Supporting Information

Synthesis of 2,3-Disubstituted Indoles via a Tandem Reaction

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Contents:

1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction.

Optical rotations were measured on a precision automated polarimeter. Infrared spectra were recorded on a 670 FT-IR spectrometer. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker APEXII mass spectrometer by means of the electrospray ionization (ESI) technique. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300MHz and 400 MHz spectrometers. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H NMR and 77.0 for ^{13}C NMR). Melting points were measured on a melting point apparatus and are uncorrected. Allyl bromide was purchased from Adamas-beta®. Substrates were purchased from TCI, Energy Chemical or Alfa Aesar and used as received. Oil bath was used as heat source for reactions above room temperature.

2. Preparation and characterization of starting materials

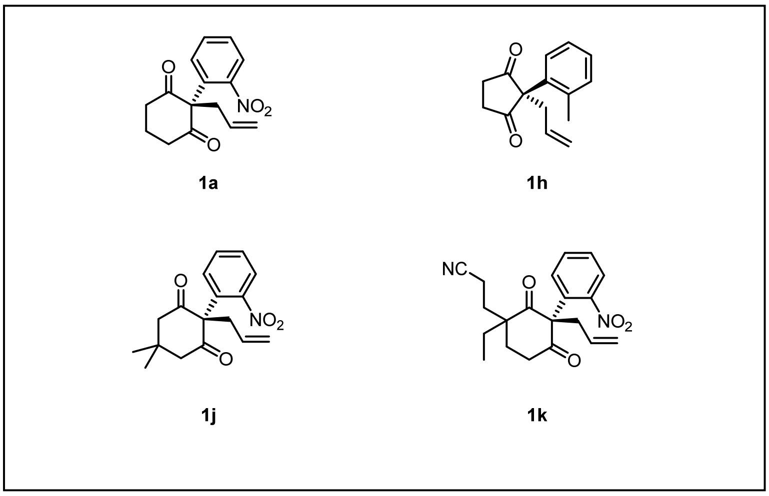


Figure. SI-1 Known Compounds

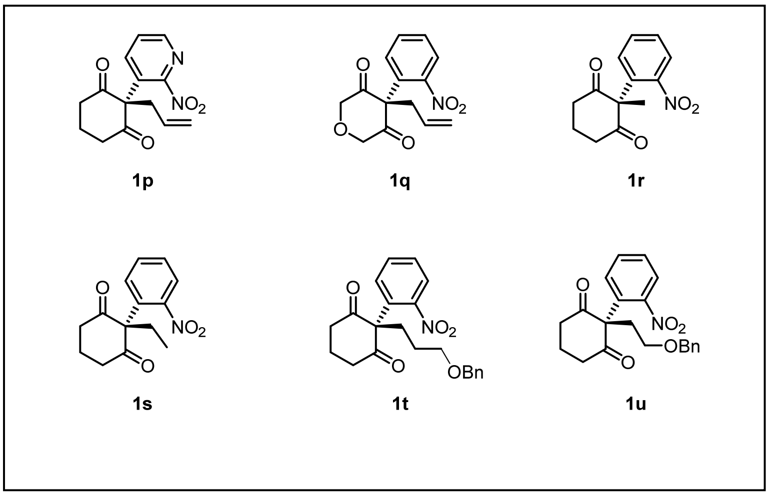
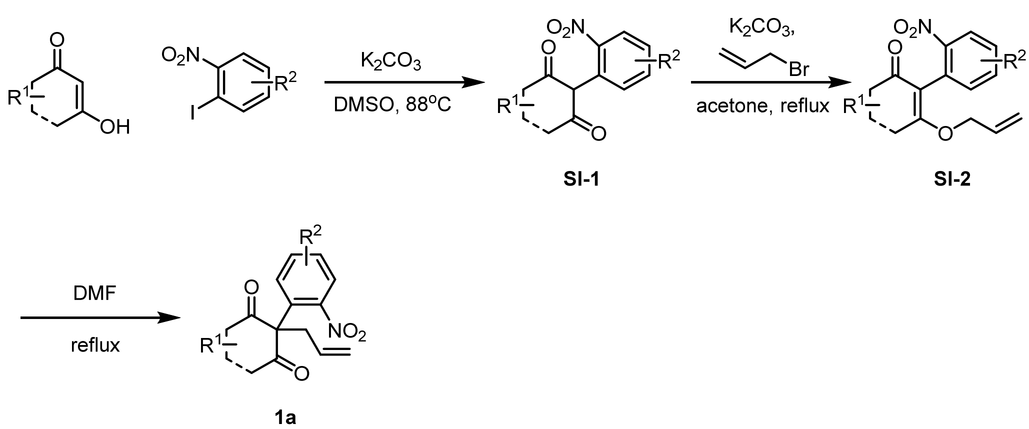


Figure. SI-2 Failed Prepared substrates

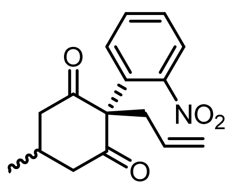
General procedure for the substrates:



A mixture of 1,3-cyclohexanedione (5 mmol, 1 equiv), anhydrous K_2CO_3 (15 mmol, 3 equiv), and *o*-iodonitrobenzene (10 mmol, 2 equiv) in dimethyl sulfoxide (50 ml) was heated to 88 °C for 15 h. After cooling, the mixture was poured into water. The resulting solution was acidified with concentrated hydrochloric acid and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated, the residue was purified by silica gel column chromatography (CH_2Cl_2-MeOH, 20:1) to afford **SI-1**.

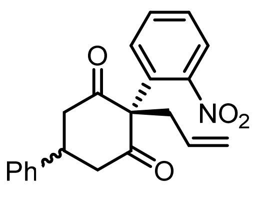
A mixture of 2-(o-nitrophenyl)-l,3-cyclohexanedione **SI-1** (5 mmol, 1equiv), K_2CO_3 (1.037 g, 7.5 mmol, 1.5 equiv) and allyl bromide (5 mmol, 1 equiv) in anhydrous acetone (50 ml) was stirred at reflux temperature for 15 h. Then, the mixture was concentrated *in vacuo*, the residue was solubilized with CH_2Cl_2 and washed with water. The aqueous layer was back-extracted with CH_2Cl_2, the combined organic layers were dried with Na_2SO_4, filtered and concentrated under vacuum, the residue was purified by silica gel column chromatography to afford **SI-2**.

A solution of 3-allyloxy-2-(o-nitrophenyl)-2-cyclohexenone (1 mmol) in anhydrous DMF (10 ml) was stirred at reflux temperature for 12 h. Then, the mixture was diluted with ether, the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum, the residue was purified by silica gel column chromatography to give the compound **1a**.



1b

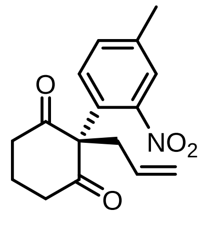
Substrate 1b 2-allyl-5-methyl-2-(2-nitrophenyl)cyclohexane-1,3-dione was obtained as a white solid. Mp: 167-168 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.05 (t, J 9.0 Hz, 1H), 7.61 (m, 2H), 7.46 (t, J = 7.5 Hz, 1H), 5.68 – 5.46 (m, 1H), 5.30 – 5.07 (m, 2H), 3.02 (dd, J = 15.6, 9.0 Hz, 2H), 2.87 – 2.42 (m, 5H), 1.15 (d, J = 5.7 Hz, 3H).; **^{13}C NMR (75 MHz, CDCl$_3$)** δ 204.8, 204.6, 147.7, 147.0, 133.5, 133.4, 132.6, 131.9, 131.6, 131.2, 131.1, 130.4, 128.4, 128.4, 125.7, 125.6, 119.7, 119.6, 71.5, 70.0, 45.3, 45.3, 38.3, 35.6, 24.2, 24.0, 21.7, 21.7; **HRMS ESI** Calcd for $C_{16}H_{17}NO_4$ $[M+H]^+$: 288.1230, Found: 288.1241.



1c

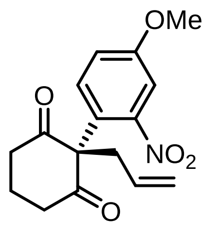
Substrate 1c 2-allyl-2-(2-nitrophenyl)-5-phenylcyclohexane-1,3-dione was obtained as a orange solid. Mp: 159-160 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.20 – 8.04 (m, 1H), 7.76 – 7.45 (m, 3H), 7.43 – 7.26 (m, 5H), 5.74 – 5.51 (m, 1H), 5.38 –

5.11 (m, 2H), 3.91 – 3.74 (m, 1H), 3.24 – 2.85 (m, 6H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 204.3, 204.1, 147.7, 147.0, 142.0, 133.7, 133.6, 131.9, 131.7, 131.2, 131.1, 130.4, 129.0, 128.7, 128.6, 127.4, 127.3, 126.6, 126.0, 125.8, 120.1, 120.0, 71.9, 44.8, 44.5, 38.6, 36.1, 35.1, 34.5; **HRMS ESI** Calcd for $C_{21}H_{19}NO_4$ $[M+H]^+$: 350.1387, Found: 350.1400.



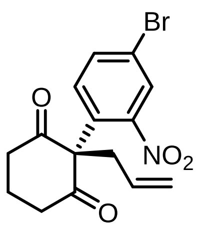
1d

Substrate 1d 2-allyl-2-(4-methyl-2-nitrophenyl)cyclohexane-1,3-dione was obtained as a light yellow solid. Mp: 134-135 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.94 (s, 1H), 7.47 (m, 2H), 5.67 – 5.49 (m, 1H), 5.31 – 5.09 (m, 2H), 3.04 (d, J = 6.6 Hz, 2H), 2.90 – 2.70 (m, 4H), 2.43 (s, 3H), 2.39 – 2.27 (m, 1H), 2.23 – 2.08 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 205.4, 147.3, 139.1, 134.3, 131.0, 130.8, 129.3, 126.4, 119.7, 72.4, 37.8, 36.8, 20.6, 16.9; **HRMS ESI** Calcd for $C_{16}H_{17}NO_4$ $[M+H]^+$: 288.1230, Found: 288.1239.



1e

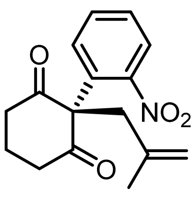
Substrate 1e 2-allyl-2-(4-methoxy-2-nitrophenyl)cyclohexane-1,3-dione was obtained as a light yellow solid. Mp: 121-122 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.65 (d, J = 2.7 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.20 (dd, J = 8.7, 3.0 Hz, 1H), 5.66 – 5.48 (m, 1H), 5.32 – 5.08 (m, 2H), 3.86 (s, 3H), 3.03 (d, J = 6.3 Hz, 2H), 2.91 – 2.70 (m, 4H), 2.43 – 2.26 (m, 1H), 2.24 – 2.09 (m, 1H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 205.5, 159.0, 148.1, 131.9, 130.8, 124.0, 119.7, 119.4, 111.1, 72.2, 55.8, 37.9, 36.8, 16.9; **HRMS ESI** Calcd for $C_{16}H_{17}NO_5$ $[M+H]^+$: 304.1179, Found: 304.1191.



1f

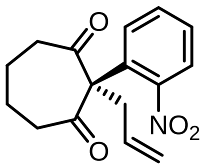
Substrate 1f 2-allyl-2-(4-bromo-2-nitrophenyl)cyclohexane-1,3-dione was obtained as a light yellow solid. Mp: 161-162 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.25 (d, J = 2.1 Hz, 1H), 7.80 (dd, J = 8.7, 2.1 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 5.61 – 5.46 (m, 1H), 5.31 – 5.14 (m, 3H), 3.05 (d, J = 6.3 Hz, 2H), 2.93 – 2.72 (m, 4H), 2.45

– 2.28 (m, 1H), 2.18 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 204.8, 148.1, 136.4, 132.7, 131.3, 130.3, 128.9, 122.0, 120.3, 72.5, 37.8, 36.7, 16.8; **HRMS ESI** Calcd for $C_{15}H_{14}BrNO_4$ $[M+H]^+$: 352.0179, 354.0159, Found: 352.0188, 354.0173.



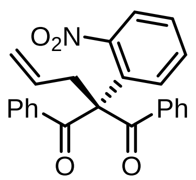
1g

Substrate 1g 2-(2-methylallyl)-2-(2-nitrophenyl)cyclohexane-1,3-dione as a white solid. Mp: 125-127 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.05 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 4.2 Hz, 2H), 7.53 – 7.42 (m, 1H), 4.88 (s, 1H), 4.61 (s, 1H), 3.04 (s, 2H), 2.97 – 2.82 (m, 2H), 2.80 – 2.65 (m, 2H), 2.36 – 2.08 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 205.0, 147.7, 138.3, 132.9, 131.9, 131.4, 128.4, 125.3, 116.8, 73.0, 40.2, 36.5, 24.3, 16.7; **HRMS ESI** Calcd for $C_{16}H_{17}NO_4$ $[M+H]^+$: 288.1230, Found: 288.1240.



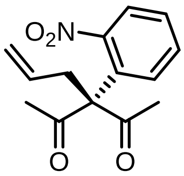
1i

Substrate 1i 2-allyl-2-(2-nitrophenyl)cycloheptane-1,3-dione was obtained as a white solid. Mp: 124-125 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.93 – 7.83 (dd, J = 7.8, 2.1 Hz, 1H), 7.63 – 7.53 (t, J = 7.5 Hz ,1H), 7.52 – 7.43 (t, J = 7.5 Hz ,1H), 7.27 – 7.19 (d, J = 7.8 Hz, 1H), 5.61 – 5.42 (m, 1H), 5.04 – 4.85 (m, 2H), 3.03 (d, J = 6.9 Hz, 2H), 2.87 – 2.72 (m, 2H), 2.68 – 2.55 (m, 2H), 2.13 – 1.86 (m, 4H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 206.6, 150.2, 132.5, 132.4, 131.0, 130.4, 128.6, 125.7, 118.9, 73.3, 42.6, 39.3, 26.2; **HRMS ESI** Calcd for $C_{16}H_{17}NO_4$ $[M+H]^+$: 288.1230, Found: 288.1241.



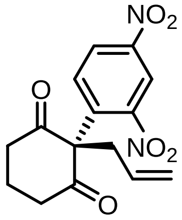
1l

Substrate 1l 2-allyl-2-(2-nitrophenyl)-1,3-diphenylpropane-1,3-dione was obtained as a yellow solid. Mp: 154-155 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.00 (dd, J = 7.8, 1.5 Hz, 1H), 7.71 – 7.64 (m, 4H), 7.55 – 7.31 (m, 5H), 7.29 (s, 1H), 7.25 – 7.22 (m, 1H), 6.95 (dd, J = 7.8, 1.5 Hz, 1H), 5.71 – 5.51 (m, 1H), 4.91 – 4.71 (m, 2H), 3.57 (d, J = 7.2 Hz, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 197.2, 149.7, 136.6, 134.3, 133.1, 132.6, 132.5, 131.5, 129.7, 128.5, 128.1, 125.7, 118.3, 74.4, 41.5; **HRMS ESI** Calcd for $C_{24}H_{19}NO_4$ [M+H]$^+$: 386.1387, Found: 386.1400.



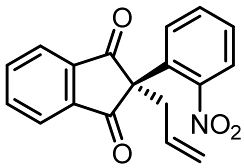
1m

Substrate 1m 3-allyl-3-(2-nitrophenyl)pentane-2,4-dione was obtained as yellow oil. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.03 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 5.63 – 5.47 (m, 1H), 5.16 – 4.97 (m, 2H), 3.22 (d, J = 6.3 Hz, 2H), 2.18 (s, 6H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 203.3, 149.4, 133.1, 133.0, 132.1, 131.3, 128.7, 125.7, 119.5, 74.7, 38.4, 28.4; **HRMS ESI** Calcd for $C_{14}H_{15}NO_4$ [M+H]$^+$: 262.1074, Found: 262.1083.



1n

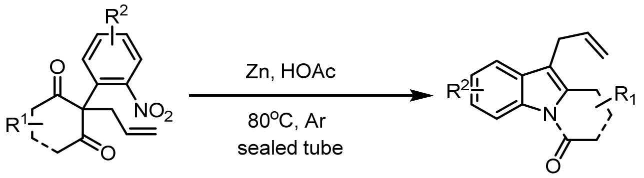
Substrate 1n 2-allyl-2-(2,4-dinitrophenyl)cyclohexane-1,3-dione was obtained as a brown solid. Mp: 174-176 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.91 (d, J = 2.4 Hz, 1H), 8.49 (dd, J = 8.7, 2.4 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 5.59 – 5.43 (m, 1H), 5.37 – 5.19 (m, 2H), 3.14 (d, J = 6.6 Hz, 2H), 2.97 – 2.74 (m, 4H), 2.45 – 2.30 (m, 1H), 2.29 – 2.15 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 204.3, 148.2, 147.1, 139.0, 133.0, 129.7, 127.1, 121.0, 120.8, 73.1, 37.9, 36.5, 16.7; **HRMS ESI** Calcd for $C_{15}H_{14}N_2O_6$ [M+H]$^+$: 319.0925, Found: 319.0934.



1o

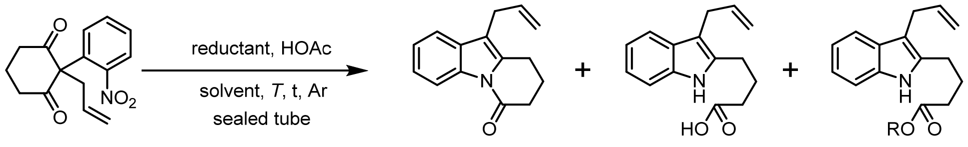
Substrate 1o 2-allyl-2-(2-nitrophenyl)-1H-indene-1,3(2H)-dione was obtained as a yellow solid. Mp: 119-120 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.04 – 7.94 (m, 2H), 7.91 – 7.79 (m, 4H), 7.72 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 5.61 – 5.42 (m, 1H), 5.14 – 4.93 (m, 2H), 3.01 (d, J = 6.9 Hz, 2H).; **^{13}C NMR (75 MHz, CDCl$_3$)** δ 198.2, 148.6, 140.4, 135.6, 133.4, 132.2, 130.8, 129.5, 128.8, 125.2, 123.5, 120.1, 61.4, 39.8.; **HRMS ESI** Calcd for $C_{18}H_{13}NO_4$ [M+H]$^+$: 308.0917, Found: 308.0930.

3. General procedure for the tandem reaction



In an oven-dried 10 mL tube equipped with a stir bar was added **1a** 2-allyl-2-(2-nitrophenyl)cyclohexane-1,3-dione (50 mg, 0.18 mmol) and zinc powder (120 mg, 1.83 mmol, 10 equiv). The tube was evacuated and refilled with dry argon (three times). HOAc (0.6 mL) was then added by syringe. The reaction mixture was required to heat to 80 °C in an oil bath and then stirred for 24 h under argon. After cooling to room temperature, the reaction mixture filtered through a plug of celite and washed with dichloromethane, the solution was evaporated *in vacuo*. The residue was diluted with dichloromethane, washed with saturated aq. $NaHCO_3$, the aqueous mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4, then concentrated under vacuum and purified by silica gel flash column chromatography (PE:EtOAc, 30:1) to afford **2a** 10-allyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (39 mg, 94%) as a white solid.

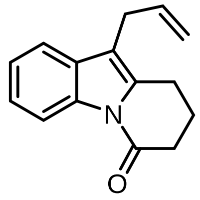
Table SI Optimization of the reaction conditions.[a]



Entry	Reductant (equiv)	Solvent	*T* (°C)	Time (h)	Yield (%)	**2a**: (**3a**+**4a**)[b]
1	Fe (10)	EtOH	80	3	10[c]	
2	Fe (10)	EtOH	80	12	58[d]	
3	Fe (10)	EtOH	80	24	89	1:1.3
4	Fe (10)	EtOH	40	24	80	1:7.7
5	Fe (10)	EtOH	60	24	86	1:16.7
6[e]	Fe (10)	EtOH	80	24	82	1:1.2
7	Zn (10)	EtOH	80	24	95	1:2.4
8	HCOOH (10)	EtOH	80	24	0	
9	Zn (10)	MeOH	80	24	88	1:2.5
10	Zn (10)	*i*-PrOH	80	24	90	6.5:1
11	Zn (10)	*t*-BuOH	80	24	92[f]	
12[e]	Zn (10)	EtOH	80	24	93	17.6:1
13	Zn (4)	EtOH	80	24	94	1:1.6
14	Zn (5)	EtOH	80	24	95	1.1:1
15	Zn (6)	EtOH	80	24	96	1:2.9
16	Zn (8)	EtOH	80	24	96	1:3.0
17[g]	Zn (10)	—	80	24	99[f]	
18[g]	Zn (3.5)	—	80	24	51[f]	
19[g]	Zn (4)	—	80	24	84[f]	
20[g]	Zn (4) AcOH (0.24mL)	—	80	24	36[f]	
21[g]	Zn (5) AcOH (0.30mL)	—	80	24	22[f]	

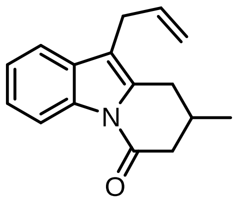
[a]Reaction conditions: **1a** (0.18 mmol), reductant, HOAc (0.6 mL), solvent (0.6 mL), Ar. The yield was determined by ^{1}H NMR using CH_3NO_2 as the internal standard. [b]The ratio was **2a** to (**3a**+**4a**). [c]Isolated yield of **4a**. [d]The starting material was recovered. [e]This reaction was carried in the air. [f]No product **3a** and product **4a** was detected. [g]Without solvent.

4. Characterization data for the products



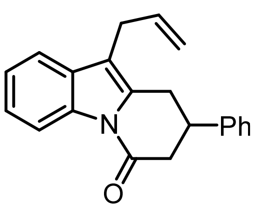
2a

Compound 2a 10-allyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 66-68 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.49 – 8.40 (m, 1H), 7.47 – 7.39 (m, 1H), 7.31 – 7.19 (m, 2H), 6.00 – 5.85 (m, 1H), 5.11 – 5.00 (m, 2H), 3.38 (d, J = 6.0 Hz, 2H), 2.91 – 2.82 (t, J = 6.3 Hz, 2H), 2.78 – 2.70 (t, J = 6.3 Hz, 2H), 2.10 – 1.98 (m, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 169.1, 135.4, 134.5, 133.9, 130.2, 124.0, 123.6, 118.1, 116.3, 115.4, 114.0, 34.4, 28.1, 21.7, 21.1; **HRMS ESI** Calcd for $C_{15}H_{15}NO$ [M+H]$^+$: 226.1226, Found: 226.1228.



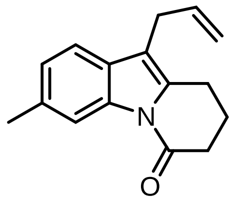
2b

Compound 2b 10-allyl-8-methyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 78-80 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.48 – 8.40 (m, 1H), 7.47 – 7.39 (m, 1H), 7.31 – 7.20 (m, 2H), 6.00 – 5.85 (m, 1H), 5.12 – 5.00 (m, 2H), 3.38 (d, J = 6.0 Hz, 2H), 3.08 – 2.97 (m, 1H), 2.85 – 2.74 (m, 1H), 2.51 – 2.37 (m, 2H), 2.36 – 2.22 (m, 1H), 1.13 (d, J = 6.3 Hz, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 168.9, 135.4, 134.5, 133.4, 130.4, 124.1, 123.6, 118.1, 116.2, 115.5, 114.2, 42.1, 29.6, 28.4, 28.1, 20.6; **HRMS ESI** Calcd for $C_{16}H_{17}NO$ [M+H]$^+$: 240.1383, Found: 240.1387.



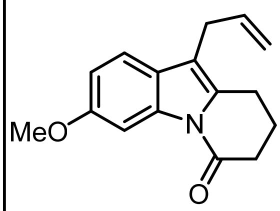
2c

Compound 2c 10-allyl-8-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 104-105 °C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.51 – 8.46 (m, 1H), 7.50 – 7.43 (m, 1H), 7.40 – 7.32 (m, 2H), 7.31 – 7.22 (m, 4H), 5.99 – 5.84 (m, 1H), 5.10 – 4.99 (m, 2H), 3.48 – 3.35 (m, 3H), 3.33 – 3.23 (m, 1H), 3.10 – 2.99 (m, 1H), 2.99 – 2.86 (m, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 168.4, 142.1, 135.2, 134.5, 132.9, 130.5, 128.9, 127.3, 126.5, 124.3, 123.8, 118.3, 116.3, 115.6, 114.6, 41.3, 38.9, 29.3, 28.1; **HRMS ESI** Calcd for $C_{21}H_{19}NO$ $[M+H]^+$: 302.1539, Found: 302.1541.



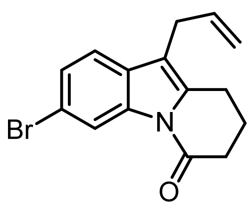
2d

Compound 2d 10-allyl-3-methyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 68-70 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 6.00 – 5.84 (m, 1H), 5.12 – 4.99 (m, 2H), 3.36 (d, J = 6.0 Hz, 2H), 2.86 (t, J = 6.3 Hz, 2H), 2.74 (t, J = 6.3 Hz, 2H), 2.46 (s, 3H), 2.10 – 1.99 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 169.3, 135.5, 135.0,134.2, 133.2, 127.9, 124.9, 117.7, 116.7, 115.4, 114.0, 34.5, 29.7, 28.2, 21.8, 21.2; **HRMS ESI** Calcd for $C_{16}H_{17}NO$ $[M+H]^+$: 240.1383, Found: 240.1385.



2e

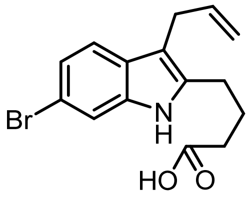
Compound 2e 10-allyl-3-methoxy-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 72-73 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.11 – 8.06 (m, 1H), 7.34 – 7.27 (m, 1H), 6.92 – 6.84 (m, 1H), 6.02 – 5.83 (m, 1H), 5.14 – 4.99 (m, 2H), 3.87 (d, J = 1.8 Hz, 3H), 3.36 (d, J = 6.0 Hz, 2H), 2.86 (t, J = 6.0 Hz, 2H), 2.75 (t, J = 6.6 Hz, 2H), 2.12 – 2.00 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 169.4, 157.7, 135.5, 135.4, 132.4, 124.0, 118.5, 115.4, 113.9, 112.4, 100.9, 55.7, 34.5, 28.2, 21.8, 21.2; **HRMS ESI** Calcd for $C_{16}H_{17}NO_2$ $[M+H]^+$: 256.1332, Found: 256.1333.



2f

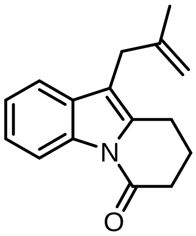
Compound 2f 10-allyl-3-bromo-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.63 (d, J = 1.5 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.27 (d, J = 8.1 Hz, 1H), 5.99 – 5.80 (m, 1H), 5.12 – 4.98 (m, 2H), 3.36 (d, J = 6.0 Hz, 2H), 2.94 – 2.83 (t, J = 6.3 Hz, 2H), 2.82 – 2.71 (t, J = 6.0 Hz, 2H), 2.16 – 2.01 (m, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 169.1, 135.1, 134.6, 132.3,129.1, 126.8, 119.4, 119.3 117.7, 115.7, 113.9, 34.3, 28.0, 21.7, 21.0; **HRMS**

ESI Calcd for $C_{15}H_{14}BrNO$ [M+H] $^{+}$: 304.0332, 306.0311, Found: 304.0335, 306.0313.



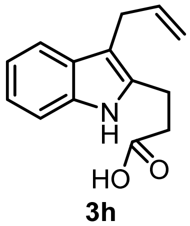
3f

Compound 3f 4-(3-allyl-6-bromo-1H-indol-2-yl)butanoic acid was obtained as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (s, 1H), 7.45 – 7.29 (m, 2H), 7.20 – 7.08 (m, 1H), 6.04 – 5.84 (m, 1H), 5.09 – 4.92 (m, 2H), 3.41 (d, J = 6.0 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.38 (t, J = 6.9 Hz, 2H), 2.08 – 1.88 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 178.9, 137.0, 136.1, 134.9, 127.5, 122.4, 119.8, 114.8, 114.7, 113.3, 109.9, 32.9, 28.4, 25.0, 24.6; **HRMS ESI** Calcd for $C_{15}H_{16}BrNO_2$ [M+H] $^{+}$: 322.0437, 324.0417, Found: 322.0439, 324.0419.



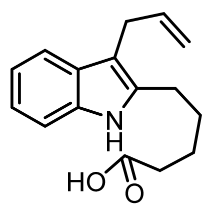
2g

Compound 2g 10-(2-methylallyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 70-72 ^{o}C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.49 – 8.41 (m, 1H), 7.48 – 7.41 (m, 1H), 7.32 – 7.19 (m, 2H), 4.76 (d, J = 15.6 Hz, 2H), 3.33 (s, 2H), 2.92 – 2.84 (t, J = 6.3 Hz, 2H), 2.80 – 2.72 (t, J = 6.6 Hz, 2H), 2.12 – 2.00 (m, 2H), 1.73 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ169.2, 143.1, 134.5, 134.2, 130.4, 124.0, 123.6, 118.2, 116.2, 114.1, 111.3, 34.4, 32.4, 22.3, 21.7, 21.1; **HRMS ESI** Calcd for $C_{16}H_{17}NO$ [M+H] $^{+}$: 240.1383, Found: 240.1387.



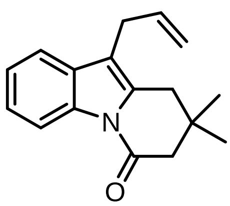
3h

Compound 3h 3-(3-allyl-1H-indol-2-yl)propanoic acid was obtained as a white solid. Mp: 103-105 ^{o}C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.15 – 7.01 (m, 2H), 6.05 – 5.89 (m, 1H), 5.10 – 4.94 (m, 2H), 3.46 (d, J = 6.0 Hz, 2H), 3.02 (t, J = 6.6 Hz, 2H), 2.70 (t, J = 6.9 Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 179.0, 137.4, 135.3, 133.7, 128.3, 121.4, 119.1, 118.5, 114.5, 110.5, 109.5, 34.1, 28.4, 20.6; **HRMS ESI** Calcd for $C_{14}H_{15}NO_2$ [M+H] $^{+}$: 230.1176, Found: 230.1176.



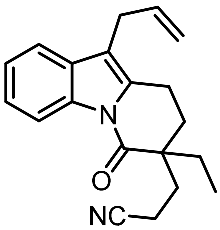
3i

Compound 3i 5-(3-allyl-1H-indol-2-yl)pentanoic acid was obtained as a yellow oil. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.87 (s, 1H), 7.54 – 7.45 (d, J = 6.9 Hz, 2H), 7.32 – 7.23 (m, 1H), 7.15 – 7.02 (m, 2H), 6.04 – 5.88 (m, 1H), 5.10 – 4.94 (m, 2H), 3.45 (m,2H), 2.74 (t, J = 6.9 Hz, 2H), 2.38 (t, J = 6.6 Hz, 2H), 1.83 – 1.62 (m, 4H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 179.2, 137.5, 135.3, 135.0, 128.6, 121.1, 119.1, 118.4, 114.4, 110.3, 109.2, 33.6, 29.0, 28.6, 25.7, 24.2; **HRMS ESI** Calcd for $C_{16}H_{19}NO_2$ [M+H]$^+$: 258.1489, Found: 258.1492.



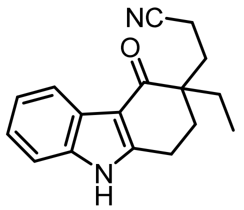
2j

Compound 2j 10-allyl-8,8-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one was obtained as a white solid. Mp: 75-77 ^{o}C. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.49 – 8.42 (m, 1H), 7.49 – 7.41 (m, 1H), 7.33 – 7.21 (m, 2H), 6.01 – 5.86 (m, 1H), 5.11 – 4.99 (m, 2H), 3.39 (d, J = 6.0 Hz, 2H), 2.72 (s, 2H), 2.59 (s, 2H), 1.09 (s, 6H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 168.7, 135.5, 134.5, 133.0, 130.5, 124.1, 123.6, 118.1, 116.3, 115.4, 115.1, 47.8, 35.4, 32.6, 28.0, 27.8; **HRMS ESI** Calcd for $C_{17}H_{19}NO$ [M+H]$^+$: 254.1539, Found: 254.1541.



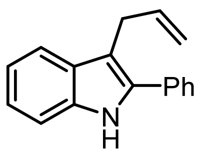
2k

Compound 2k 3-(9-allyl-3-ethyl-4-oxo-2,3,4,4a-tetrahydro-1H-fluoren-3-yl)propanenitrile was obtained as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.43 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 6.8 Hz, 1H), 7.33 – 7.26 (m, 2H), 6.02 – 5.86 (m, 1H), 5.08 (m, 2H), 3.39 (d, J = 5.6 Hz, 2H), 3.06 – 2.90 (m, 2H), 2.58 – 2.39 (m, 2H), 2.33 – 2.22 (m, 1H), 2.10 – 1.97 (m, 3H), 1.90 – 1.72 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 172.3, 135.1, 134.9, 132.6, 130.5, 124.4, 123.9, 119.8, 118.3, 116.5, 115.7, 114.6, 45.9, 30.9, 28.6, 28.1, 27.8, 17.7, 12.7, 8.0; **HRMS ESI** Calcd for $C_{20}H_{22}N_2O$ [M+H]$^+$: 307.1805, Found: 307.1808.



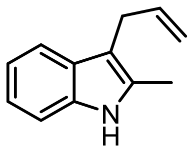
2k'

Compound 2k' 3-(3-ethyl-4-oxo-2,3,4,9-tetrahydro-1H-carbazol-3-yl)propanenitrile was obtained as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.39 (d, J = 16.0 Hz, 1H), 8.19 (dd, J = 5.6, 3.2 Hz, 1H), 7.36 (dd, J = 6.0, 2.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 3.13 – 2.93 (m, 2H), 2.43 (m, 2H), 2.27 – 2.17 (m, 1H), 2.14 (t, J = 6.4 Hz, 2H), 1.91 (m, 1H), 1.81 – 1.59 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 196.9, 149.8, 136.1, 125.0, 123.4, 122.5, 121.2, 120.4, 111.9, 111.2, 47.5, 31.1, 30.2, 27.3, 19.9, 12.6, 8.4; **HRMS ESI** Calcd for $C_{17}H_{18}N_2O$ [M+H]$^+$: 267.1492, Found: 267.1497.



2l

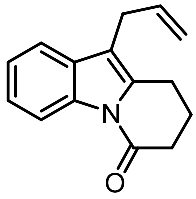
Compound 2l 3-allyl-2-phenyl-1H-indole was obtained as a yellow solid. Mp: 102-104 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.99 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.40 (m, 2H), 7.38 – 7.31 (m, 2H), 7.23 – 7.16 (m, 1H), 7.15 – 7.08 (m, 1H), 6.18 – 6.03 (m, 1H), 5.16 – 5.00 (m, 2H), 3.69 – 3.54 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 137.4, 136.0, 134.8, 133.0, 129.4, 128.8, 127.8, 127.6, 122.3, 119.6, 119.4, 115.1, 110.8, 110.5, 28.9; **HRMS ESI** Calcd for $C_{17}H_{15}N$ [M+H]$^+$: 234.1277, Found: 234.1285.



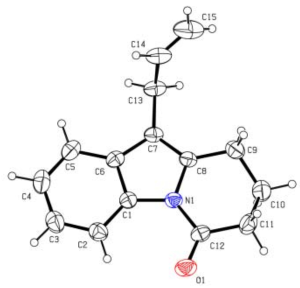
2m

Compound 2m 3-allyl-2-methyl-1H-indole was obtained as a yellow oil. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.63 – 7.38 (m, 2H), 7.21 – 6.98 (m, 3H), 6.02 – 5.85 (m, 1H), 5.09 – 4.88 (m, 2H), 3.47 – 3.34 (m, 2H), 2.25 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 137.3, 135.1, 131.3, 128.6, 120.8, 119.0, 118.1, 114.3, 110.1, 109.1, 28.5, 11.4; **HRMS ESI** Calcd for $C_{12}H_{13}N$ [M+H]$^+$: 172.1121, Found: 172.1127.

