Supporting Information

for

A Unified Strategy for the Synthesis of β-Carbolines, γ-Carbolines, and other Fused Azaheteroaromatics under Mild, Metal-free Conditions

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EXPERIMENTAL SECTION

General experimental: Glassware was dried in an oven (120 °C), heated under reduced pressure, and cooled under argon before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Reactions were monitored by thin-layer chromatography on Analtech silica gel plates using UV-light and ceric sulfate or β-naphthol for visualization. Column chromatography was performed on silica gel (230–400 mesh) using *n*-hexane/ethyl acetate, dichloromethane/methanol as eluent. Evaporation of solvents was conducted under reduced pressure at 50 °C. FTIR spectra were recorded neat on a Perkin-Elmer Spectrum 65. NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively. Deuterated chloroform was used as the solvent, and spectra were calibrated against the residual solvent peak (7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C). Chemical shifts (δ) and coupling constants (J) are given in ppm (parts per million) and Hz (Hertz), respectively. The following abbreviations were used to explain multiplicities: s=singlet, d=doublet, t=triplet, m=multiplet, bs=broad singlet. Mass spectra were obtained on VG 70–70H or LC/MSD trapSL spectrometer operating at 70 eV using a direct inlet system.

Figure 1: Structures of aldehyde starting materials (1a-z):

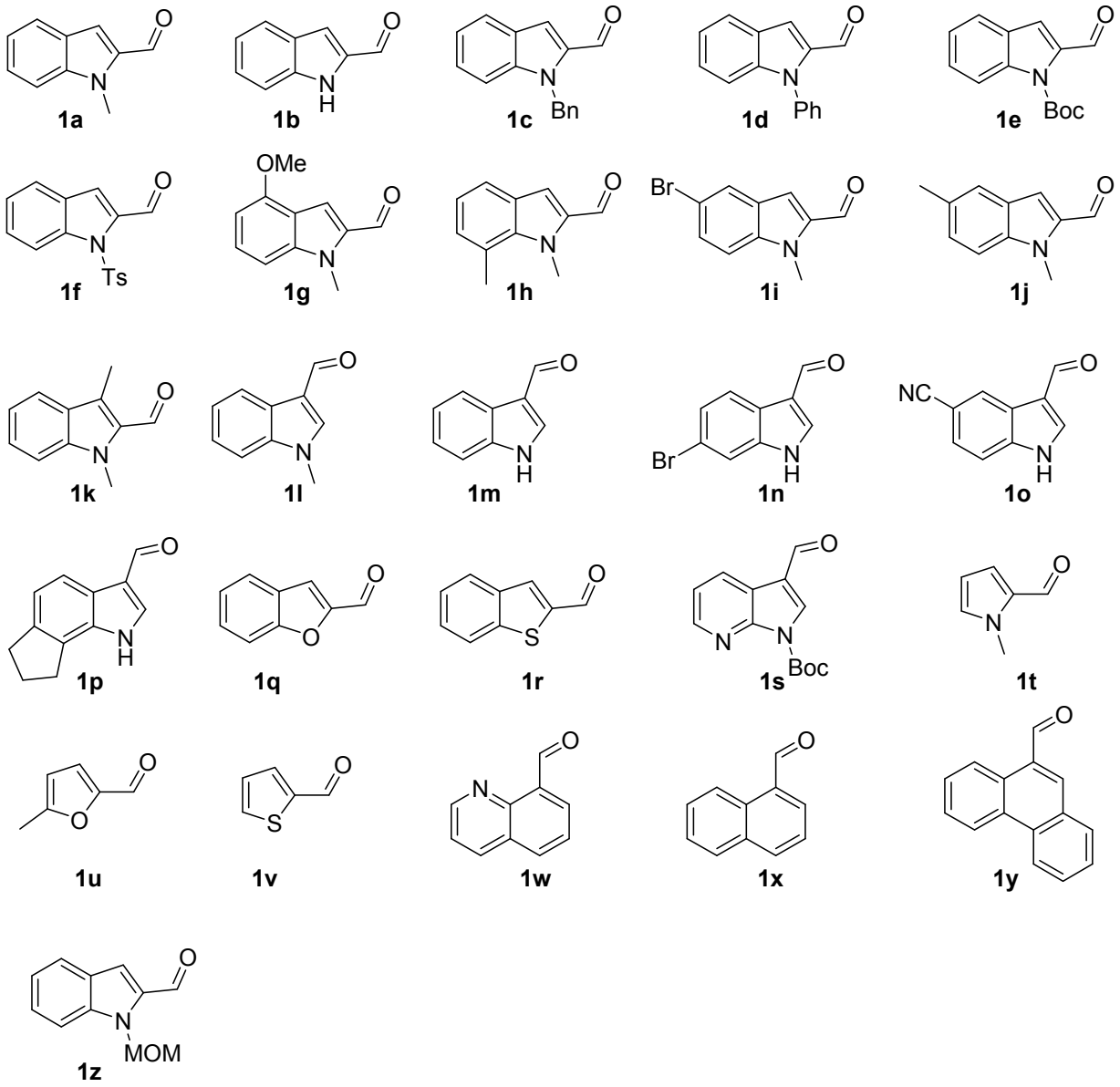
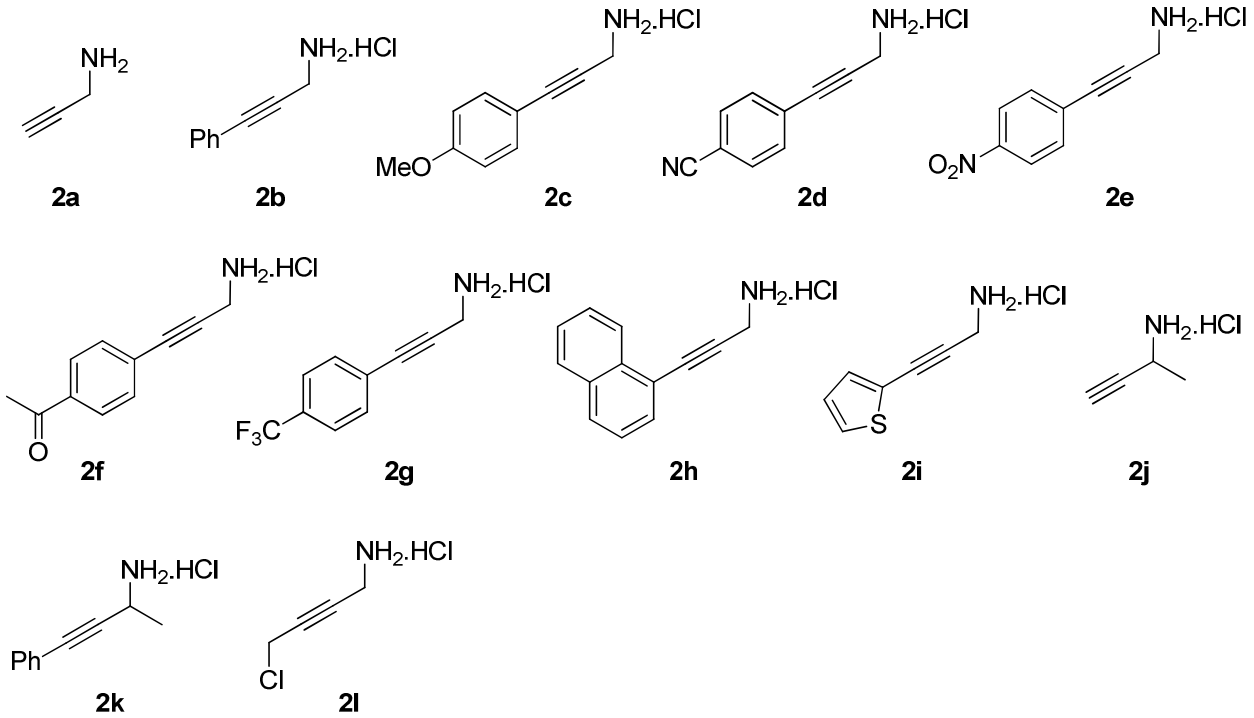


Figure 2: Structures of propargylic amines (2a-l):



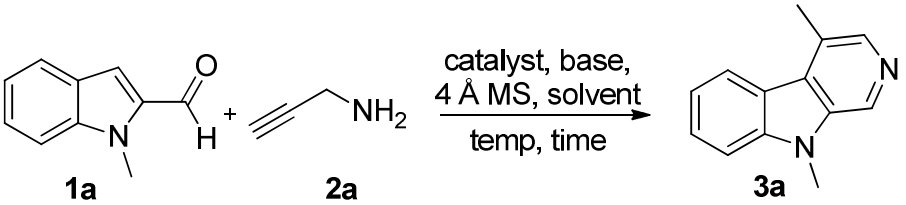
Commercially available aldehydes (**1b**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x** and **1y**) and propargylic amines (**2a**, **2b** and **2l**) were used without further purification and the other starting aldehydes (**1a**,[1] **1c**,[2] **1e**,[3]**1f** and **1z**[4]) and propargylic amines (**2c**,[5] **2d**,[5] **2e**,[5] **2i**,[6] **2j**[7] and **2k**[8]) were synthesized as described below.

Optimization studies:

For the optimization of reaction parameters, we chose 1-methyl-1*H*-indole-2-carbaldehyde (**1a**) as a model substrate in combination with propargylamine (**2a**). To our delight, the imine formation and cyclization reaction proceeded, and the corresponding β-carboline **3a** was obtained in 15% yield using 2 mol% $[Cp^*RhCl_2]_2$ and sodium acetate under an argon atmosphere in methanol at 60 °C for 24 h (Table S1, entry 1). Next, with the same catalyst and base, various

solvents were screened, including toluene, DCE, HFIP and DMF. The investigation showed that toluene and DCE gave inferior yields (entries 2 and 3), whereas DMF was a better solvent than HFIP in this reaction (entries 4 and 5). We later found that switching the catalyst to 5 mol% $Pd(OAc)_2$ was also efficient for this conversion in the presence of NaOAc in DMF at 80 °C for 24 h and delivered **3a** in 50% yield (entry 6). In sharp contrast, the replacement of NaOAc with $NaHCO_3$ as a base significantly improved the yield of **3a** within 9 h at 80 °C (entry 7). Changing the base to Cs_2CO_3 or $KHPO_4$ had a deleterious effect on the reaction under Pd-catalysis (entries 8 and 9). Interestingly, higher yield was observed with $Cu(OAc)_2$ and $NaHCO_3$ conditions to deliver **3a** in 84% yield (entry 10). Investigation of other bases with $Cu(OAc)_2$ deteriorated the reaction progress (entries 11-13). In an attempt to improve the yield of our transformation, alternative and environmentally benign conditions were screened. Interestingly and to our surprise, further examination of the optimization conditions revealed that carboline **3a** formed in good yield even in the absence of catalyst (86%, entry 14). Not surprisingly, the addition of $NaHCO_3$ was an absolute requirement for the reaction to progress and only 23% yield was realized with 10 mol% $Cu(OAc)_2$ in the absence of base (entry 15). The reaction fails to provide carboline **3a** in the absence of both base and catalyst (entry 16). Rather, the corresponding imine (**3aa**) was isolated in 85% yield. Subsequent cyclization of this intermediate to **3a** (88%) was accomplished using the optimized reaction conditions ($NaHCO_3$ in DMF at 80 °C) for 6 hours.

Table S1. Optimization of reaction parameters.[a]



entry	catalyst	base	solvent	temp (°C)	time (h)	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	NaOAc	MeOH	60	24	15
2	$[Cp^*RhCl_2]_2$	NaOAc	toluene	100	24	30
3	$[Cp^*RhCl_2]_2$	NaOAc	DCE	80	24	30
4	$[Cp^*RhCl_2]_2$	NaOAc	HFIP	80	24	45
5	$[Cp^*RhCl_2]_2$	NaOAc	DMF	80	24	48
6	$Pd(OAc)_2$	NaOAc	DMF	80	24	50
7	$Pd(OAc)_2$	$NaHCO_3$	DMF	80	9	80
8	$Pd(OAc)_2$	$CsCO_3$	DMF	80	24	47
9	$Pd(OAc)_2$	K_2HPO_4	DMF	80	24	25
10	$Cu(OAc)_2$	$NaHCO_3$	DMF	80	9	84
11	$Cu(OAc)_2$	Na_2CO_3	DMF	80	9	63
12	$Cu(OAc)_2$	K_2CO_3	DMF	80	9	67
13	$Cu(OAc)_2$	$CsCO_3$	DMF	80	9	63
14	**-**	**$NaHCO_3$**	**DMF**	**80**	**9**	**86**
15	$Cu(OAc)_2$	-	DMF	80	24	23
16[c]	-	-	DMF	80	24	0

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.9 mmol) and base (1.2 mmol); $[Cp^*RhCl_2]_2$ (2 mol%), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (10 mol%); [b]isolated yield; [c]Imine **3aa** was isolated (85%).

Mechanistic studies:

To help establish the mechanistic pathway of the current reaction and to identify the intermediates of the reaction, we monitored the conversion of imine **3aa** to carboline **3a** using ^1H

and ^{13}C NMR analysis of the reaction mixture. Imine **3aa** was treated with $NaHCO_3$ (1.1 equiv.) at 80 °C in DMF-d_7, and the reaction mixture was analyzed at 2-hour intervals (Figure S1). The appearance of a doublet of doublets at 5.4 ppm indicated the formation of an allene intermediate (**A**, terminal CH_2). Additionally, DEPT135 experiments, particularly at 2 h and 4 h intervals showed a corresponding negative peak at 80.7 ppm. The NMR analysis of the reaction clearly showed the disappearance of imine **3aa** (peaks at 4.60, 4.16, and 3.49 ppm), the formation and subsequent disappearance of the allene intermediate **A** (peaks at 5.47 and 4.19 ppm), followed by the increasing concentration of the product **3a** (peaks at 4.04 and 2.84 ppm) in the spectra in Figure S1

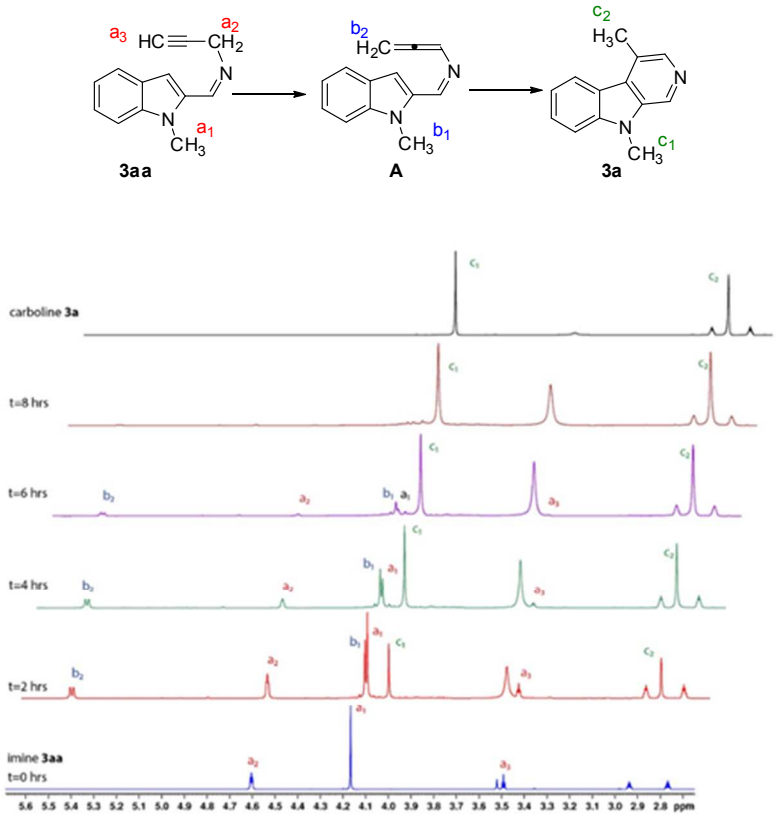
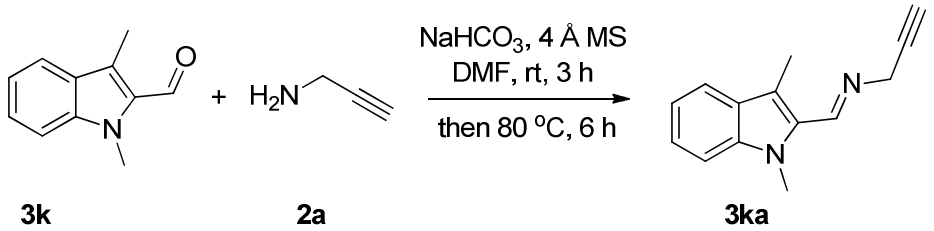


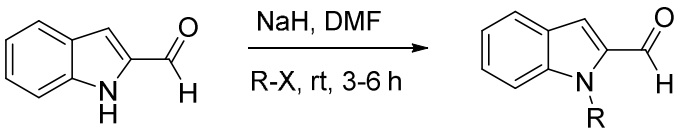
Figure S1: Stacked ^{1}H NMR spectra of reaction mixture at 2-hour intervals.

Shceme S1: Synthesis of (*E*)-*N*-((1,3-dimethyl-1*H*-indol-2-yl)methylene)prop-2-yn-1-amine (3ka):



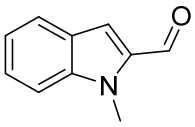
To a stirred solution of aldehyde (**1k**, 103 mg, 0.6 mmol) and propargylamine (**2a**, 49.5 mg, 0.90 mmol) in DMF (2 mL) were added 4 Å molecular sieves (200 mg) and $NaHCO_3$ (101 mg, 1.20 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred for 3 h at room temperature, followed by 6 h at 80 °C. The mixture was filtered through Celite, and water (10 mL) was added to the filtrate. The two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with ice cold water (2 x 15 mL), dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography (gradient: EtOAc/hexanes 10:90 to 40:60) on silica gel to afford **3ka** as a pale, yellow solid in 87% (110 mg) yield. R_f = 0.3 (EtOAc/hexanes 30:70), mp = 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (t, J = 1.8 Hz, 1H), 7.61 (dt, J = 8.0, 0.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.14 – 7.08 (m, 1H), 4.55 (t, J = 2.1 Hz, 2H), 4.06 (s, 3H), 2.55 (t, J = 2.5 Hz, 1H), 2.49 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 153.6, 139.1, 130.5, 127.4, 124.4, 119.8, 119.2, 118.2, 109.5, 79.3, 75.5, 47.9, 32.0, 8.8; FTIR (neat): 3015, 2932, 1613, 1479, 1437, 1297, 1183, 1101, 972, 812, 727 cm^{-1}; MS (ESI): *m/z* 211 $(M+H)^+$.

General procedure for the synthesis of *N*-protected aldehydes (1a, 1c, 1f and 1z):



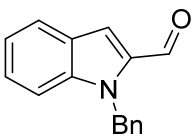
A flame-dried, 25 mL two neck round bottom flask equipped with a magnetic stir bar, was charged with NaH (60 % dispersion in mineral oil, 6.89 mmol, washed with hexanes twice and dried under vacuum) and DMF (5 mL) under argon. To this was added 1*H*-indole-2-carbaldehyde (3.44 mmol) in DMF (2 mL) at 0 °C with stirring for 30 minutes. To the stirred solution was added R-X (4.13 mmol, MeI, BnBr, MOMCl, TsCl in DMF (2 mL)) dropwise at 0 °C, then the reaction mixture was allowed to warm to room temperature and stirred until the starting material disappeared (monitored by TLC). The reaction mixture was quenched by the dropwise addition of water at 0 °C, extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with ice cold water (2 x 20 mL) and brine (30 mL). The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient, 0→30% EtOAc/hexanes) to afford the corresponding *N*-protected indole aldehyde (**1a**, **1c**, **1f** and **1z**).

1-Methyl-1*H*-indole-2-carbaldehyde (1a):



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1 H), 7.69 (d, J = 8.0 Hz, 1H), 7.31-7.40 (m, 2H), 7.13-7.16 (m, 2H), 4.02 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 182.9, 140.8, 135.6, 126.9, 126.2, 123.3, 120.8, 117.4, 110.3, 31.5.

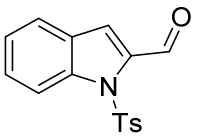
1-Benzyl-1*H*-indole-2-carbaldehyde (1c):



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.76 (dt, J = 8.1, 0.8 Hz, 1H), 7.39-7.29 (m, 3H), 7.29-7.14 (m, 4H), 7.09 (dd, J = 7.6, 1.0 Hz, 2H), 5.83 (s,

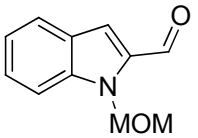
2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 182.6, 140.6, 137.7, 135.3, 128.6, 127.3, 127.2, 126.5, 126.5, 123.4, 121.2, 118.3, 111.0, 47.9.

1-Tosyl-1*H*-indole-2-carbaldehyde (1f):



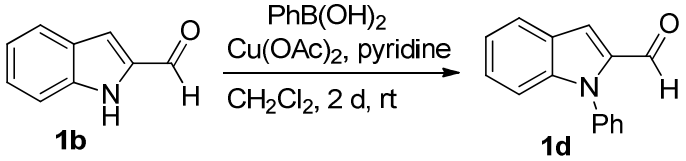
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.54 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.47 (s, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 183.3, 145.6, 138.5, 137.8, 134.6, 130.0, 128.8, 128.2, 126.6, 124.8, 123.6, 118.8, 115.4, 21.6.

1-(Methoxymethyl)-1*H*-indole-2-carbaldehyde (1z):



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.78 (dt, J = 8.1, 0.9 Hz, 1H), 7.60 (dd, J = 8.5, 0.8 Hz, 1H), 7.48 (ddd, J = 8.4, 7.0, 1.1 Hz, 1H), 7.36 (d, J = 0.8 Hz, 1H), 7.26 (ddd, J = 8.0, 5.1, 1.6 Hz, 1H), 6.01 (s, 2H), 3.32 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 182.6, 140.9, 135.7, 127.6, 126.8, 123.4, 121.8, 119.7, 111.4, 74.7, 55.9.

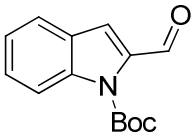
Synthesis of 1-phenyl-1*H*-indole-2-carbaldehyde (1d):



Activated molecular sieves (1 g, 4 Å) were placed in an oven dried round bottom flask and cooled to room temperature under an argon atmosphere. 1*H*-indole-2-carbaldehyde (0.5 g, 3.4 mmol), phenylboronic acid (1.26 g, 10.3 mmol), copper acetate (0.93 g, 5.17 mmol), and dichloromethane (20 mL) were added to the flask, followed by pyridine (1.08 g, 1.10 mL, 13.8 mmol). The reaction mixture was stirred at room temperature for 2 days and then filtered through Celite. The filtrate was concentrated under reduced pressure. The resultant residue was purified

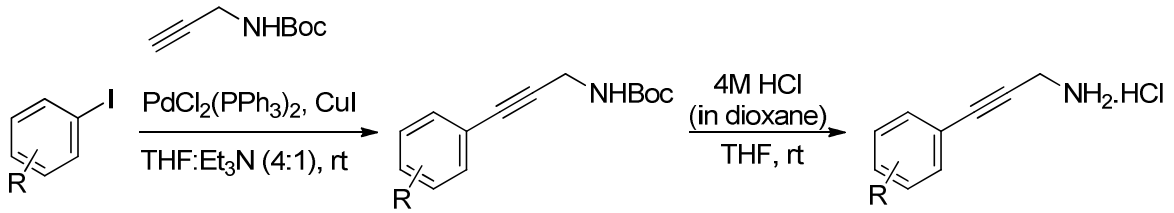
by flash column chromatography on silica gel (gradient, 0→30% EtOAc/hexanes) to give the desired product **1d** in 63% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 1H), 8.25 (dd, J = 8.6, 0.8 Hz, 1H), 7.79 (dt, J = 8.7, 1.7 Hz, 2H), 7.63 (d, J = 7.9 Hz, 1H), 7.58-7.50 (m, 2H), 7.49 (d, J = 0.6 Hz, 1H), 7.43 (dt, J = 7.5, 1.7 Hz, 2H), 7.35-7.30 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 183.2, 138.5, 137.8, 137.5, 134.3, 129.4, 128.9, 128.2, 126.6, 124.9, 123.7, 119.1, 115.3.

***tert*-Butyl 2-formyl-1*H*-indole-1-carboxylate (1e):**



To a stirred solution of 1*H*-indole-2-carbaldehyde (0.5 g, 3.4 mmol), triethylamine (0.6 mL, 4.0 mmol) and DMAP (41 mg, 0.34 mmol) in THF at 0 °C was added di-*tert*-butyl dicarbonate (0.87 g, 4.0 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight, then evaporated under vacuum. The residue was partitioned between EtOAc and water. The combined organic layer was dried over anhydrous magnesium sulfate, concentrated *in vacuo*, and purified by flash column chromatography on silica gel (gradient, 0→20% EtOAc/hexanes) to give *tert*-butyl 2-formylindole-1-carboxylate (**1e**) as a white solid in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.44 (s, 1H), 8.17 (dd, J = 8.6, 0.8 Hz, 1H), 7.72-7.64 (m, 1H), 7.49 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.44 (d, J = 0.5 Hz, 1H), 7.30 (ddd, J = 8.0, 7.3, 0.9 Hz, 1H), 1.72 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 184.2, 149.8, 137.9, 137.8, 128.2, 127.5, 123.8, 123.2, 116.4, 116.1, 85.6, 28.2.

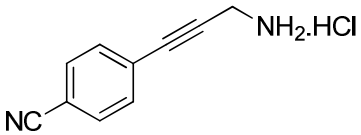
General procedure for the synthesis of propargylic amine hydrochloride salts 2c-i:



To a degassed solution of aryl iodide (5.5 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (0.77 g, 5.0 mmol) in THF/Et_3N (0.45 M, 4:1) under argon, were added CuI (38.1 mg, 0.20 mmol) and $PdCl_2(PPh_3)_2$ (70.2 mg, 0.10 mmol) at room temperature. The mixture was stirred overnight, and an aqueous solution of saturated NH_4Cl was added, and the mixture was extracted with Et_2O (3 x 30 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient, 0→20% EtOAc/hexanes) to give the corresponding propargylic amine derivatives in high yield (81-91%).

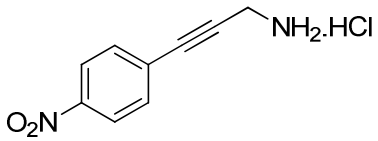
To a solution of the coupling product (4.0 mmol) in THF (4 mL) was added 4.0 M HCl in 1,4-dioxane solution (4.0 mL, 16 mmol) at room temperature, and the reaction mixture was stirred overnight. The solution was diluted with Et_2O upon completion. The organic layer was removed by decantation, and the precipitate was washed with Et_2O (3 x 15 mL). The solid compound was dried under vacuum to give the corresponding propargylic amine hydrochloride salts **2c-i**.

4-(3-Aminoprop-1-yn-1-yl)benzonitrile hydrochloride (2d):



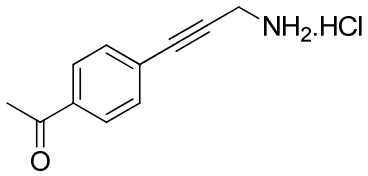
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.67 (bs, 3H), 7.92 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 4.03 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ 132.8, 132.3, 126.1, 118.3, 111.6, 87.1, 84.1, 28.9.

3-(4-Nitrophenyl)prop-2-yn-1-amine hydrochloride (2e):



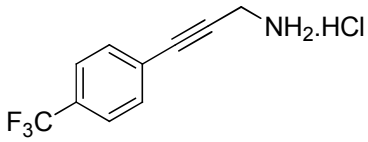
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.73 (bs, 3H), 8.35-8.18 (m, 2H), 7.80-7.66 (m, 2H), 4.05 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 147.3, 132.8, 128.0, 124.1, 88.0, 83.8, 28.9.

1-(4-(3-Aminoprop-1-yn-1-yl)phenyl)ethanone hydrochloride (2f):



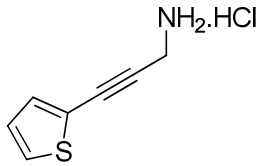
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (bs, 3H), 8.03-7.94 (m, 2H), 7.64-7.58 (m, 2H), 4.03 (s, 2H), 2.60 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 197.3, 136.7, 131.7, 128.6, 125.8, 85.9, 84.8, 28.9, 26.8.

3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-amine hydrochloride (2g):



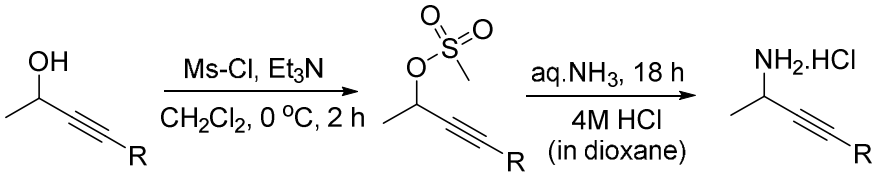
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.72 (s, 3H), 7.81 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 4.02 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 132.3, 129.1 (d, J = 32.2 Hz), 125.8 (q, J = 3.7 Hz), 125.4 (d, J = 37.0 Hz), 122.5, 85.7, 84.1, 28.8.

3-(Thiophen-2-yl)prop-2-yn-1-amine hydrochloride (2i):



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.62 (s, 3H), 7.68 (dd, J = 5.1, 1.1 Hz, 1H), 7.37 (dd, J = 3.6, 0.9 Hz, 1H), 7.11 (dd, J = 5.1, 3.7 Hz, 1H), 4.00 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 133.2, 129.2, 127.5, 120.5, 86.5, 78.7, 28.8.

Synthesis of propargylic amine hydrochlorides (2j and 2k):

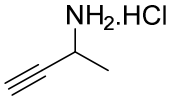


To a stirred solution of propargylic alcohol (71.4 mmol) and triethylamine (107.1 mmol) in dichloromethane (50 mL), methanesulfonylchloride (85.7 mmol) was added dropwise over 30

min at 0 °C. The mixture was stirred for 2 h before warming to room temperature. Water (50 mL) was added, and the dichloromethane layer was separated. The aqueous phase was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with brine (50 mL) before drying over magnesium sulfate. The solvent was removed under vacuum to yield a pale, yellow oil. The crude product was used in the next step without further purification.

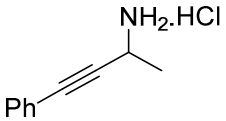
The crude methanesulfonate (70.9 mmol) was stirred for 18 h with aqueous NH_3 (1348 mmol) at room temperature. The aqueous phase was extracted with dichloromethane (3 × 30 mL), combined and dried over anhydrous magnesium sulfate. The organic phase was set up to reflux for 4 h, until the vapor above the double condenser no longer gave a positive alkali test. To the solution was added 4.0 M HCl in 1,4-dioxane solution (142 mmol) at room temperature, and the solution was stirred for 24 h. The product was filtered and washed with ice cold ether (100 mL) giving the propargylic amine hydrochloride salts (**2j** and **2k**) as pale, yellow powders.

But-3-yn-2-amine hydrochloride (2j):



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75 (bs, 3H), 4.11 (s, 1H), 3.67 (d, J = 2.3 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 81.0, 77.0, 37.4, 19.7.

4-Phenylbut-3-yn-2-amine hydrochloride (2k):

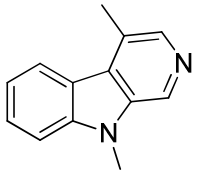


^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (bs, 3H), 7.92-7.86 (m, 2H), 7.65-7.53 (m, 3H), 3.97 (q, J = 6.8 Hz, 1H), 1.45 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 132.8, 132.3, 128.3, 118.3, 87.1, 84.1, 37.8, 24.5.

General procedure for the synthesis of β-carbolines, γ-carbolines and fused azaheterocycles:

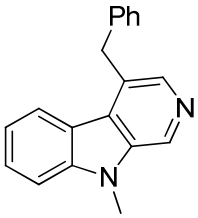
To a stirred solution of aldehyde **1a-z** (0.6 mmol) and propargylic amine/propargylic amine hydrochloride (0.9 mmol) in DMF (2 mL) were added 4 Å molecular sieves (200 mg) and $NaHCO_3$ (1.2 mmol for free propargylic amines and 1.8 mmol for propargylic amine hydrochlorides) at room temperature under an argon atmosphere. The reaction mixture was stirred for 3 h at room temperature, followed by 6 h at 80 °C (heated for 24 h at 80 °C in case of *N*-H indole aldehydes). The mixture was filtered through Celite, and water (10 mL) was added to filtrate. Two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with ice cold water (2 x 15 mL), dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the corresponding β-carbolines (**3a-s and 3z**), γ-carbolines (**3t-y**) and fused azaheterocycles (**4a-j**).

4,9-Dimethyl-9*H*-pyrido[3,4-*b*]indole (3a):



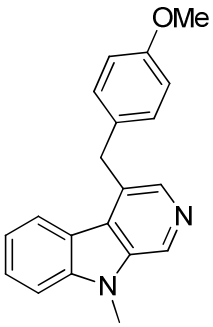
1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 101 mg (86%) of a pale, yellow solid was obtained. R_f = 0.4 (CH_2Cl_2/MeOH 95:5), mp = 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.27 (s, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 3.93 (s, 3H), 2.84 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.6, 139.4, 136.6, 129.4, 127.8, 127.1, 124.4, 123.7, 121.6, 119.7, 109.0, 29.4, 17.4; FTIR (neat): 3043, 2968, 2923, 1616, 1490, 1460, 1326, 1267, 1154, 1021, 855, 743, 728 cm^{-1}; MS (ESI): *m/z* 197 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}N_2$ $(M+H)^+$: 197.1073, found: 197.1072.

4-Benzyl-9-methyl-9*H*-pyrido[3,4-*b*]indole (3b):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 142 mg (87%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.27 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.61-7.53 (m, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.30-7.13 (m, 6H), 4.60 (s, 2H), 3.93 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.6, 140.3, 139.0, 136.8, 130.2, 129.1, 128.5, 128.5, 127.8, 126.9, 126.3, 123.9, 120.9, 119.7, 109.0, 37.1, 29.3; FTIR (neat): 3025, 2937, 1603, 1493, 1446, 1329, 1154, 1024, 981, 749, 727, 693 cm^{-1}; MS (ESI): *m/z* 273 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{17}N_2$ $(M+H)^+$: 273.1386, found: 273.1382.

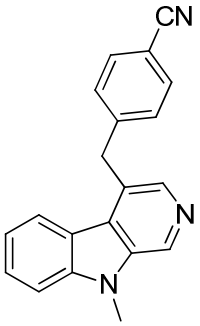
4-(4-Methoxybenzyl)-9-methyl-9*H*-pyrido[3,4-*b*]indole (3c):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-(4-methoxyphenyl)prop-2-yn-1-amine hydrochloride (**2c**, 177 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 130 mg (72%) of a white solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.26 (s, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.58 (ddd, J = 8.3, 5.6, 1.1 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.23-7.18 (m, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.84-6.75 (m, 2H), 4.55 (s, 2H), 3.96 (s, 3H), 3.75 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 158.0, 141.6, 140.3, 136.9, 131.0, 130.3, 129.5, 129.4, 127.8, 126.9, 124.0, 121.0, 119.7, 114.0, 109.0, 55.2, 36.3, 29.4; FTIR (neat): 3028, 2923, 2850, 1661, 1492, 1447, 1433, 1328, 1245, 1172, 1027, 867, 746, 729, 694 cm^{-1};

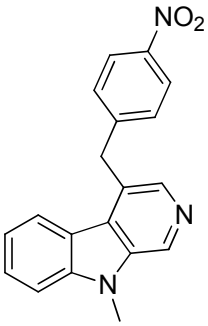
MS (ESI): *m/z* 303 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}N_2O$ $(M+H)^+$: 303.1492, found: 303.1488.

4-((9-Methyl-9*H*-pyrido[3,4-*b*]indol-4-yl)methyl)benzonitrile (3d):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 4-(3-aminoprop-1-yn-1-yl)benzonitrile hydrochloride (**2d**, 172.8 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 157 mg (88%) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 8.29 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.65-7.59 (m, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.25-7.19 (m, 1H), 4.68 (s, 2H), 4.00 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 144.7, 141.7, 140.3, 136.9, 132.4, 131.0, 129.2, 128.1, 127.2, 126.8, 123.4, 120.5, 119.9, 118.8, 110.3, 109.3, 37.2, 29.5; FTIR (neat): 3065, 2926, 2226, 1603, 1491, 1444, 1442, 1328, 1229, 1156, 1017, 913, 809, 748, 732 cm^{-1}; MS (ESI): *m/z* 298 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_3$ $(M+H)^+$: 298.1339, found: 298.1335.

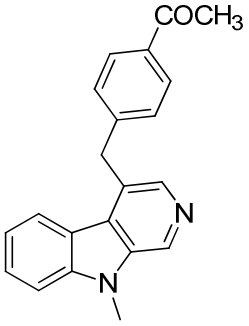
9-Methyl-4-(4-nitrobenzyl)-9*H*-pyrido[3,4-*b*]indole (3e):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-(4-nitrophenyl)prop-2-yn-1-amine hydrochloride (**2e**, 190.8 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 158 mg (83%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.29 (s, 1H), 8.12 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H),

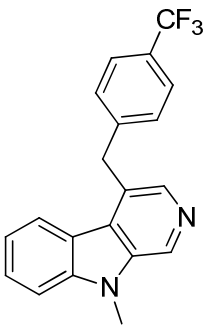
7.51 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 4.72 (s, 2H), 4.00 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 146.8, 146.7, 141.8, 140.0, 130.9, 129.2, 129.2, 128.3, 126.9, 123.9, 123.9, 123.4, 120.5, 120.0, 109.4, 37.0, 29.5; FTIR (neat): 3209, 3051, 2853, 1696, 1512, 1455, 1400, 1343, 1109, 1051, 791, 729 cm^{-1}; MS (ESI): *m/z* 318 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{16}N_3O_2$ $(M+H)^+$: 318.1237, found: 318.1231.

1-(4-((9-Methyl-9*H*-pyrido[3,4-*b*]indol-4-yl)methyl)phenyl)ethanone (3f):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 1-(4-(3-aminoprop-1-yn-1-yl)phenyl)ethanone hydrochloride (**2f**, 188 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 152 mg (81%) of a white solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 139-141 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.28 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.89-7.80 (m, 2H), 7.58 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.18 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 4.66 (s, 2H), 3.97 (s, 3H), 2.54 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 197.7, 144.7, 141.8, 140.0, 136.9, 135.5, 130.5, 128.8, 128.6, 128.4, 128.1, 127.0, 123.7, 120.7, 119.9, 109.2, 37.2, 29.5, 26.5; FTIR (neat): 3045, 2922, 2851, 1687, 1647, 1439, 1349, 1260, 1159, 996, 855, 728, 698 cm^{-1}; MS (ESI): *m/z* 315 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2O$ $(M+H)^+$: 315.1492, found: 315.1489.

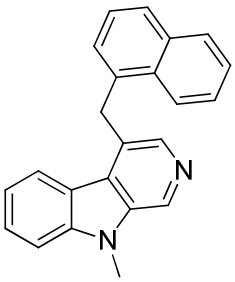
9-Methyl-4-(4-(trifluoromethyl)benzyl)-9*H*-pyrido[3,4-*b*]indole (3g):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine hydrochloride (**2g**, 211 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL were stirred for 3 h

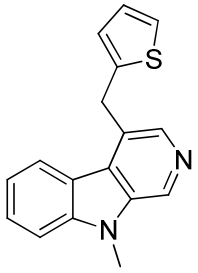
at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 190 mg (93%) of a white solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.32 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 8.1 Hz, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 4.65 (s, 2H), 3.96 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 143.2, 141.7, 140.3, 130.6, 128.8, 128.7, 128.5, 128.2, 128.0, 126.7, 125.5 (q, J = 3.7 Hz), 123.6, 122.8, 120.7, 119.8, 109.2, 37.0, 29.4; FTIR (neat): 3066, 2923, 2852, 1617, 1469, 1442, 1323, 1268, 1154, 1113, 1023, 860, 744, 726 cm^{-1}; MS (ESI): *m/z* 341 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}F_3N_2$ $(M+H)^+$: 341.1260, found: 341.1257.

9-Methyl-4-(naphthalen-1-ylmethyl)-9*H*-pyrido[3,4-*b*]indole (3h):



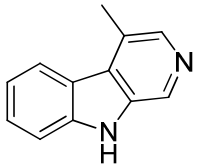
1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-(naphthalen-1-yl)prop-2-yn-1-amine hydrochloride (**2h**, 195 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 164 mg (85%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.16 (s, 1H), 8.14 (dd, J = 6.2, 3.4 Hz, 1H), 7.93 (dd, J = 6.1, 3.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.62-7.49 (m, 4H), 7.31-7.24 (m, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 6.9 Hz, 1H), 5.05 (s, 2H), 4.00 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.8, 134.2, 133.8, 132.0, 128.9, 128.9, 128.3, 128.0, 127.3, 126.4, 126.3, 126.2, 126.0, 125.8, 125.6, 125.1, 123.9, 123.5, 121.0, 119.9, 109.1, 34.4, 29.5; FTIR (neat): 3046, 2921, 2851, 1619, 1445, 1330, 1268, 1159, 1024, 980, 882, 791, 741 cm^{-1}; MS (ESI): *m/z* 323 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{23}H_{19}N_2$ $(M+H)^+$: 323.1543, found: 323.1536.

9-Methyl-4-(thiophen-2-ylmethyl)-9*H*-pyrido[3,4-*b*]indole (3i):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 3-(thiophen-2-yl)prop-2-yn-1-amine hydrochloride (**2i**, 155.7 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 135 mg (81%) of a pale, yellow solid was obtained. R_f = 0.4 (CH_2Cl_2/MeOH 95:5), mp = 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.35 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.62-7.54 (m, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.26-7.18 (m, 1H), 7.12 (dd, J = 5.1, 1.0 Hz, 1H), 6.87 (dd, J = 5.1, 3.5 Hz, 1H), 6.81-6.71 (m, 1H), 4.73 (s, 2H), 3.94 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 142.0, 141.7, 139.8, 136.9, 130.7, 128.7, 127.9, 126.9, 126.6, 125.2, 124.0, 123.9, 120.7, 119.8, 109.1, 31.8, 29.4; FTIR (neat): 3050, 2998, 2921, 1618, 1446, 1428, 1329, 1264, 1153, 1023, 813, 746, 691 cm^{-1}; MS (ESI): *m/z* 279 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}N_2S$ $(M+H)^+$: 279.0950, found: 279.0945.

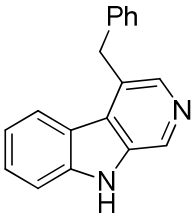
4-Methyl-9*H*-pyrido[3,4-*b*]indole (3j):



1*H*-Indole-2-carbaldehyde (**1b**, 87 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 21 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 67.7 mg (62%) of a pale, yellow solid was obtained. R_f = 0.2 (CH_2Cl_2/MeOH 95:5), mp = 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$: DMSO-d_6, 8:2): δ 11.12 (bs, 1H), 8.77 (s, 1H), 8.18 (d, J = 10.3 Hz, 2H), 7.66-7.49 (m, 2H), 7.26 (t, J = 7.3 Hz, 1H), 2.84 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$: DMSO-d_6, 8:2): δ 140.0, 137.8, 134.9, 130.9, 126.6, 126.2, 125.9, 122.5, 120.7, 118.5, 110.9, 16.5; FTIR (neat): 3049,

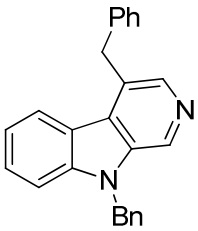
2924, 2852, 1624, 1454, 1422, 1328, 1134, 1069, 847, 733, 691 cm^{-1}; MS (ESI): *m/z* 183 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_{11}N_2$ $(M+H)^+$: 183.0917, found: 183.0918.

4-Benzyl-9*H*-pyrido[3,4-*b*]indole (3k):



1*H*-Indole-2-carbaldehyde (**1b**, 87 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 21 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 103 mg (67%) of a pale, yellow solid was obtained. R_f = 0.3 (CH_2Cl_2/MeOH 95:5), mp = 181-183 °C; ^1H NMR (400 MHz, $CDCl_3$:DMSO-d_6, 8:2): δ 11.14 (bs, 1H), 8.85 (s, 1H), 8.18 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.60-7.51 (m, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.29-7.20 (m, 4H), 7.16 (dt, J = 15.0, 5.6 Hz, 2H), 4.59 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$:DMSO-d_6, 8:2): δ 140.2, 138.8, 138.5, 135.5, 131.8, 128.2, 127.7, 127.7, 126.8, 126.1, 125.5, 122.8, 120.2, 118.6, 111.0, 36.3; FTIR (neat): 3010, 2856, 1569, 1457, 1403, 1346, 1259, 1173, 1005, 731, 697 cm^{-1}; MS (ESI): *m/z* 259 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_2$ $(M+H)^+$: 259.1230, found: 259.1231.

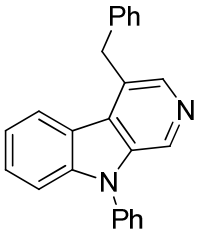
4,9-Dibenzyl-9*H*-pyrido[3,4-*b*]indole (3l):



1-Benzyl-1*H*-indole-2-carbaldehyde (**1c**, 141 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 164 mg (79%) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 135-136 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.27 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.53 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.33-7.24 (m, 7H), 7.24-7.13 (m, 4H), 5.60 (s, 2H), 4.64 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 141.3, 140.7, 138.9, 136.6, 136.4,

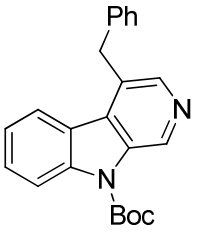
131.7, 130.7, 128.9, 128.6, 128.6, 128.0, 127.8, 127.2, 126.5, 126.4, 124.1, 121.2, 120.0, 109.5, 46.9, 37.2; MS (ESI): *m/z* 349 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{25}H_{21}N_2$ $(M+H)^+$: 349.1699, found: 349.1695.

4-Benzyl-9-(phenylsulfonyl)-9*H*-pyrido[3,4-*b*]indole (3m):



1-Phenyl-1*H*-indole-2-carbaldehyde (**1d**, 132 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 166 mg (83%) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.32 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.67-7.61 (m, 2H), 7.60-7.55 (m, 2H), 7.53-7.47 (m, 3H), 7.32-7.26 (m, 4H), 7.26-7.17 (m, 2H), 4.66 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.6, 141.4, 138.9, 137.0, 136.7, 131.7, 130.1, 129.0, 128.6, 128.5, 128.1, 128.0, 127.5, 127.1, 126.4, 123.9, 121.4, 120.6, 110.3, 37.2; FTIR (neat): 3055, 2926, 1595, 1500, 1403, 1325, 1252, 1132, 1025, 869, 743, 730, 698 cm^{-1}; MS (ESI): *m/z* 335 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{24}H_{19}N_2$ $(M+H)^+$: 335.1543, found: 335.1547.

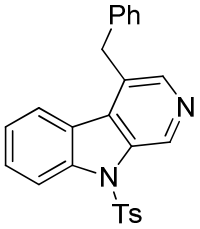
***tert*-Butyl 4-benzyl-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (3n):**



tert-Butyl 2-formyl-1*H*-indole-1-carboxylate (**1e**, 147 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 189 mg (88%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.40 (s, 1H), 7.96 (d, J =

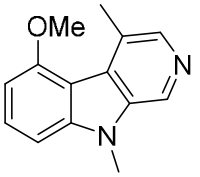
7.9 Hz, 1H), 7.59 (ddd, J = 8.5, 7.3, 1.2 Hz, 1H), 7.34-7.27 (m, 3H), 7.25-7.18 (m, 3H), 4.61 (s, 2H), 1.81 (s, 9H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 150.4, 144.5, 139.2, 138.4, 136.9, 134.8, 130.4, 129.1, 128.7, 128.5, 128.4, 126.5, 123.8, 123.5, 123.4, 116.4, 84.9, 36.9, 28.3; FTIR (neat): 3058, 2972, 1720, 1452, 1423, 1349, 1312, 1251, 1149, 1120, 824, 741, 701 cm^{-1}; MS (ESI): *m/z* 359 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{23}H_{23}N_2O_2$ $(M+H)^+$: 359.1754, found: 359.1748.

4-Benzyl-9-tosyl-9*H*-pyrido[3,4-*b*]indole (3o):



1-Tosyl-1*H*-indole-2-carbaldehyde (**1f**, 179 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 176 mg (83%) of a white solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 147-148 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 8.41 (d, J = 8.5 Hz, 1H), 8.36 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.81-7.70 (m, 2H), 7.66-7.51 (m, 1H), 7.35-7.29 (m, 1H), 7.29-7.17 (m, 3H), 7.14 (dd, J = 8.4, 7.8 Hz, 4H), 4.50 (s, 2H), 2.30 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 145.4, 145.2, 138.9, 137.9, 135.6, 134.7, 134.5, 131.0, 129.9, 129.4, 129.0, 128.7, 128.4, 126.6, 126.6, 124.4, 124.2, 123.9, 115.0, 36.8, 21.5; FTIR (neat): 3058, 2965, 1642, 1535, 1464, 1356, 1211, 1189, 1017, 936, 759, 690 cm^{-1}; MS (ESI): *m/z* 413 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{25}H_{21}N_2O_2S$ $(M+H)^+$: 413.1318, found: 413.1319.

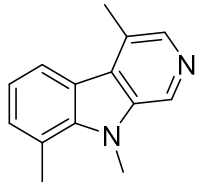
5-Methoxy-4,9-dimethyl-9*H*-pyrido[3,4-b]indole (3p):



4-Methoxy-1-methyl-1*H*-indole-2-carbaldehyde (**1g**, 113 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After

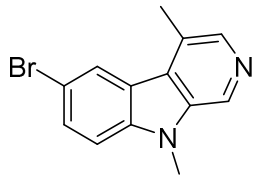
column chromatography (gradient: CH_2Cl_2/MeOH 100:0 to 99:1) 120 mg (88 %) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.22 (s, 1H), 7.50 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 8.2, 1H), 6.68 (d, J = 7.8 Hz, 1H), 4.01 (s, 3H), 3.87 (s, 3H), 2.92 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 155.9, 143.3, 141.1, 136.2, 129.3, 129.0, 127.3, 126.9, 111.2, 101.8, 100.5, 55.0, 29.5, 20.4; FTIR (neat): 2925, 1616, 1577, 1464, 1337, 1267, 1074, 785, 712 cm^{-1}; MS (ESI): *m/z* 227 $(M+H)^+$.

4,8,9-Trimethyl-9*H*-pyrido[3,4-b]indole (3q):



1,7-Dimethyl-1*H*-indole-2-carbaldehyde (**1h**, 103 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (gradient: CH_2Cl_2/MeOH 100:0 to 99:1) 105 mg (83%) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.16 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 4.01 (s, 3H), 2.78 (s, 3H), 2.70 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 140.0, 139.5, 137.0, 130.4, 129.6, 126.6, 126.4, 122.3, 121.5, 120.8, 119.5, 32.3, 20.3, 17.3; FTIR (neat): 3250, 2923, 1609, 1458, 1377, 1262, 1114, 950, 850, 745 cm^{-1}; MS (ESI): *m/z* 211 $(M+H)^+$.

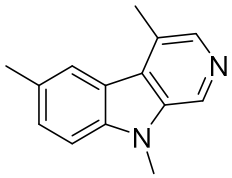
6-Bromo-4,9-dimethyl-9*H*-pyrido[3,4-b]indole (3r):



5-Bromo-1-methyl-1*H*-indole-2-carbaldehyde (**1i**, 141 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (gradient: CH_2Cl_2/MeOH 100:0 to 99:1), 130 mg (70 %) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.21 (d, J = 0.6 Hz, 1H), 8.15 (d, J = 1.7 Hz, 1H),

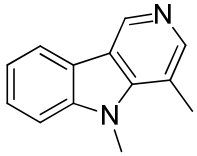
7.62 (dd, J = 8.7, 1.9 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 3.79 (s, 3H), 2.69 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 139.9, 136.5, 130.2, 130.2, 129.8, 126.9, 125.9, 125.7, 123.0, 112.1, 110.3, 29.3, 17.1; FTIR (neat): 2969, 2920, 1629, 1486, 1309, 1268, 1149, 952, 855, 804, 683 cm^{-1}; MS (ESI): m/z 275 $(M+H)^+$.

4,6,9-Trimethyl-9*H*-pyrido[3,4-b]indole (3s):



1,5-Dimethyl-1*H*-indole-2-carbaldehyde (**1j**, 103 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (gradient: CH_2Cl_2/MeOH 100:0 to 99:1) 109 mg (86 %) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 122-124 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.18 (d, J = 0.5 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.41 – 7.34 (m, 1H), 7.27 (d, J = 8.4 Hz, 1H), 3.78 (s, 3H), 2.75 (s, 3H), 2.53 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 139.7, 139.2, 136.6, 129.4, 128.9, 128.7, 126.8, 126.5, 123.3, 121.6, 108.5, 29.1, 21.4, 17.3; FTIR (neat): 3035, 2915, 1617, 1450, 1349, 1309, 1259, 1059, 857, 805 cm^{-1}; MS (ESI): m/z 211 $(M+H)^+$.

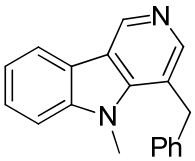
4,5-Dimethyl-5*H*-pyrido[4,3-*b*]indole (3t):



1-Methyl-1*H*-indole-3-carbaldehyde (**1l**, 95 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 108 mg (92%) of a pale, yellow solid was obtained. R_f = 0.4 (CH_2Cl_2/MeOH 95:5), mp = 129-130 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.22 (s, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 4.02 (s, 3H), 2.74 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 146.7,

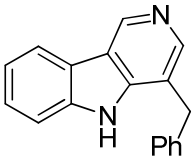
143.6, 141.1, 141.1, 126.5, 121.2, 120.4, 120.2, 119.3, 115.0, 108.8, 31.7, 17.0; FTIR (neat): 3048, 2960, 2924, 1584, 1457, 1350, 1238, 1152, 1050, 910, 878, 771, 668 cm^{-1}; MS (ESI): *m/z* 197 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}N_2$ $(M+H)^+$: 197.1073, found: 197.1071.

4-Benzyl-5-methyl-5*H*-pyrido[4,3-*b*]indole (3u):



1-Methyl-1*H*-indole-3-carbaldehyde (**1l**, 95 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 141 mg (87%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 8.38 (s, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.42-7.19 (m, 5H), 7.12 (d, J = 7.3 Hz, 2H), 4.55 (s, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 147.9, 143.6, 141.9, 141.2, 140.4, 128.8, 128.0, 126.7, 126.5, 121.3, 120.6, 120.3, 120.0, 116.8, 109.0, 36.2, 31.5; FTIR (neat): 3030, 2924, 2856, 1585, 1480, 1332, 1288, 1123, 1051, 881, 778, 695 cm^{-1}; MS (ESI): *m/z* 273 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{17}N_2$ $(M+H)^+$: 273.1386, found: 273.1383.

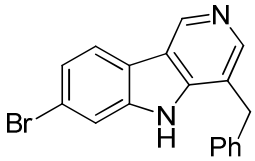
4-Benzyl-5*H*-pyrido[4,3-*b*]indole (3v):



1*H*-Indole-3-carbaldehyde (**1m**, 87 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 21 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 106 mg (69%) of a yellow solid was obtained. R_f = 0.3 (CH_2Cl_2/MeOH 95:5), mp = 197-198 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.22 (s, 1H), 8.29 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.48 (dd, J = 11.2, 4.0 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.33-7.23 (m, 3H), 7.19 (t, J = 7.2 Hz,

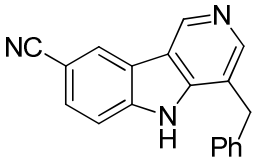
1H), 4.30 (s, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, DMSO-d_6): δ 144.6, 142.6, 141.0 (d, J = 21.2 Hz), 139.9, 139.7, 128.5, 128.5, 128.5, 126.6, 126.2, 121.0, 120.7, 120.0, 119.2, 119.1, 111.6, 33.9; FTIR (neat): 3055, 2974, 2808, 1599, 1494, 1409, 1330, 1219, 1112, 1031, 731, 692 cm^{-1}; MS (ESI): *m/z* 259 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_2$ $(M+H)^+$: 259.1230, found: 259.1232.

4-Benzyl-7-bromo-5*H*-pyrido[4,3-*b*]indole (3w):



6-Bromo-1*H*-indole-3-carbaldehyde (**1n**, 133 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 21 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 151 mg (75%) of a yellow solid was obtained. R_f = 0.3 (CH_2Cl_2/MeOH 95:5), mp = 191-192 °C; ^1H NMR (400 MHz, $CDCl_3$: DMSO-d_6, 1:1): δ 11.51 (bs, 1H), 9.15 (s, 1H), 8.29 (s, 1H), 8.00 (dt, J = 8.6, 4.3 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.68 (t, J = 1.8 Hz, 1H), 7.35 (dt, J = 8.3, 2.1 Hz, 1H), 7.27 (dd, J = 8.1, 5.2 Hz, 3H), 7.23-7.14 (m, 1H), 4.31 (s, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$: DMSO-d_6, 1:1): δ 143.9, 142.2, 139.8, 139.7, 138.1, 127.3, 127.2, 125.1, 121.9, 120.5, 119.2, 118.3, 117.8, 117.7, 113.3, 33.2; FTIR (neat): 3032, 2956, 2813, 1549, 1439, 1405, 1356, 1213, 1091, 913, 856, 779, 696 cm^{-1}; MS (ESI): *m/z* 337 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrN_2$ $(M+H)^+$: 337.0335, found: 337.0343.

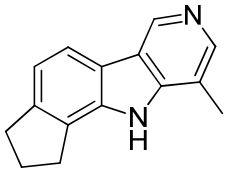
4-Benzyl-5*H*-pyrido[4,3-*b*]indole-8-carbonitrile (**3x**):



3-Formyl-1*H*-indole-5-carbonitrile (**1o**, 102 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 21 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0

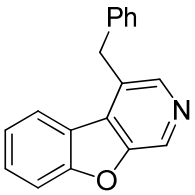
to 99:1), 113 mg (67%) of a pale, yellow solid was obtained. R_f = 0.2 (CH_2Cl_2/MeOH 95:5), mp = 179-180 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (s, 1H), 8.83 (s, 1H), 8.40 (s, 1H), 7.86 (dd, J = 8.5, 1.3 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.40-7.25 (m, 4H), 7.20 (t, J = 7.1 Hz, 1H), 4.32 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 145.9, 143.4, 141.9, 139.6, 129.7, 128.5, 128.5, 128.4, 126.3, 126.2, 121.3, 120.1, 119.7, 118.4, 112.7, 102.0, 33.8; FTIR (neat): 3032, 2920, 2813, 2223, 1585, 1477, 1411, 1243, 1221, 1120, 884, 819, 742, 696 cm^{-1}; MS (ESI): *m/z* 284 (M+H)$^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{14}N_3$ (M+H)$^+$: 284.1182, found: 284.1185.

9-Benzyl-1,2,3,10-tetrahydrocyclopenta[*g*]pyrido[4,3-*b*]indole (3y):



1, 6, 7, 8-Tetrahydrocyclopenta[g]indole-3-carbaldehyde (**1p**, 111 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 21 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 102 mg (77%) of a pale, yellow solid was obtained. R_f = 0.3 (CH_2Cl_2/MeOH 95:5), mp = 183-184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (bs, 1H), 9.13 (s, 1H), 8.21 (s, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 3.16 (t, J = 7.3 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 2.54 (s, 3H), 2.27-2.13 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 143.8, 143.4, 142.8, 140.0, 136.6, 125.8, 119.5, 119.3, 118.5, 116.7, 115.7, 33.0, 30.2, 25.1, 14.3; FTIR (neat): 2922, 2851, 1578, 1456, 1378, 1252, 1224, 1109, 804, 686 cm^{-1}; MS (ESI): *m/z* 223 (M+H)$^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}N_2$ (M+H)$^+$: 223.1230, found: 223.1232.

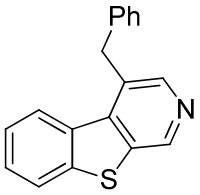
4-Benzylbenzofuro[2,3-*c*]pyridine (4a):



Benzofuran-2-carbaldehyde (**1q**, 88 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h

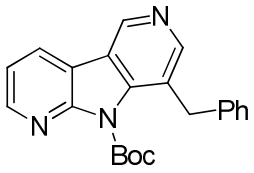
at 80 °C. After column chromatography (EtOAc/hexanes 10:90 to 40:60), 122 mg (79%) of a white solid was obtained. R_f = 0.2 (EtOAc/hexanes 30:70), mp = 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.40 (s, 1H), 7.88-7.81 (m, 1H), 7.66-7.62 (m, 1H), 7.56 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.35-7.25 (m, 3H), 7.25-7.19 (m, 3H), 4.53 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 156.6, 152.6, 144.1, 138.3, 132.7, 130.0, 129.8, 129.4, 128.7, 128.4, 126.6, 123.7, 123.4, 122.2, 112.3, 36.7; FTIR (neat): 3023, 2921, 2852, 1625,, 1448, 1416, 1268, 1201, 1151, 1041, 847, 751, 702 cm^{-1}; MS (ESI): *m/z* 260 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}NO$ $(M+H)^+$: 260.1070, found: 260.1066.

4-Benzylbenzo[4,5]thieno[2,3-*c*]pyridine (4b):



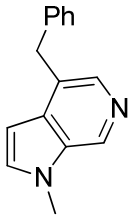
Benzo[b]thiophene-2-carbaldehyde (**1r**, 97 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (EtOAc/hexanes 10:90 to 40:60), 136 mg (83%) of a pale, yellow solid was obtained. R_f = 0.2 (EtOAc/hexanes 30:70), mp = 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.40 (s, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.51 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H), 7.37 (ddd, J = 8.3, 7.2, 1.1 Hz, 1H), 7.30-7.26 (m, 2H), 7.24-7.13 (m, 3H), 4.64 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 146.3, 143.4, 141.1, 140.1, 138.1, 136.0, 133.9, 130.3, 128.8, 128.3, 128.2, 126.6, 126.4, 124.8, 123.2, 37.7; FTIR (neat): 3027, 2922, 2851, 1493, 1441, 1405, 1254, 1228, 1132, 1072, 882, 735, 696 cm^{-1}; MS (ESI): *m/z* 276 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}NS$ $(M+H)^+$: 276.0841, found: 276.0839.

