Supplementary Information

An Effective and Versatile Strategy for the Synthesis of Structurally Diverse Heteroarylsilanes via Ir(III)-Catalyzed C−H Silylation

Zhi-Bo Yan,[a] Meng Peng,[a] Qi-Long Chen,[a] Ka Lu,[a] Yong-Qiang Tu,*[a,b] Kun-Long Dai,[a] Fu-Min Zhang,[a] Xiao-Ming Zhang[a]

[a]State Key Laboratory of Applied Organic Chemistry & College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou *730000*, P.R. China

[b]School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai *200240*, P.R. China

E-mail: tuyq@lzu.edu.cn

Table of contents

1. **General information……………………………………….………..………....3**

2. **Preparation of substrates ……………………………………………….…….4**

3. **Ir-catalyzed silylation of γ C-H bonds of heteroarenes………………..……….8**

4. **Ir-catalyzed silylation of δ C-H bonds of heteroarenes……………..………24**

5. **Ir-catalyzed silylation of α, β C-H bonds of *N, O, S*-heteroarenes……………33**

6. **Mechanism investigations…………………………….…...………...…44**

7. **DFT calculations…………………………………………………...……51**

8. **X-ray structural characterization of 2x, 6f, 1bB and 3dB………………72**

9. **References……………………………………………………………….……97**

10. **Copies of NMR spectroscopy……………………………………….......… 98**

1. General information

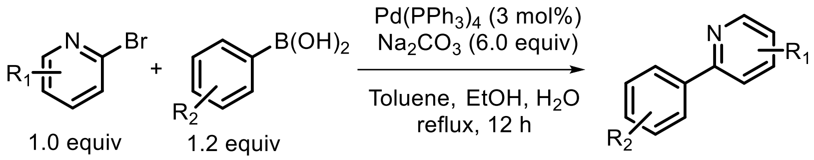
All the Ir-catalyzed α, β, γ, δ C-H silylation of heteroarenes reactions were carried out using oven-dried (150 °C) Schlenk tubes or bottles equipped with a magnetic stir bar in a glove box under argon atmosphere (H_2O < 0.5 ppm, O_2 < 0.5 ppm). In addition to commercially available chemicals, extra dry solvents including acetonitrile, 1,4-dioxane, ethanol, *N,N*-dimethylformamide (DMF), *o*-xylene, all solvents were purified by standard operating method. 1,2-Dichloroethane (DCE) was distilled from calcium hydride. Toluene and tetrahydrofuran (THF) were dried over sodium. Besides, *tert*-butylethylene, triethylsilane and *o*-xylene were purchased and degassed by freeze-pump-thaw cycle for 3 times. Analytical TLC was performed on silica gel plates with F254 indicator. Visualization was accomplished with ultraviolet light (254 nm). Products purifications were conducted with column chromatography on 200-300 mesh silica gel unless specially stated.

^{1}H, **^{13}C** and **^{19}F NMR** spectra were recorded on Bruker AM-400 MHz or Varian Mercury-600 MHz. Chemical shifts (δ) were reported in ppm relative to residual solvent peak or tetramethylsilane as internal standard ($CDCl_3$: δ_H 7.26 ppm and δ_C 77.00 ppm, C_6D_6: δ_H 7.16 ppm and δ_C 128.00 ppm). Infrared (**IR**) spectra were performed on Nicolet FT-170SX spectrometer. High-resolution mass spectral analysis (**HRMS**) data were collected on the Bruker ApexII with ESI resource. **X-ray** diffraction data were obtained on Agilent SuperNova Eos diffractometer. Gas Chromatography-Mass Spectrometry (**GC-MS**) data were collected with Shimadzu GC-MS QP2010SE by means of EI (70 eV) technique.

2. Preparation of substrates

Substrates **1a-1k**, **1o**, **1q-1w**, **3a**, **3h**, **3l-3o**, **5a-5j** and **5m-5r** were commercially available, others were prepared according to the following procedures.

2.1. General procedure for the synthesis of 2-arylpyridine derivatives 1l, 1m, 1n, 1p



According to the literatures,[1-7] to a 100 mL round-bottom flask was added $Pd(PPh_3)_4$ (79.7 mg, 3 mol%), Na_2CO_3 (1.46 g, 13.8 mmol, 6.0 equiv), and arylboronic acid (2.8 mmol, 1.2 equiv), after that, the solvent of toluene (8 mL), ethanol (1.5 mL), degassed H_2O (8 mL) combined with substituted 2-bromopyridine (2.3 mmol, 1.0 equiv) were added dropwise under argon atmosphere. The reaction was refluxed for 12 h. After the reaction was completed, the resulting mixture was cooled to room temperature. Aqueous NH_4Cl was added, the system was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual was purified by silica gel column chromatography to give products **1l**, **1m**, **1n** and **1p**.

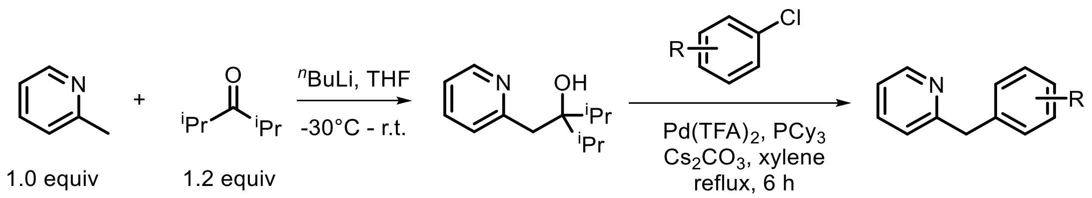
2-phenylquinoline (**1l**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.19 – 8.16 (m, 3H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.50 (m, 4H), 7.46 (t, *J* = 7.2 Hz, 1H).

2-(naphthalen-2-yl)pyridine (**1m**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.1 Hz, 1H), 8.48 (s, 1H), 8.13 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.77 (td, *J* = 7.9, 1.7 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.24 (dd, *J* = 9.3, 2.9 Hz, 1H).

2-(naphthalen-1-yl)pyridine (**1n**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 – 8.75 (m, 1H), 8.12 – 8.04 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.62 – 7.42 (m, 5H), 7.34 – 7.28 (m, 1H).

1-(naphthalen-1-yl)isoquinoline (**1p**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 8.00 – 7.90 (m, 2H), 7.78 (d, *J* = 5.8 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.66 – 7.55 (m, 3H), 7.52–7.28 (m, 4H).

2.2. General procedure for the synthesis of 2-benzylpyridine derivatives 3b-3g and 3i-3k



According to the literature,[8] to a solution of 2-methylpyridine (3.72 g, 40 mmol, 1.0 equiv) in tetrahydrofuran (40 mL) was added ^{n}BuLi (1.6 M in hexane, 27.5 mL, 44 mmol, 1.1 equiv) dropwise at -30 °C. After stirring for 0.5 h, diisopropyl ketone (5.48 g, 48 mmol, 1.2 equiv) was added. The system was reacted for 6 h at room temperature. After the reaction was completed, water was added and the mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual was purified by silica gel column chromatography to afford product 2,4-dimethyl-3-(pyridin-2-ylmethyl)pentan-3-ol.

To dry xylene (1.6 mL) were added Cs_2CO_3 (0.32 g, 0.97 mmol, 1.2 equiv), $Pd(TFA)_2$ (12.2 mg, 5 mol%), PCy_3 (0.5 M in toluene, 0.16 mL, 10 mol%), pyridyl alcohol (168 mg, 0.81 mmol, 1.0 equiv) and substituted chlorobenzene (0.97 mmol, 1.2 equiv) at room temperature. The reaction mixture was refluxed for 6 h. After the reaction was completed, the reaction was cooled to room temperature, water was added. The system was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual was purified by silica gel column chromatography to give the products **3b-3g** and **3i-3k**.

2-(4-methylbenzyl)pyridine (**3b**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.08 (dd, *J* = 13.8, 6.6 Hz, 4H), 4.11 (s, 2H), 2.30 (s, 3H).

2-(4-(tert-butyl)benzyl)pyridine (**3c**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 3.9 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.03 (m, 2H), 4.12 (s, 2H), 1.29 (s, 9H).

N,N-dimethyl-4-(pyridin-2-ylmethyl)aniline (**3d**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.0 Hz, 1H), 7.53 (td, *J* = 7.7, 1.6 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.11 – 7.03 (m, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 4.06 (s, 2H), 2.90 (s, 6H).

2-(4-methoxybenzyl)pyridine (**3e**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.57 – 8.49 (m, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.13 – 7.05 (m, 2H), 6.88 – 6.79 (m, 2H), 4.09 (s, 2H), 3.77 (s, 3H).

2-(3-methoxybenzyl)pyridine (**3f)** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.4 Hz, 1H), 7.56 (td, *J* = 7.7, 1.6 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.05 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.79 – 6.72 (m, 1H), 4.13 (s, 2H), 3.77 (s, 3H).

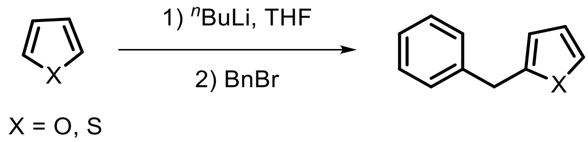
2-(2-methoxybenzyl)pyridine (**3g**) ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.13 (m, 2H), 7.11 – 7.03 (m, 2H), 6.95 – 6.83 (m, 2H), 4.17 (s, 2H), 3.79 (s, 3H).

2-(4-(trifluoromethyl)benzyl)pyridine (**3i**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.07 (m, 2H), 4.20 (s, 2H).

2-(3-(trifluoromethyl)benzyl)pyridine (**3j**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.2 Hz, 1H), 7.60 (td, *J* = 7.7, 1.6 Hz, 1H), 7.53 (s, 1H), 7.52 – 7.36 (m, 3H), 7.18 – 7.09 (m, 2H), 4.20 (s, 2H).

2-(4-fluorobenzyl)pyridine (**3k**) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.58 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.15 – 7.07 (m, 2H), 7.01 – 6.92 (m, 2H), 4.12 (s, 2H).

2.3. General procedure for the synthesis of 2-benzylthiophene 5k and 2-benzylfuran 5l



According to the literatures,[9,10] to a solution of thiophene (X = S, 1.97 g, 23.4 mmol, 2.0 equiv) or furan (X = O, 1.59 g, 23.4 mmol, 2.0 equiv) in THF (20 mL), ^{n}BuLi (1.6 M in hexane, 11 mL, 17.5 mmol, 1.5 equiv) was added dropwise under argon atmosphere at 0 °C, and stirred for 1 h. A solution of benzyl bromide (1.39 mL ,11.7 mmol, 1.0 equiv) in dry THF (10 mL) was added. After the reaction was completed, water was added and the resulting mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual was purified by silica gel column chromatography to give the products **5k** and **5l**.

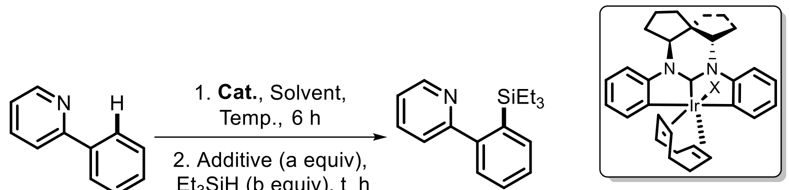
2-benzylthiophene (5k) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 7.12 (dd, J = 4.9, 0.8 Hz, 1H), 6.91 (t, J = 5.0, 3.5 Hz, 1H), 6.82 – 6.75 (m, 1H), 4.14 (s, 2H).

2-benzylfuran (5l) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 6H), 6.38 – 6.29 (m, 1H), 6.09 – 6.02 (m, 1H), 4.01 (s, 2H).

3. Ir-catalyzed silylation of γ C-H bonds of heteroarenes

3.1 Optimization conditions of γ C-H bonds of heteroarene 1a

Table S1: Reaction Optimization[a]



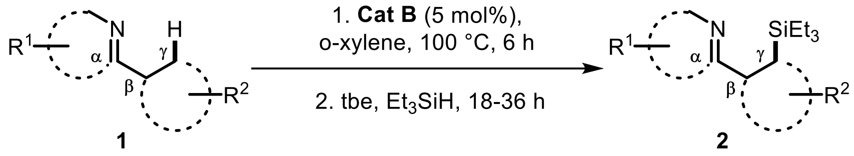
1a **2a**

Cat. A: X = H
Cat. B: X = Cl
Cat. C: X = OTf

Entry	Cat. (mol %)	Additive	Solvent	Temp. (°C)	a (equiv)	b (equiv)	t (h)	Yield (%)[b]
1	**A** (2.5)	cyclohexene	toluene	120	5	5	24	32
2	**B** (2.5)	cyclohexene	toluene	120	5	5	24	51
3	**C** (2.5)	cyclohexene	toluene	120	5	5	36	trace
4	none	cyclohexene	toluene	150	5	5	24	0
5	**B** (2.5)	none	toluene	150	5	5	24	0
6	**A** (2.5)	cyclohexene	toluene	120	3	5	24	35
7	**B** (2.5)	cyclohexene	toluene	120	3	5	24	47
8	**B** (2.5)	cyclohexene	toluene	120	3	3	18	45
9	**B** (2.5)	cyclohexene	toluene	120	3	1	24	31
10	**B** (2.5)	cyclohexene	toluene	100	3	2	18	46
11	**A** (2.5)	cyclohexene	toluene	100	3	2	18	22
12	**C** (2.5)	cyclohexene	toluene	100	3	2	18	<5
13	**B** (2.5)	nbe	toluene	100	3	2	18	26
14	**B** (2.5)	tbe	toluene	100	3	2	18	60
15	**B** (5.0)	tbe	toluene	100	3	2	18	78
16	**B** (5.0)	tbe	DCE	100	3	2	18	trace
17	**B** (5.0)	tbe	dioxane	100	3	2	18	44
18	**B** (5.0)	tbe	chlorobenzene	100	3	2	18	75(73)[c]
19	**B** (5.0)	tbe	*o*-xylene	100	3	2	18	85(80)[c]
20	**B** (5.0)	tbe	*o*-xylene	80	3	2	18	63
21[d]	**B** (5.0)	tbe	*o*-xylene	100	3	2	18	66

[a]Unless otherwise specified, reactions were conducted by pretreatment of a solution of **1a** (0.5 mmol), **Cat.** (2.5-5 mol%) and solvent (2 mL) at given temperature for 6 h, then additive (a equiv) and Et_3SiH (b equiv) were added and reacted for t h. [b]Determined by GC-MS (internal standard: dodecane). [c]Isolated yield in parentheses. [d]Without pretreatment. nbe = 2-norbornene, tbe = *tert*-butylethylene.

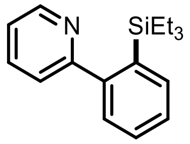
3.2 Sustrates scope of γ C-H bonds of heteroarenes



General procedure for γ C-H bonds of heteroarenes:

In glove box, to dry *o*-xylene were added substrate **1** (0.5 mmol) and **Cat. B** (5 mol%) in a 10 mL oven-dried Schlenk tube. The tube was taken out from the glove box, placed in a preheated oil bath and reacted for 6 h under stirring. After that, the mixture was cooled to room temperature, then tbe and silane source were added under argon atmosphere. The reaction system was stirred in oil bath for further reaction. After the reaction was completed, the resulting solution was concentrated *in vacuo*, and the residual was purified by silica gel column chromatography to give the silylation product **2**.

2-(2-(triethylsilyl)phenyl)pyridine (**2a**)



2a

The reaction was conducted according to the general procedure by using **1a** (77.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2a** (107.7 mg, 80% yield).

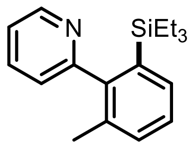
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.59 (m, 1H), 7.70 (m, 1H), 7.67 – 7.62 (m, 1H), 7.47 – 7.33 (m, 4H), 7.27 – 7.21 (m, 1H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 148.4, 147.8, 136.3, 136.0, 135.9, 129.0, 128.5, 127.1, 123.2, 121.9, 7.6, 4.5;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{17}H_{23}NSiNa$, *m/z*: 292.1492, found: 292.1485, Error 2.3 ppm;

IR (KBr): 3078, 2872, 1610, 1004, 798, 753, 724 cm^{-1}.

2-(2-methyl-6-(triethylsilyl)phenyl)pyridine (**2b**)



2b

The reaction was conducted according to the general procedure by using **1b** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2b** (117.5 mg, 83% yield).

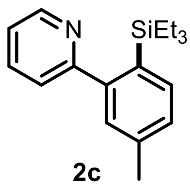
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.2 Hz, 1H), 7.70 (m, 1H), 7.43 (d, J = 6.7 Hz, 1H), 7.26 (t, J = 8.1 Hz, 4H), 2.02 (s, 3H), 0.80 (t, J = 7.9 Hz, 9H), 0.36 (q, J = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 148.9, 147.0, 135.6, 135.2, 133.1, 130.7, 127.1, 124.8, 122.0, 20.4, 7.5, 3.7;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1830, Error -0.5 ppm;

IR (KBr): 3055, 2873, 1377, 1004, 859, 791, 728 cm^{-1}.

2-(5-methyl-2-(triethylsilyl)phenyl)pyridine (**2c**)



2c

The reaction was conducted according to the general procedure by using **1c** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2c** (72.2 mg, 51% yield).

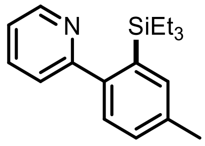
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.60 (m, 1H), 7.73 – 7.67 (m, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.26 – 7.17 (m, 3H), 2.38 (s, 3H), 0.82 (t, J = 9.4 Hz, 9H), 0.53 (q, J = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.5, 147.9, 138.3, 136.4, 135.9, 132.1, 130.0, 127.9, 123.2, 121.8, 21.2, 7.6, 4.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1830, Error -0.3 ppm;

IR (KBr): 3051, 2952, 2872, 1424, 724, 790 cm^{-1}.

2-(4-methyl-2-(triethylsilyl)phenyl)pyridine (**2d**)



2d

The reaction was conducted according to the general procedure by using **1d** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2d** (123.2 mg, 87% yield).

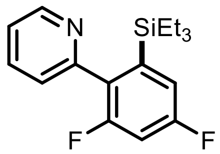
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.6 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.47 – 7.38 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.15 (m, 2H), 2.39 (s, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 148.3, 145.0, 137.0, 136.4, 135.9, 135.6, 129.2, 128.9, 123.0, 121.6, 21.3, 7.6, 4.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1834, Error -1.6 ppm;

IR (KBr): 3082, 2872, 1377, 828, 786, 732, 705 cm^{-1}.

2-(2,4-difluoro-6-(triethylsilyl)phenyl)pyridine (**2e**)



2e

The reaction was conducted according to the general procedure by using **1e** (95.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2e** (111.4 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.84 – 7.59 (m, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.16 – 7.08 (m, 1H), 6.93 – 6.82 (m, 1H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H);

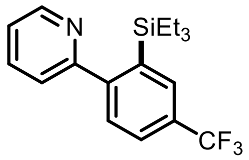
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.2, 161.3, 161.2, 160.8, 160.7, 158.8, 158.7, 155.0, 149.0, 142.2, 142.2, 135.8, 130.6, 130.5, 125.6, 125.5, 122.7, 118.2, 118.1, 118.0, 118.0, 104.4, 104.1, 103.8, 7.4, 3.8;

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0, -111.1, -112.2, -112.2;

HRMS (ESI) calcd for $[M+H]^+$ $C_{17}H_{22}F_2NSi$, *m/z*: 306.1484, found: 306.1488, Error -1.2 ppm;

IR (KBr): 3085, 2955, 2875, 1684, 1642, 1283, 994, 736 cm^{-1}.

2-(2-(triethylsilyl)-4-(trifluoromethyl)phenyl)pyridine (**2f**)



2f

The reaction was conducted according to the general procedure by using **1f** (111.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2f** (114.6 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (m, 1H), 7.87 (d, *J* = 0.5 Hz, 1H), 7.77 (m, 1H), 7.67 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (m, 1H), 7.32 (m, 1H), 0.83 (t, *J* = 7.8 Hz, 9H), 0.57 (q, *J* = 7.8 Hz, 6H);

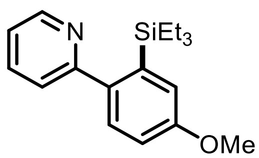
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 151.1, 148.7, 137.6, 136.4, 132.8, 132.7, 129.2, 129.1, 128.9, 125.8, 125.4, 125.4, 123.1, 122.6, 7.5, 4.2;

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.5;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{22}F_3NSiNa$, *m/z*: 360.1366, found: 360.1361, Error 1.4 ppm;

IR (KBr): 3051, 2956, 2875, 1587, 1326, 749, 739 cm^{-1}.

2-(4-methoxy-2-(triethylsilyl)phenyl)pyridine (**2g**)



2g

The reaction was conducted according to the general procedure by using **1g** (92.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2g** (139.1 mg, 93% yield).

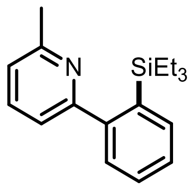
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.0 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.45 – 7.37 (m, 2H), 7.24 – 7.18 (m, 2H), 6.96 – 6.90 (m, 1H), 3.85 (s, 3H), 0.83 (t, *J* = 7.8 Hz, 9H), 0.57 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 158.5, 148.3, 140.3, 137.8, 136.0, 130.2, 122.9, 122.7, 121.5, 112.8, 55.1, 7.7, 4.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NOSi$, *m/z*: 300.1778, found: 300.1781, Error -1.0 ppm;

IR (KBr): 3004, 2952, 2872, 1274, 787, 732 cm^{-1}.

2-methyl-6-(2-(triethylsilyl)phenyl)pyridine (**2h**)



2h

The reaction was conducted according to the general procedure by using **1h** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2h** (121.8 mg, 86% yield).

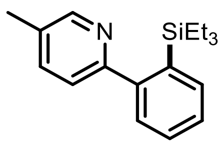
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 2.58 (s, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 157.1, 148.2, 136.2, 136.2, 135.6, 129.1, 128.4, 126.8, 121.3, 120.2, 24.1, 7.5, 4.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1825, Error 1.4 ppm;

IR (KBr): 3053, 2952, 2873, 1574, 1445, 803, 723 cm^{-1}.

5-methyl-2-(2-(triethylsilyl)phenyl)pyridine (**2i**)



2i

The reaction was conducted according to the general procedure by using **1i** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2i** (83.5 mg, 59% yield).

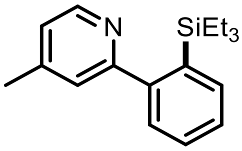
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.30 (m, 4H), 2.37 (s, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.7, 147.8, 136.6, 136.2, 135.7, 131.2, 128.9, 128.4, 126.8, 122.6, 18.2, 7.6, 4.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1828, Error 0.5 ppm;

IR (KBr): 3079, 2952, 2872, 1490, 1464, 836, 743, 724 cm^{-1}.

4-methyl-2-(2-(triethylsilyl)phenyl)pyridine (**2j**)



2j

The reaction was conducted according to the general procedure by using **1j** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2j** (65.1 mg, 46% yield).

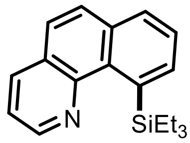
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.0 Hz, 1H), 7.63 (d, *J* = 6.7 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.07 (d, *J* = 4.4 Hz, 1H), 2.38 (s, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 148.2, 148.0, 147.0, 136.2, 135.8, 128.9, 128.4, 126.9, 124.1, 122.9, 21.1, 7.6, 4.4;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1825, Error 1.3 ppm;

IR (KBr): 3050, 2952, 2872, 1601, 1003, 890, 742, 724 cm^{-1}.

10-(triethylsilyl)benzo[h]quinoline (**2k**)



2k

The reaction was conducted according to the general procedure by using **1k** (89.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2k** (123.1 mg, 84% yield).

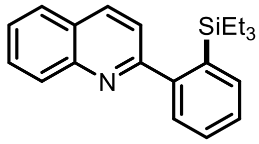
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.91 (m, 1H), 8.18 – 8.12 (m, 1H), 8.09 – 8.04 (m, 1H), 7.94 – 7.89 (m, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.51 – 7.46 (m, 1H), 1.10 – 0.98 (m, 6H), 0.91 (t, *J* = 7.7 Hz, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 145.7, 137.0, 136.9, 135.5, 135.3, 133.8, 129.2, 129.0, 127.2, 126.5, 124.6, 121.4, 8.6, 7.0;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{24}NSi$, *m/z*: 294.1673, found: 294.1664, Error 3.0 ppm;

IR (KBr): 3044, 2923, 1972, 1403, 834, 749, 618 cm^{-1}.

2-(2-(triethylsilyl)phenyl)quinoline (**2l**)



2l

The reaction was conducted according to the general procedure by using **1l** (102.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2l** (147.1 mg, 92% yield).

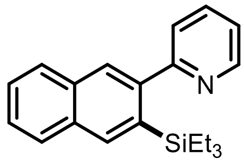
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.54 – 7.45 (m, 2H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H);

13C NMR (150 MHz, $CDCl_3$) δ 161.6, 148.1, 147.3, 136.5, 136.2, 136.2, 129.6, 129.4, 129.3, 128.5, 127.5, 127.3, 126.8, 126.2, 121.6, 7.6, 4.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{26}NSi$, *m/z*: 320.1829, found: 320.1830, Error -0.3 ppm;

IR (KBr): 3051, 2952, 2872, 1599, 1423, 792, 734 cm^{-1}.

2-(3-(triethylsilyl)naphthalen-2-yl)pyridine (**2m**)



2m

The reaction was conducted according to the general procedure by using **1m** (102.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 µL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 µL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2m** (126.1 mg, 79% yield).

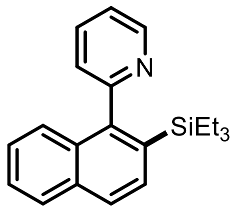
1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.0 Hz, 1H), 8.15 (d, *J* = 2.1 Hz, 1H), 7.88 (s, 2H), 7.85 – 7.79 (m, 1H), 7.74 – 7.65 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.26 – 7.18 (m, 1H), 0.93 – 0.84 (m, 9H), 0.71 – 0.60 (m, 6H);

13C NMR (100 MHz, $CDCl_3$) δ 161.6, 148.4, 144.4, 137.5, 136.2, 133.8, 133.1, 132.3, 127.9, 127.8, 127.7, 126.6, 126.1, 123.1, 121.8, 7.7, 4.6;

HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{26}NSi$, *m/z*: 320.1829, found: 320.1832, Error -0.9 ppm;

IR (KBr): 3045, 2953, 2874, 1664, 1554, 774, 730 cm^{-1}.

2-(2-(triethylsilyl)naphthalen-1-yl)pyridine (**2n**)



2n

The reaction was conducted according to the general procedure by using **1n** (102.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 µL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 µL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2n** (124.5 mg, 78% yield).

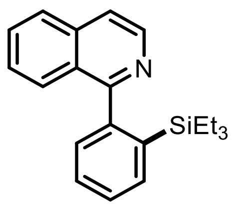
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.4 Hz, 1H), 7.84 (t, *J* = 9.5 Hz, 2H), 7.77 – 7.65 (m, 2H), 7.46 – 7.35 (m, 2H), 7.35 – 7.24 (m, 3H), 0.84 (t, *J* = 7.8 Hz, 9H), 0.45 (q, *J* = 7.7 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 149.1, 145.8, 135.4, 133.5, 133.4, 132.1, 131.2, 127.7, 126.8, 126.0, 125.9, 125.8, 122.3, 7.5, 3.7;

HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{26}NSi$, *m/z*: 320.1829, found: 320.1825, Error 1.3 ppm;

IR (KBr): 3053, 2999, 2872, 1664, 1585, 1003, 744 cm^{-1}.

1-(2-(triethylsilyl)phenyl)isoquinoline (**2o**)



2o

The reaction was conducted according to the general procedure by using **1o** (102.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2o** (143.6 mg, 90% yield).

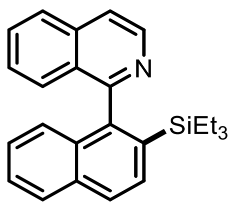
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.7 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.67 – 7.58 (m, 2H), 7.48 – 7.39 (m, 3H), 7.38 – 7.30 (m, 1H), 0.72 (t, *J* = 7.9 Hz, 9H), 0.30 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 145.8, 141.4, 136.8, 136.2, 135.9, 129.8, 129.7, 127.9, 127.8, 127.0, 126.7, 126.6, 120.0, 7.3, 3.6;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{21}H_{25}NSiNa$, *m/z*: 342.1648, found: 342.1643, Error 1.5 ppm;

IR (KBr): 3049, 2952, 2873, 1621, 1558, 845, 767 cm^{-1}.

1-(2-(triethylsilyl)naphthalen-1-yl)isoquinoline (**2p**)



2p

The reaction was conducted according to the general procedure by using **1p** (127.7 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2p** (138.4 mg, 75% yield).

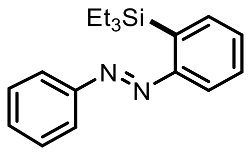
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.7 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.77 (t, *J* = 7.0 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.46 – 7.34 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 0.71 (t, *J* = 7.9 Hz, 9H), 0.38 – 0.24 (m, 3H), 0.23 – 0.10 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 144.0, 142.1, 135.8, 134.8, 133.4, 132.5, 131.3, 130.1, 129.3, 127.9, 127.7, 127.0, 126.9, 126.7, 126.2, 126.1, 125.9, 120.4, 7.3, 3.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{25}H_{28}NSi$, *m/z*: 370.1986, found: 370.1992, Error -1.7 ppm;

IR (KBr): 3050, 2953, 2874, 1620, 1261, 763, 750 cm^{-1}.

1-phenyl-2-(2-(triethylsilyl)phenyl)diazene (**2q**)



2q

The reaction was conducted according to the general procedure by using **1q** (91.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2q** (125.9 mg, 85% yield).

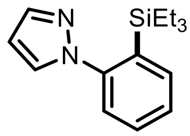
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.77 – 7.70 (m, 1H), 7.70 – 7.63 (m, 1H), 7.58 – 7.50 (m, 2H), 7.50 – 7.36 (m, 3H), 0.98 – 0.86 (m, 15H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 152.5, 138.9, 135.8, 130.9, 129.9, 129.8, 129.1, 123.2, 114.6, 7.6, 4.6;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{24}N_2SiNa$, *m/z*: 319.1601, found: 319.1590, Error 3.4 ppm;

IR (KBr): 3060, 2953, 2873, 1463, 1261, 764, 749 cm^{-1}.

1-(2-(triethylsilyl)phenyl)-1H-pyrazole (**2r**)



2r

The reaction was conducted according to the general procedure by using **1r** (72.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 18 h to give the silylation product **2r** (92.9 mg, 72% yield).

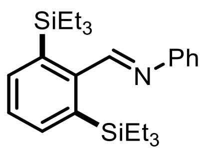
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.5 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.45 – 7.36 (m, 2H), 7.28 – 7.23 (m, 1H), 6.42 (t, *J* = 2.1 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 139.8, 136.7, 133.7, 130.3, 129.5, 127.6, 126.1, 106.5, 7.5, 3.4;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{22}N_2SiNa$, *m/z*: 281.1444, found: 281.1446, Error -0.7 ppm;

IR (KBr): 3063, 2953, 2873, 1591, 743, 727 cm^{-1}.

1-(2,6-bis(triethylsilyl)phenyl)-*N*-phenylmethanimine (**2s**)



2s

The reaction was conducted according to the general procedure by using **1s** (90.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 24 h to give the silylation product **2s** (98.2 mg, 48% yield).

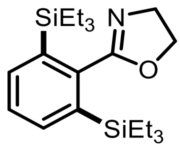
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.34 (m, 3H), 7.28 – 7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 0.95 – 0.81 (m, 30H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 151.5, 148.6, 137.7, 136.9, 129.3, 128.2, 125.9, 120.8, 7.8, 5.3;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{25}H_{39}NSi_2Na$, *m/z*: 432.2513, found: 432.2513, Error 0.0 ppm;

IR (KBr): 3047, 2953, 2873, 1628, 1592, 761, 727 cm^{-1}.

2-(2,6-bis(triethylsilyl)phenyl)-4,5-dihydrooxazole (**2t**)



2t

The reaction was conducted according to the general procedure by using **1t** (73.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 24 h to give the silylation product **2t** (88.2 mg, 47% yield).

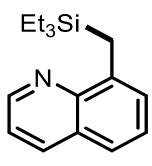
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 4.36 (t, J = 9.9 Hz, 2H), 4.07 (t, J = 9.9 Hz, 2H), 0.93 (t, J = 7.7 Hz, 18H), 0.80 (q, J = 15.1, 7.2 Hz, 12H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.1, 136.0, 135.9, 127.3, 66.7, 55.3, 7.5, 3.8;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{21}H_{37}NOSi_2Na$, *m/z*: 398.2306, found: 398.2310, Error -1.0 ppm;

IR (KBr): 3045, 2953, 2874, 1664, 1554, 774, 730 cm^{-1}.

8-((triethylsilyl)methyl)quinoline (**2u**)



2u

The reaction was conducted according to the general procedure by using **1u** (71.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 24 h to give the silylation product **2u** (122.2 mg, 95% yield).

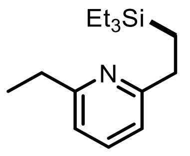
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.54 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 (dd, *J* = 8.2, 4.1 Hz, 1H), 2.85 (s, 2H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.48 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.6, 140.8, 136.1, 128.4, 127.8, 126.2, 123.7, 120.7, 16.9, 7.3, 3.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{16}H_{24}NSi$, *m/z*: 258.1673, found: 258.1671, Error 0.5 ppm;

IR (KBr): 3044, 2952, 2730, 1605, 1008, 798, 724 cm^{-1}.

2-ethyl-6-(2-(triethylsilyl)ethyl)pyridine (**2v**)



2v

The reaction was conducted according to the general procedure by using **1v** (67.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 µL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 µL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 140 °C for 36 h to give the silylation product **2v** (56.1 mg, 45% yield).

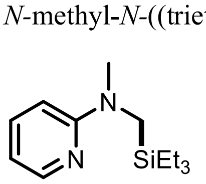
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 2.85 – 2.73 (m, 4H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.00 – 0.91 (m, 11H), 0.55 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 162.8, 136.6, 118.8, 118.7, 32.6, 31.5, 14.2, 11.7, 7.4, 3.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{15}H_{28}NSi$, *m/z*: 250.1986, found: 250.1985, Error 0.4 ppm;

IR (KBr): 3060, 2952, 2874, 1590, 1454, 1016, 764, 732 cm^{-1}.

N-methyl-*N*-((triethylsilyl)methyl)pyridin-2-amine (**2w**)



2w

The reaction was conducted according to the general procedure by using **1w** (61.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 µL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 µL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 140 °C for 36 h to give the silylation product **2w** (77.9 mg, 66% yield).

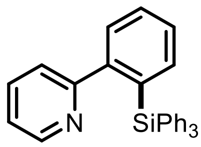
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 1H), 7.43 – 7.34 (m, 1H), 6.47 – 6.38 (m, 2H), 3.13 (s, 2H), 3.04 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 147.6, 136.7, 110.1, 105.2, 38.2, 37.2, 7.3, 3.5;

HRMS (ESI) calcd for $[M+H]^+$ $C_{13}H_{25}N_2Si$, *m/z*: 237.1782, found: 237.1781, Error 0 ppm;

IR (KBr): 3048, 2953, 2874, 1598, 1017, 764, 730 cm^{-1}.

2-(2-(triphenylsilyl)phenyl)pyridine (**2x**)



2x

The reaction was conducted according to the general procedure by using **1a** (77.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Ph_3SiH (260.4 mg, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 36 h to give the silylation product **2x** (134 mg, 65% yield). The single crystal of **2x** was grown by slow evaporation of a mixing solution of petroleum ether and ethyl acetate.

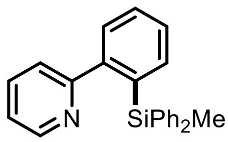
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 1H), 7.67 – 7.60 (m, 2H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 – 7.38 (m, 8H), 7.32 (td, *J* = 7.4, 1.2 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.23 – 7.17 (m, 6H), 6.77 – 6.70 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 147.0, 145.3, 140.5, 139.4, 136.2, 135.5, 133.6, 130.0, 128.3, 127.9, 127.1, 126.5, 121.9, 119.8;

HRMS (ESI) calcd for $[M+H]^+$ $C_{29}H_{24}NSi$, *m/z*: 414.1667, found: 414.1673, Error 1.2 ppm;

IR (KBr): 3361, 3066, 2923, 1589, 1426, 1101, 701, 515 cm^{-1}.

2-(2-(methyldiphenylsilyl)phenyl)pyridine (**2y**)



2y

The reaction was conducted according to the general procedure by using **1a** (77.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Ph_2MeSiH (199.3 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 24 h to give the silylation product **2y** (135.7 mg, 77% yield).

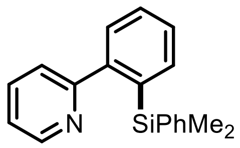
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 7.65 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.53 – 7.34 (m, 9H), 7.30 – 7.17 (m, 8H), 7.00 – 6.92 (m, 1H), 0.59 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 147.8, 146.8, 139.6, 138.8, 136.1, 135.3, 134.6, 129.5, 128.2, 127.9, 127.6, 127.4, 121.8, 121.8, -1.4;

HRMS (ESI) calcd for $[M+H]^+$ $C_{24}H_{22}NSi$, *m/z*: 352.1511, found: 352.1516, Error 1.5 ppm;

IR (KBr): 3065, 3006, 2955, 1588, 1427, 1103, 754, 495 cm^{-1}.

2-(2-(dimethyl(phenyl)silyl)phenyl)pyridine (**2z**)



2z

The reaction was conducted according to the general procedure by using **1a** (77.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), $PhMe_2SiH$ (153.3 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (2 mL) at 100 °C for 24 h to give the silylation product **2z** (119.9 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.43 (m, 1H), 7.69 – 7.60 (m, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.34 – 7.30 (m, 1H), 7.27 – 7.19 (m, 3H), 7.14 – 7.08 (m, 1H), 0.35 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 148.2, 147.1, 140.9, 137.2, 136.8, 136.1, 133.6, 129.1, 128.5, 128.2, 127.4, 127.4, 122.7, 121.8, -0.3;

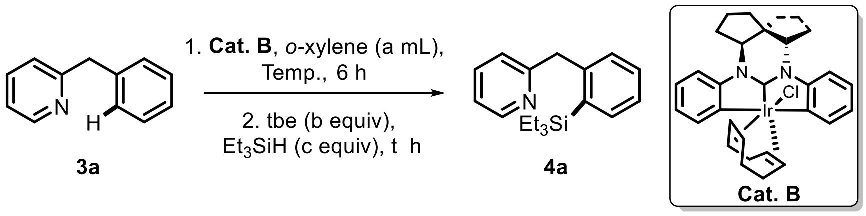
HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{20}NSi$, *m/z*: 290.1350, found: 290.1360, Error 3.5 ppm;

IR (KBr): 3065, 3001, 2952, 1587, 1426, 1108, 817, 702, 479 cm^{-1}.

4. Ir-catalyzed silylation of δ C-H bonds of heteroarenes

4.1 Optimization conditions of δ C-H bonds of heteroarene 3a

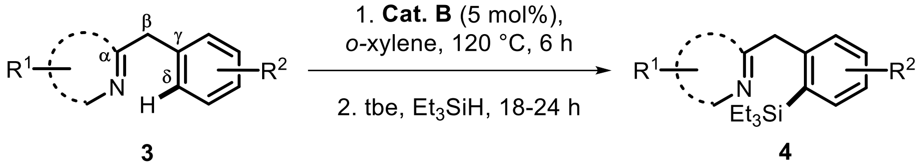
Table S2: Reaction Optimization[a]



Entry	a (mL)	Temp. (°C)	b (equiv)	c (equiv)	t (h)	Yield (%)[b]
1	2	100	3	2	18	42
2	2	100	5	5	18	38
3	2	100	3	2	24	45
4	1	100	3	2	24	66
5	0.5	100	3	2	24	73
6	0.5	100	1.5	2	24	77
7	0.5	120	1.5	2	18	80
8	0.5	120	1.5	3	18	83
9	0.5	120	1.5	3	24	84

[a]Unless otherwise specified, reactions were conducted by pretreatment of a solution of **3a** (0.5 mmol) and **Cat. B** (5 mol%) in *o*-xylene (a mL) at 120 °C for 6 h, then tbe (b equiv) and Et_3SiH (c equiv) were added and reacted for t h. [b]Isolated yield.

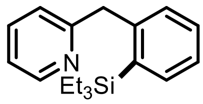
4.2 Sustrates scope of δ C-H bonds of heteroarenes



General procedure for δ C-H bonds of heteroarenes：

In glove box, to dry *o*-xylene were added substrate **3** (0.5 mmol) and **Cat. B** (5 mol%) in a 10 mL oven-dried Schlenk tube. The tube was taken out from the glove box, placed in a preheated oil bath and reacted for 6 h under stirring. After that, the mixture was cooled to room temperature, then tbe and Et_3SiH were added under argon atmosphere. After the reaction was completed, the reaction system was stirred in oil bath for further reaction. The resulting solution was concentrated *in vacuo*, and the residual was purified by silica gel column chromatography to give the silylation product **4**.

2-(2-(triethylsilyl)benzyl)pyridine (**4a**)



4a

The reaction was conducted according to the general procedure by using **3a** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4a** (117.5 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 4.34 (s, 2H), 0.95 – 0.88 (m, 9H), 0.86 – 0.77 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 149.1, 144.8, 136.2, 136.1, 135.9, 130.1, 129.1, 125.5, 123.0, 121.0, 44.5, 7.5, 4.1;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*: 284.1829, found: 284.1826, Error 1.2 ppm;

IR (KBr): 3080, 2954, 2874, 1589, 1470, 1432, 701, 731 cm^{-1}.

2-(4-methyl-2-(triethylsilyl)benzyl)pyridine (**4b**)

4b

The reaction was conducted according to the general procedure by using **3b** (91.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4b** (129.3 mg, 87% yield).

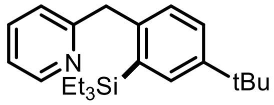
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.9 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.31 (s, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.30 (s, 2H), 2.33 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 9H), 0.84 – 0.78 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 149.0, 141.7, 136.5, 136.2, 135.9, 134.6, 130.1, 129.9, 122.9, 120.9, 44.0, 21.1, 7.5, 4.1;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{28}NSi$, *m/z*: 298.1986, found: 298.1987, Error -0.4 ppm;

IR (KBr): 3006, 2953, 2874, 1588, 1471, 788, 734 cm^{-1}.

2-(4-(tert-butyl)-2-(triethylsilyl)benzyl)pyridine (**4c**)



4c

The reaction was conducted according to the general procedure by using **3c** (112.7 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4c** (140.8 mg, 83% yield).

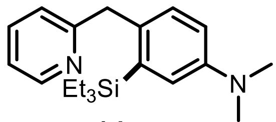
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.6 Hz, 1H), 7.55 (s, 1H), 7.51 (t, *J* = 7.7 Hz 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.11 – 7.05 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.30 (s, 2H), 1.32 (s, 9H), 0.98 – 0.89 (m, 9H), 0.86 – 0.78 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 149.0, 147.6, 141.7, 136.2, 135.4, 132.8, 129.7, 126.0, 123.1, 120.9, 44.0, 34.3, 31.3, 7.6, 4.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{22}H_{34}NSi$, *m/z*: 340.2455, found: 340.2466, Error -3.1 ppm;

IR (KBr): 3055, 2955, 2873, 1589, 1472, 750, 731 cm^{-1}.

2-ylmethyl)-3-(triethylsilyl)aniline (**4d**)



4d

The reaction was conducted according to the general procedure by using **3d** (106.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4d** (150.1 mg, 92% yield).

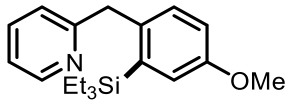
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.99 – 6.92 (m, 2H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.75 – 6.70 (m, 1H), 4.24 (s, 2H), 2.93 (s, 6H), 0.92 (t, *J* = 7.6 Hz, 9H), 0.80 (q, *J* = 7.4 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 148.8, 148.1, 136.4, 136.1, 132.6, 131.0, 122.9, 120.7, 120.2, 113.6, 43.4, 40.6, 7.5, 4.2;

HRMS (ESI) calcd for $[M+H]^+$ $C_{20}H_{31}N_2Si$, *m/z*: 327.2251, found: 327.2239, Error 3.7 ppm;

IR (KBr): 3064, 2953, 2873, 1683, 1594, 802, 732 cm^{-1}.

2-(4-methoxy-2-(triethylsilyl)benzyl)pyridine (**4e**)



4e

The reaction was conducted according to the general procedure by using **3e** (99.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4e** (144.1 mg, 92% yield).

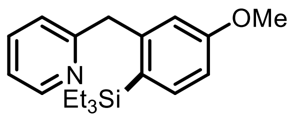
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.2 Hz, 1H), 7.58 – 7.43 (m, 1H), 7.12 – 7.06 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.78 (m, 2H), 4.27 (s, 2H), 3.79 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 9H), 0.85 – 0.76 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 157.2, 149.0, 137.7, 136.7, 136.1, 131.2, 122.9, 121.8, 120.9, 113.6, 54.9, 43.6, 7.4, 4.0;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{28}NOSi$, *m/z*: 314.1935, found: 314.1936, Error -0.3 ppm;

IR (KBr): 3065, 2953, 2874, 1589, 1229, 734, 708 cm^{-1}.

2-(5-methoxy-2-(triethylsilyl)benzyl)pyridine (**4f**)



4f

The reaction was conducted according to the general procedure by using **3f** (99.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4f** (100.2 mg, 64% yield).

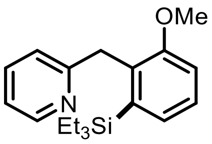
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.3 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.83 – 6.77 (m, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 4.30 (s, 2H), 3.73 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 9H), 0.83 – 0.73 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 160.4, 149.1, 146.7, 137.3, 136.3, 127.0, 123.1, 121.1, 116.2, 110.9, 54.8, 44.5, 7.5, 4.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{28}NOSi$, *m/z*: 314.1935, found: 314.1941, Error -2.1 ppm;

IR (KBr): 3065, 2953, 2873, 1591, 1227, 786, 733 cm^{-1}.

2-(2-methoxy-6-(triethylsilyl)benzyl)pyridine (**4g**)



4g

The reaction was conducted according to the general procedure by using **3g** (99.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4g** (65.9 mg, 42% yield).

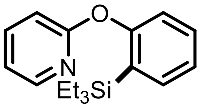
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.50 (m, 1H), 7.44 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.08 – 7.01 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 4.35 (s, 2H), 3.67 (s, 3H), 0.88 – 0.82 (m, 9H), 0.79 – 0.69 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 157.9, 148.7, 138.6, 135.9, 132.5, 127.9, 127.3, 121.4, 120.5, 111.5, 55.2, 39.1, 7.5, 4.2;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{28}NOSi$, *m/z*: 314.1935, found: 314.1936, Error 0.3 ppm;

IR (KBr): 3360, 3060, 2953, 2874, 1588, 1259, 1003, 730 cm^{-1}.

2-(2-(triethylsilyl)phenoxy)pyridine (**4h**)



4h

The reaction was conducted according to the general procedure by using **3h** (85.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4h** (134.0 mg, 94% yield).

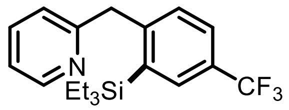
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 1H), 7.58 – 7.50 (m, 1H), 7.41 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.11 – 7.04 (m, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.88 – 6.81 (m, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 0.82 (t, *J* = 7.7 Hz, 9H), 0.73 – 0.63 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 159.0, 147.7, 139.1, 136.3, 130.2, 128.7, 124.1, 120.6, 118.1, 111.3, 7.4, 3.3;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{17}H_{23}NOSiNa$, *m/z*: 308.1441, found: 308.1439, Error 0.8 ppm;

IR (KBr): 3060, 2953, 2874, 1594, 1465, 1424, 1192, 737 cm^{-1}.

2-(2-(triethylsilyl)-4-(trifluoromethyl)benzyl)pyridine (**4i**)



4i

The reaction was conducted according to the general procedure by using **3i** (118.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4i** (147.7 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.74 (s, 1H), 7.64 – 7.46 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.38 (s, 2H), 0.96 – 0.90 (m, 9H), 0.90 – 0.84 (m, 6H);

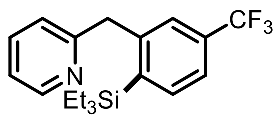
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 149.4, 149.1, 137.6, 136.5, 132.2, 132.2, 130.2, 128.3, 127.9, 127.6, 127.3, 125.9, 125.8, 123.2, 123.1, 121.4, 44.3, 7.4, 4.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3, -62.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{25}F_3NSi$, *m/z*: 352.1703, found: 352.1707, Error -1.1 ppm;

IR (KBr): 3065, 3005, 2952, 2873, 1591, 1077, 750, 733 cm^{-1}.

2-(2-(triethylsilyl)-5-(trifluoromethyl)benzyl)pyridine (**4j**)



4j

The reaction was conducted according to the general procedure by using **3j** (118.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4j** (112.4 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 3.9 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.33 (s, 1H), 7.21 – 7.11 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.38 (s, 2H), 0.95 – 0.88 (m, 9H), 0.88 – 0.81 (m, 6H);

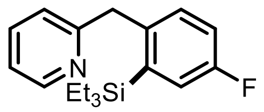
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 149.4, 145.7, 141.4, 136.6, 136.3, 131.6, 131.2, 130.9, 126.3, 126.3, 125.5, 123.0, 122.8, 122.1, 122.0, 121.4, 44.3, 7.4, 3.9;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{25}F_3NSi$, *m/z*: 352.1703, found: 352.1711, Error -2.1 ppm;

IR (KBr): 3069, 3009, 2956, 2876, 1591, 1126, 782, 732 cm^{-1}.

2-(4-fluoro-2-(triethylsilyl)benzyl)pyridine (**4k**)



4k

The reaction was conducted according to the general procedure by using **3k** (93.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 µL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 µL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4k** (132.5 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 1H), 7.58 – 7.51 (m, 1H), 7.23 – 7.16 (m, 1H), 7.14 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 7.00 – 6.93 (m, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.29 (s, 2H), 0.94 – 0.87 (m, 9H), 0.85 – 0.77 (m, 6H);

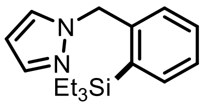
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 161.3, 159.9, 149.2, 140.4, 140.3, 139.2, 139.2, 136.3, 131.7, 131.7, 122.9, 122.1, 121.9, 121.1, 115.9, 115.7, 43.6, 7.4, 3.9;

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8, -117.8, -117.8;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{25}FNSi$, *m/z*: 302.1735, found: 302.1735, Error -0.1 ppm;

IR (KBr): 3064, 2954, 2875, 1588, 1473, 749, 707 cm^{-1}.

1-(2-(triethylsilyl)benzyl)-1H-pyrazole (**4l**)



4l

The reaction was conducted according to the general procedure by using **3l** (79.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 18 h to give the silylation product **4l** (119.8 mg, 88% yield).

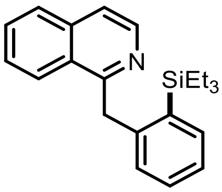
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.26 – 7.14 (m, 2H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.80 (d, *J* = 7.0 Hz, 1H), 6.17 (t, *J* = 1.9 Hz, 1H), 5.35 (s, 2H), 0.86 (t, *J* = 7.5 Hz, 9H), 0.81 – 0.72 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.3, 135.7, 135.1, 129.5, 129.2, 128.0, 127.0, 105.7, 55.8, 7.4, 4.1;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{24}N_2SiNa$, *m/z*: 295.1601, found: 295.1597, Error 1.3 ppm;

IR (KBr): 3057, 2953, 2874, 1512, 1087, 1003, 734 cm^{-1}.

1-(2-(triethylsilyl)benzyl)isoquinoline (**4m**)



4m

The reaction was conducted according to the general procedure by using **3m** (109.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4m** (123.3 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.8 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.49 – 7.42 (m, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.08 (td, *J* = 7.5, 1.4 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.82 (s, 2H), 1.07 – 0.97 (m, 15H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 145.7, 142.1, 136.4, 135.8, 135.1, 129.8, 129.1, 128.2, 127.4, 127.3, 127.1, 126.0, 125.3, 119.8, 42.9, 7.6, 4.1;

HRMS (ESI) calcd for $[M+H]^+$ $C_{22}H_{28}NSi$, *m/z*: 334.1986, found: 334.1982, Error 1.2 ppm;

IR (KBr): 3053, 2953, 2873, 1623, 1587, 823, 732 cm^{-1}.

3-(2-(triethylsilyl)benzyl)isoquinoline (**4n**)

4n

The reaction was conducted according to the general procedure by using **3n** (109.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (96.7 μL, 0.75 mmol, 1.5 equiv), Et_3SiH (239.6 μL, 1.5 mmol, 3.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **4n** (108.3 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.76 – 7.69 (m, 1H), 7.48 – 7.39 (m, 1H), 7.33 – 7.16 (m, 6H), 4.29 (s, 2H), 1.05 – 0.87 (m, 15H);

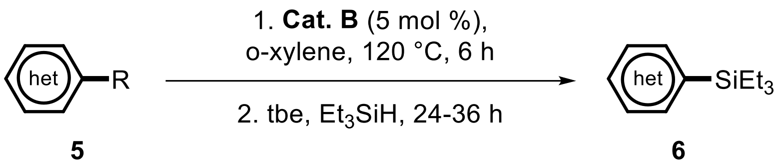
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.4, 139.8, 138.6, 136.8, 136.5, 129.2, 128.5, 128.5, 126.2, 125.9, 125.3, 120.9, 45.6, 7.8, 4.1;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{22}H_{27}NSiNa$, *m/z*: 356.1805, found: 356.1801, Error 1.2 ppm;

IR (KBr): 3057, 2951, 2872, 1600, 1494, 1007, 720 cm^{-1}.

5. Ir-catalyzed silylation of α, β C-H bonds of *N, O, S*-heteroarenes

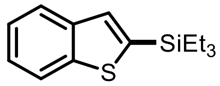
5.1 Substrates scope of α, β C-H bonds of heteroarenes



General procedure for α, β C-H bonds of heteroarenes:

In glove box, to dry *o*-xylene were added substrate **5** (0.5 mmol) and **Cat. B** (5 mol%) in a 10 mL oven-dried Schlenk tube. The tube was taken out from the glove box, placed in a preheated oil bath and reacted for 6 h under stirring. After that, the mixture was cooled to room temperature, then tbe and Et_3SiH were added under argon atmosphere. The reaction system was stirred in oil bath for further reaction. After the reaction was completed, the resulting solution was concentrated *in vacuo*, and the residual was purified by silica gel column chromatography to give the silylation product **6**.

benzo[b]thiophen-2-yl-triethylsilane (**6a**)



6a

The reaction was conducted according to the general procedure by using **5a** (67.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6a** (84.4 mg, 68% yield).

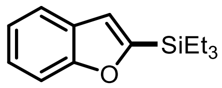
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.47 (s, 1H), 7.38 – 7.27 (m, 2H), 1.03 (t, *J* = 7.7 Hz, 9H), 0.90 – 0.82 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.0, 139.0, 131.5, 124.0, 123.9, 123.3, 122.1, 7.3, 4.2;

HRMS (ESI) calcd for $[M+H]^+$ $C_{14}H_{21}SSi$, *m/z*: 249.1128, found: 249.1125, Error 1.1 ppm;

IR (KBr): 3057, 2954, 2874, 1454, 1018, 738, 725 cm^{-1}.

benzofuran-2-yl-triethylsilane (**6b**)



6b

The reaction was conducted according to the general procedure by using **5b** (59.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6b** (89.4 mg, 77% yield).

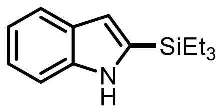
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 1.03 (t, *J* = 7.6 Hz, 9H), 0.89 – 0.81 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 158.1, 128.0, 124.1, 122.2, 120.8, 117.2, 111.3, 7.3, 3.1;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{20}OSiNa$, *m/z*: 255.1176, found: 255.1175, Error 0.2 ppm;

IR (KBr): 3101, 2955, 2876, 1525, 1296, 1009, 743 cm^{-1}.

2-(triethylsilyl)-1H-indole (**6c**)



6c

The reaction was conducted according to the general procedure by using **5c** (58.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6c** (71.7 mg, 62% yield).

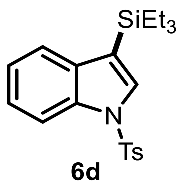
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.13 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 0.9 Hz, 1H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.84 (q, *J* = 7.4 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 135.6, 128.7, 122.1, 120.4, 119.5, 112.3, 110.7, 7.4, 3.6;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{21}NSiNa$, *m/z*: 254.1335, found: 254.1332, Error 1.5 ppm;

IR (KBr): 3424, 3051, 2954, 2874, 1497, 1013, 790, 738 cm^{-1}.

1-tosyl-3-(triethylsilyl)-1H-indole (**6d**)



6d

The reaction was conducted according to the general procedure by using **5d** (135.7 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6d** (140.6 mg, 73% yield).

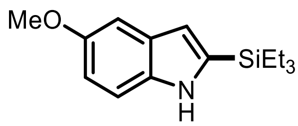
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 (s, 1H), 7.31 – 7.26 (m, 1H), 7.24 – 7.19 (m, 3H), 2.33 (s, 3H), 0.97 – 0.91 (m, 9H), 0.89 – 0.82 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 135.8, 135.2, 135.0, 132.5, 129.8, 126.8, 124.2, 123.0, 122.4, 115.1, 113.4, 21.6, 7.4, 3.6;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{21}H_{27}NO_2SSiNa$, *m/z*: 408.1424, found: 408.1419, Error 1.3 ppm;

IR (KBr): 3065, 2955, 2874, 1598, 1046, 858, 748 cm^{-1}.

5-methoxy-2-(triethylsilyl)-1H-indole (**6e**)



6e

The reaction was conducted according to the general procedure by using **5e** (73.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6e** (108.4 mg, 83% yield).

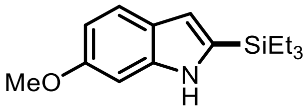
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 6.88 – 6.81 (m, 1H), 6.66 (d, *J* = 0.8 Hz, 1H), 3.84 (s, 3H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.86 – 0.77 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 136.4, 133.9, 129.0, 112.7, 111.8, 111.4, 101.6, 55.8, 7.4, 3.5;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{23}NOSiNa$, *m/z*: 284.1441, found: 284.1437, Error 1.5 ppm;

IR (KBr): 3425, 3026, 2992, 2874, 1620, 1018, 736, 705 cm^{-1}.

6-methoxy-2-(triethylsilyl)-1H-indole (**6f**)



6f

The reaction was conducted according to the general procedure by using **5f** (73.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6f** (86.2 mg, 66% yield). The single crystal of **6f** was grown by slow evaporation of a mixing solution of petroleum ether and dichloromethane.

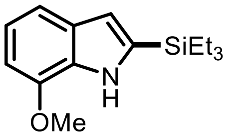
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 6.87 (s, 1H), 6.77 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.66 (d, *J* = 0.9 Hz, 1H), 3.82 (s, 3H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.81 (q, *J* = 7.7 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 139.4, 134.1, 123.0, 120.9, 112.3, 109.8, 93.9, 55.6, 7.4, 3.5;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{23}NOSNa$, *m/z*: 284.1441, found: 284.1438, Error 0.9 ppm;

IR (KBr): 3386, 3067, 2954, 2874, 1621, 1020, 737, 704 cm^{-1}.

7-methoxy-2-(triethylsilyl)-1H-indole (**6g**)



6g

The reaction was conducted according to the general procedure by using **5g** (73.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 36 h to give the silylation product **6g** (95.3 mg, 73% yield).

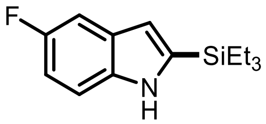
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 3.97 (s, 3H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.87 – 0.78 (m, 6H);

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 145.8, 135.0, 129.9, 129.3, 119.9, 113.1, 112.5, 101.5, 55.2, 7.4, 3.5;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{23}NOSiNa$, *m/z*: 284.1441, found: 284.1438, Error 1.1 ppm;

IR (KBr): 3429, 3067, 2954, 2874, 1580, 1105, 723 cm^{-1}.

5-fluoro-2-(triethylsilyl)-1H-indole (**6h**)



6h

The reaction was conducted according to the general procedure by using **5h** (67.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 36 h to give the silylation product **6h** (71.0 mg, 57% yield).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.30 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.26 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.93 (td, *J* = 9.0, 2.5 Hz, 1H), 6.70 – 6.67 (m, 1H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.89 – 0.78 (m, 6H);

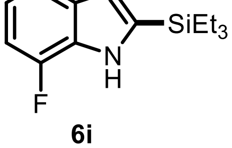
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 158.9, 156.6, 137.9, 135.1, 128.9, 128.8, 112.2, 112.1, 111.2, 111.1, 110.6, 110.4, 105.0, 104.8, 7.4, 3.4;

^{19}**F NMR** (376 MHz, $CDCl_3$) δ -125.4;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{20}FNSiNa$, *m/z*: 272.1241, found: 272.1241, Error -0.1 ppm;

IR (KBr): 3470, 3061, 2955, 2875, 1502, 1141, 764, 749 cm^{-1}.

7-fluoro-2-(triethylsilyl)-1H-indole (**6i**)



6i

The reaction was conducted according to the general procedure by using **5a** (67.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 36 h to give the silylation product **6a** (54.8 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.39 (dd, *J* = 7.9 Hz, 0.4 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.91 – 6.84 (m, 1H), 6.78 – 6.74 (m, 1H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.89 – 0.81 (m, 6H);

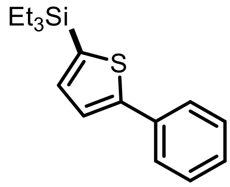
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.1, 136.7, 132.4, 132.4, 127.1, 126.9, 119.7, 119.7, 116.1, 116.1, 116.1, 112.8, 112.7, 106.7, 106.6, 7.4, 3.4;

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.2;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{20}FNSiNa$, *m/z*: 272.1241, found: 272.1247, Error -2.2 ppm;

IR (KBr): 3478, 3071, 2956, 2875, 1581, 1017, 803, 726 cm^{-1}.

triethyl(5-phenylthiophen-2-yl)silane (**6j**)



6j

The reaction was conducted according to the general procedure by using **5j** (80.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6j** (98.7 mg, 72% yield).

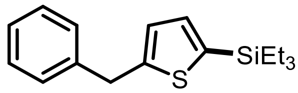
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 – 7.22 (m, 1H), 7.20 (d, *J* = 3.4 Hz, 1H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.89 – 0.76 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 136.5, 135.7, 134.4, 128.8, 127.4, 126.0, 124.3, 7.4, 4.4;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{22}SSiNa$, *m/z*: 297.1104, found: 297.1109, Error -1.8 ppm;

IR (KBr): 3058, 2953, 2874, 1600, 1237, 1004, 737 cm^{-1}.

(5-benzylthiophen-2-yl)triethylsilane (**6k**)



6k

The reaction was conducted according to the general procedure by using **5k** (87.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6k** (93.6 mg, 65% yield).

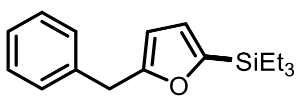
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 7.05 (d, *J* = 3.2 Hz, 1H), 6.84 (d, *J* = 3.1 Hz, 1H), 4.17 (s, 2H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.80 – 0.71 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 140.4, 135.3, 134.7, 128.7, 128.5, 126.5, 126.4, 36.0, 7.4, 4.4;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{17}H_{24}SSiNa$, *m/z*: 311.1260, found: 311.1260, Error 0.0 ppm;

IR (KBr): 3063, 3003, 2874, 1604, 1454, 737, 699 cm^{-1}.

(5-benzylfuran-2-yl)triethylsilane (**6l**)



6l

The reaction was conducted according to the general procedure by using **5l** (79.1 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6l** (96.6 mg, 71% yield).

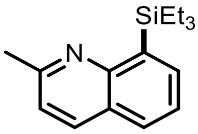
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 6.53 (d, *J* = 3.0 Hz, 1H), 5.93 (d, *J* = 2.9 Hz, 1H), 4.00 (s, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.77 – 0.69 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.0, 138.4, 128.7, 128.4, 126.3, 121.5, 106.1, 34.7, 7.3, 3.2;

HRMS (ESI) calcd for $[M+Na]^+$ $C_{17}H_{24}OSiNa$, *m/z*: 295.1489, found: 295.1482, Error 2.2 ppm;

IR (KBr): 3064, 2954, 2875, 1683, 1012, 738, 722 cm^{-1}.

2-methyl-8-(triethylsilyl)quinoline (**6m**)



6m

The reaction was conducted according to the general procedure by using **5m** (71.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6m** (79.7 mg, 62% yield).

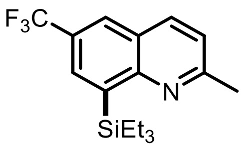
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 6.7 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.44 – 7.37 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 2.67 (s, 3H), 1.05 – 1.00 (m, 6H), 0.99 – 0.92 (m, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 152.5, 138.5, 136.6, 135.9, 128.4, 125.6, 125.0, 121.2, 25.1, 7.8, 4.3;

HRMS (ESI) calcd for $[M+H]^+$ $C_{16}H_{24}NSi$, *m/z*: 258.1673, found: 258.1671, Error 0.5 ppm;

IR (KBr): 3044, 2952, 2730, 1605, 1008, 798, 724 cm^{-1}.

2-methyl-8-(triethylsilyl)-6-(trifluoromethyl)quinoline (**6n**)



6n

The reaction was conducted according to the general procedure by using **5n** (105.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6n** (107.3 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.92 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.73 (s, 3H), 1.08 – 1.00 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 9H);

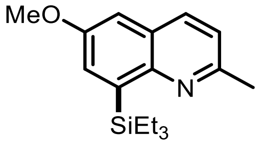
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 153.4, 140.8, 136.8, 131.7, 131.7, 126.9, 126.6, 126.4, 126.4, 125.9, 124.4, 123.2, 122.4, 25.3, 7.7, 4.0;

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.0;

HRMS (ESI) calcd for $[M+H]^+$ $C_{17}H_{23}F_3NSi$, *m/z*: 326.1546, found: 326.1558, Error -3.4 ppm;

IR (KBr): 3036, 2955, 2875, 1608, 1281, 1127, 749 cm^{-1}.

6-methoxy-2-methyl-8-(triethylsilyl)quinoline (**6o**)



6o

The reaction was conducted according to the general procedure by using **5o** (86.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6o** (123.5 mg, 86% yield).

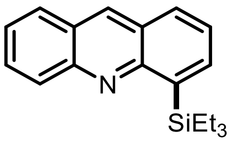
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 2.9 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 2.63 (s, 3H), 1.08 – 0.99 (m, 6H), 0.98 – 0.91 (m, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.6, 148.5, 140.6, 134.8, 129.1, 126.5, 121.4, 105.5, 55.2, 24.8, 7.8, 4.0;

HRMS (ESI) calcd for $[M+H]^+$ $C_{17}H_{26}NOSi$, *m/z*: 288.1778, found: 288.1788, Error -3.5 ppm;

IR (KBr): 3048, 2952, 2873, 1604, 1229, 851, 730 cm^{-1}.

4-(triethylsilyl)acridine (**6p**)



6p

The reaction was conducted according to the general procedure by using **5p** (89.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 120 °C for 24 h to give the silylation product **6p** (121.7 mg, 83% yield).

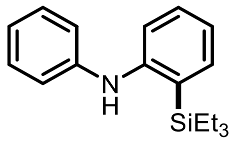
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 6.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.46 (m, 2H), 1.13 (q, *J* = 7.6 Hz, 6H), 0.99 (t, *J* = 7.7 Hz, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 148.1, 139.5, 137.8, 135.5, 129.9, 129.4, 129.1, 127.9, 126.1, 126.0, 125.4, 125.3, 7.9, 4.1;

HRMS (ESI) calcd for $[M+H]^+$ $C_{19}H_{24}NSi$, *m/z*: 294.1673, found: 294.1682, Error -3.3 ppm;

IR (KBr): 3052, 2952, 2871, 1661, 1515, 1007, 741 cm^{-1}.

N-phenyl-2-(triethylsilyl)aniline (**6q**)



6q

The reaction was conducted according to the general procedure by using **5q** (84.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 140 °C for 36 h to give the silylation product **6q** (58.1 mg, 41% yield).

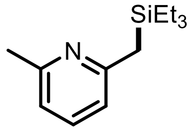
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 1H), 7.29 (d, J = 3.6 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.06 – 6.99 (m, 1H), 6.94 – 6.81 (m, 3H), 5.58 (s, 1H), 0.96 (t, J = 7.6 Hz, 9H), 0.88 – 0.79 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 144.6, 136.5, 130.0, 129.3, 128.5, 122.2, 120.4, 119.9, 116.5, 7.6, 3.8;

HRMS (ESI) calcd for $[M+H]^+$ $C_{18}H_{26}NSi$, *m/z*:284.1829, found: 284.1823, Error 2.3 ppm;

IR (KBr): 3437, 3047, 2952, 2874, 1498, 1004, 745, 692 cm^{-1}.

2-methyl-6-((triethylsilyl)methyl)pyridine (**6r**)



6r

The reaction was conducted according to the general procedure by using **5r** (53.6 mg, 0.5 mmol, 1.0 equiv), catalyst **B** (16.3 mg, 5 mol%), tbe (193.3 μL, 1.5 mmol, 3.0 equiv), Et_3SiH (159.7 μL, 1.0 mmol, 2.0 equiv) and *o*-xylene (0.5 mL) at 140 °C for 36 h to give the silylation product **6r** (60.8 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 2H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.9 Hz, 6H);

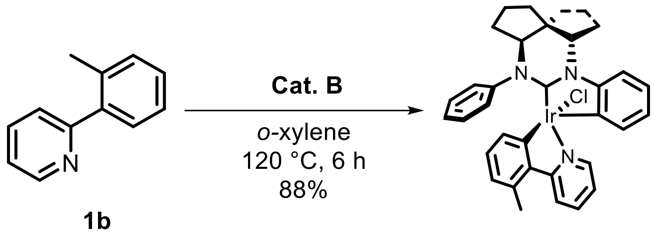
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.3, 135.9, 119.0, 118.3, 25.4, 24.5, 7.2, 3.2;

HRMS (ESI) calcd for $[M+H]^+$ $C_{13}H_{24}NSi$, *m/z*: 222.1673, found: 222.1672, Error 0.3 ppm;

IR (KBr): 3061, 2953, 2875, 1588, 1576, 1017, 797, 749 cm^{-1}.

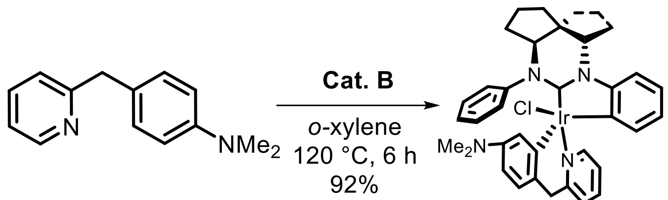
6. Mechanism investigations

6.1. Synthesis of iridicycle intermediates 1bB and 3dB



1b

1bB



3d

3dB

General procedure:

In glove box, to a solution of **Cat. B** (65 mg, 0.1 mmol, 1.0 equiv) in *o*-xylene (3 mL) was added substrates **1b** (25.4 mg, 0.15 mmol, 1.5 equiv) or **3d** (31.8 mg, 0.15 mmol, 1.5 equiv), the tubes were taken out from glove box and stirred at 120 °C for 6 h. After the reactions were completed, red-brown solutions were obtained, the resulting solutions were treated with *n*-pentane to give two brown precipitates. After that, supernatants were separated and the residuals were washed by *n*-pentane, respectively, until **1b** or **3d** was disappeared completely (monitored by TLC). Then the solvent was removed *in vacuo*, affording solid products **1bB** (62.6 mg, 88% yield) or **3dB** (69.4 mg, 92% yield). The single crystals of **1bB** and **3dB** were grown by slow evaporation of a mixing solution of petroleum ether and benzene.

Iridicycle complex 1bB:

HRMS (ESI) calcd for $[M-Cl]^+$ $C_{34}H_{33}IrN_3$, *m/z*: 676.2300, found: 676.2274, Error 3.6 ppm;

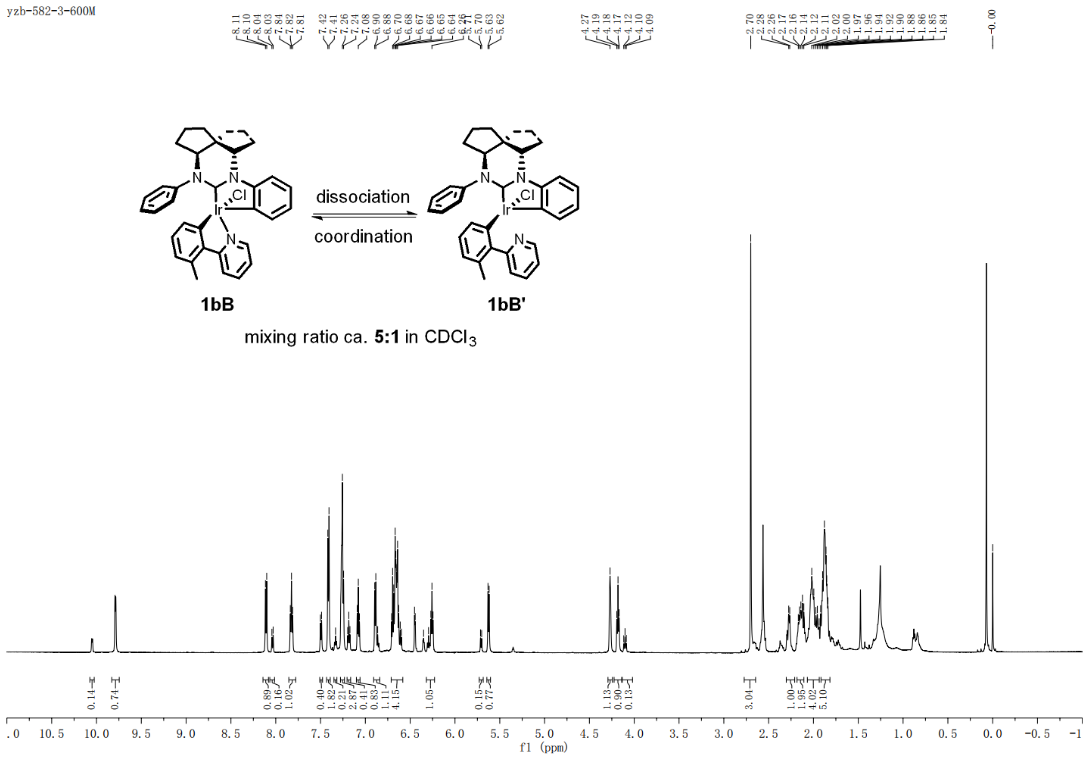
IR (KBr): 3046, 2960, 2871, 1599, 1460, 1028, 727 cm^{-1}.

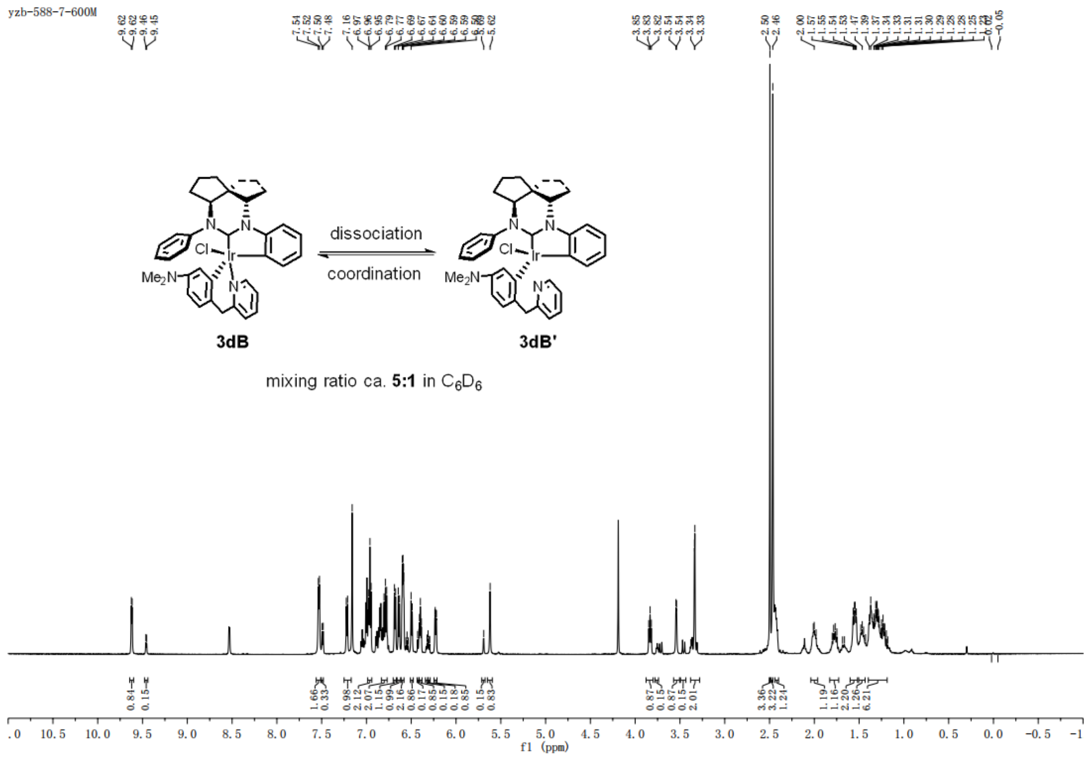
Iridicycle complex 3dB:

HRMS (ESI) calcd for $[M-Cl]^+$ $C_{36}H_{38}IrN_4$, *m/z*: 719.2722, found: 719.2699, Error 2.9 ppm;

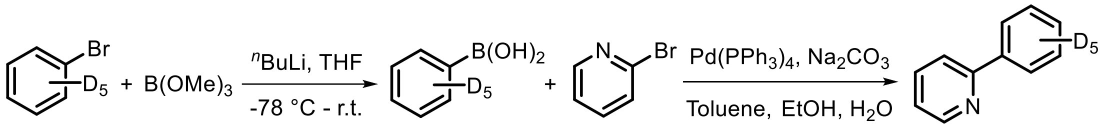
IR (KBr): 3068, 2919, 2849, 1596, 1463, 1268, 879, 760 cm^{-1}.

^{1}H NMR of single crystals of **1bB** and **3dB** indicated that, the N atom in the phenylpyridine moiety of **1bB** or benzylpyridine moiety of **3dB** might dissociate from central metal Ir in solution conditions. (see below)





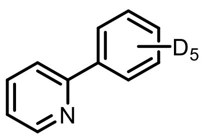
6.2 Synthesis of 2-(pentadeuteriophenyl)pyridine 1a-D_5



1a-D5

According to the literature,[11] to a solution of bromobenzene-D_5 (0.63 mL, 6 mmol, 1.0 equiv) in dry THF (20 mL) was added ^{n}BuLi (1.6 M in hexane, 9 mmol, 5.6 mL, 1.5 equiv) under argon atmosphere at -78 °C. The mixture was stirred for 1 h, then $B(OMe)_3$ (1.25 g, 12 mmol, 2.0 equiv) was added. The system was reacted for further 1 h and allowed to warm to room temperature. After the reaction was quenched by 1N HCl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*, to give an off-white solid used next step without further purification.

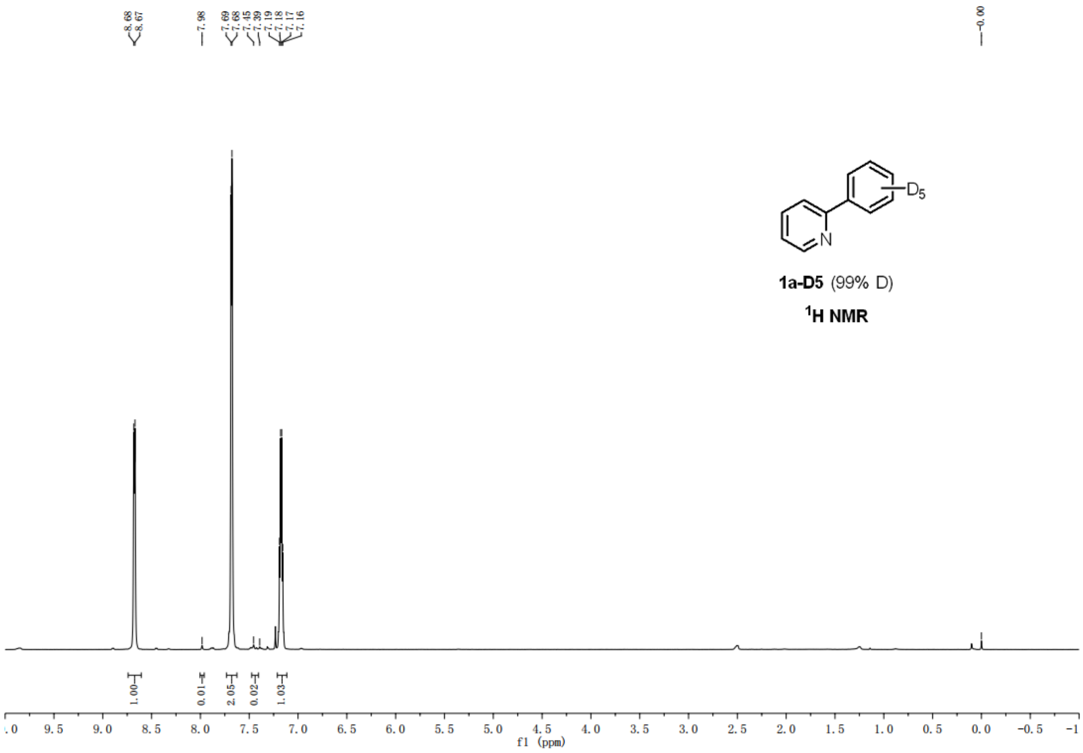
To a 100 mL round-bottom flask was added $Pd(PPh_3)_4$ (231 mg, 5 mol%), Na_2CO_3 (2.97 g, 28 mmol, 7.0 equiv), and phenylboronic acid-D_5 (0.61 g, 4.8 mmol, 1.2 equiv), after that, the solvent of toluene (15 mL), ethanol (2 mL), degassed H_2O (15 mL) combined with 2-bromopyridine (0.63 g, 4.0 mmol, 1.0 equiv) were added dropwise under argon atmosphere. The reaction mixture was refluxed for 12 h. After the reaction was completed, the mixture was cooled to room temperature. Water was added, the system was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual was purified by silica gel column chromatography to afford deuterated product **1a-D_5**.



1a-D5

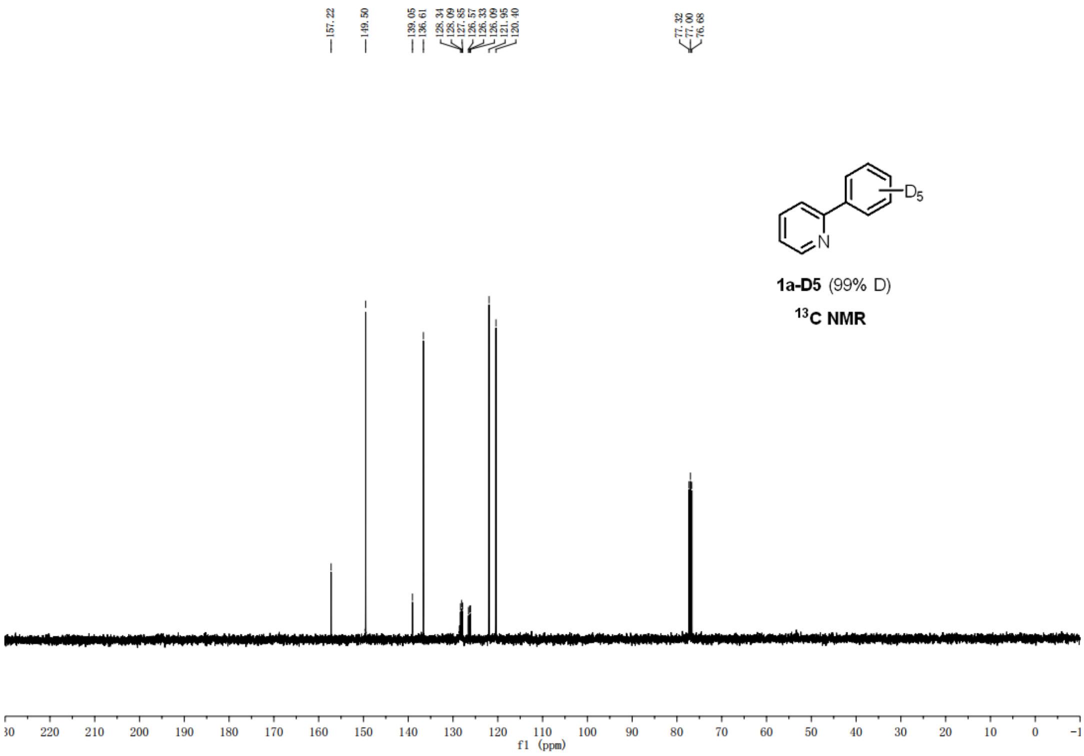
2-(pentadeuteriophenyl)pyridine (**1a-D5**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.22 – 7.13 (m, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.22, 149.50, 139.05, 136.61, 128.34, 128.09, 127.85, 127.52, 126.57, 126.33, 126.09, 121.95, 120.40.