5. X-ray crystallography data for 2a and 3h

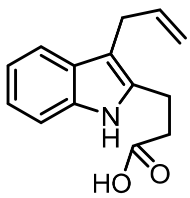


2a

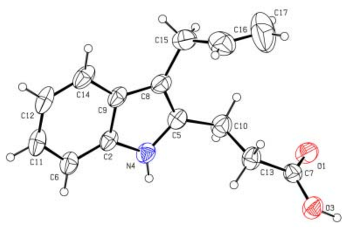


CCDC	2007714
Empirical formula	$C_{15}H_{15}NO$
Formula weight	172.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.1714(6)
b/Å	14.8338(9)
c/Å	9.4775(7)
α/°	90.00
β/°	108.911(7)
γ/°	90.00
Volume/Å^3	1219.78(14)
Z	4
ρ_{calc}g/cm^3	1.172
μ/mm^{-1}	0.076
F(000)	455.0
Crystal size/mm^3	0.17 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.57 to 28.54
Index ranges	$-11 \le h \le 9$, $-18 \le k \le 9$, $-6 \le l \le$

	12
Reflections collected	4748
Independent reflections	2772 [R_{int} = 0.0263, R_{sigma} = 0.0563]
Data/restraints/parameters	2772/0/154
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0620, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.1113, wR_2 = 0.1753
Largest diff. peak/hole / e Å^{-3}	0.18/-0.25



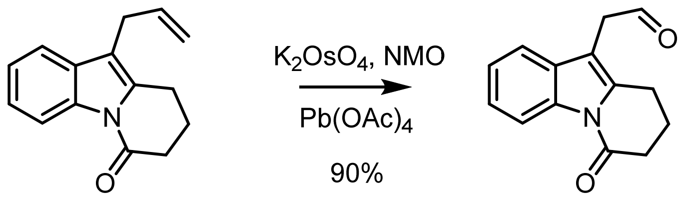
3h



CCDC	2007713
Empirical formula	$C_{14}H_{15}NO_2$
Formula weight	229.27
Temperature/K	292.60(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	25.4782(8)
b/Å	13.9470(4)
c/Å	7.1727(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2548.79(13)
Z	8

ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	0.643
F(000)	976.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.333 to 69.690
Index ranges	-28 ≤ h ≤ 30, -16 ≤ k ≤ 16, -8 ≤ l ≤ 5
Reflections collected	5439
Independent reflections	2188 [R_{int} = 0.0264, R_{sigma} = 0.0281]
Data/restraints/parameters	2188/0/158
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0589, wR_2 = 0.1593
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1683
Largest diff. peak/hole / e Å^{-3}	0.18/-0.28

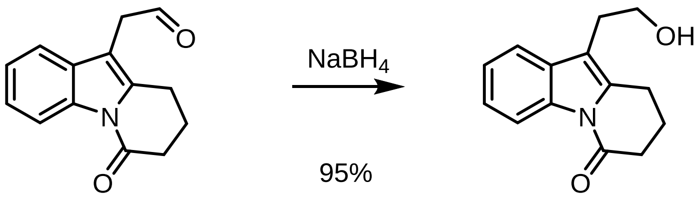
6. Formal Synthesis of Goniomitine



2a **5**

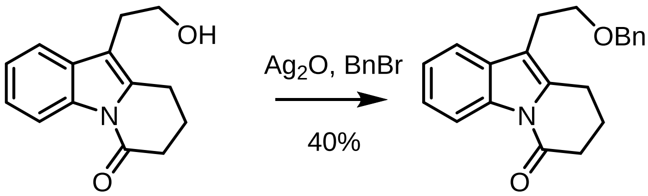
To the solution of compound **2a** (277mg, 1.23 mmol) and 4-Methylmorpholine N-oxide (720mg, 6.15mmol) in THF/H_2O=1:1 was added $K_2OsO_4 \cdot 2H_2O$ and stirred at the room temperature for 2 h, the reaction was quenched with saturated solution of $Na_2S_2O_3$ and stirred for another 1h, and then extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4, then concentrated under vacuum and used without further purification.

To the solution of the crude product in ethyl acetate (350mL) was added $Pb(OAc)_4$. After completion, the reaction mixture filtered through a plug of silica gel and washed with ethyl acetate, the solution was evaporated in vacuo, then purified by silica gel flash column chromatography to afford Compound **5** **2-(6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)acetaldehyde** as a white solid. Mp: 153-155 ^{o}C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.70 (t, J = 2.1 Hz, 1H), 8.50 – 8.44 (m, 1H), 7.41 – 7.24 (m, 3H), 3.70 (d, J = 2.1 Hz, 2H), 2.91 (t, J = 6.3 Hz, 2H), 2.83 – 2.75 (t, J = 6.6 Hz, 2H), 2.17 – 2.05 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.8, 169.1, 136.1, 134.5, 129.6, 124.7, 124.0, 117.5, 116.5, 107.0, 39.1, 34.3, 21.9, 21.0; **HRMS ESI** Calcd for $C_{14}H_{13}NO_2$ [M+H]$^+$: 228.1019, Found: 228.1020.



5 6

0°C, to the solution of compound **5** (285 mg, 1.25 mmol) in MeOH was added $NaBH_4$ (57 mg, 1.51 mmol) and stirred at the room temperature for 2 h, the reaction was quenched with saturated solution of NH4Cl. The solution was concentrated under reduced pressure, and then extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4, then concentrated under vacuum and purified by silica gel flash column chromatography to afford Compound **6** **10-(2-hydroxyethyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one** as a little red solid. Mp: 95-97 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.42 – 8.35 (m, 1H), 7.49 – 7.42 (m, 1H), 7.31 – 7.21 (m, 2H), 3.84 (t, J = 6.6 Hz, 2H), 2.87 (t, J = 6.0 Hz, 4H), 2.57 – 2.49 (t, J = 6.3 Hz, 2H), 2.48 – 2.40 (broad, 1H), 2.01 – 1.91 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 169.4, 135.0, 134.4, 130.2, 124.1, 123.7, 117.8, 116.3, 113.1, 61.8, 33.9, 27.5, 21.6, 20.9; **HRMS ESI** Calcd for $C_{14}H_{15}NO_2$ $[M+H]^+$: 230.1176, Found: 230.1177.



6 7

To the solution of compound **6** (12 mg, 0.0524 mmol) in CH_2Cl_2 was added Silver oxide (18mg, 0.00786 mmol) and benzyl bromide (7 uL, 0.0576mmol) then stirred at the room temperature for 16 h. The reaction mixture filtered through a plug of celite and washed with dichloromethane, the solution was evaporated in vacuo, then purified by silica gel flash column chromatography to afford Compound **7** **10-(2-(benzyloxy)ethyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 6.8 Hz, 1H), 7.28 (m, 7H), 4.50 (s, 2H), 3.68 (t, J = 6.8 Hz, 2H), 2.94 (m, 4H), 2.76 (t, J = 6.4 Hz, 2H), 2.05 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.3, 138.3, 134.6, 134.6, 130.3, 128.3, 127.6, 127.5, 124.1, 123.7, 117.8, 116.4, 113.5, 73.1, 69.6, 34.5, 24.9, 21.9, 21.2; **HRMS ESI** Calcd for $C_{21}H_{21}NO_2$ $[M+H]^+$: 320.1645, Found: 320.1646.

7. Computational Details

All calculations were carried out with the Gaussian 09 programs. 1 The geometries of all the species were fully optimized by using density functional theory (DFT) of the B3LYP method 2 with the 6-31G(d, p) basis set for all atoms. Vibrational frequency calculations done at the B3LYP/6-31G (d, p) level of theory were used to characterize all of the stationary points as either minima (the number of imaginary frequencies (NIMAG=0) or transition states (NIMAG=1)).

8. The Cartesian coordinates of the stationary points

1a-Int-1

6	-2.608294000	0.774186000	-0.316739000
6	-2.518950000	1.156163000	1.168351000
6	-1.167967000	1.834586000	1.545923000
6	-0.089783000	0.966475000	1.036809000
6	0.012582000	0.551516000	-0.398543000
6	-1.391866000	0.059439000	-0.894039000
7	0.810693000	0.337200000	1.746153000
6	1.571796000	-0.576255000	0.964472000
6	1.093621000	-0.501715000	-0.348673000
6	2.594001000	-1.421887000	1.369492000
6	3.150341000	-2.236662000	0.378334000
6	2.686815000	-2.186508000	-0.941930000
6	1.656565000	-1.316552000	-1.322885000
6	0.386174000	1.768599000	-1.342408000
6	1.638047000	2.494710000	-0.932967000
6	1.675577000	3.791209000	-0.623140000

8	-1.445646000	-0.740157000	-1.800532000
1	-3.470567000	0.128036000	-0.495197000
1	-2.749358000	1.673522000	-0.934408000
1	-2.635589000	0.259611000	1.779090000
1	-3.326348000	1.848833000	1.418656000
1	-1.093600000	1.988917000	2.625717000
1	-1.091684000	2.814848000	1.058982000
1	0.896449000	0.428261000	2.753786000
1	2.946656000	-1.456328000	2.395055000
1	3.952926000	-2.917753000	0.639949000
1	3.135224000	-2.836236000	-1.686162000
1	1.297920000	-1.293980000	-2.345326000
1	0.491473000	1.332765000	-2.342499000
1	-0.455432000	2.467183000	-1.381265000
1	2.555836000	1.909900000	-0.920701000
1	2.605528000	4.284064000	-0.358759000
1	0.786020000	4.416470000	-0.649214000
8	-1.494006000	-1.752437000	1.212859000
1	-2.259304000	-2.091019000	0.699359000
1	-0.872724000	-2.491211000	1.226303000
8	-3.490571000	-2.328948000	-0.604451000
1	-4.053701000	-3.089180000	-0.795652000
1	-3.024736000	-2.108586000	-1.426136000

1a-TS-1

6	2.715919000	0.270886000	-0.082546000
6	2.562507000	0.940171000	-1.452163000
6	1.307029000	1.863138000	-1.530759000
6	0.153125000	1.089172000	-1.033921000
6	0.141231000	0.407335000	0.296744000
6	1.466114000	-0.468566000	0.434999000
7	-0.925944000	0.777155000	-1.710690000
6	-1.767520000	-0.122930000	-0.995583000
6	-1.138581000	-0.393970000	0.226447000
6	-2.980813000	-0.674199000	-1.380948000
6	-3.575342000	-1.555046000	-0.471599000
6	-2.963218000	-1.854937000	0.751982000
6	-1.739768000	-1.277701000	1.117503000
6	0.149829000	1.432699000	1.490048000
6	-0.977663000	2.427757000	1.454436000
6	-0.802791000	3.749329000	1.413954000
8	1.541249000	-1.098597000	1.548950000
1	3.535538000	-0.452895000	-0.110814000
1	2.985896000	1.004741000	0.685188000
1	2.485408000	0.175780000	-2.228975000
1	3.440856000	1.551948000	-1.674244000
1	1.145252000	2.234760000	-2.546477000

1	1.448871000	2.730268000	-0.873924000
1	-1.117161000	1.105070000	-2.652680000
1	-3.448157000	-0.442435000	-2.332306000
1	-4.525500000	-2.014046000	-0.722605000
1	-3.448932000	-2.546943000	1.431975000
1	-1.265399000	-1.515773000	2.062875000
1	0.113123000	0.812070000	2.391680000
1	1.108511000	1.958602000	1.507859000
1	-1.987505000	2.022214000	1.490535000
1	-1.644438000	4.434388000	1.418332000
1	0.187766000	4.198756000	1.405134000
8	1.298464000	-1.622005000	-0.822607000
1	2.080138000	-2.483882000	-0.283999000
1	0.404315000	-1.986502000	-0.713205000
8	2.756818000	-2.925467000	0.551906000
1	2.558701000	-3.839596000	0.800571000
1	2.351743000	-2.216882000	1.262356000

1a-Int-2

6	-2.530128000	0.480917000	0.477539000
6	-2.166251000	1.366255000	1.675222000
6	-0.838814000	2.154232000	1.444035000
6	0.174721000	1.206022000	0.938972000

6	-0.058240000	0.308716000	-0.244273000
6	-1.400325000	-0.490714000	0.088656000
7	1.316903000	0.916858000	1.505376000
6	1.990721000	-0.155955000	0.851732000
6	1.178607000	-0.566565000	-0.210941000
6	3.213846000	-0.730111000	1.163446000
6	3.624839000	-1.787536000	0.345551000
6	2.831376000	-2.225246000	-0.721480000
6	1.601521000	-1.619861000	-1.013929000
6	-0.186929000	1.116029000	-1.580827000
6	0.977176000	2.028691000	-1.862256000
6	0.870021000	3.348012000	-2.025590000
8	-1.670216000	-1.252512000	-1.034414000
1	-3.404426000	-0.129966000	0.720098000
1	-2.797082000	1.087180000	-0.392794000
1	-2.055103000	0.744702000	2.567328000
1	-2.959512000	2.091860000	1.873308000
1	-0.506328000	2.659207000	2.355547000
1	-0.998165000	2.921351000	0.675510000
1	1.664321000	1.377206000	2.341698000
1	3.822576000	-0.386947000	1.993473000
1	4.573461000	-2.274362000	0.544468000
1	3.176806000	-3.050557000	-1.335265000
1	0.989369000	-1.969844000	-1.837742000

1	-0.297580000	0.361221000	-2.365766000
1	-1.113968000	1.694768000	-1.568390000
1	1.954262000	1.557030000	-1.955656000
1	1.733940000	3.964886000	-2.251267000
1	-0.088588000	3.859348000	-1.969596000
8	-1.180867000	-1.292059000	1.237350000
1	-4.311056000	-3.113846000	-0.286337000
1	-0.640476000	-2.045961000	0.958007000
8	-4.188649000	-2.258755000	-0.719125000
1	-4.772777000	-2.272113000	-1.488818000
1	-2.562981000	-1.663874000	-0.941069000

1a-TS-2

6	2.143692000	-1.586583000	-0.090077000
6	1.870096000	-1.894554000	-1.563526000
6	1.194686000	-0.702500000	-2.301722000
6	0.026764000	-0.264900000	-1.494826000
6	0.085636000	0.399590000	-0.226756000
6	0.906414000	-1.256117000	0.732467000
7	-1.221844000	-0.702677000	-1.709301000
6	-2.084012000	-0.299626000	-0.675817000
6	-1.305918000	0.424603000	0.248008000
6	-3.449218000	-0.519979000	-0.519924000
6	-4.042573000	0.018158000	0.621462000

6	-3.290824000	0.743900000	1.560597000
6	-1.922775000	0.953366000	1.386596000
6	1.047635000	1.540022000	0.081693000
6	0.729236000	2.792607000	-0.700794000
6	1.598318000	3.424218000	-1.489037000
8	1.064449000	-0.799356000	1.973862000
1	2.579155000	-2.471285000	0.391773000
1	2.869990000	-0.777389000	0.018876000
1	1.230998000	-2.779479000	-1.639381000
1	2.812850000	-2.132154000	-2.063814000
1	0.895599000	-1.003934000	-3.309758000
1	1.900072000	0.127833000	-2.401872000
1	-1.489257000	-1.307550000	-2.475251000
1	-4.028329000	-1.080418000	-1.246628000
1	-5.105395000	-0.125425000	0.784997000
1	-3.786933000	1.150862000	2.435498000
1	-1.355282000	1.516323000	2.120467000
1	0.972187000	1.744671000	1.157892000
1	2.085373000	1.252270000	-0.111435000
1	-0.283310000	3.178083000	-0.592625000
1	1.324948000	4.325580000	-2.027853000
1	2.620174000	3.073712000	-1.617236000
8	-0.042458000	-2.204361000	0.645119000
1	4.017732000	-0.128515000	2.955757000

1	-0.653228000	-2.108324000	1.394491000
8	3.417687000	0.363946000	2.378562000
1	3.451628000	1.279358000	2.688033000
1	1.933557000	-0.330546000	2.112766000

1a-Int-3

6	2.326170000	-1.765091000	-0.134387000
6	1.959708000	-1.835152000	-1.627814000
6	1.316402000	-0.530670000	-2.156669000
6	0.081673000	-0.169695000	-1.394016000
6	-0.093775000	0.726835000	-0.348027000
6	1.176886000	-1.685908000	0.822444000
7	-1.093187000	-0.871629000	-1.584022000
6	-2.046911000	-0.452976000	-0.674041000
6	-1.447878000	0.559559000	0.121788000
6	-3.368063000	-0.871765000	-0.485043000
6	-4.090818000	-0.256806000	0.530924000
6	-3.517474000	0.749175000	1.336475000
6	-2.207473000	1.164553000	1.141031000
6	0.873210000	1.779716000	0.133500000
6	0.649412000	3.128555000	-0.517187000
6	1.588108000	3.816766000	-1.164242000
8	1.216331000	-1.075708000	1.950476000
1	2.858590000	-2.686673000	0.146532000
1	3.005112000	-0.935102000	0.077876000

1	1.290994000	-2.685371000	-1.794635000
1	2.878459000	-2.044956000	-2.183697000
1	1.090460000	-0.658904000	-3.221581000
1	2.036224000	0.290664000	-2.094398000
1	-1.241049000	-1.564911000	-2.301075000
1	-3.815695000	-1.639719000	-1.108432000
1	-5.119695000	-0.554694000	0.705225000
1	-4.116639000	1.208279000	2.116008000
1	-1.782344000	1.949291000	1.760109000
1	0.751537000	1.882254000	1.224003000
1	1.910691000	1.472821000	-0.048406000
1	-0.360078000	3.528201000	-0.438943000
1	1.376812000	4.780628000	-1.615609000
1	2.605588000	3.445625000	-1.268987000
8	0.163573000	-2.471700000	0.613439000
1	3.801786000	0.296285000	3.051993000
1	-0.525726000	-2.343939000	1.293153000
8	3.214801000	0.456538000	2.298861000
1	3.027699000	1.406253000	2.287429000
1	2.026885000	-0.460256000	2.090963000

1a-TS-3

6	1.297631000	-2.296206000	-1.586085000
6	0.497436000	-3.165929000	-0.593264000

6	-0.822949000	-2.475024000	-0.183975000
6	-0.711190000	-0.980012000	-0.228231000
6	-1.632426000	-0.004456000	-0.390167000
6	1.713472000	-1.021365000	-0.913876000
7	0.634554000	-0.382677000	-0.102073000
6	0.432103000	1.064975000	-0.263965000
6	-0.943965000	1.286995000	-0.408468000
6	1.372261000	2.081947000	-0.226915000
6	0.887257000	3.387511000	-0.370999000
6	-0.480936000	3.639746000	-0.525481000
6	-1.409705000	2.597670000	-0.540296000
6	-3.124381000	-0.188726000	-0.488779000
6	-3.811940000	-0.024667000	0.851047000
6	-4.566733000	-0.959267000	1.425617000
8	2.818574000	-0.541978000	-0.879179000
1	2.200471000	-2.790114000	-1.949339000
1	0.672486000	-2.042042000	-2.453192000
1	1.115635000	-3.362524000	0.289443000
1	0.291394000	-4.136468000	-1.049856000
1	-1.129373000	-2.815917000	0.813007000
1	-1.628571000	-2.770421000	-0.864435000
1	1.074693000	-0.518185000	1.059280000
1	2.428319000	1.888561000	-0.093266000
1	1.588353000	4.215153000	-0.358261000

1	-0.824916000	4.663390000	-0.630563000
1	-2.468937000	2.804157000	-0.653012000
1	-3.519177000	0.547536000	-1.201447000
1	-3.355989000	-1.177132000	-0.898428000
1	-3.666228000	0.932846000	1.349458000
1	-5.052327000	-0.787601000	2.380883000
1	-4.743977000	-1.923718000	0.955859000
8	3.976917000	0.284676000	1.590134000
1	2.613945000	-0.311892000	2.071837000
1	4.073901000	0.070508000	0.648010000
8	1.662480000	-0.661029000	2.168863000
1	1.233196000	-0.194548000	2.901190000
1	4.815842000	0.074658000	2.021840000

2a

6	-0.380945000	-3.194261000	-0.594160000
6	-1.710446000	-2.925955000	0.127575000
6	-2.351427000	-1.635132000	-0.399209000
6	-1.373898000	-0.501925000	-0.408568000
6	-1.558142000	0.844035000	-0.336237000
6	0.569437000	-2.028663000	-0.493234000
7	0.028035000	-0.780062000	-0.541992000
6	0.716491000	0.457869000	-0.608200000
6	-0.251885000	1.474353000	-0.459781000

6	2.054290000	0.740261000	-0.876757000
6	2.432778000	2.089302000	-0.926062000
6	1.492830000	3.112582000	-0.718400000
6	0.149549000	2.814805000	-0.497658000
6	-2.877739000	1.558915000	-0.164113000
6	-3.499409000	1.345664000	1.198285000
6	-4.735465000	0.889517000	1.400614000
8	1.802009000	-2.218795000	-0.384534000
1	0.139646000	-4.070215000	-0.202619000
1	-0.561539000	-3.376737000	-1.663129000
1	-1.532121000	-2.843709000	1.205743000
1	-2.384688000	-3.772906000	-0.020349000
1	-3.217719000	-1.350896000	0.204051000
1	-2.718478000	-1.803330000	-1.422330000
1	3.603167000	-0.513202000	1.484846000
1	2.768855000	-0.043612000	-1.091296000
1	3.457974000	2.344219000	-1.179615000
1	1.812526000	4.148463000	-0.766623000
1	-0.574840000	3.613853000	-0.378922000
1	-2.716422000	2.631788000	-0.326237000
1	-3.581643000	1.239405000	-0.941038000
1	-2.872497000	1.601362000	2.051859000
1	-5.142321000	0.774179000	2.400158000
1	-5.394447000	0.635966000	0.573500000

8	3.436479000	-1.530984000	1.282236000
1	3.332436000	1.450569000	1.121198000
1	2.703267000	-1.748504000	0.521957000
8	3.841999000	0.883610000	1.729974000
1	3.715857000	1.225060000	2.626375000
1	4.266735000	-2.000165000	1.110432000

1k-Int-1’

6	-1.670938000	0.809788000	-0.110738000
6	-1.441991000	1.049233000	1.401558000
6	-0.095723000	1.745669000	1.771848000
6	0.972675000	0.919839000	1.183127000
6	1.032696000	0.628170000	-0.280255000
6	-0.397704000	0.252055000	-0.807895000
7	1.852455000	0.193507000	1.819685000
6	2.558755000	-0.683630000	0.951007000
6	2.057230000	-0.486665000	-0.339521000
6	3.555524000	-1.594229000	1.263850000
6	4.058139000	-2.348780000	0.199571000
6	3.570180000	-2.176490000	-1.100945000
6	2.569158000	-1.238940000	-1.388341000
6	1.512641000	1.887153000	-1.122006000
6	2.842433000	2.436331000	-0.684100000
6	3.017246000	3.680038000	-0.235686000

8	-0.456146000	-0.404879000	-1.823401000
1	0.001991000	1.834198000	2.857229000
1	-0.054332000	2.754960000	1.347590000
1	1.951759000	0.185272000	2.830024000
1	3.926102000	-1.724120000	2.275206000
1	4.836844000	-3.079830000	0.388059000
1	3.974826000	-2.783081000	-1.904180000
1	2.196045000	-1.118142000	-2.398623000
1	1.551764000	1.531911000	-2.157962000
1	0.754834000	2.672353000	-1.077759000
1	3.697374000	1.769359000	-0.772333000
1	3.999095000	4.049065000	0.042566000
1	2.194022000	4.386381000	-0.154902000
8	-0.316623000	-1.977606000	1.335318000
1	-0.390511000	-2.523766000	0.521292000
1	-0.675277000	-2.539850000	2.033524000
8	-0.673778000	-3.248219000	-1.092977000
1	-1.445405000	-3.802241000	-1.269707000
1	-0.705882000	-2.535940000	-1.748304000
1	-2.247472000	1.667791000	1.805909000
1	-1.461917000	0.083758000	1.911415000
6	-2.004508000	2.141276000	-0.872907000
6	-3.380455000	2.768733000	-0.614837000
1	-1.907697000	1.945764000	-1.946499000

1	-1.242556000	2.890167000	-0.628455000
1	-3.426431000	3.743969000	-1.107602000
1	-4.190123000	2.164212000	-1.029637000
1	-3.580411000	2.936267000	0.448210000
6	-2.763297000	-0.285686000	-0.338251000
6	-4.009411000	-0.250939000	0.579218000
1	-2.291208000	-1.258872000	-0.194071000
1	-3.086234000	-0.244847000	-1.381773000
1	-3.728543000	-0.279688000	1.637049000
1	-4.615246000	0.646672000	0.435171000
6	-4.844362000	-1.425714000	0.311582000
7	-5.465707000	-2.377703000	0.078797000

1k-TS-1’

6	-1.898328000	0.805263000	0.174696000
6	-1.554223000	1.260995000	1.606890000
6	-0.203442000	2.036725000	1.725257000
6	0.847385000	1.166669000	1.160608000
6	0.814931000	0.610616000	-0.213346000
6	-0.718520000	-0.041785000	-0.469587000
7	1.790420000	0.578651000	1.872714000
6	2.497762000	-0.395775000	1.117384000
6	1.914532000	-0.426771000	-0.157004000

6	3.563563000	-1.198889000	1.504586000
6	4.055199000	-2.079762000	0.538703000
6	3.492977000	-2.133385000	-0.744443000
6	2.424765000	-1.306689000	-1.108811000
6	1.101034000	1.648306000	-1.353402000
6	2.464075000	2.283845000	-1.273750000
6	2.663312000	3.593958000	-1.124925000
8	-0.878417000	-0.440444000	-1.658369000
1	0.002192000	2.293442000	2.768589000
1	-0.255005000	2.971202000	1.157663000
1	1.960456000	0.771037000	2.854818000
1	3.996913000	-1.148238000	2.498085000
1	4.886163000	-2.730871000	0.787594000
1	3.896830000	-2.830594000	-1.470939000
1	2.000430000	-1.357344000	-2.105171000
1	0.972155000	1.077476000	-2.280123000
1	0.341835000	2.427013000	-1.361484000
1	3.322257000	1.621468000	-1.369303000
1	3.662145000	4.017647000	-1.100184000
1	1.837213000	4.297448000	-1.047296000
8	-0.645945000	-1.399623000	0.544932000
1	-0.571981000	-2.383254000	-0.375029000
1	0.193935000	-1.436707000	1.025247000
8	-0.596331000	-2.900116000	-1.359989000

1	-1.445693000	-3.403282000	-1.349764000
1	-0.752254000	-2.016142000	-1.847664000
1	-2.339068000	1.920917000	1.987613000
1	-1.510223000	0.398277000	2.278369000
6	-2.153963000	2.046715000	-0.753812000
6	-3.430367000	2.869504000	-0.512568000
1	-2.142079000	1.689592000	-1.787472000
1	-1.316770000	2.741251000	-0.662722000
1	-3.377331000	3.788186000	-1.103764000
1	-4.338782000	2.347703000	-0.821255000
1	-3.551431000	3.170570000	0.533947000
6	-3.242310000	0.009381000	0.157556000
6	-3.470618000	-1.268845000	1.017339000
1	-3.470437000	-0.222457000	-0.886534000
1	-4.006693000	0.714180000	0.486221000
1	-2.835348000	-1.304865000	1.904959000
1	-4.509496000	-1.278563000	1.365491000
6	-3.265058000	-2.502005000	0.261807000
7	-3.090509000	-3.447514000	-0.388646000

1k-Int-2'

6	-1.967500000	0.712095000	0.155347000
6	-1.702019000	1.239380000	1.585181000

6	-0.370544000	2.043932000	1.728680000
6	0.718524000	1.211055000	1.180172000
6	0.723885000	0.670582000	-0.213347000
6	-0.719345000	-0.135803000	-0.319513000
7	1.672770000	0.658035000	1.889174000
6	2.443409000	-0.263245000	1.129457000
6	1.894020000	-0.294346000	-0.156132000
6	3.549696000	-1.001574000	1.523441000
6	4.128719000	-1.816137000	0.546350000
6	3.610079000	-1.860596000	-0.753522000
6	2.493213000	-1.098313000	-1.119787000
6	0.953430000	1.734728000	-1.333866000
6	2.258979000	2.478504000	-1.206531000
6	2.347546000	3.799520000	-1.047571000
8	-0.906267000	-0.542261000	-1.628476000
1	-0.191489000	2.306221000	2.775470000
1	-0.430292000	2.976793000	1.158131000
1	1.810663000	0.829593000	2.880443000
1	3.952380000	-0.951622000	2.529748000
1	4.997570000	-2.414209000	0.799019000
1	4.090432000	-2.491957000	-1.494009000
1	2.110976000	-1.134834000	-2.134356000
1	0.904392000	1.177116000	-2.275884000
1	0.137886000	2.452410000	-1.359748000

1	3.170684000	1.887526000	-1.269040000
1	3.307945000	4.300656000	-0.981462000
1	1.466172000	4.435506000	-1.002827000
8	-0.610797000	-1.197839000	0.596506000
1	-0.913099000	-3.616898000	-1.114824000
1	-0.149122000	-1.948293000	0.170485000
8	-0.076692000	-3.135974000	-1.302472000
1	0.551008000	-3.770762000	-1.668822000
1	-0.561267000	-1.454126000	-1.751900000
6	-2.267120000	1.899690000	-0.819871000
6	-3.639734000	2.583856000	-0.702373000
1	-2.136155000	1.540713000	-1.844701000
1	-1.521959000	2.683103000	-0.668791000
1	-3.639936000	3.487457000	-1.318546000
1	-4.459626000	1.956419000	-1.058256000
1	-3.871538000	2.896220000	0.321938000
6	-3.253991000	-0.179229000	0.141161000
6	-3.380247000	-1.476015000	0.987141000
1	-3.478447000	-0.422186000	-0.901057000
1	-4.064863000	0.464519000	0.486190000
1	-2.859838000	-1.407485000	1.945633000
1	-4.441369000	-1.634321000	1.213090000
6	-2.915813000	-2.682065000	0.303672000
7	-2.569787000	-3.635292000	-0.260670000

1	-2.517003000	1.898024000	1.898083000
1	-1.666057000	0.407699000	2.293455000

1k-TS-2’

6	-2.007726000	0.635378000	0.184403000
6	-1.765805000	1.092241000	1.639286000
6	-0.469211000	1.939438000	1.829980000
6	0.671738000	1.170041000	1.273448000
6	0.904371000	0.885635000	-0.125193000
6	-0.770578000	-0.173161000	-0.325021000
7	1.423016000	0.363230000	2.025402000
6	2.264898000	-0.442291000	1.235074000
6	1.992531000	-0.121732000	-0.104445000
6	3.217295000	-1.377444000	1.624754000
6	3.925581000	-2.008837000	0.601612000
6	3.683104000	-1.701639000	-0.746703000
6	2.719920000	-0.758249000	-1.113018000
6	0.980170000	1.966711000	-1.207879000
6	2.268298000	2.755433000	-1.147156000
6	2.322494000	4.079058000	-1.004576000
8	-0.823009000	-0.417750000	-1.649792000
1	-0.321865000	2.149535000	2.893544000
1	-0.557459000	2.900734000	1.317761000

1	1.335164000	0.281458000	3.030940000
1	3.409389000	-1.605353000	2.668137000
1	4.684136000	-2.741875000	0.855041000
1	4.267237000	-2.196503000	-1.516098000
1	2.553340000	-0.520162000	-2.159069000
1	0.881236000	1.460160000	-2.176078000
1	0.145633000	2.661756000	-1.143990000
1	3.192452000	2.187612000	-1.236010000
1	3.269167000	4.609200000	-0.981720000
1	1.424583000	4.687236000	-0.921293000
8	-0.543253000	-1.242221000	0.483353000
1	-0.634854000	-3.511434000	-1.438217000
1	-0.066490000	-1.948990000	-0.011527000
8	0.158046000	-2.934650000	-1.497583000
1	0.911072000	-3.468785000	-1.779797000
1	-0.369538000	-1.267203000	-1.865035000
6	-2.322363000	1.856328000	-0.738833000
6	-3.696527000	2.523426000	-0.564828000
1	-2.207878000	1.540639000	-1.779403000
1	-1.573890000	2.630120000	-0.569123000
1	-3.720343000	3.443414000	-1.155340000
1	-4.521261000	1.899324000	-0.915990000
1	-3.902270000	2.805625000	0.473312000
6	-3.273052000	-0.294175000	0.106101000

6	-3.329588000	-1.676195000	0.811204000
1	-3.518852000	-0.436396000	-0.950160000
1	-4.091114000	0.286812000	0.535750000
1	-2.820154000	-1.675841000	1.778504000
1	-4.381051000	-1.916023000	1.007125000
6	-2.787509000	-2.774397000	0.010020000
7	-2.361535000	-3.630089000	-0.647986000
1	-2.614240000	1.693005000	1.977982000
1	-1.705022000	0.223494000	2.301637000

1k-Int-3’

6	-2.179282000	0.706276000	0.111287000
6	-1.763089000	1.089068000	1.563938000
6	-0.391581000	1.808929000	1.724370000
6	0.767672000	0.975618000	1.266361000
6	1.497195000	1.008067000	0.087726000
6	-1.229441000	-0.331700000	-0.436879000
7	1.124040000	-0.154695000	1.986252000
6	2.018781000	-0.911917000	1.263790000
6	2.279836000	-0.204943000	0.057395000
6	2.576412000	-2.166617000	1.535228000
6	3.385396000	-2.733664000	0.556648000
6	3.647027000	-2.061269000	-0.660101000
6	3.116999000	-0.795326000	-0.908610000

6	1.586629000	2.114899000	-0.933835000
6	2.892211000	2.878332000	-0.844555000
6	2.980767000	4.196471000	-0.679974000
8	-0.941243000	-0.331307000	-1.697599000
1	-0.280784000	2.067911000	2.784462000
1	-0.395515000	2.757250000	1.182213000
1	0.719808000	-0.424454000	2.869452000
1	2.378773000	-2.685919000	2.467978000
1	3.831898000	-3.707066000	0.732464000
1	4.305555000	-2.521458000	-1.390409000
1	3.346654000	-0.277923000	-1.835636000
1	1.482466000	1.686600000	-1.942219000
1	0.763049000	2.825013000	-0.815489000
1	3.801020000	2.283474000	-0.921003000
1	3.940964000	4.699602000	-0.629374000
1	2.097785000	4.825812000	-0.595091000
8	-0.864977000	-1.295784000	0.335462000
1	0.173644000	-3.461853000	-1.775579000
1	-0.313416000	-1.978700000	-0.161367000
8	0.468250000	-2.593325000	-1.461502000
1	1.445475000	-2.588675000	-1.382842000
1	-0.385656000	-1.121790000	-1.939243000
6	-2.225100000	1.935137000	-0.843648000
6	-3.144235000	3.079415000	-0.399920000

1	-2.536292000	1.587441000	-1.833260000
1	-1.211708000	2.319949000	-0.972508000
1	-3.110737000	3.875554000	-1.148107000
1	-4.189029000	2.769596000	-0.309528000
1	-2.837220000	3.519292000	0.553268000
6	-3.621059000	0.047756000	0.108078000
6	-3.820919000	-1.406367000	0.605332000
1	-4.017958000	0.113279000	-0.908985000
1	-4.245804000	0.690131000	0.733248000
1	-3.363322000	-1.577298000	1.585364000
1	-4.895789000	-1.577466000	0.728488000
6	-3.303900000	-2.413292000	-0.329913000
7	-2.824784000	-3.153599000	-1.085302000
1	-2.543523000	1.743794000	1.961220000
1	-1.773263000	0.190047000	2.188634000

