Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed C(*sp*^{3})-C(*sp*^{2}) Cross-Coupling of Homoleptic Rare-Earth Metal Trialkyl Complexes with Aryl Bromides: Efficient Synthesis of Functionalized Benzyltrimethylsilanes

Guilong Cai, Yingda Huang, Tingting Du, Shaowen Zhang, Bo Yao* and Xiaofang Li*

Key Laboratory of Cluster Science of Ministry of Education, Department of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China

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General Information

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. THF, Et_2O, hexane and toluene were dried and distilled over sodium. Palladium catalysts (98% purity), phosphine ligands, rare-earth metal trichlorides and $LiCH_2SiMe_3$ are purchased from *J&K Scientic* and used without further purification. The real purity of $Pd_2(dba)_3$ was determined as 92% according to the method in the literature (S. S. Zalesskiy, V. P. Ananikov, *Organometallics*, **2012**, *31*, 2302-2309). Other chemicals including aryl bromides, iodides, and α-bromostyrene were purchased from *Energy Chemical* and used without further purification. Chromatographic purification was conducted with technical grade solvents (petroleum ether, dichloromethane and ethyl acetate) and silica gel 40-63 μm. TLC was performed on Merck silica gel 60 F_{254} TLC aluminium plates and visualized with UV light (254 nm), permanganate stain, CAN stain or PMA stain. ^{1}H NMR spectra were recorded on a Brucker Advance 400 MHz spectrometer in $CDCl_3$ or toluene-*d₈* (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, or the internal toluene signal at 7.00 ppm as standard). ^{13}C NMR spectra were recorded with ^{1}H-decoupling on a Brucker Advance 101 MHz spectrometer in $CDCl_3$ or toluene-d_8 (all signals are reported in ppm with the internal chloroform signal at 77.16 ppm, or the internal DMSO signal at 20.43 ppm as standard). Gas chromatographic analysis was conducted by a Shimadzu GC2014C gas chromatograph instrument.

Preparation of The (Trimethylsilyl)methyl Complexes 1a-1c.

$$LnCl_3 \xrightarrow[\text{2) } LiCH_2SiMe_3 \text{ (3.1 equiv)}]{\text{1) THF, reflux, 30 min}} Ln(CH_2SiMe_3)_3(THF)_2$$

(Ln = Y, Sc, Lu) **1a-1c**, 80-90%

General Procedure: Anhydrous YCl_3 (488 mg, 2.5 mmol) was slurried in THF (60 mL) and stirred at 60 °C for 7 days. To the resulting suspension of $YCl_3(THF)_x$ was added dropwise a solution of $LiCH_2SiMe_3$ (7.75 mmol) in 10 mL of THF at ambient temperature. The mixture was stirred for 3 h and the solvent was removed under reduced pressure. The resulting residue was extracted with 3×10 mL of hexane. The solvent was evaporated in *vacuo* to give $Y(CH_2SiMe_3)_3(THF)_2$ (**1a**, 1100 mg, 90% yield) as a white solid. ^{1}H NMR (400 MHz, toluene-d8) δ 4.09 (t, *J* = 6.4 Hz, 8H), 1.61-1.33 (m, 8H), 0.18 (s, 27H), -0.38 (s, 6H). The NMR data is in good agreement with that reported in the literature.[1]

$Sc(CH_2SiMe_3)_3(THF)_2$ (**1b**): prepared from $ScCl_3$, 80% yield. ^{1}H NMR (400 MHz, toluene-d8) δ 4.06 (t, *J* = 6.5 Hz, 8H), 1.52-1.37 (m, 8H), 0.18 (s, 27H), -0.39 (s, 6H). The NMR data is in good agreement with that reported in the literature.[1]

$Lu(CH_2SiMe_3)_3(THF)_2$ (**1c**): prepared from $LuCl_3$, 85% yield. ^1H NMR (400 MHz, C_6D_6) δ 3.96 (t, *J* = 6.4 Hz, 8H), 1.29 (t, *J* = 6.5 Hz, 8H), 0.29 (s, 27H), -0.89 (s, 6H). The NMR data is in good agreement with that reported in the literature.[2]

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[1] M. F. Lappert, R. Pearce, *J. Chem. Soc., Chem. Commun.*, **1973**, 126.
[2] S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics,* **2000**, *19*, 4690-4700.

Reaction of 1a-1c with 4-Bromoanisole

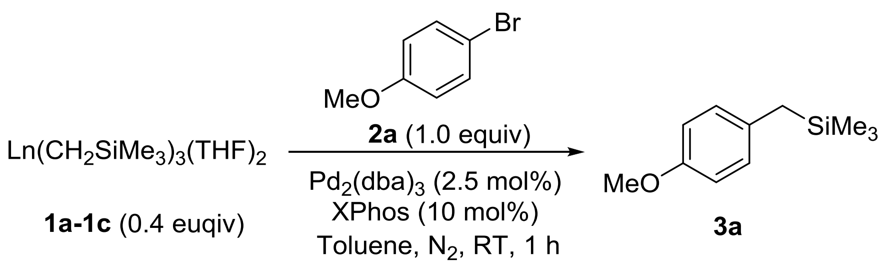
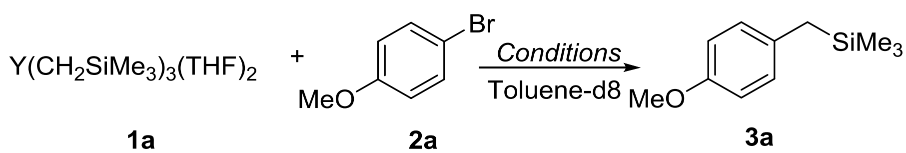


Table S1. Reaction of **1a-1c** with 4-bromoanisole **2a** in the presence of $Pd_2(dba)_3$/XPhos

Entry	Ln	$Ln(CH_2SiMe_3)_3(THF)_2$	Yield[b]
1	Y	**1a**	92%
2	Sc	**1b**	95%
3	Lu	**1e**	89%

[a] Conditions: 4-bromoanisole **2a** (1.0 equiv, 0.3 mmol), $Pd_2(dba)_3$ (2.5 mol%, 0.0075 mmol), XPhos (10 mol%, 0.03 mmol) and $Ln(CH_2SiMe_3)_3(THF)_2$ **1** (0.4 equiv, 0.12 mmol) in toluene (4 mL) at room temperature, 1h. [b]All yields of **3a** are reported after silica gel chromatographic purification.

Complete Table for Condition Optimization

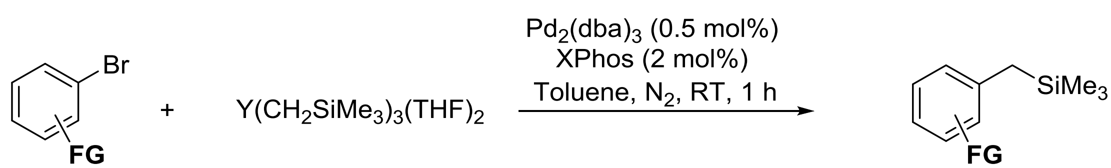


General Procedure: In a dry Schlenk flask, to a mixture of Pd catalyst, ligand and 4-bromoanisole **2a** (1.0 equiv, 0.075 mmol) in 0.8 mL of dry toluene-d8 was added a solution of (trimethylsilyl)methyl yttrium complex **1a** (0.33-0.4 equiv) in 0.2 mL of dry toluene-d8 dropwise. After being stirred at room temperature for 1 h, the reaction mixture was submitted to ^{1}H NMR analysis to calculate the conversion of **2a**. Then the reaction was quenched with saturated NH_4Cl aqueous solution (10 mL). The resulting mixture was extracted by ethyl acetate (3 × 5 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel chromatography with petroleum ether/dichloromethane (100:0 to 90:10) as the eluent to give the product **3a**.

Table S2. Condition optimization for the cross-coupling of **1a** with **2a**.

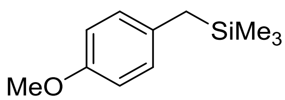
Entry	[Pd] (mol%)	Ligand (mol%)	**1a** (equiv)	Solvent	Conv. of **2a** (%)
1	-	-	0.4	Toluene	0
2	$Pd_2(dba)_3$ (2.5)	-	0.4	Toluene	0
3	$Pd_2(dba)_3$ (2.5)	XPhos (10)	0.4	Toluene	100
4	$Pd_2(dba)_3$ (2.5)	SPhos (10)	0.4	Toluene	55
5	$Pd(P\textit{t}Bu_3)_2$ (5)	-	0.4	Toluene	17
6	$Pd_2(dba)_3$ (2.5)	XPhos (10)	0.4	THF	33
7	$Pd_2(dba)_3$ (2.5)	XPhos (10)	0.4	Et_2O	6
8	$Pd_2(dba)_3$ (1)	XPhos (4)	0.33	Toluene	100
9	$Pd_2(dba)_3$ (0.5)	XPhos (2)	0.33	Toluene	100
10	$Pd_2(dba)_3$ (0.25)	XPhos (1)	0.33	Toluene	85
11	$Pd_2(dba)_3$ (0.5)	XPhos (1)	0.33	Toluene	100
12	$Pd_2(dba)_3$ (2.5)	PPh_3 (10)	0.4	Toluene	0

Substrate Scope



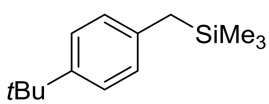
2 (1.0 equiv) **1a** (0.33 euqiv) **3**

General Procedure: In a dry Schlenk flask, to a mixture of $Pd_2(dba)_3$, XPhos and arylbromide **2** (1.0 equiv, 0.3 mmol) in 3.2 mL of dry toluene was added a solution of (trimethylsilyl)methyl yttrium complex **1a** (0.33 equiv) in 0.8 mL of dry toluene dropwise. After being stirred at room temperature for 1 h, the reaction was quenched with saturated NH_4Cl aqueous solution (20 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **3**.



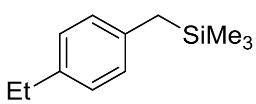
3a: 89%

From the reaction of 4-bromoanisole **2a** with **1a**. R_f = 0.45 (Petroleum ether/ethyl acetate 150:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.01 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 132.5, 128.9, 113.8, 55.4, 25.8, -1.8. The NMR data is in good agreement with that reported in the literature.[3]



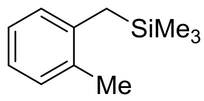
3b: 85%

From the reaction of 4-*tert*-butylphenyl bromide **2b** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 2.04 (s, 2H), 1.31 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 137.3, 127.8, 125.1, 34.3, 31.6, 26.5, -1.7. The NMR data is in good agreement with that reported in the literature.[4]



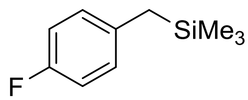
3c: 91%

From the reaction of 4-ethylphenyl bromide **2c** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.6, 128.1, 127.7, 28.5, 26.6, 15.8, -1.7. The NMR data is in good agreement with that reported in the literature.[5]



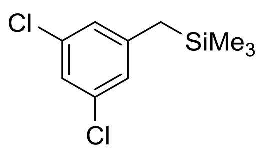
3d: 99%

From the reaction of 2-methylphenyl iodide **2d** with **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 2.23 (s, 3H), 2.10 (s, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 134.7, 130.2, 128.8, 125.7, 124.2, 23.8, 20.5, -1.2. The NMR data is in good agreement with that reported in the literature.[6]



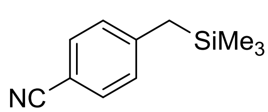
3e: 88%

From the reaction of 4-fluorophenyl bromide **2e** with **1a**. R_f = 0.5 (Petroleum ether/ethyl acetate 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.84 (m, 4H), 2.04 (s, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ160.4 (d, *J* = 241.1 Hz), 136.1 (d, *J* = 3.1 Hz), 129.2 (d, *J* = 7.5 Hz), 115.0 (d, *J* = 21.0 Hz), 26.2, -1.9. The NMR data is in good agreement with that reported in the literature.[7]



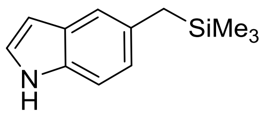
3f: 72%

From the reaction of 3,5-dichlorophenyl bromide **2f** with **1a**. R_f = 0.5 (Petroleum ether/ethyl acetate 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 1.9 Hz, 1H), 6.87 (d, *J* = 1.9 Hz, 2H), 2.04 (s, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 134.6, 126.4, 124.3, 27.2, -1.8. The NMR data is in good agreement with that reported in the literature.[8]



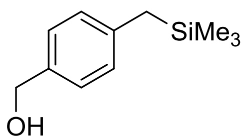
3g: 81%

From the reaction of 4-cyanophenyl bromide **2g** with **1a**. R_f = 0.5 (Petroleum ether/ethyl acetate 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 2H), -0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 132.1, 128.6, 119.6, 107.7, 28.4, -1.9. The NMR data is in good agreement with that reported in the literature.[9]



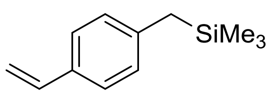
3h: 90%

From the reaction of 5-bromoindole **2h** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.28 – 7.22 (m, 2H), 7.17 – 7.12 (m, 1H), 6.86 (dd, J = 8.4, 1.4 Hz, 1H), 6.45 (t, J = 2.2 Hz, 1H), 2.15 (s, 2H), -0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6, 131.6, 128.4, 124.1, 123.4, 119.2, 110.6, 102.1, 29.9, 26.7, -1.7. The NMR data is in good agreement with that reported in the literature.[4]



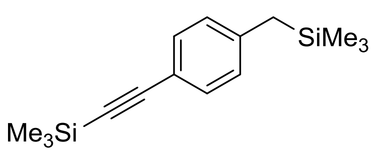
3i: 85%

From the reaction of 4-bromobenzyl alcohol **2i** with **1a**. R_f = 0.3 (Petroleum ether/ethyl acetate 80:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 4.63 (d, J = 5.6 Hz, 2H), 2.08 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 136.5, 128.3, 127.3, 65.6, 27.0, -1.8. The NMR data is in good agreement with that reported in the literature.[10]



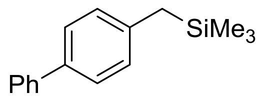
3j: 90%

From the reaction of 4-bromostyrene **2j** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.68 (d, J = 17.6 Hz, 1H), 5.16 (d, J = 10.9 Hz, 1H), 2.09 (s, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 137.0, 133.5, 128.3, 126.2, 112.1, 27.1, -1.8. The NMR data is in good agreement with that reported in the literature.[11]



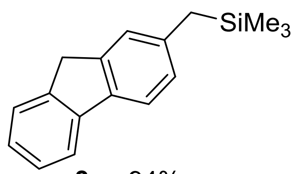
3k: 97%

From the reaction of ((4-bromophenyl)ethynyl)trimethylsilane **2k** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 2.09 (s, 2H), 0.25 (s, 9H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 132.0, 128.0, 118.6, 105.8, 93.0, 27.6, 0.2, -1.8. The NMR data is in good agreement with that reported in the literature.[12]



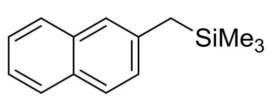
3l: 94%

From the reaction of 4-bromobiphenyl **2l** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 2.19 (s, 2H), 0.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.9, 136.9, 128.8, 128.6, 127.0, 126.9, 126.8, 26.9, -1.7. The NMR data is in good agreement with that reported in the literature.[4]



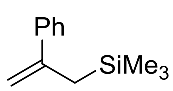
3m: 94%

From the reaction of 2-fluorenyl bromide **2m** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, C_7D_8) δ 7.57 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.26 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 6.98 (s, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.49 (s, 2H), 2.02 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, C_7D_8) δ 143.9, 143.2, 142.5, 139.2, 138.5, 126.9, 126.2, 125.3, 125.1, 124.8, 119.9, 119.6, 36.9, 27.3, -1.8. The NMR data is in good agreement with that reported in the literature.[10]



3n: 93%

From the reaction of 2-naphthyl bromide **2n** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 8.0 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.19 (dd, J = 8.4, 1.3 Hz, 1H), 2.27 (s, 2H), 0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 134.0, 131.1, 128.0, 127.7, 127.6, 127.1, 125.9, 125.3, 124.5, 27.5, -1.7. The NMR data is in good agreement with that reported in the literature.[4]



3o: 76%

From the reaction of α-bromostyrene **2o** with **1a**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 2H), 7.35 – 7.21 (m, 4H), 5.12 (s, 1H), 4.87 (s, 1H), 2.02 (s, 2H), -0.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 142.9, 128.2, 127.3, 126.5, 110.2, 26.3, -1.3. The NMR data is in good agreement with that reported in the literature.[13]

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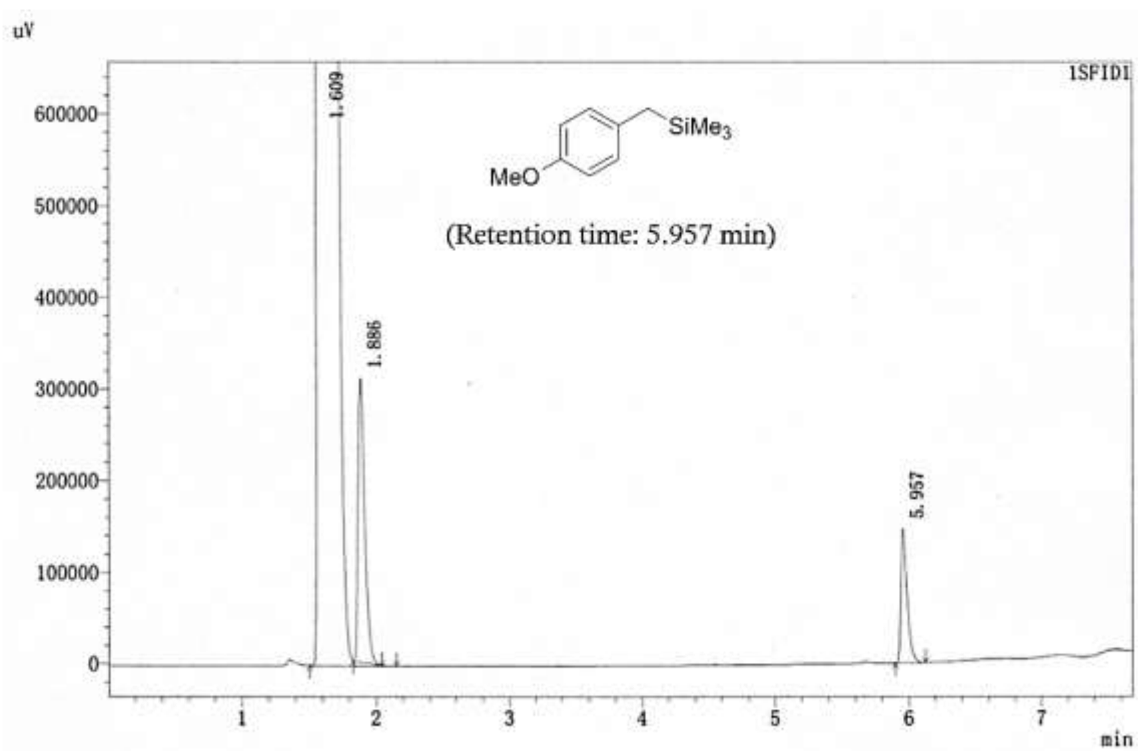
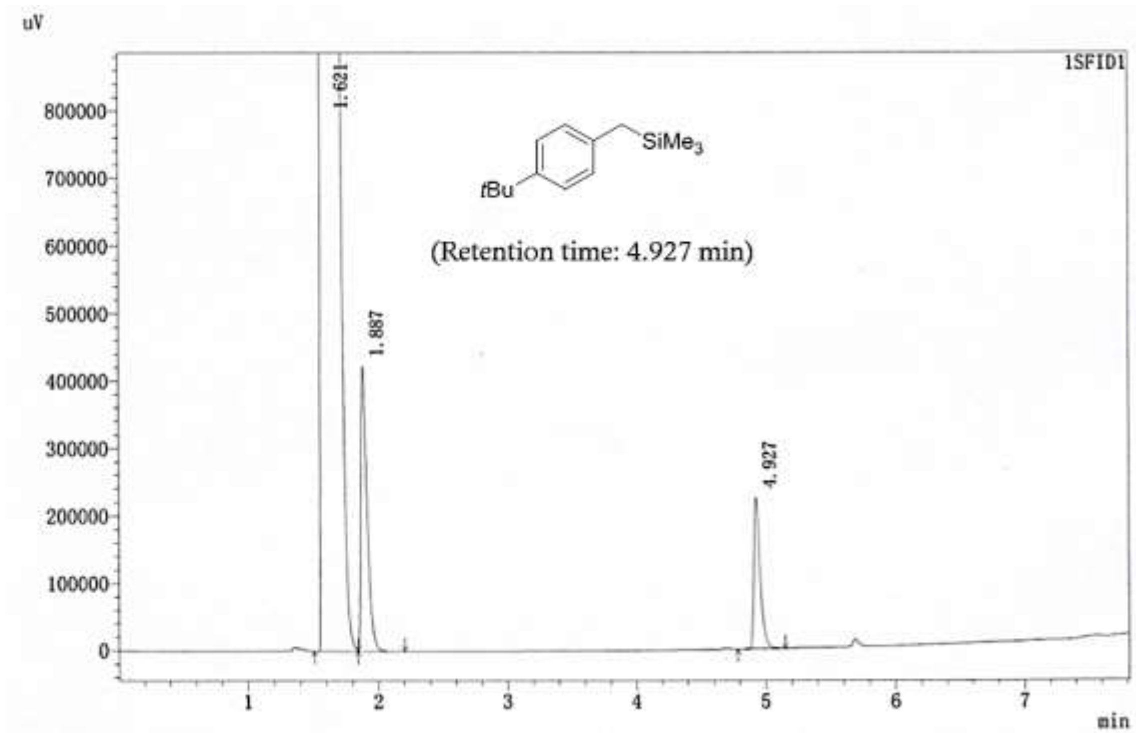
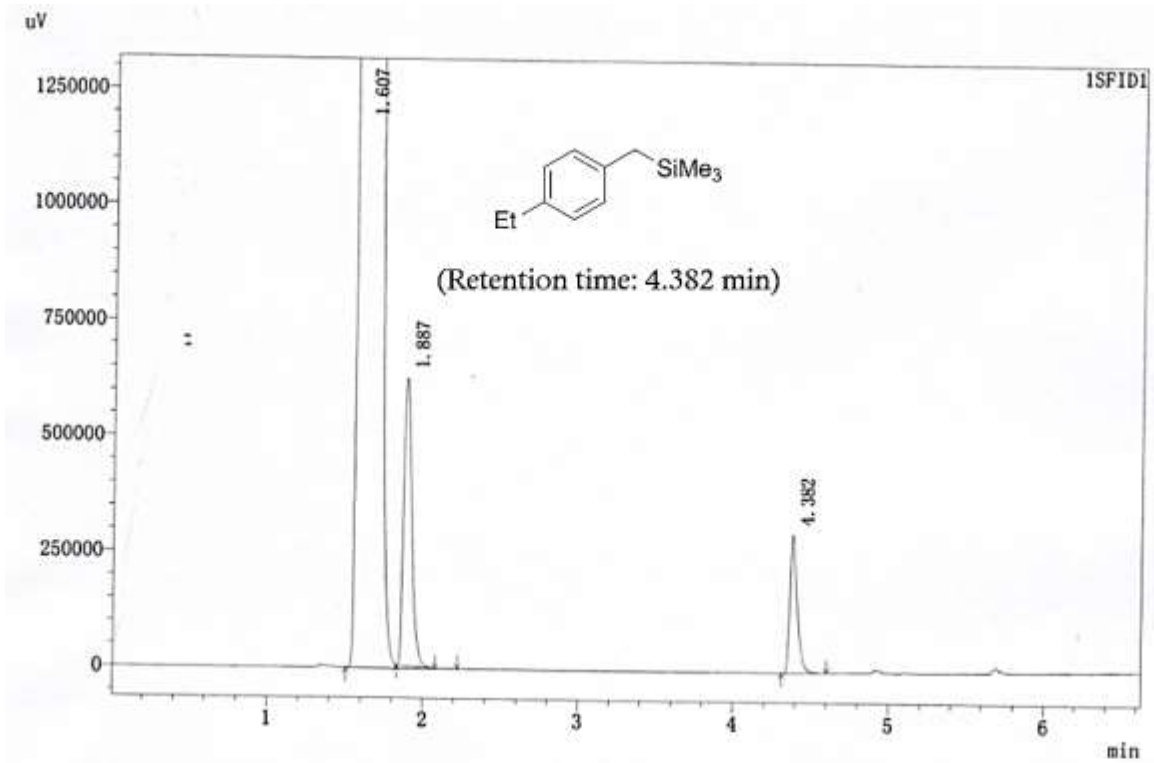
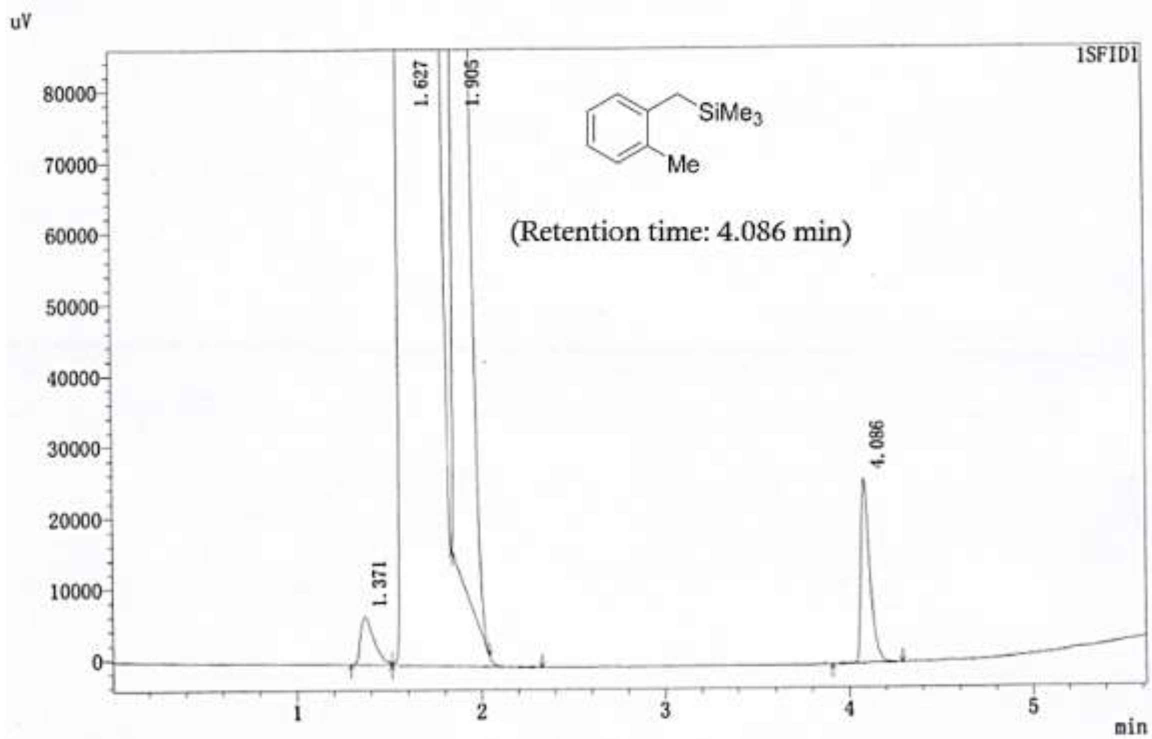
Gas Chromatographic Analysis of the Products