1a-D5 (99% D)

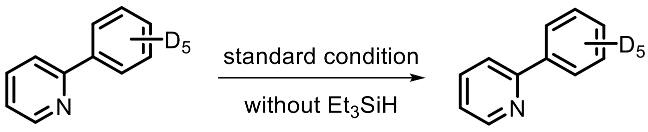
^{1}H NMR



1a-D5 (99% D)

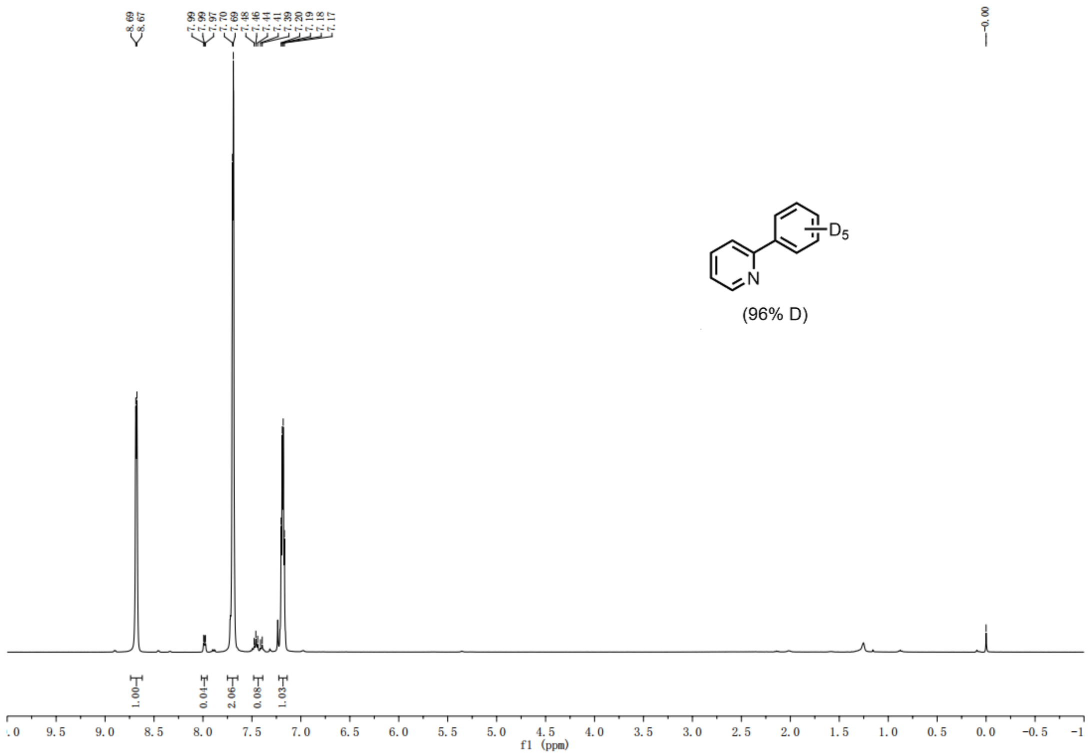
^{13}C NMR

6.3. Hydrogen-deuterium exchange experiment

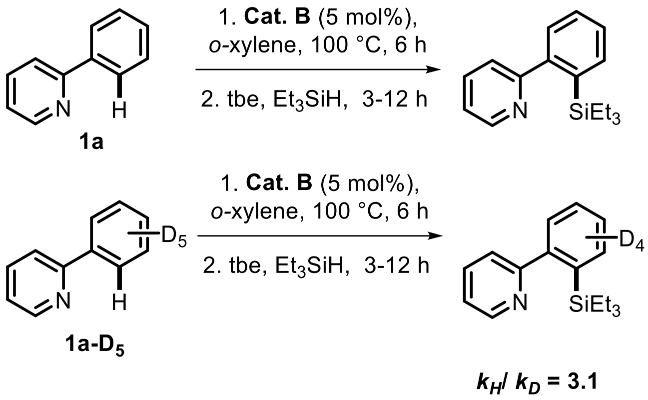


1a-D$_5$ (99% D) (96% D)

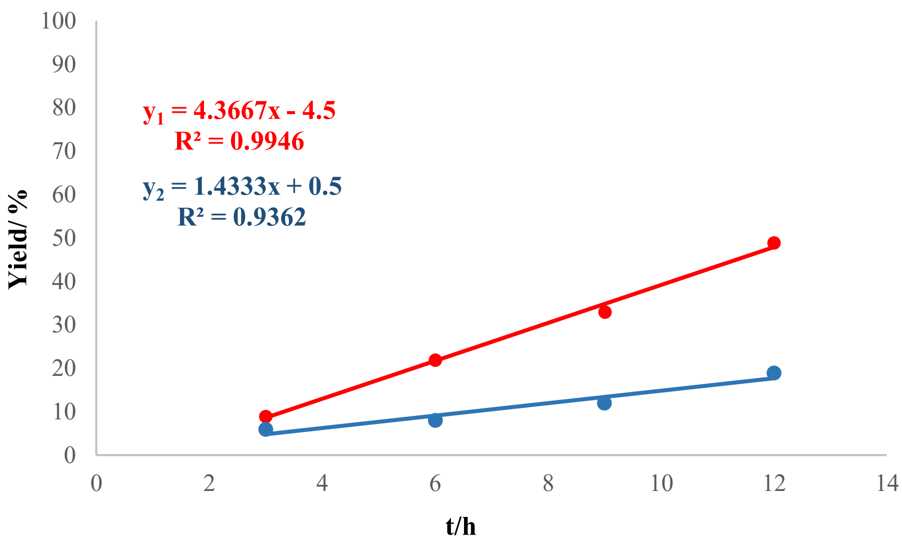
In glove box, to dry *o*-xylene (2 mL) were added **1a-D5** (99% D, 80.1 mg, 0.5 mmol, 1.0 equiv) and **Cat. B** (16.3 mg, 5 mol%) in a 10 mL oven-dried Schlenk tube. The system reacted at 100 °C outside of glove box for 6 h. After that, the mixture was cooled down to room temperature, then tbe (193.3 μL, 1.5 mmol, 3.0 equiv) was added under argon atmosphere. The system was stirred at 100 °C for 18 h. The resulting solution was concentrated *in vacuo*, and the residual was purified by silica gel column chromatography to give the corresponding product (96% D).



6.4. KIE determined from parallel reactions

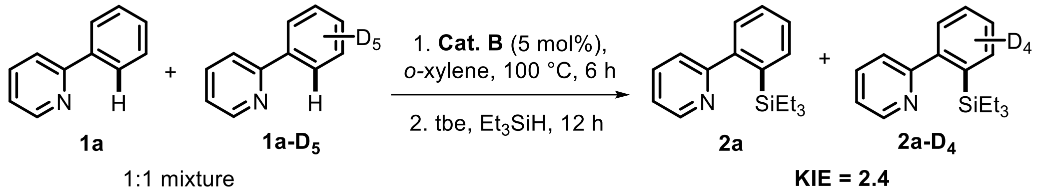


In glove box, to dry *o*-xylene (2 mL) were added substrate **1a** (77.6 mg, 0.5 mmol, 1.0 equiv) or **1a-D5** (80.1 mg, 0.5 mmol, 1.0 equiv) and **Cat. B** (16.3 mg, 5 mol%) in a 10 mL oven-dried Schlenk tube. The system reacted at 100 °C outside of glove box for 6 h. After that, the mixture was cooled to room temperature, then tbe (193.3 µL, 1.5 mmol, 3.0 equiv) and Et_3SiH (159.7 µL, 1.0 mmol, 2.0 equiv) were added under argon atmosphere. The reaction system was stirred at 100 °C and quenched after reacting for 3 h, 6 h, 9 h and 12 h respectively. Yield was determined by GC-MS using dodecane as internal standard.

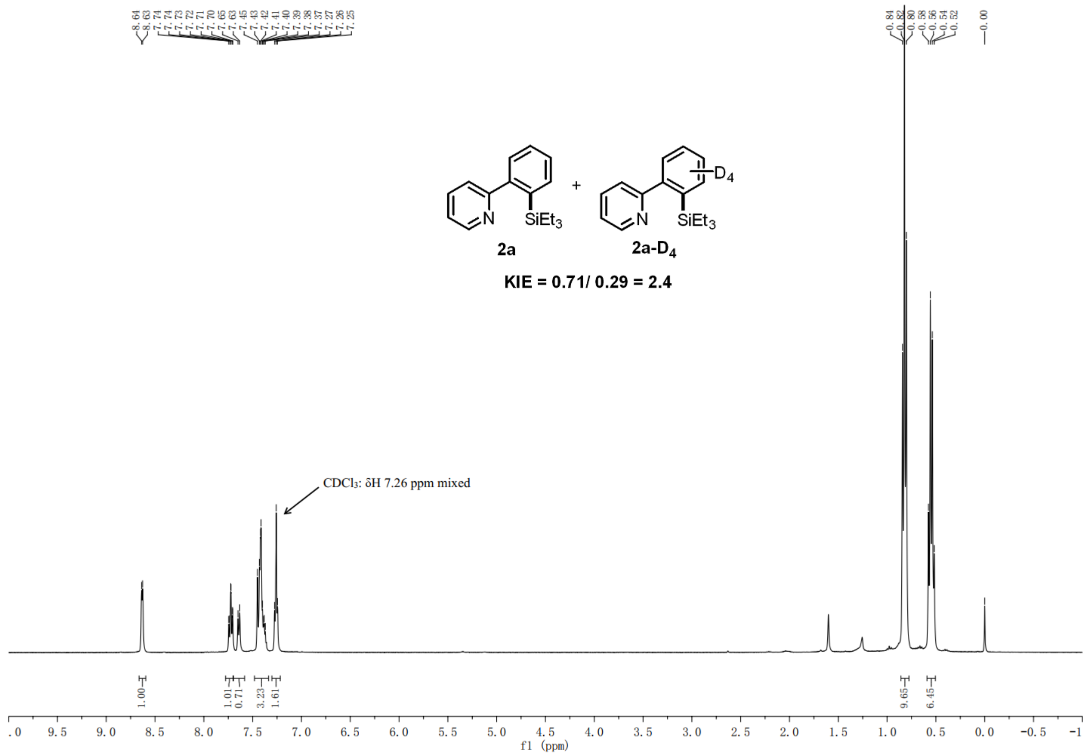


KIE from parallel reactions of **1a**/**1a-D5** was determined to $k_H/ k_D = 4.4/ 1.4 = 3.1$

6.5. KIE determined from intermolecular competition



In glove box, to dry *o*-xylene (4 mL) were added substrate **1a** (77.6 mg, 0.5 mmol) and **1a-D5** (80.1 mg, 0.5 mmol) and **Cat. B** (32.5 mg) in a 25 mL oven-dried Schlenk tube. The system reacted at 100 °C outside of glove box for 6 h. After that, the mixture cooled to room temperature, then tbe (386.6 µL, 3 mmol) and Et_3SiH (319.4 µL, 2 mmol) were added under argon atmosphere. After the reaction system was stirred at 100 °C for 12 h, the resulting solution was concentrated *in vacuo* and purified by silica gel column chromatography to give the mixed products of **2a** and **2a-D4** in a total yield of 33%, the ratio was determined by ^{1}H NMR spectrum.



KIE from intermolecular competition of **1a**/**1a-D5** was determined to 0.71/ 0.29 = 2.4

7. DFT calculations

7.1. Computational methods:

The DFT optimization calculations were carried out at the ωB97XD functional[12] theory level by Gaussian 09 programs.[13] The Pople's basis set 6-311G(d,p) was applied for the C, H, N, Cl and Si atoms, while the basis set LANL2TZ(f) with pseudopotential considered was used to simulate the Ir atom. The single point energy calculations were taken by using Dunning's correlation consistent basis sets Def2-TZVP for C, H, N, Cl and Si atoms, while Def2-QZVP for Ir atom to obtain more accurate energies given that TZVP and QZVP behave well in basis set superposition error (BSSE).[14] The SMD solvation model[15] was used to evaluate the solvation effect of *o*-xylene, and the temperatures were set to 393.15 K according to the experimental conditions during all the calculations. To ensure that the optimized catalyst, reactants, intermediates, and products had no imaginary frequencies while the transition states have only one imaginary frequency, vibrational frequency analyses were carried out. And the intrinsic reaction coordinate (IRC)[16,17] analyses were employed to confirm the transition states were connect the reactants and products. The Gibbs free energies were obtained by the addition of thermal correction of free energy and single point energy.

7.2. Cartesian Coordinates and energies

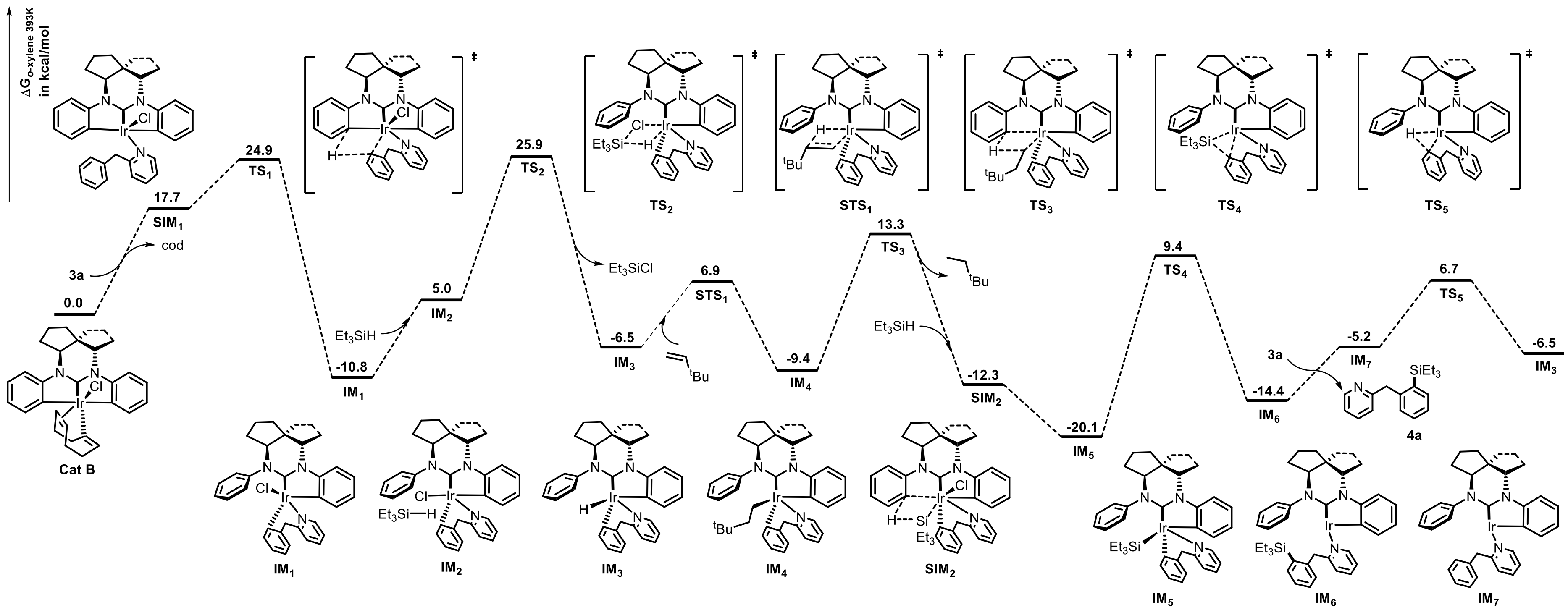


Figure S1. Complete energy profiles for the Ir-catalyzed silylation of 2-benzylpyridine **3a** at 120 °C.

(**SIM$_1$**, **STS$_1$**, **SIM$_2$** were omitted in manuscript due to the limited page space)

Cat. B

Sum of Thermal Correction to Free Energies and Electronic Energy = -1837.472989

Electronic Energy (EE) = -1837.972370

C	0.84151400	-2.18719200	-0.50097900
C	0.54801500	-2.01814600	-0.62696300
C	1.24653300	-3.10414800	-1.14522300
C	0.62193500	-4.31039900	-1.45832400
C	0.74411300	-4.45268100	-1.27823100
C	1.49035600	-3.37720700	-0.80960800
H	2.30803000	-3.01932500	-1.34202400
H	1.20852000	-5.13231600	-1.85479000
H	1.24042000	-5.38569300	-1.52028700
H	2.56406600	-3.47520100	-0.71064200
N	1.56363900	-1.01872900	-0.12177300
C	0.83417800	0.10246700	-0.16866500
Ir	1.15531700	-0.03250700	-0.17321800
N	1.40907600	1.30369300	-0.11378900
C	0.51840600	2.40443500	-0.24009400
C	0.97835100	3.71047800	-0.35087800
C	0.84552100	2.06785800	-0.27396300
C	0.05702300	4.74156500	-0.49734500
H	2.03737200	3.93829100	-0.34558500
C	1.73101900	3.12856300	-0.43719500
C	1.29646800	4.44896400	-0.54289700
H	0.40484100	5.76446500	-0.58700600
H	2.79671800	2.94140700	-0.48973000
H	2.02232100	5.24528800	-0.66882300
C	2.85311100	1.45329400	-0.10126300
H	3.08650900	2.36675200	0.45095100
C	3.00082800	-1.07846800	0.17811400
C	3.52265100	0.29865800	0.63472700
C	4.98890800	0.47108000	0.21038900
C	3.50878200	1.48326000	-1.49046800
H	2.94694900	0.82932900	-2.16195900
H	3.48747400	2.48237100	-1.92727600
C	4.94099000	0.94853200	-1.25922500
H	5.69536100	1.71572900	-1.44131100
H	5.15532400	0.12766400	-1.94608800
H	5.44824600	1.23470500	0.84607600
H	5.57134900	-0.44458900	0.33654100
H	3.51259500	-1.41428100	-0.72797700
C	3.27764400	-2.02018100	1.38333200
H	4.03103200	-2.76796300	1.12904400
H	2.36798200	-2.56585400	1.63693800
C	3.73007300	-1.12523900	2.55497900
H	3.29868200	-1.44313300	3.50566000
H	4.81737300	-1.16130400	2.66445000
C	3.29905600	0.28177400	2.14732400
H	3.85387800	1.07500000	2.65410400
H	2.23427100	0.43266800	2.36232300
Cl	1.38851600	0.17741900	-2.58681100
C	3.21303100	-0.89165500	-0.08915400
H	3.42870800	-1.24258000	-1.09343800
C	3.30449200	0.48064400	0.12520800
H	3.58264700	1.08251500	-0.73211000
C	3.58911500	1.06663700	1.50253900
H	4.16044400	1.98907000	1.38185100
H	4.24039700	0.37550200	2.04577800
C	3.35835600	-1.91463900	1.01770100
H	4.39079400	-1.89171400	1.38740500
H	3.20748700	-2.90589100	0.59315500
C	2.37035700	-1.71154900	2.17726600
H	2.86728400	-1.23176700	3.02637000
H	2.02970300	-2.68587700	2.53162900
C	2.32340500	1.36270400	2.32309200
H	2.51142200	1.21321200	3.39363500
H	2.04811900	2.41013500	2.19602300
C	1.14574500	-0.88166800	1.81092400
H	0.19516100	-1.38249900	1.96673200
C	1.12989900	0.52750400	1.91368200
H	0.17336800	0.98656800	2.15007300

3a

Sum of Thermal Correction to Free Energies and Electronic Energy = -518.524460

Electronic Energy (EE) = -518.670533

C	2.87966300	1.22726500	-0.02048500
C	3.48987800	0.31108000	-0.86445700
C	2.94181700	-0.96208900	-0.95303800
C	1.81652100	-1.25799900	-0.20084400
C	1.27207800	-0.27175400	0.62171700
N	1.79881200	0.95229600	0.71018100
H	3.38473600	-1.71192300	-1.59910700
H	3.27746200	2.23339800	0.07878400
H	4.36864000	0.58936600	-1.43318200
H	1.35648600	-2.23848400	-0.24758400
C	0.01930100	-0.53186800	1.42596700

H	-0.00981100	-1.57852600	1.73863600
H	0.06099000	0.08675700	2.32532600
C	-1.23204800	-0.20473500	0.63592500
C	-2.09885000	-1.21095900	0.21620600
C	-1.52367200	1.11783100	0.29681000
C	-3.23751300	-0.90616800	-0.52314700
H	-1.88472100	-2.24376700	0.47350400
C	-2.65890400	1.42434200	-0.44057100
H	-0.84577300	1.90514900	0.61004000
C	-3.52073900	0.41246300	-0.85327600
H	-3.90331900	-1.70173100	-0.83972500
H	-2.87338600	2.45674300	-0.69449900
H	-4.40818600	0.65249000	-1.42830200

cod

Sum of Thermal Correction to Free Energies and

Electronic Energy = -311.916311

Electronic Energy (EE) = -312.052739

C	-1.19041100	-1.23272400	-0.50709200
H	-1.78182300	-1.82376800	-1.20476100
C	0.03454700	-1.68426400	-0.24254500
H	0.33937900	-2.58891400	-0.76526200
C	1.08205100	-1.09286600	0.66809800
H	1.77360100	-1.88982700	0.95762800
H	0.64199800	-0.73299400	1.59792800
C	-1.91412000	-0.01684800	0.00582000
H	-2.69128700	-0.34453500	0.70912000
H	-2.45849700	0.41890700	-0.84081900
C	-1.08203800	1.09283900	0.66818100
H	-0.64196600	0.73294300	1.59799400
H	-1.77358800	1.88978400	0.95774700
C	1.91412000	0.01683600	0.00575100
H	2.69132800	0.34448300	0.70902400
H	2.45844700	-0.41888500	-0.84093800
C	-0.03455000	1.68427900	-0.24245700
H	-0.33938300	2.58896700	-0.76510500
C	1.19040000	1.23274800	-0.50706400
H	1.78179700	1.82383500	-1.20470800

Et_3SiH

Sum of Thermal Correction to Free Energies and

Electronic Energy = -527.666358

Electronic Energy (EE) = -527.822722

Si	0.00324900	0.00015100	-1.01683800
H	0.00538200	0.00092900	-2.51280500
C	-0.34341700	1.76925100	-0.44935600
C	-0.86038800	1.92507100	0.98643600
H	-1.07316900	2.20257700	-1.14386900
H	0.57296200	2.35746000	-0.58378700
H	-1.02261300	2.97796900	1.23754600
H	-1.81493900	1.40817600	1.12321100
H	-0.15995500	1.51945000	1.72174000
C	1.70866200	-0.58204300	-0.44833200
C	2.09492400	-0.22599500	0.99312700
H	2.44847200	-0.15380700	-1.13530600
H	1.76723700	-1.66767300	-0.59551000
H	3.09024600	-0.60678700	1.24245600
H	2.11650500	0.85768800	1.14262800
H	1.39459000	-0.64352800	1.72187300
C	-1.35718400	-1.18468800	-0.45415900
C	-1.24751600	-1.70215300	0.98558700
H	-1.35842200	-2.03706900	-1.14418700
H	-2.32438500	-0.68789000	-0.60127100
H	-2.07967900	-2.36892700	1.23209800
H	-0.32338100	-2.26870500	1.13473400
H	-1.25481900	-0.88863800	1.71636100

Et_3SiCl

Sum of Thermal Correction to Free Energies and

Electronic Energy = -987.357103

Electronic Energy (EE) = -987.502965

Si	-0.36770100	-0.00061800	0.00016300
C	0.14873700	-1.33706500	-1.21144400
C	1.59201100	-1.22373000	-1.72254300
H	-0.54122500	-1.30154000	-2.06196900
H	-0.01117000	-2.31244300	-0.73697400
H	1.82730200	-2.04424800	-2.40627100
H	1.74816900	-0.28995300	-2.27018600
H	2.32316000	-1.25733200	-0.91019300
C	0.14797600	-0.38168100	1.76353500
C	1.59184700	-0.87918900	1.92120600
H	-0.54105200	-1.13706300	2.15769000
H	-0.01340900	0.51649300	2.37127700
H	1.82723000	-1.05997200	2.97383100
H	1.74890100	-1.82075500	1.38729000
H	2.32213800	-0.15839500	1.54338500
C	0.14787900	1.71744700	-0.55049600
C	1.59140000	2.10454800	-0.19952900

H	-0.54143400	2.43533900	-0.09198000
H	-0.01476300	1.79585700	-1.63192100
H	1.82350800	3.10883900	-0.56506900
H	1.75070200	2.10846800	0.88254600
H	2.32274500	1.42104400	-0.63937300
Cl	-2.48247600	0.00013800	-0.00051400

3,3-dimethyl-1-butene

Sum of Thermal Correction to Free Energies and Electronic Energy = -235.744223

Electronic Energy (EE) = -235.865700

C	-1.11460200	-0.46294000	1.25252000
C	-0.35226500	0.00197600	0.00000000
H	-1.19956700	-1.55397000	1.28142200
H	-0.60473600	-0.14041200	2.16516700
H	-2.12772300	-0.04800500	1.26278100
C	-0.25412200	1.52853000	-0.00029400
C	-1.11457700	-0.46343100	-1.25235100
H	0.27171000	1.89635600	-0.88648500
H	-1.25553100	1.96930600	-0.00035900
H	0.27174600	1.89669300	0.88573500
H	-2.12768300	-0.04846500	-1.26282100
H	-0.60466700	-0.14129900	-2.16511300
H	-1.19958100	-1.55447000	-1.28080400
C	1.00513200	-0.66639100	0.00013700
C	2.19554800	-0.07948700	0.00001700
H	0.96399900	-1.75638400	0.00035700
H	3.10717500	-0.66840000	0.00013300
H	2.31417500	0.99950600	-0.00019100

3,3-dimethyl-1-butane

Sum of Thermal Correction to Free Energies and Electronic Energy = -236.961372

Electronic Energy (EE) = -237.104929

H	0.85460000	1.48659400	-0.87719400
C	1.61617200	0.97755700	-0.00003800
C	0.43373700	0.00079100	-0.00000100
H	1.59551300	1.62243200	0.88489600
H	1.59557100	1.62228900	-0.88507700
H	2.56990400	0.43974500	0.00003600
C	0.51790300	-0.88140500	-1.25142000
C	0.51785300	-0.88124600	1.25153300
H	0.26552200	-1.64450400	-1.26428100
H	1.48068700	-1.40113700	-1.29337000
H	0.42133300	-0.28323100	-2.16392400
H	1.48063800	-1.40096800	1.29359100
H	0.26556800	-1.64434900	1.26445200
H	0.42123700	-0.28296000	2.16396000
C	0.86988700	0.82763900	-0.00007700
C	2.17549200	0.03685600	-0.00000600
H	0.85460200	1.48675100	0.87692200
H	3.03124600	0.71778400	-0.00006700
H	2.26753100	-0.59972200	0.88443100
H	2.26753300	-0.59988200	-0.88432700

SIM_1

Sum of Thermal Correction to Free Energies and Electronic Energy = -2044.052954

Electronic Energy (EE) = -2044.558830

C	1.01507700	-2.27838000	0.56587100
C	-0.37337000	-2.12250800	0.34915900
C	-1.15013600	-3.26127300	0.55088300
C	-0.60742100	-4.47235000	0.98777500
C	0.75078000	-4.56511100	1.24610700
C	1.57385200	-3.45996600	1.03394400
H	-2.21978800	-3.21064600	0.35857500
H	-1.24773300	-5.33748200	1.12873400
H	1.18244400	-5.49362900	1.60327400
H	2.63730900	-3.54342400	1.22574700
N	1.82635100	-1.12096800	0.30573600
C	1.12644900	-0.00204800	0.06998700
Ir	-0.80104900	-0.12774000	-0.15087200
N	1.71491600	1.18293500	-0.11183600
C	0.83159800	2.25127700	-0.47289800
C	1.28386800	3.55211000	-0.64471200
C	-0.52213500	1.88269200	-0.62819400
C	0.37831900	4.53510700	-1.04169400
H	2.32044900	3.82197900	-0.47700200
C	-1.38328200	2.89369100	-1.04586200
C	-0.95053200	4.20373600	-1.25821300
H	0.72260800	5.55374000	-1.18431800
H	-2.43496900	2.65992400	-1.19485500
H	-1.65352500	4.96491900	-1.58237100
C	3.15232200	1.32177500	0.00849300
H	3.46722500	2.14861600	-0.63168900
C	3.28122300	-1.23921900	0.09760900
C	3.87314500	0.06929600	-0.48293200
C	5.29983800	0.28740900	0.05346000

C	3.67216800	1.53238600	1.43410900
H	3.11979200	0.87224700	2.10744500
H	3.52643600	2.55575300	1.78467200
C	5.15250900	1.10860700	1.36098700
H	5.81058500	1.97946900	1.33760100
H	5.43414800	0.52544400	2.23958100
H	5.87378000	0.85157900	-0.68725900
H	5.82787500	-0.65588800	0.21126700
H	3.73517400	-1.47561100	1.06456600
C	3.61668200	-2.32027200	-0.97252100
H	4.26931900	-3.09355200	-0.56287800
H	2.69642200	-2.81222200	-1.28661700
C	4.25838900	-1.58888100	-2.16530600
H	3.95240900	-2.02182000	-3.11900800
H	5.35006200	-1.64555600	-2.11323300
C	3.80200300	-0.14421300	-1.99539000
H	4.41358600	0.57974500	-2.53995400
H	2.76547600	-0.03312200	-2.33295600
Cl	-0.28294000	-0.68319300	-2.40826000
C	-3.42471300	-0.24165200	-1.84591200
C	-4.77158000	-0.41055500	-2.11453200
C	-5.63762100	-0.67653800	-1.06530900
C	-5.12195500	-0.74995900	0.21973700
C	-3.76133700	-0.57002400	0.41634600
N	-2.92123000	-0.32851800	-0.60790000
H	-6.69799400	-0.81397900	-1.24195600
H	-2.71002600	-0.03587700	-2.63125700
H	-5.12381500	-0.32959800	-3.13466100
H	-5.76182400	-0.94053600	1.07249600
C	-3.10390000	-0.61050000	1.76057900
H	-3.84086400	-0.43572000	2.54851700
H	-2.67711400	-1.60373400	1.92253600
C	-2.00617100	0.43171100	1.84140800
C	-0.70517500	0.09186200	2.25653200
C	-2.39158600	1.80736200	1.88374400
C	0.17374800	1.11284500	2.72175200
H	-0.47150700	-0.93772700	2.49329700
C	-1.52530700	2.76865000	2.30818400
C	-0.22069600	2.41725400	2.73335900
H	1.15083100	0.82661100	3.08992600
H	-1.83162600	3.80780100	2.32364500
H	0.45337700	3.18946500	3.08575400
H	-3.39833800	2.07300600	1.57864500

TS_1

Sum of Thermal Correction to Free Energies and Electronic Energy = -2044.041396

Electronic Energy (EE) = -2044.543664

Value of imaginary frequency = -595.26 cm^{-1}

Ir	0.69331300	0.23592900	-0.23173200
N	-1.99248800	0.96436700	0.41725000
N	-1.71109400	-1.26736900	-0.22973500
C	-1.21105900	-0.05841400	0.04479100
C	-3.46451600	0.96091600	0.31186900
C	-4.01001400	-0.39434900	-0.21253500
C	-3.09256500	-1.57696100	0.08501400
C	-3.96310400	2.01549300	-0.72079900
C	-4.81087900	1.25799900	-1.75179800
C	-4.24051600	-0.15354500	-1.70579600
C	-5.27674300	-0.78933300	0.56218200
C	-4.77446300	-1.45012400	1.86240700
C	-3.33872700	-1.93973400	1.56163500
C	-1.28801000	2.18528600	0.67064500
C	0.09153100	2.17793100	0.38455300
C	0.78381700	3.37175600	0.54697300
C	0.14868000	4.52868200	0.99886600
C	-1.19839200	4.49292100	1.32309300
C	-1.92673500	3.31716700	1.15845200
C	-0.77262300	-2.21541600	-0.74397900
C	-1.12286800	-3.52865800	-1.02269600
C	-0.14830000	-4.39737400	-1.50990100
C	1.14991600	-3.95086400	-1.69901900
C	1.48280900	-2.63010900	-1.39462300
C	0.54007000	-1.73041200	-0.91404300
H	-3.85439400	1.16548700	1.31235500
H	-3.41144300	-2.39448400	-0.56244800
H	-0.41392400	-5.42486500	-1.73263900
H	0.71046500	5.45034500	1.10698700
H	-1.69635500	5.37957500	1.69915000
H	-2.98128100	3.30570900	1.40391100
H	-2.12958600	-3.89672300	-0.86451700
H	-4.89474400	-0.91142400	-2.14424500
H	-3.28112100	-0.18848800	-2.23464300
H	-4.74941000	1.71374700	-2.74145100
H	-5.86510700	1.24765500	-1.45762500
H	-4.51531500	2.82463500	-0.24090700
H	-3.09752500	2.46254800	-1.21242500
H	-5.93823700	0.05961700	0.74950200

H	-5.83969600	-1.51159300	-0.03782900
H	-5.43272900	-2.26452900	2.16925600
H	-4.76182300	-0.72937300	2.68298600
H	-2.61167400	-1.41707900	2.18804600
H	-3.20406000	-3.00853500	1.73632900
H	1.84300000	3.40586400	0.31004100
H	2.51190900	-2.30655000	-1.52213900
H	1.90896500	-4.63098400	-2.07134600
H	0.77641200	0.70967600	1.27716700
C	5.47739100	0.64832500	-1.55835900
C	5.11621800	0.81073900	-0.23269700
C	3.77856900	0.72533400	0.13807300
C	3.17100600	0.32063600	-2.05297400
C	4.47995000	0.39551100	-2.48697400
H	6.51671500	0.71273000	-1.85889700
H	5.86261600	1.00057600	0.52841700
H	2.36310600	0.12443400	-2.74397200
H	4.69991700	0.25210100	-3.53677000
C	2.63133700	-0.33242200	2.09706700
C	1.39219800	-0.69508500	1.54774900
C	3.17083900	-1.06436500	3.15320400
C	0.68610900	-1.73910000	2.15435800
C	2.47866100	-2.12788500	3.71191600
H	4.14008900	-0.77971600	3.55109000
C	1.22255100	-2.45261500	3.21595200
H	-0.29091100	-2.01936100	1.78371400
H	2.90773300	-2.68537600	4.53683800
H	0.65680200	-3.26915400	3.65120900
N	2.81328800	0.48790400	-0.76839400
Cl	0.04464800	0.95206000	-2.48401400
C	3.36843100	0.87686800	1.57287100
H	4.25301900	1.06648700	2.18131700
H	2.72308400	1.75836300	1.65844900

IM_1

Sum of Thermal Correction to Free Energies and Electronic Energy = -2044.098337

Electronic Energy (EE) = -2044.602813

C	1.00811000	-2.23077300	-0.23122700
C	0.84363500	-2.96535700	0.93874700
C	0.04923400	-4.10260500	0.93022500
C	-0.58228900	-4.50624100	-0.24258600
C	-0.41794000	-3.76829700	-1.40810800
C	0.38269100	-2.62993500	-1.40871800
H	-0.09260700	-4.66327800	1.84680400
H	-1.20784200	-5.39169600	-0.24419200
H	-0.91077600	-4.07350600	-2.32394700
H	0.51658500	-2.04316200	-2.30959500
N	1.82300000	-1.04886900	-0.20375900
C	1.16887000	0.12120500	-0.18461100
Ir	-0.77125300	0.26364100	-0.40289900
N	1.85198200	1.26386600	0.00736700
C	1.02504500	2.40207700	0.15656700
C	1.50826400	3.66985400	0.44161800
C	-0.35502900	2.13365600	0.05550100
C	0.60416600	4.71114300	0.64093200
H	2.57245900	3.85866900	0.52157200
C	-1.23287400	3.18595600	0.29288900
C	-0.75889900	4.46707800	0.57605800
H	0.97383300	5.70584400	0.86267100
H	-2.30223600	3.01015500	0.27543400
H	-1.46393400	5.27194600	0.75436800
C	3.27774900	1.29636000	0.26262600
H	3.67777900	2.20603300	-0.19427900
C	3.28083100	-1.22029400	-0.06972600
C	3.99105100	0.10873600	-0.38324100
C	5.35540200	0.16721400	0.32142700
C	3.65760000	1.23434300	1.75172200
H	2.92536400	0.61297000	2.27472300
H	3.63339900	2.21969800	2.21917500
C	5.05888200	0.58175800	1.77837200
H	5.82124700	1.26712600	2.15256500
H	5.06293500	-0.28529800	2.44236000
H	5.96300100	0.93135900	-0.17305200
H	5.90739800	-0.77279500	0.25135000
H	3.49902300	-1.58407800	0.93928000
C	3.80878600	-2.15512800	-1.15847700
H	4.83247200	-2.43824000	-0.89821600
H	3.23188600	-3.07705700	-1.24708700
C	3.78561600	-1.28929400	-2.42344800
H	2.80380100	-1.34816400	-2.89887000
H	4.52080800	-1.62136600	-3.15824200
C	4.04753000	0.15068800	-1.92803100
H	5.01976000	0.52552800	-2.25679400
H	3.28885500	0.83422000	-2.31742500
Cl	-0.56894200	0.54676000	-2.88342300
C	-3.50221400	1.28781600	-1.38689300
C	-4.87161400	1.36188400	-1.55046100

C	-5.66601100	0.40878100	-0.92953000
C	-5.05693100	-0.58584900	-0.18235600
C	-3.67277800	-0.60588400	-0.05888000
N	-2.91403400	0.33802700	-0.64430300
H	-6.74466500	0.43526100	-1.03246900
H	-2.83389500	1.99347200	-1.86279200
H	-5.29639200	2.15124000	-2.15656800
H	-5.64277300	-1.35432100	0.30620500
C	-2.96025300	-1.68401000	0.71463100
H	-3.69937800	-2.38300500	1.10933200
H	-2.33785600	-2.25602500	0.01400100
C	-2.10302000	-1.13225700	1.83730900
C	-2.32858000	-1.56170400	3.14268200
C	-1.07967400	-0.21049600	1.53997500
C	-1.55061900	-1.08926000	4.19264200
H	-3.12092700	-2.27900500	3.33951900
C	-0.32566800	0.26551400	2.62202900
C	-0.54846600	-0.16540700	3.92534900
H	-1.73280000	-1.43134900	5.20563500
H	0.45655700	0.99720500	2.44522200
H	0.06026800	0.22717400	4.73406600
H	1.30686900	-2.61964500	1.85543500

IM_2

Sum of Thermal Correction to Free Energies and Electronic Energy = -2571.739532

Electronic Energy (EE) = -2572.430611

C	-3.42897500	0.54520700	0.57219200
H	-4.04538500	0.34541500	1.44833800
C	-3.11904200	-0.12706400	-1.82026300
C	-4.12343800	-0.05940300	-0.64222700
C	-5.22622400	0.96915600	-0.90893500
C	-3.39008100	2.06220600	0.30283400
H	-2.44192200	2.33028000	-0.16571900
H	-3.45836400	2.62563600	1.23444100
C	-4.57112400	2.33971100	-0.65501400
H	-5.28365600	3.05343700	-0.23815500
H	-4.20290300	2.76966900	-1.58970500
H	-6.04111600	0.79723500	-0.19762800
H	-5.64748000	0.87032300	-1.91336600
H	-3.33237800	0.67217000	-2.53041300
C	-3.34568000	-1.51842400	-2.43885500
H	-4.19940500	-1.45802200	-3.12290100
H	-2.48792600	-1.86863700	-3.01436200
C	-3.70218700	-2.39880400	-1.24279500
H	-2.80420100	-2.63422100	-0.66534500
H	-4.16135700	-3.34530700	-1.53455100
C	-4.63427200	-1.50303700	-0.42906300
H	-5.65584500	-1.58359300	-0.81490000
H	-4.66329600	-1.76967000	0.63031100
Ir	0.79219500	-0.24031200	-0.03520800
N	-1.70679500	0.04460000	-1.41380600
N	-2.12630100	-0.07284200	0.82972700
C	-1.20590700	-0.13503200	-0.16055500
C	-0.73071500	0.08554500	-2.44835700
C	0.58496700	-0.15872100	-2.02135400
C	1.56241600	-0.25204800	-3.01302200
C	1.26444500	-0.03668000	-4.35659000
C	-0.03277700	0.27052500	-4.73873300
C	-1.04333700	0.32003800	-3.78294600
C	-1.94327900	-0.69355900	2.10198400
C	-2.24219000	0.00949300	3.26497800
C	-2.11214800	-0.60998100	4.49848400
C	-1.67843600	-1.92874800	4.57800300
C	-1.39446200	-2.62997800	3.41341300
C	-1.54273900	-2.02142200	2.17514500
H	-2.33074500	-0.05290200	5.40252300
H	2.04756800	-0.11605700	-5.10339900
H	-0.27325600	0.45001700	-5.78059500
H	-2.05786100	0.52182900	-4.10280800
H	-2.54710300	1.04854800	3.20666500
H	2.57967600	-0.50814700	-2.73915700
H	-1.06051400	-3.66019700	3.46130800
H	-1.56458500	-2.40680300	5.54436100
H	-1.32573200	-2.56877400	1.26730300
C	5.72427800	-0.15860100	-0.14502600
C	5.06291500	-1.18849900	0.49647100
C	3.67002800	-1.22123400	0.52571400
C	3.59674400	0.73304100	-0.71017300
C	4.97088200	0.82808500	-0.76527700
H	6.80748600	-0.12691100	-0.16522500
H	5.61416300	-1.98059600	0.98736900
H	2.97234200	1.46881000	-1.19858700
H	5.43067300	1.65653600	-1.28808500
C	0.86391300	-2.26249500	-0.19508000
C	1.92249700	-4.39364300	0.31868800
C	-0.04884000	-2.98792900	-0.97470700
C	0.97590800	-5.08912300	-0.41984000

H	2.71508400	-4.93985500	0.82271500
C	-0.01205700	-4.37184600	-1.08058600
H	-0.81511600	-2.45559500	-1.52304500
H	1.02057500	-6.17048500	-0.48991100
H	-0.75243900	-4.88438100	-1.68696500
N	2.94799800	-0.25888000	-0.07745600
Si	0.74028500	2.98979100	0.44549100
C	0.13181600	3.89617900	-1.08642600
H	-0.89951600	3.58276600	-1.28844700
H	0.08087900	4.97055600	-0.87014200
C	2.47410100	3.50369700	0.93802300
H	2.87754300	2.71777800	1.58530600
H	3.11570300	3.53836900	0.05137400
C	-0.47071000	3.08781600	1.86966000
H	0.08546900	2.91436300	2.79453200
H	-1.15266600	2.23967800	1.78791600
C	-1.24794600	4.40739200	1.94018200
H	-1.94585100	4.40651300	2.78338000
H	-1.83100800	4.58852500	1.03216100
H	-0.58220300	5.26563000	2.07517200
C	2.51347900	4.85621700	1.66187300
H	2.12308300	5.66565400	1.03629800
H	3.53719000	5.12463200	1.93837500
H	1.92446200	4.83379300	2.58349400
C	0.99919200	3.64236800	-2.32484700
H	2.02865600	3.98210700	-2.17119200
H	0.61235700	4.17201800	-3.20022400
H	1.02987900	2.57792100	-2.57727200
C	1.88158200	-3.00296500	0.43356000
C	2.95063600	-2.32066800	1.25272100
H	2.49609300	-1.87267400	2.14195700
H	3.68766100	-3.05248400	1.58703100
H	0.88353100	1.58895300	-0.14240900
Cl	1.13570900	0.14190600	2.46573900

TS_2

Sum of Thermal Correction to Free Energies and Electronic Energy = -2571.706197

Electronic Energy (EE) = -2572.400013

Value of imaginary frequency = -97.97 cm^{-1}

C	-3.30735800	1.31270700	0.15255400
H	-3.75861800	1.83522200	0.99635600
C	-3.48083600	-0.78323700	-1.20301600
C	-4.23928400	0.17917500	-0.25488100
C	-5.34395600	0.93788100	-0.99676500
C	-3.26267200	2.24649400	-1.06882100
H	-2.44886600	1.94605500	-1.72814200
H	-3.07896500	3.28028200	-0.77020200
C	-4.62464300	2.05715100	-1.77561000
H	-5.21527000	2.97485600	-1.78488500
H	-4.47051200	1.77026100	-2.81822800
H	-6.02590100	1.36654300	-0.25499500
H	-5.93779100	0.27882000	-1.63635900
H	-3.76747400	-0.58547500	-2.23688000
C	-3.91775200	-2.18491500	-0.74070800
H	-4.89237900	-2.40727000	-1.18930200
H	-3.22665100	-2.96933600	-1.05081000
C	-4.06353400	-2.04164800	0.77283900
H	-3.07775900	-2.02297000	1.24440400
H	-4.62738000	-2.86030000	1.22450000
C	-4.74645100	-0.68379600	0.92402100
H	-5.83203000	-0.80068400	0.84390100
H	-4.54010800	-0.21124300	1.88758700
Ir	0.66566100	-0.42090500	-0.14077100
N	-2.00907500	-0.64256800	-1.14659600
N	-2.01019800	0.81425100	0.61494500
C	-1.29105000	-0.04063600	-0.15923600
C	-1.23777400	-1.43710700	-2.03333200
C	0.11965000	-1.54604000	-1.68572300
C	0.89335700	-2.42200200	-2.45072600
C	0.36705100	-3.09308900	-3.55119300
C	-0.96078800	-2.91184200	-3.90913400
C	-1.77526100	-2.08940600	-3.13811300
C	-1.61390900	1.17174200	1.93433300
C	-1.63231300	2.50842100	2.32211900
C	-1.27130800	2.85904100	3.61507100
C	-0.88353700	1.88012400	4.52287900
C	-0.88237200	0.54539400	4.13600700
C	-1.26377500	0.18624400	2.85062000
H	-1.27453900	3.90320900	3.90720900
H	0.99767100	-3.76662100	-4.12223500
H	-1.37674900	-3.42397300	-4.76949400
H	-2.82077300	-1.98854800	-3.40131300
H	-1.90450100	3.27422500	1.60379600
H	1.92447200	-2.60939300	-2.17605800
H	-0.59100500	-0.22796700	4.83778900
H	-0.58856200	2.15708500	5.52859400
H	-1.26614500	-0.85333100	2.54851900

C	5.47818500	-1.45989600	-0.52022500
C	4.82173300	-1.65013700	0.68157500
C	3.46219300	-1.36634500	0.79218700
C	3.41042900	-0.72439000	-1.43084800
C	4.75264300	-0.98863800	-1.60506600
H	6.53587300	-1.67901800	-0.61065400
H	5.35042000	-2.02326300	1.54982500
H	2.80234400	-0.35472600	-2.24463200
H	5.21043300	-0.82315400	-2.57149100
C	0.50195200	-2.11393200	1.05714600
C	1.41956500	-3.57152700	2.79212700
C	-0.56461400	-3.02193800	0.97372400
C	0.32431600	-4.42107800	2.71593200
H	2.21844400	-3.78885700	3.49639600
C	-0.66907800	-4.14501300	1.78586500
H	-1.34059900	-2.85437500	0.23653600
H	0.25919700	-5.29224100	3.35888700
H	-1.52367100	-4.80718800	1.68391600
N	2.76870100	-0.90098500	-0.26399400
Si	1.41155400	2.67934400	-0.52911800
C	0.12801200	3.11355100	-1.85672600
H	-0.81889700	3.33990900	-1.35756400
H	0.48649400	4.08107300	-2.23458900
C	3.13300000	2.52767800	-1.28383100
H	3.77240200	1.96403000	-0.59789800
H	3.04605000	1.91936600	-2.18895400
C	1.33871400	4.25040500	0.56895000
H	2.26668900	4.27103700	1.15402200
H	0.54577700	4.09925300	1.30966600
C	1.12534300	5.60679500	-0.11266200
H	1.19832300	6.42244800	0.61481000
H	0.13586900	5.67608400	-0.57321800
H	1.86353700	5.80570000	-0.89444500
C	3.79612100	3.86470800	-1.63292600
H	3.20140300	4.43726800	-2.35136900
H	4.78071600	3.70490900	-2.08382800
H	3.93987900	4.49032900	-0.74782000
C	-0.08670700	2.16311300	-3.02822700
H	0.85532500	1.94455400	-3.54184500
H	-0.76927000	2.59307800	-3.76914500
H	-0.49842800	1.20407800	-2.70681200
C	1.51460600	-2.44153200	1.97877200
C	2.74769300	-1.57312100	2.09896500
H	2.47564100	-0.59163900	2.49681800
H	3.45143000	-2.01746600	2.80464000
H	1.02357400	0.95364800	-1.10318100
Cl	1.51609800	1.47491600	1.44571900

IM_3

Sum of Thermal Correction to Free Energies and Electronic Energy = -1584.400818

Electronic Energy (EE) = -1584.911293

C	-3.31728100	1.17442200	-0.53919300
H	-3.73195100	2.14032600	-0.24182200
C	-3.25985800	-1.26541400	0.17210300
C	-4.03110000	0.08434200	0.26306000
C	-5.36698800	-0.00507200	-0.48038400
C	-3.66576900	0.88459600	-2.01622100
H	-2.87415900	0.28694800	-2.47311800
H	-3.74479100	1.80954100	-2.58992700
C	-5.00257300	0.10620900	-1.97275000
H	-5.79066000	0.60355600	-2.54084800
H	-4.87425100	-0.88594200	-2.41173900
H	-5.99207800	0.84128500	-0.17533200
H	-5.91711400	-0.91837900	-0.23720800
H	-3.73517400	-1.92545800	-0.55652600
C	-3.33389400	-1.83821200	1.59809700
H	-4.30827600	-2.32155900	1.73171500
H	-2.56197400	-2.58436300	1.79008000
C	-3.23693800	-0.60147300	2.48677000
H	-2.20545200	-0.23764400	2.50522100
H	-3.53668100	-0.79357400	3.51894600
C	-4.14669500	0.40028200	1.77380600
H	-5.18328300	0.25568600	2.09550400
H	-3.87996900	1.43810500	1.98884100
Ir	0.74494200	-0.00573900	-0.54419900
N	-1.86150400	-1.10156900	-0.24744700
N	-1.89878300	1.20485900	-0.21441500
C	-1.17159700	0.06317500	-0.28210700
C	-1.04151500	-2.23011300	-0.47677100
C	0.32711900	-1.92460100	-0.64146400
C	1.20278900	-2.99809400	-0.80589900
C	0.73712500	-4.31005000	-0.85677100
C	-0.61867100	-4.57954800	-0.73397400
C	-1.51635000	-3.53430100	-0.53393300
C	-1.18764300	2.43539500	-0.19419600
C	-1.34041400	3.37141000	-1.21552500
C	-0.62772500	4.56244800	-1.17538400

C	0.25325400	4.82138000	-0.13116300
C	0.40180300	3.88965400	0.88896200
C	-0.32631300	2.70554900	0.86952000
H	-0.74824100	5.28382600	-1.97559300
H	1.44306000	-5.12413700	-0.98486800
H	-0.98368700	-5.59955500	-0.77594200
H	-2.57103300	-3.75163300	-0.41319600
H	-1.99675800	3.15773700	-2.05009900
H	2.26869500	-2.81443300	-0.87769000
H	1.07127100	4.08675200	1.71888300
H	0.81525600	5.74803500	-0.11021800
H	-0.23816800	1.99239800	1.67929000
C	5.59531200	-0.22557100	-1.52486200
C	5.14047000	0.46966300	-0.41865100
C	3.77402500	0.55698400	-0.16632700
C	3.32529800	-0.68932800	-2.06661700
C	4.66552000	-0.81261900	-2.37239500
H	6.65727300	-0.30276800	-1.72791400
H	5.83415400	0.94906500	0.26068800
H	2.55748800	-1.12107200	-2.69491300
H	4.96509000	-1.35796600	-3.25782200
C	1.30040700	-0.21191700	1.47991900
C	2.83188100	0.37146000	3.29895500
C	0.60909700	-0.99916800	2.41394500
C	2.11159900	-0.40434200	4.19934100
H	3.71368000	0.90980100	3.63764700
C	0.99434800	-1.09570000	3.74742600
H	-0.26022700	-1.56428000	2.08779900
H	2.42320900	-0.47182400	5.23630500
H	0.42385500	-1.71555400	4.43292100
N	2.88204400	-0.03679500	-0.97936300
C	2.43398900	0.46659900	1.96604500
C	3.24537200	1.32571500	1.01455300
H	2.62634400	2.14786800	0.63323400
H	4.08565400	1.78642200	1.53751900
H	0.48755100	0.24667300	-2.17542900

STS_1

Sum of Thermal Correction to Free Energies and Electronic Energy = -1820.123579

Electronic Energy (EE) = -1820.792282

Value of imaginary frequency = -541.13 cm^{-1}

Ir	0.71380900	-0.20210400	-0.29903700
N	-1.95586600	-1.18464800	-0.49381200
N	-2.02725600	1.01706500	0.12117800
C	-1.24800400	-0.07886100	-0.15569900
C	-1.18126100	-2.34140100	-0.79539800
C	0.20887500	-2.15062700	-0.71628300
C	0.99796800	-3.28769300	-0.90216500
C	0.44858000	-4.53338300	-1.19421100
C	-0.92782300	-4.67598300	-1.29875000
C	-1.75340100	-3.57740700	-1.08561100
C	-1.57184000	2.11546000	0.89832500
C	-1.82111200	3.42538000	0.48827900
C	-1.42830500	4.49521500	1.28349900
C	-0.76004700	4.27305000	2.47978500
C	-0.50826500	2.96685900	2.88647300
C	-0.92615100	1.89422600	2.11375300
H	-1.62969200	5.50750800	0.95078600
H	1.09607100	-5.39407100	-1.32881200
H	-1.36835700	-5.64087800	-1.52441700
H	-2.82630200	-3.71528500	-1.13522700
H	-2.30674600	3.61741600	-0.46192700
H	2.07518900	-3.21446400	-0.79298900
H	0.00451000	2.77329000	3.82200400
H	-0.44359200	5.10880800	3.09331800
H	-0.74361700	0.88072500	2.44419500
C	5.55486500	-1.11723900	-0.77098100
C	5.06426300	-0.51360500	0.37259300
C	3.70445000	-0.24011000	0.49114000
C	3.32418100	-1.16235000	-1.59453200
C	4.66165400	-1.45049800	-1.77856800
H	6.61314300	-1.32827800	-0.87280200
H	5.72619400	-0.24185400	1.18534500
H	2.59041600	-1.41873900	-2.34594000
H	4.98448200	-1.93190100	-2.69251100
C	2.12007600	-0.41428900	2.40805700
C	0.97867000	-0.81344800	1.68851200
C	2.32434700	-0.79678200	3.73400900
C	0.08409400	-1.64622500	2.37988800
C	1.39887500	-1.59235500	4.39629000
H	3.21965500	-0.46609200	4.25443900
C	0.27393500	-2.02377700	3.70415200
H	-0.79175500	-2.02482700	1.86366200
H	1.56061000	-1.88008300	5.42969200
H	-0.45481700	-2.66434900	4.19209600
N	2.84378000	-0.56352200	-0.49343100
H	0.98407400	1.41703000	0.06962000

C	0.66296600	0.56946300	-2.32577400
H	1.53359400	0.34879900	-2.93876800
H	-0.27109700	0.36394900	-2.84076700
C	0.72515500	1.72867400	-1.47391800
H	-0.23808000	2.20437200	-1.30212300
C	1.78855500	2.83103400	-1.63069900
C	1.40639800	3.57559500	-2.92215300
H	1.50234900	2.92319800	-3.79473600
H	2.05690700	4.44332000	-3.07078100
H	0.37255600	3.93446800	-2.88193900
C	3.22284100	2.32079700	-1.76290400
H	3.32145500	1.54825400	-2.52893100
H	3.58851000	1.91680700	-0.81883900
H	3.88141800	3.14926400	-2.04238700
C	1.71376700	3.80882200	-0.45540900
H	0.72617300	4.26991300	-0.38520000
H	2.45371700	4.60732000	-0.57071400
H	1.90796300	3.30494300	0.49604700
C	3.16027500	0.43552200	1.71717000
H	3.98798100	0.66336300	2.39140800
H	2.70509200	1.38478000	1.40887400
C	-3.31431000	1.15752700	-0.56758300
H	-3.79958800	2.03000500	-0.13394600
C	-3.38289300	-1.34852500	-0.20808800
C	-4.22632300	-0.04868500	-0.32495100
C	-5.08976600	-0.07500800	-1.59361300
C	-3.20187300	1.32876900	-2.10778600
H	-2.16509900	1.26059500	-2.43863600
H	-3.56840100	2.31921400	-2.39132400
C	-4.08929600	0.22789600	-2.71157500
H	-4.57015900	0.53050700	-3.64352600
H	-3.48688700	-0.66086300	-2.92602600
H	-5.84184500	0.72096400	-1.53899500
H	-5.62045400	-1.02246300	-1.72150700
H	-3.76606600	-2.04929400	-0.94933400
C	-3.64913400	-1.90209600	1.20249600
H	-3.52266300	-2.98468600	1.25563900
H	-2.94050400	-1.44565300	1.90050000
C	-5.05858200	-1.41018500	1.51660500
H	-5.30473300	-1.47459600	2.57831200
H	-5.80258500	-1.99651400	0.96577300
C	-5.01309400	0.02655500	0.99667900
H	-5.99715200	0.48105700	0.85916600
H	-4.45964900	0.64289200	1.71423800

IM_4

Sum of Thermal Correction to Free Energies and Electronic Energy = -1820.149608

Electronic Energy (EE) = -1820.814936

Ir	0.60719900	-0.35162900	-0.17599700
N	-2.13391800	-0.56359000	-0.87194400
N	-1.85011200	0.93322200	0.85188600
C	-1.28592500	0.02912600	0.00543100
C	-1.48082500	-1.41101700	-1.79347800
C	-0.08171100	-1.47580100	-1.62363700
C	0.62008900	-2.35233600	-2.45348800
C	-0.02995900	-3.09000600	-3.43989100
C	-1.40335500	-2.98100200	-3.60859000
C	-2.13799900	-2.14568600	-2.77225100
C	-1.03385100	1.53416900	1.84592900
C	-0.90586400	2.91953600	1.92367600
C	-0.08542400	3.48843900	2.88851600
C	0.62418500	2.68385000	3.77289900
C	0.48302600	1.30282900	3.70545000
C	-0.35670700	0.72629300	2.75985100
H	0.01525200	4.56708400	2.93353600
H	0.54252700	-3.76415900	-4.06862400
H	-1.91200000	-3.55636800	-4.37378600
H	-3.21357100	-2.08733600	-2.88860500
H	-1.42026500	3.55171600	1.21083300
H	1.68596600	-2.48779100	-2.31366500
H	1.01117400	0.66287100	4.40353800
H	1.27418200	3.13141800	4.51586300
H	-0.49321500	-0.34724600	2.72645700
C	5.46880600	-1.07625800	-0.86700500
C	4.90367000	-1.20457200	0.38951100
C	3.53899400	-0.99383500	0.56092100
C	3.30322000	-0.54317000	-1.69681400
C	4.64994600	-0.73352800	-1.93410000
H	6.53083100	-1.23728300	-1.01172800
H	5.50900000	-1.46485200	1.24879000
H	2.62605500	-0.27327300	-2.49584300
H	5.03952800	-0.61518300	-2.93674700
C	1.79565900	-2.14802000	1.95796500
C	0.70030700	-2.02959700	1.07856500
C	1.90647300	-3.20664600	2.85779900
C	-0.25163000	-3.05877300	1.14671600
C	0.92898100	-4.19308600	2.91422900

H	2.76479700	-3.26130500	3.52304500
C	-0.15164900	-4.11752300	2.04403700
H	-1.09877800	-3.03784200	0.46633500
H	1.01679000	-5.01195100	3.62040200
H	-0.91785100	-4.88724500	2.06093400
N	2.75044000	-0.67607100	-0.48152600
H	2.77599400	2.00947900	-0.49040600
C	0.83486800	1.49419800	-1.28878400
H	1.23269900	1.28892800	-2.29206300
H	-0.12689500	1.98985400	-1.46432900
C	1.77544800	2.45961500	-0.55541200
H	1.44073000	2.58961800	0.48443800
C	1.96084200	3.87926300	-1.14523500
C	0.64408100	4.66237300	-1.10379700
H	-0.13761200	4.16859900	-1.68773300
H	0.77614100	5.67067800	-1.51169300
H	0.28401900	4.76263900	-0.07471800
C	2.46151700	3.79612900	-2.59056700
H	1.71505000	3.33990100	-3.24642100
H	3.37540100	3.19434100	-2.65443300
H	2.68838600	4.79297300	-2.98441700
C	3.00015600	4.61806900	-0.29358800
H	2.68552500	4.66275400	0.75510700
H	3.14757500	5.64568600	-0.64408500
H	3.96987000	4.10975900	-0.32867800
C	2.89370200	-1.09962700	1.91528100
H	3.66446400	-1.32410300	2.65533100
H	2.48948700	-0.11309400	2.17796300
C	-3.12551400	1.55564100	0.50796000
H	-3.45887000	2.08753500	1.40147700
C	-3.58679200	-0.64071600	-0.70798900
C	-4.18093900	0.50059800	0.16962500
C	-5.19723300	1.31792100	-0.63867400
C	-3.08810300	2.52932100	-0.70180700
H	-2.16306400	2.40292300	-1.26539500
H	-3.11708700	3.56436800	-0.35352800
C	-4.32610900	2.18581000	-1.55428700
H	-4.85276200	3.07207000	-1.91214700
H	-4.02274600	1.61474900	-2.43632500
H	-5.77223300	1.95047500	0.04727200
H	-5.90800600	0.69096800	-1.18355600
H	-4.01687000	-0.56823100	-1.70873100
C	-4.02431400	-1.96295900	-0.03392000
H	-4.25999700	-2.74419500	-0.75795900
H	-3.19707300	-2.32418100	0.58365100
C	-5.19877300	-1.57685600	0.86454500
H	-5.37991600	-2.30921900	1.65381300
H	-6.12069800	-1.48385300	0.28029000
C	-4.76727300	-0.21188600	1.39439900
H	-5.57480000	0.36384600	1.85341800
H	-3.98046400	-0.34771600	2.14601300

TS_3

Sum of Thermal Correction to Free Energies and Electronic Energy = -1820.113448

Electronic Energy (EE) = -1820.780782

Value of imaginary frequency = -1023.86 cm^{-1}

C	-0.97833500	-0.18623400	2.29302000
C	0.29911600	0.38654100	2.09726300
C	0.92923600	0.91338600	3.22435900
C	0.38236600	0.79890500	4.50086000
C	-0.83389700	0.15662800	4.66915300
C	-1.52387300	-0.33081000	3.56314700
H	1.87209300	1.43781800	3.10292100
H	0.90698800	1.21101900	5.35600200
H	-1.26471700	0.04471700	5.65779000
H	-2.48165500	-0.81387700	3.70820000
N	-1.66939300	-0.61476800	1.12704900
C	-0.94255100	-0.55050200	-0.00689400
Ir	0.84475700	0.17685800	0.01411600
N	-1.45210300	-0.99924000	-1.16674900
C	-0.57025100	-0.88030200	-2.28287300
C	-0.92095000	-1.30355300	-3.55725400
C	0.69668400	-0.32826100	-1.98374100
C	0.00281200	-1.17432000	-4.59271700
H	-1.89142600	-1.73813600	-3.76598300
C	1.59001500	-0.22937100	-3.04708700
C	1.25624400	-0.64086700	-4.33843300
H	-0.26415600	-1.50320300	-5.59101900
H	2.58976200	0.15521300	-2.86774200
H	1.98293500	-0.55521400	-5.13997800
C	-2.66973400	-1.79100800	-1.18134900
H	-3.10361800	-1.72882000	-2.18054400
C	-3.11085800	-0.91230600	1.18649900
C	-3.70873900	-1.24281800	-0.20727000
C	-4.69015200	-2.42213200	-0.09802300
C	-2.47349900	-3.26285900	-0.77473900
H	-1.68683400	-3.32033000	-0.01951300

H	-2.15504000	-3.87583200	-1.61951900
C	-3.82736000	-3.70014300	-0.17436700
H	-4.31810400	-4.46291700	-0.78142900
H	-3.67790200	-4.13468300	0.81617300
H	-5.37896500	-2.37930000	-0.94760700
H	-5.29773000	-2.37667400	0.80889000
H	-3.23079800	-1.77091700	1.85219700
C	-3.92287600	0.31620400	1.69088200
H	-4.34912300	0.14850600	2.68075400
H	-3.24709100	1.17009900	1.77291100
C	-4.99648400	0.59843700	0.63083700
H	-5.24804700	1.65928400	0.57631400
H	-5.91807600	0.05480200	0.86041800
C	-4.38221400	0.05623600	-0.65498500
H	-5.10958400	-0.11723100	-1.45204300
H	-3.62814400	0.75048200	-1.04019000
C	3.19242300	1.90644000	-0.96689300
C	4.46510000	2.41012600	-1.14450000
C	5.49519400	1.89034600	-0.37434800
C	5.19818800	0.89137500	0.53404500
C	3.88998500	0.43138000	0.66991400
N	2.89485200	0.94274100	-0.07933400
H	6.51090700	2.25234400	-0.48410000
H	2.36862100	2.27324200	-1.56256400
H	4.63509400	3.18661800	-1.87895700
H	5.97390100	0.45142500	1.14824000
C	3.56168100	-0.65335300	1.65295000
H	4.47866200	-0.94298000	2.16906500
H	2.88402700	-0.24591100	2.40538200
C	2.91436200	-1.86179500	1.01664200
C	3.52941100	-3.10325500	1.18133600
C	1.72196400	-1.72059800	0.28361500
C	2.97758500	-4.25426100	0.63696800
H	4.45290400	-3.16832500	1.75073800
C	1.20587000	-2.90202600	-0.26849700
C	1.80417200	-4.14480200	-0.09572800
H	3.46076500	-5.21531800	0.77716400
H	0.31300500	-2.85970000	-0.87970000
H	1.35529800	-5.02509800	-0.54598200
H	-1.47536700	2.56675000	0.96684900
C	-3.36765600	4.03867600	-0.19030200
C	-1.90069700	3.94584900	-0.62827800
H	-3.95872100	3.23013300	-0.63322800
H	-3.45971700	3.96722100	0.89891500
H	-3.81566500	4.98809900	-0.50205900
C	-1.12215900	5.11671700	-0.01941300
C	-1.83231900	4.01963000	-2.15781300
H	-0.07699500	5.11758900	-0.34177000
H	-1.55991800	6.07415200	-0.32109200
H	-1.13619900	5.07163300	1.07504900
H	-2.32495500	4.92588300	-2.52579100
H	-0.79938600	4.03730700	-2.51607400
H	-2.32782400	3.15710100	-2.61673100
C	-1.34625800	2.59662000	-0.12398400
C	0.09981400	2.26440200	-0.48408400
H	-1.99034700	1.80752400	-0.52233900
H	0.21090100	2.23047300	-1.56853900
H	0.77093500	3.04811400	-0.11340200
H	0.40136500	1.44377700	0.91274000

SIM$_2$

Sum of Thermal Correction to Free Energies and

Electronic Energy = -2110.859136

Electronic Energy (EE) = -2111.544821

C	-1.08265400	0.63728900	-2.05746300
C	0.30754900	0.49103200	-1.82988800
C	1.12969200	0.86987700	-2.89125000
C	0.63361700	1.36175100	-4.09832100
C	-0.73358900	1.49021700	-4.27774900
C	-1.59949900	1.12715900	-3.25072700
H	2.20586300	0.80894200	-2.77127500
H	1.31905300	1.64879600	-4.88890400
H	-1.13631600	1.87732700	-5.20714300
H	-2.66497800	1.25110900	-3.39382300
N	-1.94300700	0.33997500	-0.95207500
C	-1.29034100	0.02525100	0.17263600
Ir	0.68945000	-0.21014600	0.14837400
N	-1.95404100	-0.21486500	1.31591400
C	-1.14985700	-0.74367100	2.37306800
C	-1.67904200	-1.07495700	3.61351600
C	0.21127800	-0.95902800	2.05283800
C	-0.85415300	-1.66869800	4.56733100
H	-2.71625900	-0.88102300	3.85996700
C	0.99630900	-1.56038900	3.03049800
C	0.47583000	-1.92340500	4.27400800
H	-1.26325300	-1.92903600	5.53740600
H	2.04512700	-1.74095400	2.81877700
H	1.11594500	-2.39293300	5.01372100

C	-3.33806300	0.18847000	1.46644500
H	-3.78780700	-0.42320600	2.24917500
C	-3.40115800	0.29725800	-1.12048200
C	-4.14350600	-0.07993600	0.19296300
C	-5.34870100	0.85067500	0.39556800
C	-3.52309600	1.68782000	1.79763000
H	-2.62380700	2.24269500	1.52051200
H	-3.66794400	1.82980400	2.86995800
C	-4.74620100	2.14192000	0.97101700
H	-5.47224400	2.70007900	1.56406300
H	-4.42423700	2.80141800	0.16060900
H	-6.02846500	0.39259100	1.12251500
H	-5.91613400	1.01801100	-0.52330500
H	-3.71426500	1.29168700	-1.44981100
C	-3.81885800	-0.79066500	-2.15235500
H	-4.18105100	-0.35811400	-3.08561800
H	-2.93949200	-1.39134400	-2.39784700
C	-4.87686500	-1.66088100	-1.46363800
H	-4.87328300	-2.68644600	-1.83799000
H	-5.87936300	-1.25497300	-1.63032100
C	-4.51300300	-1.55476200	0.01164500
H	-5.31407400	-1.86018100	0.68948000
H	-3.63719300	-2.17855800	0.22902800
C	-0.60412300	-2.94044000	-0.27609700
C	-0.82842300	-4.23924100	-0.67841000
C	0.11436300	-4.85097300	-1.49195200
C	1.23055100	-4.12597400	-1.85999200
C	1.39465700	-2.80981700	-1.42982900
N	0.47430800	-2.22477400	-0.64119400
H	-0.01596700	-5.87331200	-1.82726600
H	-1.30991700	-2.44640000	0.37516400
H	-1.71998600	-4.75439300	-0.34545200
H	1.99509700	-4.56528200	-2.48824400
C	2.59622900	-2.02559900	-1.85986600
H	3.22788400	-2.67592000	-2.46749000
H	2.23915800	-1.22673700	-2.51280500
C	3.39523700	-1.43894500	-0.71681000
C	4.75260100	-1.75532600	-0.63379700
C	2.76772300	-0.59685100	0.22140000
C	5.54676500	-1.23967600	0.38067300
H	5.19487900	-2.41246500	-1.37853800
C	3.60447200	-0.11417600	1.24507700
C	4.95920500	-0.41183100	1.32891100
H	6.60217300	-1.48523300	0.43224100
H	3.18233900	0.52385500	2.01695400
H	5.55408000	-0.00134700	2.13946000
Si	1.17669600	2.26469100	0.26907600
H	0.94298500	0.81240500	1.31980600
C	-0.25417300	3.24257300	-0.51411900
C	-0.41337300	4.70310300	-0.08005700
H	-1.18272300	2.70892300	-0.28653900
H	-0.14997700	3.19417700	-1.60166600
H	-1.26962800	5.16344700	-0.58466300
H	-0.58542400	4.79332300	0.99639800
H	0.46497900	5.30518800	-0.32687300
C	2.83689500	2.61327700	-0.57425800
C	2.87851300	3.90914400	-1.38973200
H	3.11181300	1.76583900	-1.20196100
H	3.60130800	2.64157900	0.20928800
H	3.85635100	4.04386700	-1.86375200
H	2.12643100	3.90679400	-2.18473300
H	2.69694000	4.79015900	-0.76653300
C	1.33042400	2.91632300	2.06642200
C	2.09589300	4.23188000	2.24905000
H	1.81382300	2.14816500	2.68177100
H	0.31587100	3.00825500	2.47705100
H	2.12984800	4.52753400	3.30292900
H	3.13079300	4.13827700	1.90709600
H	1.64407400	5.05813100	1.69540600

IM_5

Sum of Thermal Correction to Free Energies and Electronic Energy = -2110.871658

Electronic Energy (EE) = -2111.559537

C	-1.02500600	0.90853800	2.01842900
C	0.35426000	0.73186400	1.78472800
C	1.21935400	1.00634600	2.84455700
C	0.74320400	1.46294300	4.07158700
C	-0.61698900	1.65654200	4.26361100
C	-1.51041700	1.37661600	3.23267400
H	2.28465000	0.85713100	2.70484300
H	1.44155900	1.66727000	4.87632400
H	-0.99257400	2.01755600	5.21439800
H	-2.57148500	1.51886600	3.39694500
N	-1.86515500	0.50572800	0.94620400
C	-1.19351200	-0.06581200	-0.08016400
Ir	0.80261900	0.14082900	-0.04146000
N	-1.94200300	-0.64456100	-1.05989300

C	-1.29634500	-1.28917100	-2.15520200
C	-0.18760100	-0.71858800	-2.78892900
C	-1.76428500	-2.51787800	-2.62203300
C	0.46643100	-1.38644800	-3.81482300
H	0.16669300	0.26731200	-2.50908000
C	-1.12215300	-3.16776100	-3.66798200
C	0.00438700	-2.61649300	-4.26220700
H	1.33664100	-0.92662300	-4.26878300
H	-1.49936500	-4.12750100	-4.00268000
H	0.51260500	-3.13604300	-5.06575800
C	-3.36774800	-0.90320900	-0.84938500
H	-3.80604200	-1.05524300	-1.83840300
C	-3.27642100	0.89175600	0.96328700
C	-4.07379600	0.29855500	-0.22379500
C	-5.37028000	-0.33973800	0.29395000
C	-3.70249100	-2.11092300	0.06355100
H	-2.84262300	-2.36666200	0.68441200
H	-3.93759600	-2.99403100	-0.53302700
C	-4.91296200	-1.66842400	0.91343000
H	-5.71187400	-2.41154100	0.92142100
H	-4.60808900	-1.51939200	1.95246300
H	-6.03815900	-0.52482900	-0.55464300
H	-5.90514800	0.30048600	0.99998700
H	-3.69707100	0.52707900	1.90255200
C	-3.43277900	2.43353700	0.84986900
H	-3.71109000	2.89218100	1.79961200
H	-2.46734800	2.85735000	0.56016000
C	-4.47013500	2.67410500	-0.25286300
H	-4.32497500	3.63330200	-0.75456700
H	-5.48250500	2.67268900	0.16291400
C	-4.28699000	1.47544000	-1.17950900
H	-5.12919600	1.30624700	-1.85512500
H	-3.39045900	1.61126100	-1.79544100
C	-0.48908800	2.65896300	-1.57846200
C	-0.74952900	3.94810400	-1.99935800
C	0.15165600	4.94424800	-1.64982500
C	1.25915800	4.59955300	-0.89687200
C	1.45454700	3.27644700	-0.50026100
N	0.58318200	2.31652500	-0.85052800
H	-0.00661000	5.97127100	-1.95835900
H	-1.17164000	1.85631700	-1.83002600
H	-1.63523100	4.15704200	-2.58582400
H	1.98253300	5.34945900	-0.60157300
C	2.63141400	2.90780500	0.36291100
H	3.26027200	3.79303400	0.47882200
H	2.23725500	2.66550200	1.35345100
C	3.44976400	1.75027300	-0.16687900
C	4.76658600	2.00067600	-0.55379700
C	2.86872500	0.46863600	-0.28948100
C	5.55770100	0.99570600	-1.09612500
H	5.17895200	2.99952500	-0.43459700
C	3.69955100	-0.51266400	-0.86543800
C	5.01046900	-0.26896200	-1.26250000
H	6.58136400	1.20204700	-1.39058800
H	3.31064400	-1.51698300	-1.01085500
H	5.60356300	-1.06896100	-1.69552900
Si	1.08349500	-2.01926900	0.89987100
C	-0.29687400	-2.45214800	2.15860500
C	-0.66096700	-3.93095100	2.32184000
H	-1.19726700	-1.89513600	1.88127000
H	-0.00185500	-2.03317800	3.12878500
H	-1.48044200	-4.07032000	3.03695800
H	-0.98214400	-4.37291100	1.37256900
H	0.18463600	-4.52324400	2.68212800
C	2.72941700	-2.23195100	1.85114400
C	2.78675400	-3.33607800	2.91227500
H	2.95330400	-1.26996800	2.32418600
H	3.53570600	-2.38116700	1.12559800
H	3.76322600	-3.36312400	3.40948000
H	2.03378600	-3.18451900	3.69195200
H	2.61706900	-4.32788200	2.48313400
C	1.02486600	-3.34083400	-0.48647100
C	1.73512700	-4.67271600	-0.22573600
H	1.43270800	-2.89430800	-1.40113300
H	-0.03157500	-3.52604100	-0.71416100
H	1.65975300	-5.34523700	-1.08825200
H	2.80060900	-4.52416300	-0.02345000
H	1.31259300	-5.20005600	0.63419300
H	-2.61252100	-2.99718000	-2.15310400

TS_4

Sum of Thermal Correction to Free Energies and Electronic Energy = -2110.824656

Electronic Energy (EE) = -2111.510405

Value of imaginary frequency = -113.59 cm^{-1}

C	-1.58415200	2.26409800	0.59378500
C	-0.21154600	2.27132200	0.28073100
C	0.47543800	3.46463700	0.56157600

C	-0.16443400	4.57008400	1.11493600	C	1.94868100	2.34047600	-2.15664500
C	-1.51915500	4.51702900	1.41986700	C	2.85287800	3.18564000	-2.77111100
C	-2.23455300	3.35201200	1.16166800	C	4.13849800	3.27071400	-2.25695400
H	1.53991700	3.53458400	0.36036600	C	4.47020200	2.48310600	-1.16718500
H	0.40085200	5.47557400	1.31336400	C	3.51535200	1.63840400	-0.61340800
H	-2.01999800	5.37181400	1.86087900	N	2.26146600	1.58208200	-1.09339800
H	-3.28840600	3.30712200	1.41262400	H	4.87136100	3.93502400	-2.70003700
N	-2.22350300	1.04060300	0.29301800	H	0.92448000	2.26970800	-2.49807600
C	-1.33770400	0.06898400	-0.12352300	H	2.54193800	3.77239200	-3.62555700
Ir	0.55145000	0.50341900	-0.20755500	H	5.46544300	2.50926300	-0.74063000
N	-1.98011600	-1.08715000	-0.52758600	C	3.84397800	0.69603000	0.51193700
C	-1.35975600	-2.01883600	-1.38516600	H	4.90044300	0.78288000	0.77030800
C	-0.66003300	-1.58331000	-2.51175100	H	3.25750400	0.97391700	1.39329000
C	-1.46718200	-3.38975200	-1.13808000	C	3.50433400	-0.69692300	0.03970700
C	-0.05338600	-2.50318300	-3.35580400	C	4.47129700	-1.43847100	-0.61833100
H	-0.60003300	-0.52146600	-2.71838600	C	2.17386200	-1.16465900	0.14981600
C	-0.87385300	-4.30430800	-1.99739300	C	4.14768500	-2.65658600	-1.21433500
C	-0.15733800	-3.86595600	-3.10590800	H	5.48627900	-1.05775600	-0.68521800
H	0.49840200	-2.14905700	-4.21924600	C	1.88019700	-2.38503700	-0.47049200
H	-0.95902000	-5.36475100	-1.78759600	C	2.84541300	-3.11985400	-1.15658300
H	0.31302000	-4.58146900	-3.77063600	H	4.91383400	-3.22971700	-1.72534900
C	-3.34059100	-1.36367700	-0.06984800	H	0.88101900	-2.78909800	-0.40047500
H	-3.66970800	-2.26012500	-0.59624300	H	2.57065200	-4.05685000	-1.62813900
C	-3.62137200	1.13544700	-0.15562900	Si	1.18538600	-0.88248500	1.94150700
C	-4.29165000	-0.23243000	-0.44833900	C	0.75210300	0.62136000	3.06536500
C	-5.47658500	-0.48358900	0.49084700	C	-0.70875800	0.70466500	3.51693700
C	-3.50721500	-1.56480900	1.45636000	H	1.01733100	1.54775200	2.55189200
H	-2.66258400	-1.13317300	1.99035700	H	1.39359100	0.56988000	3.95218900
H	-3.53153000	-2.62962500	1.69996500	H	-0.90794500	1.64744200	4.03670500
C	-4.82096300	-0.84539000	1.83121900	H	-1.39583100	0.65234900	2.66990500
H	-5.47461400	-1.45550100	2.45717700	H	-0.96154200	-0.10804000	4.20601500
H	-4.59438900	0.06350000	2.39615400	C	2.71255100	-1.59014200	2.89273700
H	-6.05552300	-1.33331400	0.11111700	C	2.48746400	-1.81353600	4.39476500
H	-6.15472900	0.37146800	0.55902100	H	3.58441800	-0.94004000	2.75635900
H	-4.17265100	1.61985600	0.65193900	H	2.98071700	-2.53730600	2.41129700
C	-3.76024600	1.96423800	-1.45461500	H	3.22513800	-2.50708300	4.81333800
H	-3.92324300	3.02436400	-1.25666000	H	2.57068700	-0.88157600	4.96039600
H	-2.82808600	1.87765900	-2.02203800	H	1.49713900	-2.22766300	4.61297100
C	-4.89892000	1.29423100	-2.22182300	C	-0.10054400	-2.27913600	2.12101200
H	-4.89173500	1.53803400	-3.28651700	C	0.39945600	-3.71946100	2.28502200
H	-5.86967500	1.60336700	-1.81856300	H	-0.77868200	-2.23102800	1.26971200
C	-4.65513500	-0.18643700	-1.93832400	H	-0.71710900	-2.02287400	2.99018500
H	-5.50566100	-0.83151300	-2.17260100	H	-0.44221300	-4.41877300	2.34701700
H	-3.80047900	-0.53023700	-2.53293900	H	1.02448300	-4.03908200	1.44748100

H	0.99182200	-3.85042800	3.19386900
H	-1.99300900	-3.73957100	-0.25680400

IM$_6$

Sum of Thermal Correction to Free Energies and

Electronic Energy = -2110.862522

Electronic Energy (EE) = -2111.544051

C	-1.26662400	0.11504600	-2.39535900
C	-0.01549000	-0.54574500	-2.27244500
C	0.84378300	-0.45600600	-3.37552900
C	0.49374200	0.25267900	-4.52586300
C	-0.73730700	0.88539800	-4.61035500
C	-1.62831400	0.81216400	-3.53709800
H	1.81239500	-0.94580700	-3.33564300
H	1.18787900	0.30306600	-5.35928900
H	-1.01688000	1.43289700	-5.50368900
H	-2.59119600	1.30463900	-3.61388100
N	-2.06482500	0.02720300	-1.23347100
C	-1.47743200	-0.71988100	-0.24495500
Ir	0.27587800	-1.39420700	-0.54847900
N	-2.20653000	-0.77751300	0.93010500
C	-1.72007800	-1.58382400	1.98398000
C	-1.28563800	-2.89106300	1.72560500
C	-1.68598600	-1.12037600	3.30145700
C	-0.79668200	-3.68930800	2.75085500
H	-1.35577700	-3.28019600	0.71581800
C	-1.23006600	-1.94016000	4.32549700
C	-0.77092100	-3.22334400	4.05977700
H	-0.46303000	-4.69564100	2.52228800
H	-1.21458300	-1.55757900	5.34021600
H	-0.40675800	-3.85451900	4.86219900
C	-3.09617100	0.33310600	1.25546800
H	-3.66560300	0.03117300	2.13608000
C	-3.47333300	0.38467400	-1.27506300
C	-4.10892800	0.59450600	0.13162000
C	-4.44762300	2.07625400	0.34732400
C	-2.38040700	1.68730200	1.52906000
H	-1.31106100	1.60772500	1.32733700
H	-2.49129100	1.95977100	2.58269900
C	-3.08270400	2.71212800	0.62328100
H	-3.15587400	3.70375200	1.07457200
H	-2.52881900	2.81930800	-0.31399600
H	-5.09442300	2.17720700	1.22710700
H	-4.97380600	2.51768400	-0.50330900
H	-3.54110600	1.33246100	-1.81432800
C	-4.34442400	-0.67058100	-1.98630900
H	-4.37105100	-0.52596500	-3.06784100
H	-3.91838700	-1.66040700	-1.79441000
C	-5.70508600	-0.54747900	-1.30462000
H	-6.34496700	-1.41678000	-1.47056900
H	-6.24132300	0.33388900	-1.67433600
C	-5.31521600	-0.35814700	0.16102100
H	-6.12335000	0.02438000	0.78998900
H	-4.99906900	-1.32403100	0.57238300
C	2.49732000	-3.27567100	-1.35532000
C	3.74909100	-3.81160000	-1.59148900
C	4.86418200	-3.02710200	-1.33677500
C	4.67420200	-1.73882100	-0.86334300
C	3.38824500	-1.25508400	-0.64937400
N	2.30900300	-2.02874300	-0.89040300
H	5.86404400	-3.40926900	-1.50610300
H	1.59481700	-3.84307700	-1.54838400
H	3.83739000	-4.82216200	-1.96890100
H	5.51951600	-1.09465200	-0.65477400
C	3.15936000	0.15008200	-0.16417700
H	4.12375200	0.66603000	-0.15259900
H	2.52942400	0.65025100	-0.90512500
C	2.51222200	0.27006000	1.20761200
C	2.61168900	-0.79332300	2.10560100
C	1.84149500	1.45091500	1.58587800
C	2.03208700	-0.73034800	3.36528400
H	3.13551800	-1.69742200	1.81272600
C	1.26527900	1.48268800	2.86154600
C	1.34828600	0.41298200	3.74390200
H	2.10320400	-1.57801100	4.03738800
H	0.72308700	2.36556700	3.18224500
H	0.87696800	0.47390700	4.71836600
Si	1.65953900	2.99615600	0.48730000
C	0.49837100	2.65849400	-0.96114700
C	-0.20188900	3.88481100	-1.55782300
H	-0.25019600	1.93505800	-0.62651400
H	1.04613500	2.13604700	-1.75291100
H	-0.85442500	3.58887400	-2.38524200
H	-0.81982500	4.40139100	-0.81726100
H	0.51027000	4.61621900	-1.95202300
C	3.36334000	3.56155500	-0.11257700
C	3.36317100	4.90870400	-0.84601500
H	3.78585600	2.79968600	-0.77495100

H	4.03222400	3.60755100	0.75588200
H	4.37909700	5.21930400	-1.10989600
H	2.79044900	4.85398500	-1.77626300
H	2.92640700	5.70765600	-0.23879600
C	0.94138300	4.39729900	1.53527000
C	1.85955800	4.93963400	2.63696800
H	-0.02162600	4.08200000	1.95611200
H	0.69459000	5.21136900	0.84352000
H	1.37379900	5.73642900	3.20916900
H	2.15852000	4.16158300	3.34530800
H	2.77899100	5.35744100	2.21548700
H	-1.98853300	-0.10736900	3.53303300

IM_7

Sum of Thermal Correction to Free Energies and

Electronic Energy = -1584.381768

Electronic Energy (EE) = -1584.892140

Ir	0.83179900	-0.23865000	-0.56700800
N	-1.78791800	-1.28844700	-0.28691700
N	-1.82848000	0.99136000	-0.65107400
C	-1.06178500	-0.13935400	-0.50295800
C	-3.11959000	-1.29406800	0.31719600
C	-3.99106400	-0.05953600	-0.06506100
C	-3.23608500	0.87500900	-1.01479200
C	-3.07213500	-1.31759300	1.86161200
C	-4.32282100	-0.55290600	2.28794100
C	-4.35913800	0.59064100	1.27673200
C	-5.18783500	-0.48400500	-0.92504500
C	-4.56730200	-0.75197300	-2.30110100
C	-3.48098700	0.33136700	-2.44994300
C	-0.94117900	-2.40436900	-0.07052700
C	0.44557800	-2.09993200	-0.13204800
C	1.31986900	-3.15657900	0.15698800
C	0.85857100	-4.44228700	0.44279200
C	-0.50142800	-4.70995000	0.45585200
C	-1.40945400	-3.67920600	0.20577200
C	-1.19967500	2.26130100	-0.72716700
C	-1.70208700	3.31886900	0.03319100
C	-1.08523300	4.56118400	0.00576900
C	0.05376000	4.76886800	-0.76684300
C	0.55652500	3.72296900	-1.52902900
C	-0.07537600	2.48414500	-1.52564200
H	-3.62982400	-2.18934200	-0.04574200
H	-3.67398100	1.87059800	-0.92702500
H	-1.48568700	5.36843000	0.60905200
H	1.56966400	-5.23257100	0.66409300
H	-0.86667200	-5.70726400	0.67560800
H	-2.47292100	-3.88832600	0.24284500
H	-2.56502300	3.15525500	0.66846500
H	-5.31624600	1.11678200	1.22900700
H	-3.58529200	1.31936800	1.54638300
H	-4.27959900	-0.21089600	3.32449300
H	-5.21397700	-1.18212600	2.18356500
H	-3.01347400	-2.33089500	2.26146200
H	-2.17477600	-0.78158000	2.18779400
H	-5.72172800	-1.34467700	-0.51292500
H	-5.89922400	0.34823800	-0.98819200
H	-5.30552500	-0.72980800	-3.10524300
H	-4.10320100	-1.74252500	-2.31221600
H	-2.55904500	-0.07513800	-2.86739600
H	-3.80759800	1.14264600	-3.10455900
H	2.38968500	-2.97305000	0.17948600
H	1.43461600	3.86993900	-2.14841300
H	0.53919400	5.73791100	-0.77619100
H	0.29475600	1.67024100	-2.15292700
C	5.75185500	-0.59661500	-1.02510700
C	5.21816700	0.40661700	-0.23291000
C	3.83911600	0.54144500	-0.10751500
C	3.52324600	-1.27840800	-1.50614700
C	4.88249300	-1.45038500	-1.68660700
H	6.82536700	-0.70646900	-1.12578200
H	5.86473000	1.09947600	0.29160100
H	2.80563700	-1.93050700	-1.98691000
H	5.24063900	-2.24701300	-2.32575800
C	2.27783700	1.34208100	1.77326300
C	1.19775900	2.18701000	2.02619800
C	2.43272900	0.19543300	2.55070300
C	0.27472600	1.87736800	3.01624100
C	1.50794300	-0.11813000	3.53667100
H	3.25815600	-0.48157100	2.35645300
C	0.42294400	0.71916000	3.76954900
H	-0.57216300	2.53388600	3.18421200
H	1.62464300	-1.02992200	4.11138600
H	-0.30709500	0.46509400	4.53015600
N	2.99879700	-0.31733400	-0.72465500
H	1.05637100	3.07439400	1.41651500
C	3.26095500	1.69480500	0.67633800
H	2.76474100	2.36815600	-0.03281900

H	4.09411500	2.26238100	1.10149700

TS_5

Sum of Thermal Correction to Free Energies and Electronic Energy = -1584.362894

Electronic Energy (EE) = -1584.870868

Value of imaginary frequency = -634.22 cm^{-1}

Ir	-0.87285900	0.32806500	-0.15051000
N	1.86282900	1.19704500	-0.02546900
N	1.74431600	-1.04109600	-0.54356800
C	1.07080000	0.09198000	-0.21139700
C	3.28016300	1.18512300	0.35555400
C	3.95897800	-0.18526900	0.11892500
C	3.16456700	-1.01280700	-0.87620300
C	3.46523200	1.48288800	1.87218100
C	4.39696700	0.38999400	2.40934900
C	4.08677200	-0.80449400	1.51222800
C	5.29259200	-0.00875300	-0.62041800
C	4.90558500	0.20577900	-2.09874300
C	3.50124800	-0.42280300	-2.26190700
C	1.14680500	2.41688700	0.05396300
C	-0.25472800	2.30435900	-0.08280800
C	-0.97549700	3.48985800	0.08673000
C	-0.36150700	4.72330700	0.30914700
C	1.01926300	4.79629000	0.37685200
C	1.78262700	3.63651000	0.26400200
C	1.05451800	-2.20828100	-1.00847900
C	1.06074800	-3.36264400	-0.23776400
C	0.40681900	-4.50132000	-0.69315300
C	-0.23747200	-4.48971100	-1.92385800
C	-0.21942900	-3.33879400	-2.70574800
C	0.42857800	-2.19901100	-2.25175500
H	3.77863800	1.94191100	-0.25450100
H	3.52009400	-2.04516900	-0.82245800
H	0.39489600	-5.39480600	-0.07955600
H	-0.96349200	5.61763800	0.43397700
H	1.51505700	5.74733800	0.53974500
H	2.85864700	3.70920000	0.35604600
H	1.55335300	-3.35712400	0.72697600
H	4.84301100	-1.59315000	1.54517100
H	3.12596400	-1.24660600	1.80262600
H	4.23098800	0.18880400	3.46962100
H	5.44528500	0.68325700	2.29089600
H	3.84599000	2.48825900	2.05687300
H	2.48717900	1.41591900	2.35595200
H	5.89518600	0.80884500	-0.21711200
H	5.87679000	-0.92857500	-0.51084500
H	5.64102700	-0.24401800	-2.76799400
H	4.87053700	1.27094700	-2.33837600
H	2.76295000	0.33952000	-2.52000700
H	3.46450200	-1.18977200	-3.03722100
H	-2.06052700	3.46487100	0.07107100
H	-0.71904100	-3.32589400	-3.66778300
H	-0.75146100	-5.37730100	-2.27554400
H	0.43009300	-1.28729400	-2.83668400
C	-5.60641900	1.37151200	-1.20986100
C	-5.31908900	0.25971400	-0.43980500
C	-3.99740700	-0.07304500	-0.15104200
C	-3.26394600	1.75904300	-1.34480400
C	-4.54754700	2.12117700	-1.70017400
H	-6.63229000	1.63580400	-1.43873500
H	-6.11289000	-0.37746900	-0.06957100
H	-2.41415400	2.32265400	-1.70129600
H	-4.70198800	2.98168600	-2.33812300
C	-2.62274600	-1.49635200	1.52930300
C	-1.29103500	-1.14498600	1.20621800
C	-2.93205600	-2.02544800	2.77938700
C	-0.29720400	-1.50821500	2.14307900
C	-1.94453600	-2.29372600	3.71712200
H	-3.96883000	-2.25280400	3.01147200
C	-0.61779600	-2.05171200	3.37550700
H	0.74220700	-1.32010500	1.90736600
H	-2.20298800	-2.70766000	4.68515800
H	0.17666200	-2.27746600	4.08005600
N	-2.97637900	0.70739400	-0.55318200
H	-1.12383300	-1.34664800	-0.18453000
C	-3.69792900	-1.40378900	0.48333200
H	-3.39828400	-2.05436700	-0.35295500
H	-4.62998900	-1.81439100	0.87535800

4a

Sum of Thermal Correction to Free Energies and Electronic Energy = -1044.990564

Electronic Energy (EE) = -1045.303886

C	-3.33393100	-1.45468500	-1.42664600
C	-4.61304900	-1.51354100	-0.88715300
C	-4.79404900	-1.06187600	0.41147000
C	-3.69763700	-0.57216300	1.10787400

C	-2.45287700	-0.54791700	0.48207500	C	2.66058600	-2.00698100	2.05335600
N	-2.27820600	-0.98507100	-0.76835600	H	1.34334500	-0.33927700	2.43652600
H	-5.77325200	-1.08864000	0.87654000	H	3.00098900	0.12946800	2.19029800
H	-3.14820300	-1.80134800	-2.43957000	H	2.85583800	-2.20424000	3.11219200
H	-5.43742200	-1.90329400	-1.47166000	H	1.88842800	-2.71096100	1.72758000
H	-3.80062100	-0.21183500	2.12502400	H	3.57399500	-2.25110500	1.50358800
C	-1.22510500	-0.01160200	1.18204600	C	3.48872300	0.52547000	-0.74832700
H	-1.46846000	0.19944700	2.22767500	C	4.73047500	-0.31944700	-0.43190700
H	-0.47522800	-0.80279200	1.18818800	H	3.66861200	1.54373000	-0.38380200
C	-0.68434800	1.24840100	0.52611100	H	3.36311900	0.61272400	-1.83455900
C	-1.53487800	2.35462900	0.48093800	H	5.62280500	0.09984700	-0.90726500
C	0.60772400	1.33321000	-0.02597600	H	4.92432800	-0.35194000	0.64444000
C	-1.14485900	3.54315600	-0.11618700	H	4.63288100	-1.35078500	-0.77876000
H	-2.52803000	2.27680200	0.91416600	C	1.19042600	-1.55861600	-0.96435000
C	0.97281800	2.54470000	-0.63305300	C	2.22401000	-2.52904000	-1.54726500
C	0.11750100	3.63680400	-0.68564300	H	0.57622800	-1.14677800	-1.77252500
H	-1.82478300	4.38780900	-0.14119000	H	0.48298700	-2.11246700	-0.33770300
H	1.95388400	2.64454500	-1.08475800	H	1.73380600	-3.33796000	-2.09832000
H	0.43696400	4.55491500	-1.16656500	H	2.89895500	-2.02496300	-2.24527000
Si	1.87057200	-0.08987300	0.01830600	H	2.83894100	-2.99217900	-0.77009700
C	2.22502500	-0.55467100	1.82397800				

8. X-ray structural characterization of 2x, 6f, 1bB and 3Db

8.1 X-ray ellipsoid plots of 2x

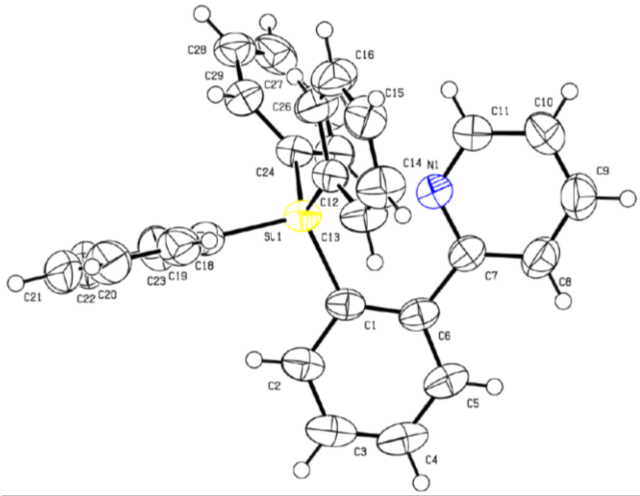


Table S3: Crystal data and structure refinement for 2x.

