Supporting Information

Transition-metal-free Chemoselective Catalytic Hydrosilylation of Tertiary Amides to Hemiaminals by Me_2SiH_2 Generated from Controllable Disproportionation of 1,1,3,3-Tetramethyldisiloxane

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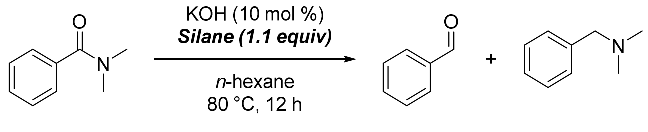
1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. Anhydrous THF was freshly distilled from Sodium. ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 MHz and 400 MHz spectrometer. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (0.00 ppm) and deuterochloroform (7.26 ppm) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.1 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh).
(Caution! combustible gas (Me_2SiH_2) is generated under standard conditions)

2. Optimization of the Reaction Conditions of Alkoxide-Catalyzed Hydrosilylation of Amides

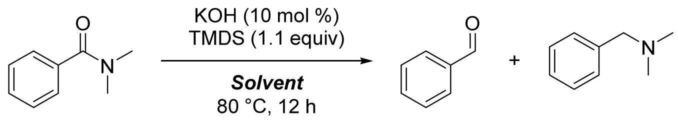
Table S1 Screening of silane



Entry	Silane	Conv. (%)	Yield (%)	
			2a	**3a**
1	Ph_2SiH_2	99	15	60
2	$PhSiH_3$	90	3	63
3	Ph_3SiH	71	21	38
4	Ph_2MeSiH	69	26	22
5	Et_3SiH	13	6	0
6	$(EtO)_3SiH$	47	4	8
7	$(MeO)_2MeSiH$	33	8	0
8	TMDS	98	62	23
9	PMHS	7	4	0

Reaction conditions: **1a** (298 mg, 2.0 mmol), KOH (11.2 mg, 0.2 mmol, 10 mol%), silane (1.1 equiv) and *n*-hexane (4.0 mL), 80 °C, 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

Table S2 Screening of solvent

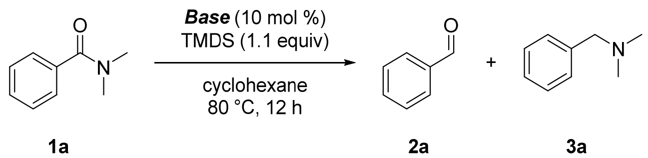


Entry	Solvent	Conv. (%)	Yield (%)

			2a	3a
1	Hexane	98	62	23
2	Cyclohexane	99	65	12
3	Heptane	99	56	29
4	THF	56	17	37
5	Dioxane	92	46	32
6	Diglyme	97	43	34
7	Toluene	95	40	35
8	PhF	26	9	10
9	CH_3CN	0	0	0
10	DCE	0	0	0
11	HMPA	31	0	18
12	None	72	31	40

Reaction conditions: **1a** (298 mg, 2.0 mmol), KOH (11.2 mg, 0.2 mmol, 10 mol%), TMDS (295.5 mg, 2.2 mmol, 1.1 equiv) and solvent (4.0 mL), 80 °C, 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

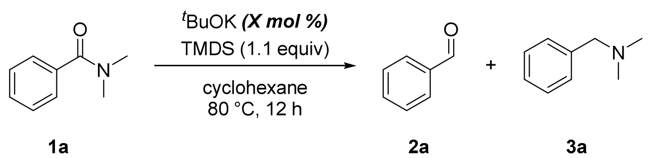
Table S3 Screening of catalysts



Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	3a
1	^{t}BuOK	99	71	11
2	TMSOK	99	67	16
3	CH_3CH_2OK	99	51	28
4	CH_3OK	79	23	38
5	KOH	99	65	12
6	K_2CO_3	12	6	0
7	KF	0	0	0
8	DBU	0	0	0
9	2,6-Lutidine	0	0	0
10	^{t}BuONa	29	21	0
11	^{t}BuOLi	5	3	0

Reaction conditions: **1a** (298 mg, 2.0 mmol), base (10 mol%), TMDS (295.5 mg, 2.2 mmol, 1.1 equiv) and cyclohexane (4.0 mL), 80 °C, 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

Table S4 Screening of catalyst loading

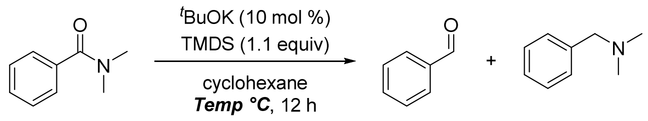


Entry	X mol%	Conv. (%)	Yield (%)

			2a	3a
1	5	78	58	6
2	10	99	71	11
3	20	99	68	21
4	40	99	54	38

Reaction conditions: **1a** (298 mg, 2.0 mmol), ^{t}BuOK (X mol%), TMDS (295.5 mg, 2.2 mmol, 1.1 equiv) and cyclohexane (4.0 mL), 80 °C, 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

Table S5 Screening of temperature

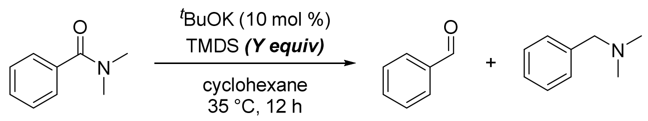


1a **2a** **3a**

Entry	Temp(°C)	Conv. (%)	Yield (%)	
			2a	**3a**
1	35	96	76	5
2	50	98	72	9
3	80	99	71	11
4	100[a]	93	41	47

Reaction conditions: **1a** (298 mg, 2.0 mmol), ^{t}BuOK (22.4 mg, 0.2 mmol, 10 mol%), TMDS (295.5 mg, 2.2 mmol, 1.1 equiv) and cyclohexane (4.0 mL), 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution. [a] *n*-heptane as solvent.

Table S6 Screening of silane dosage



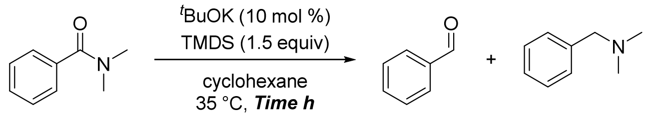
1a **2a** **3a**

Entry	Y (equiv)	Conv. (%)	Yield (%)	
			2a	**7a**
1	1.1	96	76	5
2	1.5	99	78	4
3	2.1	99	71	7
4	4.1	99	68	18
5	0.8	64	57	3
6	0.6	49	43	2

Reaction conditions: **1a** (298 mg, 2.0 mmol), ^{t}BuOK (22.4 mg, 0.2 mmol, 10 mol%), TMDS (Y equiv) and cyclohexane (4.0 mL), 35 °C, 12 h. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

3. Time-Course of Hydrosilylation Reduction

Table S7 Time-course at 0.5 M concentration in cyclohexane



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

Entry	Time (h)	Conv. (%)	Yield (%)	
			2a	**3a**
1	0.5	13	8	0
2	1.0	27	21	0
3	1.5	48	37	1
4	2.0	56	44	2
5	3.0	74	61	3
6	4.0	84	69	10
7	6.0	88	60	17
8	8.0	90	35	29
9	12.0	92	29	38

Reaction conditions: **1a** (298 mg, 2.0 mmol), ^{t}BuOK (22.4 mg, 0.2 mmol, 10 mol%), TMDS (402.9 mg, 3.0 mmol, 1.5 equiv) and cyclohexane (4.0 mL), 35 °C. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

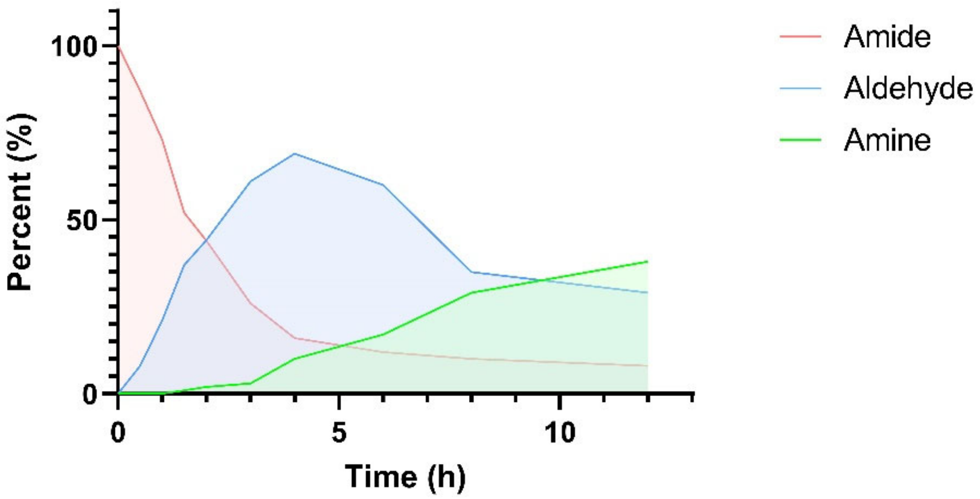
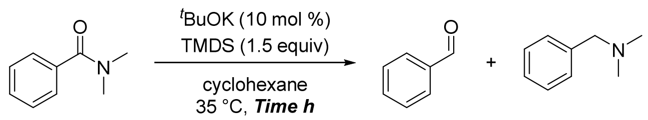


Figure S1. Time-course diagram of reduction at 0.5 M concentration in cyclohexane

Table S8 Time-course at 0.3 M concentration in cyclohexane



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

Entey	Time (h)	Conv. (%)	Yield (%)	
			2a	**3a**
1	0.5	23	9	0
2	1.0	37	33	0

3	1.5	60	56	1
4	2.0	71	65	2
5	3.0	89	81	2
6	4.0	95	84	4
7	6.0	99	90	4
8	8.0	99	85	6
9	12.0	99	82	7

Reaction conditions: **1a** (149 mg, 1.0 mmol), ^{t}BuOK (11.2 mg, 0.1 mmol, 10 mol%), TMDS (201 mg, 1.5 mmol, 1.5 equiv) and cyclohexane (3.0 mL), 35 °C. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

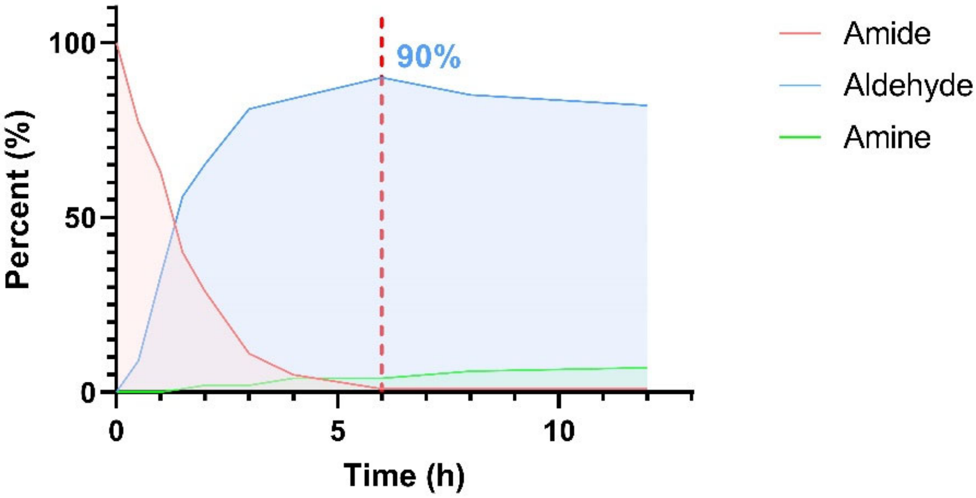
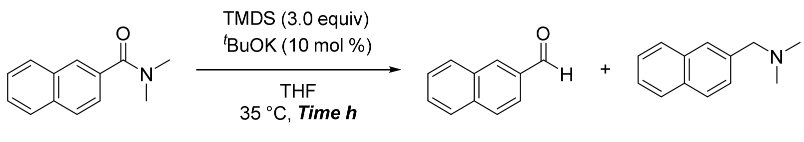


Figure S2. Time-course diagram of reduction at 0.3 M concentration in cyclohexane

Table S9 Time-course of 1n at 0.3 M concentration in THF



1y **2y** **3y**

Entry	Time (h)	Conv. (%)	Yield (%)	
			2w	**3w**
1	0	0	0	0
2	1	60	50	10
3	2	92	72	20
4	3	98	67	29
5	4	99	37	48
6	5	99	23	71
7	6	99	11	86
8	7	99	5	90
9	8	99	1	91

Reaction conditions: **1n** (199 mg, 1.0 mmol), ^{t}BuOK (11.2 mg, 0.1 mmol, 10 mol%), TMDS (402.9 mg, 3.0 mmol, 3.0 equiv) and THF (3.0 ml), 35 °C. Conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard. Reaction was quenched by HCl (aq.)/THF solution.

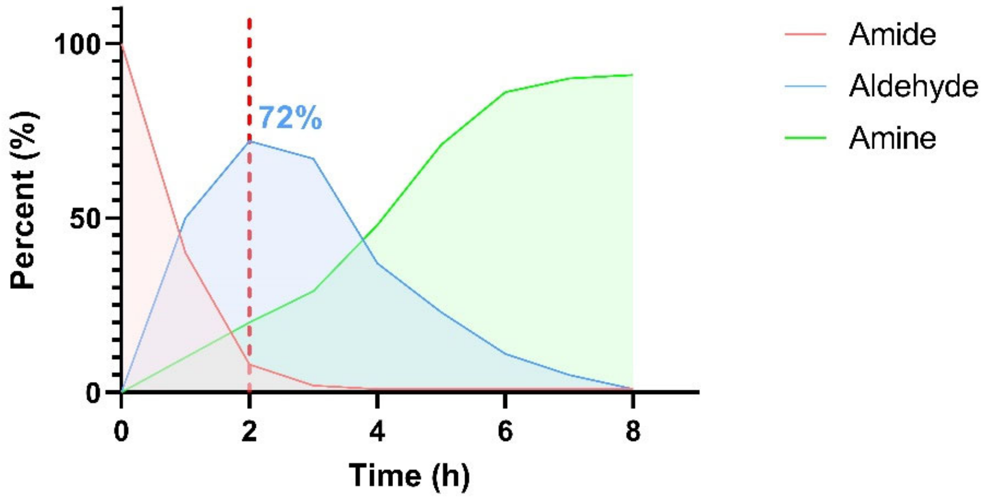
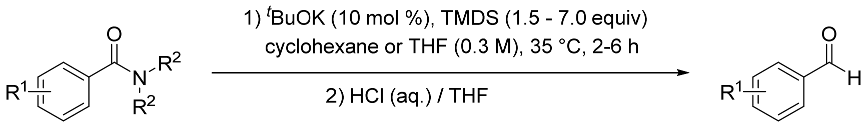


Figure S3. Time-course diagram of reduction at 0.3 M concentration in THF

4. Alkoxide-Catalyzed Hydrosilylation of Amides

4.1 General Experimental Procedures

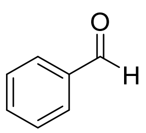


A dry reaction tube containing a magnetic stir bar was charged with amide (**1**, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 10 mol%), cyclohexane (3.0 mL) or THF (3.0 mL) was then added into the tube *via* syringe. TMDS was added dropwise into the tube slowly, the amount of TMDS depended on the kind of amide (the actual amount was listed in the manuscript). Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 2-6 h, removed from the oil bath, and allowed to cool to room temperature. HCl (aq.)/THF solution (*conc.* HCl : THF = 1 : 5, 2.0 mL) was added to quench the reaction for 10 min. The mixture was extracted with EtOAc (3.0 mL × 3), the combined organic phase was washed with brine and dried over Na_2SO_4. After removing the solvent under vacuum carefully, the residue was purified by column chromatography (silica gel) to give the product with Petroleum ether and EtOAc as eluent.

Specially: If the amide is liquid, the amide can be added dropwise after the solvent.

Caution! Combustible gas (Me_2SiH_2) is generated under standard conditions

4.2 Characterization of Aldehydes

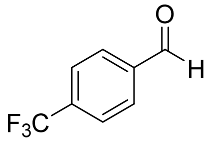


Benzaldehyde (2a)[1]: colorless liquid, the yields of **2a** prepared from various substituted amides are given in manuscript. 87% yield from **1a**.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 50 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.90 – 7.88 (m, 2H), 7.65 – 7.62 (m, 1H), 7.55 – 7.52 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 192.5, 136.5, 134.6, 129.9, 129.1.



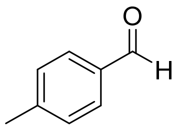
4-(Trifluoromethyl)benzaldehyde (2b)[2]: colorless liquid, 140 mg, 80% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 50 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 191.2, 138.8, 135.7 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 130.0, 126.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $^{1}J_{C\text{-}F}$ = 271.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -63.3.

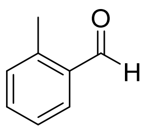


4-Methylbenzaldehyde (2c)[1]: colorless liquid, 108 mg, 90% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 30 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1, 145.7, 134.3, 130.0, 129.8, 22.0.

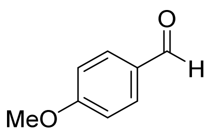


2-Methylbenzaldehyde (2d)[2]: colorless liquid, 86 mg, 72% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (s, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 2.69 (s, 3H).

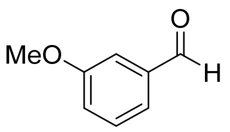
^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 140.7, 134.3, 133.7, 132.1, 131.9, 126.4, 19.7.



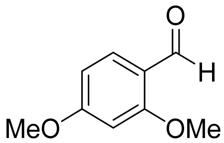
4-Methoxybenzaldehyde (2f)[1]: colorless liquid, 101 mg, 74% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).

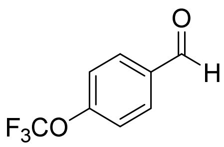
^{1}H NMR (500 MHz, CDCl$_3$): δ 9.82 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 190.7, 164.6, 131.9, 129.9, 114.3, 55.5.



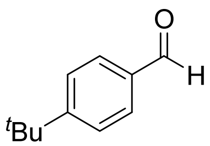
3-Methoxybenzaldehyde (2g)[3]: colorless liquid, 125 mg, 92% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 9.88 (s, 1H), 7.38 – 7.30 (m, 3H), 7.10 – 7.07 (m, 1H), 3.77 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 192.3, 160.3, 137.9, 130.2, 123.7, 121.7, 112.2, 55.6.



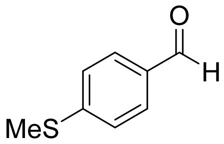
2,4-Dimethoxybenzaldehyde (2h)[4]: white solid, 150 mg, 90% yield, mp 58 – 60 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 10.27 (s, 1H), 7.79 (d, *J* = 11.0 Hz, 1H), 6.53 (dd, *J* = 11.0, 3.0 Hz, 1H), 6.43 (d, *J* = 3.0 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 188.5, 166.3, 163.7, 130.9, 119.1, 105.9, 98.0, 55.74, 55.71.



4-(Trifluoromethoxy)benzaldehyde (2i)[5]: colorless liquid, 173 mg, 91% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 10.01 (s, 1H), 7.96 – 7.93 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 190.6, 153.7 (q, $^{3}J_{C\text{-}F}$ = 2.0 Hz), 134.6, 131.7, 121.0, 120.4 (q, $^{1}J_{C\text{-}F}$ = 257.9 Hz).
^{19}F NMR (470 MHz, CDCl$_3$): δ -57.6.



4-(*tert*-Butyl)benzaldehyde (2j)[4]: white solid, 148 mg, 91% yield, mp 148 – 150 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 9.98 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 192.2, 158.6, 134.2, 129.8, 126.1, 35.5, 31.2.

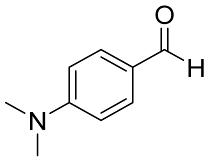


4-(Methylthio)benzaldehyde (2k)[3]: light yellow oil, 134 mg, 88% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.91 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 191.3, 148.0, 133.0, 130.1, 125.3, 14.8.

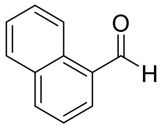


4-(Dimethylamino)benzaldehyde (2l)[6]: yellow solid, 107 mg, 72% yield, mp 70 – 72 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 3 : 1).

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.74 (s, 1H), 7.74 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 3.08 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 190.4, 154.5, 132.1, 125.3, 111.1, 40.2.

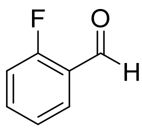


1-Naphthaldehyde (2m)[3]: yellow oil, 114 mg, 73% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 10.39 (s, 1H), 9.26 – 9.25 (m, 1H), 8.08 – 8.07 (m, 1H), 7.98 – 7.95 (m, 1H), 7.91 – 7.90 (m, 1H), 7.70 – 7.67 (m, 1H), 7.62 – 7.60 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 193.6, 136.7, 135.4, 133.8, 131.5, 130.6, 129.1, 128.6, 127.0, 125.0.



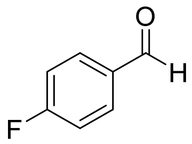
2-Fluorobenzaldehyde (2n)[7]: colorless liquid, 84 mg, 68% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 10.33 (s, 1H), 7.85 – 7.82 (m, 1H), 7.60 – 7.55 (m, 1H), 7.25 – 7.22 (m, 1H), 7.16 – 7.12 (m, 1H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 187.2 (d, $^3J_{C-F}$ = 6.5 Hz), 164.7 (d, $^1J_{C-F}$ = 257.1 Hz), 136.4 (d, $^3J_{C-F}$ = 9.1 Hz), 128.8 (d, $^4J_{C-F}$ = 1.9 Hz), 124.7 (d, $^3J_{C-F}$ = 3.7 Hz), 124.2 (d, $^2J_{C-F}$ = 8.0 Hz), 116.6 (d, $^2J_{C-F}$ = 20.4 Hz).

^{19}F NMR (470 MHz, CDCl$_3$): δ -122.0.



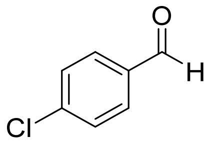
4-Fluorobenzaldehyde (2o)[3]: colorless liquid, 113 mg, 91% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 30 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.97 (s, 1H), 7.93 – 7.90 (m, 2H), 7.24 – 7.20 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 190.5, 166.5 (d, $^{1}J_{C\text{-}F}$ = 255.1 Hz), 133.0 (d, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 132.2 (d, $^{2}J_{C\text{-}F}$ = 9.6 Hz).

^{19}F NMR (470 MHz, CDCl$_3$): δ -102.4.

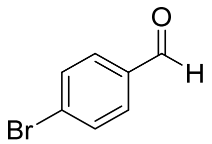


4-Chlorobenzaldehyde (2p)[3]: white solid, 118 mg, 84% yield, mp 44 – 46 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.99 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 191.0, 141.1, 134.9, 131.0, 129.6.

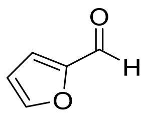


4-Chlorobenzaldehyde (2q)[3]: white solid, 115 mg, 62% yield, mp 53 – 55 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.96 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 191.2, 135.2, 132.5, 131.1, 129.9.

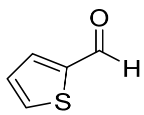


Furan-2-carbaldehyde (2r)[3]: yellow oil, 61 mg, 64% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.58 (s, 1H), 7.63 (s, 1H), 7.20 – 7.19 (m, 1H), 6.54 – 6.53 (m, 1H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 177.8, 152.9, 148.1, 121.2, 112.6.

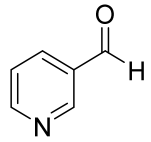


Furan-2-carbaldehyde (2s)[6]: orange oil, 85 mg, 76% yield.

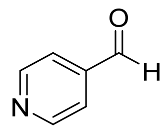
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 20 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.92 (s, 1H), 7.77 – 7.74 (m, 2H), 7.20 – 7.19 (m, 1H).

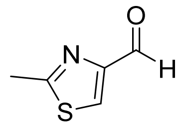
^{13}C NMR (125 MHz, CDCl$_3$): δ 183.1, 144.1, 136.4, 135.2, 128.4.



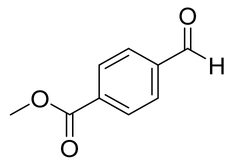
Nicotinaldehyde (2t)[3]: yellow oil, 91 mg, 85% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.99 (s, 1H), 8.75 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.41 (dd, J = 8.0, 5.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 190.8, 154.7, 152.0, 135.8, 131.4, 124.0.



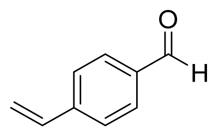
Isonicotinaldehyde (2u)[8]: yellow oil, 88 mg, 82% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.79 – 8.78 (m, 2H), 7.62 – 7.61 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 191.5, 151.2, 141.4, 122.0.



2-Methylthiazole-4-carbaldehyde (2v)[9]: yellow solid, 108 mg, 85% yield, mp 46 – 48 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.04 (s, 1H), 2.77 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 184.5, 167.8, 154.8, 128.4, 19.4.

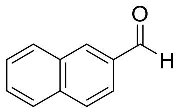


Methyl 4-formylbenzoate (2w)[3]: white solid, 71 mg, 43% yield, mp 83 – 85 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.17 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 8.5 Hz, 2H), 3.96 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 191.7, 166.2, 139.3, 135.2, 130.3, 129.7, 129.6, 52.7.

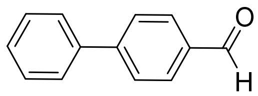


4-Vinylbenzaldehyde (2x)[10]: light yellow oil, 41 mg, 31% yield.

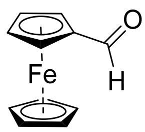
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 9.98 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 6.77 (dd, *J* = 11.0 Hz, 18.0 Hz, 1H), 5.91 (d, *J* = 18.0 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 191.9, 143.6, 136.0, 135.8, 130.2, 126.9, 117.6.



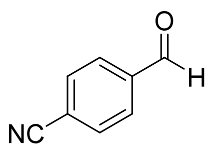
2-Naphthaldehyde (2y)[3]: white solid, 111 mg, 71% yield, mp 58 – 60 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 10.16 (s, 1H), 8.34 (s, 1H), 8.02 – 8.00 (m, 1H), 7.97 – 7.90 (m, 3H), 7.66 – 7.63 (m, 1H), 7.61 – 7.58 (m, 1H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 192.4, 136.6, 134.7, 134.3, 132.8, 129.7, 129.25, 129.23, 128.2, 127.2, 122.9.



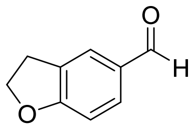
[1,1'-Biphenyl]-4-carbaldehyde (2z)[3]: white solid, 128 mg, 70% yield, mp 54 – 56 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 10.06 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 192.0, 147.3, 139.8, 135.3, 130.3, 129.1, 128.6, 127.8, 127.4.



Ferrocenecarboxaldehyde (2aa)[11]: orange solid, 150 mg, 70% yield, mp 115 – 117 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 10 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 9.95 (s, 1H), 4.79 (t, *J* = 2.0 Hz, 2H), 4.60 (t, *J* = 2.0 Hz, 2H), 4.27 (s, 5H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 193.6, 77.5, 76.8, 73.3, 69.8.



4-Formylbenzonitrile (2bb)[3]: white solid, 99 mg, 76% yield, mp 98 – 100 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 10.10 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 190.7, 138.9, 133.0, 130.0, 117.8, 117.7.

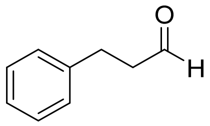


2,3-Dihydrobenzofuran-5-carbaldehyde (2cc)[12]: white solid, 104 mg, 70% yield, mp 189 – 191 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 3 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.73 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.67 (t, *J* = 8.5 Hz, 2H), 3.25 (t, *J* = 8.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 165.7, 133.1, 130.5, 128.5, 126.0, 109.7, 72.5, 28.8.

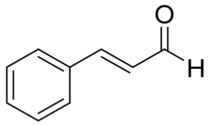


3-Phenylpropanal (2dd)[6]: colorless liquid, 83 mg, 62% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.34 – 7.31 (m, 2H), 7.25 – 7.21 (m, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 140.4, 128.6, 128.3, 126.3, 45.2, 28.1.

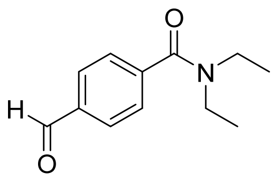


Cinnamaldehyde (2ee)[6]: colorless liquid, 71 mg, 53% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 5 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.70 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.49 – 7.46 (m, 1H), 7.44 – 7.42 (m, 3H), 6.74 – 6.69 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 152.9, 134.1, 131.4, 129.2, 128.7, 128.6.

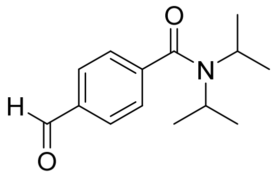


***N,N*-Diethyl-4-formylbenzamide (2nn)**[13]: yellow oil, 172 mg, 84% yield in cyclohexane; 155 mg, 76% yield in THF.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 3 : 1).

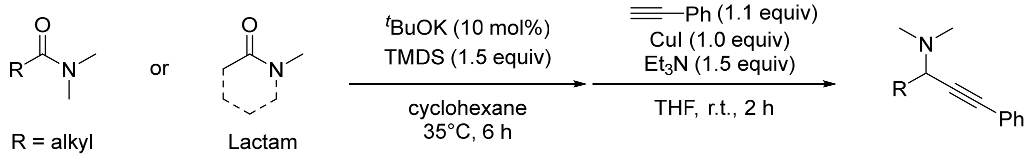
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 3.73 (q, *J* = 7.5 Hz, 2H), 3.54 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 8.5 Hz, 3H), 1.01 (t, *J* = 8.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 191.7, 170.0, 143.1, 136.6, 130.0, 127.0, 43.3, 39.5, 14.3, 13.0.

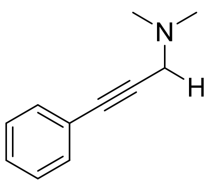


4-Formyl-*N,N*-diisopropylbenzamide (2pp)[14]: white solid: 189 mg, 81% yield, mp 83 – 85 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 3 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 10.03 (s, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 3.73 (s, 1H), 3.54 (s, 1H), 1.55 (s, 6H), 1.15 (s, 6H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 191.7, 169.7, 144.5, 136.3, 130.2, 126.3, 51.1, 46.2, 20.7.

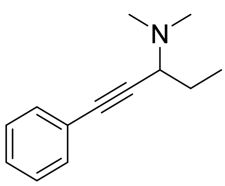
4.3 Tandem Reduction and Nucleophilic Attack of Alkyl Amides and Lactams



A dry reaction tube containing a magnetic stir bar was charged with amide (**1**, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), cyclohexane (3.0 mL) was then added into the tube *via* syringe. TMDS (201 mg, 1.5 mmol, 1.5 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to room temperature. Then the mixture was transferred into another reaction tube containing a magnetic stir bar which was charged with alkyne (1.1 mmol, 1.1 equiv), CuI (190 mg, 1.0 mmol, 1.0 equiv), Et$_3$N (152 mg, 1.5 mmol, 1.5 equiv) and THF (4.0 mL). The reaction mixture was quenched by addition of 15% KOH solution and extracted with EtOAc (5.0 mL × 3). The combined organic phase was washed with brine and dried over Na$_2$SO$_4$. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give the product with Petroleum ether and EtOAc as eluent.

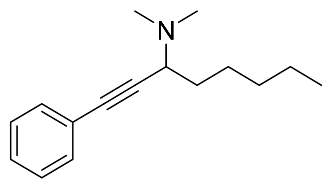


***N,N*-Dimethyl-3-phenylprop-2-yn-1-amine (4qq)[15]**: pale orange oil: 133 mg, 84% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.43 (m, 2H), 7.31 – 7.28 (m, 3H), 3.47 (s, 2H), 2.37 (s, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 131.8, 128.4, 128.1, 123.4, 85.4, 84.7, 48.7, 44.4.

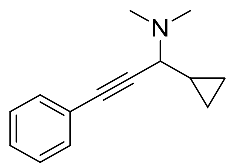


***N,N*-Dimethyl-1-phenylpent-1-yn-3-amine (4rr)[16]**: pale orange oil: 142 mg, 76% yield.

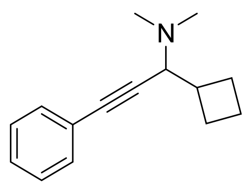
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.42 (m, 2H), 7.31 – 7.28 (m, 3H), 3.43 (t, *J* = 7.2 Hz, 1H), 2.31 (s, 6H), 1.75 – 1.68 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 131.9, 128.4, 128.0, 123.6, 87.1, 86.1, 60.1, 41.7, 27.3, 11.5.



***N,N*-Dimethyl-1-phenyloct-1-yn-3-amine (4ss)**: colorless oil: 170 mg, 74% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 5 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.41 (m, 2H), 7.31 – 7.28 (m, 3H), 3.51 (t, *J* = 7.6 Hz, 1H), 2.32 (s, 6H), 1.73 – 1.66 (m, 2H), 1.59 – 1.44 (m, 2H), 1.37 – 1.33 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 131.9, 128.3, 128.0, 123.6, 87.2, 86.1, 58.4, 41.6, 34.1, 31.8, 26.5, 22.7, 14.2.
IR (KBr) *ν*(cm^{-1}): 3419, 2935, 1597, 1489, 1467, 1456, 1259, 1070, 1042, 1028, 803, 755.
HRMS – ESI (m/z): [M + H]$^+$ called for $C_{16}H_{24}N$, 230.1909, found 230.1916.

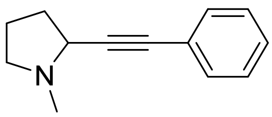


1-Cyclopropyl-*N,N*-dimethyl-3-phenylprop-2-yn-1-amine (4tt): colorless oil: 187 mg, 94% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.40 (m, 2H), 7.31 – 7.27 (m, 3H), 3.51 (d, *J* = 5.6 Hz, 1H), 2.39 (s, 6H), 1.15 – 1.07 (m, 1H), 0.63 – 0.49 (m, 3H), 0.44 – 0.38 (m, 1H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 131.9, 128.4, 128.1, 123.4, 86.5, 84.3, 61.7, 42.0, 13.6, 3.2, 2.5.
IR (KBr) *ν*(cm^{-1}): 3419, 3080, 3003, 2965, 2924, 1597, 1489, 1469, 1454, 1357, 1302, 1259, 1030, 914, 756.
HRMS – ESI (m/z): [M + H]$^+$ called for $C_{14}H_{18}N$, 200.1439, found 200.1440.

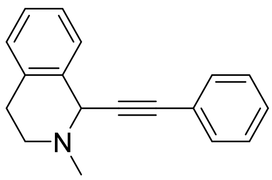


1-Cyclobutyl-*N,N*-dimethyl-3-phenylprop-2-yn-1-amine (4uu): colorless oil: 151 mg, 71% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.42 (m, 2H), 7.31 – 7.28 (m, 3H), 3.48 (d, *J* = 8.4 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.29 (s, 6H), 2.13 – 1.98 (m, 4H), 1.86 – 1.79 (m, 2H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 131.9, 128.4, 128.0, 123.6, 86.9, 85.5, 64.1, 42.0, 38.3, 26.5, 26.3, 18.3.
IR (KBr) *ν*(cm^{-1}): 3423, 3079, 2973, 2937, 2860, 2822, 2823, 2778, 1597, 1488, 1468, 1454, 1442, 1330, 1272, 1257, 1016, 755.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{15}H_{19}N$, 214.1596, found 214.1600.

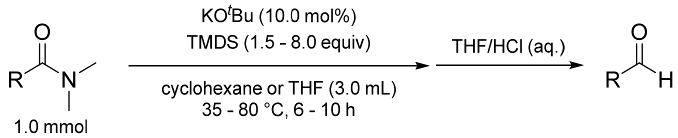


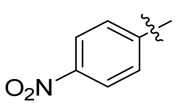
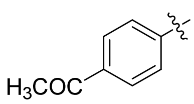
1-Methyl-2-(phenylethynyl)pyrrolidine (4vv)[17]: pale orange oil: 57 mg, 31% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA : MeOH= 1 : 10 : 0.05).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.31 – 7.27 (m, 3H), 3.39 (t, *J* = 6.8 Hz, 1H), 2.97 – 2.92 (m, 1H), 2.51 (s, 3H), 2.48 – 2.44 (m, 1H), 2.26 – 2.18 (m, 1H), 2.08 – 1.91 (m, 2H), 1.87 – 1.78 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 128.3, 128.1, 123.3, 88.5, 84.7, 57.2, 54.9, 39.9, 32.4, 22.5.

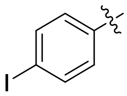
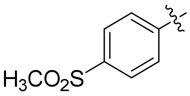
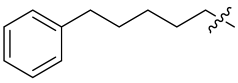
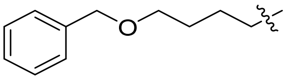
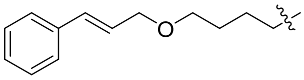
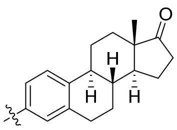
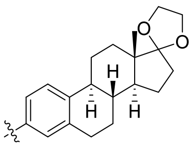
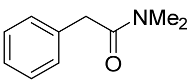
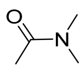
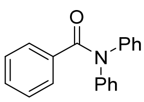
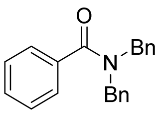


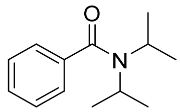
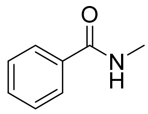
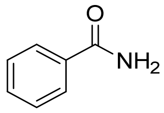
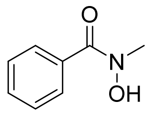
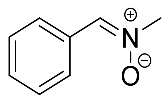
2-Methyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4ww)[18]: pale yellow oil: 210 mg, 85% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 5 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.27 – 7.23 (m, 3H), 7.20 – 7.15 (m, 2H), 7.13 – 7.10 (m, 1H), 4.70 (s, 1H), 3.08 – 2.85 (m, 3H), 2.73 – 2.67 (m, 1H), 2.62 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 133.6, 131.9, 129.0, 128.3, 128.1, 127.7, 127.1, 126.0, 123.3, 87.6, 86.4, 57.1, 48.8, 43.9, 28.9.

4.4 Unsuccessful Substrates

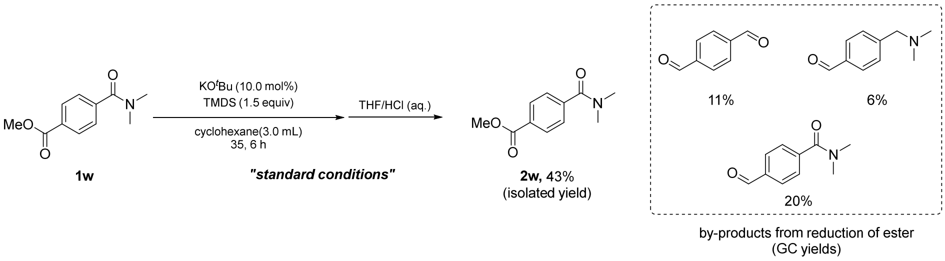


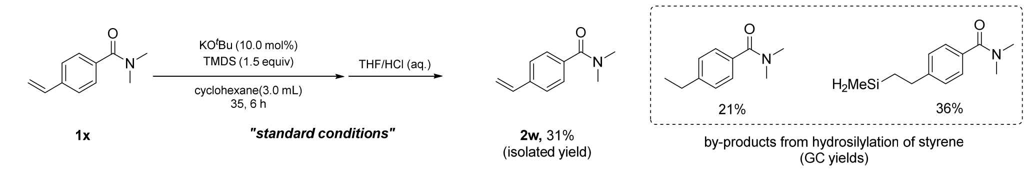
R/Amide	Solvent	TMDS (X equiv)	Temperature (˚C)	Result
 O$_2$N	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
 H$_3$COC	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble

	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	Conv.% <10%
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	Conv.% = 15%
	cyclohexane	1.5	35	Conv.% <10%
	THF	8.0	80	Conv.% <10%
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	Conv.% <10%
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Conv.% <10%
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	No Detection
	THF	8.0	80	No Detection
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble

	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	No Reaction
	THF	8.0	80	No Reaction
	cyclohexane	1.5	35	Insoluble
	THF	8.0	80	No Reaction
	THF	2.0	35	 57%

For the substrates **1w** and **1x**



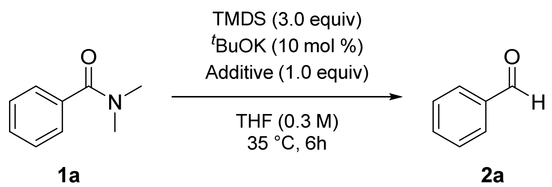


5. Competitive Experiments

Experiment Procedure: A dry reaction tube containing a magnetic stir bar was charged with amide *N*,*N*-dimethylbenzamide (**1a**, 149 mg, 1.0 mmol, 1.0 equiv), additive (1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), THF (3.0 mL) was then added into the tube *via* syringe. TMDS (402 mg, 3.0 mmol, 3.0 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to the room temperature. HCl (aq.)/THF solution (*conc.* HCl : THF = 1 : 5, 2.0 mL) was added to quench the reaction for 10 min. The mixture was extracted with EtOAc (3.0 mL × 3), the combined organic phase was washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give **1a**, **2a** and additive.

Result: Under standard conditions (Part 4.4 of Supporting Information), most of the amides which are insoluble in cyclohexane cannot be reduced successfully, including the amides bearing nitro, iodine, ketones, cyano, and methylsulfonyl. In order to understand whether the failures are caused by poor solubility, we change the solvent into THF to exclude the differences in solubility. Delightedly, model amide **1a** also can be reduced in good conversion but moderate chemoselectivity to give aldehyde. From the Table S9, we observed that cyano group cannot inhibit the model reaction, indicating that the amide **2bb** cannot be reduced, just because of its poor solubility; however, other additives, such as nitrobenzene, iodobenzene, benzenesulfone, and acetophenone, completely inhibited the occurrence of model reaction, and the significant reduction of this equivalent of additives were not detected. Based on the following studies on mechanism, we proposed a reasonable explanation that these strongly coordinative groups can competitively hinder the approach of amide to silane, thereby the disproportionation of TMDS is difficult to occur, and the reduction fail.

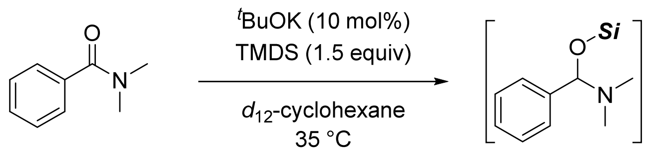
Table S10 Competitive Experiments



Entry	Additive	Yield% of **2a**	Additive recovery (%)	Conv. % of **1a**
1	none	74	0	>99
2	$PhNO_2$	0	99	0
3	PhI	0	96	0
4	$PhSO_2CH_3$	0	87	0
5	PhCN	62	99	94
6	$PhCOCH_3$	0	91	6

6. Mechanistic Experiments

6.1 NMR Analysis



A dry reaction tube containing a magnetic stir bar was charged with *N*,*N*-dimethylbenzamide (**1**, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (0.1 mmol, 0.1 equiv), d_{12}-cyclohexane (3.0 mL) was then added into the tube *via* syringe. TMDS was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The reaction was monitored by ^{1}H NMR at reaction time of 10 min, 120 min, 360 min, 600 min and 1440 min, respectively.

From the spectrum, *N,N*-dimethylbenzamide was consumed (the peak at 3.8 ppm gradually disappears) in 6 h, the intermediate was gradually formed at the same time (the peak at 5.5 ppm appears). After 1440 min (24 h), the disappearance of the peak at 5.5 ppm meant that the intermediate was further transformed completely to amine. By the comparison with prior reports[19], this intermediate was identified as the hemiaminal rather than imine (because there is not α-H, the formation of enamine is impossible).

Also from the spectrum, an unusual phenomenon was appeared that the original TMDS (the peak at 4.7 ppm) consumed rapidly in initial minutes and completely converted into newly active Si-H compound (the peak at 3.8 ppm), which was identified as Me_2SiH_2. Although Me_2SiH_2 is gas at room temperature, it can still dissolve well in organic solvents, like cyclohexane and THF, and thus can maintain a comparative low concentration which is benefited for the chemoselective reduction, indeed, the integral of Me_2SiH_2 was just half of the integral of original TMDS.

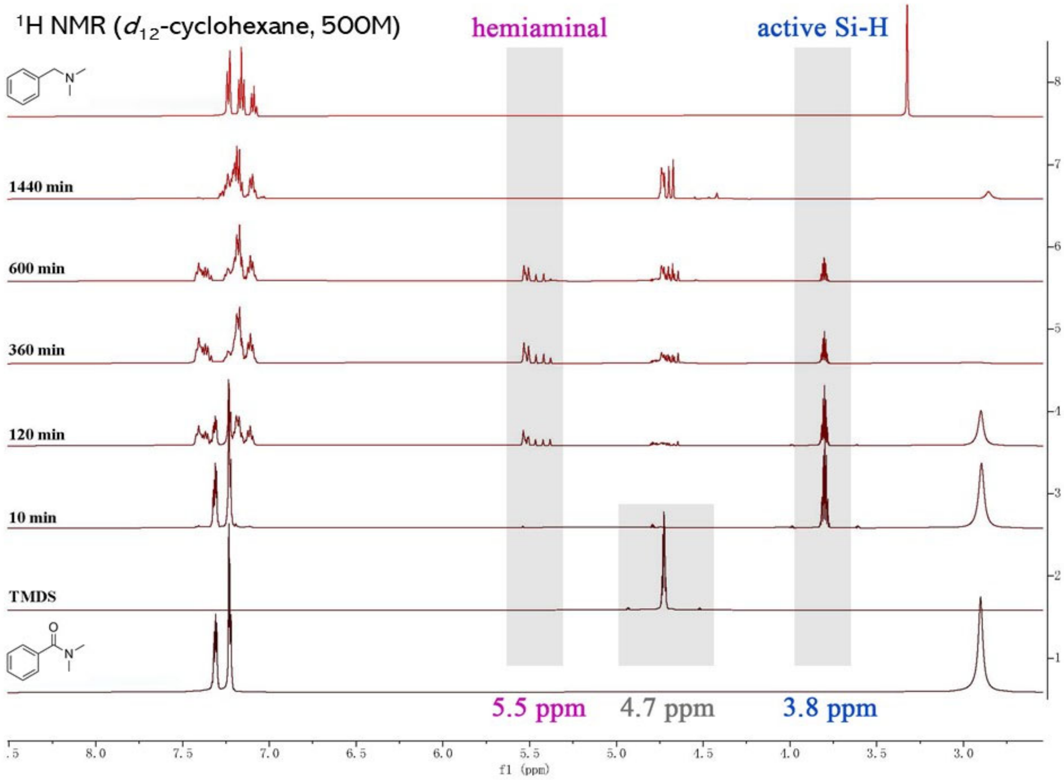


Figure S4. ^{1}H NMR experiments of hydrosilylation reduction of *N,N*-dimethylbenzamide

In order to further clarify this special activation process of silane, we also monitored the reaction by ^{29}Si NMR at reaction time of 10 min, 120 min, 360 min, 600 min and 1440 min, respectively.

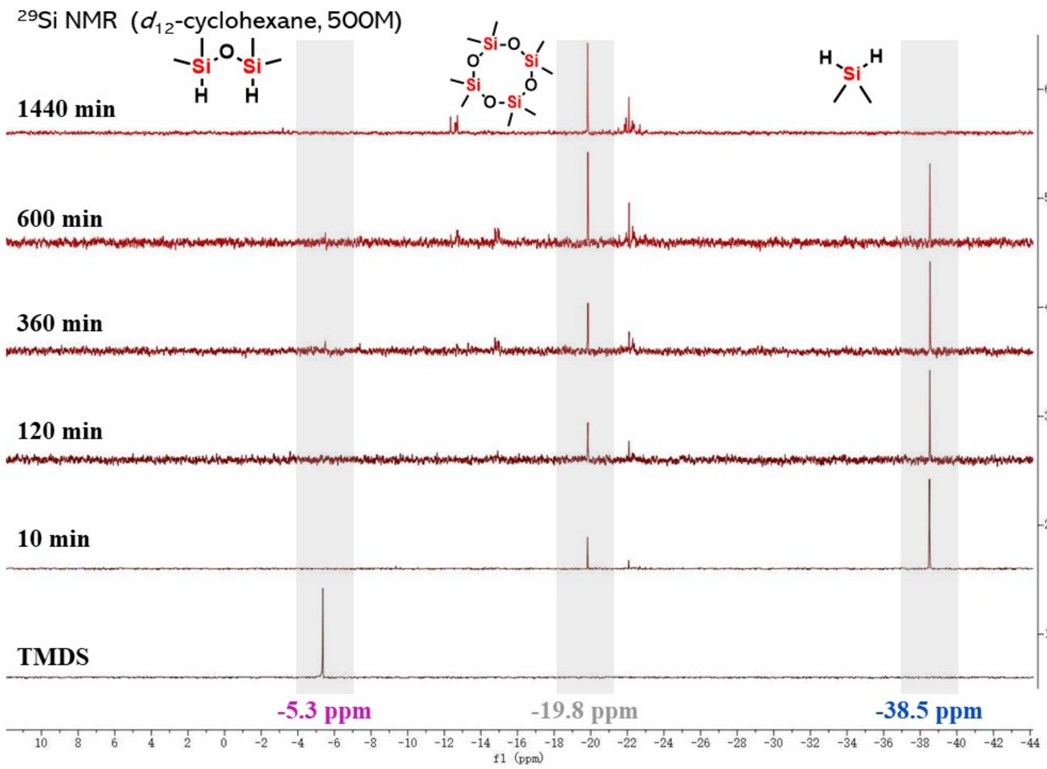


Figure S5. ^{29}Si NMR experiments of hydrosilylation reduction of *N,N*-dimethylbenzamide

From the spectrum, TMDS was authentically disappeared (the peak at -5.3 ppm) rapidly in initial minutes and completely converted into mainly two parts (the peak at -19.8 ppm and -38.5 ppm), indicating that this activation process is actual a disproportionation of TMDS. From previous literatures, the peak at -19.8 ppm is refer to octamethylcyclotetrasiloxane[20] (D_4) and the peak at -19.8 ppm is refer to dimethylsilane[20]. From the contrastive spectrum, we can discover that the amount of octamethylcyclotetrasiloxane do not decrease with the reaction but will increase evidently, while the amount of dimethylsilane decrease slowly, so we speculated that dimethylsilane is the actual reductant for the reduction.

Additionally, we also studied the effort of alkoxide and amides in this disproportionation process. The test procedure is following: A dry reaction tube containing a magnetic stir bar was charged with *N*,*N*-dimethylbenzamide (**1**) or ^{t}BuOK, and then d_{12}-cyclohexane (3.0 mL) was added into the tube *via* syringe. Then the tube was inserted into an oil bath preheated to 35 ˚C for 10 mins. Then TMDS was added quickly within 10 secs and the mixture kept stirring for 1 min. Then the NMR tests were carried out within 3 mins.

As shown in Figure S6, we found that amide play a crucial role in promoting the disproportionation, the disproportionation cannot occur in absent of alkoxide or amide (1.0 equiv). Specially, when no amide was added, KO^{t}Bu hardly caused any disproportionation or activation of TMDS, and even the stoichiometric amount did not work.

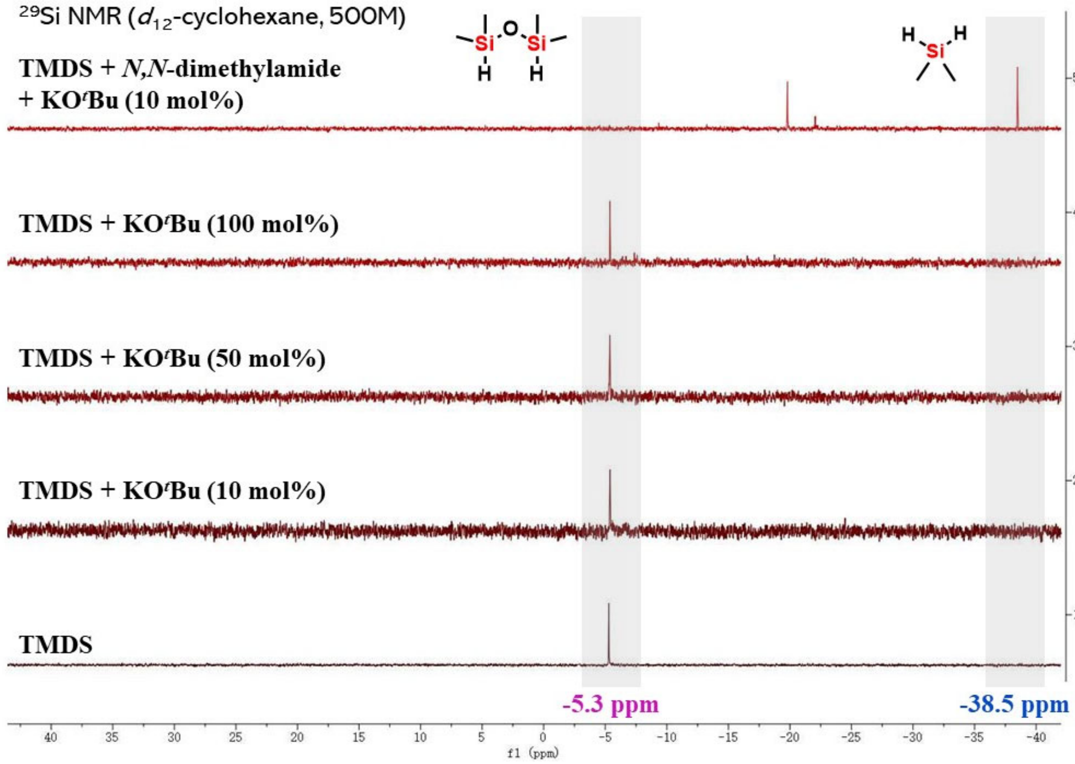


Figure S6. [1]H NMR experiments for the influence of KO^{t}Bu in absent of amide

However, in the present of amides, the disproportionation occurred too rapidly to detect the behavior of the amides and alkoxide by NMR or ReactIR, as shown in Figure S7. Even very low loading of alkoxide (1.0 mol%) can make the disproportionation complete, further reducing the loading of alkoxide (< 0.5 mol%) made the disproportionation incomplete slightly (not listed). Another finding is that, with the increasing loading of alkoxide, the mode of disproportionation would be changed. Although the generation of Me_2SiH_2 was always maintained, octamethylcyclotetrasiloxane would be no longer produced when the loading of alkoxide is more than 50 mol%, and hexamethylcyclortrisiloxane would be the main product. The reason for this change is unknown so far.

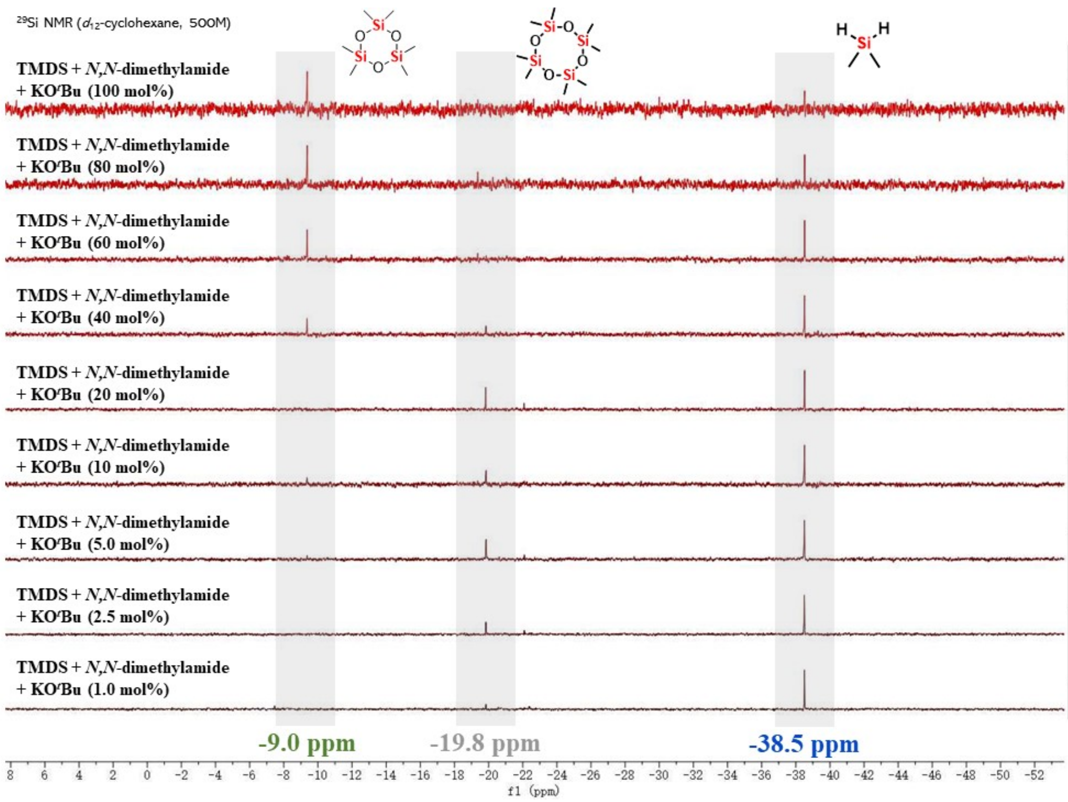
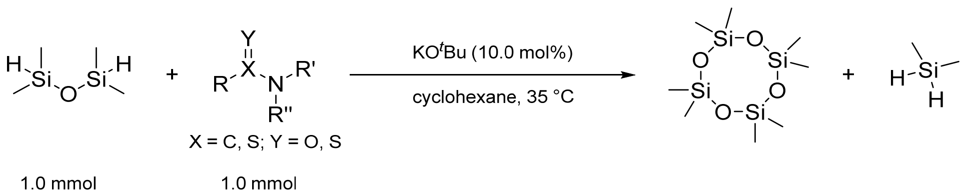
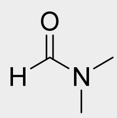
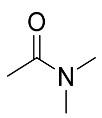


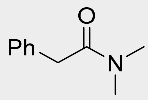
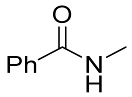
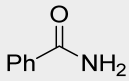
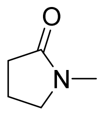
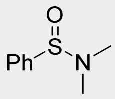
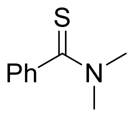
Figure S7. ^{1}H NMR experiments for the influence of KOtBu in present of amide

We tried to detected the relationship of amide, alkoxide and silanes, however, all attempts were failed, no directed evidence can indicate the interaction among them, no visible difference was found in the displacement and shapes of characteristic peaks in NMR analysis and ReactIR. But we still have some findings to inspire our following research:

1) wide scope of amides can promote this kind of disproportionation of TMDS to produce Me_2SiH_2 and cyclosiloxane, including DMF and DMA in cyclohexane as listed.

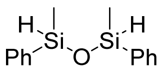
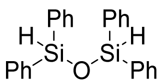
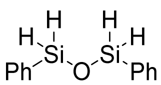
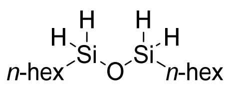
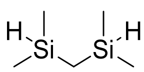
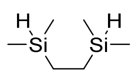
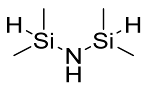


Amide	Disproportionation of TMDS	Reduction of amide
	√	√
	√	×

	√	×
	×	×
	×	×
	√	√
	×	×
	×	×

2) Silanes with similar structure to TMDS as listed, can undergo the same kind of disproportionation to produce corresponding secondary silane and cyclosiloxane, however, other common kinds of silane are failed to be converted in this system.

silane —[**1a** (1.0 equiv), KO^{t}Bu (10.0 mol%); cyclohexane, 35 °C, 3 min]→ secondary silane + cyclosiloxane

Silane	Products	
	silane	cyclosiloxane
	$PhMeSiH_2$	$(PhMeSiO)_4$
	Ph_2SiH_2	$(Ph_2SiO)_4$
	Messy	
	Messy	
	No Reaction	
	No Reaction	
	Messy	
$(EtO)_3SiH$	No Reaction	

Et_3SiH	No Reaction
Et_2SiH_2	No Reaction
Ph_2SiH_2	No Reaction
$PhSiH_3$	No Reaction

6.2 ReactIR Analysis

For the detailed evident of the generation of hemiaminal, we carried out the online ReactIR experiment in a 5.0 gram-scale reaction for 2 hours, the result was shown in Figure S8. As the reaction proceeded, the peak at 1655 cm^{-1} gradually weakened and disappeared in 2 hours, at the same time the peak at 2517 cm^{-1} is rapidly and maintained at a high intensity until the end of the test. By the comparison with prior reports[21], the peak at 1655 cm^{-1} is refer to the carbonyl in *N,N*-dimethylbenzamide, and the peak at 2517 cm^{-1} is refer to the C-H bond in hemiaminal, there were no detectable characteristic peaks of imines and aldehydes. These phenomena exactly matched our expectations and NMR analysis.

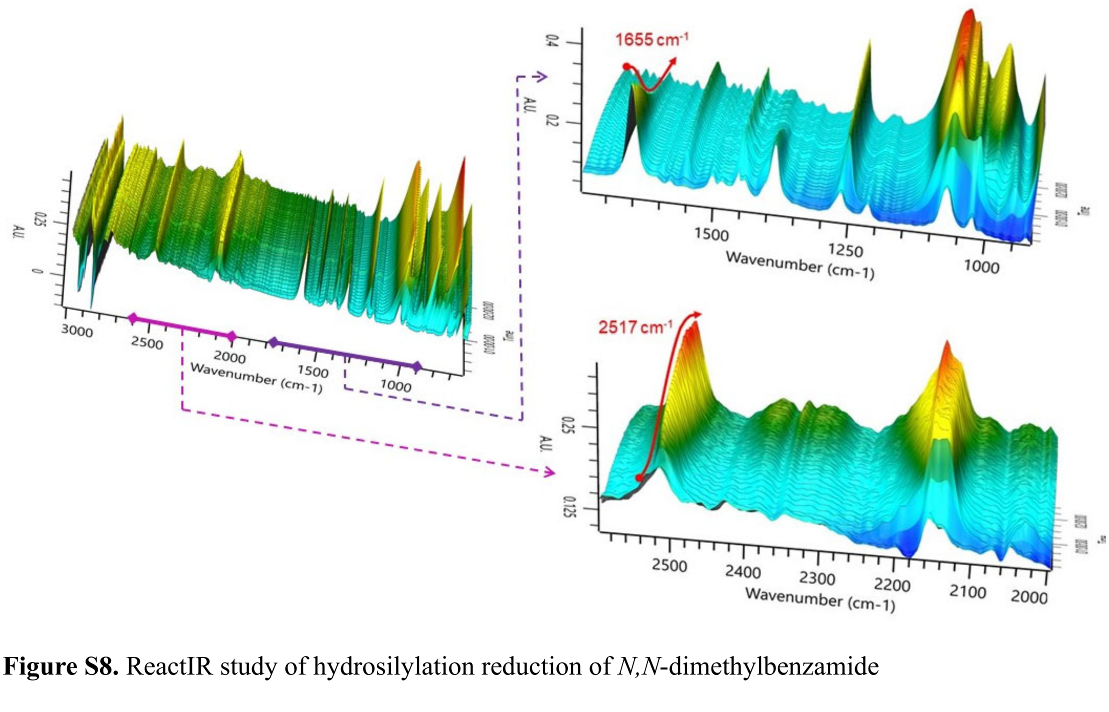
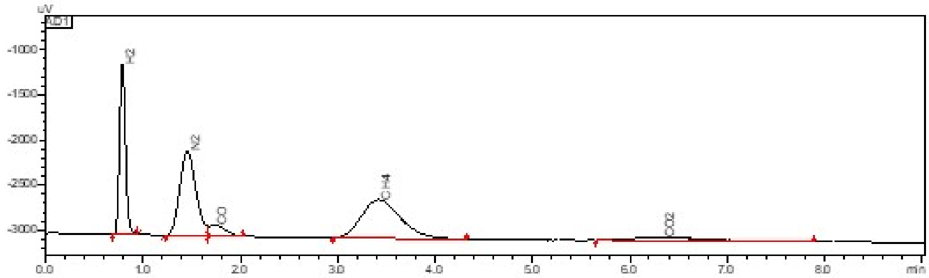


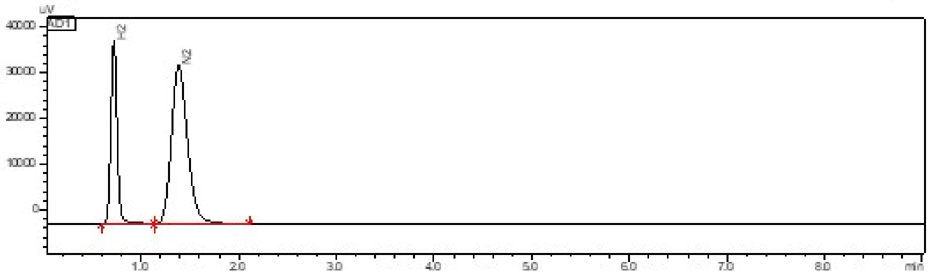
Figure S8. ReactIR study of hydrosilylation reduction of *N,N*-dimethylbenzamide

6.3 GC-MS Analysis

In the actual research process, in order to characterize the actual workable reductant, we mainly based on the results of GC-MS analysis. Firstly, we studied the light components in headspace gas, by comparison with the standard mixed gas, hydrogen and nitrogen can be detected. The nitrogen inevitably exists as inert protective gas, while the hydrogen maybe generated from the activation process of silane. However, the amount of hydrogen is very lower than amides (< 0.01 mmol), thus hydrogen are not the effective reductant.



Mixed Standard Gas — 0.1 mL					
Entry	Name	R. Time	Area	Height	Conc.%
1	H_2	0.787	8083	1879	0.100
2	N_2	1.456	10986	935	0.100
3	CO	1.741	1336	115	0.100
4	CH_4	3.421	11880	427	0.100
5	CO_2	6.328	1634	30	0.100



Reaction Top Gas — 1.0 mL					
Entry	Name	R. Time	Area	Height	Conc.%
1	H_2	0.722	184740	40073	2.286
2	N_2	1.383	402005	34687	3.659
3	CO	1.741	0	0	0.000
4	CH_4	3.421	0	0	0.000
5	CO_2	6.328	0	0	0.000

Figure S9. GC-MS analysis of hydrosilylation reduction of *N,N*-dimethylbenzamide (light components in headspace gas)

Then we analyzed the heavy components in headspace gas, two substances were detected. One is the cyclohexane, which is the solvent, and the another is the Me_2SiH_2, which is the actual workable reductant. Although dimethylsilane usually exists in gaseous form, it has sufficient solubility in organic solvents to participate in the reduction reaction, which is consist with NMR data. And because of this property, it can also maintain a relatively stable and low concentration in the system, so as to effectively realize the chemoselectivity control of reduction reaction.

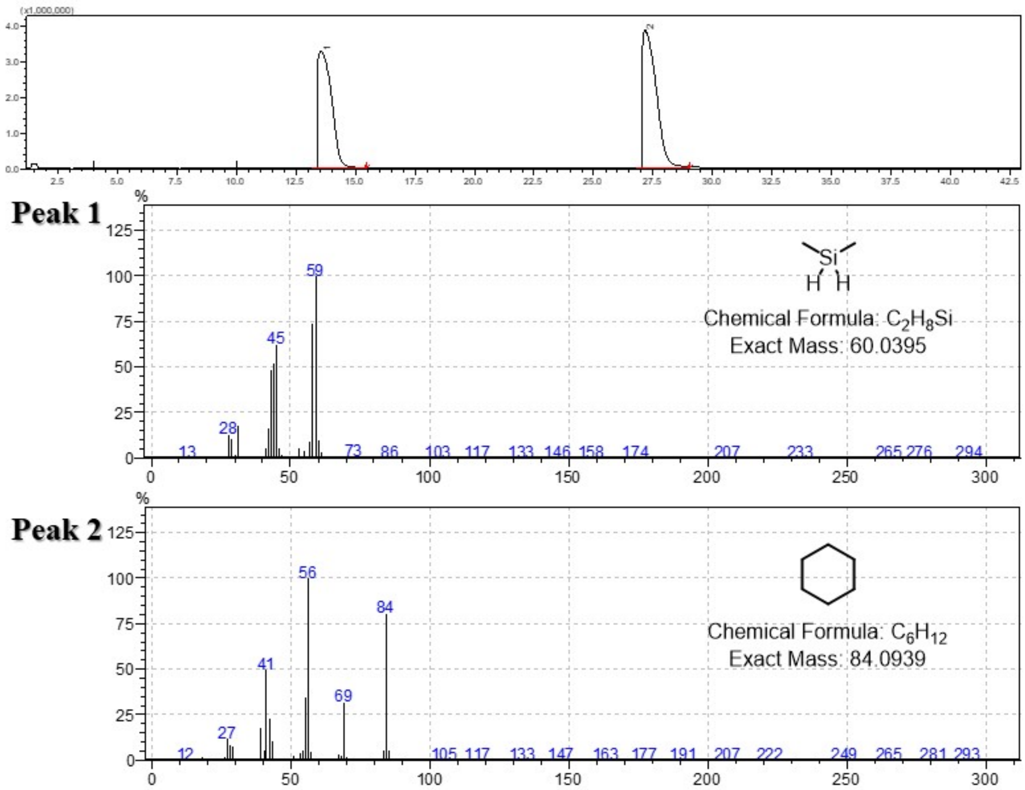


Figure S10. GC-MS analysis of hydrosilylation reduction of *N,N*-dimethylbenzamide (heavy components in headspace gas)

6.4 Control Experiments

Because it is difficult to obtain gaseous dimethylsilane, we carried out comparative experiments with other analogues, showing the special reduction ability of dimethylsilane, including: a) when commercially available diethylsilane was used as reductant, the reduction efficiency will be greatly reduced, indicating that the reducing ability of dimethylsilane is more efficient than diethylsilane; b) when 1,1,2,2-tetramethyldisilane (**6a**), which has quite similar properties to dimethylsilane, was used as reductant, **6a** also exhibited the very similar reduction efficiency to dimethylsilane under standard conditions, indicating that dimethylsilane is indeed the effective reductant for this system. However, the reduction would not occur in absent of KO^{t}Bu, showing that the dimethylsilane must be activated by alkoxide to reduce amides; c) although we believe that hydrogen cannot be used as H-donor in this system, we have conducted validation test. It turns out that hydrogen is completely inactive for this reaction.

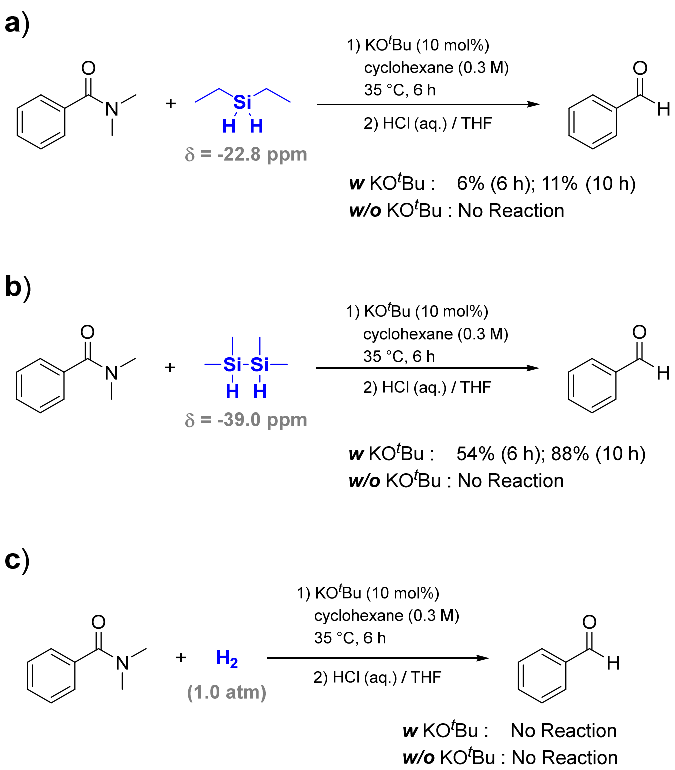


Figure S11. Control experiments

6.5 Kinetic Experiments

To understanding the rate determination step of our reaction, we conduct the kinetic experiments. A 25 mL three-neck round-bottom flask containing a magnetic stir bar, which was dried under vacuum, was charged with **1a** (X mmol) and *t*-BuOK (Z mmol). Dry cyclohexane (10.0 mL) was then added into the tube *via* syringe. An IR detector was fixed at one of three necks and the probe should be placed below the solvent surface. Then the flask was put into oil-bath at 35 ºC. Meanwhile, IR data was allowed to be collected. TMDS (Y mmol) was added dropwise into the flask *via* syringe in 5-10 seconds. The mixture was further stirred at 35 ºC for one hour. Then stop IR data acquisition and remove the detector from the flask. Repeat the above operations for different concentrations of each component. The data was listed in Table S11. It should be noted that we use the average rate of consumption of amide (1650 cm^{-1}) in the first 15 minutes to refer to the initial rate of the reaction.

Through analysis and calculation, the reaction order is first order with respect to [TMDS] and [*t*-BuOK], nearly zero order with respect to [amide], meaning that silane and base are involved in RDS as reactants and amide is not transformed in RDS. Combined above data, we conjecture that the activation of silane to generate the pentavalent silicate is most likely to be the RDS.

Table S11 Summary of Dynamic Data

Entry	Amide (mmol)	TMDS (mmol)	*t*-BuOK (mmol)	k_0 (M/s)
1	1.0	4.0	0.2	-0.5570
2	2.0			-0.4941
3	4.0			-0.5869
4	8.0			-0.5968

5	2.0	2.0	0.2	-0.3945
6		4.0		-0.4941
7		8.0		-0.8012
8		16.0		-1.1448
9	2.0	4.0	0.1	-0.1009
10			0.2	-0.4941
11			0.4	-1.7458
12			0.8	-4.1247

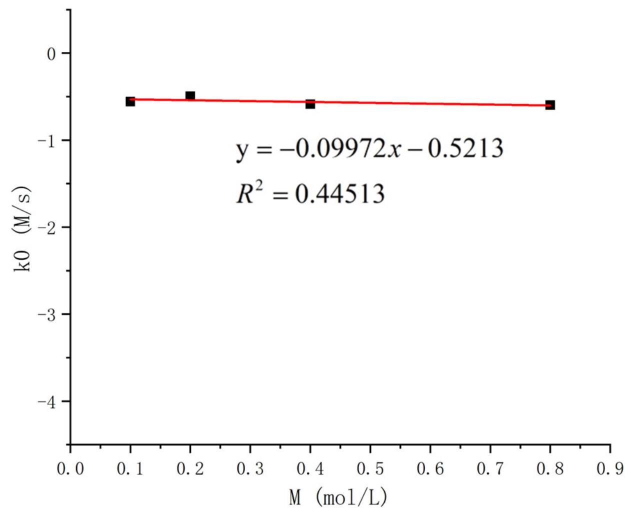


Figure S12. Determination of the Reaction Order in [amide (**1a**)]

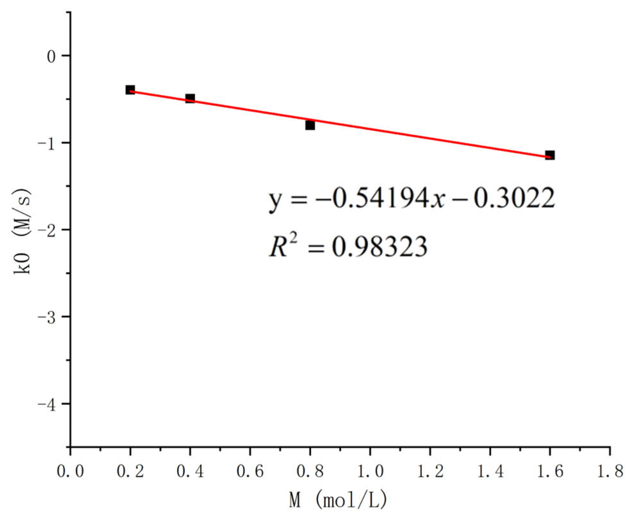


Figure S13. Determination of the Reaction Order in [TMDS]

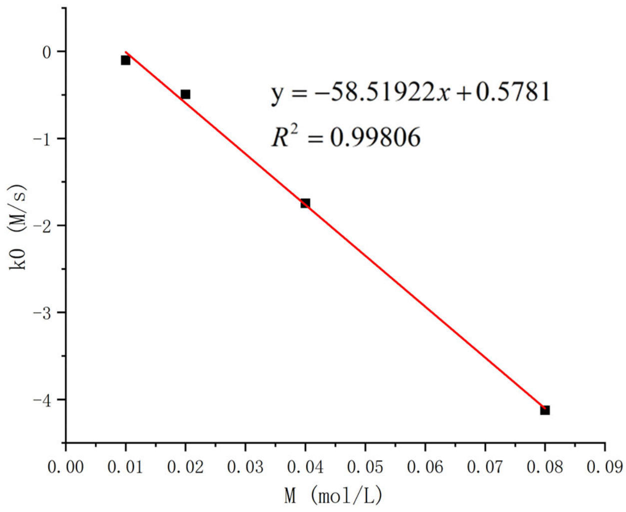
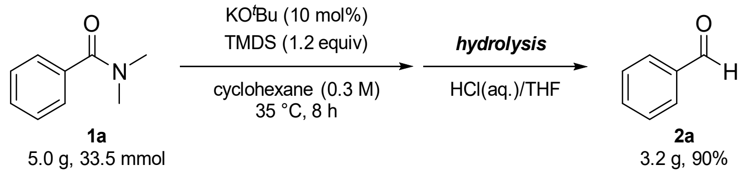


Figure S14. Determination of the Reaction Order in [*t*-BuOK]

7. Synthetic Application Research

7.1 Gram-scale Reaction

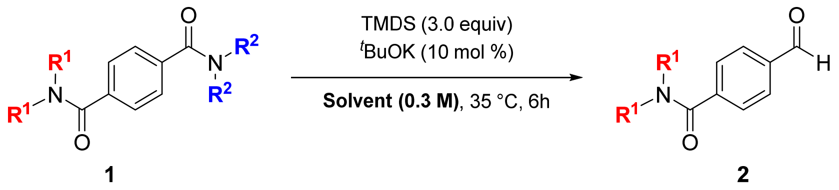


A dry reaction tube containing a magnetic stir bar was charged with amide *N*,*N*-dimethylbenzamide (**1a**, 5.0 g, 33.5 mmol, 1.0 equiv) and ^{t}BuOK (376 mg, 3.35 mmol, 0.1 equiv), cyclohexane (100.0 mL) was then added into the tube *via* syringe. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 ˚C. TMDS (5.4 g, 40.0 mmol, 1.2 equiv) was added dropwise into the tube slowly within 15 min. The mixture was stirred for 8 h, removed from the oil bath, and allowed to cool to the room temperature. HCl (aq.)/THF solution (30.0 mL) was added to quench the reaction for 10 min. The mixture was extracted with EtOAc (20.0 mL × 3), the combined organic phase was washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum carefully, **2a** was obtained from the residue by distillation (177-178 ˚C) in 90% yield as colorless liquid.

7.2 Chemoselective Reduction of Diamides

A dry reaction tube containing a magnetic stir bar was charged with diamide (**1**, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), cyclohexane or THF (3.0 mL) was then added into the tube *via* syringe. TMDS (402 mg, 3.0 mmol, 3.0 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 ˚C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to the room temperature. HCl (aq.)/THF solution (2.0 mL) was added to quench the reaction for 10 min. The mixture was extracted with EtOAc

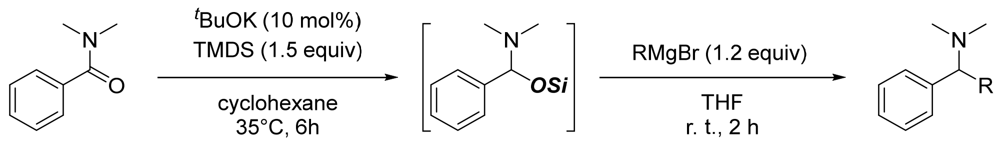
(3.0 mL × 3), the combined organic phase was washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give **2**.



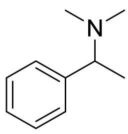
Entry	R^1	R^2	Solvent	Isolate yield of **2** (%)
1	Et	Me	cyclohexane	84
2	Et	Me	THF	76
3	*i*-Pr	Et	THF	81

7.3 Tandem Deoxygenative Functionalization

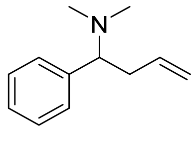
7.3.1 Alkylation



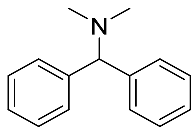
A dry reaction tube containing a magnetic stir bar was charged with *N*,*N*-dimethylbenzamide (**1a**, 149 g, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), cyclohexane (3.0 mL) was then added into the tube *via* syringe. TMDS (201 mg, 1.5 mmol, 1.5 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to room temperature. Then Grignard reagent (1.0 M in THF, 1.2 equiv) was added dropwise into the tube slowly *via* syringe. The mixture was stirred for 2 h at room temperature. Then EtOH (3.0 mL) was added to quench the reaction for 10 min. The mixture was extracted with EtOAc (3.0 mL × 3), the combined organic phase was extracted with *conc.* HCl (5.0 mL × 2). Then the water phase was adjusted to neutral with 15% KOH solution and extracted with DCM (5.0 mL × 3). The combined organic phase washed by brine and dried over Na_2SO_4. The product was afforded after removing the solvent under vacuum.
Specially: If the product was not pure, it can be purified by column chromatography (silica gel).



***N*,*N*-dimethyl-1-phenylethan-1-amine (5a)**[22]: colorless liquid: 125 mg, 84% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA : MeOH = 1 : 1 : 0.01).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 3.24 (q, J = 6.5 Hz, 1H), 2.20 (s, 6H), 1.37 (d, J = 6.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 128.3, 127.7, 127.0, 66.1, 43.4, 20.4.

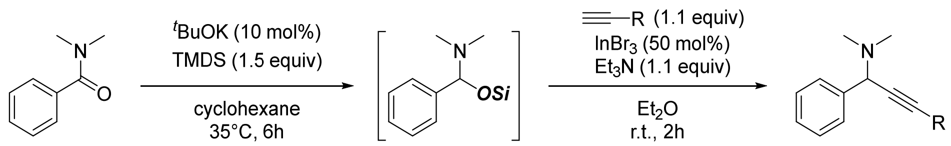


***N,N*-Dimethyl-1-phenylbut-3-en-1-amine (5b)**[23]: colorless liquid: 159 mg, 91% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 5.66 – 5.56 (m, 1H), 5.00 – 4.90 (m, 2H), 3.28 – 3.24 (m, 1H), 2.68 – 2.62 (m, 1H), 2.56 – 2.48 (m, 1H), 2.19 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 135.8, 128.7, 128.1, 127.2, 116.5, 70.7, 42.8, 37.9.

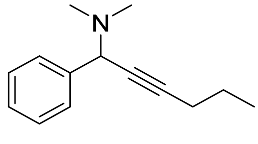


***N,N*-Dimethyl-1,1-diphenylmethanamine (5c)**[24]: white solid: 185 mg, 88% yield, mp 61 – 63 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 4H), 7.27 (m, 4H), 7.17 (t, *J* = 7.0 Hz, 2H), 4.07 (s, 1H), 2.20 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 128.6, 127.9, 127.0, 78.2, 44.9.

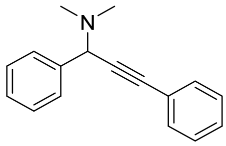
7.3.2 Alkynylation



A dry reaction tube containing a magnetic stir bar was charged with *N*,*N*-dimethylbenzamide (**1a**, 149 mg, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), cyclohexane (3.0 mL) was then added into the tube *via* syringe. TMDS (201 mg, 1.5 mmol, 1.5 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to room temperature. Then the mixture was transferred into another reaction tube containing a magnetic stir bar which was charged with alkyne (1.1 equiv), $InBr_3$ (177 mg, 50 mol%, 0.2 equiv), Et_3N (112 mg, 1.1 mmol, 1.1 equiv) and Et_2O (4.0 mL). The mixture was stirred for 2 h at room temperature then was extracted with EtOAc (3.0 mL × 3). The combined organic phase was extracted with *conc.* HCl (5.0 mL × 2). Then the water phase was adjusted to neutral with 15% KOH solution and extracted with DCM (5.0 mL × 3). The combined organic phase washed by brine and dried over Na_2SO_4. The product was afforded after removing the solvent under vacuum.
Specially: If the product was not pure, it can be purified by column chromatography (silica gel).

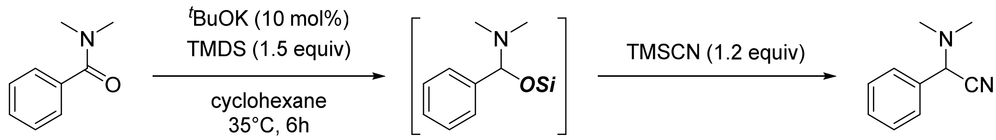


***N,N*-Dimethyl-1-phenylhex-2-yn-1-amine (6a)**: yellow liquid: 148 mg, 74% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 4.57 (s, 1H), 2.33 – 2.30 (m, 2H), 2.23 (s, 6H), 1.65 – 1.60 (m, 2H), 1.07 – 1.04 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4, 128.6, 128.2, 127.5, 88.5, 75.1, 61.9, 41.6, 22.7, 20.9, 13.7.
IR (KBr) *ν*(cm^{-1}): 3476, 2929, 1632, 1394, 1265, 1216, 1085, 735, 636.
HRMS – ESI (m/z): $[M + H]^+$ called for $C_{14}H_{20}N$, 202.1596, found 202.1598.

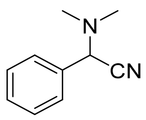


***N,N*-Dimethyl-1,3-diphenylprop-2-yn-1-amine (6b)[25]**: yellow liquid: 227 mg, 97% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.54 (m, 2H), 7.41 – 7.31 (m, 6H), 4.86 (s, 1H), 2.35 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 131.9, 128.6, 128.4, 128.32, 128.28, 128.0, 123.3, 88.5, 84.9, 62.3, 41.7.

7.3.3 Cyanation

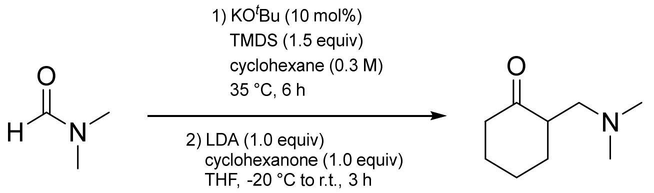


A dry reaction tube containing a magnetic stir bar was charged with *N*,*N*-dimethylbenzamide (**1a**, 149 mg, 1.0 mmol, 1.0 equiv) and ^{t}BuOK (11.2 mg, 0.1 mmol, 0.1 equiv), cyclohexane (3.0 mL) was then added into the tube *via* syringe. TMDS (201 mg, 1.5 mmol, 1.5 equiv) was added dropwise into the tube slowly. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h. Then TMSCN (119 mg, 1.2 mmol, 1.2 equiv) was added into the tube *via* syringe, and the mixture continued being stirred for another 2 h. Until the reaction completed, the mixture was removed from oil bath and cooled to room temperature. Then the solvent was evaporated and the desired product was obtained by column chromatography (silica gel).



2-(Dimethylamino)-2-phenylacetonitrile (7a)[26]: colorless oil: 125 mg, 78% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 10 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.50 (m, 2H), 7.43 – 7.35 (m, 3H), 4.85 (s, 1H), 2.33 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6, 128.8, 128.7, 127.7, 115.0, 63.0, 41.7.

7.4 Preparation of Pharmaceutical Intermediates

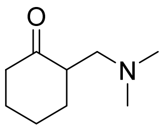


1.46 g, 20.0 mmol **5d**, 81%

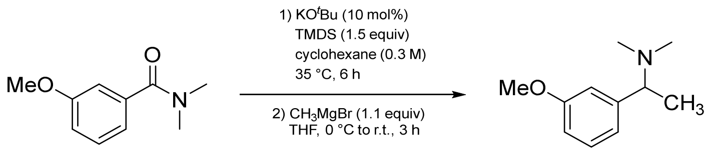
Reaction bottle A: a dry round-bottom flask containing a magnetic stir bar was charged with DMF (20.0 mmol, 1.0 equiv, 1.46 g), and ^{t}BuOK (2.0 mmol, 0.1 equiv), cyclohexane (60.0 mL) was then added into the tube *via* syringe. TMDS (30.0 mmol, 1.5 equiv) was added dropwise into the tube slowly within 15 min. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to room temperature.

Reaction bottle B: a dry round-bottom flask containing a magnetic stir bar was charged with cyclohexanone (20.0 mmol, 1.0 equiv), and THF (30.0 mL), then cooled to -20 °C. LDA (20.0 mmol, 1.0 equiv, 1.0 M in THF) was then added into the flask *via* funnel. Until the addition of LDA was completed, the reaction maintained at -20 °C, then slowly raise to room temperature for 1 h.

When both reactions have been ready, the mixture in **bottle A** was carefully transferred into funnel *via* syringe and funnel, and then slowly added into **bottle B** at 0 °C. Until the addition finished, the reaction continued at room temperature for 3 h. Then the saturated NH_4Cl (aq., 10.0 mL) was added to quench the reaction, and the saturated Na_2CO_3 (aq., 20 mL) was added to ensure the pH > 7.0. Then the mixture was transferred into separating funnel and extracted with EtOAc (30.0 mL × 3). The combined organic phase washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum carefully, the **5d** was obtained from the residue by distillation as colorless oil.

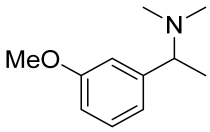


2-((Dimethylamino)methyl)cyclohexan-1-one (5d)[27]: colorless oil: 2.51 g, 81% yield.
Purification: Distillation (87 – 89 °C, 10 mmHg).
^{1}H NMR (400 MHz, CDCl$_3$): δ 2.69 – 2.64 (m, 1H), 2.51 – 2.43 (m, 1H), 2.41 – 2.36 (m, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.16 (m, 8H), 2.05 – 1.95 (m, 1H), 1.87 – 1.81 (m, 1H), 1.74 – 1.59 (m, 2H), 1.43 – 1.33 (m, 1H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 212.8, 59.1, 49.1, 45.9, 42.1, 32.6, 28.1, 24.7.



1.78 g, 10.0 mmol **5e**, 90%

A dry round-bottom flask containing a magnetic stir bar was charged with **1g** (10.0 mmol, 1.0 equiv, 1.78 g), and ^{t}BuOK (1.0 mmol, 0.1 equiv), cyclohexane (30.0 mL) was then added into the tube *via* syringe. TMDS (15.0 mmol, 1.5 equiv) was added dropwise into the tube slowly within 15 min. Then the tube was sealed with a rubber stopper and inserted into an oil bath preheated to 35 °C. The mixture was stirred for 6 h, removed from the oil bath, and allowed to cool to 0 °C in an ice bath. Then Grignard reagent (1.0 M in THF, 1.1 equiv) was added dropwise into the tube slowly *via* syringe. The mixture was stirred for 2 h and gradually returned to room temperature. Then EtOH (5.0 mL) was added to quench the reaction for 10 min. Then the mixture was transferred into separating funnel and extracted with EtOAc (10.0 mL × 3). The combined organic phase washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum carefully, the **5e** was obtained from the residue by distillation as pale-yellow oil.

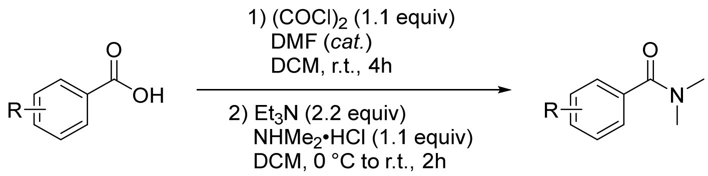


1-(3-Methoxyphenyl)-*N,N*-dimethylethan-1-amine (5e)[28]: pale yellow oil: 1.61 g, 90% yield.
Purification: Distillation (101 – 103 °C, 10 mmHg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 1H), 6.87 – 6.86 (m, 2H), 6.80 – 6.77 (m, 1H), 3.81 (s, 3H), 3.21 (q, *J* = 6.8 Hz, 1H), 2.19 (s, 6H), 1.36 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 145.9, 129.3, 120.2, 113.2, 112.4, 66.2, 55.3, 43.4, 20.5.

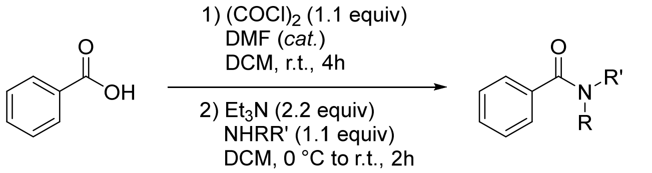
8. Synthesis and Characterization of Reactants

8.1 General Synthesis Procedure for Amides

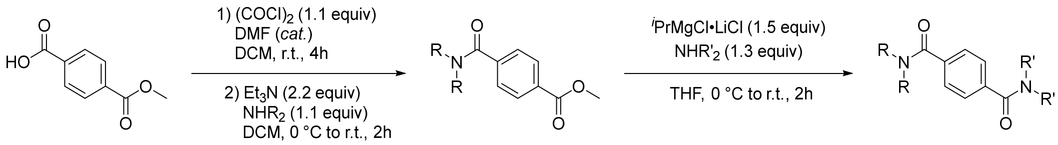
1h, **1pp**, **1qq**, **1tt**, **1uu**, **1xx** and almost silanes are commercially available compounds. Methods for the preparation of the remaining amides and 1,1,2,2-tetramethyldisilane (**6a**) are described below. Their characterization data are also listed.



Method A: A dry flask containing a magnetic stir bar was charged with carboxylic acid (10.0 mmol, 1.0 equiv), DMF (0.1 mL) and DCM (40 mL). $(COCl)_2$ (1.5 g, 12.0 mmol, 1.2 equiv) was added dropwise into the flask slowly at room temperature. The mixture was stirred for 4 h after no more bubbles were generated. The solvent and excess oxalyl chloride were removed under reduced pressure to give the acid chloride product. The amine hydrochloride (15.0 mmol, 1.5 equiv) and DCM (40 mL) were added to the flask containing the acid chloride and a magnetic stir bar. Et_3N (25.0 mmol, 2.5 equiv) in DCM (15 mL) solution was added dropwise into the flask *via* funnel at 0 °C. The mixture was stirred for 2 h and gradually returned to room temperature. The mixture was washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give the product.

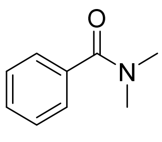


Method B: A dry flask containing a magnetic stir bar was charged with carboxylic acid (10.0 mmol, 1.0 equiv), DMF (0.1 mL) and DCM (40 mL). $(COCl)_2$ (1.5 g, 12.0 mmol, 1.2 equiv) was added dropwise into the flask slowly at room temperature. The mixture was stirred for 4 h after no more bubbles were generated. The solvent and excess oxalyl chloride were removed under reduced pressure to give the acid chloride product. The DCM (40 mL) was added to the flask containing the acid chloride and a magnetic stir bar. Et_3N (25.0 mmol, 2.5 equiv) and amine (15.0 mmol, 1.5 equiv) in DCM (15 mL) solution was added dropwise into the flask *via* funnel at 0 °C. The mixture was stirred for 2 h and gradually returned to room temperature. The mixture was washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give the product.

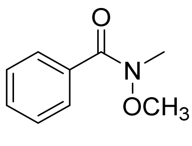


Method C: The methyl ester amides were prepared by **method A**. A dry flask containing a magnetic stir bar was charged with ^{i}PrMgCl•LiCl (1.0 M in THF, 7.5 mmol, 1.5 equiv). Amine (6.5 mmol, 1.3 equiv) was added dropwise into the flask slowly at 0 °C. The mixture was stirred for 1h. Methyl ester amide (5.0 mmol, 1.0 equiv) was dissolved in anhydrous THF and slowly added to the flask. The mixture was stirred for 2 h at 0 °C. Then EtOH (3.0 mL) and H_2O (5.0 mL) was added to quench the reaction for 10 min. The mixture was filtered to remove solids or insolubles. The liquid was extracted with DCM (5.0 mL × 3). The combined organic phase washed by brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel) to give the product.

8.2 Characterization of amides

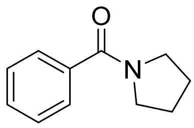


***N*,*N*-Dimethylbenzamide (1a)**[1]: prepared by method A, white solid: 1.13 g, 75% yield, mp 43 – 45 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.35 (m, 5H), 3.08 (s, 3H), 2.94 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 136.4, 129.5, 128.4, 127.1, 39.6, 35.3.

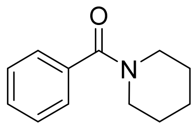


***N*-Methoxy-*N*-methylbenzamide (1ff)**[1]: prepared by method B, light yellow liquid: 1.29 g, 78% yield.

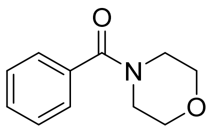
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.61 – 7.60 (m, 2H), 7.40 – 7.31 (m, 3H), 3.48 (s, 3H), 3.28 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 169.8, 134.1, 130.4, 128.0, 127.92, 127.89, 60.9, 33.6.



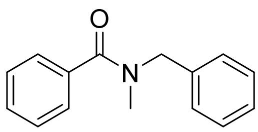
Phenyl(pyrrolidin-1-yl)methanone (1gg)[29]: prepared by method B, colorless oil: 1.51 g, 86% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 1 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54 – 7.48 (m, 2H), 7.42 – 7.36 (m, 3H), 3.63 – 3.48 (br, 4H), 1.91 (s, 4H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 169.8, 137.4, 129.8, 128.3, 127.2, 49.7, 46.3, 26.5, 24.6.



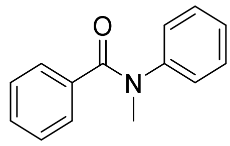
Phenyl(piperidin-1-yl)methanone (1hh)[30]: prepared by method B, light yellow liquid: 1.47 g, 78% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36 – 7.35 (m, 5H), 3.68 (s, 2H), 3.30 (s, 2H), 1.63 (s, 4H), 1.47 (s, 2H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 170.2, 136.4, 129.2, 128.3, 126.7, 48.6, 43.0, 26.4, 25.5, 24.5.



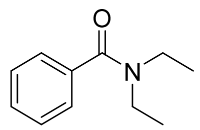
Morpholino(phenyl)methanone (1ii)[29]: prepared by method B, colorless oil: 1.49 g, 79% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 – 7.38 (m, 5H), 3.83 – 3.42 (m, 8H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 170.6, 135.5, 130.0, 128.7, 127.2, 67.0, 48.0, 42.8.



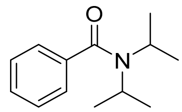
***N*-Benzyl-*N*-methylbenzamide (1jj)[29]**: prepared by method B, colorless oil: 1.73 g, 77% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.47 – 7.31 (m, 9H), 7.18 (s, 1H), 4.77 – 4.51 (br, 2H), 3.03 – 2.87 (br, 2H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 172.3, 171.7, 137.2, 136.7, 136.4, 129.7, 128.9, 128.6, 128.3, 127.7, 127.1, 126.9, 55.3, 50.9, 37.6, 32.3.



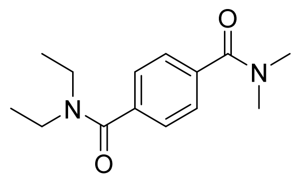
***N*-Methyl-*N*-phenylbenzamide (1kk)**[31]: prepared by method B, pale orange oil: 1.69 g, 80% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 7.17 – 7.13 (m, 3H), 7.05 – 7.02 (m, 2H), 3.50 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 145.0, 136.0, 129.7, 129.2, 128.8, 127.8, 127.0, 126.6, 39.5.



***N*,*N*-Diethylbenzamide (1ll)**[1]: prepared by method B, light yellow liquid: 1.45 g, 82% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 5H), 3.50 (s, 2H), 3.22 (s, 2H), 1.21 (s, 3H), 1.07 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 137.3, 129.1, 128.4, 126.3, 43.3, 39.2, 14.2, 12.9.

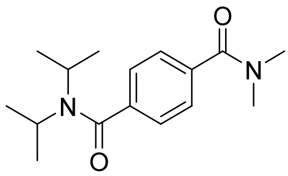


***N*,*N*-Diisopropylbenzamide (1mm)**[1]: prepared by method B, white solid: 1.38 g, 67% yield, mp 61 – 63 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA = 2 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.35 (m, 3H), 7.31 – 7.29 (m, 2H), 3.82 (s, 1H), 3.53 (s, 1H), 1.52 (s, 6H), 1.16 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 139.1, 128.7, 128.6, 125.7, 50.9, 45.9, 20.9.



***N^1*,*N^1*-Diethyl-*N^4*,*N^4*-dimethylterephthalamide (1nn)**: prepared by method C, white solid: 0.98 g, 79% yield, mp 121 – 123 ˚C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.53 (s, 2H), 3.21 (s, 2H), 3.10 (s, 3H), 2.95 (s, 3H), 1.24 (s, 3H), 1.07 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 170.7, 138.5, 137.2, 127.3, 126.5, 43.3, 39.6, 39.4, 35.5, 14.3, 13.0.
IR (KBr) *ν*(cm^{-1}): 3428, 2986, 2935, 1618, 1517, 1430, 1393, 1095, 881, 737, 591.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{14}H_{21}N_2O_2$, 249.1603, found 249.1604.



***N*[1],*N*[1]-Diisopropyl-*N*[4],*N*[4]-dimethylterephthalamide (1oo)**: prepared by method C, white solid: 0.92 g, 67% yield, mp 152 – 154 °C.

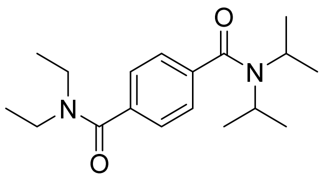
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 1H), 3.51 (br, 1H), 3.11 (s, 3H), 2.96 (s, 3H), 1.53 (s, 6H), 1.12 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 170.4, 140.1, 136.8, 127.3, 125.8, 51.1, 46.1, 39.7, 35.5, 20.8.

IR (KBr) *ν*(cm^{-1}): 3444, 3974, 2931, 1627, 1513, 1442, 1395, 1341, 1079, 855, 754.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{16}H_{24}N_2O_2Na$, 299.1735, found 299.1734.



***N*[1],*N*[1]-Diethyl-*N*[4],*N*[4]-diisopropylterephthalamide (1pp)**: prepared by method C, white solid: 0.78 g, 51% yield, mp 171 – 173 °C.

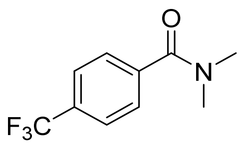
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.36 (m, 2H), 7.33 – 7.31 (m, 2H), 3.81 (br, 1H), 3.56 – 3.48 (m, 3H), 3.23 – 3.21 (m, 2H), 1.53 (s, 6H), 1.25 – 1.06 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 170.5, 139.7, 137.7, 126.6, 125.9, 51.0, 46.1, 43.4, 39.4, 20.8, 14.3, 13.0.

IR (KBr) *ν*(cm^{-1}): 3428, 2969, 3931, 1624, 1510, 1443, 1424, 1344, 1099, 1037, 858, 830, 594.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{18}H_{29}N_2O_2$, 305.2229, found 305.2228.



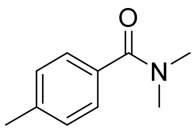
***N*,*N*-Dimethyl-4-(trifluoromethyl)benzamide (1b)[2]**: prepared by method A, white solid: 1.63 g, 75% yield, mp 89 – 91 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 3.12 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 140.0, 131.6 (q, $^2J_{C-F}$ = 32.5 Hz), 127.5, 125.6 (q, $^3J_{C-F}$ = 3.6 Hz), 123.9 (q, $^3J_{C-F}$ = 270.5 Hz), 39.5, 35.4.

^{19}F NMR (470 MHz, $CDCl_3$): δ -62.9.

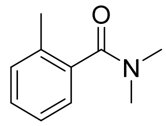


***N,N*,4-Trimethylbenzamide (1c)**[1]: prepared by method A, white solid: 1.37 g, 84% yield, mp 42 – 44 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 3.08 (s, 3H), 2.98 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 139.7, 133.5, 129.0, 127.3, 39.7, 35.5, 21.5.

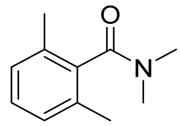


***N,N*,2-Trimethylbenzamide (1d)**[2]: prepared by method A, colorless liquid: 1.27 g, 78% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.17 (m, 4H), 3.15 (s, 3H), 2.85 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 136.8, 134.1, 130.4, 128.9, 126.0, 125.9, 38.5, 34.7, 19.0.

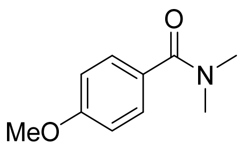


***N,N*,2,6-Tetramethylbenzamide (1e)**[32]: prepared by method A, beige solid: 1.16 g, 65% yield, mp 55 – 57 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 2H), 3.14 (s, 3H), 2.78 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 136.8, 133.6, 128.3, 127.5, 37.5, 34.2, 19.0.

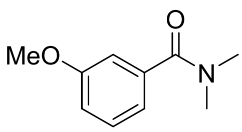


4-Methoxy-*N,N*-dimethylbenzamide (1f)[1]: prepared by method A, colorless liquid: 1.53 g, 85% yield.

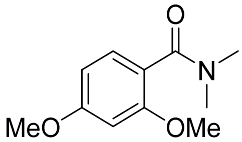
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.38 (m, 2H), 6.91 – 6.88 (m, 2H), 3.82 (s, 3H), 3.04 (s, 6H).

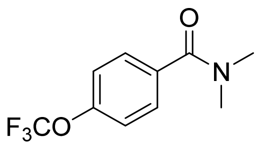
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6, 160.7, 129.2, 128.5, 113.7, 55.4, 39.9, 35.7.



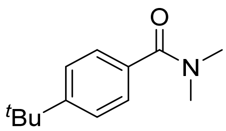
3-Methoxy-*N,N*-dimethylbenzamide (1g)[33]: prepared by method A, colorless oil: 1.56 g, 87% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.6 Hz, 1H), 6.97 – 6.93 (m, 3H), 3.81 (s, 3H), 3.10 (s, 3H), 2.97 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 159.5, 137.7, 129.5, 119.1, 115.4, 112.4, 55.3, 39.5, 35.3.



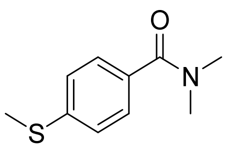
3-Methoxy-*N,N*-dimethylbenzamide (1h)[34]: prepared by method A, pale yellow oil: 1.88 g, 90% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.5 Hz, 1H), 6.46 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 3.772 (s, 3H), 3.765 (s, 3H), 3.05 (s, 3H), 2.81 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 161.6, 156.7, 129.0, 119.1, 104.8, 98.5, 55.6, 55.5, 38.4, 34.9.



***N,N*-Dimethyl-4-(trifluoromethoxy)benzamide (1i)**[2]: prepared by method A, white solid: 1.72 g, 74% yield, mp 58 – 60 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.10 (s, 3H), 2.97 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 150.0 (q, $^{3}J_{C\text{-}F}$ = 1.8 Hz), 135.0, 129.0, 120.9, 120.5 (q, $^{1}J_{C\text{-}F}$ = 256.3 Hz), 39.7, 35.5.
^{19}F NMR (470 MHz, $CDCl_3$): δ -57.8.



4-(*tert*-Butyl)-*N,N*-dimethylbenzamide (1j)[2]: prepared by method A, white solid: 1.60 g, 78% yield, mp 85 – 87 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.09 (s, 3H), 3.00 (s, 3H), 1.31 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 152.8, 133.5, 127.1, 125.3, 39.8, 35.5, 34.9, 31.3.

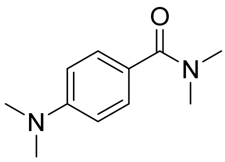


N,N-Dimethyl-4-(methylthio)benzamide (1k)[35]: prepared by method A, light yellow oil: 1.48 g, 76% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.05 (s, 3H), 2.97 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 140.8, 132.6, 127.8, 125.7, 39.7, 35.5, 15.4.

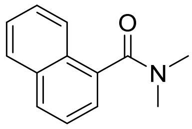


4-(Nimethylamino)-N,N-dimethylbenzamide (1l)[2]: prepared by method A, yellow solid: 1.69 g, 88% yield, mp 89 – 91 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 6H), 2.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 1172.2, 151.4, 129.3, 123.2, 111.1, 40.3 (4C).

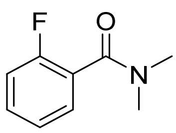


N,N-Dimethyl-1-naphthamideimethylbenzamide (1m)[35]: prepared by method A, yellow liquid: 1.44 g, 72% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.82 (m, 2H), 7.78 – 7.76 (m, 1H), 7.51 – 7.43 (m, 3H), 7.40 – 7.38 (m, 1H), 3.21 (s, 3H), 2.75 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 134.7, 133.4, 129.4, 128.9, 128.4, 126.9, 126.3, 125.1, 124.8, 123.8, 38.8, 34.8.



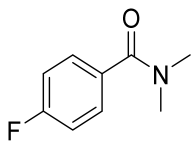
2-Fluoro-N,N-dimethylbenzamide (1n)[36]: prepared by method A, colorless liquid: 1.14 g, 68% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

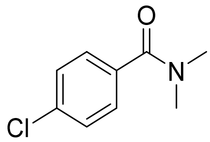
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 9.0 Hz, 1H), 3.05 (s, 3H), 2.85 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 158.1 (d, $^{1}J_{C-F}$ = 246.0 Hz), 131.1 (d, $^{3}J_{C-F}$ = 7.9 Hz), 128.9 (d, $^{2}J_{C-F}$ = 3.7 Hz), 124.7, 124.5 (d, $^{3}J_{C-F}$ = 3.5 Hz), 115.6 (d, $^{2}J_{C-F}$ = 21.4 Hz), 38.2 (d, J_{C-F} = 2.7 Hz), 34.9.

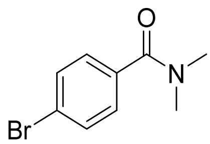
^{19}F NMR (470 MHz, $CDCl_3$): δ -115.3.



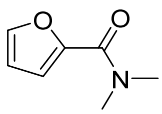
4-Fluoro-*N*,*N*-dimethylbenzamide (1o)[2]: prepared by method A, light yellow liquid: 1.20 g, 72% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.43 – 7.40 (m, 2H), 7.09 – 7.05 (m, 2H), 3.09 (s, 3H), 2.98 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 170.8, 163.4 (d, $^{1}J_{C\text{-}F}$ = 248.0 Hz), 132.4 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 129.4 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 115.5 (d, $^{3}J_{C\text{-}F}$ = 21.6 Hz), 39.8, 35.6.
^{19}F NMR (470 MHz, CDCl$_3$): δ -110.8.



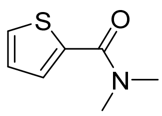
4-Chloro-*N*,*N*-dimethylbenzamide (1p)[1]: prepared by method A, colorless liquid: 1.38 g, 75% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.33 (s, 4H), 3.06 (s, 3H), 2.93 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 170.5, 135.6, 134.7, 128.65, 128.63, 39.6, 35.4.



4-Bromo-*N*,*N*-dimethylbenzamide (1q)[37]: prepared by method A, white solid: 1.86 g, 82% yield, mp 52 – 54 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55 – 7.53 (m, 2H), 7.31 – 7.29 (m, 2H), 3.10 (s, 3H), 2.97 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 170.5, 135.1, 131.6, 128.8, 123.8, 39.5, 35.4.

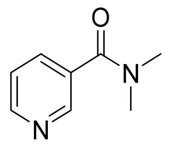


***N*,*N*-Dimethylfuran-2-carboxamide (1r)**[35]: prepared by method A, brown solid: 0.99 g, 71% yield, mp 32 – 34 °C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 4 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.43 – 7.42 (m, 1H), 6.91 – 6.90 (m, 1H), 6.40 – 6.39 (m, 1H), 3.20 (s, 3H), 3.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 160.3, 148.1, 143.7, 115.9, 111.1, 38.2, 36.3.

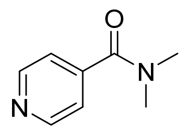


***N*,*N*-Dimethylthiophene-2-carboxamide (1s)**[35]: prepared by method A, yellow liquid: 1.21 g, 78%

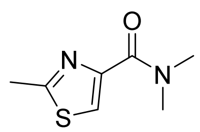
yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 4 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.41 – 7.40 (m, 1H), 7.32 – 7.31 (m, 1H), 7.01 – 6.99 (m, 1H), 3.14 (s, 6H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 164.4, 137.9, 129.2, 128.8, 126.7, 39.5, 36.6.



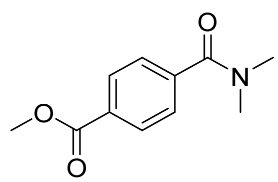
***N,N*-Dimethylnicotinamide (1t)[38]**: prepared by method A, white solid: 1.23 g, 82% yield, mp 45 – 47 ˚C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 4 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.63 – 8.62 (m, 1H), 8.60 – 8.59 (m, 1H), 7.72 – 7.70 (m, 1H), 7.31 – 7.29 (m, 1H), 3.07 (s, 3H), 2.96 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 169.0, 150.6, 148.0, 134.9, 132.1, 123.4, 39.5, 35.4.



***N,N*-Dimethylisonicotinamide (1u)[38]**: prepared by method A, brown solid: 1.14 g, 76% yield, mp 44 – 46 ˚C.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 4 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.67 – 8.66 (m, 2H), 7.28 – 7.27 (m, 2H), 3.10 (s, 3H), 2.93 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 169.1, 150.3, 144.0, 121.3, 39.3, 35.3.



***N,N*,2-Trimethylthiazole-4-carboxamide (1v)**: prepared by method A, yellow liquid: 1.24 g, 73% yield.
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 5 : 1).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 (s, 1H), 3.21 (s, 3H), 3.07 (s, 3H), 2.70 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 165.1, 164.5, 150.5, 123.0, 39.0, 36.1, 19.2.
IR (KBr) *ν*(cm^{-1}): 3457, 2927, 1631, 1517, 1394, 1253, 1167, 961, 832, 748.
HRMS – ESI (m/z): [M + Na]$^+$ called for $C_7H_{10}N_2OSNa$, 193.0412, found 193.0410.

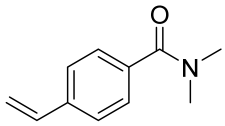


Methyl 4-(dimethylcarbamoyl)benzoate (1w)[35]: prepared by method A, white solid: 1.53 g, 74% yield, mp 96 – 98 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.5 Hz, 2H,), 7.47 (d, *J* = 8.5 Hz, 2H,), 3.92 (s, 3H), 3.12 (s, 3H), 2.94 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 166.5, 140.8, 131.1, 129.8, 127.1, 52.4, 39.5, 35.4.

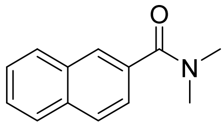


***N,N*-Dimethyl-4-vinylbenzamide (1x)[39]**: prepared by method A, yellow solid: 1.21 g, 69% yield, mp 51 – 53 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.73 – 6.67 (m, 1H), 5.78 (d, *J* = 18.0 Hz, 1H), 5.29 (d, *J* = 11.0 Hz, 1H,), 3.08 (s, 3H), 2.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 138.7, 136.1, 135.5, 127.5, 126.1, 115.1, 39.6, 35.4.

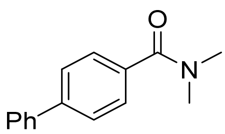


***N,N*-Dimethyl-2-naphthamideimethylbenzamide (1y)[40]**: prepared by method A, white solid: 1.56 g, 78% yield, mp 84 – 86 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.88 – 7.84 (m, 3H), 7.53 – 7.50 (m, 3H), 3.16 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 133.8, 133.7, 132.8, 128.5, 128.3, 127.9, 127.1, 127.0, 126.7, 124.5, 39.8, 35.6.

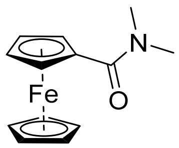


***N,N*-Dimethyl-[1,1'-biphenyl]-4-carboxamide (1z)[40]**: prepared by method A, white solid: 1.78 g, 79% yield, mp 104 – 106 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.59 (m, 4H), 7.51 – 7.49 (m, 2H), 7.46 – 7.43 (m, 2H), 7.38 – 7.35 (m, 1H), 3.13 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 142.5, 140.4, 135.2, 128.9, 127.79, 127.73, 127.2, 127.1, 39.7, 35.5.



***N,N*-Dimethyl-ferrocenecarboxamide (1aa)[40]**: prepared by method A, orange solid: 2.10 g, 82% yield, mp 110 – 112 °C.

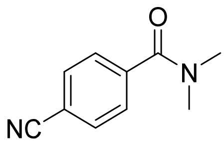
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.62 (s, 2H), 4.30 (s, 2H), 4.22 (s, 5H), 3.12 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 78.6, 70.7, 69.9, 69.4.

IR (KBr) *v*(cm^{-1}): 3443, 3080, 2941, 1612, 1503, 1391, 1265, 1106, 1035, 819, 762, 682.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{13}H_{16}FeNO$, 258.0581, found 258.0590.

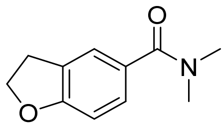


4-Cyano-*N,N*-dimethyl-3-phenylacrylamide (1bb)[35]: prepared by method A, beige solid: 1.39 g, 80% yield, mp 91 – 93 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.65 (m, 2H), 7.47 – 7.45 (m, 2H), 3.05 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 140.7, 132.3, 127.7, 118.1, 113.2, 39.2, 35.2.



