Supplementary Materials for

Amide Synthesis via Molecular Shuffling of Carboxylic Acids

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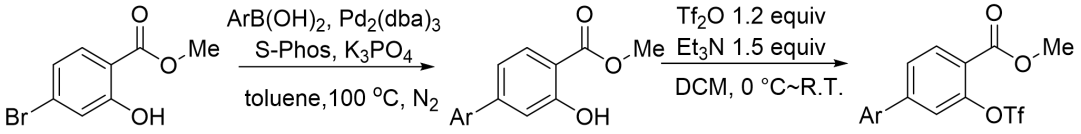
1. General Information

The reactions were carried out in Schlenk tubes of 25 mL under N_2 atmosphere. All heating and stirring were conducted on the IKA (Model: RCT B S025). Reagents were used as received unless otherwise noted, and solvents were purified according to standard operation procedure. Column chromatography was performed using Silica Gel 60 (300 – 400 mesh). The reactions were monitored by GC and GC-MS. GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2010 plus. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, 100 MHz, and 376 MHz, respectively, and chemical shifts were reported in parts per million (ppm) with deuterated chloroform as solvent. The atmospheric pressure chemical ionization (APCI) and electron ionization methods were used for the HRMS measurement, and the mass analyzer type is TOF for APCI and EI. All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, and Aladdin.

2. Experimental Procedure

2.1 Preparation of the starting materials

General Procedure A for the preparation of triflates:

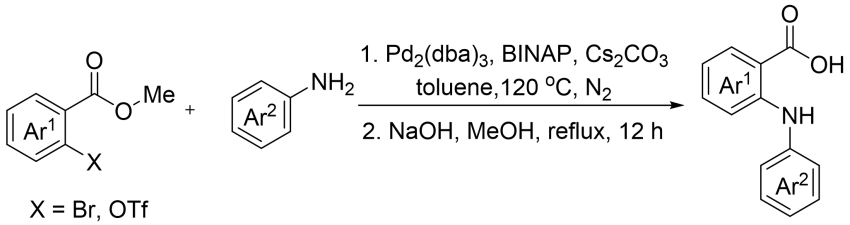


1. In a dry Schlenk tube filled with N_2, methyl bromosalicylate (230.0 mg, 1 mmol, 1.0 equiv), $ArB(OH)_2$ (2 mmol, 2.0 equiv), $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 0.05 equiv), S-Phos (41.0 mg, 0.1 mmol, 0.1 equiv) and K_3PO_4 (530.7 mg, 2.5 mmol, 2.5 equiv) were dissolved in toluene (5.0 mL). The reaction mixture was heated at 100 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum/EtOAc (10 : 1) as the eluent to give the desired products **39a**, **41a**–**45a** precursor for next step.

2. General procedure for the preparation of substrate triflate according to Ganem's procedure: To a solution DCM (50 mL) of phenols (10 mmol) and NEt_3 (2.1 mL, 1.5 equiv) was slowly

added trifluoromethanesulfonic anhydride (2.0 mL, 1.2 equiv) at 0 °C. Then the reaction mixture was warm up to room temperature and stirred for overnight. The reaction mixture was transferred to a 100 mL separator funnel and extracted with DCM (25 mL × 3). The organic phase was collected and washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel on column chromatography, eluting with EtOAc/petroleum ether.

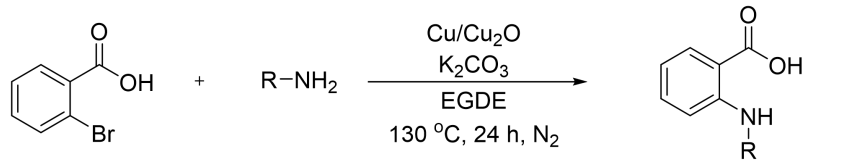
General procedure B for the preparation of carboxylic acids 2a–20a, 22a–45a:



1. To a solution of bromide (or triflate) (10 mmol) in toluene (0.1 M) was added amine (1.2 equiv), Cs_2CO_3 (2 equiv), BINAP (7.5 mol%), and $Pd_2(dba)_3$ (5 mol%) at room temperature. The reaction mixture was allowed to stir at 120 °C for 24 h. Once the reaction appeared to be complete by consumption of the bromide (or triflate) by TLC analysis, the mixture was allowed to cool to room temperature, diluted with EtOAc, washed with 2 M aq HCl (× 3), brine, and dried over sodium sulfate. The solution was concentrated, loaded on silica gel, and purified by silica gel chromatography.

2. To a solution of the methyl ester (1 equiv) in MeOH (0.2 M) was added NaOH (2 equiv per ester) in water (0.2 M) at room temperature. The reaction mixture was allowed to stir under reflux for 12 h. Once the reaction appeared complete by TLC analysis, MeOH was evaporated from the reaction mixture, the resultant solution was cooled to 0 °C and acidified to pH 2 with 2 M aq HCl. The resultant precipitated product was collected by vacuum filtration and washed with water.

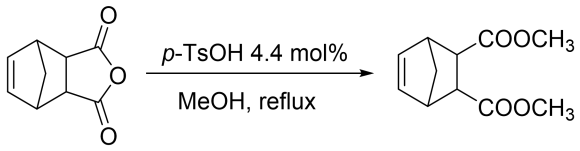
General procedure C for the preparation of carboxylic acids 46a–48a:



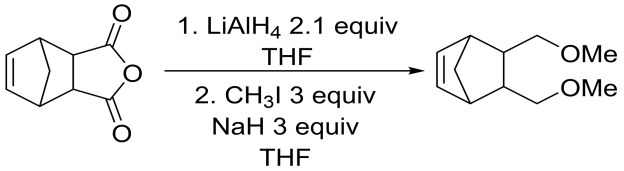
R = Bn, cyclohexyl, octyl

A mixture of 2-bromobenzoic acid (10 mmol), alkylamine (2 euqiv, 20 mmol), K_2CO_3 (1 equiv, 10 mmol), Cu powder (10 mol%, 1 mmol), Cu_2O (5 mol%, 0.5 mmol) and ethylene glycol diethyl ether (5 mL) was heated to 130 °C for 24 h under nitrogen. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was poured into H_2O (30 mL), treated with charcoal and the mixture was filtrated through celite. Acidification of the filtrate (pH 5) with dilute HCl gave a precipitate, which was dissolved in aq Na_2CO_3 (5%, 100 mL) and the solution was filtered through celite and subjected to precipitation as described above. Flash chromatography (EtOAc/petroleum = 1:5) afforded the desired *N*-alkyl anthranilic acids.

General Procedure for the preparation of *NBE*s:



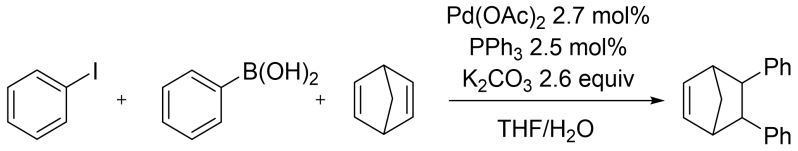
Procedure D: Nadic anhydride (5 mmol) and *p*-TsOH (4.4 mol%) as the catalyst were dissolved in 20 mL of methanol in a 100 mL flask. The mixture was kept refluxing for approximately 12 hours. After methanol was removed by evaporation, the mixture was then distilled in vacuum and purified by silica gel chromatography.



Procedure E: 1. A flame-dried flask was charged with $LiAlH_4$ (10.5 mmol, 2.1 equiv) and cooled to 0 °C. THF (10 mL, 0.5 M) was added dropwise and the suspension was stirred at 0 °C

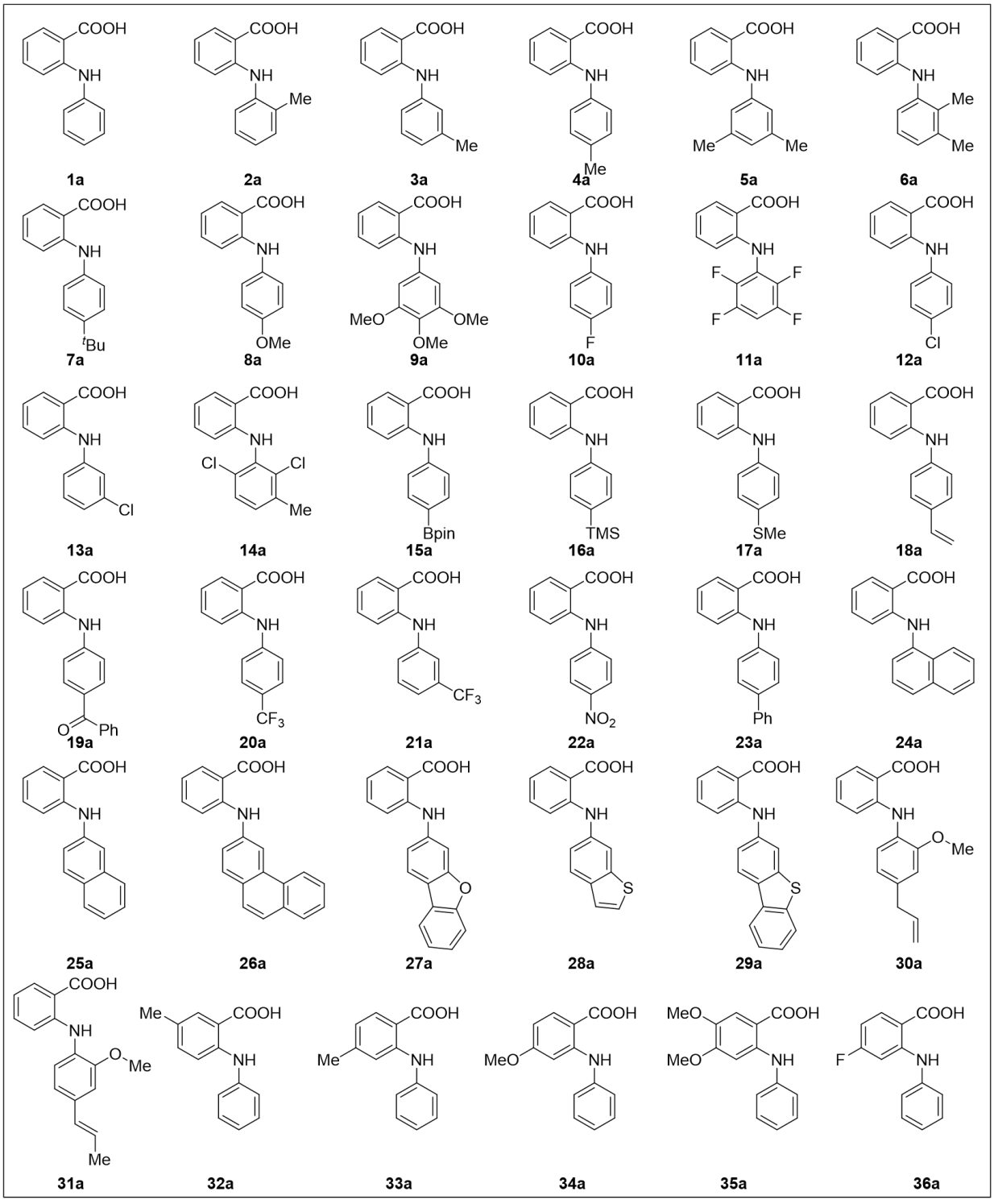
for 5 min. The nadic anhydride (5 mmol, 1.0 equiv) was added portion-wise over 10 min and the reaction mixture was allowed to warm to room temperature and stirred for an additional 15 h. The crude mixture was cooled to 0 ºC and 1 mL of deionized H_2O was added dropwise, followed by 1 mL of 15% NaOH and then 2 mL of deionized H_2O. The mixture was filtered and concentrated to yield a white solid. The crude diol was used without any further purification.

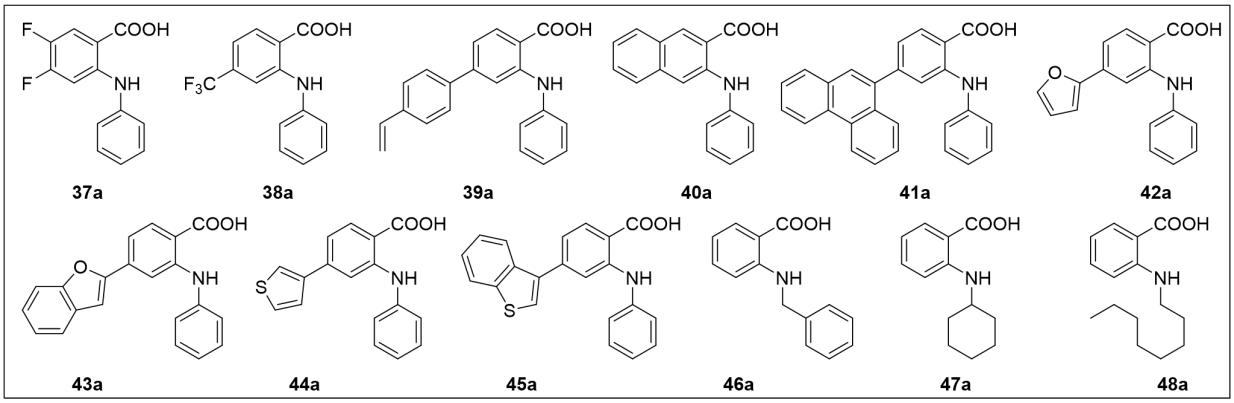
2. A flame-dried flask was charged with NaH (3 equiv) and the mineral oil was removed via washing three times with hexanes. The flask was cooled to 0 ºC and THF (10 mL) was added slowly. In a separate flask the crude diol (1.0 equiv) was diluted in THF (2 mL) and cannulated over the suspension at 0 ºC. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was cooled to 0 ºC and MeI (3.0 equiv) was added dropwise. The reaction was warmed to room temperature and stirred for 18 h. The reaction mixture was cooled to 0 ºC and quenched with MeOH (until reaction mixture turned transparent) after which the volatiles were evaporated. The crude mixture was diluted with H_2O and extracted three times with Et_2O. The combined organic layers were washed once with H_2O, brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography.



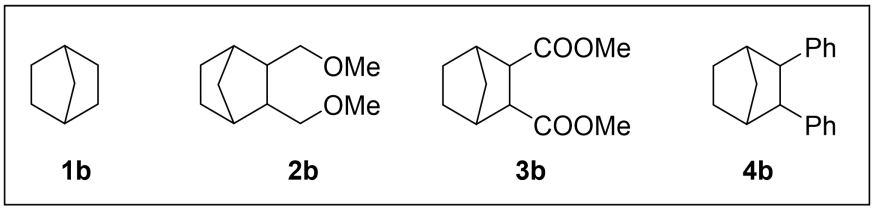
Procedure F: A 25 mL Schlenk flask was charged with iodobenzene (2.5 mmol, 1 equiv), phenylboronic acid(2.75 mmol, 1.1 equiv), 2,5-norbornadiene (2.75 mmol, 1.1 equiv), triphenylphosphine (16 mg, 0.062 mmol, 2.5 mol%), K_2CO_3 (0.912 g, 6.6 mmol. 2.6 equiv), THF (5 mL), water (5 mL), and a stirbar. The mixture was then degassed via three freeze-pump-thaw cycles, and $Pd(OAc)_2$ (6 mg, 2.7 mol% in 250 µL of degassed THF) was added via syringe under a nitrogen backflow. The reaction was degassed once more and heated in 60 ºC overnight. The two phases were separated, and the aqueous phase was extracted with 2 × 15 mL of CH_2Cl_2. The organic layers were combined, extracted with 5% NaCN (1 × 25 mL) to remove colored palladium impurities, and dried over Na_2SO_4. Afterward, the solvent was removed with a rotary evaporator. The resulting resin left in the pot was purified by column chromatography (silica gel) and/or recrystallization.

Starting materials of carboxylic acids

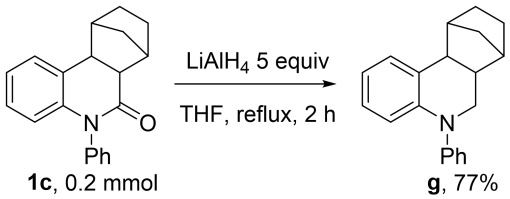




Starting materials of *NBE*s



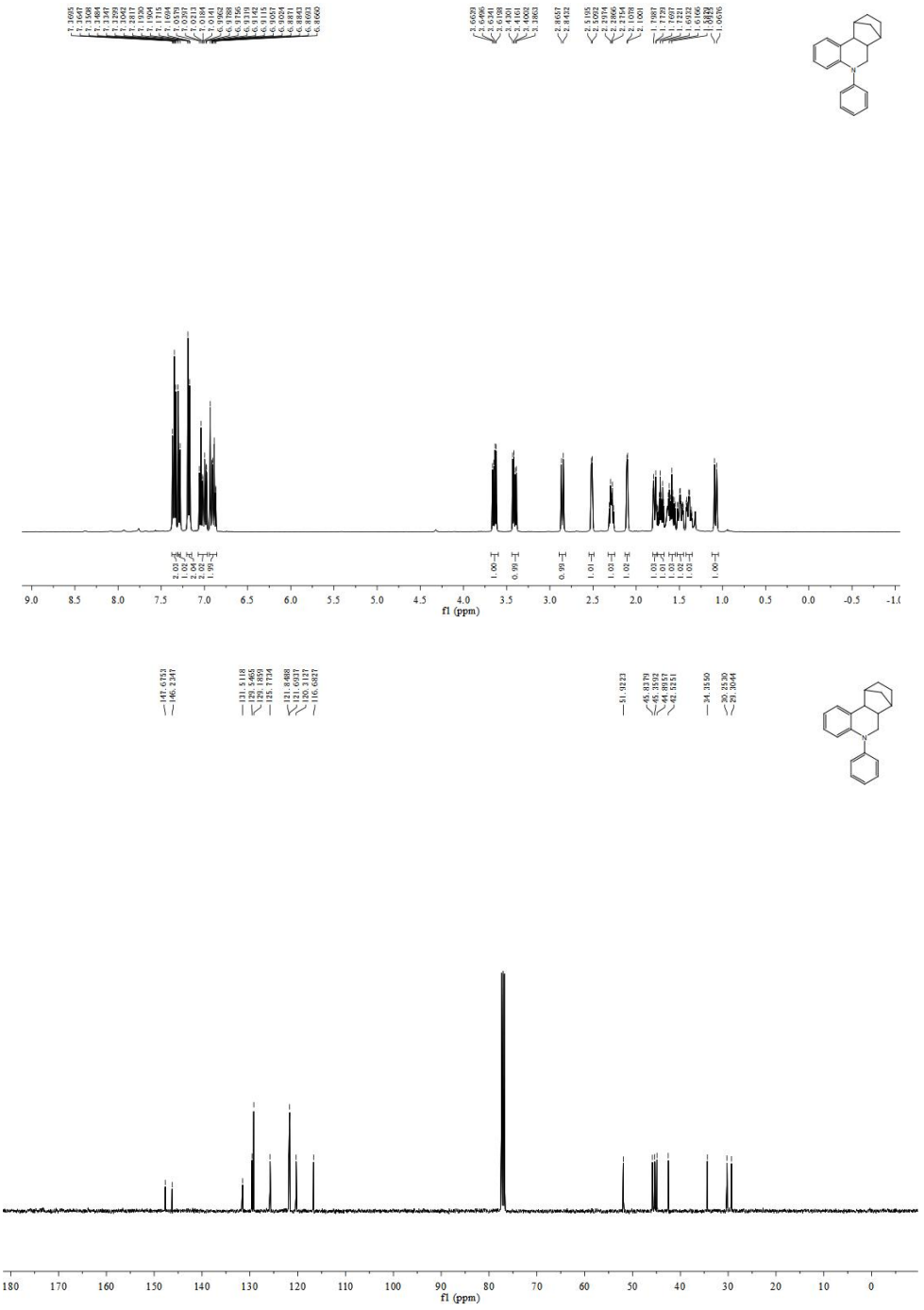
2.2 Synthetic applications

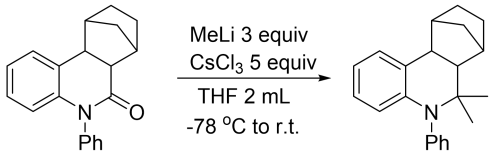


To a solution of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**1c**) (56 mg, 0.2 mmol) in dry THF (8 mL) was added $LiAlH_4$ (41 mg, 1.1 mmol, 5 equiv) in two portions at 0 °C. The resulting solution was allowed to warm up to room temperature and then refluxed. Upon completion, the resulting solution was cool down to 0 °C and slowly quenched with a saturated aqueous solution of and stirred for 1 hour. The resulting aqueous phase was extracted with EA (3 × 20 mL). The combined organic phases was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography over silica gel eluting with PE to afford the desired product as an colorless oil (42.4 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.4, 1.8 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 1H), 7.22–7.14 (m, 2H), 7.08–6.96 (m, 2H), 6.94–6.86 (m, 2H), 3.64 (dd, *J* = 11.8, 5.6 Hz, 1H), 3.41 (dd, *J* = 11.8, 5.6 Hz, 1H), 2.85 (d, *J* = 9.0 Hz, 1H), 2.51 (d, *J* = 4.2 Hz, 1H),

2.29 (dt, *J* = 10.0, 5.6 Hz, 1H), 2.10 (d, *J* = 3.1 Hz, 1H), 1.82–1.76 (m, 1H), 1.72 (ddd, *J* = 15.8, 8.2, 4.2 Hz, 1H), 1.59 (tt, *J* = 11.4, 4.0 Hz, 1H), 1.53–1.45 (m, 1H), 1.42–1.35 (m, 1H), 1.08 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.68, 146.23, 131.51, 129.55, 129.19, 125.77, 121.85, 121.69, 120.31, 116.68, 51.92, 45.84, 45.36, 44.90, 42.53, 34.35, 30.25, 29.30.

5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**g**)

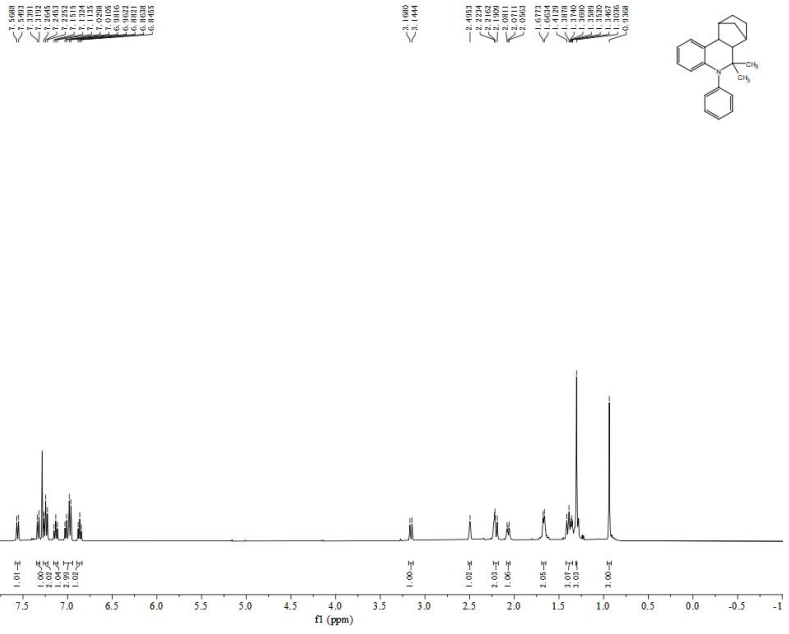


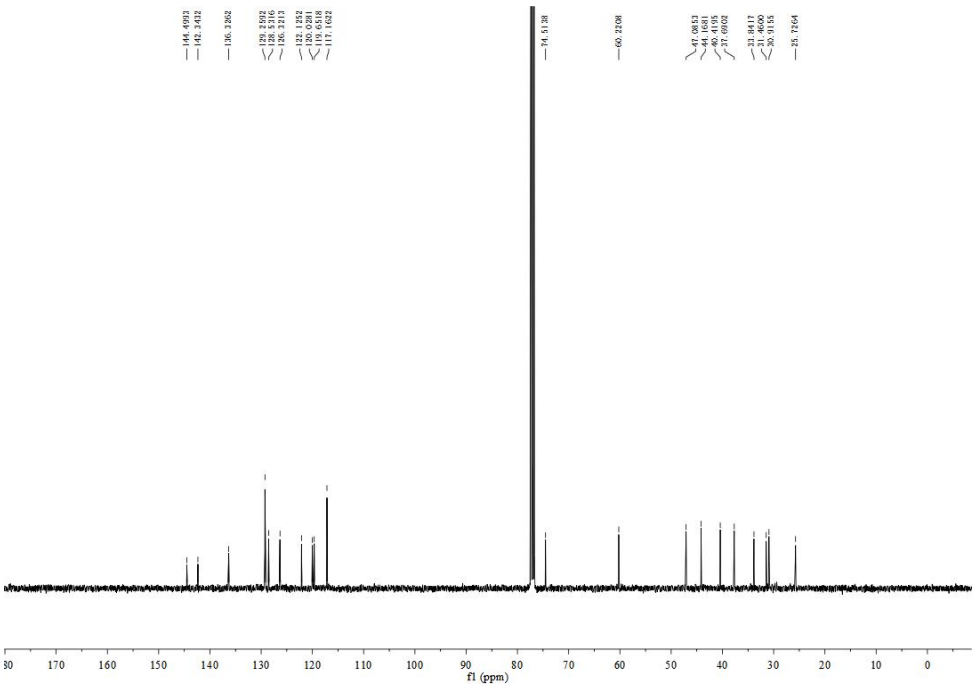


1c, 0.2 mmol **h**, 72%

A solution of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**1c**) (0.2 mmol, 1 equiv) and $CeCl_3$ (5 equiv) in THF (2 mL) was stirred at -78 °C for 1 h. A solution of MeLi 1.3 M in diethyl ether (3 equiv) was added dropwise, keeping the internal temperature below -78 °C. After warming to room temperature over 4 hours, Then the reaction mixture was quenched with 1 mol/L HCl aqueous solution, and diluted with DCM. The organic layer was washed with water, and brine, sequentially. After that, the organic layer was dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography to afford the product **h** in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 19.2, 7.6 Hz, 3H), 6.86 (t, *J* = 7.2 Hz, 1H), 3.16 (d, *J* = 9.4 Hz, 1H), 2.50 (s, 1H), 2.25–2.17 (m, 2H), 2.10–2.03 (m, 1H), 1.67 (d, *J* = 5.6 Hz, 2H), 1.41–1.35 (m, 3H), 1.30 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.3, 136.3, 129.2, 128.5, 126.3, 122.1, 120.0, 119.6, 117.1, 74.5, 60.2, 47.1, 44.2, 40.4, 37.7, 33.8, 31.5, 30.9, 25.7.

6,6-dimethyl-5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**h**)

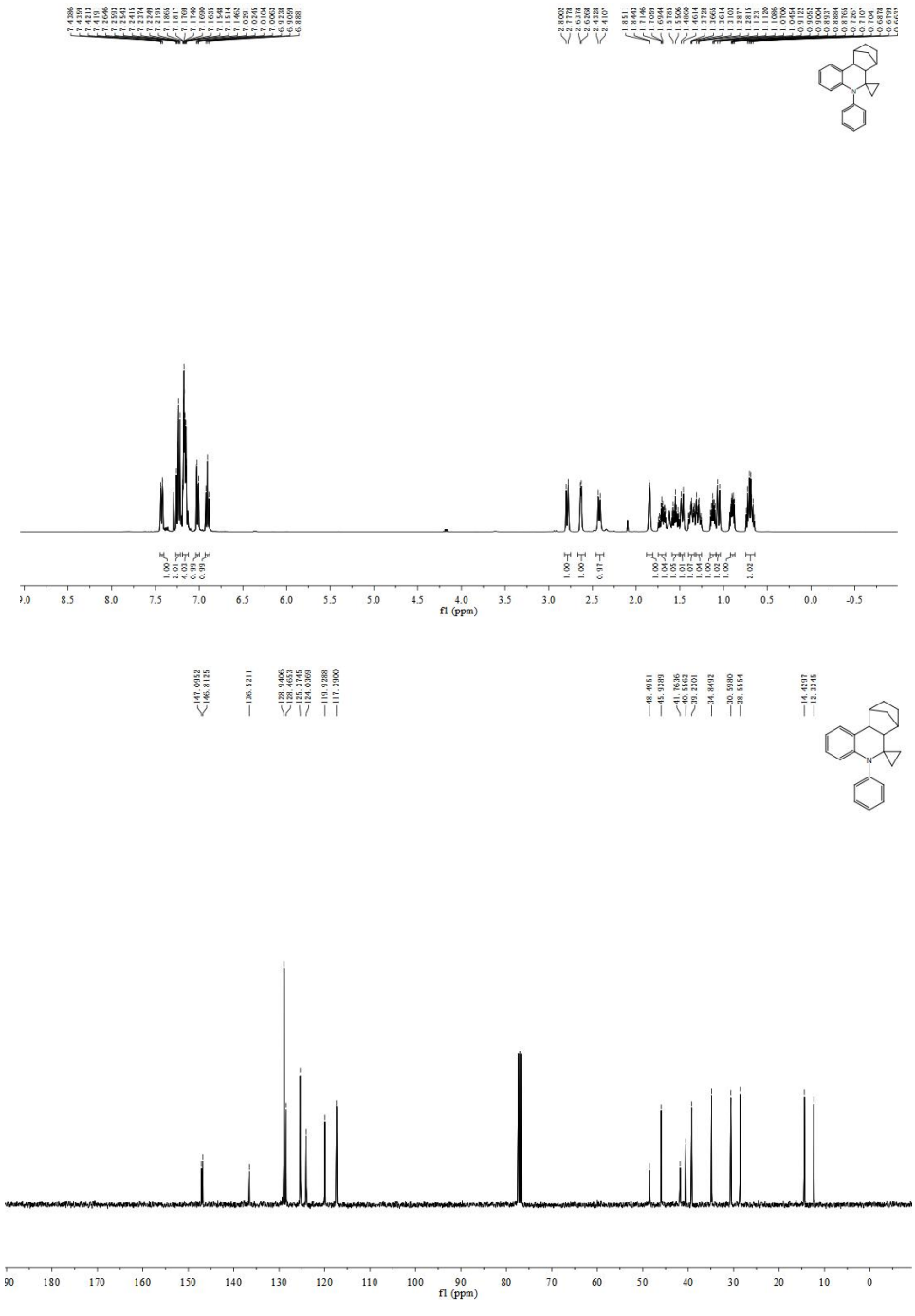




To a solution of EtMgBr (3.0 M in Et_2O, 2.5 eq.) in THF (4.0 M Grignard) was added $Ti(OiPr)_4$ (1.1 eq.) at -78 °C and stirred for 5–10 min. A solution of **1c** (1.0 eq.) in THF (1.0 M lactam) was added dropwise at the same temperature, the mixture was allowed to warm up to rt within 1-2 h and was subsequently heated to reflux (70 °C) for 24 h. Upon warming to room temperature the reaction mixture was quenched with 10% aq. NaOH (0.5 M) and diluted with Et_2O. Anhydrous Na_2SO_4 and NaOH pellets were added and the mixture was stirred at rt until the colour changed to white/yellow and a fine precipitate was formed. The suspension was filtered, the precipitate was washed with Et_2O and the combined filtrates were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the product **i** in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 1H), 7.29–7.20 (m, 2H), 7.19–7.12 (m, 4H), 7.02 (dd, J = 7.4, 1.6 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 2.79 (d, J = 8.8 Hz, 1H), 2.63 (d, J = 4.4 Hz, 1H), 2.42 (d, J = 8.8 Hz, 1H), 1.86–1.81 (m, 1H), 1.76–1.66 (m, 1H), 1.55 (tt, J = 12.2, 4.2 Hz, 1H), 1.47 (d, J = 9.8 Hz, 1H),

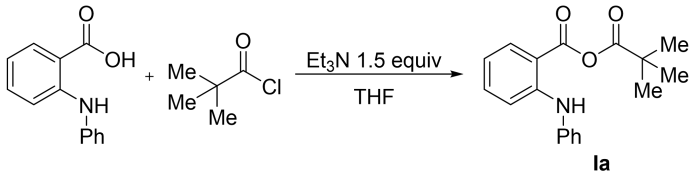
1.40–1.33 (m, 1H), 1.31–1.25 (m, 1H), 1.12 (ddd, J = 10.6, 6.2, 4.8 Hz, 1H), 1.06 (d, J = 9.8 Hz, 1H), 0.93–0.87 (m, 1H), 0.75–0.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 146.8, 136.5, 128.9, 128.5, 125.4, 124.0, 119.9, 117.4, 48.5, 45.9, 41.7, 40.5, 39.2, 34.8, 30.6, 28.5, 14.4, 12.3.

