Supporting Information

Nitrative Bicyclization of 1,7-Diynes for Accessing Skeletally Diverse Tricyclic Pyrroles

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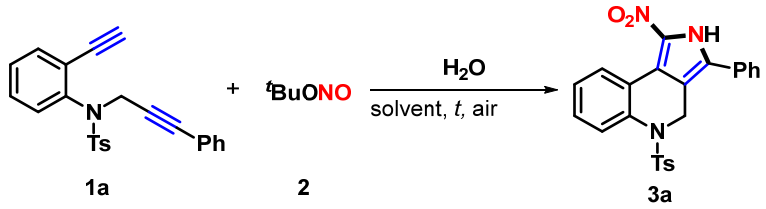
General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-d_6) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI and ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. The melting points were measured with digital melting point detector.

Table S1. Optimization of the Reaction Conditions for Forming 3a[a]

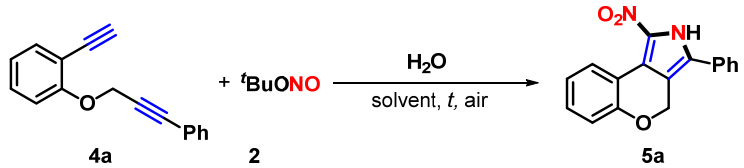


1a 2 3a

entry	solvent	H_2O (mmol)	t (°C)	yield (%)[b]
1	DMSO	0.46	60	68
2	MeCN	0.46	60	trace
3	1,4-dioxane	0.46	60	trace
4	DMF	0.46	60	trace
5	DCE	0.46	60	36
6	Toluene	0.46	60	43
7	THF	0.46	60	65
8	DMSO	0.46	25	34
9	DMSO	0.46	80	70
10	DMSO	0.46	100	82
11	DMSO	0.46	110	66
12[c]	DMSO	0.46	100	58
13	DMSO	0.23	100	55
14	DMSO	0.69	100	57
15[d]	DMSO	7.8	100	70

[a]Reaction conditions: **1a** (0.2 mmol), ^{t}BuONO (**2**, 3.5 equiv.) and DMSO (3 mL) under air conditions for 5 h. [b]Isolated yield. [c]Under Ar atmosphere. [d]**1a** (1.54 g, 4 mmol).

Table S2. Optimization of the Reaction Conditions for Forming 5a[a]



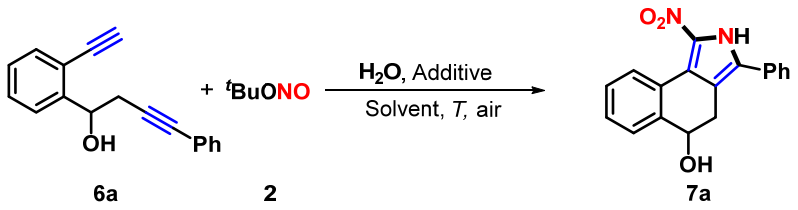
4a 2 5a

entry	solvent	H_2O (mmol)	t (°C)	yield (%)[b]
1	DMSO	0.46	100	40
2	DMSO	0.46	70	42
4	DMSO	0.46	50	48
5	DMSO	0.46	30	trace

6	THF	0.46	50	64
7	Toluene	0.46	50	trace
8	1,4-dioxane	0.46	50	20
9	MeCN	0.46	50	40

[a] Reaction conditions: **4** (0.2 mmol), ^{t}BuONO (**2**, 3.5 equiv), and solvent (3 mL) under air conditions for 8 h.

Table S3. Optimization of the Reaction Conditions for Forming 7a[a]

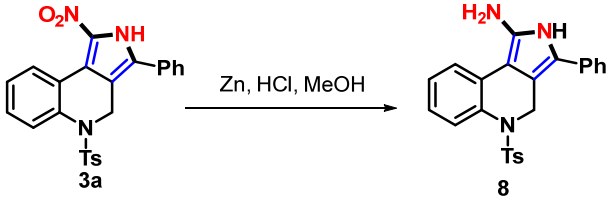


6a **2** **7a**

entry	solvent	H_2O (mmol)	additive (equiv)	*t* (°C)	yield (%)[b]
1	DMSO	0.46	-	100	25
2	DMSO	0.46	-	80	28
3	DMSO	0.46	-	60	31
4	THF	0.46	-	60	40
5	MeCN	0.46	-	60	32
6	DMF	0.46	-	60	trace
7	Toluene	0.46	-	60	22
8	1,4-dioxane	0.46	-	60	trace
9	THF	0.46	-	55	46
10	THF	0.46	-	50	43
11	THF	0.46	$Co(NO_3)_2$•$6H_2O$	55	60
12	THF	0.46	$Co(C_5H_7O_2)_2$	100	trace
13	THF	0.46	$CH_3CO_2)_2Co$•$4H_2O$	100	20
14	THF	0.46	$CoCl_2$	100	40

[a]Reaction conditions: **6a** (0.2 mmol), ^{t}BuONO (**2**, 3.5 equiv), $Co(NO_3)_2$•$6H_2O$ (1.0 equiv) and solvent (3 mL) under air conditions for 8 h.

The presence of the nitro group provides great possibilities for late-stage modifications (Scheme S1). For instance, treatment of **3a** with Zn powder in the presence of HCl resulted in product **8** in 93% yield.[1]

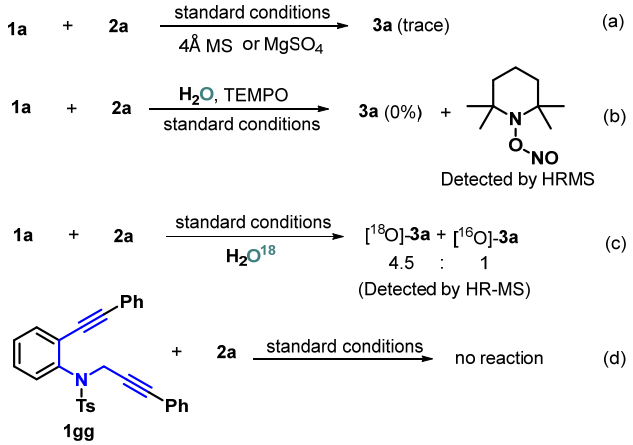


3a **8**

Scheme S1. Synthetic Application of 3a

To gain insight into this mechanism of the nitrative bicyclization, some controlled experiments were carried out (Scheme S2). Firstly, the formation of product **3a** was substantially inhibited and starting material **1a** was almost completely recovered with the existence of the dehydrating agents such as 4Å molecular sieve (4Å MS) and anhydrous magnesium, revealing that H_2O is crucial for this transformation (Scheme S2a). Then, the reaction process was severely suppressed when 2,2,6,6-tetramethyl-piperidine-*N*-oxyl (TEMPO) as the radical scavenger was placed into the reaction system, in which TEMPO-NO adduct was detected by HR-MS analysis (Scheme S2b),

indicating that a radical process may be included. Next, an ^{18}O-labeling experiment gave a mixture of [^{18}O]-**3a** and [^{16}O]-**3a** with a 4.5:1 ratio (Scheme S2c), thus demonstrating that one of the oxygen atoms of the nitro group may come from H_2O and oxygen in air. Moreover, 1,7-diyne **1gg** with two internal alkyne units was subjected with standard conditions. The reaction did not proceed with starting material **1gg** being recovered (Scheme S2d). These results showed that the terminal alkyne at the 1,7-diyne substrate is essential for this transformation.



Scheme S2. Control Experiments

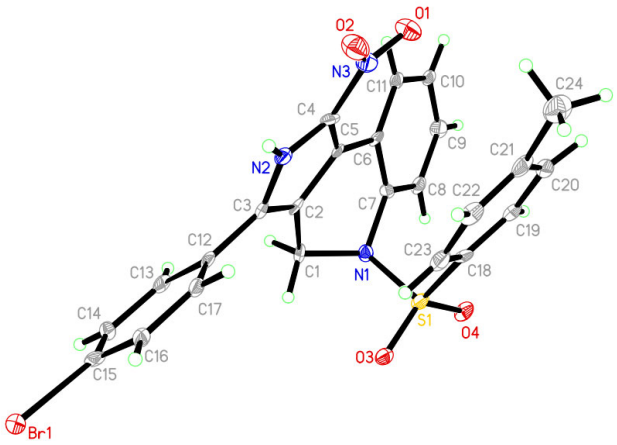
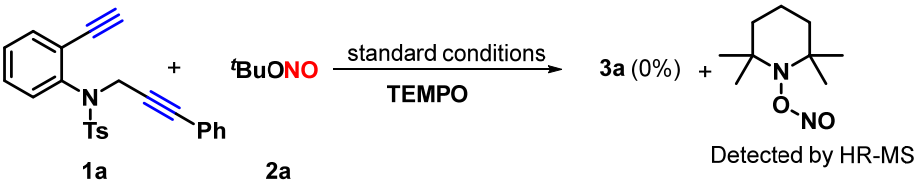


Figure S1 X-Ray Structure of 3l (2141386)

Radical-Trapping Experiment:

TEMPO as the radical trapping reagent — General procedure



To a 25-mL Pressure tube under air conditions, 1,7-diyne **1a** (0.2 mmol, 77 mg), *tert*-butyl nitrite (**2a**, 0.7 mmol, 72.1mg, 3.5 equiv) and TEMPO (0.6 mmol, 94 mg) in DMSO (3.0 mL, about 0.46 mmol H_2O in 3mL DMSO) was stirred at 100 °C for 5 hours. The corresponding product (**3a**) was not detected according to TLC analysis. After completion of the reaction, the solution was detected by HR-MS analysis (Figure S2).

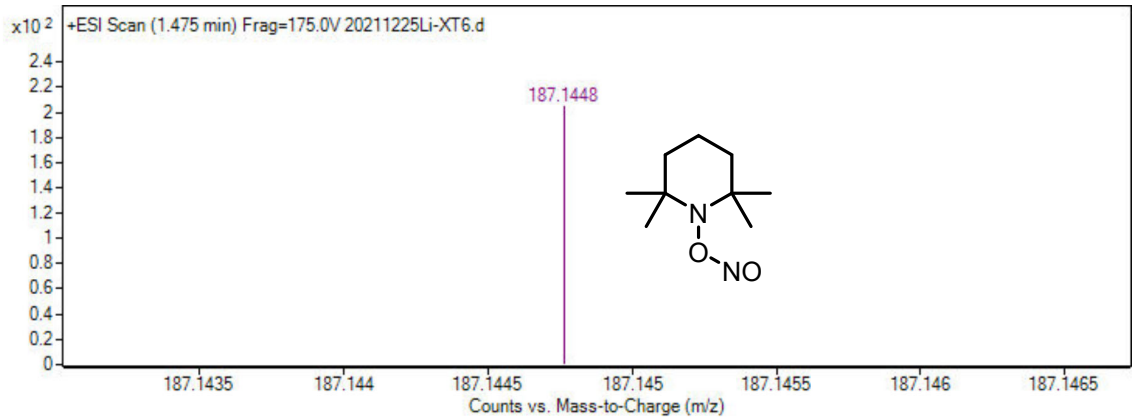


Figure S2. Copy of HR-MS Spectrum of TEMPO-NO adduct $[M+H]^+$

Intermediate Detection

To a 25-mL Pressure tube under air conditions, 1,7-diyne **1a** (0.2 mmol, 77 mg), *tert*-butyl nitrite (**2a**, 0.7 mmol, 72.1mg, 3.5 equiv), H_2O (0.46 mmol, 8 mg,) and DMSO (3.0 mL, about 0.46 mmol H_2O in 3mL DMSO) was stirred at 100 °C for 1 hours. Then the reaction system was directly measured by LC-MS analysis. The key intermediates **C** and **F** were detected by HR-MS (Figures S3-S4).

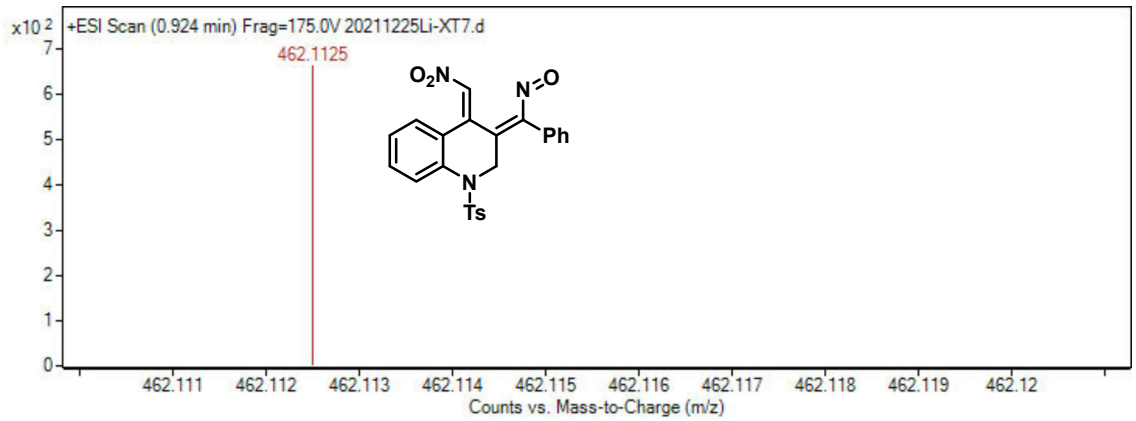


Figure S3. Copy of HR-MS Spectrum of Intermediate C $[M+H]^+$

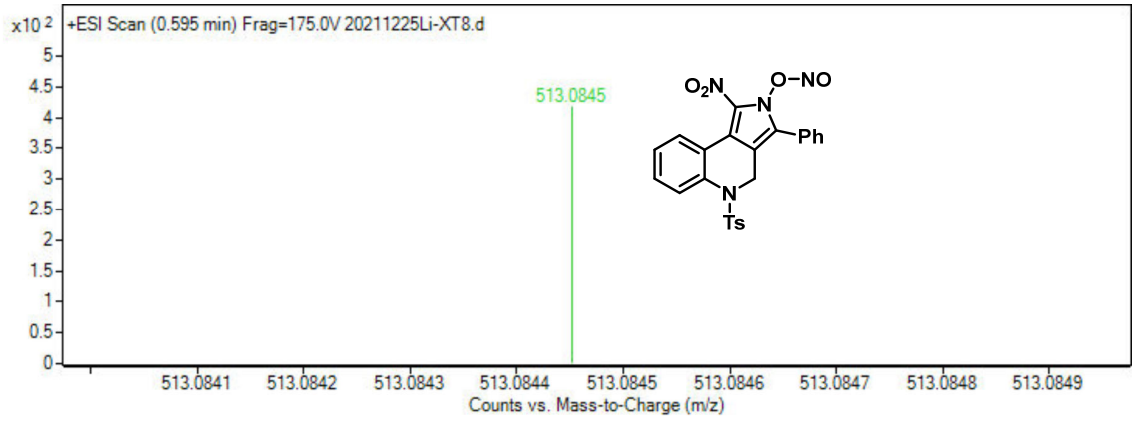
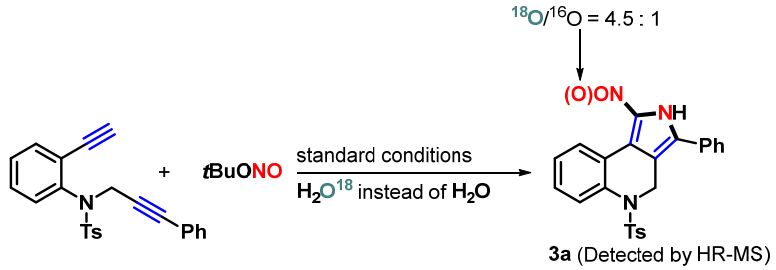


Figure S4. Copy of HR-MS Spectrum of Intermediate F $[M+Na]^+$

Mechanistic Investigations Control Experiment with $H_2{}^{18}O$



To a 25-mL Pressure tube under air conditions, 1,7-diyne **1a** (0.2 mmol, 77 mg), *tert*-butyl nitrite (**2**, 0.7 mmol, 72.1 mg, 3.5 equiv), $H_2{}^{18}O$ (0.46 mmol, 10 mg,) and DMSO (3.0 mL, about 0.46 mmol H_2O in 3mL DMSO) was stirred at 100 °C for 5 hours until complete consumption of **1a** as monitored by TLC analysis. The product was detected by HRMS (Figure S5).

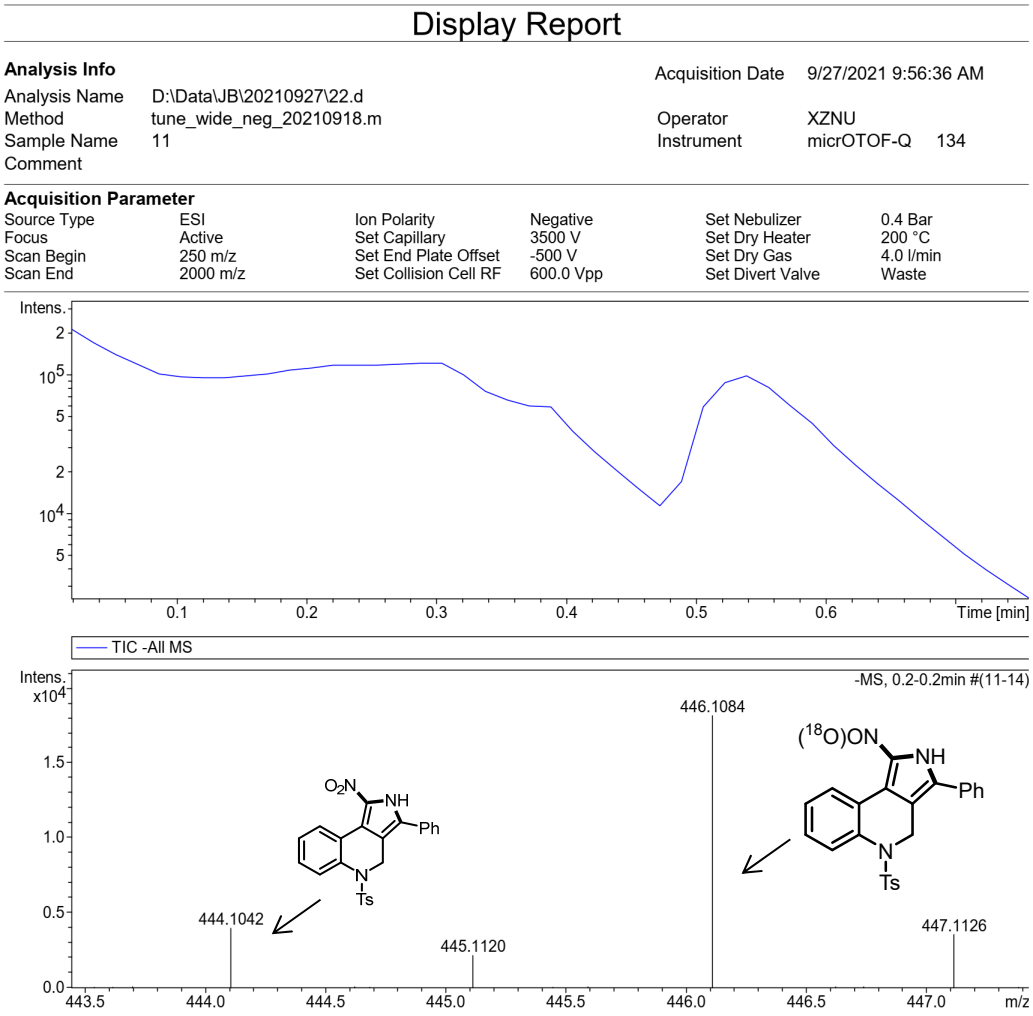
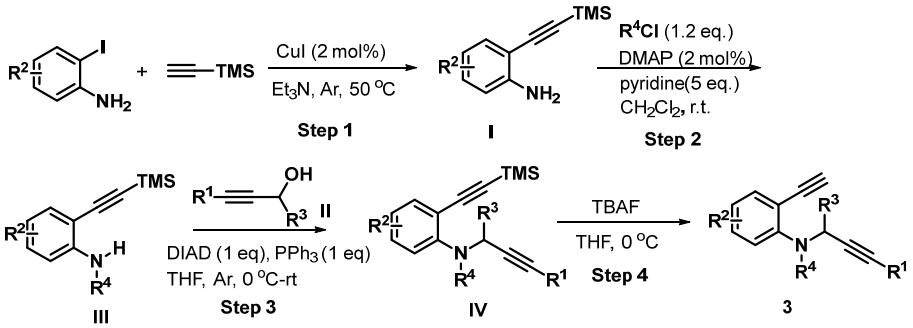


Figure S5. Copy of HR-MS Spectrum of O^{18}-containing Product 3a $[M-H]^-$

General procedure for the synthesis of substrates 1a-1ff[2]



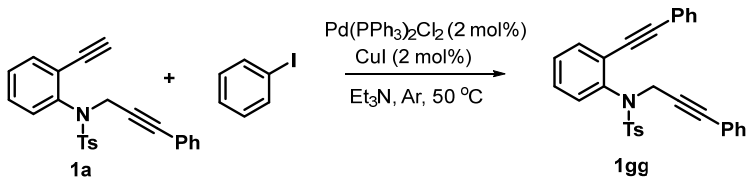
Step 1: Under Ar conditions, a mixture of 2-iodoaniline (10.0 mmol), CuI (38 mg, 2 mol %), $PdCl_2(PPh_3)_2$ (140 mg, 2 mol %), and Et_3N (60 mL) was stirred at 50 °C in oil bath. Then, trimethylsilylacetylene (1.0 g, 10.5 mmol, 1.05 equiv) was dropwise added into the reaction system. The resulting reaction mixture was stirred until thin-layer chromatography (TLC) indicated complete consumption of the starting material., the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford compound **I** (90-95% yield).

Step 2: To a solution of **I** (1.0 equiv) in CH_2Cl_2 (solvent, c = 0.2 M) was added pyridine (5.0 equiv), catalytic DMAP (2 mol %), and R^4Cl (1.2 equiv) sequentially. After the reaction was completed at room temperature (monitored by TLC), the reaction mixture was quenched with 1 N HCl and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography (eluent: hexanes/EtOAc) on silica gel to afford product **V**.

Step 3: To an 100-mL oven-dried flask containing a magnetic stirring bar, **III** (9 mmol), PPh_3 (2.358 g, 9 mmol), and **II** (9 mmol) in distilled THF (30 mL), DIAD (diisopropyl azodicarboxylate, 9 mmol) was added dropwise at 0 °C under nitrogen. Then the solution stirred for 30 minutes and the temperature was warmed to room temperature slowly. The reaction was quenched by adding aqueous sodium hydroxide solution (0.5 M, 50 mL). The mixture was then diluted with Et_2O (50 mL) and washed with NaOH (0.5 M, 50 mL) and brine (50 mL) in sequence. The combined organic layers were dried with Na_2SO_4, and concentrated in vacuo after filtration. The residue was purified by flash chromatography on silica gel (eluted with petroleum ether/ethyl acetate = 10:1) to give pure compound **IV**.

Step 4: Under Ar conditions, compound **IV** (6 mmol), TBAF•$3H_2O$ (4.8 mmol, 1.56 g, 0.8 equiv) and THF (10 mL) were added into a dried flask. Then, the mixture was cooled down to 0 °C. After stirring at this temperature for 1.0 h, and it was quenched by saturated aqueous NH_4Cl. Then the mixture was extracted with DCM and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (200-300 mesh) using mixtures of petroleum ether/ethyl acetate (5:1, v/v) afforded substrate **3** (78%-90% yield).

General procedure for the synthesis of substrate 1gg

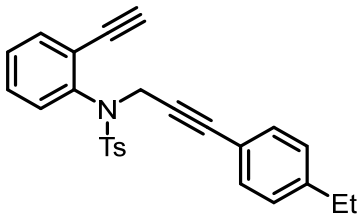


Under Ar conditions, a mixture of **1a** (5 mmol), CuI (19 mg, 2 mol %), $PdCl_2(PPh_3)_2$ (70 mg, 2 mol %), iodobenzene (1.1 equiv) and Et_3N (20 mL) was stirred at 50 °C in oil bath. The resulting reaction mixture was stirred until thin-layer chromatography (TLC) indicated complete consumption of the starting material. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford product **1gg** (1.84 g, 80% yield).

Reference

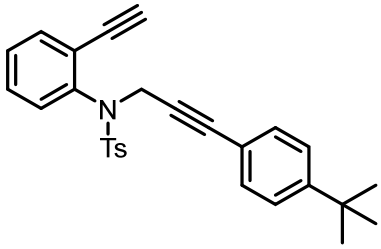
1. B. M. Trost, D. A. Bringley and B. M. O'Keefe, *Org. Lett.* 2013, **15**, 5630.
2. (a) D. Wu, W.-J. Hao, Q. Rao, Y. Lu, S.-J. Tu and B. Jiang, *Chem. Commun.,* 2021, **57**, 1911. (b) M. He, N. Chen, T. Zhou, Q. Li, H.-G. Li, M. Lang, J. Wang, S.-Y. Peng, *Org. Lett.,* 2019, **21**, 9559.

N-(3-(4-ethylphenyl)prop-2-yn-1-yl)-N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1f)



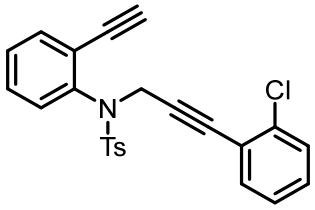
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.85 g, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.73 (d, J = 8.0 Hz, 2H), 7.57–7.51 (m, 1H), 7.34–7.28 (m, 2H), 7.25 (d, J = 5.2 Hz, 3H), 7.13–7.05 (m, 4H), 4.74 (s, 2H), 3.12 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 2.41 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 144.9, 143.6, 140.6, 137.2, 134.1, 131.5, 131.1, 129.5, 129.3, 128.6, 128.1, 127.8, 123.8, 119.7, 85.7, 82.8, 82.2, 80.0, 41.4, 28.8, 21.6, 15.4. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{23}NO_2SNa$ 436.1347; Found 436.1346

N-(3-(4-(tert-butyl)phenyl)prop-2-yn-1-yl)-N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1g)



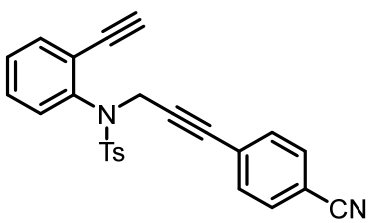
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.87 g, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.73 (d, J = 8.0 Hz, 2H), 7.57–7.51 (m, 1H), 7.34–7.28 (m, 3H), 7.27–7.23 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 4.75 (s, 2H), 3.13 (s, 1H), 2.41 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 151.7, 143.6, 140.6, 137.2, 134.1, 131.3, 131.1, 129.5, 129.3, 128.6, 128.1, 125.2, 123.8, 119.5, 85.7, 82.8, 82.2, 80.0, 41.4, 34.8, 31.2, 21.6. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{27}NO_2SNa$ 464.166; Found 464.1636

N-(3-(2-chlorophenyl)prop-2-yn-1-yl)-N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1k)



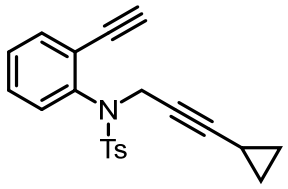
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.51 g, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (d, J = 8.0 Hz, 2H), 7.57–7.51 (m, 1H), 7.36–7.28 (m, 4H), 7.26–7.18 (m, 4H), 7.13 (d, J = 7.2 Hz, 1H), 4.83 (s, 2H), 3.13 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.7, 140.4, 137.0, 135.8, 134.2, 133.5, 131.3, 129.5, 129.5, 129.4, 129.2, 128.7, 128.1, 126.4, 123.7, 122.4, 88.8, 82.3, 82.3, 80.0, 41.4, 21.6. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}ClNO_2SNa$ 442.0644; Found 442.0641

N-(3-(4-cyanophenyl)prop-2-yn-1-yl)-N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1m)



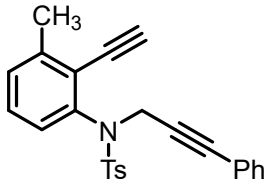
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.30 g, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.69 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 3H), 7.36–7.28 (m, 4H), 7.27–7.24 (m, 3H), 4.76 (s, 2H), 3.07 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.9, 140.4, 136.9, 134.3, 132.1, 132.0, 131.2, 129.6, 129.52, 128.9, 128.1, 127.4, 123.5, 118.4, 111.9, 88.4, 83.9, 82.4, 79.9, 41.3, 21.7. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{18}N_2O_2SNa$ 433.0987; Found 433.0951

N-(3-cyclopropylprop-2-yn-1-yl)-N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1o)



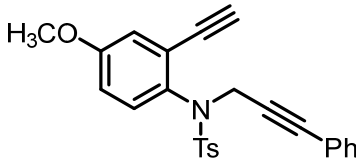
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 1.99 g, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.67 (d, J = 8.0 Hz, 2H), 7.53–7.48 (m, 1H), 7.34–7.28 (m, 2H), 7.25 (d, J = 5.2 Hz, 2H), 7.20–7.15 (m, 1H), 4.46 (s, 2H), 3.06 (s, 1H), 2.43 (s, 3H), 1.14–0.98 (m, 1H), 0.67–0.60 (m, 2H), 0.45–0.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.5, 140.7, 137.3, 134.1, 131.2, 129.4, 129.2, 128.5, 128.1, 123.7, 89.4, 82.1, 80.0, 77.3, 69.4, 41.1, 21.7, 7.99, 0.1. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}NO_2SNa$ 372.1034; Found 372.1029

N-(2-ethynyl-3-methylphenyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1p)



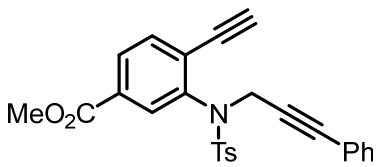
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 1.40 g, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.76 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 12.0 Hz, 5H), 7.22–7.13 (m, 4H), 7.03 (d, J = 7.6 Hz, 1H), 4.73 (s, 2H), 3.39 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.5, 143.1, 140.8, 137.4, 131.5, 129.9, 129.4、, 128.5, 128.4, 128.2, 128.1, 127.9, 123.8, 122.6, 86.5, 85.4, 83.8, 78.7, 41.4, 21.6, 21.1. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}NO_3SNa$ 422.1191; Found 422.1198.

N-(2-ethynyl-4-methoxyphenyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1r)



Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.24 g, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.2 Hz, 5H), 7.21 (d, J = 6.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 1H), 7.04 (d, J = 2.8 Hz, 1H), 6.83 (m, 1H), 4.73 (s, 2H), 3.79 (s, 3H), 3.10 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 159.2, 143.5, 137.2, 133.2, 132.0, 131.6, 129.5, 128.4, 128.2, 128.1, 124.8, 122.5, 118.5, 115.6, 85.4, 83.8, 81.9, 79.9, 55.6, 41.6, 21.6. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}NO_3SNa$ 438.1140; Found 438.1146.

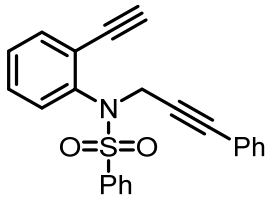
methyl 4-ethynyl-3-((4-methyl-N-(3-phenylprop-2-yn-1-yl)phenyl)sulfonamido)benzoate (1t)



Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.44 g, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.21 (d, J = 2.0 Hz, 1H), 8.00–7.96 (m, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.29–7.24 (m, 5H),

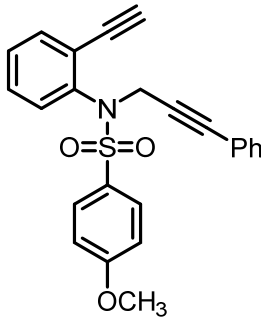
7.19 (d, *J* = 7.2 Hz, 2H), 4.77 (s, 2H), 3.92 (s, 3H), 3.17 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 165.6, 144.4, 144.0, 136.7, 135.4, 131.6, 131.2, 130.4, 130.3, 129.6, 128.6, 128.3, 128.1, 123.9, 122.2, 85.9, 83.2, 83.1, 79.1, 52.6, 41.2, 21.6. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}NO_4SNa$ 466.1089; Found 466.1076

N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1v)



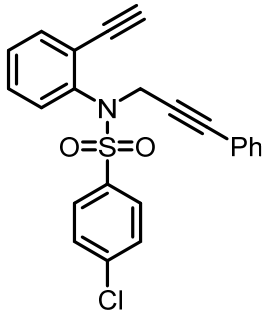
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.78 g, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.90 (d, *J* = 8.0 Hz, 2H), 7.65–7.58 (m, 2H), 7.55–7.50 (m, 2H), 7.40–7.36 (m, 2H), 7.34–7.29 (m, 4H), 7.26 (d, *J* = 6.8 Hz, 2H), 4.84 (s, 2H), 3.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 140.4, 140.1, 134.3, 132.9, 131.6, 131.4, 129.5, 129.0, 128.8, 128.6, 128.3, 128.1, 123.7, 122.5, 85.7, 83.5, 82.3, 79.9, 41.5. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{17}NO_2SNa$ 394.0878; Found 394.0851

N-(2-ethynylphenyl)-4-methoxy-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1w)



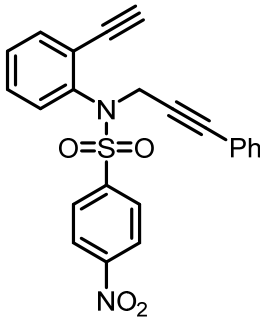
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 3.05g, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.83 (d, *J* = 8.8 Hz, 2H), 7.62–7.58 (m, 1H), 7.39–7.36 (m, 2H), 7.35–7.30 (m, 4H), 7.26 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.80 (s, 2H), 3.88 (s, 3H), 3.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 163.2, 140.7, 134.2, 131.7, 131.6, 131.1, 130.3, 129.6, 129.4, 128.7, 128.5, 128.3, 123.8, 122.6, 114.3, 114.1, 85.6, 83.7, 82.3, 80.1, 55.7, 41.4. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}NO_3SNa$ 424.0983; Found 424.0959

4-chloro-N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1x)



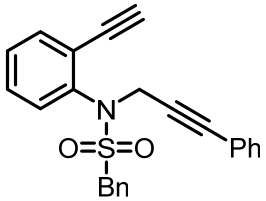
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.59g, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.77 (d, *J* = 8.8 Hz, 2H), 7.58–7.53 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36–7.32 (m, 2H), 7.30–7.24 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 2H), 4.76 (s, 2H), 3.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 140.1, 139.4, 138.6, 134.3, 131.5, 131.3, 129.5, 129.5, 129.2, 128.9, 128.6, 128.3, 123.5, 122.3, 85.8, 83.2, 82.4, 79.8, 41.6. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{16}ClNO_2SNa$ 428.0488; Found 428.0486

N-(2-ethynylphenyl)-4-nitro-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1y)



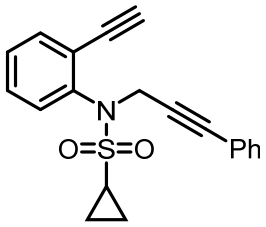
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.37g, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 7.58–7.52 (m, 1H), 7.40–7.35 (m, 2H), 7.34–7.26 (m, 3H), 7.26–7.19 (m, 3H), 4.80 (s, 2H), 3.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 150.2, 145.9, 139.6, 134.5, 131.5, 131.4, 129.8, 129.3, 129.3, 128.9, 128.5, 124.1, 123.3, 122.0, 86.2, 82.8, 82.6, 79.6, 41.9. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{16}N_2O_4SNa$ 439.0728; Found 439.0725

N-(2-ethynylphenyl)-1-phenyl-N-(3-phenylprop-2-yn-1-yl)methanesulfonamide (1z)



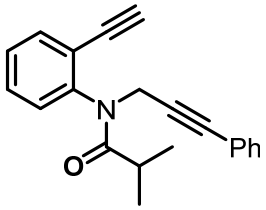
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.70g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.63–7.58 (m, 1H), 7.52–7.48 (m, 2H), 7.38–7.29 (m, 10H), 7.24–7.20 (m, 1H), 4.69 (s, 2H), 4.51 (s, 2H), 3.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 140.8, 134.3, 131.9, 131.7, 131.2, 129.8, 128.8, 128.8, 128.7, 128.5, 123.4, 122.5, 85.8, 84.0, 83.0, 80.7, 60.2, 41.9. HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_2S$ 386.1215; Found 386.1211

N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)cyclopropanesulfonamide (1aa)



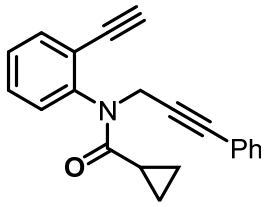
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.28g, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.64 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.42 (s, 1H), 7.38–7.27 (m, 6H), 4.77 (s, 2H), 3.35 (s, 1H), 2.71–2.63 (m, 1H), 1.16–1.10 (m, 2H), 1.02–0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 140.8, 134.1, 132.0, 131.6, 129.7, 128.7, 128.5, 128.4, 123.5, 122.6, 85.5, 84.2, 82.5, 80.5, 41.5, 31.0, 6.1. HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2S$ 336.1058; Found 336.1057

N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)isobutyramide (1bb)



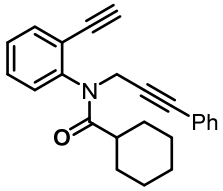
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.14g, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.62 (d, J = 7.6 Hz, 1H), 7.47–7.35 (m, 3H), 7.31–7.25 (m, 5H), 5.27 (d, J = 17.6 Hz, 1H), 4.31 (d, J = 17.2 Hz, 1H), 3.27 (s, 1H), 2.41–2.33 (m, 1H), 1.10 (d, J = 6.4 Hz, 3H), 1.03 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 177.0, 143.5, 133.9, 131.7, 130.1, 129.9, 128.5, 128.3, 128.2, 123.1, 122.4, 84.7, 84.5, 82.9, 79.7, 38.0, 32.0, 19.9, 19.5. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}NONa$ 324.1364; Found 324.1351

N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)cyclopropanecarboxamide (1cc)



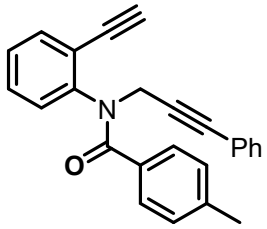
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.03g, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.63 (d, J = 7.6 Hz, 1H), 7.50–7.42 (m, 2H), 7.40–7.35 (m, 1H), 7.32–7.29 (m, 2H), 7.28–7.25 (m, 3H), 5.27 (d, J = 17.2 Hz, 1H), 4.36 (d, J = 17.6 Hz, 1H), 3.27 (s, 1H), 1.27–1.21 (m, 1H), 1.10–1.01 (m, 2H), 0.72–0.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 173.3, 143.5, 133.9, 131.7, 130.5, 129.9, 128.4, 128.4, 128.3, 128.2, 123.1, 122.7, 84.7, 84.4, 82.8, 79.7, 38.1, 12.8, 9.1, 8.6. HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; Found 300.1385

N-(2-ethynylphenyl)-N-(3-phenylprop-2-yn-1-yl)cyclohexanecarboxamide (1dd)



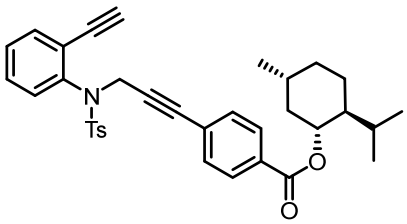
Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.28g, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.62 (d, J = 6.8 Hz, 1H), 7.47–7.35 (m, 3H), 7.31–7.23 (m, 6H), 5.26 (d, J = 17.62 Hz, 1H), 4.29 (d, J = 17.2 Hz, 1H), 3.25 (s, 1H), 2.09–2.00 (m, 1H), 1.78 (d, J = 12.8 Hz, 1H), 1.70–1.44 (m, 6H), 1.23–1.12 (m, 1H), 1.06–0.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 175.9, 143.5, 133.9, 131.7, 130.1, 129.8, 128.5, 128.3, 128.2, 123.1, 122.4, 84.8, 84.4, 82.9, 79.7, 42.2, 37.8, 29.8, 29.2, 25.7, 25.5. HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{23}NONa$ 364.1677; Found 364.1690

N-(2-ethynylphenyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzamide (1ee)



Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.51g, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.48 (d, J = 6.4 Hz, 1H), 7.35–7.28 (m, 4H), 7.27–7.16 (m, 6H), 6.96 (d, J = 7.2 Hz, 2H), 5.37 (d, J = 16.8 Hz, 1H), 4.58 (d, J = 17.2 Hz, 1H), 3.37 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 170.7, 144.7, 140.2, 133.8, 132.7, 131.8, 131.8, 130.7, 129.6, 128.7, 128.4, 128.3, 127.8, 123.0, 121., 84.6, 83.4, 80.2, 53.6, 39.2, 21.5. HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}NO$ 350.1545; Found 350.1543

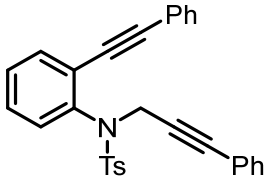
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl
74-(3-((N-(2-ethynylphenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1ff)



Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 2.83g, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.97 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.62–7.57 (m, 1H), 7.41–7.36 (m, 2H), 7.33 (s, 2H), 7.30 (d, J = 7.8 Hz, 3H), 5.01–4.92 (m, 1H), 4.82 (s, 2H), 3.16 (s, 1H), 2.47 (s, 3H), 2.15 (d, J = 11.2 Hz, 1H), 2.01–1.93 (m, 1H), 1.78 (d, J = 11.6 Hz, 2H), 1.69–1.58 (m, 3H), 1.18 (s, 2H), 1.02–0.93 (m, 7H), 0.83 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 165.5, 143.7, 140.5, 137.0, 134.2, 131.4, 131.1, 130.5, 129.5, 129.4, 129.4, 128.7, 128.1, 126.9, 123.7, 86.53, 84.9, 82.3, 79.9, 75.2, 47.3, 41.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.1, 21.6, 20.8, 16.6.

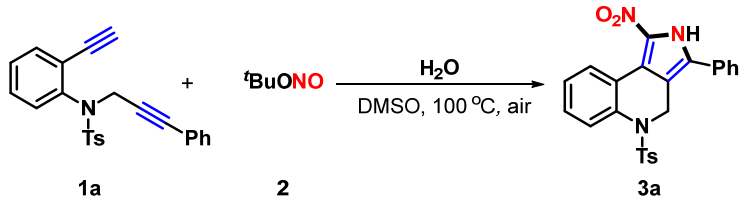
HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{35}H_{38}NO_4S$ 568.2522; Found 568.2519

4-methyl-N-(2-(phenylethynyl)phenyl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1gg)



Isolation by column chromatography (PE/EA= 5/1 v/v) White solid; 1.84 g, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.75 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 9.2 Hz, 1H), 7.45–7.29 (m, 10H), 7.23 (d, J = 7.6 Hz, 3H), 7.15 (d, J = 8.0 Hz, 2H), 4.83 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.5, 139.9, 137.4, 133.4, 132.1, 131.8, 131.7, 131.6, 129.7, 129.6, 128.9, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.3, 124.3, 122.9, 122.6, 94.5, 86.0, 85.4, 83.8, 51.7, 41.2, 21.5. HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{24}NO_2S$ 462.1528; Found 462.1524

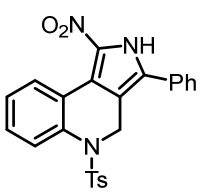
General Procedure for the Synthesis of Product 3.



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

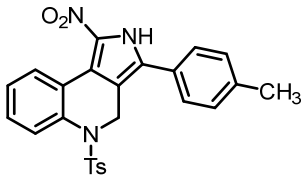
To a pressure tube were added 1,7-diyne **1a** (0.2 mmol, 77 mg), *tert*-butyl nitrite (**2**, 0.7 mmol, 72.1 mg, 3.5 equiv), and DMSO (3 mL, about 0.46 mmol H_2O in 3 mL). Then the mixture was stirred at 100 °C (metal bath temperature) for 8 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in ethyl acetate, and washed with H_2O. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent, petroleum ether/ethyl acetate = 10:1) to afford the desired product **3a** as yellow solid in 82% yield.

1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3a)



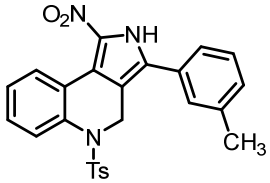
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 73.0 mg, 82% yield; mp: 240-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.24 (s, 1H), 8.27 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.63–7.43 (m, 7H), 6.90–6.80 (m, 4H), 4.85 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.7, 136.5, 133.8, 131.4, 130.2, 130.0, 129.9, 129.2, 128.6, 128.5, 128.4, 128.0, 127.1, 127.0, 125.5, 119.68, 117.0, 43.5, 21.3. IR (KBr, v, cm^{-1}): 3262, 1596, 1473, 1397, 1244, 1154, 1052, 844, 775; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}N_3O_4S$ 446.1175; Found 446.1176;

1-nitro-3-(p-tolyl)-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3b)



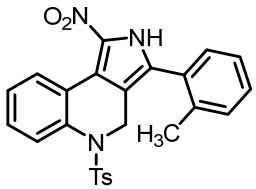
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 80.8 mg, 88% yield; mp: 260-261 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.99 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.55–7.48 (m, 4H), 7.43 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.61 (d, J = 8.0 Hz, 2H), 4.74 (s, 2H), 2.44 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 143.8, 139.6, 136.4, 133.6, 133.4, 132.6, 130.1, 129.5, 129.1, 128.8, 128.6, 128.5, 128.1, 126.5, 126.5, 126.1, 118.7, 116.6, 43.7, 21.5, 21.1. IR (KBr, v, cm^{-1}): 3258, 1472, 1395, 1275, 1156, 1053, 842, 749; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_4S$ 460.1331; Found 460.1332;

1-nitro-3-(m-tolyl)-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3c)



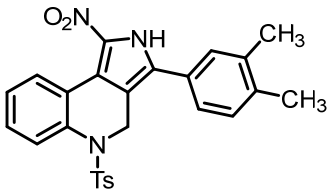
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 76.2 mg, 83% yield; mp: 218-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.26 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.52–7.43 (m, 3H), 7.35 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 12.4 Hz, 2H), 6.88–6.81 (m, 4H), 4.84 (s, 2H), 2.50 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.6, 139.8, 136.5, 133.8, 131.7, 131.0, 129.9, 129.8, 129.2, 128.5, 128.4, 128.3, 127.9, 127.6, 127.0, 125.5, 124.1, 119.6, 116.9, 43.5, 21.7, 21.2. IR (KBr, v, cm^{-1}): 3447, 1637, 1473, 1350, 1221, 1163, 1056, 855, 764; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_4S$ 460.1331; Found 460.1331;

1-nitro-3-(o-tolyl)-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3d)



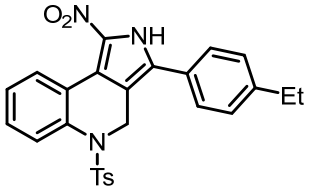
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 71.6 mg, 78% yield; mp: 224-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.17 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.52–7.38 (m, 5H), 7.33 (d, J = 7.6 Hz, 1H), 6.95–6.86 (m, 4H), 4.59 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.8, 136.9, 136.4, 134.0, 131.8, 131.7, 131.0, 130.4, 129.9, 129.3, 129.2, 128.5, 128.5, 128.0, 127.9, 127.0, 126.9, 125.8, 118.7, 118.4, 43.78, 21.27, 19.9. IR (KBr, v, cm^{-1}): 3263, 1596, 1474, 1392, 1273, 1162, 1059, 850, 765; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_4S$ 460.1331; Found 460.1325;

3-(3,4-dimethylphenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3e)



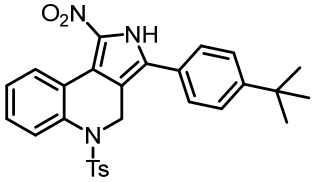
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 80.4 mg, 85% yield; mp: 238-239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.23 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.52–7.43 (m, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.88–6.80 (m, 4H), 4.83 (s, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.7, 139.4, 138.5, 136.5, 133.9, 132.0, 131.8, 131.2, 129.9, 129.2, 128.6, 128.3, 128.1, 127.9, 127.0, 126.0, 125.7, 124.5, 119.8, 116.7, 43.6, 21.3, 20.2, 19.9. IR (KBr, v, cm^{-1}): 3445, 1636, 1471, 1352, 1267, 1164, 1056, 855, 749; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_3O_4S$ 474.1488; Found 474.1487;

3-(4-ethylphenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3f)



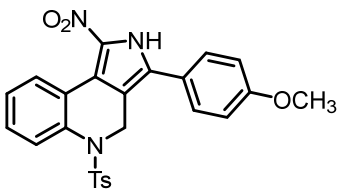
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 80.4 mg, 85% yield; mp: 213-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.21 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.52–7.40 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 6.92–6.79 (m, 4H), 4.84 (s, 2H), 2.77 (q, J = 7.6 Hz, 2H), 2.24 (s, 3H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 146.8, 143.7, 136.5, 133.9, 131.9, 131.8, 129.9, 129.5, 129.2, 128.6, 128.34, 127.9, 127.0, 127.0, 125.9, 125.6, 119.8, 116.8, 43.5, 28.9, 21.3, 15.4. IR (KBr, v, cm^{-1}): 3258, 1471, 1393, 1271, 1150, 1049, 834, 749; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_3O_4S$ 474.1488; Found 474.1489;

3-(4-(tert-butyl)phenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3g)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 76.2 mg, 76% yield; mp: 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.19 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.53–7.42 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.90–6.79 (m, 4H), 4.86 (s, 2H), 2.25 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 153.7, 143.7, 136.5, 133.8, 131.9, 131.7, 129.9, 129.2, 128.6, 128.3, 128.0, 127.0, 127.0, 126.8, 125.7, 125.6, 119.8, 116.8, 43.5, 35.1, 31.2, 21.3. IR (KBr, v, cm^{-1}): 3218, 1476, 1395, 1242, 1165, 1059, 838, 765; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{28}N_3O_4S$ 502.1801; Found 502.1799;

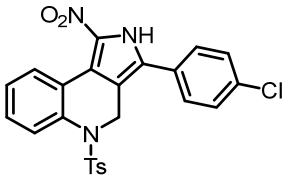
3-(4-methoxyphenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3h)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 80.8 mg, 85% yield; mp: 227-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.92 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.55–7.45 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H), 3.89 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 160.6, 143.8, 136.4, 133.6, 133.4, 132.4, 130.2, 129.5,

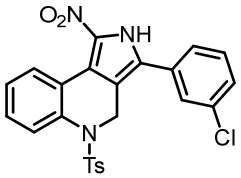
129.1, 128.8, 128.5, 128.1, 126.6, 126.5, 121.3, 118.9, 116.3, 115.0, 55.9, 43.7, 21.1. IR (KBr, *v*, cm^{-1}): 3445, 1634, 1469, 1391, 1265, 1156, 832, 745; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_5S$ 476.1280; Found 476.1281;

3-(4-chlorophenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3i)



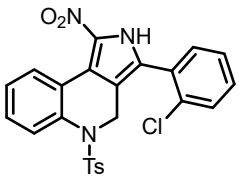
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 63.2 mg, 66% yield; mp: 224-225 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.14 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.75–7.58 (m, 5H), 7.56–7.46 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.73 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 144.0, 136.5, 134.7, 133.7, 133.0, 131.8, 130.5, 129.7, 129.2, 129.0, 128.6, 128.3, 127.8, 126.6, 126.4, 118.6, 117.3, 43.7, 21.2. IR (KBr, *v*, cm^{-1}): 3459, 1471, 1338, 1262, 1161, 1016, 800, 764; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}ClN_3O_4S$ 480.0785; Found 480.0781;

3-(3-chlorophenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3j)



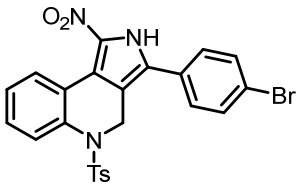
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 71.9 mg, 75% yield; mp: 223-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 9.28 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.56–7.45 (m, 4H), 7.38 (s, 1H), 7.34 (d, *J* = 6.4 Hz, 1H), 6.89–6.81 (m, 4H), 4.82 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 143.8, 136.5, 136.0, 133.8, 131.2, 130.2, 130.1, 130.0, 129.5, 129.2, 128.5, 128.3, 128.0, 126.9, 125.2, 125.2, 119.4, 117.5, 43.3, 21.2. IR (KBr, *v*, cm^{-1}): 3054, 1563, 1470, 1304, 1265, 1160, 1056, 847, 766; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}ClN_3O_4S$ 480.0785; Found 480.0783;

3-(2-chlorophenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3k)



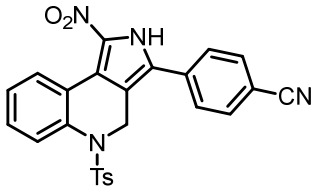
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 70.9 mg, 74% yield; mp: 217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 9.56 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.63–7.58 (m, 1H), 7.53–7.43 (m, 4H), 7.37–7.32 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 143.8, 136.4, 133.7, 132.6, 132.0, 131.4, 131.4, 131.1, 129.9, 129.2, 128.6, 128.5, 128.0, 127.9, 127.9, 127.0, 125.6, 119.3, 118.5, 44.1, 21.2. IR (KBr, *v*, cm^{-1}): 3272, 1596, 1470, 1306, 1238, 1163, 1059, 848, 764; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}ClN_3O_4S$ 480.0785; Found 480.0782;

3-(4-bromophenyl)-1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3l)



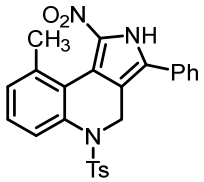
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 64.9 mg, 62% yield; mp: 245-246 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.14 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.54–7.46 (m, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 143.9, 136.5, 133.7, 133.1, 132.6, 131.8, 130.7, 129.7, 129.2, 129.0, 128.6, 128.3, 128.2, 126.6, 126.4, 123.5, 118.6, 117.3, 43.7, 21.2. IR (KBr, v, cm^{-1}): 3447, 1637, 1470, 1330, 1262, 1153, 1051, 843, 749; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{24}H_{19}BrN_3O_4S$ 524.0280; Found 524.0279;

4-(1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinolin-3-yl)benzonitrile (3m)



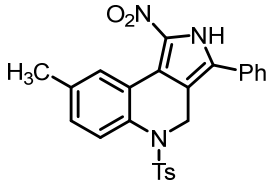
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 65.8 mg, 70% yield; mp: 209-210 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.30 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.56–7.47 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 4.76 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 143.9, 136.4, 133.6, 133.4, 133.2, 130.7, 129.7, 129.3, 129.1, 128.9, 128.5, 128.2, 126.5, 126.1, 119.0, 118.4, 118.3, 112.0, 43.6, 21.1. IR (KBr, v, cm^{-1}): 3447, 1636, 1474, 1399, 1316, 1152, 845, 764; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{25}H_{19}N_4O_4S$ 471.1127; Found 471.1125;

9-methyl-1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3p)



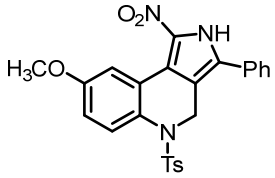
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 70.3 mg, 71% yield; mp: 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.30 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.63–7.53 (m, 3H), 7.48 (d, J = 8.0 Hz, 2H), 7.44–7.40 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 6.90–6.83 (m, 4H), 5.33 (d, J = 16.0 Hz, 1H), 4.18 (d, J = 16.0 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.4, 138.1, 137.4, 134.4, 131.4, 130.2, 130.1, 129.9, 129.0, 128.5, 128.4, 127.1, 126.4, 126.1, 125.7, 119.6, 118.9, 43.9, 31.6, 22.7, 21.2, 20.7, 14.2. IR (KBr, v, cm^{-1}): 3340, 1733, 1470, 1275, 1163, 1090, 924, 749; HRMS (ESI -TOF) m/z: [M+Na]$^+$ Calcd for $C_{25}H_{21}N_3O_4SNa$ 482.1150; Found 482.1161.

8-methyl-1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3q)



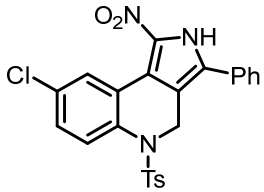
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 79.9 mg, 87% yield; mp: 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.23 (s, 1H), 8.07 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.63–7.52 (m, 3H), 7.44 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 8.4 Hz, 1H), 6.89–6.81 (m, 4H), 4.82 (s, 2H), 2.46 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.6, 137.9, 134.0, 133.9, 132.0, 131.4, 130.8, 130.1, 130.0, 128.9, 128.6, 128.3, 127.1, 127.0, 125.2, 119.9, 117.1, 43.5, 21.6, 21.3. IR (KBr, v, cm^{-1}): 3189, 1470, 1394, 1271, 1195, 1161, 1054, 860, 766; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{25}H_{22}N_3O_4S$ 460.1331; Found 460.1326;

8-methoxy-1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3r)



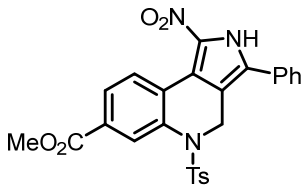
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 76.0 mg, 80% yield; mp: 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.26 (s, 1H), 7.84 (d, J = 2.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.63–7.53 (m, 3H), 7.44 (d, J = 7.6 Hz, 2H), 7.07–7.02 (m, 1H), 6.91–6.81 (m, 4H), 4.82 (s, 2H), 3.90 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 158.7, 143.6, 133.6, 131.4, 130.1, 130.1, 129.9, 129.2, 128.5, 128.3, 127.0, 126.4, 119.8, 1167.0, 116.2, 112.7, 55.7, 43.6, 21.2. IR (KBr, v, cm^{-1}): 3005, 1663, 1478, 1349, 1275, 1163, 1089, 812, 750; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}N_3O_5SNa$ 498.1100; Found 498.1113.

8-chloro-1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3s)



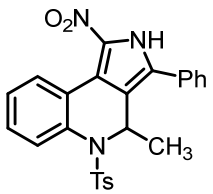
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 67.1 mg, 70% yield; mp: 230-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.29 (s, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.82 (s, 1H), 7.63–7.53 (m, 3H), 7.47–7.40 (m, 3H), 6.88 (s, 4H), 4.84 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 144.0, 137.7, 135.2, 133.8, 132.0, 131.6, 130.3, 130.0, 129.5, 129.3, 128.5, 128.4, 128.2, 127.1, 127.0, 124.0, 118.8, 116.7, 43.4, 21.3. IR (KBr, v, cm^{-1}): 3445, 1634, 1470, 1343, 1259, 1157, 1055, 849, 750; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}ClN_3O_4SNa$ 502.0604; Found 502.0601;

methyl 1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline-7-carboxylate (3t)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 72.4 mg, 72% yield; mp: 203-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.35 (s, 1H), 8.94 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.63–7.55 (m, 3H), 7.45 (d, J = 7.6 Hz, 2H), 6.89–6.83 (m, 4H), 4.87 (s, 2H), 3.98 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 166.4, 144.0, 140.4, 133.9, 131.3, 130.8, 130.3, 130.0, 129.9, 129.5, 129.2, 128.6, 128.34, 127.1, 126.9, 125.5, 118.7, 116.9, 52.6, 43.4, 21.3. IR (KBr, v, cm^{-1}):3445, 1698, 1471, 1353, 1267, 1161, 1038, 810, 746; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}N_3O_6SNa$ 526.1049; Found 526.1043;

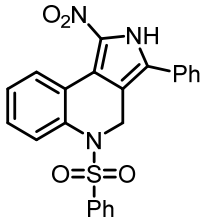
4-methyl-1-nitro-3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3u)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 78.1 mg, 85% yield; mp: 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.25 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63–7.43 (m, 7H), 6.82 (m, 4H), 5.58–5.51 (m, 1H), 2.23 (s, 3H), 1.34 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 143.59, 133.96, 133.37, 132.05, 130.55, 130.46, 130.11, 130.02, 128.75, 128.36, 128.29, 127.86, 126.95, 126.83, 124.88,

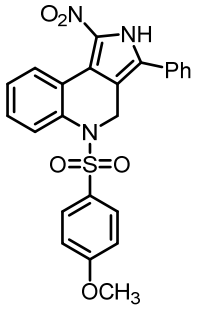
122.12, 118.27, 48.76, 21.24, 21.04. IR (KBr, *v*, cm^{-1}): 3380, 1478, 1392, 1234, 1163, 1078, 1005, 896, 764; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_4S$ 460.1331; Found 460.1330;

1-nitro-3-phenyl-5-(phenylsulfonyl)-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3v)



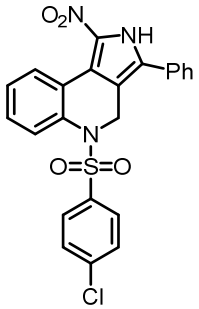
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 67.3 mg, 78% yield; mp: 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.27 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.62–7.54 (m, 3H), 7.52–7.41 (m, 4H), 7.32–7.27 (m, 1H), 7.10–7.05 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 137.2, 136.3, 132.5, 132.0, 131.3, 130.2, 130.0, 129.2, 128.5, 128.5, 128.0, 127.8, 127.1, 127.0, 125.4, 119.6, 117.1, 43.4. IR (KBr, *v*, cm^{-1}): 3425, 1636, 1474, 1350, 1268, 1165, 1088, 847, 766; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N_3O_4S$ $[M+H]^+$ 432.1018; Found 432.1012;

5-((4-methoxyphenyl)sulfonyl)-1-nitro-3-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3w)



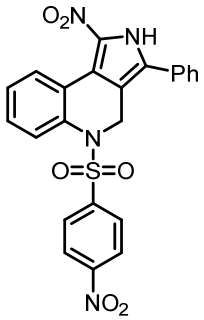
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 75.6 mg, 82% yield; mp: 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.31 (s, 1H), 8.30–8.26 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.61–7.53 (m, 3H), 7.51–7.42 (m, 4H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.84 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 162.9, 136.6, 132.1, 131.5, 130.2, 130.0, 129.4, 129.1, 128.6, 128.5, 127.9, 127.1, 125.5, 119.8, 117.2, 112.9, 55.8, 43.4. IR (KBr, *v*, cm^{-1}): 3347, 1593, 1474, 1346, 1267, 1155, 1021, 846, 766; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}N_3O_5SNa$ 484.0943; Found 484.0941;

5-((4-chlorophenyl)sulfonyl)-1-nitro-3-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3x)



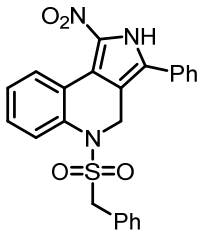
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 66.4 mg, 71% yield; mp: 222-223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.42 (s, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.63–7.55 (m, 3H), 7.53–7.46 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 139.3, 136.1, 135.4, 132.1, 131.2, 130.2, 130.0, 130.0, 129.2, 128.6, 128.3, 128.2, 128.1, 127.0, 125.2, 119.1, 116.7, 43.4. IR (KBr, *v*, cm^{-1}): 3418, 1634, 1583, 1474, 1395, 1357, 1243, 1166, 1090, 847, 765; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{16}ClN_3O_4SNa$ 488.0448; Found 488.0446;

1-nitro-5-((4-nitrophenyl)sulfonyl)-3-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3y)



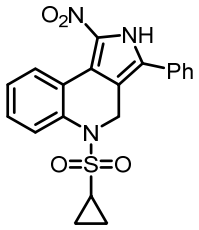
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 66.7 mg, 70% yield; mp: 244-245 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.22 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 4.0 Hz, 4H), 7.61–7.52 (m, 3H), 7.00 (d, J = 8.4 Hz, 2H), 4.81 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 149.7, 141.7, 135.6, 133.2, 132.7, 130.0, 129.6, 129.0, 128.8, 128.55, 128.2, 126.3, 123.6, 118.5, 117.0, 44.0. IR (KBr, v, cm^{-1}): 3445, 1635, 1531, 1473, 1362, 1274, 1161, 848, 749; HRMS (ESI -TOF) m/z: [M+Na]$^+$ Calcd for $C_{23}H_{16}N_4O_6SNa$ 499.0688; Found 499.0683;

5-(benzylsulfonyl)-1-nitro-3-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3z)



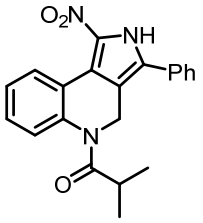
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 60.5 mg, 68% yield; mp: 250-251 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.35 (s, 1H), 8.41 (d, J = 8.4 Hz, 1H), 7.60–7.48 (m, 5H), 7.41–7.35 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.19 (m, 2H), 7.12 (d, J = 7.6 Hz, 2H), 4.64 (s, 2H), 4.35 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 136.7, 133.6, 132.3, 131.2, 129.7, 129.5, 129.4, 1292, 129.1, 128.9, 128.6, 128.5, 126.6, 126.3, 124.9, 119.5, 119.2, 57.9, 43.1. IR (KBr, v, cm^{-1}): 3445, 1602, 1563, 1481, 1455, 1351, 1243, 1152, 1086, 901, 751; HRMS (ESI -TOF) m/z: [M+Na]$^+$ Calcd for $C_{24}H_{19}N_3O_4SNa$ 468.0994; Found 468.0992;

5-(cyclopropylsulfonyl)-1-nitro-3-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline (3aa)



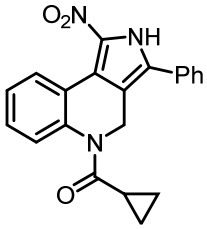
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 43.5 mg, 55% yield; mp: 230-231 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.45 (s, 1H), 8.51–8.47 (m, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.61–7.55 (m, 3H), 7.54 (d, J = 7.2 Hz, 1H), 7.50–7.44 (m, 2H), 4.75 (s, 2H), 1.92–1.86 (m, 1H), 0.55–0.48 (m, 2H), 0.41 (d, J = 11.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 136.8, 133.7, 132.7, 129.8, 129.6, 129.5, 129.2, 128.9, 128.5, 128.4, 127.6, 126.0, 119.3, 119.1, 43.4, 28.8, 5.2. IR (KBr, v, cm^{-1}): 3448, 1637, 1559, 1474, 1389, 1266, 1146, 749; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{20}H_{18}N_3O_4S$ 396.1018; Found 396.1018;

2-methyl-1-(1-nitro-3-phenyl-2,4-dihydro-5H-pyrrolo[3,4-c]quinolin-5-yl)propan-1-one (3bb)



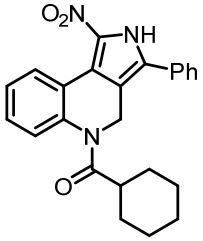
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 54.2 mg, 75% yield; mp: 211-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.78 (s, 1H), 8.60–8.55 (m, 1H), 7.56–7.48 (m, 4H), 7.46 (d, J = 7.2 Hz, 1H), 7.43–7.38 (m, 2H), 7.33 (s, 1H), 3.17–3.09 (m, 1H), 1.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 177.4, 138.3, 132.7, 131.5, 129.8, 129.6, 129.3, 129.0, 128.7, 127.3, 126.7, 125.2, 124.5, 120.9, 120.5, 39.0, 30.5, 19.9. IR (KBr, v, cm^{-1}): 3445, 1635, 1532, 1478, 1367, 1274, 1157, 1093, 849, 749; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_3$ 362.1505; Found 362.1505;

cyclopropyl(1-nitro-3-phenyl-2,4-dihydro-5H-pyrrolo[3,4-c]quinolin-5-yl)methanone (3cc)



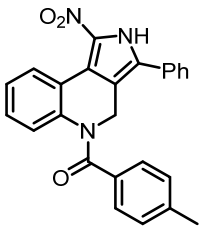
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 48.8 mg, 68% yield; mp: 240-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.67 (s, 1H), 8.60 (d, J = 6.8 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 4.4 Hz, 4H), 7.48–7.37 (m, 3H), 1.97–1.90 (m, 1H), 1.11 (s, 2H), 0.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 173.2, 138.4, 132.7, 131.4, 129.9, 129.7, 129.2, 128.9, 128.8, 127.3, 126.3, 125.5, 124.1, 120.6, 120.6, 39.1, 13.3, 9.8. IR (KBr, v, cm^{-1}): 3447, 1636, 1570, 1478, 1366, 1265, 1160, 748; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}N_3O_3$ 360.1348; Found 360.1343;

cyclohexyl(1-nitro-3-phenyl-2,4-dihydro-5H-pyrrolo[3,4-c]quinolin-5-yl)methanone (3dd)



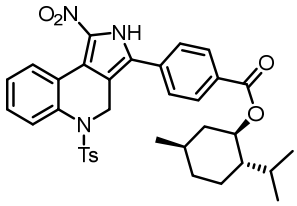
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 59.4 mg, 74% yield; mp: 236-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.77 (s, 1H), 8.66–8.61 (m, 1H), 7.58 (d, J = 6.4 Hz, 4H), 7.52 (d, J = 6.8 Hz, 1H), 7.49–7.44 (m, 2H), 7.39–7.34 (m, 1H), 2.91–2.82 (m, 1H), 1.89–1.60 (m, 6H), 1.36–1.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 176.2, 138.3, 132.7, 131.4, 129.8, 129.6, 129.2, 128.9, 128.6, 127.3, 126.6, 125.4, 125.0, 124.4, 121.0, 120.5, 40.8, 38.9, 29.8, 25.7, 25.5. IR (KBr, v, cm^{-1}):3445, 1625, 1569, 1480, 1368, 1275, 1157, 1025, 853, 750; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O_3$ 402.1818; Found 402.1822;

(1-nitro-3-phenyl-2,4-dihydro-5H-pyrrolo[3,4-c]quinolin-5-yl)(p-tolyl)methanone (3ee)



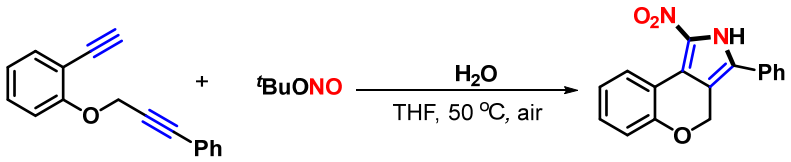
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 65.5 mg, 80% yield; mp: 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.78 (s, 1H), 8.58 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 4.4 Hz, 4H), 7.50–7.46 (m, 1H), 7.24 (d, J = 7.2 Hz, 3H), 7.03 (d, J = 7.6 Hz, 3H), 6.70 (d, J = 8.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 169.5, 141.3, 139.2, 131.8, 131.5, 129.9, 129.7, 129.6, 128.9, 128.4, 127.3, 126.3, 125.6, 122.7, 120.4, 120.0, 40.2, 21.6. IR (KBr, v, cm^{-1}): 3448, 1629, 1570, 1479, 1365, 1247, 1145, 1026, 830, 747; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{19}N_3O_3Na$ $[M+Na]^+$ 432.1324; Found 432.1318;

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(1-nitro-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinolin-3-yl)benzoate (3ff)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 77.8 mg, 62% yield; mp: 232-233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.44 (s, 1H), 8.29–8.22 (m, 3H), 7.81 (d, J = 7.6 Hz, 1H), 7.54–7.43 (m, 4H), 6.88–6.77 (m, 4H), 5.03–4.96 (m, 1H), 4.85 (d, J = 4.0 Hz, 2H), 2.24 (s, 3H), 2.16 (d, J = 12.4 Hz, 1H), 2.05–1.97 (m, 1H), 1.80–1.73 (m, 2H), 1.65–1.54 (m, 2H), 1.21–1.11 (m, 2H), 1.01–0.92 (m, 7H), 0.84 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 165.2, 143.8, 136.5, 133.9, 132.6, 132.4, 132.1, 131.1, 130.1, 130.1, 129.2, 128.6, 128.4, 128.0, 127.0, 126.9, 125.3, 119.5, 118.0, 75.7, 47.4, 43.4, 41.1, 34.4, 31.6, 26.7, 23.7, 22.2, 21.3, 20.9, 16.7. IR (KBr, v, cm^{-1}): 3418, 3271, 2955, 2869, 1712, 1612, 1476, 1407, 1353, 1274, 1165, 1108, 957, 858, 765, 578; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{35}H_{38}N_3O_6S$ 628.2481; Found 628.2477;

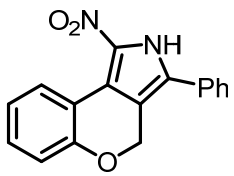
General Procedure for the Synthesis of Product 5.