Identification code	**2x**
Empirical formula	$C_{29}H_{23}NSi$
Formula weight	413.57
Temperature/K	290.73(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.84377(18)
b/Å	16.7777(3)
c/Å	13.6685(2)
α/°	90
β/°	93.7231(17)
γ/°	90
Volume/Å^3	2252.67(7)
Z	4
ρ_{calc}g/cm^3	1.219
μ/mm^{-1}	1.024
F(000)	872.0
Crystal size/mm^3	0.17 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.436 to 133.164
Index ranges	$-11 \le h \le 11, -19 \le k \le 19, -9 \le l \le 16$
Reflections collected	8193
Independent reflections	3972 [R_{int} = 0.0211, R_{sigma} = 0.0264]
Data/restraints/parameters	3972/0/280
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1168

Final R indexes [all data] R_1 = 0.0495, wR_2 = 0.1235
Largest diff. peak/hole / e $Å^{-3}$ 0.26/-0.25

Table S4: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2x. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	3518.3(4)	2209.3(3)	4825.3(3)	43.32(15)
N1	1420.7(14)	1444.1(10)	5326.5(10)	54.5(4)
C1	2702.3(16)	1746.4(10)	3660.3(11)	44.7(4)
C2	3342.5(19)	1837.5(11)	2783.0(12)	53.8(4)
C3	2792(2)	1515.6(13)	1901.5(13)	64.2(5)
C4	1606(2)	1088.3(13)	1883.0(13)	66.1(5)
C5	946(2)	987.6(12)	2728.1(13)	58.6(5)
C6	1461.5(16)	1319.3(10)	3612.7(12)	46.2(4)
C7	714.4(16)	1228.1(10)	4510.0(12)	46.6(4)
C8	-628.7(19)	961.7(13)	4539.2(15)	64.6(5)
C9	-1210(2)	919.6(14)	5422.2(17)	72.3(6)
C10	-468(2)	1139.2(14)	6259.4(16)	68.8(5)
C11	839(2)	1396.4(14)	6179.8(14)	66.4(5)
C12	2462.3(17)	3000.1(10)	5387.0(11)	46.1(4)
C13	1372(2)	3359.3(12)	4862.3(14)	61.2(5)
C14	639(2)	3968.2(13)	5249.3(16)	71.1(6)
C15	972(2)	4233.2(13)	6185.8(15)	66.4(5)
C16	2013(2)	3883.3(15)	6725.9(15)	71.5(6)
C17	2757.1(19)	3276.4(13)	6337.0(13)	62.2(5)
C18	5010.5(18)	2821.1(11)	4387.8(12)	51.0(4)
C19	4917(2)	3640.9(12)	4227.9(14)	63.7(5)
C20	6006(3)	4078.0(15)	3917.3(16)	81.0(7)
C21	7212(3)	3703.4(17)	3748.4(17)	84.2(7)
C22	7337(2)	2899.2(17)	3896.0(18)	80.7(7)
C23	6249(2)	2467.4(14)	4215.8(16)	66.6(5)
C24	4411.7(16)	1509.4(9)	5733.3(11)	43.3(3)
C25	4189.4(19)	693.6(10)	5761.0(13)	54.6(4)
C26	4915(2)	205.5(12)	6426.3(15)	68.8(5)
C27	5874(2)	524.3(14)	7086.3(14)	66.8(6)
C28	6106.0(19)	1325.1(13)	7083.7(13)	61.1(5)
C29	5402.1(17)	1812.1(11)	6412.0(12)	51.1(4)

Table S5: Anisotropic Displacement Parameters ($Å^2×10^3$) for 2x. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	51.0(3)	42.3(3)	36.3(2)	0.98(16)	-0.34(17)	2.43(17)
N1	50.4(8)	69.1(10)	43.6(7)	-3.9(7)	0.4(6)	-7.8(7)
C1	51.9(9)	44.6(9)	37.1(8)	1.1(6)	0.4(6)	10.4(7)
C2	60.6(10)	60.5(11)	40.5(8)	2.8(7)	4.4(7)	13.4(8)
C3	80.4(13)	76.3(13)	35.9(9)	0.2(8)	3.6(8)	26.8(11)
C4	78.7(13)	74.4(13)	42.9(9)	-11.2(9)	-14.2(9)	20.9(11)
C5	62.4(10)	62.2(11)	48.9(10)	-6.7(8)	-13.3(8)	9.6(9)
C6	51.0(9)	44.9(9)	41.6(8)	-1.7(7)	-6.2(6)	10.7(7)
C7	46.2(8)	43.8(8)	48.7(9)	-0.8(7)	-4.6(7)	4.8(7)
C8	48.0(9)	78.3(13)	66.2(12)	-8.3(10)	-6.9(8)	-3.2(9)
C9	49.9(10)	84.9(15)	82.9(14)	-5.9(12)	10.6(10)	-8.5(10)
C10	64.1(11)	78.9(14)	65.2(12)	0.4(10)	18.3(9)	-3.2(10)
C11	63.2(11)	88.9(15)	47.2(10)	-4.9(10)	4.7(8)	-13.5(10)
C12	50.6(8)	47.6(9)	40.1(8)	0.3(7)	3.5(6)	0.0(7)
C13	73.9(12)	63.1(11)	45.3(9)	-1.8(8)	-6.0(8)	14.3(9)
C14	73.3(13)	70.2(13)	68.7(12)	1.0(10)	-5.1(10)	22.6(10)
C15	62.4(11)	63.9(12)	73.9(13)	-16.2(10)	13.5(9)	7.5(9)
C16	67.2(12)	91.3(16)	55.6(11)	-27.5(11)	0.5(9)	7.2(11)
C17	56.8(10)	79.0(13)	49.5(10)	-14.1(9)	-6.1(8)	10.5(9)
C18	58.1(10)	52.9(10)	41.5(8)	4.3(7)	-0.7(7)	-4.4(7)
C19	79.4(13)	55.7(11)	55.2(10)	11.2(8)	-1.5(9)	-5.1(9)
C20	102.9(18)	67.5(14)	71.0(14)	20.5(11)	-6.2(12)	-24.8(13)
C21	79.1(15)	102.4(19)	69.5(14)	22.0(13)	-7.3(11)	-38.7(14)
C22	57.5(12)	103.7(19)	81.2(15)	13.9(13)	7.0(10)	-9.8(11)
C23	59.0(11)	67.7(12)	73.9(13)	8.8(10)	9.5(9)	-1.8(9)
C24	51.4(9)	41.9(8)	36.7(7)	0.7(6)	3.7(6)	2.5(7)
C25	64.4(10)	44.4(9)	55.0(10)	-0.6(7)	3.5(8)	-1.6(8)
C26	84.2(14)	47.1(10)	76.9(13)	18.1(9)	17.5(11)	9.2(9)
C27	63.8(11)	81.4(14)	56.1(11)	29.1(10)	10.0(9)	18.1(10)
C28	54.6(10)	85.3(14)	42.8(9)	4.6(9)	-2.1(7)	10.0(9)
C29	52.7(9)	50.1(10)	49.9(9)	-1.3(7)	-2.4(7)	2.0(7)

Table S6: Bond Lengths for 2x.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C1	1.9020(16)	C12	C17	1.391(2)
Si1	C12	1.8799(17)	C13	C14	1.376(3)

Si1	C18	1.9192(18)	C14	C15	1.374(3)
Si1	C24	1.8845(16)	C15	C16	1.357(3)
N1	C7	1.326(2)	C16	C17	1.381(3)
N1	C11	1.335(2)	C18	C19	1.395(3)
C1	C2	1.399(2)	C18	C23	1.389(3)
C1	C6	1.414(2)	C19	C20	1.388(3)
C2	C3	1.397(3)	C20	C21	1.376(4)
C3	C4	1.369(3)	C21	C22	1.369(4)
C4	C5	1.372(3)	C22	C23	1.387(3)
C5	C6	1.396(2)	C24	C25	1.387(2)
C6	C7	1.478(2)	C24	C29	1.397(2)
C7	C8	1.399(2)	C25	C26	1.387(3)
C8	C9	1.371(3)	C26	C27	1.371(3)
C9	C10	1.368(3)	C27	C28	1.363(3)
C10	C11	1.368(3)	C28	C29	1.381(2)
C12	C13	1.389(2)			

Table S7: Bond Angles for 2x.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Si1	C18	104.34(7)	C13	C12	Si1	121.63(13)
C12	Si1	C1	114.55(7)	C13	C12	C17	116.40(16)
C12	Si1	C18	101.80(8)	C17	C12	Si1	121.93(13)
C12	Si1	C24	114.68(7)	C14	C13	C12	122.03(17)
C24	Si1	C1	116.78(7)	C15	C14	C13	119.94(18)
C24	Si1	C18	101.81(7)	C16	C15	C14	119.50(18)
C7	N1	C11	119.19(16)	C15	C16	C17	120.69(18)
C2	C1	Si1	118.93(13)	C16	C17	C12	121.42(17)
C2	C1	C6	116.86(15)	C19	C18	Si1	122.16(15)
C6	C1	Si1	124.20(12)	C23	C18	Si1	121.46(14)
C3	C2	C1	121.73(18)	C23	C18	C19	116.39(18)
C4	C3	C2	120.06(18)	C20	C19	C18	121.6(2)
C3	C4	C5	119.94(17)	C21	C20	C19	120.1(2)
C4	C5	C6	120.96(19)	C22	C21	C20	119.7(2)
C1	C6	C7	119.28(14)	C21	C22	C23	119.8(2)
C5	C6	C1	120.41(16)	C22	C23	C18	122.3(2)
C5	C6	C7	120.31(16)	C25	C24	Si1	124.41(13)
N1	C7	C6	114.07(14)	C25	C24	C29	116.44(15)
N1	C7	C8	120.54(17)	C29	C24	Si1	119.11(12)
C8	C7	C6	125.36(16)	C26	C25	C24	121.67(18)

C9	C8	C7	119.42(18)	C27	C26	C25	120.29(19)
C10	C9	C8	119.47(18)	C28	C27	C26	119.42(17)
C9	C10	C11	118.19(19)	C27	C28	C29	120.53(18)
N1	C11	C10	123.19(18)	C28	C29	C24	121.64(17)

Table S8: Torsion Angles for 2x.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Si1	C1	C2	C3	-179.67(14)	C9	C10	C11	N1	0.1(4)
Si1	C1	C6	C5	-178.96(12)	C11	N1	C7	C6	179.14(17)
Si1	C1	C6	C7	1.1(2)	C11	N1	C7	C8	0.7(3)
Si1	C12	C13	C14	-176.45(17)	C12	Si1	C24	C25	118.43(15)
Si1	C12	C17	C16	176.96(17)	C12	Si1	C24	C29	-63.80(15)
Si1	C18	C19	C20	179.59(15)	C12	C13	C14	C15	-0.6(4)
Si1	C18	C23	C22	179.75(17)	C13	C12	C17	C16	-0.9(3)
Si1	C24	C25	C26	177.67(14)	C13	C14	C15	C16	-0.8(4)
Si1	C24	C29	C28	-178.89(13)	C14	C15	C16	C17	1.3(4)
N1	C7	C8	C9	-0.5(3)	C15	C16	C17	C12	-0.5(4)
C1	Si1	C12	C13	-16.35(18)	C17	C12	C13	C14	1.4(3)
C1	Si1	C12	C17	165.88(15)	C18	Si1	C12	C13	95.59(16)
C1	Si1	C24	C25	-19.66(17)	C18	Si1	C12	C17	-82.18(17)
C1	Si1	C24	C29	158.11(12)	C18	Si1	C24	C25	-132.54(15)
C1	C2	C3	C4	-1.0(3)	C18	Si1	C24	C29	45.22(14)
C1	C6	C7	N1	-11.4(2)	C18	C19	C20	C21	0.7(3)
C1	C6	C7	C8	166.95(17)	C19	C18	C23	C22	-0.4(3)
C2	C1	C6	C5	2.0(2)	C19	C20	C21	C22	-0.5(4)
C2	C1	C6	C7	-177.89(14)	C20	C21	C22	C23	-0.1(4)
C2	C3	C4	C5	1.1(3)	C21	C22	C23	C18	0.6(4)
C3	C4	C5	C6	0.3(3)	C23	C18	C19	C20	-0.2(3)
C4	C5	C6	C1	-2.0(3)	C24	Si1	C12	C13	-155.39(15)
C4	C5	C6	C7	177.97(16)	C24	Si1	C12	C17	26.85(19)
C5	C6	C7	N1	168.66(16)	C24	C25	C26	C27	0.6(3)
C5	C6	C7	C8	-13.0(3)	C25	C24	C29	C28	-0.9(2)
C6	C1	C2	C3	-0.6(2)	C25	C26	C27	C28	0.1(3)
C6	C7	C8	C9	-178.71(18)	C26	C27	C28	C29	-1.2(3)
C7	N1	C11	C10	-0.5(3)	C27	C28	C29	C24	1.6(3)
C7	C8	C9	C10	0.0(3)	C29	C24	C25	C26	-0.1(3)
C8	C9	C10	C11	0.1(3)					

Table S9: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2x.

Atom	*x*	*y*	*z*	U(eq)
H2	4155.89	2119.71	2786.56	65
H3	3231.6	1591.75	1326.76	77
H4	1248.49	866.29	1298.3	79
H5	142.98	694.26	2711.4	70
H8	-1122.88	814.4	3964.58	78
H9	-2102.37	743.16	5451.6	87
H10	-842.03	1114.33	6866.35	83
H11	1347.1	1545.22	6747.89	80
H13	1130.13	3182.83	4229.88	73
H14	-80.53	4200.1	4877.57	85
H15	486.93	4649.18	6447.45	80
H16	2227.67	4054.08	7364.61	86
H17	3470.66	3047.39	6718.09	75
H19	4104.9	3901.07	4332.14	76
H20	5920.21	4625.12	3823.03	97
H21	7939.74	3995.44	3535.05	101
H22	8149.52	2642.78	3782.02	97
H23	6351.71	1922.17	4318.79	80
H25	3537.02	468.15	5322.4	66
H26	4751.16	-340.35	6424.62	83
H27	6361.33	196.94	7531.91	80
H28	6743.36	1545.36	7537.79	73
H29	5592.25	2355.1	6411.62	61

8.2 X-ray ellipsoid plots of 6f (CCDC 2068360)

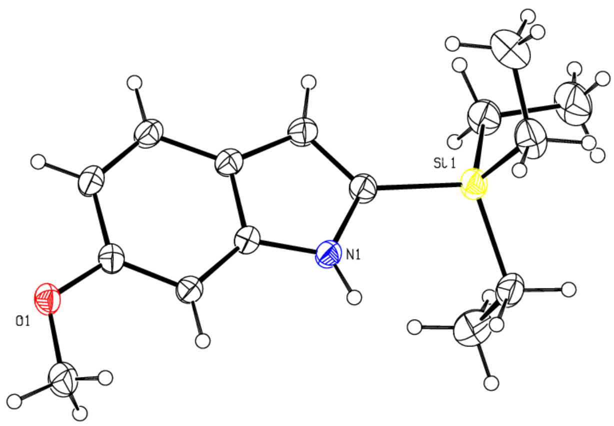


Table S10: Crystal data and structure refinement for 6f.

Identification code	**6f**

Empirical formula	$C_{15}H_{23}NOSi$
Formula weight	261.43
Temperature/K	149.96(10)
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	17.07243(19)
b/Å	17.07243(19)
c/Å	21.9046(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6384.49(18)
Z	16
ρ_{calc}g/cm^3	1.088
μ/mm^{-1}	1.206
F(000)	2272.0
Crystal size/mm^3	0.12 × 0.09 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.564 to 152.462
Index ranges	$-19 \leq h \leq 14$, $-21 \leq k \leq 21$, $-21 \leq l \leq 26$
Reflections collected	9382
Independent reflections	3209 [R_{int} = 0.0359, R_{sigma} = 0.0346]
Data/restraints/parameters	3209/0/167
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1321
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1356
Largest diff. peak/hole / e Å^{-3}	0.31/-0.29

Table S11: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	8043.8(3)	6799.8(3)	1120.2(2)	42.48(17)
O1	8892.9(6)	6292.2(6)	-2320.5(5)	40.0(3)
N1	8338.7(8)	6913.4(7)	-170.3(6)	37.5(3)
C1	8481.4(8)	6477.4(8)	-684.7(7)	34.4(3)
C2	8612.8(9)	6727.3(9)	-1284.0(7)	35.5(3)
C3	8744.3(8)	6147.1(9)	-1711.8(7)	35.3(3)
C4	8745.4(9)	5347.8(9)	-1552.9(7)	39.0(3)
C5	8604.3(9)	5114.0(9)	-963.9(8)	41.2(4)

C6	8467.5(9)	5683.1(9)	-511.3(7)	37.3(3)
C7	8300.1(10)	5666.6(9)	127.4(7)	42.9(4)
C8	8225.6(10)	6422.4(9)	331.0(7)	39.6(3)
C9	8861.5(13)	7086.3(11)	-2515.1(8)	54.7(5)
C10	7481.6(14)	7738.3(11)	1060.5(8)	56.8(5)
C11	6647.2(17)	7633.5(16)	820.5(13)	81.7(7)
C12	7480.9(13)	6040.7(11)	1545.0(9)	55.9(5)
C13	7333.9(17)	6252.4(16)	2216.9(10)	76.6(7)
C14	9008.4(13)	6966.3(13)	1501.5(9)	61.4(5)
C15	9475.7(15)	6220.8(16)	1617.8(11)	74.0(6)

Table S12: Anisotropic Displacement Parameters ($Å^2×10^3$) for 6f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	57.7(3)	37.5(2)	32.2(3)	0.53(16)	7.95(18)	-6.46(18)
O1	39.1(6)	48.2(6)	32.7(5)	-6.5(4)	1.6(4)	4.2(4)
N1	50.7(7)	29.3(6)	32.6(6)	-0.6(5)	5.8(5)	-0.4(5)
C1	35.9(7)	33.1(7)	34.3(7)	-3.9(5)	1.3(6)	0.6(5)
C2	37.7(7)	33.2(7)	35.7(7)	-1.4(6)	1.3(6)	1.7(5)
C3	28.4(6)	43.4(8)	34.0(7)	-5.9(6)	-1.4(5)	2.3(5)
C4	35.6(7)	38.3(8)	43.2(8)	-12.3(6)	-2.9(6)	3.1(6)
C5	44.5(8)	31.4(7)	47.6(9)	-5.2(6)	-2.4(7)	0.0(6)
C6	39.5(7)	31.9(7)	40.4(8)	-1.6(6)	-0.2(6)	-0.5(5)
C7	55.4(9)	32.4(7)	40.8(8)	2.7(6)	2.6(7)	-3.5(6)
C8	48.9(8)	35.8(7)	34.2(7)	1.2(6)	5.3(6)	-3.5(6)
C9	73.8(13)	52.7(10)	37.4(9)	-0.4(7)	10.2(8)	-0.2(9)
C10	88.1(14)	41.5(9)	40.9(9)	-5.8(7)	13.0(9)	3.1(9)
C11	93.1(18)	71.5(15)	80.6(16)	-9.4(12)	-5.1(14)	27.8(13)
C12	71.0(12)	51.0(10)	45.8(10)	5.7(8)	13.2(9)	-9.7(9)
C13	97.9(18)	83.8(16)	48.2(11)	11.3(11)	24.6(11)	-15.0(13)
C14	70.4(13)	68.1(12)	45.6(10)	-1.6(9)	1.7(9)	-17.0(10)
C15	74.6(15)	90.6(17)	56.8(12)	13.5(11)	-8.5(10)	-2.4(12)

Table S13: Bond Lengths for 6f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C8	1.8708(16)	C2	C3	1.382(2)
Si1	C10	1.872(2)	C3	C4	1.408(2)

Si1	C12	1.8626(18)	C4	C5	1.372(2)
Si1	C14	1.868(2)	C5	C6	1.408(2)
O1	C3	1.3796(18)	C6	C7	1.428(2)
O1	C9	1.422(2)	C7	C8	1.371(2)
N1	C1	1.3723(19)	C10	C11	1.529(4)
N1	C8	1.3948(19)	C12	C13	1.536(3)
C1	C2	1.398(2)	C14	C15	1.524(3)
C1	C6	1.408(2)			

Table S14: Bond Angles for 6f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	Si1	C10	108.38(8)	C2	C3	C4	121.81(14)
C12	Si1	C8	107.91(8)	C5	C4	C3	120.95(14)
C12	Si1	C10	111.46(10)	C4	C5	C6	119.38(14)
C12	Si1	C14	109.71(10)	C1	C6	C7	106.65(13)
C14	Si1	C8	108.62(9)	C5	C6	C1	118.16(14)
C14	Si1	C10	110.67(10)	C5	C6	C7	135.19(15)
C3	O1	C9	117.00(12)	C8	C7	C6	108.58(13)
C1	N1	C8	110.18(12)	N1	C8	Si1	122.91(11)
N1	C1	C2	129.33(13)	C7	C8	Si1	129.80(12)
N1	C1	C6	107.33(13)	C7	C8	N1	107.26(13)
C2	C1	C6	123.34(13)	C11	C10	Si1	113.67(15)
C3	C2	C1	116.36(14)	C13	C12	Si1	113.53(15)
O1	C3	C2	123.82(14)	C15	C14	Si1	114.16(16)
O1	C3	C4	114.37(13)				

Table S15: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6f.

Atom	*x*	*y*	*z*	U(eq)
H2	8321.54	7416.64	-158.61	45
H4	8611.72	7255.13	-1388.93	43
H7	8843.19	4973.19	-1851.54	47
H6	8599.12	4584.36	-864.6	49
H10	8249.97	5218.29	365.32	51
H12A	8972.38	7114.08	-2944.23	82
H12B	9242.83	7387.1	-2294.24	82
H12C	8348.24	7293.61	-2438.28	82

H11A	7458.58	7980.61	1460.67	68
H11B	7761.51	8092.05	791.28	68
H16A	6662.81	7377.64	430.46	123
H16B	6402.85	8137.02	778.09	123
H16C	6351.92	7320.03	1102.37	123
H14A	6980.67	5962.52	1344.1	67
H14B	7765.55	5549.48	1527.51	67
H15A	7038.7	6730.21	2238.61	115
H15B	7826.32	6320.74	2421.7	115
H15C	7044.88	5838.75	2410.13	115
H13A	9319.32	7314.63	1249.25	74
H13B	8918.31	7227.38	1888.51	74
H17A	9534.06	5936.55	1242.39	111
H17B	9204.17	5901.09	1909.72	111
H17C	9983.41	6354.87	1774.59	111

8.3 X-ray ellipsoid plots of 1bB (CCDC 2054626)

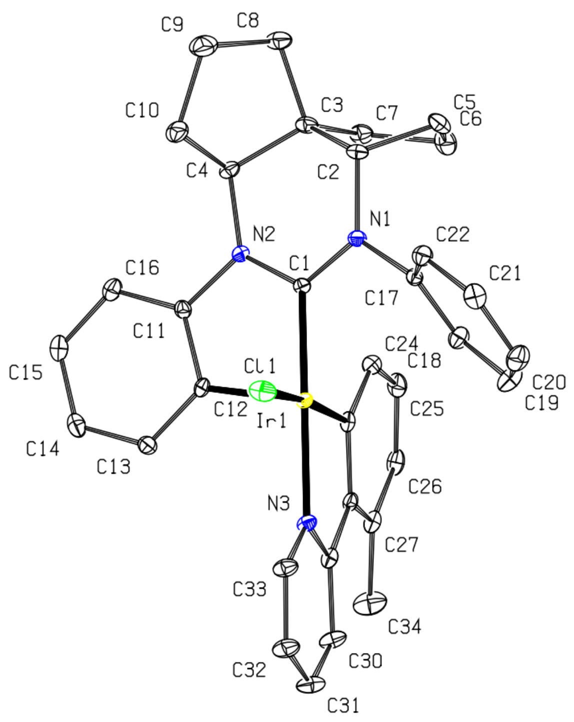


Table S16: Crystal data and structure refinement for 1bB.

Identification code	**1bB**
Empirical formula	$C_{34}H_{33}ClIrN_3$
Formula weight	711.28
Temperature/K	173.00(10)

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.6492(2)
b/Å	11.05361(16)
c/Å	16.4956(2)
α/°	90
β/°	102.7731(15)
γ/°	90
Volume/Å^3	2782.80(7)
Z	4
ρ_{calc}g/cm^3	1.698
μ/mm^{-1}	10.383
F(000)	1408.0
Crystal size/mm^3	0.07 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.048 to 133.178
Index ranges	$-16 \leq h \leq 18$, $-13 \leq k \leq 8$, $-19 \leq l \leq 19$
Reflections collected	10206
Independent reflections	4916 [R_{int} = 0.0184, R_{sigma} = 0.0239]
Data/restraints/parameters	4916/0/353
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0188, wR_2 = 0.0470
Final R indexes [all data]	R_1 = 0.0202, wR_2 = 0.0480
Largest diff. peak/hole / e Å^{-3}	0.53/-0.66

Table S17: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1bB. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ir1	125.8(2)	3833.5(2)	2308.8(2)	12.21(5)
Cl1	657.8(4)	3474.4(6)	1051.1(4)	25.03(14)
N1	-8.0(14)	6395(2)	2129.9(14)	15.5(4)
N2	-1168.3(13)	5412(2)	1260.5(12)	15.3(4)
N3	699.5(14)	2260.7(19)	2908.0(13)	16.3(4)
C1	1027.4(16)	4983(2)	2864.6(15)	14.7(5)
C2	1833.4(16)	4732(3)	3398.1(16)	19.5(5)
C3	2403.2(17)	5664(3)	3725.3(16)	22.9(6)
C4	2184.1(17)	6856(3)	3532.6(17)	23.4(6)
C5	1386.2(18)	7131(3)	3002.0(16)	21.6(6)
C6	816.3(17)	6206(2)	2681.6(16)	15.4(5)

C7	-316.5(17)	7592(2)	1834.5(16)	17.8(5)
C8	95.9(18)	8083(3)	1134.9(18)	26.1(6)
C9	-582(2)	8969(3)	646(2)	37.7(8)
C10	-1419(2)	8802(2)	983.6(19)	27.0(6)
C11	-1303.9(17)	7611(2)	1471.5(15)	18.6(5)
C12	-1890.9(17)	7522(2)	2112.0(16)	21.8(6)
C13	-2657.3(18)	6670(3)	1739.6(18)	27.9(6)
C14	-2581.8(17)	6456(3)	839.9(17)	24.4(6)
C15	-1597.3(16)	6535(2)	883.3(15)	17.2(5)
C16	-419.8(15)	5355(2)	1847.3(14)	12.5(5)
C17	-1497.3(15)	4259(2)	916.5(15)	15.3(5)
C18	-1680.8(17)	3363(3)	1447.3(16)	22.1(6)
C19	-1932(2)	2217(3)	1124.6(18)	30.1(7)
C20	-2022.8(19)	1992(3)	283.5(19)	28.9(6)
C21	-1860.6(18)	2906(3)	-232.2(17)	24.4(6)
C22	-1588.0(17)	4039(3)	76.5(16)	20.7(5)
C23	-330.3(16)	3869(2)	3359.5(15)	14.9(5)
C24	-912.8(16)	4722(2)	3546.4(16)	19.9(5)
C25	-1153.7(17)	4709(3)	4307.9(17)	22.1(6)
C26	-792.1(18)	3872(2)	4904.0(17)	21.8(6)
C27	-209.3(17)	2994(2)	4755.8(16)	19.5(5)
C28	5.1(16)	2966(2)	3967.4(15)	15.4(5)
C29	561.4(16)	2048(2)	3687.2(15)	16.8(5)
C30	923(2)	1010(2)	4110.7(18)	24.9(6)
C31	1438(2)	234(3)	3765.3(18)	28.2(6)
C32	1587.7(19)	487(3)	2990.6(18)	26.4(6)
C33	1202.5(19)	1500(3)	2582.1(17)	22.4(6)
C34	173(2)	2173(3)	5479.3(17)	35.1(7)

Table S18: Anisotropic Displacement Parameters (Å^2×10^3) for 1bB. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	13.94(7)	10.36(7)	13.31(7)	0.93(4)	5.14(4)	0.73(4)
Cl1	29.3(3)	30.6(4)	19.0(3)	5.2(3)	13.7(3)	11.0(3)
N1	15.2(10)	12.3(11)	19.2(10)	1.7(9)	3.9(8)	0.2(8)
N2	15.7(10)	13.6(11)	16.5(10)	1.7(8)	3.6(8)	2.1(8)
N3	20.0(10)	12.0(10)	18.4(10)	0.9(8)	7.0(8)	1.2(9)
C1	15.3(11)	15.4(12)	15.2(11)	0.0(10)	7.4(9)	-3.0(10)
C2	15.8(12)	22.4(14)	20.6(13)	5.8(11)	4.8(10)	1.9(10)

C3	15.9(12)	34.1(17)	18.1(12)	1.6(12)	2.5(10)	-2.7(12)
C4	20.1(13)	27.5(15)	23.6(13)	-5.5(11)	7.1(11)	-7.3(11)
C5	23.6(13)	17.9(14)	24.1(13)	-3.3(11)	7.2(11)	-4.4(11)
C6	13.2(12)	17.0(14)	16.9(12)	-0.6(9)	5.1(10)	0.8(9)
C7	22.4(13)	11.3(12)	20.7(12)	0.5(10)	7.2(10)	0.8(10)
C8	25.9(14)	24.6(15)	31.9(15)	8.6(12)	14.8(12)	1.2(12)
C9	37.6(18)	33.6(18)	44.7(19)	19.1(15)	15.3(15)	6.9(14)
C10	32.1(16)	19.4(15)	30.4(15)	6.0(11)	9.2(13)	8.6(11)
C11	21.1(13)	16.3(13)	19.5(12)	1.5(11)	7.2(10)	6.5(10)
C12	24.5(13)	18.9(14)	23.9(13)	-0.7(11)	9.3(11)	6.1(11)
C13	20.3(13)	33.8(17)	32.6(15)	-4.0(13)	12.3(12)	2.7(13)
C14	17.0(13)	26.7(15)	26.7(14)	-0.8(12)	-0.9(11)	6.3(11)
C15	20.1(12)	15.4(13)	16.2(12)	3.0(10)	4.1(10)	6.5(11)
C16	13.2(11)	12.3(12)	14.3(11)	0.1(9)	7.8(9)	3.2(9)
C17	12.7(11)	13.1(12)	20.2(12)	-1.3(10)	3.8(9)	0.6(10)
C18	24.6(13)	21.9(15)	20.6(13)	-0.2(11)	6.9(11)	-3.0(11)
C19	41.2(17)	20.6(15)	30.6(15)	0.2(12)	12.2(13)	-7.7(13)
C20	33.9(15)	20.5(15)	32.8(15)	-8.8(12)	8.6(13)	-5.6(12)
C21	24.4(13)	29.2(16)	20.4(13)	-7.4(11)	7.0(11)	-0.9(12)
C22	21.2(13)	22.0(14)	20.1(13)	1.7(11)	6.8(11)	0.0(11)
C23	13.8(12)	16.8(13)	14.8(12)	-2.7(9)	5.2(10)	-4.1(9)
C24	18.9(12)	18.2(13)	23.0(13)	1.3(11)	5.3(10)	0.0(10)
C25	18.3(12)	24.5(14)	26.6(14)	-5.2(11)	11.7(10)	-0.6(11)
C26	21.4(13)	27.5(16)	20.5(13)	-4.3(11)	13.0(11)	-7.6(11)
C27	20.5(12)	19.3(13)	19.7(13)	-1.6(10)	6.5(10)	-6.5(10)
C28	14.9(11)	12.4(12)	19.1(12)	-2.4(10)	4.5(9)	-4.0(9)
C29	18.1(12)	16.0(13)	16.6(12)	-1.4(10)	4.8(10)	-4.4(10)
C30	38.8(16)	17.0(14)	20.2(13)	6.3(11)	9.1(12)	3.2(12)
C31	40.4(17)	15.7(14)	27.3(14)	4.0(11)	4.6(13)	7.6(12)
C32	35.7(16)	15.7(14)	30.0(15)	1.1(12)	12.2(13)	7.7(12)
C33	29.9(14)	17.1(13)	23.7(13)	3.3(11)	13.7(11)	6.4(12)
C34	55(2)	33.1(18)	22.5(14)	6.4(13)	19.7(14)	9.1(16)

Table S19: Bond Lengths for 1bB.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	Cl1	2.4329(6)	C11	C12	1.549(3)
Ir1	N3	2.101(2)	C11	C15	1.540(4)
Ir1	C1	1.968(2)	C12	C13	1.542(4)
Ir1	C16	1.962(2)	C13	C14	1.533(4)

Ir1	C23	2.015(2)	C14	C15	1.529(4)
N1	C6	1.420(3)	C17	C18	1.394(4)
N1	C7	1.455(3)	C17	C22	1.383(4)
N1	C16	1.350(3)	C18	C19	1.396(4)
N2	C15	1.481(3)	C19	C20	1.385(4)
N2	C16	1.346(3)	C20	C21	1.380(4)
N2	C17	1.442(3)	C21	C22	1.383(4)
N3	C29	1.370(3)	C23	C24	1.393(4)
N3	C33	1.342(3)	C23	C28	1.430(4)
C1	C2	1.397(3)	C24	C25	1.389(4)
C1	C6	1.409(3)	C25	C26	1.378(4)
C2	C3	1.391(4)	C26	C27	1.390(4)
C3	C4	1.380(4)	C27	C28	1.413(3)
C4	C5	1.391(4)	C27	C34	1.513(4)
C5	C6	1.383(4)	C28	C29	1.476(3)
C7	C8	1.540(3)	C29	C30	1.396(4)
C7	C11	1.529(3)	C30	C31	1.382(4)
C8	C9	1.536(4)	C31	C32	1.378(4)
C9	C10	1.543(4)	C32	C33	1.376(4)
C10	C11	1.532(3)			

Table S20: Bond Angles for 1bB.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	Ir1	Cl1	94.30(6)	C10	C11	C15	110.4(2)
C1	Ir1	Cl1	99.05(7)	C15	C11	C12	104.0(2)
C1	Ir1	N3	97.30(9)	C13	C12	C11	107.1(2)
C1	Ir1	C23	86.61(10)	C14	C13	C12	105.1(2)
C16	Ir1	Cl1	90.60(7)	C15	C14	C13	103.8(2)
C16	Ir1	N3	174.87(8)	N2	C15	C11	109.8(2)
C16	Ir1	C1	80.41(10)	N2	C15	C14	109.3(2)
C16	Ir1	C23	96.36(10)	C14	C15	C11	103.3(2)
C23	Ir1	Cl1	171.70(7)	N1	C16	Ir1	117.55(17)
C23	Ir1	N3	78.88(9)	N2	C16	Ir1	123.66(18)
C6	N1	C7	122.4(2)	N2	C16	N1	118.8(2)
C16	N1	C6	113.1(2)	C18	C17	N2	119.1(2)
C16	N1	C7	124.1(2)	C22	C17	N2	119.9(2)
C16	N2	C15	125.7(2)	C22	C17	C18	121.0(2)
C16	N2	C17	114.8(2)	C19	C18	C17	119.0(3)
C17	N2	C15	119.1(2)	C20	C19	C18	120.2(3)

C29	N3	Ir1	116.36(17)	C21	C20	C19	119.6(3)
C33	N3	Ir1	123.85(17)	C20	C21	C22	121.3(3)
C33	N3	C29	119.8(2)	C21	C22	C17	118.9(3)
C2	C1	Ir1	128.3(2)	C24	C23	Ir1	125.24(19)
C2	C1	C6	117.5(2)	C24	C23	C28	118.3(2)
C6	C1	Ir1	114.19(18)	C28	C23	Ir1	116.42(18)
C3	C2	C1	120.6(3)	C25	C24	C23	121.0(2)
C4	C3	C2	120.8(2)	C26	C25	C24	120.1(3)
C3	C4	C5	119.8(3)	C25	C26	C27	121.7(2)
C6	C5	C4	119.5(3)	C26	C27	C28	118.4(2)
C1	C6	N1	114.5(2)	C26	C27	C34	116.1(2)
C5	C6	N1	123.6(2)	C28	C27	C34	125.5(2)
C5	C6	C1	121.8(2)	C23	C28	C29	114.2(2)
N1	C7	C8	114.1(2)	C27	C28	C23	120.4(2)
N1	C7	C11	112.1(2)	C27	C28	C29	125.4(2)
C11	C7	C8	104.8(2)	N3	C29	C28	113.7(2)
C9	C8	C7	105.2(2)	N3	C29	C30	118.7(2)
C8	C9	C10	106.1(2)	C30	C29	C28	127.6(2)
C11	C10	C9	106.4(2)	C31	C30	C29	120.8(3)
C7	C11	C10	102.1(2)	C32	C31	C30	119.4(3)
C7	C11	C12	115.6(2)	C33	C32	C31	118.2(3)
C7	C11	C15	111.7(2)	N3	C33	C32	123.1(2)
C10	C11	C12	113.3(2)				

Table S21: Torsion Angles for 1bB.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ir1	N3	C29	C28	1.3(3)	C12	C11	C15	C14	35.3(2)
Ir1	N3	C29	C30	179.6(2)	C12	C13	C14	C15	31.1(3)
Ir1	N3	C33	C32	178.7(2)	C13	C14	C15	N2	75.4(3)
Ir1	C1	C2	C3	178.71(19)	C13	C14	C15	C11	-41.5(3)
Ir1	C1	C6	N1	0.0(3)	C15	N2	C16	Ir1	-178.93(17)
Ir1	C1	C6	C5	-178.3(2)	C15	N2	C16	N1	0.0(3)
Ir1	C23	C24	C25	-176.5(2)	C15	N2	C17	C18	-129.6(2)
Ir1	C23	C28	C27	173.66(18)	C15	N2	C17	C22	53.4(3)
Ir1	C23	C28	C29	-7.0(3)	C15	C11	C12	C13	-16.1(3)
N1	C7	C8	C9	153.6(2)	C16	N1	C6	C1	-3.2(3)
N1	C7	C11	C10	-163.8(2)	C16	N1	C6	C5	175.0(2)
N1	C7	C11	C12	72.9(3)	C16	N1	C7	C8	-94.5(3)
N1	C7	C11	C15	-45.8(3)	C16	N1	C7	C11	24.5(3)

N2	C17	C18	C19	-174.9(2)	C16	N2	C15	C11	-22.7(3)
N2	C17	C22	C21	176.6(2)	C16	N2	C15	C14	-135.4(2)
N3	C29	C30	C31	2.3(4)	C16	N2	C17	C18	57.9(3)
C1	C2	C3	C4	0.2(4)	C16	N2	C17	C22	-119.2(3)
C2	C1	C6	N1	179.4(2)	C17	N2	C15	C11	165.6(2)
C2	C1	C6	C5	1.1(4)	C17	N2	C15	C14	52.9(3)
C2	C3	C4	C5	-0.3(4)	C17	N2	C16	Ir1	-6.9(3)
C3	C4	C5	C6	0.8(4)	C17	N2	C16	N1	172.0(2)
C4	C5	C6	N1	-179.4(2)	C17	C18	C19	C20	-2.1(4)
C4	C5	C6	C1	-1.2(4)	C18	C17	C22	C21	-0.4(4)
C6	N1	C7	C8	78.1(3)	C18	C19	C20	C21	0.3(5)
C6	N1	C7	C11	-162.9(2)	C19	C20	C21	C22	1.5(4)
C6	N1	C16	Ir1	5.1(3)	C20	C21	C22	C17	-1.5(4)
C6	N1	C16	N2	-173.9(2)	C22	C17	C18	C19	2.1(4)
C6	C1	C2	C3	-0.6(4)	C23	C24	C25	C26	2.3(4)
C7	N1	C6	C1	-176.6(2)	C23	C28	C29	N3	3.5(3)
C7	N1	C6	C5	1.7(4)	C23	C28	C29	C30	-174.6(3)
C7	N1	C16	Ir1	178.36(17)	C24	C23	C28	C27	-3.9(4)
C7	N1	C16	N2	-0.6(3)	C24	C23	C28	C29	175.4(2)
C7	C8	C9	C10	-9.3(3)	C24	C25	C26	C27	-2.5(4)
C7	C11	C12	C13	-139.0(2)	C25	C26	C27	C28	-0.5(4)
C7	C11	C15	N2	44.2(3)	C25	C26	C27	C34	177.0(3)
C7	C11	C15	C14	160.7(2)	C26	C27	C28	C23	3.8(4)
C8	C7	C11	C10	-39.5(3)	C26	C27	C28	C29	-175.5(2)
C8	C7	C11	C12	-162.8(2)	C27	C28	C29	N3	-177.1(2)
C8	C7	C11	C15	78.5(3)	C27	C28	C29	C30	4.8(4)
C8	C9	C10	C11	-15.3(3)	C28	C23	C24	C25	0.9(4)
C9	C10	C11	C7	33.7(3)	C28	C29	C30	C31	-179.7(3)
C9	C10	C11	C12	158.6(3)	C29	N3	C33	C32	0.9(4)
C9	C10	C11	C15	-85.3(3)	C29	C30	C31	C32	-0.5(5)
C10	C11	C12	C13	103.7(3)	C30	C31	C32	C33	-1.1(5)
C10	C11	C15	N2	157.0(2)	C31	C32	C33	N3	1.0(5)
C10	C11	C15	C14	-86.5(3)	C33	N3	C29	C28	179.3(2)
C11	C7	C8	C9	30.5(3)	C33	N3	C29	C30	-2.5(4)
C11	C12	C13	C14	-9.1(3)	C34	C27	C28	C23	-173.5(3)
C12	C11	C15	N2	-81.2(2)	C34	C27	C28	C29	7.2(4)

Table S22: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1bB.

Atom	*x*	*y*	*z*	U(eq)
H2	1990.56	3934.33	3536.01	23
H3	2938.31	5482.42	4078.1	28
H4	2568.65	7472.46	3756.75	28
H5	1237.12	7931.1	2863.83	26
H7	-185	8155.87	2303.86	21
H8A	643.29	8494.55	1364.21	31
H8B	208.18	7430.47	779.02	31
H9A	-699.05	8789.39	56.51	45
H9B	-370.95	9794.8	731.2	45
H10A	-1489.33	9471.02	1343.55	32
H10B	-1931.52	8763.56	529.31	32
H12A	-1558.62	7199.74	2634.2	26
H12B	-2110.54	8314.73	2214.09	26
H13A	-2607.39	5912.89	2044.14	33
H13B	-3214.25	7042.94	1755.59	33
H14A	-2808.93	5666.38	645.04	29
H14B	-2897.47	7071.39	472.97	29
H15	-1476.57	6680.43	333.39	21
H18	-1636.83	3525.59	2008.19	27
H19	-2037.75	1603.07	1475.09	36
H20	-2192.18	1230.12	67.8	35
H21	-1936.14	2757.93	-798.61	29
H22	-1467.5	4642.02	-275	25
H24	-1143.89	5309.09	3155.42	24
H25	-1559.68	5267.03	4415.47	26
H26	-941.73	3894.59	5418.96	26
H30	817.06	838.8	4631.59	30
H31	1680.18	-452.11	4053.1	34
H32	1940.02	-14.84	2750.28	32
H33	1294.95	1666.7	2055.44	27
H34A	0.93	2457.11	5969.85	53
H34B	800.04	2176.34	5570.75	53
H34C	-41.14	1364.36	5356.47	53

8.4 X-ray ellipsoid plots of 3dB (CCDC 2054624)

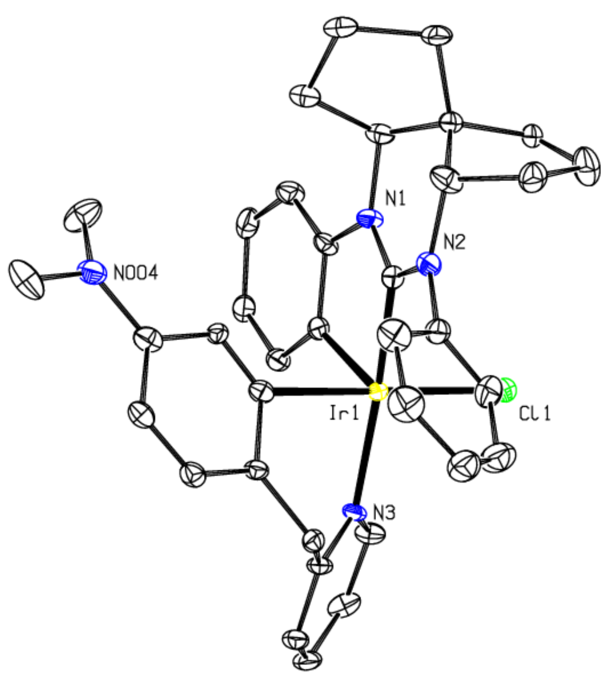


Table S23: Crystal data and structure refinement for 3dB.

Identification code	**3dB**
Empirical formula	$C_{36}H_{38}ClIrN_4$
Formula weight	754.35
Temperature/K	270.82(19)
Crystal system	hexagonal
Space group	$P6_1$
a/Å	26.9599(4)
b/Å	26.9599(4)
c/Å	11.3490(2)
α/°	90
β/°	90
γ/°	120
Volume/$Å^3$	7143.7(2)
Z	6
ρ_{calc}g/cm^3	1.052
μ/mm^{-1}	6.097
F(000)	2256.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.024 to 152.184
Index ranges	$-23 \leq h \leq 32$, $-32 \leq k \leq 32$, $-13 \leq l \leq 12$
Reflections collected	27060
Independent reflections	8514 [R_{int} = 0.0421, R_{sigma} = 0.0382]

Data/restraints/parameters	8514/25/381
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1154
Largest diff. peak/hole / e Å^{-3}	0.79/-0.76
Flack parameter	0.118(15)

Table S24: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3dB. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ir1	8497.5(2)	4924.7(2)	6879.5(2)	50.96(12)
Cl1	8976.8(11)	5012.3(15)	8715(3)	84.9(8)
N1	9523(3)	5182(4)	5624(9)	73(2)
N2	9442(4)	5993(4)	6011(10)	75(2)
N3	7681(3)	4367(3)	7665(8)	59.0(18)
N4	8165(4)	4889(5)	1963(15)	91(3)
C1	10394(4)	6119(6)	5492(10)	76(3)
C2	10075(4)	5510(5)	5037(12)	76(3)
C3	10027(5)	5547(6)	3670(16)	97(4)
C4	10568(6)	6112(8)	3335(17)	114(6)
C5	10869(5)	6396(6)	4568(14)	96(4)
C6	10020(5)	6391(5)	5472(19)	101(5)
C7	10343(7)	6897(6)	6306(15)	102(5)
C8	10614(8)	6681(8)	7256(19)	127(7)
C9	10612(4)	6184(6)	6731(11)	78(3)
C10	9242(4)	5441(5)	6040(10)	66(2)
C11	9219(4)	4579(4)	5642(11)	66(3)
C12	8678(4)	4341(5)	6187(9)	63(2)
C13	8350(4)	3747(4)	6285(11)	68(3)
C14	8547(5)	3399(5)	5818(11)	73(3)
C15	9079(6)	3656(6)	5196(13)	91(4)
C16	9409(5)	4249(5)	5139(14)	81(3)
C17	9057(5)	6195(5)	6309(12)	78(3)
C18	8865(8)	6418(8)	5470(20)	121(5)
C19	8483(10)	6577(10)	5860(30)	147(7)
C20	8317(8)	6587(9)	7050(20)	128(6)
C21	8501(9)	6346(9)	7740(20)	135(7)
C22	8877(7)	6142(7)	7444(17)	109(5)

C23	7620(4)	3948(4)	8395(13)	76(3)
C24	7092(6)	3533(6)	8755(13)	91(4)
C25	6613(5)	3571(5)	8452(13)	87(4)
C26	6686(4)	4020(5)	7754(12)	79(3)
C27	7222(4)	4419(4)	7370(10)	65(3)
C28	7337(4)	4936(5)	6671(10)	63(2)
C29	7560(4)	4934(4)	5438(9)	61(2)
C30	8063(4)	4897(4)	5143(12)	65(2)
C31	8255(4)	4898(4)	4172(9)	55(2)
C32	7961(5)	4901(5)	3151(13)	80(4)
C33	7471(4)	4966(5)	3382(13)	74(3)
C34	7294(5)	4970(5)	4468(13)	74(3)
C35	8487(9)	4602(9)	1792(19)	132(7)
C36	7874(7)	4934(7)	970(20)	139(8)

Table S25: Anisotropic Displacement Parameters (Å^2×10^3) for 3dB. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	41.26(16)	67.1(2)	41.44(17)	-3.61(16)	2.84(14)	24.74(15)
Cl1	62.7(13)	129(2)	62.7(17)	-14.8(15)	-9.6(11)	47.4(14)
N1	45(4)	97(6)	77(6)	0(5)	9(4)	36(4)
N2	62(5)	77(6)	84(7)	-14(5)	-3(4)	33(4)
N3	31(3)	73(5)	61(5)	8(4)	9(3)	18(3)
N4	65(5)	97(7)	109(9)	-3(7)	8(7)	38(5)
C1	53(5)	104(8)	58(7)	0(5)	4(4)	29(5)
C2	51(5)	92(7)	87(9)	16(6)	15(5)	36(5)
C3	62(6)	110(9)	110(12)	2(9)	19(7)	36(6)
C4	77(8)	140(12)	115(14)	4(11)	43(9)	46(8)
C5	64(6)	98(9)	102(11)	6(7)	37(7)	22(6)
C6	69(6)	72(7)	153(16)	1(8)	3(8)	28(6)
C7	114(11)	85(8)	104(12)	-17(8)	3(9)	47(8)
C8	132(13)	133(13)	130(16)	-29(11)	-57(12)	77(11)
C9	57(5)	110(8)	51(6)	-11(6)	-7(5)	29(5)
C10	60(5)	76(6)	59(6)	-6(5)	-2(4)	32(5)
C11	42(4)	72(6)	83(7)	-3(5)	-7(4)	29(4)
C12	57(5)	87(7)	50(5)	-3(5)	-9(4)	40(5)
C13	56(5)	61(5)	84(8)	-15(5)	3(5)	27(4)
C14	79(7)	82(7)	69(7)	-17(5)	-15(5)	48(6)
C15	109(9)	120(10)	76(8)	-36(8)	-28(8)	82(8)

C16	62(5)	93(7)	96(9)	0(8)	4(6)	46(5)
C17	75(7)	66(6)	86(9)	-13(6)	7(6)	30(5)
C18	122(9)	116(9)	139(12)	7(8)	-3(8)	69(8)
C19	149(12)	143(11)	160(13)	1(10)	-6(10)	83(10)
C20	129(10)	129(10)	127(12)	-14(9)	14(9)	67(8)
C21	136(11)	145(11)	136(12)	-11(9)	32(9)	78(9)
C22	123(12)	105(10)	99(12)	-27(9)	-7(9)	57(10)
C23	62(5)	73(6)	90(9)	25(6)	22(6)	33(5)
C24	113(10)	100(8)	79(9)	24(7)	35(7)	68(8)
C25	63(6)	82(7)	88(9)	-3(7)	36(6)	17(5)
C26	49(5)	83(7)	97(9)	-19(6)	15(5)	27(5)
C27	43(4)	64(5)	82(7)	-6(5)	19(4)	22(4)
C28	61(5)	80(6)	57(6)	-8(5)	-7(4)	41(5)
C29	47(4)	76(6)	64(6)	7(5)	6(4)	34(4)
C30	56(5)	67(5)	78(7)	3(5)	0(5)	35(4)
C31	52(4)	74(5)	49(5)	-2(4)	0(4)	37(4)
C32	67(6)	60(5)	121(12)	-7(6)	4(6)	36(5)
C33	63(5)	78(6)	92(9)	6(6)	-16(6)	43(5)
C34	63(6)	74(6)	93(9)	-10(6)	-8(6)	41(5)
C35	188(17)	199(18)	83(11)	28(14)	24(12)	151(16)
C36	97(11)	84(9)	210(20)	11(12)	-50(13)	23(8)

Table S26: Bond Lengths for 3dB.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	Cl1	2.400(3)	C9	C8	1.46(2)
Ir1	N3	2.142(7)	C11	C16	1.357(16)
Ir1	C10	2.020(11)	C12	C11	1.409(14)
Ir1	C12	2.023(11)	C12	C13	1.395(15)
Ir1	C30	2.274(13)	C13	C14	1.392(15)
N1	C2	1.458(13)	C15	C14	1.43(2)
N1	C10	1.348(14)	C16	C15	1.388(18)
N1	C11	1.407(14)	C17	C18	1.35(2)
N2	C6	1.510(17)	C17	C22	1.36(2)
N2	C10	1.304(14)	C18	C19	1.37(3)
N2	C17	1.434(15)	C20	C19	1.42(4)
N3	C23	1.342(14)	C21	C20	1.27(3)
N3	C27	1.355(13)	C22	C21	1.41(3)
N4	C32	1.46(2)	C24	C23	1.361(17)
N4	C35	1.435(18)	C25	C24	1.388(19)

N4	C36	1.41(2)	C26	C25	1.38(2)
C1	C2	1.513(18)	C26	C27	1.372(14)
C1	C5	1.530(15)	C27	C28	1.494(15)
C1	C6	1.515(18)	C29	C28	1.523(14)
C2	C3	1.56(2)	C29	C34	1.343(16)
C4	C3	1.54(2)	C30	C29	1.451(13)
C4	C5	1.61(2)	C30	C31	1.217(16)
C6	C7	1.53(2)	C32	C31	1.407(17)
C7	C8	1.57(2)	C32	C33	1.441(15)
C9	C1	1.501(16)	C34	C33	1.323(19)

Table S27: Bond Angles for 3dB.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	Ir1	Cl1	91.2(2)	N2	C10	Ir1	120.0(8)
N3	Ir1	C30	90.3(3)	N2	C10	N1	124.3(10)
C10	Ir1	Cl1	92.3(3)	N1	C11	C12	114.0(9)
C10	Ir1	N3	176.4(4)	C16	C11	N1	123.9(9)
C10	Ir1	C30	86.1(4)	C16	C11	C12	122.1(10)
C12	Ir1	Cl1	95.0(3)	C11	C12	Ir1	114.4(8)
C12	Ir1	N3	100.2(4)	C13	C12	Ir1	127.0(7)
C12	Ir1	C10	79.1(4)	C13	C12	C11	118.4(9)
C12	Ir1	C30	87.6(4)	C14	C13	C12	120.5(10)
C30	Ir1	Cl1	176.7(3)	C13	C14	C15	119.3(11)
C10	N1	C2	120.9(10)	C16	C15	C14	119.4(11)
C10	N1	C11	116.0(8)	C11	C16	C15	120.1(11)
C11	N1	C2	122.5(9)	C18	C17	N2	120.9(14)
C10	N2	C6	120.9(10)	C18	C17	C22	121.0(15)
C10	N2	C17	117.5(10)	C22	C17	N2	118.2(14)
C17	N2	C6	120.7(10)	C17	C18	C19	115(2)
C23	N3	Ir1	119.9(6)	C18	C19	C20	127(2)
C23	N3	C27	120.3(8)	C21	C20	C19	112(2)
C27	N3	Ir1	119.7(7)	C20	C21	C22	126(2)
C35	N4	C32	118.2(13)	C17	C22	C21	118.3(19)
C36	N4	C32	120.1(13)	N3	C23	C24	121.0(11)
C36	N4	C35	116.7(16)	C23	C24	C25	119.7(11)
C2	C1	C5	100.2(10)	C26	C25	C24	118.5(10)
C2	C1	C6	111.6(9)	C27	C26	C25	120.3(11)
C6	C1	C5	110.5(12)	N3	C27	C26	119.9(11)
C9	C1	C2	115.1(11)	N3	C27	C28	117.0(8)

C9	C1	C5	113.6(10)	C26	C27	C28	123.1(10)
C9	C1	C6	105.9(12)	C27	C28	C29	112.5(8)
N1	C2	C1	110.8(10)	C30	C29	C28	126.6(10)
N1	C2	C3	113.6(10)	C34	C29	C28	121.9(9)
C1	C2	C3	106.8(10)	C34	C29	C30	111.5(10)
C4	C3	C2	103.9(13)	C29	C30	Ir1	106.4(8)
C3	C4	C5	105.0(13)	C31	C30	Ir1	125.0(7)
C1	C5	C4	105.3(10)	C31	C30	C29	128.4(11)
N2	C6	C1	110.4(11)	C30	C31	C32	120.3(9)
N2	C6	C7	108.0(14)	C31	C32	N4	122.6(10)
C1	C6	C7	101.7(12)	C31	C32	C33	113.9(12)
C6	C7	C8	105.0(13)	C33	C32	N4	123.3(12)
C9	C8	C7	105.7(14)	C34	C33	C32	121.8(11)
C8	C9	C1	108.1(13)	C33	C34	C29	123.8(10)
N1	C10	Ir1	115.5(8)				

Table S28: Torsion Angles for 3dB.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Ir1	N3	C23	C24	-169.3(11)	C10	N1	C11	C12	-4.9(14)
Ir1	N3	C27	C26	171.9(8)	C10	N1	C11	C16	172.3(12)
Ir1	N3	C27	C28	-10.8(12)	C10	N2	C6	C1	-24(2)
Ir1	C12	C11	N1	-3.2(12)	C10	N2	C6	C7	-134.4(13)
Ir1	C12	C11	C16	179.6(10)	C10	N2	C17	C18	-109.5(15)
Ir1	C12	C13	C14	-176.1(9)	C10	N2	C17	C22	68.8(16)
Ir1	C30	C29	C28	-5.2(12)	C11	N1	C2	C1	-160.6(10)
Ir1	C30	C29	C34	174.8(8)	C11	N1	C2	C3	79.2(14)
Ir1	C30	C31	C32	-177.6(7)	C11	N1	C10	Ir1	10.8(13)
N1	C2	C3	C4	152.8(11)	C11	N1	C10	N2	-174.8(11)
N1	C11	C16	C15	-179.7(12)	C11	C12	C13	C14	-2.1(16)
N2	C6	C7	C8	82.7(16)	C11	C16	C15	C14	-2(2)
N2	C17	C18	C19	177.7(16)	C12	C11	C16	C15	-3(2)
N2	C17	C22	C21	179.4(14)	C12	C13	C14	C15	-2.4(18)
N3	C27	C28	C29	66.5(12)	C13	C12	C11	N1	-177.9(10)
N4	C32	C31	C30	-178.5(10)	C13	C12	C11	C16	4.9(17)
N4	C32	C33	C34	179.4(11)	C16	C15	C14	C13	4.5(19)
C1	C2	C3	C4	30.4(13)	C17	N2	C6	C1	167.4(12)
C1	C6	C7	C8	-33.4(17)	C17	N2	C6	C7	57.0(17)
C1	C9	C8	C7	4.0(18)	C17	N2	C10	Ir1	-15.8(15)
C2	N1	C10	Ir1	-177.9(8)	C17	N2	C10	N1	170.0(11)

C2	N1	C10	N2	-3.5(18)	C17	C18	C19	C20	7(3)
C2	N1	C11	C12	-176.1(10)	C17	C22	C21	C20	-1(3)
C2	N1	C11	C16	1.1(18)	C18	C17	C22	C21	-2(2)
C2	C1	C5	C4	38.9(14)	C21	C20	C19	C18	-10(3)
C2	C1	C6	N2	47.9(17)	C22	C17	C18	C19	0(3)
C2	C1	C6	C7	162.3(12)	C22	C21	C20	C19	7(3)
C3	C4	C5	C1	-21.3(16)	C23	N3	C27	C26	-4.5(16)
C5	C1	C2	N1	-167.4(11)	C23	N3	C27	C28	172.9(10)
C5	C1	C2	C3	-43.3(12)	C25	C24	C23	N3	-6(2)
C5	C1	C6	N2	158.5(12)	C25	C26	C27	N3	1.0(18)
C5	C1	C6	C7	-87.1(15)	C25	C26	C27	C28	-176.2(11)
C5	C4	C3	C2	-5.0(15)	C26	C25	C24	C23	2(2)
C6	N2	C10	Ir1	175.2(11)	C26	C27	C28	C29	-116.2(11)
C6	N2	C10	N1	1.0(19)	C27	N3	C23	C24	7.0(19)
C6	N2	C17	C18	59.5(19)	C27	C26	C25	C24	0.0(19)
C6	N2	C17	C22	-122.3(16)	C28	C29	C34	C33	-179.5(11)
C6	C1	C2	N1	-50.4(15)	C29	C30	C31	C32	-4.3(17)
C6	C1	C2	C3	73.8(13)	C29	C34	C33	C32	2.2(19)
C6	C1	C5	C4	-78.9(15)	C30	C29	C28	C27	-56.8(13)
C6	C7	C8	C9	18.8(19)	C30	C29	C34	C33	0.5(16)
C8	C9	C1	C2	-149.4(12)	C31	C30	C29	C28	-179.5(11)
C8	C9	C1	C5	95.8(15)	C31	C30	C29	C34	0.5(16)
C8	C9	C1	C6	-25.7(15)	C31	C32	C33	C34	-5.5(16)
C9	C1	C2	N1	70.3(12)	C33	C32	C31	C30	6.4(15)
C9	C1	C2	C3	-165.5(9)	C34	C29	C28	C27	123.2(11)
C9	C1	C5	C4	162.2(13)	C35	N4	C32	C31	30.2(19)
C9	C1	C6	N2	-78.0(14)	C35	N4	C32	C33	-155.2(14)
C9	C1	C6	C7	36.4(14)	C36	N4	C32	C31	-175.6(12)
C10	N1	C2	C1	28.6(15)	C36	N4	C32	C33	-0.9(18)
C10	N1	C2	C3	-91.6(14)					

Table S29: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3dB.

Atom	*x*	*y*	*z*	U(eq)
H00Q	10305.31	5328.92	5203.81	92
H00X	10021.65	5223.81	3281.21	117
H00Y	9683.2	5556.19	3458.68	117
H00R	10467.03	6360.77	2908.58	137
H00S	10820.15	6039.07	2847.97	137

H01A	11175.64	6317.56	4739.61	116
H01B	11025.74	6807.46	4549.31	116
H00V	9985.75	6514.61	4678.22	121
H01C	10083.43	7002.88	6671.09	123
H01D	10638.17	7226.4	5887.6	123
H01E	11002.19	6978.1	7439.58	153
H01F	10389.45	6573.2	7974.78	153
H00E	10367.07	5842.16	7183.15	94
H00F	10996.71	6240.15	6729.55	94
H00O	7997.11	3581.48	6664.71	82
H00W	8334.15	3003.89	5909.12	87
H00T	9203.37	3428.67	4831.78	109
H00M	9761.42	4419.95	4756.79	97
H00U	8984.91	6460	4693.68	146
H68	8313.42	6689.36	5288.21	176
H015	8100.84	6750.78	7287.89	153
H014	8377.79	6299.6	8521.74	162
H013	8997.92	5976.4	8009.89	131
H00L	7942.97	3941.62	8659.73	91
H00H	7052.04	3226.04	9200.67	109
H00G	6250.6	3298.44	8714.74	104
H00B	6370.52	4052.64	7540.86	95
H00A	7616.63	5276.86	7085.04	76
H00C	6986.35	4951.55	6609.04	76
H00D	8598.47	4896.56	4104.62	67
H00J	7273.13	5005.71	2750.9	89
H00I	6967.11	4999.49	4564.46	88
H	8837.39	4852.66	1388.04	198
H00Z	8571.96	4498.76	2542.96	198
HA	8265.78	4262.77	1329.48	198
H00K	7561.78	4561.33	770.66	208
H00N	8133.52	5084.97	317.32	208
H00P	7727.4	5184.58	1149.82	208

9. References

(1) C. M. M. Gómez, V. V. Kouznetsov, M. A. Sortino, S. L. Álvarez and S. A. Zacchino, In vitro antifungal activity of polyfunctionalized 2-(hetero)arylquinolines prepared through imino Diels–Alder reactions. *Bioorganic & Medicinal Chemistry*, 2008, **16**, 7908–7320.

(2) A. Ros, B. Estepa, R. López-Rodríguez, E. Álvarez, R. Fernández and J. M. Lassaletta, Use of Hemilabile *N,N* Ligands in Nitrogen-Directed Iridium-Catalyzed Borylations of Arenes. *Angew. Chem. Int. Ed.* 2011, **50**, 11724–11728.

(3) O. Kobayashi, D. Uraguchi and T. Yamakawa, Cp_2Ni-KOt-Bu-BEt_3 (or PPh_3) Catalyst System for Direct C−H Arylation of Benzene, Naphthalene, and Pyridine. *Org. Lett.* 2009, **11**, 2679–2682.

(4) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim and S. Chang Rhodium-Catalyzed Intermolecular Amidation of Arenes with Sulfonyl Azides via Chelation-Assisted C–H Bond Activation. *J. Am. Chem. Soc.* 2012, **134**, 9110–9113.

(5) G.-F. Zhang, Y. Li, X.-Q. Xie and C.-R. Ding, Ru-Catalyzed Regioselective Direct Hydroxymethylation of (Hetero)Arenes via C–H Activation. *Org. Lett.* 2017, **19**, 1216–1219.

(6) Z.-Y. Li, H. H. C. Lakmal and X. Cui, Enabling Catalytic Arene C–H Amidomethylation via Bis(tosylamido)methane as a Sustainable Formaldimine Releaser. *Org. Lett.* 2019, **21**, 3735–3740.

(7) Z. Ibrahim Mohamed Allaoui, E. le Gall, A. Fihey, R. Plaza-Pedroche, C. Katan, F. Robin-le Guen, J. Rodríguez-López and S. Achelle, Push-Pull (Iso)quinoline Chromophores: Synthesis, Photophysical Properties, and Use for White-Light Emission. *Chemistry - A European Journal* 2020, **26**, 8153–8161.

(8) T. Niwa, H. Yorimitsu and K. Oshima, Palladium-Catalyzed 2-Pyridylmethyl Transfer from 2-(2-Pyridyl)ethanol Derivatives to Organic Halides by Chelation-Assisted Cleavage of Unstrained C_{sp3}–C_{sp3} bonds. *Angew. Chem. Int. Ed.* 2007, **46**, 2643–2645.

(9) A. Skrzyńska, A. Przydacz and Ł. Albrecht, Organocatalytic Nonclassical Trienamine Activation in the Remote Alkylation of Furan Derivatives. *Org. Lett.* 2015, **17**, 5682–5685.

(10) M. J. Burns, I. J. S. Fairlamb, A. R. Kapdi, P. Sehnal, R. J. K. Taylor, Simple Palladium(II) Precatalyst for Suzuki−Miyaura Couplings: Efficient Reactions of Benzylic, Aryl, Heteroaryl, and Vinyl Coupling Partners. *Org. Lett.* 2007, **9**, 5397–5400.

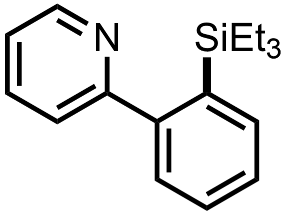
(11) Y.-X. Tan, X.-Y. Liu, Y.-S. Zhao, P. Tian and G.-Q. Lin, Arylation/Intramolecular Conjugate Addition of 1,6-Enynes Enabled by Manganese(I)-Catalyzed C–H Bond Activation. *Org. Lett.* 2019, **21**, 5–9.

(12) J.-D. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.,* 2008, **10**, 6615–6620.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; T. Nakajima; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas,

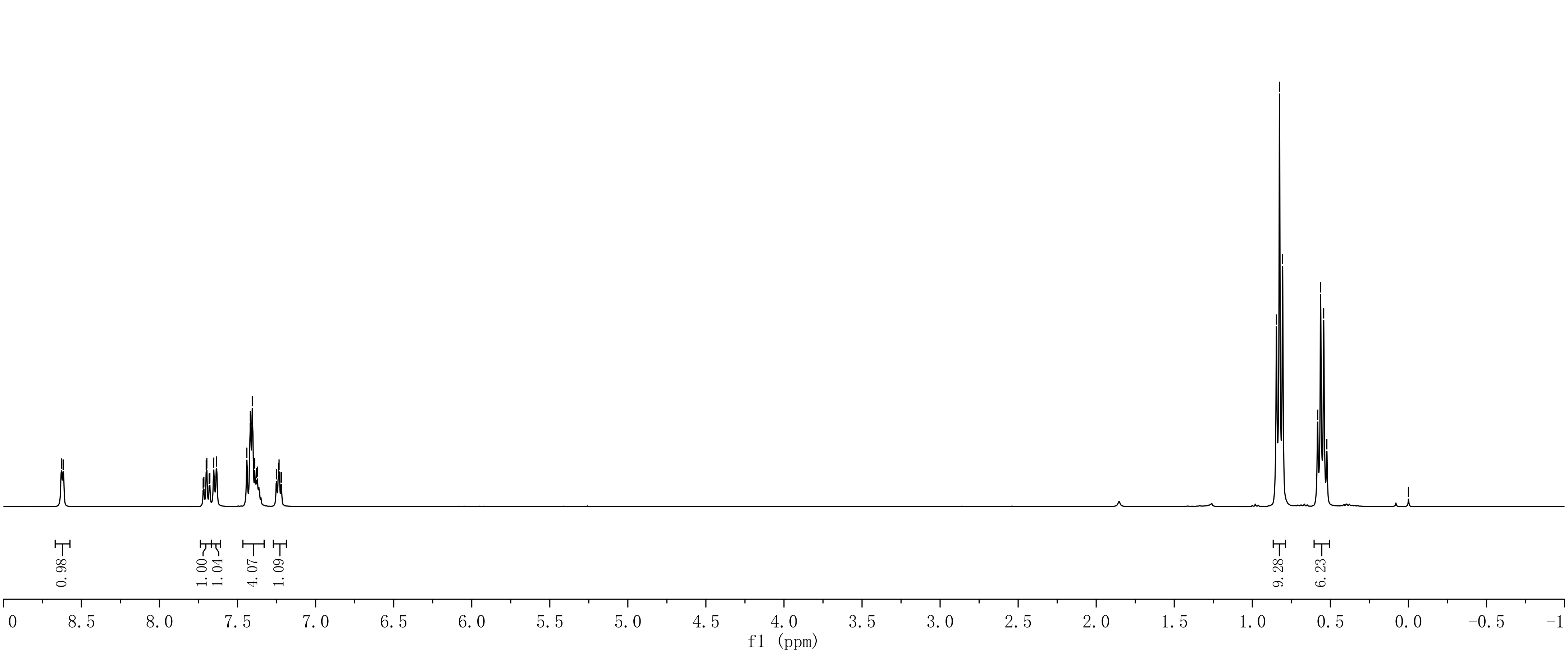
O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
(14), A. Armstrong, R. A. Boto, P. Dingwall, J. Contreras-Garcia, M. J. Harvey, N. J. Mason and H. S. Rzepa, The Houk-List transition states for organocatalytic mechanisms revisited. *Chem. Sci.* 2014, **5**, 2057–2071.
(15) A. V. Marenich, C. J. Cramer and D. G. Truhlar, Performance of SM6, SM8, and SMD on the SAMPL1 Test set for the prediction of small-molecule solvation free energies. *J. Phys. Chem. B* 2009, **113**, 4538–4543.
(16) K. Fukui, The path of chemical reactions-the IRC approach. *Acc. Chem. Res.* 1981, **14**, 363–368.
(17) C. Gonzalez and B. Schlegel, An improved algorithm for reaction path following. *J. Chem. Phys.* 1989, **90**, 2154–2161.