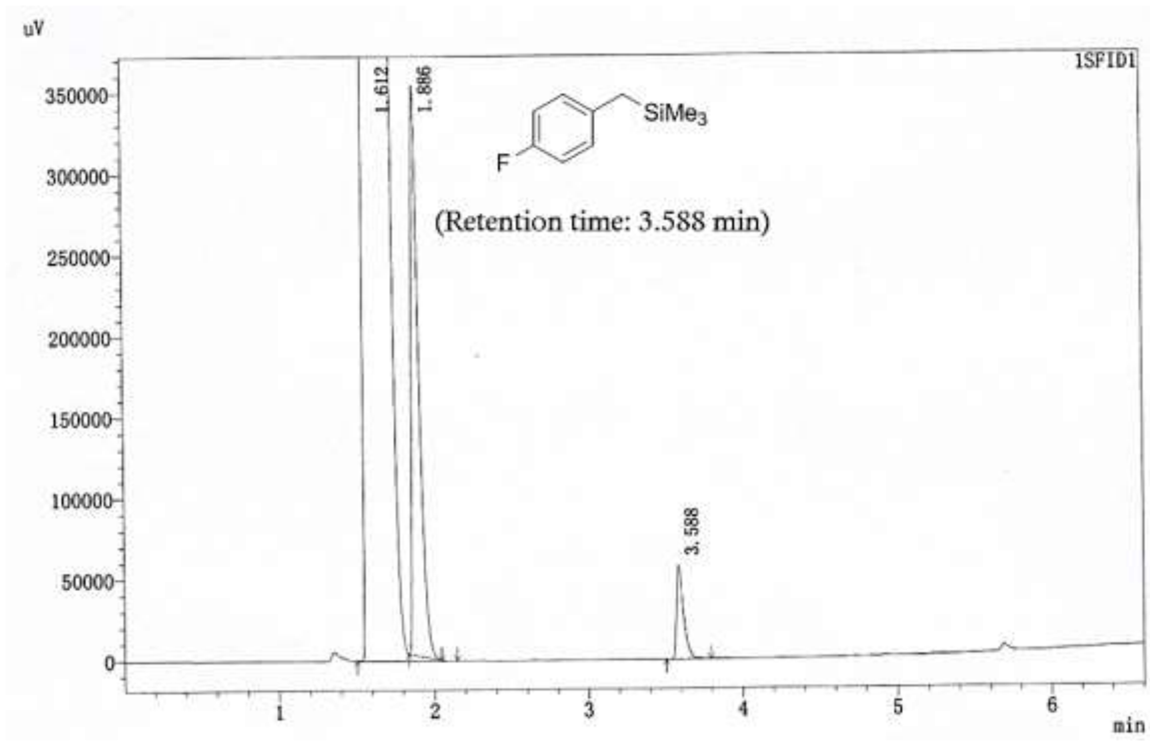
Conditions: SPL temperature, 250 ℃; SFID temperature, 250 ℃; Column (WondaCAP WAX) 80 ℃ for 1 min, heated to 250 ℃ at the rate of 20 ℃/min.

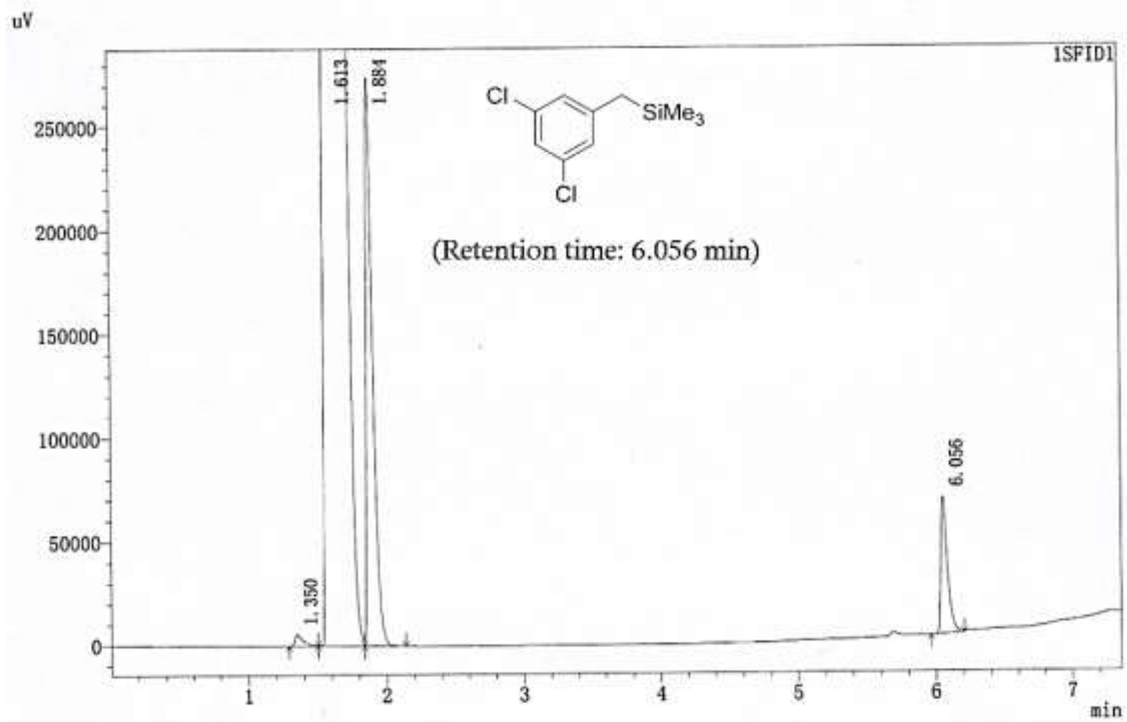


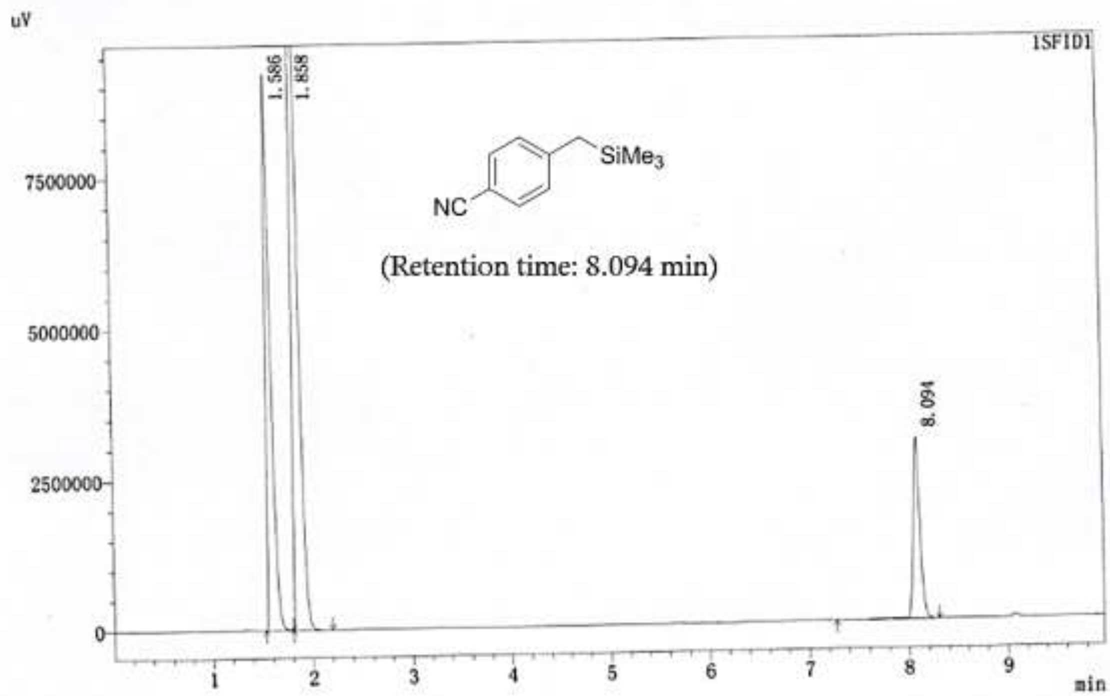

uV
1SFID1
(Retention time: 4.927 min)
1.621
1.887
4.927
min

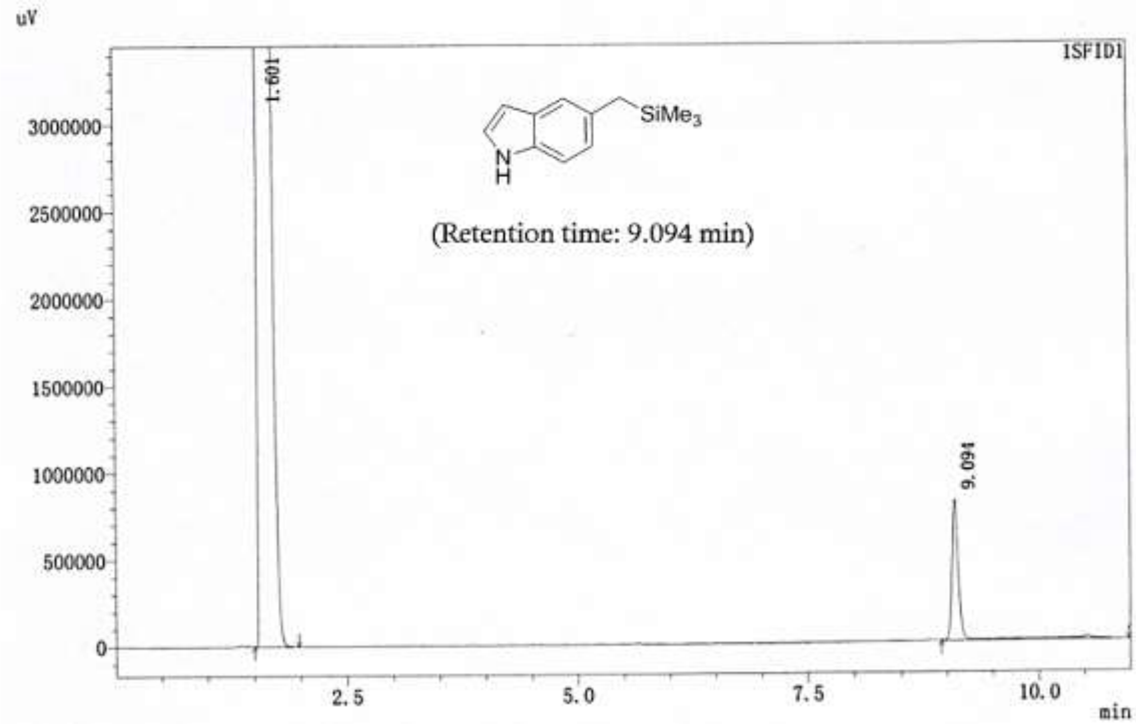

uV
1SFID1
(Retention time: 4.382 min)
1.607
1.887
4.382
min

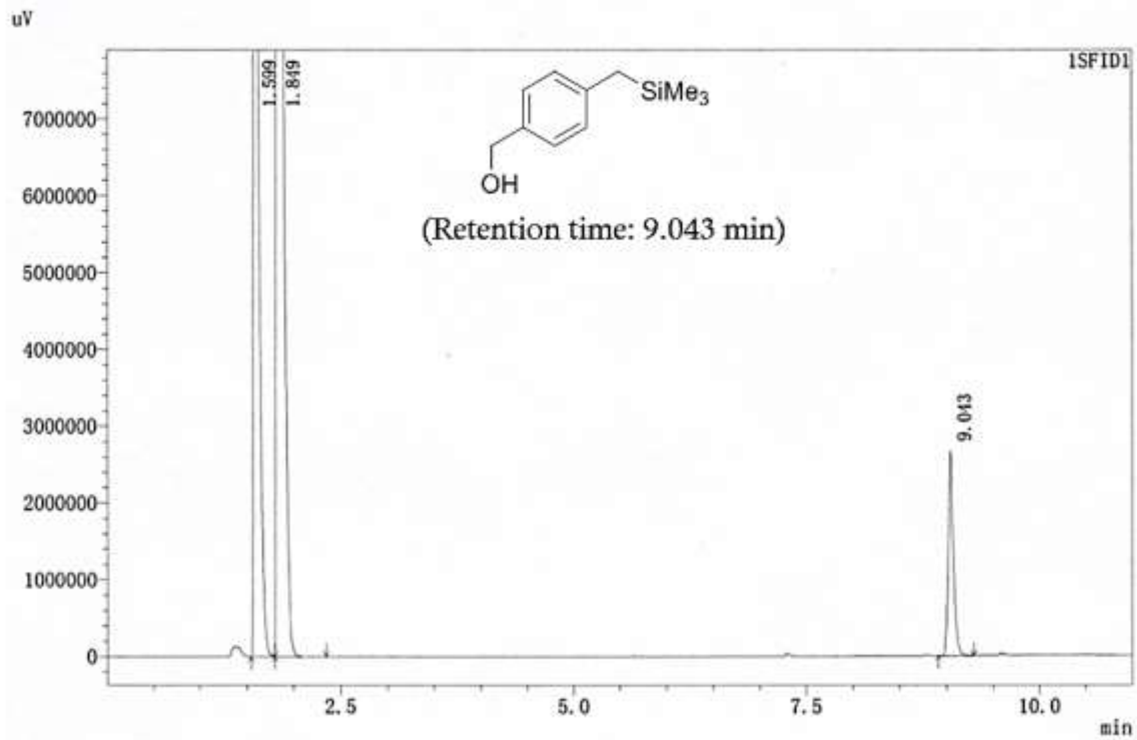

uV
1SFID1
SiMe3
Me
(Retention time: 4.086 min)
1.371
1.627
1.905
4.086
min

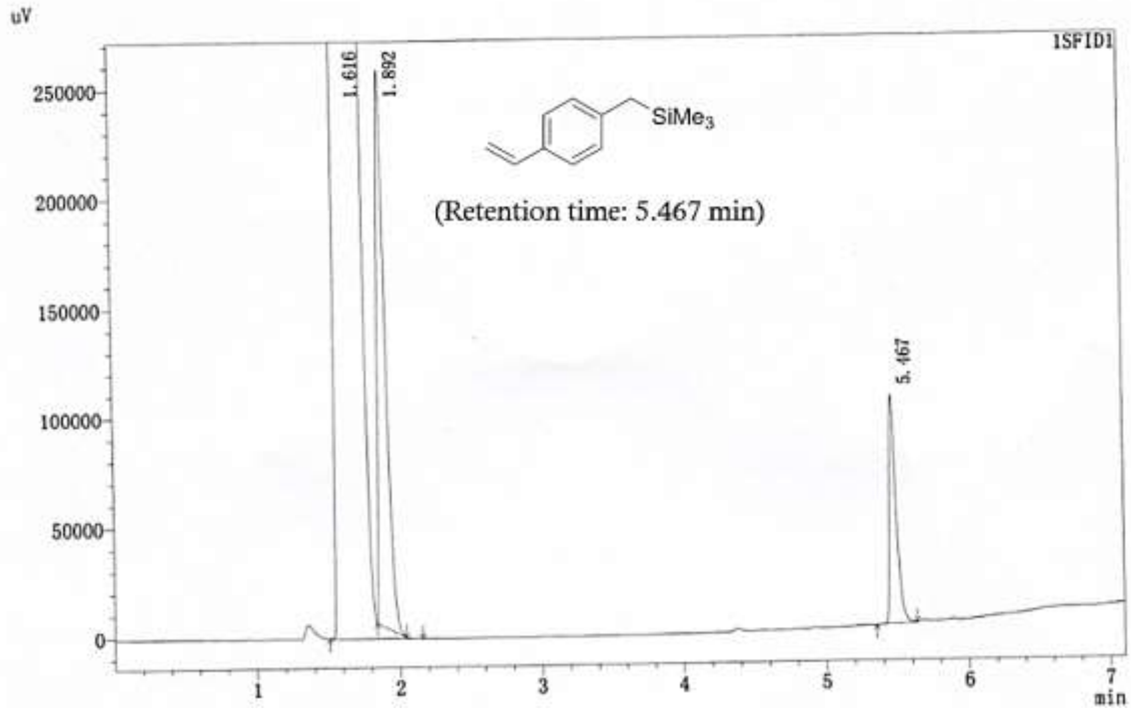

uV
1SFID1
SiMe3
F
(Retention time: 3.588 min)
1.612
1.886
3.588
min

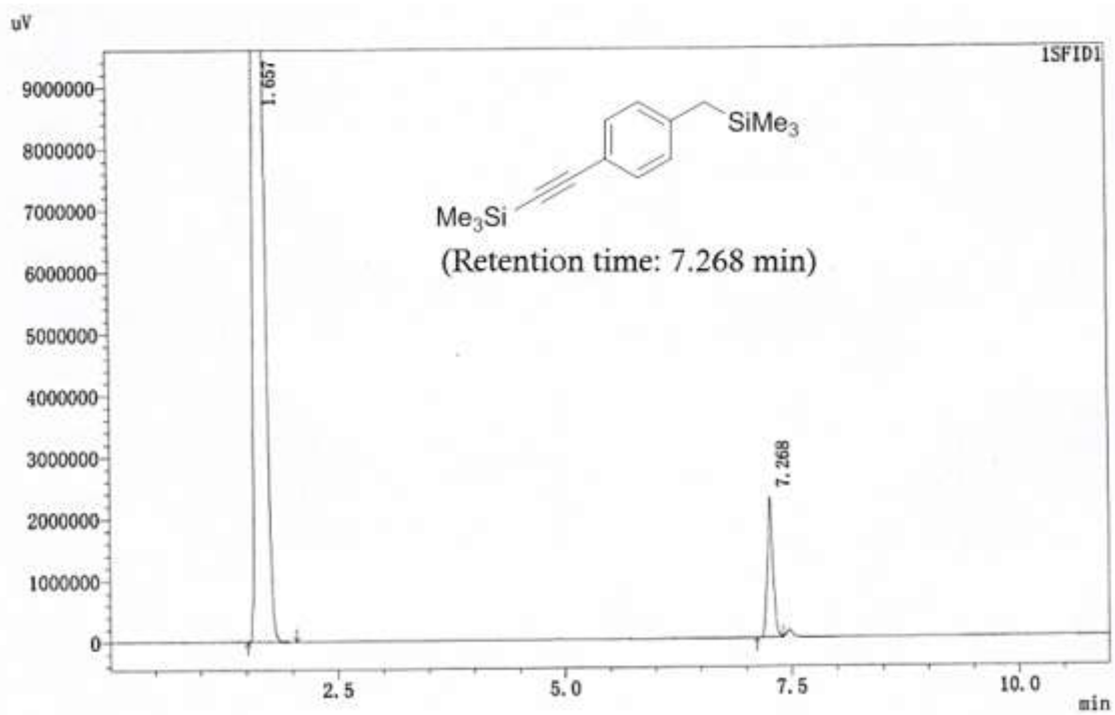

uV
1SFID1
250000
200000
150000
100000
50000
0
1.350
1.613
1.884
6.056
Cl
SiMe3
Cl
(Retention time: 6.056 min)
1
2
3
4
5
6
7
min