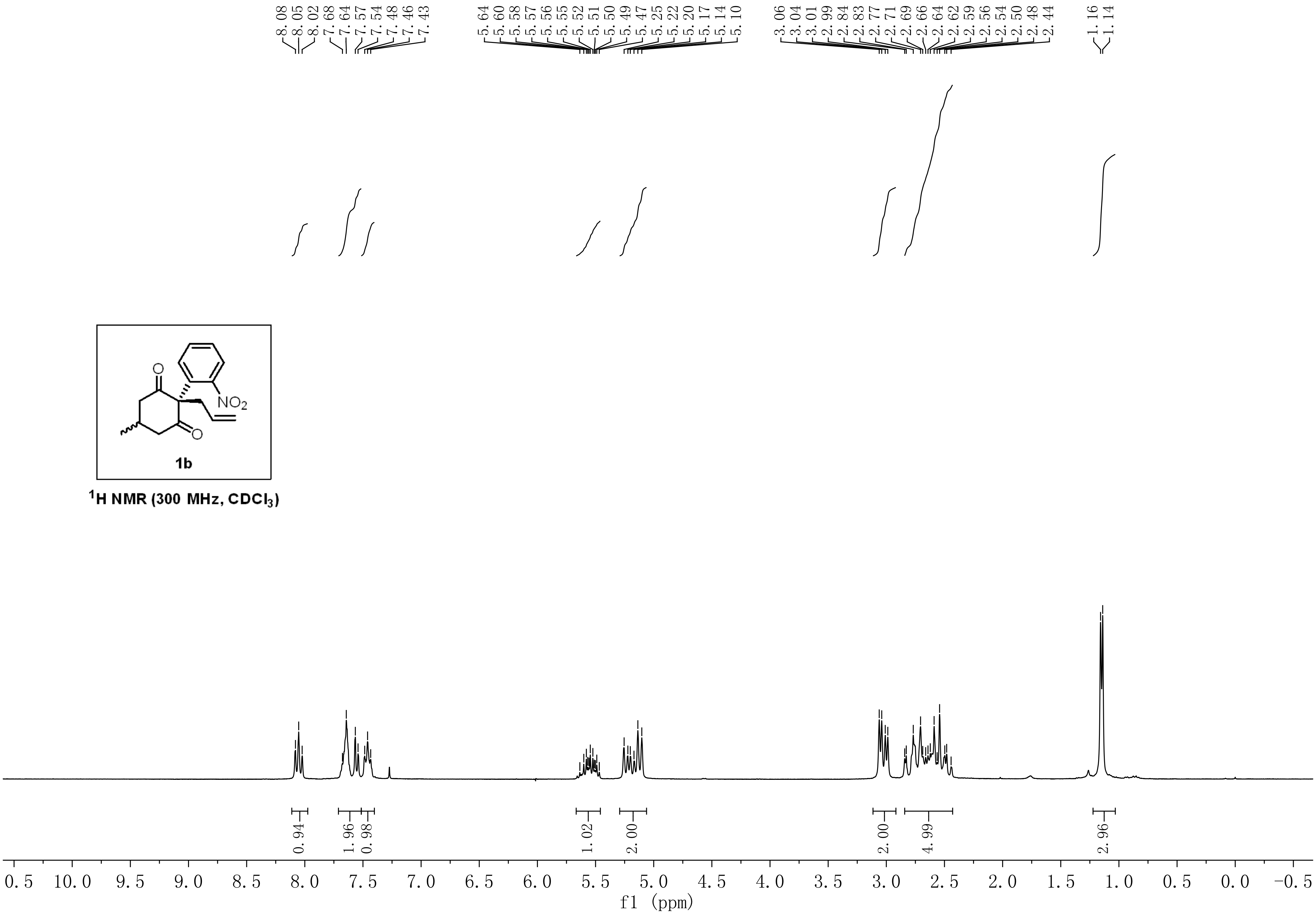
9. References

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

B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

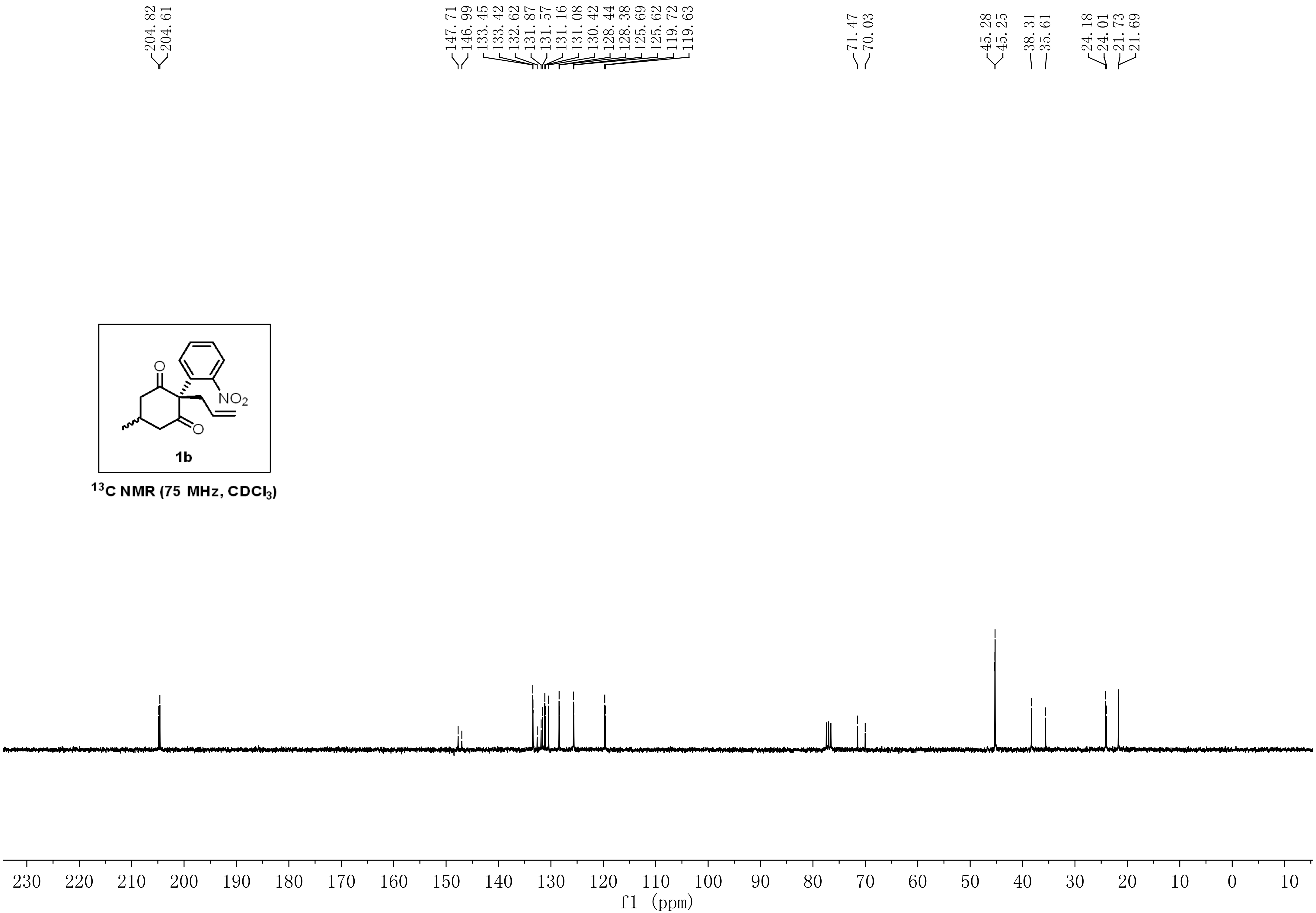
[2] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

10. NMR Spectra of New Compounds



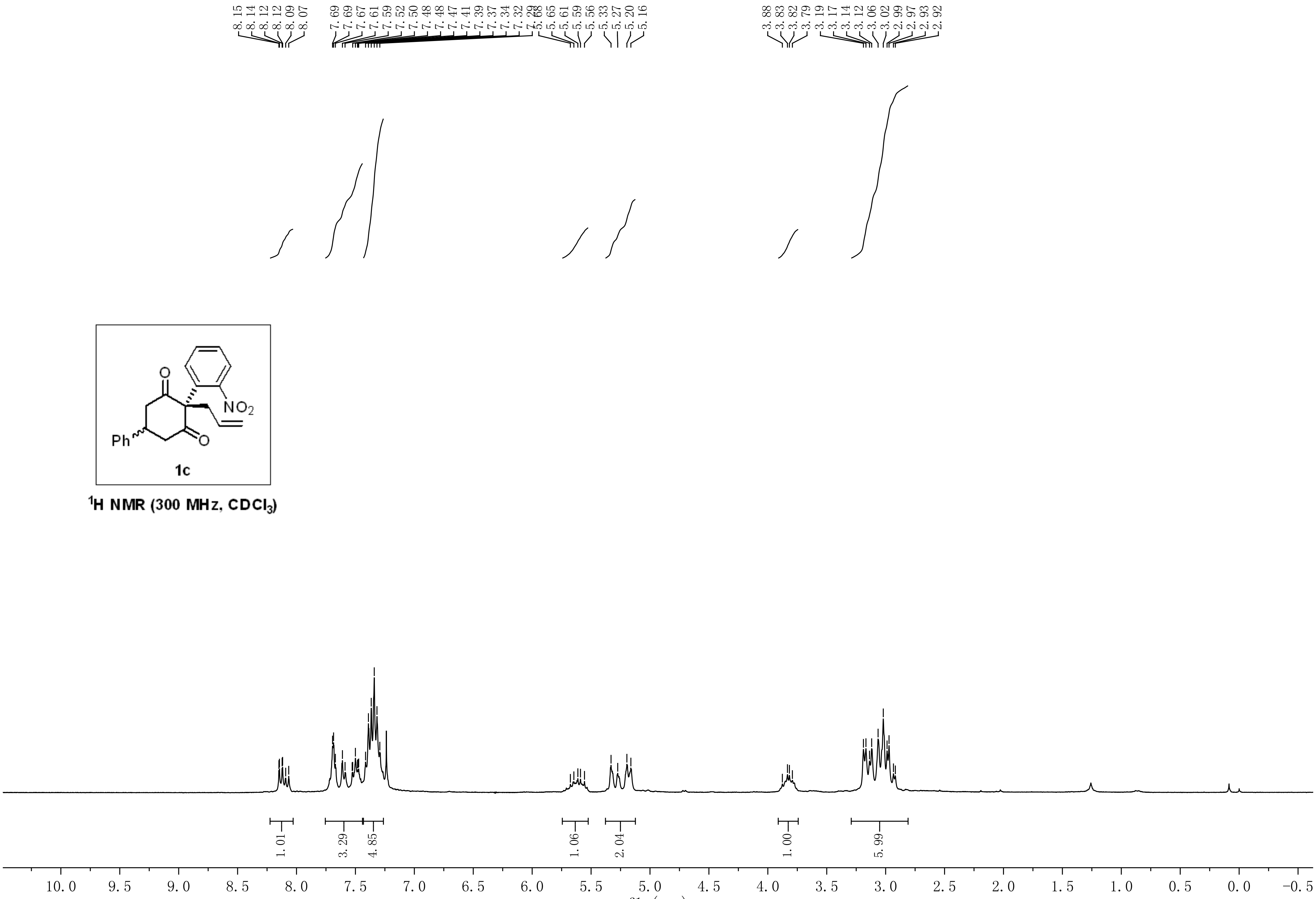
1b

^{1}H NMR (300 MHz, $CDCl_3$)



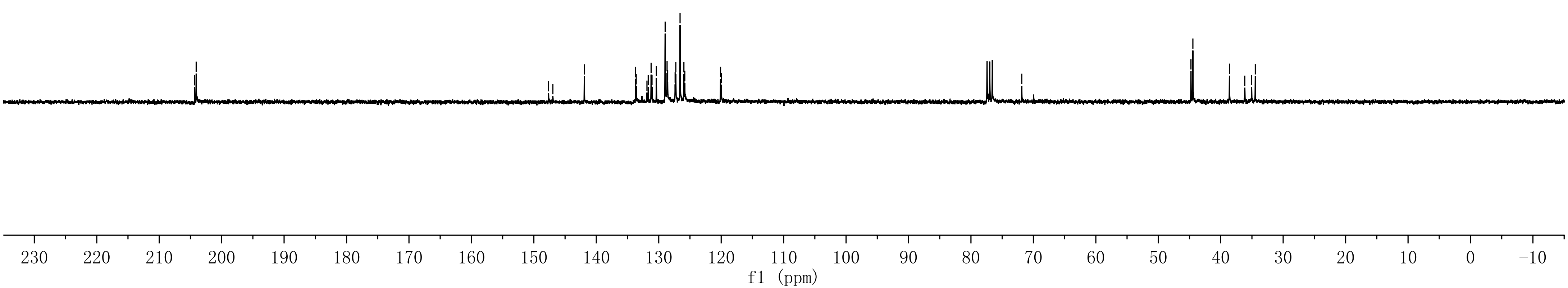
1b

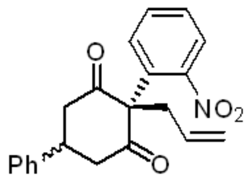
^{13}C NMR (75 MHz, $CDCl_3$)



1c

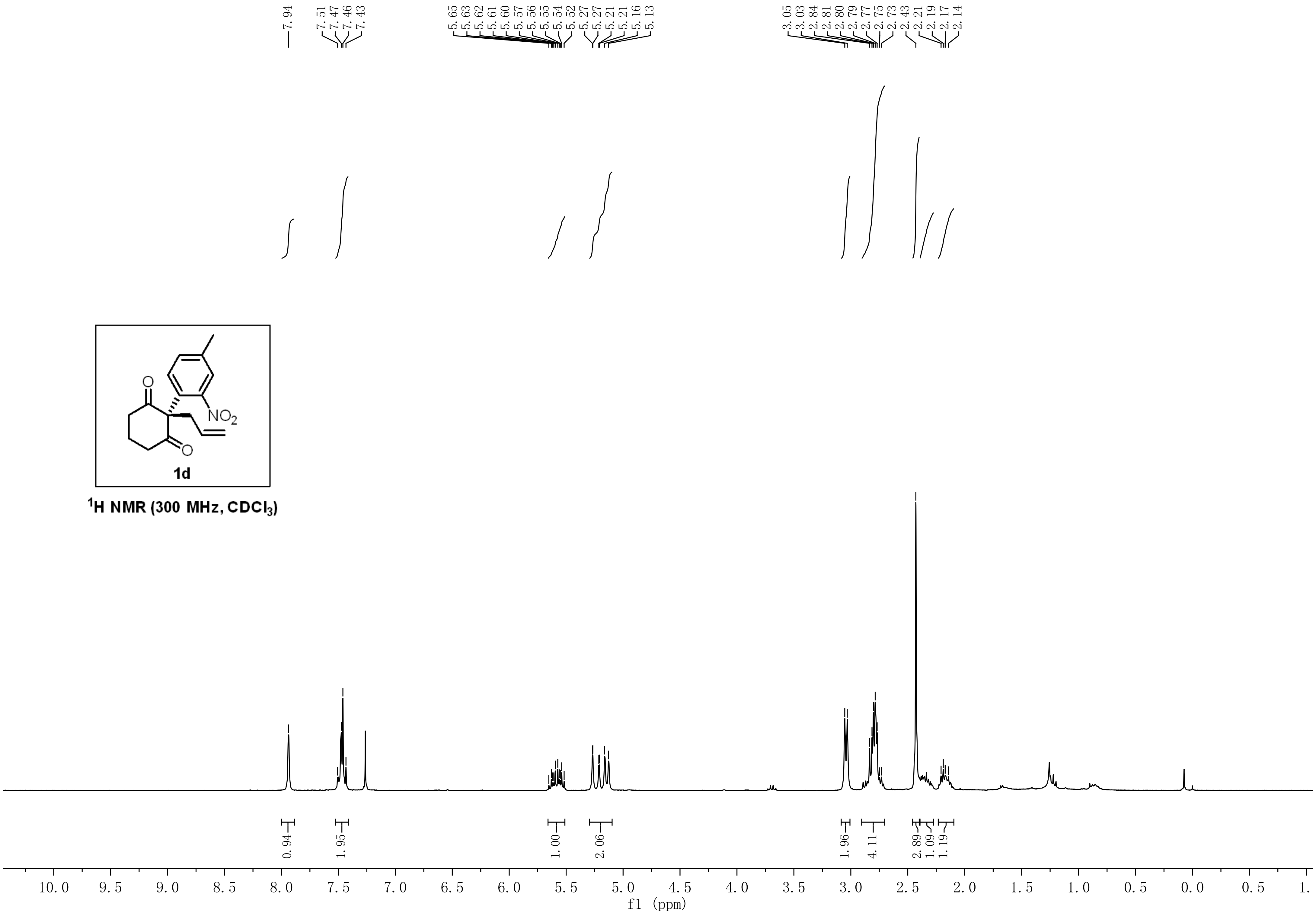
^{1}H NMR (300 MHz, $CDCl_3$)



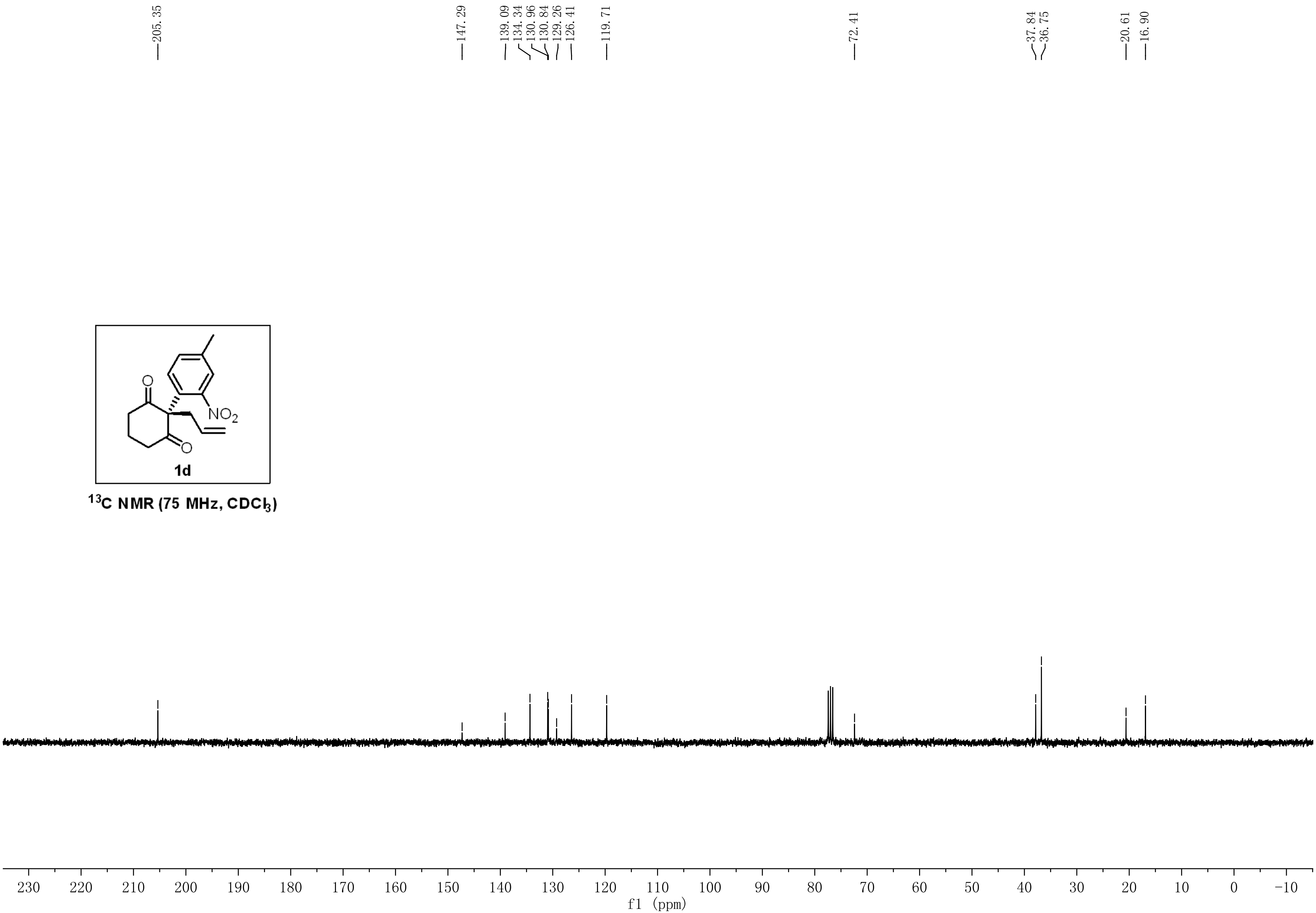


1c

^{13}C NMR (75 MHz, CDCl$_3$)

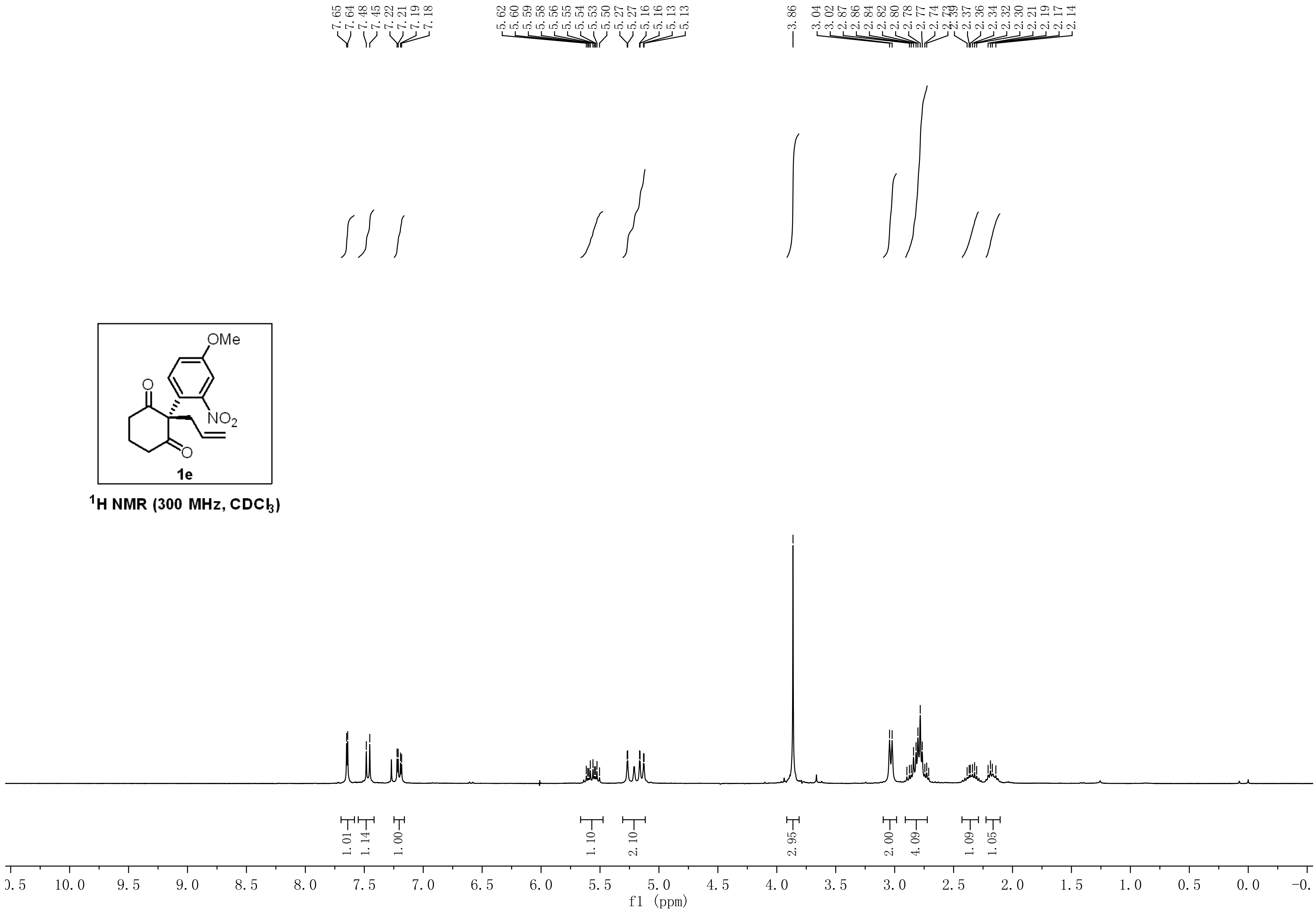


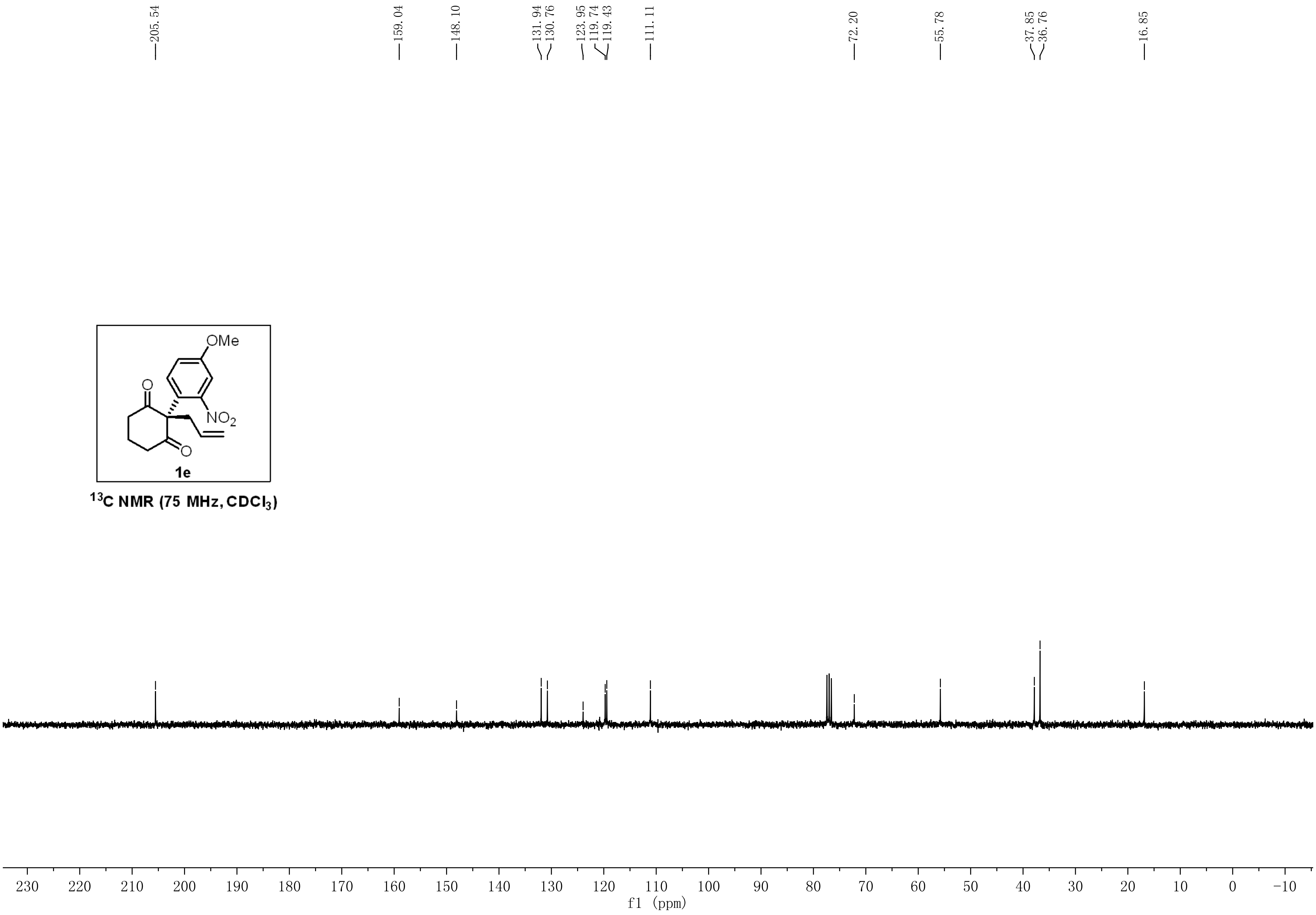
^1H NMR (300 MHz, $CDCl_3$)



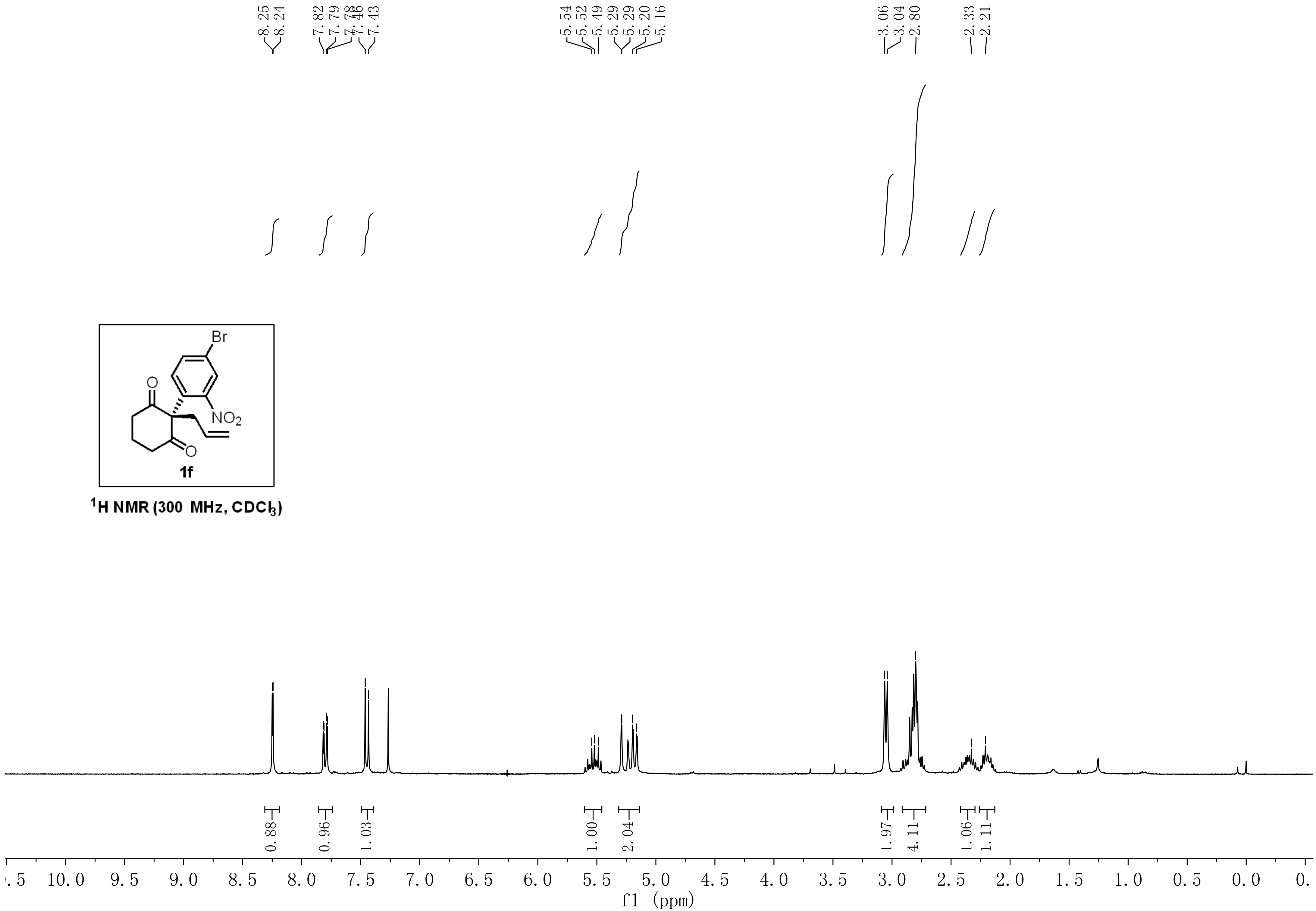
1d

^{13}C NMR (75 MHz, $CDCl_3$)

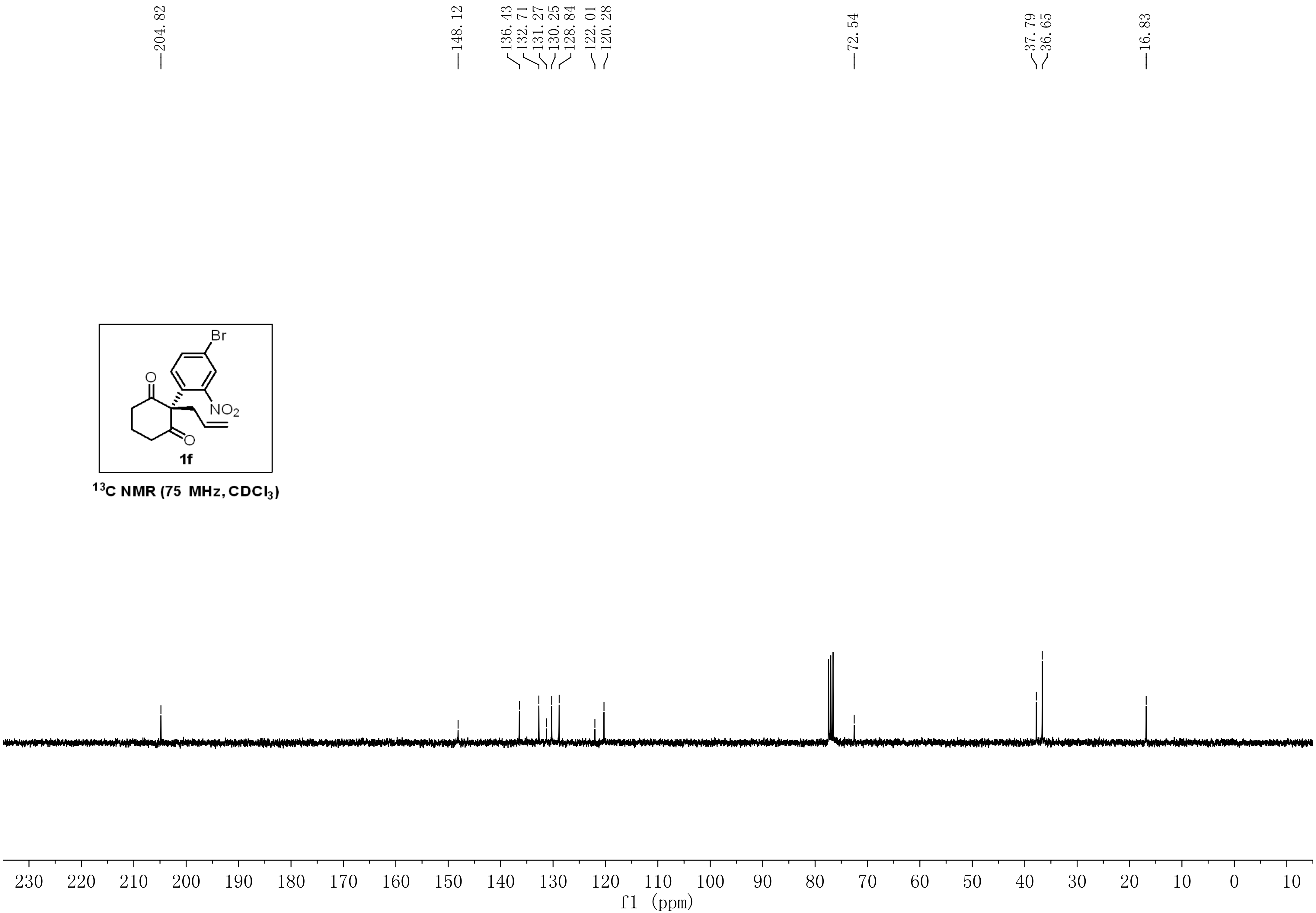

7.65 7.64 7.48 7.45 7.22 7.21 7.19 7.18
5.62 5.60 5.59 5.58 5.56 5.55 5.54 5.53 5.50 5.27 5.27 5.16 5.16 5.13 5.13
3.86
3.04 3.02 2.87 2.86 2.84 2.82 2.80 2.78 2.77 2.74 2.73 2.39 2.37 2.36 2.34 2.32 2.30 2.21 2.19 2.17 2.14
OMe
O
NO2
O
1e
1H NMR (300 MHz, CDCl3)
1.01 1.14 1.00 1.10 2.10 2.95 2.00 4.09 1.09 1.05
0.5 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)



^{13}C NMR (75 MHz, $CDCl_3$)