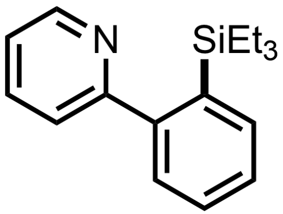
10. Copies of NMR spectroscopy



2a

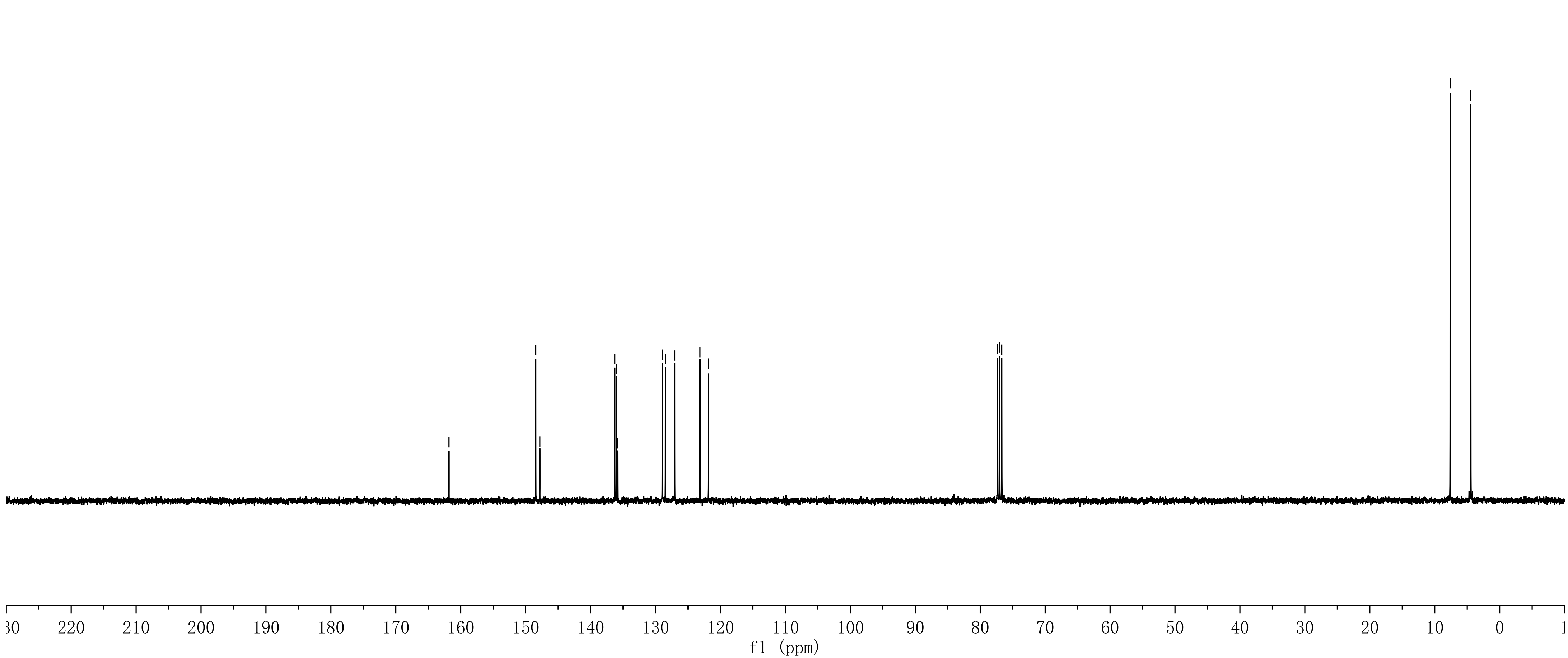
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

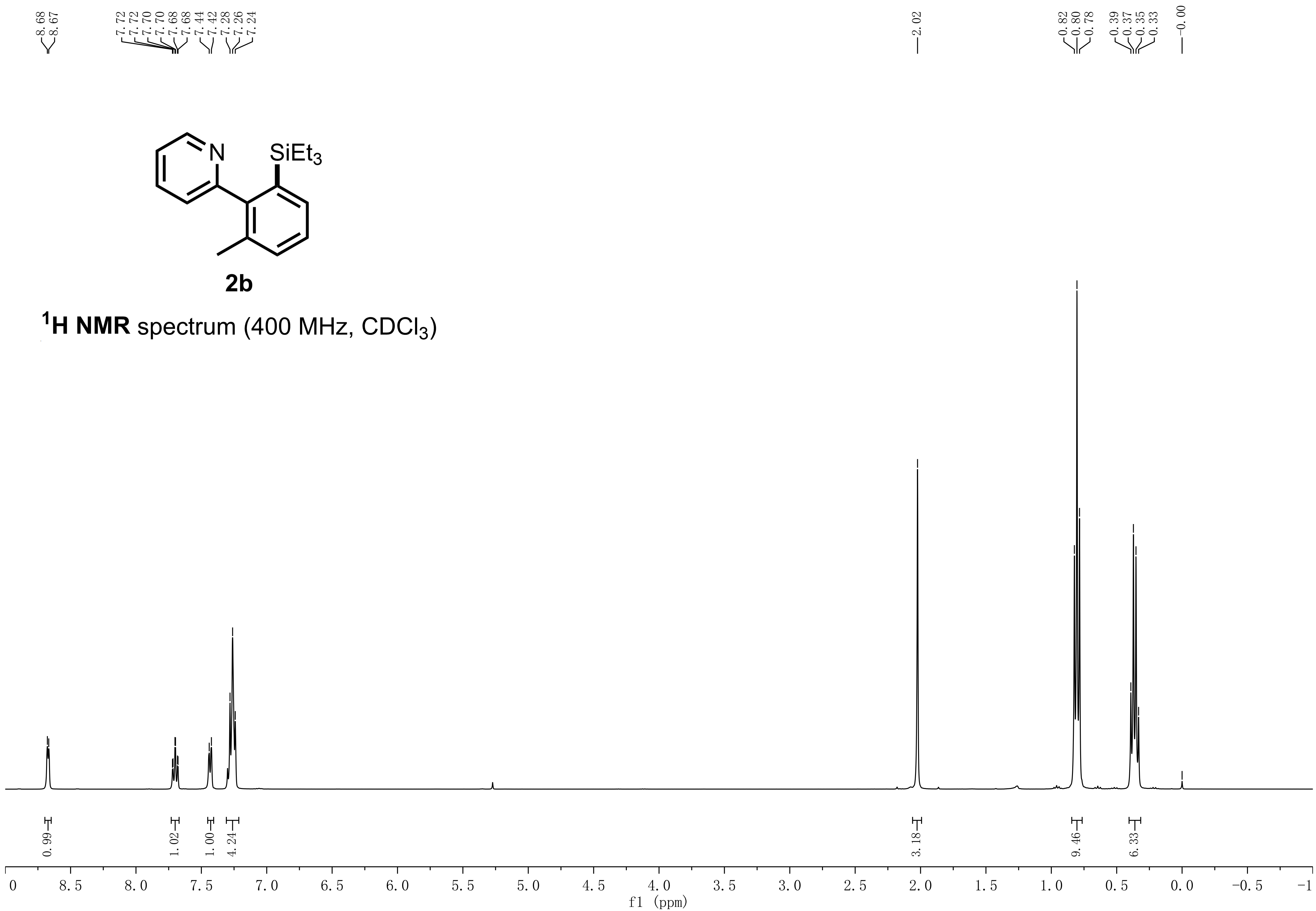


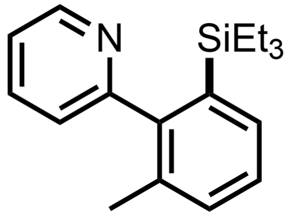


2a

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

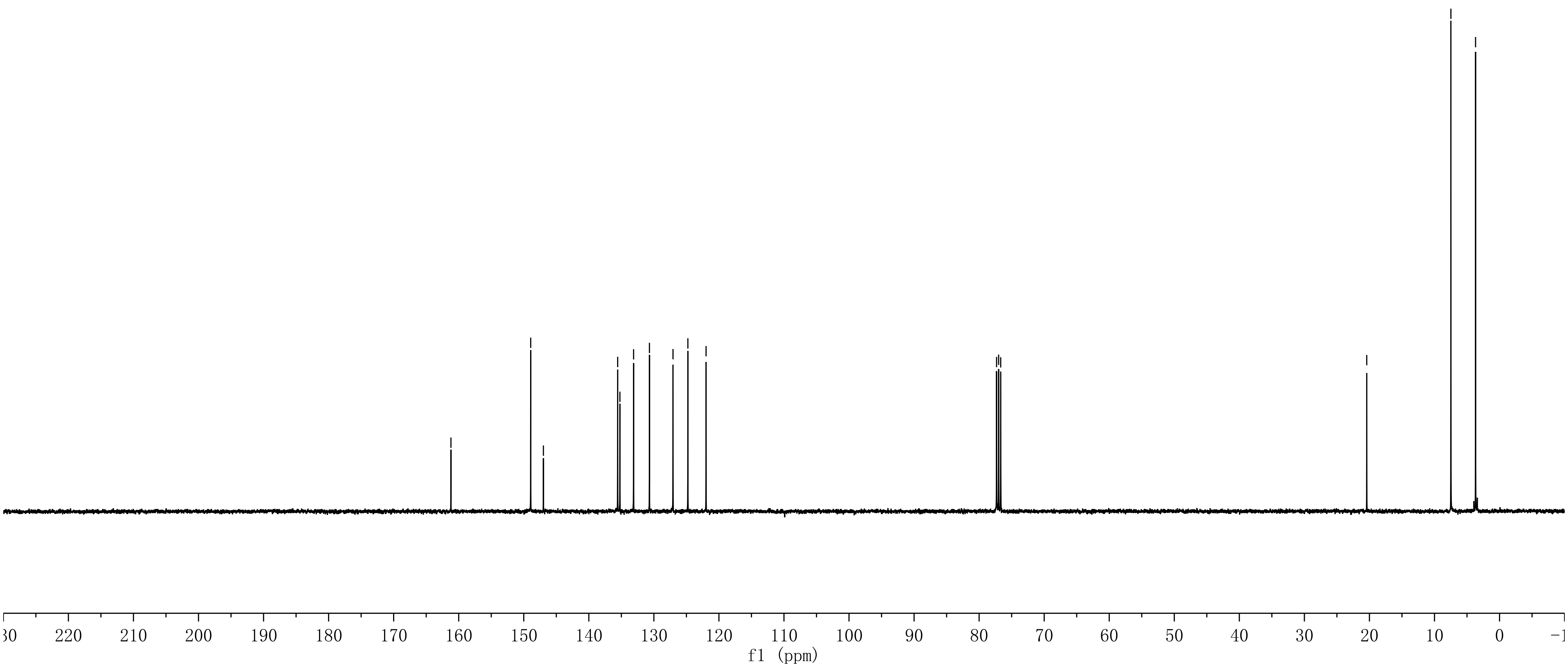


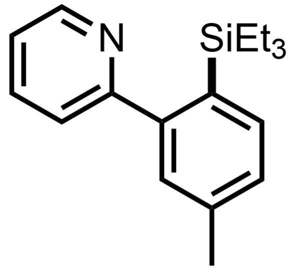

8.68
8.67
7.72
7.72
7.70
7.70
7.68
7.68
7.44
7.42
7.28
7.26
7.24
2.02
0.82
0.80
0.78
0.39
0.37
0.35
0.33
-0.00
SiEt3
N
2b
1H NMR spectrum (400 MHz, CDCl3)
0.99
1.02
1.00
4.24
3.18
9.46
6.33
f1 (ppm)



2b

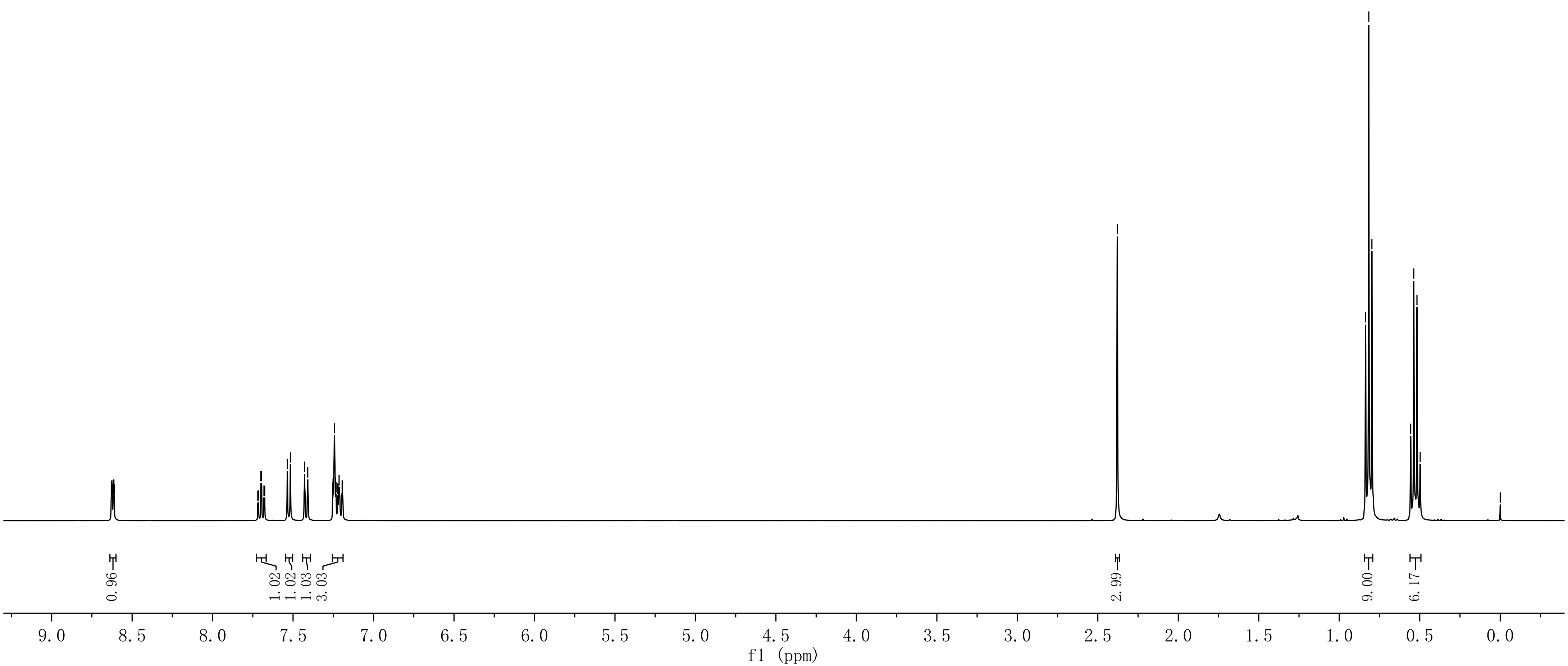
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

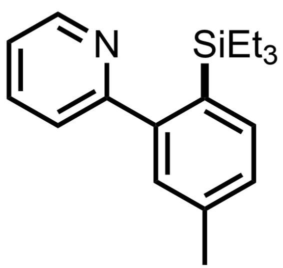




2c

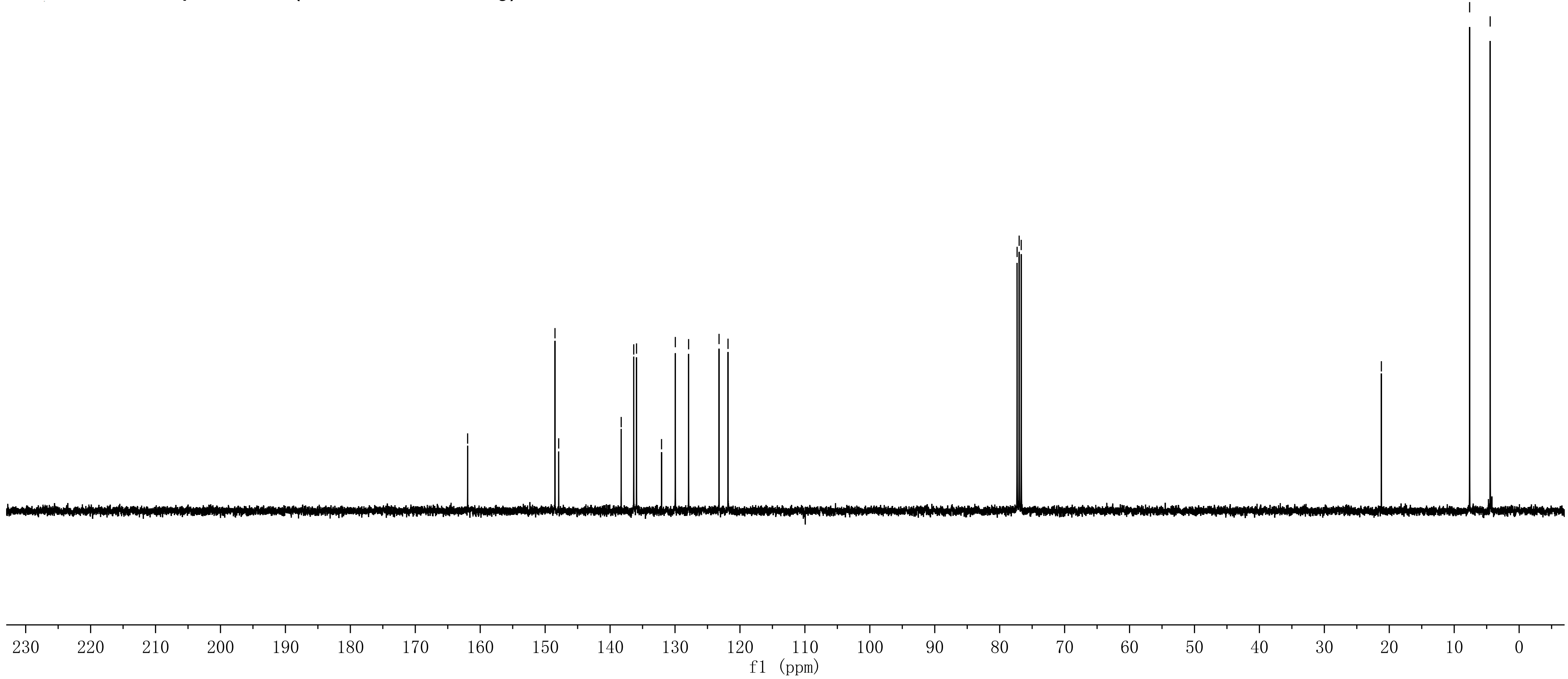
[1]H NMR spectrum (400 MHz, $CDCl_3$)

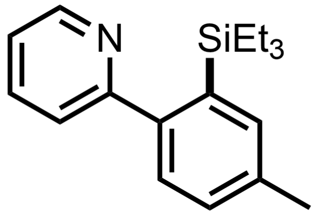




2c

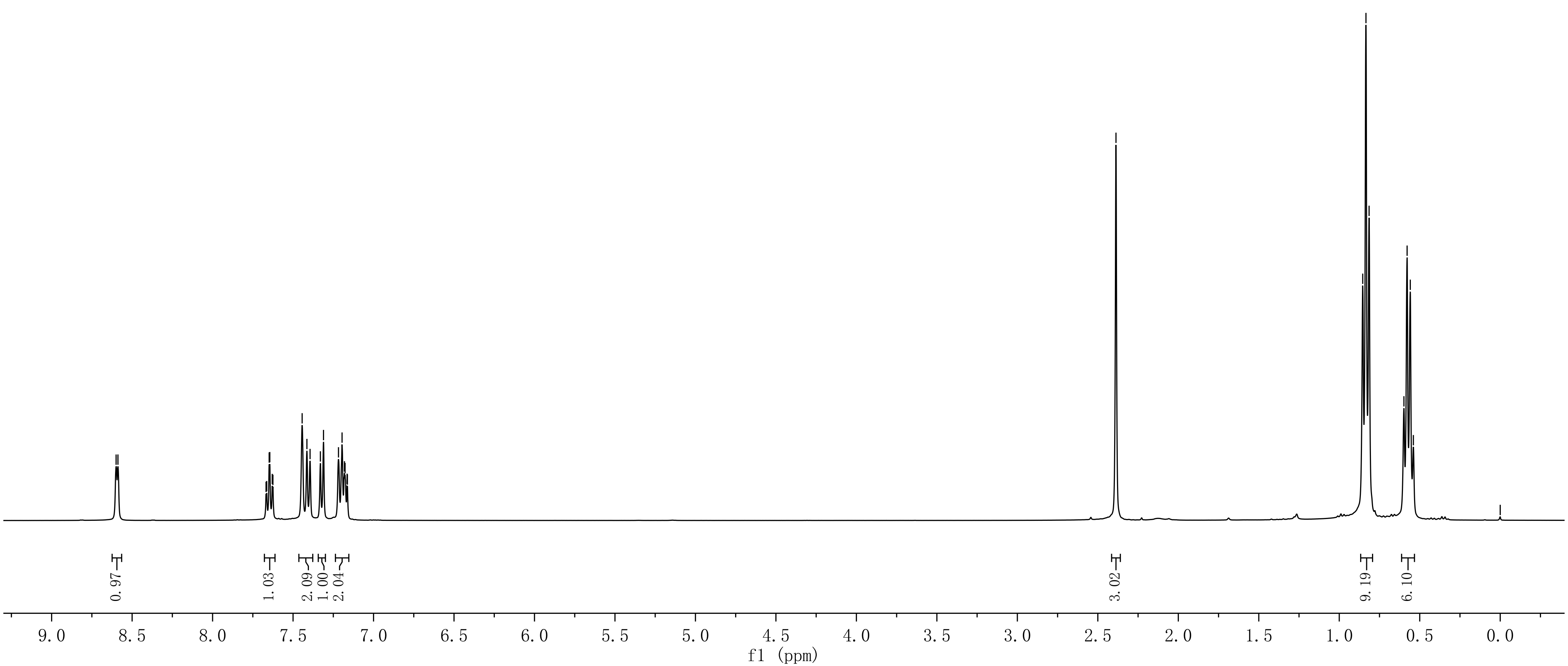
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

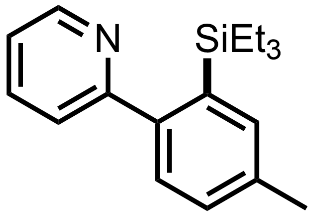




2d

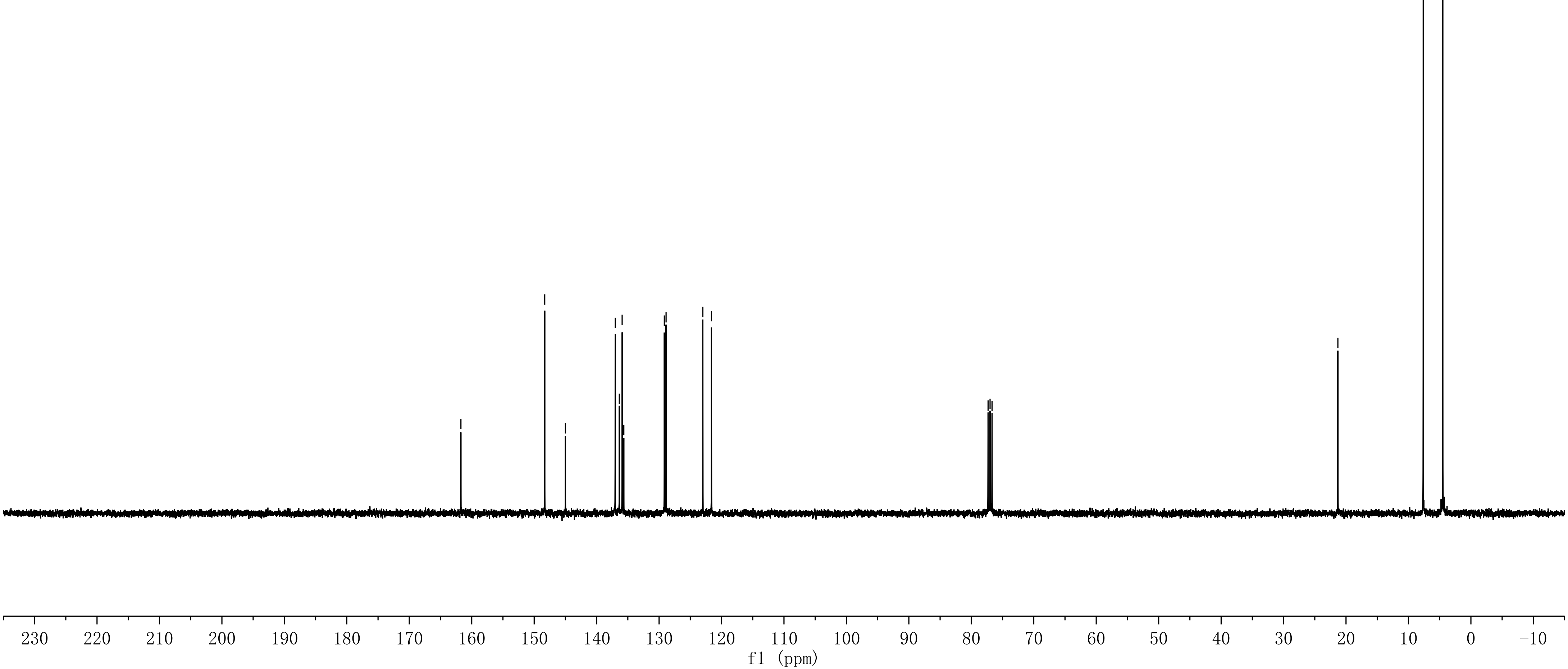
[1]H NMR spectrum (400 MHz, $CDCl_3$)

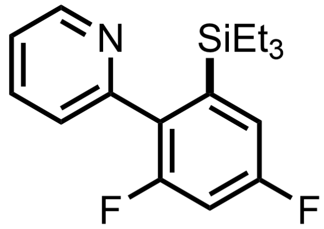




2d

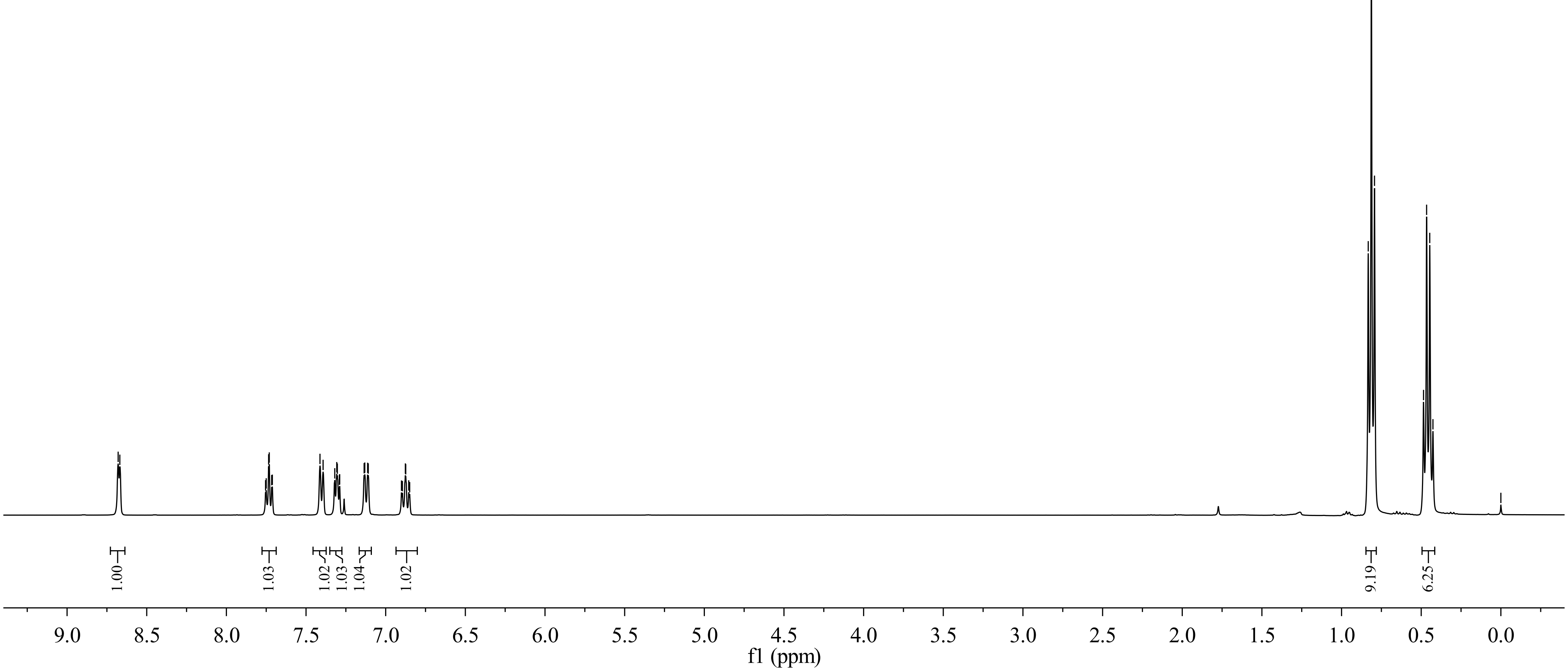
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

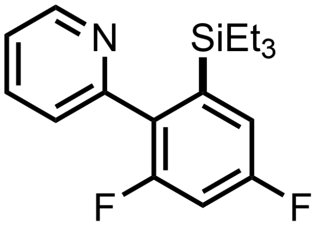




2e

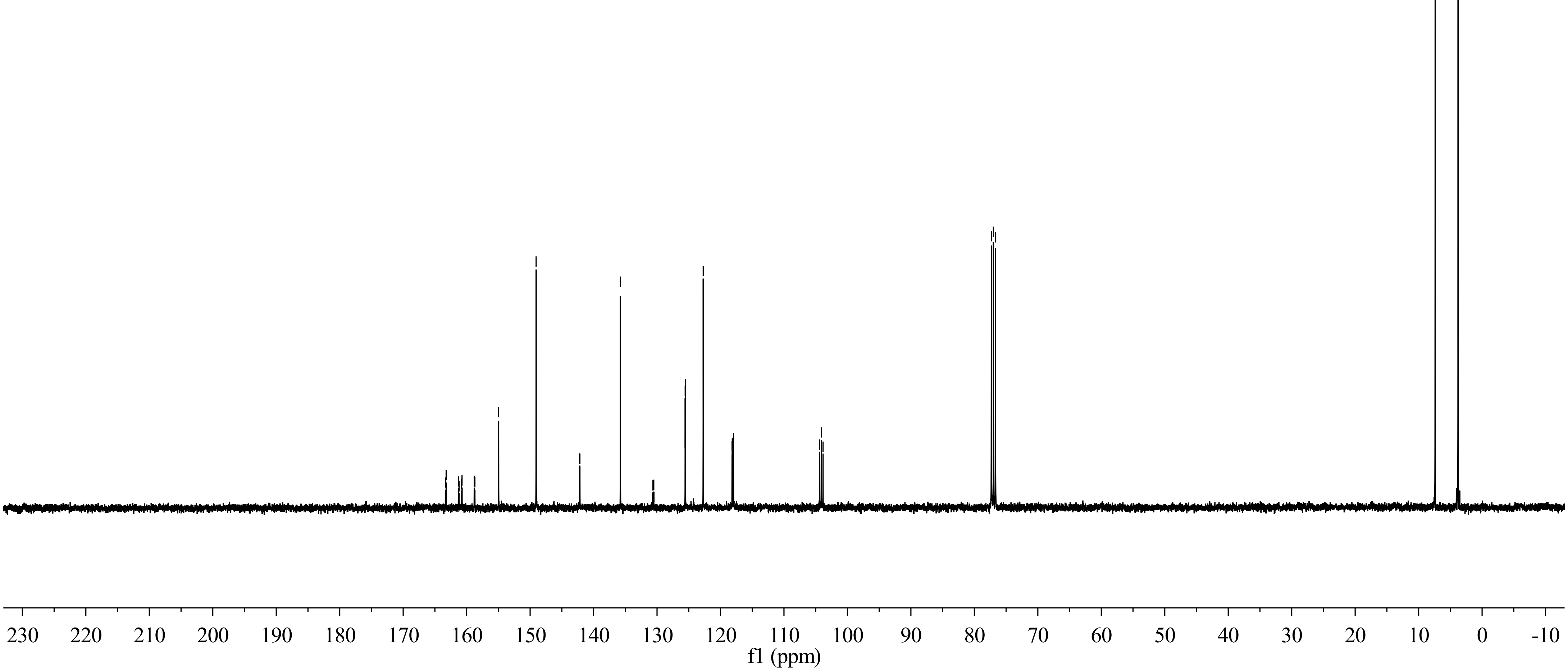
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

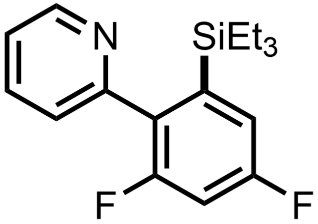




2e

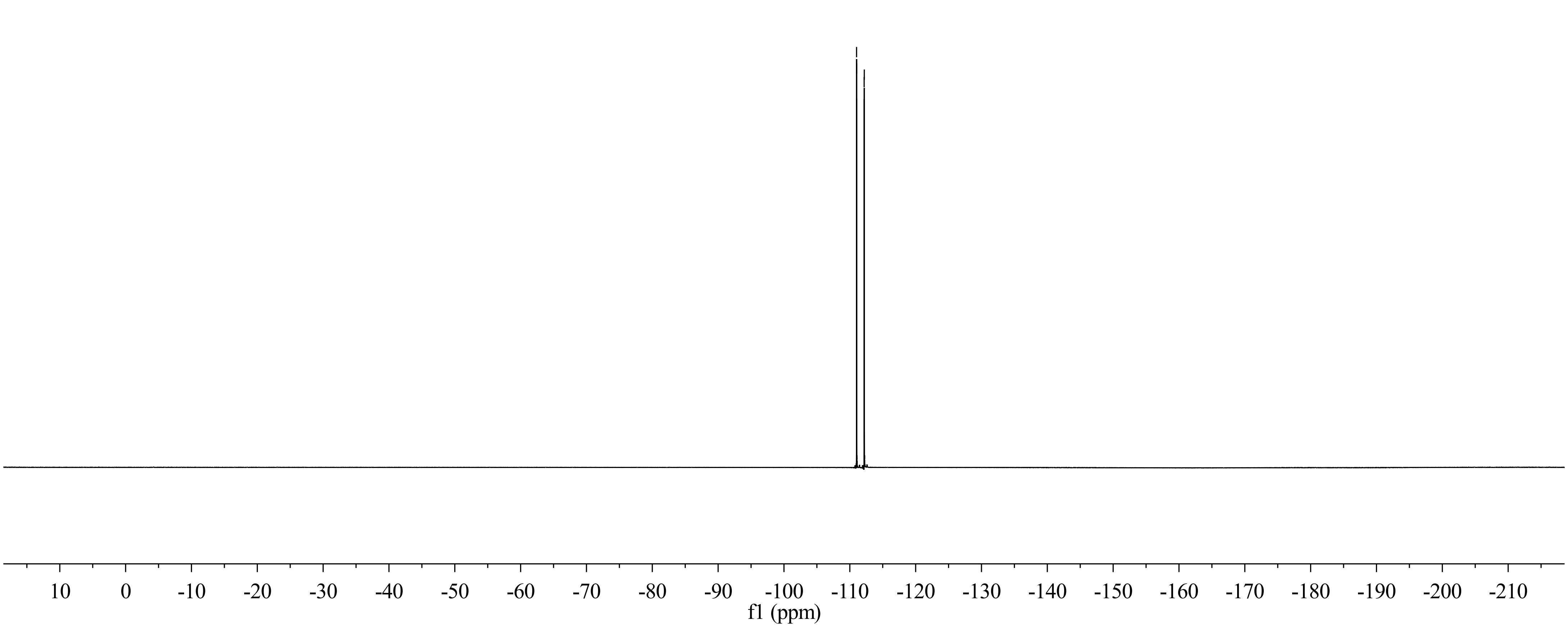
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

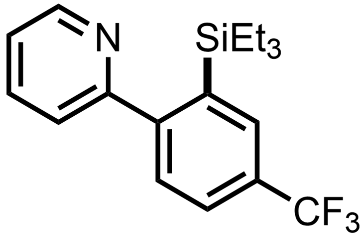




2e

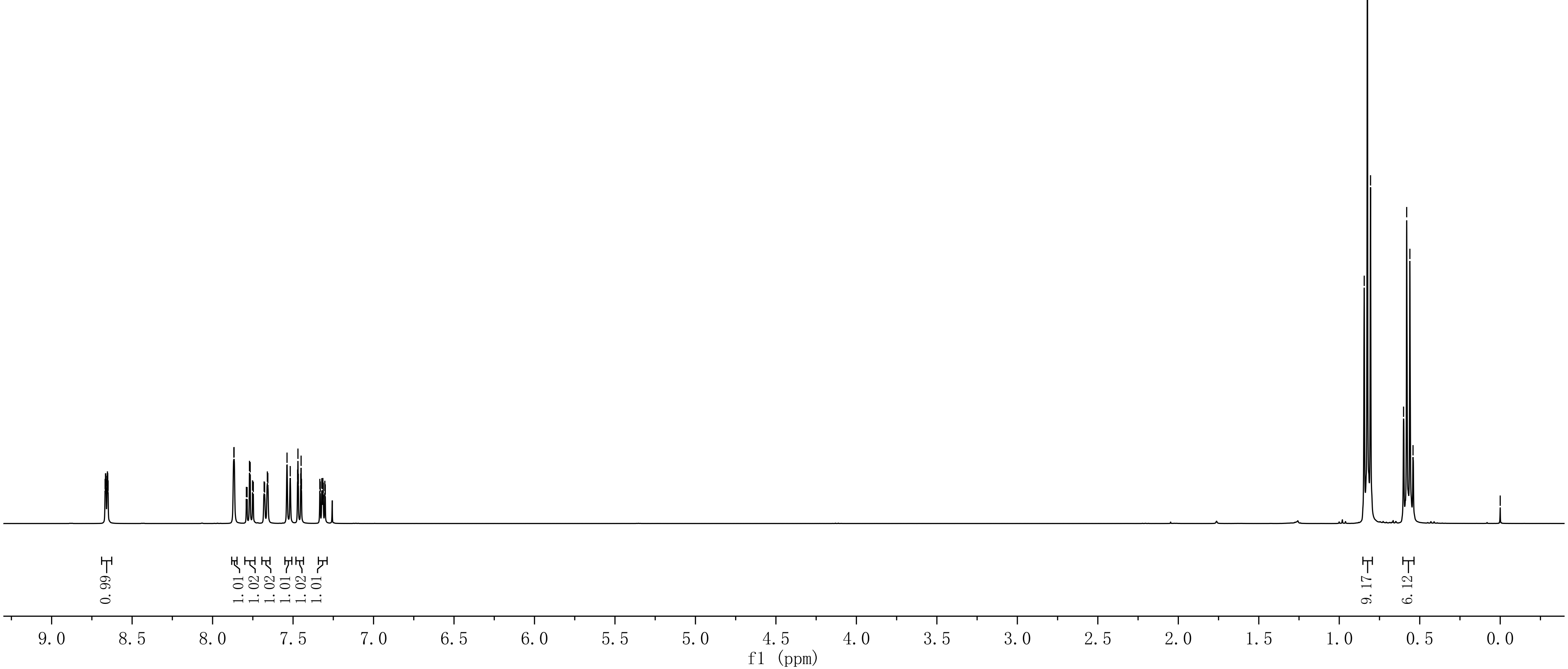
^{19}F NMR spectrum (376 MHz, $CDCl_3$)

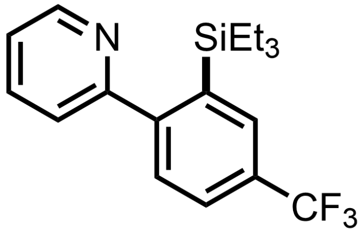




2f

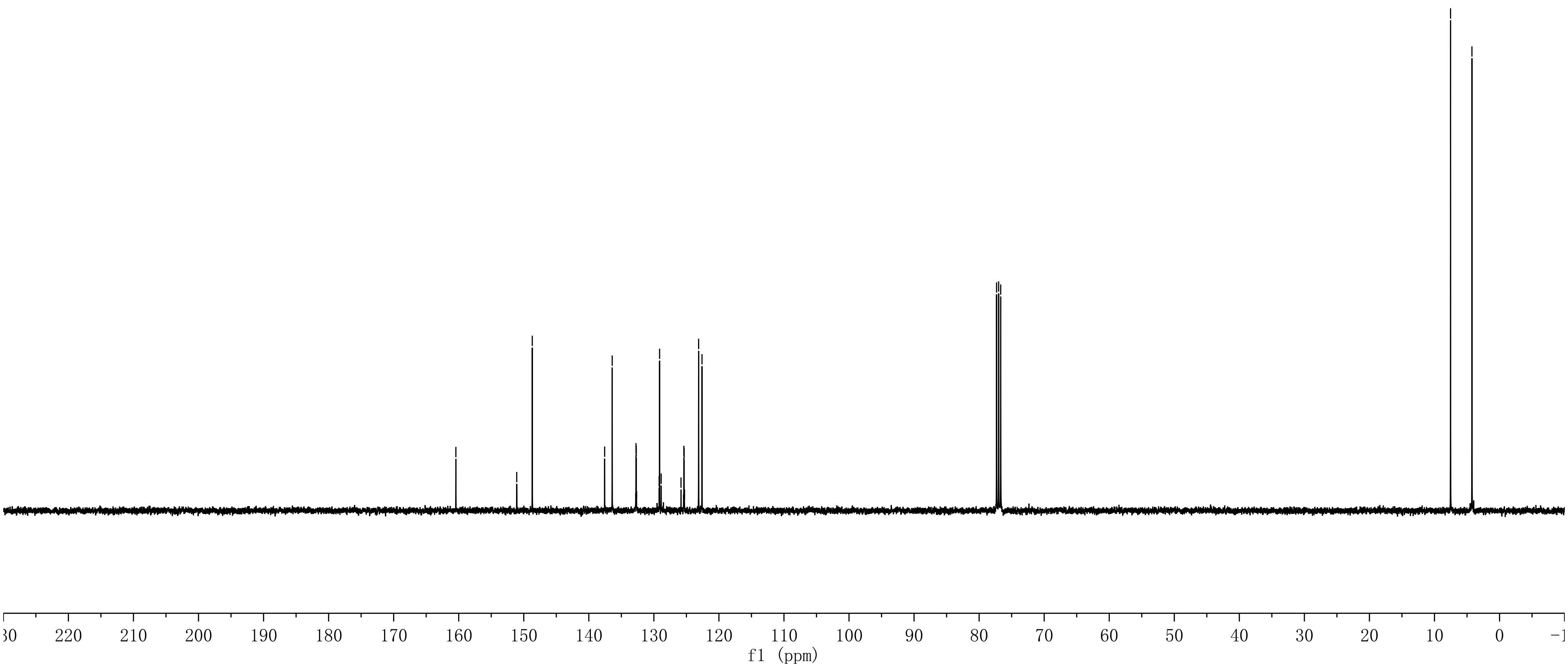
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

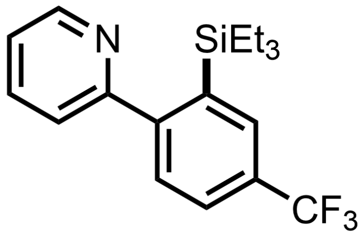




2f

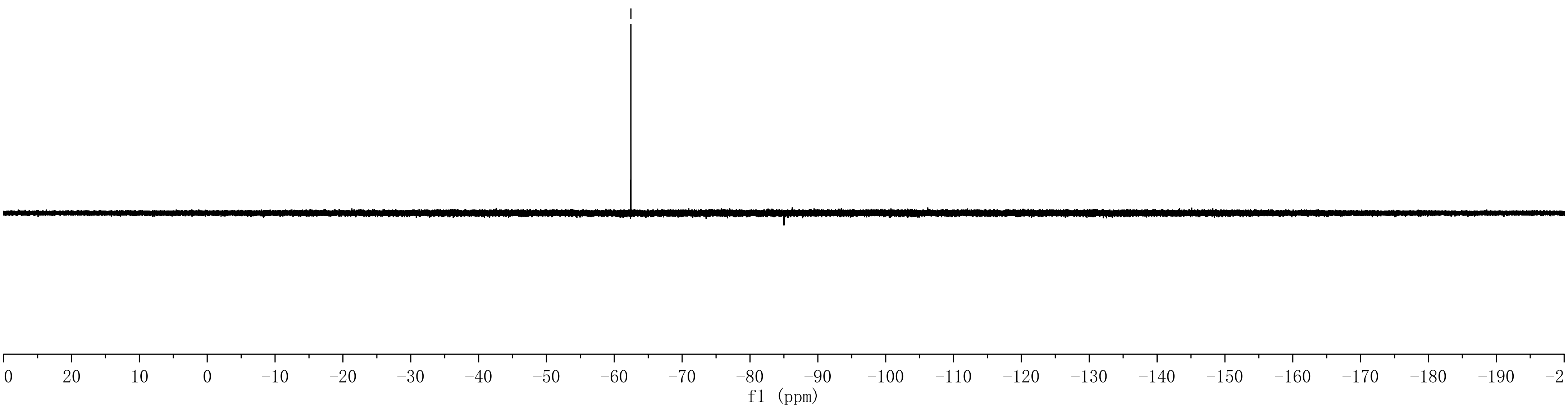
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

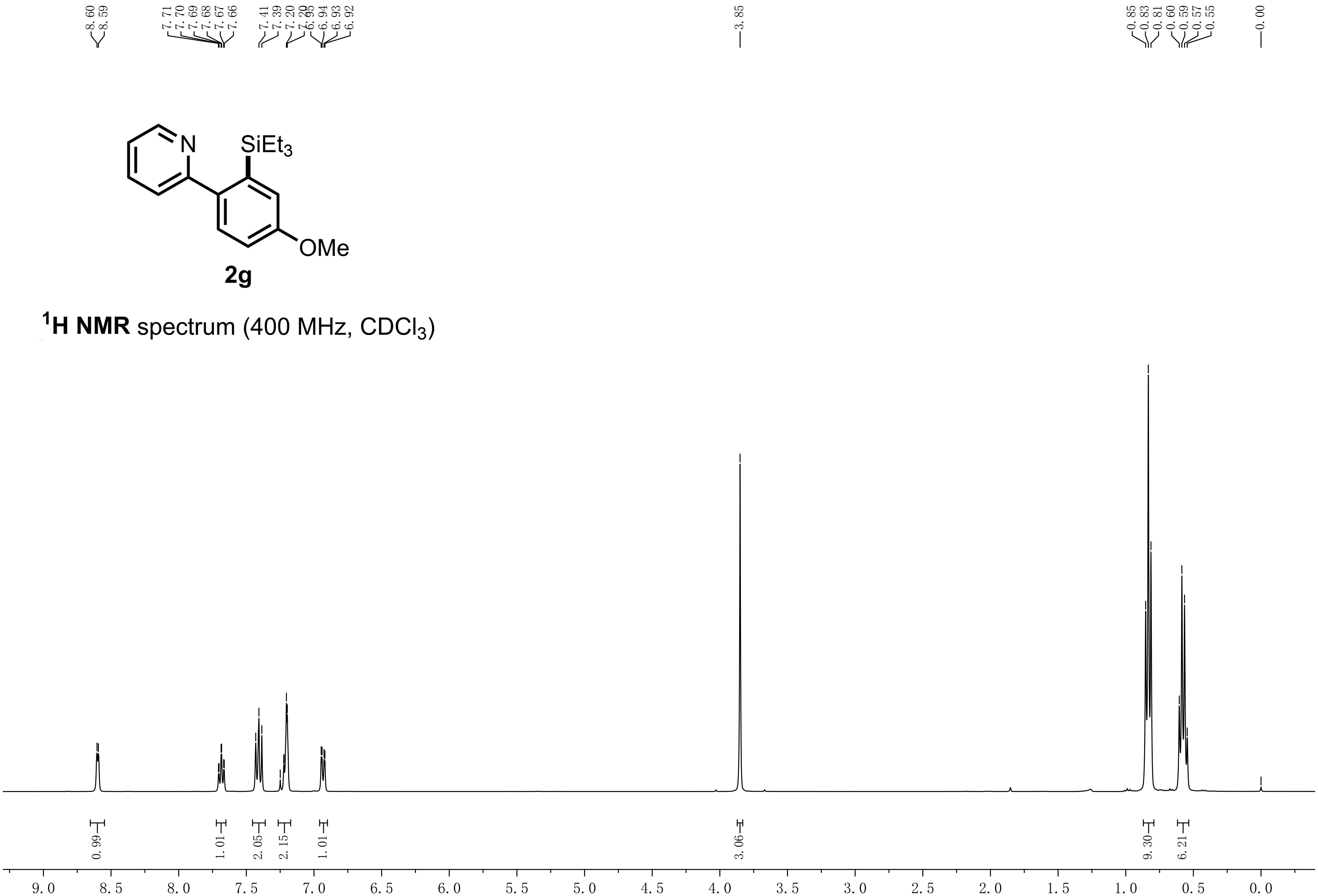




2f

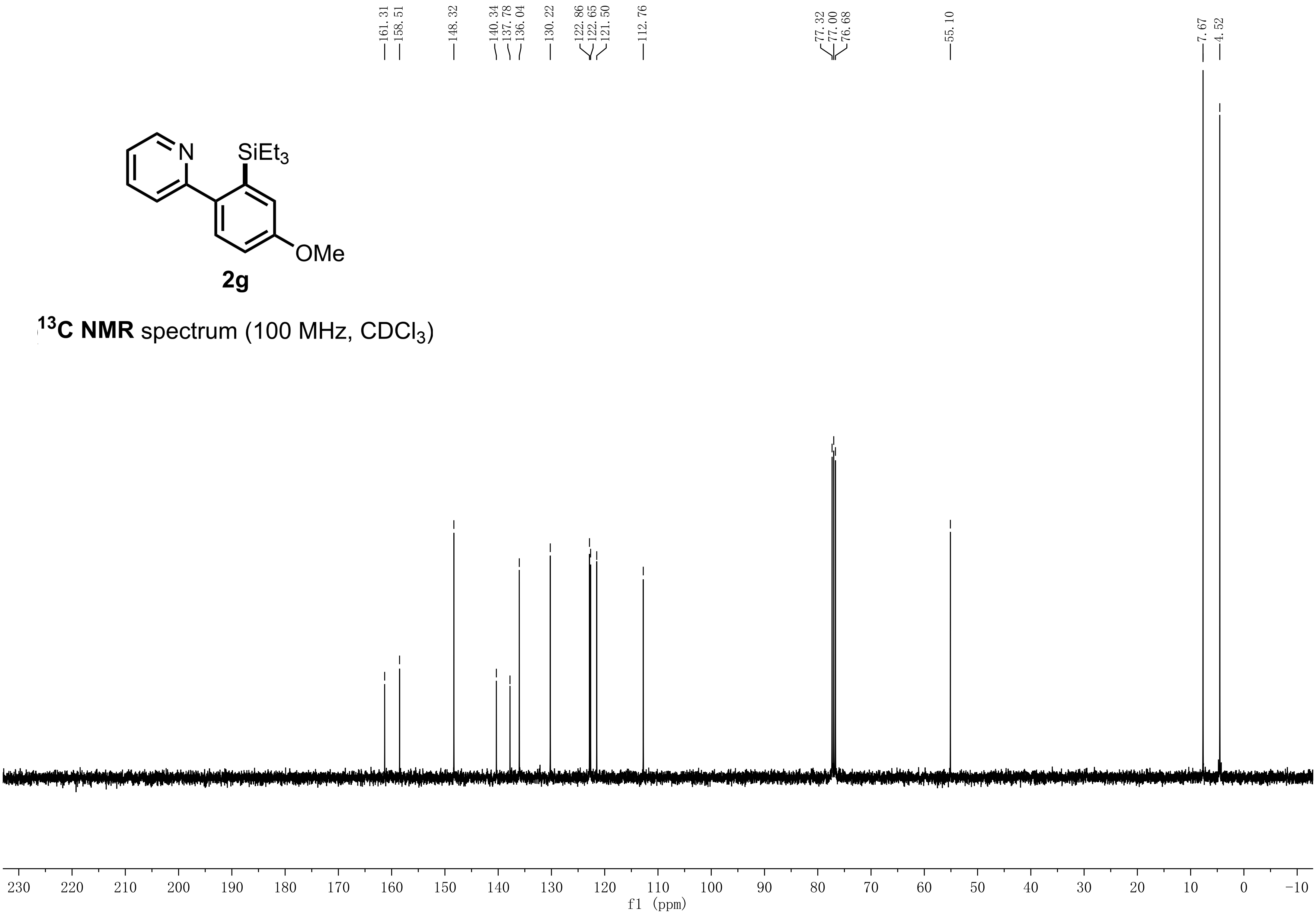
^{19}F NMR spectrum (564 MHz, $CDCl_3$)





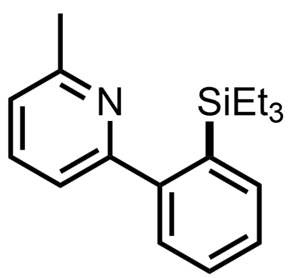
2g

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



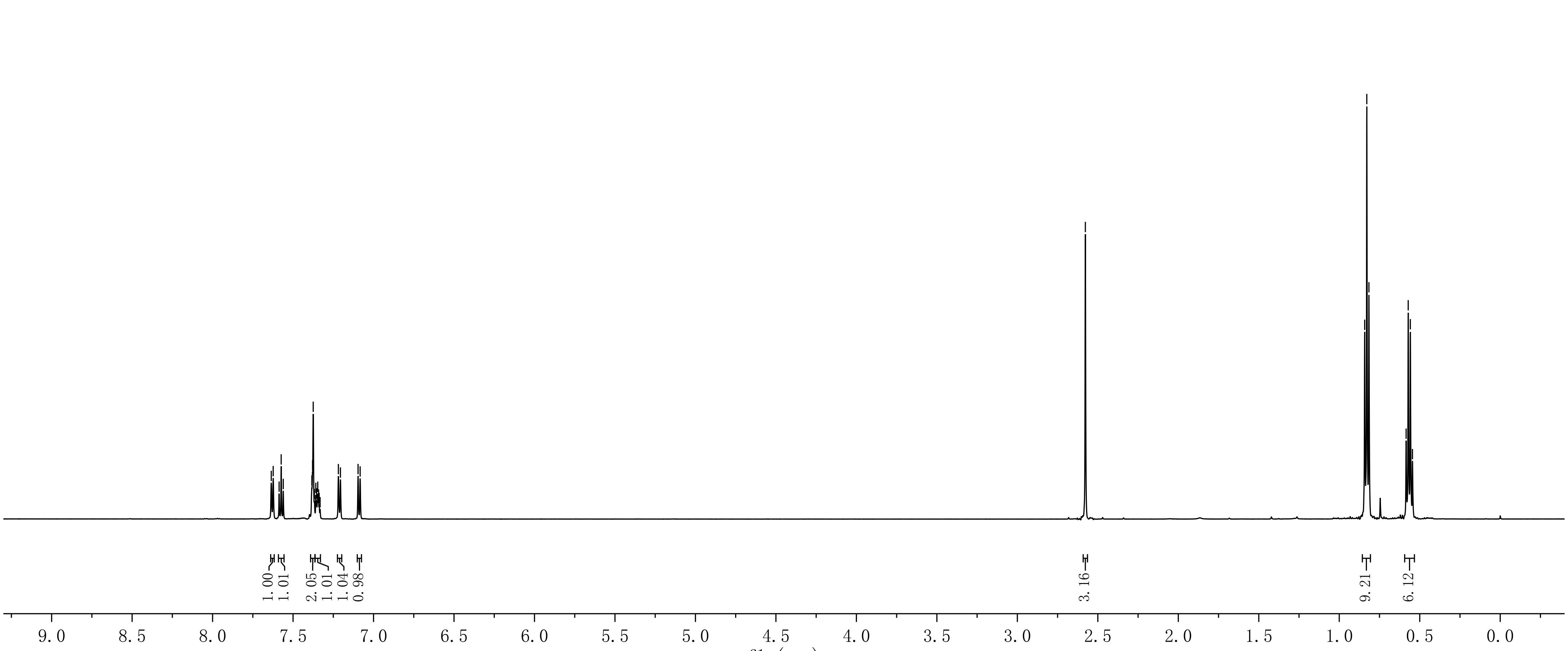
2g

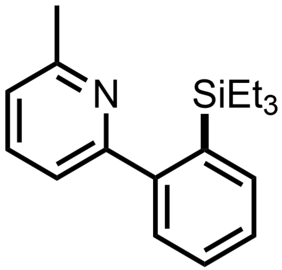
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



2h

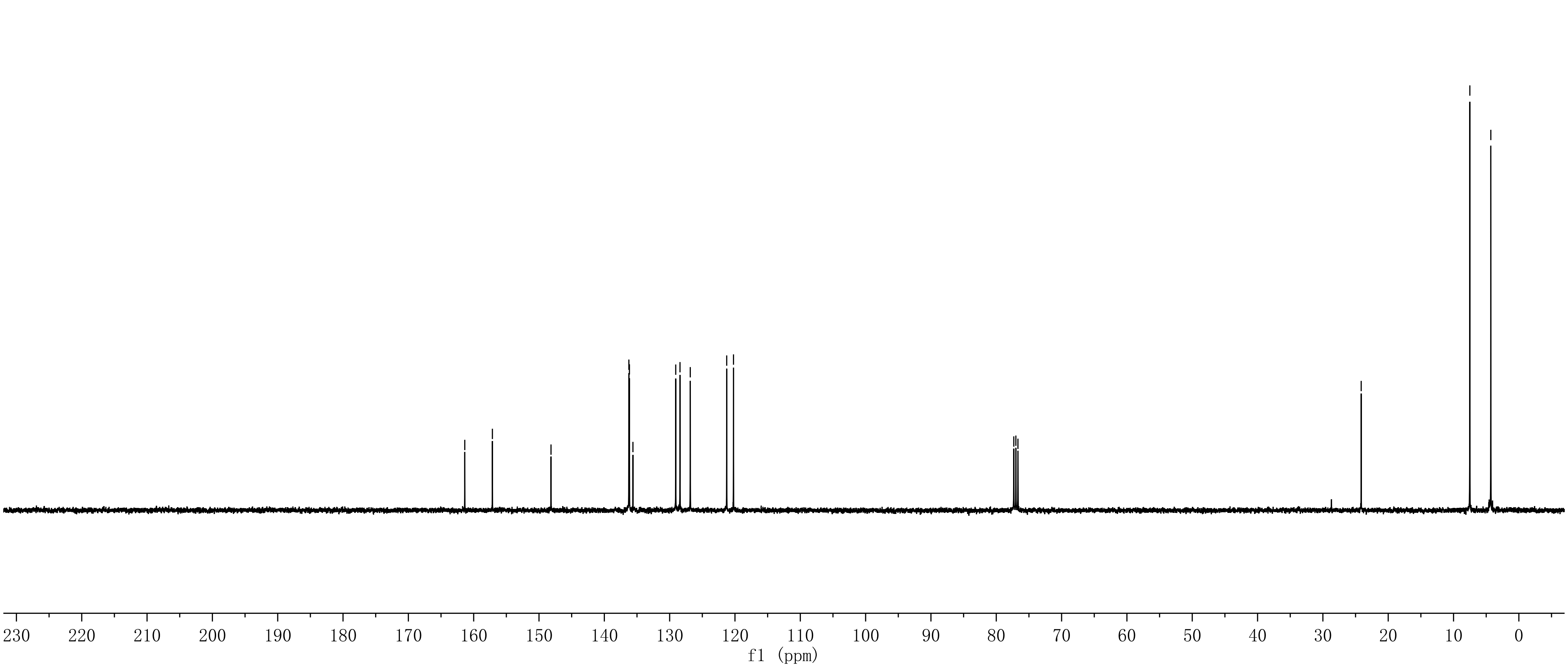
^{1}H NMR spectrum (600 MHz, $CDCl_3$)

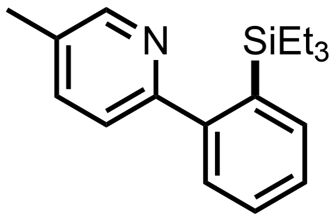




2h

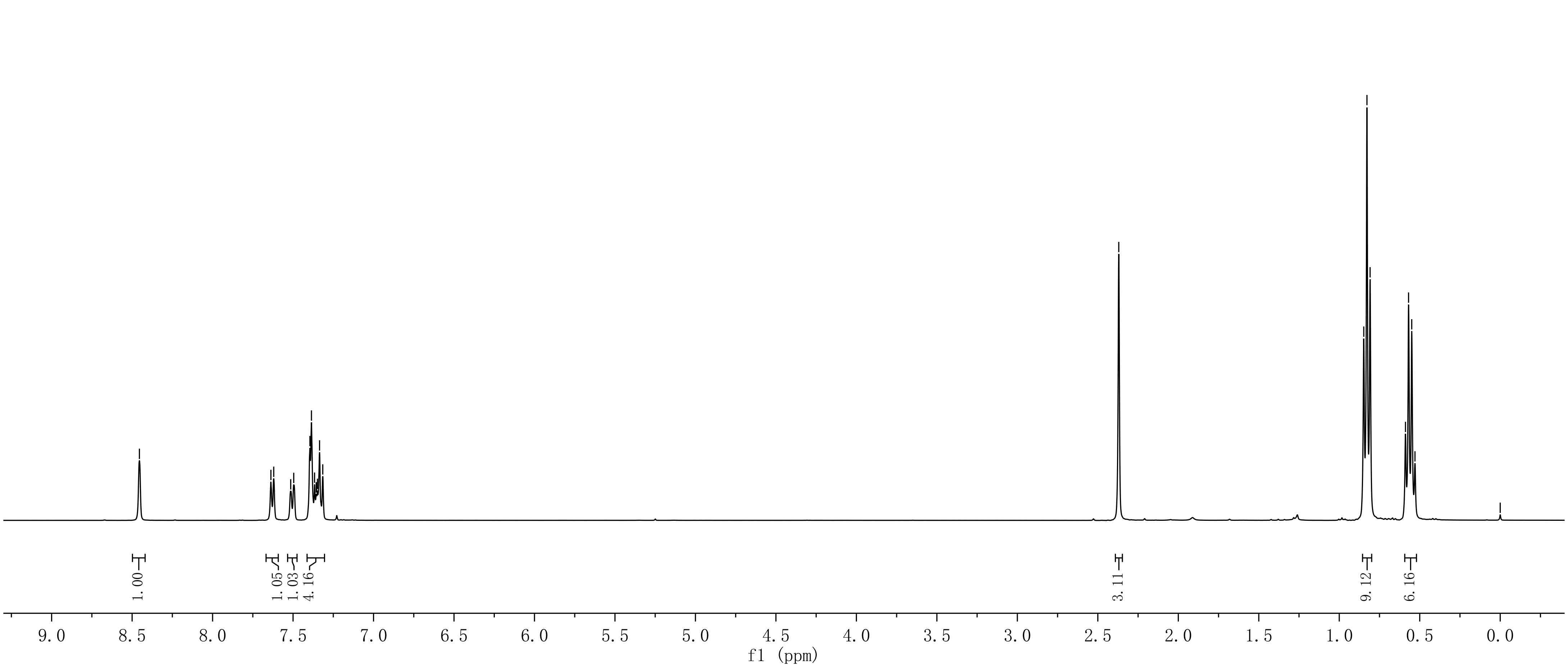
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

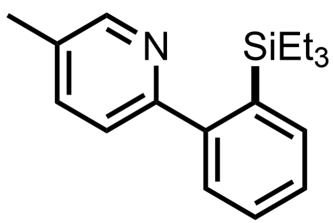




2i

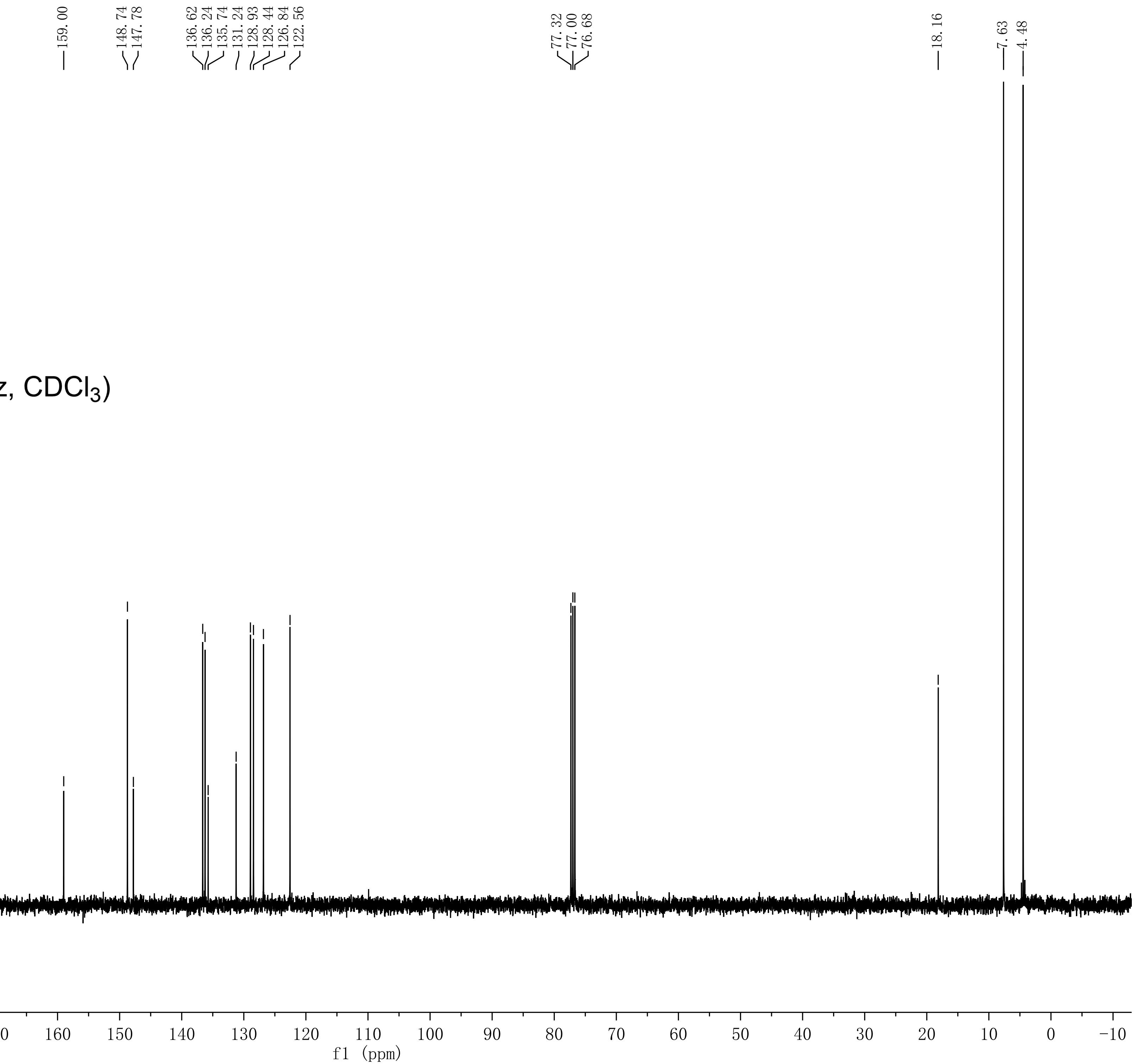
[1]H NMR spectrum (400 MHz, $CDCl_3$)

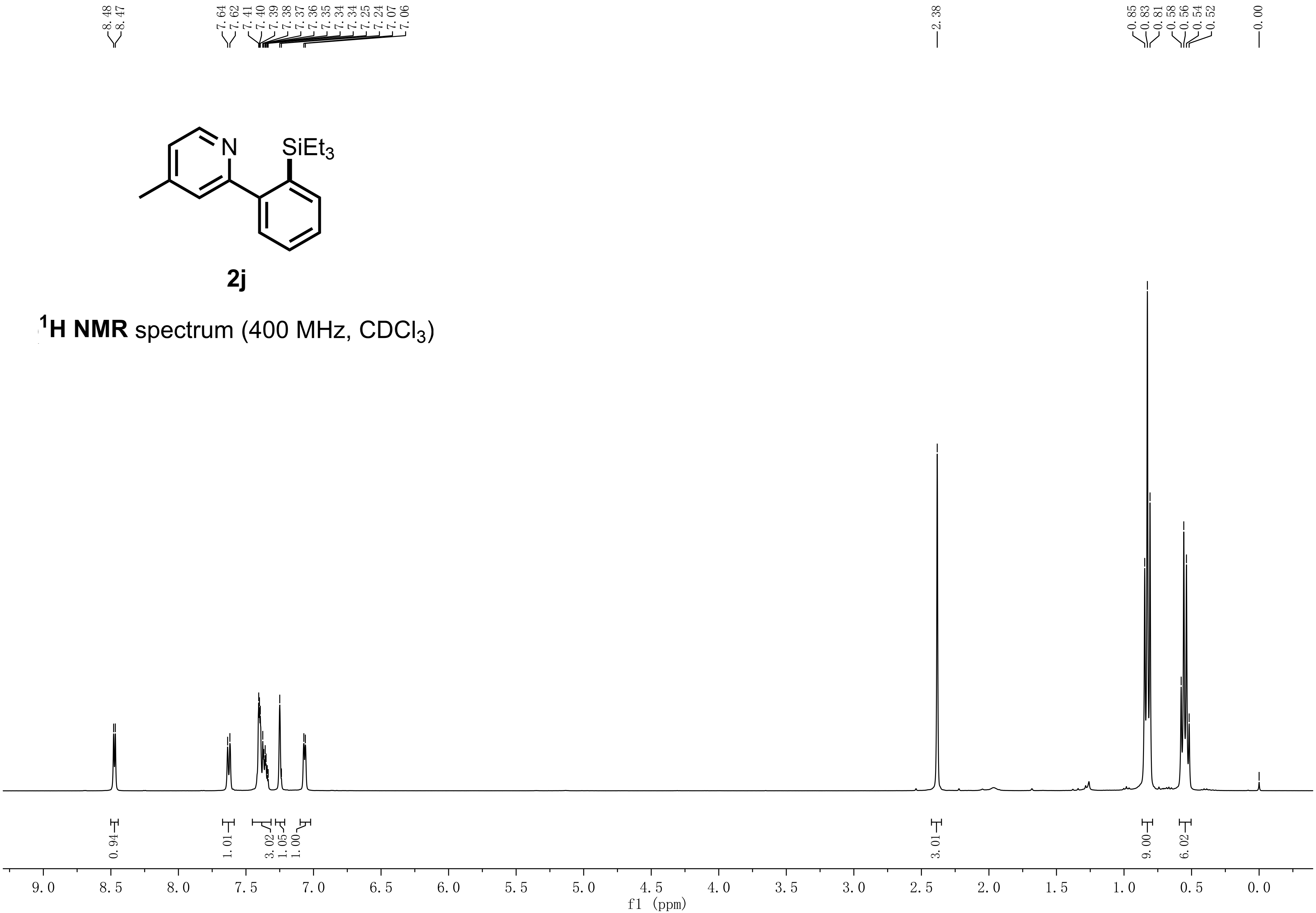


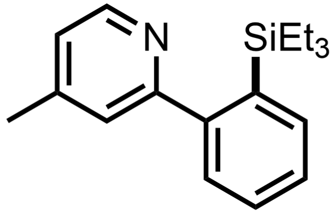


2i

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

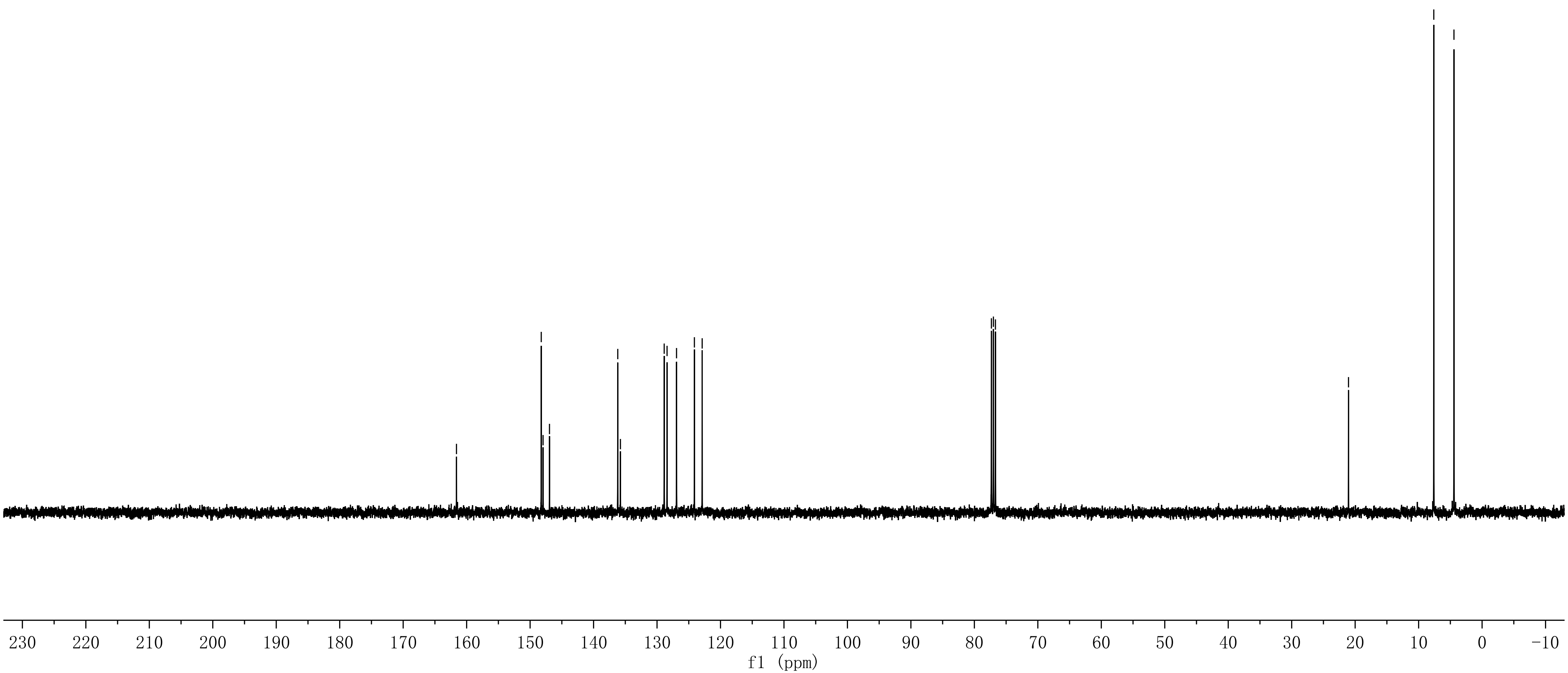


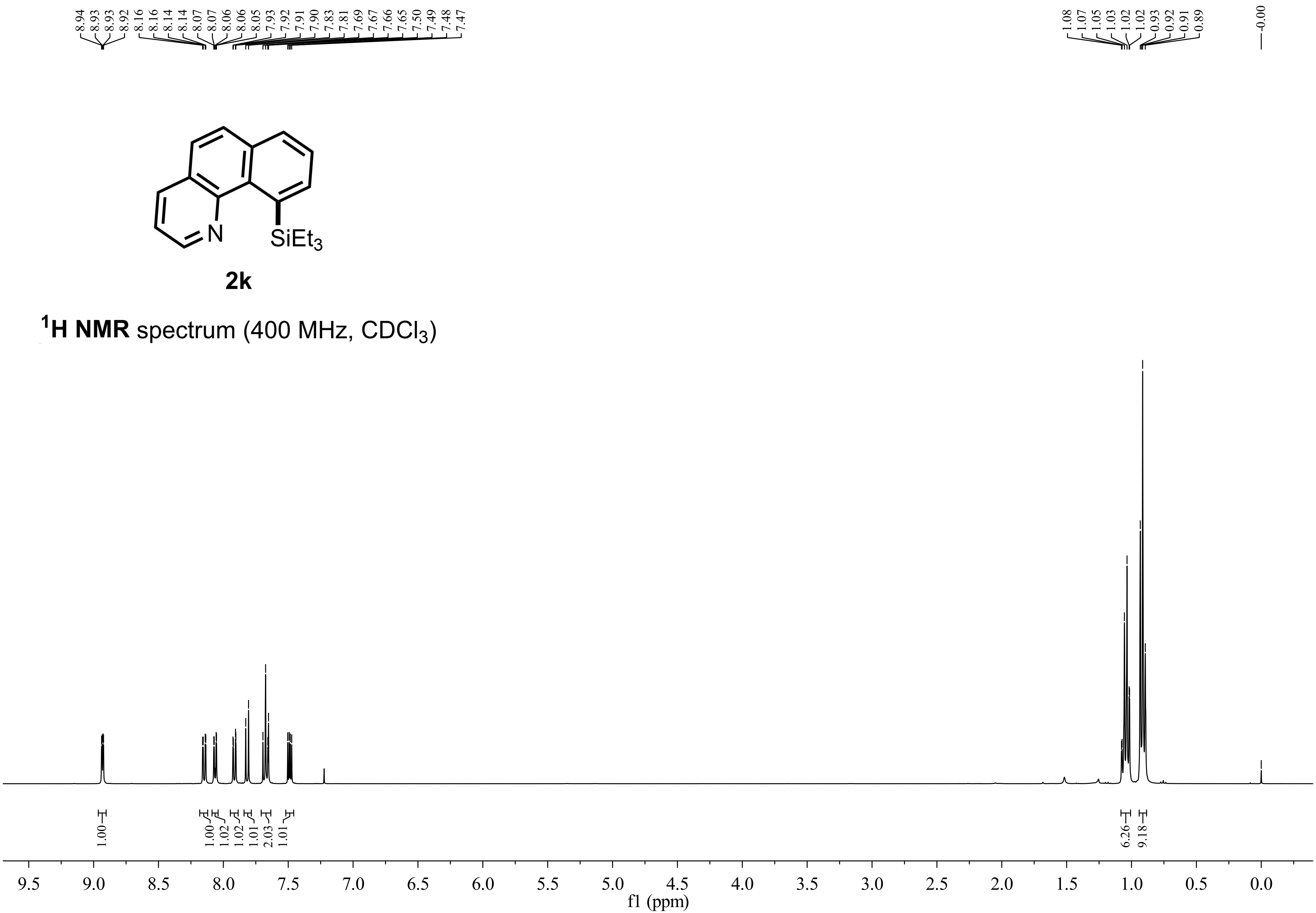

8.48
8.47
7.64
7.62
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.25
7.24
7.07
7.06
2.38
0.85
0.83
0.81
0.58
0.56
0.54
0.52
0.00
N
SiEt3
2j
1H NMR spectrum (400 MHz, CDCl3)
0.94
1.01
3.02
1.05
1.00
3.01
9.00
6.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

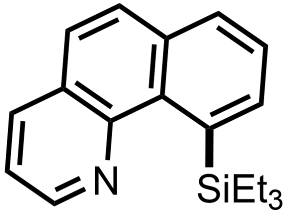


2j

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

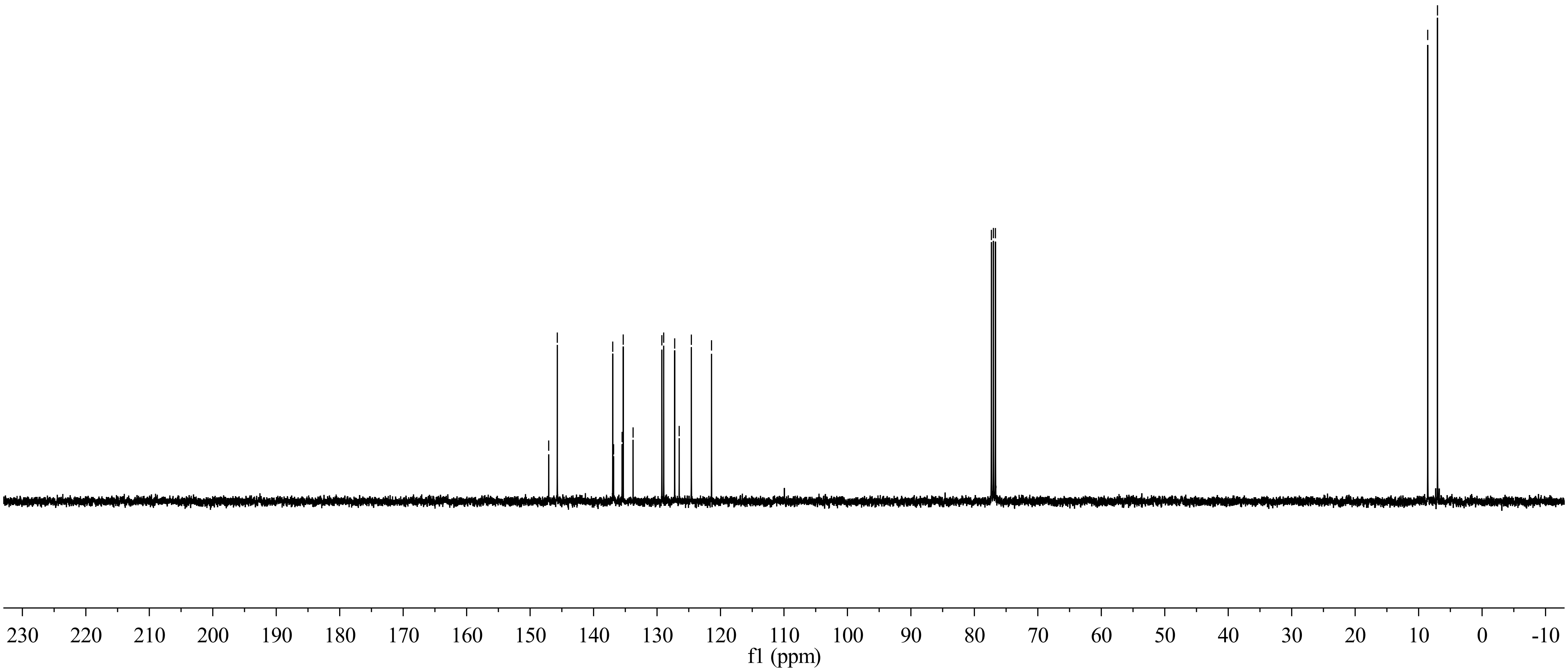


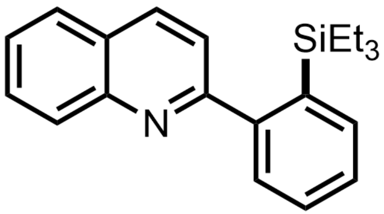

8.94
8.93
8.93
8.92
8.16
8.16
8.14
8.14
8.07
8.07
8.06
8.06
8.05
7.93
7.92
7.91
7.90
7.83
7.81
7.69
7.67
7.66
7.65
7.50
7.49
7.48
7.47
1.08
1.07
1.05
1.03
1.02
1.02
0.93
0.92
0.91
0.89
-0.00
N
SiEt3
2k
1H NMR spectrum (400 MHz, CDCl3)
1.00
1.00
1.02
1.02
1.01
2.03
1.01
6.26
9.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2k

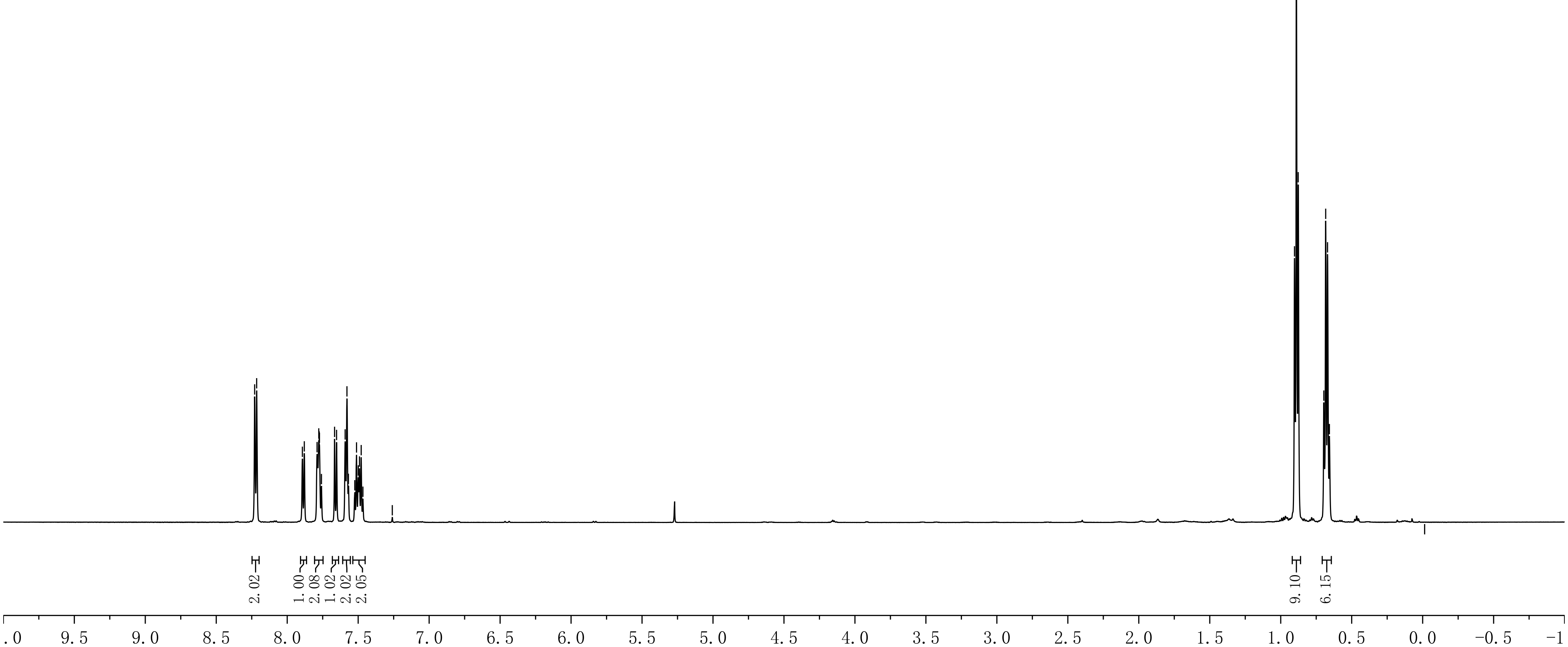
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

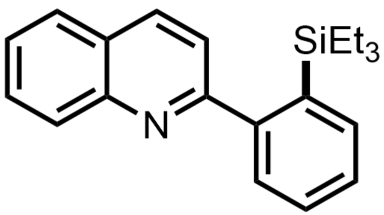




2l

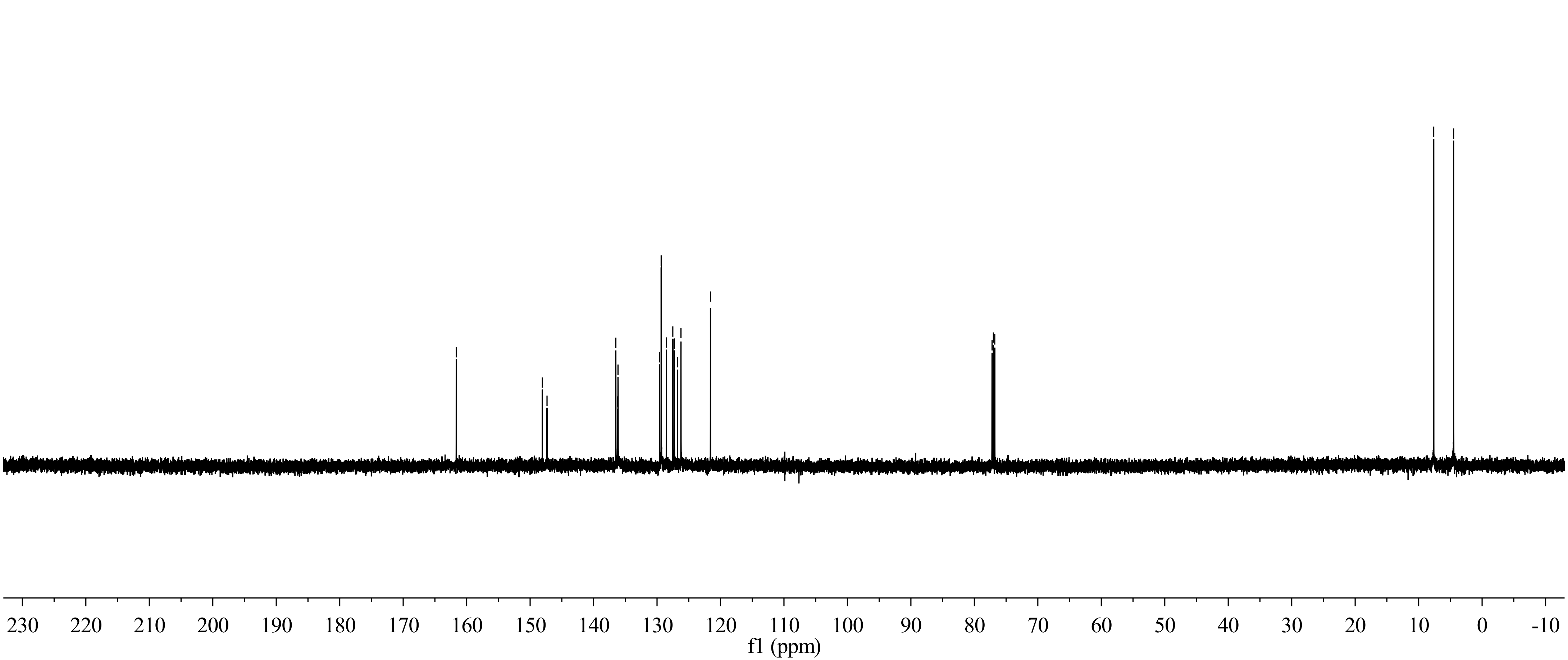
[1]**H NMR** spectrum (600 MHz, $CDCl_3$)

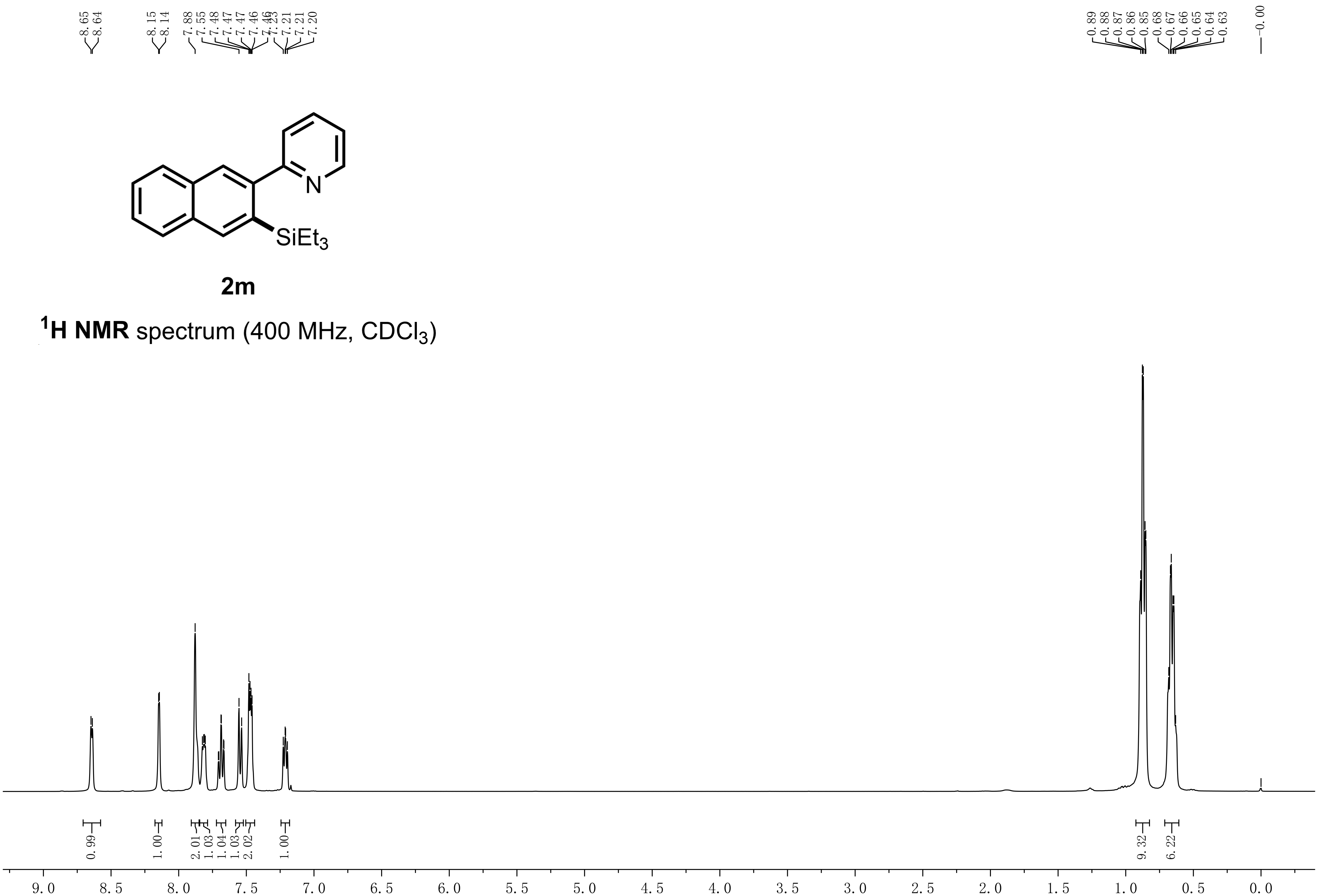




2l

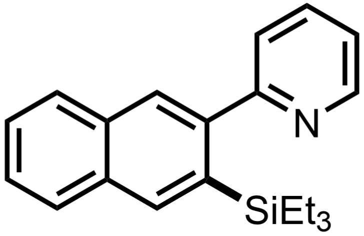
^{13}C NMR spectrum (150 MHz, $CDCl_3$)