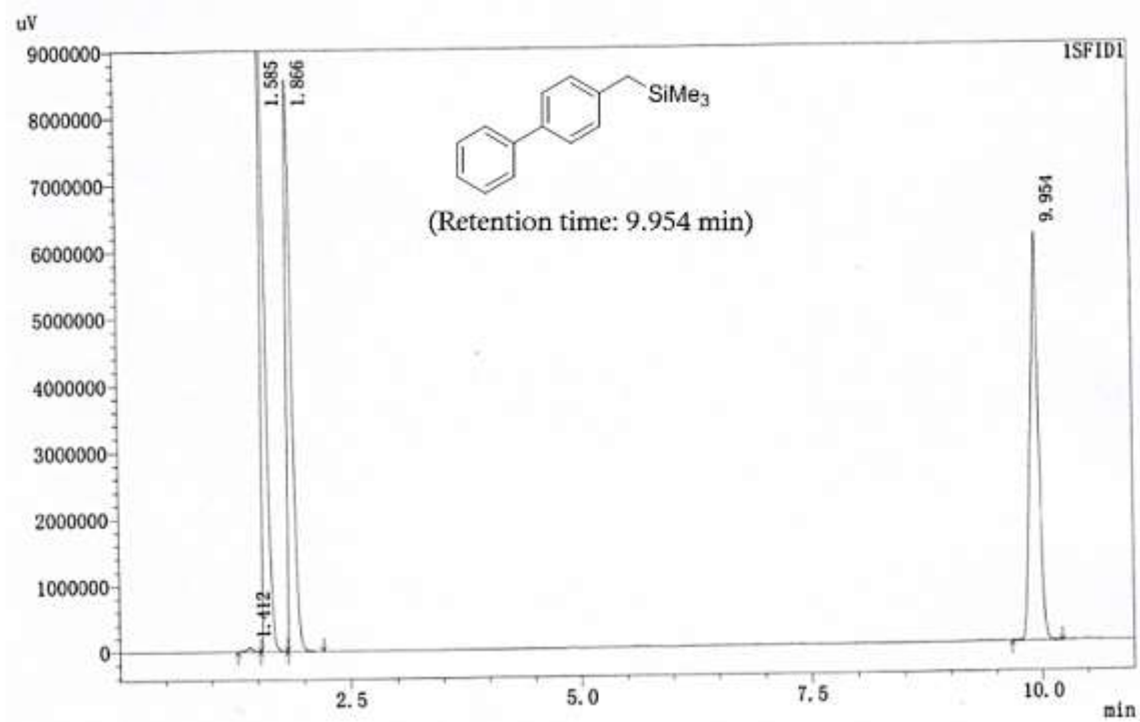

uV
1SFID1
7500000
5000000
2500000
0
1.586
1.858
8.094
SiMe3
NC
(Retention time: 8.094 min)
1
2
3
4
5
6
7
8
9
min

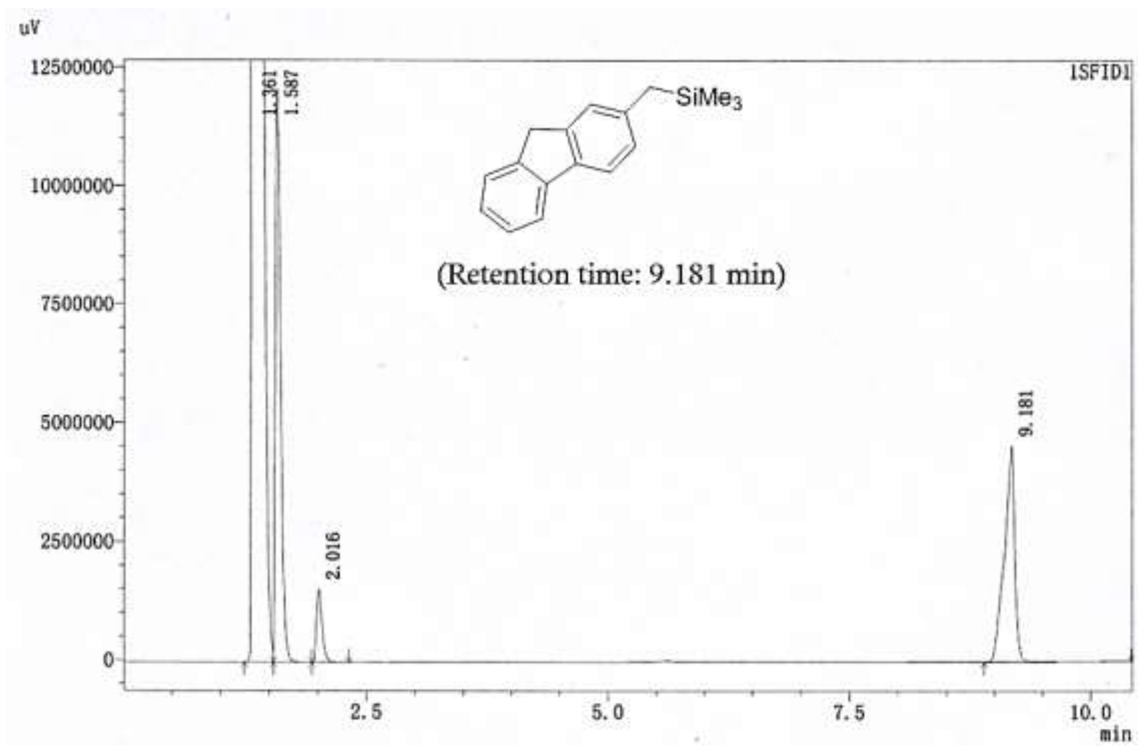

uV
1SFID1
SiMe3
N
H
(Retention time: 9.094 min)
1.601
9.094
3000000
2500000
2000000
1500000
1000000
500000
0
2.5
5.0
7.5
10.0
min

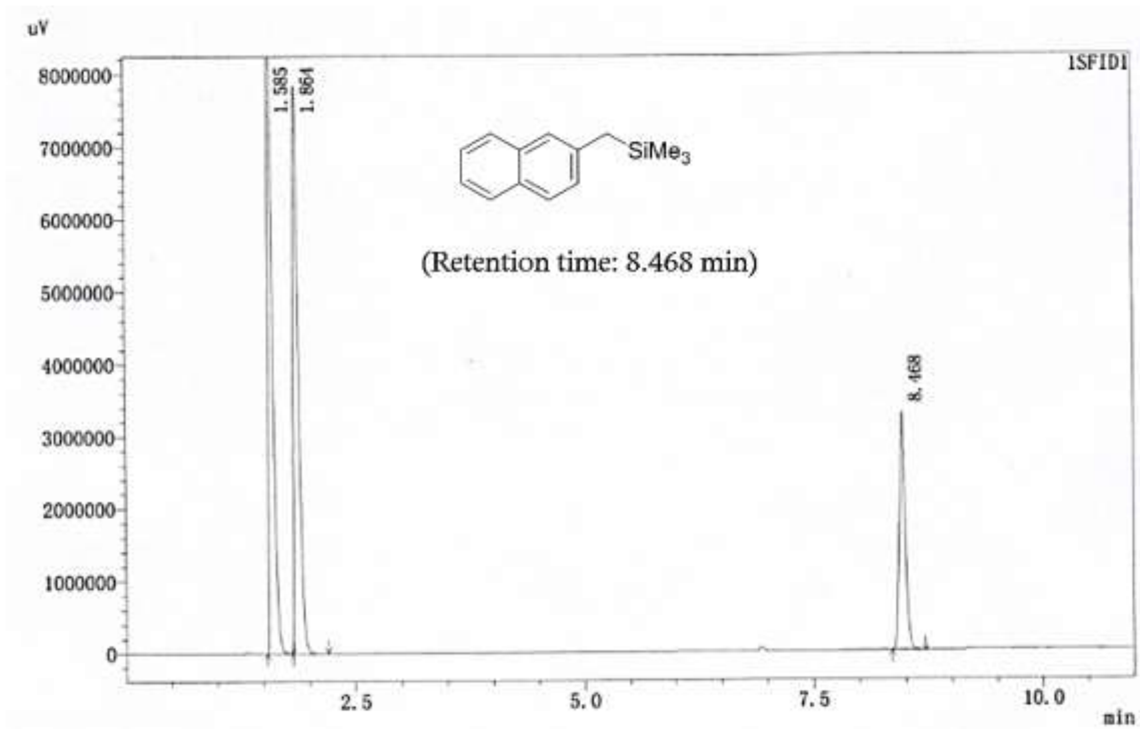

uV
1SFID1
SiMe3
OH
(Retention time: 9.043 min)
1.599
1.849
9.043
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
2.5
5.0
7.5
10.0
min

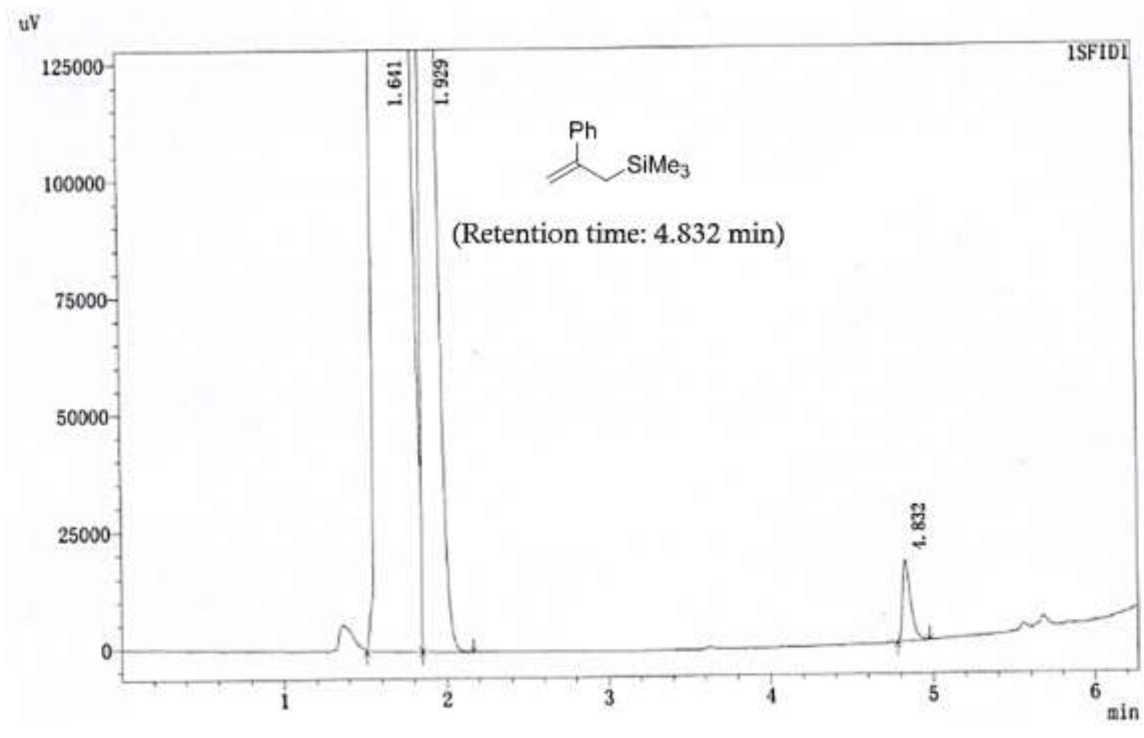

uV
1SFID1
SiMe3
(Retention time: 5.467 min)
1.616
1.892
5.467
250000
200000
150000
100000
50000
0
1
2
3
4
5
6
7
min


uV
1SFID1
SiMe3
Me3Si
(Retention time: 7.268 min)
1.657
7.268
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
2.5
5.0
7.5
10.0
min


uV
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
1SFID1
1.585
1.866
1.412
9.954
SiMe3
(Retention time: 9.954 min)
2.5
5.0
7.5
10.0
min

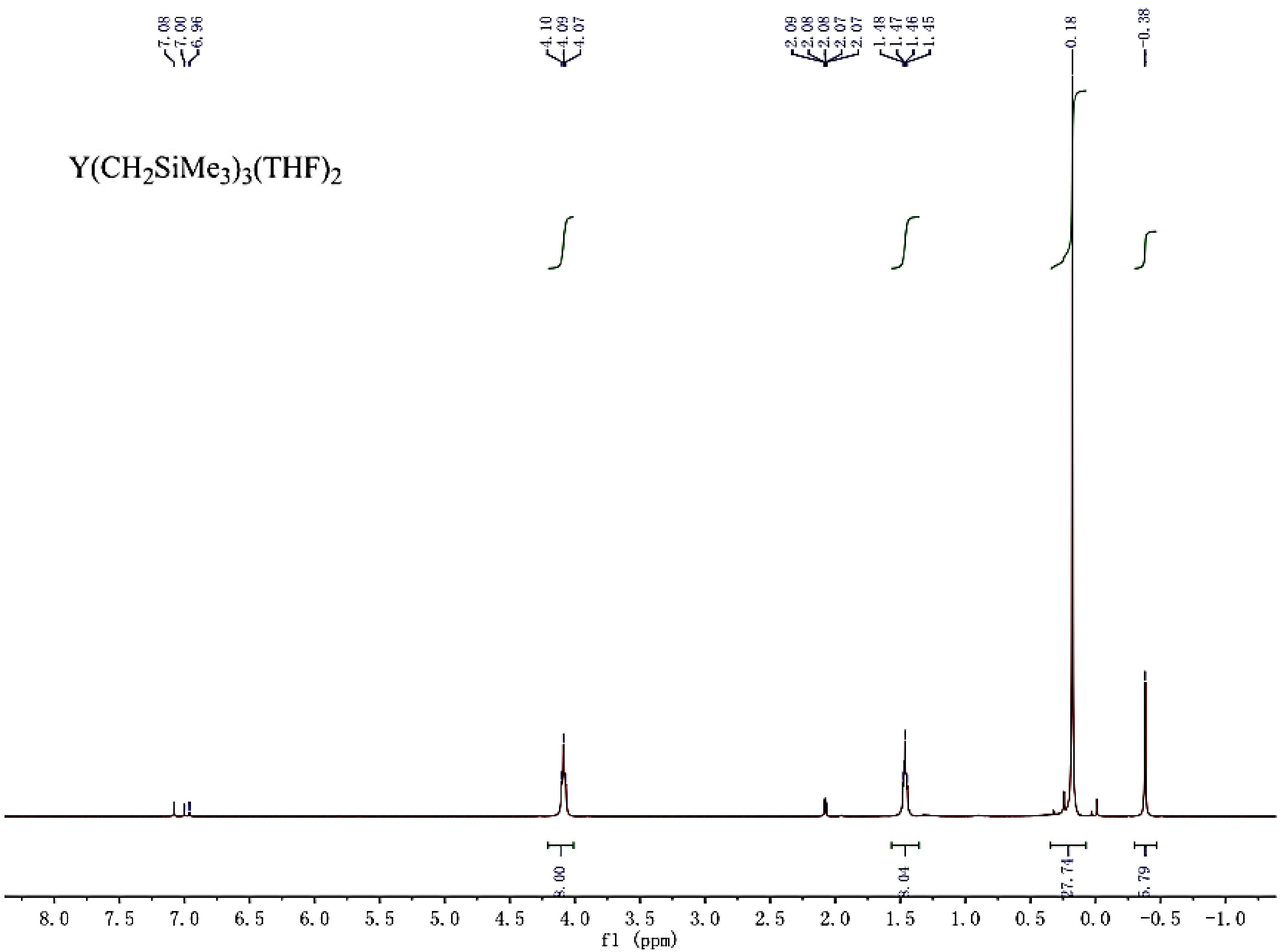

uV
12500000
10000000
7500000
5000000
2500000
0
1SFID1
1.361
1.587
2.016
9.181
SiMe3
(Retention time: 9.181 min)
2.5
5.0
7.5
10.0
min





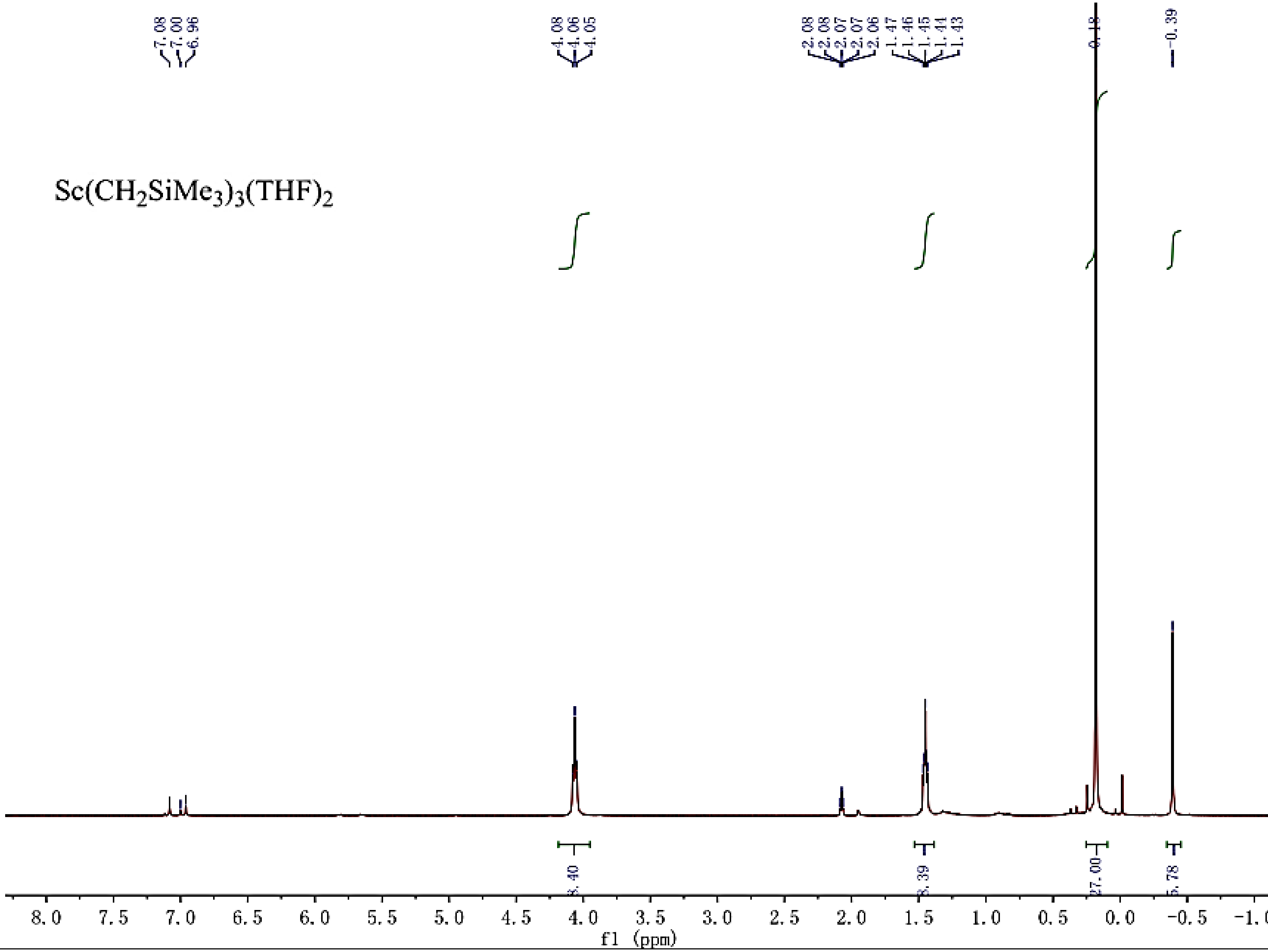
Copies of ^{1}H and ^{13}C NMR Spectra

^{1}H NMR of **1a**



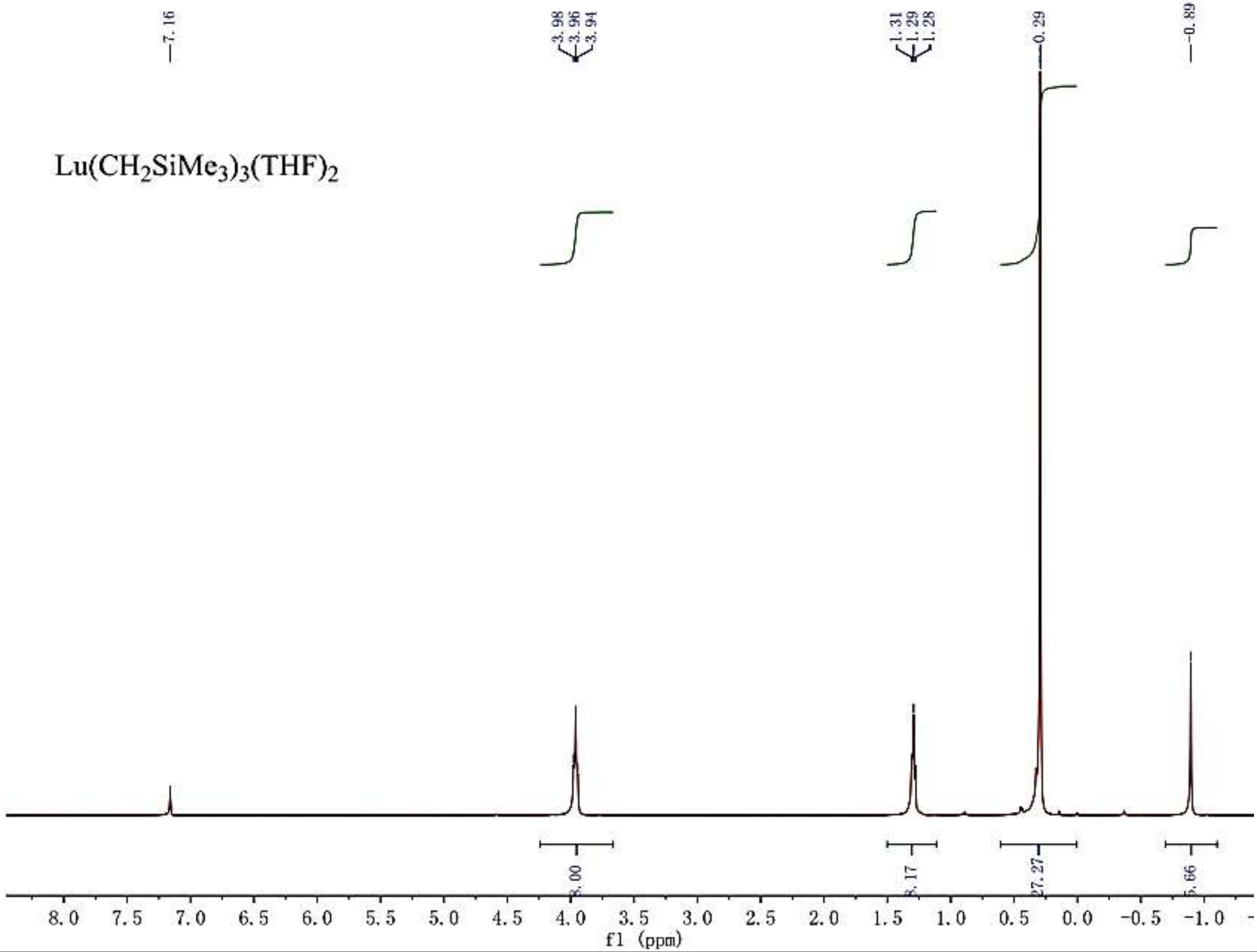
Y(CH2SiMe3)3(THF)2
7.08
7.00
6.96
4.10
4.09
4.07
2.09
2.08
2.08
2.07
2.07
1.48
1.47
1.46
1.45
0.18
-0.38
6.00
6.04
27.74
5.79
f1 (ppm)