5'-phenyl-6a',7',8',9',10',10a'-hexahydro-5'H-spiro[cyclopropane-1,6'-[7,10] methanophenanthridine] (**i**)



2.3 Control experiments

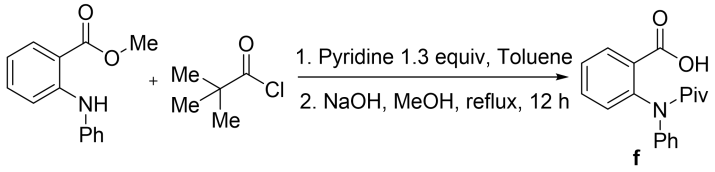
Synthesis of mixed anhydride e and its characterization



Ia

To an oven-dried round bottom flask equipped with a stirring bar containing a solution of pivaloyl chloride (1.5 equiv) in anhydrous THF (2.0 mL) was added dropwise triethylamine (1.5 equiv) in THF (4.0 mL) at -15 ºC. Subsequently, *N*-phenylanthranilic acid (2 mmol, 1 equiv) in THF (2.0 mL) was added dropwise into the solution at -15 °C. The reaction mixture was stirred at -15 ºC overnight and poured into ice-cold saturated aqueous $NaHCO_3$ solution. The aqueous solution was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give mixed anhydride **Ia**.

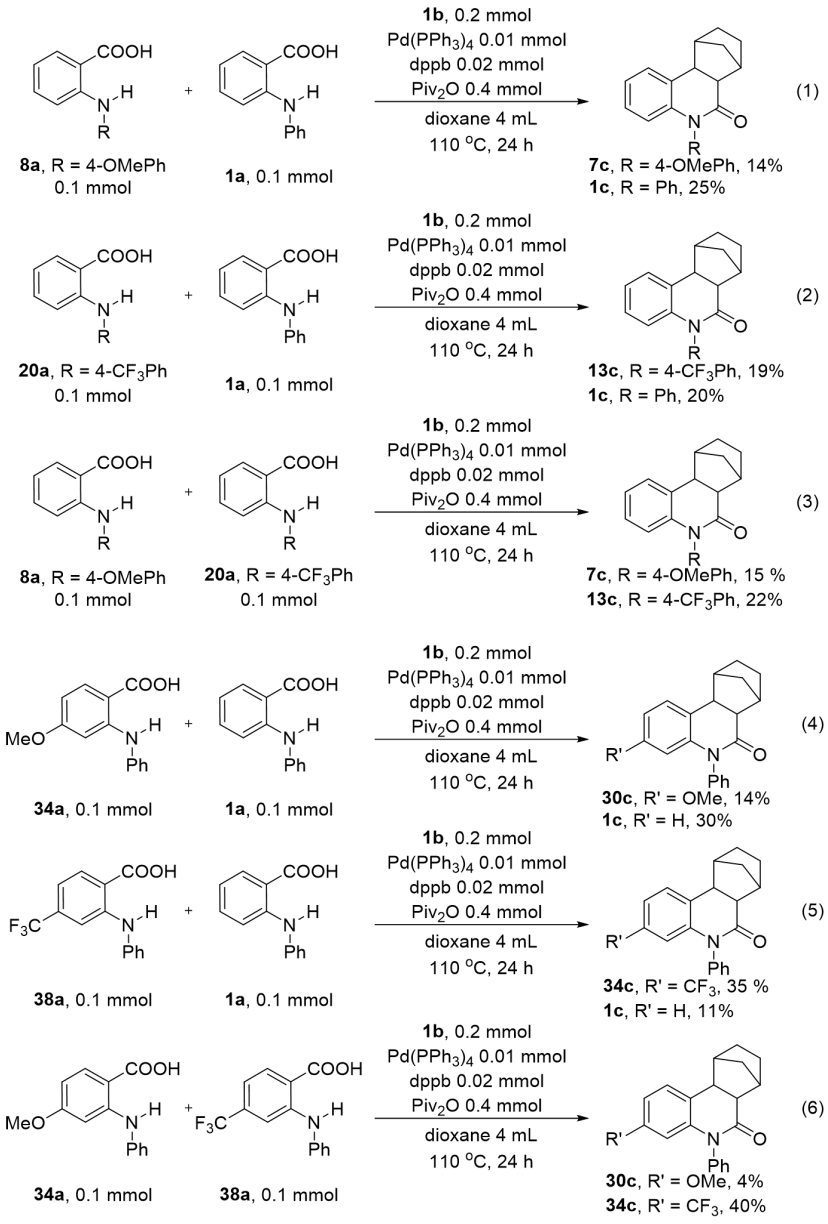
Synthesis of 2-(N-phenylpivalamido)benzoic acid f and its characterization



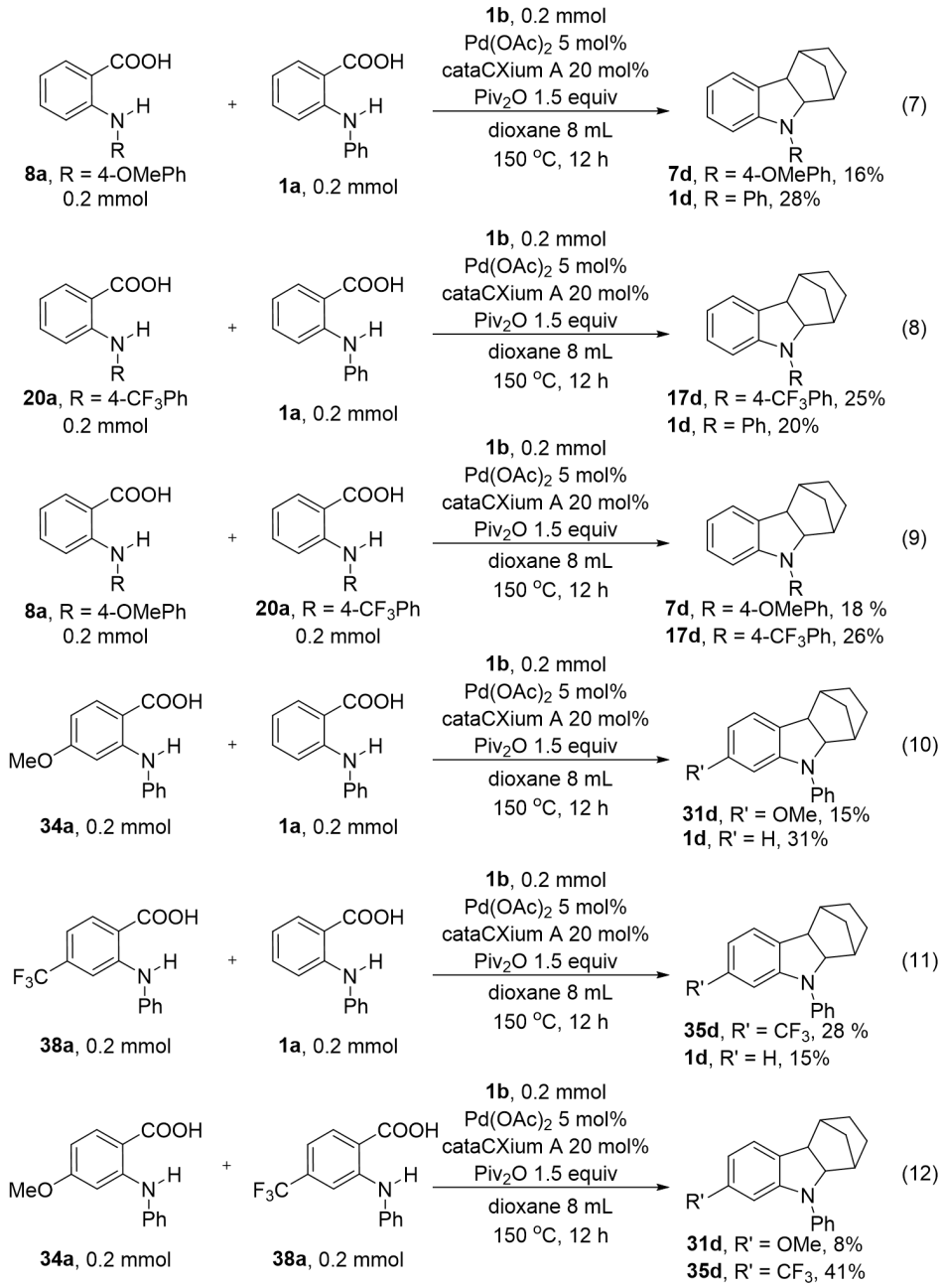
f

Pivaloyl chloride (735 µL, 6.0 mmol) was added to a solution of amine (5.0 mmol) and pyridine (604 µL, 7.5 mmol) in toluene (25 mL) at room temperature, and the resulting mixture was refluxed for 72 h. Then, the mixture was cooled to room temperature, diluted with DCM (75 mL) and washed with water (4 × 150 mL). The combined aqueous phases were washed with DCM (1 × 80 mL) and then the combined organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel.

2.4 Intermolecular Competition Experiments

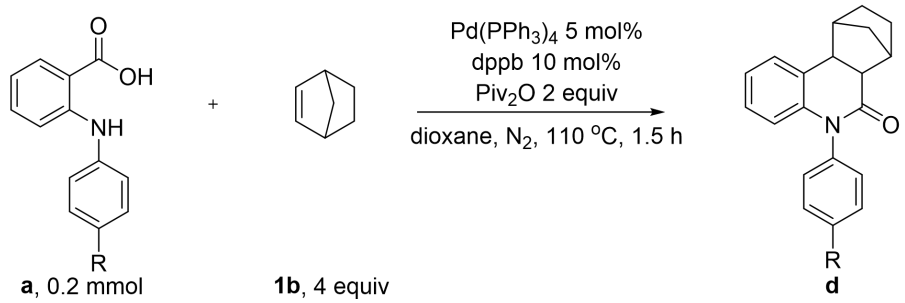


Experimental procedure taking eq 1 as an example: An oven dried 25 mL Schlenk tube was charged with 2-((4-methoxyphenyl)amino)benzoic acid **8a** (0.2 mmol, 1.0 equiv), 2-(phenylamino)benzoic acid **1a** (0.2 mmol, 1.0 equiv), *NBE* **1b** (0.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5 mol%) and dppb (10 mol%). Subsequently, Piv_2O (2.0 equiv), and dioxane (4 mL) were added under N_2. The reaction mixture was allowed to react at 110 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard.

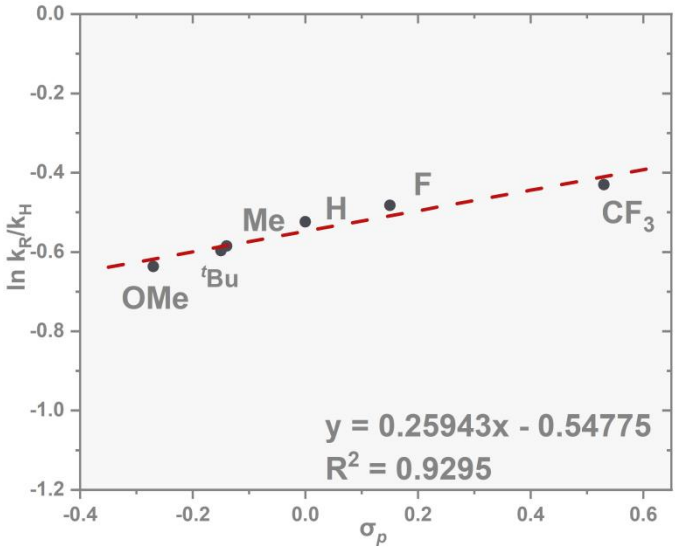


Experimental procedure taking eq 7 as an example: An oven dried 25 mL Schlenk tube was charged with 2-((4-methoxyphenyl)amino)benzoic acid **8a** (0.2 mmol, 1.0 equiv), 2-(phenylamino)benzoic acid **1a** (0.2 mmol, 1.0 equiv), *NBE* **1b** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv_2O (1.5 equiv), and dioxane (8 mL) were added under N_2. The reaction mixture was allowed to react at 150 °C for 12 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard.

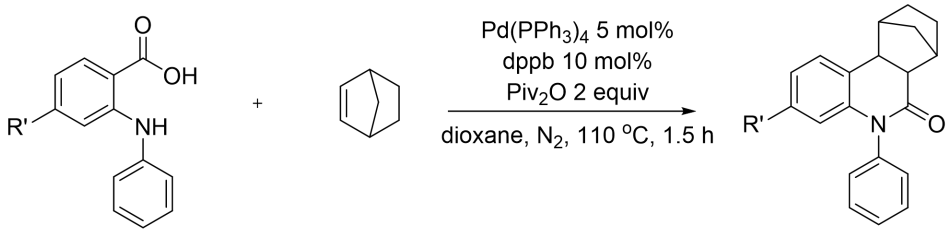
2.5 Substituent Effect of Substrates



R	OMe	^{t}Bu	Me	H	F	CF_3
Yield	25.5 %	26.6 %	26.9 %	28.6 %	29.8 %	31.4 %

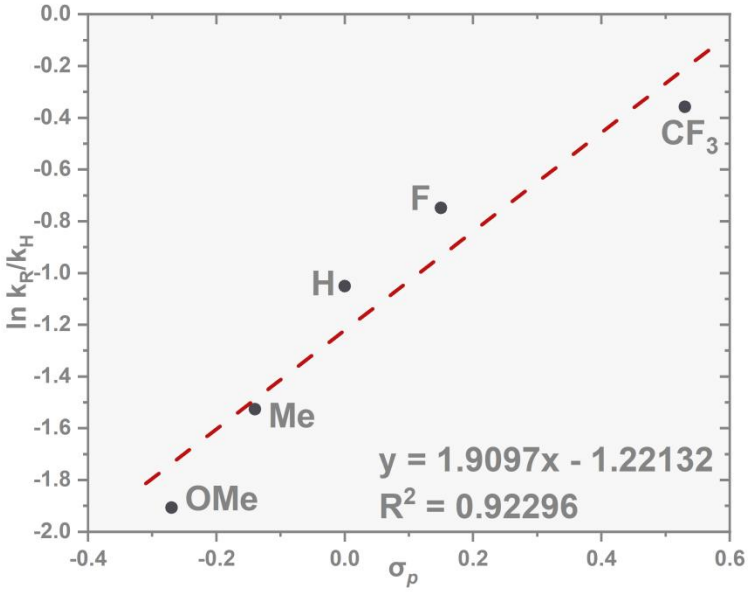


A typical experimental procedure of CO reinsertion process: An oven dried 25 mL Schlenk tube was charged with substitued 2-(phenylamino)benzoic acid **a** (0.2 mmol), *NBE* **1b** (4 equiv), $Pd(PPh_3)_4$ (5 mol%) and dppb (10 mol%). Subsequently, Piv_2O (2 equiv) and dioxane (4 mL) was added under N_2. The reaction mixture was allowed to react at 110 °C for 1.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

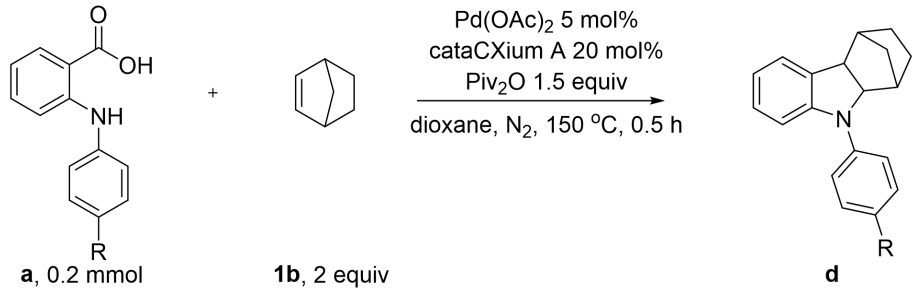


a, 0.2 mmol **1b**, 4 equiv **d**

R	OMe	Me	H	F	CF_3
Yield	8.2 %	12 %	19.3 %	26.1 %	38.6 %

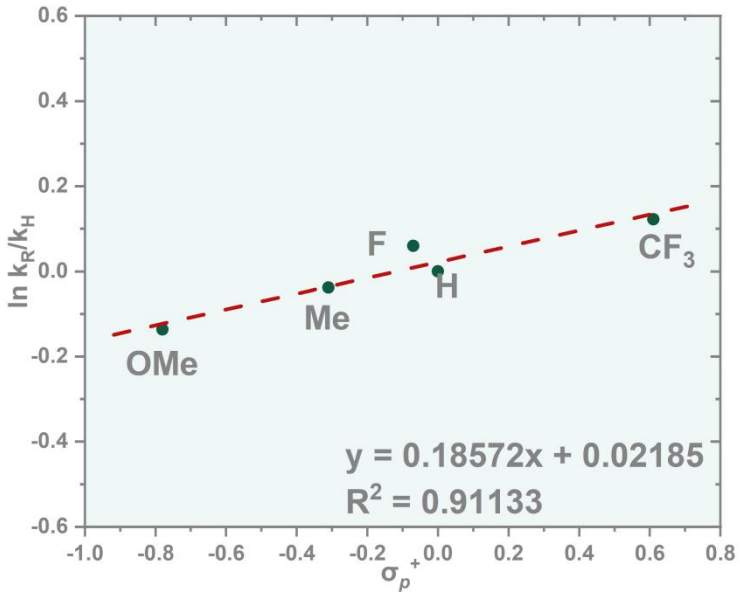


A typical experimental procedure of CO reinsertion process: An oven dried 25 mL Schlenk tube was charged with substitued 2-(phenylamino)benzoic acid **a** (0.2 mmol), *NBE* **1b** (4 equiv), $Pd(PPh_3)_4$ (5 mol%) and dppb (10 mol%). Subsequently, Piv_2O (2 equiv) and dioxane (4 mL) was added under N_2. The reaction mixture was allowed to react at 110 °C for 1.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

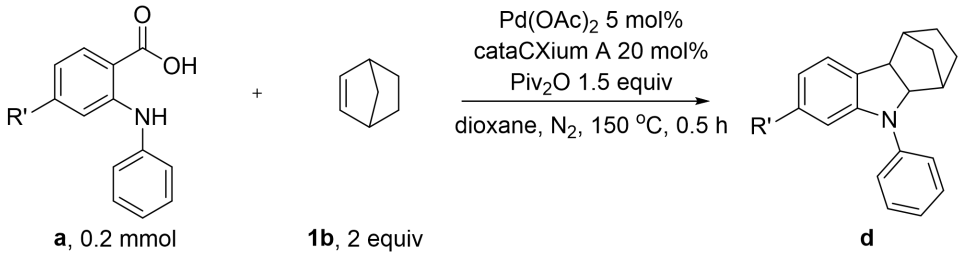


a, 0.2 mmol **1b**, 2 equiv **d**

R	OMe	Me	H	F	CF_3
Yield	31.0%	34.2%	35.5%	37.7%	40.1%

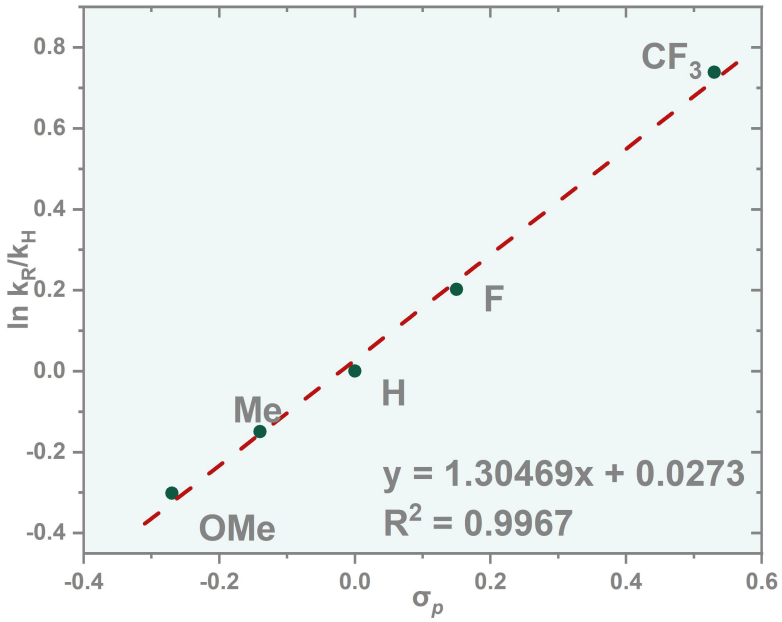


A typical experimental procedure of decarbonylative process: An oven dried 25 mL Schlenk tube was charged with substitued 2-(phenylamino)benzoic acid **a** (0.2 mmol), *NBE* **1b** (2 equiv), $Pd(OAc)_2$ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv_2O (1.5 equiv) and dioxane (8 mL) was added under N_2. The reaction mixture was allowed to react at 150 °C for 0.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.



a, 0.2 mmol **1b**, 2 equiv **d**

R'	OMe	Me	H	F	CF_3
Yield	18.8%	21.9%	25.4%	31.1%	53.2%



A typical experimental procedure of decarbonylative process: An oven dried 25 mL Schlenk tube was charged with substitued 2-(phenylamino)benzoic acid **a** (0.2 mmol), *NBE* **1b** (2 equiv), $Pd(OAc)_2$ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv_2O (1.5 equiv) and dioxane (8 mL) was added under N_2. The reaction mixture was allowed to react at 150 °C for 0.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

2.6 Reaction progress kinetic analysis

To provide further information about the reaction mechanism, kinetic experiments were performed to establish the rate laws of the cyclization using the reaction of **1a** and **1b** as a model reaction. All the kinetic data were taken at the time points in the early stage of reaction. With the help of GC tracking on product formation, we evaluated the dependence of the average rate after the initiation period on the **1a**, **1b**, Pd catalyst and **1c** or **1d** concentrations in each case. (Note: Every indicated times represent one independent experiment).

The rate on the concentration of 1a in CO reinsertion process

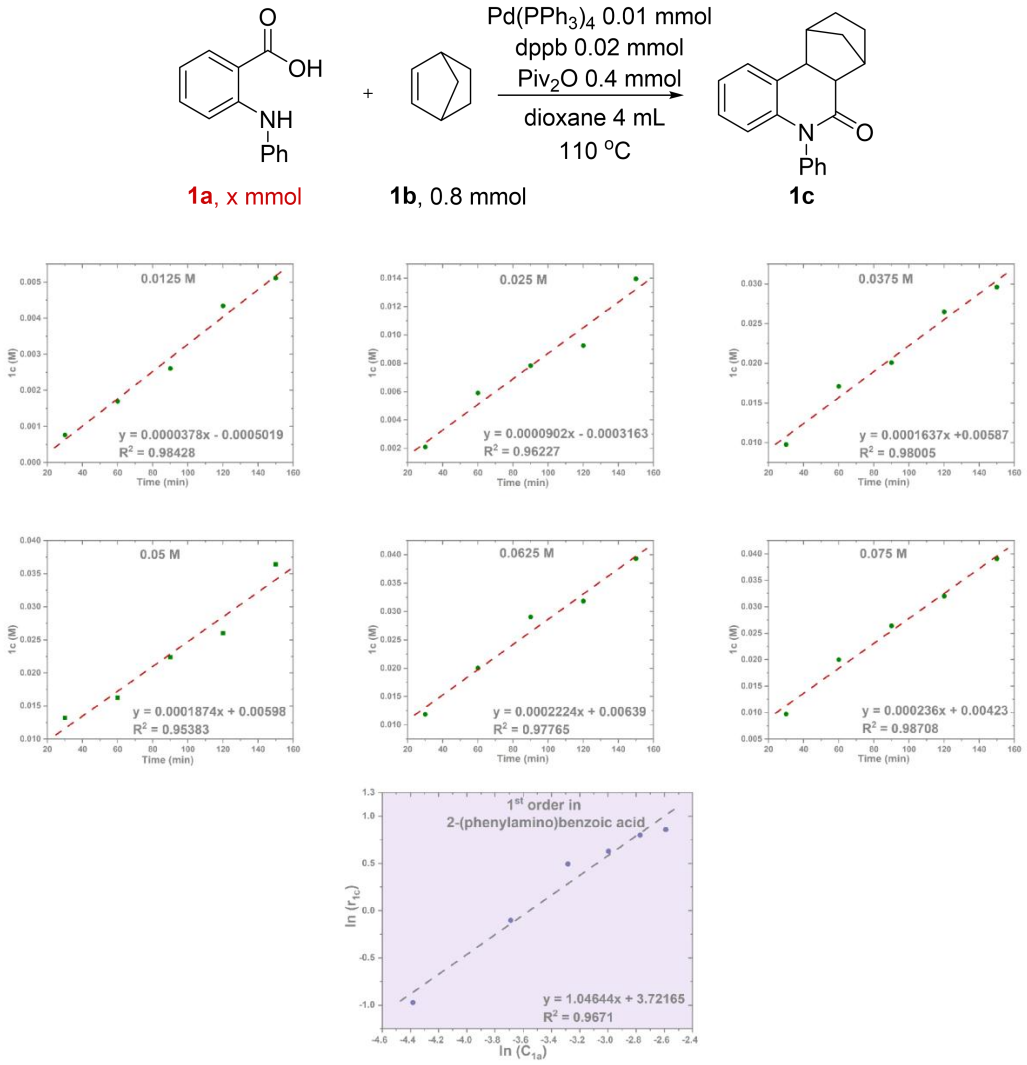


Fig. S3. Plot of the rise of product and the rate on the concentration of **1a** from the reaction of **1b** (0.8 mmol), $Pd(PPh_3)_4$ (0.01 mmol), dppb (0.02 mmol), Piv_2O (0.4 mmol) with 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol, 0.25 mmol, 0.3 mmol of **1a**.