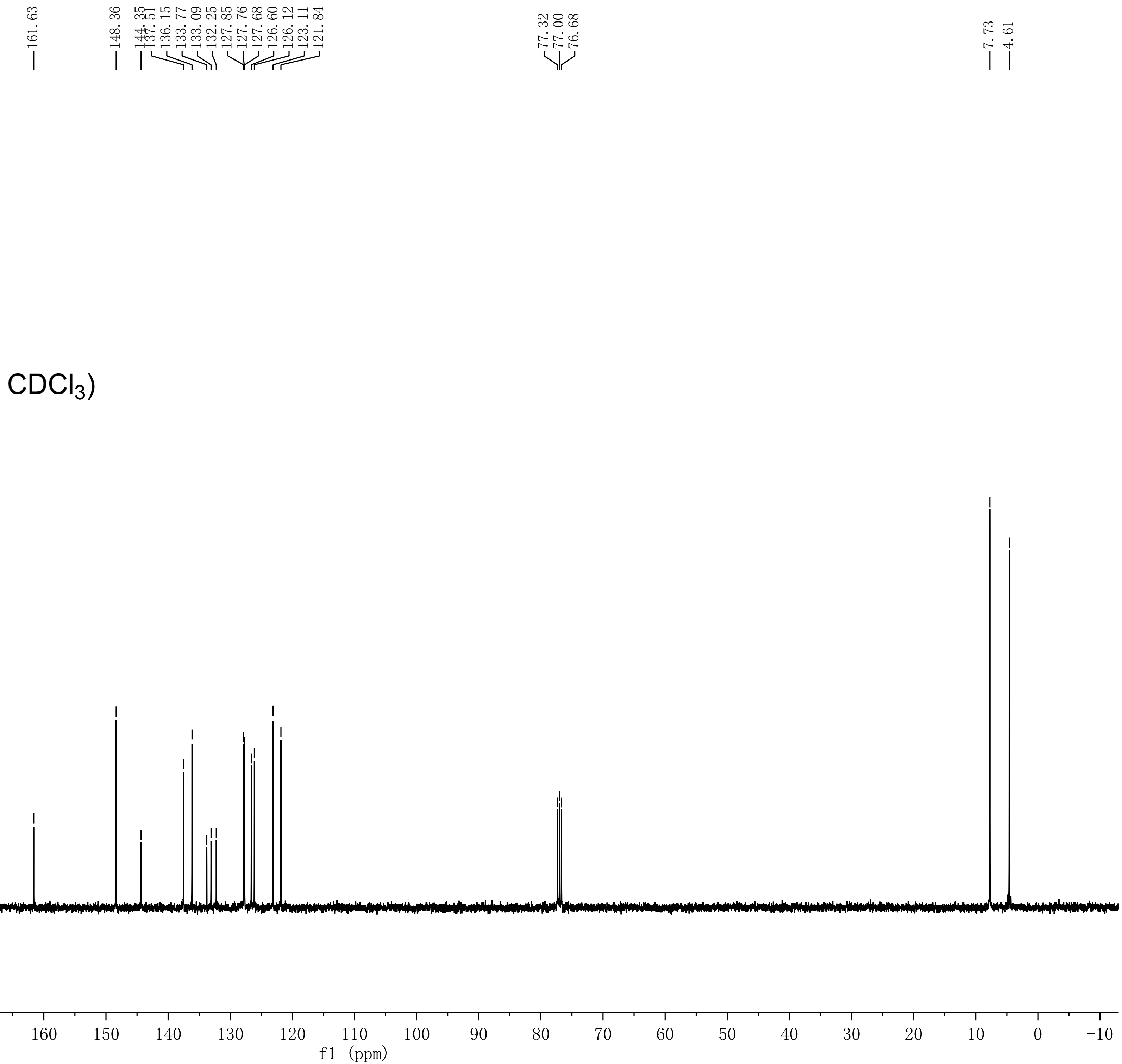
2m

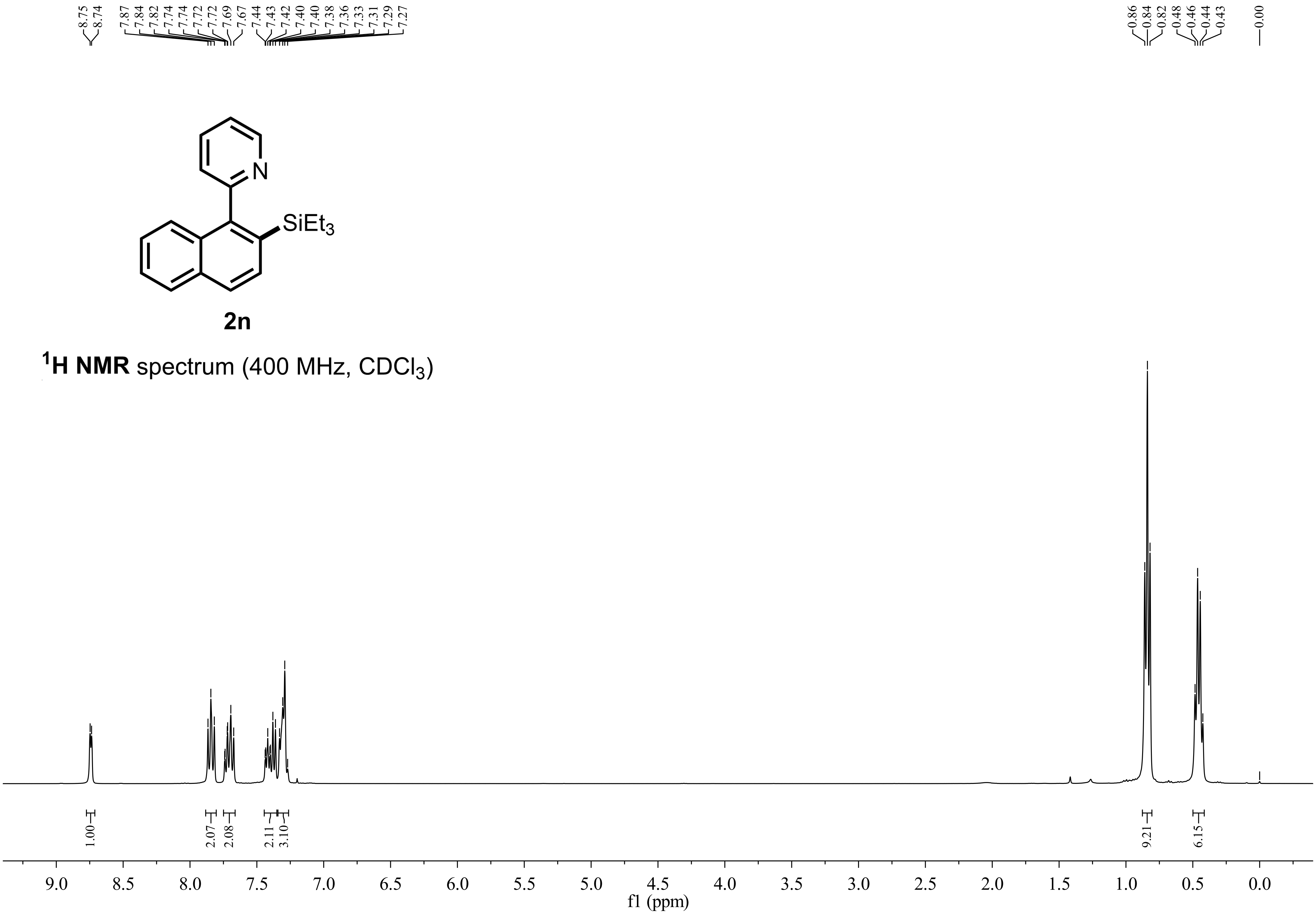
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



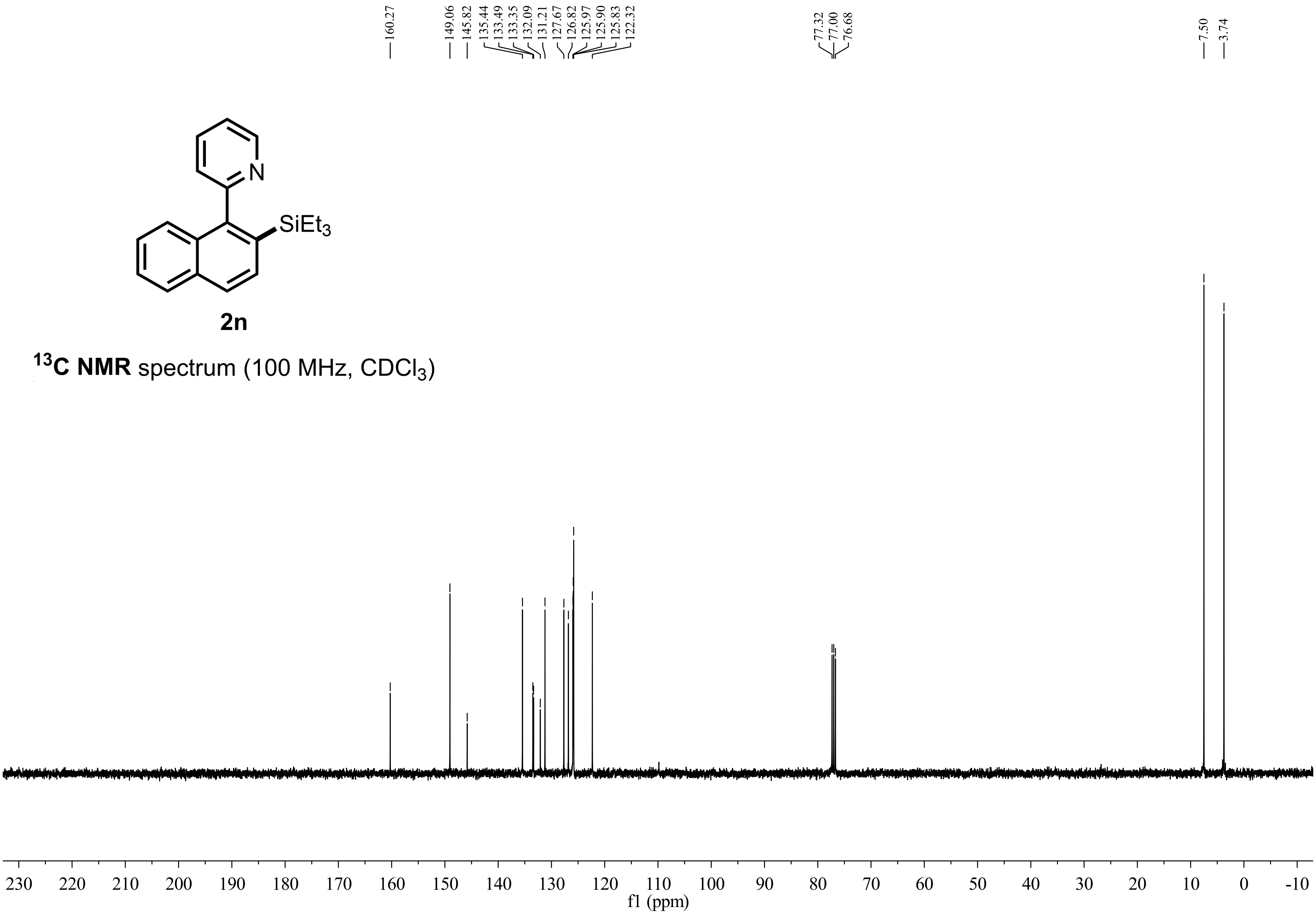
2m

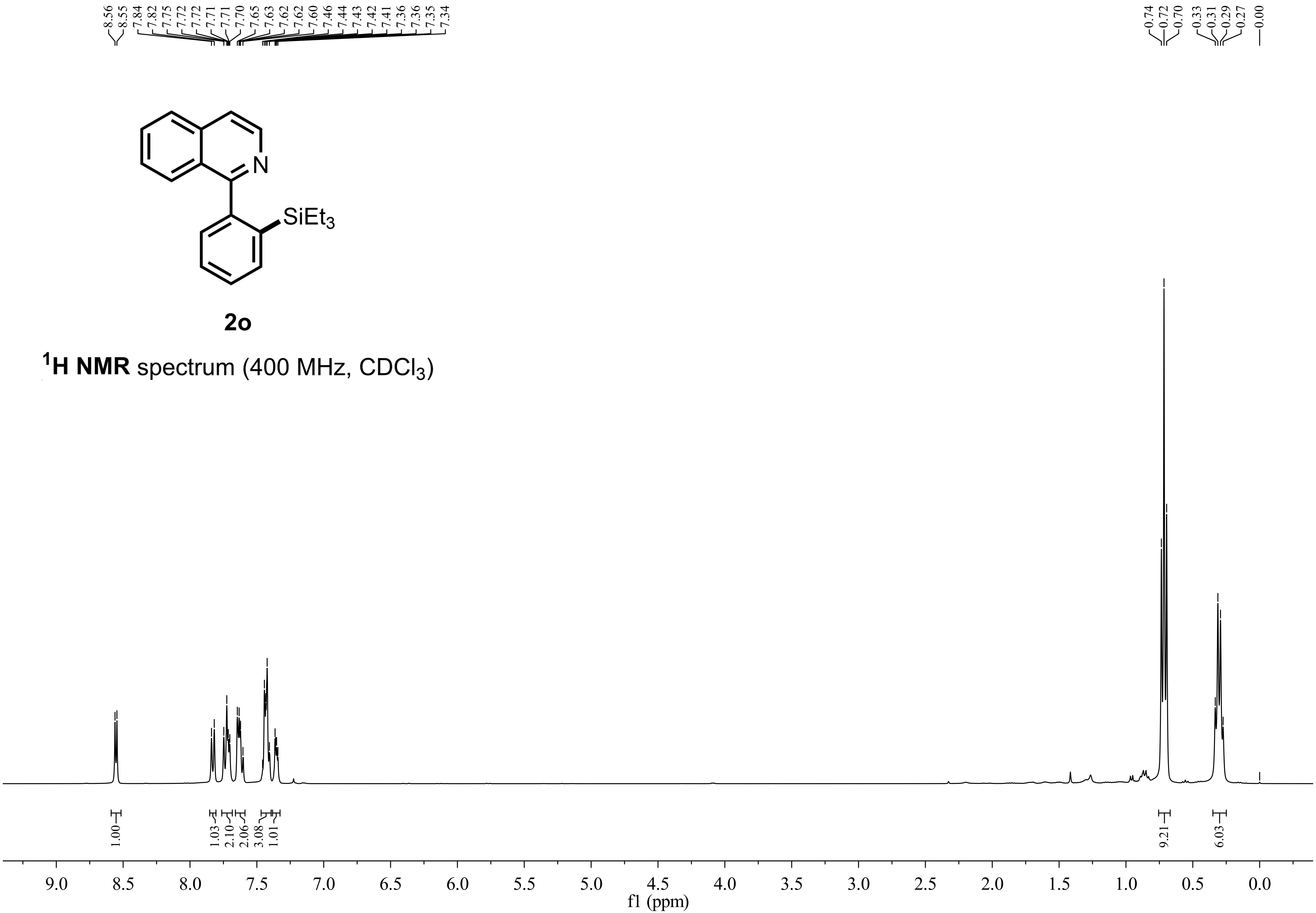
^{13}C NMR spectrum (100 MHz, $CDCl_3$)





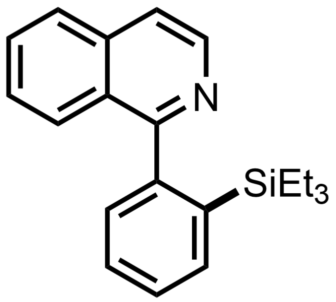
8.75
8.74
7.87
7.84
7.82
7.74
7.74
7.72
7.72
7.69
7.67
7.44
7.43
7.42
7.40
7.40
7.38
7.36
7.33
7.31
7.29
7.27
0.86
0.84
0.82
0.48
0.46
0.44
0.43
0.00
N
SiEt3
2n
1H NMR spectrum (400 MHz, CDCl3)
1.00
2.07
2.08
2.11
3.10
9.21
6.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.27
149.06
145.82
135.44
133.49
133.35
132.09
131.21
127.67
126.82
125.97
125.90
125.83
122.32
77.32
77.00
76.68
7.50
3.74
N
SiEt3
2n
13C NMR spectrum (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



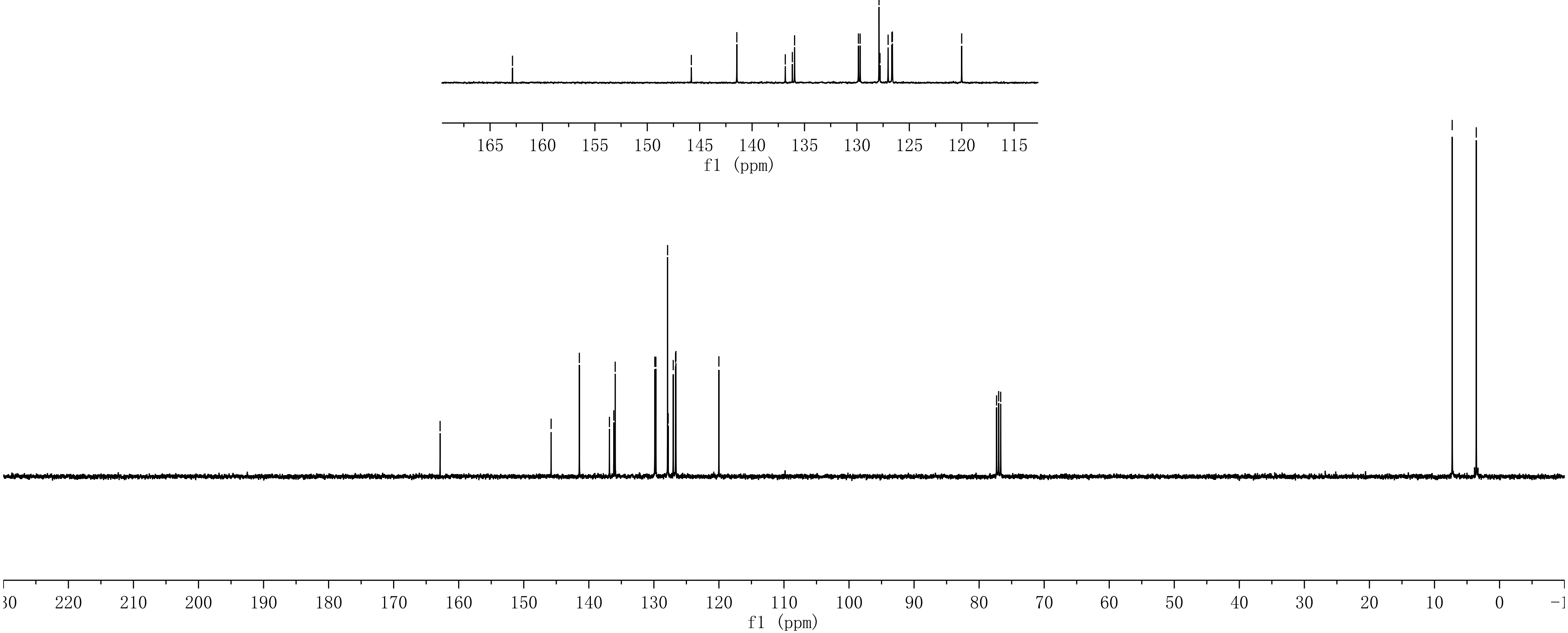
2o

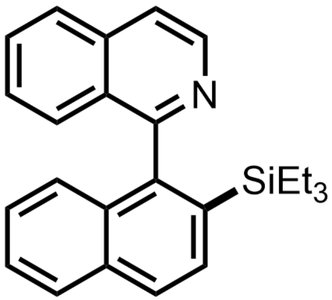
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



2o

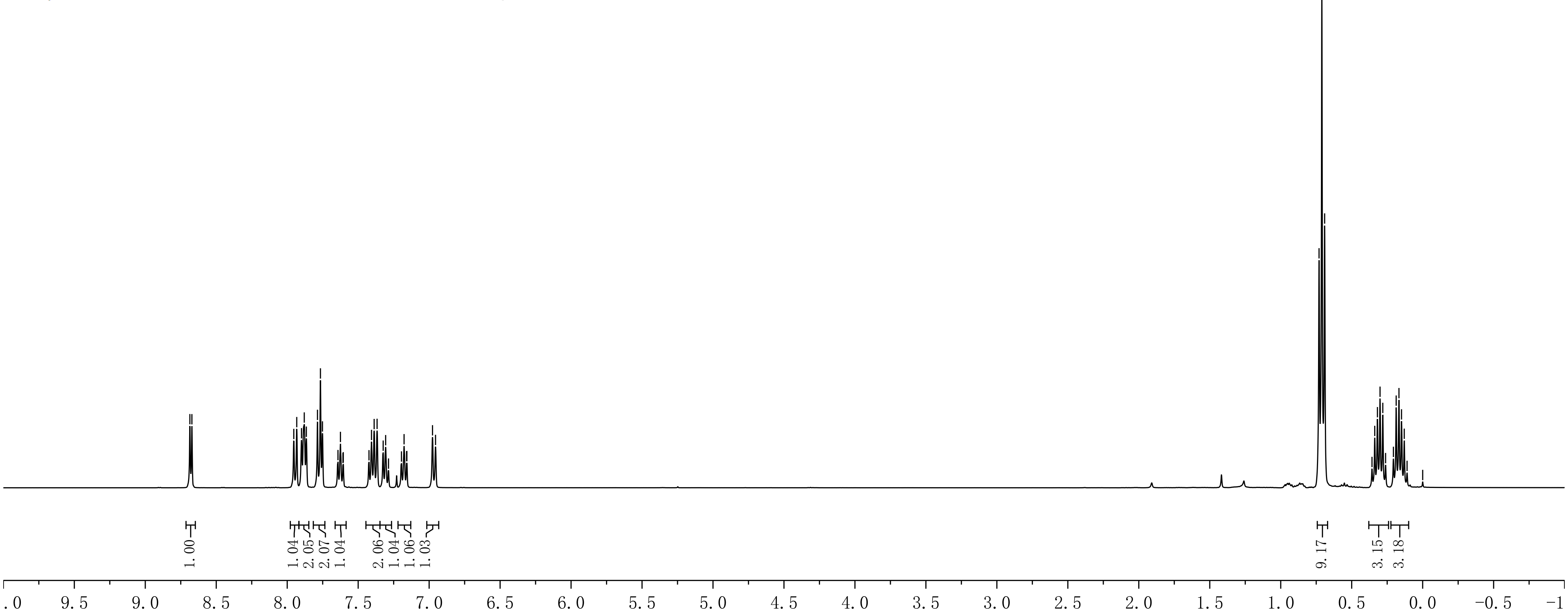
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

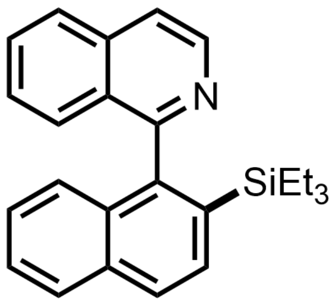




2p

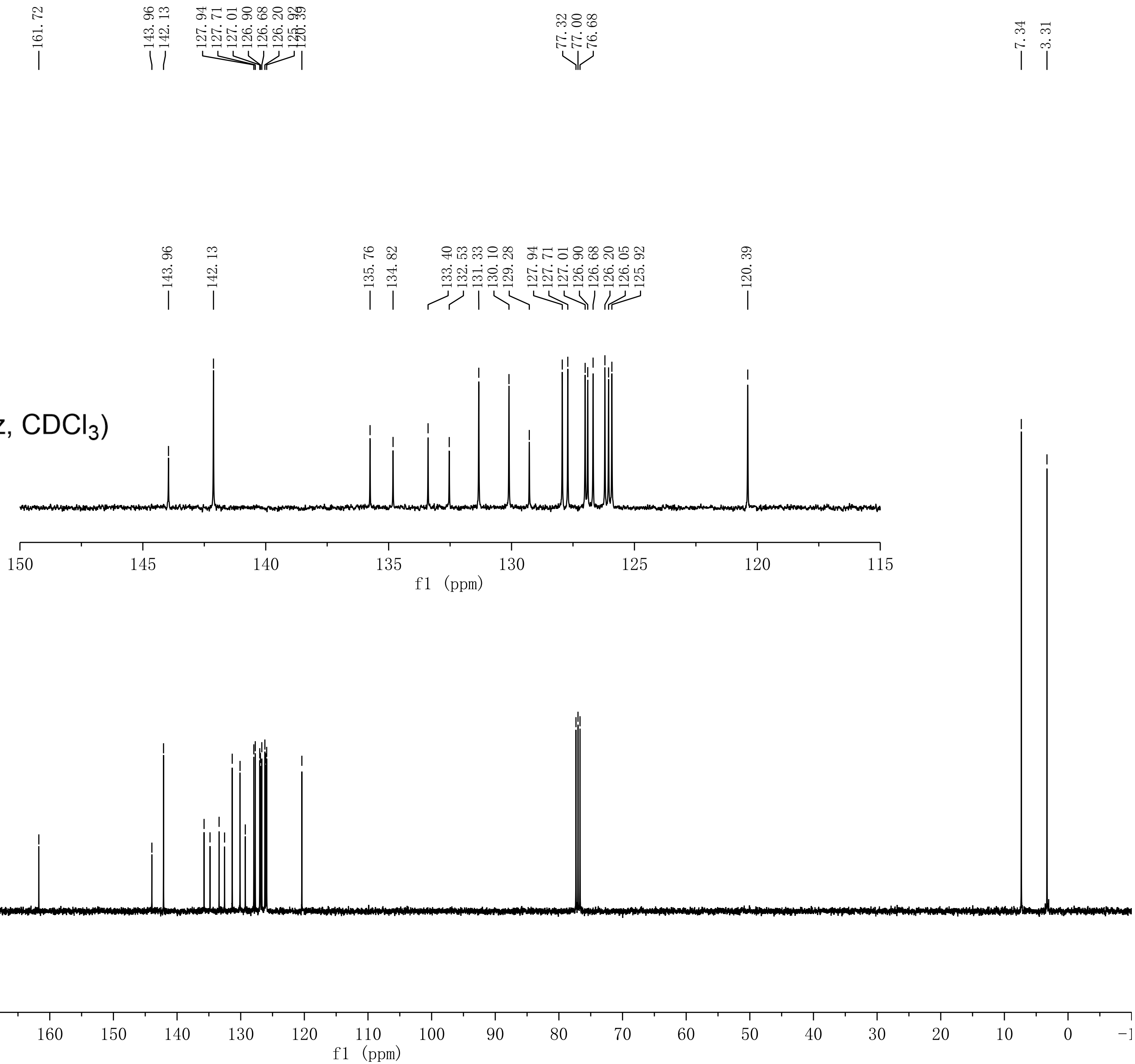
[1]H NMR spectrum (400 MHz, $CDCl_3$)

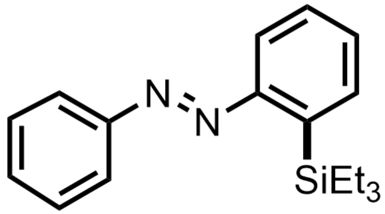




2p

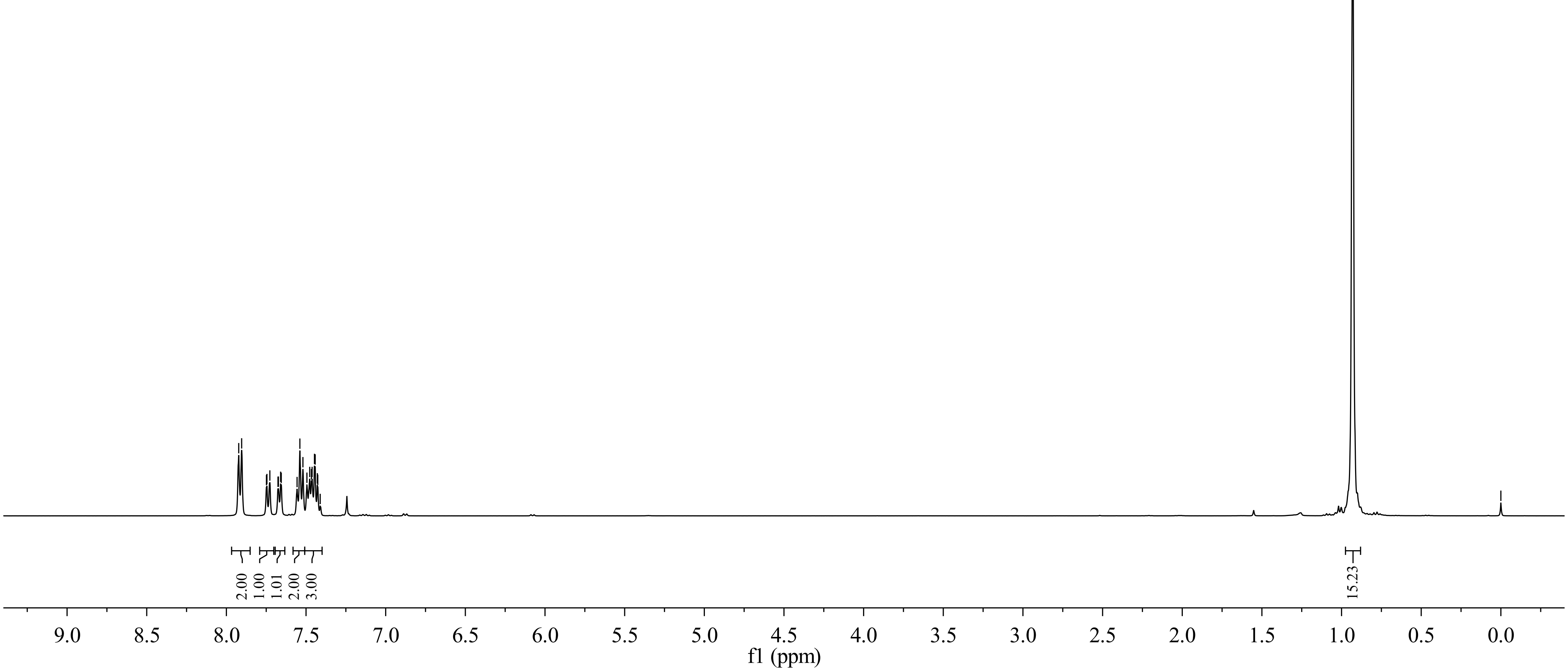
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

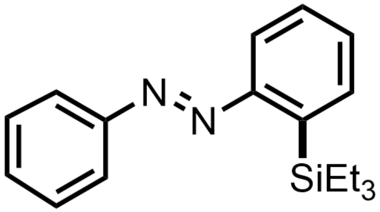




2q

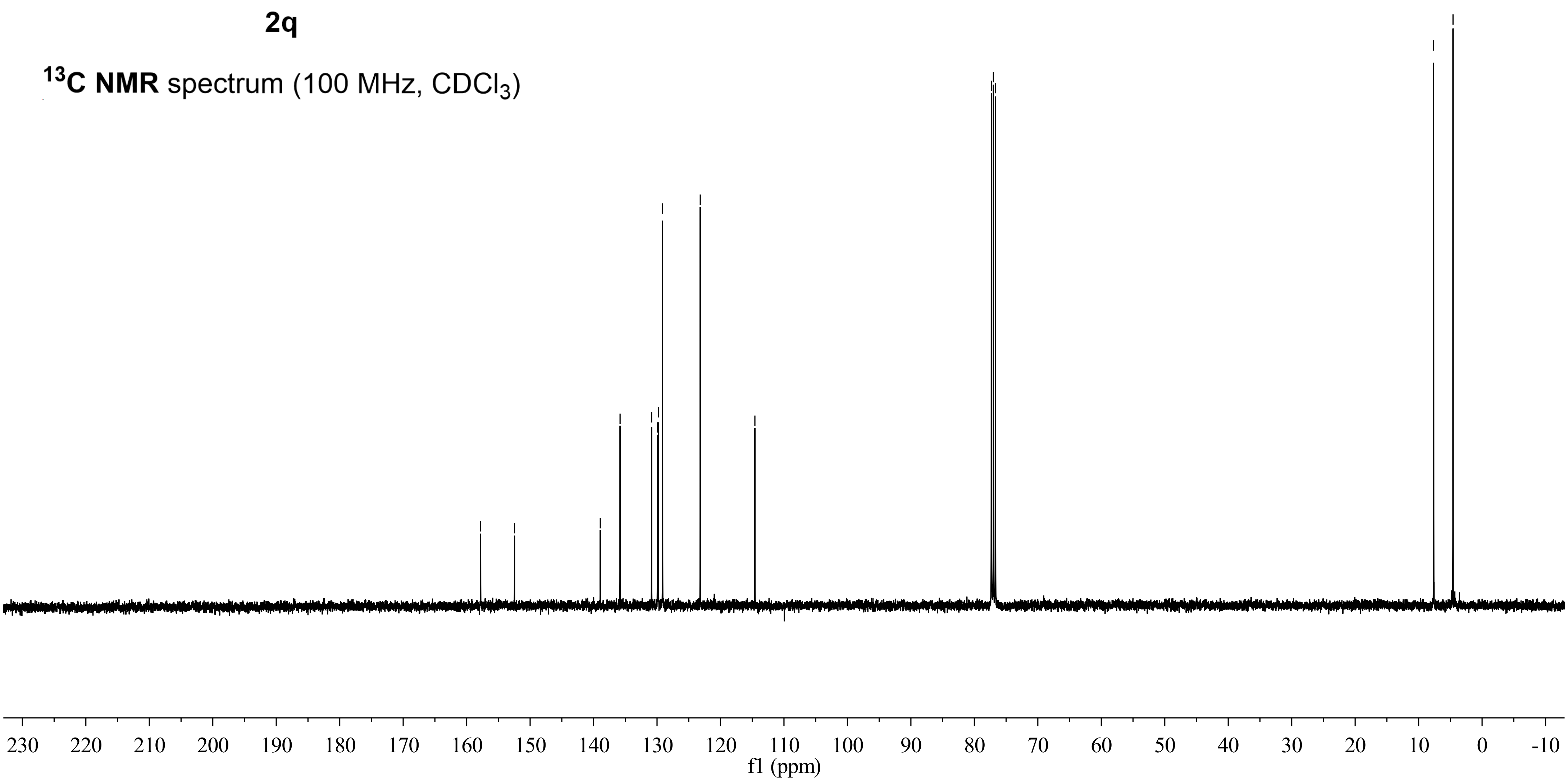
[1]H NMR spectrum (400 MHz, $CDCl_3$)

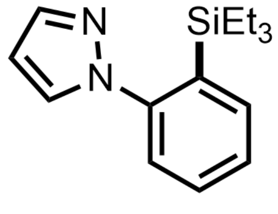




2q

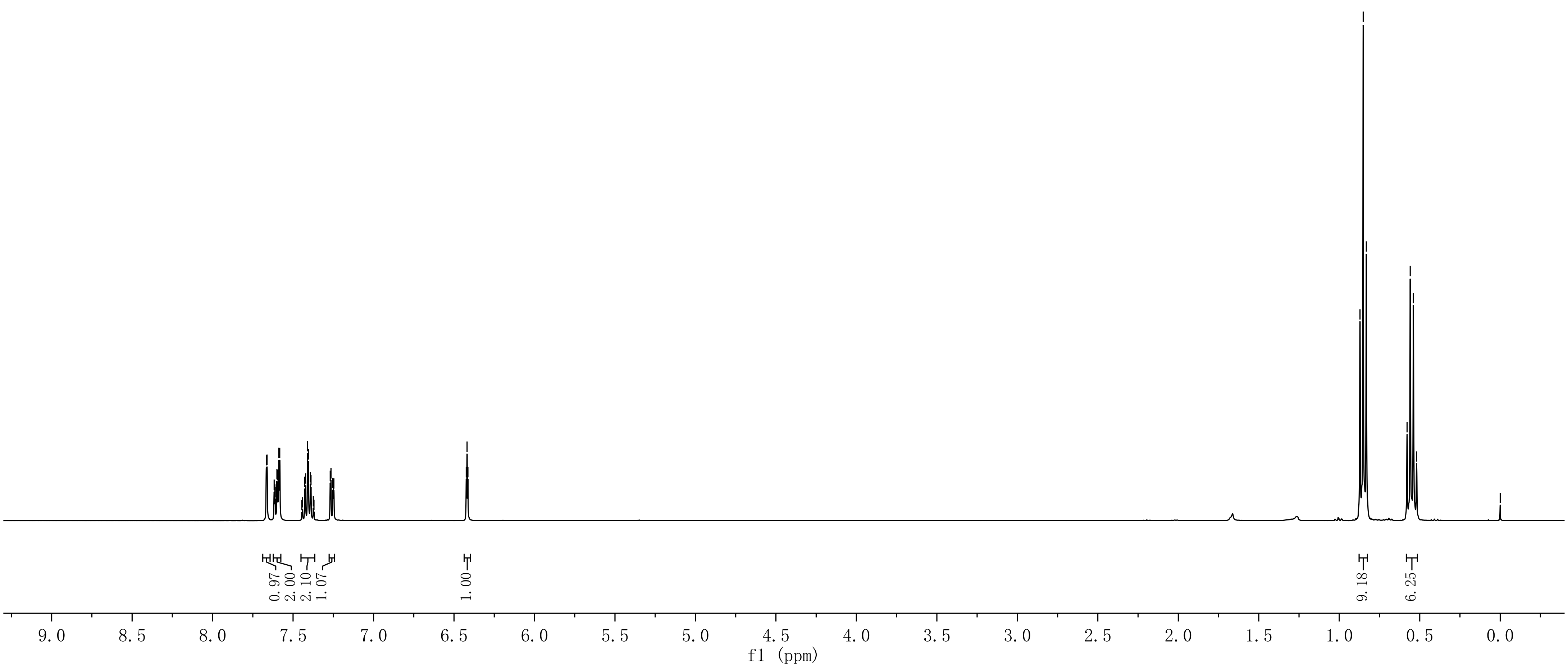
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

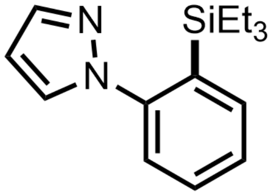




2r

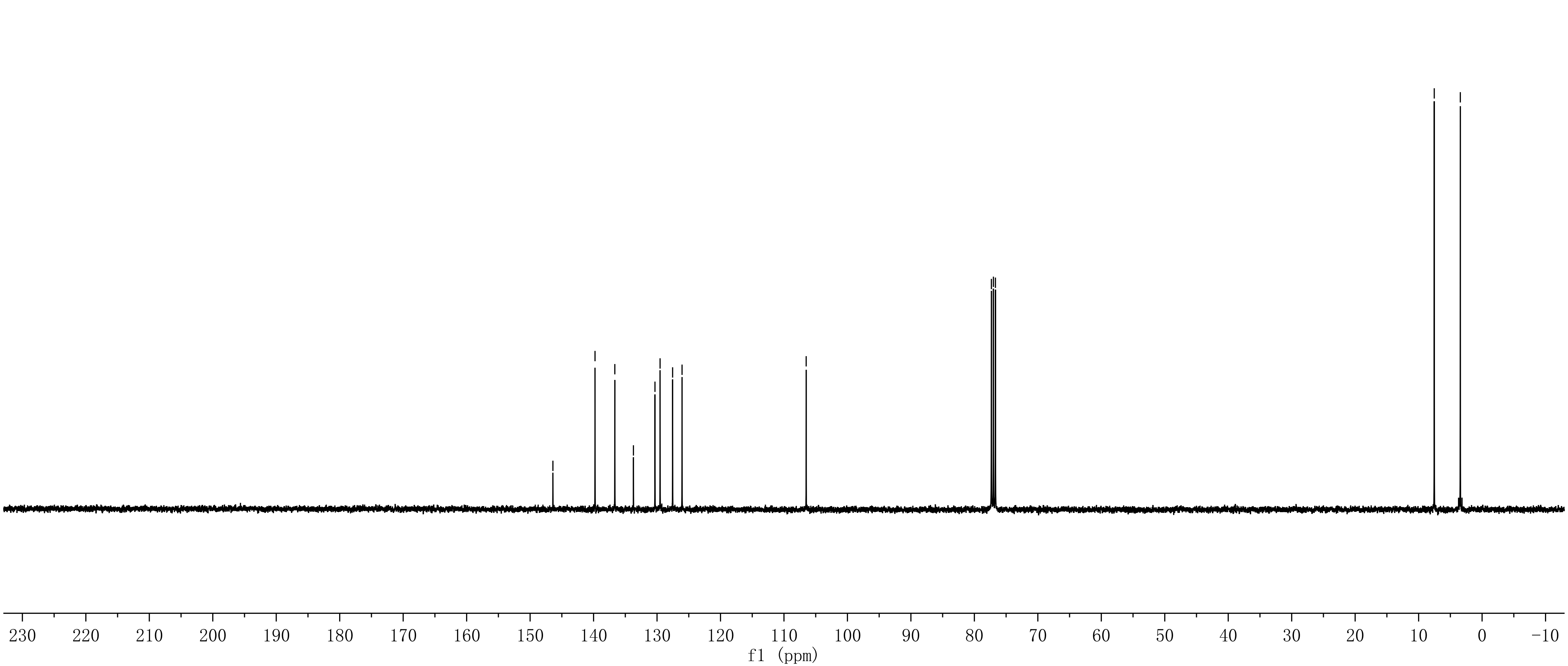
[1]H NMR spectrum (400 MHz, $CDCl_3$)

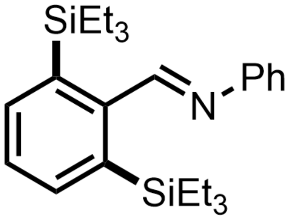




2r

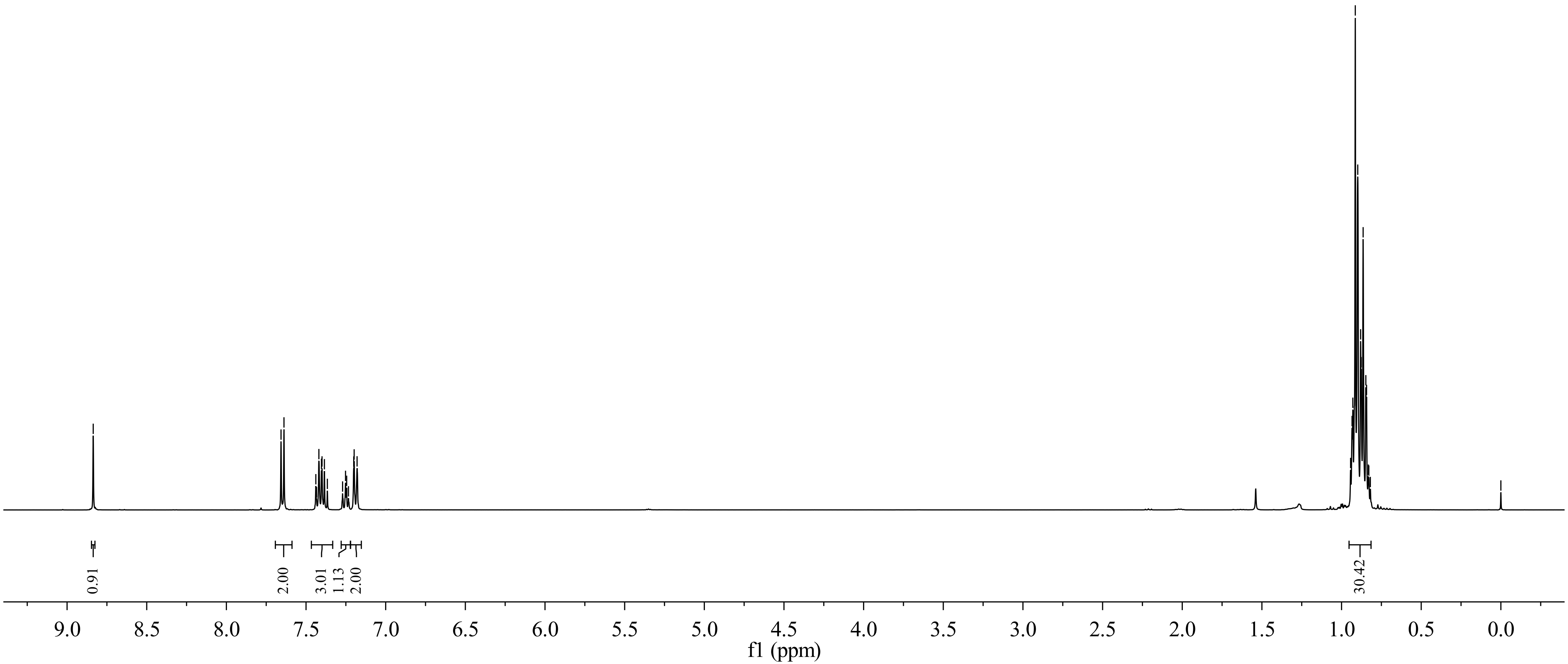
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

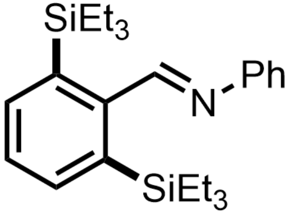




2s

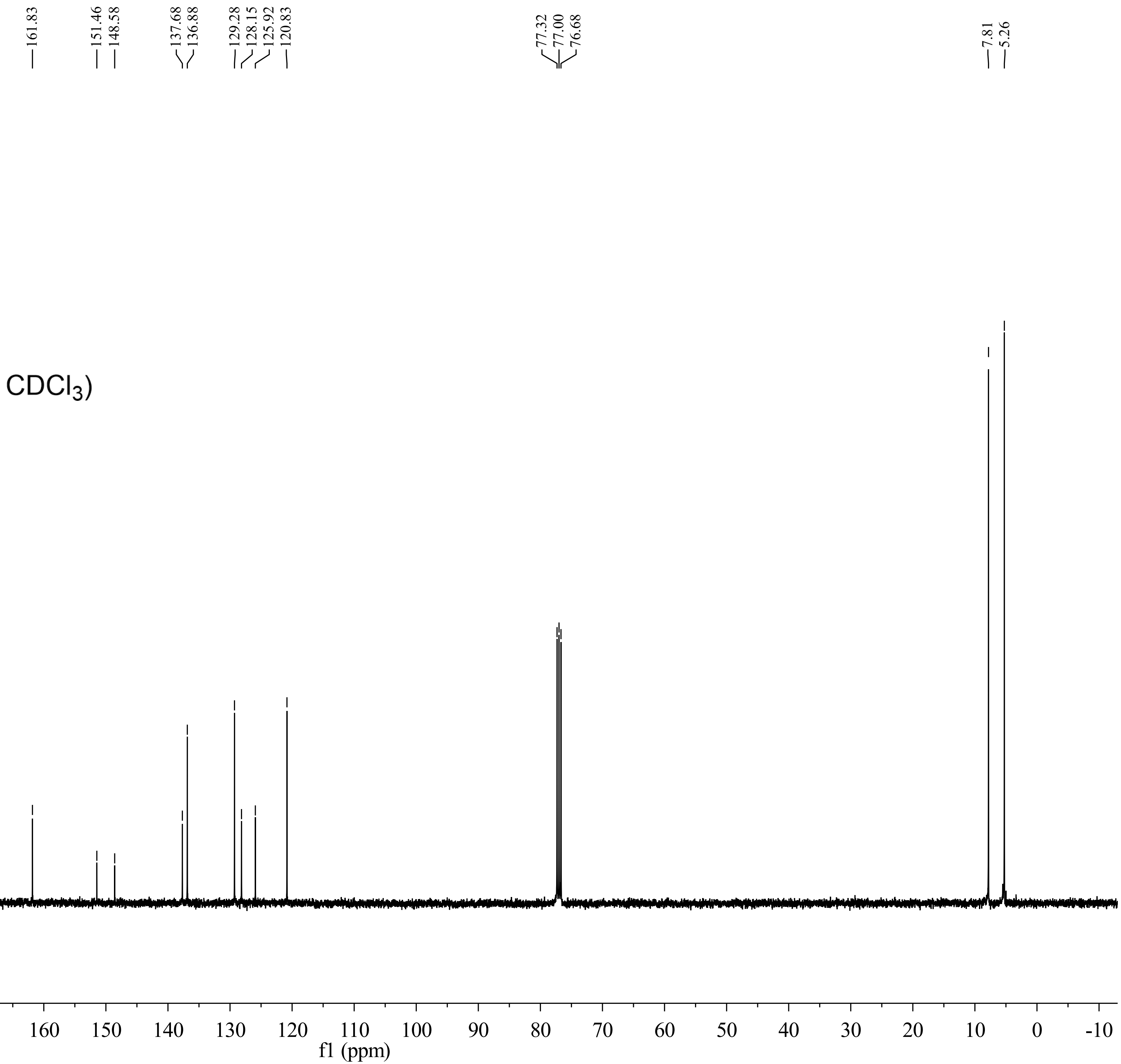
[1]H NMR spectrum (400 MHz, $CDCl_3$)

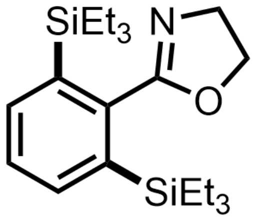




2s

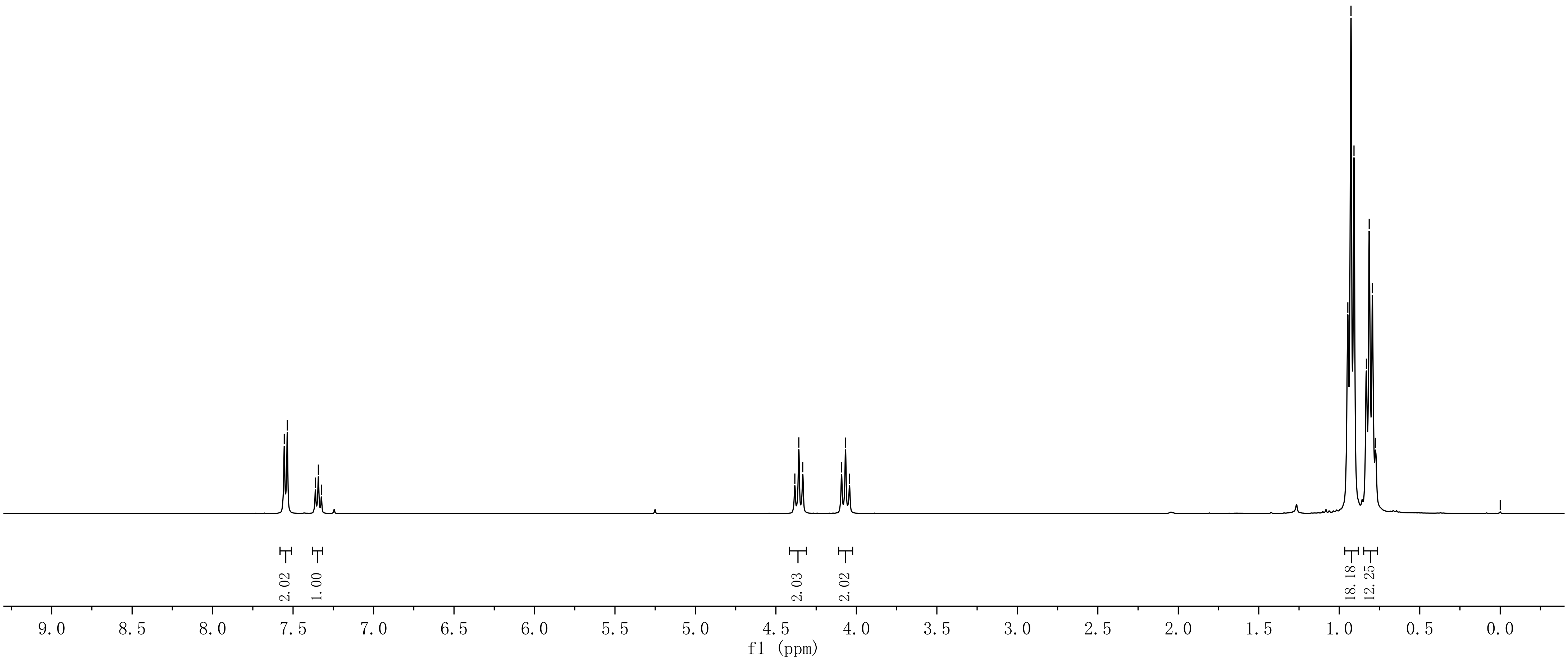
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

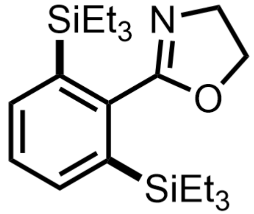




2t

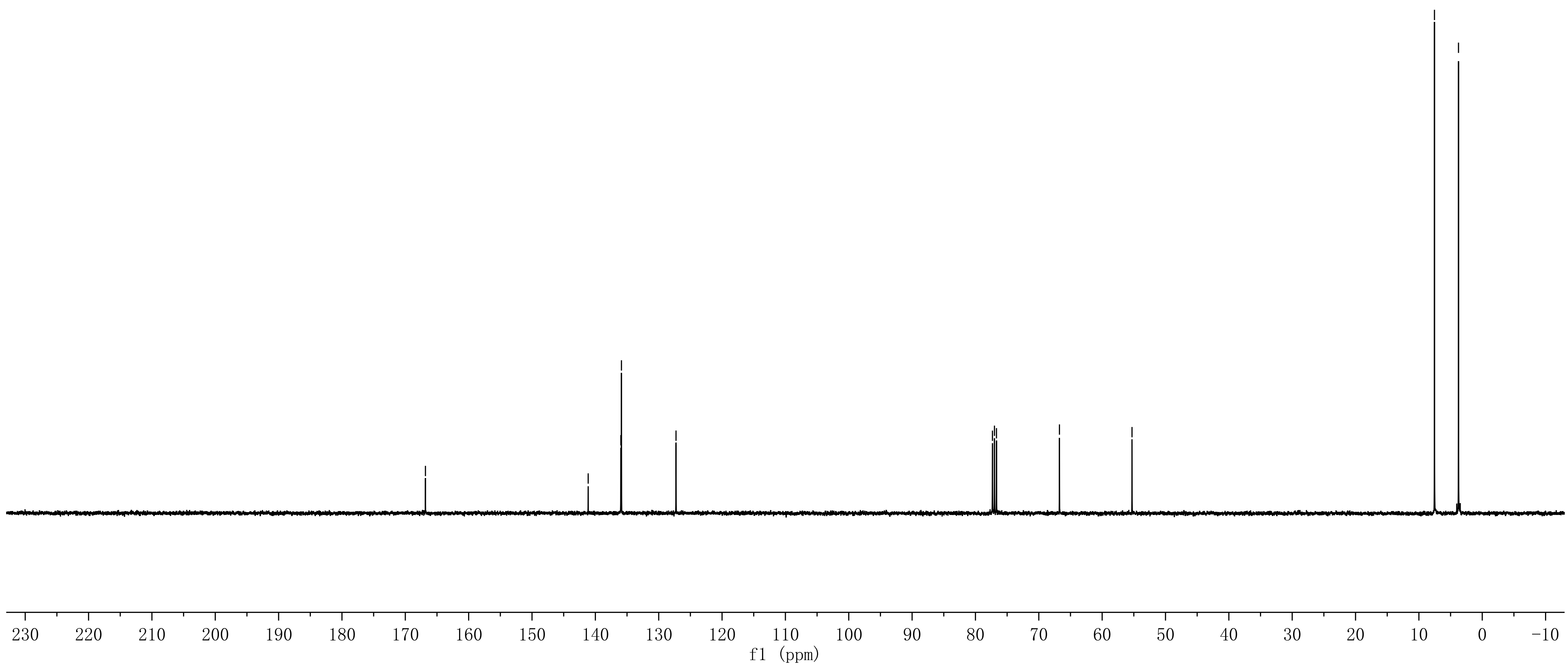
[1]H NMR spectrum (400 MHz, CDCl3)

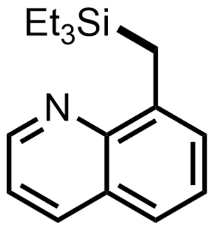




2t

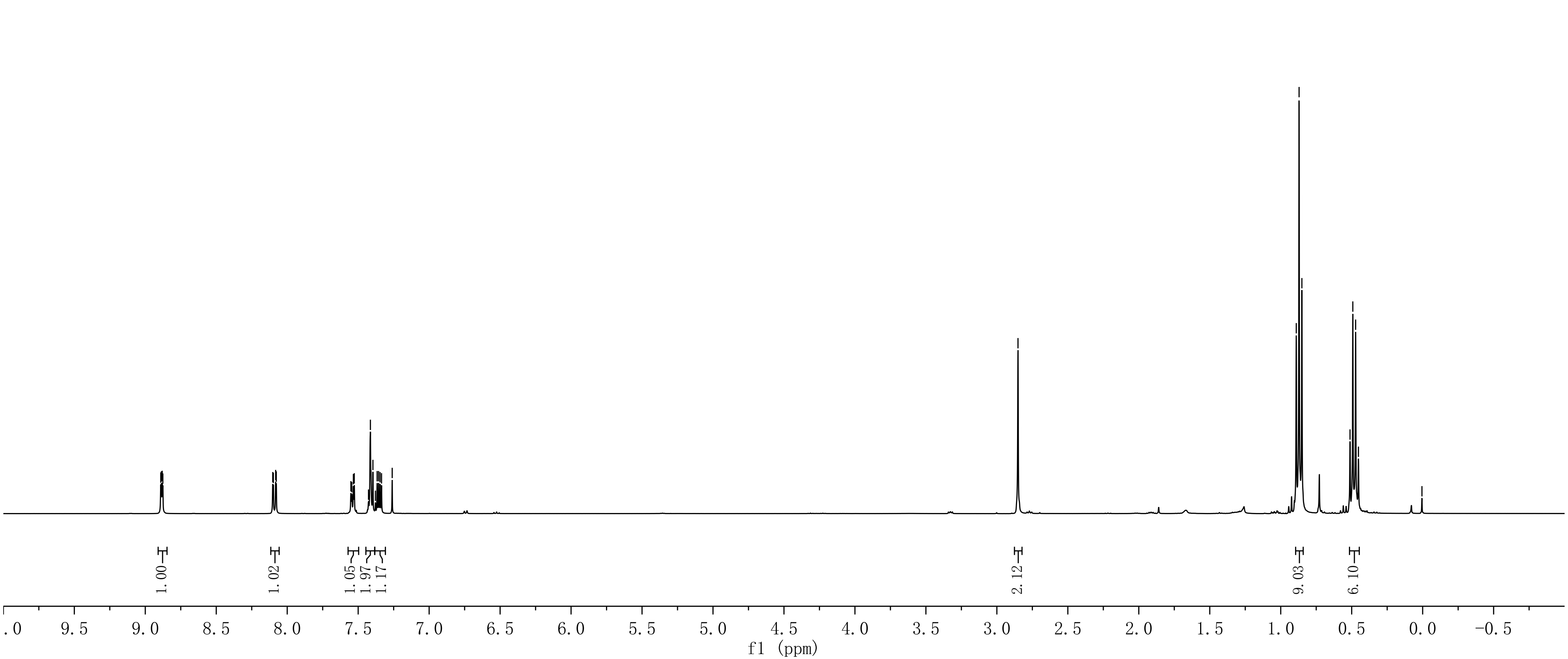
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

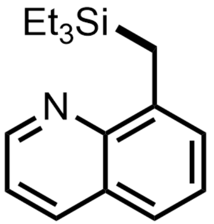




2u

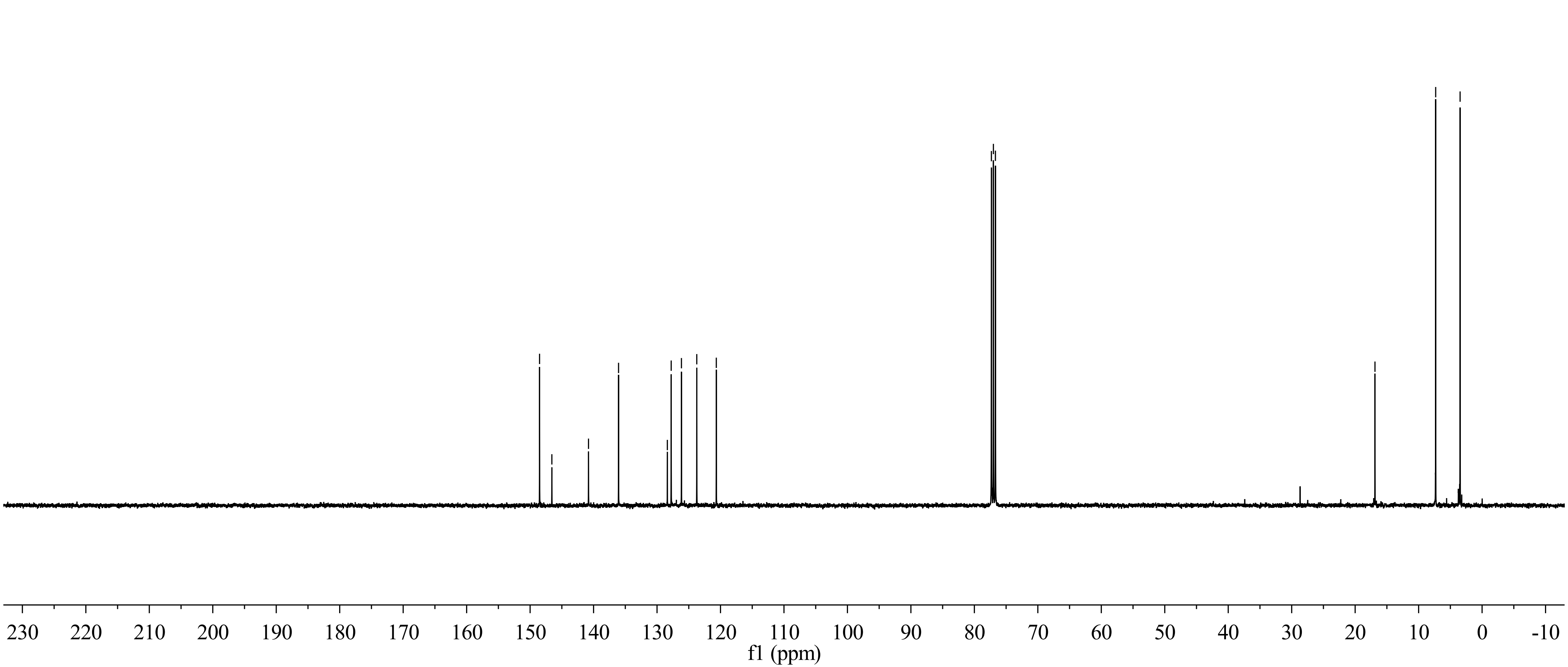
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

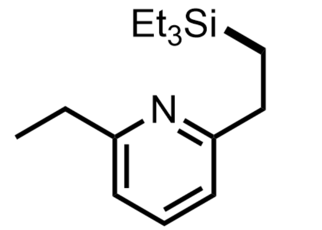




2u

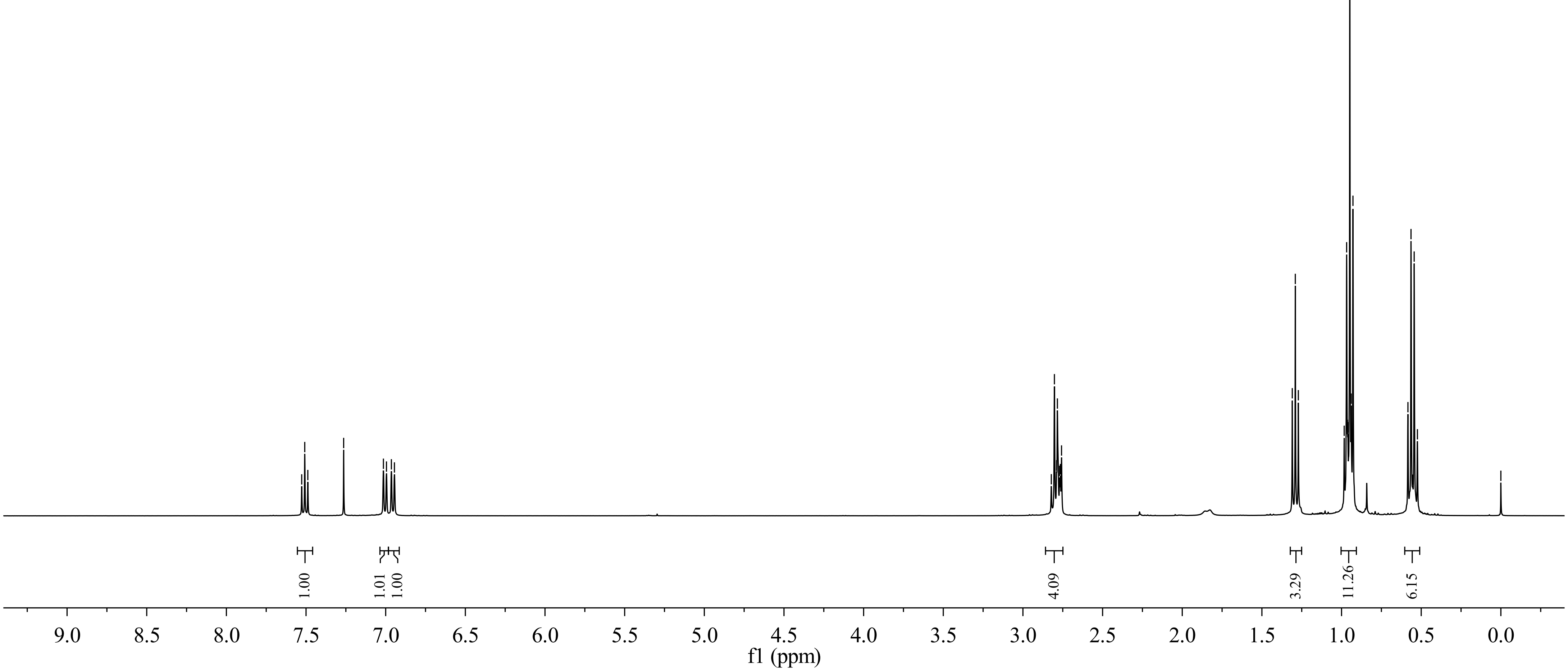
[13]C NMR spectrum (100 MHz, $CDCl_3$)

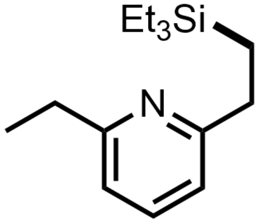




2v

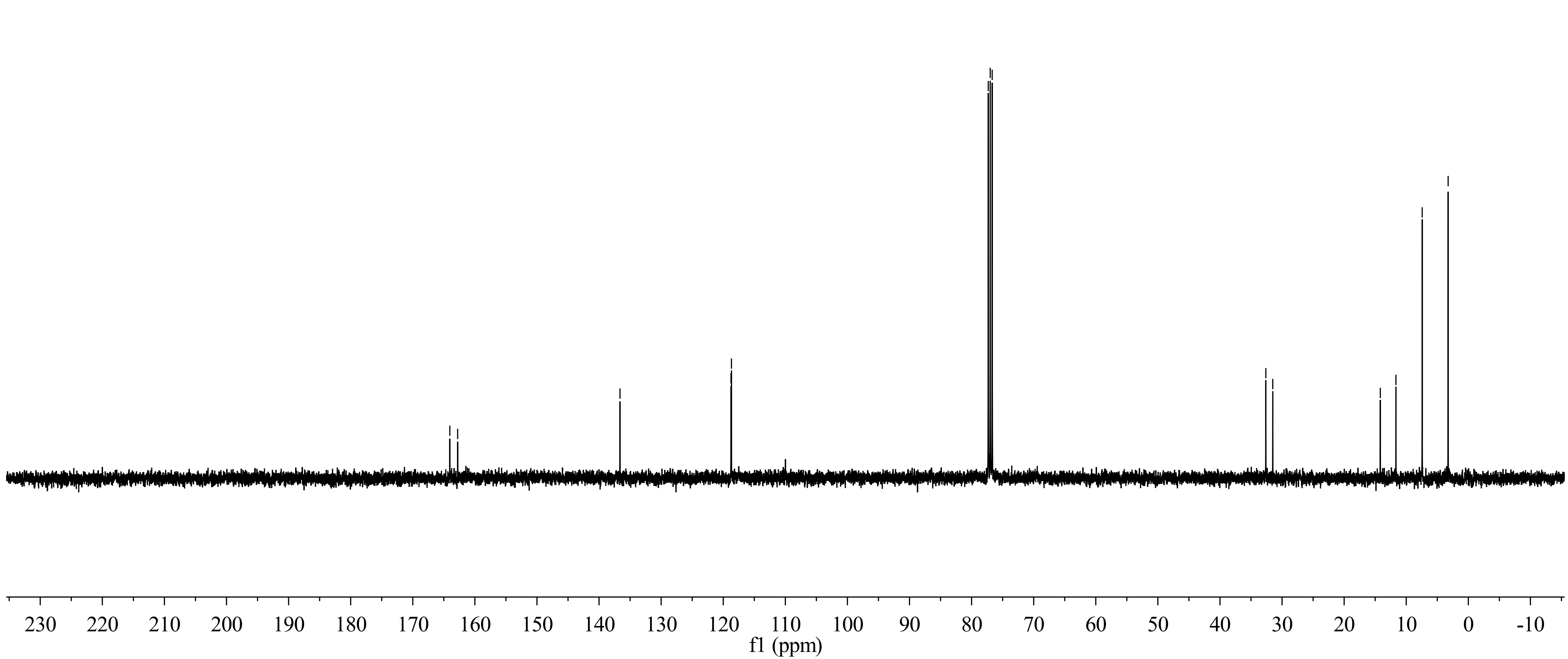
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

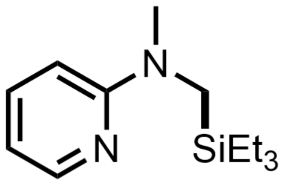




2v

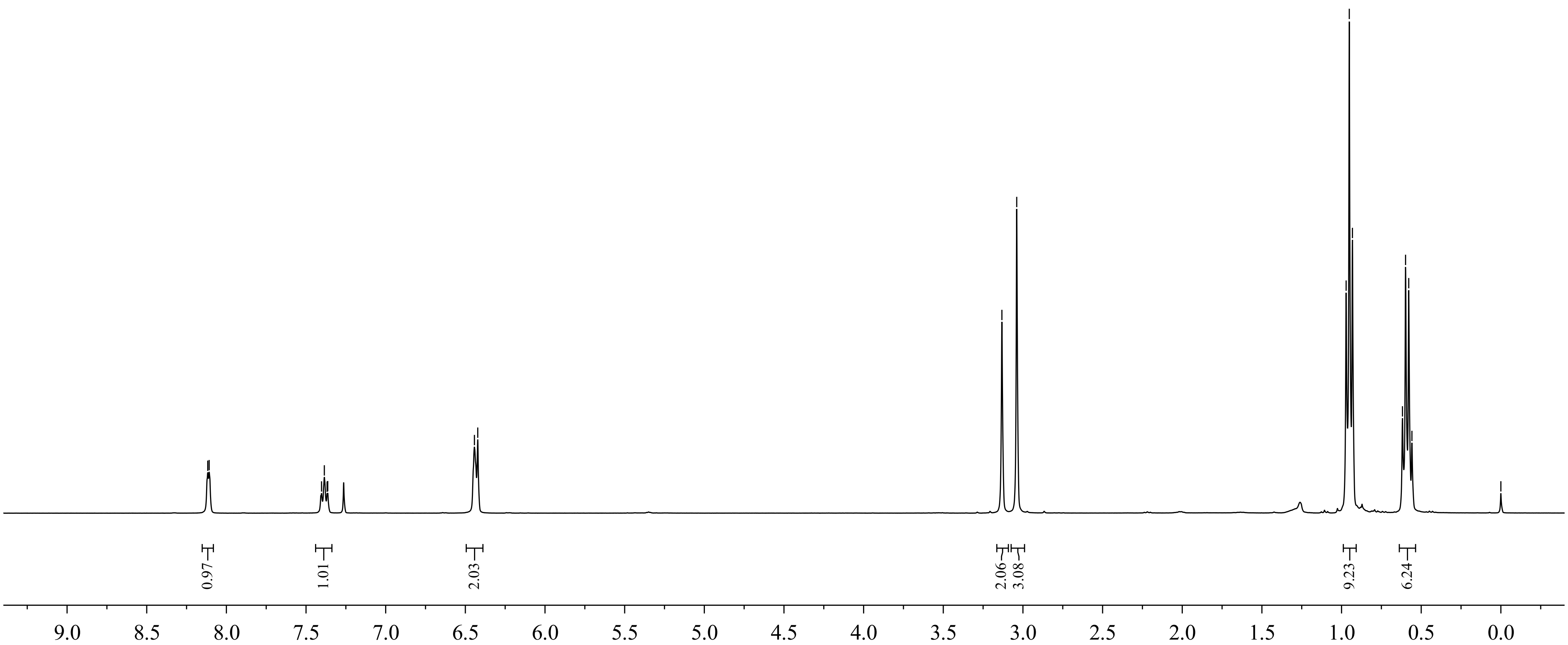
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

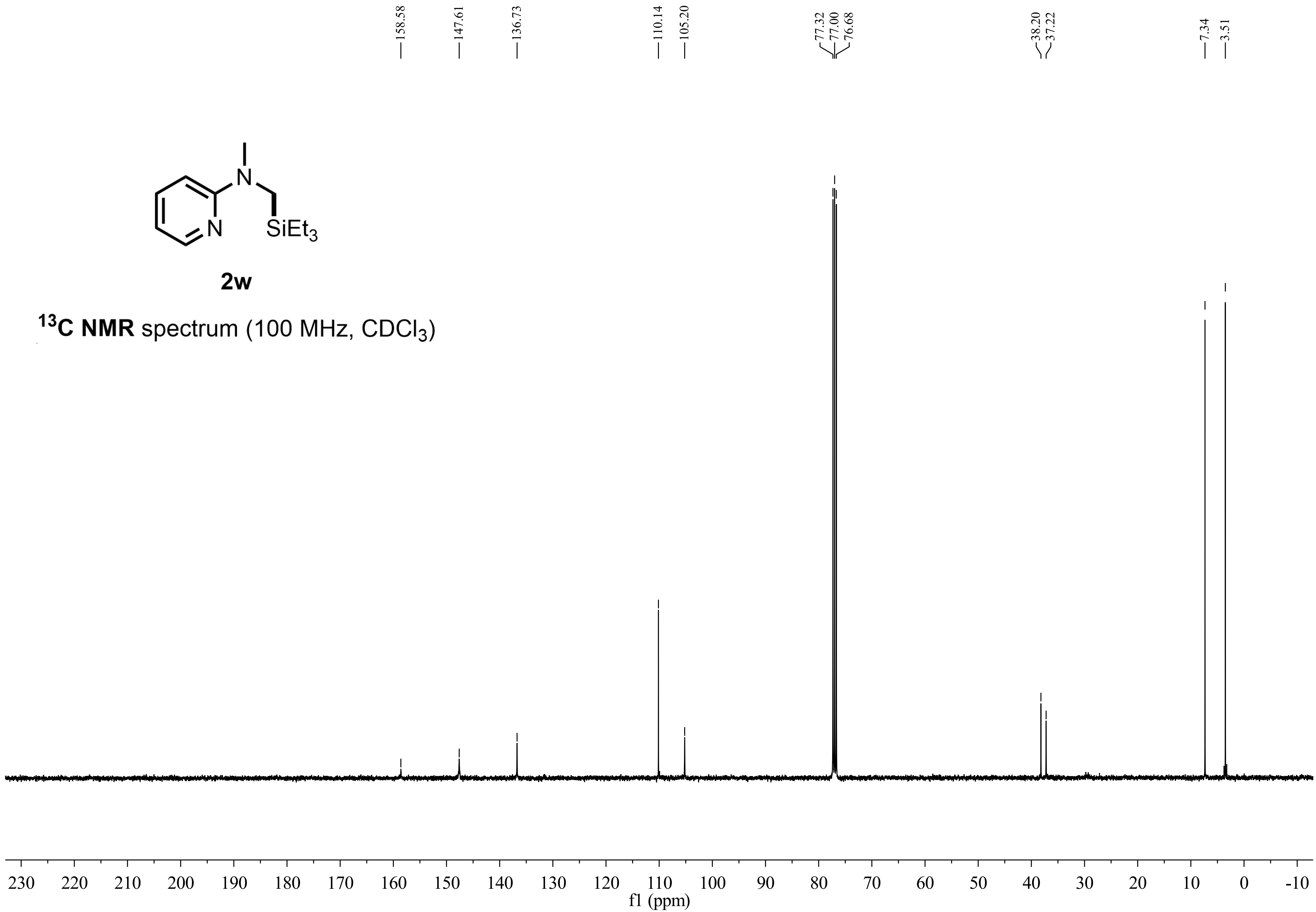




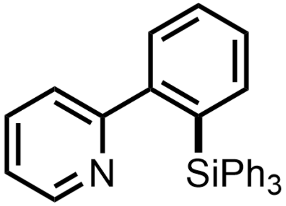
2w

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



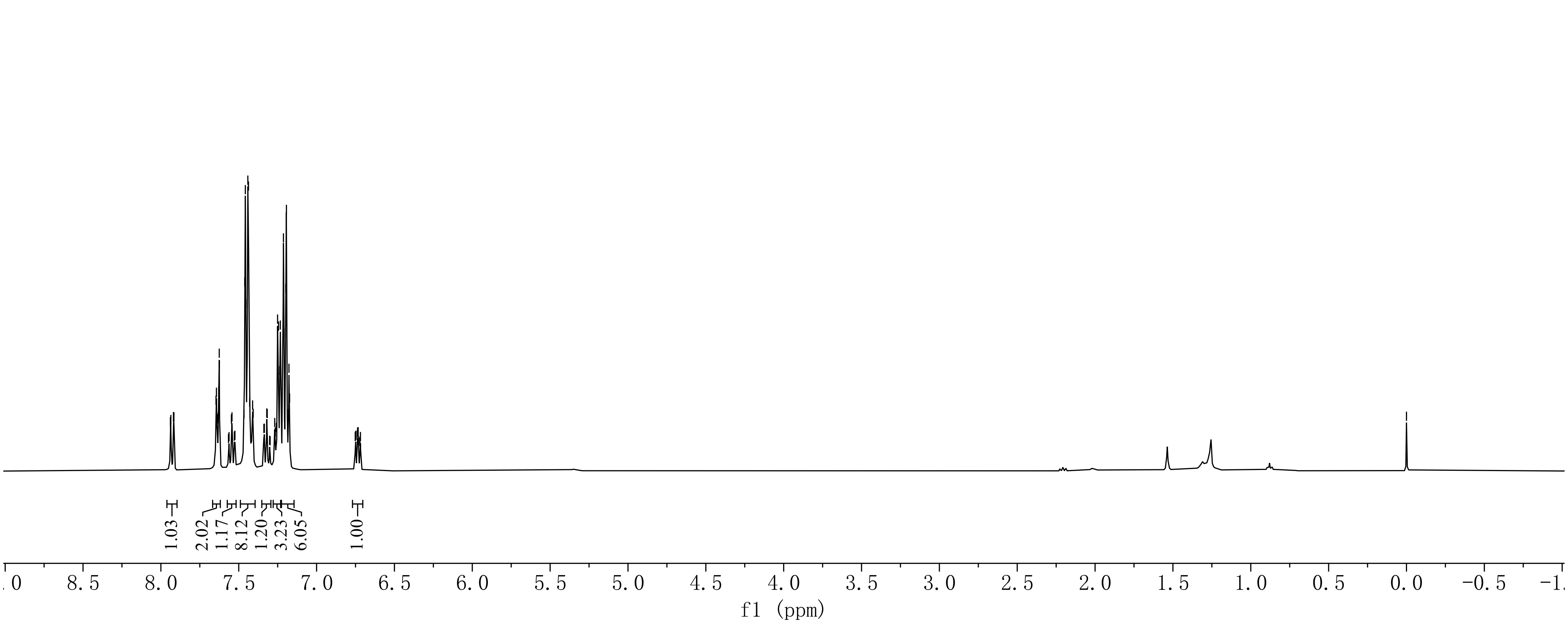


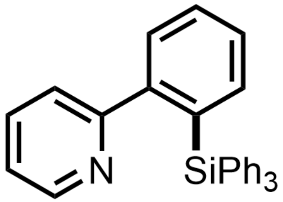
158.58
147.61
136.73
110.14
105.20
77.32
77.00
76.68
38.20
37.22
7.34
3.51
N
N
SiEt3
2w
13C NMR spectrum (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2x

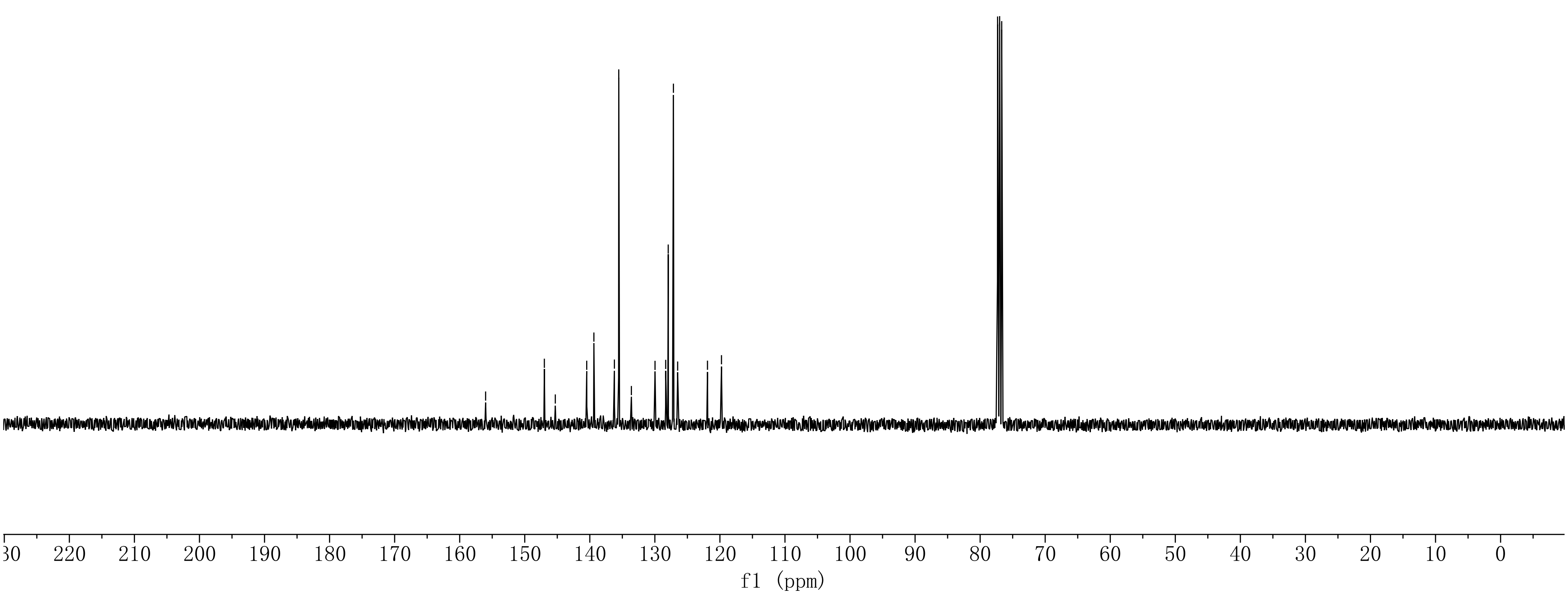
¹H NMR spectrum (400 MHz, $CDCl_3$)