***tert*-Butyl 8-benzyl-9*H*-pyrrolo[2,3-*b*:4,5-*c*']dipyridine-9-carboxylate (4c):**



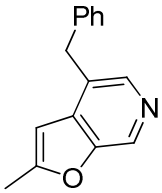
tert-Butyl 3-formyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (**1s**, 147 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 174 mg (81%) of a pale, yellow solid was obtained. R_f = 0.4 (CH_2Cl_2/MeOH 95:5), mp = 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.55 (dd, J = 4.8, 1.7 Hz, 1H), 8.47 (s, 1H), 8.35 (dd, J = 7.7, 1.7 Hz, 1H), 7.34 (dd, J = 7.7, 4.8 Hz, 1H), 7.24-7.17 (m, 3H), 7.05 (d, J = 6.8 Hz, 2H), 4.46 (s, 2H), 1.59 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 151.6, 149.7, 149.2, 148.0, 141.5, 141.2, 138.7, 132.6, 128.5, 128.4, 126.4, 121.7, 119.2, 118.9, 115.5, 85.5, 37.0, 27.8; FTIR (neat): 3063, 2976, 2925, 1739, 1576, 1495, 1400, 1254, 11456, 892, 757, 706 cm^{-1}; MS (ESI): *m/z* 360 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}N_3O_2$ $(M+H)^+$: 360.1707, found: 360.1709.

4-Benzyl-1-methyl-1*H*-pyrrolo[2,3-*c*]pyridine (4d):



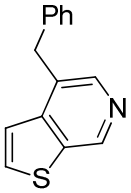
1-Methyl-1H-pyrrole-2-carbaldehyde (**1t**, 65 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 62 mg (62%) of a pale, yellow solid was obtained. R_f = 0.1 (CH_2Cl_2/MeOH 95:5), mp = 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.13 (s, 1H), 7.28-7.22 (m, 4H), 7.20-7.15 (m, 1H), 7.12 (d, J = 3.0 Hz, 1H), 6.37 (dd, J = 3.0, 0.5 Hz, 1H), 4.23 (s, 2H), 3.88 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 140.3, 138.5, 133.0, 132.0, 131.3, 128.7, 128.4, 128.4, 127.5, 126.1, 99.4, 37.2, 33.2; FTIR (neat): 3019, 2917, 2850, 1669, 1503, 1447, 1350, 1251, 1117, 1080, 864, 758, 699 cm^{-1}; MS (ESI): *m/z* 223 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}N_2$ $(M+H)^+$: 223.1230, found: 223.1228.

4-Benzyl-2-methylfuro[2,3-*c*]pyridine (4t):



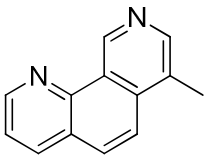
5-Methylfuran-2-carbaldehyde (**1u**, 66 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 115 mg (86%) of a white solid was obtained. R_f = 0.7 (CH_2Cl_2/MeOH 95:5), mp = 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.25 (s, 1H), 7.31-7.25 (m, 2H), 7.24-7.17 (m, 3H), 6.25 (s, 1H), 4.16 (s, 2H), 2.45 (d, J = 1.0 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 158.9, 142.3, 139.6, 135.3, 131.3, 128.7, 128.6, 128.6, 128.0, 126.4, 101.1, 37.0, 14.2; FTIR (neat): 3026, 2919, 2851, 1594, 1494, 1417, 1264, 1205, 1030, 939, 865, 730, 698 cm^{-1}; MS (ESI): *m/z* 224 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}NO$ $(M+H)^+$: 224.1070, found: 224.1067.

4-Benzylthieno[2,3-*c*]pyridine (4f):



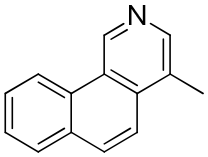
Thiophene-2-carbaldehyde (**1v**, 67 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 101 mg (75%) of a pale, yellow solid was obtained. R_f = 0.7 (CH_2Cl_2/MeOH 95:5), mp = 147-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.38 (s, 1H), 7.67 (d, J = 5.4 Hz, 1H), 7.34 (d, J = 5.4 Hz, 1H), 7.31-7.24 (m, 2H), 7.21 (t, J = 6.7 Hz, 3H), 4.31 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 144.4, 143.1, 142.9, 139.4, 132.0, 130.2, 128.6, 128.6, 128.4, 126.5, 121.6, 37.4; FTIR (neat): 3097, 3084, 2920, 1567, 1491, 1401, 1340, 1257, 1225, 957, 779, 746, 695 cm^{-1}; MS (ESI): *m/z* 226 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{12}NS$ $(M+H)^+$: 226.0685, found: 226.0681.

7-Methyl-1,9-phenanthroline (4g):



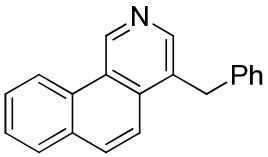
Quinoline-8-carbaldehyde (**1w**, 94 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 73 mg (63%) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 9.08 (dd, J = 4.4, 1.8 Hz, 1H), 8.67 (d, J = 0.7 Hz, 1H), 8.24 (dd, J = 8.1, 1.8 Hz, 1H), 7.96 (s, 2H), 7.60 (dd, J = 8.1, 4.4 Hz, 1H), 2.72 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 150.1, 147.3, 146.8, 146.3, 136.4, 135.9, 129.9, 127.3, 126.1, 125.2, 122.5, 122.3, 16.2; FTIR (neat): 3050, 2936, 2925, 1725, 1539, 1487, 1439, 1254, 1453, 903, 765, 720 cm^{-1}; MS (ESI): *m/z* 195 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}N_2$ $(M+H)^+$: 195.0917, found: 195.0913.

4-Methylbenzo[*h*]isoquinoline (4h):



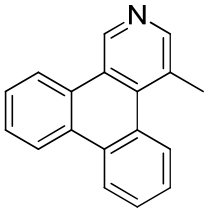
1-Naphthaldehyde (**1x**, 94 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (EtOAc/hexanes 10:90 to 40:60), 101 mg (87%) of a pale, yellow solid was obtained. R_f = 0.3 (EtOAc/hexanes 30:70), mp = 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.82 (d, J = 8.3 Hz, 1H), 8.57 (s, 1H), 8.02 (d, J = 9.1 Hz, 1H), 7.96 (dd, J = 7.9, 1.2 Hz, 1H), 7.89 (d, J = 9.1 Hz, 1H), 7.76 (ddd, J = 8.4, 7.1, 1.4 Hz, 1H), 7.68 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 2.71 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 144.8, 144.7, 135.1, 131.8, 131.7, 129.6, 128.9, 128.2, 128.0, 127.4, 124.4, 122.2, 121.1, 16.3; FTIR (neat): 3035, 2980, 2869, 1576, 1475, 1356, 1283, 1136, 996, 789, 699 cm^{-1}; MS (ESI): *m/z* 194 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{12}N$ $(M+H)^+$: 194.0959, found: 194.0964.

4-Benzylbenzo[*h*]isoquinoline (4i):



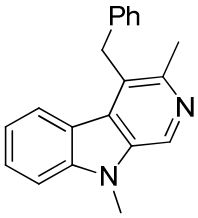
1-Naphthaldehyde (**1x**, 94 mg, 0.60 mmol), 3-phenylprop-2-yn-1-amine hydrochloride (**2b**, 150 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (EtOAc/hexanes 10:90 to 40:60), 95 mg (82%) of a pale, yellow solid was obtained. R_f = 0.3 (EtOAc/hexanes 30:70), mp = 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.85 (d, J = 8.3 Hz, 1H), 8.64 (s, 1H), 7.96-7.88 (m, 2H), 7.84 (d, J = 9.1 Hz, 1H), 7.80-7.73 (m, 1H), 7.68 (dd, J = 11.0, 4.0 Hz, 1H), 7.34-7.26 (m, 2H), 7.22 (dd, J = 6.9, 4.4 Hz, 3H), 4.49 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 146.1, 145.9, 139.8, 134.7, 131.7, 130.2, 129.7, 128.8, 128.6, 128.6, 128.5, 127.9, 127.4, 126.3, 124.9, 122.2, 121.4, 36.4; FTIR (neat): 3043, 2959, 2876, 1577, 1483, 1371, 1239, 1121, 887, 779, 696 cm^{-1}; MS (ESI): *m/z* 270 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N$ $(M+H)^+$: 270.1277, found: 270.1278.

4-Methyldibenzo[*f,h*]isoquinoline (4j):



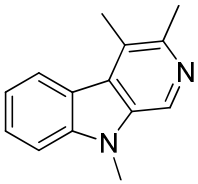
Phenanthrene-9-carbaldehyde (**1y**, 123 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 123 mg (85%) of a white solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.76 (d, J = 8.2 Hz, 1H), 8.73-8.68 (m, 2H), 8.66-8.59 (m, 2H), 7.75 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.72-7.62 (m, 3H), 3.04 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 150.0, 144.8, 135.1, 132.3, 130.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 126.4, 125.2, 123.5, 123.2, 123.0, 23.6; FTIR (neat): 3057, 2961, 2871, 1587, 1416, 1375, 1249, 1156, 882, 752, 713 cm^{-1}; MS (ESI): *m/z* 244 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N$ $(M+H)^+$: 244.1121, found: 244.1122.

4-Benzyl-3,9-dimethyl-9*H*-pyrido[3,4-*b*]indole (5a):



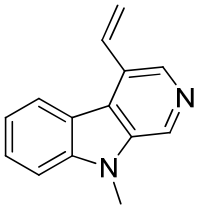
1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 4-phenylbut-3-yn-2-amine hydrochloride (**2k**, 162 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 139 mg (81%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 161-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.60-7.51 (m, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.25-7.19 (m, 2H), 7.16 (t, J = 7.16 Hz, 4H), 4.65 (s, 2H), 3.92 (s, 3H), 2.66 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 146.6, 142.1, 138.4, 136.1, 128.9, 128.6, 128.3, 128.1, 127.7, 126.6, 126.2, 123.8, 121.0, 119.5, 109.0, 35.4, 29.3, 21.5; FTIR (neat): 3026, 2918, 1492, 1452, 1329, 1277, 1074, 938, 742, 729, 696 cm^{-1}; MS (ESI): *m/z* 287 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}N_2$ $(M+H)^+$: 287.1543, found: 287.1547.

3,4,9-Trimethyl-9*H*-pyrido[3,4-*b*]indole (5b):



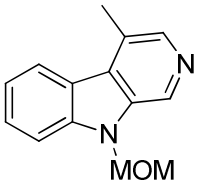
1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), but-3-yn-2-amine hydrochloride (**2j**, 94.5 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 114 mg (91%) of a pale, yellow solid was obtained. R_f = 0.6 (CH_2Cl_2/MeOH 95:5), mp = 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.59-7.53 (m, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.28-7.23 (m, 1H), 3.82 (s, 3H), 2.76 (s, 3H), 2.69 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 145.3, 141.9, 135.8, 127.7, 127.7, 127.4, 124.8, 123.8, 121.6, 119.2, 108.8, 29.1, 21.8, 15.9; FTIR (neat): 3059, 2921, 1620, 1460, 1327, 1282, 1159, 1002, 956, 725 cm^{-1}; MS (ESI): *m/z* 211 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}N_2$ $(M+H)^+$: 211.1230, found: 211.1235.

9-Methyl-4-vinyl-9*H*-pyrido[3,4-*b*]indole (5c):



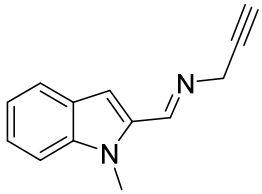
1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), 4-chlorobut-2-yn-1-amine hydrochloride (**2l**, 125 mg, 0.90 mmol) and $NaHCO_3$ (151 mg, 1.80 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 78 mg (63%) of a pale, yellow solid was obtained. R_f = 0.4 (CH_2Cl_2/MeOH 95:5), mp = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.58 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.68-7.55 (m, 2H), 7.51 (d, J = 8.3 Hz, 1H), 7.33 (ddd, J = 11.3, 6.2, 2.6 Hz, 1H), 6.00 (dd, J = 17.5, 1.3 Hz, 1H), 5.64 (dd, J = 11.0, 1.2 Hz, 1H), 3.97 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.8, 136.7, 136.7, 132.5, 130.6, 128.4, 128.0, 125.3, 124.1, 121.2, 119.8, 118.2, 109.1, 29.4; FTIR (neat): 3050, 2922, 1617, 1466, 1441, 1326, 1264, 1136, 1098, 916, 745, 730 cm^{-1}; MS (ESI): *m/z* 209 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_2$ $(M+H)^+$: 209.1073, found: 209.1076.

9-(Methoxymethyl)-4-methyl-9*H*-pyrido[3,4-b]indole (3z):



1-(Methoxymethyl)-1*H*-indole-2-carbaldehyde (**1z**, 113 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1), 126 mg (93 %) of a pale, yellow solid was obtained. R_f = 0.5 (CH_2Cl_2/MeOH 95:5), mp = 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.30 (s, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.68-7.54 (m, 2H), 7.43-7.31 (m, 1H), 5.74 (s, 2H), 3.30 (s, 3H), 2.84 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 141.1, 140.8, 136.3, 130.3, 128.0, 127.7, 127.1, 123.7, 122.4, 120.7, 109.8, 74.3, 56.3, 17.4; FTIR (neat): 2944, 1617, 1451, 1327, 1263, 1135, 1068, 1101, 911, 753, 689 cm^{-1}; MS (ESI): *m/z* 227 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}N_2O$ $(M+H)^+$: 227.1179, found: 227.1181.

(*E*)-*N*-((1-methyl-1*H*-indol-2-yl)methylene)prop-2-yn-1-amine (3aa):



1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and 4 Å molecular sieves in DMF (3 mL) were stirred for 3 h at room temperature followed by 6 h at 80 °C. After column chromatography (EtOAc/hexanes 1:99 to 5:95), 100 mg (85%) of a pale, yellow solid was obtained. R_f = 0.5 (EtOAc/hexanes 10:90), mp = 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (t, J = 1.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.33 (ddd, J = 14.4, 8.3, 4.0 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.87 (s, 1H), 4.54 (t, J = 2.1 Hz, 2H), 4.11 (s, 3H), 2.54 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 155.1, 140.0, 135.1, 126.9, 124.1, 121.8, 120.0, 110.0, 109.7, 79.0, 75.7, 47.5, 31.9; FTIR (neat): 3242, 2940, 2869, 1638, 1469, 1322, 1182, 1122, 1026, 920, 804, 740 cm^{-1}; MS (ESI): *m/z* 197 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}N_2$ $(M+H)^+$: 197.1073, found: 197.1072.

Synthesis of carboline 3a from imine intermediate 3aa:

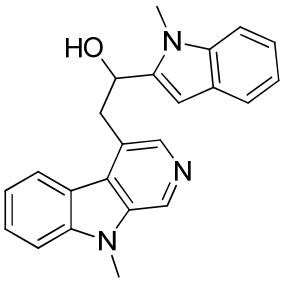
To a stirred solution of imine **3aa** (0.6 mmol) in DMF (2 mL) was added $NaHCO_3$ (1.2 mmol) at room temperature under argon. The reaction mixture was stirred for 6 h at 80 °C. After completion of the reaction, water (10 mL) was added. The two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with ice cold water (2 x 15 mL), dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford β-carboline **3a** in 88% yield.

Gram-scale synthesis of 3a:

1-Methyl-1*H*-indole-2-carbaldehyde (**1a**, 95 mg, 0.60 mmol), propargylamine (**2a**, 49.5 mg, 0.90 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in DMF (3 mL) were stirred for 3 h at room

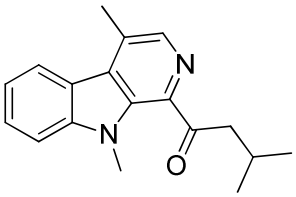
temperature followed by 6 h at 80 °C. Column chromatography (CH_2Cl_2/MeOH 100:0 to 99:1) gave **3a** (79%) and **5** (5%).

1-(1-Methyl-1*H*-indol-2-yl)-2-(9-methyl-9*H*-pyrido[3,4-*b*]indol-4-yl)ethanol (6):



Pale, yellow solid. mp = 145-147 °C; R_f = 0.6 (EtOAc/hexanes 30:70), ^{1}H NMR (400 MHz, $CDCl_3$: DMSO-d_6, 2:8): δ 8.88 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 8.17 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 6.54 (s, 1H), 5.65 (d, J = 6.1 Hz, 1H), 5.26 (dd, J = 13.0, 6.3 Hz, 1H), 3.98 (s, 3H), 3.87-3.75 (m, 2H), 3.69 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$: DMSO-d_6, 2:8): δ 140.1, 139.4, 138.2, 135.5, 134.5, 128.7, 125.7, 125.4, 124.8, 123.8, 121.3, 119.0, 118.3, 118.1, 117.7, 117.0, 108.0, 107.4, 96.7, 63.1, 36.0, 28.0, 27.3; FTIR (neat): 3049, 2924, 1659, 1466, 1423, 1326, 1132, 1066, 911, 847, 743, 687 cm^{-1}; MS (ESI): *m/z* 356 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_3O$ $(M+H)^+$: 356.1757, found: 356.1759.

Synthesis of oxopropaline analogue (7):[9]



To a solution of **3a** (0.2 mmol), isovaleraldehyde (0.8 mmol) and $TMSN_3$ (0.4 mmol) in benzene (1.5 mL), phenyliodinebis(trifluoroacetate) (PIFA) (0.4 mmol) was added portionwise over a 10 minute period at room temperature. After stirring for 2 h at room temperature, triethylamine (0.5 mL) was added and the mixture was stirred for 10 min. The volatiles were removed under reduced pressure. Flash column chromatography (EtOAc/hexanes 1:99 to 5:95) gave the product **7** as a semisolid in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 0.6 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.61 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.32 (ddd, J = 8.0, 7.2, 0.9 Hz, 1H), 3.87 (s, 3H), 3.28 (d, J = 7.0 Hz, 2H), 2.86

(d, J = 0.5 Hz, 3H), 2.47-2.34 (m, 1H), 1.07 (d, J = 6.7 Hz, 6H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 203.5, 143.2, 138.5, 138.3, 135.0, 130.7, 130.0, 128.2, 123.4, 121.3, 120.2, 109.9, 48.8, 34.0, 25.0, 22.8, 17.8; FTIR (neat): 2954, 2869, 1680, 1615, 1464, 1275, 1183, 1108, 1011, 934, 734 cm^{-1}; MS (ESI): *m/z* 281 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{21}N_2O$ $(M+H)^+$: 281.1648, found: 281.1652.

NMR analysis of the conversion of 3aa to 3a:

To a stirred solution of (*E*)-*N*-((1-methyl-1*H*-indol-2-yl)methylene)prop-2-yn-1-amine (**3aa**) (50 mg, 0.25 mmol) in DMF-d_7 (2.5 mL) was added $NaHCO_3$ (25.2 mg, 0.3 mmol) at room temperature under argon. The solution was heated to 80 °C and stirred for 2 h. An aliquot was analyzed by ^{1}H and DEPT135 NMR every 2 hours for 8 hours. The spectra allowed for monitoring the progress of the reaction, allene intermediate formation, and product formation by NMR.

References:

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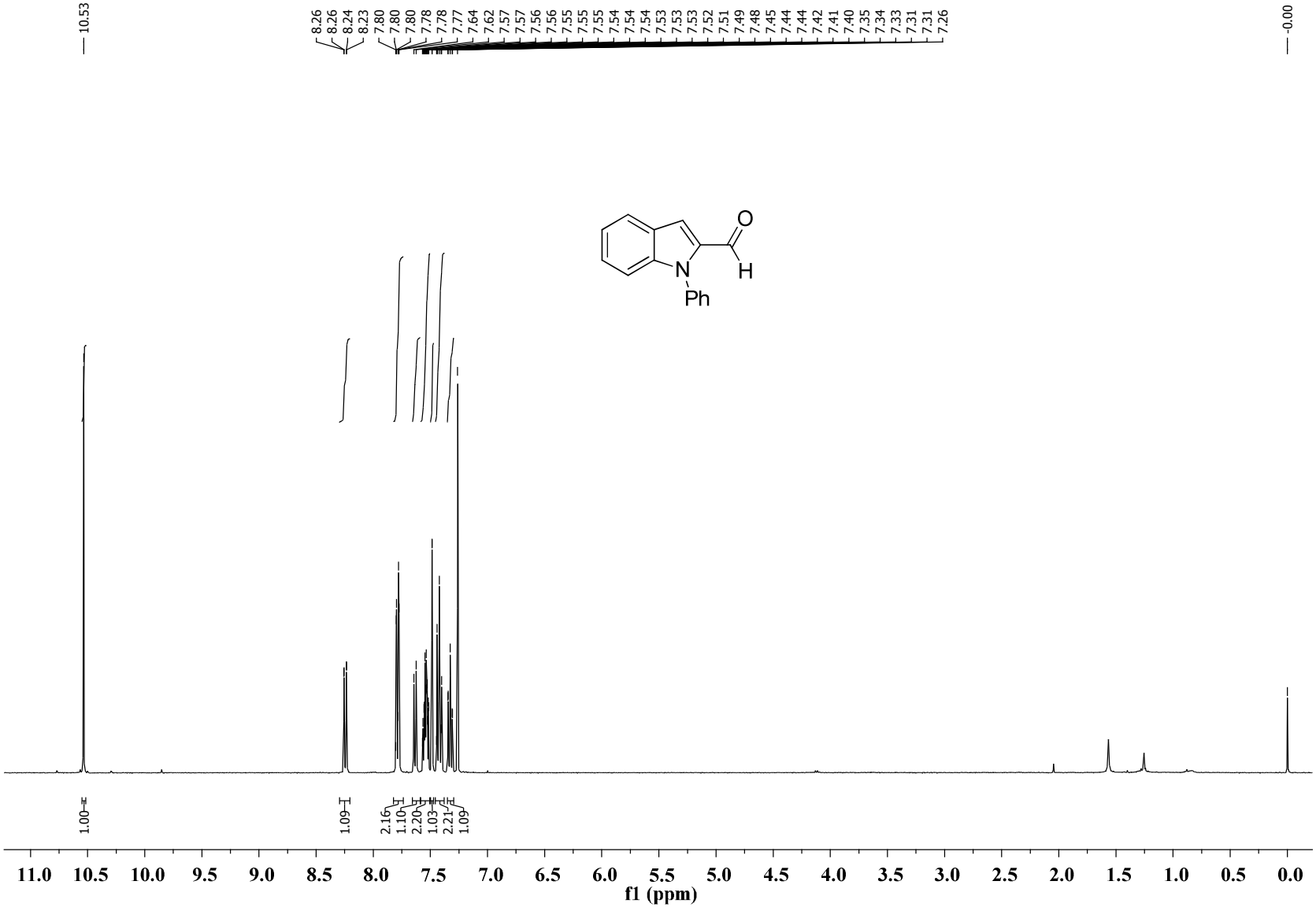
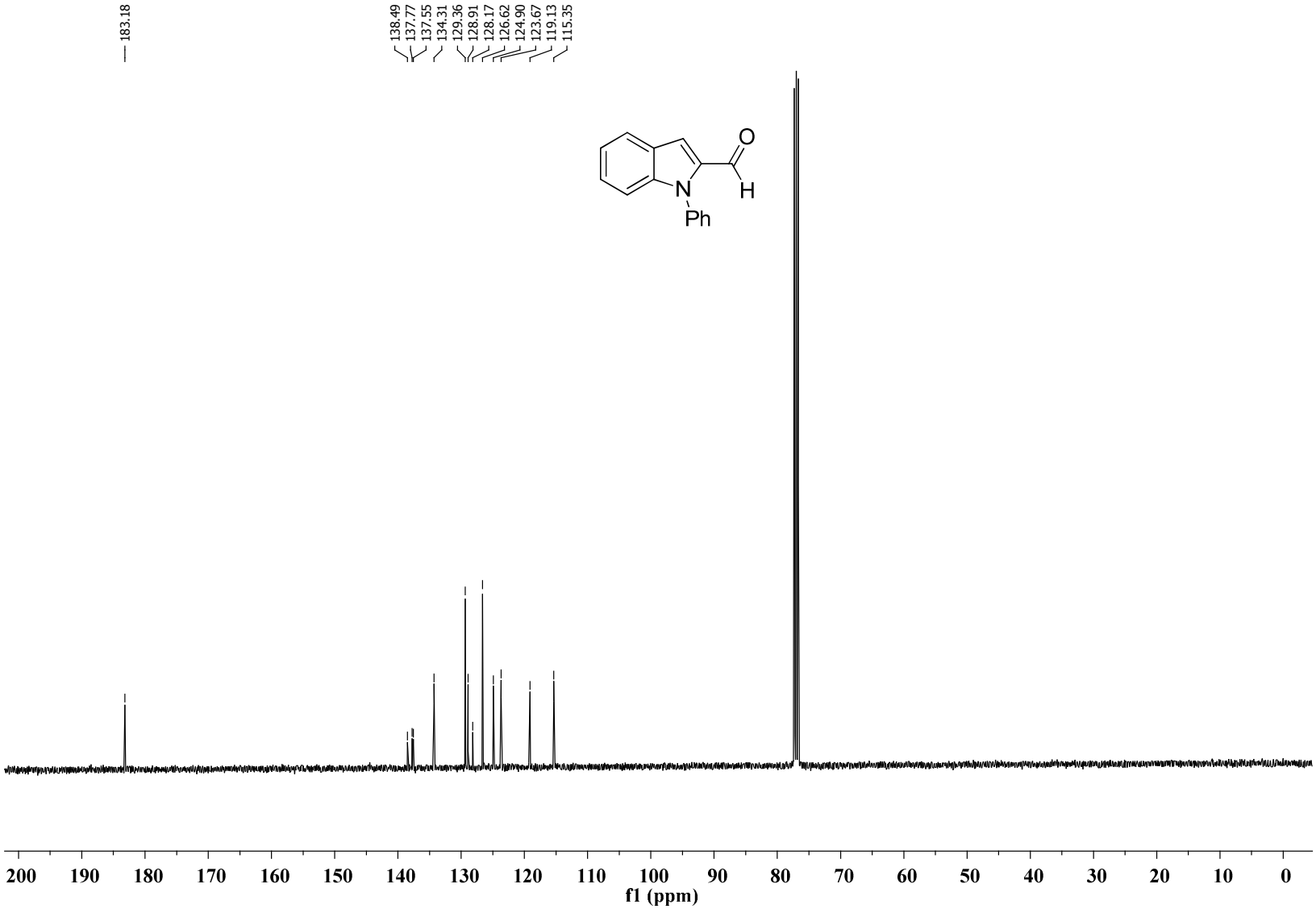
9. Kiran, M.; P., A. A., *Angew. Chem. Int. Ed.* **2013**, *52*, 2082-2086.

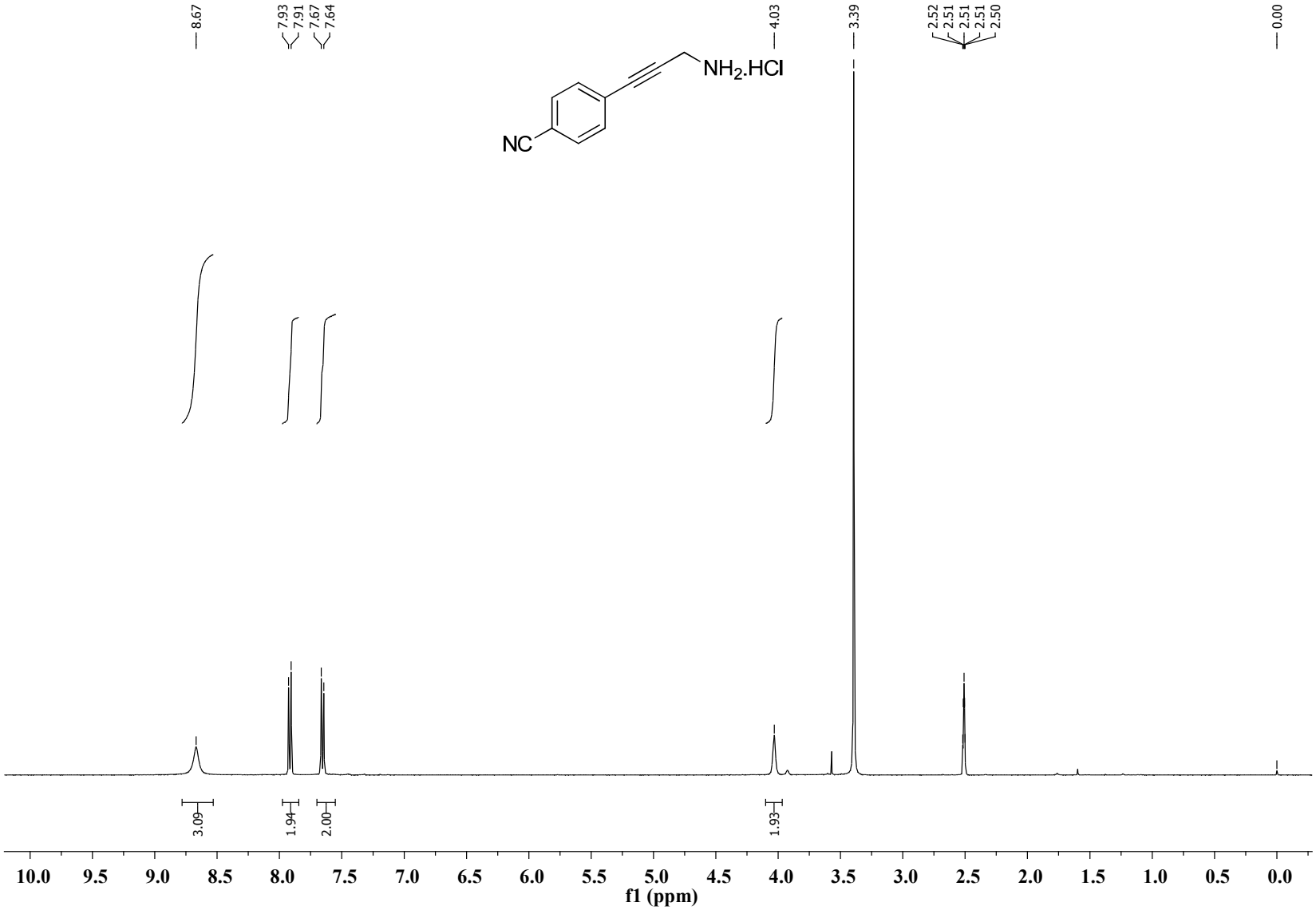
^{1}H NMR spectrum of **1d** ($CDCl_3$, 400 MHz)**:**



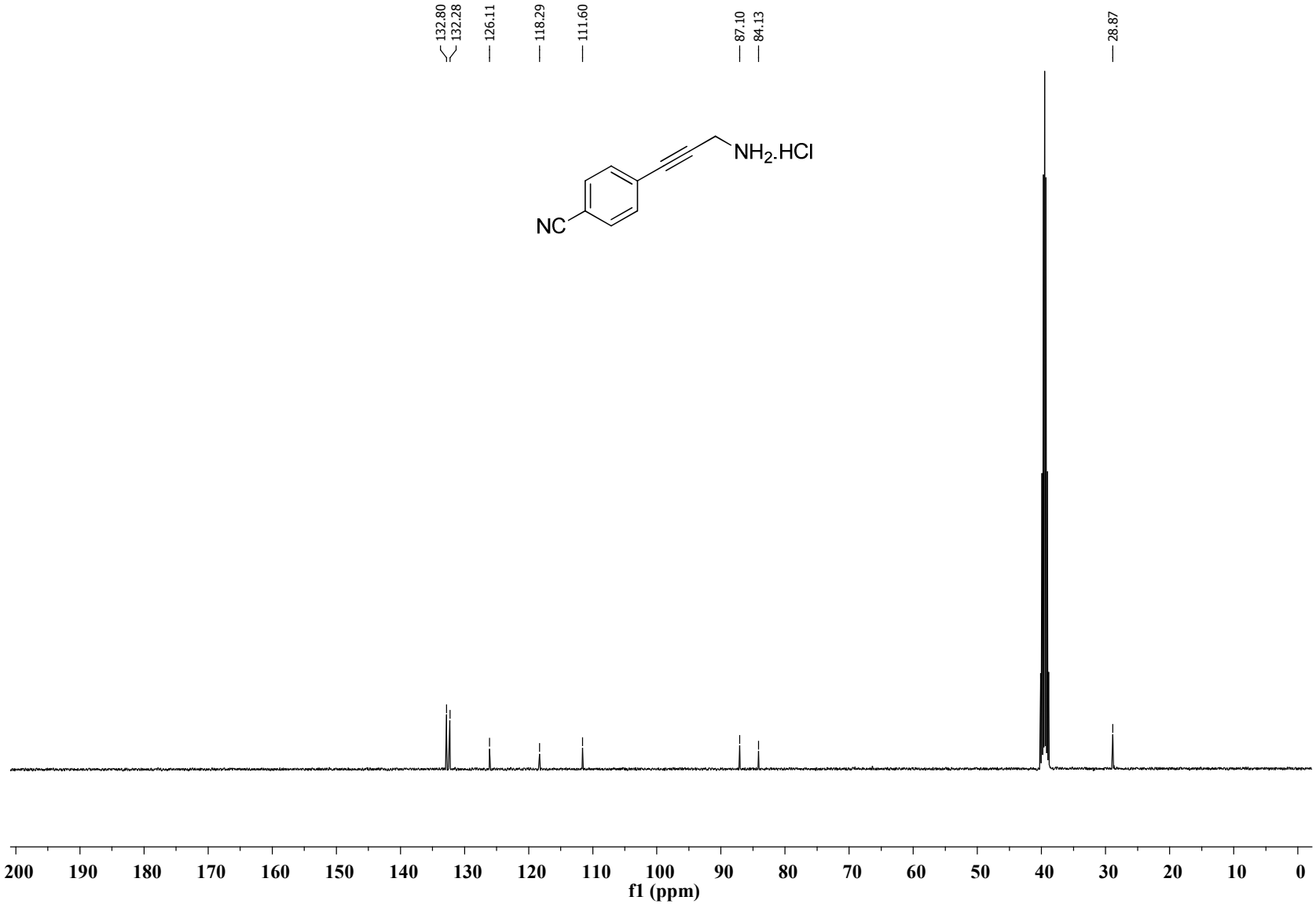
$^{13}C\{^{1}H\}$NMR spectrum of **1d** ($CDCl_3$, 100 MHz)**:**



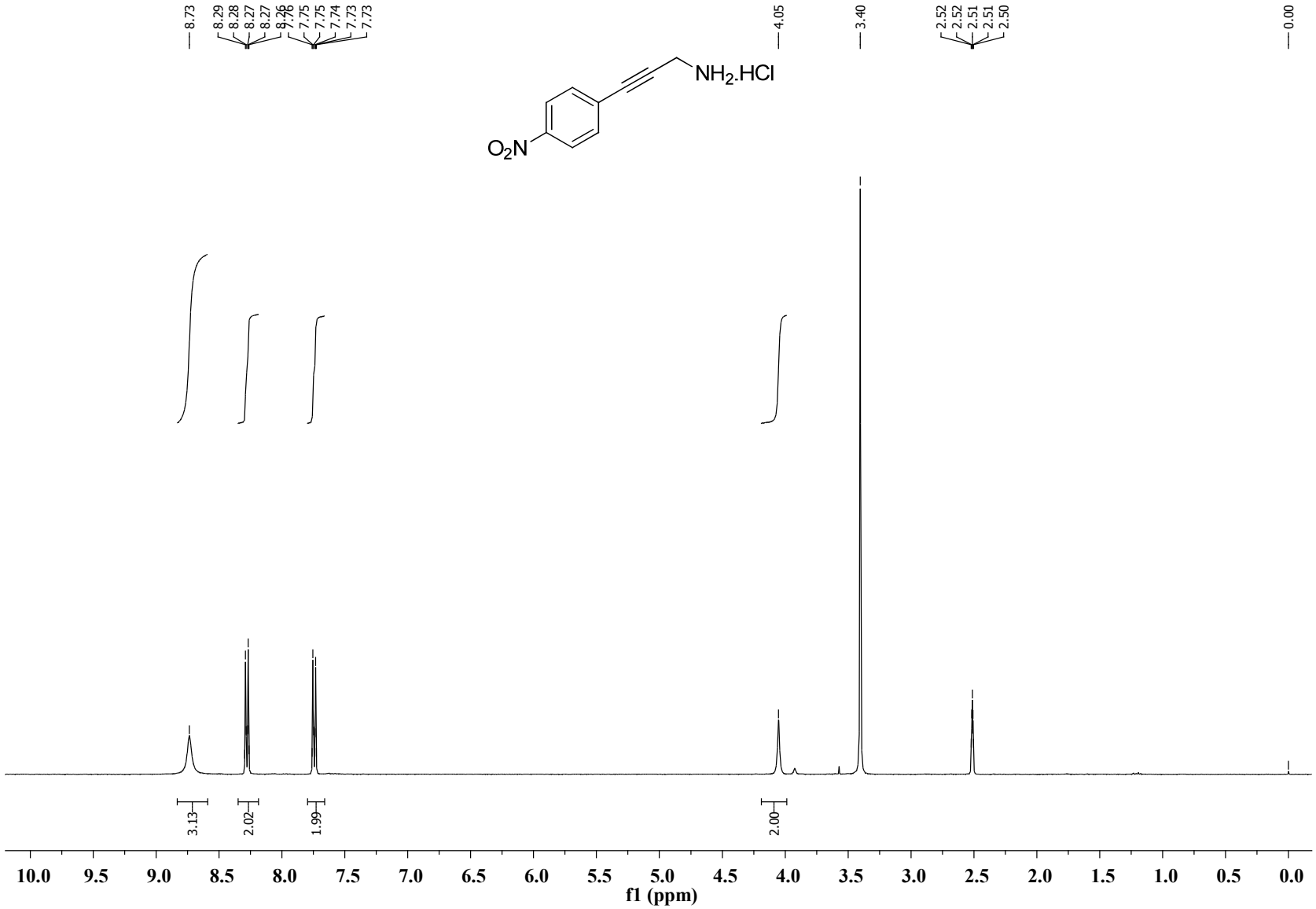
^{1}H NMR spectrum of **2d** (DMSO-d_6, 400 MHz)**:**



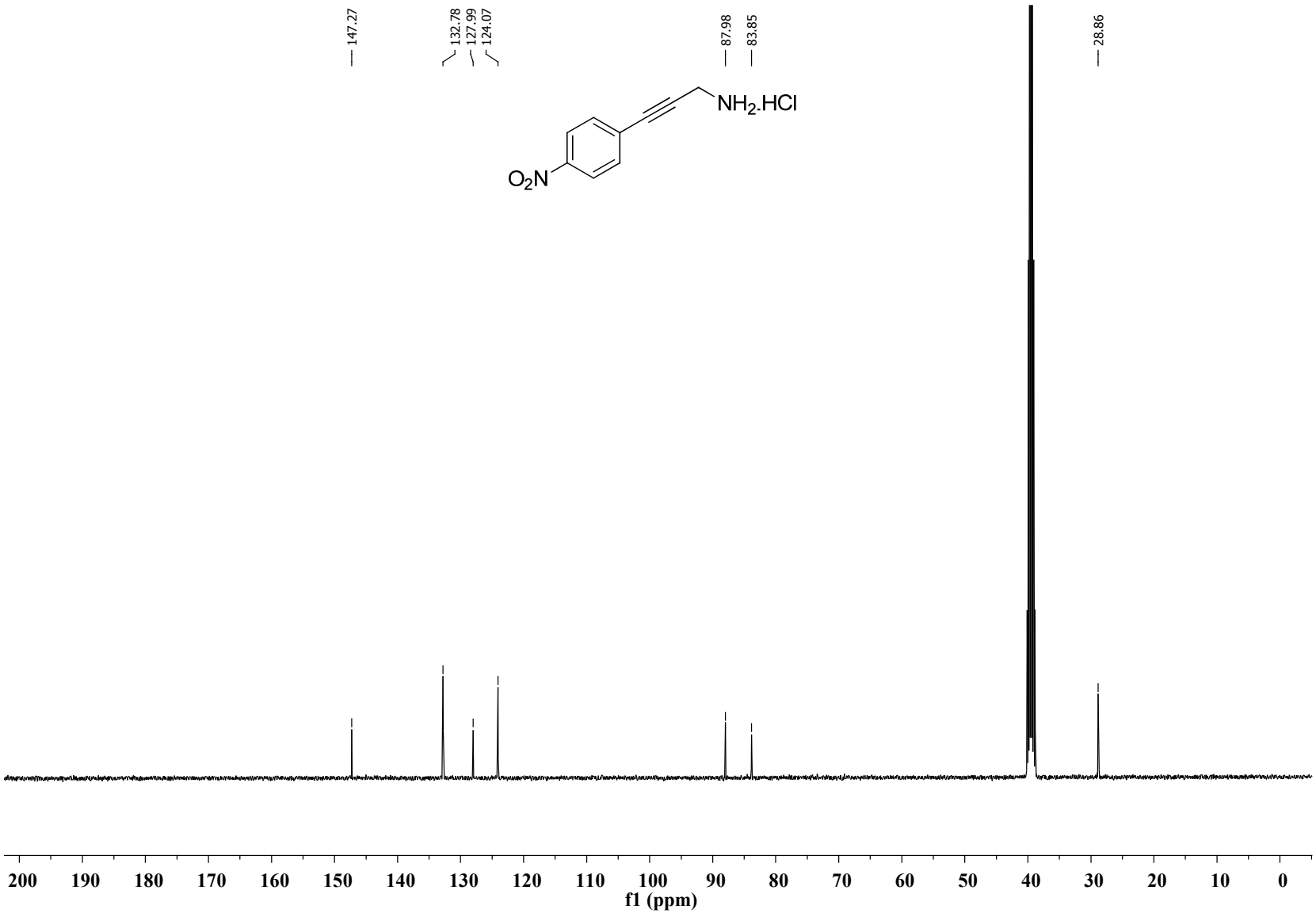
$^{13}C\{^{1}H\}$NMR spectrum of **2d** (DMSO-d_6, 100 MHz)**:**



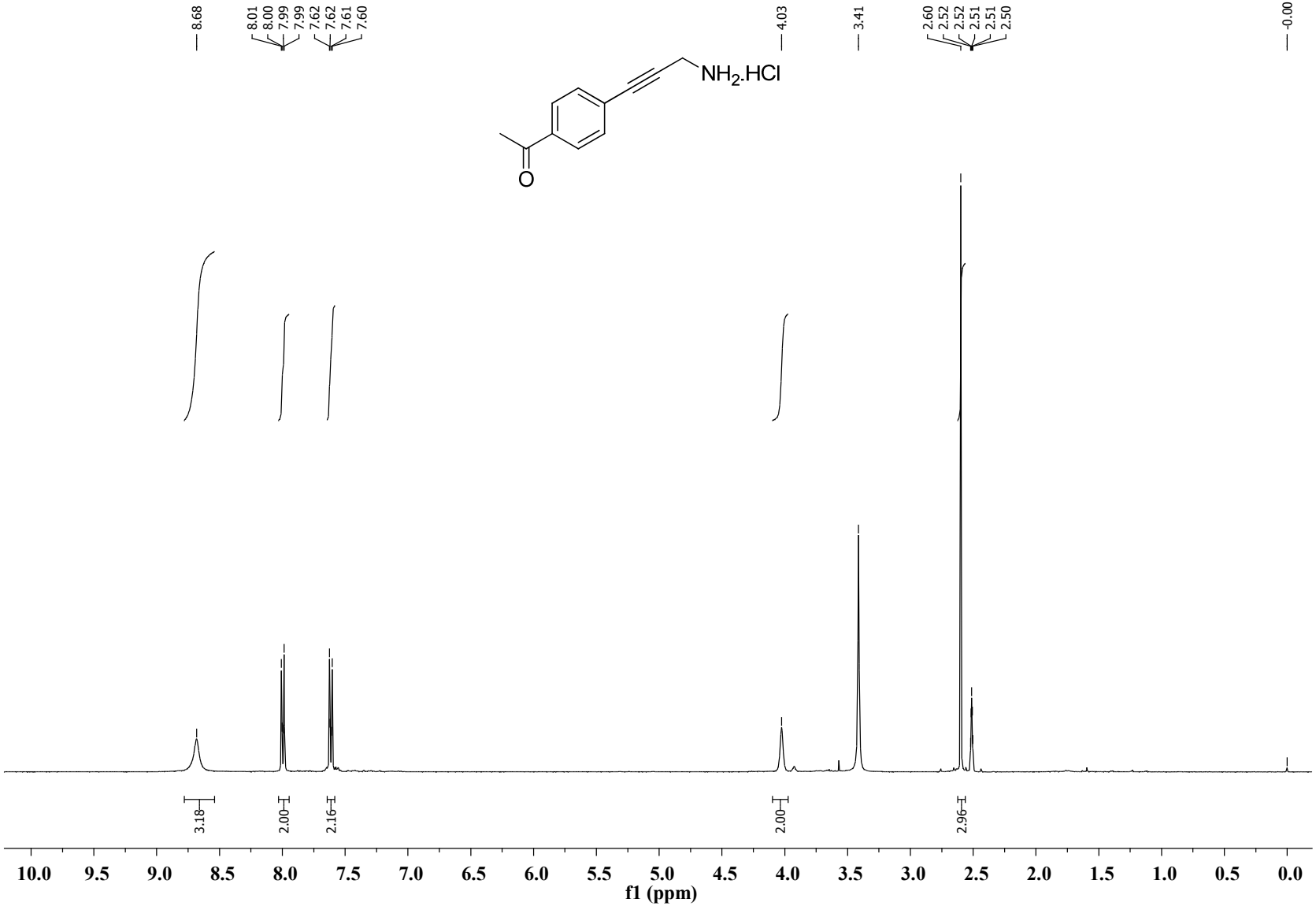
^{1}H NMR spectrum of **2e** (DMSO-d_6, 400 MHz)**:**



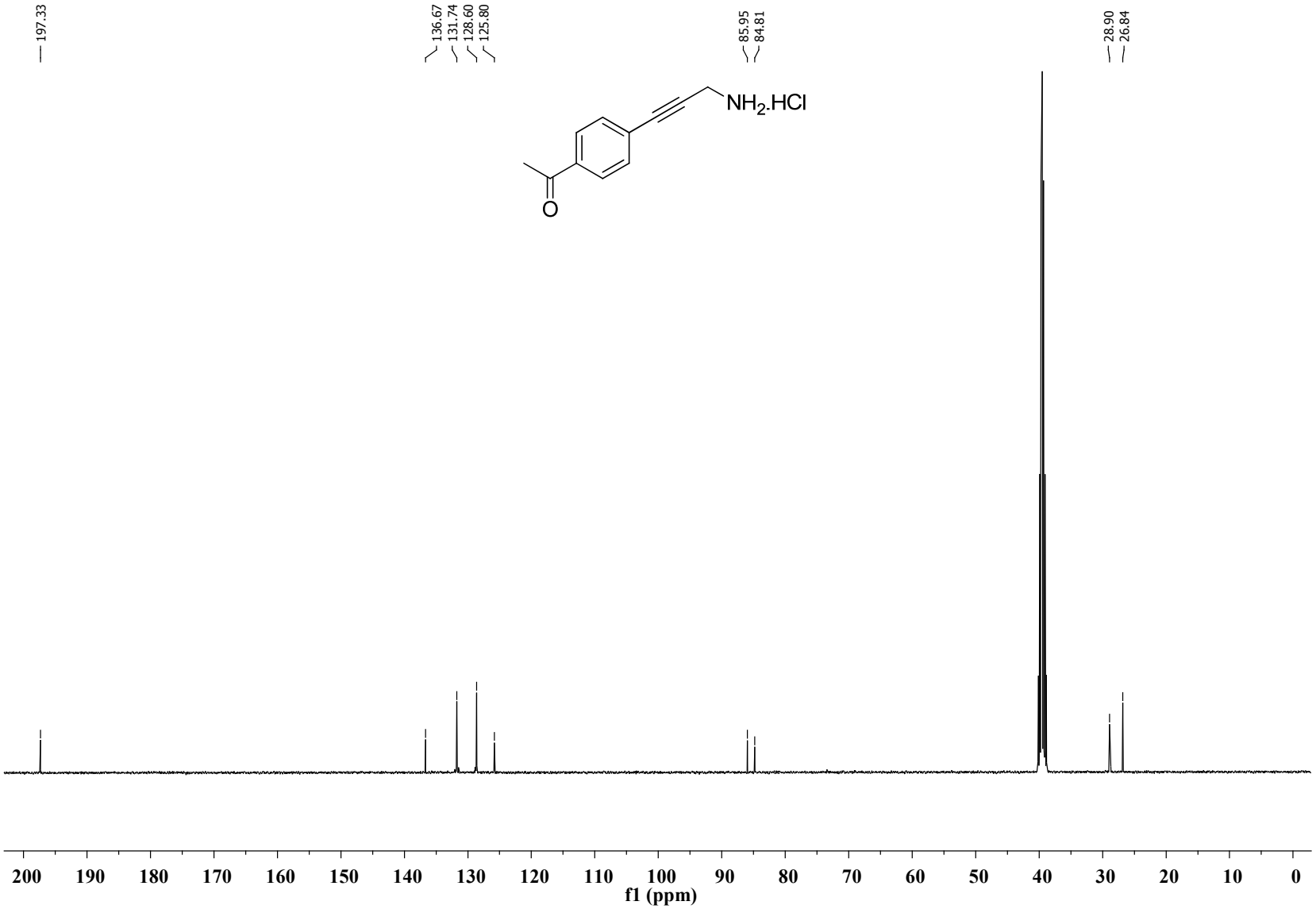
$^{13}C\{^{1}H\}$NMR spectrum of **2e** (DMSO-d_6, 100 MHz)**:**



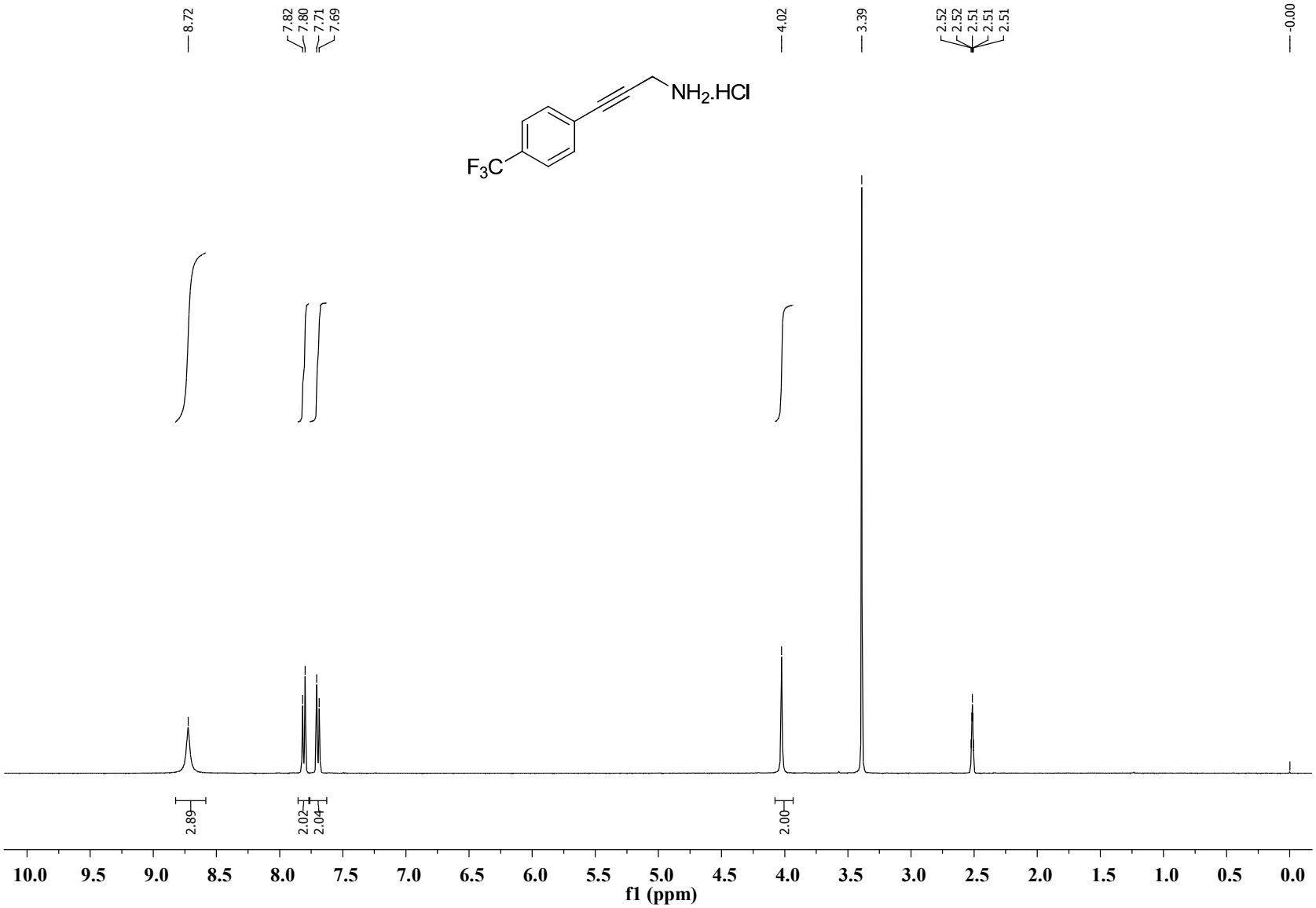
^{1}H NMR spectrum of **2f** (DMSO-d_6, 400 MHz)**:**



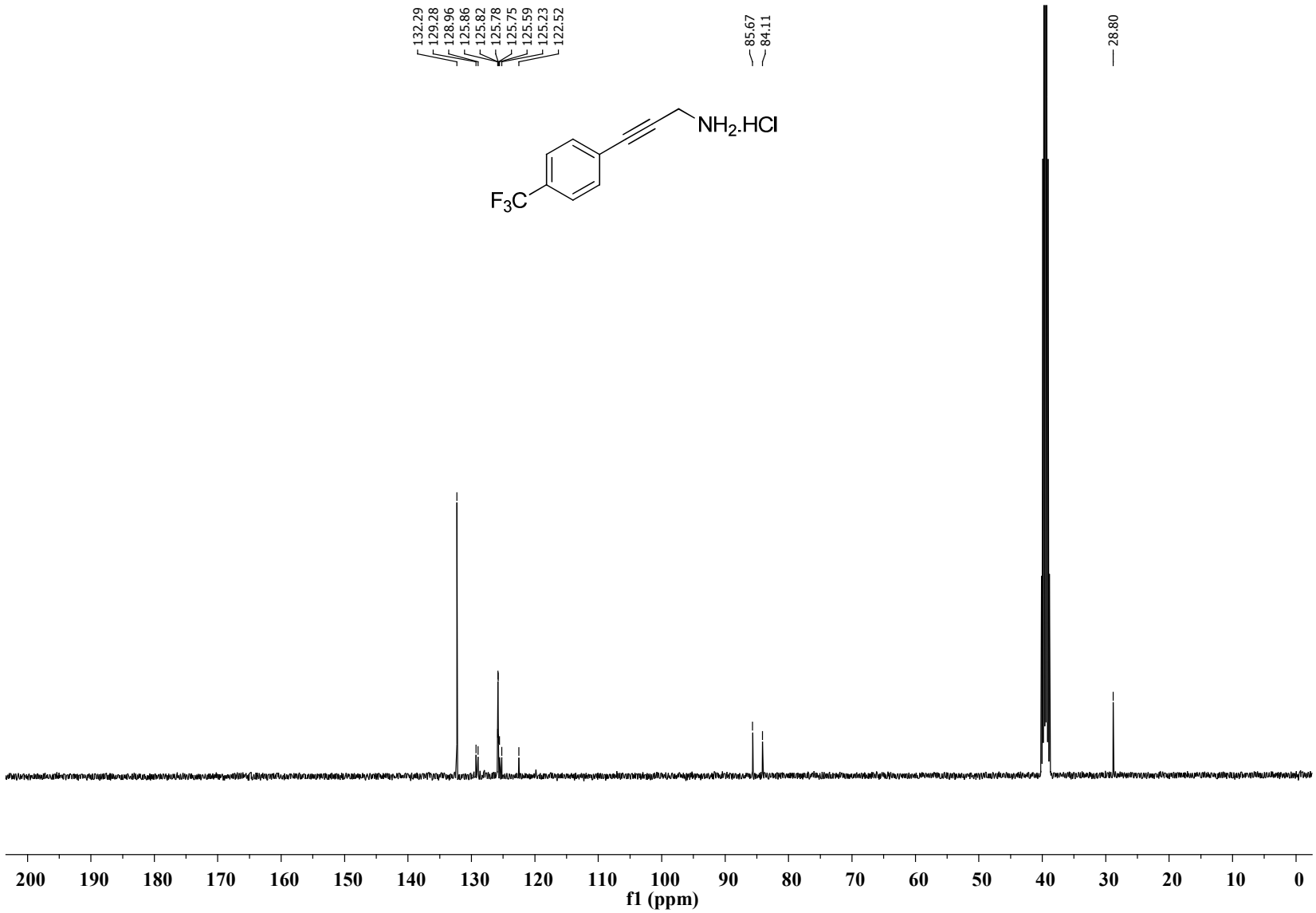
$^{13}C\{^{1}H\}$NMR spectrum of **2f** (DMSO-d_6, 100 MHz)**:**



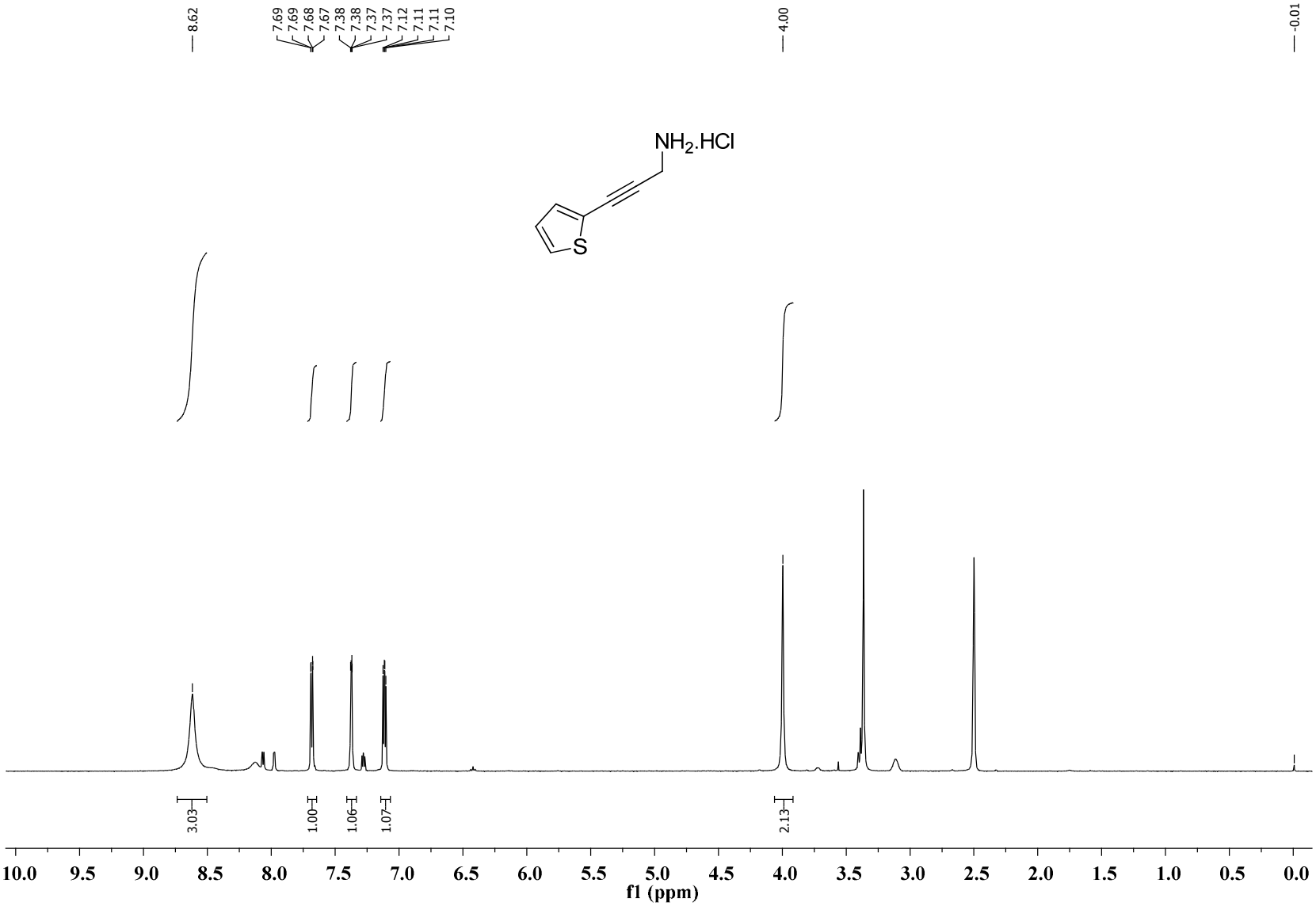
^{1}H NMR spectrum of **2g** (DMSO-d_6, 400 MHz)**:**



