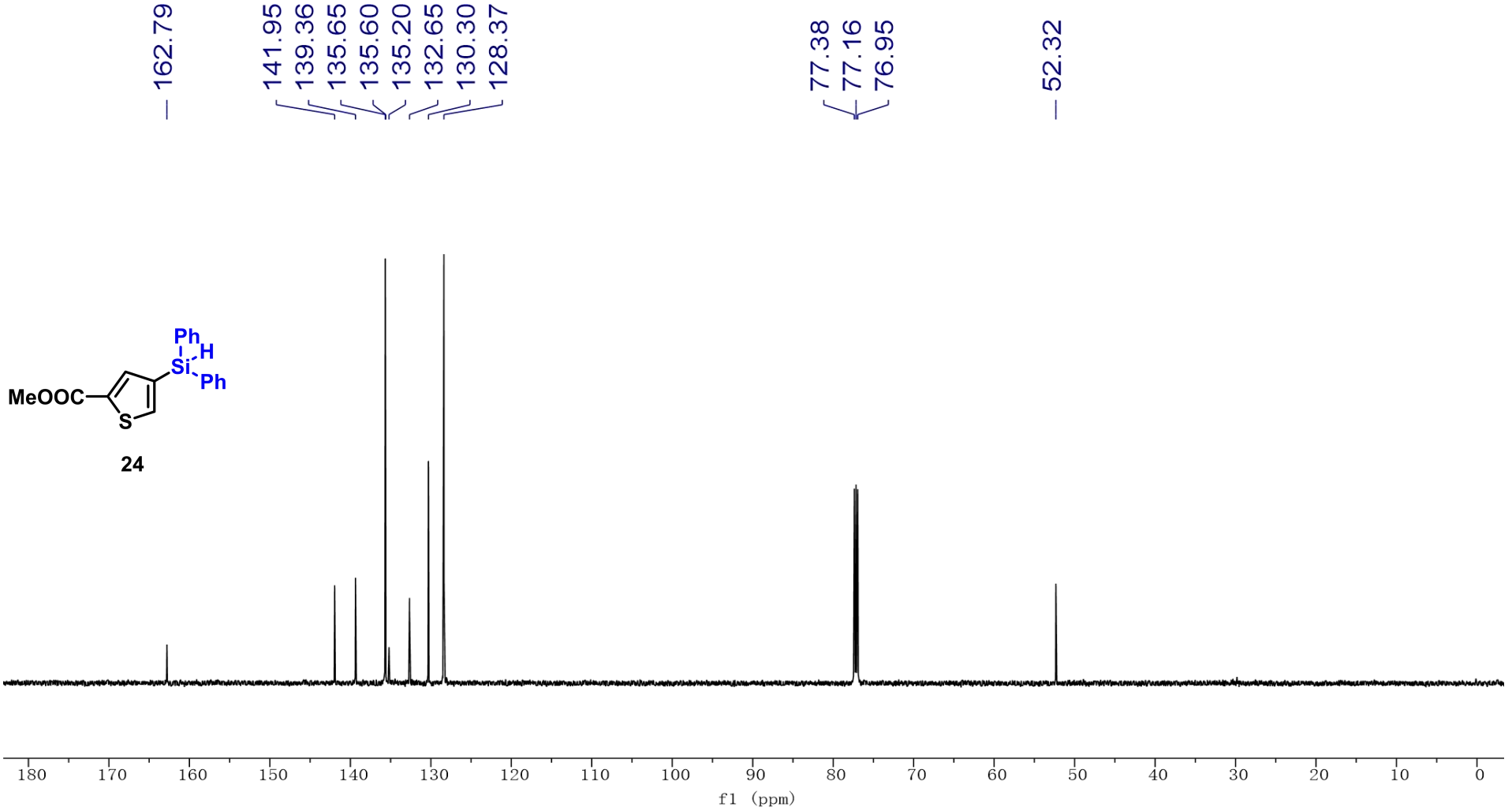
^{13}C NMR of 23 (151 MHz, $CDCl_3$)