***N,N*-Dimethyl-2,3-dihydrobenzofuran-5-carboxamide (1cc)**: prepared by method A, yellow solid: 1.64 g, 86% yield, mp 63 – 65 °C.

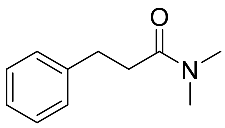
Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (s, 1H), 7.20 – 7.18 (m, 1H), 6.77 – 6.75 (m, 1H), 4.60 (t, J = 9.0 Hz, 2H), 3.22 (t, J = 8.5 Hz, 2H), 3.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 161.4, 128.5, 128.0, 127.3, 124.8, 108.8, 71.7, 39.9, 35.7, 29.5.

IR (KBr) *v*(cm^{-1}): 3463, 2927, 1627, 1591, 1484, 1390, 1240, 982, 758.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{11}H_{14}NO_2$, 192.1025, found 192.1016.

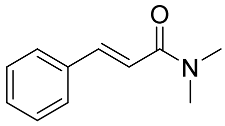


***N,N*-Dimethyl-3-phenylpropanamide (1dd)[41]**: prepared by method A, light yellow liquid: 1.49 g, 84% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 2.99 (t, J = 8.5 Hz, 2H,), 2.96 (s, 3H), 2.94 (s, 3H), 2.63 (t, J = 8.5 Hz, 2H,).

^{13}C NMR (125 MHz, CDCl$_3$): δ 172.3, 141.6, 128.53, 128.49, 126.2, 37.2, 35.5, 35.4, 31.4.

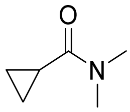


***N,N*-Dimethylcinnamamide (1ee)[33]**: prepared by method A, white solid: 1.50 g, 86% yield, mp 93 – 95 °C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.66 (d, *J* = 15.5 Hz, 1H,), 7.52 – 7.51 (m, 2H), 7.37 – 7.33 (m, 3H), 6.88 (d, *J* = 15.5 Hz, 1H), 3.16 (s, 3H), 3.06 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 166.8, 142.4, 135.5, 129.6, 128.9, 127.9, 117.6, 37.5, 36.0.

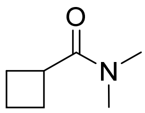


***N,N*-Dimethylcyclopropanecarboxamide (1tt)[42]**: prepared by method A, colorless oil: 1.03 g, 91% yield.

Purification: Distillation (70 – 71 °C, 5.0 mmHg).

^{1}H NMR (500 MHz, CDCl$_3$): δ 3.14 (s, 3H), 2.93 (s, 3H), 1.74 – 1.69 (m, 1H), 0.94 – 0.91 (m, 2H), 0.73 – 0.70 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 173.5, 37.3, 35.9, 11.1, 7.4.

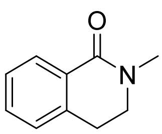


***N,N*-Dimethylcyclobutanecarboxamide (1uu)[43]**: prepared by method A, colorless oil: 1.13 g, 89% yield.

Purification: Distillation (68 – 70 °C, 0.1 mmHg).

^{1}H NMR (400 MHz, CDCl$_3$): δ 3.23 (m, 1H), 2.89 (s, 3H), 2.87 (s, 3H), 2.34 – 2.24 (m, 2H), 2.15 – 2.07 (m, 2H), 1.96 – 1.76 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 174.6, 37.5, 36.6, 35.4, 25.1, 17.9.

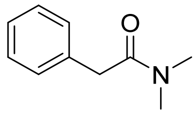


2-Methyl-3,4-dihydroisoquinolin-1(*2H*)-one (1ww)[44]: pale yellow oil: 1.47 g, 91% yield.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 2).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 8.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.56 (m, *J* = 6.5 Hz, 2H), 3.15 (s, 3H), 3.00 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 164.9, 138.1, 131.6, 129.5, 128.2, 127.1, 127.0, 48.2, 35.3, 28.0.

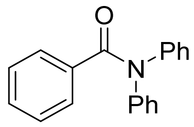


***N,N*-Dimethyl-2-phenylacetamide (1xx)**[45]: prepared by method A, white solid: 1.16 g, 71% yield, mp 105 – 107 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 3 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 2H), 7.29 – 7.24 (m, 3H), 3.74 (s, 2H), 3.01 (s, 3H), 2.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 135.2, 128.8, 128.7, 126.8, 41.1, 37.8, 35.7.

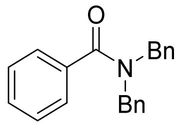


***N,N*-Diphenylbenzamide (1zz)**[46]: prepared by method B, white solid: 2.64 g, 96% yield, mp 176 – 178 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA : DCM = 2 : 1 : 0.05).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.45 (m, 2H), 7.30 – 7.27 (m, 5H), 7.22 – 7.15 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 144.0, 136.2, 130.3, 129.3, 129.2, 128.0, 127.6, 126.5.

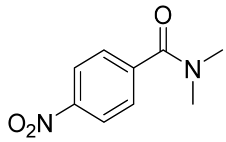


***N,N*-Ddibenzylbenzamide (1aaa)**[46]: prepared by method B, white solid: 2.58 g, 86% yield, mp 109 – 111 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA : DCM = 2 : 1 : 0.05).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2H), 7.40 – 7.35 (m, 11H), 7.16 – 7.14 (m, 2H), 4.71 (s, 2H), 4.41 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 137.1, 136.6, 136.3, 129.8, 129.0, 128.8, 128.7, 128.5, 127.8, 127.7, 127.2, 126.8, 51.7, 47.0.

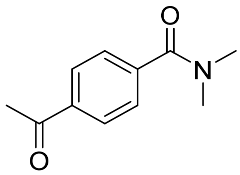


***N,N*-Dimethyl-4-nitrobenzamide (1bbb)**[36]: prepared by method A, white solid: 1.48 g, 76% yield, mp 94 – 96 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 1 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 3.13 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 148.4, 142.6, 128.2, 123.9, 39.4, 35.4.

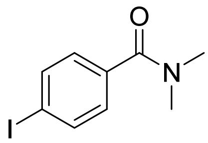


4-Acetyl-*N*,*N*-dimethylbenzamide (1ccc)[47]: prepared by method A, orange solid: 1.42 g, 74% yield, mp 61 – 63 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 3.09 (s, 3H), 2.92 (s, 3H), 2.59 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 170.5, 140.8, 137.7, 128.5, 127.3, 39.4, 35.3, 26.8.

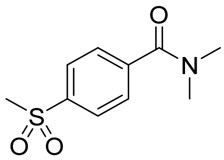


4-Iodo-*N*,*N*-dimethylbenzamide (1ddd)[37]: prepared by method A, white solid: 1.84 g, 67% yield, mp 111 – 113 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.74 (m, 2H), 7.17 – 7.15 (m, 2H), 3.09 (s, 3H), 2.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 137.7, 135.8, 129.0, 95.8, 39.6, 35.5.



***N*,*N*-Dimethyl-4-(methylsulfonyl)benzamide (1eee)**: prepared by method A, white solid: 1.77 g, 78% yield, mp 152 – 154 ˚C.

Purification: flash column chromatography (300-400 mesh silica gel, PE : EA= 2 : 1).

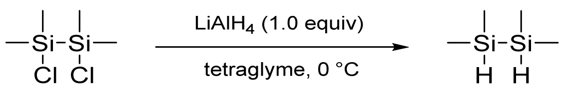
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 6.5 Hz, 2H), 7.59 (d, *J* = 6.5 Hz, 2H), 3.12 (s, 3H), 3.05 (s, 3H), 2.94 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 141.9, 141.5, 128.0, 127.8, 44.5, 39.4, 35.4.

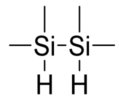
IR (KBr) *ν*(cm^{-1}): 3461, 3004, 2917, 1629, 1510, 1395, 1303, 1285, 1150, 1091, 1078, 966, 782.

HRMS – ESI (m/z): $[M + H]^+$ called for $C_{10}H_{14}NO_3S$, 228.0694, found 228.0682.

8.3 General Synthesis Procedure and Characterization for Silane



$LiAlH_4$ (759 mg, 20.0 mmol, 1.0 equiv) and dry tetraglyme (20.0 mL) were stirred in a dry three-neck round-bottomed flask at 0 ˚C until there are no bubbles. The solution of 1,2-dichloro-1,1,2,2-tetramethyldisilane (3.74 g, 20.0 mmol, 1.0 equiv) in dry tetraglyme (10.0 mL) was added dropwise into the flask within 10 min. The mixture was stirred for 15 min at 0 ˚C and for 2 h at room temperature. Then the product, 1,1,2,2-tetramethyldisilane, was vacuum-transferred into a clean cold trap (-40 ˚C).



1,1,2,2-Tetramethyldisilane[48]: colorless liquid: 2.10 g, 89% yield.

Purification: trapped in cold (-40 ˚C) under vacuum (1.0 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (m, 2H), 0.17 – 0.16 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ -6.3.

^{29}Si NMR (99 MHz, $CDCl_3$): δ -39.0.

9. References

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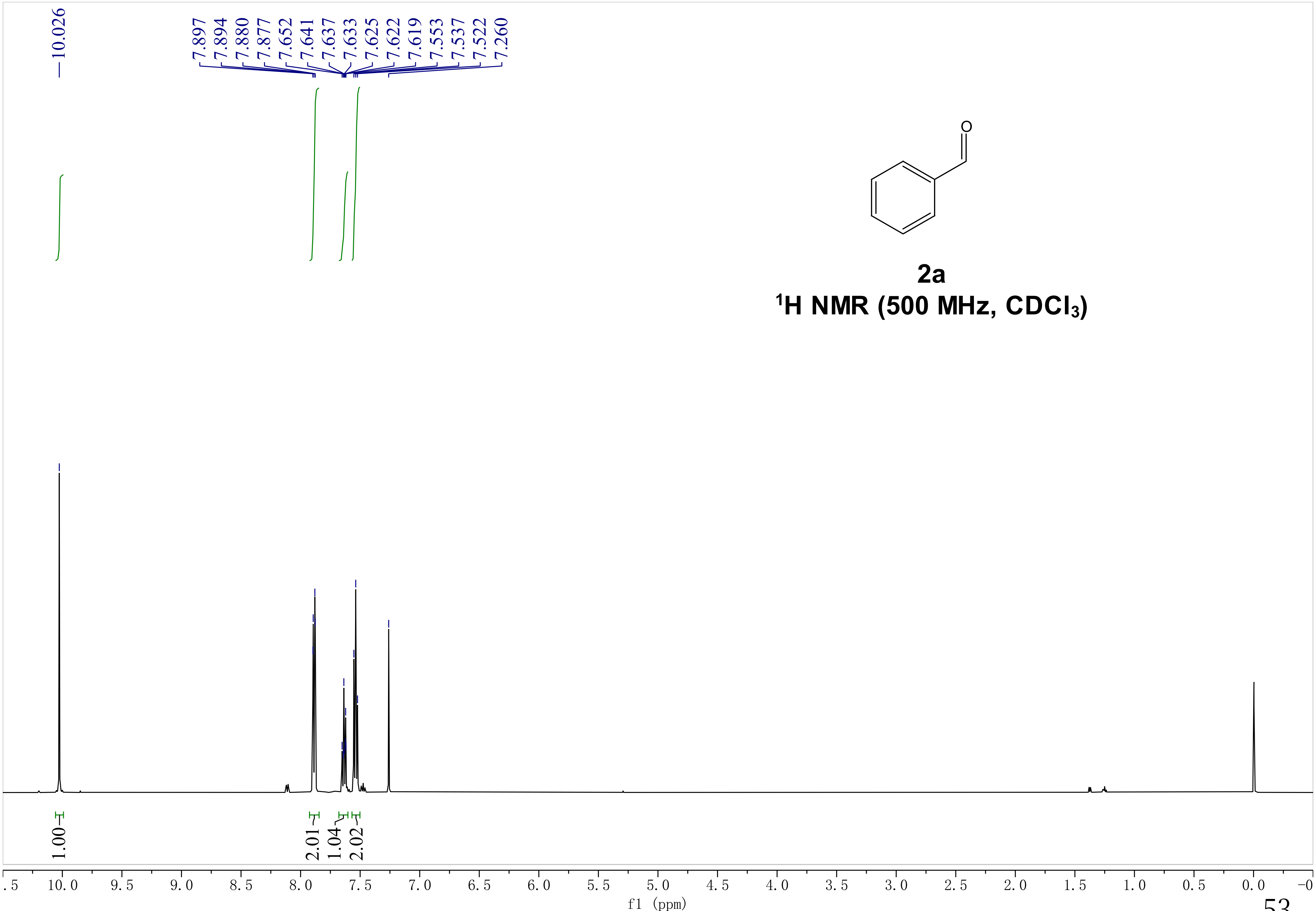
10. NMR Spectra Copies of the Amides, Aldehydes and Amines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7.652
7.641
7.637
7.633
7.625
7.622
7.619
7.553
7.537
7.522
7.260
O
2a
^{1}H NMR (500 MHz, $CDCl_3$)
1.00
2.01
1.04
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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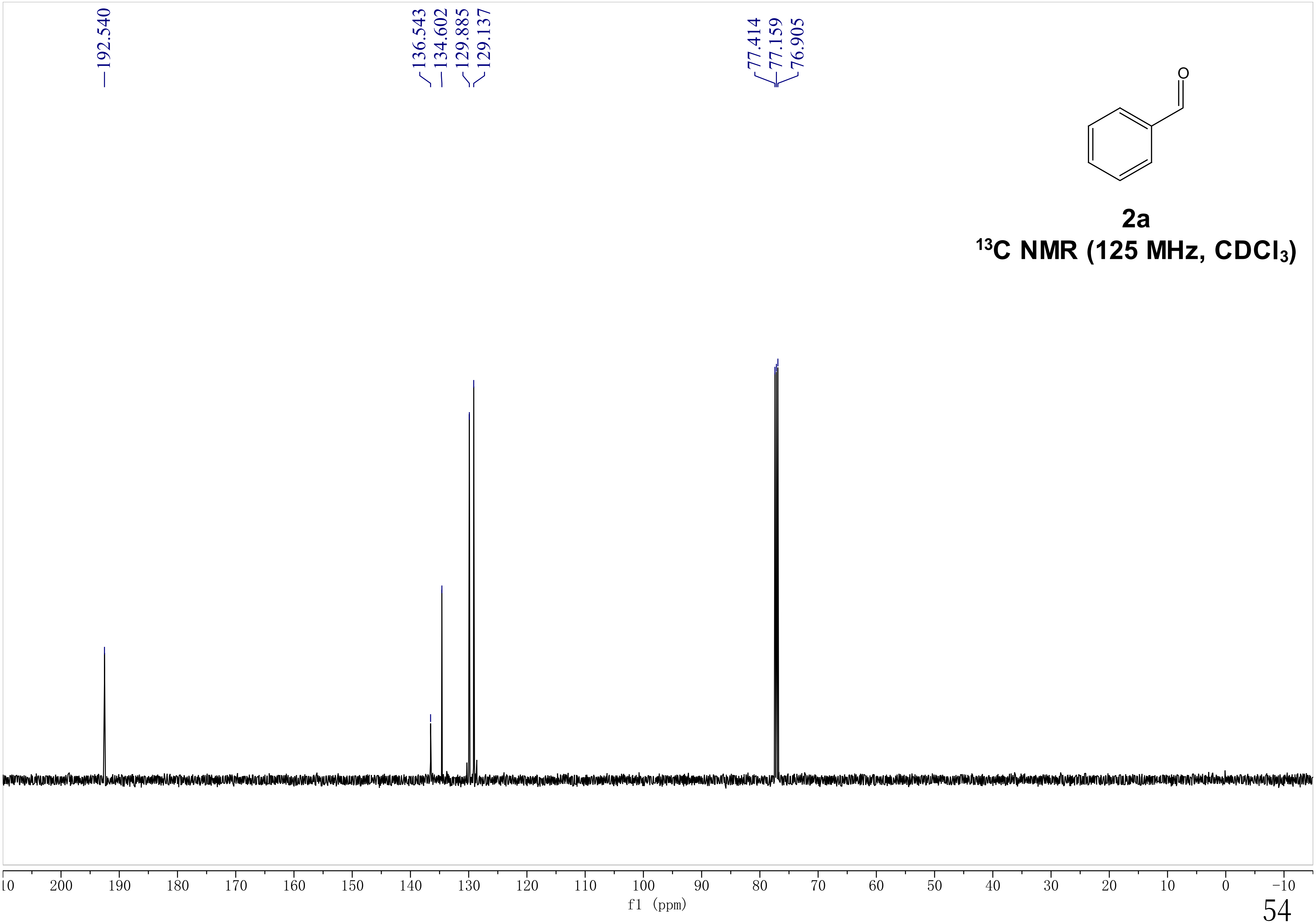
f1 (ppm)


192.540
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2a
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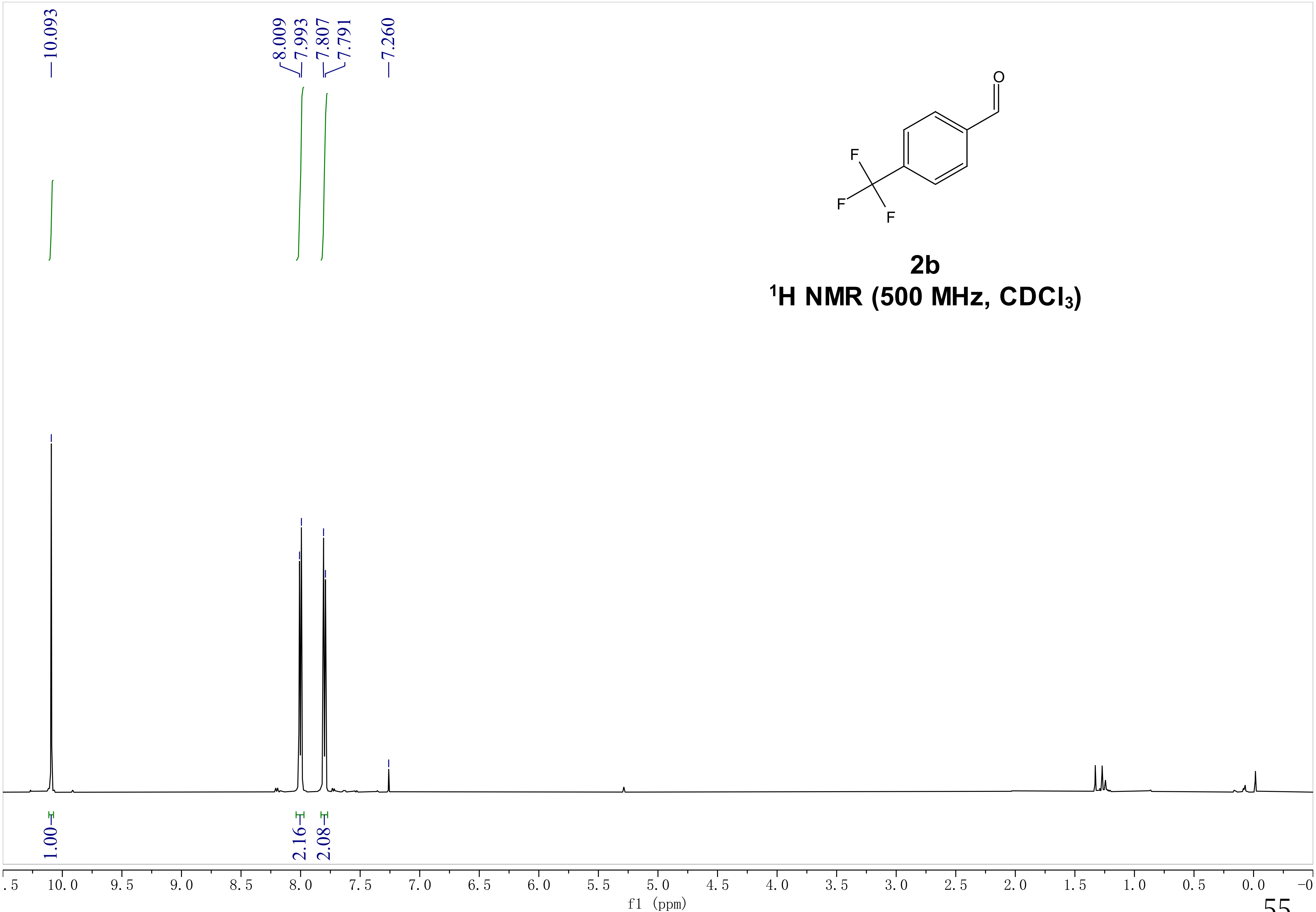
f1 (ppm)


10.093
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7.993
7.807
7.791
7.260
O
F
F
F
2b
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1.00
2.16
2.08
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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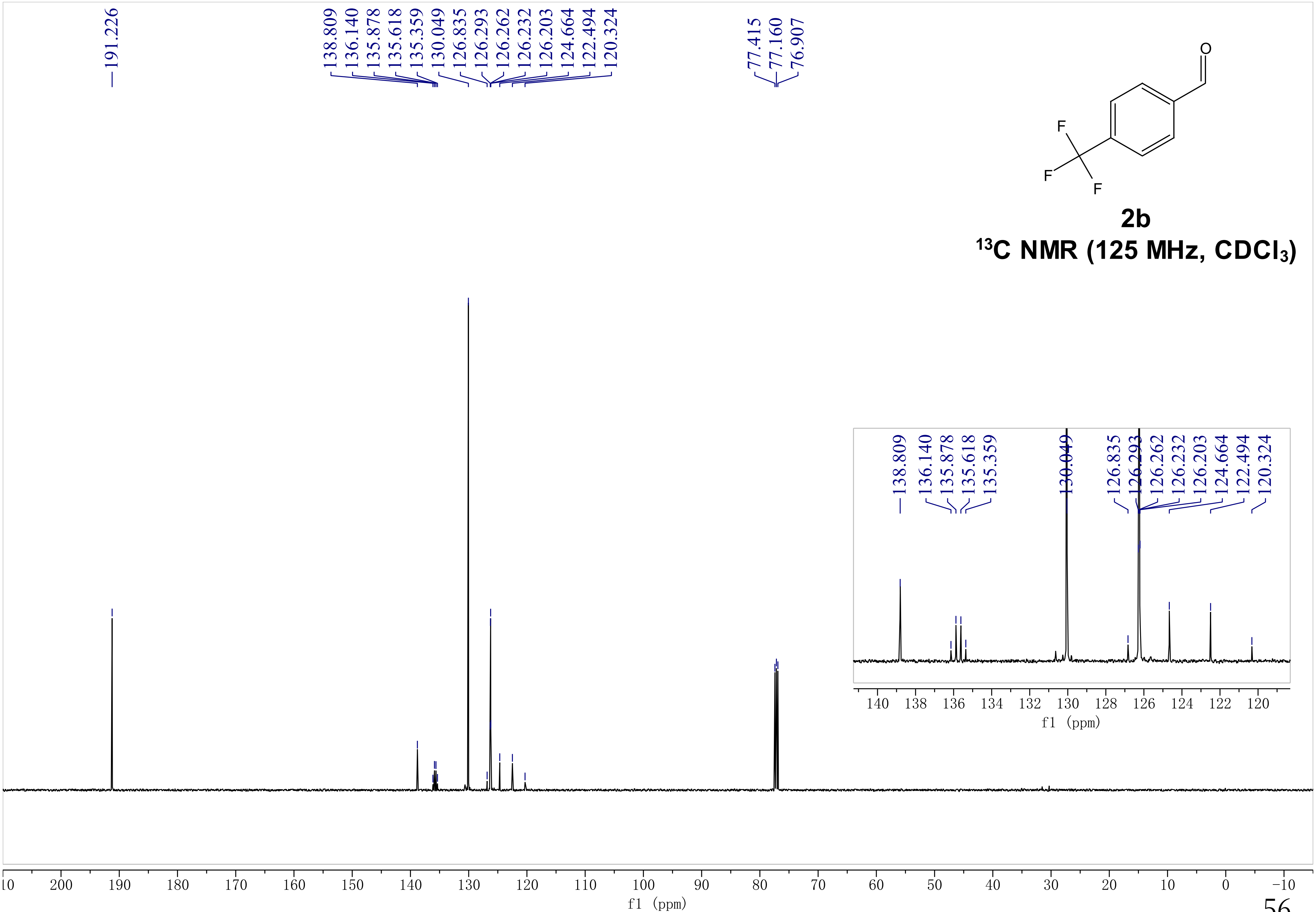
0.5
0.0
-0
f1 (ppm)



2b

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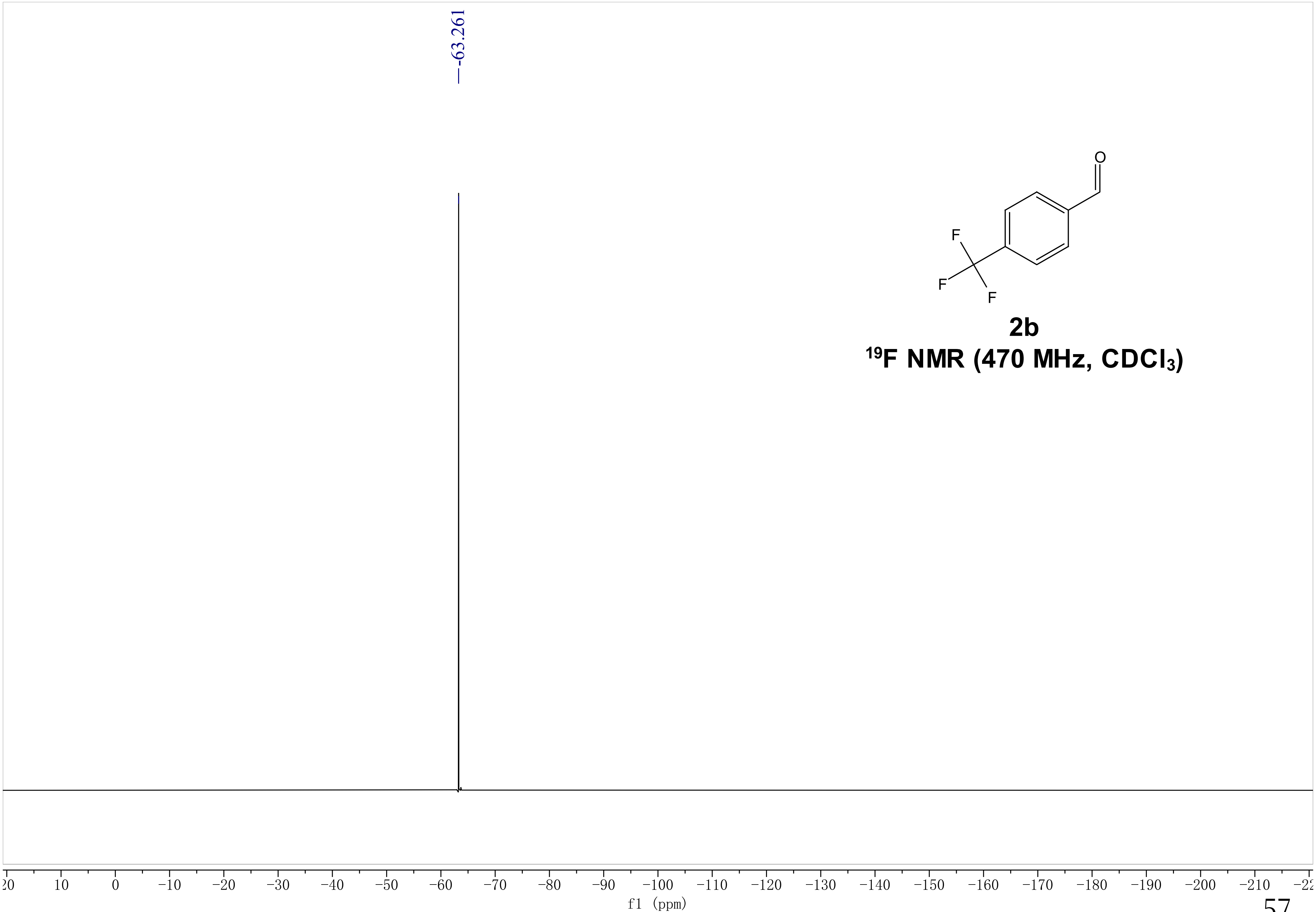
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O
F
F
F
2b
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20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
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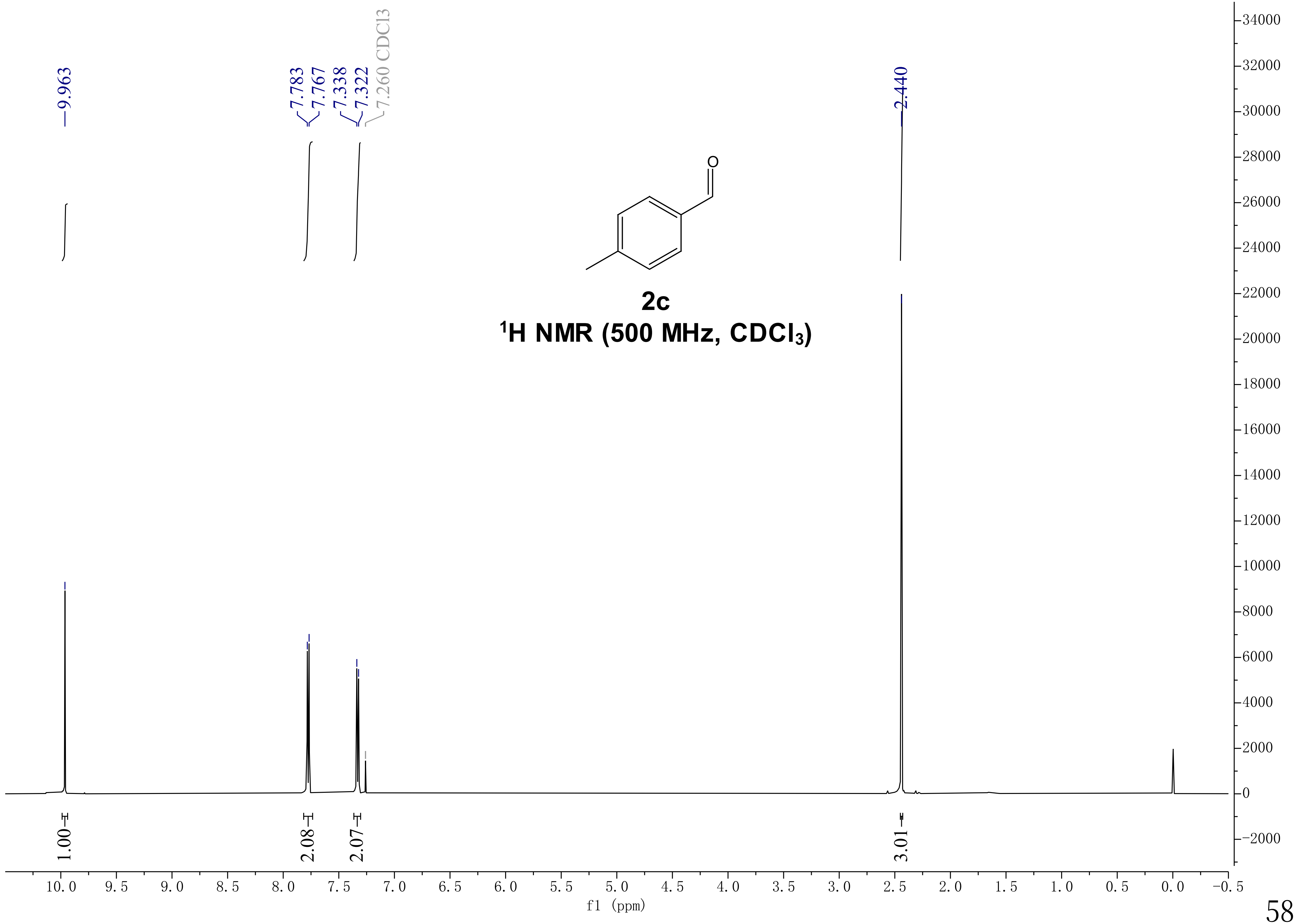
−210
−22
f1 (ppm)



9.963
7.783
7.767
7.338
7.322
7.260 CDCl3
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O
2c
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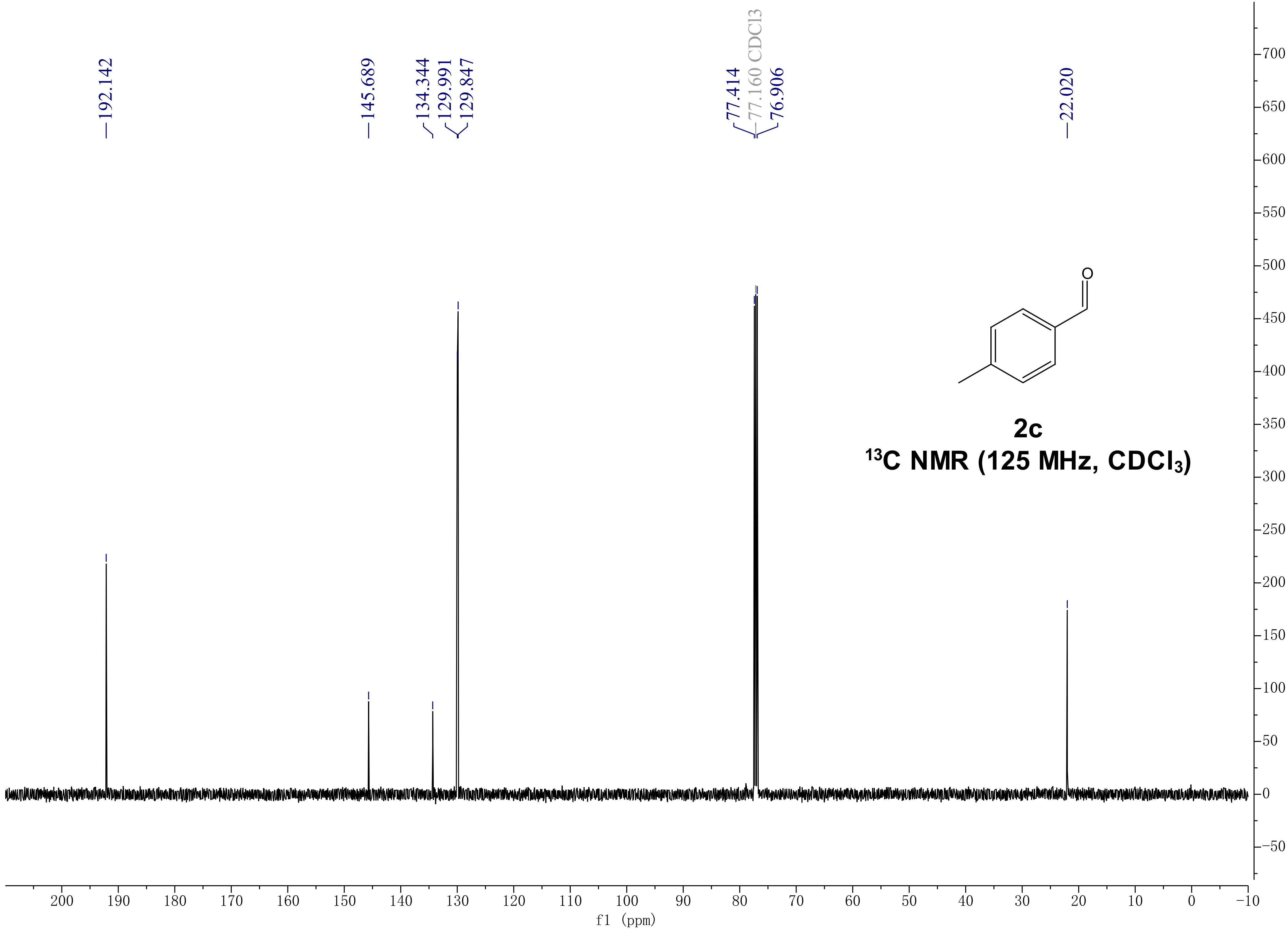
2.07
3.01
f1 (ppm)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22.020
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2c
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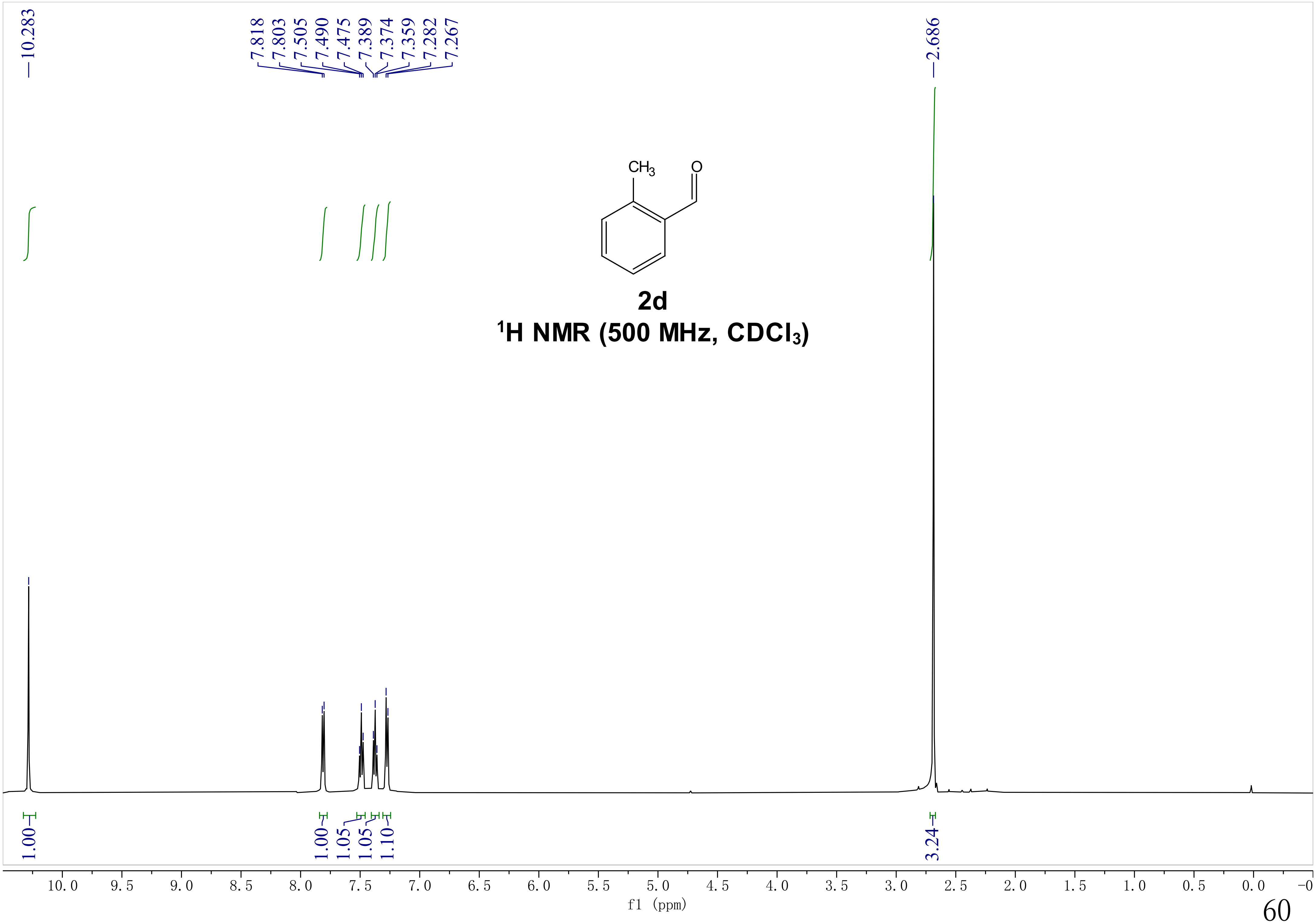
f1 (ppm)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7.374
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CH3
O
2d
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.05
1.05
1.10
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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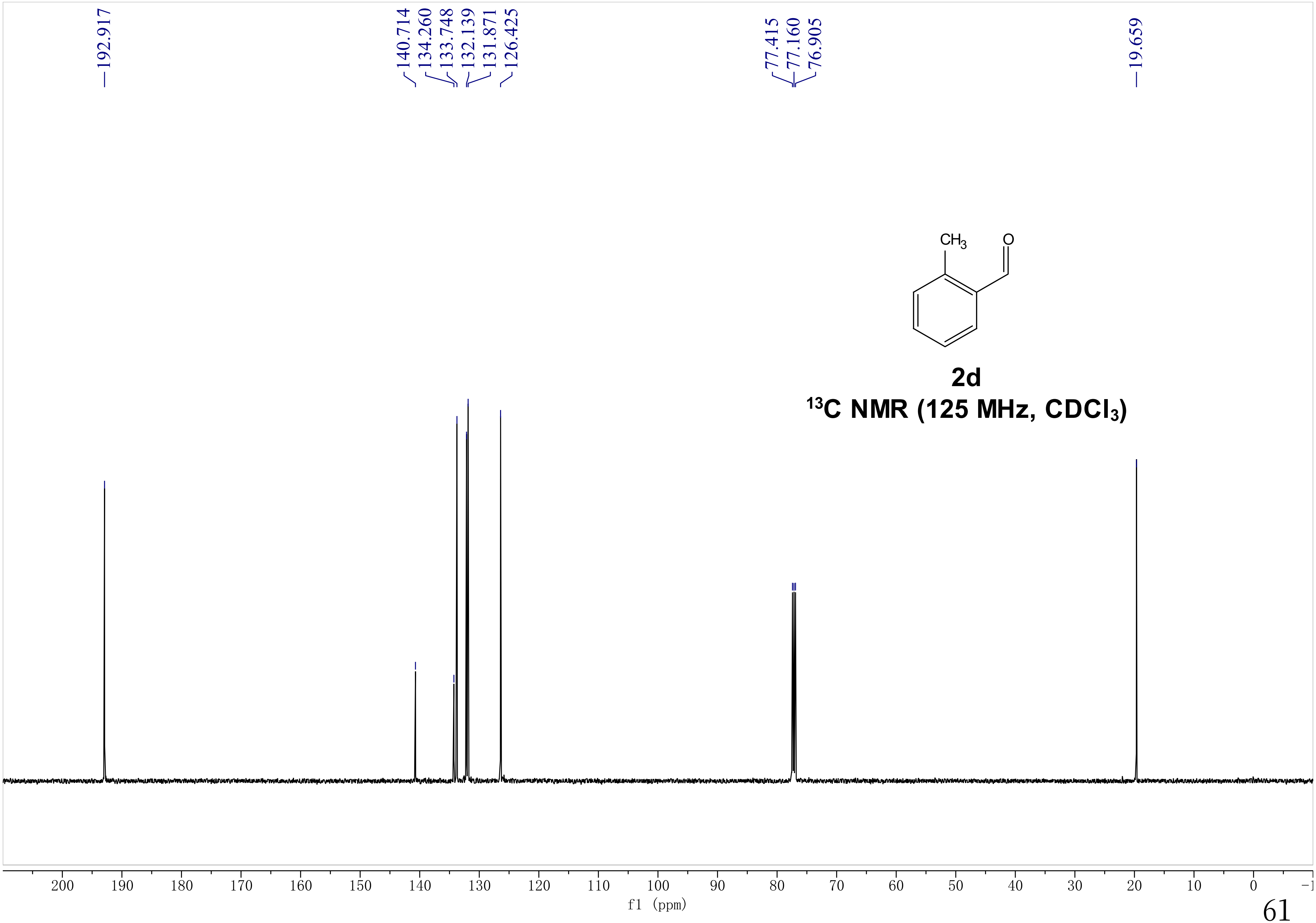
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2d

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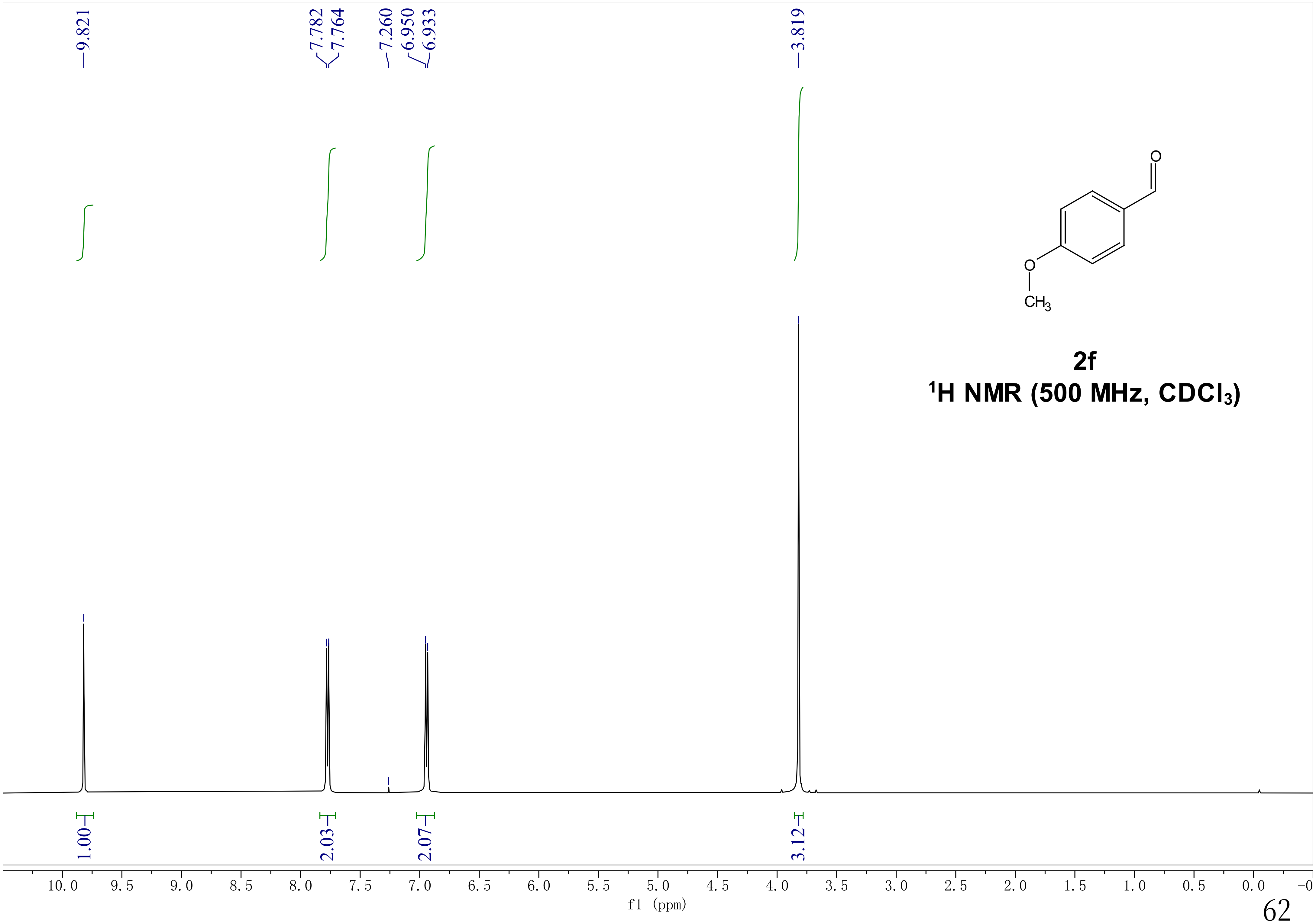
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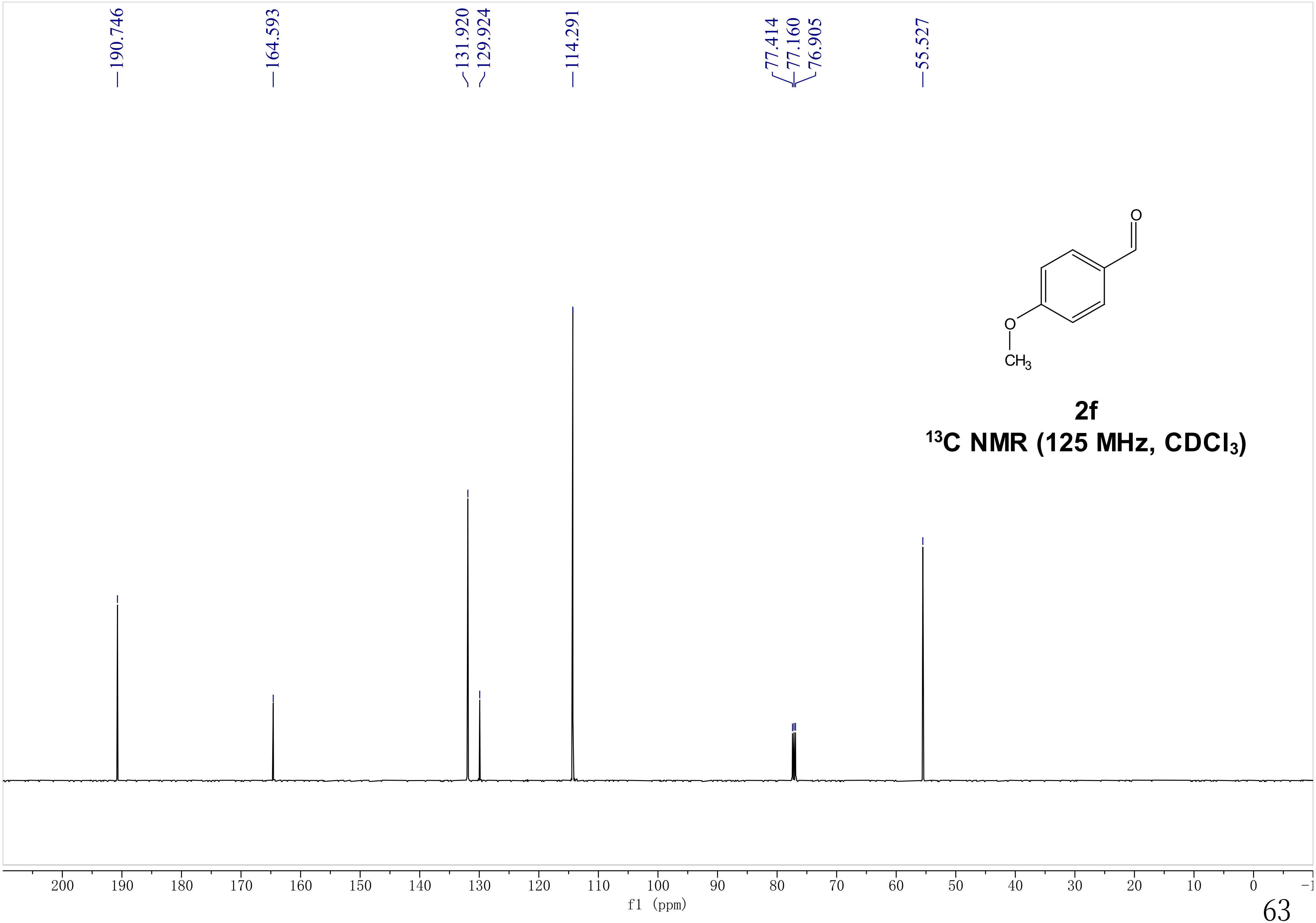
7.782
7.764
7.260
6.950
6.933
3.819
O
O
CH3
2f
1H NMR (500 MHz, CDCl3)
1.00
2.03
2.07
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.746
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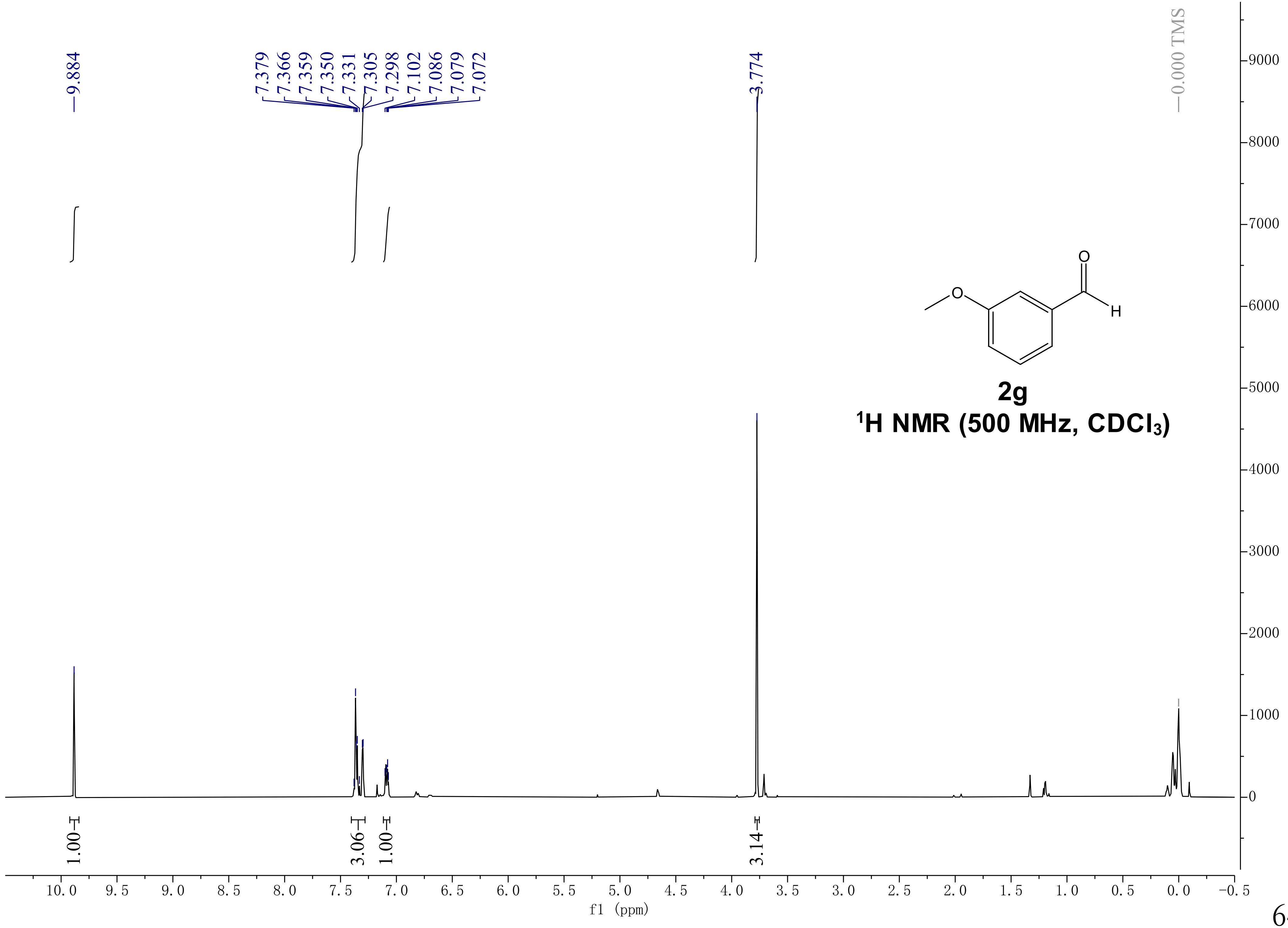
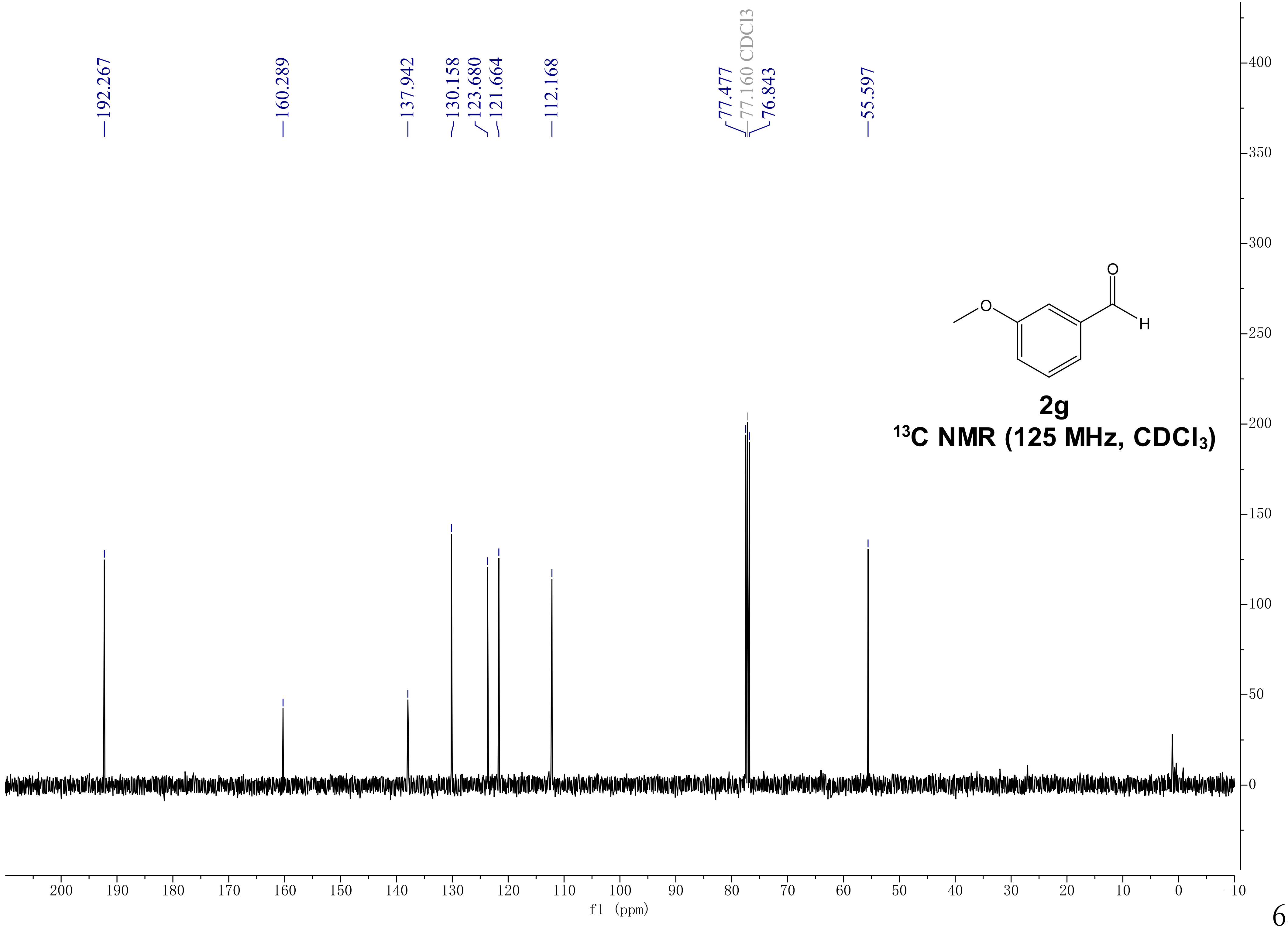
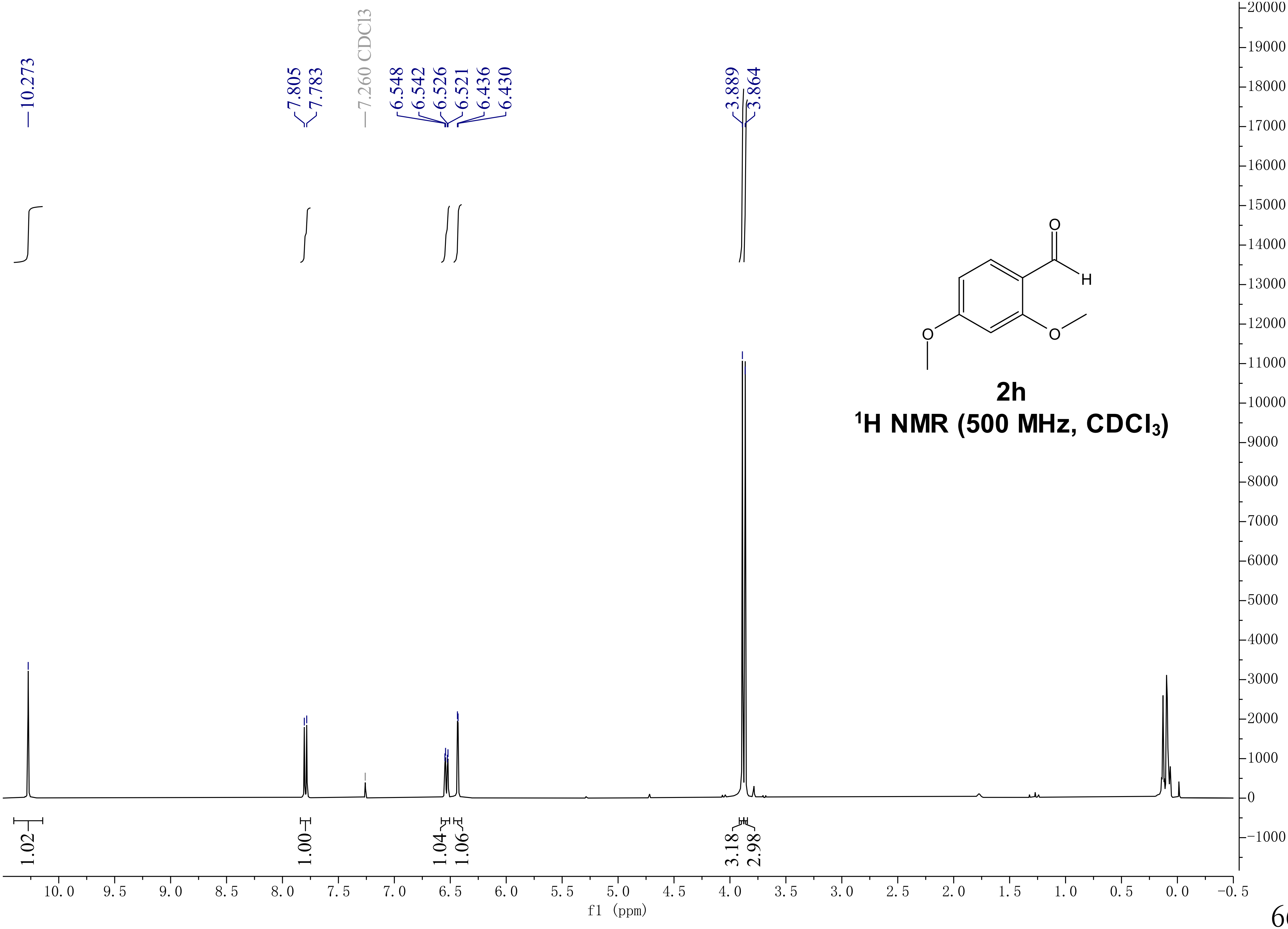
55.527
2f
13C NMR (125 MHz, CDCl3)
f1 (ppm)



2g

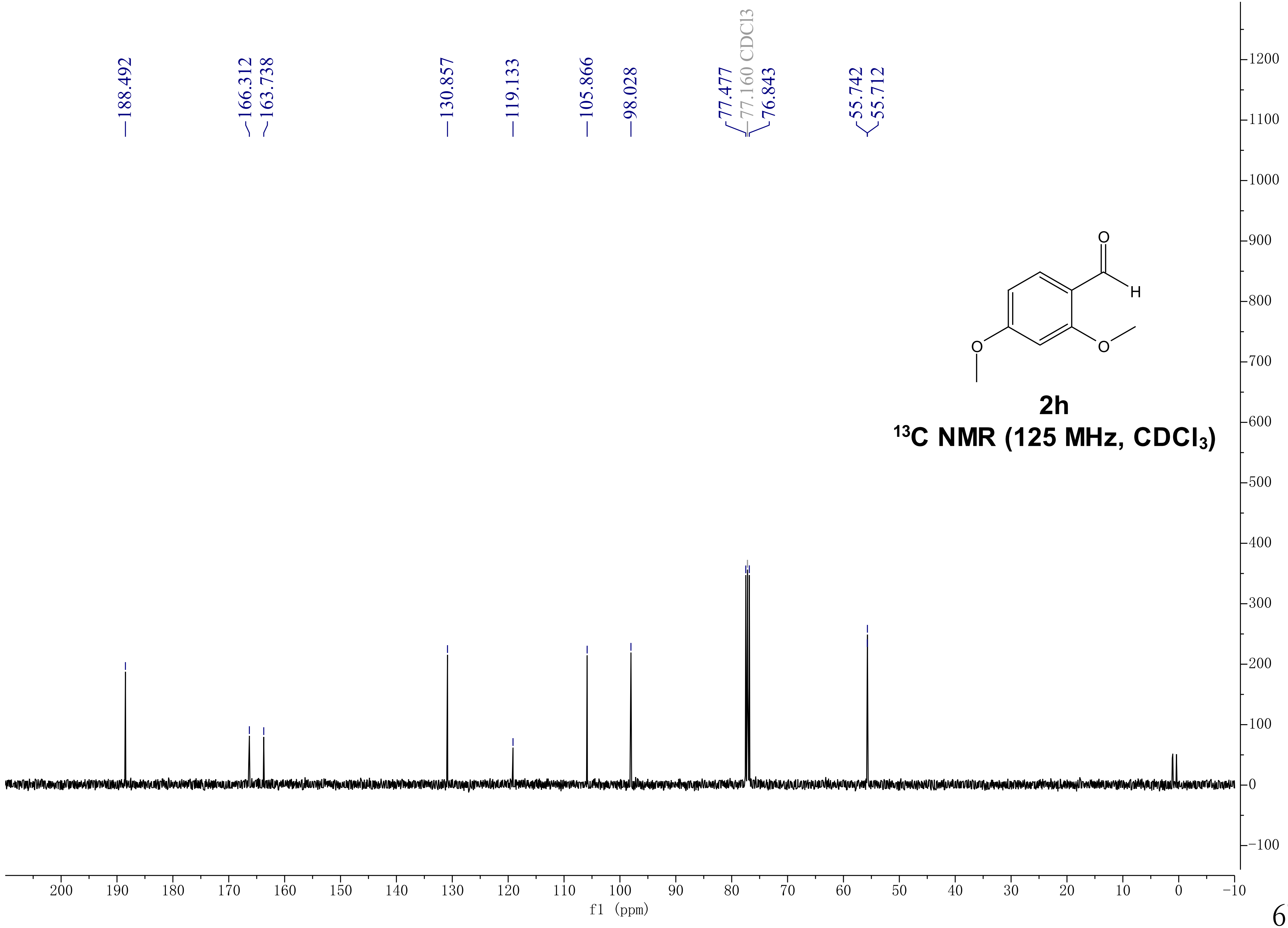
^{1}H NMR (500 MHz, $CDCl_3$)

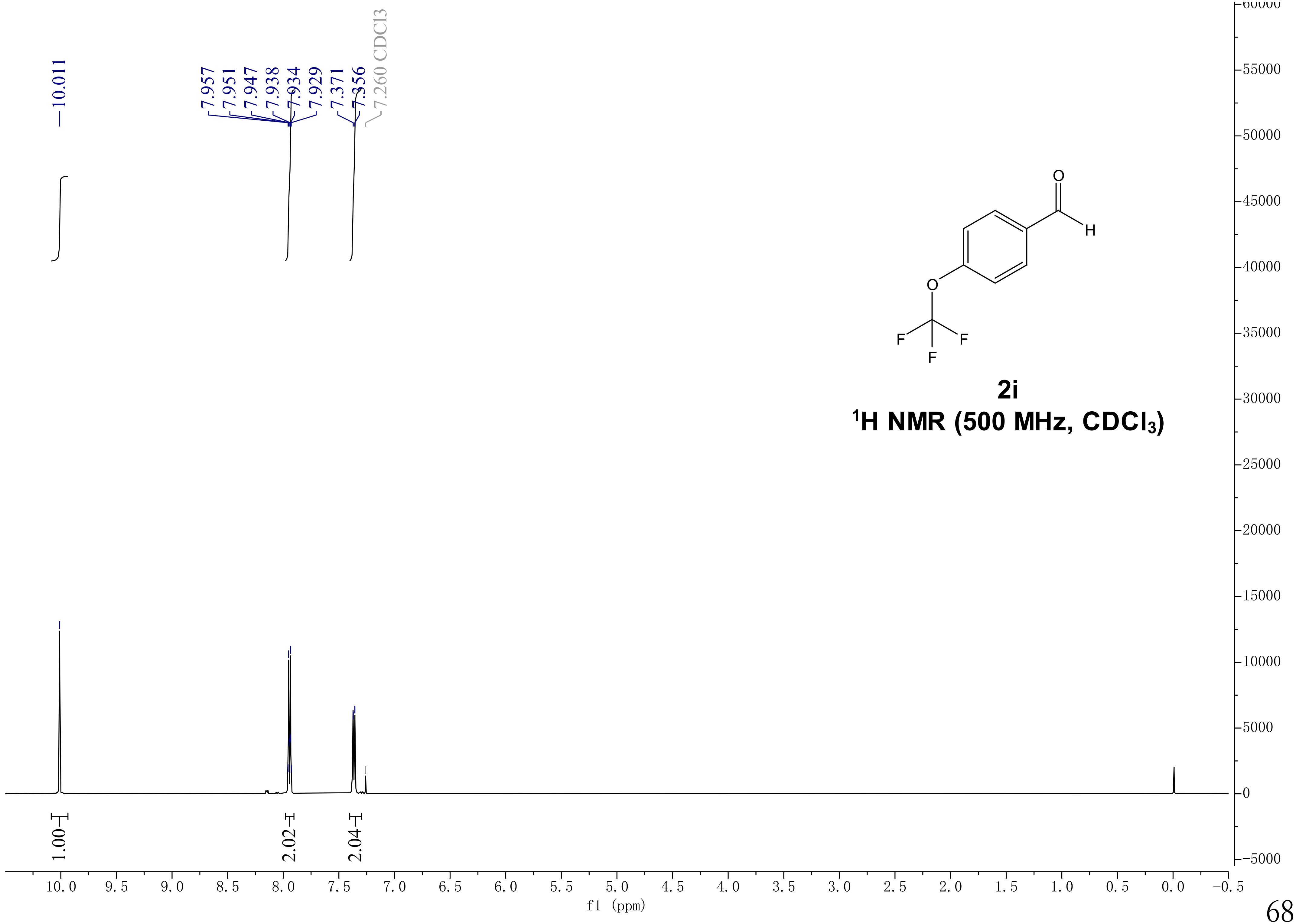

192.267
160.289
137.942
130.158
123.680
121.664
112.168
77.477
77.160 CDCl3
76.843
55.597
O
O
H
2g
13C NMR (125 MHz, CDCl3)
f1 (ppm)

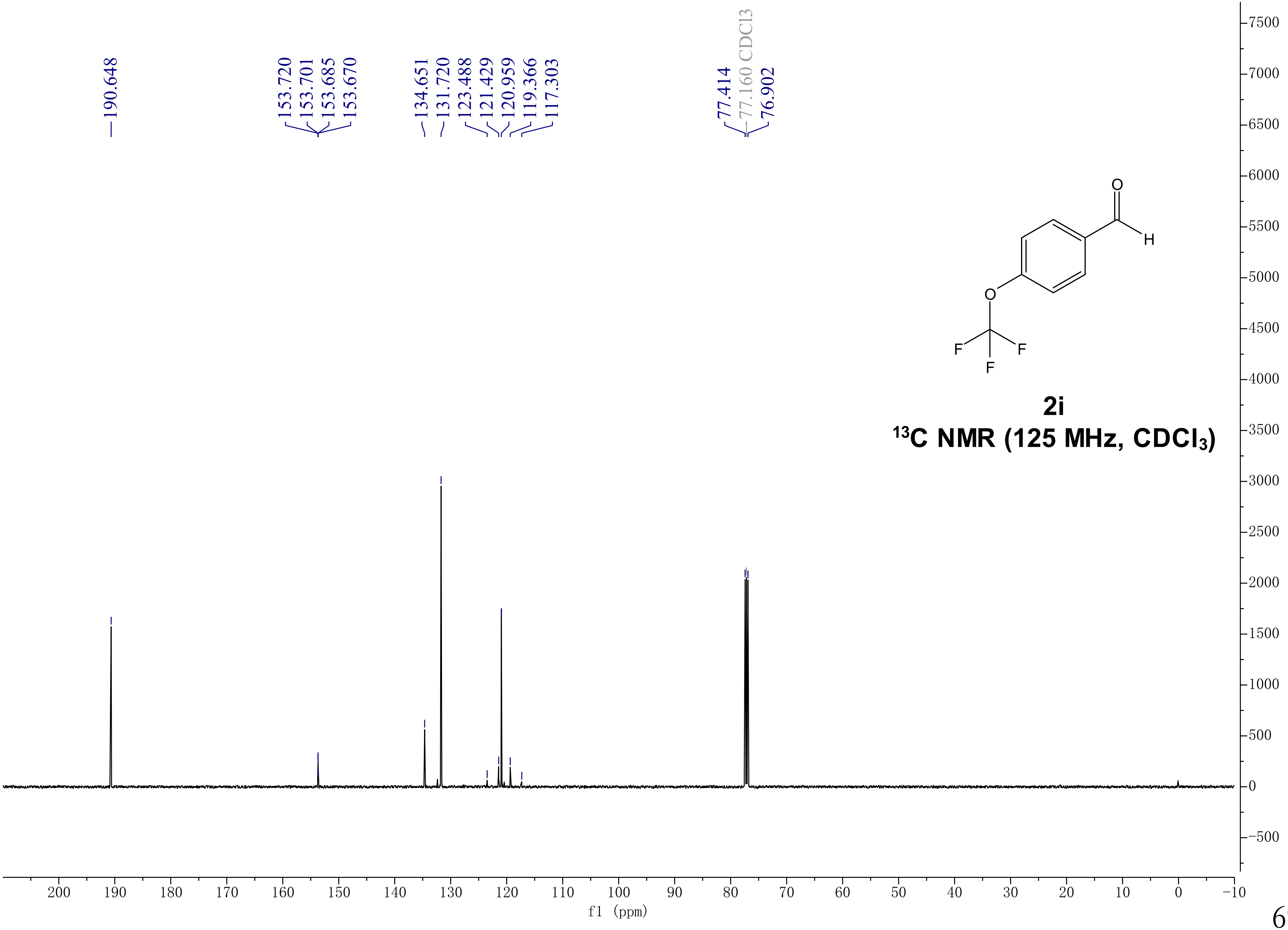


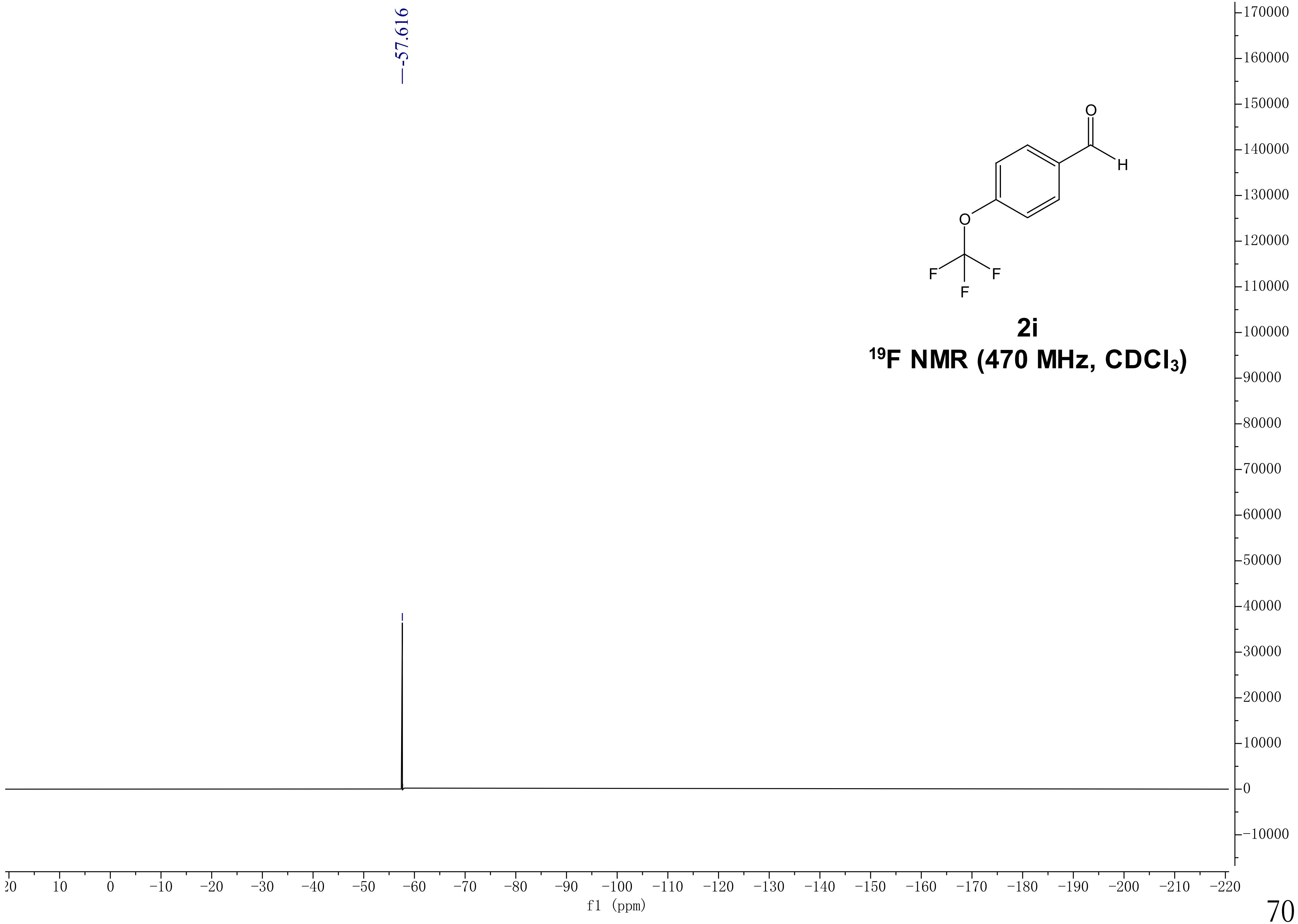
2h

^{1}H NMR (500 MHz, $CDCl_3$)

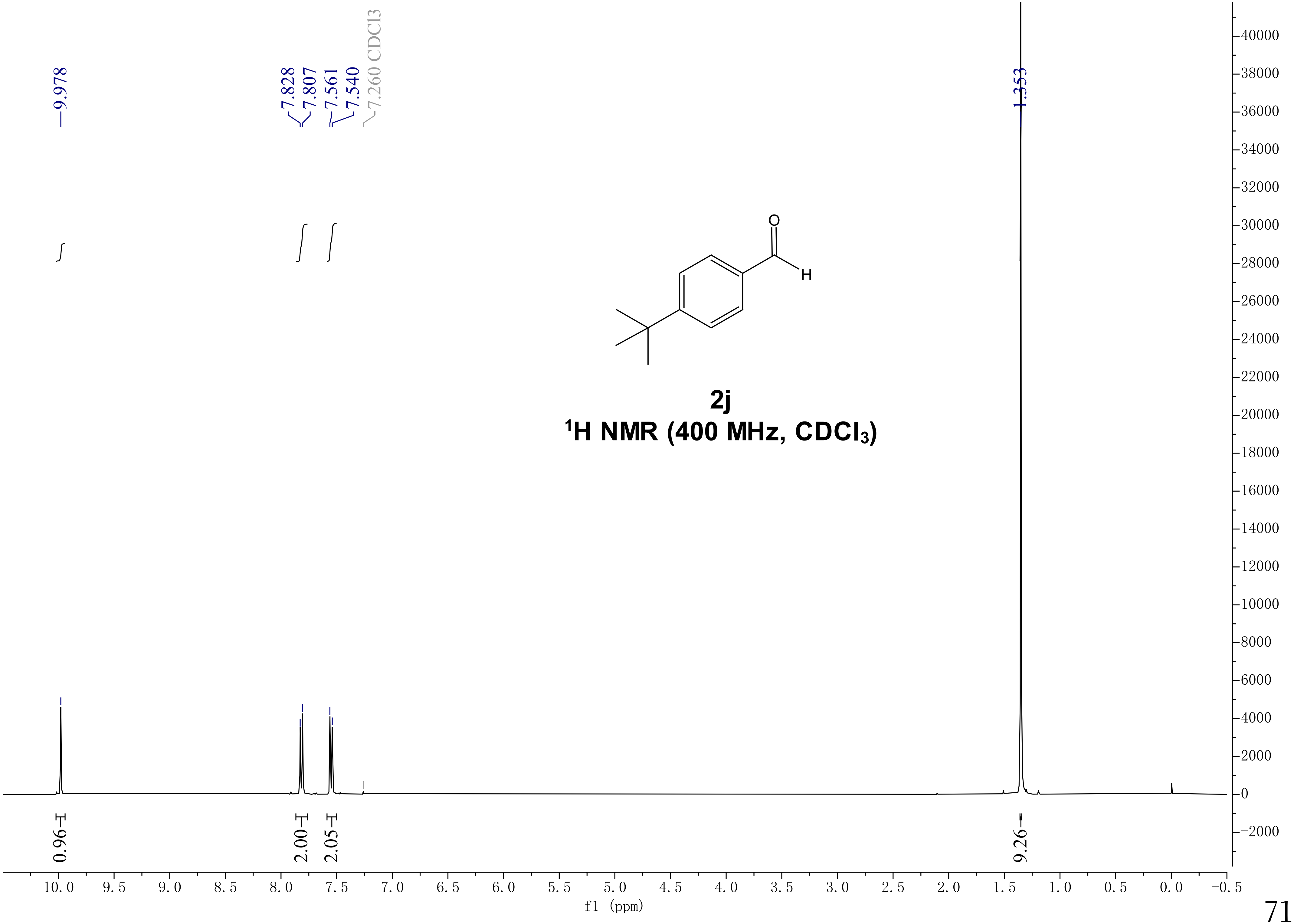

188.492
166.312
163.738
130.857
119.133
105.866
98.028
77.477
77.160 CDCl3
76.843
55.742
55.712
2h
13C NMR (125 MHz, CDCl3)
f1 (ppm)


10.011
7.957
7.951
7.947
7.938
7.934
7.929
7.371
7.356
7.260 CDCl3
2i
¹H NMR (500 MHz, CDCl₃)
1.00
2.02
2.04
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000


190.648
153.720
153.701
153.685
153.670
134.651
131.720
123.488
121.429
120.959
119.366
117.303
77.414
77.160 CDCl3
76.902
O
H
O
F
F
F
2i
13C NMR (125 MHz, CDCl3)
f1 (ppm)

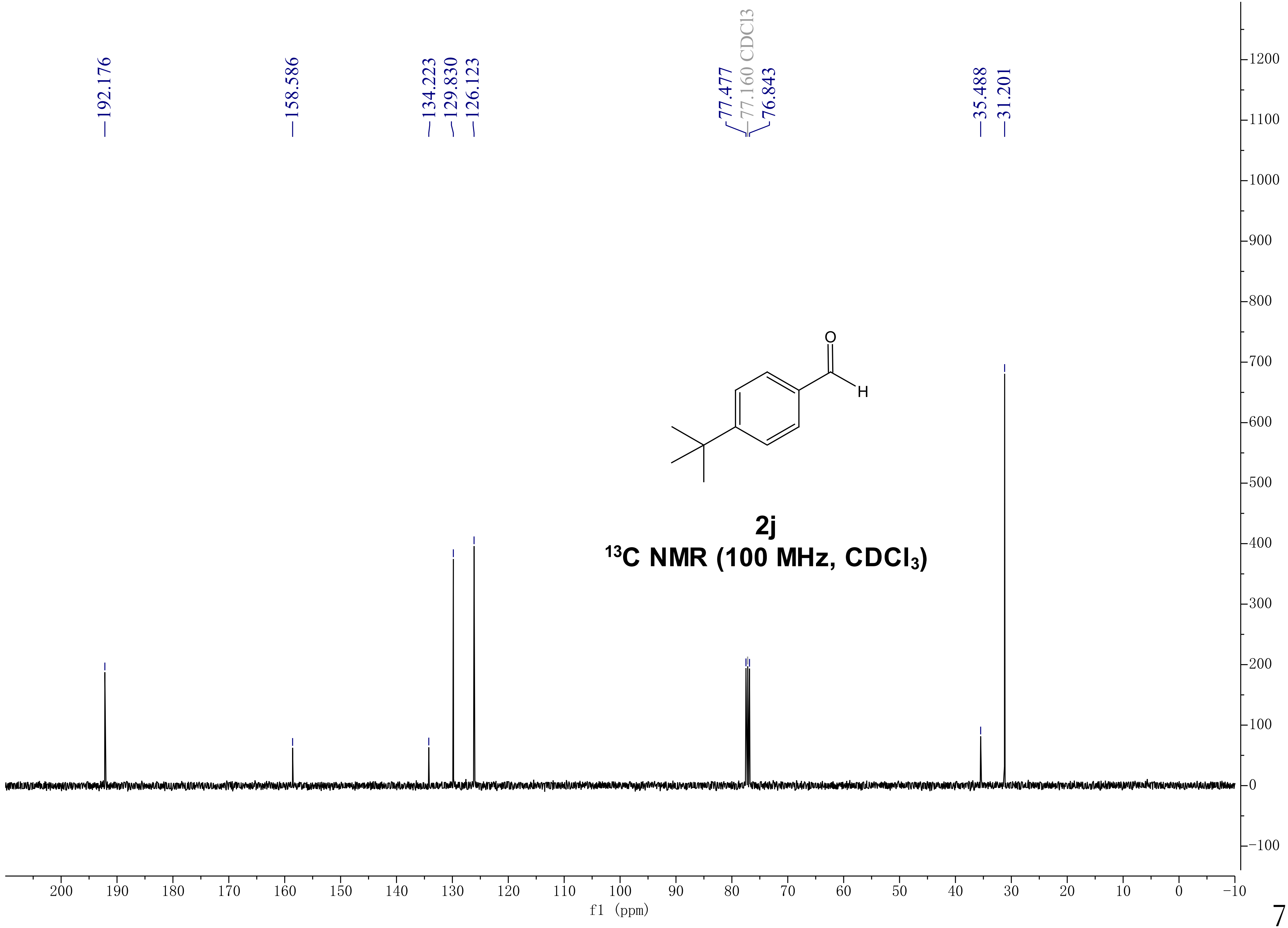


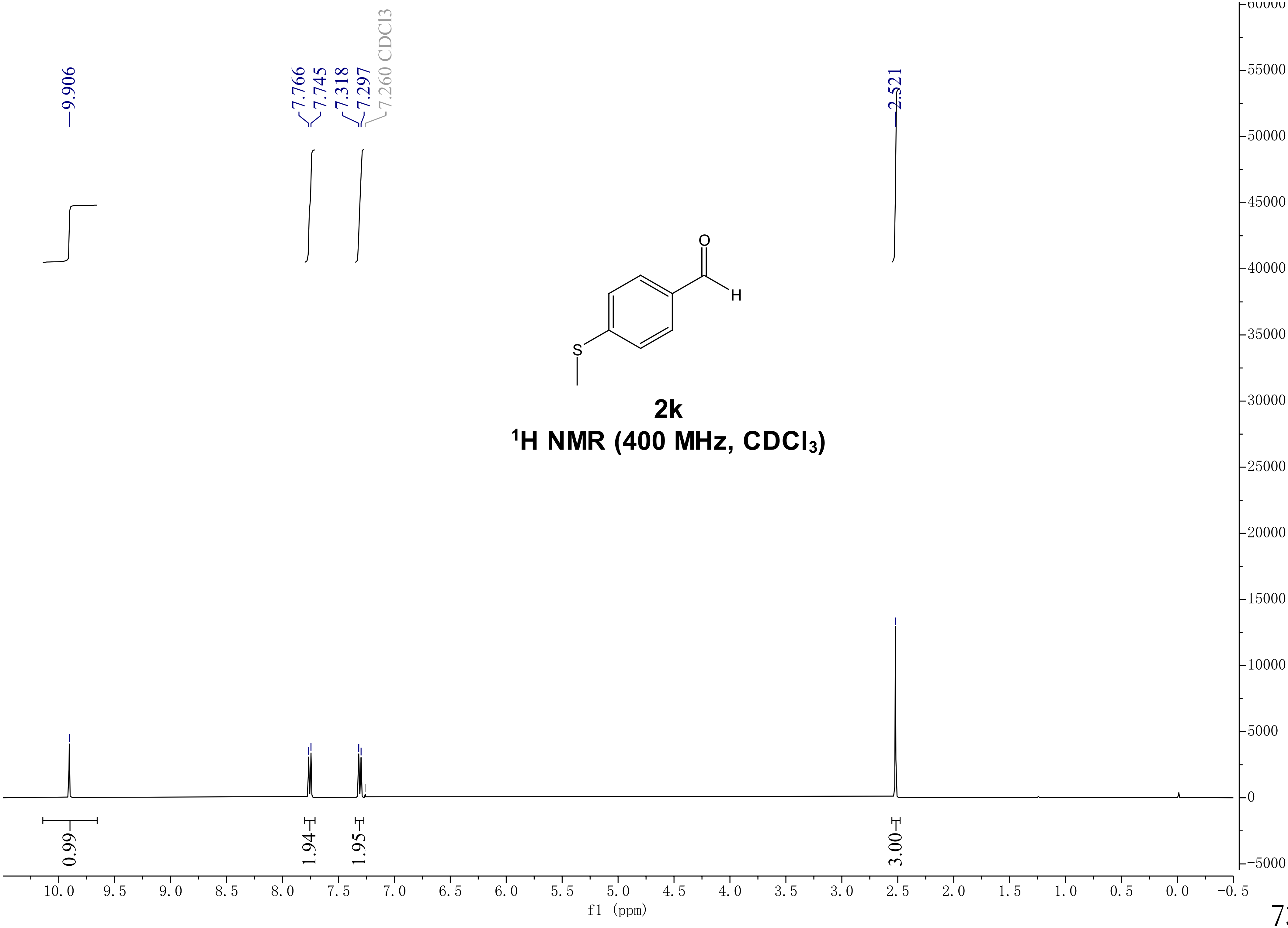
—-57.616
O
H
O
F
F
F
2i
^{19}F NMR (470 MHz, CDCl$_3$)
f1 (ppm)



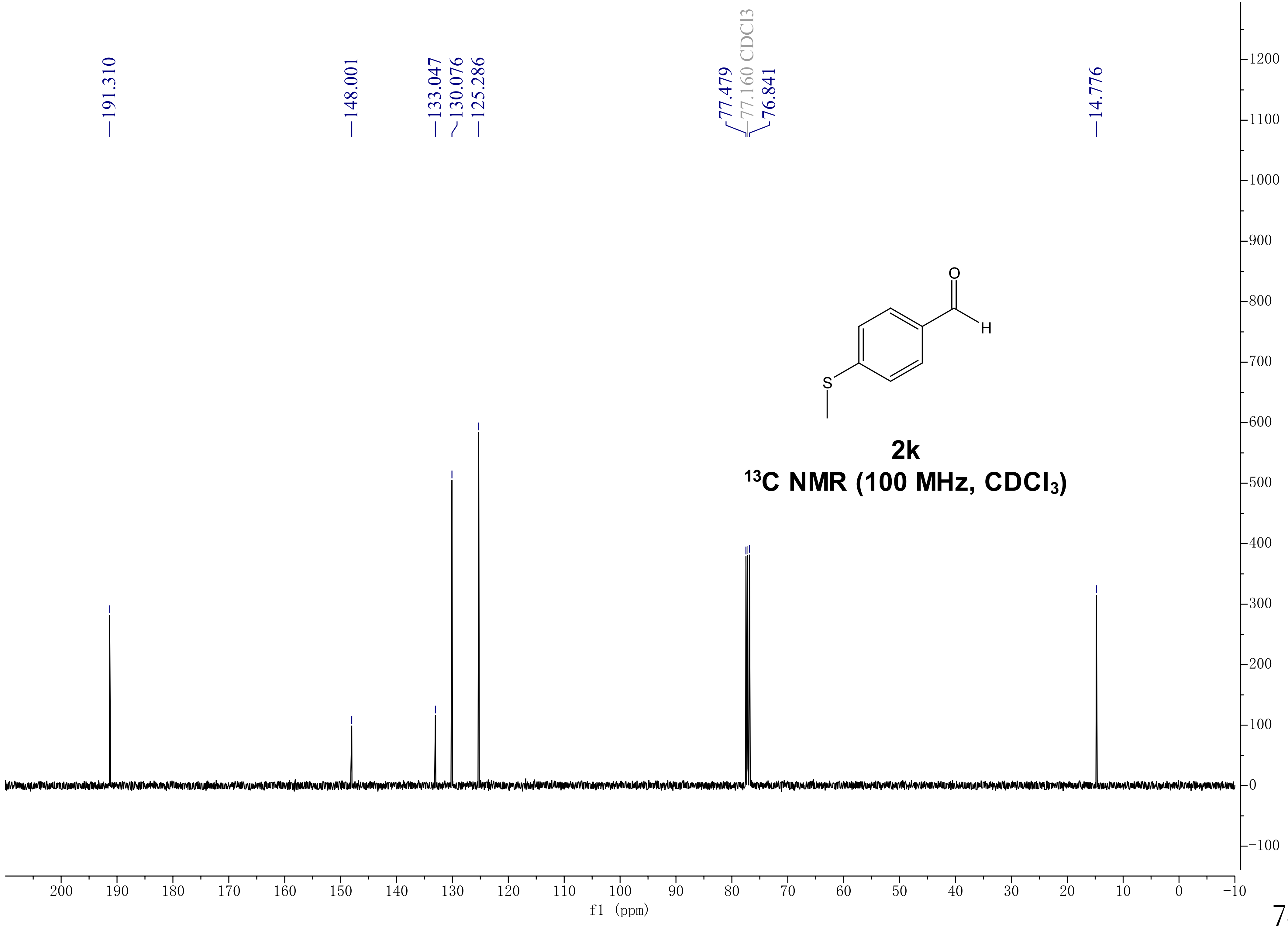
2j

^1H NMR (400 MHz, $CDCl_3$)

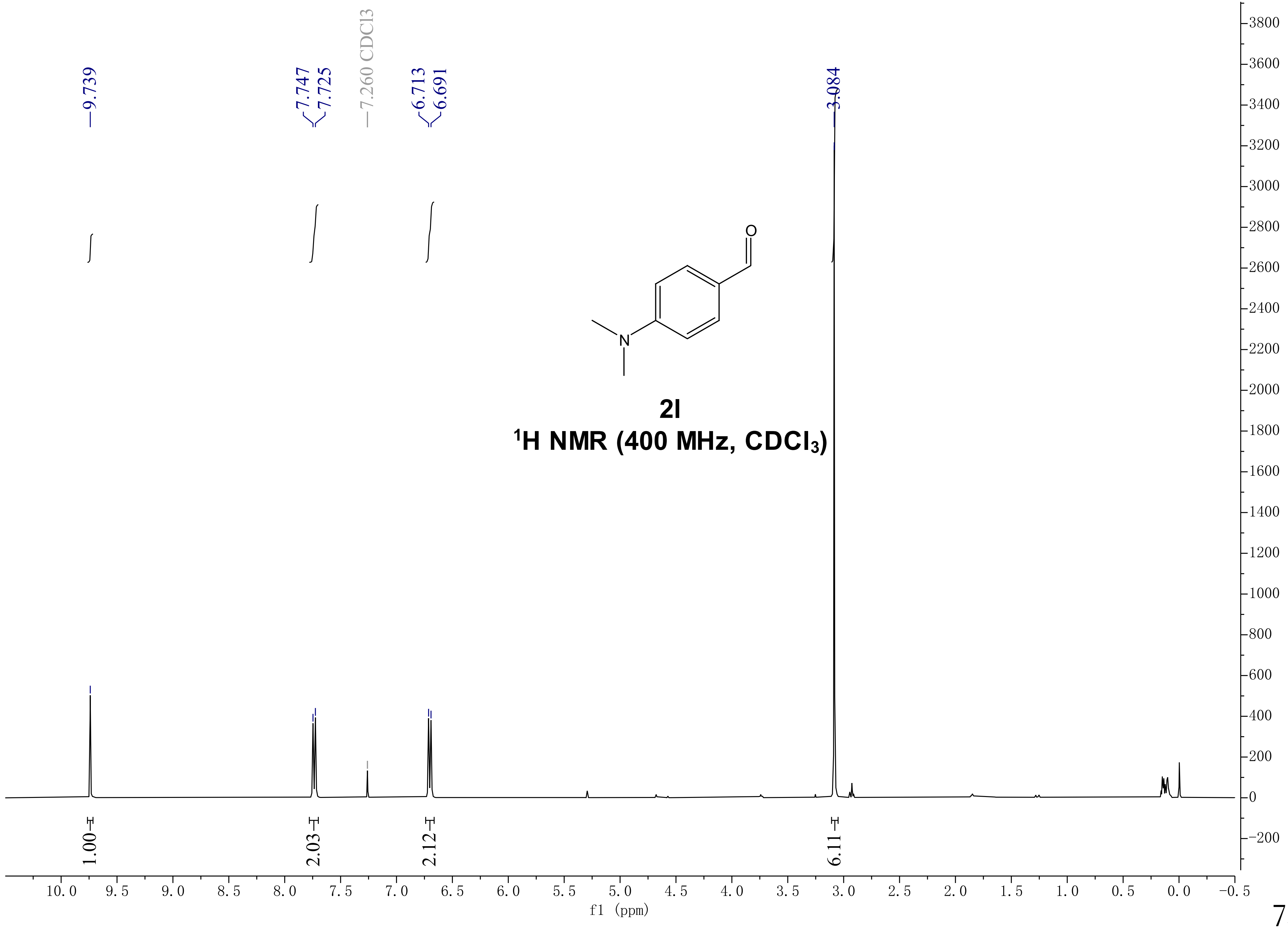

192.176
158.586
134.223
129.830
126.123
77.477
77.160 CDCl3
76.843
35.488
31.201
O
H
2j
13C NMR (100 MHz, CDCl3)
f1 (ppm)



9.906
7.766
7.745
7.318
7.297
7.260 CDCl3
2.521
O
H
S
2k
1H NMR (400 MHz, CDCl3)
0.99
1.94
1.95
3.00
f1 (ppm)

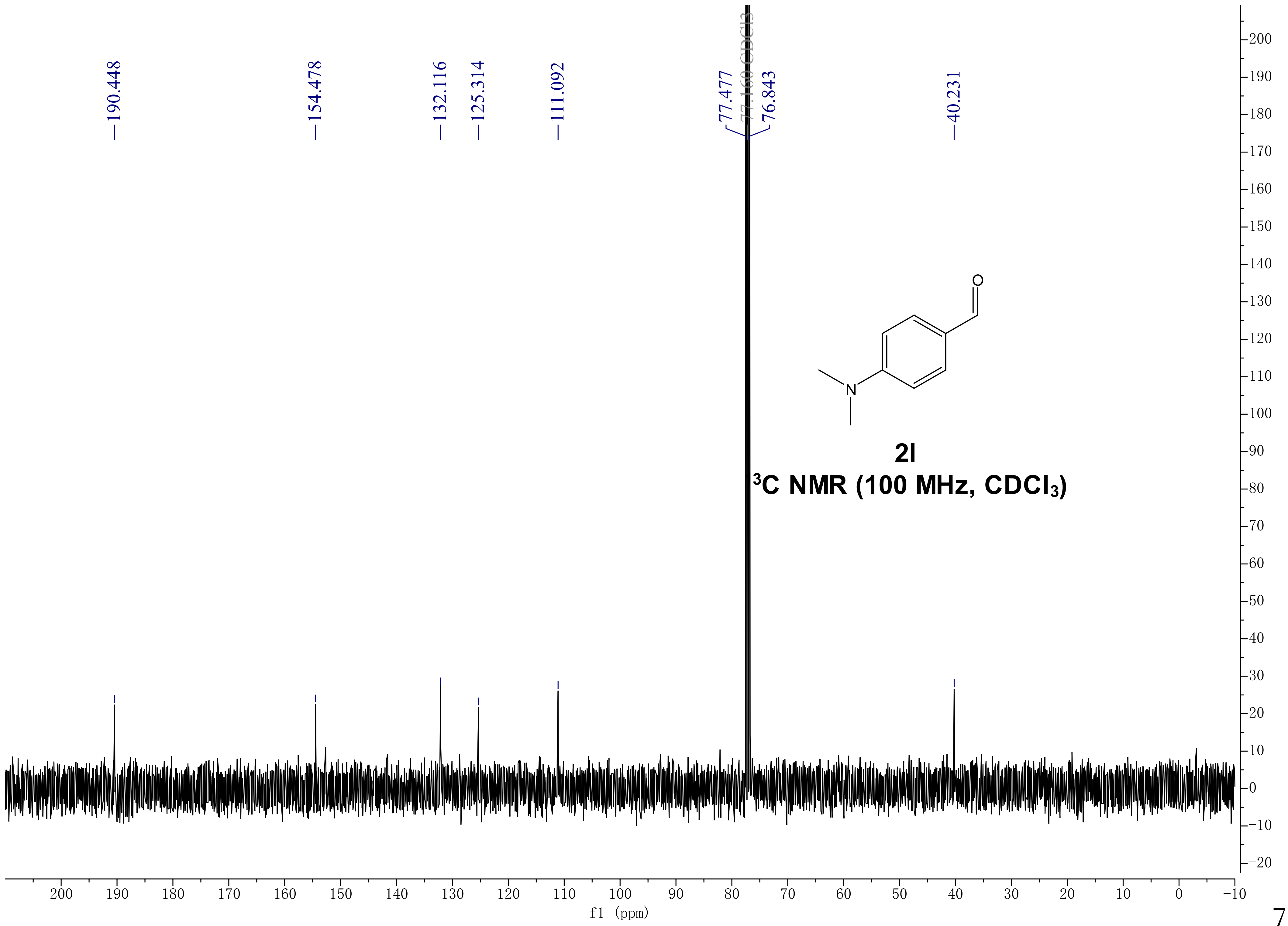


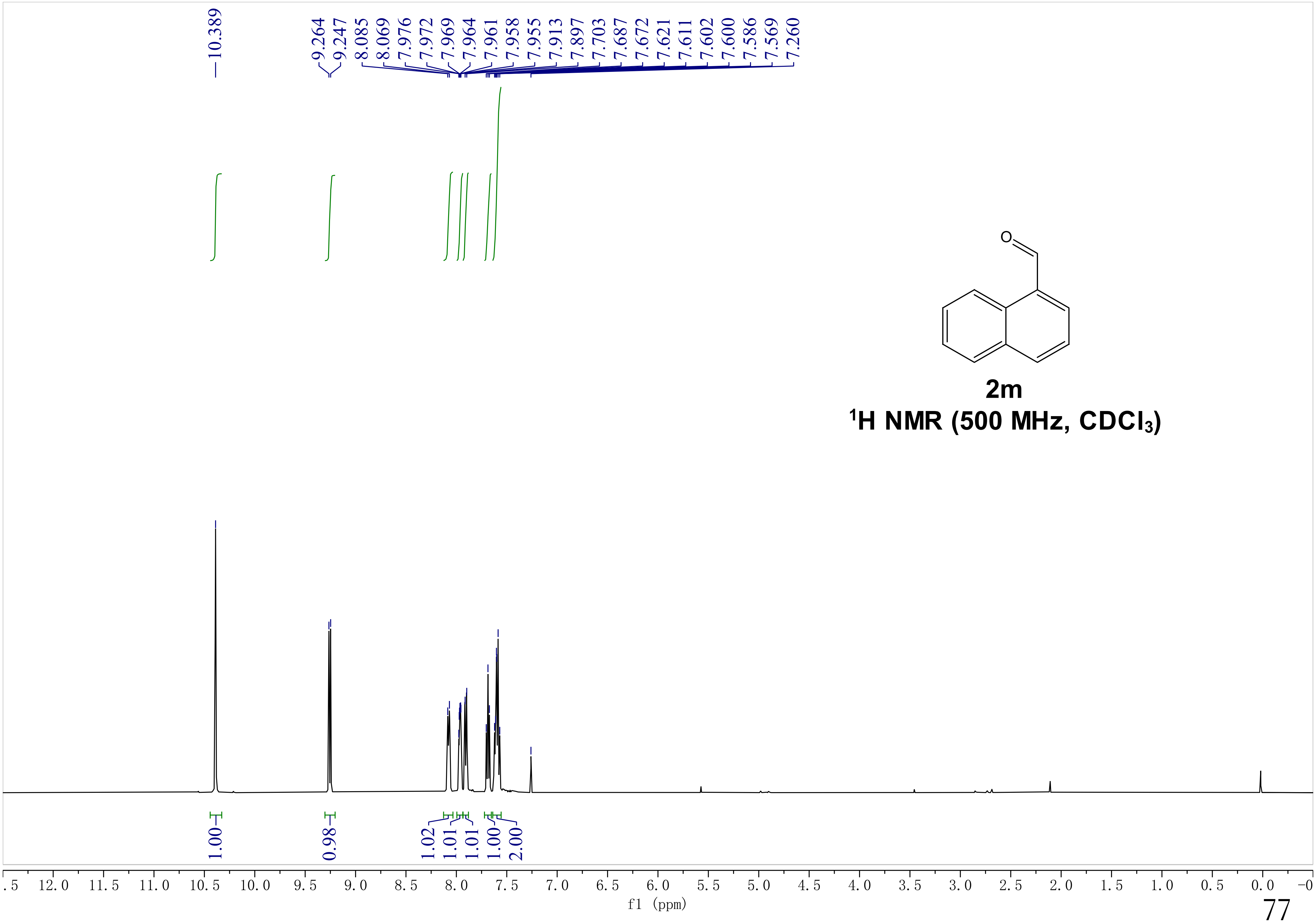
191.310
148.001
133.047
130.076
125.286
77.479
77.160 CDCl3
76.841
14.776
2k
13C NMR (100 MHz, CDCl3)
f1 (ppm)

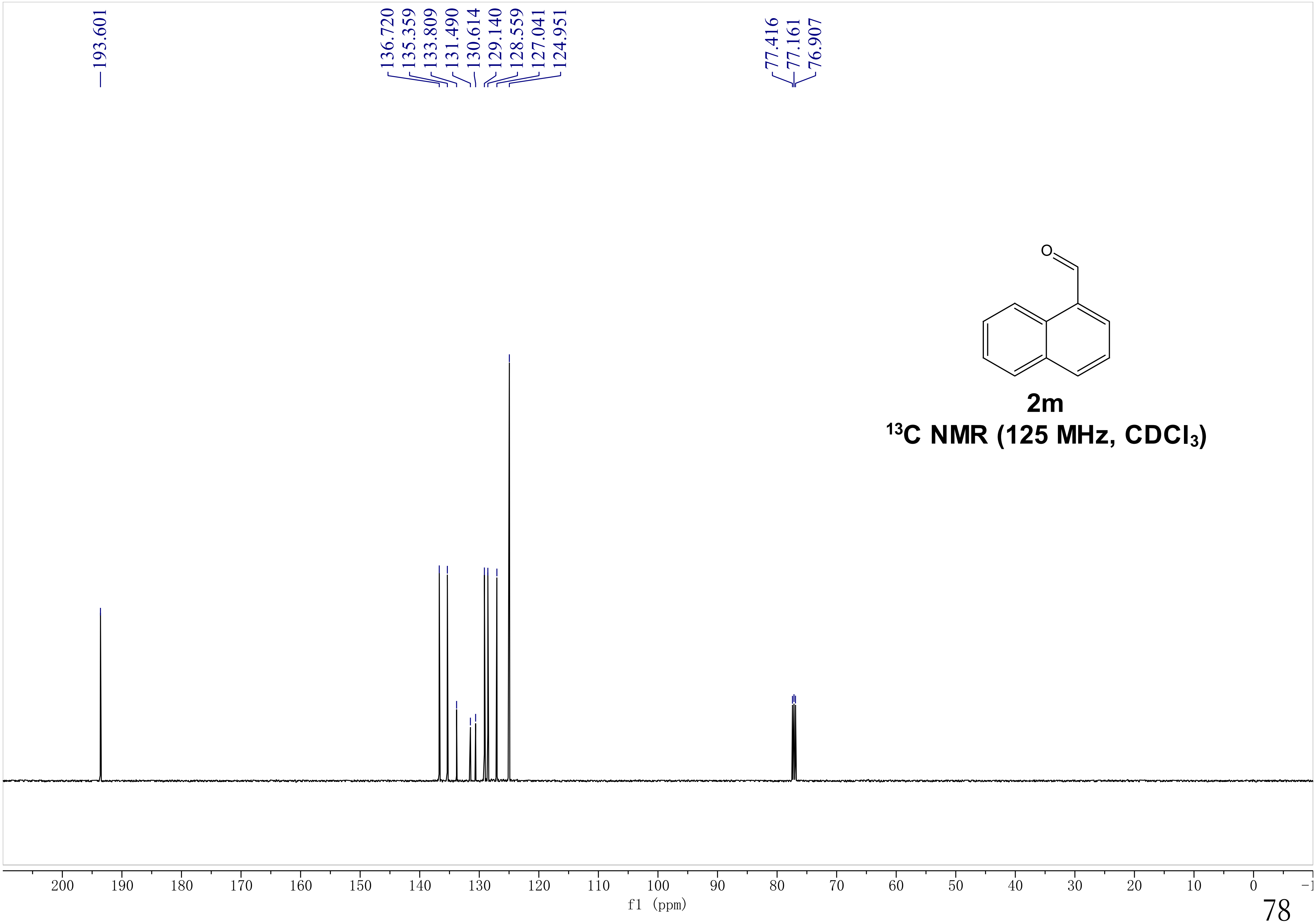


2l

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

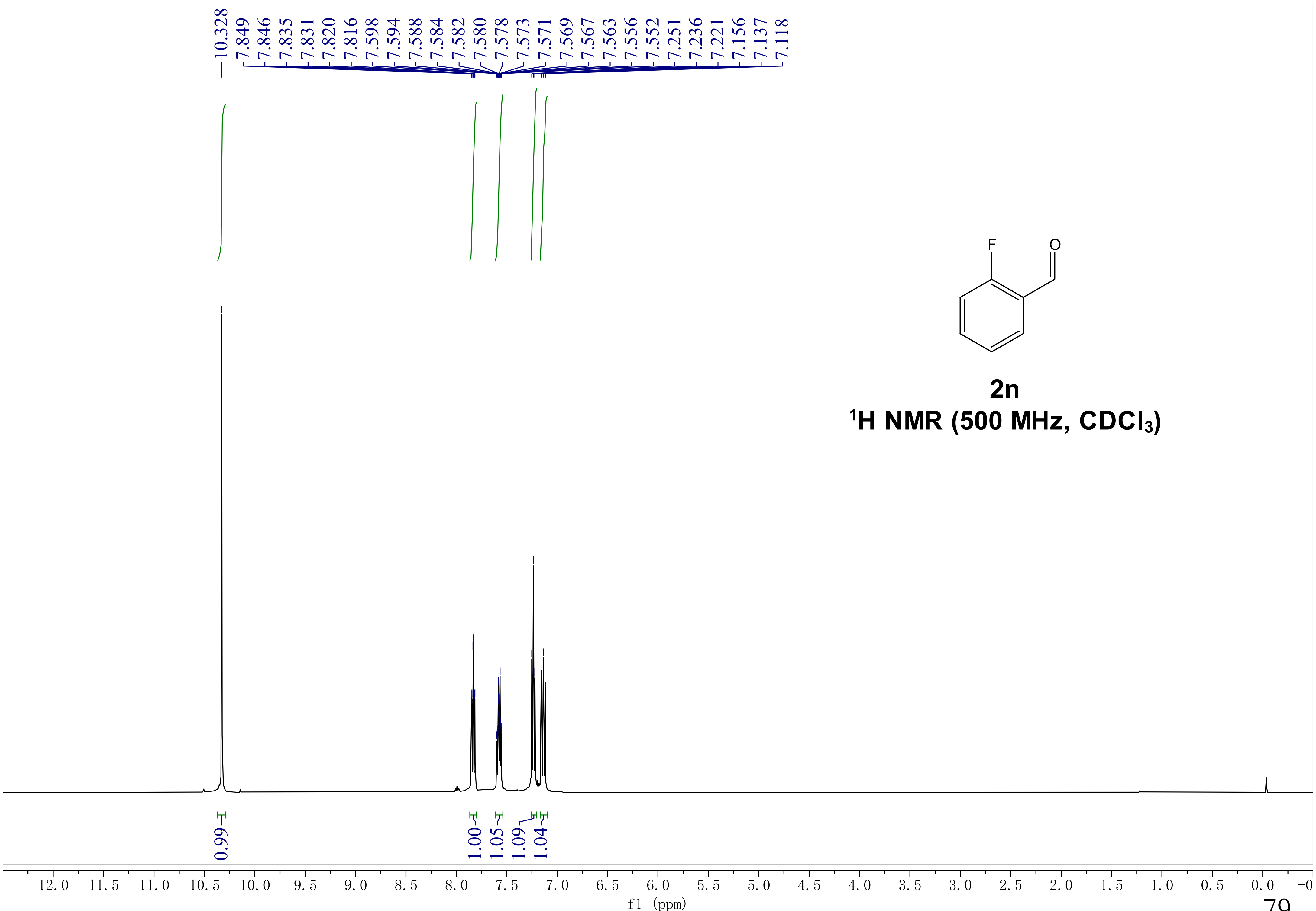

190.448
154.478
132.116
125.314
111.092
77.477
77.160 CDCl3
76.843
40.231
O
N
2l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

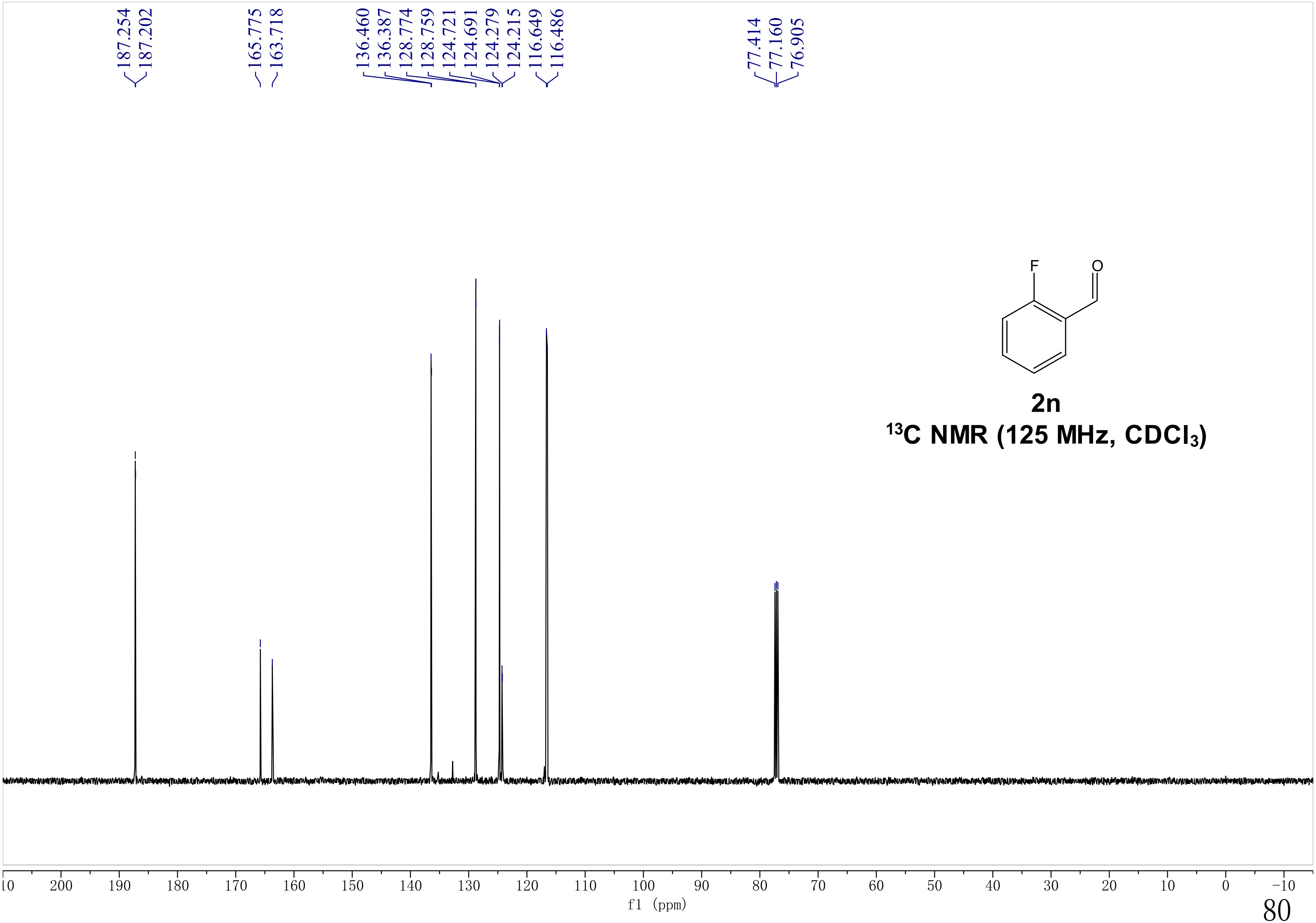

10.389
9.264
9.247
8.085
8.069
7.976
7.972
7.969
7.964
7.961
7.958
7.955
7.913
7.897
7.703
7.687
7.672
7.621
7.611
7.602
7.600
7.586
7.569
7.260
O
2m
1H NMR (500 MHz, CDCl3)
1.00
0.98
1.02
1.01
1.01
1.00
2.00
f1 (ppm)

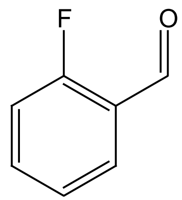


2m

^{13}C NMR (125 MHz, $CDCl_3$)