4a **2** **5a**

To a pressure tube were added 1,7-diyne **4a** (0.2 mmol, 46.4 mg), *tert*-butyl nitrite (**2**, 0.7 mmol, 72.1 mg, 3.5 equiv), and THF (3 mL, about 0.46 mmol H_2O in 3 mL). Then the mixture was stirred in oil bath at 50 °C for 8 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in ethyl acetate, and washed with H_2O. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent, petroleum ether/ethyl acetate = 15:1) to afford the desired product **5a** as yellow solid in 64% yield.

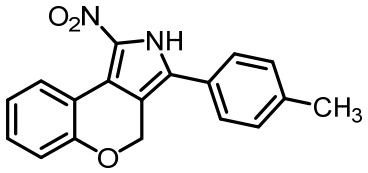
1-nitro-3-phenyl-2,4-dihydrochromeno[3,4-c]pyrrole (5a)



Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 37.3 mg, 64% yield; mp: 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.57 (s, 1H), 8.61 (d, J = 7.2 Hz, 1H), 7.57–7.46 (m, 3H), 7.42 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.15–7.10 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 5.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 155.0,

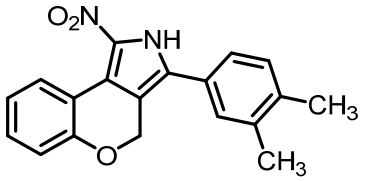
131.0, 130.7, 129.8, 129.6, 128.9, 128.5, 127.1, 122.4, 118.9, 117.8, 117.5, 116.9, 62.5. IR (KBr, *v*, cm^{-1}): 3445, 1634, 1532, 1456, 1304, 1237, 1108, 851, 747; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}N_2O_3$ 293.0926; Found 293.0924;

1-nitro-3-(p-tolyl)-2,4-dihydrochromeno[3,4-c]pyrrole (5b)



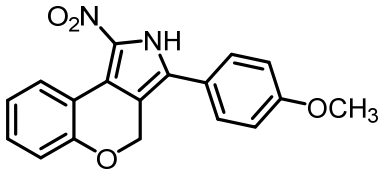
Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 30.6 mg, 50% yield; mp: 229-230 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.26 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 3H), 7.15–7.10 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 5.18 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 155.2, 139.5, 133.2, 132.8, 131.0, 130.0, 128.7, 128.2, 126.4, 122.5, 118.6, 118.0, 117.9, 117.0, 63.0, 21.5. IR (KBr, *v*, cm^{-1}): 3445, 1634, 1480, 1397, 1322, 1274, 1109, 810, 743; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}N_2O_3Na$ 329.0902; Found 329.0897;

3-(3,4-dimethylphenyl)-1-nitro-2,4-dihydrochromeno[3,4-c]pyrrole (5c)



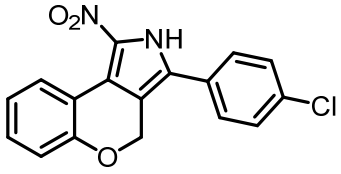
Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 41.6 mg, 65% yield; mp: 230-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 9.53 (s, 1H), 8.61 (d, J = 8.0 Hz, 1H), 7.35–7.27 (m, 2H), 7.19 (s, 1H), 7.15–7.10 (m, 2H), 7.04 (d, J = 8.4 Hz, 1H), 5.20 (s, 2H), 2.34 (d, J = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 155.0, 138.9, 138.2, 131.2, 131.0, 130.8, 128.5, 128.0, 126.4, 124.6, 122.4, 119.1, 117.9, 117.5, 116.5, 62.6, 20.0, 19.8. IR (KBr, *v*, cm^{-1}): 3445, 1634, 1557, 1441, 1371, 1265, 1109, 1045, 812, 743; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O_3$ 321.1239; Found 321.1235;

3-(4-methoxyphenyl)-1-nitro-2,4-dihydrochromeno[3,4-c]pyrrole (5d)



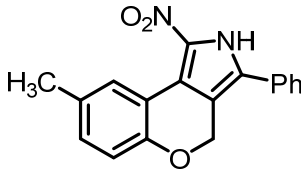
Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 36.7 mg, 57% yield; mp: 220-221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 9.51 (s, 1H), 8.62 (d, J = 8.0 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.16 – 7.10 (m, 1H), 7.05 (d, J = 8.8 Hz, 3H), 5.19 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 160.9, 155.1, 131.0, 128.6, 122.4, 121.3, 119.2, 117.9, 117.5, 116.2, 115.1, 62.6, 55.6. IR (KBr, *v*, cm^{-1}): 3445, 1651, 1538, 1447, 1373, 1255, 1183, 835, 740; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_4$ 323.1032; Found 323.1035;

3-(4-chlorophenyl)-1-nitro-2,4-dihydrochromeno[3,4-c]pyrrole (5e)



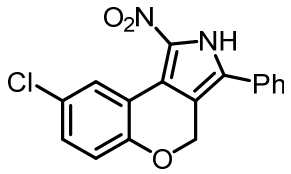
Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 40.4 mg, 62% yield; mp: 232-233 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.40 (s, 1H), 8.44 (d, J = 8.0 Hz, 1H), 7.65–7.58 (m, 4H), 7.36–7.31 (m, 1H), 7.15–7.10 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 5.19 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 155.2, 134.5, 133.6, 131.2, 131.1, 130.5, 129.5, 128.2, 128.1, 122.5, 118.5, 117.9, 117.8, 117.6, 62.8. IR (KBr, v, cm^{-1}): 3445, 1634, 1473, 1319, 1275, 1099, 746; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}ClN_2O_3$ 327.0356; Found 327.0354;

8-methyl-1-nitro-3-phenyl-2,4-dihydrochromeno[3,4-c]pyrrole (5f)



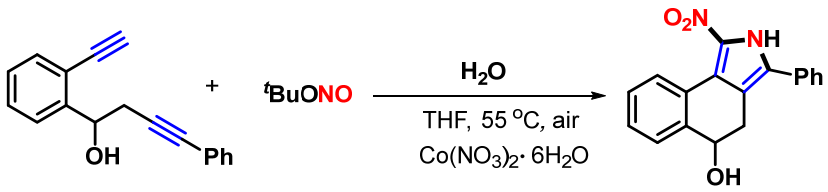
Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 36.7 mg, 60% yield; mp: 232-233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.58 (s, 1H), 8.40 (s, 1H), 7.57–7.45 (m, 3H), 7.41 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 152.9, 132.7, 131.7, 130.8, 129.8, 129.7, 129.0, 128.7, 127.1, 119.2, 117.5, 117.2, 117.1, 62.6, 21.1. IR (KBr, v, cm^{-1}): 3445, 1634, 1465, 1377, 1275, 1152, 1018, 815, 749; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_3$ 307.1083; Found 307.1079;

8-chloro-1-nitro-3-phenyl-2,4-dihydrochromeno[3,4-c]pyrrole (5f)



Isolation by column chromatography (PE/EA= 15/1 v/v) Yellow solid; 43.0 mg, 66% yield; mp: 229-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.63 (s, 1H), 8.62 (s, 1H), 7.66–7.44 (m, 4H), 7.41 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 8.8 Hz, 1H), 5.21 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 153.8, 133.4, 132.4, 130.4, 129.8, 129.4, 128.9, 128.7, 127.4, 126.0, 120.0, 119.6, 117.0, 116.4, 63.1. IR (KBr, v, cm^{-1}): 3459, 1634, 1456, 1376, 1274, 1116, 888, 748; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}ClN_2O_3$ 327.0356; Found 0357;

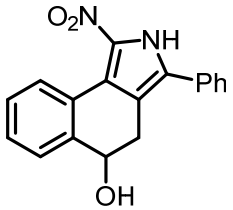
General Procedure for the Synthesis of Product 7



6a **2** **7a**

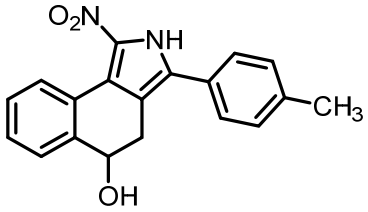
To a pressure tube were added 1,7-diyne **6a** (0.2 mmol, 49.2 mg), *tert*-butyl nitrite (**2**, 0.7 mmol, 72.1 mg, 3.5 equiv), $Co(NO_3)_2$•$6H_2O$(0.2 mmol, 58.2 mg, 1.0 equiv) and THF (3 mL, about 0.46 mmol H_2O in 3 mL). Then the mixture was stirred in oil bath at 55 °C for 8 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in ethyl acetate, and washed with H_2O. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent, petroleum ether/ethyl acetate = 10:1) to afford the desired product **7a** as yellow solid in 60% yield.

1-nitro-3-phenyl-4,5-dihydro-2H-benzo[e]isoindol-5-ol (7a)



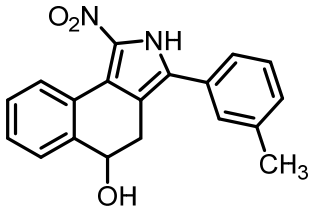
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 36.7 mg, 60% yield; mp: 184-185 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.07 (s, 1H), 8.36–8.30 (m, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.60–7.52 (m, 3H), 7.50–7.46 (m, 1H), 7.42–7.37 (m, 2H), 5.45 (d, J = 4.4 Hz, 1H), 4.73–4.66 (m, 1H), 2.97–2.90 (m, 1H), 2.78–2.71 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 141.5, 134.5, 133.6, 129.9, 129.3, 129.1, 128.9, 127.7, 127.7, 127.5, 126.4, 122.2, 119.4, 67.9, 30.3. IR (KBr, v, cm^{-1}): 3418, 3266, 1473, 1398, 1245, 1161, 1052, 845, 775; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_3$ 307.1083; Found 307.1081;

1-nitro-3-(p-tolyl)-4,5-dihydro-2H-benzo[e]isoindol-5-ol (7b)



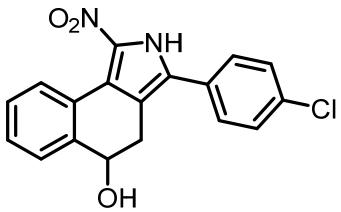
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 39.7 mg, 62% yield; mp: 215-216 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.00 (s, 1H), 8.36–8.31 (m, 1H), 7.58 (d, J = 8.0 Hz, 3H), 7.42–7.37 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.44 (d, J = 4.8 Hz, 1H), 4.71–4.66 (m, 1H), 2.96–2.89 (m, 1H), 2.77–2.69 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 141.6, 139.1, 134.9, 133.5, 129.8, 129.0, 128.9, 127.8, 127.8, 127.5, 127.1, 126.5, 122.5, 119.3, 68.0, 30.4, 21.5. IR (KBr, v, cm^{-1}): 3445, 1634, 1538, 1447, 1359, 1255, 1183, 835, 740; HRMS (ESI -TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O_3$ 321.1239; Found 321.1239;

1-nitro-3-(m-tolyl)-4,5-dihydro-2H-benzo[e]isoindol-5-ol (7c)



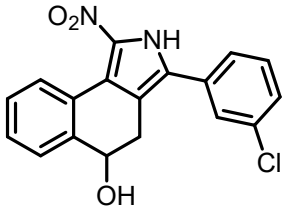
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 38.4 mg, 60% yield; mp: 202-203 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.00 (s, 1H), 8.38–8.29 (m, 1H), 7.61–7.56 (m, 1H), 7.53 (s, 1H), 7.49–7.42 (m, 2H), 7.41–7.37 (m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 5.44 (s, 1H), 4.73–4.65 (m, 1H), 2.98–2.90 (m, 1H), 2.79–2.70 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 141.5, 138.4, 134.7, 133.5, 130.0, 129.8, 129.4, 129.0, 128.9, 127.7, 127.7, 127.5, 126.4, 126.0, 122.2, 119.4, 67.9, 30.3, 21.5. IR (KBr, v, cm^{-1}): 3445, 1634, 1538, 1445, 1360, 1275, 1183, 835, 749; HRMS (ESI -TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}N_2O_3Na$ 343.1059; Found 343.1056;

3-(4-chlorophenyl)-1-nitro-4,5-dihydro-2H-benzo[e]isoindol-5-ol (7d)



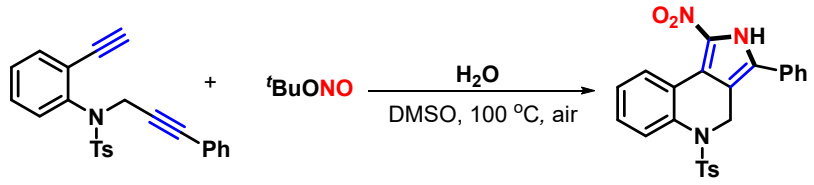
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 40.8 mg, 60% yield; mp: 203-204 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.13 (s, 1H), 8.36–8.28 (m, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.64–7.55 (m, 3H), 7.43–7.36 (m, 2H), 5.45 (d, J = 4.8 Hz, 1H), 4.74–4.65 (m, 1H), 2.97–2.87 (m, 1H), 2.79–2.69 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 141.5, 134.0, 133.7, 133.1, 130.6, 129.2, 128.9, 128.7, 127.7, 127.6, 127.5, 126.4, 122.1, 119.7, 67.9, 30.2. IR (KBr, v, cm^{-1}): 3445, 1634, 1474, 1361, 1275, 1092, 832, 749; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{18}H_{13}ClN_2O_3$ 341.0693; Found 341.0692;

3-(3-chlorophenyl)-1-nitro-4,5-dihydro-2H-benzo[e]isoindol-5-ol (7e)



Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid; 39.4 mg, 58% yield; mp: 193-194 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 13.17 (s, 1H), 8.34–8.28 (m, 1H), 7.80 (s, 1H), 7.64–7.53 (m, 4H), 7.43–7.37 (m, 2H), 5.46 (d, J = 4.4 Hz, 1H), 4.73–4.67 (m, 1H), 2.97–2.90 (m, 1H), 2.80–2.72 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 141.4, 133.9, 133.8, 132.6, 131.9, 131.0, 129.1, 129.0, 128.4, 127.6, 127.6, 127.5, 126.4, 122.0, 119.9, 67.8, 30.2. IR (KBr, v, cm^{-1}): 3440, 1634, 1458, 1390, 1275, 1202, 1025, 860, 749; HRMS (ESI -TOF) m/z: [M+H]$^+$ Calcd for $C_{18}H_{14}ClN_2O_3$ 341.0693; Found 341.0694;

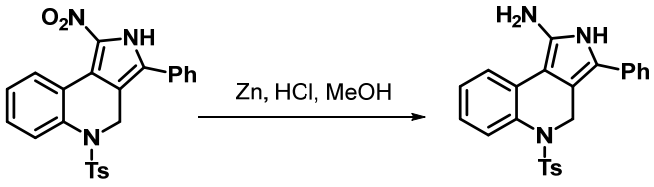
General Procedure for Scale-Up Experiment of 3a



1a (4 mmol) **2** (14 mmol) **3a** (1.246 g, 70% yield)

To an 100-mL oven-dried flask under Ar conditions, 1,7-diyne (**1a**, 4 mmol, 1.54 g, 1 equiv), *t*BuONO(**2**, 14 mmol, 1.24 g, 3.5 equiv), H_2O (7.8 mmol, 0.14 g, 0.46 equiv) and DMSO (50 mL) were successively added. The resulting mixture was stirring in oil bath at 100 °C for 5 h. After the reaction was complete (by TLC), the reaction mixture was cooled to room temperature and washed with H_2O (80 ml) and extracted with ethyl acetate (3 ×50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 10:1 v/v) to afford the desired product **3a** as yellow solid in 70% yield.

General Procedure for the Synthesis of Product 8

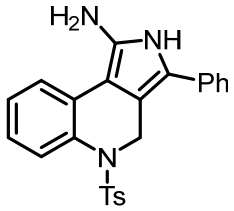


3a **8**

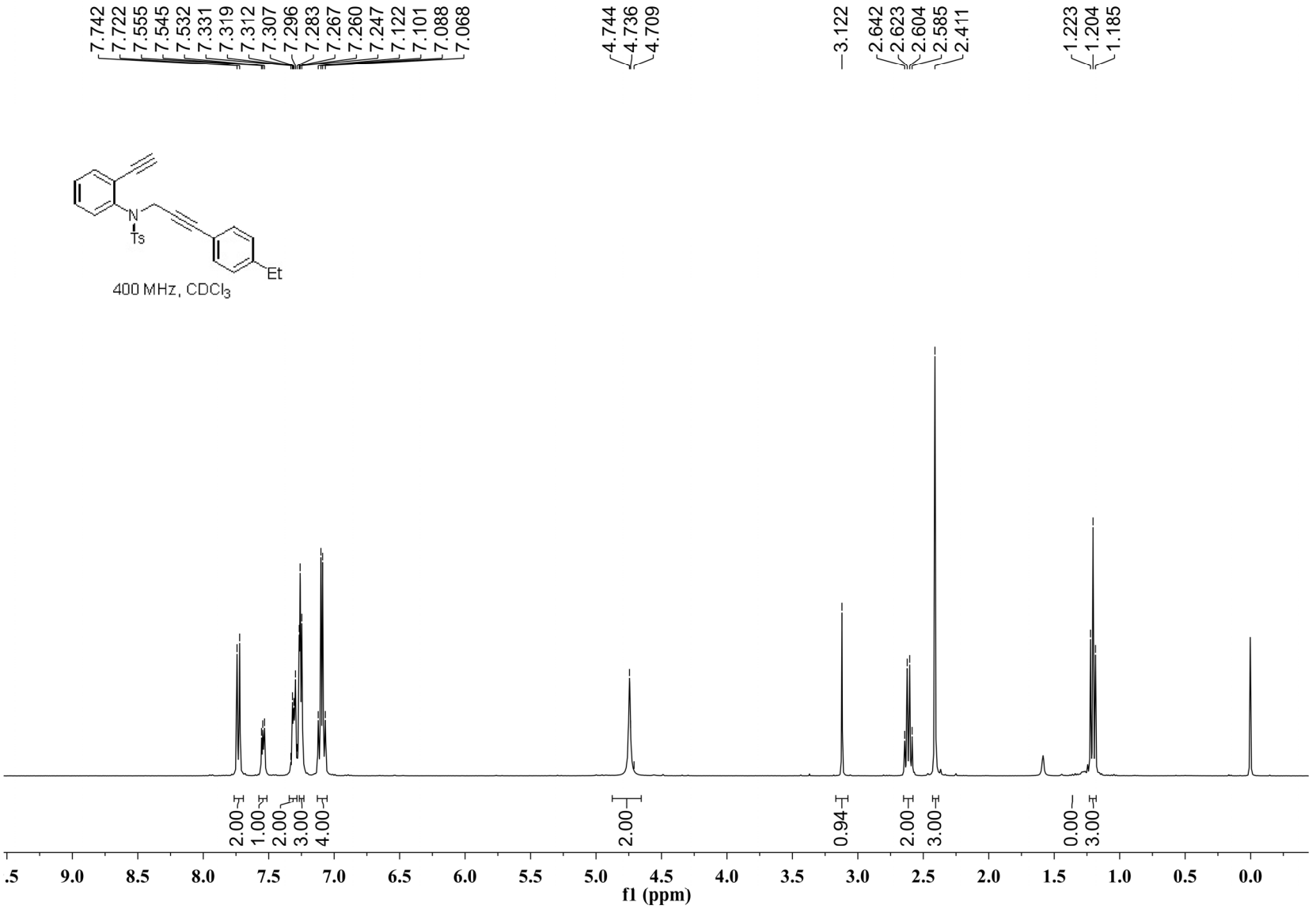
A suspension of **3a** (0.2 mmol, 89 mg, 1 equiv) in concentrated HCl (378 μL, 4.56 mmol) and methanol (2.0 mL) was placed in an ambient water bath. Zinc dust (261.6 mg, 4.0 mmol) was carefully added with vigorous stirring over 1 minute, and the mixture was stirred for 10 minutes. The reaction was then quenched with sat. $NaHCO_3$ (30 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous

Na_2SO_4 and concentrated. The residue was purified by column chromatography (eluent, petroleum ether/ethyl acetate = 5:1) on silica gel to afford **8** (77.2 mg, 93%).

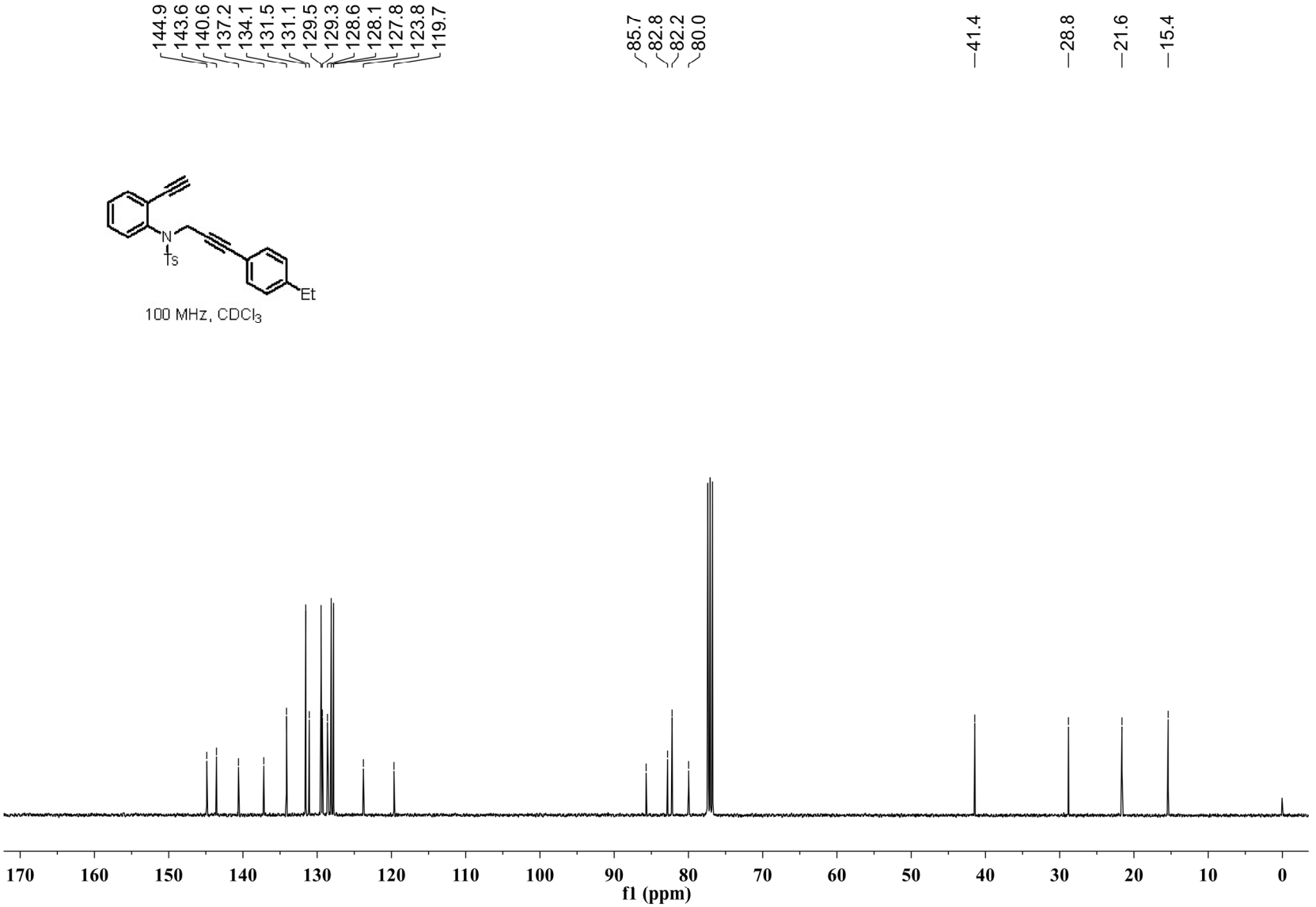
3-phenyl-5-tosyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinolin-1-amine (8)



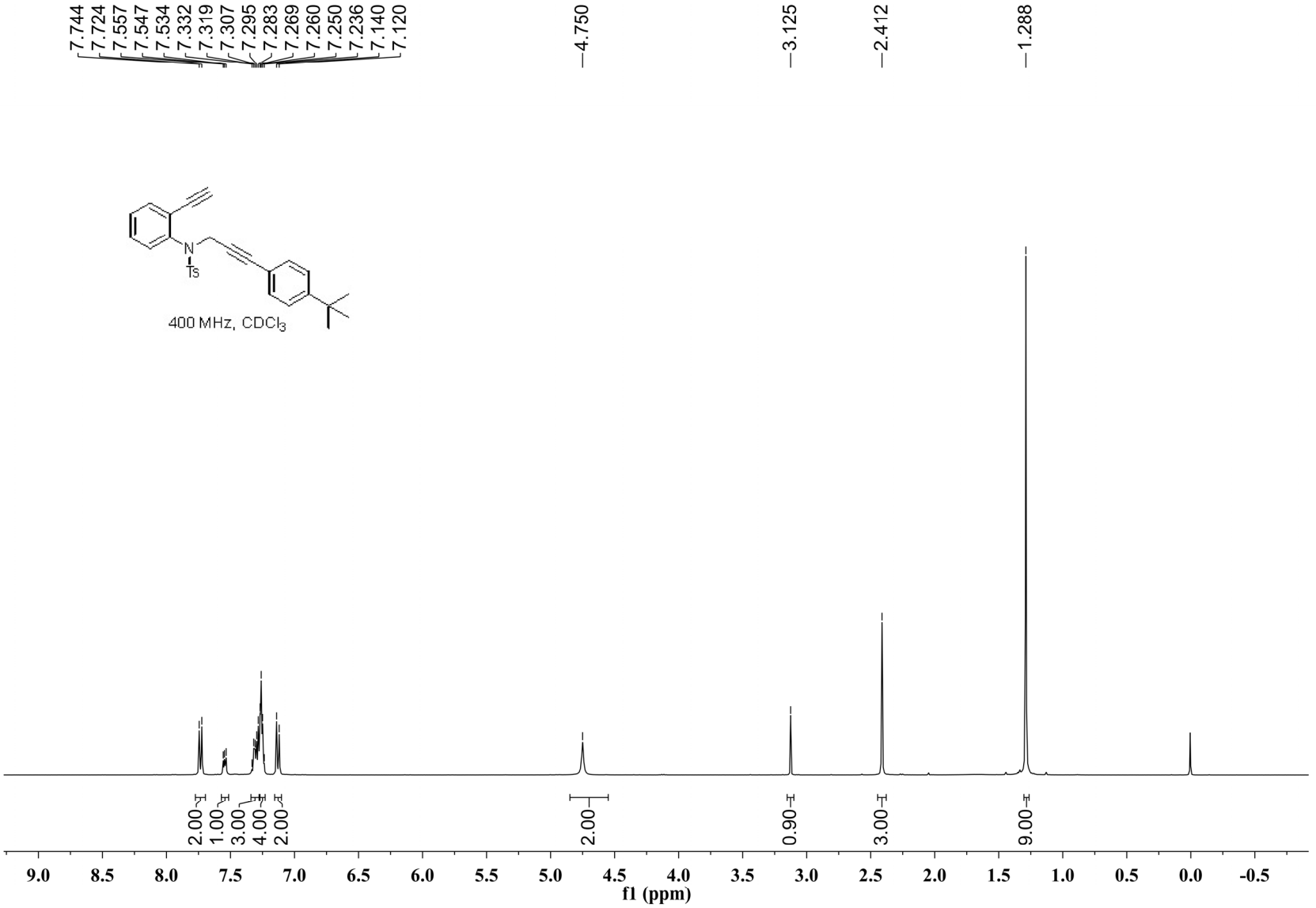
Blue solid; 77.2 mg, 93% yield; mp: 186-187 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.06 (s, 1H), 7.47–7.41 (m, 3H), 7.36 (d, J = 8.0 Hz, 1H), 7.27–7.20 (m, 3H), 7.19–7.14 (m, 1H), 7.06–7.02 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 4.79 (s, 2H), 4.62 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 143.2, 137.4, 134.8, 133.1, 132.3, 131.2, 129.3, 128.4, 128.2, 127.7, 126.7, 124.7, 124.5, 122.9, 122.8, 117.2, 112.2, 98.1, 44.7, 21.4. IR (KBr, v, cm^{-1}): 3428, 1624, 1508, 1338, 1265, 1157, 1030, 809, 757; HRMS (ESI -TOF) m/z: $[M-H]^-$ Calcd for $C_{24}H_{20}N_3O_2S$ 414.1276; Found 414.1250;