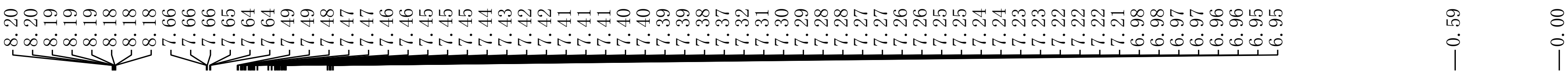


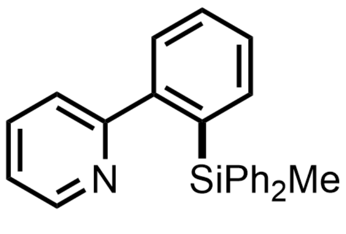


2x

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

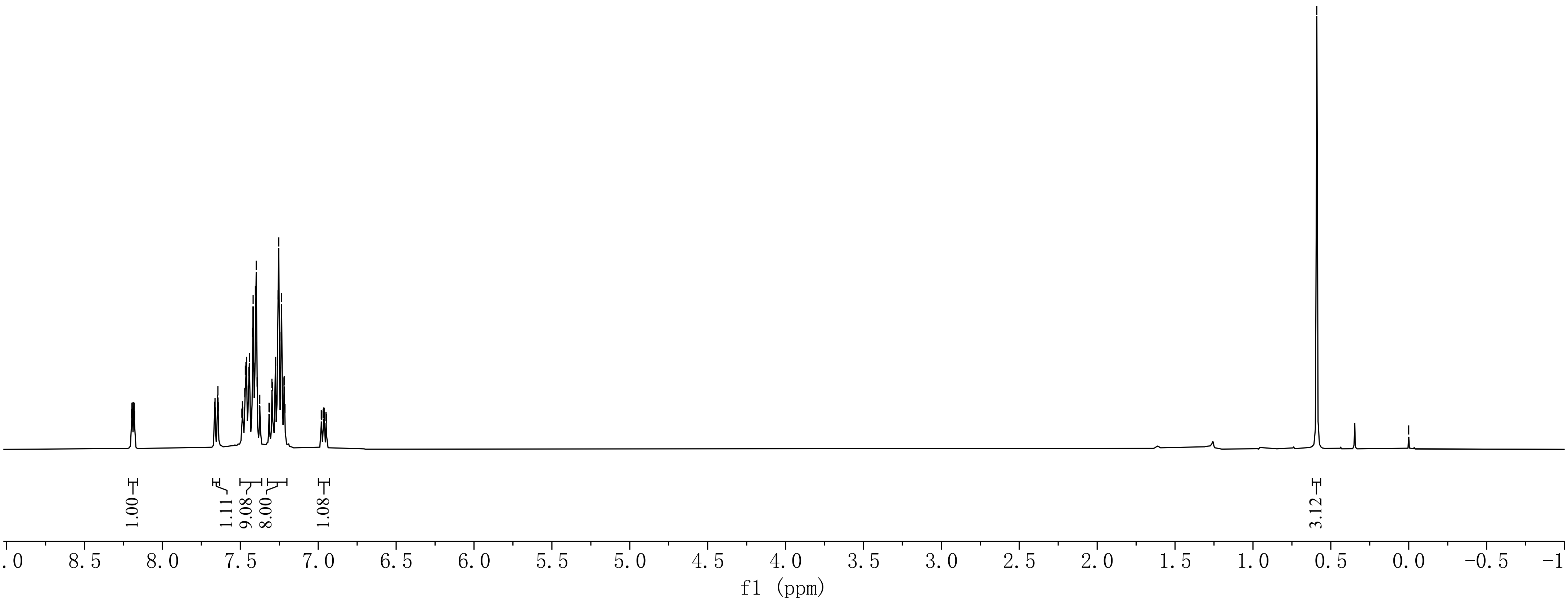


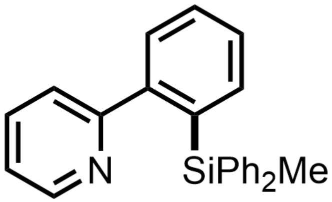




2y

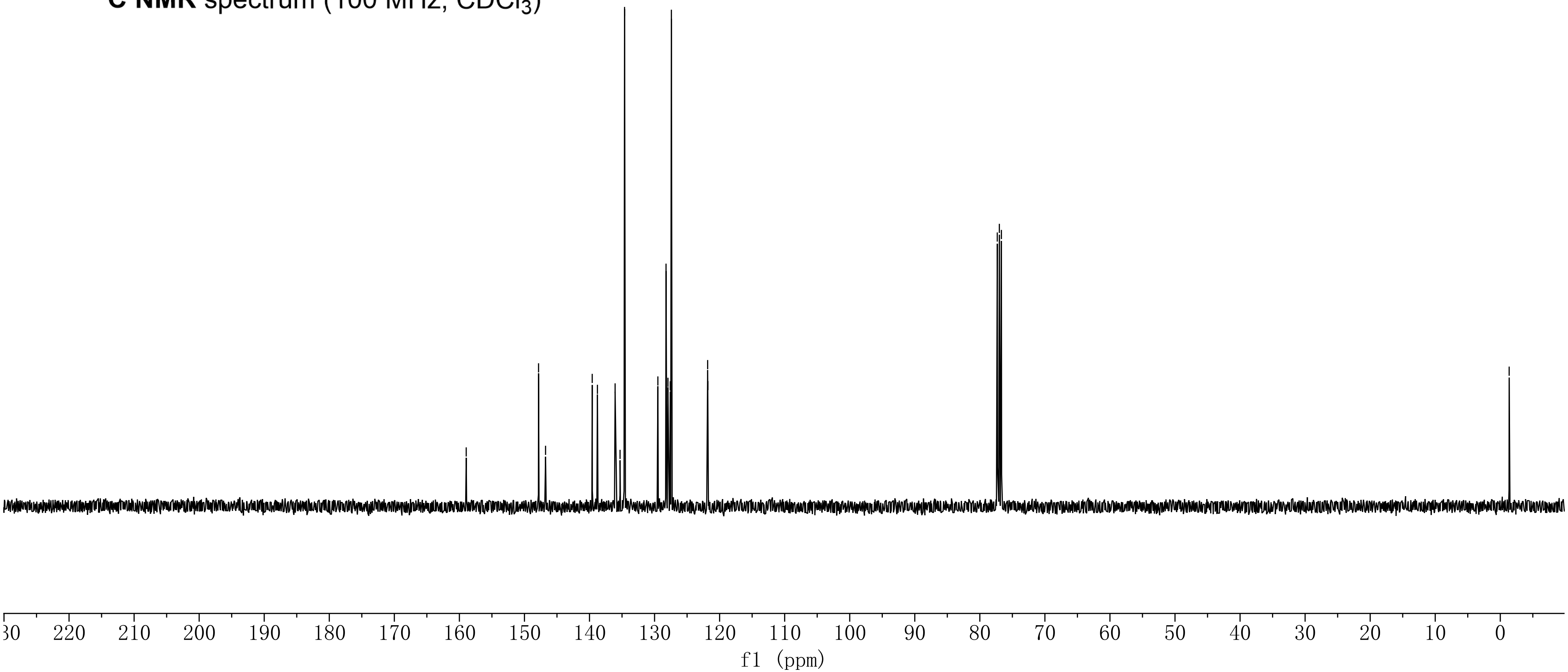
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





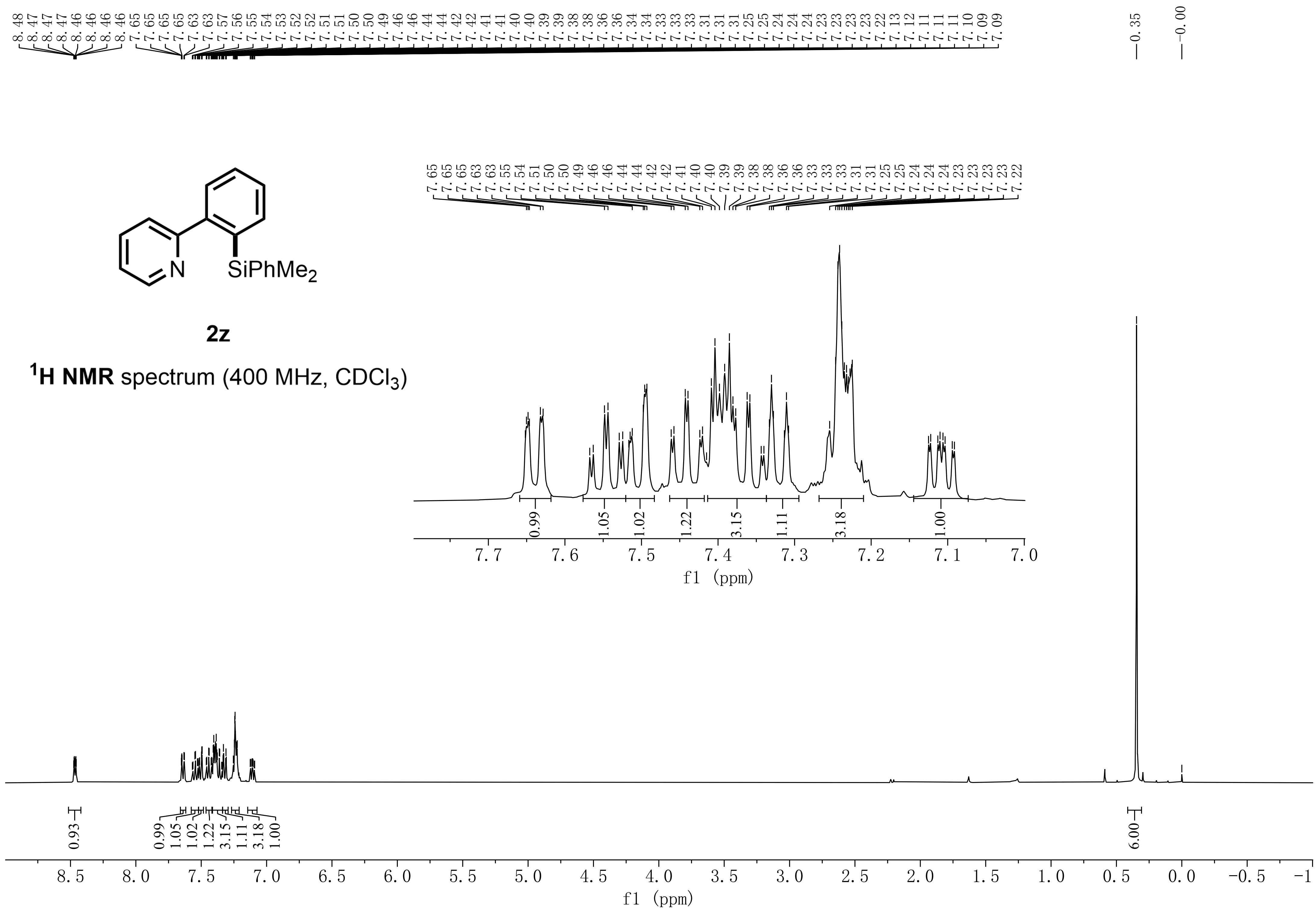
2y

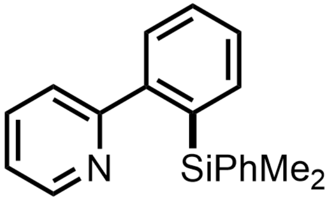
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



2z

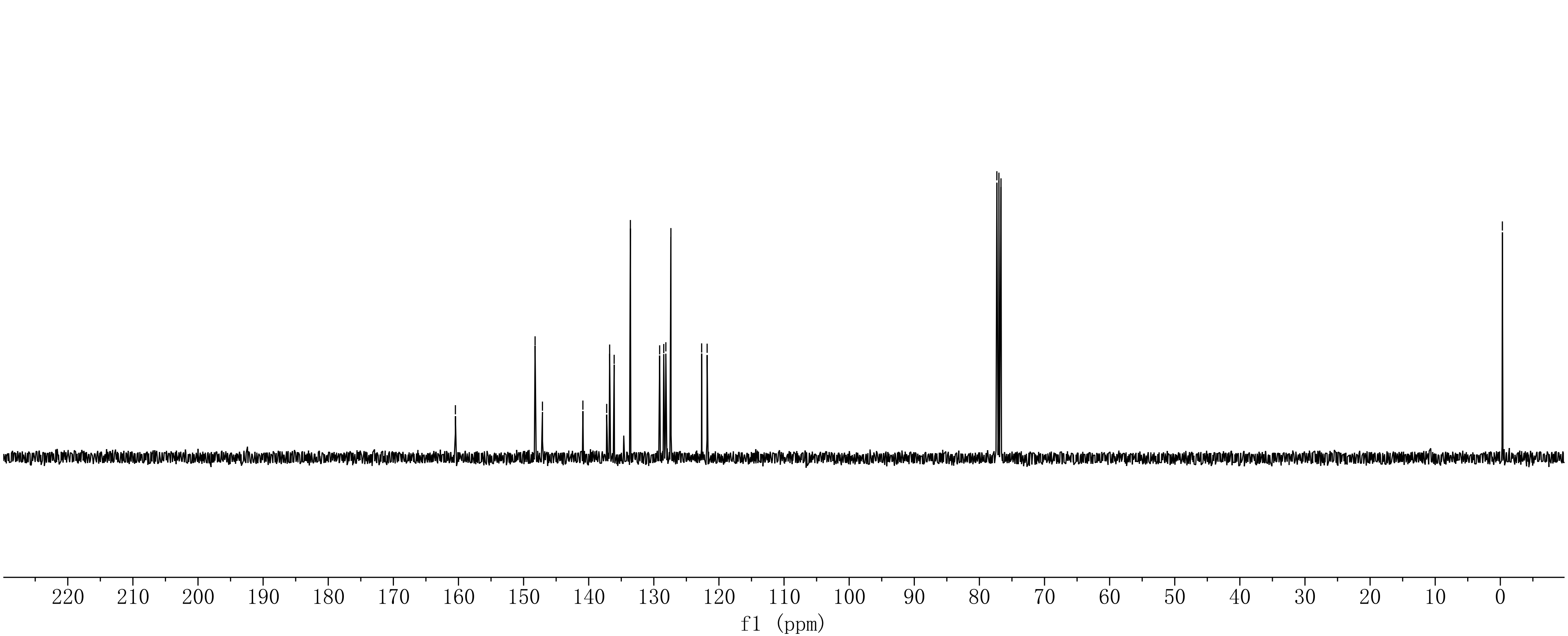
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

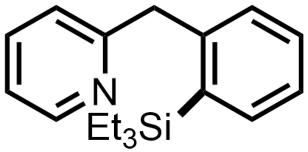




2z

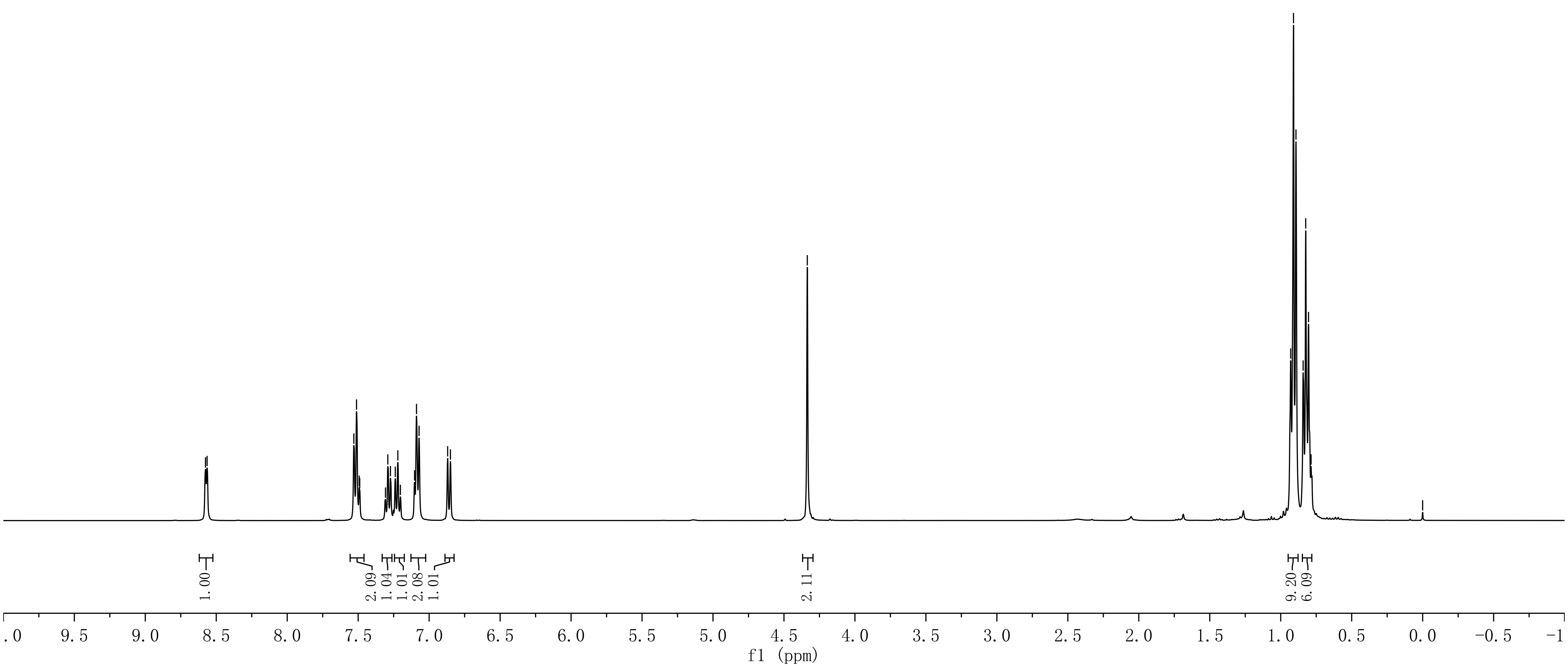
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

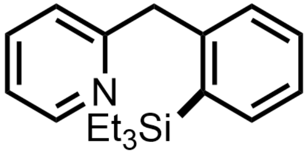




4a

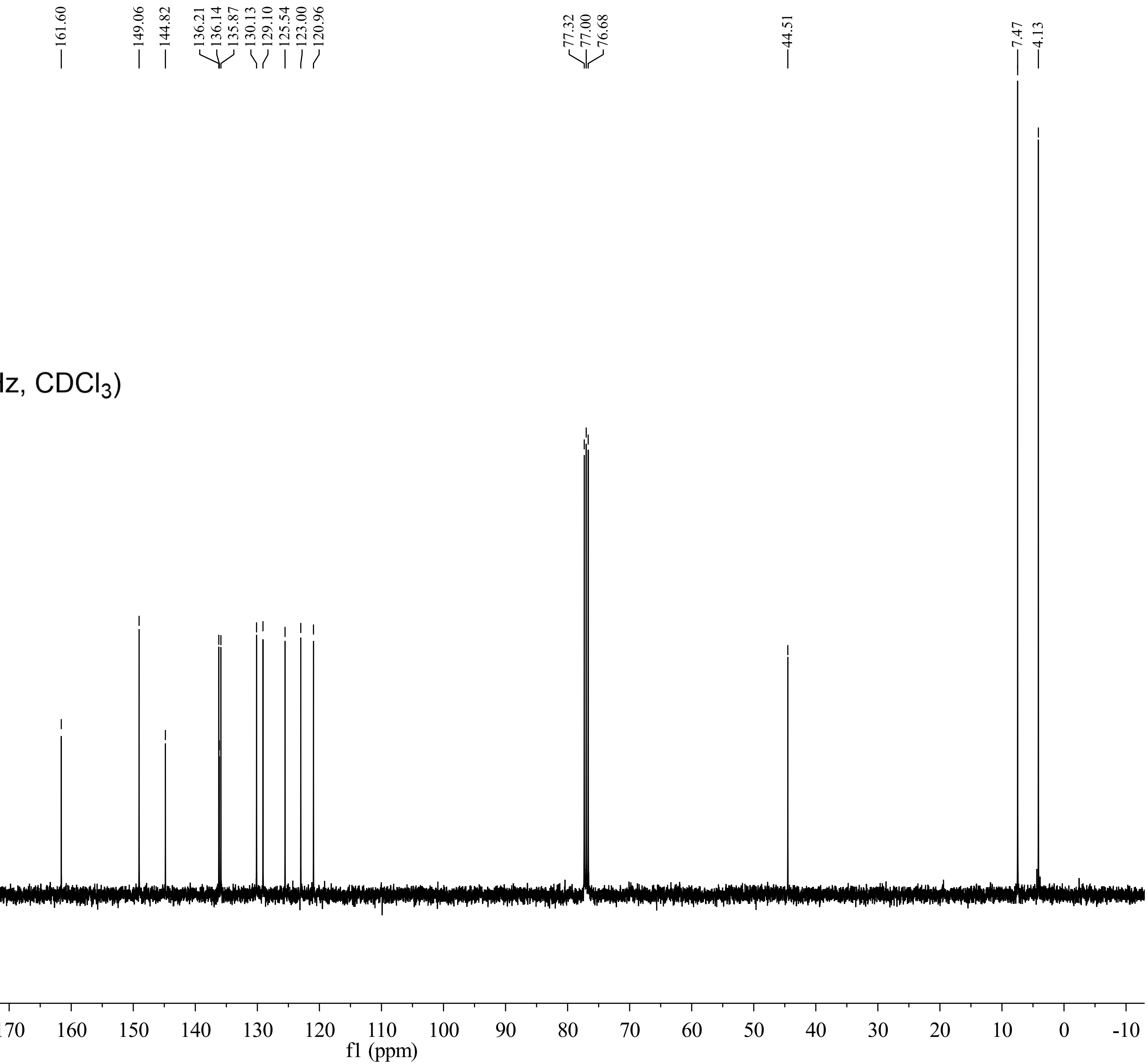
[1]H NMR spectrum (400 MHz, $CDCl_3$)

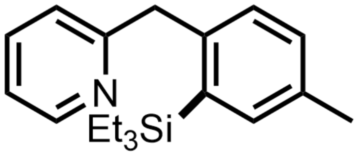




4a

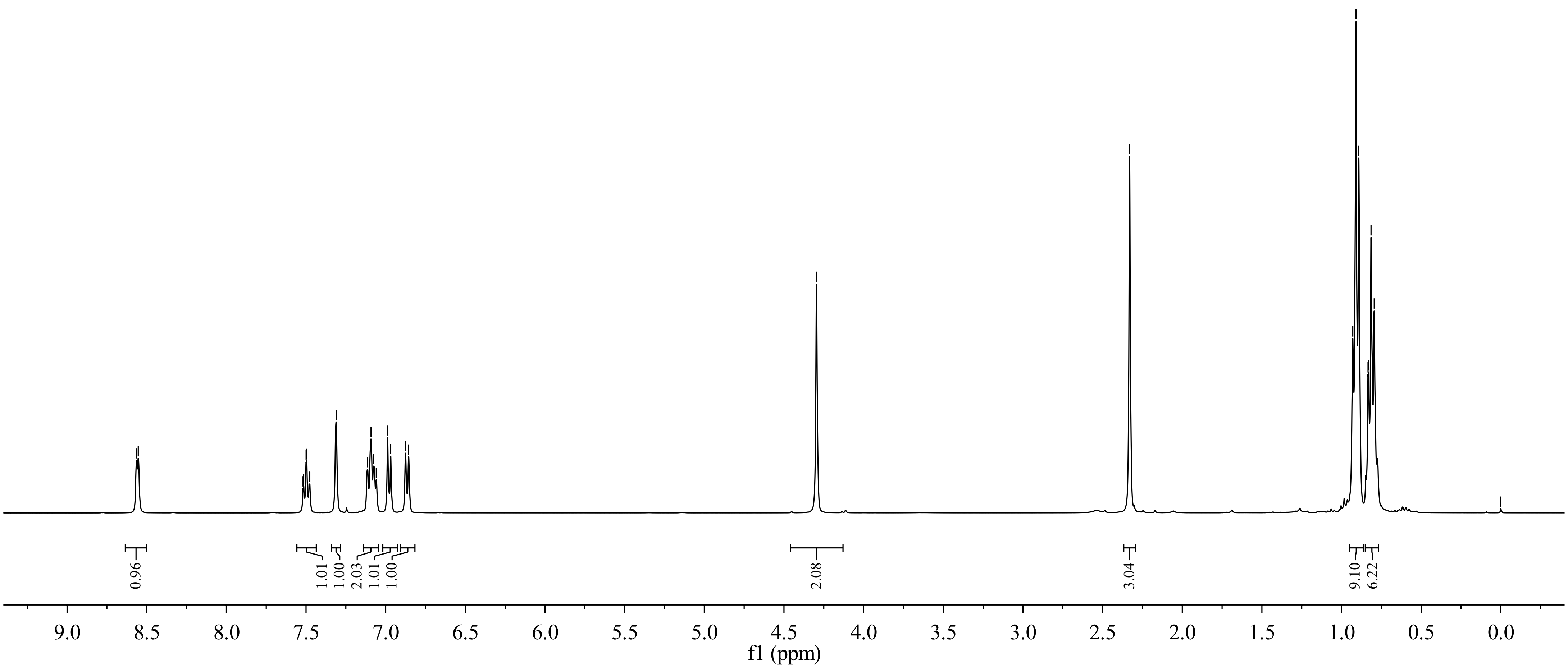
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

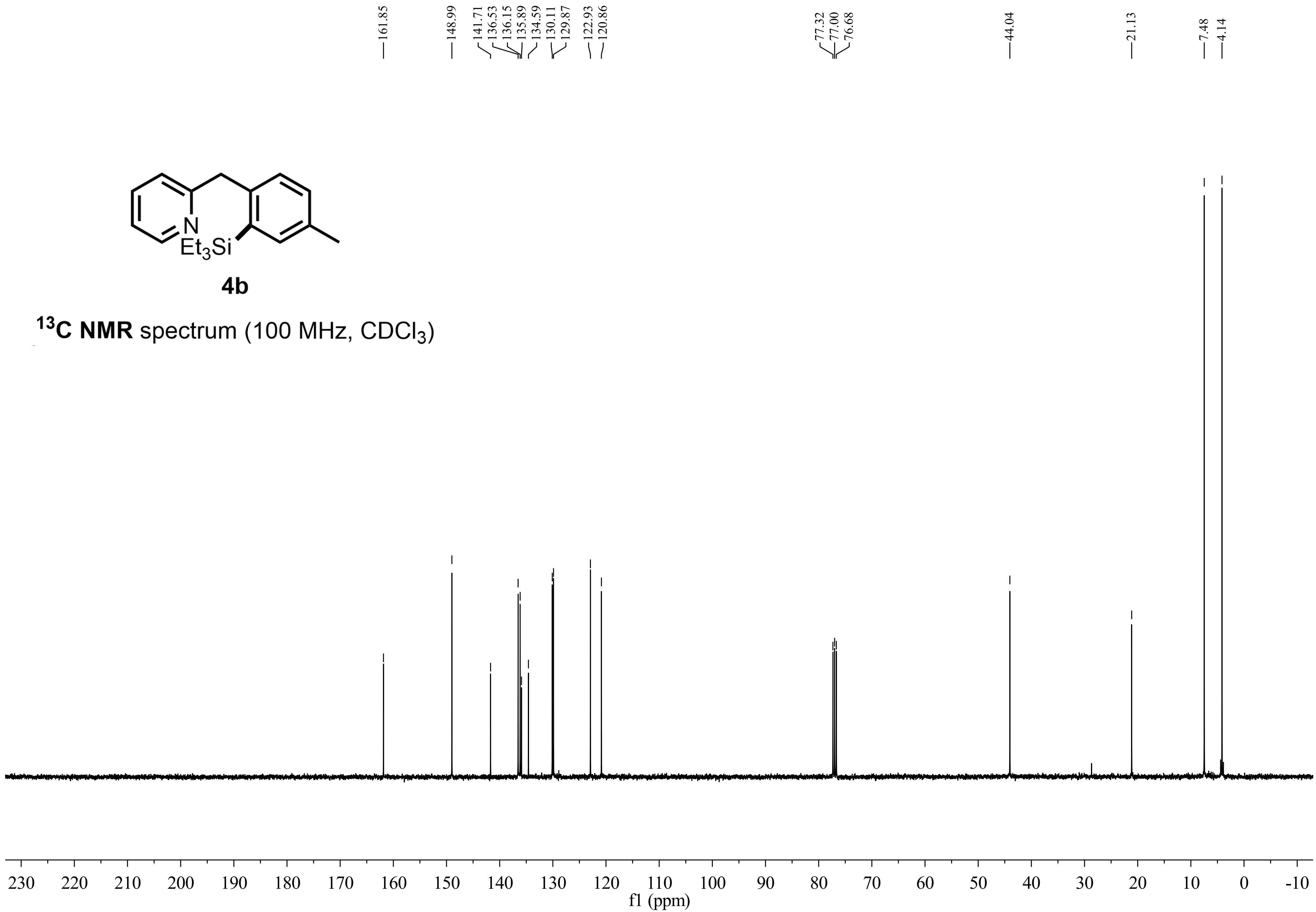




4b

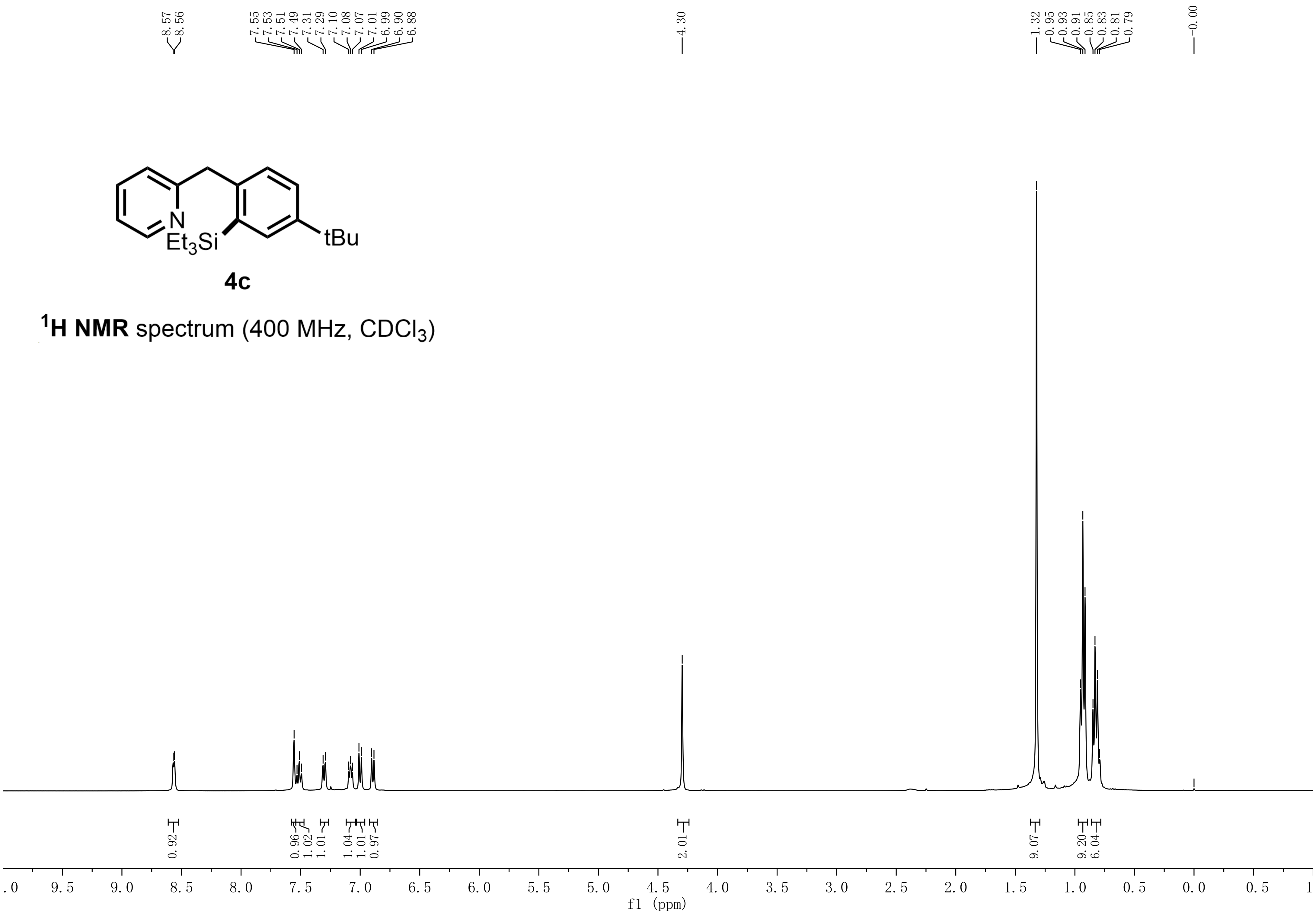
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

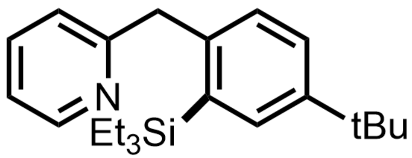




4b

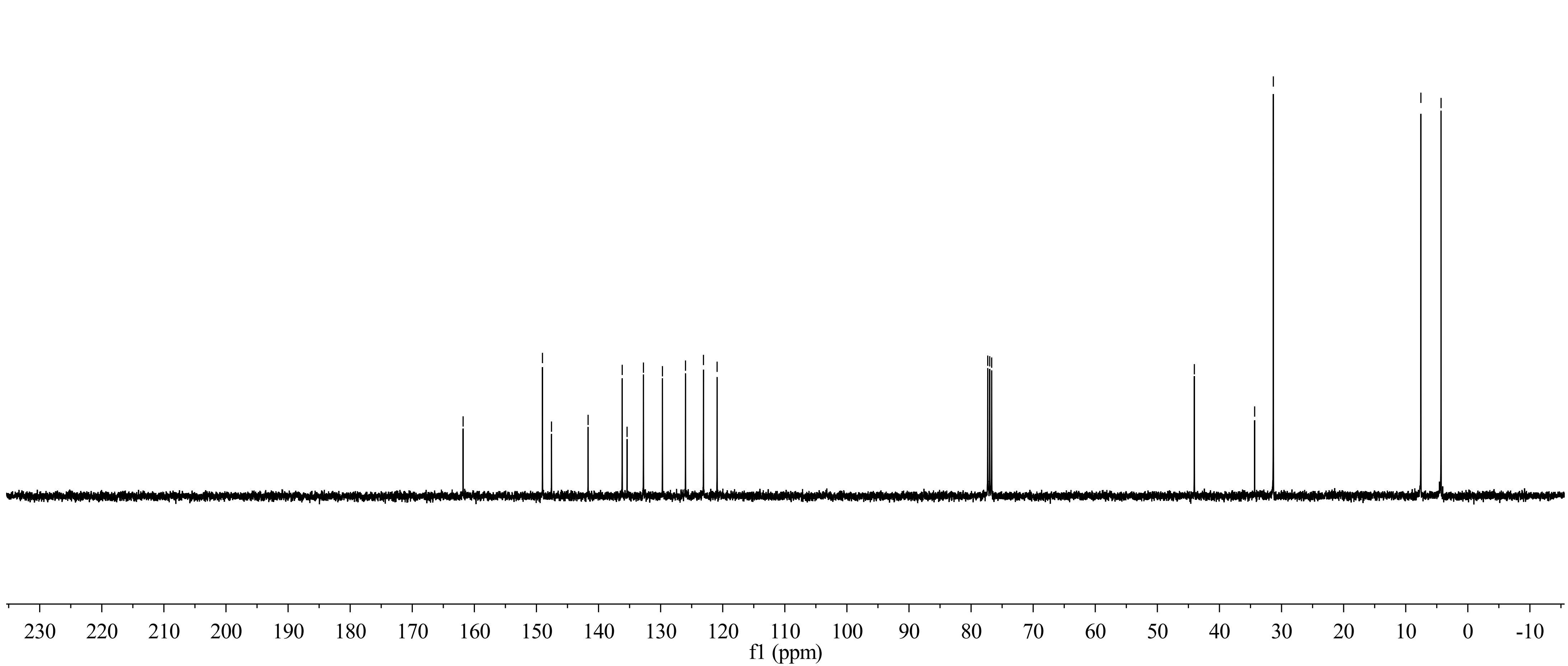
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

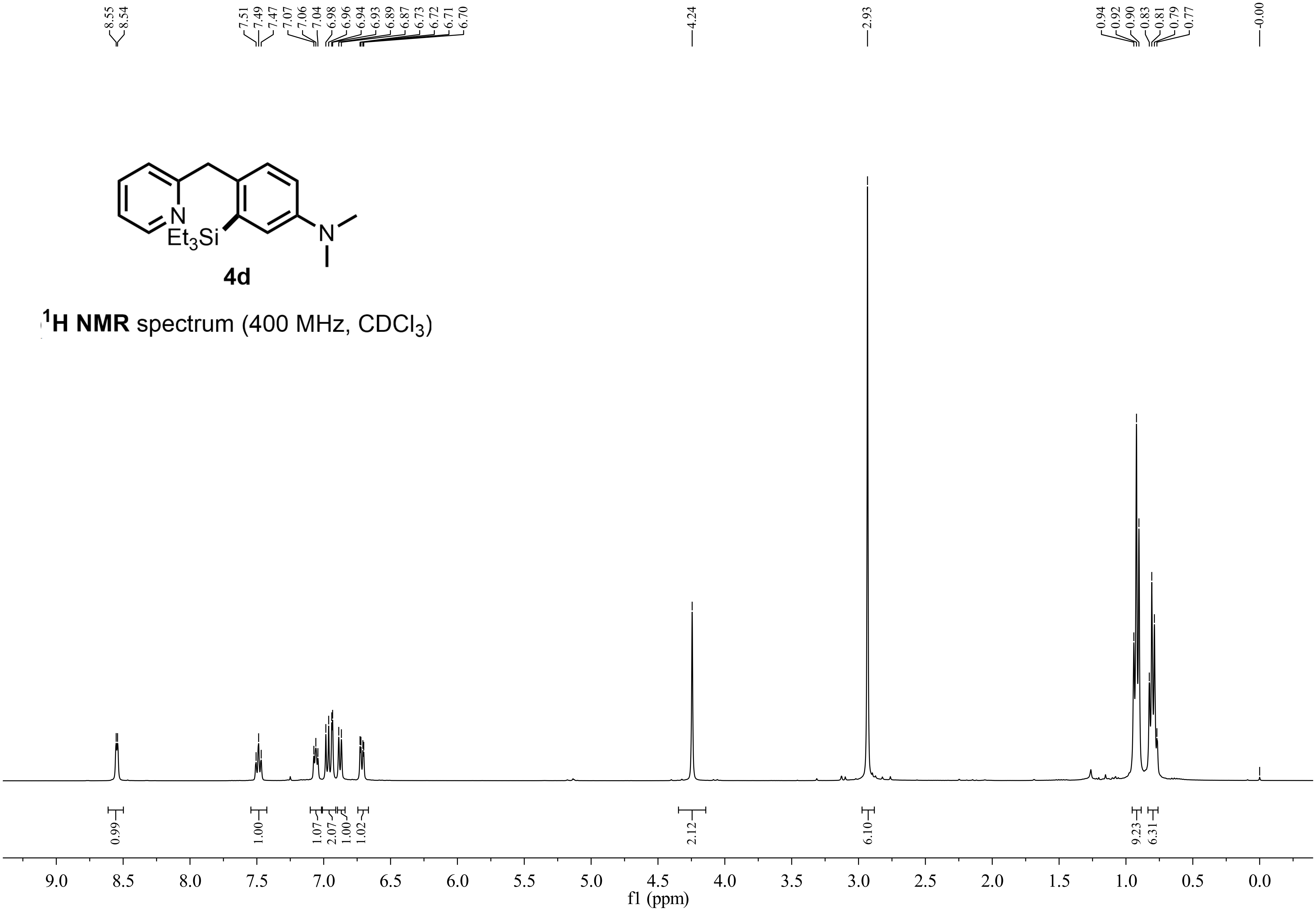

8.57
8.56
7.55
7.53
7.51
7.49
7.31
7.29
7.10
7.08
7.07
7.01
6.99
6.90
6.88
4.30
1.32
0.95
0.93
0.91
0.85
0.83
0.81
0.79
-0.00
N
Et3Si
tBu
4c
1H NMR spectrum (400 MHz, CDCl3)
0.92
0.96
1.02
1.01
1.04
1.01
0.97
2.01
9.07
9.20
6.04
f1 (ppm)

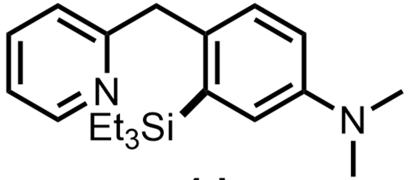


4c

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

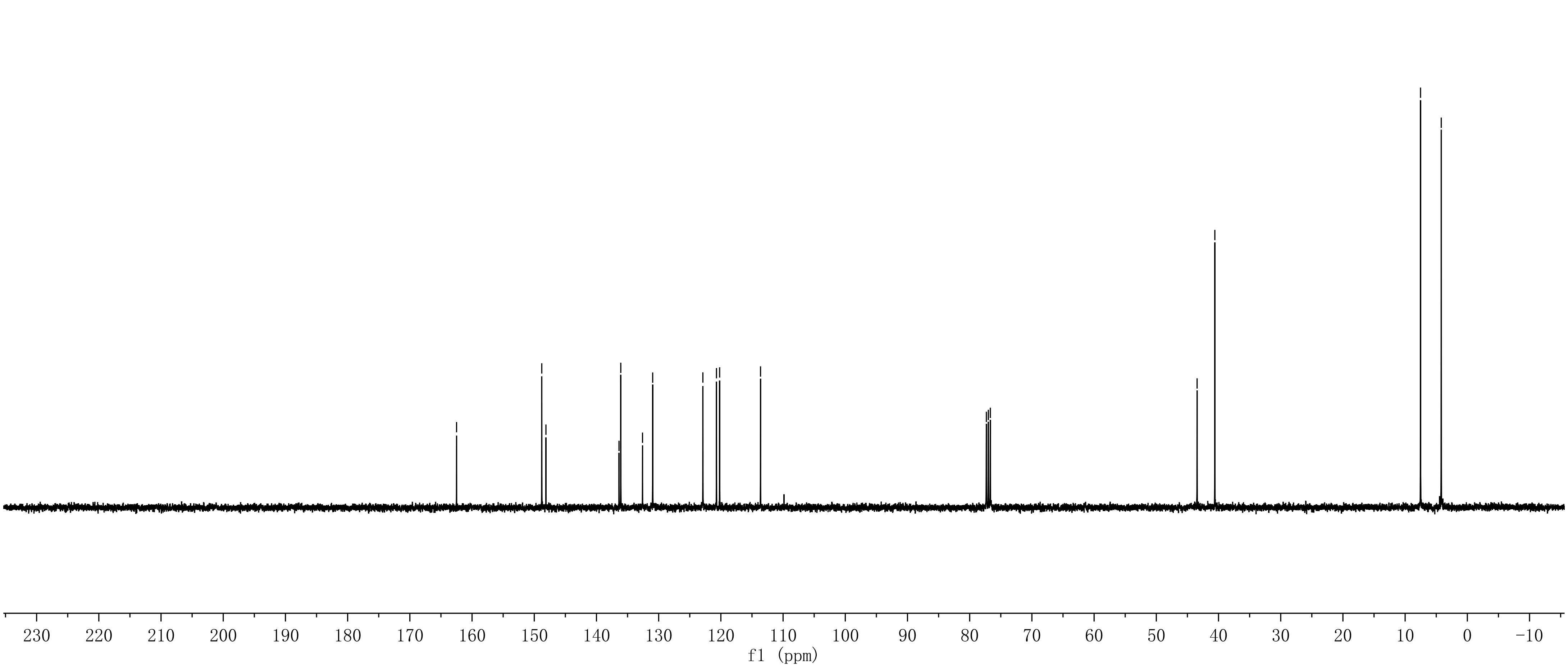


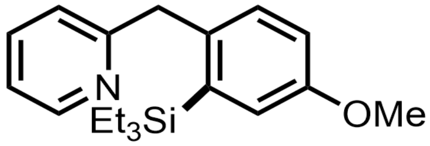

8.55
8.54
7.51
7.49
7.47
7.07
7.06
7.04
6.98
6.96
6.94
6.93
6.89
6.87
6.73
6.72
6.71
6.70
4.24
2.93
0.94
0.92
0.90
0.83
0.81
0.79
0.77
-0.00
N
Et_3Si
N
4d
1H NMR spectrum (400 MHz, $CDCl_3$)
0.99
1.00
1.07
2.07
1.00
1.02
2.12
6.10
9.23
6.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4d

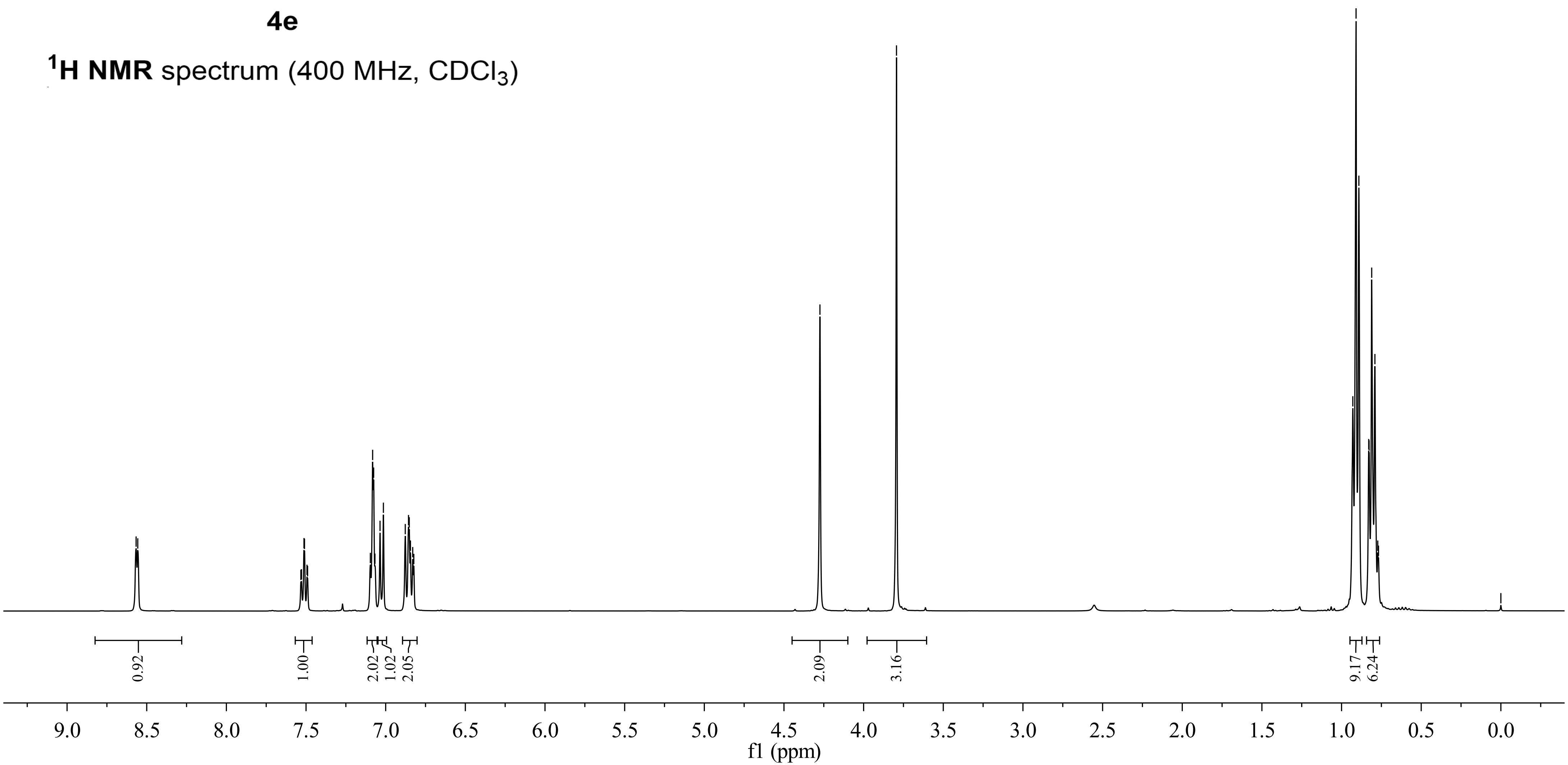
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

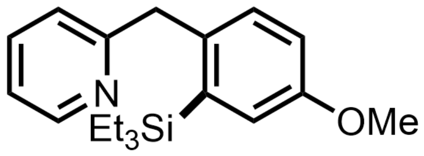




4e

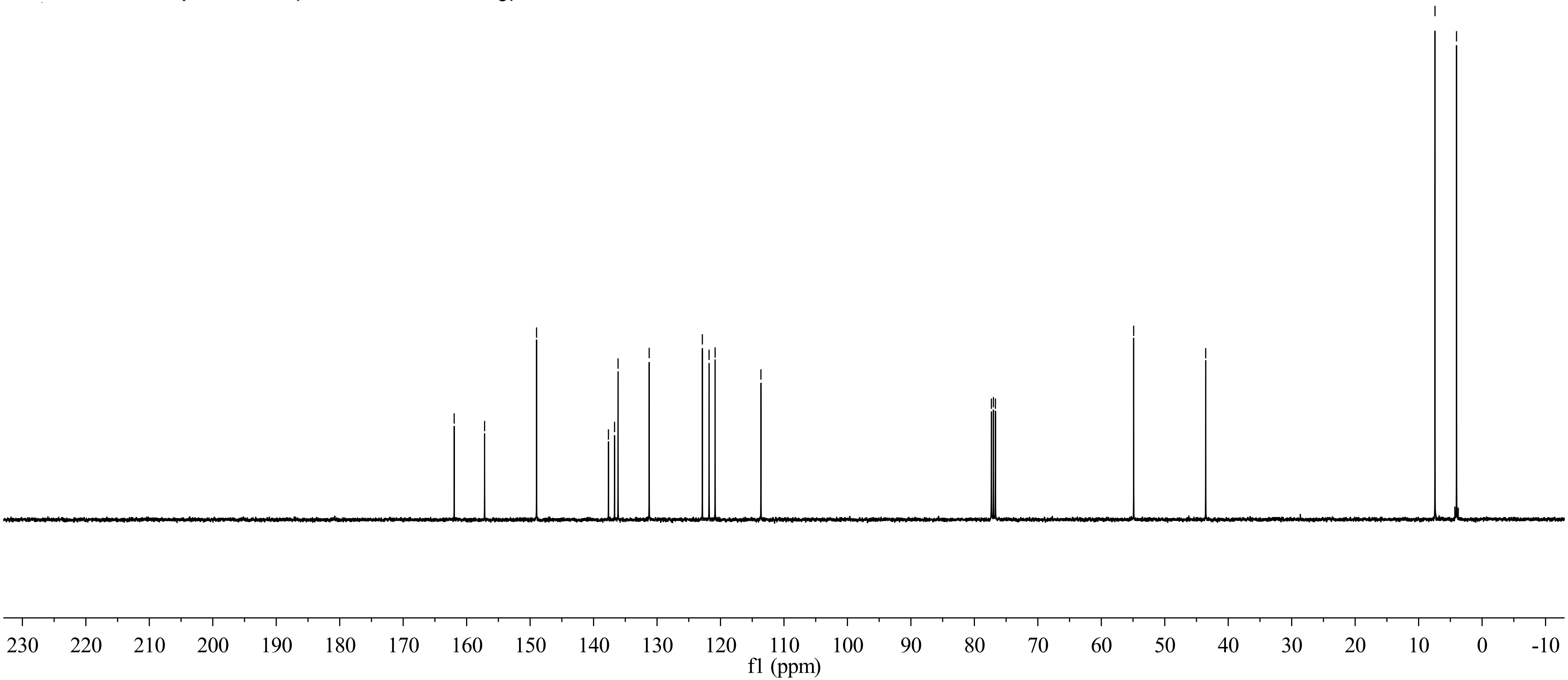
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

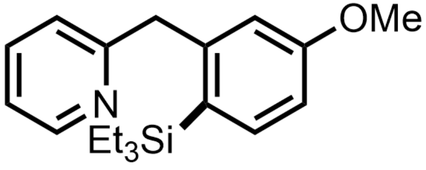




4e

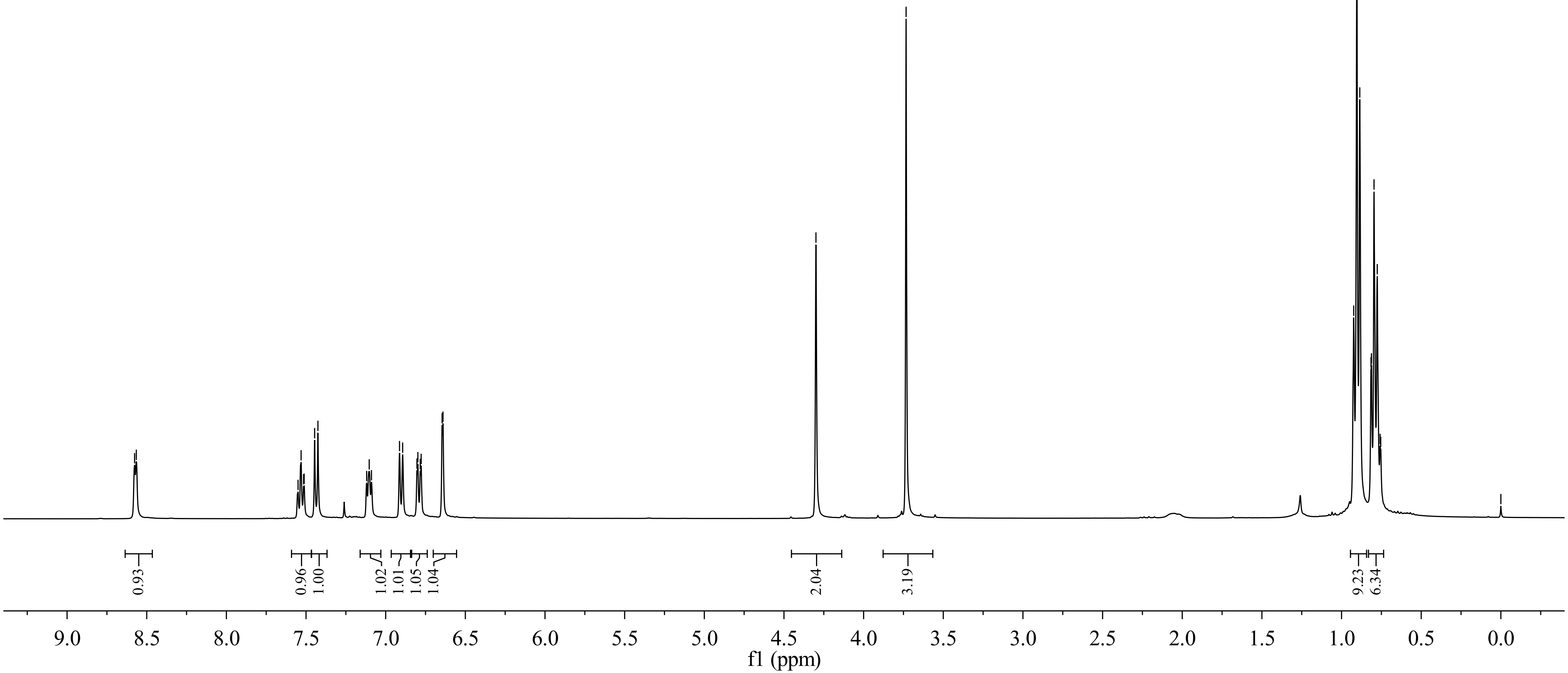
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

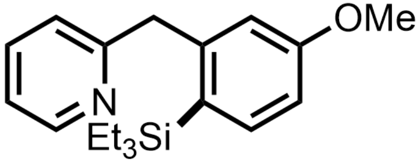




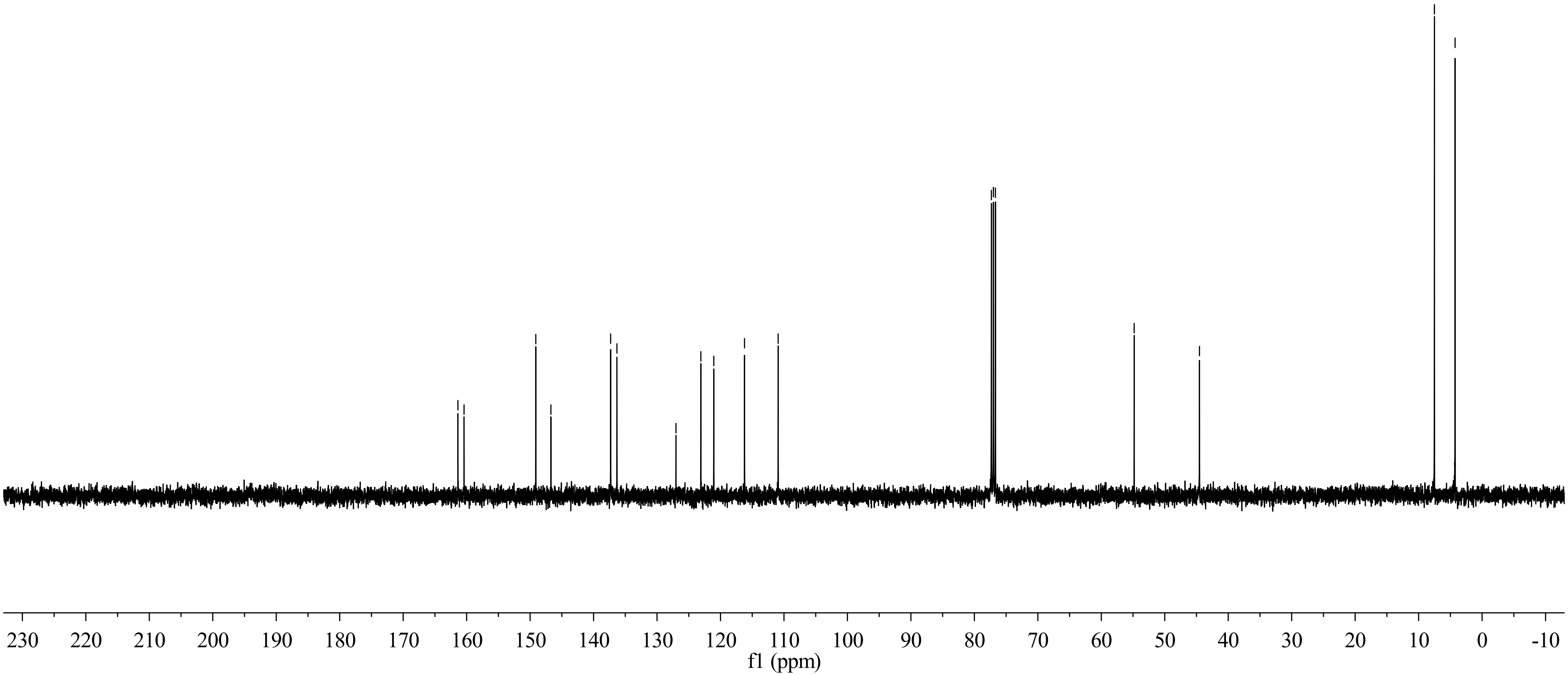
4f

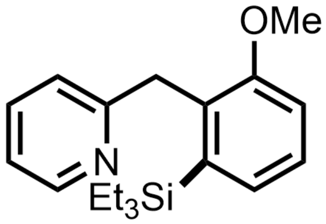
^{1}H NMR spectrum (400 MHz, $CDCl_3$)




OMe
N
Et_3Si

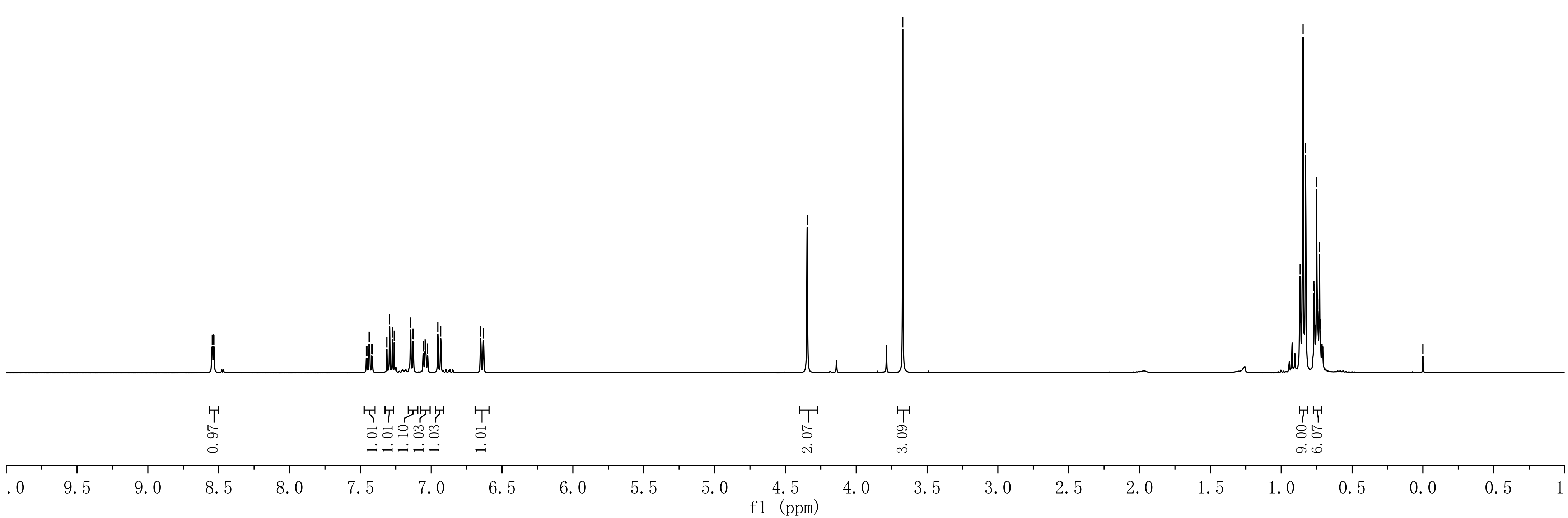
4f

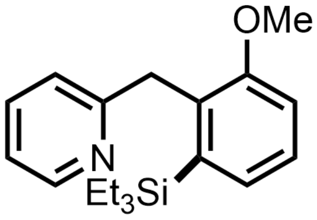

^{13}C NMR spectrum (100 MHz, $CDCl_3$)
161.38
160.41
149.10
146.72
137.31
136.32
127.02
123.10
121.06
116.22
110.92
77.32
77.00
76.68
54.82
44.53
7.51
4.25
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4g

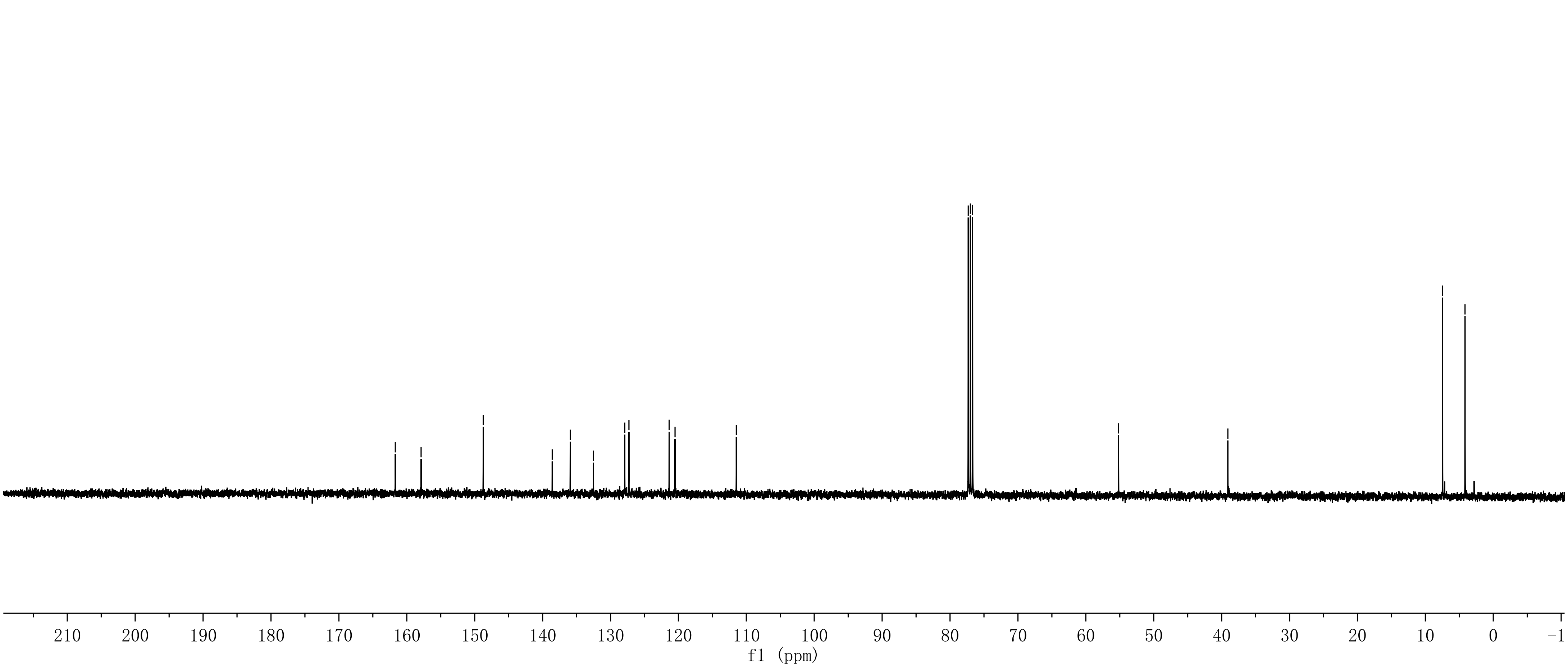
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

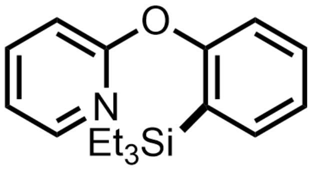




4g

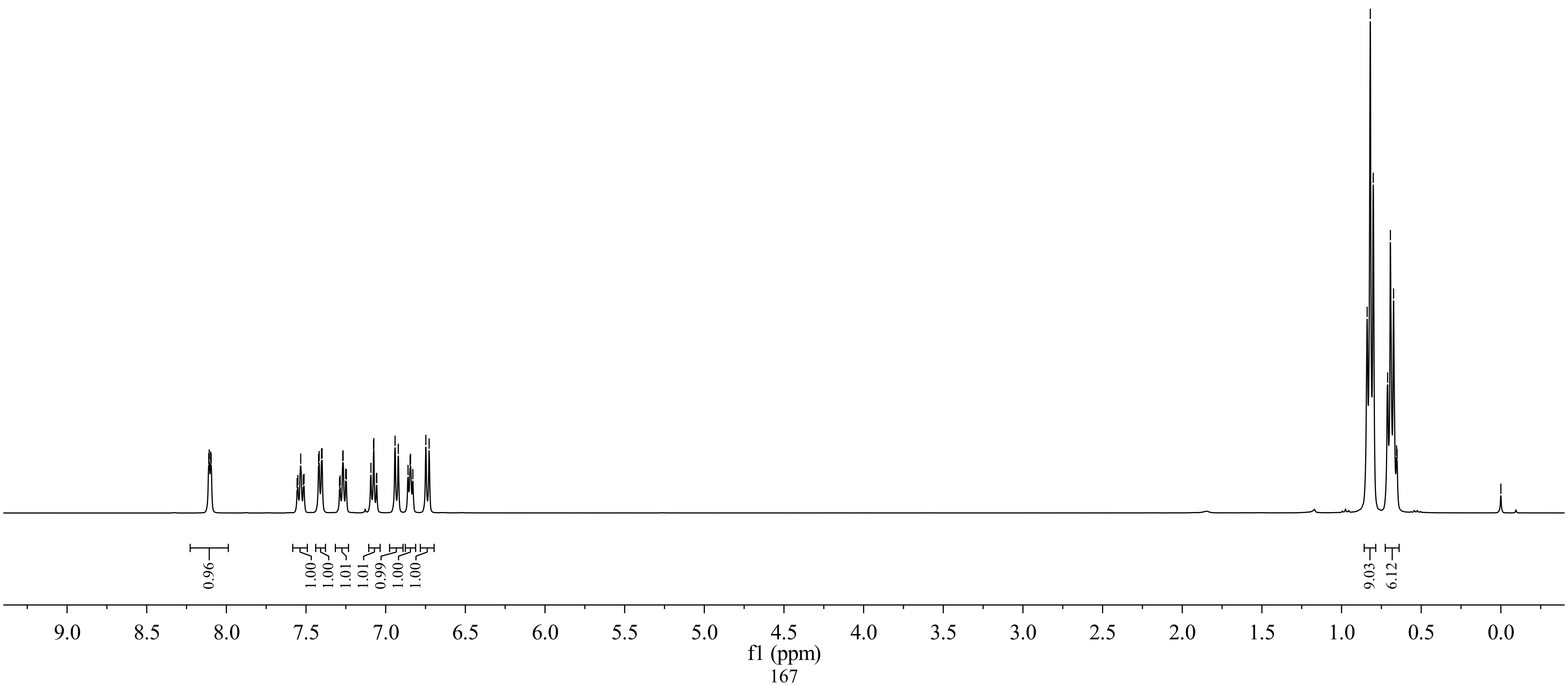
^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)





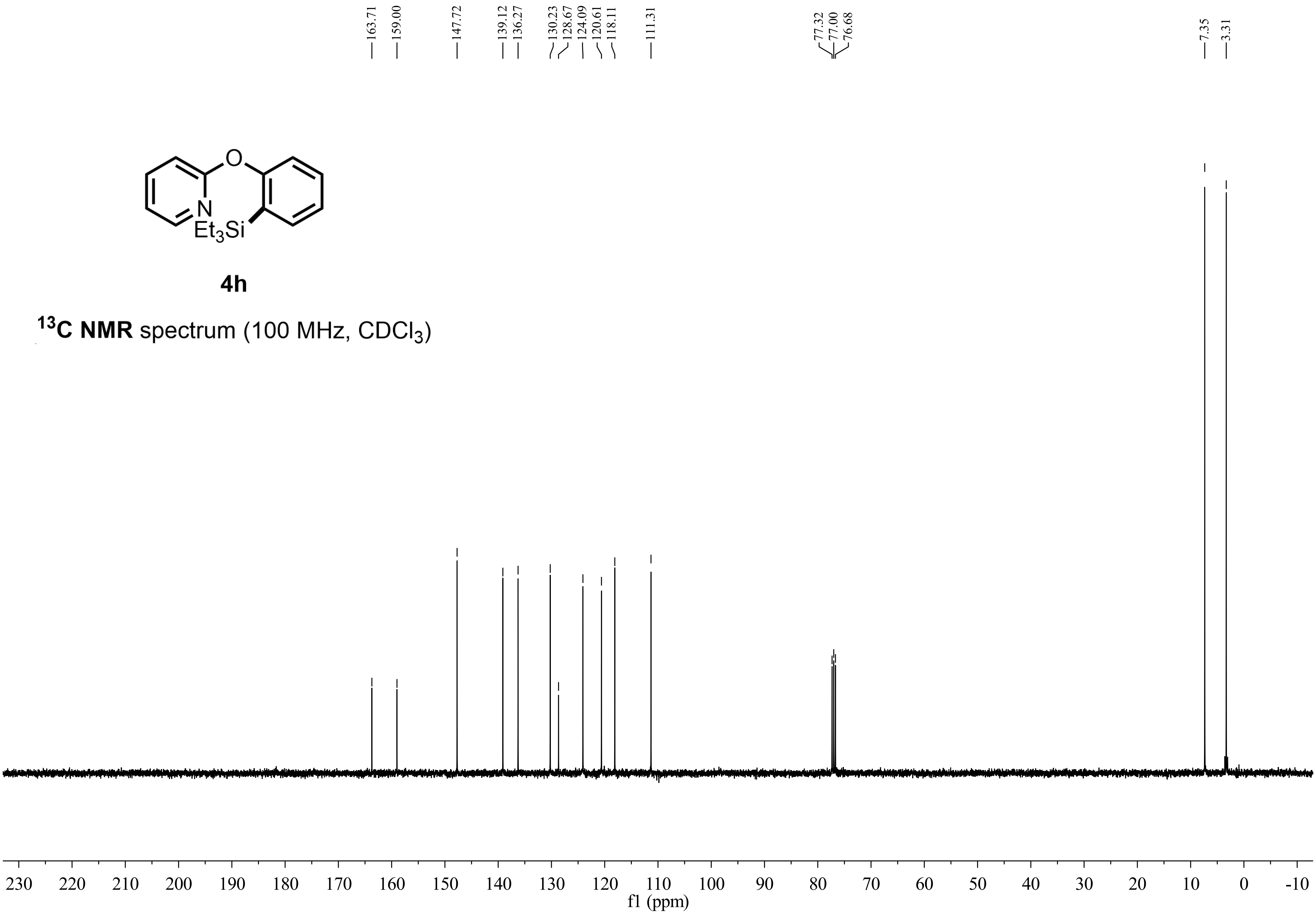
4h

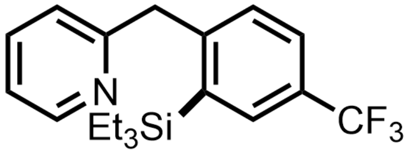
[1]H NMR spectrum (400 MHz, $CDCl_3$)



4h

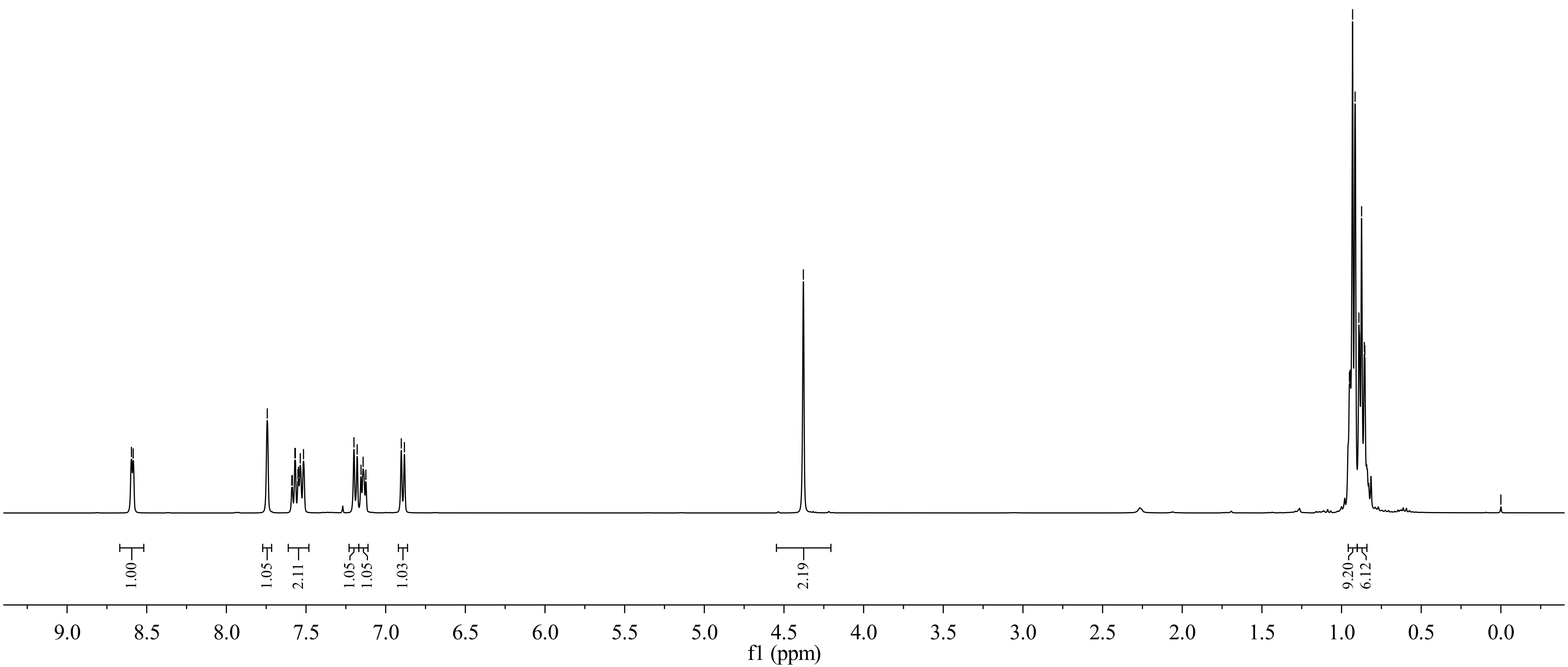
^{13}C NMR spectrum (100 MHz, $CDCl_3$)





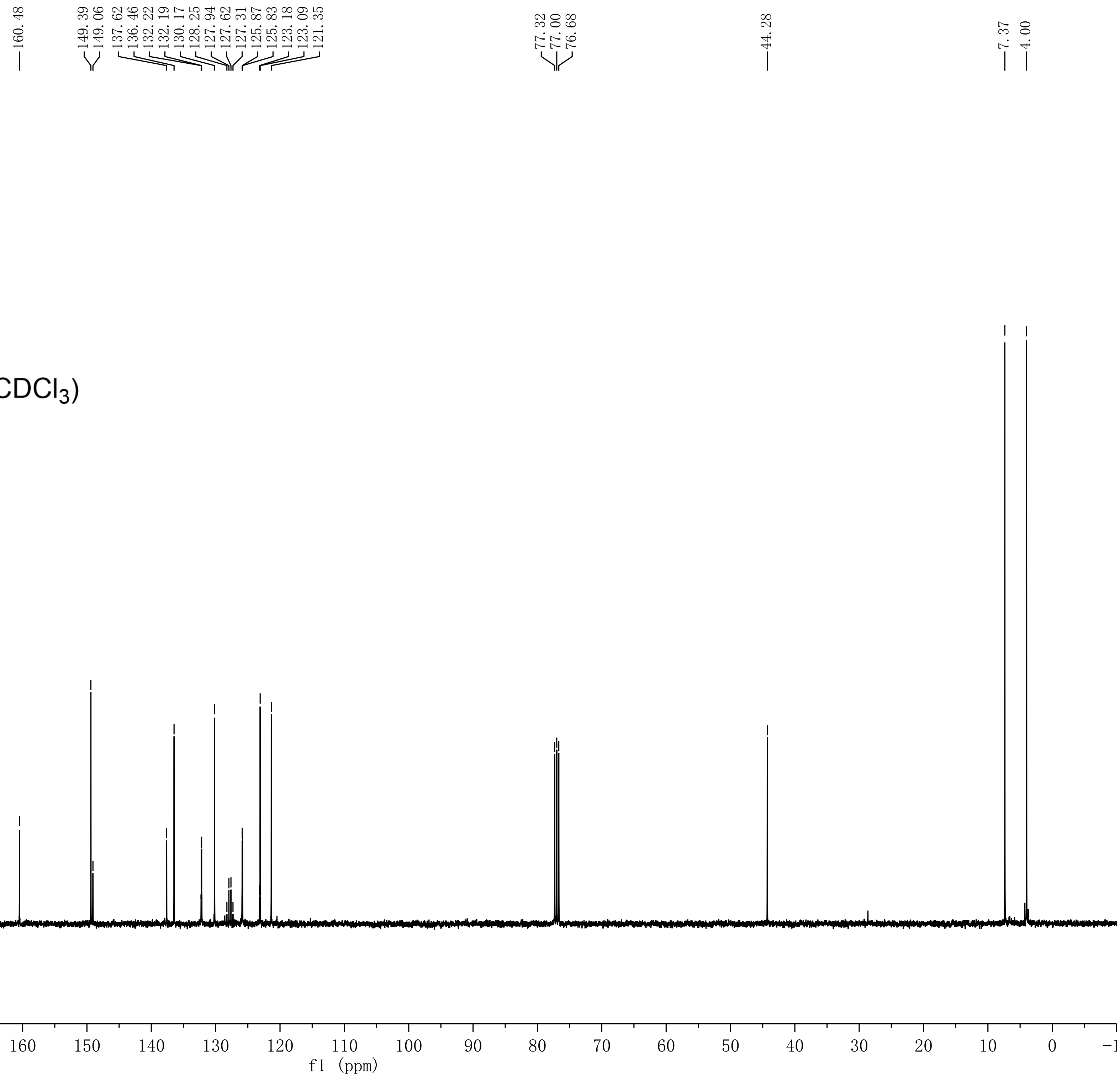
4i

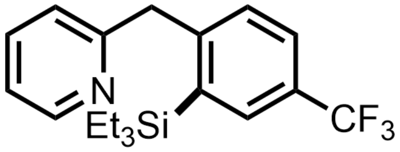
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



4i

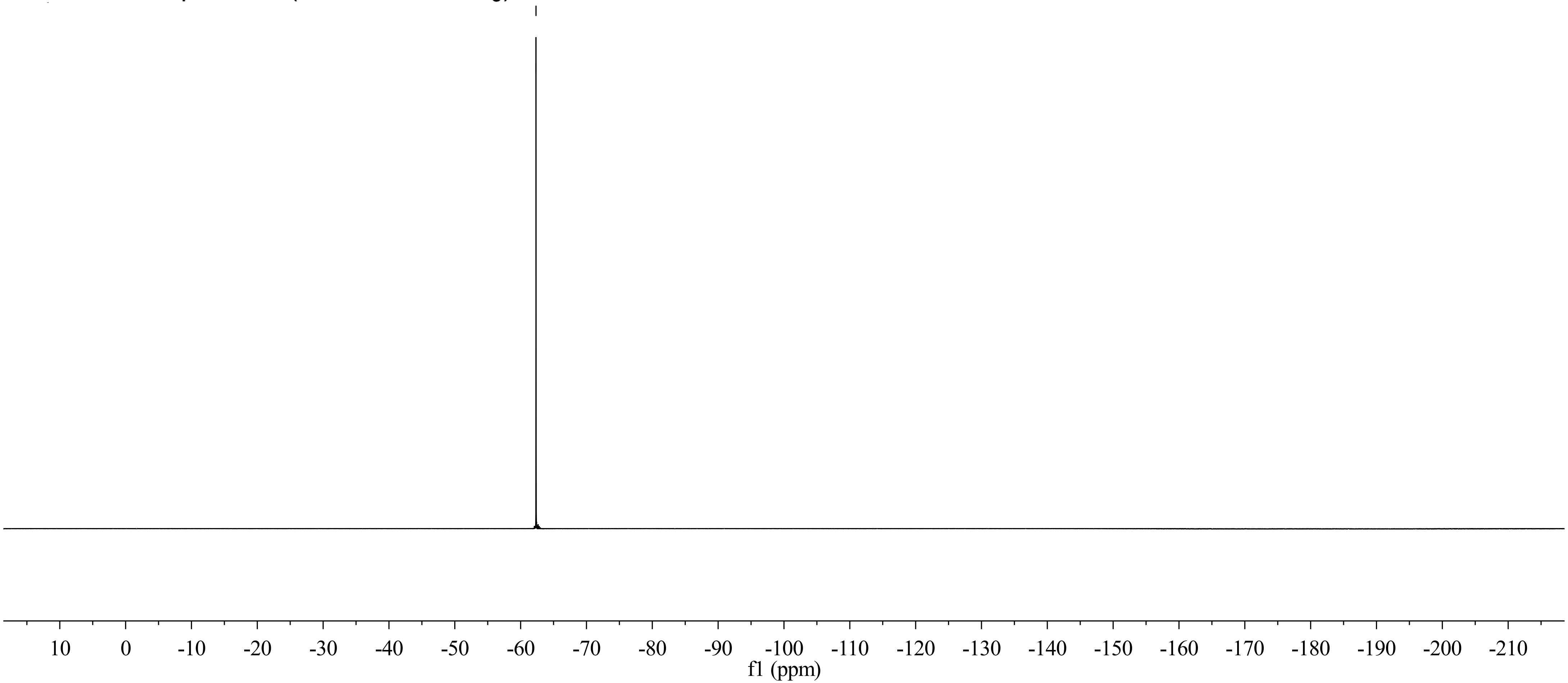
[13]C NMR spectrum (100 MHz, $CDCl_3$)

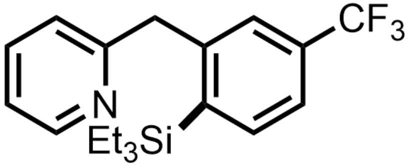




4i

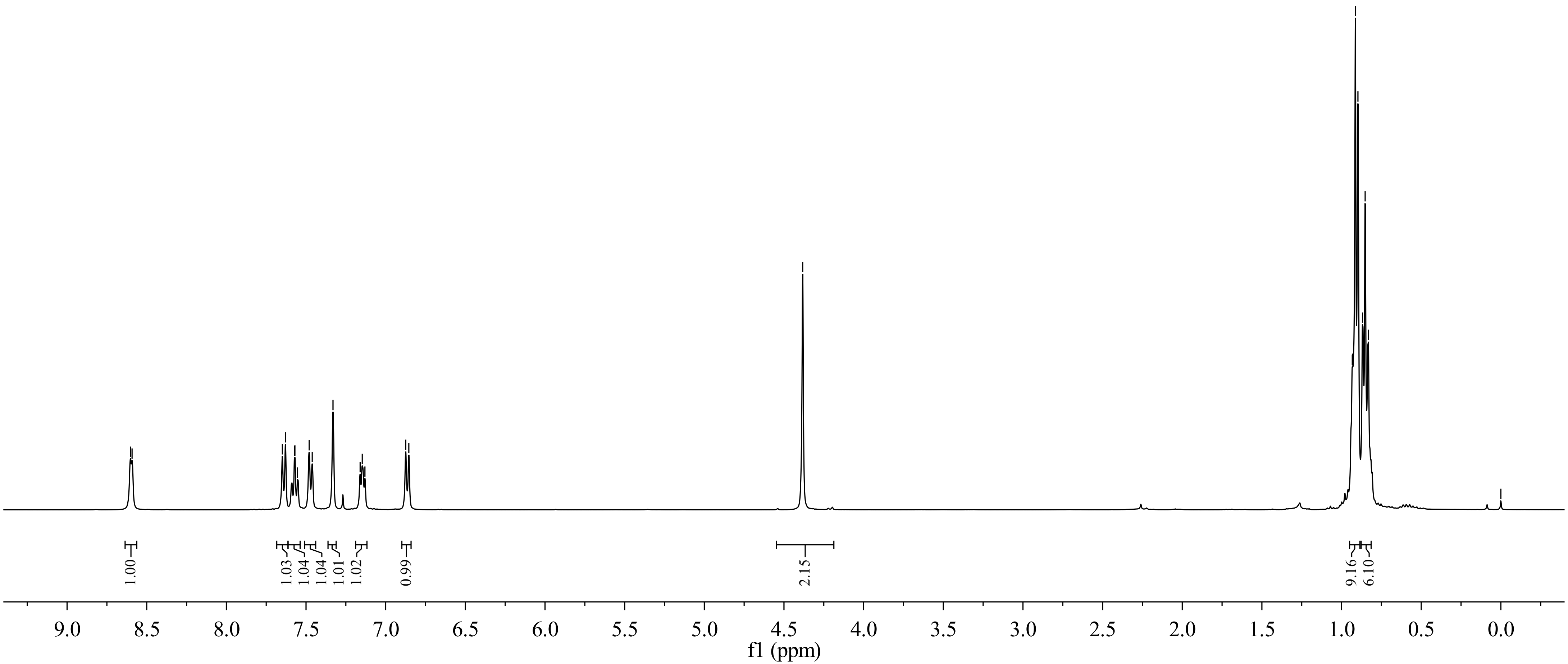
^{19}F NMR spectrum (376 MHz, $CDCl_3$)