[1]H NMR of **1b**

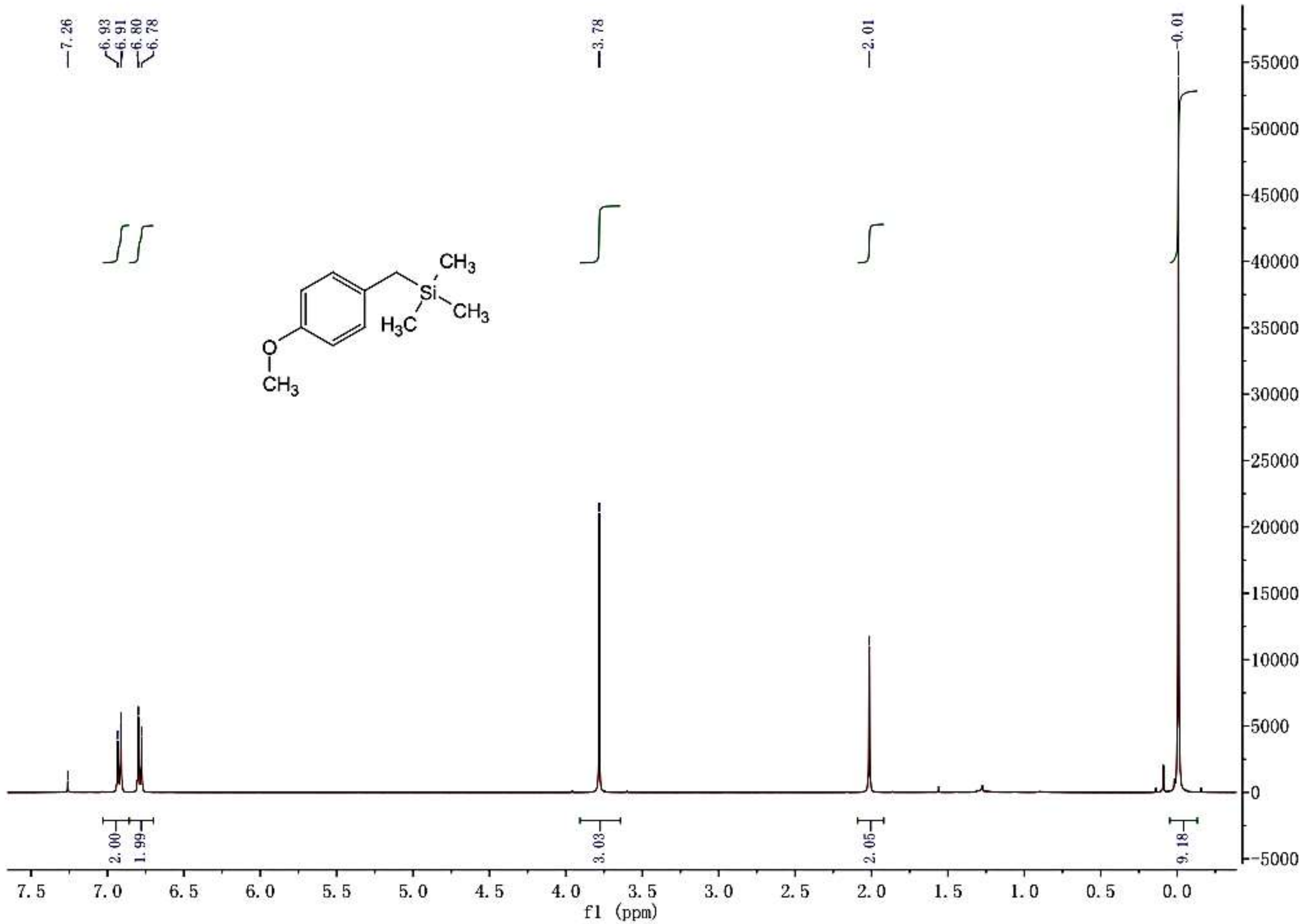


7.08
7.00
6.96
4.08
4.06
4.05
2.08
2.08
2.07
2.07
2.06
1.47
1.46
1.45
1.44
1.43
0.18
-0.39
Sc(CH2SiMe3)3(THF)2
8.40
8.39
27.00
5.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

^{1}H NMR of **1c**

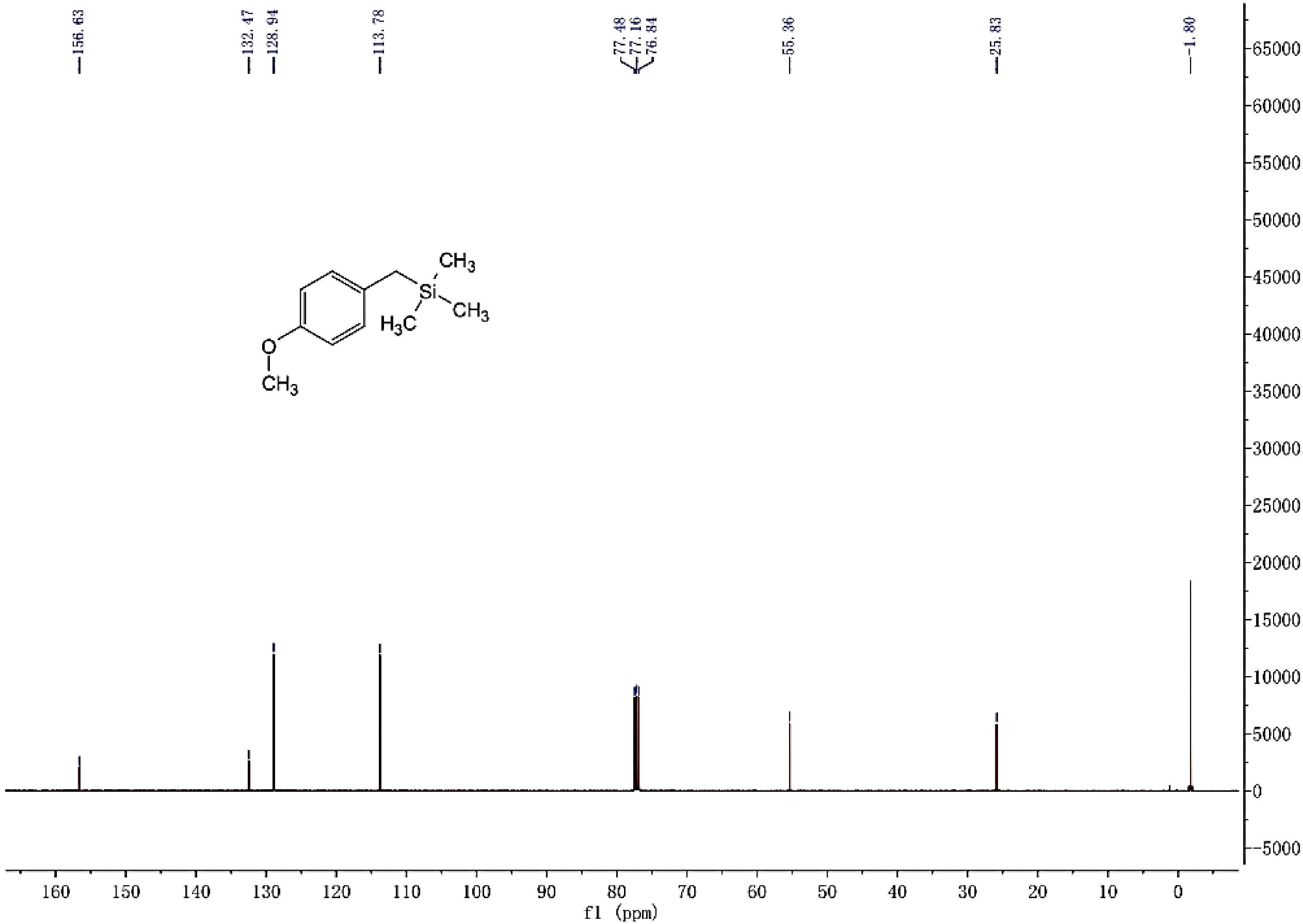


^{1}H NMR of **3a**

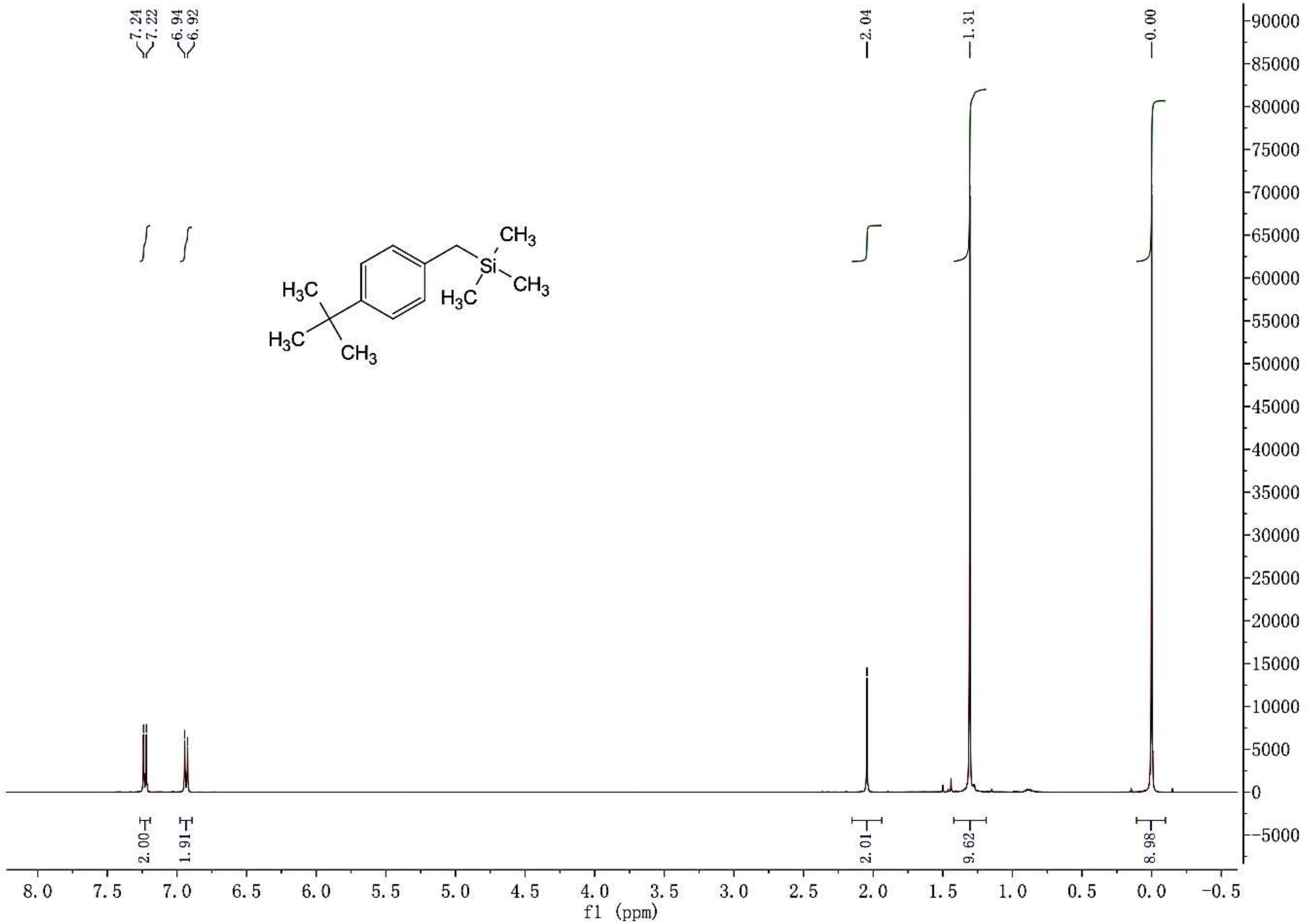


7.26
6.93
6.91
6.80
6.78
3.78
2.01
0.01
CH3
Si
H3C
CH3
O
CH3
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
2.00
1.99
3.03
2.05
9.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

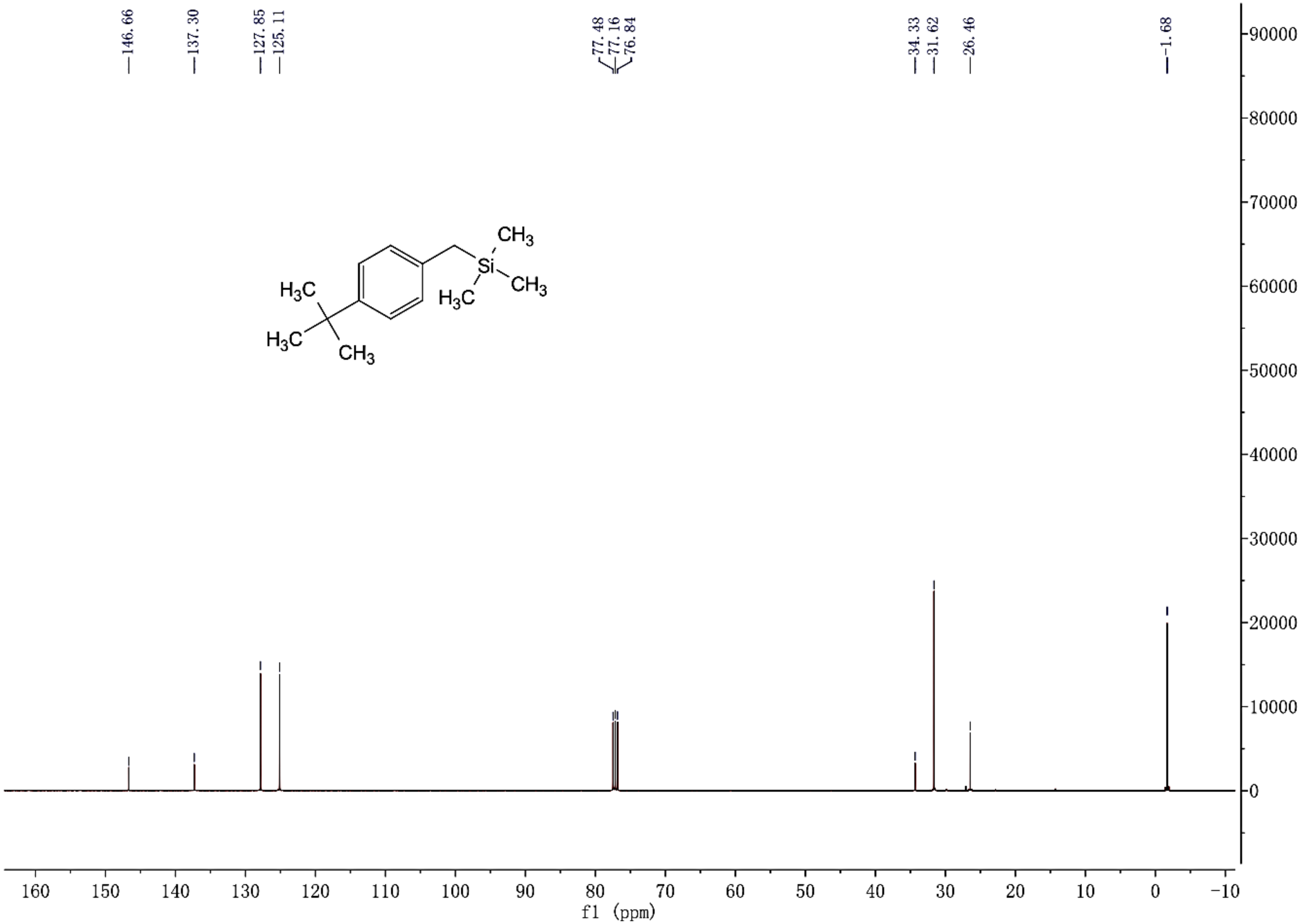
^{13}C NMR of **3a**



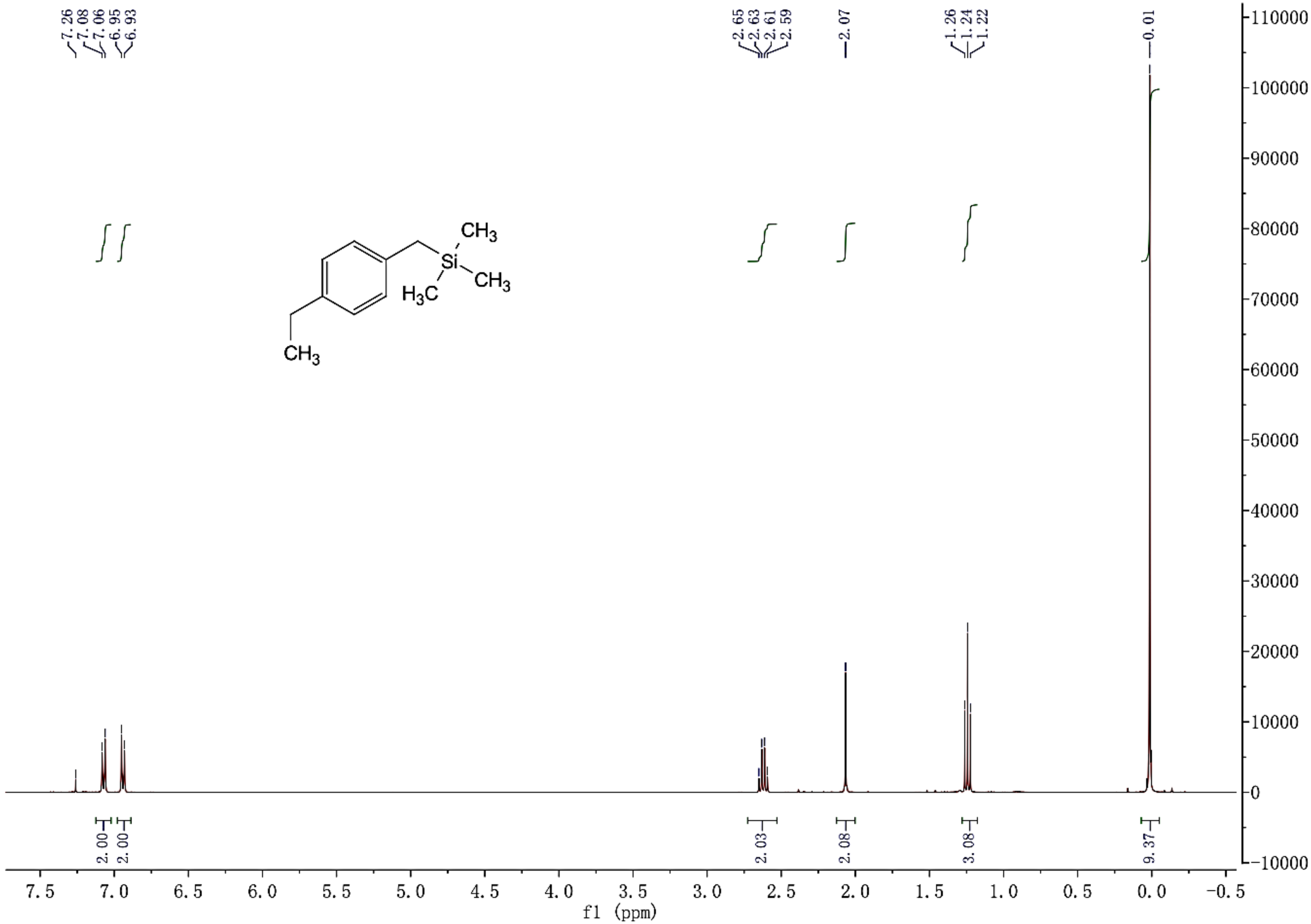
156.63
132.47
128.94
113.78
77.48
77.16
76.84
55.36
25.83
-1.80
CH3
Si
CH3
H3C
O
CH3
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.24
7.22
6.94
6.92
2.04
1.31
0.00
CH3
Si
CH3
H3C
H3C
H3C
CH3
2.00
1.91
2.01
9.62
8.98
f1 (ppm)

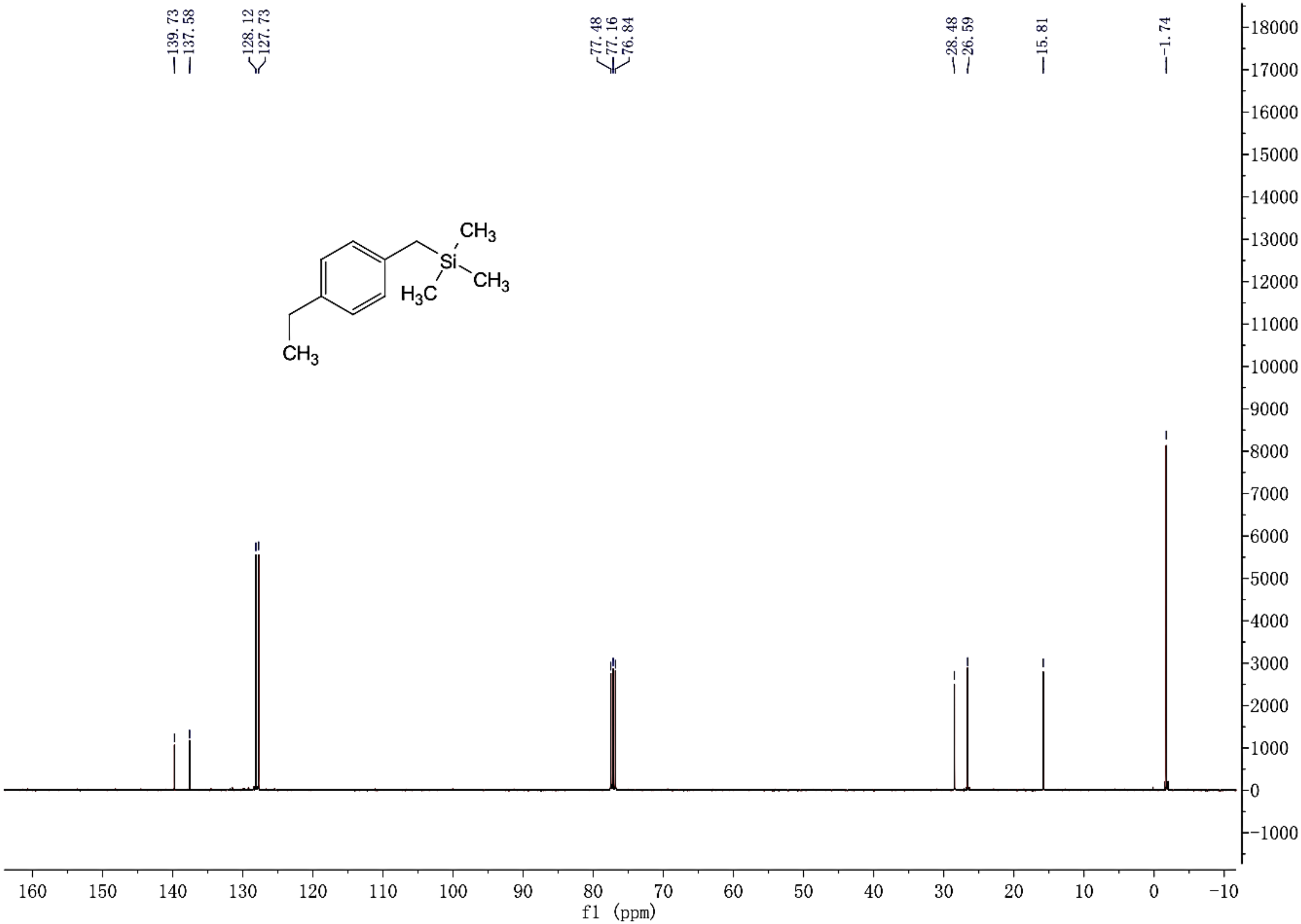
^{13}C NMR of **3b**


146.66
137.30
127.85
125.11
77.48
77.16
76.84
34.33
31.62
26.46
-1.68
CH3
Si
CH3
H3C
H3C
H3C
CH3
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