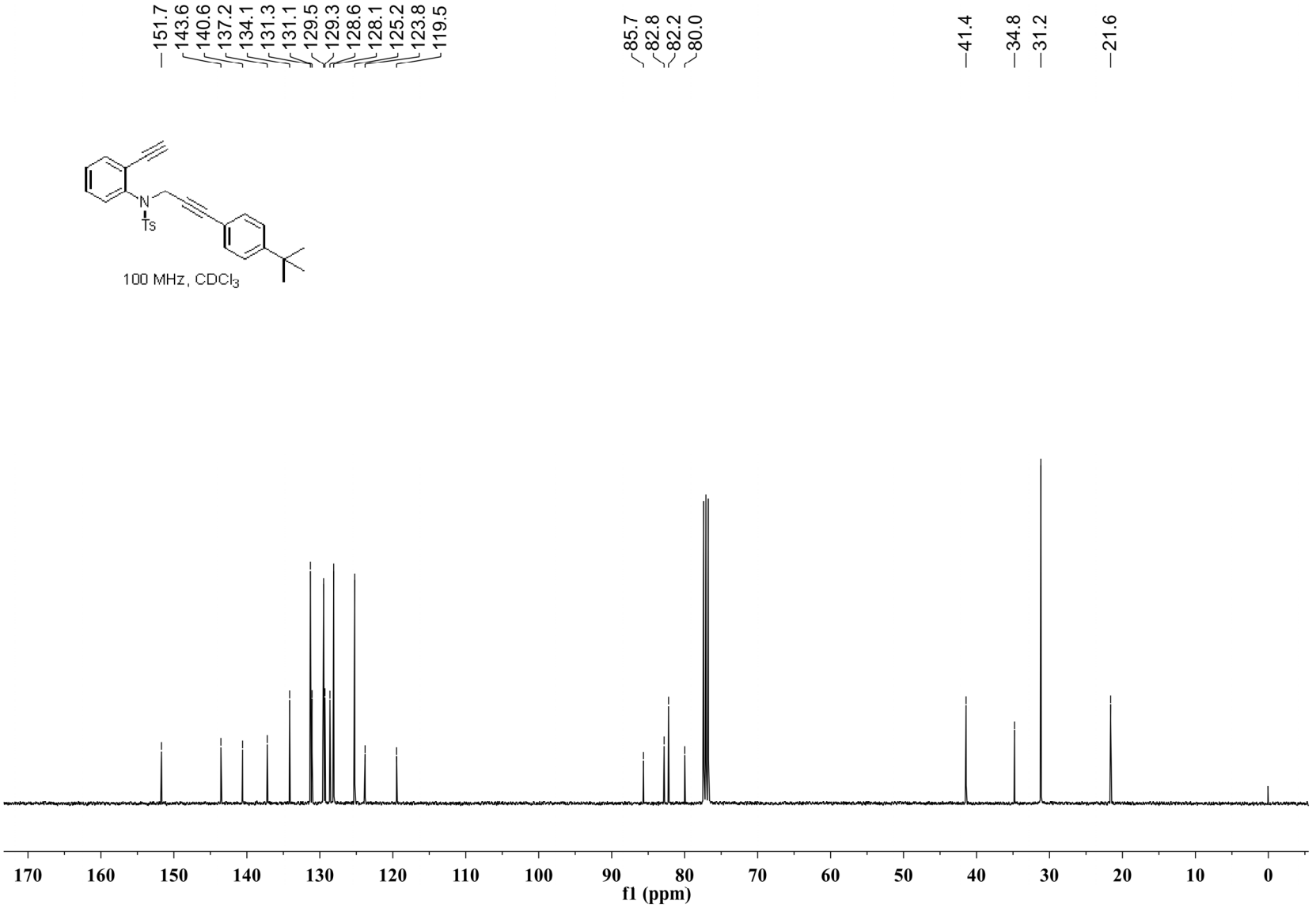
^{1}H NMR Spectrum of Compound 1f



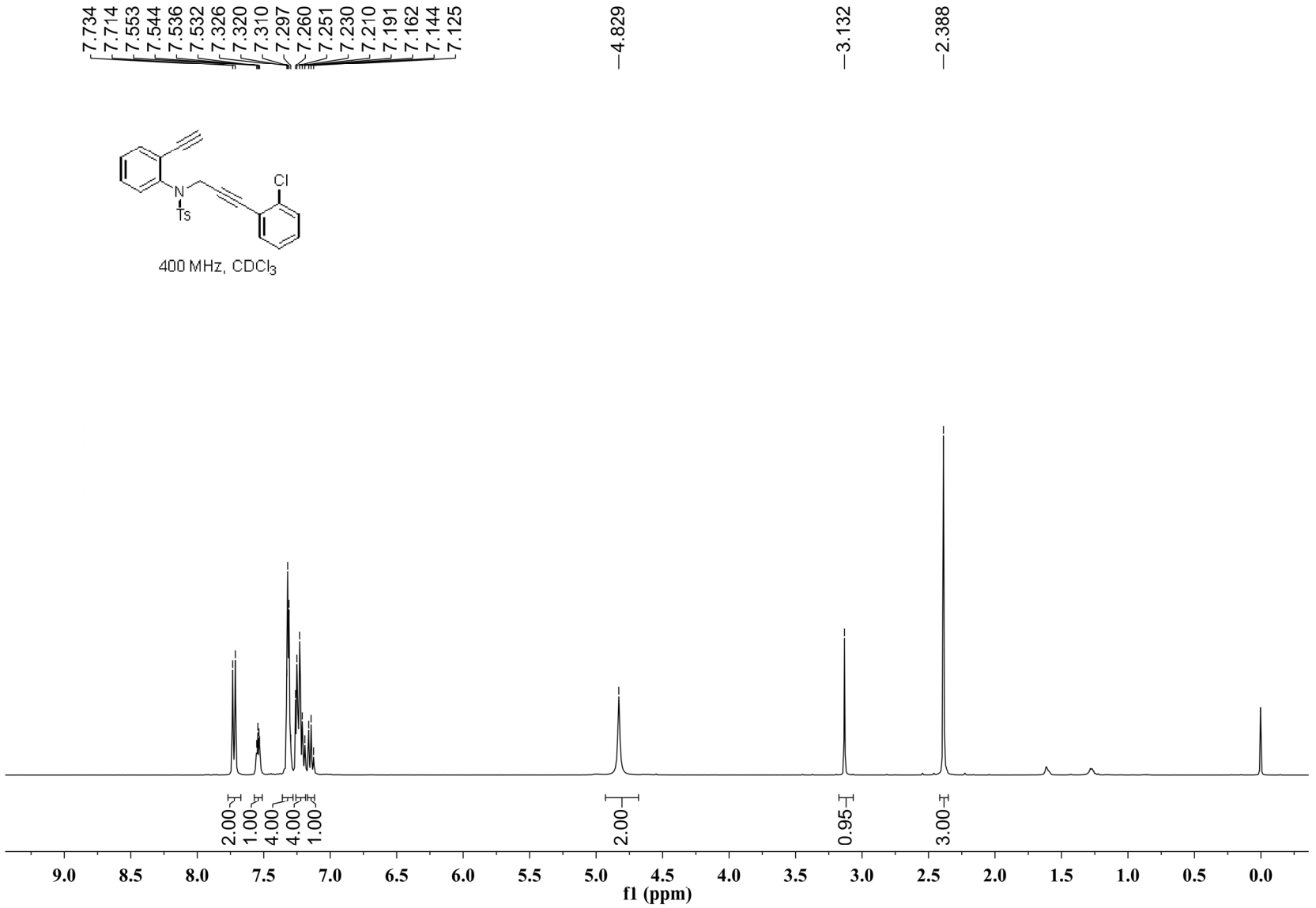
^{13}C NMR Spectrum of Compound 1f



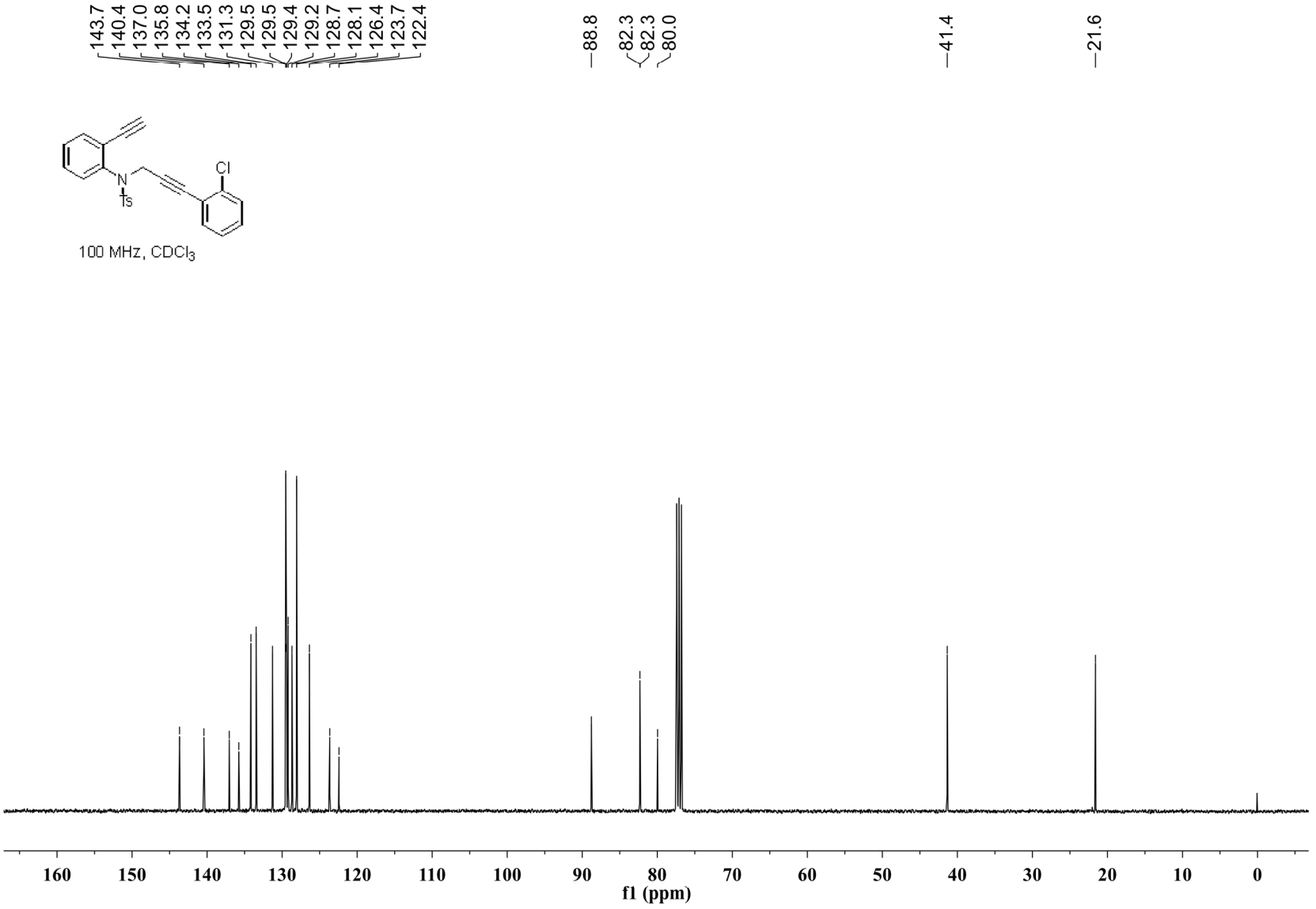
^{1}H NMR Spectrum of Compound 1g



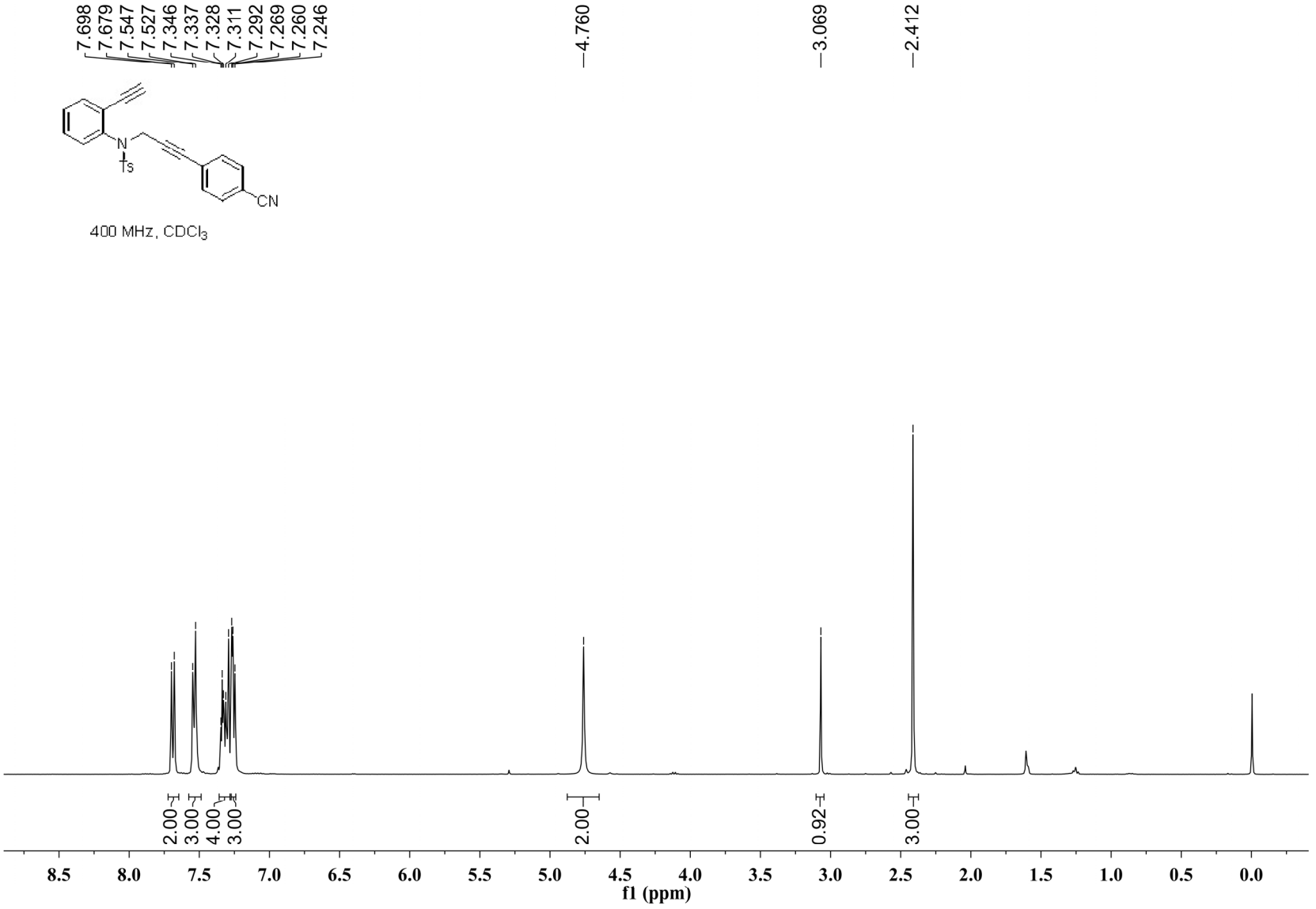
^{13}C NMR Spectrum of Compound 1g



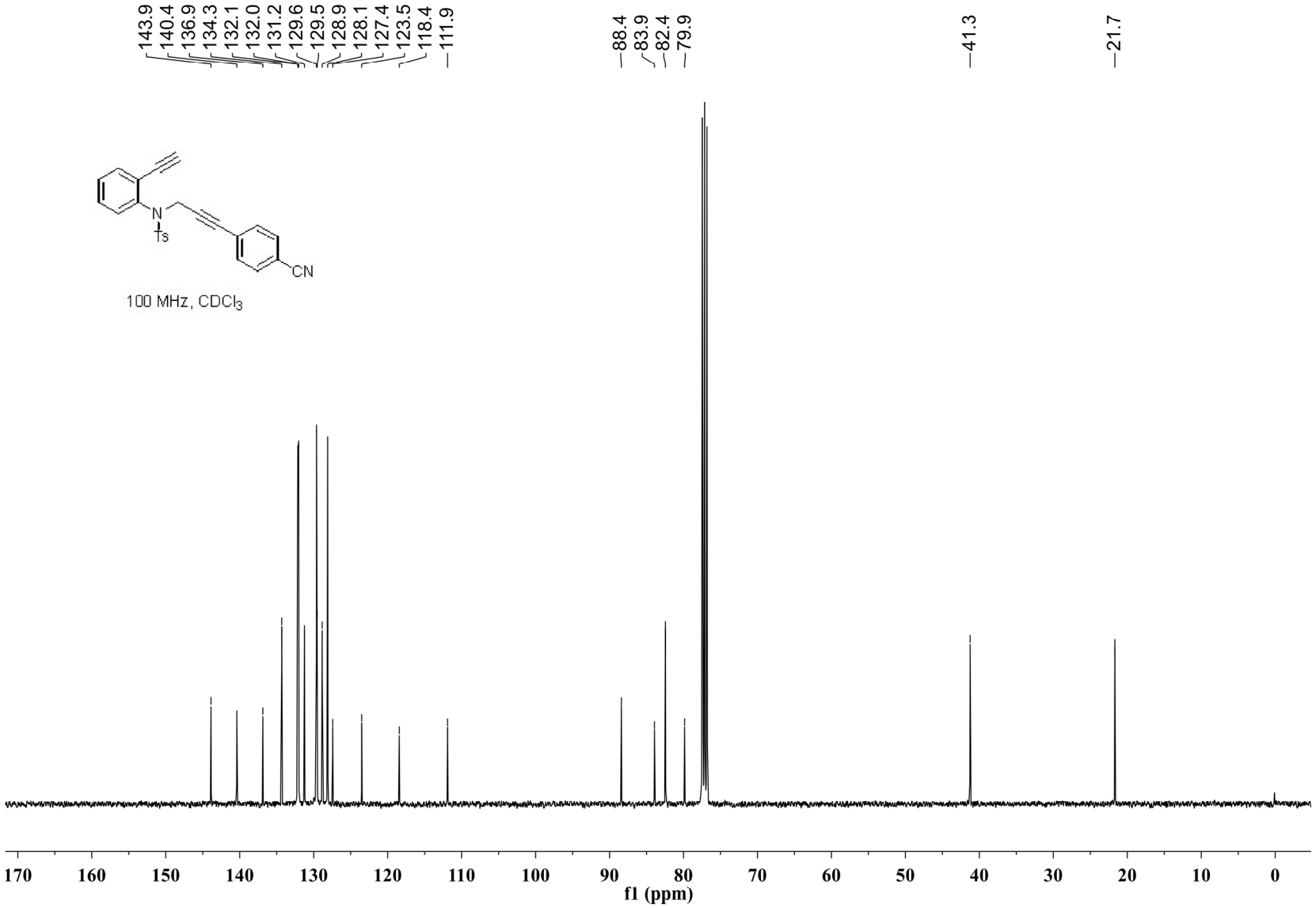
^{1}H NMR Spectrum of Compound 1k



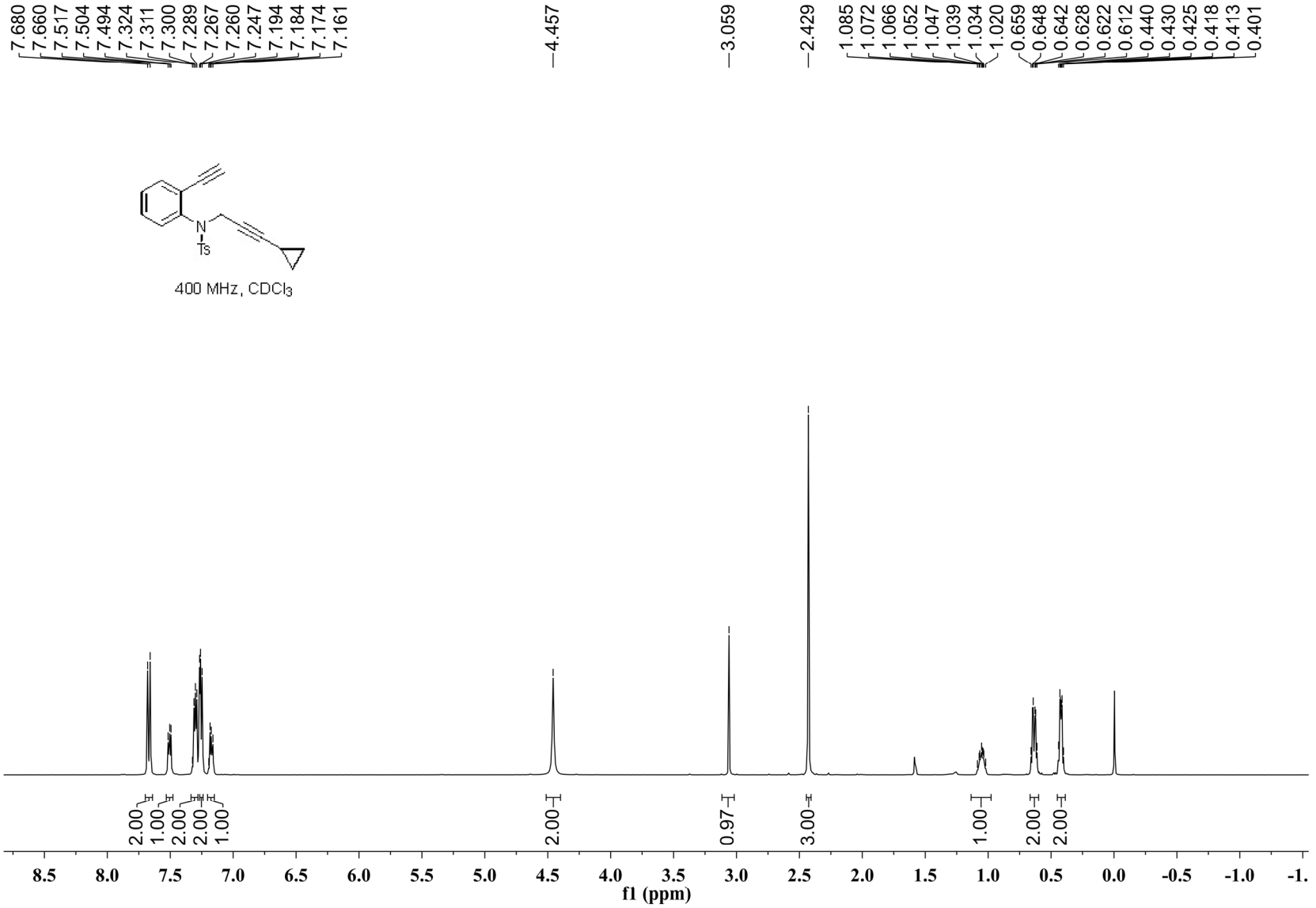
^{13}C NMR Spectrum of Compound 1k



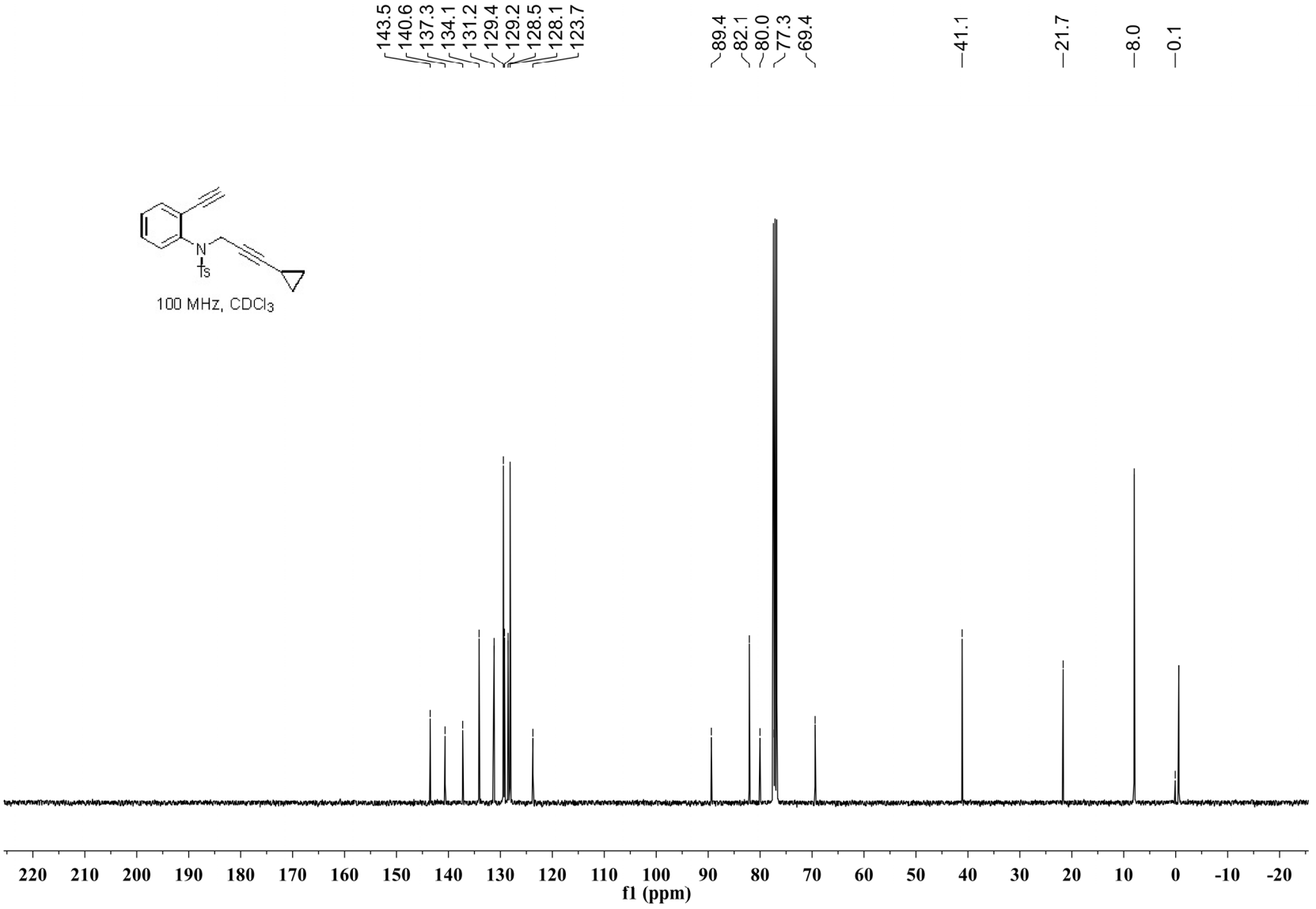
^{1}H NMR Spectrum of Compound 1m



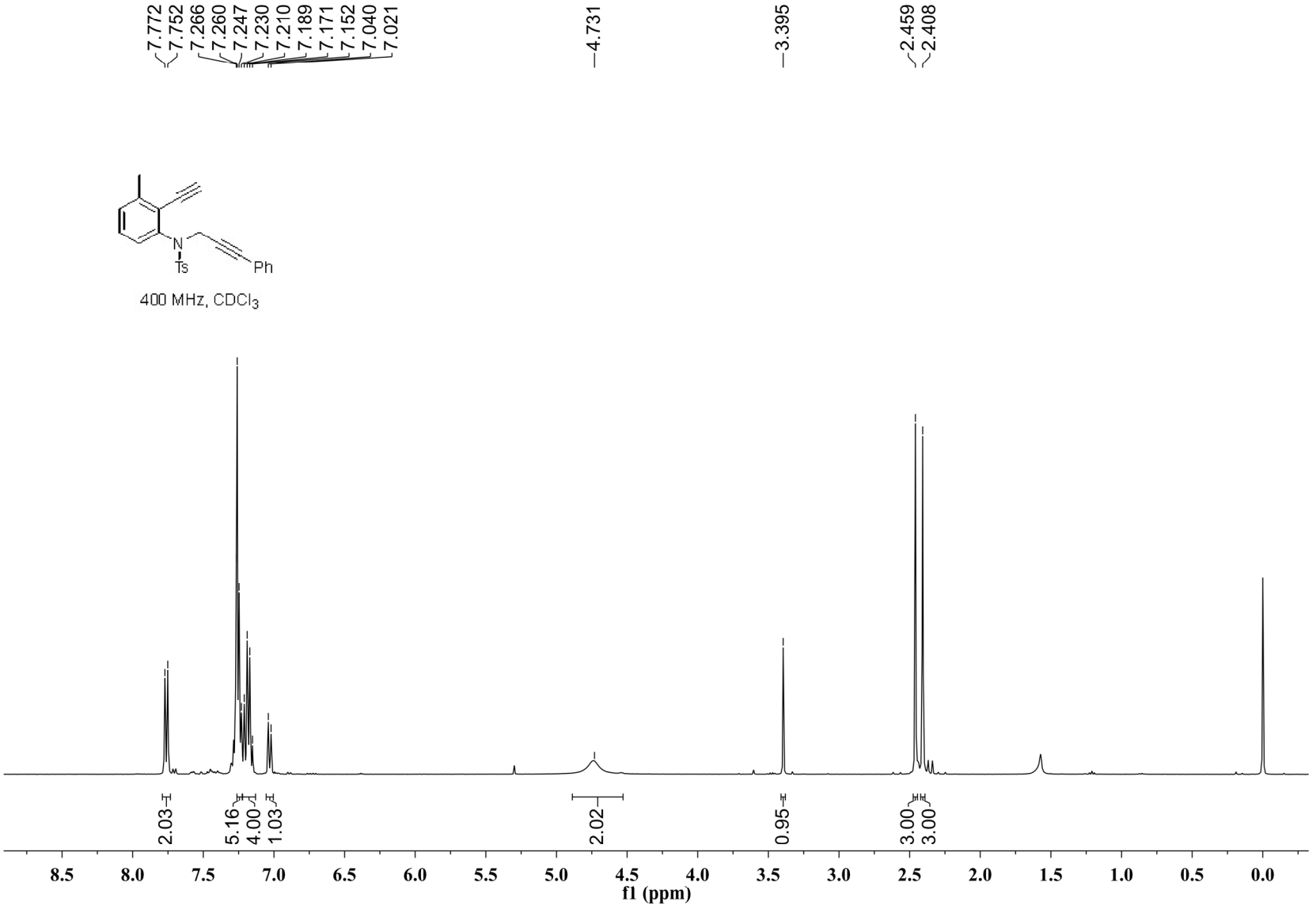
^{13}C NMR Spectrum of Compound 1m



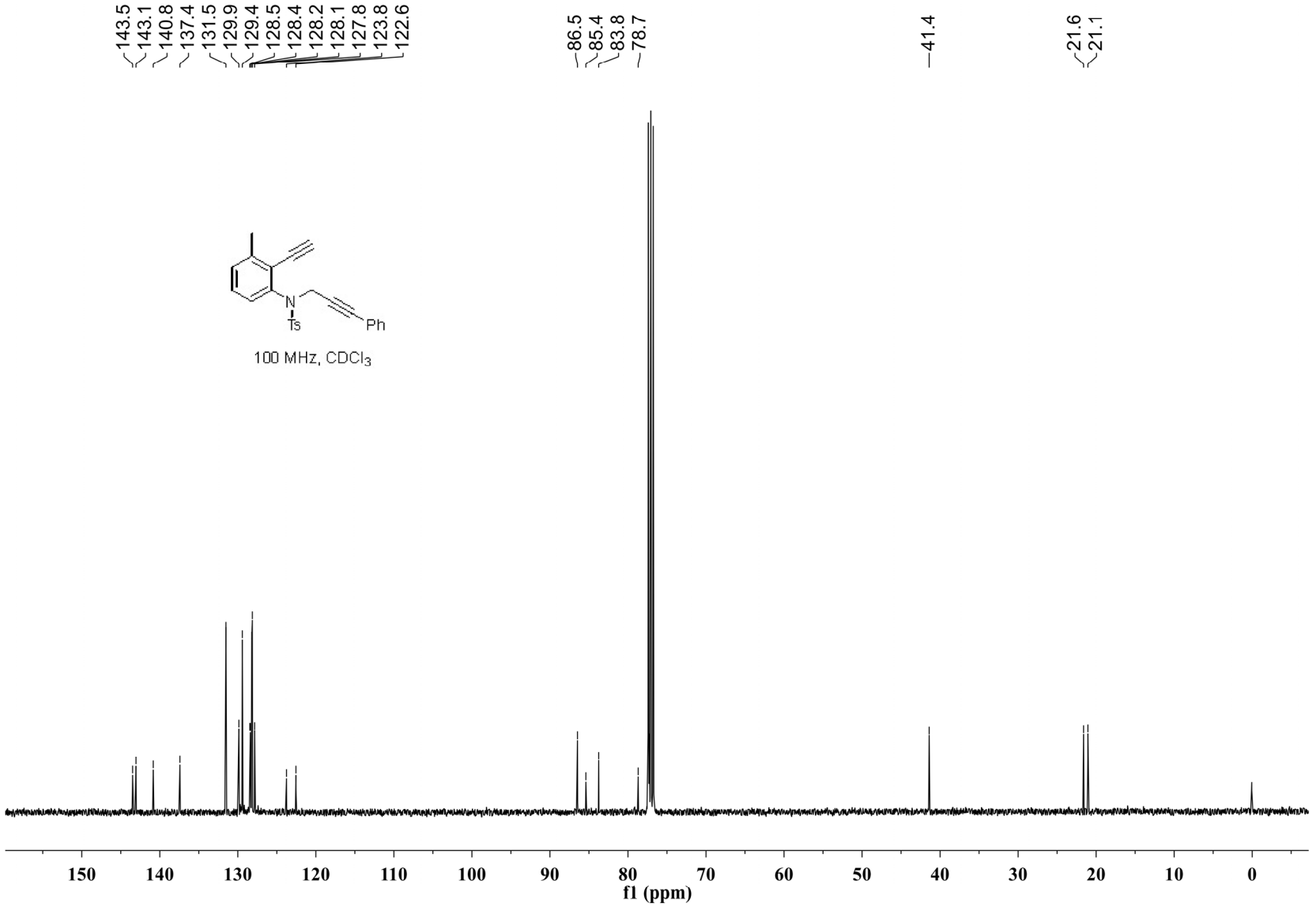
^{1}H NMR Spectrum of Compound 1o



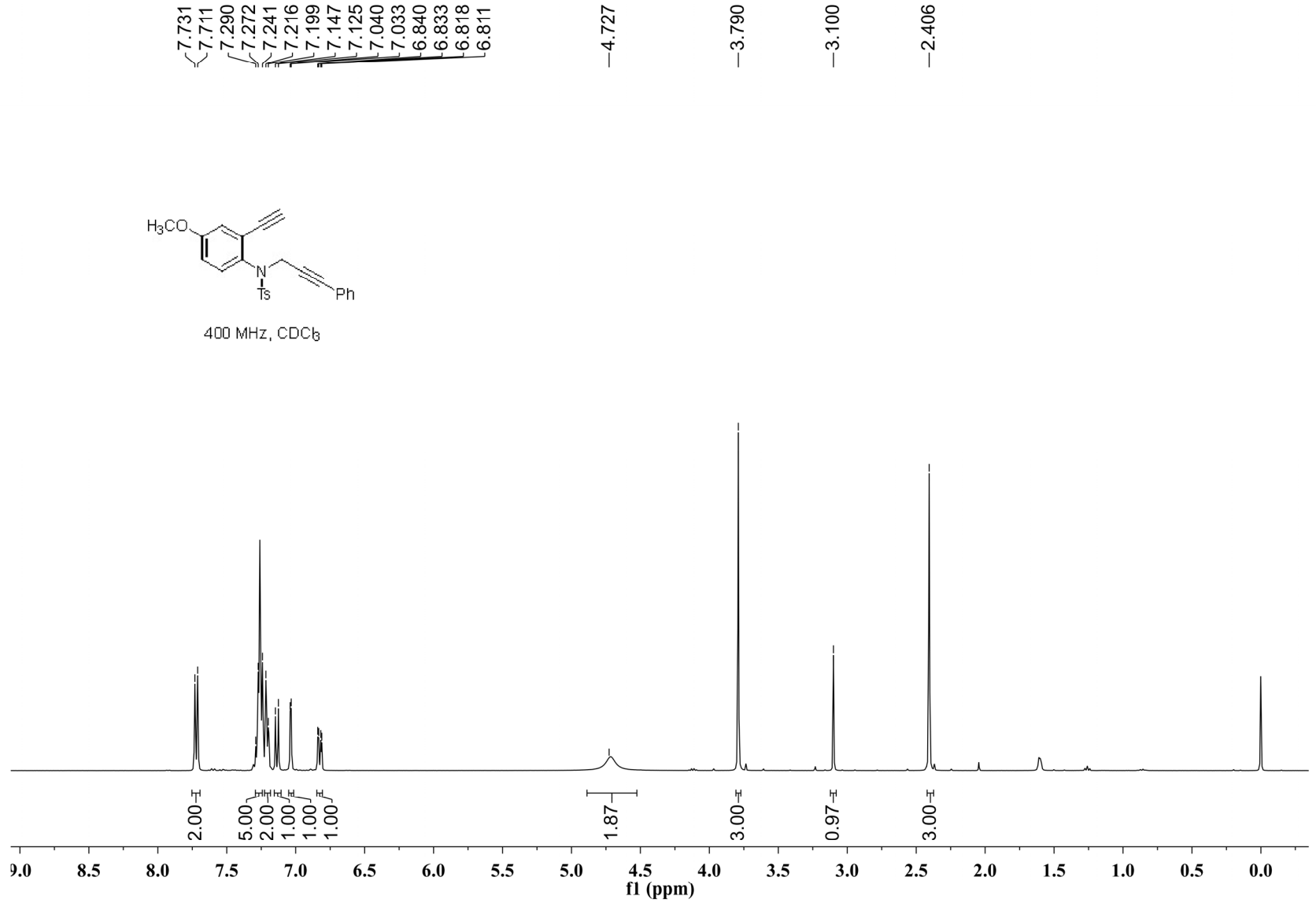
^{13}C NMR Spectrum of Compound 1o



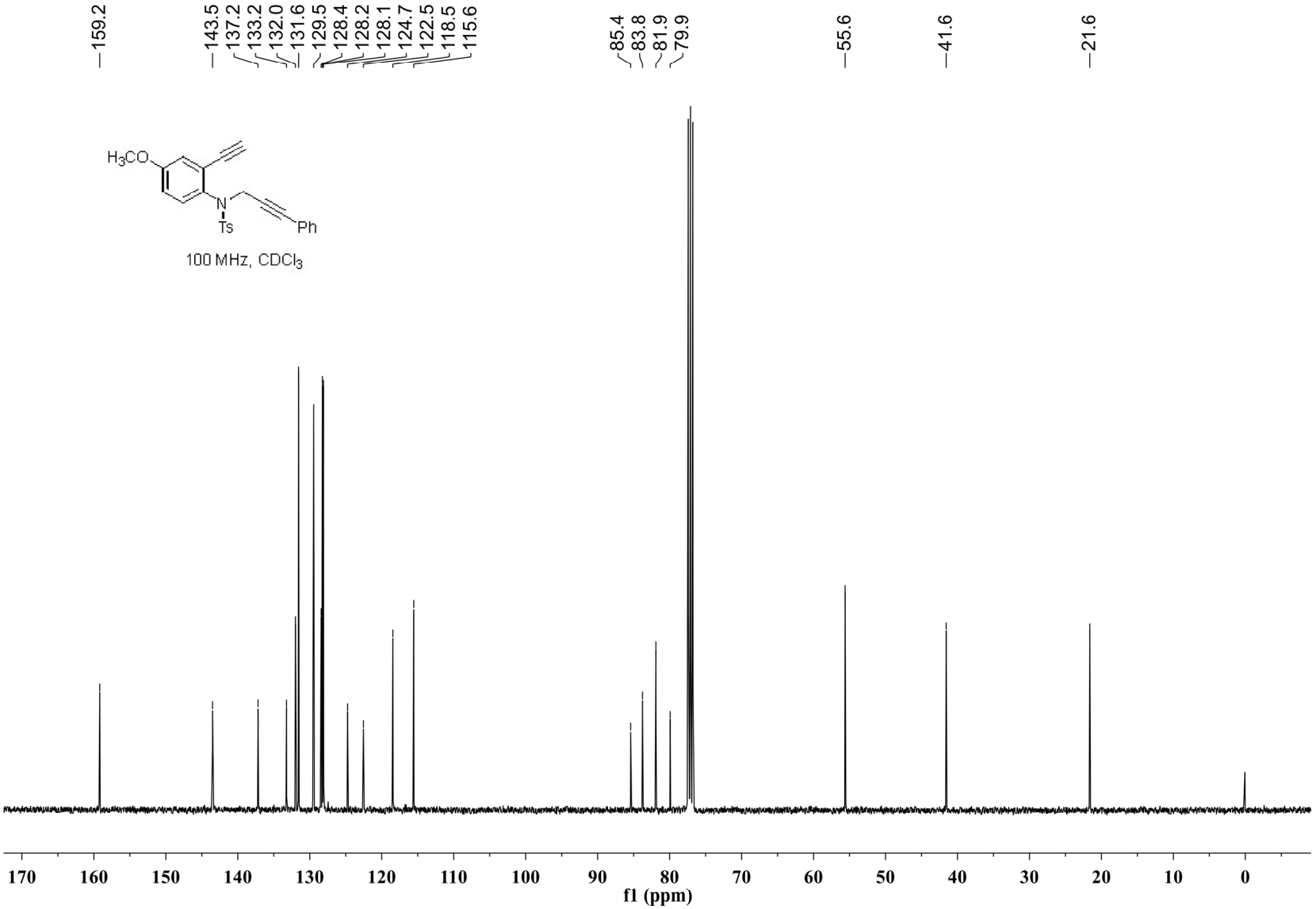
^{1}H NMR Spectrum of Compound 1p



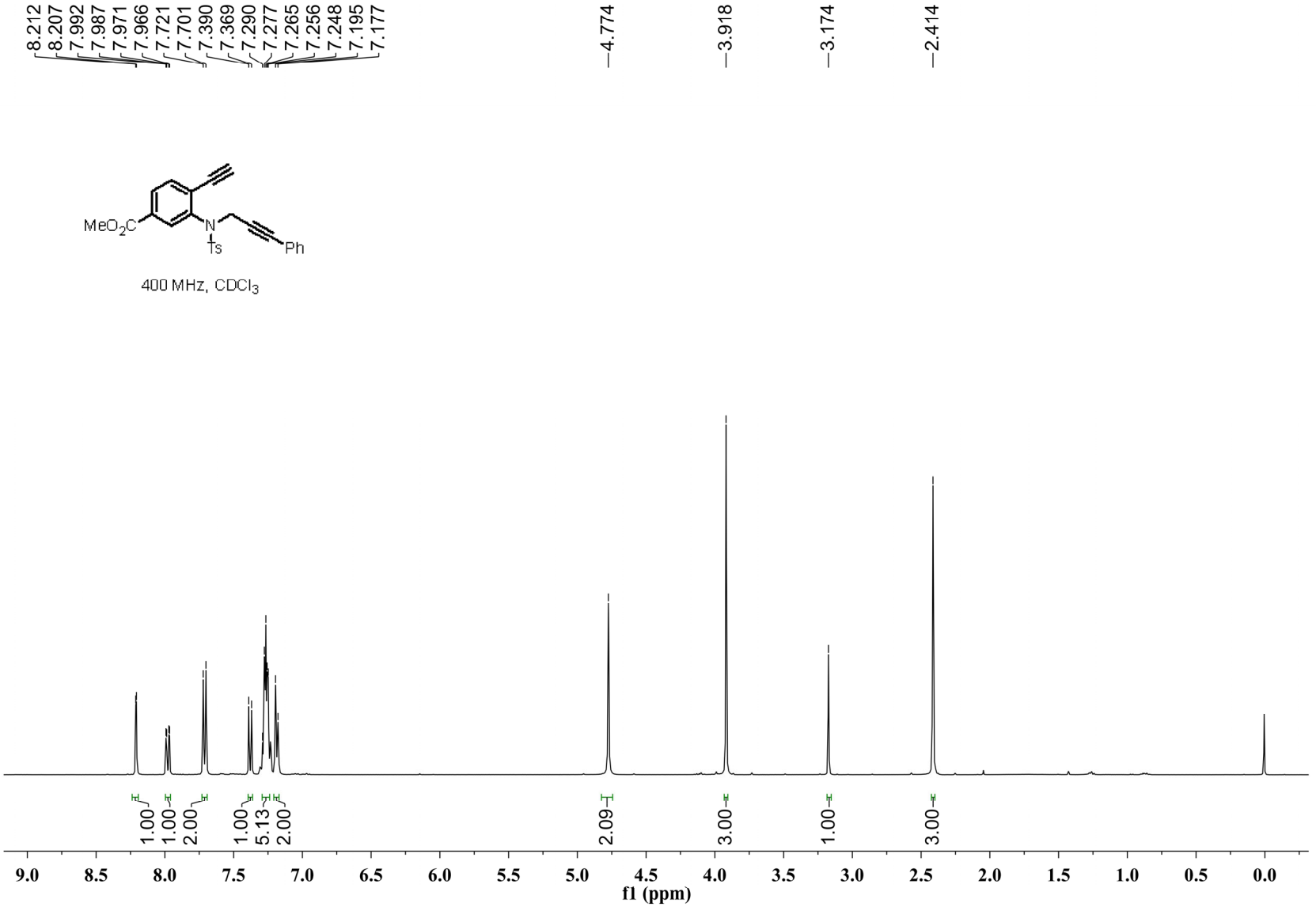
^{13}C NMR Spectrum of Compound 1p



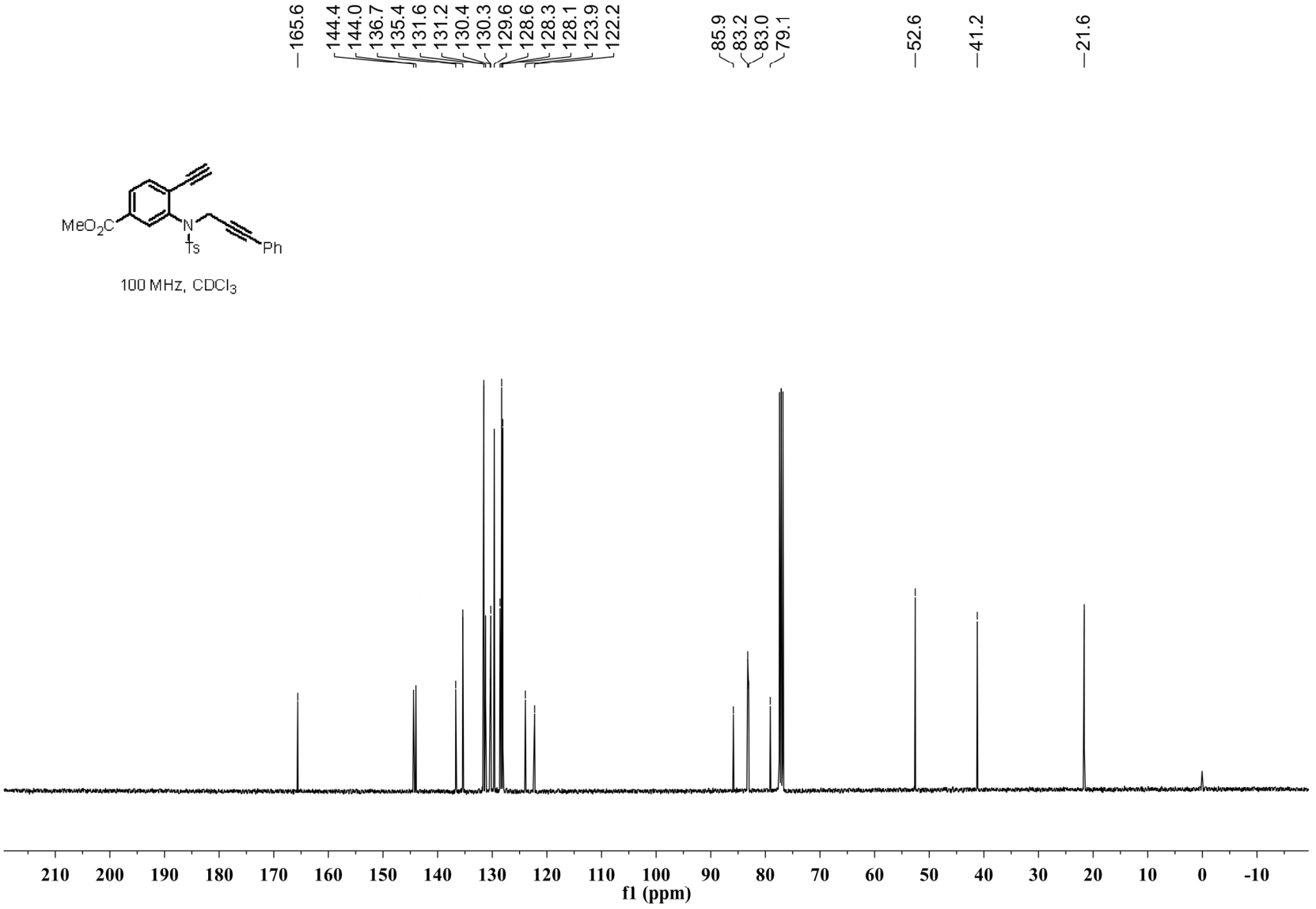
^{1}H NMR Spectrum of Compound 1r



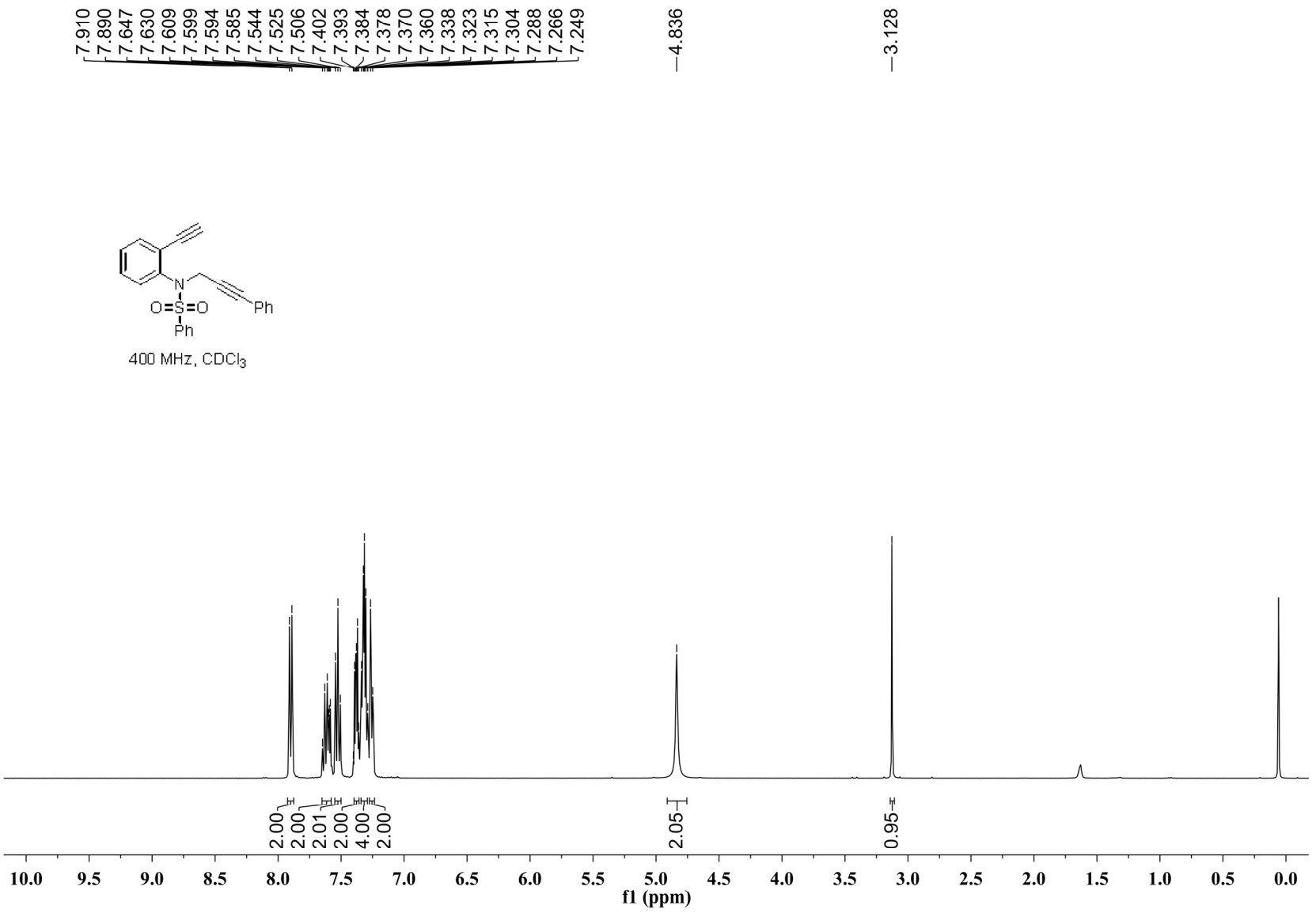
^{13}C NMR Spectrum of Compound 1r



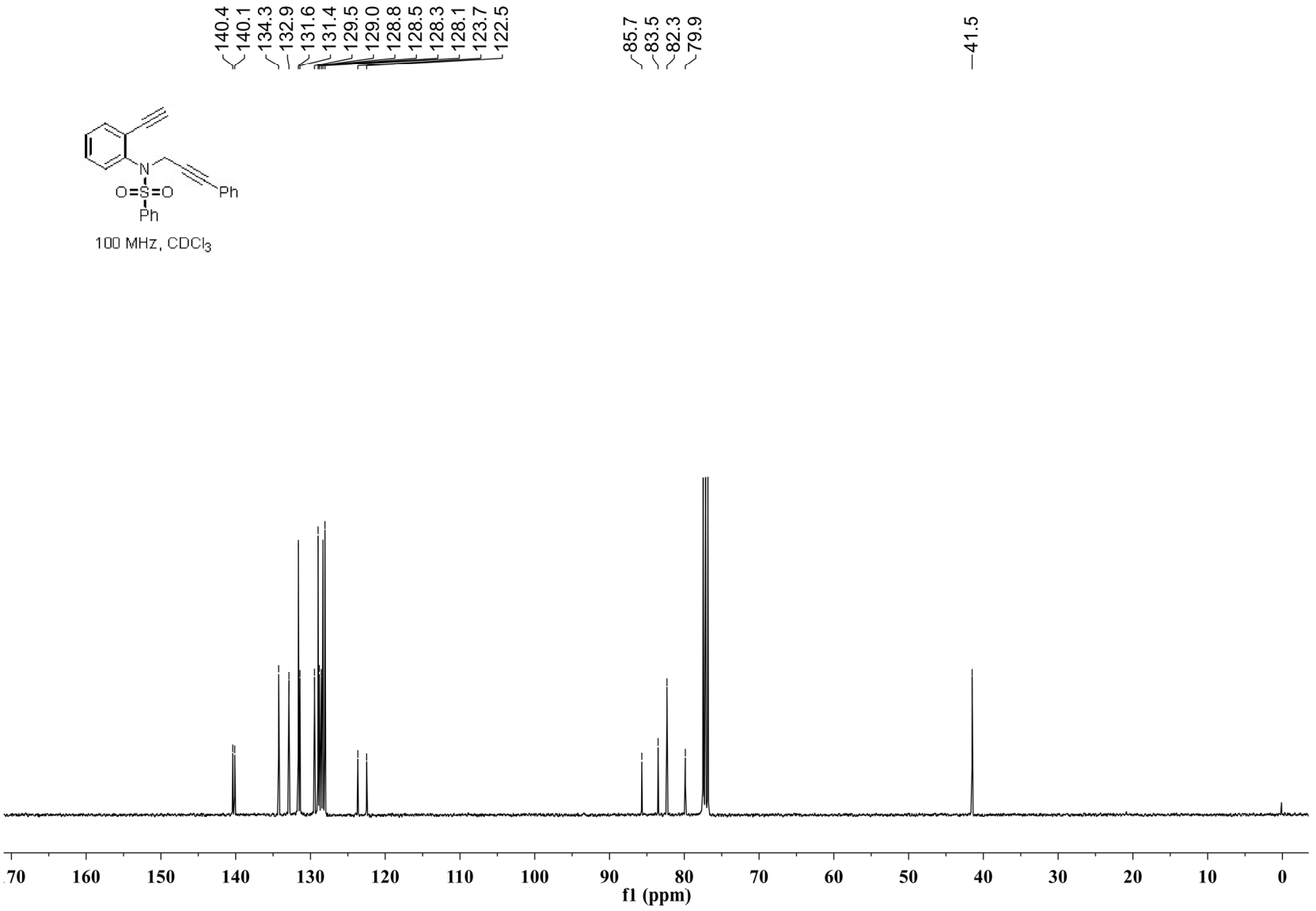
^{1}H NMR Spectrum of Compound 1t



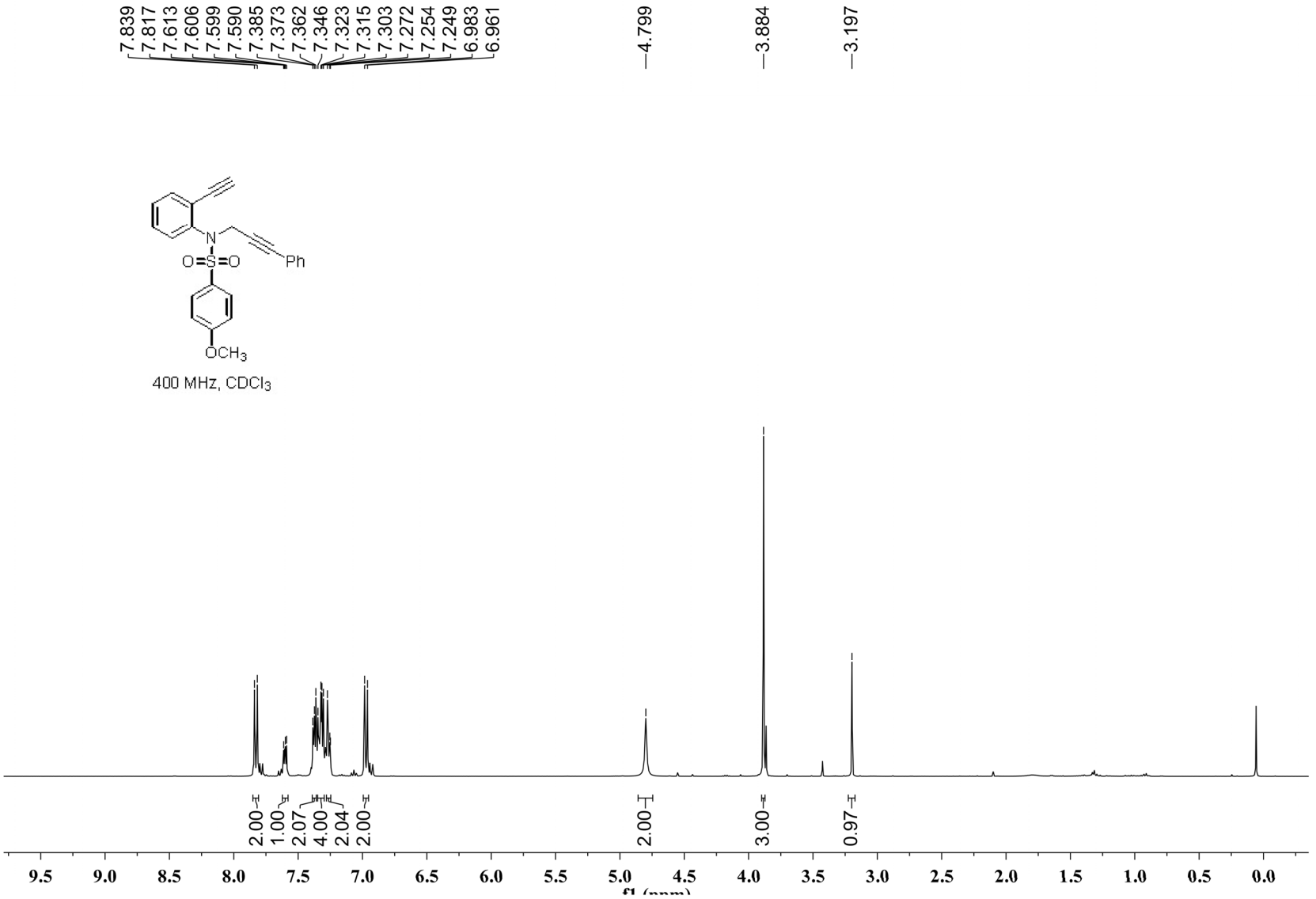
^{13}C NMR Spectrum of Compound 1t



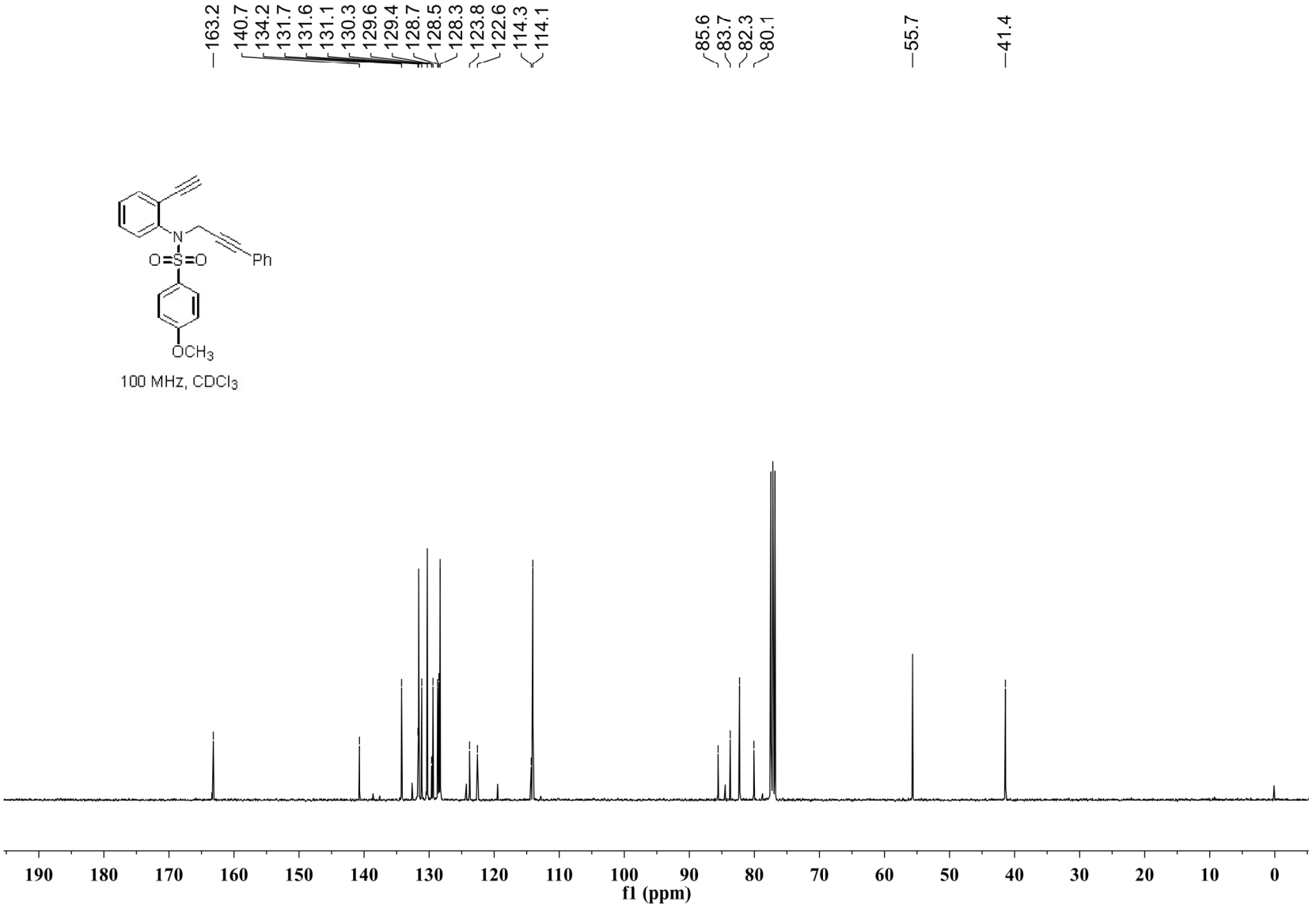
^{1}H NMR Spectrum of Compound 1v



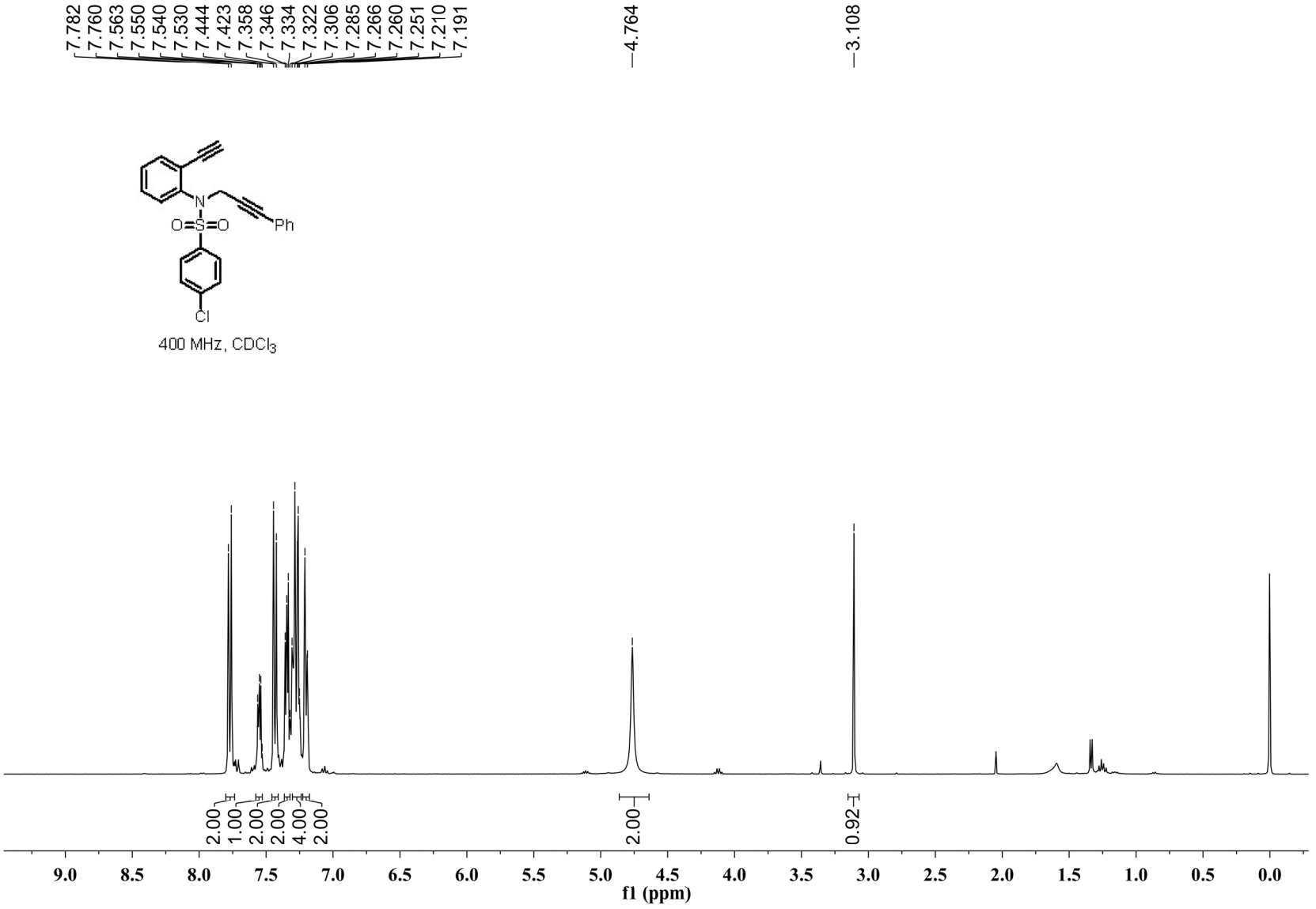
^{13}C NMR Spectrum of Compound 1v



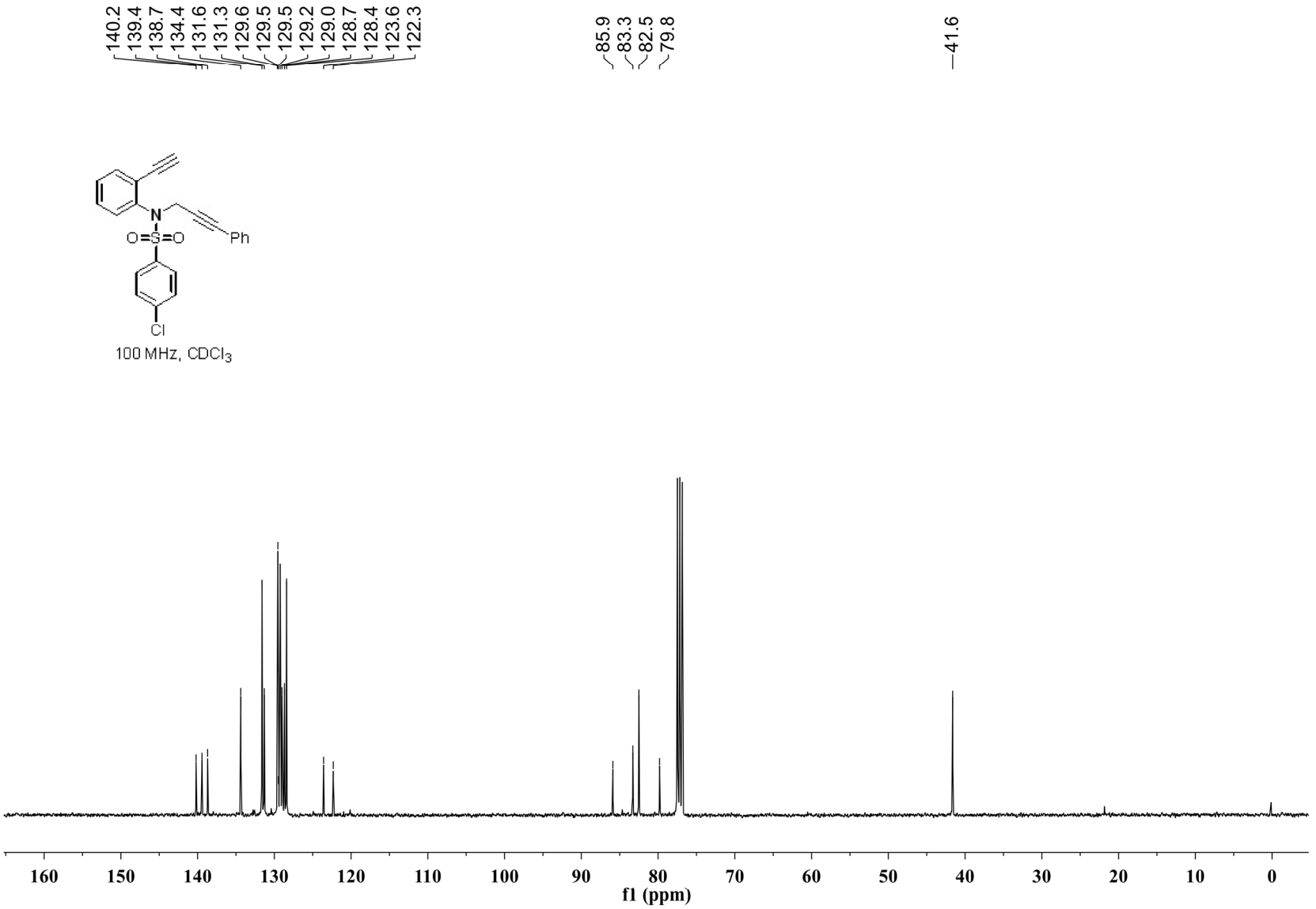
^{1}H NMR Spectrum of Compound 1w



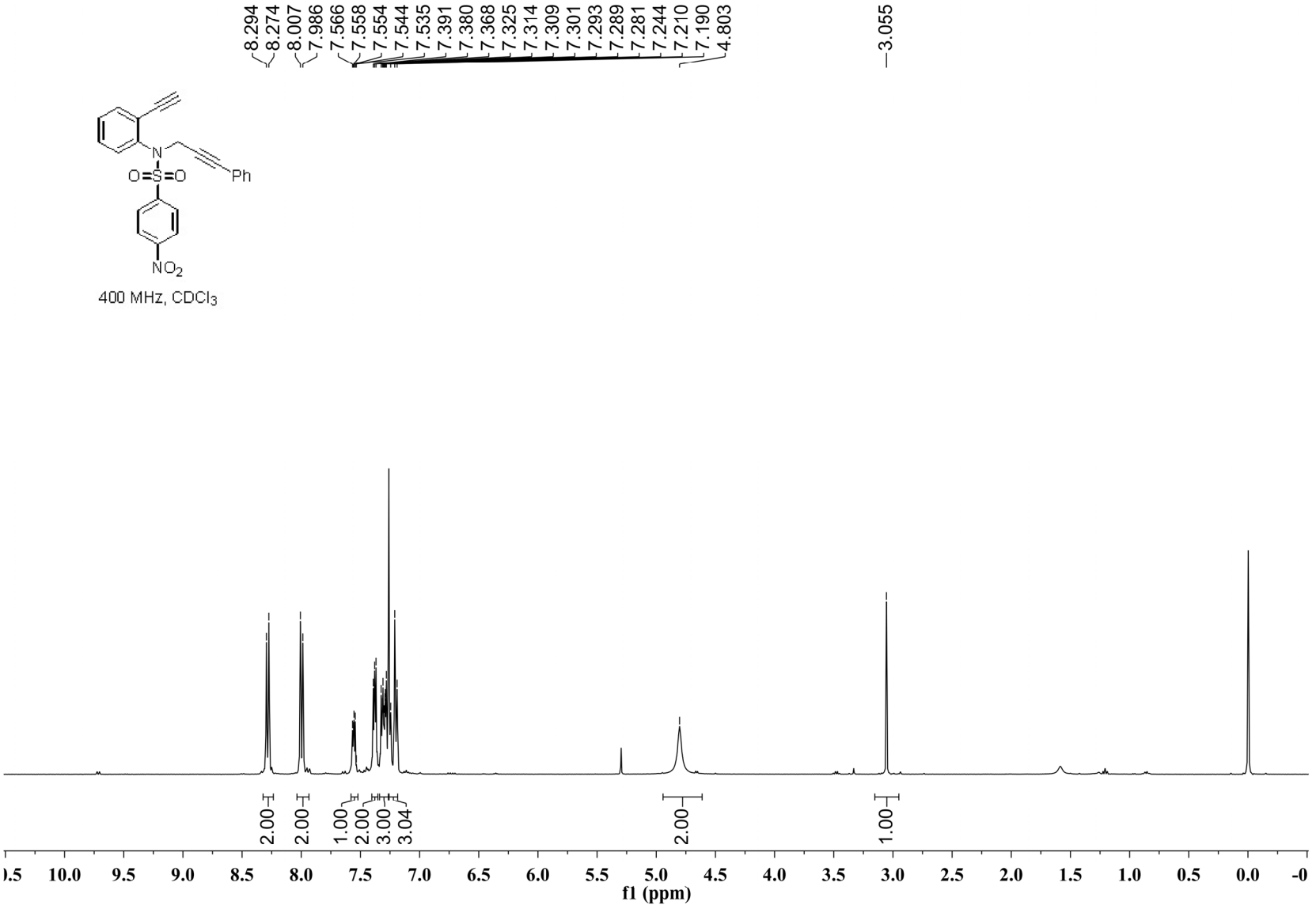
^{13}C NMR Spectrum of Compound 1w



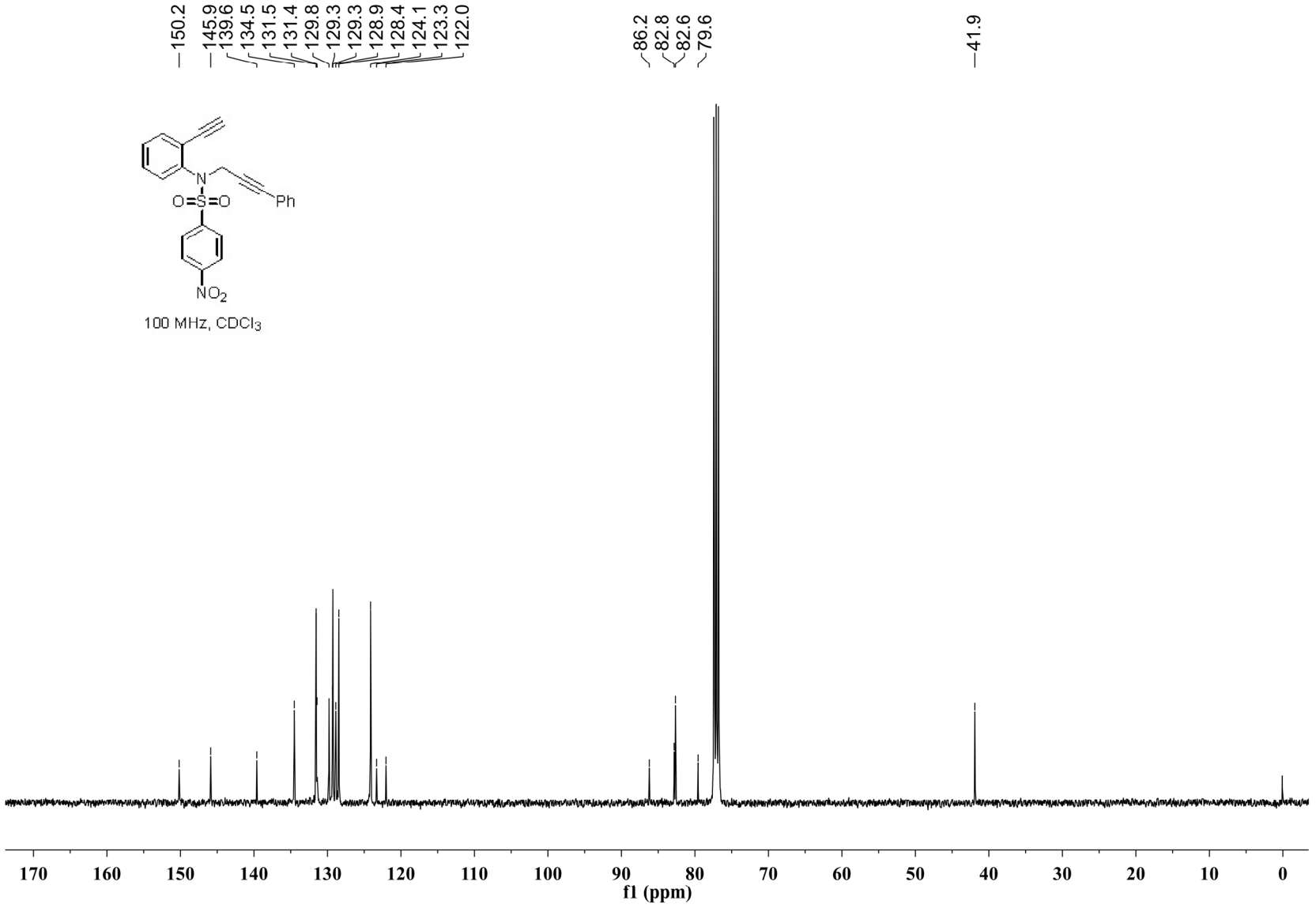
^{1}H NMR Spectrum of Compound 1x