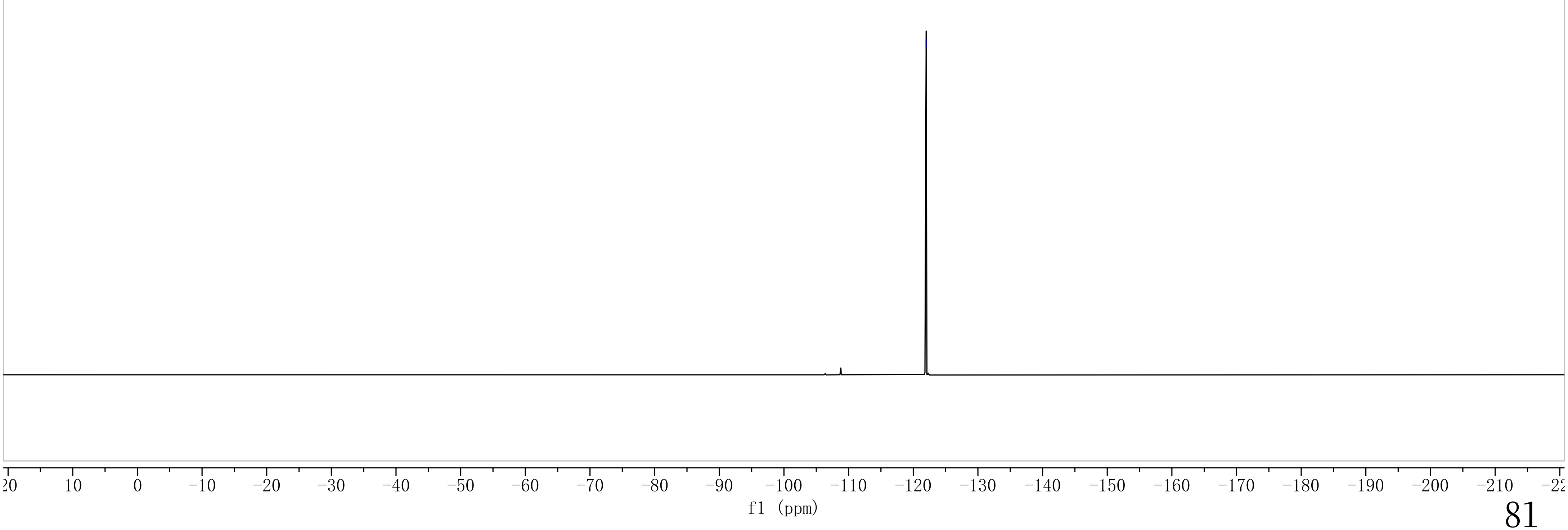

10.328
7.849
7.846
7.835
7.831
7.820
7.816
7.598
7.594
7.588
7.584
7.582
7.580
7.578
7.573
7.571
7.569
7.567
7.563
7.556
7.552
7.251
7.236
7.221
7.156
7.137
7.118
F
O
2n
1H NMR (500 MHz, CDCl3)
0.99
1.00
1.05
1.09
1.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

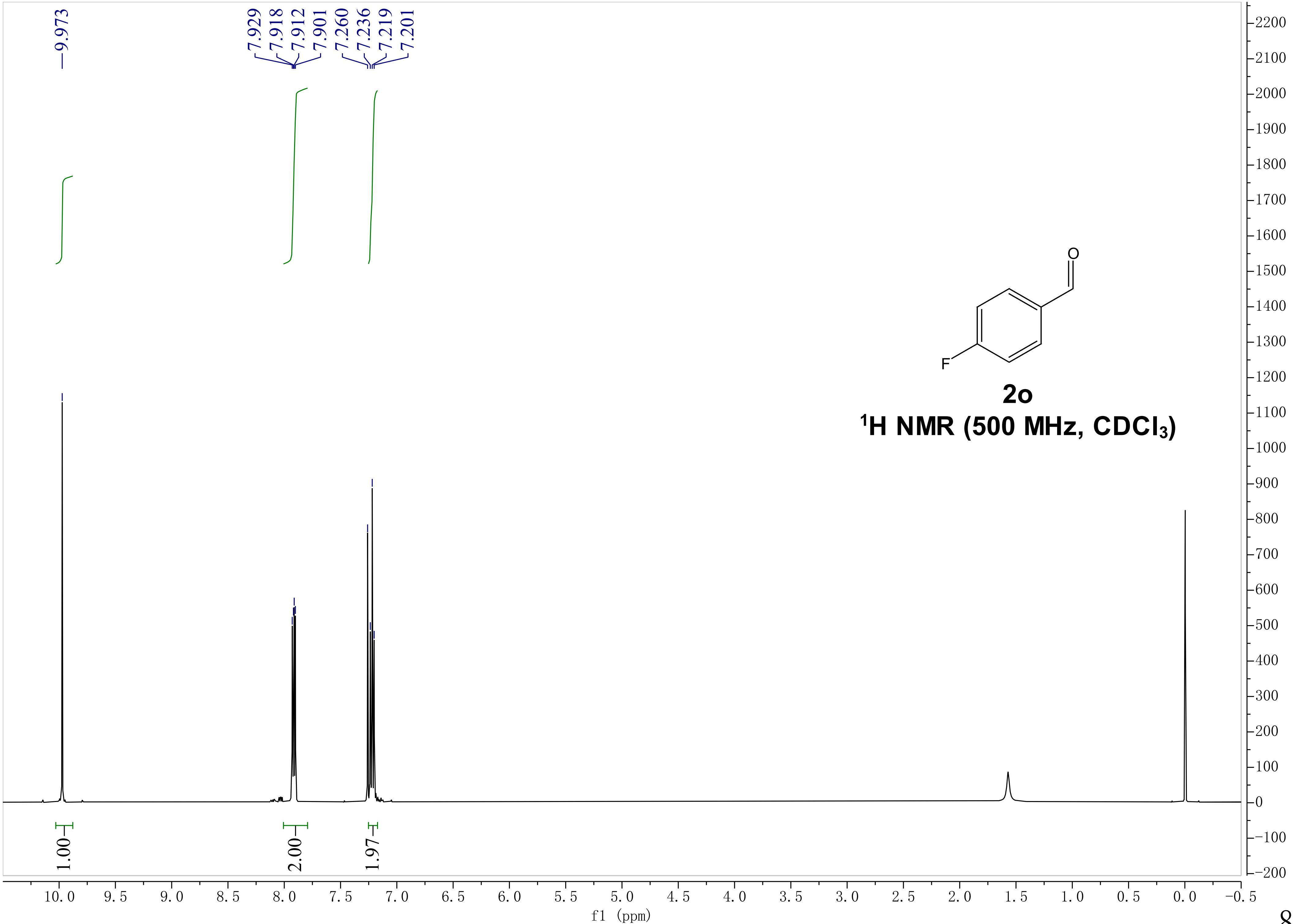

187.254
187.202
165.775
163.718
136.460
136.387
128.774
128.759
124.721
124.691
124.279
124.215
116.649
116.486
77.414
77.160
76.905
F
O
2n
^{13}C NMR (125 MHz, CDCl$_3$)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



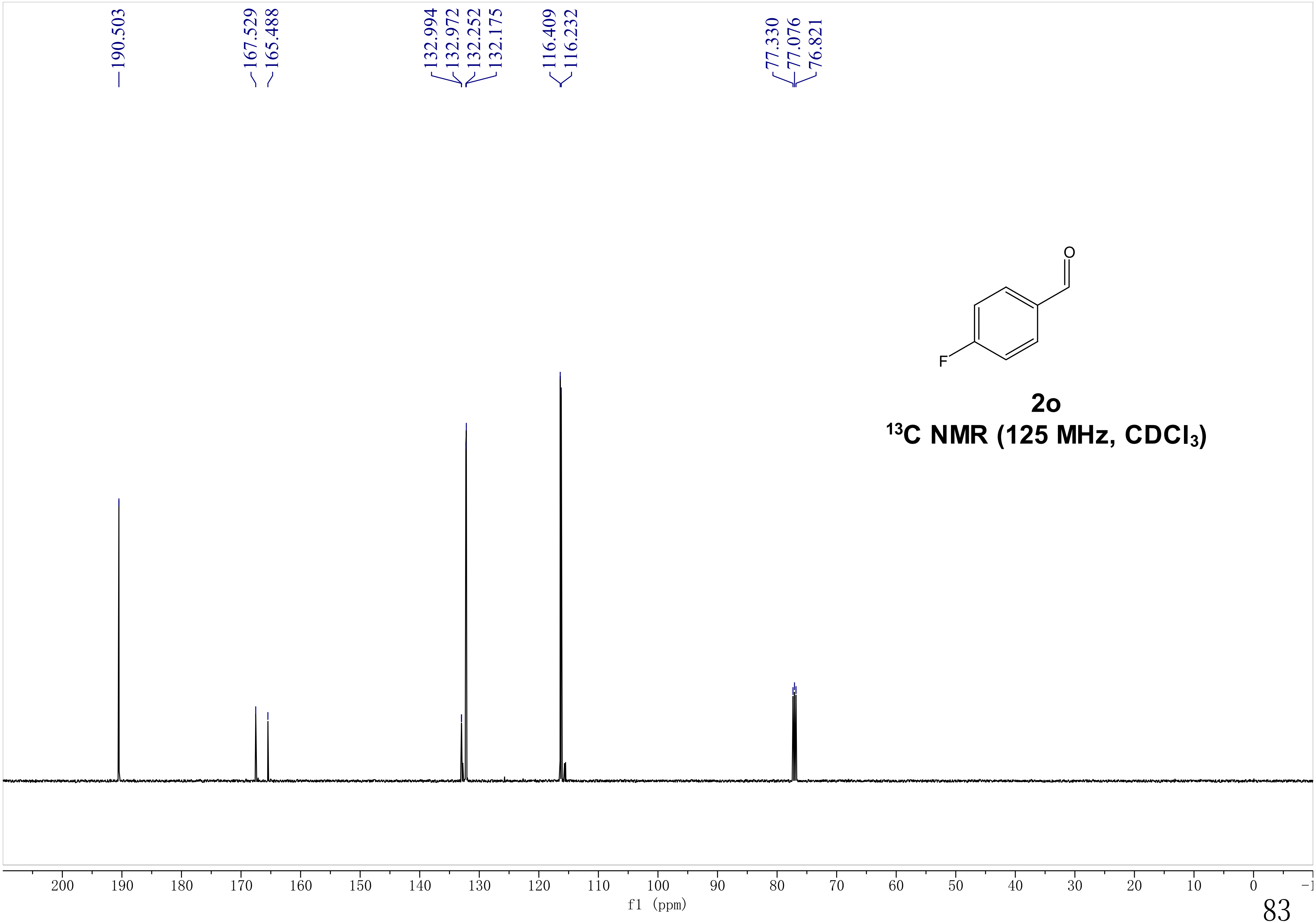
2n

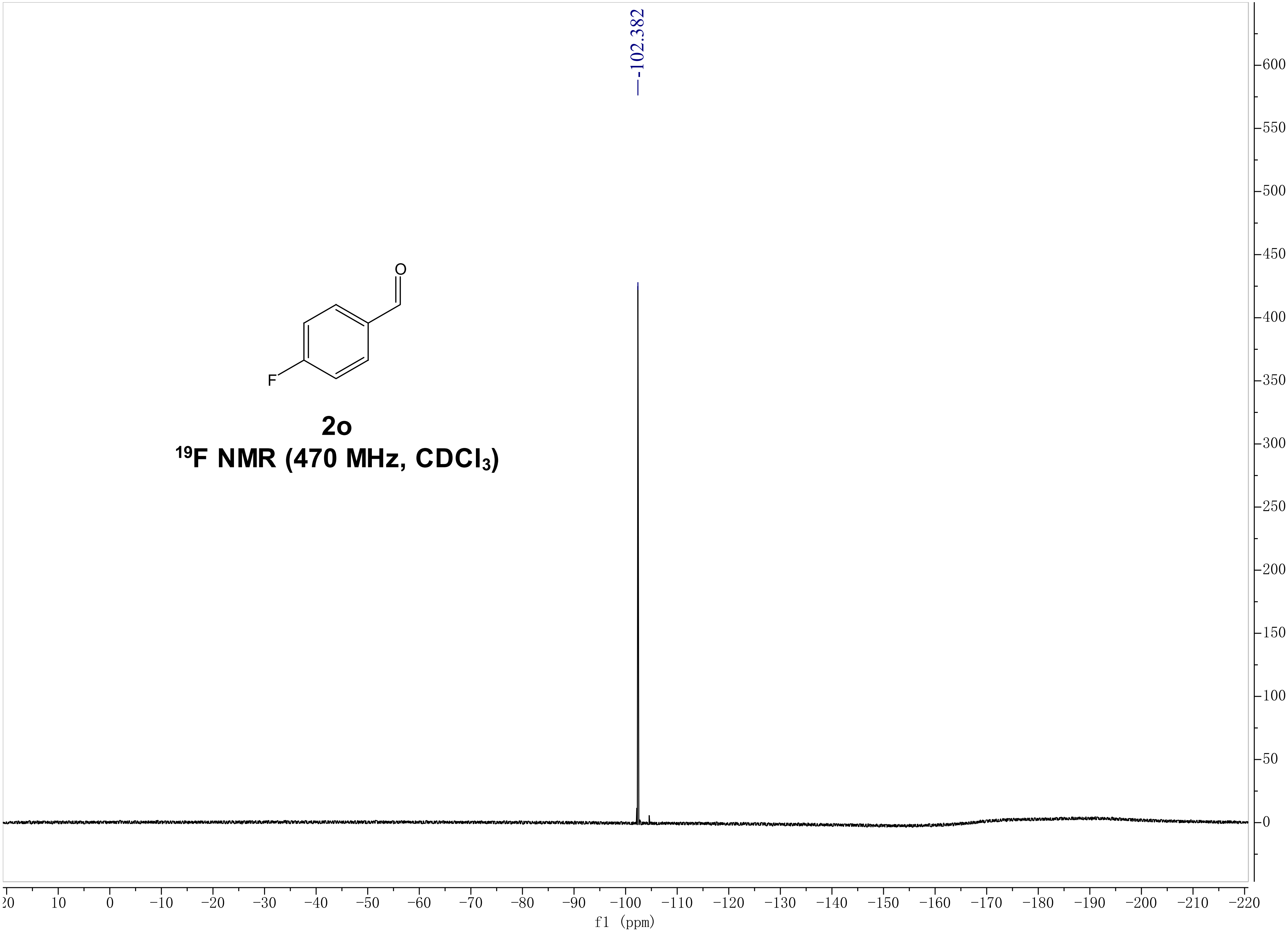
^{19}F NMR (470 MHz, $CDCl_3$)





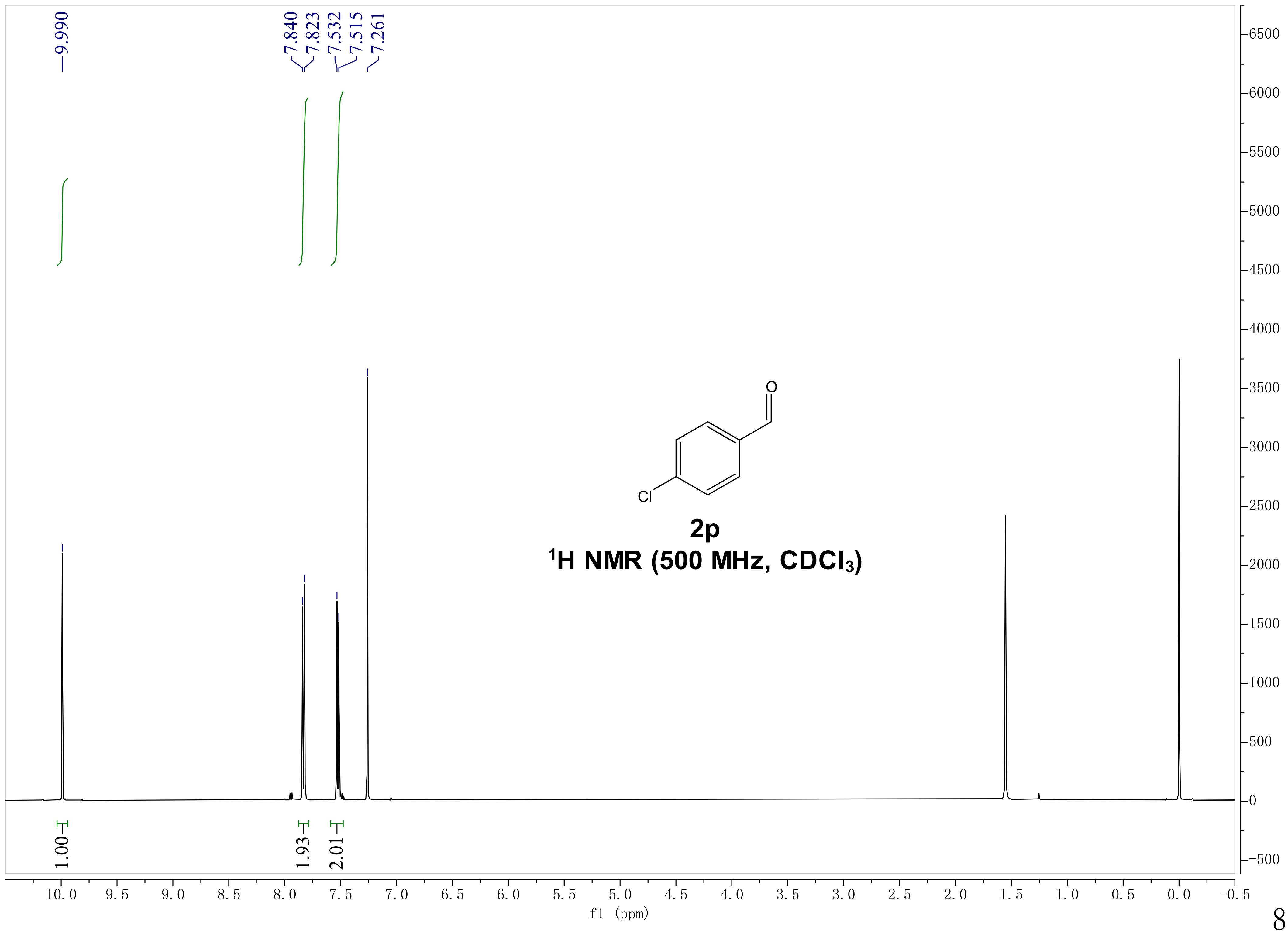
9.973
7.929
7.918
7.912
7.901
7.260
7.236
7.219
7.201
O
F
2o
¹H NMR (500 MHz, CDCl₃)
1.00
2.00
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


190.503
167.529
165.488
132.994
132.972
132.252
132.175
116.409
116.232
77.330
77.076
76.821
O
F
2o
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

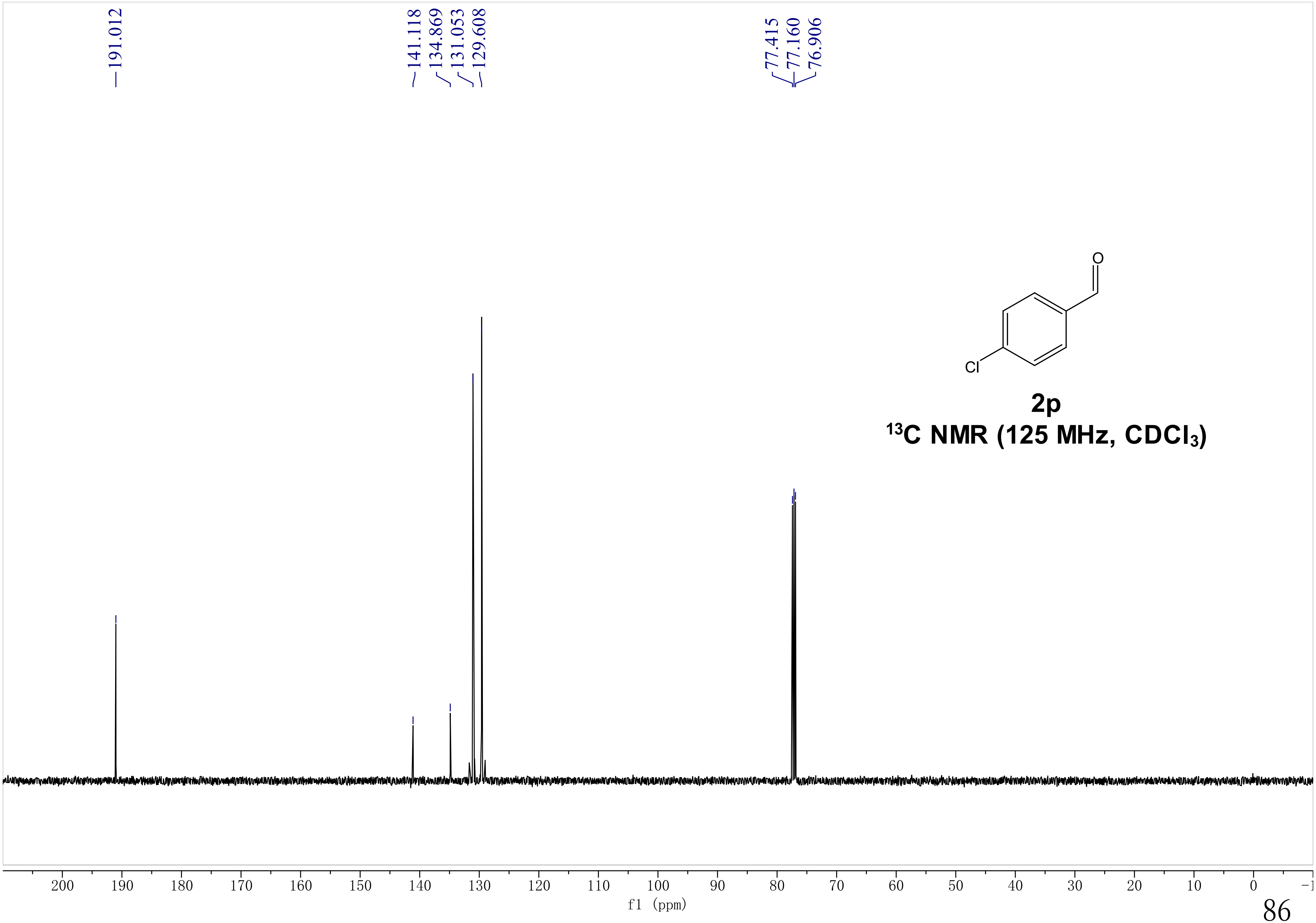


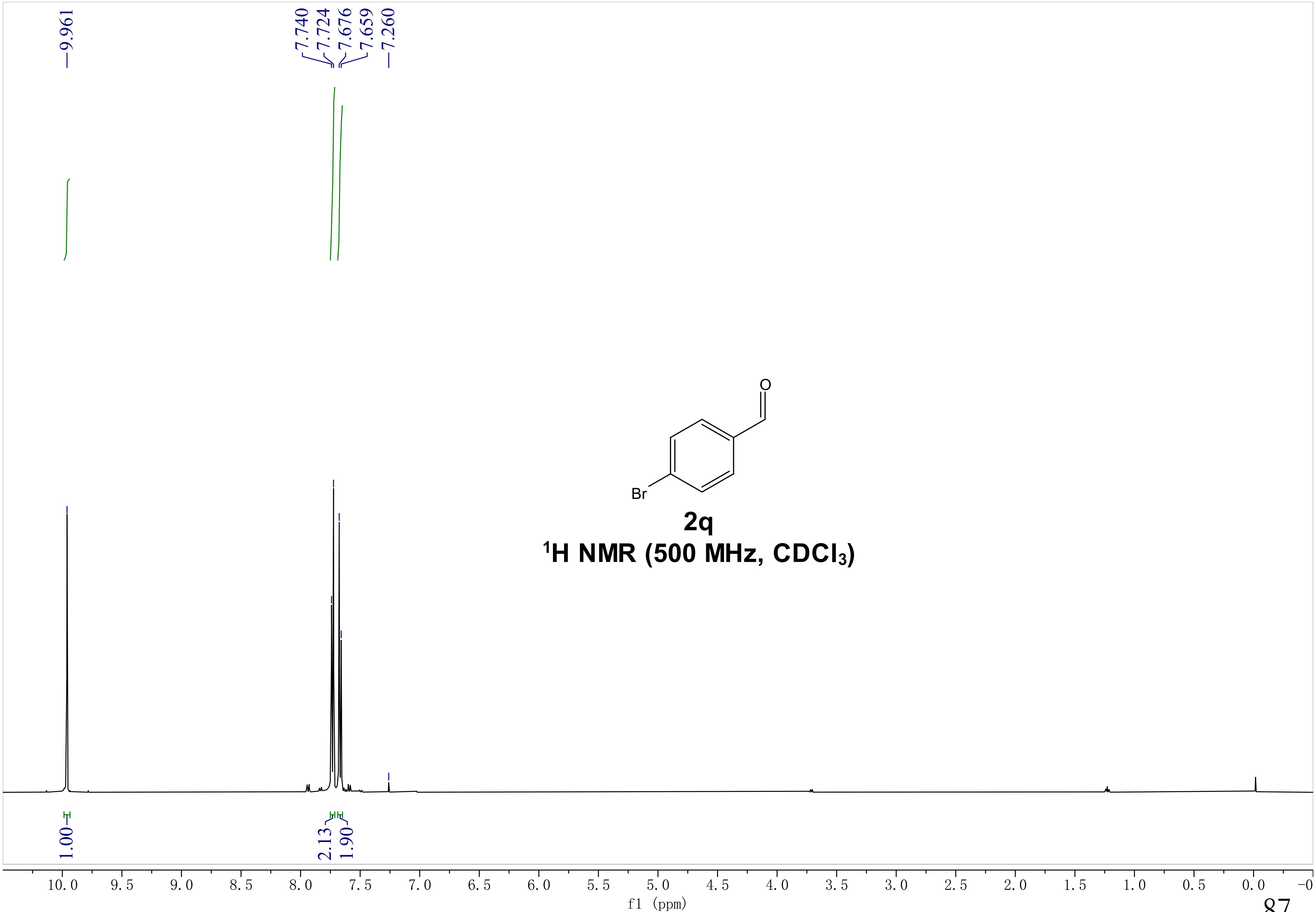
2o

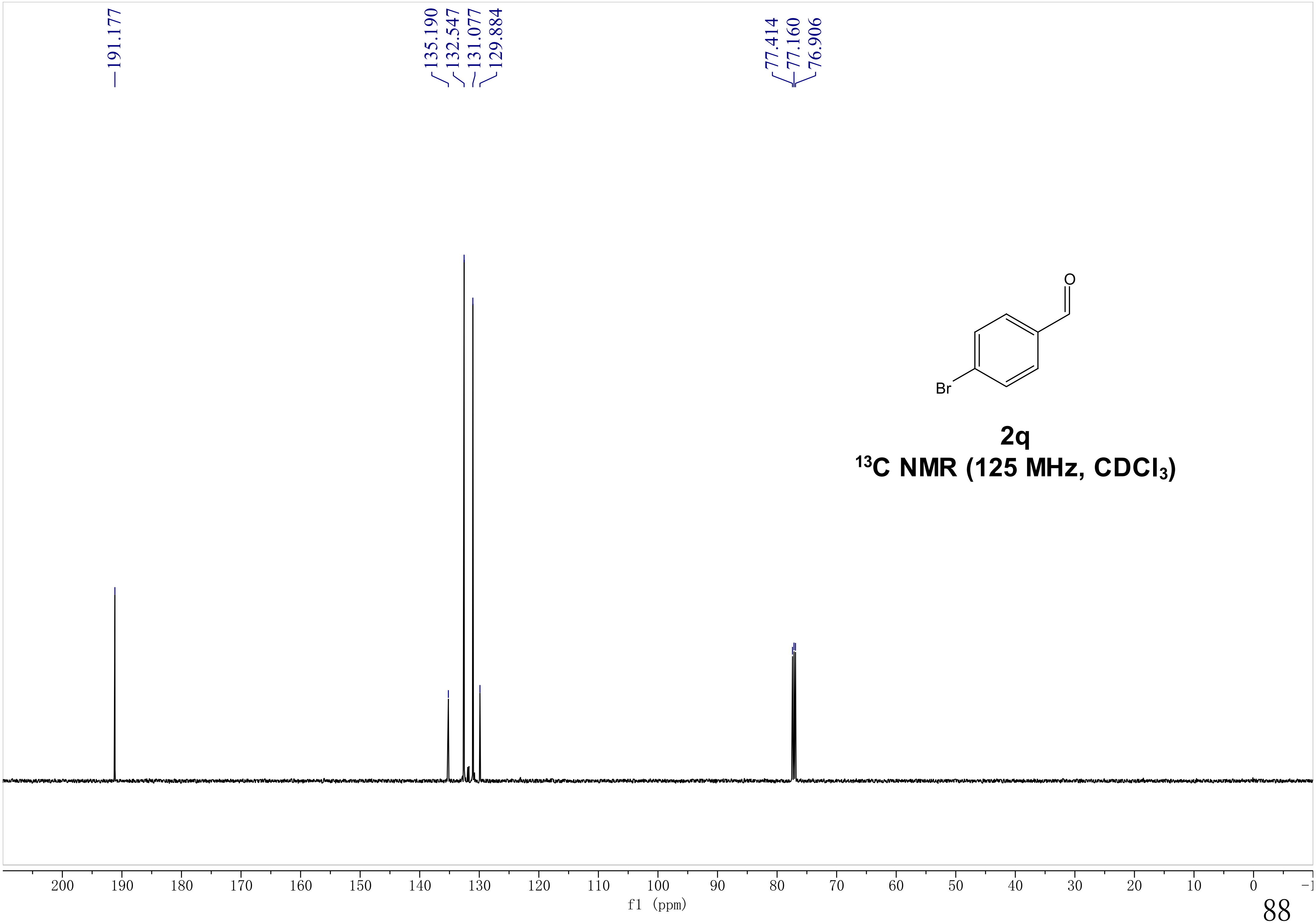
^{19}F NMR (470 MHz, $CDCl_3$)

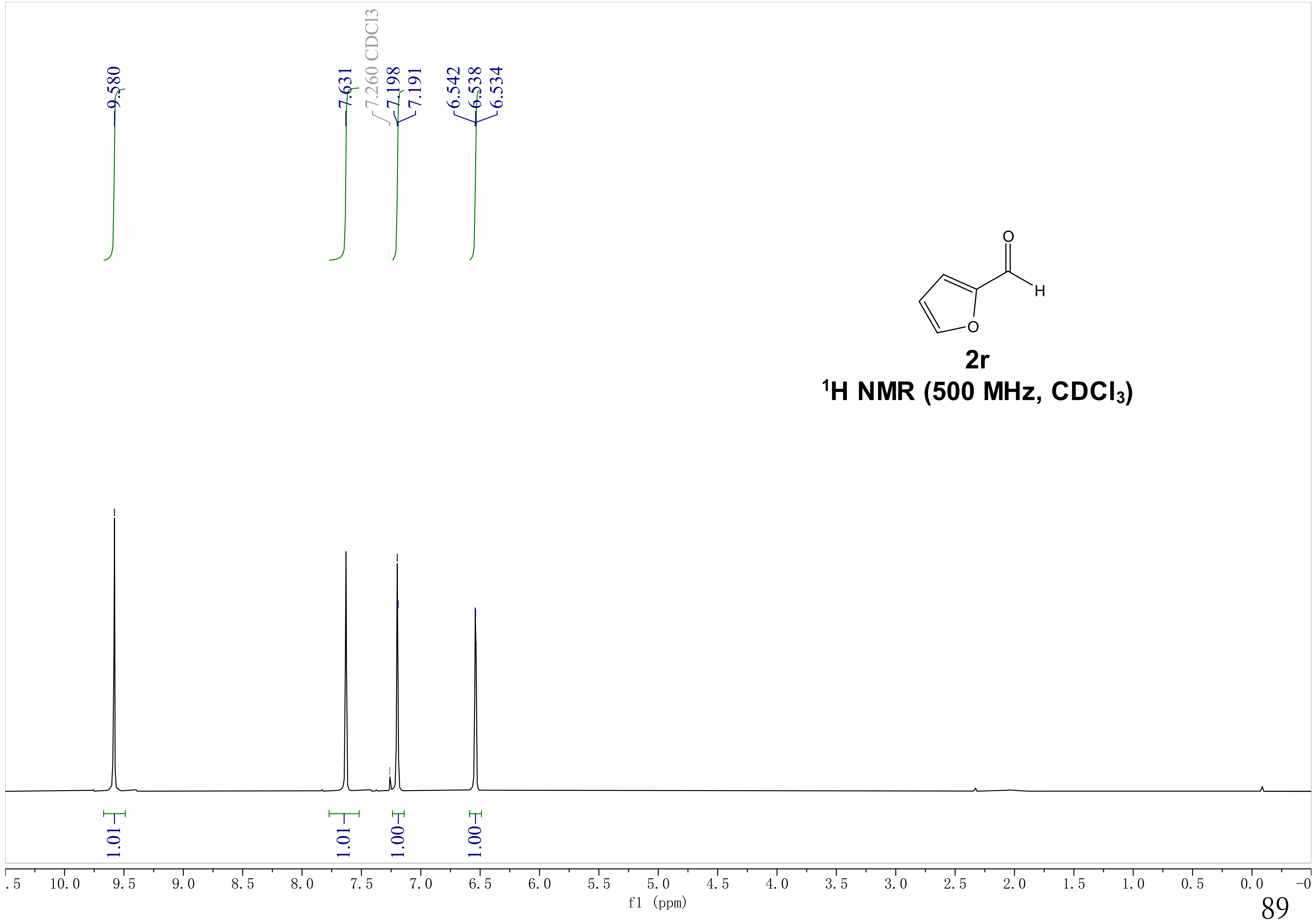


9.990
7.840
7.823
7.532
7.515
7.261
O
Cl
2p
1H NMR (500 MHz, CDCl3)
1.00
1.93
2.01
f1 (ppm)


191.012
141.118
134.869
131.053
129.608
77.415
77.160
76.906
O
Cl
2p
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

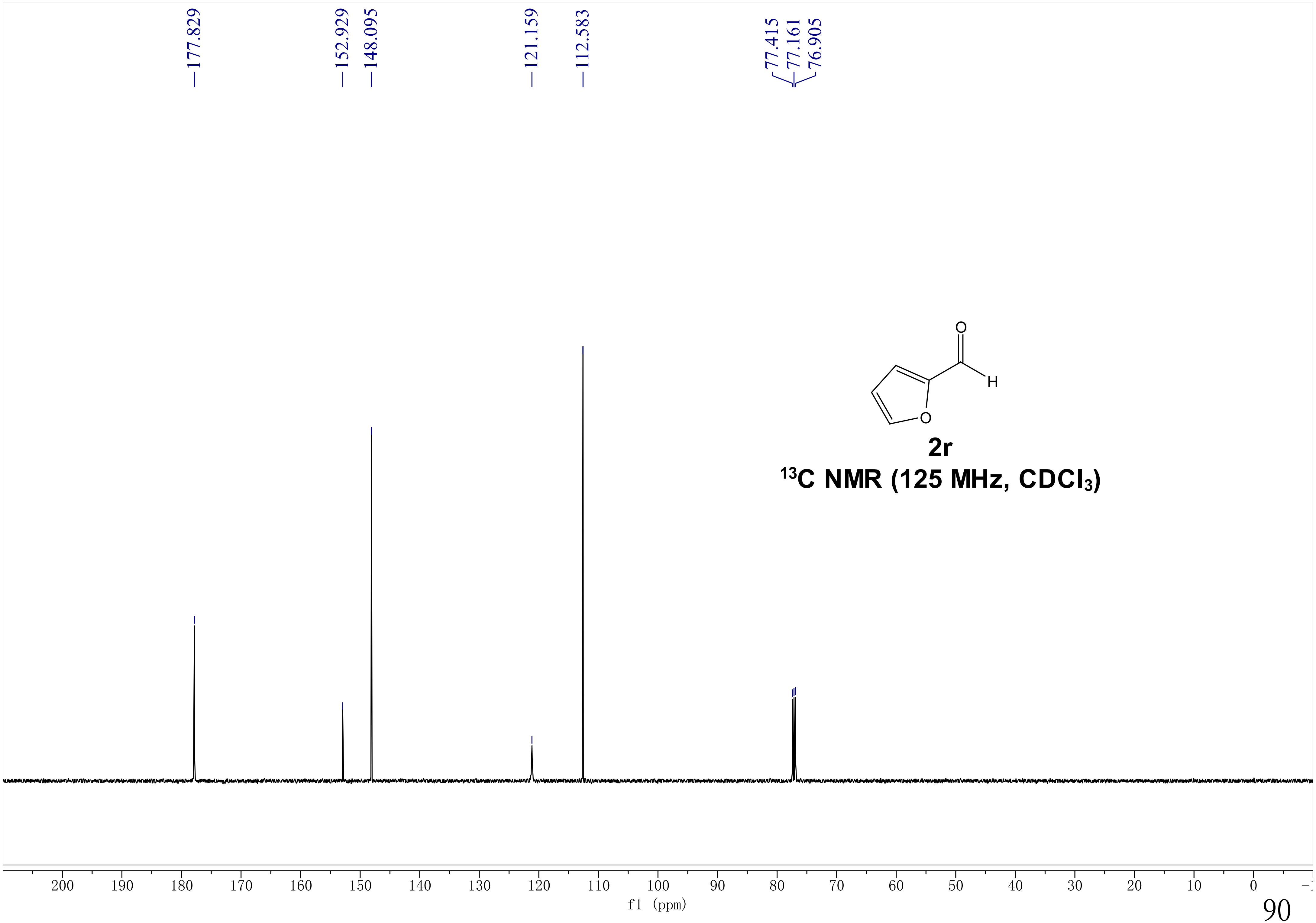

9.961
7.740
7.724
7.676
7.659
7.260
O
Br
2q
1H NMR (500 MHz, CDCl3)
1.00
2.13
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

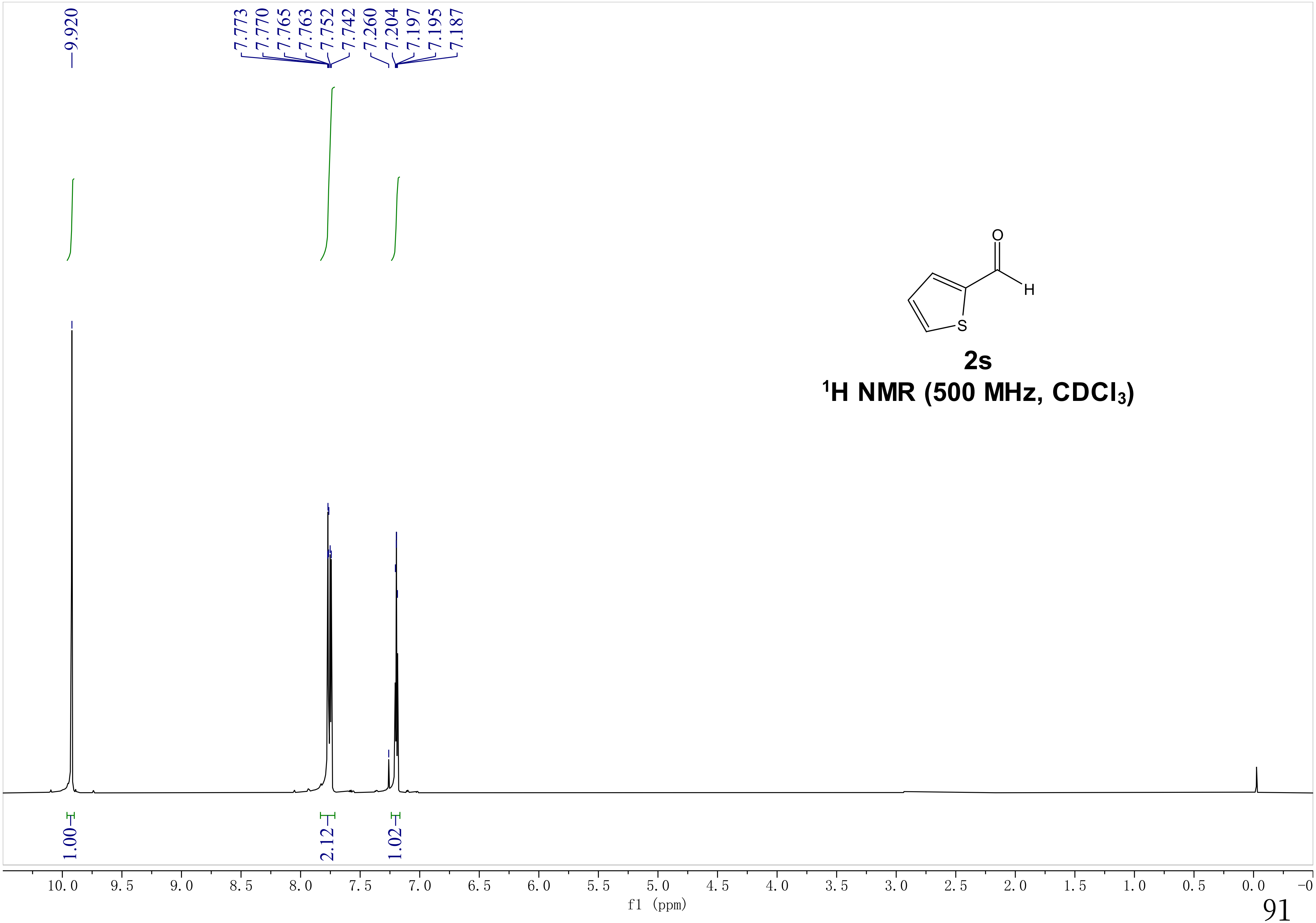

191.177
135.190
132.547
131.077
129.884
77.414
77.160
76.906
O
Br
2q
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



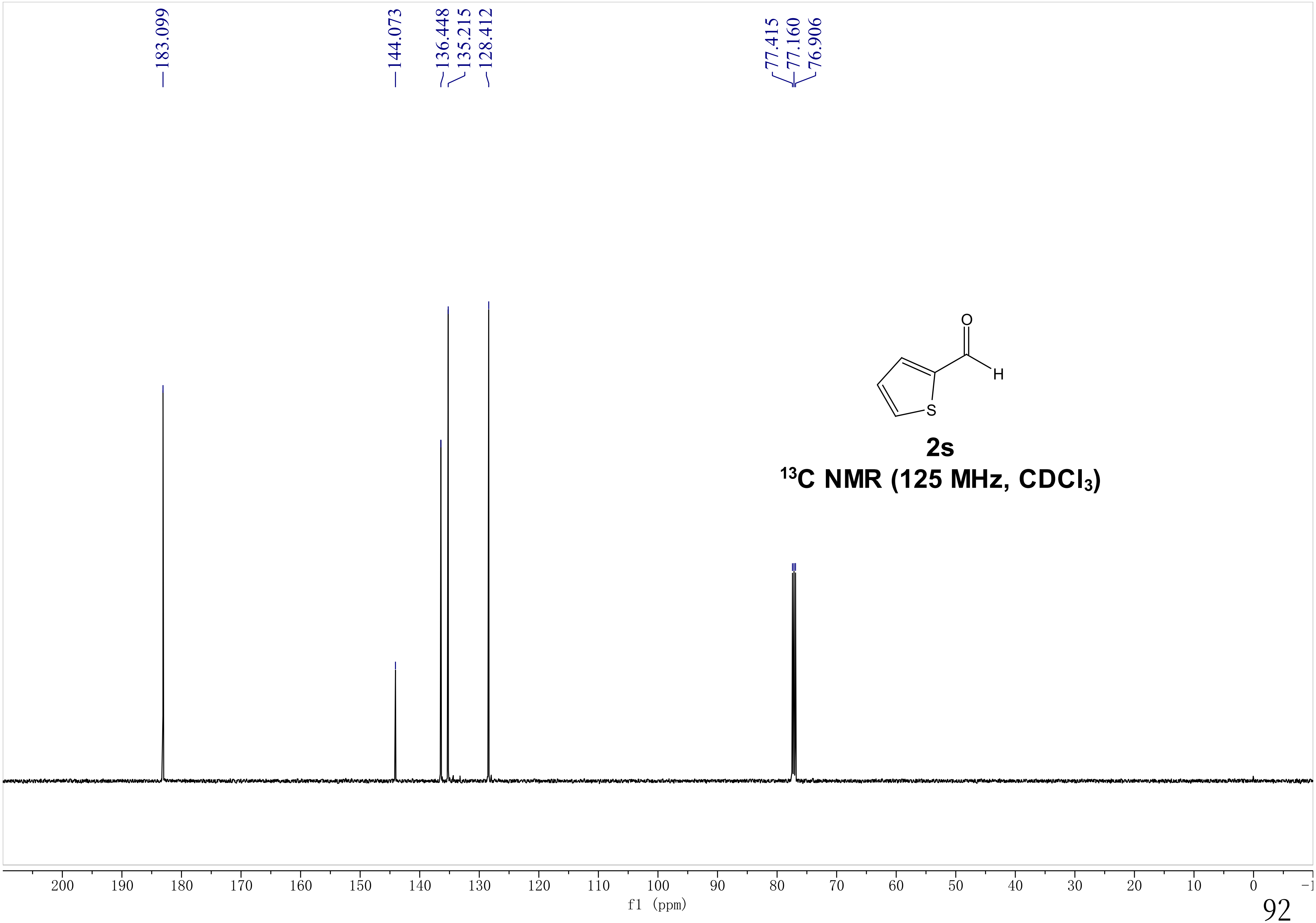
2r

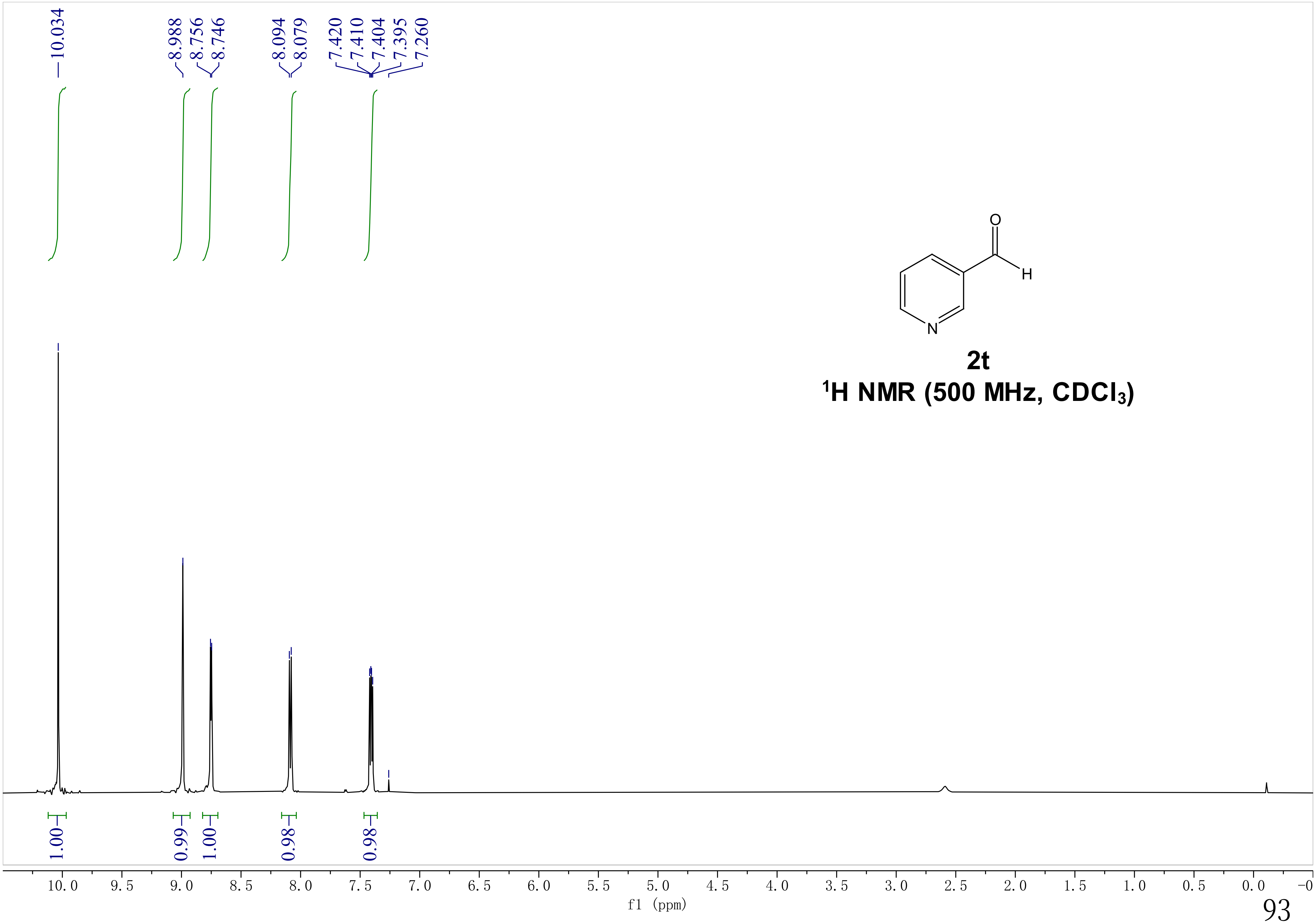
^1H NMR (500 MHz, $CDCl_3$)

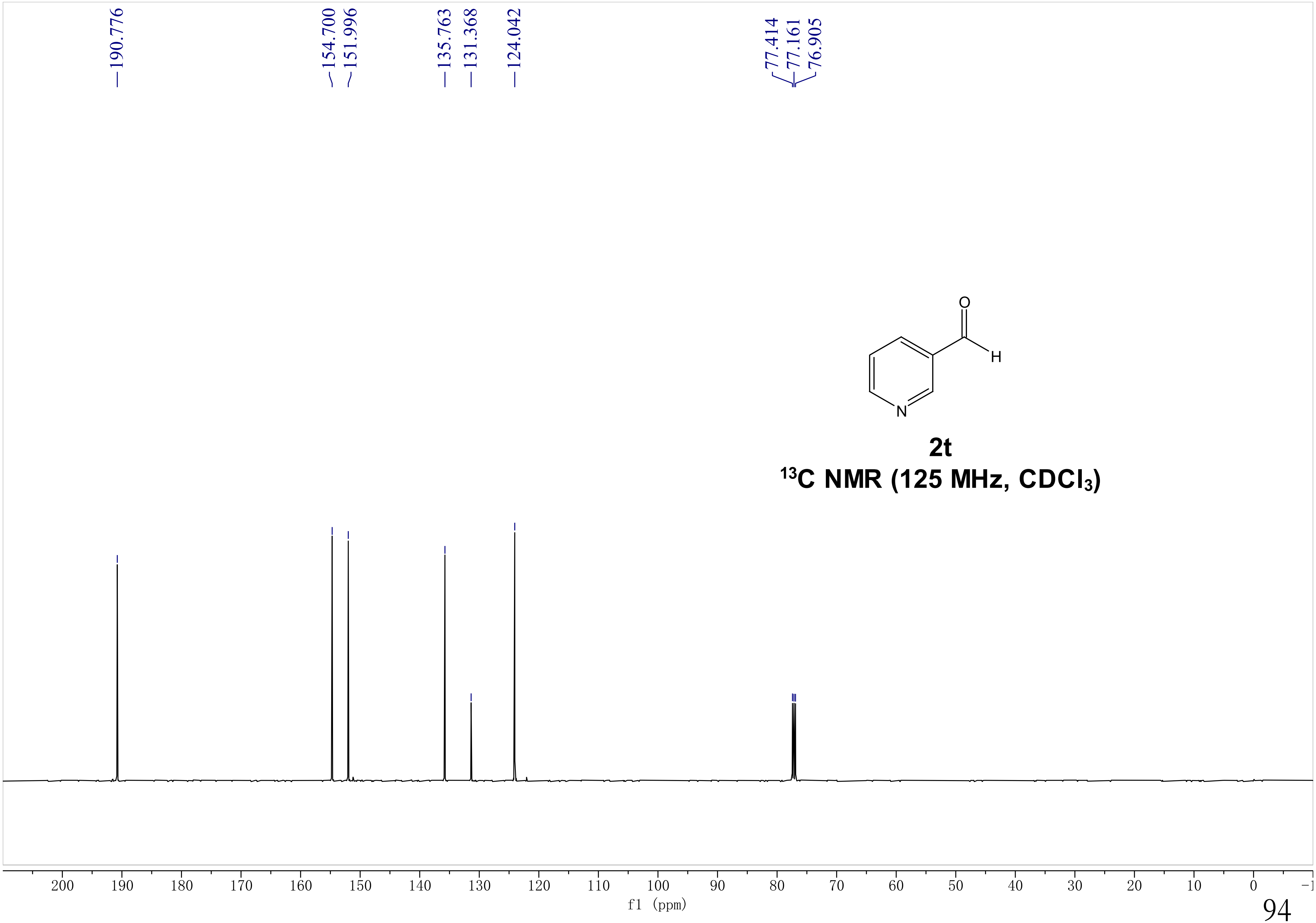

177.829
152.929
148.095
121.159
112.583
77.415
77.161
76.905
O
H
O
2r
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



9.920
7.773
7.770
7.765
7.763
7.752
7.742
7.260
7.204
7.197
7.195
7.187
O
H
S
2s
¹H NMR (500 MHz, CDCl₃)
1.00
2.12
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

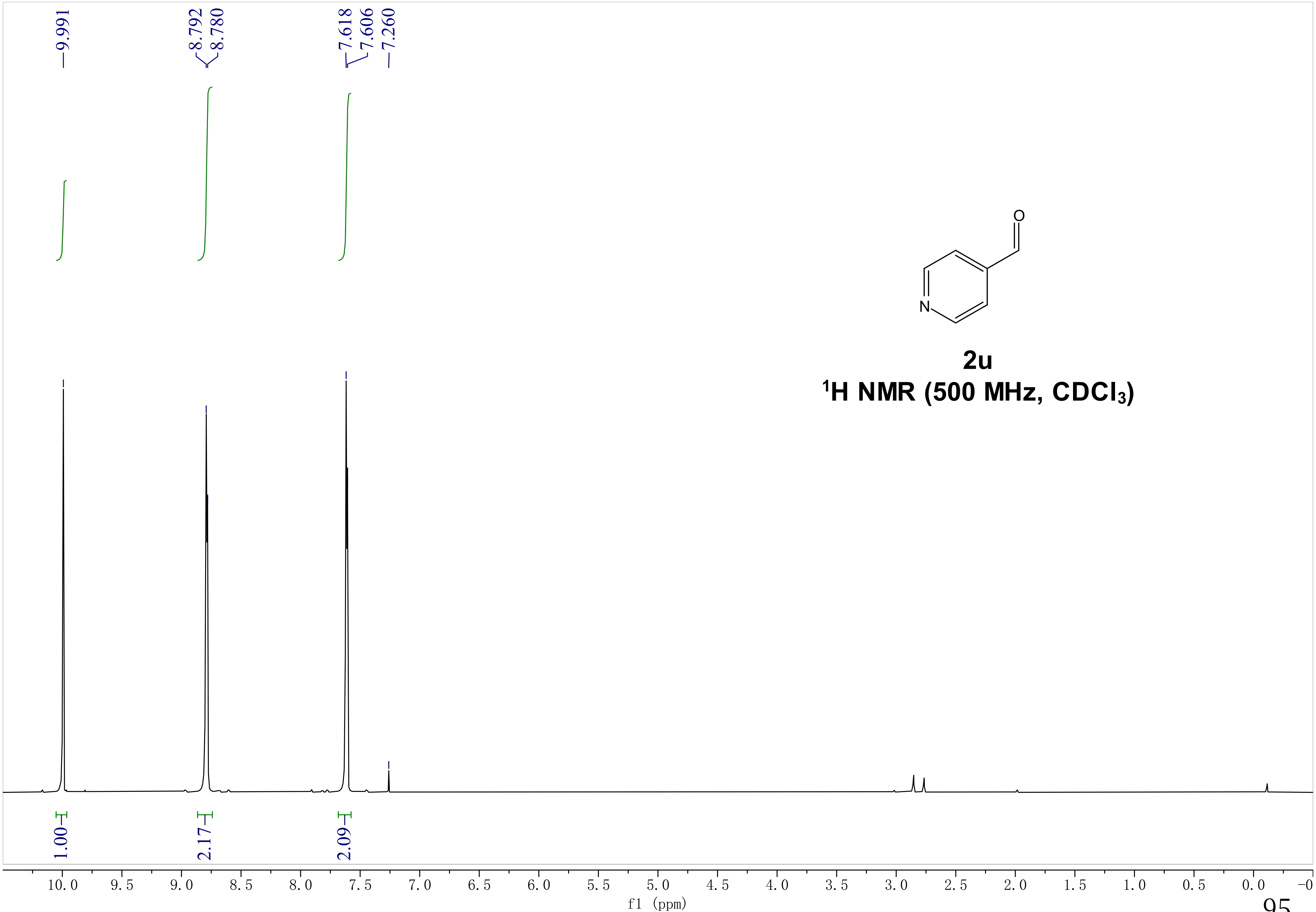

183.099
144.073
136.448
135.215
128.412
77.415
77.160
76.906
O
H
S
2s
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.034
8.988
8.756
8.746
8.094
8.079
7.420
7.410
7.404
7.395
7.260
O
H
N
2t
^{1}H NMR (500 MHz, $CDCl_3$)
1.00
0.99
1.00
0.98
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



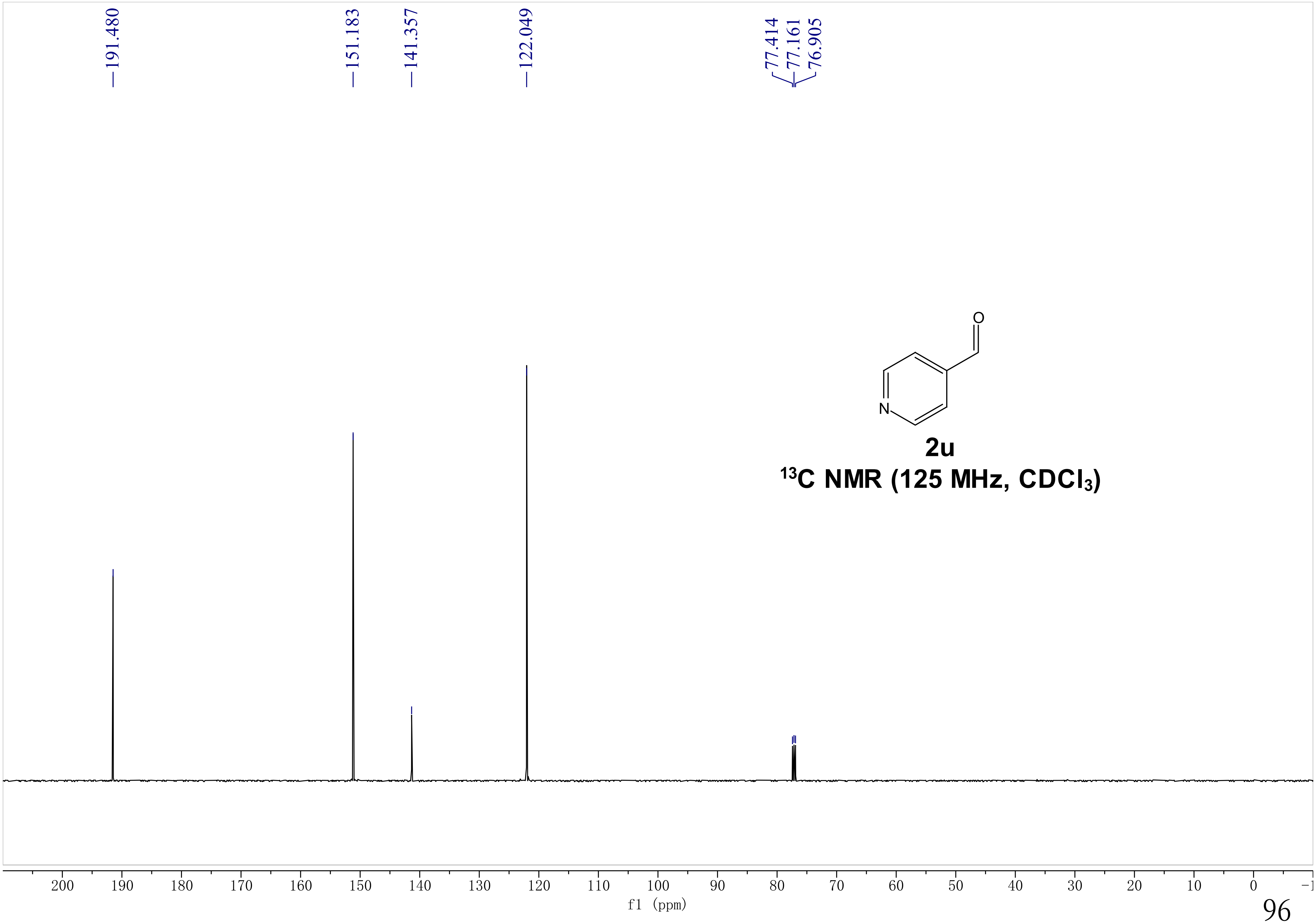
2t

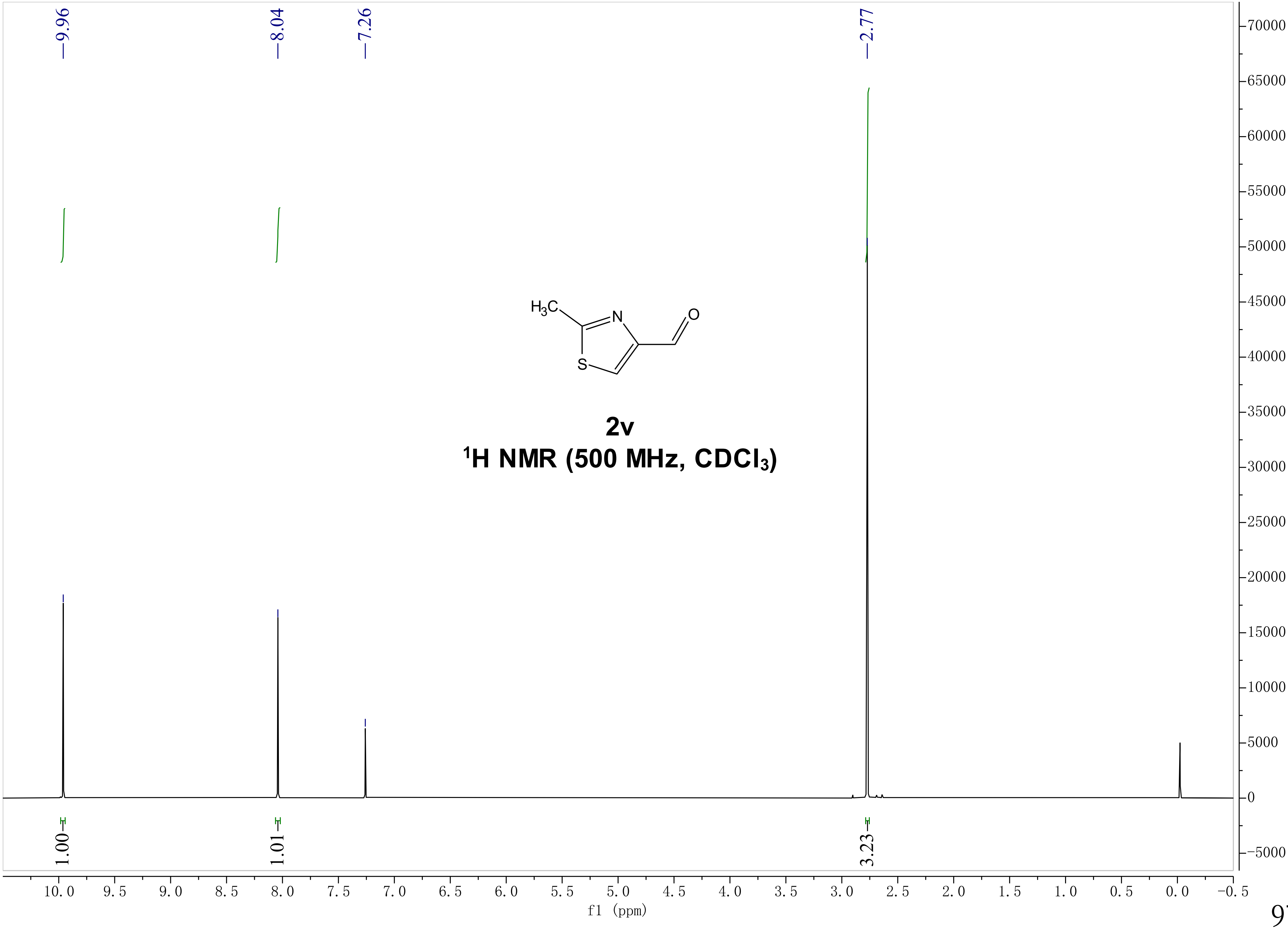
^{13}C NMR (125 MHz, $CDCl_3$)



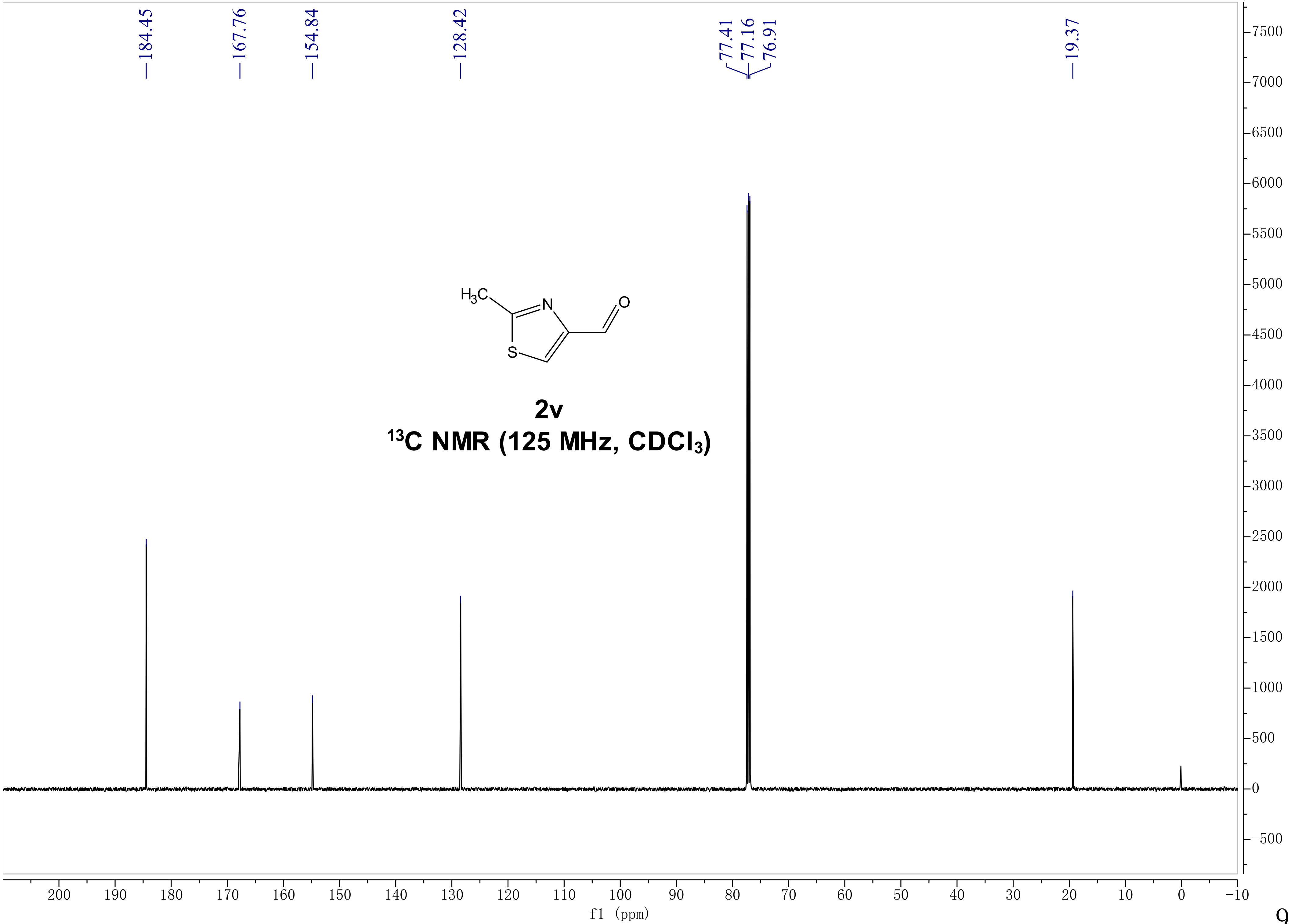
2u

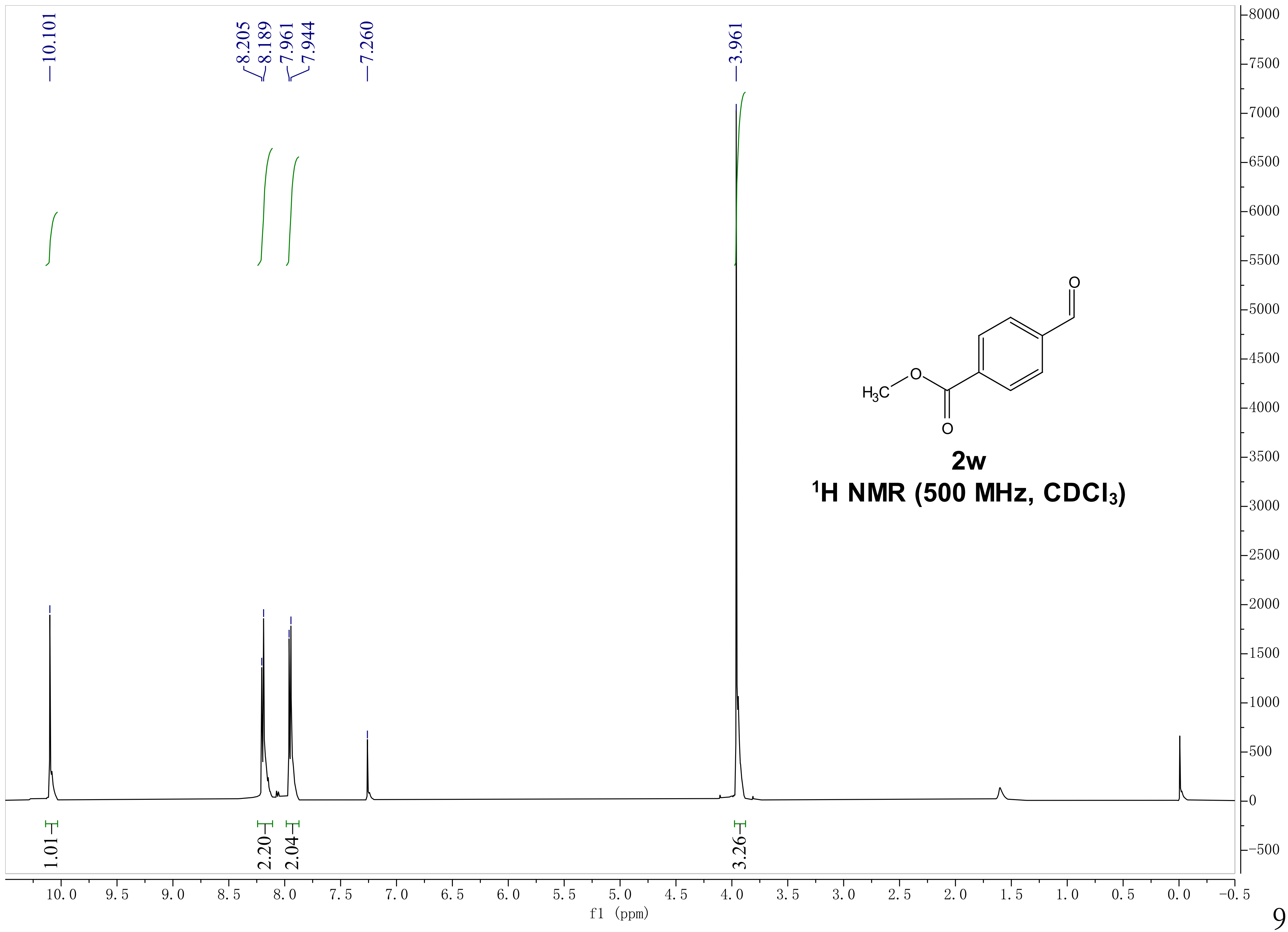
^{1}H NMR (500 MHz, $CDCl_3$)

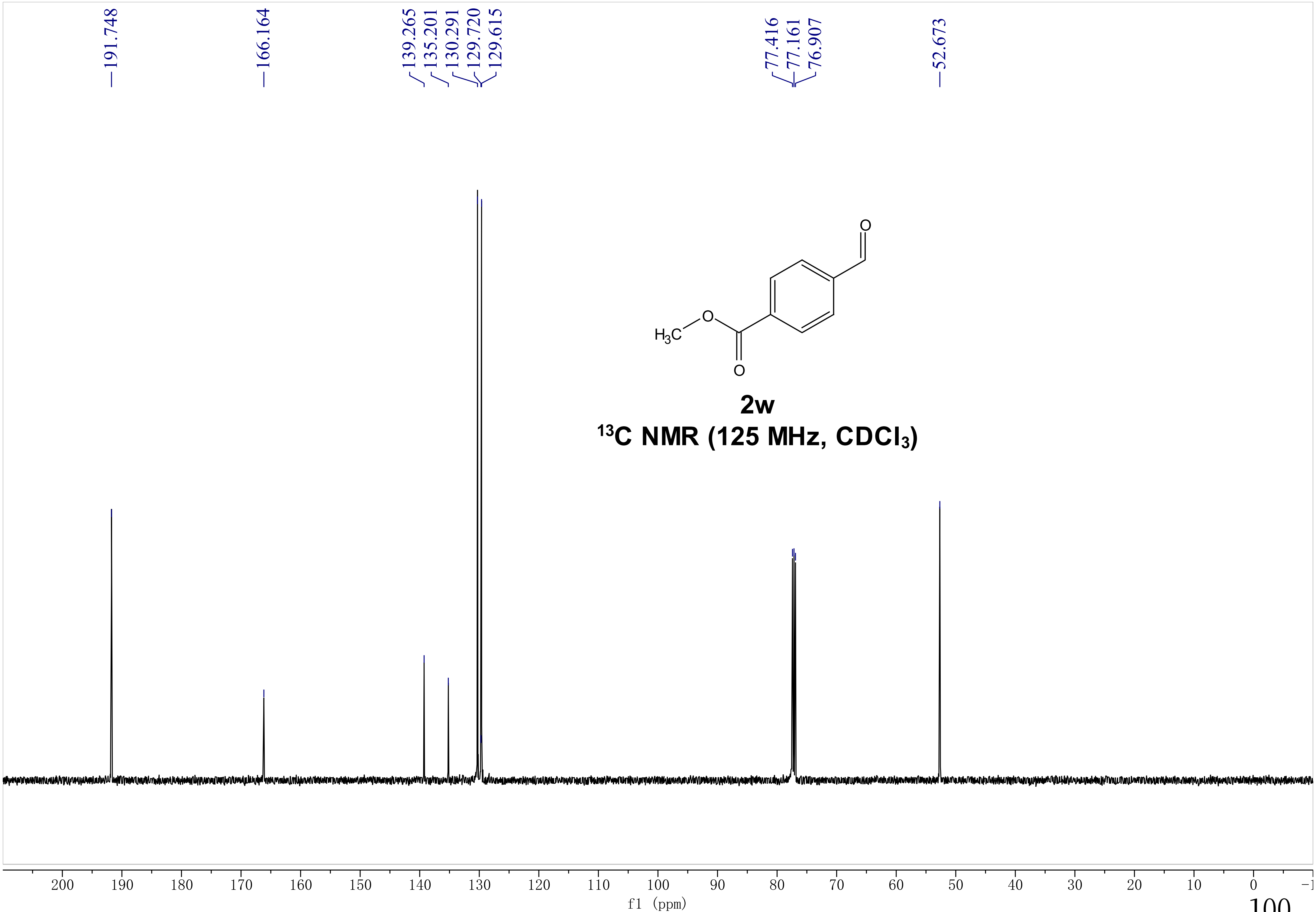

191.480
151.183
141.357
122.049
77.414
77.161
76.905
O
N
2u
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

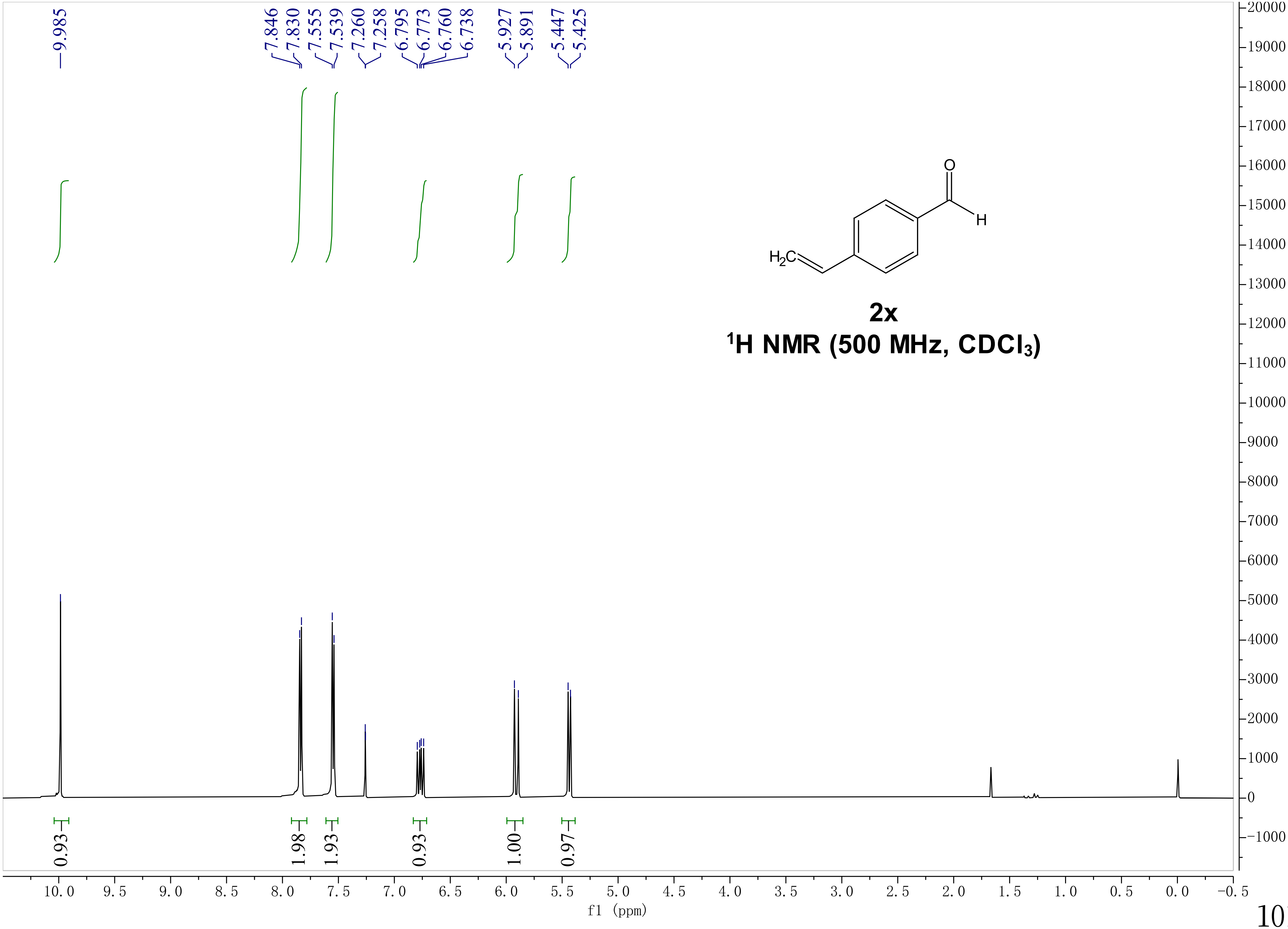


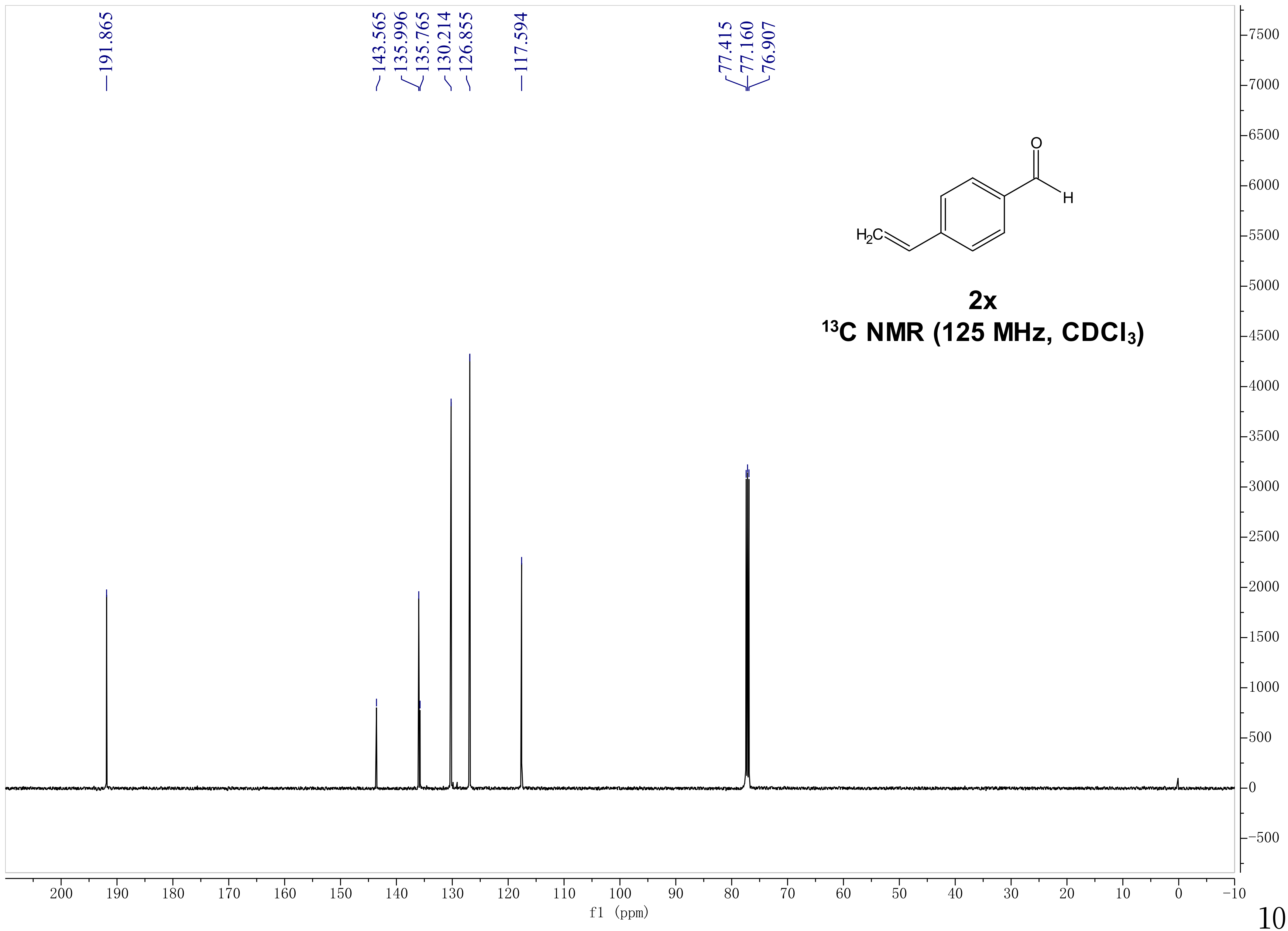
2v
¹H NMR (500 MHz, CDCl3)
H3C
N
O
S
9.96
8.04
7.26
2.77
1.00
1.01
3.23
f1 (ppm)

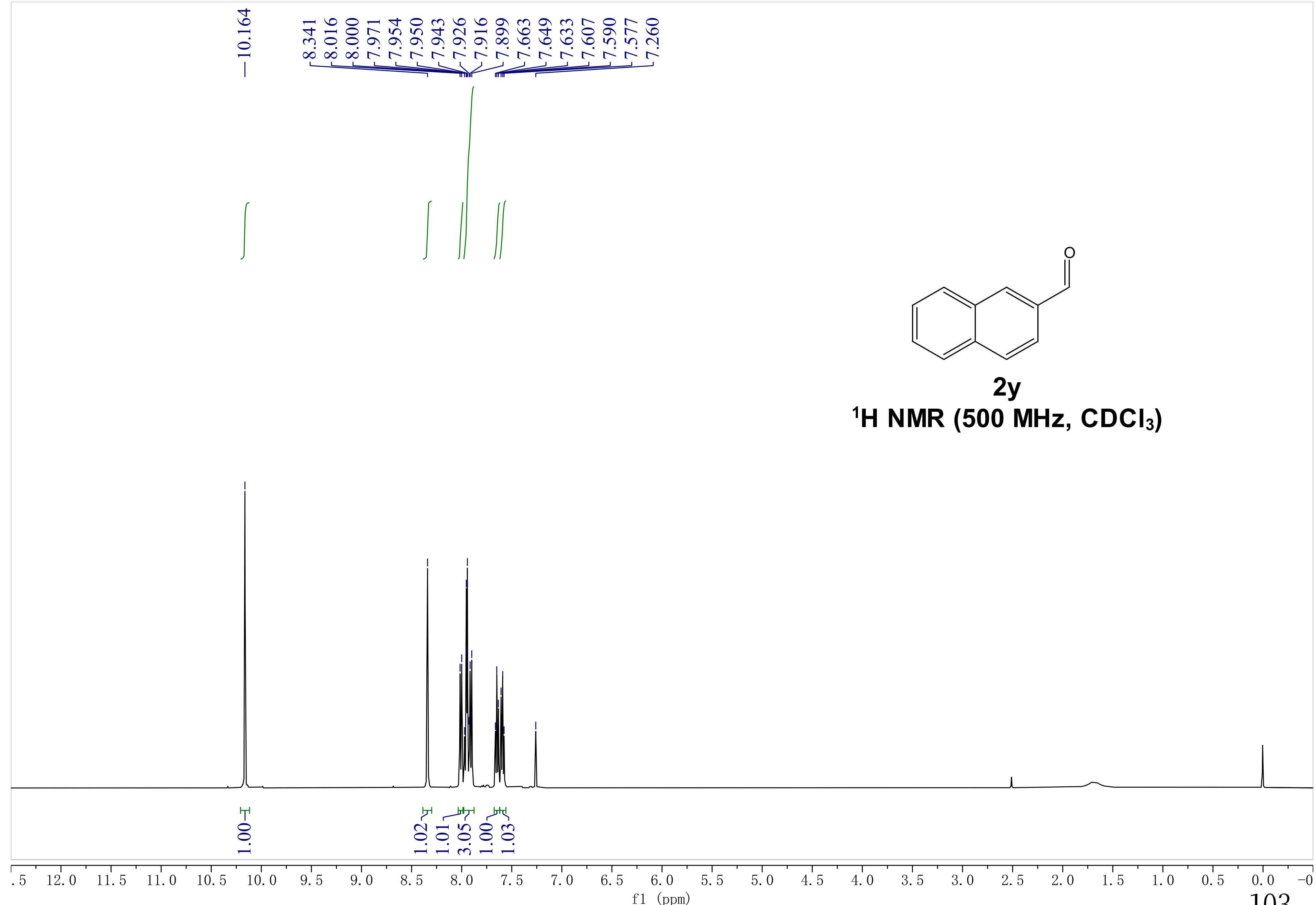

184.45
167.76
154.84
128.42
77.41
77.16
76.91
19.37
H3C
N
O
S
2v
13C NMR (125 MHz, CDCl3)
f1 (ppm)

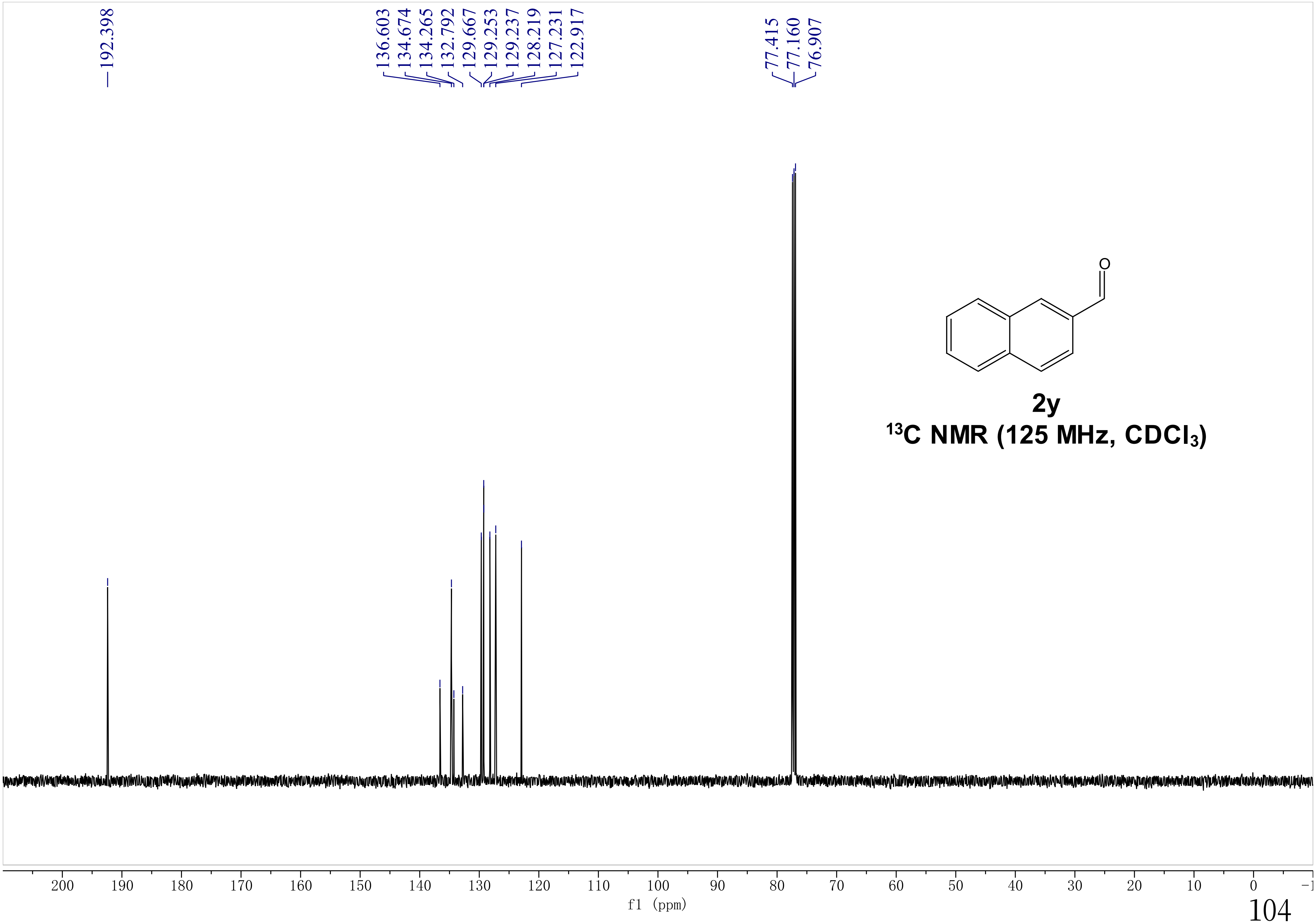

10.101
8.205
8.189
7.961
7.944
7.260
3.961
H3C
O
O
O
2w
1H NMR (500 MHz, CDCl3)
1.01
2.20
2.04
3.26
f1 (ppm)

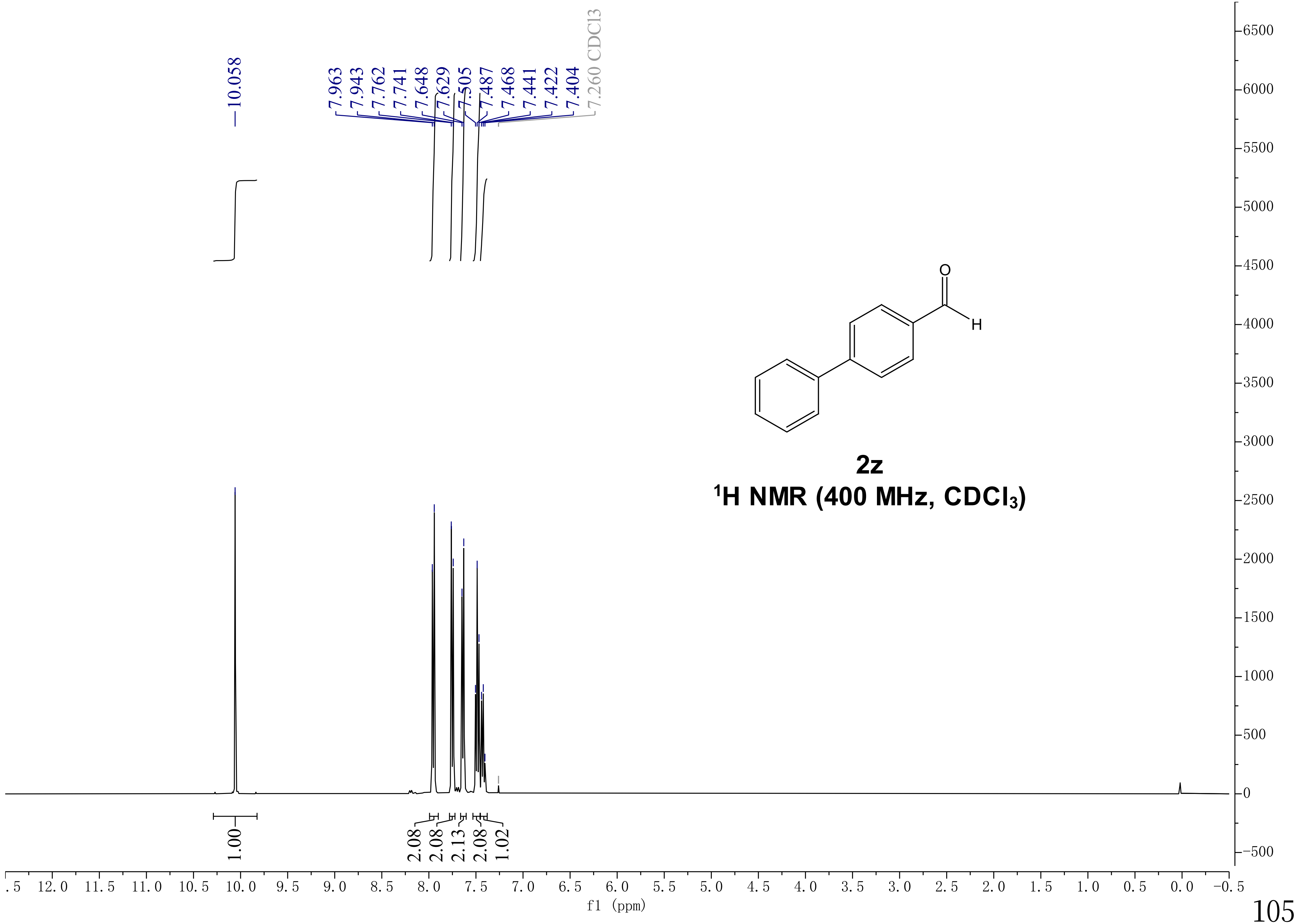

191.748
166.164
139.265
135.201
130.291
129.720
129.615
77.416
77.161
76.907
52.673
O
H3C
O
O
2w
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

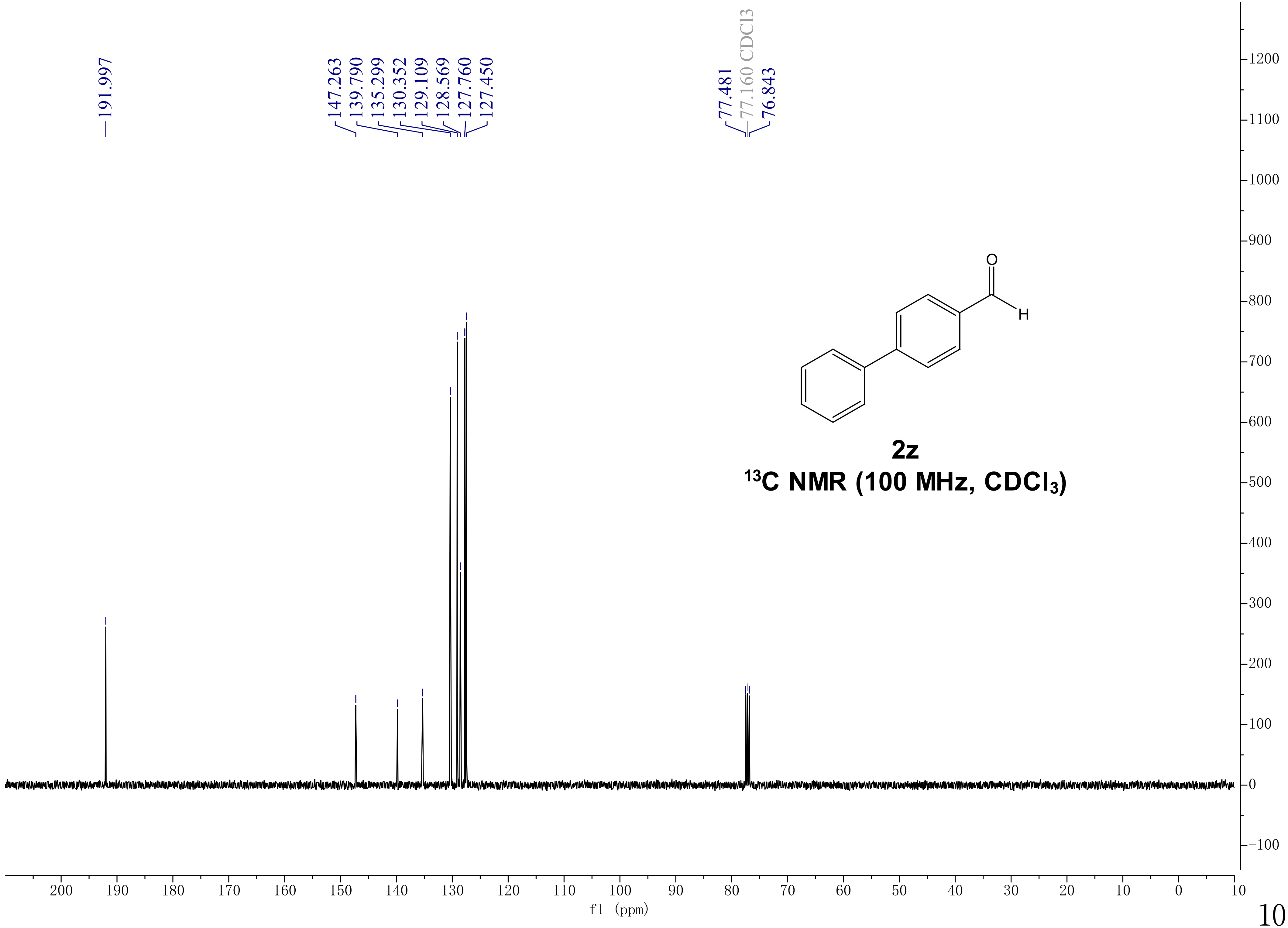

9.985
7.846
7.830
7.555
7.539
7.260
7.258
6.795
6.773
6.760
6.738
5.927
5.891
5.447
5.425
2x
1H NMR (500 MHz, CDCl3)
0.93
1.98
1.93
0.93
1.00
0.97
f1 (ppm)

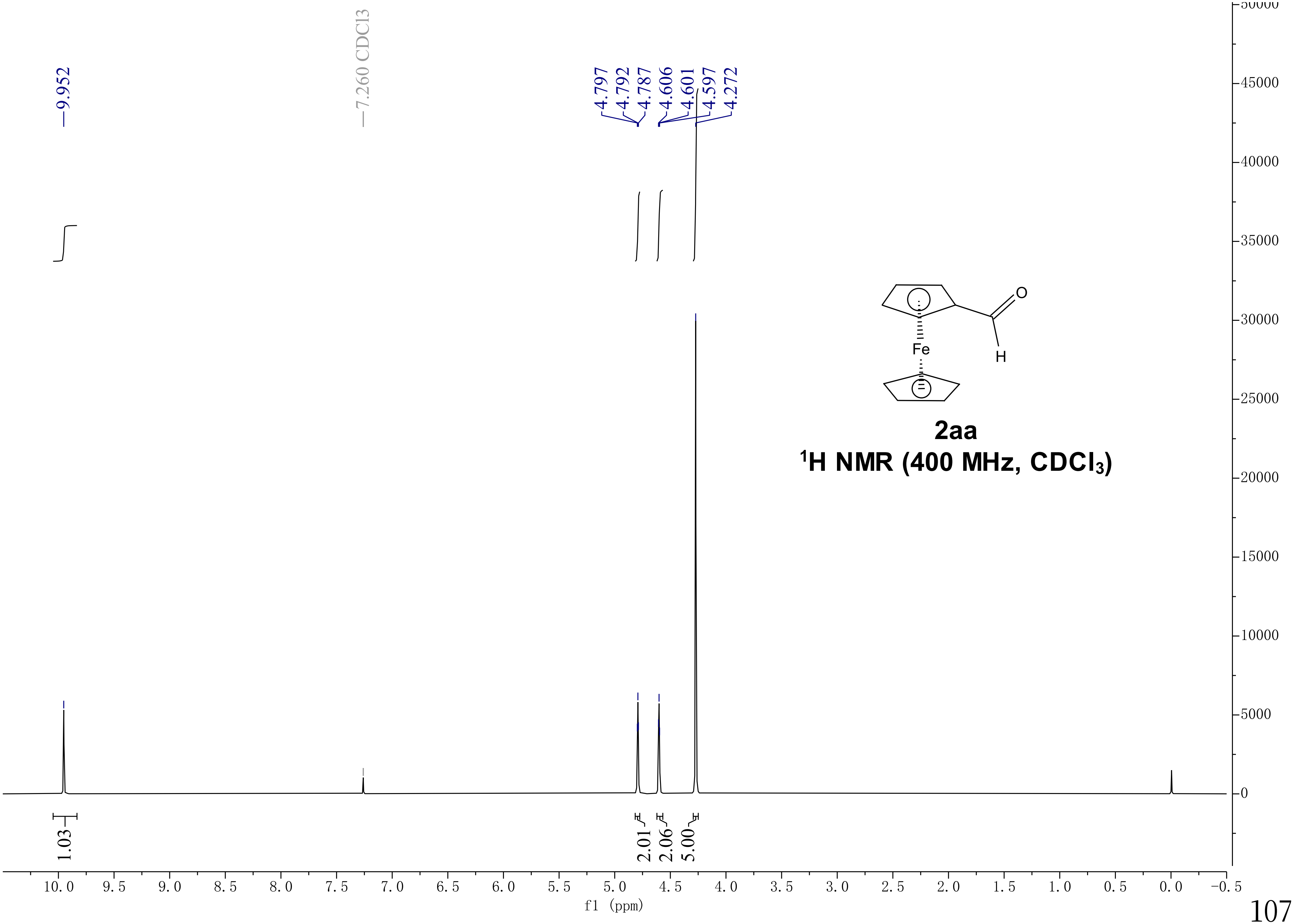

191.865
143.565
135.996
135.765
130.214
126.855
117.594
77.415
77.160
76.907
O
H
H2C
2x
13C NMR (125 MHz, CDCl3)
f1 (ppm)


10.164
8.341
8.016
8.000
7.971
7.954
7.950
7.943
7.926
7.916
7.899
7.663
7.649
7.633
7.607
7.590
7.577
7.260
O
2y
1H NMR (500 MHz, CDCl3)
1.00
1.02
1.01
3.05
1.00
1.03
f1 (ppm)

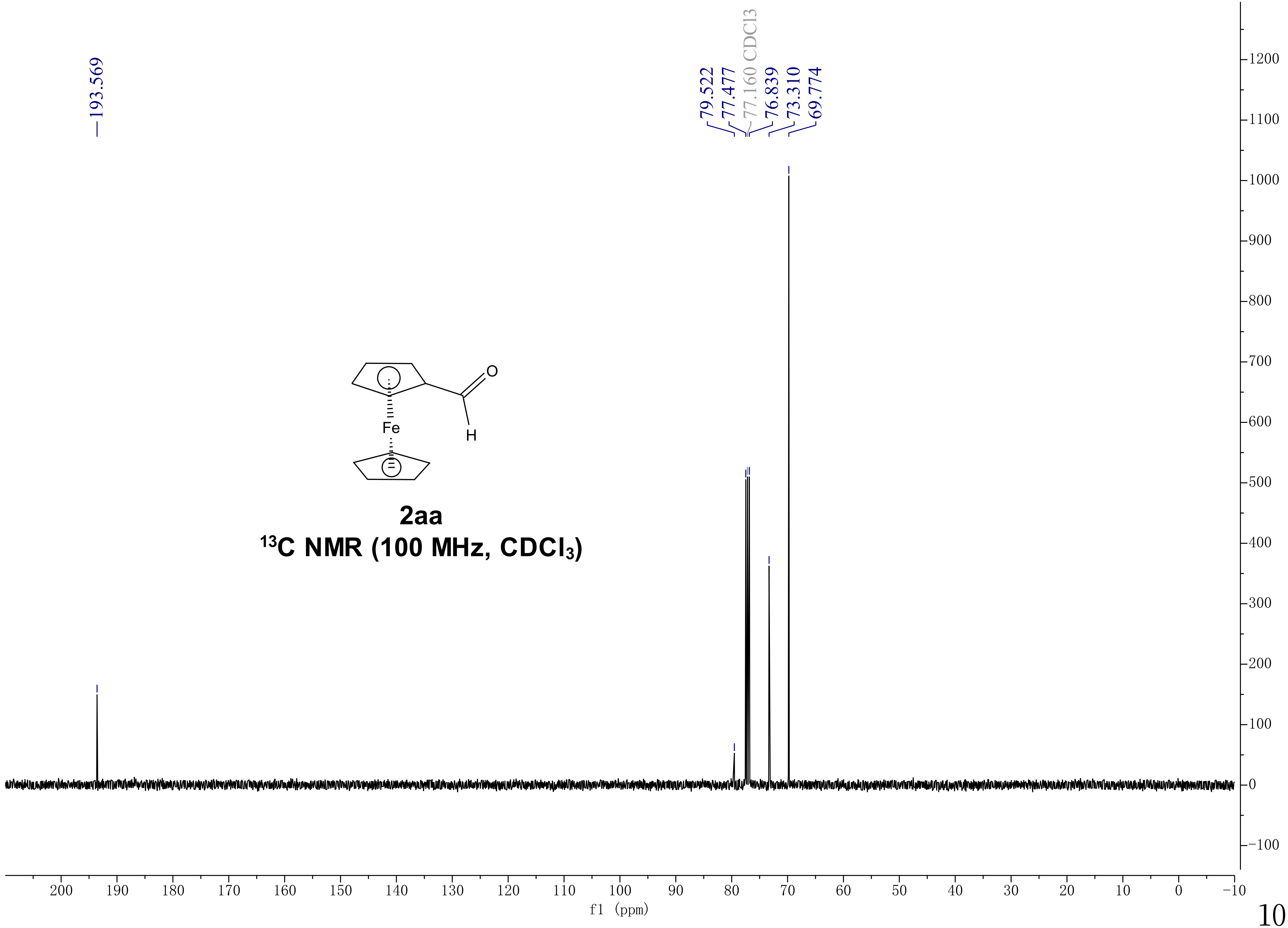

192.398
136.603
134.674
134.265
132.792
129.667
129.253
129.237
128.219
127.231
122.917
77.415
77.160
76.907
O
2y
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.058
7.963
7.943
7.762
7.741
7.648
7.629
7.505
7.487
7.468
7.441
7.422
7.404
7.260 CDCl3
O
H
2z
1H NMR (400 MHz, CDCl3)
1.00
2.08
2.08
2.13
2.08
1.02
f1 (ppm)

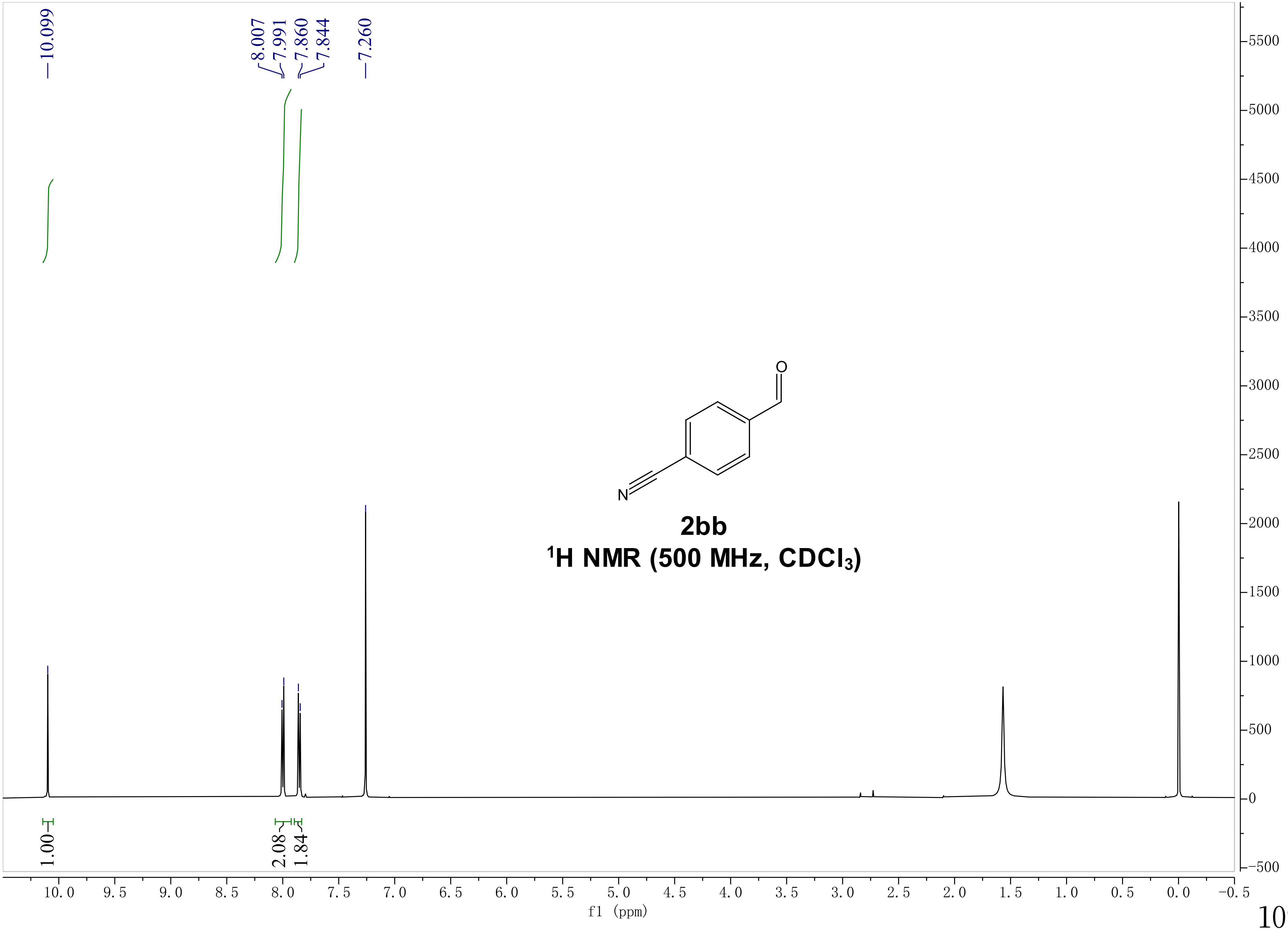

191.997
147.263
139.790
135.299
130.352
129.109
128.569
127.760
127.450
77.481
77.160 CDCl3
76.843
O
H
2z
13C NMR (100 MHz, CDCl3)
f1 (ppm)

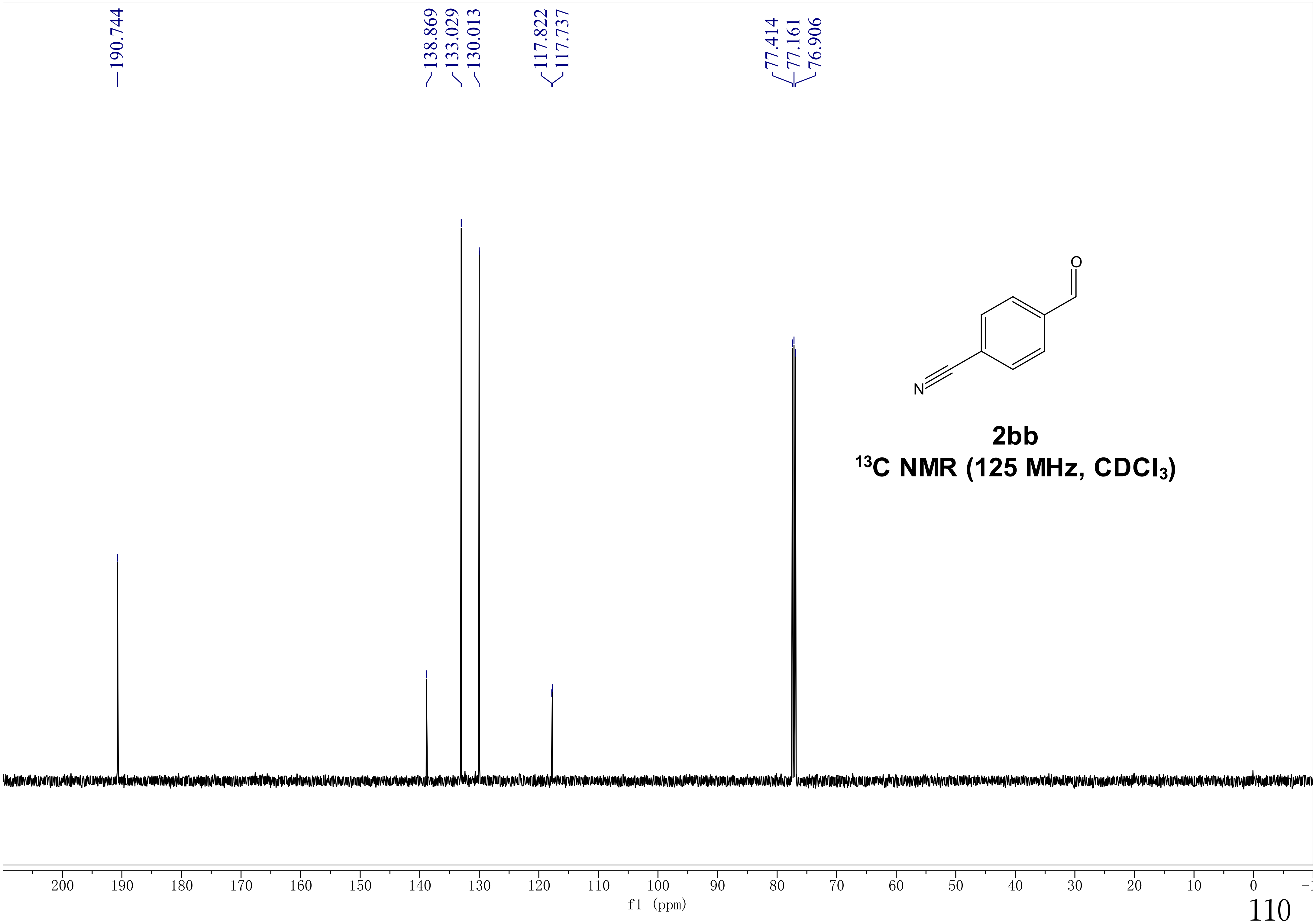


9.952
7.260 CDCl3
4.797
4.792
4.787
4.606
4.601
4.597
4.272
1.03
2.01
2.06
5.00
2aa
1H NMR (400 MHz, CDCl3)
Fe
O
H
f1 (ppm)



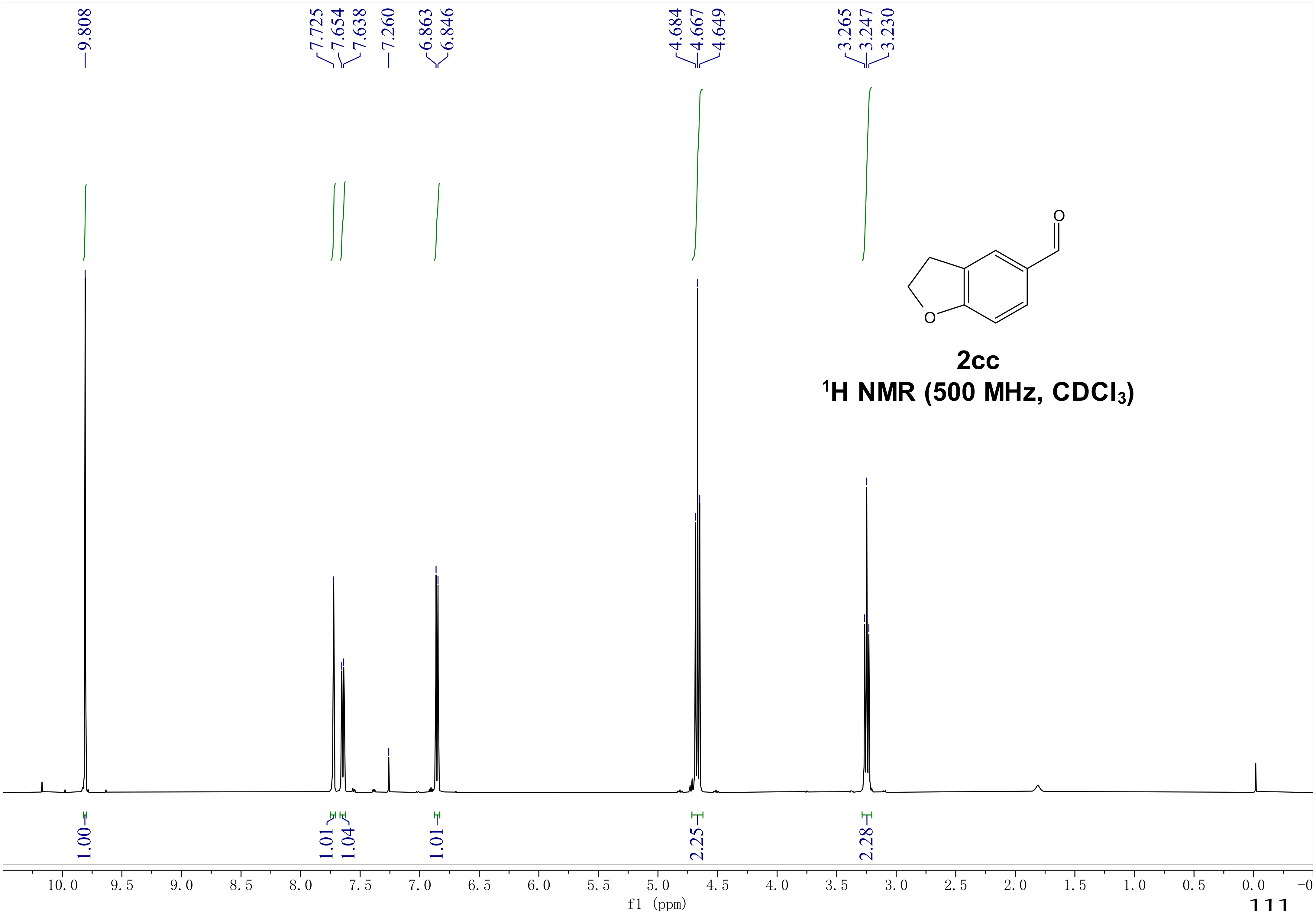
193.569
79.522
77.477
77.160 CDCl3
76.839
73.310
69.774
O
Fe
H
2aa
13C NMR (100 MHz, CDCl3)
f1 (ppm)