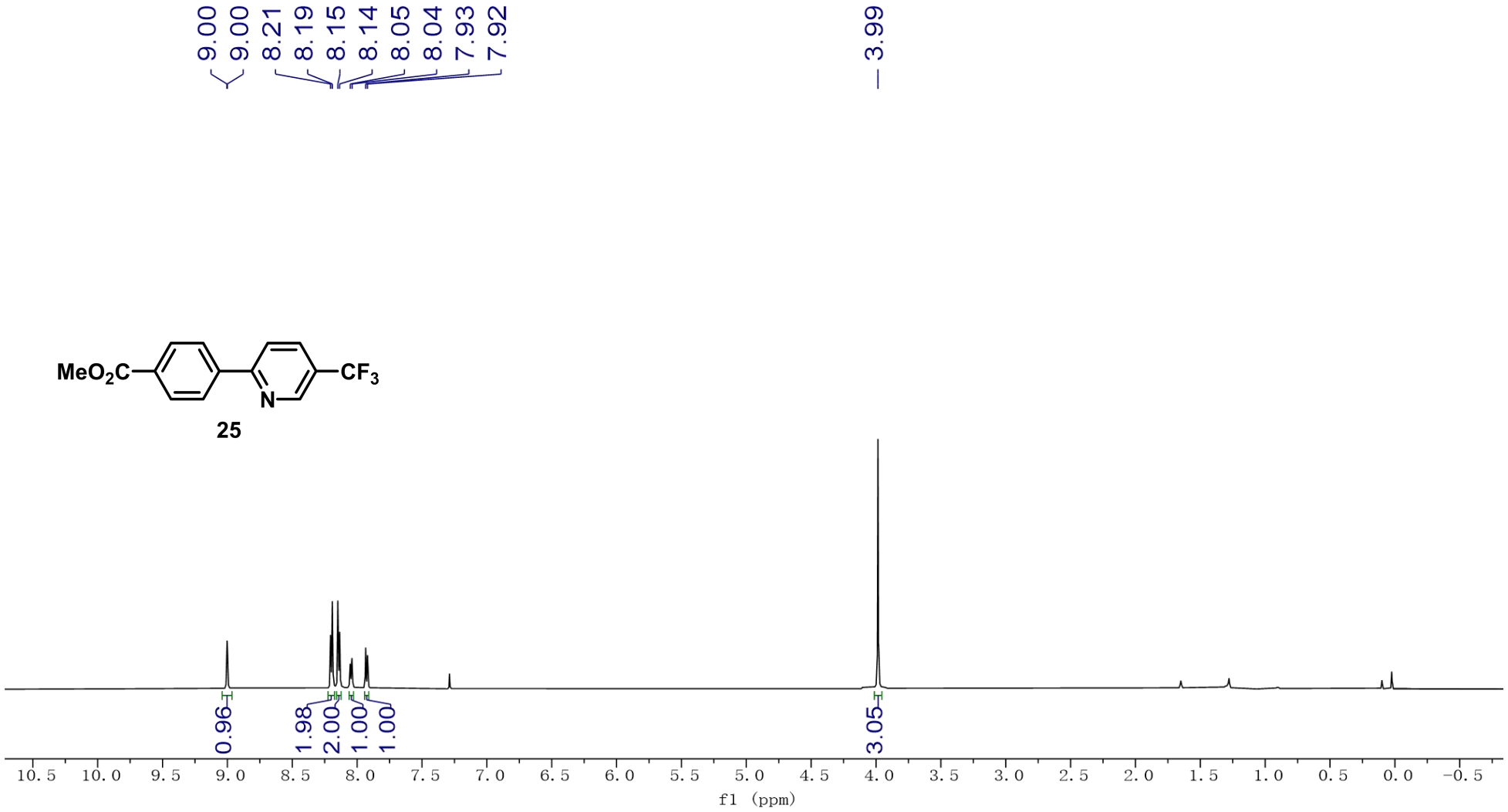
^{1}H NMR of 24 (400 MHz, $CDCl_3$)