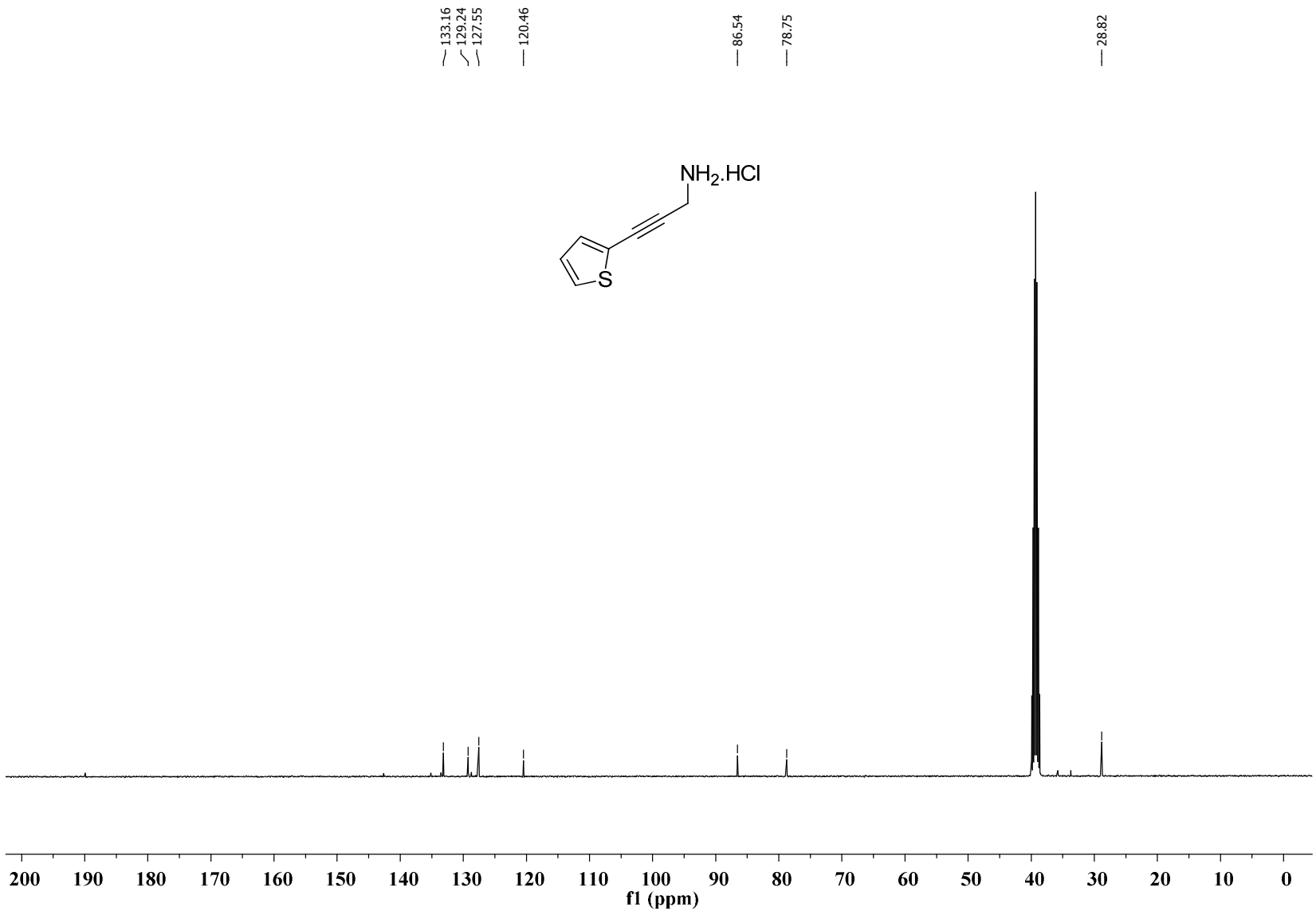
$^{13}C\{^{1}H\}$NMR spectrum of **2g** (DMSO-d_6, 100 MHz)**:**



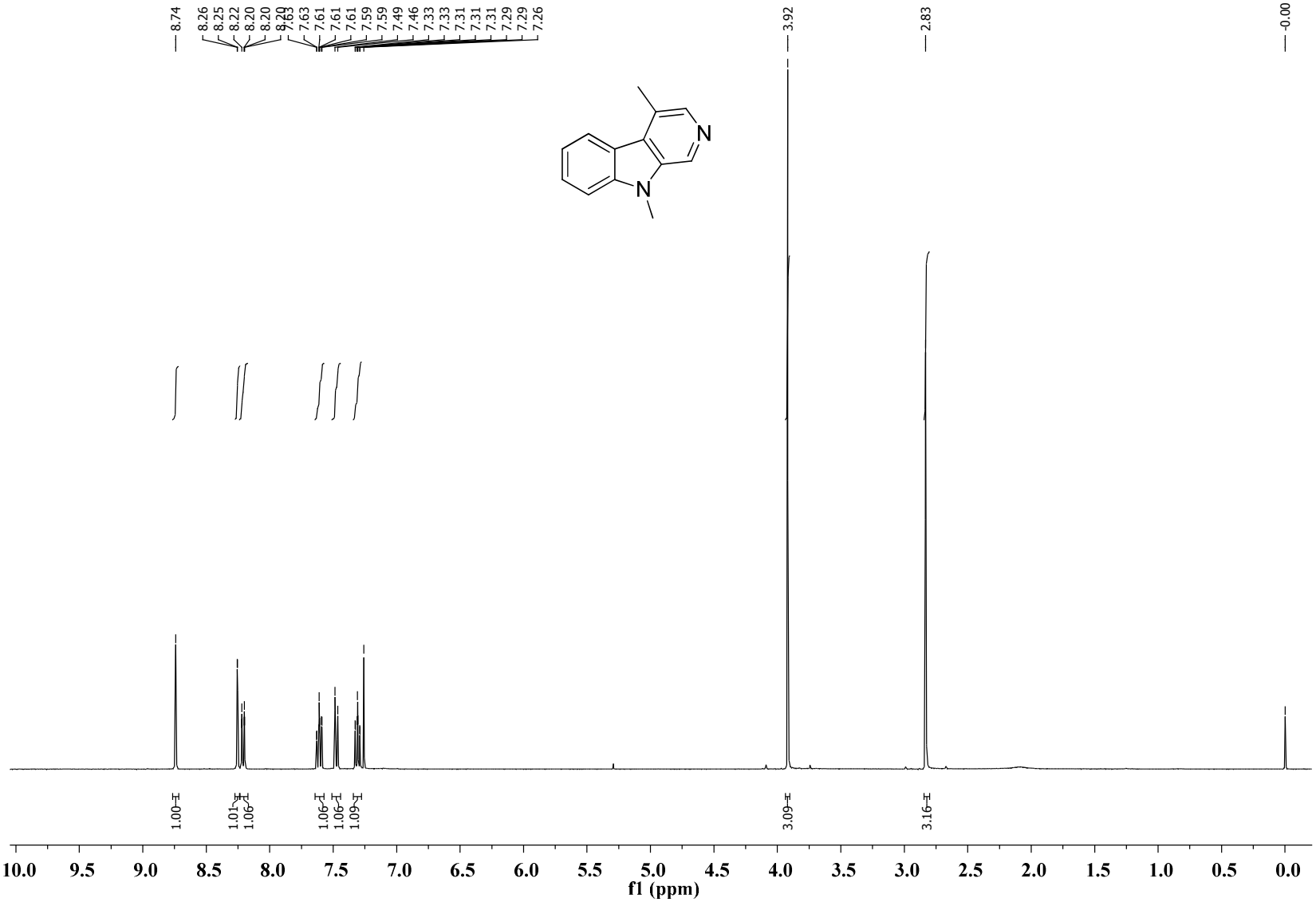
^{1}H NMR spectrum of **2i** (DMSO-d_6, 400 MHz)**:**



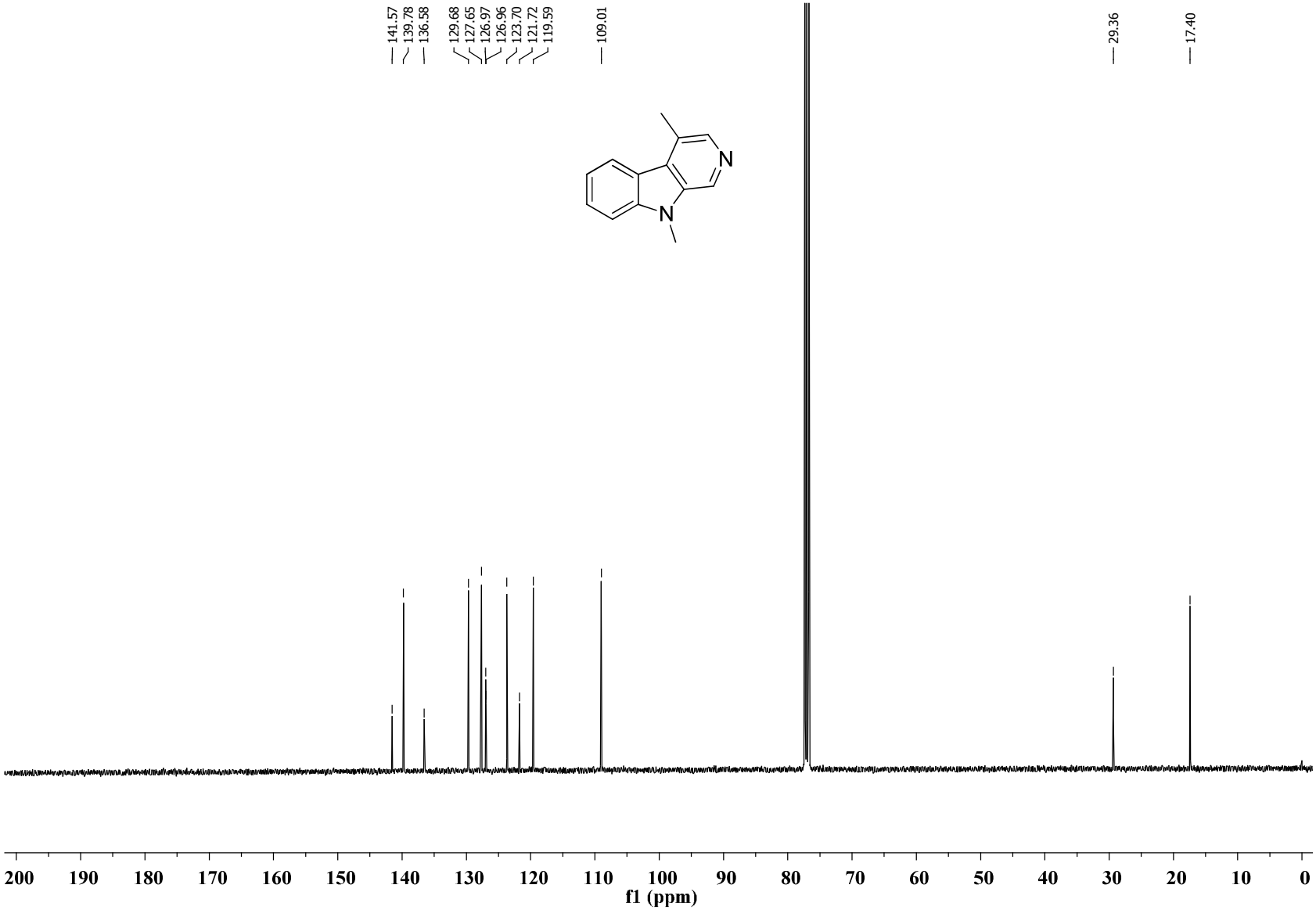
$^{13}C\{1H\}$NMR spectrum of **2i** (DMSO-d_6, 100 MHz)**:**



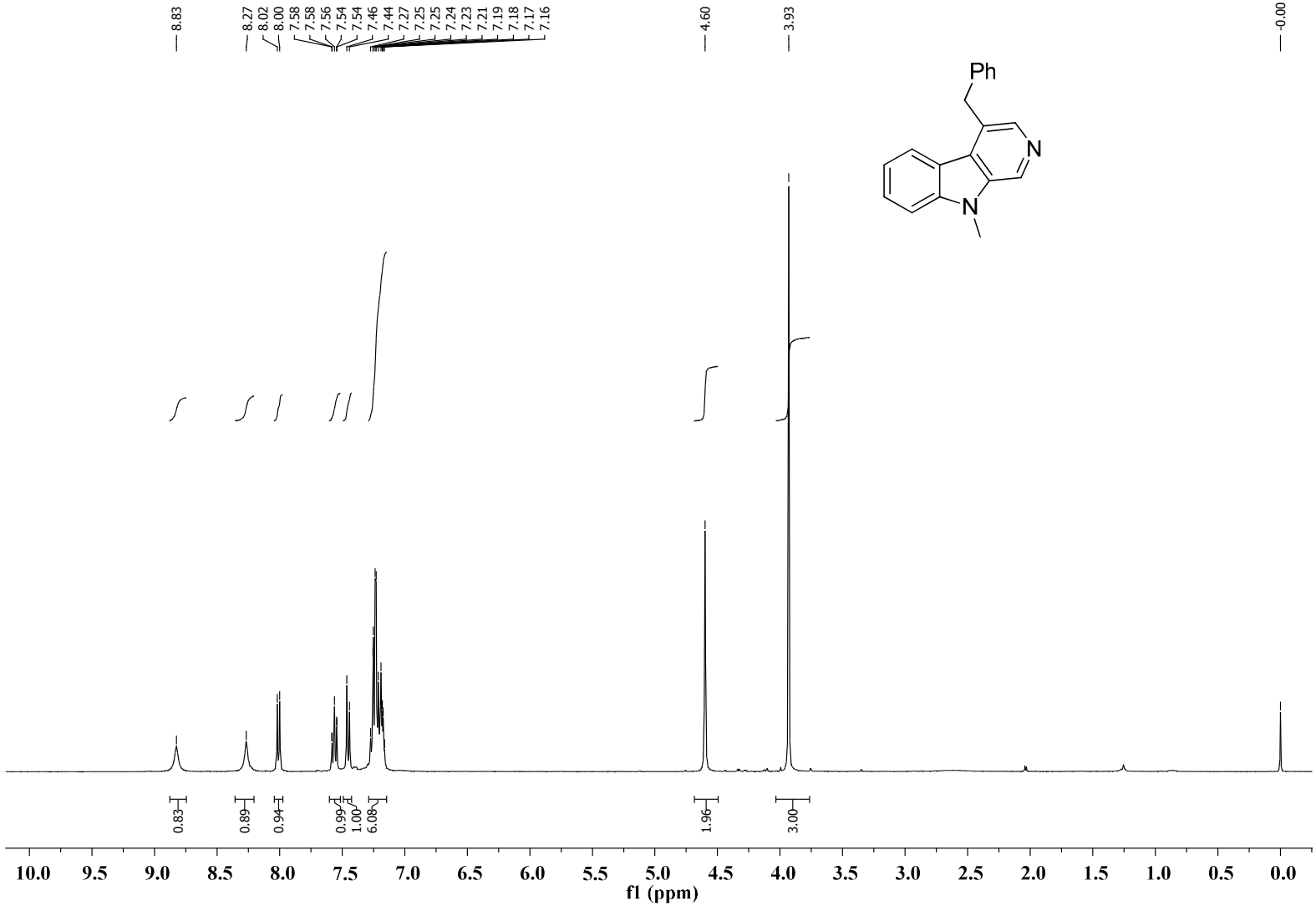
^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz)**:**



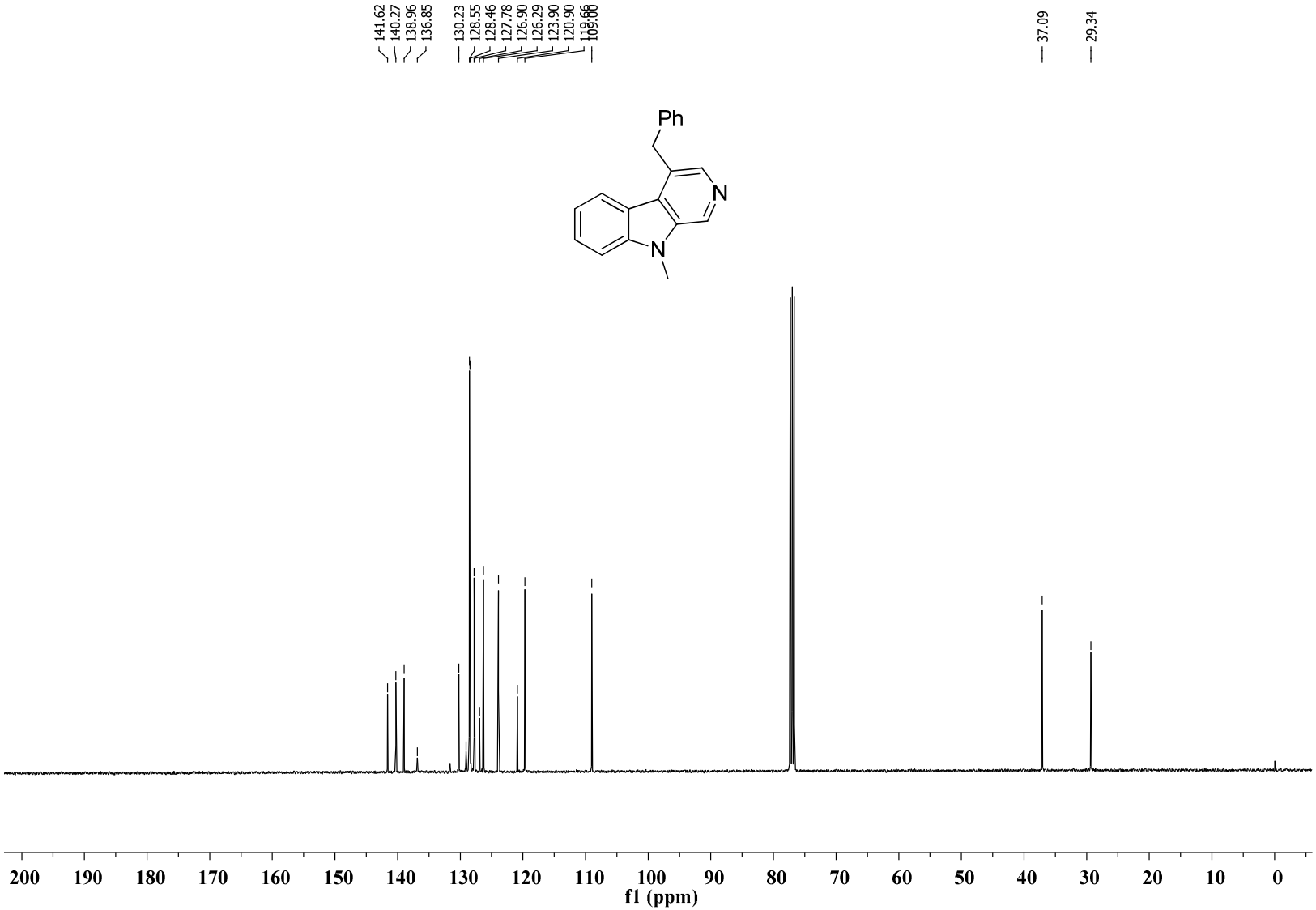
$^{13}C\{1H\}$NMR spectrum of **3a** ($CDCl_3$, 100 MHz)**:**



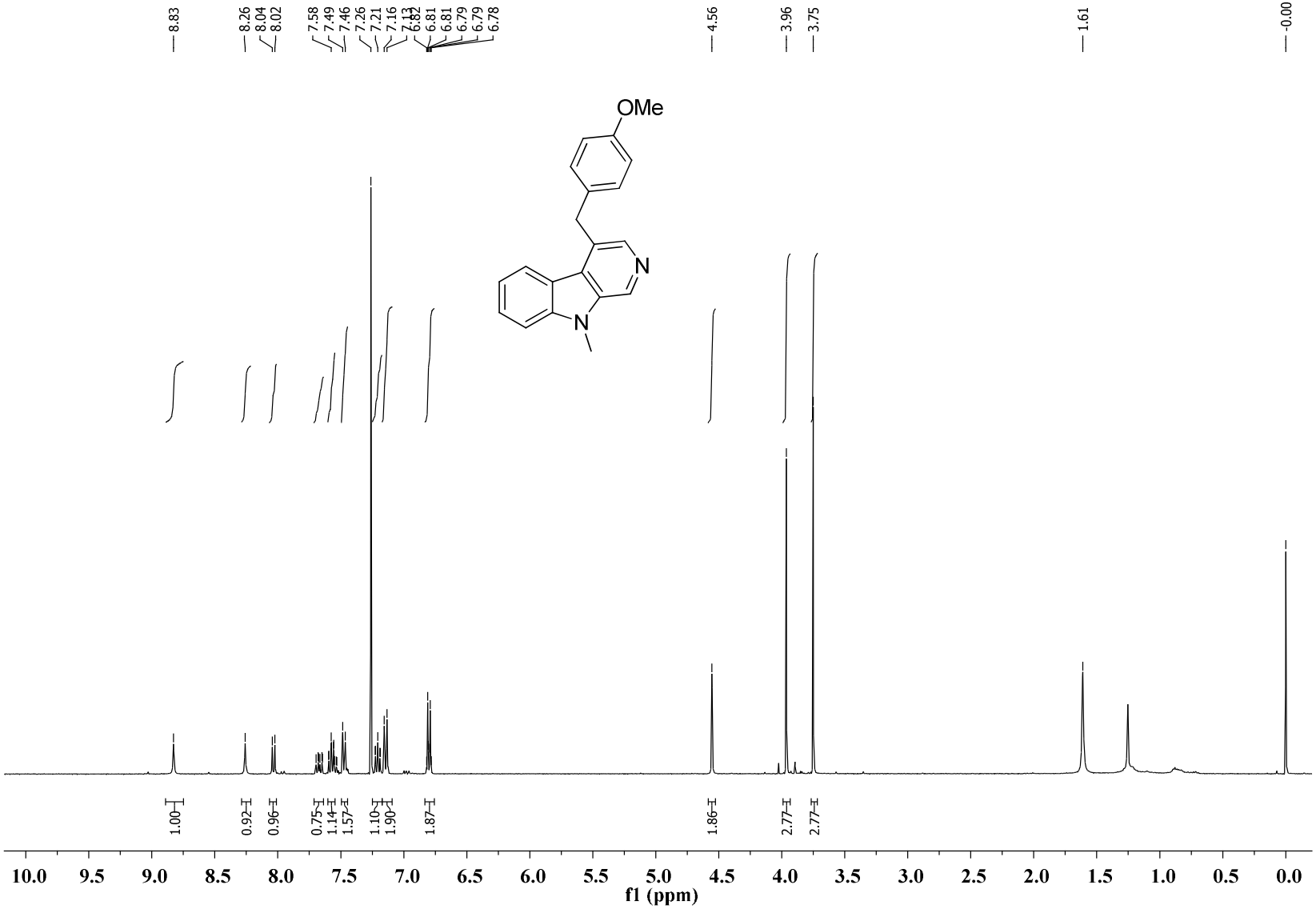
^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz)**:**



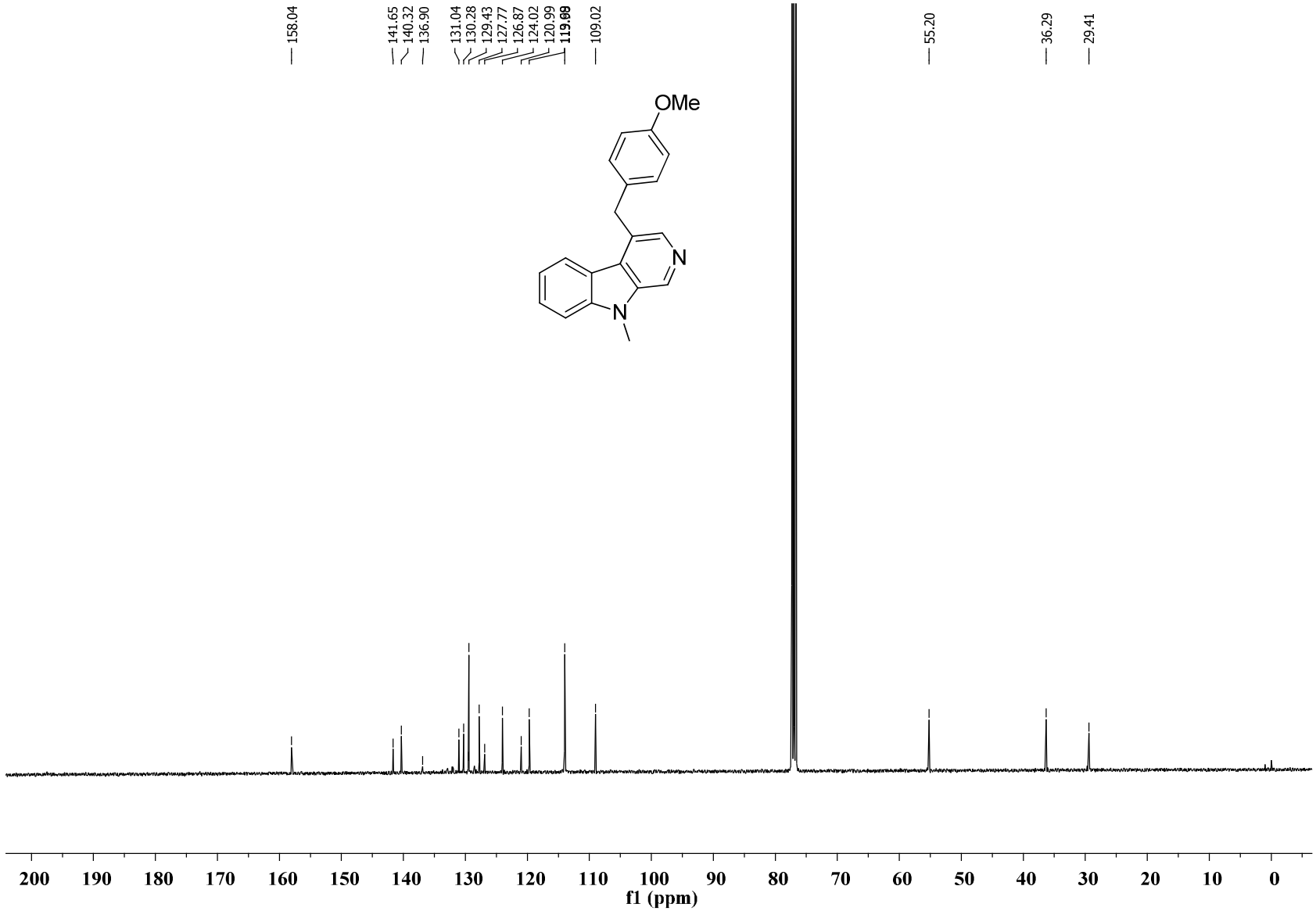
$^{13}C\{1H\}$NMR spectrum of **3b** ($CDCl_3$, 100 MHz)**:**



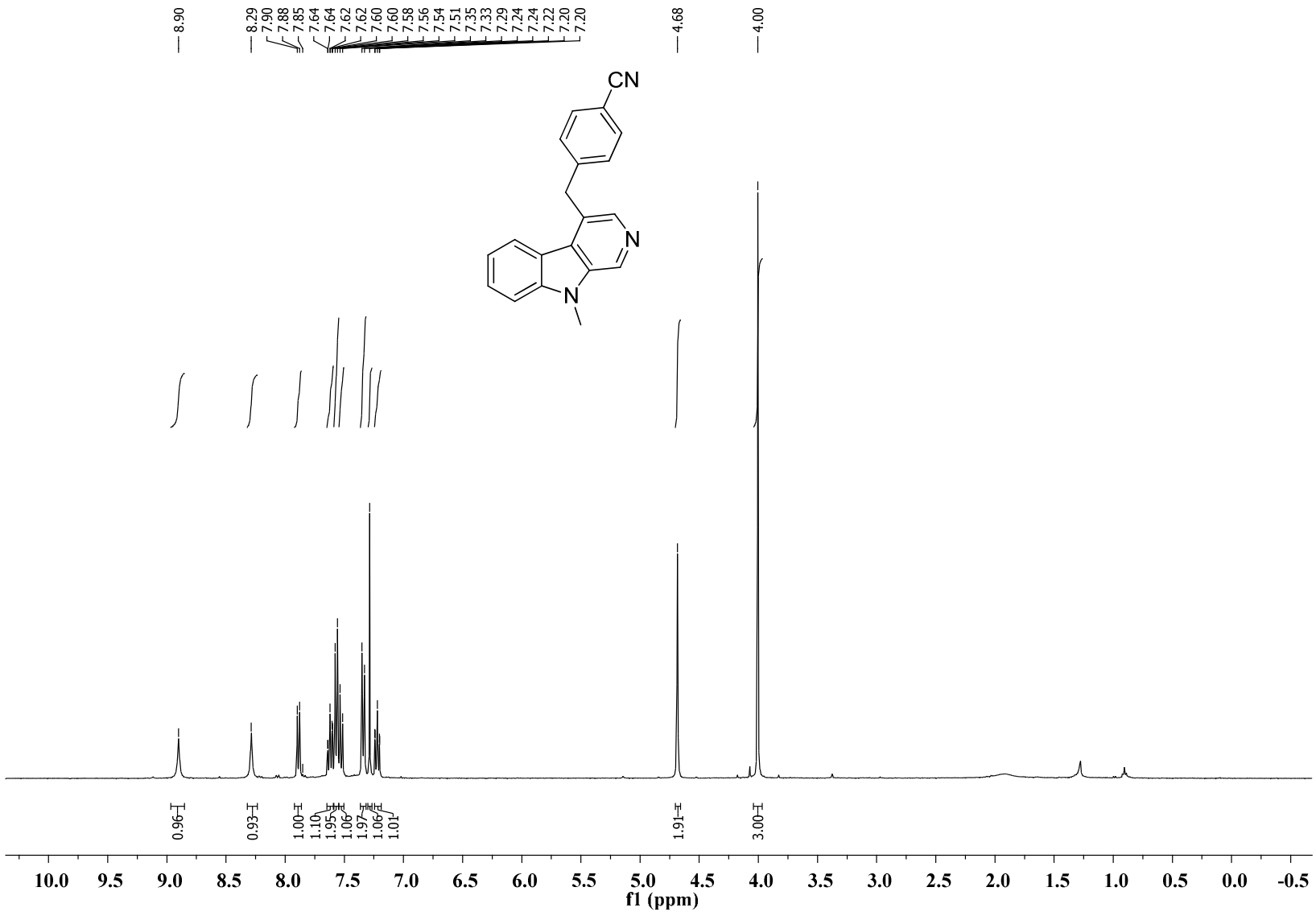
^{1}H NMR spectrum of **3c** ($CDCl_3$, 400 MHz)**:**



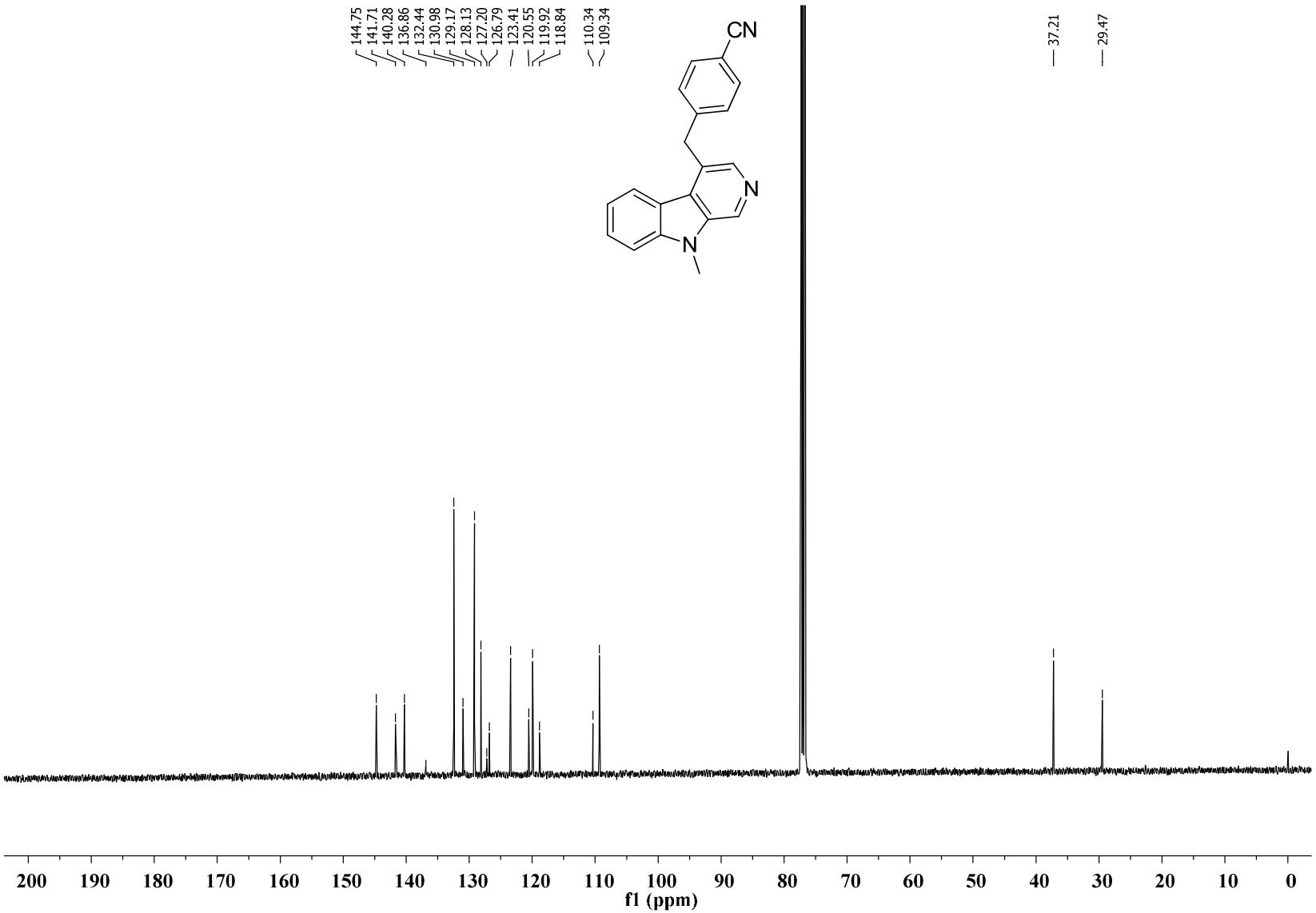
$^{13}C\{1H\}$NMR spectrum of **3c** ($CDCl_3$, 100 MHz)**:**



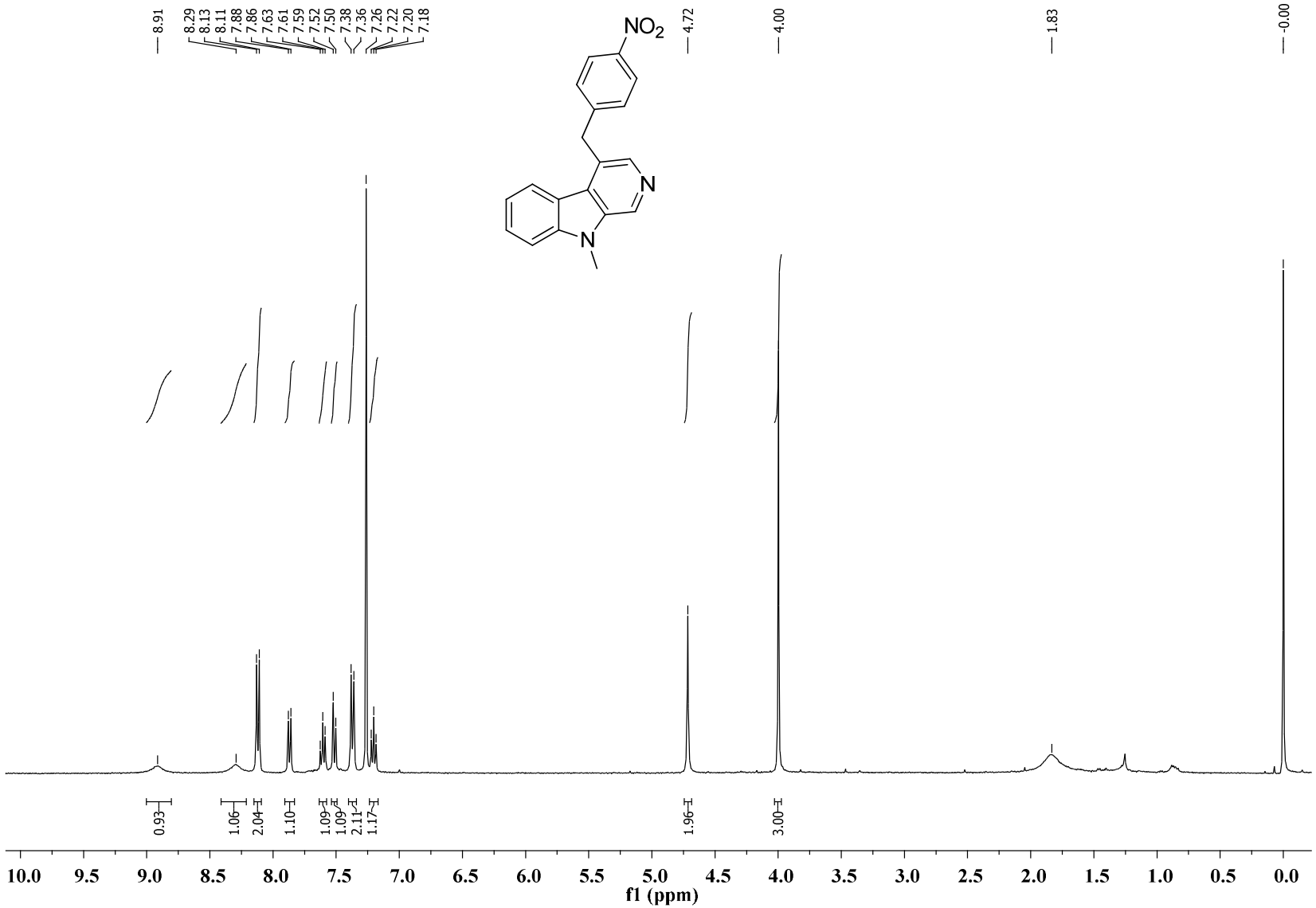
^{1}H NMR spectrum of **3d** ($CDCl_3$, 400 MHz)**:**



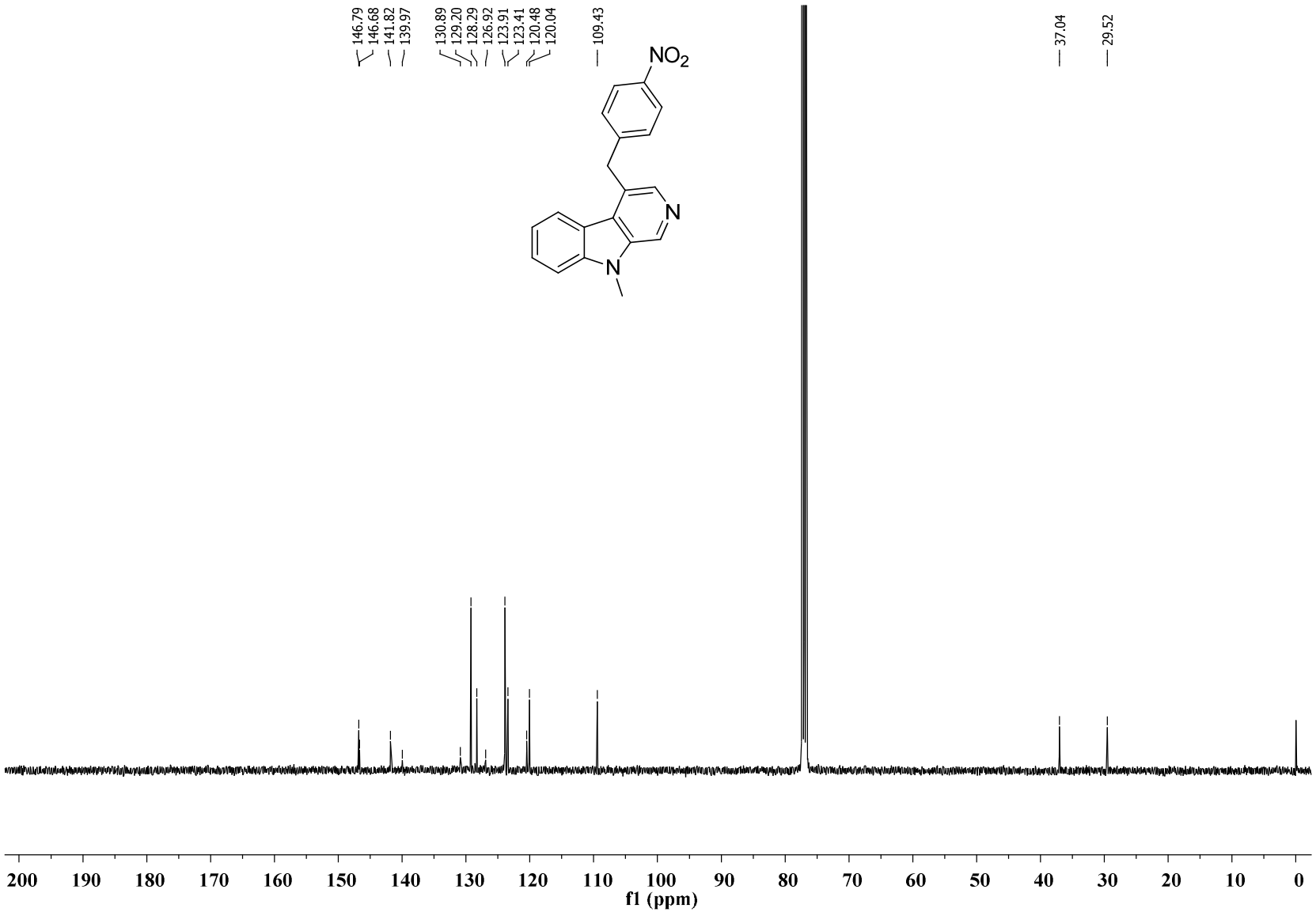
$^{13}C\{1H\}$NMR spectrum of **3d** ($CDCl_3$, 100 MHz)**:**



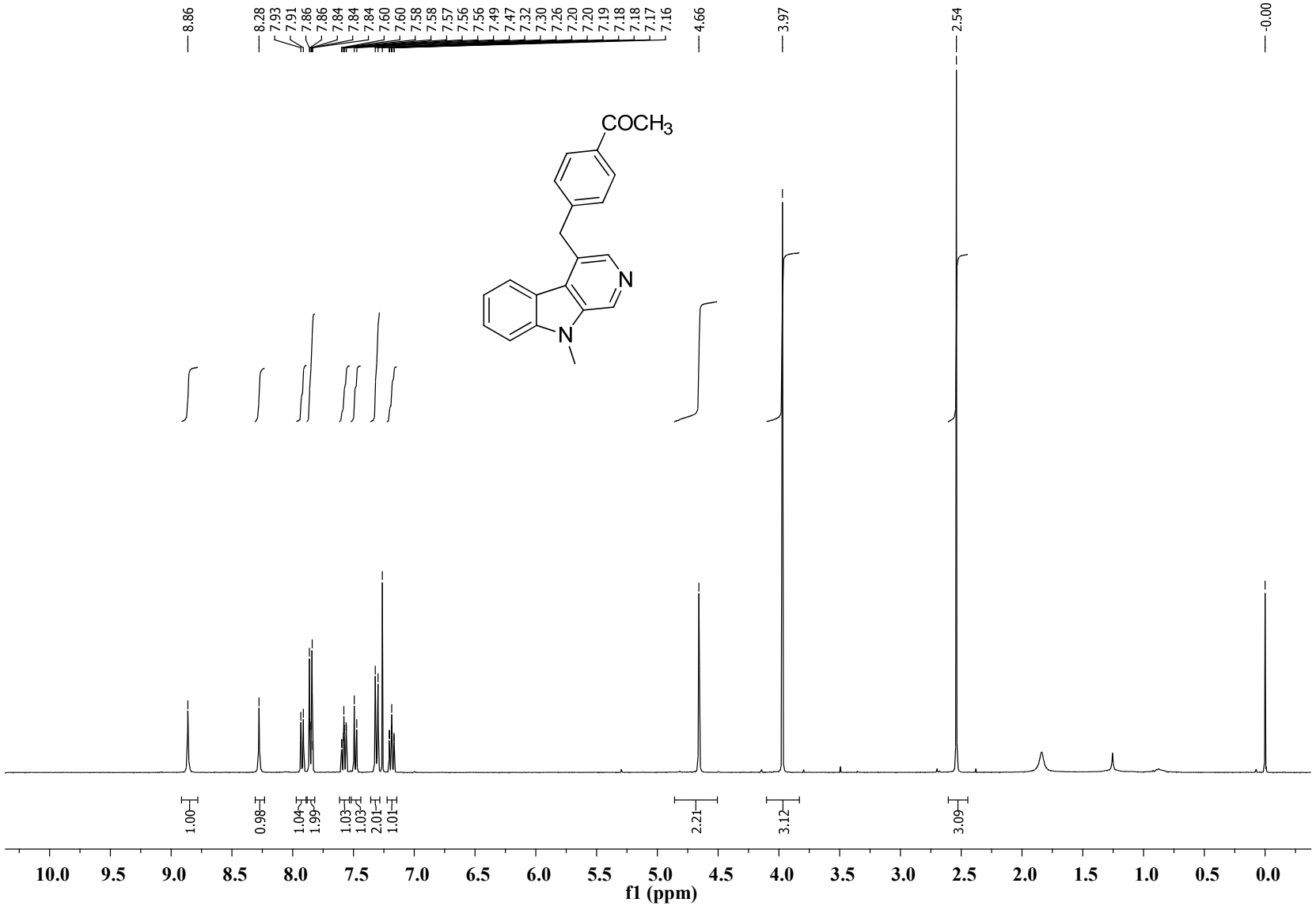
^{1}H NMR spectrum of **3e** ($CDCl_3$, 400 MHz)**:**



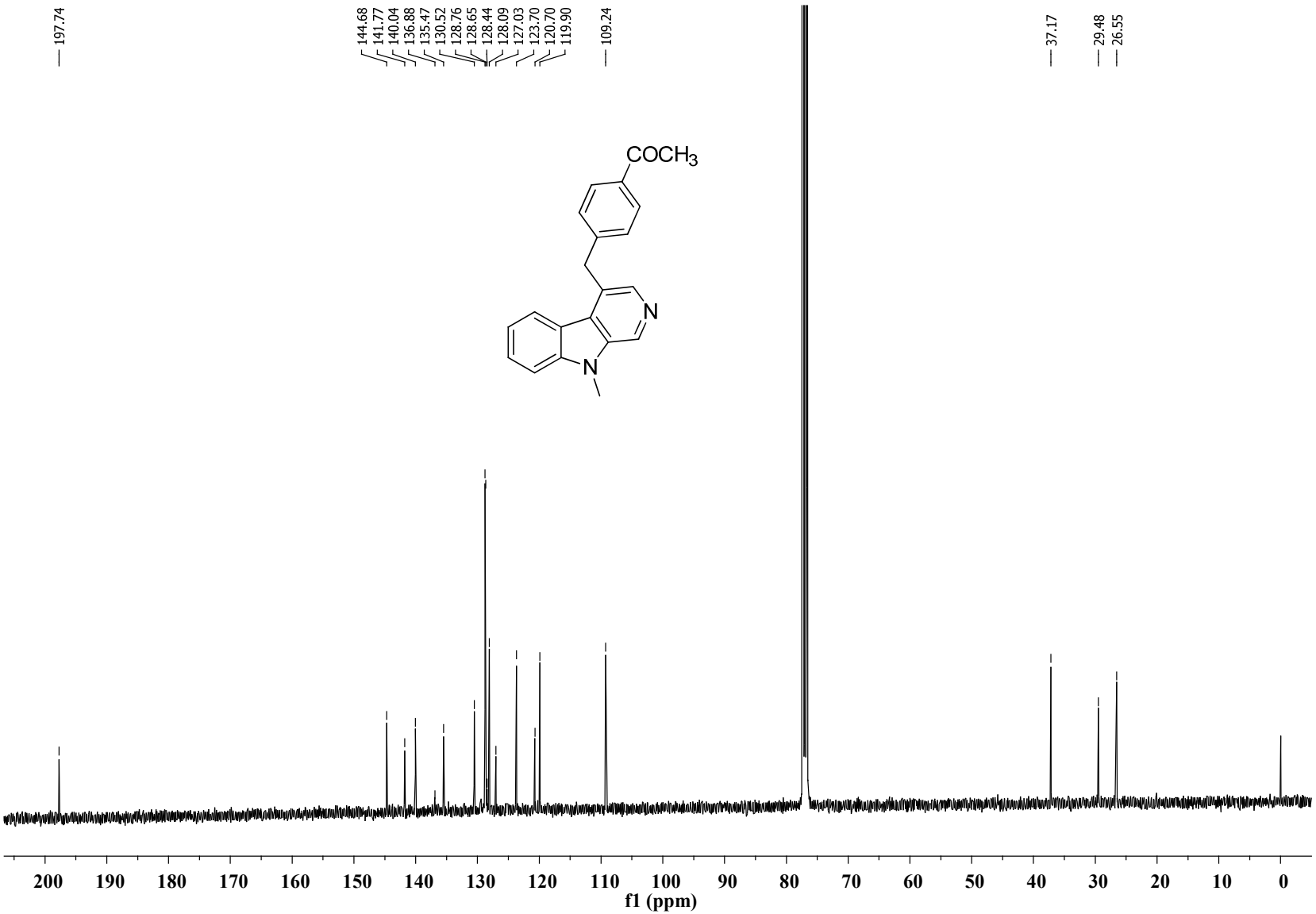
$^{13}C\{1H\}$NMR spectrum of **3e** ($CDCl_3$, 100 MHz)**:**



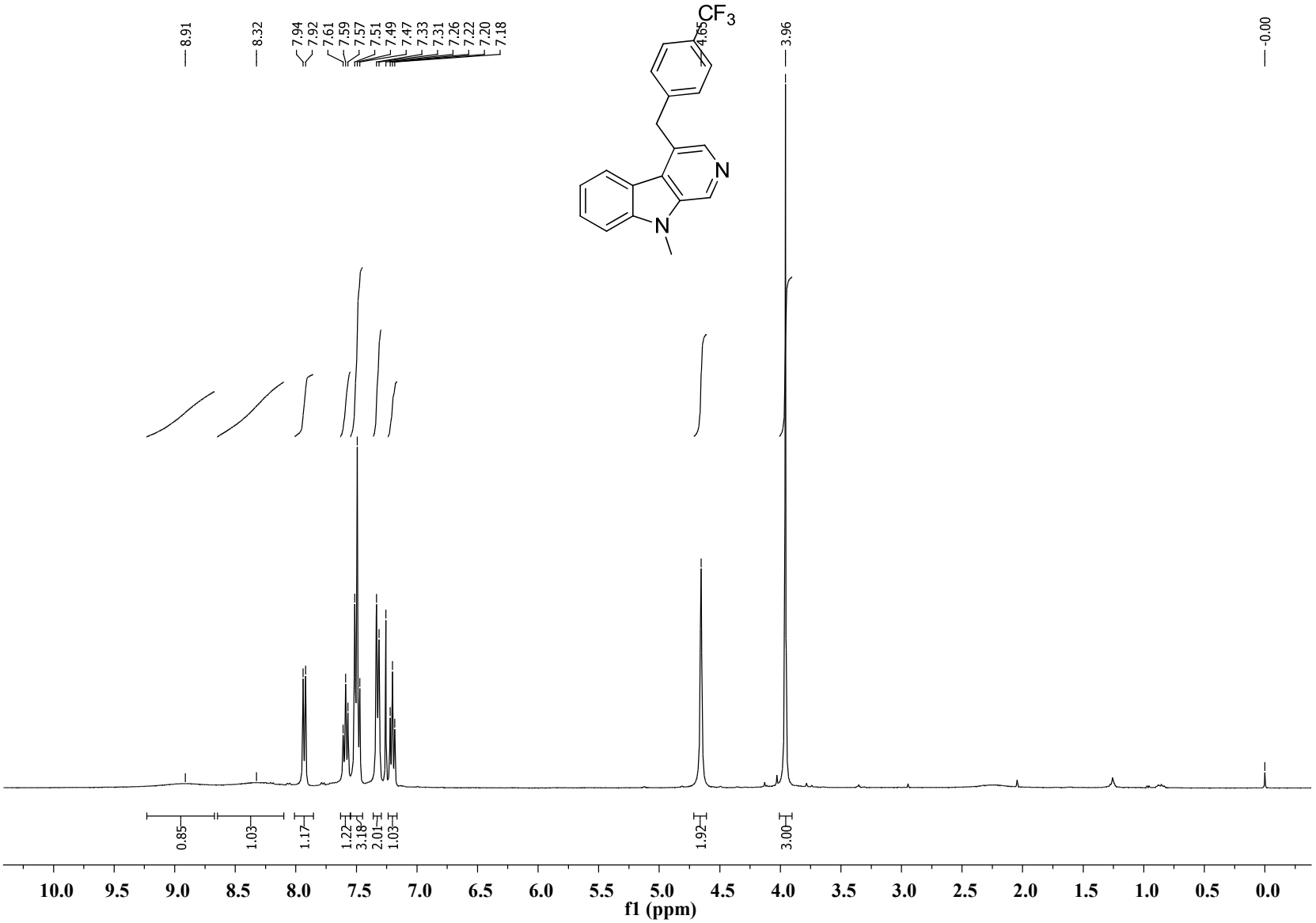
^{1}H NMR spectrum of **3f** ($CDCl_3$, 400 MHz)**:**



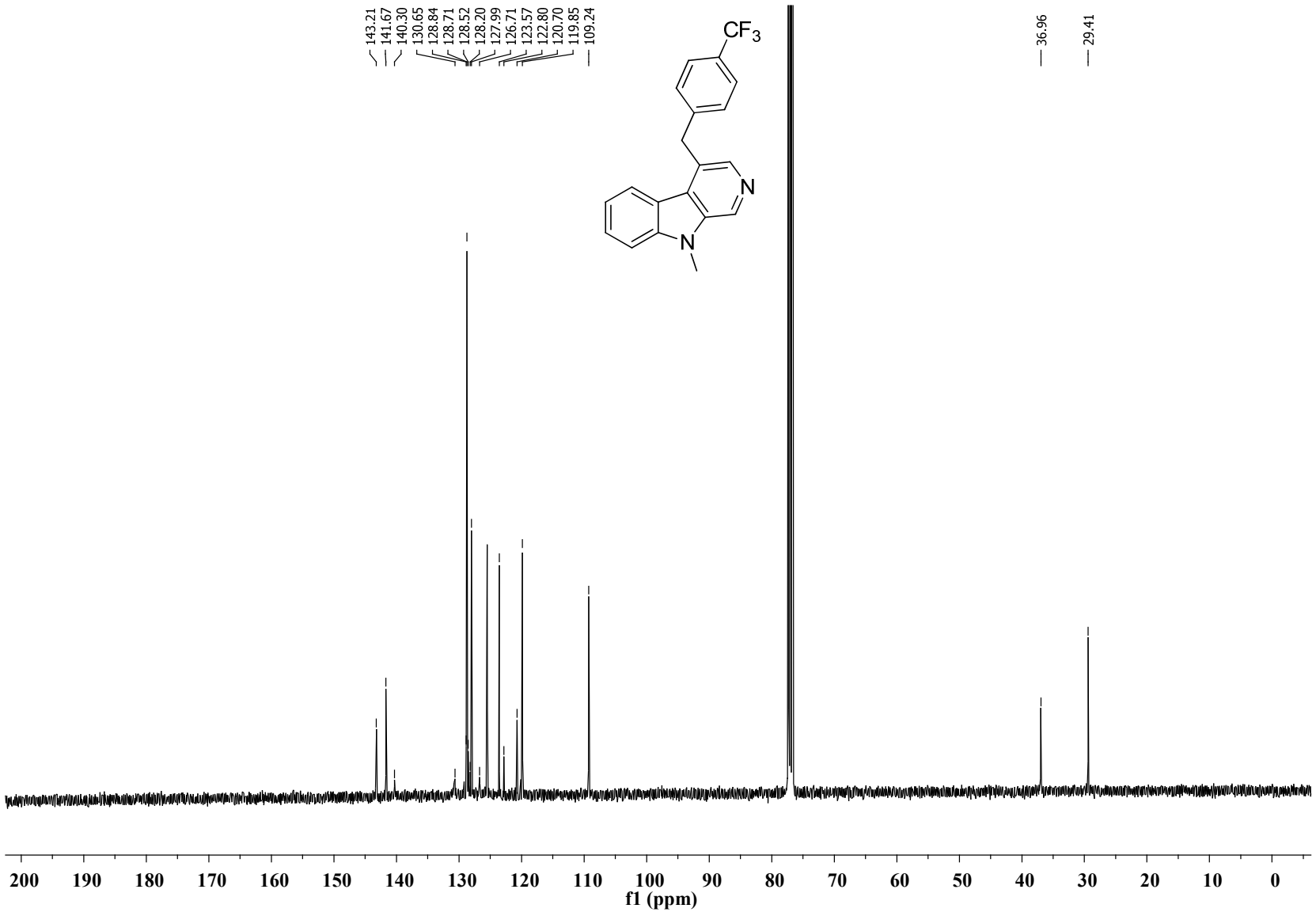
$^{13}C\{1H\}$NMR spectrum of **3f** ($CDCl_3$, 100 MHz)**:**



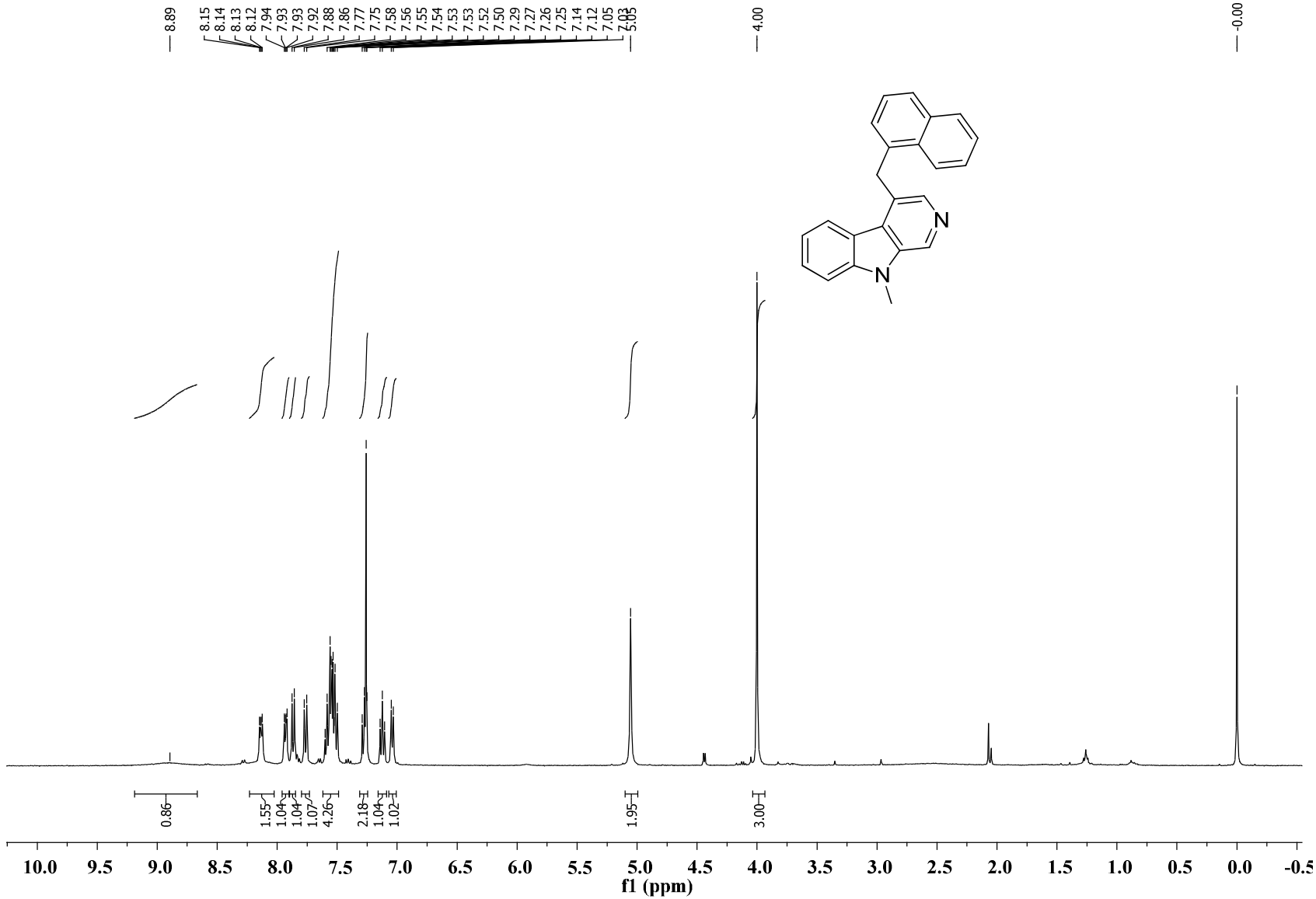
^{1}H NMR spectrum of **3g** ($CDCl_3$, 400 MHz)**:**