The rate on the concentration of 1b in CO reinsertion process

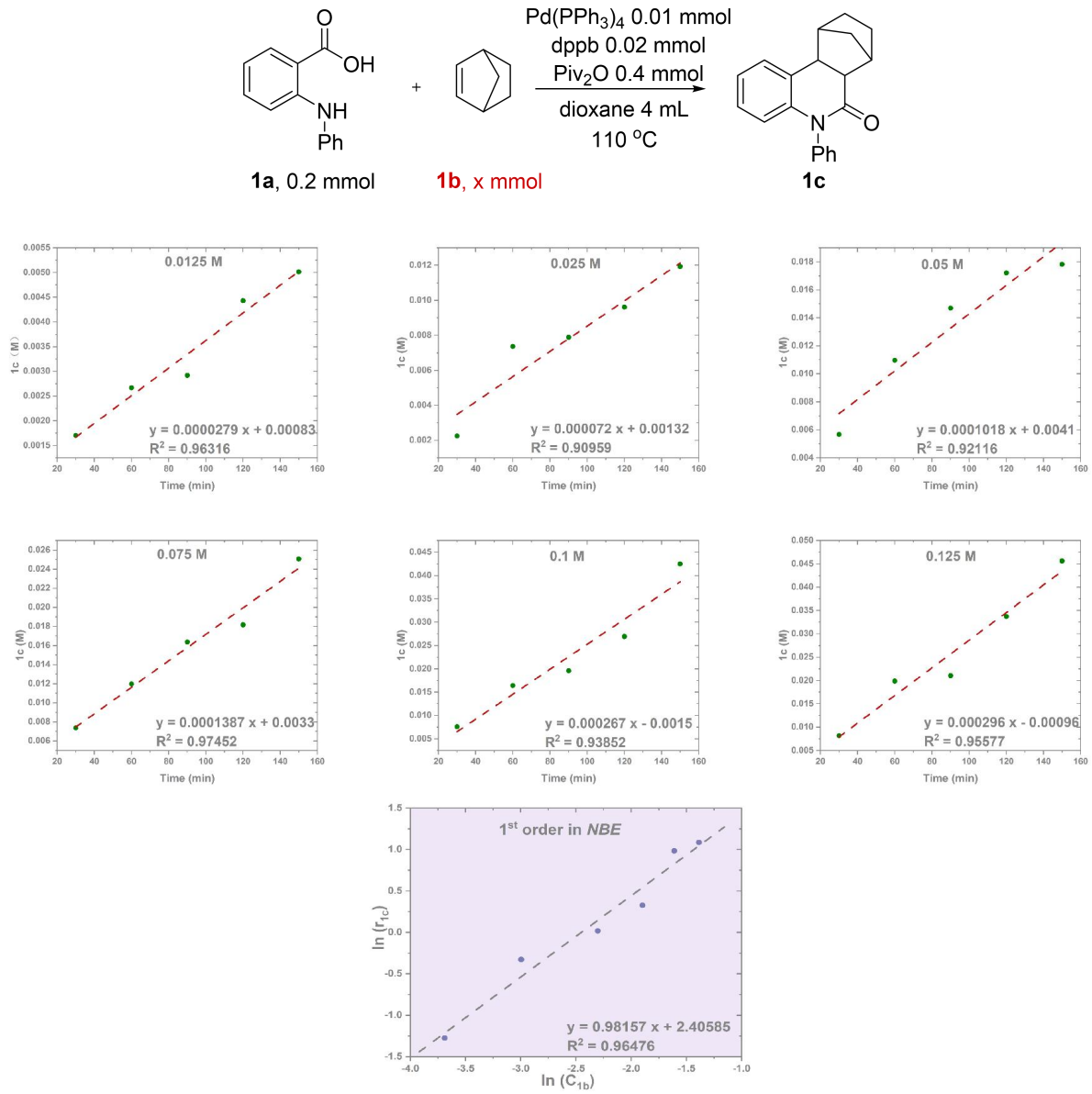


Fig. S4. Plot of the rise of product and the rate on the concentration of **1b** from the reaction of **1a** (0.2 mmol), $Pd(PPh_3)_4$ (0.01 mmol), dppb (0.02 mmol), Piv_2O (0.4 mmol) with 0.1 mmol, 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1 mmol of **1b**.

The rate on the concentration of $Pd(PPh_3)_4$ in CO reinsertion process

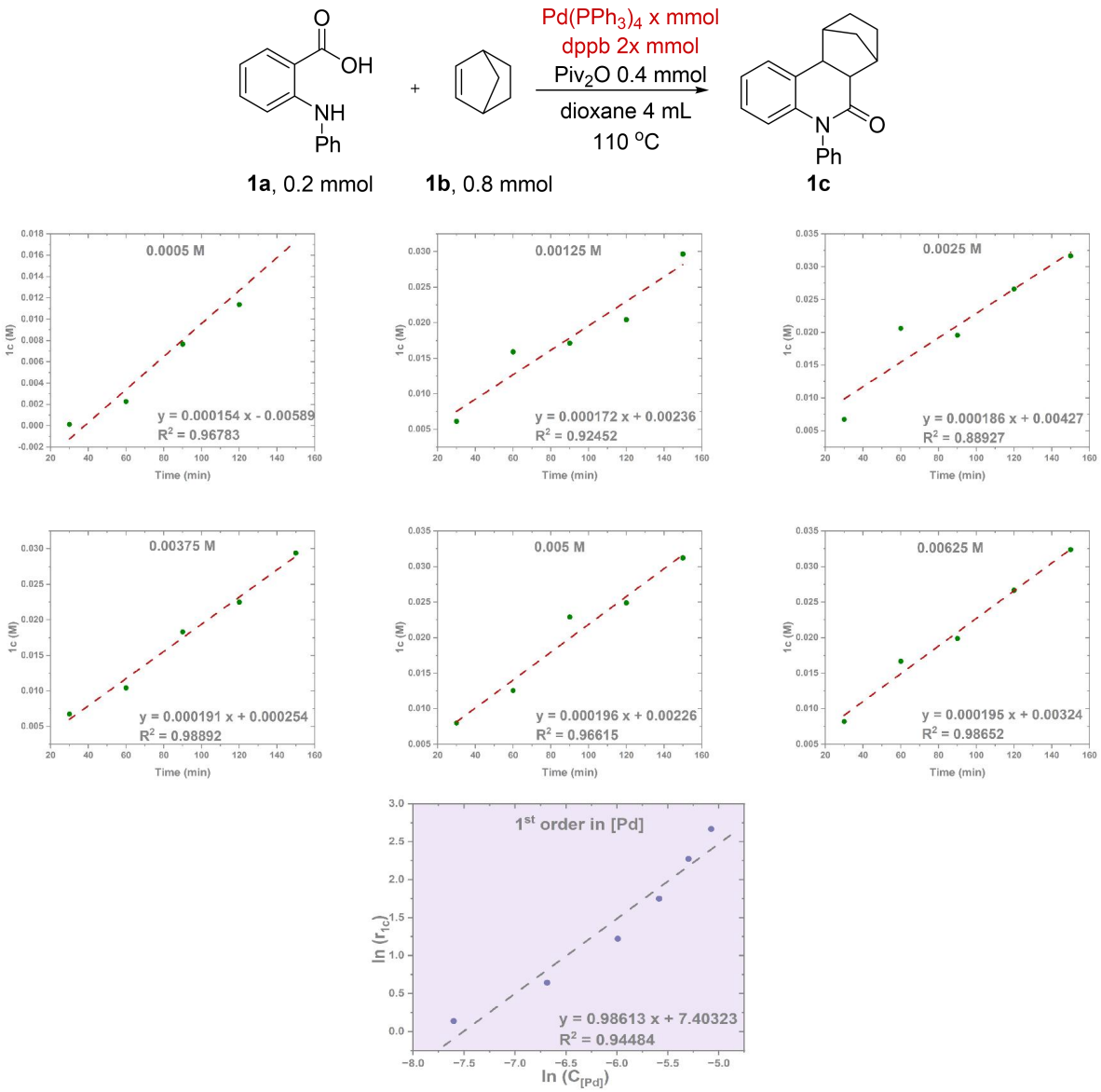
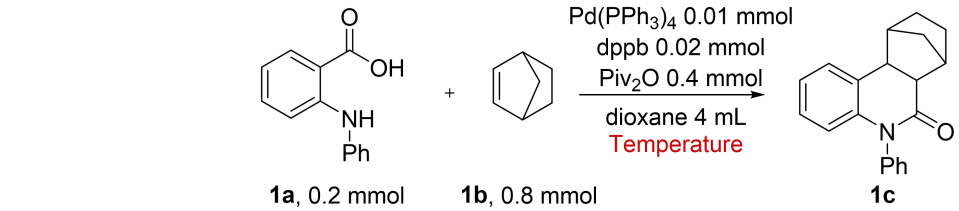


Fig. S5. Plot of the rise of product and the rate on the concentration of [Pd] from the reaction of **1a** (0.2 mmol), **1b** (0.8 mmol), Piv_2O (0.4 mmol) with 0.002 mmol, 0.005 mmol, 0.01 mmol, 0.015 mmol, 0.02 mmol, 0.025 mmol of [Pd].

Arrhenius plot: plot of ln*k* *vs* 1/T



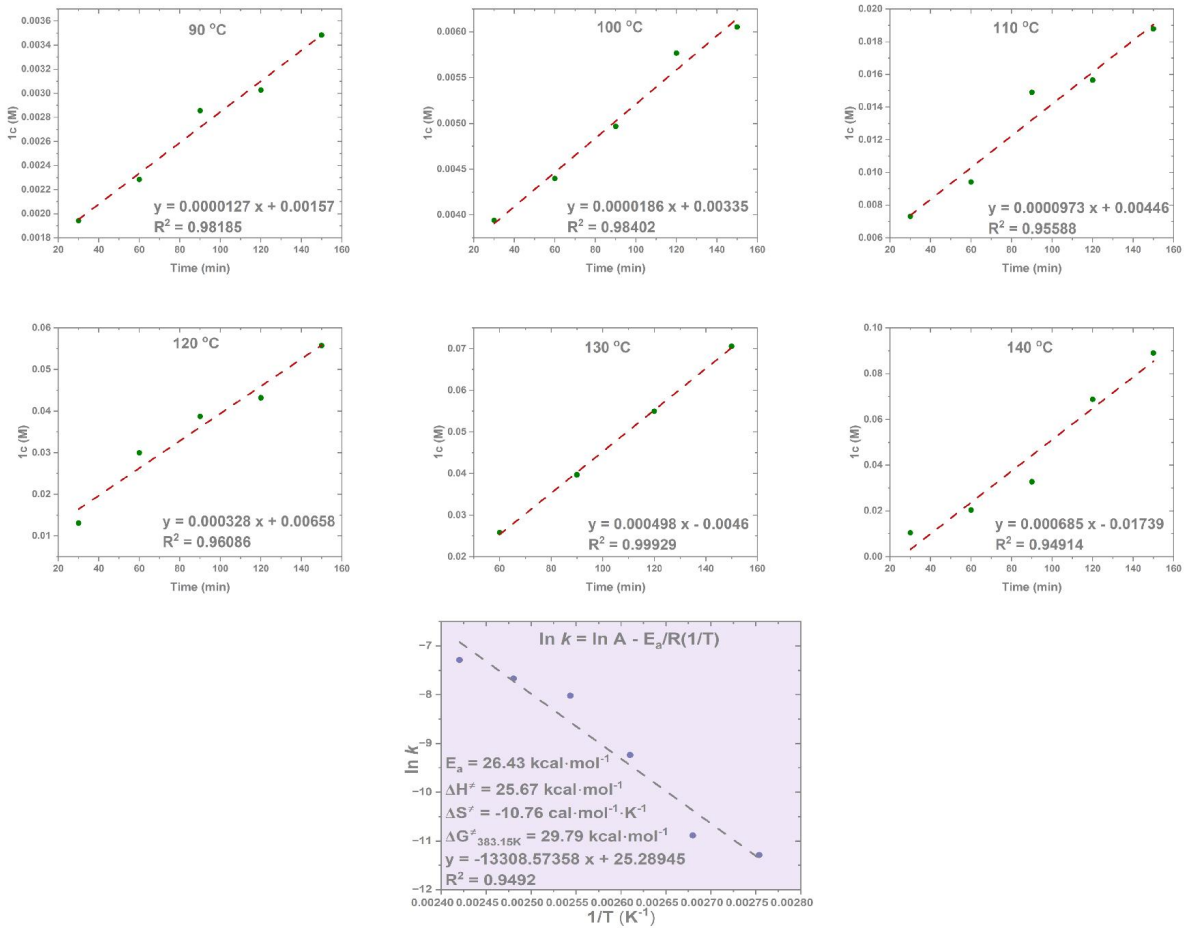


Fig. S6. Comparison of the temperature dependence of the rate constant for the **1a** and **1b**; an arrhenius plot of ln *k* vs. 1/T for the reaction of **1a** and **1b**.

The rate on the concentration of 1a in decarbonylative process

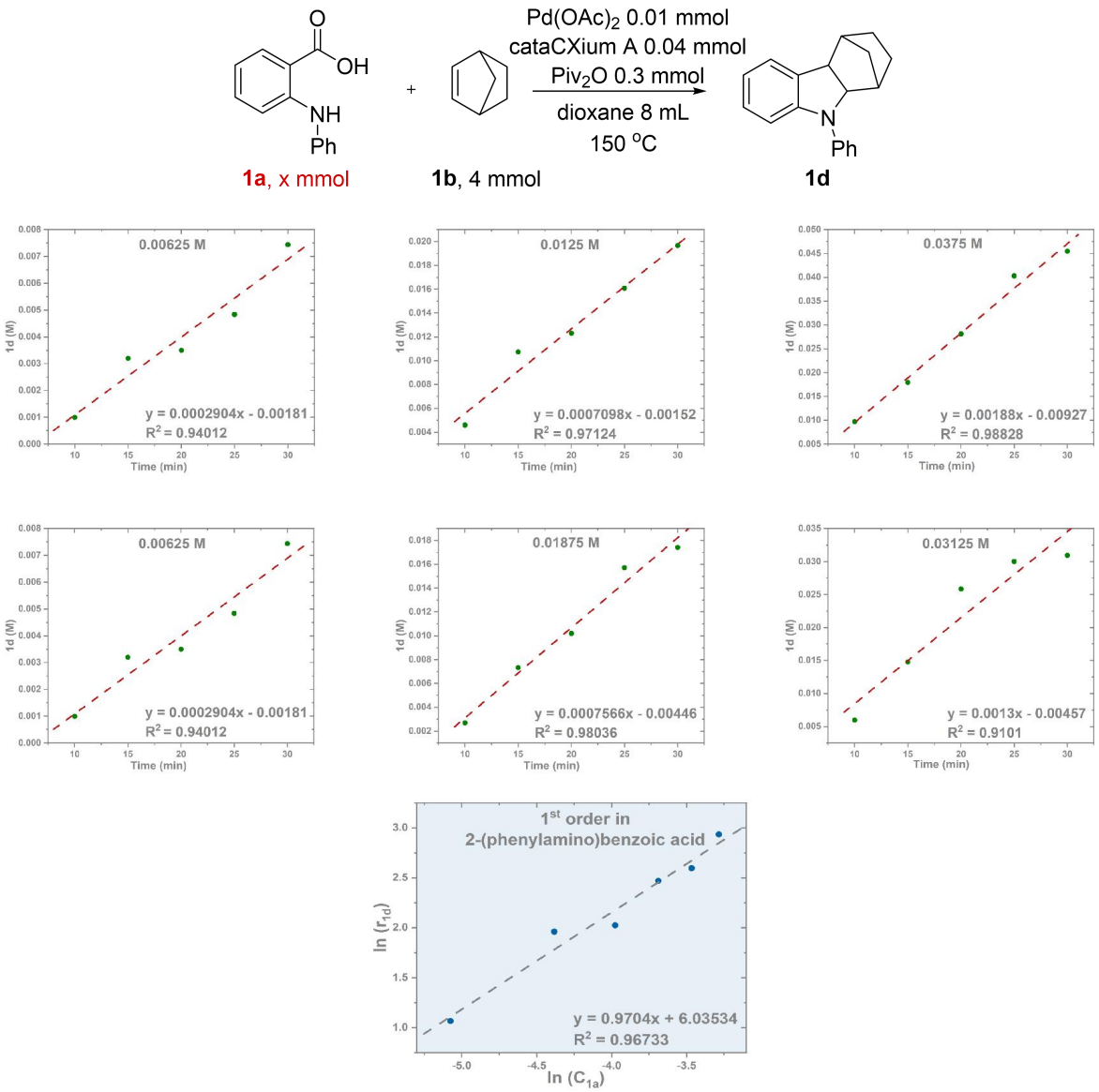


Fig. S7. Plot of the rise of product and the rate on the concentration of **1a** from the reaction of **1b** (0.4 mmol), $Pd(OAc)_2$ (0.01 mmol), cataCXium A (0.04 mmol), Piv_2O (0.3 mmol) with 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol, 0.25 mmol, 0.3 mmol of **1a**.

The rate on the concentration of 1b in decarbonylative process

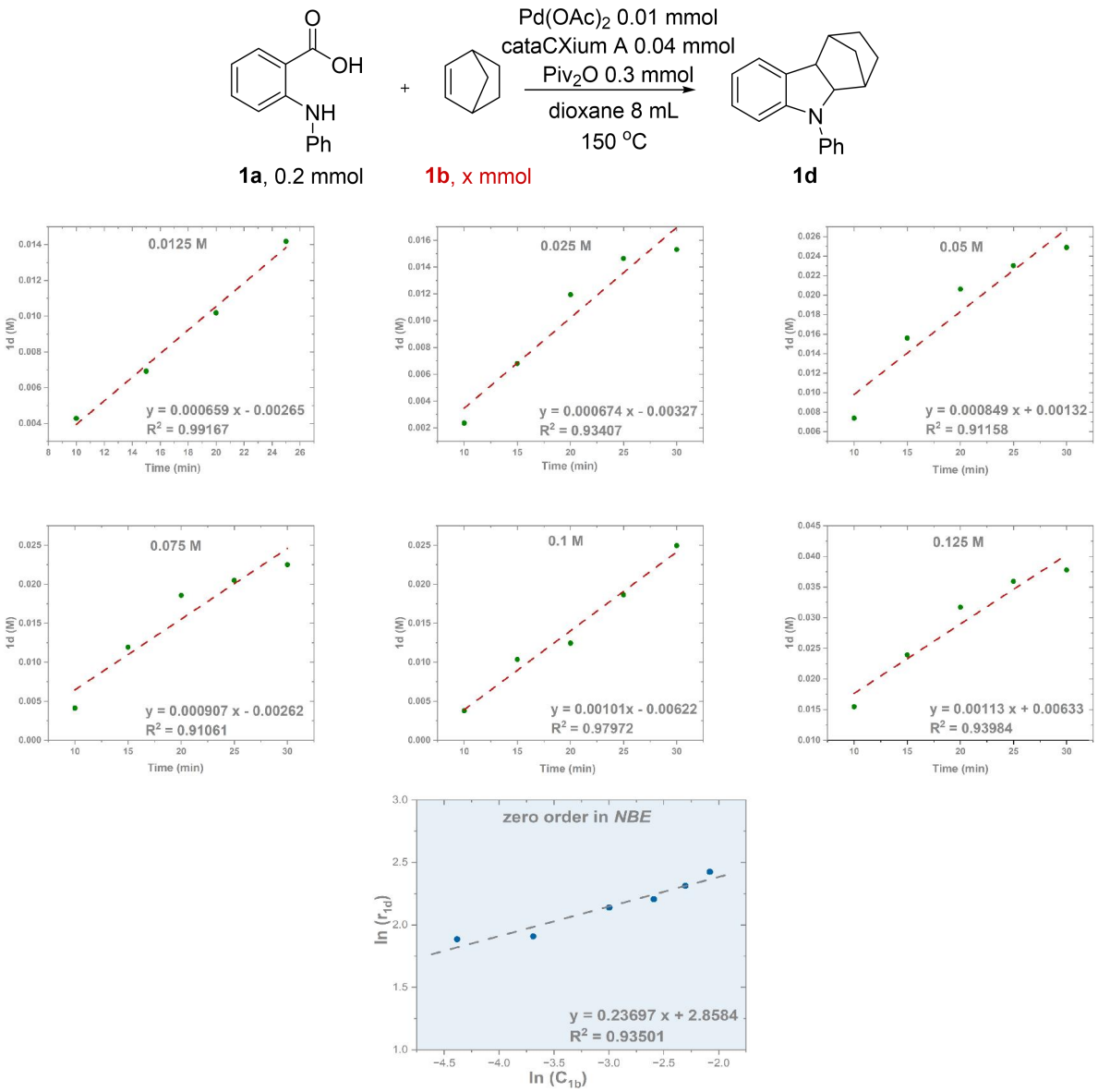


Fig. S8. Plot of the rise of product and the rate on the concentration of **1b** from the reaction of **1a** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), cataCXium A (0.04 mmol), Piv_2O (0.3 mmol) with 0.1 mmol, 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1 mmol of **1b**.

The rate on the concentration of $Pd(OAc)_2$ in decarbonylative process

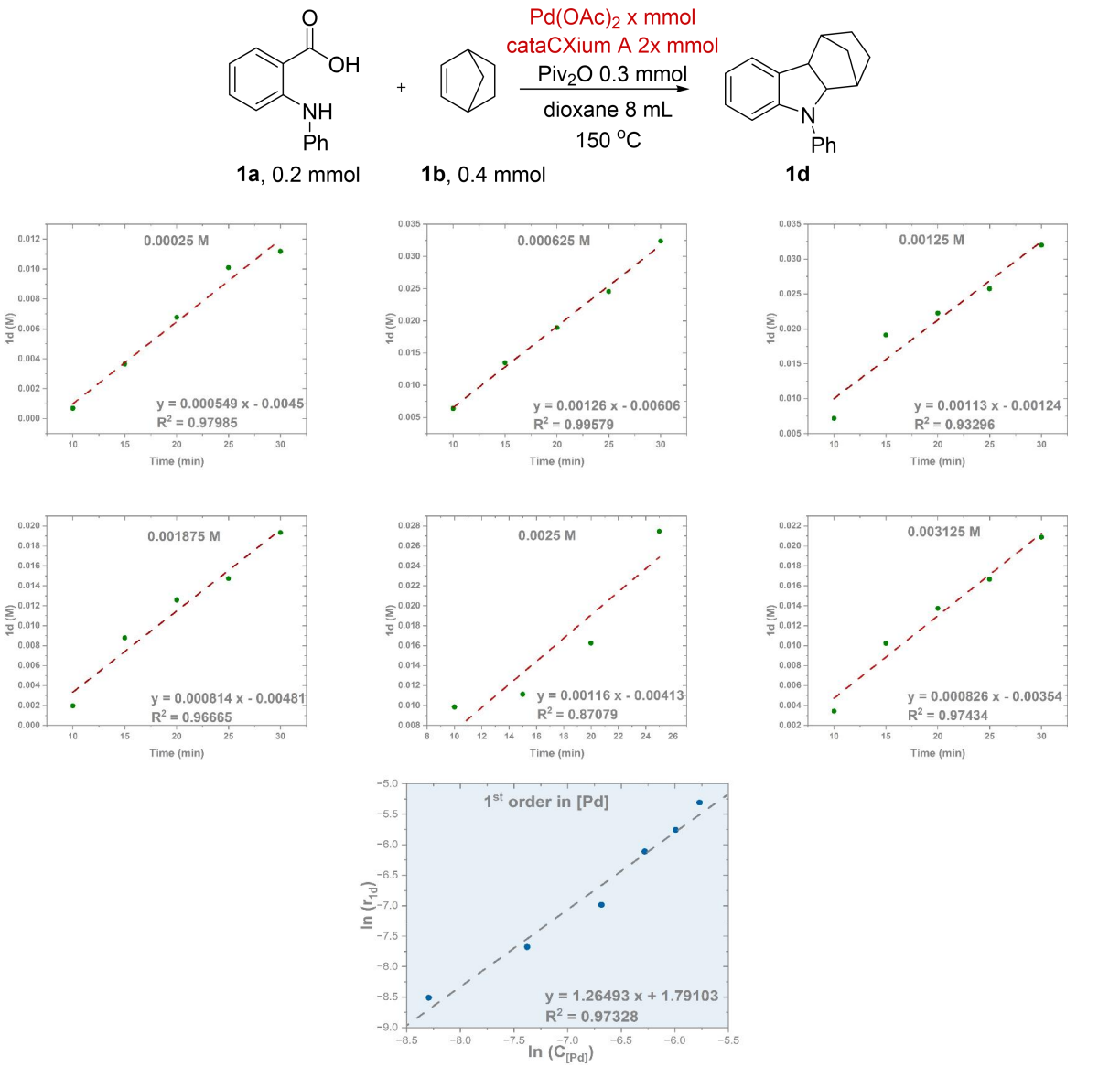


Fig. S9. Plot of the rise of product and the rate on the concentration of [Pd] from the reaction of **1a** (0.2 mmol), **1b** (0.4 mmol), Piv_2O (0.3 mmol) with 0.002 mmol, 0.005 mmol, 0.01 mmol, 0.015 mmol, 0.02 mmol, 0.025 mmol of [Pd].

Arrhenius plot: plot of lnk vs 1/T

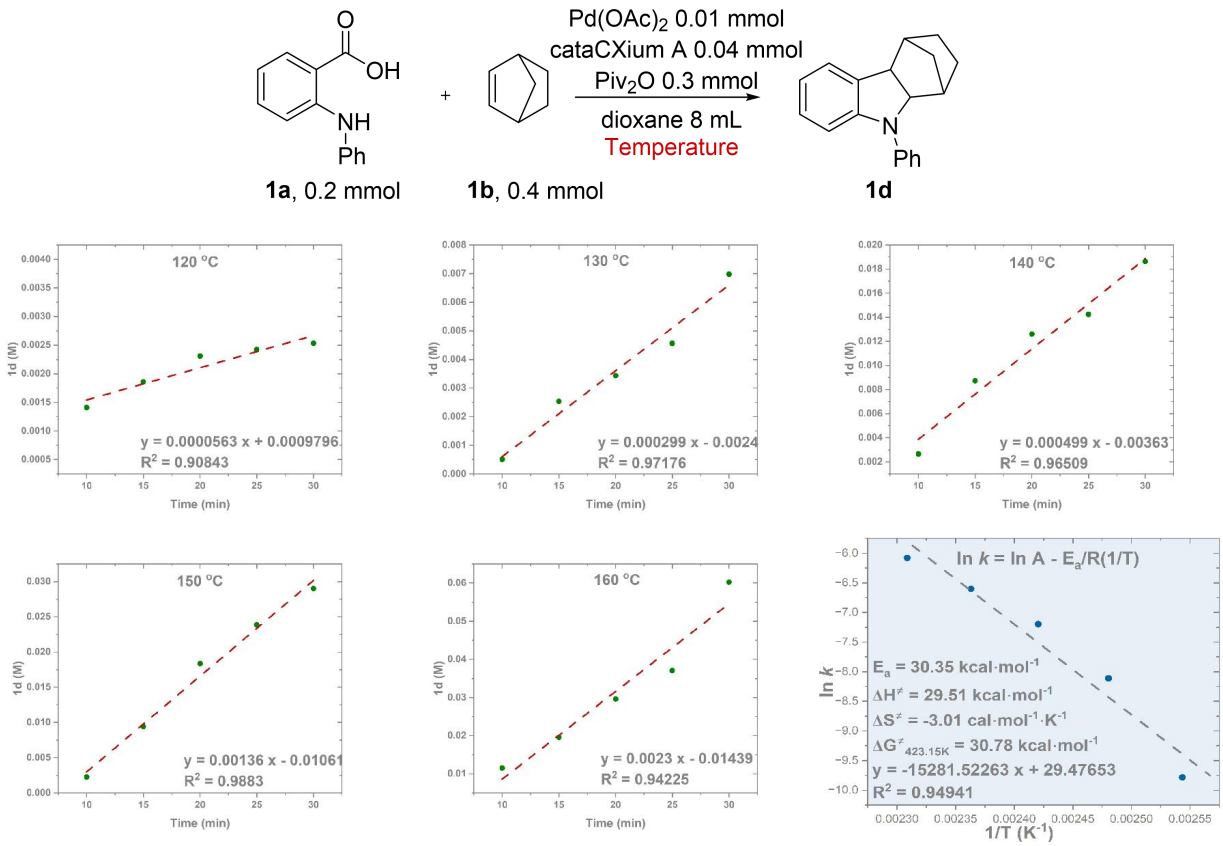
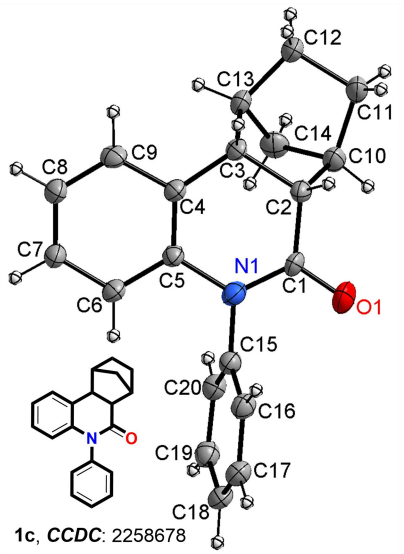


Fig. S10. Comparison of the temperature dependence of the rate constant for the **1a** and **1b**; an arrhenius plot of ln k vs. 1/T for the reaction of **1a** and **1b**.