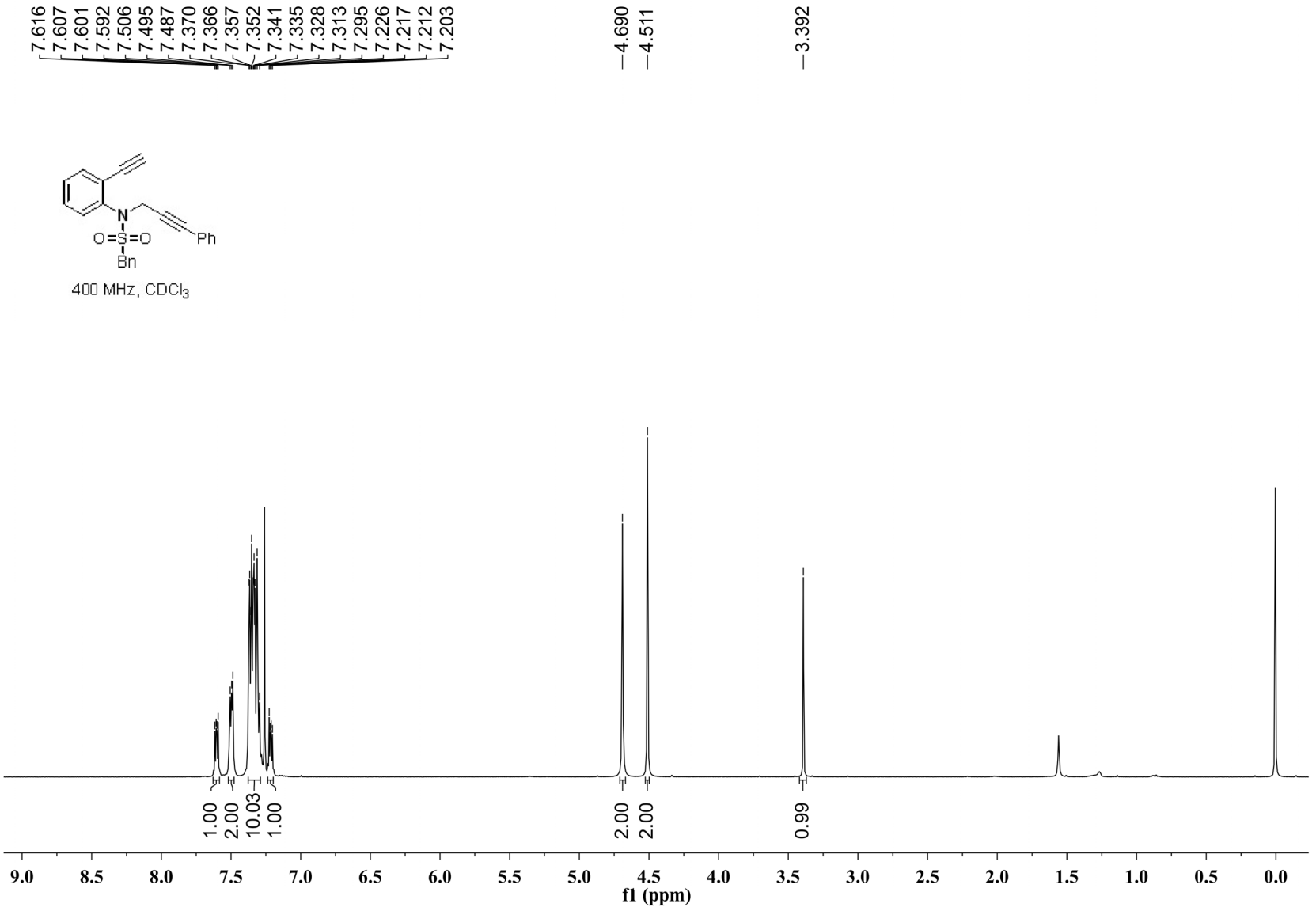
^{13}C NMR Spectrum of Compound 1x



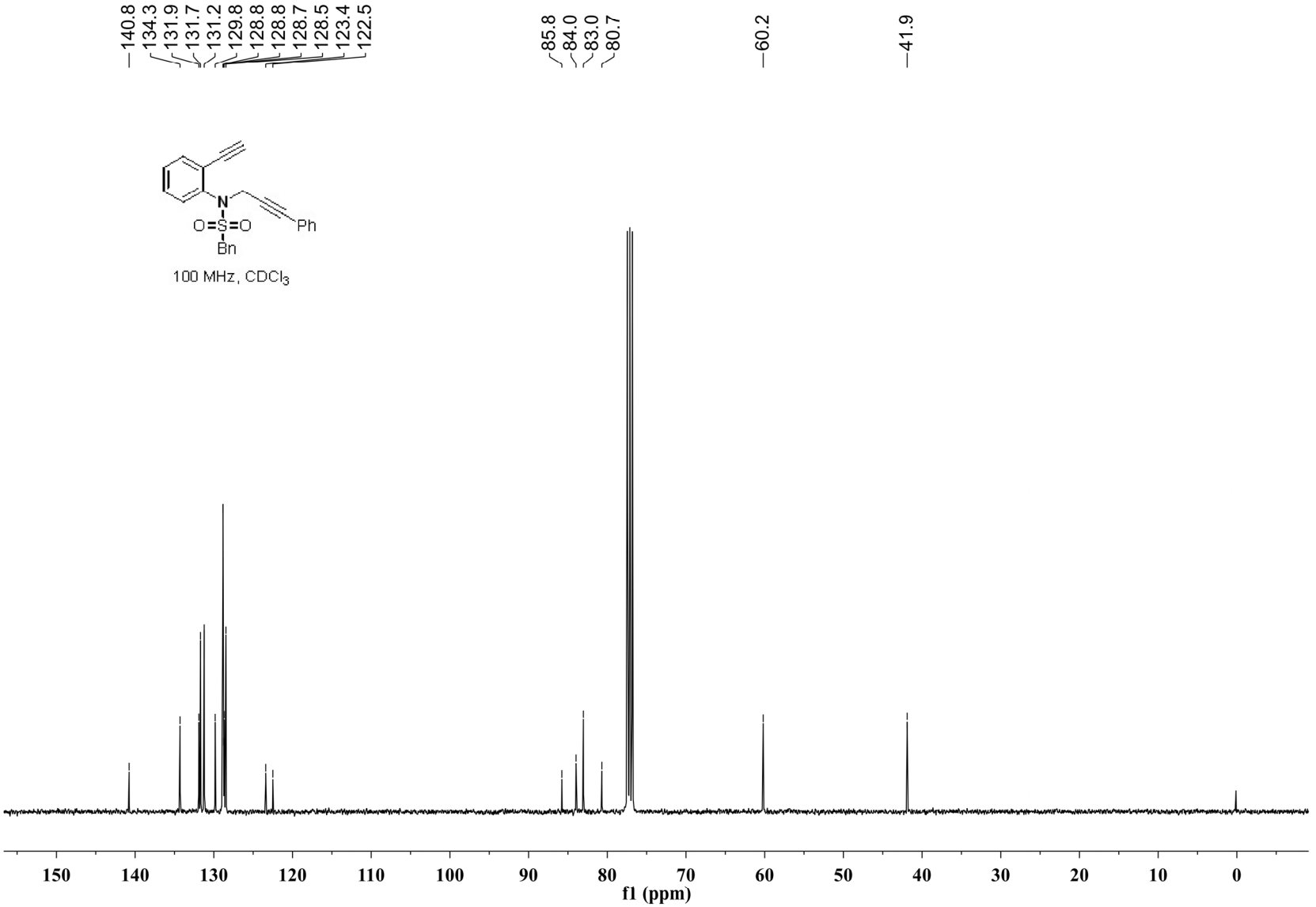
^{1}H NMR Spectrum of Compound 1y



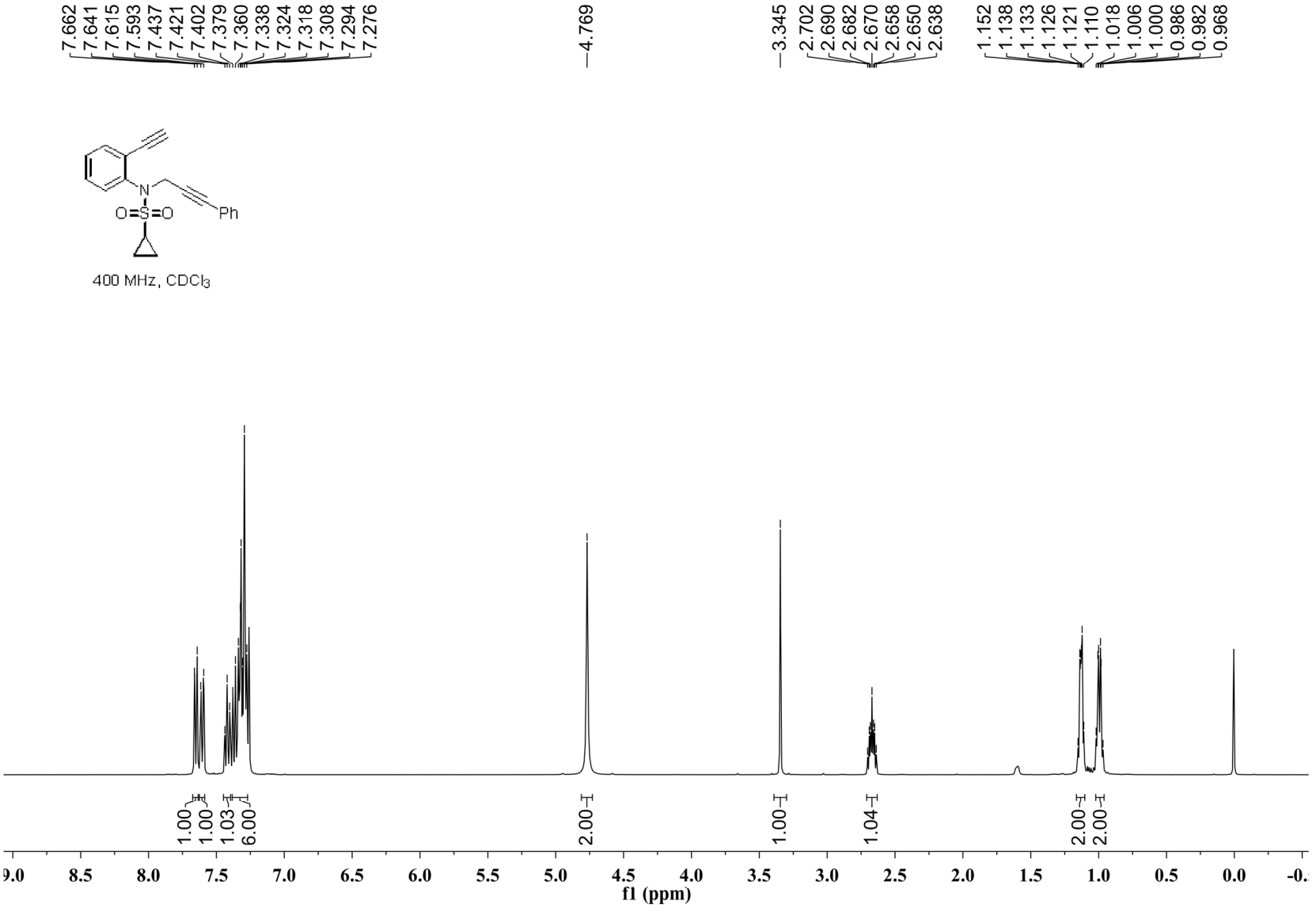
^{13}C NMR Spectrum of Compound 1y



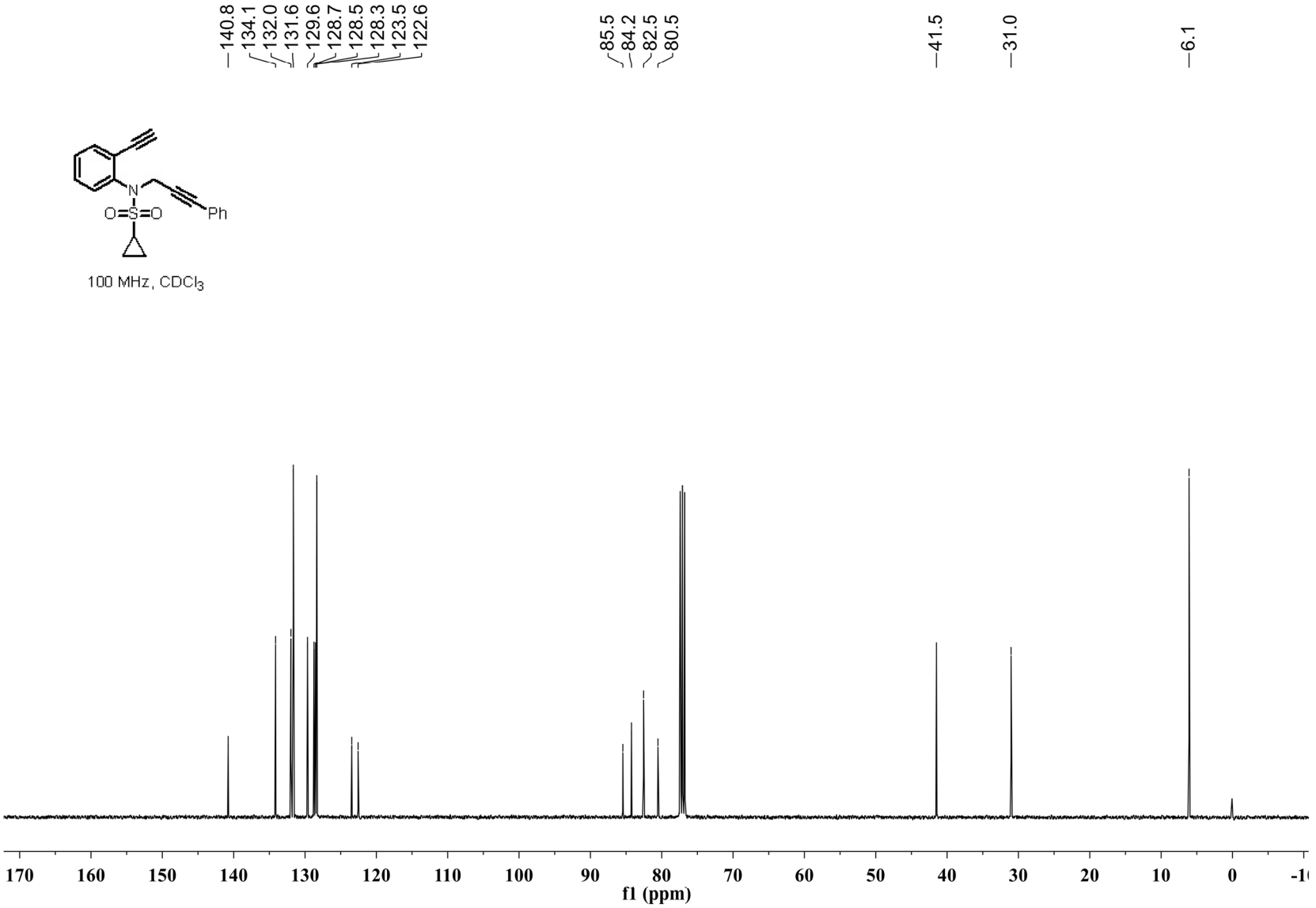
^{1}H NMR Spectrum of Compound 1z



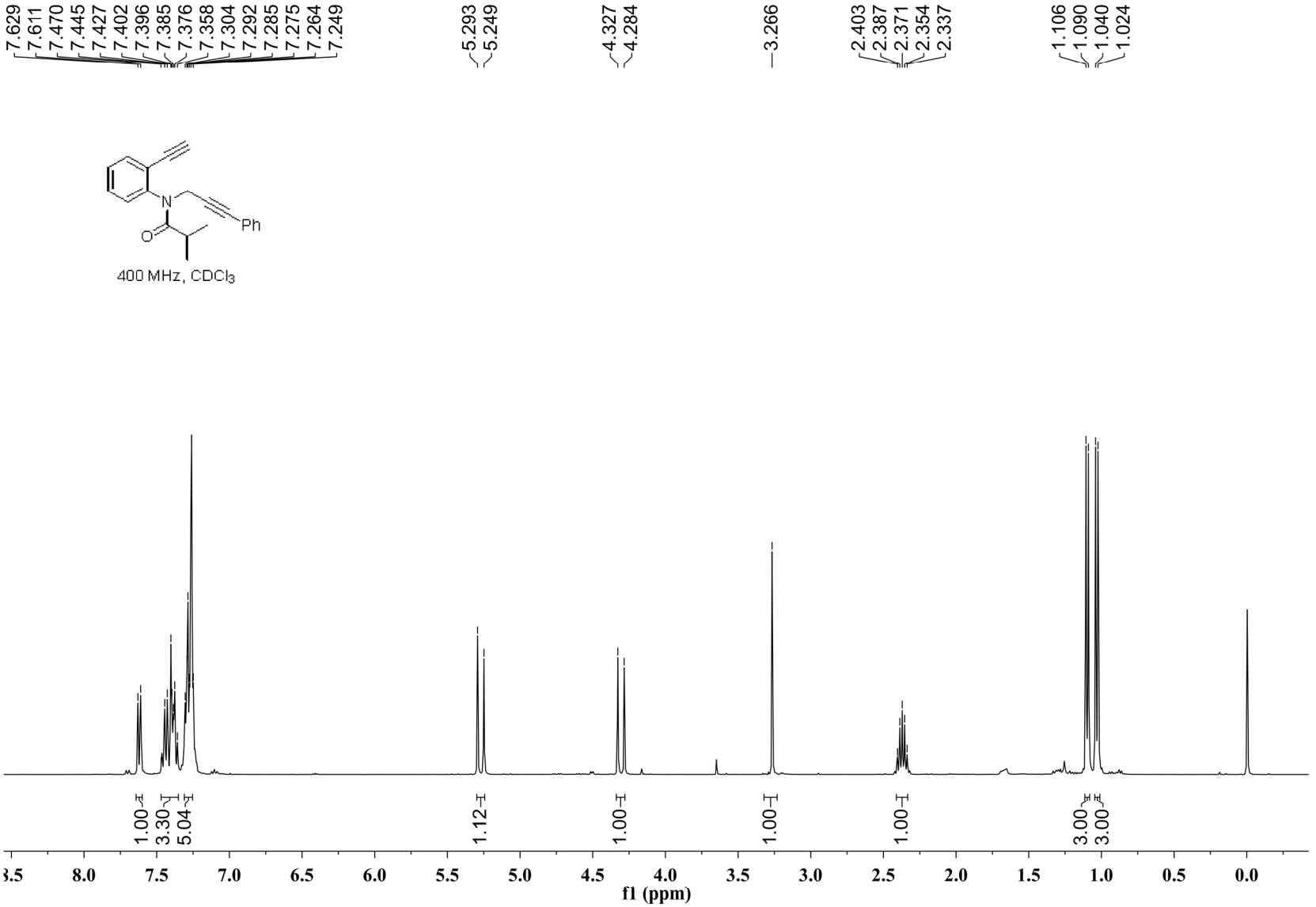
^{13}C NMR Spectrum of Compound 1z



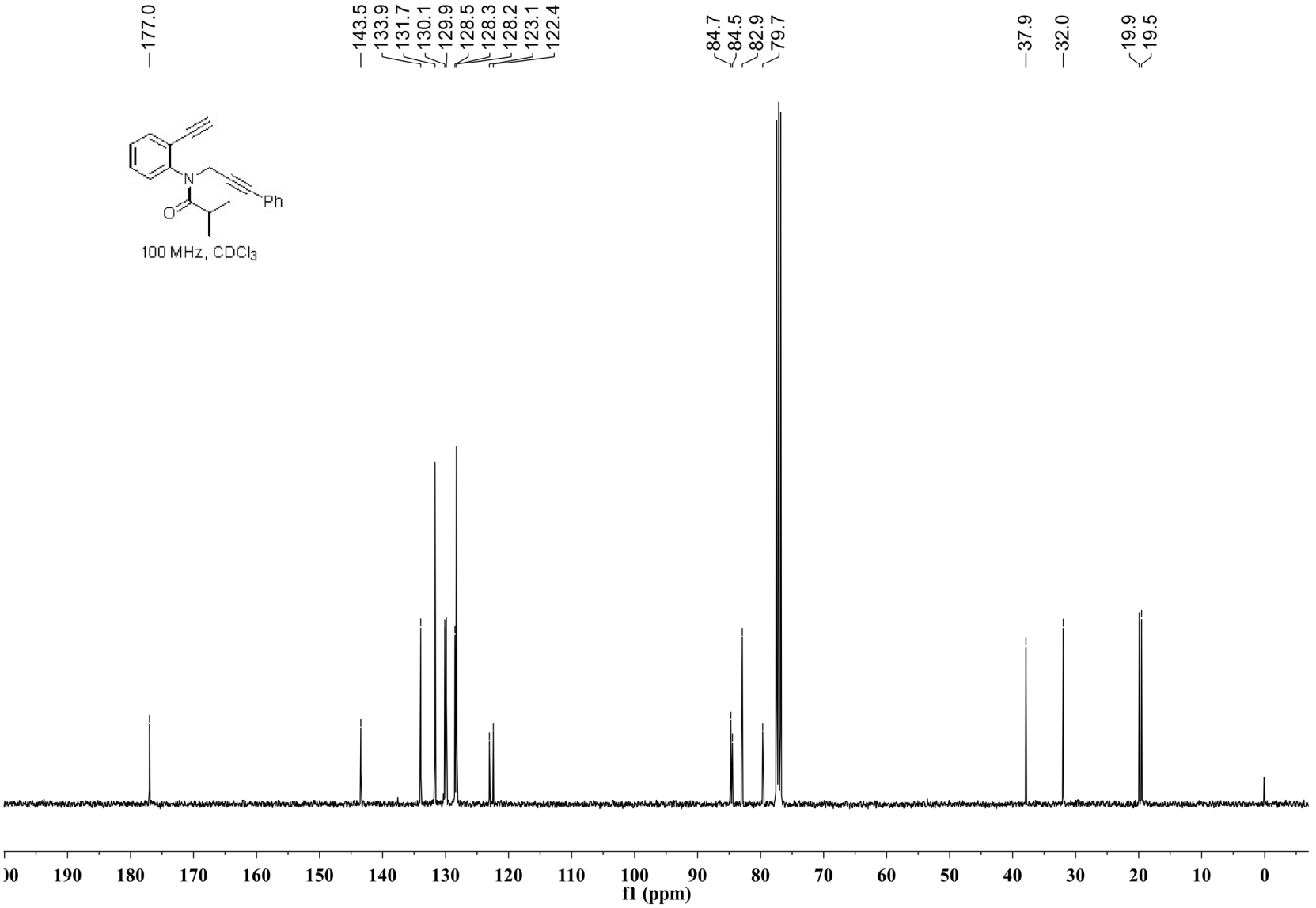
^{1}H NMR Spectrum of Compound 1aa



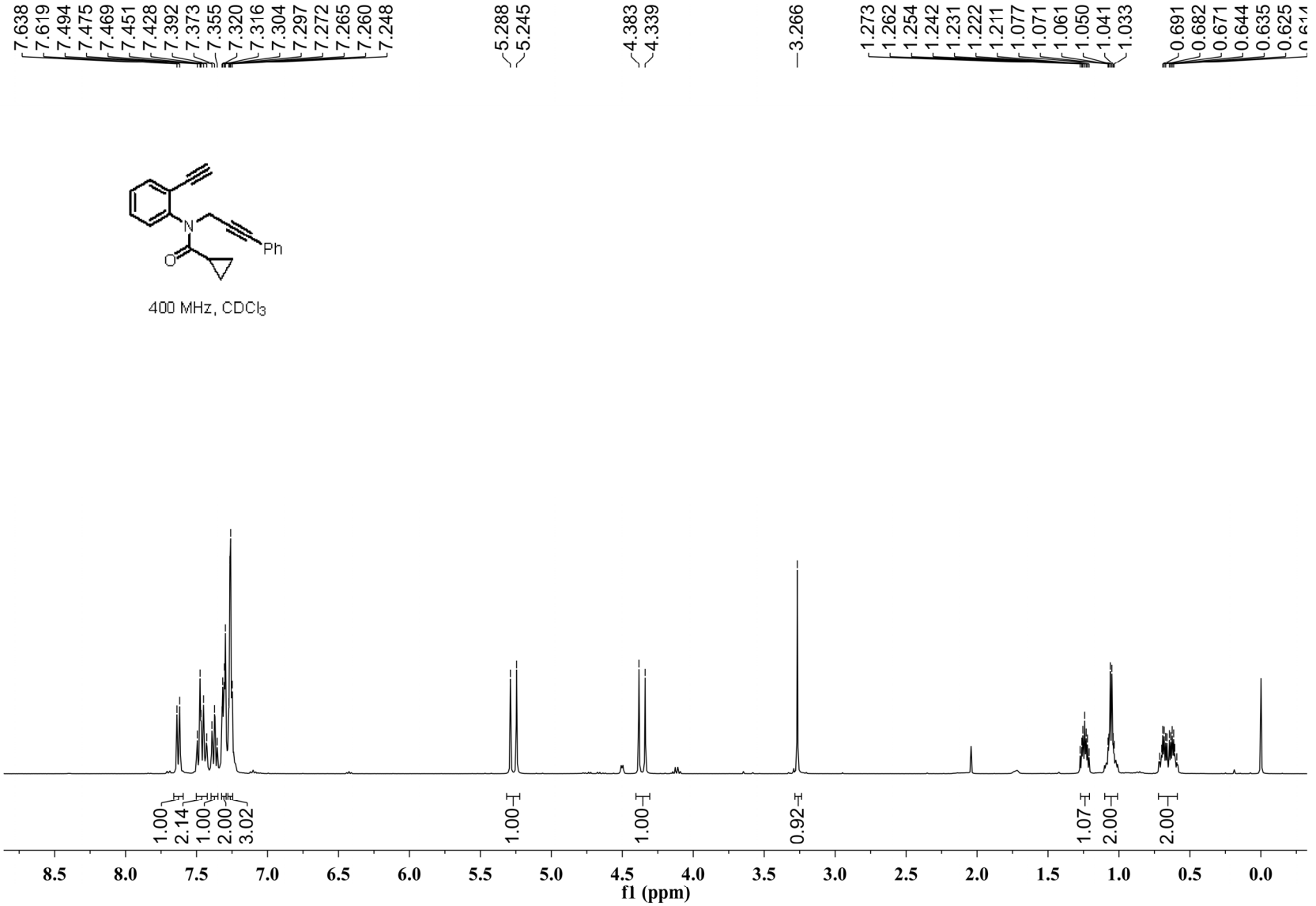
^{13}C NMR Spectrum of Compound 1aa



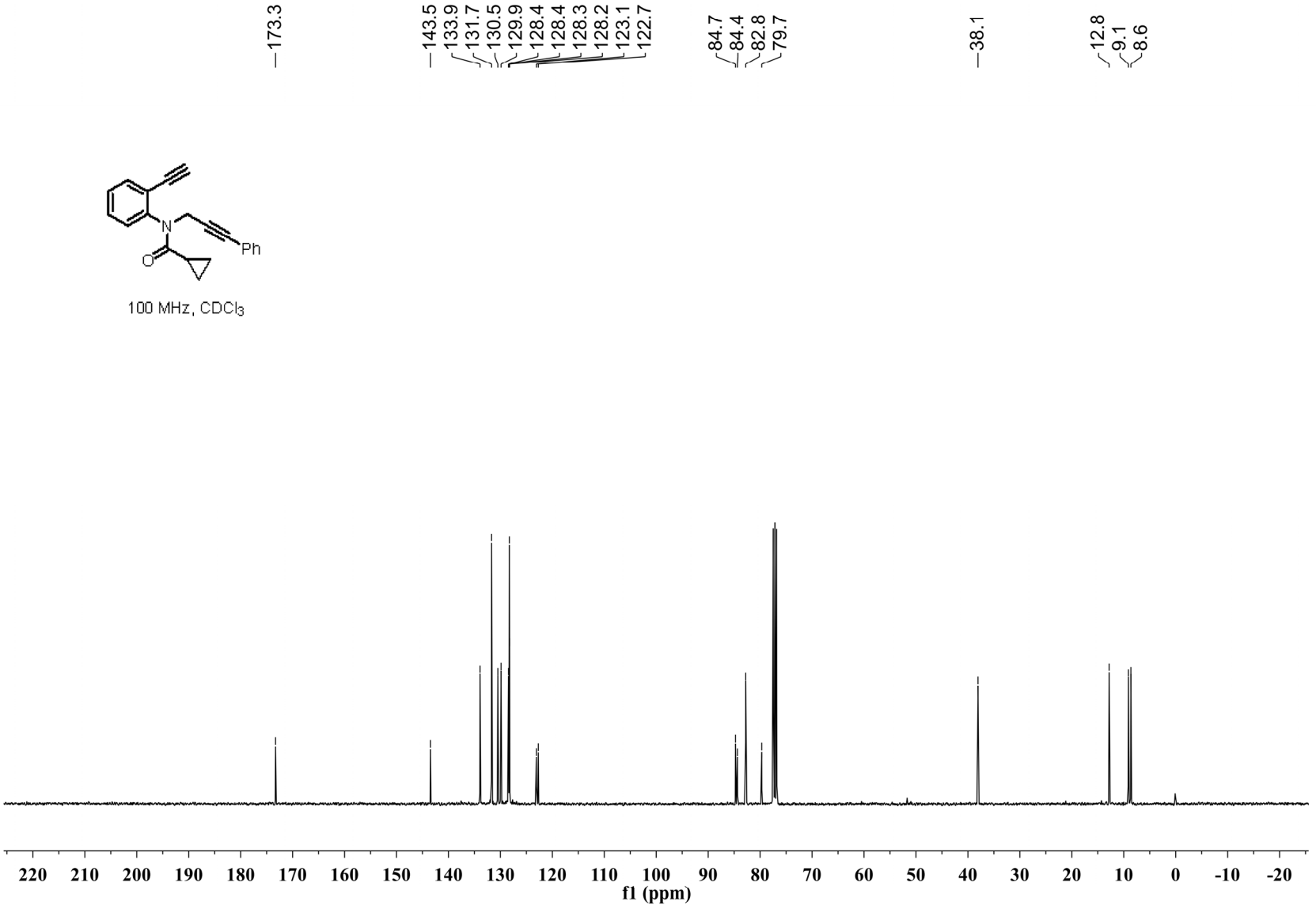
^{1}H NMR Spectrum of Compound 1bb



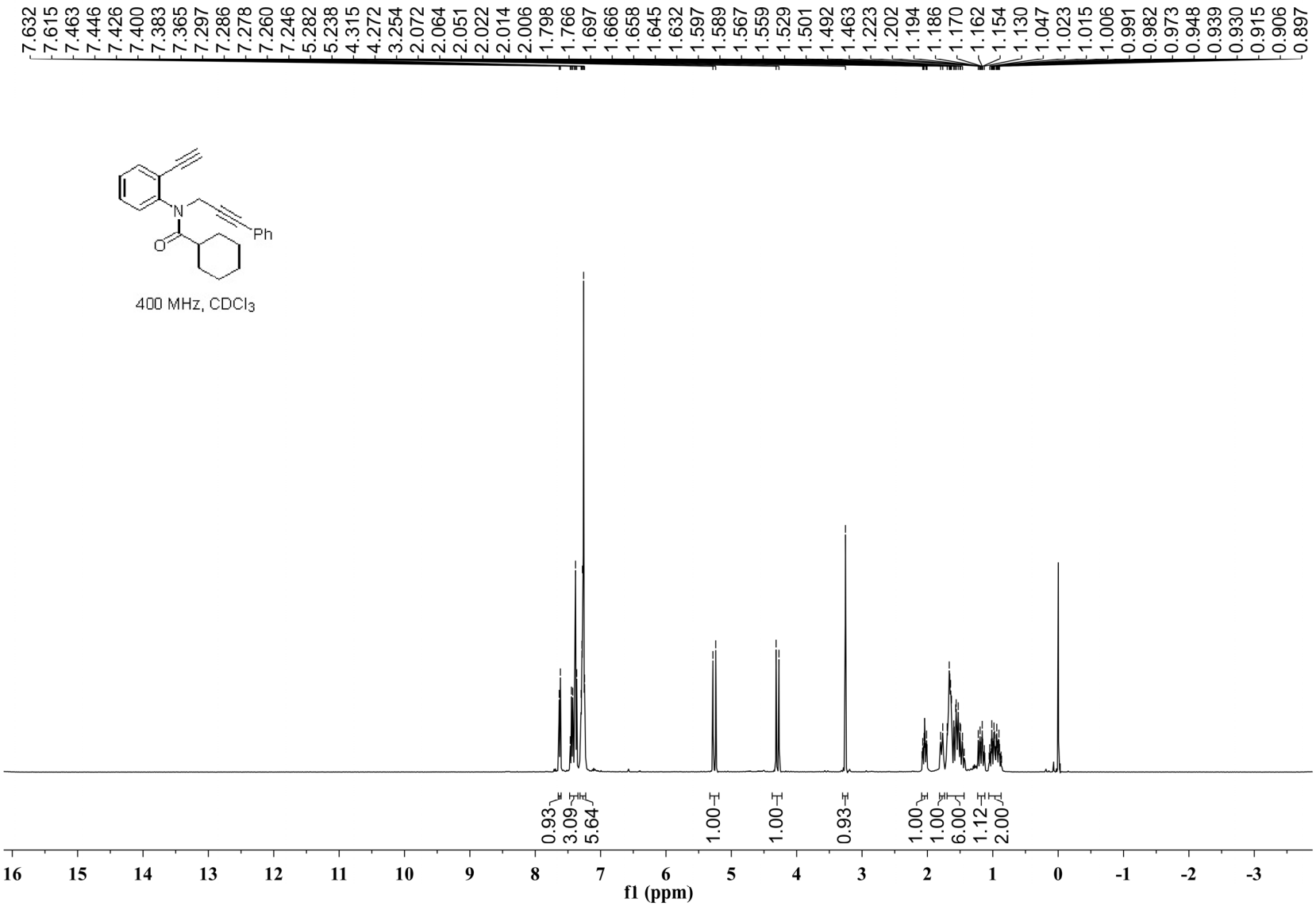
^{13}C NMR Spectrum of Compound 1bb



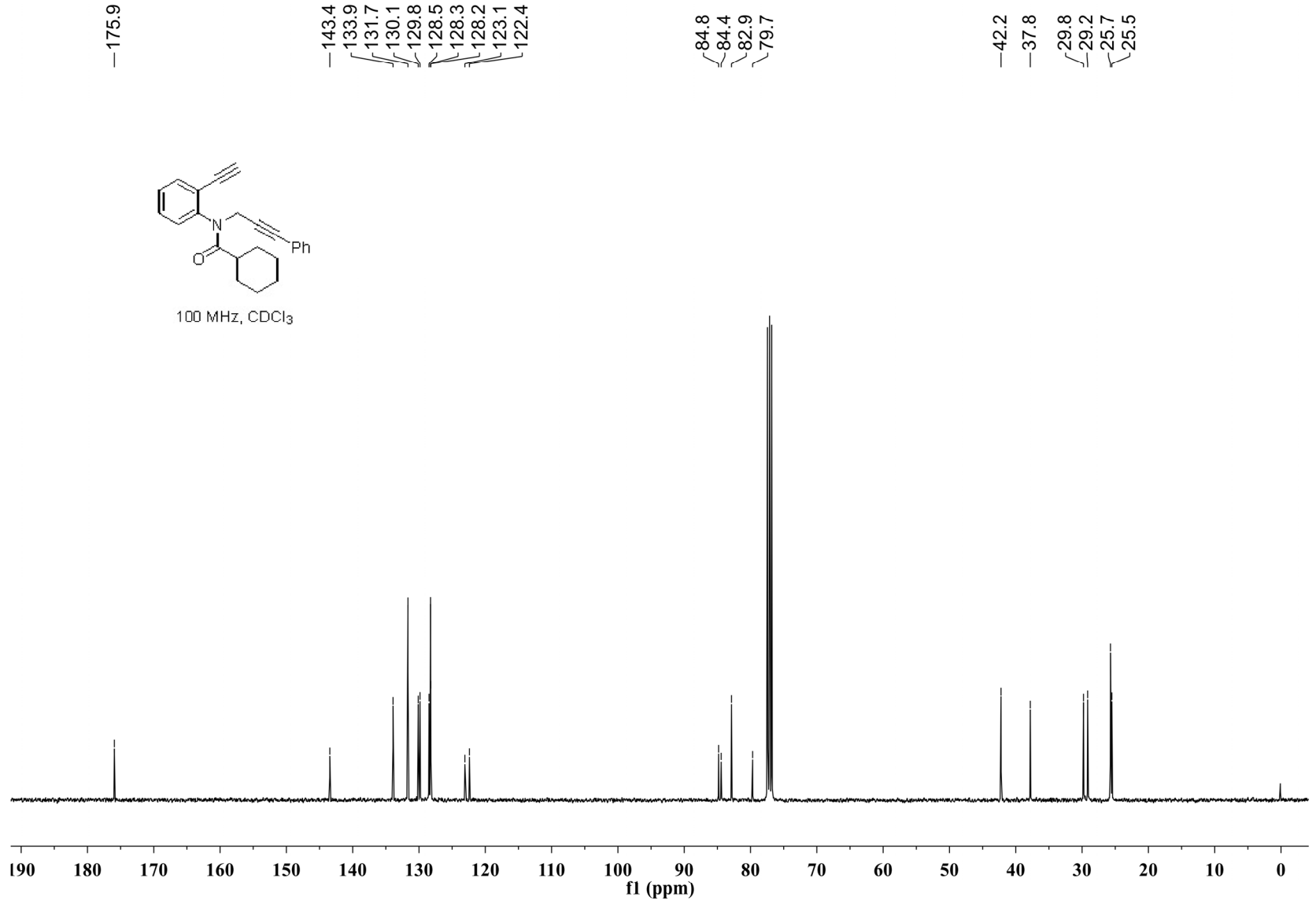
^{1}H NMR Spectrum of Compound 1cc



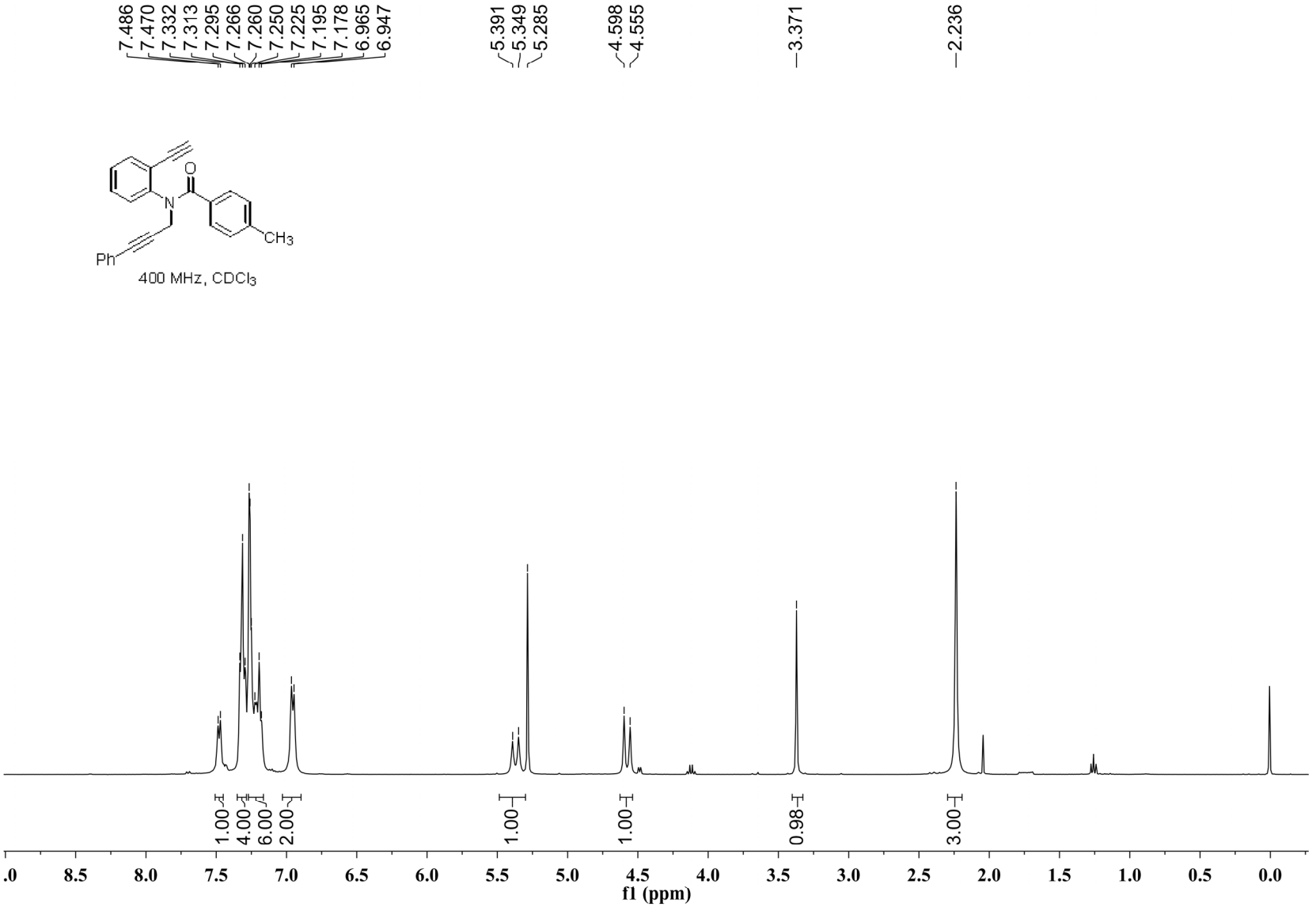
^{13}C NMR Spectrum of Compound 1cc



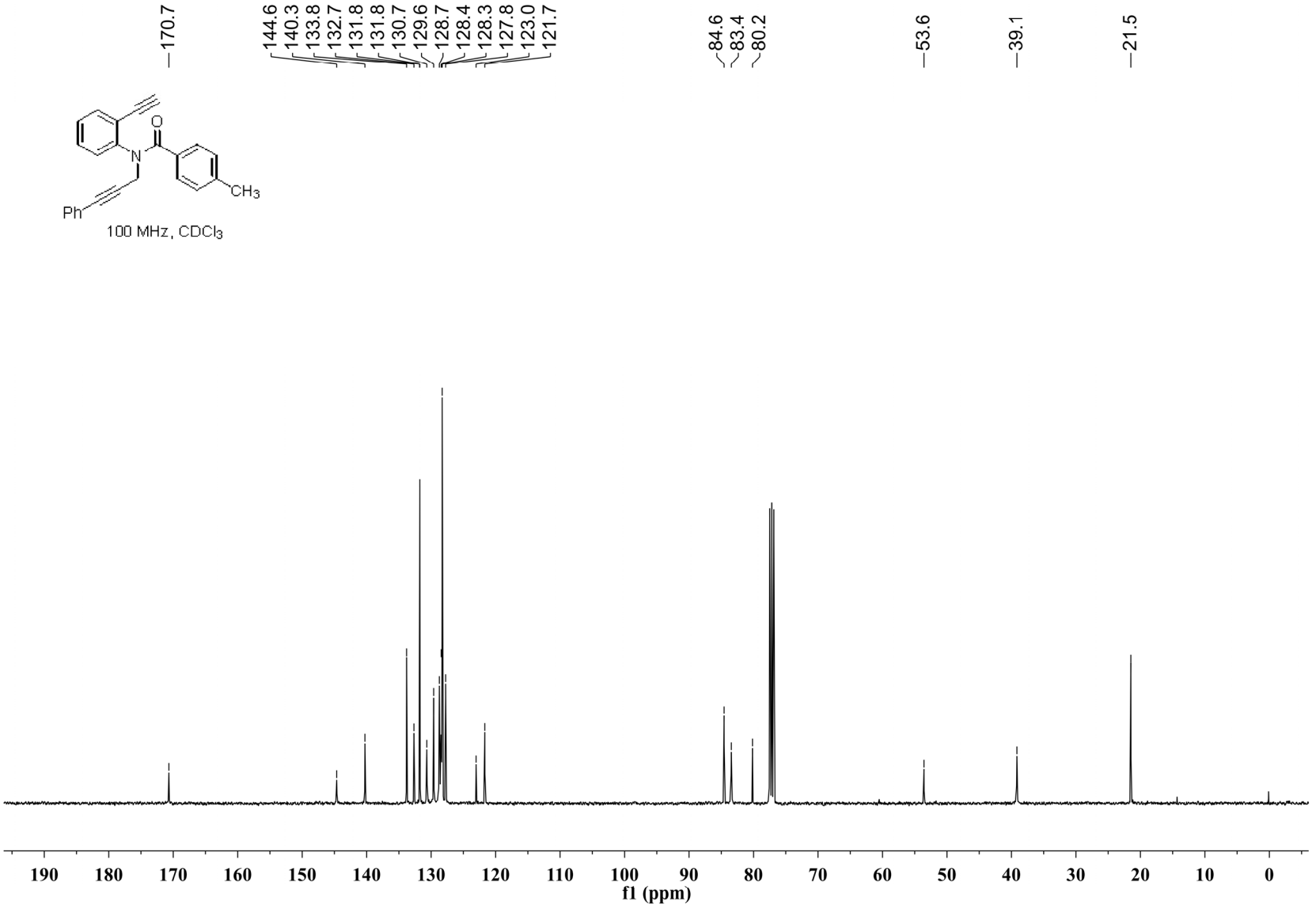
^{1}H NMR Spectrum of Compound 1dd



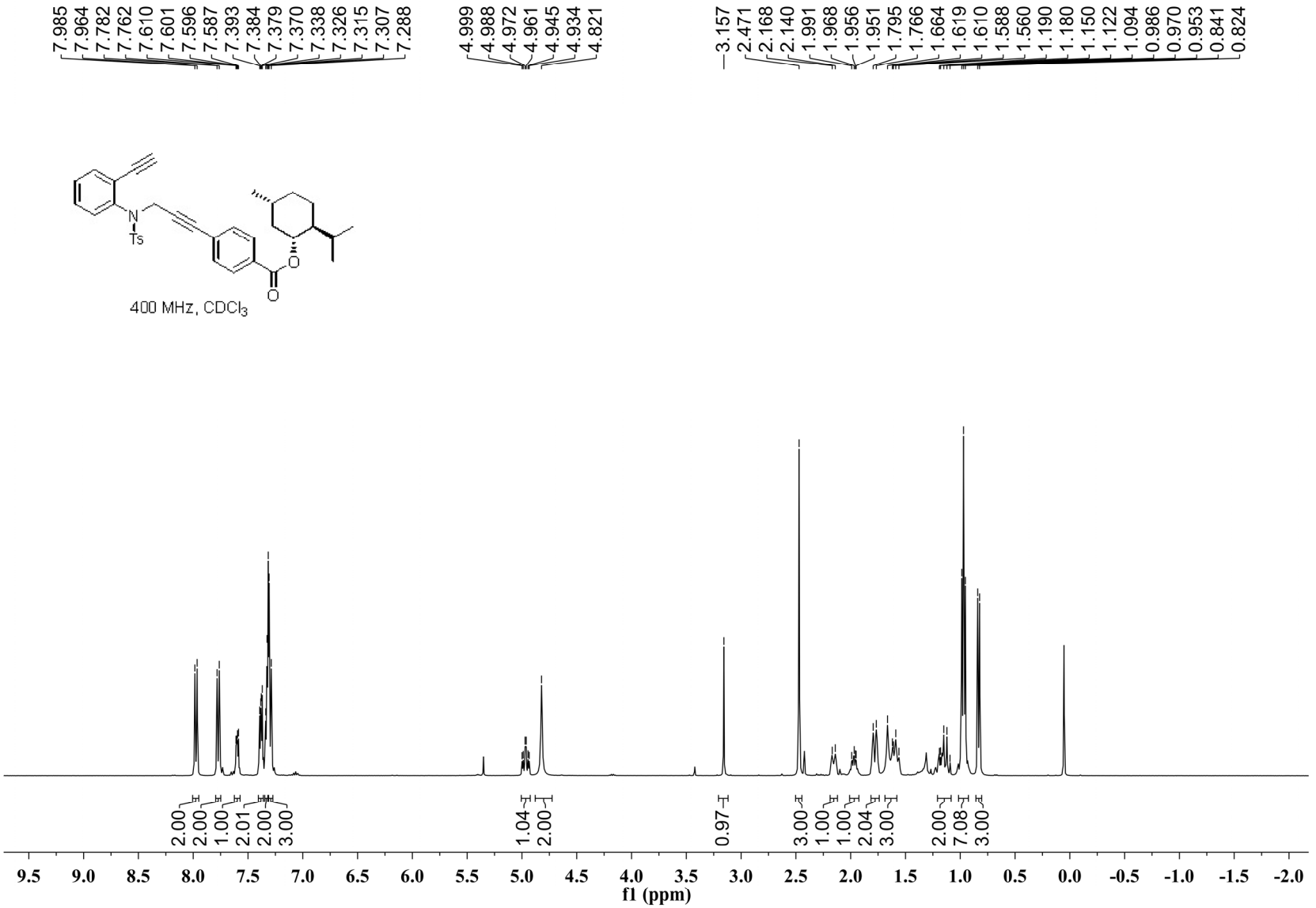
^{13}C NMR Spectrum of Compound 1dd



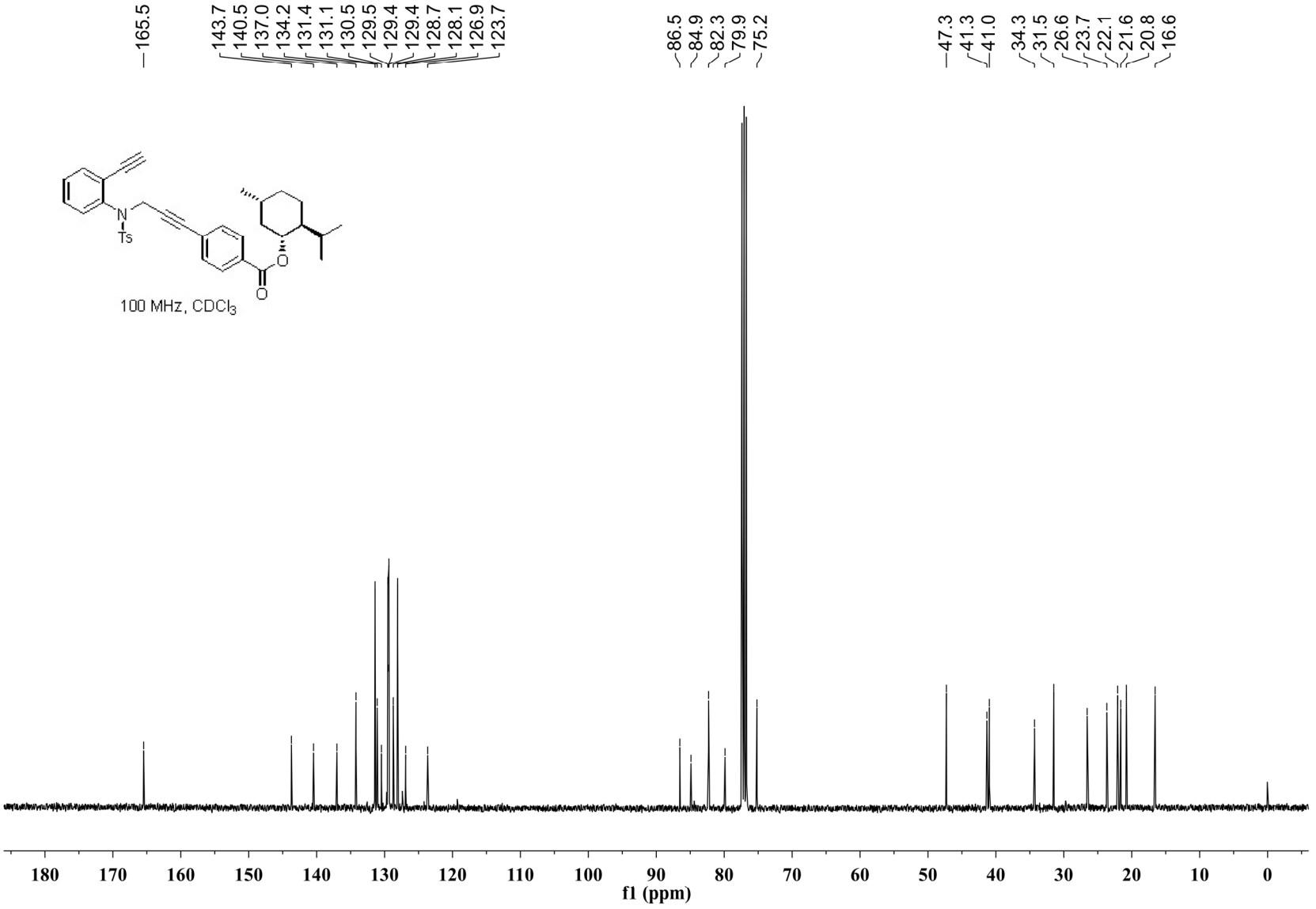
^{1}H NMR Spectrum of Compound 1ee



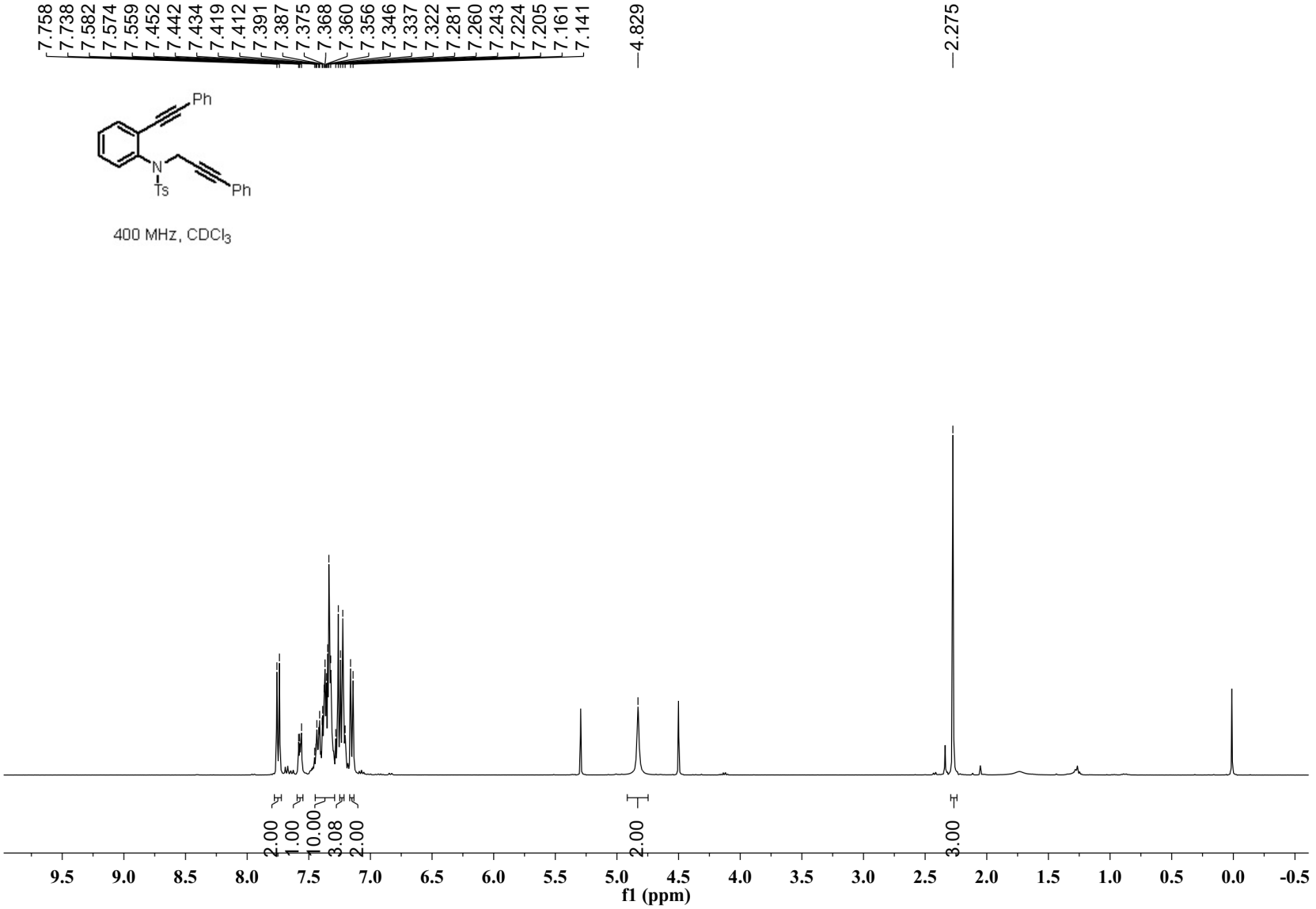
^{13}C NMR Spectrum of Compound 1ee



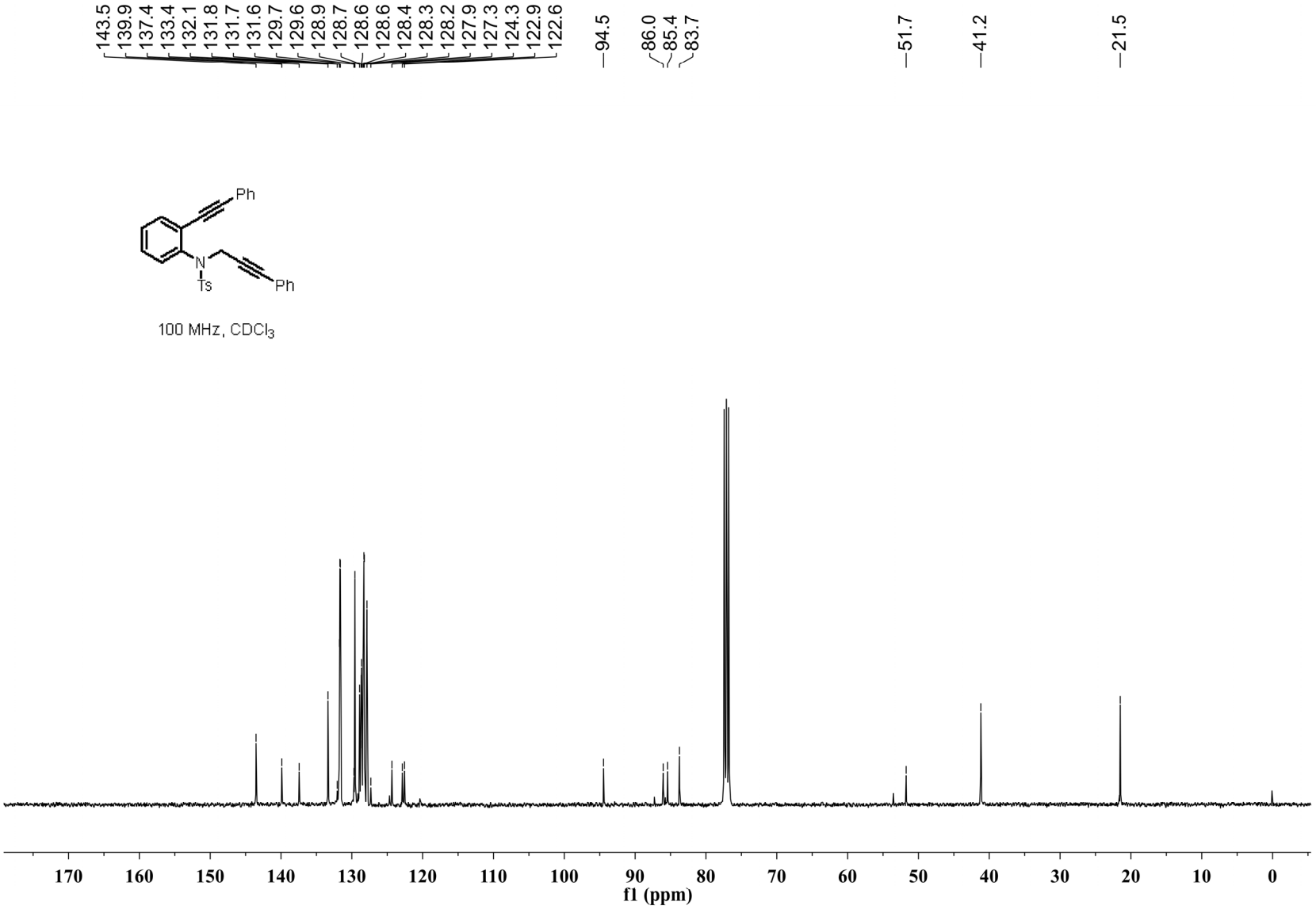
^{1}H NMR Spectrum of Compound 1ff



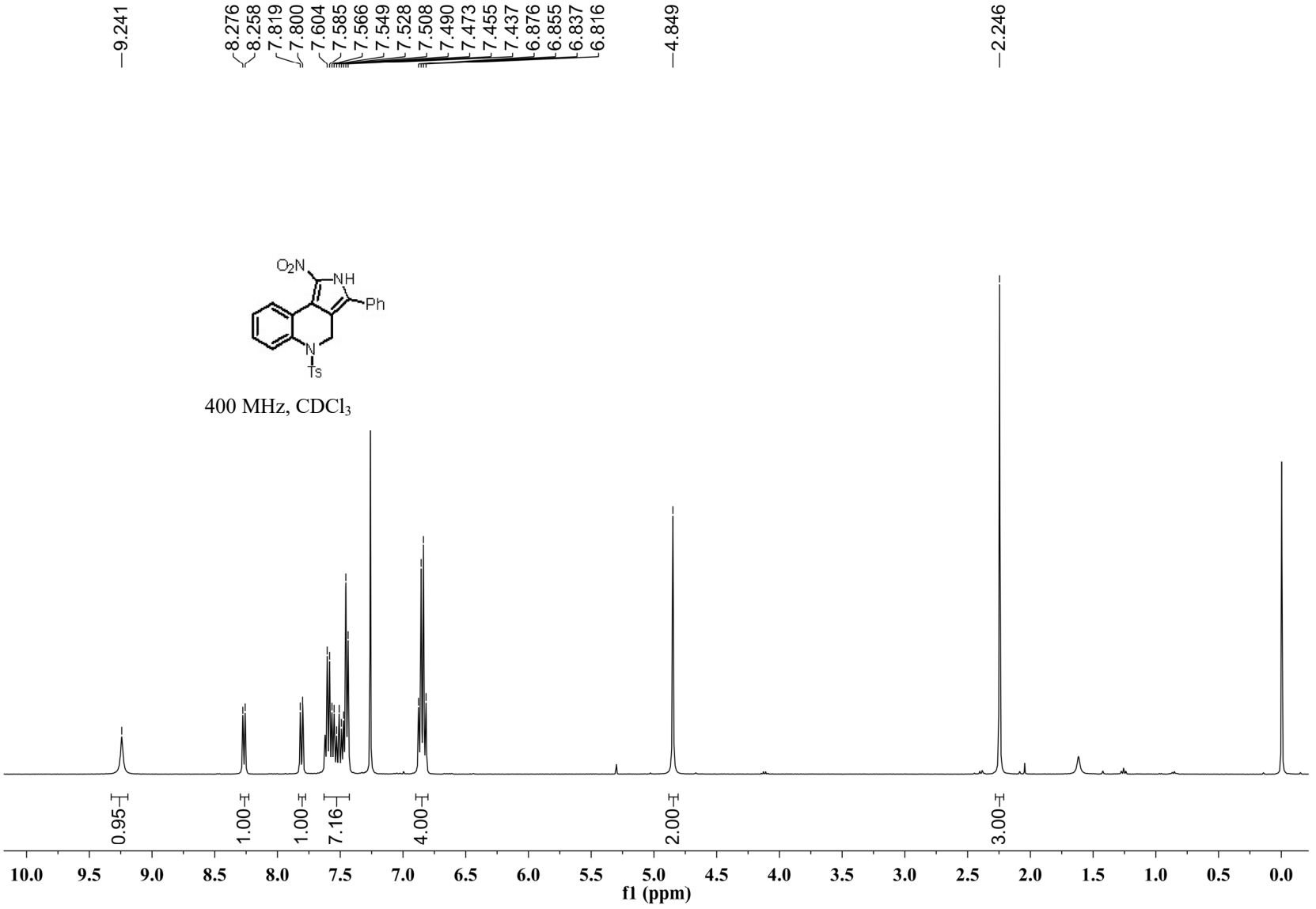
^{13}C NMR Spectrum of Compound 1ff



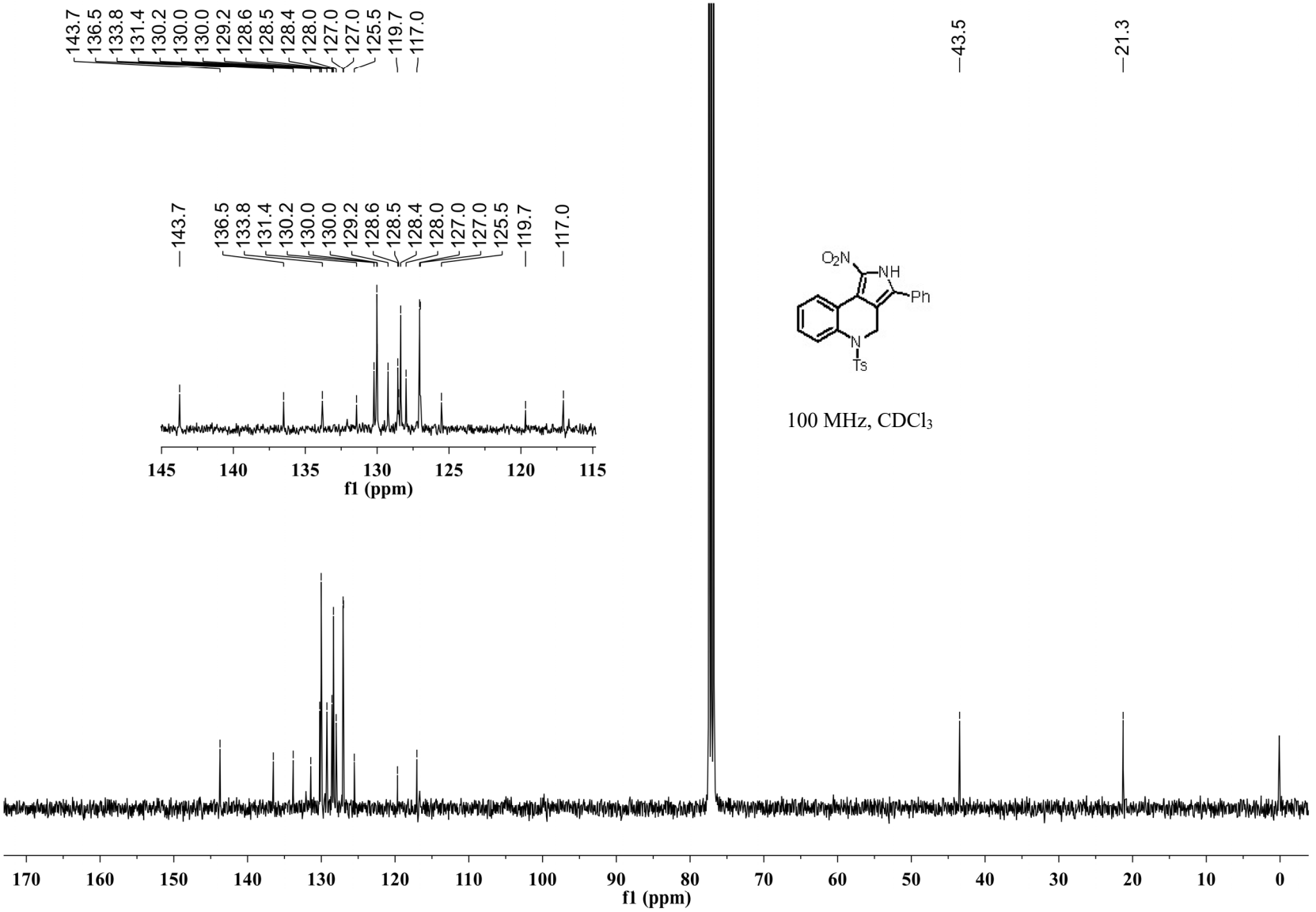
^{1}H NMR Spectrum of Compound 1gg



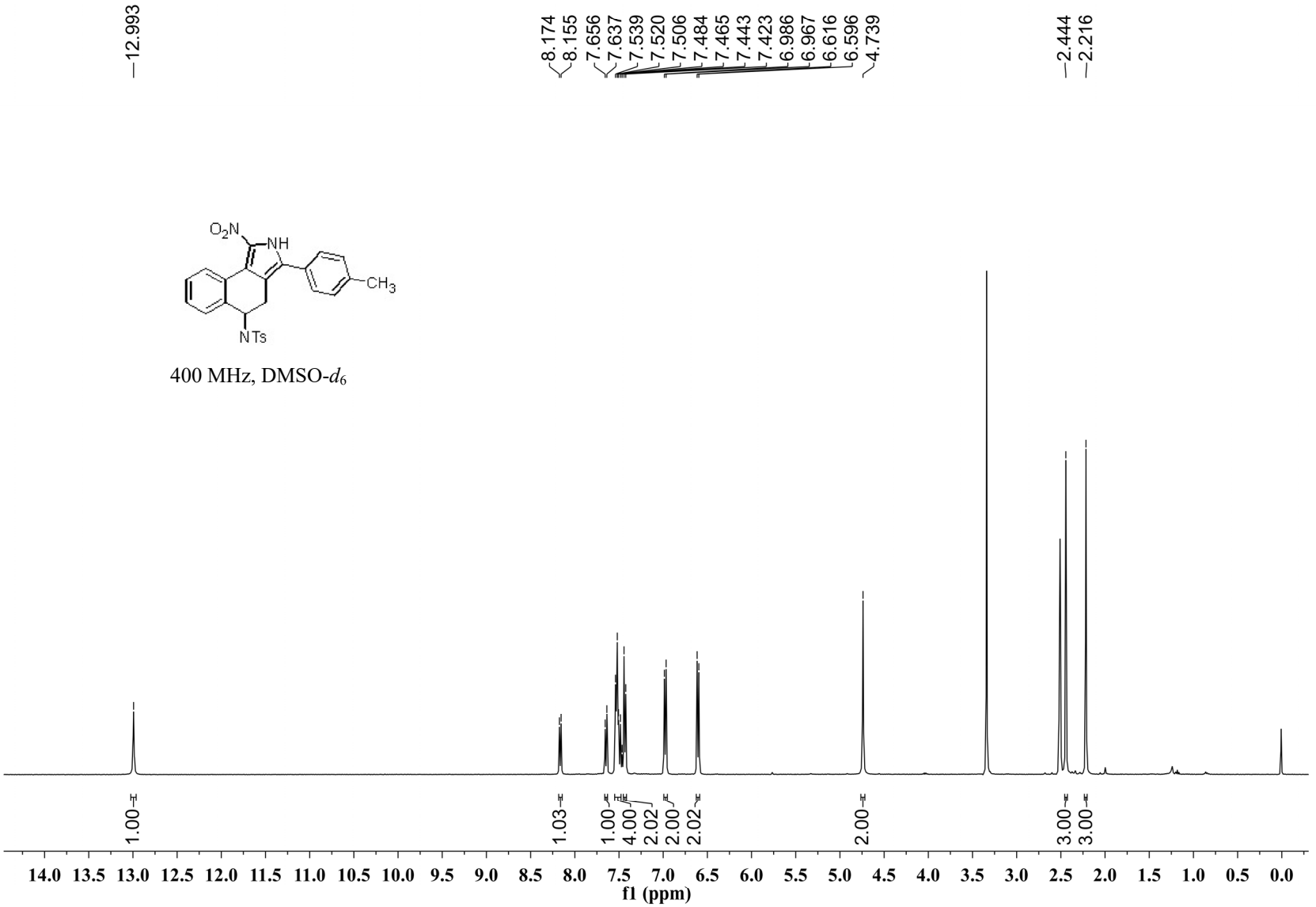
^{13}C NMR Spectrum of Compound 1gg



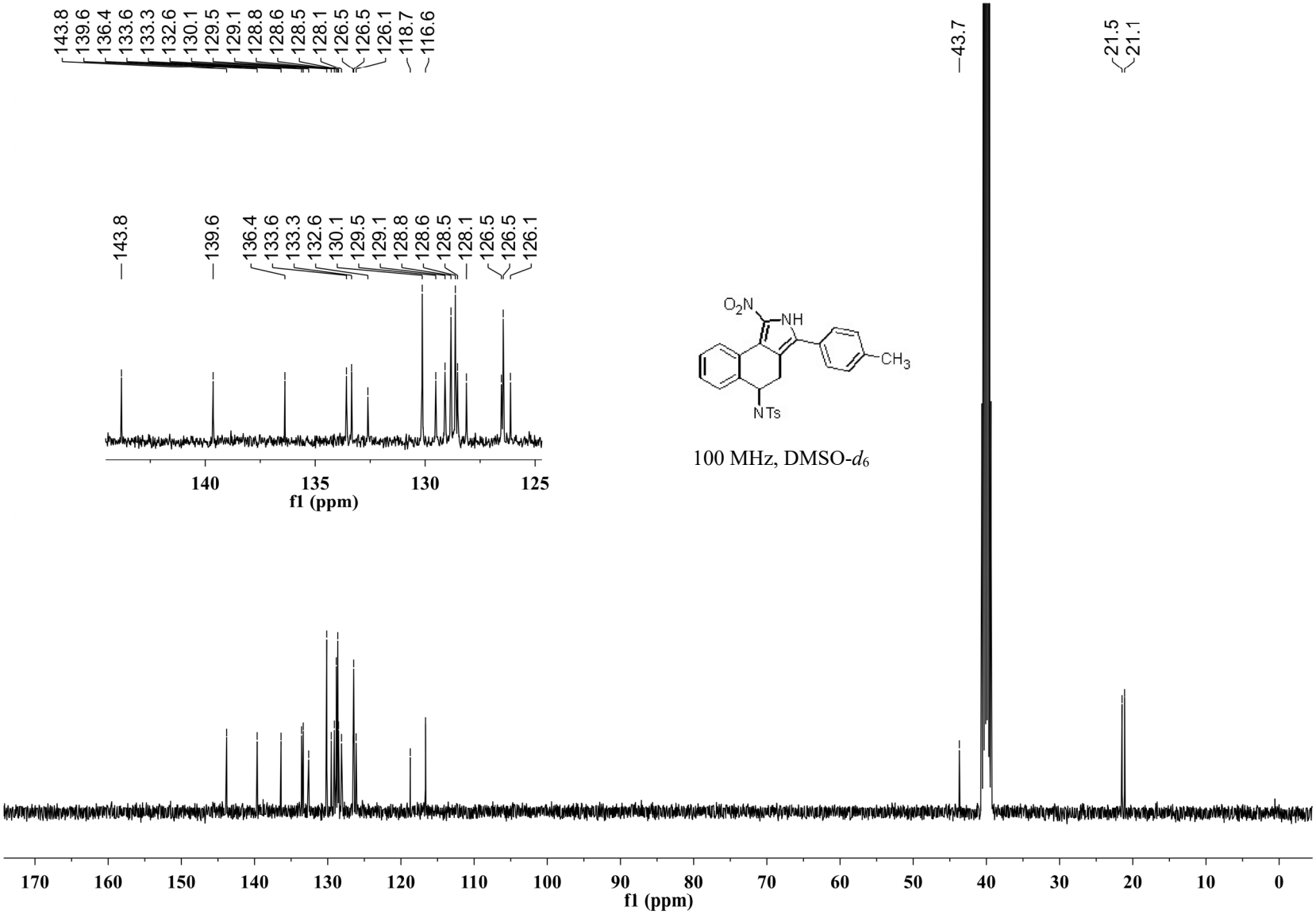
^{1}H NMR Spectrum of Compound 3a



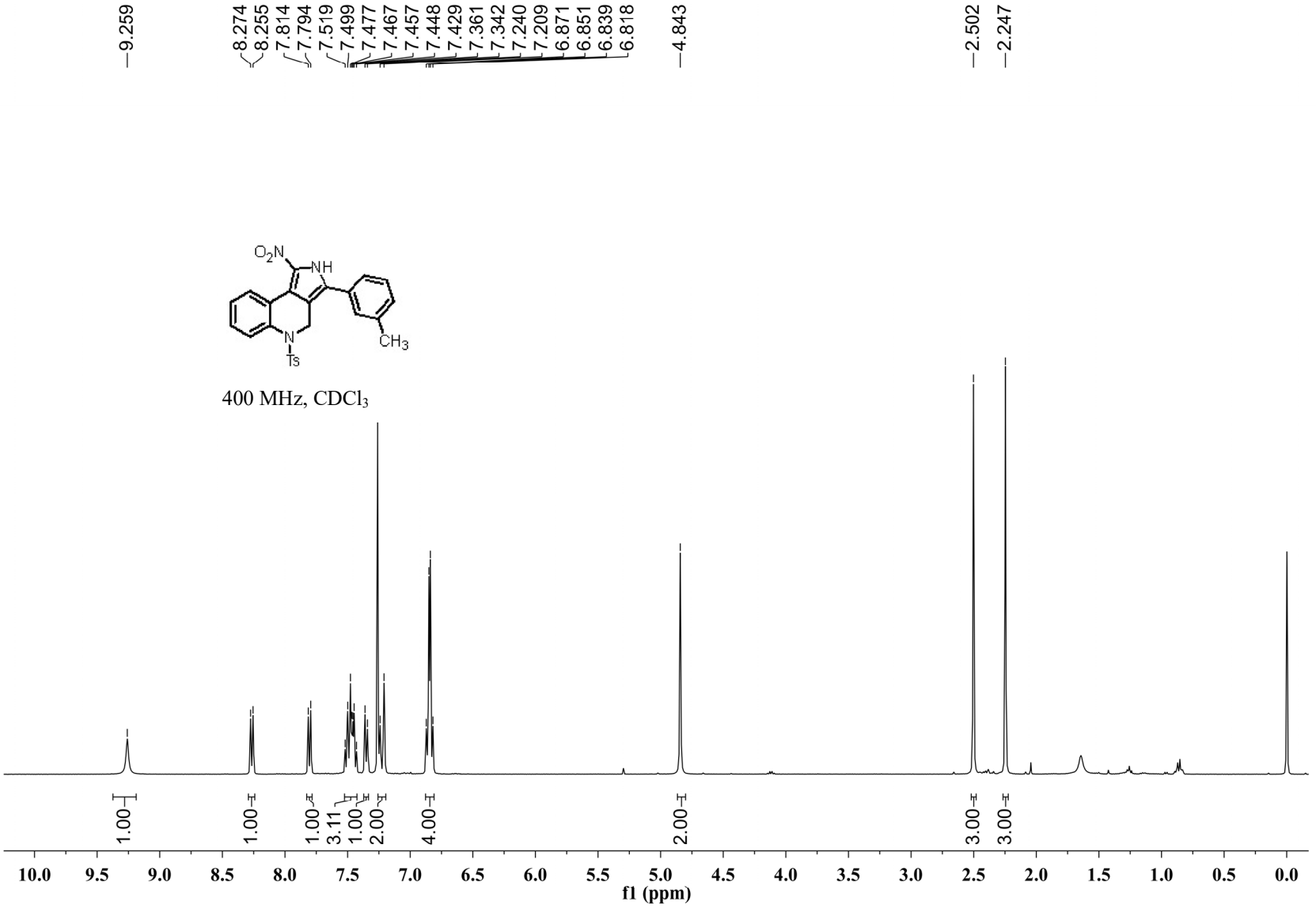