[1]H NMR of **3c**

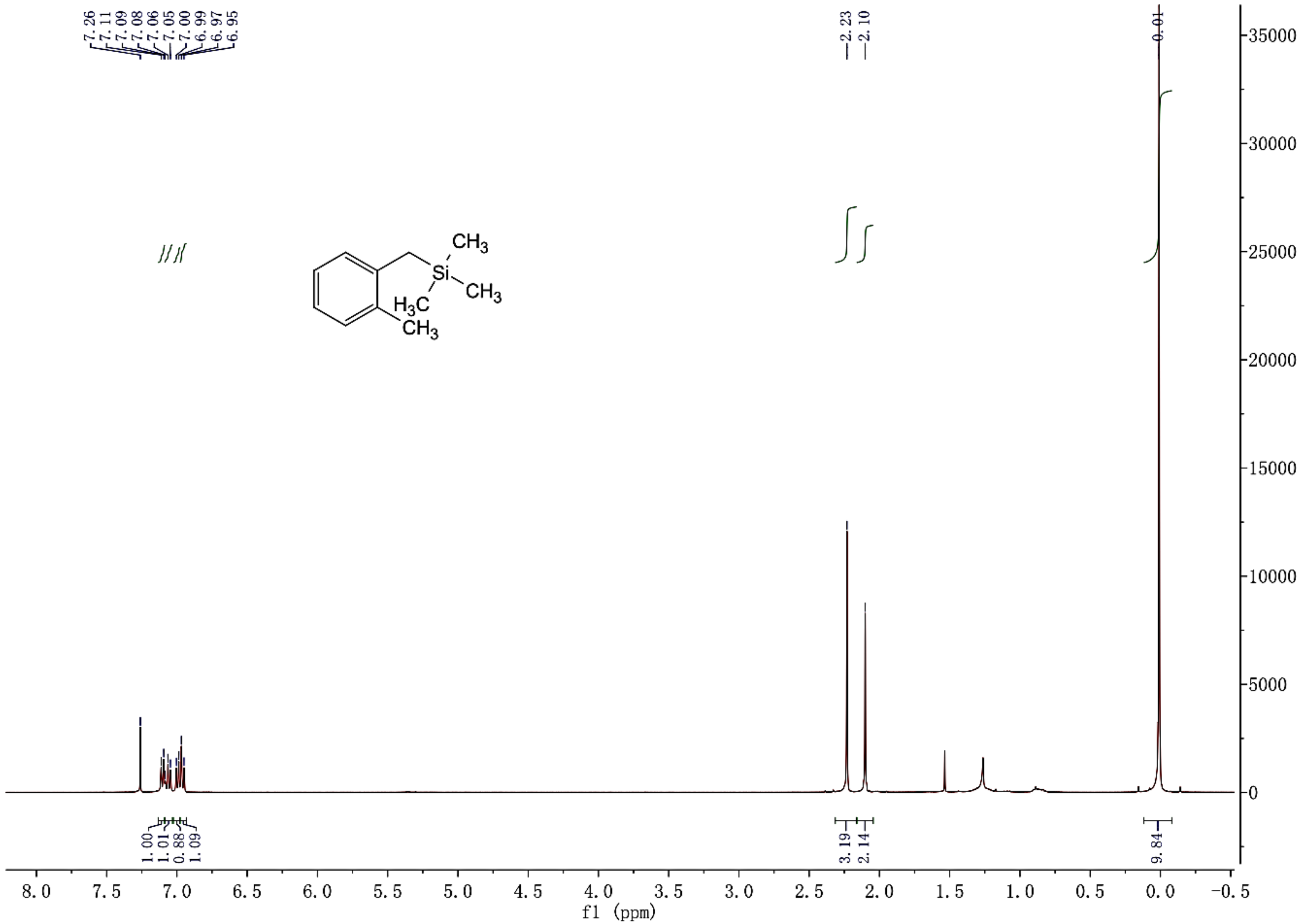

7.26
7.08
7.06
6.95
6.93
2.65
2.63
2.61
2.59
2.07
1.26
1.24
1.22
0.01
CH3
Si
CH3
H3C
CH3
2.00
2.00
2.03
2.08
3.08
9.37
f1 (ppm)

^{13}C NMR of **3c**



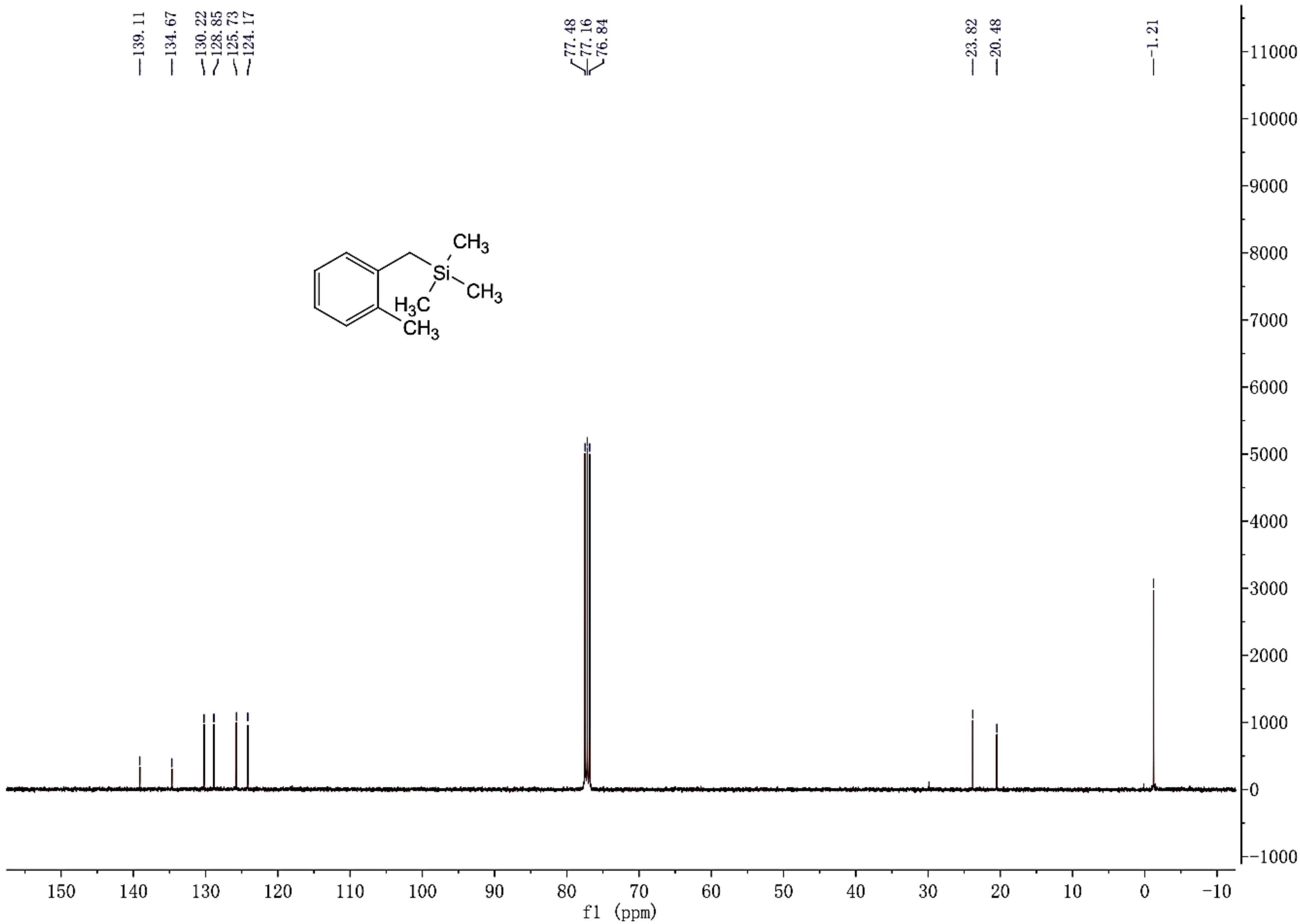
139.73
137.58
128.12
127.73
77.48
77.16
76.84
28.48
26.59
15.81
-1.74
CH3
Si
CH3
H3C
CH3
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of **3d**

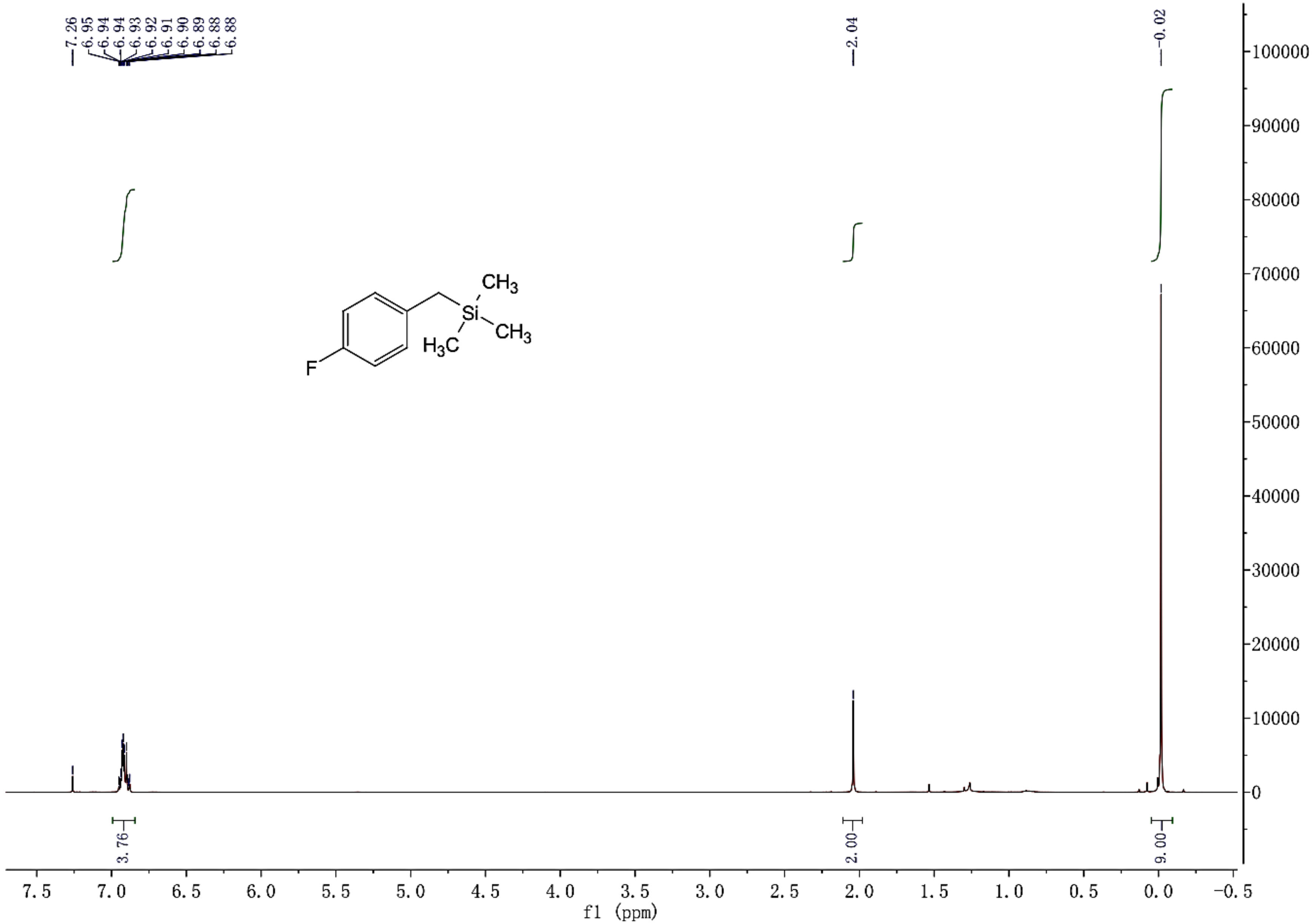


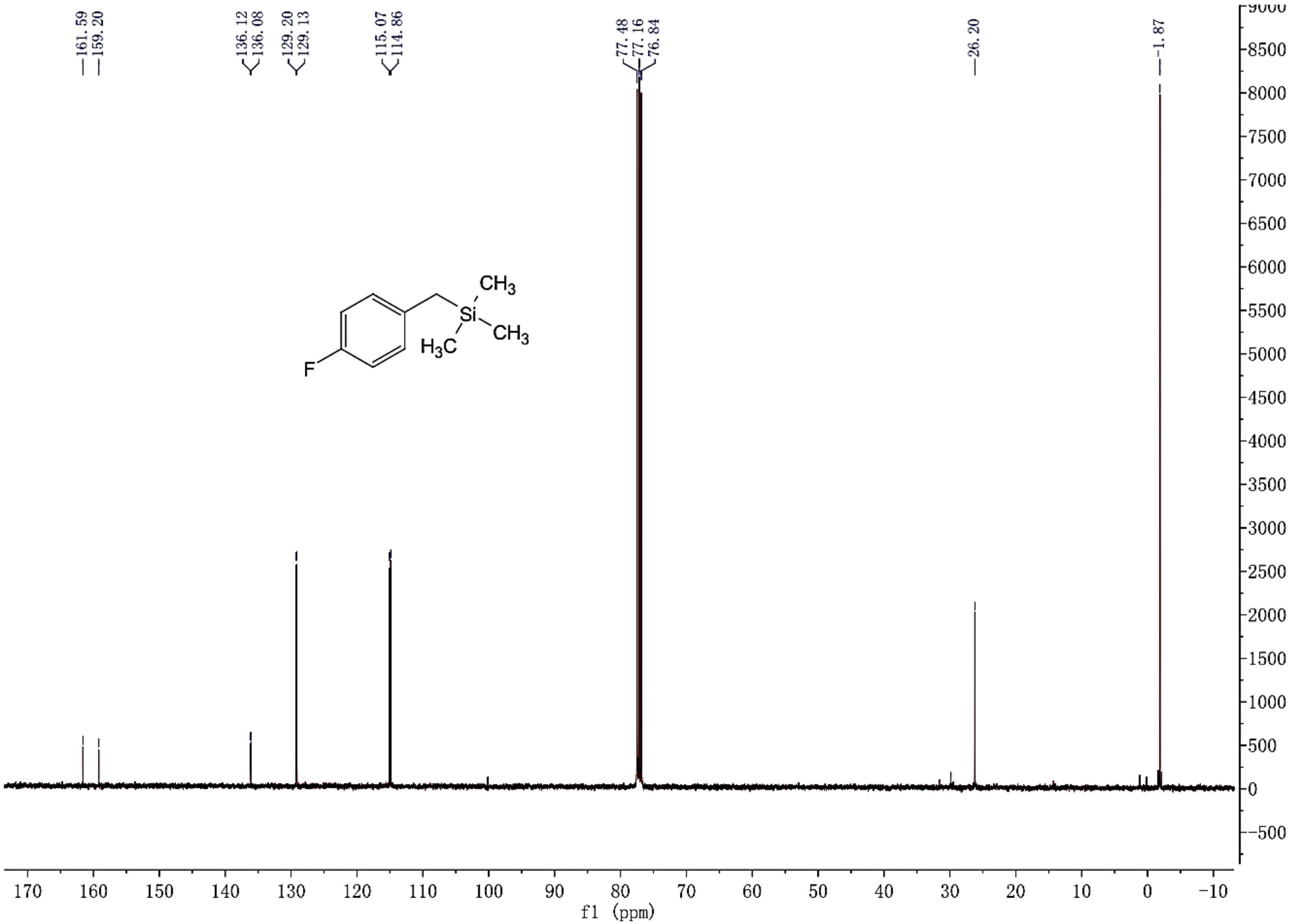
7.26
7.11
7.09
7.08
7.06
7.05
7.00
6.99
6.97
6.95
2.23
2.10
0.01
CH3
Si
CH3
H3C
CH3
1.00
1.01
0.88
1.09
3.19
2.14
9.84
f1 (ppm)

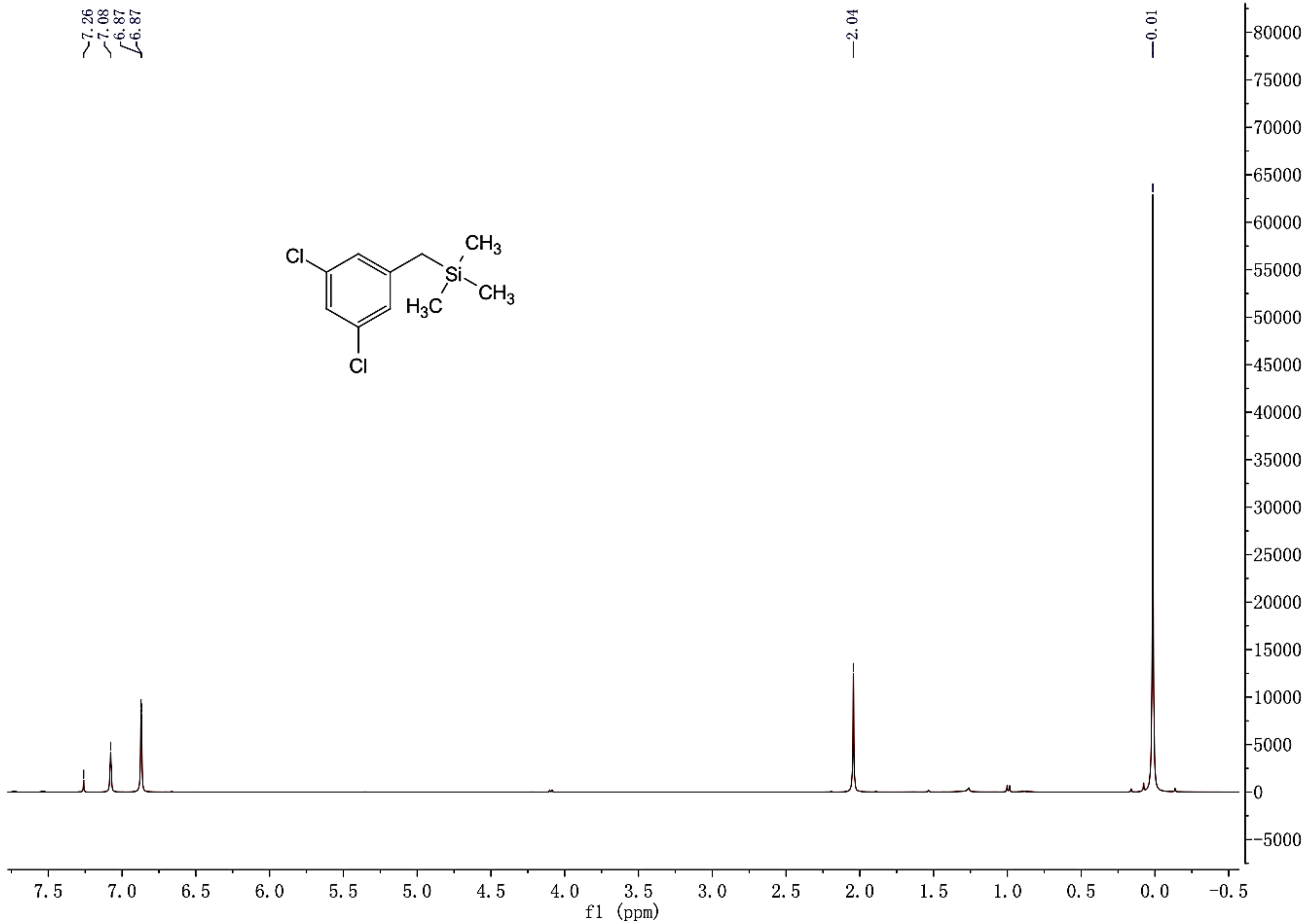
^{13}C NMR of **3d**



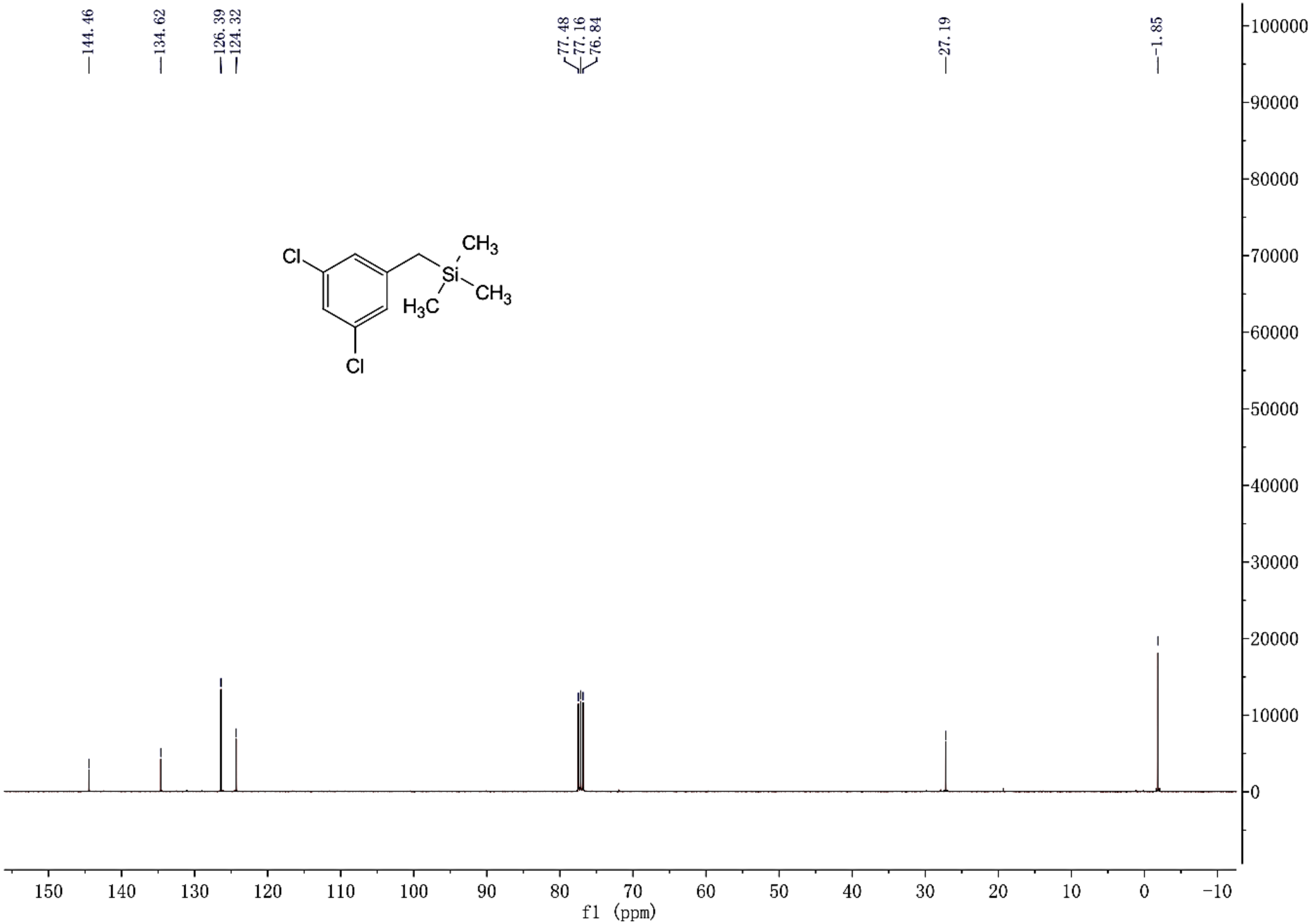
139.11
134.67
130.22
128.85
125.73
124.17
77.48
77.16
76.84
23.82
20.48
-1.21
CH3
Si
CH3
H3C
CH3
f1 (ppm)


7.26
6.95
6.94
6.94
6.93
6.92
6.91
6.90
6.89
6.88
6.88
2.04
-0.02
CH3
Si
CH3
H3C
F
3.76
2.00
9.00
f1 (ppm)