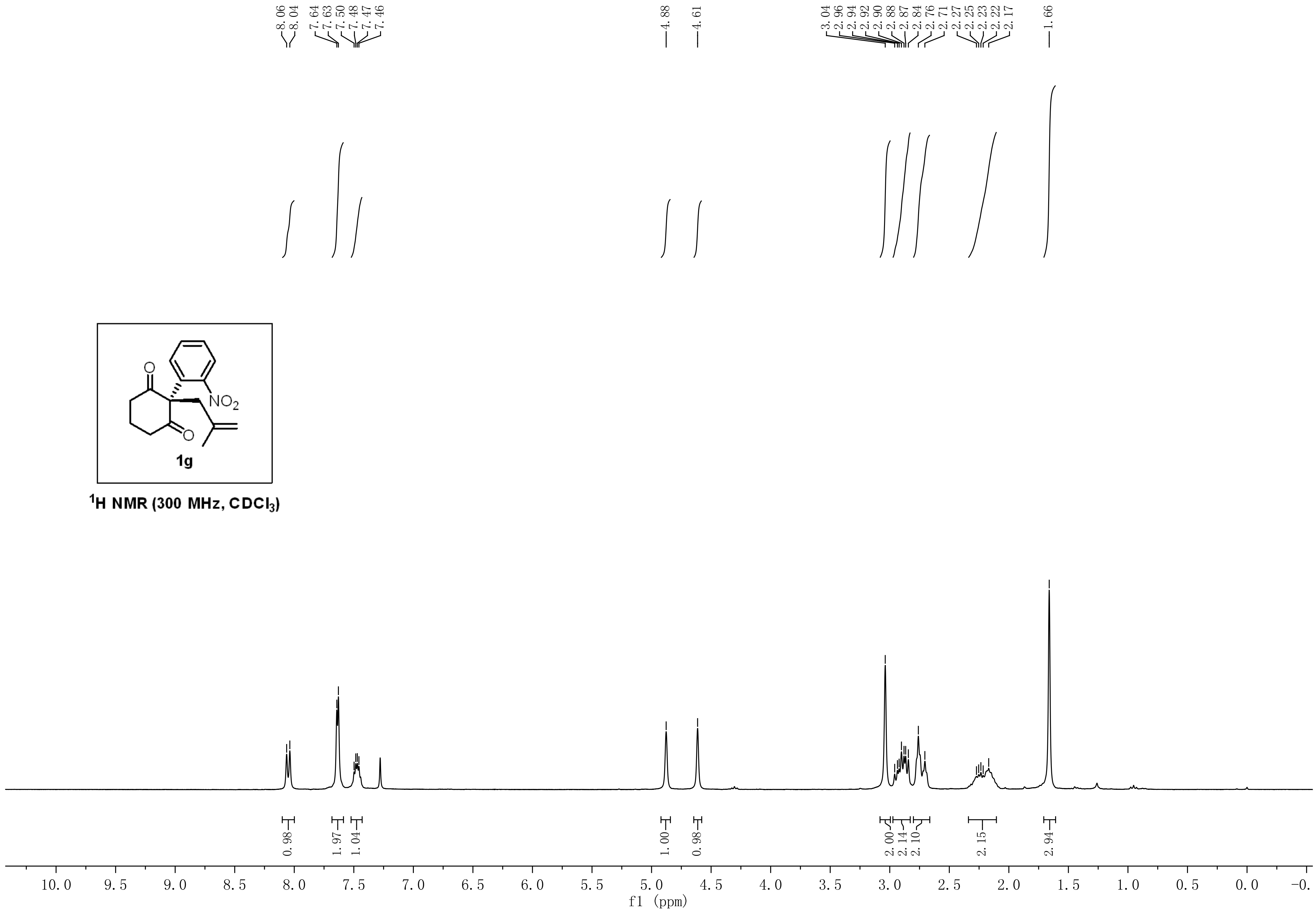


8.25
8.24
7.82
7.79
7.78
7.46
7.43
5.54
5.52
5.49
5.29
5.29
5.20
5.16
3.06
3.04
2.80
2.33
2.21
Br
O
NO_2
O
1f
^{1}H NMR (300 MHz, $CDCl_3$)
0.88
0.96
1.03
1.00
2.04
1.97
4.11
1.06
1.11
5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)

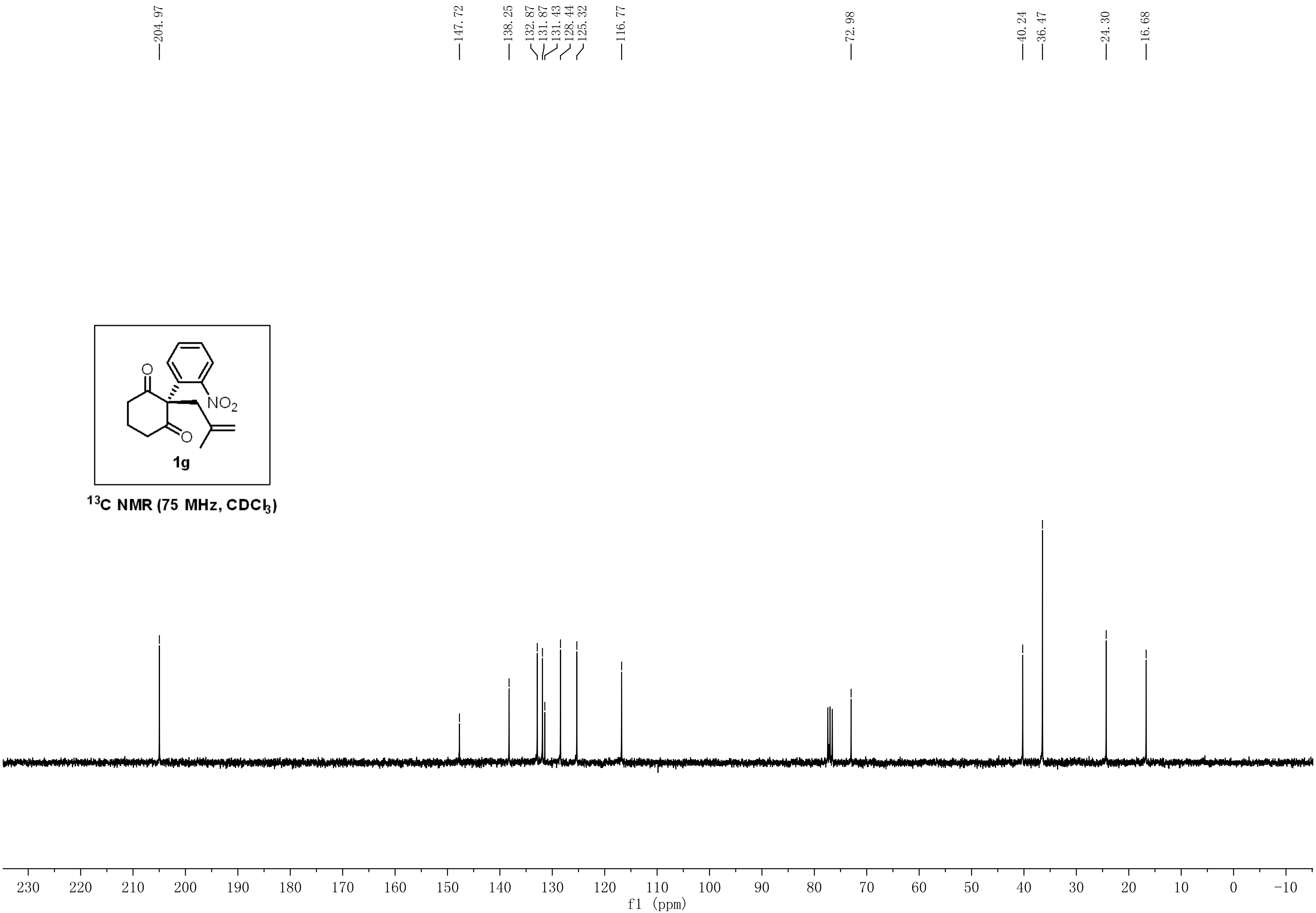


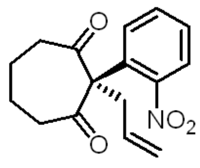
1f

^{13}C NMR (75 MHz, $CDCl_3$)



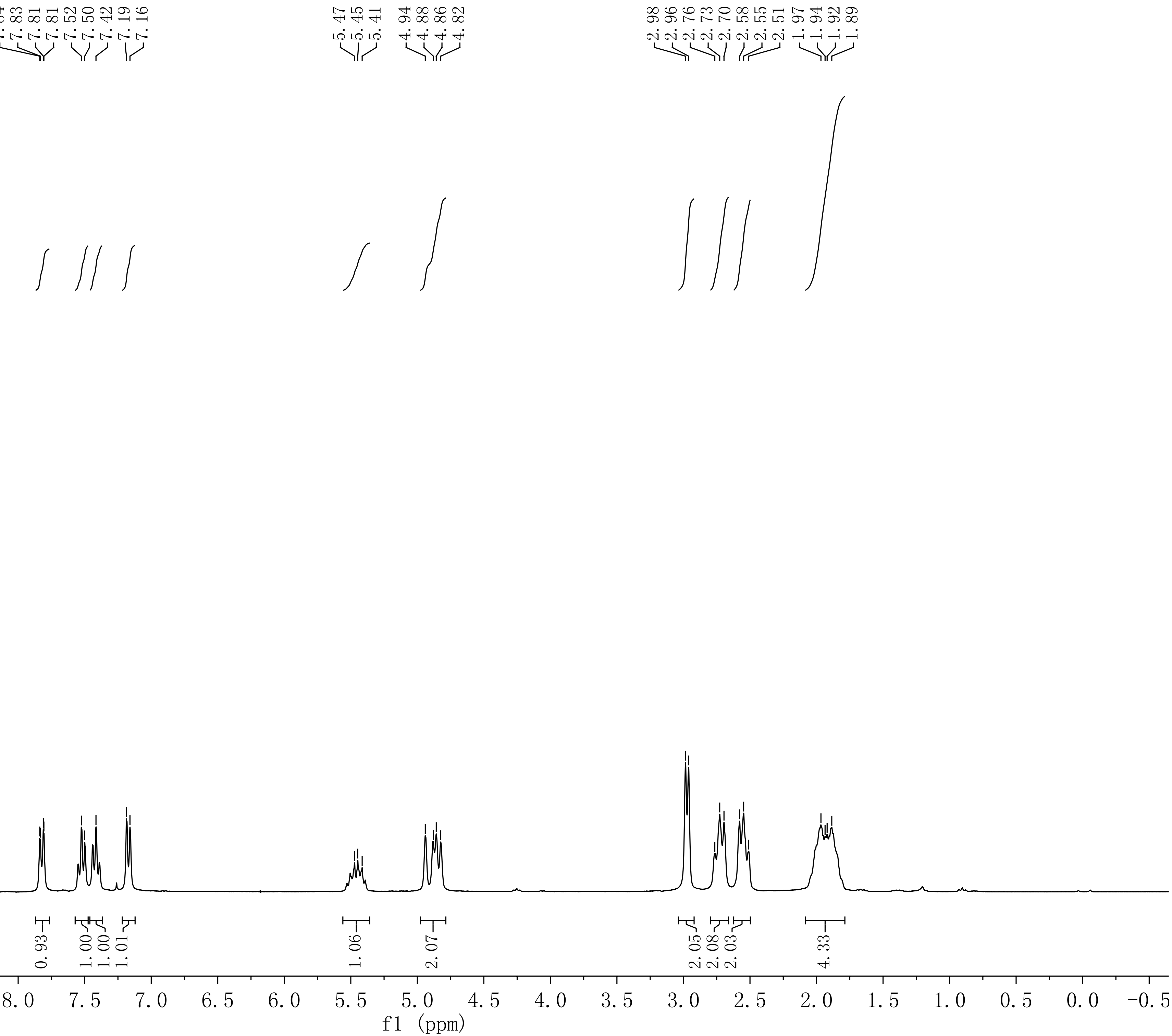
^{1}H NMR (300 MHz, $CDCl_3$)

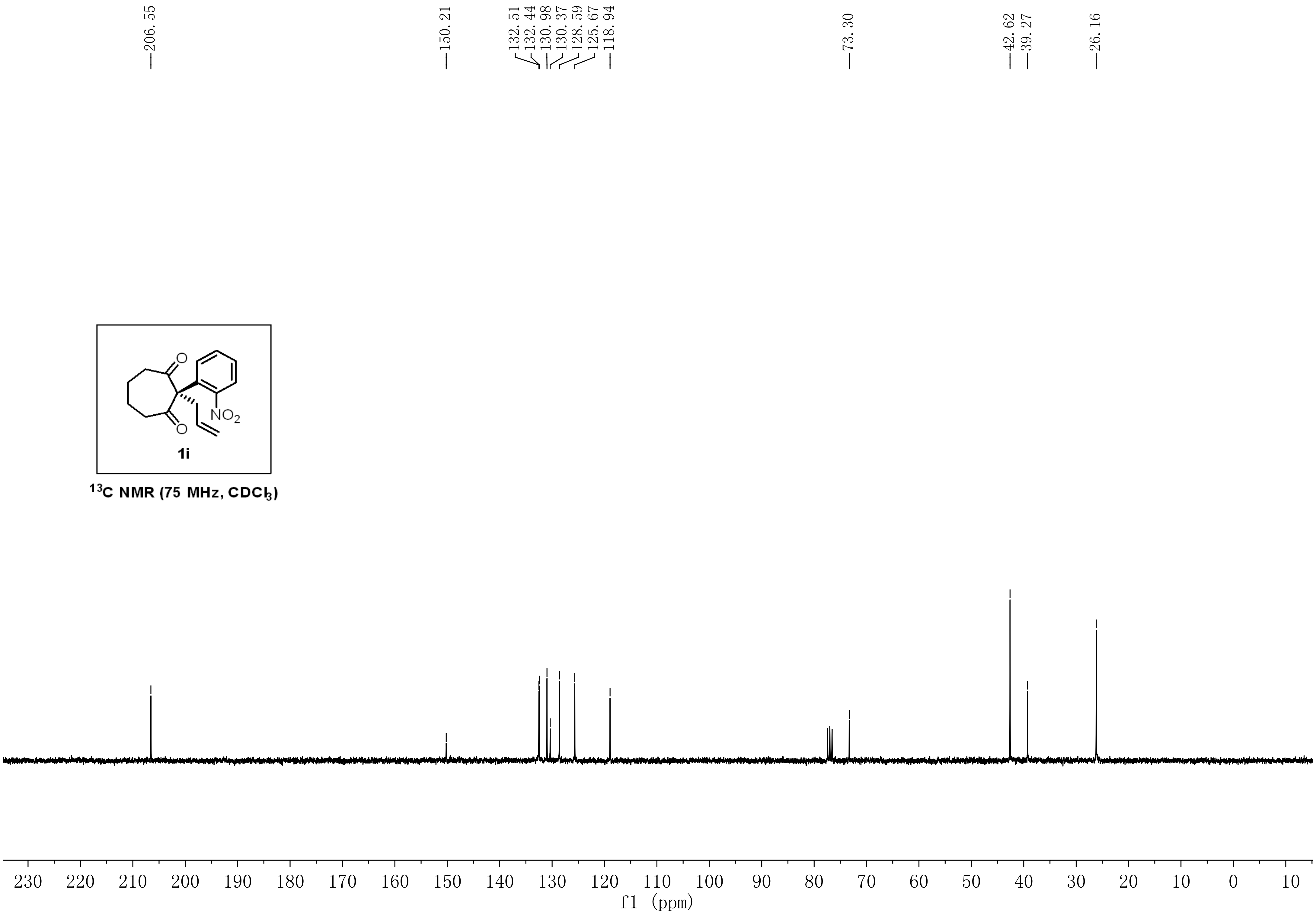

204.97
147.72
138.25
132.87
131.87
131.43
128.44
125.32
116.77
72.98
40.24
36.47
24.30
16.68
NO2
1g
13C NMR (75 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



1i

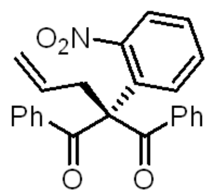
^{1}H NMR (300 MHz, CDCl$_3$)





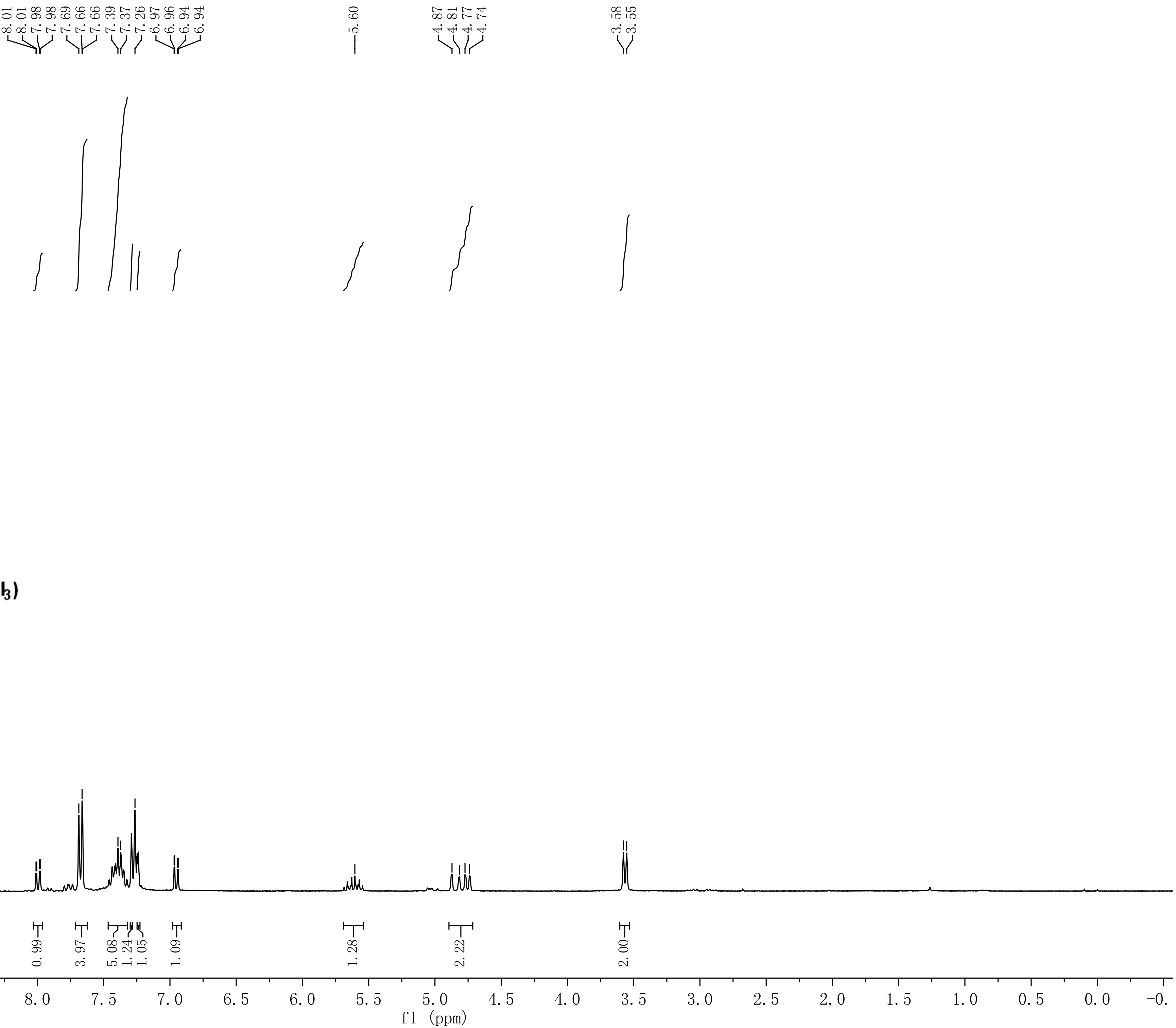
1i

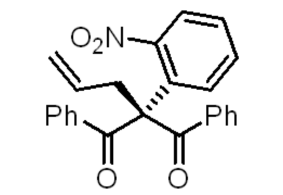
^{13}C NMR (75 MHz, CDCl$_3$)



1l

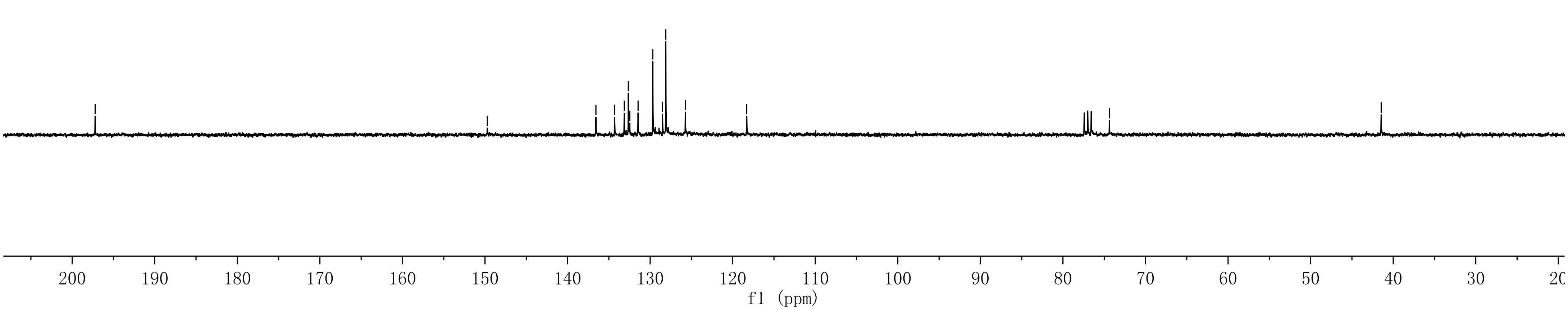
^1H NMR (300 MHz, $CDCl_3$)

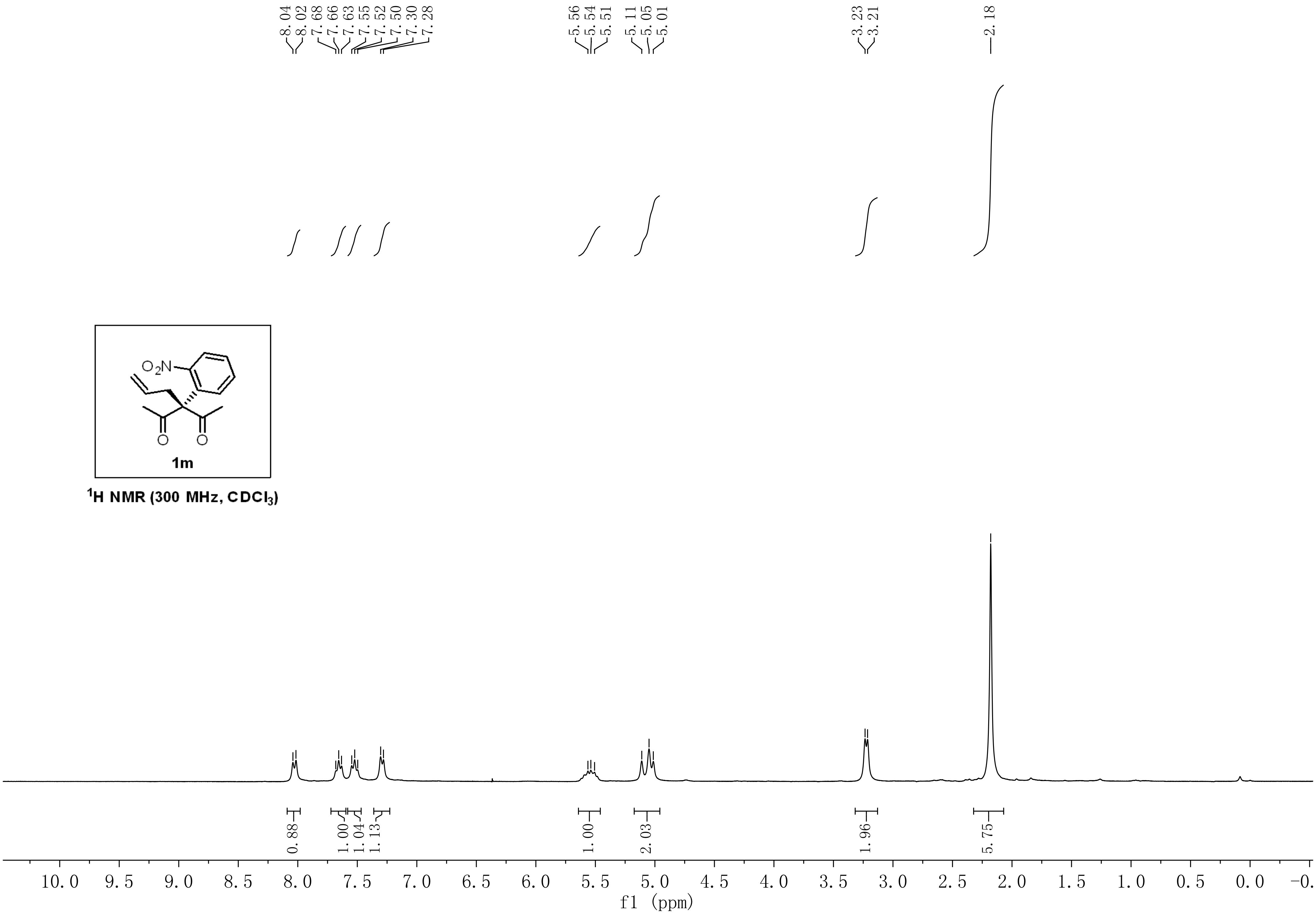




1l

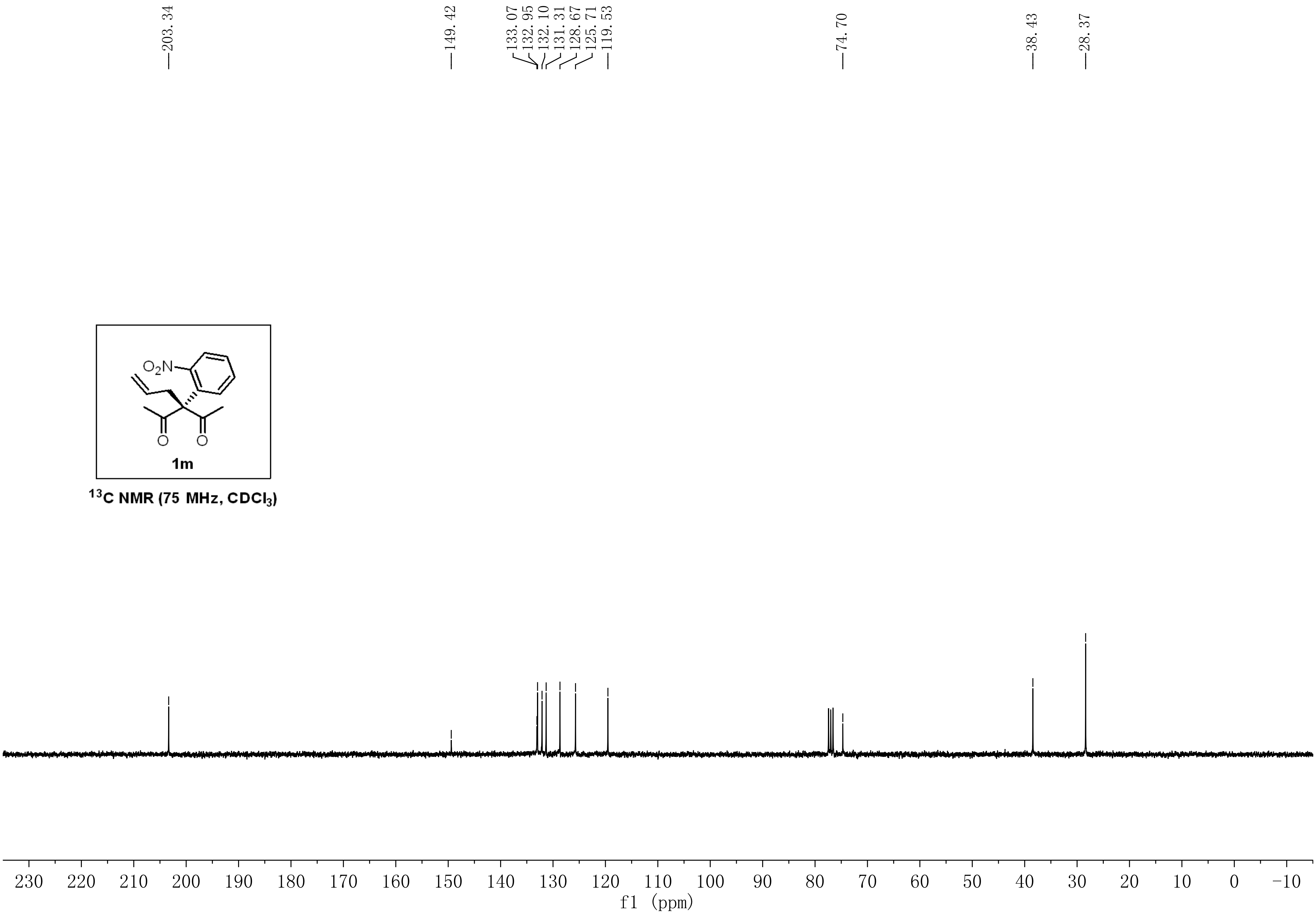
^{13}C NMR (75 MHz, $CDCl_3$)



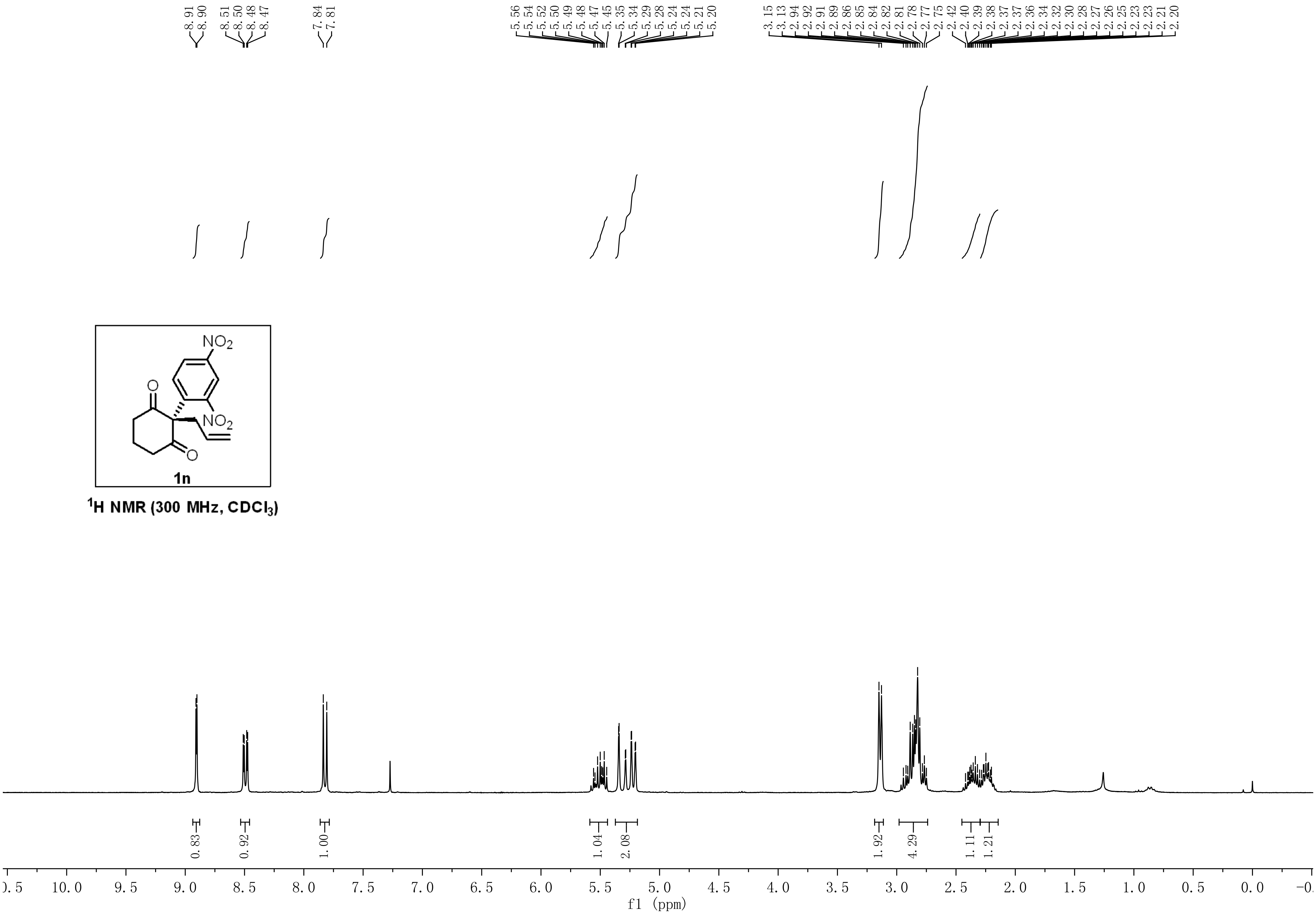


1m

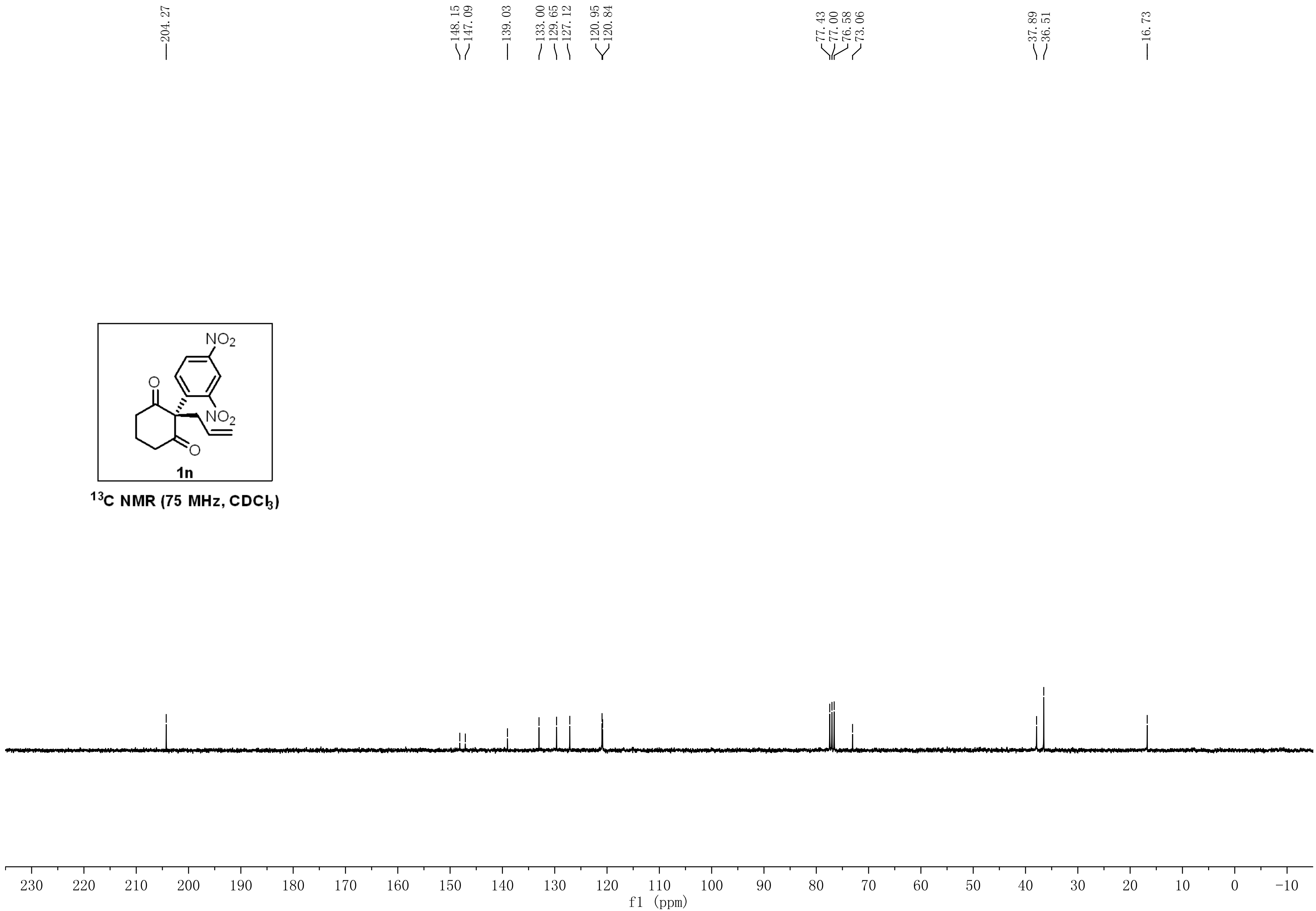
^{1}H NMR (300 MHz, $CDCl_3$)