^{1}H NMR Spectrum of Compound 3a



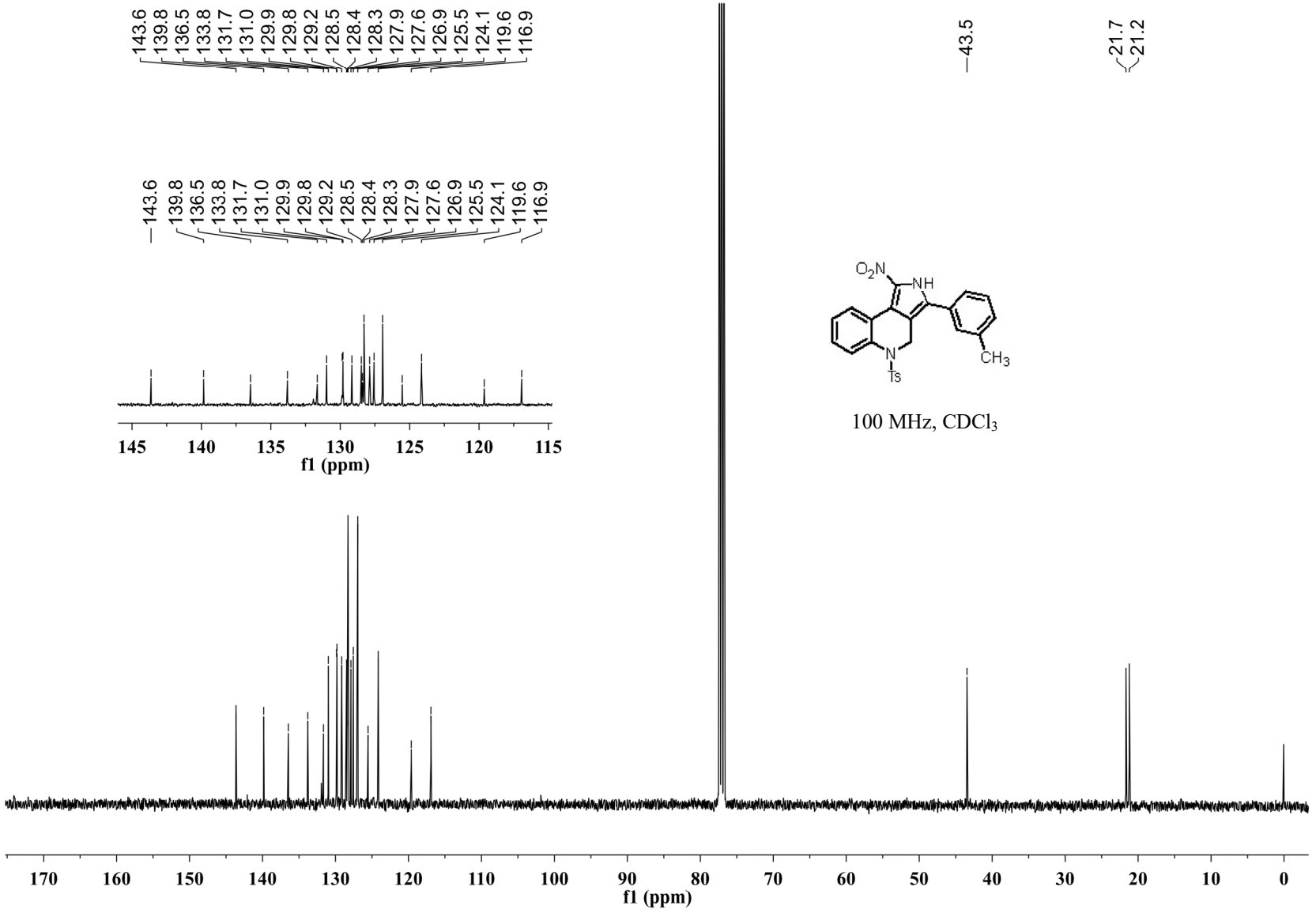
^{1}H NMR Spectrum of Compound 3b



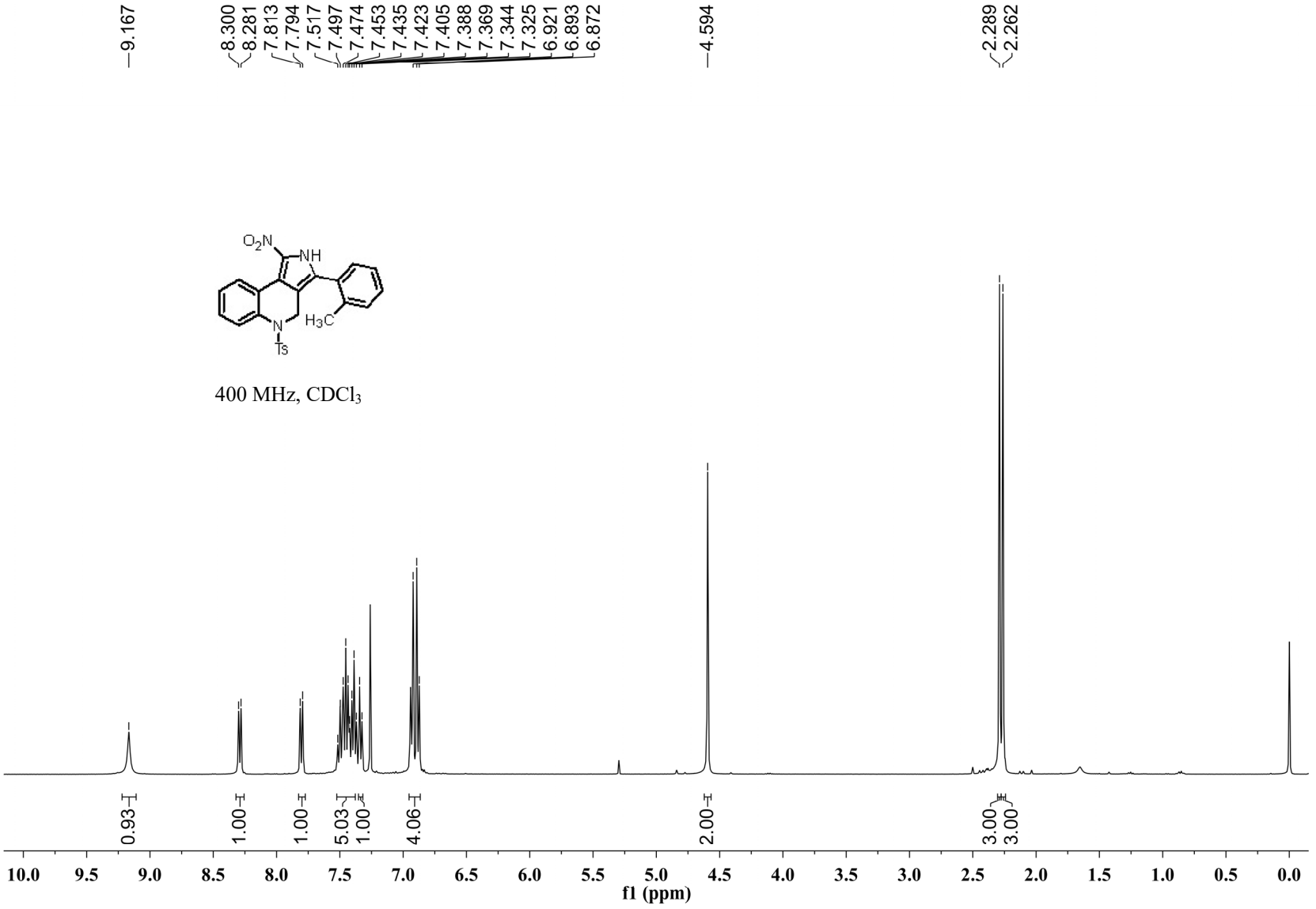
^{13}C NMR Spectrum of Compound 3b



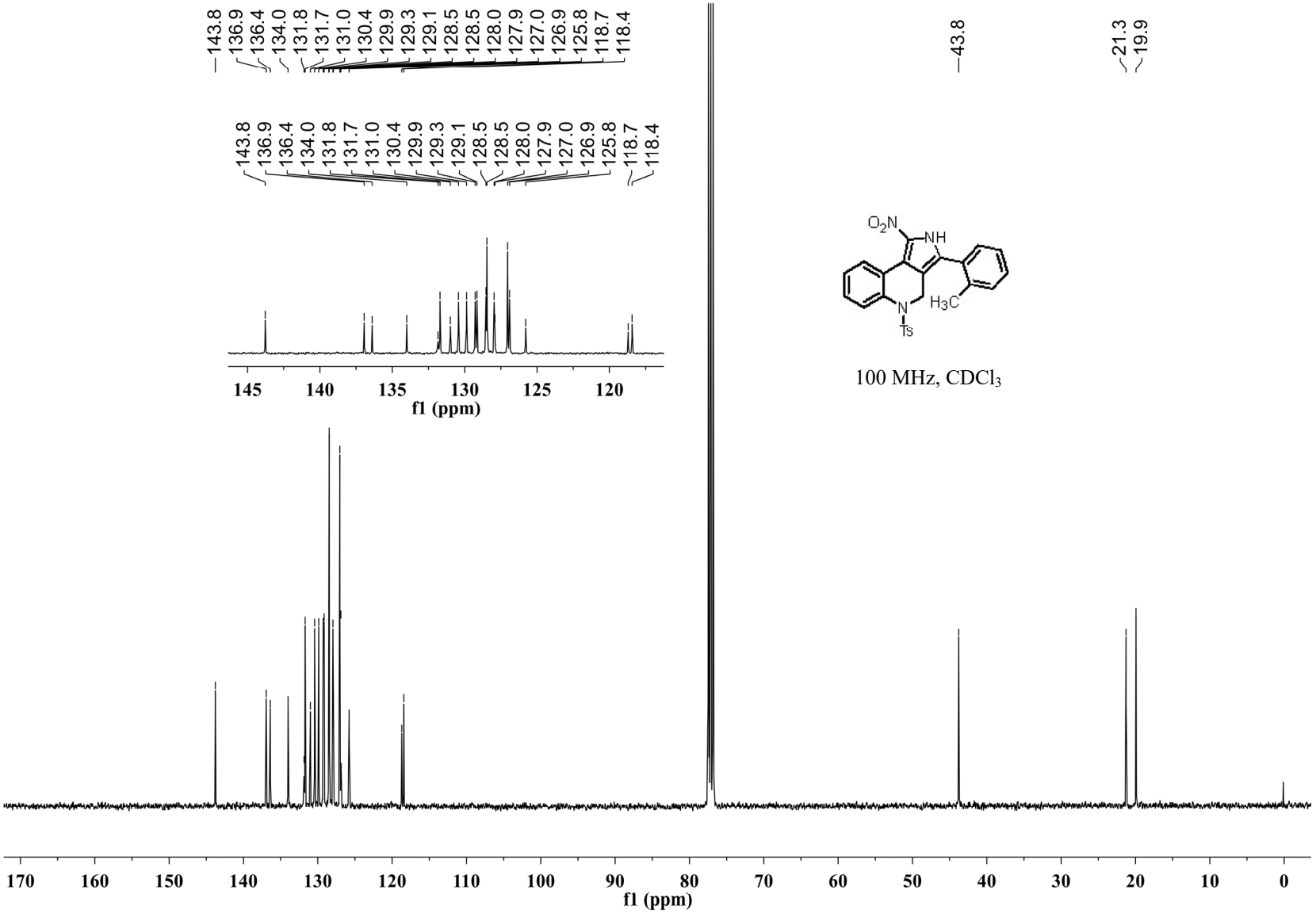
^{1}H NMR Spectrum of Compound 3c



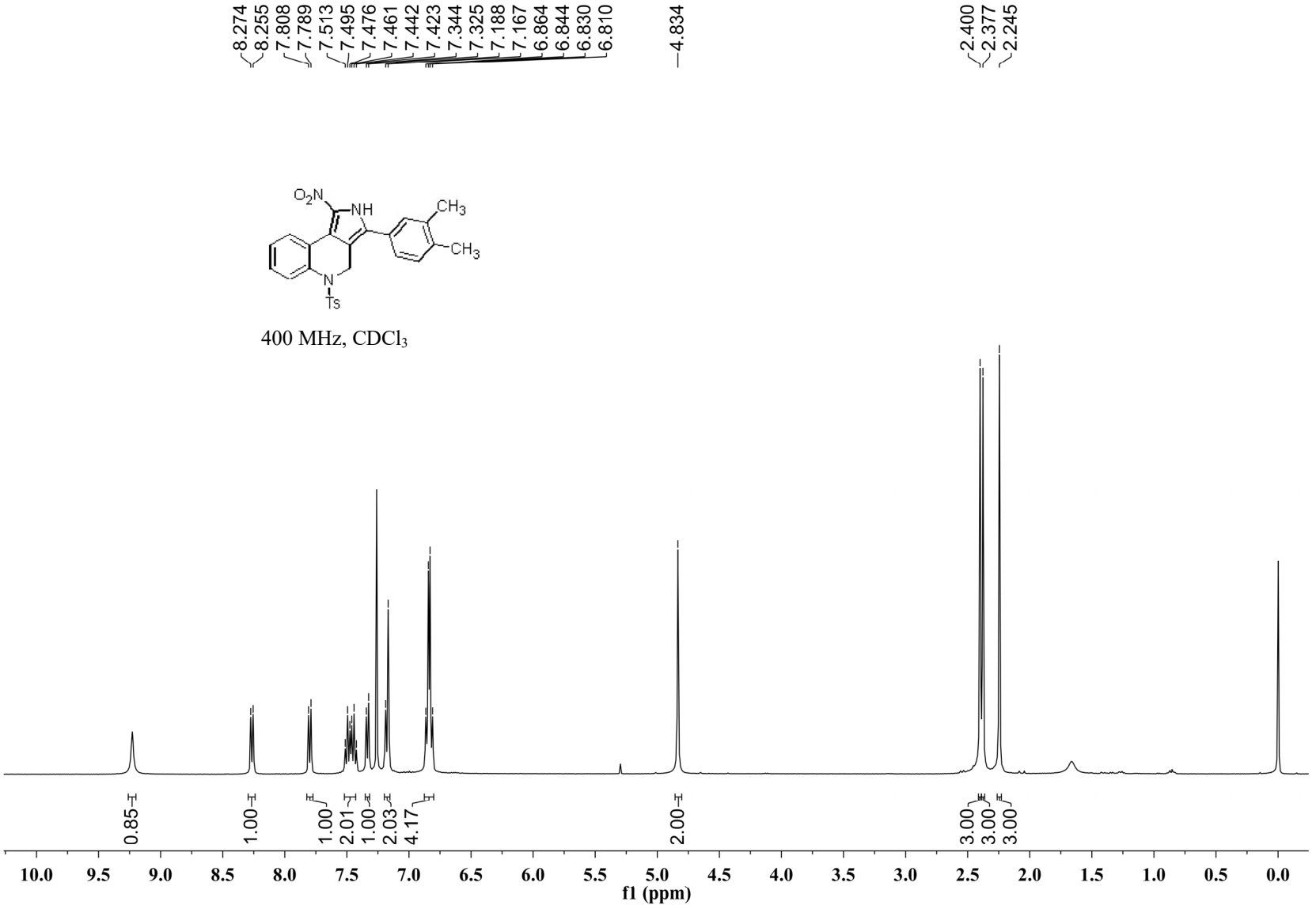
^{13}C NMR Spectrum of Compound 3c



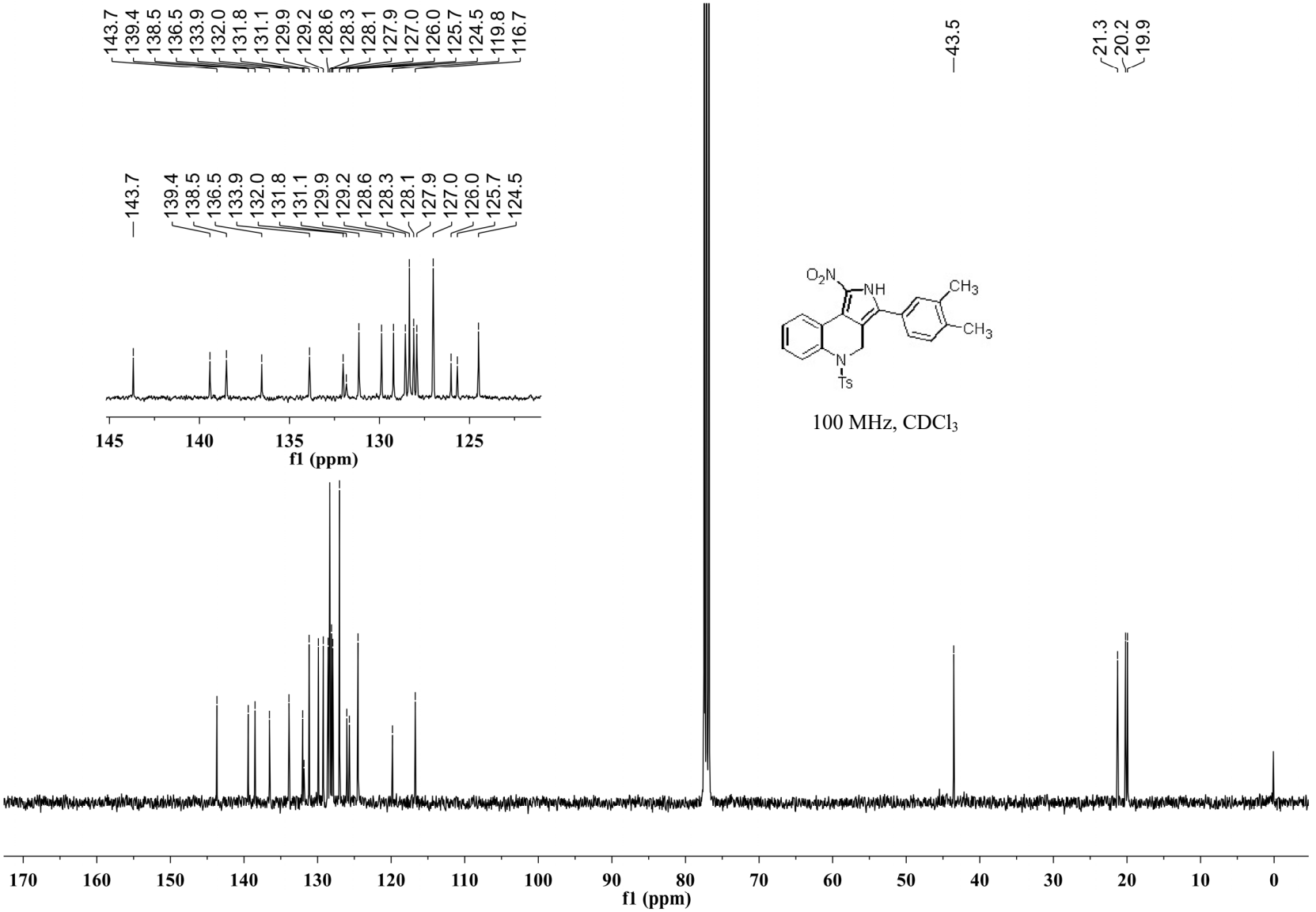
^{1}H NMR Spectrum of Compound 3d



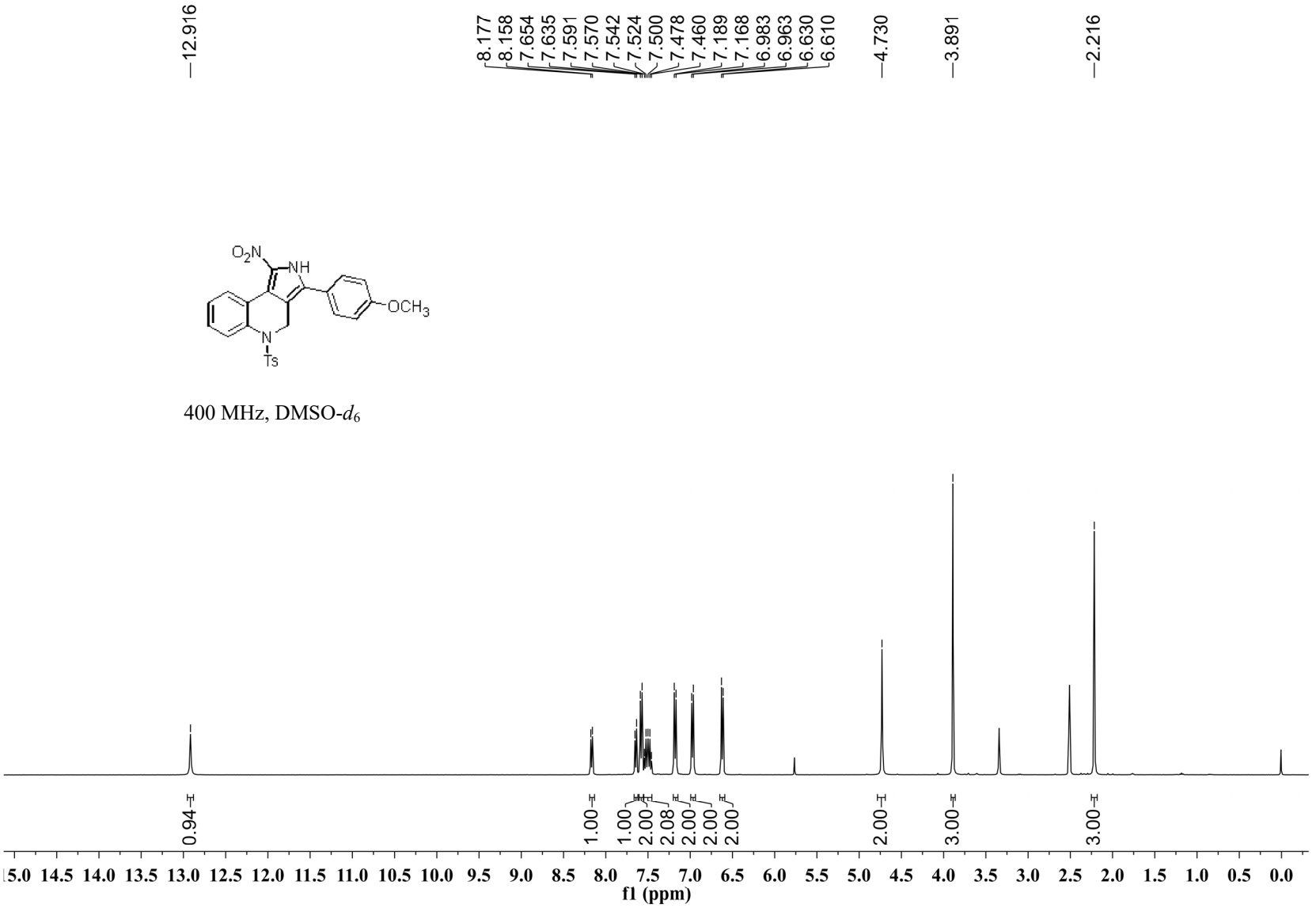
^{13}C NMR Spectrum of Compound 3d



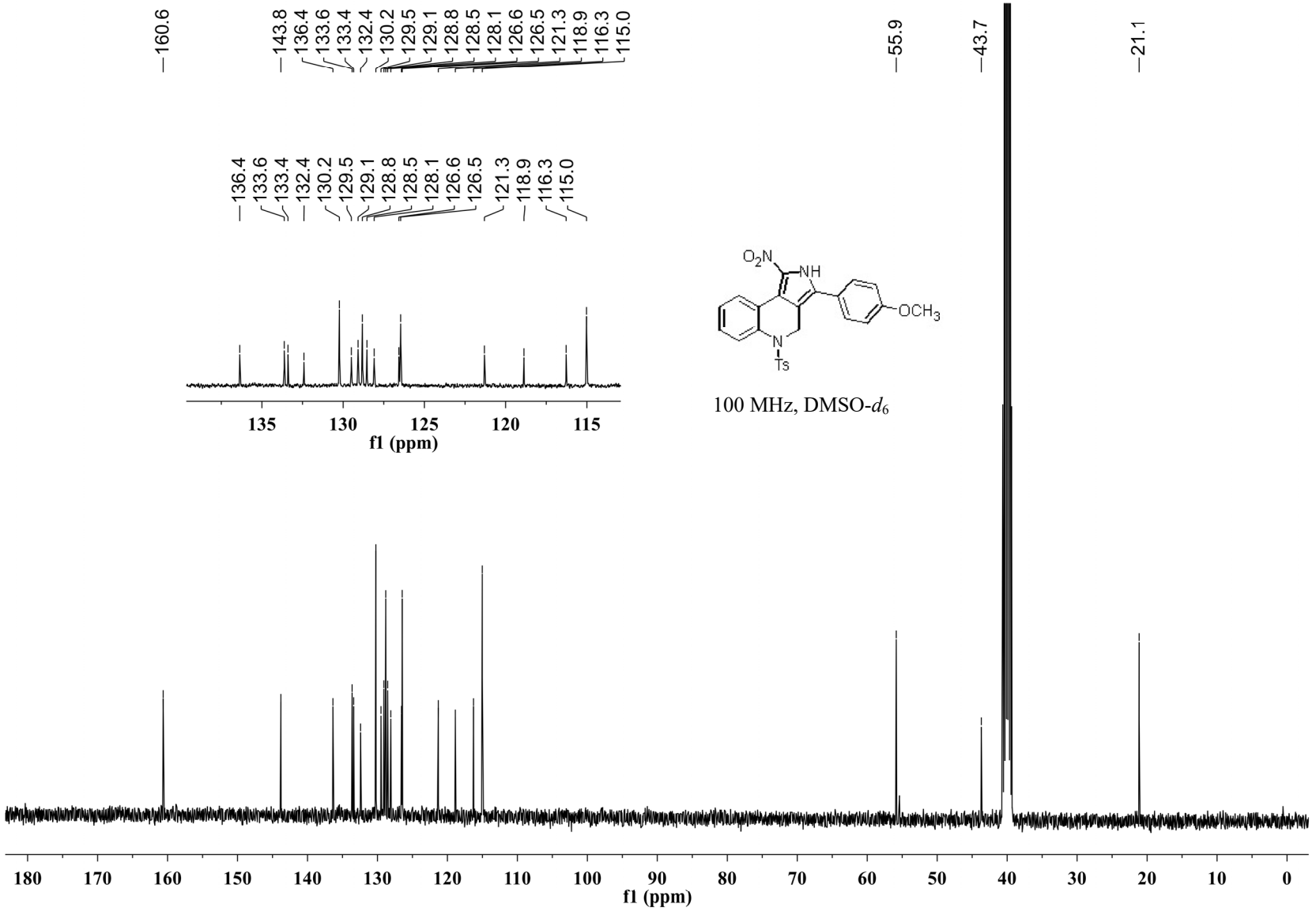
^{1}H NMR Spectrum of Compound 3e



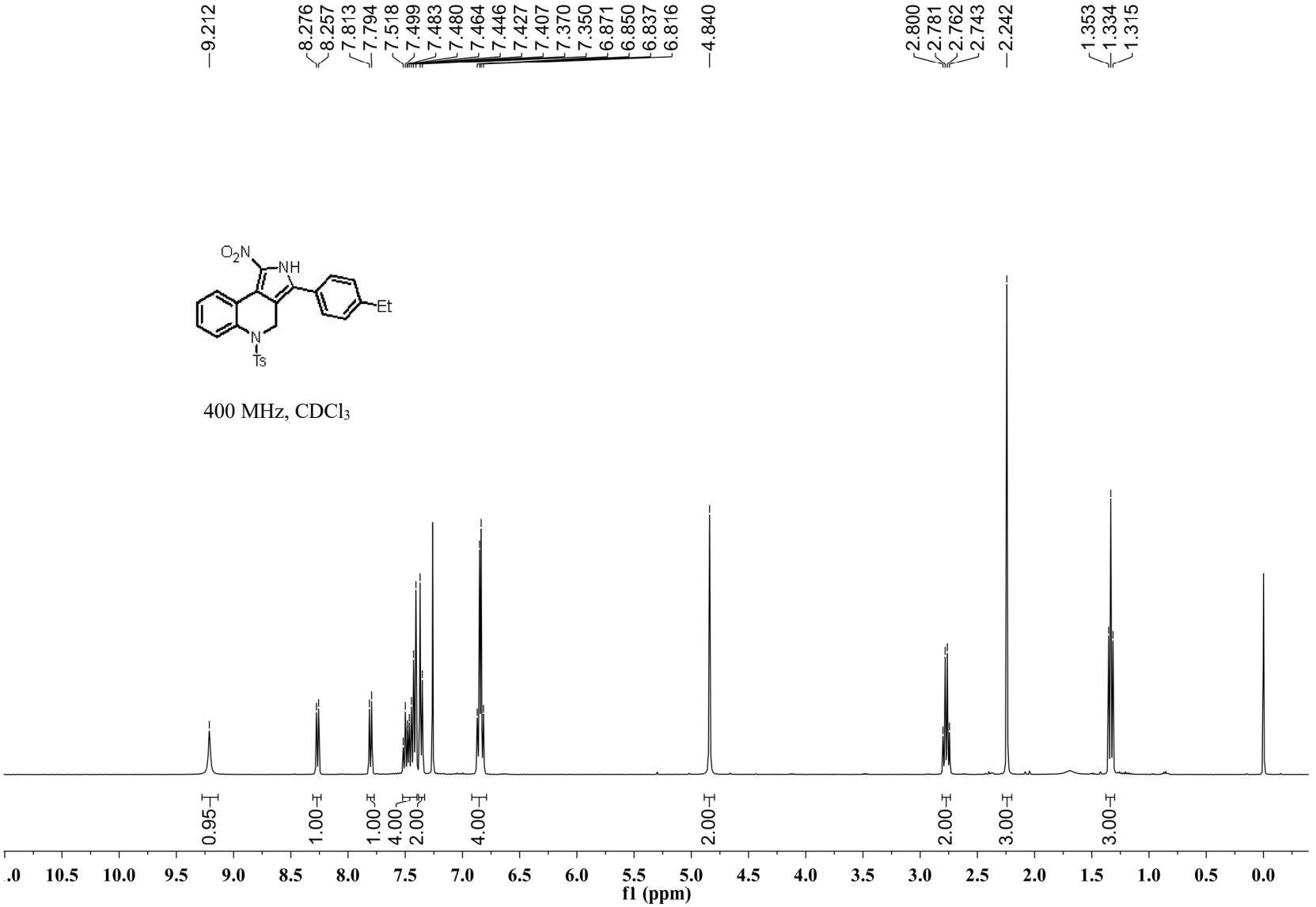
^{13}C NMR Spectrum of Compound 3e



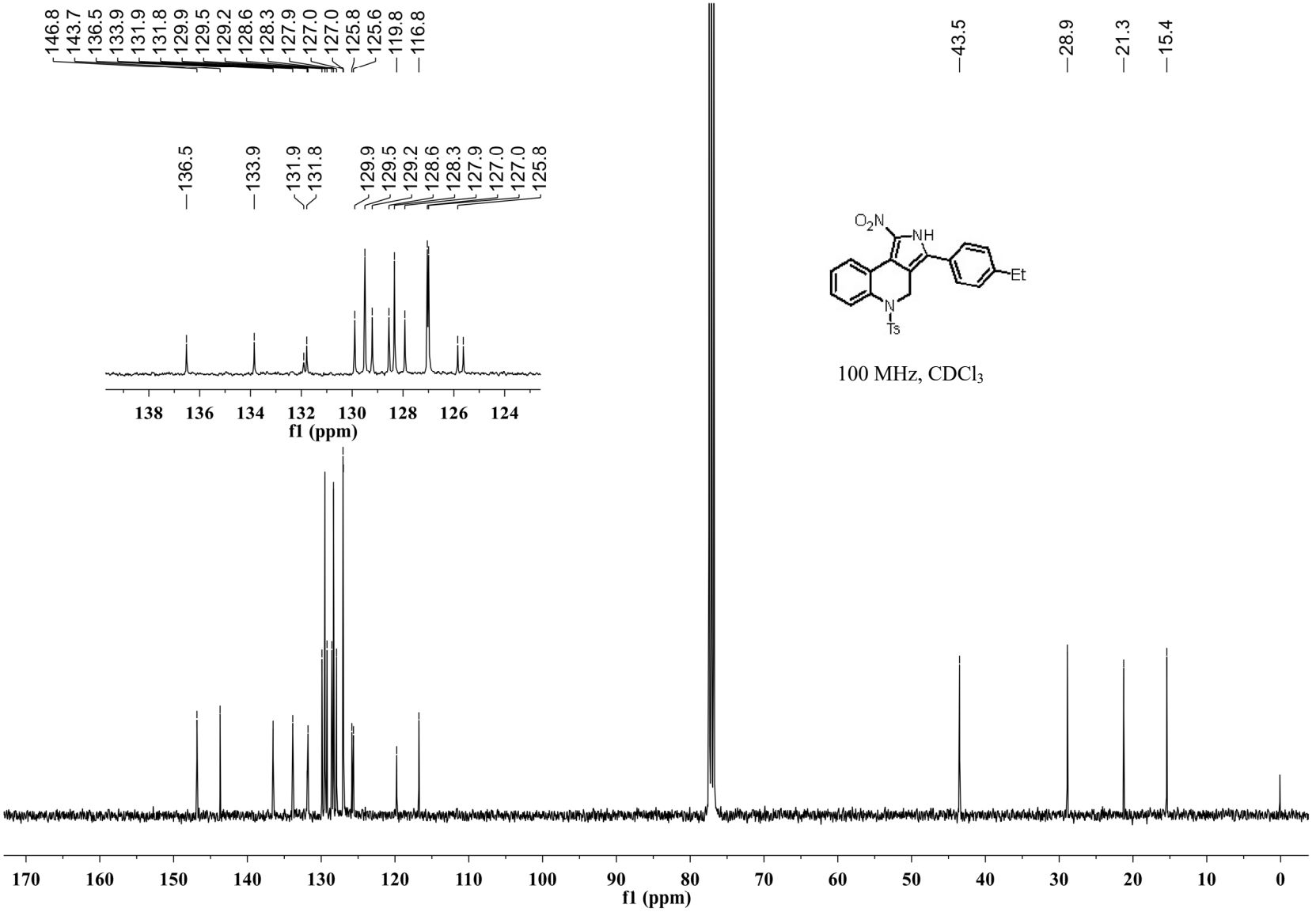
^{1}H NMR Spectrum of Compound 3f



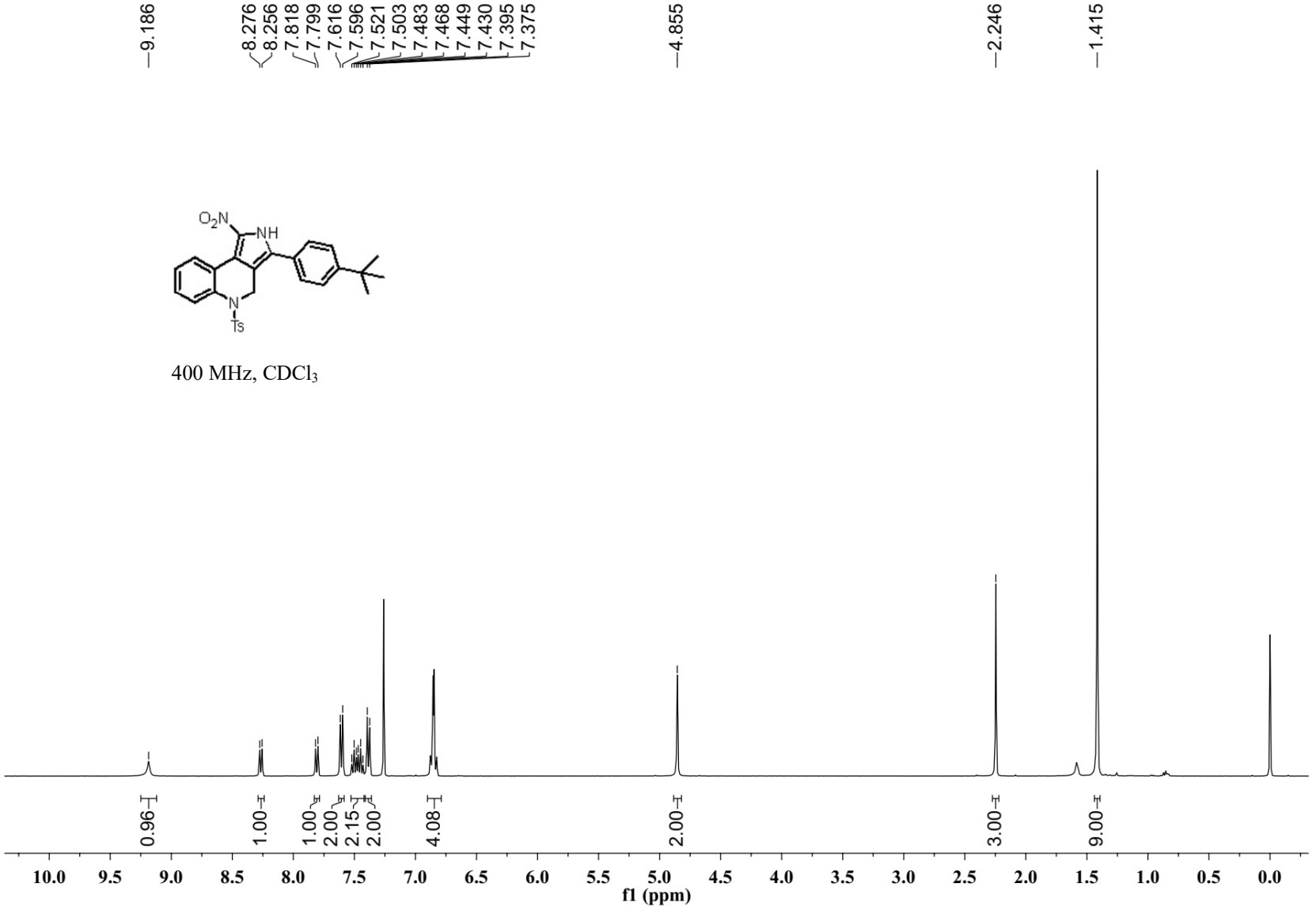
^{13}C NMR Spectrum of Compound 3f



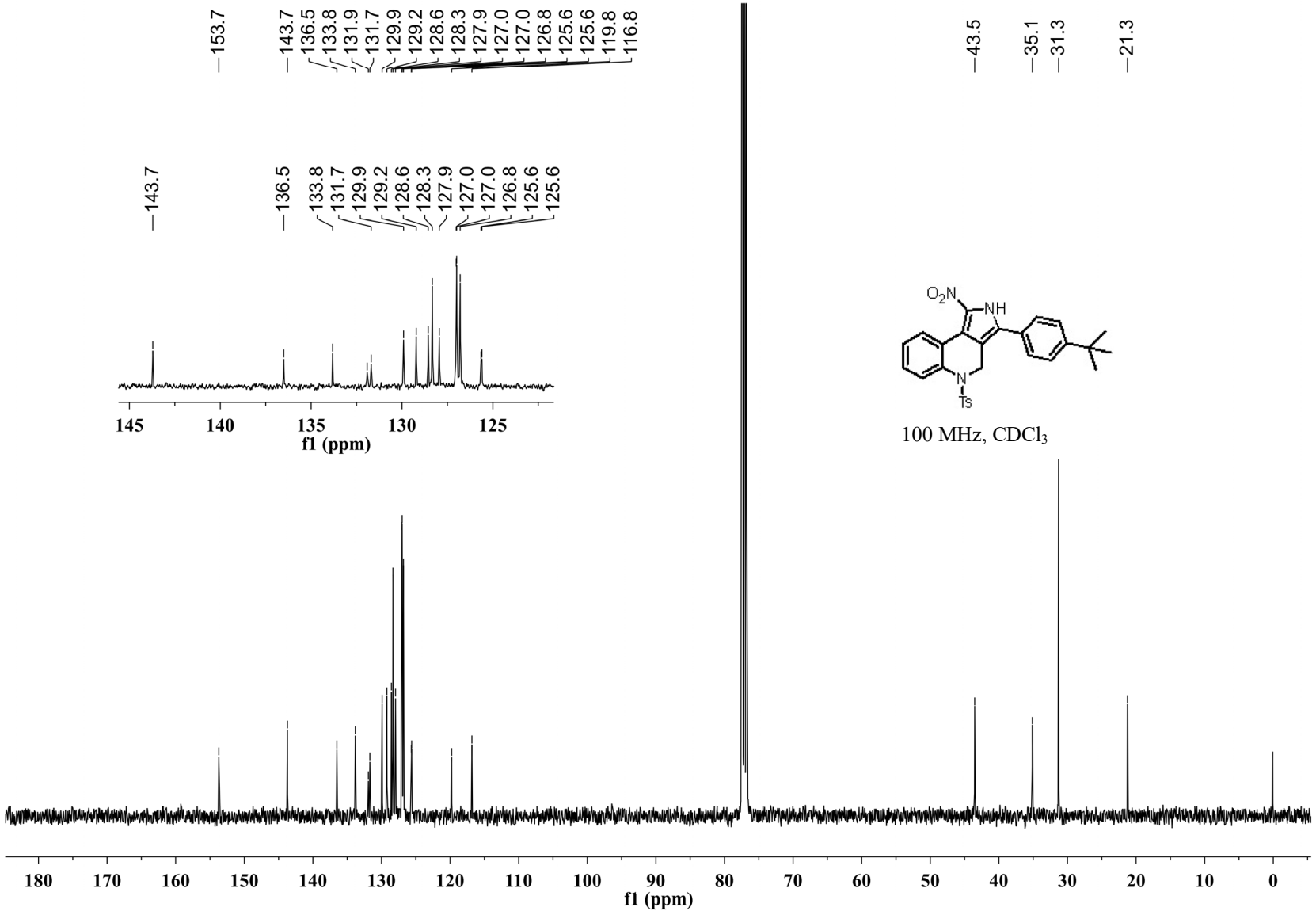
^{1}H NMR Spectrum of Compound 3g



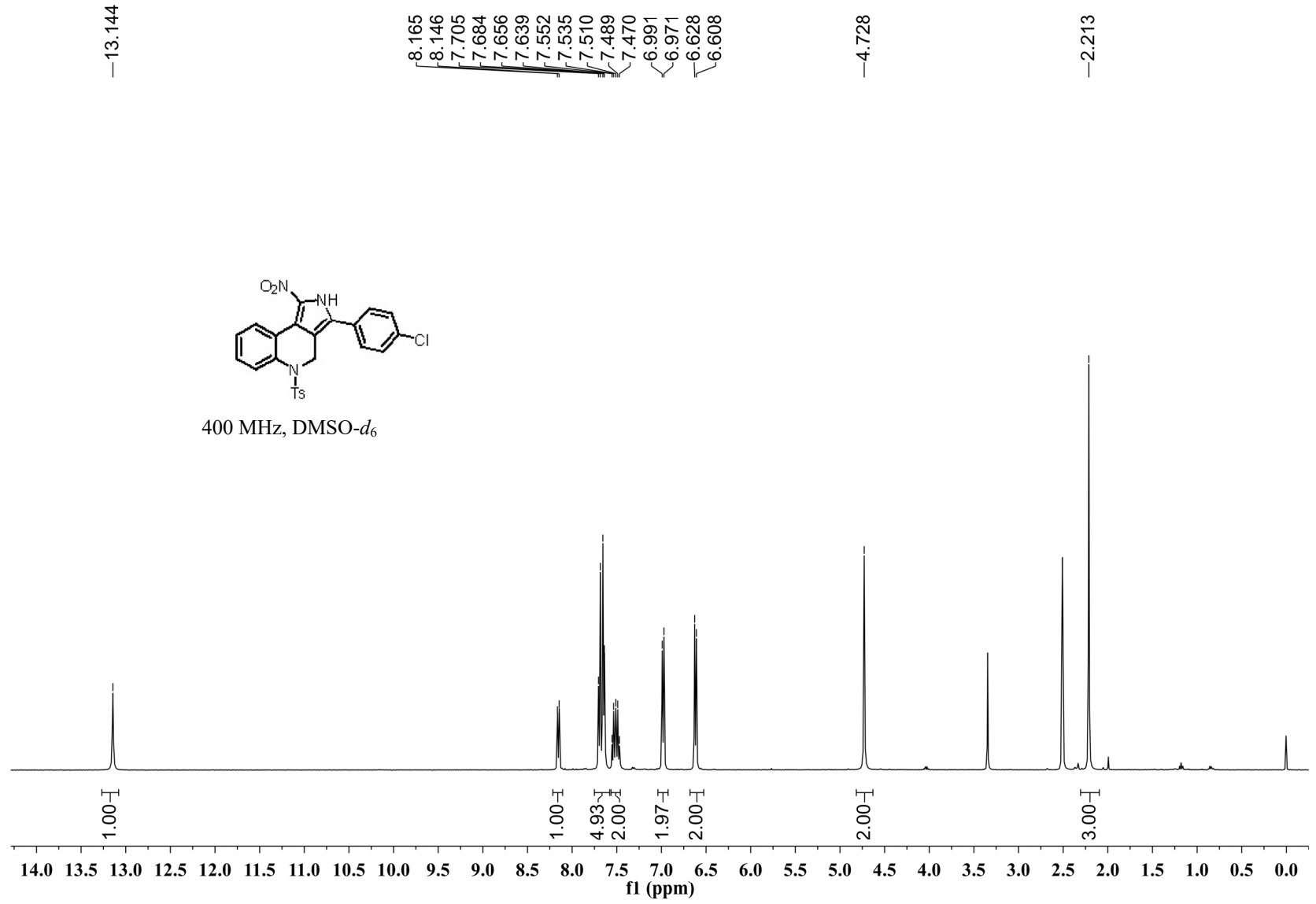
^{13}C NMR Spectrum of Compound 3g



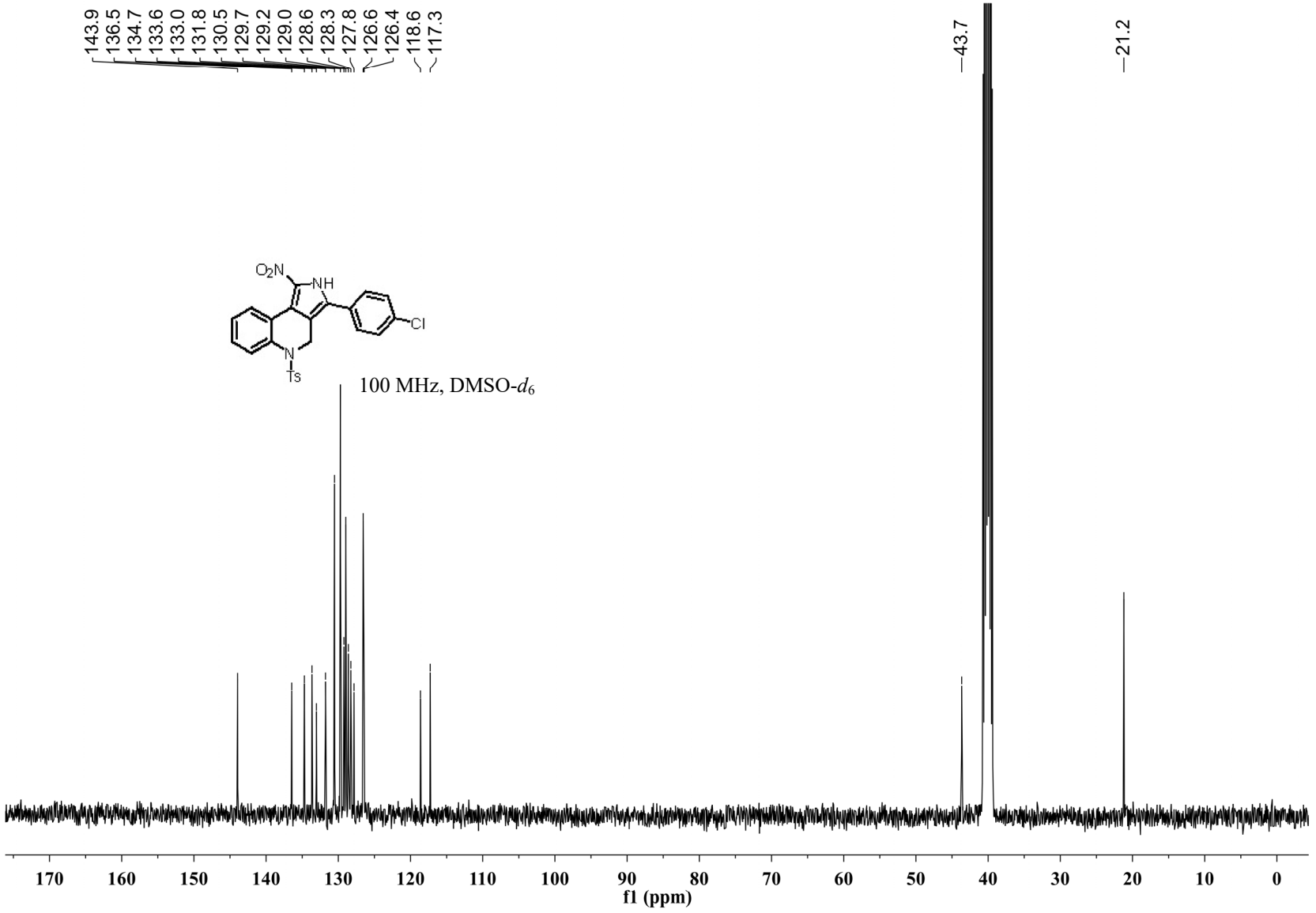
^{1}H NMR Spectrum of Compound 3h



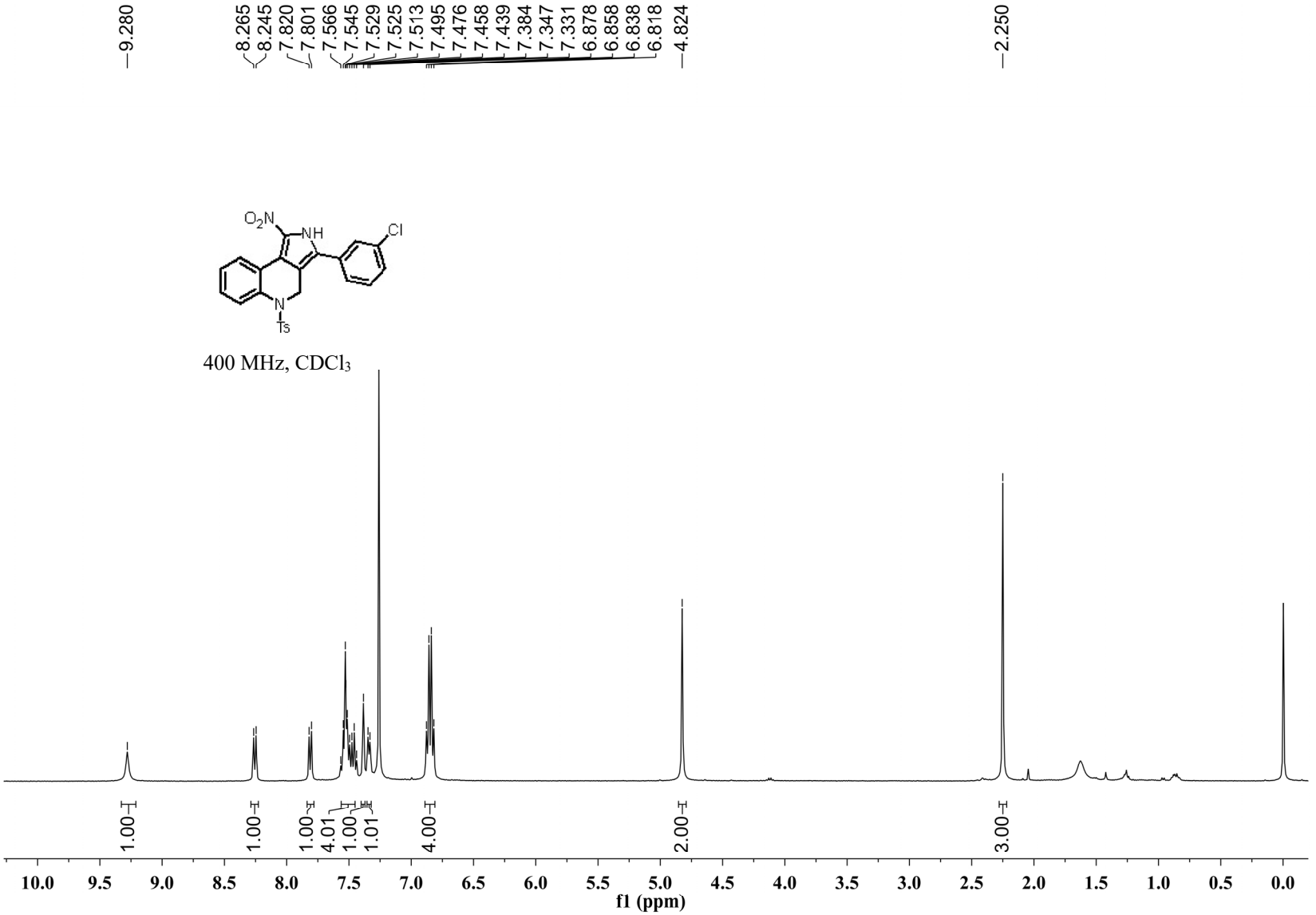
^{13}C NMR Spectrum of Compound 3h



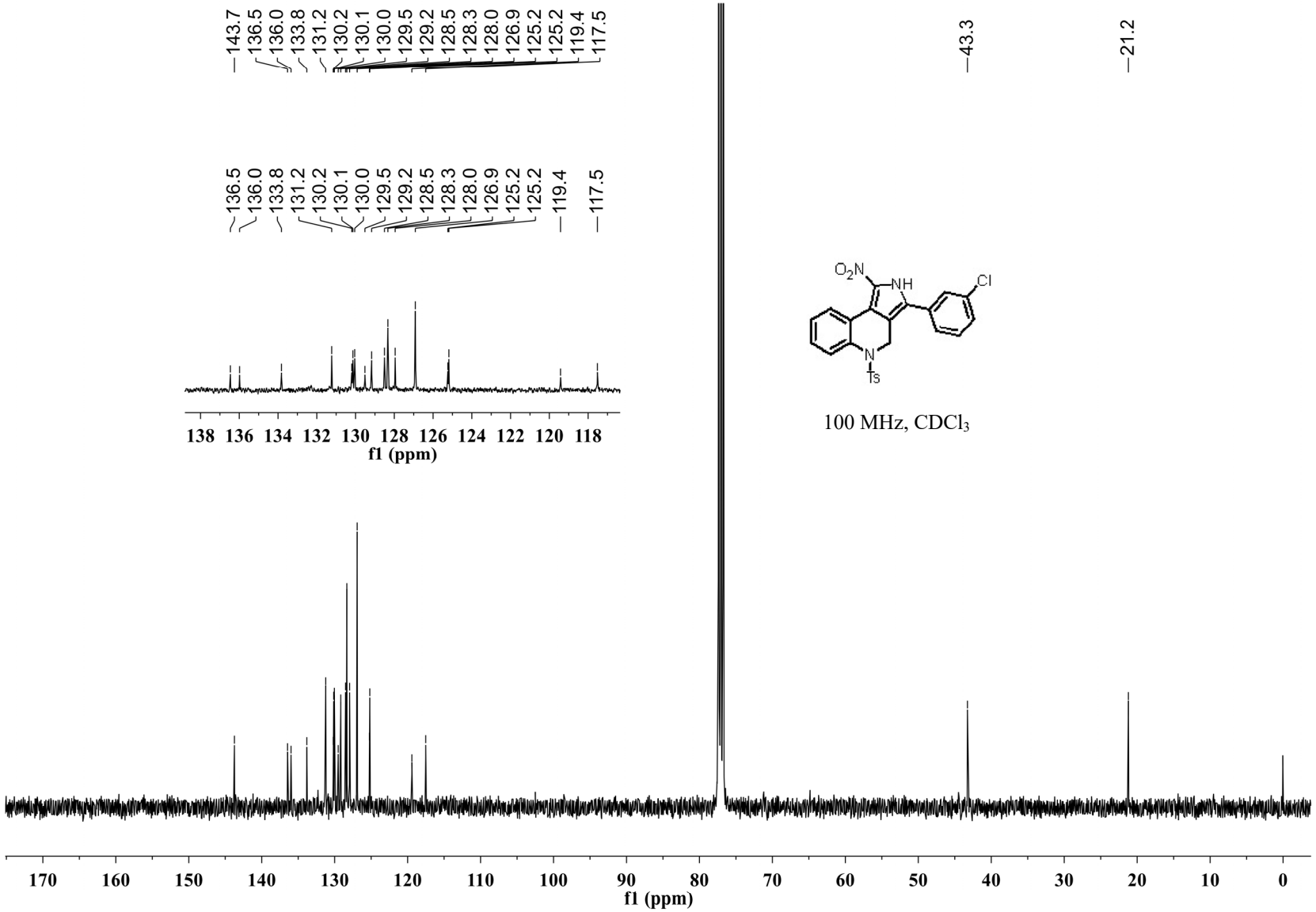
^{1}H NMR Spectrum of Compound 3i



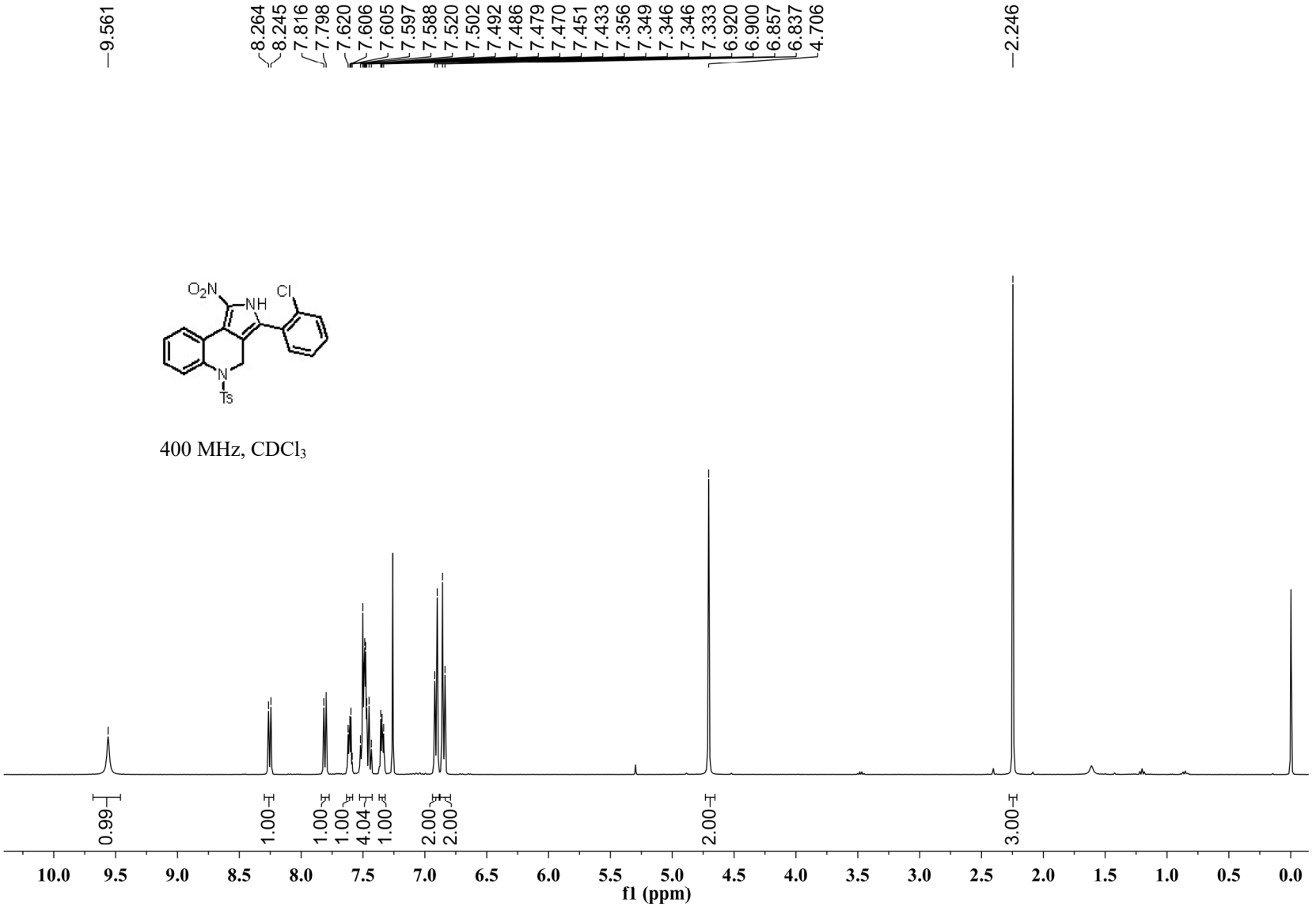
^{13}C NMR Spectrum of Compound 3i



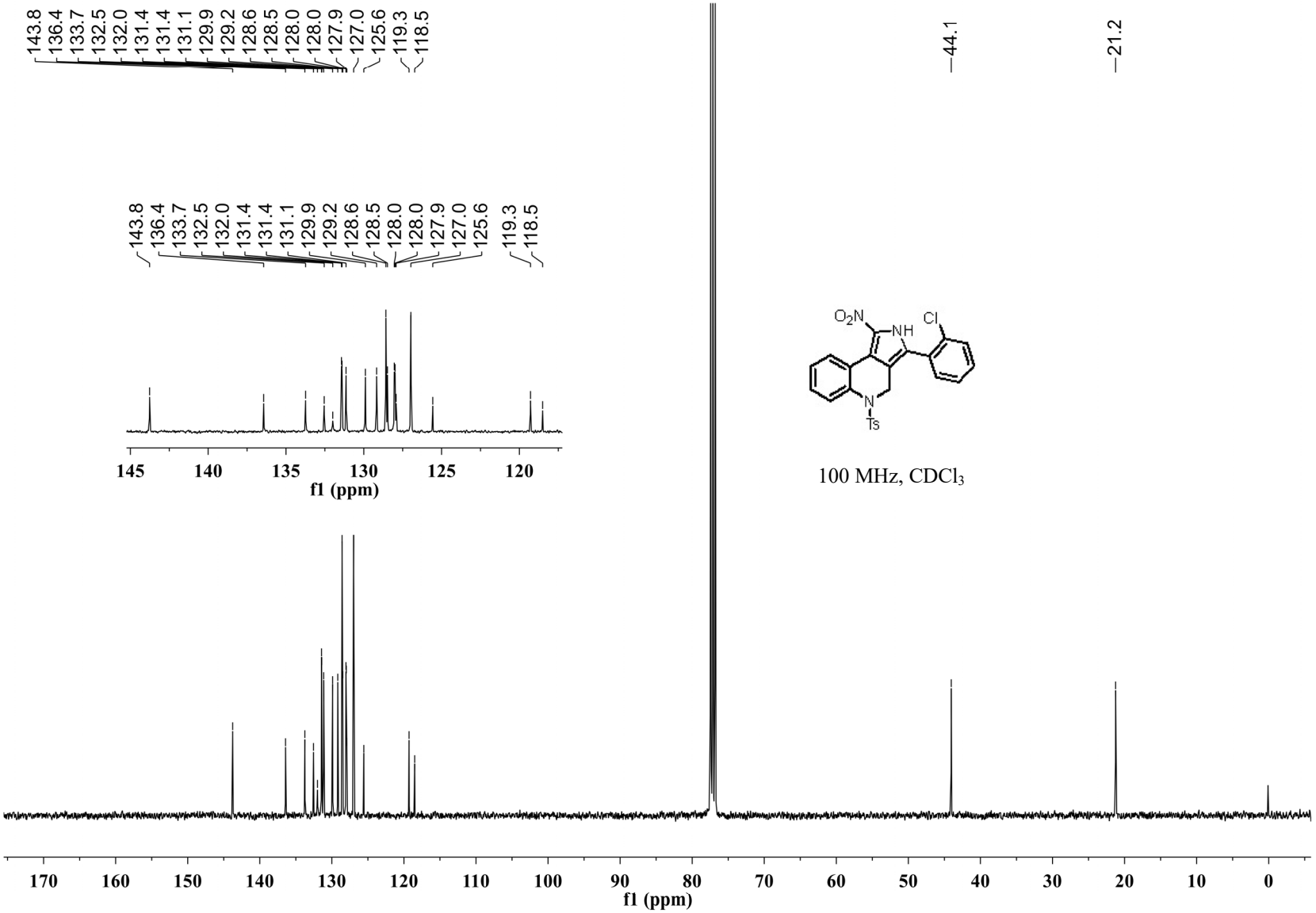
^{1}H NMR Spectrum of Compound 3j



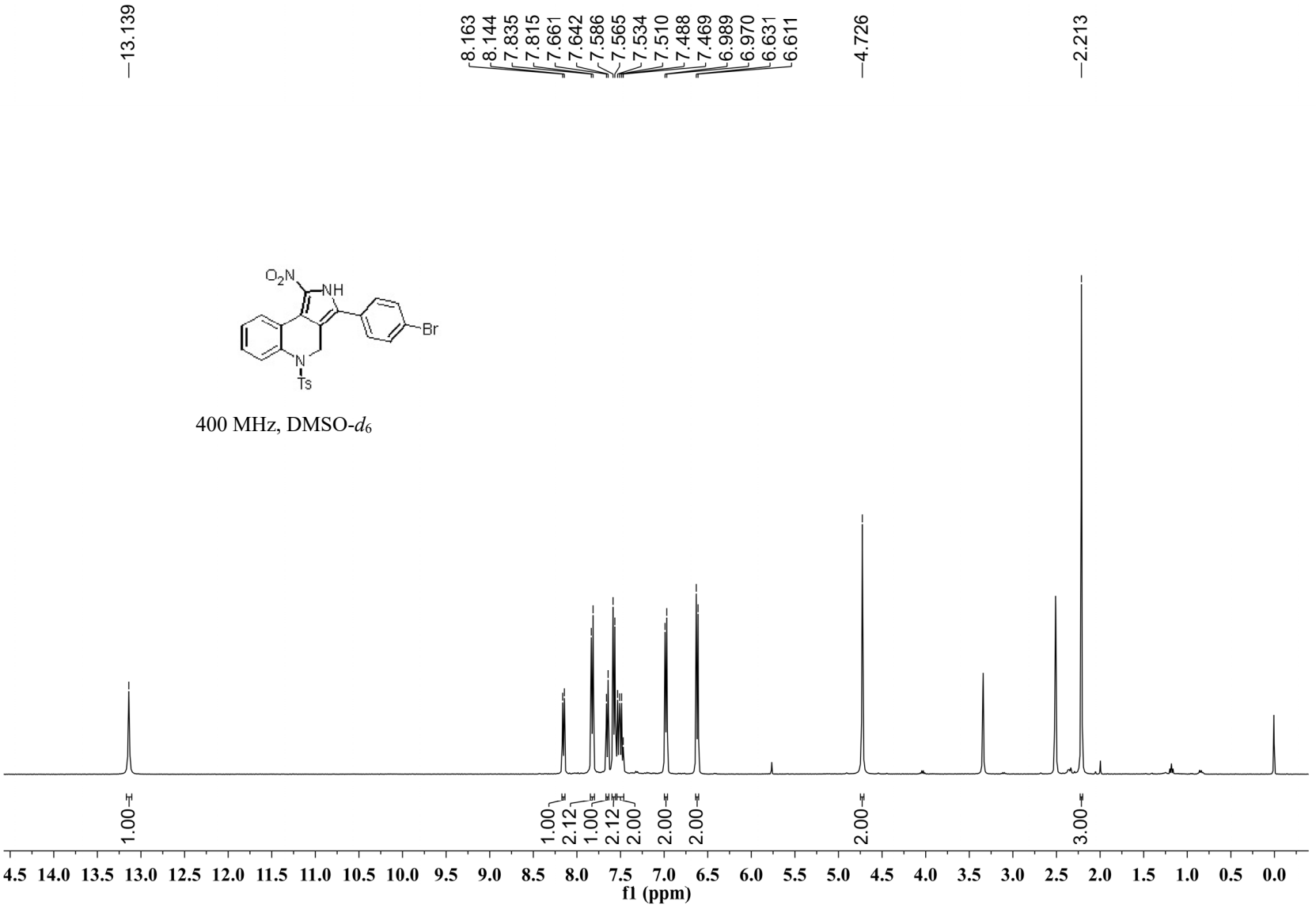
^{13}C NMR Spectrum of Compound 3j



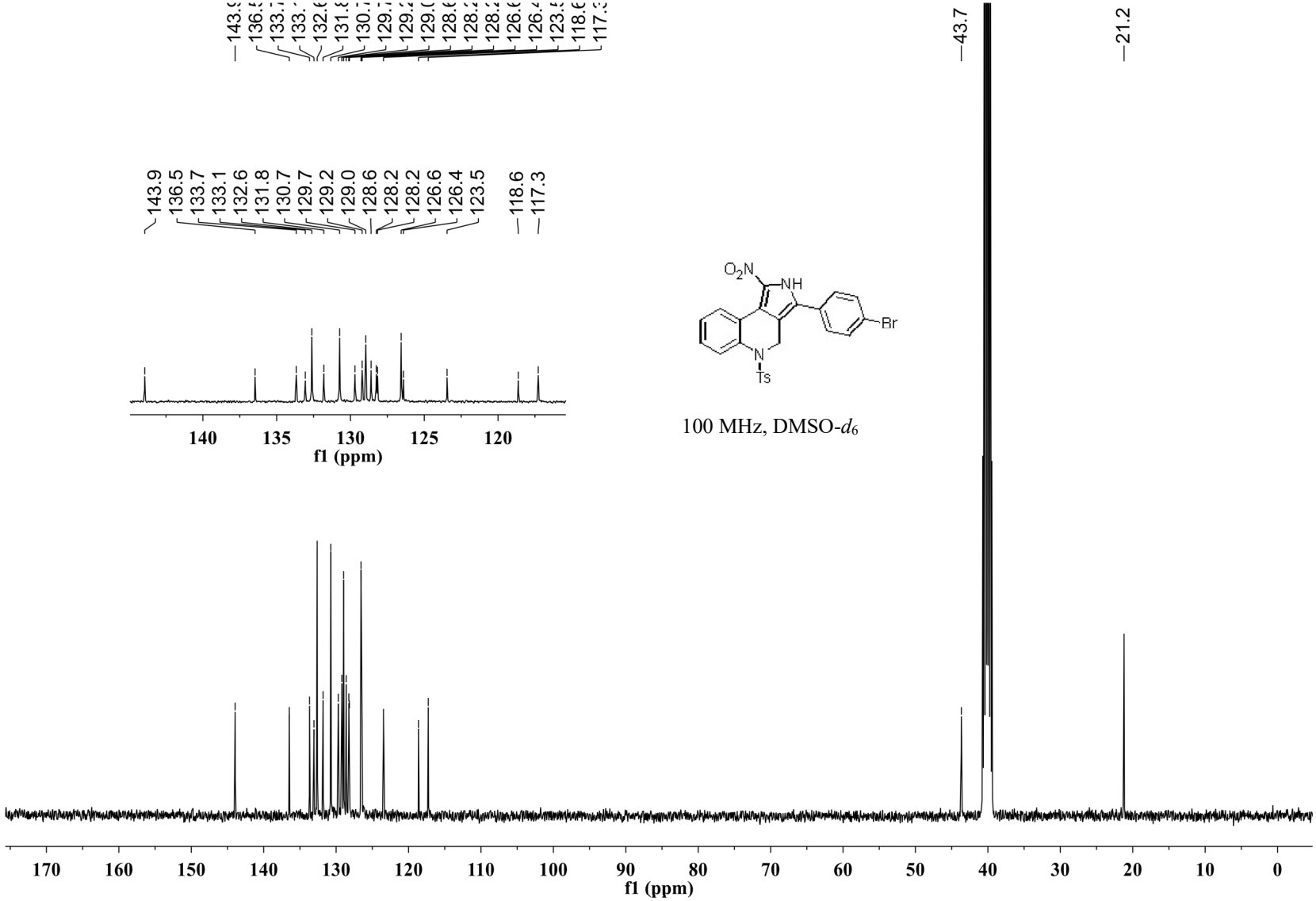
^{1}H NMR Spectrum of Compound 3k



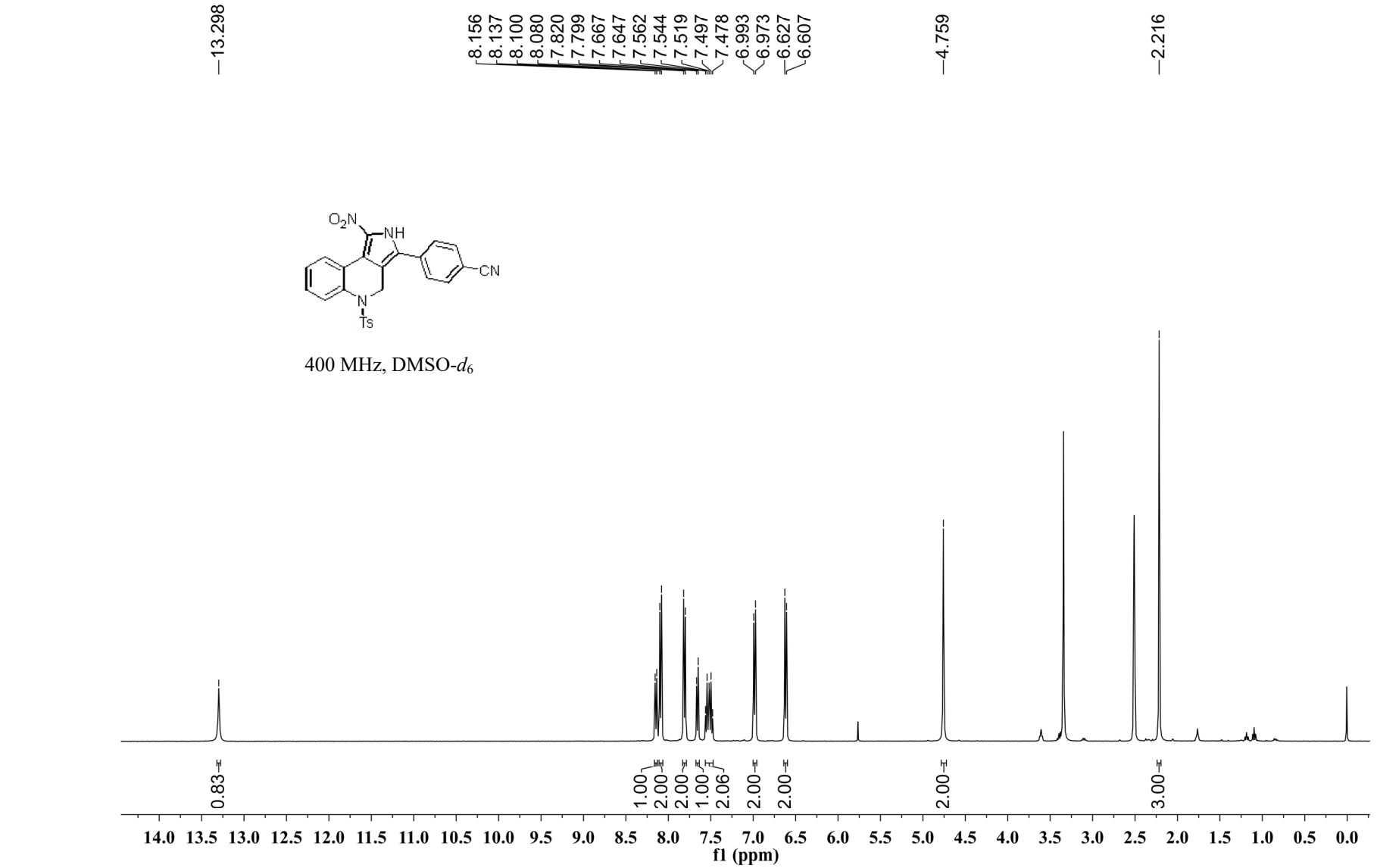
^{13}C NMR Spectrum of Compound 3k



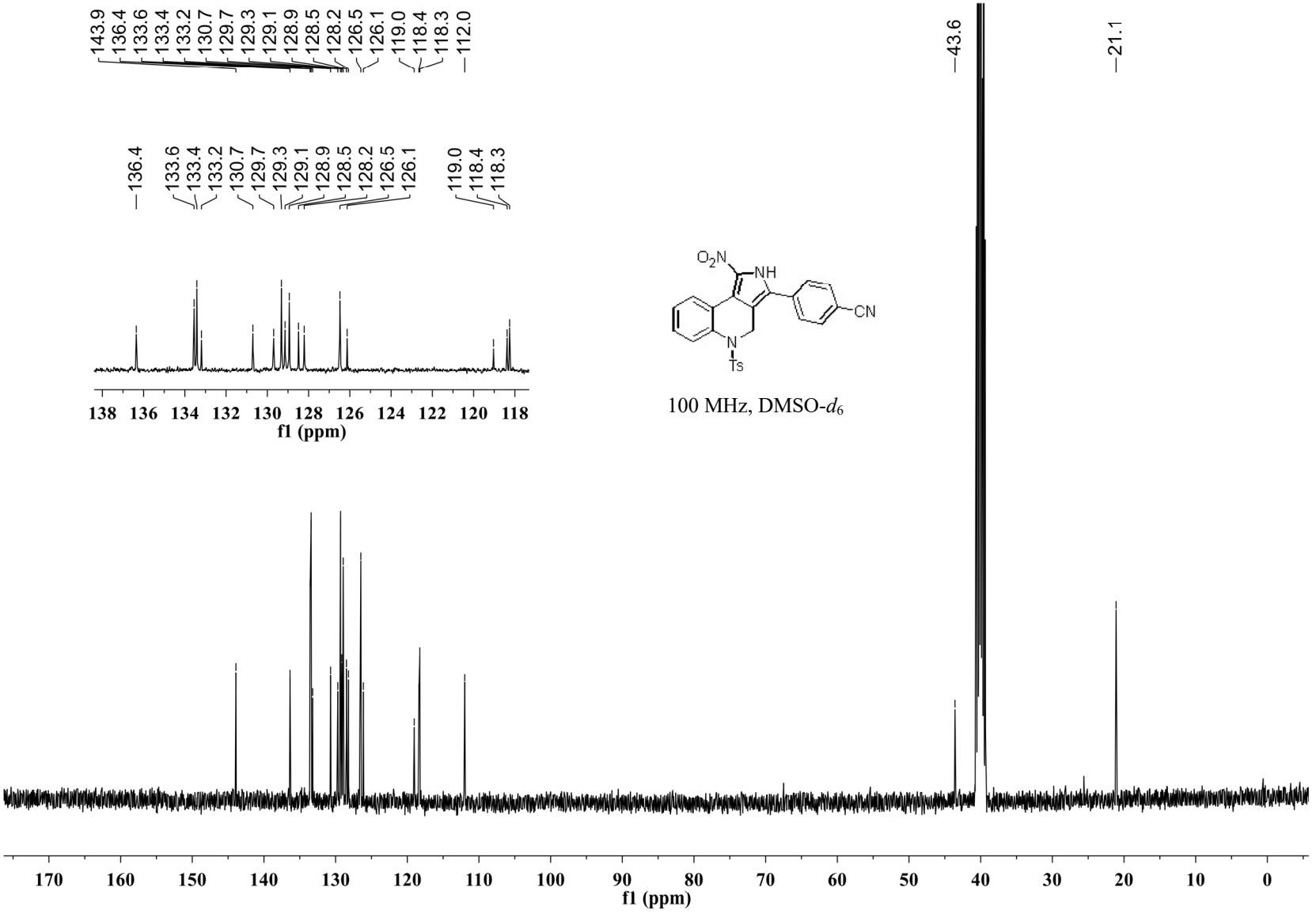