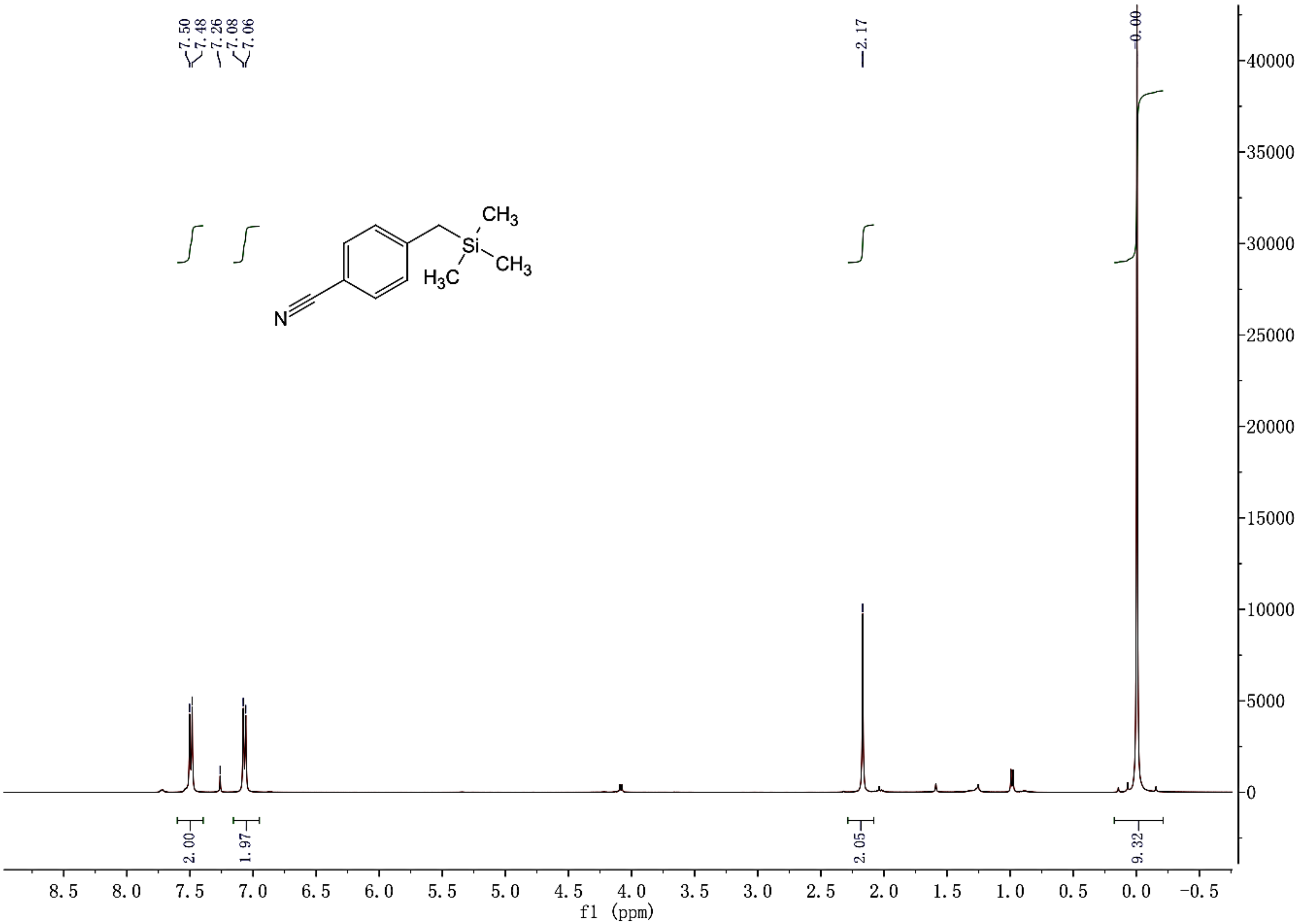

161.59
159.20
136.12
136.08
129.20
129.13
115.07
114.86
77.48
77.16
76.84
26.20
-1.87
CH3
Si
CH3
H3C
F
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
7.08
6.87
6.87
2.04
0.01
Cl
Cl
CH3
Si
CH3
H3C
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

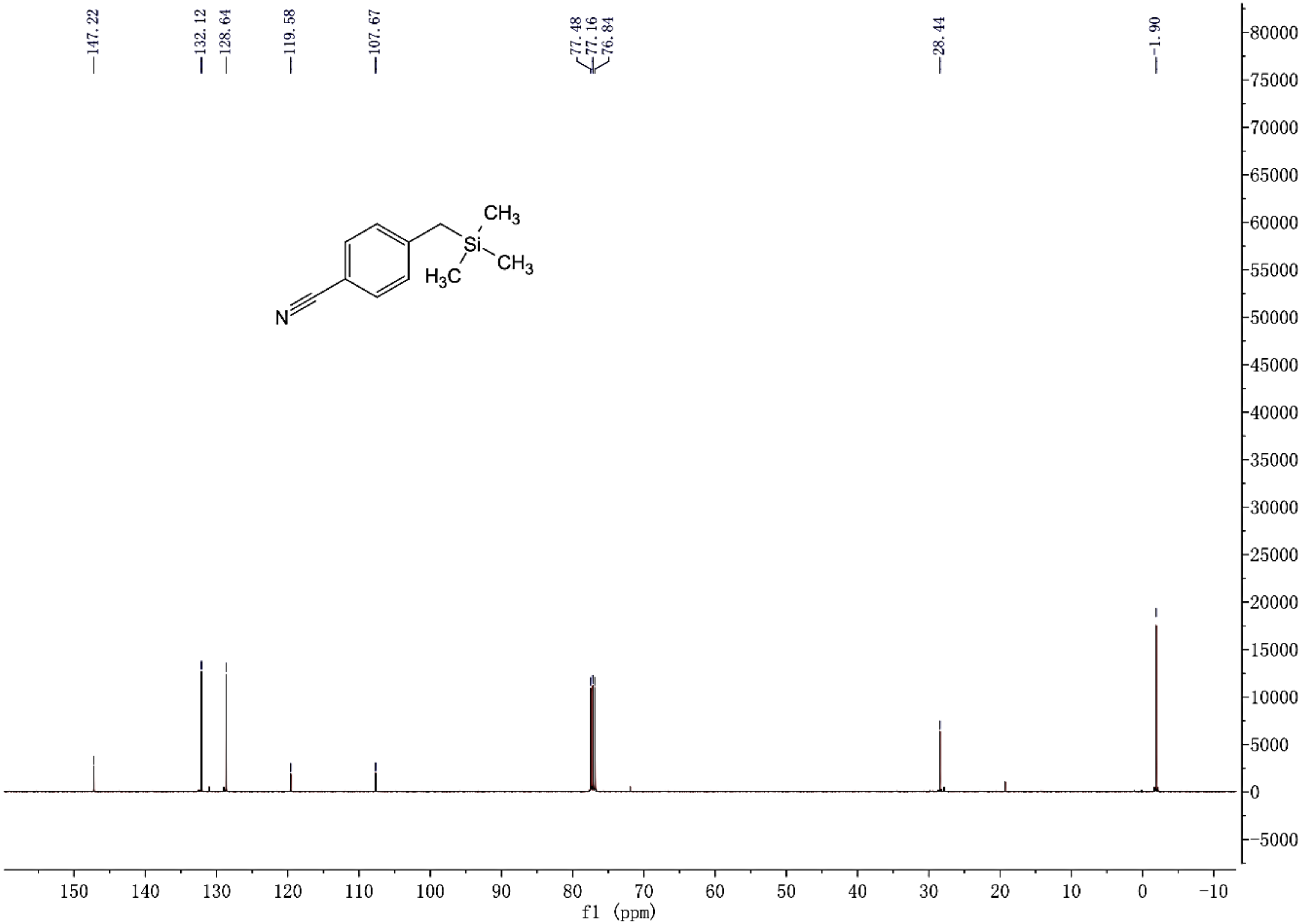
^{13}C NMR of **3f**


144.46
134.62
126.39
124.32
77.48
77.16
76.84
27.19
-1.85
Cl
Cl
CH3
Si
CH3
H3C
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR of **3g**

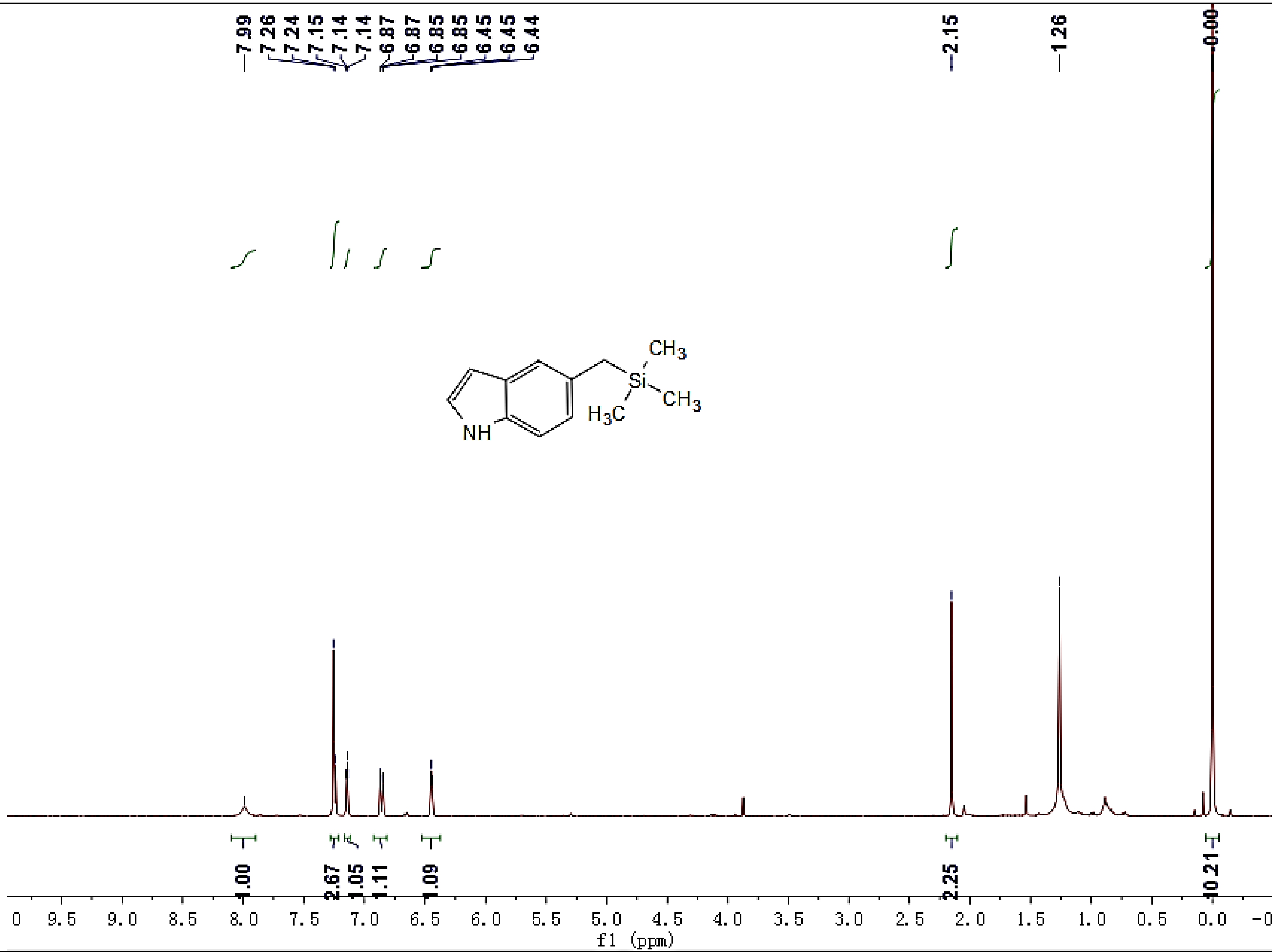

7.50
7.48
7.26
7.08
7.06
2.17
0.00
CH3
Si
CH3
H3C
N
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
1.97
2.05
9.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{13}C NMR of **3g**



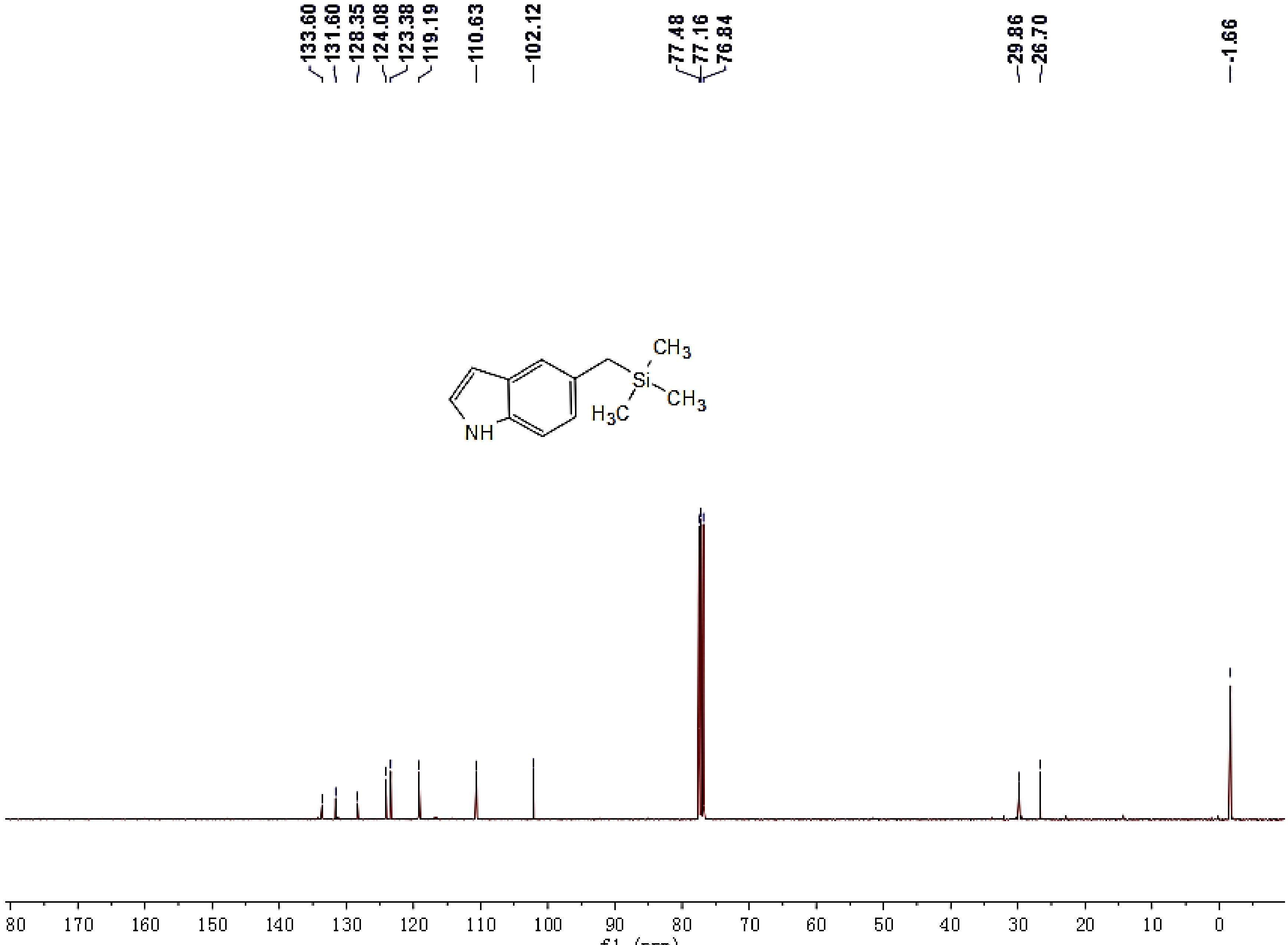
147.22
132.12
128.64
119.58
107.67
77.48
77.16
76.84
28.44
-1.90
CH3
Si
CH3
H3C
N
f1 (ppm)

^{1}H NMR of **3h**



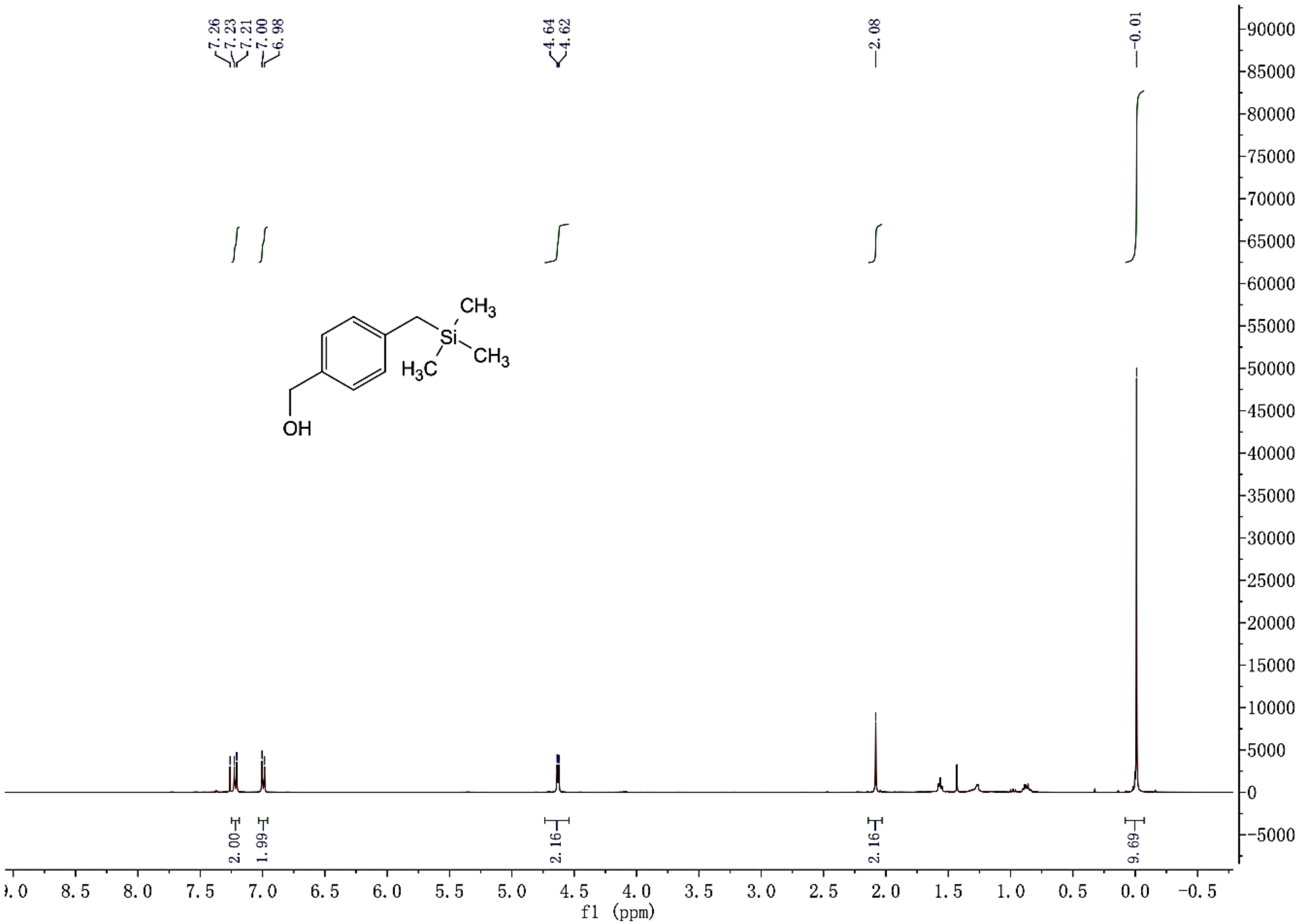
7.99
7.26
7.24
7.15
7.14
7.14
6.87
6.87
6.85
6.85
6.45
6.45
6.44
2.15
1.26
0.00
CH3
Si
CH3
H3C
NH
1.00
2.67
1.05
1.11
1.09
2.25
10.21
f1 (ppm)

^{13}C NMR of **3h**



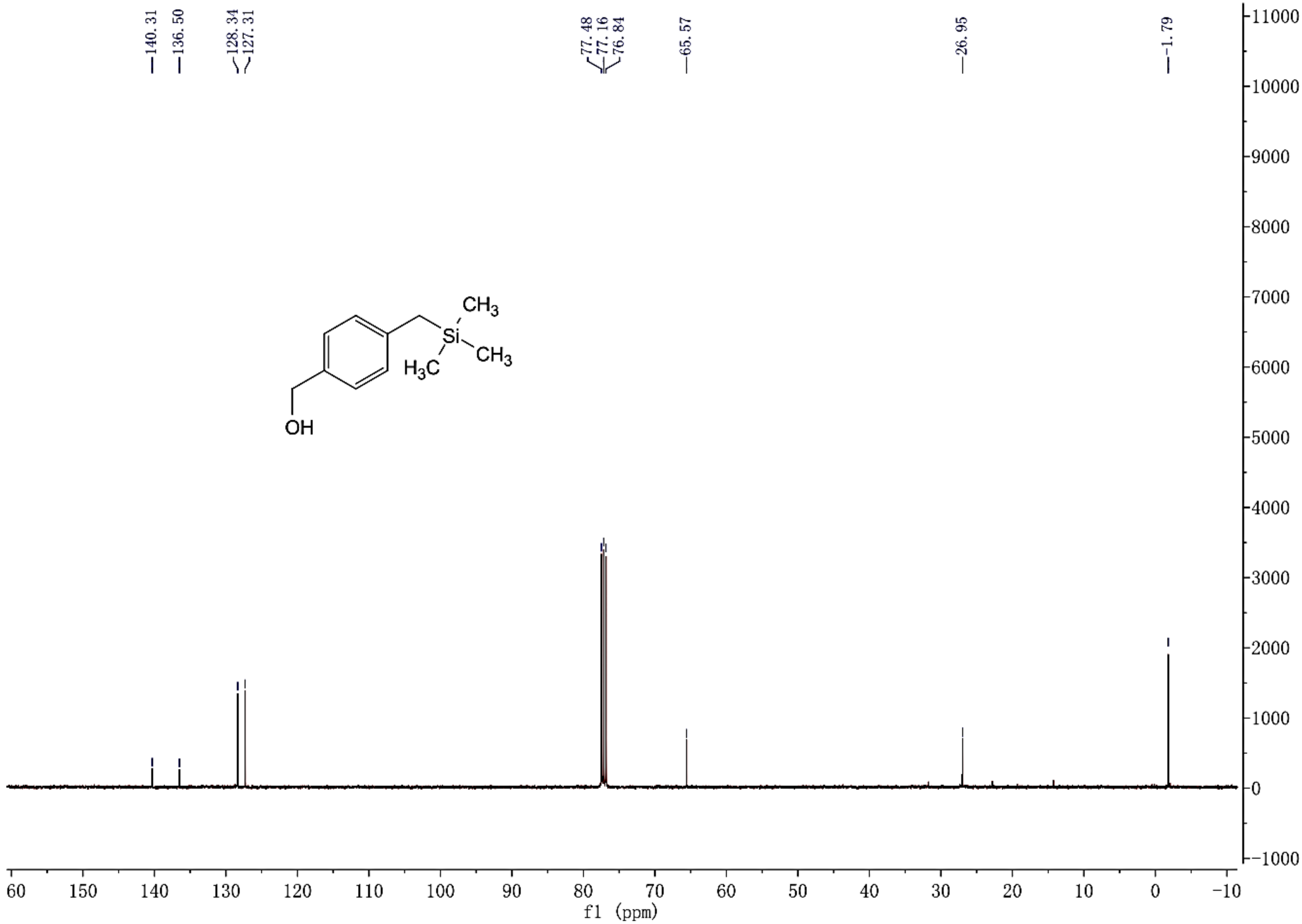
133.60
131.60
128.35
124.08
123.38
119.19
110.63
102.12
77.48
77.16
76.84
29.86
26.70
-1.66
CH3
Si
CH3
H3C
NH
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of **3i**