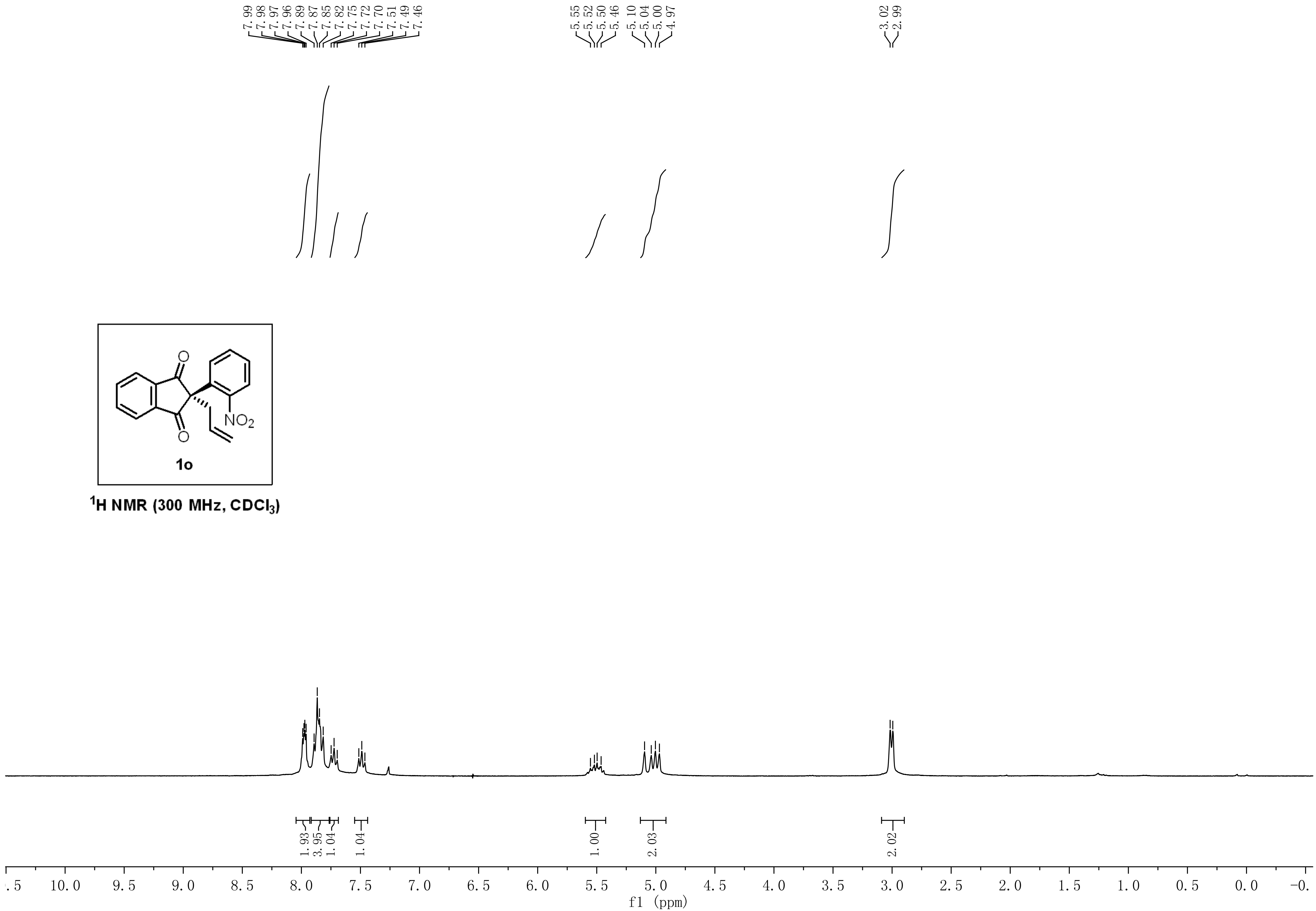


203.34
149.42
133.07
132.95
132.10
131.31
128.67
125.71
119.53
74.70
38.43
28.37
O_2N
O
O
1m
^{13}C NMR (75 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



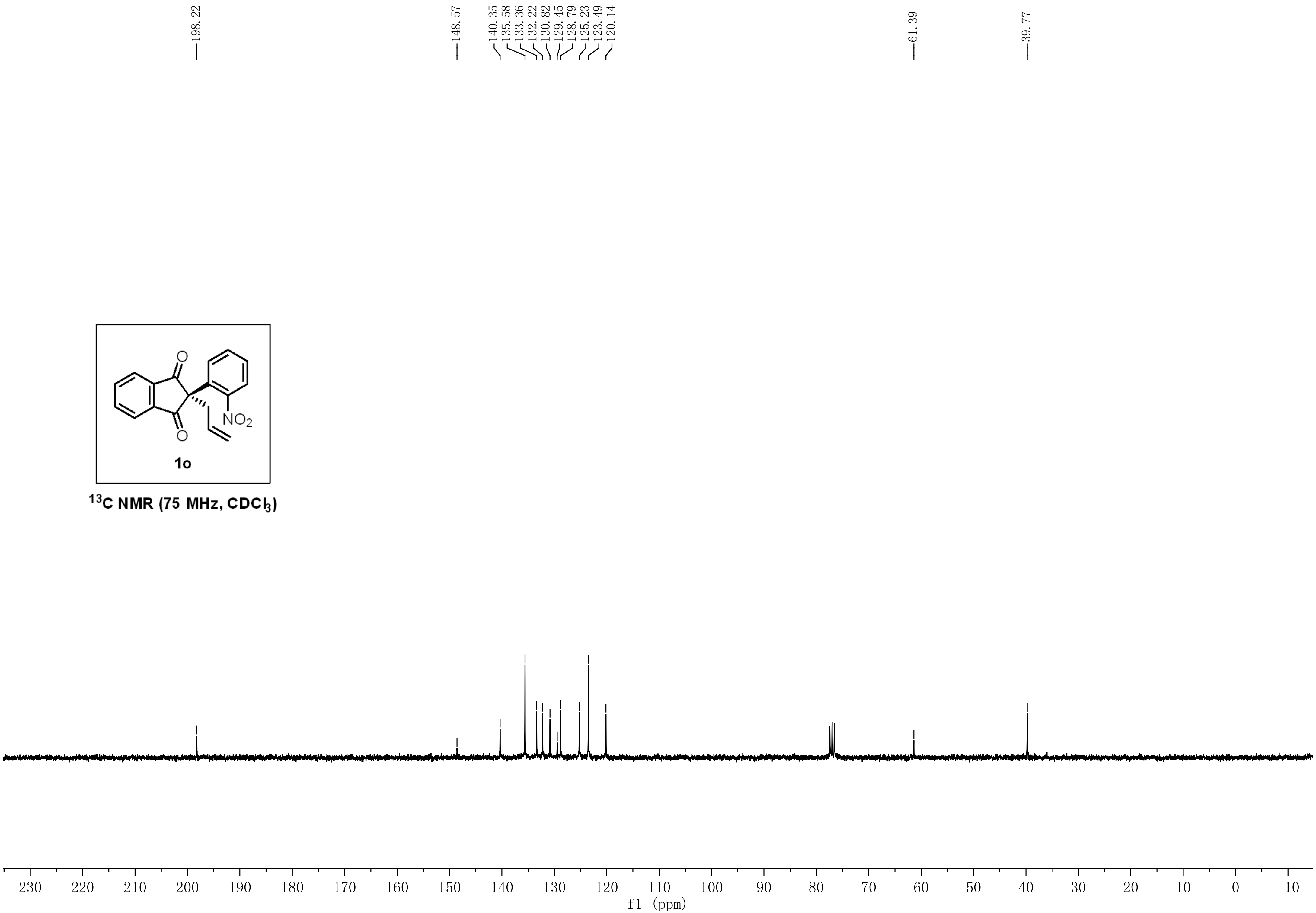
^{1}H NMR (300 MHz, CDCl$_3$)


204.27
148.15
147.09
139.03
133.00
129.65
127.12
120.95
120.84
77.43
77.00
76.58
73.06
37.89
36.51
16.73
NO_2
O
NO_2
O
1n
^{13}C NMR (75 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



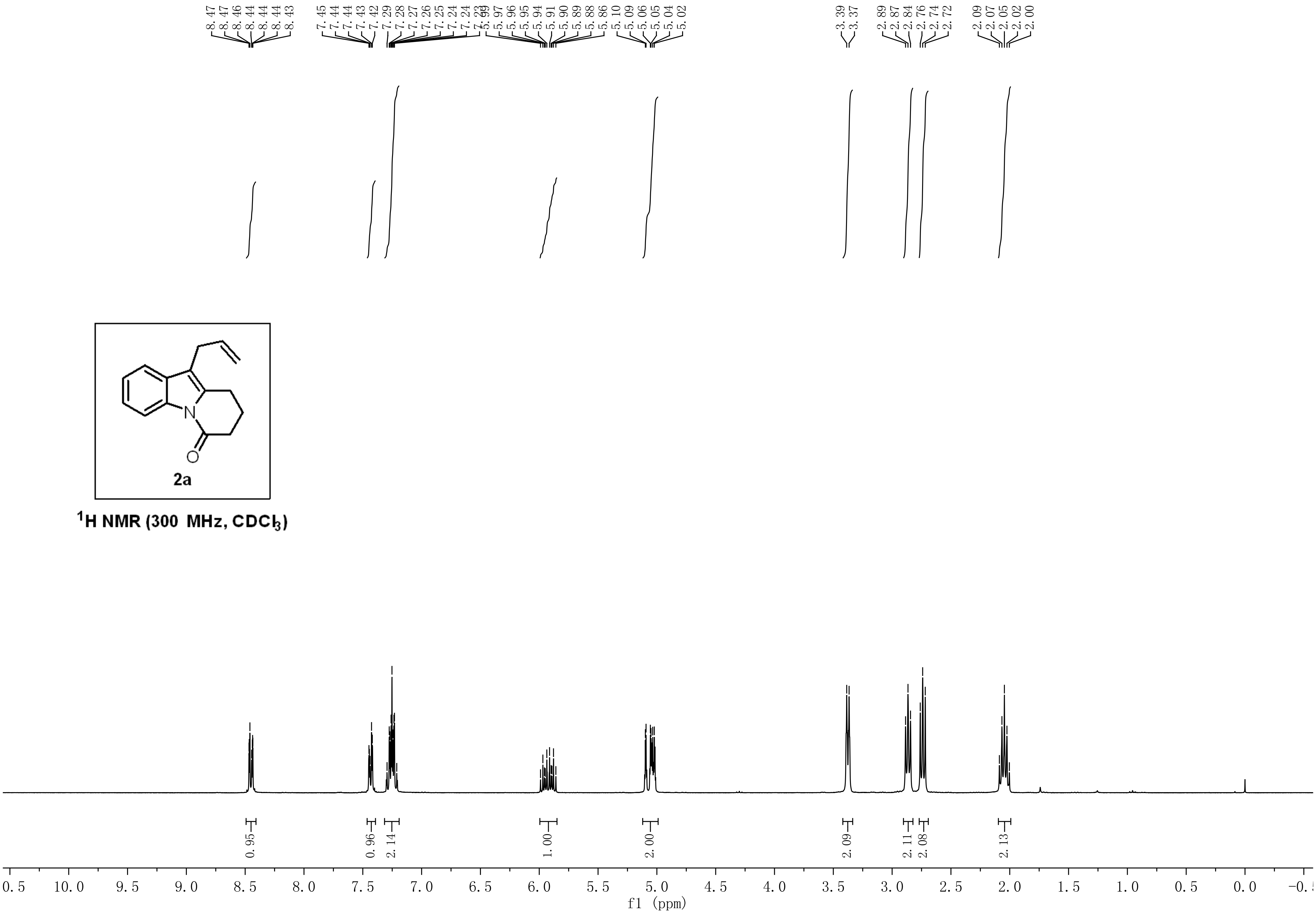
1o

^{1}H NMR (300 MHz, $CDCl_3$)



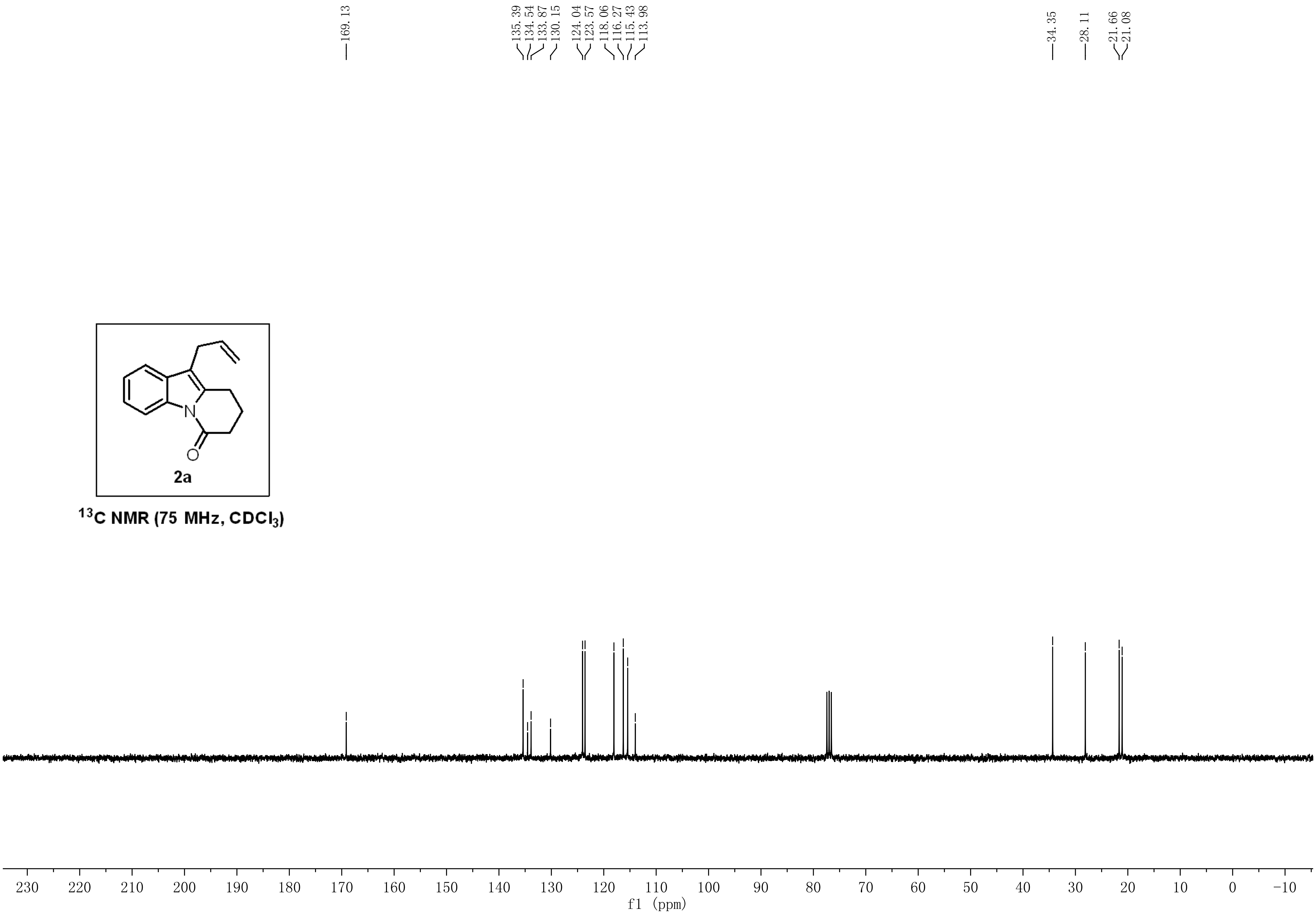
1o

^{13}C NMR (75 MHz, $CDCl_3$)



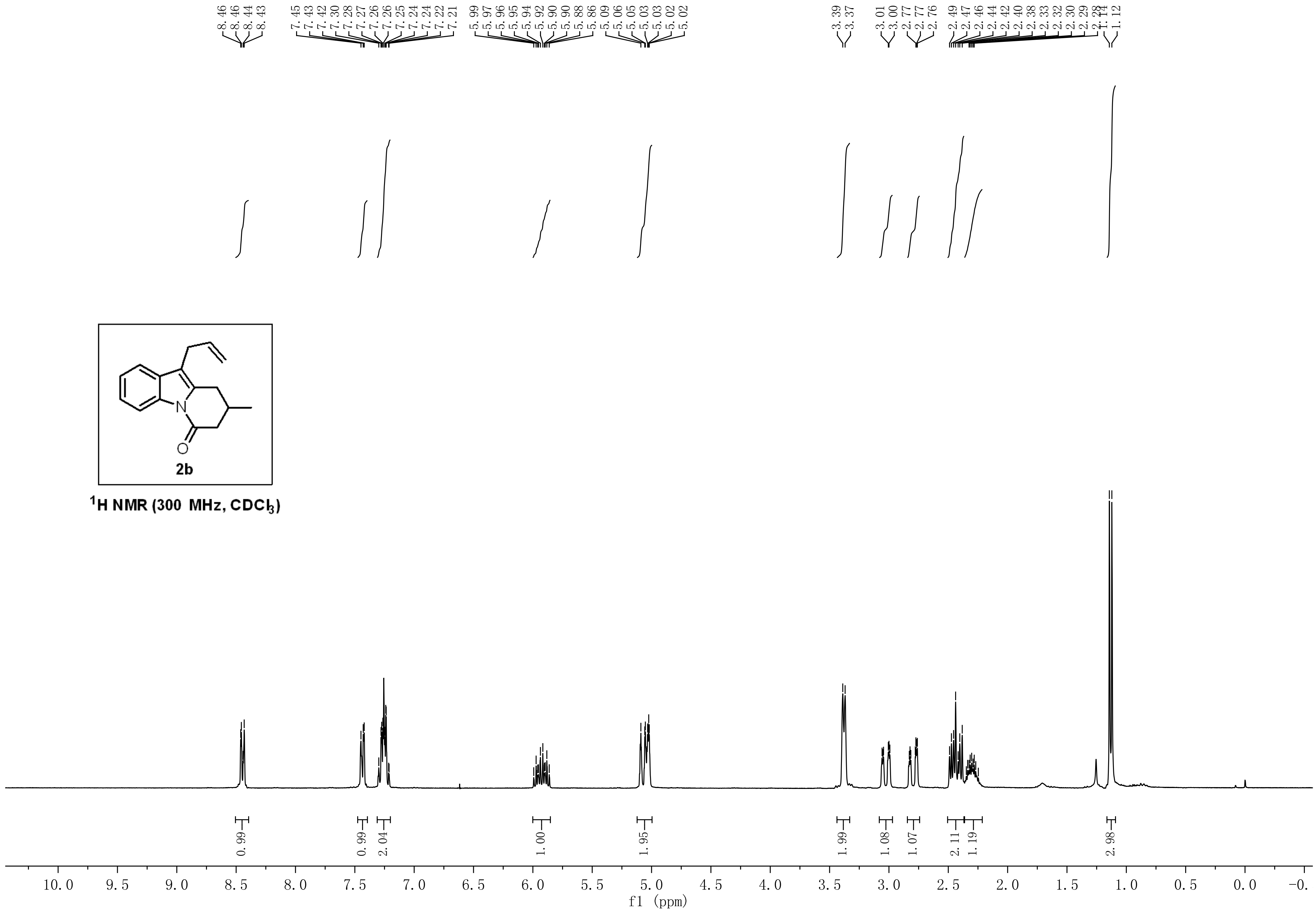
2a

^{1}H NMR (300 MHz, CDCl$_3$)



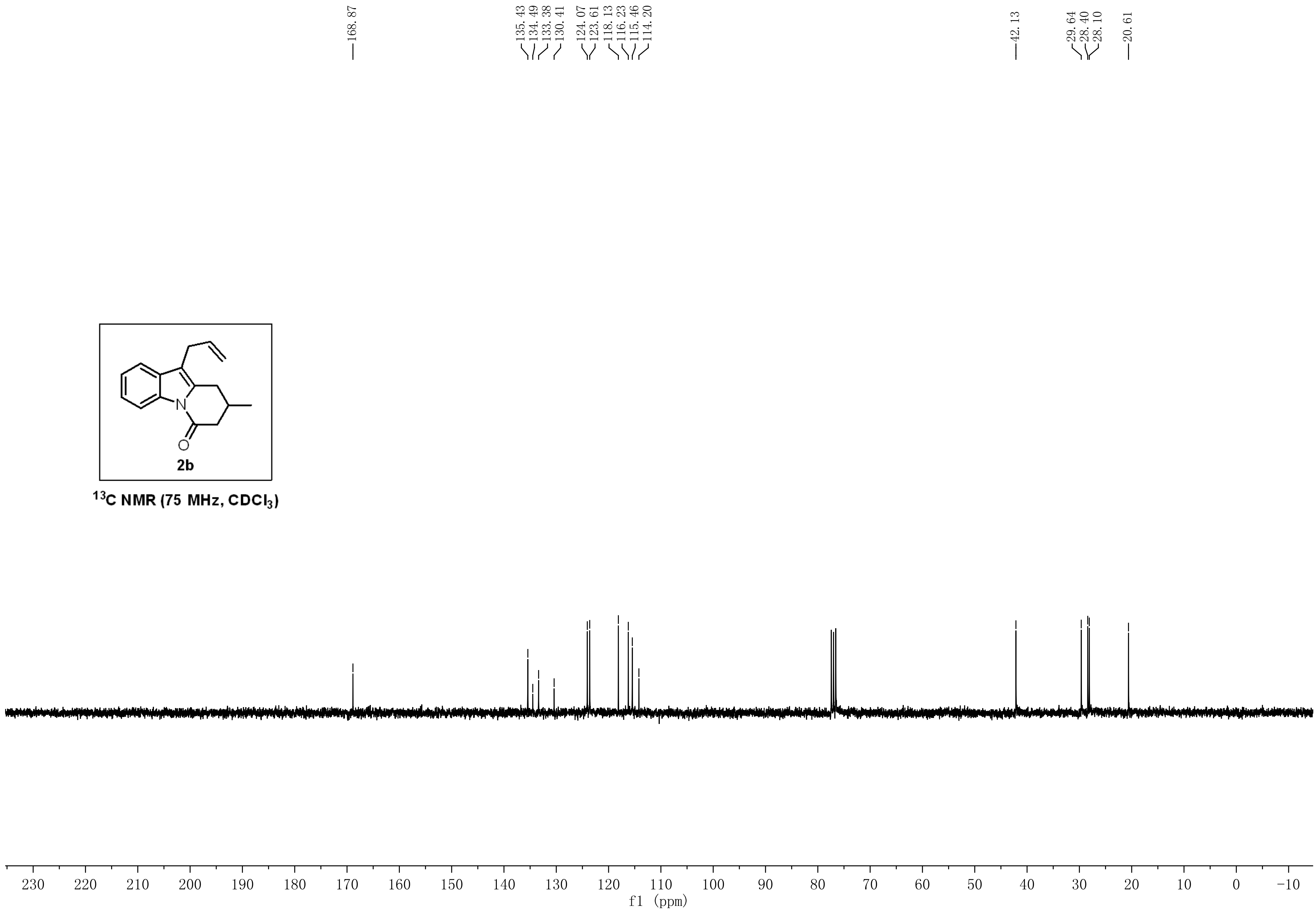
2a

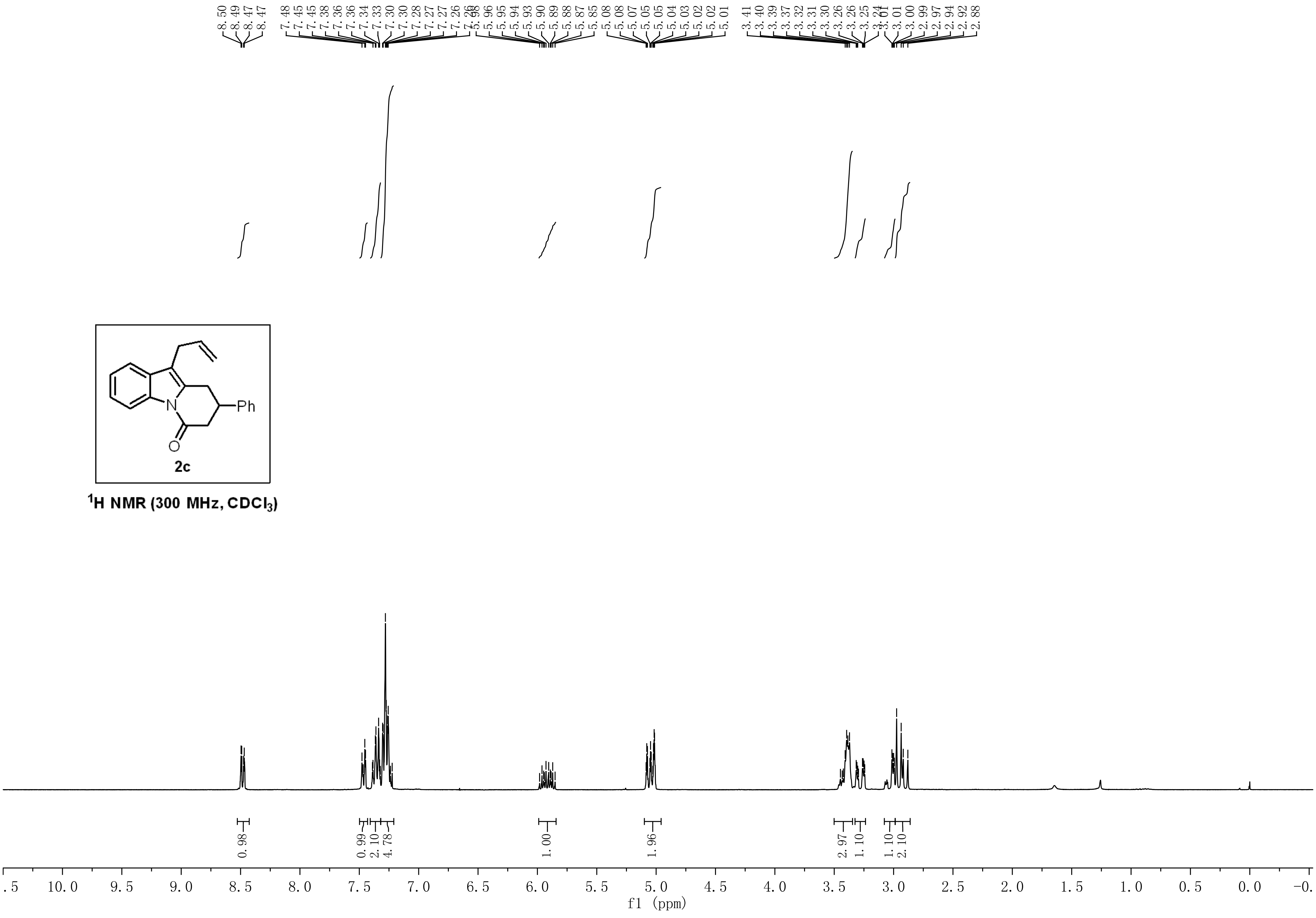
^{13}C NMR (75 MHz, $CDCl_3$)



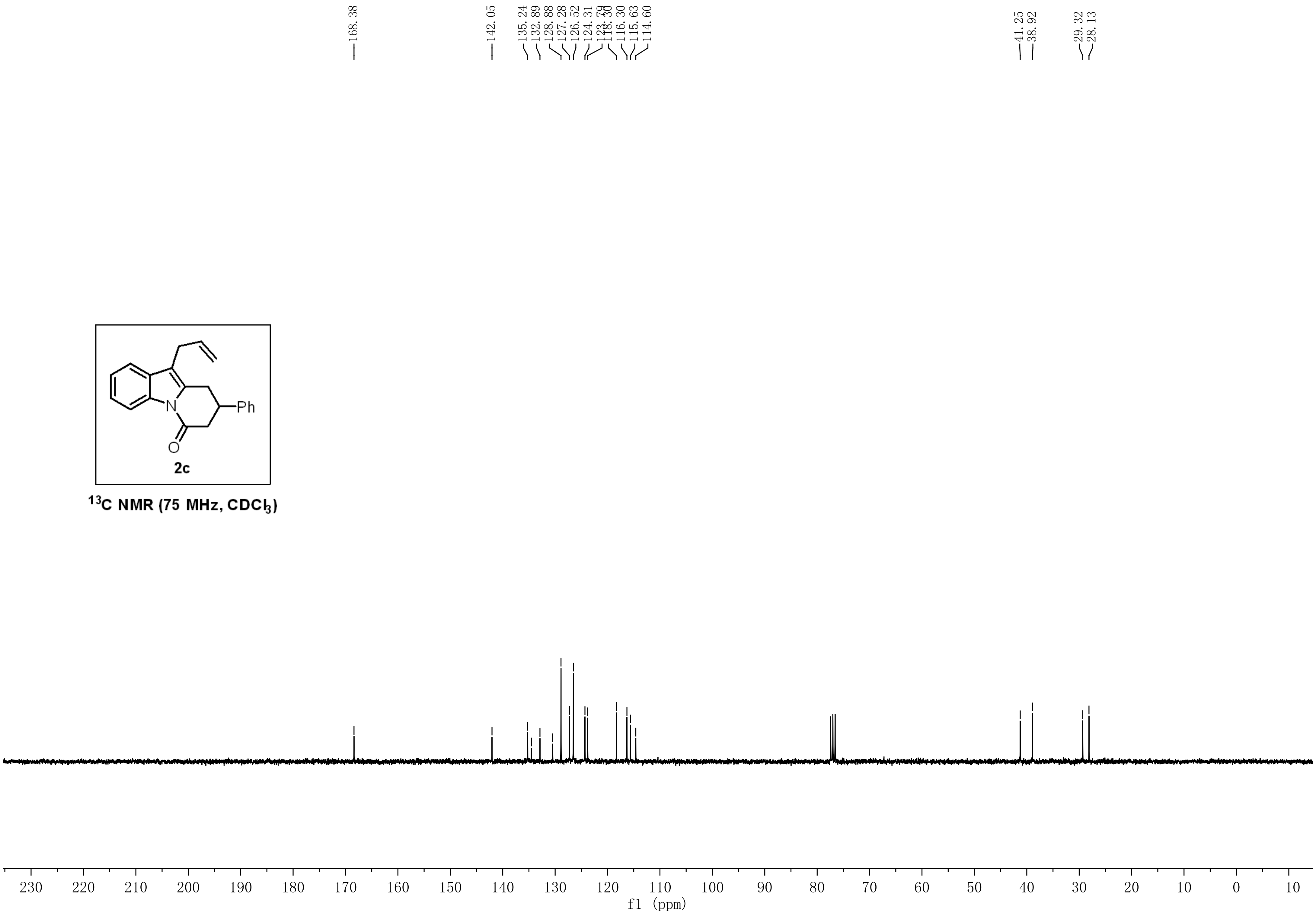
2b

^{1}H NMR (300 MHz, CDCl$_3$)


168.87
135.43
134.49
133.38
130.41
124.07
123.61
118.13
116.23
115.46
114.20
42.13
29.64
28.40
28.10
20.61
2b
^{13}C NMR (75 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

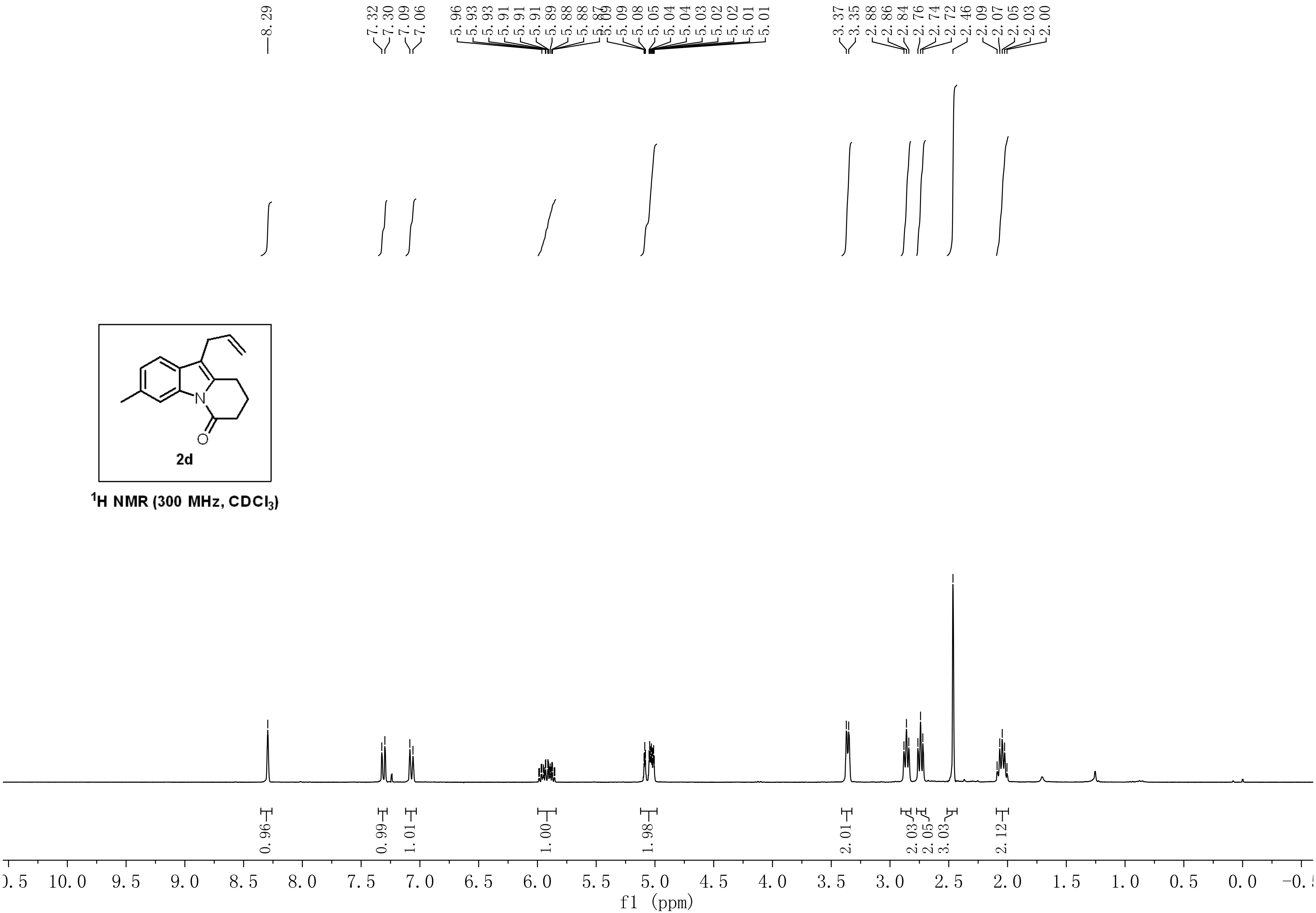


^{1}H NMR (300 MHz, $CDCl_3$)