2.X-ray Crystallographic Data

X-ray data for compound **1c**, CCDC: 2258678



Supplementary Table 1. Crystal data and structure refinement for **1c**

chemical formula	$C_{20}H_{19}NO$
formula weight	289.36
crystal size (mm)	0.21×0.17×0.05
temperature (K)	298(2)
radiation	0.71073
crystal system	Monoclinic
space group	$P2_{(1)}/n$
a(Å)	5.6735(6)
b(Å)	19.723(2)
c(Å)	14.1155(17)
α(°)	90.00
β(°)	101.542(4)
γ(°)	90.00
V(Å^3)	1547.6(3)
Z	4
$\rho_{(calc)}$ (g/cm^3)	1.242
F (000)	616
absorp.coeff. (mm^{-1})	0.076
θ range (deg)	2.537 to 28.307

Supplementary Table 2. Bond distance data of compound **1c**

Bond		Length(Å)
N1	C1	1.370(14)

N1	C15	1.433(14)
N1	C5	1.474(15)
O1	C1	1.232(13)
C1	C2	1.507(16)
C2	C10	1.539(17)
C2	C3	1.576(16)
C2	H2	0.98
C3	C4	1.502(15)
C3	C13	1.525(16)
C3	H3	0.98
C4	C5	1.349(16)
C4	C9	1.443(17)
C5	C6	1.405(15)
C6	C7	1.400(17)
C6	H6	0.93
C7	C8	1.339(16)
C7	H7	0.93
C8	C9	1.375(16)
C8	H8	0.93
C9	H9	0.93
C10	C14	1.519(17)
C10	C11	1.538(18)
C10	H10	0.98
C11	C12	1.551(17)
C11	H11A	0.97
C11	H11B	0.97
C12	C13	1.527(16)
C12	H12A	0.97
C12	H12B	0.97
C13	C14	1.538(18)
C13	H13	0.98
C14	H14A	0.97
C14	H14B	0.97
C15	C20	1.381(8)
C15	C16	1.385(8)
C16	C17	1.388(8)
C16	H16	0.93
C17	C18	1.382(8)
C17	H17	0.93
C18	C19	1.382(8)
C18	H18	0.93
C19	C20	1.389(8)
C19	H19	0.93
C20	H20	0.93

Supplementary Table 3. Bond angle data of compound **1c**

Angle			Degree(°)
C1	N1	C15	119.2(11)
C1	N1	C5	121.3(10)
C15	N1	C5	119.4(10)
O1	C1	N1	119.1(12)
O1	C1	C2	119.6(12)
N1	C1	C2	121.2(11)
C1	C2	C10	110.1(11)
C1	C2	C3	118.3(10)
C10	C2	C3	103.0(10)
C1	C2	H2	108.3
C10	C2	H2	108.3
C3	C2	H2	108.3
C4	C3	C13	112.3(10)
C4	C3	C2	113.0(10)
C13	C3	C2	101.9(9)
C4	C3	H3	109.8
C13	C3	H3	109.8
C2	C3	H3	109.8
C5	C4	C9	117.9(12)
C5	C4	C3	125.2(12)
C9	C4	C3	116.9(11)
C4	C5	C6	122.2(12)
C4	C5	N1	120.8(11)
C6	C5	N1	116.9(11)
C7	C6	C5	118.1(12)
C7	C6	H6	120.9
C5	C6	H6	120.9
C8	C7	C6	120.8(13)
C8	C7	H7	119.6
C6	C7	H7	119.6
C7	C8	C9	121.6(13)
C7	C8	H8	119.2
C9	C8	H8	119.2
C8	C9	C4	119.3(12)
C8	C9	H9	120.3
C4	C9	H9	120.3
C14	C10	C11	101.0(11)
C14	C10	C2	100.5(10)
C11	C10	C2	109.6(12)
C14	C10	H10	114.7
C11	C10	H10	114.7
C2	C10	H10	114.7
C10	C11	C12	104.5(11)

C10	C11	H11S	110.8
C12	C11	H11A	110.8
C10	C11	H11B	110.8
C12	C11	H11B	110.8
H11A	C11	H11B	108.9
C13	C12	C11	101.4(10)
C13	C12	H12A	111.5
C11	C12	H12A	111.5
C13	C12	H12B	111.5
C11	C12	H12B	111.5
H12A	C12	H12B	109.3
C3	C13	C12	109.6(11)
C3	C13	C14	102.4(10)
C12	C13	C14	102.6(11)
C3	C13	H13	113.7
C12	C13	H13	113.7
C14	C13	H13	113.7
C10	C14	C13	94.2(11)
C10	C14	H14A	112.9
C13	C14	H14A	112.9
C10	C14	H14B	112.9
C13	C14	H114B	112.9
H14A	C14	H14B	110.3
C20	C15	C16	118.9(12)
C20	C15	N1	121.2(10)
C16	C15	N1	119.9(10)
C15	C16	C17	120.4(12)
C15	C16	H16	119.8
C17	C16	H16	119.8
C18	C17	C16	120.4(13)
C18	C17	H17	119.8
C16	C17	H17	119.8
C19	C18	C17	119.4(12)
C19	C18	H18	120.3
C17	C18	H18	120.3
C18	C18	C20	120.0(13)
C18	C18	H19	120.0
C20	C19	H19	120.0
C15	C20	C19	120.7(12)
C15	C20	H20	119.6
C19	C20	H20	119.6

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 230417a

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Bond precision:   C-C = 0.0177 A          Wavelength=0.71073

Cell:             a=5.6735(6)     b=19.723(2)         c=14.1155(17)
                  alpha=90        beta=101.542(4)     gamma=90
Temperature:      298 K

                  Calculated                  Reported
Volume            1547.6(3)                   1547.6(3)
Space group       P 21/c                      P2(1)/c
Hall group        -P 2ybc                     ?
Moiety formula    C20 H19 N O                 ?
Sum formula       C20 H19 N O                 C20 H19 N O
Mr                289.36                      289.36
Dx,g cm-3         1.242                       1.242
Z                 4                           4
Mu (mm-1)         0.076                       0.076
F000              616.0                       616.0
F000'             616.24
h,k,lmax          6,23,16                     6,23,16
Nref              2741                        2652
Tmin,Tmax         0.985,0.996                 0.984,0.996
Tmin'             0.984

Correction method= # Reported T Limits: Tmin=0.984 Tmax=0.996
AbsCorr = MULTI-SCAN

Data completeness= 0.968          Theta(max)= 25.020

R(reflections)= 0.1981( 876)                  wR2(reflections)=
                                              0.4151( 2652)
S = 1.237                 Npar= 201
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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
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Alert level B

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PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low ..        33% Check
PLAT031_ALERT_4_B Refined Extinction Parameter Within Range of ...     1.857 Sigma
PLAT082_ALERT_2_B High R1 Value ..................................      0.20 Report
PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ...................      0.42 Report
PLAT340_ALERT_3_B Low Bond Precision on  C-C Bonds ...............   0.01768 Ang.
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Alert level C

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PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .     0.968 Why?
PLAT234_ALERT_4_C Large Hirshfeld Difference C13      --C14      .      0.18 Ang.
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Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         6 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        16 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical         ? Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      6.75 Why ?
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT793_ALERT_4_G Model has Chirality at C2           (Centro SPGR)        S Verify
PLAT793_ALERT_4_G Model has Chirality at C3           (Centro SPGR)        R Verify
PLAT793_ALERT_4_G Model has Chirality at C10          (Centro SPGR)        R Verify
PLAT793_ALERT_4_G Model has Chirality at C13          (Centro SPGR)        S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       396 Note
PLAT881_ALERT_1_G No Datum for _diffrn_reflns_av_R_equivalents ...     Please Do !
PLAT899_ALERT_4_G SHELXL97  is Deprecated and Succeeded by SHELXL-     2019/2 Note
```

```
   0 ALERT level A - Most likely a serious problem - resolve or explain
   5 ALERT level B - A potentially serious problem, consider carefully
   2 ALERT level C - Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G - General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

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# start Validation Reply Form
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;
PROBLEM: Ratio Observed / Unique Reflections (too) Low ..        33% Check
RESPONSE: ...
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;
_vrf_PLAT031_230417a
;
PROBLEM: Refined Extinction Parameter Within Range of ...      1.857 Sigma
RESPONSE: ...
;
_vrf_PLAT082_230417a
;
PROBLEM: High R1 Value ..................................       0.20 Report
RESPONSE: ...
;
_vrf_PLAT084_230417a
;
PROBLEM: High wR2 Value (i.e. > 0.25) ...................       0.42 Report
RESPONSE: ...
;
_vrf_PLAT340_230417a
;
PROBLEM: Low Bond Precision on  C-C Bonds ...............    0.01768 Ang.
RESPONSE: ...
;
_vrf_PLAT029_230417a
;
PROBLEM: _diffrn_measured_fraction_theta_full value Low .      0.968 Why?
RESPONSE: ...
;
_vrf_PLAT234_230417a
;
PROBLEM: Large Hirshfeld Difference C13      --C14      .       0.18 Ang.
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

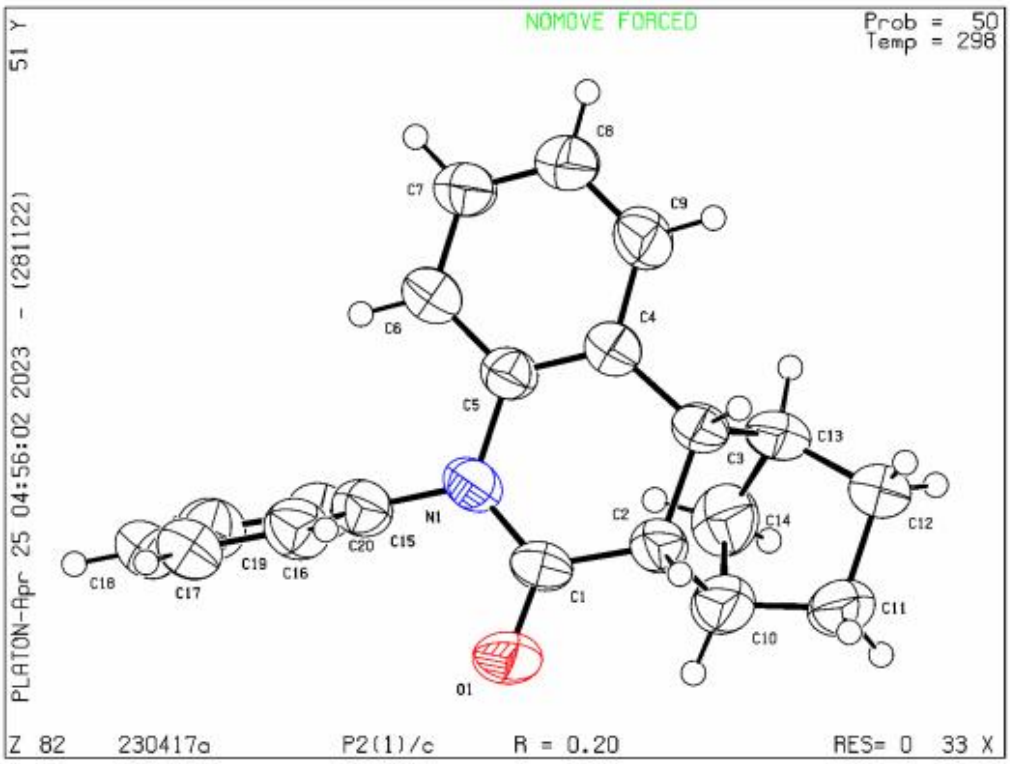
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

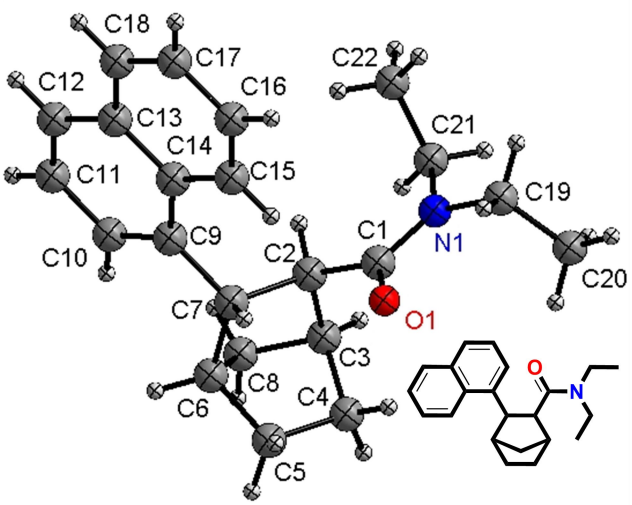
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock 230417a - ellipsoid plot



X-ray data for compound **1e**, CCDC: 2442307



Supplementary Table 2. Crystal data and structure refinement for **1e**

chemical formula	C22H27NO
formula weight	321.45
crystal size (mm)	0.40×0.35×0.33
temperature (K)	298(2)
radiation	0.71073
crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
a(Å)	10.1122(11)
b(Å)	11.5702(12)
c(Å)	15.3663(13)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	1797.9(3)
Z	4
ρ$_{(calc)}$ (g/cm^3)	1.188
F (000)	696
absorp.coeff. (mm^{-1})	0.072
θ range (deg)	2.20 to 25.02

Supplementary Table 2. Bond distance data of compound **1c**

Bond		Length(Å)
N1	C1	1.343(3)
N1	C21	1.447(3)
N1	C19	1.450(3)
O1	C1	1.213(2)
C1	C2	1.499(3)

C2	C3	1.524(3)
C2	C7	1.558(3)
C2	H2	0.98
C3	C4	1.504(4)
C3	C8	1.508(3)
C3	H3	0.98
C4	C5	1.543(4)
C4	H4A	0.97
C4	H4B	0.97
C5	C6	1.527(4)
C5	H5A	0.97
C5	H5B	0.97
C6	C8	1.512(3)
C6	C7	1.516(3)
C6	H6	0.98
C7	C9	1.501(3)
C7	H7	0.98
C8	H8A	0.97
C8	H8B	0.97
C9	C10	1.366(3)
C9	C14	1.417(3)
C10	C11	1.387(3)
C10	H10	0.93
C11	C12	1.340(3)
C11	H11	0.93
C12	C13	1.403(3)
C12	H12	0.93
C13	C18	1.394(3)
C13	C14	1.410(3)
C14	C15	1.402(3)
C15	C16	1.362(4)
C15	H15	0.93
C16	C17	1.377(4)
C16	H16	0.93
C17	C18	1.339(4)
C17	H17	0.93
C18	H18	0.93
C19	C20	1.469(4)
C19	H19A	0.97
C19	H19B	0.97
C20	H20A	0.96
C20	H20B	0.96
C20	H20C	0.96
C21	C22	1.495(4)
C21	H21A	0.97

C21	H21B	0.97
C22	H22A	0.96
C22	H22B	0.96
C22	H22C	0.96

Supplementary Table 3. Bond angle data of compound **1c**

Angle			Degree(°)
C1	N1	C21	124.7(2)
C1	N1	C19	118.84(19)
C21	N1	C19	116.1(2)
O1	C1	N1	120.3(2)
O1	C1	C2	121.5(2)
N1	C1	C2	118.1(2)
C1	C2	C3	113.34(19)
C1	C2	C7	115.32(17)
C3	C2	C7	103.12(18)
C1	C2	H2	108.2
C3	C2	H2	108.2
C7	C2	H2	108.2
C4	C3	C8	101.5(2)
C4	C3	C2	110.4(2)
C8	C3	C2	101.0(2)
C4	C3	H3	114.2
C8	C3	H3	114.2
C2	C3	H3	114.2
C3	C4	C5	102.6(2)
C3	C4	H4A	111.2
C5	C4	H4A	111.2
C3	C4	H4B	111.2
C5	C4	H4B	111.2
H4A	C4	H4B	109.2
C6	C5	C4	103.4(2)
C6	C5	H5A	111.1
C4	C5	H5A	111.1
C6	C5	H5B	111.1
C4	C5	H5B	111.1
H5A	C5	H5B	109.1
C8	C6	C7	102.62(19)
C8	C6	C5	100.8(2)
C7	C6	C5	107.6(2)
C8	C6	H6	114.8
C7	C6	H6	114.8
C5	C6	H6	114.8
C9	C7	C6	116.81(19)
C9	C7	C2	112.71(17)

C6	C7	C2	102.21(17)
C9	C7	H7	108.2
C6	C7	H7	108.2
C2	C7	H7	108.2
C3	C8	C6	94.9(2)
C3	C8	H8A	112.8
C6	C8	H8A	112.8
C3	C8	H8B	112.8
C6	C8	H8B	112.8
H8A	C8	H8B	110.2
C10	C9	C14	117.6(2)
C10	C9	C7	121.4(2)
C14	C9	C7	121.01(19)
C9	C10	C11	122.5(2)
C9	C10	H10	118.7
C11	C10	H10	118.7
C12	C11	C10	120.7(2)
C12	C11	H11	119.6
C10	C11	H11	119.6
C11	C12	C13	119.7(2)
C11	C12	H12	120.1
C13	C12	H12	120.1
C18	C13	C12	120.2(2)
C18	C13	C14	119.9(2)
C12	C13	C14	119.9(2)
C15	C14	C13	117.8(2)
C15	C14	C9	122.7(2)
C13	C14	C9	119.5(2)
C16	C15	C14	120.1(3)
C16	C15	H15	119.9
C14	C15	H15	119.9
C15	C16	C17	121.3(3)
C15	C16	H16	119.3
C17	C16	H16	119.3
C18	C17	C16	120.1(3)
C18	C17	H17	119.9
C16	C17	H17	119.9
C17	C18	C13	120.8(3)
C17	C18	H18	119.6
C13	C18	H18	119.6
N1	C19	C20	113.8(2)
N1	C19	H19A	108.8
C20	C19	H19A	108.8
N1	C19	H19B	108.8
C20	C19	H19B	108.8

H19A	C19	H19B	107.7
C19	C20	H20A	109.5
C19	C20	H20B	109.5
H20A	C20	H20B	109.5
C19	C20	H20C	109.5
H20A	C20	H20C	109.5
H20B	C20	H20C	109.5
N1	C21	C22	112.9(3)
N1	C21	H21A	109
C22	C21	H21A	109
N1	C21	H21B	109
C22	C21	H21B	109
H21A	C21	H21B	107.8
C21	C22	H22A	109.5
C21	C22	H22B	109.5
H22A	C22	H22B	109.5
C21	C22	H22C	109.5
H22A	C22	H22C	109.5
H22B	C22	H22C	109.5

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 220514d

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Bond precision:   C-C = 0.0035 A          Wavelength=0.71073

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                  alpha=90          beta=90           gamma=90
Temperature:      298 K

                  Calculated                Reported
Volume            1797.9(3)                 1797.9(3)
Space group       P 21 21 21                P2(1)2(1)2(
Hall group        P 2ac 2ab                 ?
Moiety formula    C22 H27 N O               ?
Sum formula       C22 H27 N O               C22 H27 N O
Mr                321.45                    321.45
Dx,g cm-3         1.188                     1.188
Z                 4                         4
Mu (mm-1)         0.072                     0.072
F000              696.0                     696.0
F000'             696.26
h,k,lmax          12,13,18                  12,13,18
Nref              3166[ 1822]               3137
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Tmin'             0.972

Correction method= # Reported T Limits: Tmin=0.972 Tmax=0.977
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.99        Theta(max)= 25.020

R(reflections)= 0.0414( 2189)                wR2(reflections)=
                                             0.1069( 3137)
S = 1.030                  Npar= 220
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```
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level B

```
PLAT035_ALERT_1_B _chemical_absolute_configuration Info  Not Given     Please Do !
```

Alert level C

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STRVA01_ALERT_4_C           Flack parameter is too small
          From the CIF: _refine_ls_abs_structure_Flack   -2.000
          From the CIF: _refine_ls_abs_structure_Flack_su    2.000
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C17      --C18      .        5.5 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C21 Check
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      2.000 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT791_ALERT_4_G Model has Chirality at C2         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C3         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C6         (Sohncke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C7         (Sohncke SpGr)          S Verify
PLAT899_ALERT_4_G SHELXL-97  is Outdated   and Succeeded by SHELXL     2019/3 Note
```

```
   0 ALERT level A - Most likely a serious problem - resolve or explain
   1 ALERT level B - A potentially serious problem, consider carefully
   3 ALERT level C - Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G - General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_STRVA01_220514d
;
PROBLEM: Flack parameter is too small
RESPONSE: ...
;
_vrf_PLAT035_220514d
;
PROBLEM: _chemical_absolute_configuration Info  Not Given     Please Do !
RESPONSE: ...
```