10.099
8.007
7.991
7.860
7.844
7.260
2bb
1H NMR (500 MHz, CDCl3)
1.00
2.08
1.84
f1 (ppm)



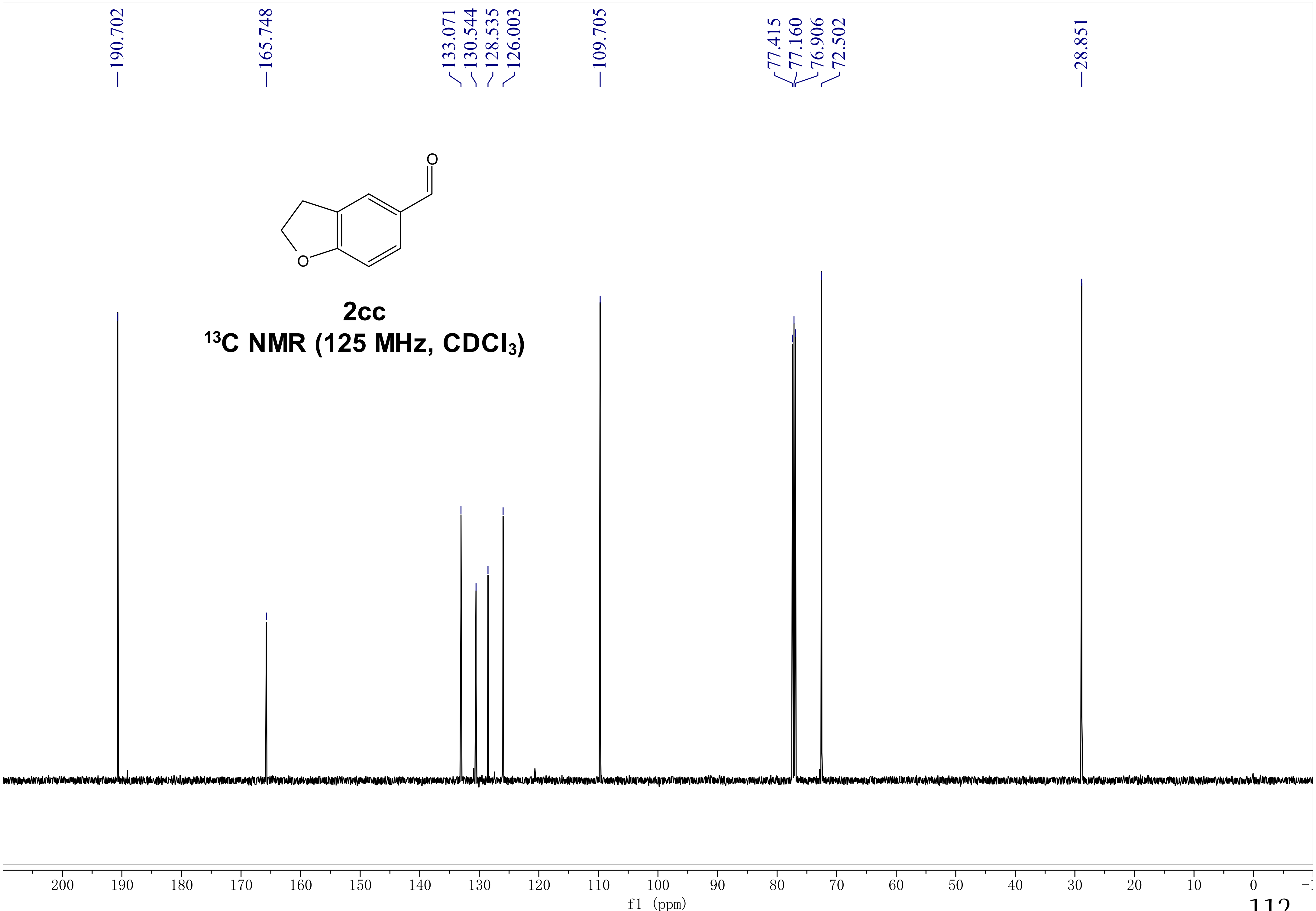
2bb

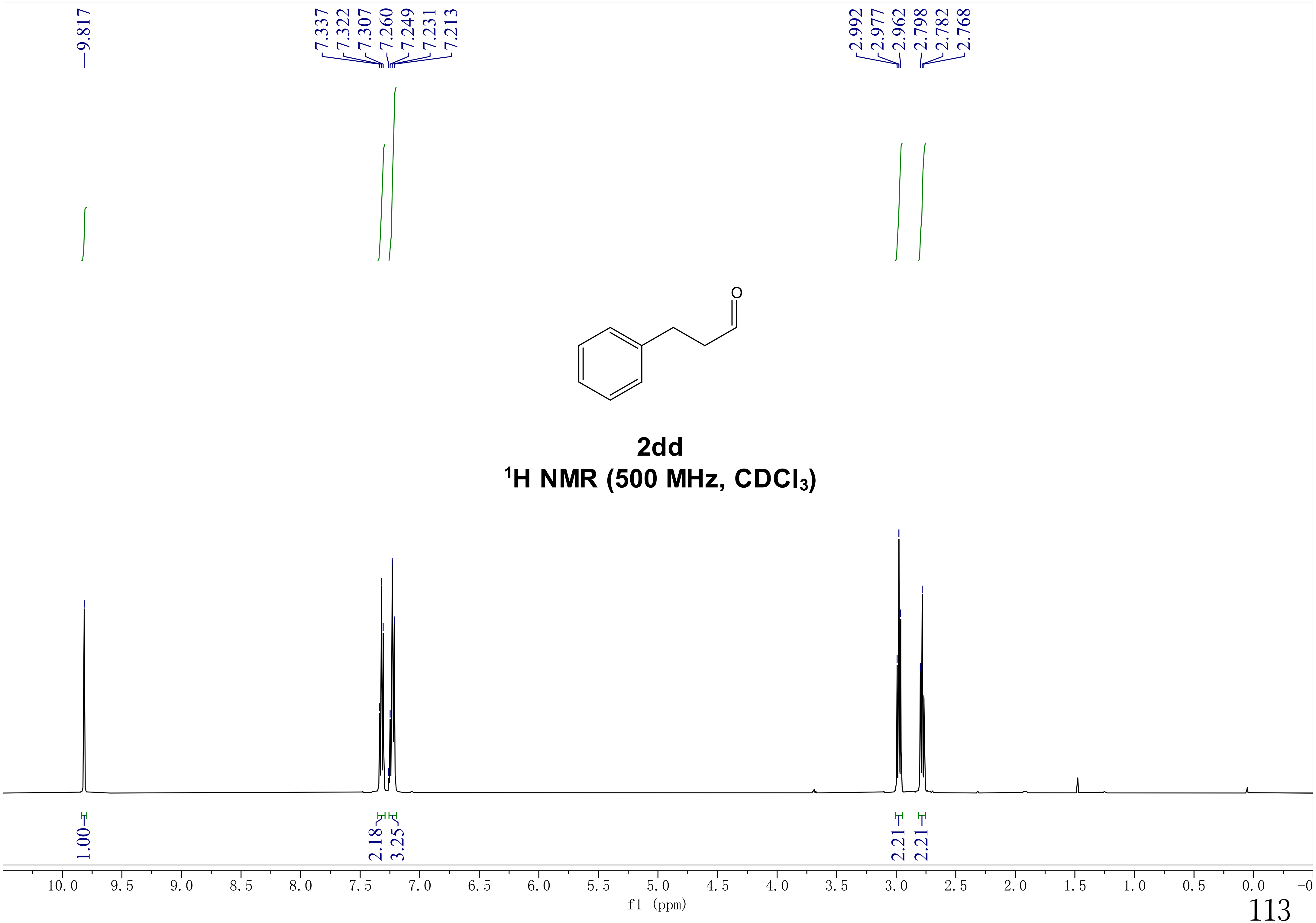
^{13}C NMR (125 MHz, $CDCl_3$)



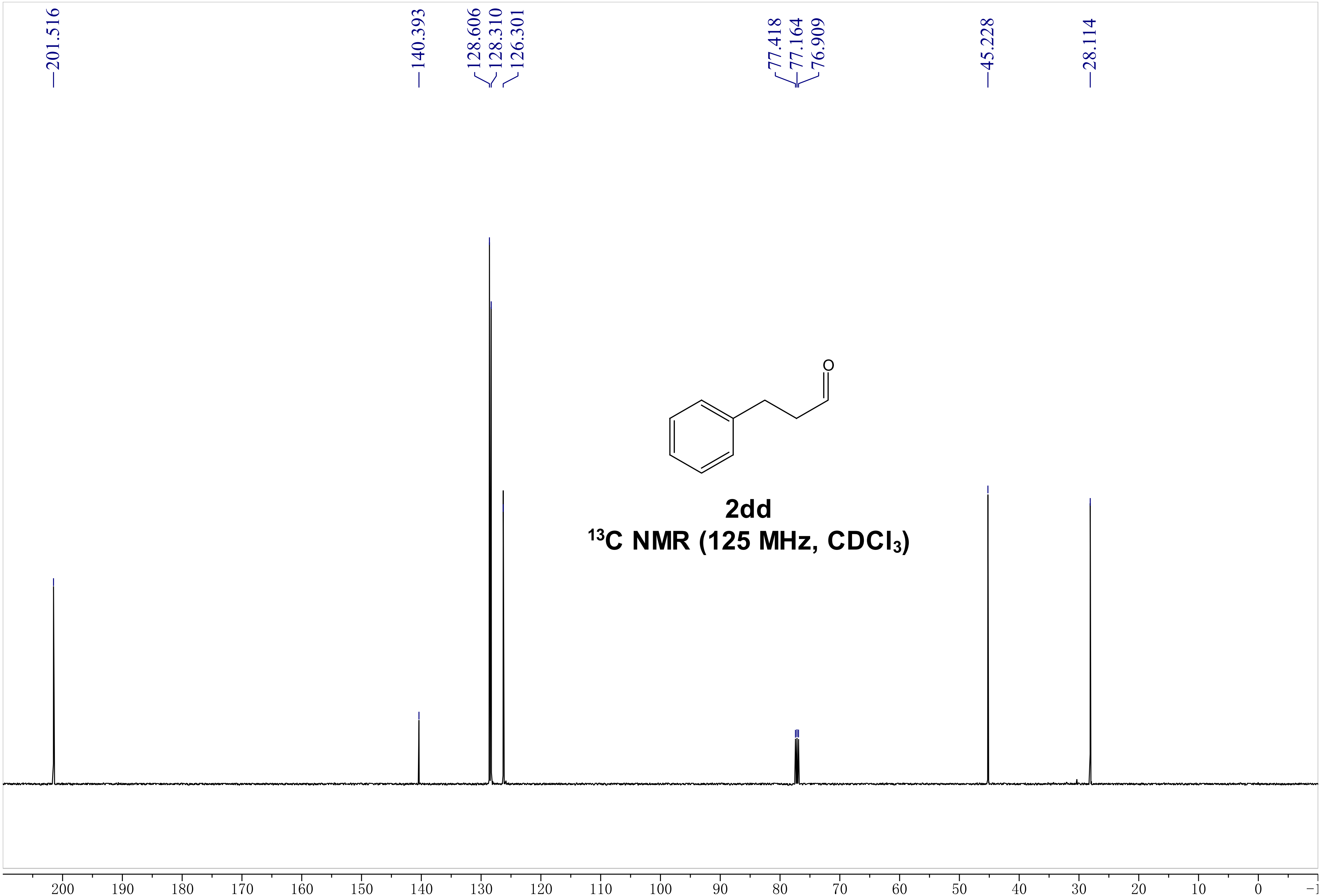
2cc

^{1}H NMR (500 MHz, $CDCl_3$)


190.702
165.748
133.071
130.544
128.535
126.003
109.705
77.415
77.160
76.906
72.502
28.851
2cc
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

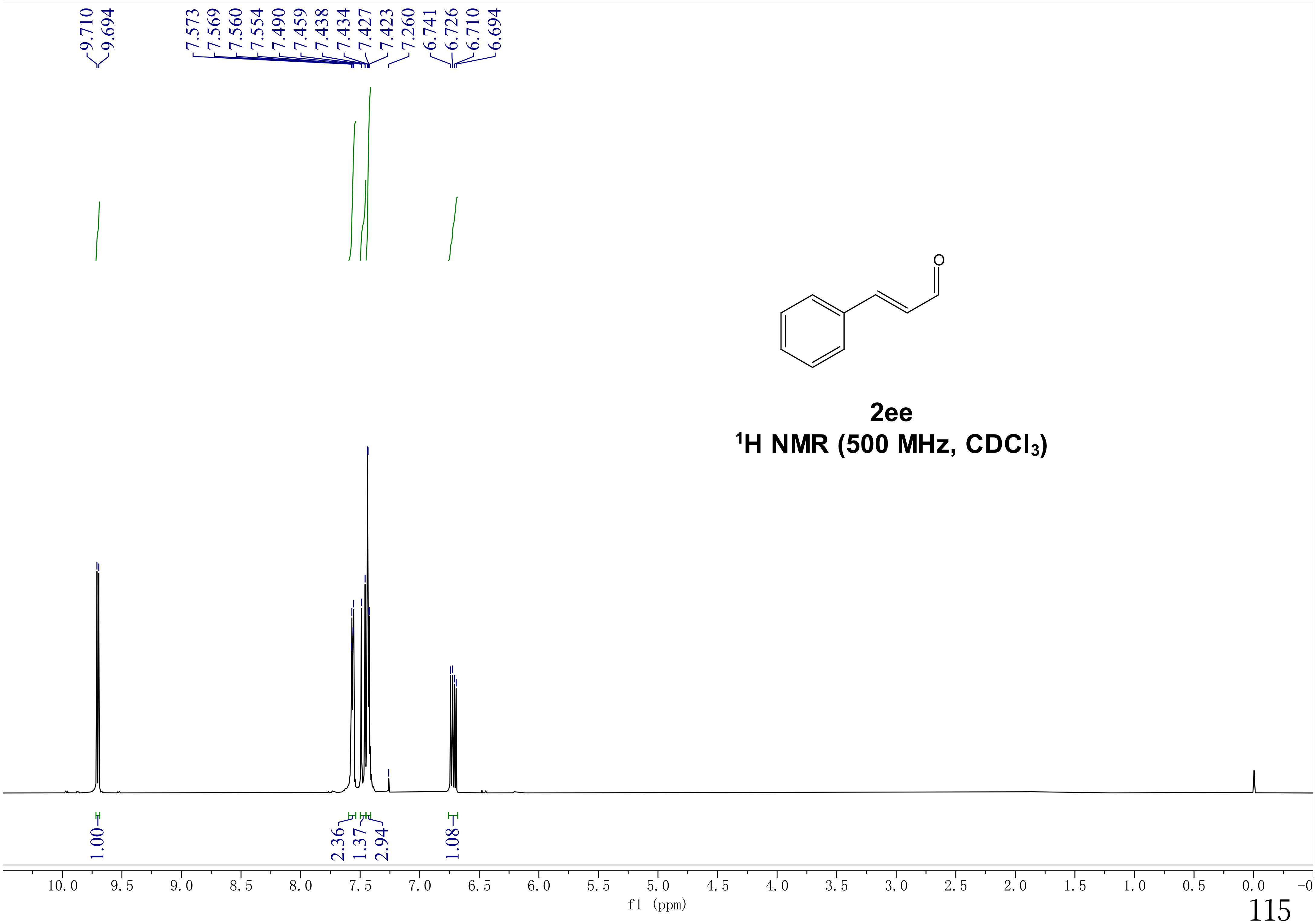


9.817
7.337
7.322
7.307
7.260
7.249
7.231
7.213
2.992
2.977
2.962
2.798
2.782
2.768
O
2dd
1H NMR (500 MHz, CDCl3)
1.00
2.18
3.25
2.21
2.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



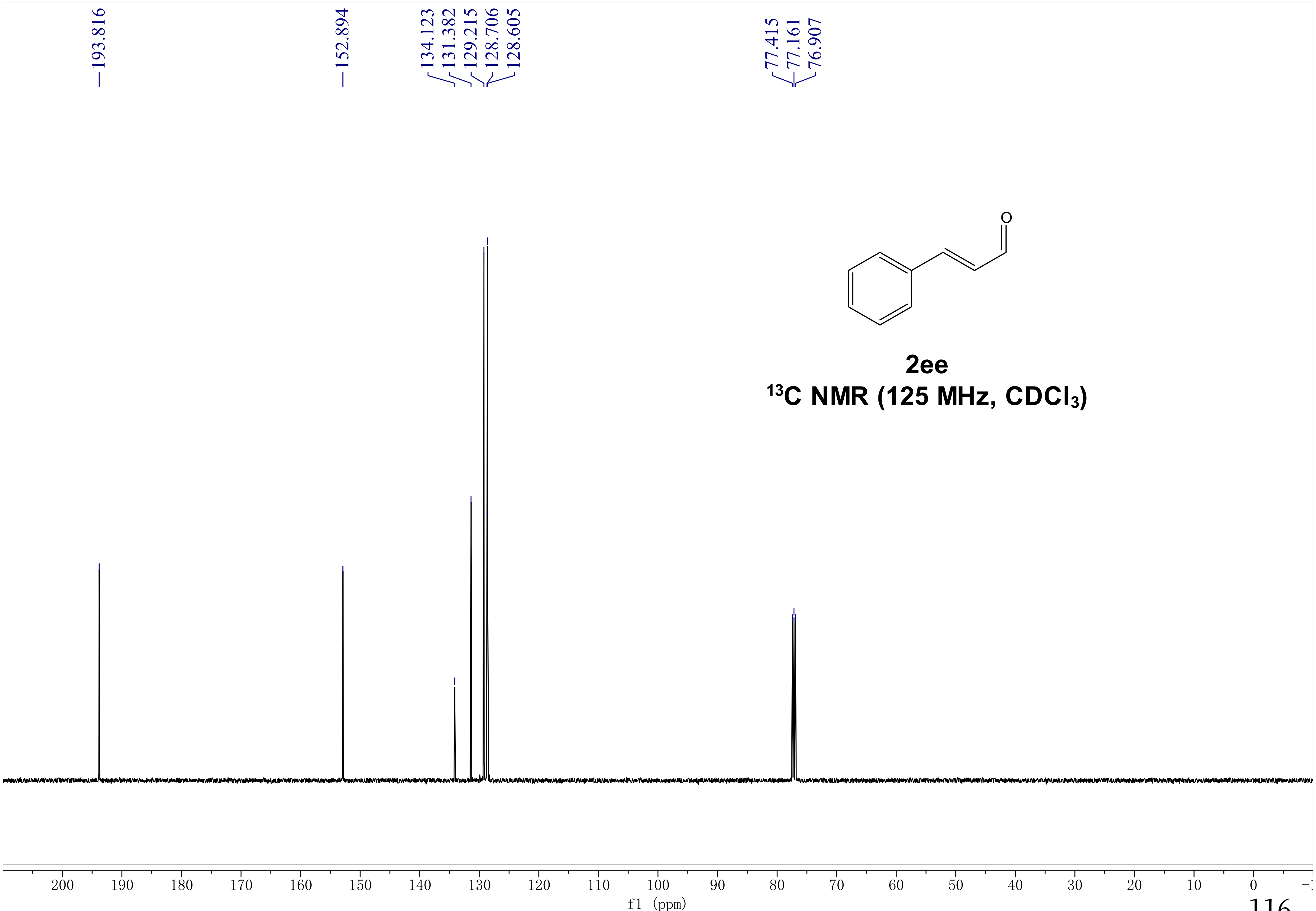
2dd

^{13}C NMR (125 MHz, $CDCl_3$)



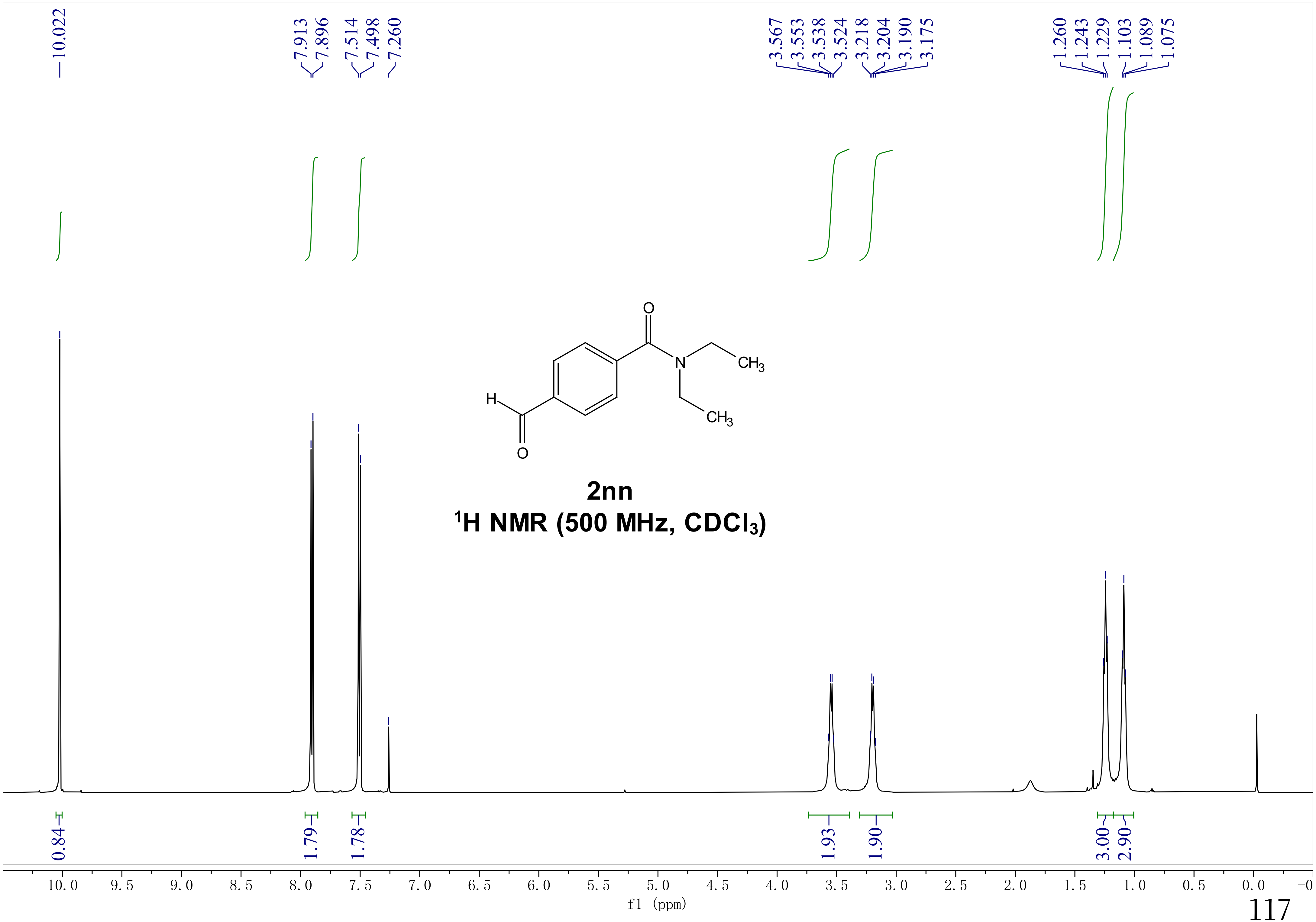
2ee

^{1}H NMR (500 MHz, $CDCl_3$)

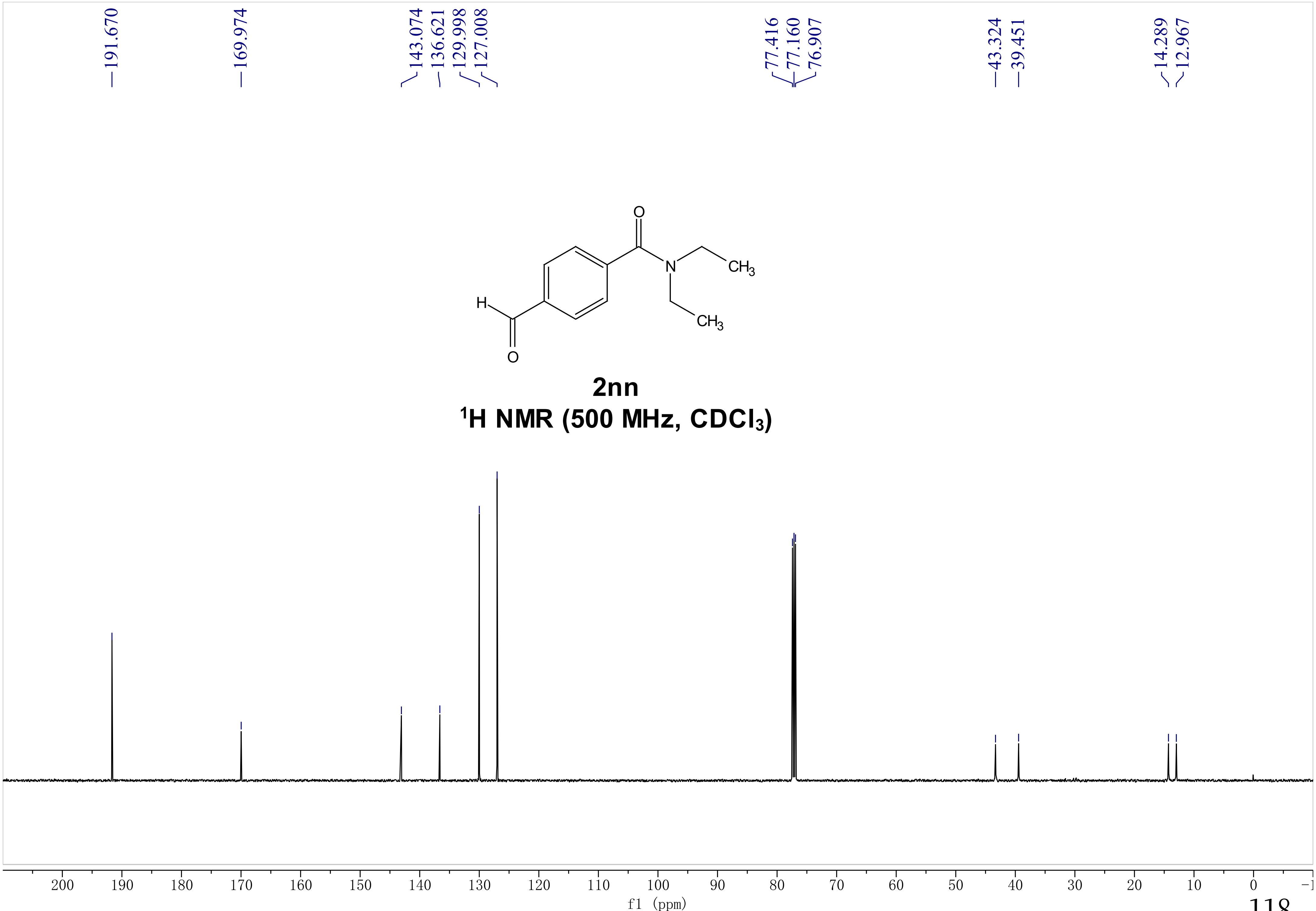


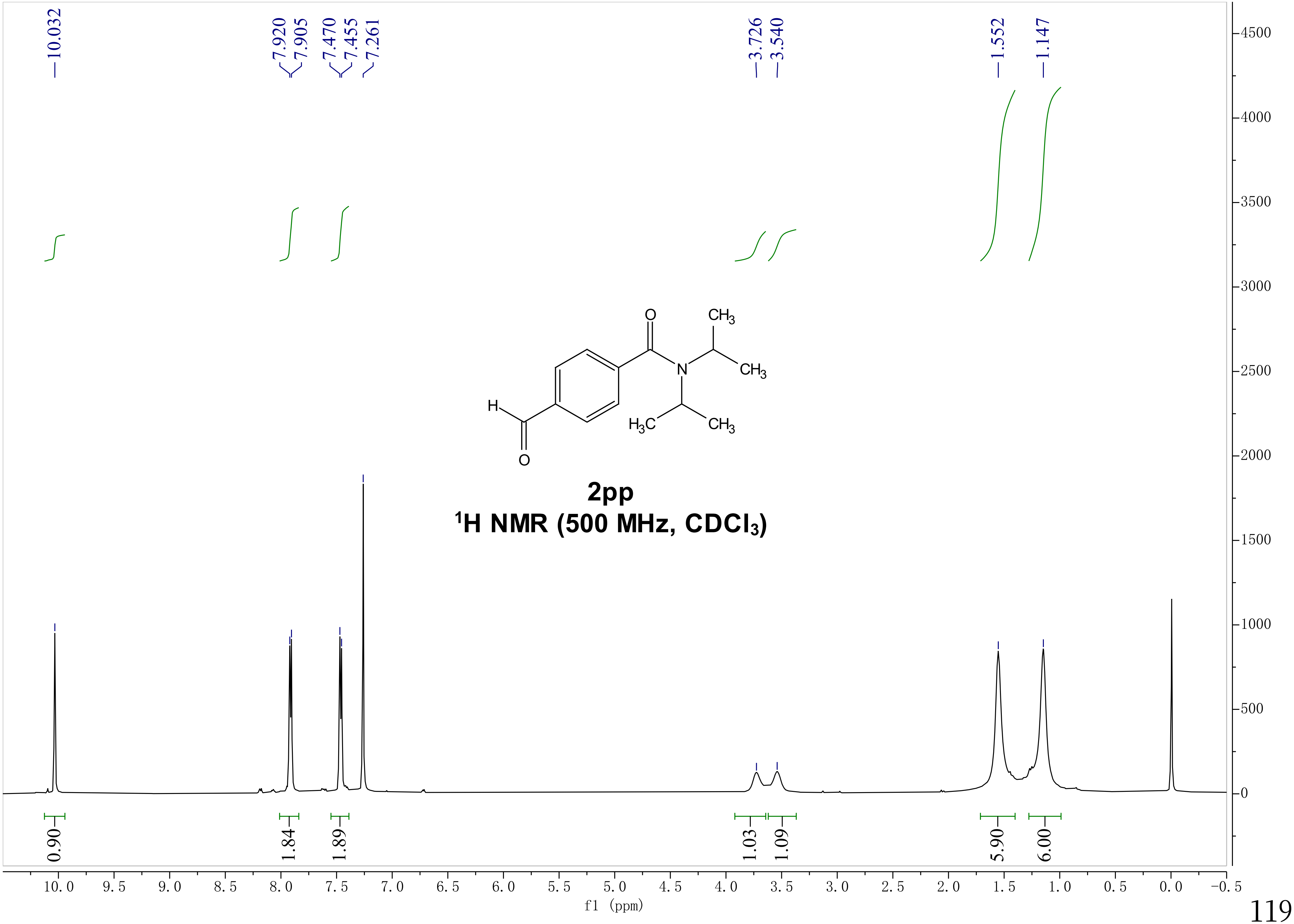
2ee

^{13}C NMR (125 MHz, $CDCl_3$)



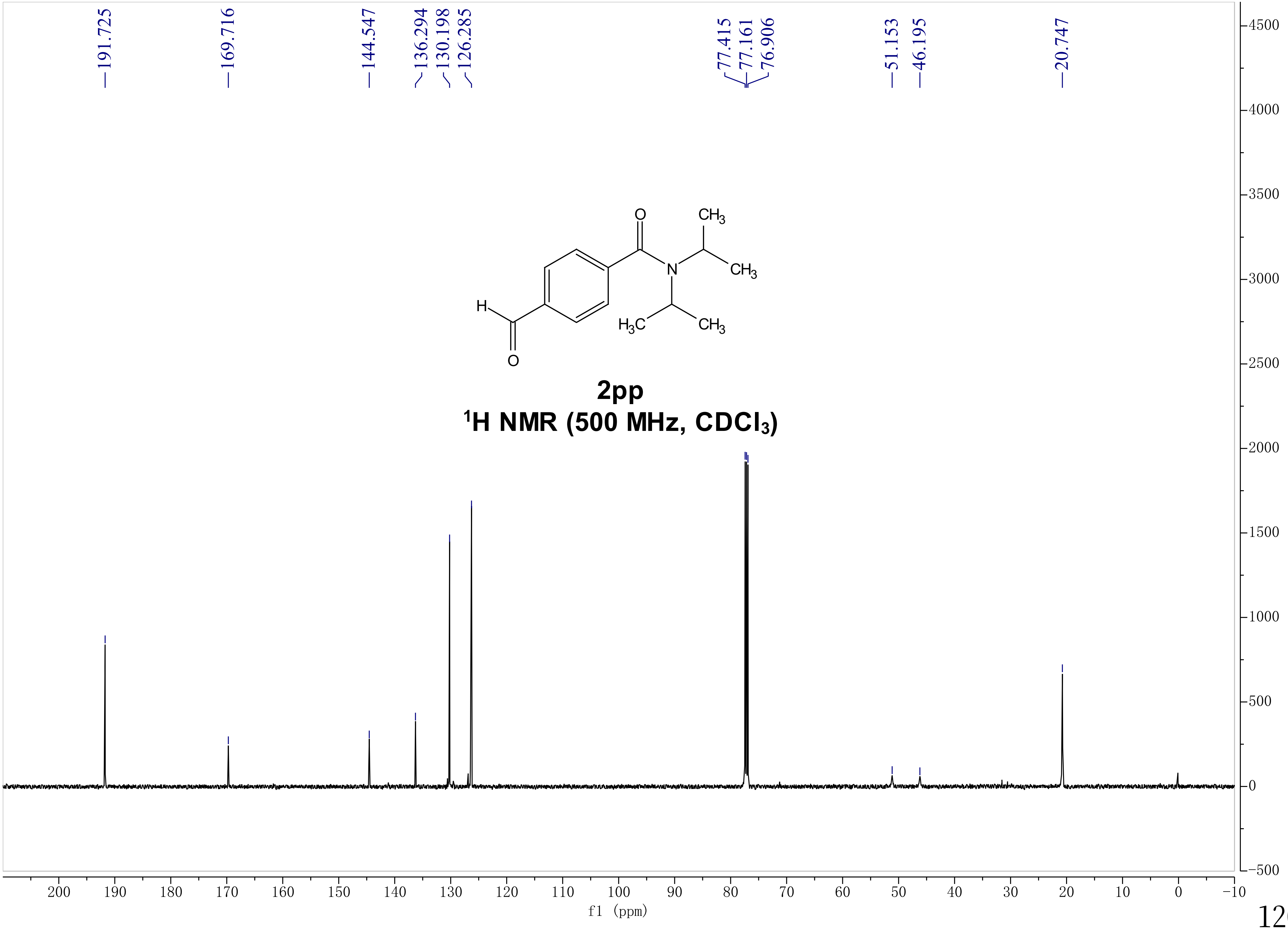
10.022
7.913
7.896
7.514
7.498
7.260
3.567
3.553
3.538
3.524
3.218
3.204
3.190
3.175
1.260
1.243
1.229
1.103
1.089
1.075
2nn
¹H NMR (500 MHz, CDCl3)
0.84
1.79
1.78
1.93
1.90
3.00
2.90
f1 (ppm)

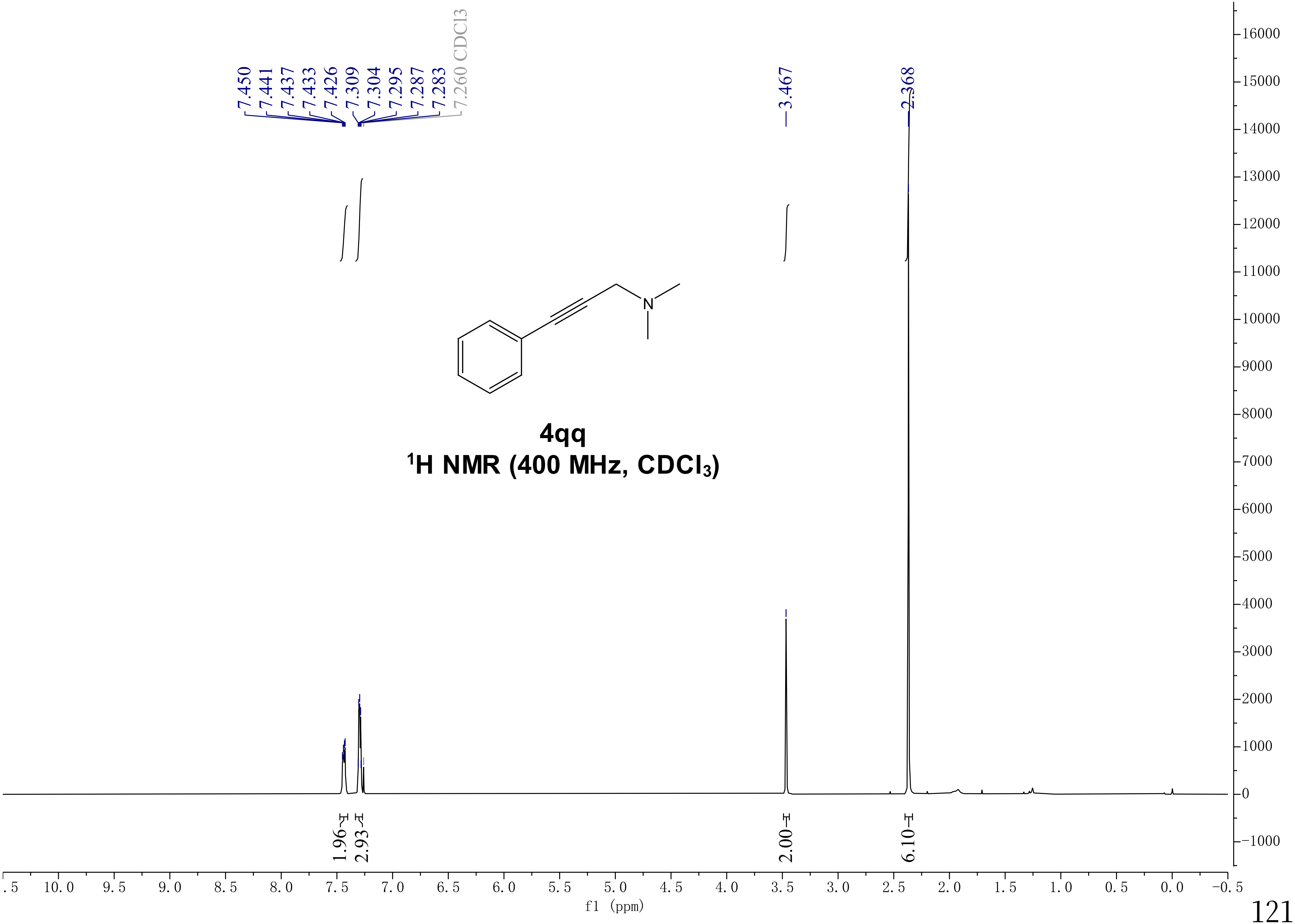

191.670
169.974
143.074
136.621
129.998
127.008
77.416
77.160
76.907
43.324
39.451
14.289
12.967
O
N
CH3
CH3
H
O
2nn
1H NMR (500 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



2pp

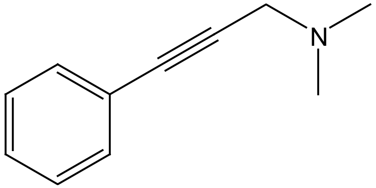
^{1}H NMR (500 MHz, $CDCl_3$)


191.725
169.716
144.547
136.294
130.198
126.285
77.415
77.161
76.906
51.153
46.195
20.747
O
CH3
N
CH3
H
H3C
CH3
O
2pp
1H NMR (500 MHz, CDCl3)
f1 (ppm)



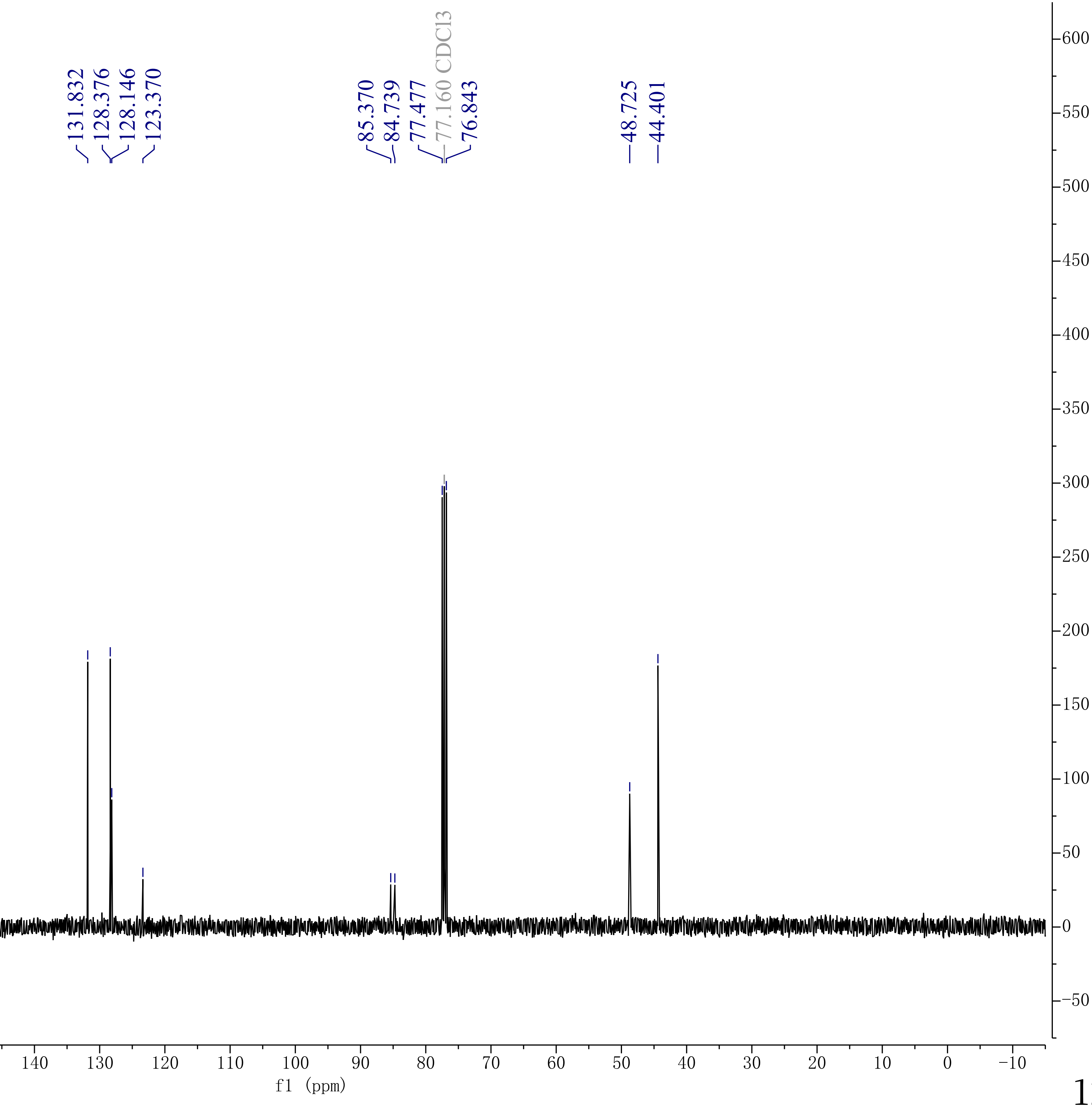
4qq

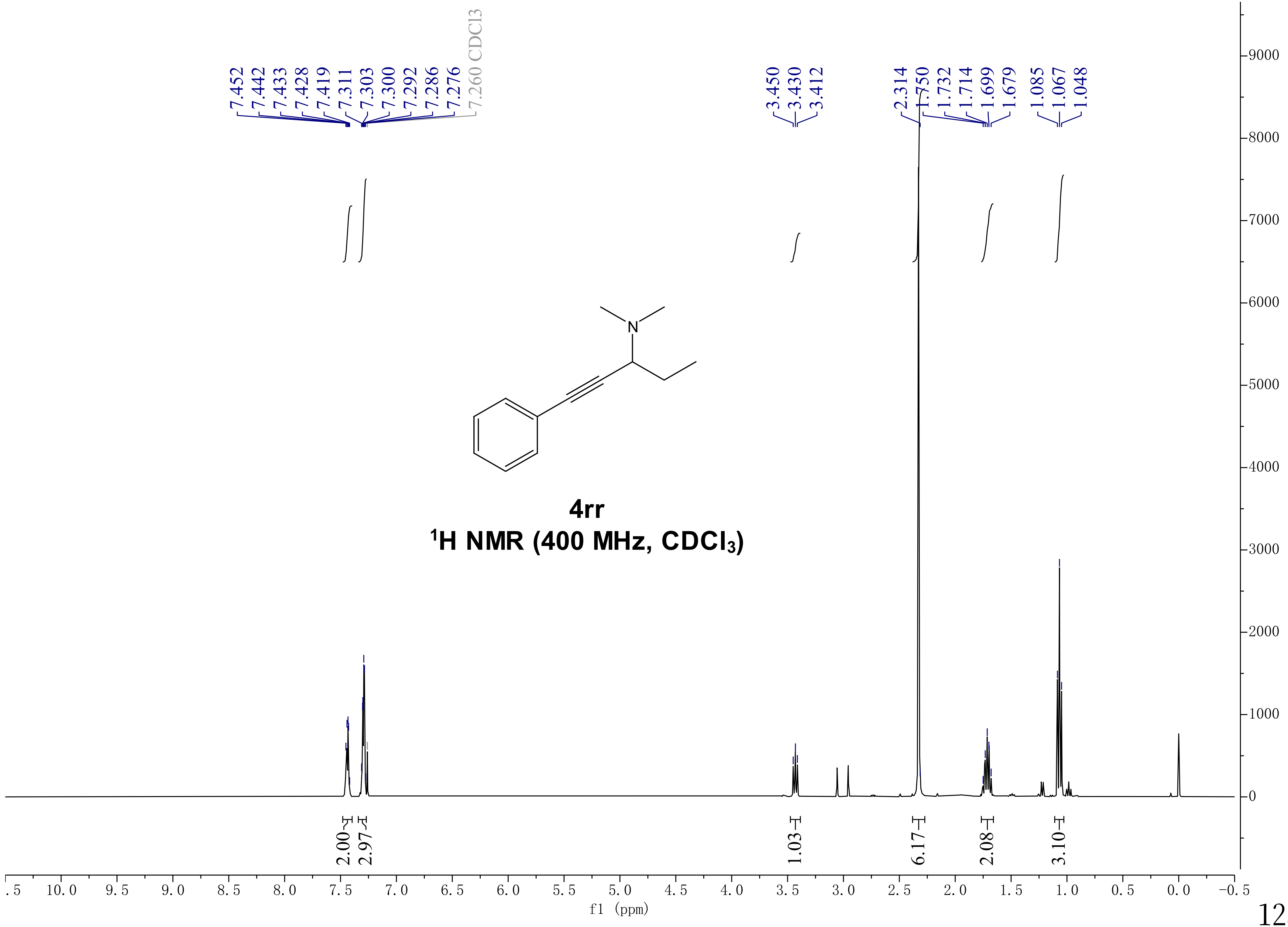
^{1}H NMR (400 MHz, $CDCl_3$)

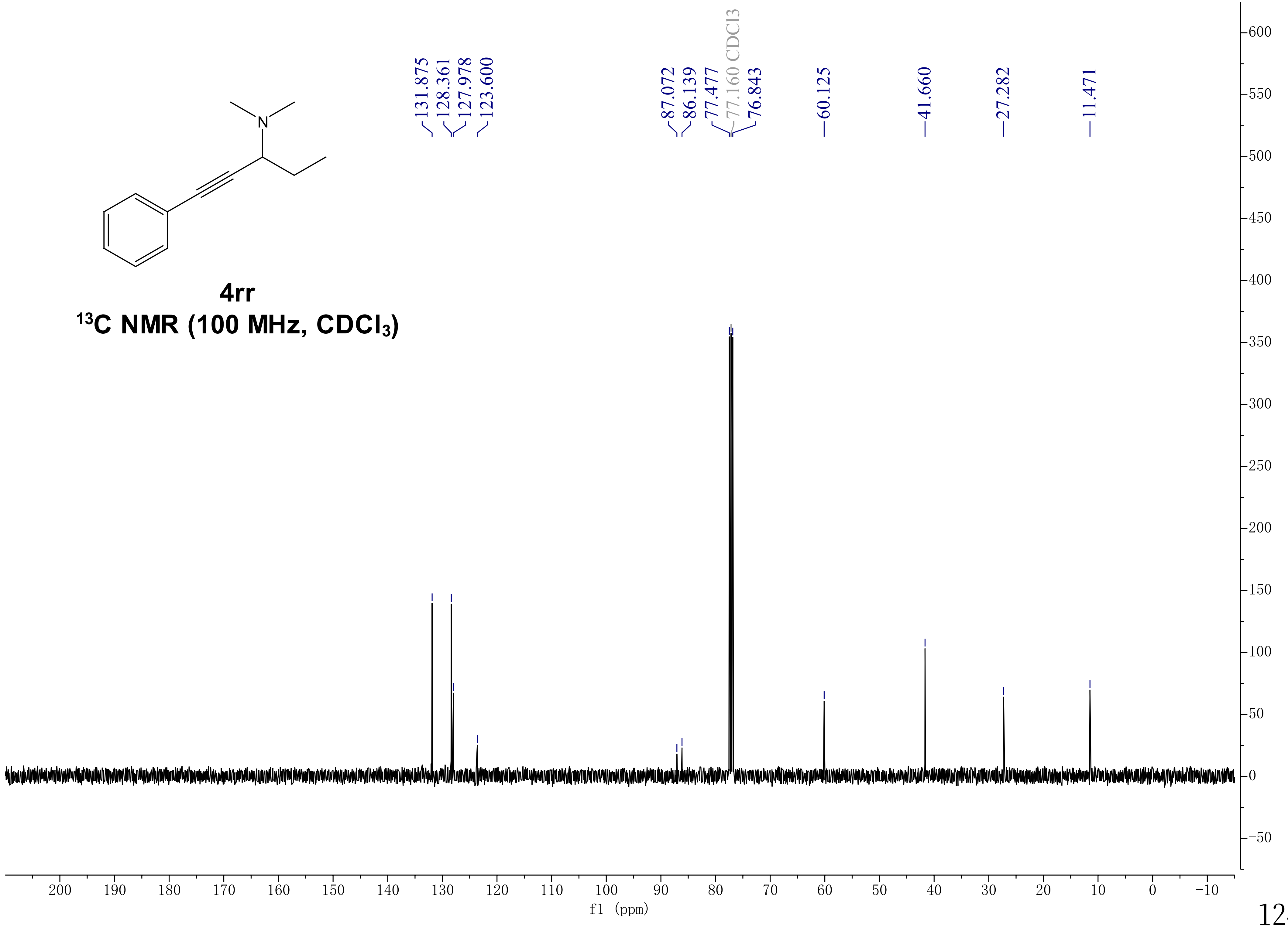


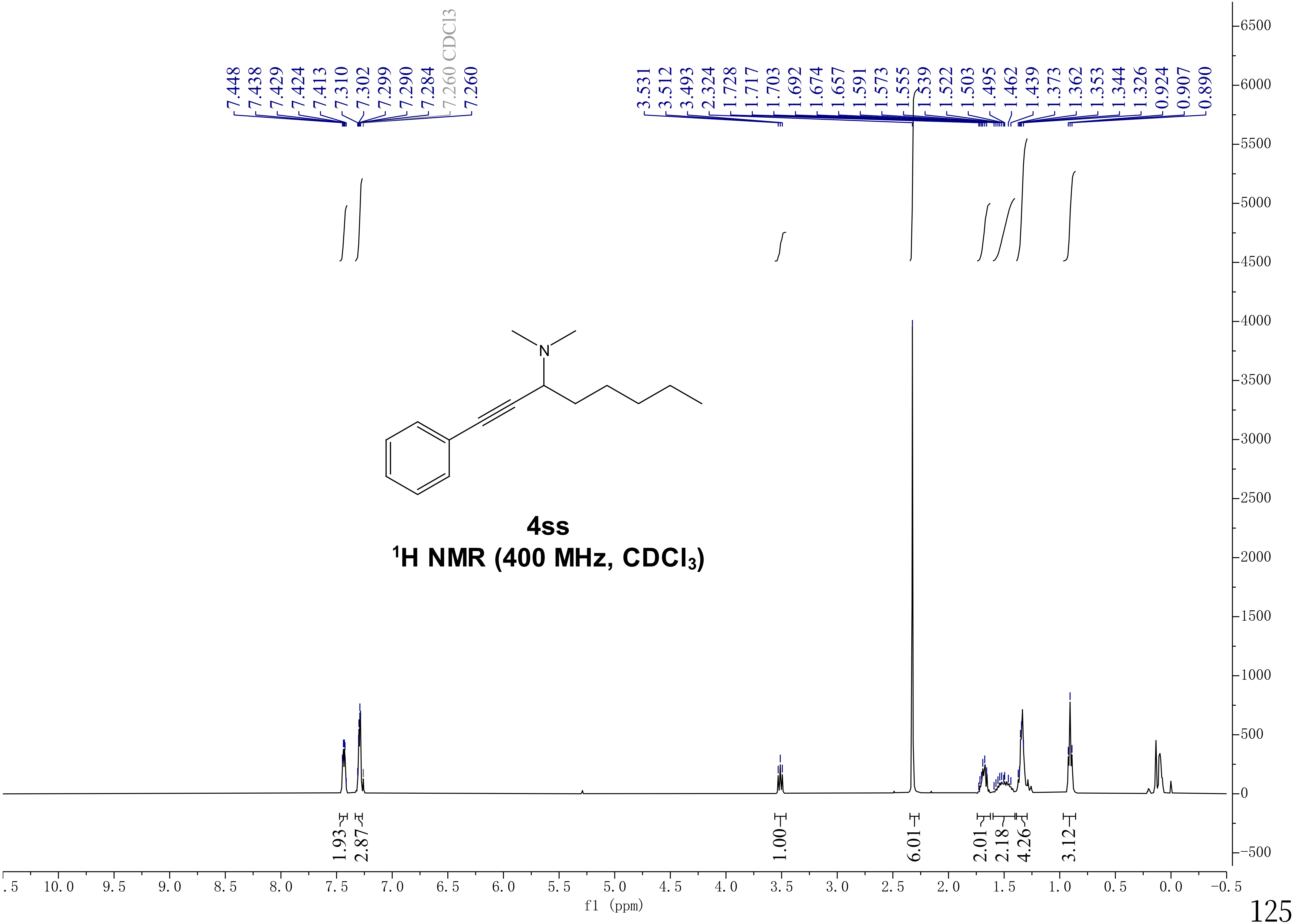
4qq

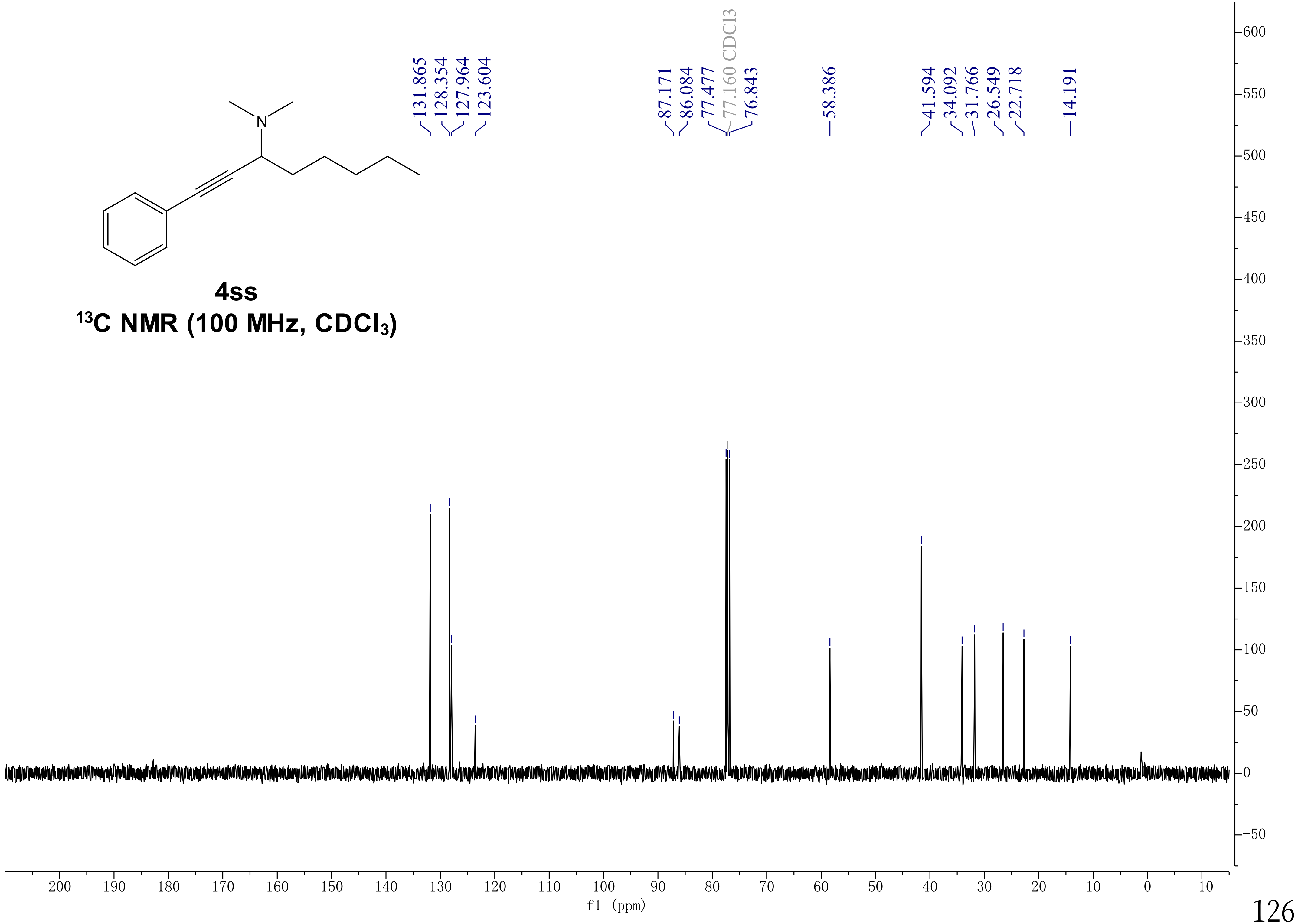
^{13}C NMR (100 MHz, $CDCl_3$)




7.452
7.442
7.433
7.428
7.419
7.311
7.303
7.300
7.292
7.286
7.276
7.260 CDCl3
3.450
3.430
3.412
2.314
1.750
1.732
1.714
1.699
1.679
1.085
1.067
1.048
N
4rr
1H NMR (400 MHz, CDCl3)
2.00
2.97
1.03
6.17
2.08
3.10
f1 (ppm)

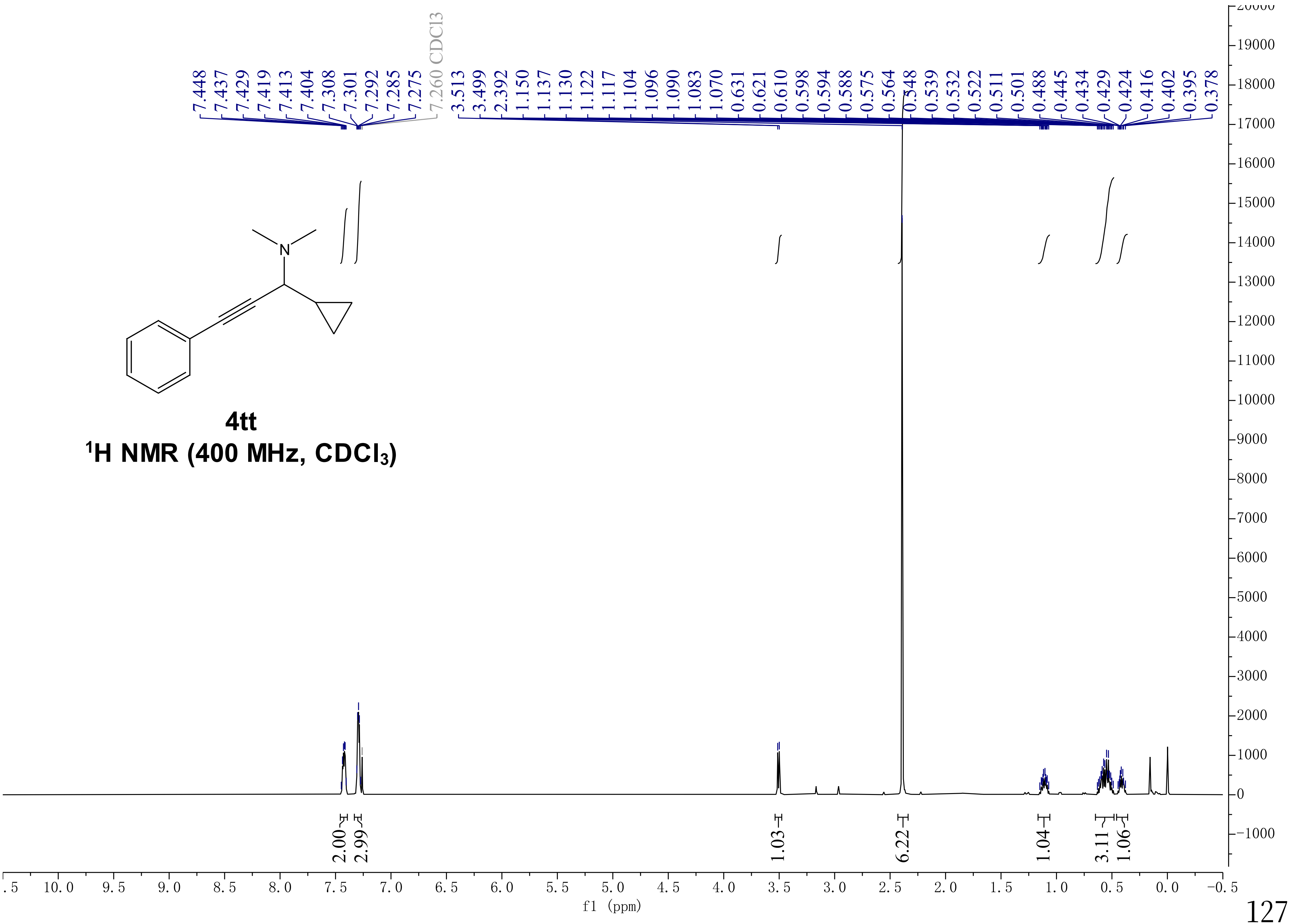

4rr
^{13}C NMR (100 MHz, $CDCl_3$)
131.875
128.361
127.978
123.600
87.072
86.139
77.477
77.160 CDCl3
76.843
60.125
41.660
27.282
11.471
f1 (ppm)

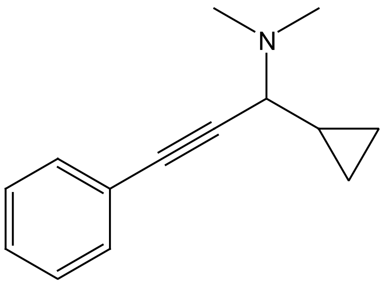

7.448
7.438
7.429
7.424
7.413
7.310
7.302
7.299
7.290
7.284
7.260 CDCl3
7.260
3.531
3.512
3.493
2.324
1.728
1.717
1.703
1.692
1.674
1.657
1.591
1.573
1.555
1.539
1.522
1.503
1.495
1.462
1.439
1.373
1.362
1.353
1.344
1.326
0.924
0.907
0.890
N
4ss
1H NMR (400 MHz, CDCl3)
1.93
2.87
1.00
6.01
2.01
2.18
4.26
3.12
f1 (ppm)



4ss

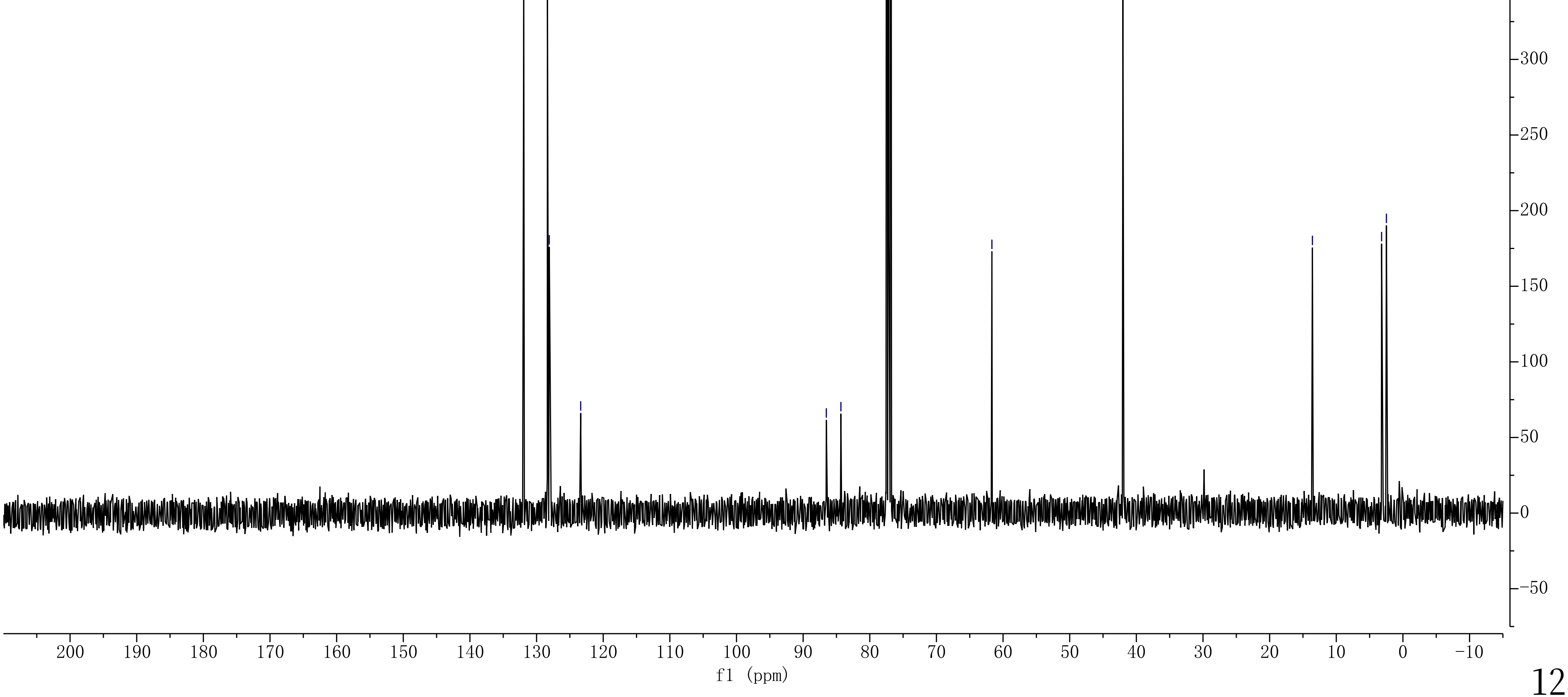
^{13}C NMR (100 MHz, $CDCl_3$)

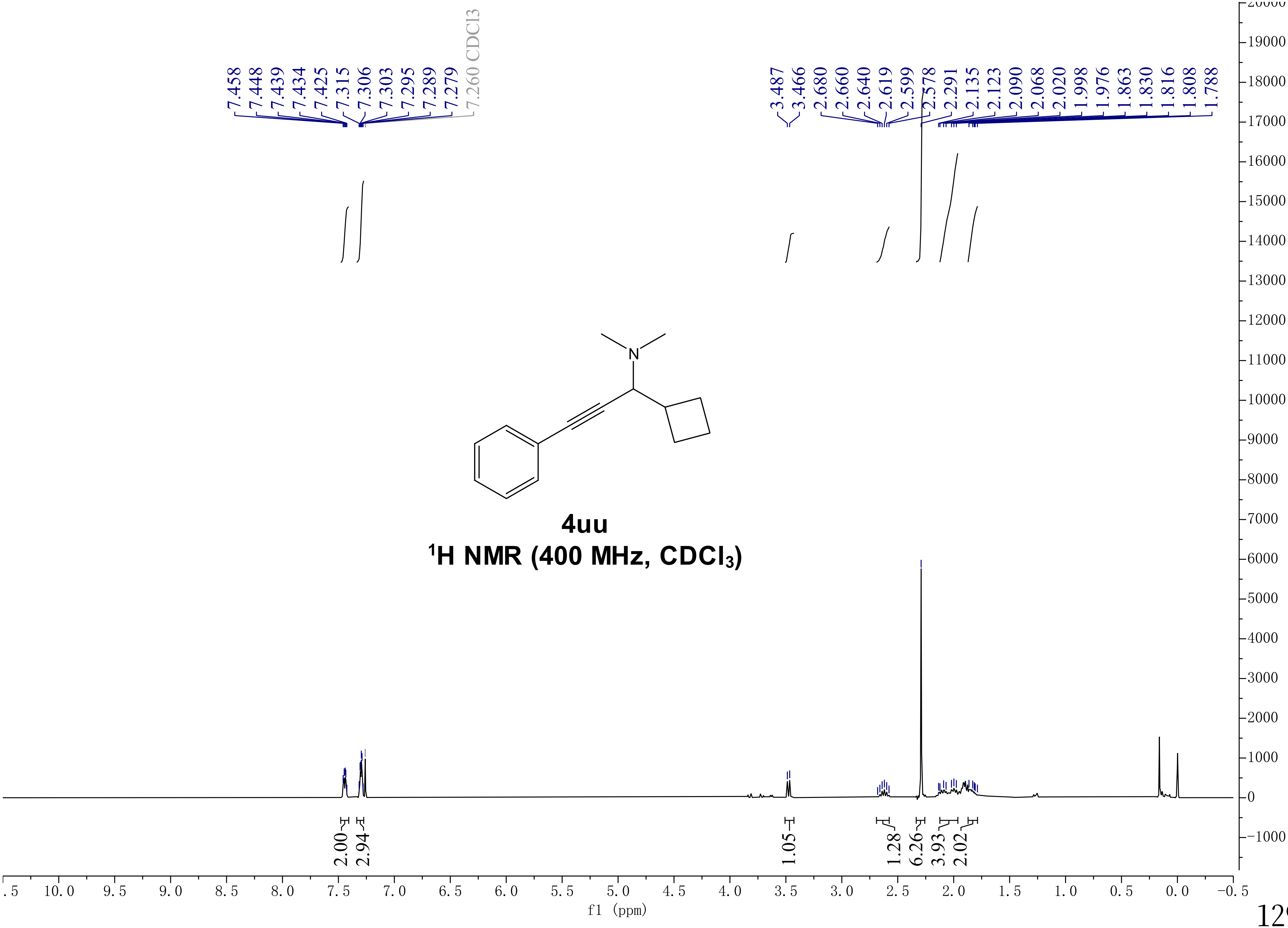

7.448
7.437
7.429
7.419
7.413
7.404
7.308
7.301
7.292
7.285
7.275
7.260 CDCl3
3.513
3.499
2.392
1.150
1.137
1.130
1.122
1.117
1.104
1.096
1.090
1.083
1.070
0.631
0.621
0.610
0.598
0.594
0.588
0.575
0.564
0.548
0.539
0.532
0.522
0.511
0.501
0.488
0.445
0.434
0.429
0.424
0.416
0.402
0.395
0.378
N
4tt
1H NMR (400 MHz, CDCl3)
2.00
2.99
1.03
6.22
1.04
3.11
1.06
f1 (ppm)

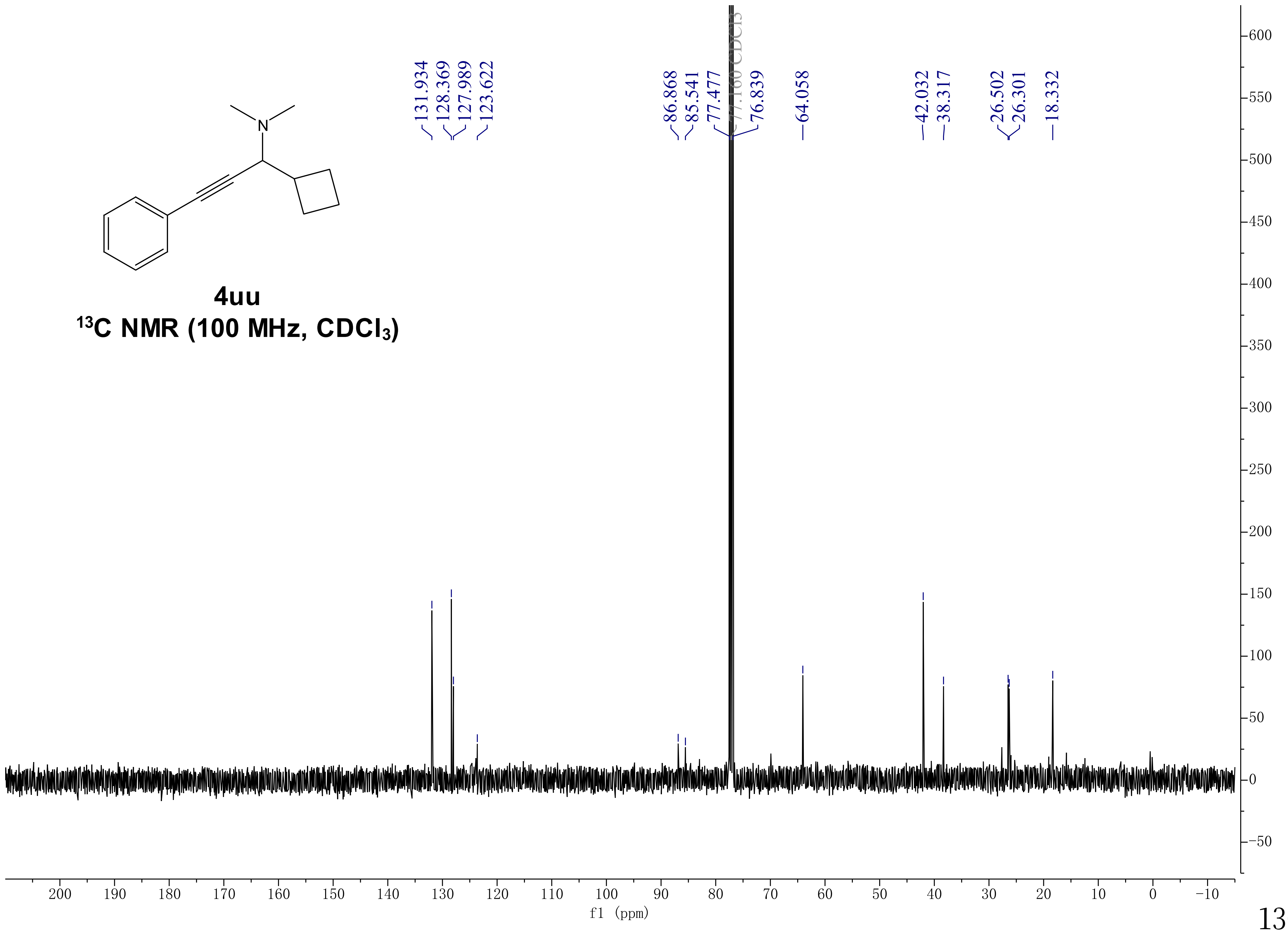


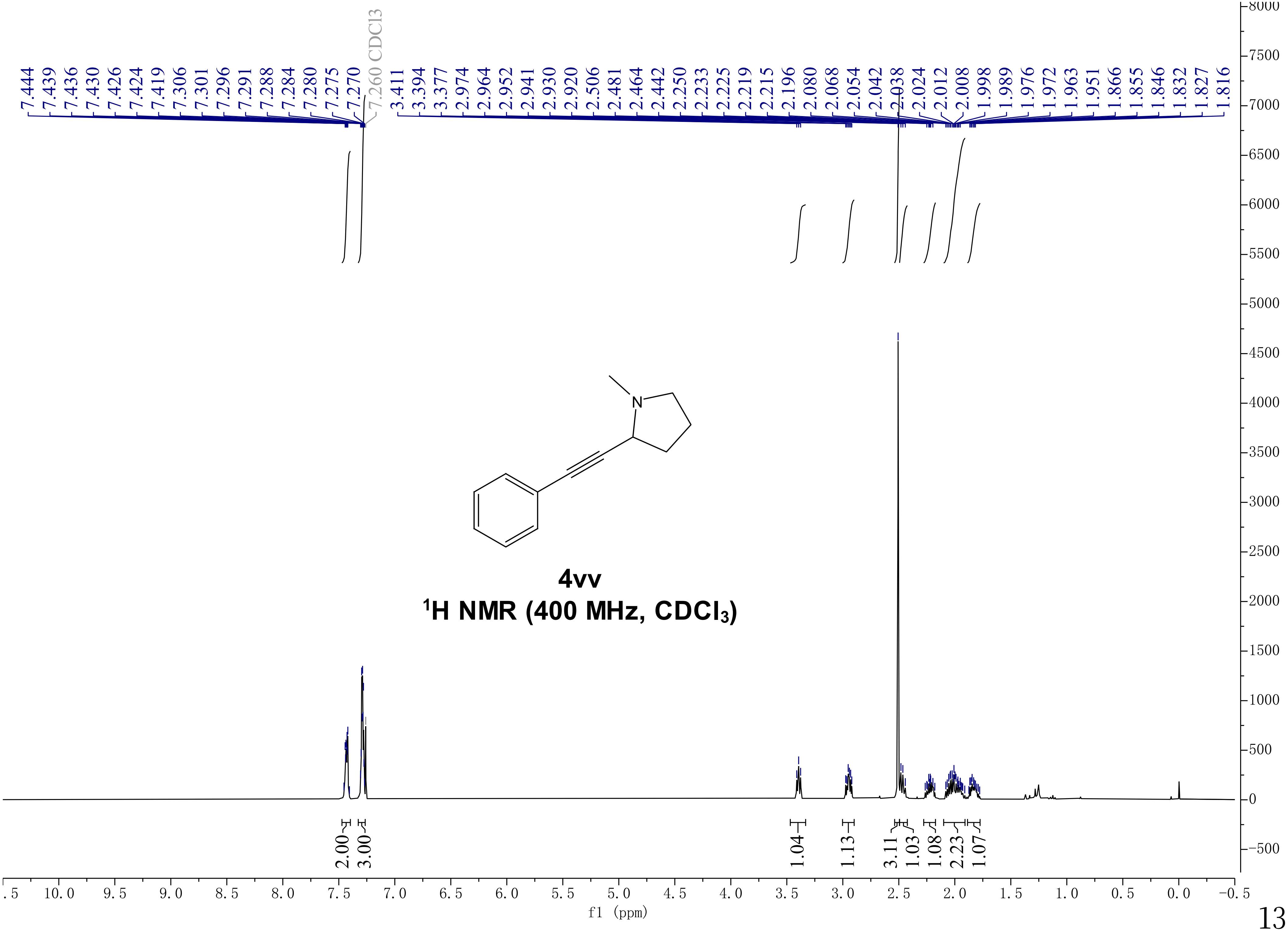
4tt

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



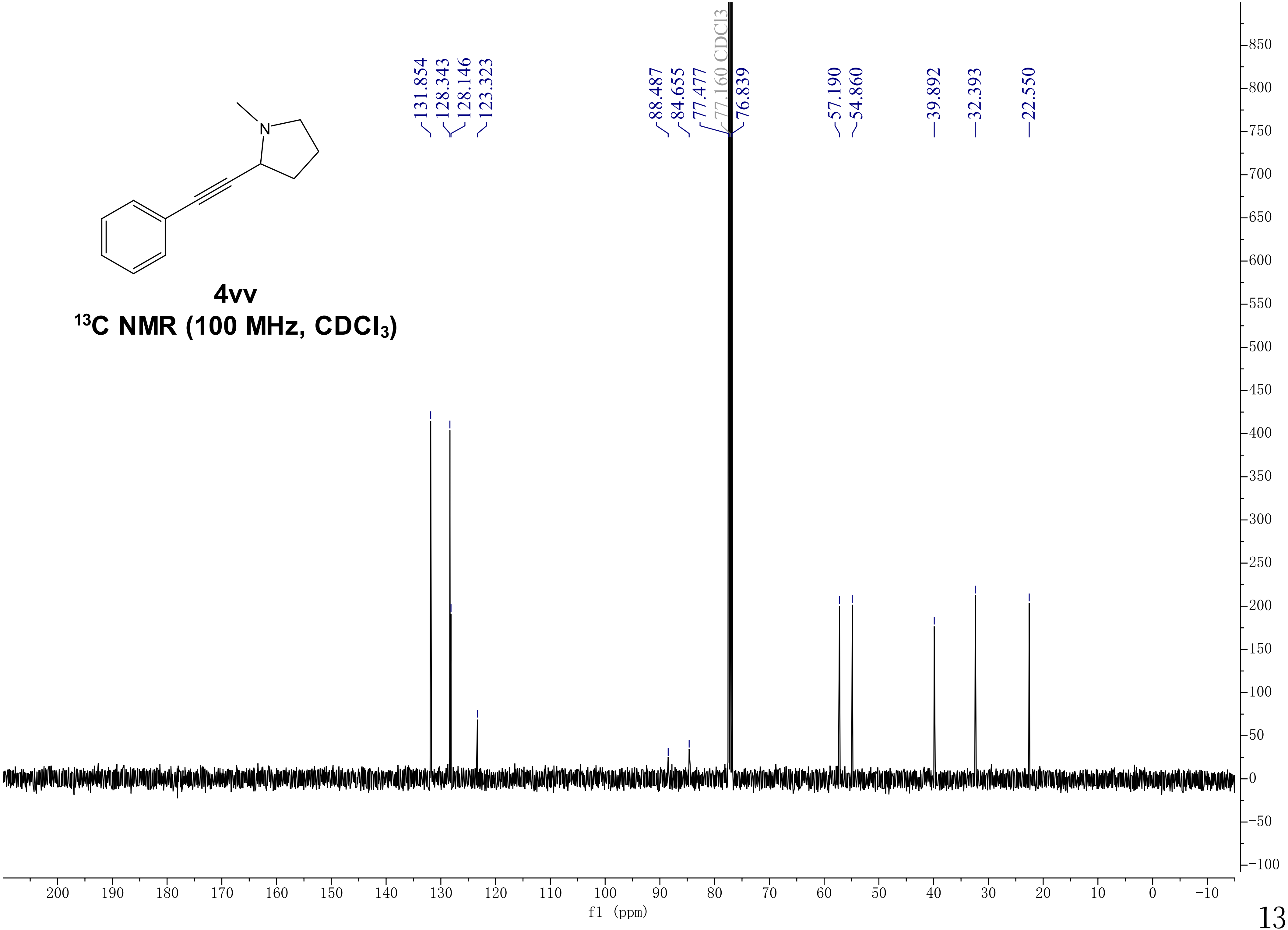

7.458 7.448 7.439 7.434 7.425 7.315 7.306 7.303 7.295 7.289 7.279 7.260 CDCl3
3.487 3.466 2.680 2.660 2.640 2.619 2.599 2.578 2.291 2.135 2.123 2.090 2.068 2.020 1.998 1.976 1.863 1.830 1.816 1.808 1.788
N
4uu
^{1}H NMR (400 MHz, CDCl$_3$)
2.00 2.94 1.05 1.28 6.26 3.93 2.02
f1 (ppm)

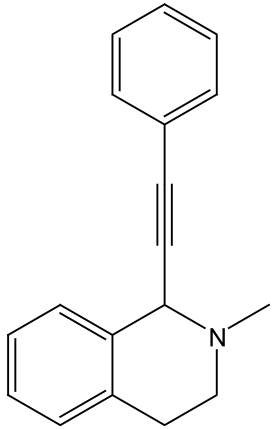

N
4uu
^{13}C NMR (100 MHz, CDCl$_3$)
131.934
128.369
127.989
123.622
86.868
85.541
77.477
77.160 CDCl3
76.839
64.058
42.032
38.317
26.502
26.301
18.332
f1 (ppm)



4vv

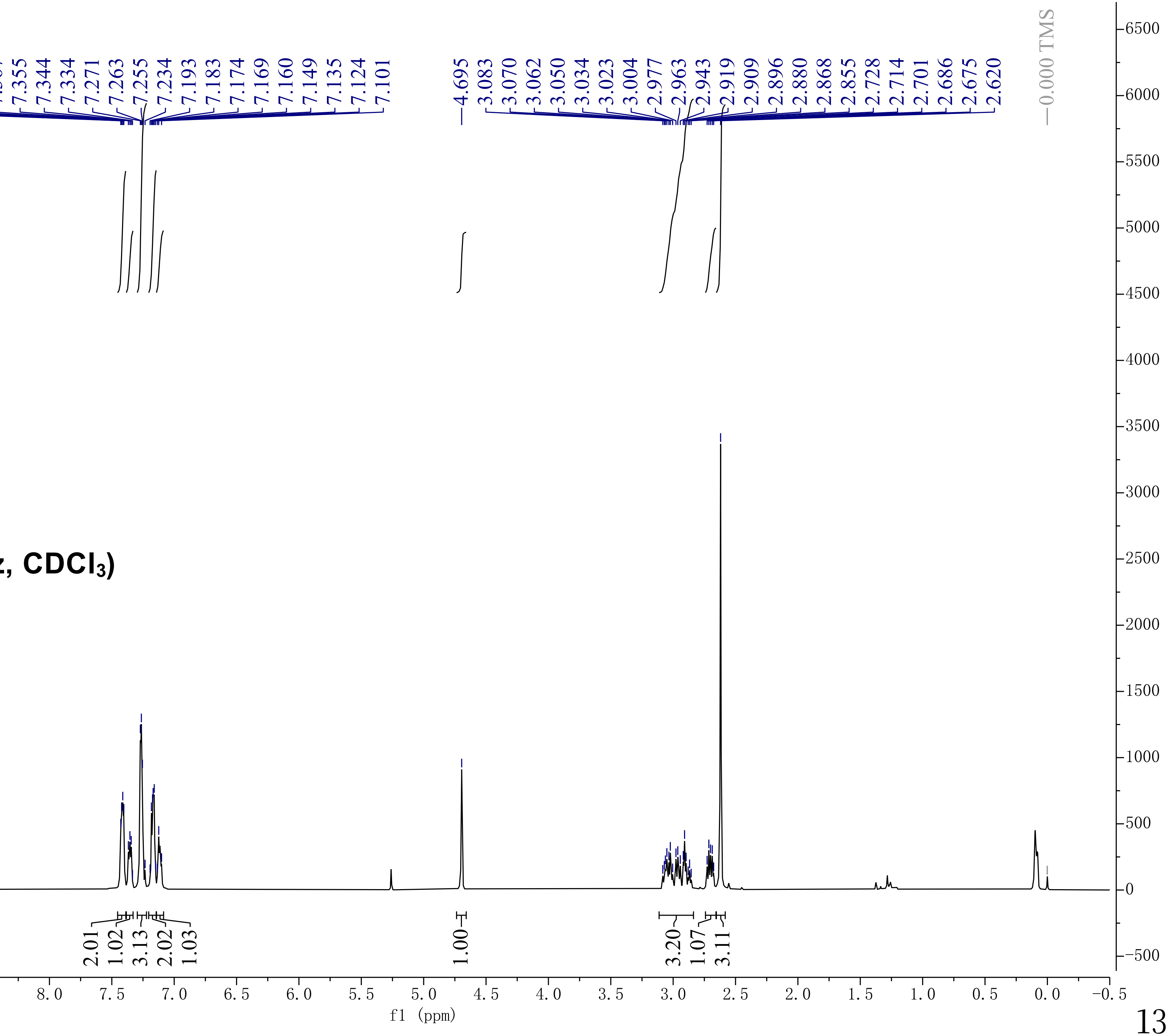
^{1}H NMR (400 MHz, $CDCl_3$)


4vv
^{13}C NMR (100 MHz, CDCl$_3$)
131.854
128.343
128.146
123.323
88.487
84.655
77.477
77.160 CDCl3
76.839
57.190
54.860
39.892
32.393
22.550
f1 (ppm)

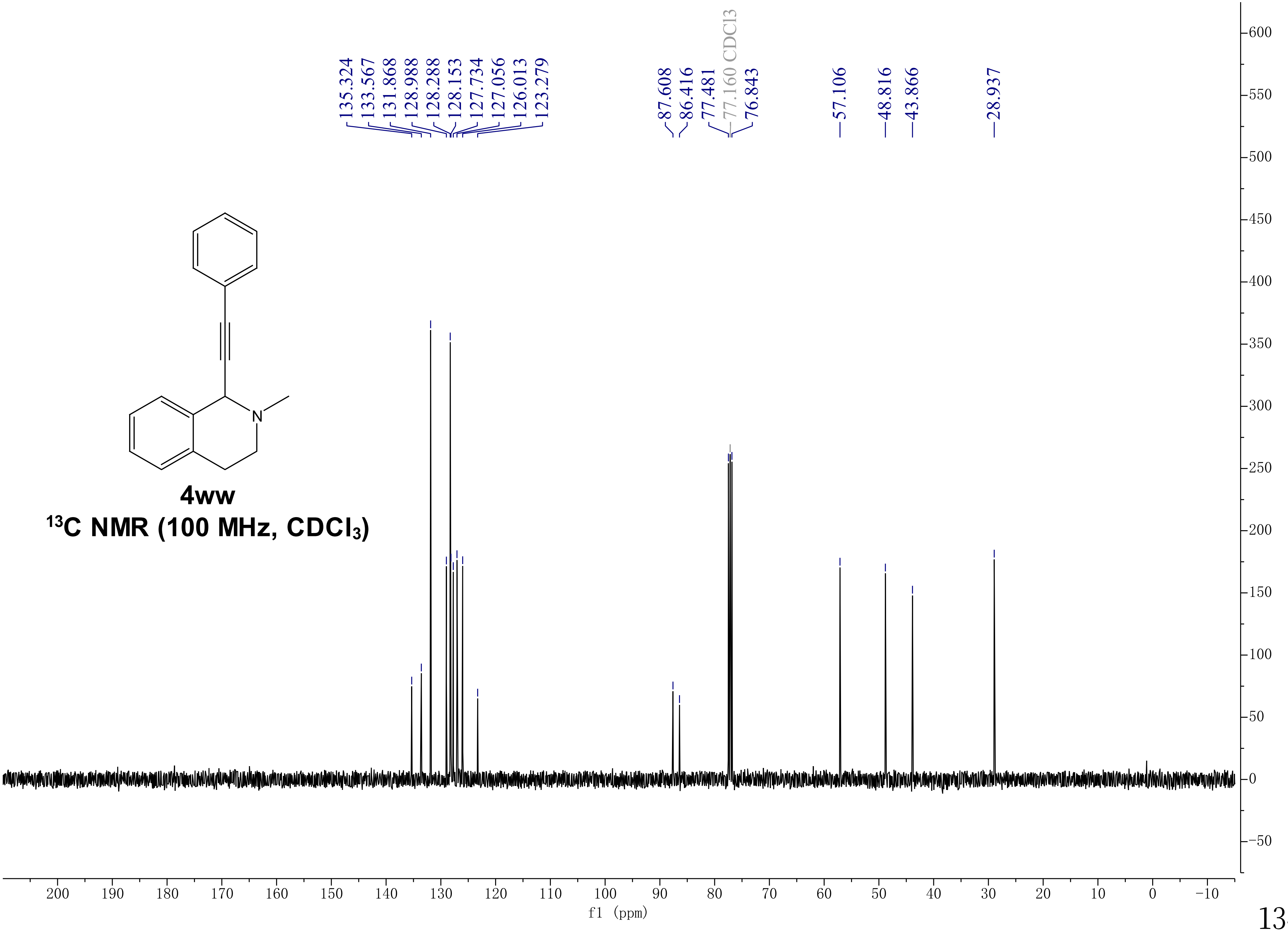


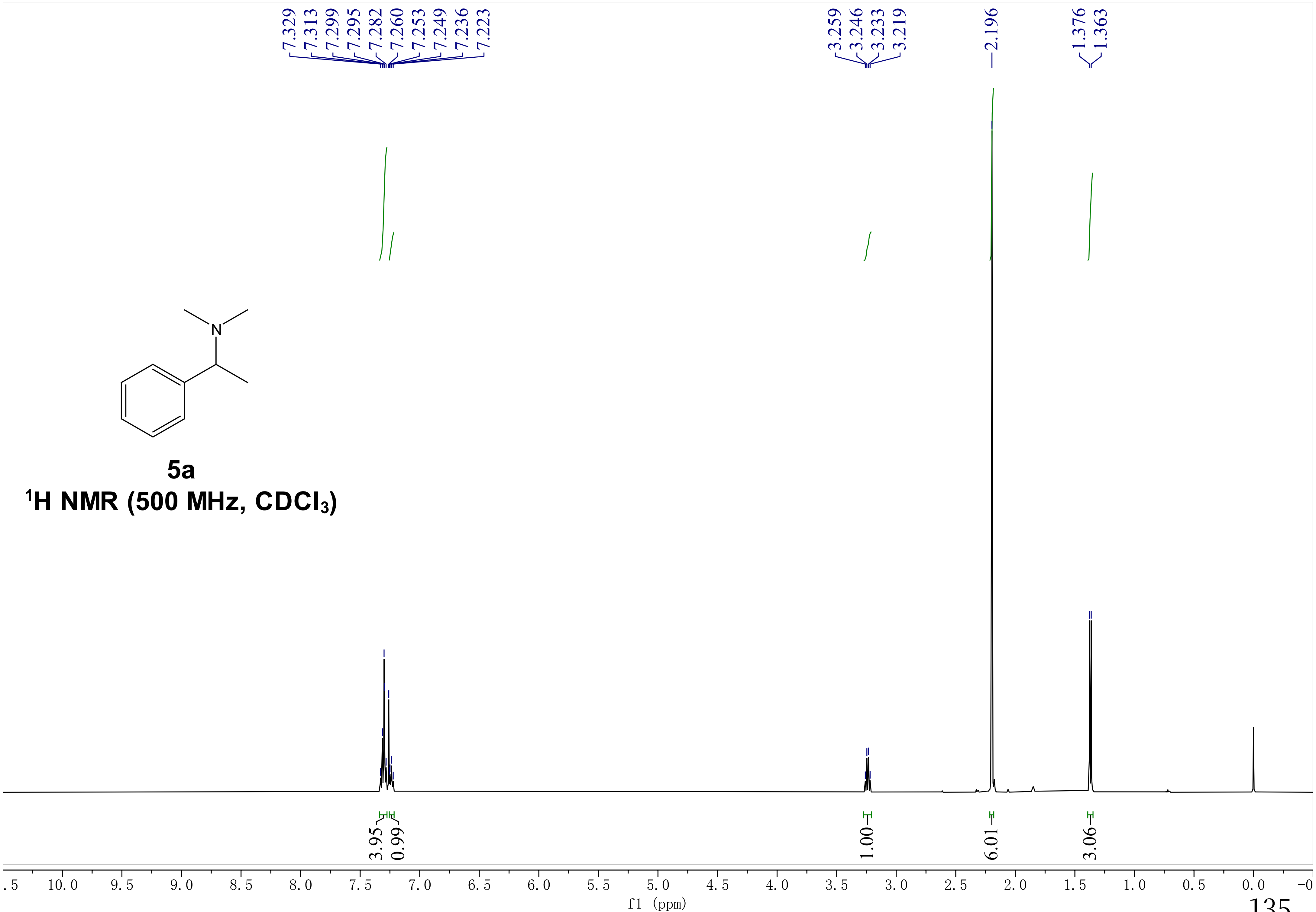
4ww

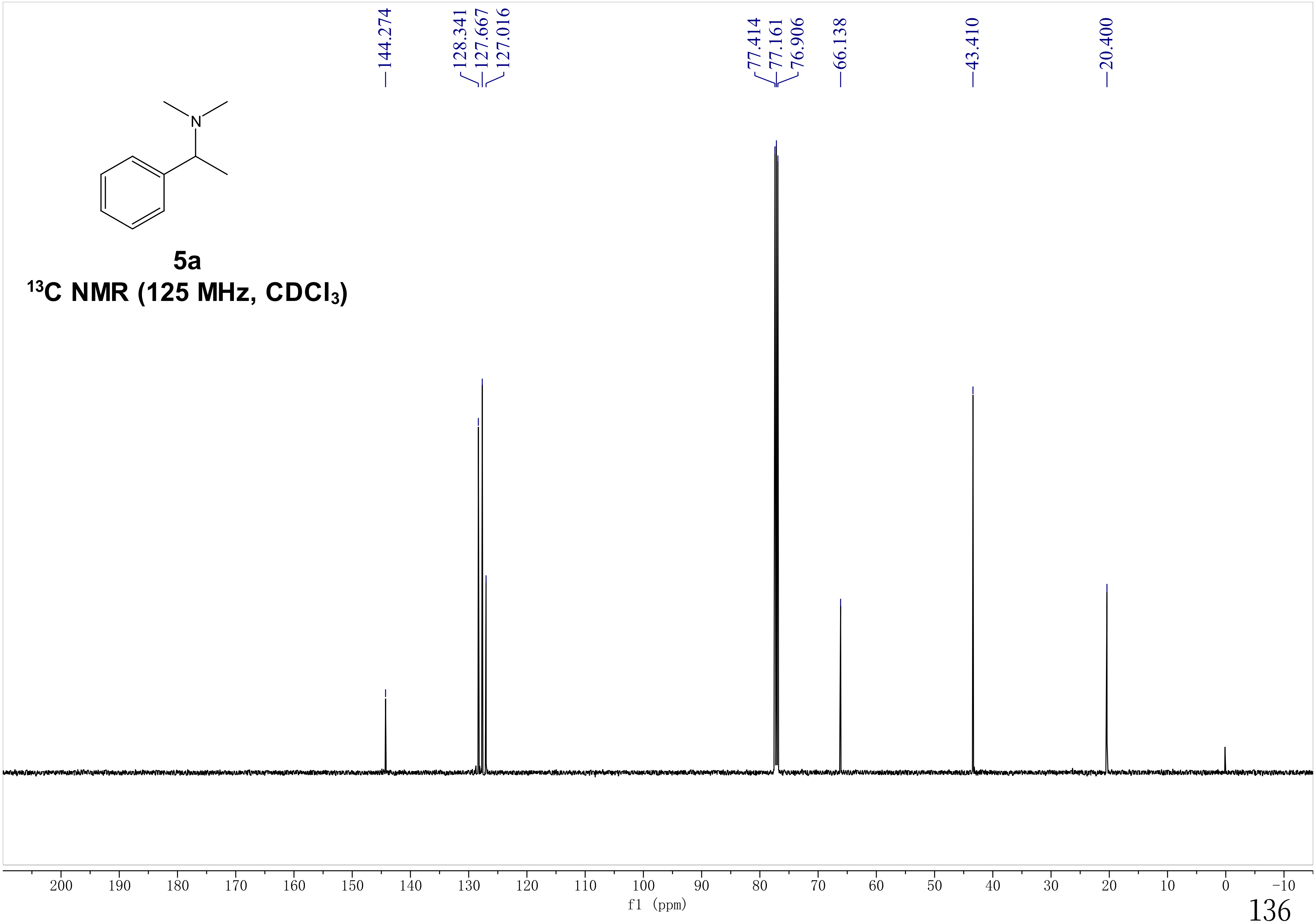
^{1}H NMR (400 MHz, $CDCl_3$)

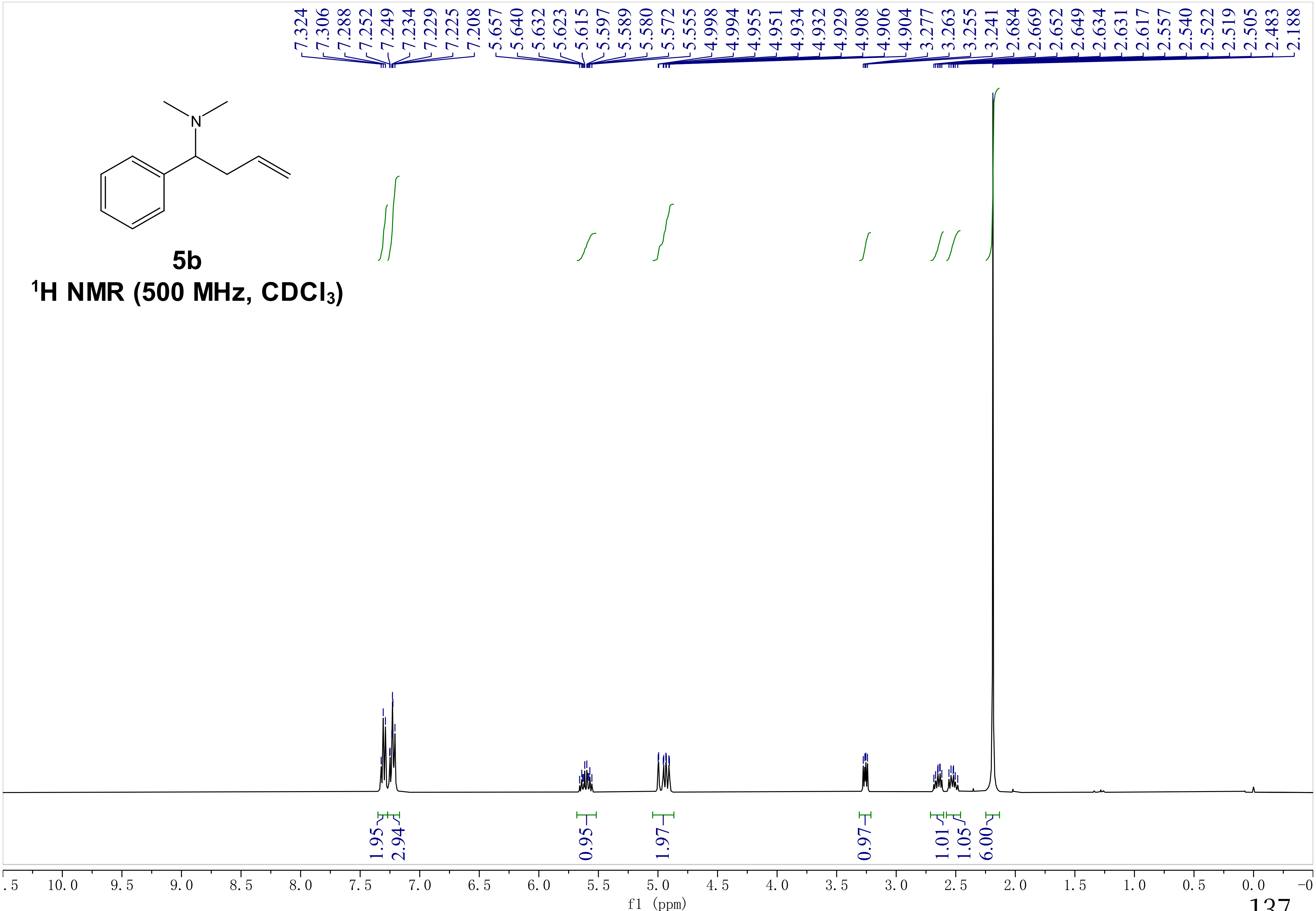


4ww
^{13}C NMR (100 MHz, $CDCl_3$)

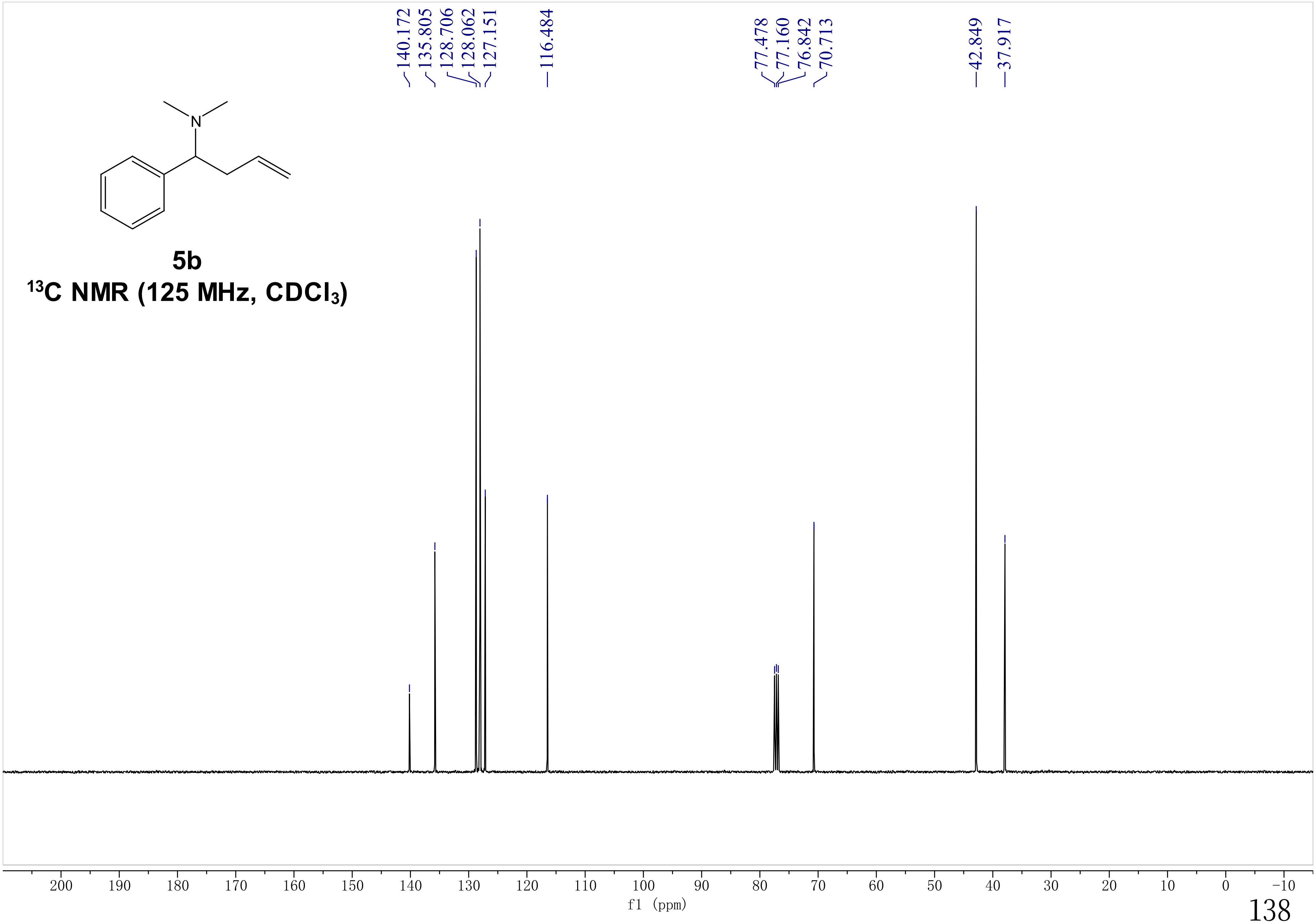


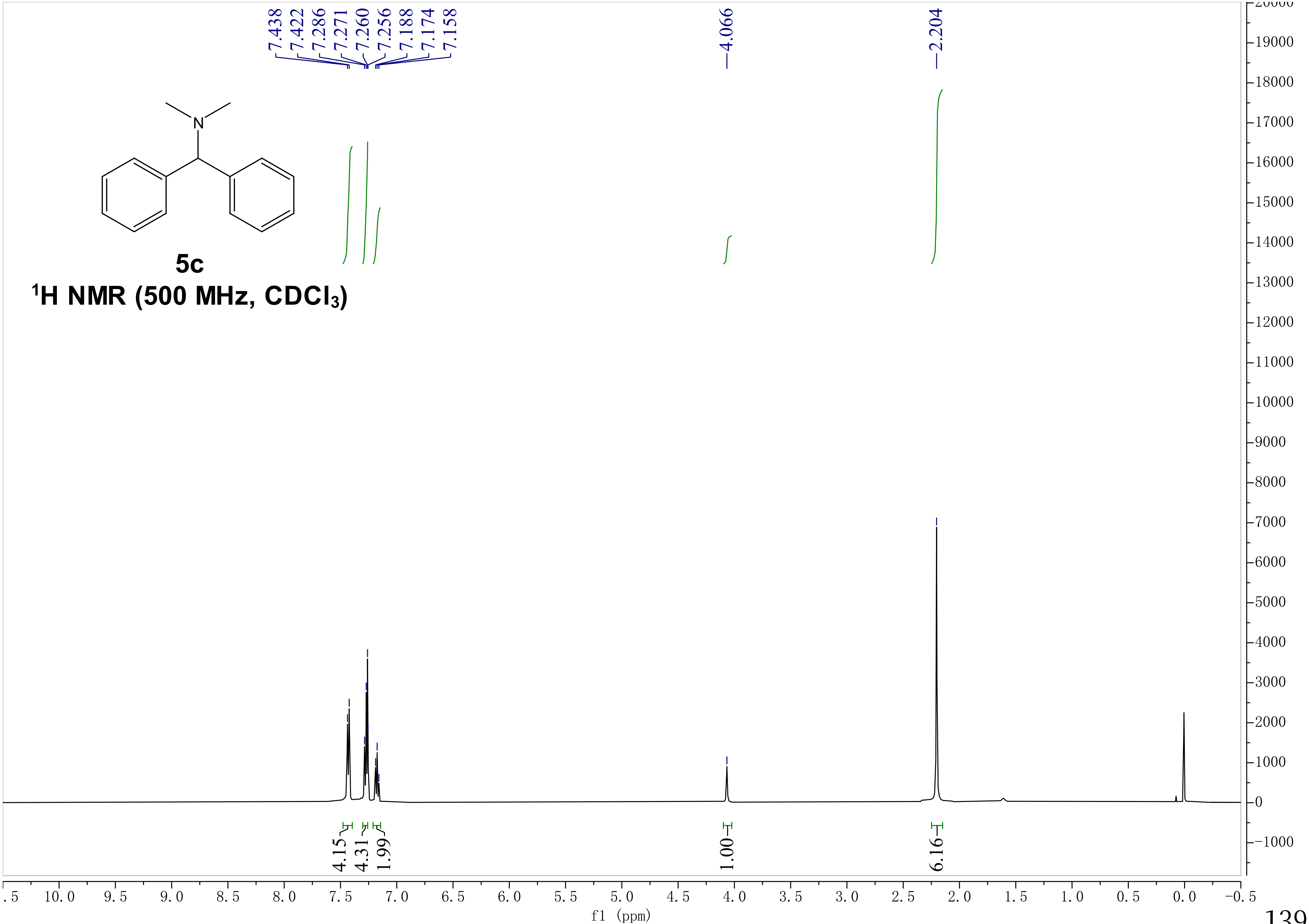

7.329
7.313
7.299
7.295
7.282
7.260
7.253
7.249
7.236
7.223
3.259
3.246
3.233
3.219
2.196
1.376
1.363
N
5a
^{1}H NMR (500 MHz, $CDCl_3$)
3.95
0.99
1.00
6.01
3.06
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)


144.274
128.341
127.667
127.016
77.414
77.161
76.906
66.138
43.410
20.400
N
5a
^{13}C NMR (125 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

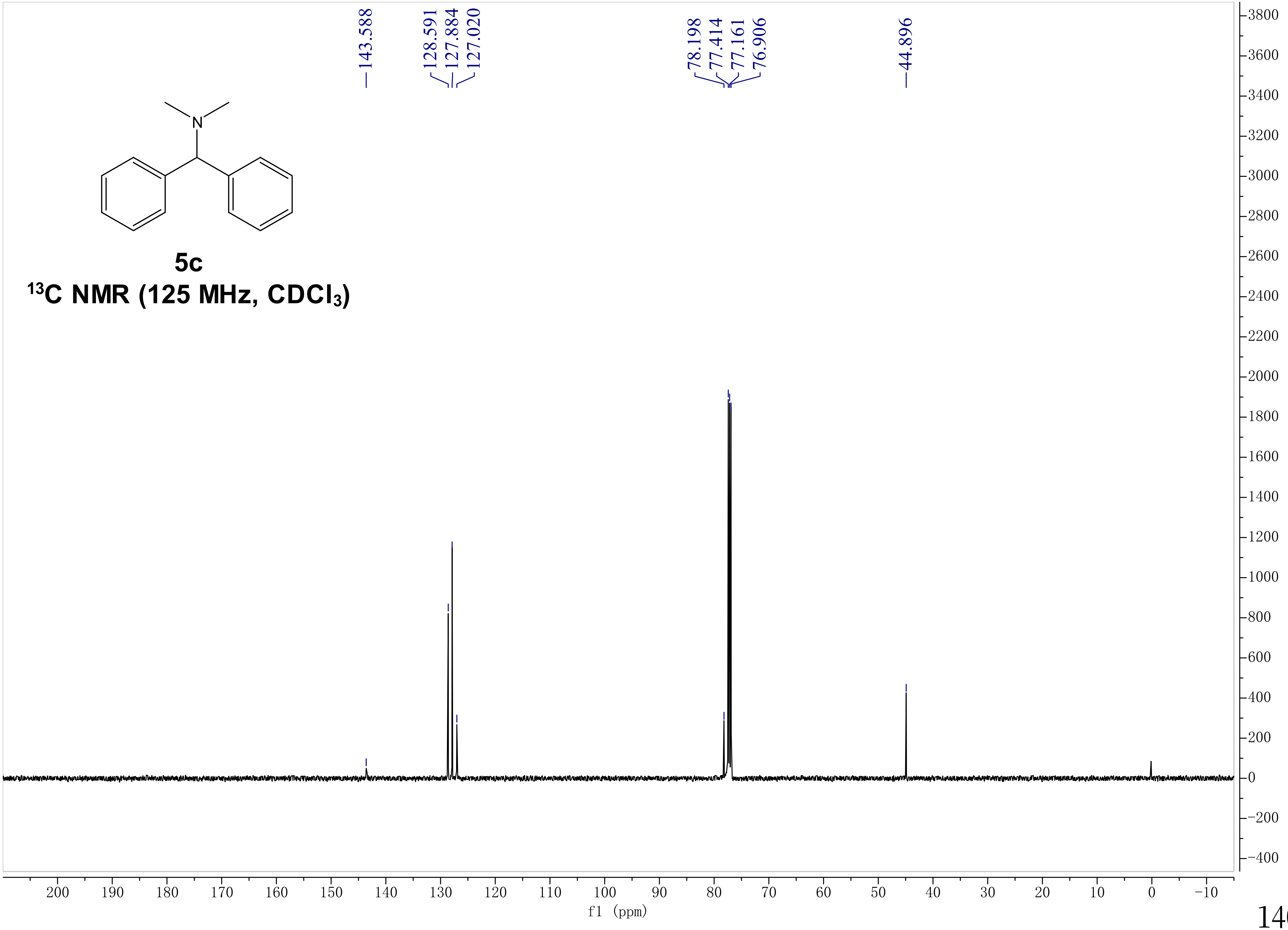


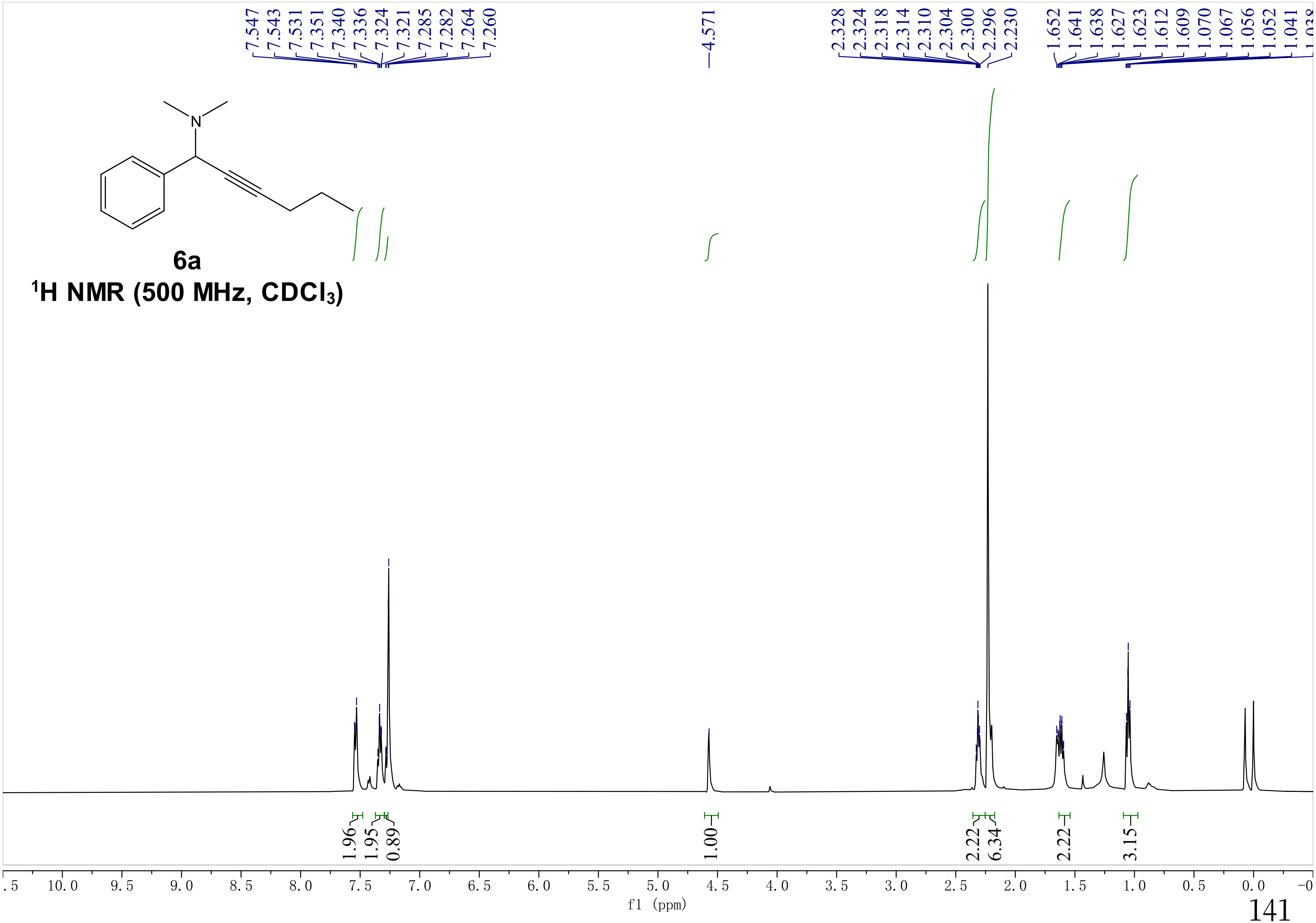
5b
1H NMR (500 MHz, CDCl3)
7.324 7.306 7.288 7.252 7.249 7.234 7.229 7.225 7.208 5.657 5.640 5.632 5.623 5.615 5.597 5.589 5.580 5.572 5.555 4.998 4.994 4.955 4.951 4.934 4.932 4.929 4.908 4.906 4.904 3.277 3.263 3.255 3.241 2.684 2.669 2.652 2.649 2.634 2.631 2.617 2.557 2.540 2.522 2.519 2.505 2.483 2.188
1.95 2.94 0.95 1.97 0.97 1.01 1.05 6.00
f1 (ppm)