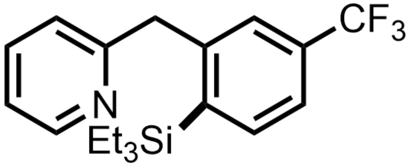




4j

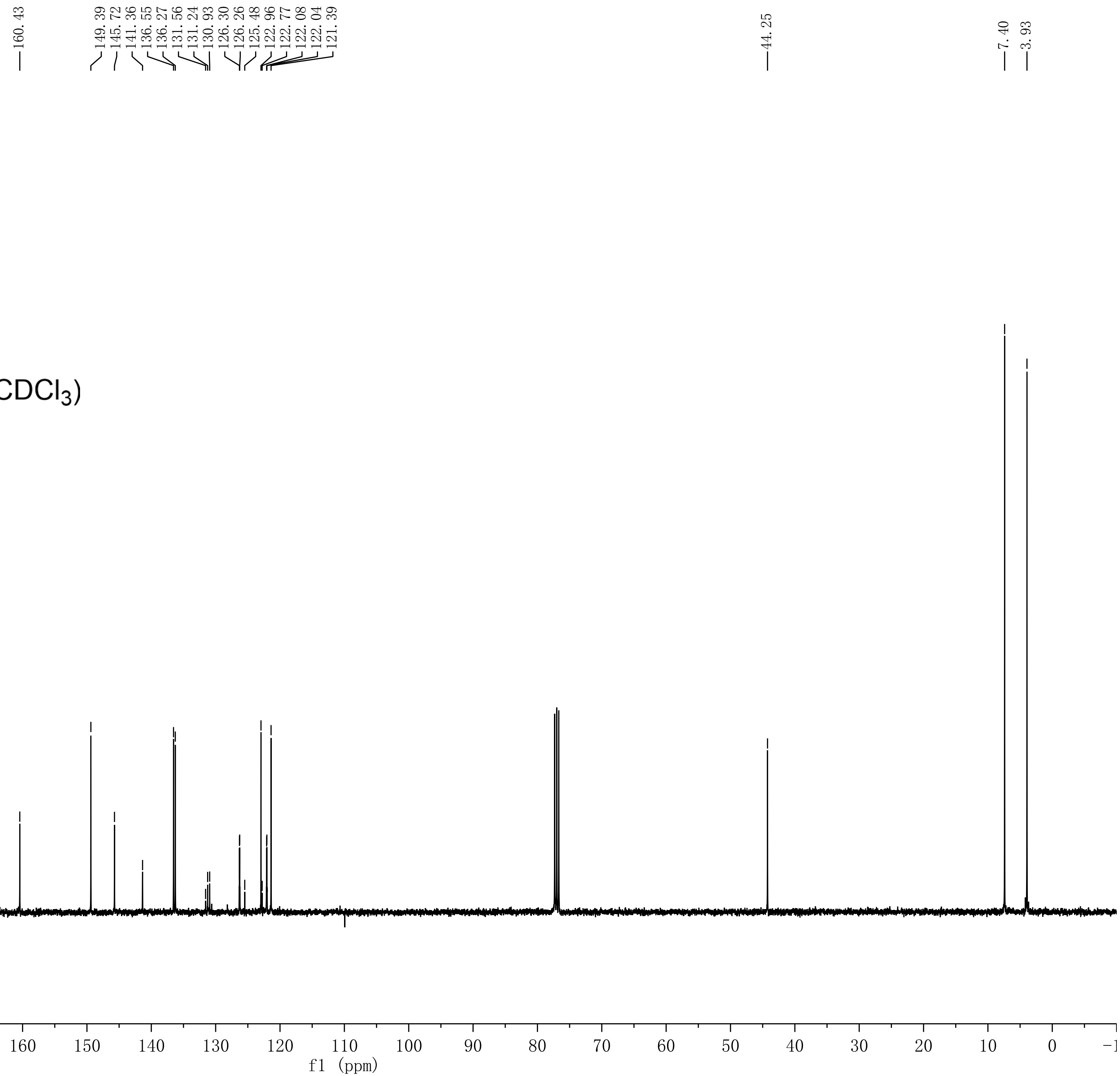
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

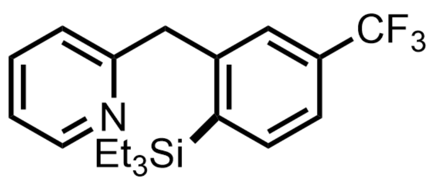




4j

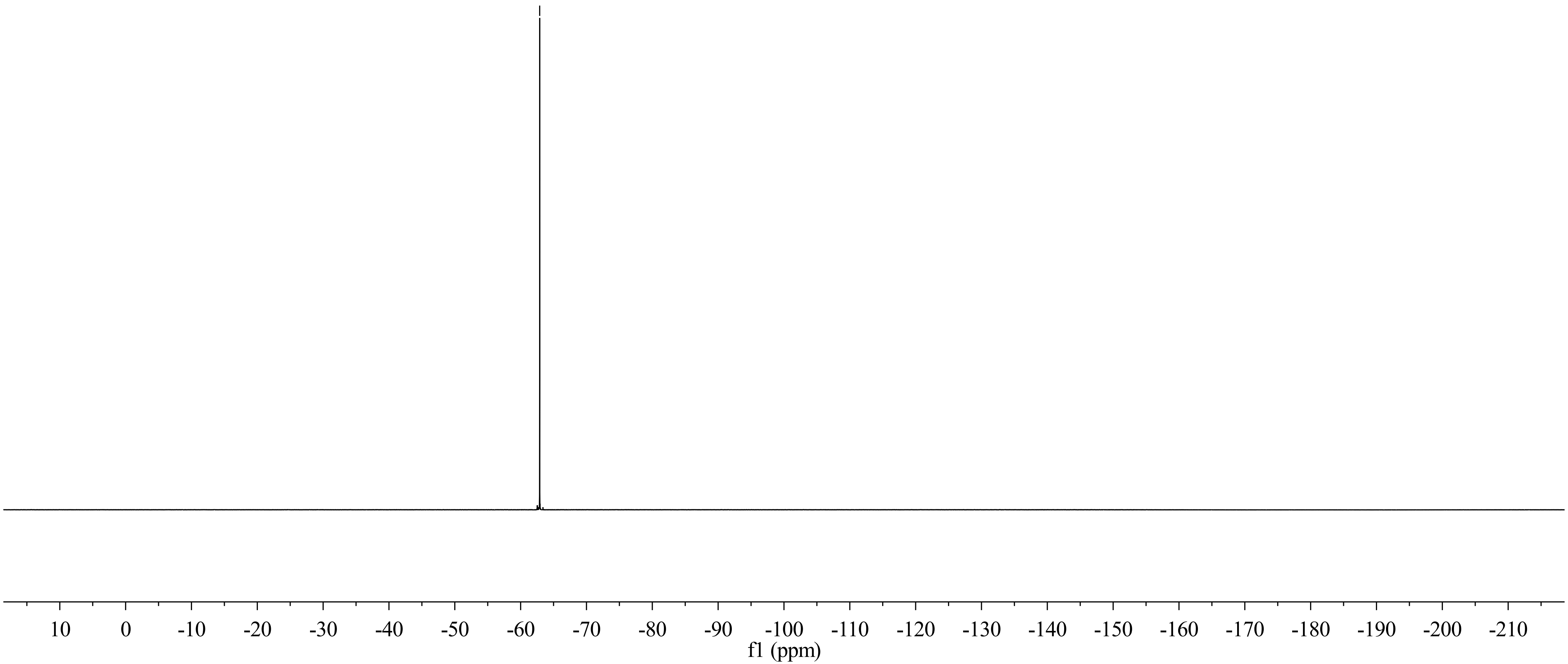
[13]C NMR spectrum (100 MHz, $CDCl_3$)

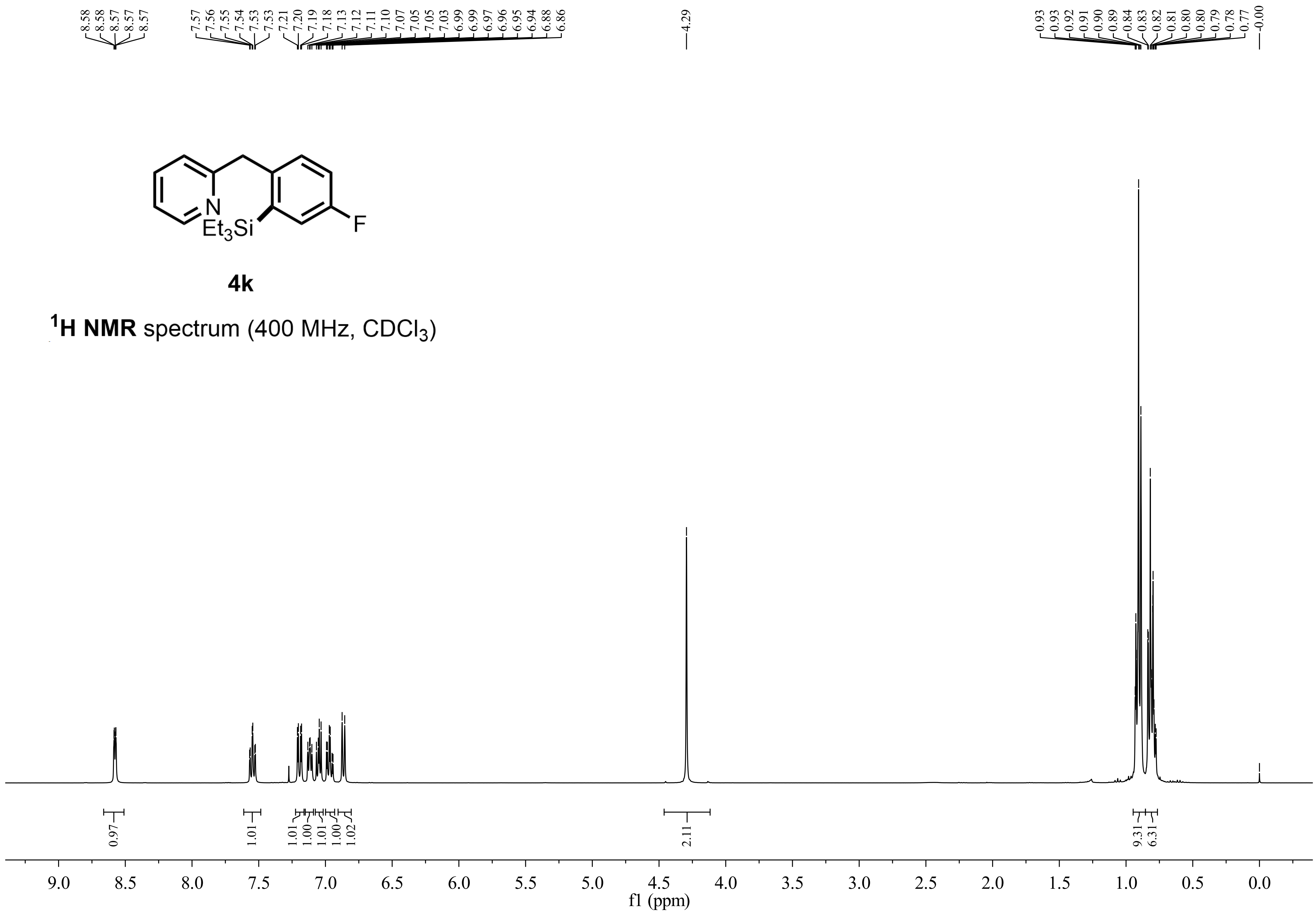




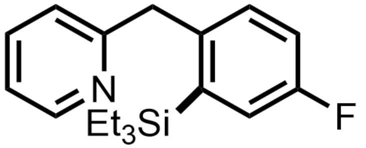
4j

^{19}F NMR spectrum (376 MHz, $CDCl_3$)



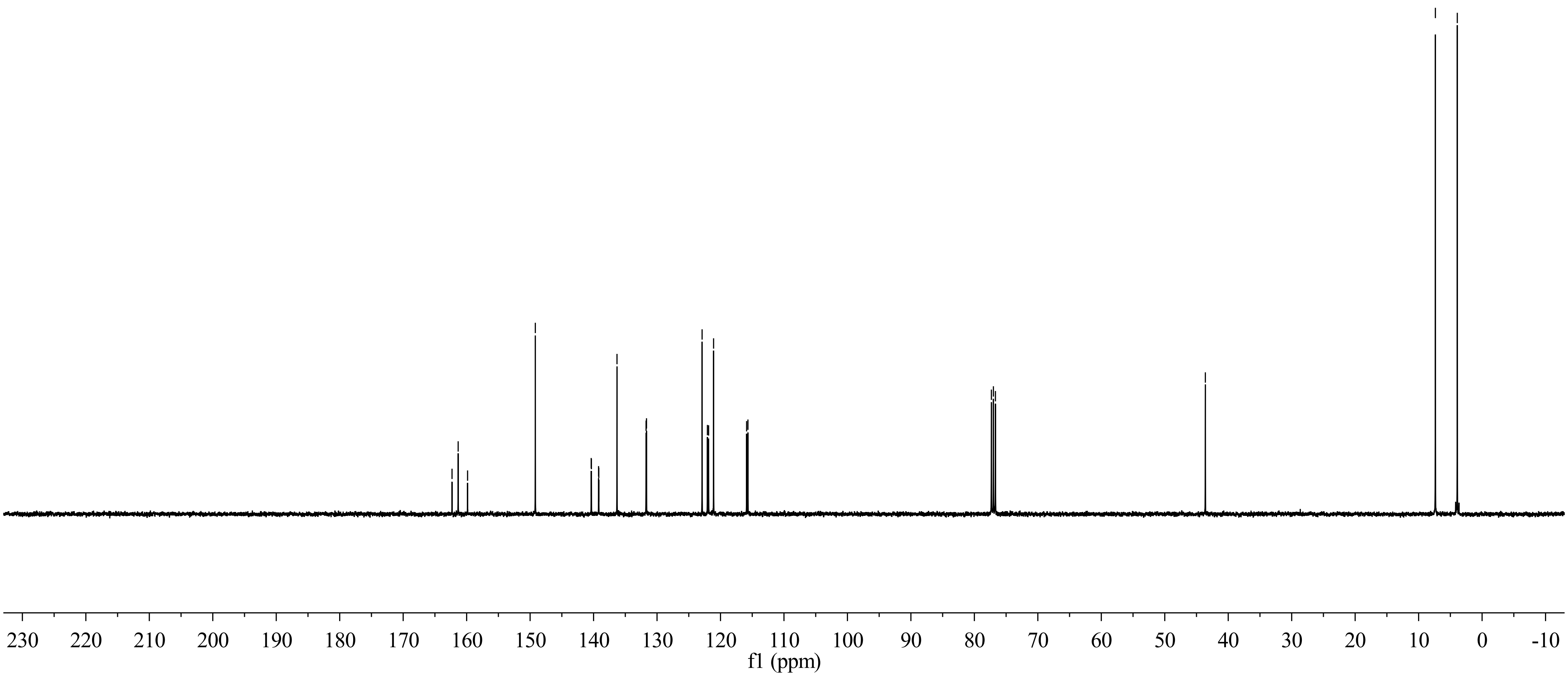


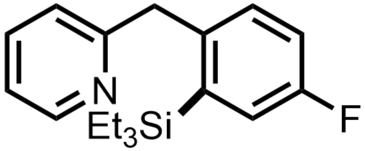
4k
¹H NMR spectrum (400 MHz, CDCl3)
8.58 8.58 8.57 8.57 8.57
7.57 7.56 7.55 7.54 7.53 7.53 7.21 7.20 7.19 7.18 7.13 7.12 7.11 7.10 7.07 7.05 7.05 7.03 6.99 6.99 6.97 6.96 6.95 6.94 6.88 6.86
4.29
0.93 0.93 0.92 0.91 0.90 0.89 0.84 0.83 0.82 0.81 0.80 0.80 0.79 0.78 0.77 -0.00
0.97 1.01 1.01 1.00 1.01 1.00 1.02 2.11 9.31 6.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4k

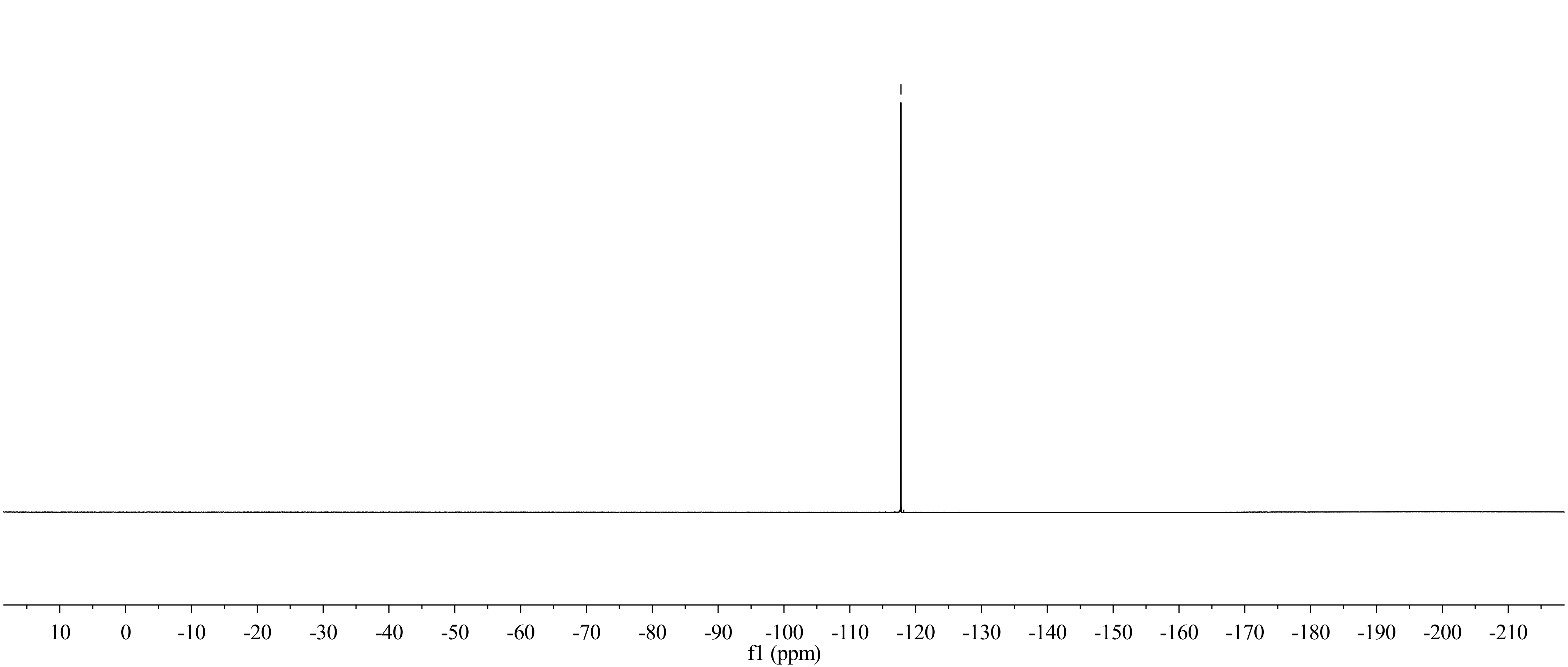
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

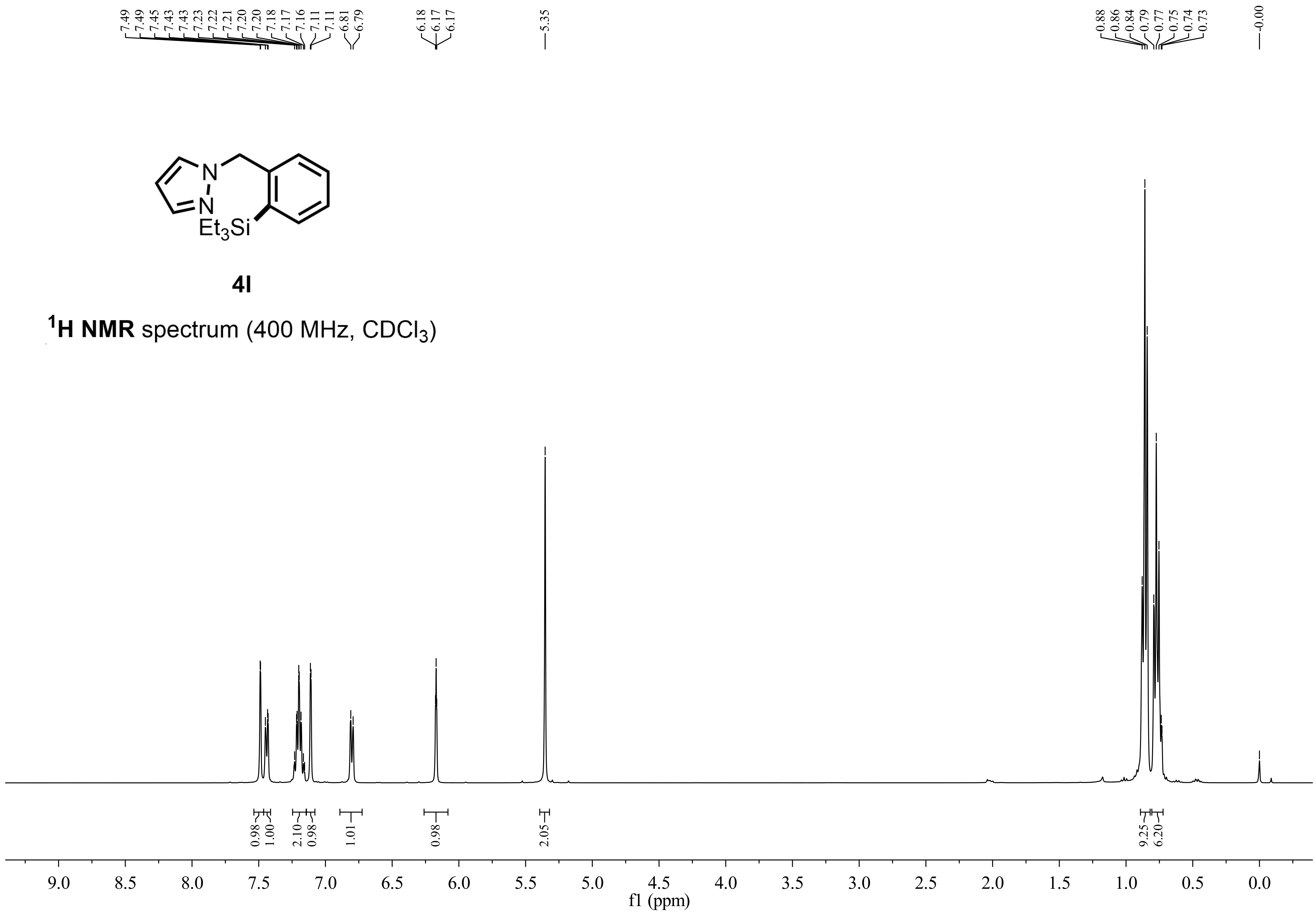




4k

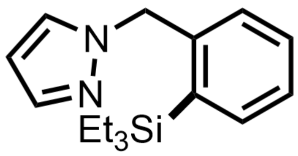
^{19}F NMR spectrum (376 MHz, $CDCl_3$)





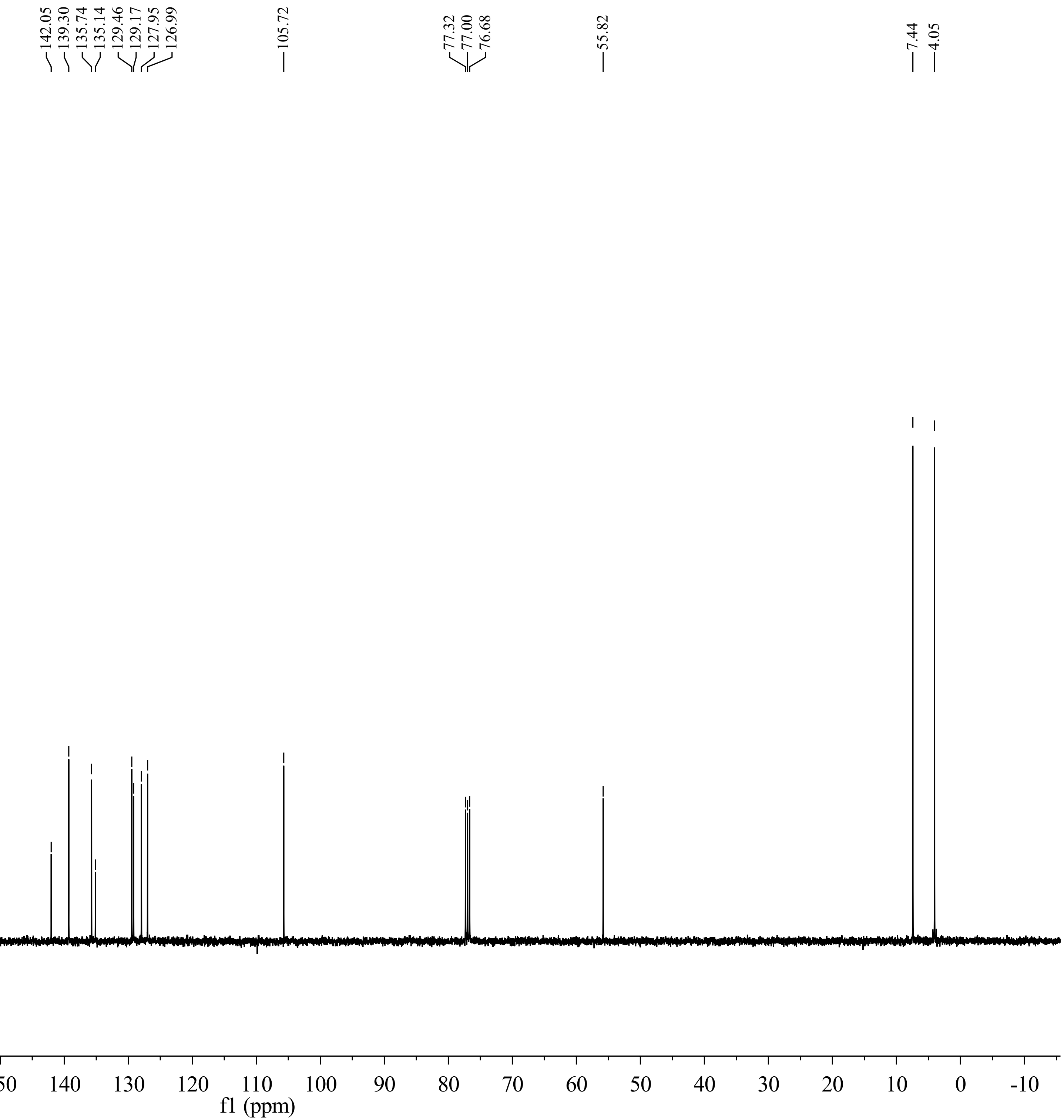
4l

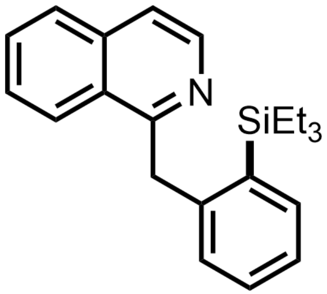
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



4l

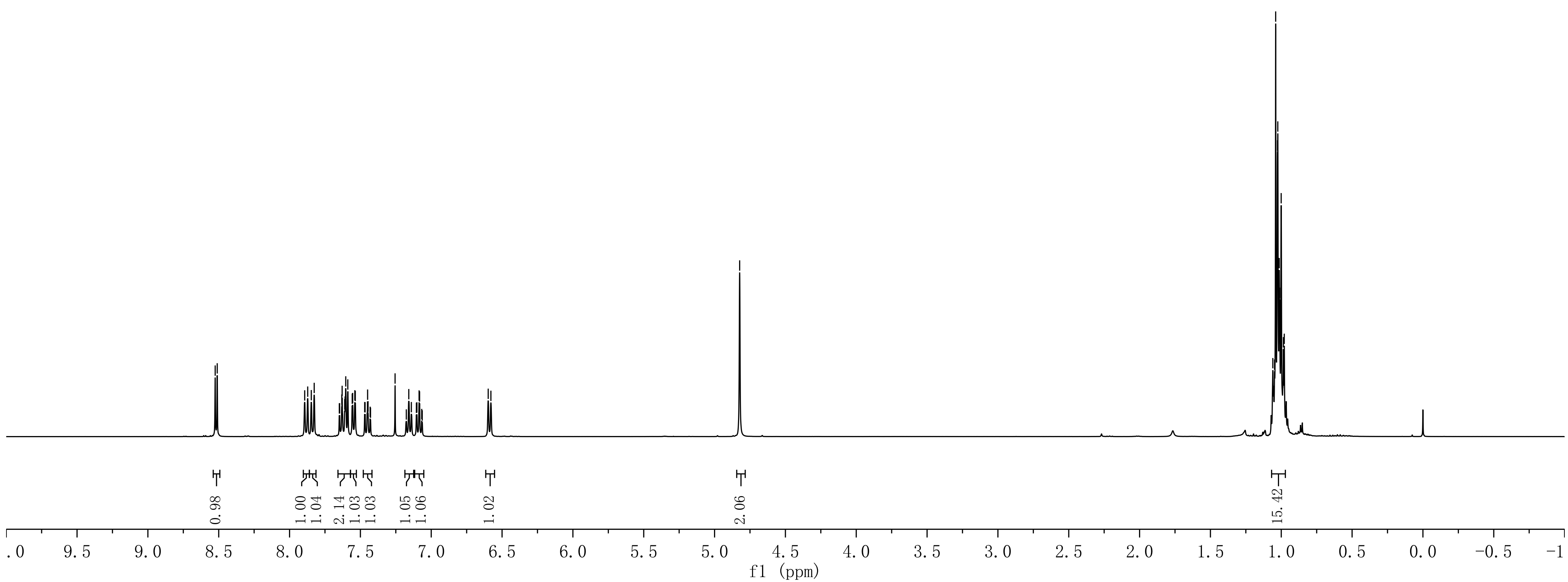
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

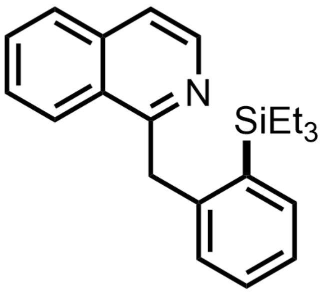




4m

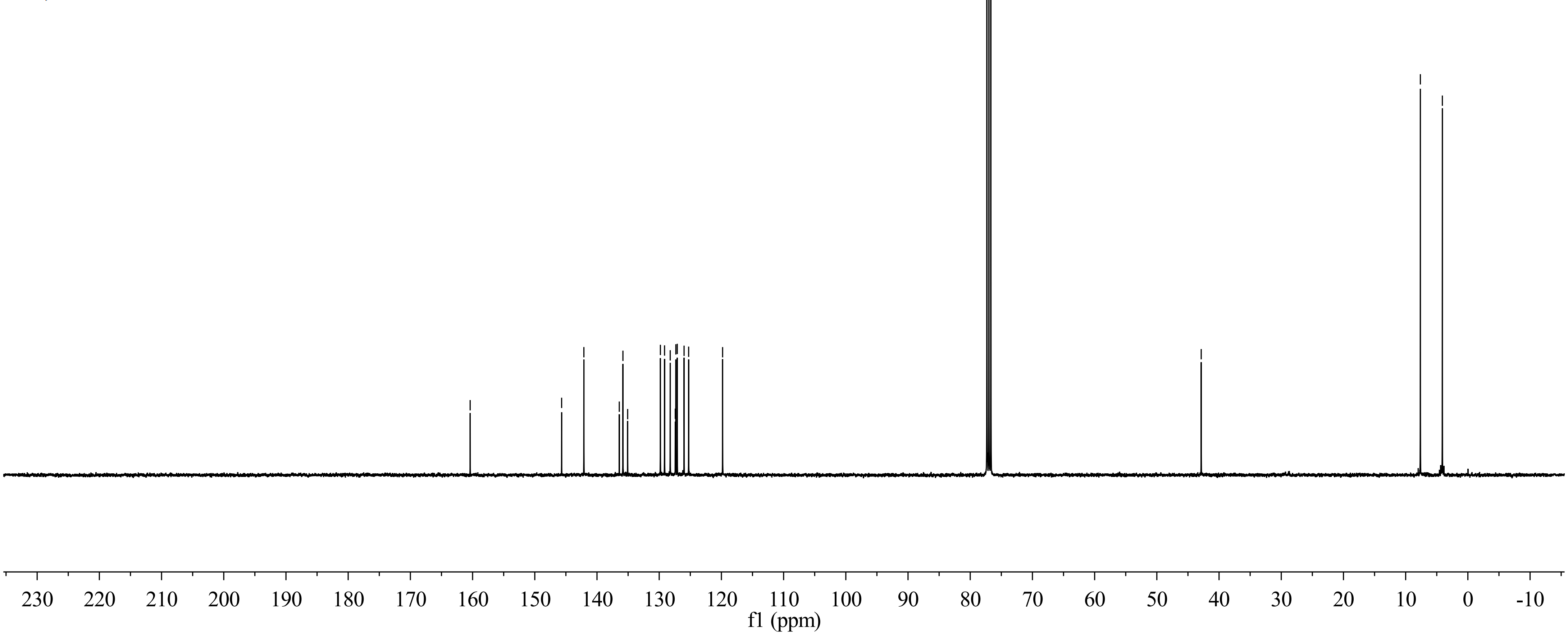
[1]H NMR spectrum (400 MHz, $CDCl_3$)

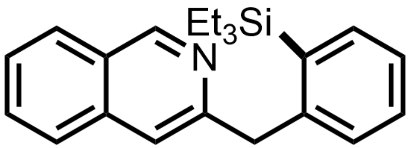




4m

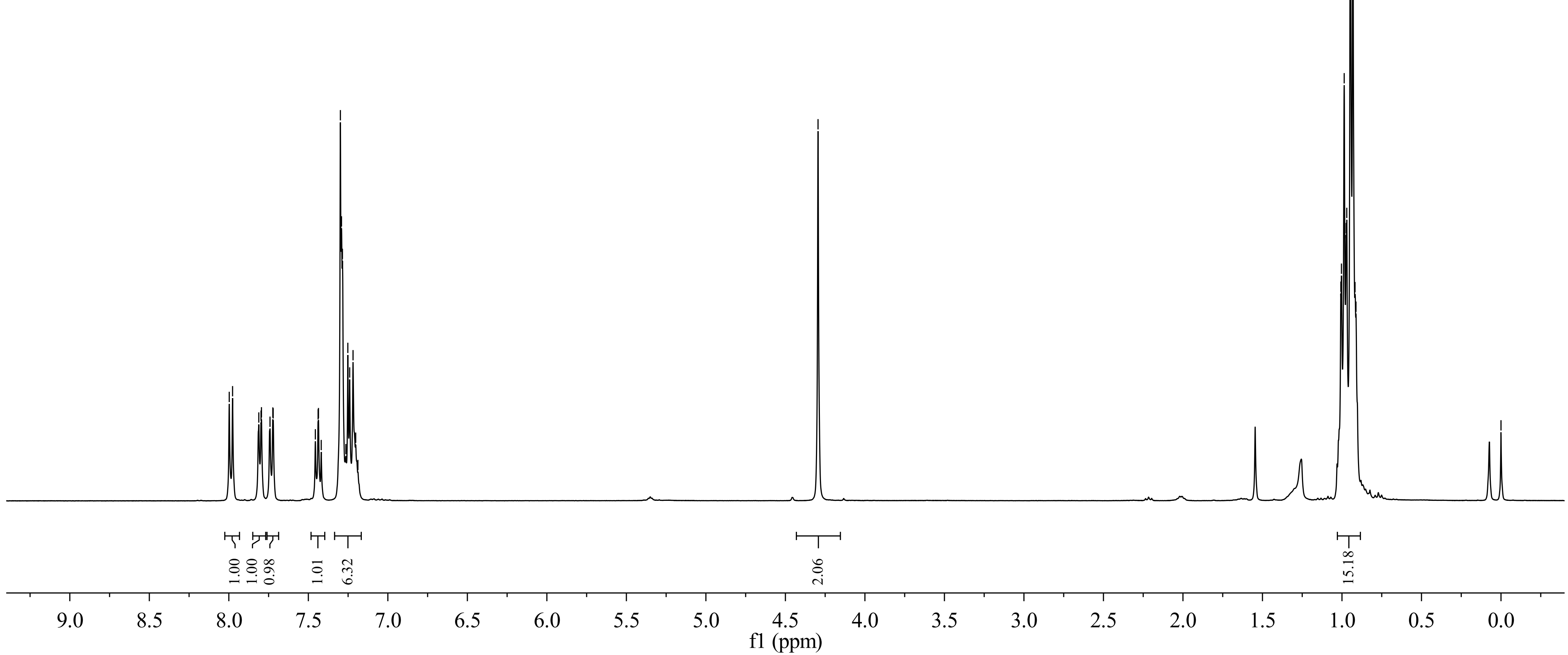
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

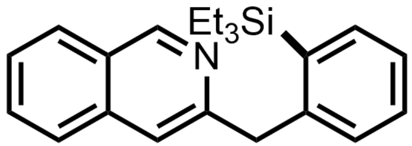




4n

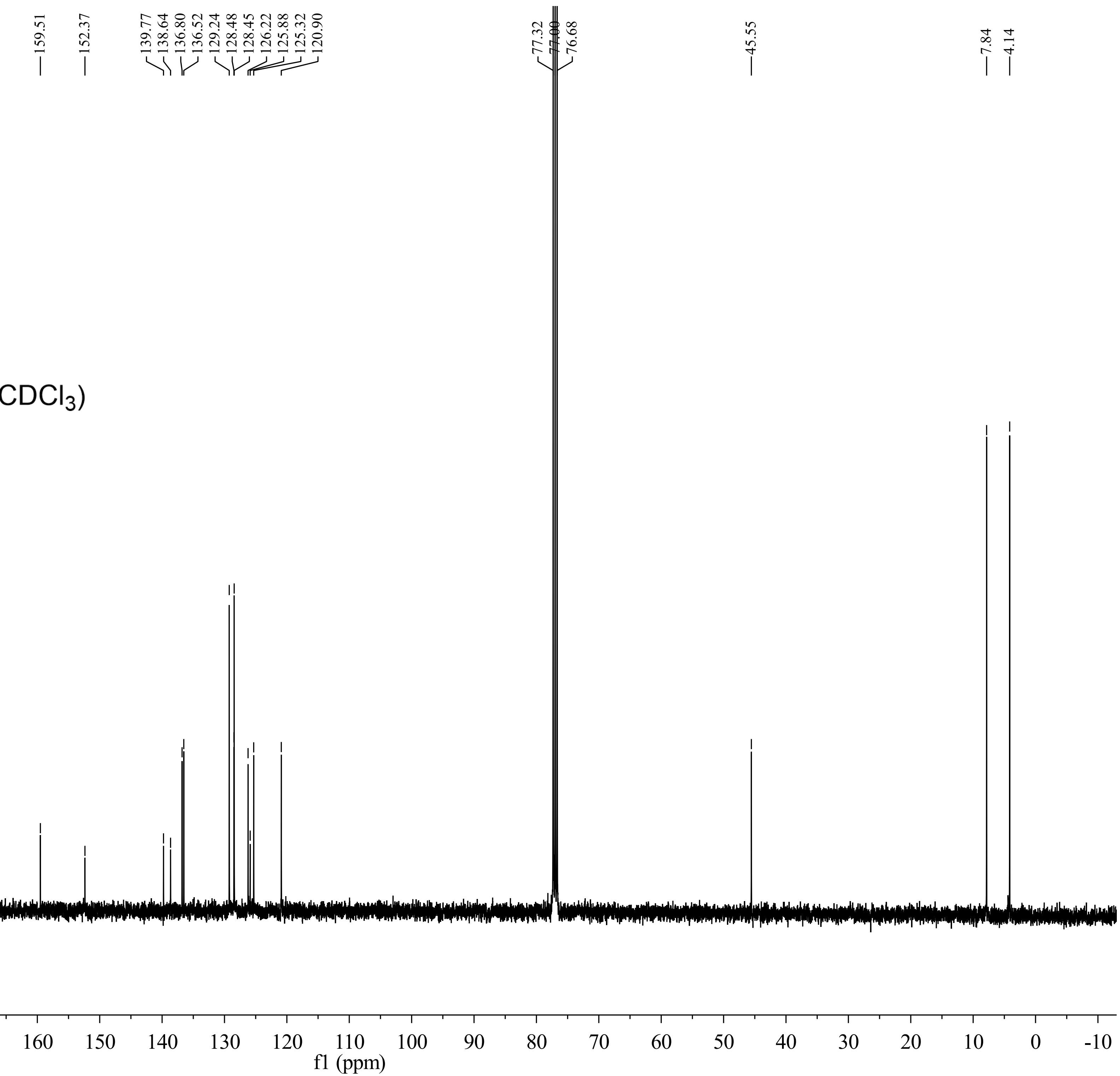
[1]H NMR spectrum (400 MHz, $CDCl_3$)

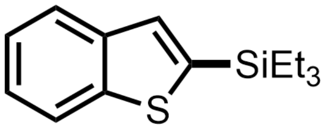




4n

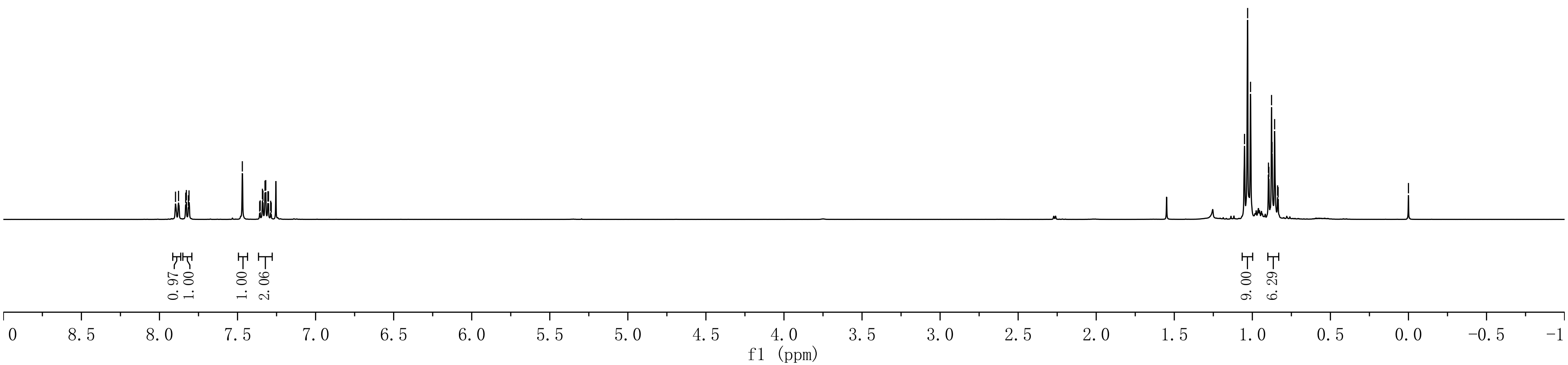
^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)

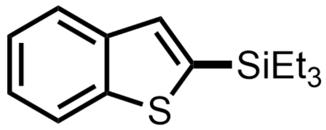




6a

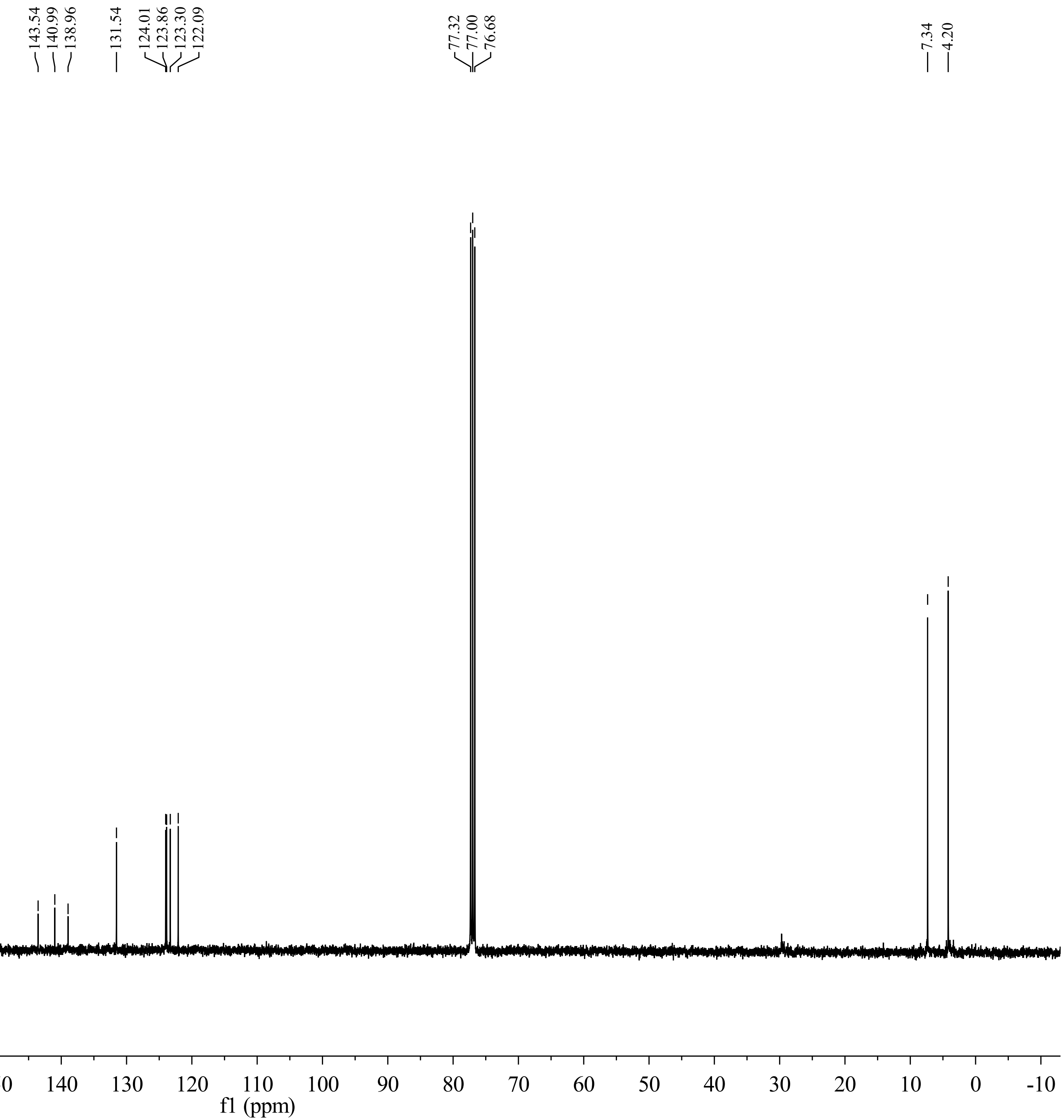
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

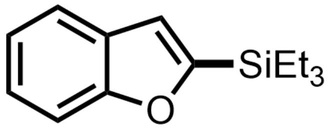




6a

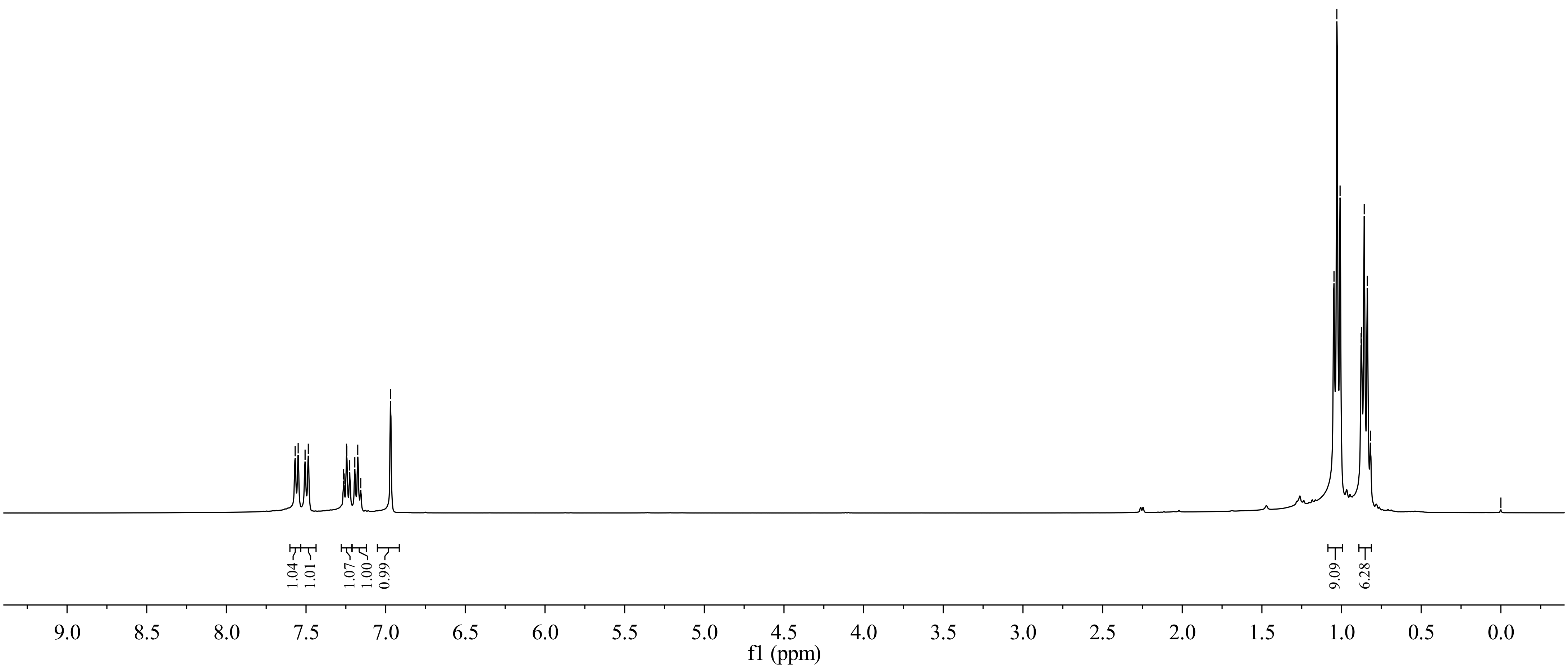
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

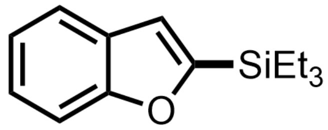




6b

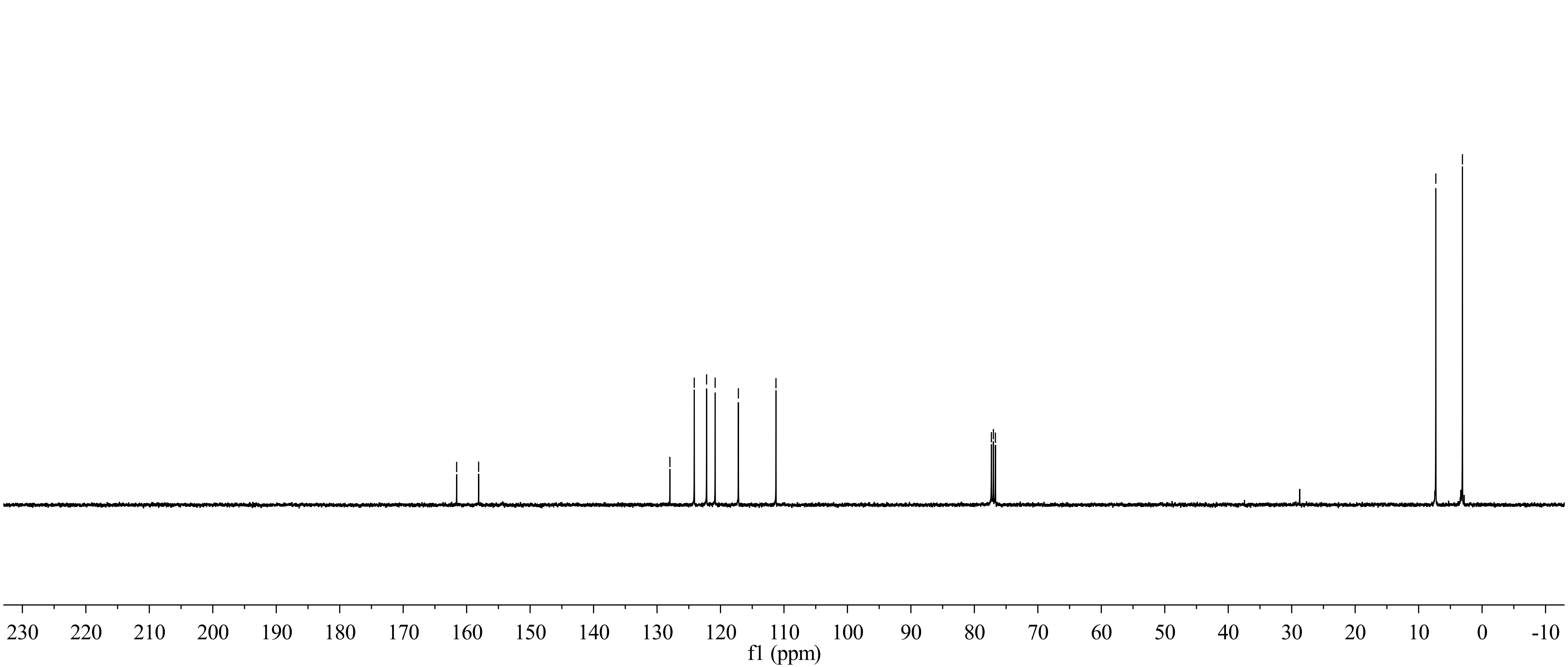
[1]H NMR spectrum (400 MHz, $CDCl_3$)

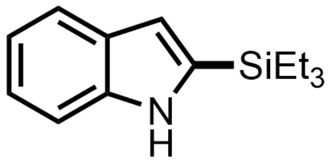




6b

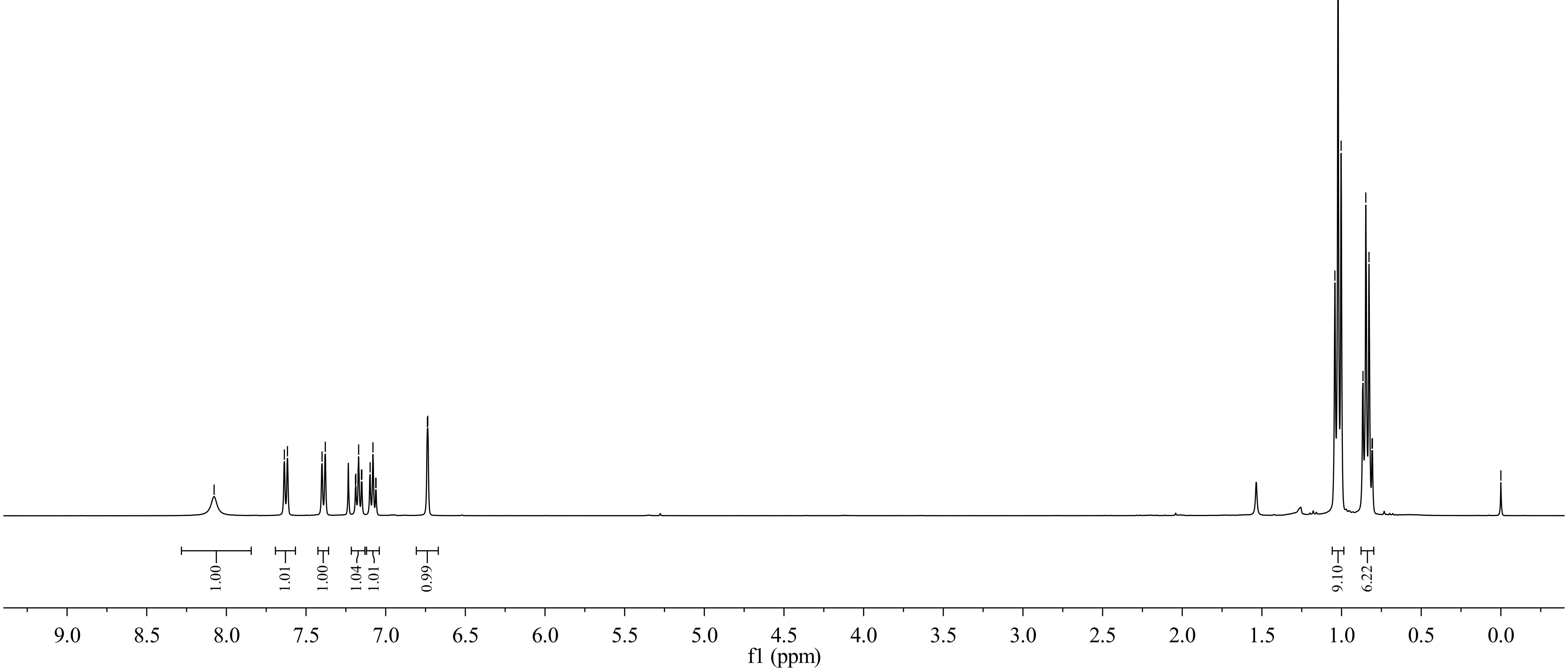
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

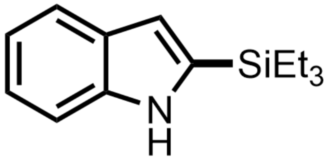




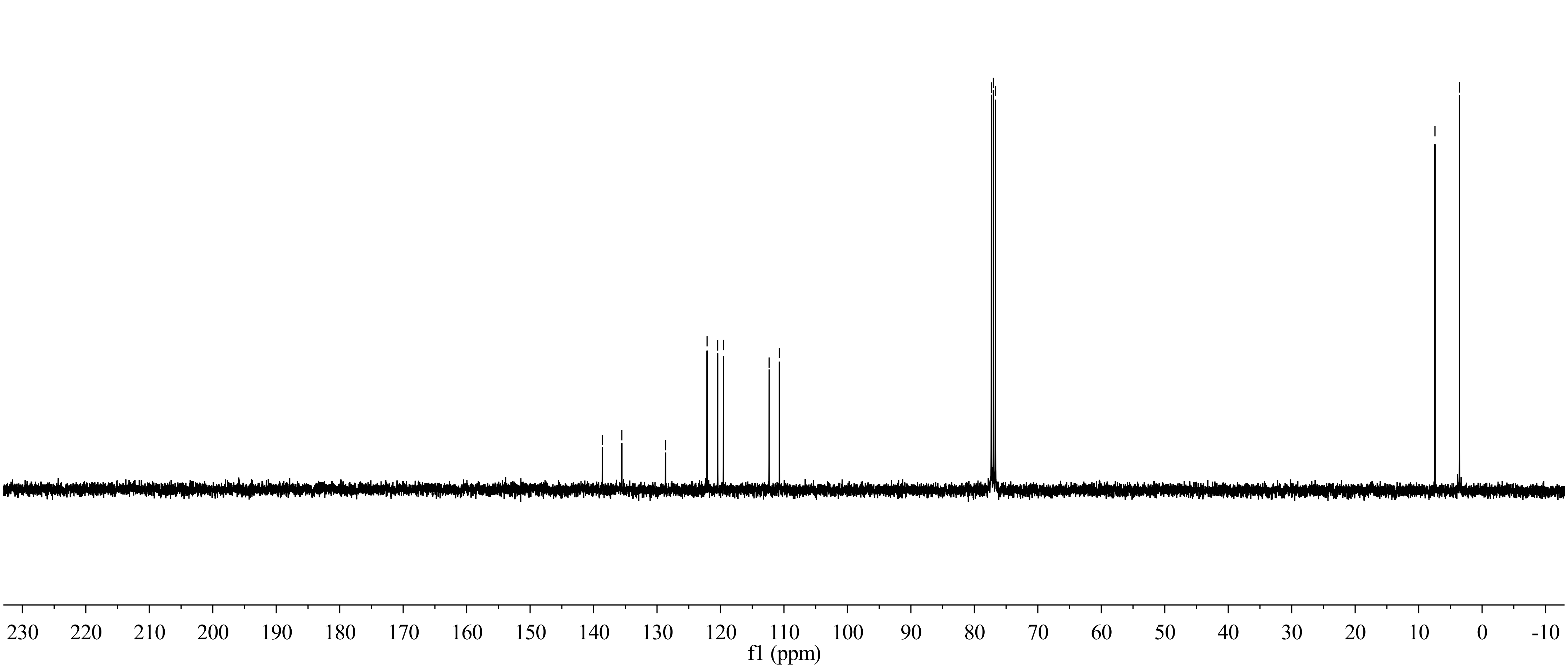
6c

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

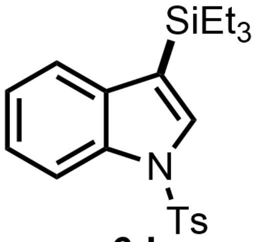




6c

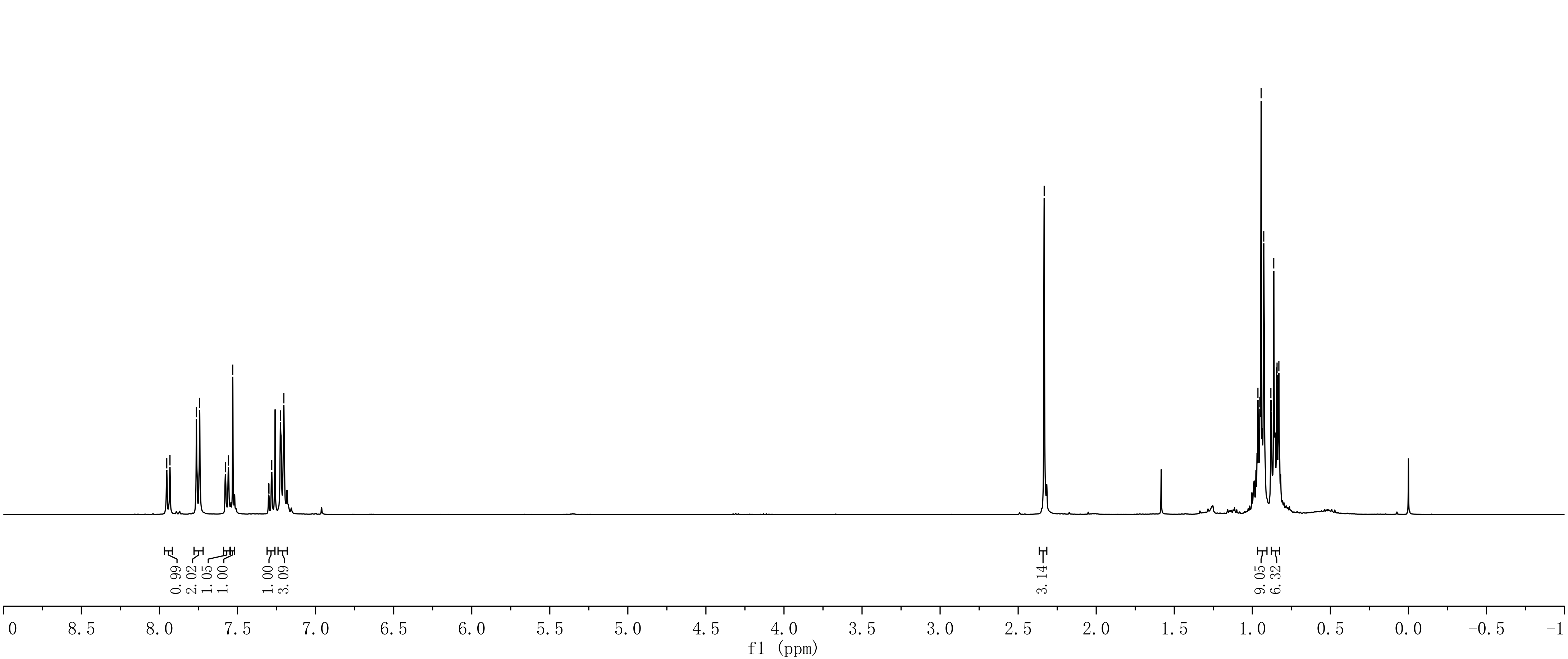


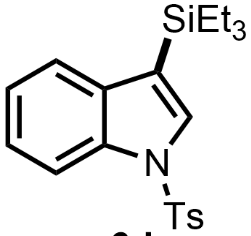
^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)



6d

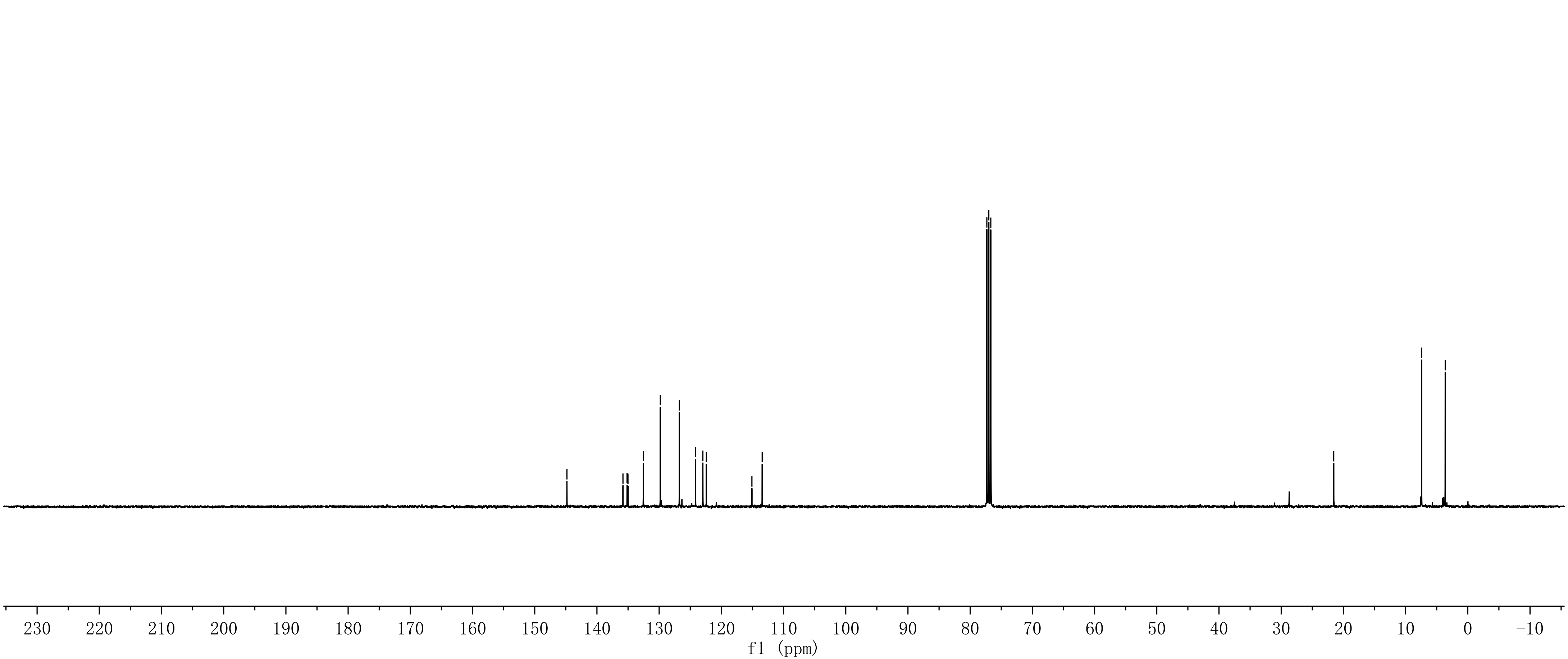
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

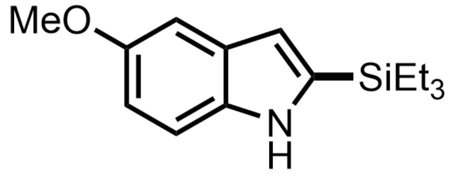




6d

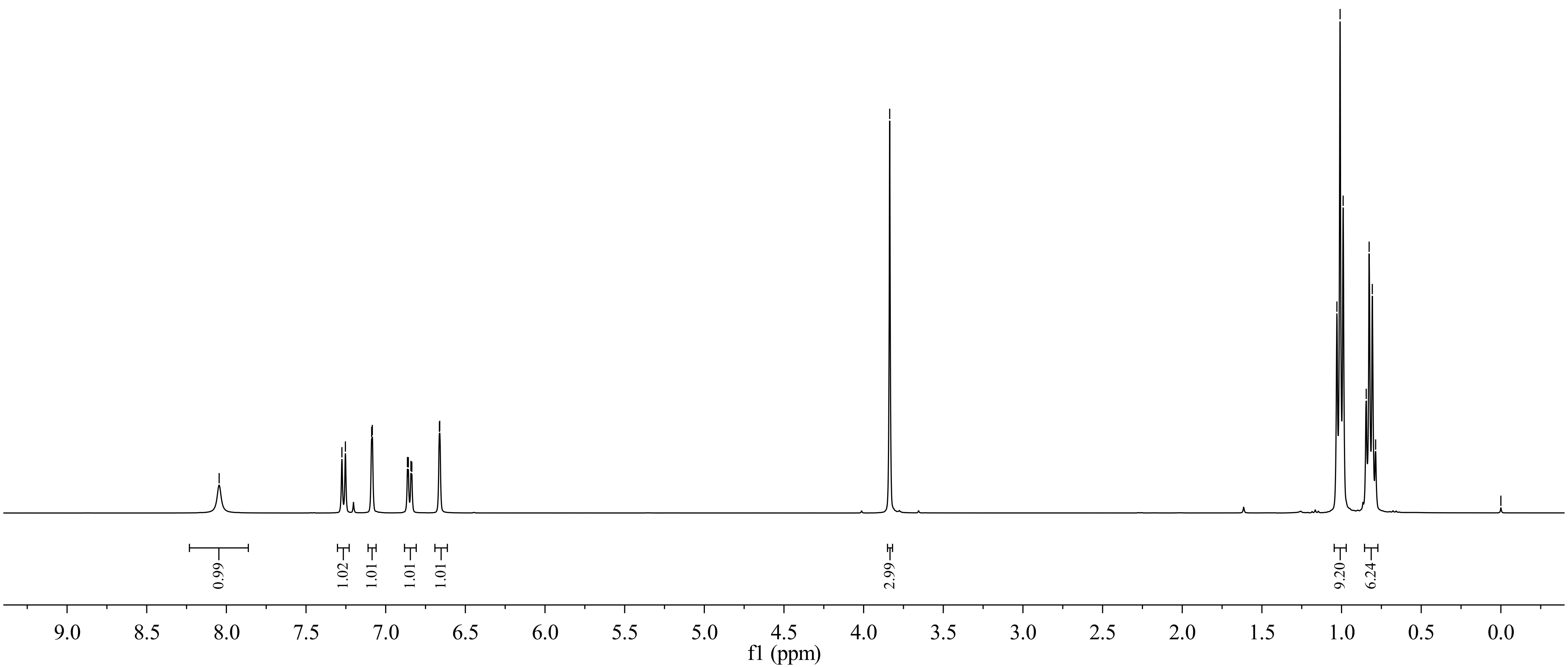
[13]C NMR spectrum (100 MHz, $CDCl_3$)

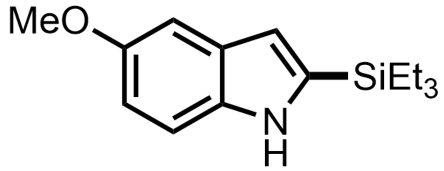




6e

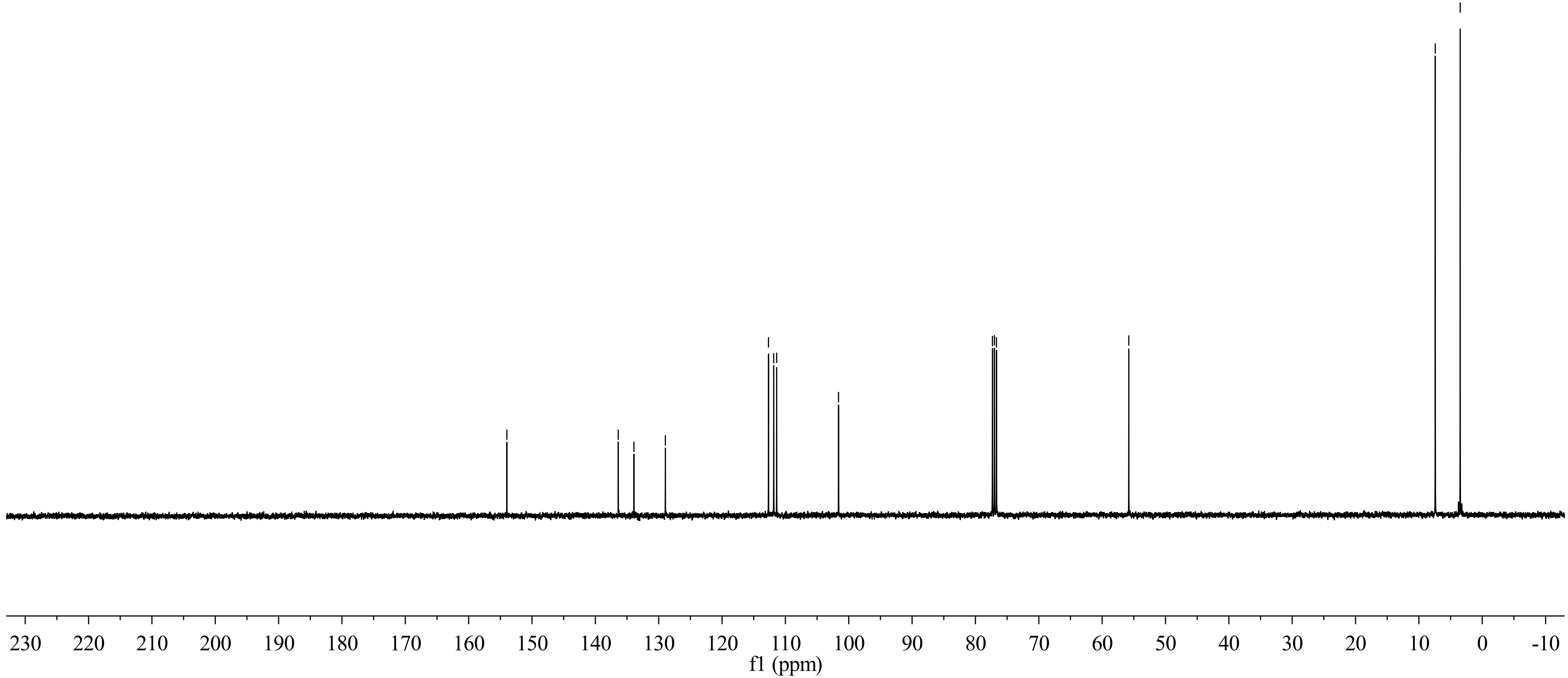
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

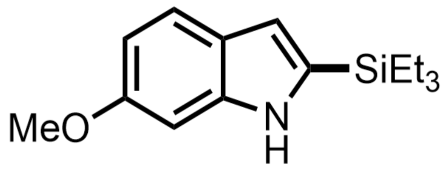




6e

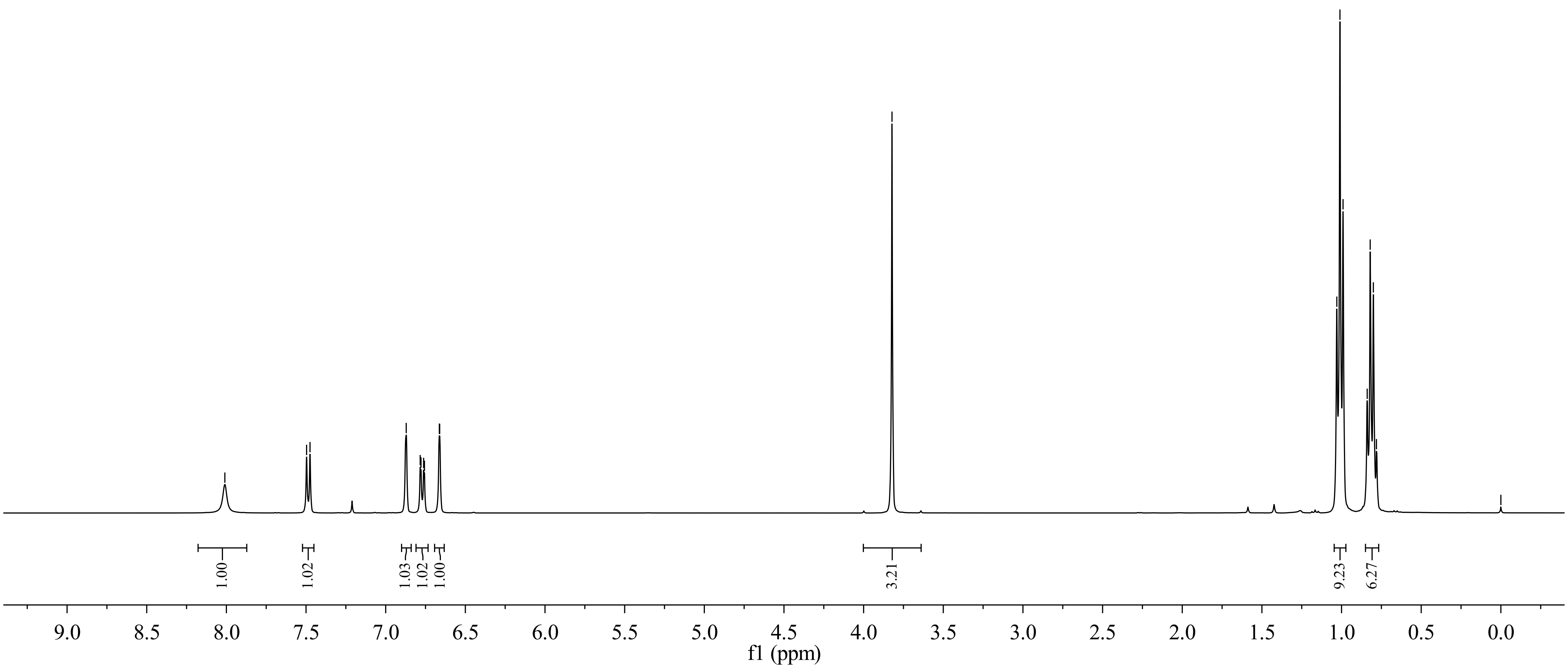
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

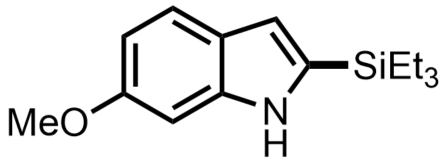




6f

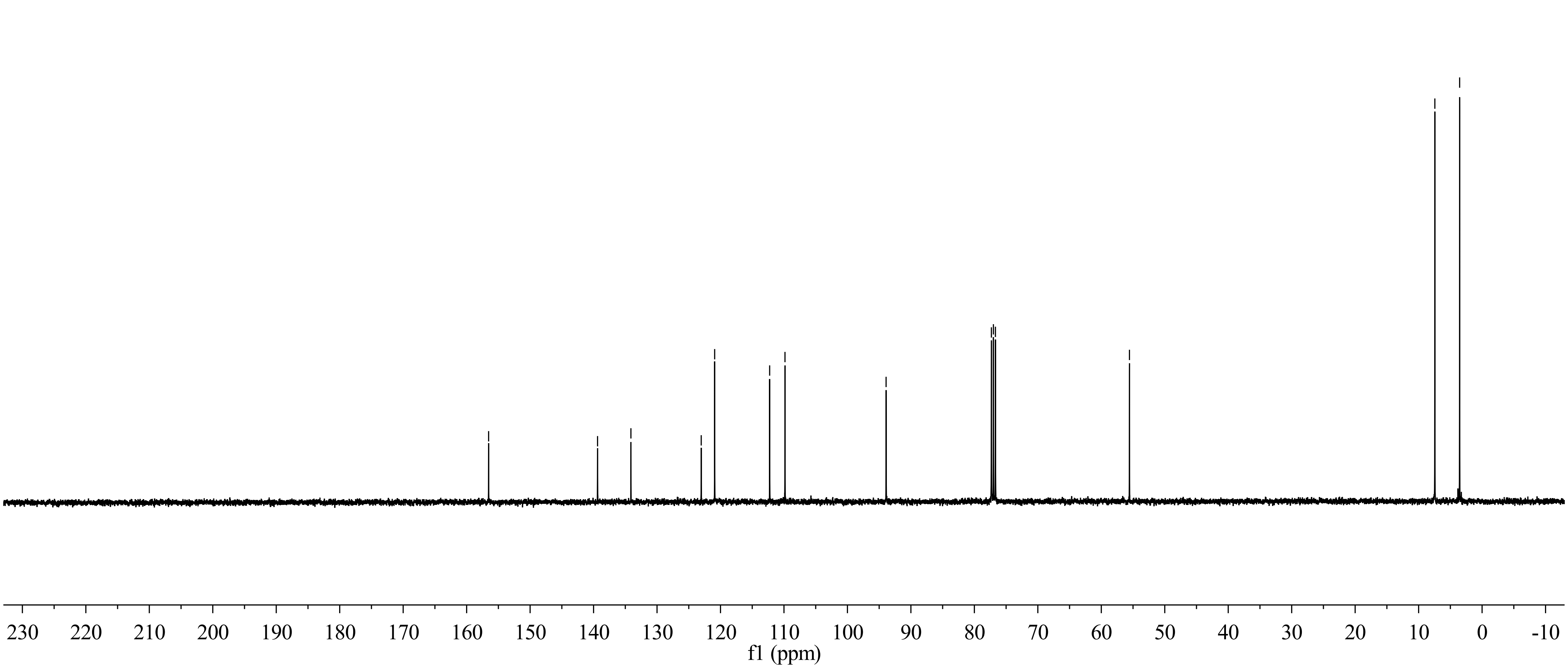
[1]H NMR spectrum (400 MHz, $CDCl_3$)

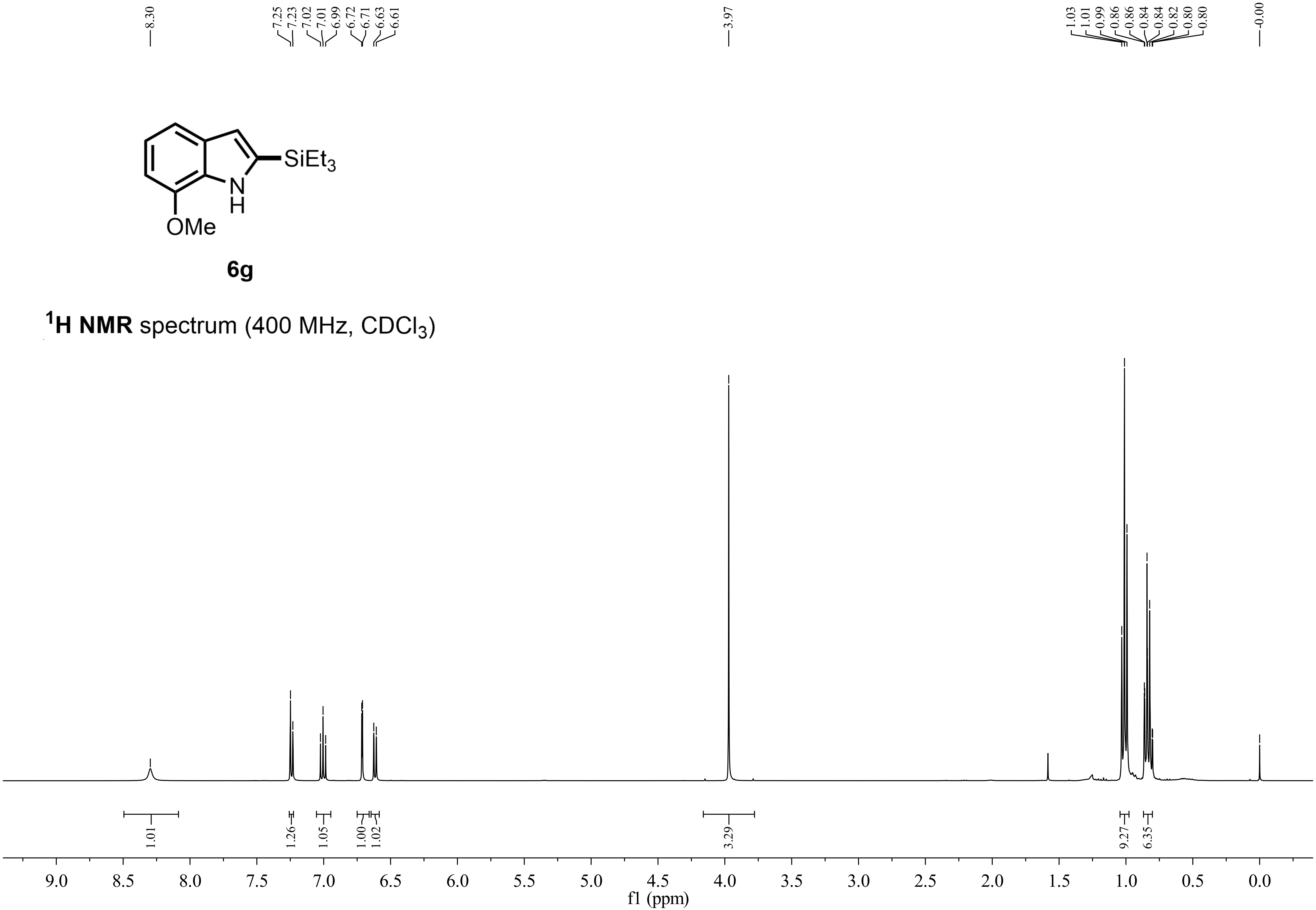




6f

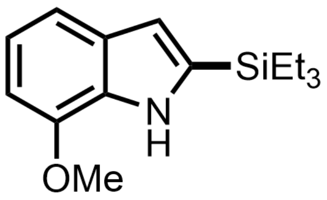
^{13}C NMR spectrum (100 MHz, $CDCl_3$)





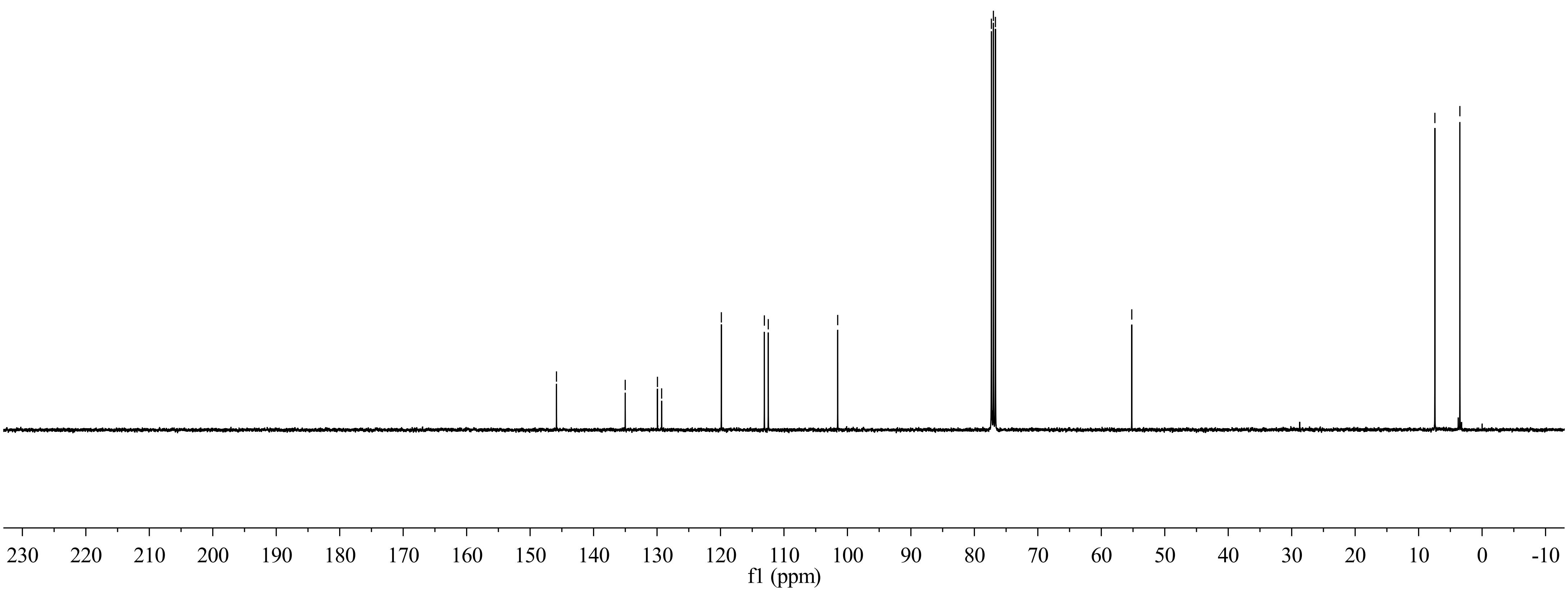
6g

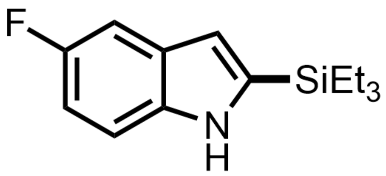
¹H NMR spectrum (400 MHz, $CDCl_3$)