```
;
_vrf_PLAT230_220514d
;
PROBLEM: Hirshfeld Test Diff for    C17      --C18      .        5.5 s.u.
RESPONSE: ...
;
_vrf_PLAT242_220514d
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of       C21 Check
RESPONSE: ...
;
# end Validation Reply Form
```

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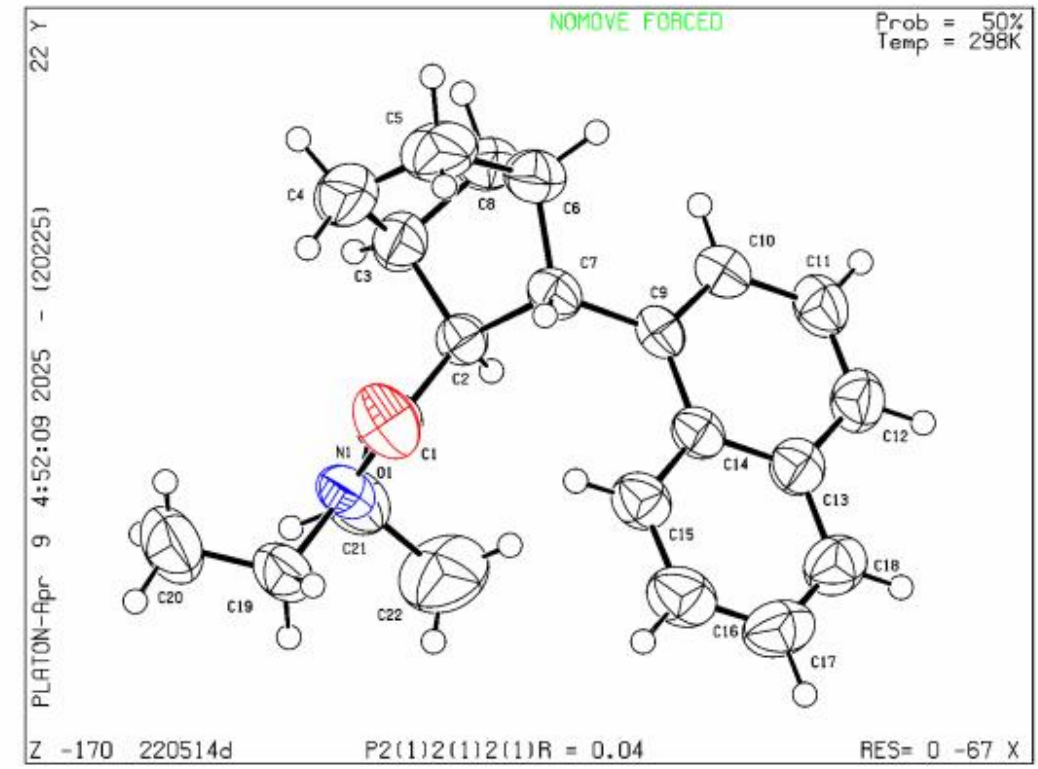
Publication of your CIF in other journals

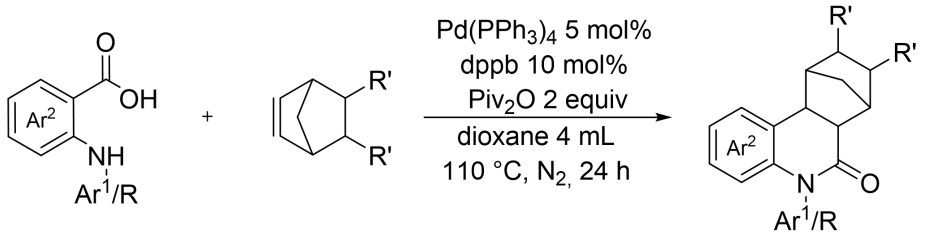
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 02/02/2025; check.def file version of 02/02/2025

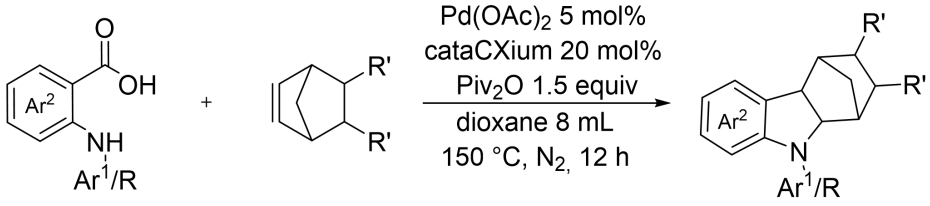
Datablock 220514d - ellipsoid plot



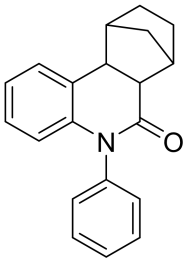
3.Characterization Data for the Products



An oven dried 25 mL Schlenk tube was charged with 2-aminobenzoic acid **a** (0.2 mmol, 1.0 equiv), *NBE* **b** (0.8 mmol, 4.0 equiv) $Pd(PPh_3)_4$ (5 mol%), and dppb (10 mol%). Subsequently, Piv_2O (0.4 mmol, 2.0 equiv), and dioxane (4 mL) were added under N_2. The reaction mixture was allowed to react at 110 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give a desired product compound **1c**–**50c**.

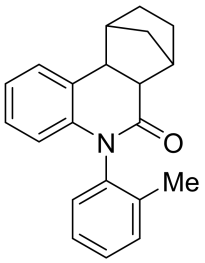


An oven dried 25 mL Schlenk tube was charged with 2-aminobenzoic acid **a** (0.2 mmol, 1.0 equiv), *NBE* **b** (0.4 mmol, 2.0 equiv) $Pd(OAc)_2$ (5 mol%), and cataCXium (20 mol%). Subsequently, Piv_2O (0.3 mmol, 1.5 equiv), and dioxane (8 mL) were added under N_2. The reaction mixture was allowed to react at 150 °C for 12 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give a desired product compound **1d**–**45d**.



5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**1c**)

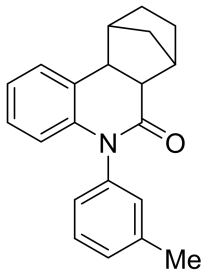
The representative general procedure mentioned above was followed. The desired product 1c was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, R_f = 0.51) as a white solid in 93% yield (53.8 mg). mp: 240–244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.00 (dtd, *J* = 17.0, 7.2, 1.2 Hz, 2H), 6.16 (d, *J* = 7.8 Hz, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.98 (d, *J* = 9.8 Hz, 2H), 2.56 (d, *J* = 2.4 Hz, 1H), 1.83–1.70 (m, 2H), 1.63 (t, *J* = 8.2 Hz, 3H), 1.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 139.8, 138.6, 130.1, 129.7, 128.3, 126.8, 125.0, 122.9, 116.1, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3. HRMS (ESI) calcd for $C_{20}H_{19}NO$ $[M+H]^+$: 290.1539, found: 290.1539.



5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**2c**)

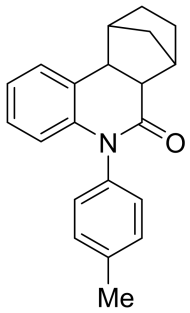
The representative general procedure mentioned above was followed. The desired product **2c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, R_f = 0.53) as a white solid in 82% yield (49.7 mg). mp: 241–244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.10 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.00 (dt, *J* = 19.8, 7.2 Hz, 2H), 6.06 (d, *J* = 7.8 Hz, 1H), 3.33–3.23 (m, 1H), 3.01–2.95 (m, 2H), 2.57 (s, 1H), 2.13 (d, *J* = 26.0 Hz, 3H), 1.82– .70 (m, 2H), 1.69–1.59 (m, 3H), 1.33–1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 138.9, 137.3, 136.5, 131.5, 129.8, 129.3, 128.6, 127.8, 127.1, 125.1,

123.0, 115.4, 49.3, 48.6, 45.2, 34.8, 29.7, 29.4, 28.9, 17.7. HRMS (ESI) calcd for $C_{21}H_{21}NO$ $[M+H]^+$: 304.1696, found: 304.1692.



5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**3c**)

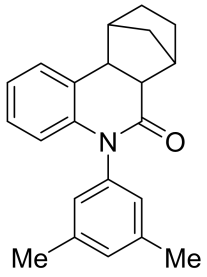
The representative general procedure mentioned above was followed. The desired product **3c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 79% yield (47.9 mg). mp: 239–241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.8 Hz, 1H), 7.26–7.18 (m, 2H), 6.96 (qd, *J* = 8.0, 7.6, 1.6 Hz, 4H), 6.13 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 2.93 (dd, *J* = 6.4, 2.6 Hz, 2H), 2.53–2.48 (m, 1H), 2.39 (s, 3H), 1.78–1.66 (m, 2H), 1.58 (t, *J* = 8.2 Hz, 3H), 1.24 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.8, 138.4, 129.9, 129.6, 129.1, 126.8, 125.0, 122.9, 116.2, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.2, 21.4. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M+H]+ : 304.1696, found: 304.1696.



5-(*p*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**4c**)

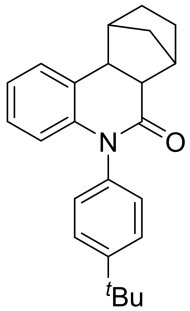
The representative general procedure mentioned above was followed. The desired product **4c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 84% yield (50.9 mg). mp: 239–241 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.24–7.20 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.95 (pd, *J* = 7.2, 1.4 Hz, 2H), 6.19–6.12 (m, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 2.97–2.89 (m, 2H), 2.50 (d, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 1.77–1.66 (m, 2H), 1.62–1.55 (m, 3H), 1.24 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 139.9, 138.1, 135.8, 130.7, 129.6, 126.8, 125.0, 122.8, 116.2, 49.4, 48.6, 45.2, 45.2, 34.7, 29.4, 29.2, 21.3. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M+H]+ : 304.1696, found: 304.1699.



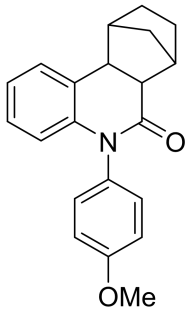
5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**5c**)

The representative general procedure mentioned above was followed. The desired product **5c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 84% yield (53.2 mg). mp: 241–244 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 1H), 7.05 (s, 1H), 6.99–6.91 (m, 2H), 6.78 (d, *J* = 4.4 Hz, 2H), 6.14 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 2H), 2.49 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 6H), 1.78–1.64 (m, 2H), 1.58 (t, *J* = 8.2 Hz, 3H), 1.27–1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.9, 139.8, 139.7, 138.3, 130.1, 129.6, 126.8, 126.7, 126.4, 124.9, 122.8, 116.3, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3, 21.3. HRMS (ESI) calcd for $C_{22}H_{23}NO$ [M+H]+ : 318.1852, found: 318.1850.



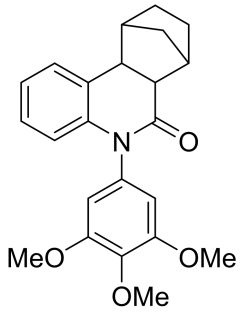
5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**6c**)

The representative general procedure mentioned above was followed. The desired product **6c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.53) as a white solid in 90% yield (62.1 mg). mp: 240–242 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.05–6.96 (m, 2H), 6.20 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 3.01–2.94 (m, 2H), 2.55 (d, *J* = 2.6 Hz, 1H), 1.83–1.71 (m, 2H), 1.64 (dd, *J* = 14.8, 5.0 Hz, 3H), 1.42 (s, 9H), 1.32–1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 151.1, 139.9, 135.7, 129.6, 127.0, 126.8, 125.0, 122.8, 116.2, 49.4, 48.7, 45.2, 45.2, 34.7, 34.7, 31.4, 29.4, 29.3. HRMS (ESI) calcd for $C_{24}H_{27}NO$ [M+H]+ : 346.2165, found: 346.2163.



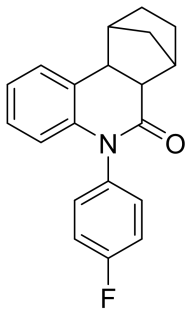
5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**7c**)

The representative general procedure mentioned above was followed. The desired product **7c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.48) as a white solid in 80% yield (51.0 mg). mp: 233–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.09 (t, *J* = 11.4 Hz, 4H), 7.05–6.97 (m, 2H), 6.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.91 (s, 3H), 3.25 (d, *J* = 10.0 Hz, 1H), 2.97 (d, *J* = 9.6 Hz, 2H), 2.55 (d, *J* = 2.4 Hz, 1H), 1.78 (ddd, *J* = 13.0, 8.4, 3.8 Hz, 2H), 1.66 (s, 1H), 1.64–1.61 (m, 2H), 1.29 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 159.2, 140.1, 131.1, 130.3, 129.9, 129.7, 126.8, 125.1, 122.9, 116.2, 115.4, 55.5, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3. HRMS (ESI) calcd for $C_{21}H_{21}NO_2$ [M+H]+ : 320.1645, found: 320.1644.



5-(3,4,5-trimethoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**8c**)

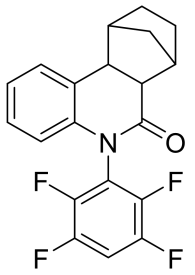
The representative general procedure mentioned above was followed. The desired product **8c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.45) as a white solid in 82% yield (62.2 mg). mp: 228–230 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.14 (m, 1H), 6.97–6.89 (m, 2H), 6.30 (d, *J* = 13.2 Hz, 2H), 6.16–6.11 (m, 1H), 3.83 (s, 3H), 3.76 (d, *J* = 9.4 Hz, 6H), 3.14 (d, *J* = 9.8 Hz, 1H), 2.86 (d, *J* = 10.2 Hz, 2H), 2.45 (d, *J* = 2.8 Hz, 1H), 1.74–1.57 (m, 2H), 1.51 (d, *J* = 8.8 Hz, 3H), 1.19 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 154.4, 154.3, 139.7, 137.6, 134.1, 129.6, 126.9, 124.9, 123.0, 116.2, 106.2, 105.7, 60.9, 56.1, 49.3, 48.7, 45.2, 45.1, 34.8, 29.4, 29.3. HRMS (ESI) calcd for $C_{23}H_{25}NO_4$ [M+H]+ : 380.1856, found: 380.1852.



5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**9c**)

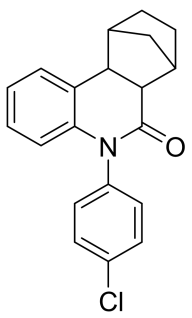
The representative general procedure mentioned above was followed. The desired product **9c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.57) as a white solid in 85% yield (52.2 mg). mp: 175–177 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.22–7.16 (m, 2H), 7.02 (pd, *J* = 7.2, 1.4 Hz, 2H), 6.18–6.14 (m, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.97 (d, *J* = 9.8 Hz, 2H), 2.55 (d, *J* = 2.2 Hz, 1H), 1.84–1.67 (m,

2H), 1.63 (t, *J* = 8.8 Hz, 3H), 1.29 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 169.9, 161.4 (d, *J* = 243.4 Hz), 141.2 (d, *J* = 9.6 Hz), 138.1, 130.9, 130.9, 130.3, 129.1 (d, *J* = 37.4 Hz), 128.7, 120.6 (d, *J* = 3.2 Hz), 109.6, 109.4, 103.7, 103.4, 49.3, 48.6, 45.2, 44.7, 34.7, 29.4, 29.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.17. HRMS (ESI) calcd for $C_{20}H_{18}FNO$ [M+H]+ : 308.1445, found: 308.1442.



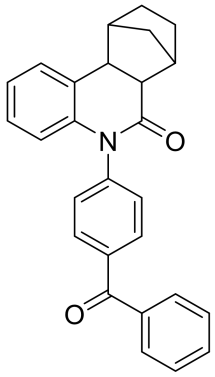
5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**10c**)

The representative general procedure mentioned above was followed. The desired product **10c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 82% yield (59.2 mg). mp:120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 10.0, 4.0 Hz, 1H), 7.29–7.21 (m, 1H), 7.14–7.06 (m, 2H), 6.24 (d, *J* = 8.0 Hz, 1H), 3.29 (d, *J* = 9.8 Hz, 1H), 3.02 (d, *J* = 9.8 Hz, 1H), 2.95 (d, *J* = 2.8 Hz, 1H), 2.56 (s, 1H), 1.84–1.71 (m, 2H), 1.68–1.59 (m, 3H), 1.30 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 147.8–147.5 (m), 145.7–144.7 (m), 143.3–141.7 (m), 137.1, 130.3, 127.5, 125.2, 124.0, 117.9 (t, *J* = 15.5 Hz), 114.1, 106.7 (t, *J* = 22.6 Hz), 49.3, 48.6, 45.4, 45.2, 34.6, 29.3, 29.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.82 (ddd, *J* = 21.2, 17.6, 10.4 Hz, 2F), -143.94–-144.18 (m, 1F), -145.00–-145.24 (m, 1F). HRMS (ESI) calcd for $C_{20}H_{15}F_4NO$ [M+H]+ : 362.1163, found: 362.1160.



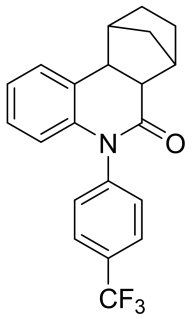
5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**11c**)

The representative general procedure mentioned above was followed. The desired product **11c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 89% yield (57.5 mg). mp: 229–231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.03–6.93 (m, 2H), 6.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.21 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 2H), 2.51 (d, *J* = 2.6 Hz, 1H), 1.77–1.64 (m, 2H), 1.62–1.52 (m, 3H), 1.24 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.5, 137.1, 134.2, 130.3, 129.8, 126.9, 125.1, 123.2, 115.9, 49.3, 48.7, 45.2, 34.7, 29.4, 29.2. HRMS (ESI) calcd for $C_{20}H_{18}ClNO$ [M+H]+ : 324.1150, found: 324.1150.



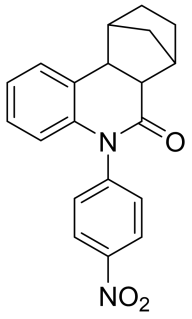
5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**12c**)

The representative general procedure mentioned above was followed. The desired product **12c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.45) as a white solid in 71% yield (55.8 mg). mp: 240–244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.91–7.84 (m, 2H), 7.66–7.57 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.29–7.22 (m, 1H), 7.01 (td, *J* = 7.4, 1.4 Hz, 1H), 6.96 (td, *J* = 7.6, 1.6 Hz, 1H), 6.13 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.24 (d, *J* = 9.8 Hz, 1H), 2.96 (d, *J* = 9.8 Hz, 2H), 2.53 (d, *J* = 2.8 Hz, 1H), 1.82–1.65 (m, 2H), 1.64–1.53 (m, 3H), 1.27 (dt, *J* = 10.2, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 169.9, 142.4, 139.2, 137.4, 137.3, 132.7, 131.8, 130.1, 129.9, 129.5, 128.4, 126.9, 125.0, 123.3, 115.9, 49.3, 48.7, 45.2, 34.8, 29.4, 29.2. HRMS (ESI) calcd for $C_{27}H_{23}NO_2$ [M+H]+ : 394.1802, found: 394.1804.



5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**13c**)

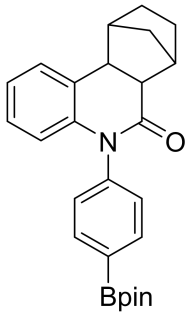
The representative general procedure mentioned above was followed. The desired product **13c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 76% yield (54.3 mg). mp: 188–190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 1H), 7.05 (td, *J* = 7.4, 1.2 Hz, 1H), 7.00 (td, *J* = 7.8, 7.4, 1.4 Hz, 1H), 6.12–6.08 (m, 1H), 3.27 (d, *J* = 9.8 Hz, 1H), 3.00–2.94 (m, 2H), 2.56 (s, 1H), 1.83–1.70 (m, 2H), 1.63 (t, *J* = 8.4 Hz, 3H), 1.30 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 141.9, 139.2, 130.5 (d, *J* = 32.8 Hz), 129.9, 127.2 (q, *J* = 3.7 Hz), 126.9, 125.1, 123.9 (q, *J* = 270.8) 123.3, 115.8, 49.3, 48.6, 45.2, 34.8, 29.4, 29.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55. HRMS (ESI) calcd for $C_{21}H_{18}F_3NO$ [M+H]+ : 358.1413, found: 358.1411.



5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**14c**)

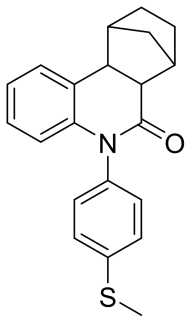
The representative general procedure mentioned above was followed. The desired product **14c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 82% yield (54.8 mg). mp: 235–236 ^{o}C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.44 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 3.29 (d, *J* = 9.8 Hz, 1H), 3.02–2.94 (m, 2H), 2.58 (s, 1H), 1.84–1.72 (m, 2H), 1.63 (dd, *J* = 12.0, 6.8 Hz, 3H), 1.32 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 147.5, 144.7, 138.8, 130.7, 130.1, 127.1, 125.4, 125.1, 123.6, 115.6, 49.3, 48.7, 45.2, 45.2, 34.8, 29.4, 29.1. HRMS (ESI) calcd for $C_{20}H_{18}N_2O_3$ [M+H]+ : 335.1390, found: 335.1390.



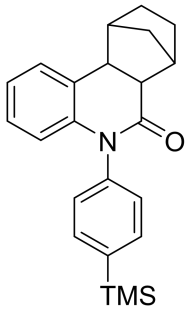
5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**15c**)

The representative general procedure mentioned above was followed. The desired product **15c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.47) as a white solid in 64% yield (53.1 mg). mp: 220–223 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.48–7.33 (m, 1H), 7.17–7.05 (m, 3H), 6.94–6.80 (m, 2H), 6.06–5.98 (m, 1H), 3.14 (d, *J* = 9.6 Hz, 1H), 2.86 (d, *J* = 10.0 Hz, 2H), 2.43 (s, 1H), 1.70–1.57 (m, 2H), 1.55–1.46 (m, 3H), 1.29 (s, 9H), 1.18 (d, *J* = 2.4 Hz, 2H), 1.15 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 141.3, 139.7, 136.6, 129.7, 126.8, 124.9, 122.9, 116.1, 84.0, 49.3, 48.7, 45.2, 45.2, 34.7, 29.4, 29.2, 24.9, 24.9. HRMS (ESI) calcd for $C_{26}H_{30}BNO_3$ [M+H]+ : 416.2392, found: 416.2393.



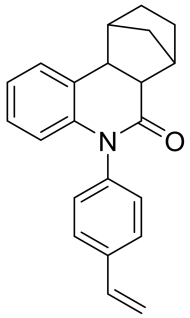
5-(4-(methylthio)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**16c**)

The representative general procedure mentioned above was followed. The desired product **16c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 88% yield (59.0 mg). mp: 207–210 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.00 (pd, *J* = 7.4, 1.6 Hz, 2H), 6.20 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.24 (d, *J* = 10.0 Hz, 1H), 2.96 (d, *J* = 9.6 Hz, 2H), 2.56 (s, 3H), 2.55–2.52 (m, 1H), 1.78–1.68 (m, 2H), 1.60 (d, *J* = 8.6 Hz, 3H), 1.30–1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.7, 138.9, 135.3, 129.7, 127.8, 126.8, 125.0, 122.9, 116.1, 49.3, 48.7, 45.2, 34.7, 29.4, 29.2, 15.7. HRMS (ESI) calcd for $C_{21}H_{21}NOS$ [M+H]+ : 336.1417, found: 336.1416.



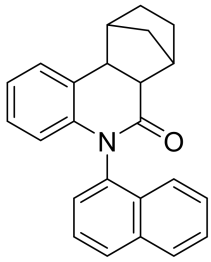
5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**17c**)

The representative general procedure mentioned above was followed. The desired product **17c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 75% yield (54.2 mg). mp: 203–205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 6.9 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.01 – 6.89 (m, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 3.21 (d, *J* = 10.0 Hz, 1H), 2.93 (d, *J* = 9.9 Hz, 2H), 2.50 (s, 1H), 1.77 – 1.64 (m, 2H), 1.59 (t, *J* = 10.4 Hz, 3H), 1.26 – 1.18 (m, 1H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 142.1, 141.1, 140.3, 136.4, 130.9, 128.1, 126.3, 124.2, 117.5, 50.7, 49.9, 46.5, 46.5, 36.0, 30.7, 30.6, 0.3. HRMS (ESI) calcd for $C_{23}H_{27}NOSi$ [M+H]+ : 362.1935, found: 362.1932.



5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**18c**)

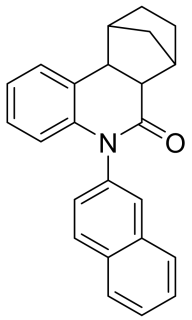
The representative general procedure mentioned above was followed. The desired product **18c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.58) as a white solid in 83% yield (52.3 mg). mp: 221–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.18–7.13 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.95–6.82 (m, 2H), 6.69 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.13–6.06 (m, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.8 Hz, 1H), 3.13 (d, *J* = 10.0 Hz, 1H), 2.89–2.82 (m, 2H), 2.46–2.40 (m, 1H), 1.70–1.58 (m, 2H), 1.50 (t, *J* = 8.0 Hz, 3H), 1.17 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.7, 137.9, 137.6, 136.1, 129.7, 127.8, 126.8, 125.0, 122.9, 116.1, 114.9, 49.3, 48.7, 45.2, 45.1, 34.7, 29.4, 29.2. HRMS (ESI) calcd for $C_{22}H_{21}NO$ [M+H]+ : 316.1696, found: 316.1693.



5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**19c**)

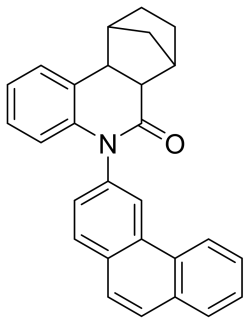
The representative general procedure mentioned above was followed. The desired product **19c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.56) as a white solid in 65% yield (44.1 mg). mp: 245–249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.61 – 7.55 (m, 1H), 7.50 (q, *J* = 6.0, 5.0 Hz, 1H), 7.43 (dd, *J* = 15.0, 8.0 Hz, 1H), 7.35 (t, *J* = 6.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 8.4 Hz, 1H), 3.34 (d, *J* = 10.0 Hz, 1H),

3.06 (d, J = 13.6 Hz, 1H), 3.01 (d, J = 8.7 Hz, 1H), 2.60 (d, J = 23.9 Hz, 1H), 1.83 – 1.70 (m, 3H), 1.63 (d, J = 7.6 Hz, 2H), 1.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.6, 135.4, 135.1, 134.8, 130.3, 129.7, 129.0, 128.6, 127.4, 127.0, 126.5, 126.2, 124.9, 123.0, 122.3, 116.3, 49.5, 48.7, 45.3, 35.4, 34.9, 29.7, 29.4. HRMS (ESI) calcd for $C_{24}H_{21}NO$ [M+H]+ : 340.1696, found: 340.1697.



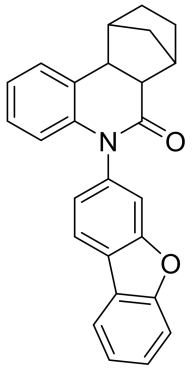
5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**20c**)

The representative general procedure mentioned above was followed. The desired product **20c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 82% yield (55.6 mg). mp: 233–236 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.79–7.72 (m, 1H), 7.62 (s, 1H), 7.45 (pd, *J* = 6.8, 3.4 Hz, 2H), 7.18 (d, *J* = 6.2 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.06 (d, *J* = 8.2 Hz, 1H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.90 (d, *J* = 10.0 Hz, 2H), 2.46 (s, 1H), 1.71–1.59 (m, 2H), 1.58–1.48 (m, 3H), 1.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.8, 136.1, 134.1, 132.9, 130.2, 129.7, 128.1, 127.9, 126.9, 126.7, 126.5, 125.1, 123.0, 116.3, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. HRMS (ESI) calcd for $C_{24}H_{21}NO$ [M+H]+ : 340.1696, found: 340.1694.



5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**21c**)

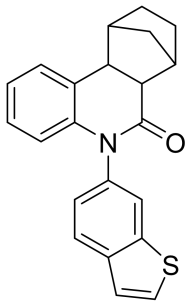
The representative general procedure mentioned above was followed. The desired product **21c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.54) as a white solid in 74% yield (57.6 mg). mp: 240–242 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.79–7.70 (m, 3H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 10.0 Hz, 1H), 3.04 (d, *J* = 10.4 Hz, 2H), 2.59 (s, 1H), 1.82–1.72 (m, 2H), 1.68–1.62 (m, 3H), 1.31 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.9, 133.2, 132.3, 130.1, 130.0, 129.7, 128.7, 127.7, 126.9, 126.9, 126.8, 126.6, 125.1, 124.9, 123.0, 122.9, 116.3, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. HRMS (ESI) calcd for $C_{28}H_{23}NO$ [M+H]+ : 390.1852, found: 390.1852.



5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**22c**)

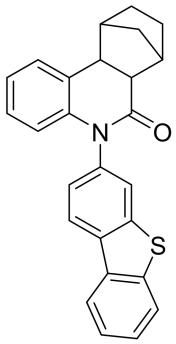
The representative general procedure mentioned above was followed. The desired product **22c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 85% yield (64.5 mg). mp: 216–217 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.51–7.45 (m, 1H), 7.42 (d, *J* = 5.4 Hz, 1H), 7.39–7.34 (m, 1H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.99 (td, *J* = 7.4, 1.2 Hz, 1H), 6.92 (td, *J* = 8.0, 1.4 Hz, 1H), 6.15 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.24 (d, *J* = 10.0 Hz, 1H), 2.98 (d, *J* = 9.8 Hz, 2H), 2.53 (d, *J* = 2.4 Hz, 1H), 1.82–1.67 (m, 2H), 1.68–1.55 (m, 3H), 1.28 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 156.9,

139.9, 137.4, 129.7, 127.6, 126.9, 125.0, 124.5, 123.7, 123.1, 123.0 121.8, 120.8, 116.2, 111.9, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. HRMS (ESI) calcd for $C_{26}H_{21}NO_2$ [M+H]+ : 380.1645, found: 380.1645.



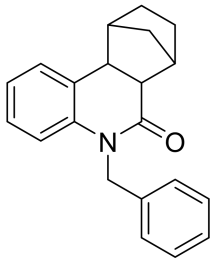
5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**23c**)

The representative general procedure mentioned above was followed. The desired product **23c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.54) as a white solid in 76% yield (52.4 mg). mp: 228–232 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.55 (d, *J* = 5.4 Hz, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 8.2 Hz, 1H), 3.28 (d, *J* = 9.8 Hz, 1H), 3.01 (d, *J* = 10.4 Hz, 2H), 2.57 (s, 1H), 1.78 (m, 2H), 1.70–1.59 (m, 3H), 1.31 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.0, 140.0, 139.6, 135.1, 129.7, 127.8, 126.8, 125.3, 125.0, 124.9, 124.4, 124.1, 123.9, 122.9, 116.3, 49.4, 48.7, 45.3, 34.8, 29.4, 29.2. HRMS (ESI) calcd for $C_{22}H_{19}NOS$ [M+H]+ : 346.1260, found: 346.1261.



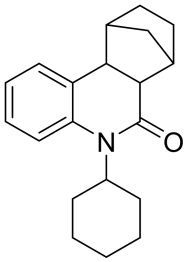
5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**24c**)