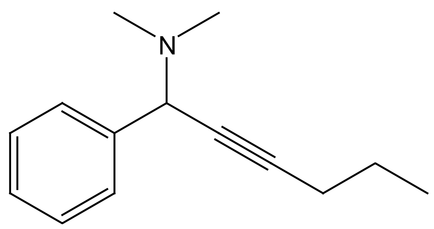

140.172
135.805
128.706
128.062
127.151
116.484
77.478
77.160
76.842
70.713
42.849
37.917
N
5b
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



5c
¹H NMR (500 MHz, CDCl3)
7.438
7.422
7.286
7.271
7.260
7.256
7.188
7.174
7.158
4.066
2.204
4.15
4.31
1.99
1.00
6.16
f1 (ppm)

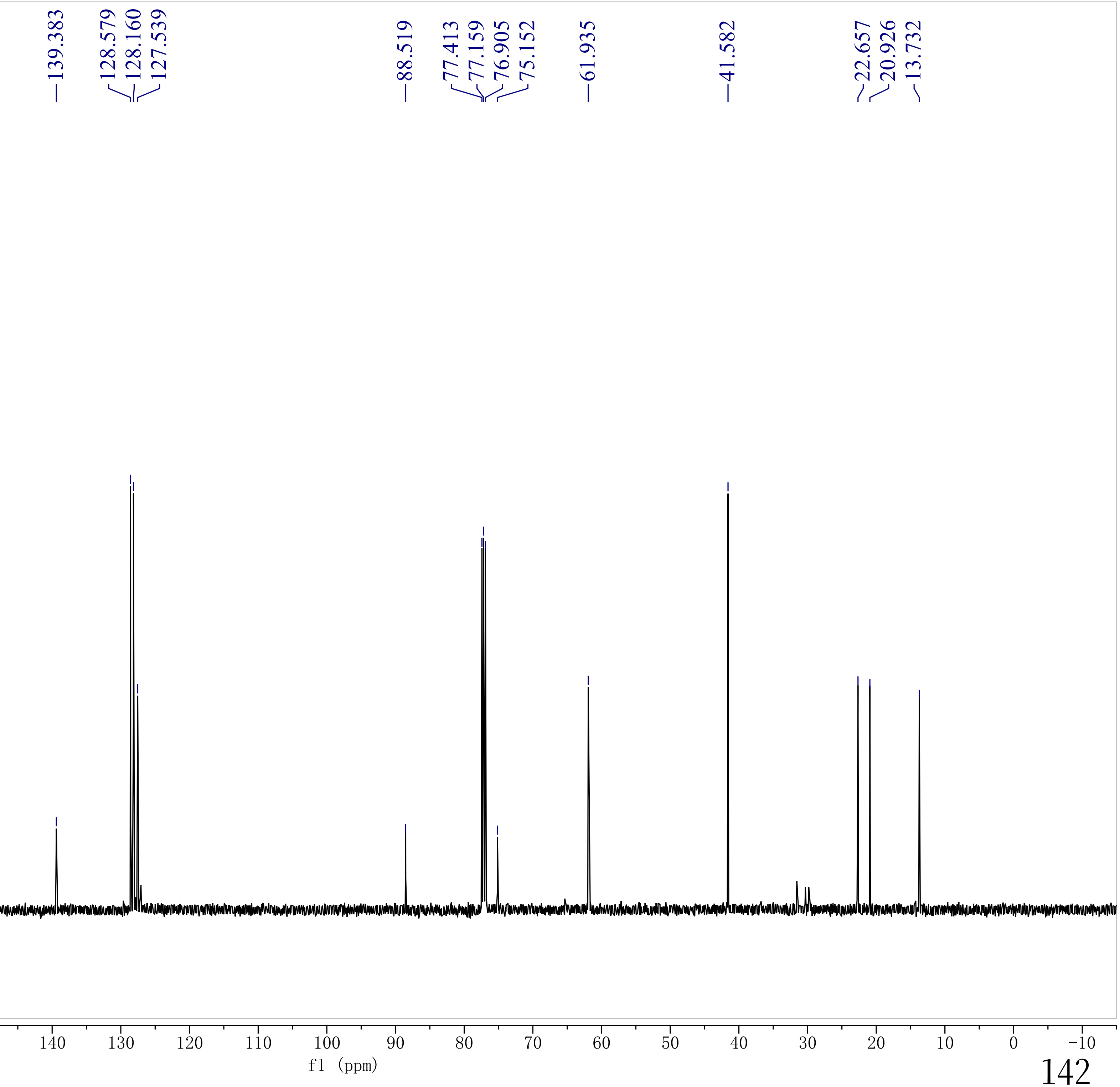

5c
13C NMR (125 MHz, CDCl3)
143.588
128.591
127.884
127.020
78.198
77.414
77.161
76.906
44.896
f1 (ppm)

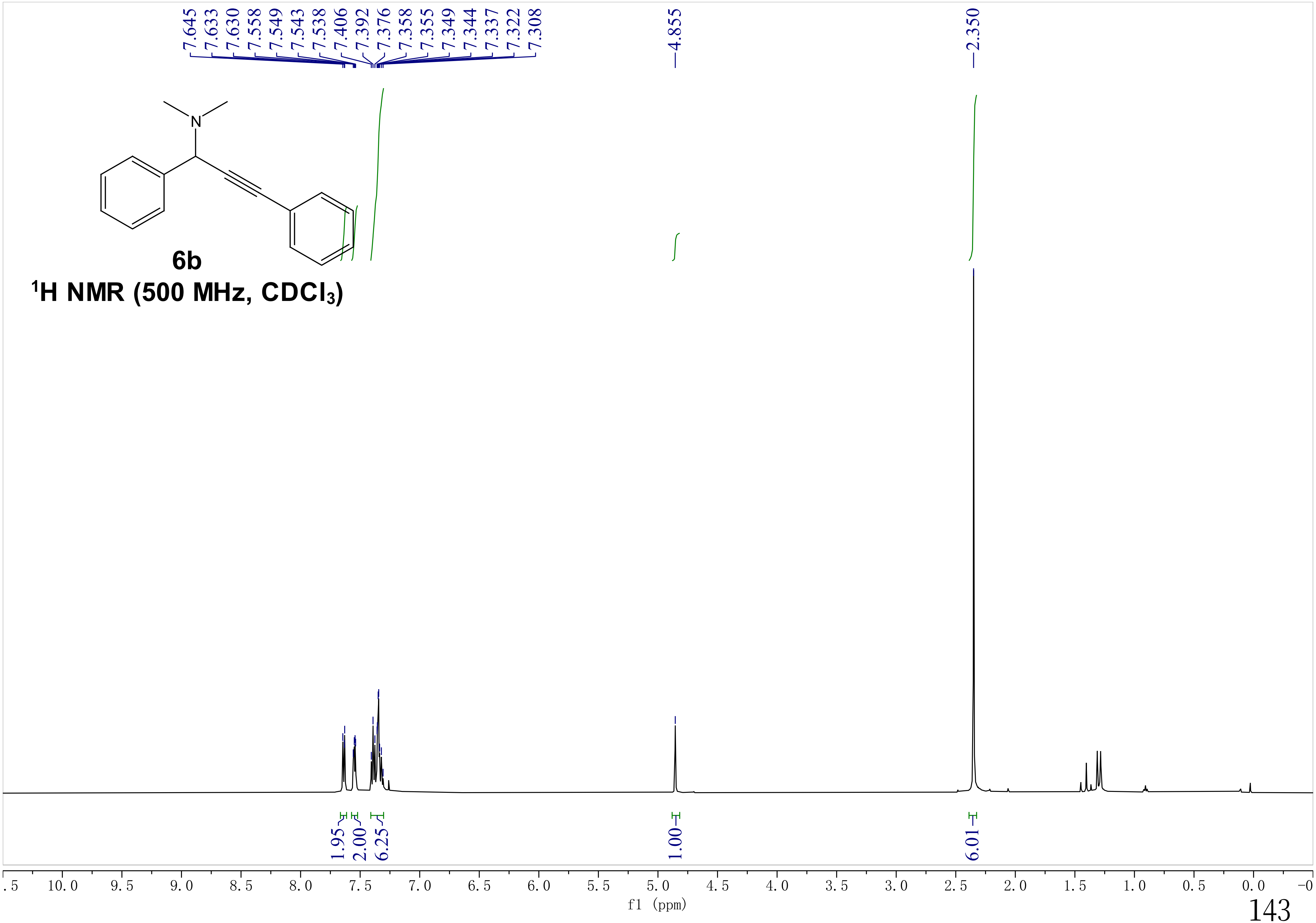

7.547 7.543 7.531 7.351 7.340 7.336 7.324 7.321 7.285 7.282 7.264 7.260
4.571
2.328 2.324 2.318 2.314 2.310 2.304 2.300 2.296 2.230
1.652 1.641 1.638 1.627 1.623 1.612 1.609 1.070 1.067 1.056 1.052 1.041
N
6a
^{1}H NMR (500 MHz, $CDCl_3$)
1.96 1.95 0.89
1.00
2.22 6.34
2.22
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

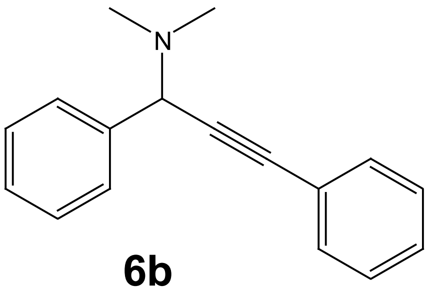


6a

^{13}C NMR (125 MHz, $CDCl_3$)

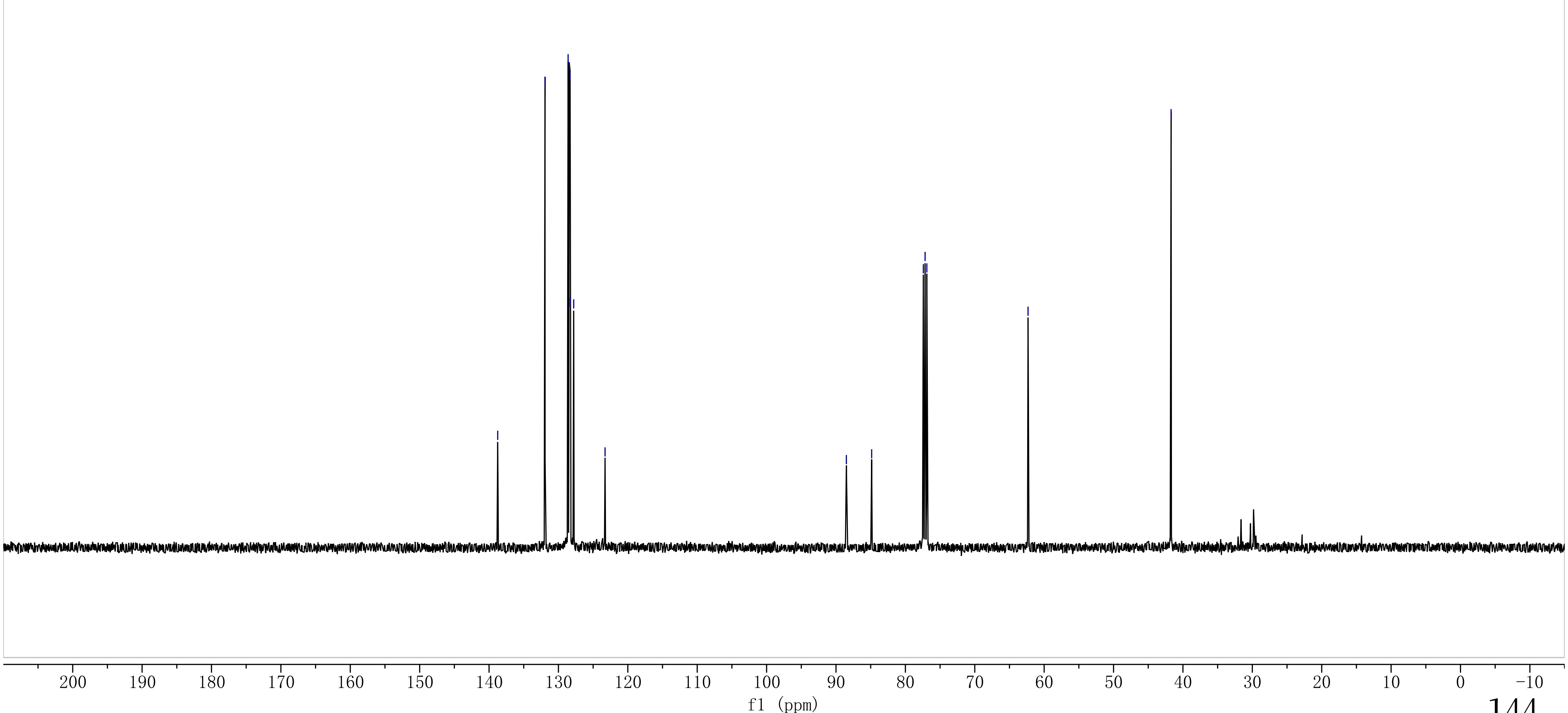



7.645
7.633
7.630
7.558
7.549
7.543
7.538
7.406
7.392
7.376
7.358
7.355
7.349
7.344
7.337
7.322
7.308
4.855
2.350
N
6b
^{1}H NMR (500 MHz, $CDCl_3$)
1.95
2.00
6.25
1.00
6.01
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)



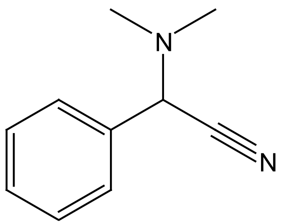
6b

^{13}C NMR (125 MHz, $CDCl_3$)



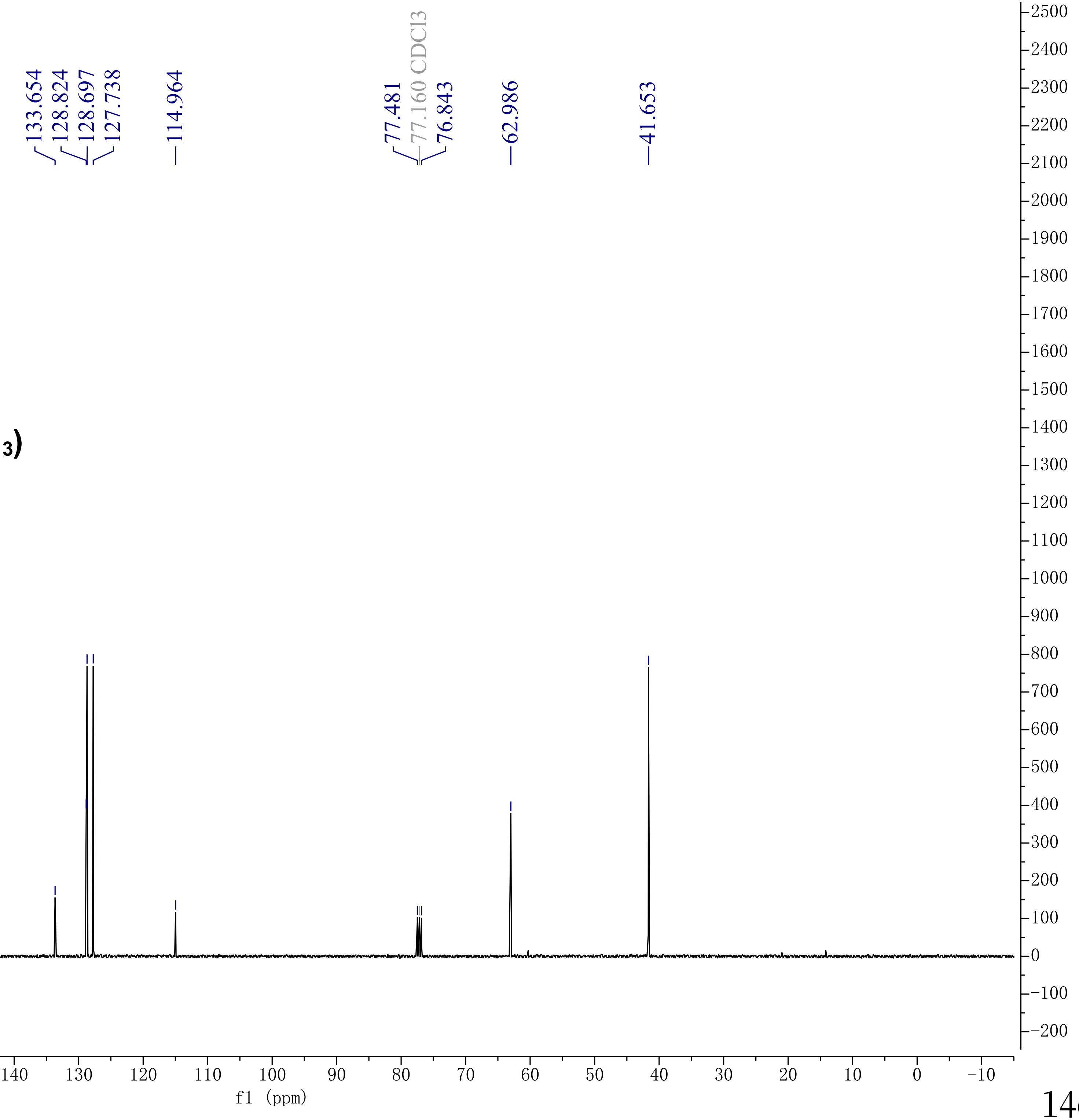
7a

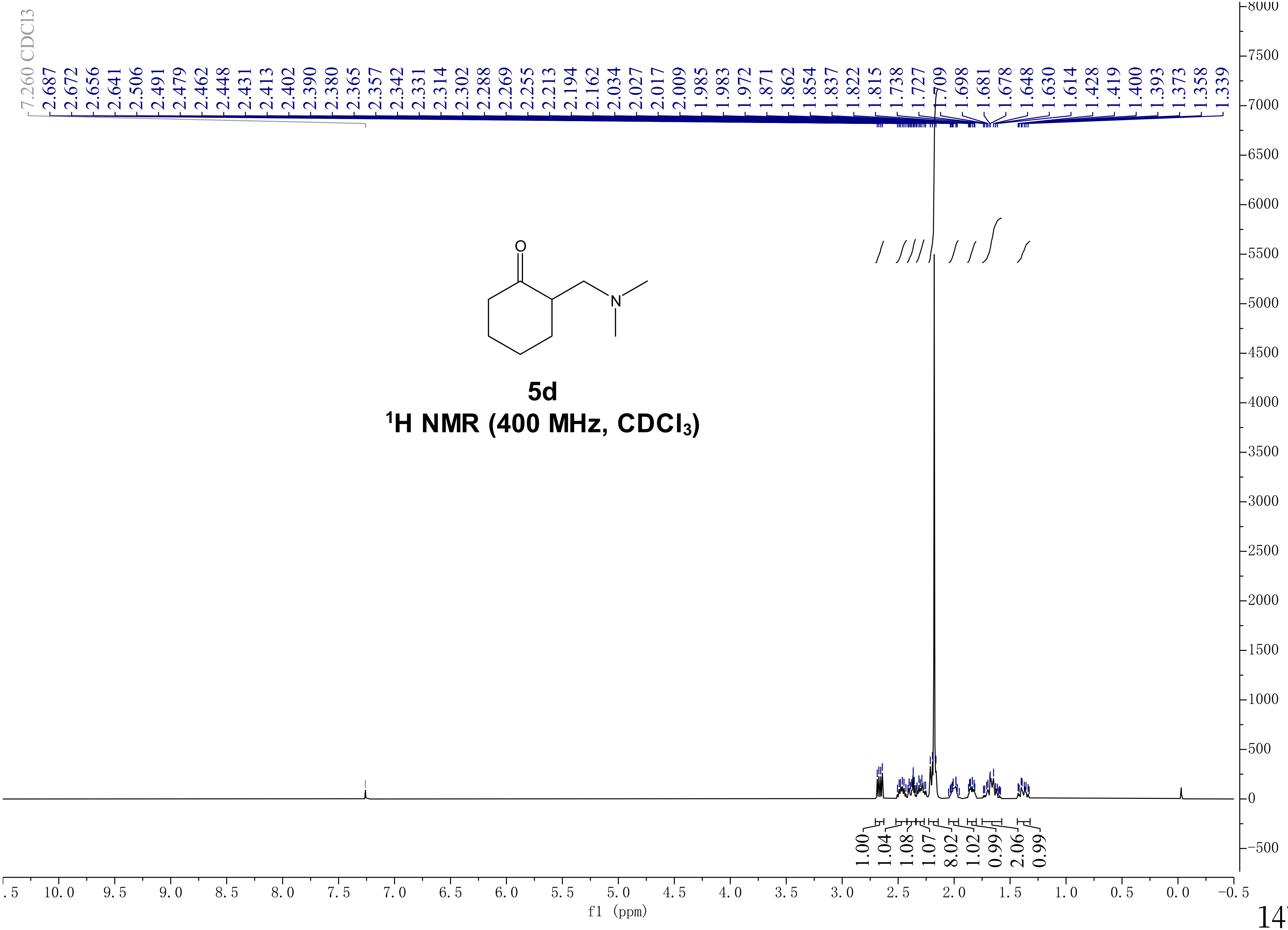
^{1}H NMR (400 MHz, $CDCl_3$)

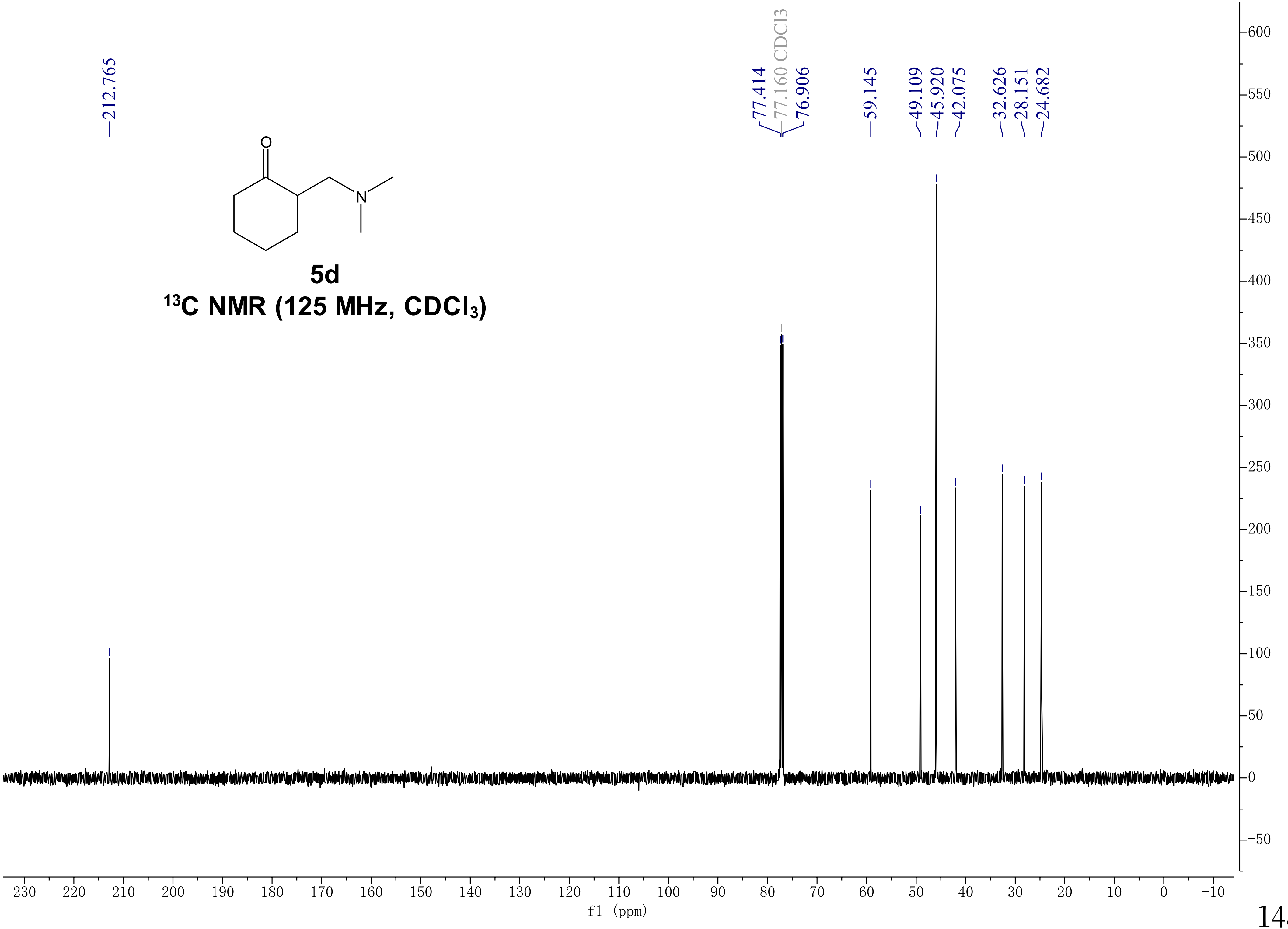


7a

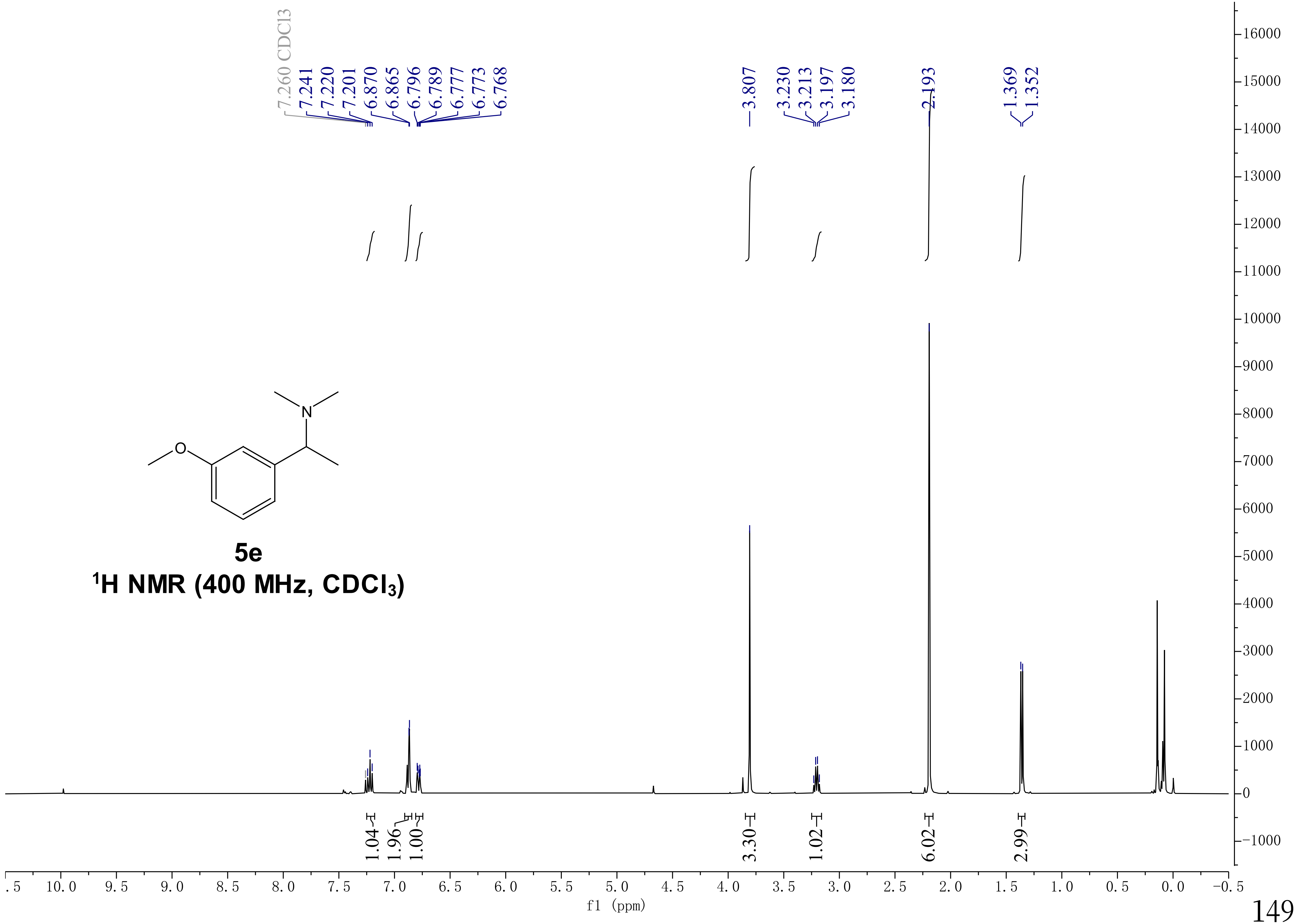
^{13}C NMR (100 MHz, $CDCl_3$)

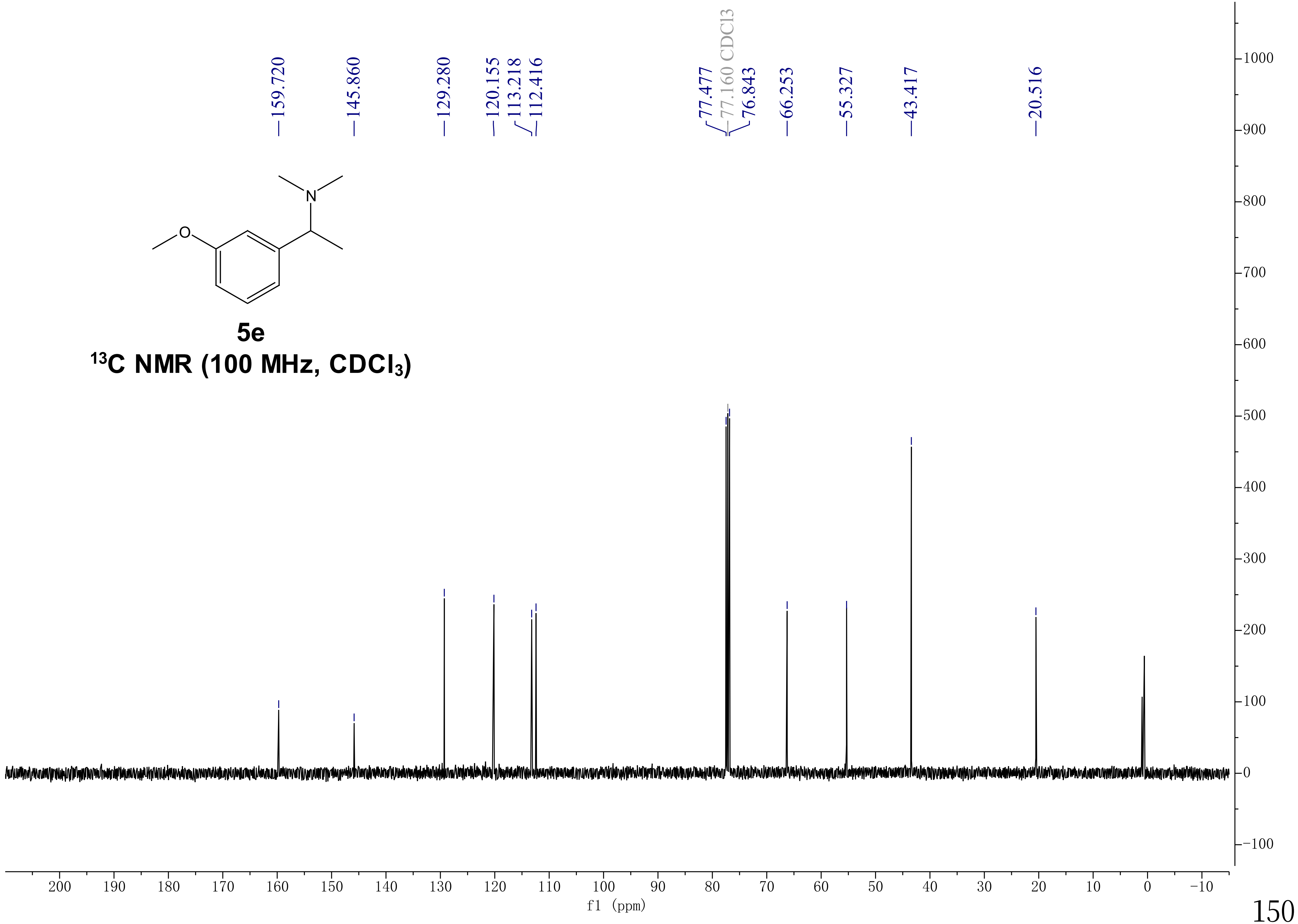


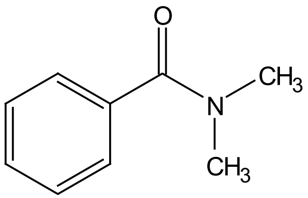

7.260 CDCl3
2.687 2.672 2.656 2.641 2.506 2.491 2.479 2.462 2.448 2.431 2.413 2.402 2.390 2.380 2.365 2.357 2.342 2.331 2.314 2.302 2.288 2.269 2.255 2.213 2.194 2.162 2.034 2.027 2.017 2.009 1.985 1.983 1.972 1.871 1.862 1.854 1.837 1.822 1.815 1.738 1.727 1.709 1.698 1.681 1.678 1.648 1.630 1.614 1.428 1.419 1.400 1.393 1.373 1.358 1.339
O
N
5d
1H NMR (400 MHz, CDCl3)
1.00 1.04 1.08 1.07 8.02 1.02 0.99 2.06 0.99
f1 (ppm)



212.765
77.414
77.160 CDCl3
76.906
59.145
49.109
45.920
42.075
32.626
28.151
24.682
O
N
5d
13C NMR (125 MHz, CDCl3)
f1 (ppm)

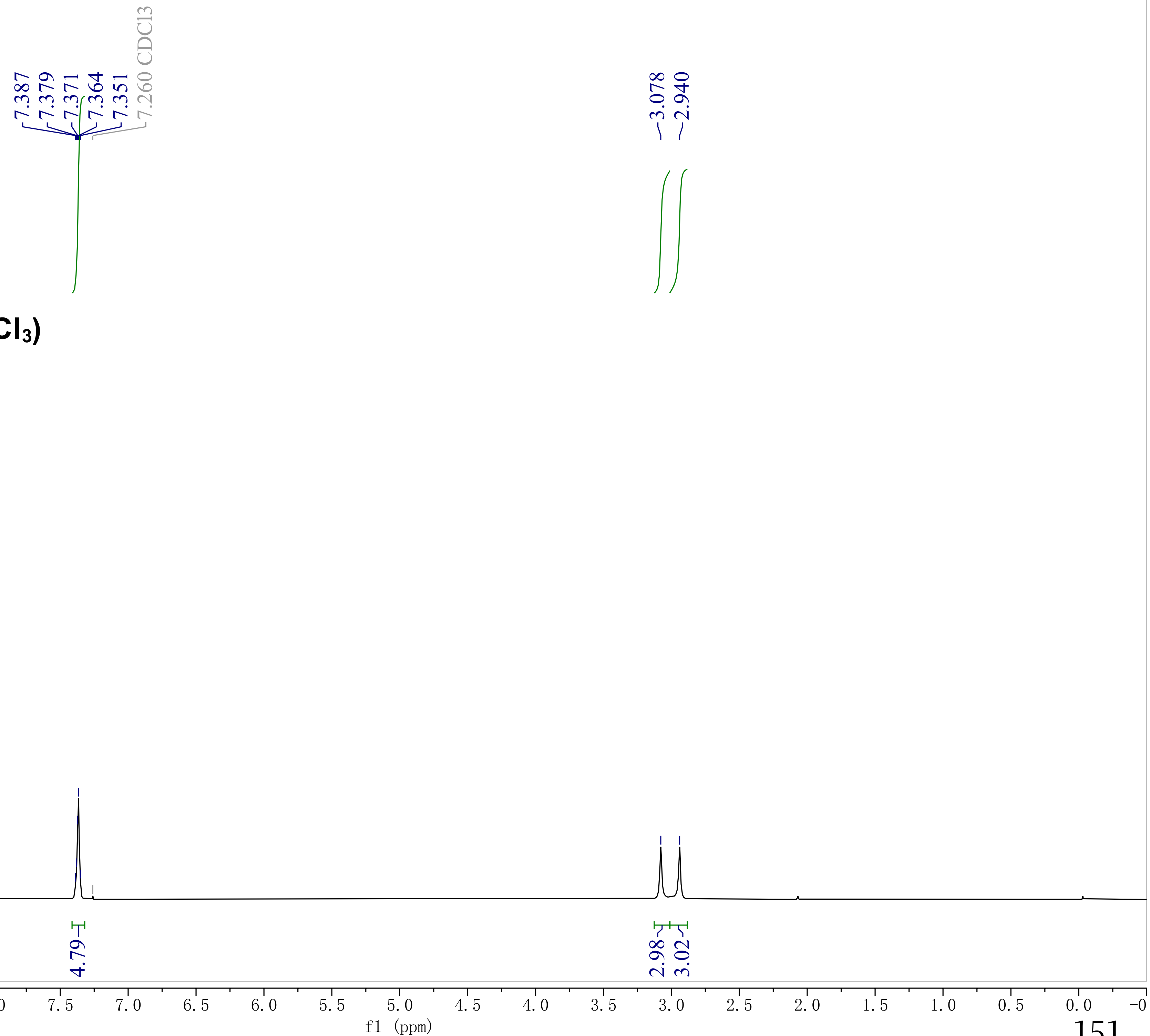

7.260 CDCl3
7.241
7.220
7.201
6.870
6.865
6.796
6.789
6.777
6.773
6.768
3.807
3.230
3.213
3.197
3.180
2.193
1.369
1.352
N
O
5e
^{1}H NMR (400 MHz, $CDCl_3$)
1.04
1.96
1.00
3.30
1.02
6.02
2.99
f1 (ppm)

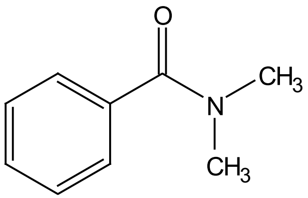

159.720
145.860
129.280
120.155
113.218
112.416
77.477
77.160 CDCl3
76.843
66.253
55.327
43.417
20.516
N
O
5e
13C NMR (100 MHz, CDCl3)
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
1000 900 800 700 600 500 400 300 200 100 0 −100



1a

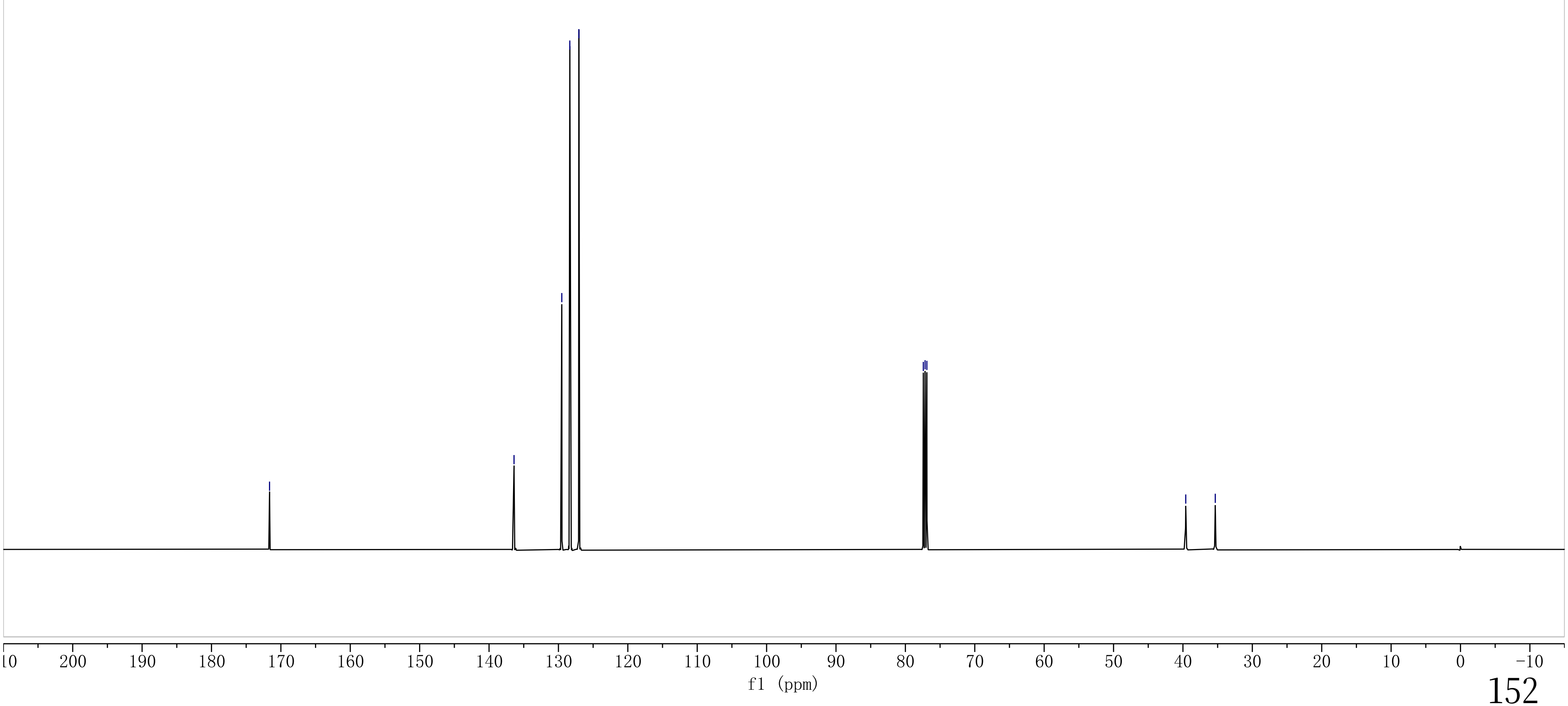
^{1}H NMR (500 MHz, $CDCl_3$)

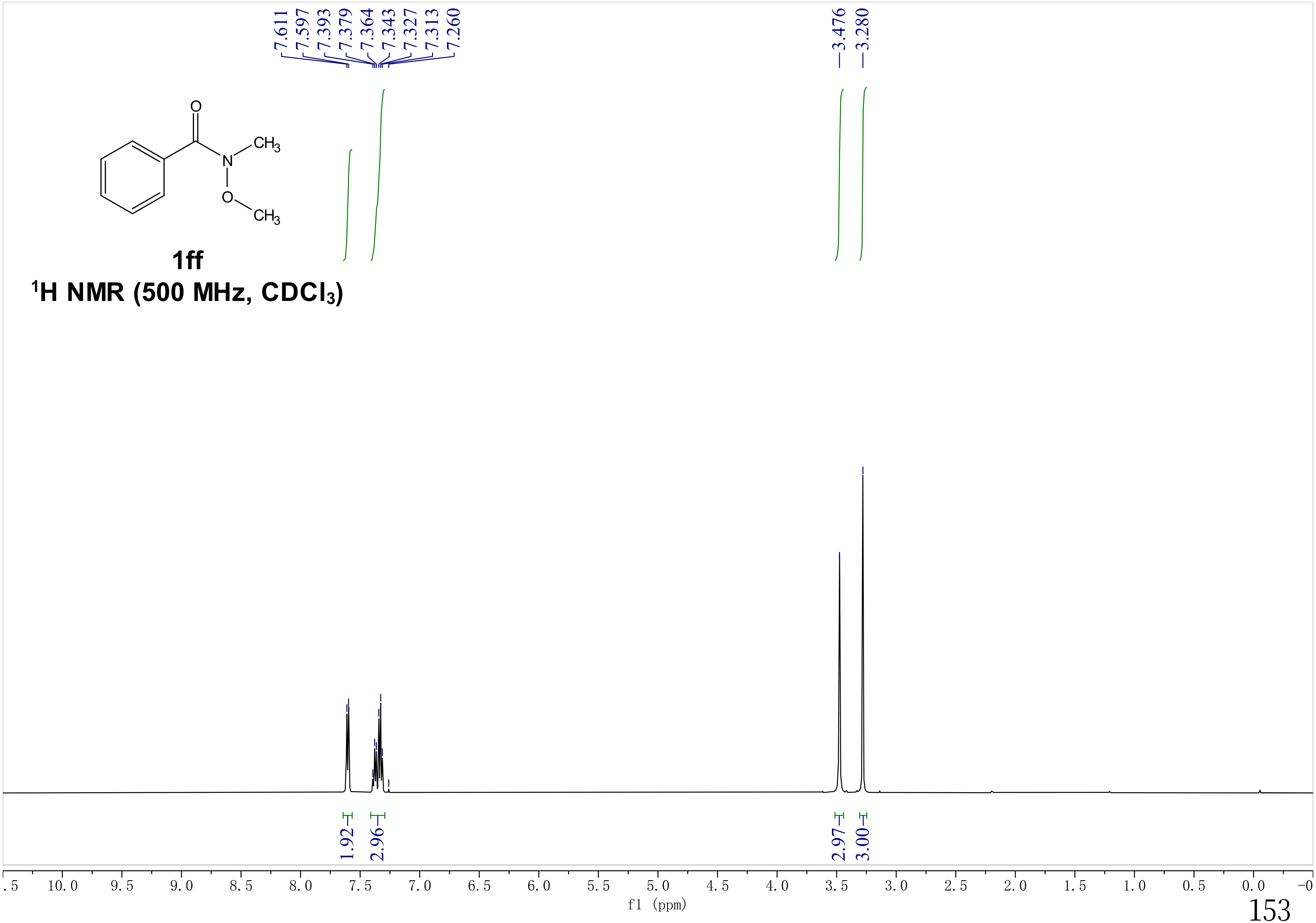


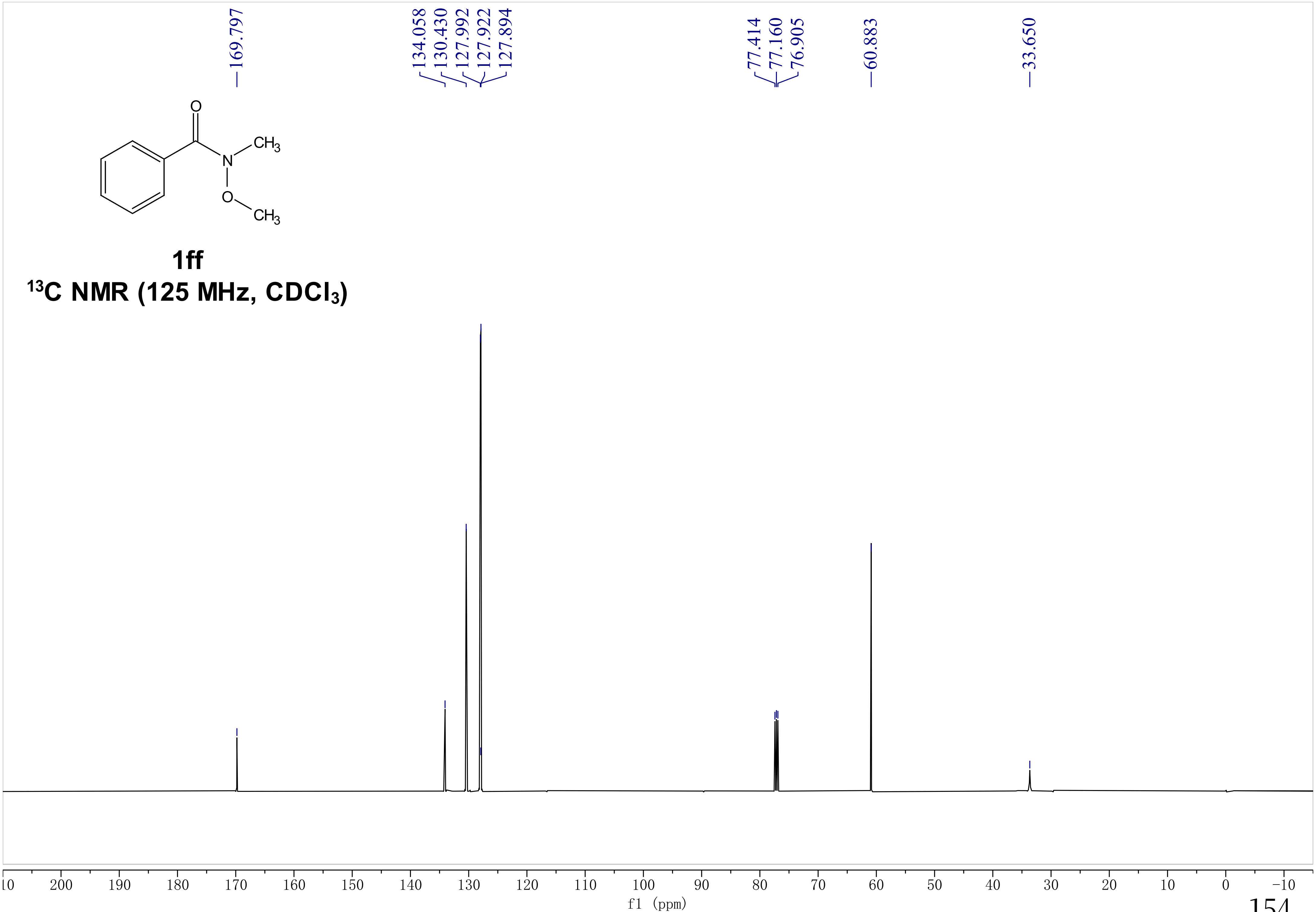


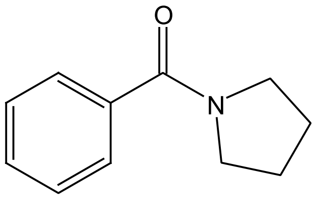
1a

^{13}C NMR (125 MHz, CDCl$_3$)



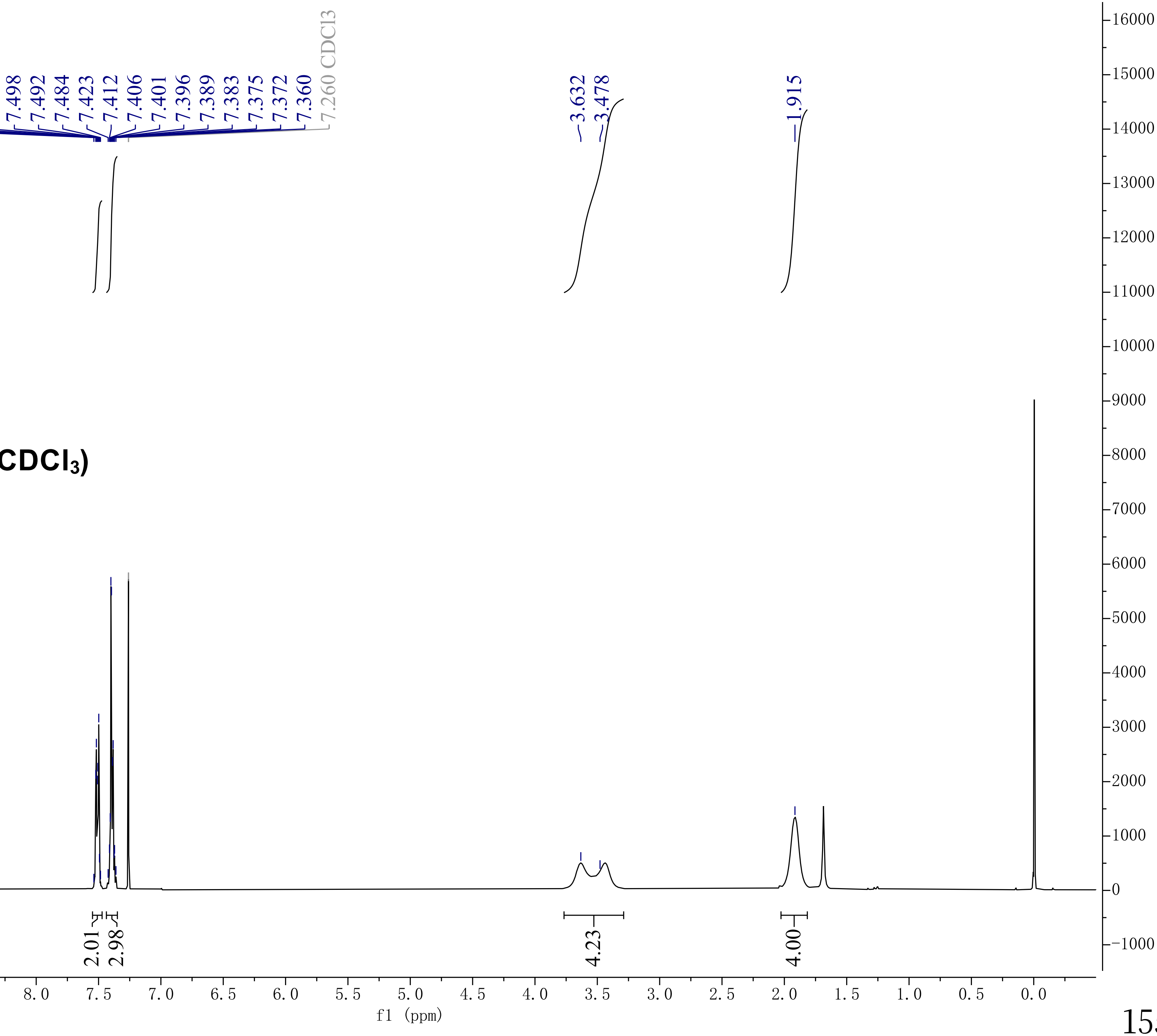

1ff
^{1}H NMR (500 MHz, CDCl$_3$)
7.611
7.597
7.393
7.379
7.364
7.343
7.327
7.313
7.260
3.476
3.280
1.92
2.96
2.97
3.00
f1 (ppm)

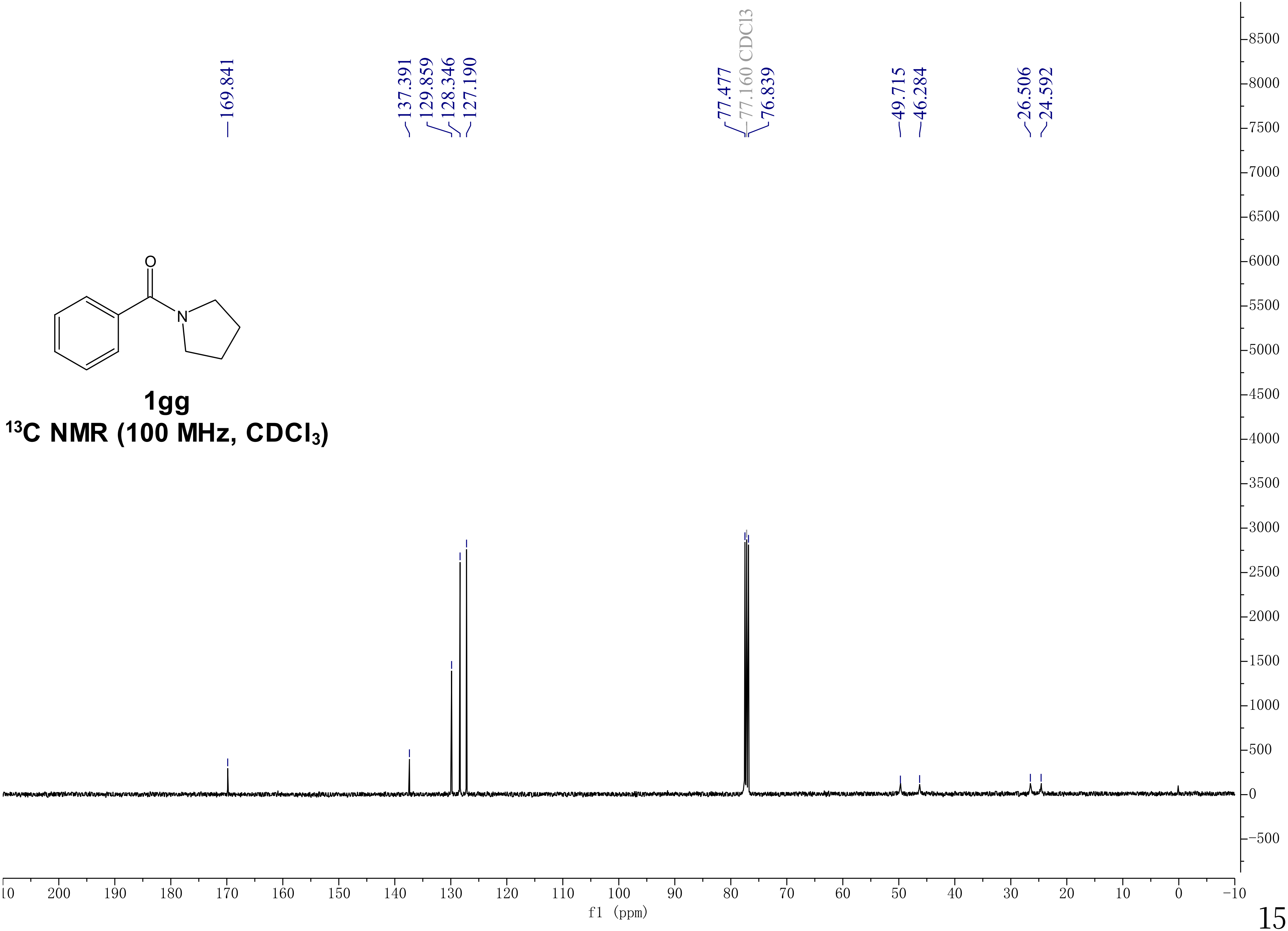

169.797
134.058
130.430
127.992
127.922
127.894
77.414
77.160
76.905
60.883
33.650
O
N
CH3
O
CH3
1ff
13C NMR (125 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



1gg

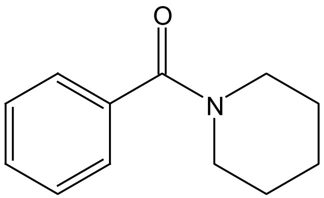
^1H NMR (400 MHz, $CDCl_3$)





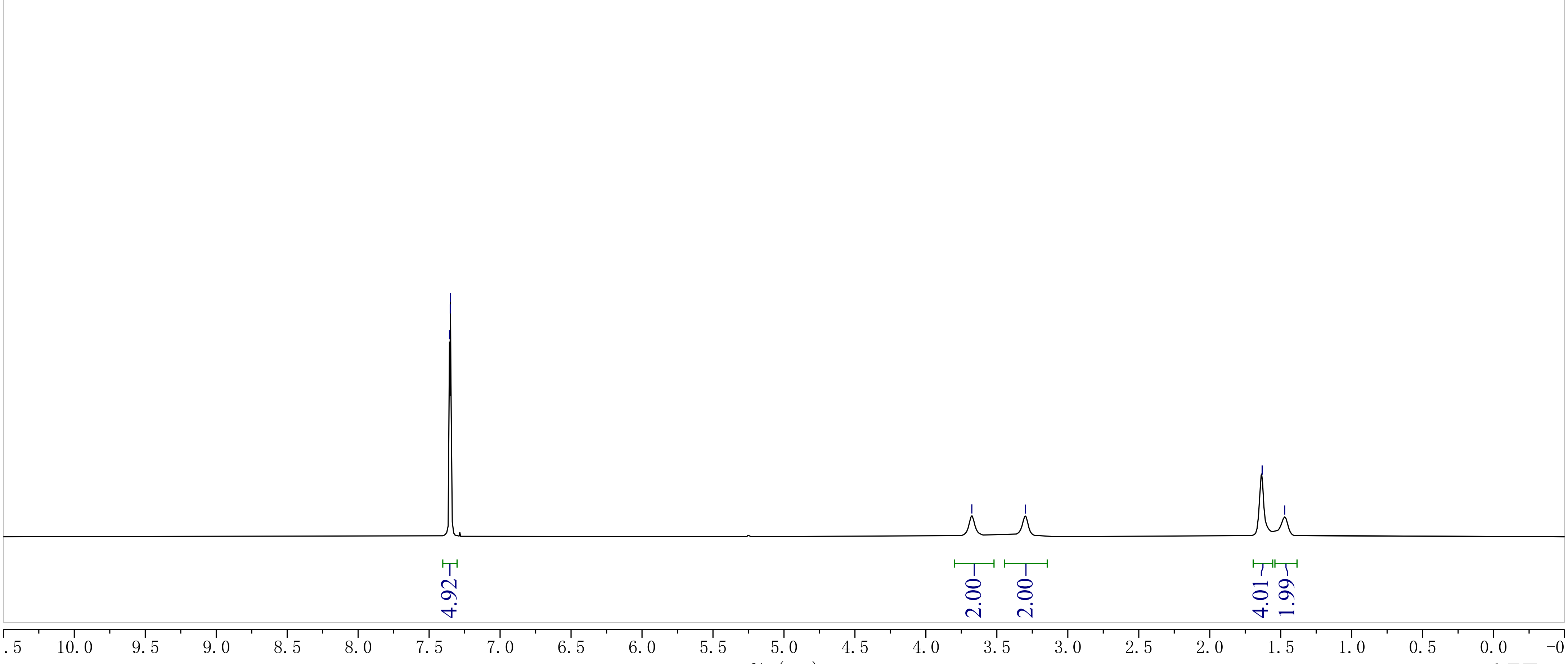
1gg

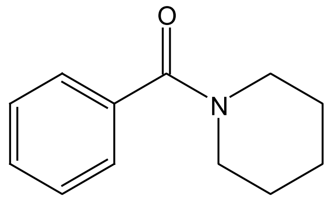
^{13}C NMR (100 MHz, $CDCl_3$)



1hh

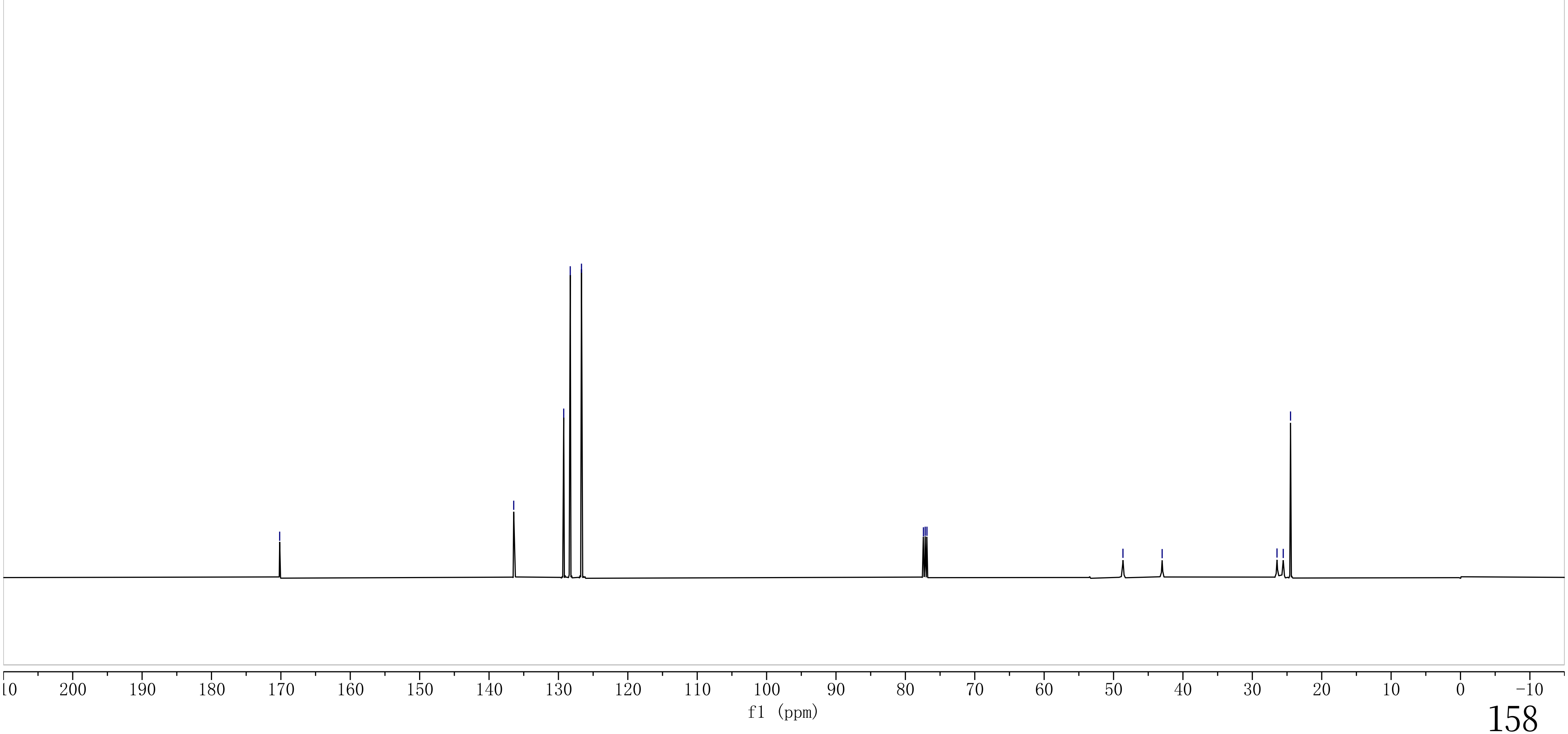
^{1}H NMR (500 MHz, $CDCl_3$)

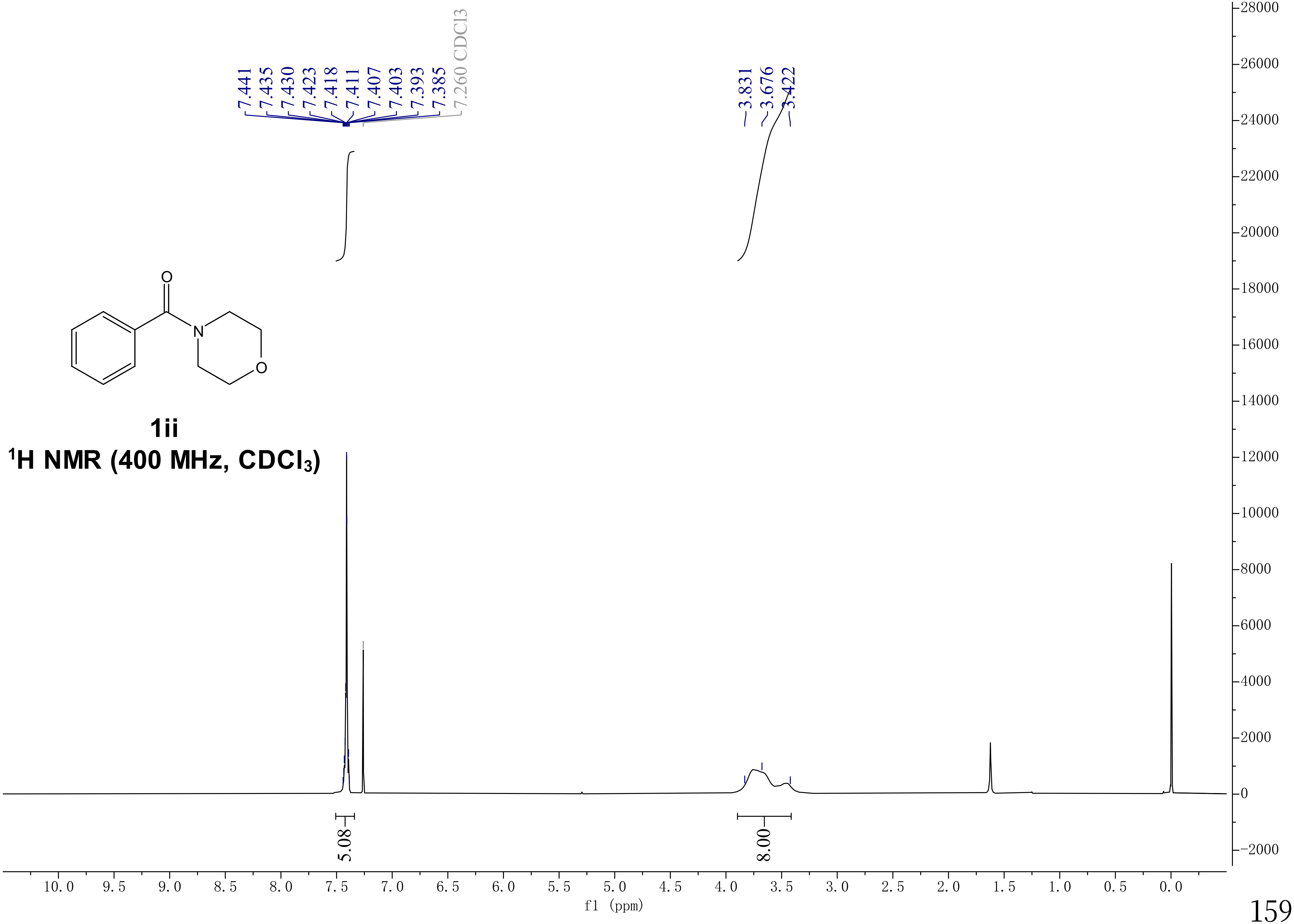


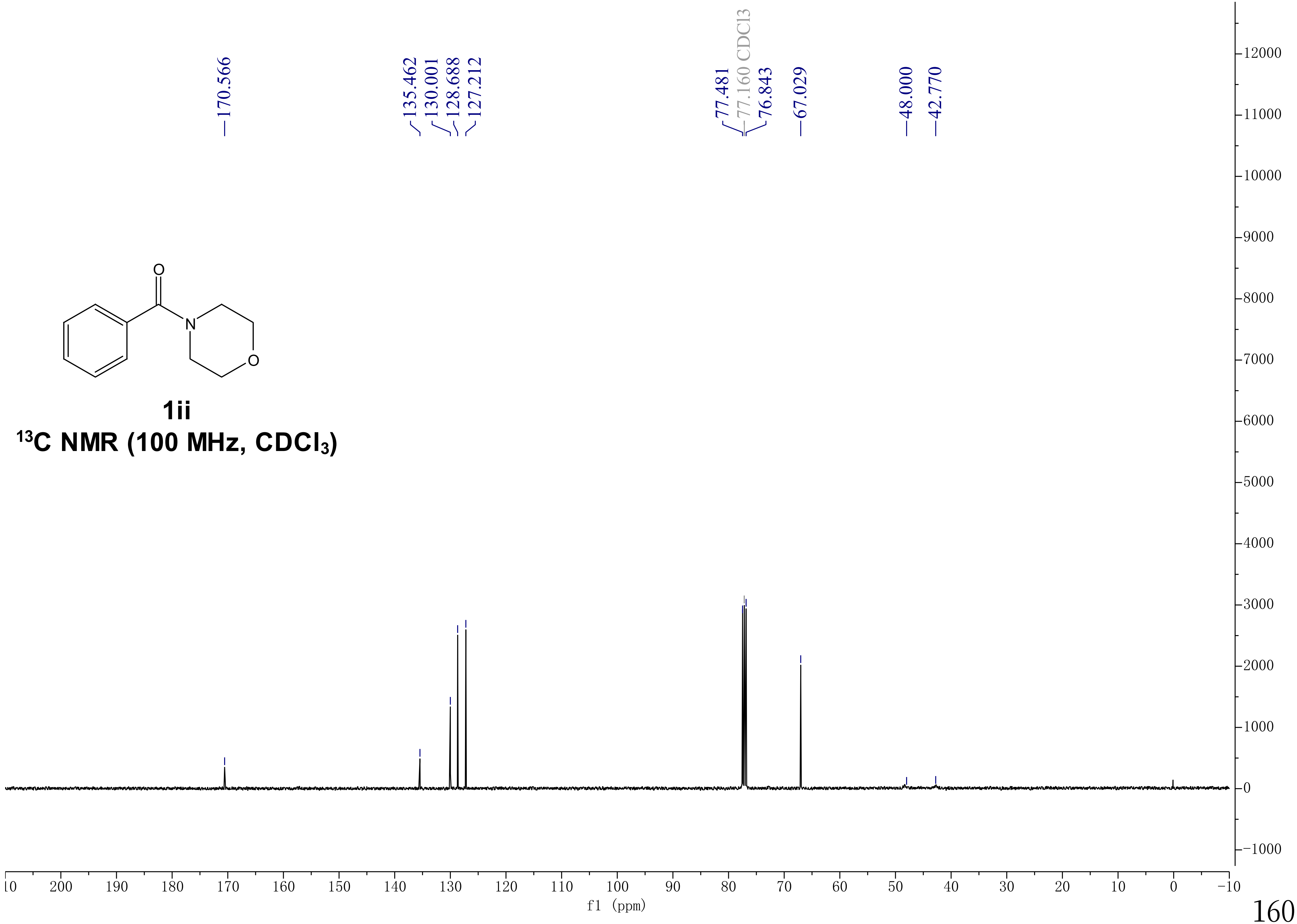


1hh

^{13}C NMR (125 MHz, $CDCl_3$)

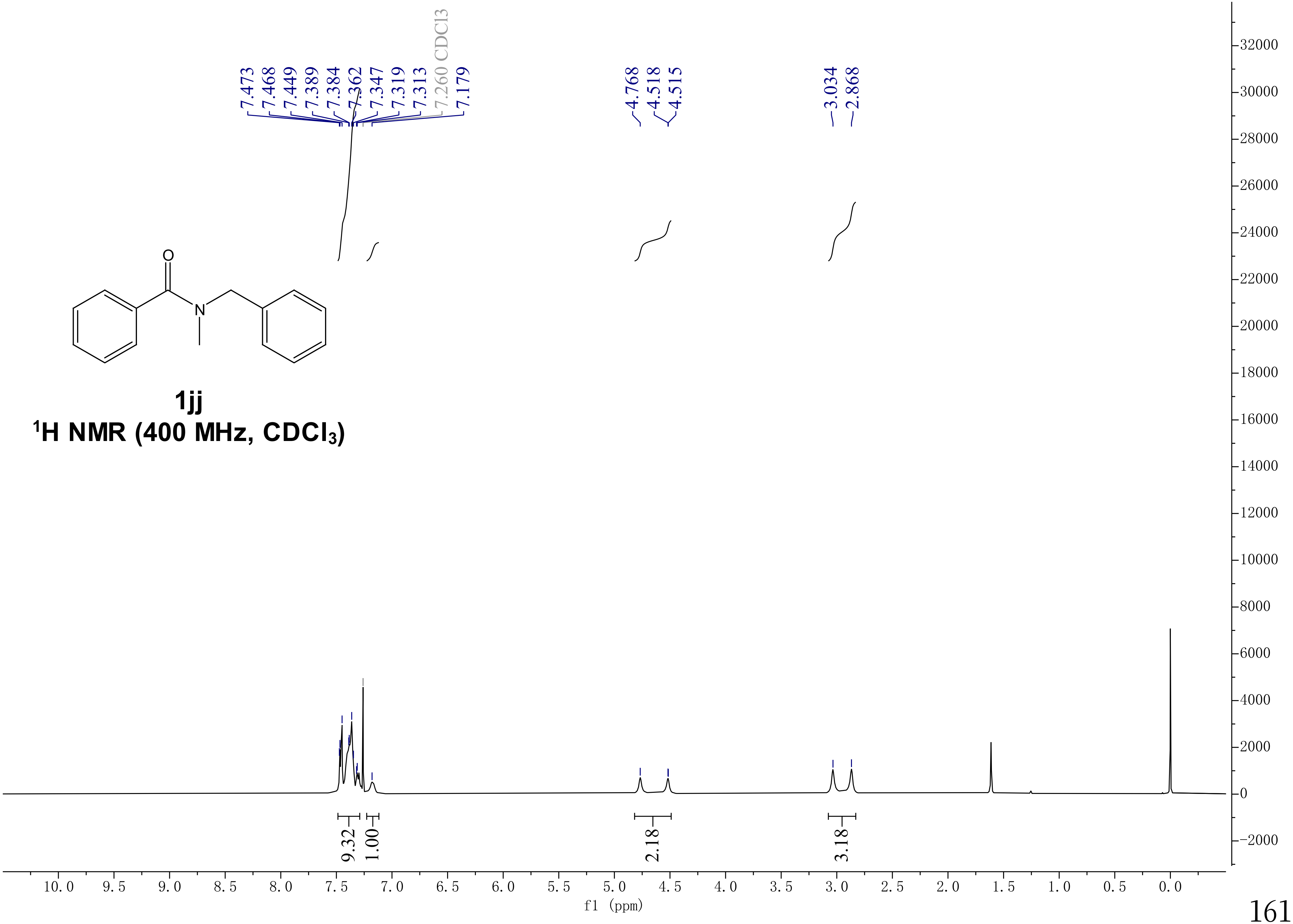



1ii
^{1}H NMR (400 MHz, CDCl$_3$)
7.441
7.435
7.430
7.423
7.418
7.411
7.407
7.403
7.393
7.385
7.260 CDCl3
3.831
3.676
3.422
5.08
8.00
f1 (ppm)



1ii

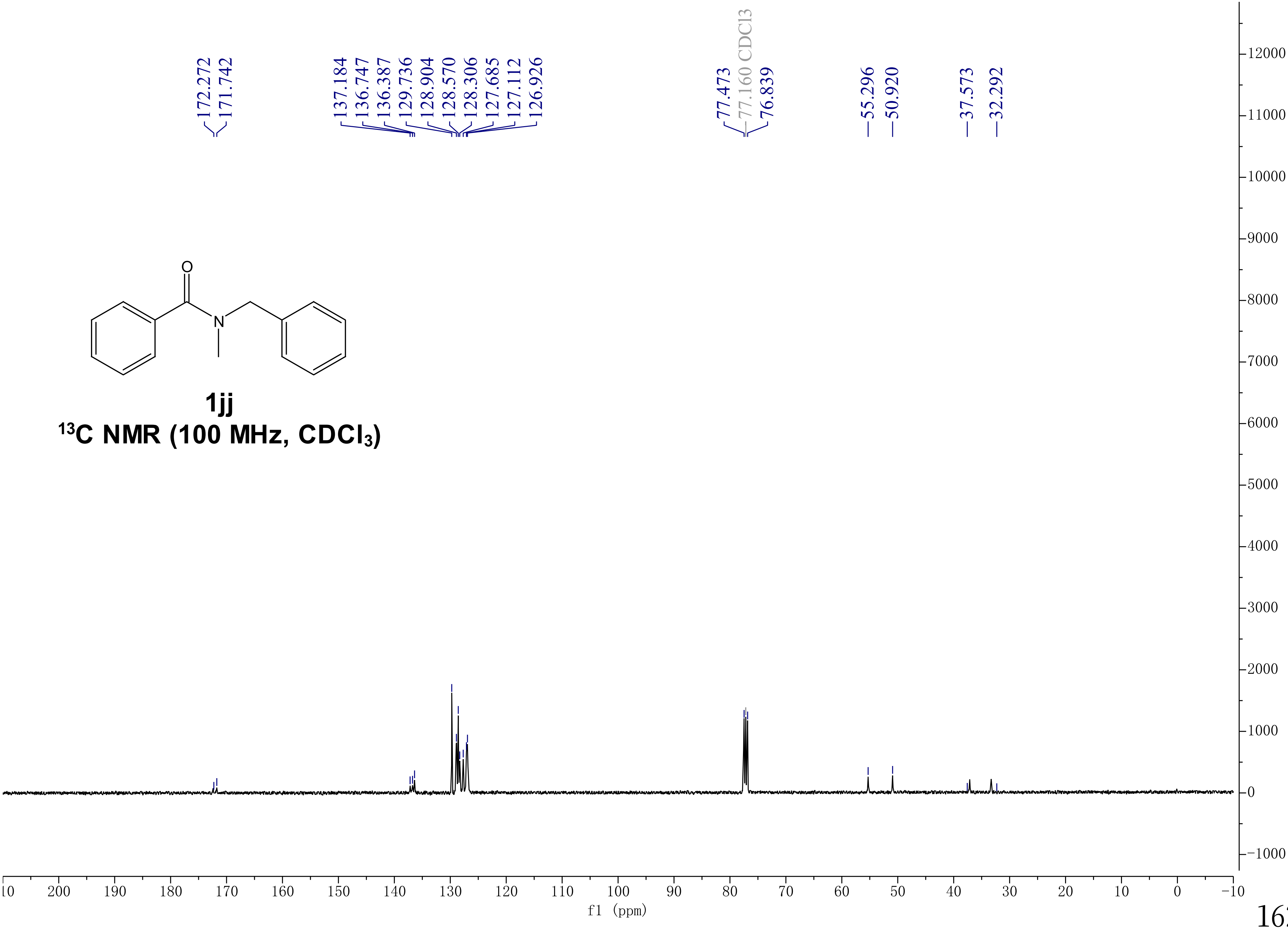
^{13}C NMR (100 MHz, $CDCl_3$)

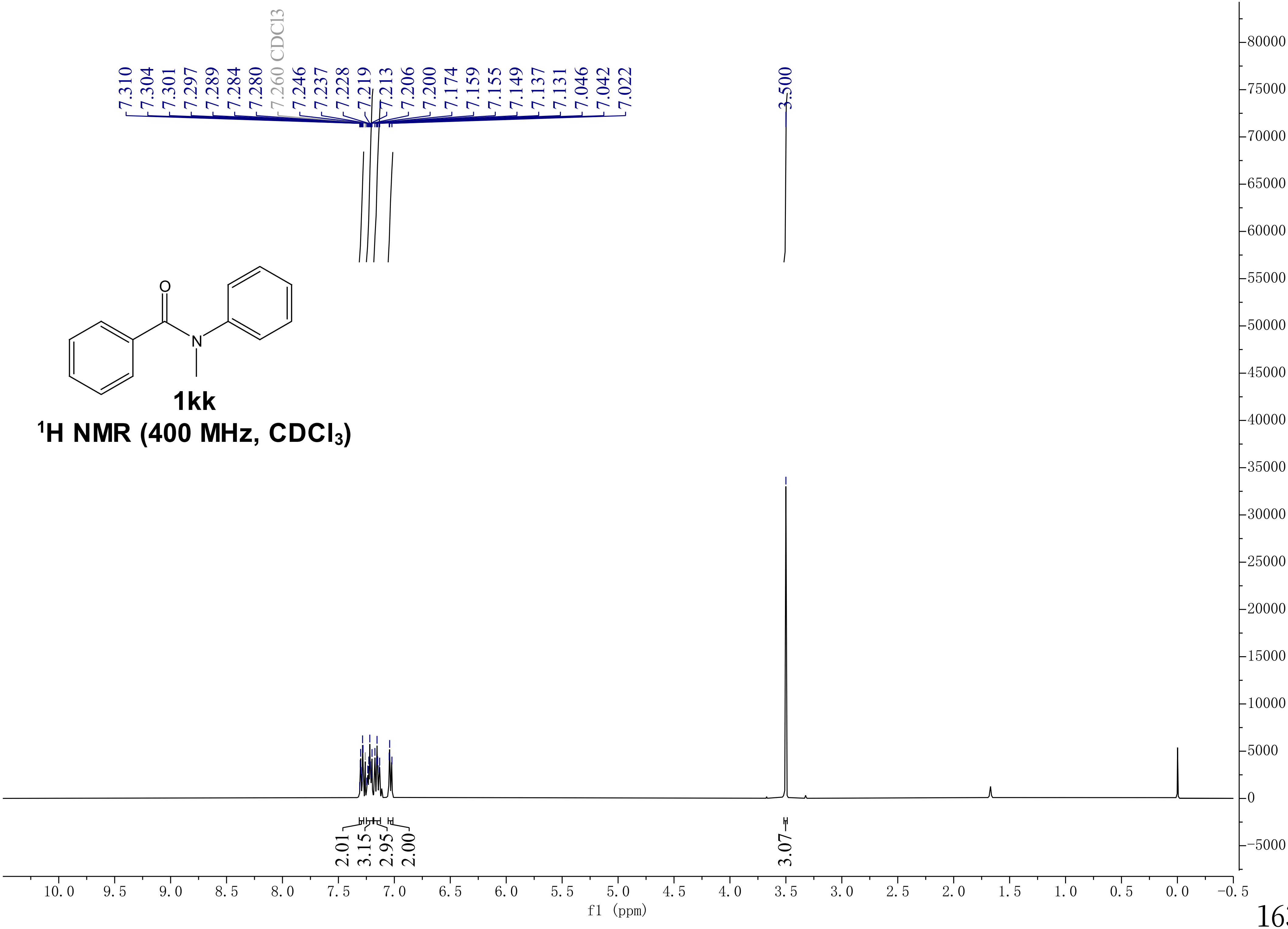


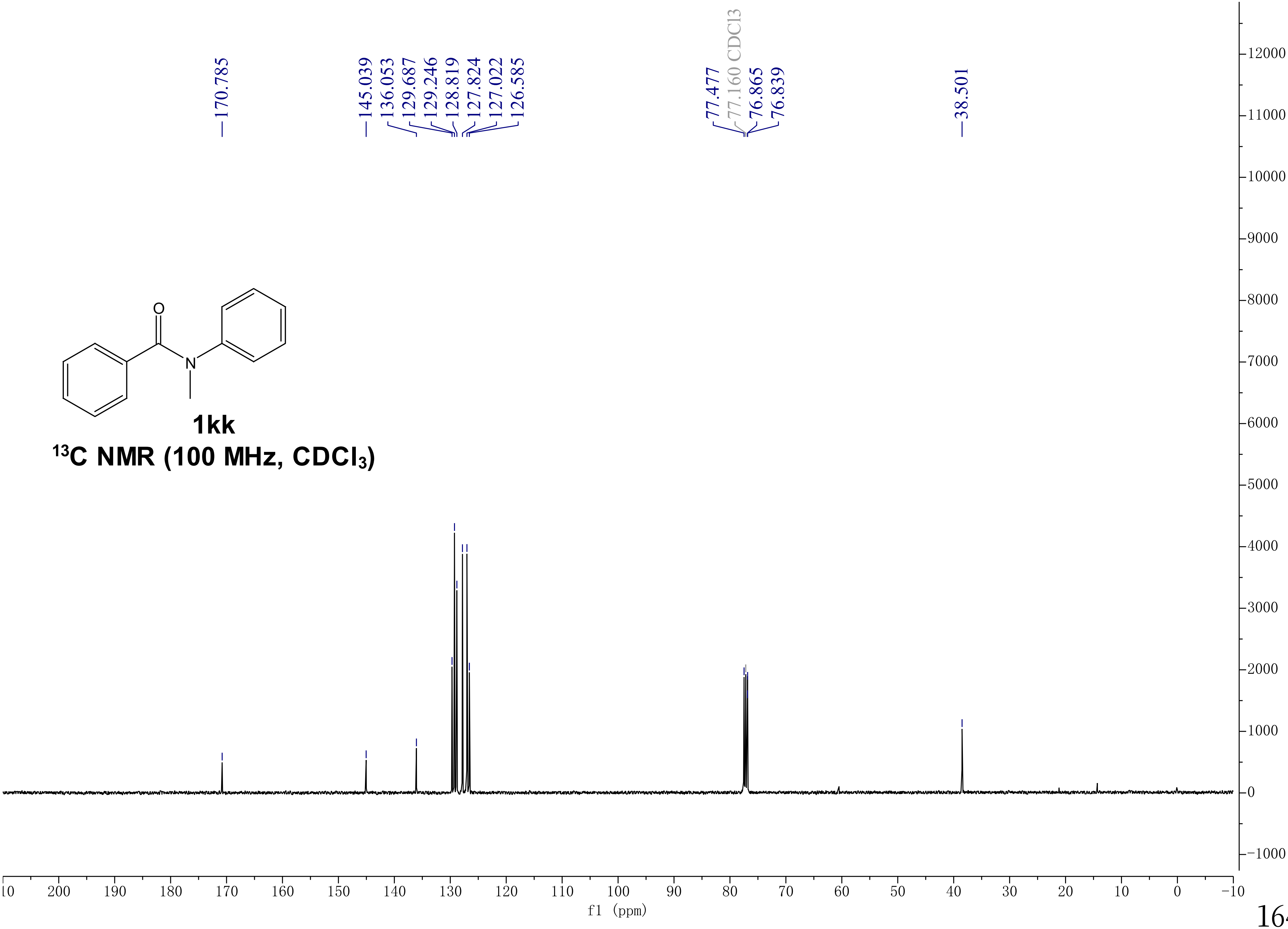
1jj
^{1}H NMR (400 MHz, $CDCl_3$)

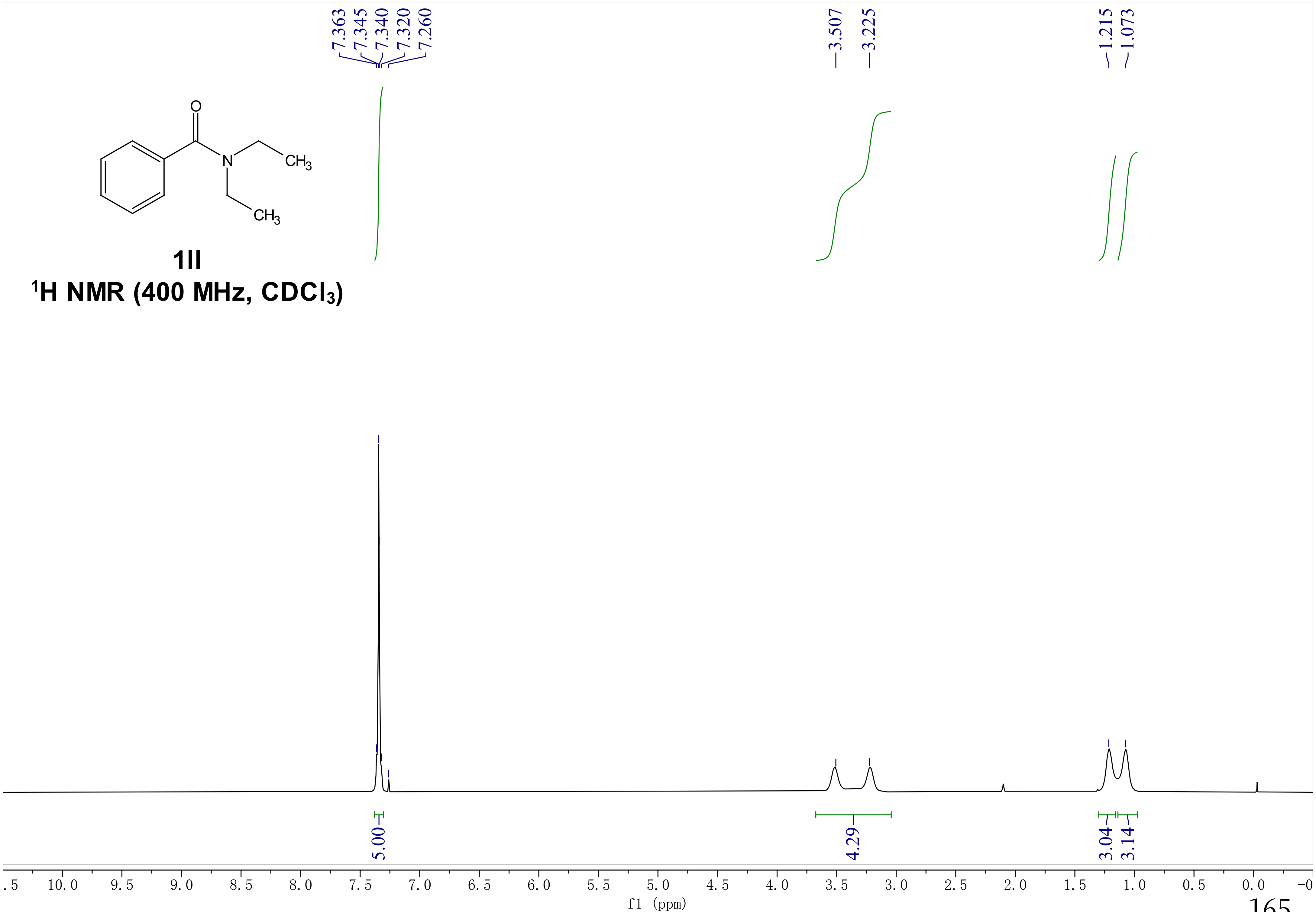
1jj

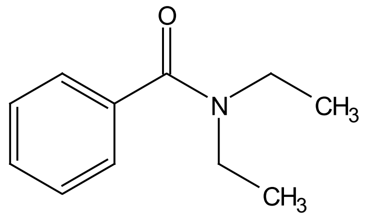
^{13}C NMR (100 MHz, $CDCl_3$)




7.310
7.304
7.301
7.297
7.289
7.284
7.280
7.260 CDCl3
7.246
7.237
7.228
7.219
7.213
7.206
7.200
7.174
7.159
7.155
7.149
7.137
7.131
7.046
7.042
7.022
3.500
O
N
1kk
^{1}H NMR (400 MHz, $CDCl_3$)
2.01
3.15
2.95
2.00
3.07
f1 (ppm)

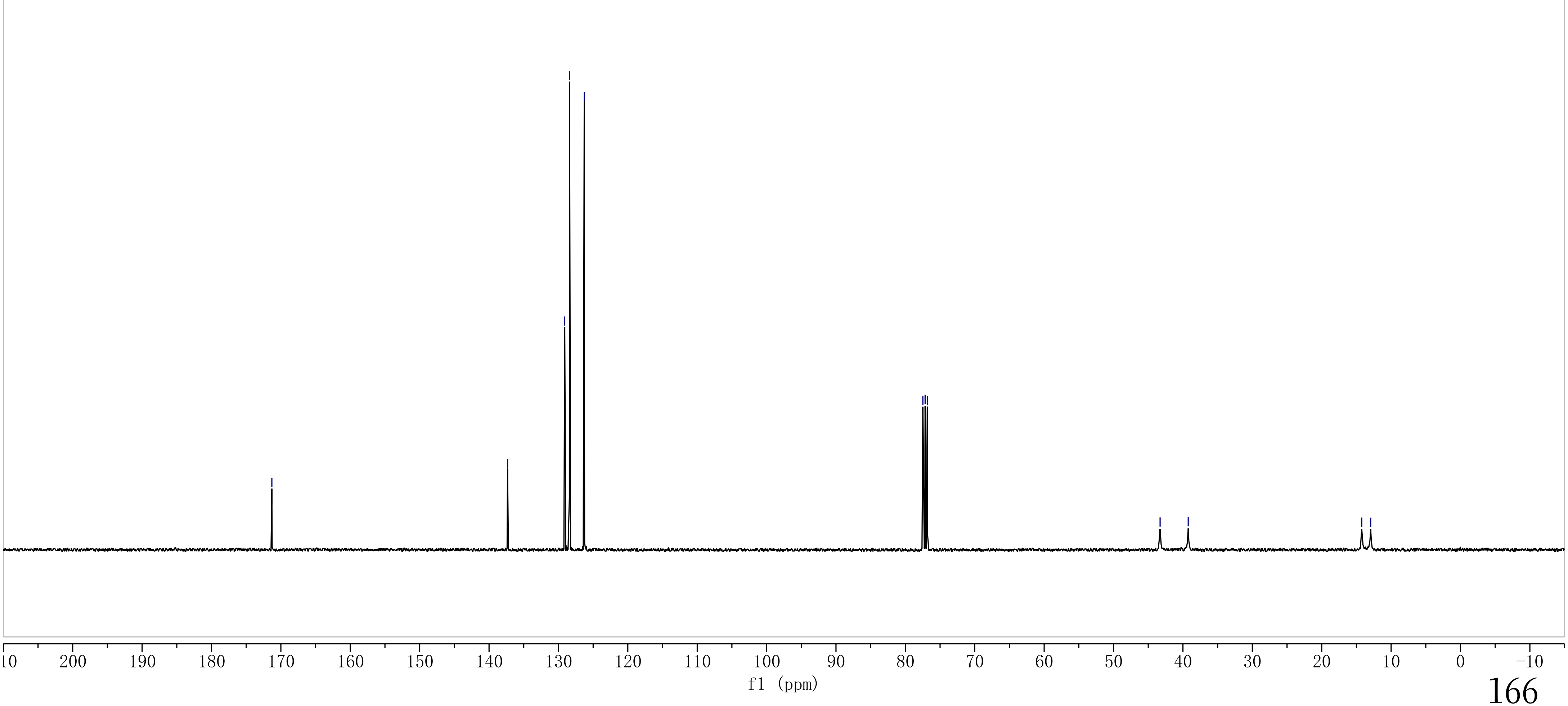

170.785
145.039
136.053
129.687
129.246
128.819
127.824
127.022
126.585
77.477
77.160 CDCl3
76.865
76.839
38.501
1kk
13C NMR (100 MHz, CDCl3)
f1 (ppm)

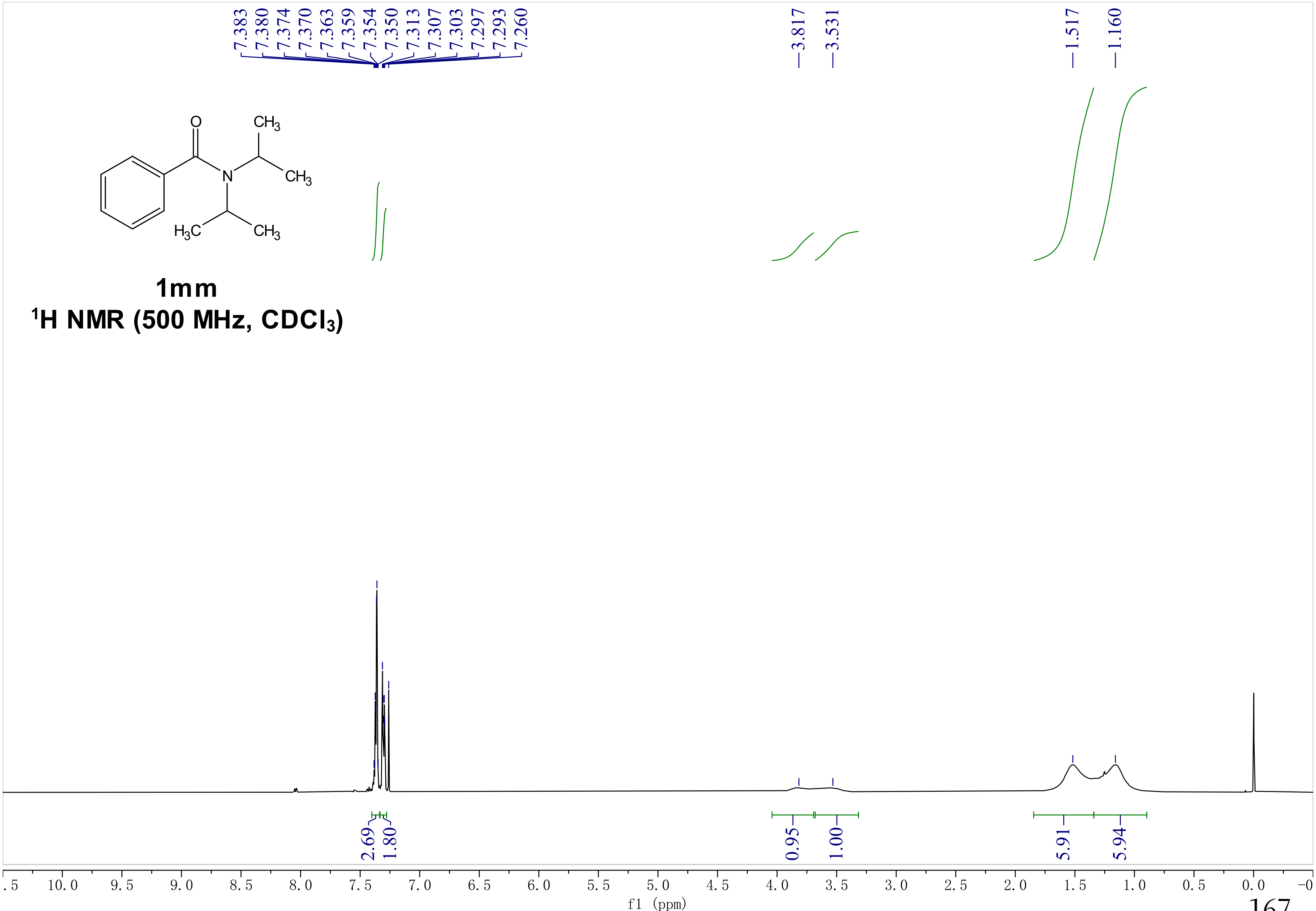

7.363
7.345
7.340
7.320
7.260
3.507
3.225
1.215
1.073
1ll
1H NMR (400 MHz, CDCl3)
O
N
CH3
CH3
5.00
4.29
3.04
3.14
f1 (ppm)

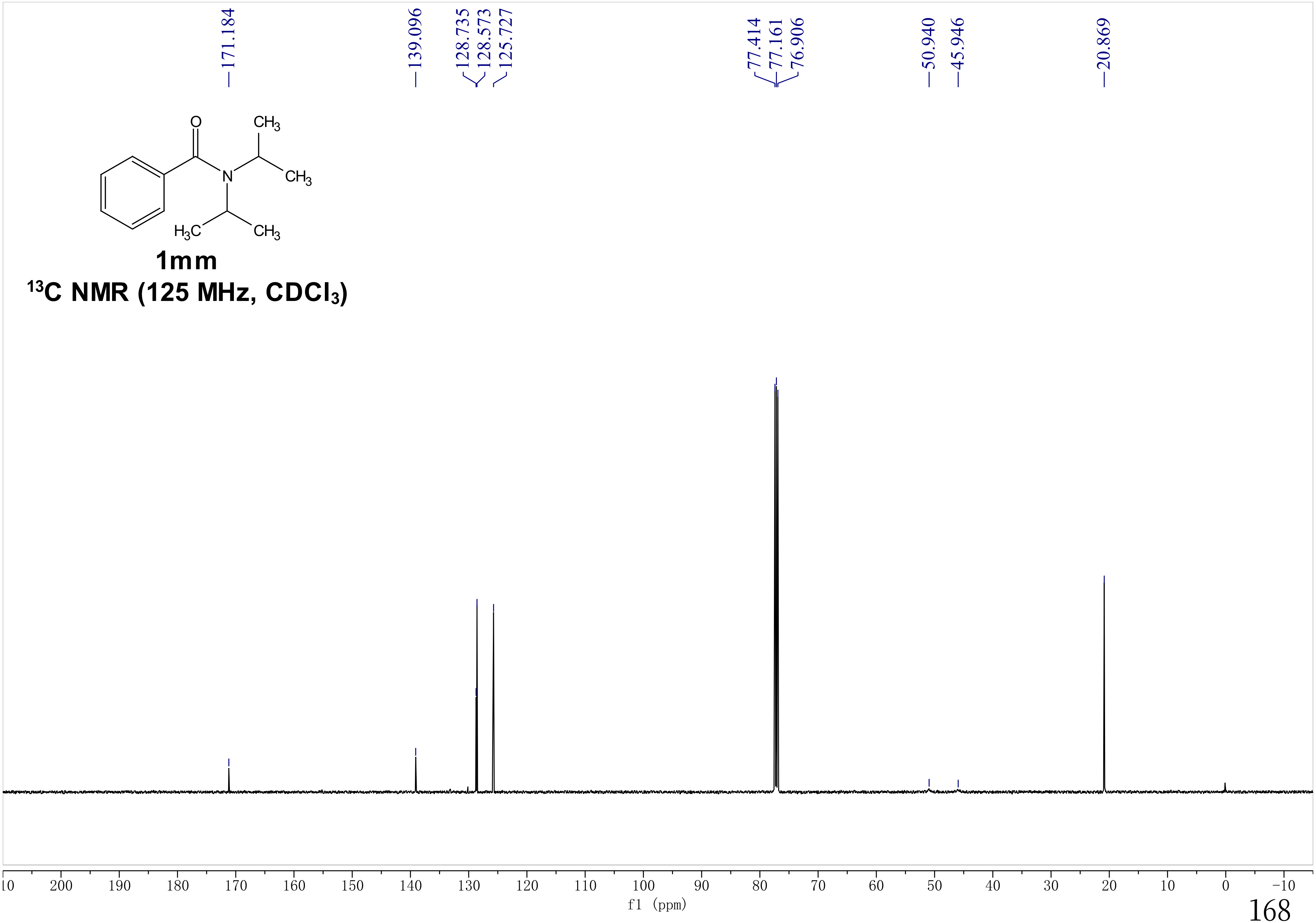


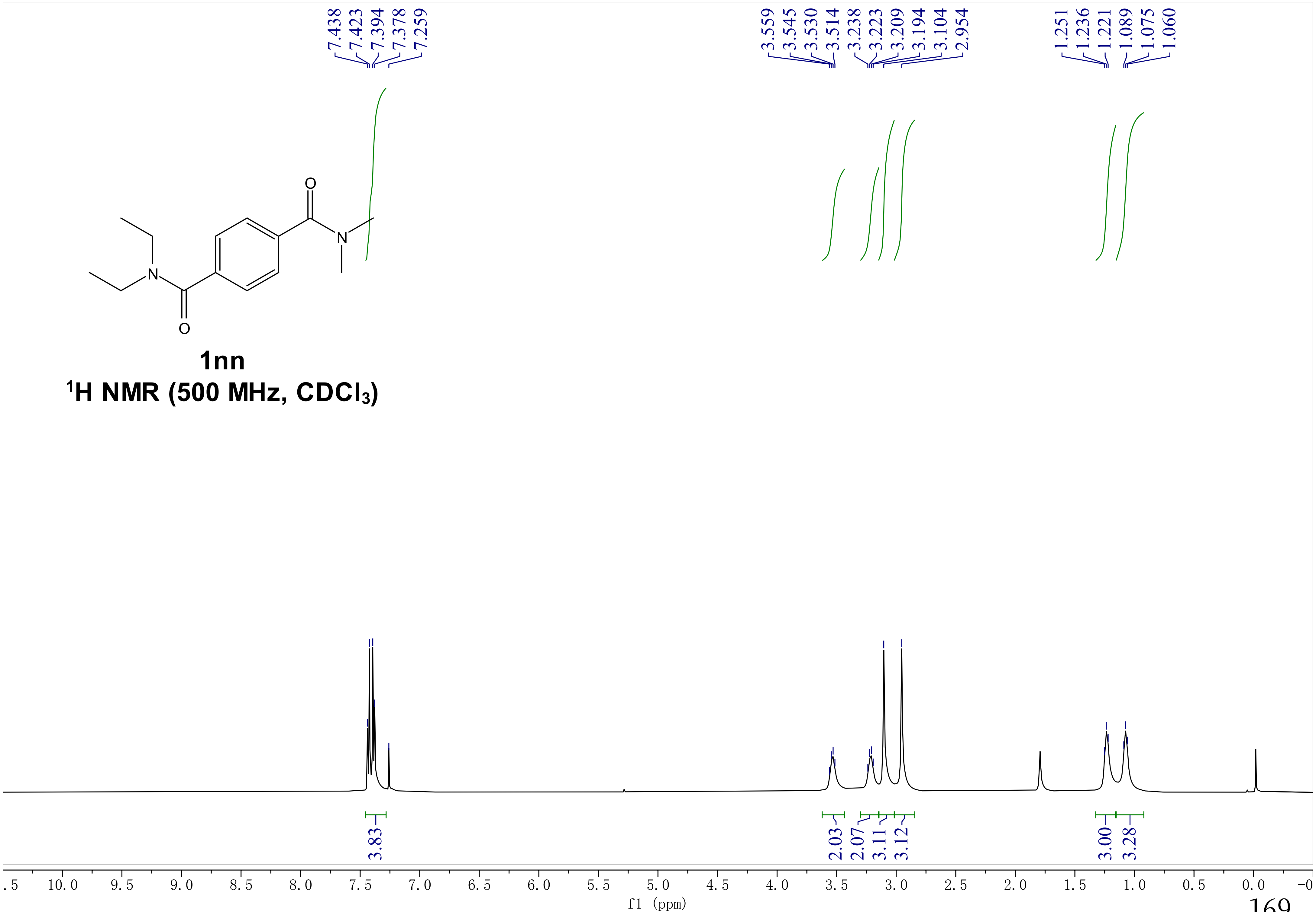
1ll

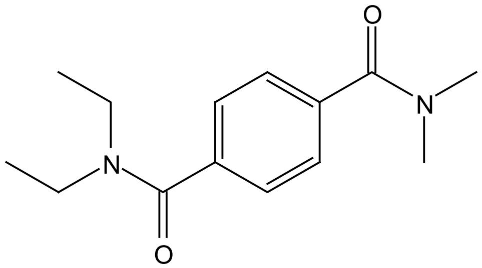
^{13}C NMR (100 MHz, $CDCl_3$)




7.383
7.380
7.374
7.370
7.363
7.359
7.354
7.350
7.313
7.307
7.303
7.297
7.293
7.260
3.817
3.531
1.517
1.160
O
CH3
N
CH3
H3C
CH3
1mm
1H NMR (500 MHz, CDCl3)
2.69
1.80
0.95
1.00
5.91
5.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

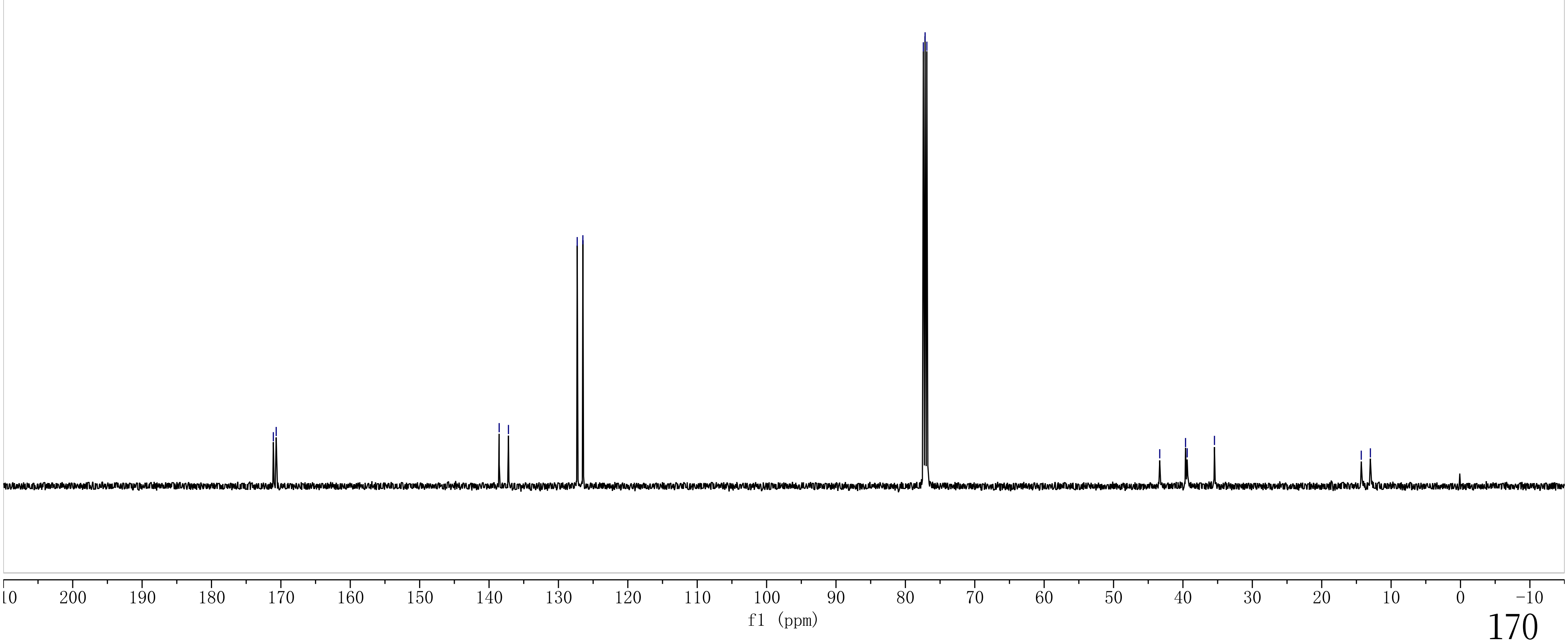

171.184
139.096
128.735
128.573
125.727
77.414
77.161
76.906
50.940
45.946
20.869
O
CH3
N
CH3
H3C
CH3
1mm
13C NMR (125 MHz, CDCl3)
f1 (ppm)

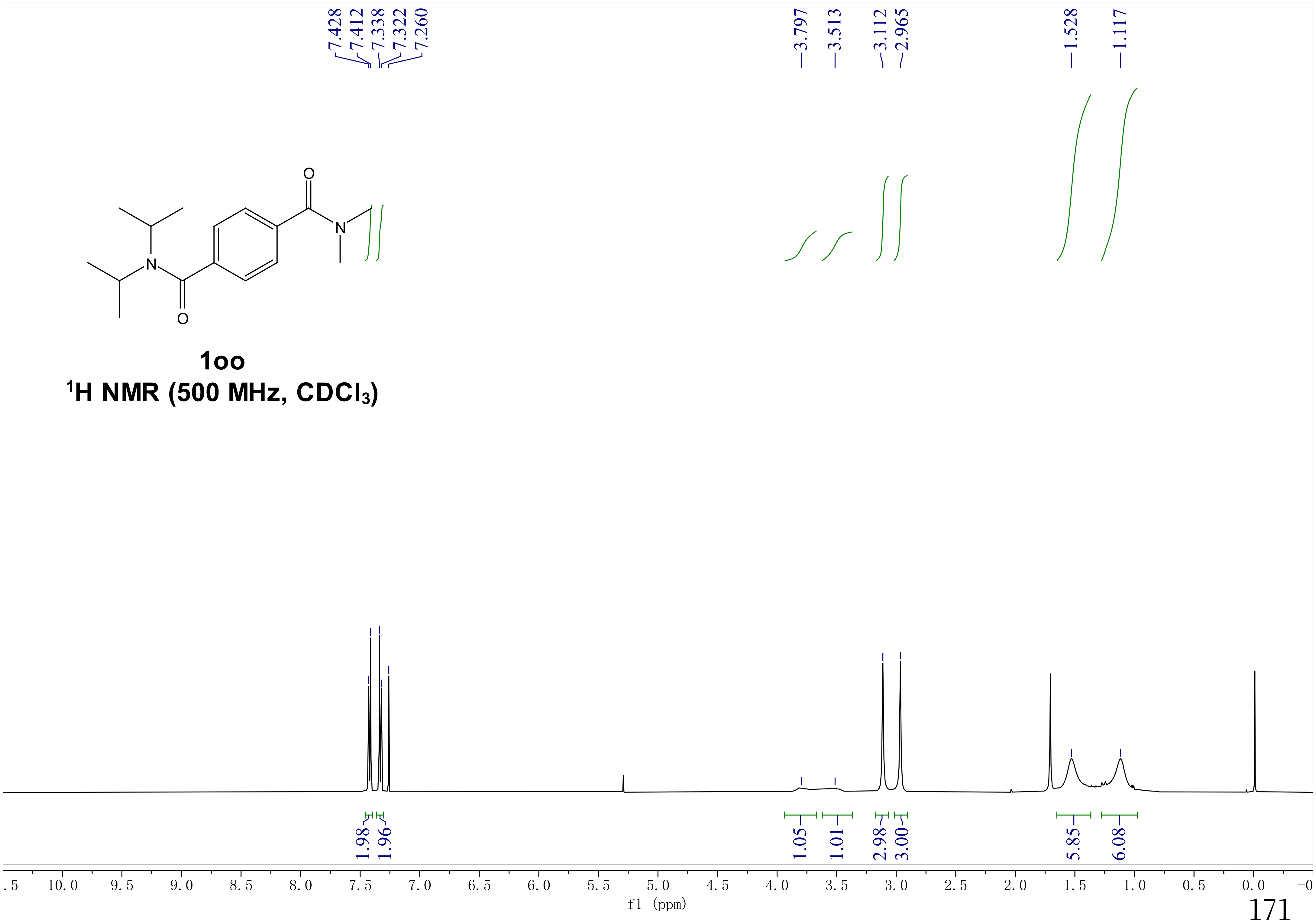

7.438
7.423
7.394
7.378
7.259
3.559
3.545
3.530
3.514
3.238
3.223
3.209
3.194
3.104
2.954
1.251
1.236
1.221
1.089
1.075
1.060
O
N
N
O
1nn
^{1}H NMR (500 MHz, CDCl$_3$)
3.83
2.03
2.07
3.11
3.12
3.00
3.28
f1 (ppm)