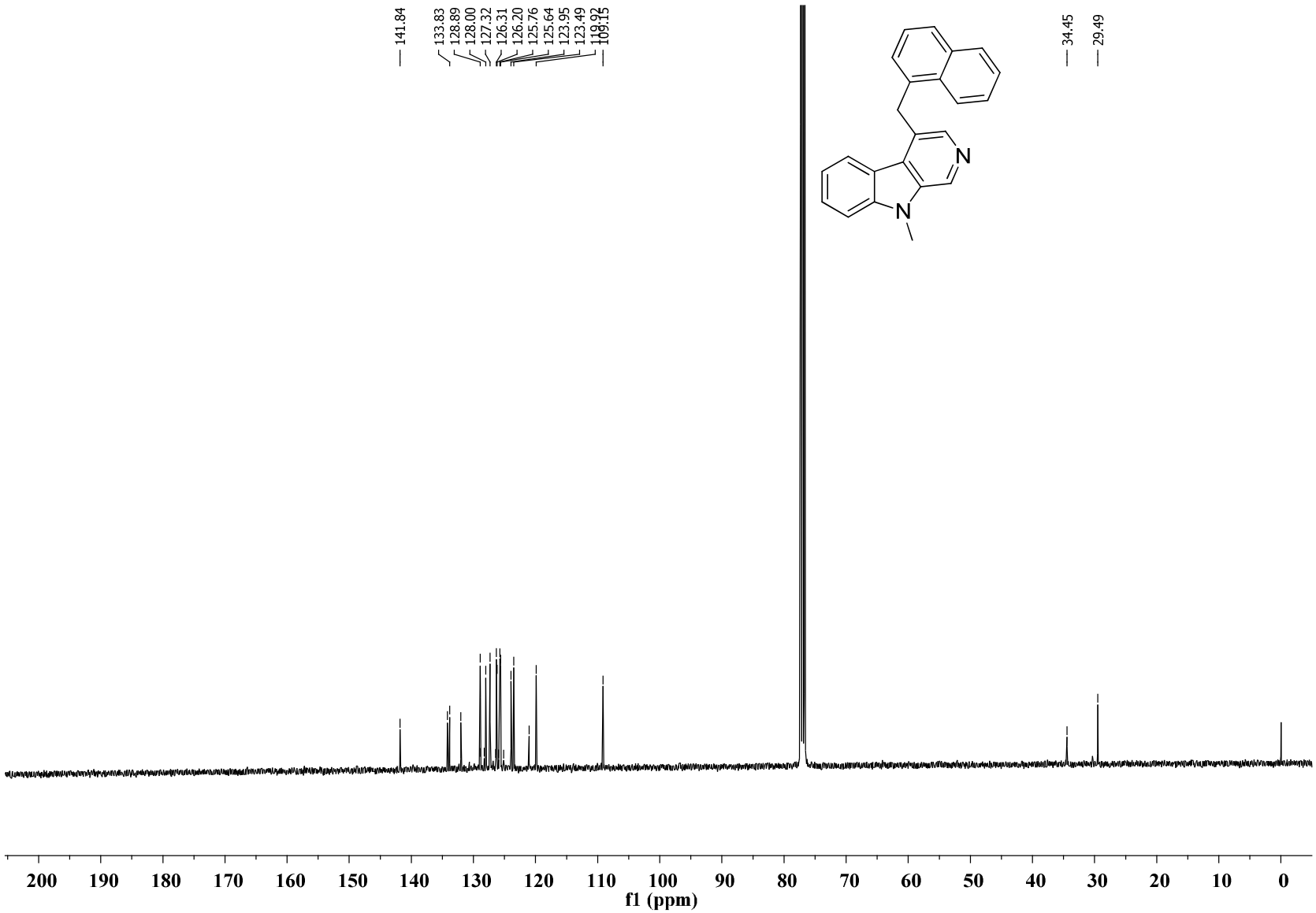
$^{13}C\{1H\}$NMR spectrum of **3g** ($CDCl_3$, 100 MHz)**:**



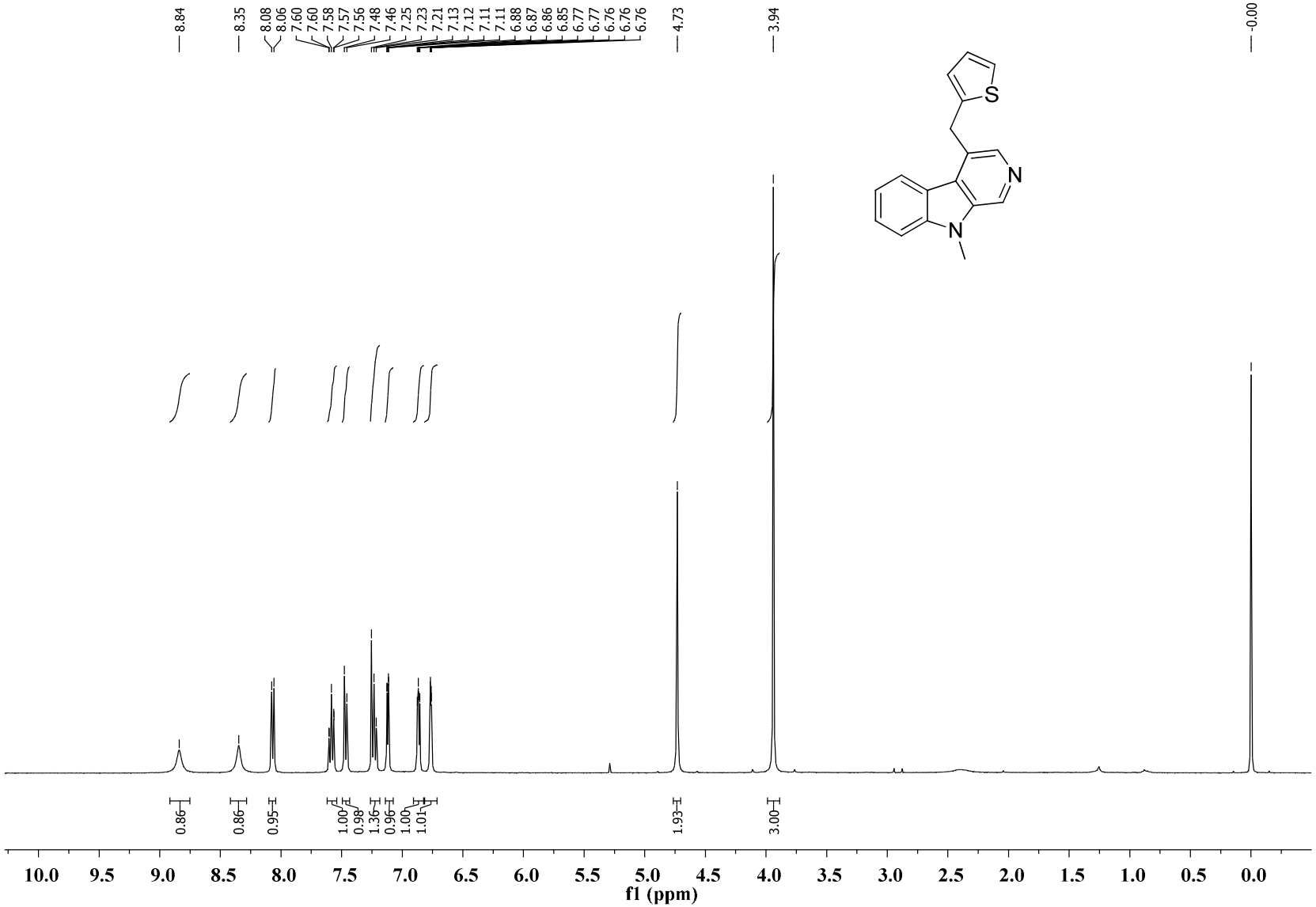
^{1}H NMR spectrum of **3h** ($CDCl_3$, 400 MHz)**:**



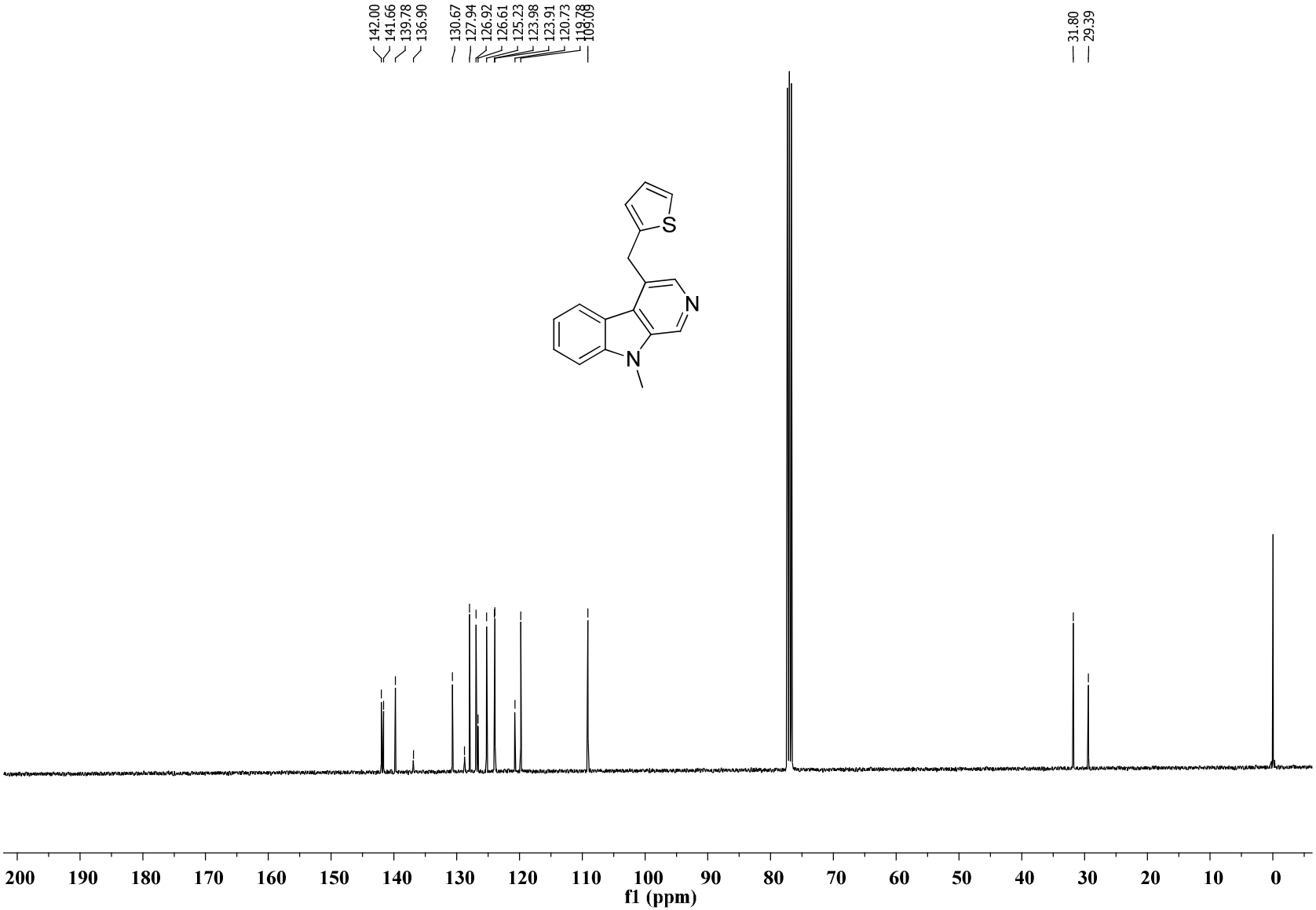
$^{13}C\{1H\}$NMR spectrum of **3h** ($CDCl_3$, 100 MHz)**:**



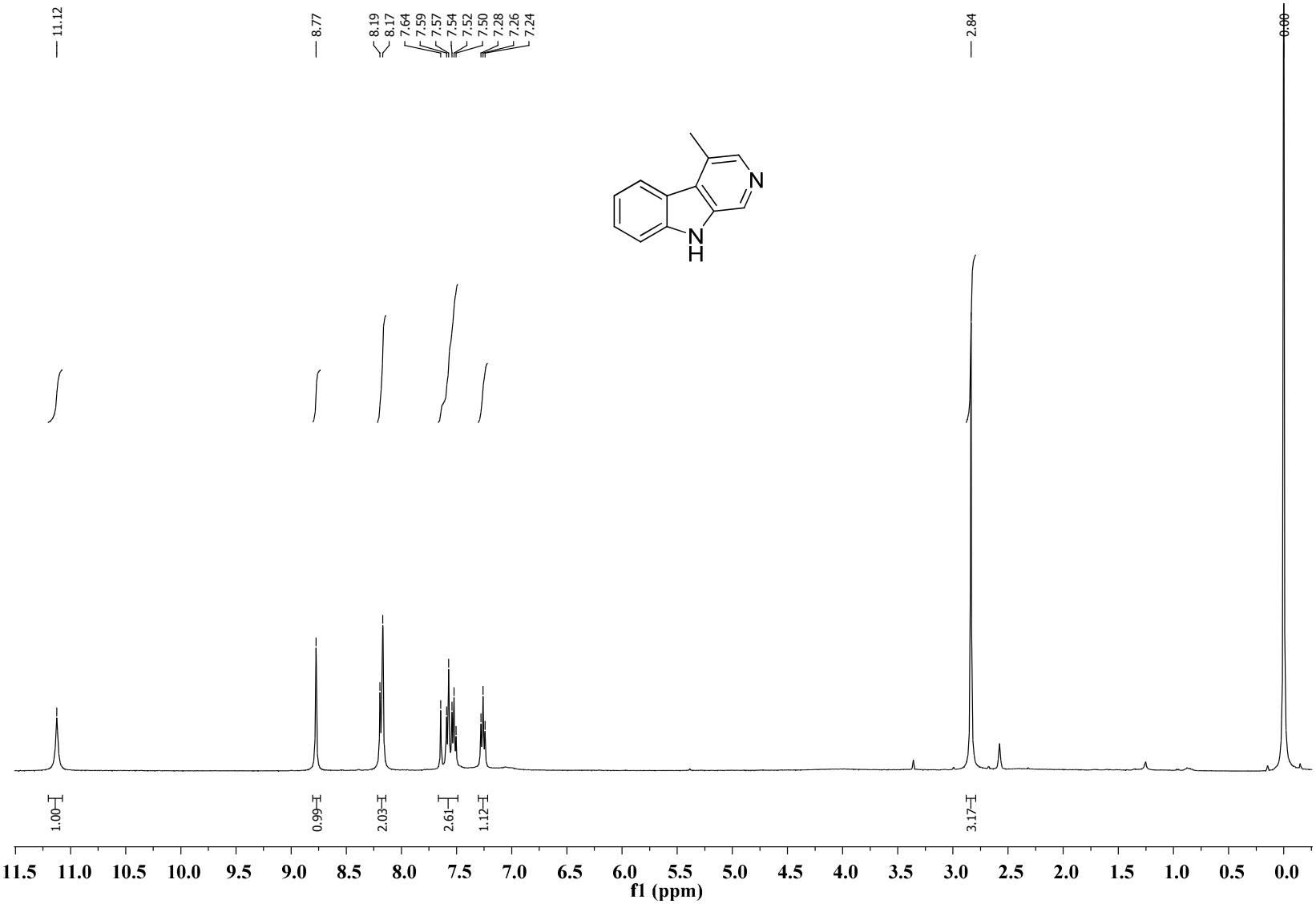
^{1}H NMR spectrum of **3i** ($CDCl_3$, 400 MHz)**:**



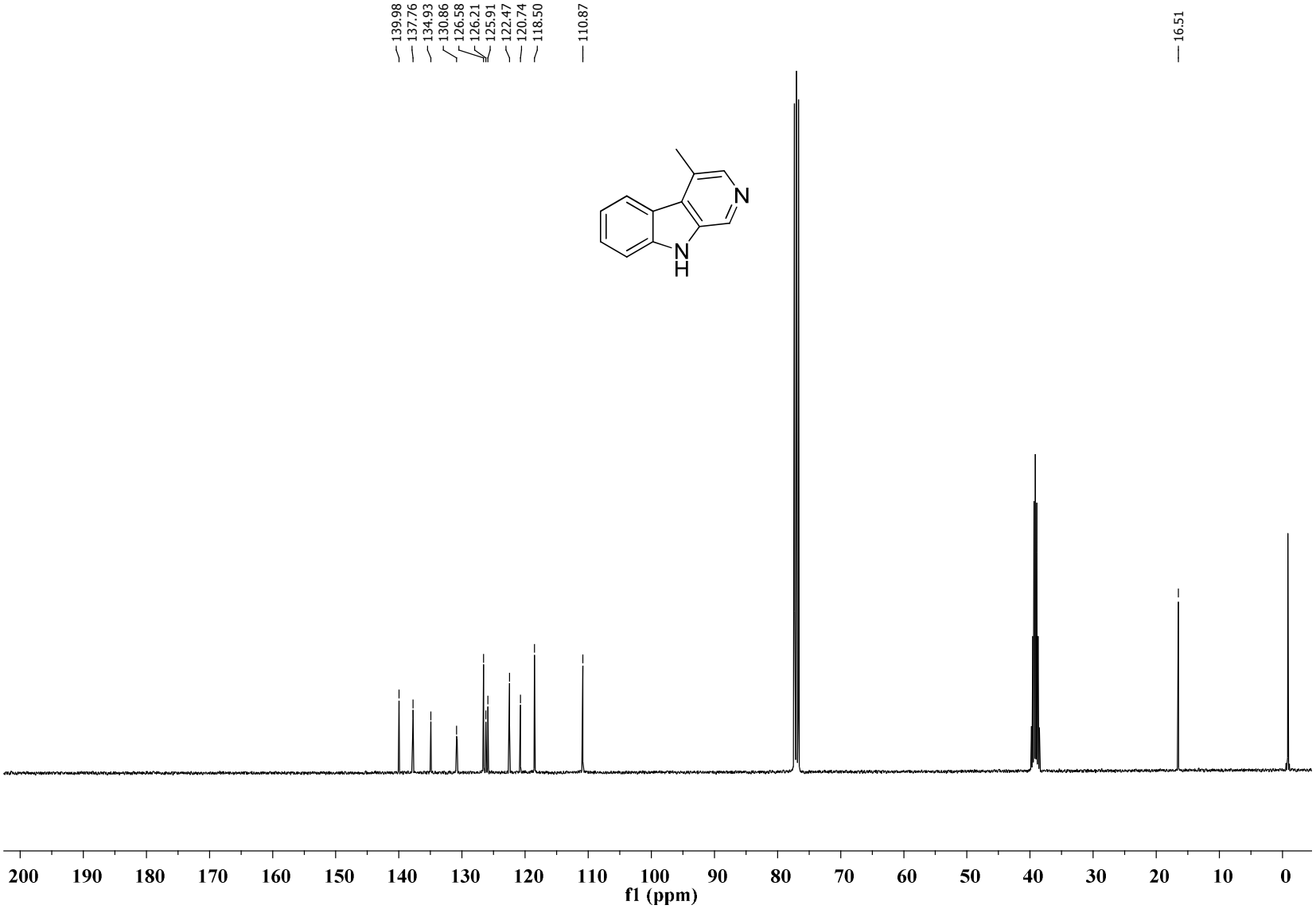
$^{13}C\{1H\}$NMR spectrum of **3i** ($CDCl_3$, 100 MHz)**:**



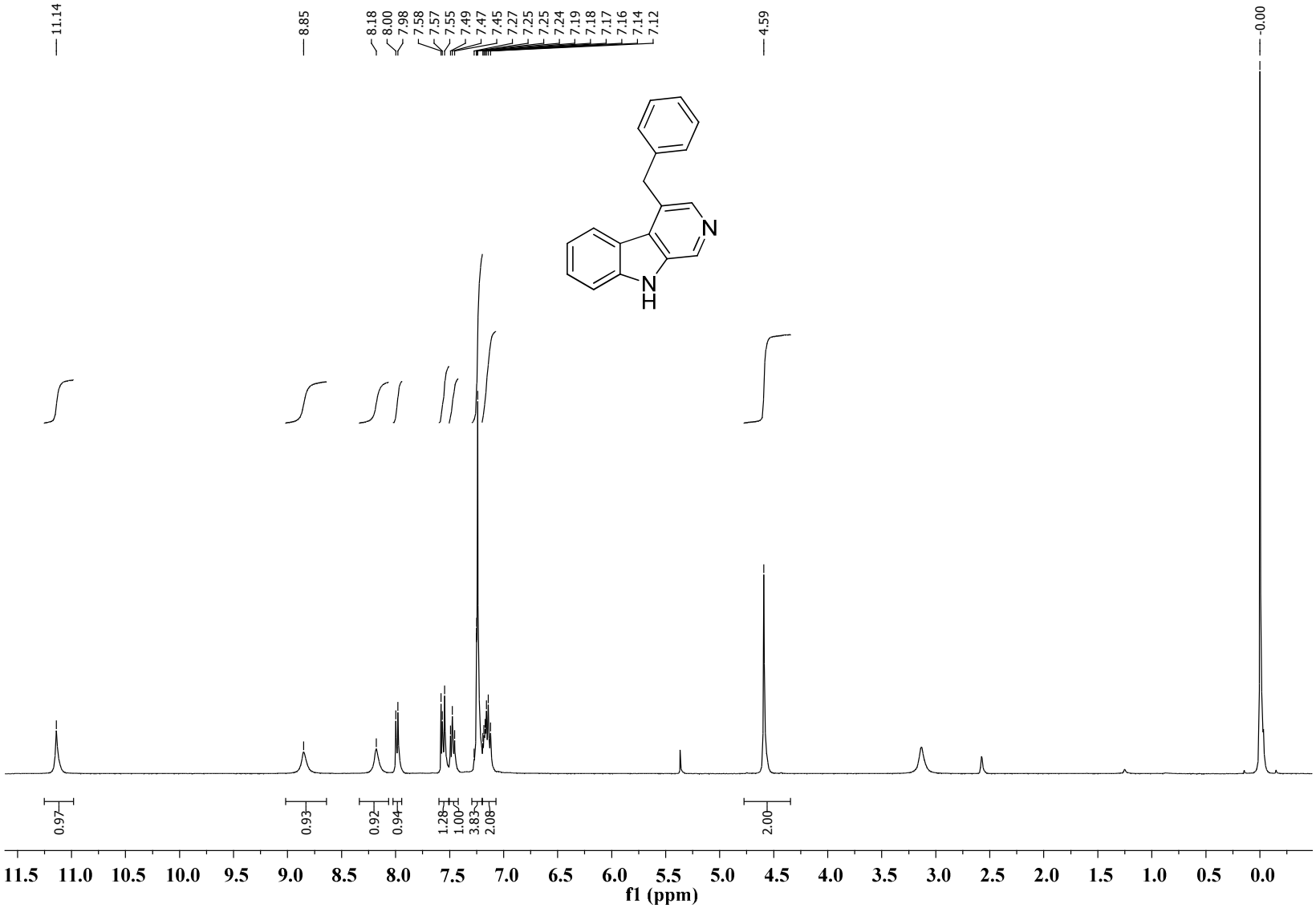
^{1}H NMR spectrum of **3j** ($CDCl_3$: DMSO-d_6, 8:2, 400 MHz)**:**



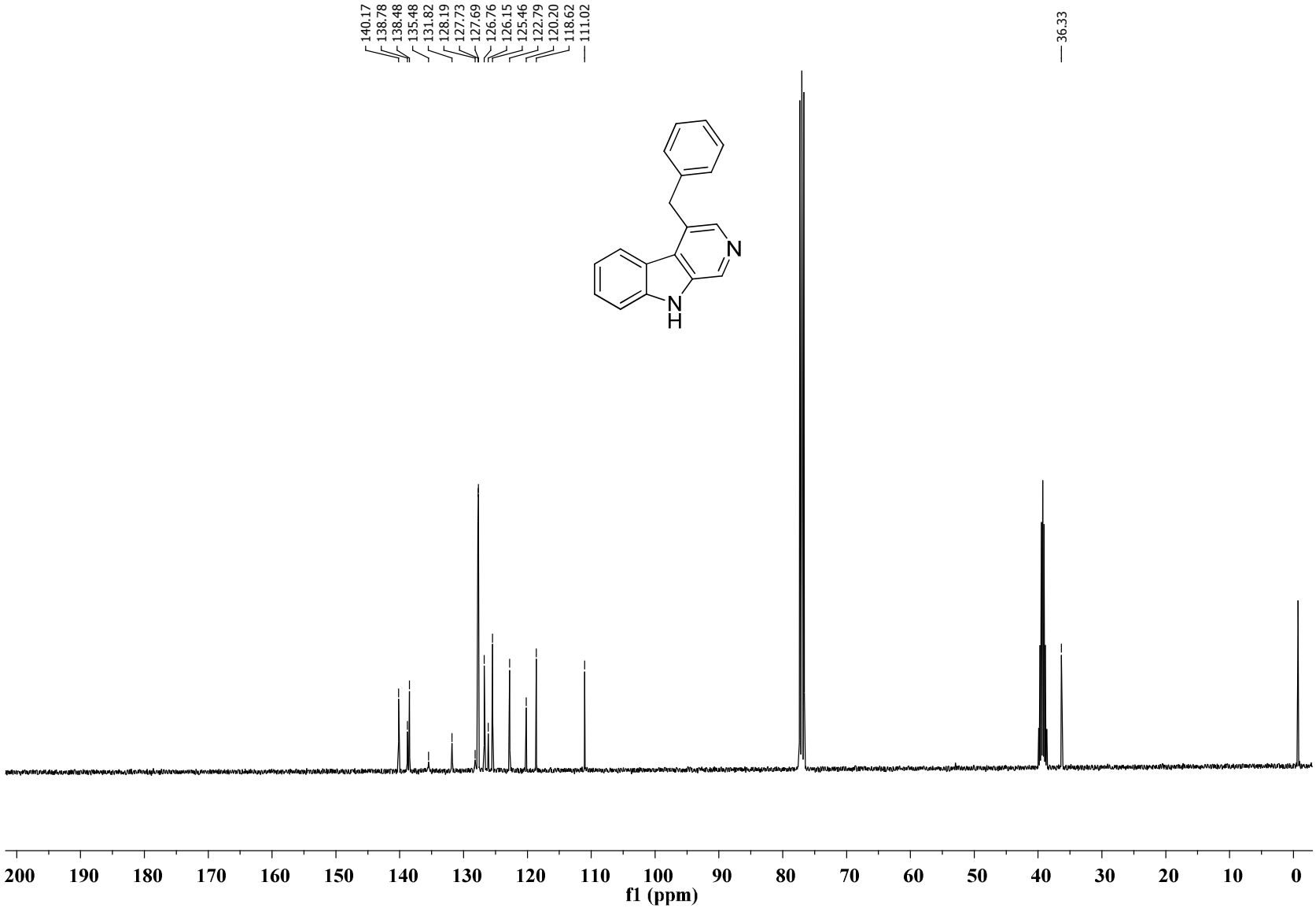
$^{13}C\{1H\}$NMR spectrum of **3j** ($CDCl_3$: DMSO-d_6, 8:2, 100 MHz)**:**



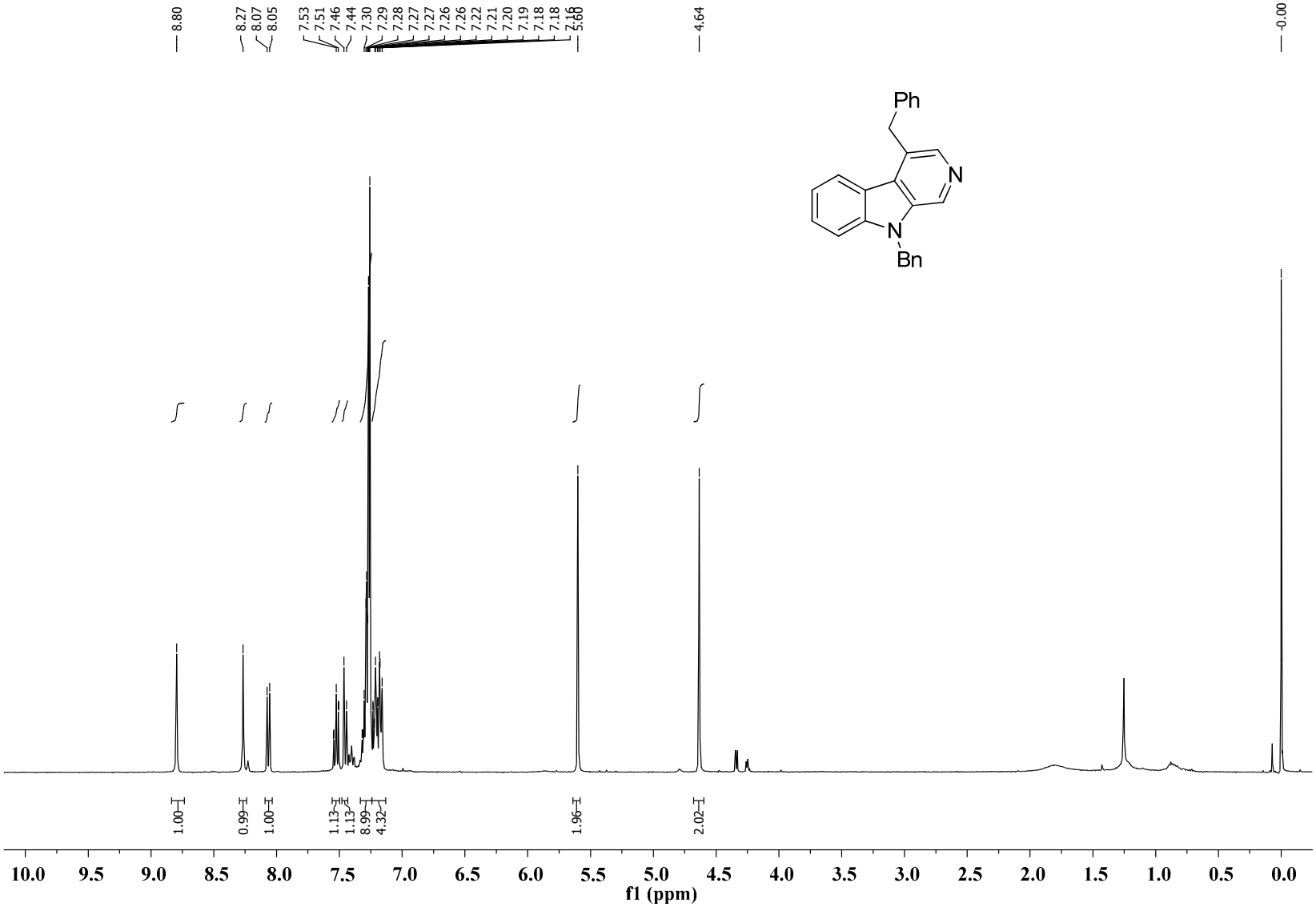
^{1}H NMR spectrum of **3k** ($CDCl_3$: DMSO-d_6, 8:2, 400 MHz)**:**



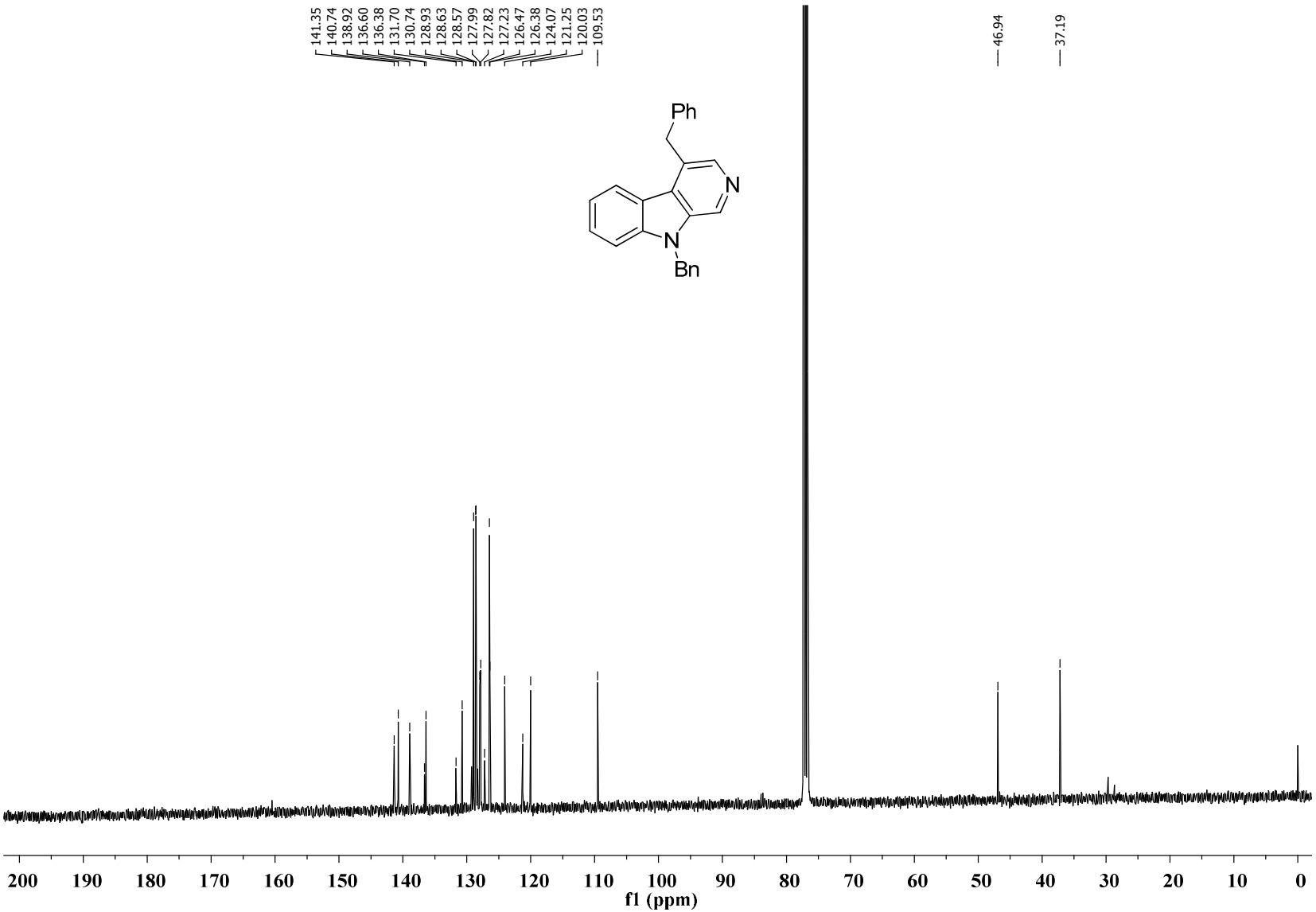
$^{13}C\{1H\}$NMR spectrum of **3k** ($CDCl_3$: DMSO-d_6, 8:2, 100 MHz)**:**



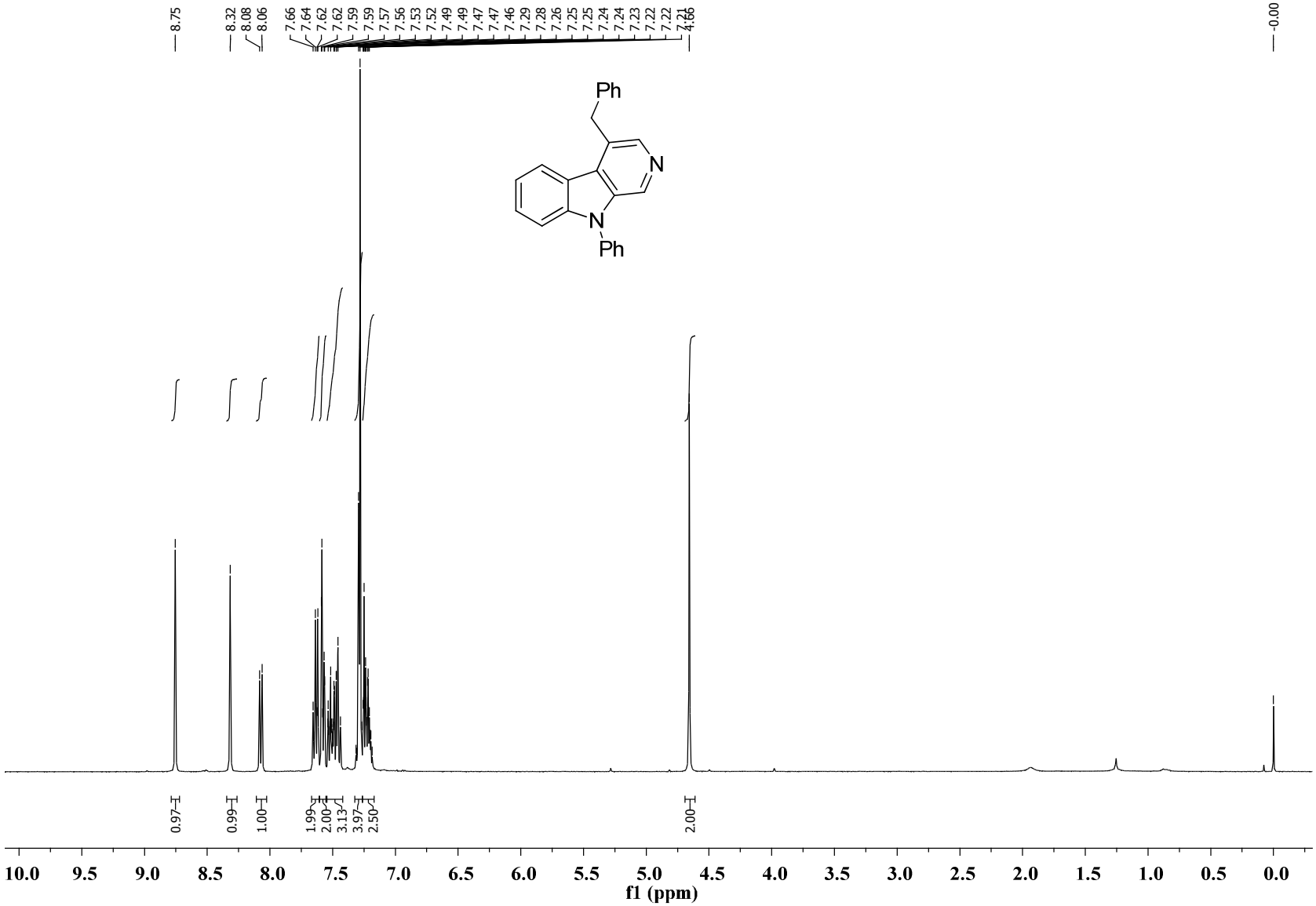
^{1}H NMR spectrum of **3l** ($CDCl_3$, 400 MHz)**:**



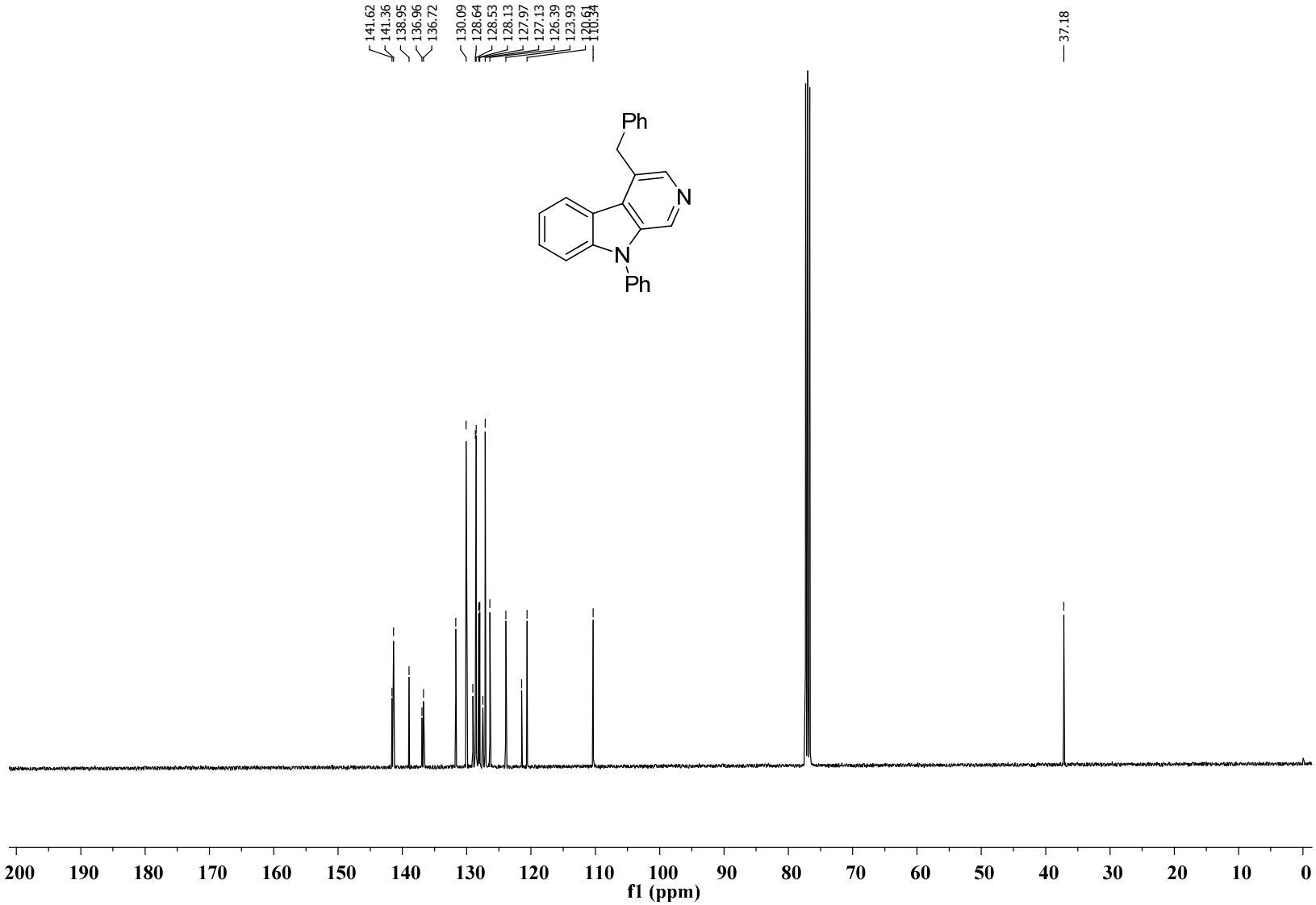
$^{13}C\{1H\}$NMR spectrum of **3l** ($CDCl_3$, 100 MHz)**:**



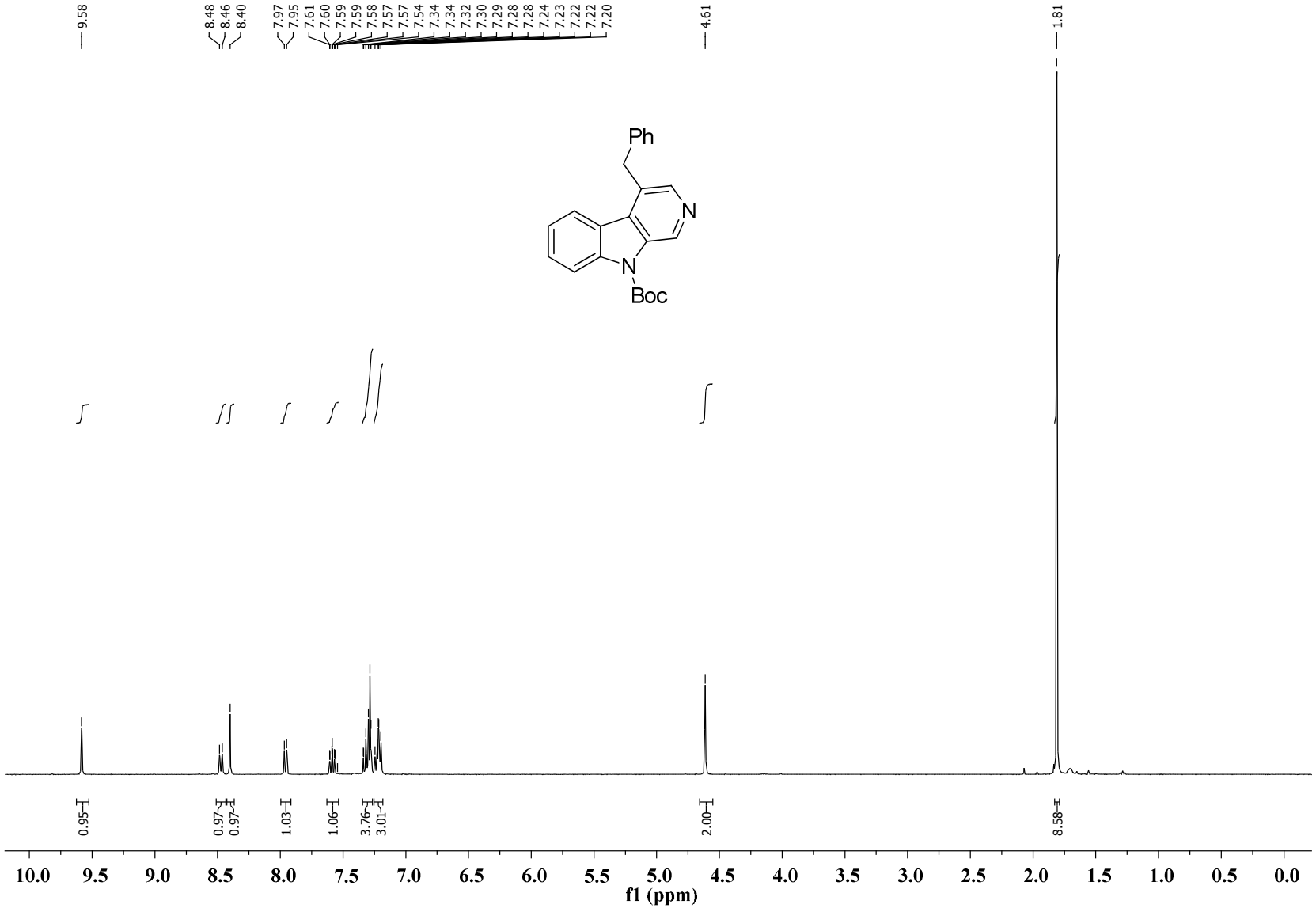
^{1}H NMR spectrum of **3m** ($CDCl_3$, 400 MHz)**:**



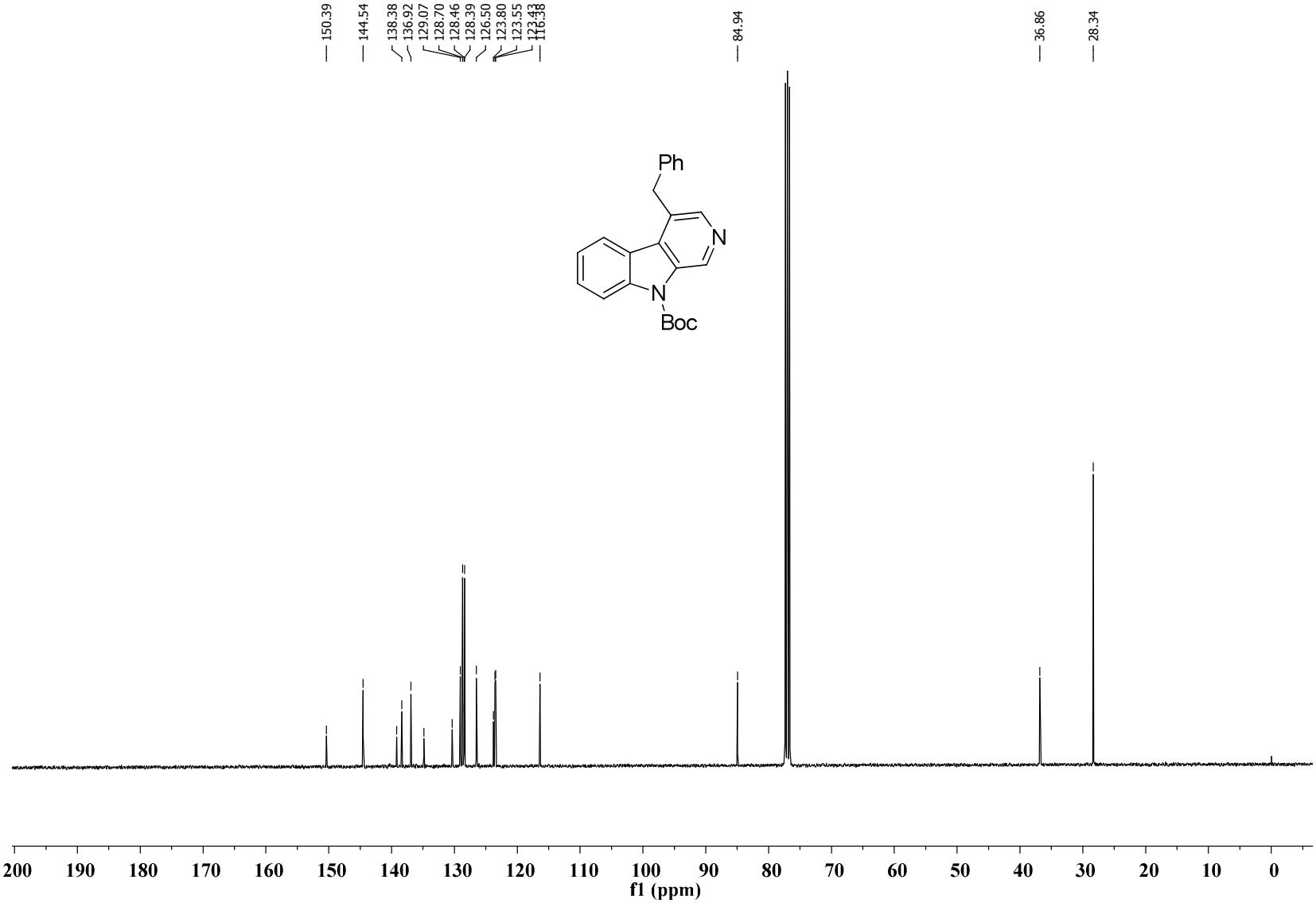
$^{13}C\{1H\}$NMR spectrum of **3m** ($CDCl_3$, 100 MHz)**:**



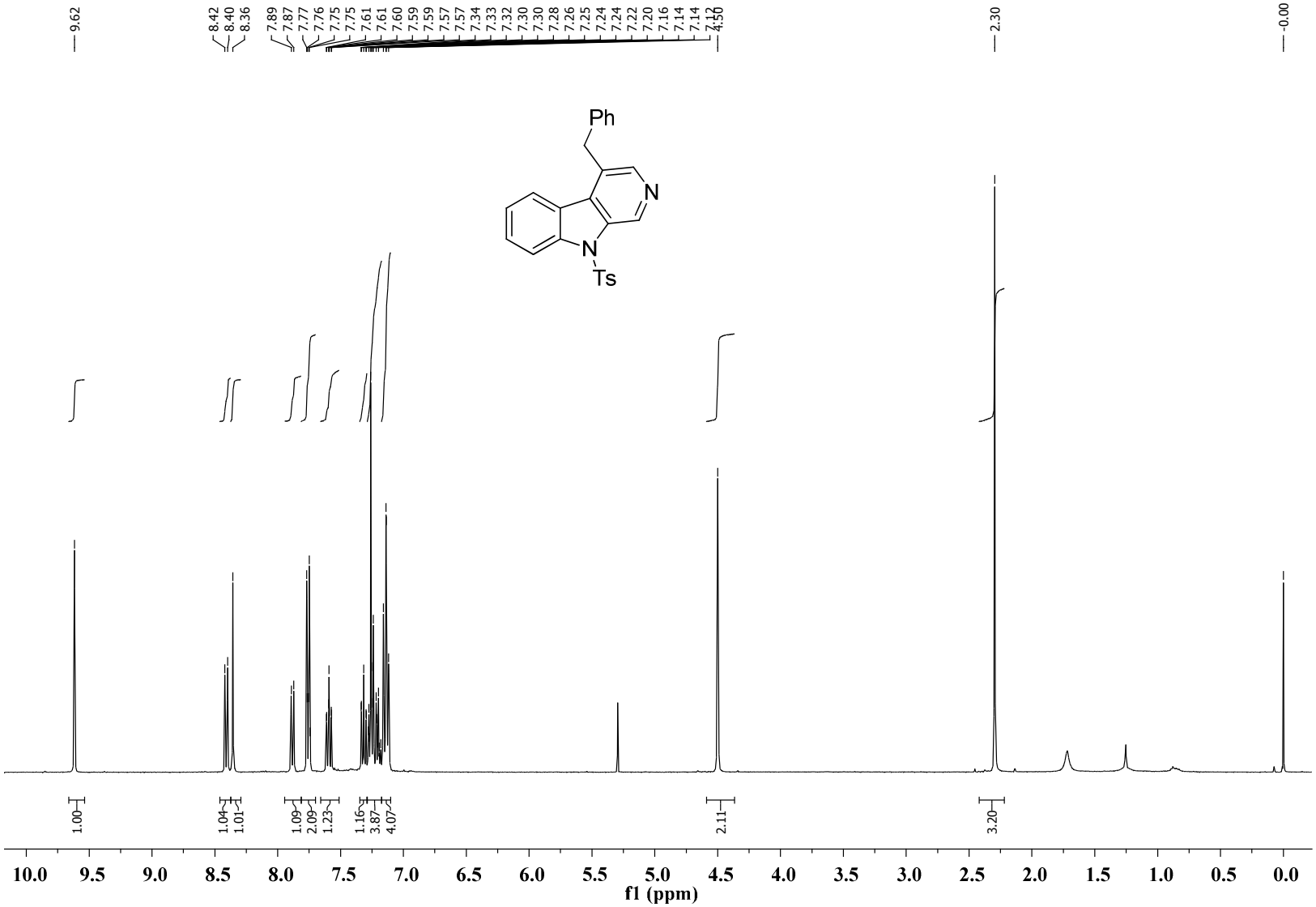
^{1}H NMR spectrum of **3n** ($CDCl_3$, 400 MHz)**:**



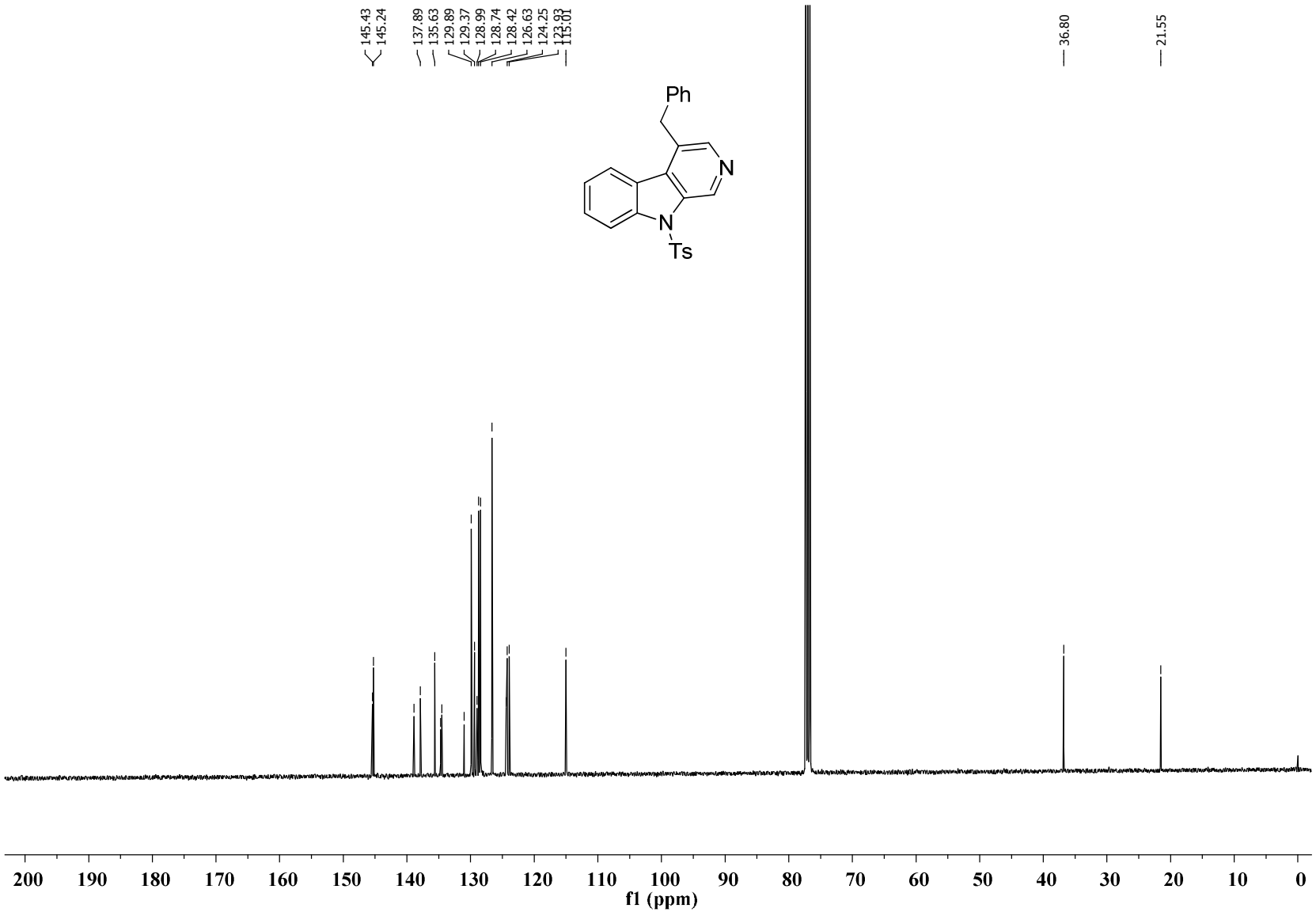
$^{13}C\{1H\}$NMR spectrum of **3n** ($CDCl_3$, 100 MHz)**:**



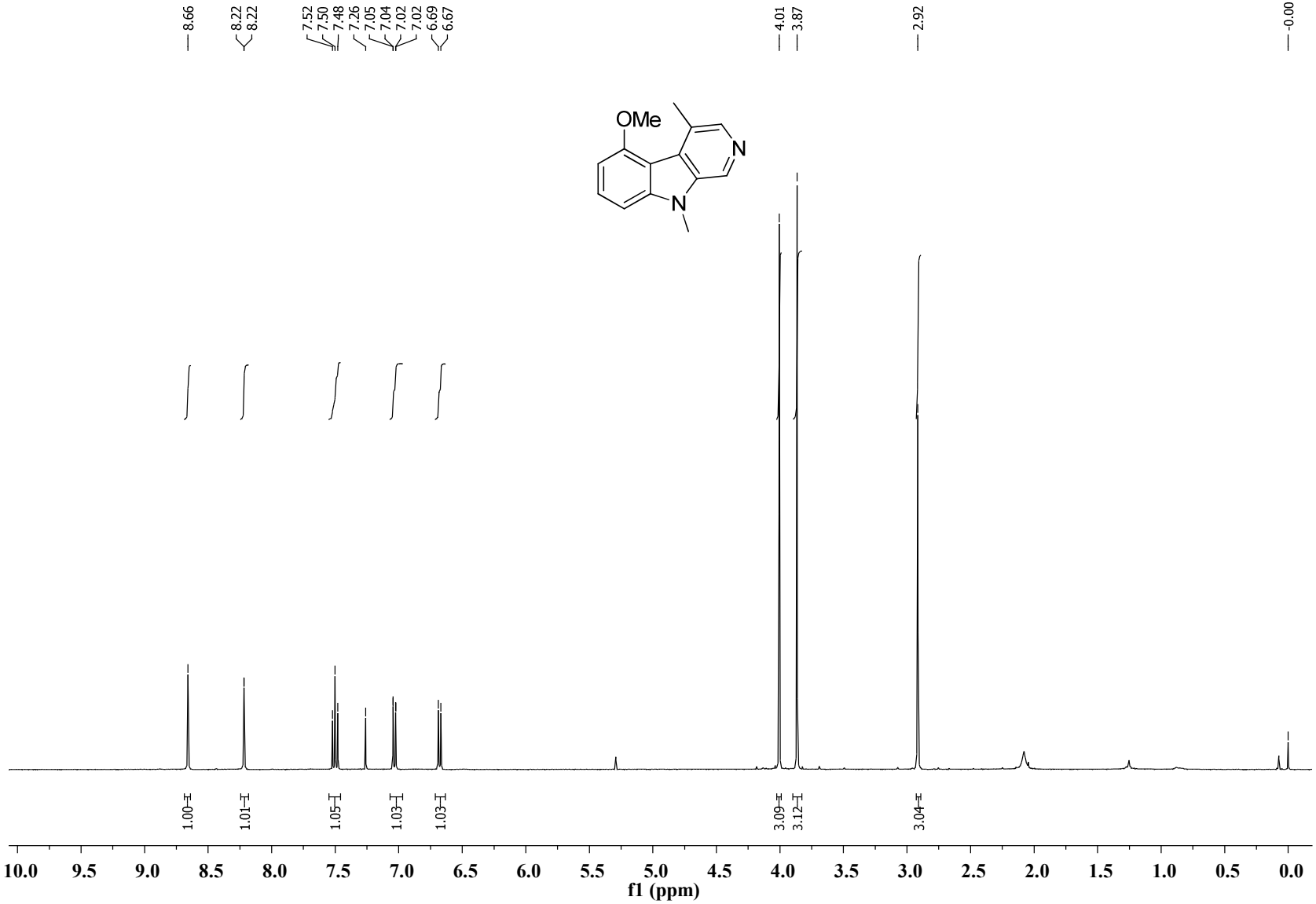
^{1}H NMR spectrum of **3o** ($CDCl_3$, 400 MHz)**:**