The representative general procedure mentioned above was followed. The desired product **24c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 82% yield (64.8 mg). mp: 230–232 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (s, 1H), 7.64 (t, *J* = 8.8 Hz, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 6.84 (s, 1H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.04 (d, *J* = 9.9 Hz, 1H), 3.01 (s, 1H), 2.64 (s, 1H), 1.83 – 1.74 (m, 2H), 1.70 – 1.64 (m, 3H), 1.31 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.9, 138.6, 137.9, 135.1, 134.4, 133.8, 130.3, 128.6, 126.8, 125.5, 124.2, 123.5, 122.9, 121.4, 108.4, 49.9, 48.6, 45.5, 45.3, 34.8, 29.4, 29.3. HRMS (ESI) calcd for $C_{26}H_{21}NOS$ [M+H]+ : 396.1417, found: 396.1416.



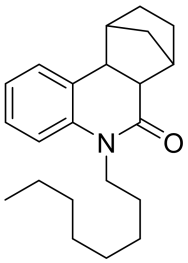
5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**25c**)

The representative general procedure mentioned above was followed. The desired product **25c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 76% yield (46.1 mg). mp: 233–235 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (td, *J* = 6.8, 2.2 Hz, 2H), 7.19–7.08 (m, 4H), 6.98–6.84 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.93 (s, 1H), 3.09 (d, *J* = 10.0 Hz, 1H), 2.94–2.81 (m, 2H), 2.38 (s, 1H), 1.70–1.55 (m, 2H), 1.49 (tt, *J* = 11.4, 5.4 Hz, 2H), 1.43–1.35 (m, 1H), 1.20–1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 137.7, 136.9, 129.8, 128.8, 127.2, 127.0, 126.3, 125.8, 122.9, 115.2, 49.3, 48.3, 45.6, 45.3, 45.0, 34.7, 29.6, 29.1. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M+H]+ : 304.1696, found: 304.1692.



5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**26c**)

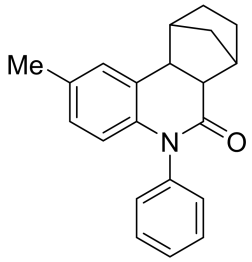
The representative general procedure mentioned above was followed. The desired product **26c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 70% yield (41.3 mg). mp: 210–212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.97 (td, *J* = 7.4, 1.2 Hz, 1H), 4.07 (s, 1H), 2.98 (d, *J* = 9.8 Hz, 1H), 2.77 (d, *J* = 4.0 Hz, 1H), 2.71 (d, *J* = 9.8 Hz, 1H), 2.52 (qd, *J* = 12.2, 3.4 Hz, 1H), 2.45–2.34 (m, 2H), 1.92–1.81 (m, 2H), 1.77–1.62 (m, 4H), 1.52–1.44 (m, 3H), 1.40–1.23 (m, 4H), 1.12 (dt, *J* = 10.0, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.2, 130.2, 126.9, 126.8, 122.3, 114.6, 57.3, 49.7, 49.0, 45.5, 45.4, 34.3, 29.4, 29.3, 29.2, 29.0, 26.8, 26.5, 25.5. HRMS (ESI) calcd for $C_{20}H_{25}NO$ [M+H]+ : 296.2009, found: 296.2009.



5-octyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**27c**)

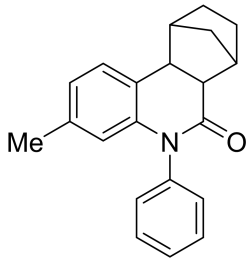
The representative general procedure mentioned above was followed. The desired product **27c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 62% yield (40.3 mg). mp: 232–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.07–3.95 (m, 1H), 3.92–3.80 (m, 1H), 3.11 (d, *J* = 10.0 Hz, 1H), 2.87 (d, *J* = 3.2 Hz, 1H), 2.80 (d, *J* = 10.0 Hz, 1H), 2.43 (s, 1H), 1.76–1.58 (m, 5H), 1.56 (dd, *J* = 6.4, 3.2 Hz, 1H), 1.40–1.27 (m, 11H), 1.16 (d, *J* = 10.2 Hz, 1H), 0.91 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.6,

130.1, 127.2, 125.9, 122.5, 114.1, 49.3, 48.2, 45.1, 44.9, 41.6, 34.4, 31.8, 29.4, 29.4, 29.3, 29.2, 27.0, 26.9, 22.6, 14.1. HRMS (ESI) calcd for $C_{22}H_{31}NO$ [M+H]+ : 326.2478, found: 326.2478.



2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**28c**)

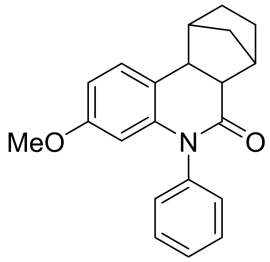
The representative general procedure mentioned above was followed. The desired product **28c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 95% yield (57.6 mg). mp: 224–228 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.04 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.91 (d, *J* = 9.8 Hz, 2H), 2.51 (s, 1H), 2.26 (s, 3H), 1.78 – 1.66 (m, 2H), 1.58 (t, *J* = 8.6 Hz, 3H), 1.24 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.7, 137.5, 132.4, 130.2, 130.0, 128.2, 127.4, 124.8, 116.0, 49.3, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3, 20.5. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M+H]+ : 304.1696, found: 304.1696.



3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**29c**)

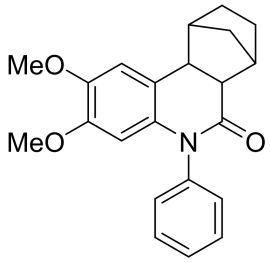
The representative general procedure mentioned above was followed. The desired product **29c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 82% yield (49.7 mg). mp: 224–228 ^{o}C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.91 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 1H), 2.10 (s, 3H), 1.74 – 1.65 (m, 2H), 1.57 (t, *J* = 9.6 Hz, 3H), 1.23 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.6, 138.6, 136.7, 130.1, 129.6, 128.3, 123.8, 122.1, 116.6, 49.3, 48.7, 45.2, 44.9, 34.7, 29.5, 29.2, 21.3. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M+H]+ : 304.1696, found: 304.1694



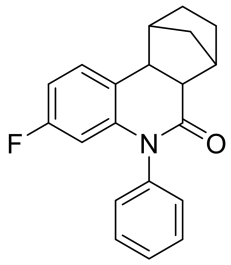
3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**30c**)

The representative general procedure mentioned above was followed. The desired product **30c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.45) as a white solid in 85% yield (54.2 mg). mp: 234–236 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.46 (m, 2H), 7.46–7.37 (m, 1H), 7.20–7.09 (m, 3H), 6.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.68 (d, *J* = 2.4 Hz, 1H), 3.59 (s, 3H), 3.15 (d, *J* = 10.0 Hz, 1H), 2.94–2.87 (m, 2H), 2.45 (d, *J* = 2.8 Hz, 1H), 1.74–1.64 (m, 2H), 1.63–1.50 (m, 3H), 1.29–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 158.3, 140.8, 138.5, 130.5, 130.0, 129.4, 129.0, 128.4, 117.4, 107.6, 102.9, 55.1, 49.2, 48.6, 45.1, 44.5, 34.6, 29.5, 29.0. HRMS (ESI) calcd for $C_{21}H_{21}NO_2$ [M+H]+ : 320.1645, found: 320.1642.



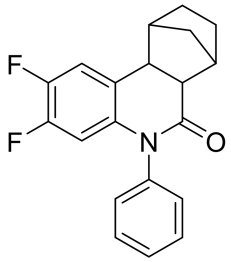
2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**31c**)

The representative general procedure mentioned above was followed. The desired product **31c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.42) as a white solid in 73% yield (51.0 mg). mp: 221–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 1H), 5.59 (s, 1H), 3.79 (s, 3H), 3.41 (s, 3H), 3.07 (d, *J* = 10.0 Hz, 1H), 2.84 (d, *J* = 9.8 Hz, 2H), 2.42 (s, 1H), 1.64 (d, *J* = 10.8 Hz, 2H), 1.51 (dd, *J* = 15.4, 8.4 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 147.5, 144.8, 138.6, 133.3, 130.0, 128.3, 116.4, 112.5, 101.13, 56.4, 55.7, 48.9, 48.6, 45.2, 45.1, 34.6, 29.4, 29.1. HRMS (ESI) calcd for $C_{22}H_{23}NO_3$ [M+H]+ : 350.1751, found: 350.1750.



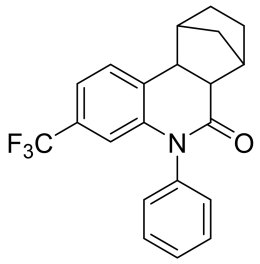
3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**32c**)

The representative general procedure mentioned above was followed. The desired product **32c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 85% yield (52.2 mg). mp: 177–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 11.4, 4.4 Hz, 2H), 7.48–7.42 (m, 1H), 7.17 (dd, *J* = 7.8, 6.6 Hz, 3H), 6.67 (td, *J* = 8.2, 2.4 Hz, 1H), 5.84 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 2H), 2.46 (d, *J* = 2.6 Hz, 1H), 1.77–1.64 (m, 2H), 1.60–1.51 (m, 3H), 1.28–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.5, 160.1, 141.2 (d, *J* = 9.7 Hz), 130.9 (d, *J* = 9.3 Hz), 130.2, 129.1 (d, *J* = 38.4 Hz), 128.6, 120.6 (d, *J* = 3.2 Hz), 109.6, 109.4, 103.7, 103.4, 49.3, 48.5, 45.2, 44.7, 34.7, 29.4, 29.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.32. HRMS (ESI) calcd for $C_{20}H_{18}FNO$ [M+H]+ : 308.1445, found: 308.1445.



2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**33c**)

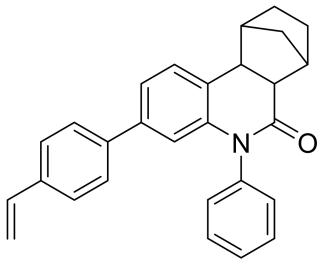
The representative general procedure mentioned above was followed. The desired product **33c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 92% yield (59.8 mg). mp: 129–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.53 (m, 2H), 7.53–7.45 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.05 (dd, *J* = 10.2, 8.8 Hz, 1H), 5.97 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.94 (d, *J* = 9.4 Hz, 2H), 2.49 (s, 1H), 1.82–1.67 (m, 2H), 1.63–1.54 (m, 3H), 1.35–1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 149.6 (d, *J* = 13.4 Hz), 147.1 (dd, *J* = 13.1, 6.0 Hz), 144.7 (d, *J* = 12.9 Hz), 138.1, 136.4 (d, *J* = 5.3 Hz), 130.4, 128.8, 121.1 (t, *J* = 4.3 Hz), 117.8, 117.7, 105.6, 105.4, 49.3, 48.3, 45.2, 44.8, 34.7, 29.3, 28.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.52 (ddd, *J* = 21.6, 11.9, 8.9 Hz), -143.53–-150.55 (m). HRMS (ESI) calcd for $C_{20}H_{17}F_2NO$ [M+H]+ :326.1351, found: 326.1352.



5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**34c**)

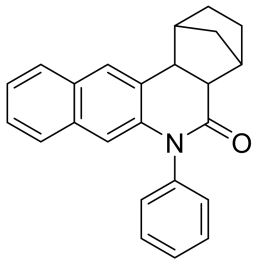
The representative general procedure mentioned above was followed. The desired product **34c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.53) as a white solid in 89% yield (63.5 mg). mp: 178–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.45 (m, 2H), 7.43–7.36 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.16–7.12 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.27 (s, 1H), 3.17 (d, *J* = 9.8 Hz, 1H), 2.92–2.84 (m, 2H), 2.44 (d, *J* =

2.6 Hz, 1H), 1.74–1.59 (m, 2H), 1.55–1.47 (m, 3H), 1.20 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 140.4, 137.8, 130.4, 130.3, 129.3 (q, *J* = 128.6), 128.8, 125.0, 122.3, 119.4 (q, *J* = 3.8 Hz), 112.7 (q, *J* = 4.1 Hz), 49.54, 48.52, 45.22, 45.17; ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.52 (ddd, *J* = 21.6, 11.9, 8.9 Hz), -143.53–-150.55 (m). HRMS (ESI) calcd for $C_{21}H_{18}F_3NO$ [M+H]+ : 358.1413, found: 358.1412.



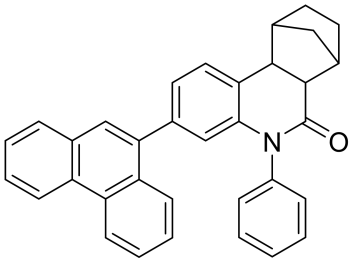
5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**35c**)

The representative general procedure mentioned above was followed. The desired product **35c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 81% yield (63.3 mg). mp: 230–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.32–7.29 (m, 2H), 7.28–7.23 (m, 3H), 6.73 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.39 (d, *J* = 1.2 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 3.29 (d, *J* = 9.8 Hz, 1H), 3.01 (d, *J* = 9.8 Hz, 2H), 2.59 (s, 1H), 1.84–1.75 (m, 2H), 1.66 (dd, *J* = 18.8, 8.6 Hz, 3H), 1.32 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 140.3, 139.9, 139.5, 138.5, 136.7, 136.2, 130.2, 128.5, 126.9, 126.6, 124.2, 121.5, 114.6, 114.1, 49.4, 48.7, 45.2, 45.0, 34.8, 29.4, 29.3. HRMS (ESI) calcd for $C_{28}H_{25}NO$ [M+H]+ : 392.2009, found: 392.2006.



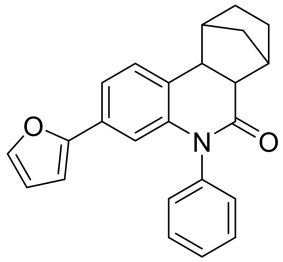
6-phenyl-2,3,4,4a,6,12b-hexahydro-1,4-methanobenzo[b]phenanthridin-5(*1H*)-one (**36c**)

The representative general procedure mentioned above was followed. The desired product **36c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 92% yield (62.4 mg). mp: 240–242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.71 (m, 2H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49–7.45 (m, 1H), 7.39–7.31 (m, 2H), 7.30–7.26 (m, 2H), 6.50 (s, 1H), 3.47 (d, *J* = 9.8 Hz, 1H), 3.07–2.98 (m, 2H), 2.65 (s, 1H), 1.85–1.75 (m, 2H), 1.73–1.61 (m, 3H), 1.30 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 138.9, 138.8, 132.4, 130.2, 129.9, 128.8, 128.5, 127.2, 126.9, 126.2, 126.1, 124.8, 112.3, 50.3, 48.6, 45.4, 45.3, 34.7, 29.5, 29.3. HRMS (ESI) calcd for $C_{24}H_{21}NO$ [M+H]+ : 340.1696, found: 340.1696.



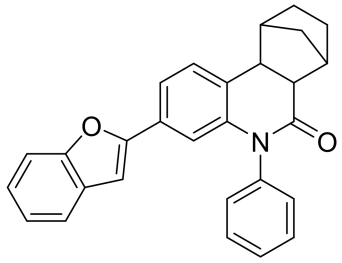
3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**37c**)

The representative general procedure mentioned above was followed. The desired product **37c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.55) as a white solid in 80% yield (74.4 mg). mp: 241–243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 21.8, 8.2 Hz, 2H), 7.92–7.83 (m, 2H), 7.74–7.58 (m, 3H), 7.58–7.53 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.40 (d, *J* = 1.4 Hz, 1H), 3.37 (d, *J* = 10.0 Hz, 1H), 3.07 (d, *J* = 9.8 Hz, 2H), 2.68 (s, 1H), 1.90–1.73 (m, 3H), 1.72–1.62 (m, 2H), 1.39 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.9, 139.5, 138.5, 138.0, 131.4, 130.8, 130.6, 130.1, 129.9, 129.6, 128.6, 128.4, 127.3, 126.9, 126.7, 126.7, 126.5, 126.4, 124.8, 124.2, 122.9, 122.5, 117.7, 49.4, 48.8, 45.2, 45.2, 34.9, 29.5, 29.3. HRMS (ESI) calcd for $C_{34}H_{27}NO$ [M+H]+ : 466.2165, found: 466.2162.



3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**38c**)

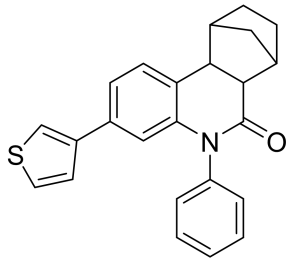
The representative general procedure mentioned above was followed. The desired product **38c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 81% yield (57.5 mg). mp: 212–215 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 11.6, 4.4 Hz, 2H), 7.55–7.48 (m, 1H), 7.36 (t, *J* = 1.2 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.27 (dt, *J* = 9.8, 5.0 Hz, 3H), 6.46 (d, *J* = 1.6 Hz, 1H), 6.39 (d, *J* = 1.2 Hz, 2H), 3.25 (d, *J* = 9.8 Hz, 1H), 2.99 (d, *J* = 9.8 Hz, 2H), 2.55 (d, *J* = 2.6 Hz, 1H), 1.82–1.69 (m, 2H), 1.66–1.58 (m, 3H), 1.30 (dd, *J* = 6.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 153.3, 142.1, 140.2, 138.4, 130.2, 130.1, 129.7, 128.5, 124.2, 118.6, 111.5, 111.4, 105.1, 49.3, 48.7, 45.2, 45.1, 34.7, 29.5, 29.2. HRMS (ESI) calcd for $C_{24}H_{21}NO_2$ [M+H]+ : 356.1645, found: 356.1644.



3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**39c**)

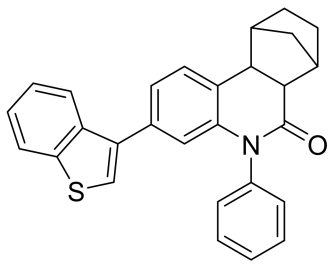
The representative general procedure mentioned above was followed. The desired product **39c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 86% yield (69.7 mg). mp: 210–213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 7.6 Hz, 2H), 7.59–7.51 (m, 3H), 7.47–7.43 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32–7.24 (m, 3H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 6.72 (s, 1H), 6.63 (d, *J* = 1.6 Hz, 1H),

3.28 (d, *J* = 9.8 Hz, 1H), 3.01 (d, *J* = 10.0 Hz, 2H), 2.59 (d, *J* = 2.4 Hz, 1H), 1.86–1.72 (m, 2H), 1.68–1.62 (m, 3H), 1.32 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.3, 154.7, 140.3, 138.3, 130.3, 129.2, 129.0, 128.6, 125.6, 124.3, 122.9), 120.8, 119.6, 112.4, 111.2, 101.4, 49.4, 48.7, 45.2, 34.8, 29.4, 29.3. HRMS (ESI) calcd for $C_{28}H_{23}NO_2$ [M+H]+ : 406.1802, found: 406.1803.



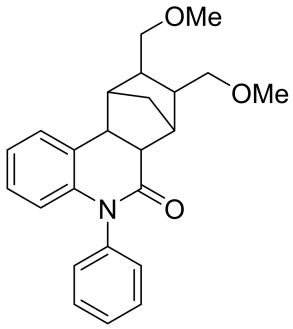
5-phenyl-3-(thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**40c**)

The representative general procedure mentioned above was followed. The desired product **40c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.48) as a white solid in 79% yield (58.6 mg). mp: 218–224 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.33–7.28 (m, 2H), 7.28–7.23 (m, 2H), 7.19 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.38 (d, *J* = 1.2 Hz, 1H), 3.27 (d, *J* = 9.8 Hz, 1H), 3.00 (d, *J* = 9.8 Hz, 2H), 2.57 (s, 1H), 1.84–1.71 (m, 2H), 1.70–1.59 (m, 3H), 1.31 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 141.7, 140.3, 138.4, 134.6, 130.2, 128.5, 126.2, 126.1, 123.9, 121.1, 120.3, 114.1, 49.3, 48.7, 45.2, 45.0, 34.8, 29.5, 29.2. HRMS (ESI) calcd for $C_{24}H_{21}NOS$ [M+H]+ : 372.1417, found: 372.1419.



3-(benzo[*b*]thiophen-3-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**41c**)

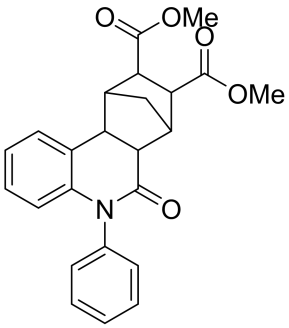
The representative general procedure mentioned above was followed. The desired product **41c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.45) as a white solid in 88% yield (74.1 mg). mp: 239–240 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.71 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40–7.31 (m, 3H), 7.30–7.25 (m, 4H), 6.42 (d, *J* = 1.2 Hz, 1H), 3.33 (d, *J* = 10.0 Hz, 1H), 3.04 (d, *J* = 9.8 Hz, 2H), 2.63 (s, 1H), 1.89–1.71 (m, 3H), 1.69–1.57 (m, 2H), 1.35 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 140.6, 140.2, 138.5, 137.5, 137.3, 134.6, 130.1, 128.5, 124.4, 124.4, 124.3, 123.4, 123.1, 122.9, 122.7, 116.3, 49.3, 48.7, 45.2, 45.2, 34.9, 29.5, 29.3. HRMS (ESI) calcd for $C_{28}H_{23}NOS$ [M+H]+ : 422.1573, found: 422.1573.



8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**42c**)

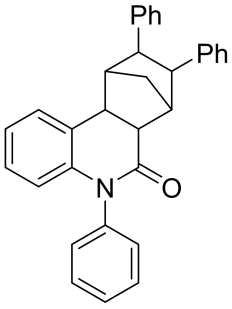
The representative general procedure mentioned above was followed. The desired product **42c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 80% yield (60.3 mg). mp: 238–245 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.20–7.14 (m, 3H), 7.03–6.90 (m, 2H), 6.18–6.10 (m, 1H), 3.72 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.62 (t, *J* = 9.4 Hz, 1H), 3.51 (d, *J* = 6.4 Hz, 2H), 3.46 (s, 3H), 3.36 (s, 3H), 3.10 (d, *J* = 10.0 Hz, 1H), 2.96 (s, 1H), 2.60 (s, 1H), 2.47–2.34 (m, 2H), 1.71 (d, *J* = 10.4 Hz, 1H), 1.41 (d, *J* = 10.4 Hz, 1H), 1.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 140.1, 138.5, 130.0, 129.6, 128.3, 126.7, 124.9, 123.0, 116.1, 71.1, 70.1, 59.1,

58.9, 52.3, 48.4, 42.4, 40.2, 40.0, 37.0, 35.8. HRMS (ESI) calcd for $C_{24}H_{27}NO_3$ [M+H]+ : 378.2064, found: 378.2064.



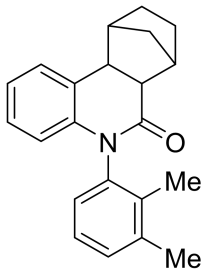
dimethyl 6-oxo-5-phenyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydro-7, 10-methanophenanthridine-8, 9-dicarboxylate (**43c**)

The representative general procedure mentioned above was followed. The desired product **43c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2/1, Rf = 0.52) as a white solid in 70% yield (56.7 mg). mp: 241–244 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (q, *J* = 7.3 Hz, 3H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.16 (s, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.13 (d, *J* = 8.2 Hz, 1H), 4.08 (d, *J* = 10.1 Hz, 1H), 3.72 (d, *J* = 9.5 Hz, 6H), 3.37 (dd, *J* = 11.8, 4.7 Hz, 1H), 3.30 (d, *J* = 4.1 Hz, 1H), 3.25 (d, *J* = 10.1 Hz, 1H), 2.96 (dd, *J* = 11.8, 3.2 Hz, 1H), 2.74 (s, 1H), 1.79 (d, *J* = 10.6 Hz, 1H), 1.46 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 172.4, 169.4, 139.5, 138.4, 130.1, 130.0, 129.5, 128.4, 127.0, 124.4, 123.3, 116.2, 52.1, 51.7, 51.1, 48.0, 47.5, 45.6, 44.1, 37.9, 36.5. HRMS (ESI) calcd for $C_{24}H_{23}NO_5$ [M+H]+ : 406.1649, found: 406.1649.



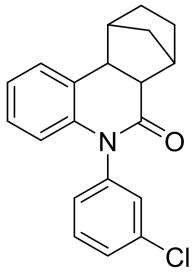
5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**44c**)

The representative general procedure mentioned above was followed. The desired product **44c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.53) as a white solid in 91% yield (80.3 mg). mp: 239–241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.37–7.32 (m, 1H), 7.31–7.27 (m, 2H), 7.11–7.00 (m, 7H), 6.96 (q, *J* = 7.0 Hz, 5H), 6.24 (dt, *J* = 7.8, 2.8 Hz, 1H), 3.75 (s, 2H), 3.63 (d, *J* = 10.0 Hz, 1H), 3.40 (s, 1H), 3.33 (d, *J* = 10.0 Hz, 1H), 2.95 (s, 1H), 2.37 (d, *J* = 11.0 Hz, 1H), 2.02 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 141.8, 141.5, 139.9, 138.5, 130.2, 129.9, 128.7, 128.6, 128.5, 127.6, 127.5, 127.2, 125.5, 125.4, 124.3, 123.2, 116.3, 54.8, 54.3, 54.1, 50.3, 49.5, 46.5, 34.1. HRMS (ESI) calcd for $C_{32}H_{27}NO$ [M+H]+ : 442.2165, found: 442.2166.



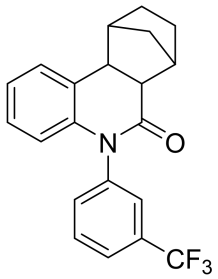
5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**45c**)

The representative general procedure mentioned above was followed. The desired product **45c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 92% yield (58.4 mg). mp: 218–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 3H), 7.01–6.88 (m, 3H), 6.02 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.28–3.18 (m, 1H), 2.99–2.91 (m, 2H), 2.52 (t, *J* = 5.4 Hz, 1H), 2.35 (s, 3H), 1.98 (d, *J* = 28.8 Hz, 3H), 1.79–1.67 (m, 2H), 1.64–1.55 (m, 3H), 1.29–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 139.1, 138.6, 137.3, 135.3, 130.1, 129.7, 127.0 126.2, 124.9, 122.9, 115.7, 49.4, 48.5, 45.2, 45.2, 34.7, 29.3, 29.3, 20.5, 13.9. HRMS (ESI) calcd for $C_{22}H_{23}NO$ [M+H]+ : 318.1852, found: 318.1852.



5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**46c**)

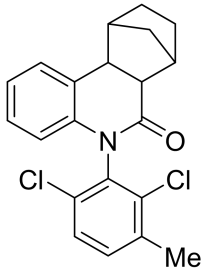
The representative general procedure mentioned above was followed. The desired product **46c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.56) as a white solid in 94% yield (60.7 mg). mp: 211–214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 1H), 7.48 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.32–7.24 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.04 (pd, *J* = 7.4, 1.6 Hz, 2H), 6.17 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.27 (d, *J* = 10.0 Hz, 1H), 2.98 (d, *J* = 9.8 Hz, 2H), 2.57 (d, *J* = 2.2 Hz, 1H), 1.86–1.69 (m, 2H), 1.64 (t, *J* = 8.8 Hz, 3H), 1.31 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.8, 139.4, 135.5, 131.0, 129.9, 128.7, 126.9, 125.0, 123.3, 115.9, 49.3, 48.7, 45.2, 34.8, 29.5, 29.2. HRMS (ESI) calcd for $C_{20}H_{18}ClNO$ [M+H]+ : 324.1150, found: 324.1151.



5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**47c**)

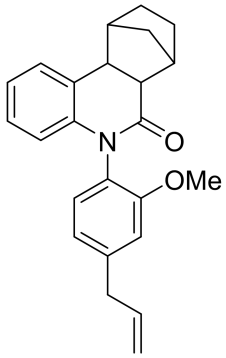
The representative general procedure mentioned above was followed. The desired product **47c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.54) as a white solid in 75% yield (53.5 mg). mp: 188–190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55, 7.41 (dt, *J* = 15.6, 8.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.79–6.72 (m, 1H), 4.23 (d, *J* = 8.2 Hz, 1H), 3.31 (S, 1H), 2.49 (d, *J* = 2.8 Hz, 1H), 2.36 (S, 1H), 1.63–1.55 (m, 2H), 1.44 (dd, *J* = 19.6, 9.8

Hz, 2H), 1.26 (S, 1H), 1.14–1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.2 (d, *J* = 13.5 Hz), 130.7, 127.0, 125.2 (d, *J* = 23.0 Hz), 123.4 (d, *J* = 270.0), 115.8, 49.3, 48.7, 45.2, 34.8, 29.4, 29.2, 27.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48. HRMS (ESI) calcd for $C_{21}H_{18}F_3NO$ [M+H]+ : 358.1413, found: 358.1412.



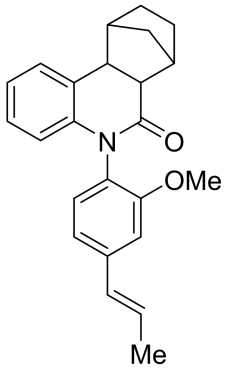
5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**48c**)

The representative general procedure mentioned above was followed. The desired product **48c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.52) as a white solid in 83% yield (61.6 mg). mp: 210–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.00 (dtd, *J* = 16.8, 7.4, 1.2 Hz, 2H), 5.96 (dd, *J* = 5.4, 3.8 Hz, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.97 (d, *J* = 10.2 Hz, 2H), 2.53 (s, 1H), 2.42 (d, *J* = 2.8 Hz, 3H), 1.81–1.66 (m, 3H), 1.60–1.55 (m, 2H), 1.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 136.9, 135.3, 133.7, 132.2, 131.4, 130.1, 128.1, 127.3, 125.0, 123.4, 114.1, 49.2, 48.5, 45.2, 45.0, 34.9, 29.5, 29.3, 20.5. HRMS (ESI) calcd for $C_{21}H_{19}Cl_2NO$ [M+H]+ : 372.0916, found: 372.0914.



5-(4-allyl-2-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**49c**)

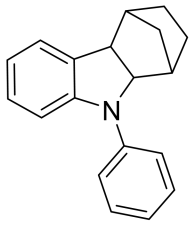