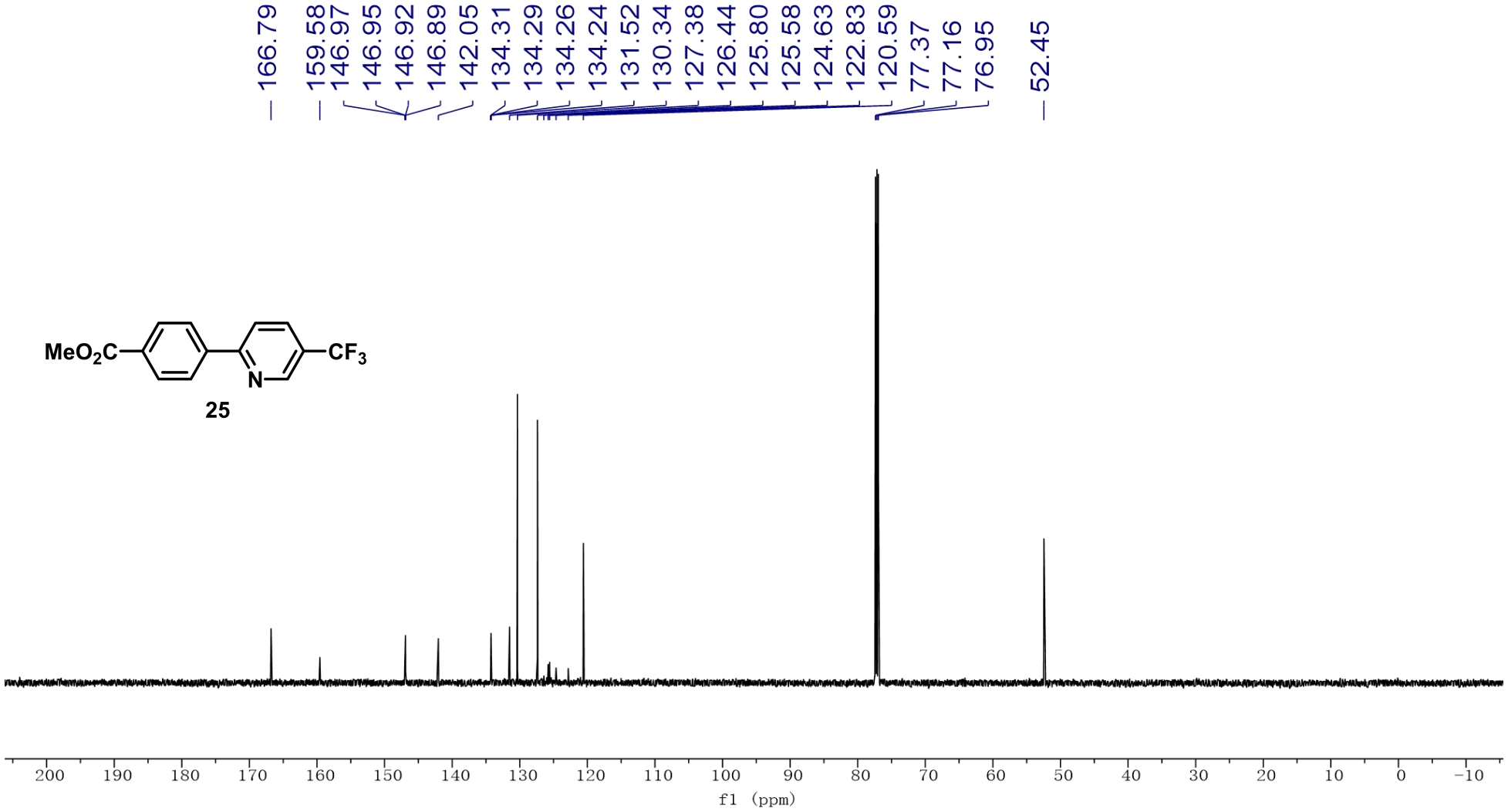
^{13}C NMR of 24 (101 MHz, $CDCl_3$)



^{1}H NMR of Hiyama coupling product (600 MHz, $CDCl_3$)



^{13}C NMR of Hiyama coupling product (151 MHz, $CDCl_3$)



^{19}F NMR of Hiyama coupling product (565 MHz, $CDCl_3$)