6g

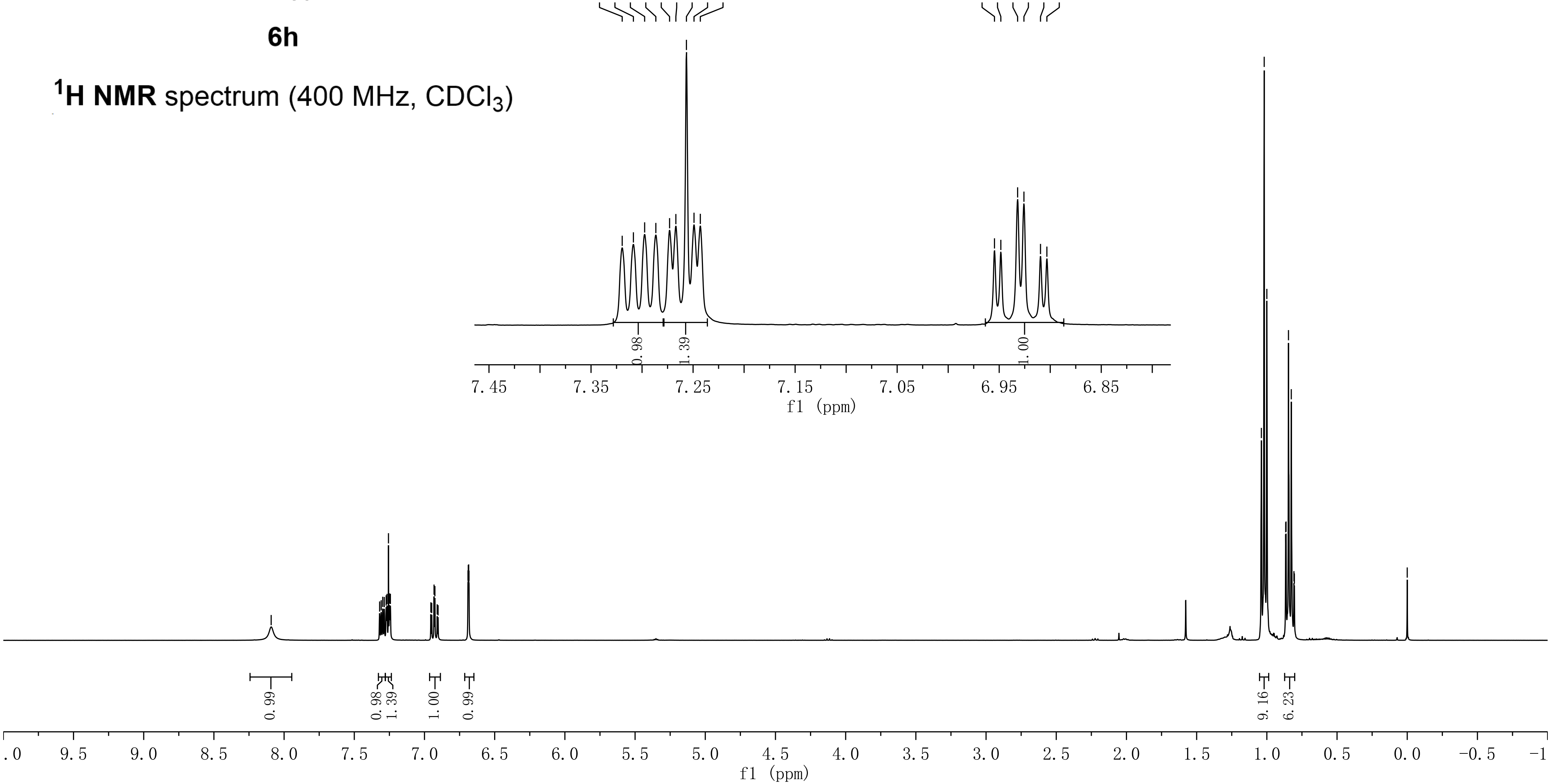
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

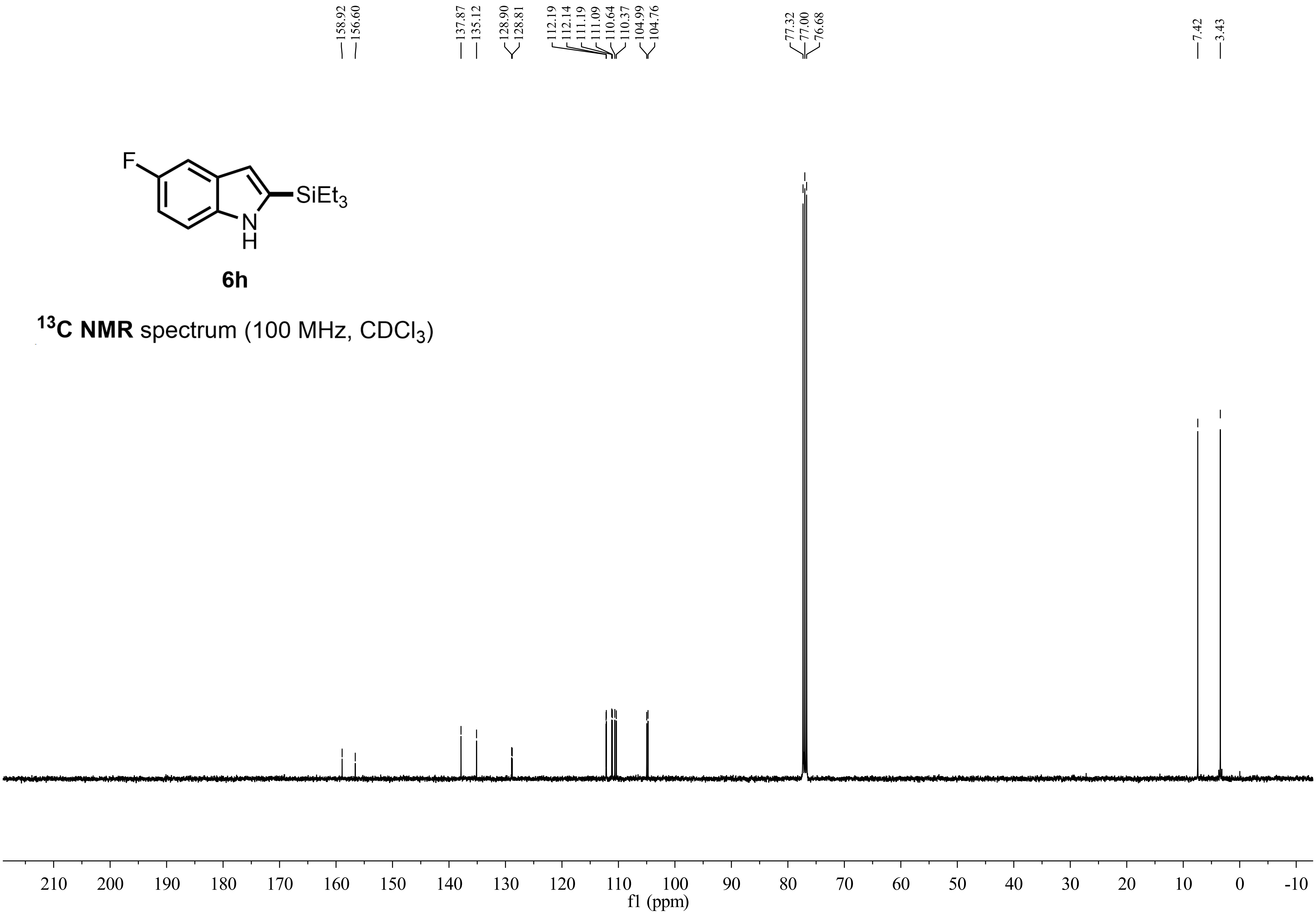




6h

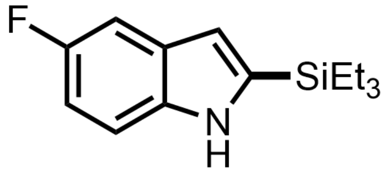
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





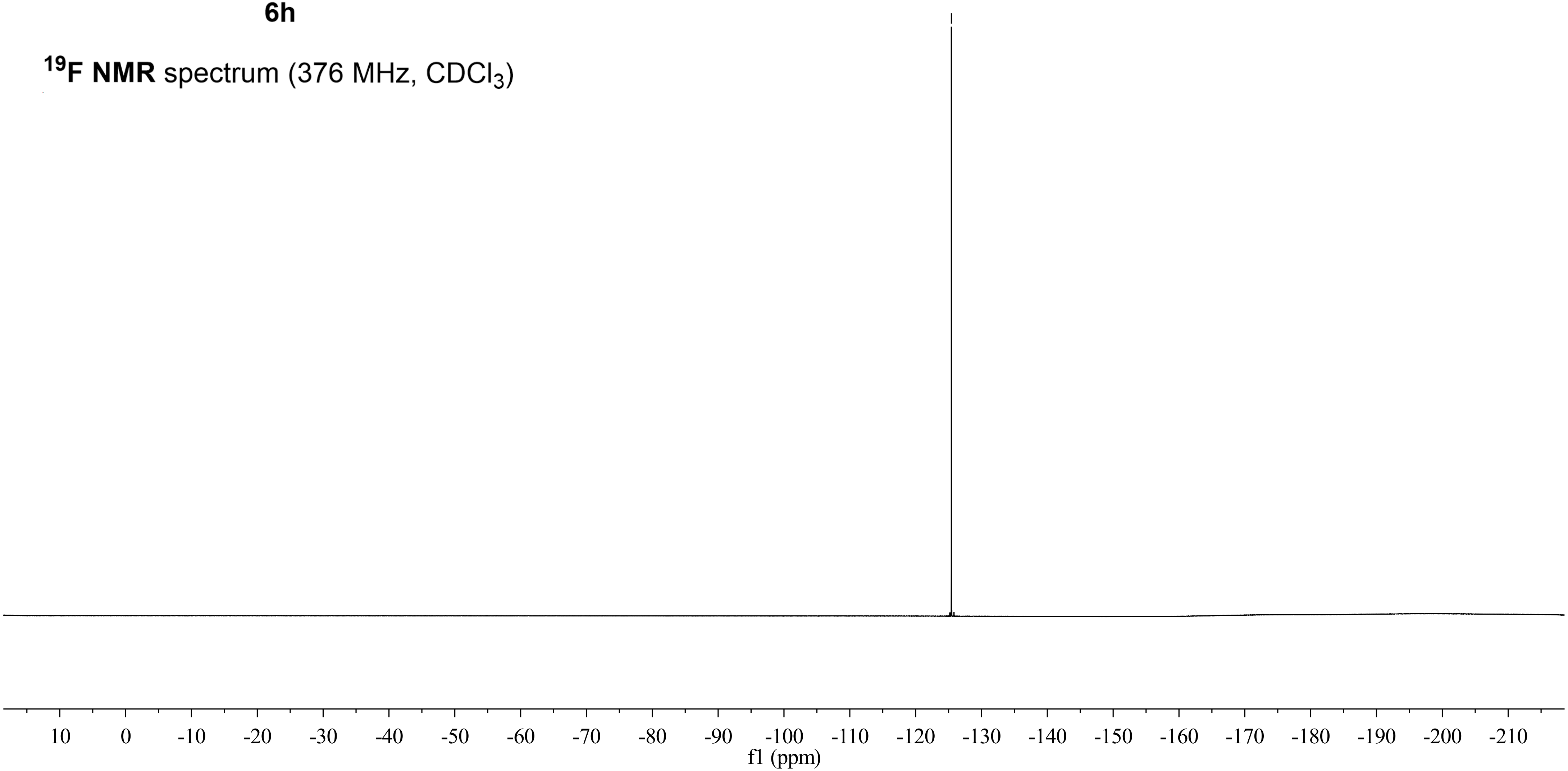
6h

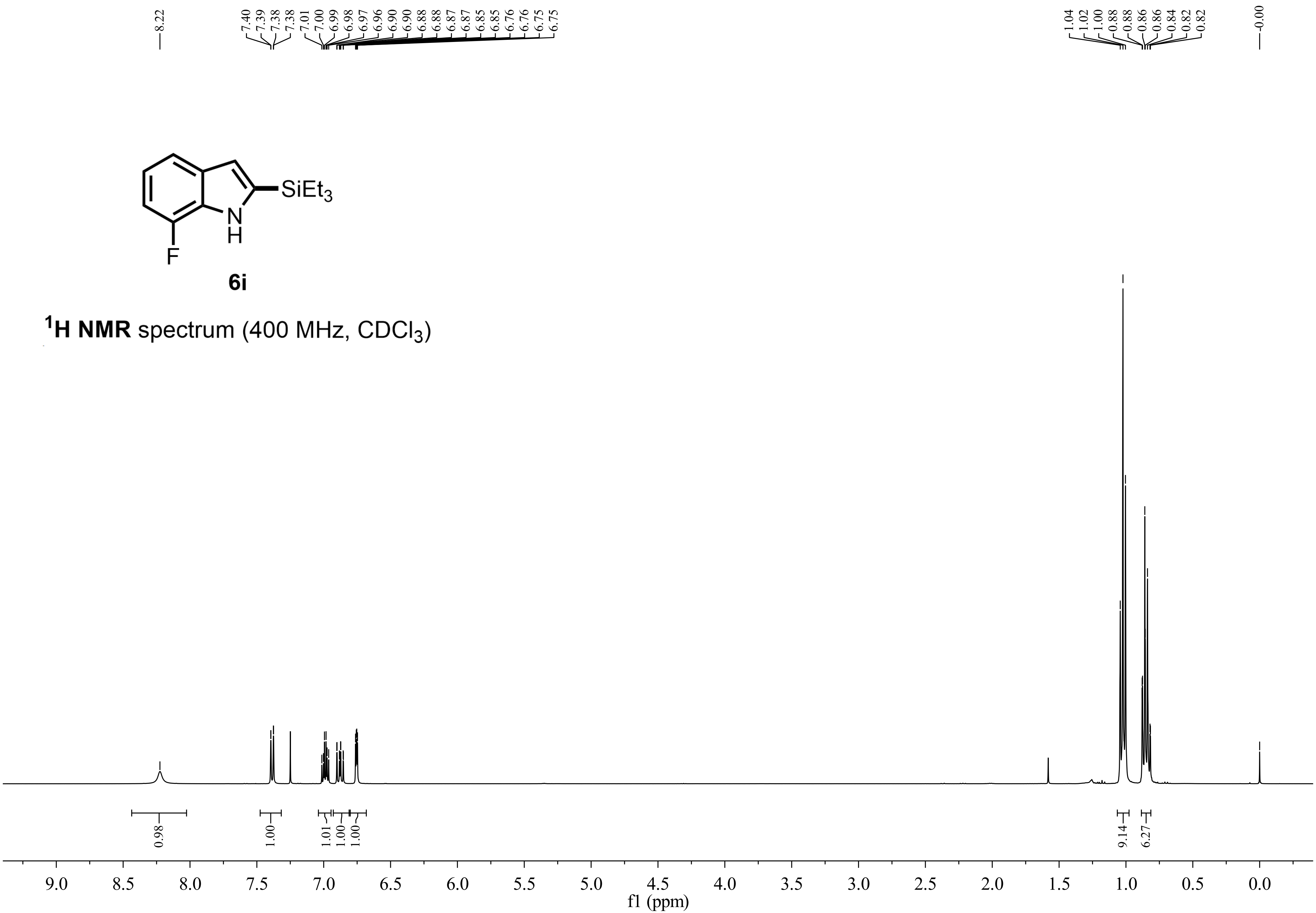
^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)

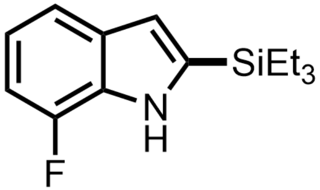


6h

^{19}F NMR spectrum (376 MHz, $CDCl_3$)

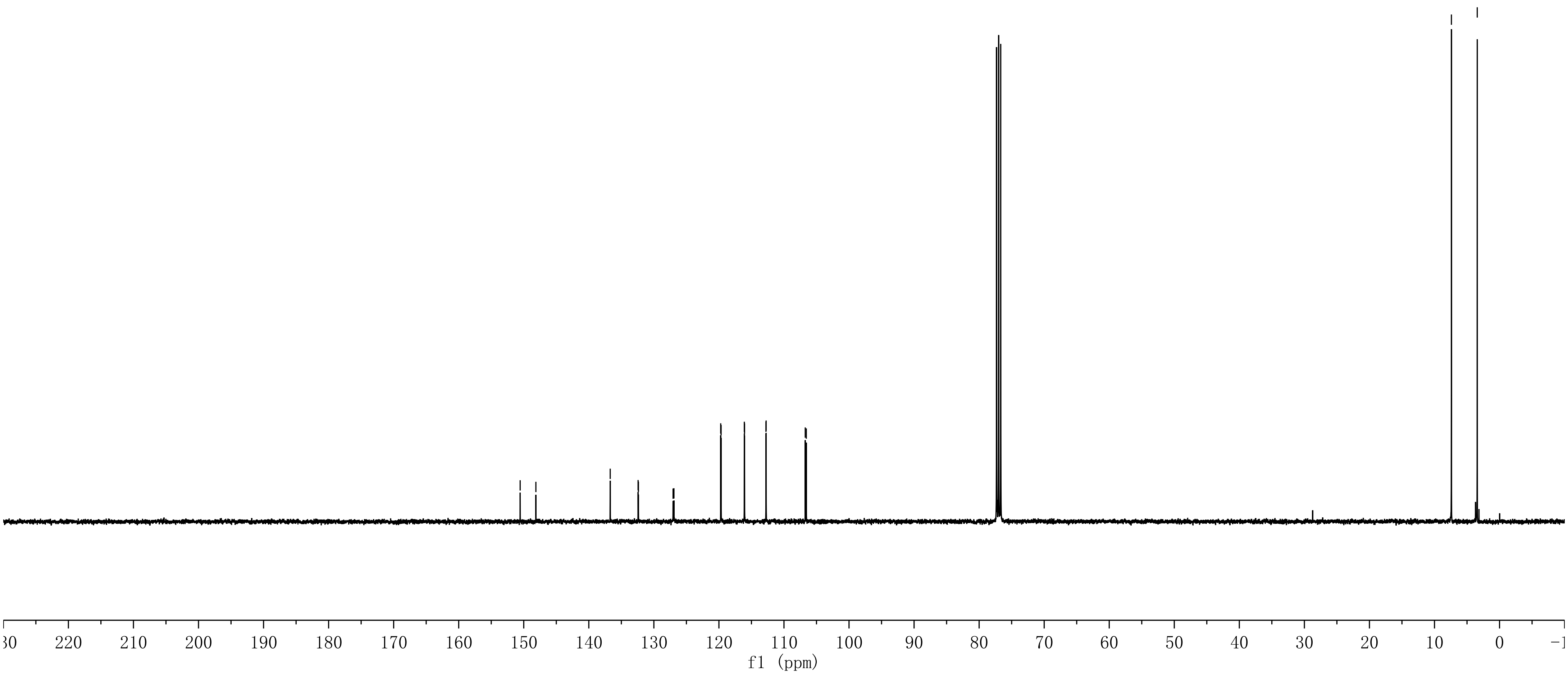


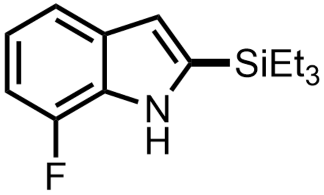

8.22
7.40 7.39 7.38 7.38 7.01 7.00 6.99 6.98 6.97 6.96 6.90 6.90 6.88 6.88 6.87 6.87 6.85 6.85 6.76 6.76 6.75 6.75
1.04 1.02 1.00 0.88 0.88 0.86 0.86 0.84 0.82 0.82
-0.00
SiEt3
N
H
F
6i
1H NMR spectrum (400 MHz, CDCl3)
0.98
1.00
1.01
1.00
1.00
9.14
6.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



6i

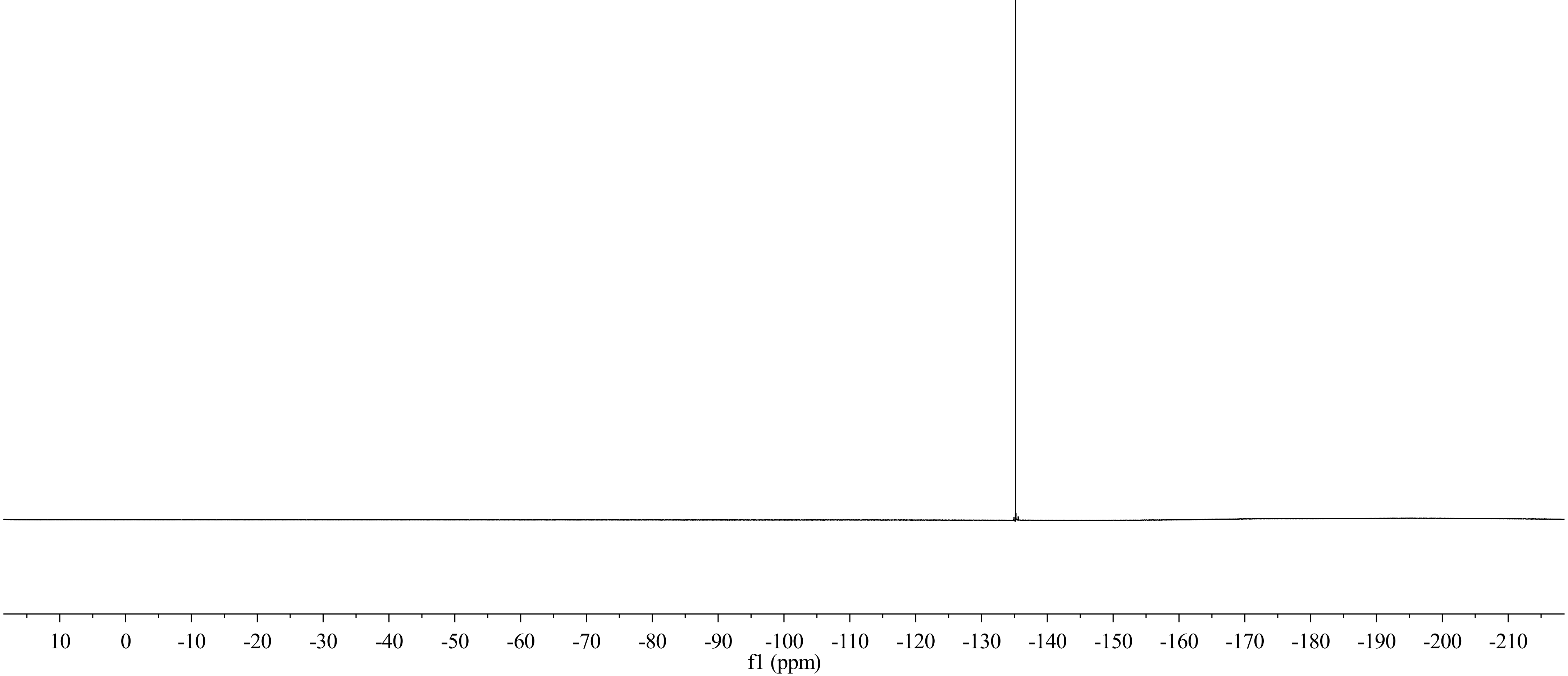
^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)

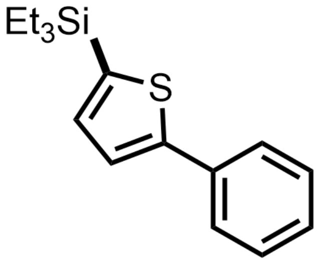




6i

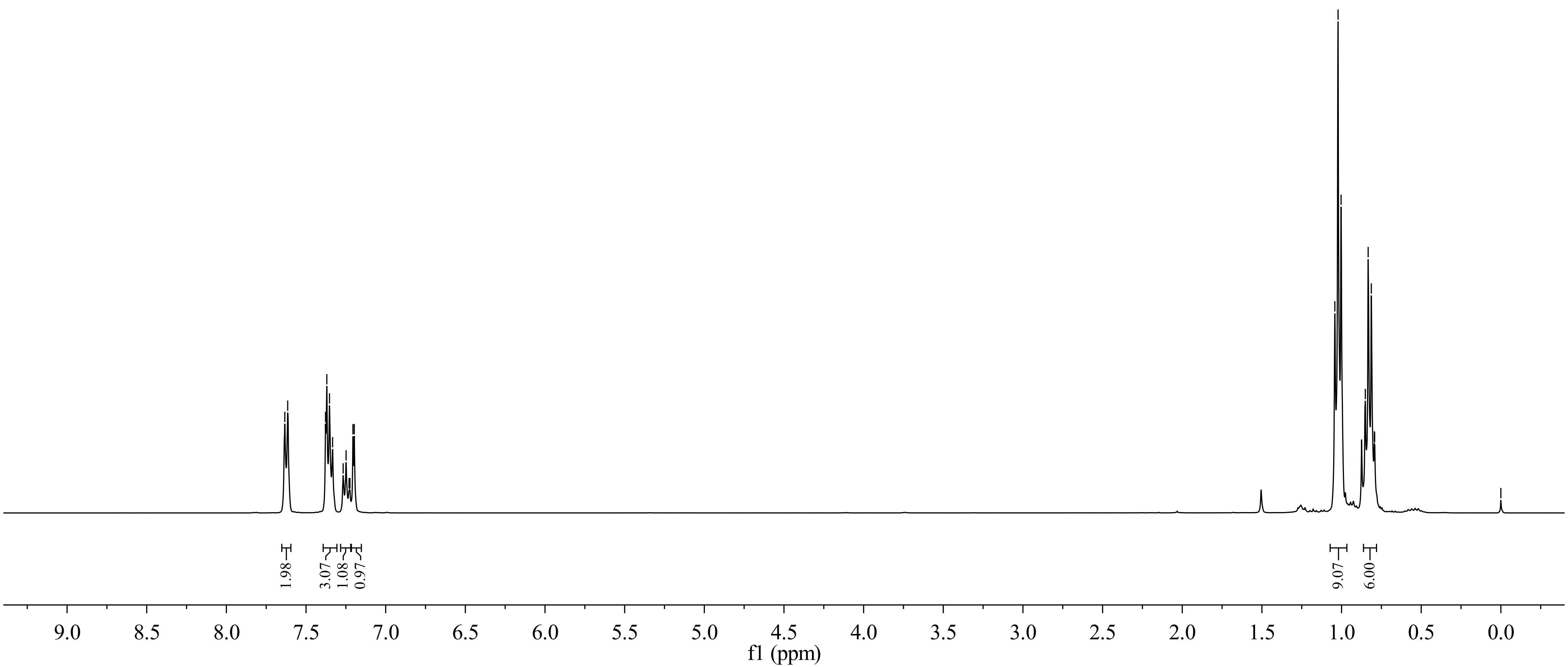
[19]F NMR spectrum (376 MHz, $CDCl_3$)

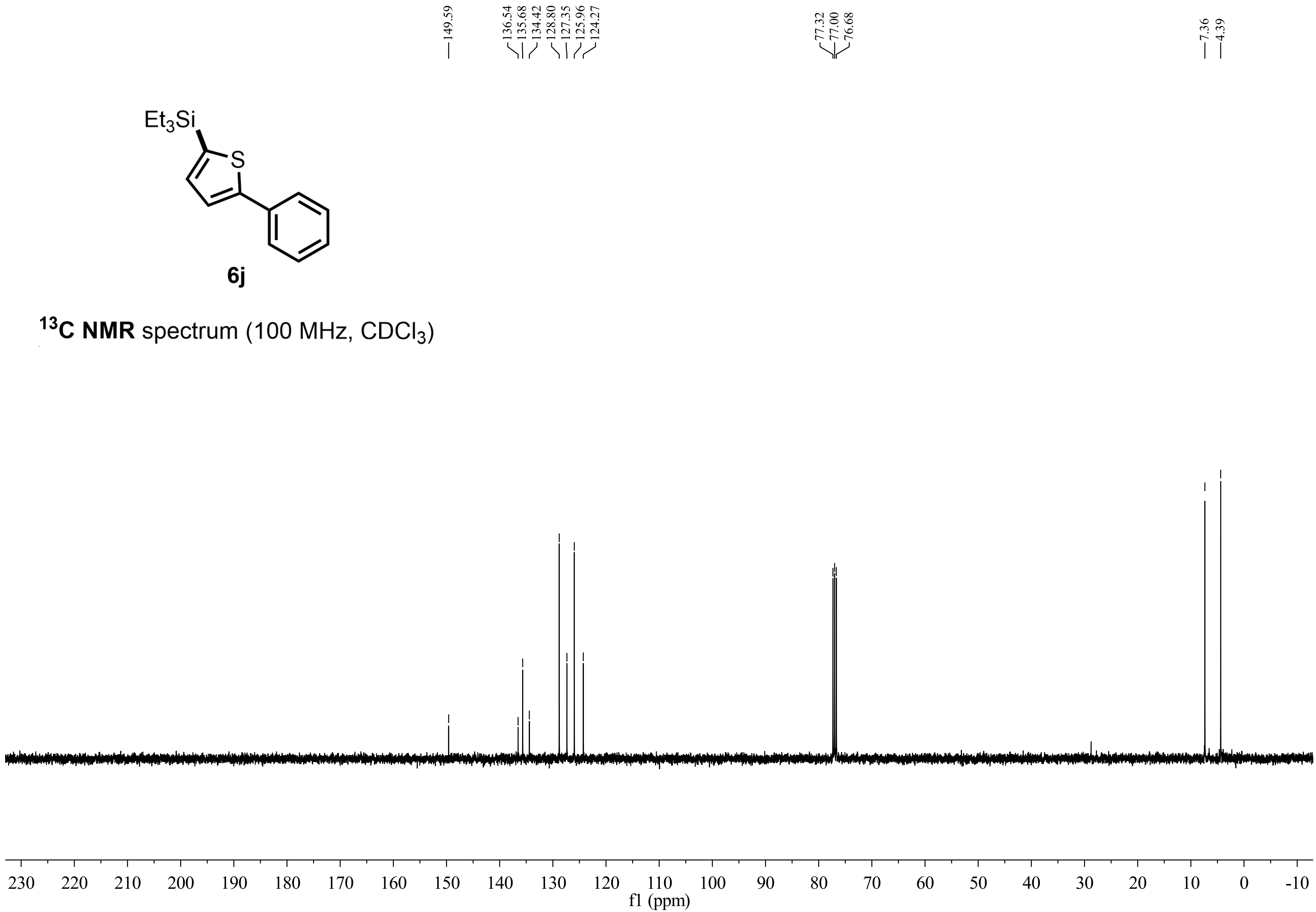




6j

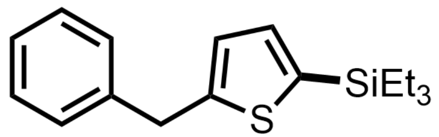
[1]H NMR spectrum (400 MHz, $CDCl_3$)





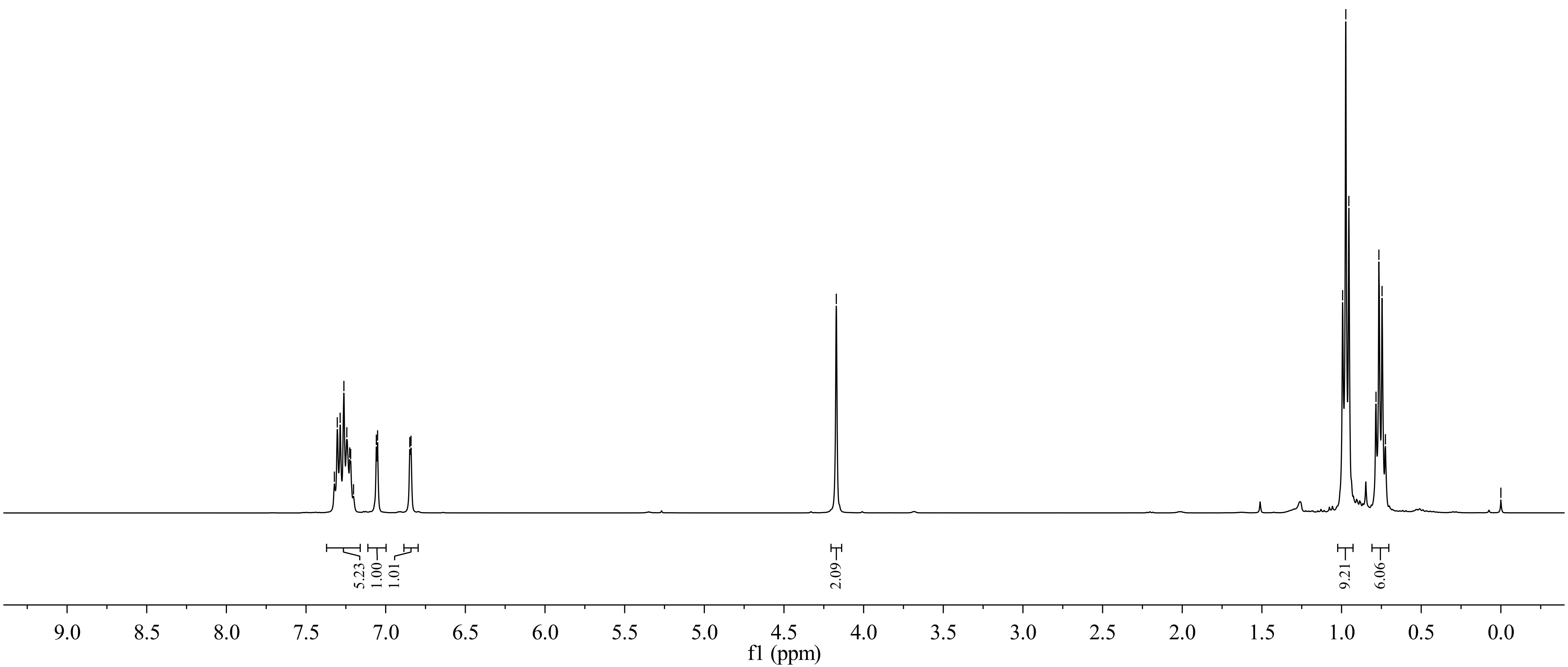
6j

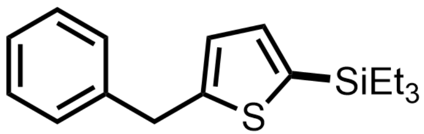
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



6k

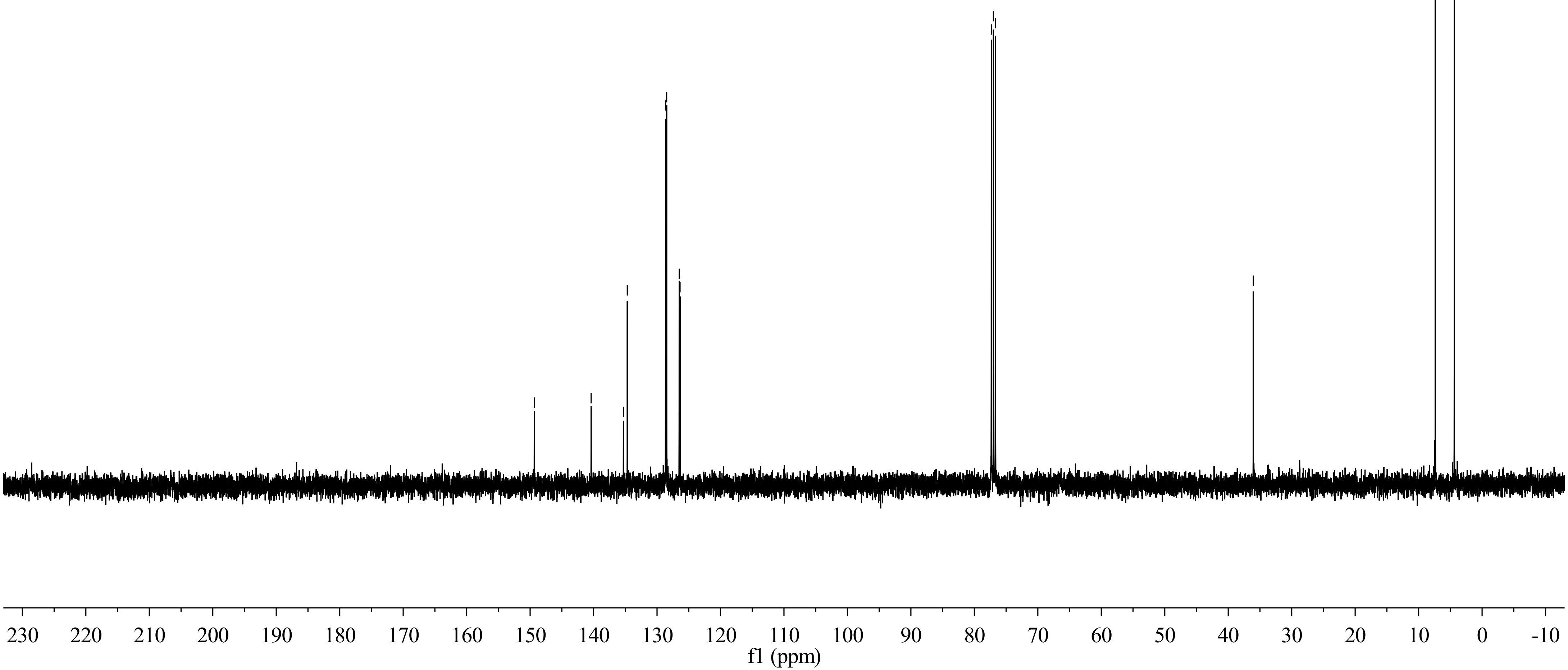
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

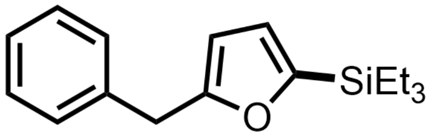




6k

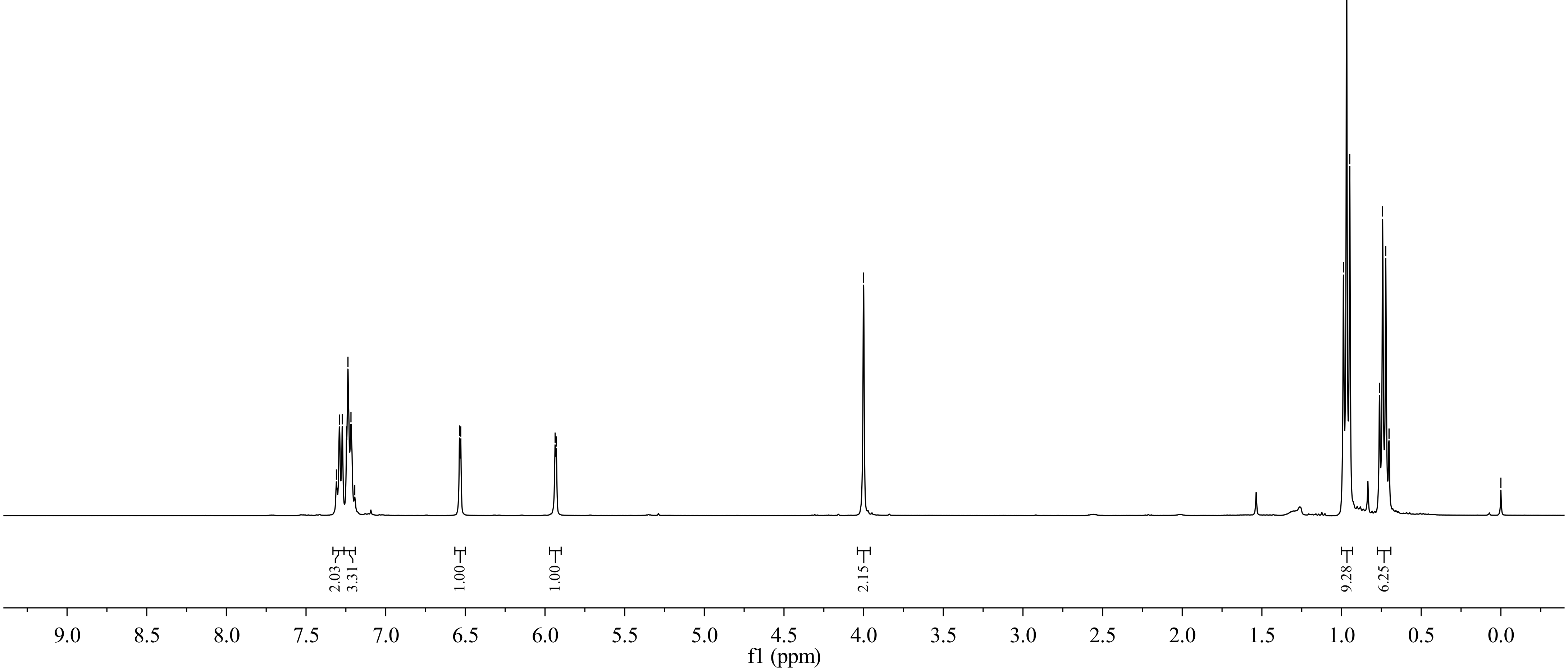
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

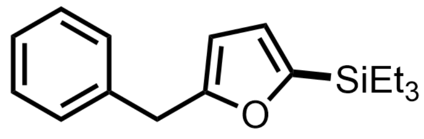




6l

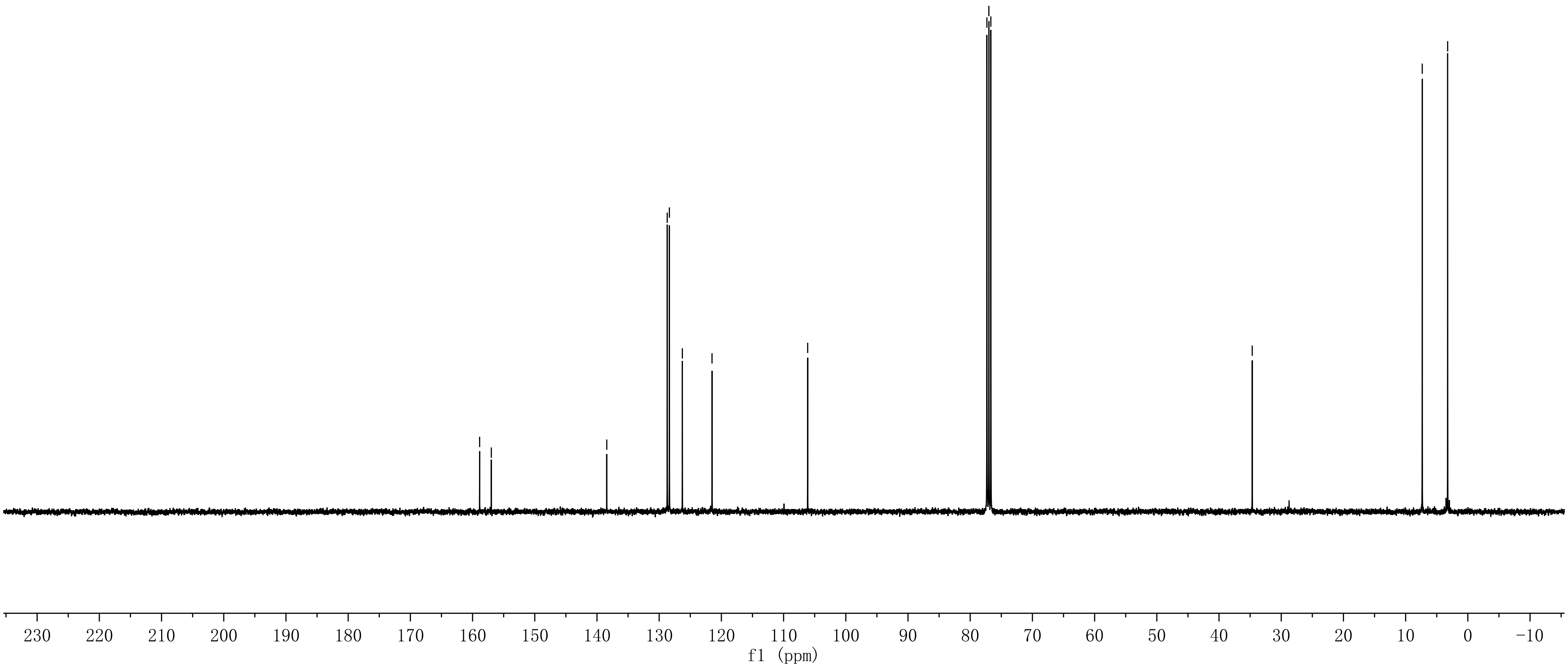
[1]H NMR spectrum (400 MHz, CDCl3)

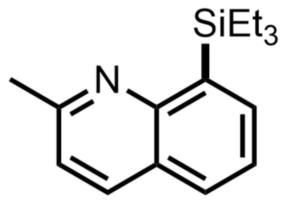




6l

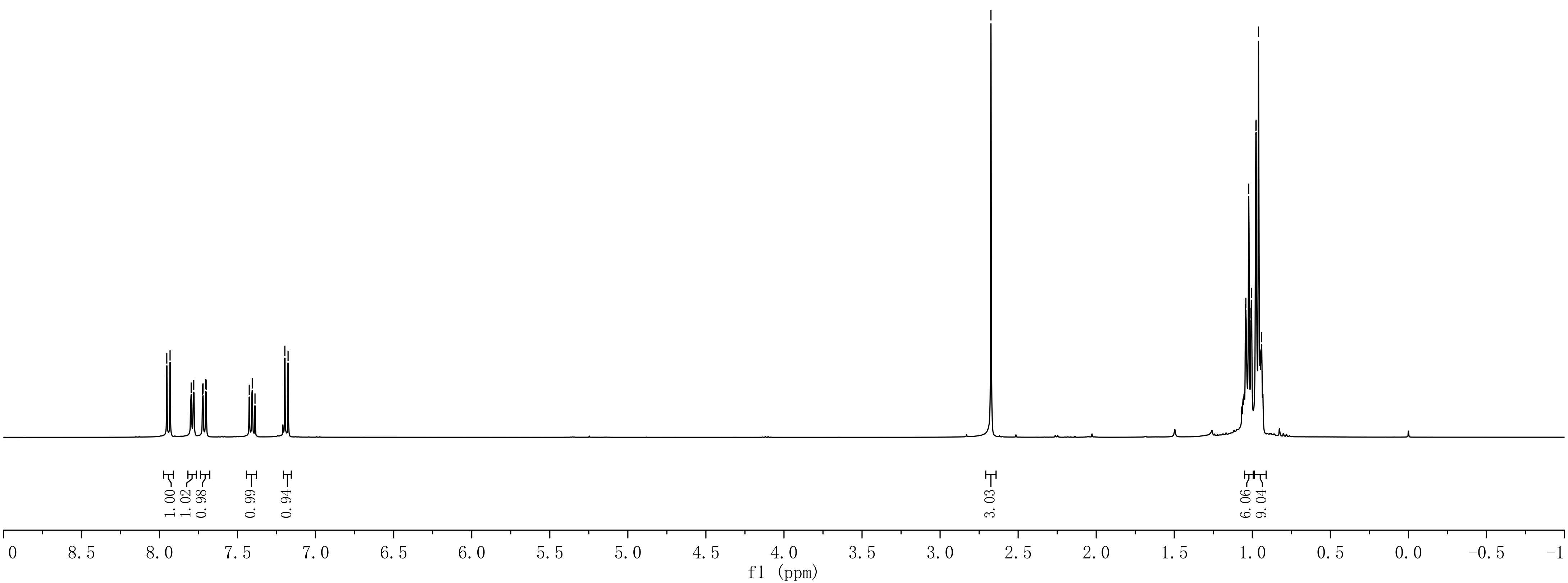
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

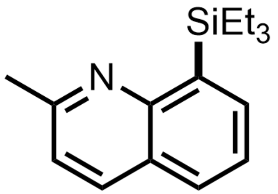




6m

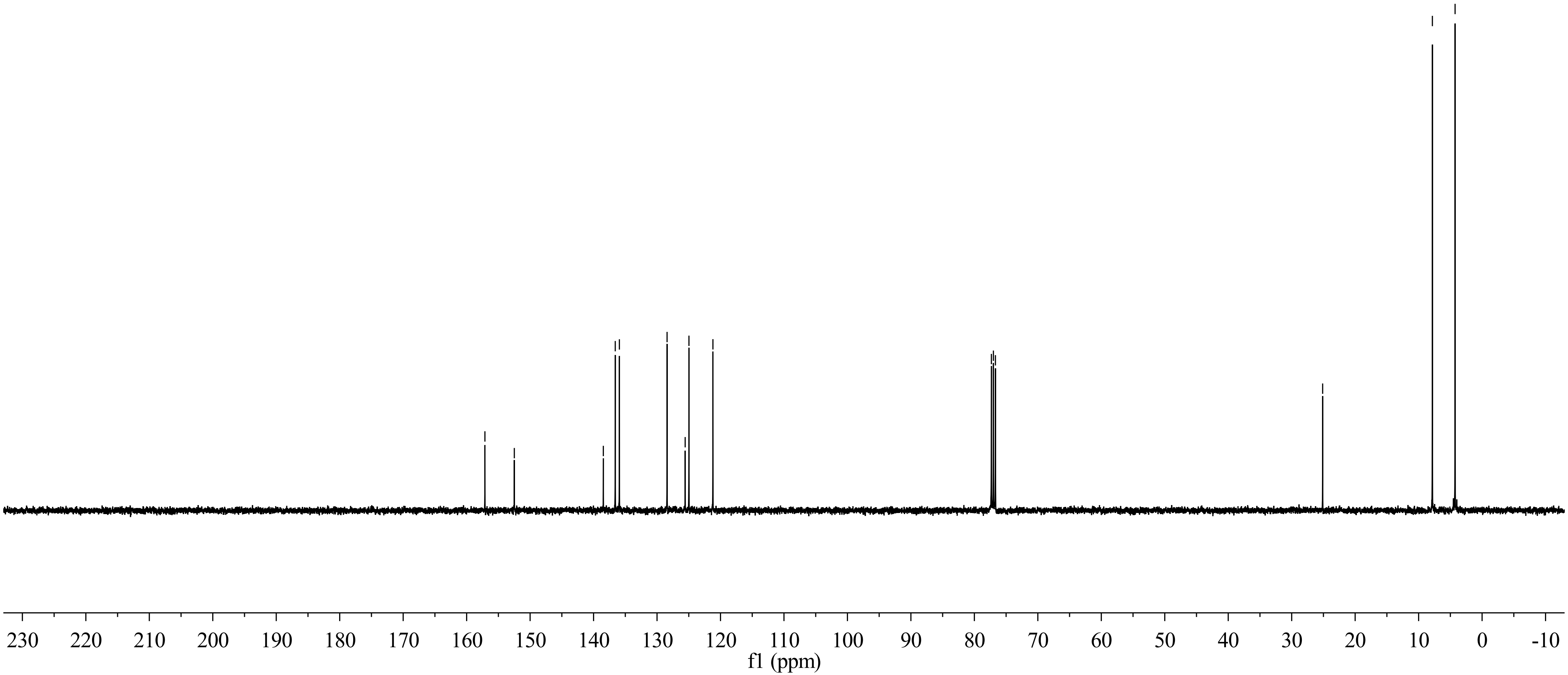
[1]H NMR spectrum (400 MHz, $CDCl_3$)

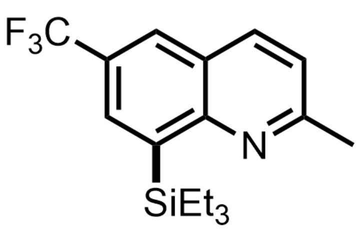




6m

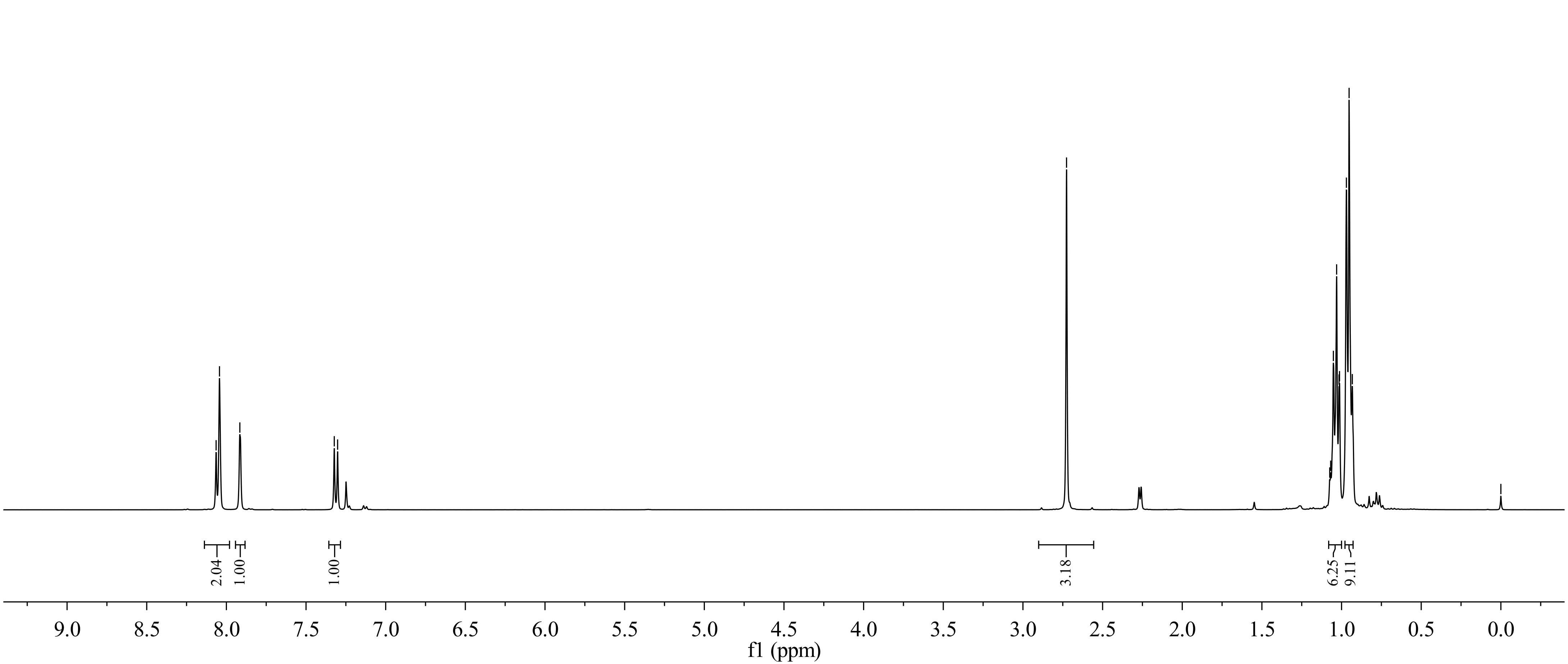
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

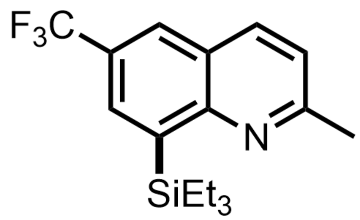




6n

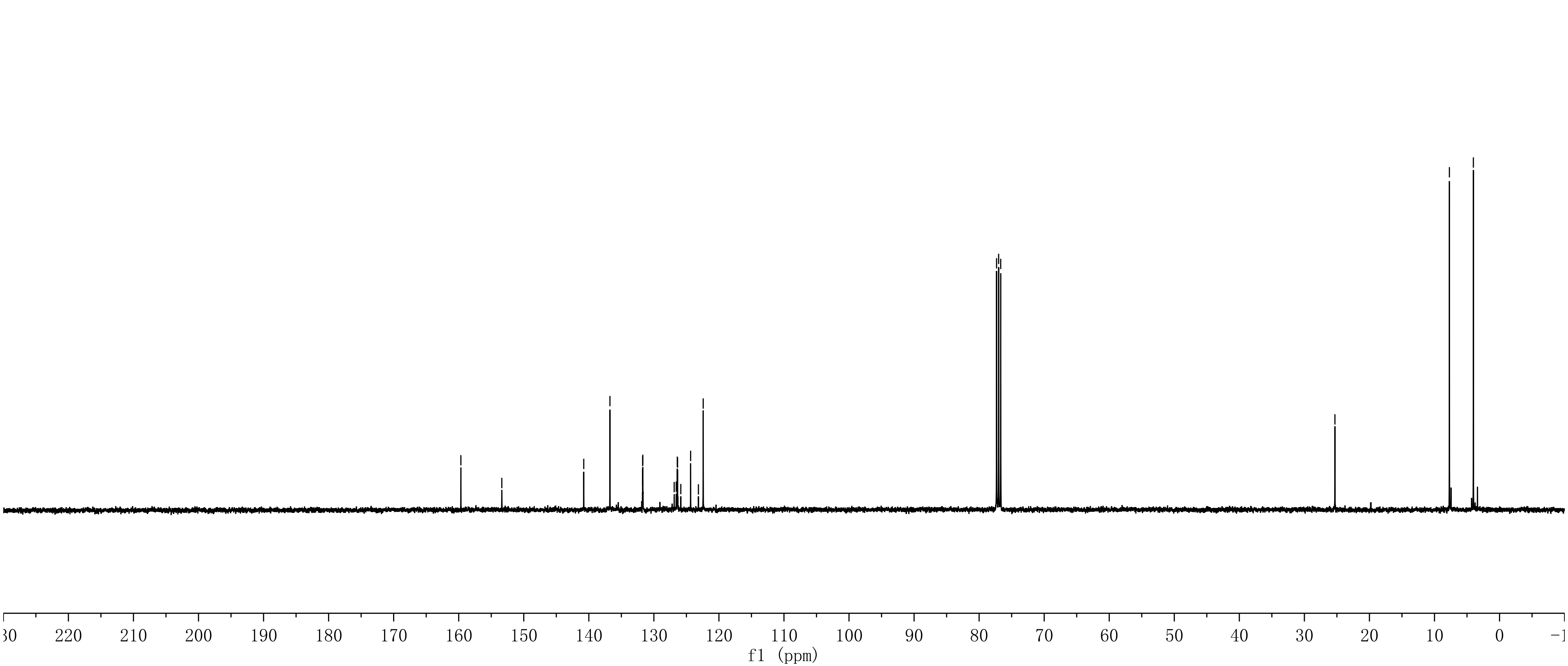
[1]H NMR spectrum (400 MHz, $CDCl_3$)

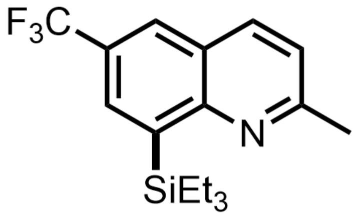




6n

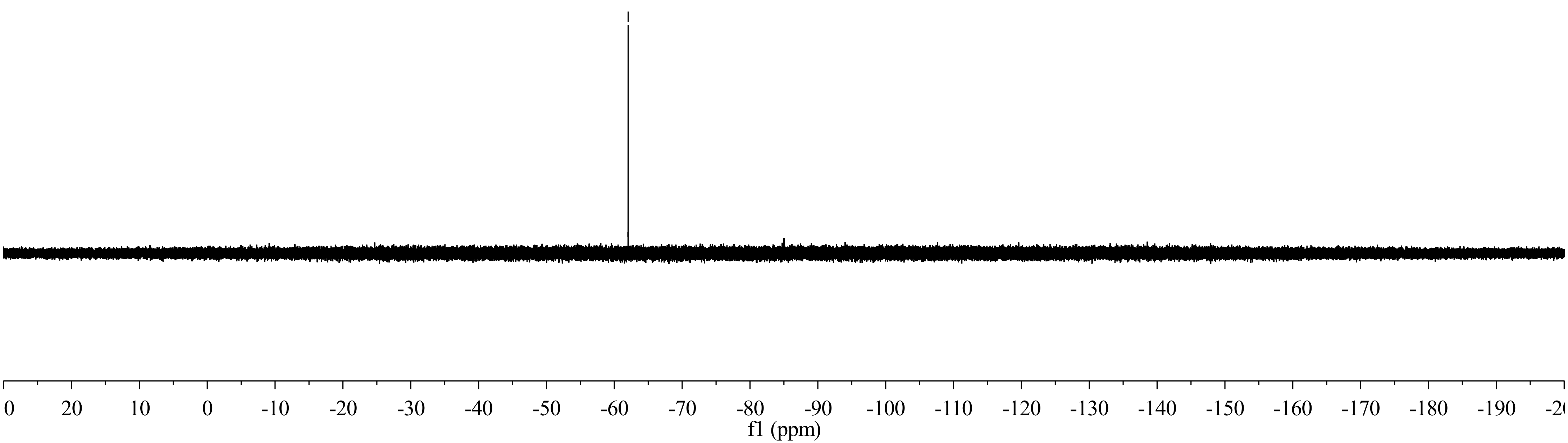
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

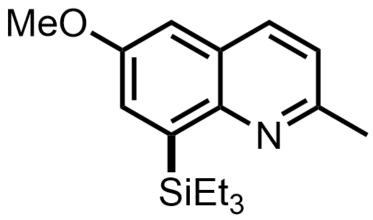




6n

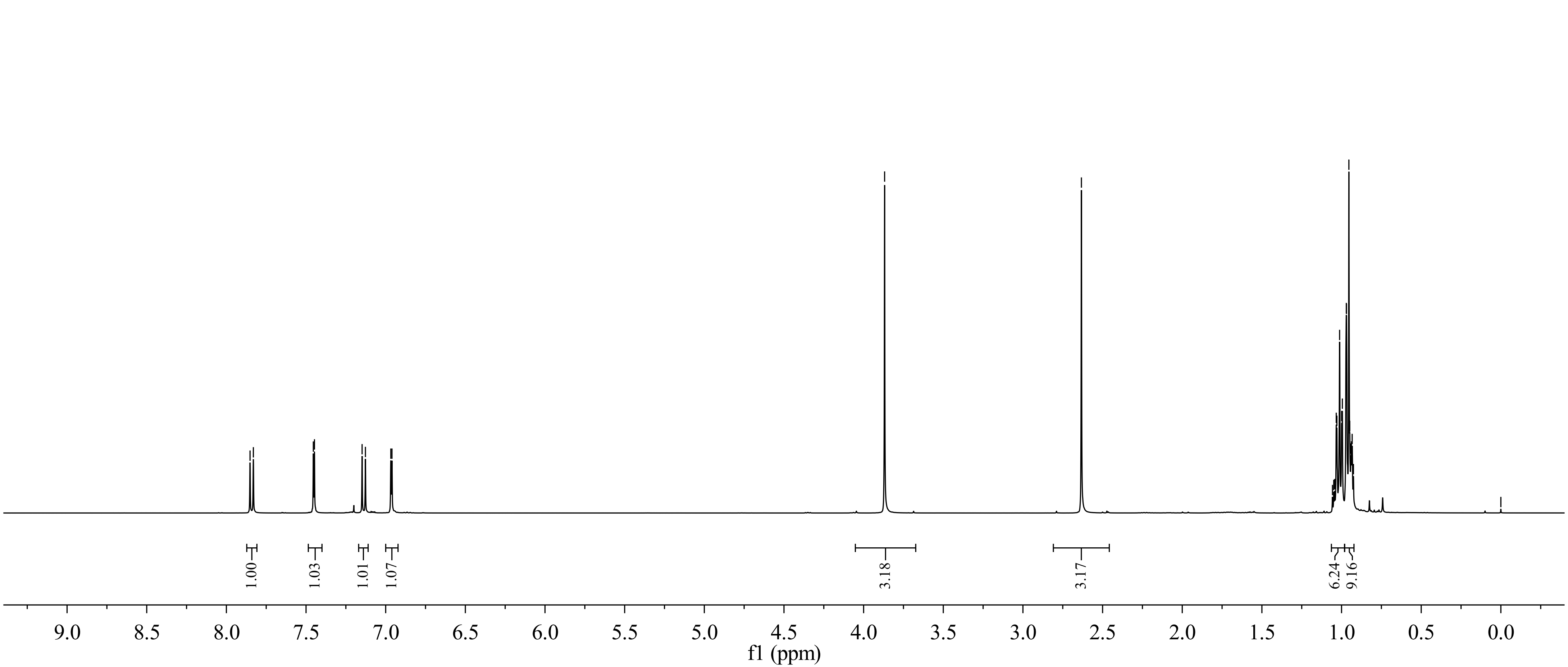
^{19}F NMR spectrum (564 MHz, $CDCl_3$)

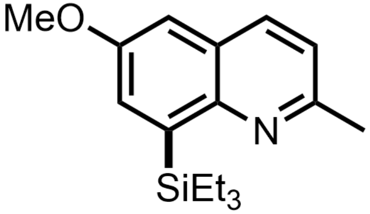




6o

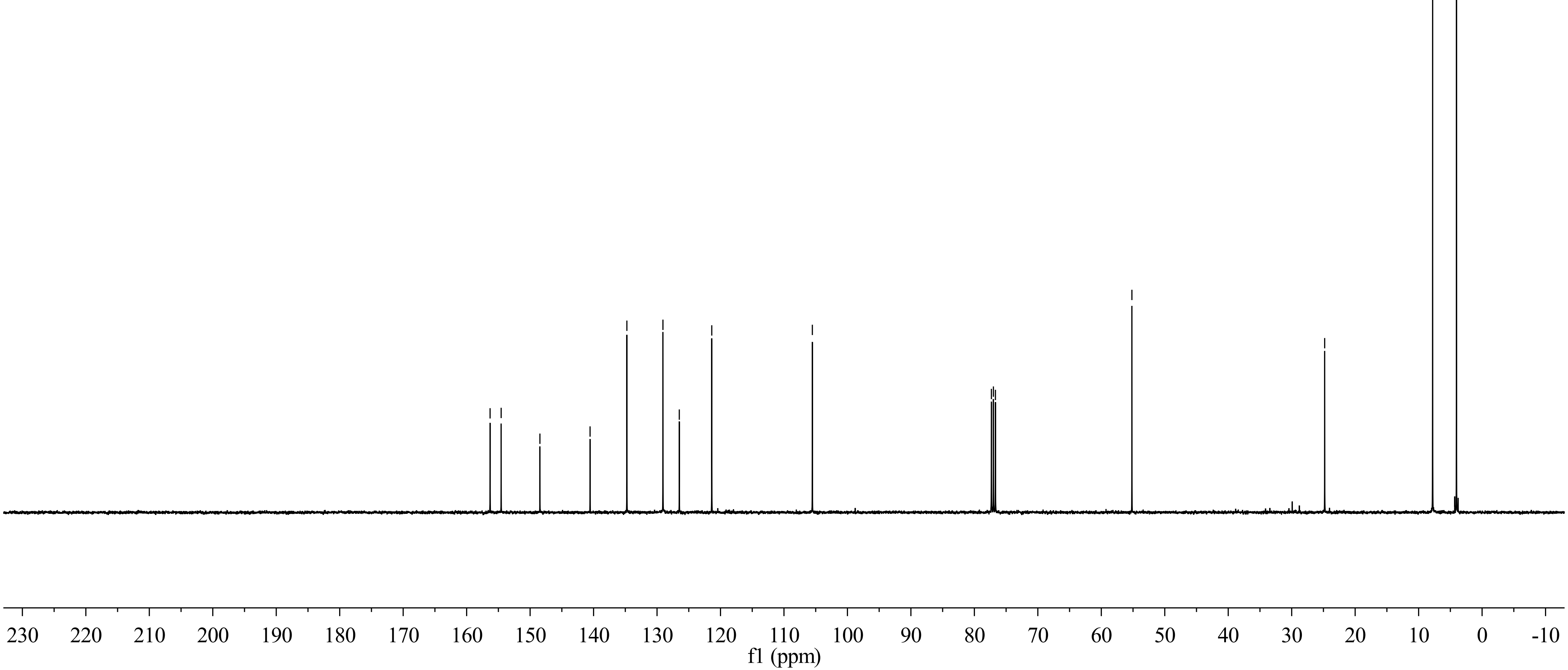
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

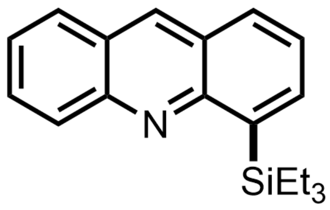




6o

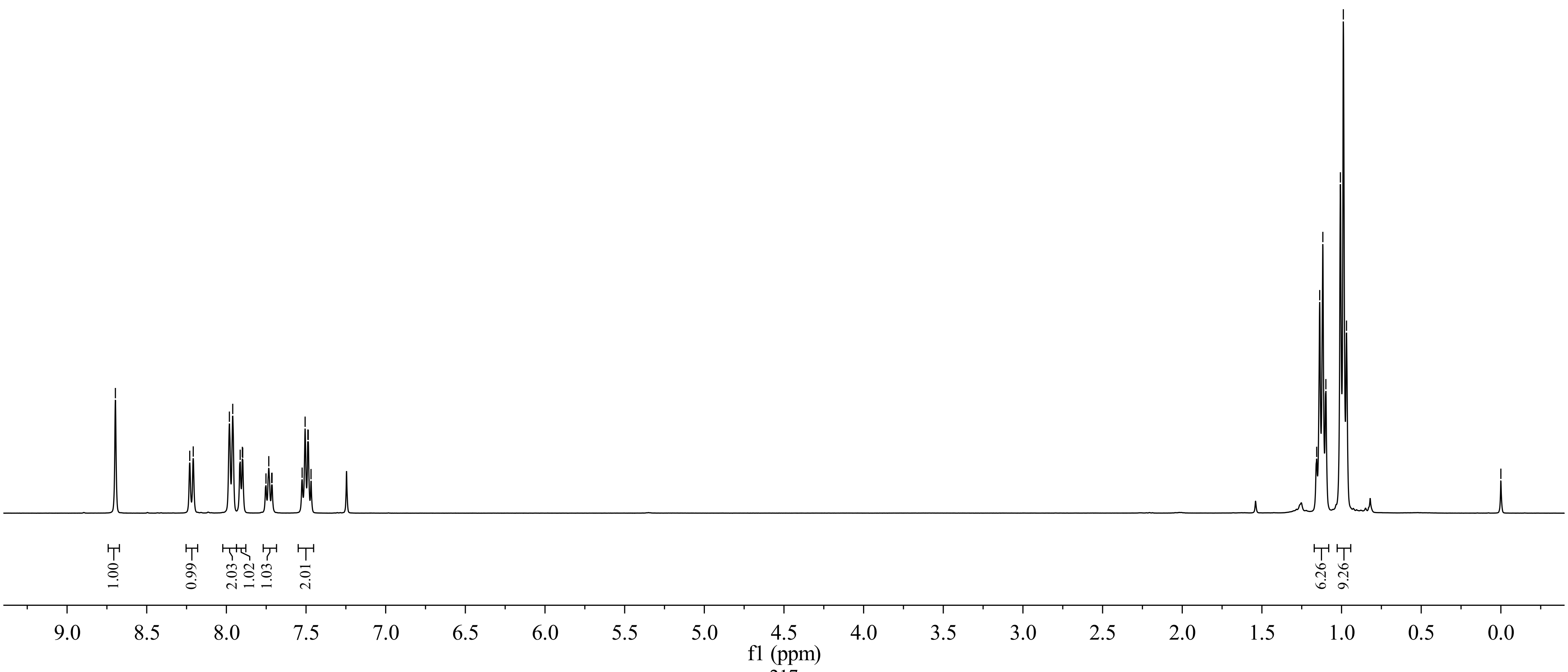
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

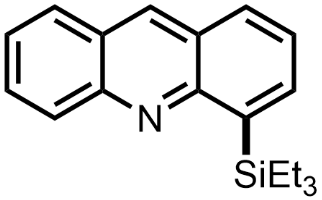




6p

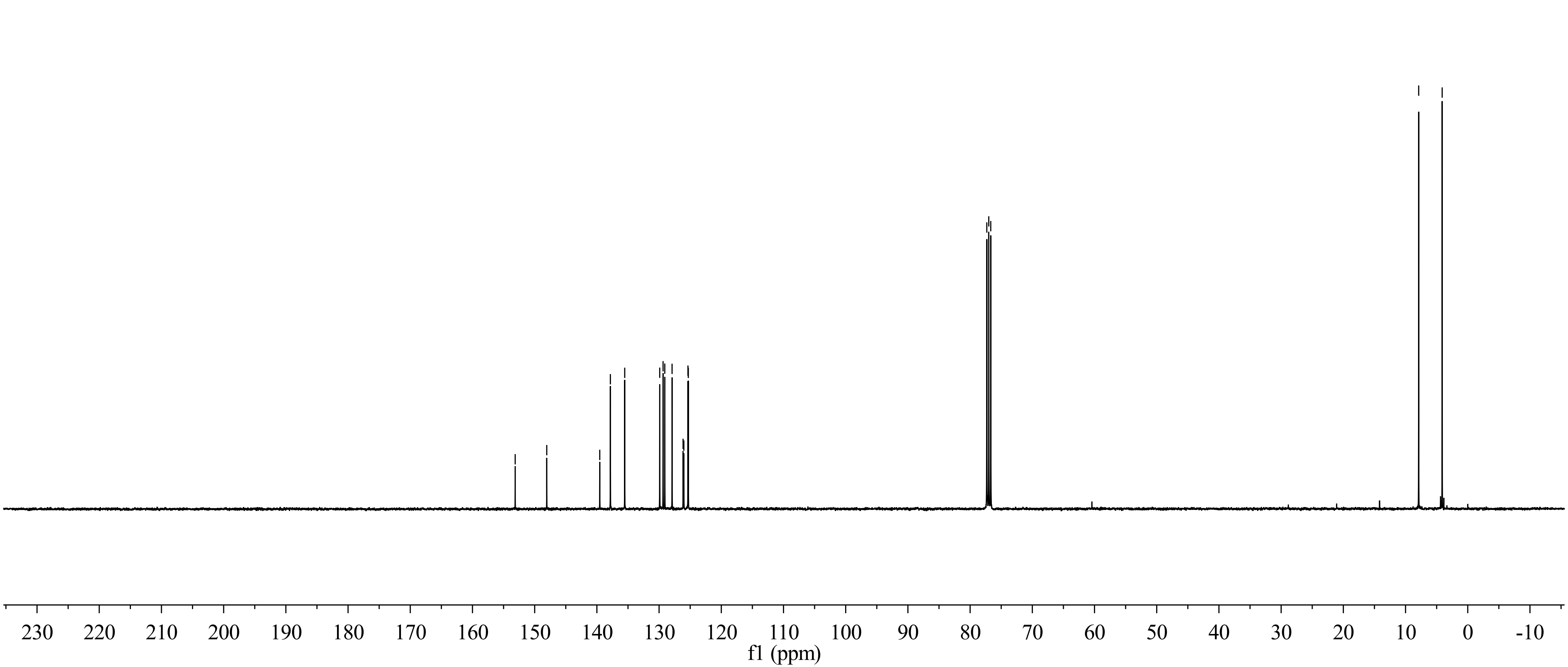
[1]H NMR spectrum (400 MHz, $CDCl_3$)

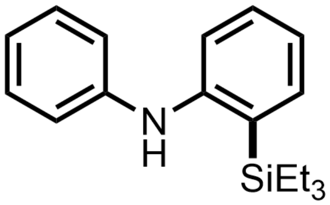




6p

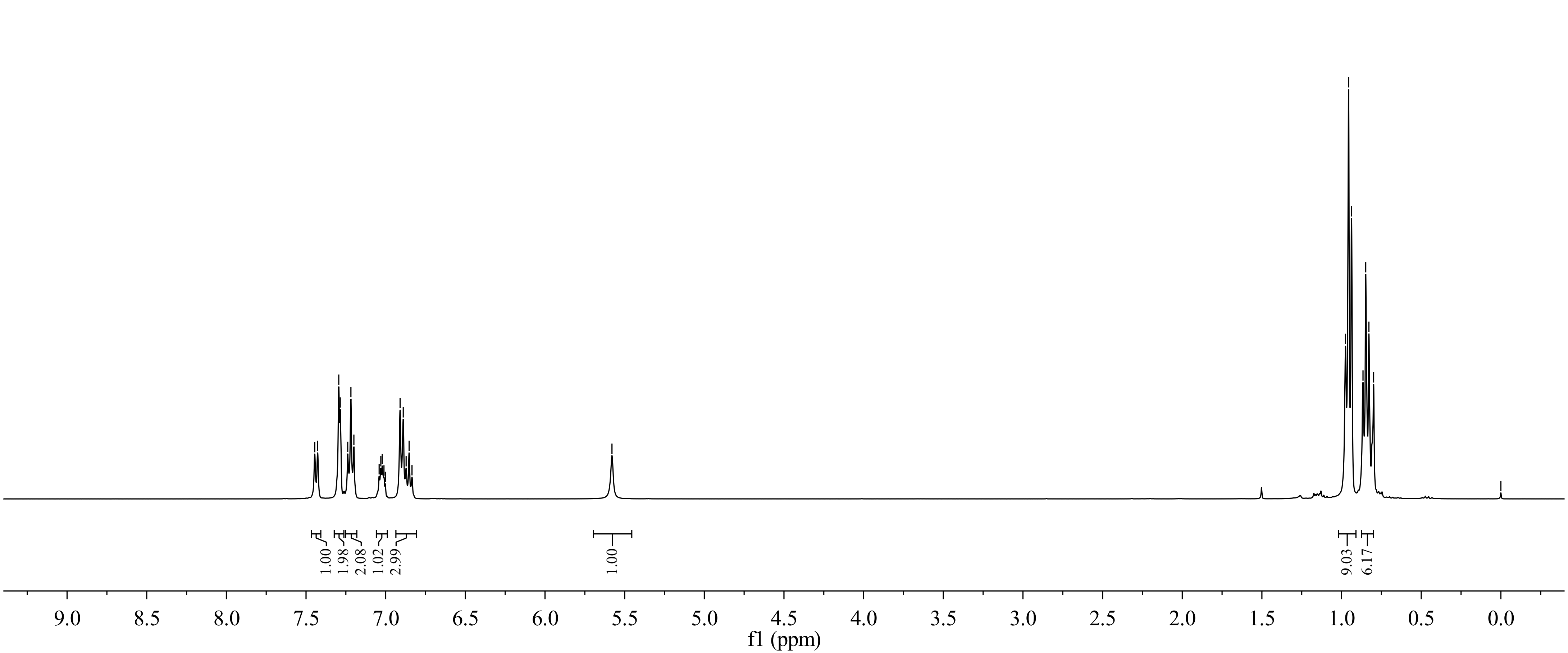
^{13}C NMR spectrum (100 MHz, CDCl$_3$)

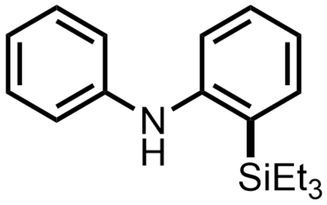




6q

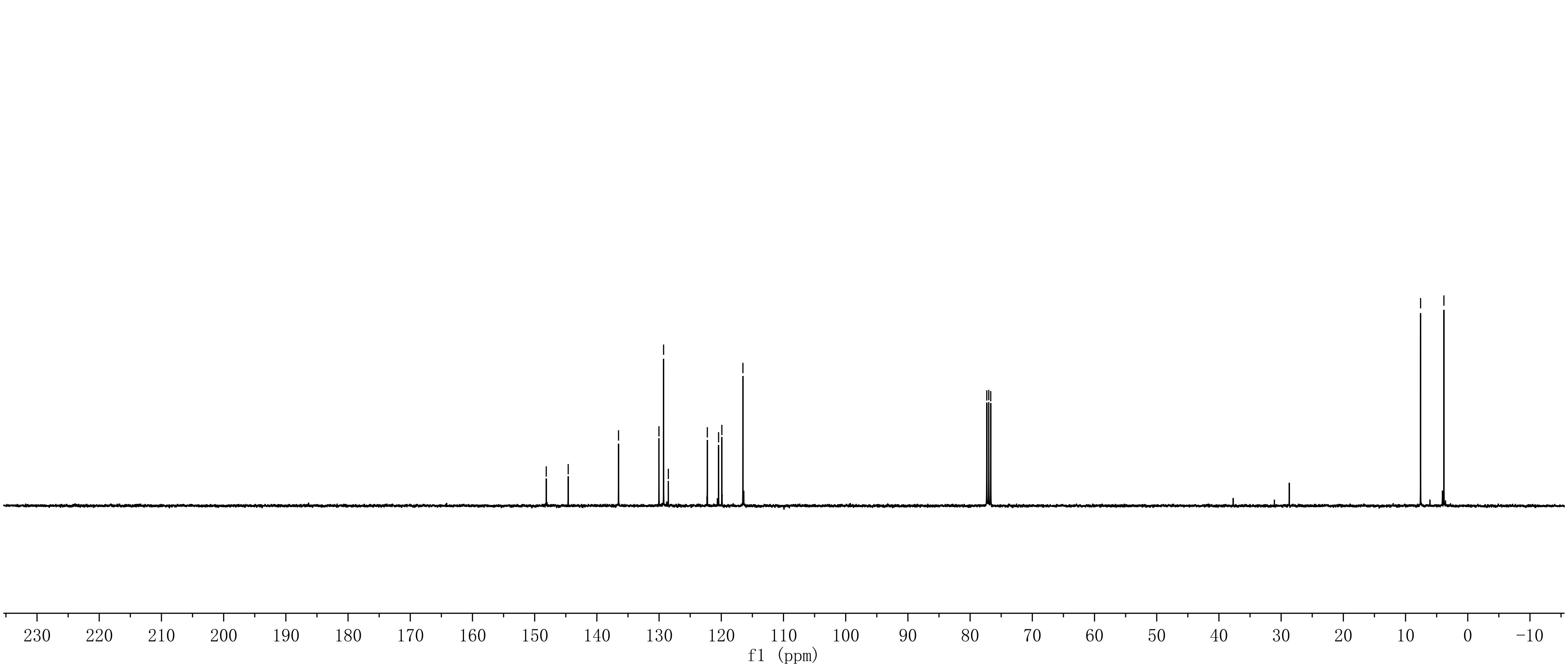
¹H NMR spectrum (400 MHz, $CDCl_3$)

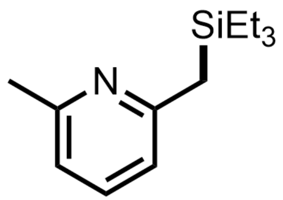




6q

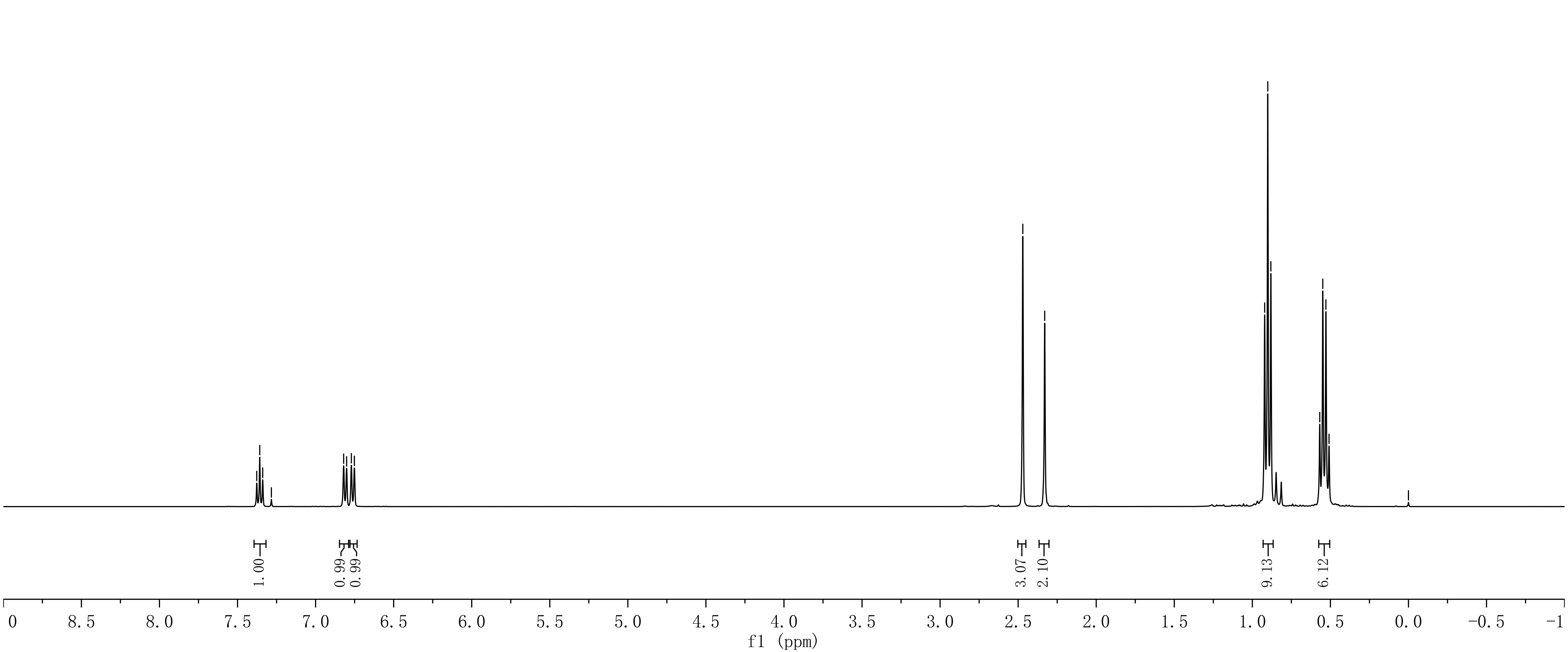
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

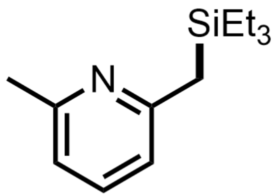




6r

[1]H NMR spectrum (400 MHz, $CDCl_3$)





6r

^{13}**C NMR** spectrum (100 MHz, $CDCl_3$)