The representative general procedure mentioned above was followed. The desired product **49c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.50) as a white solid in 91% yield (65.3 mg). mp: 221–224 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.1 Hz, 1H), 7.13 – 6.88 (m, 6H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.35 – 6.22 (m, 1H), 6.17 (ddd, *J* = 8.0, 4.0, 1.8 Hz, 1H), 3.73 (s, 3H), 3.19 (dd, *J* = 10.1, 5.6 Hz, 1H), 2.91 (q, *J* = 5.7 Hz, 2H), 2.48 (dd, *J* = 11.4, 3.6 Hz, 1H), 1.91 (dd, *J* = 6.5, 1.6 Hz, 2H), 1.73 (dddd, *J* = 27.0, 13.0, 7.9, 3.1 Hz, 3H), 1.56 (dt, *J* = 7.6, 4.2 Hz, 2H), 1.23 – 1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.3, 139.8, 139.4, 130.7, 130.2, 129.6, 126.9, 125.2, 119.0, 115.4, 109.7, 55.7, 49.5, 48.8, 45.3, 45.2, 34.3, 29.3, 18.6. HRMS (ESI) calcd for $C_{24}H_{25}NO_2$ [M+H]+ : 360.1958, found: 360.1955.



(*E*)-5-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin -6(*5H*)-one (**50c**)

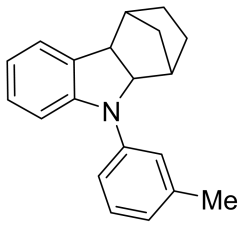
The representative general procedure mentioned above was followed. The desired product **50c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5/1, Rf = 0.51) as a white solid in 89% yield (63.9 mg). mp: 231–233 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.99 (td, *J* = 7.3, 1.8 Hz, 2H), 6.48 (dd, *J* = 15.7, 1.8 Hz, 1H), 6.38 – 6.27 (m, 1H), 6.22 (ddd, *J* = 7.8, 3.7, 1.9 Hz, 1H), 3.77 (d, *J* = 1.6 Hz, 3H), 3.24 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.02 – 2.91 (m, 2H), 2.57 – 2.48 (m, 1H), 1.95 (dd, *J* = 6.5, 1.6 Hz, 3H), 1.85 – 1.74 (m, 2H), 1.67 – 1.55 (m, 3H), 1.27 – 1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.3, 139.9, 139.3, 130.7, 130.2, 129.7,

126.9, 125.1, 119.0, 115.4, 109.7, 55.7, 49.6, 48.7, 45.3, 45.2, 34.3, 29.4, 27.2, 18.6. HRMS (ESI) calcd for $C_{24}H_{25}NO_2$ [M+H]+ : 360.1958, found: 360.1955.



9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**1d**)

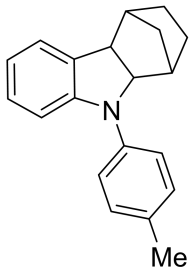
The representative general procedure mentioned above was followed. The desired product **1d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.60) as a colorless oil in 96% yield (49.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.2 Hz, 4H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 3.39 (d, *J* = 8.2 Hz, 1H), 2.58 (d, *J* = 3.0 Hz, 1H), 2.44 (s, 1H), 1.69–1.57 (m, 3H), 1.52–1.44 (m, 1H), 1.35 (d, *J* = 7.0 Hz, 1H), 1.19 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 143.7, 133.7, 129.2, 127.2, 125.0, 121.5, 119.4, 118.5, 108.2, 71.1, 50.5, 43.5, 41.2, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{19}H_{19}N$ [M+H]+ : 262.1590, found: 262.1590.



9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**2d**)

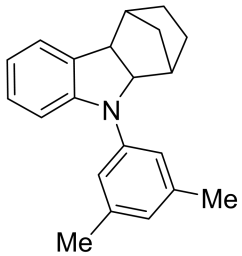
The representative general procedure mentioned above was followed. The desired product **2d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.52) as a colorless oil in 90% yield (49.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 12.2, 4.4 Hz, 1H), 7.13 (s, 1H), 7.11–7.06 (m, 2H), 7.00 (ddd, *J* = 8.0, 7.4, 0.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.67 (td, *J* = 7.3, 1.0 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.47 (d, *J* = 3.4 Hz, 1H), 2.34 (s, 3H), 1.58–1.48 (m, 3H), 1.41–1.34 (m,

1H), 1.26 (dd, *J* = 4.8, 2.6 Hz, 1H), 1.13–1.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 143.7, 138.9, 133.6, 128.9, 127.2, 124.9, 122.4, 120.2, 118.3, 116.8, 108.2, 71.1, 50.4, 43.5, 41.1, 32.4, 28.6, 25.3, 21.7. HRMS (ESI) calcd for $C_{20}H_{21}N$ [M+H]+ : 276.1747, found: 276.1747.



9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**3d**)

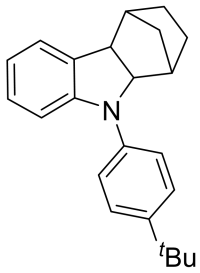
The representative general procedure mentioned above was followed. The desired product **3d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 92% yield (50.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 3.35 (d, *J* = 8.4 Hz, 1H), 2.51 (d, *J* = 3.4 Hz, 1H), 2.38 (s, 3H), 1.64–1.57 (m, 3H), 1.44 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.32 (s, 2H), 1.20–1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 141.1, 133.4, 131.3, 129.7, 127.2, 124.9, 120.0, 118.0, 107.7, 71.3, 50.5, 43.5, 41.1, 32.4, 29.8, 28.6, 25.3, 20.8. HRMS (ESI) calcd for $C_{20}H_{21}N$ [M+H]+ : 276.1747, found: 276.1742.



9-(3,5-dimethylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**4d**)

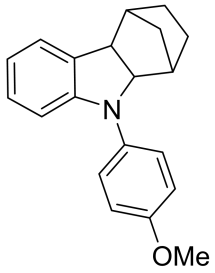
The representative general procedure mentioned above was followed. The desired product **4d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.53) as a colorless oil in 91% yield (52.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.2 Hz, 1H), 7.02–6.97 (m, 1H), 6.94–6.88 (m, 3H), 6.66 (td, *J* = 7.4, 0.8 Hz, 1H), 6.63 (s, 1H), 4.21 (d,

J = 8.4 Hz, 1H), 3.27 (d, *J* = 8.4 Hz, 1H), 2.47 (d, *J* = 3.2 Hz, 1H), 2.33 (s, 1H), 2.30 (s, 6H), 1.58–1.49 (m, 3H), 1.41–1.34 (m, 1H), 1.26 (dd, *J* = 4.8, 2.6 Hz, 1H), 1.13–1.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 143.6, 138.7, 133.5, 127.2, 124.9, 123.6, 118.2, 117.5, 108.2, 71.2, 50.4, 43.5, 41.2, 32.4, 28.6, 25.3, 21.6. HRMS (ESI) calcd for $C_{21}H_{23}N$ [M+H]+ : 290.1903, found: 290.1902.



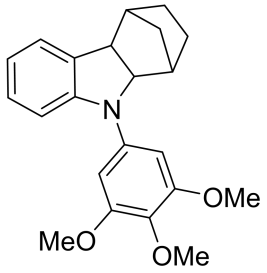
9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**5d**)

The representative general procedure mentioned above was followed. The desired product **5d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.57) as a colorless oil in 93% yield (59.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.31–7.27 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.35 (d, *J* = 8.2 Hz, 1H), 2.54 (d, *J* = 3.2 Hz, 1H), 2.39 (s, 1H), 1.63–1.55 (m, 3H), 1.37 (s, 9H), 1.30 (d, *J* = 4.4 Hz, 2H), 1.15 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 144.3, 141.0, 133.4, 127.2, 125.9, 124.8, 119.2, 118.1, 107.9, 71.2, 50.4, 43.4, 41.2, 34.3, 32.4, 31.5, 28.6, 25.3. HRMS (ESI) calcd for $C_{23}H_{27}N$ [M+H]+ : 318.2216, found: 318.2216.



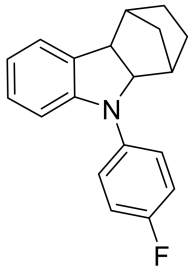
9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**6d**)

The representative general procedure mentioned above was followed. The desired product **6d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.51) as a colorless oil in 88% yield (51.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.98–6.93 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.36 (d, *J* = 8.2 Hz, 1H), 2.46 (d, *J* = 3.8 Hz, 1H), 2.41 (s, 1H), 1.68–1.57 (m, 3H), 1.50–1.41 (m, 1H), 1.30–1.26 (m, 1H), 1.22–1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 150.3, 137.0, 132.9, 127.3, 124.8, 122.8, 117.6, 114.6, 106.9, 71.9, 55.6, 50.6, 43.5, 41.2, 32.4, 28.7, 25.2. HRMS (ESI) calcd for $C_{20}H_{21}NO$ [M+H]+ : 292.1696, found: 292.1694.



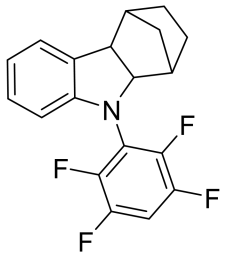
10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**7d**)

The representative general procedure mentioned above was followed. The desired product **7d** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (10/1, Rf = 0.50) as a colorless oil in 88% yield (61.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.2 Hz, 1H), 7.01 (ddd, *J* = 8.0, 7.4, 0.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.67 (td, *J* = 7.4, 0.8 Hz, 1H), 6.53 (s, 2H), 4.17 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 9H), 3.30 (d, *J* = 8.4 Hz, 1H), 2.48 (d, *J* = 3.2 Hz, 1H), 2.35 (s, 1H), 1.62–1.49 (m, 3H), 1.46–1.35 (m, 1H), 1.26 (s, 1H), 1.17–1.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.3, 139.9, 133.4, 127.3, 124.9, 118.2, 107.8, 98.3, 71.8, 61.0, 56.2, 50.5, 43.4, 41.4, 32.5, 28.5, 25.2. HRMS (ESI) calcd for $C_{22}H_{25}NO_3$ [M+H]+ : 352.1907, found: 352.1905.



9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**8d**)

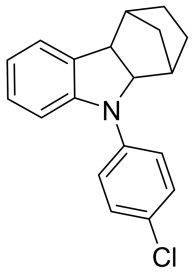
The representative general procedure mentioned above was followed. The desired product **8d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.57) as a colorless oil in 90 % yield (50.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.09–7.02 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 3.36 (d, *J* = 8.4 Hz, 1H), 2.46 (d, *J* = 3.4 Hz, 1H), 2.40 (s, 1H), 1.65–1.55 (m, 3H), 1.44 (t, *J* = 8.4 Hz, 1H), 1.31 (s, 1H), 1.17 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, *J* = 241.2 Hz), 149.3, 139.9, 133.2, 127.3, 124.9, 121.8 (d, *J* = 7.7 Hz), 118.3, 115.8 (d, *J* = 22.3 Hz), 107.4, 71.7, 50.5, 43.4, 41.2, 32.3, 28.6, 25.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.00. HRMS (ESI) calcd for $C_{19}H_{18}FN$ [M+H]+ : 280.1496, found: 280.1496.



9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**9d**)

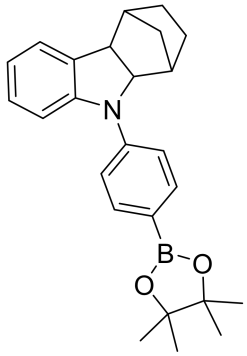
The representative general procedure mentioned above was followed. The desired product **9d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 90 % yield (60.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.4 Hz, 1H), 7.04–6.97 (m, 1H), 6.90 (tt, *J* = 9.8, 7.2 Hz, 1H), 6.73 (td, *J* = 7.4, 0.8 Hz, 1H), 6.26–6.19 (m, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.35 (d, *J* = 8.2 Hz, 1H), 2.38 (s, 1H), 2.13 (d, *J* = 3.8 Hz, 1H), 1.65 (d, *J* = 10.4 Hz, 1H), 1.60–1.48 (m, 2H), 1.43–1.34 (m, 1H), 1.19 (ddd, *J* = 11.1, 4.4, 1.7 Hz, 1H), 1.15–1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 147.8 (t, *J* = 12.2 Hz),

145.3 (d, *J* = 15.9 Hz), 131.7, 127.4, 124.7, 121.7 (t, *J* = 13.2 Hz), 119.1, 107.1 (t, *J* = 8.2 Hz), 101.6 (t, *J* = 23.1 Hz), 70.7, 51.2, 43.5, 40.9, 32.2, 28.4, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.32, -140.97, -145.62. HRMS (ESI) calcd for $C_{19}H_{15}F_4N$ [M+H]+ : 334.1213, found: 334.1214.



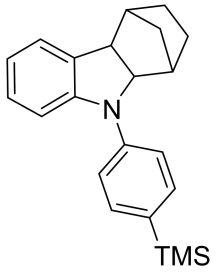
9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**10d**)

The representative general procedure mentioned above was followed. The desired product **10d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.61) as a colorless oil in 45 % yield (26.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 4H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 4.19 (d, *J* = 8.2 Hz, 1H), 2.46 (d, *J* = 3.2 Hz, 1H), 2.35 (s, 1H), 1.60 (ddd, *J* = 13.8, 7.2, 3.6 Hz, 2H), 1.47 (d, *J* = 10.2 Hz, 1H), 1.43–1.36 (m, 1H), 1.26 (d, *J* = 4.8 Hz, 1H), 1.11 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 142.3, 133.6, 129.1, 127.2, 125.9, 125.0, 120.4, 118.9, 108.2, 71.1, 50.4, 43.4, 40.9, 32.3, 28.5, 25.2. HRMS (ESI) calcd for $C_{19}H_{18}ClN$ [M+H]+ : 296.1201, found: 296.1203.



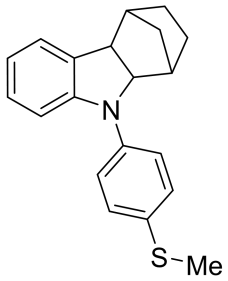
10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**)

The representative general procedure mentioned above was followed. The desired product **11d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.5) as a colorless oil in 82 % yield (63.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.19–7.05 (m, 3H), 6.78 (td, *J* = 7.0, 1.2 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 3.35 (d, *J* = 8.2 Hz, 1H), 2.58 (s, 1H), 2.40 (s, 1H), 1.63 (dt, *J* = 10.8, 5.2 Hz, 2H), 1.56–1.46 (m, 2H), 1.39 (s, 12H), 1.36–1.29 (m, 1H), 1.14 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.2, 135.9, 134.0, 127.2, 125.0, 119.2, 117.4, 109.1, 83.5, 70.6, 50.3, 43.4, 40.8, 32.3, 29.7, 28.5, 25.2, 24.8. HRMS (ESI) calcd for $C_{25}H_{30}BNO_2$ [M+H]+ : 388.2442, found: 388.2444.



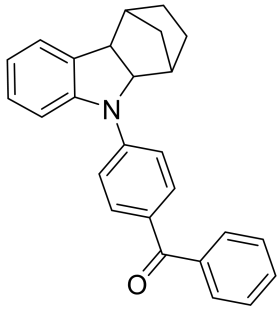
9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**12d**)

The representative general procedure mentioned above was followed. The desired product **12d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.6) as a colorless oil in 92 % yield (61.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.21–7.14 (m, 1H), 7.13–7.07 (m, 2H), 6.84–6.73 (m, 1H), 4.34 (d, *J* = 8.2 Hz, 1H), 3.38 (d, *J* = 8.2 Hz, 1H), 2.60 (s, 1H), 2.43 (s, 1H), 1.72–1.62 (m, 2H), 1.61–1.55 (m, 1H), 1.51–1.44 (m, 1H), 1.34 (dd, *J* = 12.8, 3.8 Hz, 1H), 1.18 (d, *J* = 10.4 Hz, 1H), 0.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 144.4, 134.5, 134.1, 132.0, 127.4, 125.2, 119.6, 118.9, 118.3, 108.8, 70.9, 50.6, 43.6, 41.3, 32.7, 28.8, 25.5, 1.6. HRMS (ESI) calcd for $C_{22}H_{27}NSi$ [M+H]+ : 334.1986, found: 334.1986.



9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**13d**)

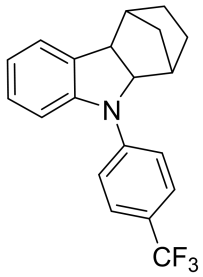
The representative general procedure mentioned above was followed. The desired product **13d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 78 % yield (47.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 4H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.62 (t, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 8.2 Hz, 1H), 3.22 (d, *J* = 8.2 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 1H), 1.59–1.52 (m, 1H), 1.50 (tt, *J* = 8.8, 4.4 Hz, 1H), 1.42 (d, *J* = 10.3 Hz, 1H), 1.36–1.28 (m, 1H), 1.18 (dd, *J* = 5.0, 2.2 Hz, 1H), 1.03 (dt, *J* = 10.6, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.7, 133.6, 129.6, 129.2, 127.3, 124.9, 120.0, 118.6, 108.2, 71.2, 50.4, 43.4, 41.0, 32.3, 28.5, 25.2, 17.6. HRMS (ESI) calcd for $C_{20}H_{21}NS$ [M+H]+ : 308.1467, found: 308.1466.



(4-(1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazol-9-yl)phenyl)(phenyl)methanone (**14d**)

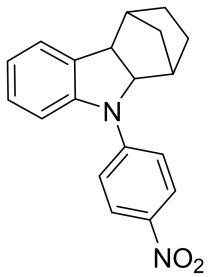
The representative general procedure mentioned above was followed. The desired product **14d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.49) as a colorless oil in 81 % yield (59.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.86–7.80 (m, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 3.40 (d, *J* = 8.0 Hz, 1H), 2.66 (s, 1H), 2.43 (s, 1H), 1.66 (dq, *J*

= 12.4, 7.6, 6.2 Hz, 2H), 1.47 (d, *J* = 7.6 Hz, 2H), 1.39 (d, *J* = 5.8 Hz, 1H), 1.17 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 147.7, 146.8, 138.7, 134.6, 132.2, 131.6, 129.7, 128.9, 128.2, 127.3, 125.3, 120.5, 116.3, 110.1, 70.6, 50.3, 43.3, 40.9, 32.4, 28.3, 25.3. HRMS (ESI) calcd for $C_{26}H_{23}NO$ [M+H]+ : 366.1852, found: 366.1851.



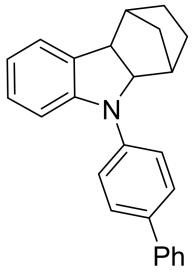
9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**15d**)

The representative general procedure mentioned above was followed. The desired product **15d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.59) as a colorless oil in 92 % yield (60.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.16–7.11 (m, 1H), 7.11–7.04 (m, 2H), 6.81–6.75 (m, 1H), 4.24 (d, *J* = 8.2 Hz, 1H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.53 (d, *J* = 3.2 Hz, 1H), 2.37 (s, 1H), 1.65–1.54 (m, 2H), 1.46–1.38 (m, 2H), 1.28 (dd, *J* = 13.6, 2.4 Hz, 1H), 1.14–1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.6, 134.2, 127.2, 126.3 (q, *J* = 3.8 Hz), 125.2, 124.6 (q, 278.0) 121.9 (q, *J* = 32.7 Hz), 120.0, 117.4, 109.3, 70.8, 50.3, 43.3, 40.8, 32.3, 28.4, 25.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.51. HRMS (ESI) calcd for $C_{20}H_{18}F_3N$ [M+H]+ : 330.1464, found: 330.1464.



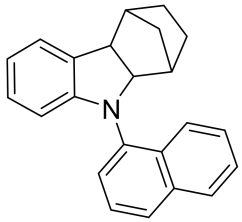
9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**16d**)

The representative general procedure mentioned above was followed. The desired product **16d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.61) as a colorless oil in 88 % yield (53.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.18 (m, 2H), 7.39–7.31 (m, 2H), 7.31–7.24 (m, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.22–7.13 (m, 1H), 6.94 (td, *J* = 7.4, 0.8 Hz, 1H), 4.28 (d, *J* = 8.0 Hz, 1H), 3.42 (d, *J* = 8.0 Hz, 1H), 2.63 (s, 1H), 2.44 (s, 1H), 1.67 (dq, *J* = 12.0, 7.4, 5.8 Hz, 2H), 1.48 (td, *J* = 9.0, 7.8, 2.2 Hz, 1H), 1.38 (t, *J* = 9.4 Hz, 2H), 1.17 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 145.9, 139.7, 134.9, 127.4, 125.7, 125.5, 121.7, 115.8, 110.8, 70.8, 50.3, 43.2, 40.9, 32.4, 28.2, 25.4. HRMS (ESI) calcd for $C_{19}H_{18}N_2O_2$ [M+H]+ : 307.1441, found: 307.1441.



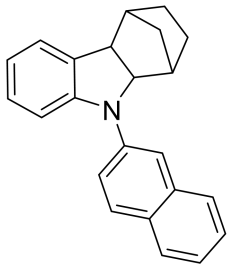
9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**17d**)

The representative general procedure mentioned above was followed. The desired product **17d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.62) as a colorless oil in 89 % yield (60.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.56–7.53 (m, 2H), 7.44–7.39 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.26 (m, 1H), 7.12–7.08 (m, 1H), 7.07–7.01 (m, 2H), 6.71 (ddd, *J* = 7.4, 6.0, 2.4 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 8.2 Hz, 1H), 2.54 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 1H), 1.64–1.55 (m, 2H), 1.52 (dd, *J* = 7.0, 5.0 Hz, 1H), 1.43–1.37 (m, 1H), 1.30–1.24 (m, 1H), 1.14–1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.9, 140.9, 133.9, 133.8, 128.8, 127.7, 127.3, 126.7, 126.6, 125.0, 119.2, 118.7, 108.5, 71.0, 50.4, 43.5, 41.1, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{25}H_{23}N$ [M+H]+ : 338.1903, found: 338.1903.



9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**18d**)

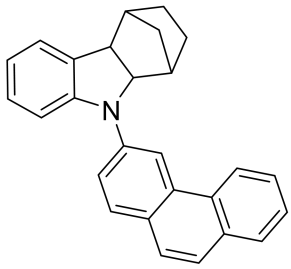
The representative general procedure mentioned above was followed. The desired product **18d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.60) as a colorless oil in 81 % yield (50.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.41 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.31 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.14–7.08 (m, 1H), 7.05 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.72 (ddd, *J* = 7.2, 5.4, 3.0 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.50 (s, 1H), 2.36 (s, 1H), 1.64–1.48 (m, 3H), 1.43–1.37 (m, 1H), 1.31–1.22 (m, 1H), 1.10 (dt, *J* = 10.2, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 141.3, 134.4, 133.8, 129.4, 128.9, 127.6, 127.3, 126.8, 126.4, 125.1, 123.9, 120.6, 118.8, 115.1, 108.2, 71.1, 50.5, 43.5, 41.1, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{23}H_{21}N$ [M+H]+ : 312.1747, found: 312.1747.



9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**19d**)

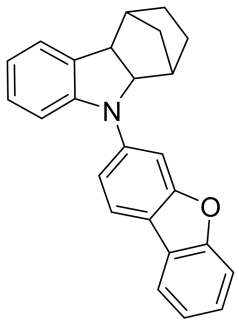
The representative general procedure mentioned above was followed. The desired product **19d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.62) as a colorless oil in 96 % yield (59.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.41 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.31 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.11 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.07–7.00 (m, 2H), 6.75–6.68 (m, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.50 (d, *J* = 3.4 Hz, 1H), 2.36 (s, 1H), 1.60–1.51 (m, 3H), 1.44–1.36 (m, 1H), 1.30–1.23 (m, 1H), 1.13–

1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.3, 134.4, 133.8, 129.4, 128.8, 127.6, 127.3, 126.8, 126.4, 125.1, 123.9, 120.6, 118.8, 115.1, 108.2, 71.2, 50.5, 43.5, 41.2, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{23}H_{27}N$ [M+H]+ : 312.1747, found: 312.1745.



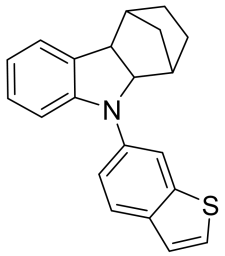
9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**20d**)

The representative general procedure mentioned above was followed. The desired product **20d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.65) as a colorless oil in 75 % yield (54.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 12.0, 5.6 Hz, 2H), 7.53 (dt, *J* = 14.8, 6.0 Hz, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 7.2, 4.8 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.25 (d, *J* = 8.2 Hz, 1H), 2.47 (s, 1H), 2.29 (s, 1H), 1.51–1.45 (m, 3H), 1.32 (t, *J* = 8.2 Hz, 1H), 1.24–1.16 (m, 1H), 1.03 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 133.9, 133.2, 131.2, 130.5, 128.6, 127.5, 127.3, 126.7, 126.6, 125.6, 125.1, 124.9, 123.7, 122.1, 119.6, 118.9, 116.2, 108.4, 71.1, 50.5, 43.5, 41.2, 32.5, 28.6, 25.4. HRMS (ESI) calcd for $C_{27}H_{23}N$ [M+H]+ : 362.1903, found: 362.1905.



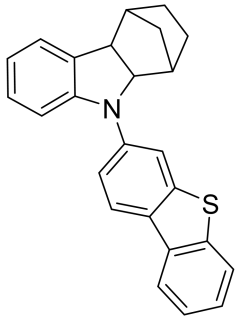
9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**21d**)

The representative general procedure mentioned above was followed. The desired product **21d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.51) as a colorless oil in 89 % yield (62.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 2H), 7.50 (t, *J* = 5.4 Hz, 2H), 7.35 (td, *J* = 7.8, 1.4 Hz, 1H), 7.32–7.26 (m, 2H), 7.08 (dt, *J* = 14.6, 7.6 Hz, 3H), 6.74 (ddd, *J* = 8.2, 6.8, 1.8 Hz, 1H), 4.30 (d, *J* = 8.2 Hz, 1H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.53 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 1H), 1.61–1.50 (m, 3H), 1.43–1.36 (m, 1H), 1.26 (dd, *J* = 12.4, 3.8 Hz, 1H), 1.14–1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.4, 148.4, 143.5, 133.9, 127.3, 125.9, 125.1, 124.6, 122.8, 120.9, 119.8, 119.1, 117.9, 114.9, 111.4, 108.5, 101.9, 71.5, 50.5, 43.5, 41.1, 32.4, 28.5, 25.3. HRMS (ESI) calcd for $C_{25}H_{21}NO$ [M+H]+ : 352.1696, found: 352.1694.



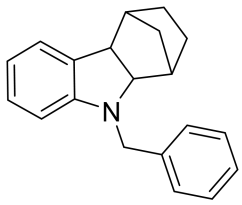
9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**22d**)

The representative general procedure mentioned above was followed. The desired product **22d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.50) as a colorless oil in 77 % yield (48.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.25 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.17–7.13 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.60 (t, *J* = 7.4 Hz, 1H), 4.20 (d, *J* = 8.2 Hz, 1H), 3.23 (d, *J* = 8.2 Hz, 1H), 2.38 (d, *J* = 3.6 Hz, 1H), 2.28 (s, 1H), 1.50–1.44 (m, 3H), 1.30 (dd, *J* = 12.6, 6.4 Hz, 1H), 1.19–1.11 (m, 2H), 1.03 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 140.8, 140.7, 133.5, 133.4, 127.3, 124.9, 123.6, 122.9, 118.8, 118.3, 114.7, 107.6, 71.8, 50.6, 43.5, 41.1, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{21}H_{19}NS$ [M+H]+ : 318.1311, found: 318.1312.



9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**23d**)

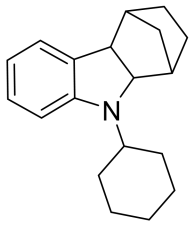