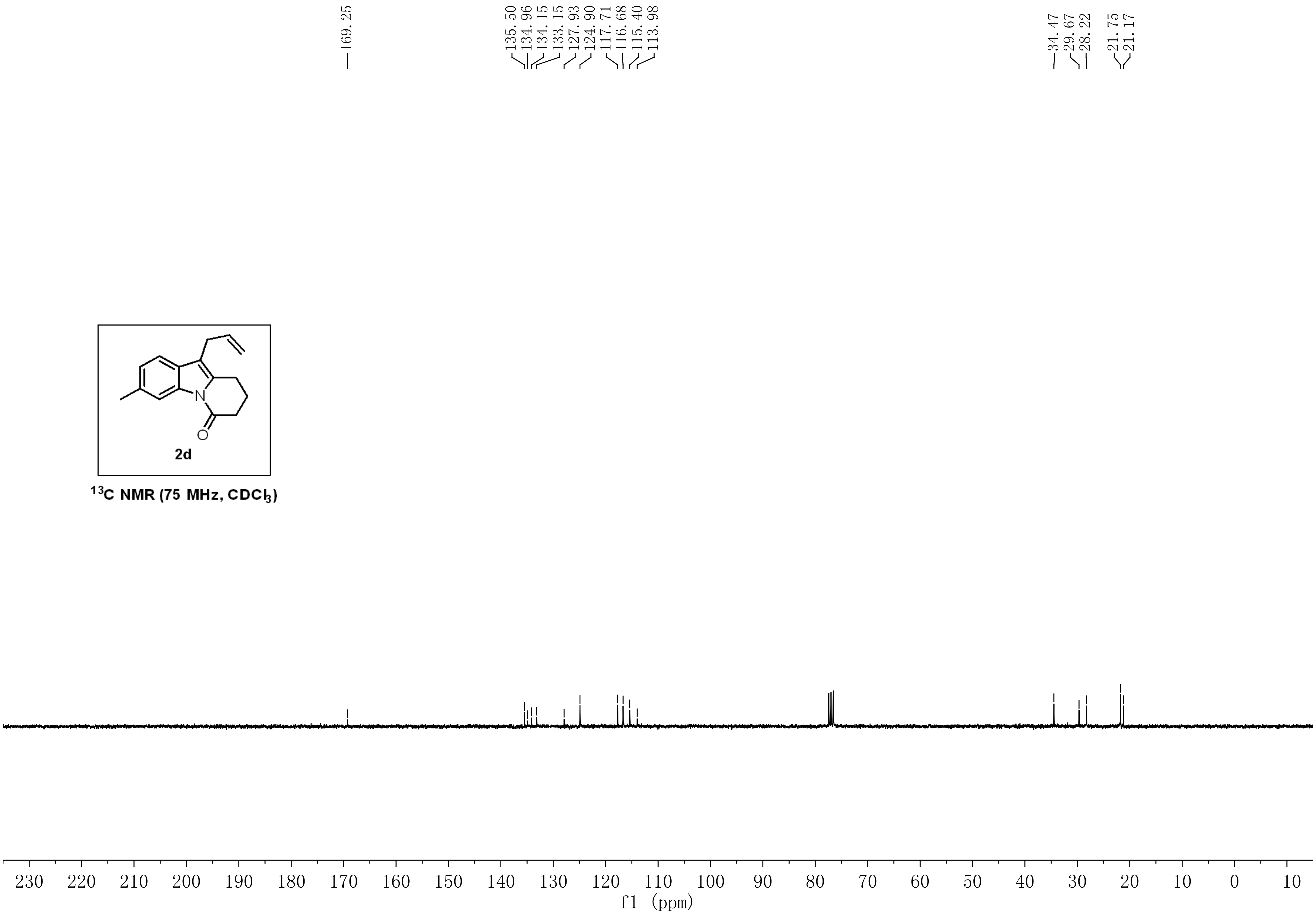


2c

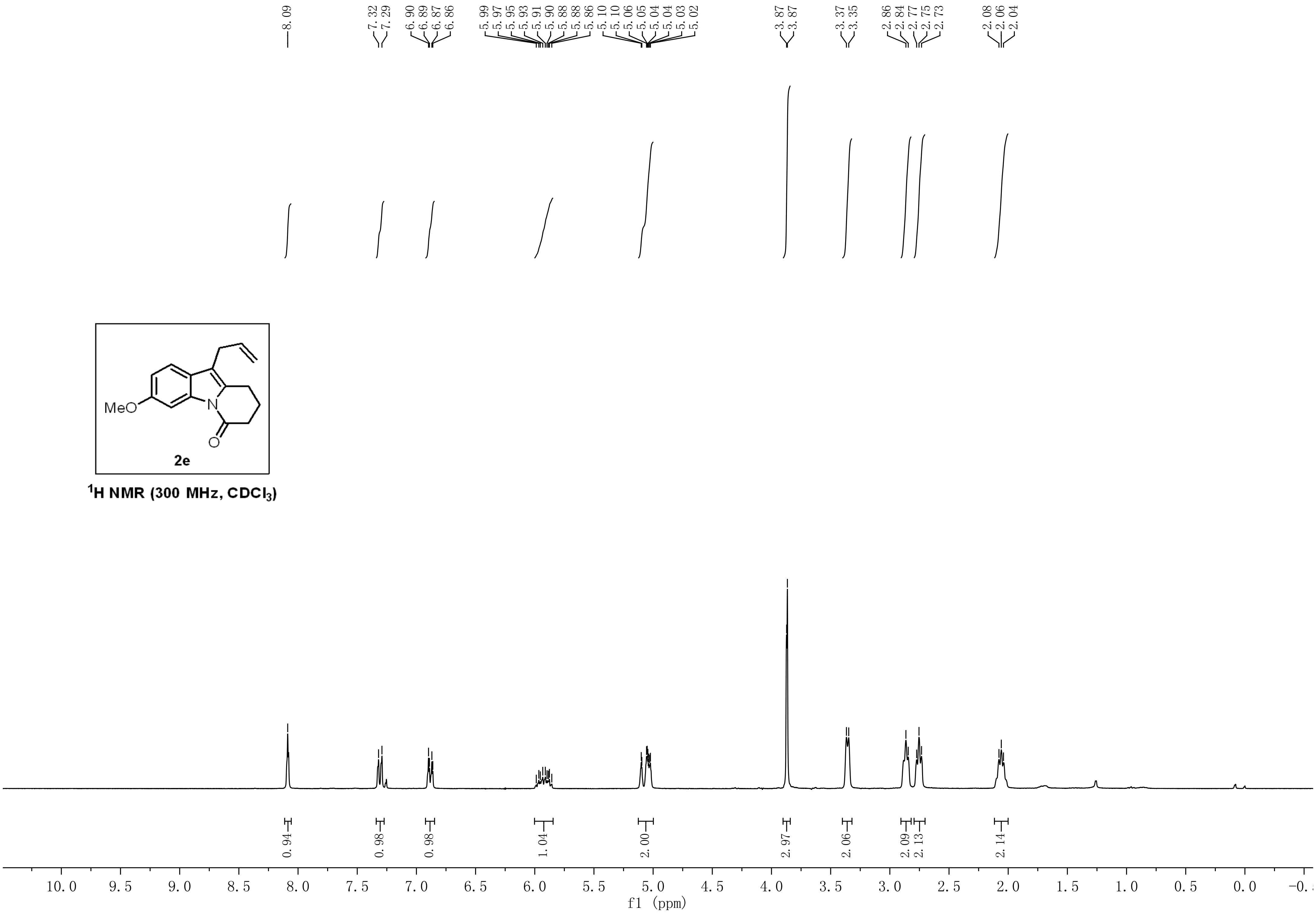
^{13}C NMR (75 MHz, $CDCl_3$)

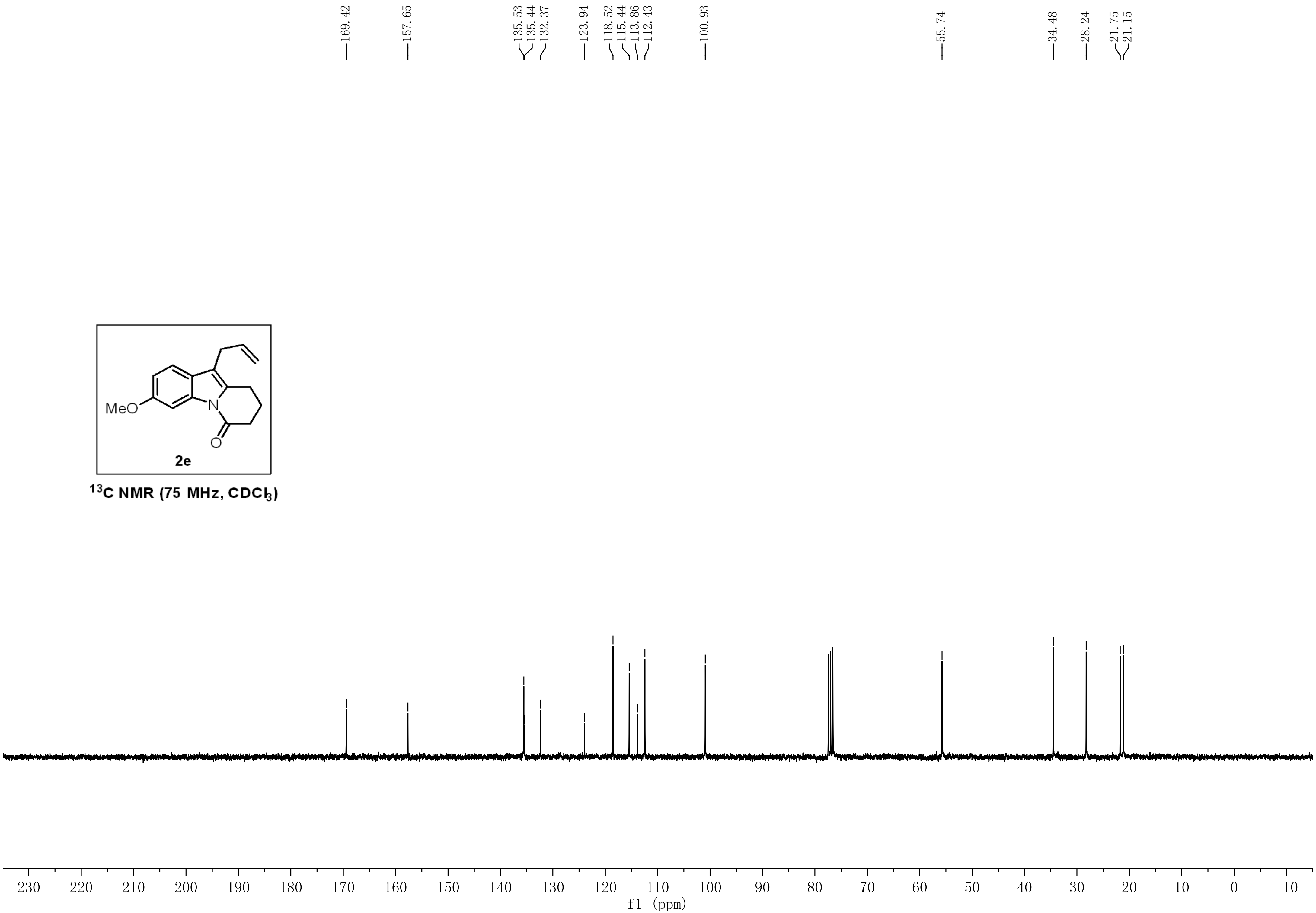


^{1}H NMR (300 MHz, $CDCl_3$)

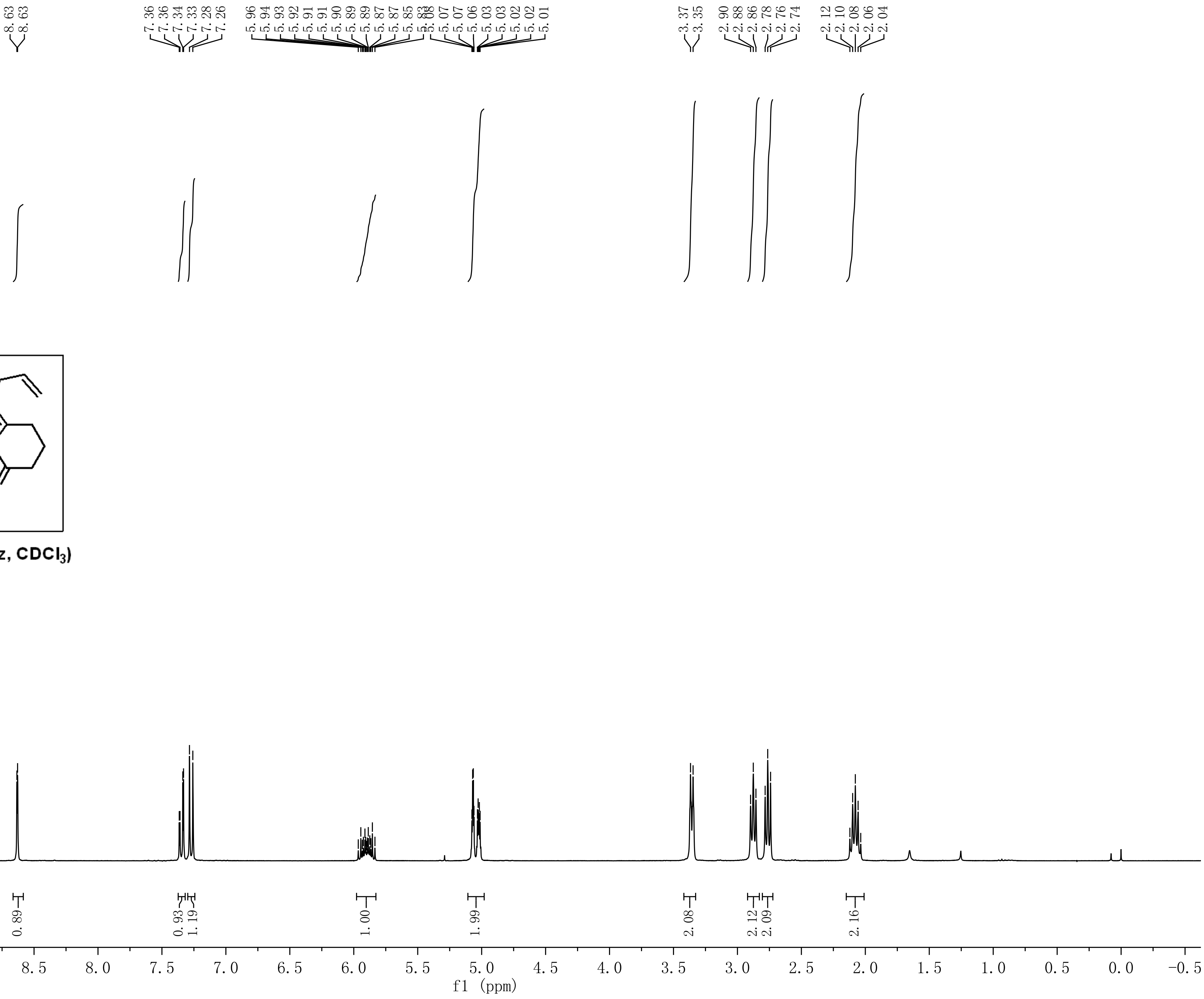


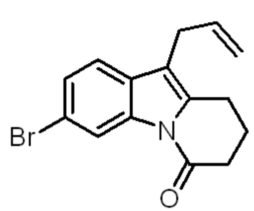
^{13}C NMR (75 MHz, $CDCl_3$)


8.09
7.32 7.29
6.90 6.89 6.87 6.86
5.99 5.97 5.95 5.93 5.91 5.90 5.88 5.88 5.86
5.10 5.10 5.06 5.05 5.04 5.04 5.03 5.02
3.87 3.87
3.37 3.35
2.86 2.84 2.77 2.75 2.73
2.08 2.06 2.04
MeO
N
O
2e
1H NMR (300 MHz, CDCl3)
0.94
0.98
0.98
1.04
2.00
2.97
2.06
2.09
2.13
2.14
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)



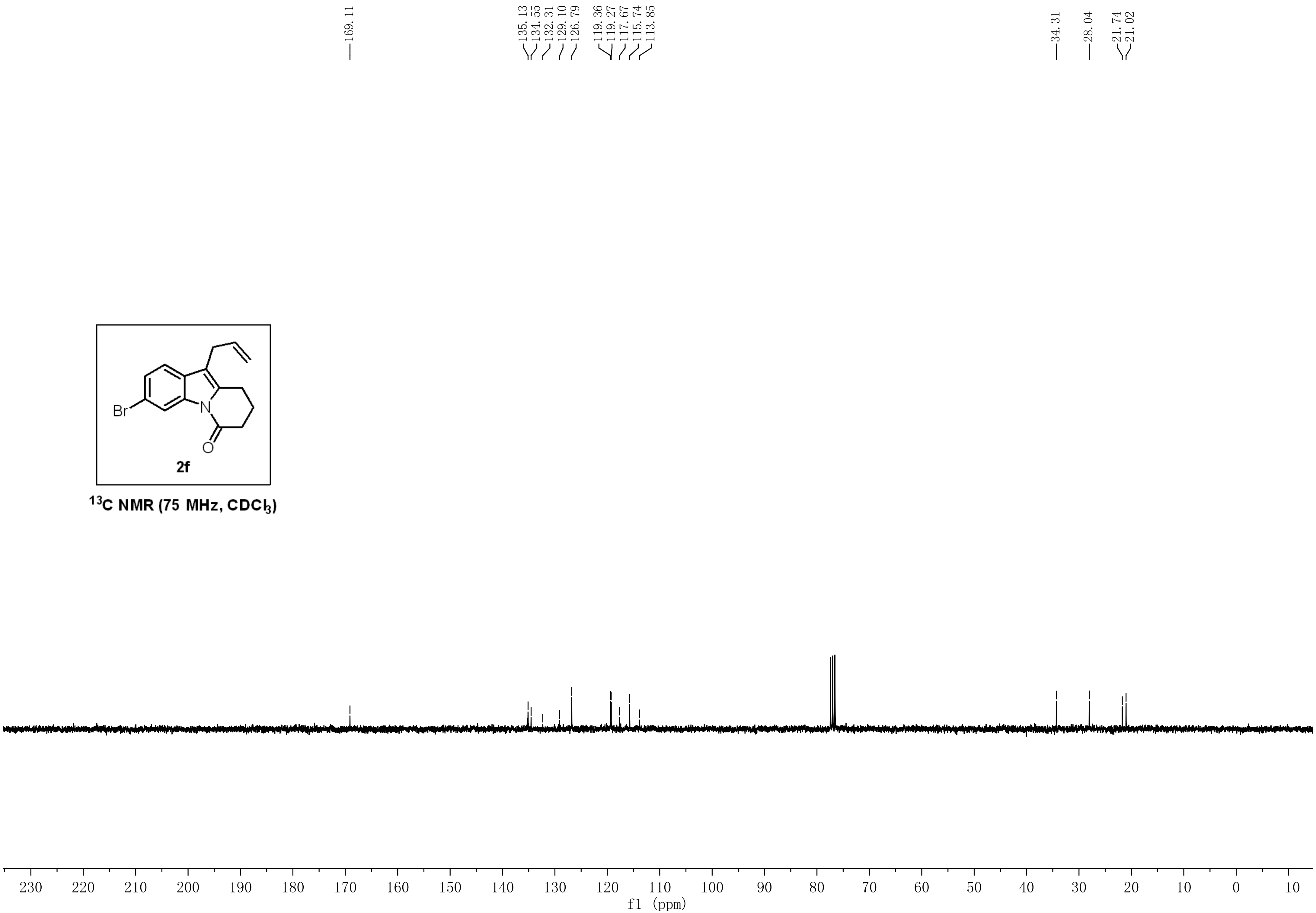
169.42
157.65
135.53
135.44
132.37
123.94
118.52
115.44
113.86
112.43
100.93
55.74
34.48
28.24
21.75
21.15
MeO
N
O
2e
^{13}C NMR (75 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

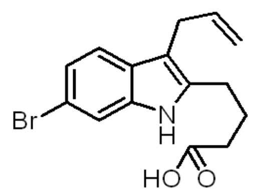




2f

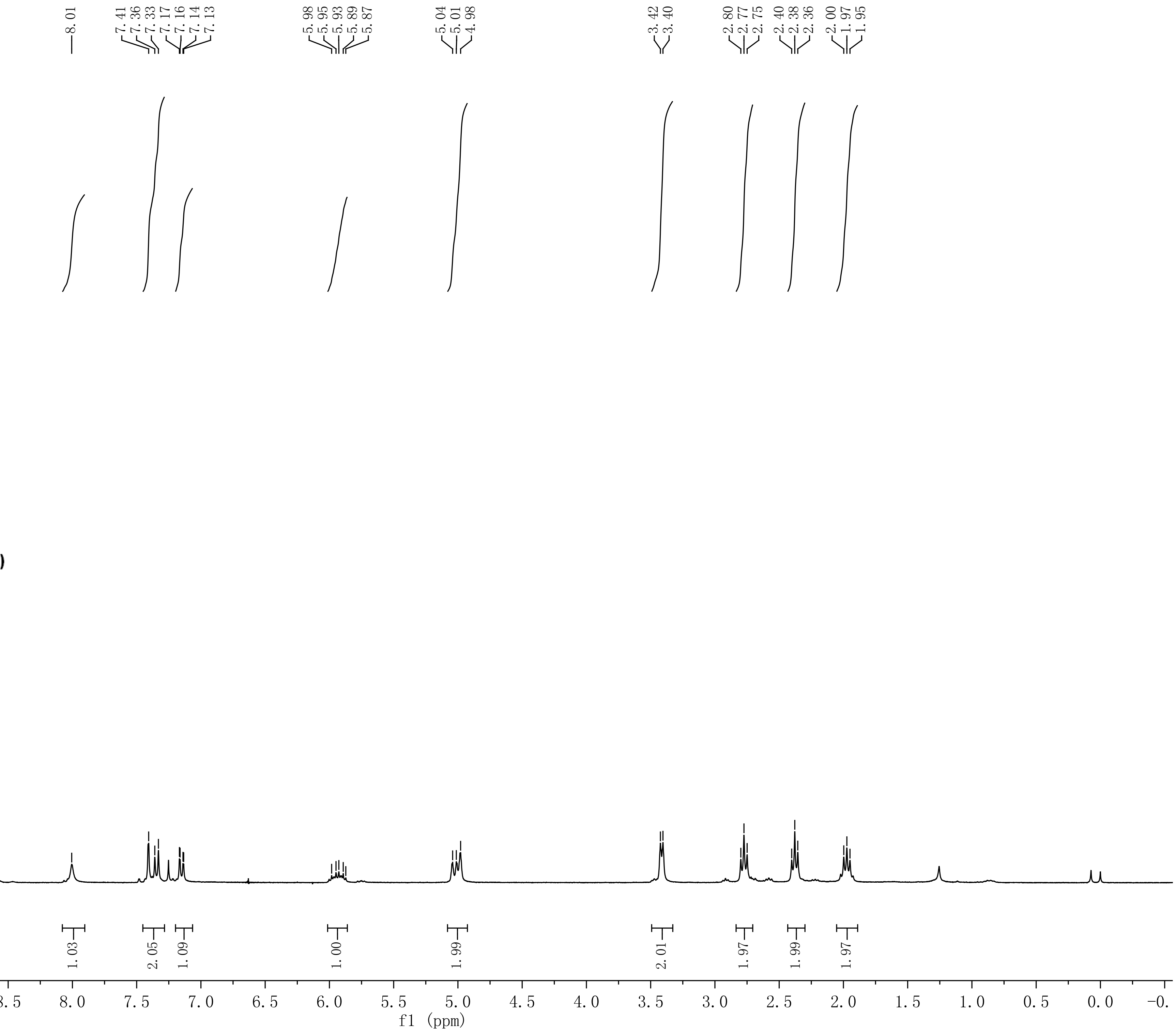
^{1}H NMR (300 MHz, $CDCl_3$)

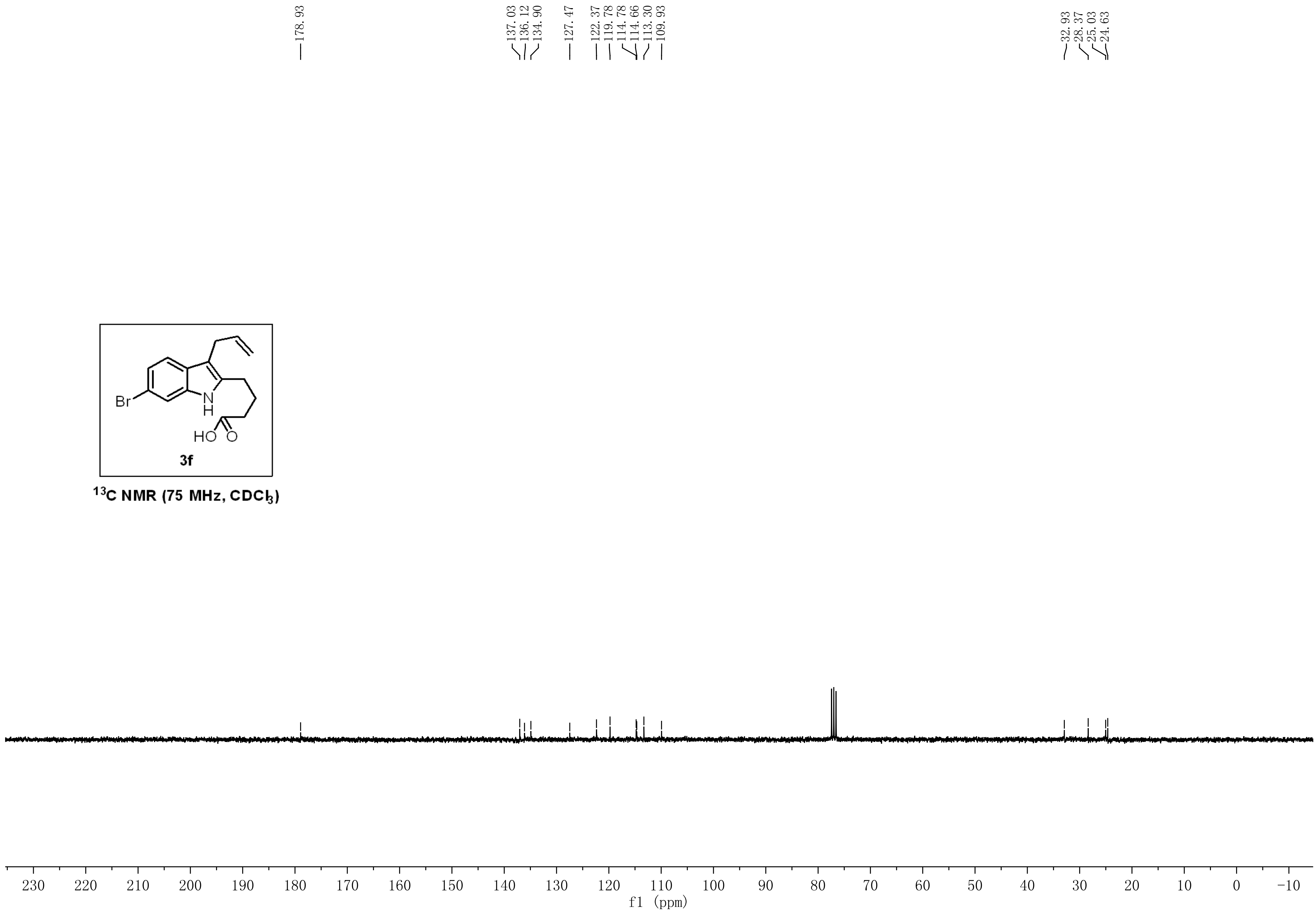

169.11
135.13
134.55
132.31
129.10
126.79
119.36
119.27
117.67
115.74
113.85
34.31
28.04
21.74
21.02
Br
N
O
2f
13C NMR (75 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

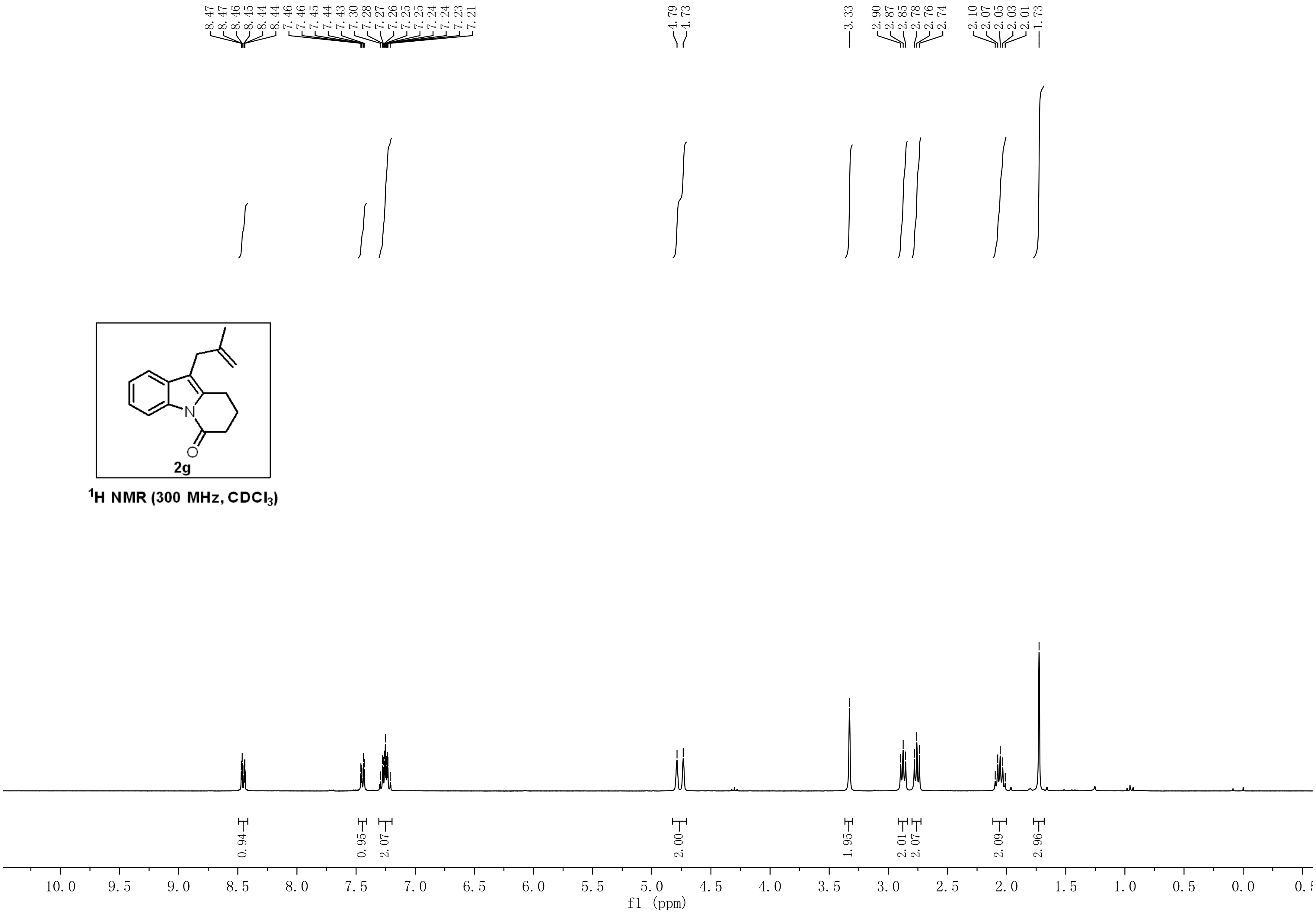


3f

^{13}C NMR (75 MHz, CDCl$_3$)

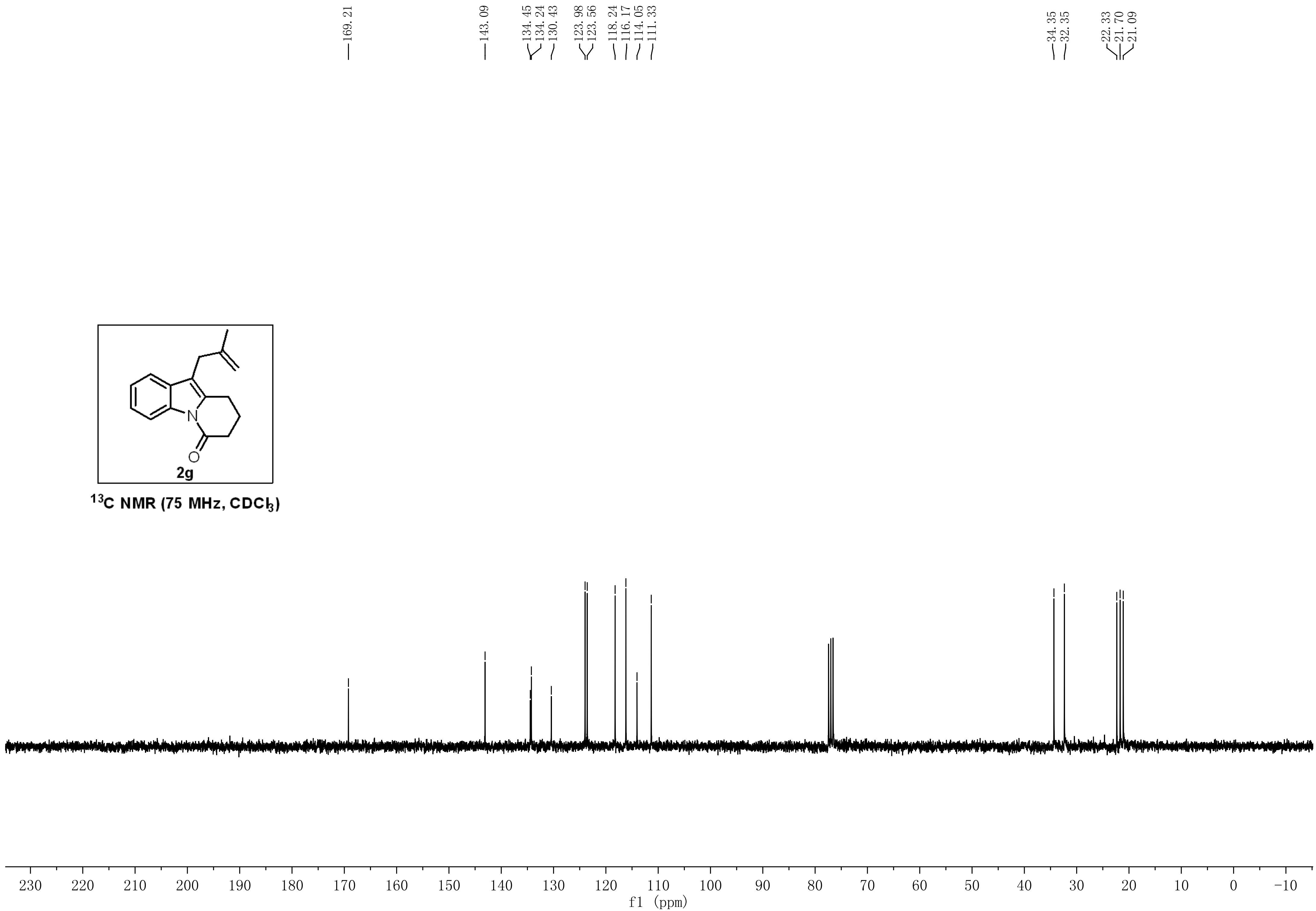


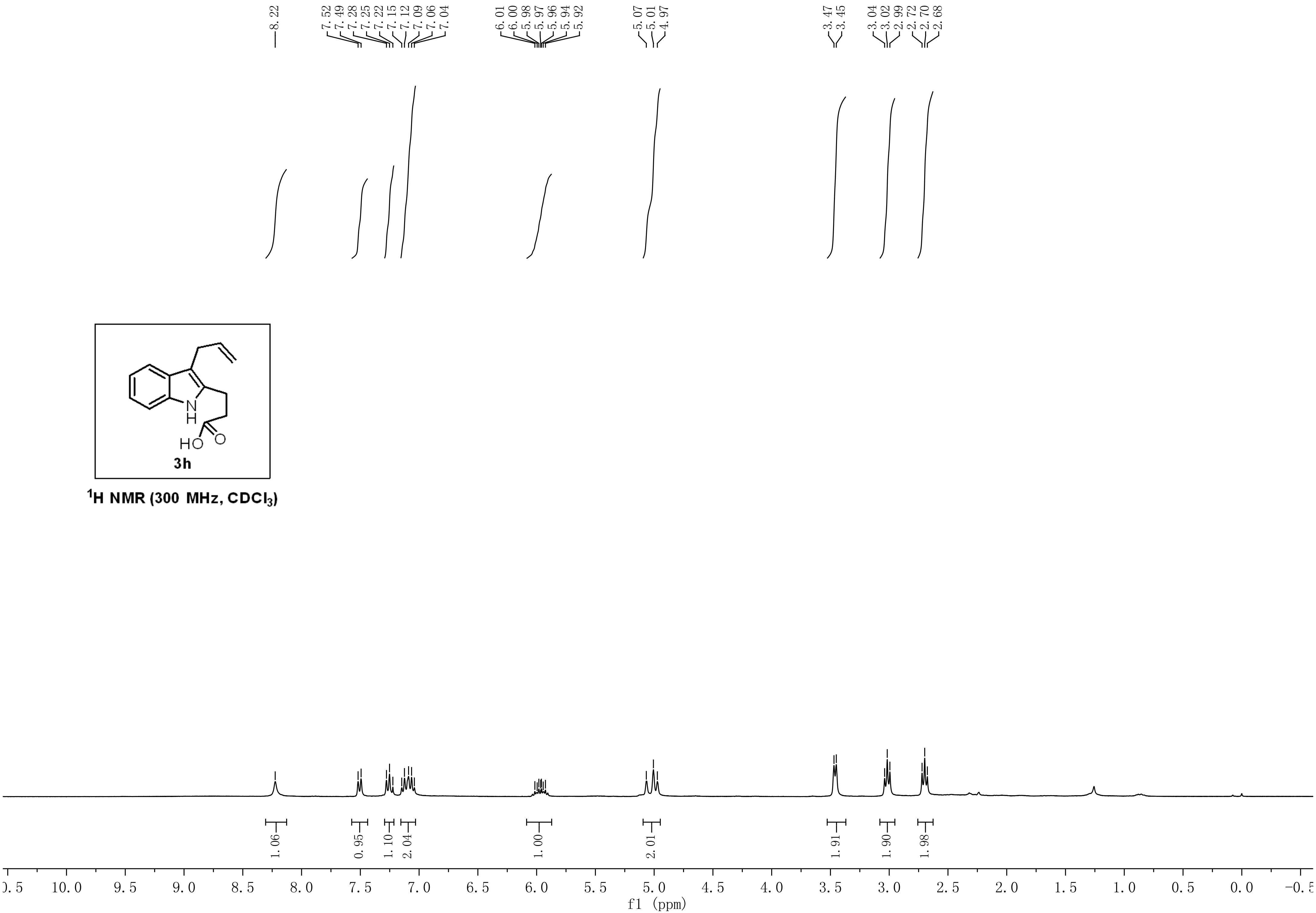

178.93
137.03
136.12
134.90
127.47
122.37
119.78
114.78
114.66
113.30
109.93
32.93
28.37
25.03
24.63
Br
N
H
HO
O
3f
13C NMR (75 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