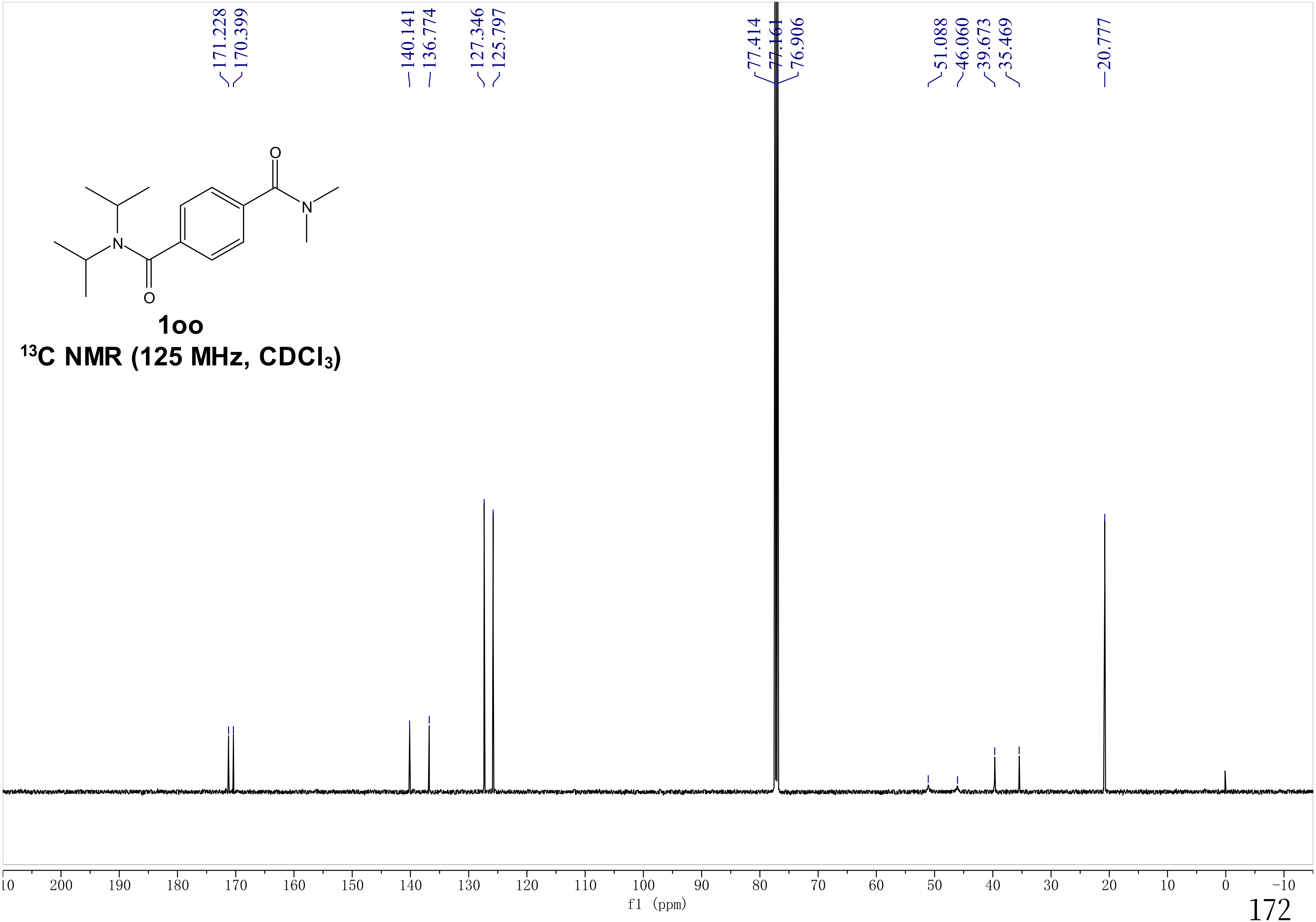


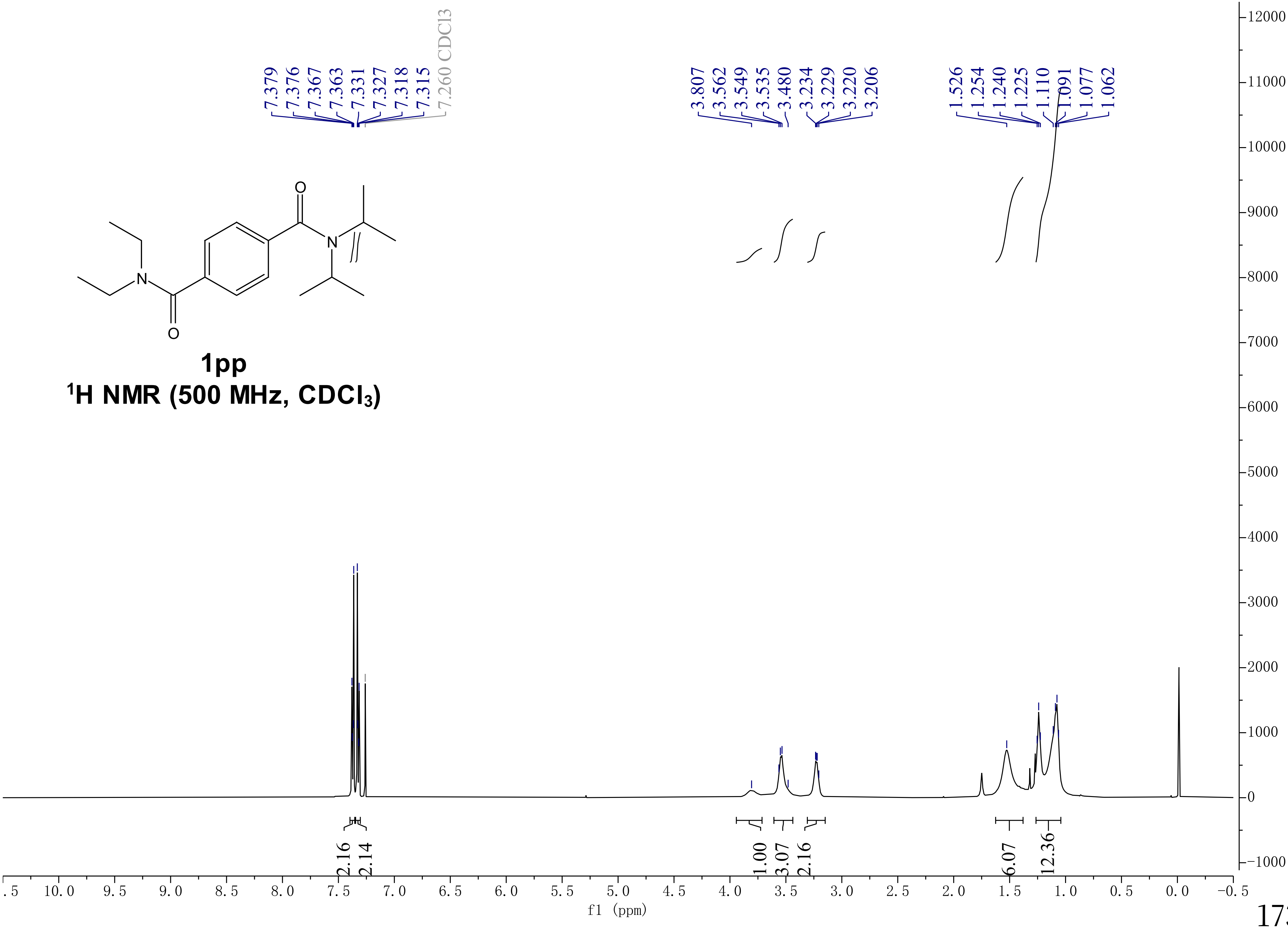
1nn

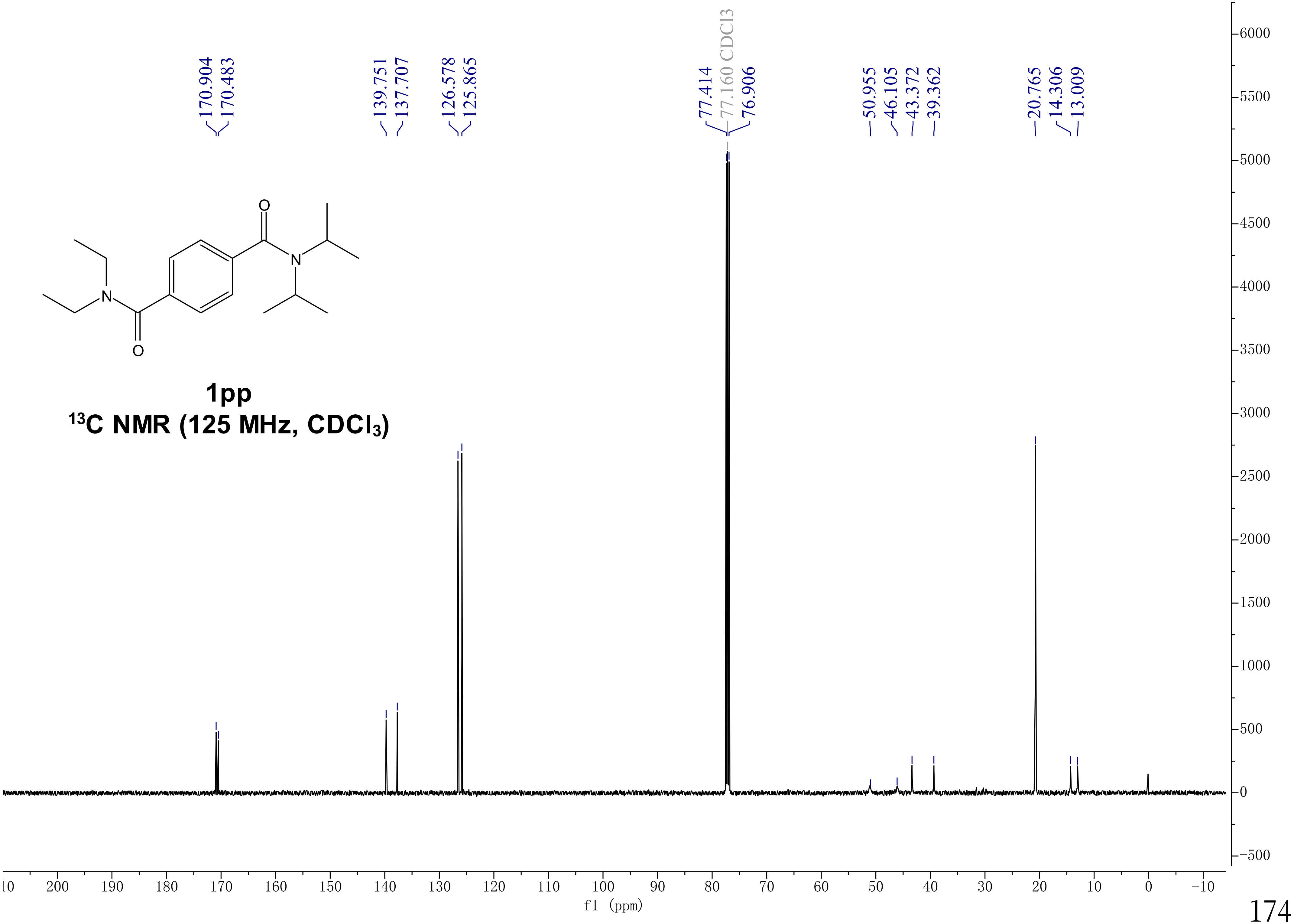
^{13}C NMR (125 MHz, $CDCl_3$)




1oo
^{1}H NMR (500 MHz, CDCl$_3$)
7.428
7.412
7.338
7.322
7.260
3.797
3.513
3.112
2.965
1.528
1.117
1.98
1.96
1.05
1.01
2.98
3.00
5.85
6.08
f1 (ppm)

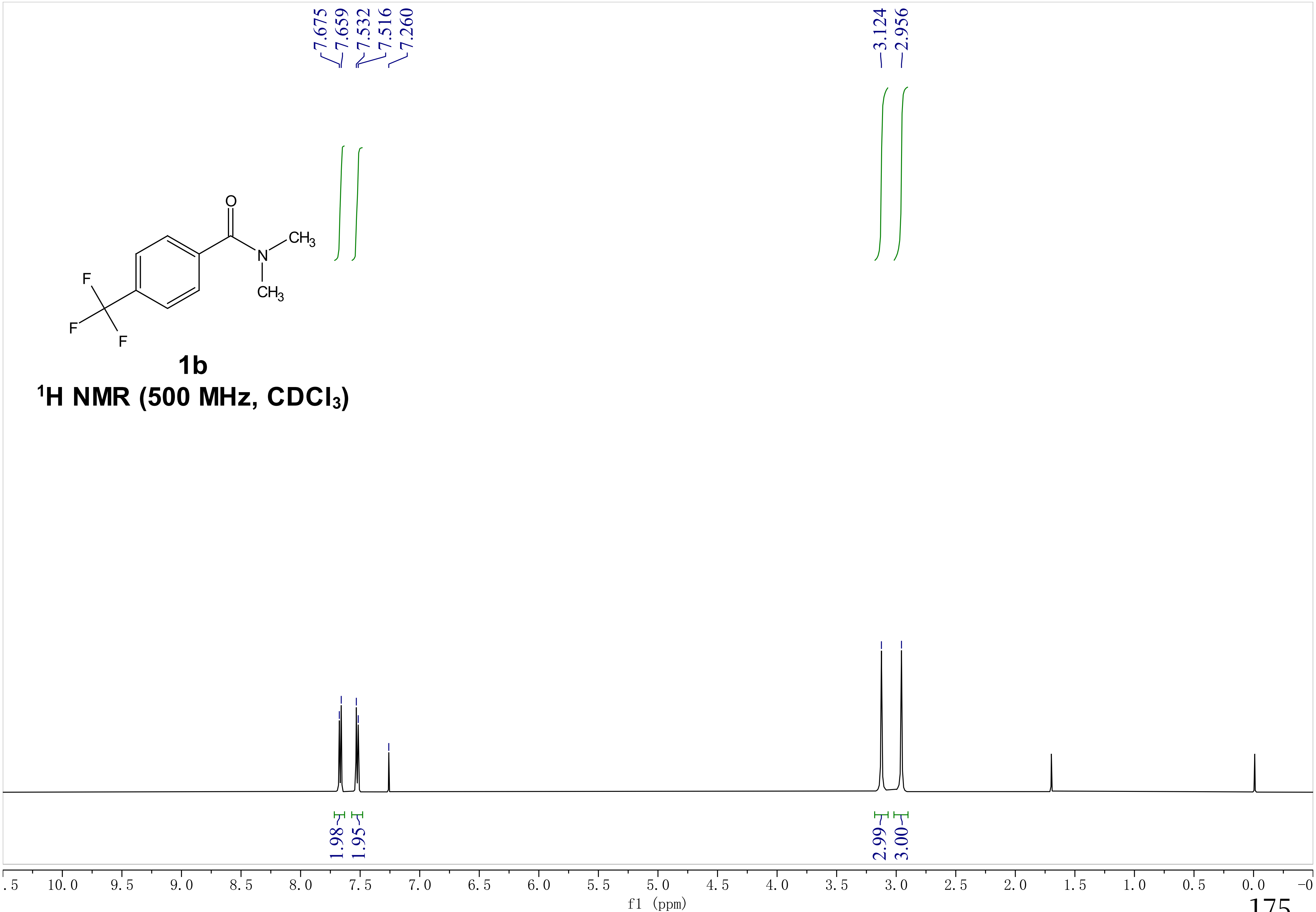

171.228
170.399
140.141
136.774
127.346
125.797
77.414
77.161
76.906
51.088
46.060
39.673
35.469
20.777
O
N
N
O
1oo
13C NMR (125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

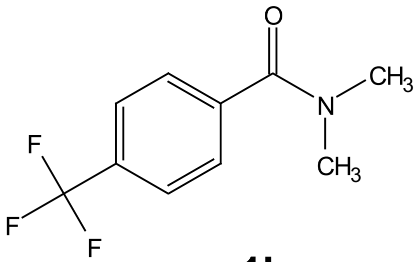

7.379
7.376
7.367
7.363
7.331
7.327
7.318
7.315
7.260 CDCl3
3.807
3.562
3.549
3.535
3.480
3.234
3.229
3.220
3.206
1.526
1.254
1.240
1.225
1.110
1.091
1.077
1.062
O
N
N
O
1pp
^{1}H NMR (500 MHz, $CDCl_3$)
2.16
2.14
1.00
3.07
2.16
6.07
12.36
f1 (ppm)



1pp

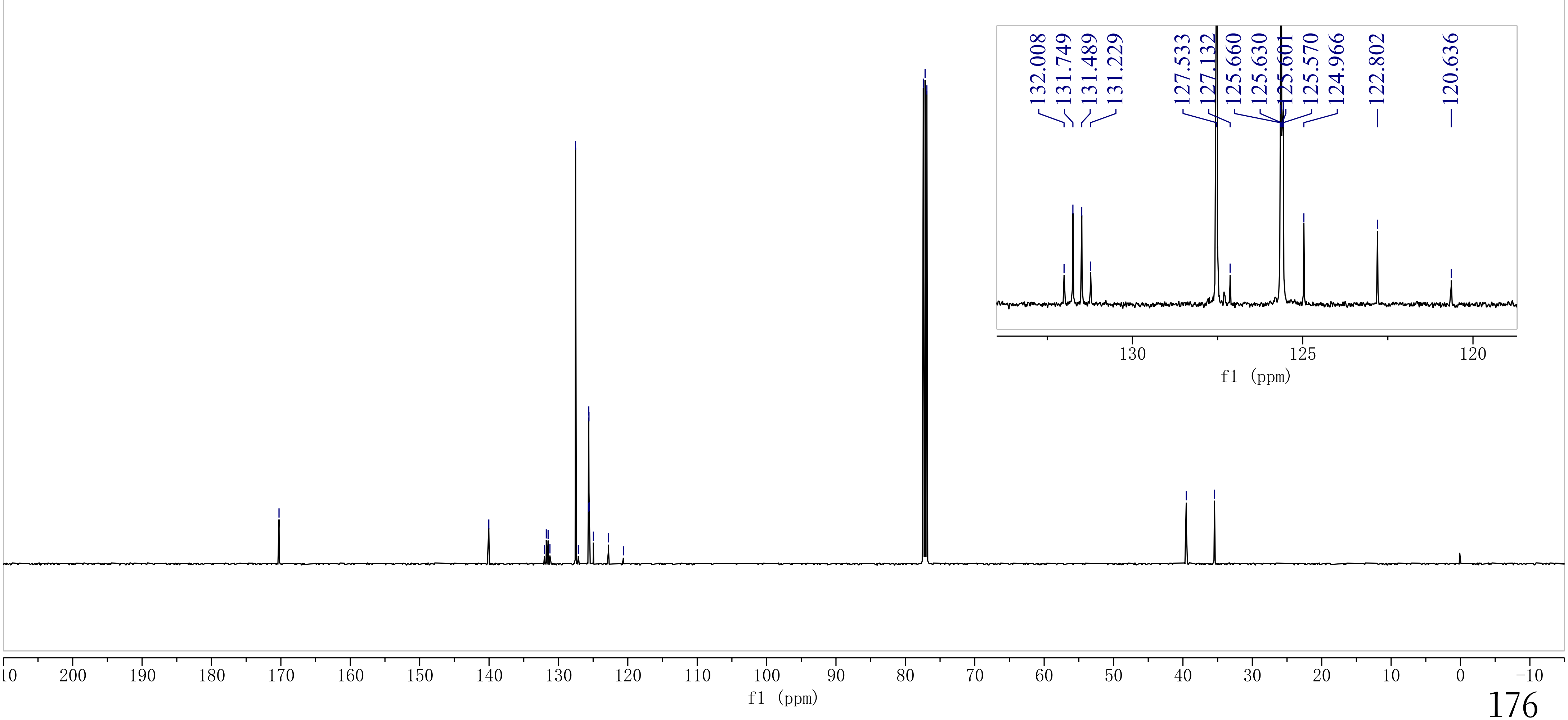
^{13}C NMR (125 MHz, $CDCl_3$)

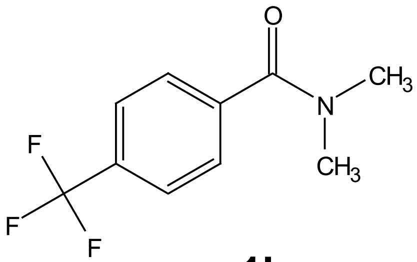

7.675
7.659
7.532
7.516
7.260
3.124
2.956
O
N
CH3
CH3
F
F
F
1b
1H NMR (500 MHz, CDCl3)
1.98
1.95
2.99
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



1b

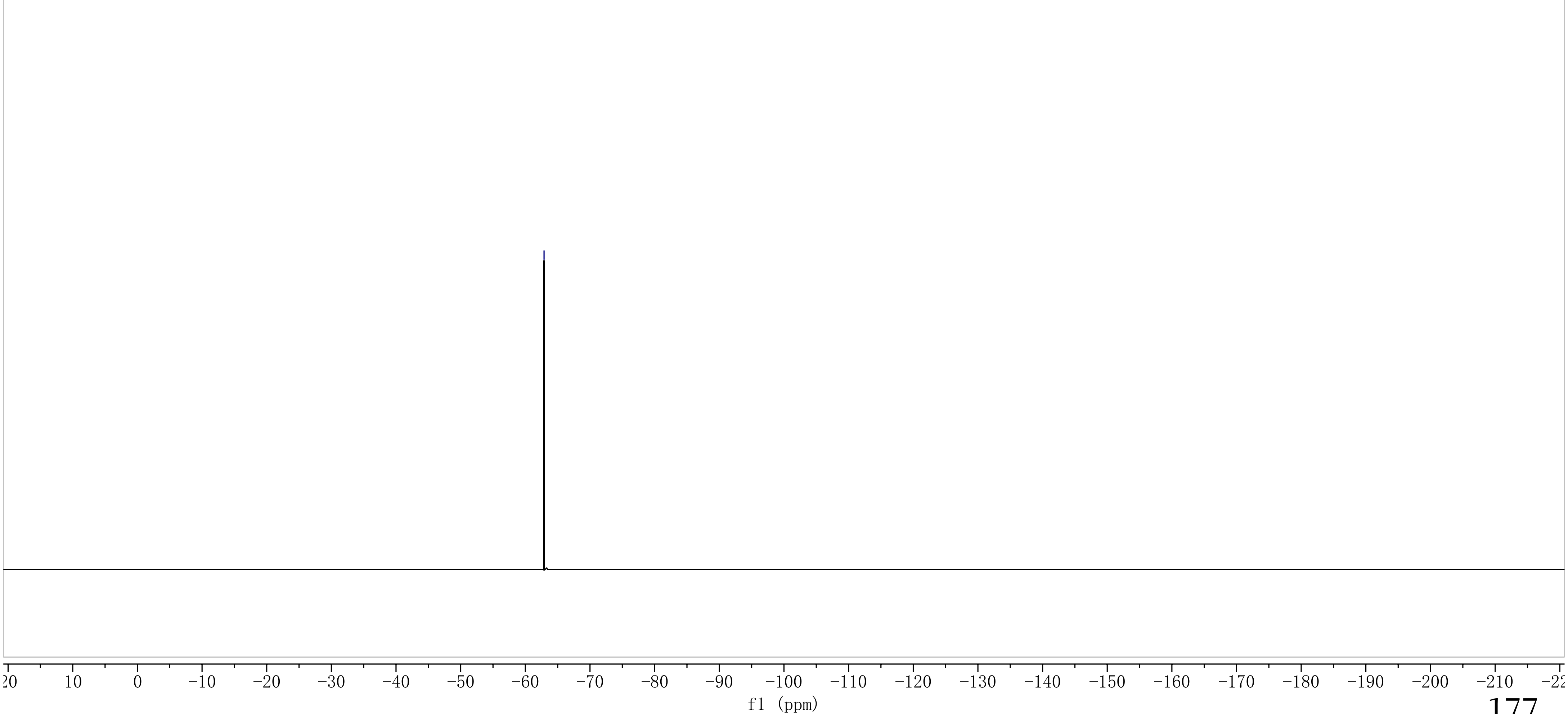
^{13}C NMR (125 MHz, $CDCl_3$)

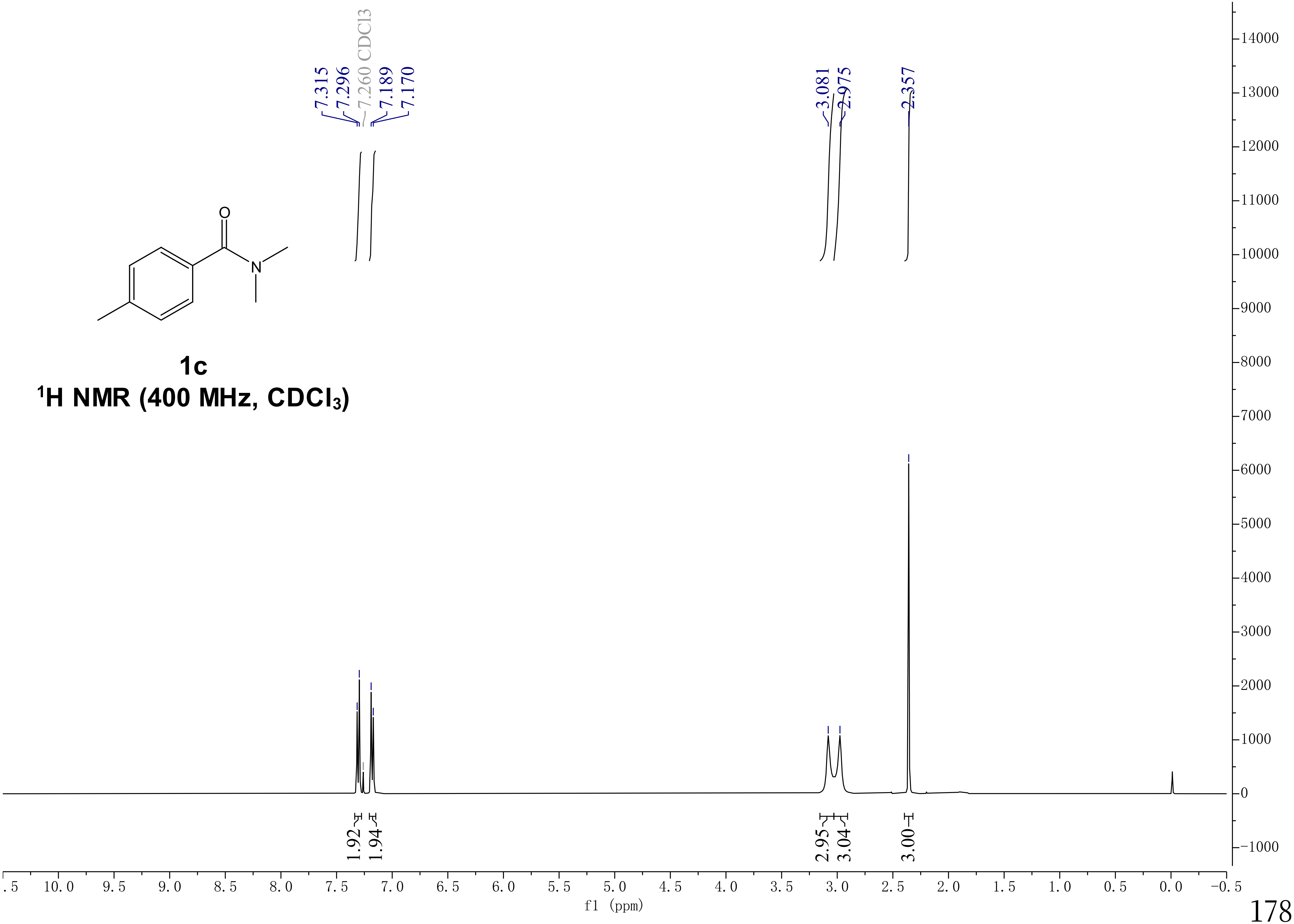


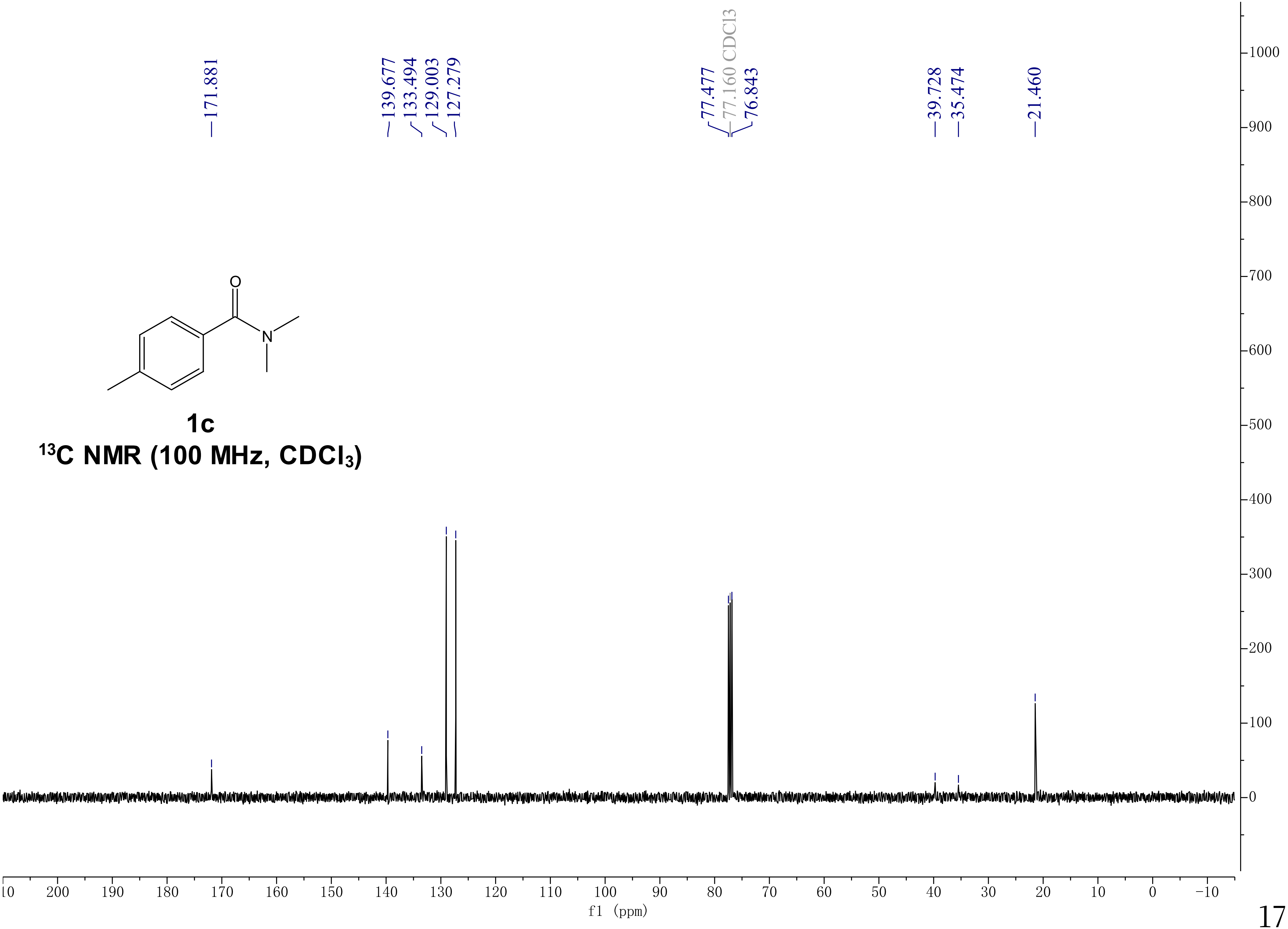


1b

^{19}F NMR (470 MHz, $CDCl_3$)

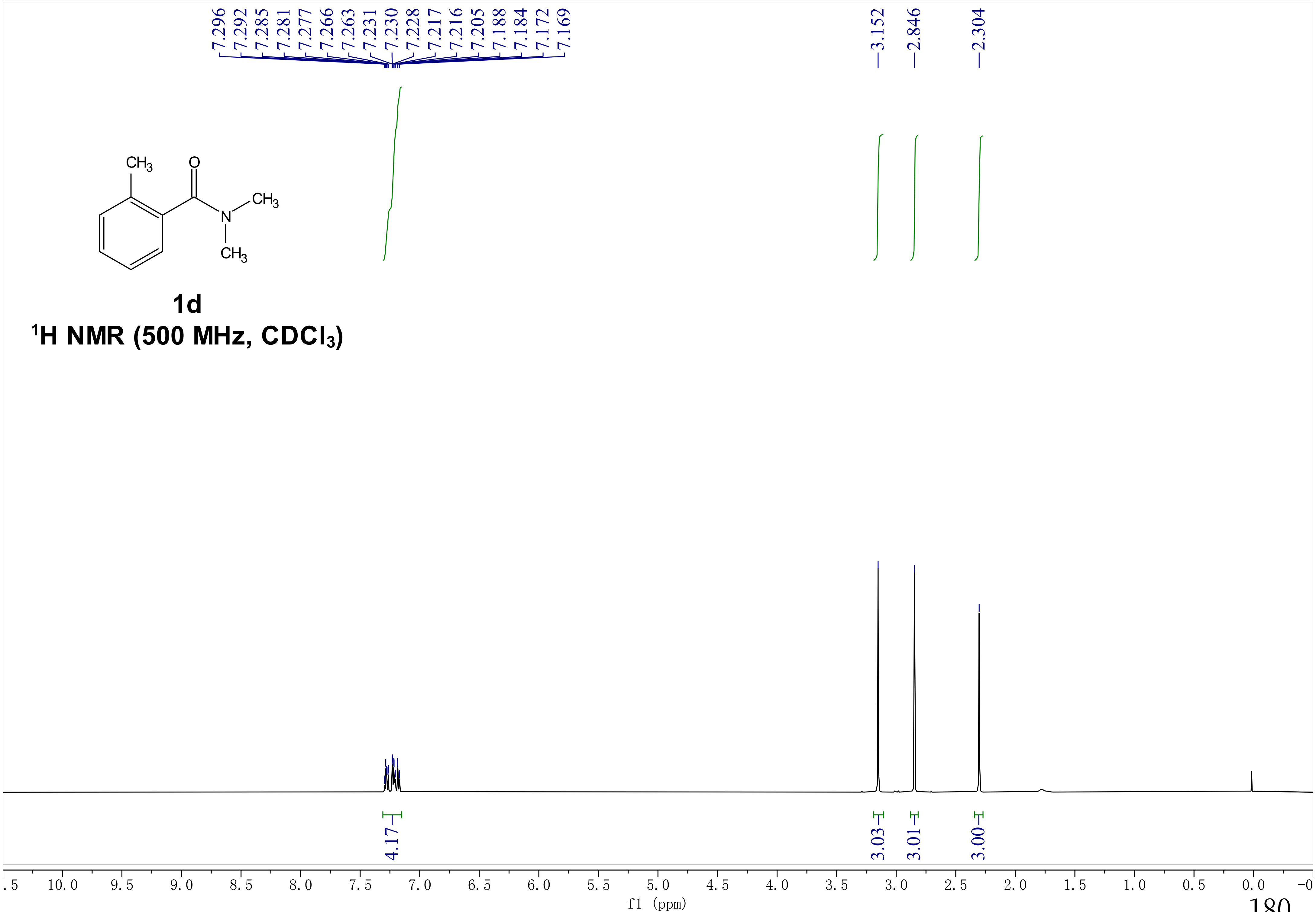



7.315
7.296
7.260 CDCl3
7.189
7.170
3.081
2.975
2.357
1c
¹H NMR (400 MHz, CDCl₃)
1.92
1.94
2.95
3.04
3.00
f1 (ppm)



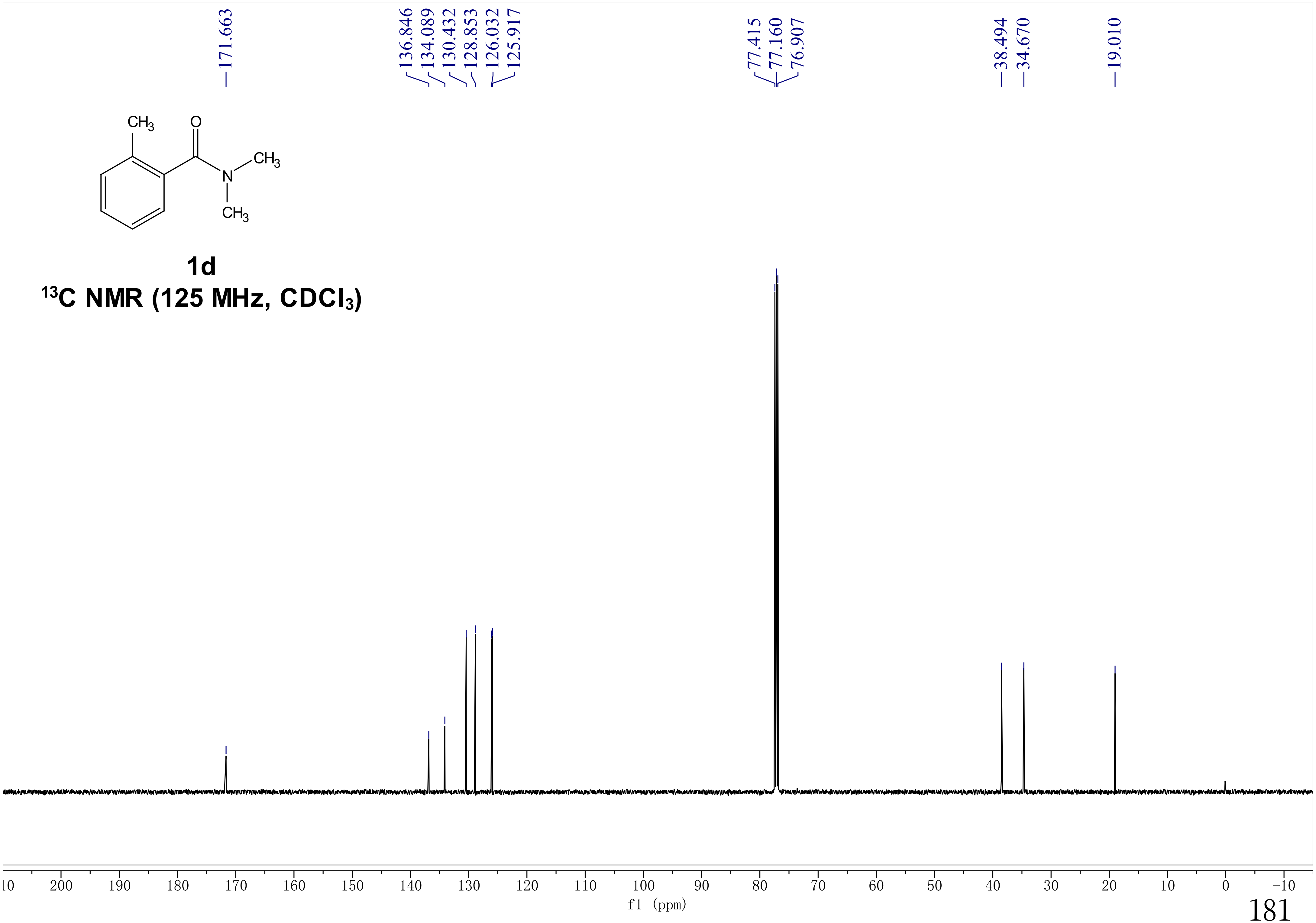
1c

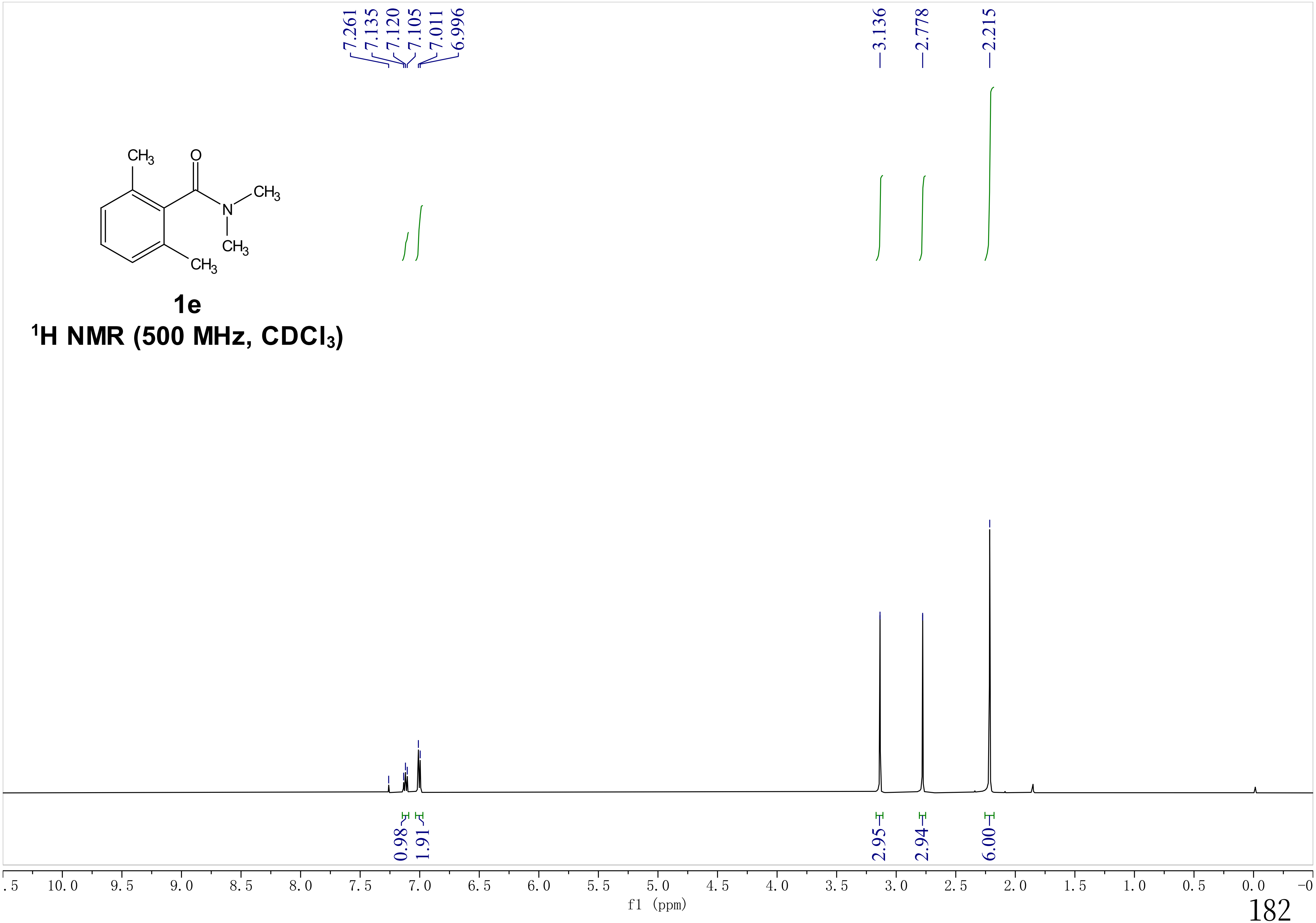
^{13}C NMR (100 MHz, CDCl$_3$)



1d

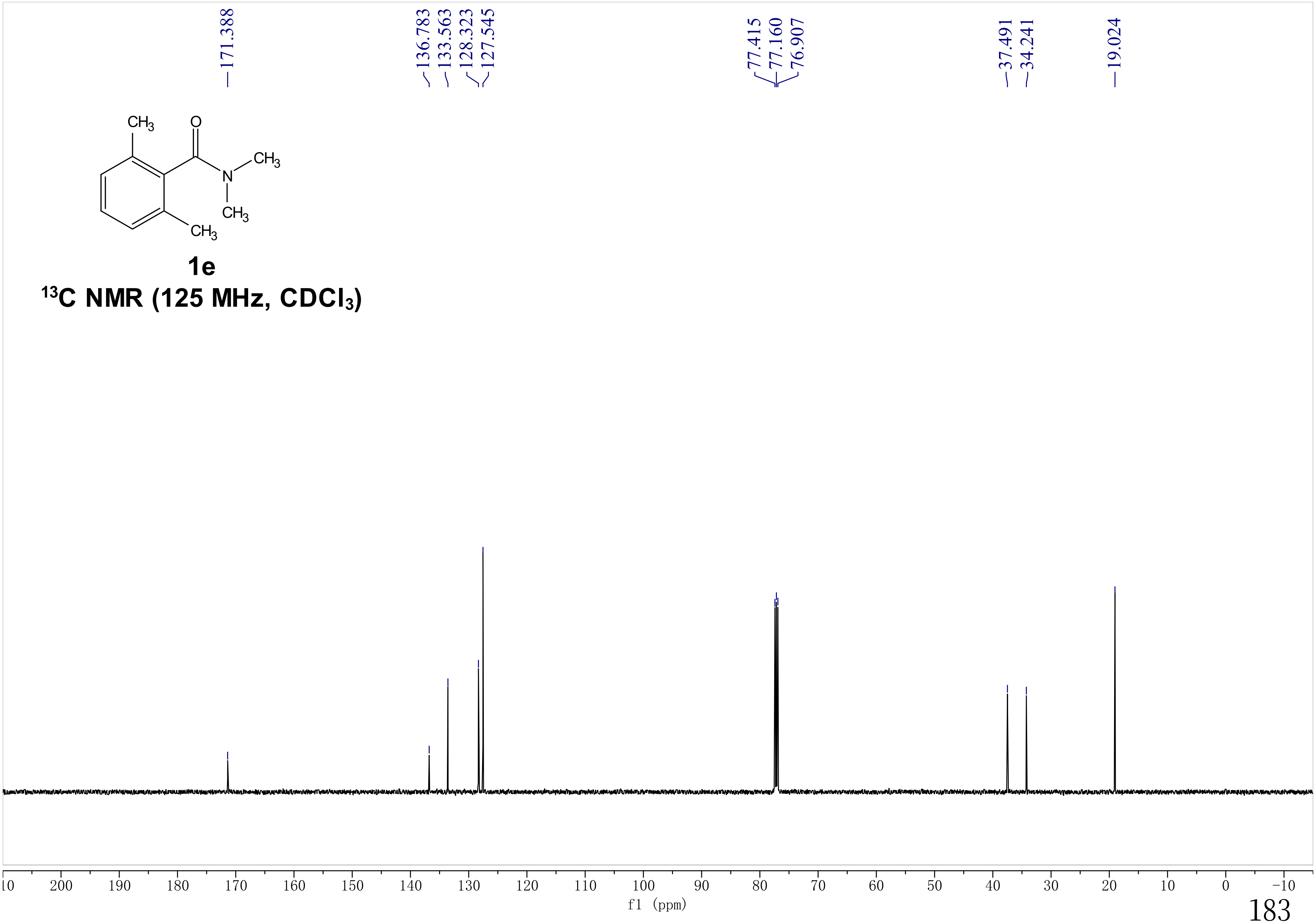
^{1}H NMR (500 MHz, $CDCl_3$)

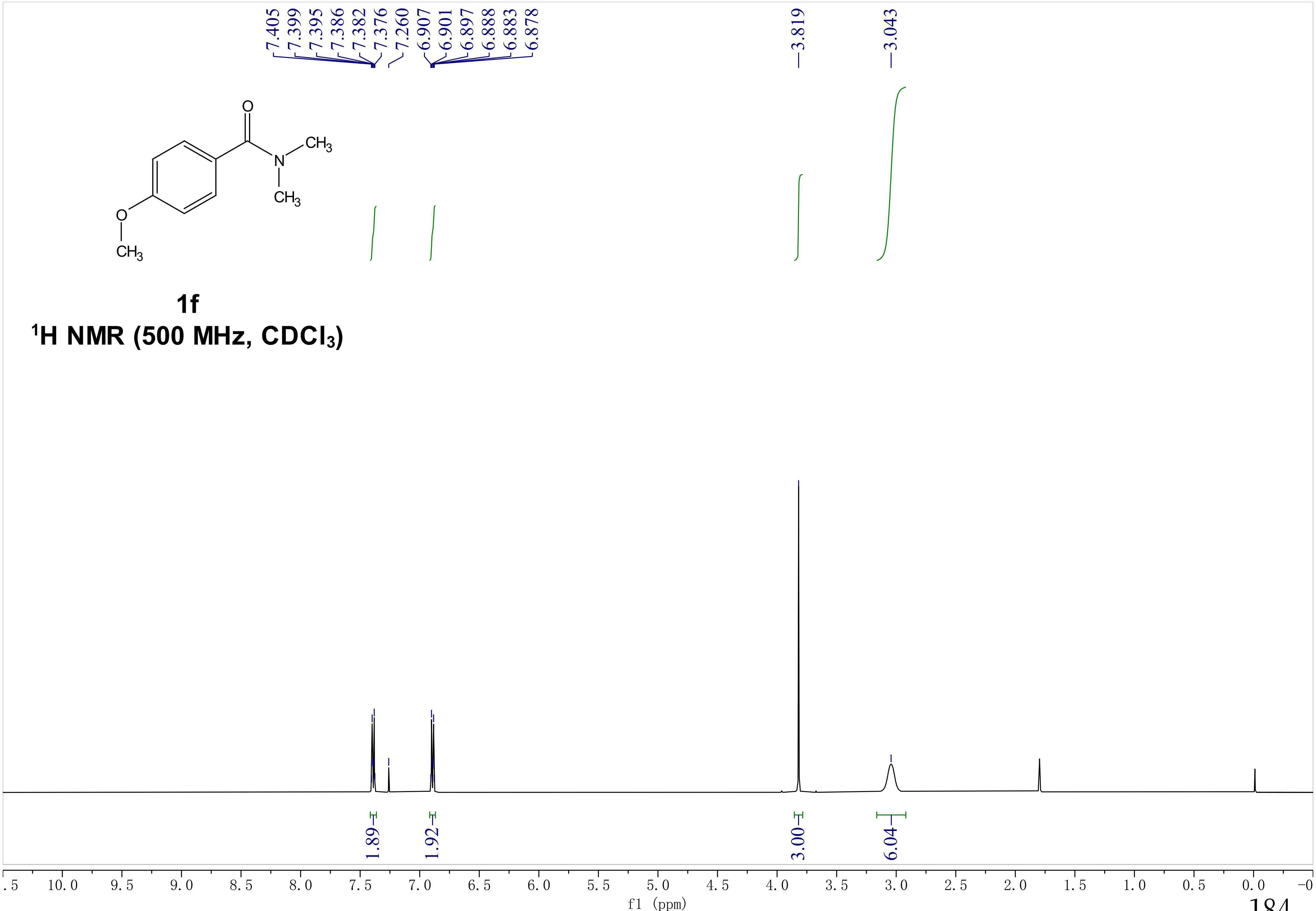

171.663
136.846
134.089
130.432
128.853
126.032
125.917
77.415
77.160
76.907
38.494
34.670
19.010
1d
13C NMR (125 MHz, CDCl3)
f1 (ppm)



1e

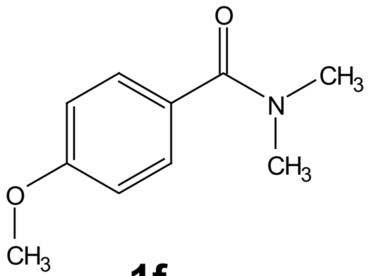
¹H NMR (500 MHz, CDCl$_3$)


171.388
136.783
133.563
128.323
127.545
77.415
77.160
76.907
37.491
34.241
19.024
CH3
O
N
CH3
CH3
CH3
1e
13C NMR (125 MHz, CDCl3)
f1 (ppm)



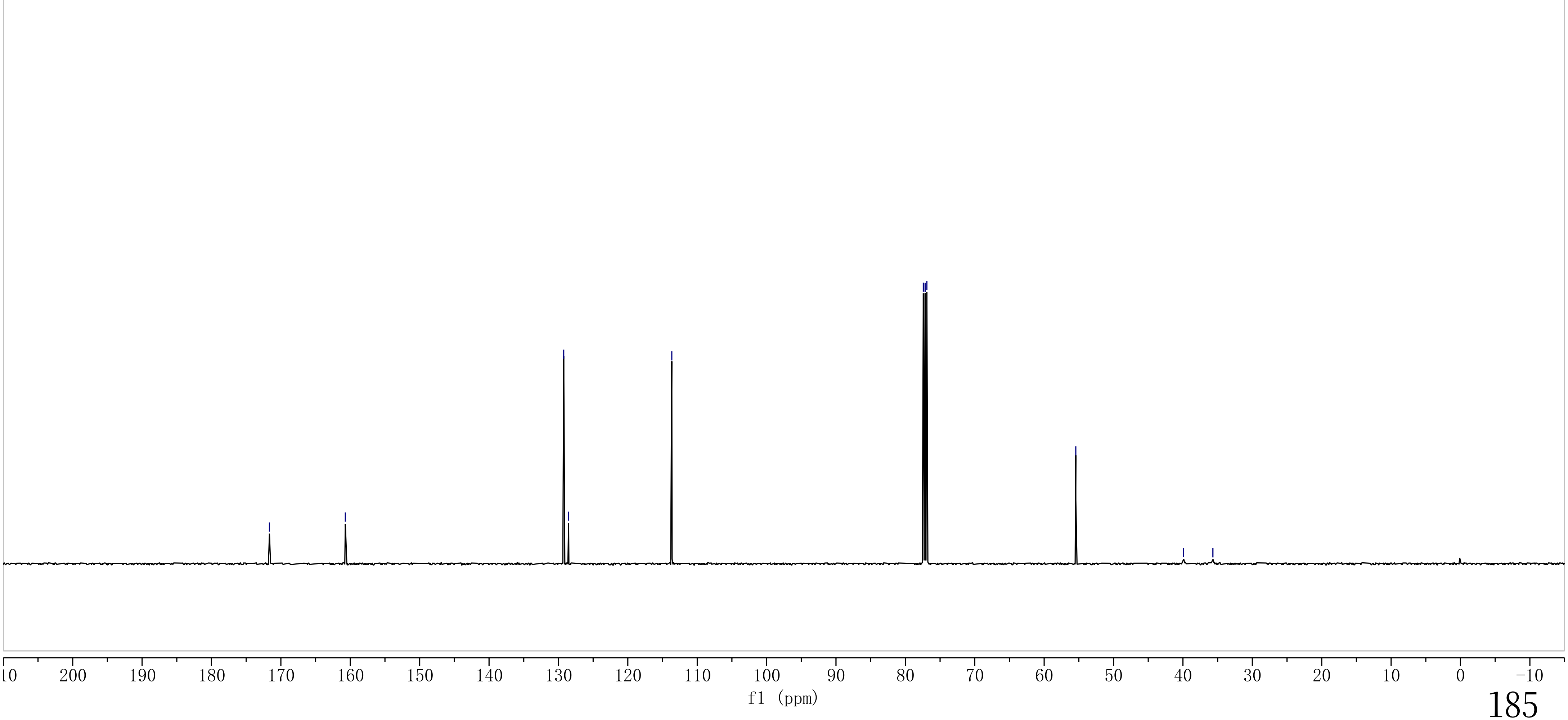
1f

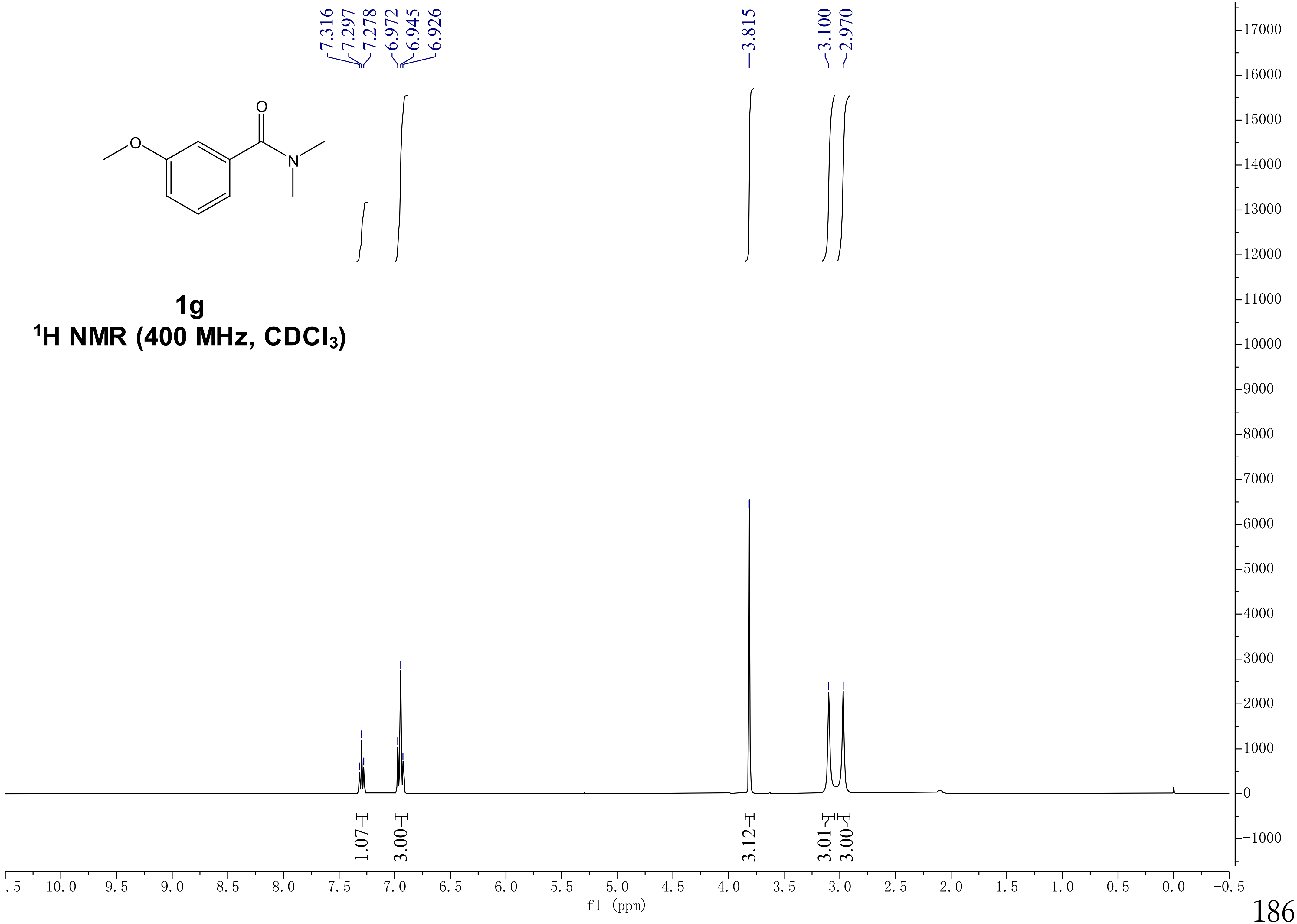
^{1}H NMR (500 MHz, $CDCl_3$)

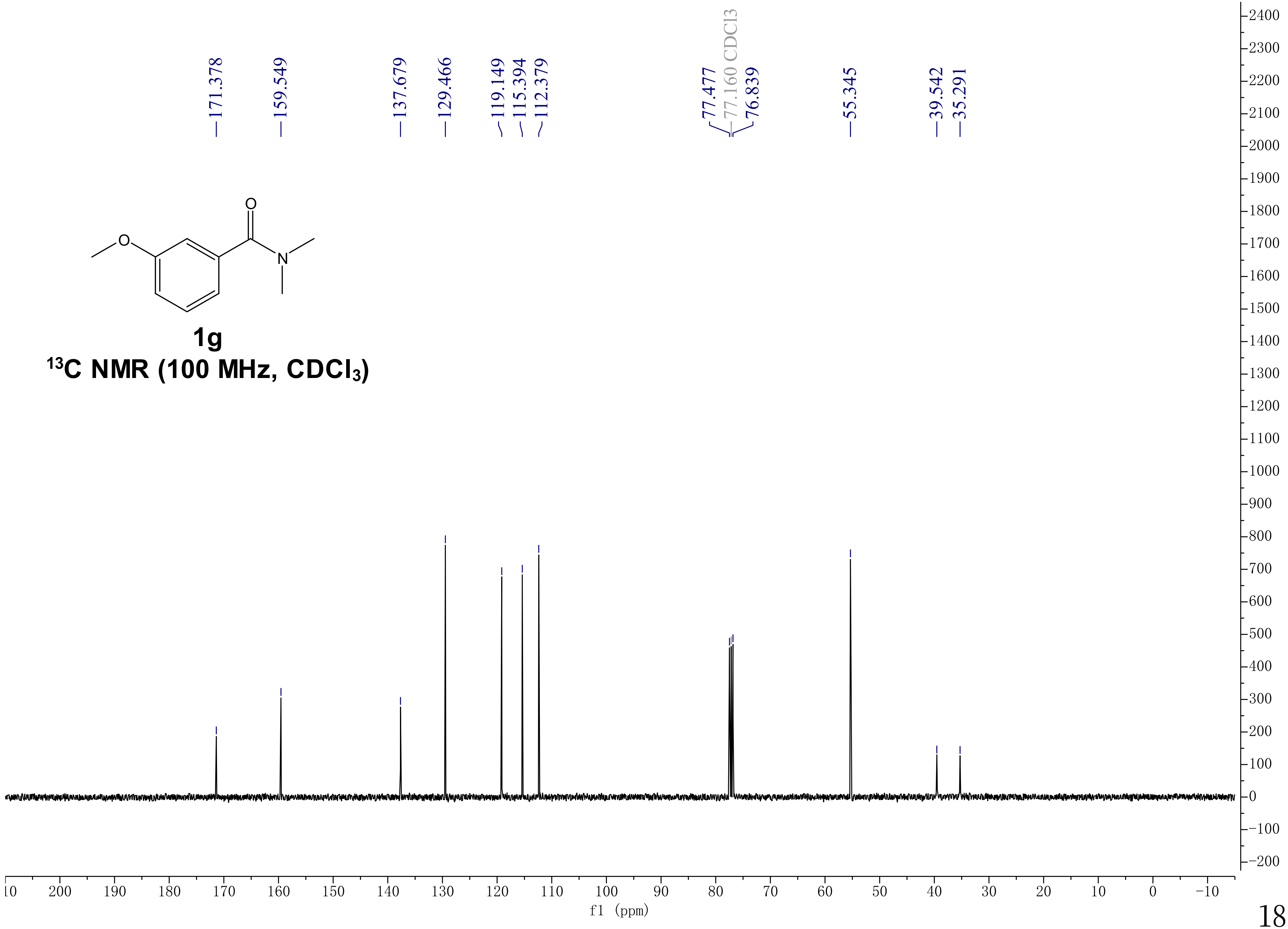


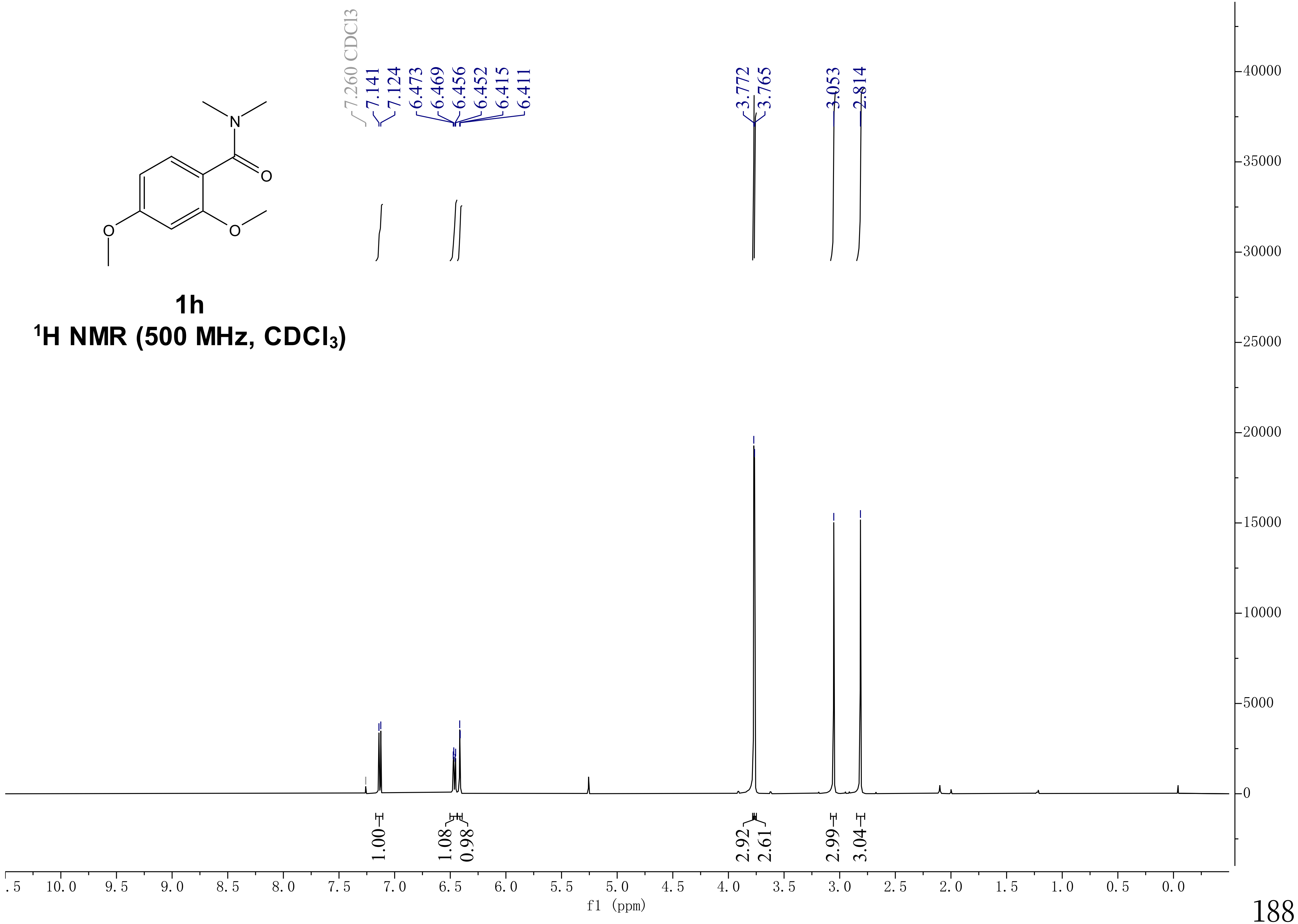
1f

^{13}C NMR (125 MHz, $CDCl_3$)



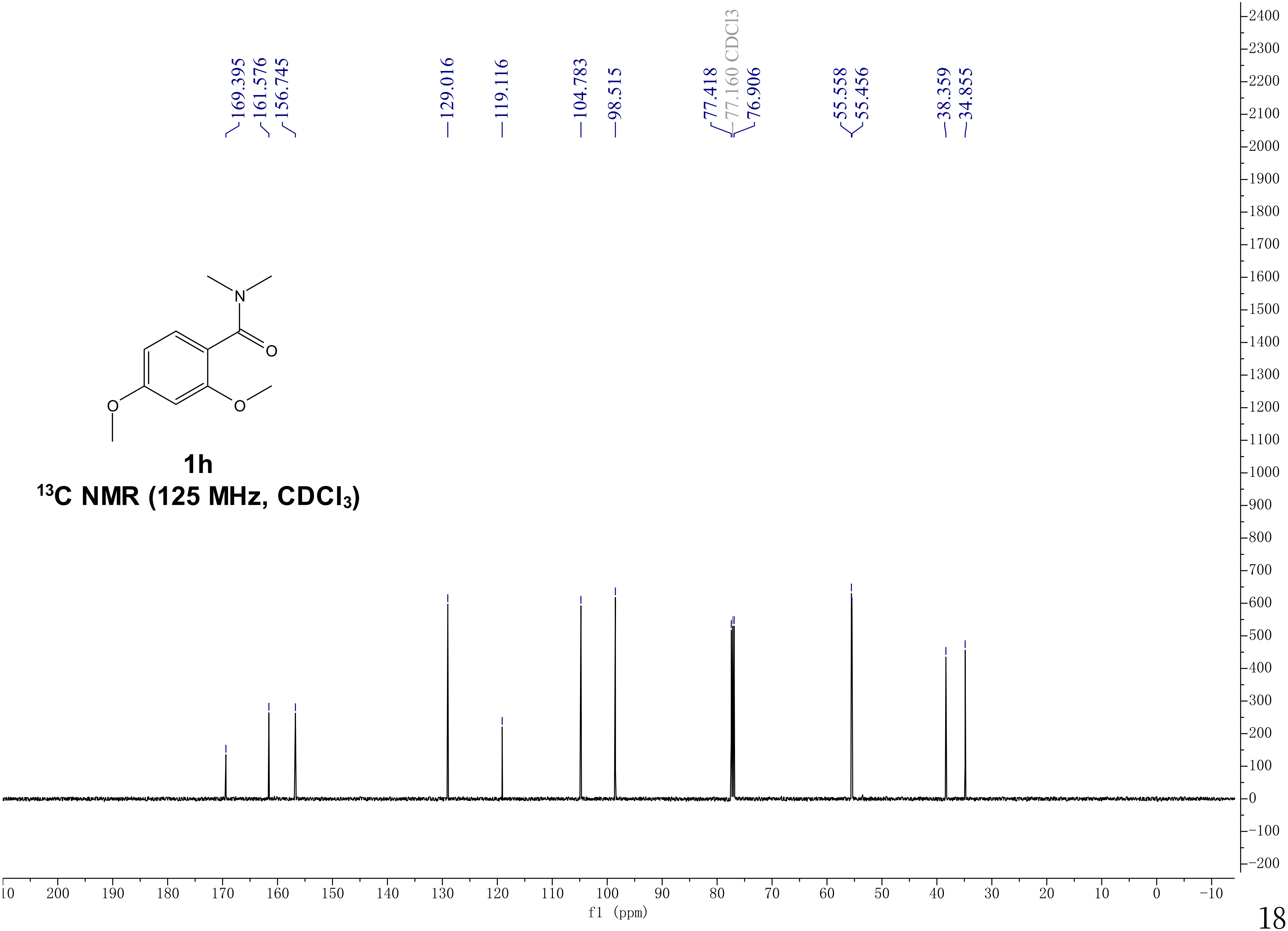

7.316
7.297
7.278
6.972
6.945
6.926
3.815
3.100
2.970
O
O
N
1g
¹H NMR (400 MHz, CDCl₃)
1.07
3.00
3.12
3.01
3.00
f1 (ppm)


171.378
159.549
137.679
129.466
119.149
115.394
112.379
77.477
77.160 CDCl3
76.839
55.345
39.542
35.291
O
N
1g
13C NMR (100 MHz, CDCl3)
f1 (ppm)



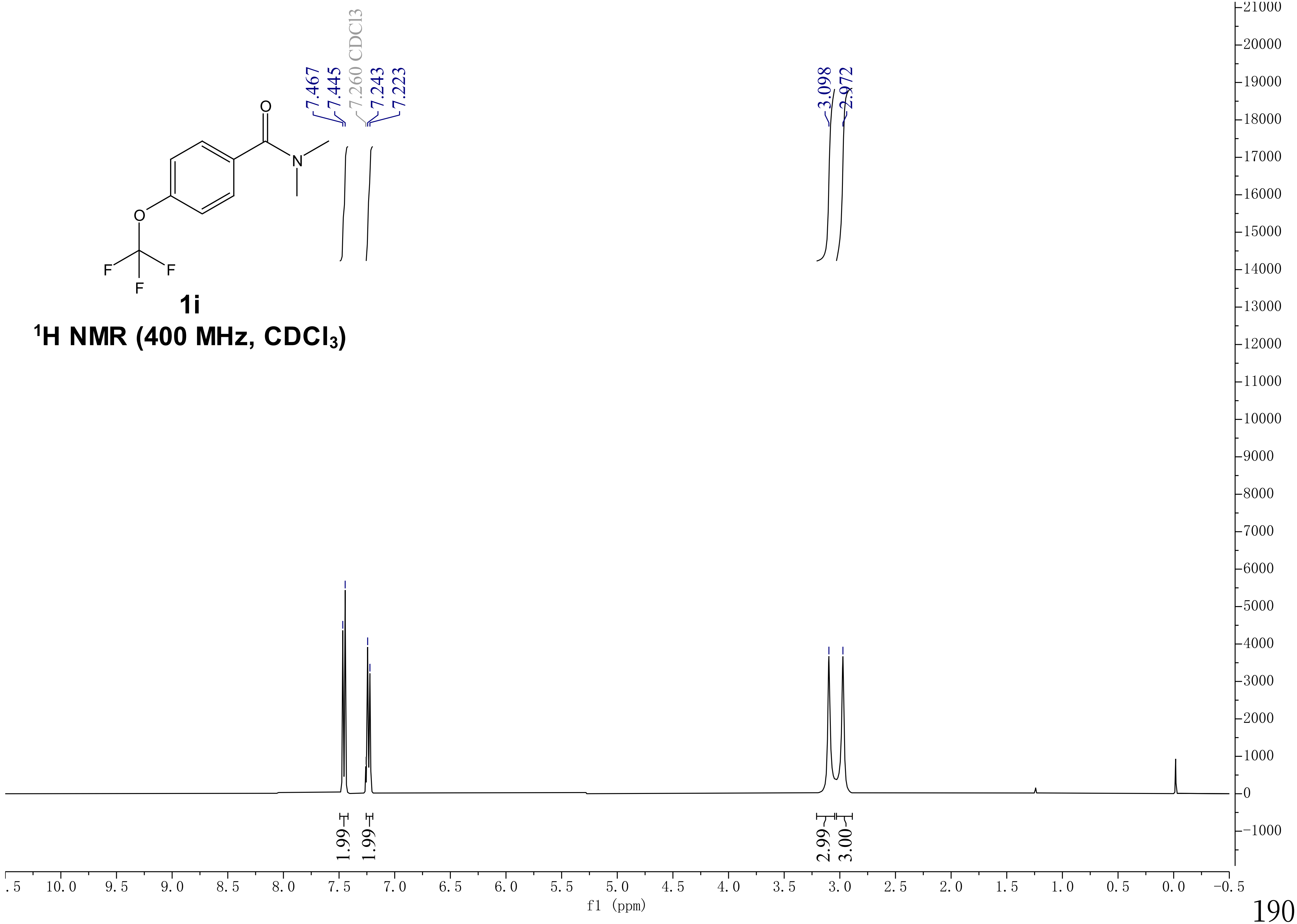
1h

^{1}H NMR (500 MHz, $CDCl_3$)

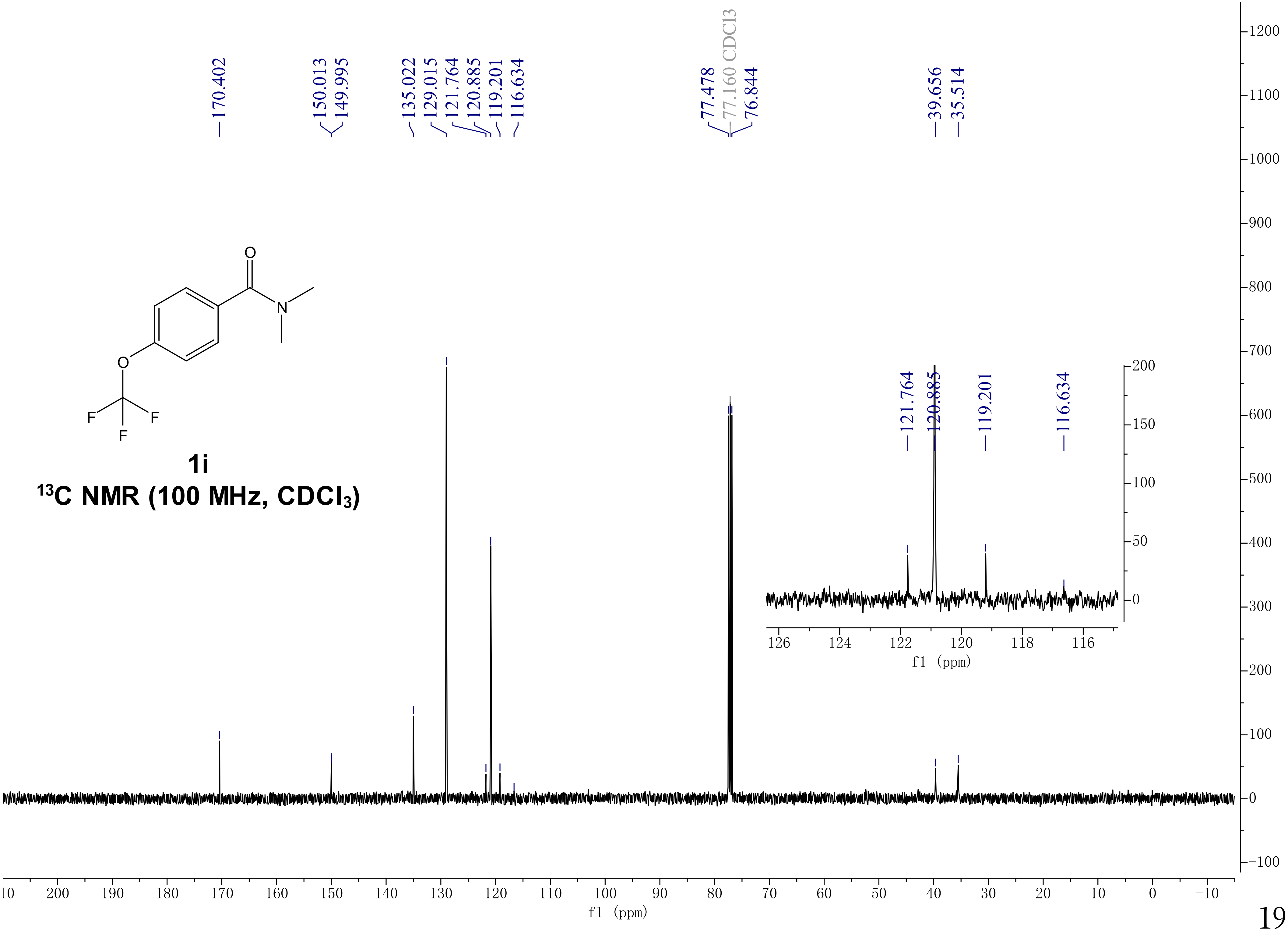


1h

^{13}C NMR (125 MHz, $CDCl_3$)



7.467
7.445
7.260 CDCl3
7.243
7.223
3.098
2.972
1i
^{1}H NMR (400 MHz, CDCl$_3$)
1.99
1.99
2.99
3.00
f1 (ppm)

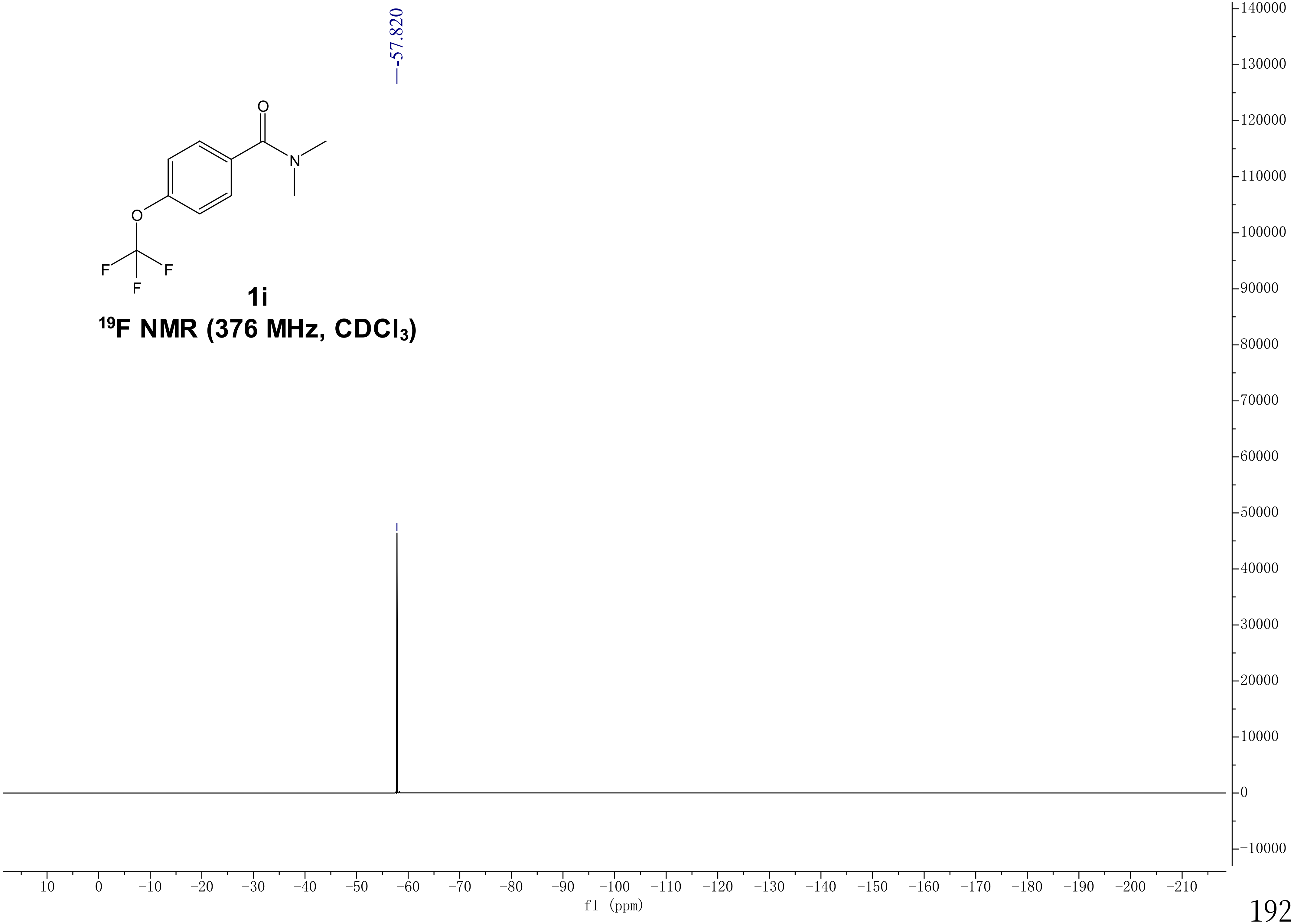


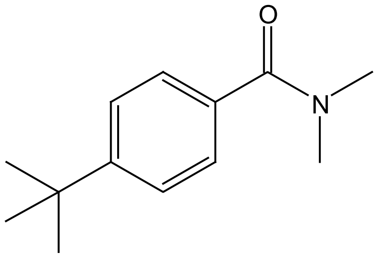
1i

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

1i

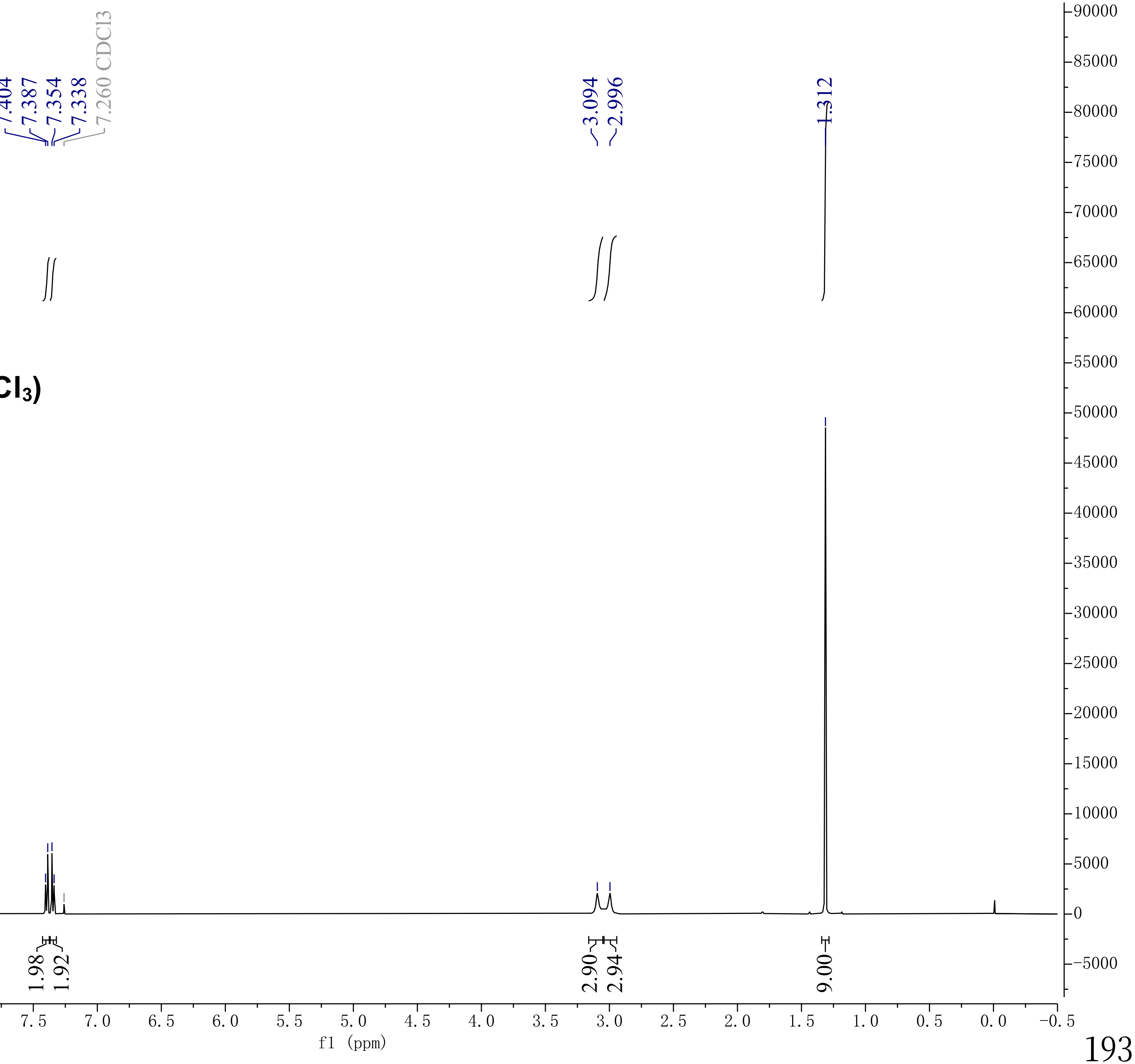
^{19}F NMR (376 MHz, $CDCl_3$)

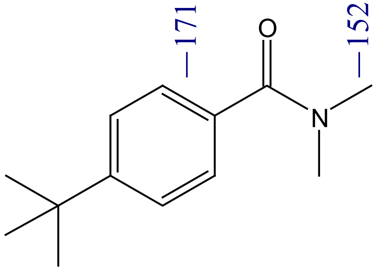




1j

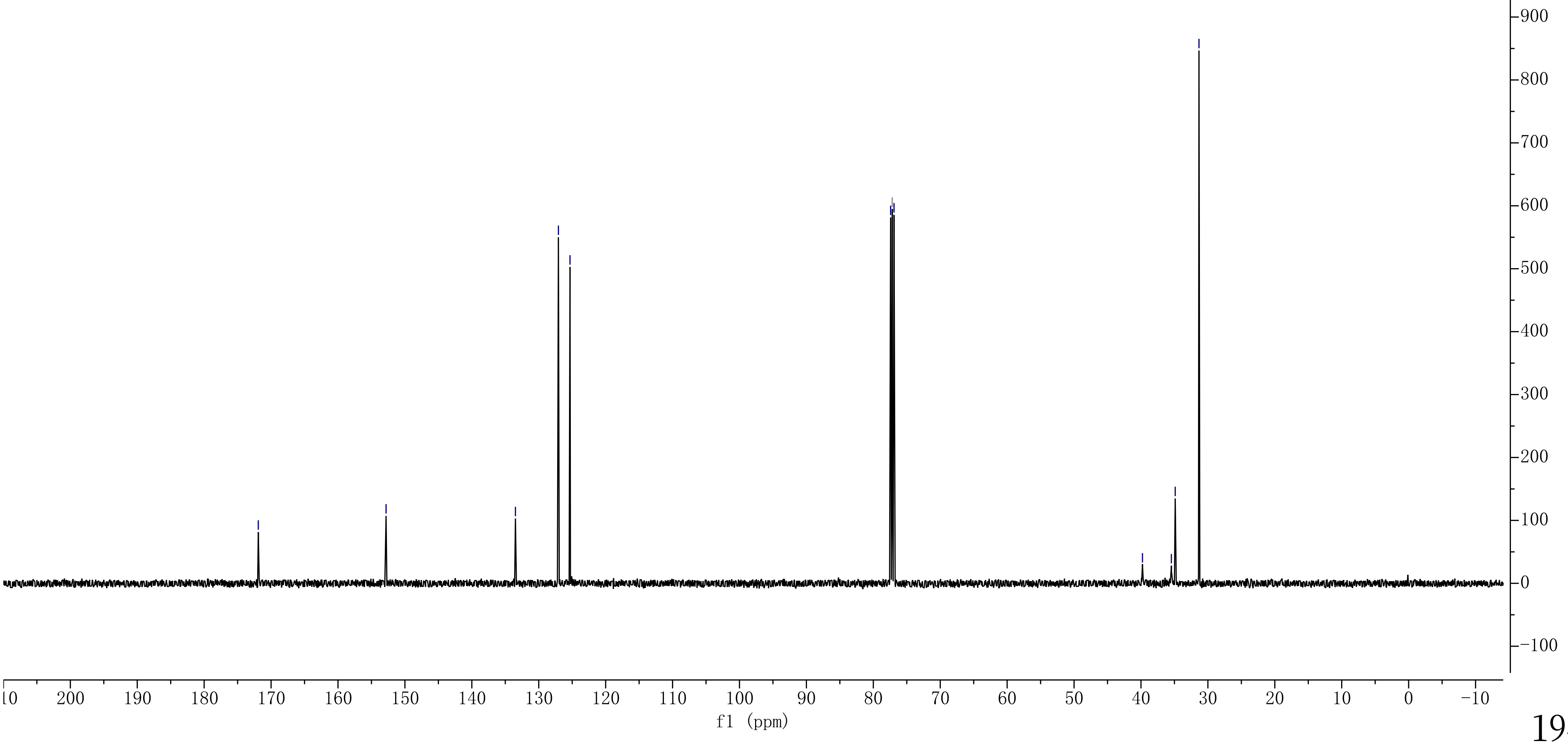
^{1}H NMR (500 MHz, $CDCl_3$)

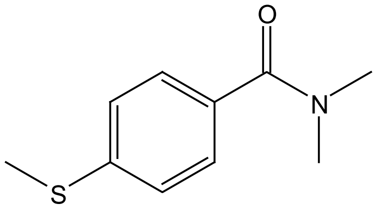




1j

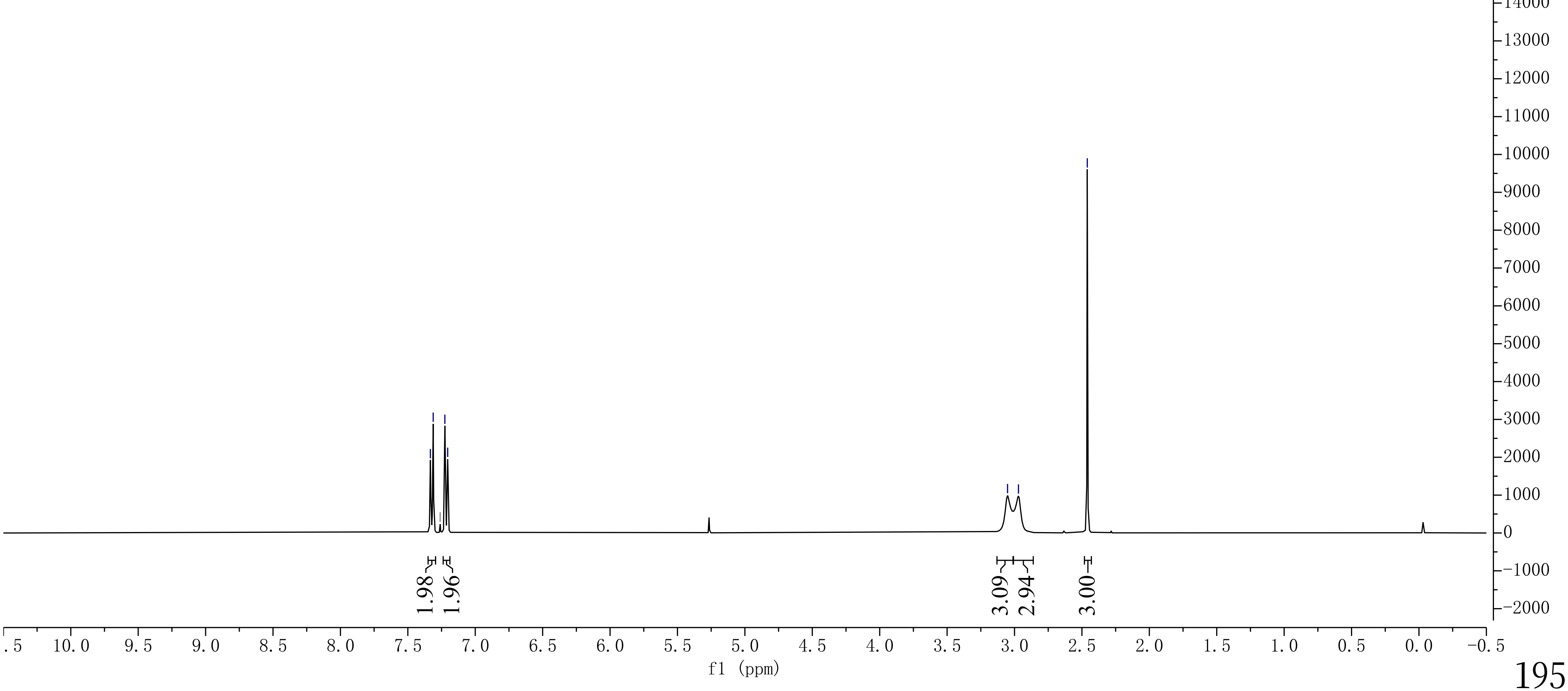
^{13}C NMR (125 MHz, $CDCl_3$)

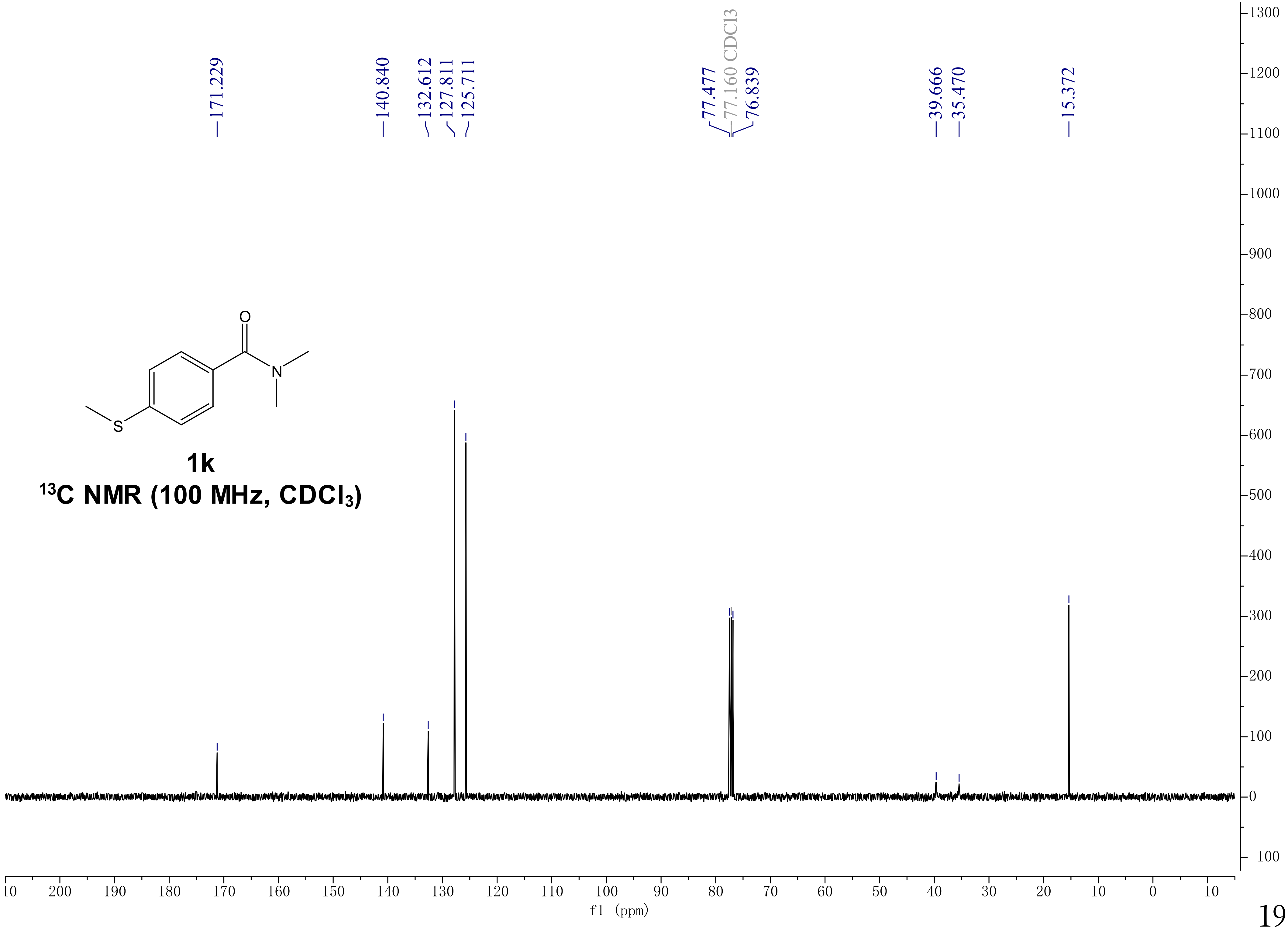


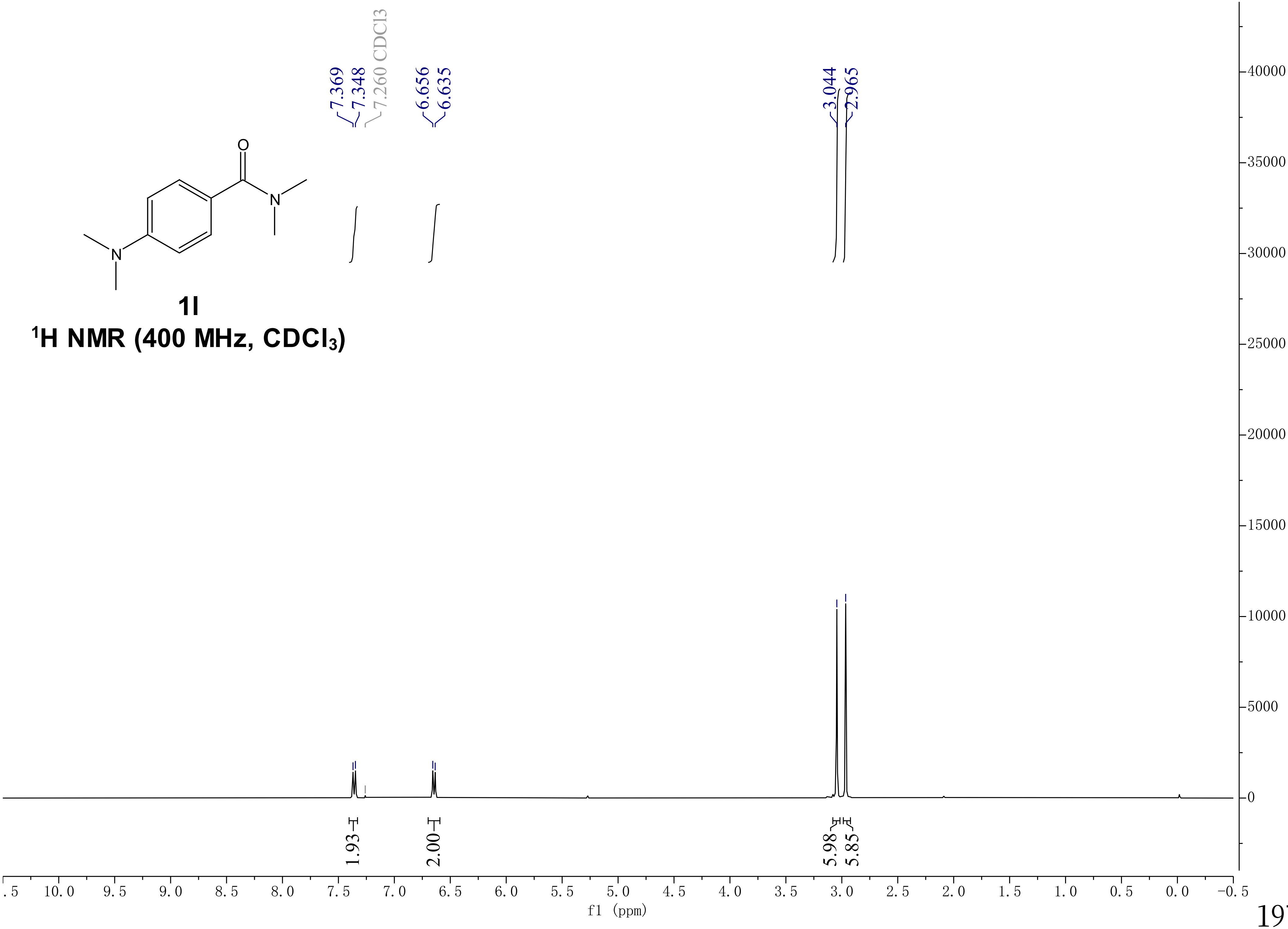


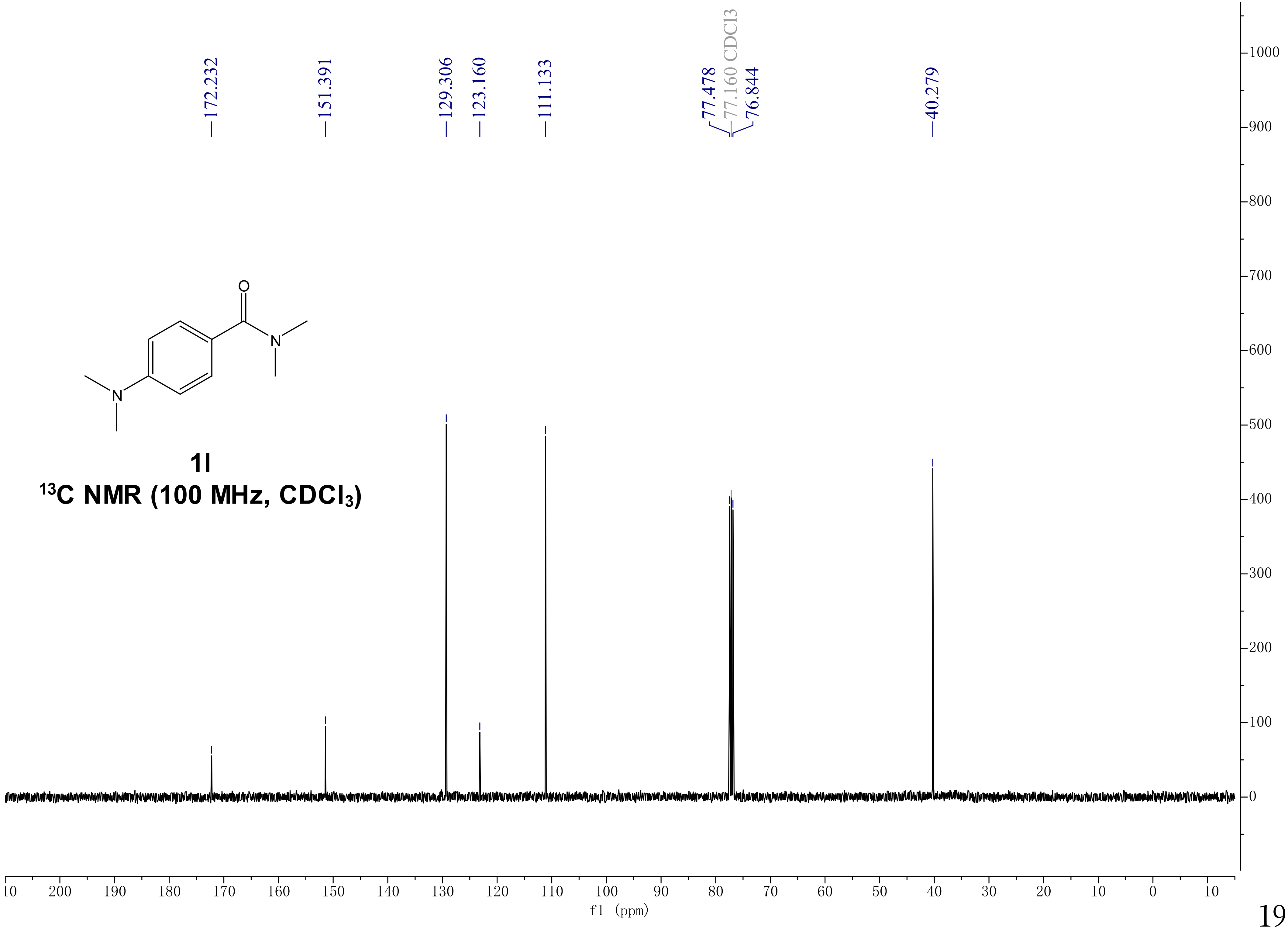
1k

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

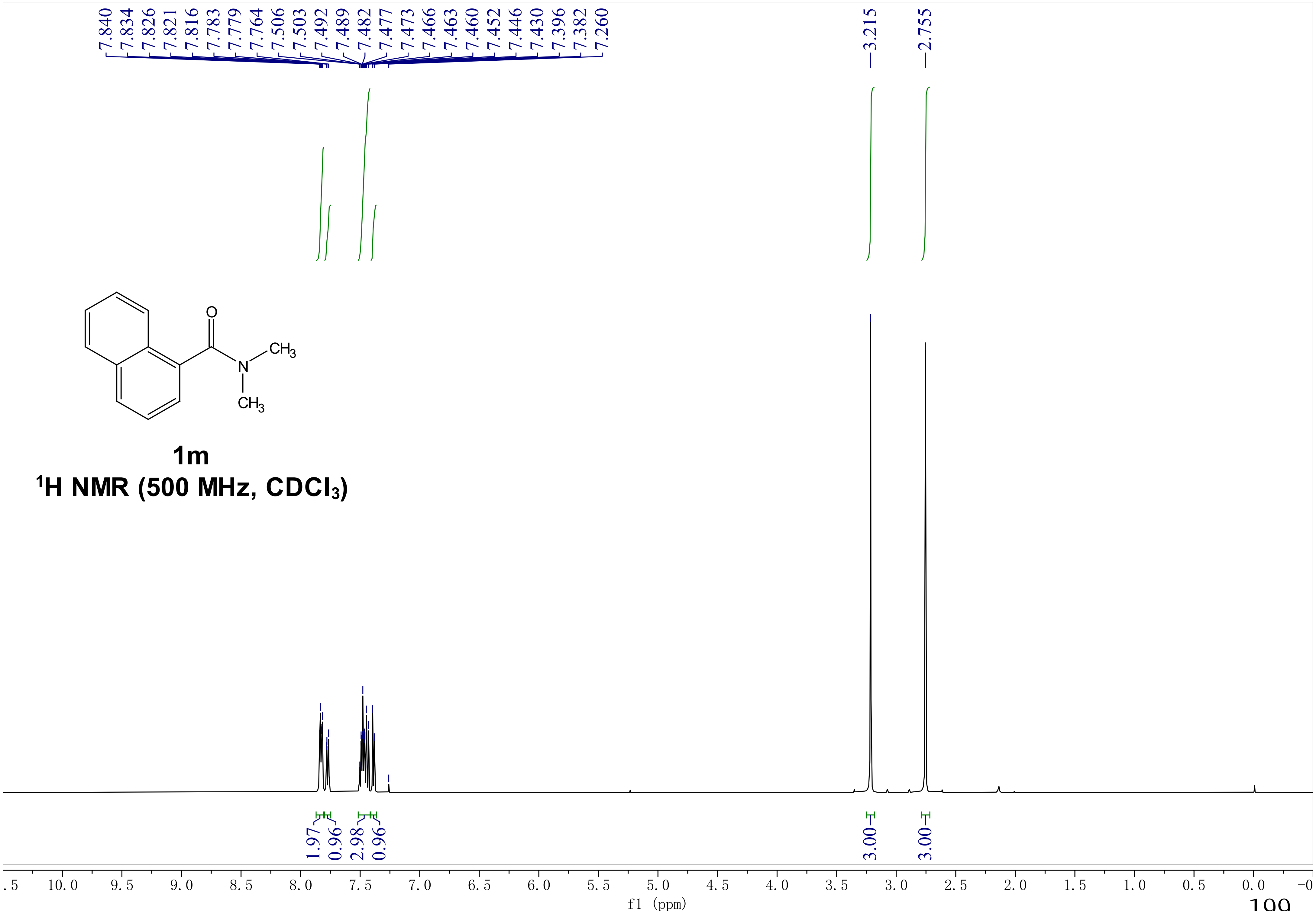



171.229
140.840
132.612
127.811
125.711
77.477
77.160 CDCl3
76.839
39.666
35.470
15.372
1k
13C NMR (100 MHz, CDCl3)
f1 (ppm)


1l
^{1}H NMR (400 MHz, CDCl$_3$)
7.369
7.348
7.260 CDCl3
6.656
6.635
3.044
2.965
1.93
2.00
5.98
5.85
f1 (ppm)

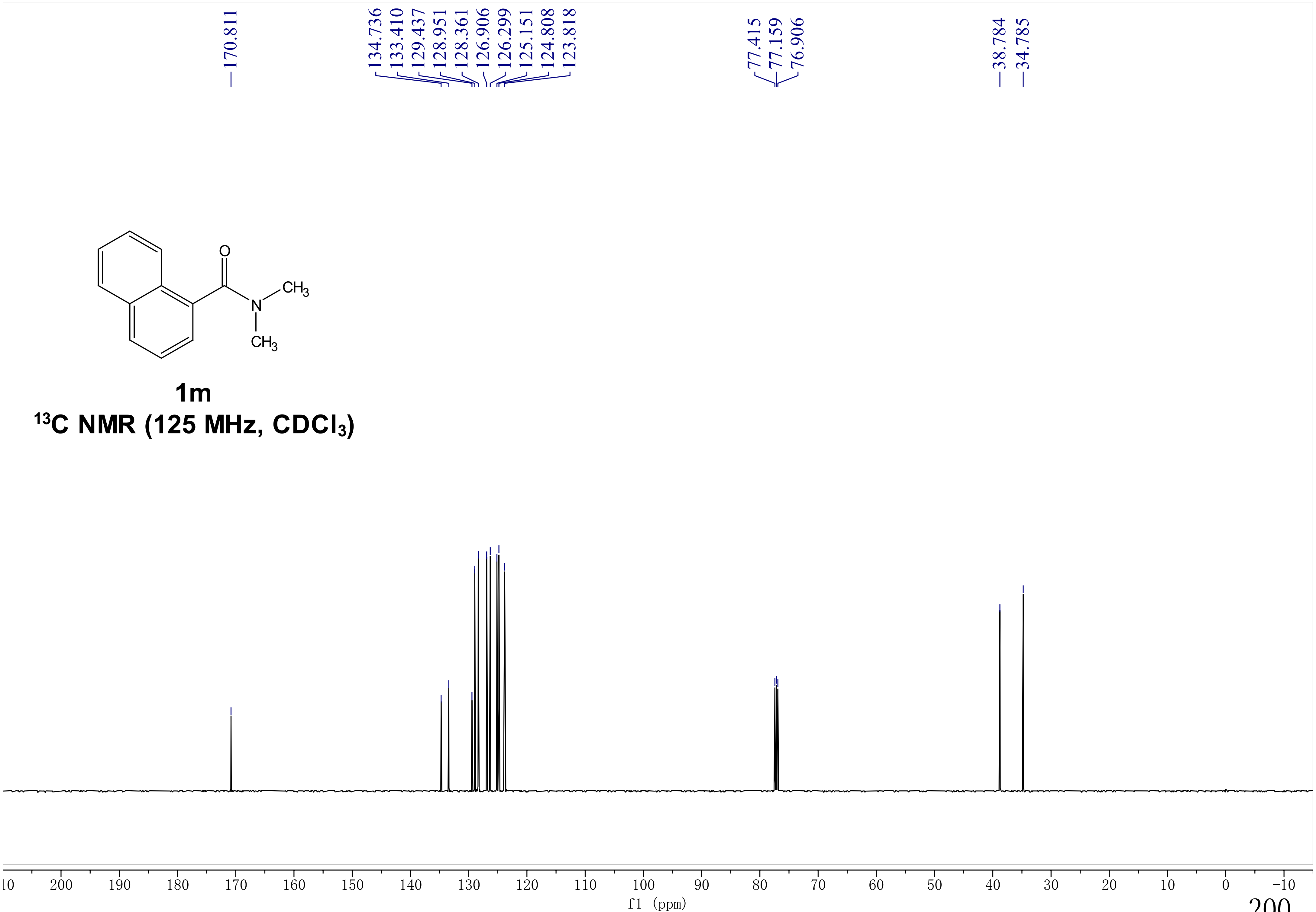


172.232
151.391
129.306
123.160
111.133
77.478
77.160 CDCl3
76.844
40.279
O
N
N
1l
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

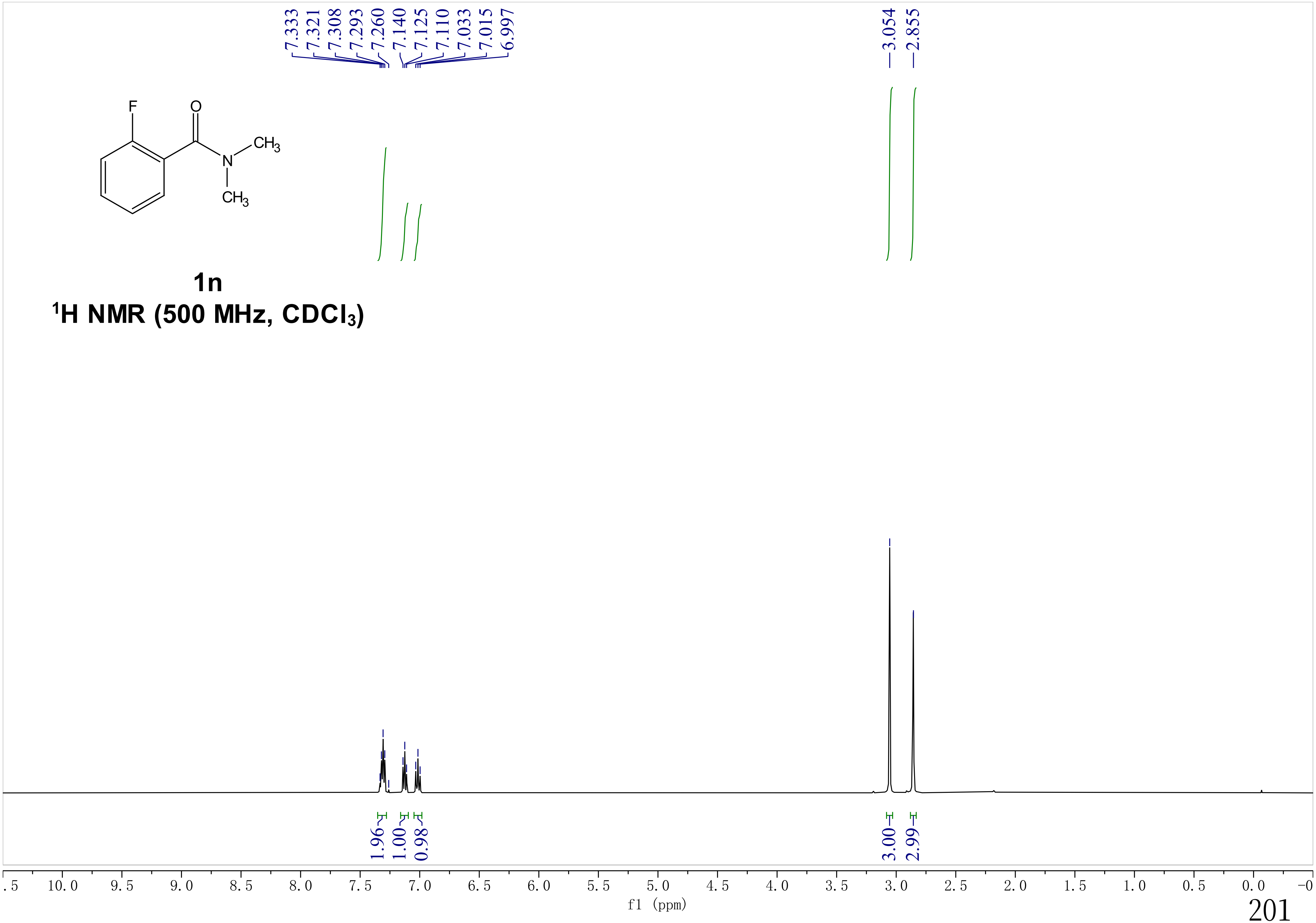


1m

^{1}H NMR (500 MHz, $CDCl_3$)