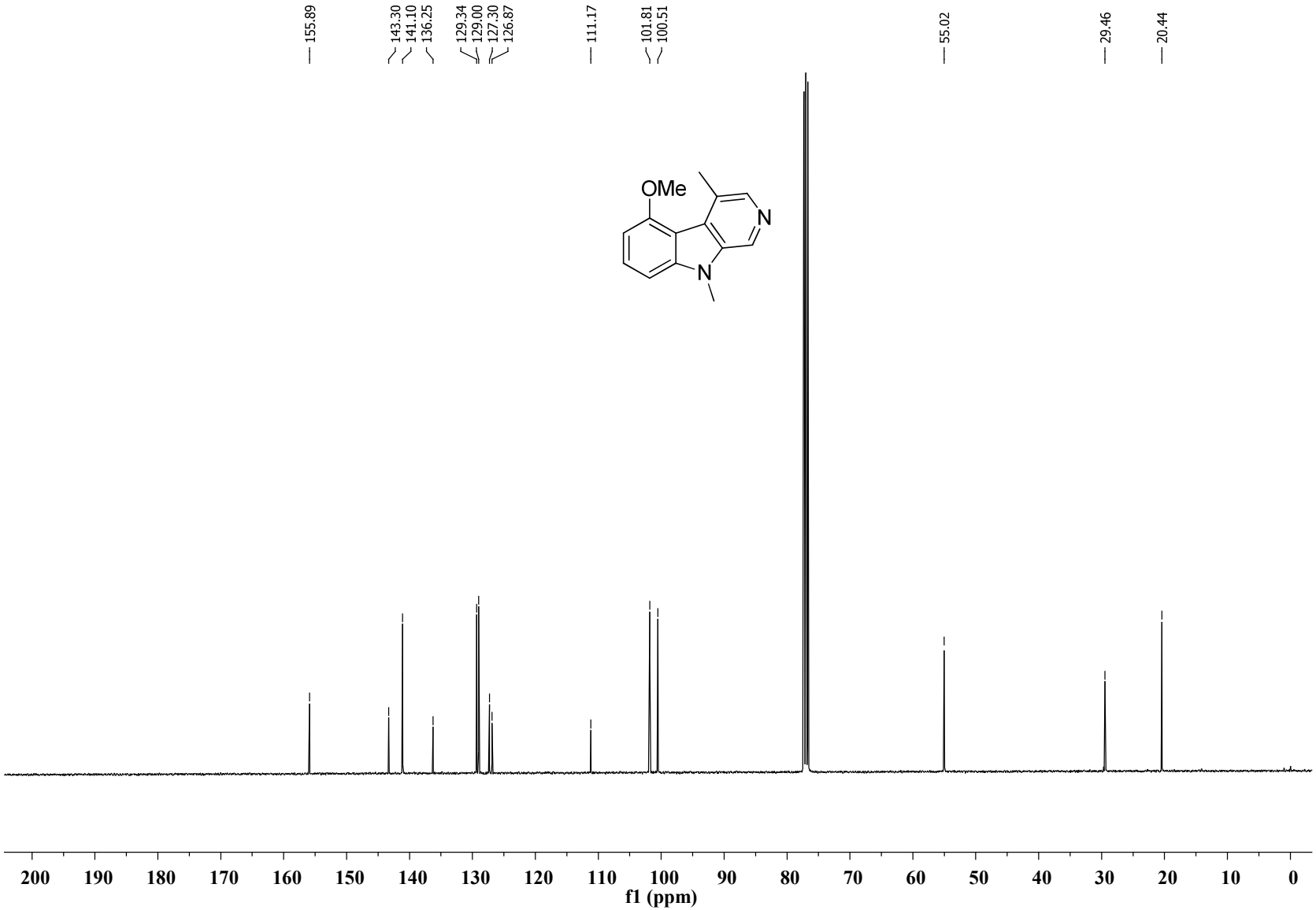
$^{13}C\{1H\}$NMR spectrum of **3o** ($CDCl_3$, 100 MHz)**:**



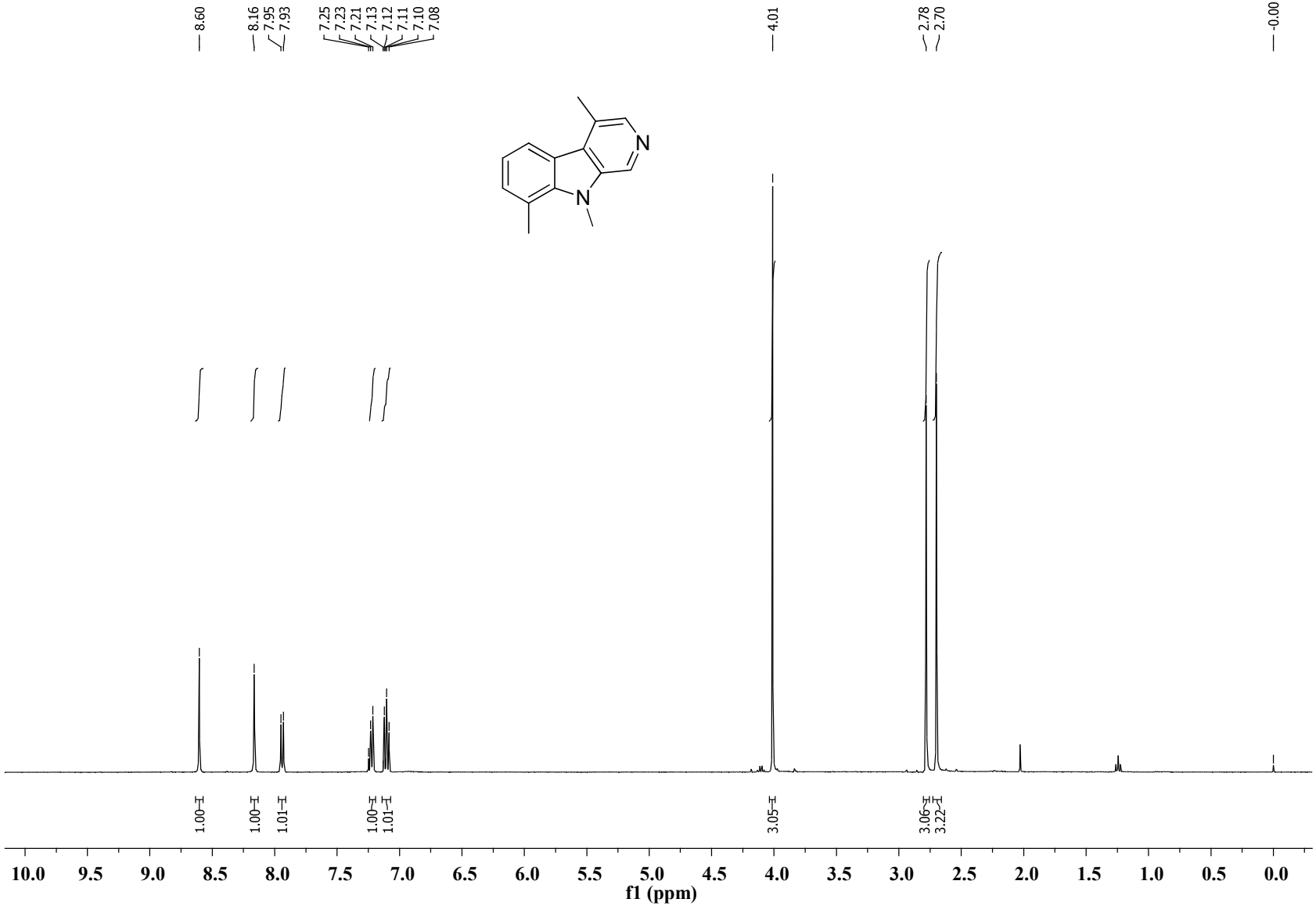
^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 400 MHz)**:**



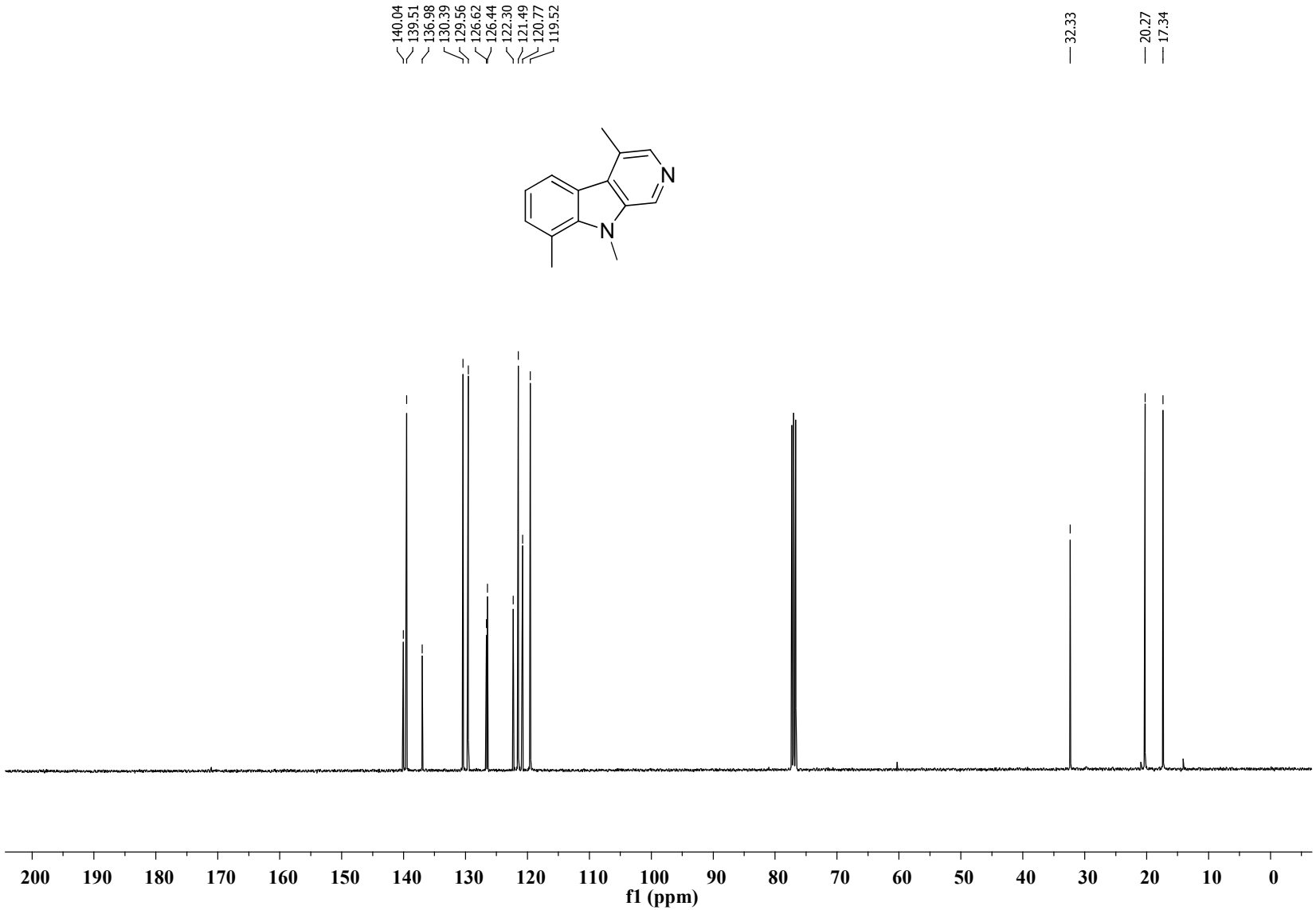
$^{13}C\{1H\}$NMR spectrum of compound **3p** ($CDCl_3$, 100 MHz)**:**



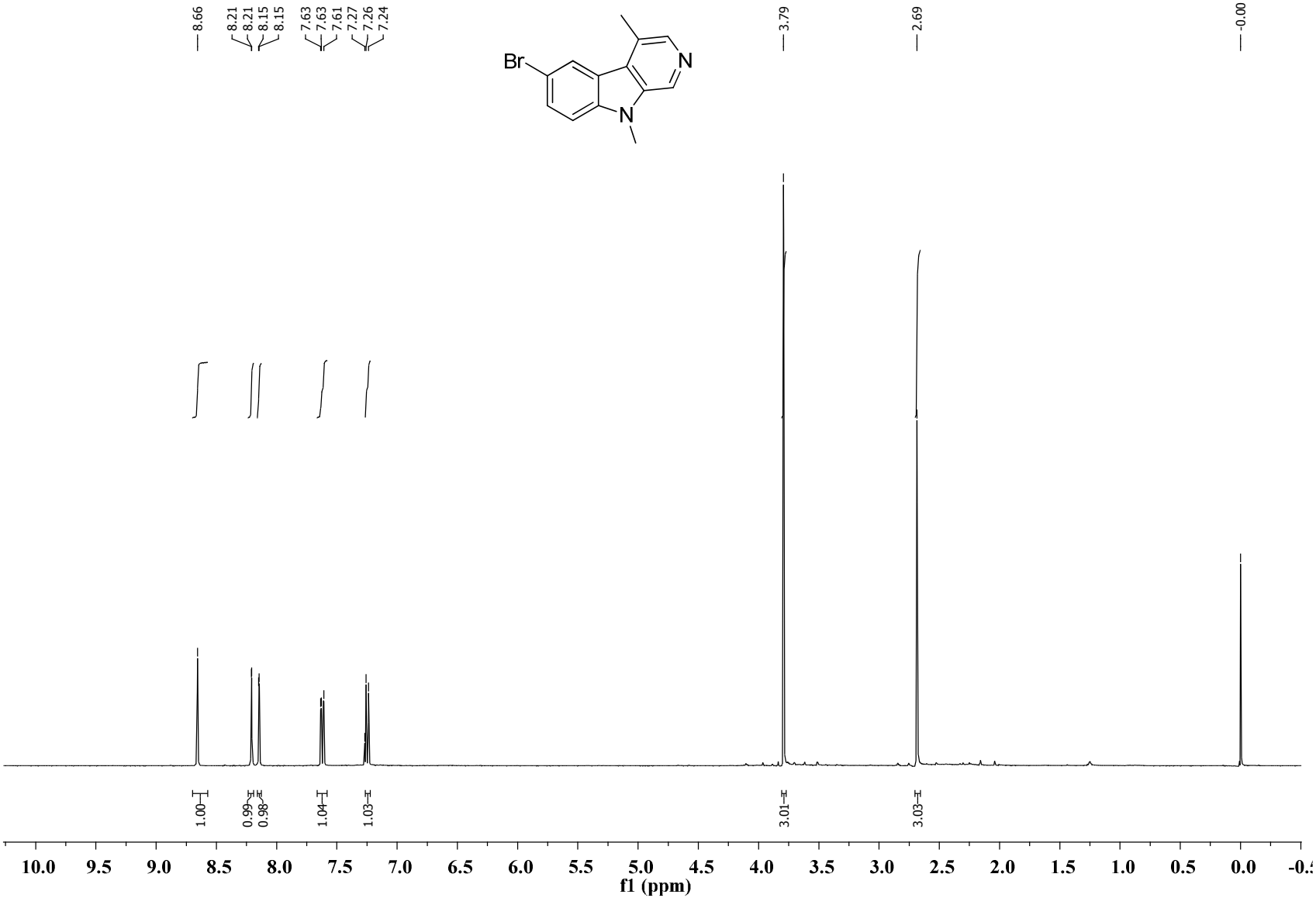
^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 400 MHz)**:**



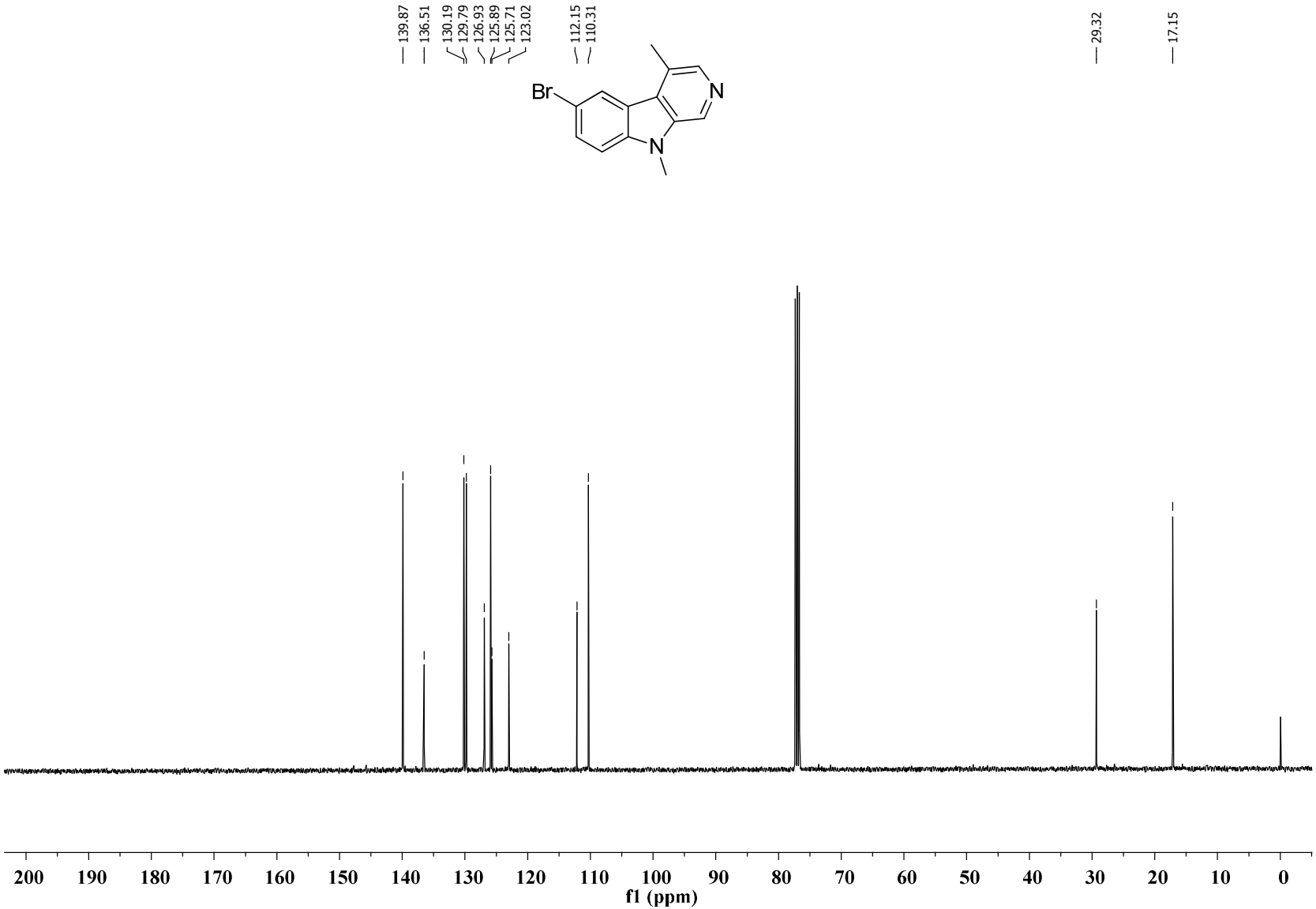
$^{13}C\{1H\}$NMR spectrum of compound **3q** ($CDCl_3$, 100 MHz)**:**



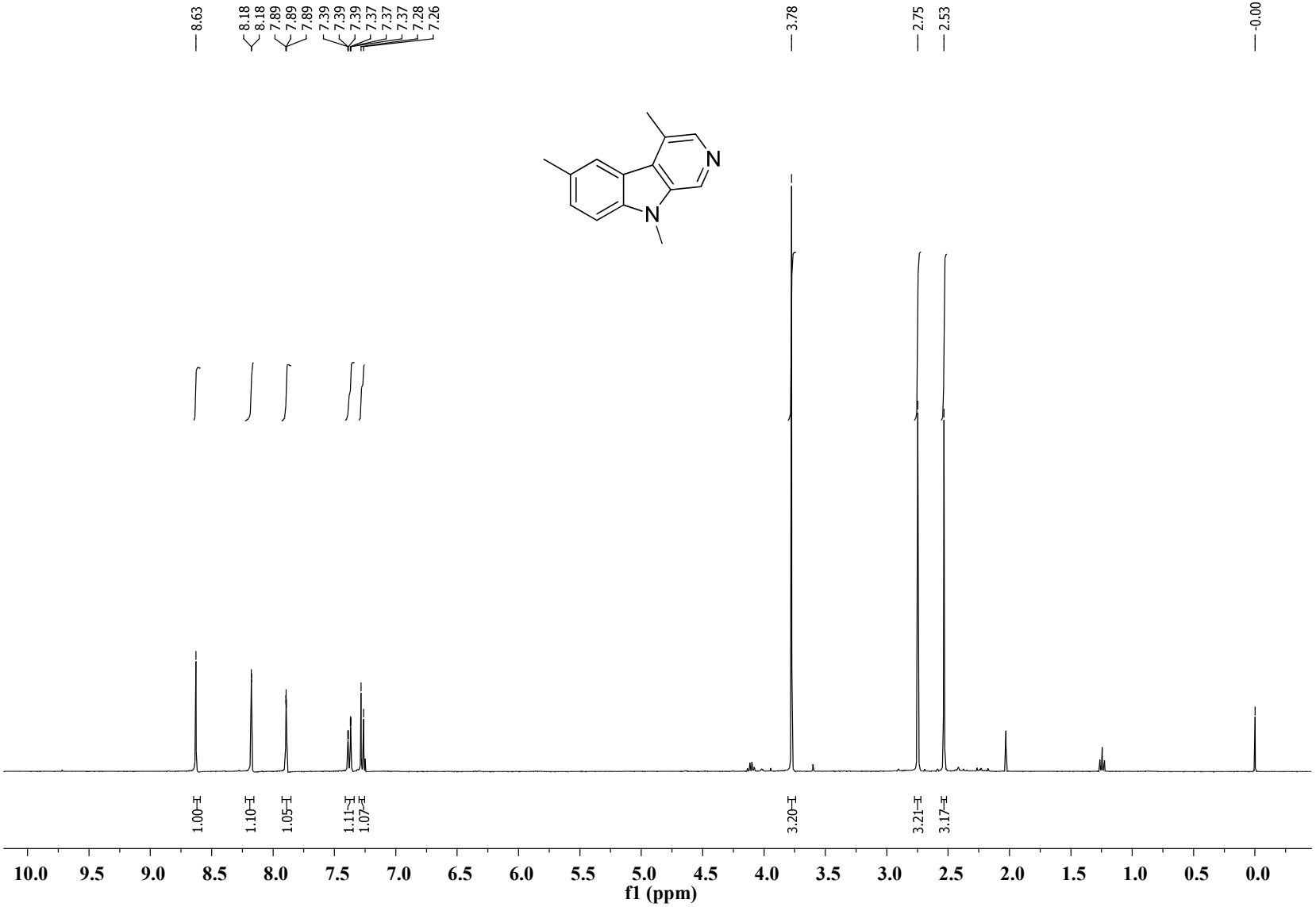
^{1}H NMR spectrum of compound **3r** ($CDCl_3$, 400 MHz)**:**



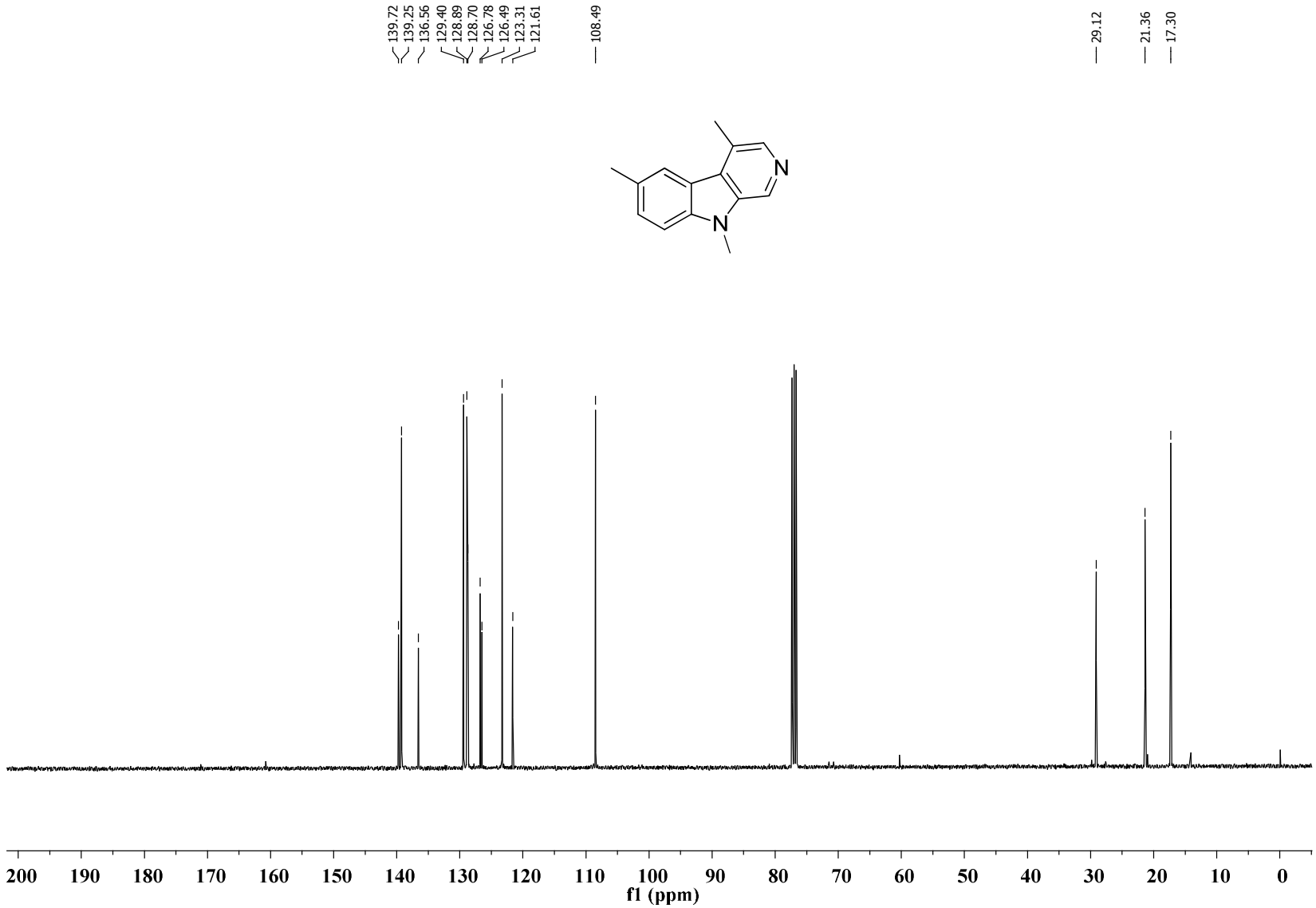
$^{13}C\{1H\}$NMR spectrum of compound **3r** ($CDCl_3$, 100 MHz)**:**



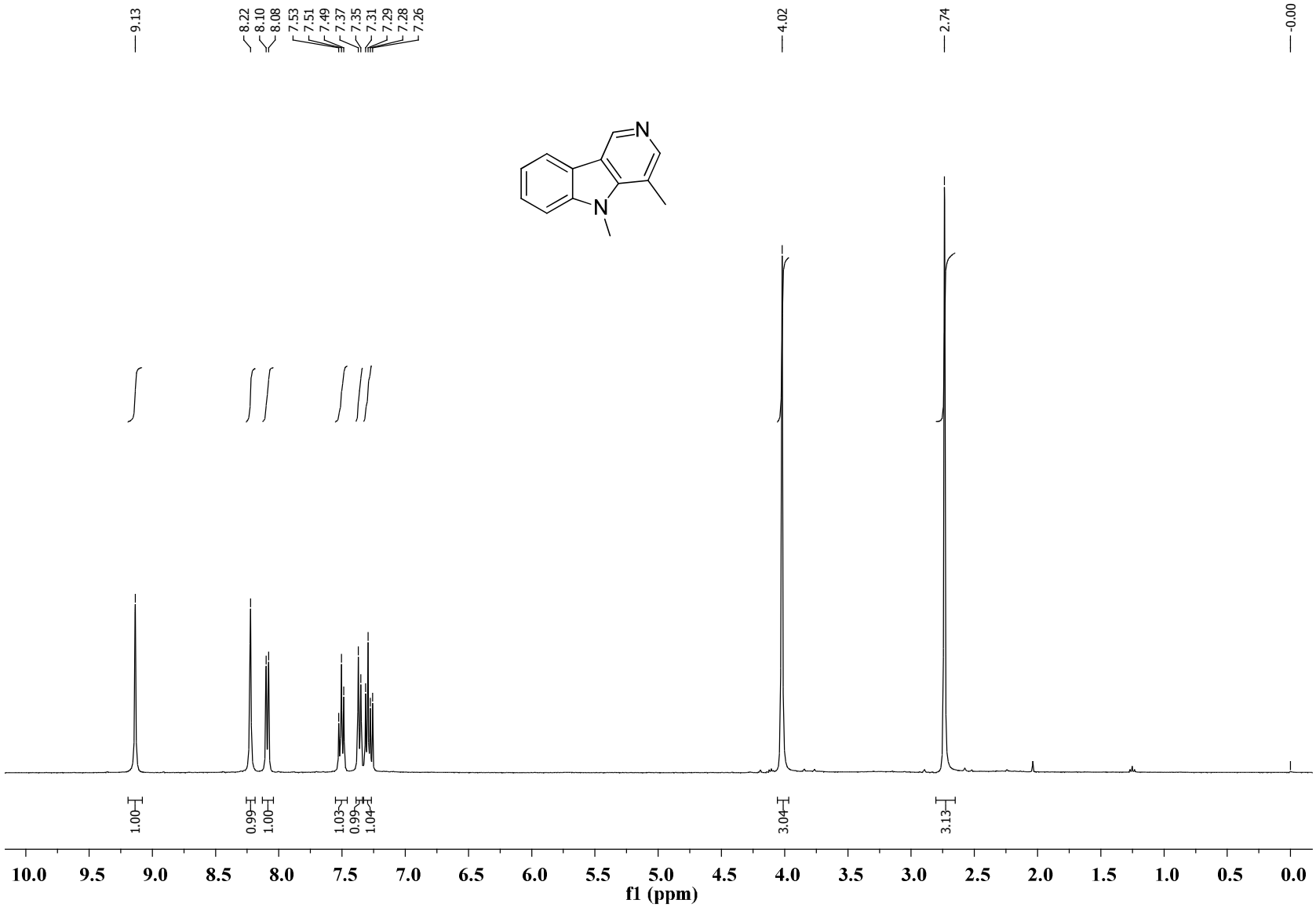
^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 400 MHz)**:**



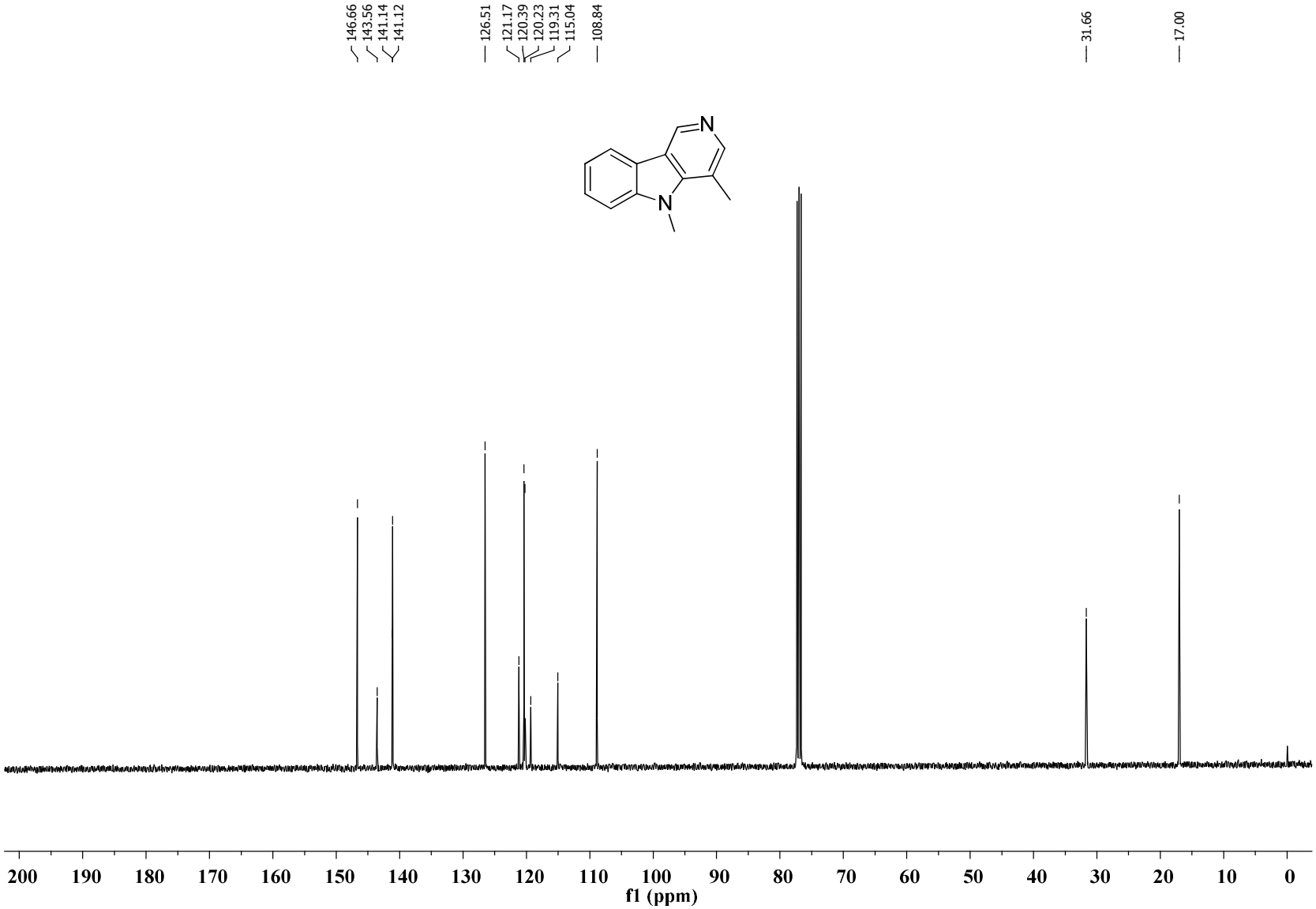
$^{13}C\{1H\}$NMR spectrum of compound **3s** ($CDCl_3$, 100 MHz)**:**



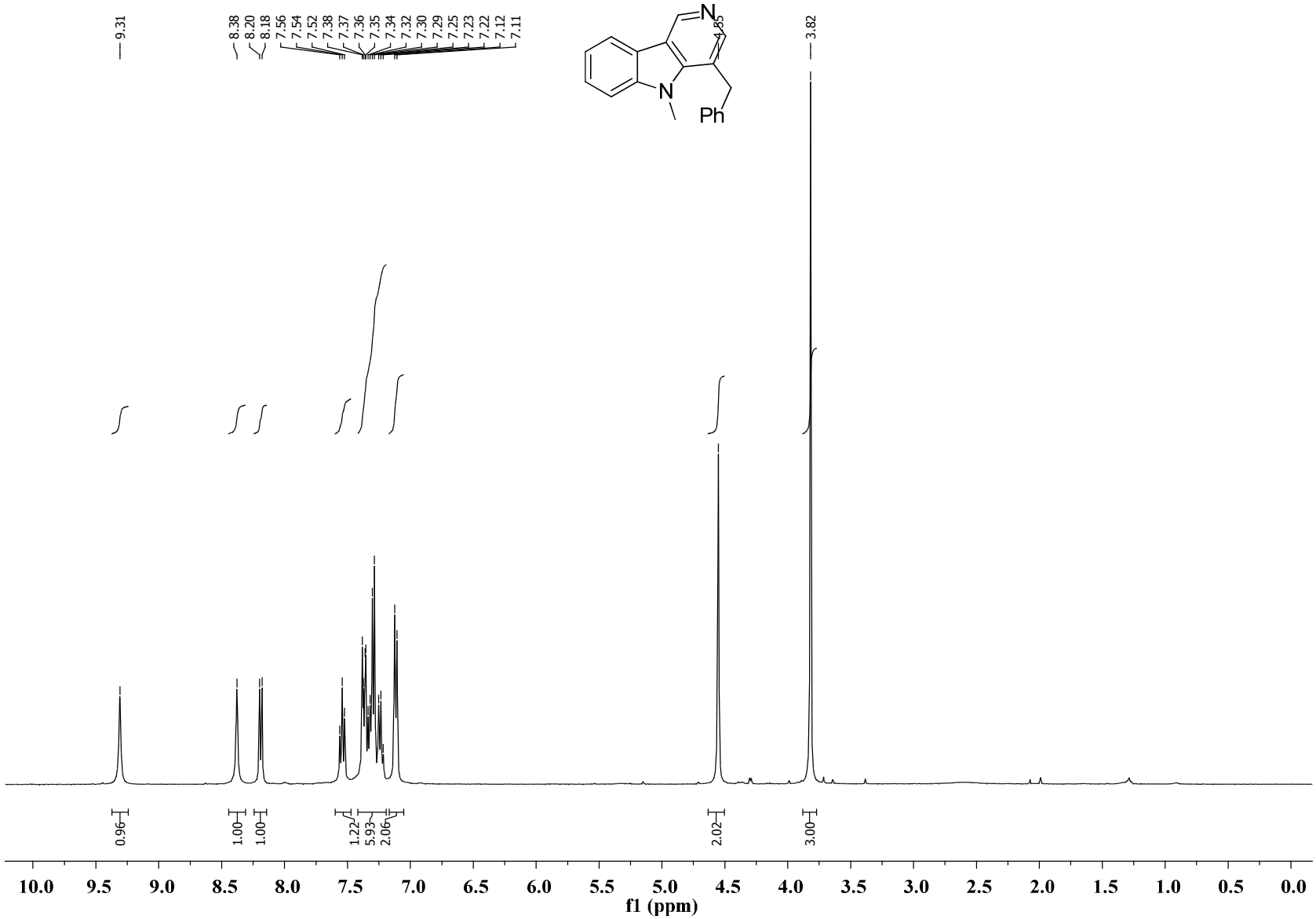
^{1}H NMR spectrum of **3t** ($CDCl_3$, 400 MHz)**:**



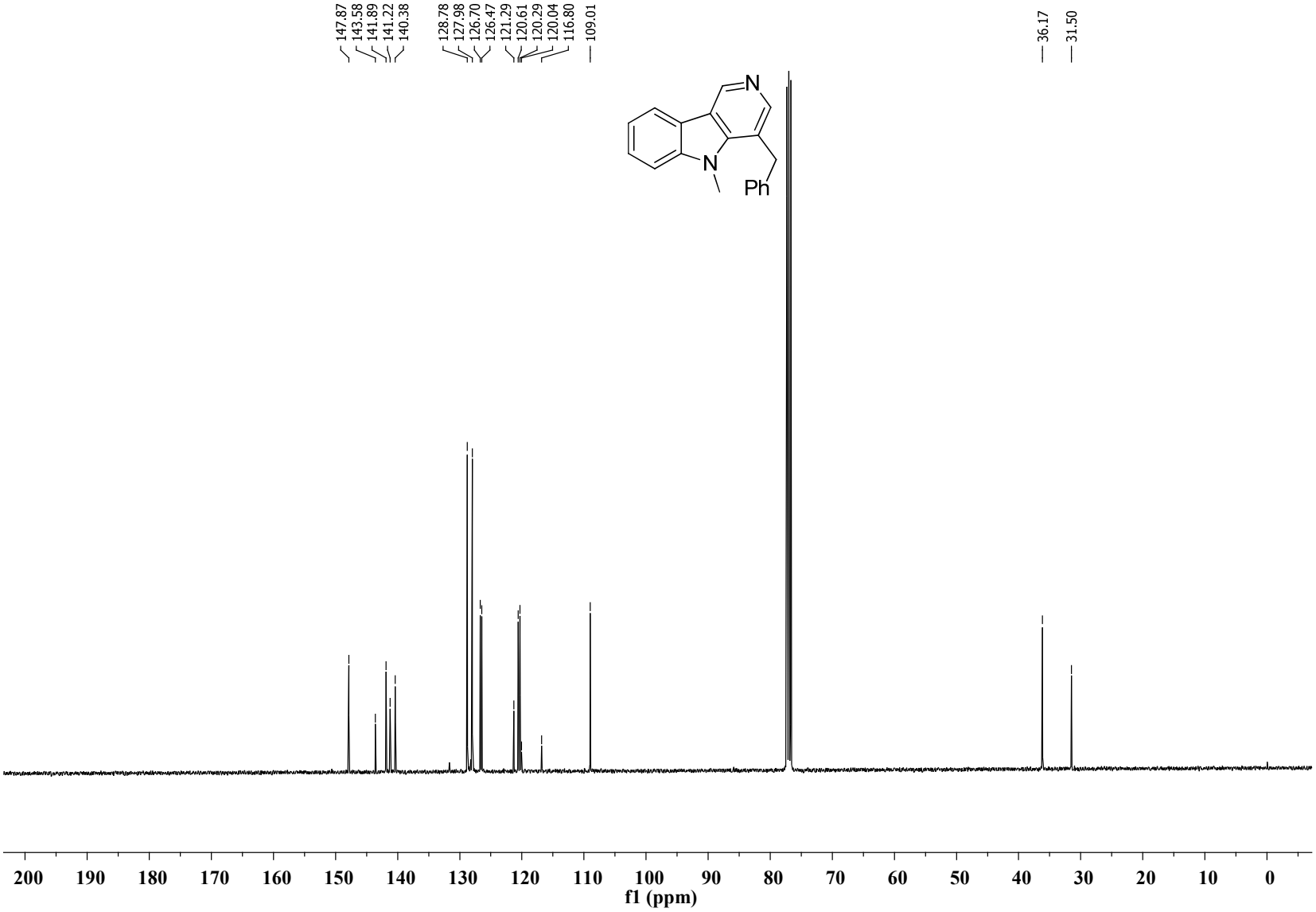
$^{13}C\{1H\}$NMR spectrum of **3t** ($CDCl_3$, 100 MHz)**:**



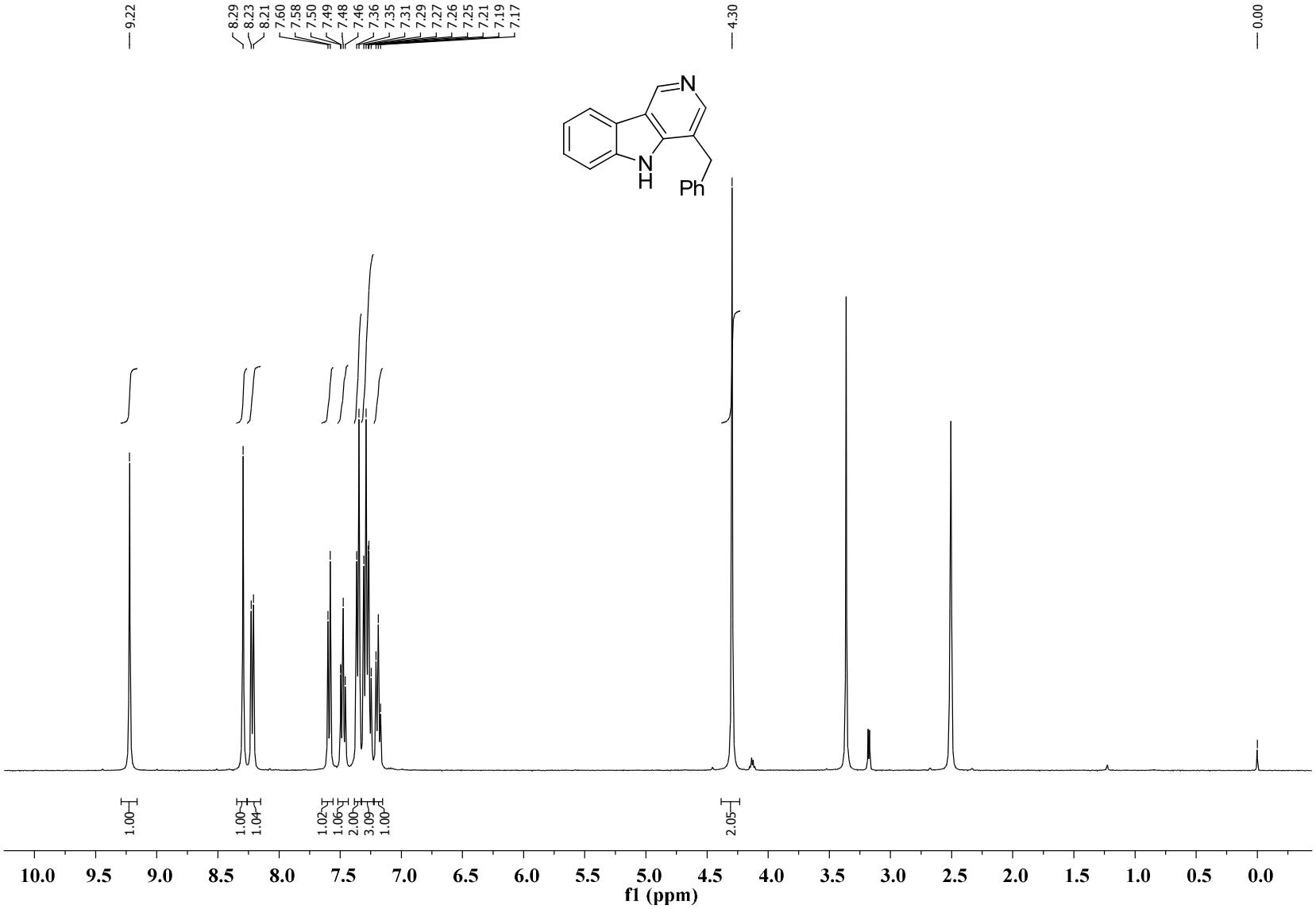
^{1}H NMR spectrum of **3u** ($CDCl_3$, 400 MHz)**:**



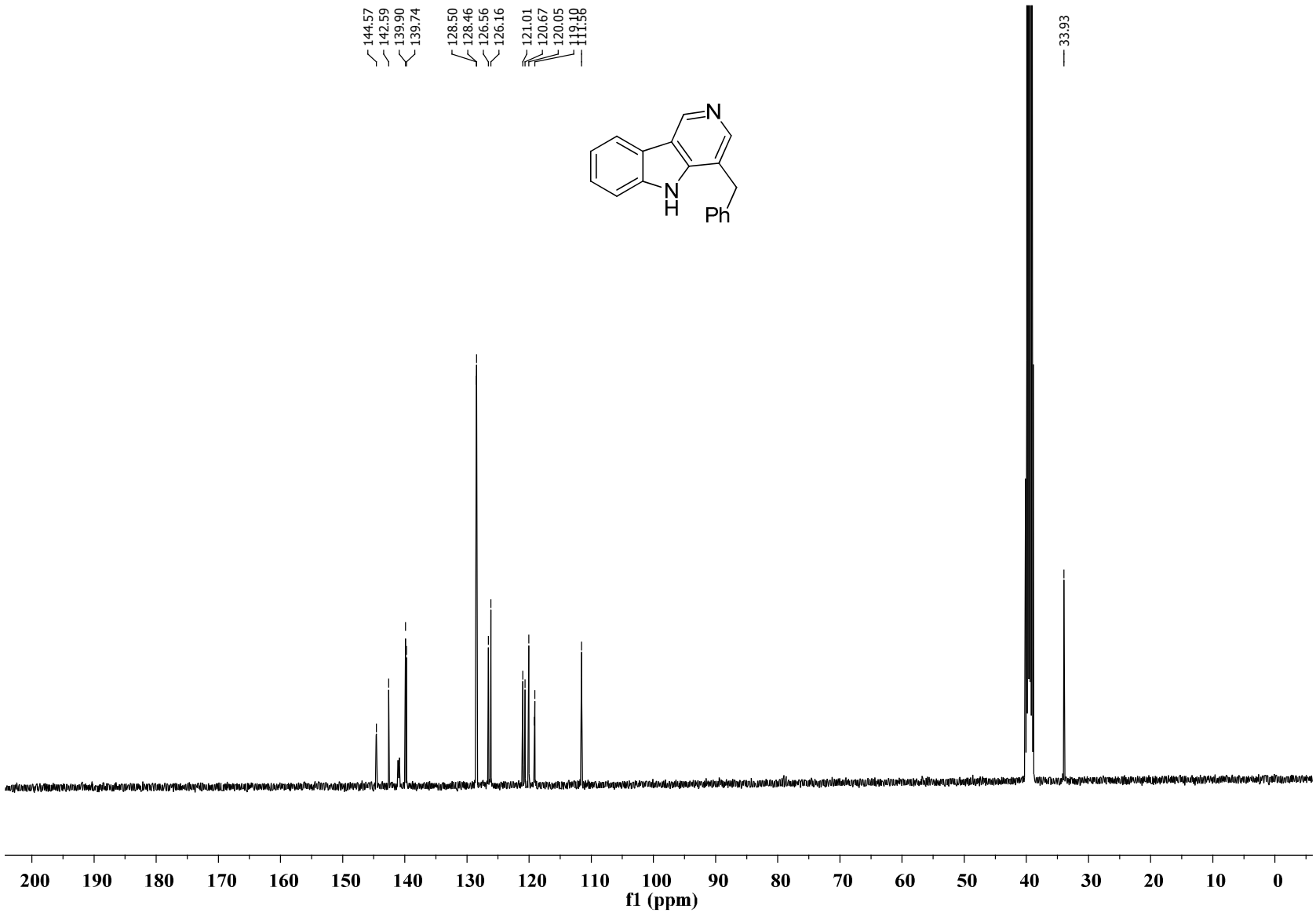
$^{13}C\{1H\}$NMR spectrum of **3u** ($CDCl_3$, 100 MHz)**:**



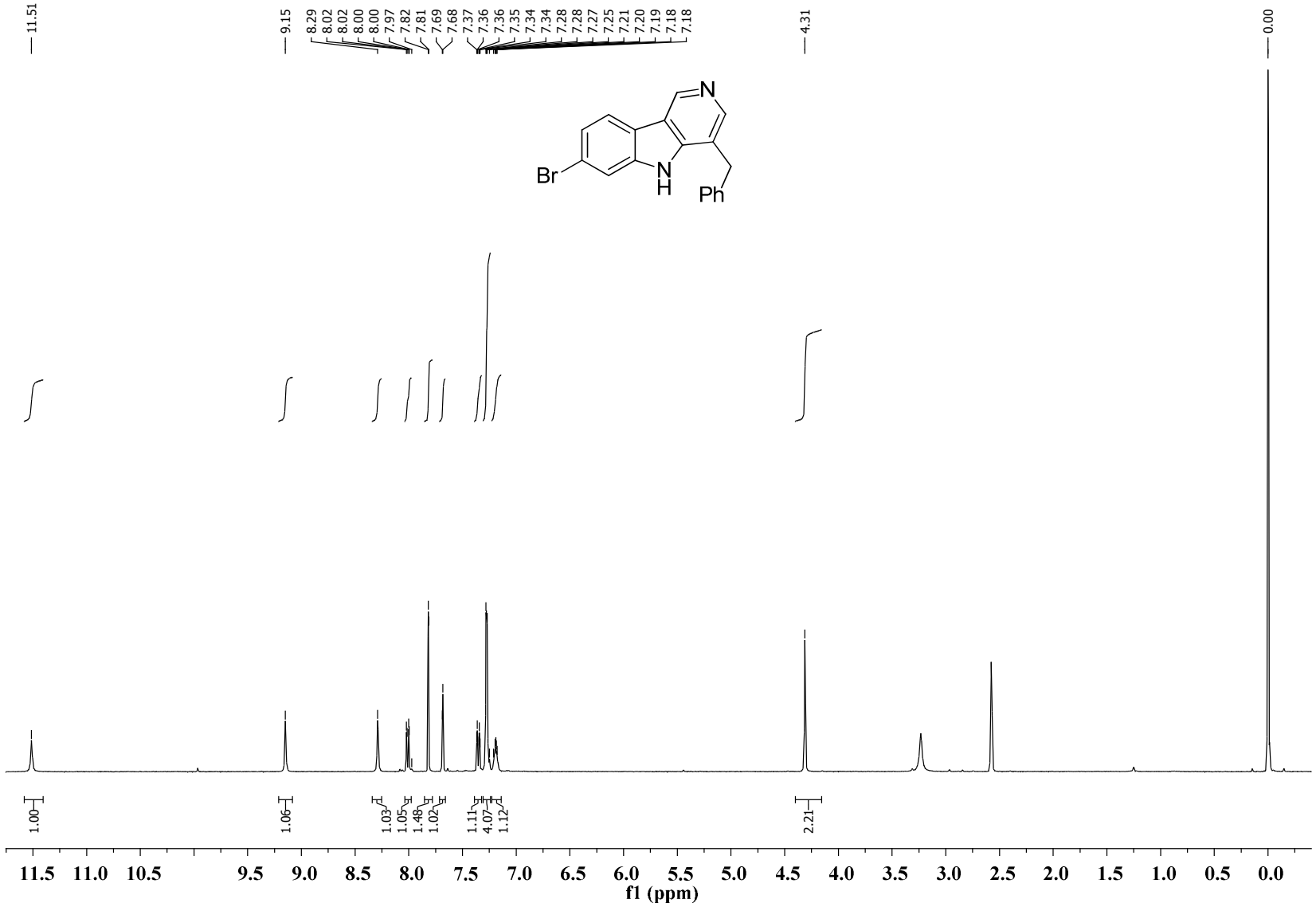
^{1}H NMR spectrum of **3v** (DMSO-d_6, 400 MHz)**:**



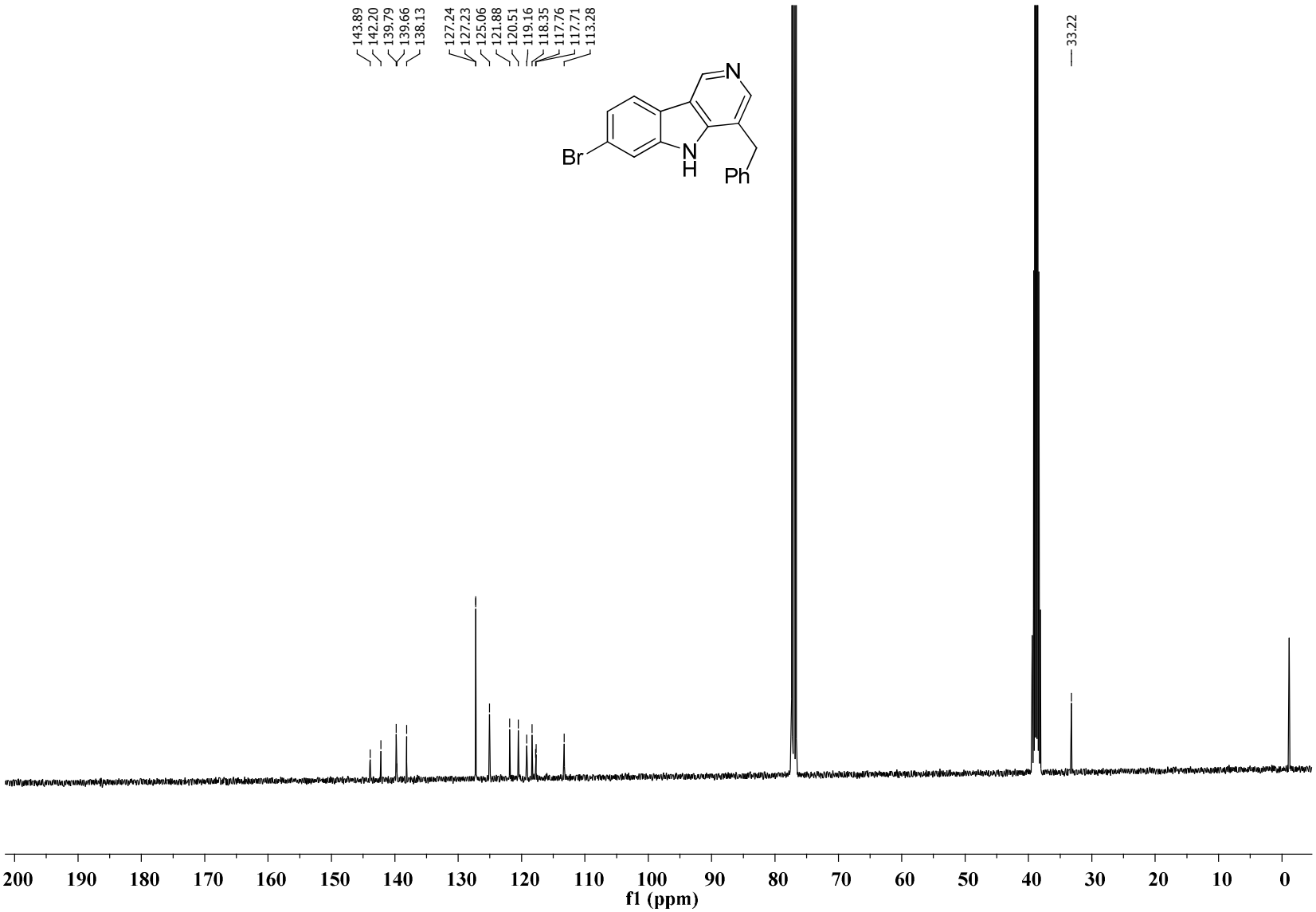
$^{13}C\{1H\}$NMR spectrum of **3v** (DMSO-d_6, 100 MHz)**:**



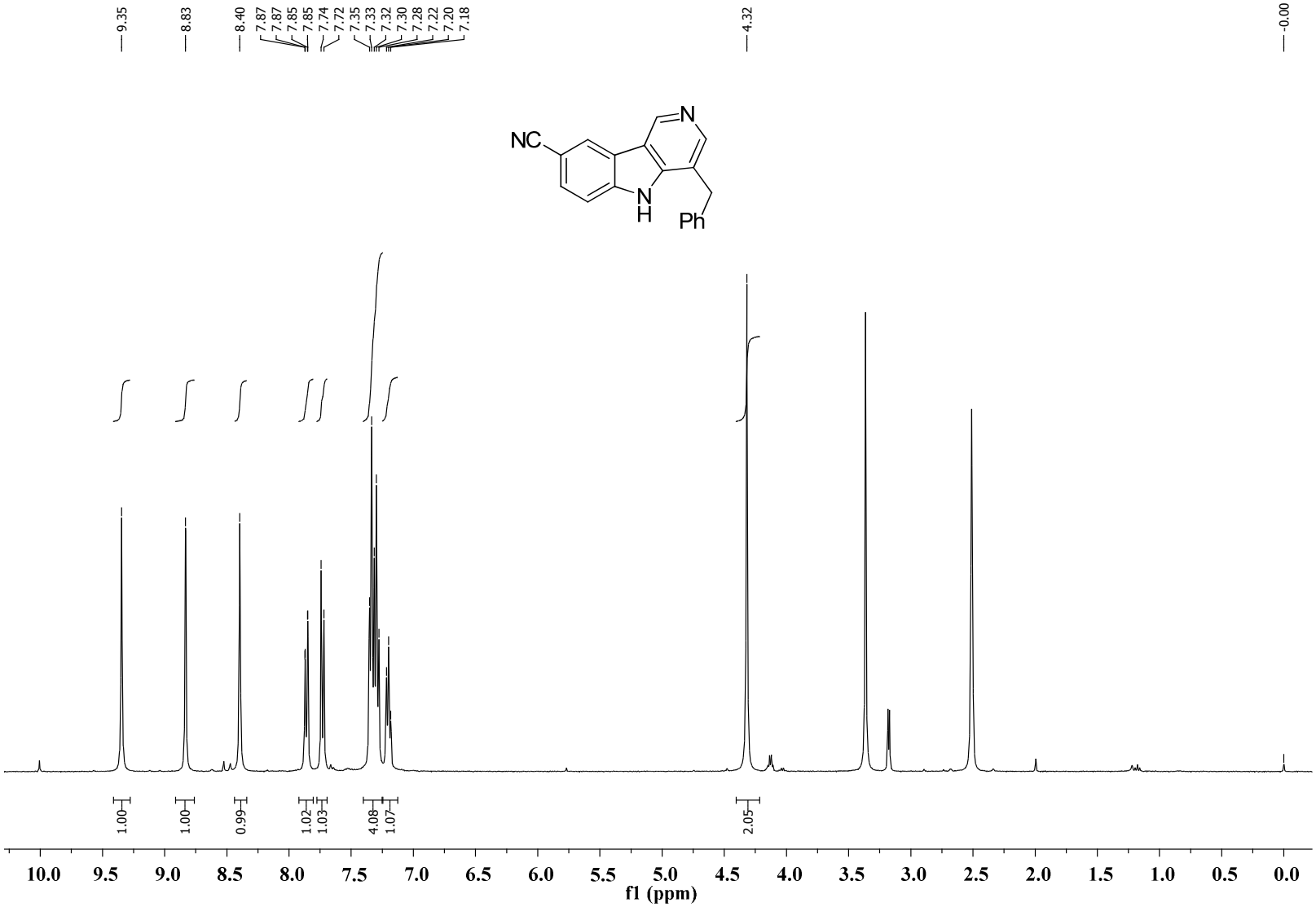
^{1}H NMR spectrum of **3w** ($CDCl_3$: DMSO-d_6, 1:1, 400 MHz)**:**



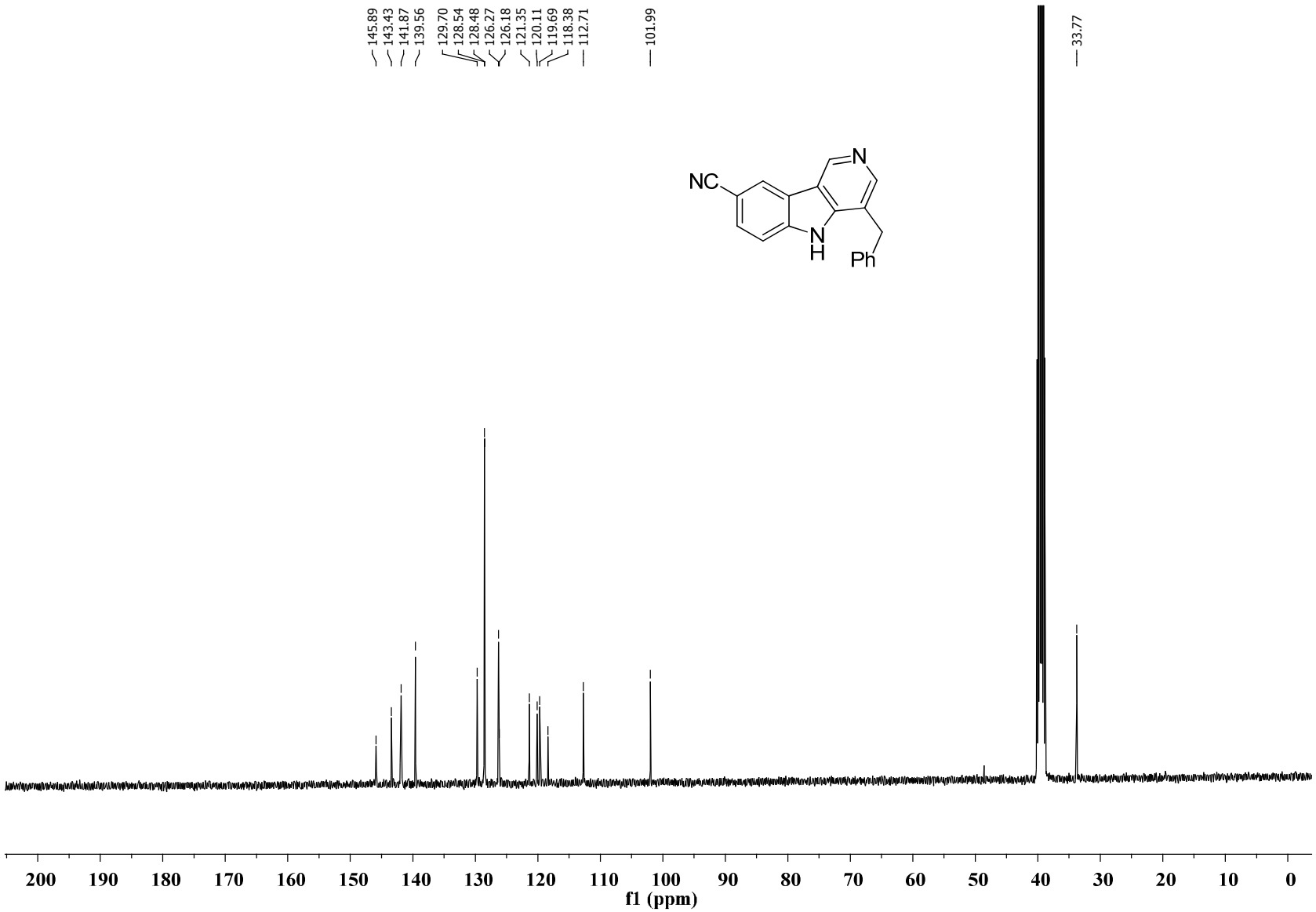
$^{13}C\{1H\}$NMR spectrum of **3w** ($CDCl_3$: DMSO-d_6, 1:1, 100 MHz)**:**