2g

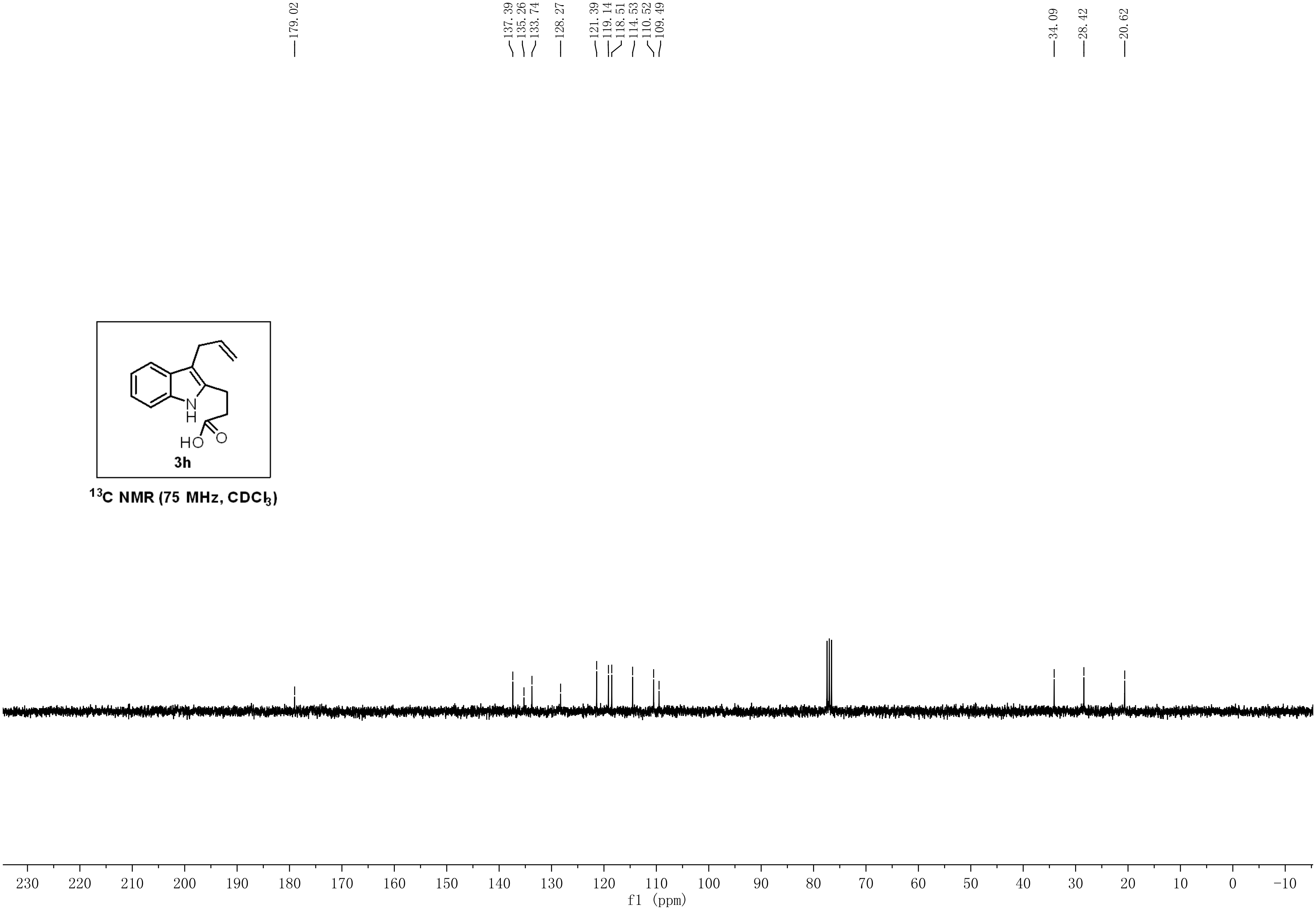
^{1}H NMR (300 MHz, $CDCl_3$)


169.21
143.09
134.45
134.24
130.43
123.98
123.56
118.24
116.17
114.05
111.33
34.35
32.35
22.33
21.70
21.09
2g
13C NMR (75 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



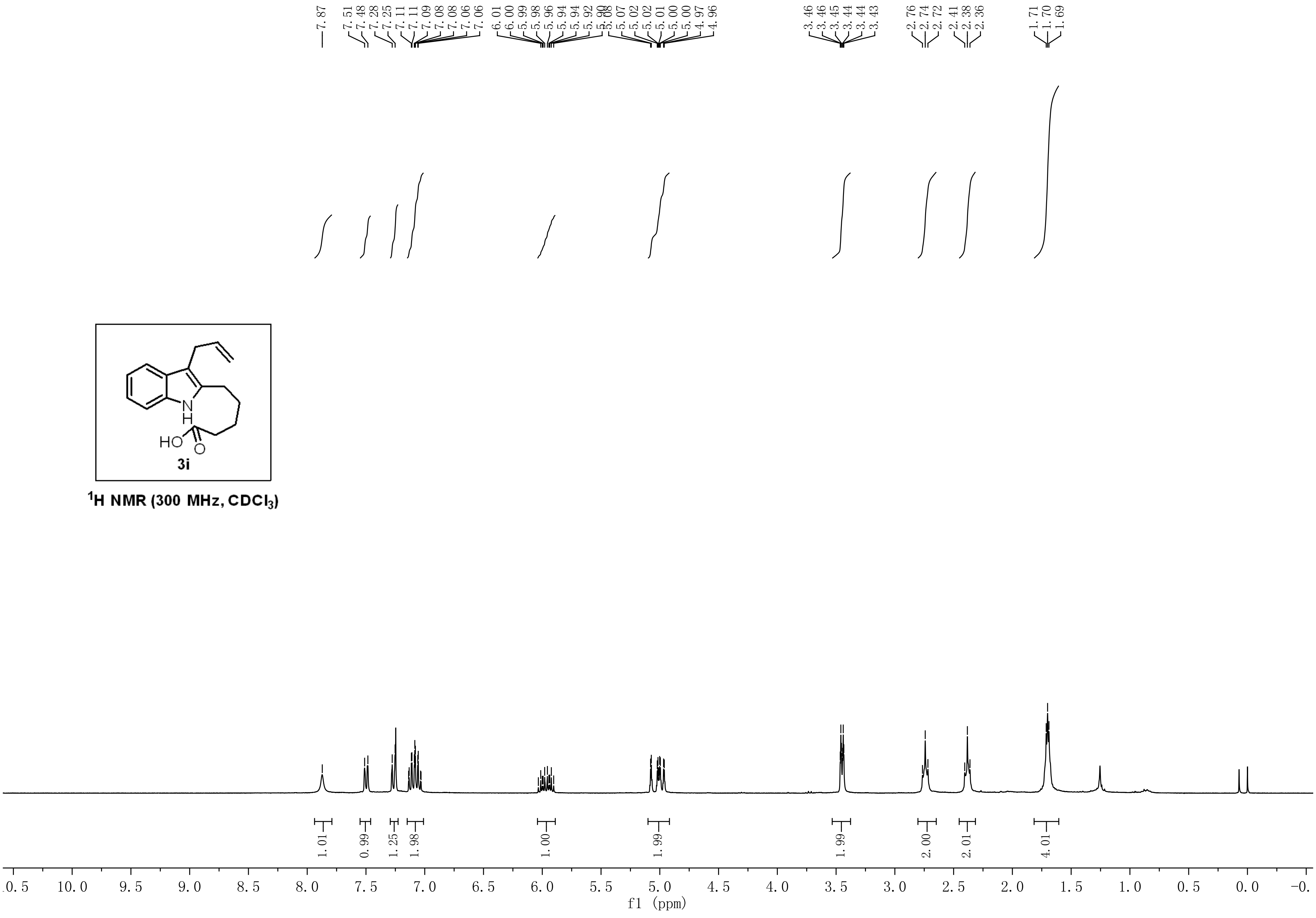
3h

^{1}H NMR (300 MHz, $CDCl_3$)

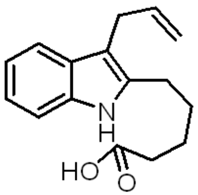


3h

^{13}C NMR (75 MHz, $CDCl_3$)

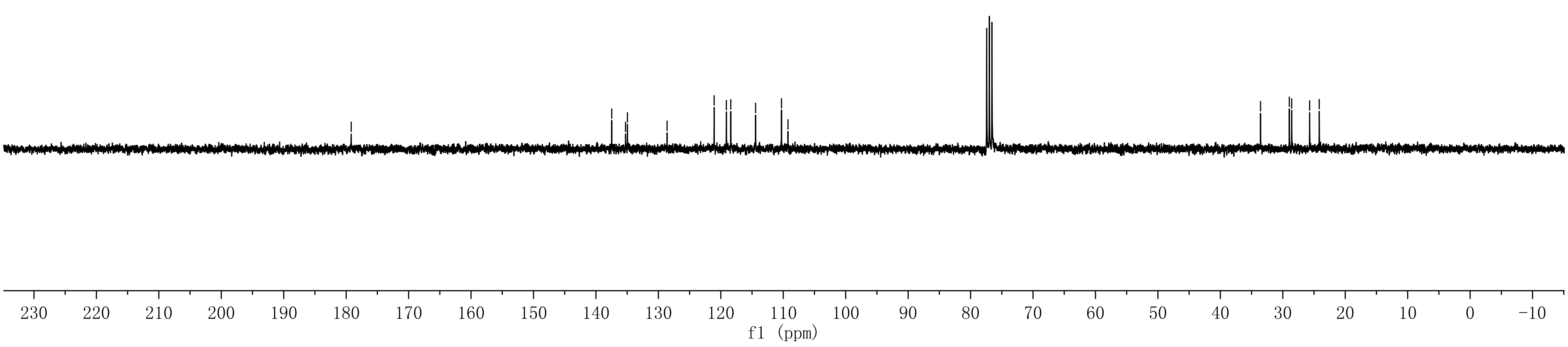


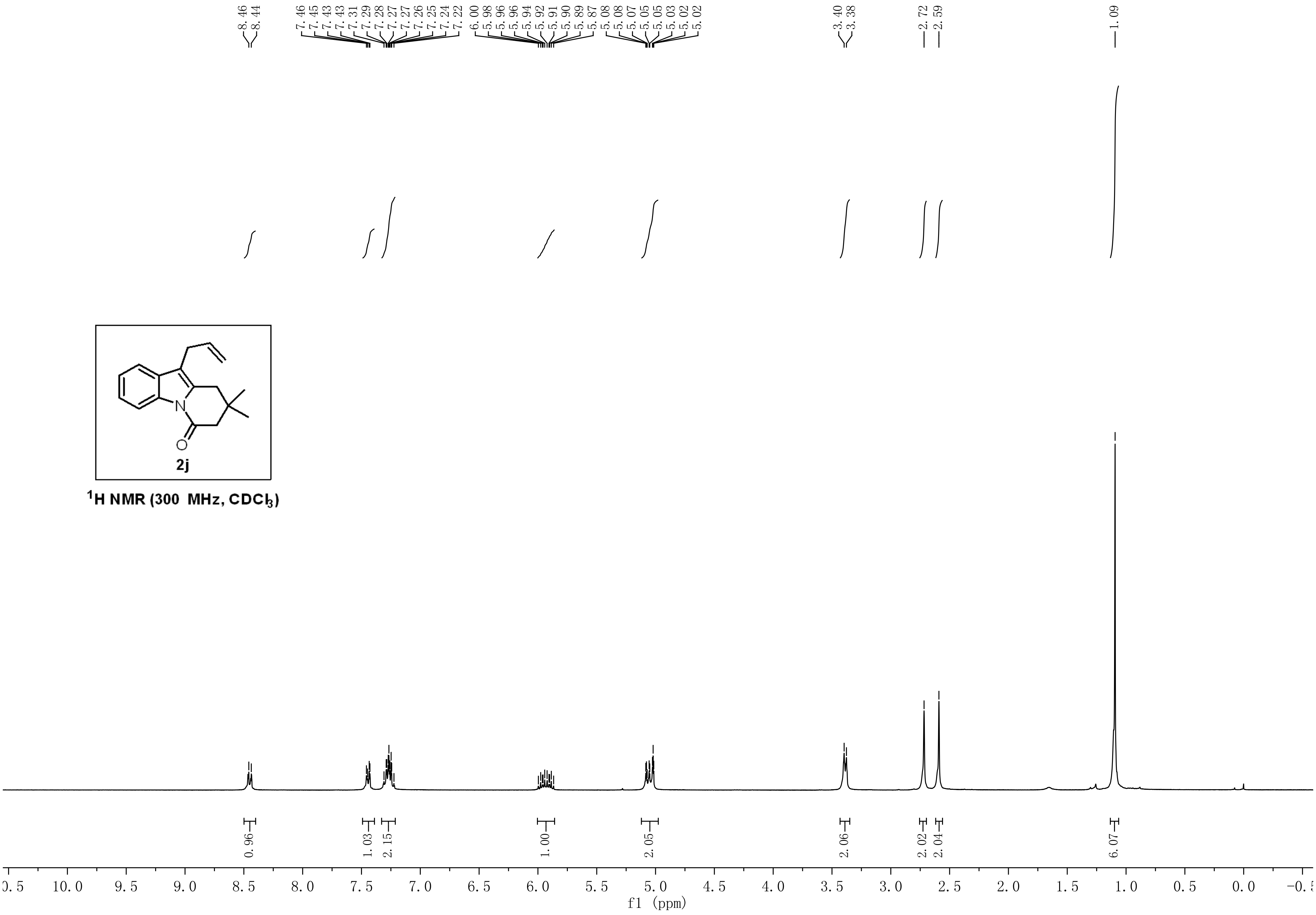
^1H NMR (300 MHz, $CDCl_3$)

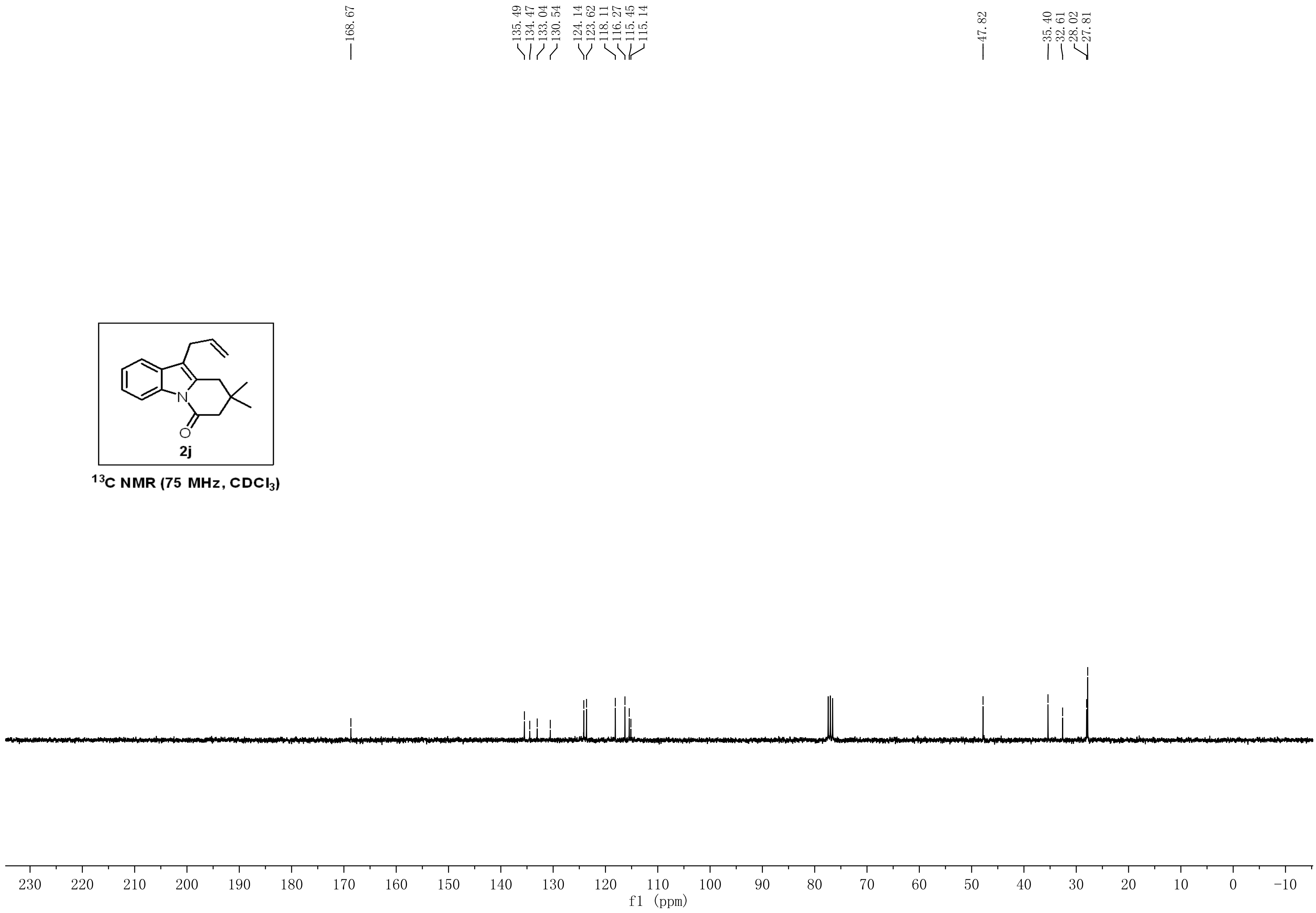


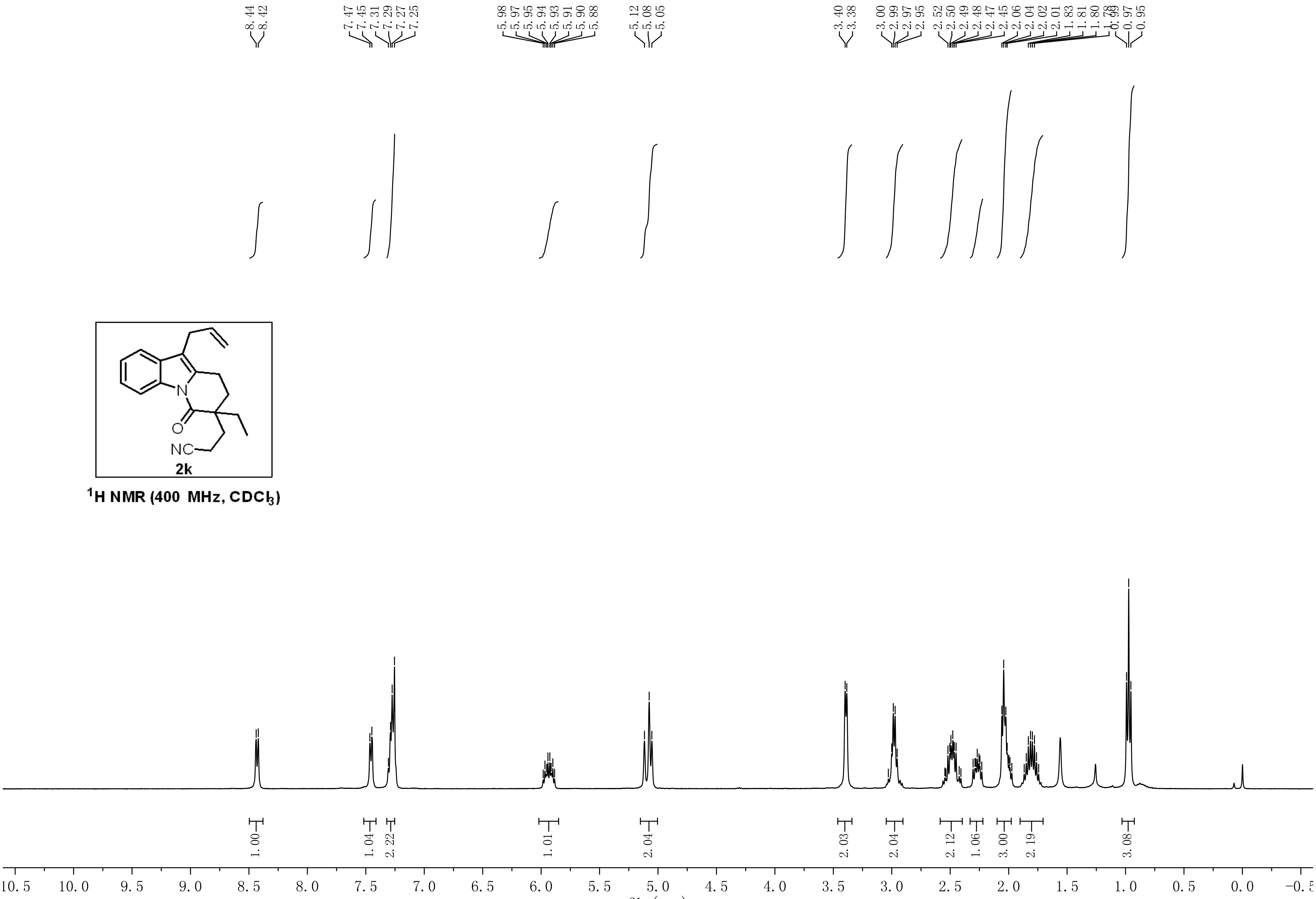
3i

^{13}C NMR (75 MHz, $CDCl_3$)

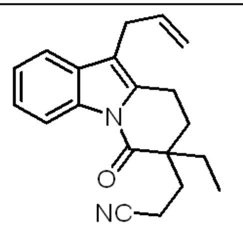



8.46
8.44
7.46
7.45
7.43
7.43
7.31
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.22
6.00
5.98
5.96
5.96
5.94
5.92
5.91
5.90
5.89
5.87
5.08
5.08
5.07
5.05
5.05
5.03
5.02
5.02
3.40
3.38
2.72
2.59
1.09
N
O
2j
^{1}H NMR (300 MHz, $CDCl_3$)
0.96
1.03
2.15
1.00
2.05
2.06
2.02
2.04
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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)


168.67
135.49
134.47
133.04
130.54
124.14
123.62
118.11
116.27
115.45
115.14
47.82
35.40
32.61
28.02
27.81
N
O
2j
^{13}C NMR (75 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

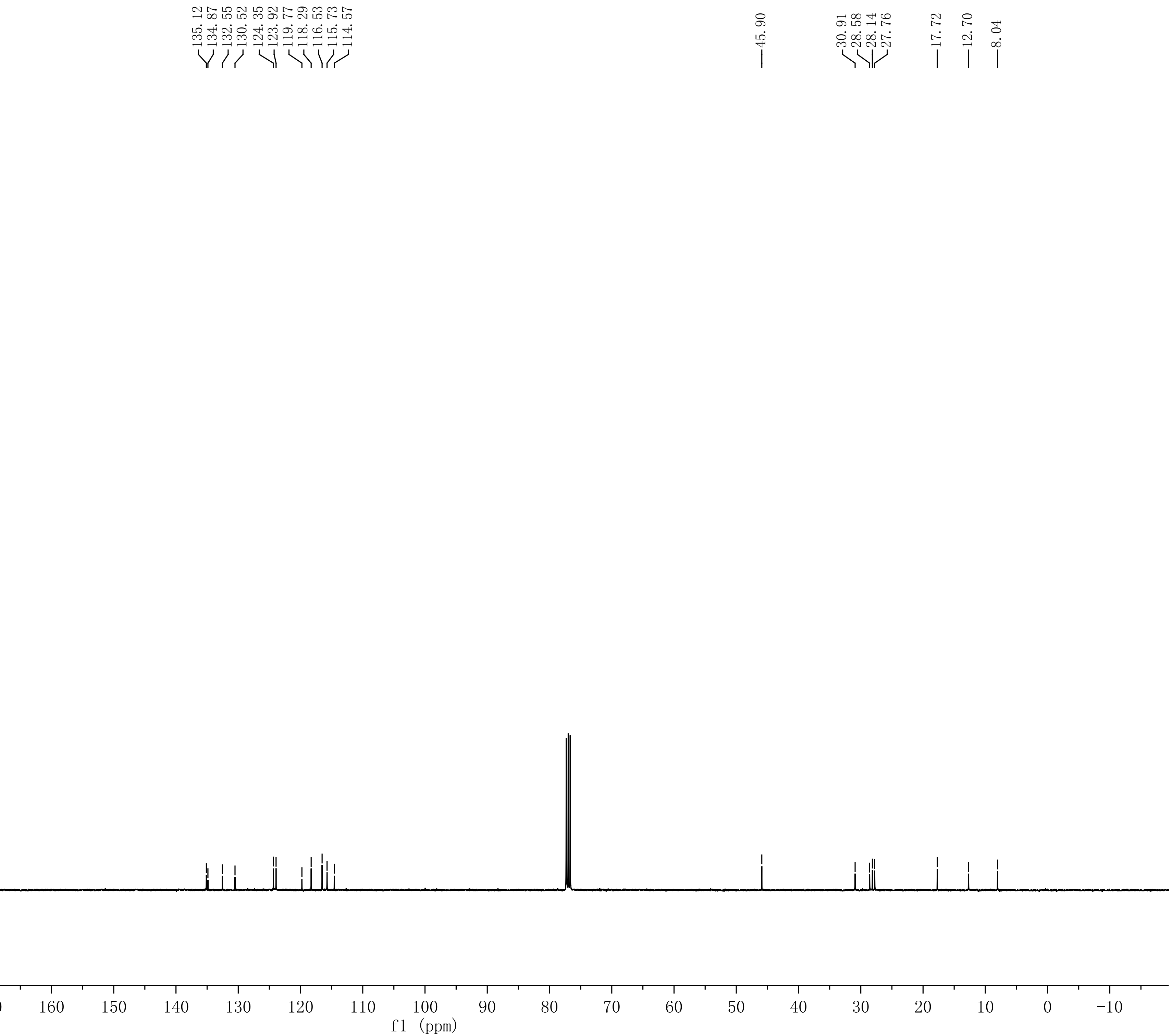


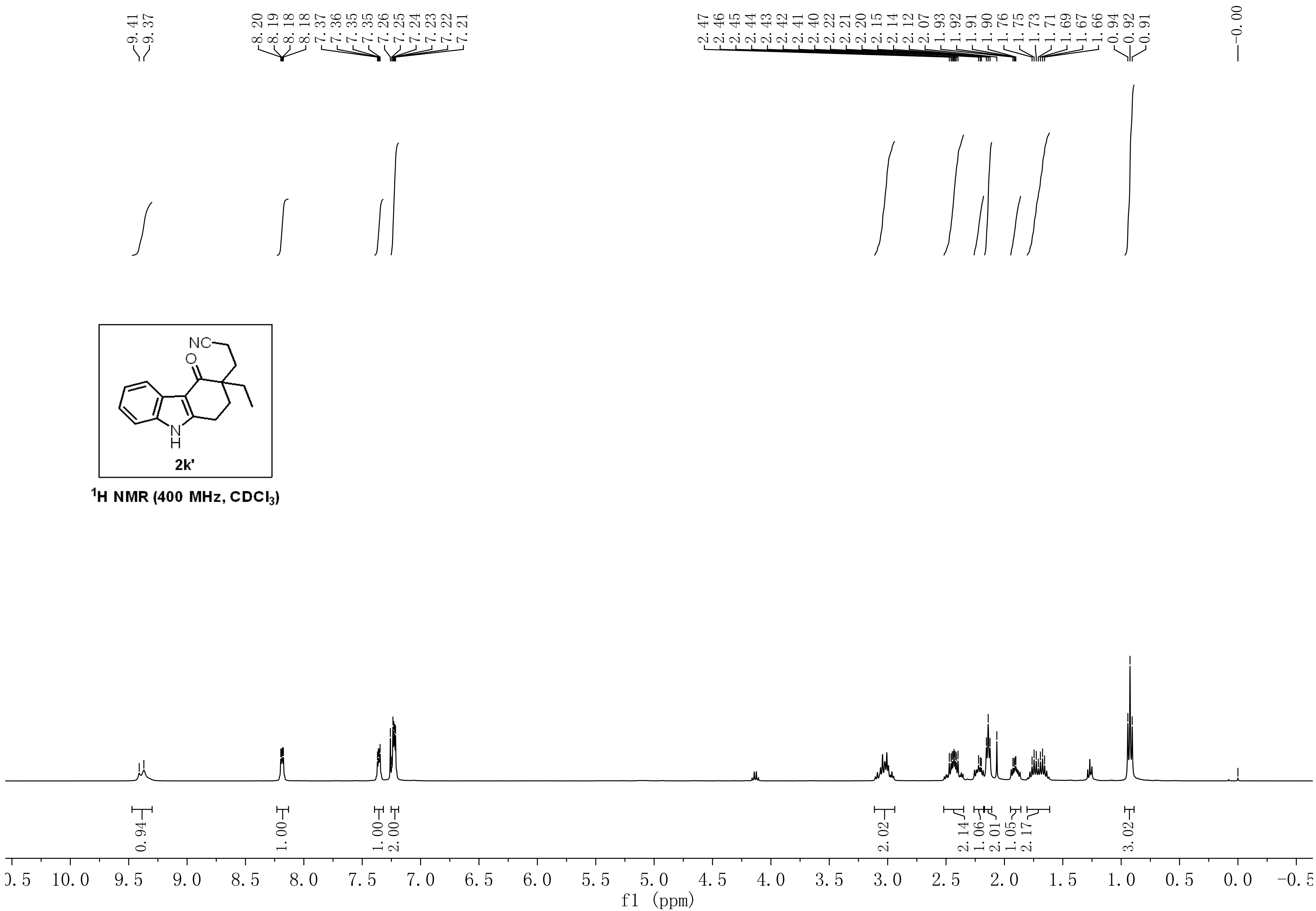
^{1}H NMR (400 MHz, $CDCl_3$)

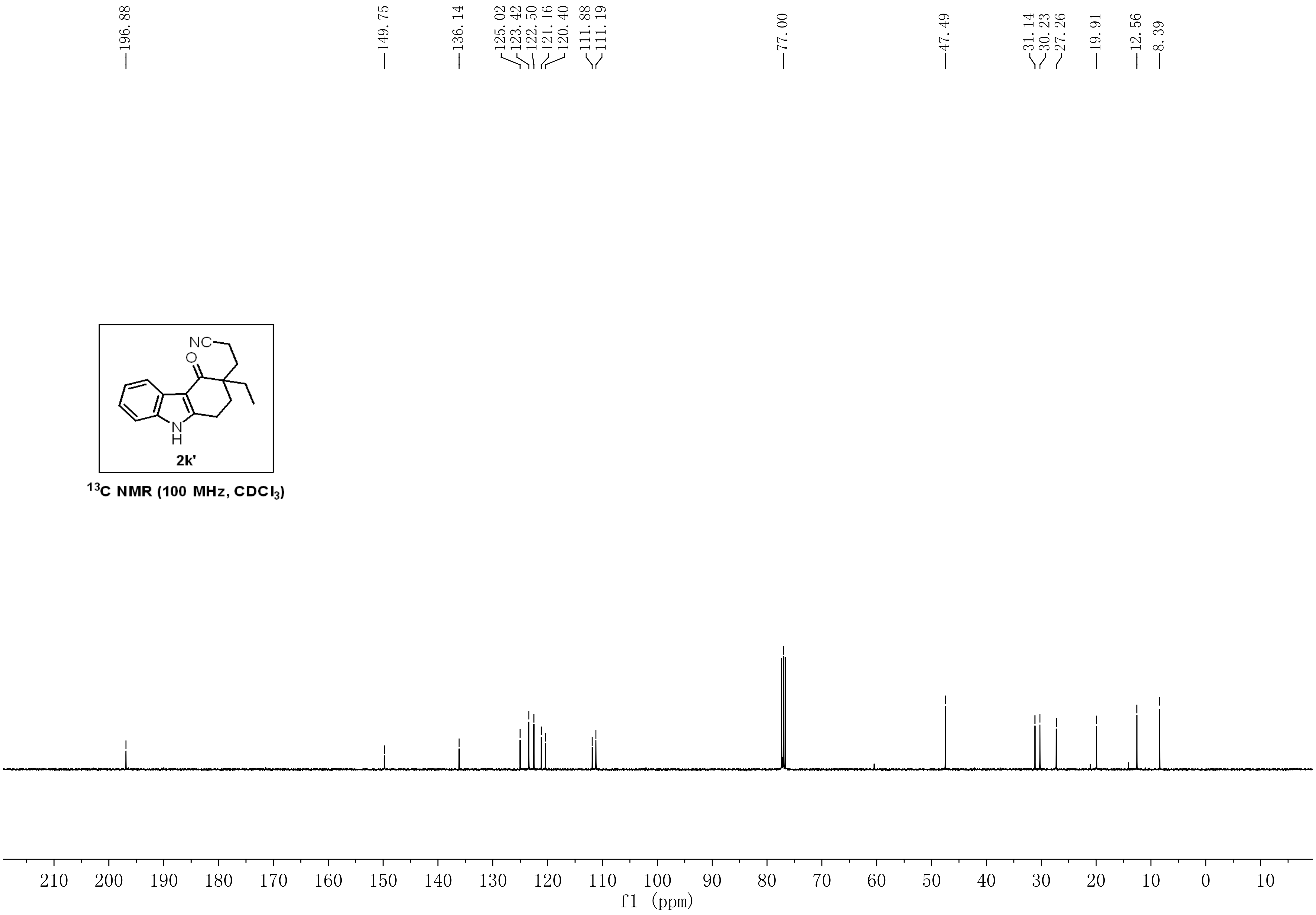


2k

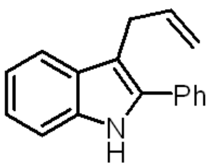
^{13}C NMR (100 MHz, CDCl$_3$)




9.41
9.37
8.20
8.19
8.18
8.18
7.37
7.36
7.35
7.35
7.26
7.25
7.24
7.23
7.22
7.21
2.47
2.46
2.45
2.44
2.43
2.42
2.41
2.40
2.22
2.21
2.20
2.15
2.14
2.12
2.07
1.93
1.92
1.91
1.90
1.76
1.75
1.73
1.71
1.69
1.67
1.66
0.94
0.92
0.91
-0.00
NC
O
N
H
2k'
1H NMR (400 MHz, CDCl3)
0.94
1.00
1.00
2.00
2.02
2.14
1.06
2.01
1.05
2.17
3.02
0.5
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
-0.5
f1 (ppm)