^{1}H NMR Spectrum of Compound 3l



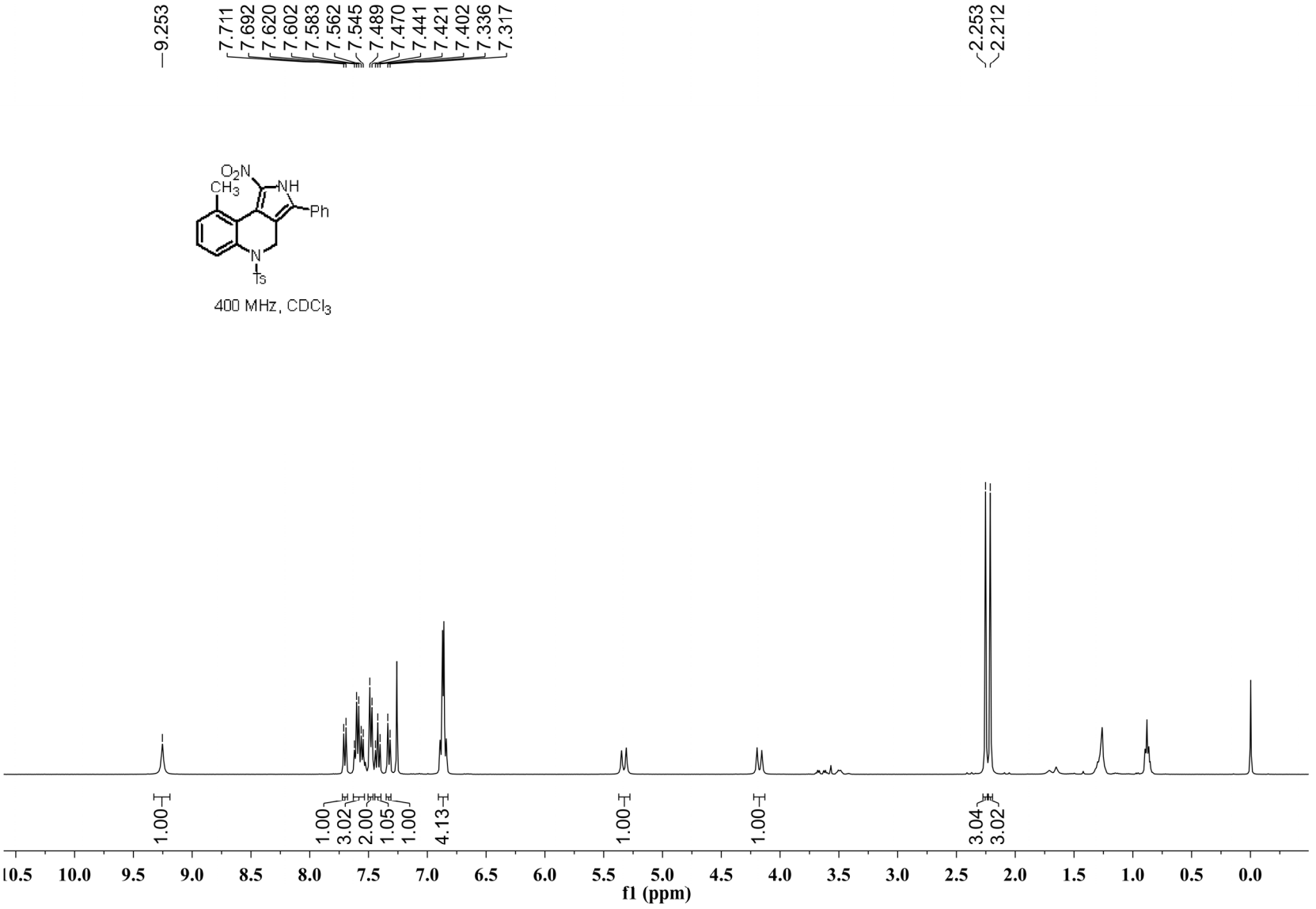
^{13}C NMR Spectrum of Compound 3l



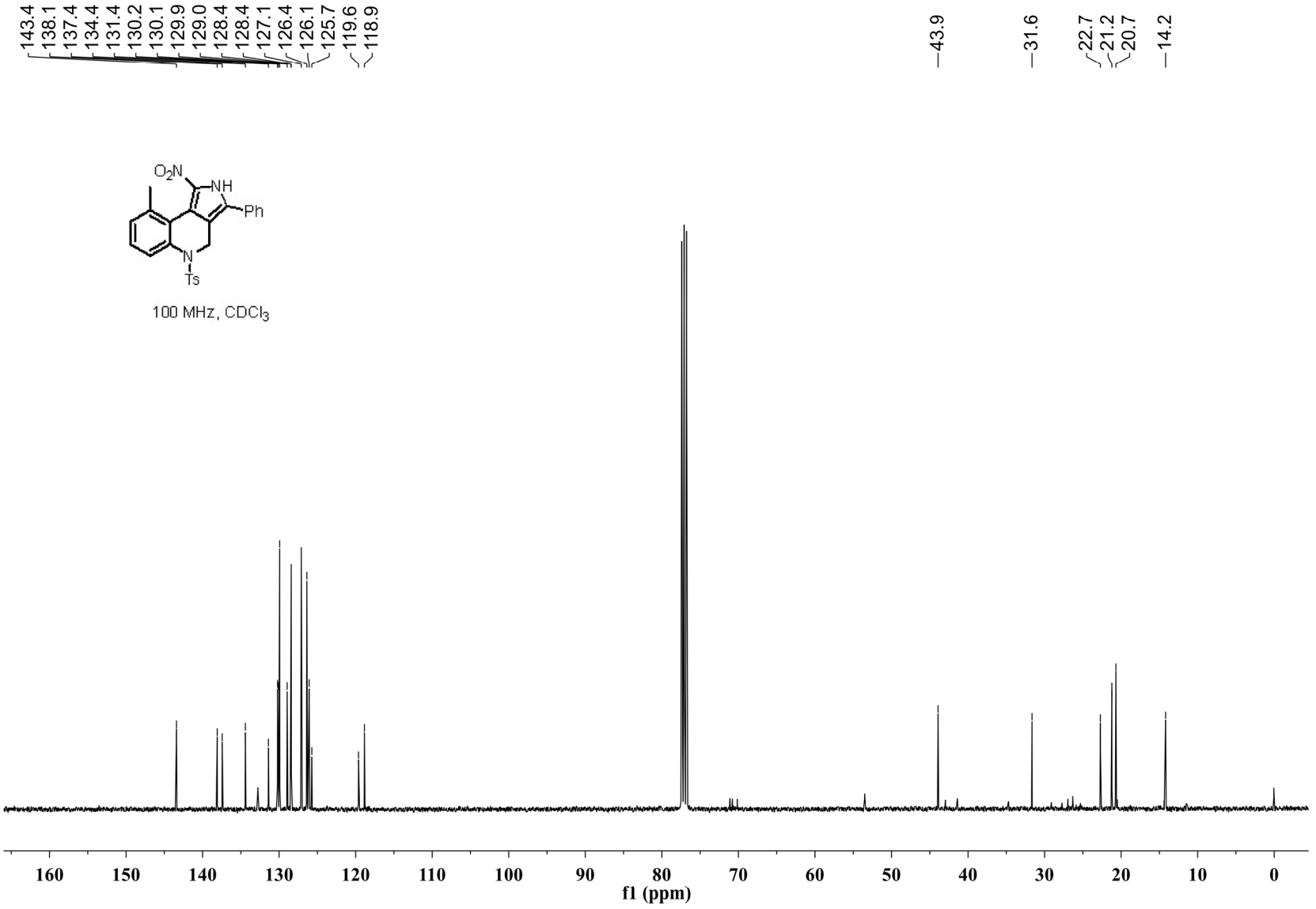
^{1}H NMR Spectrum of Compound 3m



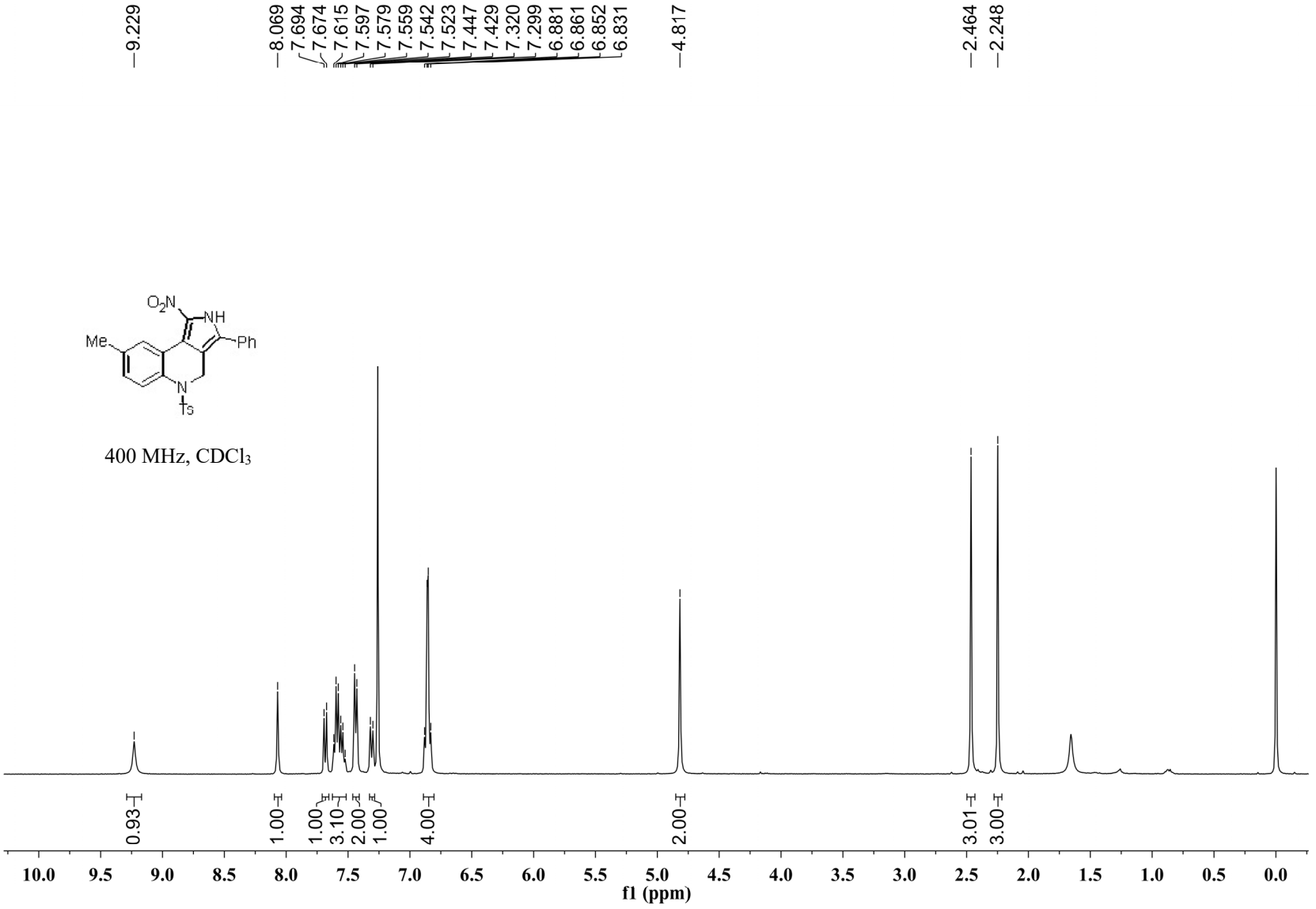
^{13}C NMR Spectrum of Compound 3m



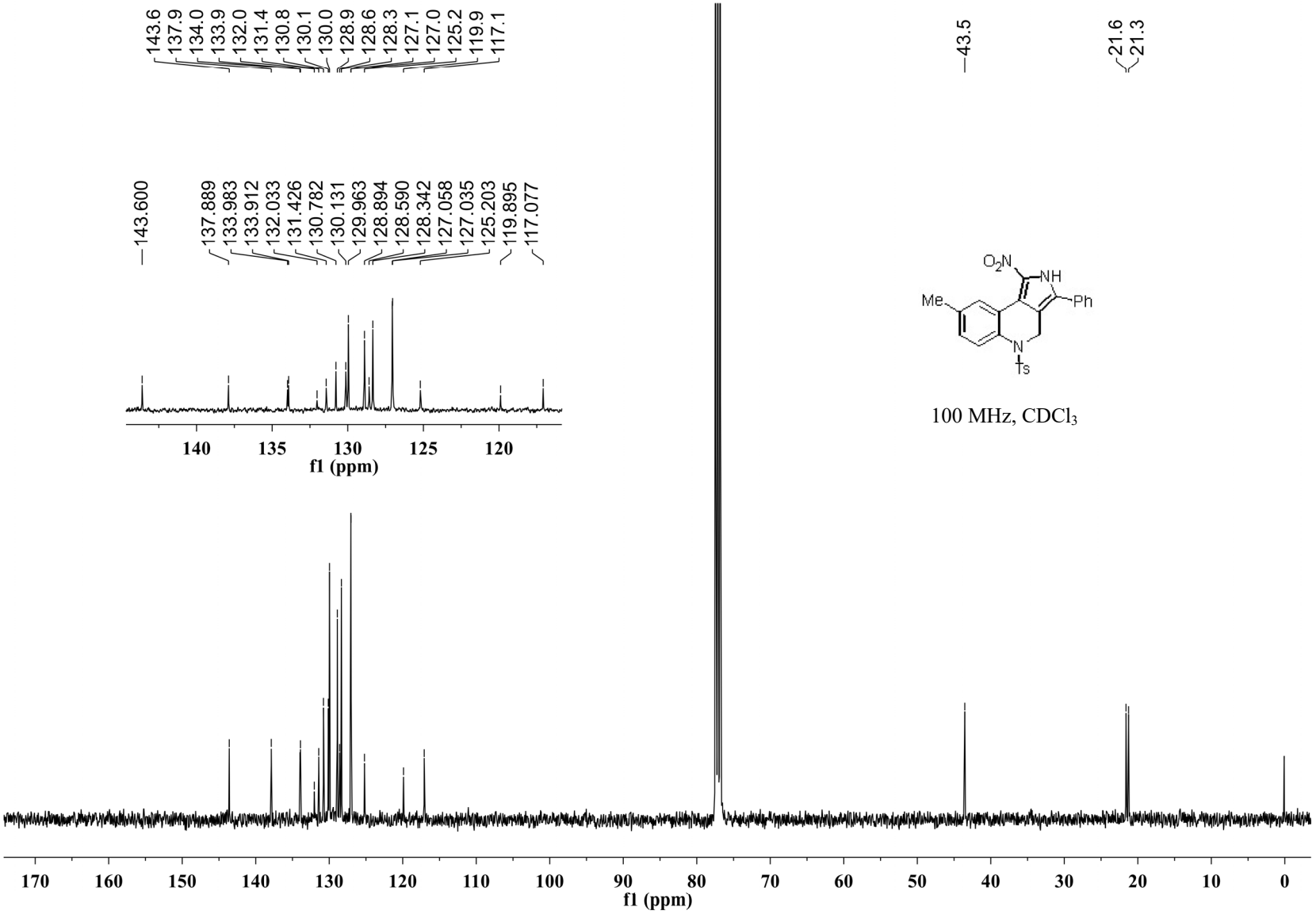
^{1}H NMR Spectrum of Compound 3p



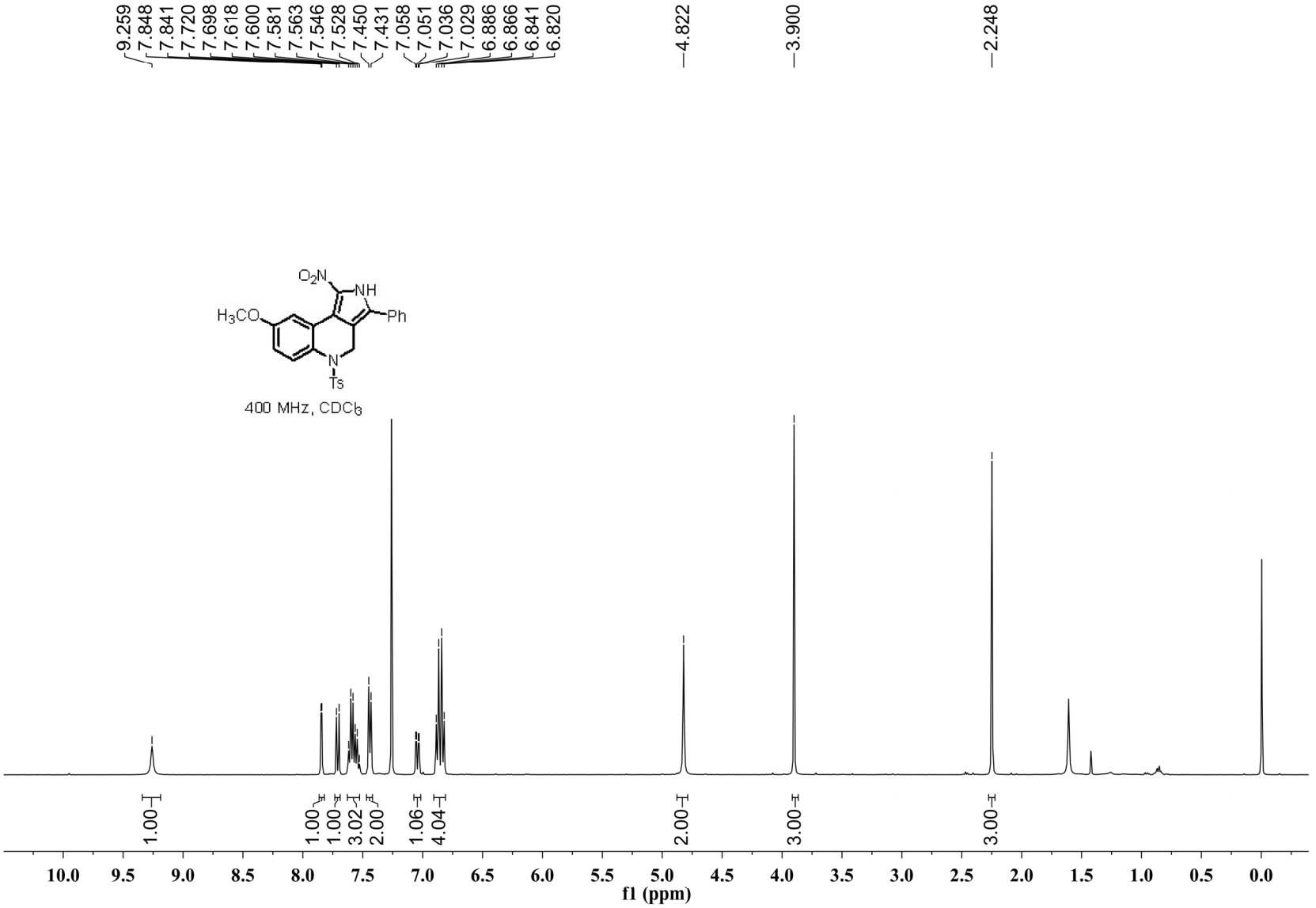
^{13}C NMR Spectrum of Compound 3p



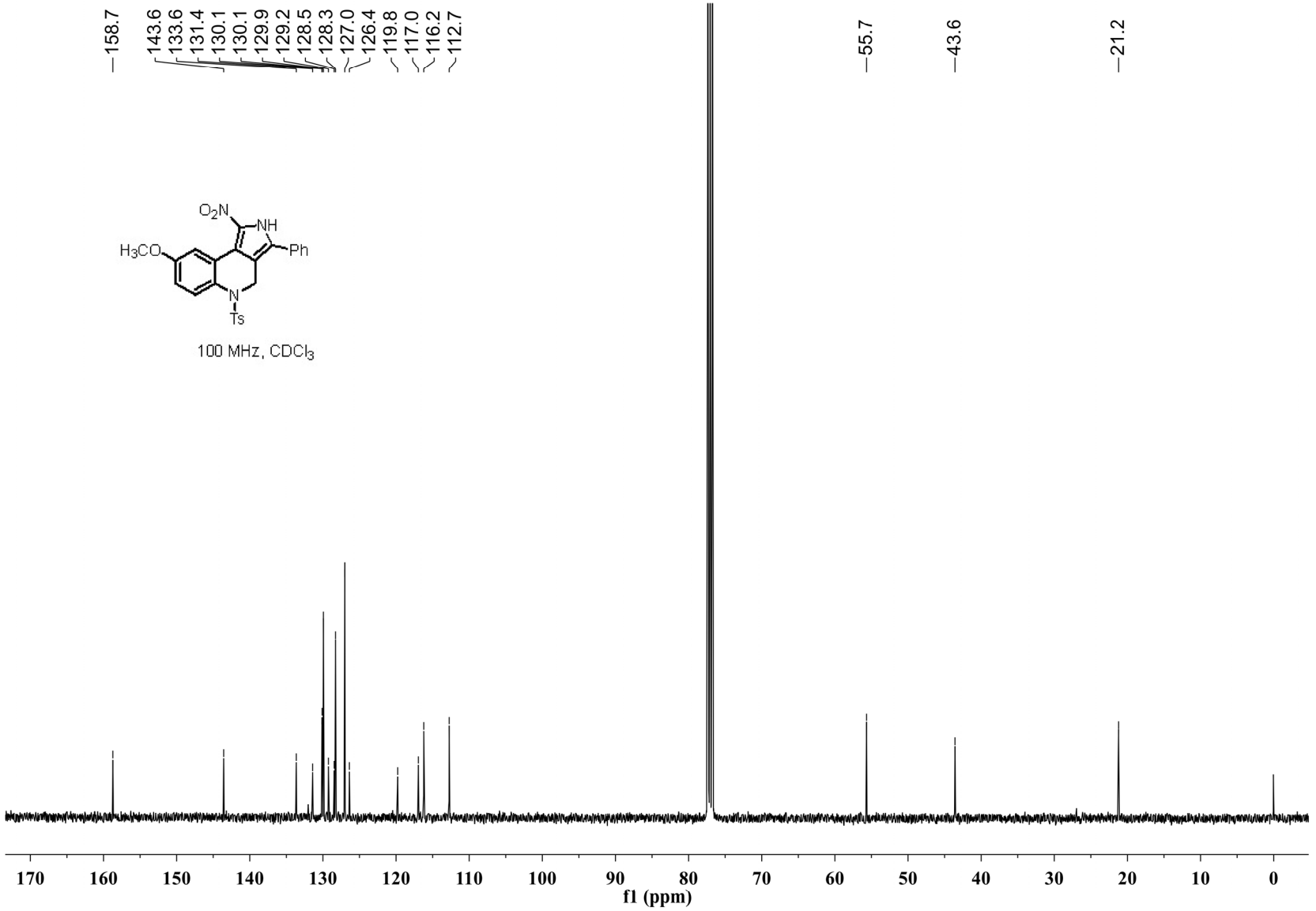
^{1}H NMR Spectrum of Compound 3q



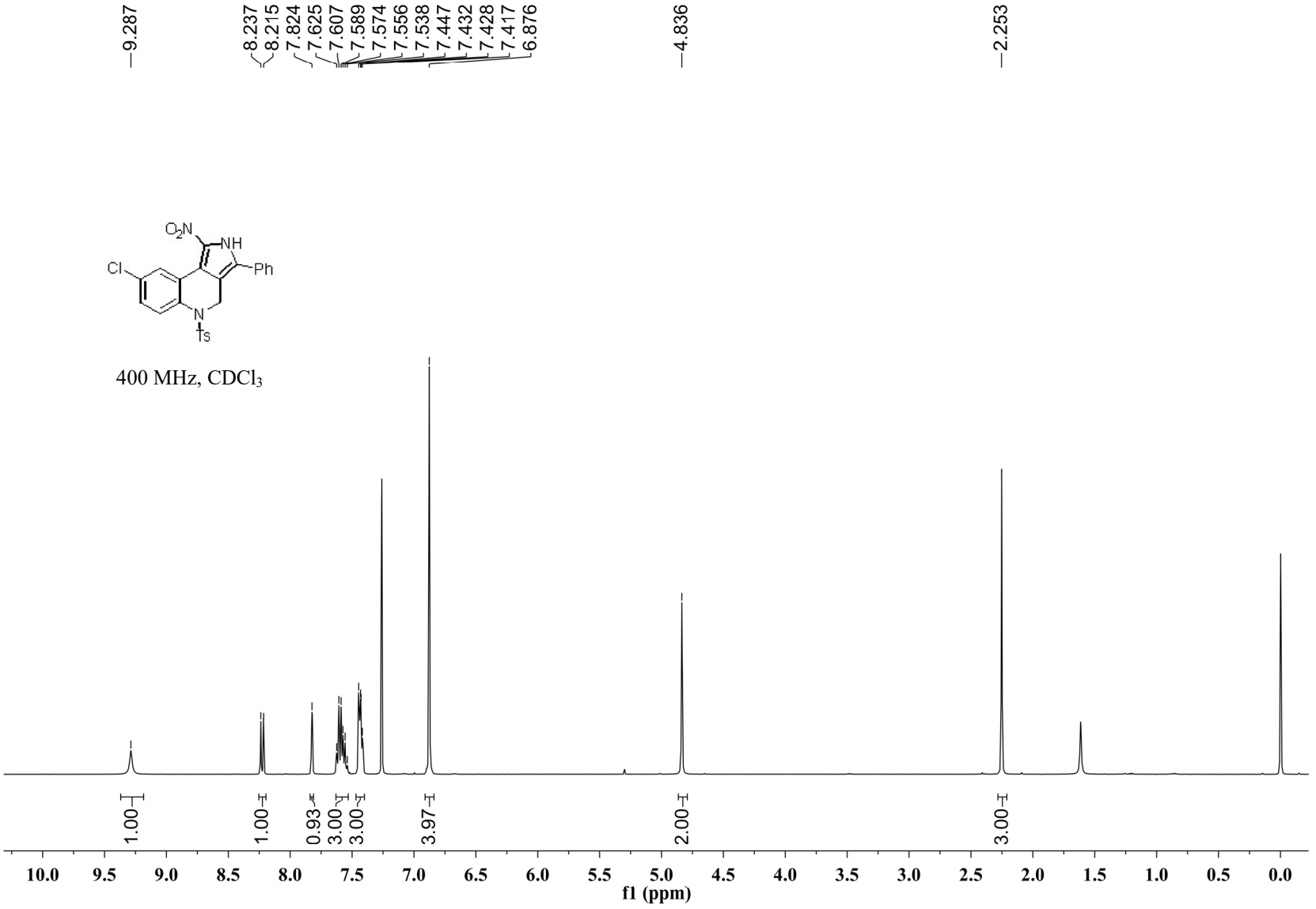
^{13}C NMR Spectrum of Compound 3q



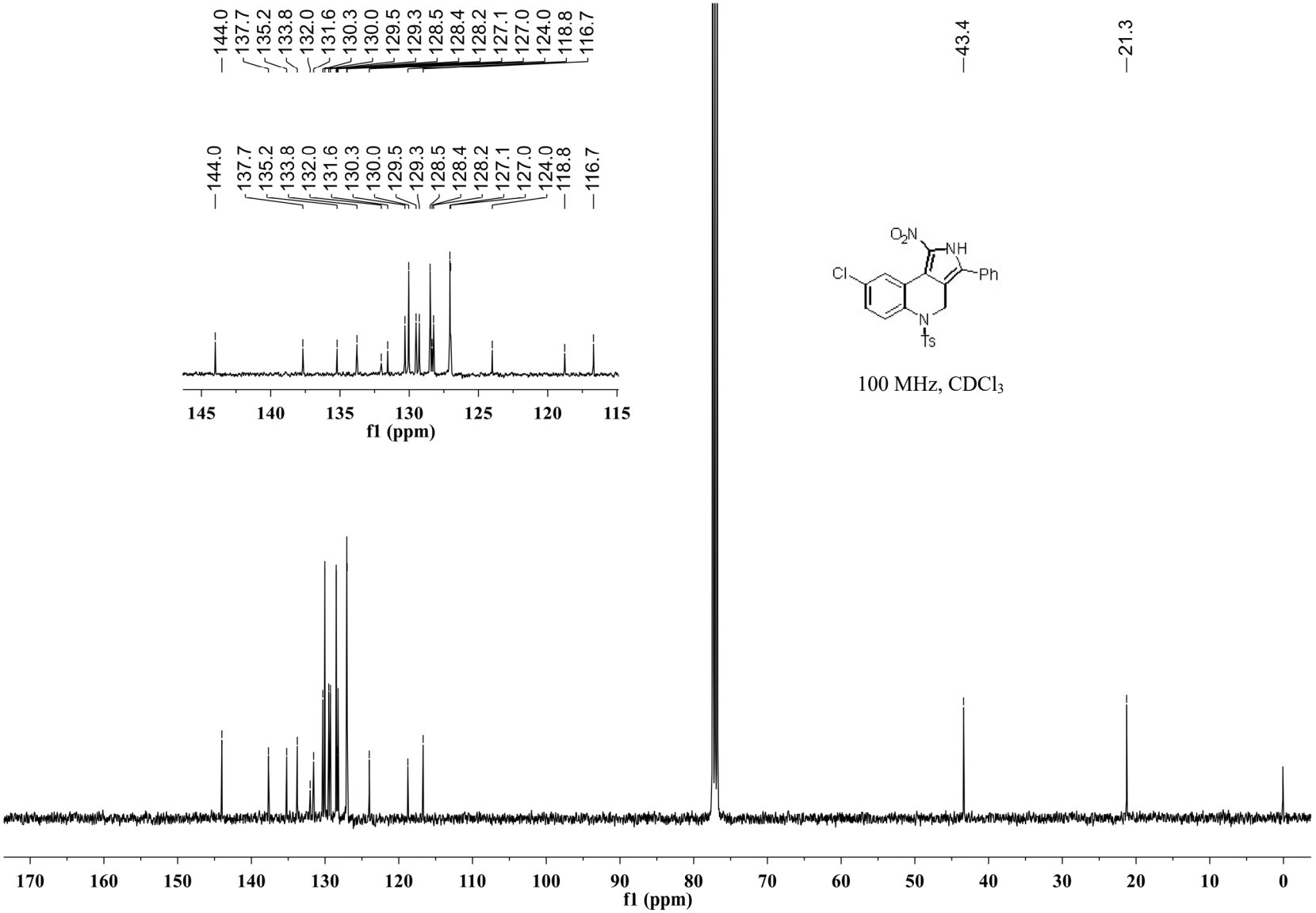
^{1}H NMR Spectrum of Compound 3r



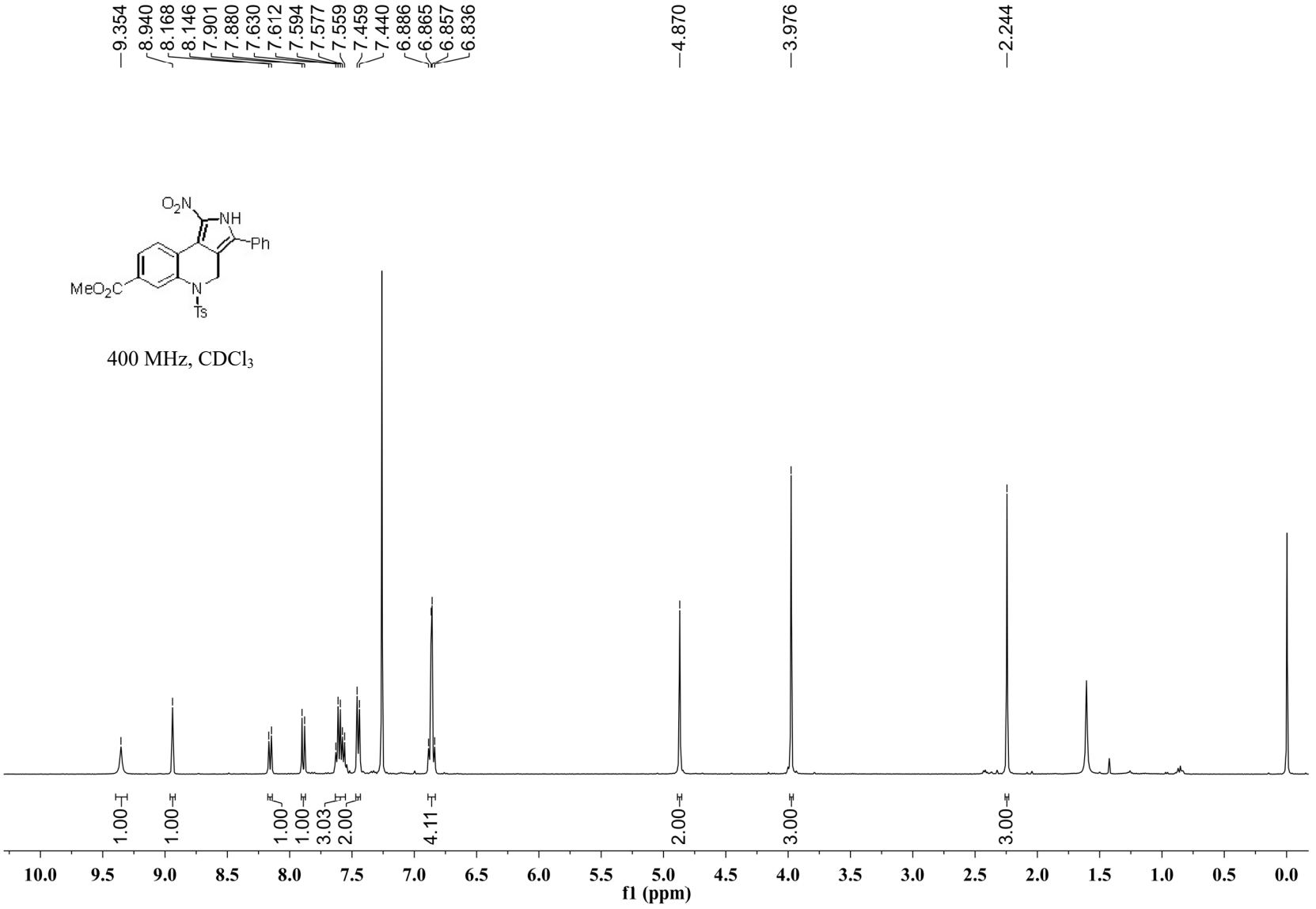
^{13}C NMR Spectrum of Compound 3r



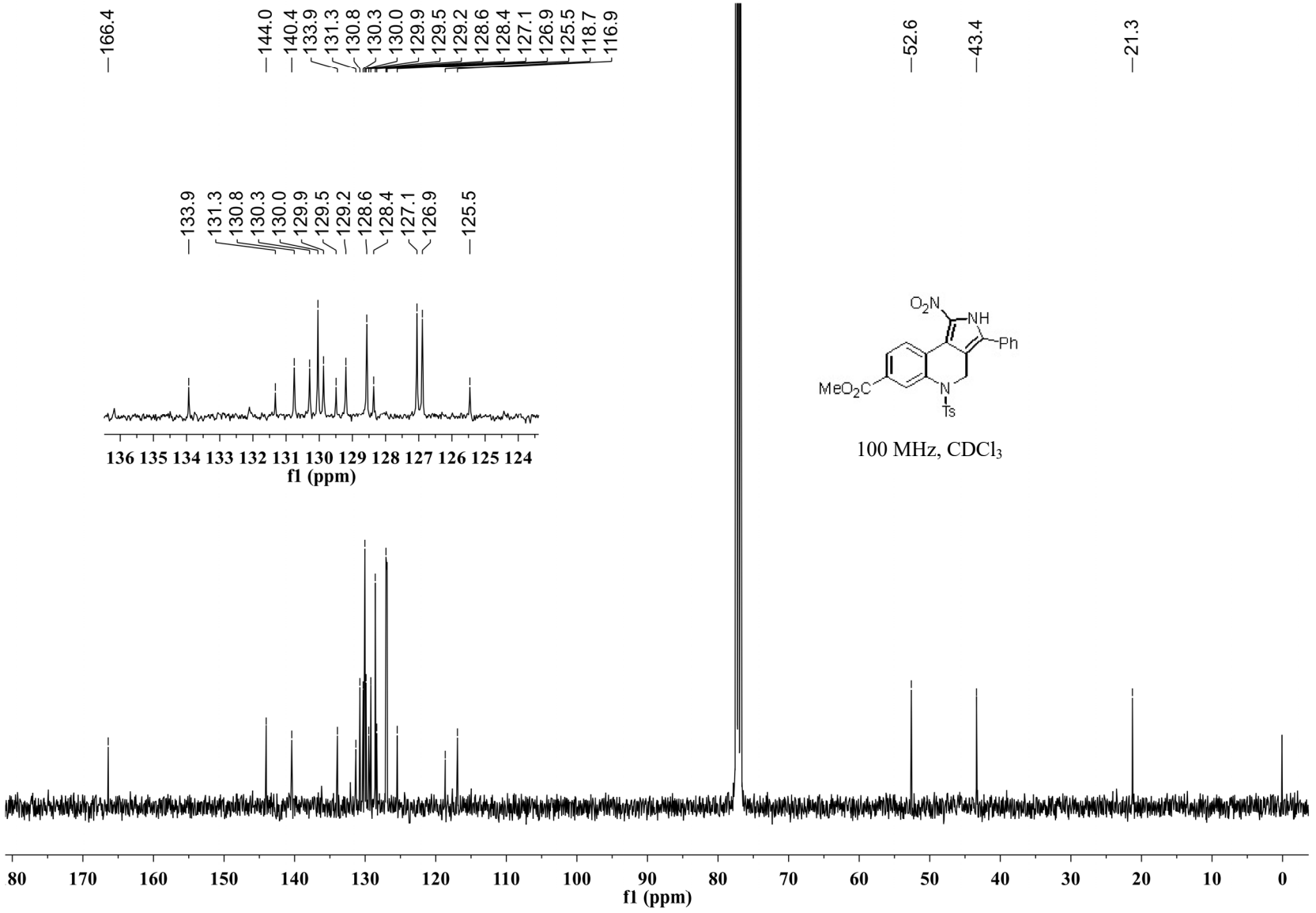
^{1}H NMR Spectrum of Compound 3s



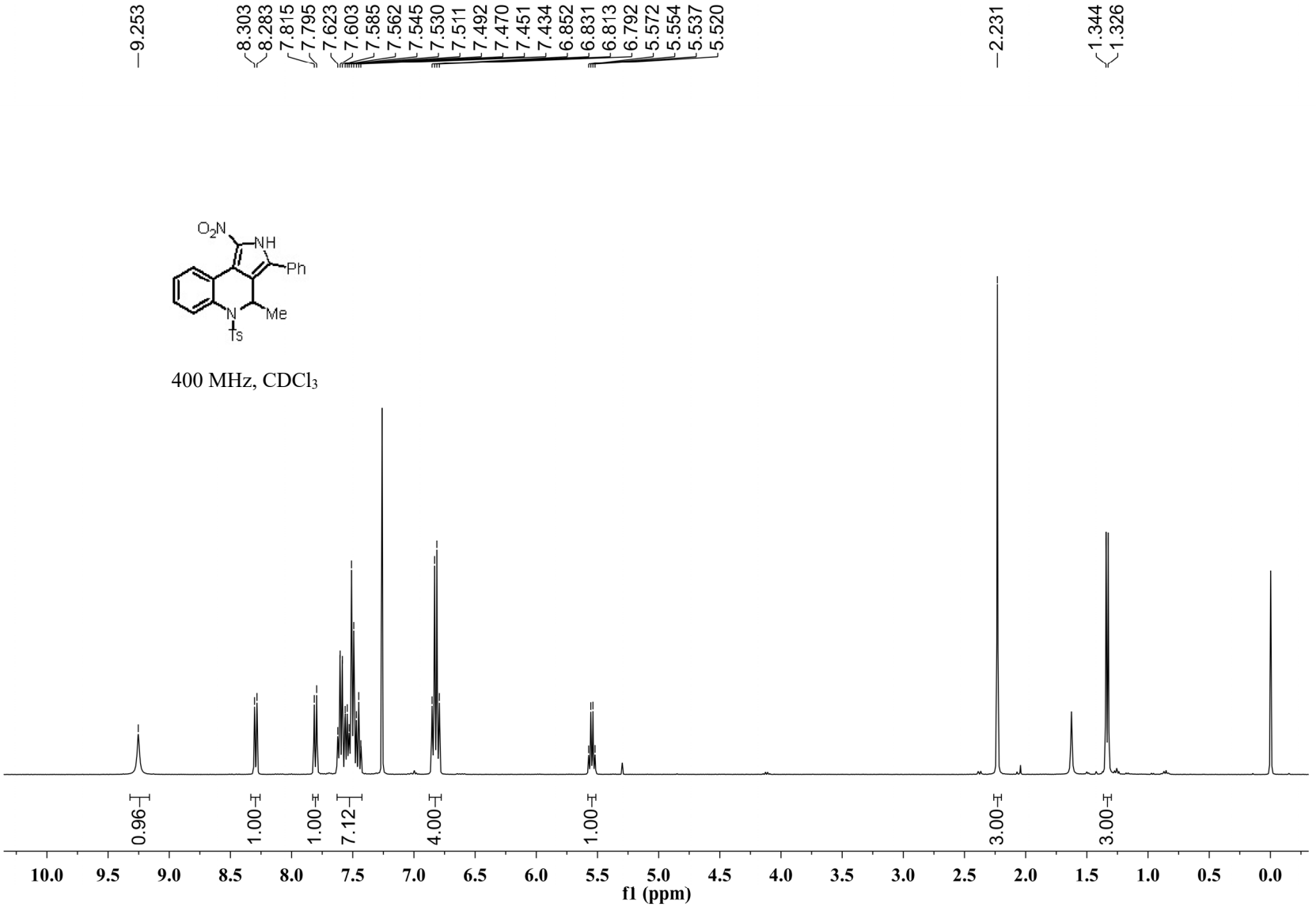
^{13}C NMR Spectrum of Compound 3s



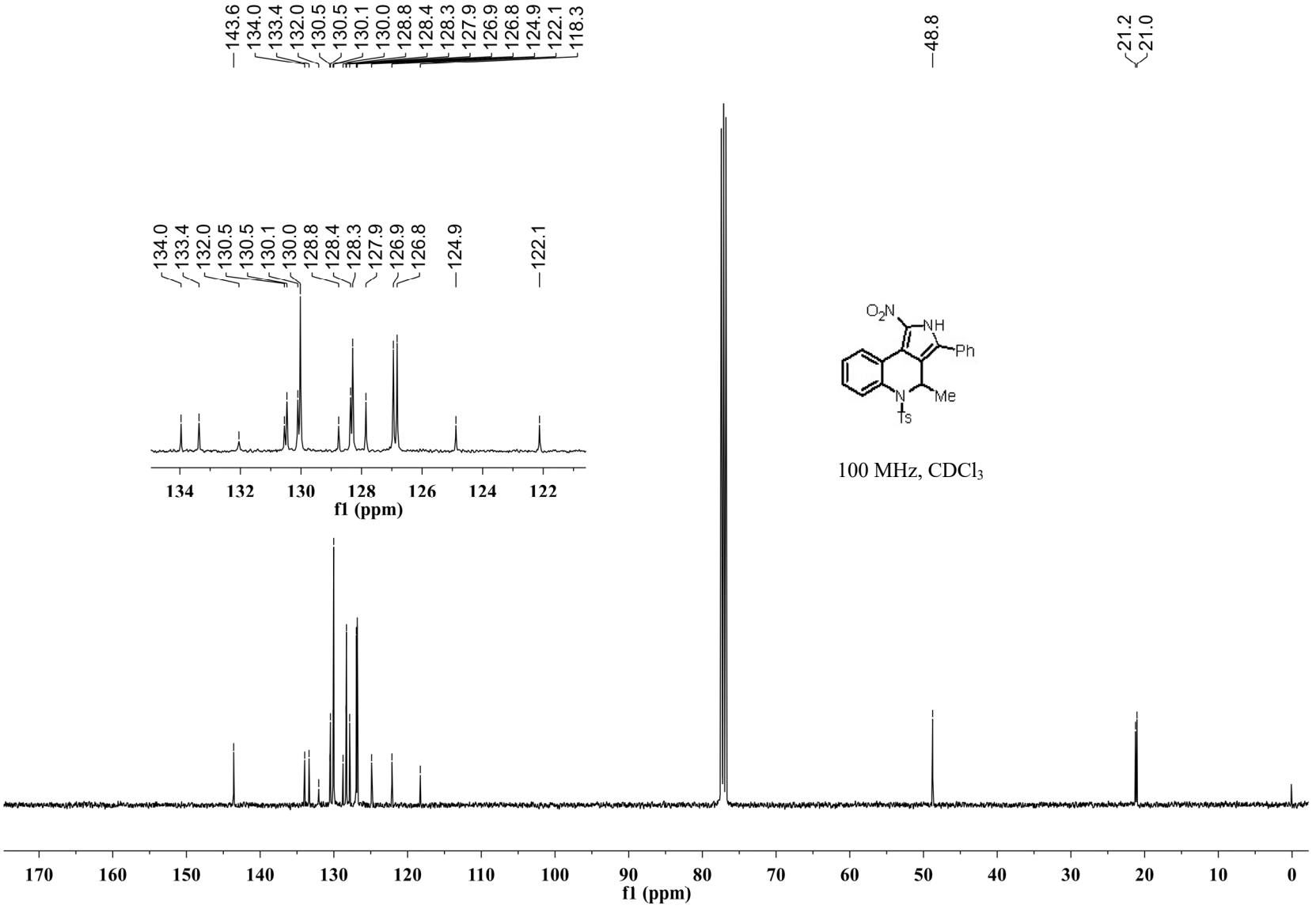
^{1}H NMR Spectrum of Compound 3t



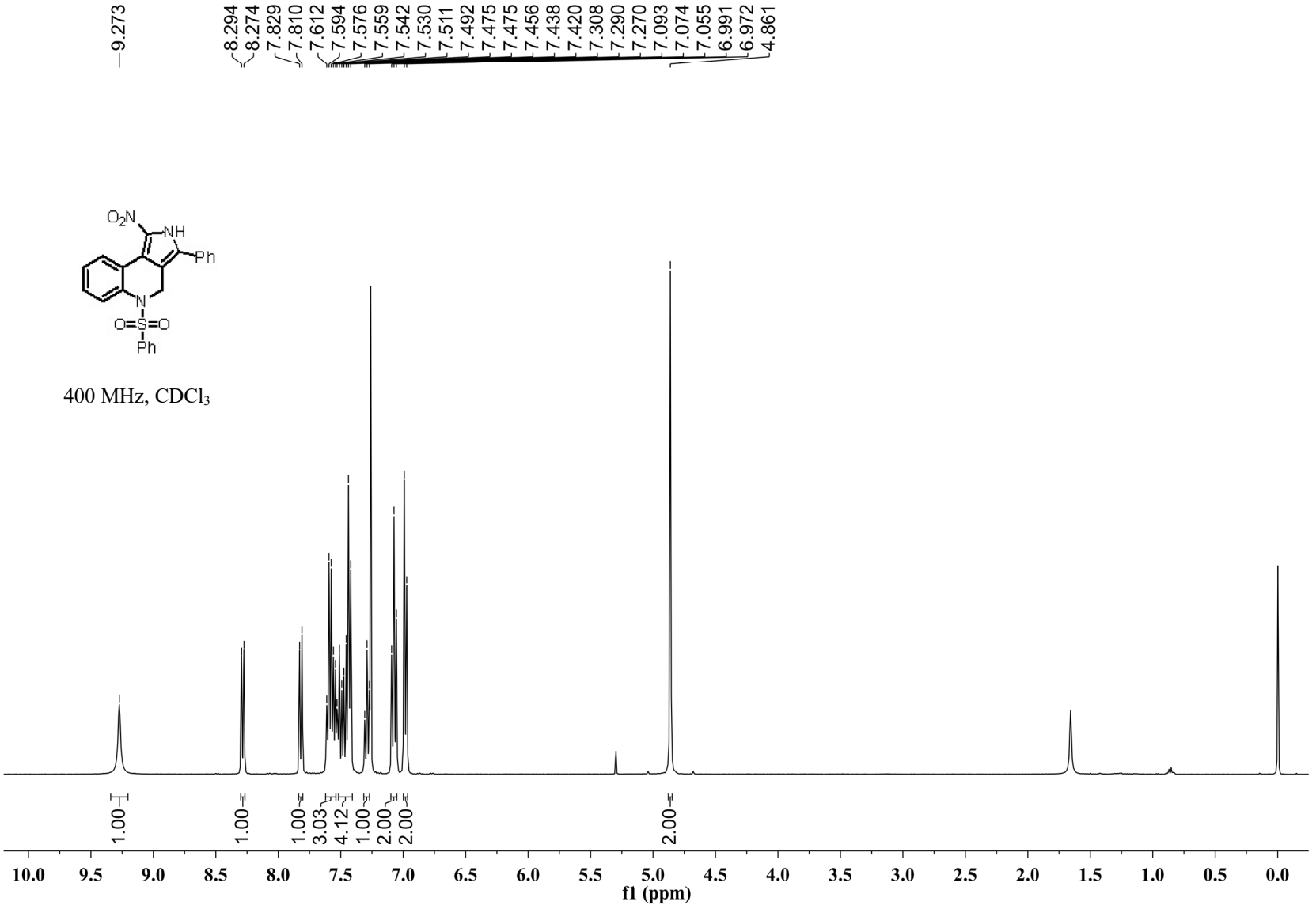
^{13}C NMR Spectrum of Compound 3t



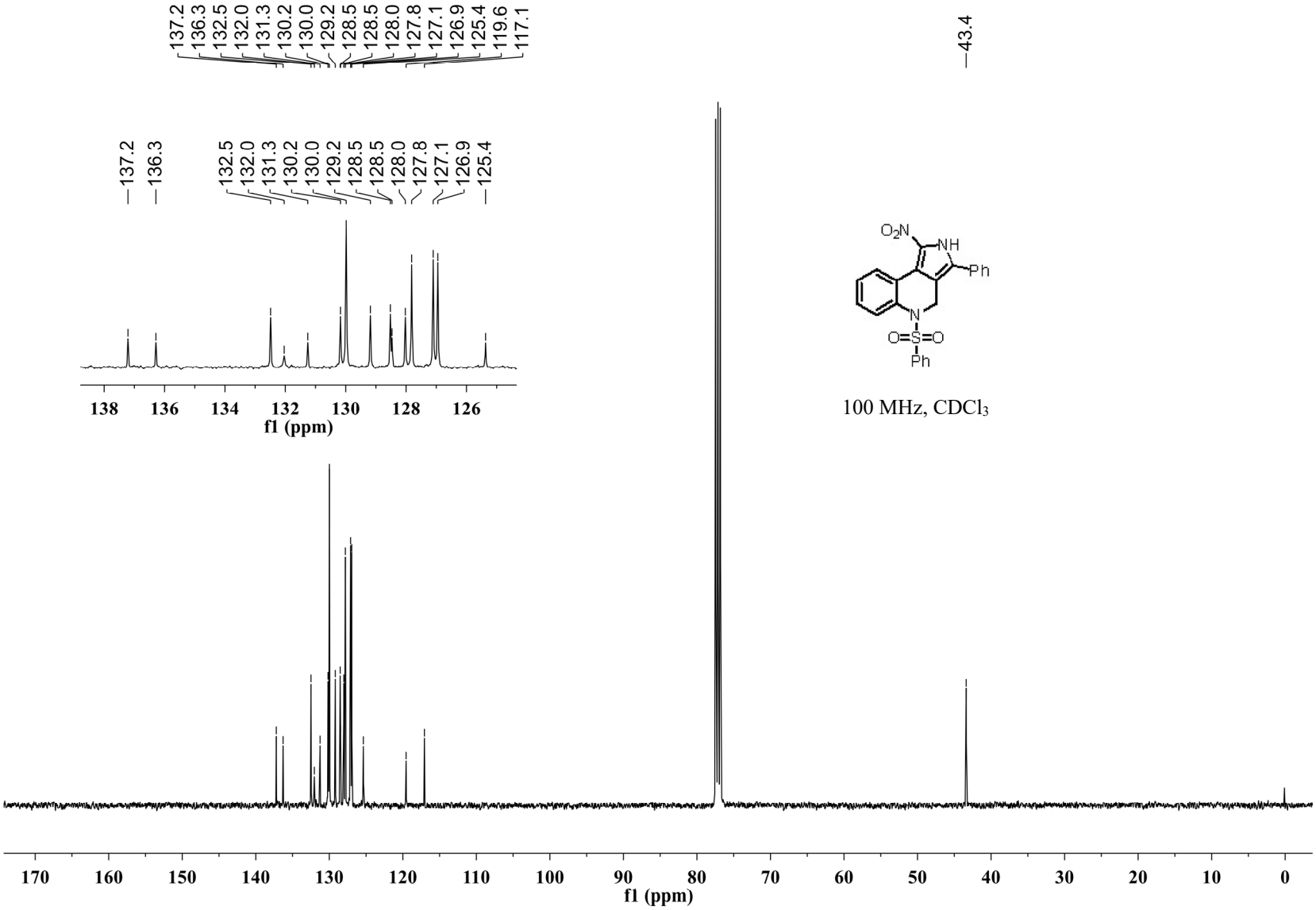
^{1}H NMR Spectrum of Compound 3u



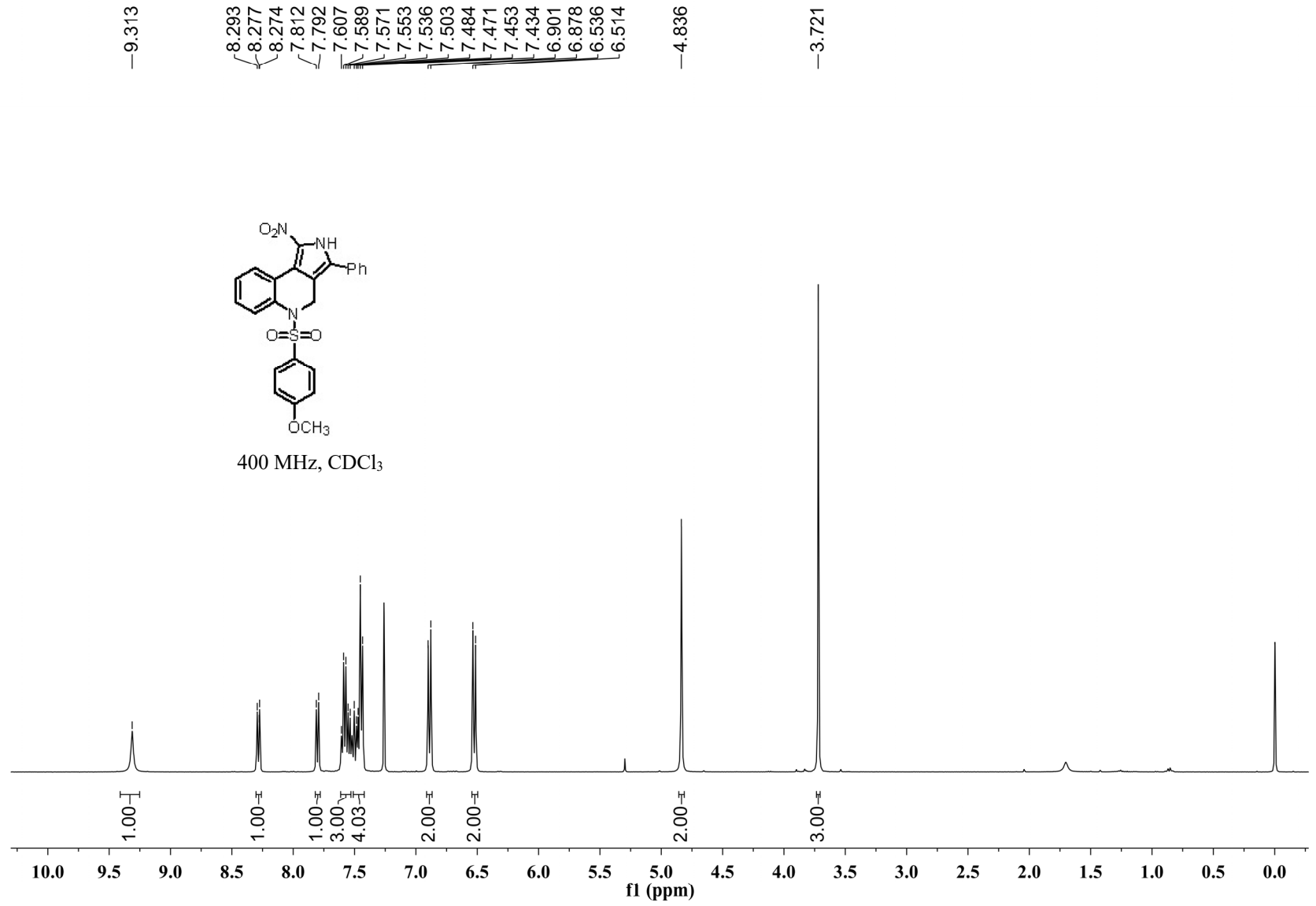
^{13}C NMR Spectrum of Compound 3u



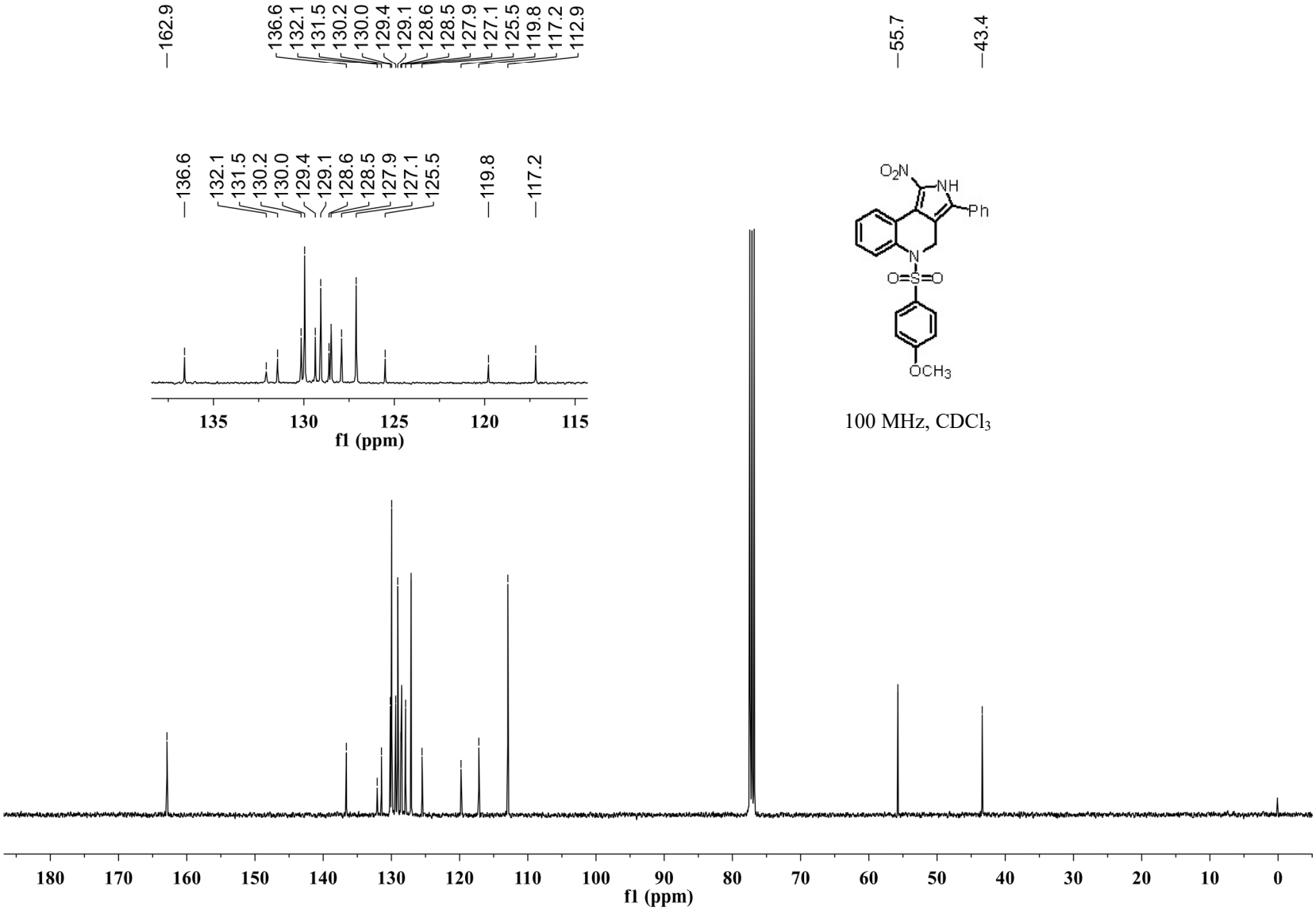
^{1}H NMR Spectrum of Compound 3v



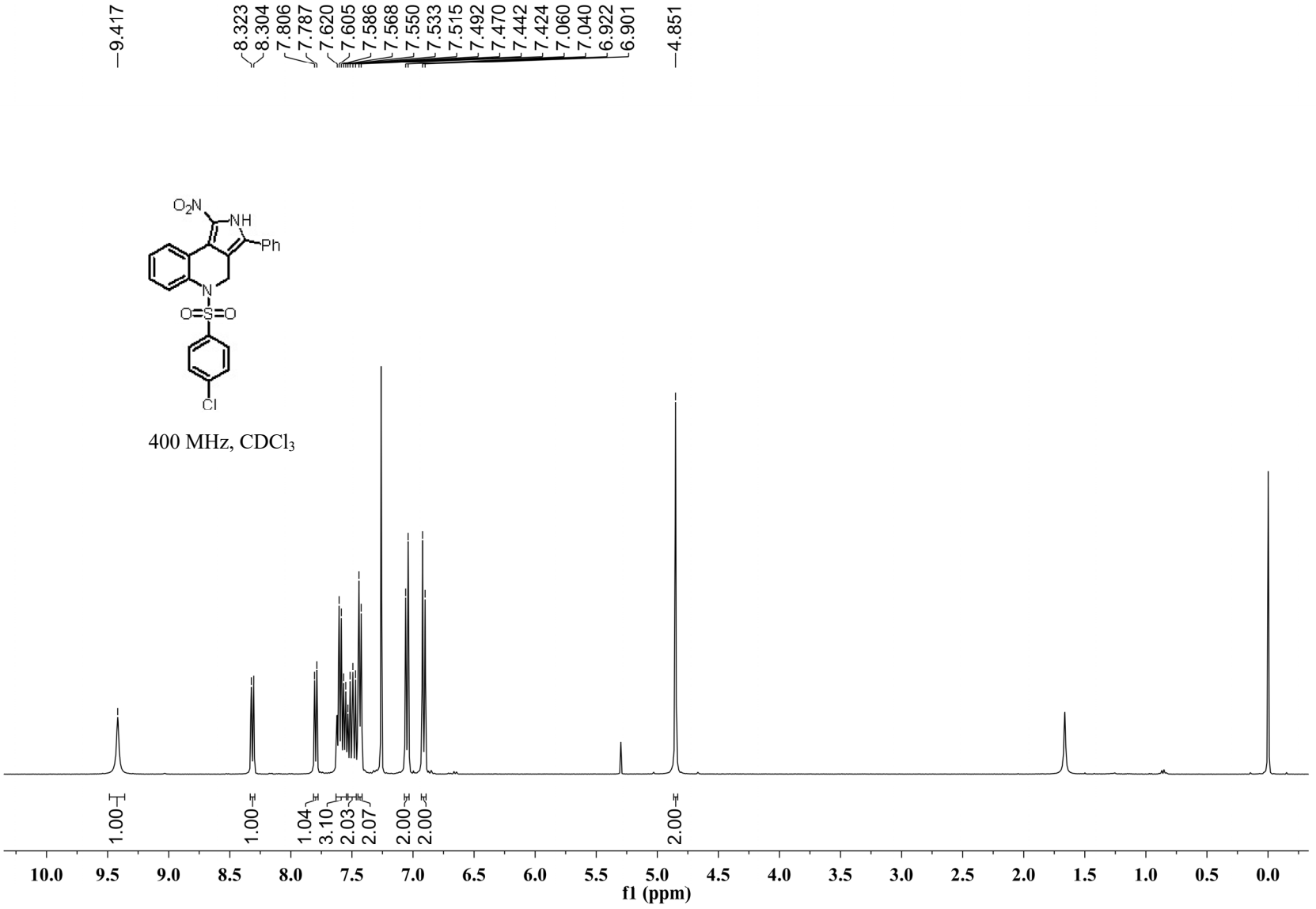
^{13}C NMR Spectrum of Compound 3v



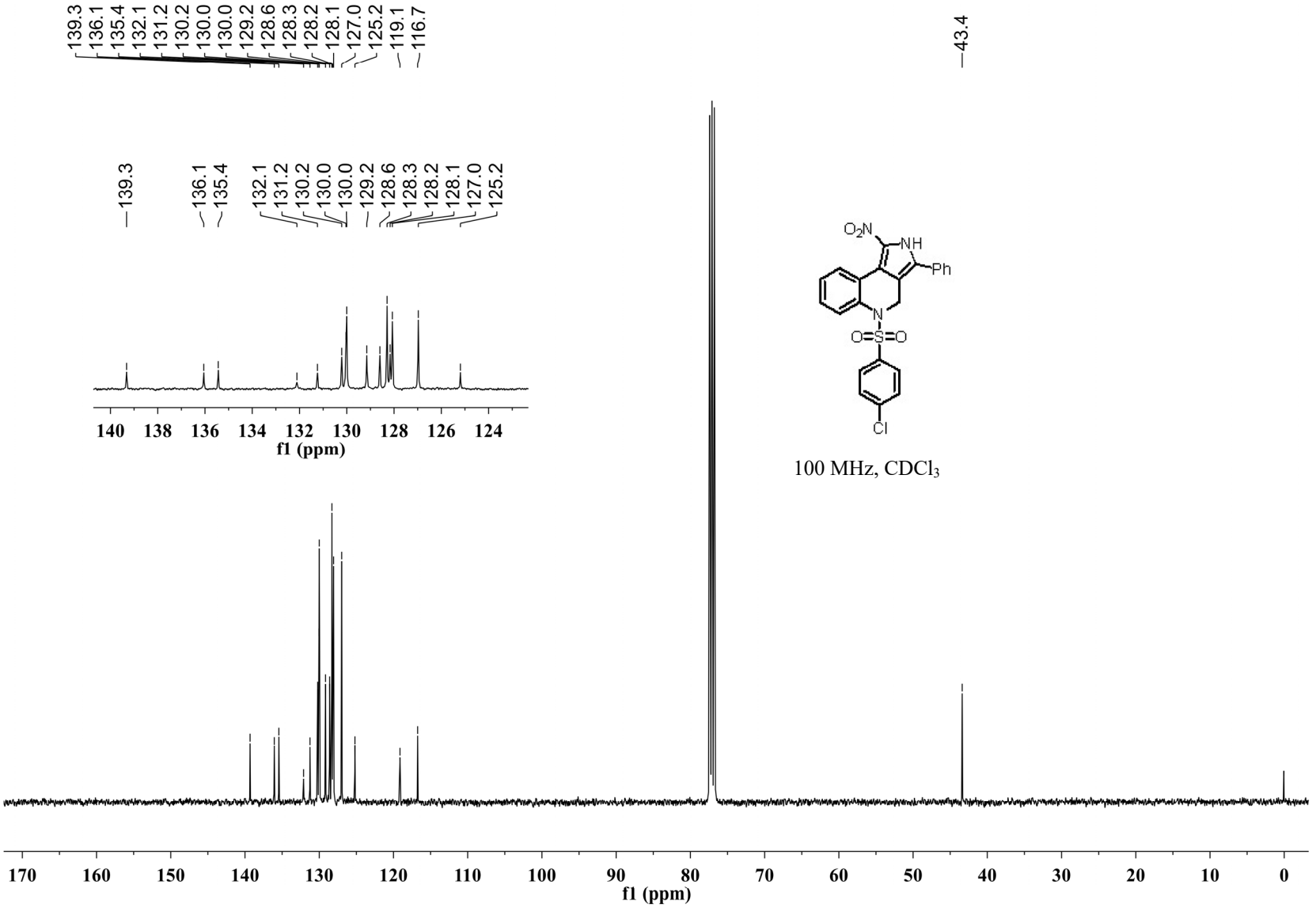
^{1}H NMR Spectrum of Compound 3w



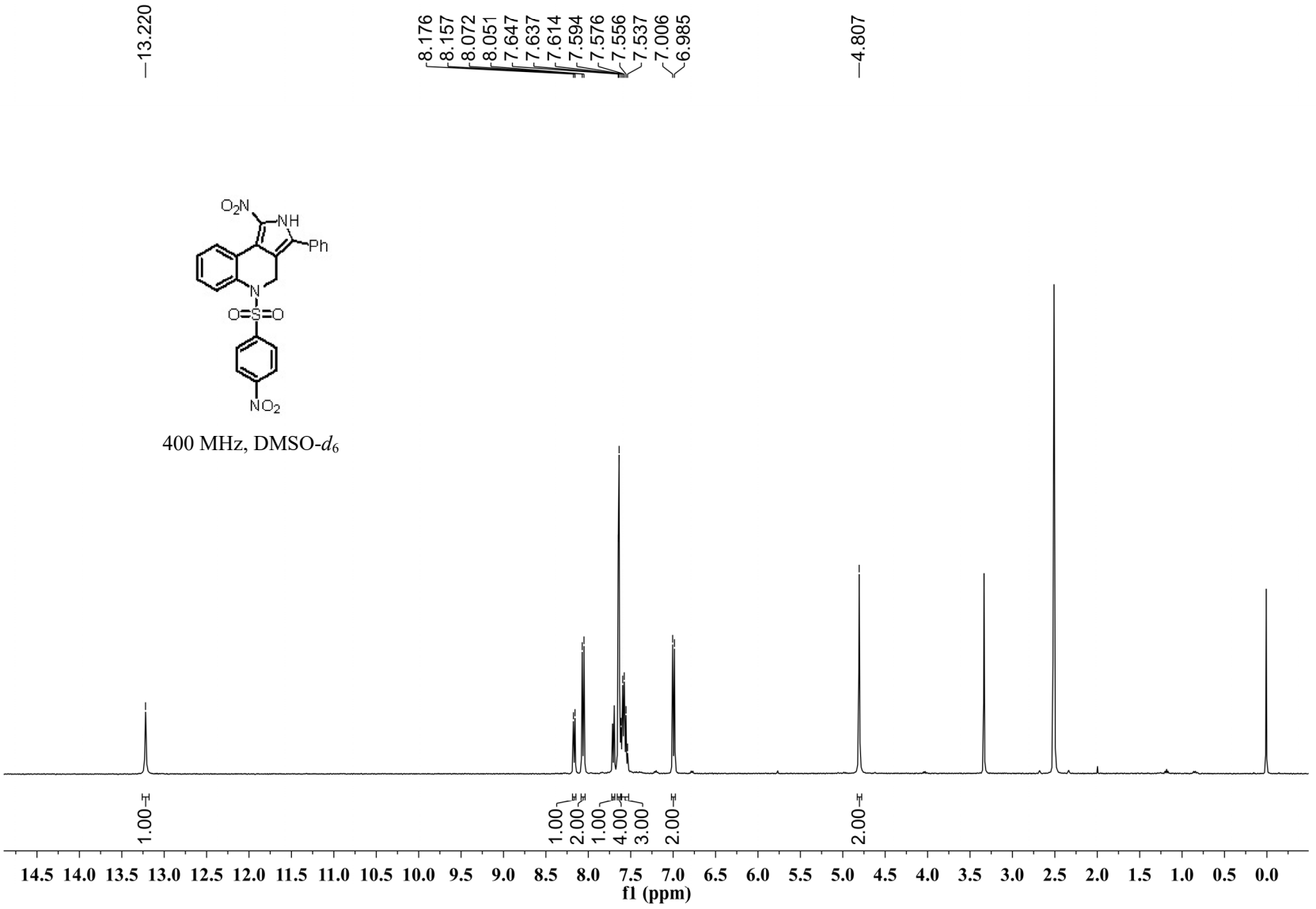
^{13}C NMR Spectrum of Compound 3w



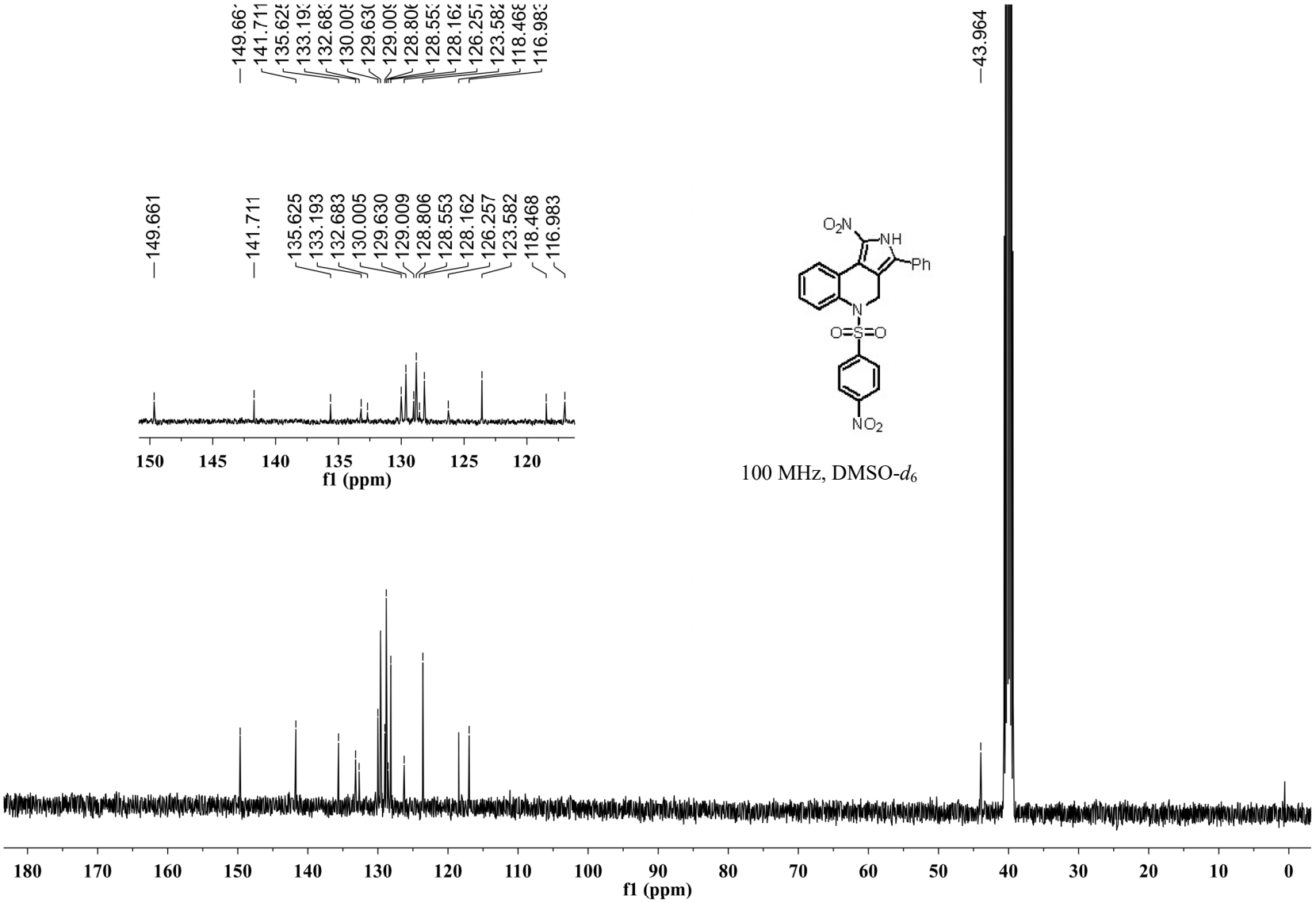
^{1}H NMR Spectrum of Compound 3x



^{13}C NMR Spectrum of Compound 3x