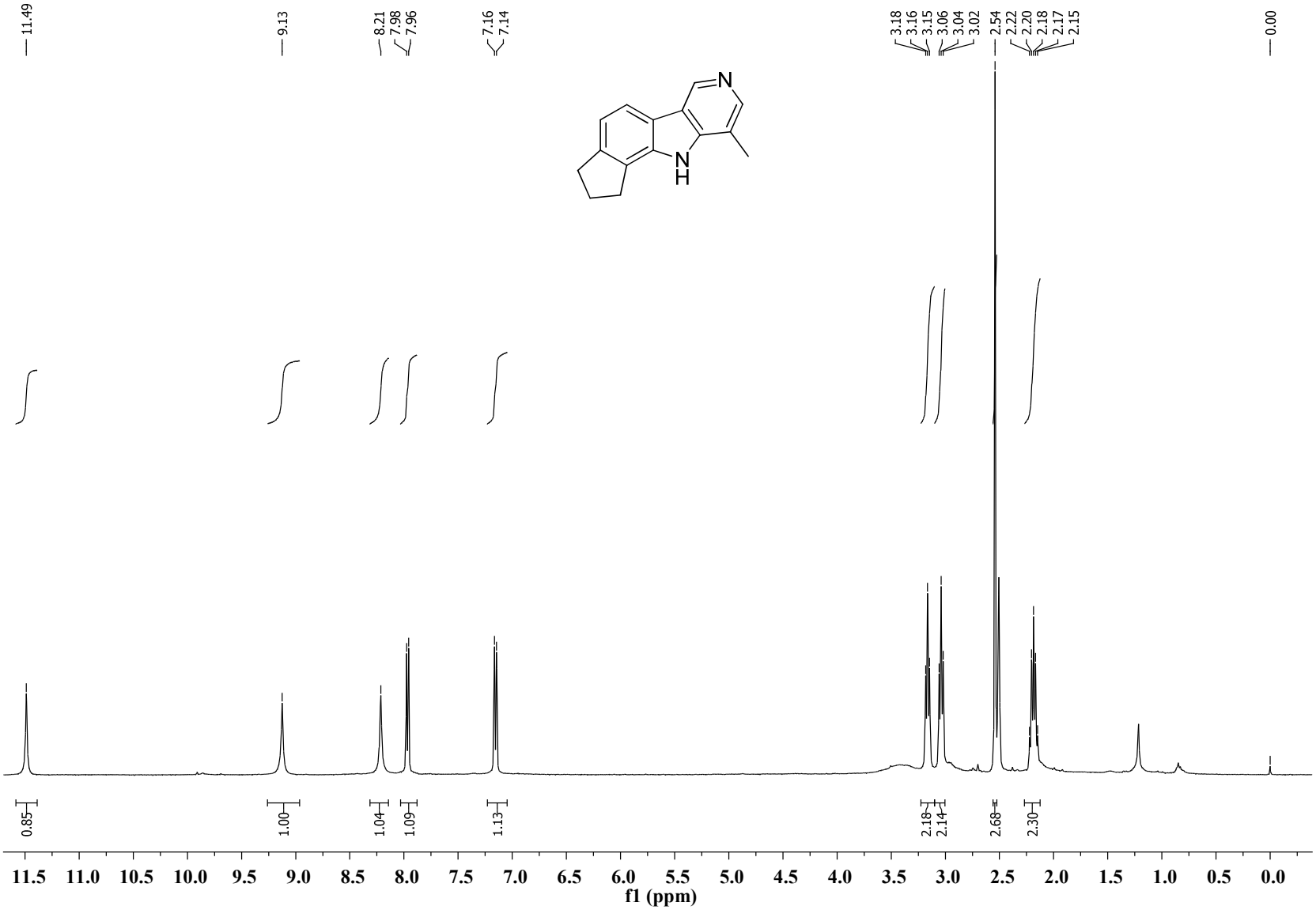
^{1}H NMR spectrum of **3x** (DMSO-d_6, 400 MHz)**:**



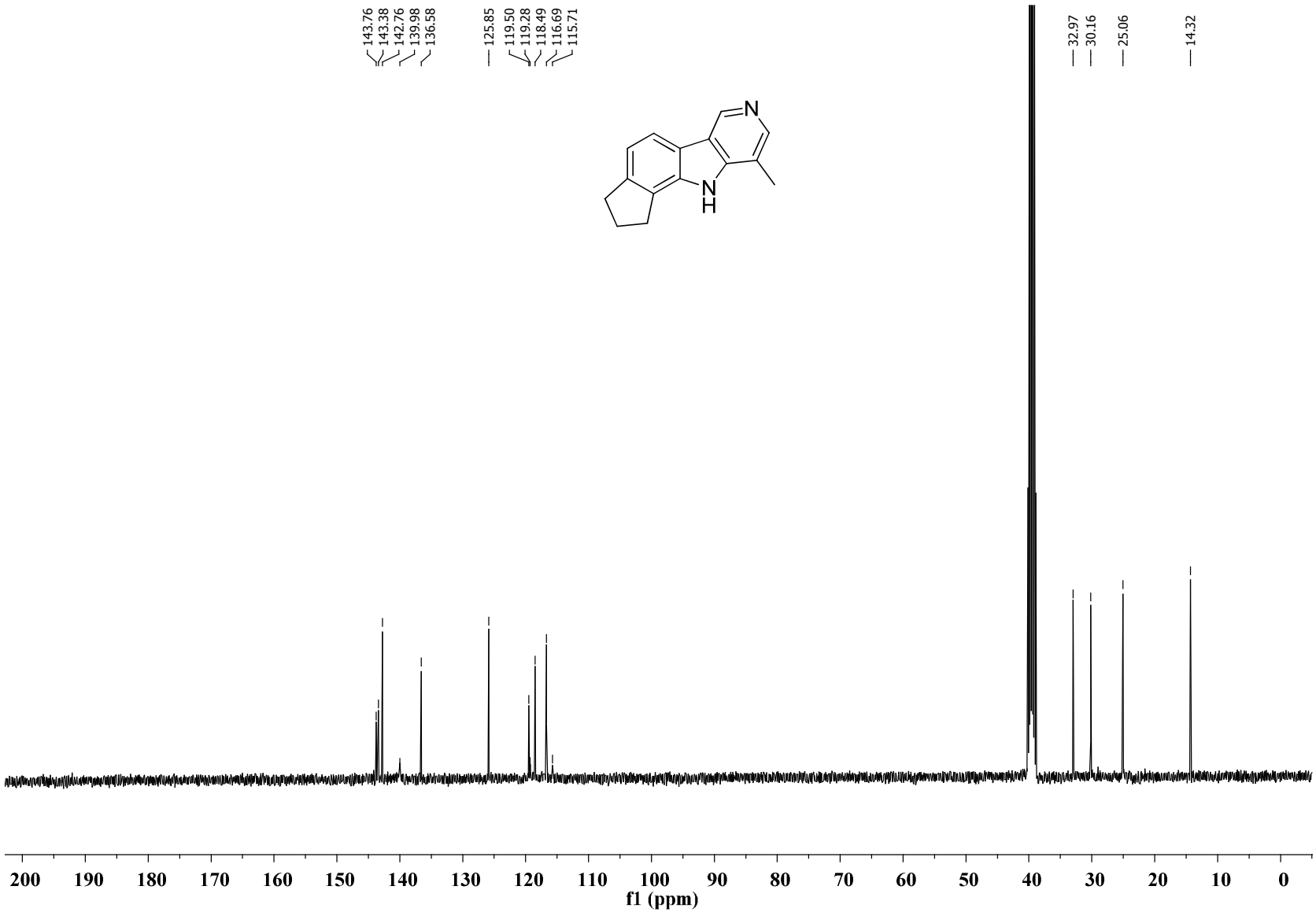
^{13}C{1H}NMR spectrum of **3x** (DMSO-d_6, 100 MHz)**:**



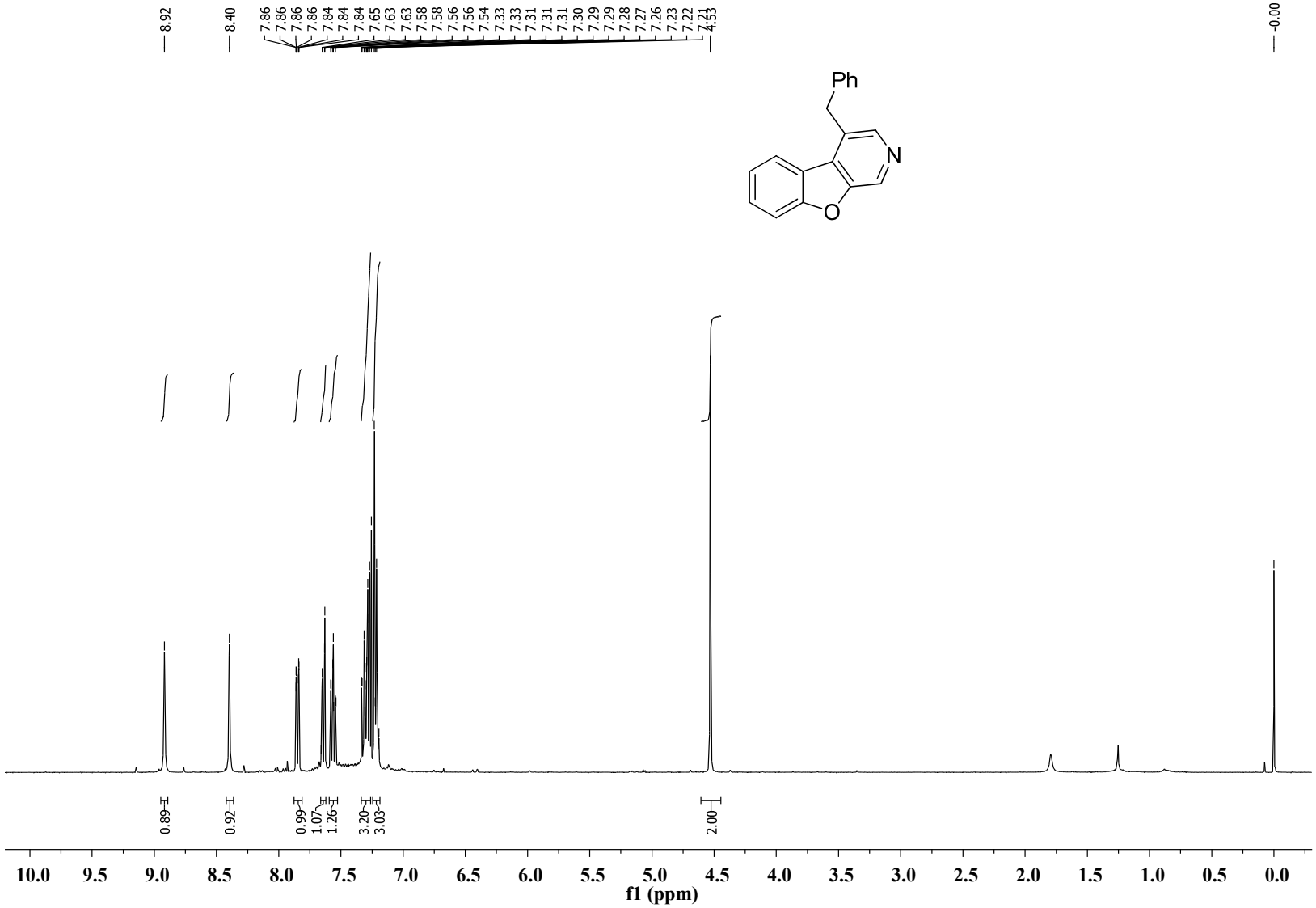
^{1}H NMR spectrum of **3y** (DMSO-d_6, 400 MHz)**:**



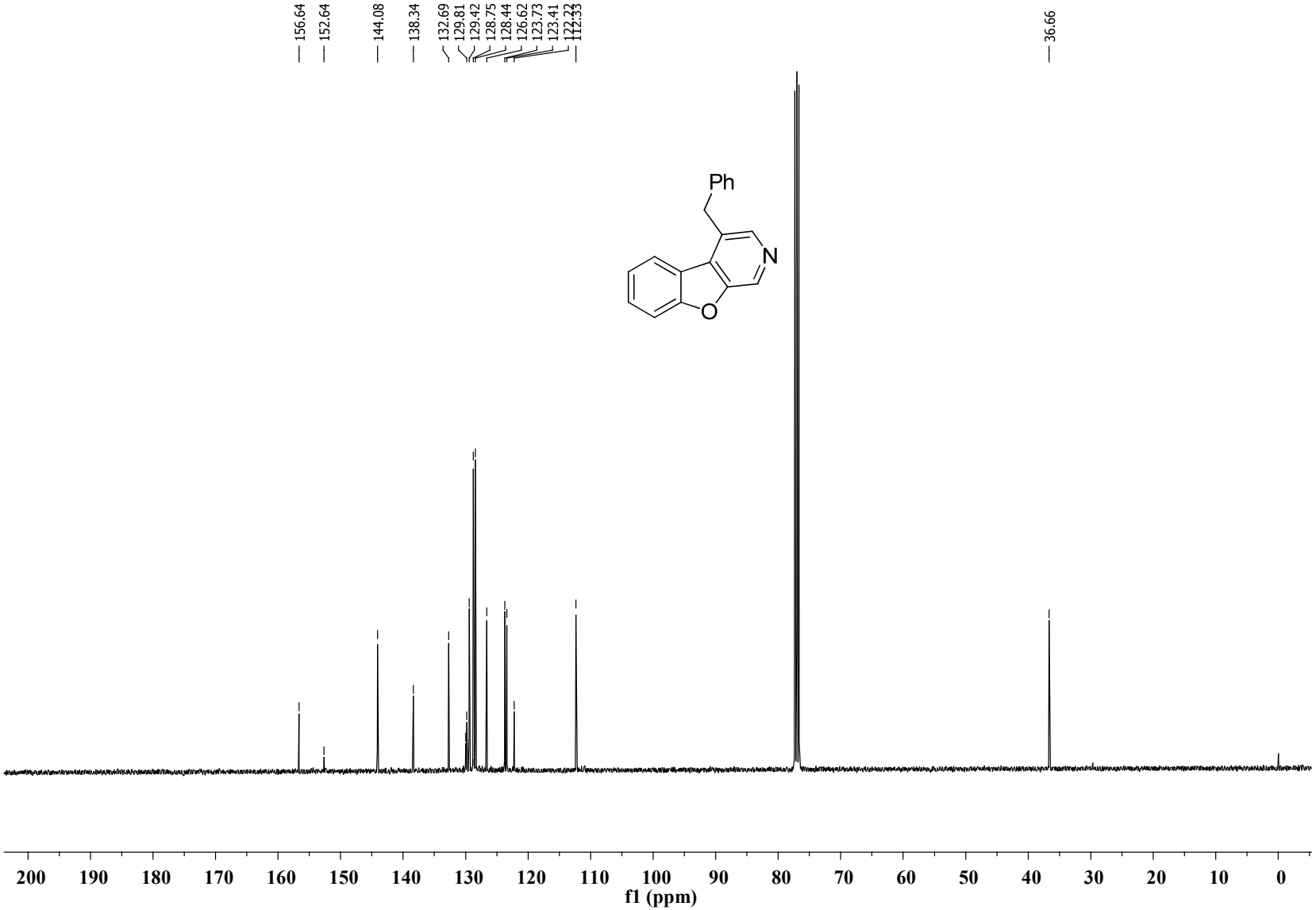
^{13}C{1H}NMR spectrum of **3y** (DMSO-d_6, 100 MHz)**:**



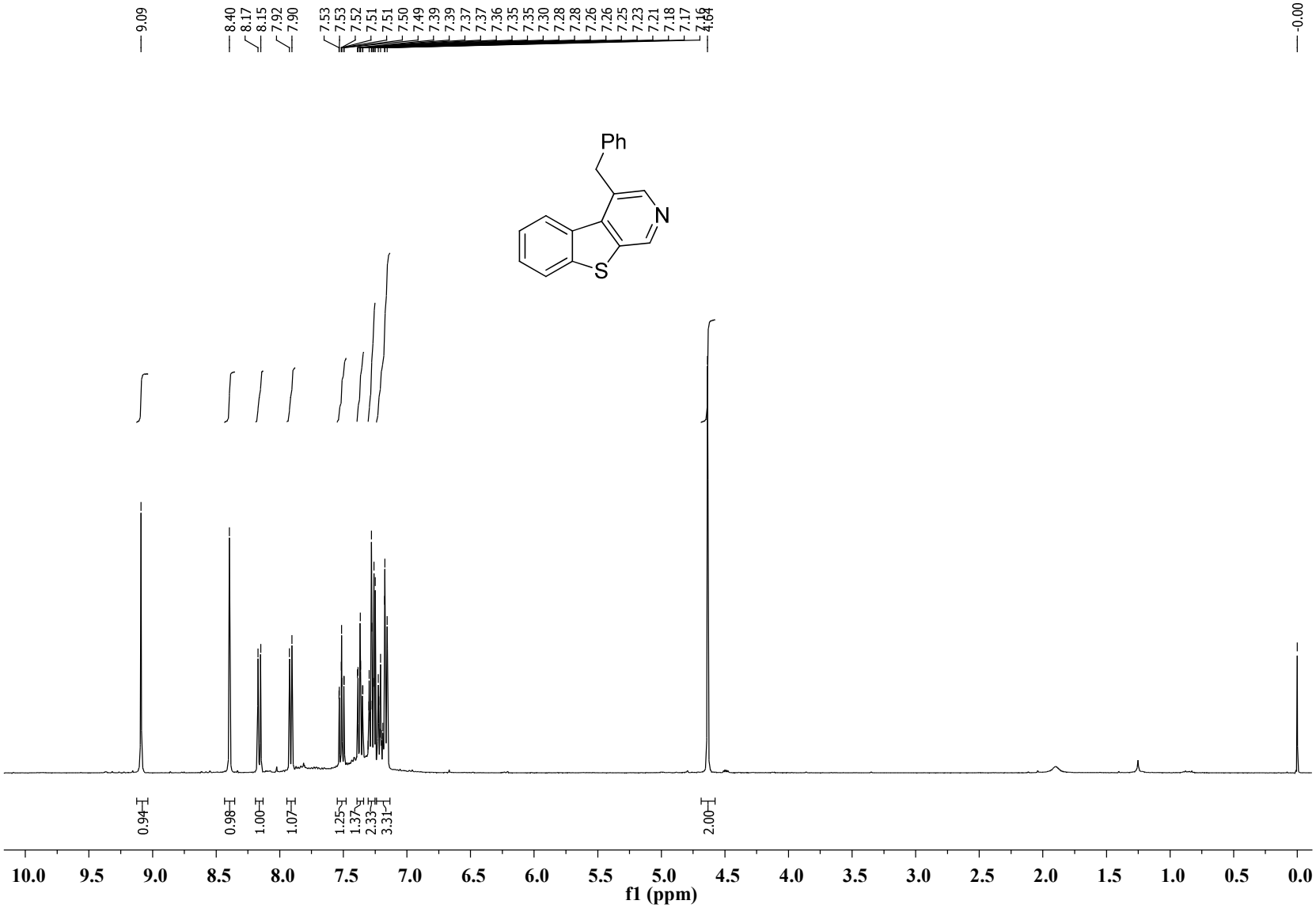
^{1}H NMR spectrum of **4a** ($CDCl_3$, 400 MHz)**:**



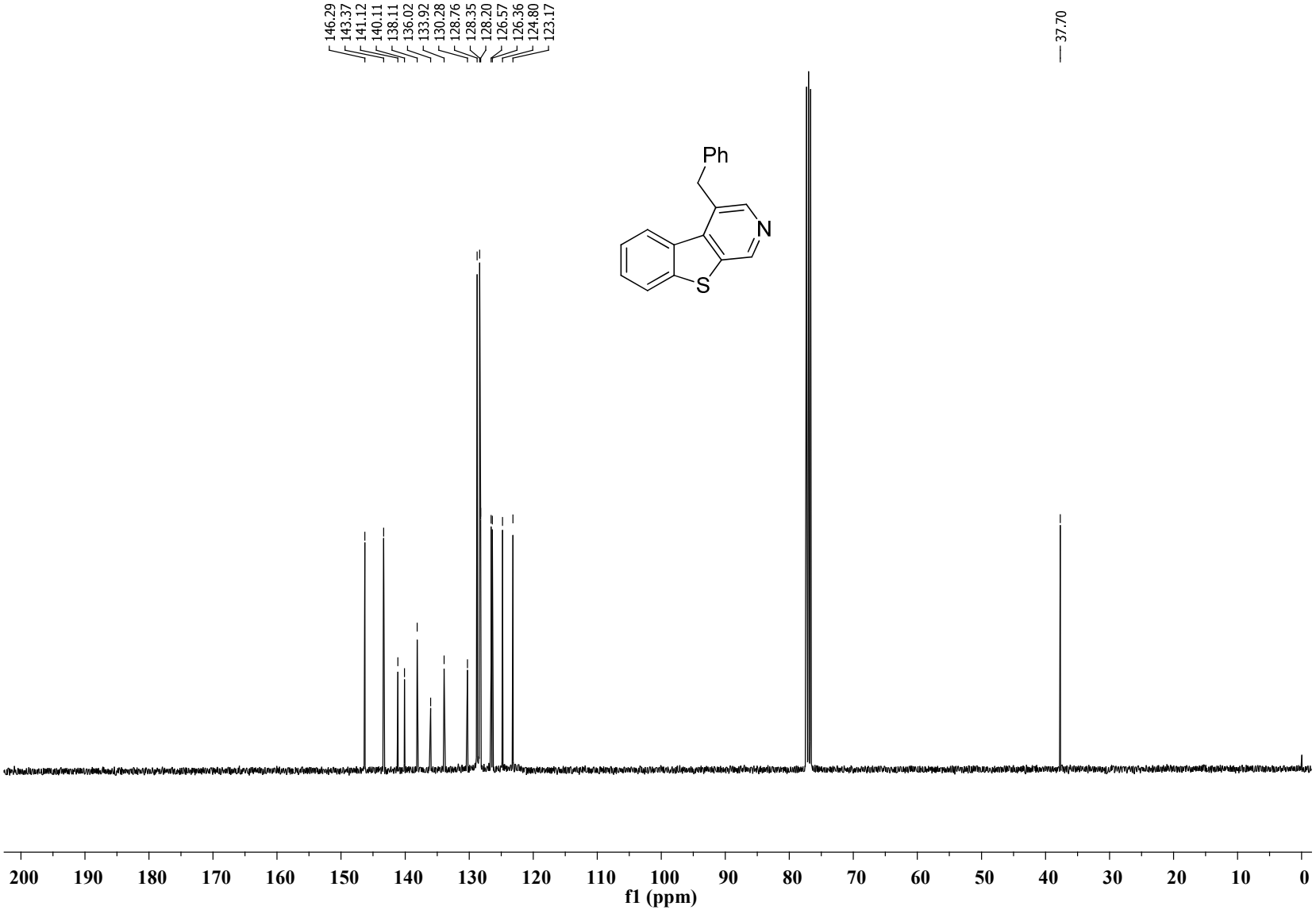
$^{13}C\{1H\}$NMR spectrum of **4a** ($CDCl_3$, 100 MHz)**:**



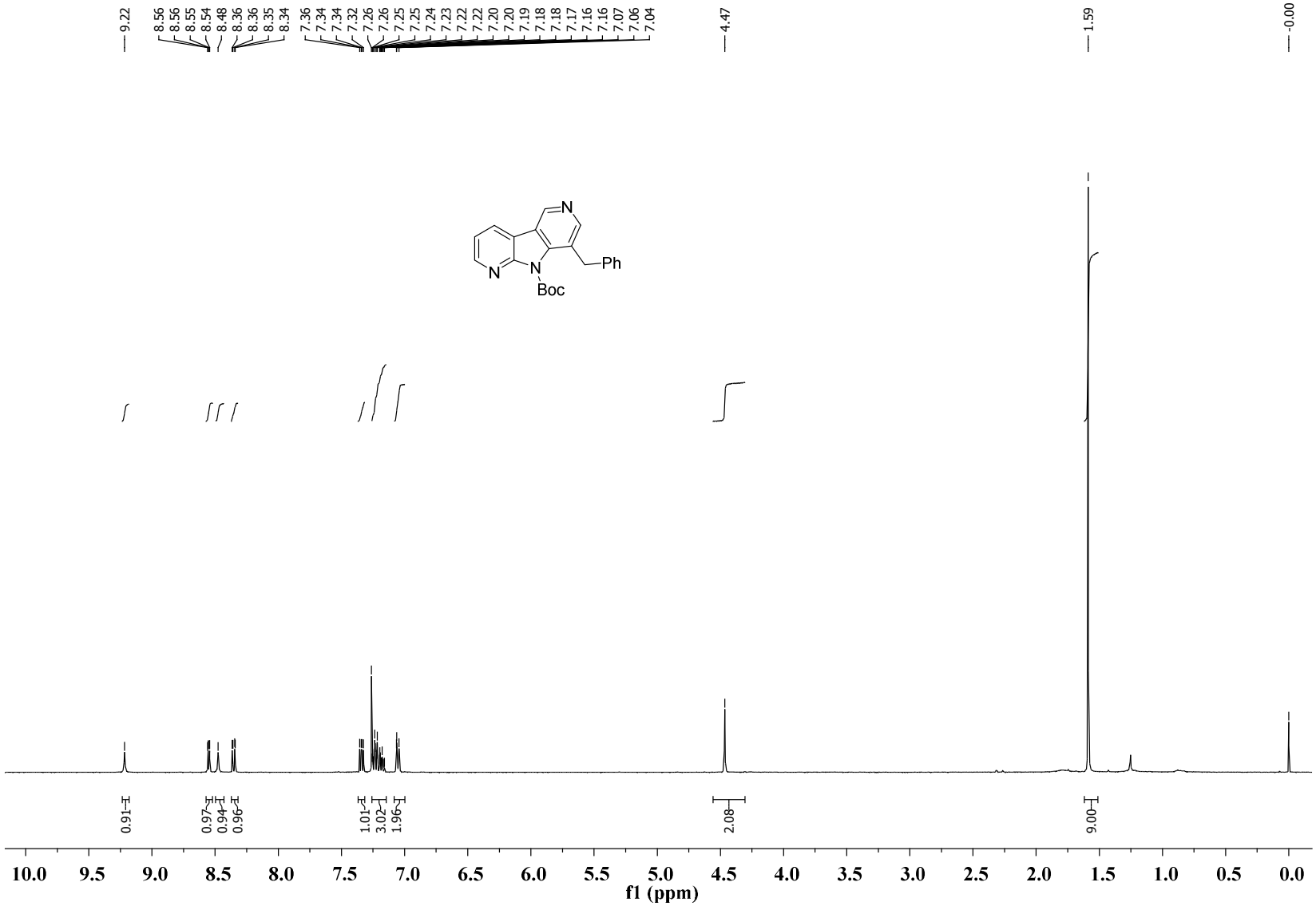
^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz)**:**



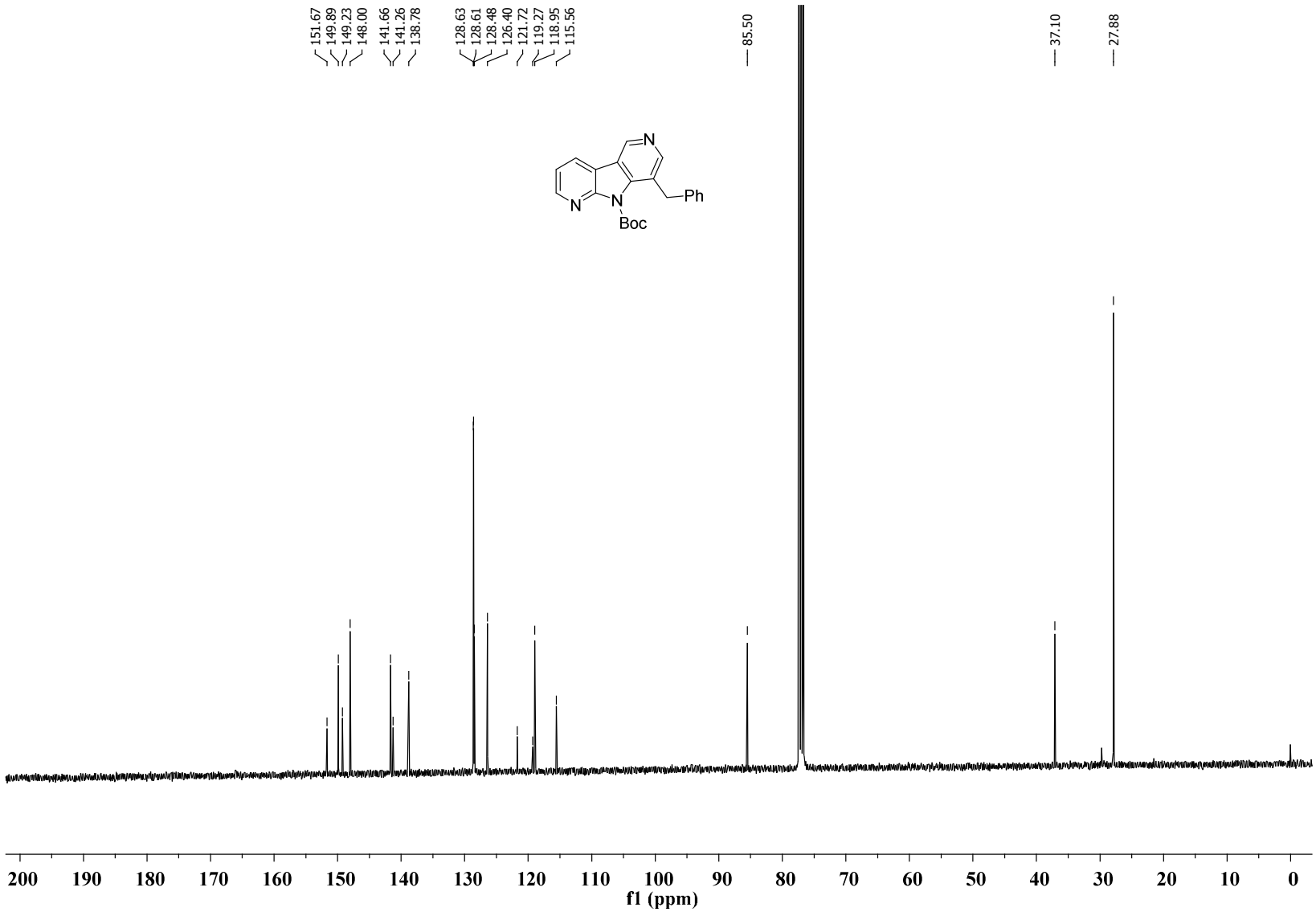
$^{13}C\{1H\}$NMR spectrum of **4b** ($CDCl_3$, 100 MHz)**:**



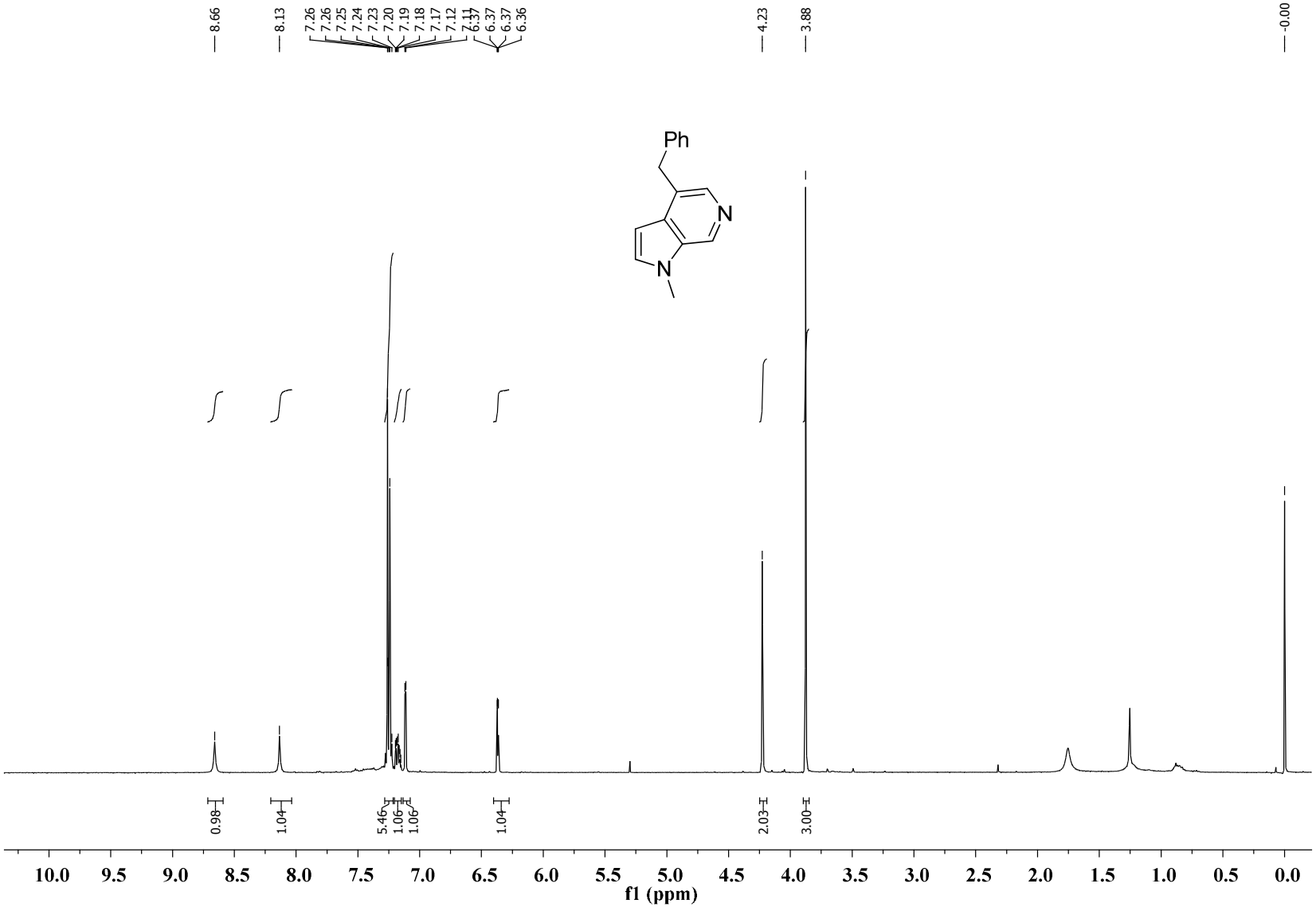
^{1}H NMR spectrum of **4c** ($CDCl_3$, 400 MHz)**:**



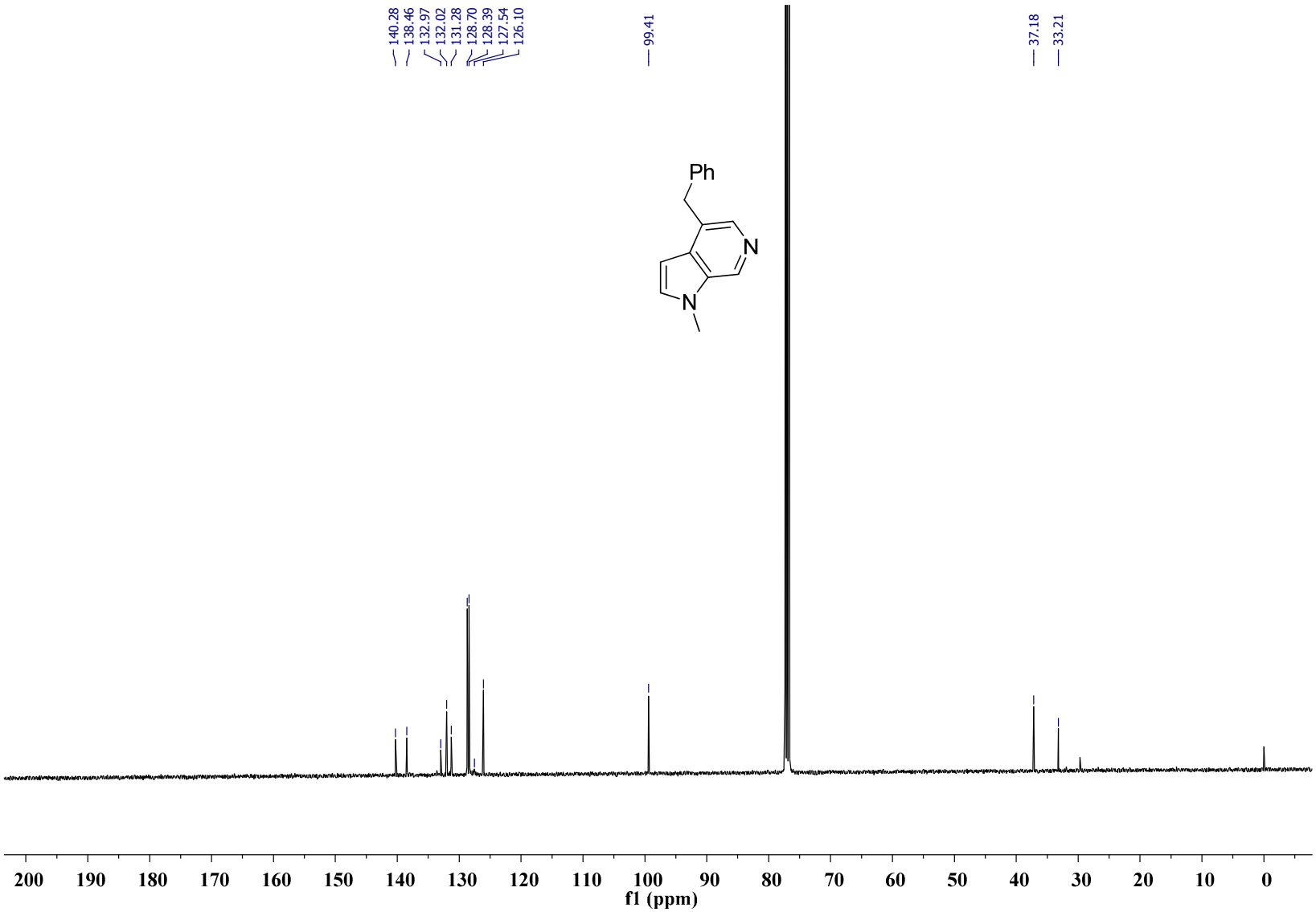
$^{13}C\{1H\}$NMR spectrum of **4c** ($CDCl_3$, 100 MHz)**:**



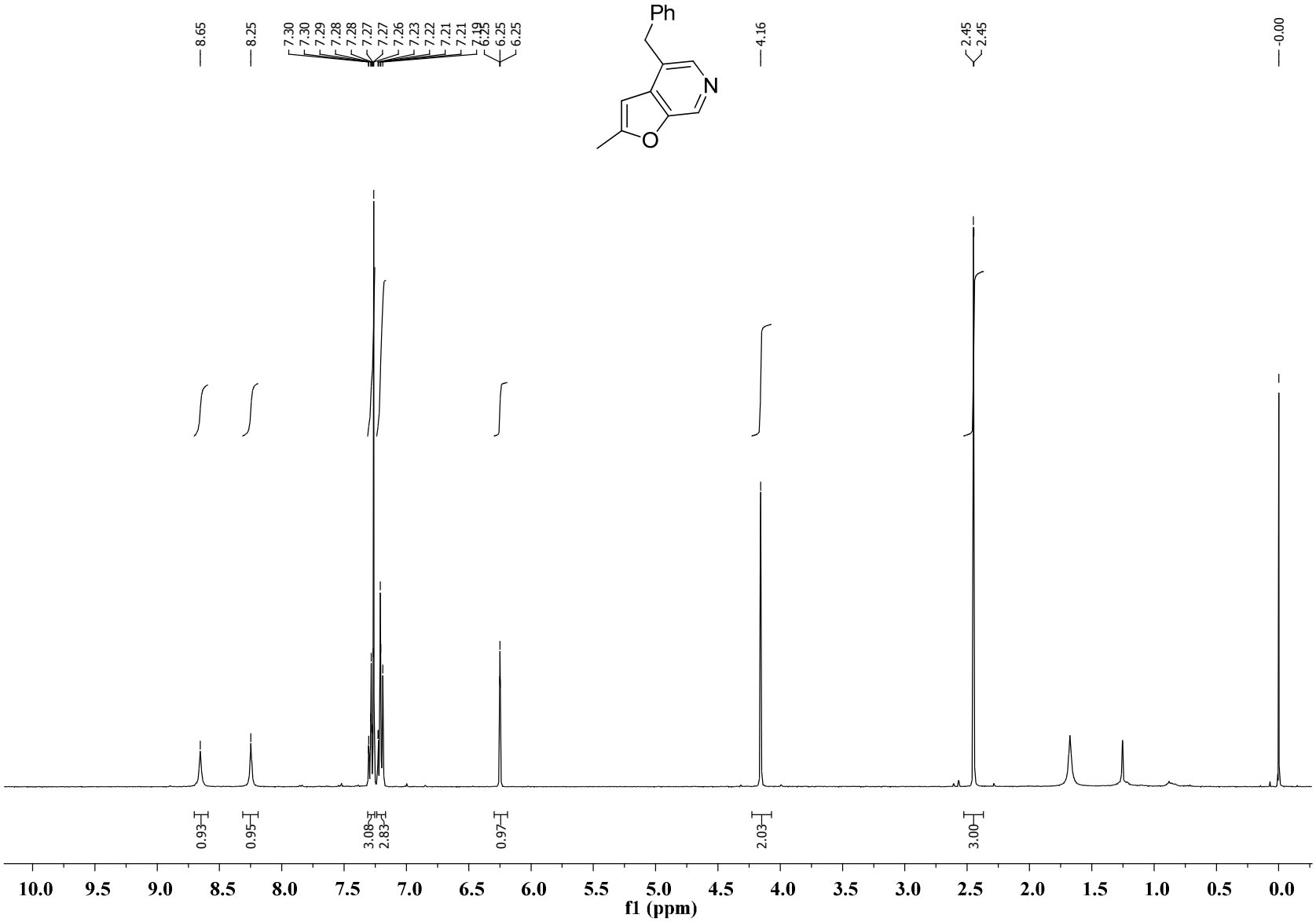
^{1}H NMR spectrum of **4d** ($CDCl_3$, 400 MHz)**:**



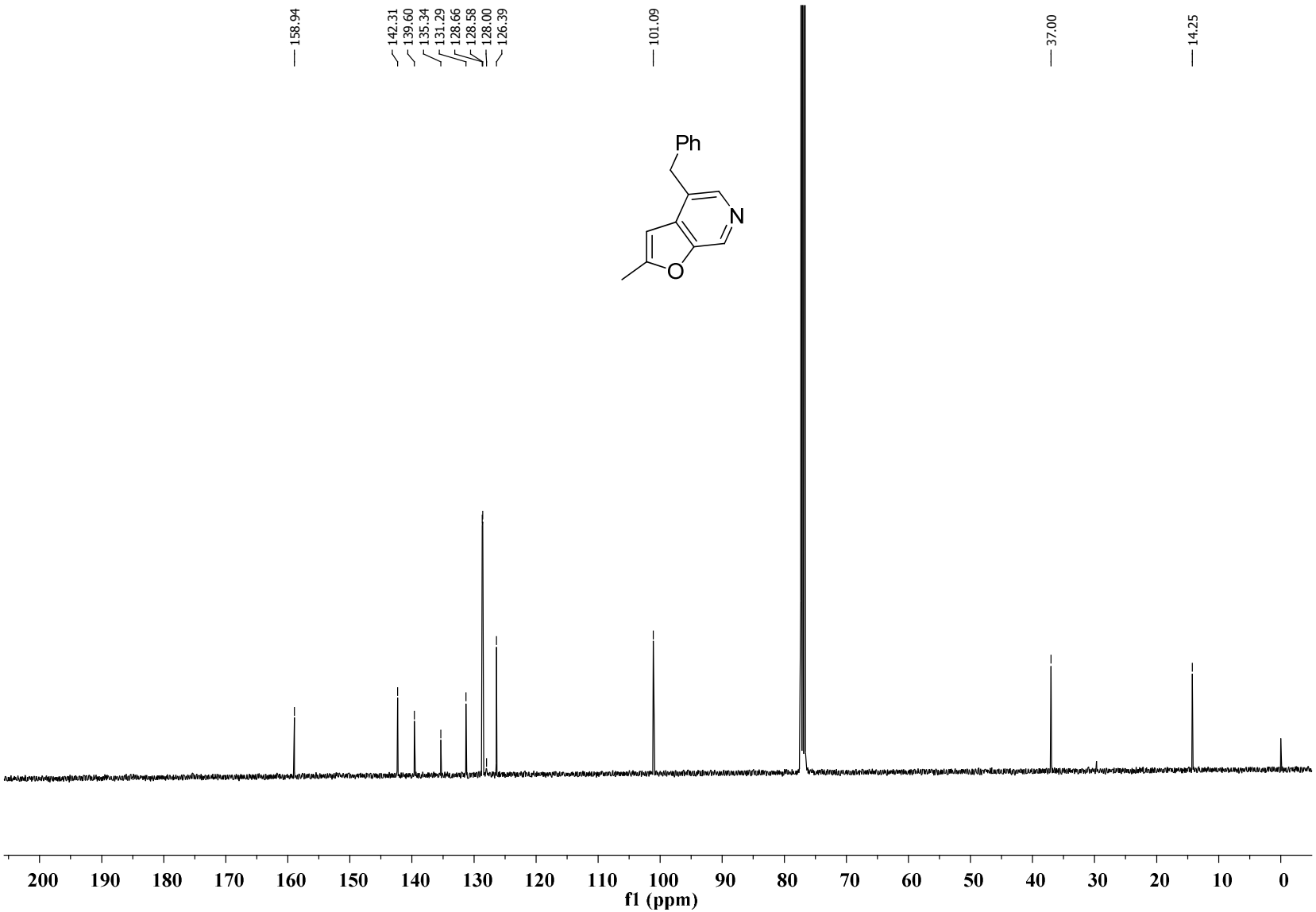
$^{13}C\{1H\}$NMR spectrum of **4d** ($CDCl_3$, 100 MHz)**:**



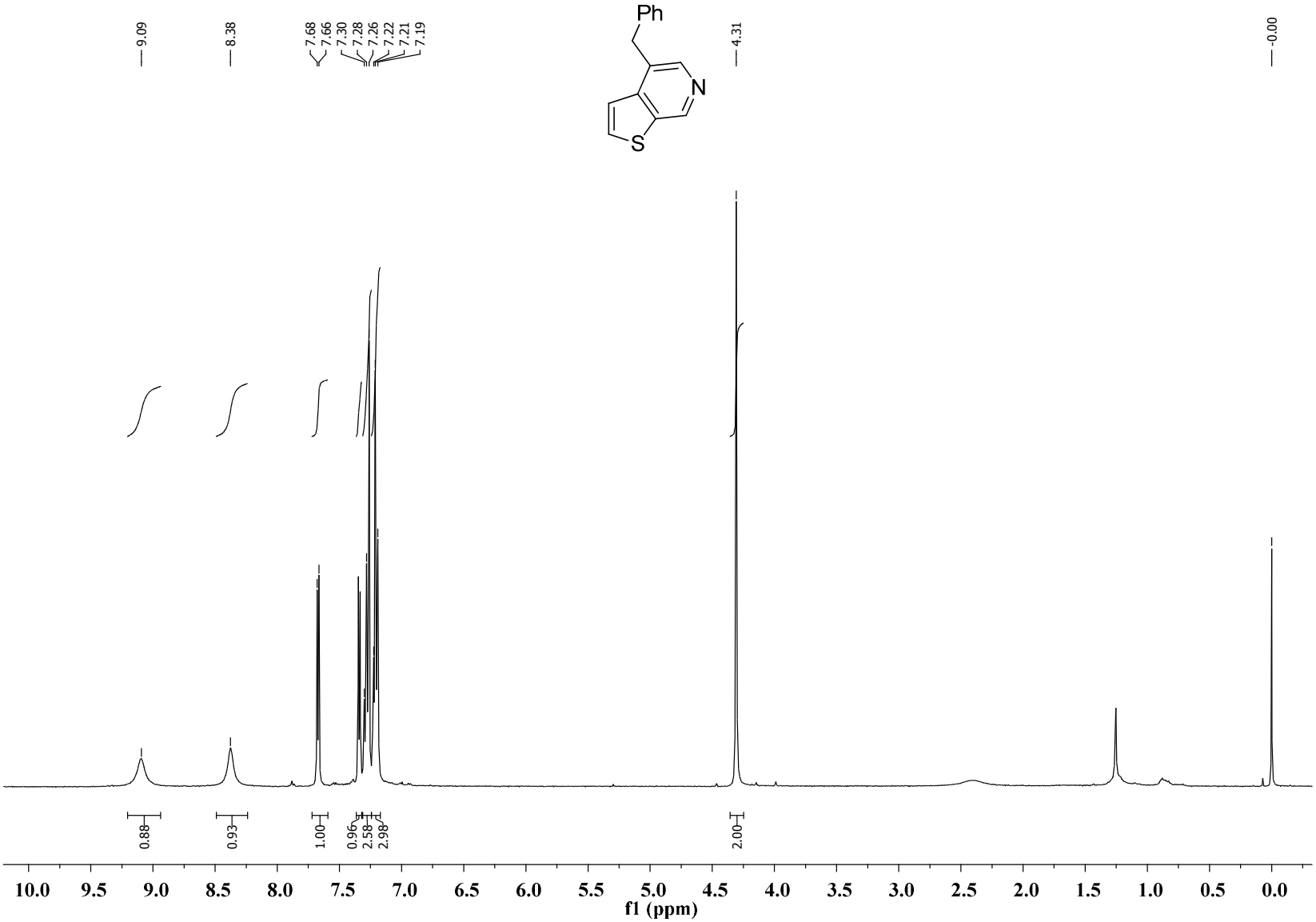
^{1}H NMR spectrum of **4e** ($CDCl_3$, 400 MHz)**:**



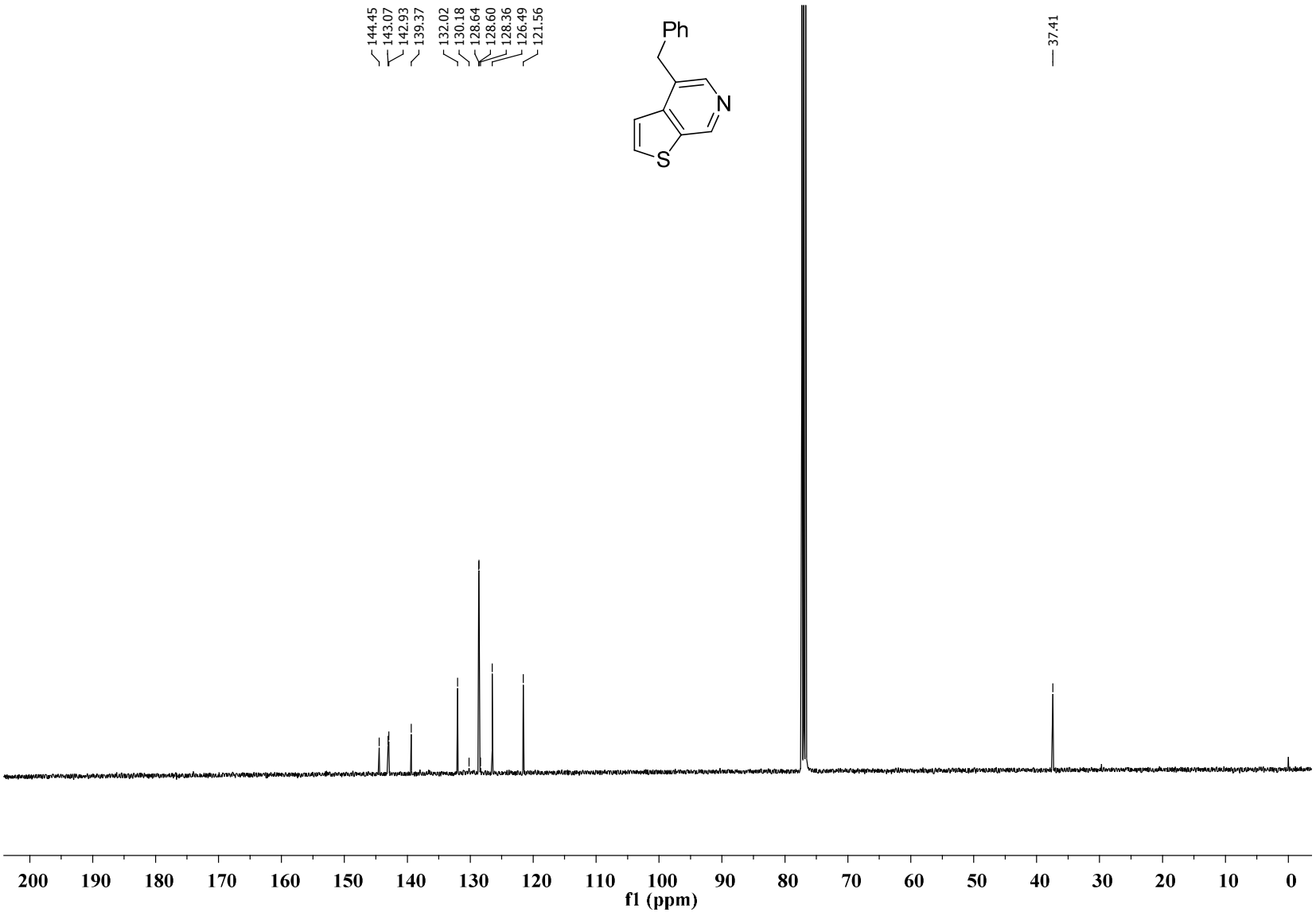
$^{13}C\{1H\}$NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)**:**



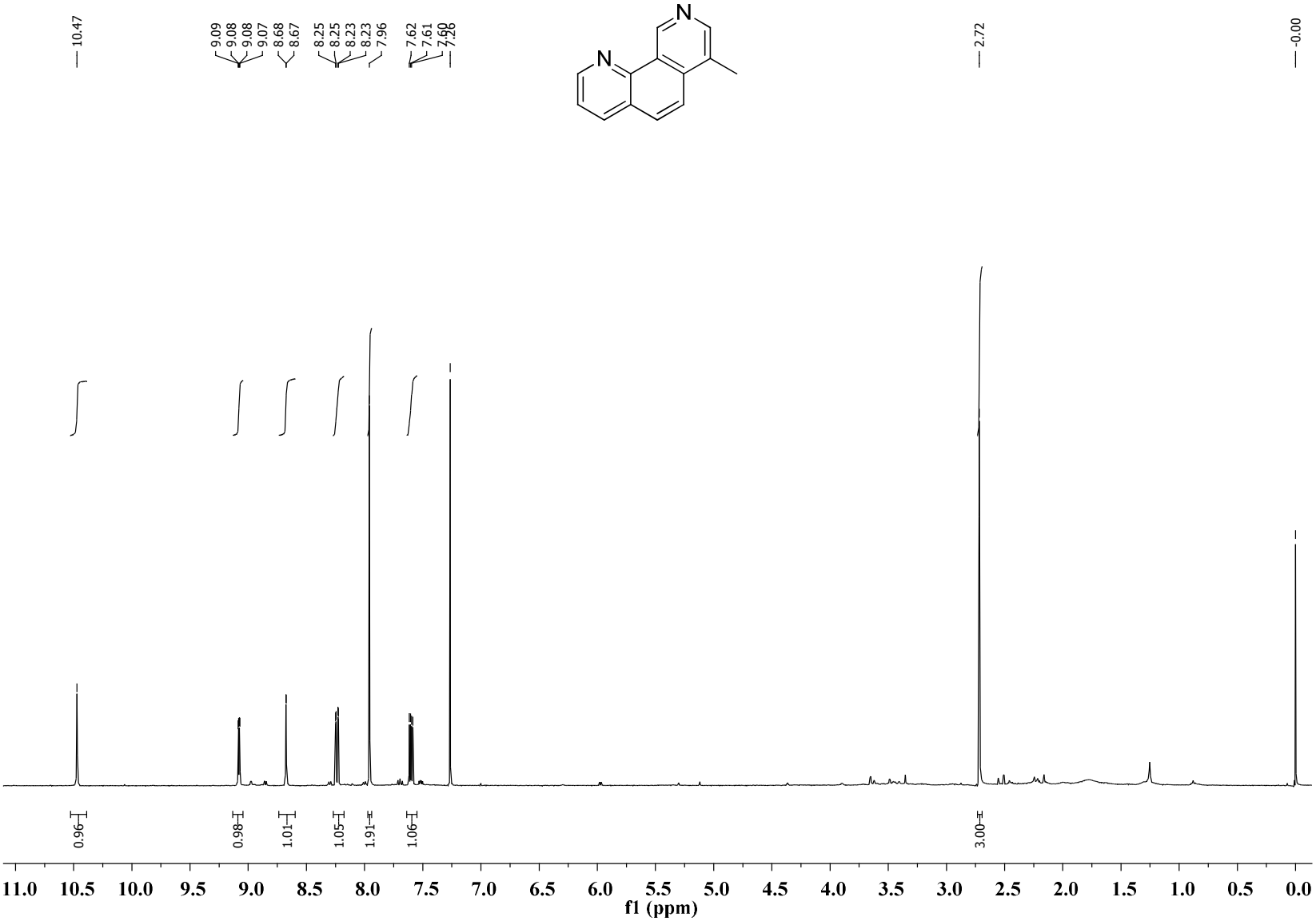
^{1}H NMR spectrum of **4f** ($CDCl_3$, 400 MHz)**:**



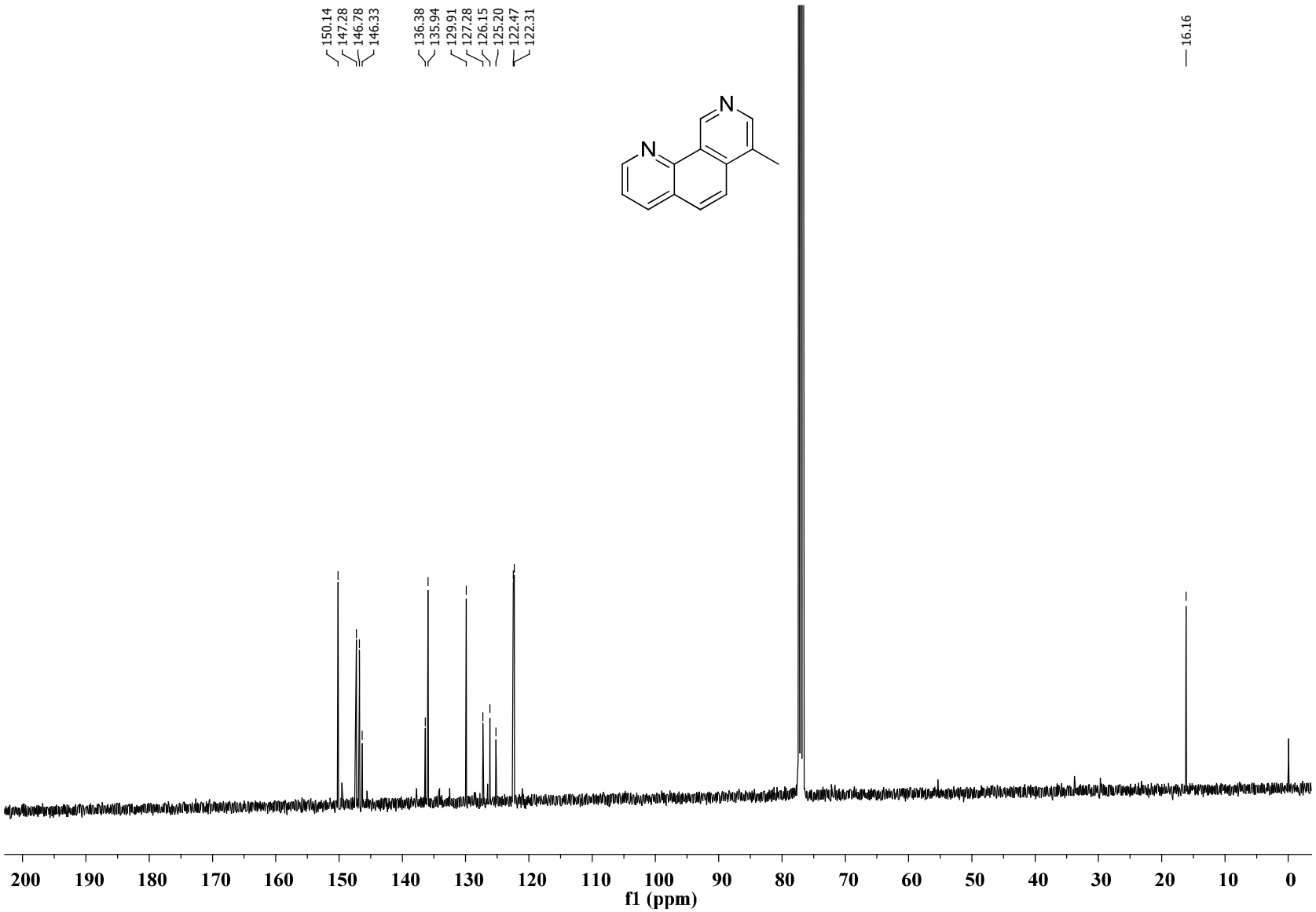
$^{13}C\{1H\}$NMR spectrum of **4f** ($CDCl_3$, 100 MHz)**:**