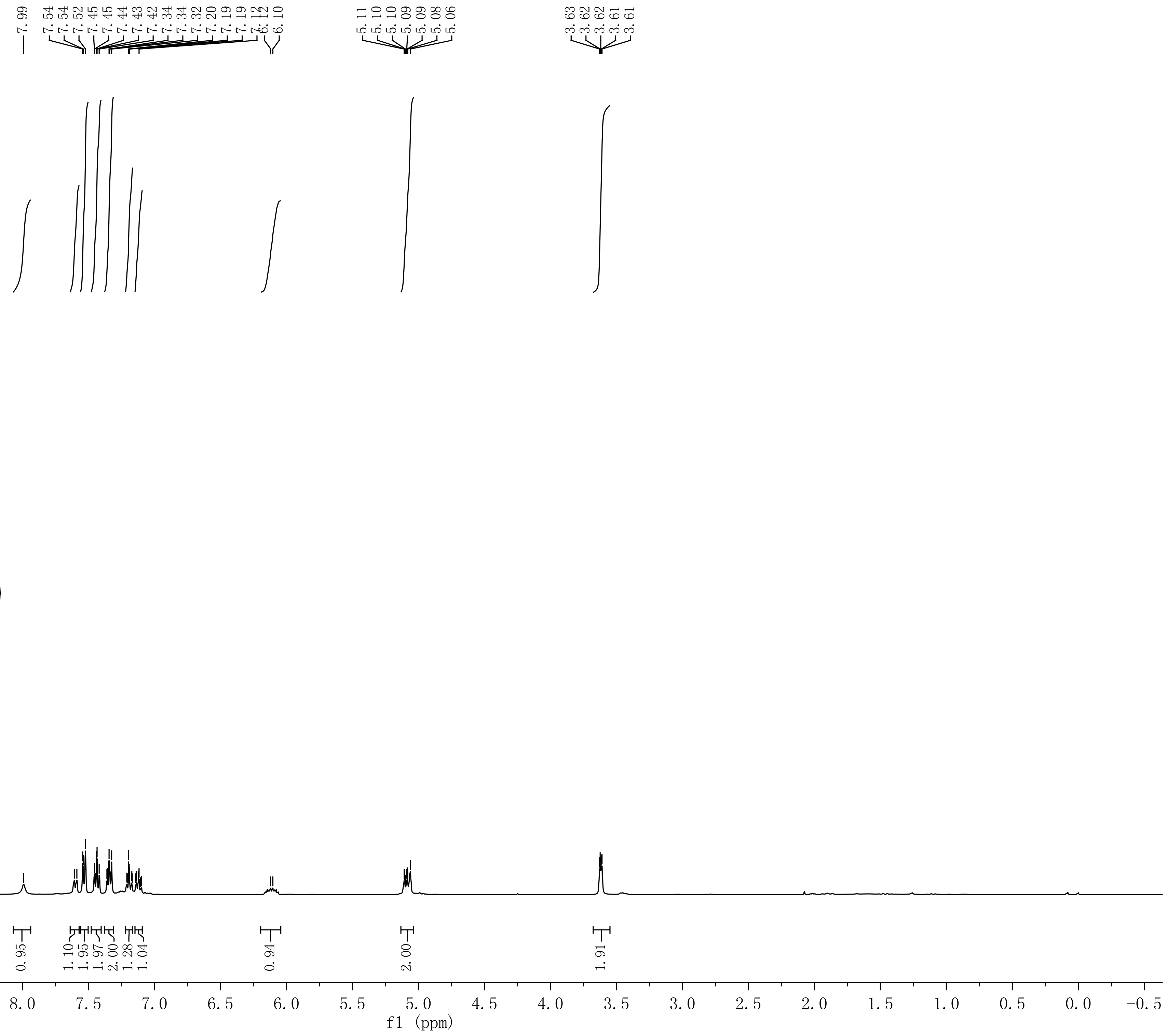


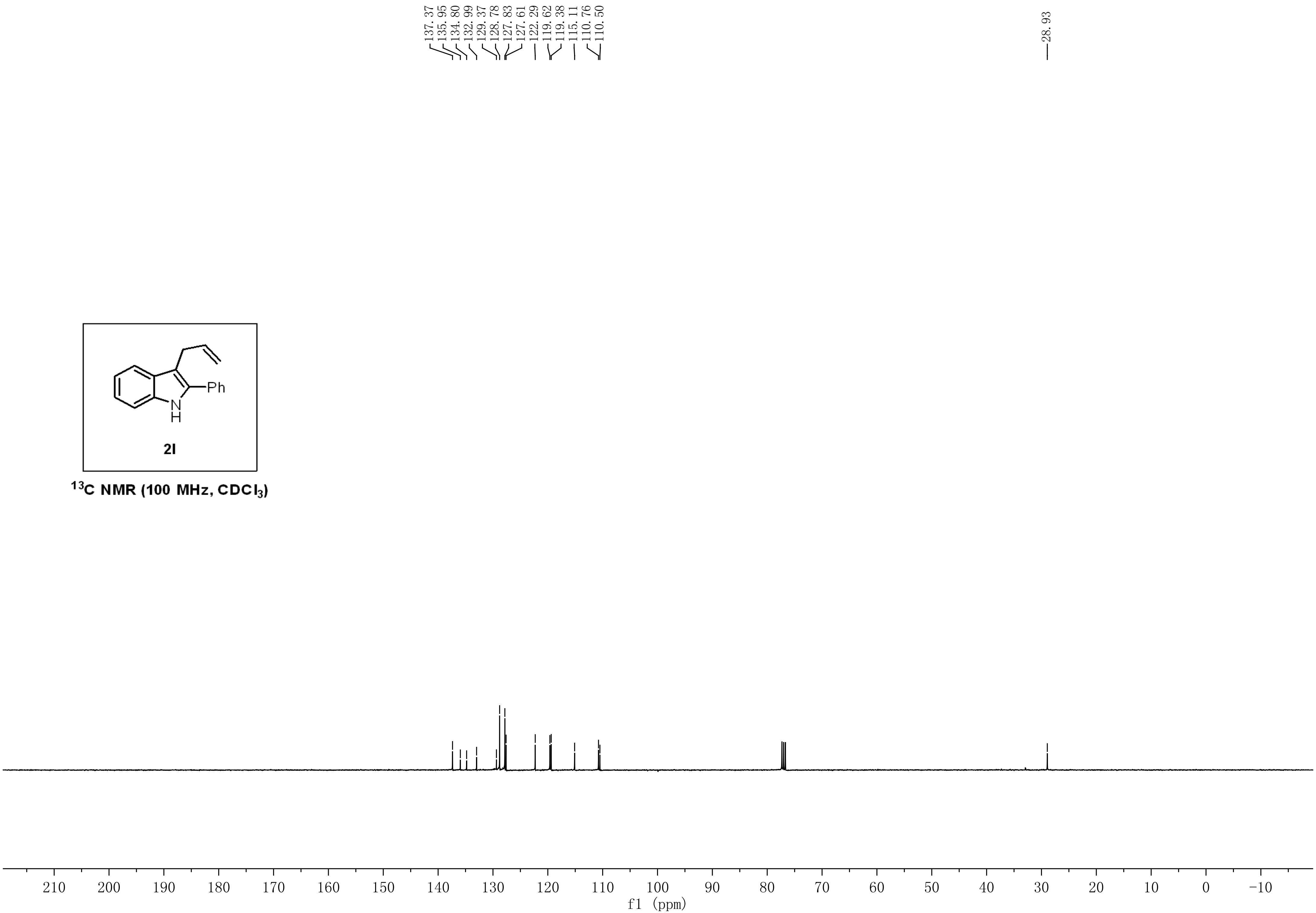
196.88
149.75
136.14
125.02
123.42
122.50
121.16
120.40
111.88
111.19
77.00
47.49
31.14
30.23
27.26
19.91
12.56
8.39
NC
O
N
H
2k'
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



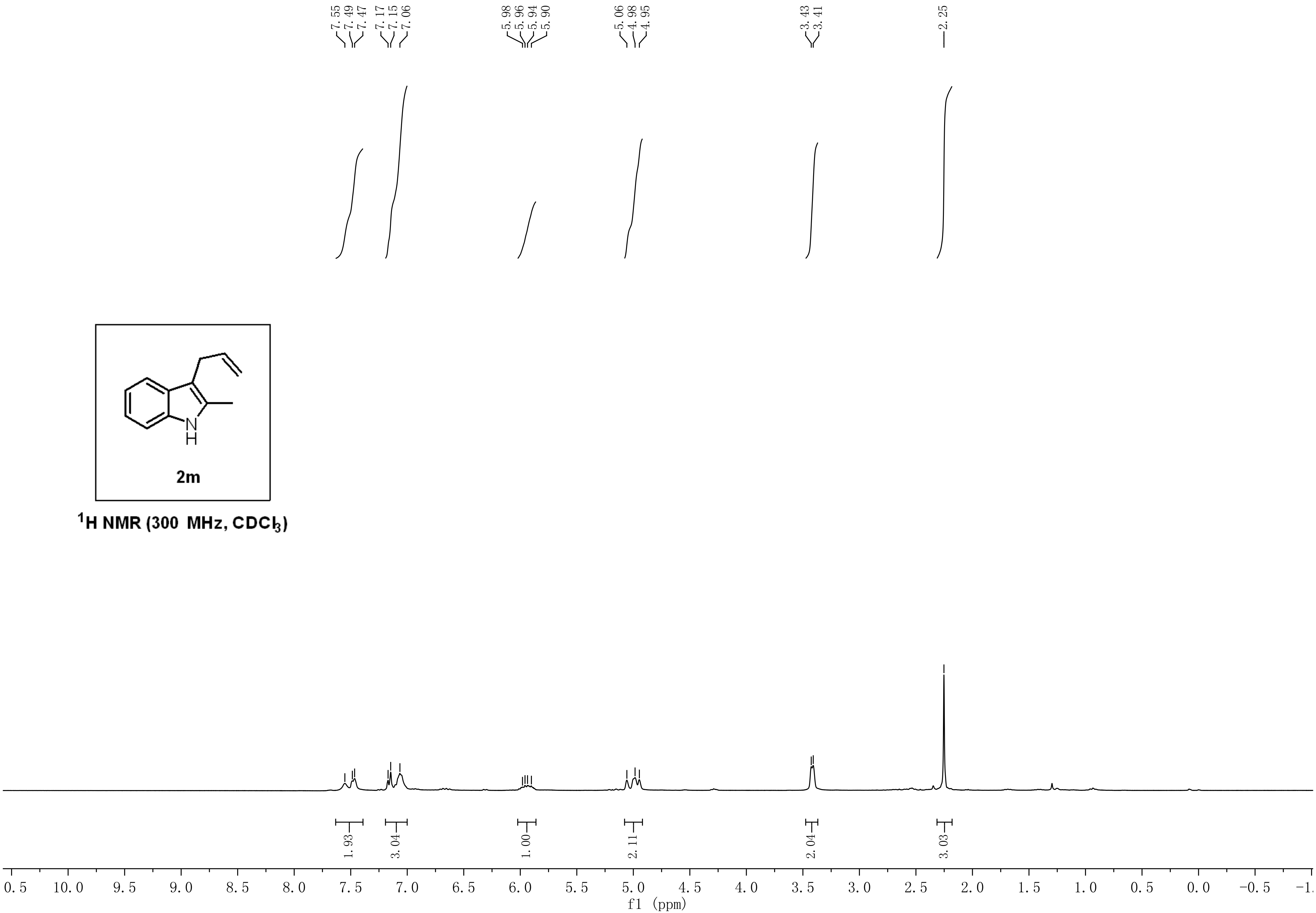
2l

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

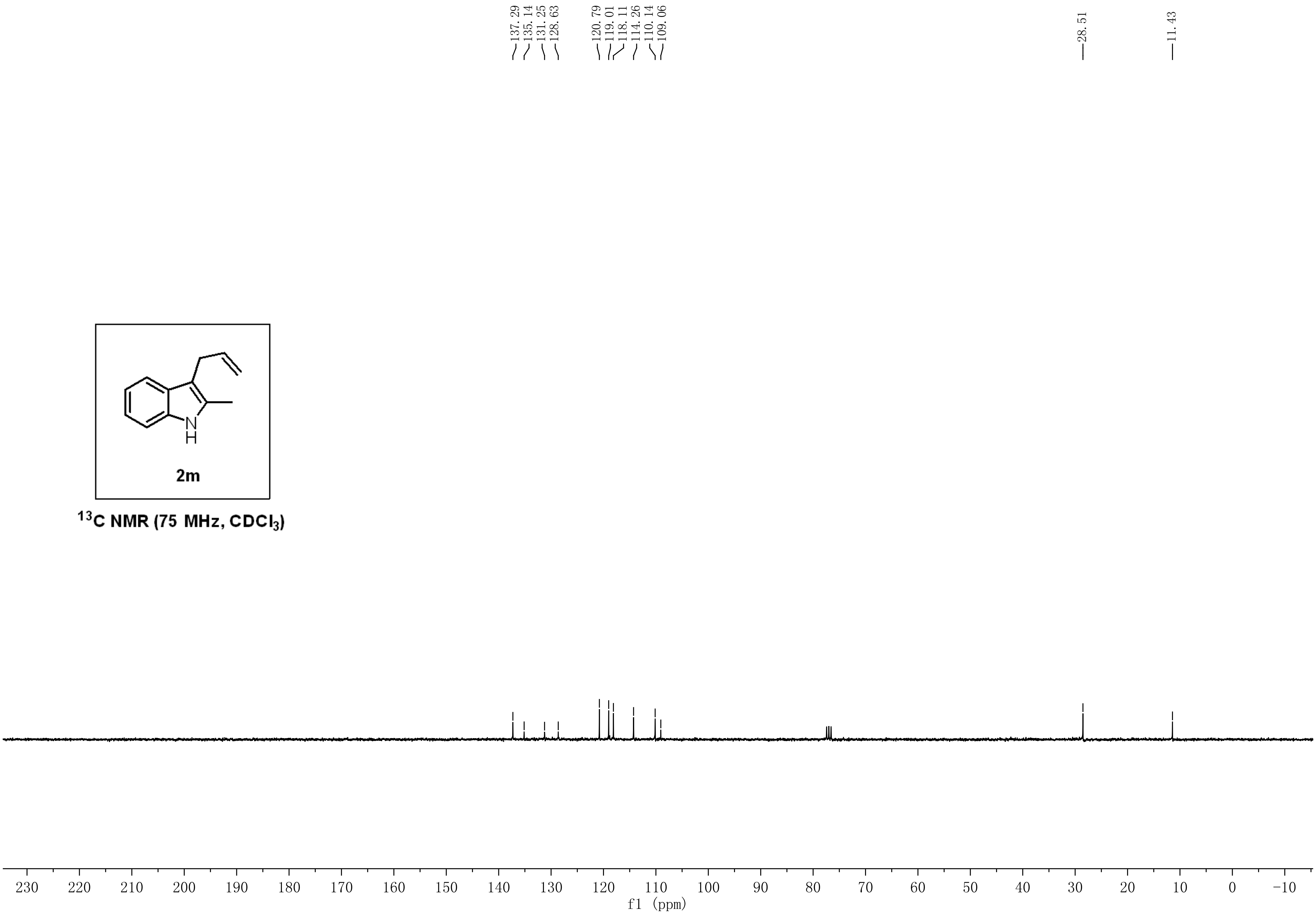




^{13}C NMR (100 MHz, $CDCl_3$)

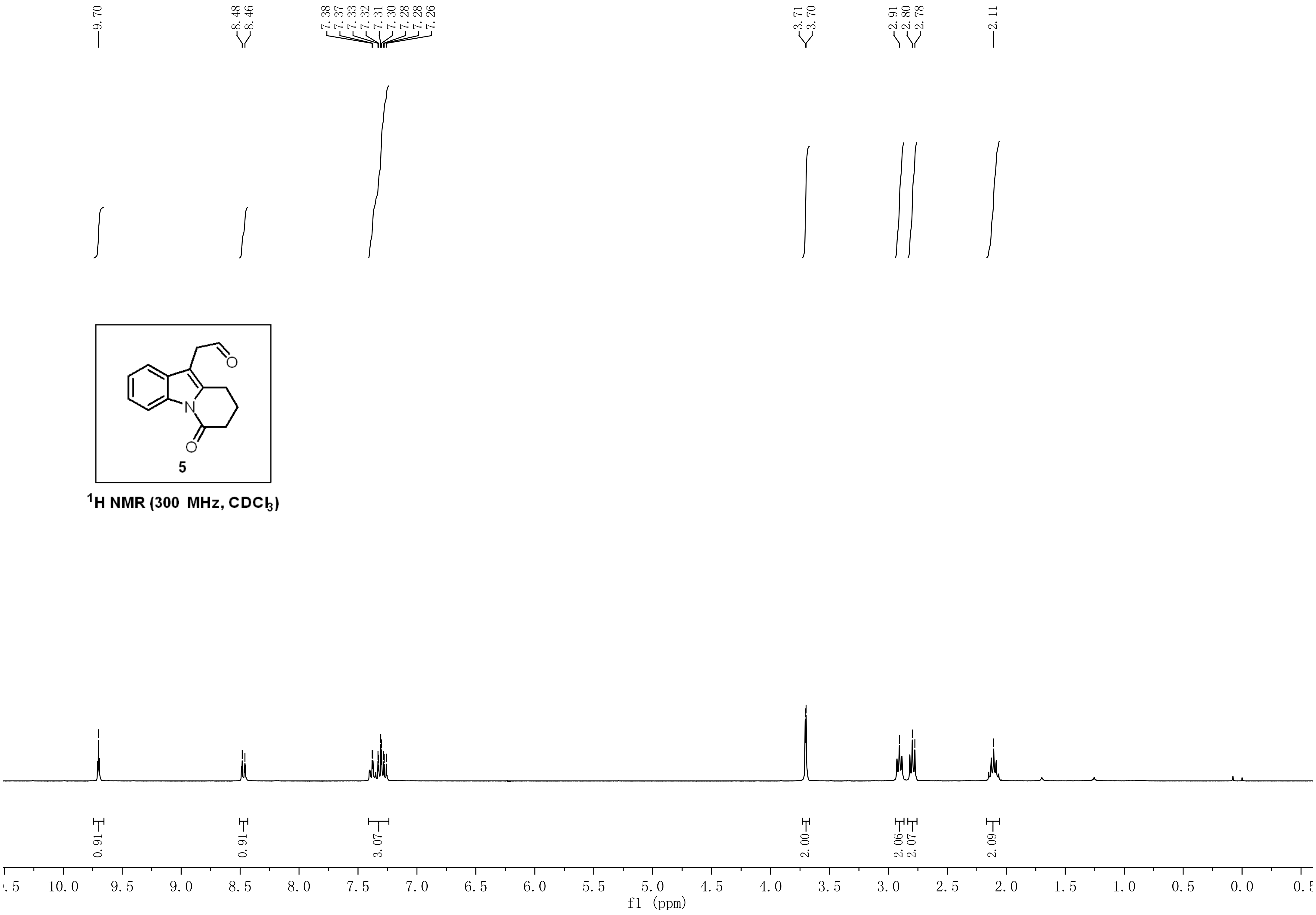


^1H NMR (300 MHz, $CDCl_3$)



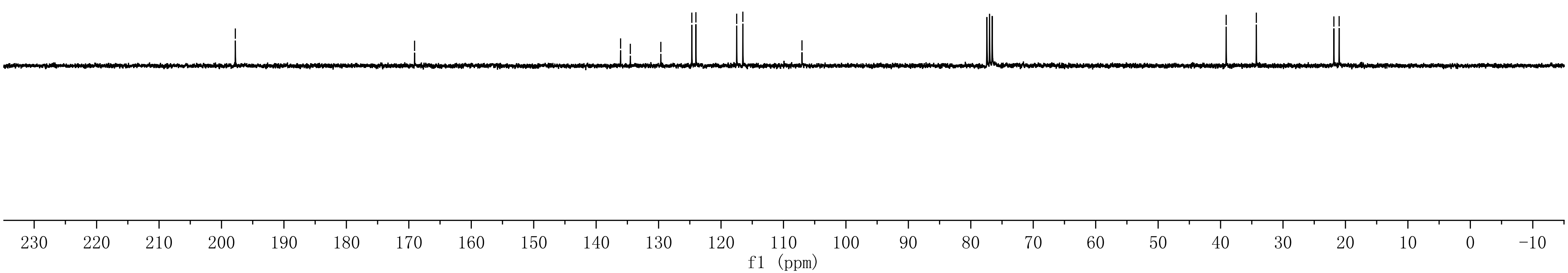
2m

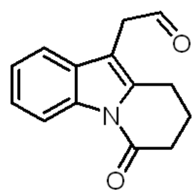
^{13}C NMR (75 MHz, $CDCl_3$)



5

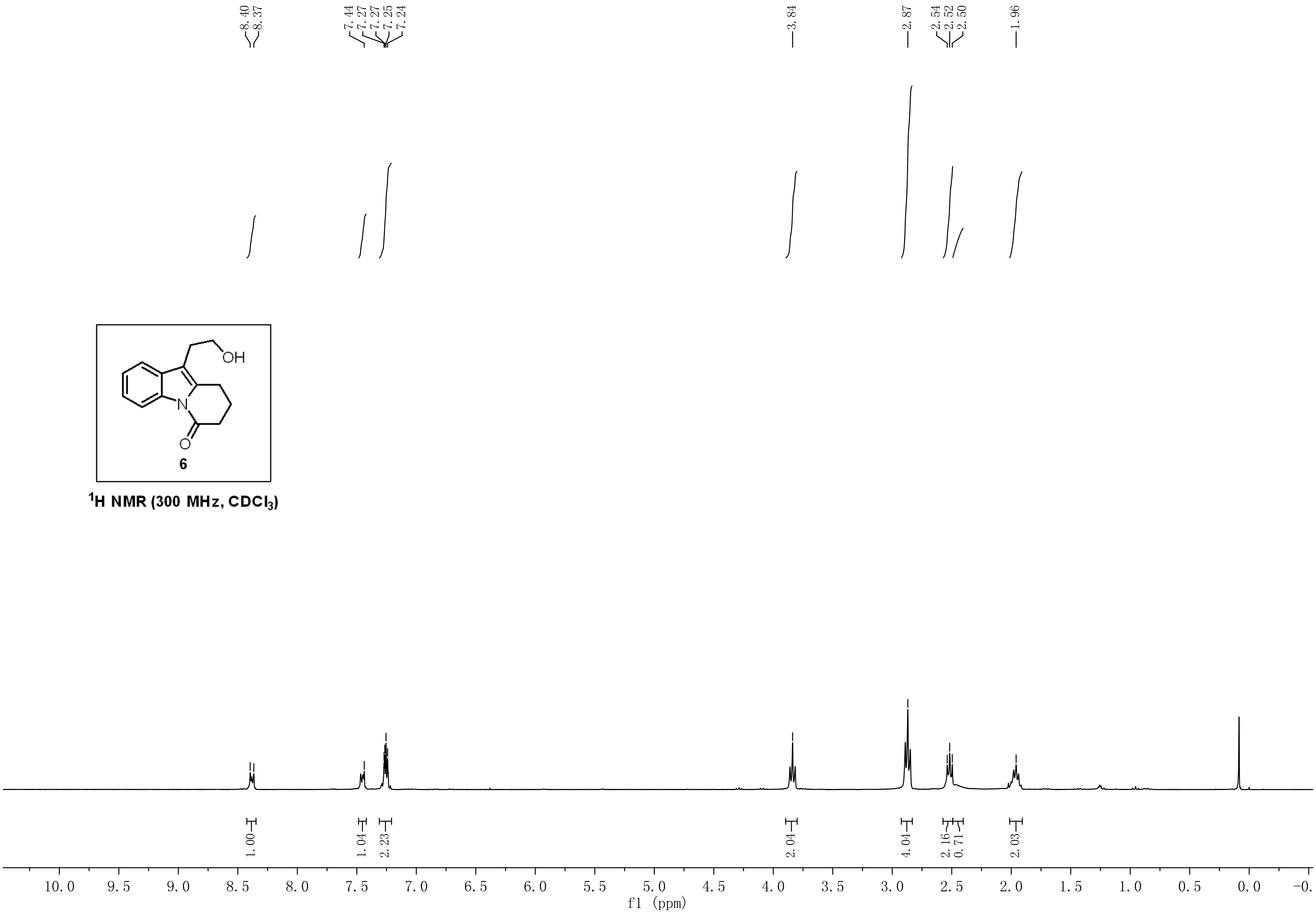
^{1}H NMR (300 MHz, $CDCl_3$)

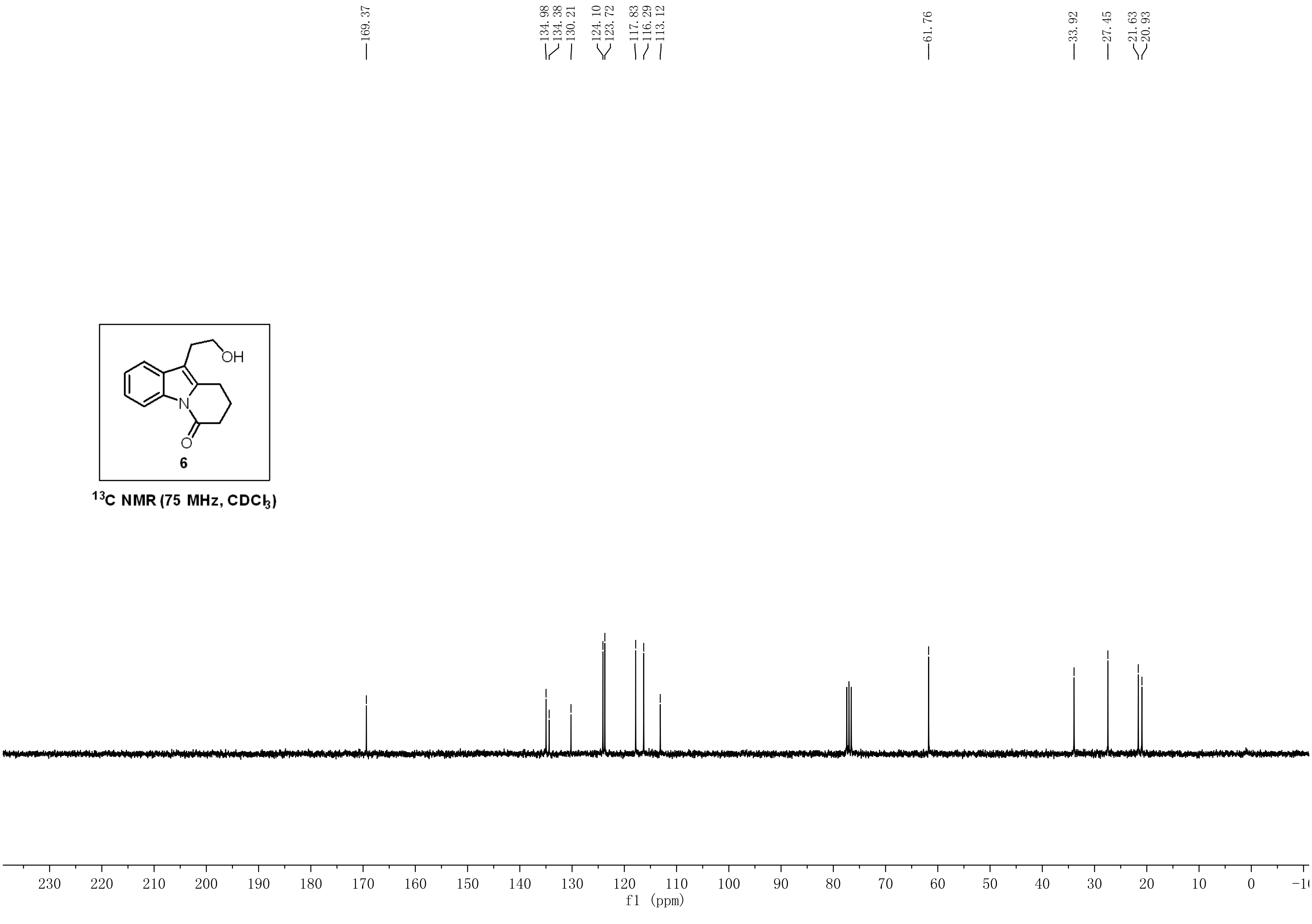




5

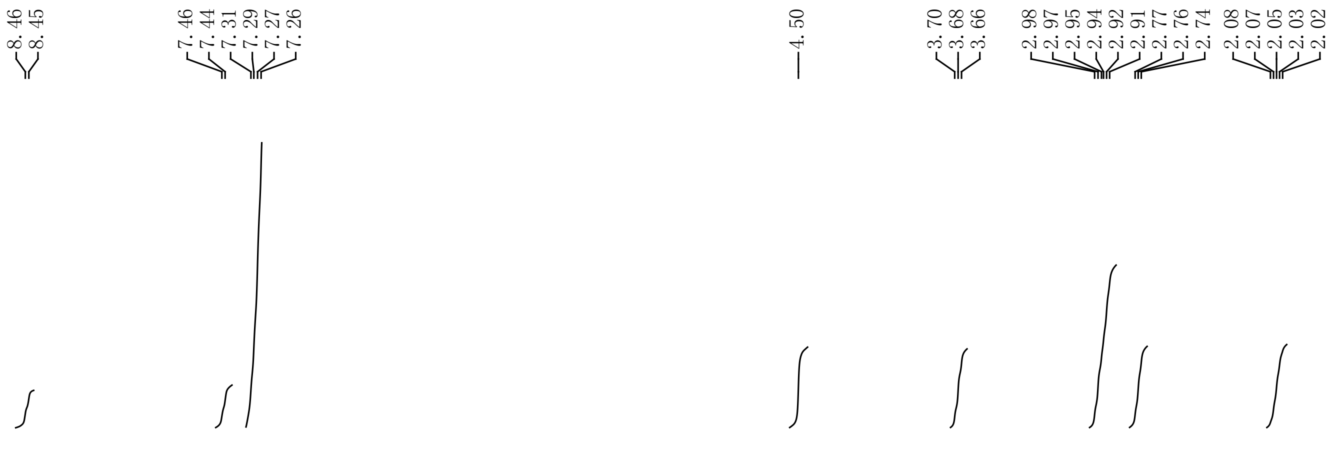
^{13}C NMR (75 MHz, $CDCl_3$)

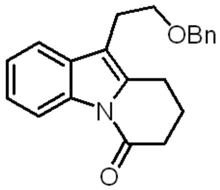

8.40
8.37
7.44
7.27
7.27
7.25
7.24
3.84
2.87
2.54
2.52
2.50
1.96
OH
N
O
6
1H NMR (300 MHz, CDCl3)
1.00
1.04
2.23
2.04
4.04
2.16
0.71
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)



6

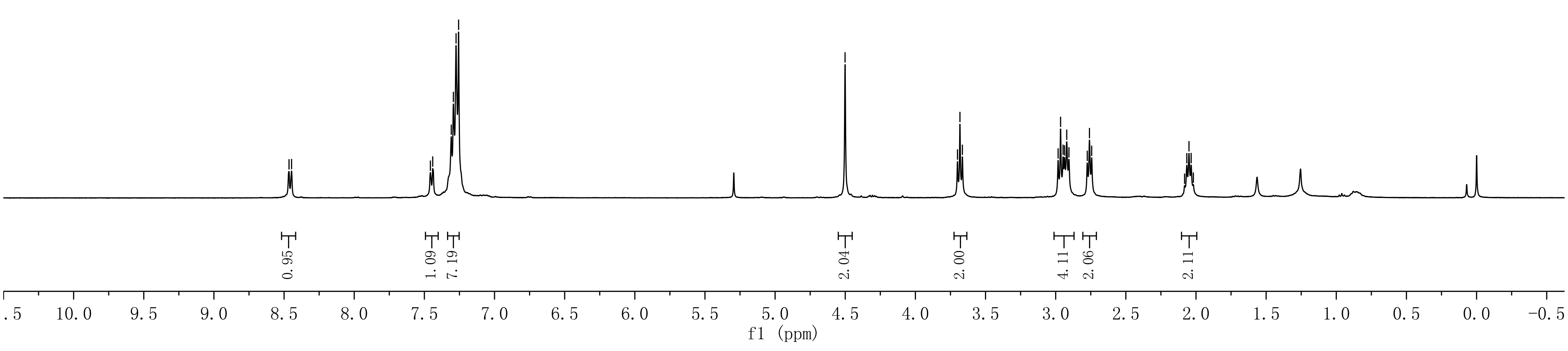
^{13}C NMR (75 MHz, $CDCl_3$)

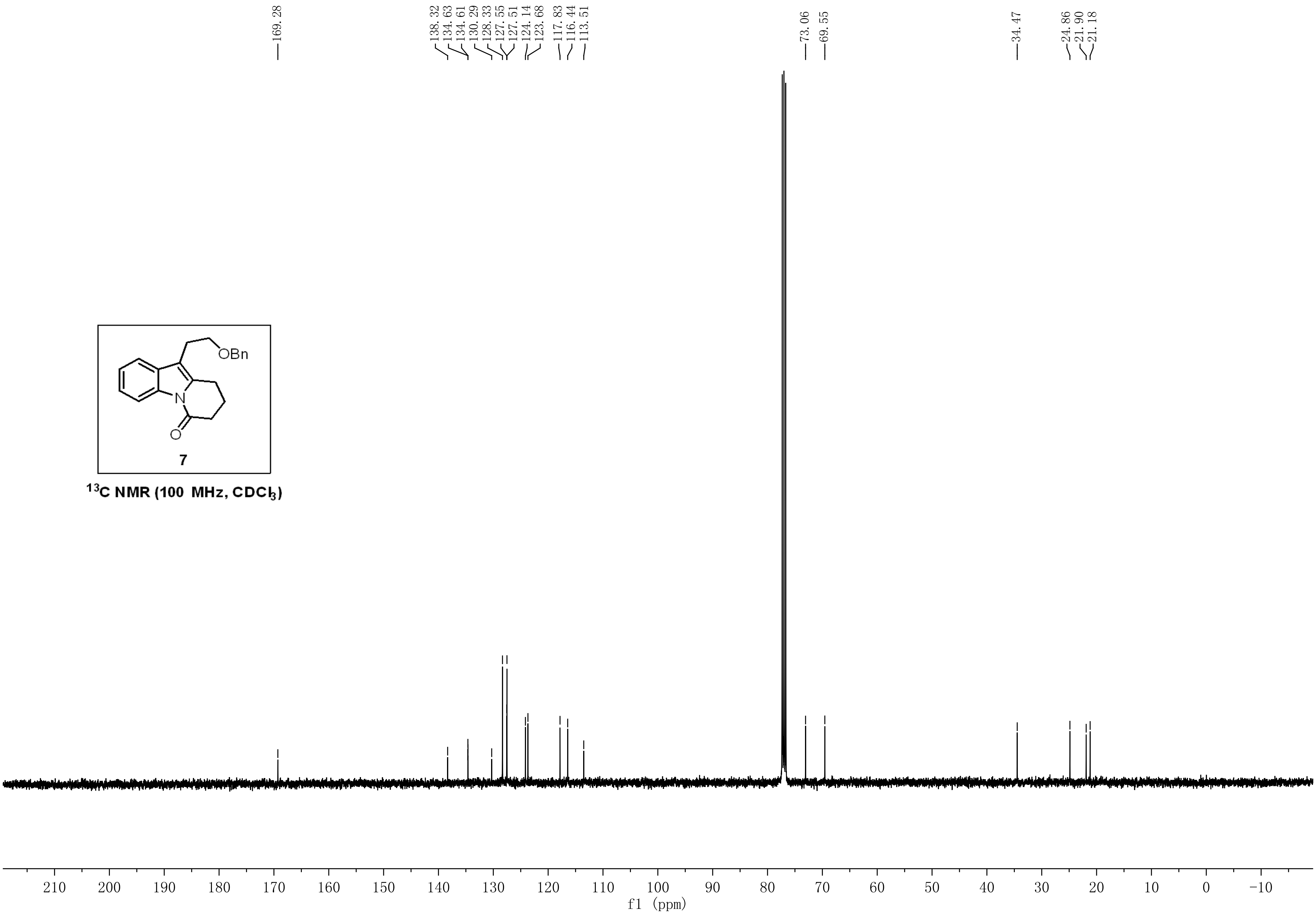




7

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





7

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