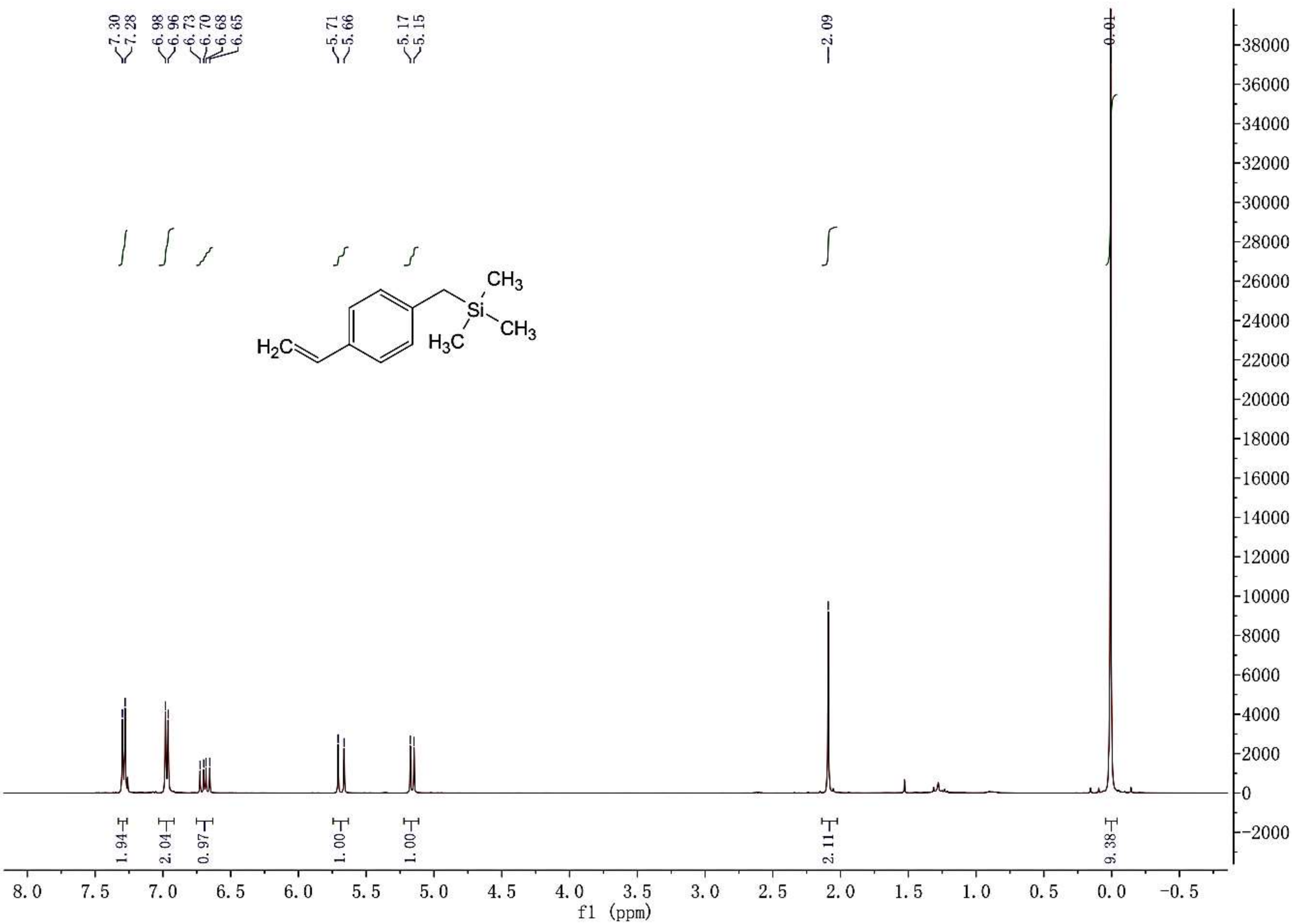
7.26
7.23
7.21
7.00
6.98
4.64
4.62
2.08
-0.01
CH3
Si
CH3
H3C
OH
2.00
1.99
2.16
2.16
9.69
f1 (ppm)

^{13}C NMR of **3i**

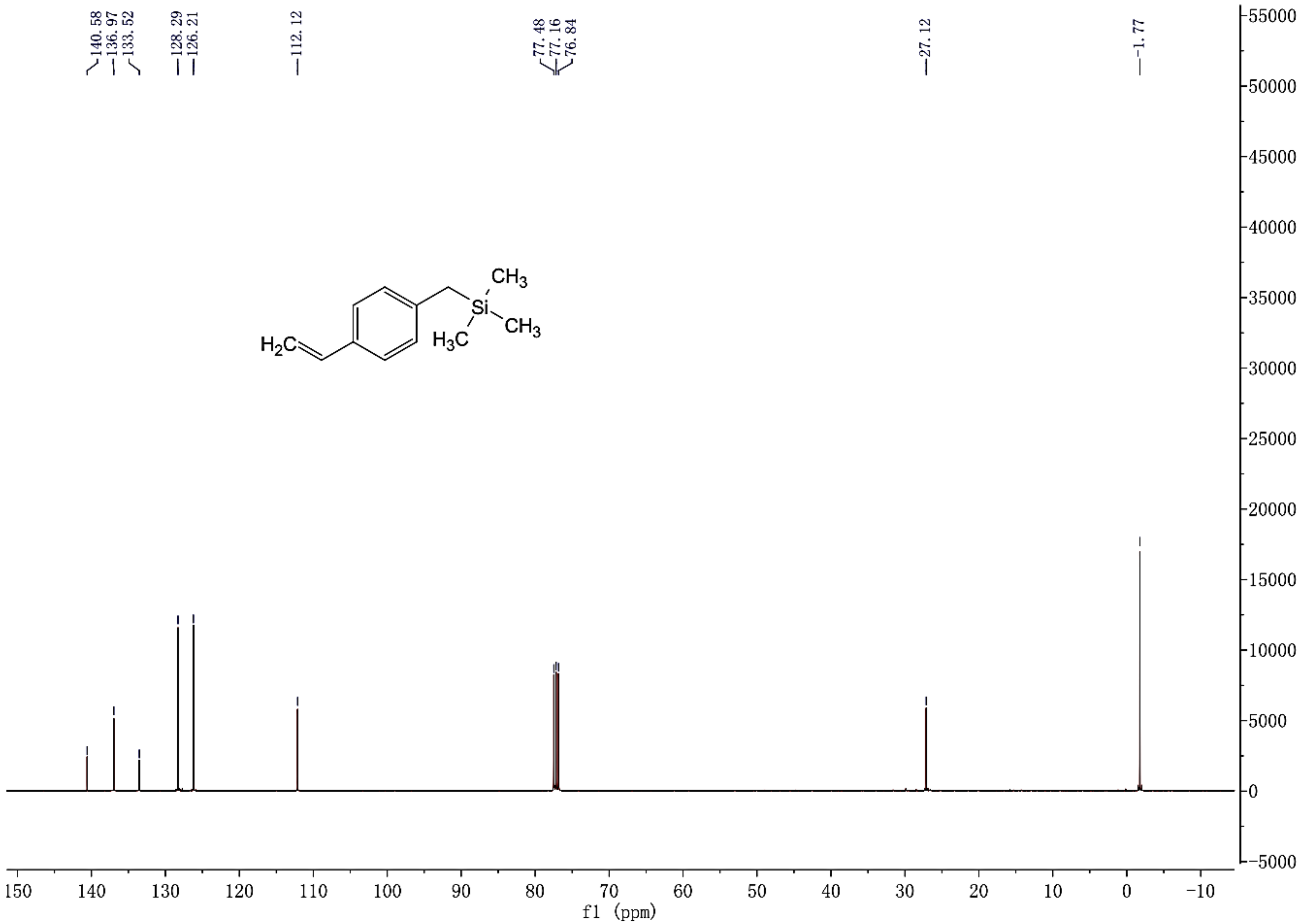


140.31
136.50
128.34
127.31
77.48
77.16
76.84
65.57
26.95
−1.79
CH3
Si
CH3
H3C
OH
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

[1]H NMR of **3j**

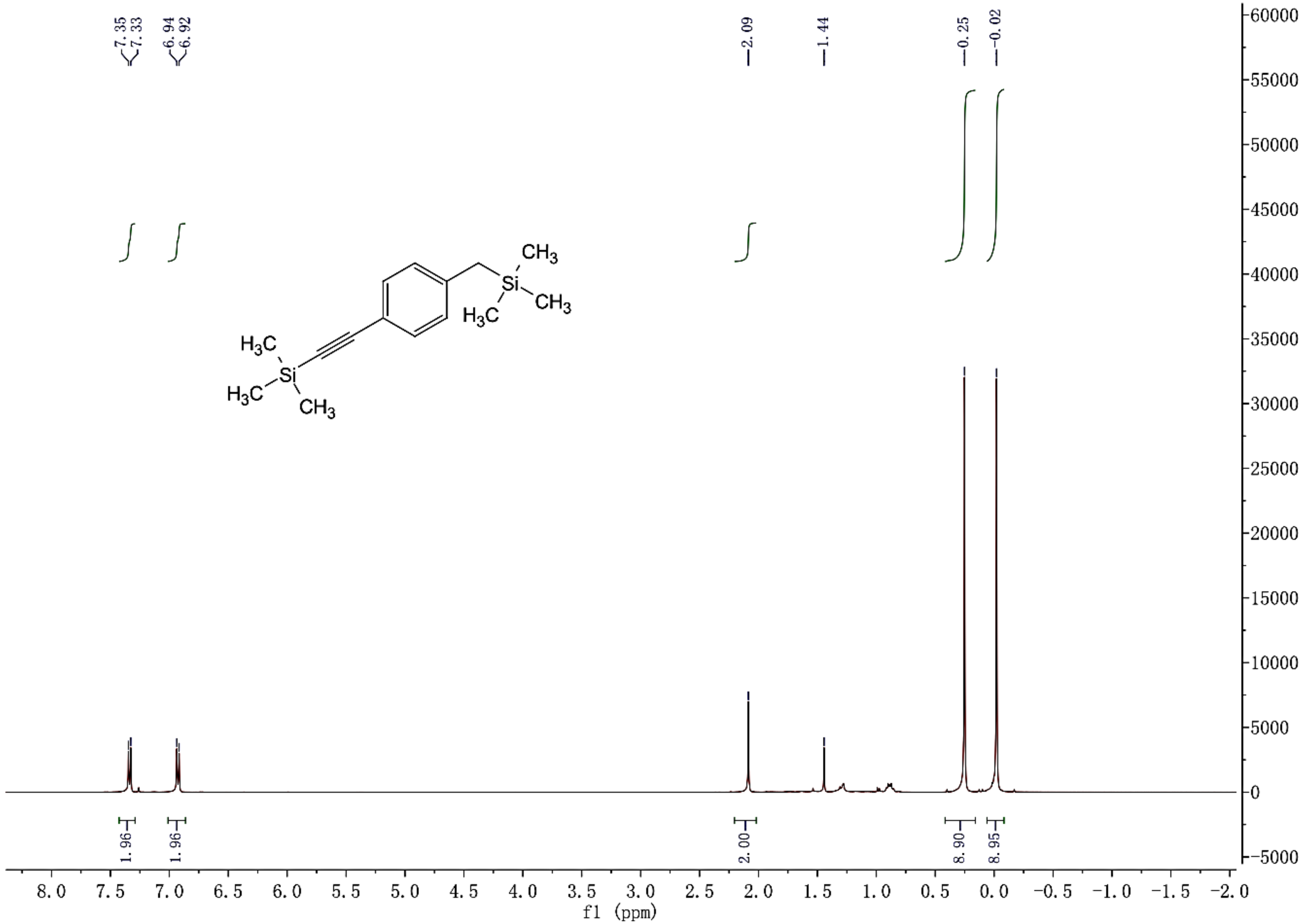


^{13}C NMR of **3j**



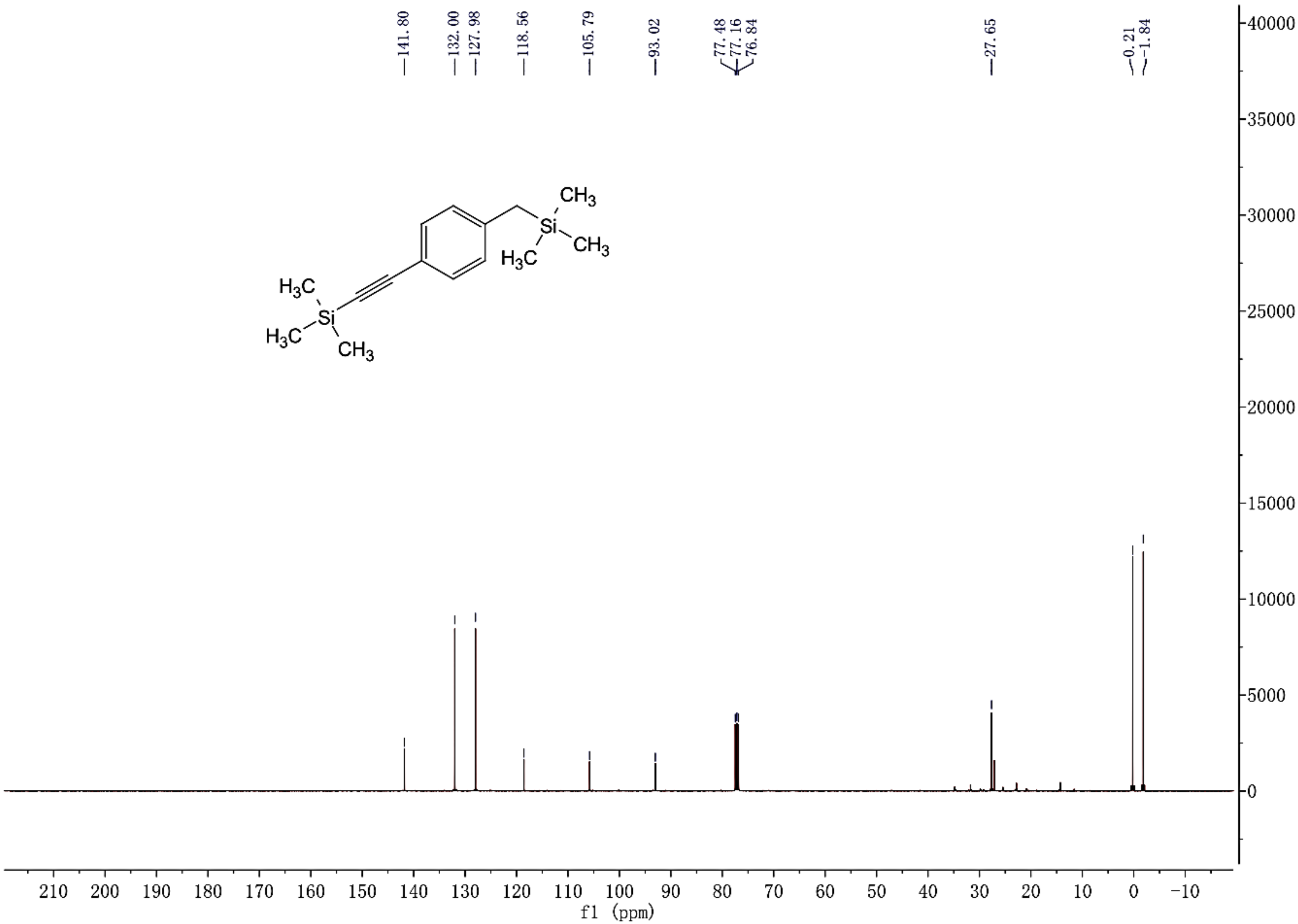
140.58
136.97
133.52
128.29
126.21
112.12
77.48
77.16
76.84
27.12
-1.77
CH3
Si
CH3
H3C
H2C
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

[1]H NMR of **3k**

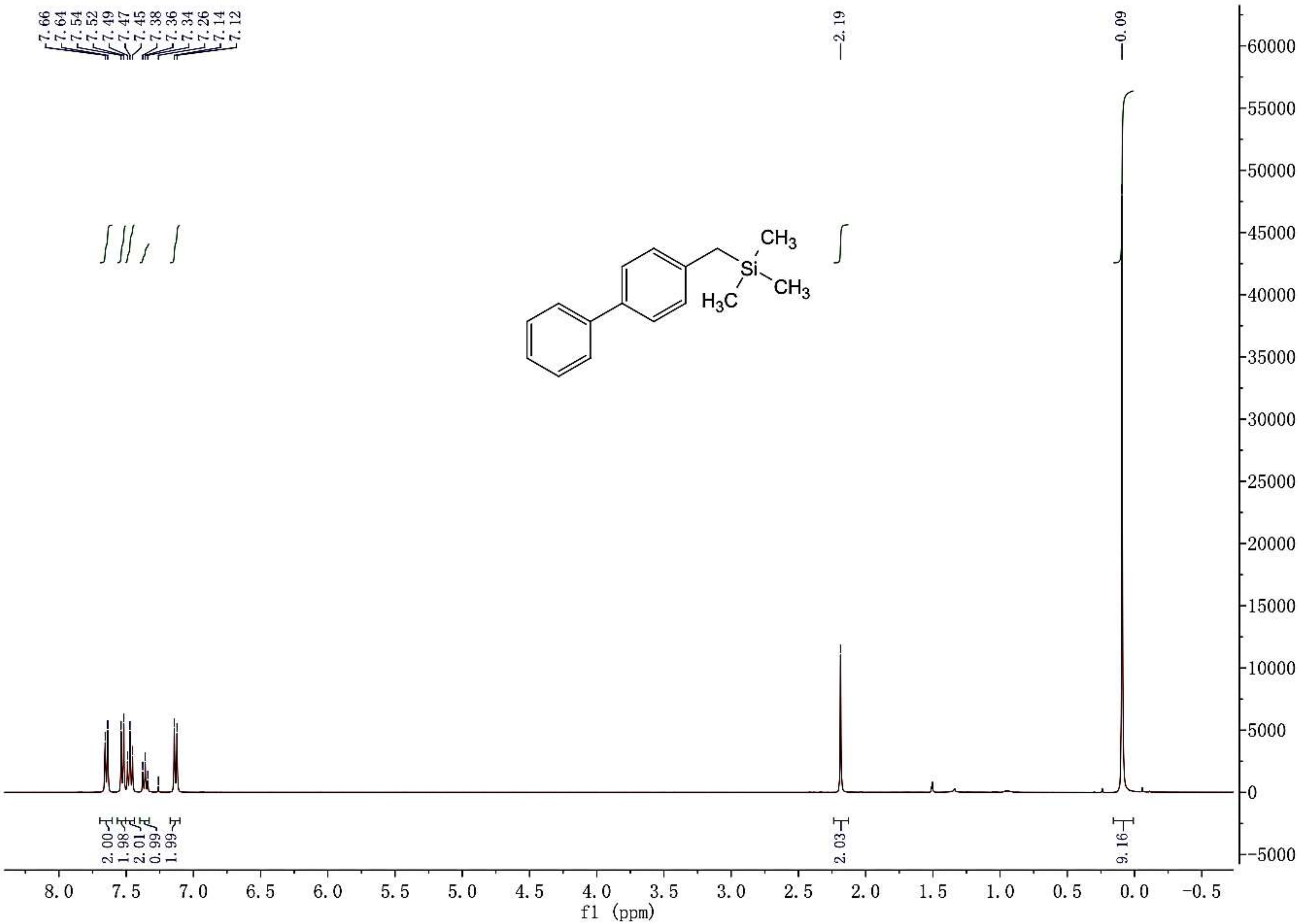


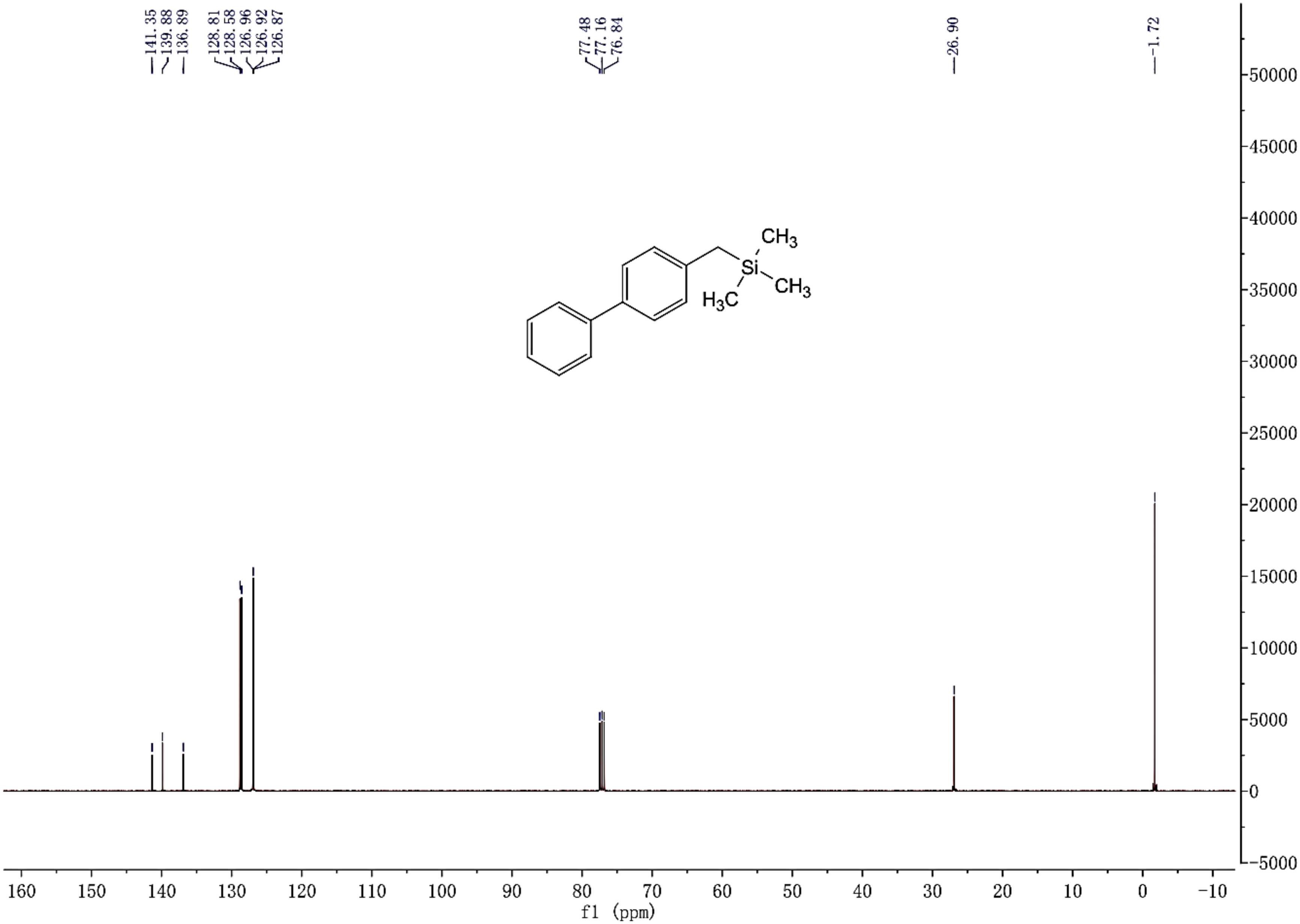
7.35
7.33
6.94
6.92
2.09
1.44
0.25
0.02
CH3
Si
CH3
H3C
H3C
Si
H3C
CH3
1.96
1.96
2.00
8.90
8.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