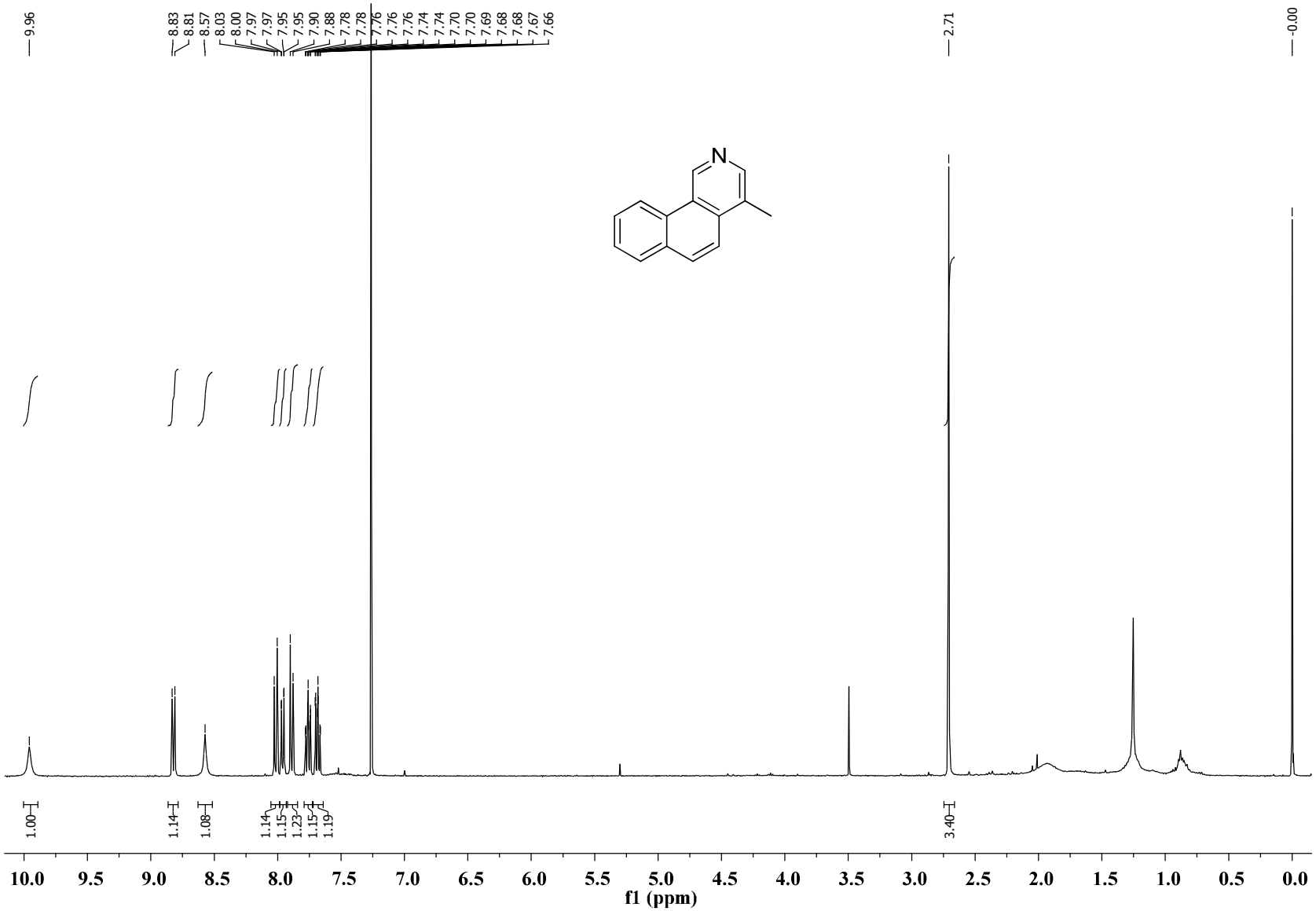
^{1}H NMR spectrum of **4g** ($CDCl_3$, 400 MHz)**:**



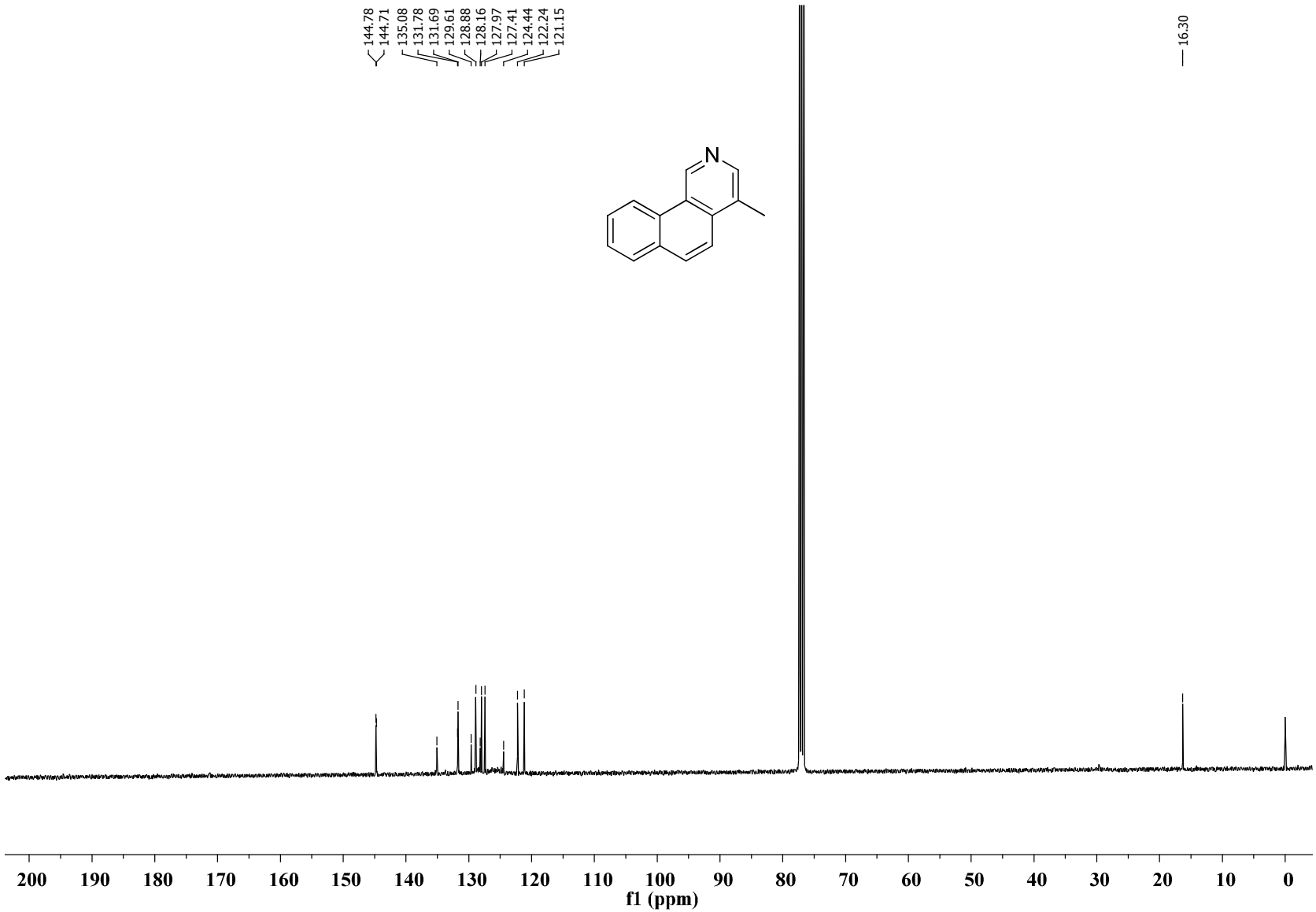
$^{13}C\{1H\}$NMR spectrum of **4g** ($CDCl_3$, 100 MHz)**:**



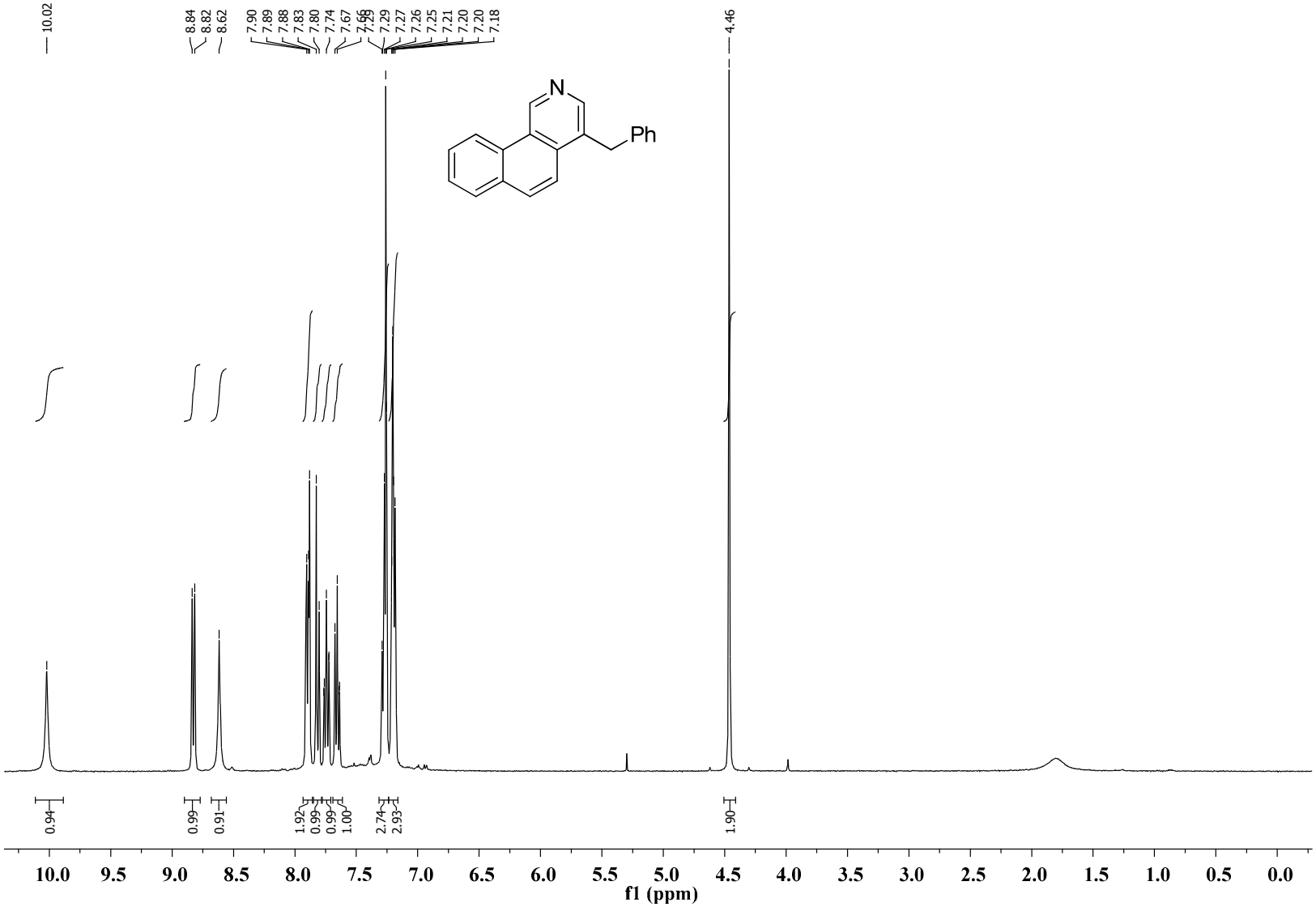
^{1}H NMR spectrum of **4h** ($CDCl_3$, 400 MHz)**:**



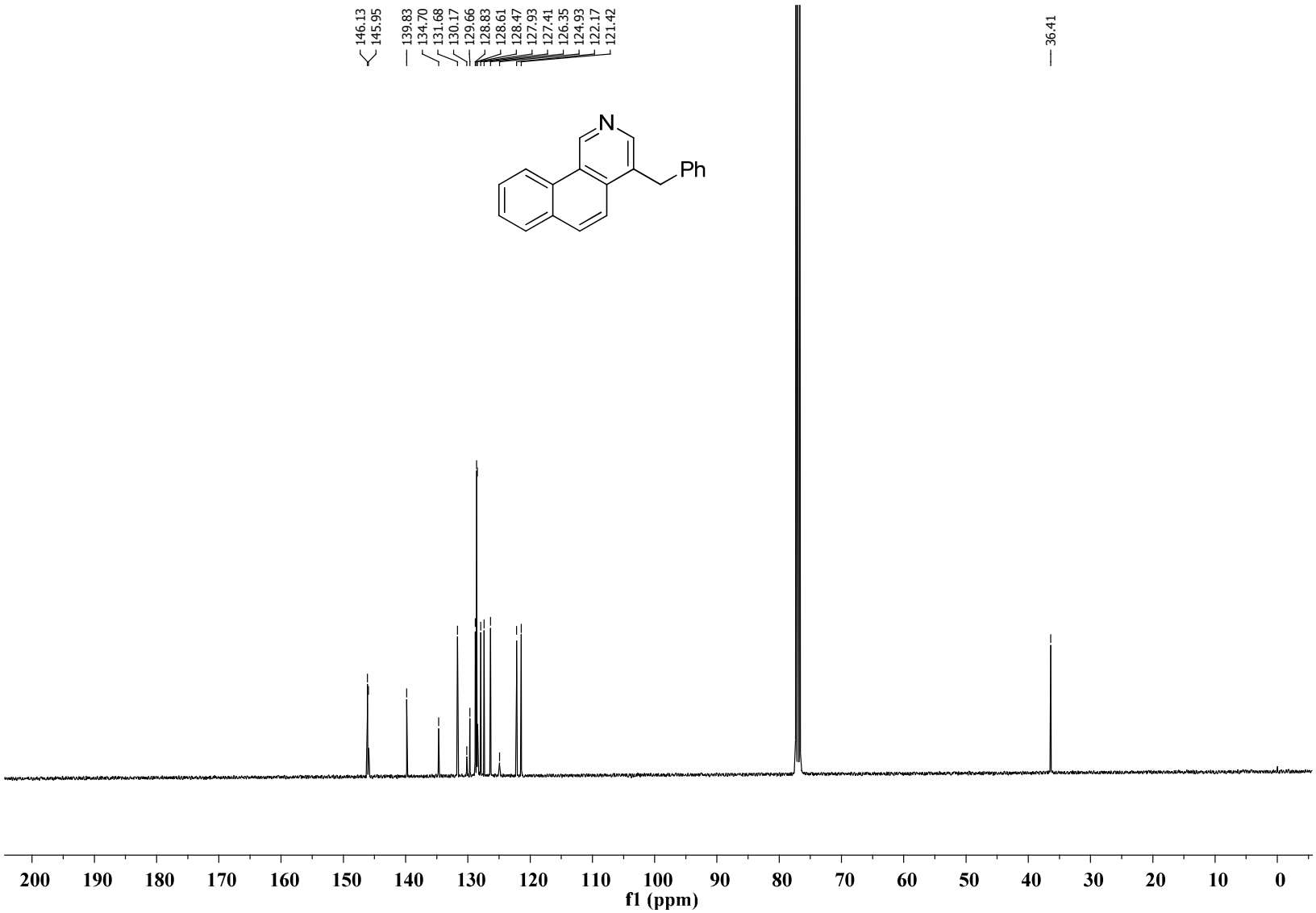
$^{13}C\{1H\}$NMR spectrum of **4h** ($CDCl_3$, 100 MHz)**:**



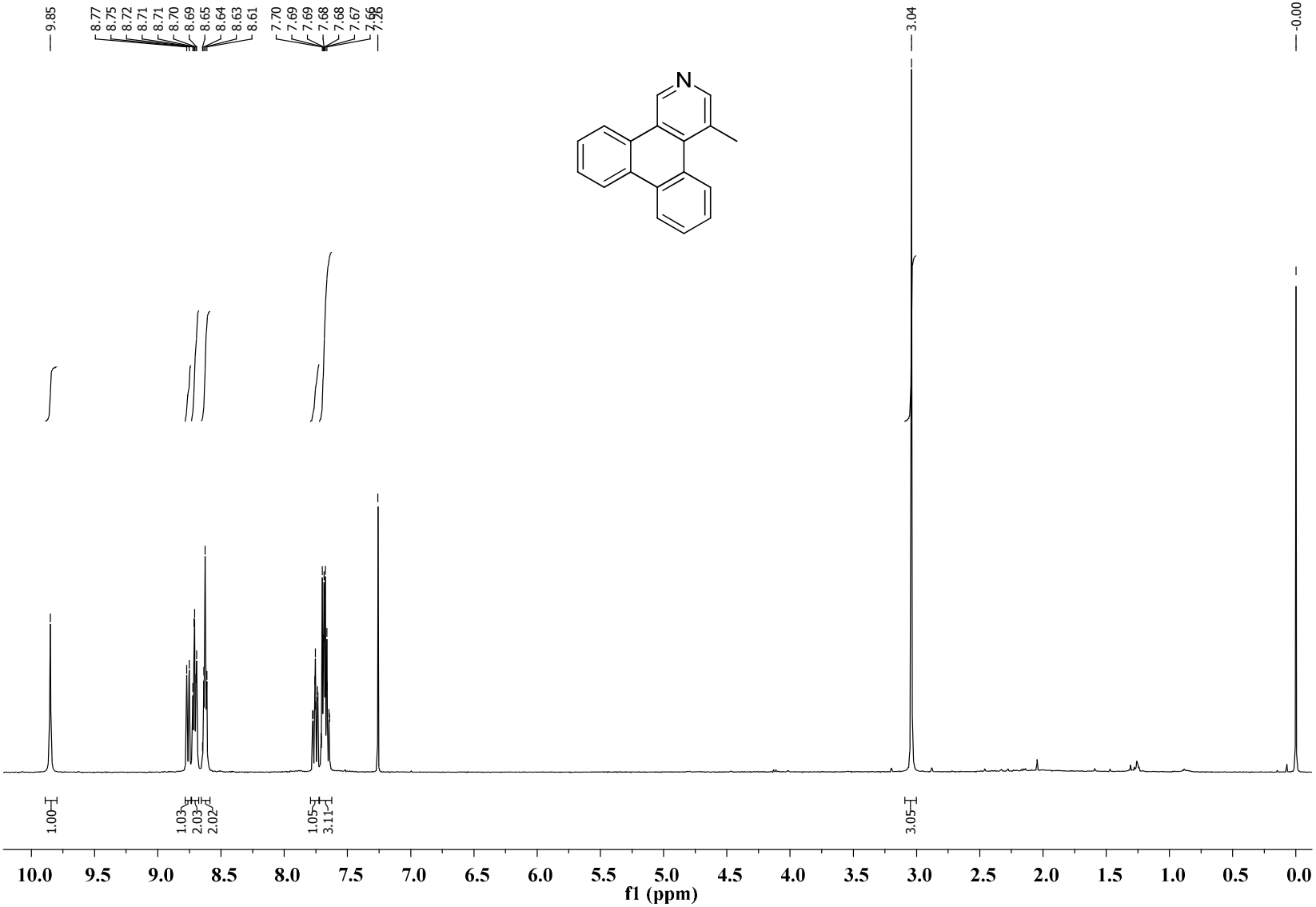
^{1}H NMR spectrum of **4i** ($CDCl_3$, 400 MHz)**:**



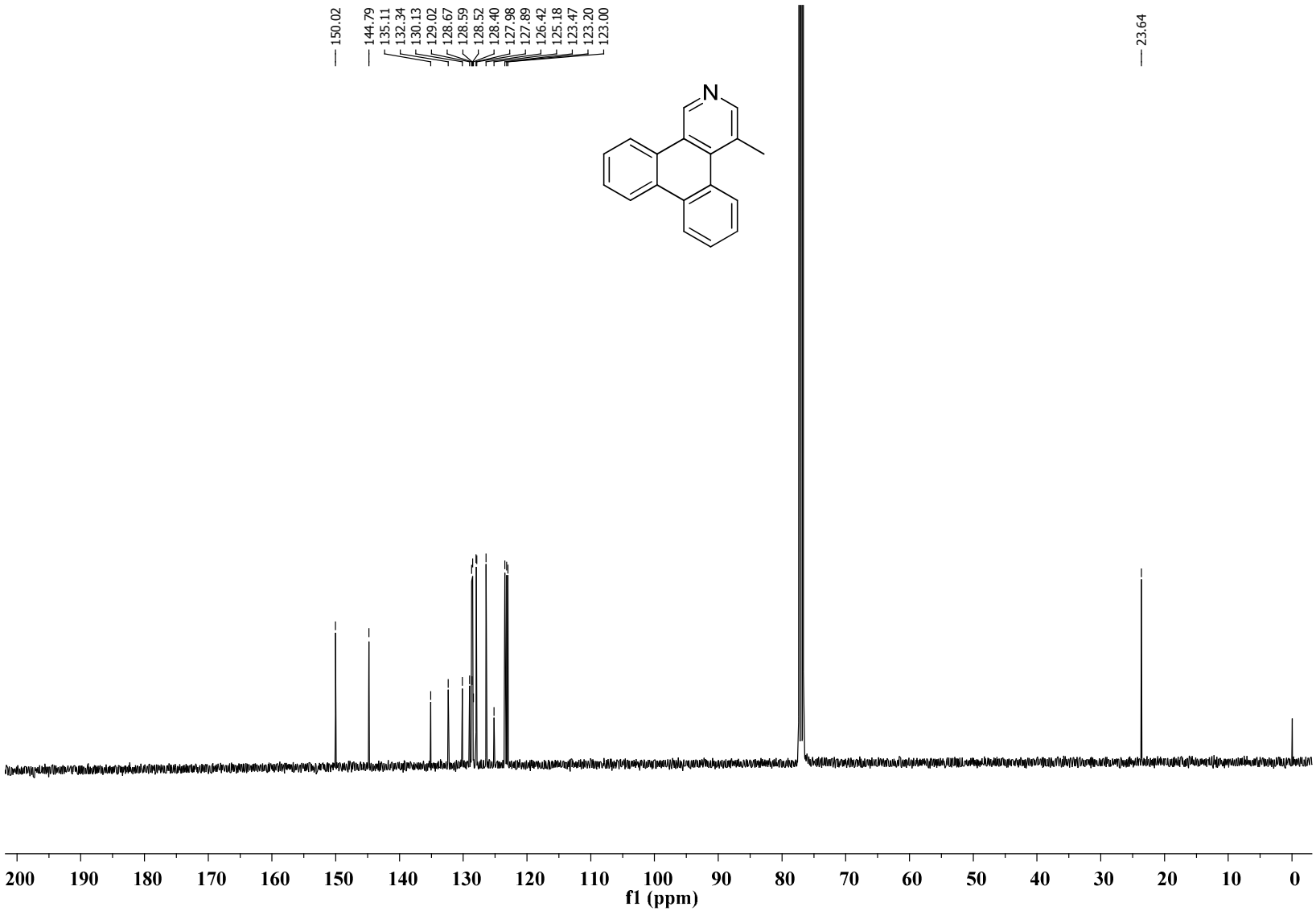
$^{13}C\{1H\}$NMR spectrum of **4i** ($CDCl_3$, 100 MHz)**:**



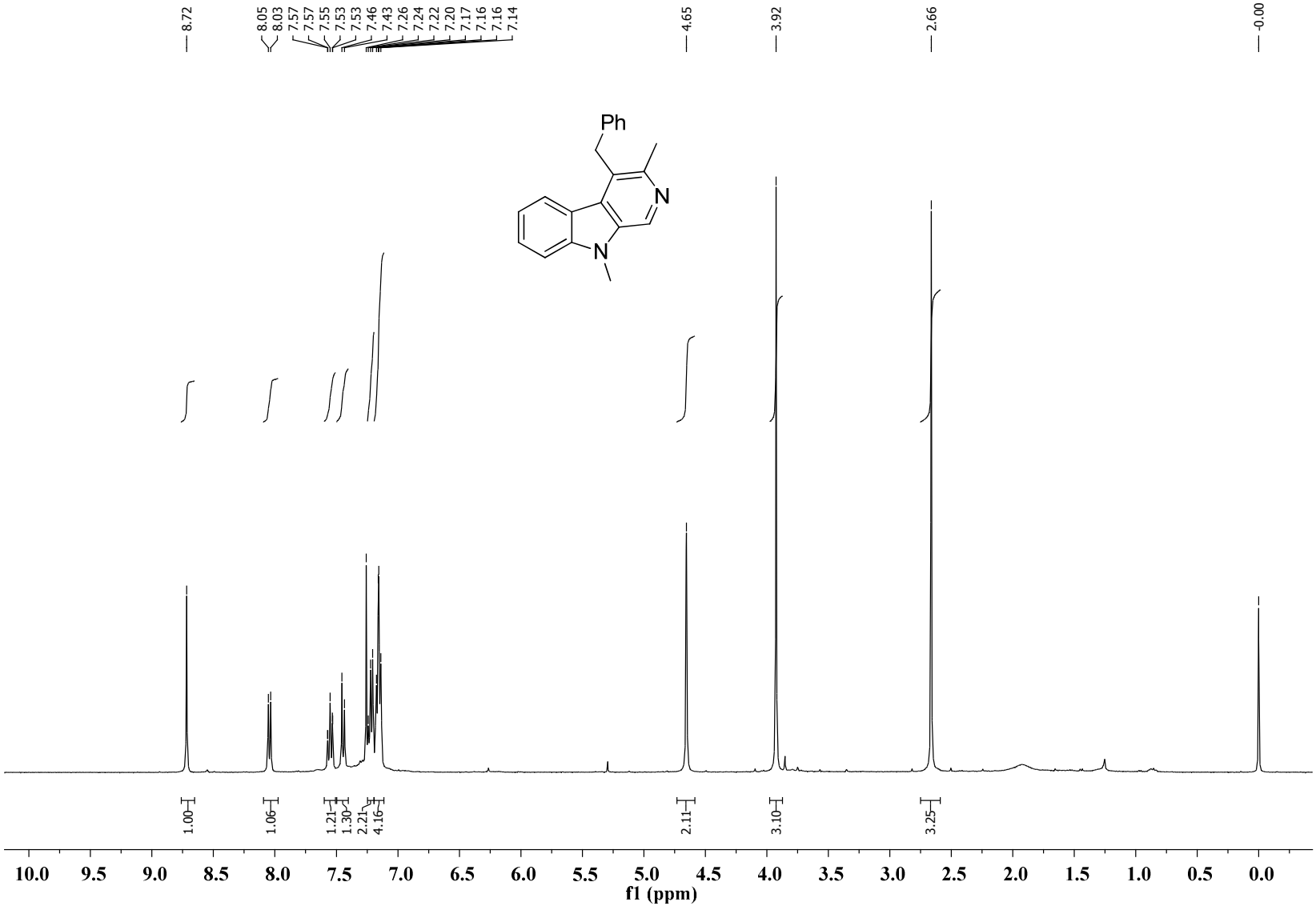
^{1}H NMR spectrum of **4j** ($CDCl_3$, 400 MHz)**:**



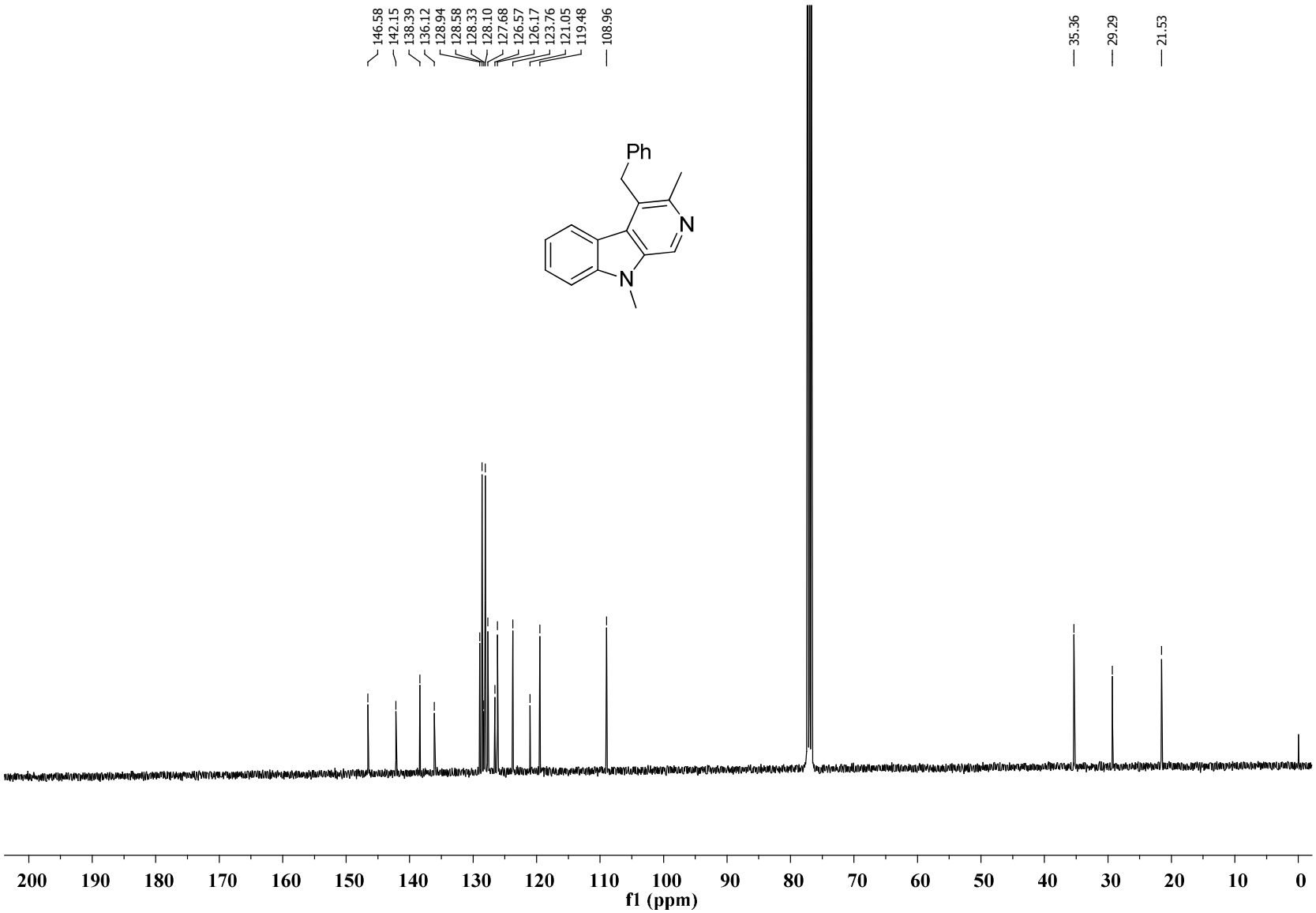
$^{13}C\{1H\}$NMR spectrum of **4j** ($CDCl_3$, 100 MHz)**:**



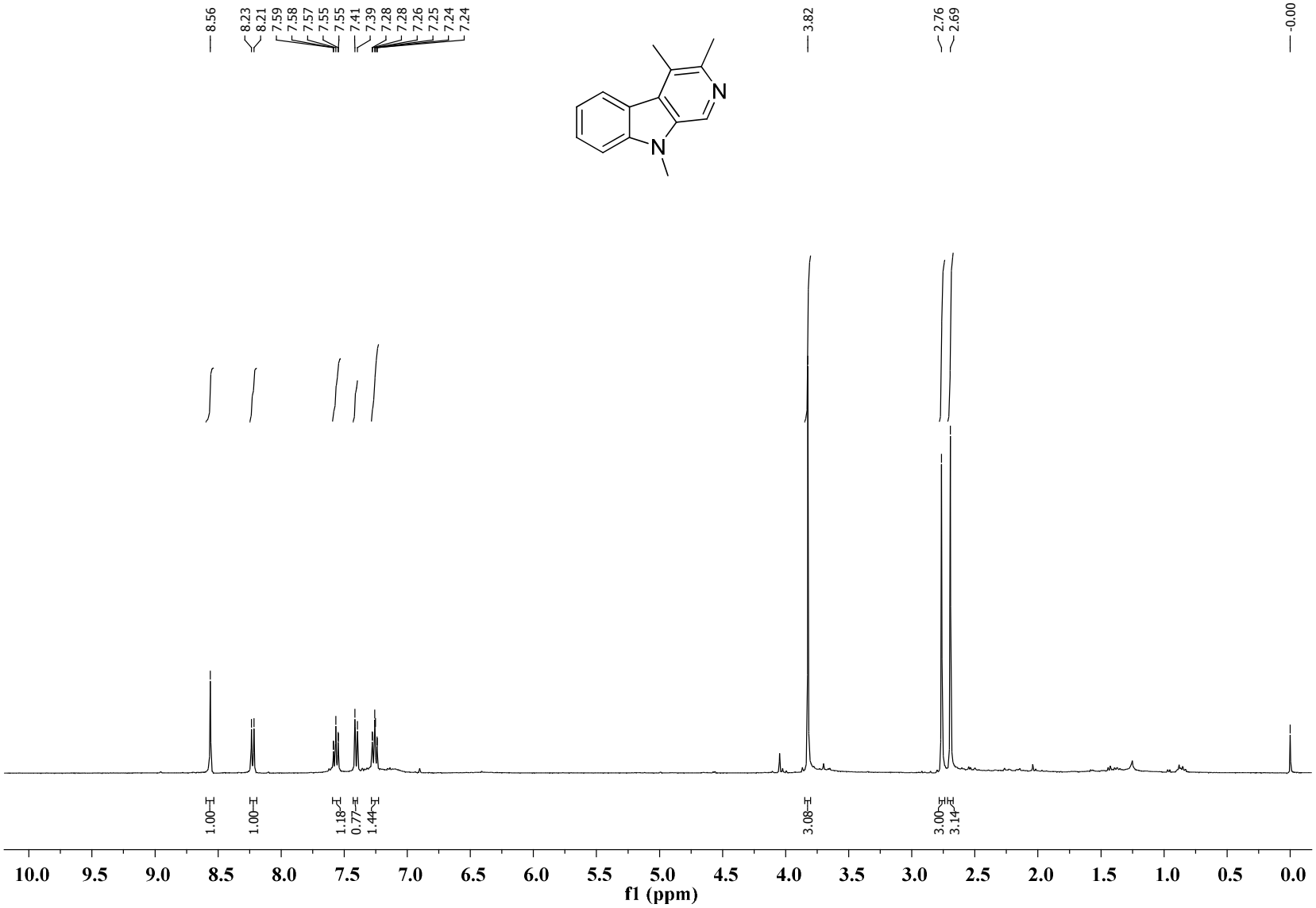
^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz)**:**



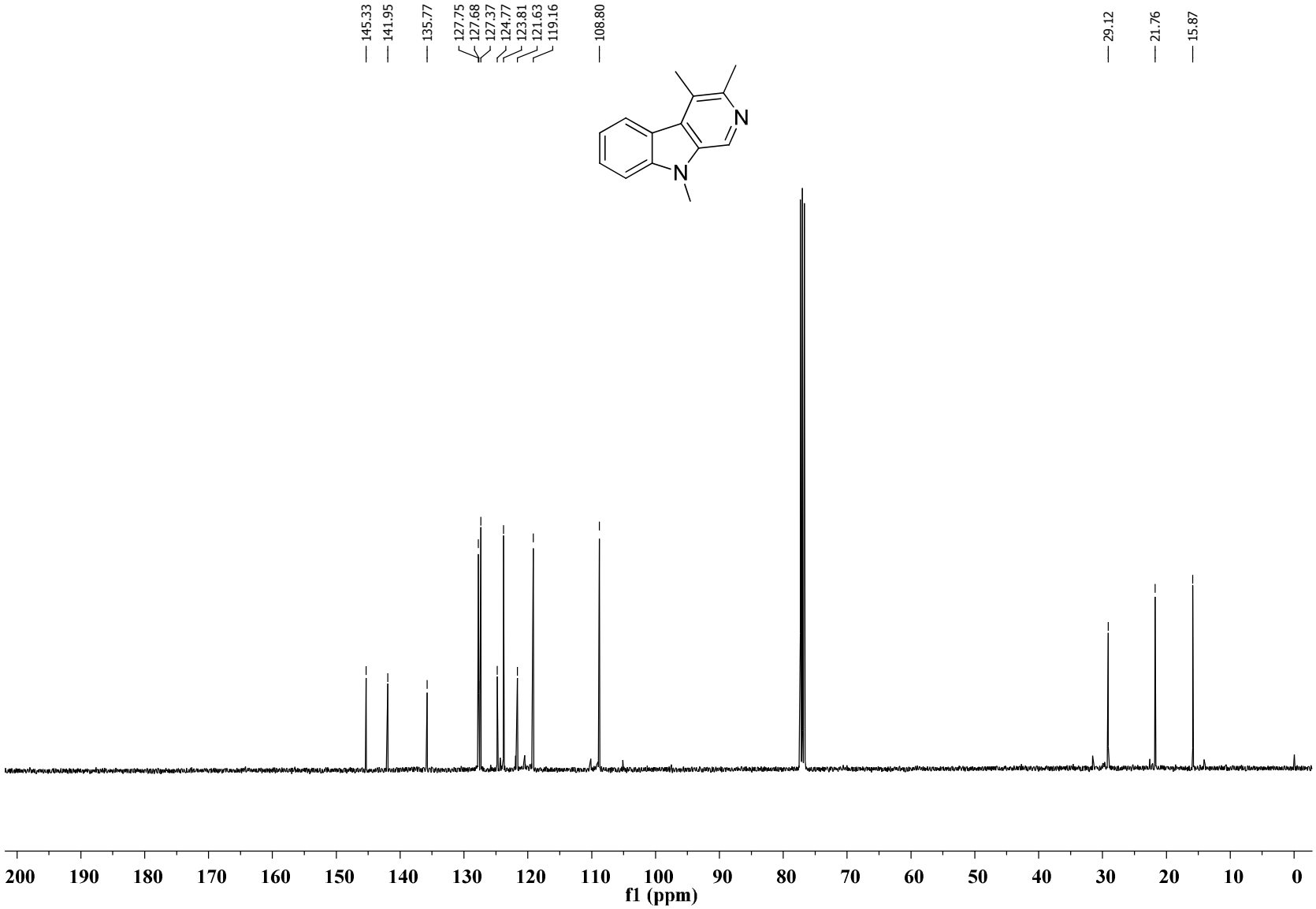
$^{13}C\{1H\}$NMR spectrum of **5a** ($CDCl_3$, 100 MHz)**:**



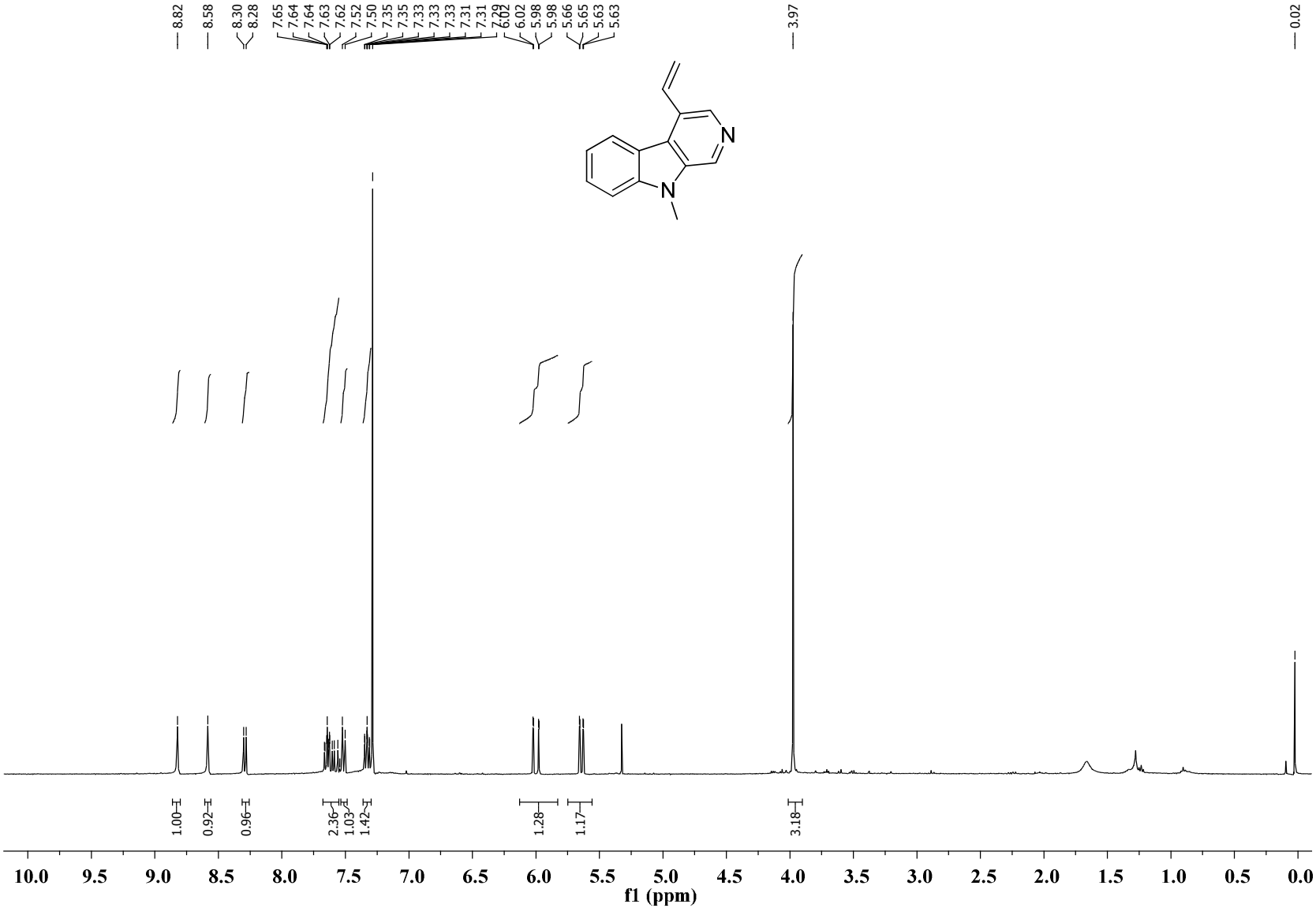
^{1}H NMR spectrum of **5b** ($CDCl_3$, 400 MHz)**:**



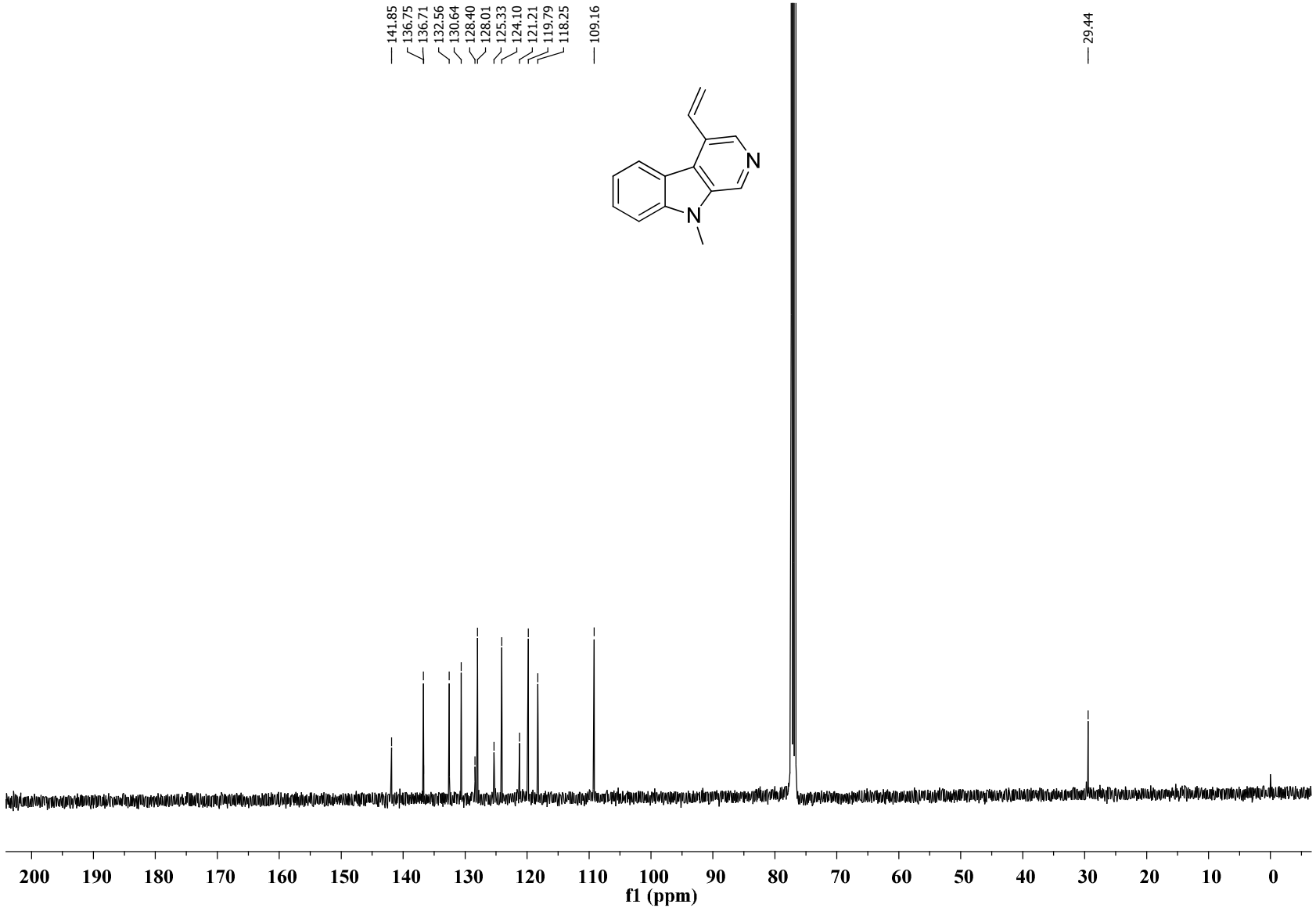
$^{13}C\{1H\}$NMR spectrum of **5b** ($CDCl_3$, 100 MHz)**:**



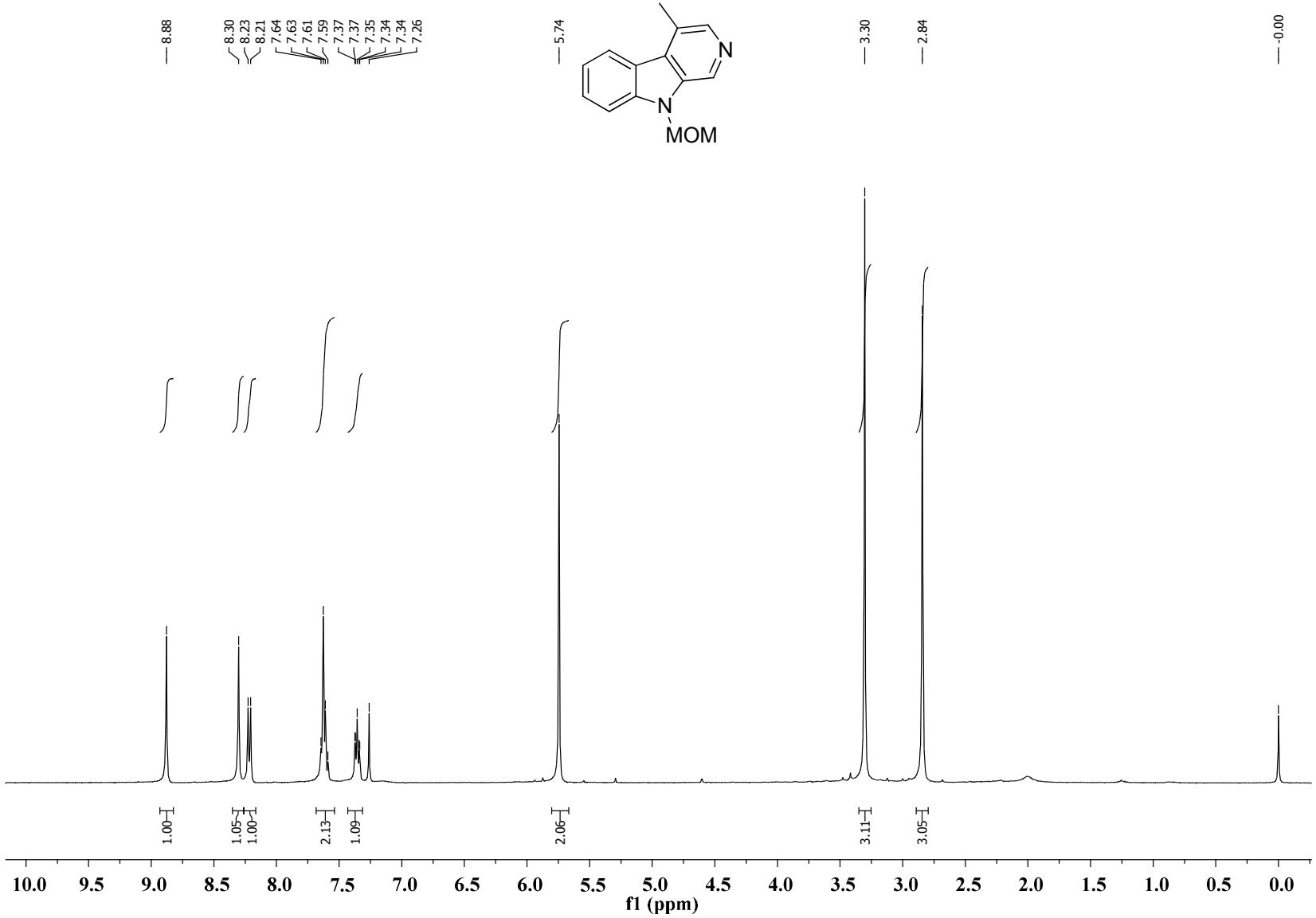
^{1}H NMR spectrum of **5c** ($CDCl_3$, 400 MHz)**:**



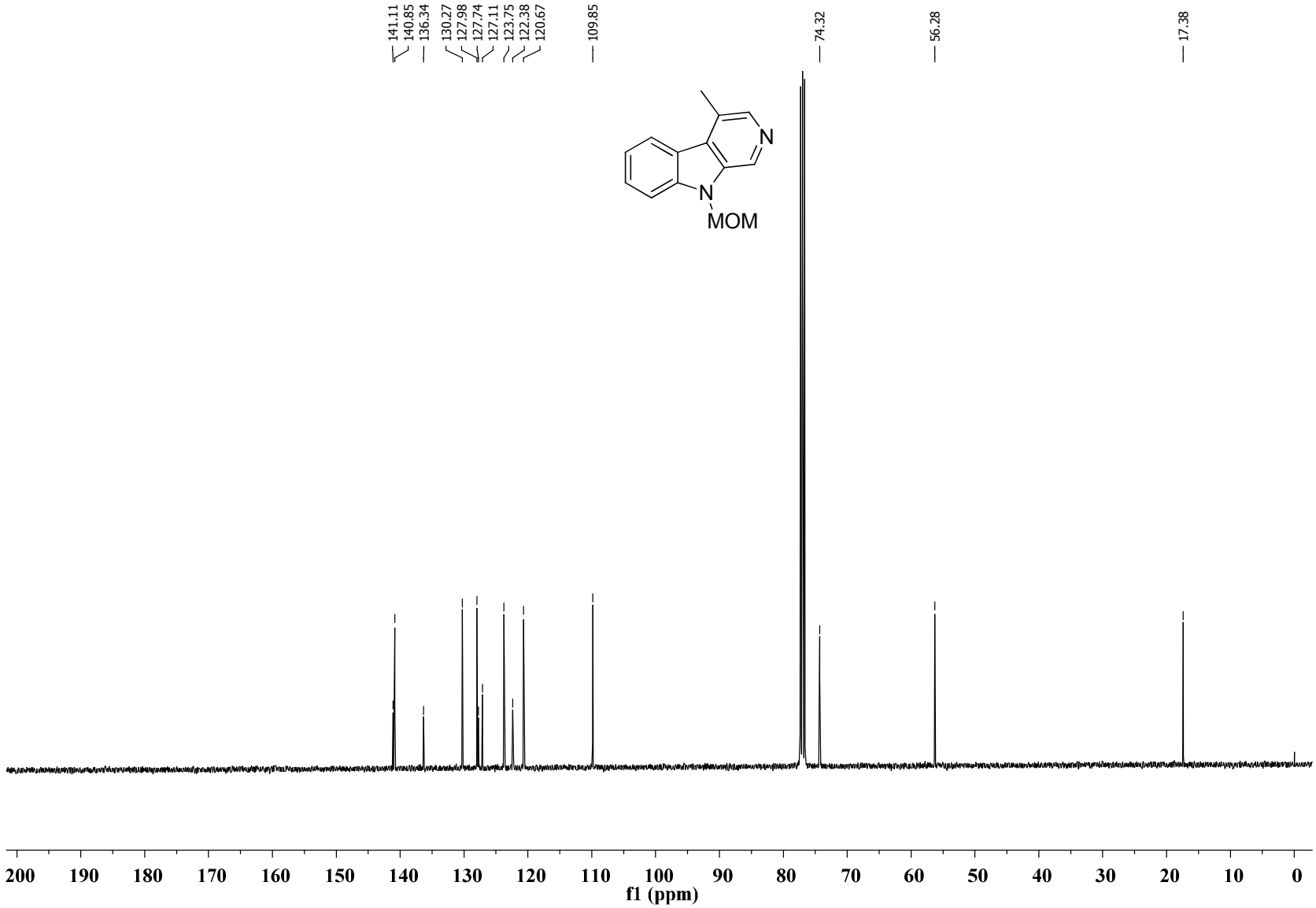
$^{13}C\{1H\}$NMR spectrum of **5c** ($CDCl_3$, 100 MHz)**:**



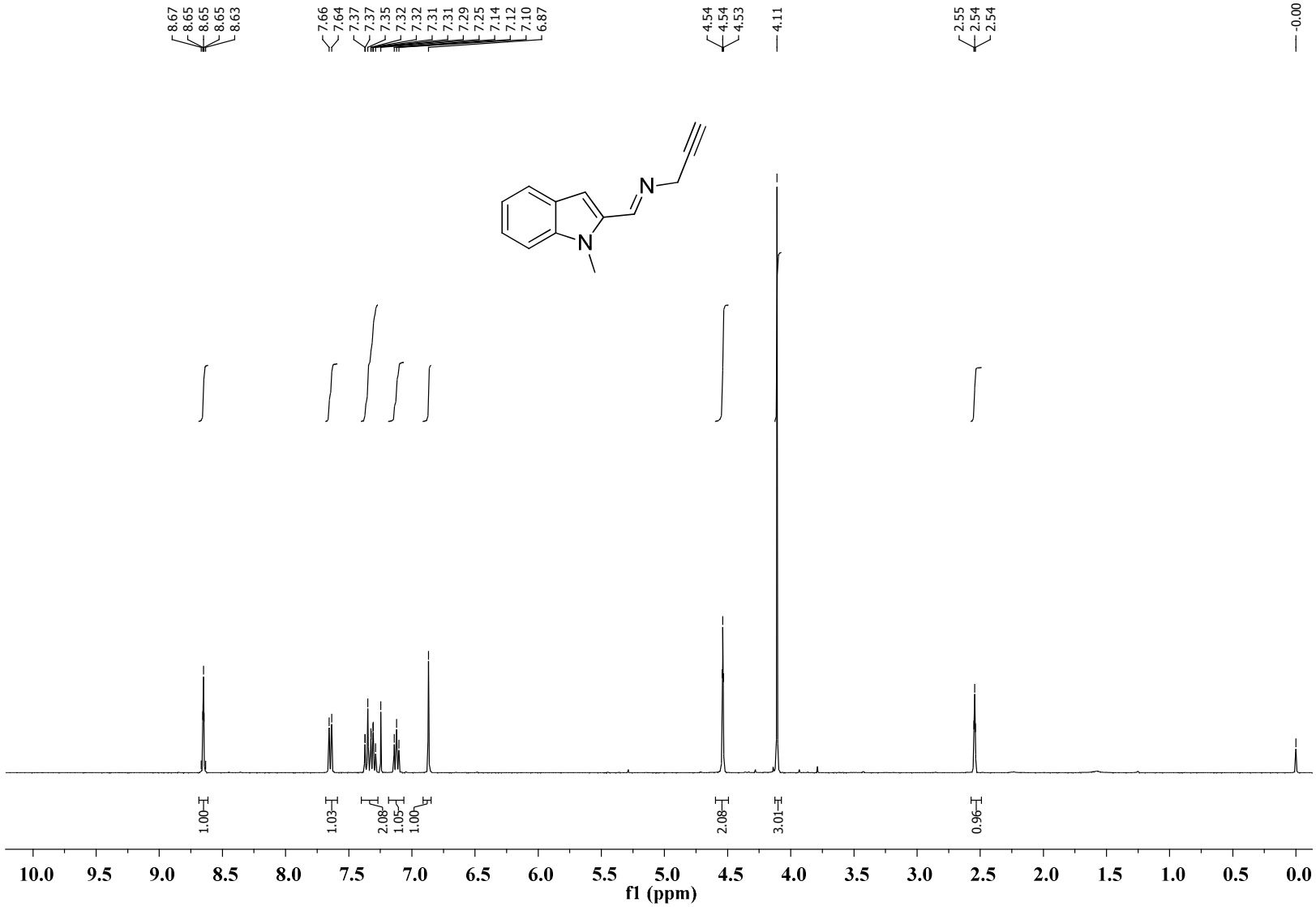
^{1}H NMR spectrum of **3z** ($CDCl_3$, 400 MHz)**:**



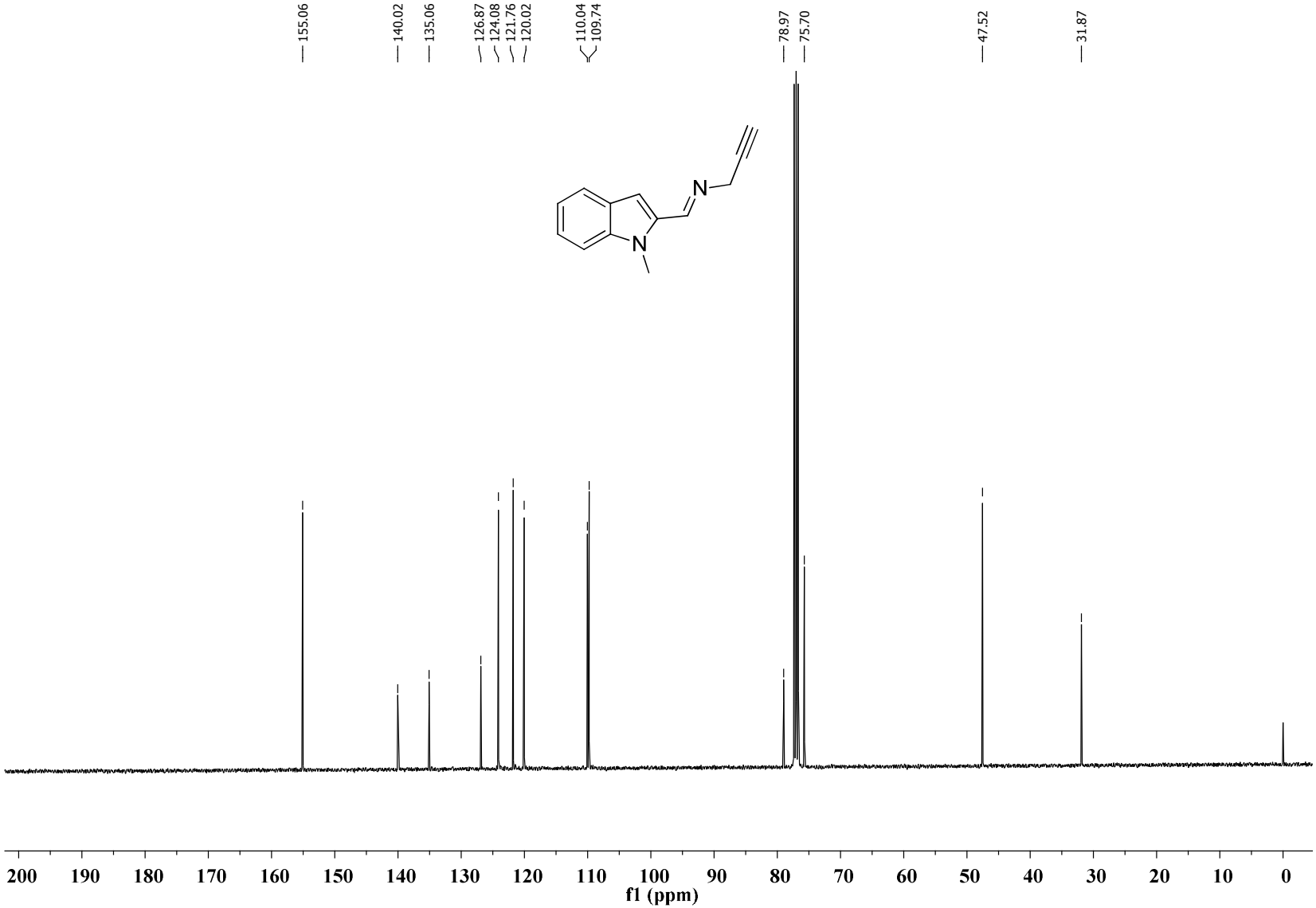
$^{13}C\{1H\}$NMR spectrum of **3z** ($CDCl_3$, 100 MHz)**:**