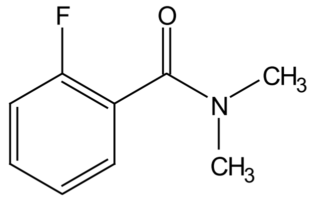


170.811
134.736
133.410
129.437
128.951
128.361
126.906
126.299
125.151
124.808
123.818
77.415
77.159
76.906
38.784
34.785
O
N
CH3
CH3
1m
13C NMR (125 MHz, CDCl3)
f1 (ppm)



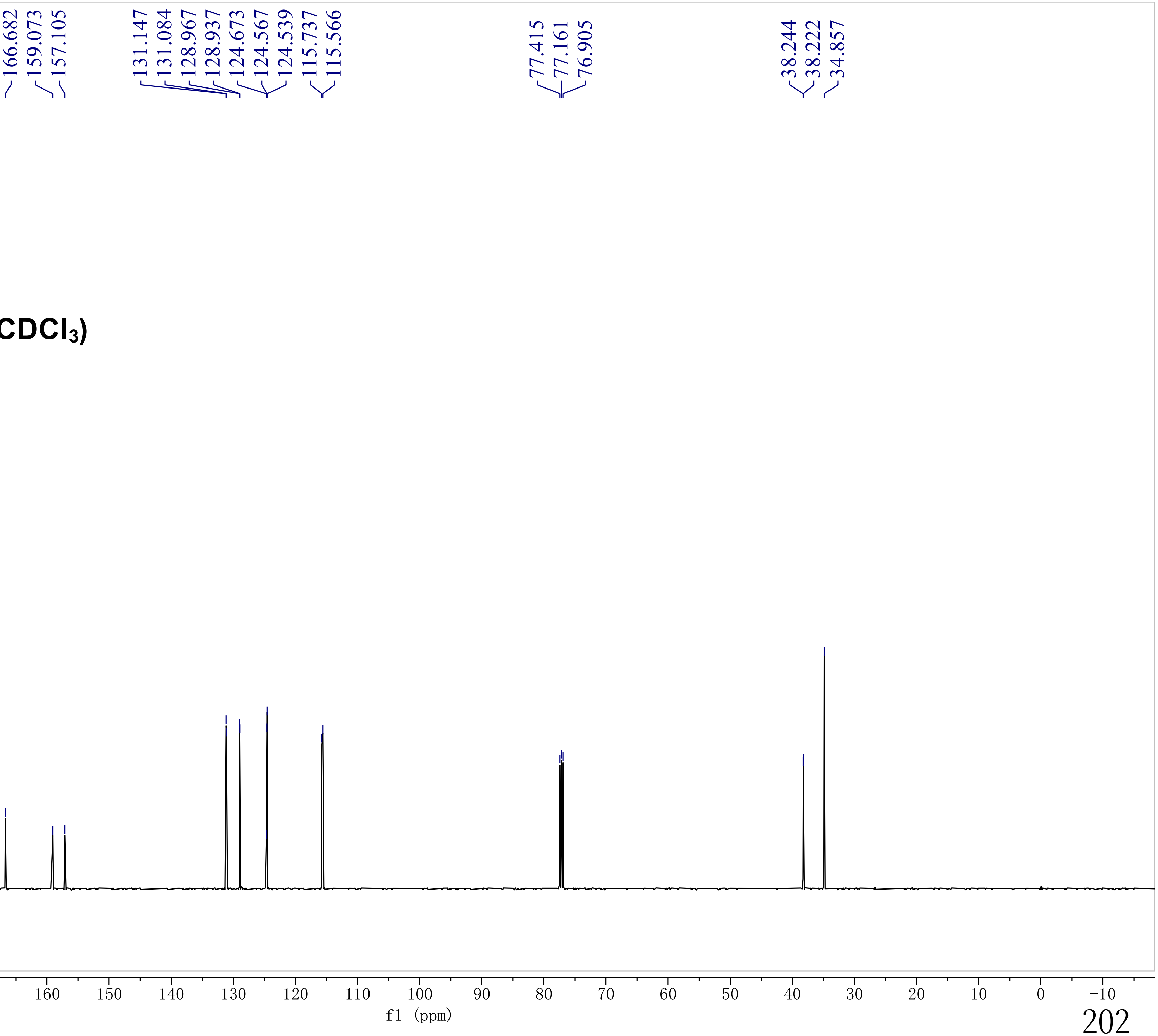
1n

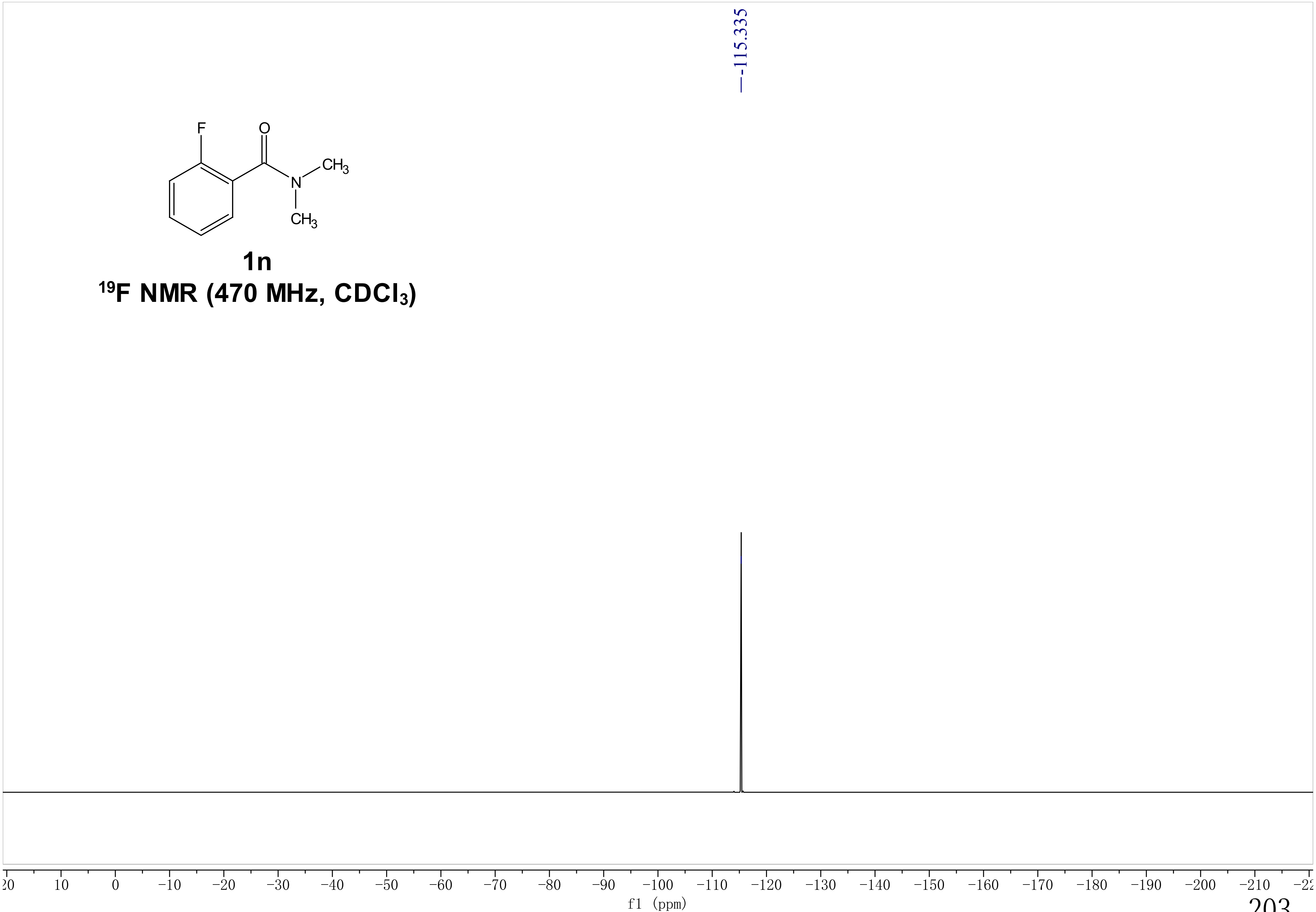
^{1}H NMR (500 MHz, $CDCl_3$)

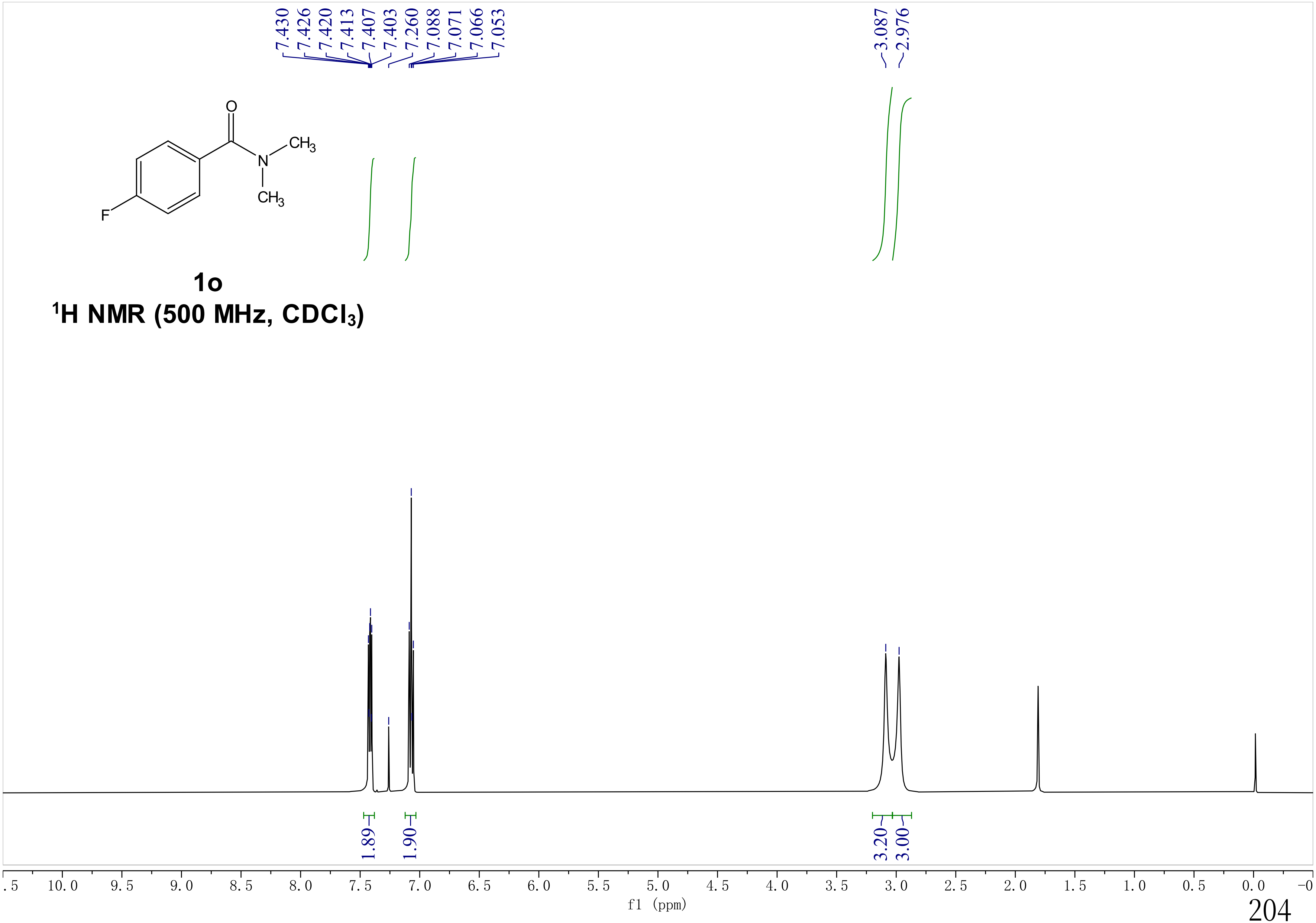


1n

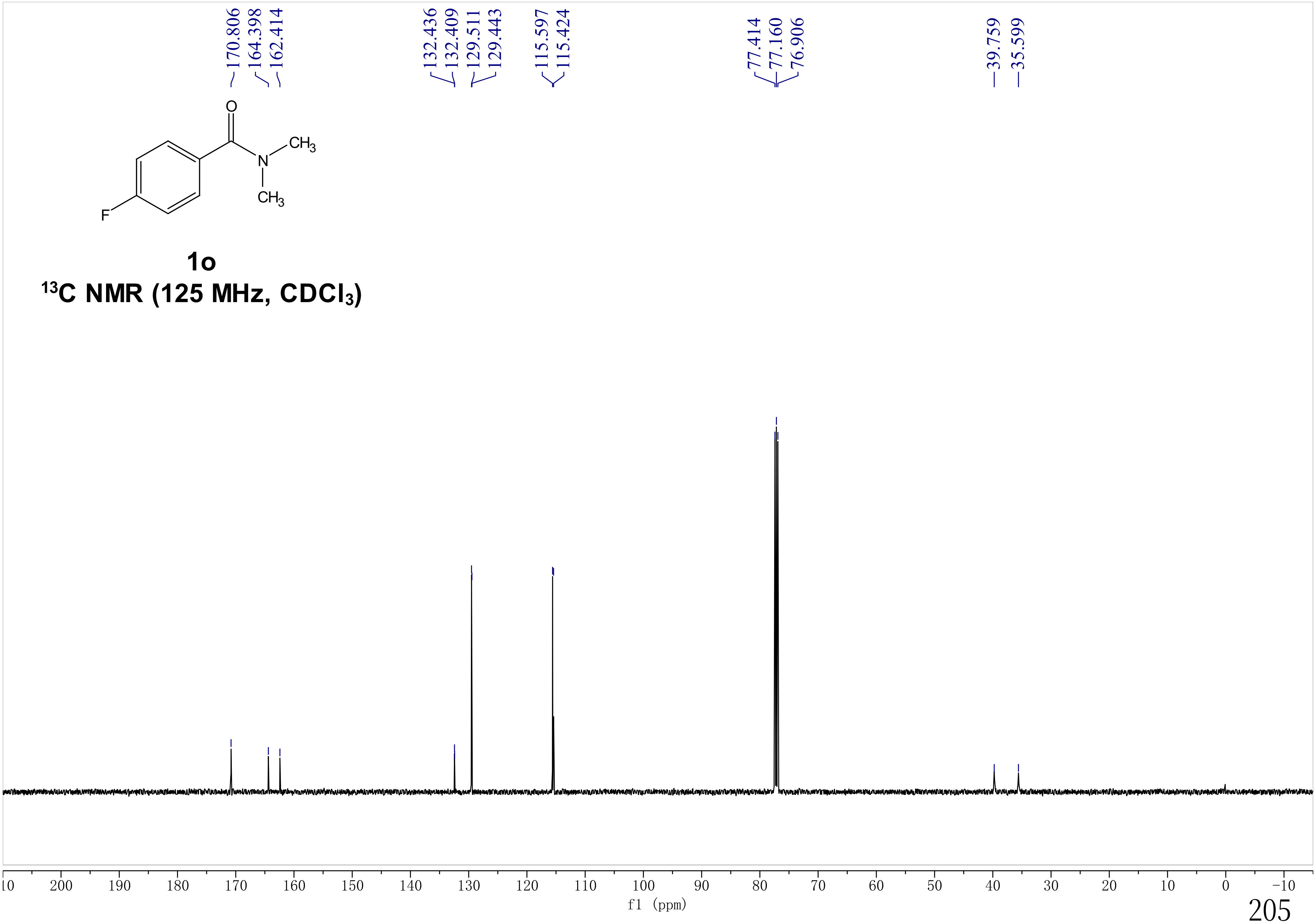
^{13}C NMR (125 MHz, $CDCl_3$)




-115.335
F
O
N
CH3
CH3
1n
19F NMR (470 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−22
f1 (ppm)

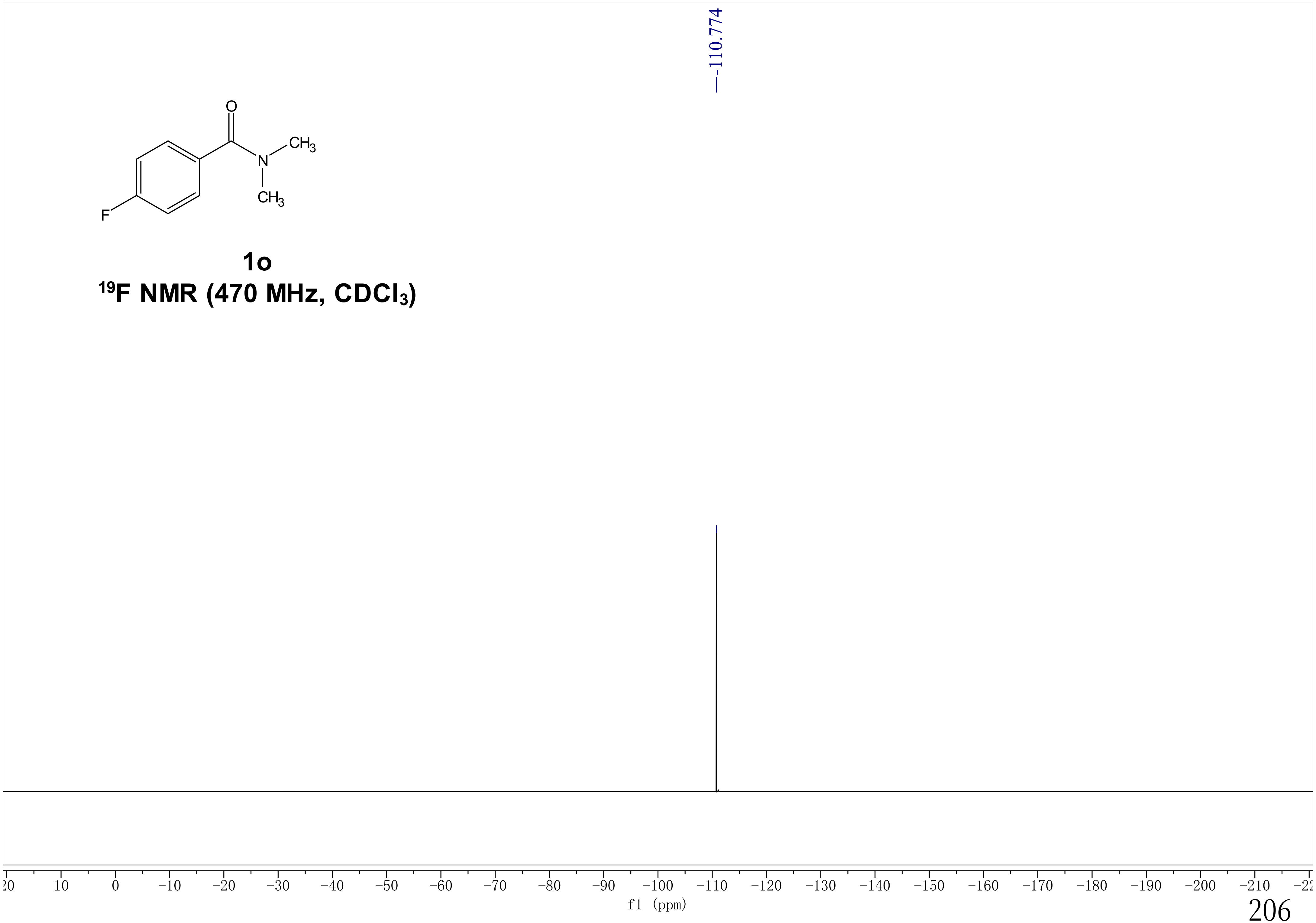


7.430
7.426
7.420
7.413
7.407
7.403
7.260
7.088
7.071
7.066
7.053
3.087
2.976
O
N
CH3
CH3
F
1o
1H NMR (500 MHz, CDCl3)
1.89
1.90
3.20
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)



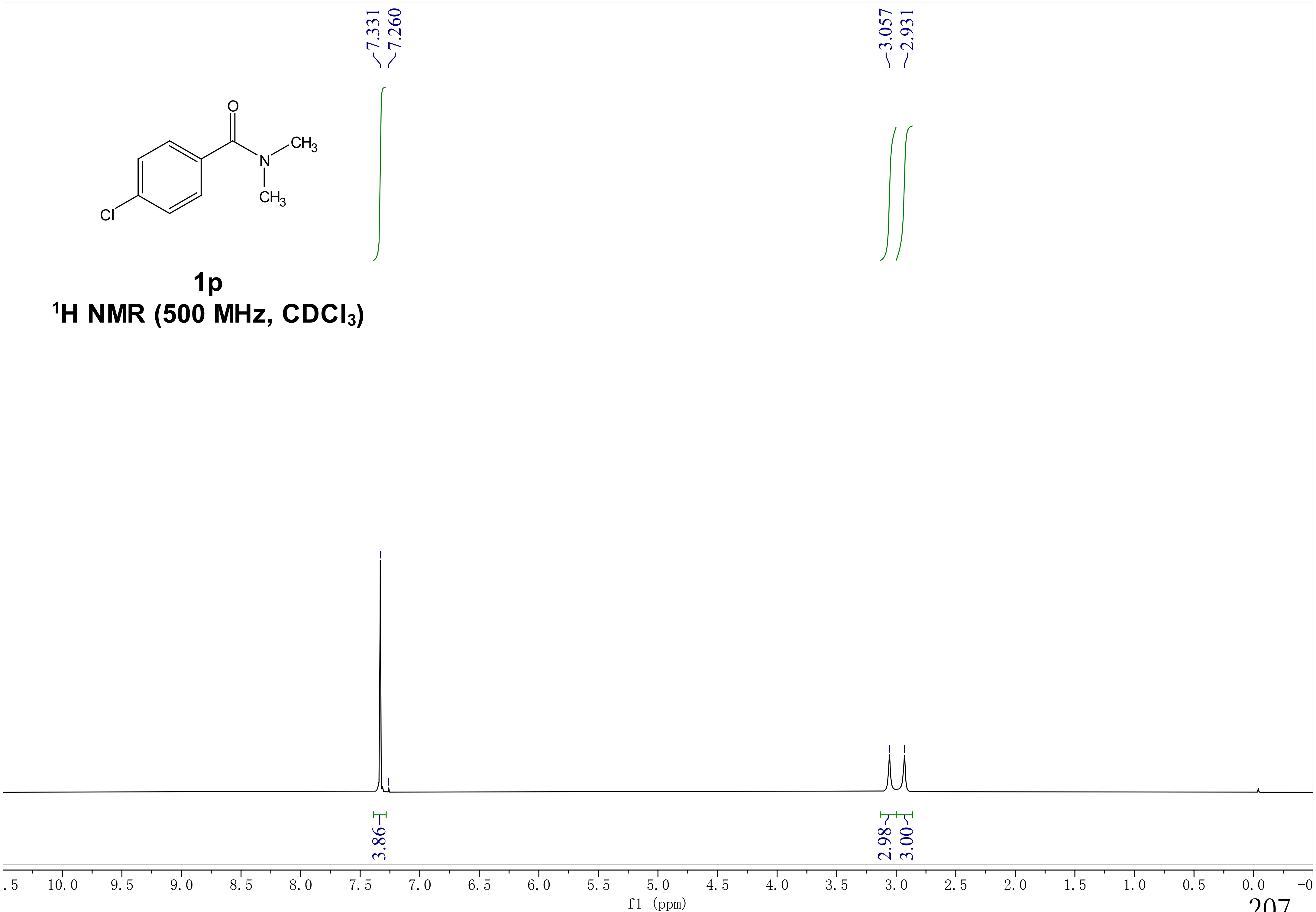
1o

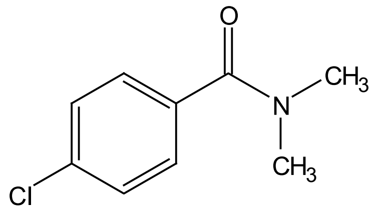
^{13}C NMR (125 MHz, $CDCl_3$)



1o

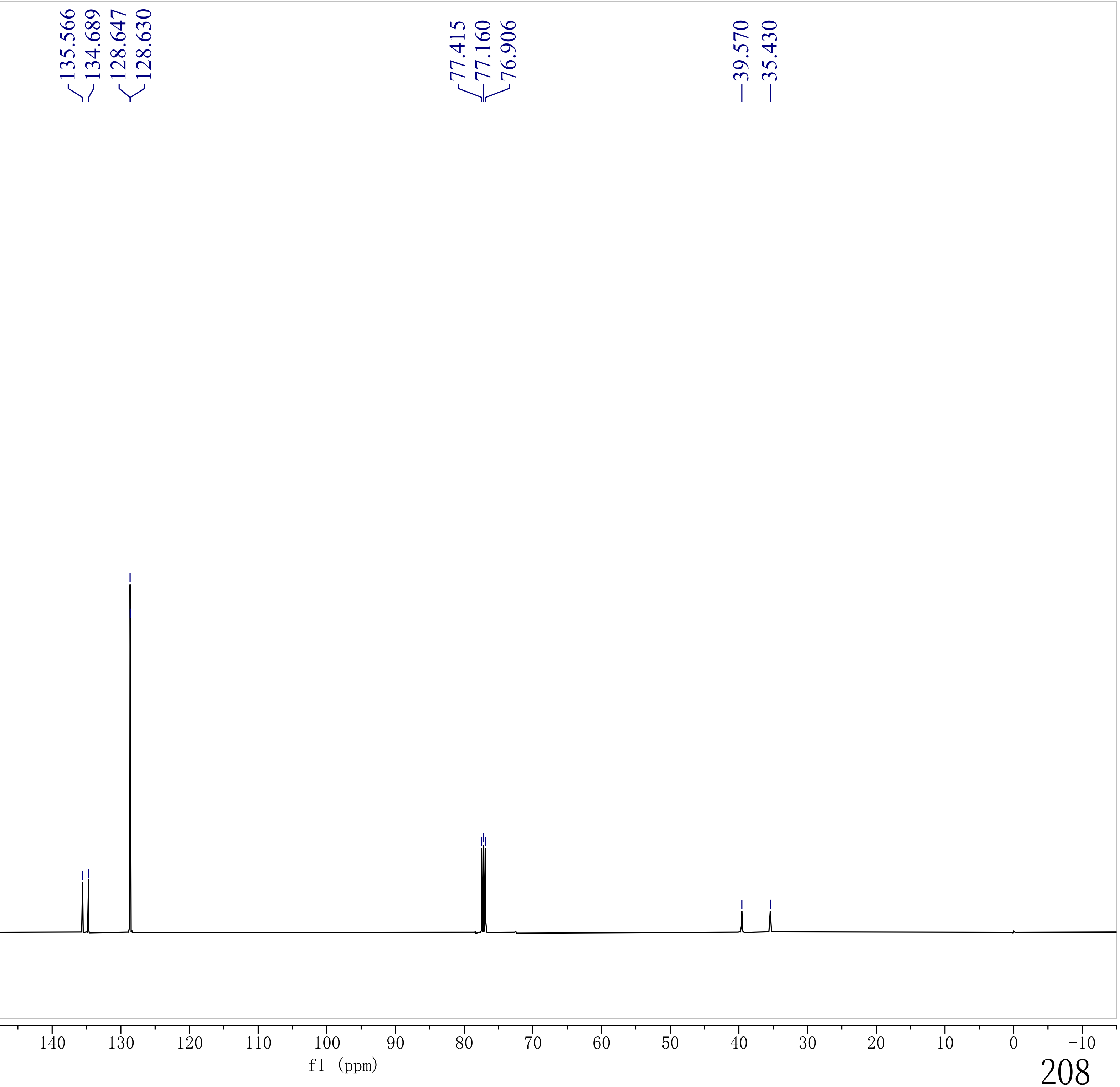
^{19}F NMR (470 MHz, $CDCl_3$)

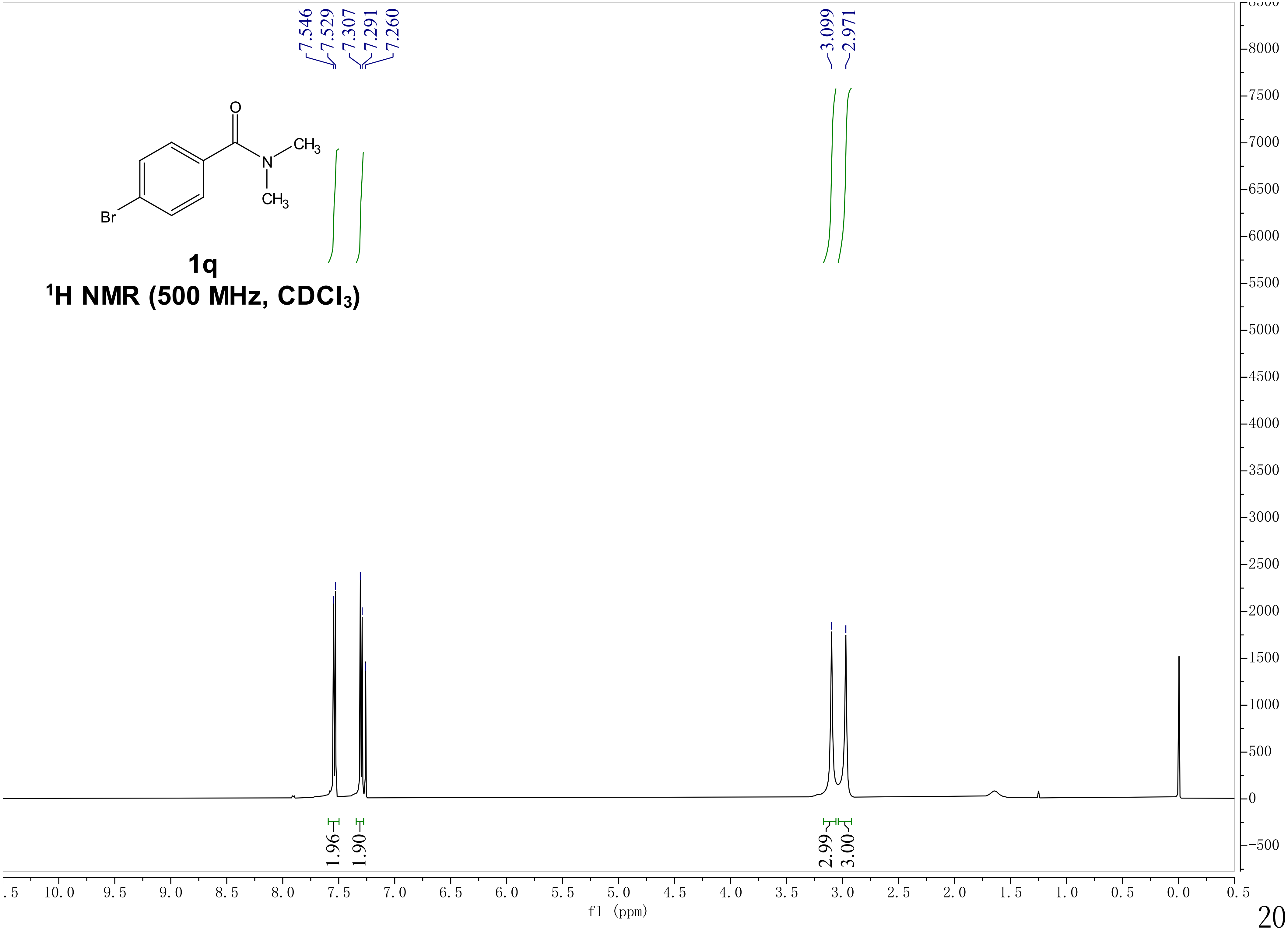

O
CH3
N
CH3
Cl
1p
1H NMR (500 MHz, CDCl3)
7.331
7.260
3.057
2.931
3.86
2.98
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

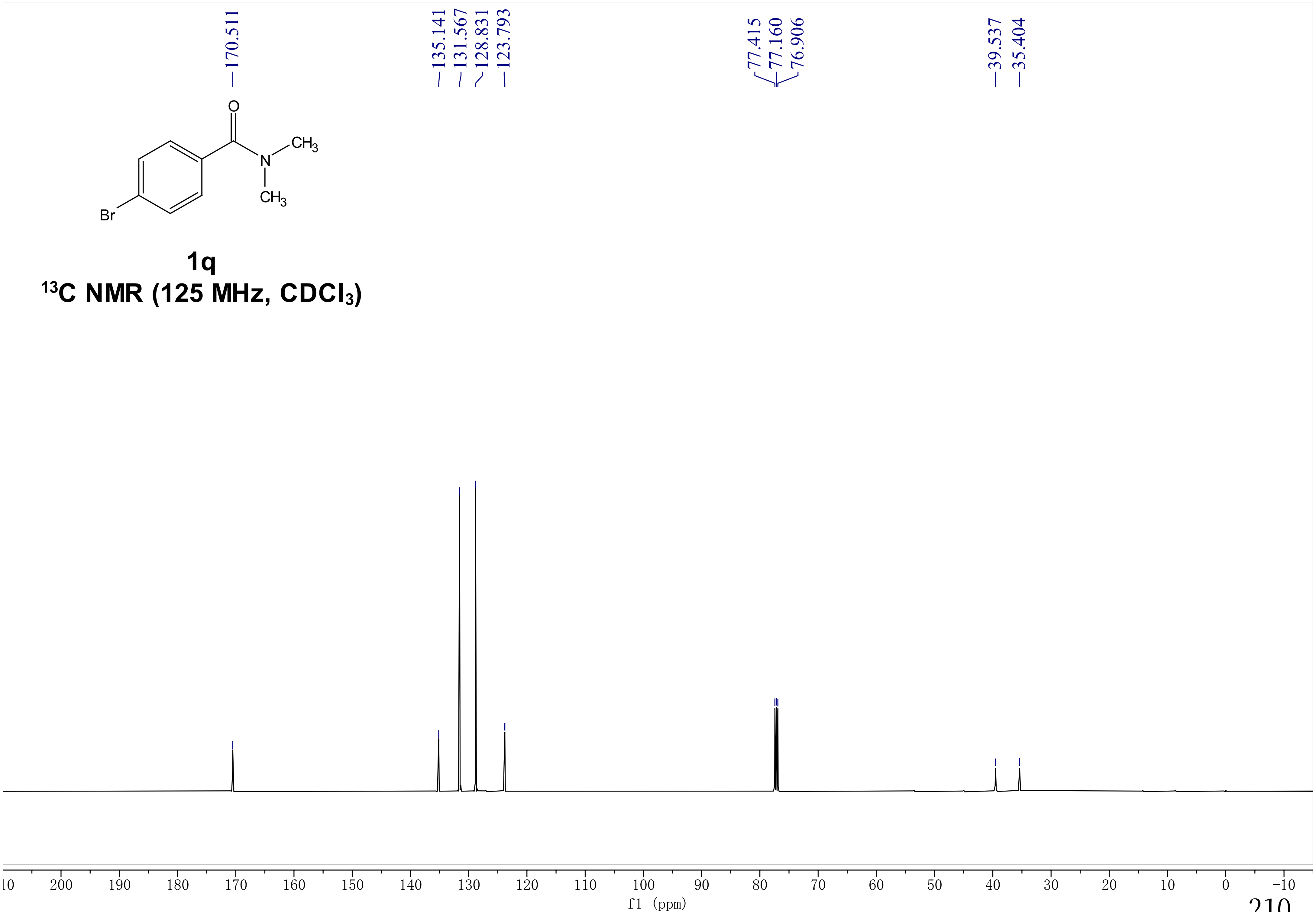


1p

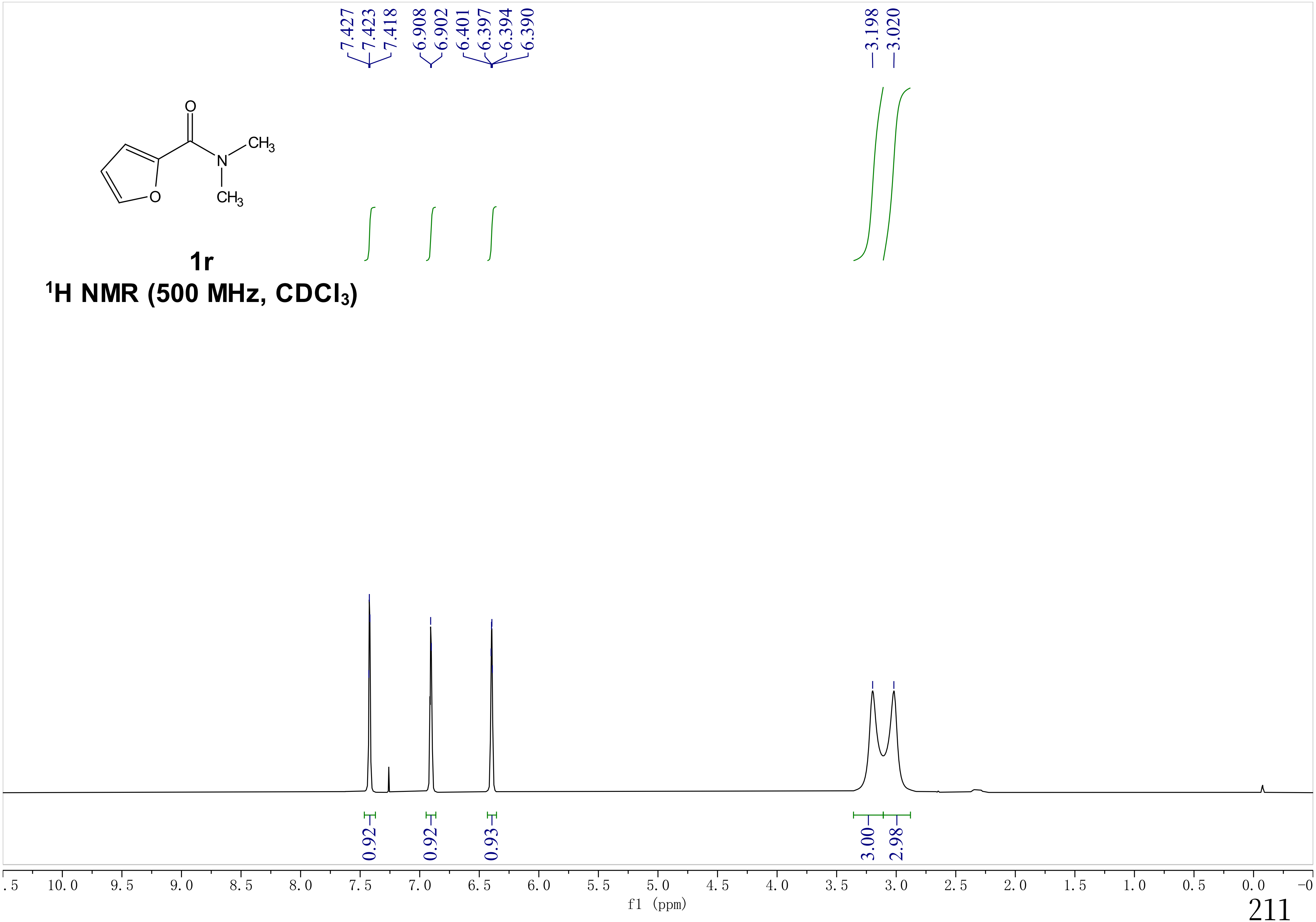
^{13}C NMR (125 MHz, $CDCl_3$)



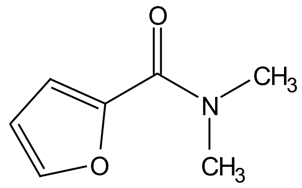

1q
^{1}H NMR (500 MHz, $CDCl_3$)
7.546
7.529
7.307
7.291
7.260
3.099
2.971
1.96
1.90
2.99
3.00
f1 (ppm)



1q
^{13}C NMR (125 MHz, $CDCl_3$)

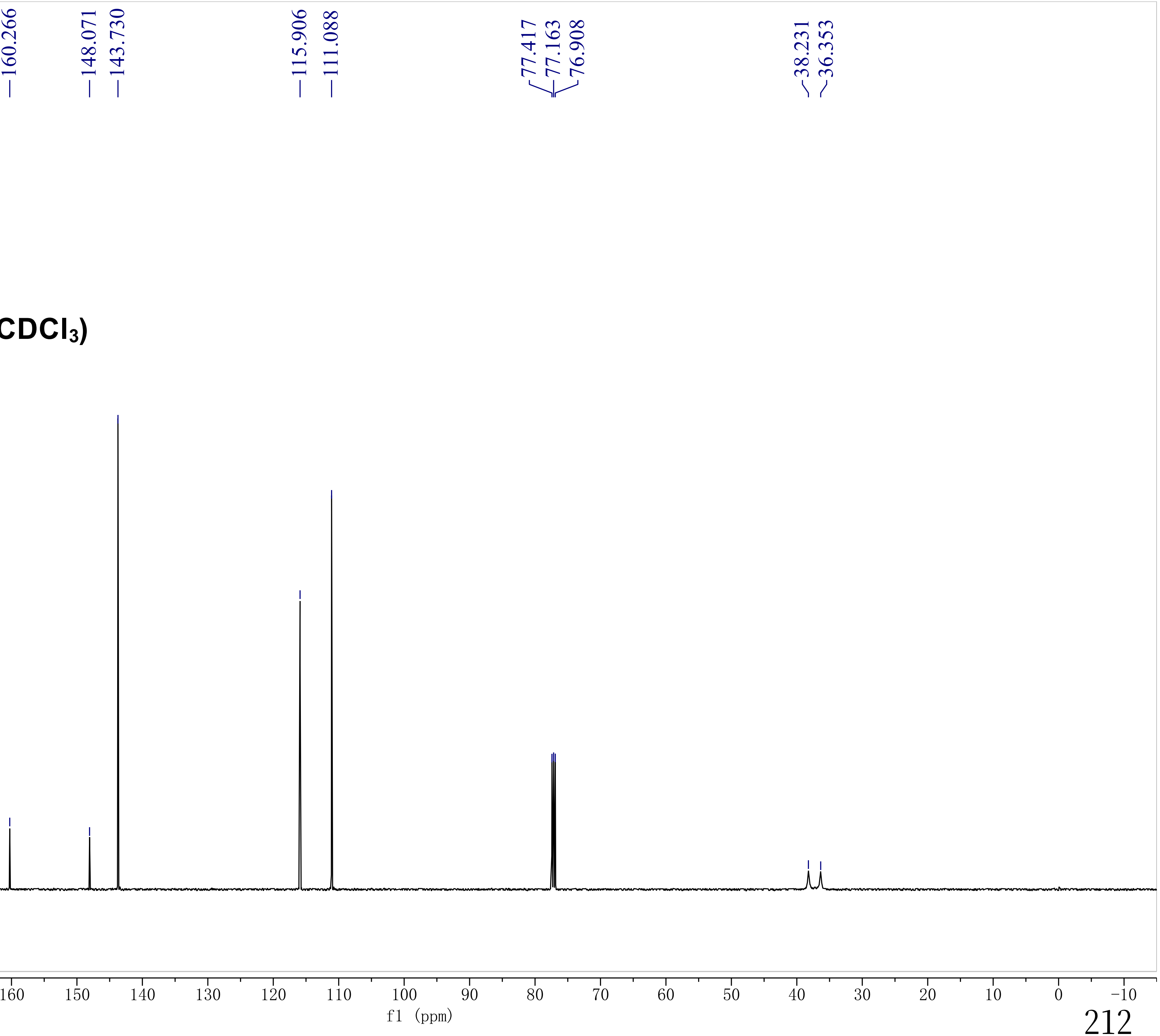


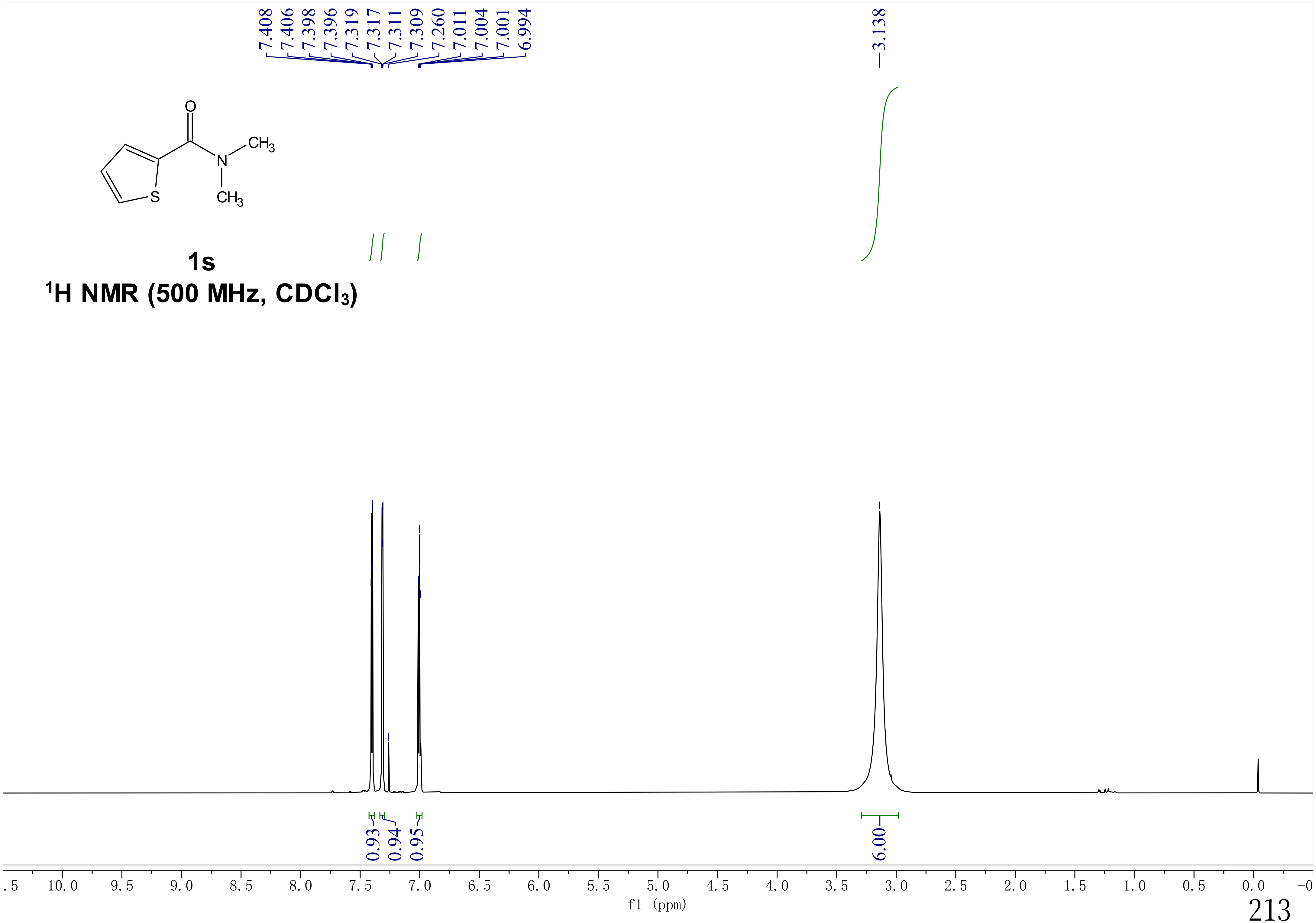
1r
^{1}H NMR (500 MHz, CDCl$_3$)
7.427
7.423
7.418
6.908
6.902
6.401
6.397
6.394
6.390
3.198
3.020
0.92
0.92
0.93
3.00
2.98
f1 (ppm)



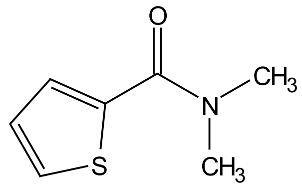
1r

^{13}C NMR (125 MHz, $CDCl_3$)



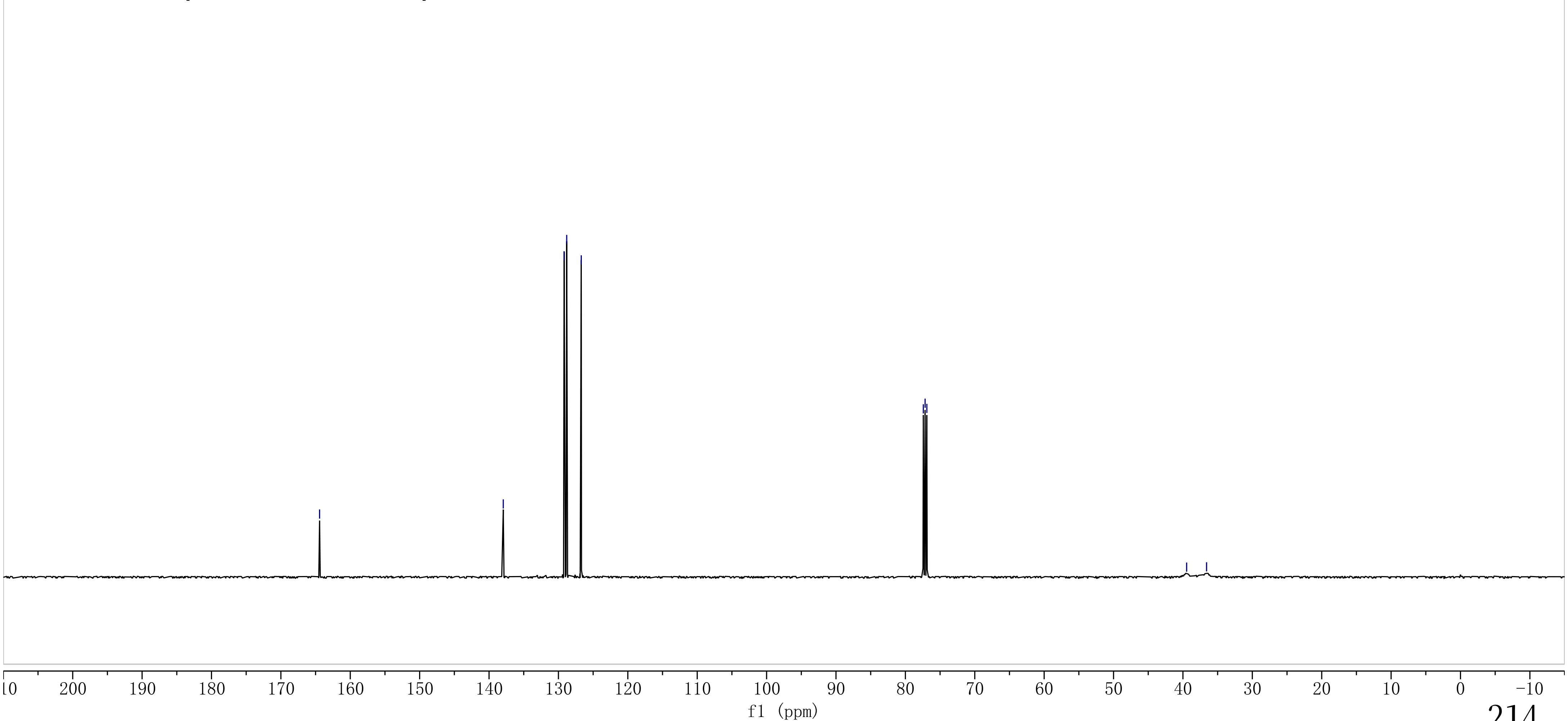


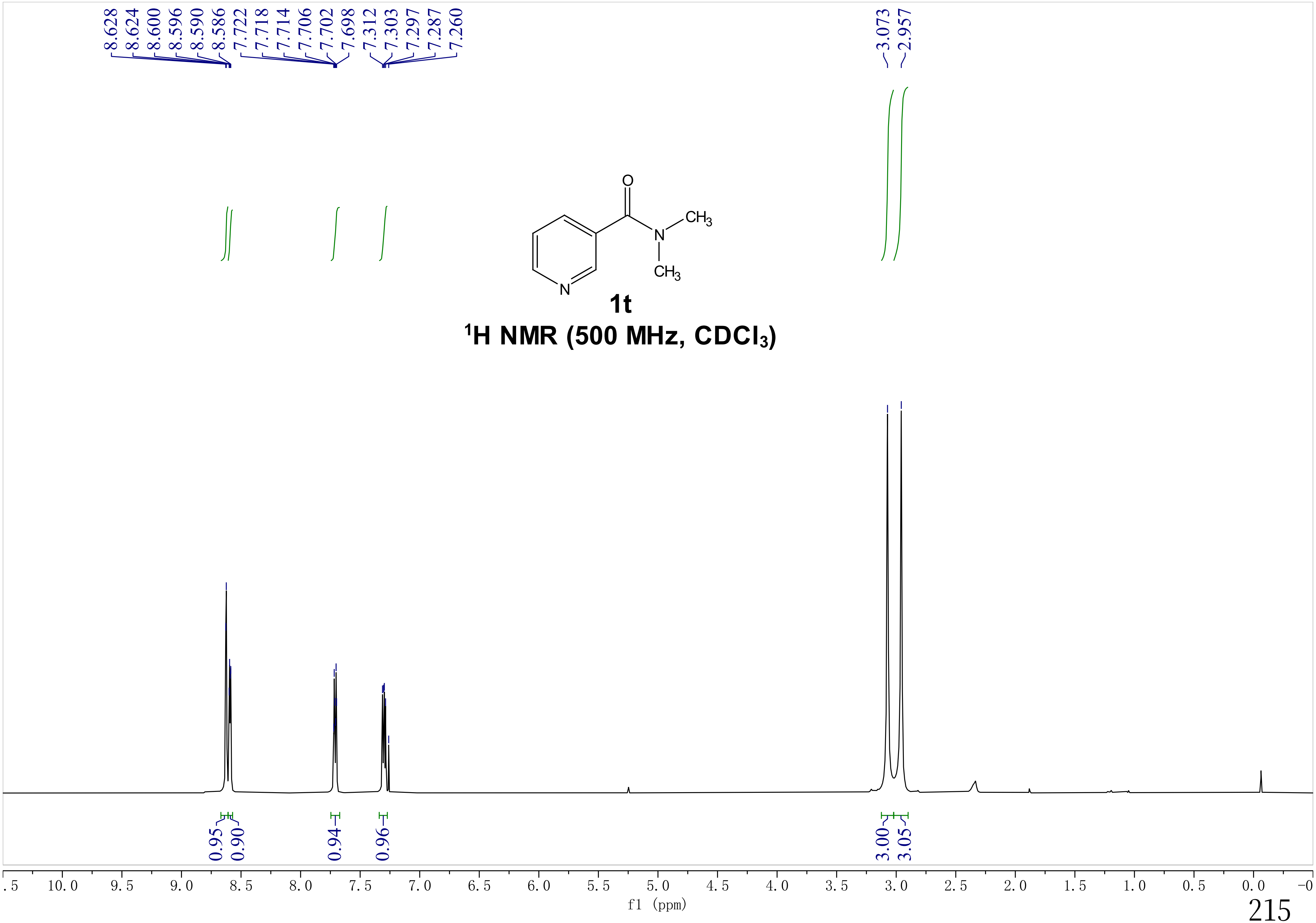
7.408
7.406
7.398
7.396
7.319
7.317
7.311
7.309
7.260
7.011
7.004
7.001
6.994
3.138
1s
¹H NMR (500 MHz, CDCl₃)
0.93
0.94
0.95
6.00
f1 (ppm)



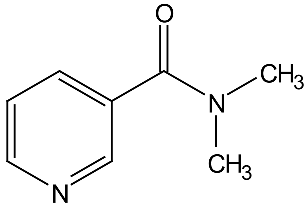
1s

^{13}C NMR (125 MHz, $CDCl_3$)



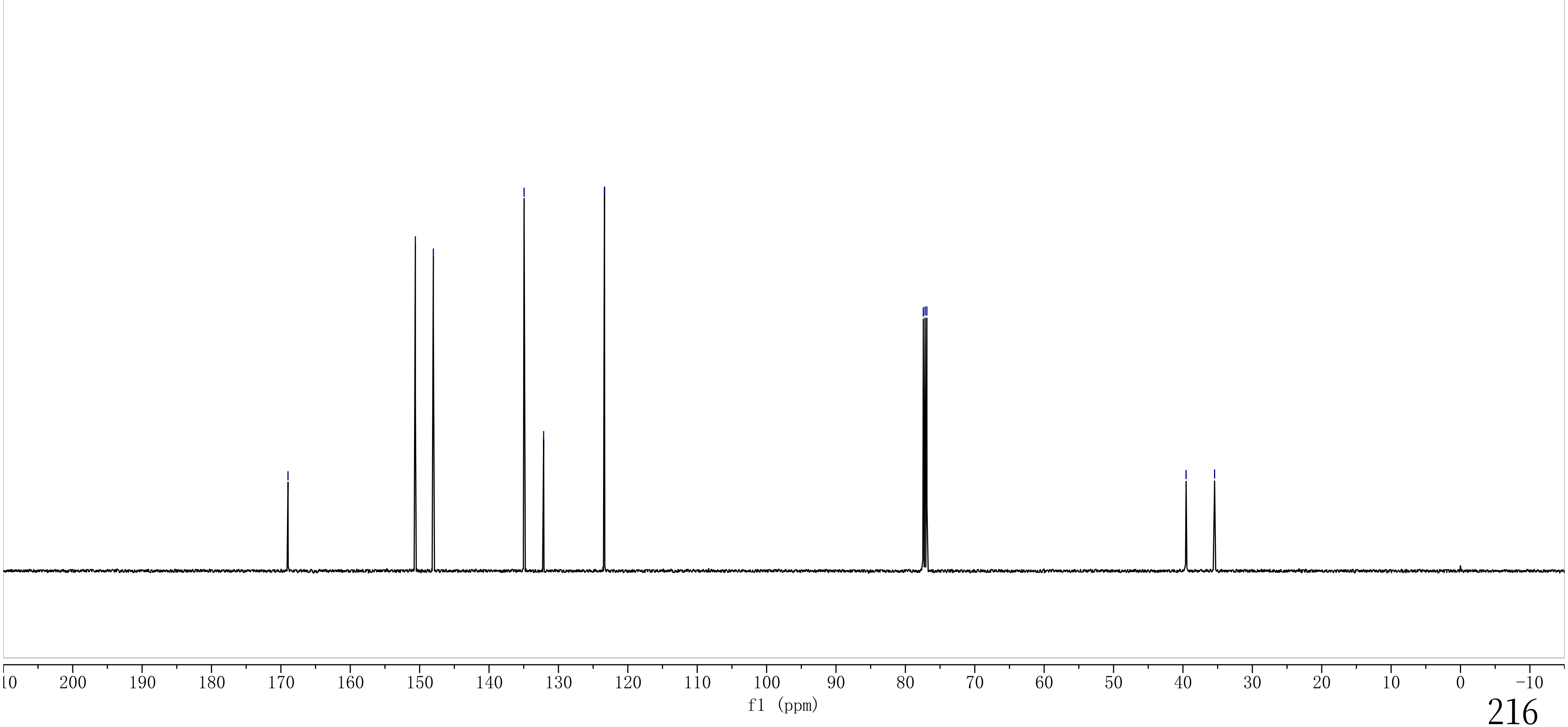


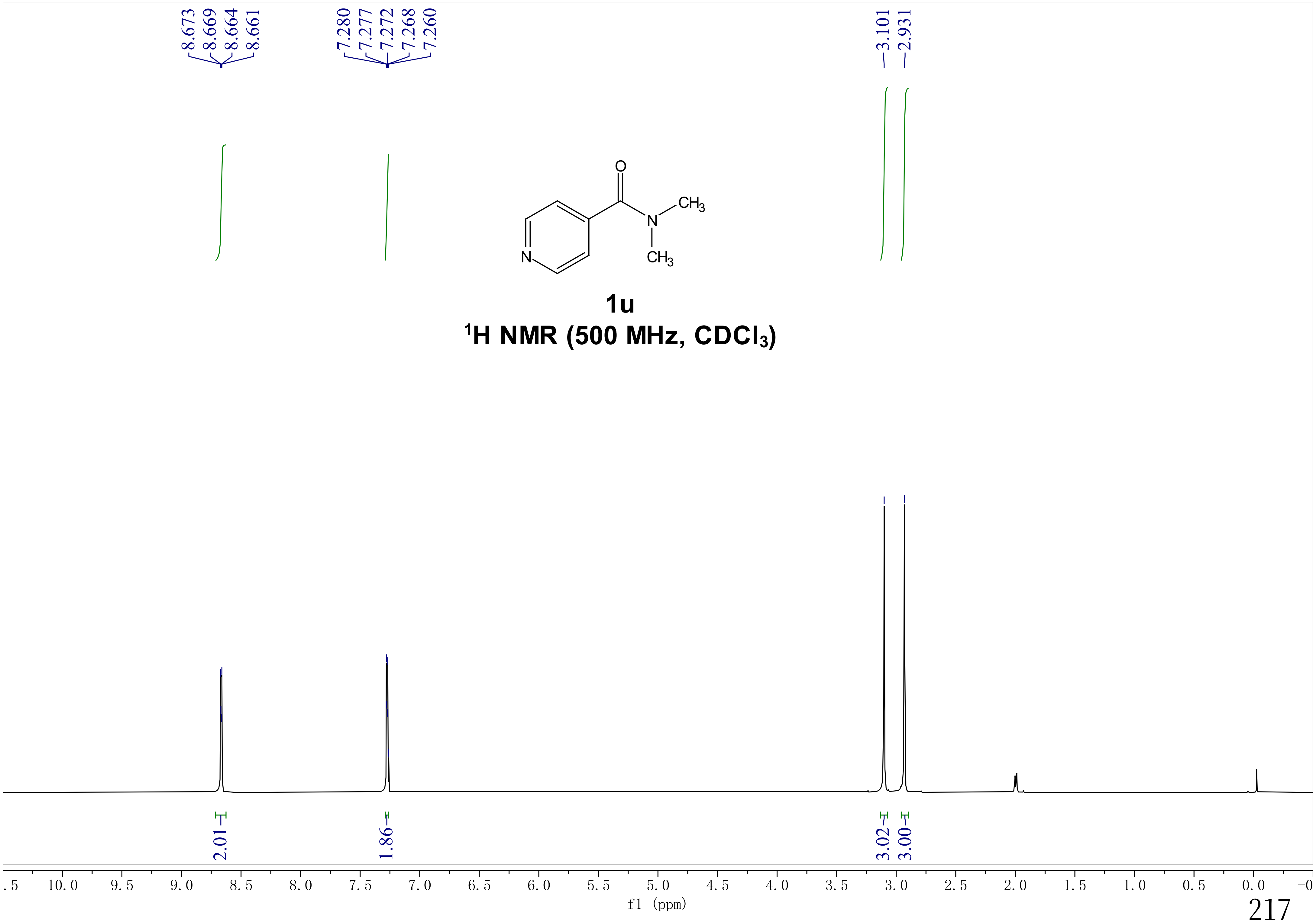
8.628
8.624
8.600
8.596
8.590
8.586
7.722
7.718
7.714
7.706
7.702
7.698
7.312
7.303
7.297
7.287
7.260
3.073
2.957
O
N
CH3
CH3
N
1t
¹H NMR (500 MHz, CDCl3)
0.95
0.90
0.94
0.96
3.00
3.05
f1 (ppm)



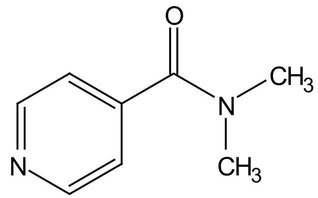
1t

^{13}C NMR (125 MHz, $CDCl_3$)



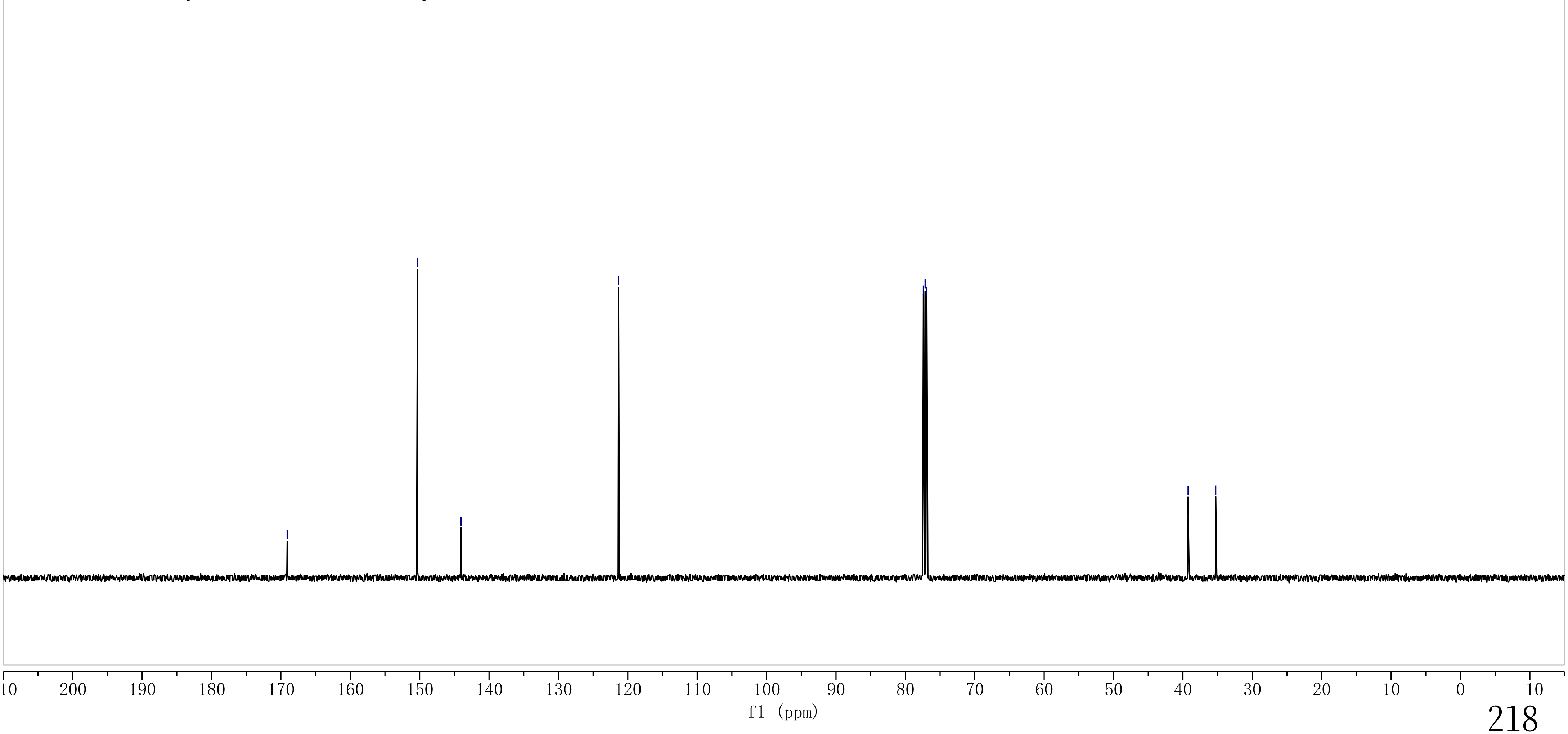


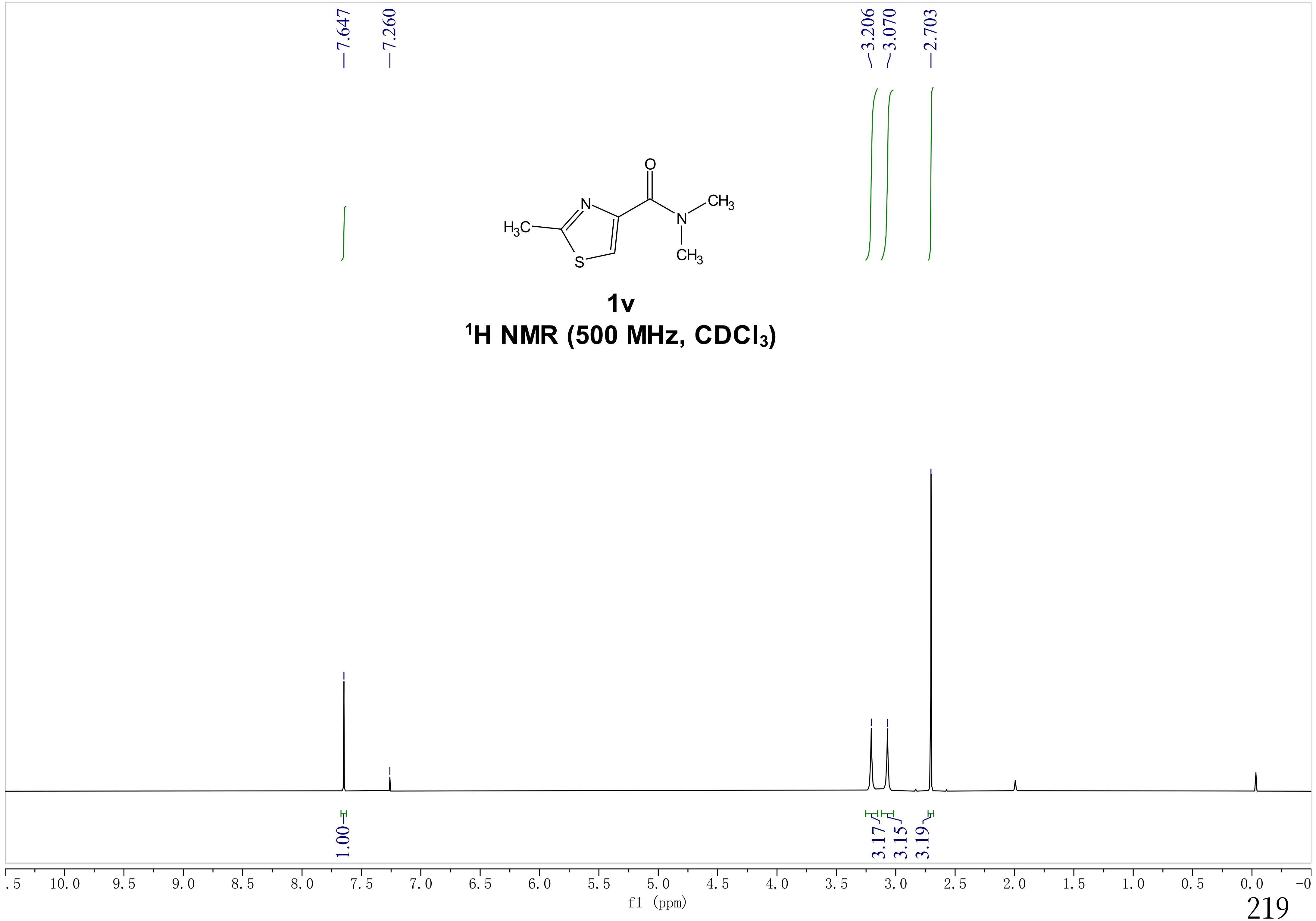
8.673
8.669
8.664
8.661
7.280
7.277
7.272
7.268
7.260
3.101
2.931
O
CH3
N
N
CH3
1u
¹H NMR (500 MHz, CDCl3)
2.01
1.86
3.02
3.00
f1 (ppm)

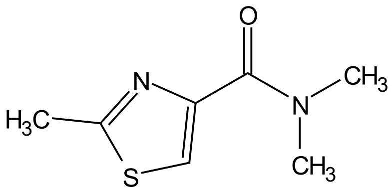


1u

^{13}C NMR (125 MHz, $CDCl_3$)

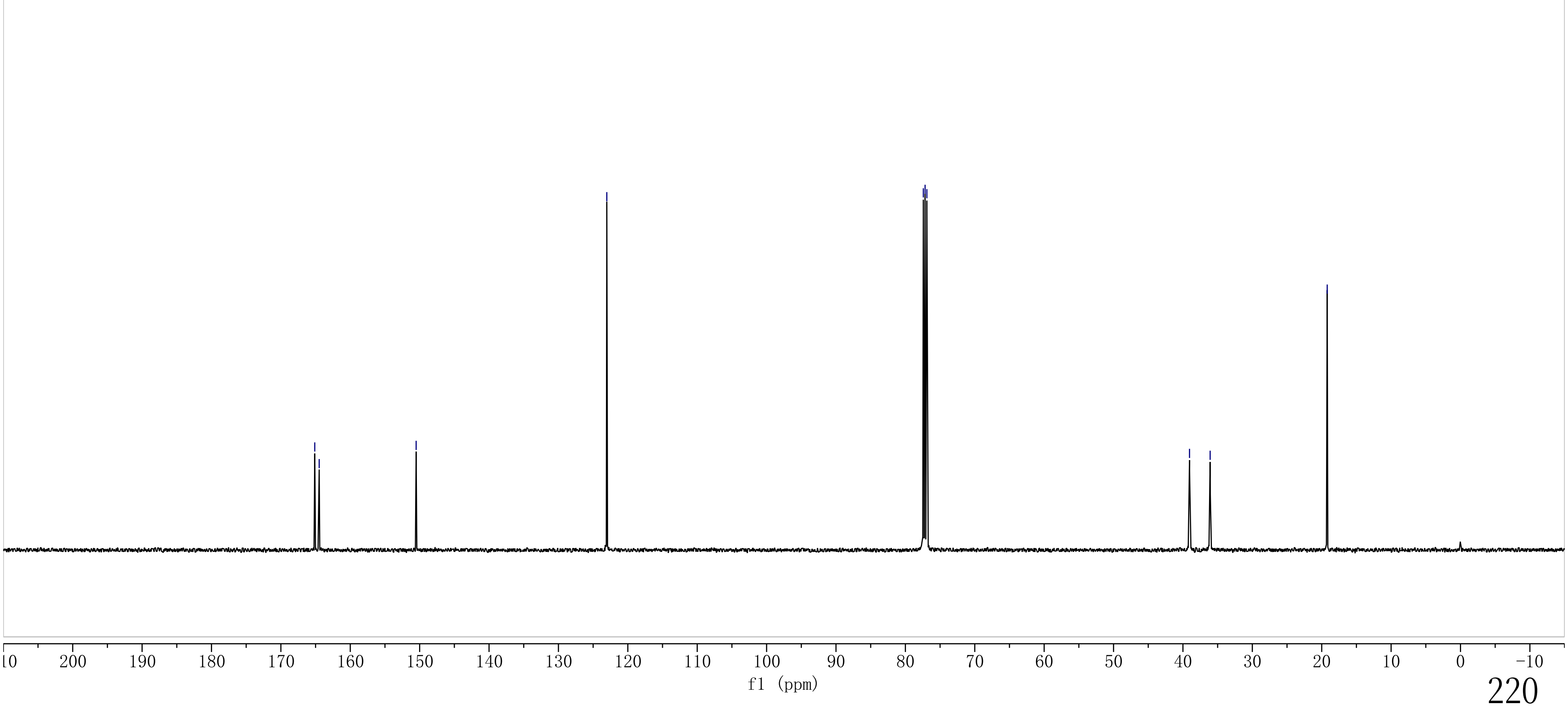


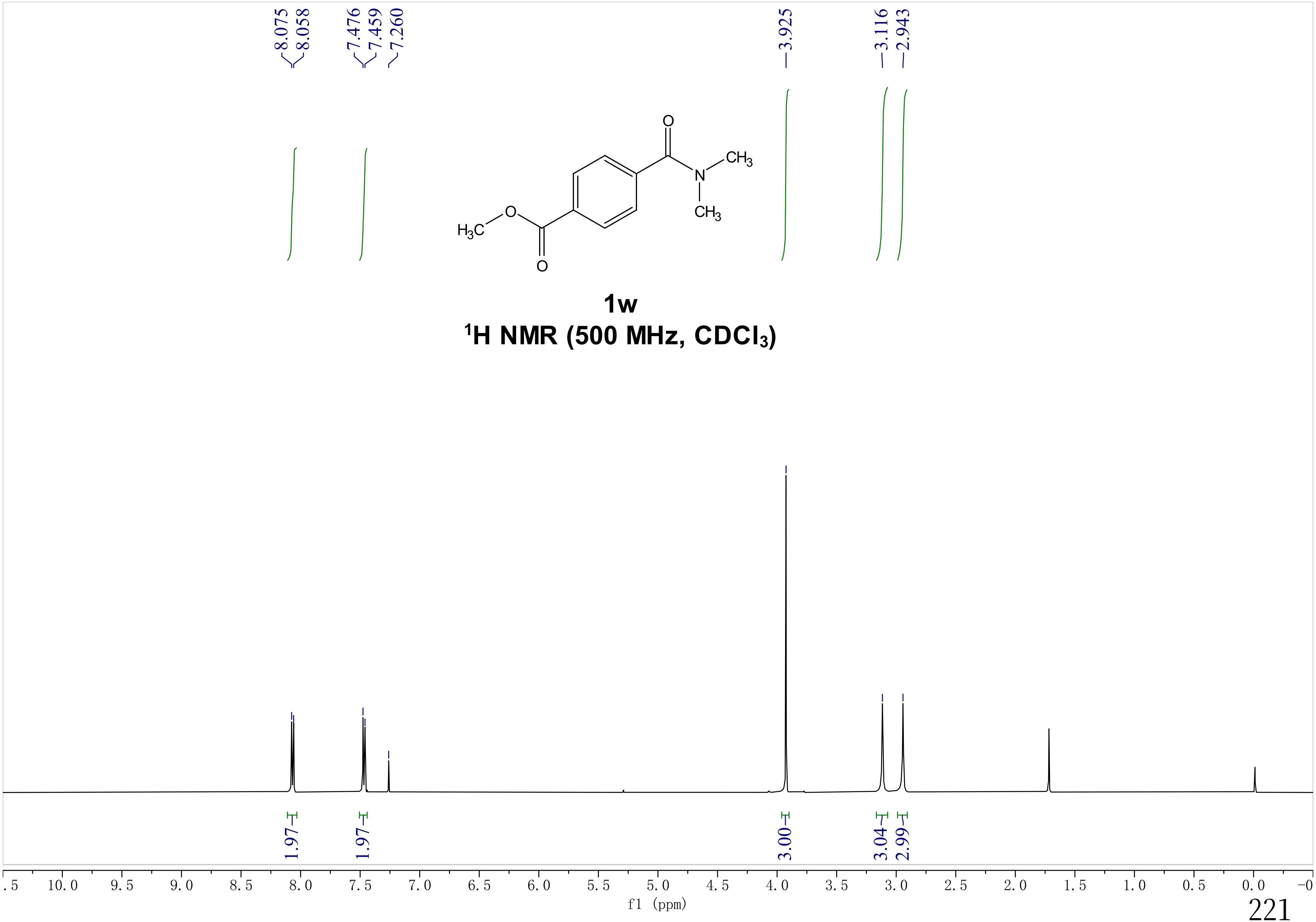

7.647
7.260
3.206
3.070
2.703
1v
1H NMR (500 MHz, CDCl3)
1.00
3.17
3.15
3.19
f1 (ppm)

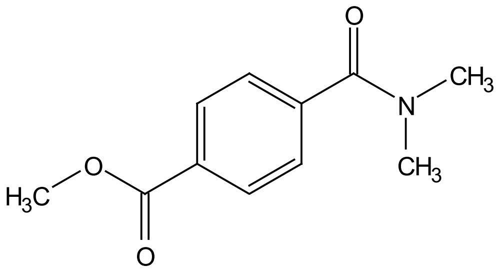


1v

^{13}C NMR (125 MHz, $CDCl_3$)

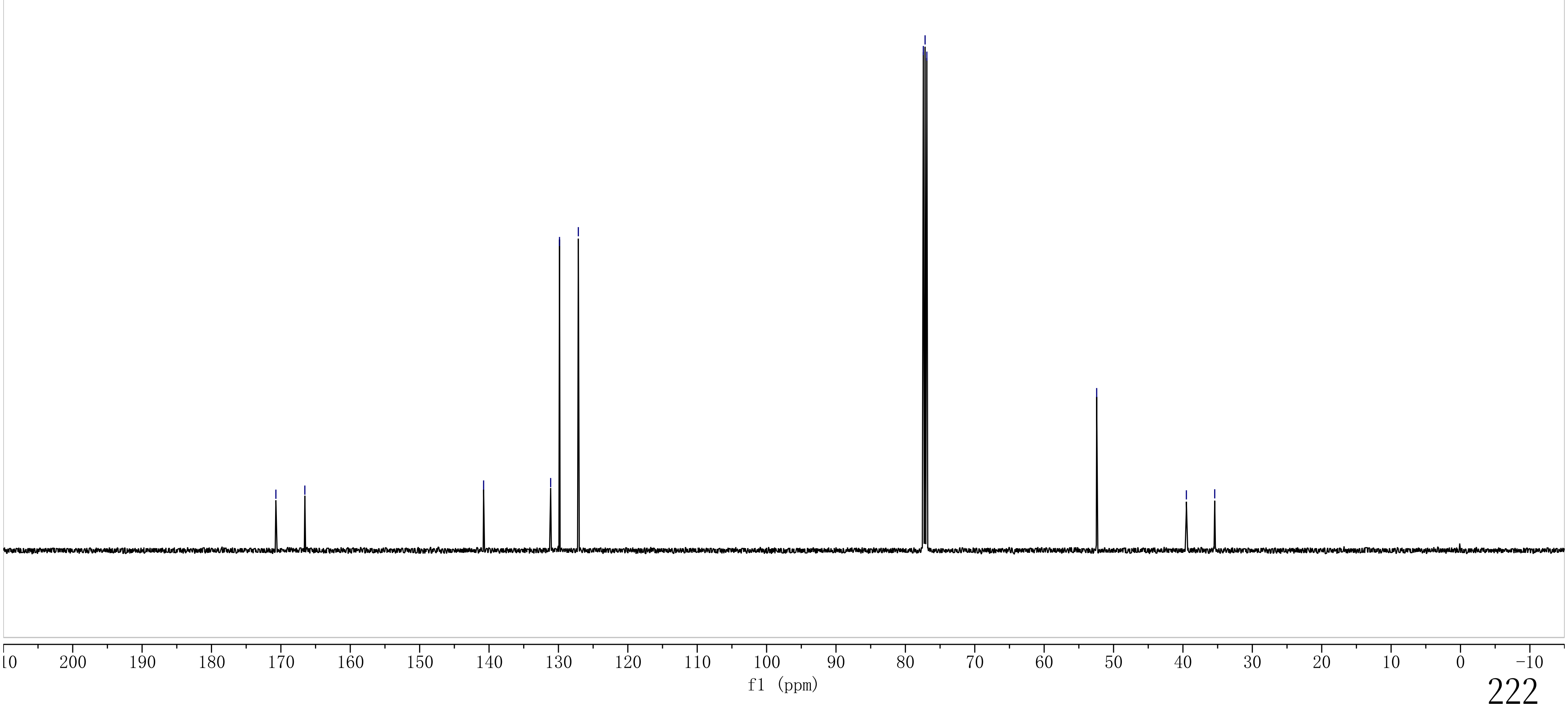


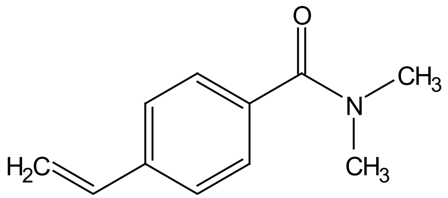

8.075
8.058
7.476
7.459
7.260
3.925
3.116
2.943
1w
¹H NMR (500 MHz, CDCl₃)
1.97
1.97
3.00
3.04
2.99
f1 (ppm)



1w

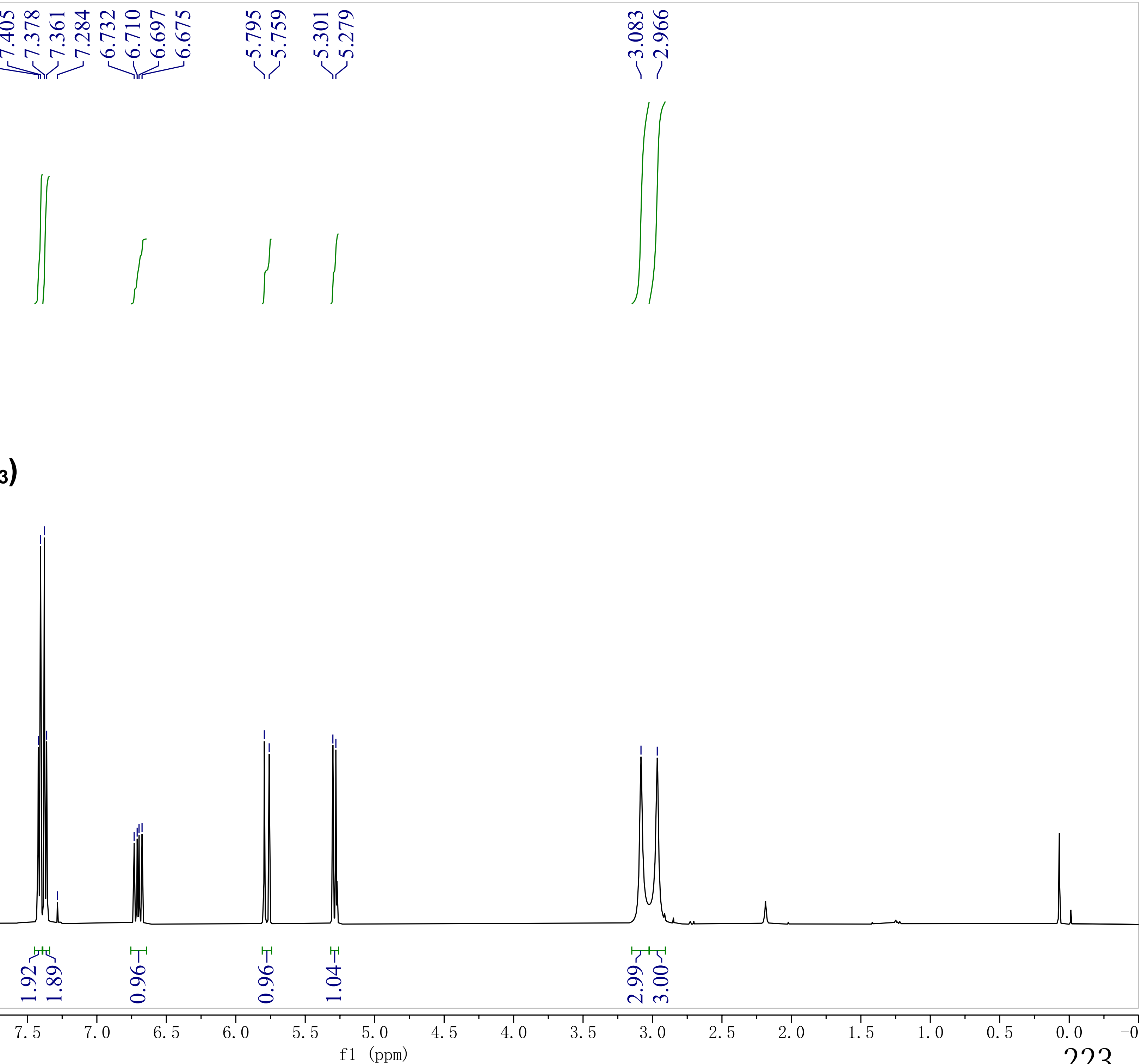
^{13}C NMR (125 MHz, $CDCl_3$)

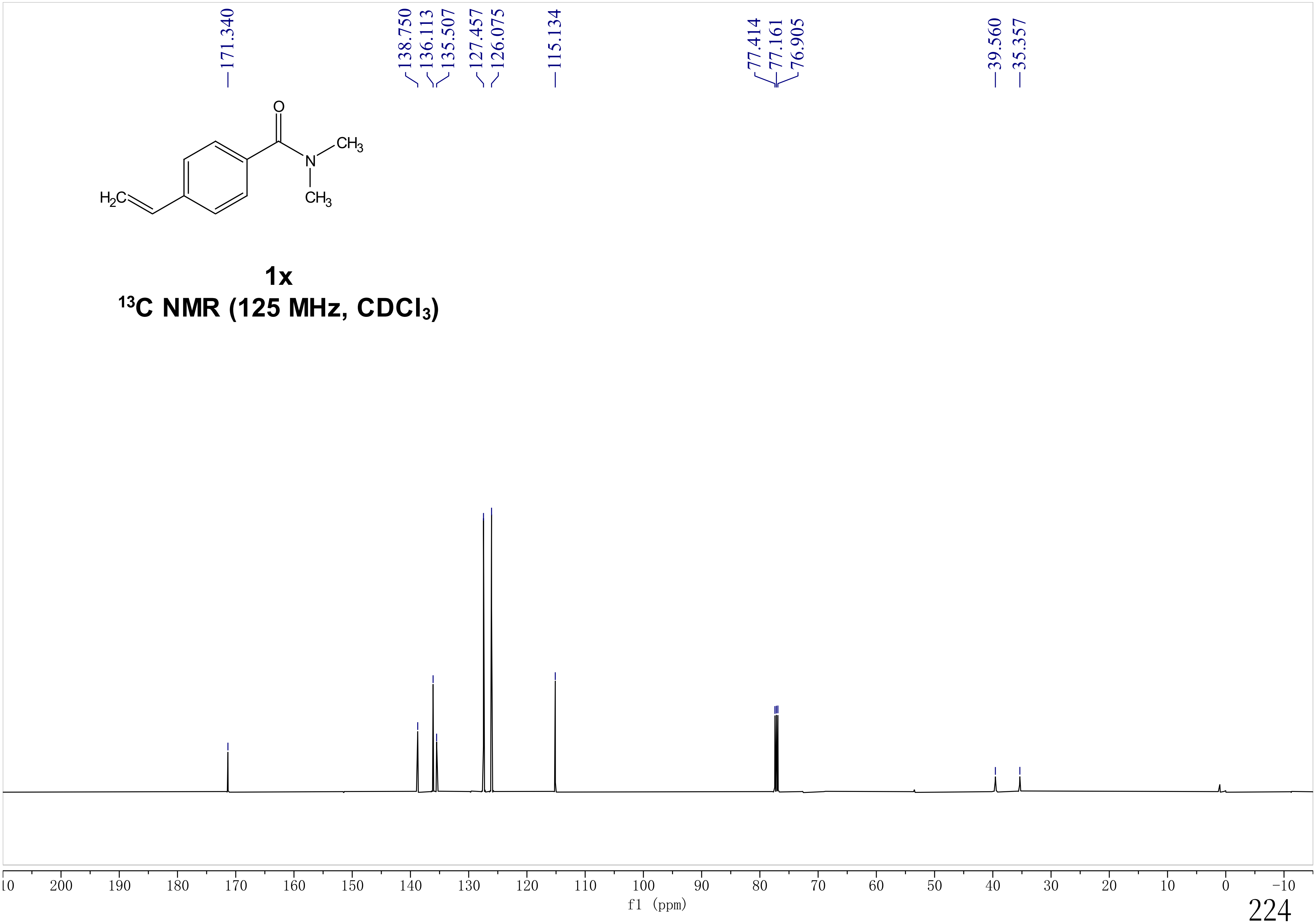




1x

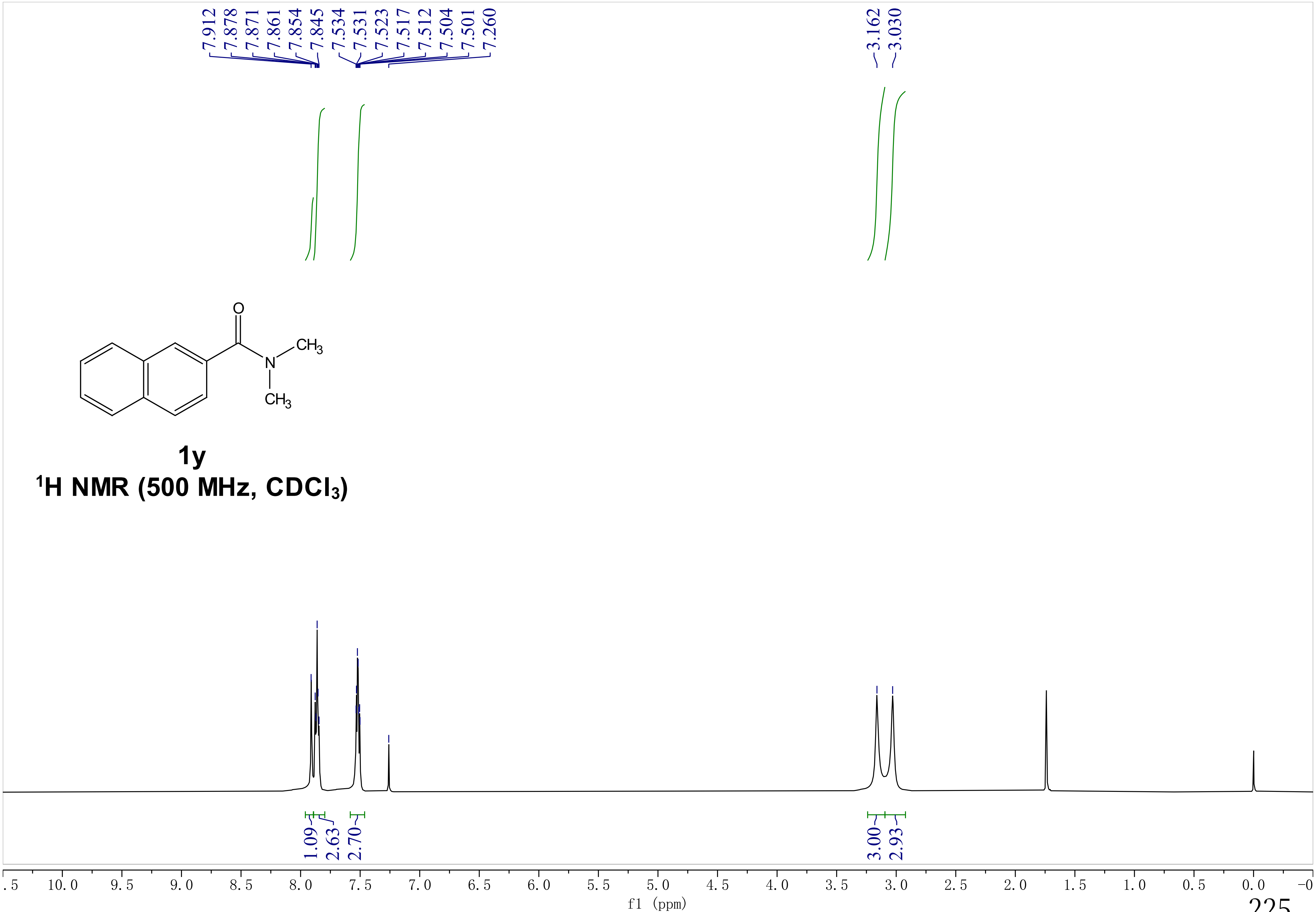
^{1}H NMR (500 MHz, $CDCl_3$)

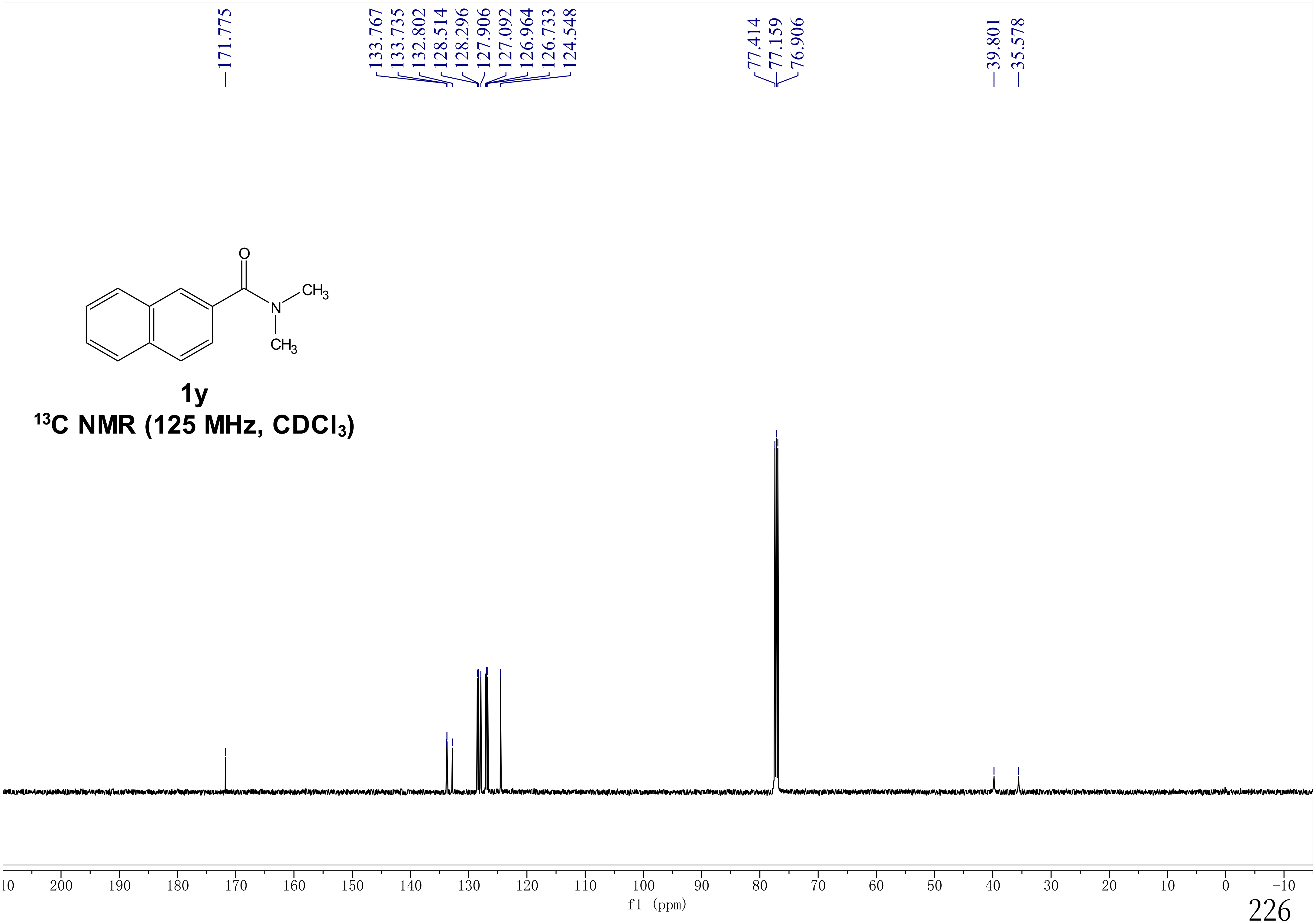


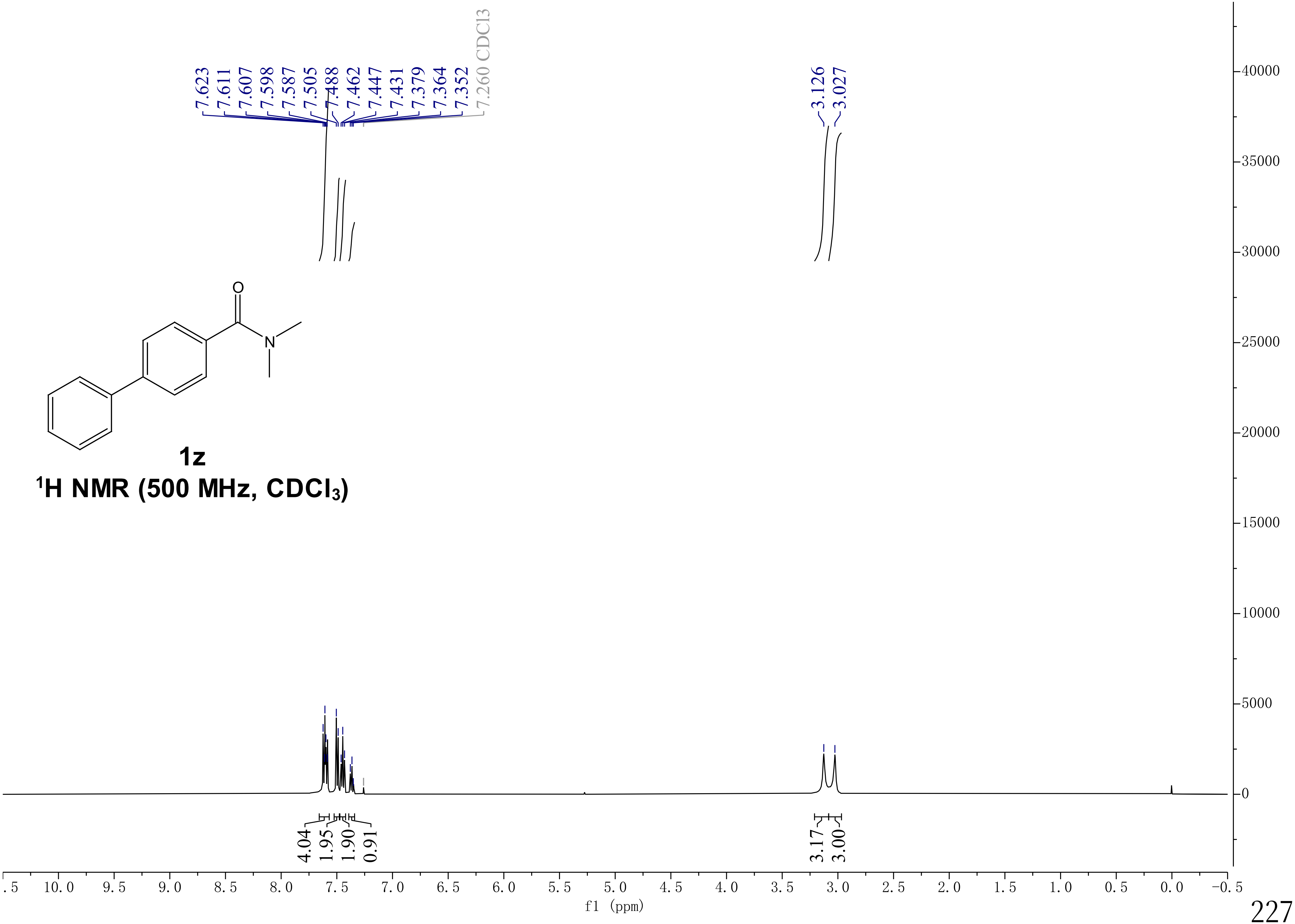


1x

^{13}C NMR (125 MHz, CDCl$_3$)

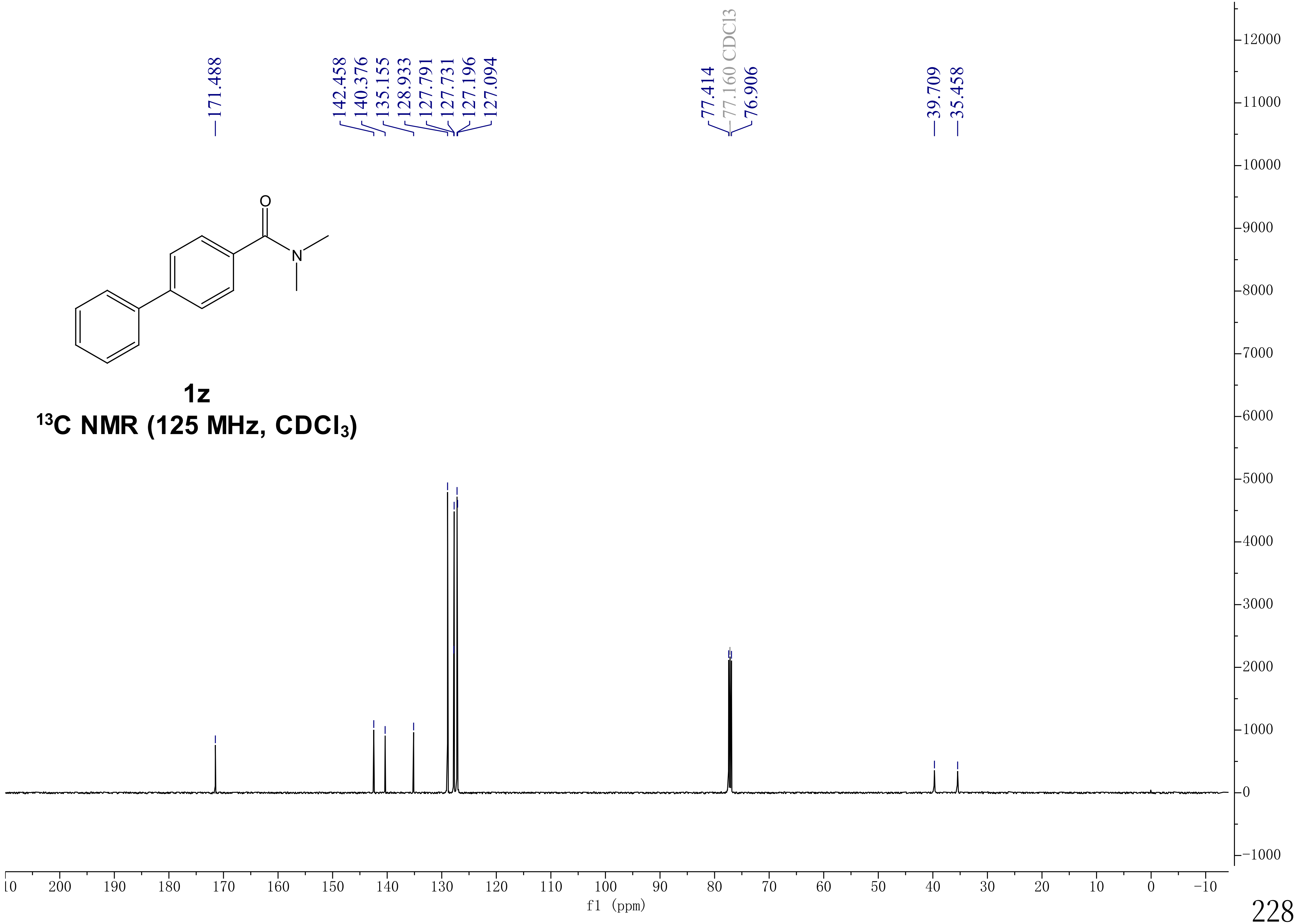

7.912
7.878
7.871
7.861
7.854
7.845
7.534
7.531
7.523
7.517
7.512
7.504
7.501
7.260
3.162
3.030
O
CH3
N
CH3
1y
1H NMR (500 MHz, CDCl3)
1.09
2.63
2.70
3.00
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

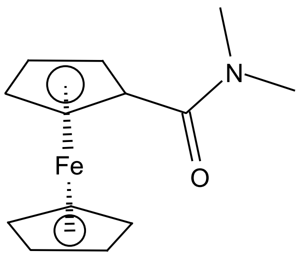

171.775
133.767
133.735
132.802
128.514
128.296
127.906
127.092
126.964
126.733
124.548
77.414
77.159
76.906
39.801
35.578
O
N
CH3
CH3
1y
13C NMR (125 MHz, CDCl3)
f1 (ppm)


1z
^{1}H NMR (500 MHz, $CDCl_3$)
7.623
7.611
7.607
7.598
7.587
7.505
7.488
7.462
7.447
7.431
7.379
7.364
7.352
7.260 CDCl3
3.126
3.027
4.04
1.95
1.90
0.91
3.17
3.00
f1 (ppm)

1z

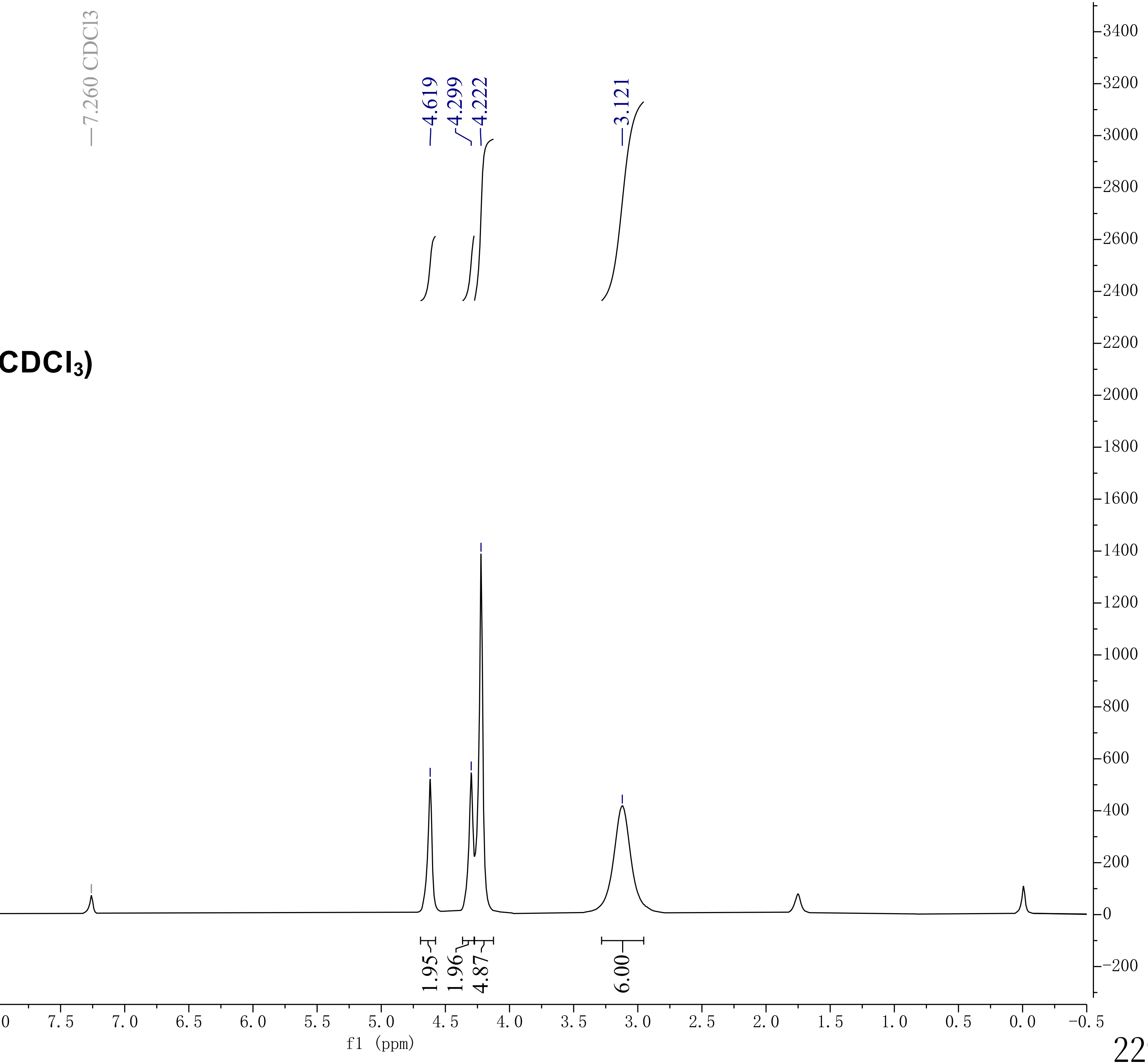
^{13}C NMR (125 MHz, $CDCl_3$)