^{13}C NMR of **3k**

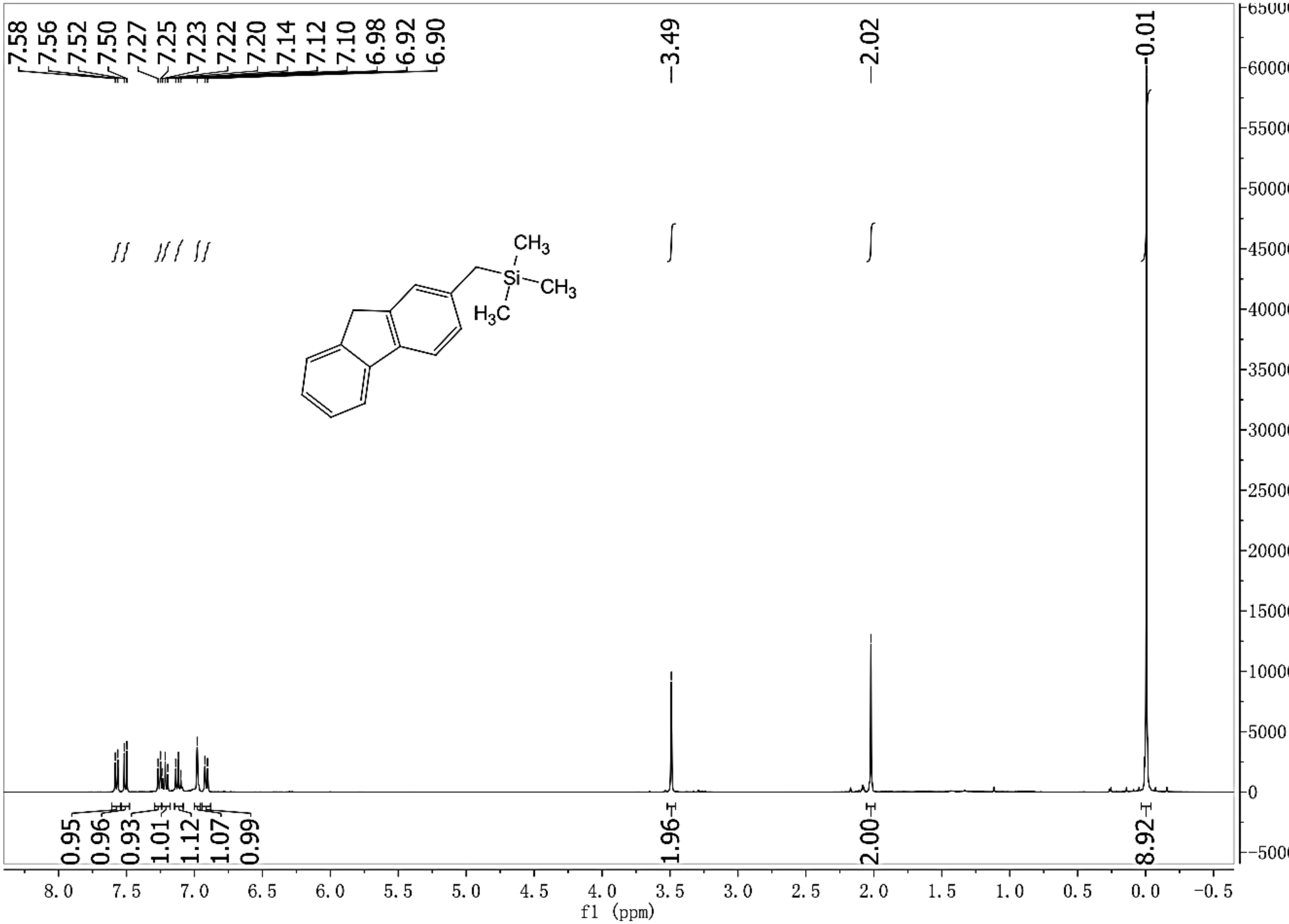

141.80
132.00
127.98
118.56
105.79
93.02
77.48
77.16
76.84
27.65
0.21
-1.84
CH3
Si
CH3
H3C
H3C
Si
H3C
CH3
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of **3l**

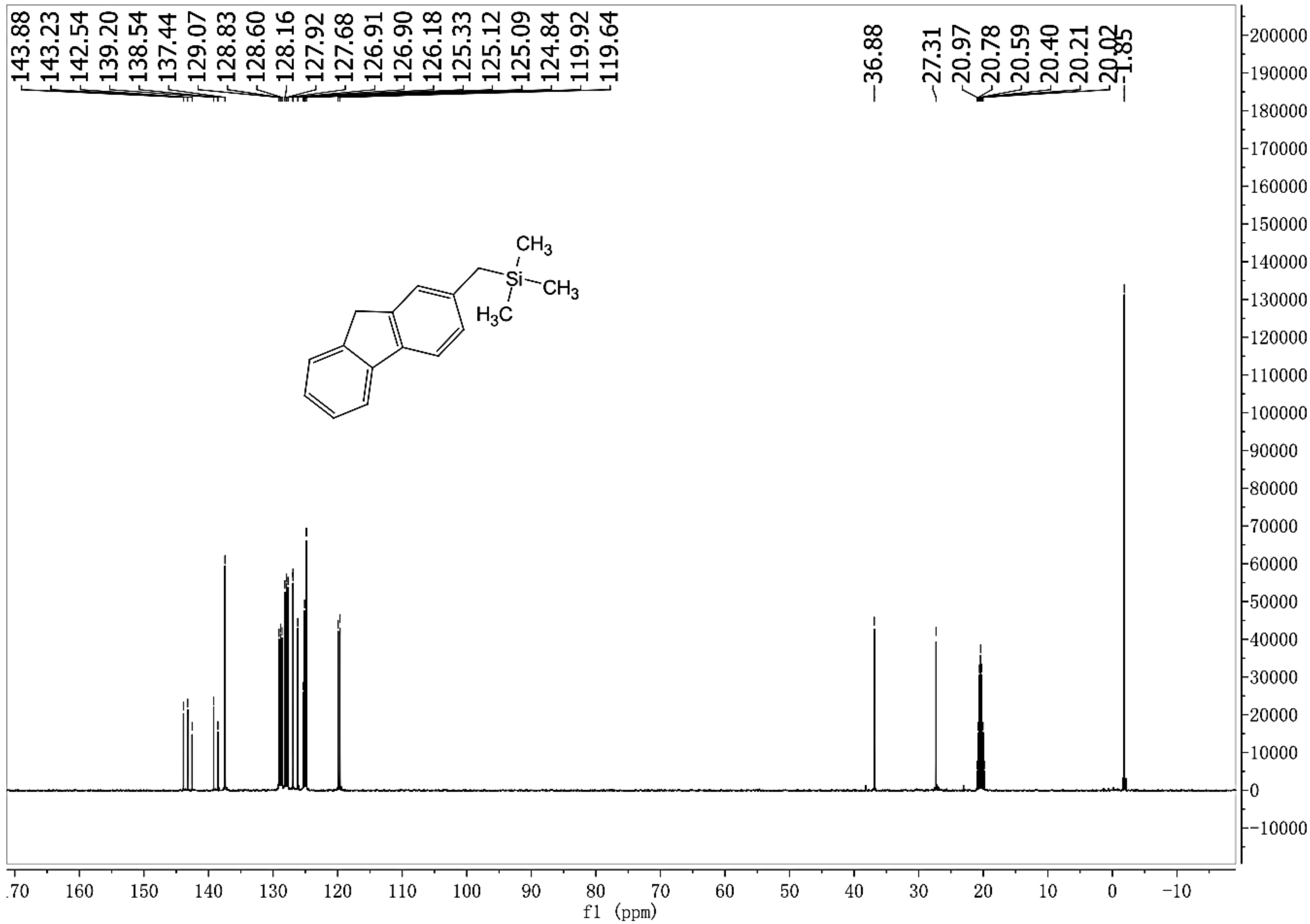

7.66
7.64
7.54
7.52
7.49
7.47
7.45
7.38
7.36
7.34
7.26
7.14
7.12
2.19
0.09
CH3
Si
CH3
H3C
2.00
1.98
2.01
0.99
1.99
2.03
9.16
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


141.35
139.88
136.89
128.81
128.58
126.96
126.92
126.87
77.48
77.16
76.84
26.90
-1.72
CH3
Si
CH3
H3C
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

[1]H NMR of **3m**

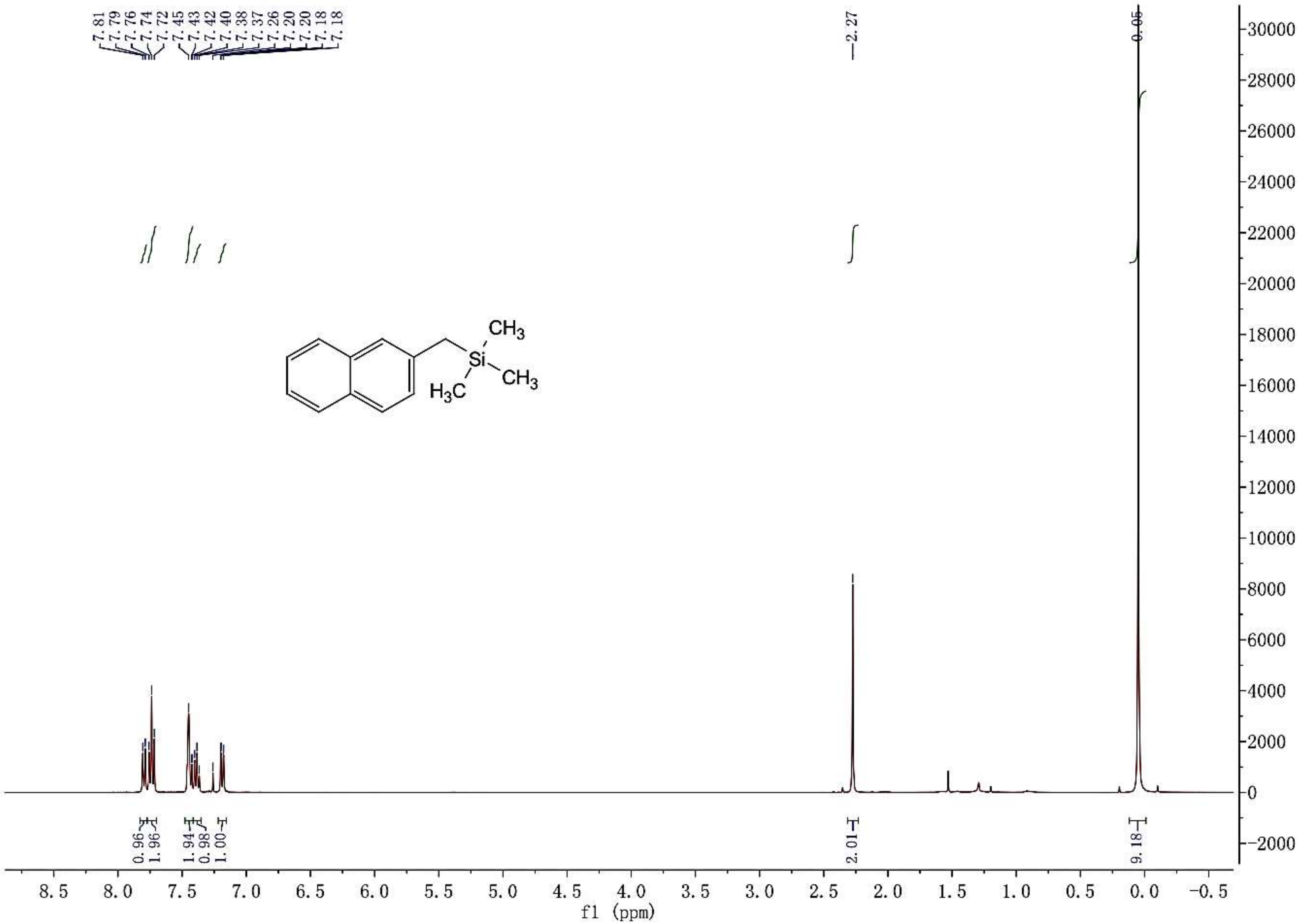

7.58
7.56
7.52
7.50
7.27
7.25
7.23
7.22
7.20
7.14
7.12
7.10
6.98
6.92
6.90
3.49
2.02
-0.01
CH3
Si
CH3
H3C
0.95
0.96
0.93
1.01
1.12
1.07
0.99
1.96
2.00
8.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

^{13}C NMR of **3m**

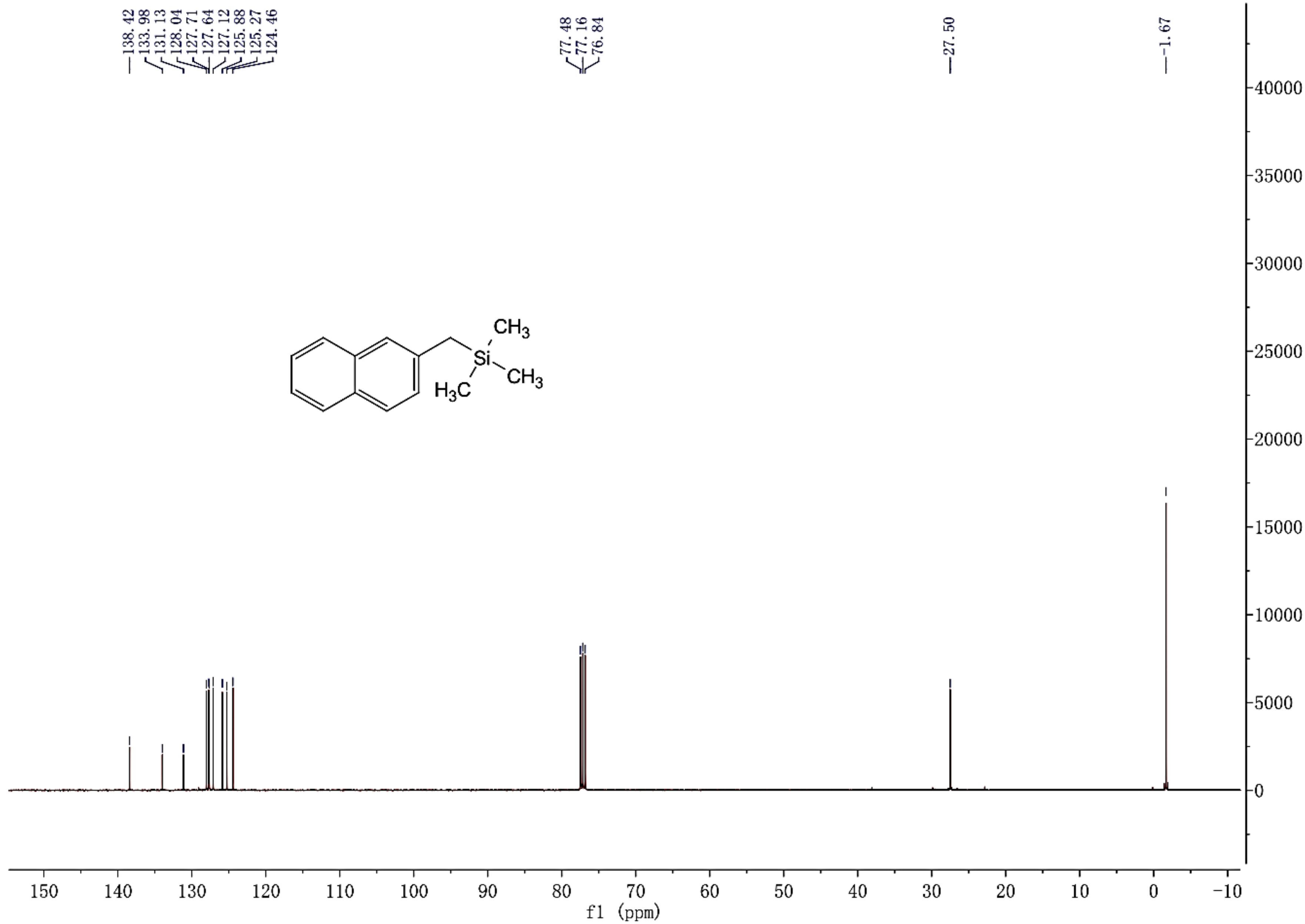


143.88
143.23
142.54
139.20
138.54
137.44
129.07
128.83
128.60
128.16
127.92
127.68
126.91
126.90
126.18
125.33
125.12
125.09
124.84
119.92
119.64
36.88
27.31
20.97
20.78
20.59
20.40
20.21
20.02
-1.85
CH3
Si
CH3
H3C
f1 (ppm)

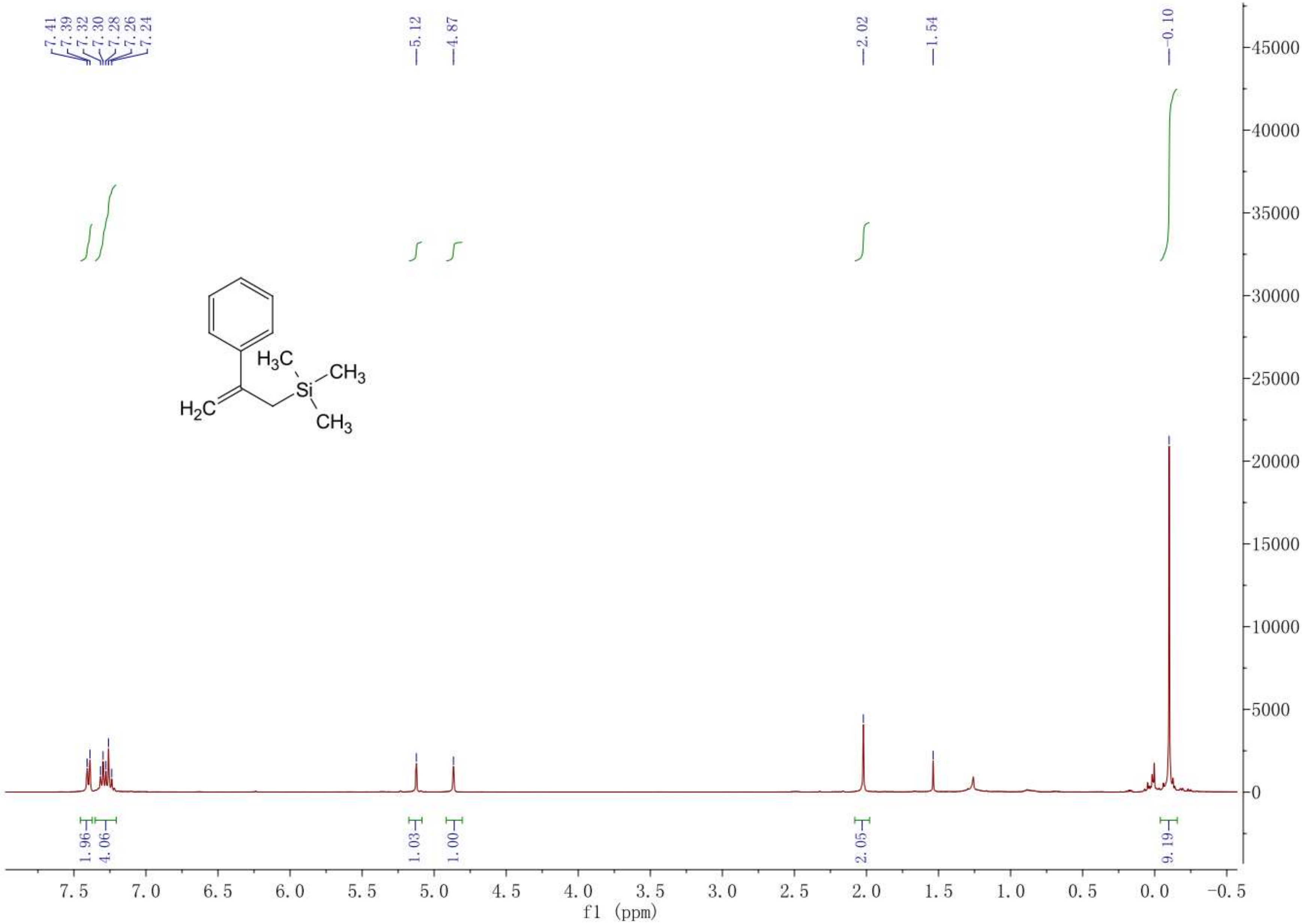
^{1}H NMR of **3n**


7.81
7.79
7.76
7.74
7.72
7.45
7.43
7.42
7.40
7.38
7.37
7.26
7.20
7.20
7.18
7.18
2.27
0.05
CH3
Si
CH3
H3C
0.96
1.96
1.94
0.98
1.00
2.01
9.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

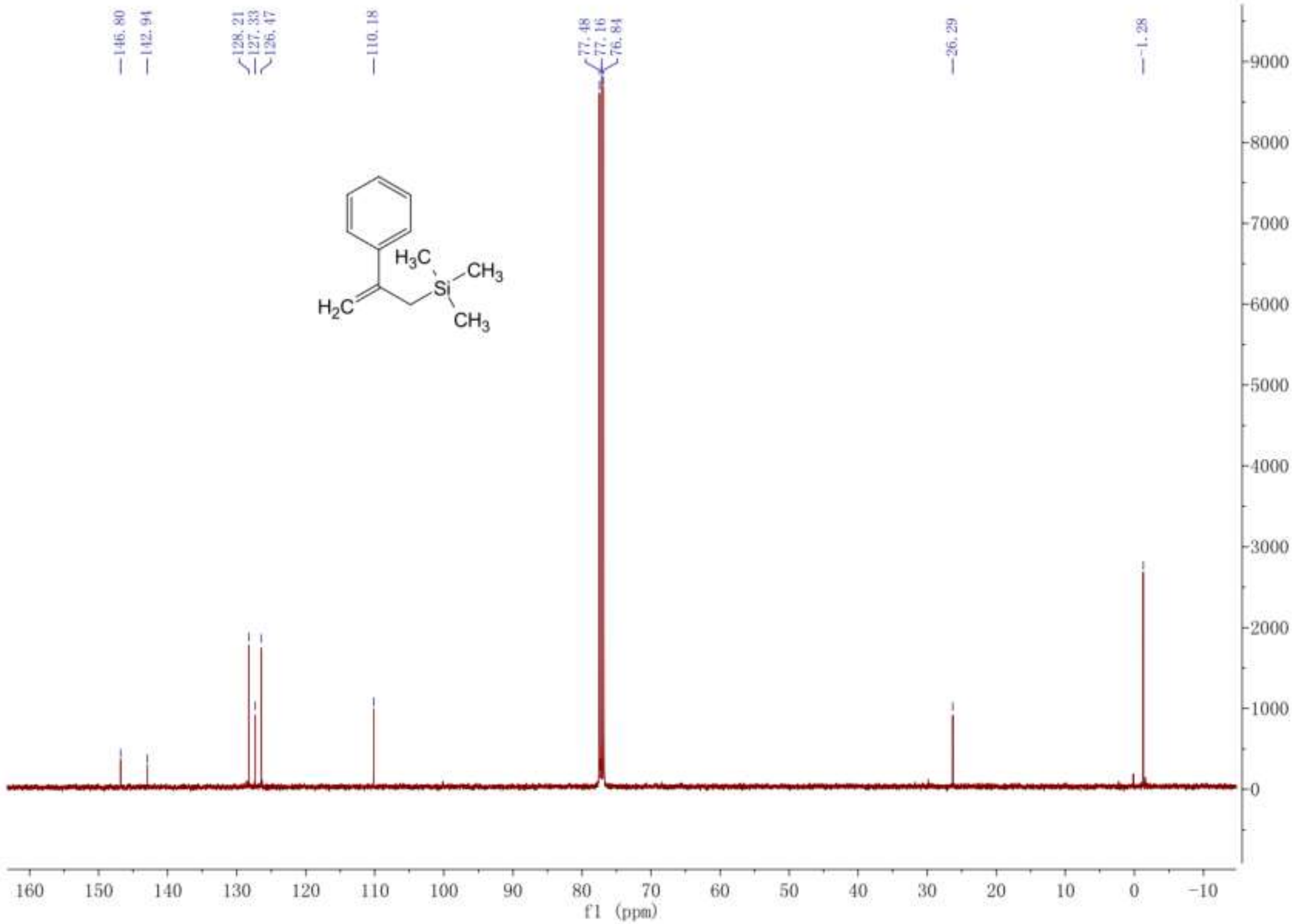
^{13}C NMR of **3n**


138.42
133.98
131.13
128.04
127.71
127.64
127.12
125.88
125.27
124.46
77.48
77.16
76.84
27.50
-1.67
CH3
Si
CH3
H3C
40000
35000
30000
25000
20000
15000
10000
5000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

[1]H NMR of **3o**


7.41
7.39
7.32
7.30
7.28
7.26
7.24
5.12
4.87
2.02
1.54
0.10
H3C
CH3
Si
CH3
H2C
1.96
4.06
1.03
1.00
2.05
9.19
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C NMR of **3o**


146.80
142.94
128.21
127.33
126.47
110.18
77.48
77.16
76.84
26.29
-1.28
H3C
CH3
Si
H2C
CH3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)