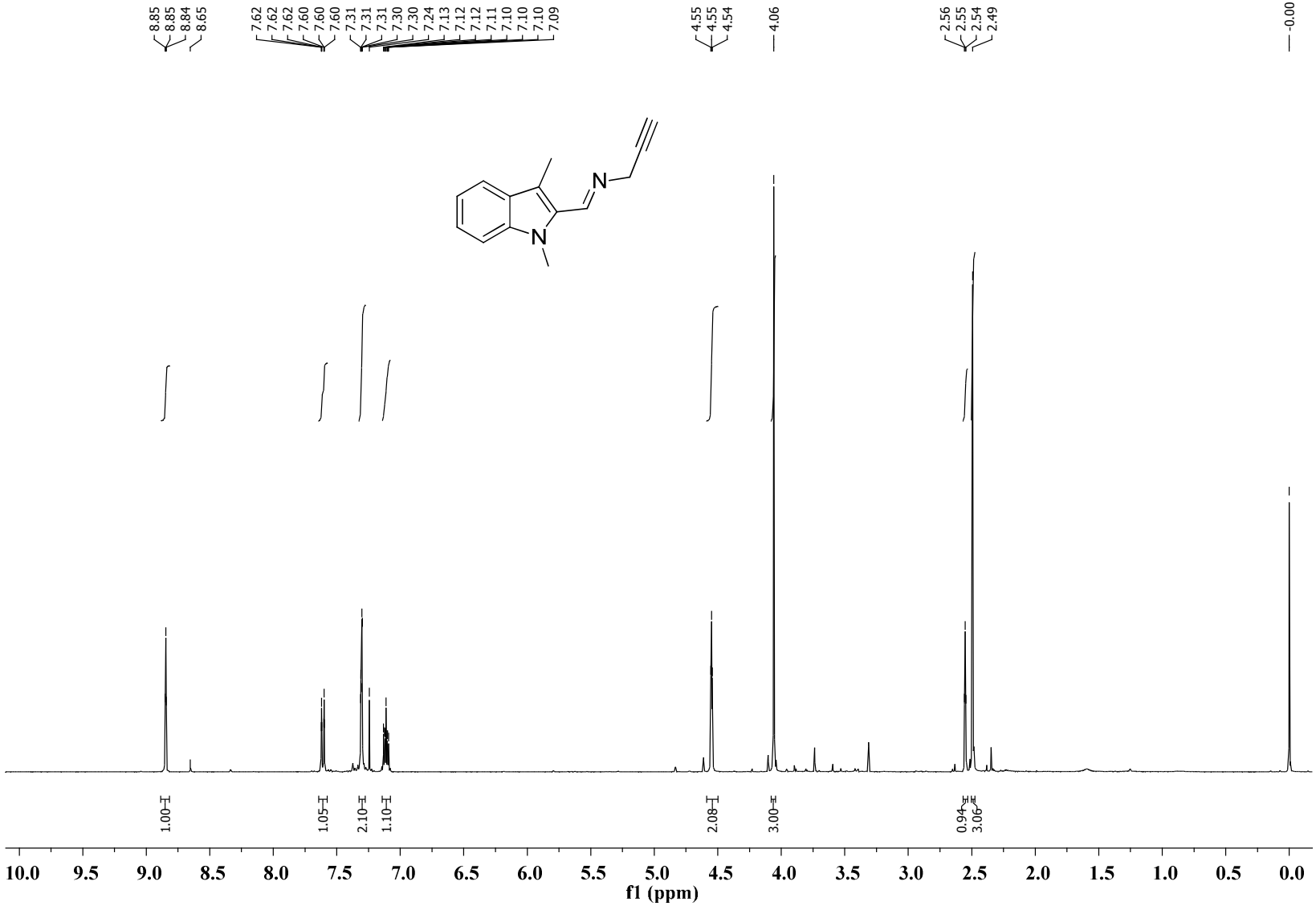
^{1}H NMR spectrum of **3aa** ($CDCl_3$, 400 MHz)**:**



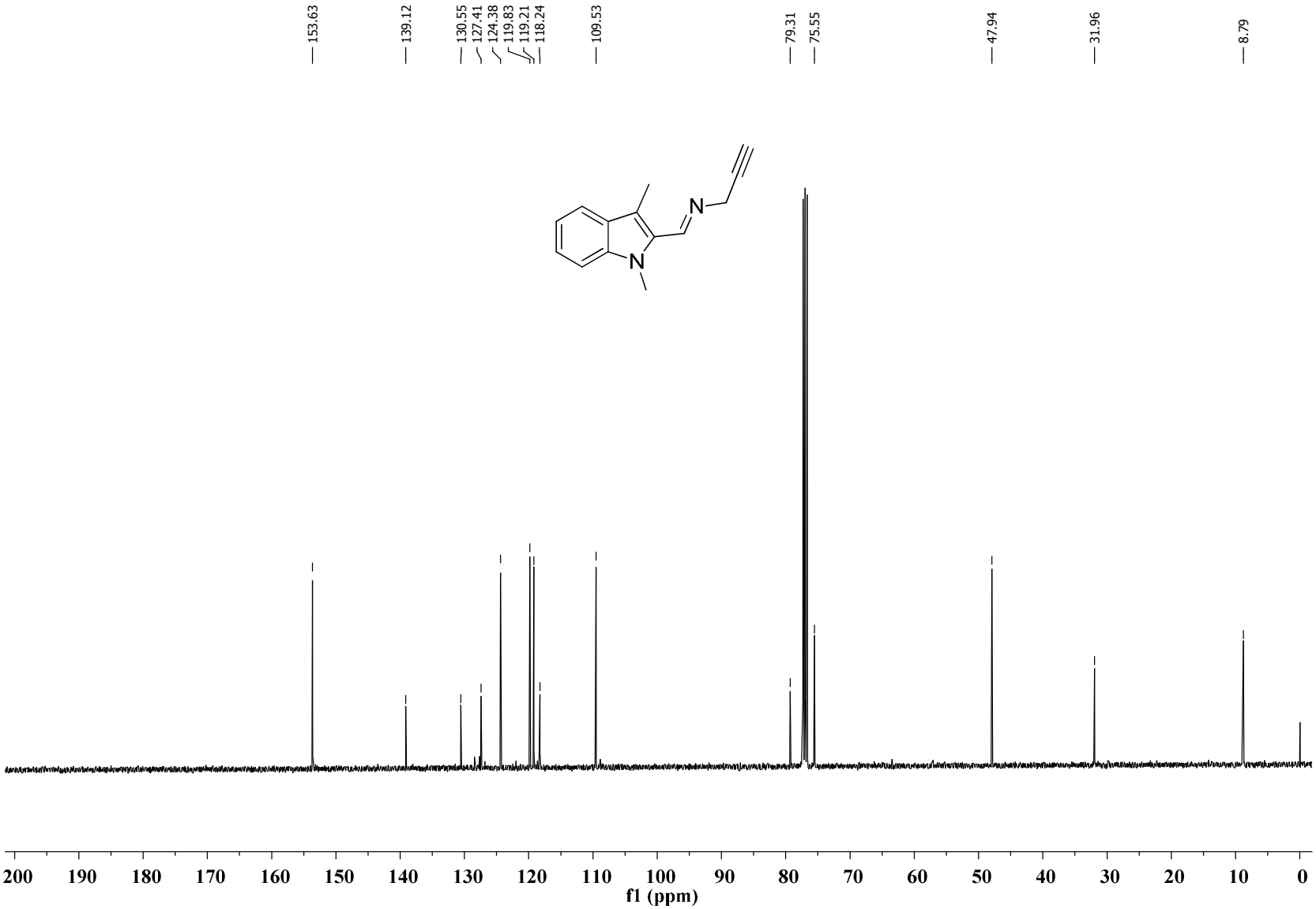
$^{13}C\{1H\}$NMR spectrum of **3aa** ($CDCl_3$, 100 MHz)**:**



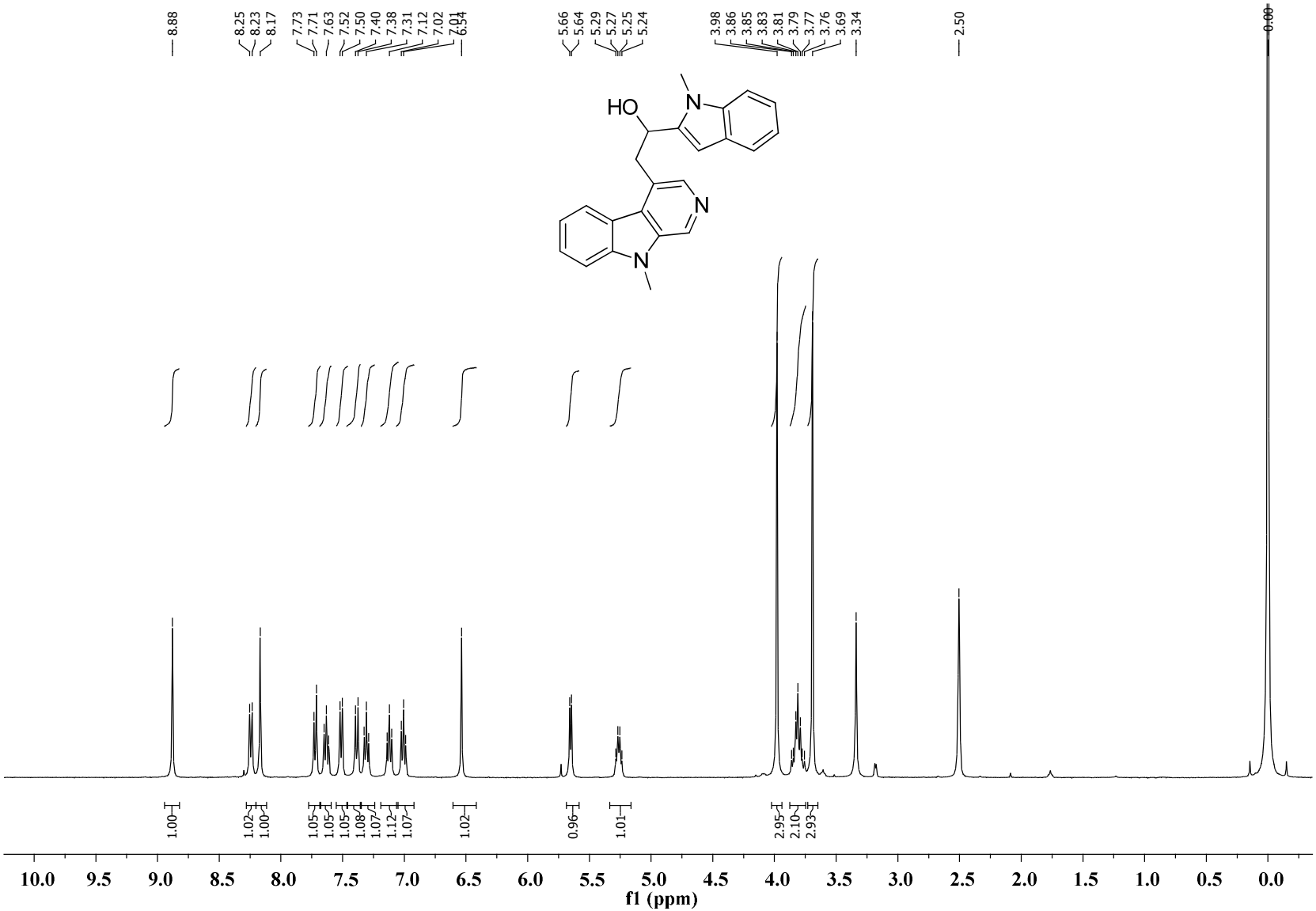
^{1}H NMR spectrum of compound **3ka** ($CDCl_3$, 400 MHz)**:**



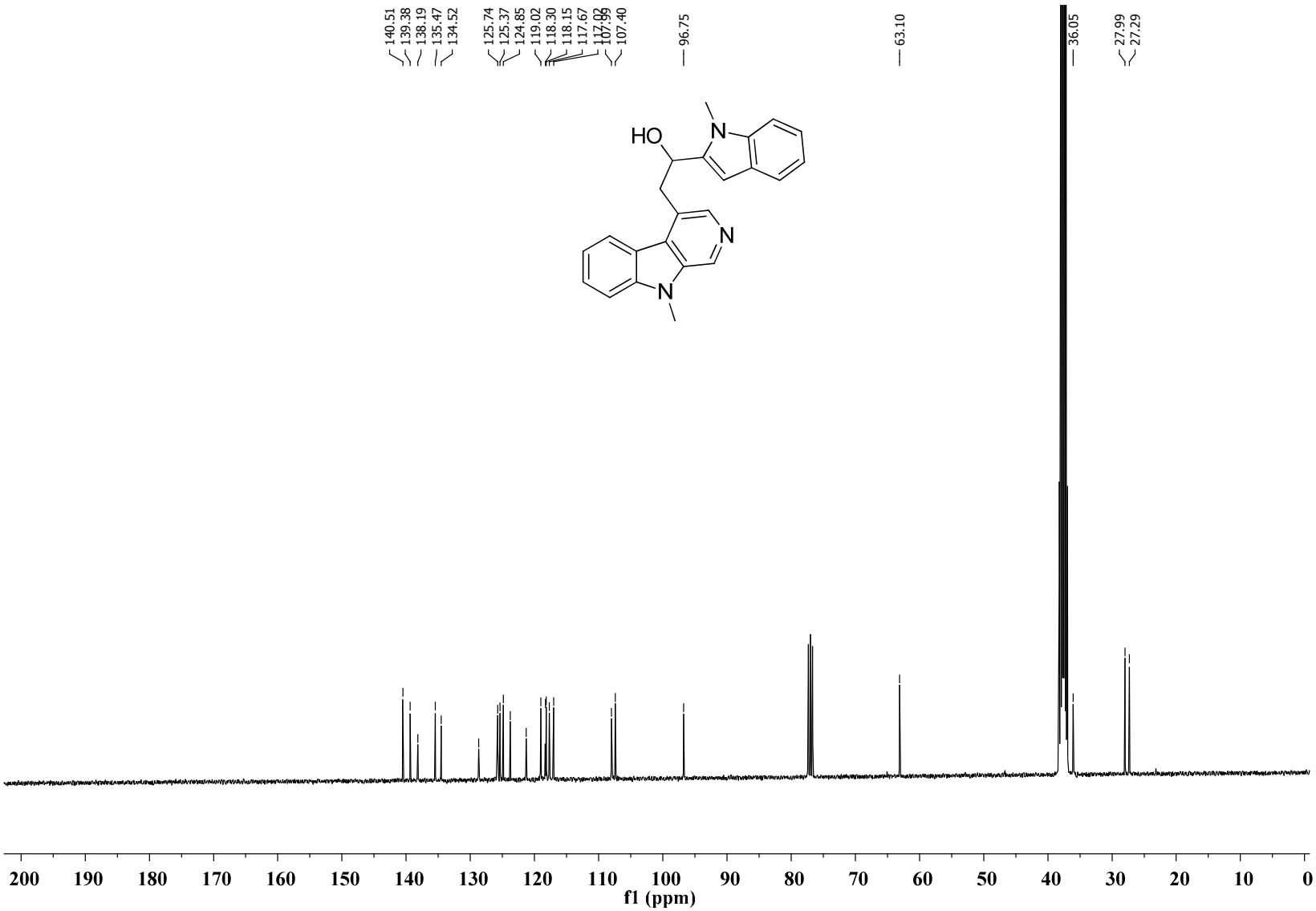
$^{13}C\{1H\}$NMR spectrum of compound **3ka** ($CDCl_3$, 100 MHz)**:**



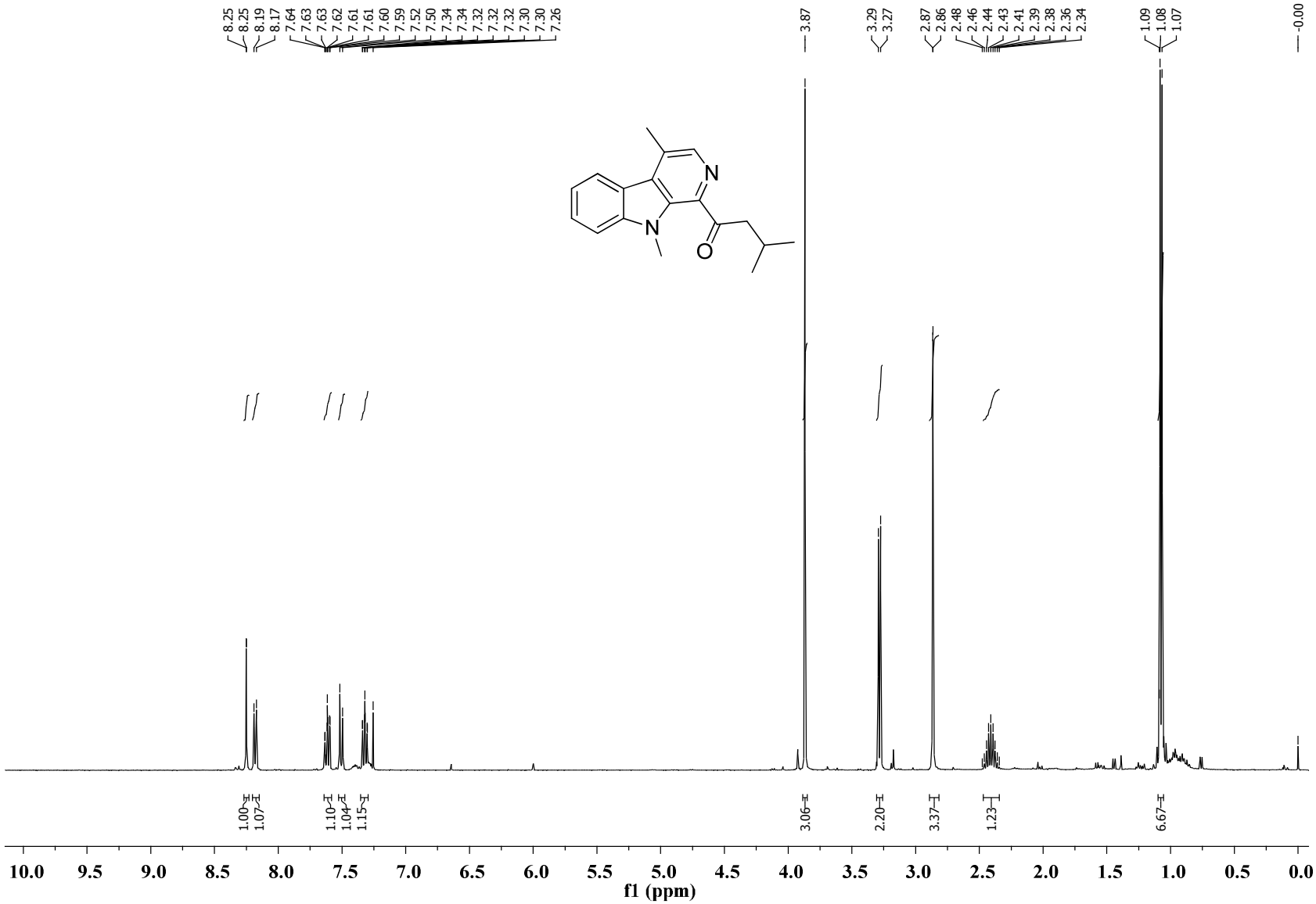
^{1}H NMR spectrum of **6** ($CDCl_3$: DMSO-d_6, 2:8, 400 MHz)**:**



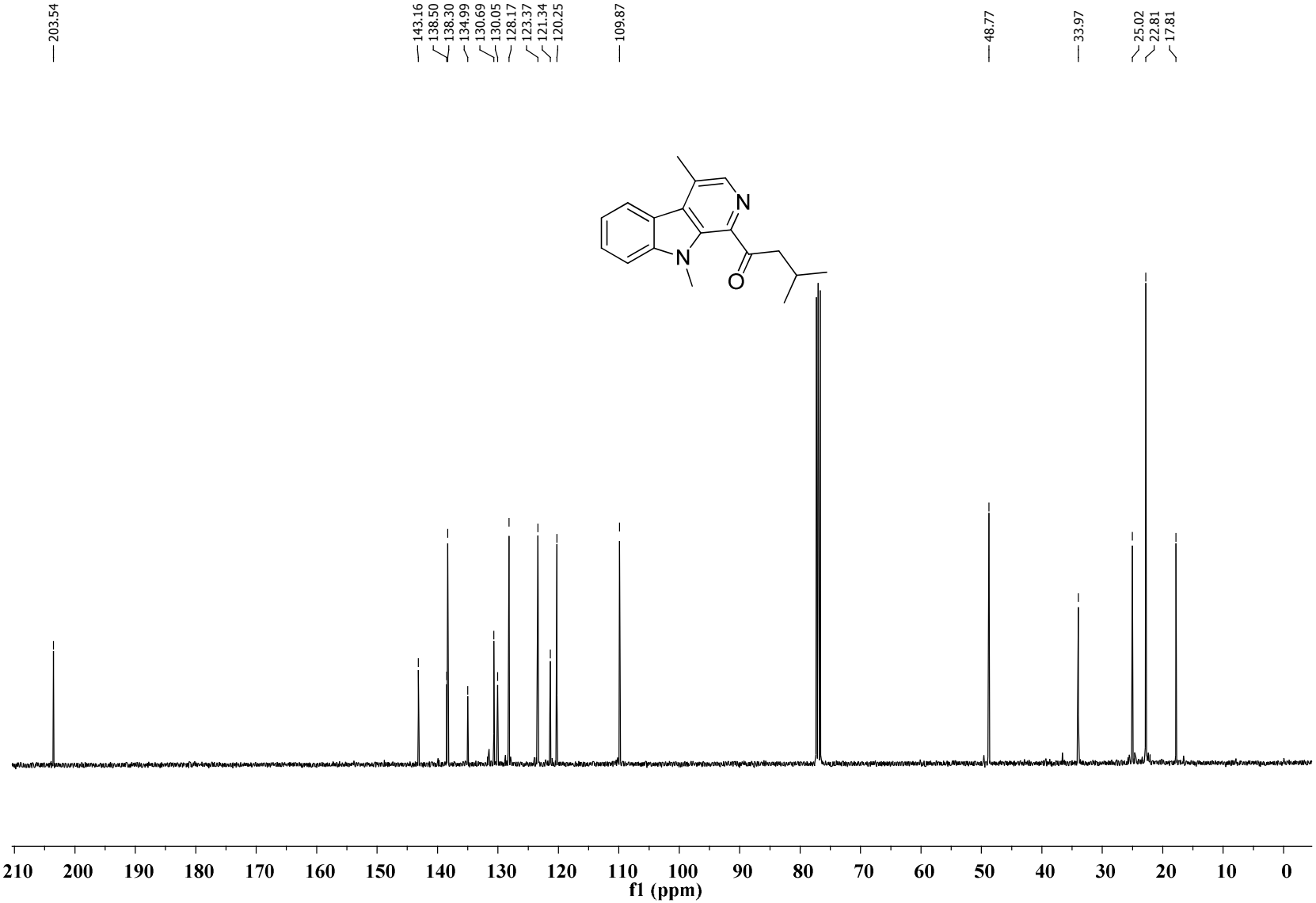
$^{13}C\{1H\}$NMR spectrum of **6** ($CDCl_3$:DMSO-d_6, 2:8, 100 MHz)**:**



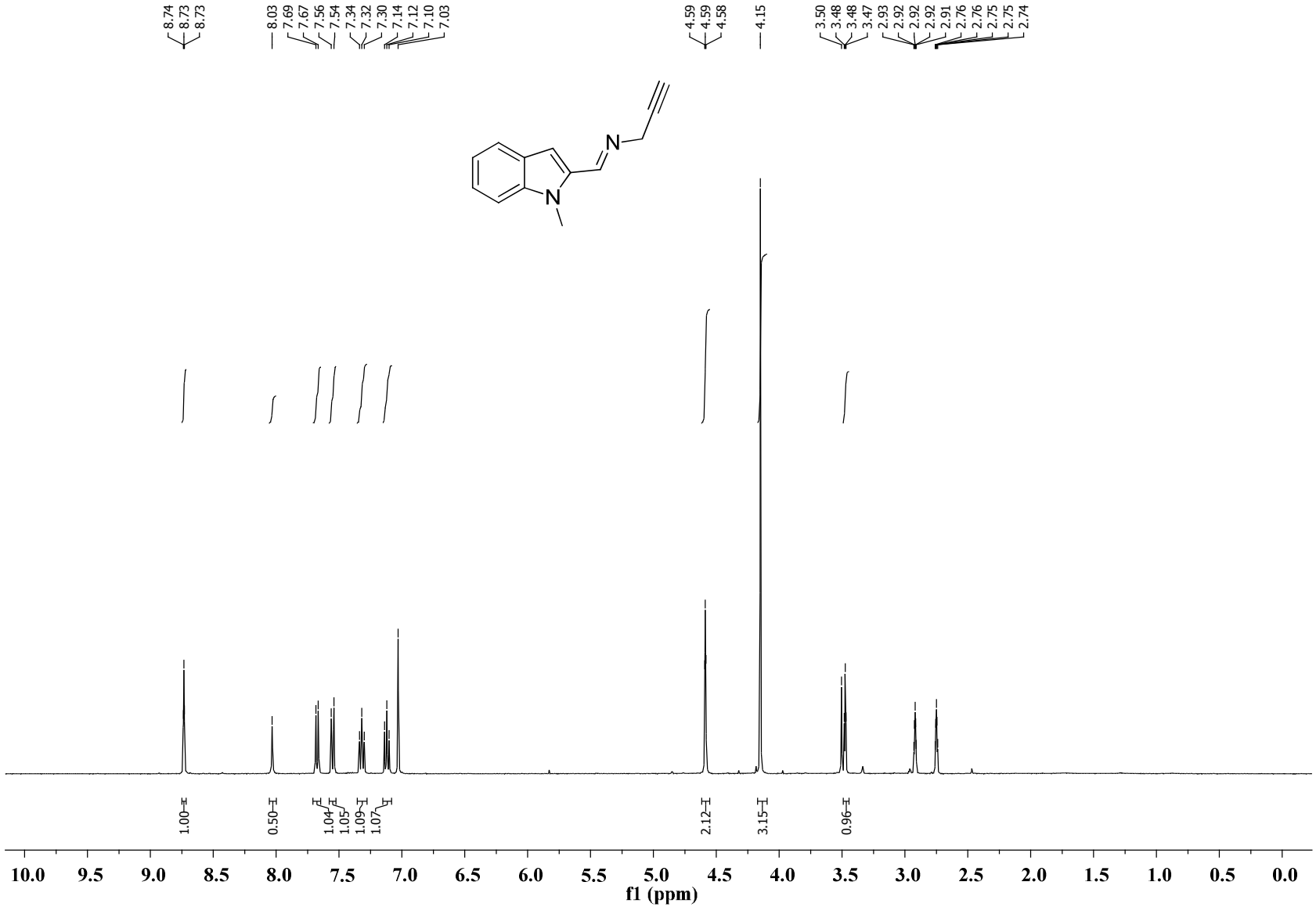
^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz)**:**



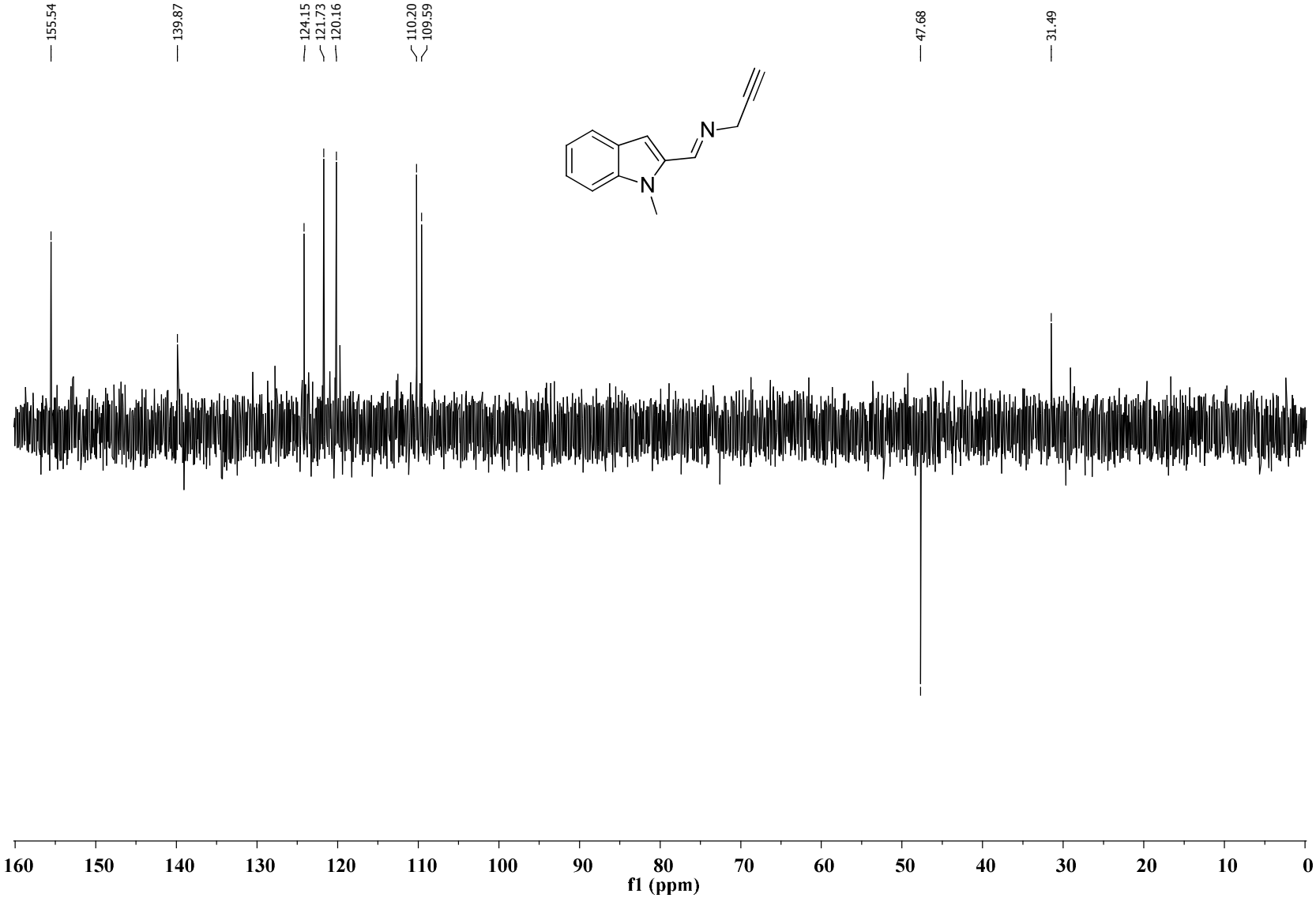
$^{13}C\{1H\}$NMR spectrum of **7** ($CDCl_3$, 100 MHz)**:**



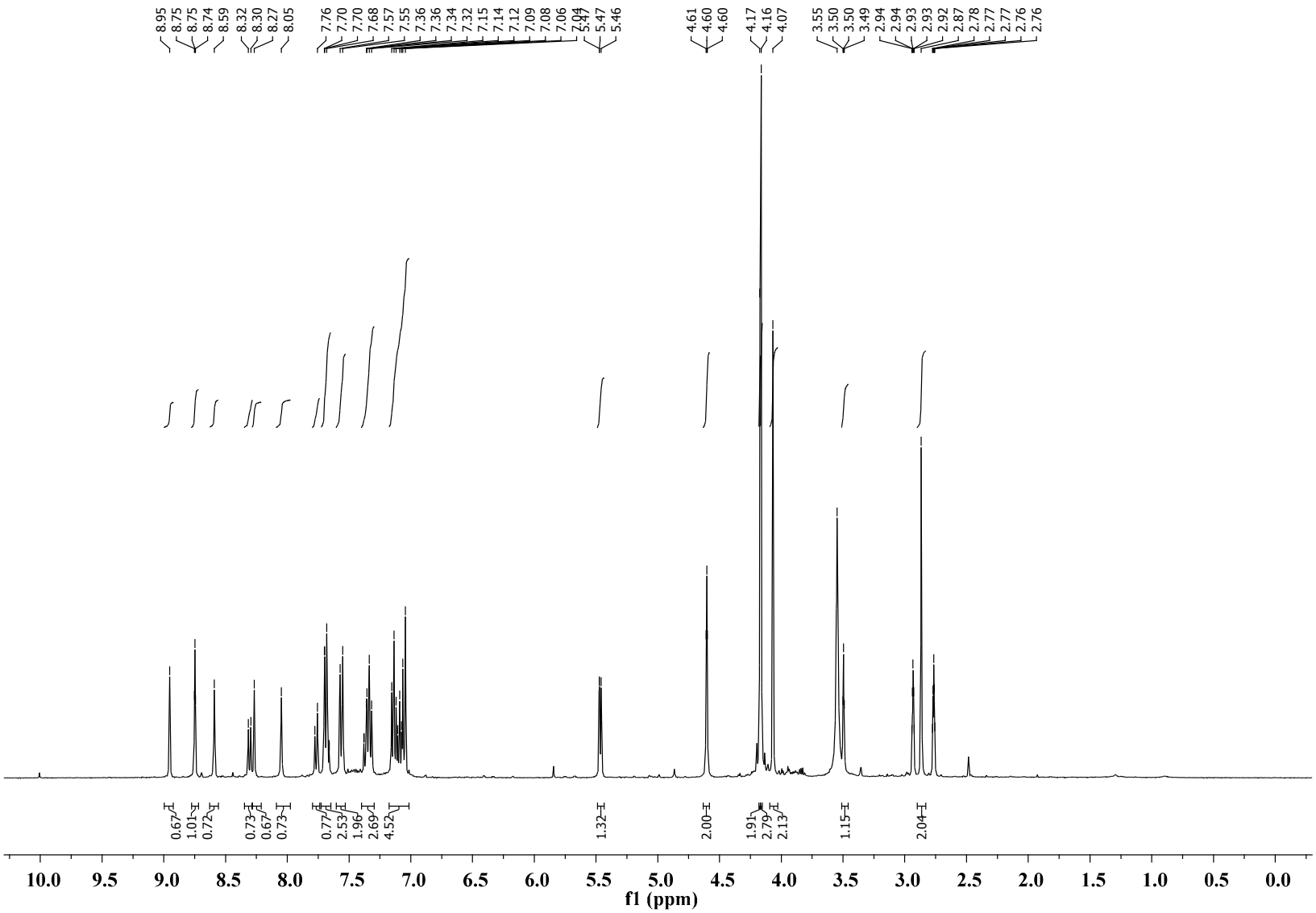
^{1}H NMR spectrum of **3aa** (DMF-d_7, 400 MHz)**:**



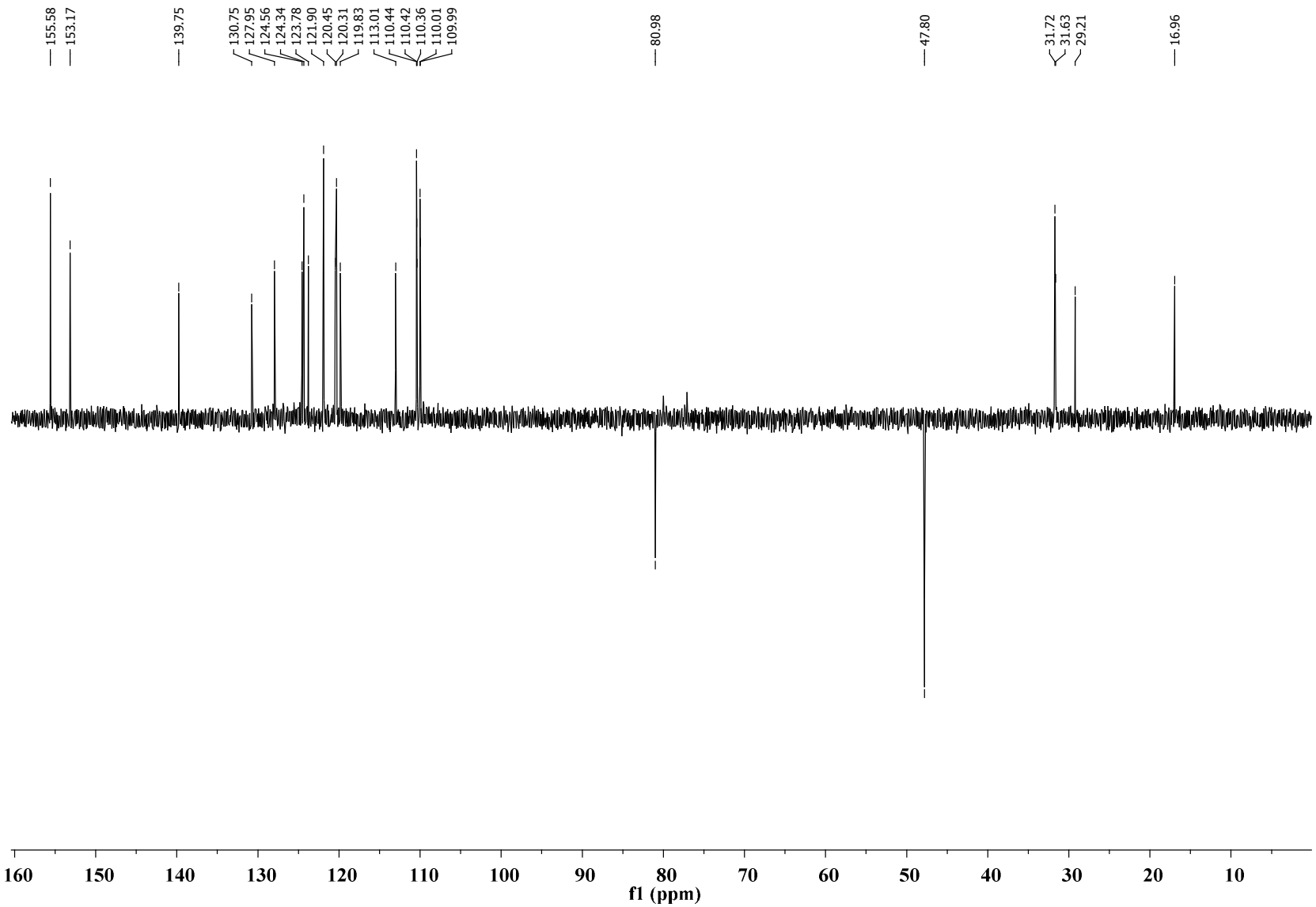
DEPT135 NMR spectrum of **3aa** (DMF-d_7, 100 MHz)**:**



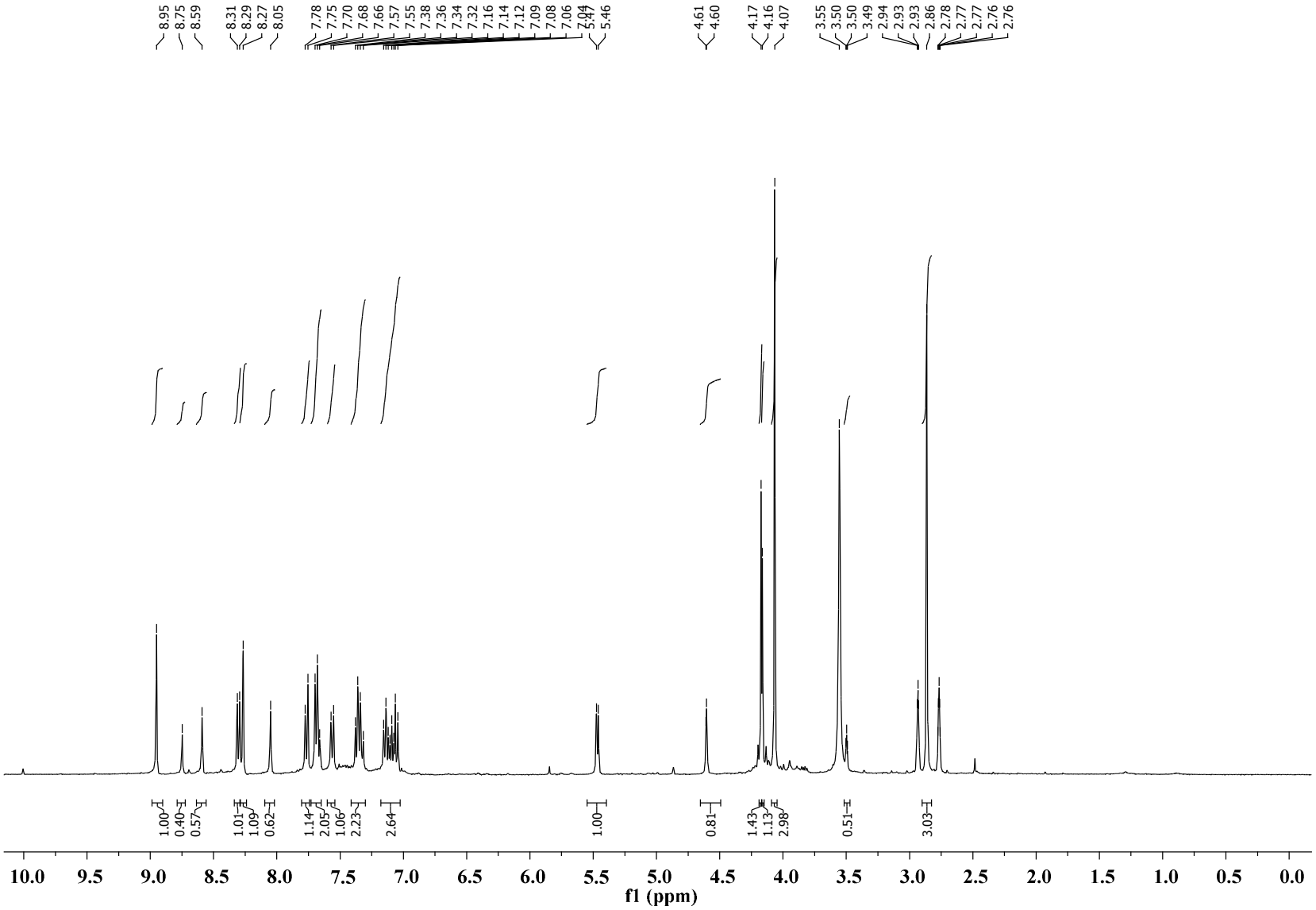
^{1}H NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 2 hours (DMF-d_7, 400 MHz)**:**



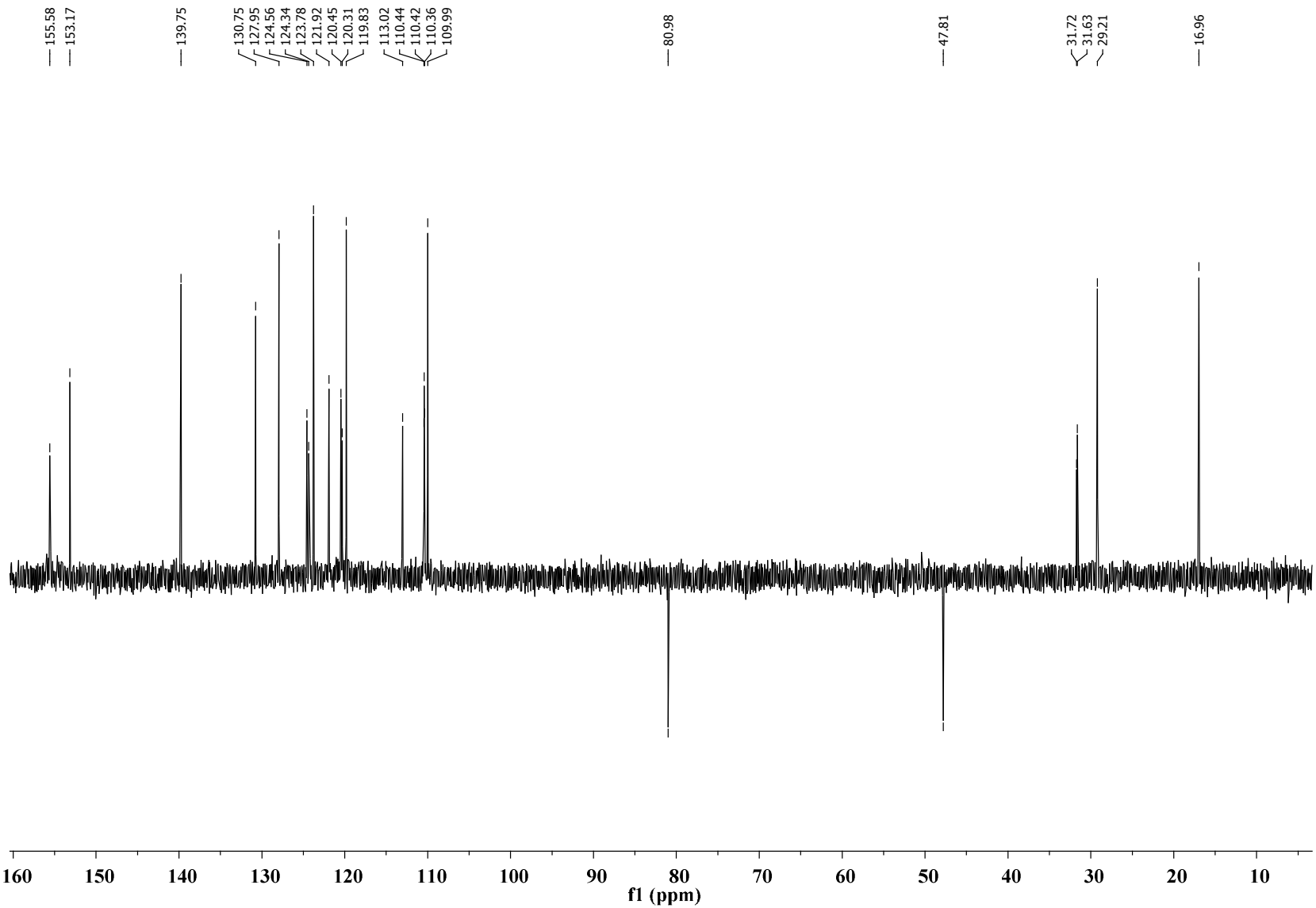
DEPT135 NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 2 hours (DMF-d_7, 100 MHz)**:**



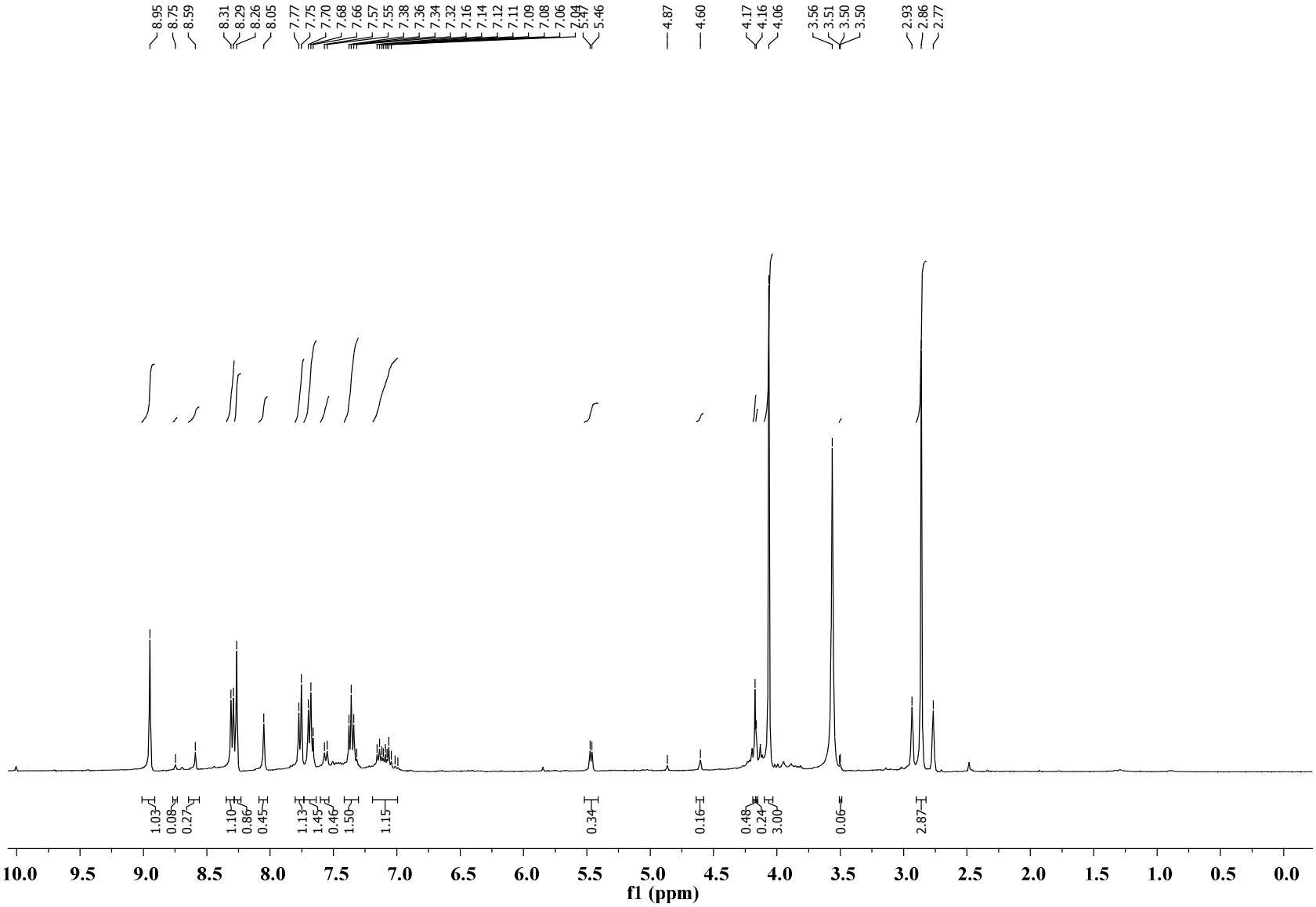
^{1}H NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 4 hours (DMF-d_7, 400 MHz)**:**



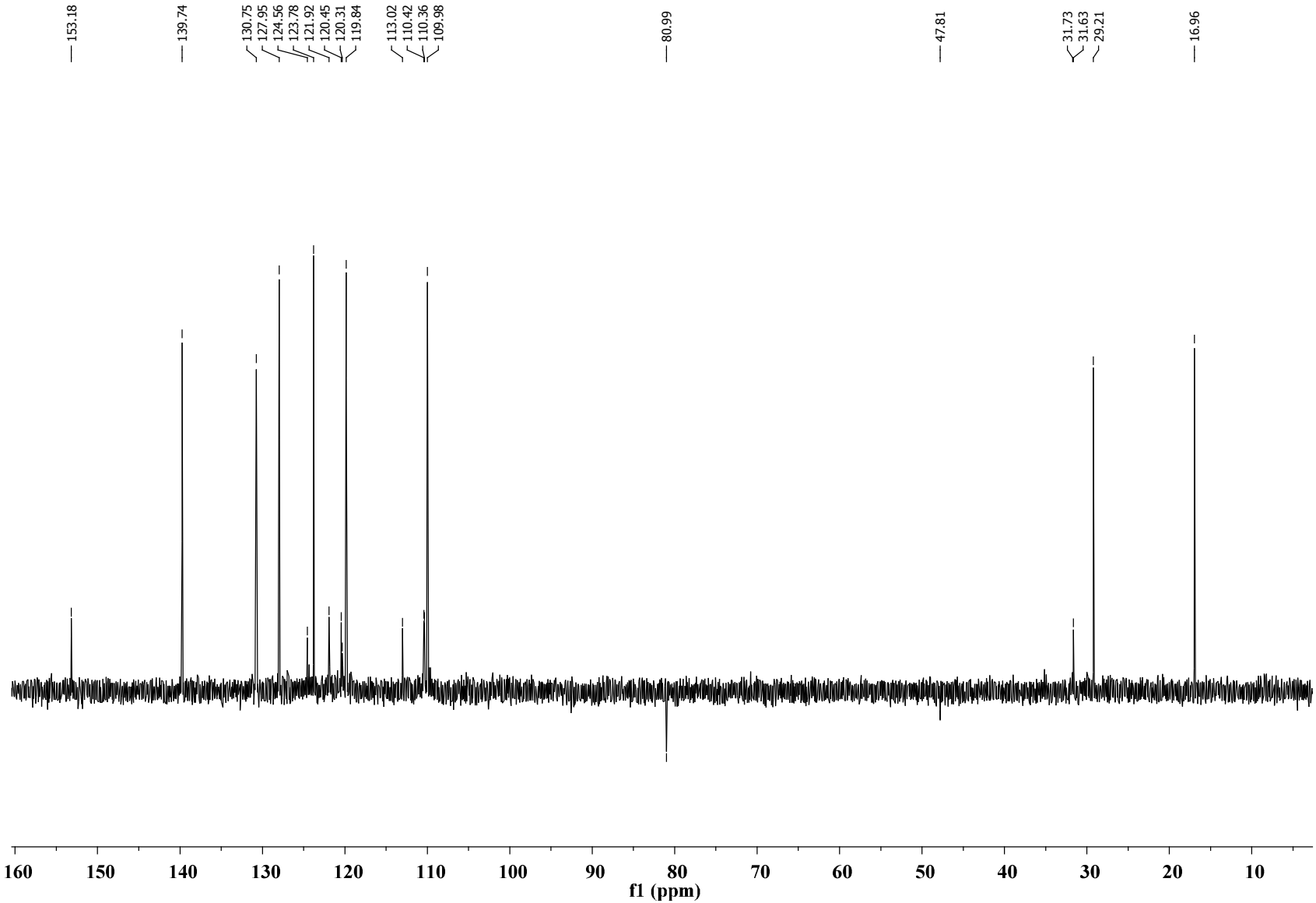
DEPT135 NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 4 hours (DMF-d_7, 100 MHz)**:**



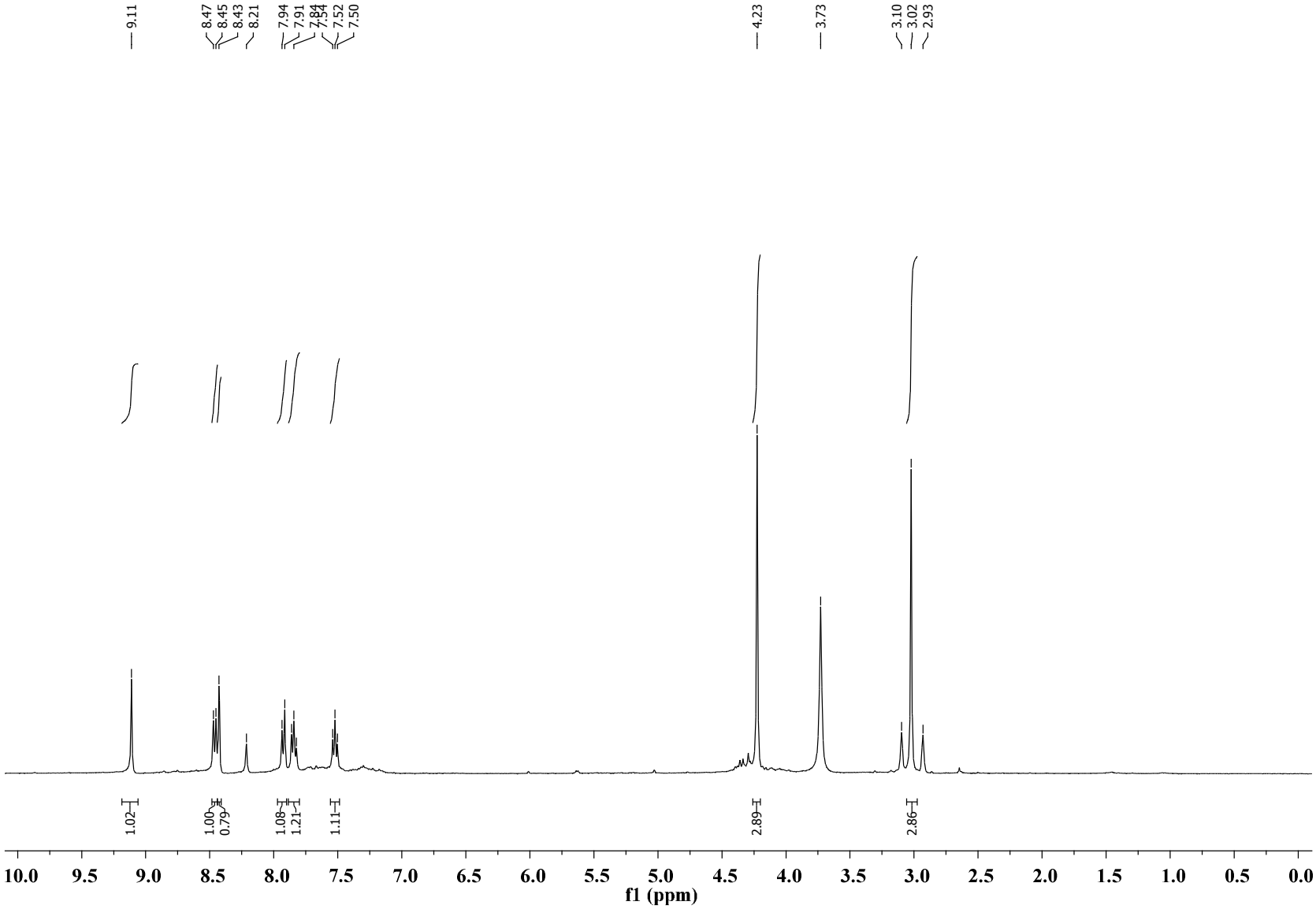
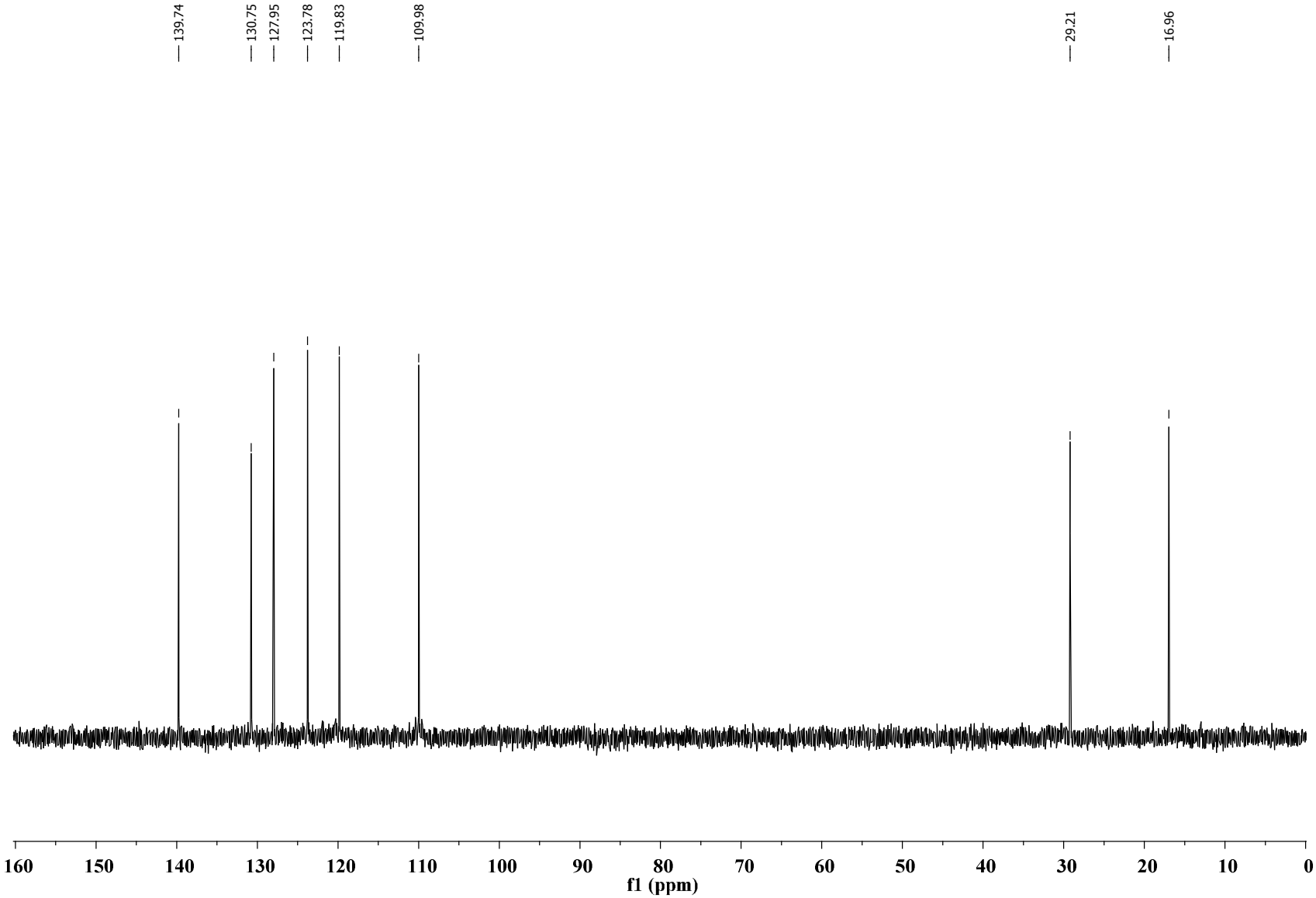
^{1}H NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 6 hours (DMF-d_7, 400 MHz)**:**



DEPT135 spectrum of reaction mixture of **3aa** to **3a** conversion at 6 hours (DMF-d_7, 100 MHz)**:**



^{1}H NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 8 hours (DMF-d_7, 400 MHz)**:**



DEPT135 NMR spectrum of reaction mixture of **3aa** to **3a** conversion at 8 hours (DMF-d_7, 100 MHz)**:**