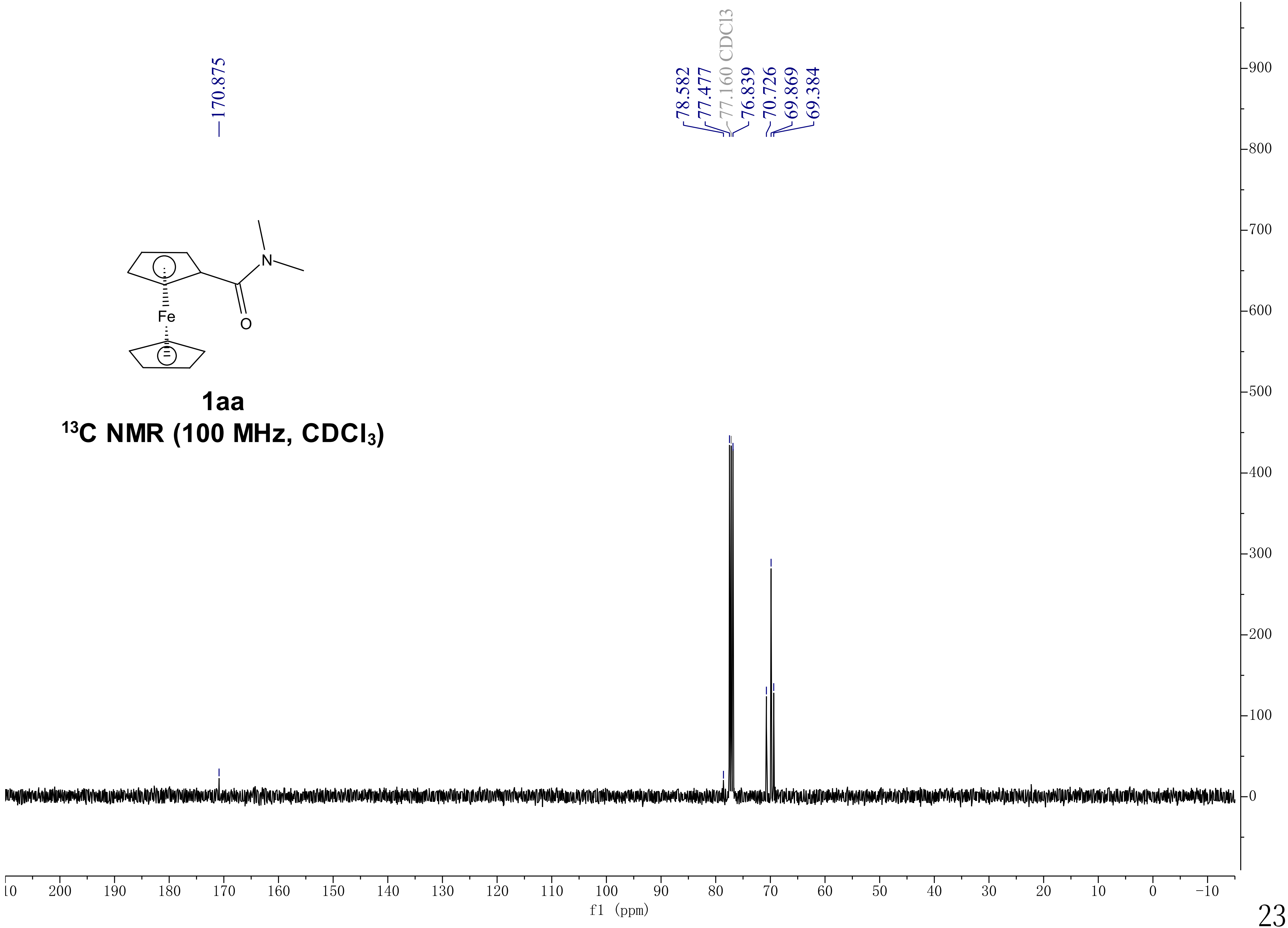


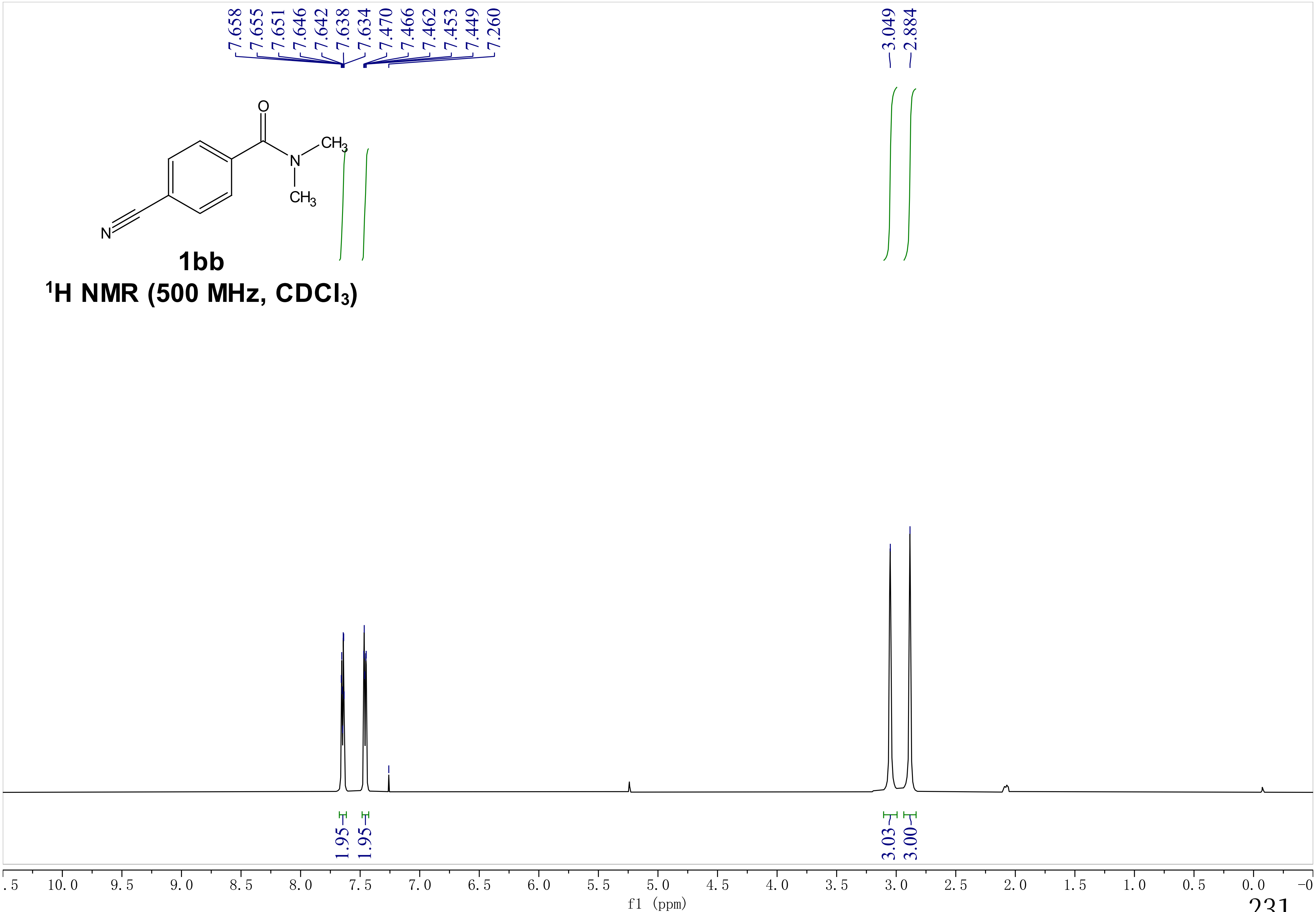


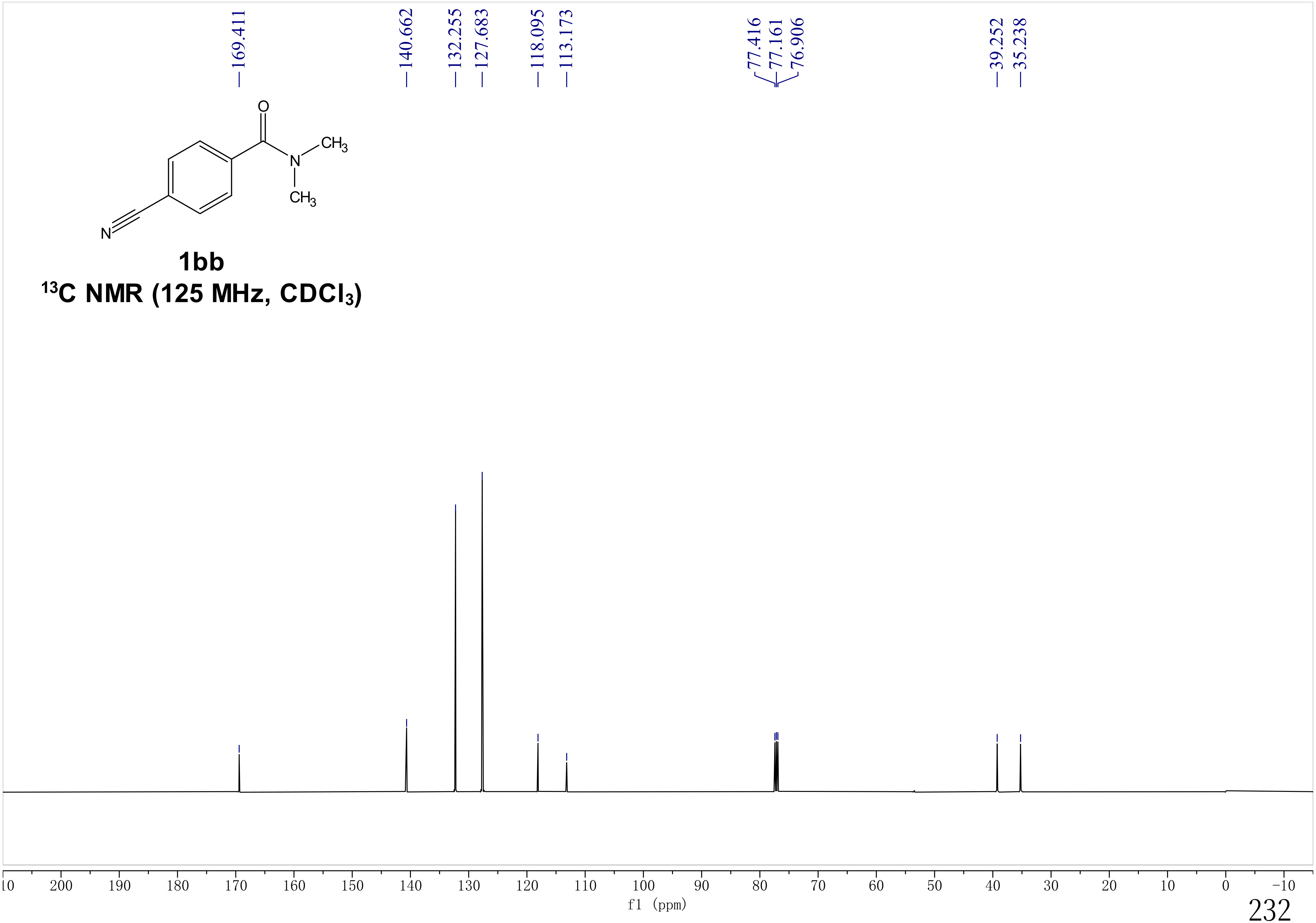
1aa

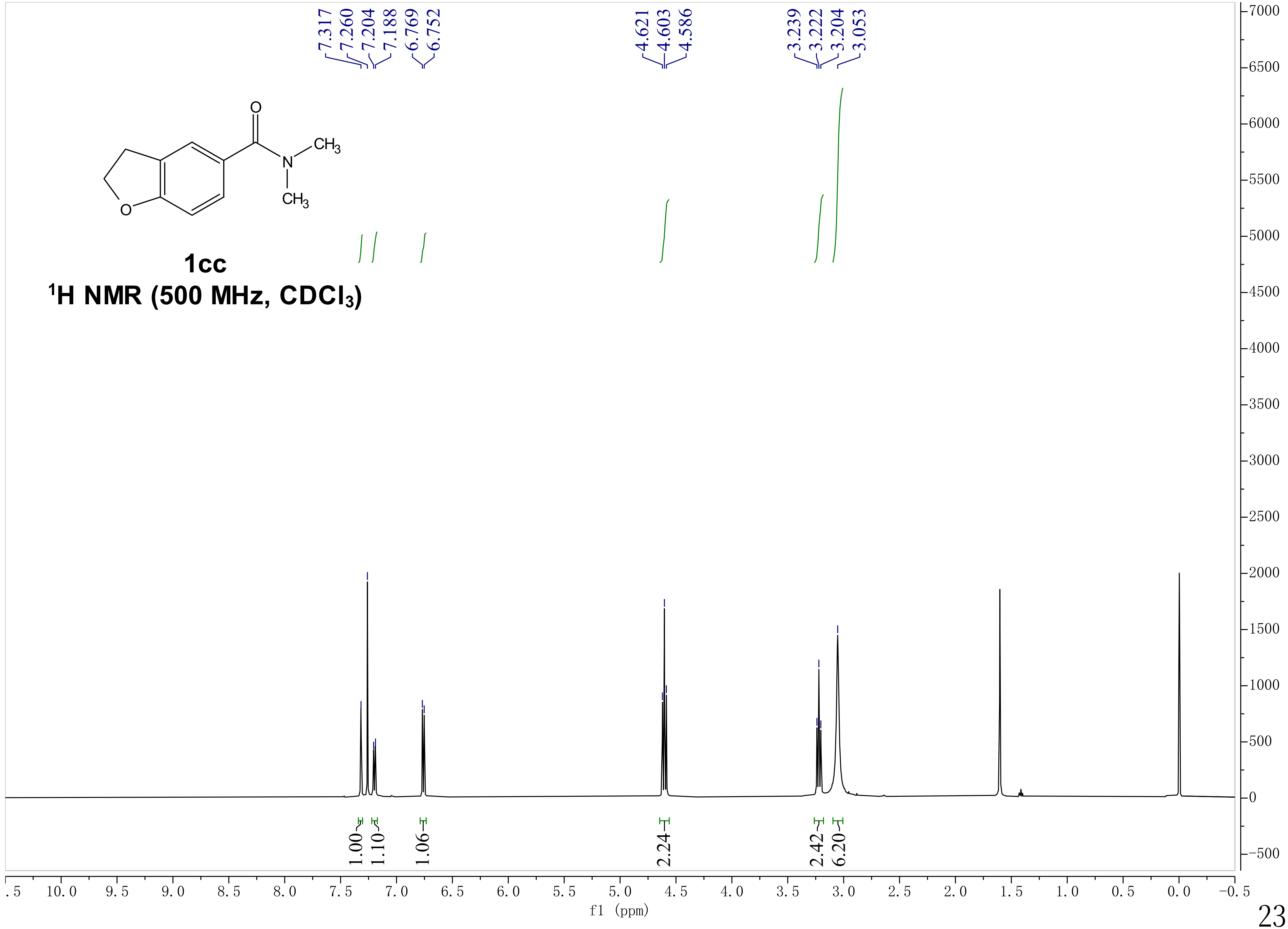
^{1}H NMR (400 MHz, $CDCl_3$)

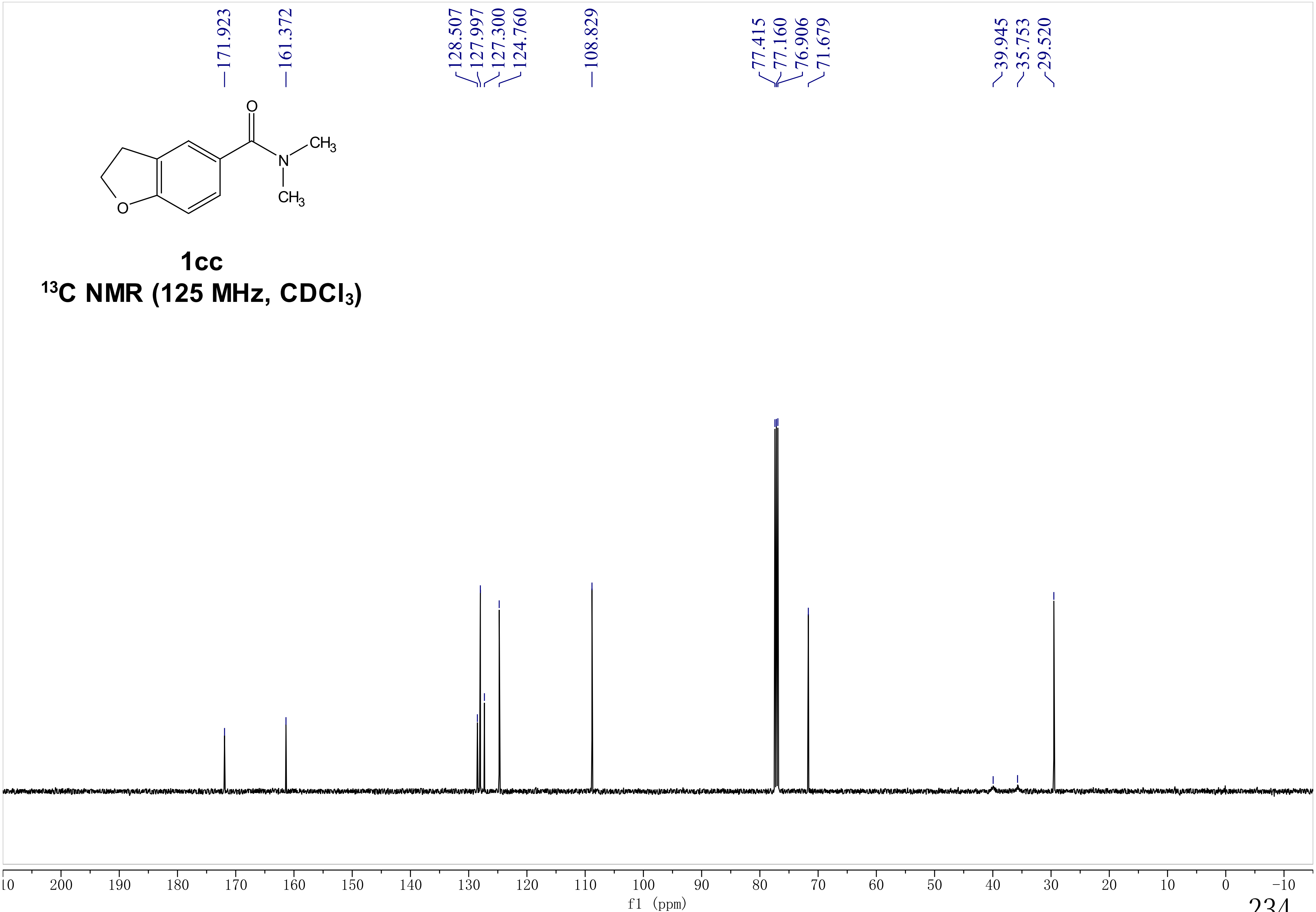



170.875
78.582
77.477
77.160 CDCl3
76.839
70.726
69.869
69.384
Fe
N
O
1aa
13C NMR (100 MHz, CDCl3)
900
800
700
600
500
400
300
200
100
0
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

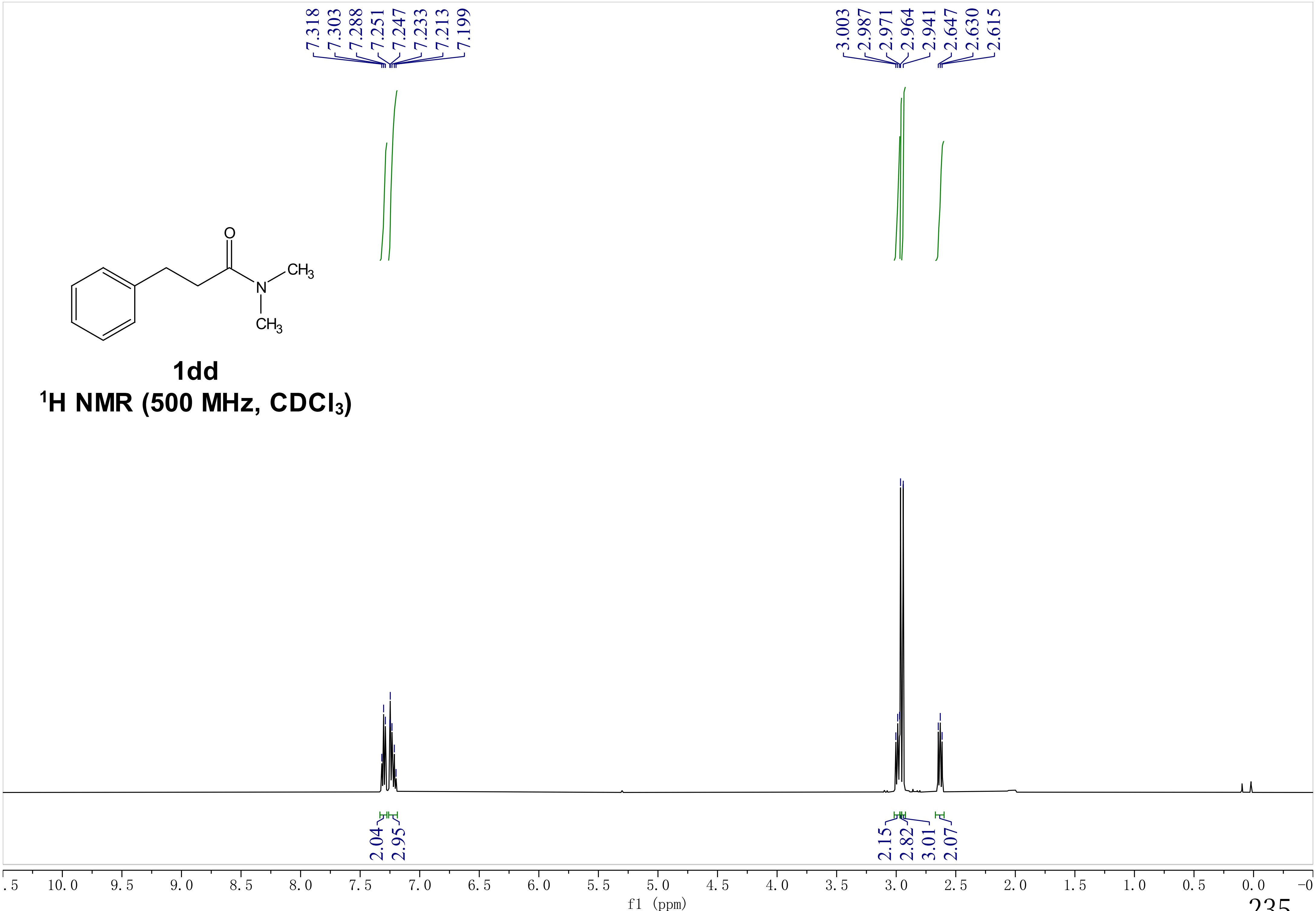

7.658
7.655
7.651
7.646
7.642
7.638
7.634
7.470
7.466
7.462
7.453
7.449
7.260
3.049
2.884
1bb
1H NMR (500 MHz, CDCl3)
1.95
1.95
3.03
3.00
f1 (ppm)

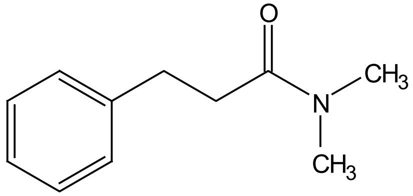

169.411
140.662
132.255
127.683
118.095
113.173
77.416
77.161
76.906
39.252
35.238
O
CH3
N
CH3
N
1bb
13C NMR (125 MHz, CDCl3)
f1 (ppm)


7.317
7.260
7.204
7.188
6.769
6.752
4.621
4.603
4.586
3.239
3.222
3.204
3.053
O
N
CH3
CH3
O
1cc
1H NMR (500 MHz, CDCl3)
1.00
1.10
1.06
2.24
2.42
6.20
f1 (ppm)



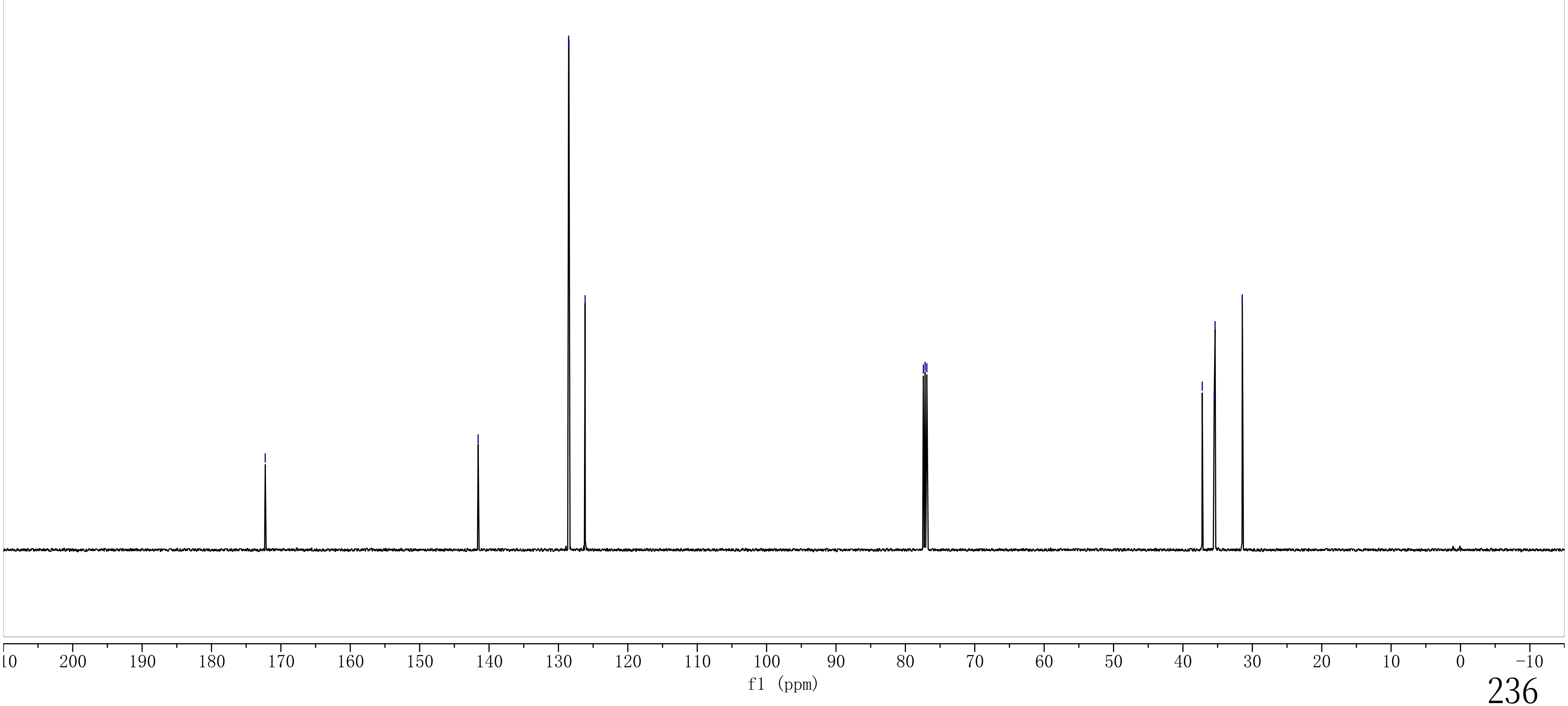
171.923
161.372
128.507
127.997
127.300
124.760
108.829
77.415
77.160
76.906
71.679
39.945
35.753
29.520
O
CH3
N
CH3
O
1cc
13C NMR (125 MHz, CDCl3)
f1 (ppm)

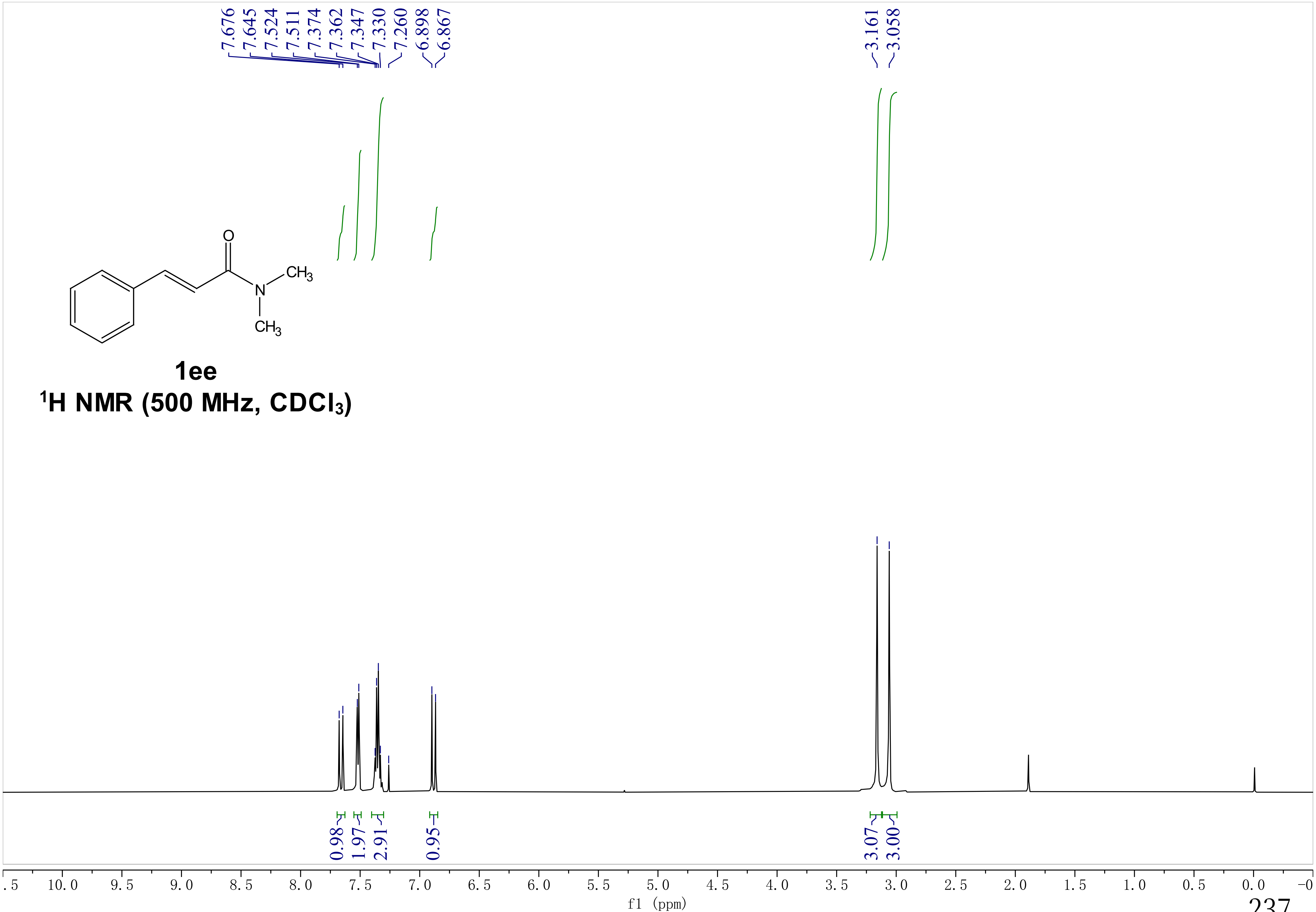

7.318
7.303
7.288
7.251
7.247
7.233
7.213
7.199
3.003
2.987
2.971
2.964
2.941
2.647
2.630
2.615
O
N
CH3
CH3
1dd
1H NMR (500 MHz, CDCl3)
2.04
2.95
2.15
2.82
3.01
2.07
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



1dd

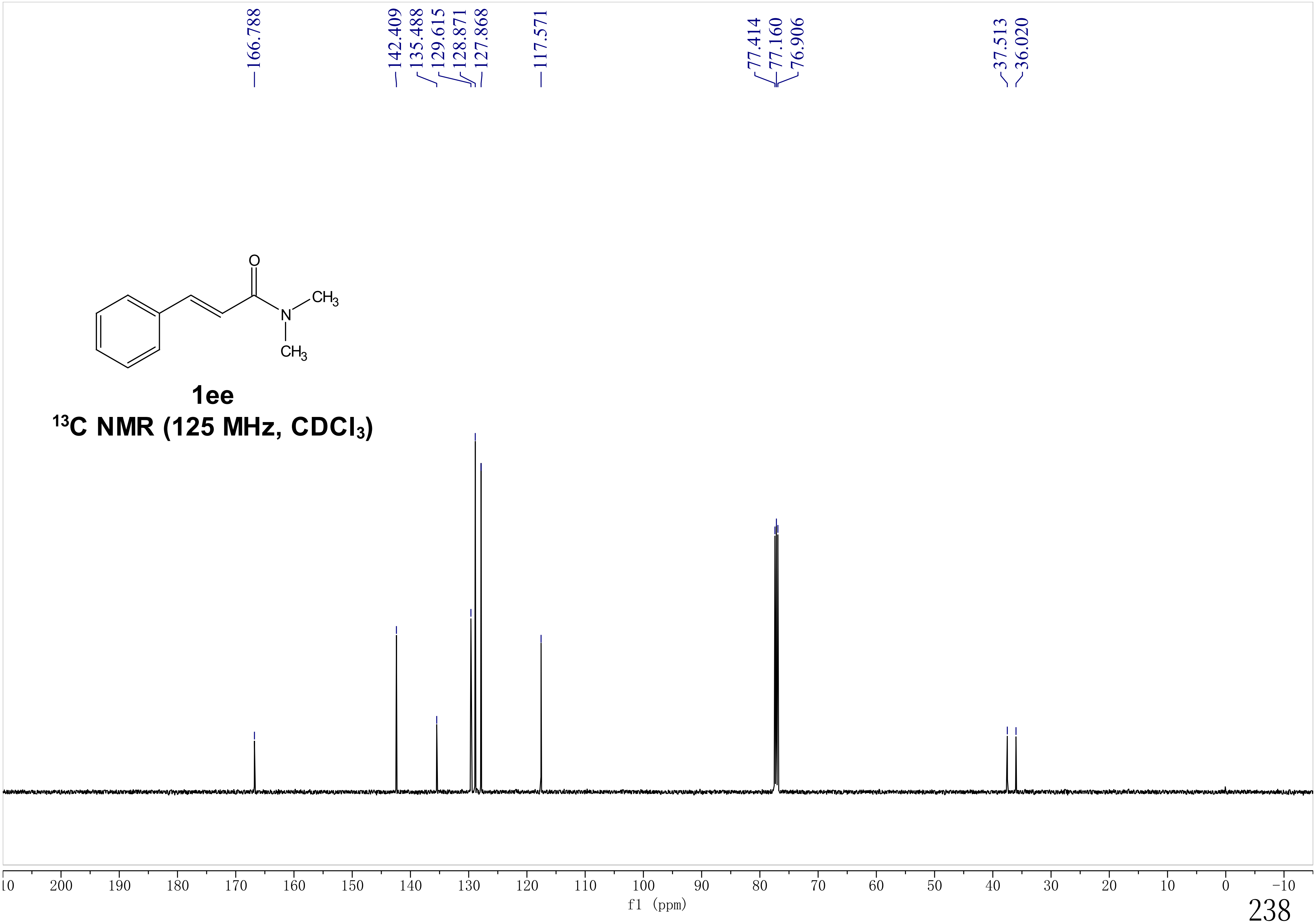
^{13}C NMR (125 MHz, $CDCl_3$)

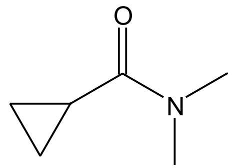




1ee

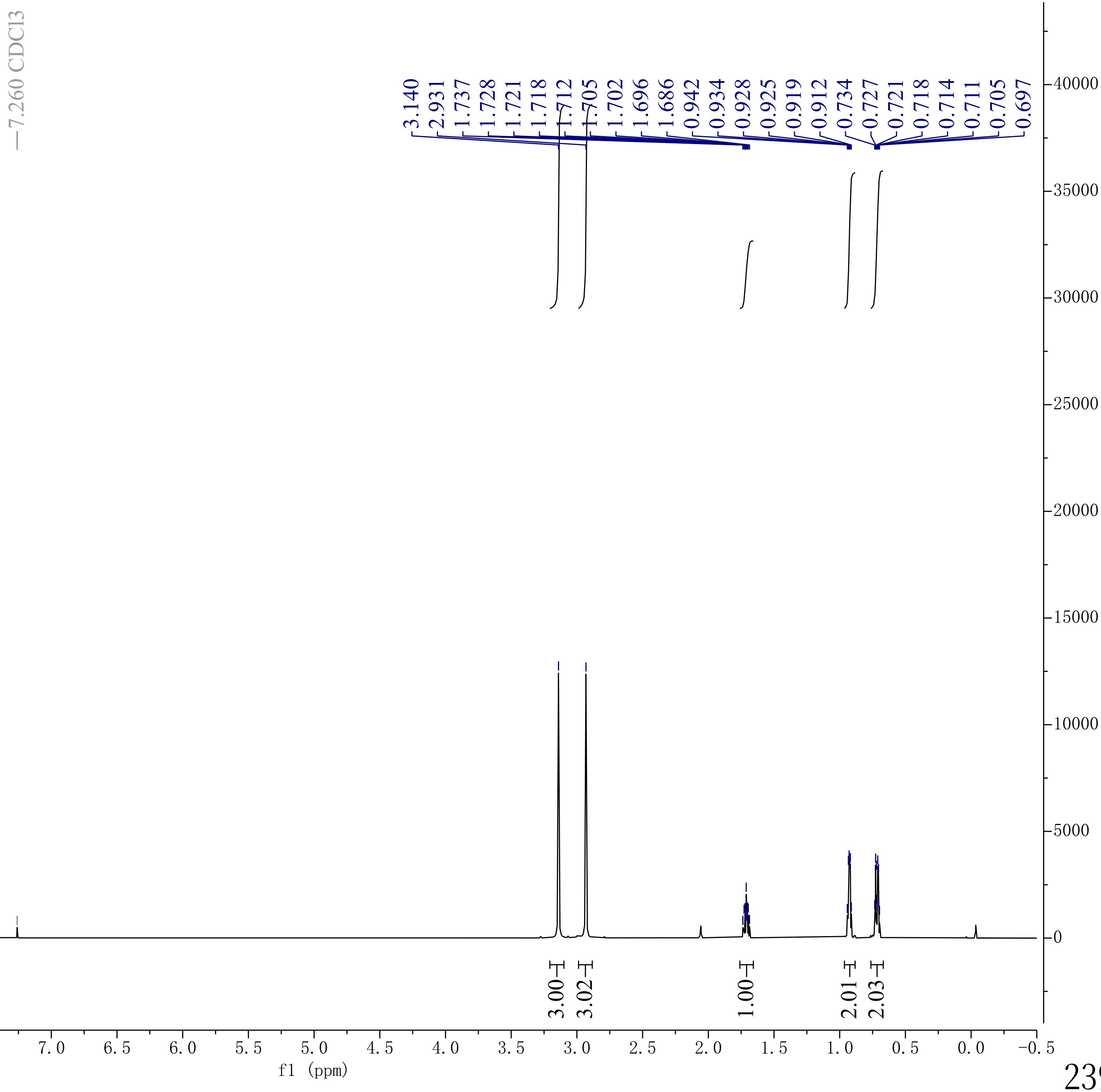
^{1}H NMR (500 MHz, $CDCl_3$)

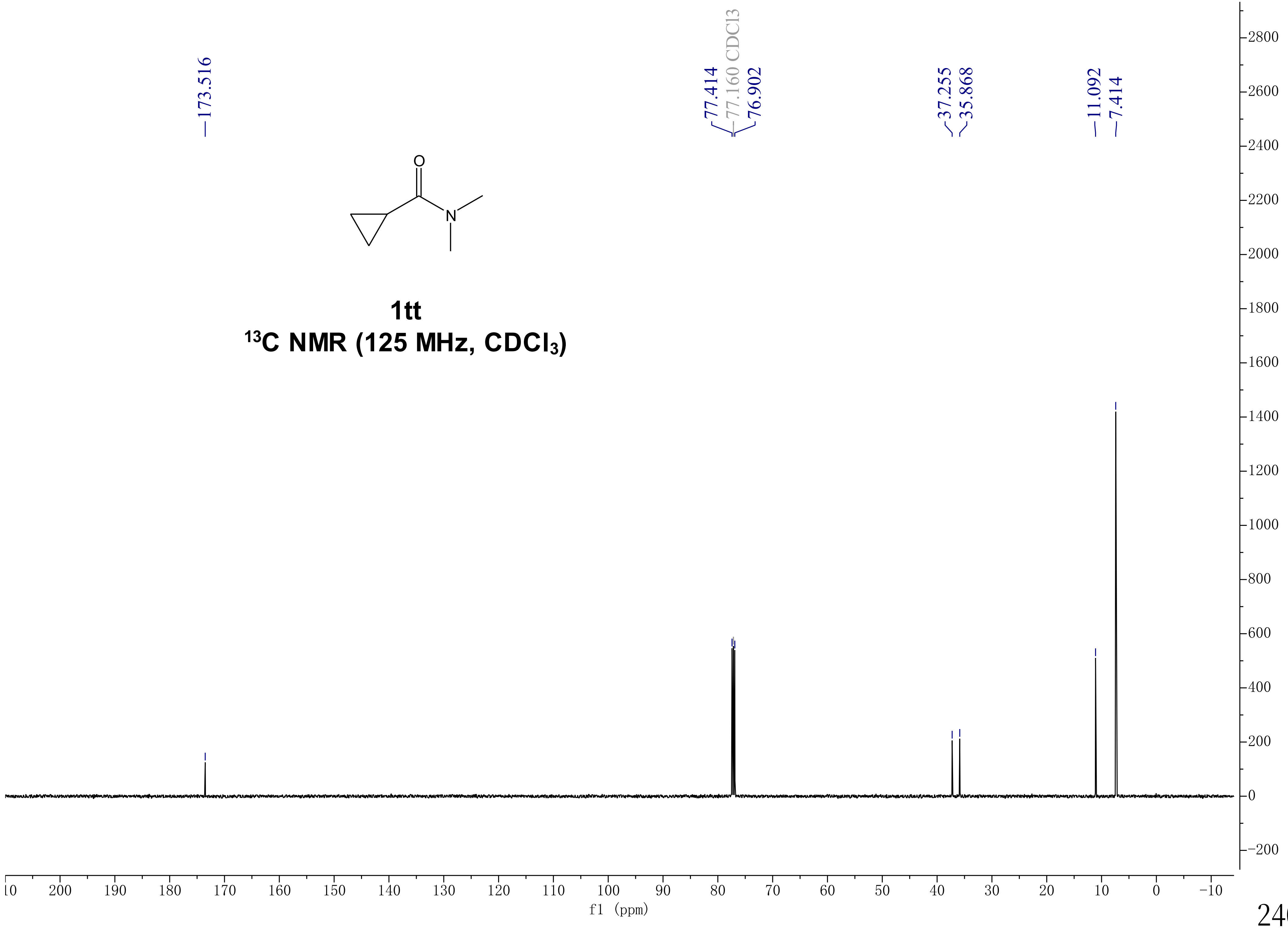

166.788
142.409
135.488
129.615
128.871
127.868
117.571
77.414
77.160
76.906
37.513
36.020
O
CH3
N
CH3
1ee
13C NMR (125 MHz, CDCl3)
f1 (ppm)



1tt

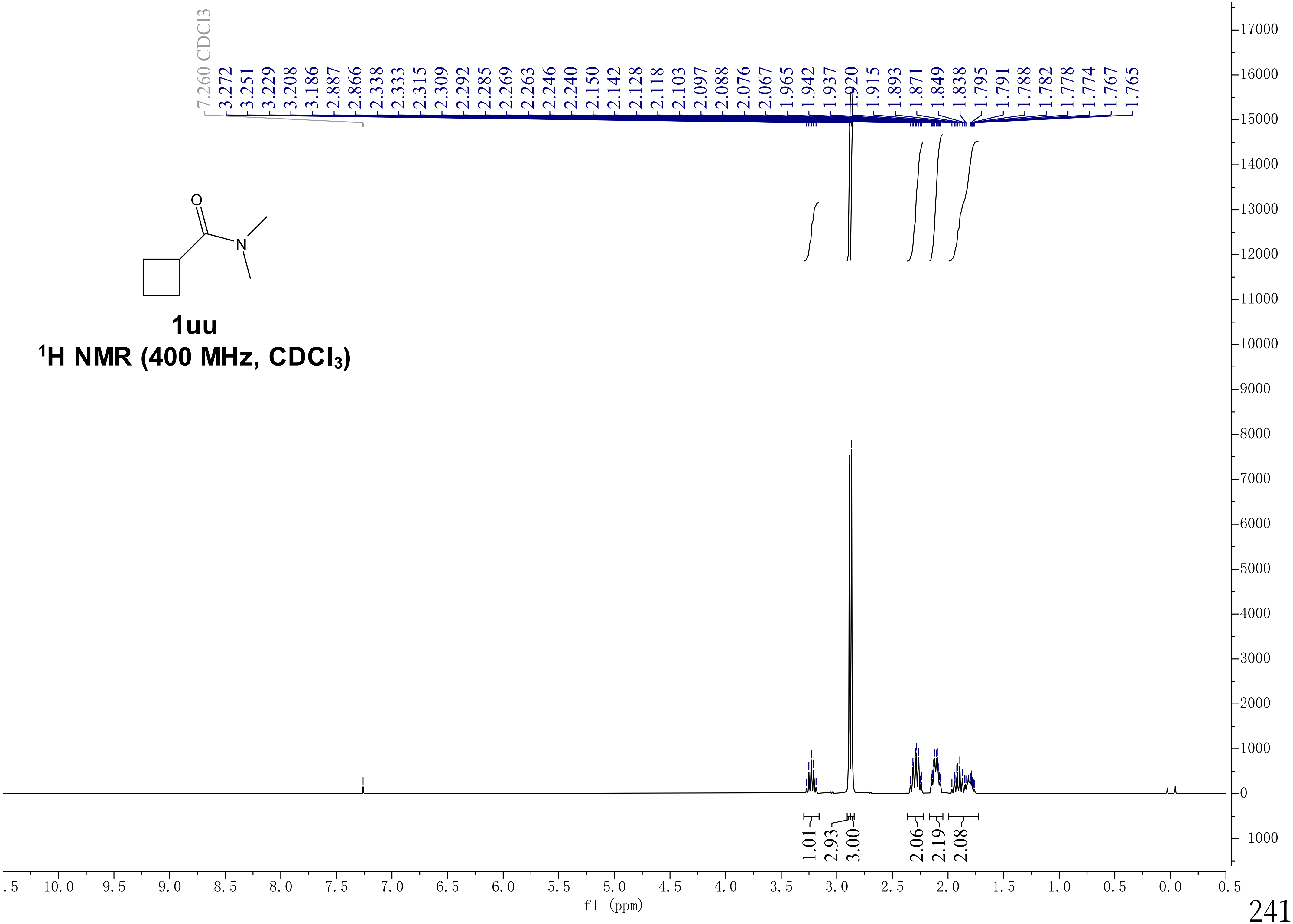
^{1}H NMR (500 MHz, $CDCl_3$)





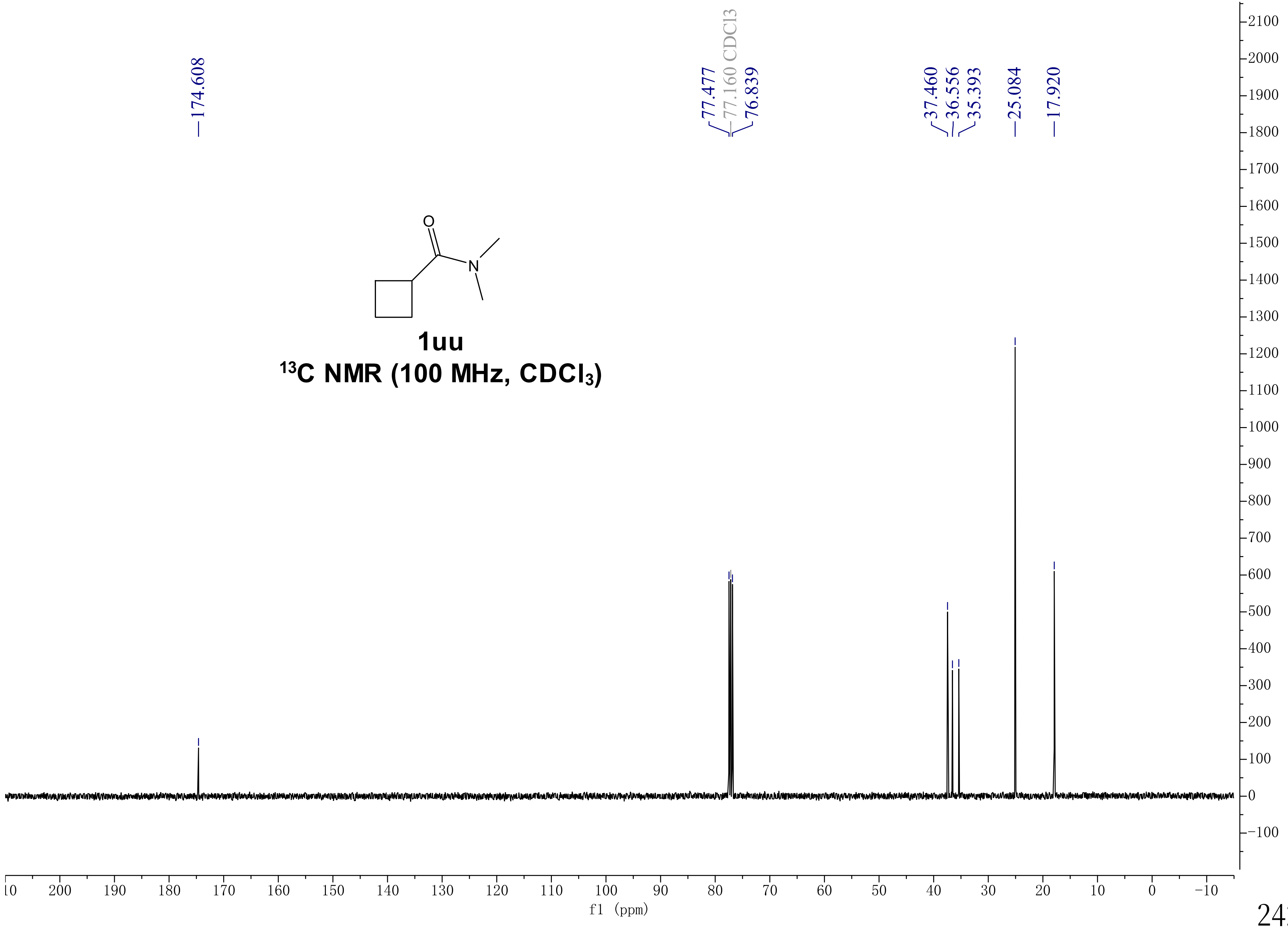
1tt

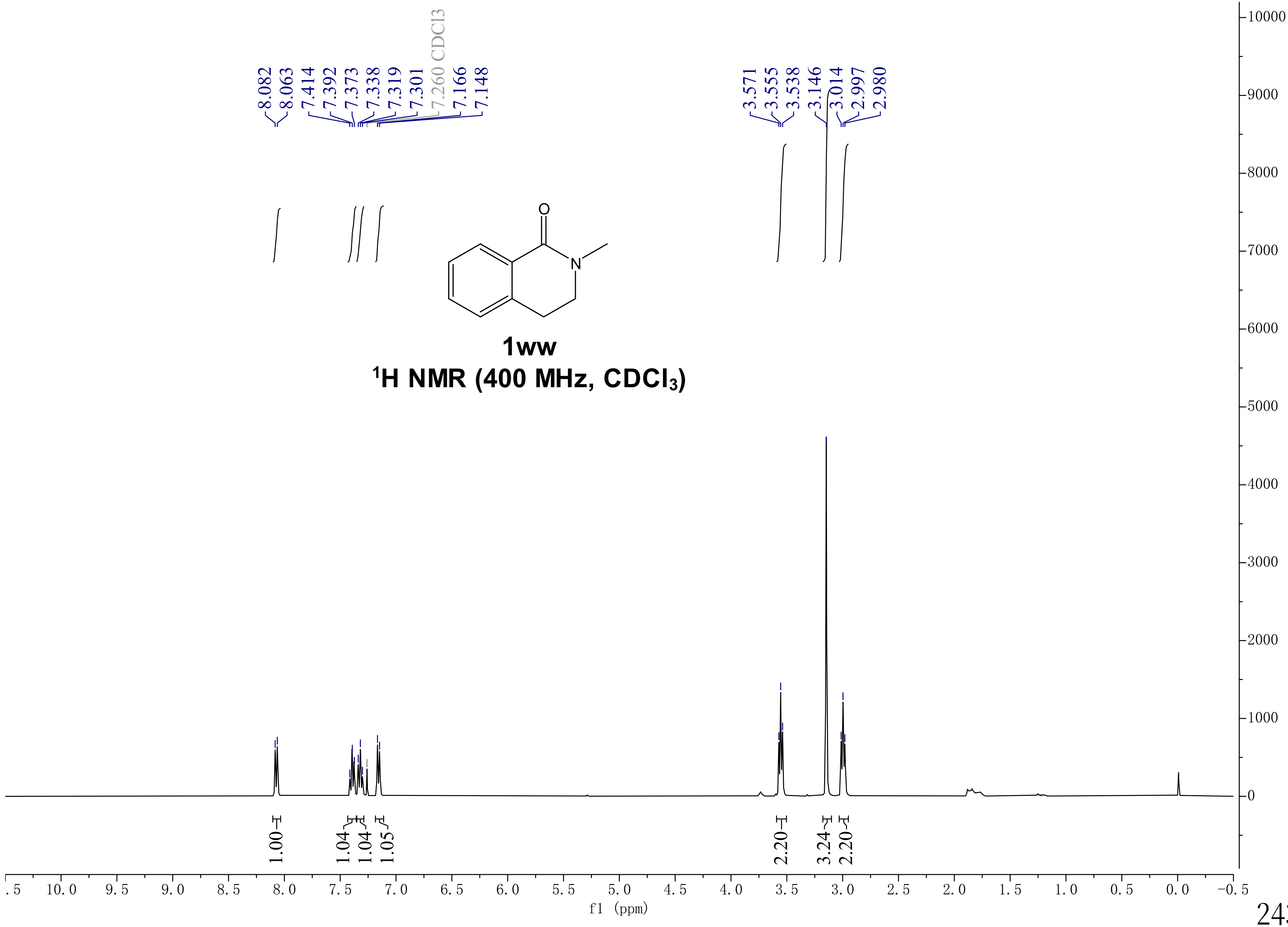
^{13}C NMR (125 MHz, $CDCl_3$)

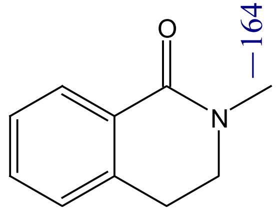


1uu

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

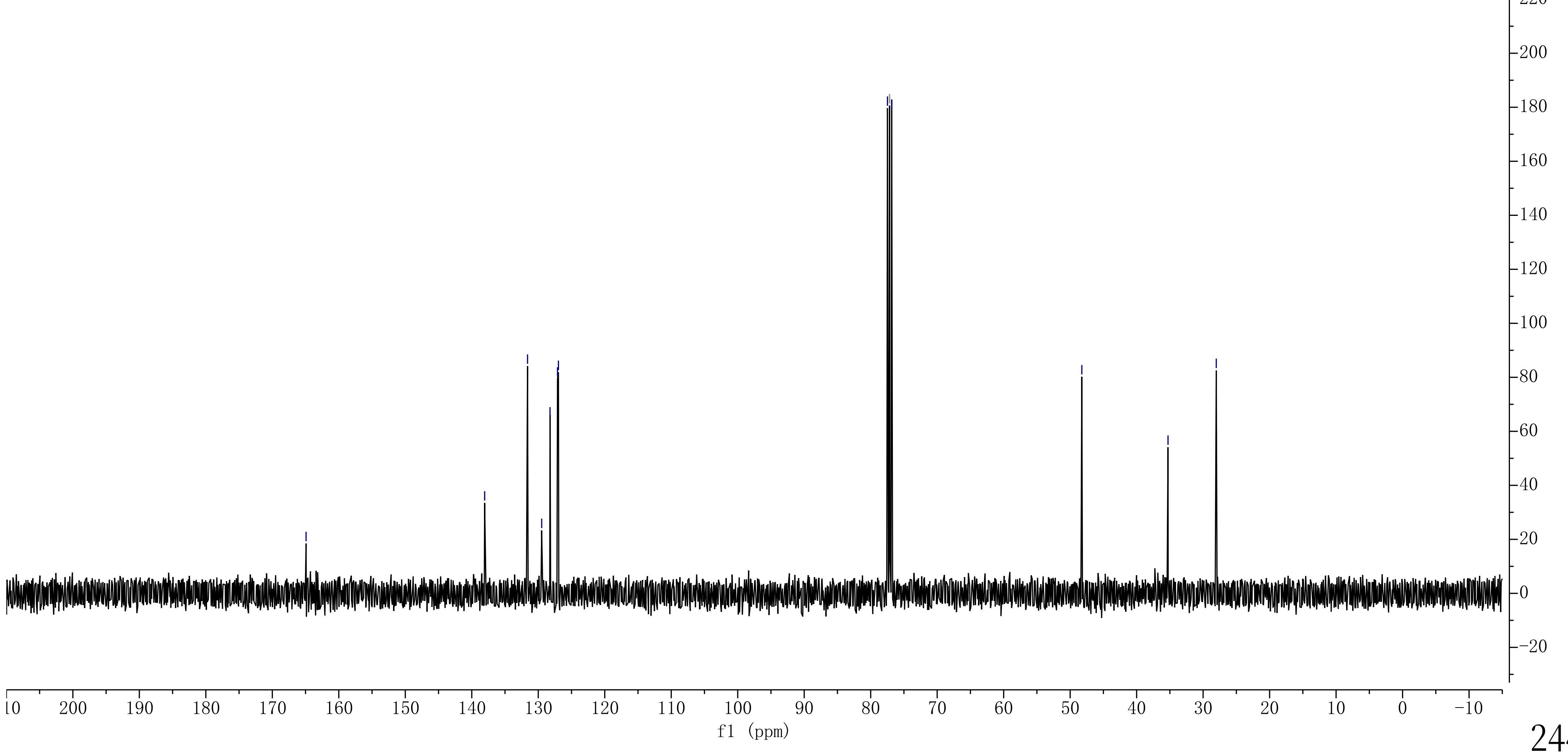

174.608
77.477
77.160 CDCl3
76.839
37.460
36.556
35.393
25.084
17.920
O
N
1uu
13C NMR (100 MHz, CDCl3)
f1 (ppm)

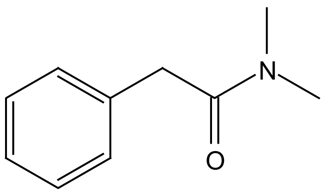

8.082
8.063
7.414
7.392
7.373
7.338
7.319
7.301
7.260 CDCl3
7.166
7.148
3.571
3.555
3.538
3.146
3.014
2.997
2.980
O
N
1ww
1H NMR (400 MHz, CDCl3)
1.00
1.04
1.04
1.05
2.20
3.24
2.20
f1 (ppm)



1ww

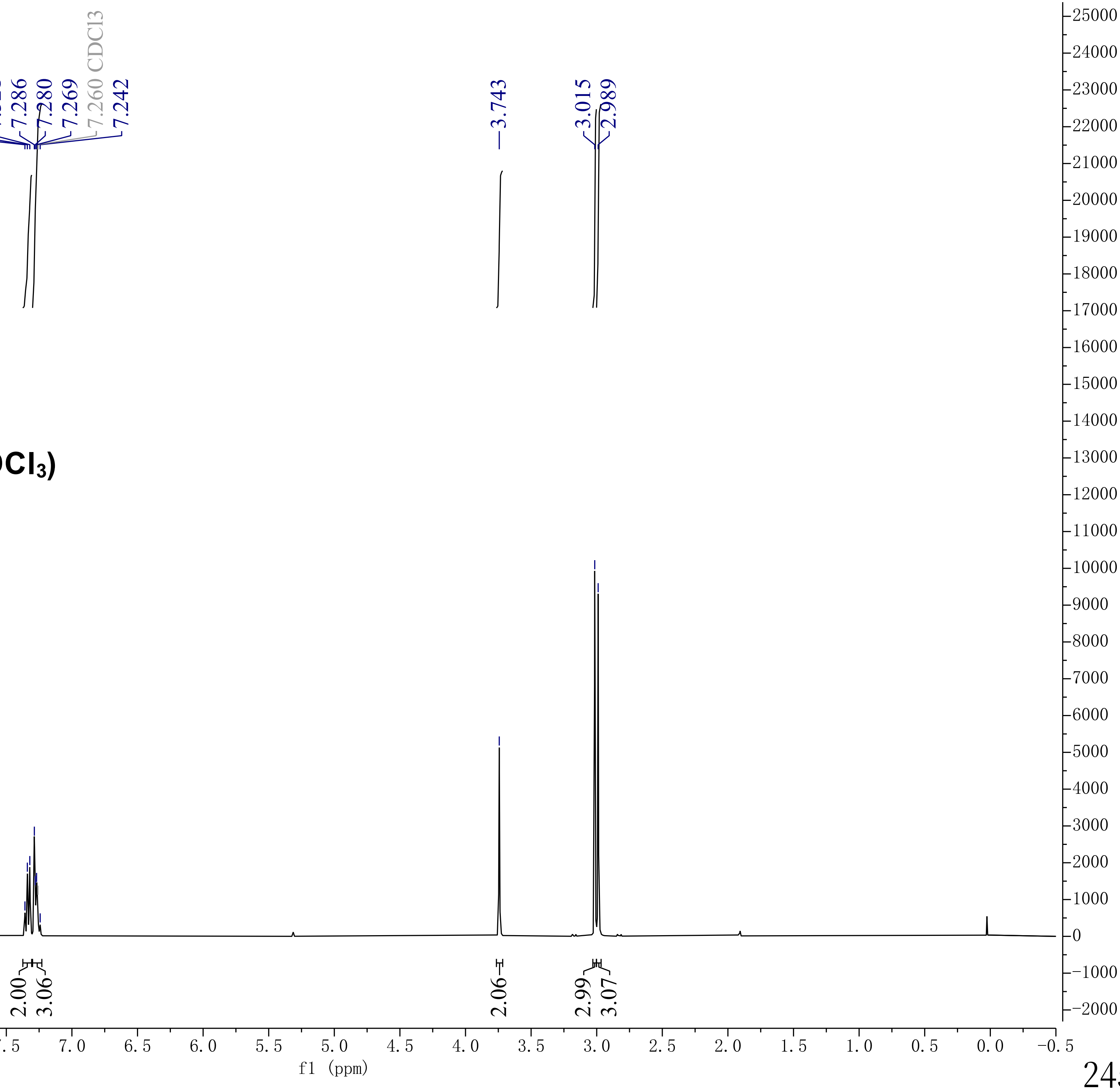
^{13}C NMR (100 MHz, $CDCl_3$)

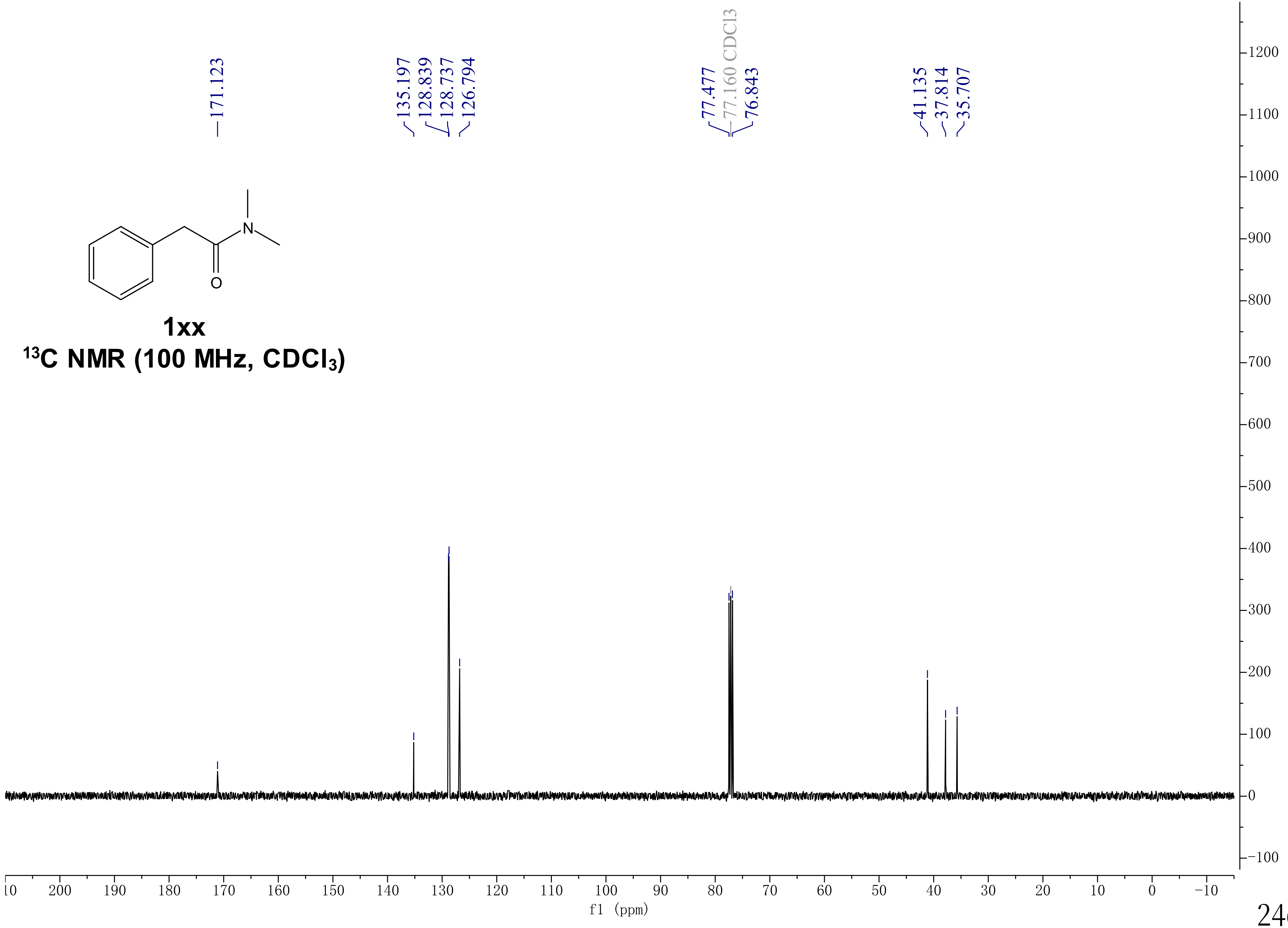


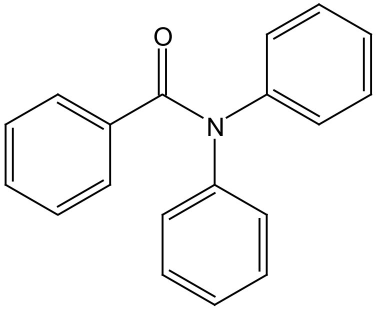


1xx

^{1}H NMR (400 MHz, CDCl$_3$)

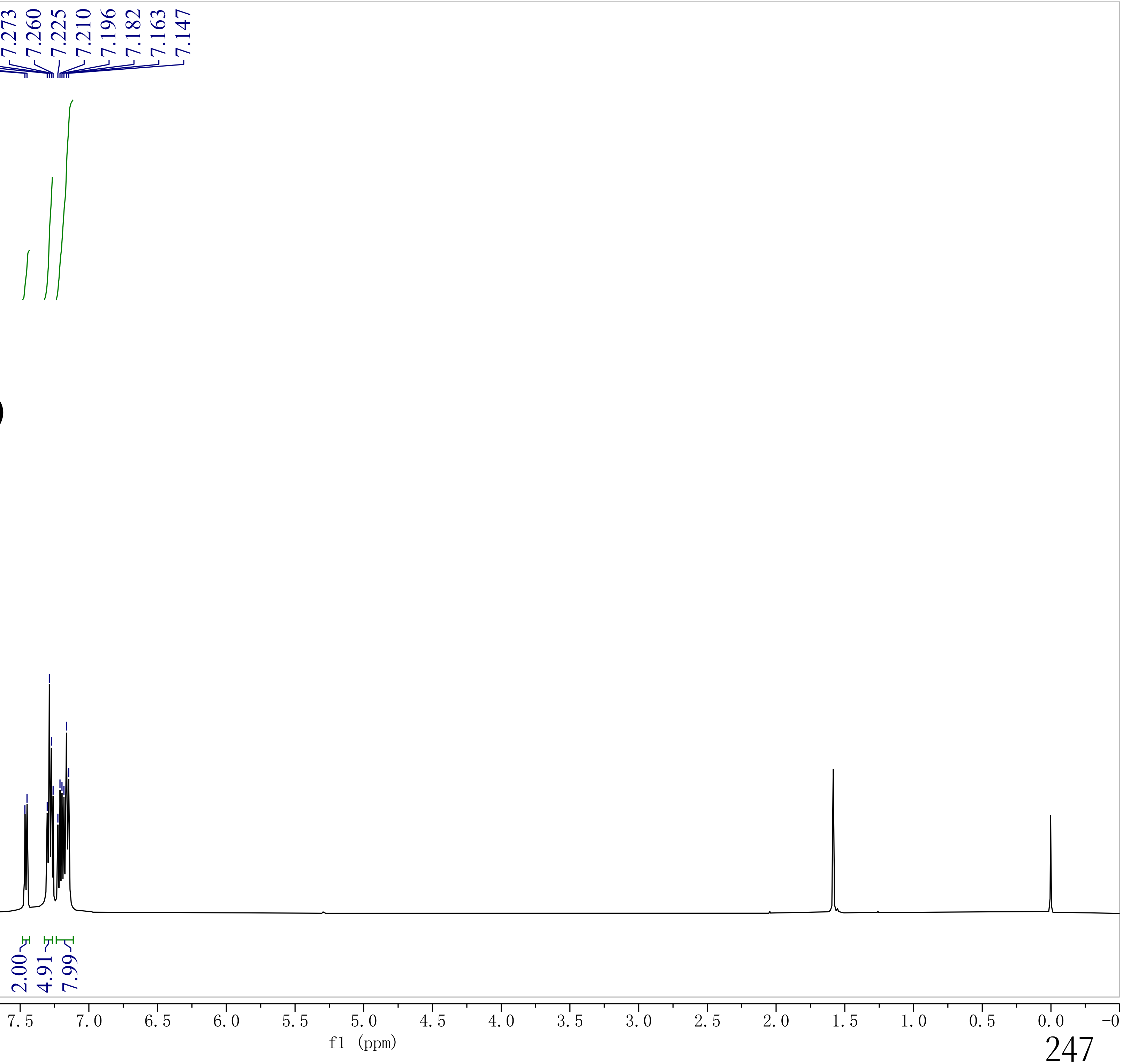


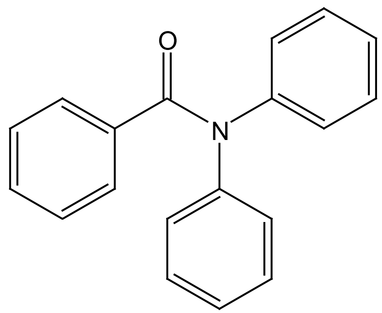

171.123
135.197
128.839
128.737
126.794
77.477
77.160 CDCl3
76.843
41.135
37.814
35.707
O
N
1xx
13C NMR (100 MHz, CDCl3)
f1 (ppm)



1zz

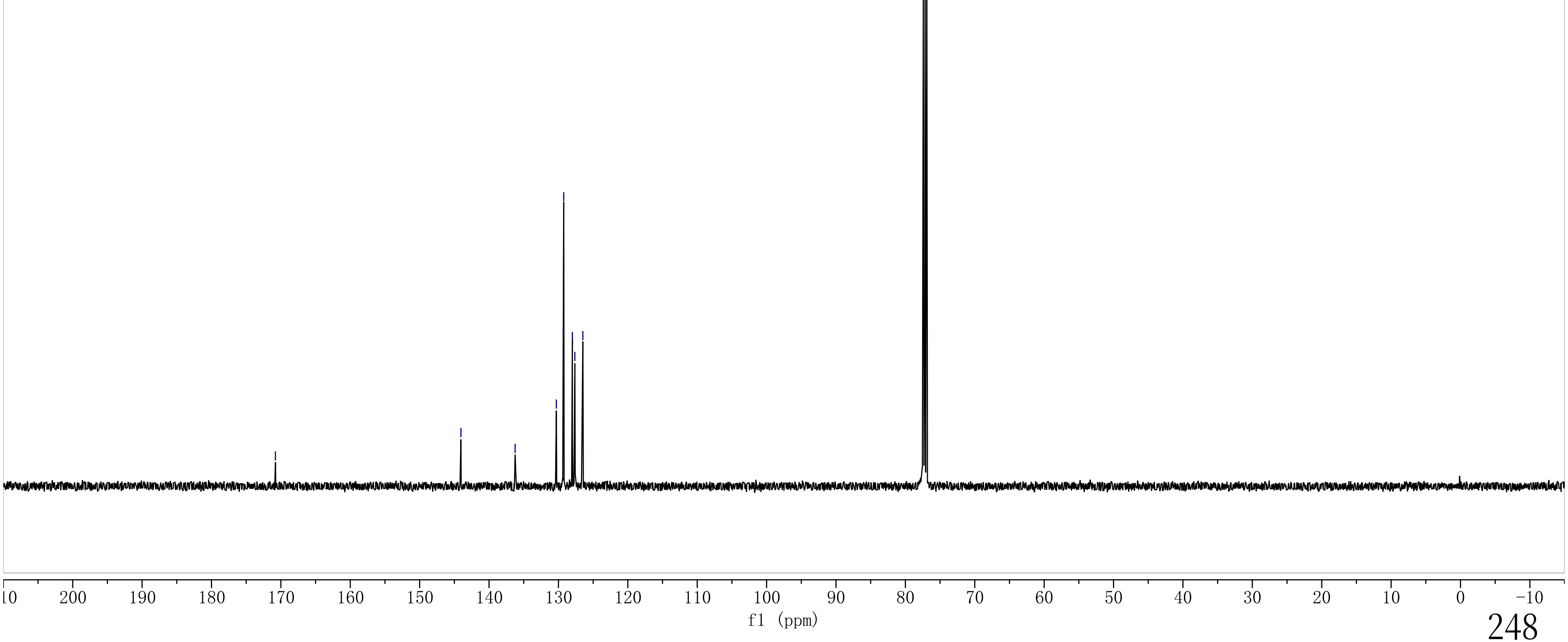
^{1}H NMR (500 MHz, $CDCl_3$)

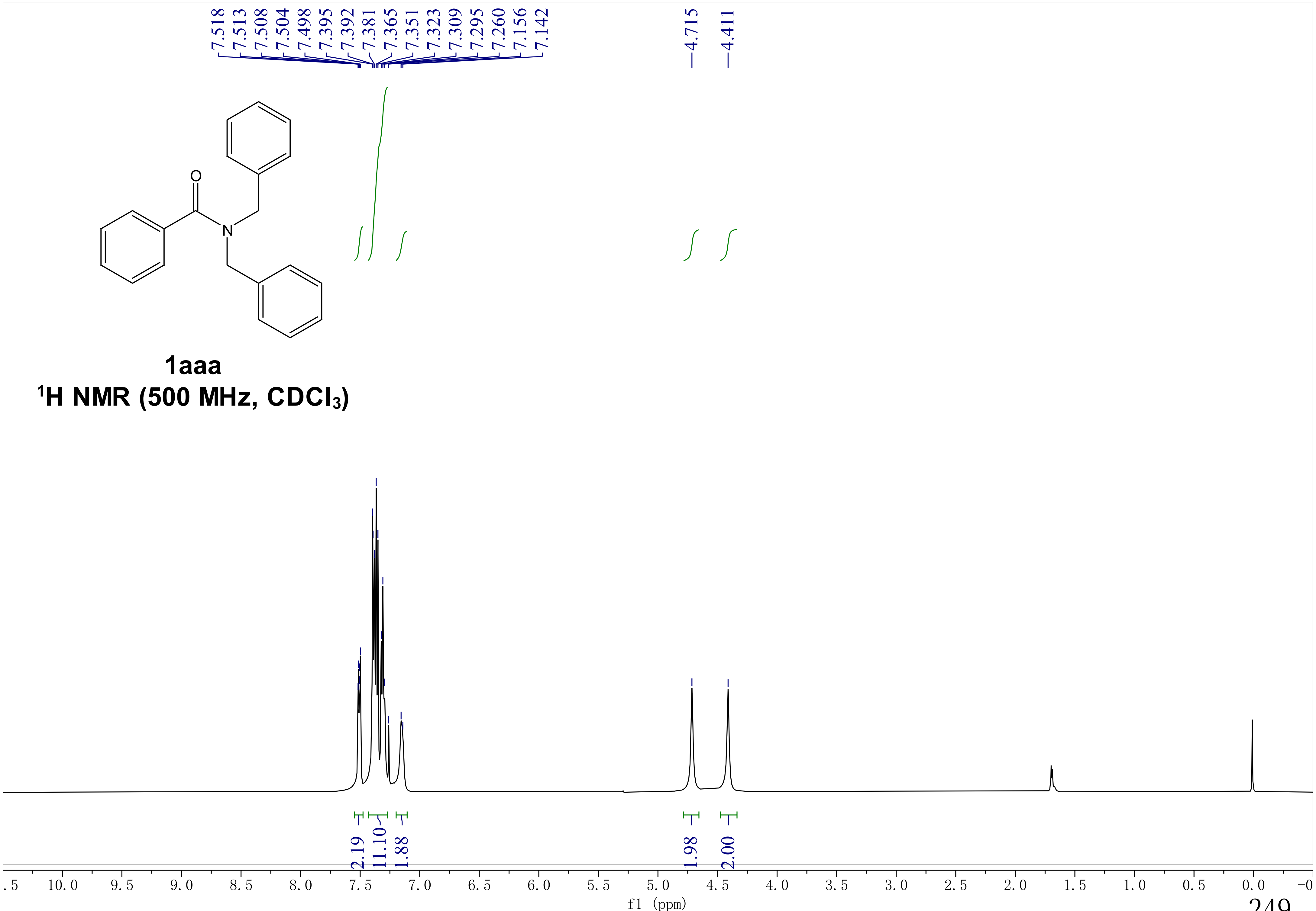


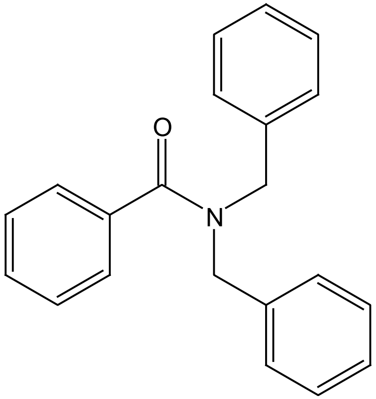


1zz

^{13}C NMR (125 MHz, CDCl$_3$)

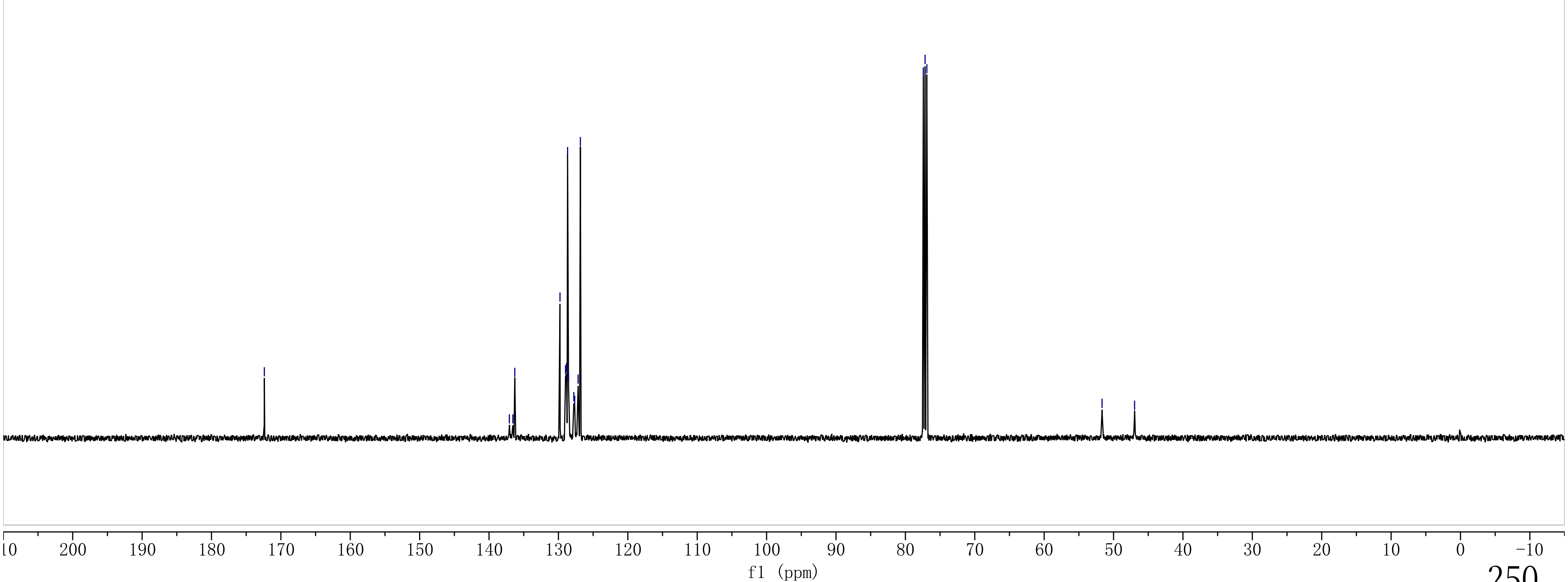


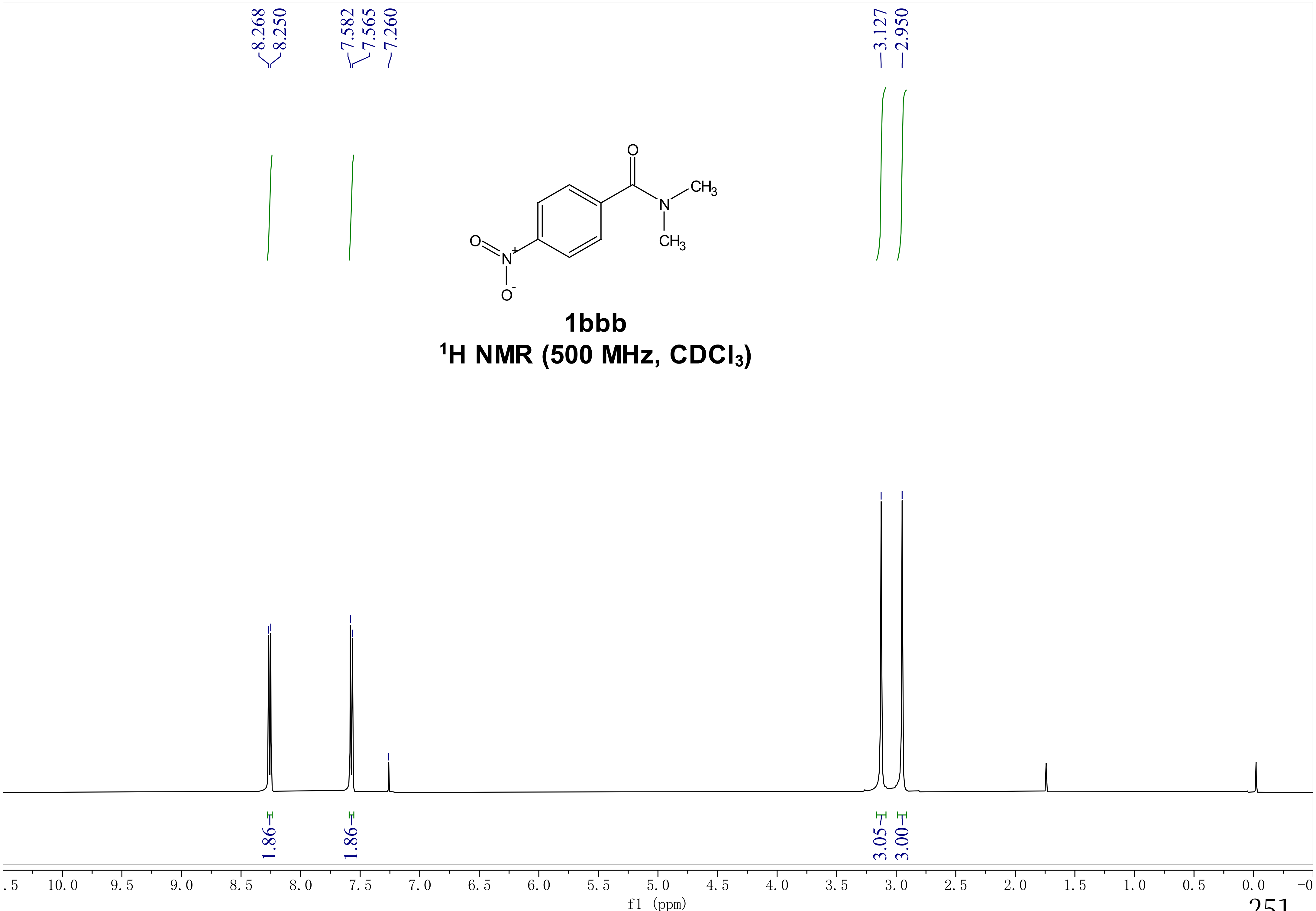

7.518
7.513
7.508
7.504
7.498
7.395
7.392
7.381
7.365
7.351
7.323
7.309
7.295
7.260
7.156
7.142
4.715
4.411
O
N
1aaa
^{1}H NMR (500 MHz, $CDCl_3$)
2.19
11.10
1.88
1.98
2.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

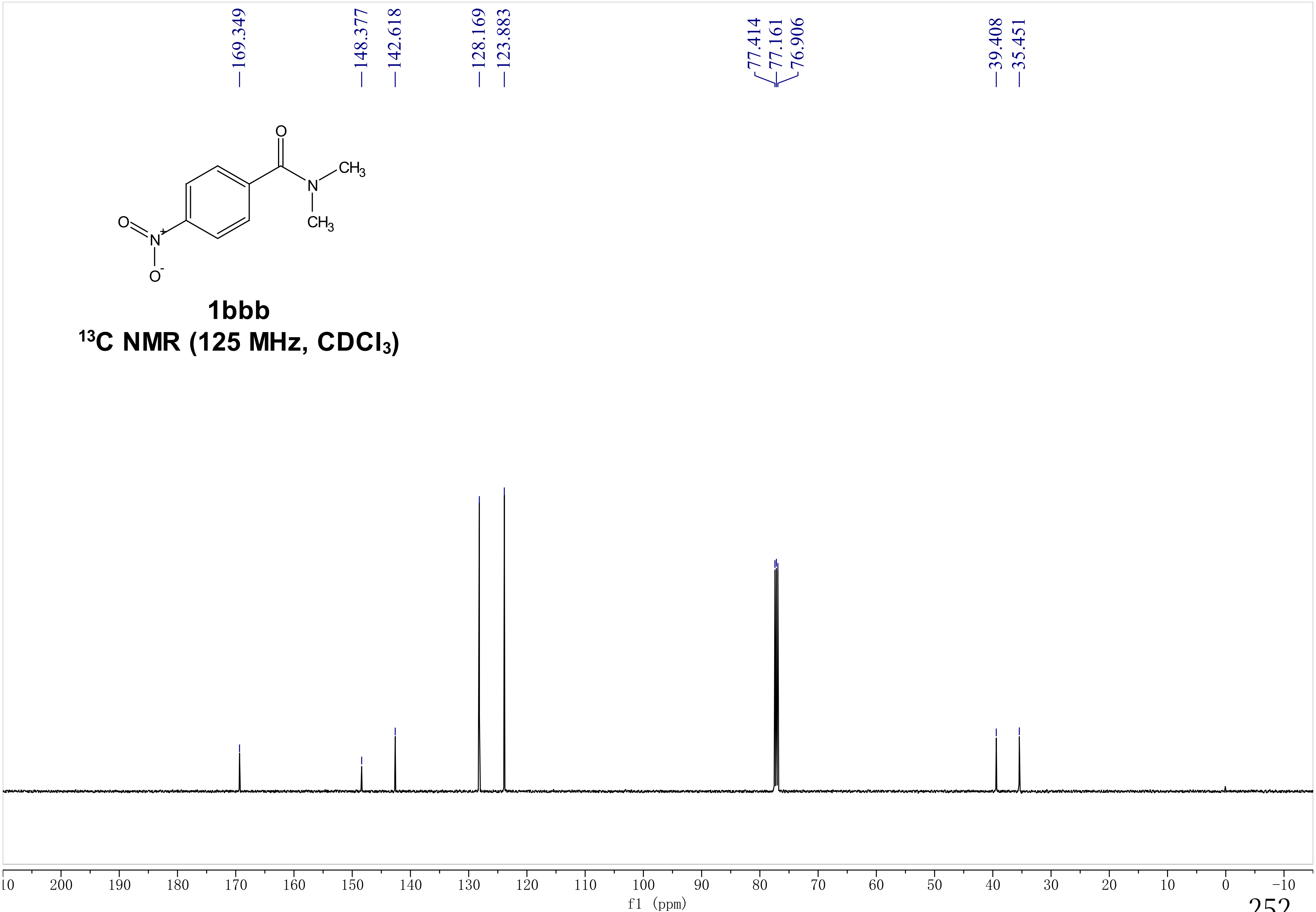


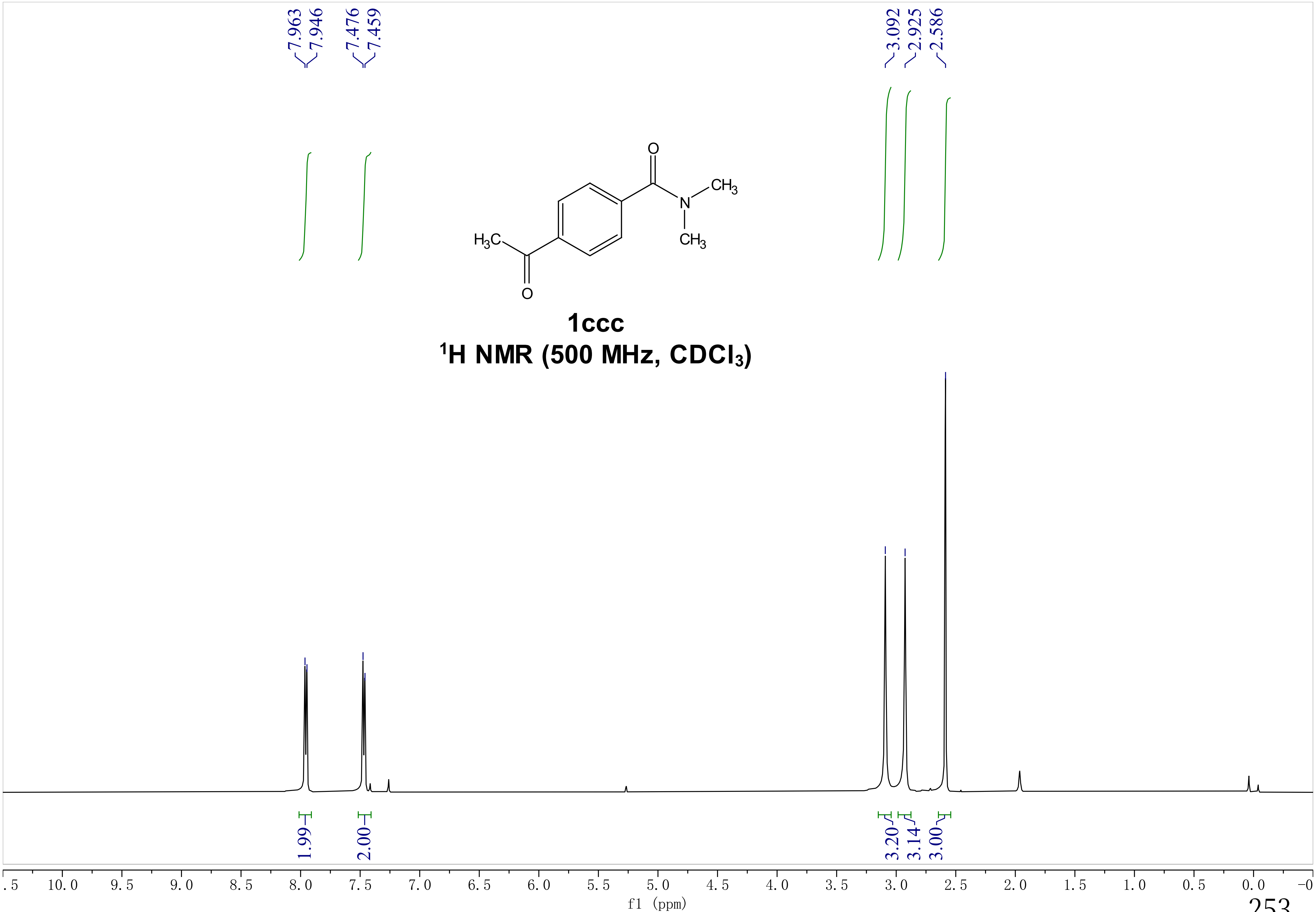
1aaa

^{13}C NMR (125 MHz, $CDCl_3$)

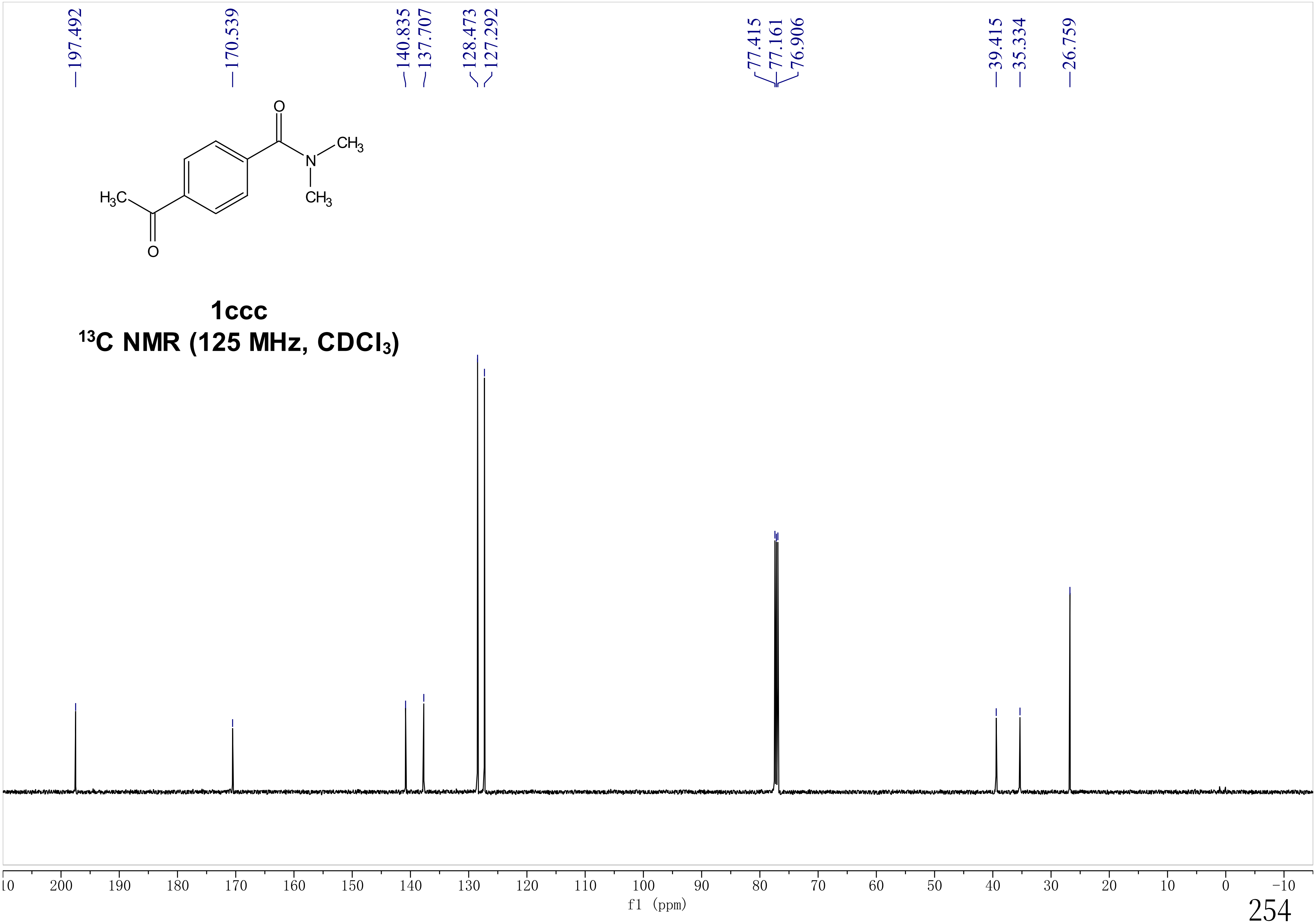


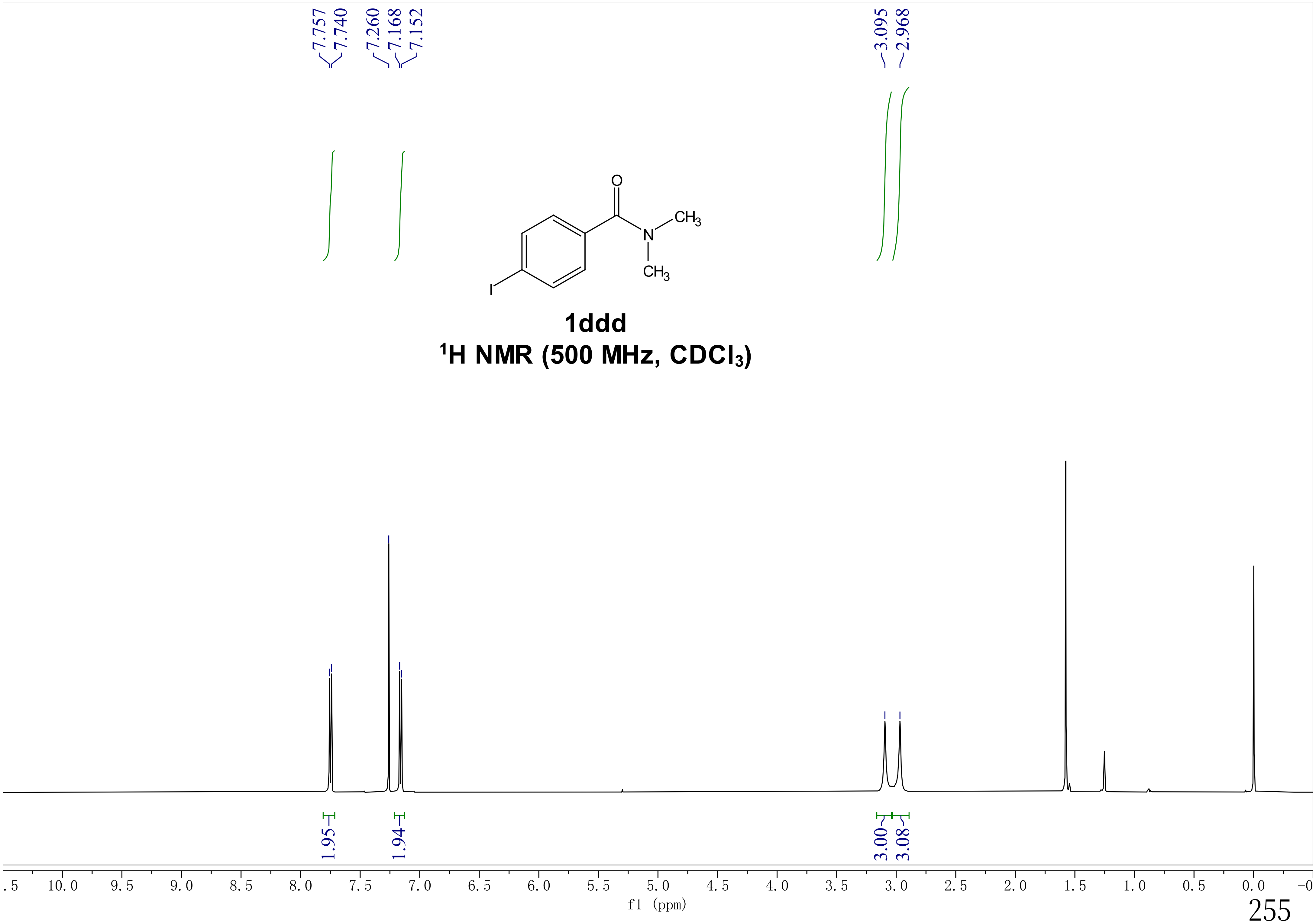

8.268
8.250
7.582
7.565
7.260
3.127
2.950
O
N
CH3
CH3
N+
O
O-
1bbb
1H NMR (500 MHz, CDCl3)
1.86
1.86
3.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

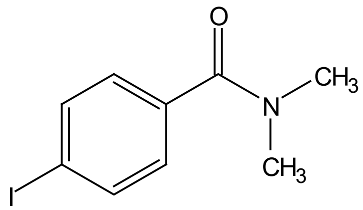

169.349
148.377
142.618
128.169
123.883
77.414
77.161
76.906
39.408
35.451
1bbb
^{13}C NMR (125 MHz, $CDCl_3$)
f1 (ppm)



7.963
7.946
7.476
7.459
3.092
2.925
2.586
1ccc
1H NMR (500 MHz, CDCl3)
1.99
2.00
3.20
3.14
3.00
f1 (ppm)

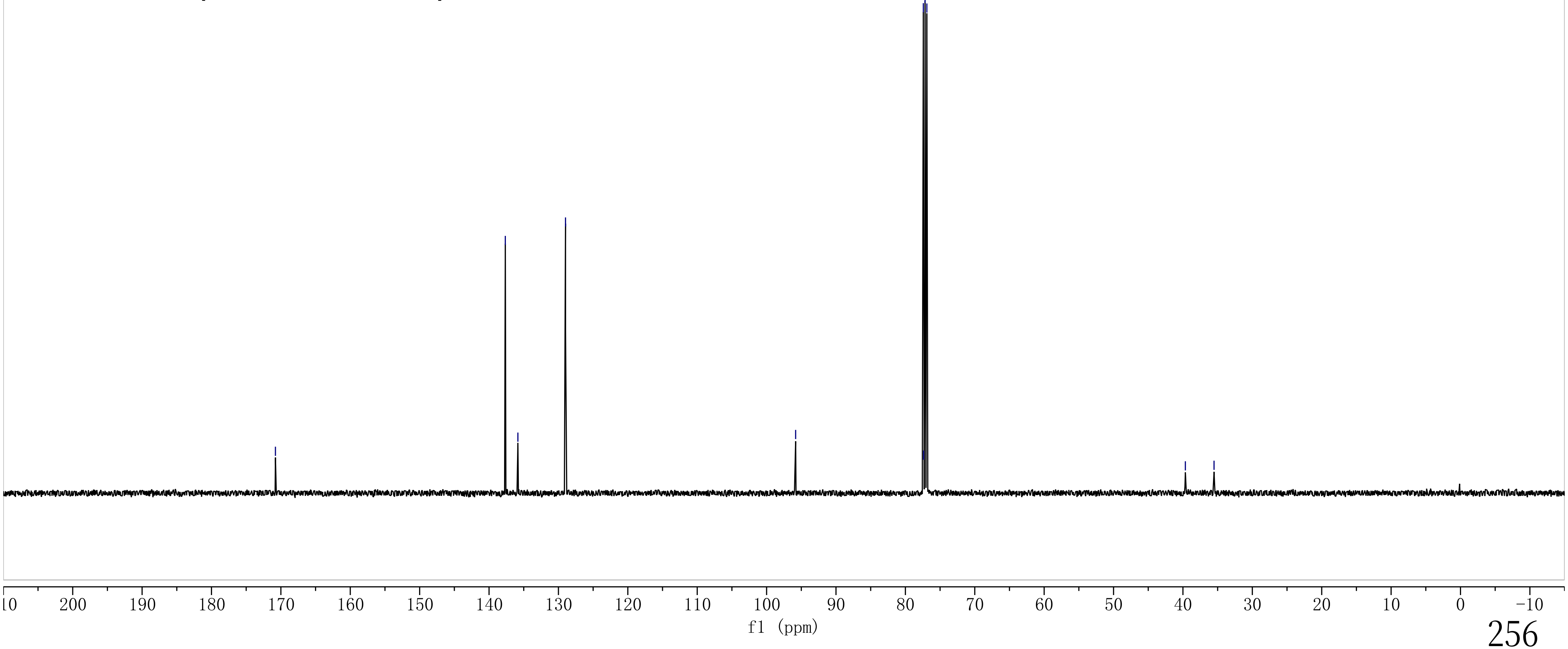

197.492
170.539
140.835
137.707
128.473
127.292
77.415
77.161
76.906
39.415
35.334
26.759
O
CH3
N
CH3
H3C
O
1ccc
13C NMR (125 MHz, CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

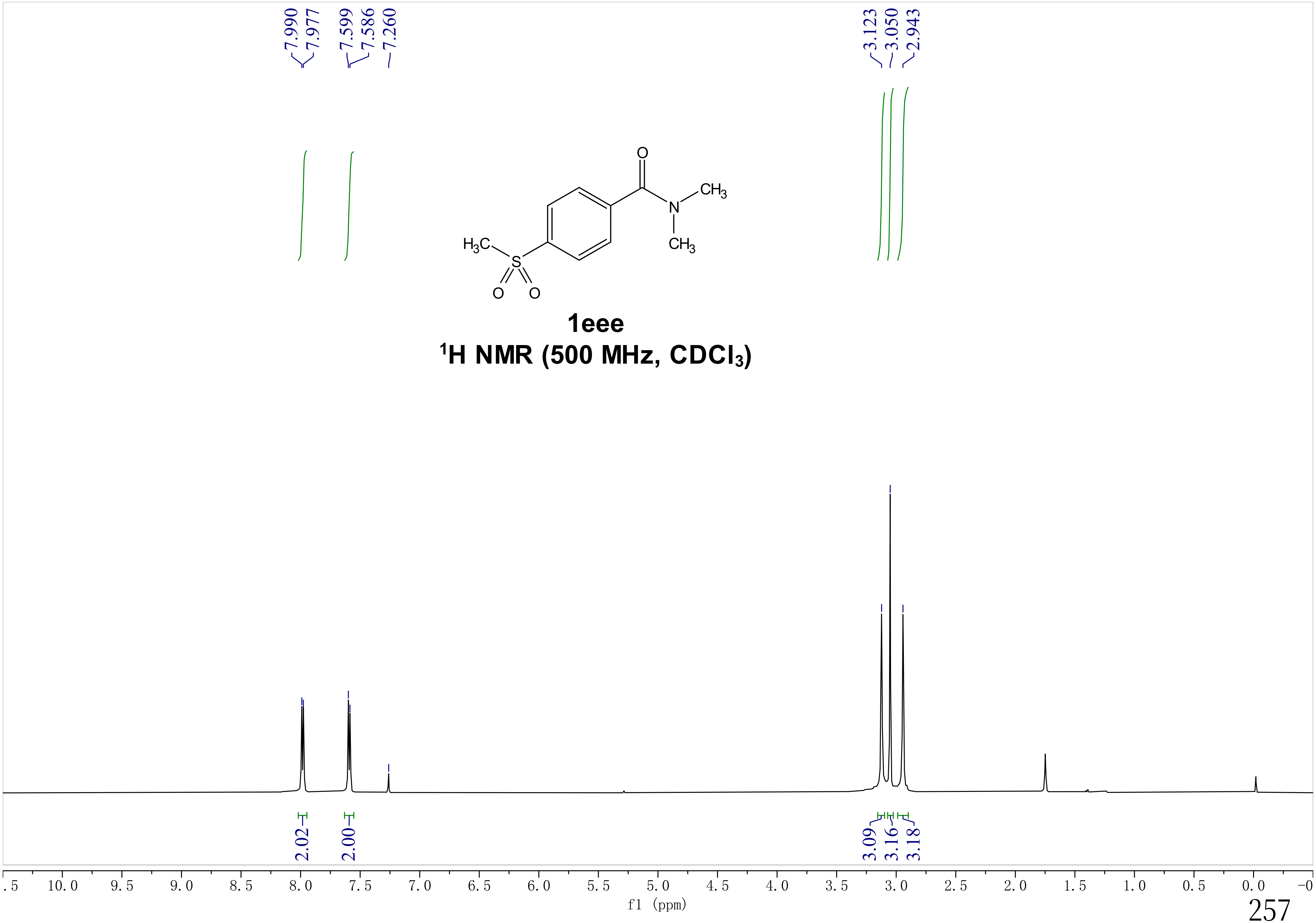

7.757
7.740
7.260
7.168
7.152
3.095
2.968
1ddd
1H NMR (500 MHz, CDCl3)
1.95
1.94
3.00
3.08
f1 (ppm)

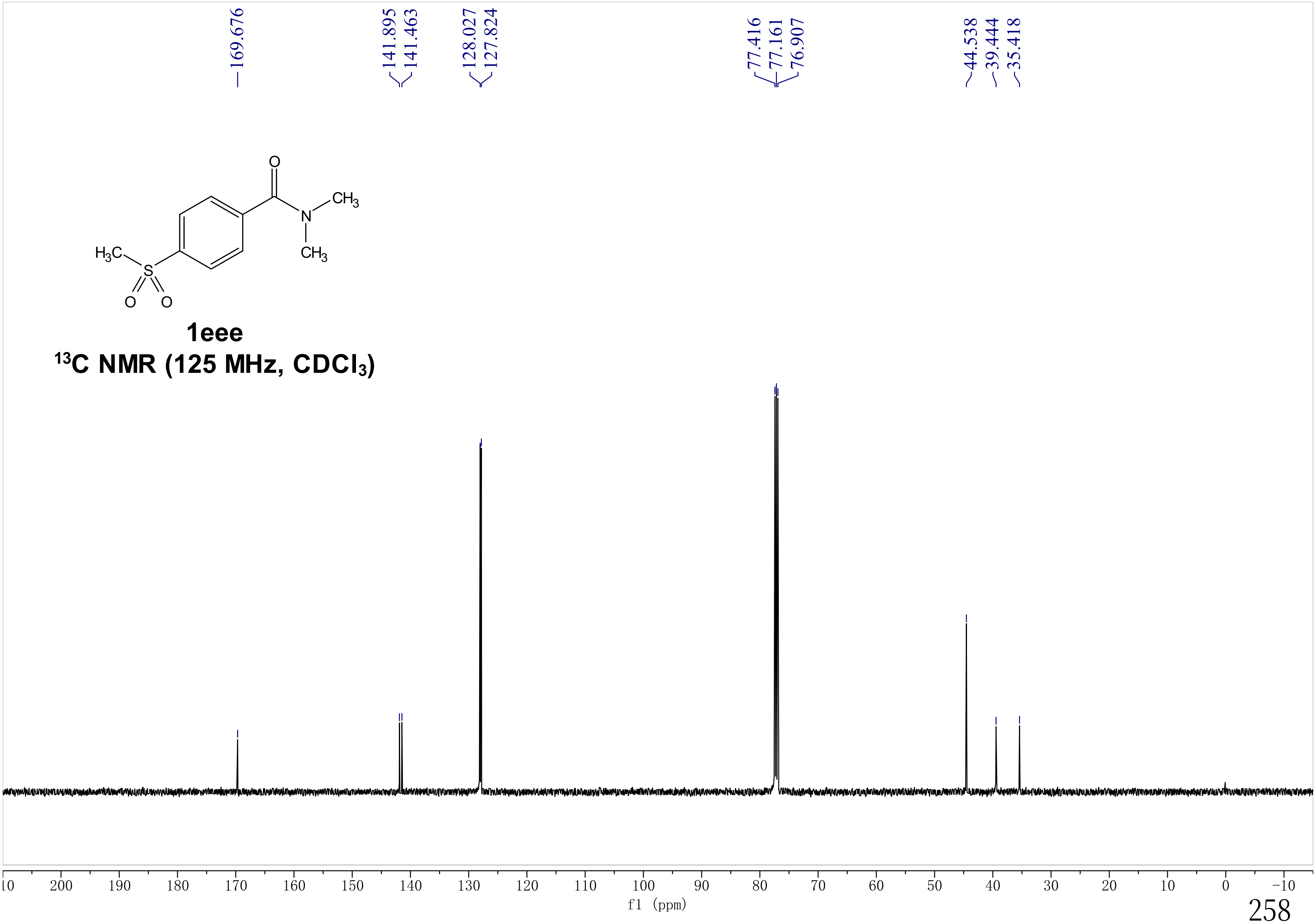


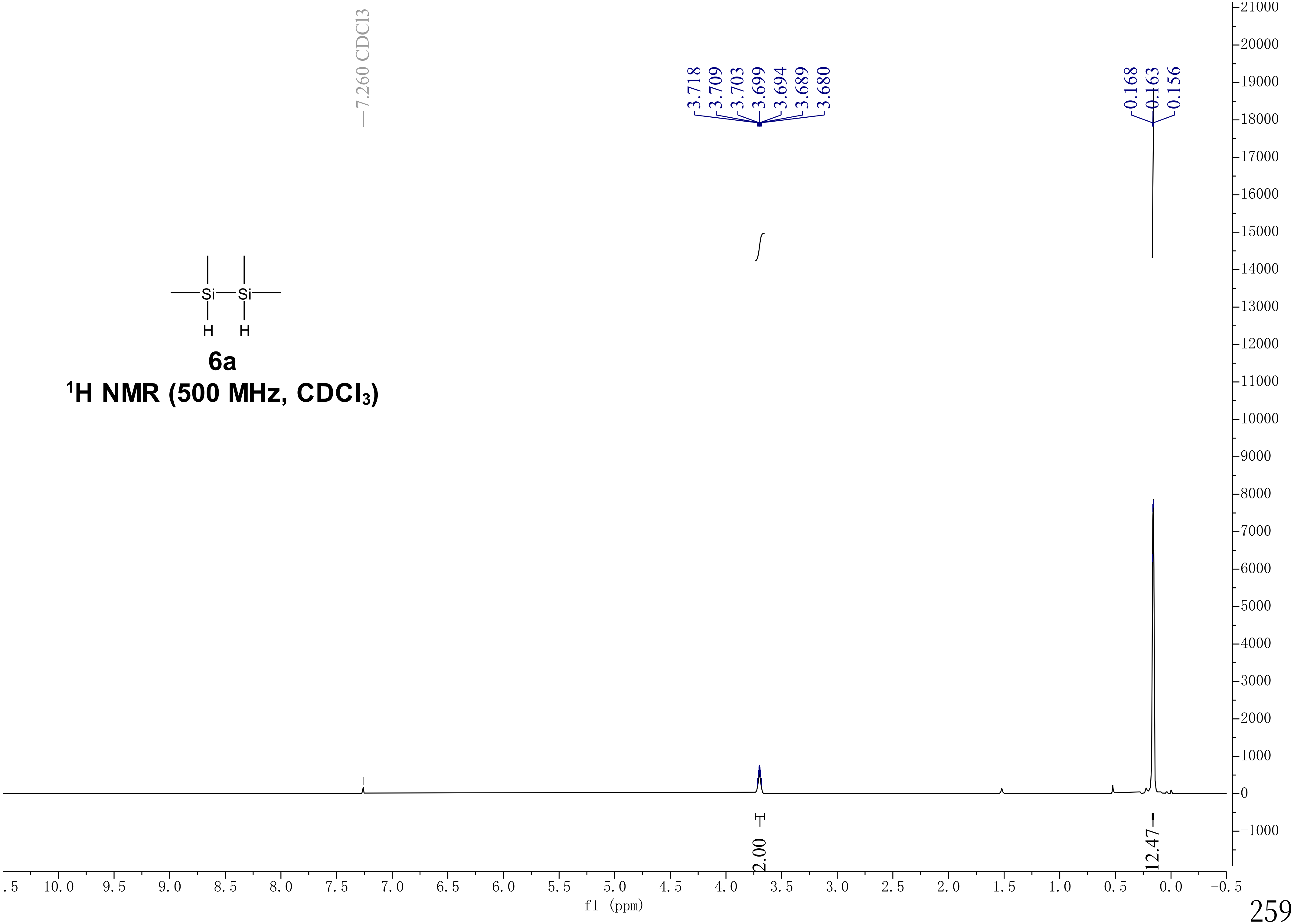
1ddd

^{13}C NMR (125 MHz, $CDCl_3$)




7.990
7.977
7.599
7.586
7.260
3.123
3.050
2.943
1eee
^{1}H NMR (500 MHz, CDCl$_3$)
2.02
2.00
3.09
3.16
3.18
f1 (ppm)


169.676
141.895
141.463
128.027
127.824
77.416
77.161
76.907
44.538
39.444
35.418
1eee
^{13}C NMR (125 MHz, $CDCl_3$)
f1 (ppm)

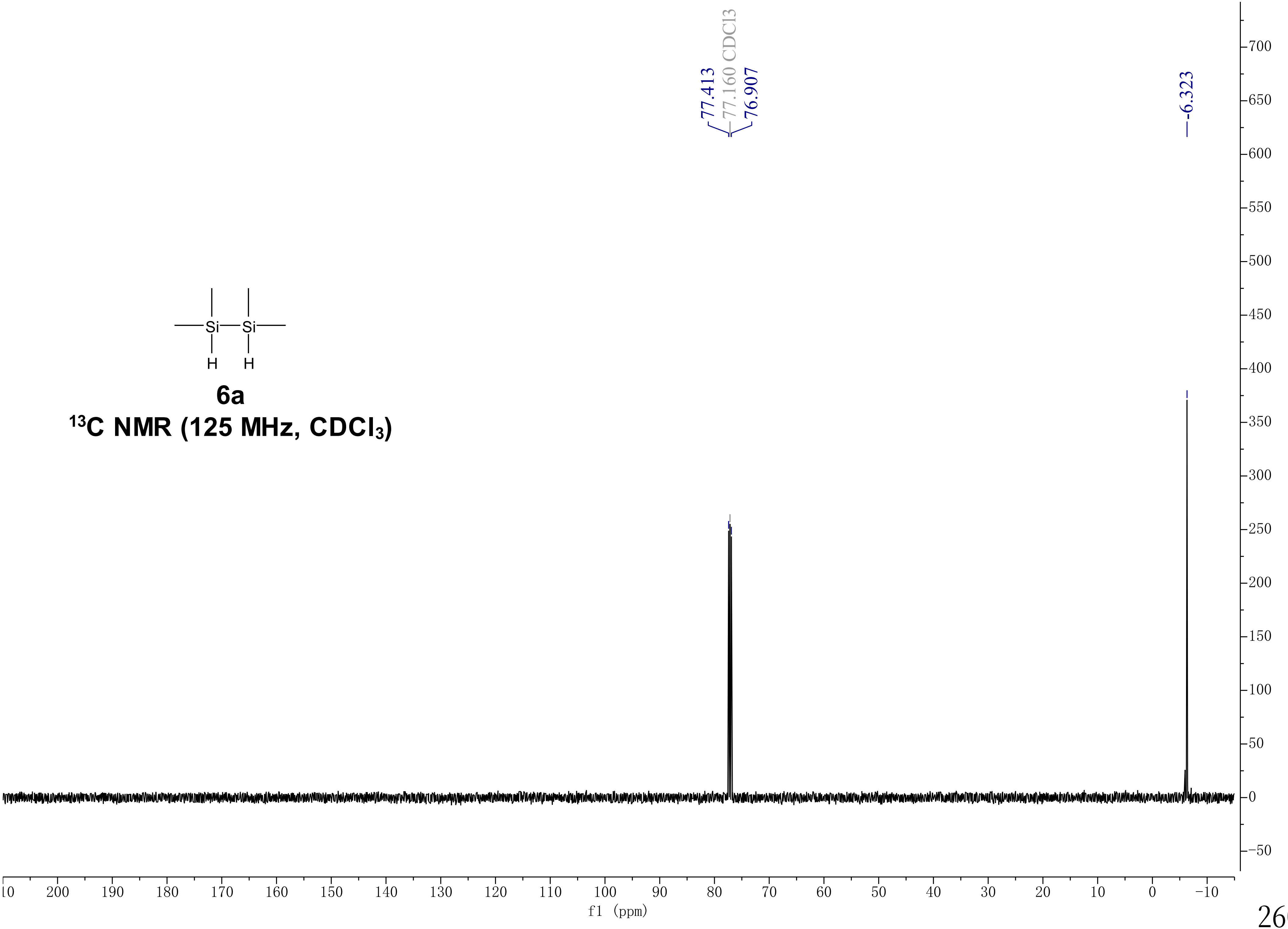


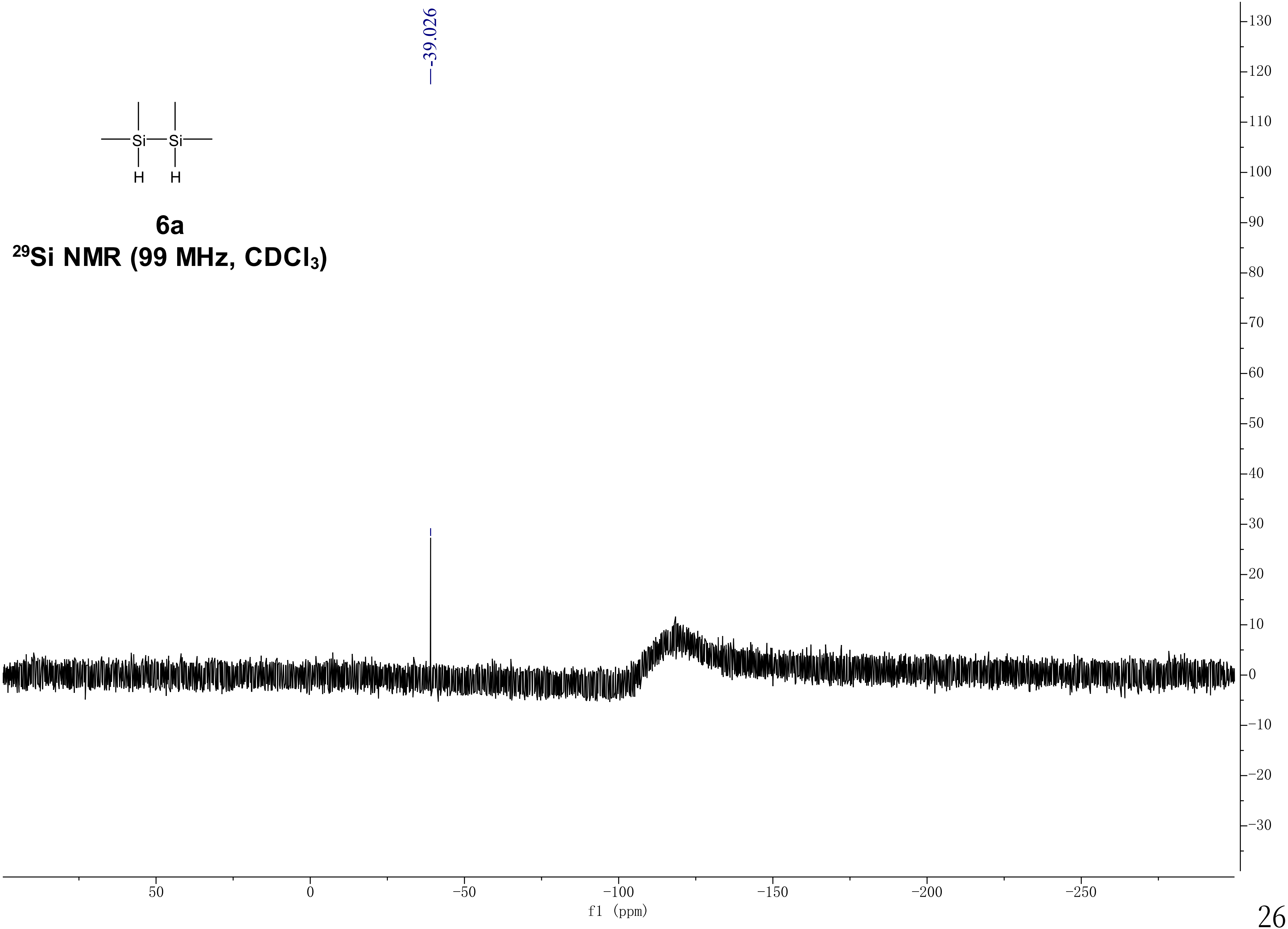
6a

^1H NMR (500 MHz, $CDCl_3$)

6a

^{13}C NMR (125 MHz, $CDCl_3$)





-39.026
Si
Si
H
H
6a
²⁹Si NMR (99 MHz, CDCl₃)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
50
0
−50
−100
−150
−200
−250
f1 (ppm)