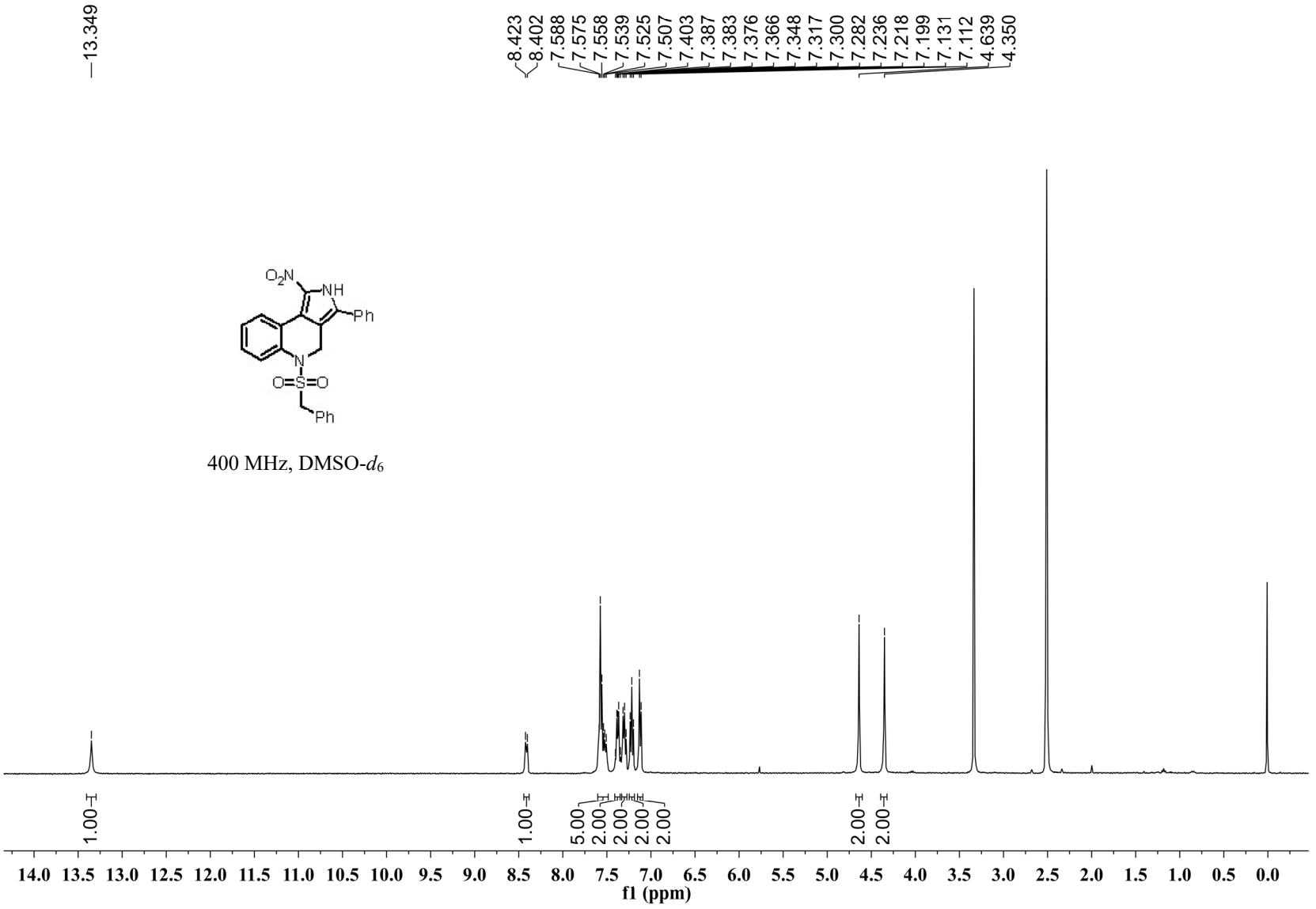


^{1}H NMR Spectrum of Compound 3y

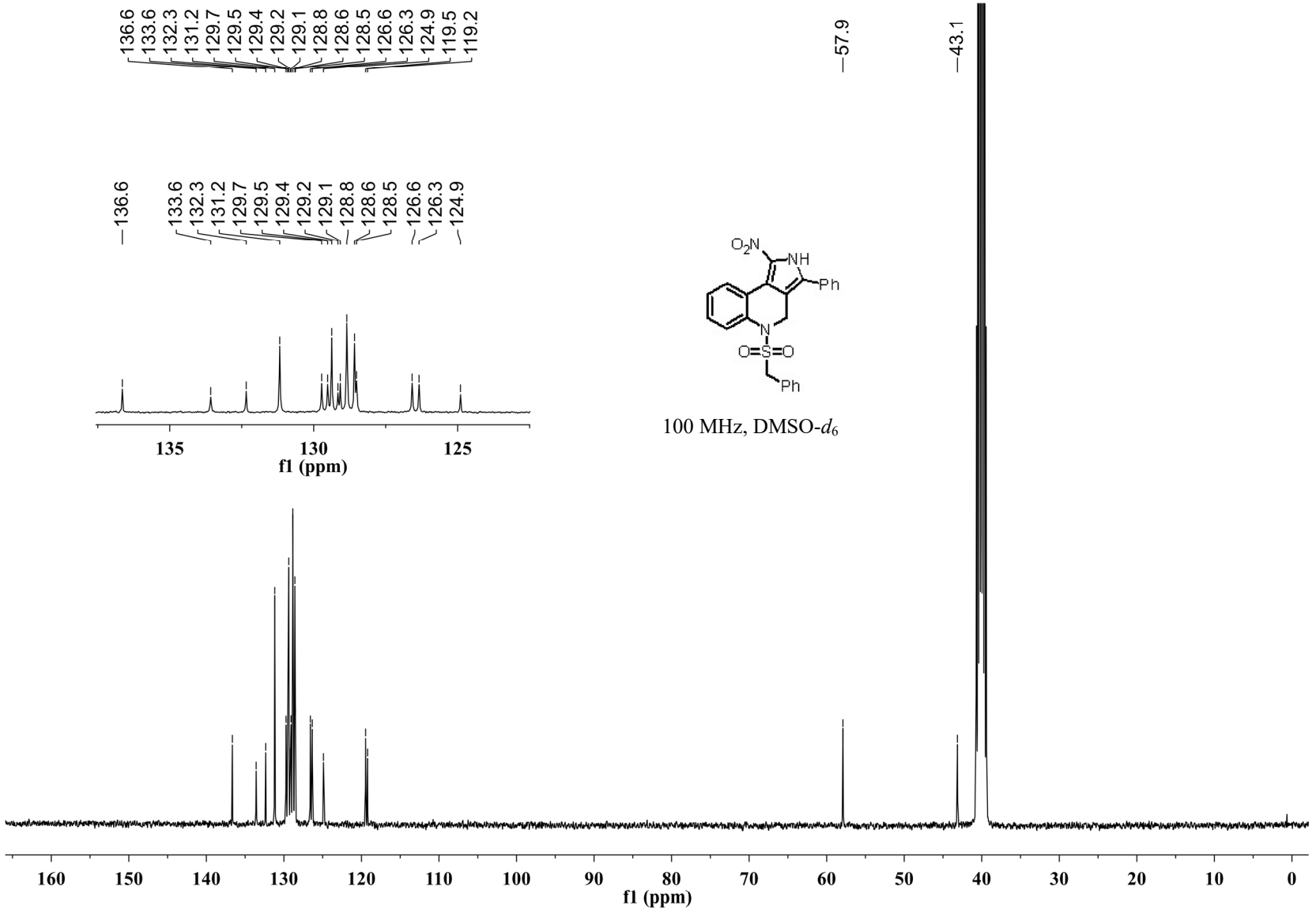


100 MHz, DMSO-d_6

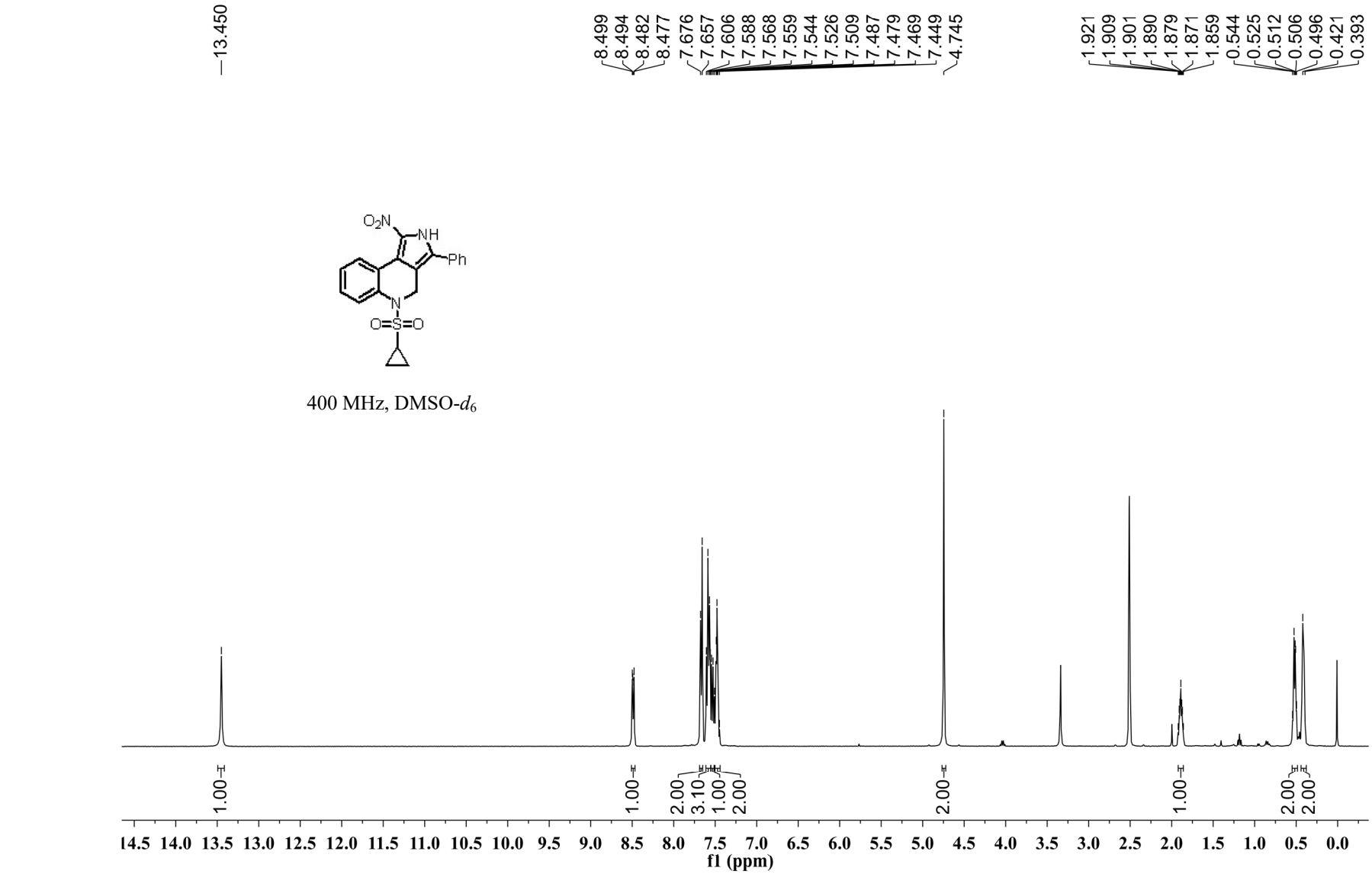
^{13}C NMR Spectrum of Compound 3y



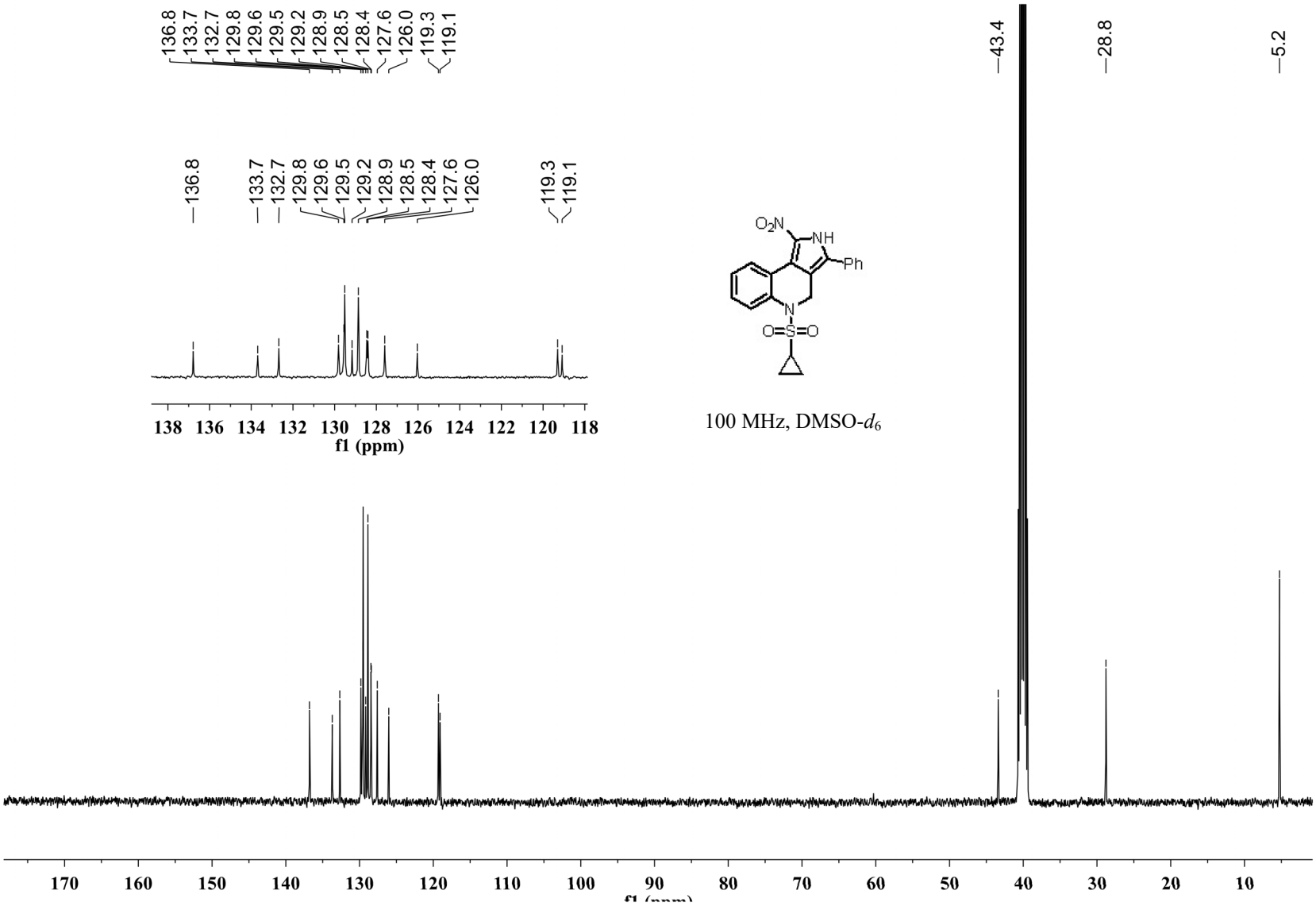
^{1}H NMR Spectrum of Compound 3z



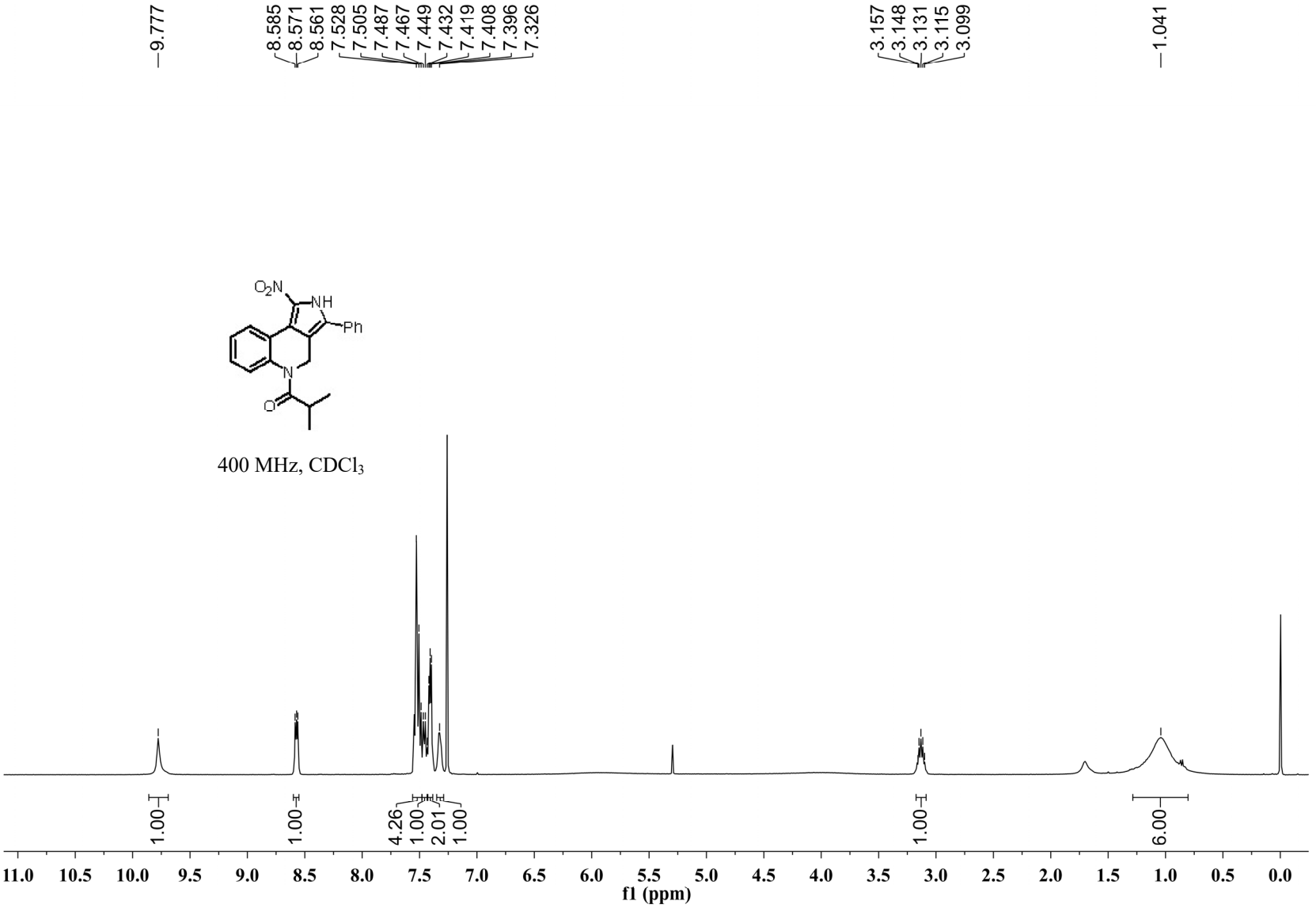
^{13}C NMR Spectrum of Compound 3z



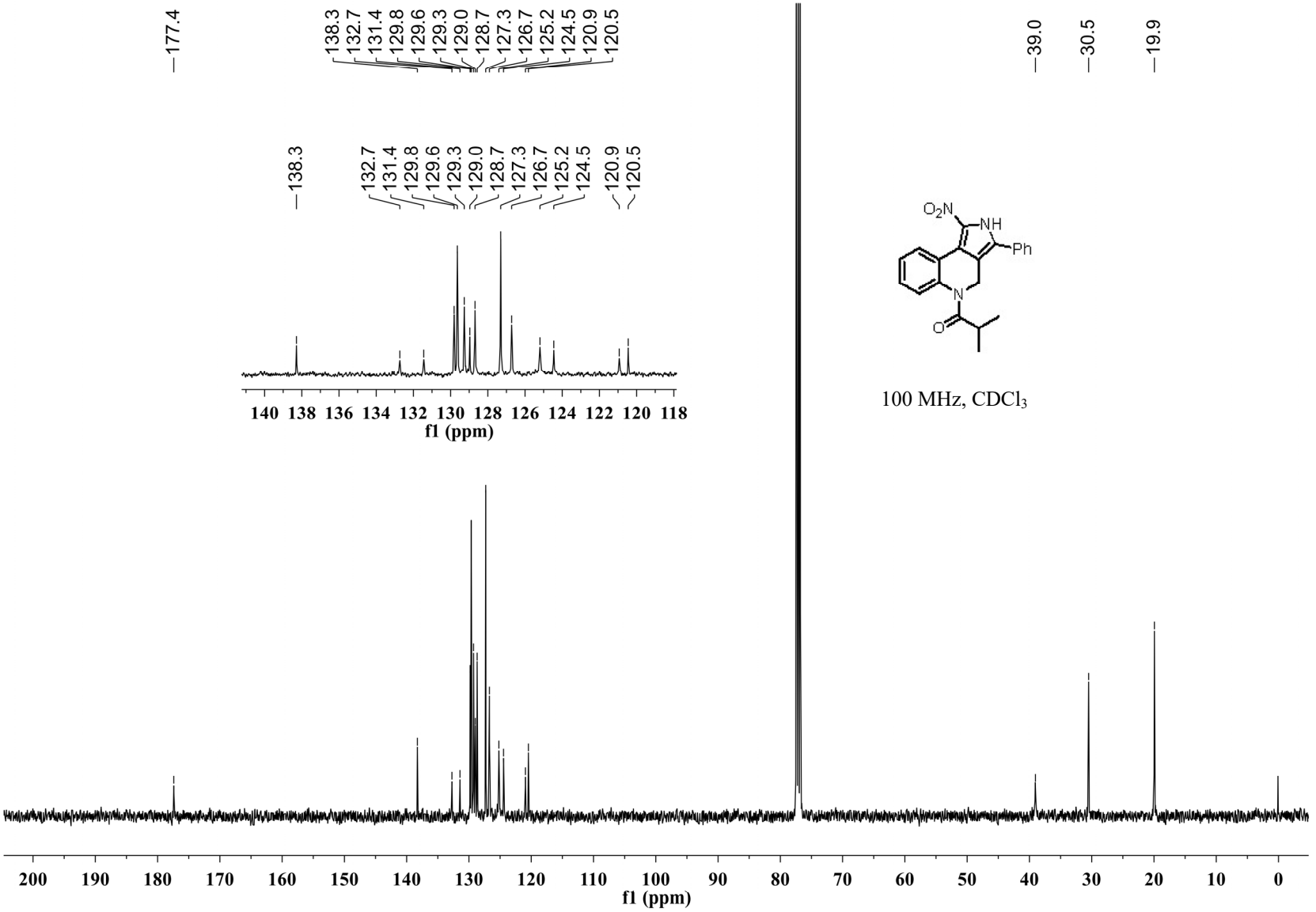
^{1}H NMR Spectrum of Compound 3aa



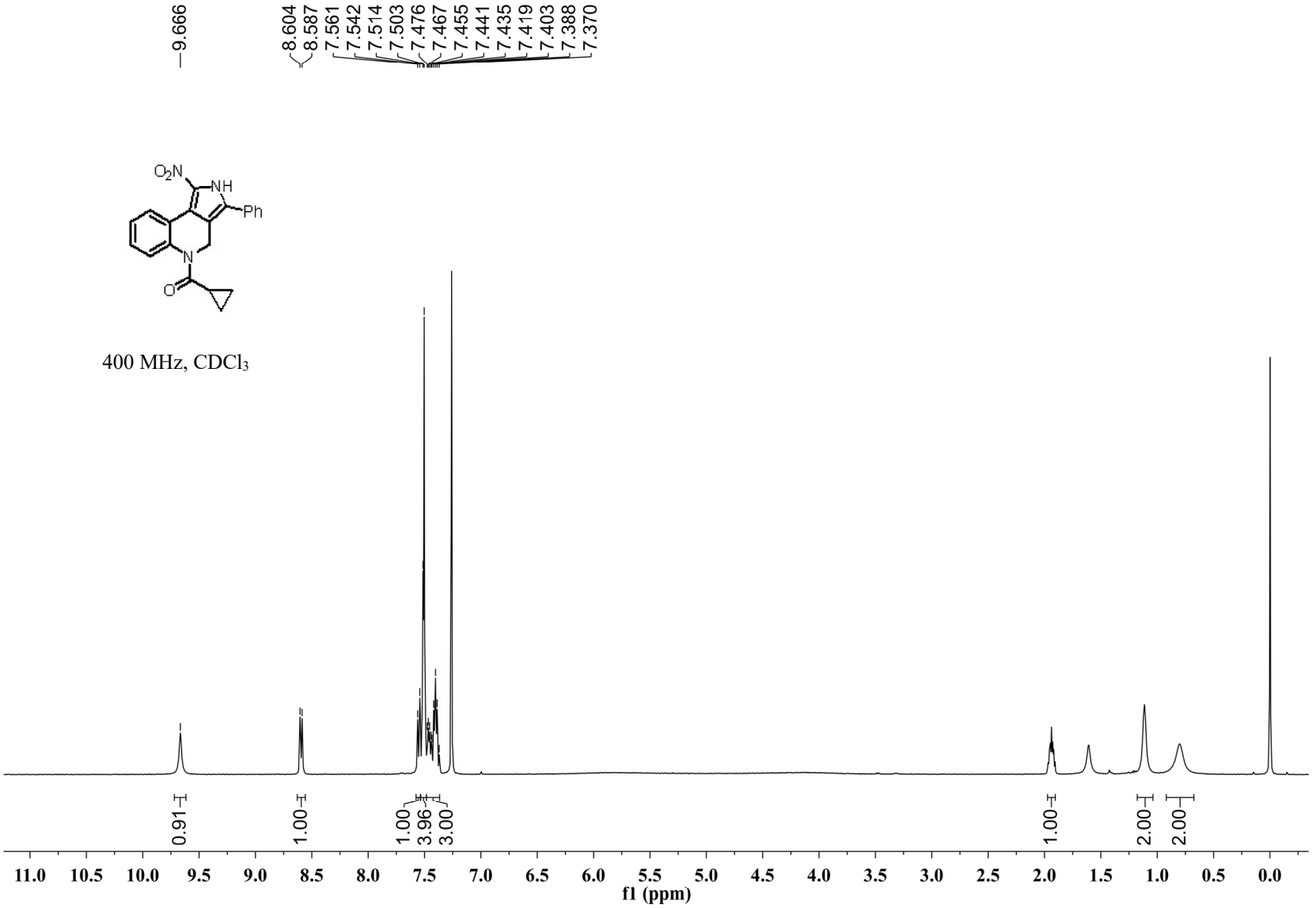
^{13}C NMR Spectrum of Compound 3aa



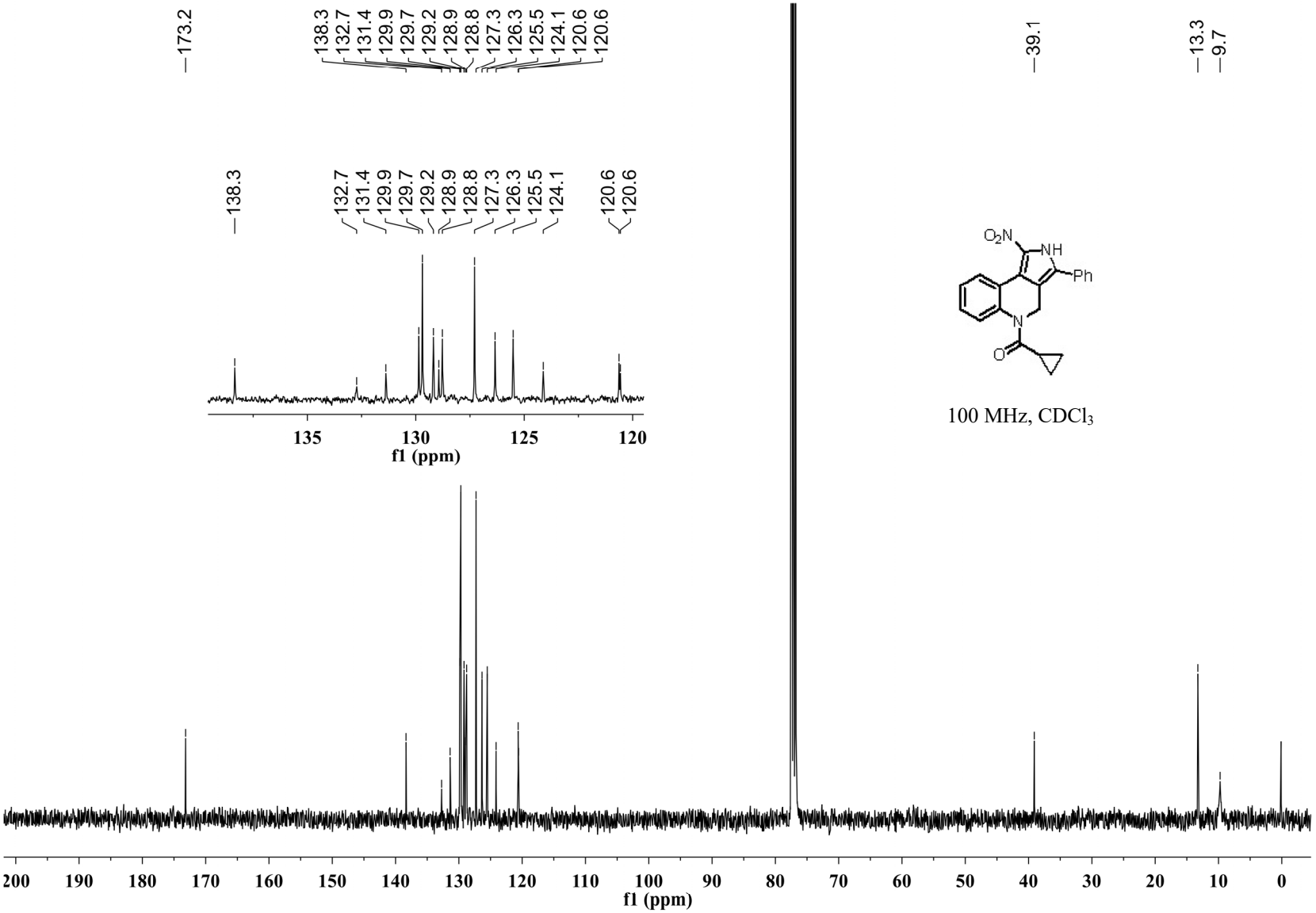
^{1}H NMR Spectrum of Compound 3bb



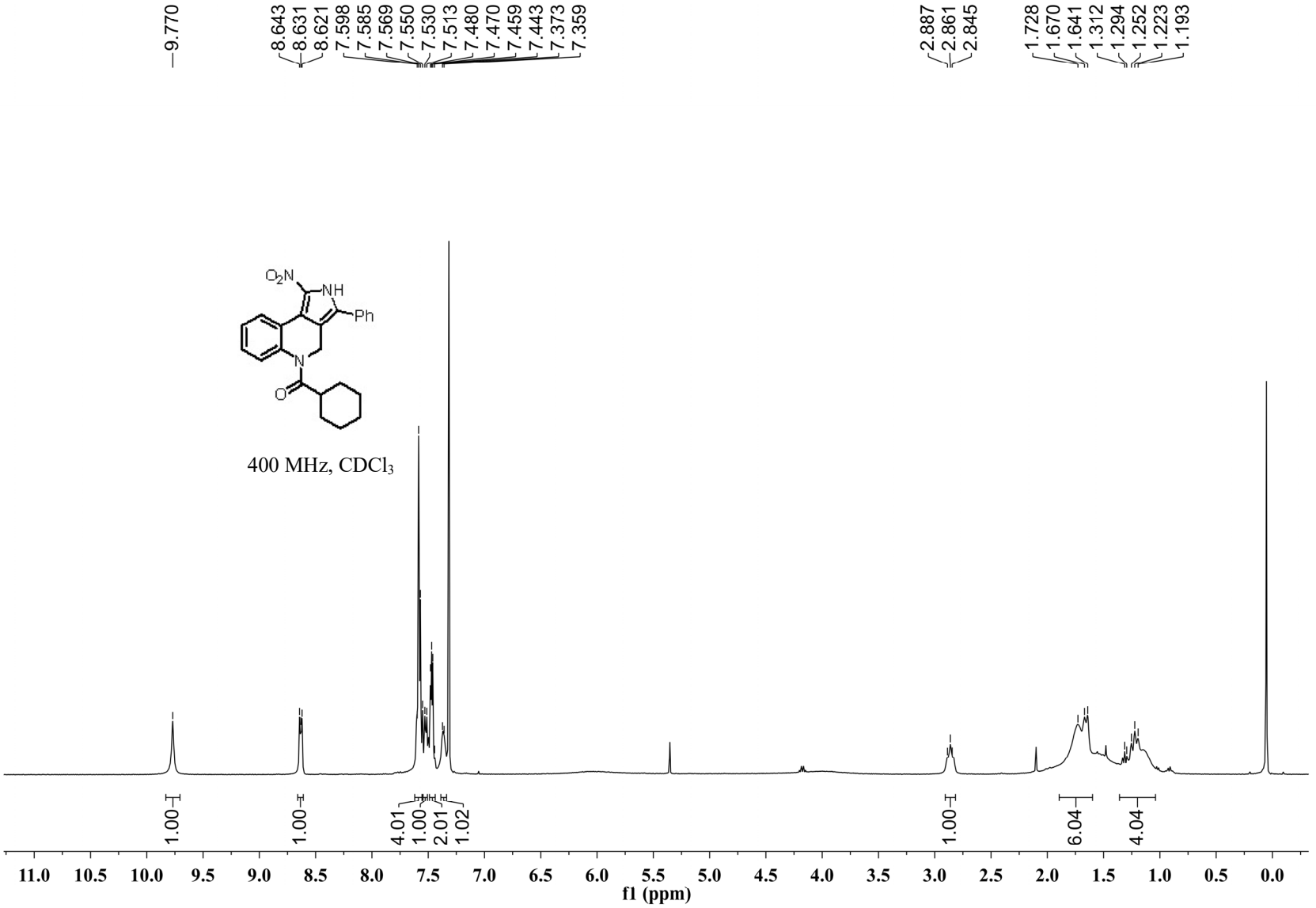
^{13}C NMR Spectrum of Compound 3bb



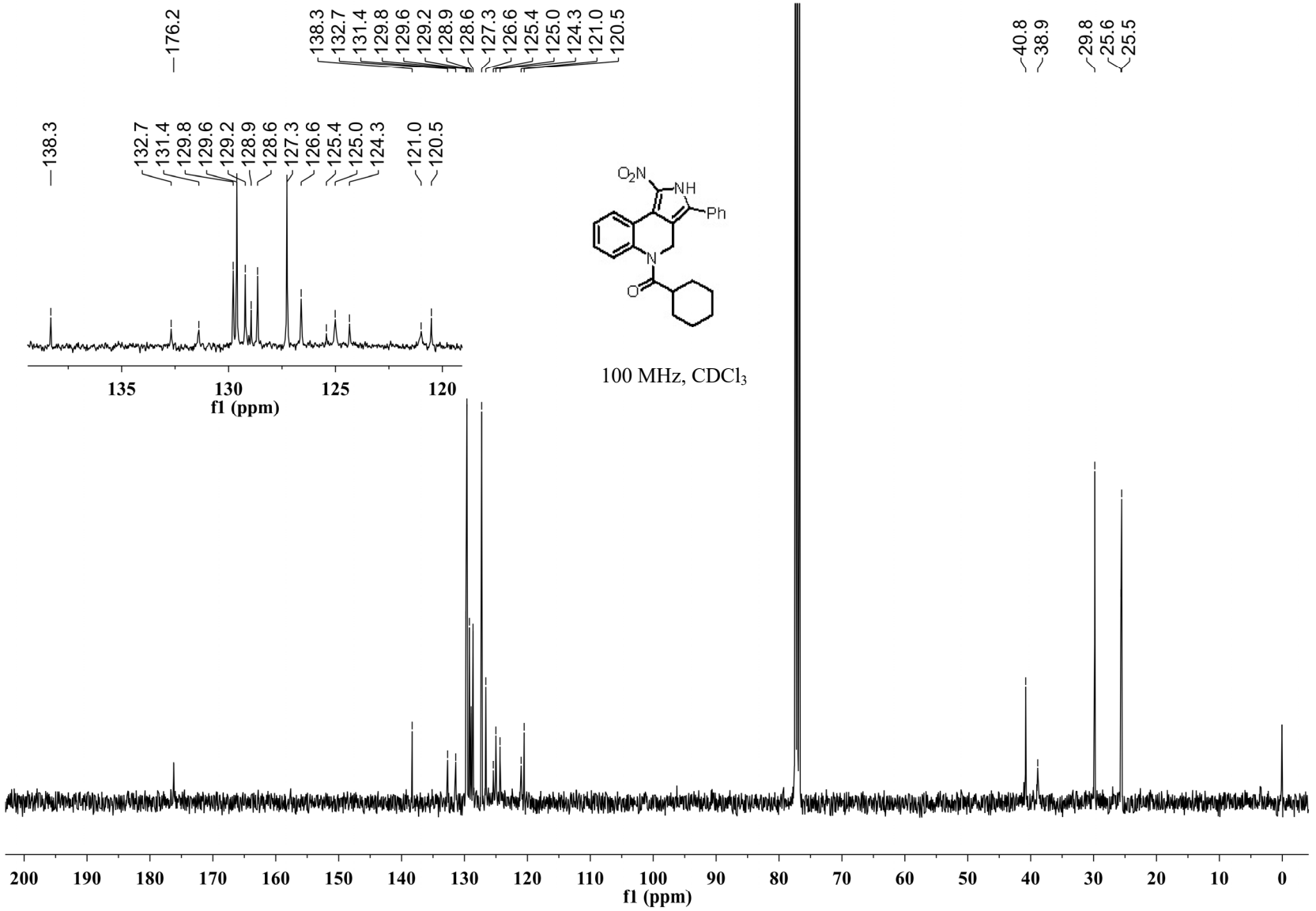
^{1}H NMR Spectrum of Compound 3cc



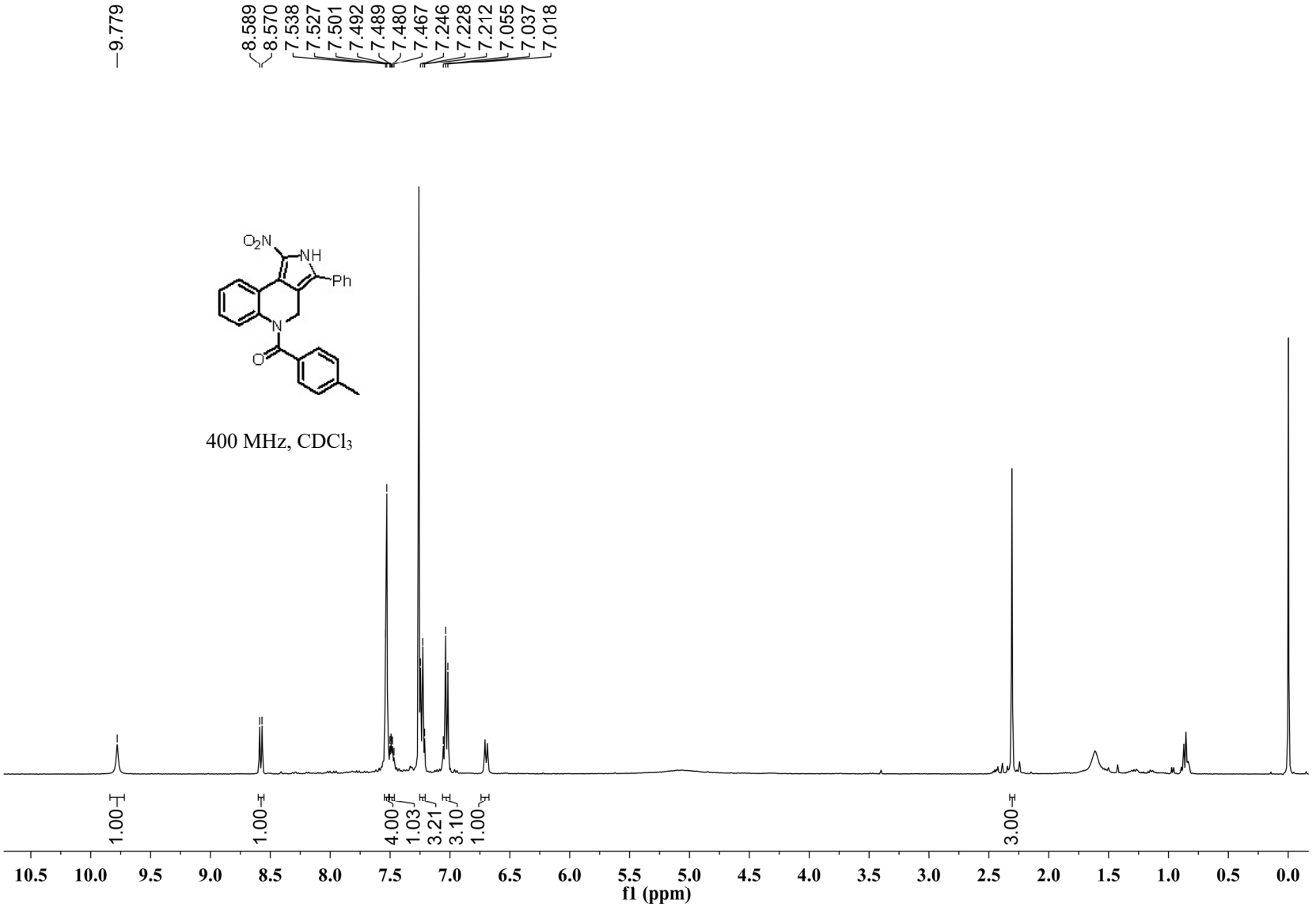
^{13}C NMR Spectrum of Compound 3cc



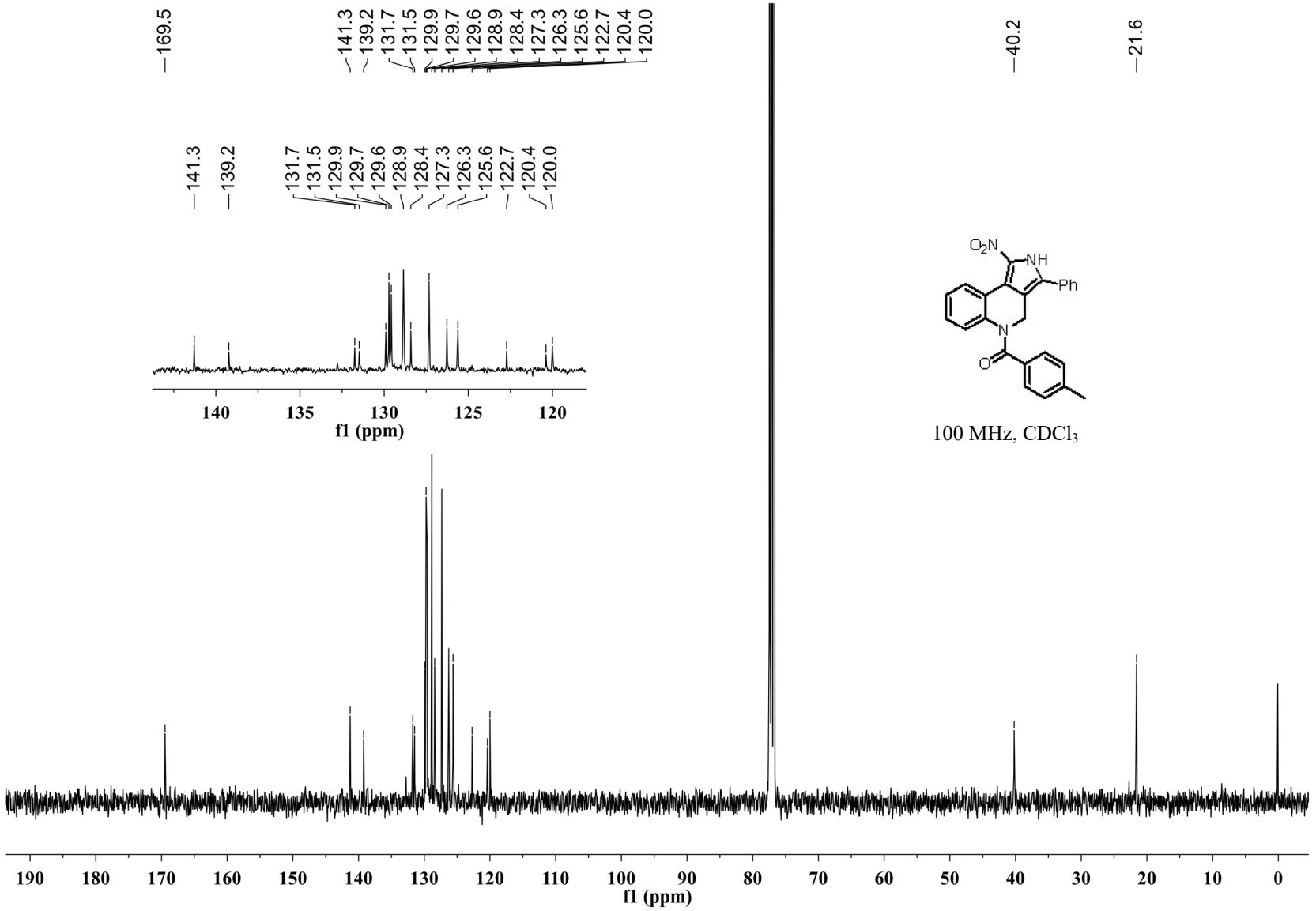
^{1}H NMR Spectrum of Compound 3dd



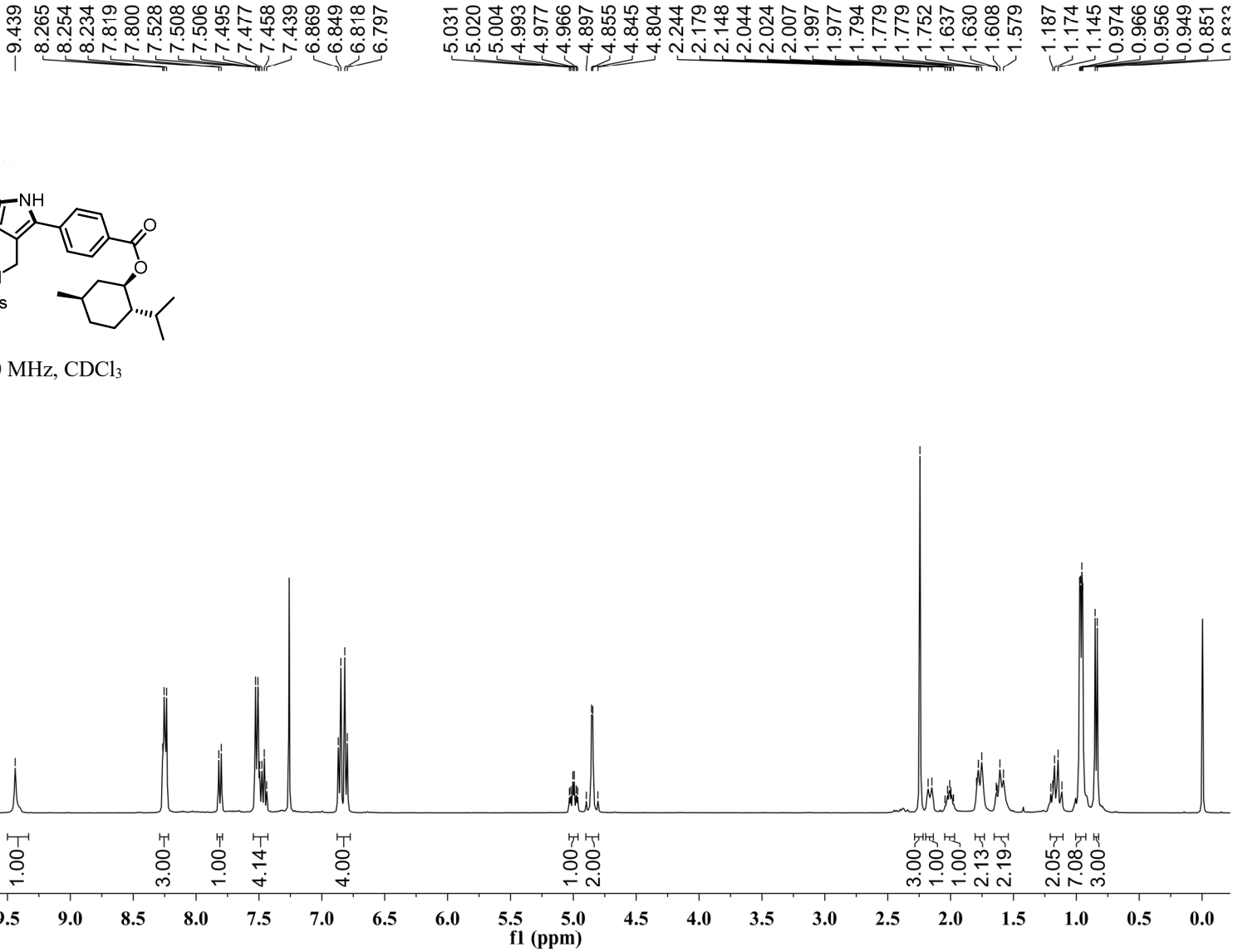
^{13}C NMR Spectrum of Compound 3dd



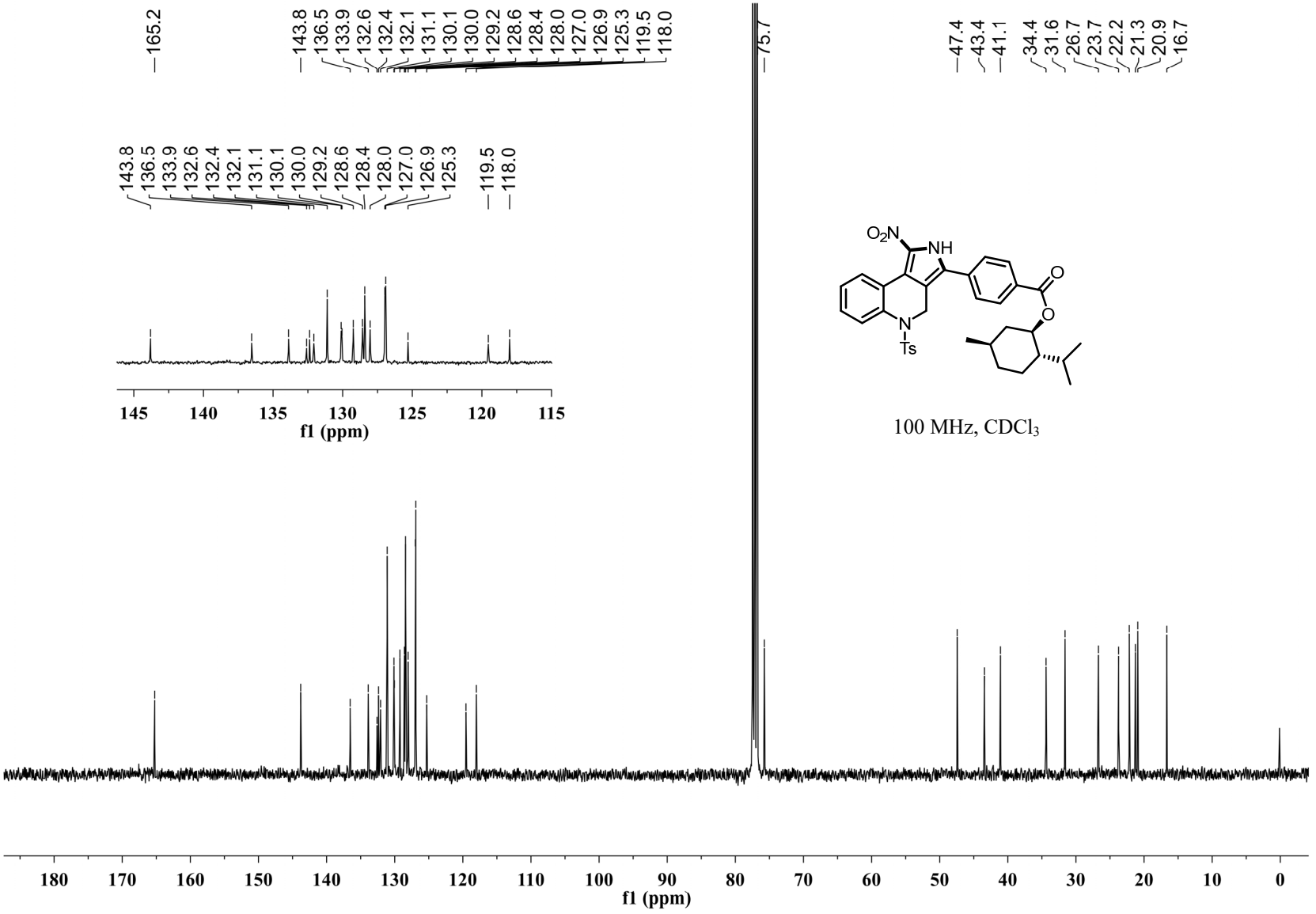
^{1}H NMR Spectrum of Compound 3ee



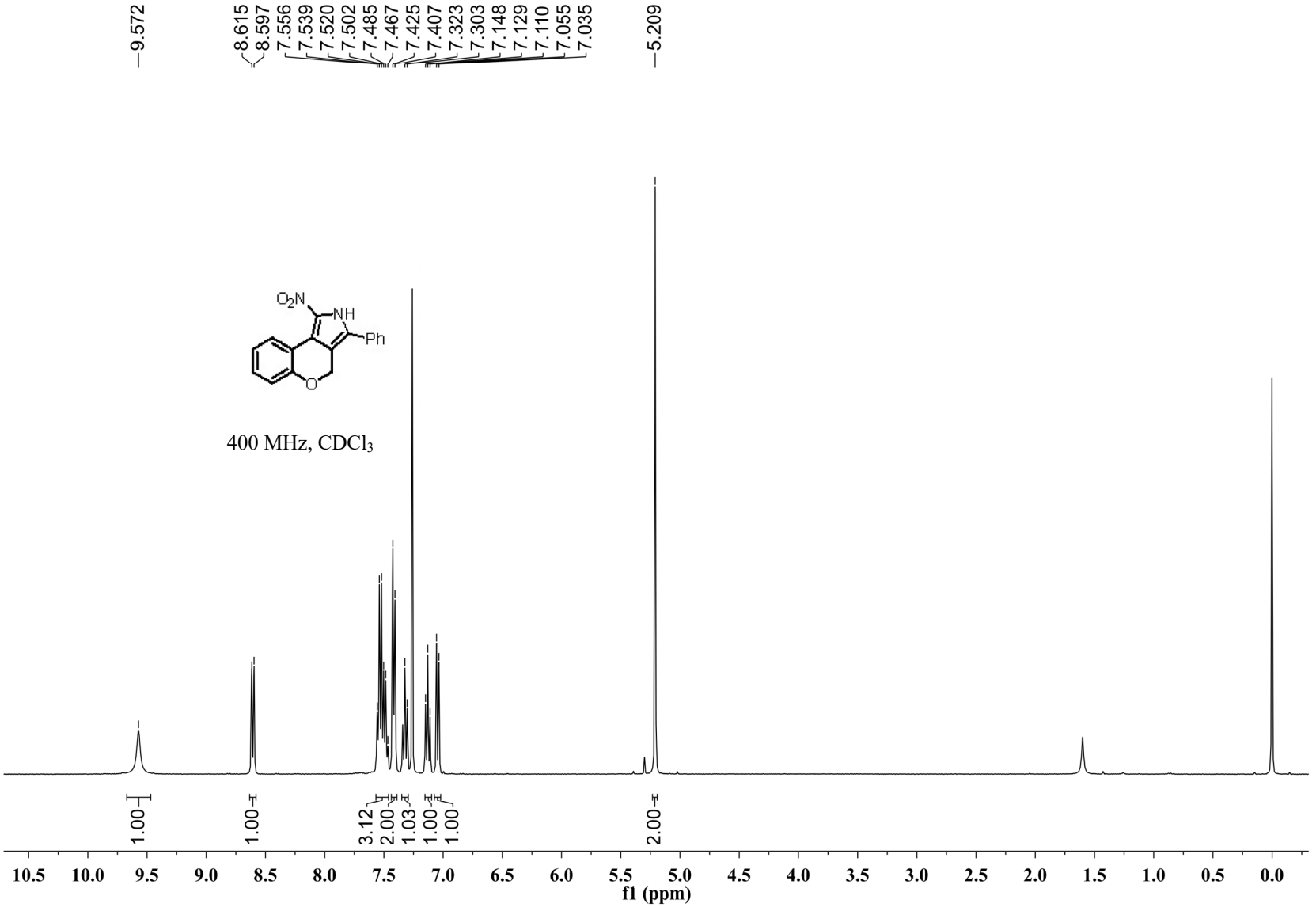
^{13}C NMR Spectrum of Compound 3ee



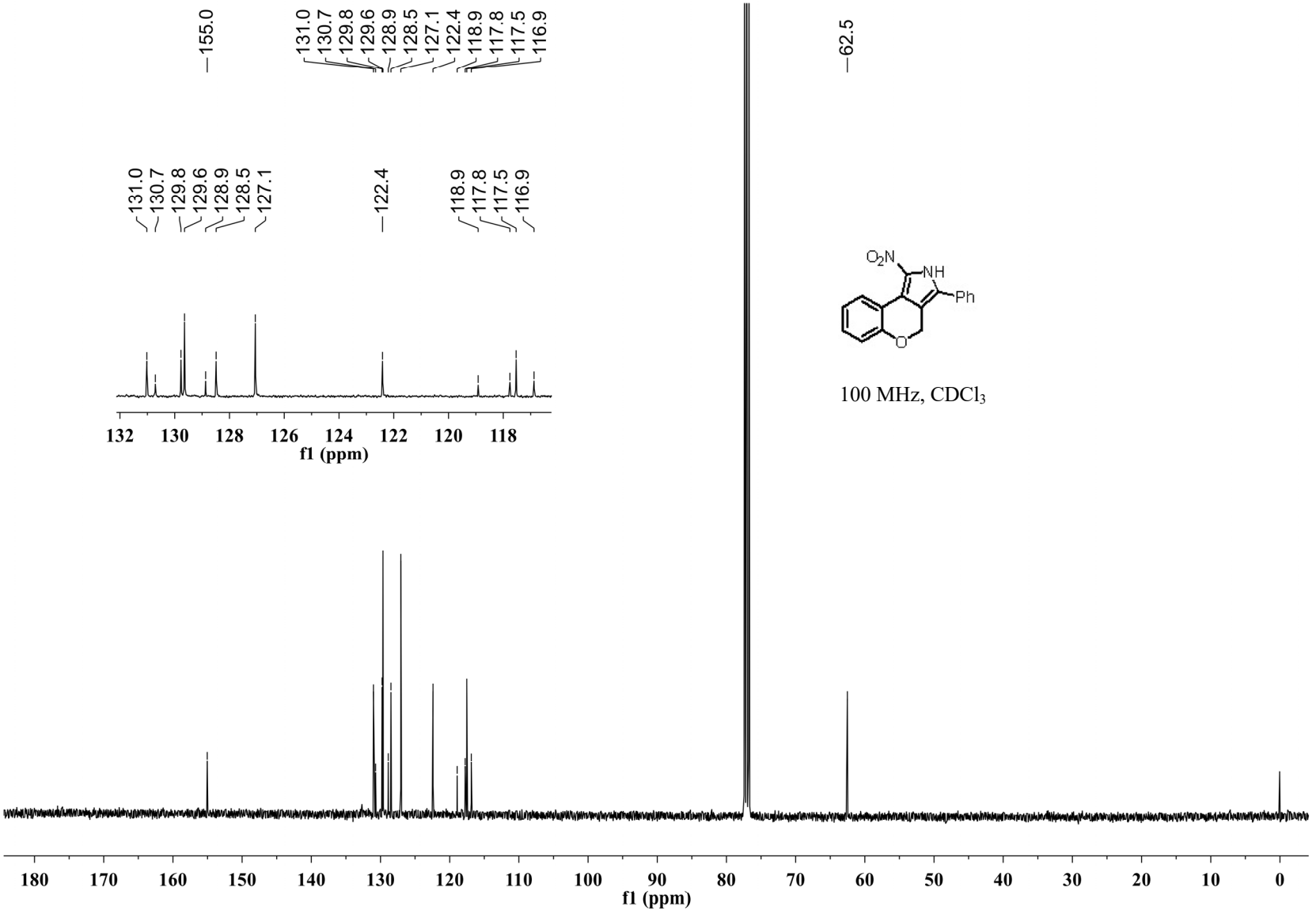
^{1}H NMR Spectrum of Compound 3ff



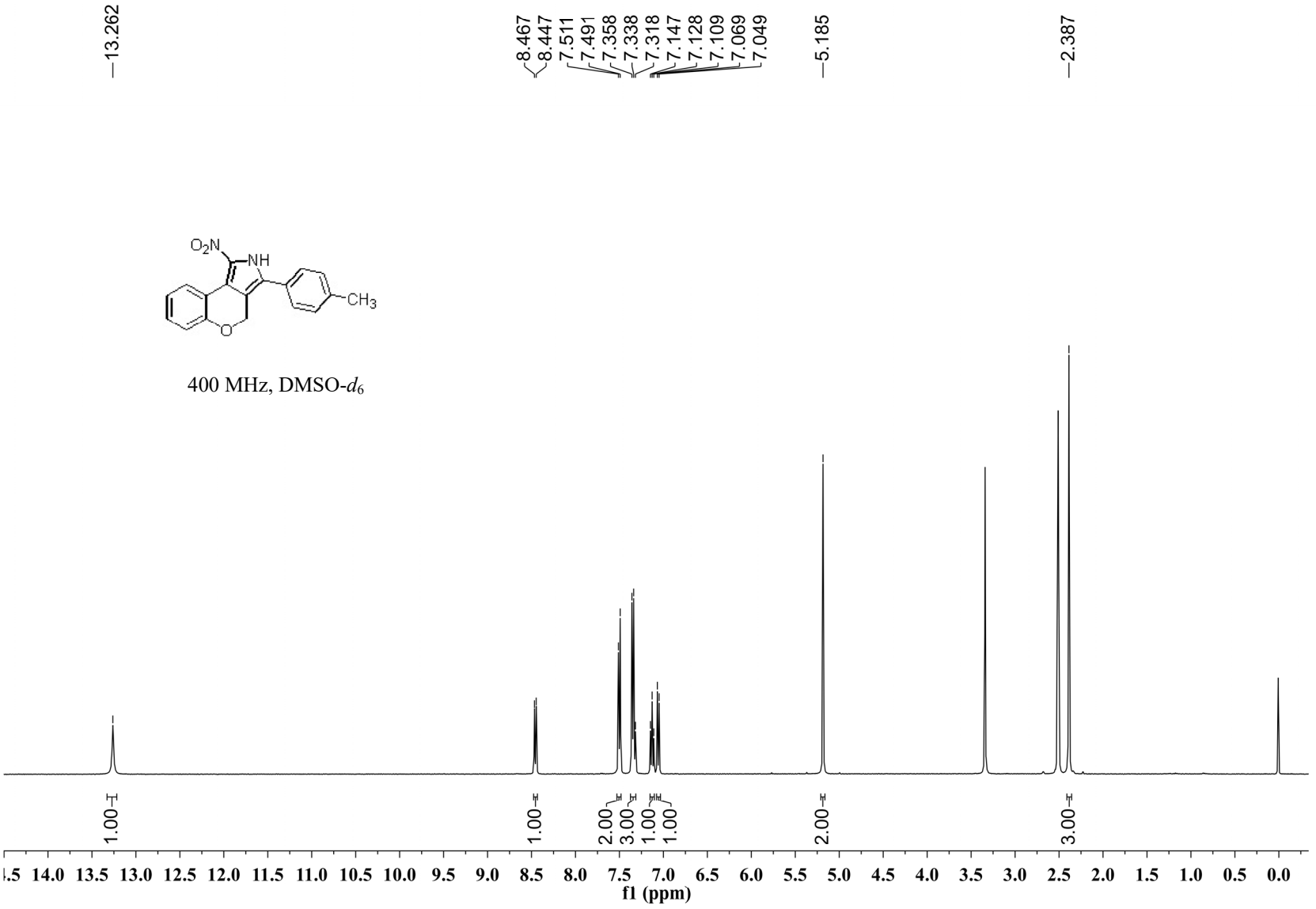
^{13}C NMR Spectrum of Compound 3ff



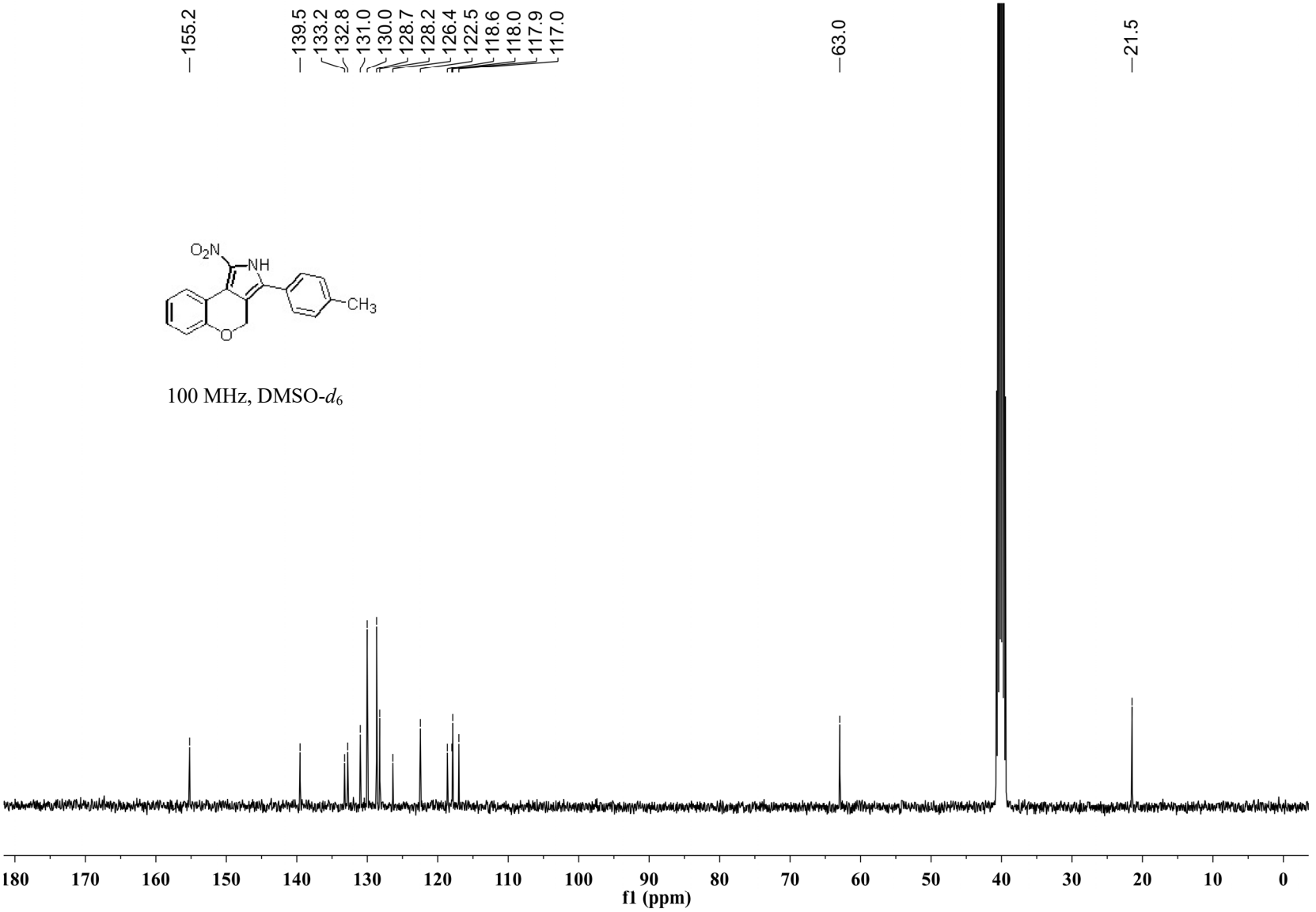
^{1}H NMR Spectrum of Compound 5a



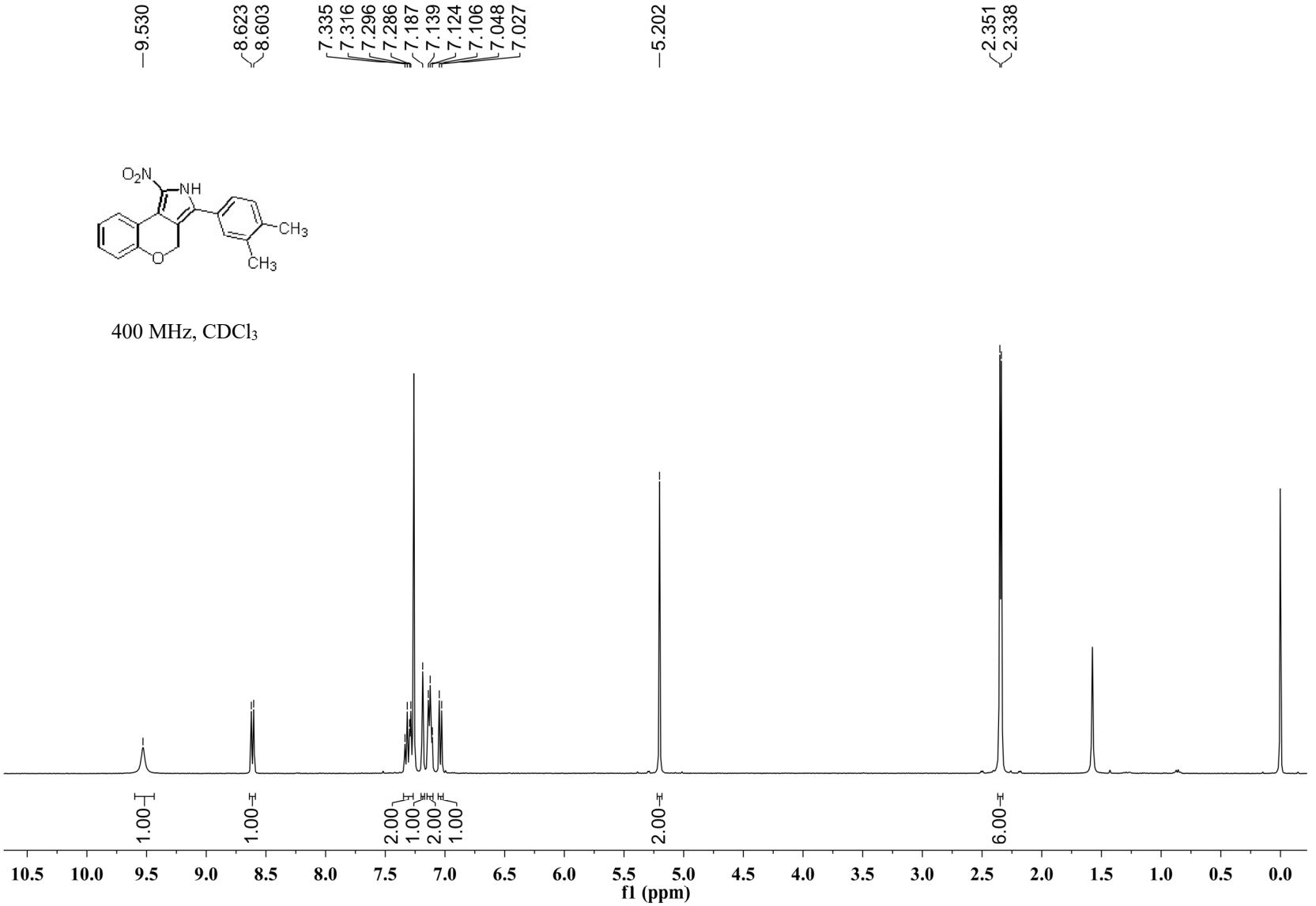
^{13}C NMR Spectrum of Compound 5a



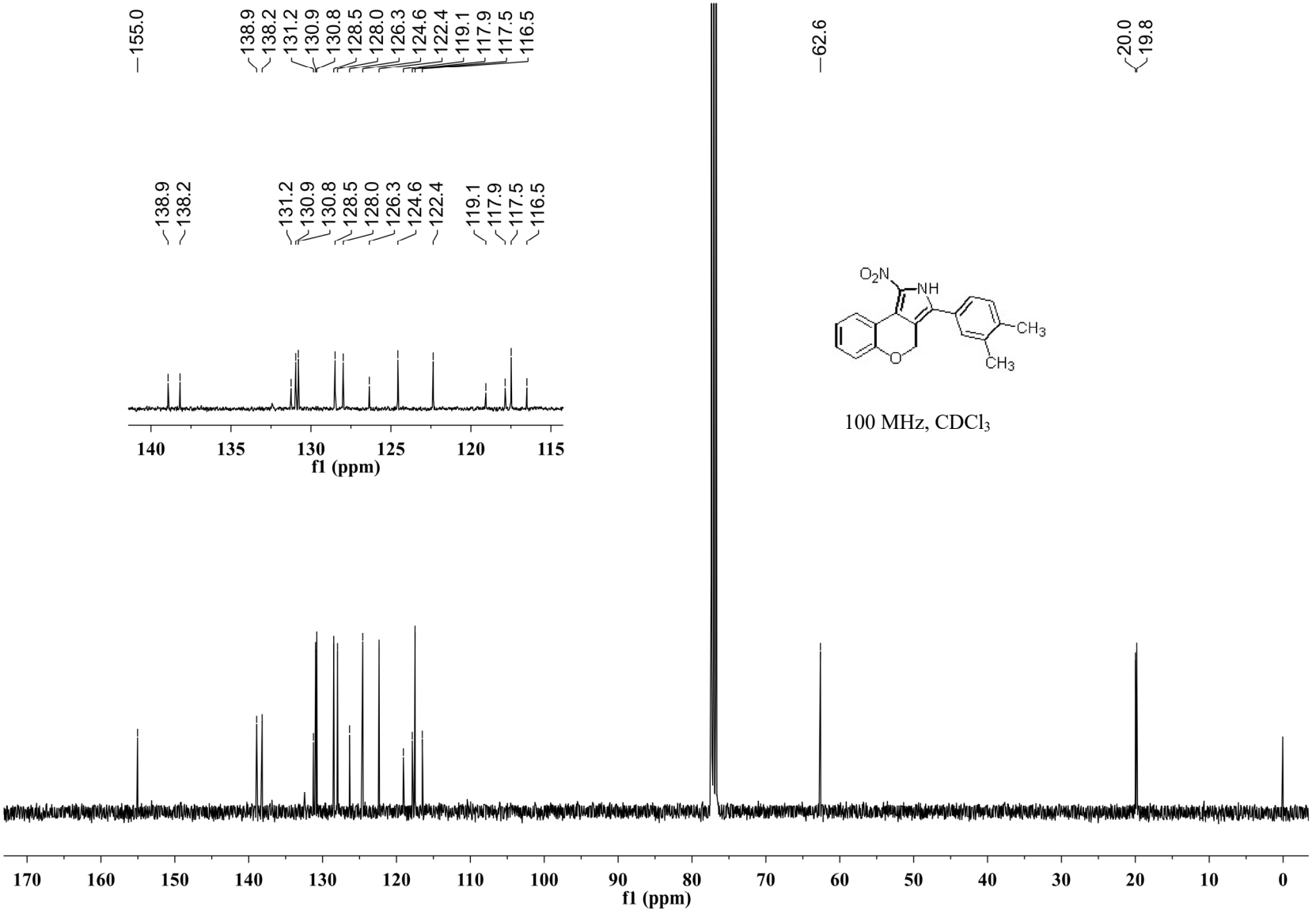
^{1}H NMR Spectrum of Compound 5b



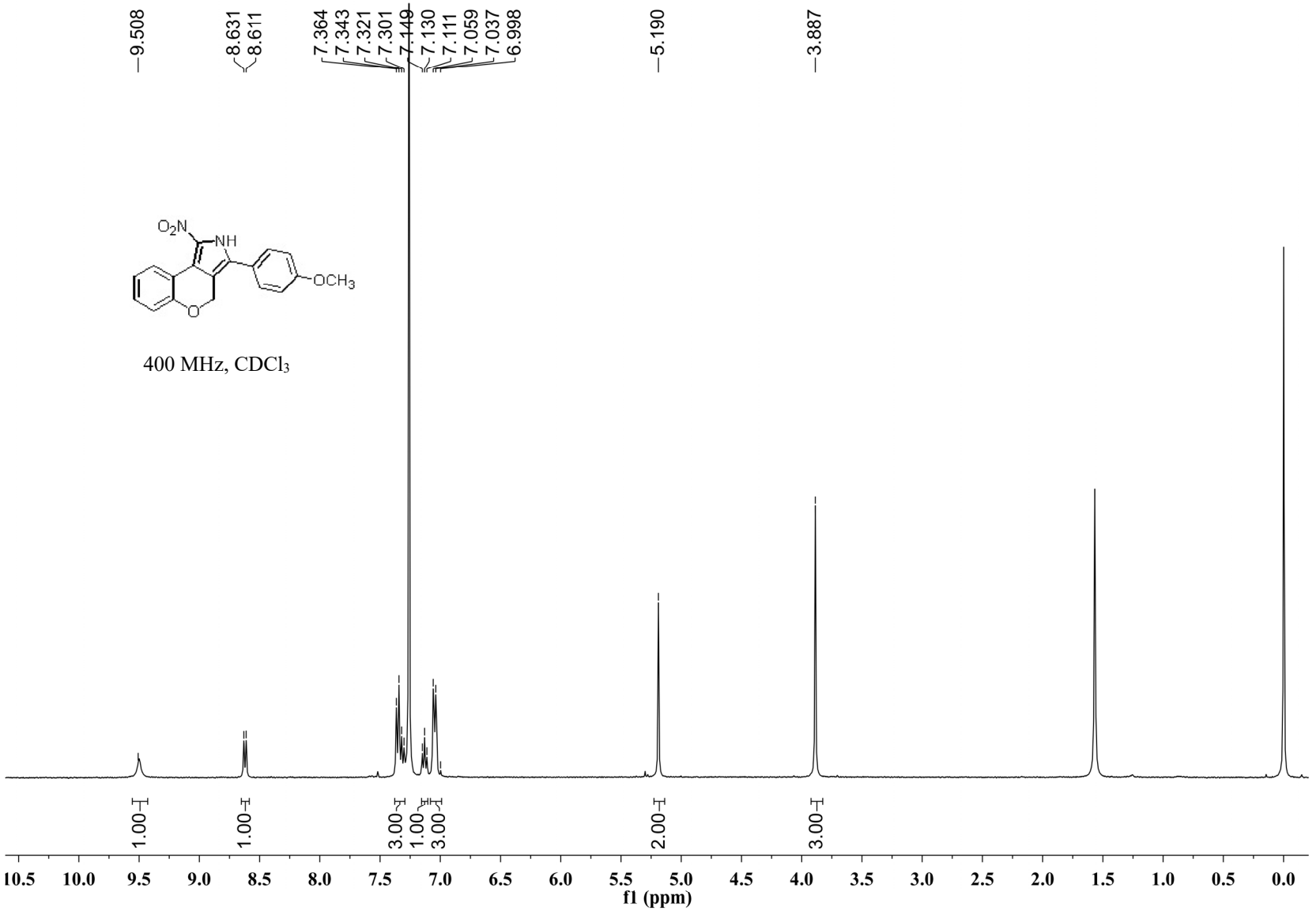
^{13}C NMR Spectrum of Compound 5b



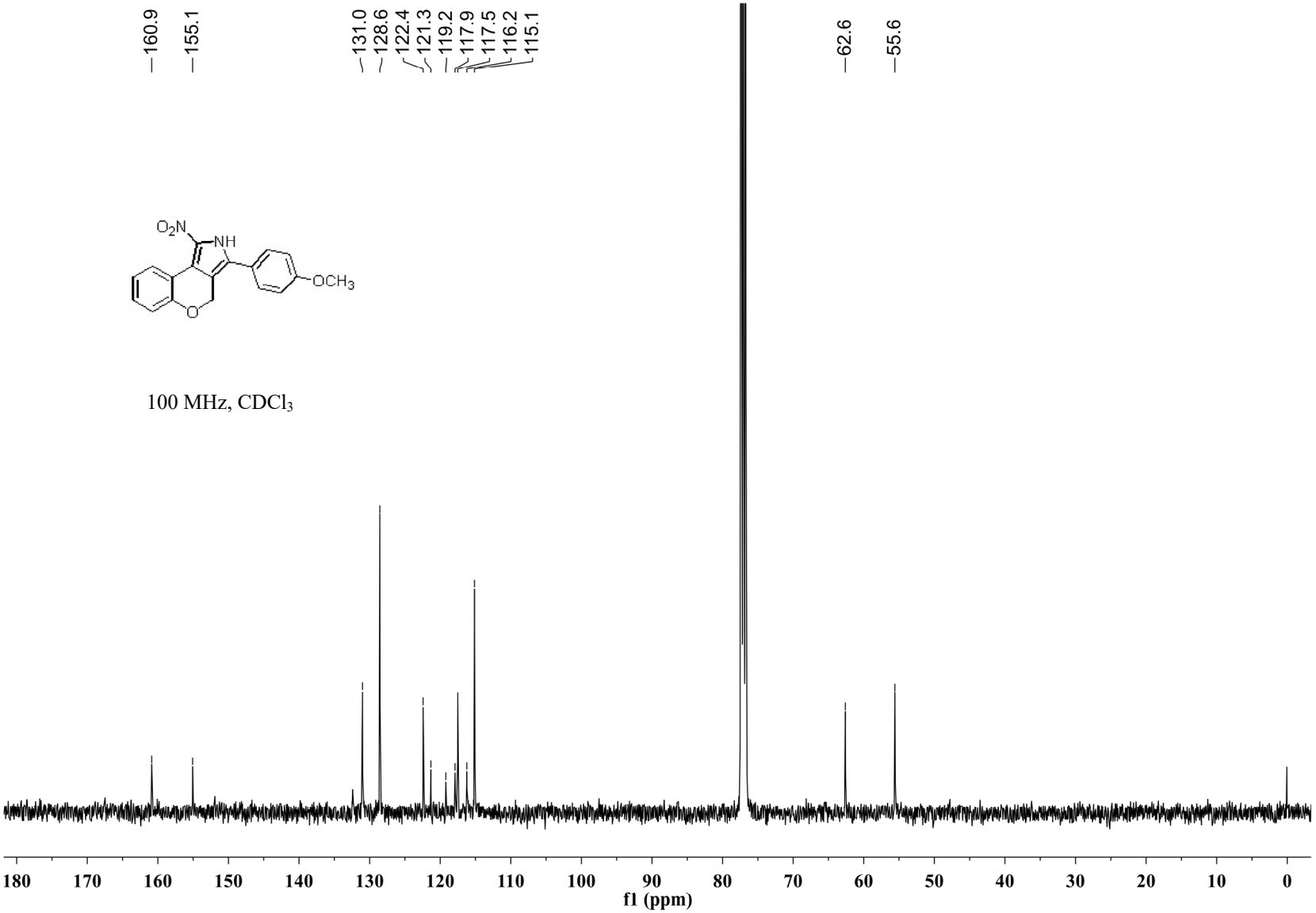
^{1}H NMR Spectrum of Compound 5c



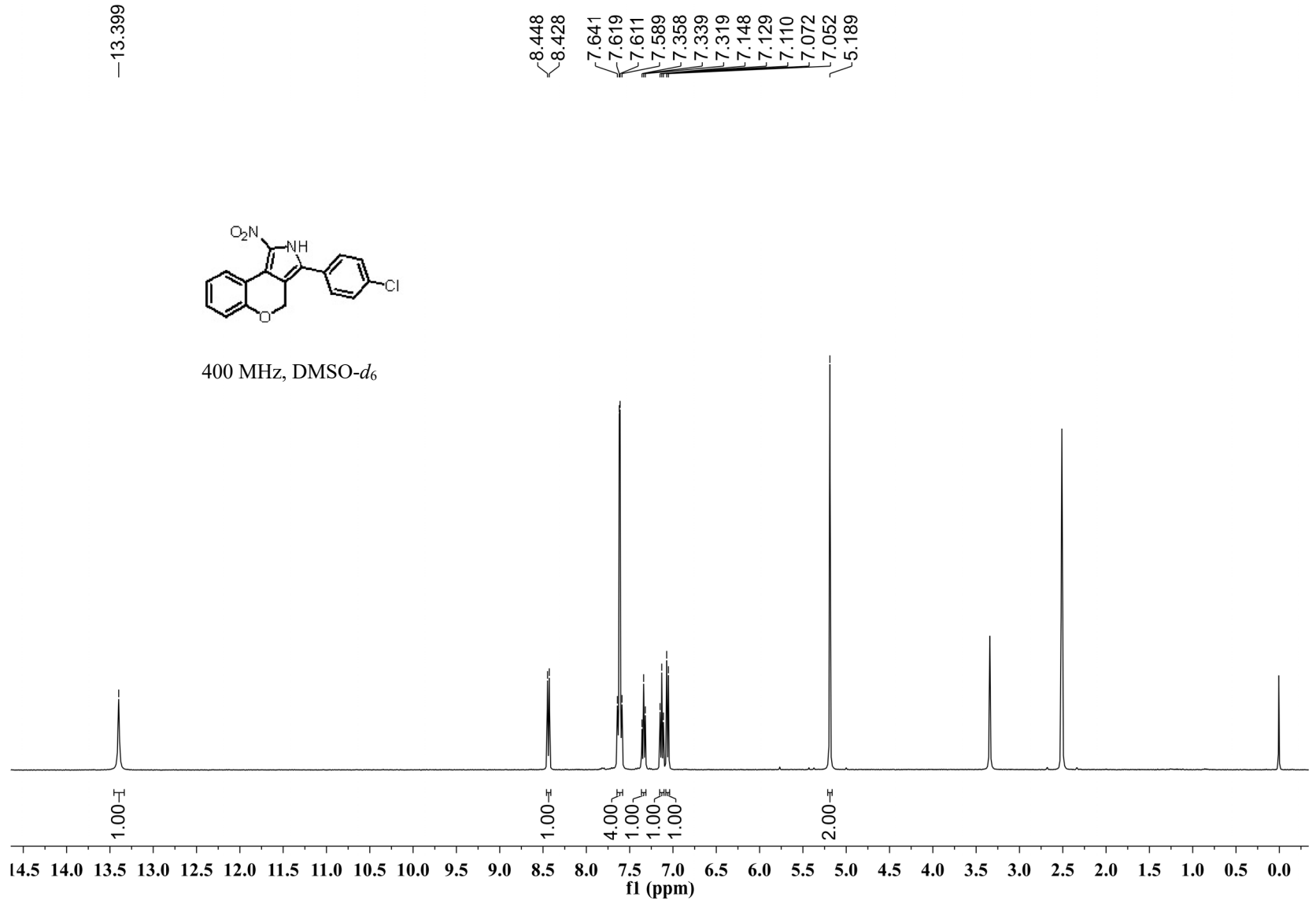
^{13}C NMR Spectrum of Compound 5c



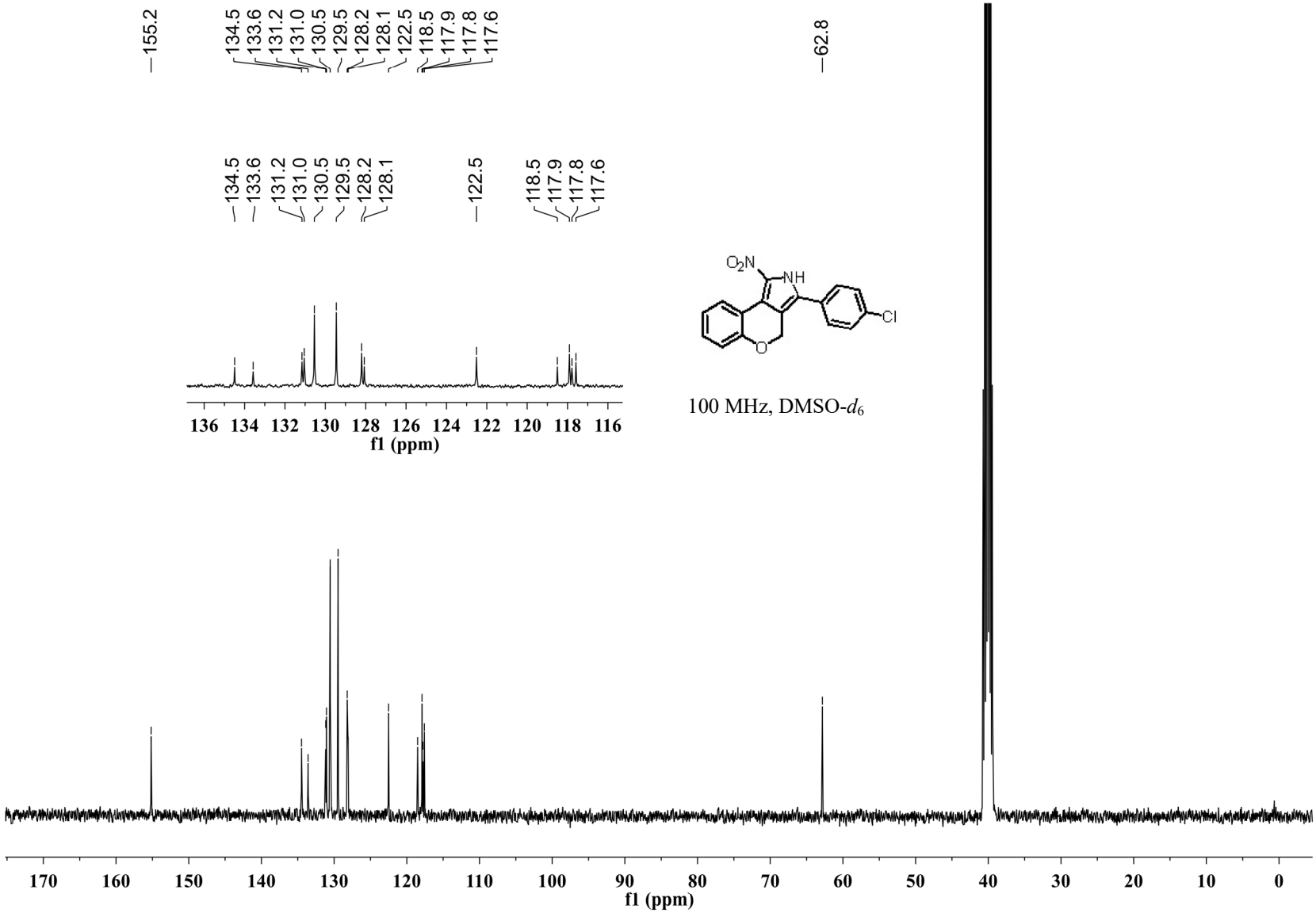
^{1}H NMR Spectrum of Compound 5d



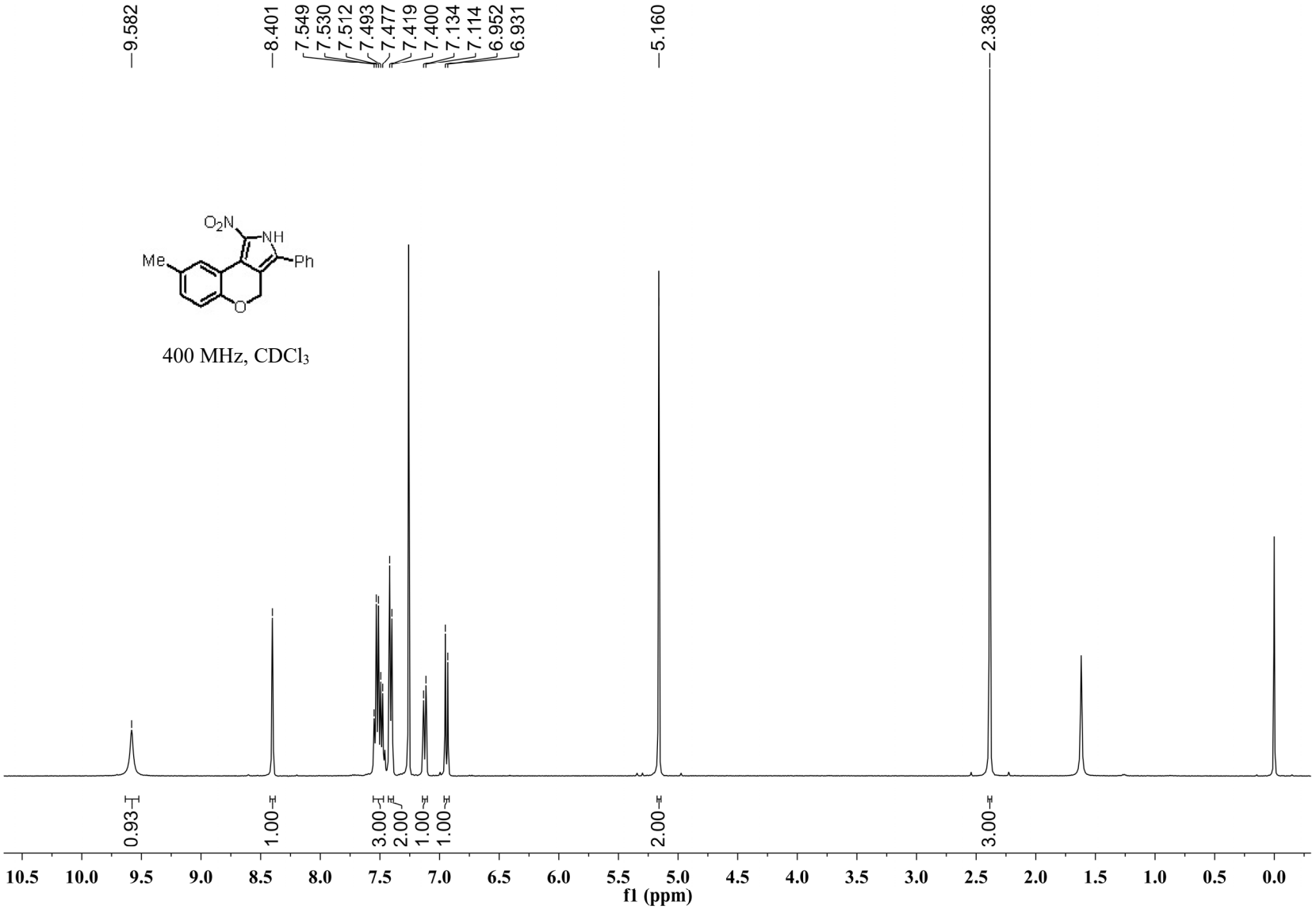
^{13}C NMR Spectrum of Compound 5d



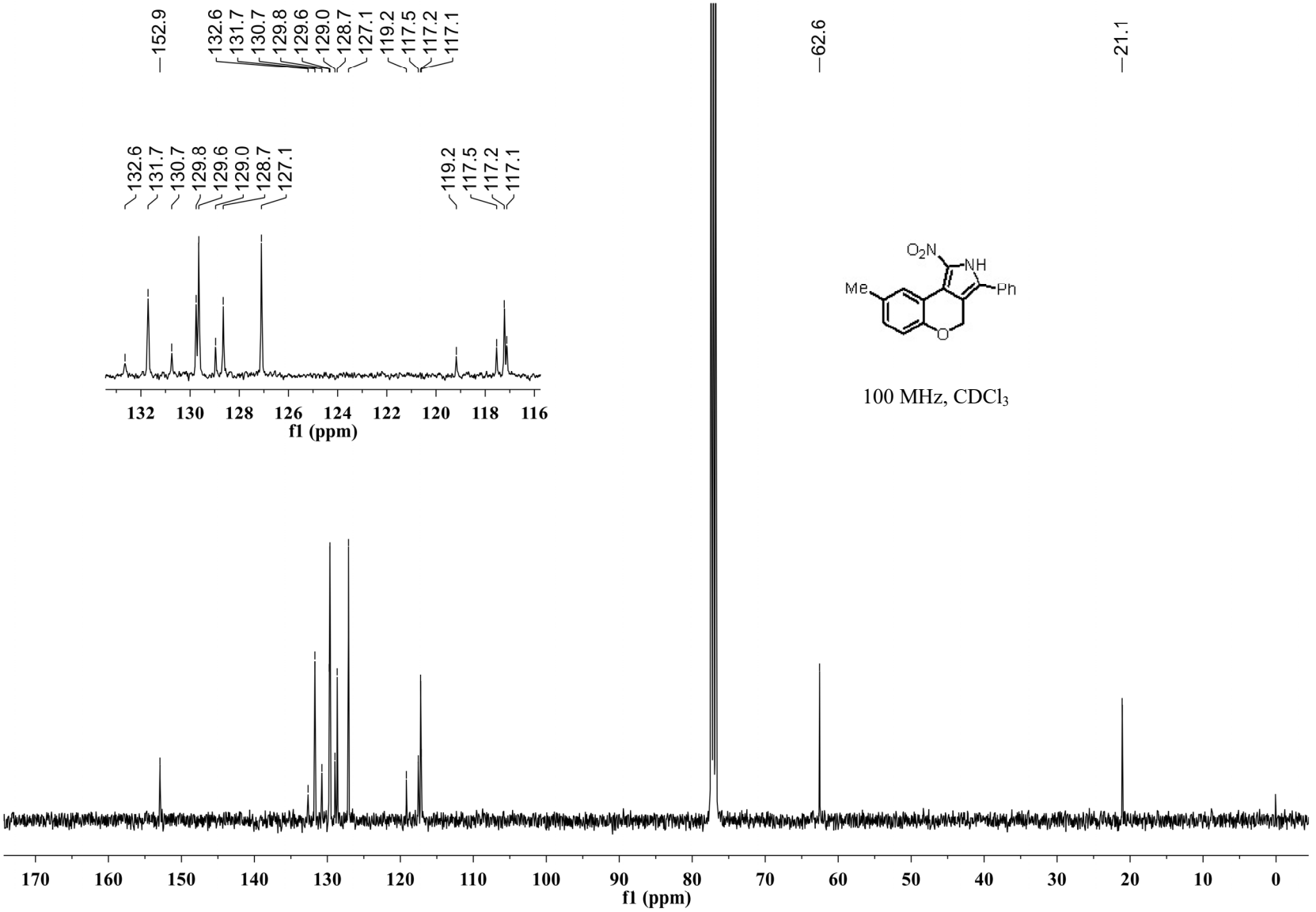
^{1}H NMR Spectrum of Compound 5e



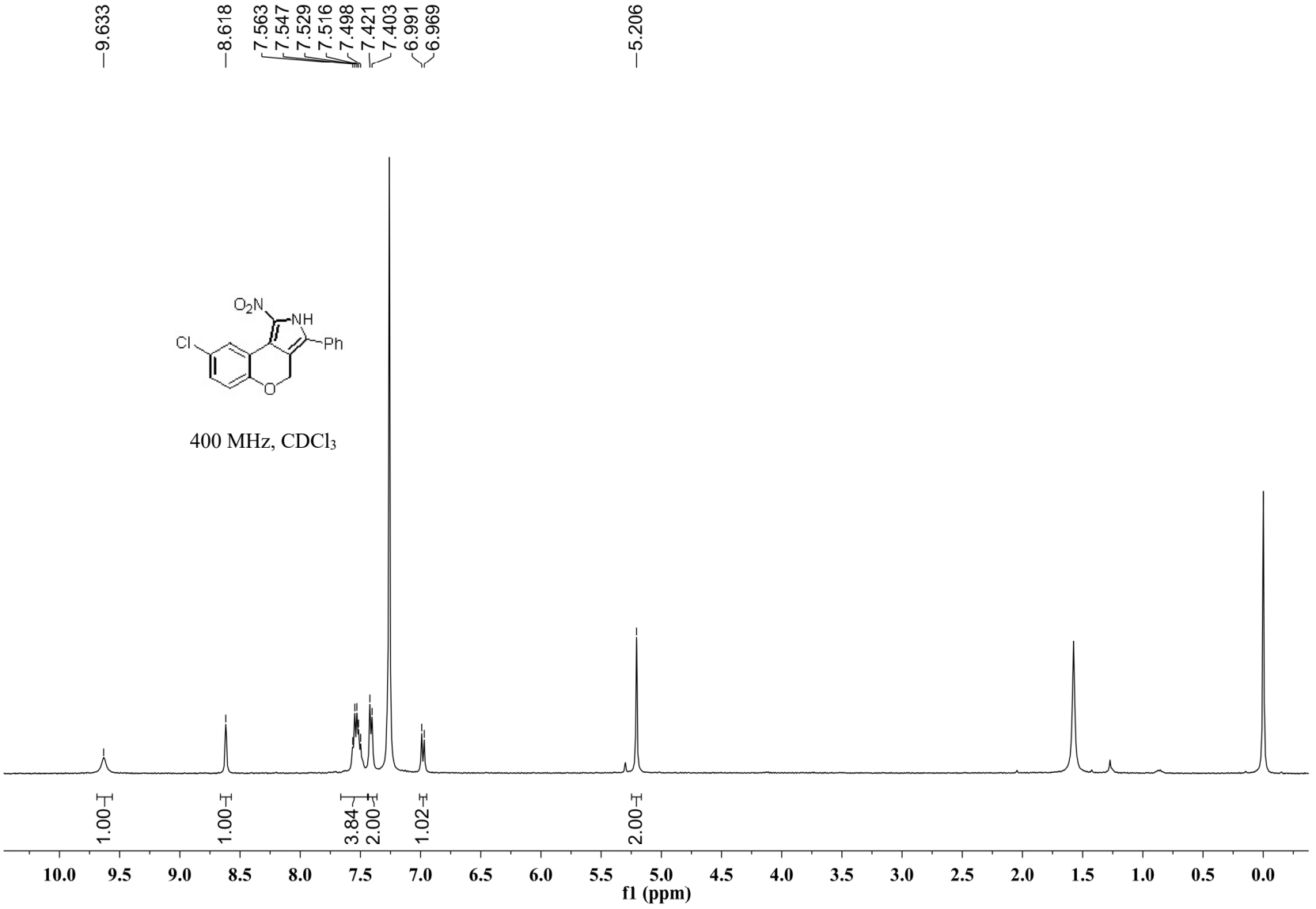
^{13}C NMR Spectrum of Compound 5e



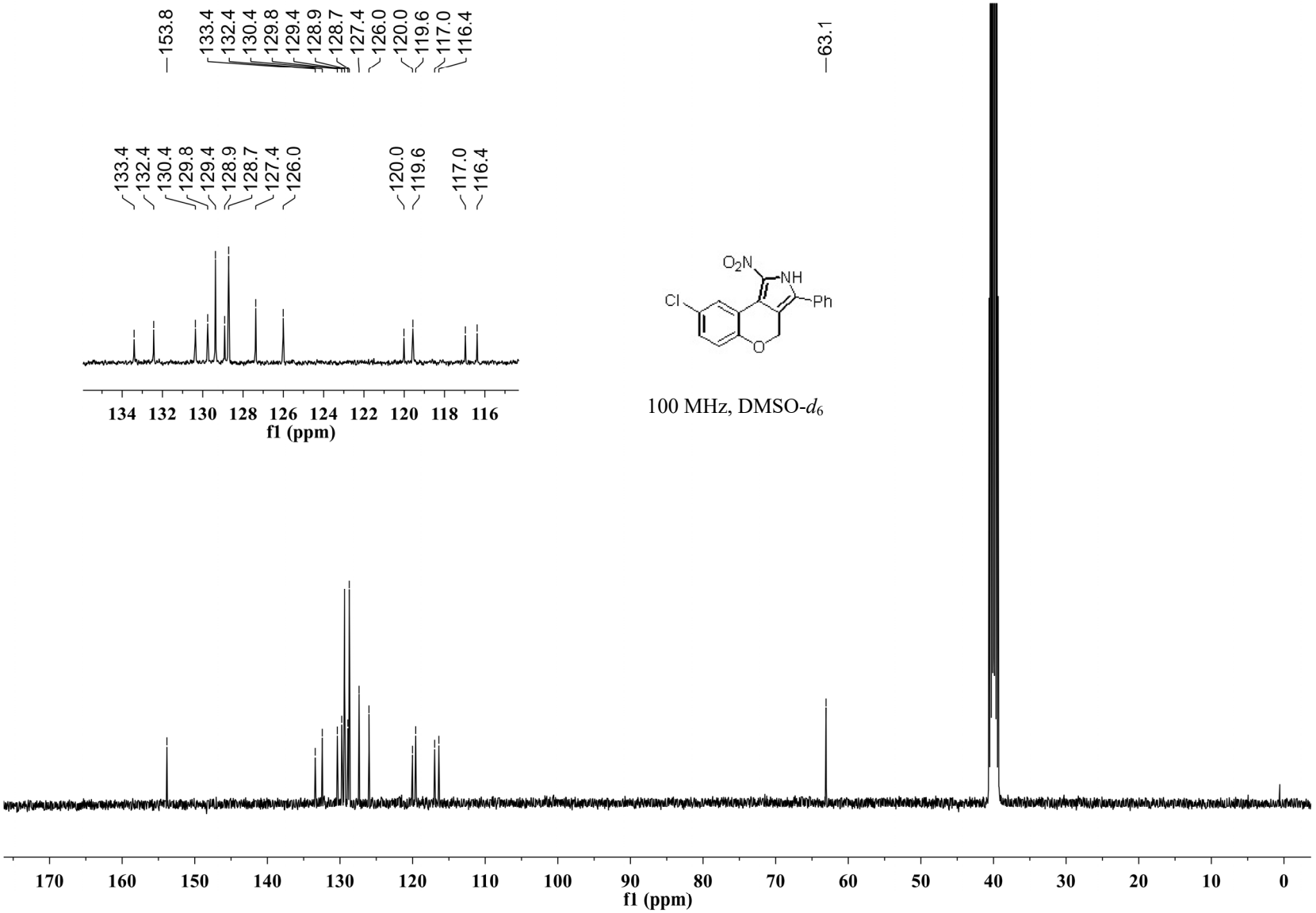
^{1}H NMR Spectrum of Compound 5f



^{13}C NMR Spectrum of Compound 5f

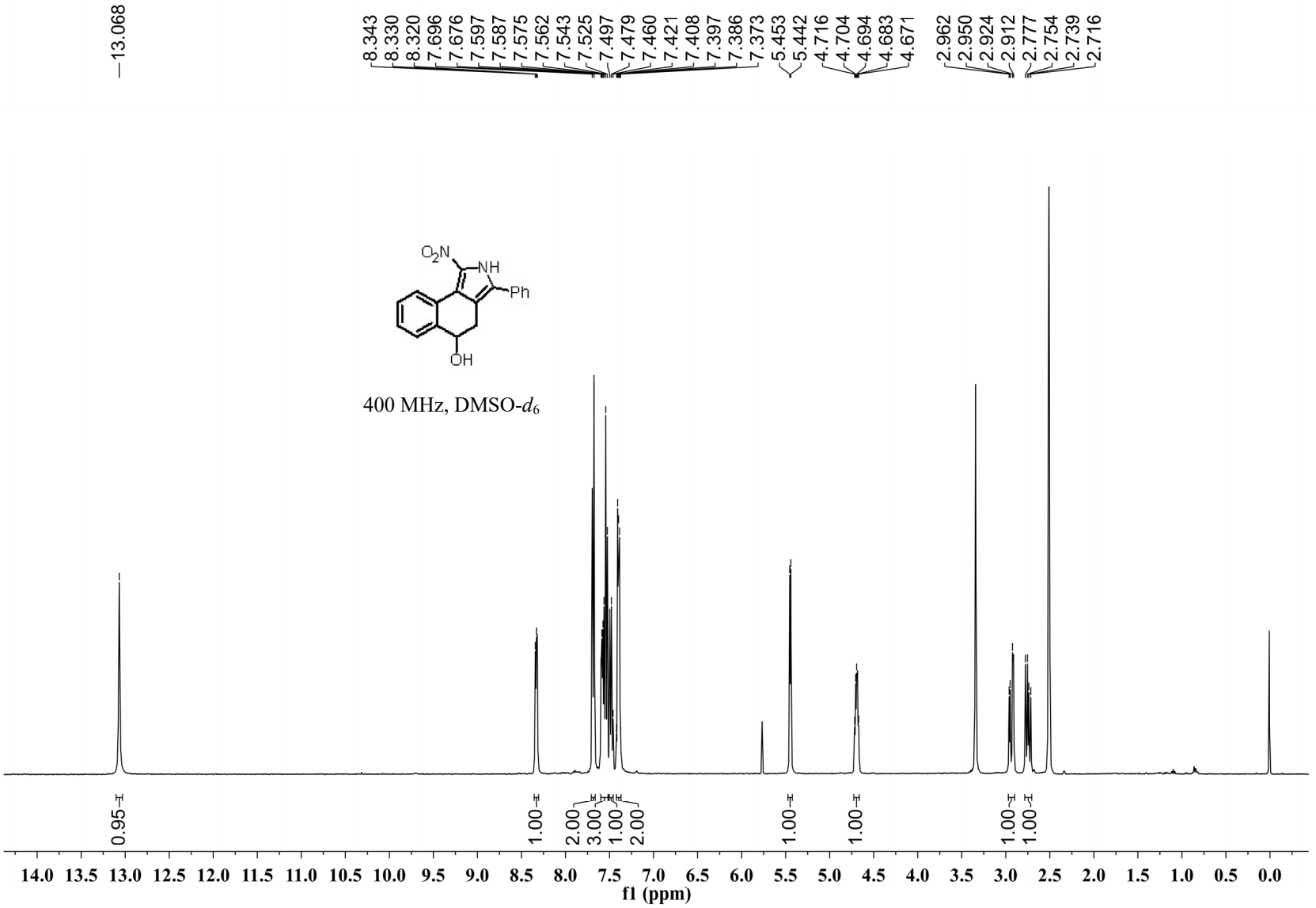


^{1}H NMR Spectrum of Compound 5g

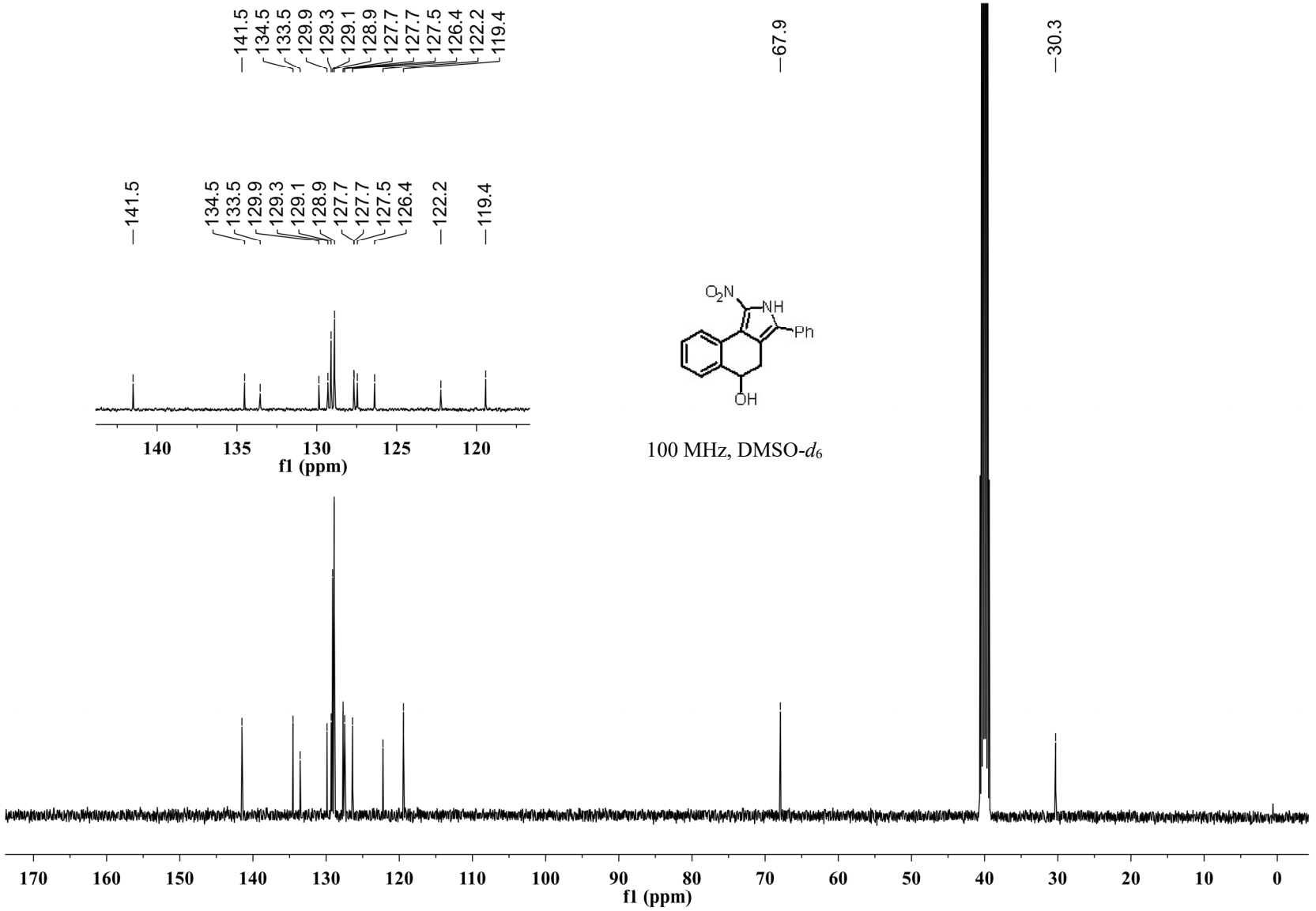


100 MHz, DMSO-d_6

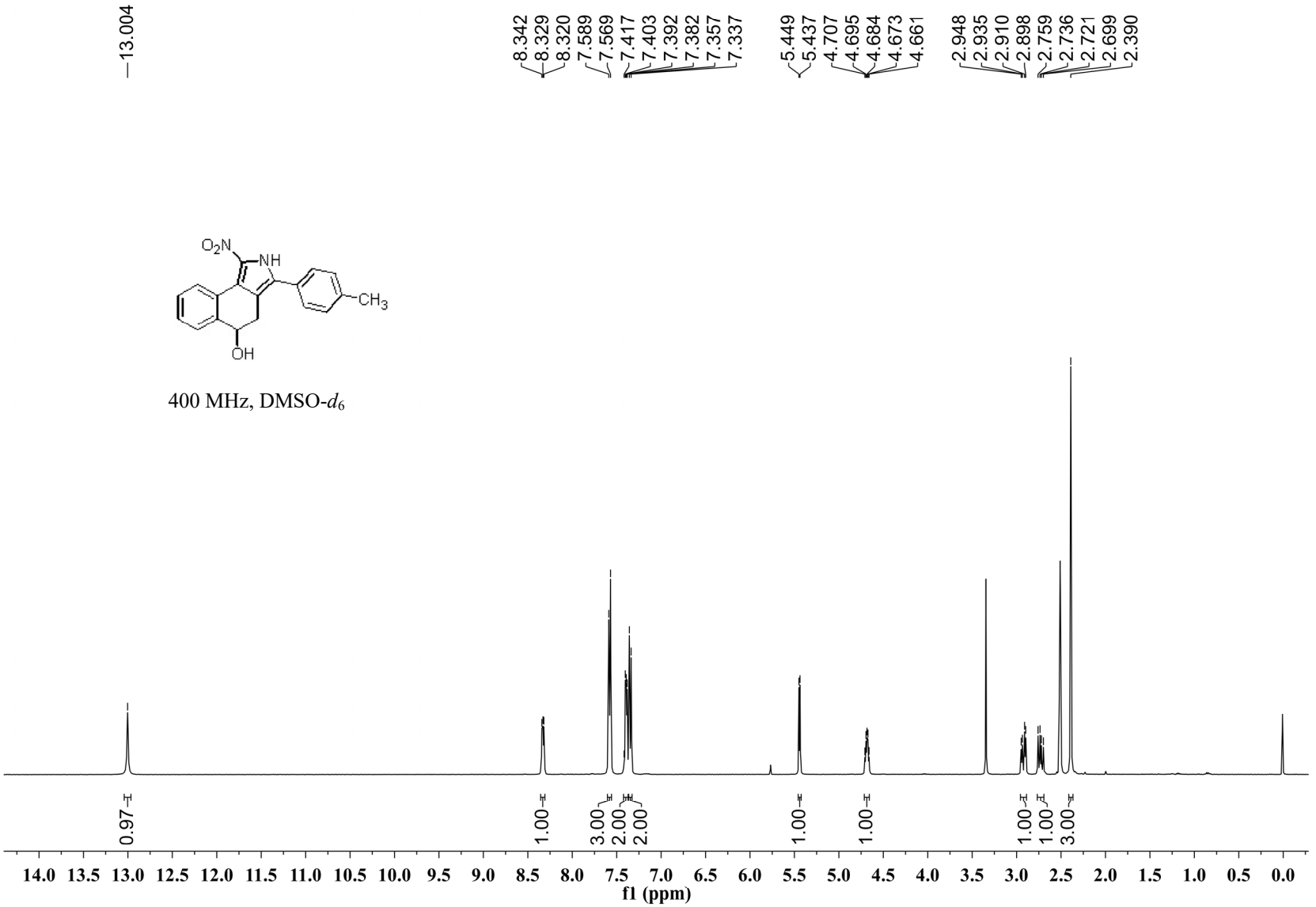
^{13}C NMR Spectrum of Compound 5g



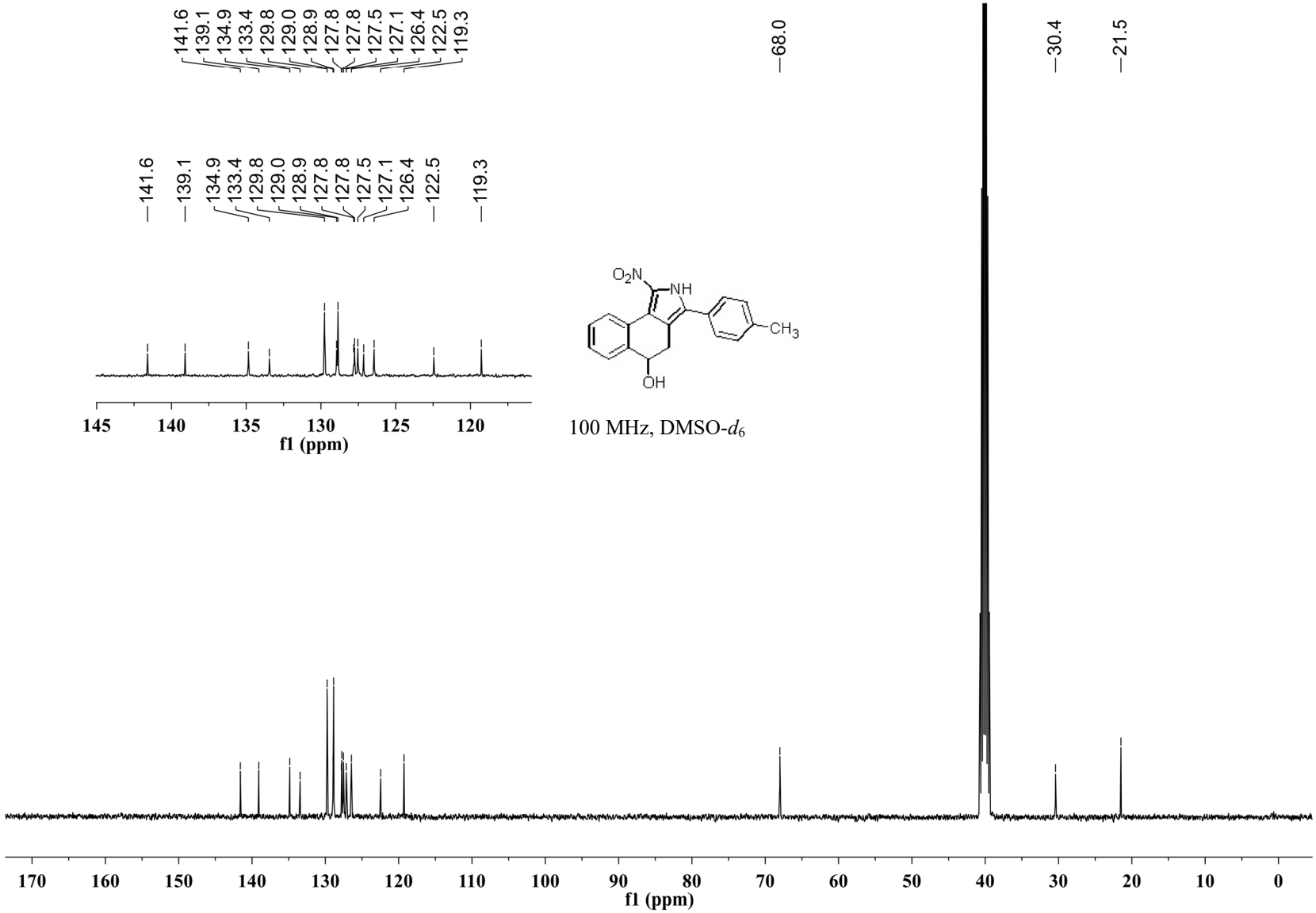
^{1}H NMR Spectrum of Compound 7a



^{13}C NMR Spectrum of Compound 7a

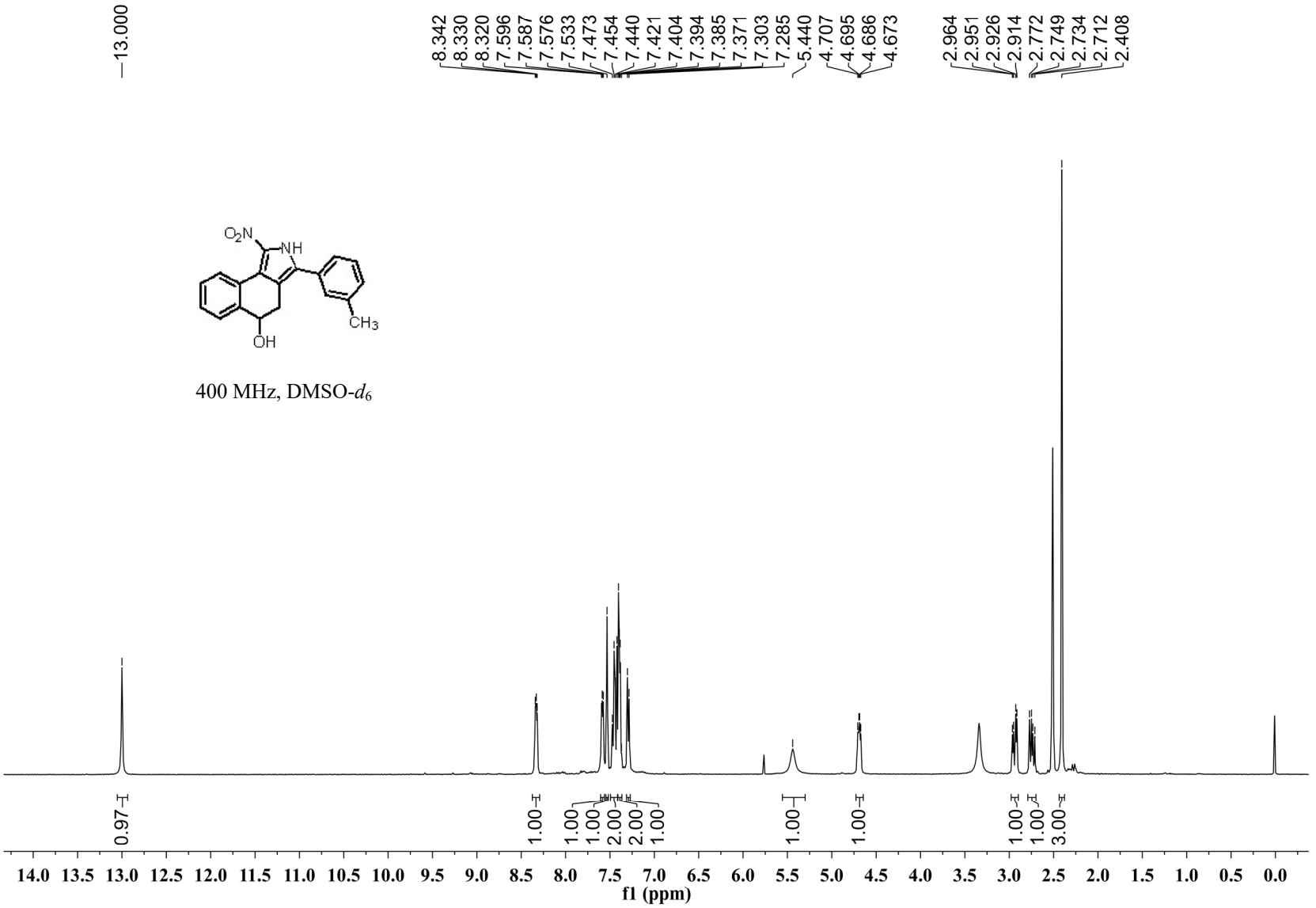


^{1}H NMR Spectrum of Compound 7b

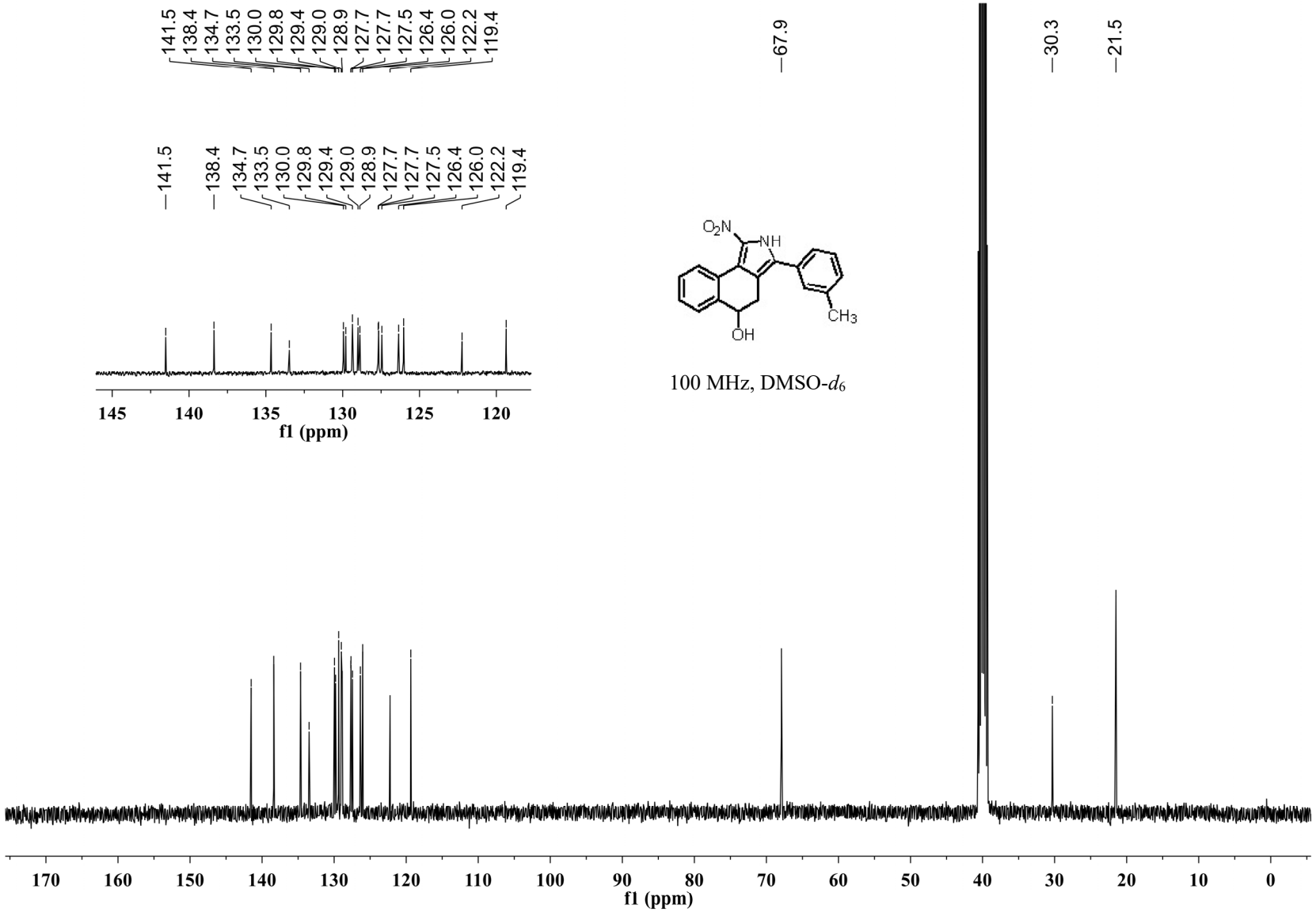


100 MHz, DMSO-d_6

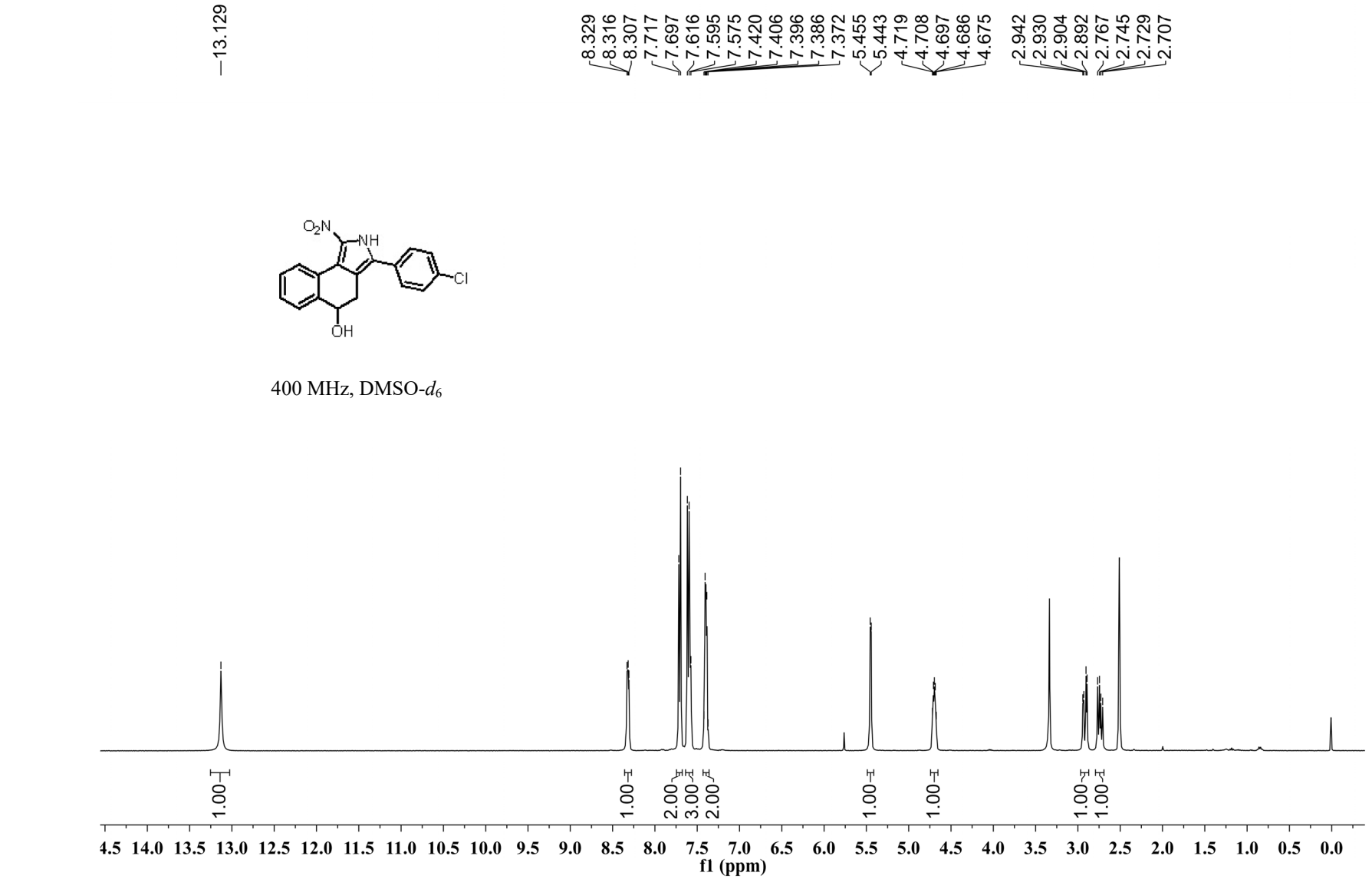
^{13}C NMR Spectrum of Compound 7b



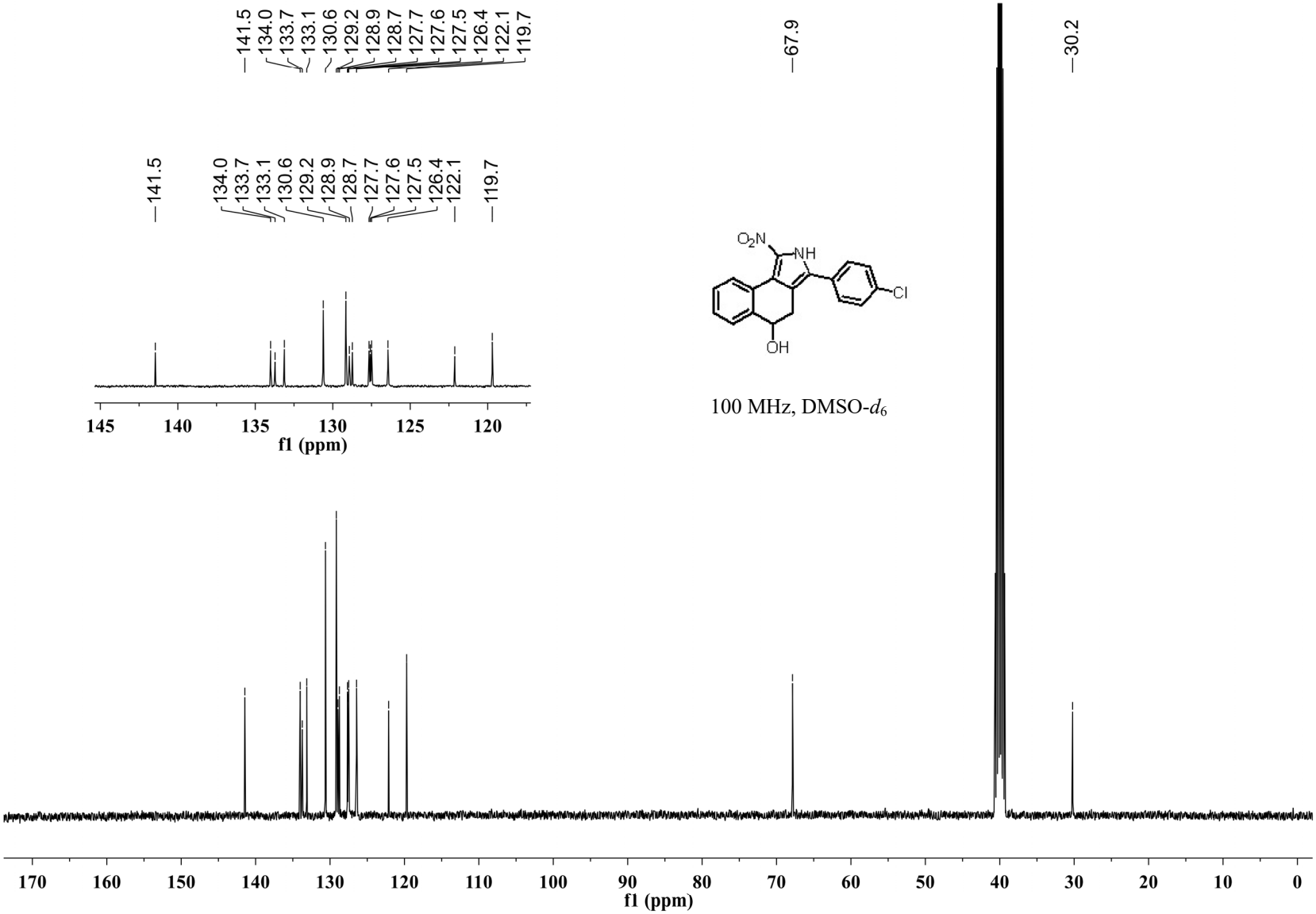
^{1}H NMR Spectrum of Compound 7c



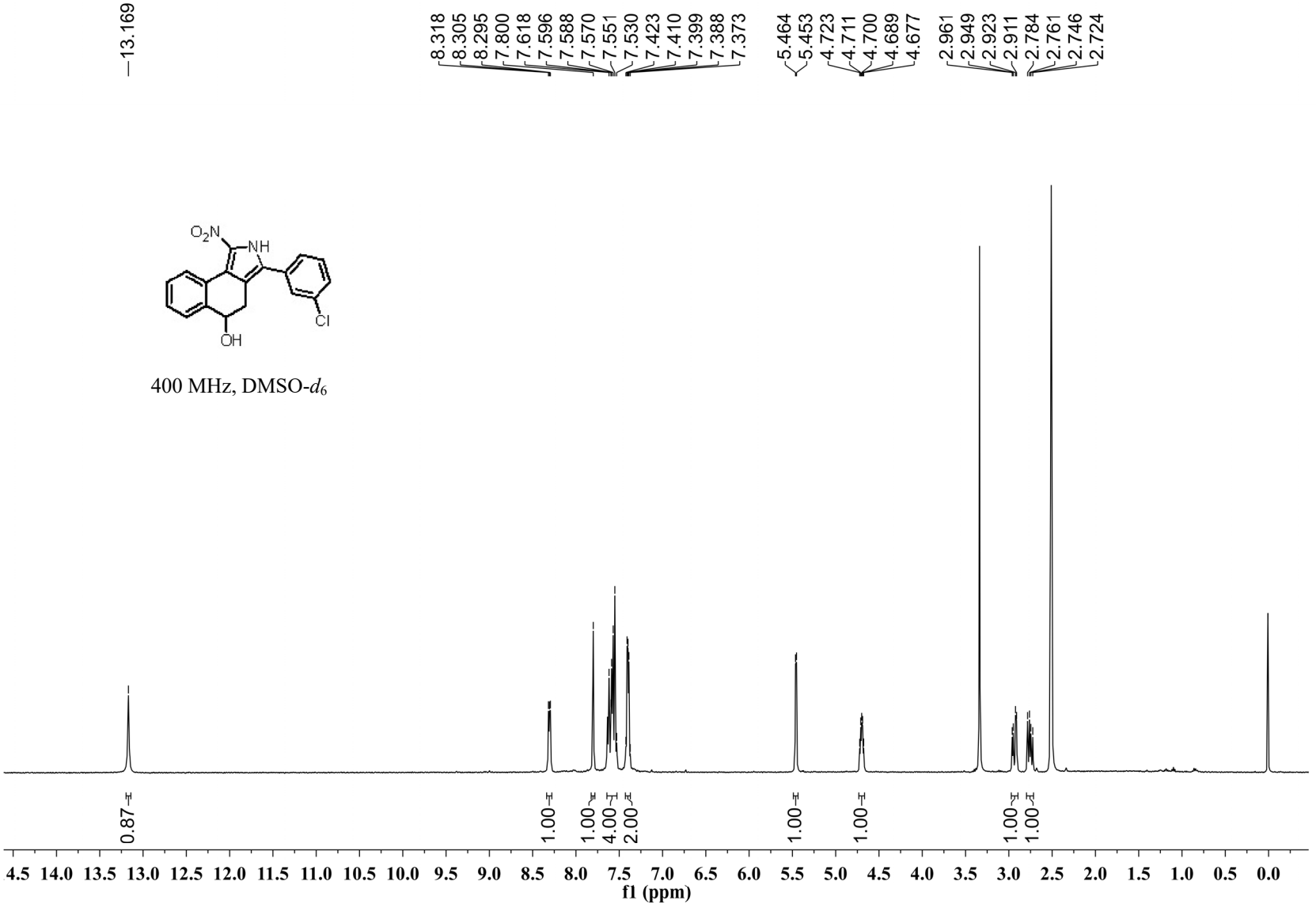
^{13}C NMR Spectrum of Compound 7c



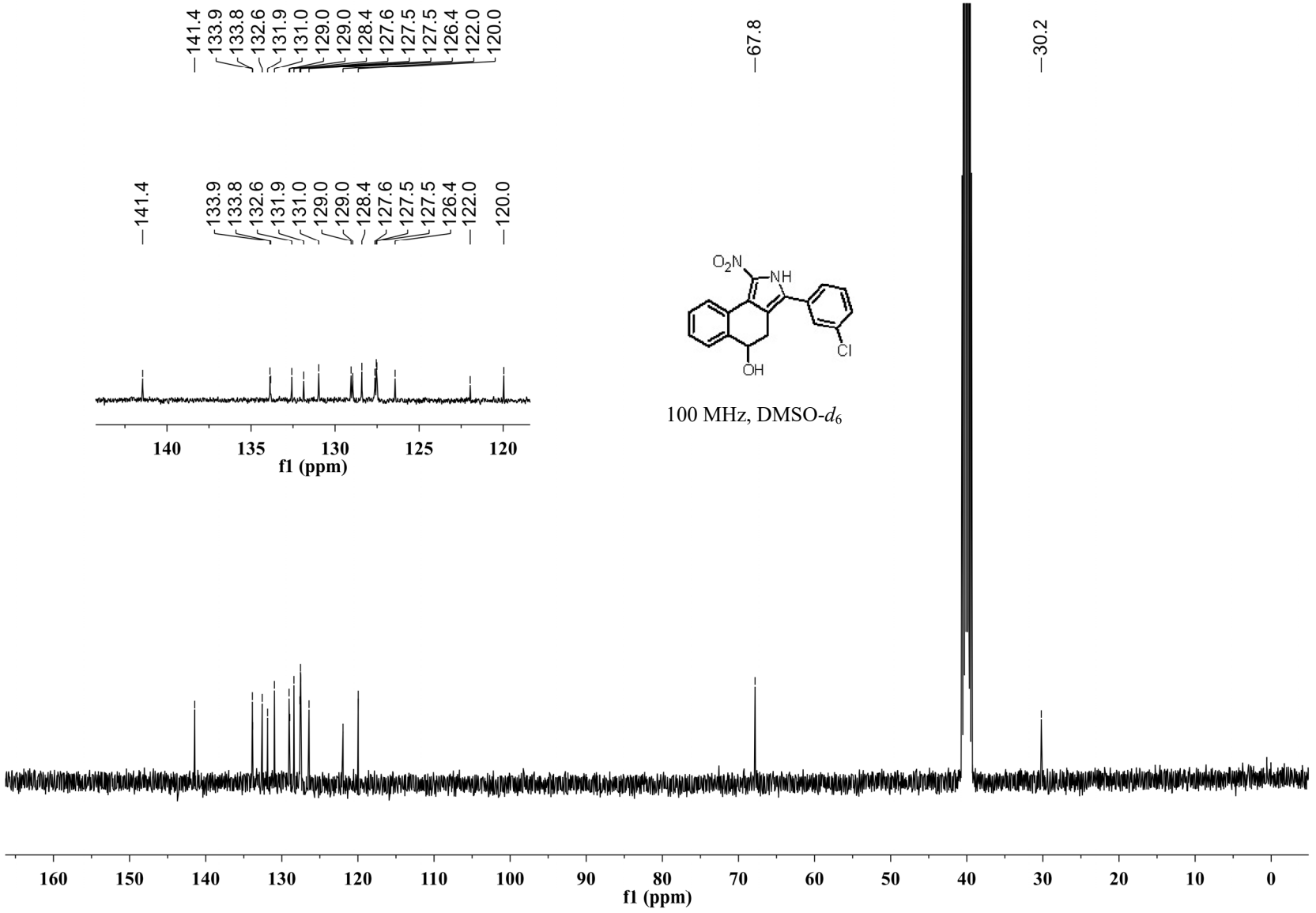
^{1}H NMR Spectrum of Compound 7d



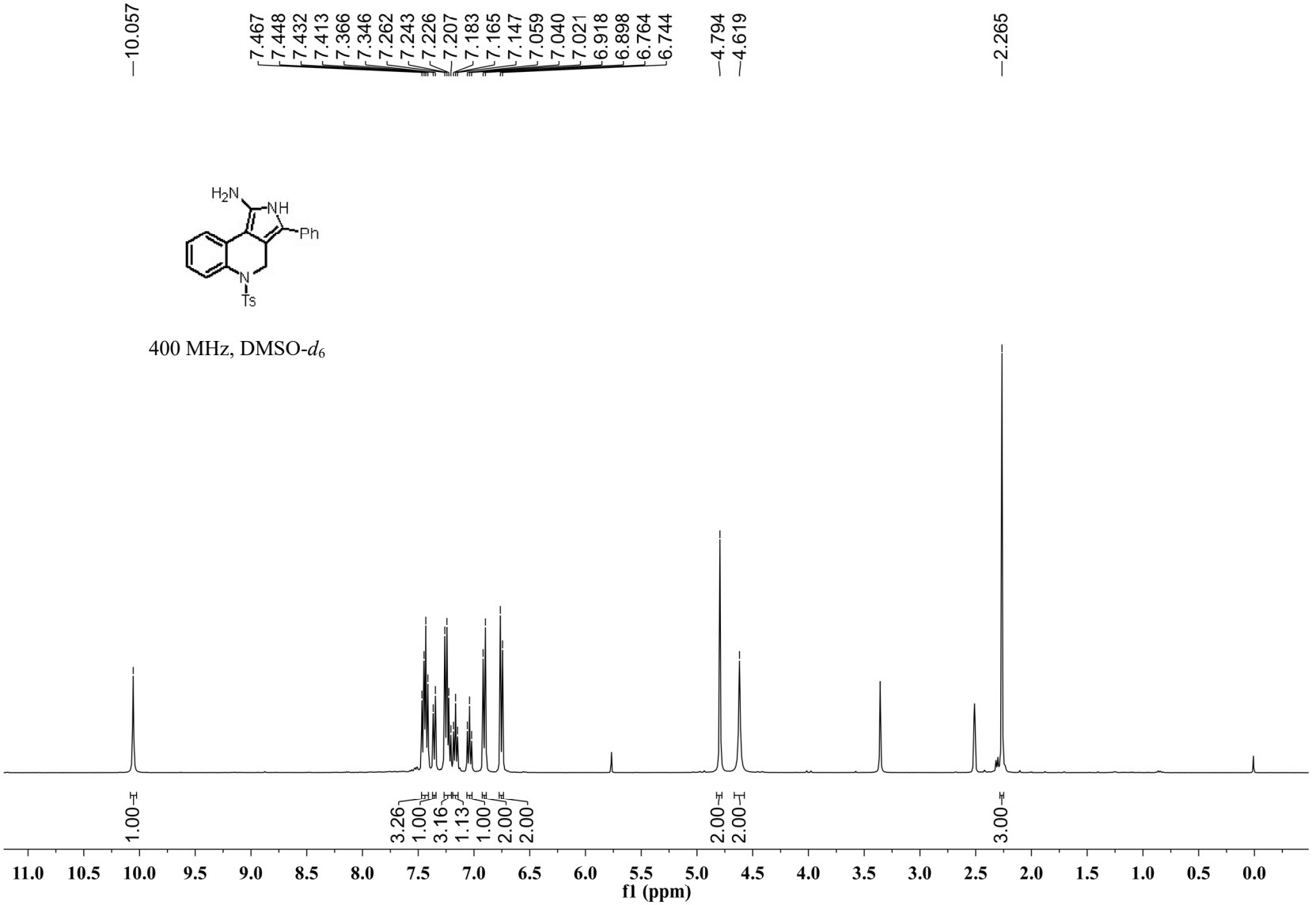
^{13}C NMR Spectrum of Compound 7d



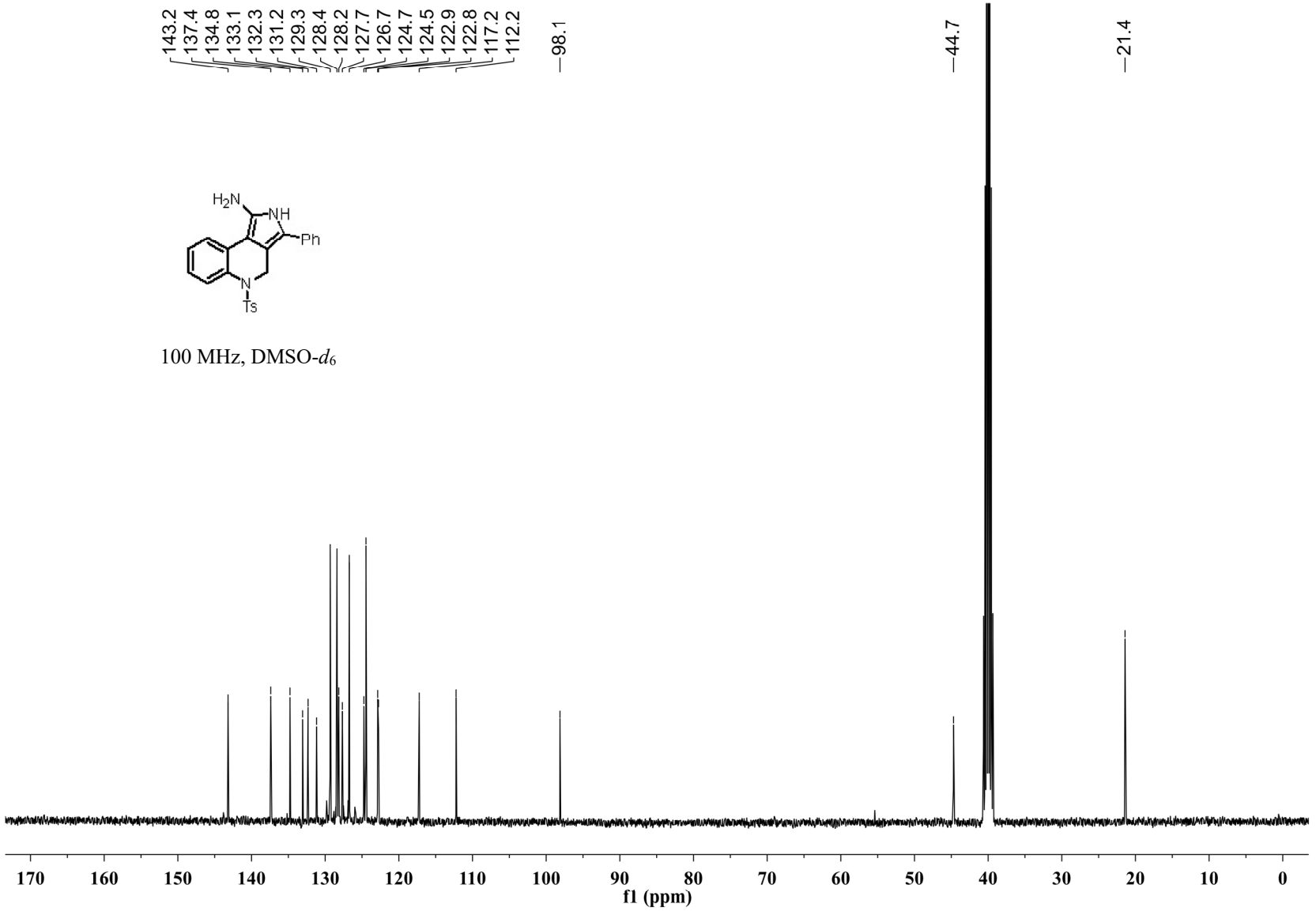
^{1}H NMR Spectrum of Compound 7e



^{13}C NMR Spectrum of Compound 7e



^{1}H NMR Spectrum of Compound 8



^{13}C NMR Spectrum of Compound 8