The representative general procedure mentioned above was followed. The desired product **23d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.54) as a colorless oil in 80 % yield (58.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.96 (m, 2H), 7.75–7.71 (m, 1H), 7.67 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.33 (ddt, *J* = 7.4, 6.0, 3.4 Hz, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.62 (td, *J* = 7.4, 0.8 Hz, 1H), 4.24 (d, *J* = 8.2 Hz, 1H), 3.25 (d, *J* = 8.2 Hz, 1H), 2.40 (d, *J* = 2.8 Hz, 1H), 2.29 (s, 1H), 1.48 (ddd, *J* = 11.4, 10.2, 7.2 Hz, 3H), 1.31 (t, *J* = 8.4 Hz, 1H), 1.16 (dd, *J* = 12.8, 3.8 Hz, 1H), 1.04 (dd, *J* = 10.2, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 140.9, 140.4, 136.6, 135.4, 133.5, 132.7, 127.4, 126.8, 125.1, 124.3, 123.4, 123.0, 121.7, 120.7, 118.5, 112.9, 107.6, 71.8, 50.6, 43.5, 41.2, 32.4, 28.6, 25.3. HRMS (ESI) calcd for $C_{25}H_{21}NS$ [M+H]+ : 368.1467, found: 368.1466.



9-benzyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**24d**)

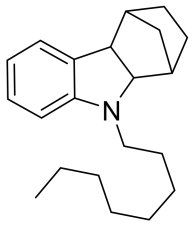
The representative general procedure mentioned above was followed. The desired product **24d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.59) as a colorless oil in 77 % yield (42.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 4H), 7.29 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.58 (td, *J* = 7.4, 0.8 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1H), 4.48–4.36 (m, 2H), 3.69 (d, *J* = 8.4 Hz, 1H), 3.32 (d,

J = 8.4 Hz, 1H), 2.36 (d, *J* = 3.0 Hz, 1H), 2.29 (d, *J* = 4.4 Hz, 1H), 1.64 (dd, *J* = 10.0, 1.6 Hz, 1H), 1.56 (ddt, *J* = 14.8, 12.0, 4.0 Hz, 2H), 1.40–1.35 (m, 1H), 1.21–1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 139.5, 131.6, 128.5, 127.7, 127.1, 126.8, 124.3, 116.1, 104.6, 71.9, 51.2, 51.0, 43.3, 41.2, 32.7, 28.8, 25.0. HRMS (ESI) calcd for $C_{20}H_{21}N$ [M+H]+ : 276.1747, found: 276.1747.



9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**25d**)

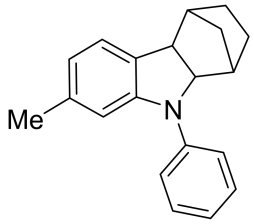
The representative general procedure mentioned above was followed. The desired product **25d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.54) as a colorless oil in 61 % yield (32.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.97 (td, *J* = 7.4, 1.2 Hz, 1H), 4.07 (s, 1H), 2.98 (d, *J* = 9.8 Hz, 1H), 2.77 (d, *J* = 4.0 Hz, 1H), 2.71 (d, *J* = 9.8 Hz, 1H), 2.52 (qd, *J* = 12.2, 3.4 Hz, 1H), 2.46–2.33 (m, 2H), 1.92–1.81 (m, 2H), 1.80–1.62 (m, 4H), 1.54–1.43 (m, 3H), 1.40–1.23 (m, 4H), 1.12 (dt, *J* = 10.0, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 127.4, 124.2, 115.9, 106.0, 67.1, 55.9, 51.2, 44.1, 43.3, 32.4, 29.7, 29.4, 28.8, 28.1, 27.2, 26.0, 25.4, 14.2. HRMS (ESI) calcd for $C_{19}H_{25}N$ [M+H]+ : 268.2060, found: 268.2062.



9-octyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**26d**)

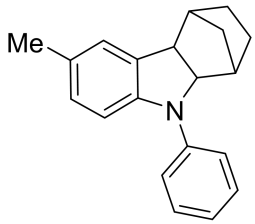
The representative general procedure mentioned above was followed. The desired product **26d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.58) as a colorless oil in 55 % yield (32.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–6.94 (m,

2H), 6.51 (t, *J* = 6.8 Hz, 1H), 6.25 (d, *J* = 7.4 Hz, 1H), 3.60 (d, *J* = 8.4 Hz, 1H), 3.24 (d, *J* = 8.2 Hz, 1H), 3.14 (t, *J* = 7.4 Hz, 2H), 2.33 (d, *J* = 21.0 Hz, 2H), 1.63–1.55 (m, 6H), 1.34 (dd, *J* = 17.0, 5.8 Hz, 10H), 1.23–1.12 (m, 2H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 131.8, 127.6, 124.2, 115.5, 104.4, 71.4, 50.9, 47.2, 43.3, 41.6, 32.5, 31.9, 29.5, 29.3, 28.8, 27.8, 27.3, 25.2, 22.7, 14.1. HRMS (ESI) calcd for $C_{21}H_{31}N$ [M+H]+ : 298.2529, found: 298.2526.



7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**27d**)

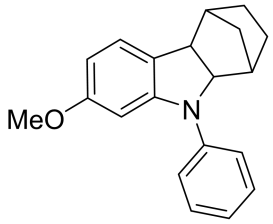
The representative general procedure mentioned above was followed. The desired product **27d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.59) as a colorless oil in 97 % yield (53.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.19 (m, 4H), 6.88 (td, *J* = 6.2, 3.2 Hz, 2H), 6.70 (s, 1H), 6.47–6.40 (m, 1H), 4.16 (d, *J* = 8.2 Hz, 1H), 3.17 (d, *J* = 8.2 Hz, 1H), 2.38 (d, *J* = 3.4 Hz, 1H), 2.24 (s, 1H), 2.18 (s, 3H), 150–1.41 (m, 3H), 1.34–1.24 (m, 1H), 1.17–1.08 (m, 1H), 1.01 (dt, *J* = 10.2, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 143.7, 137.0, 130.8, 129.1, 124.6, 121.4, 119.6, 119.2, 108.9, 71.4, 50.1, 43.4, 41.0, 32.3, 28.5, 25.3, 21.8. HRMS (ESI) calcd for $C_{20}H_{21}N$ [M+H]+ : 276.1747, found: 276.1746.



6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**28d**)

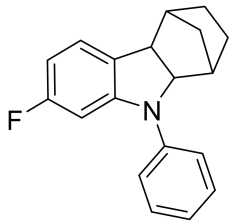
The representative general procedure mentioned above was followed. The desired product **28d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf =

0.55) as a colorless oil in 92 % yield (50.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 4H), 7.01–6.94 (m, 3H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 8.2 Hz, 1H), 3.33 (d, *J* = 8.2 Hz, 1H), 2.56 (s, 1H), 2.41–2.36 (m, 1H), 2.32 (s, 3H), 1.62 (td, *J* = 10.8, 10.0, 4.2 Hz, 2H), 1.55 (d, *J* = 10.4 Hz, 1H), 1.48–1.40 (m, 1H), 1.32 (d, *J* = 5.4 Hz, 1H), 1.16 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 144.2, 133.9, 129.1, 127.9, 127.4, 125.8, 120.8, 118.6, 108.4, 71.3, 50.4, 43.4, 41.2, 32.4, 28.6, 25.3, 20.7. HRMS (ESI) calcd for $C_{20}H_{21}N$ [M+H]+ : 276.1747, found: 276.1747.



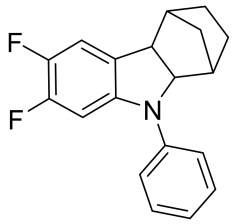
7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**29d**)

The representative general procedure mentioned above was followed. The desired product **29d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.49) as a colorless oil in 88 % yield (51.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 4H), 6.89 (ddd, *J* = 5.8, 4.0, 2.0 Hz, 2H), 6.45 (d, *J* = 2.4 Hz, 1H), 6.15 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.19 (d, *J* = 8.0 Hz, 1H), 3.66 (s, 3H), 3.15 (d, *J* = 8.2 Hz, 1H), 2.37 (d, *J* = 3.2 Hz, 1H), 2.22 (s, 1H), 1.51–1.42 (m, 3H), 1.34–1.24 (m, 1H), 1.22–1.11 (m, 1H), 1.07–0.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 150.1, 143.4, 129.2, 126.2, 124.9, 121.7, 119.8, 102.6, 95.4, 71.9, 55.4, 49.7, 43.5, 40.9, 32.3, 28.4, 25.2. HRMS (ESI) calcd for $C_{20}H_{21}NO$ [M+H]+ : 292.1696, found: 292.1696.



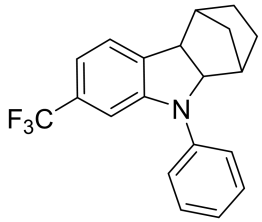
7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**30d**)

The representative general procedure mentioned above was followed. The desired product **30d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 92 % yield (51.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.27 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.00 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.95 (ddd, *J* = 7.8, 5.8, 0.8 Hz, 1H), 6.58 (dd, *J* = 11.0, 2.2 Hz, 1H), 6.33 (ddd, *J* = 9.2, 8.0, 2.4 Hz, 1H), 4.30 (d, *J* = 8.2 Hz, 1H), 3.23 (d, *J* = 8.2 Hz, 1H), 2.43 (d, *J* = 3.4 Hz, 1H), 2.30 (s, 1H), 1.59–1.49 (m, 3H), 1.41–1.33 (m, 1H), 1.27–1.18 (m, 1H), 1.13–1.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 240.5 Hz), 150.4 (d, *J* = 12.0 Hz), 142.8, 129.3, 128.9 (d, *J* = 2.1 Hz), 125.0 (d, *J* = 10.8 Hz), 122.3, 120.1, 104.2, 103.9, 95.8, 95.5, 72.0, 49.7, 43.5, 40.9, 32.2, 28.4, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38. HRMS (ESI) calcd for $C_{19}H_{18}FN$ [M+H]+ : 280.1402, found: 280.1403.



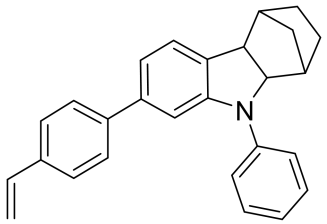
6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**31d**)

The representative general procedure mentioned above was followed. The desired product **31d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.57) as a colorless oil in 90 % yield (53.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 3.8, 1.8 Hz, 2H), 7.23 (dd, *J* = 8.6, 1.2 Hz, 2H), 6.99 (dd, *J* = 10.4, 4.2 Hz, 1H), 6.87–6.81 (m, 1H), 6.66 (dd, *J* = 12.0, 6.6 Hz, 1H), 4.25 (d, *J* = 8.2 Hz, 1H), 3.23 (d, *J* = 8.2 Hz, 1H), 2.45 (d, *J* = 3.6 Hz, 1H), 2.29 (s, 1H), 1.59–1.46 (m, 3H), 1.40–1.32 (m, 1H), 1.27–1.18 (m, 1H), 1.16–1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, *J* = 242.1), 145.2 (d, *J* = 10.4 Hz), 144.4 (d, *J* = 13.6 Hz), 143.1, 142.1 (d, *J* = 13.8 Hz), 129.3, 128.6 (dd, *J* = 5.3, 2.8 Hz), 122.2, 119.5, 113.4 (d, *J* = 1.4 Hz), 113.3 (d, *J* = 1.3 Hz), 97.2, 96.9, 71.9, 49.9, 43.3, 41.2, 32.3, 28.3, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.43–-139.69 (m), -150.75–-151.33 (m). HRMS (ESI) calcd for $C_{19}H_{17}F_2N$ [M+H]+ : 298.1402, found: 298.1404.



9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**32d**)

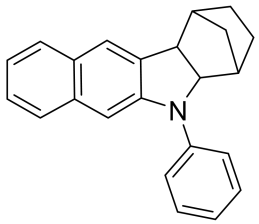
The representative general procedure mentioned above was followed. The desired product **32d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.59) as a colorless oil in 95 % yield (62.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.23–7.19 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00–6.94 (m, 2H), 6.83 (dd, *J* = 7.6, 0.6 Hz, 1H), 4.24 (d, *J* = 8.4 Hz, 1H), 3.22 (d, *J* = 8.2 Hz, 1H), 2.37 (d, *J* = 3.6 Hz, 1H), 2.28 (s, 1H), 1.52–1.41 (m, 3H), 1.35–1.29 (m, 1H), 1.17 (dd, *J* = 4.8, 2.8 Hz, 1H), 1.09–1.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 142.6, 137.4, 129.7 (q, *J* = 31.1 Hz), 129.46, 124.84, 124.6 (d, J = 270.7 Hz) 122.8, 120.4, 115.2 (q, *J* = 4.0 Hz), 103.6 (q, *J* = 3.8 Hz), 71.5, 50.1, 43.5, 41.0, 32.4, 28.5, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.61 (d, *J* = 29.0 Hz). HRMS (ESI) calcd for $C_{20}H_{18}F_3N$ [M+H]+ : 330.1464, found: 330.1464.



9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**33d**)

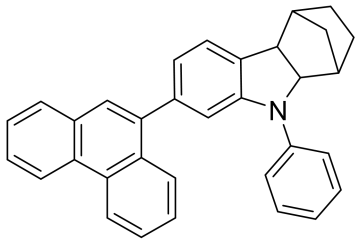
The representative general procedure mentioned above was followed. The desired product **33d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.63) as a colorless oil in 88 % yield (58.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.44–7.37 (m, 4H), 7.23–7.19 (m, 2H), 7.06 (td, *J* = 6.4, 1.2 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.80 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.39 (d, *J* = 8.2 Hz, 1H), 2.56 (s, 1H), 2.45 (s, 1H), 1.65 (dd, *J* = 12.6, 6.6 Hz, 3H), 1.51–1.44 (m, 1H), 1.33 (s, 1H), 1.20 (d, *J* = 10.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 143.5, 141.4, 140.3, 136.5, 136.3, 133.1, 129.3, 127.3, 126.5, 125.1, 121.8, 119.9, 117.6, 113.7, 106.6, 71.6, 50.2, 43.5, 41.1, 32.5, 28.6, 25.3. HRMS (ESI) calcd for $C_{27}H_{25}N$ [M+H]+ : 364.2060, found: 364.2062.



5-phenyl-2,3,4,4a,5,11b-hexahydro-*1H*-1,4-methanobenzo[*b*]carbazole (**34d**)

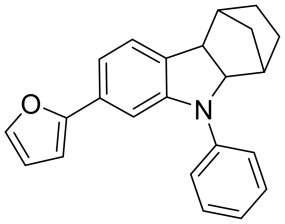
The representative general procedure mentioned above was followed. The desired product **34d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.59) as a colorless oil in 95 % yield (59.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.55 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.49–7.43 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.19 (s, 1H), 7.15–7.09 (m, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 2.53 (d, *J* = 8.6 Hz, 2H), 1.66 (td, *J* = 11.0, 3.8 Hz, 2H), 1.57 (d, *J* = 9.2 Hz, 1H), 1.51 (t, *J* = 8.4 Hz, 1H), 1.34 (s, 2H), 1.18 (dd, *J* = 10.2, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 143.1, 136.9, 134.6, 129.3, 128.8, 127.2, 126.1, 125.7, 123.4, 122.3, 122.2, 120.5, 100.7, 70.9, 49.6, 44.1, 40.7, 32.4, 28.6, 25.2. HRMS (ESI) calcd for $C_{23}H_{21}N$ [M+H]+ : 312.1747, found: 312.1746.



7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**35d)**

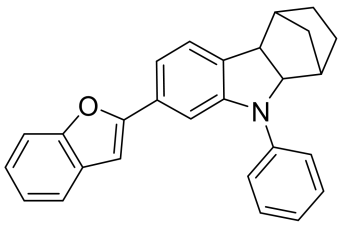
The representative general procedure mentioned above was followed. The desired product **35d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.58) as a colorless oil in 92 % yield (80.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.2 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.77 (s, 1H),

7.74–7.69 (m, 2H), 7.68–7.64 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37–7.30 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.23–7.19 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.95 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.43 (d, *J* = 8.2 Hz, 1H), 3.49 (d, *J* = 8.2 Hz, 1H), 2.64 (d, *J* = 3.2 Hz, 1H), 2.53 (s, 1H), 1.78–1.65 (m, 3H), 1.59–1.47 (m, 1H), 1.41–1.33 (m, 1H), 1.32–1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 143.5, 139.98, 139.5, 132.9, 131.7, 131.4, 130.6, 129.9, 129.2, 128.6, 127.2, 127.2, 126.8, 126.4, 126.4, 124.6, 122.8, 122.5, 121.6, 120.7, 119.5, 109.9, 71.5, 50.3, 43.5, 41.1, 32.6, 28.6, 25.3. HRMS (ESI) calcd for $C_{33}H_{27}N$ [M+H]+ : 438.2216, found: 438.2218.



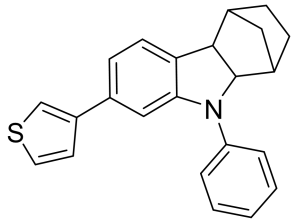
7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**36d**)

The representative general procedure mentioned above was followed. The desired product **36d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.51) as a colorless oil in 95 % yield (62.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 4.2 Hz, 4H), 7.31–7.29 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (ddd, *J* = 13.6, 7.0, 2.8 Hz, 2H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 3.35 (d, *J* = 8.2 Hz, 1H), 2.54 (d, *J* = 3.4 Hz, 1H), 2.41 (s, 1H), 1.66–1.57 (m, 3H), 1.44 (dd, *J* = 12.2, 6.4 Hz, 1H), 1.33–1.29 (m, 1H), 1.20–1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 149.2, 143.6, 141.6, 133.2, 130.2, 129.3, 125.0, 121.9, 119.9, 114.7, 111.5, 104.5, 103.5, 71.7, 50.2, 43.4, 41.1, 32.4, 28.5, 25.3. HRMS (ESI) calcd for $C_{23}H_{21}NO$ [M+H]+ : 328.1696, found: 328.1692.



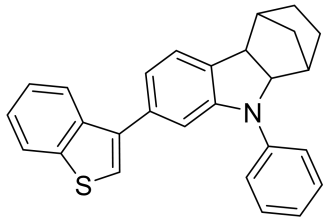
7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**37d**)

The representative general procedure mentioned above was followed. The desired product **37d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.50) as a colorless oil in 91 % yield (68.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 4.6 Hz, 5H), 7.34–7.23 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.10 (p, *J* = 4.2 Hz, 1H), 6.96 (s, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 3.38 (d, *J* = 8.2 Hz, 1H), 2.55 (s, 1H), 2.44 (s, 1H), 1.72–1.56 (m, 3H), 1.46 (t, *J* = 8.4 Hz, 1H), 1.37–1.27 (m, 3H), 1.20 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 154.7, 149.4, 143.4, 134.6, 129.7, 129.4, 125.1, 123.9, 122.8, 122.2, 120.7, 120.2, 115.9, 111.1, 104.2, 100.8, 71.7, 50.3, 43.5, 41.1, 32.5, 28.5, 25.3. HRMS (ESI) calcd for $C_{27}H_{23}NO$ [M+H]+ : 378.1852, found: 378.1850.



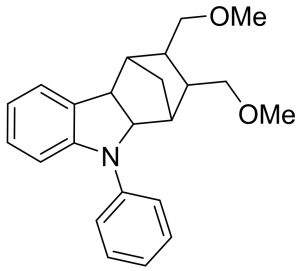
9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**38d**)

The representative general procedure mentioned above was followed. The desired product **38d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.52) as a colorless oil in 90 % yield (61.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.8 Hz, 5H), 7.38 (d, *J* = 2.2 Hz, 2H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.07 (ddd, *J* = 8.4, 5.8, 2.4 Hz, 1H), 7.00 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 3.38 (d, *J* = 8.2 Hz, 1H), 2.56 (d, *J* = 3.4 Hz, 1H), 2.44 (s, 1H), 1.68–1.57 (m, 3H), 1.47 (t, *J* = 8.4 Hz, 1H), 1.37–1.30 (m, 1H), 1.20 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 143.6, 143.1, 135.3, 132.9, 129.3, 126.7, 125.8, 125.1, 121.9, 119.9, 119.9, 117.3, 106.3, 71.7, 50.2, 43.4, 41.1, 32.5, 28.6, 25.3. HRMS (ESI) calcd for $C_{23}H_{21}NS$ [M+H]+ : 344.1467, found: 344.1466.



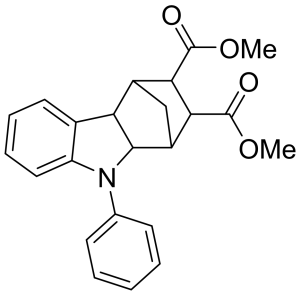
7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**39d**)

The representative general procedure mentioned above was followed. The desired product **39d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 88 % yield (69.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.00 (m, 1H), 7.99–7.93 (m, 1H), 7.45–7.40 (m, 5H), 7.40–7.35 (m, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 1.2 Hz, 1H), 7.04 (tt, *J* = 7.2, 1.4 Hz, 1H), 6.99 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 3.43 (d, *J* = 8.2 Hz, 1H), 2.59 (d, *J* = 3.4 Hz, 1H), 2.49 (s, 1H), 1.74–1.63 (m, 3H), 1.50 (dd, *J* = 11.6, 5.2 Hz, 1H), 1.35 (s, 1H), 1.24 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 143.5, 140.7, 138.9, 138.2, 135.2, 133.3, 129.3, 125.0, 124.3, 123.3 122.9, 121.8, 119.8, 119.2, 108.2, 71.5, 50.3, 43.6, 41.1, 32.5, 28.6, 25.3. HRMS (ESI) calcd for $C_{27}H_{23}NS$ [M+H]+ : 394.1624, found: 394.1622.



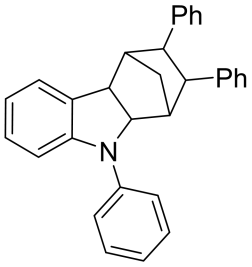
2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**40d**)

The representative general procedure mentioned above was followed. The desired product **40d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.50) as a colorless oil in 91 % yield (63.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.32–7.27 (m, 2H), 7.09–7.02 (m, 3H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.74–6.69 (m, 1H), 4.45 (d, *J* = 8.2 Hz, 1H), 3.61–3.54 (m, 2H), 3.52 (d, *J* = 7.2 Hz, 2H), 3.47 (t, *J* = 9.2 Hz, 1H), 3.41 (s, 3H), 3.38 (s, 3H), 2.69 (s, 1H), 2.43 (s, 1H), 2.41–2.32 (m, 2H), 1.58 (d, *J* = 10.4 Hz, 1H), 1.27–1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.9, 133.8, 129.1, 127.1, 124.8, 120.8, 118.9, 117.8, 109.3, 70.4, 69.9, 65.2, 58.9, 58.8, 46.6, 44.9, 43.5, 40.0, 38.9, 33.5. HRMS (ESI) calcd for $C_{23}H_{27}NO_2$ [M+H]+ : 350.2115, found: 350.2116.



dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole-2,3-dicarboxylate (**41d**)

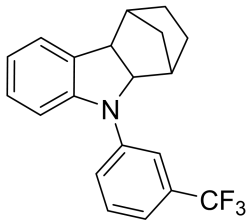
The representative general procedure mentioned above was followed. The desired product **41d** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (10/1, Rf = 0.50) as a colorless oil in 85 % yield (64.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.75 (dq, *J* = 8.0, 4.2 Hz, 1H), 4.94 (d, *J* = 8.2 Hz, 1H), 3.89 (d, *J* = 8.2 Hz, 1H), 3.76 (d, *J* = 4.6 Hz, 6H), 3.20 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.08 (dd, *J* = 11.8, 4.4 Hz, 1H), 2.87 (d, *J* = 3.8 Hz, 1H), 2.73 (d, *J* = 3.6 Hz, 1H), 1.76 (d, *J* = 10.6 Hz, 1H), 1.28 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 172.3, 148.7, 143.3, 132.7, 129.2, 127.4, 124.8, 121.3, 118.8, 118.7, 108.7, 65.3, 51.8, 51.6, 46.9, 46.2, 45.1, 44.7, 44.7. HRMS (ESI) calcd for $C_{23}H_{23}NO_4$ [M+H]+ : 378.1700, found: 378.1702.



2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**42d**)

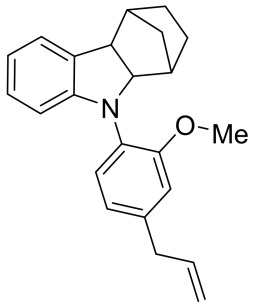
The representative general procedure mentioned above was followed. The desired product **42d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.57) as a colorless oil in 94 % yield (77.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.16 (m, 4H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.95–6.86 (m, 6H), 6.85–6.82 (m, 2H), 6.81–6.77 (m, 4H), 6.65 (td, *J* = 7.2, 0.8 Hz, 1H), 4.48 (d, *J* = 8.2 Hz, 1H), 3.57 (d, *J* = 8.2 Hz,

1H), 3.42 (d, *J* = 9.6 Hz, 1H), 3.29 (d, *J* = 9.6 Hz, 1H), 2.77 (s, 1H), 2.69 (s, 1H), 2.11 (d, *J* = 11.0 Hz, 1H), 1.83 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 142.3, 140.7, 140.6, 131.4, 128.2, 127.7, 127.6, 126.5, 126.5, 126.4, 124.4, 124.3, 124.1, 120.7, 118.5, 117.7, 107.2, 70.9, 52.4, 50.6, 49.4, 47.6, 46.1, 30.6. HRMS (ESI) calcd for $C_{31}H_{27}N$ [M+H]+ : 414.2216, found: 414.2216.



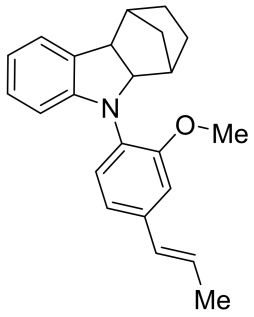
9-(3-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**43d**)

The representative general procedure mentioned above was followed. The desired product **43d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.56) as a colorless oil in 90 % yield (59.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.47 (dt, *J* = 15.6, 8.4 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.87–6.75 (m, 1H), 4.29 (d, *J* = 8.2 Hz, 1H), 3.39 (d, *J* = 8.2 Hz, 1H), 2.55 (d, *J* = 2.8 Hz, 1H), 2.43 (s, 1H), 1.71–1.58 (m, 2H), 1.56–1.45 (m, 2H), 1.35–1.31 (m, 1H), 1.18 (dt, *J* = 10.2, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.2, 133.9, 131.5 (d, J = 32.0 Hz), 129.6, 127.3, 125.2, 124.2 (d, *J* = 270.9 Hz) 121.6, 119.6, 117.4 (q, J = 3.6 Hz), 114.9 (q, J = 3.6 Hz), 108.6, 71.0, 50.4, 43.4, 41.0, 32.4, 28.4, 25.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48 (d, *J* = 17.1 Hz). HRMS (ESI) calcd for $C_{20}H_{18}F_3N$ [M+H]+ : 330.1464, found: 330.1464.



9-(4-allyl-2-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**44d**)

The representative general procedure mentioned above was followed. The desired product **44d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.51) as a colorless oil in 93 % yield (61.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.00–6.94 (m, 3H), 6.63 (dd, *J* = 10.6, 4.0 Hz, 1H), 6.42 (dd, *J* = 16.8, 11.8 Hz, 2H), 6.31–6.20 (m, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.88 (d, *J* = 1.2 Hz, 3H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.37 (s, 1H), 2.15 (s, 1H), 1.95 (dd, *J* = 6.6, 1.4 Hz, 3H), 1.67 (d, *J* = 10.0 Hz, 1H), 1.60–1.47 (m, 2H), 1.41 (t, *J* = 10.2 Hz, 1H), 1.24–1.16 (m, 1H), 1.12 (dd, *J* = 10.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 151.2, 135.6, 132.4, 130.8, 130.3, 127.2, 125.9, 125.1, 124.5, 118.6, 117.1, 109.8, 106.9, 70.5, 55.6, 50.9, 43.5, 40.6, 32.3, 28.7, 25.2, 18.5. HRMS (ESI) calcd for $C_{23}H_{25}NO$ [M+H]+ : 332.2009, found: 332.2010.

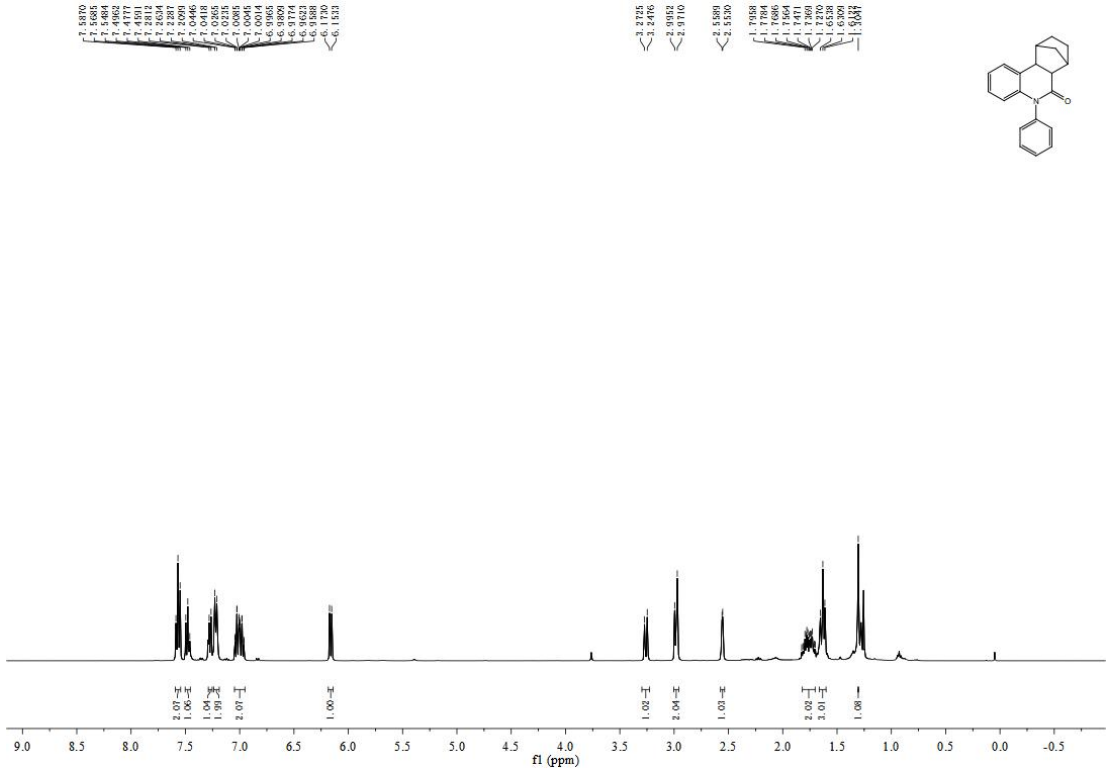


(*E*)-9-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**45d**)

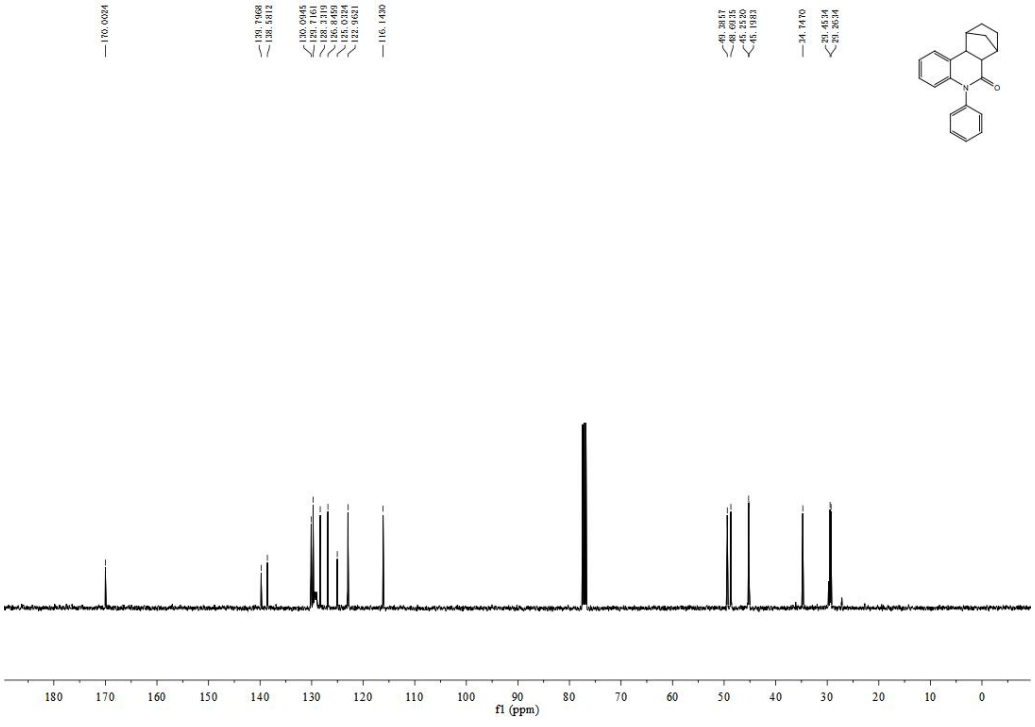
The representative general procedure mentioned above was followed. The desired product **45d** was isolated by column chromatography over silica gel and eluted with petroleum ether (Rf = 0.55) as a colorless oil in 91 % yield (60.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.00–6.93 (m, 3H), 6.64 (td, *J* = 7.2, 0.8 Hz, 1H), 6.48–6.37 (m, 2H), 6.25 (dq, *J* = 15.6, 6.6 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.32 (d, *J* = 8.2 Hz, 1H), 2.37 (d, *J* = 3.2 Hz, 1H), 2.15 (d, *J* = 4.4 Hz, 1H), 1.95 (dd, *J* = 6.6, 1.4 Hz, 3H), 1.67 (d, *J* = 10.0 Hz, 1H), 1.61–1.48 (m, 2H), 1.45–1.36 (m, 1H), 1.25–1.15 (m, 1H), 1.11 (dt, *J* = 10.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 151.2, 135.6, 132.4, 130.8, 130.3, 127.1, 125.9, 125.1, 124.5, 118.6, 117.1, 109.8, 106.9, 70.5, 55.6, 50.8, 43.5, 40.6, 32.3, 28.7, 25.2, 18.5. HRMS (ESI) calcd for $C_{23}H_{25}NO$ [M+H]+ : 332.2009, found: 332.2009.

4.Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of the products

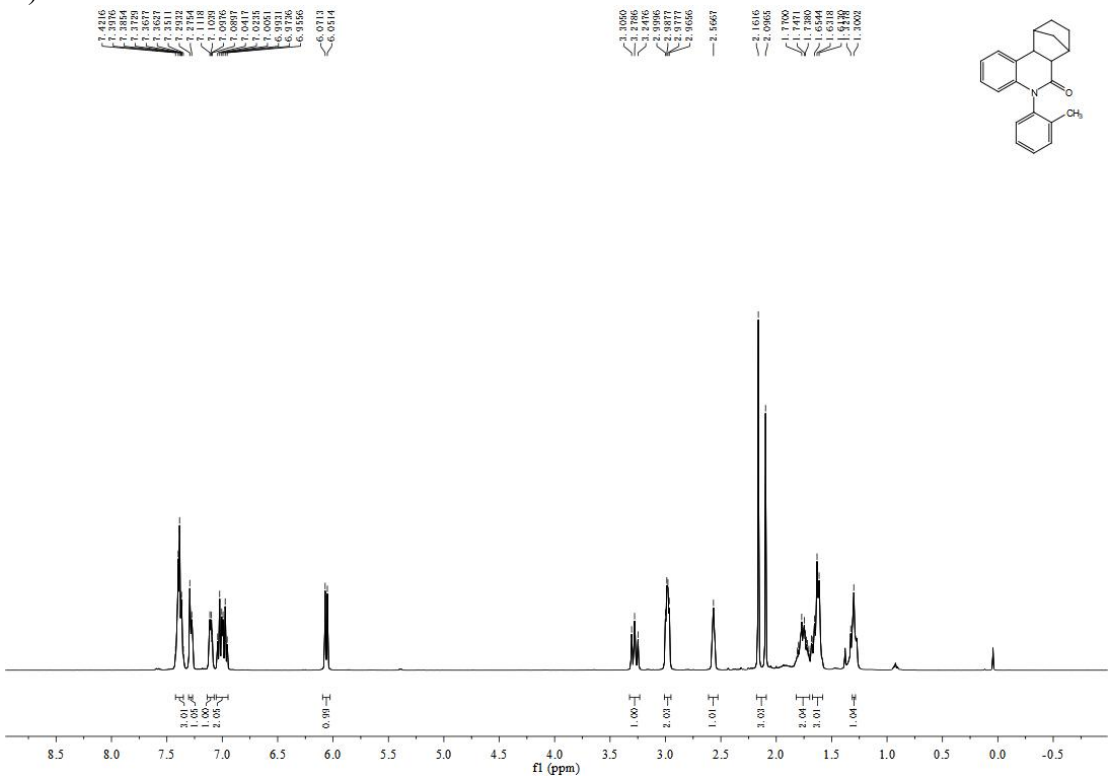
^{1}H NMR spectrum of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**1c**)



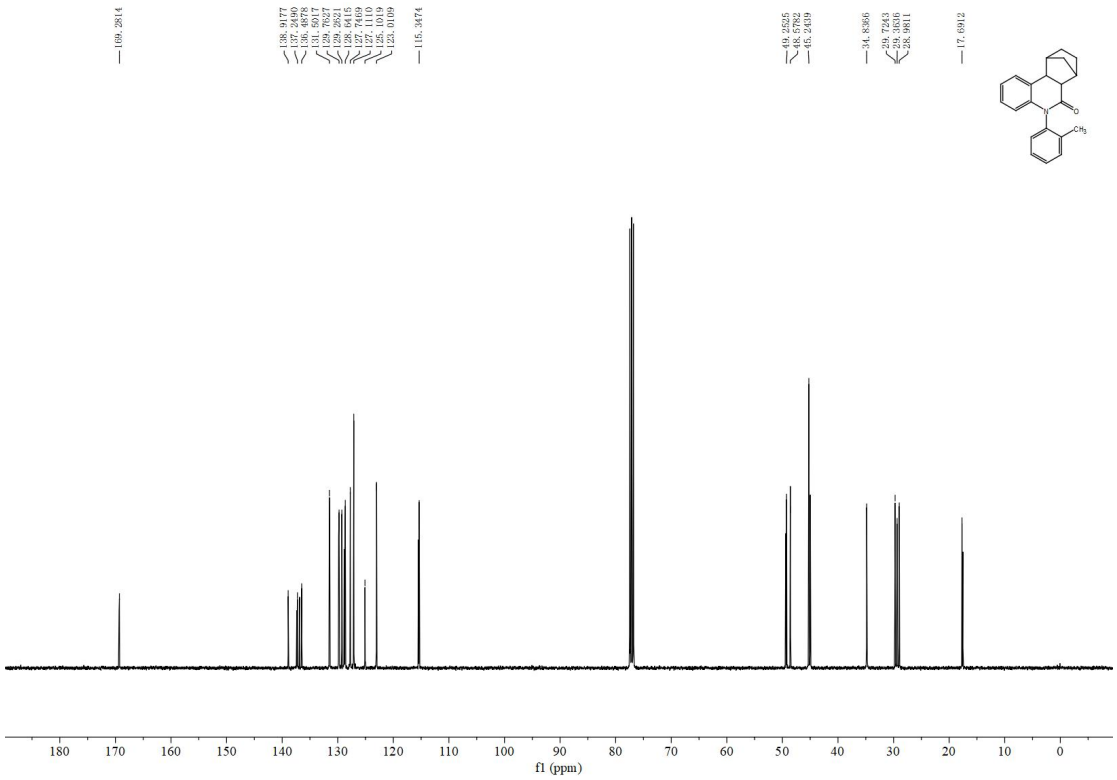
^{13}C NMR spectrum of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**1c**)



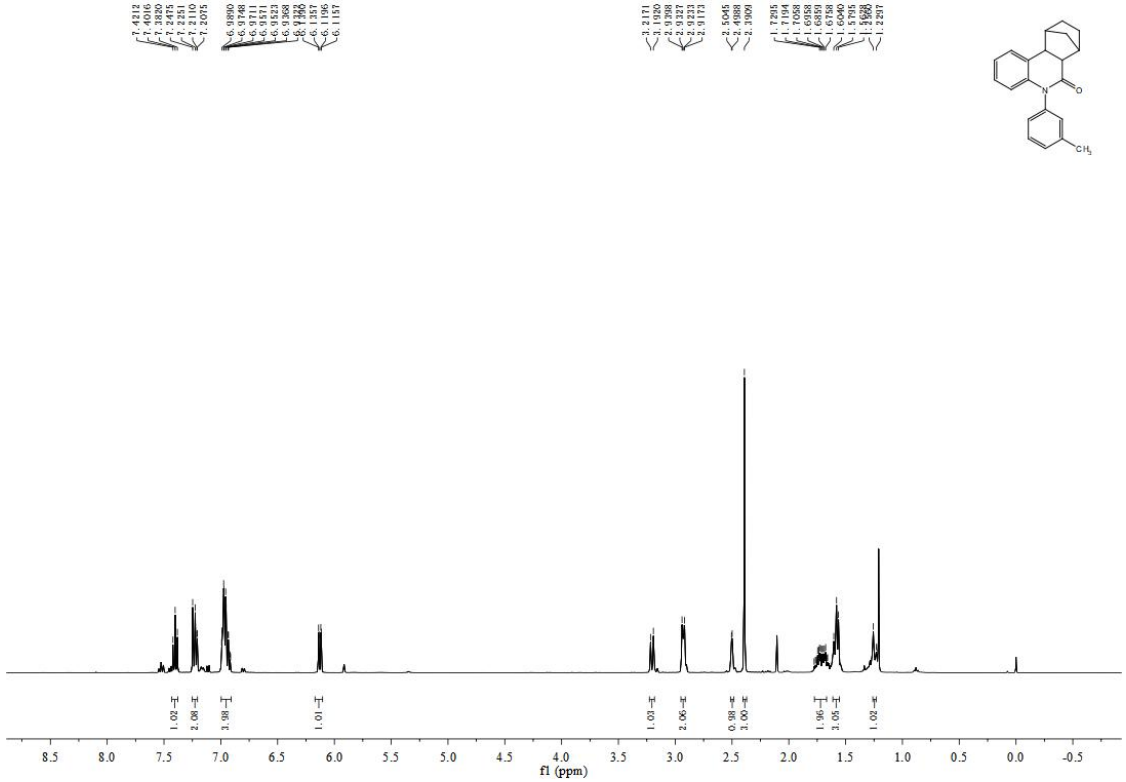
^{1}H NMR spectrum of 5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**2c**)



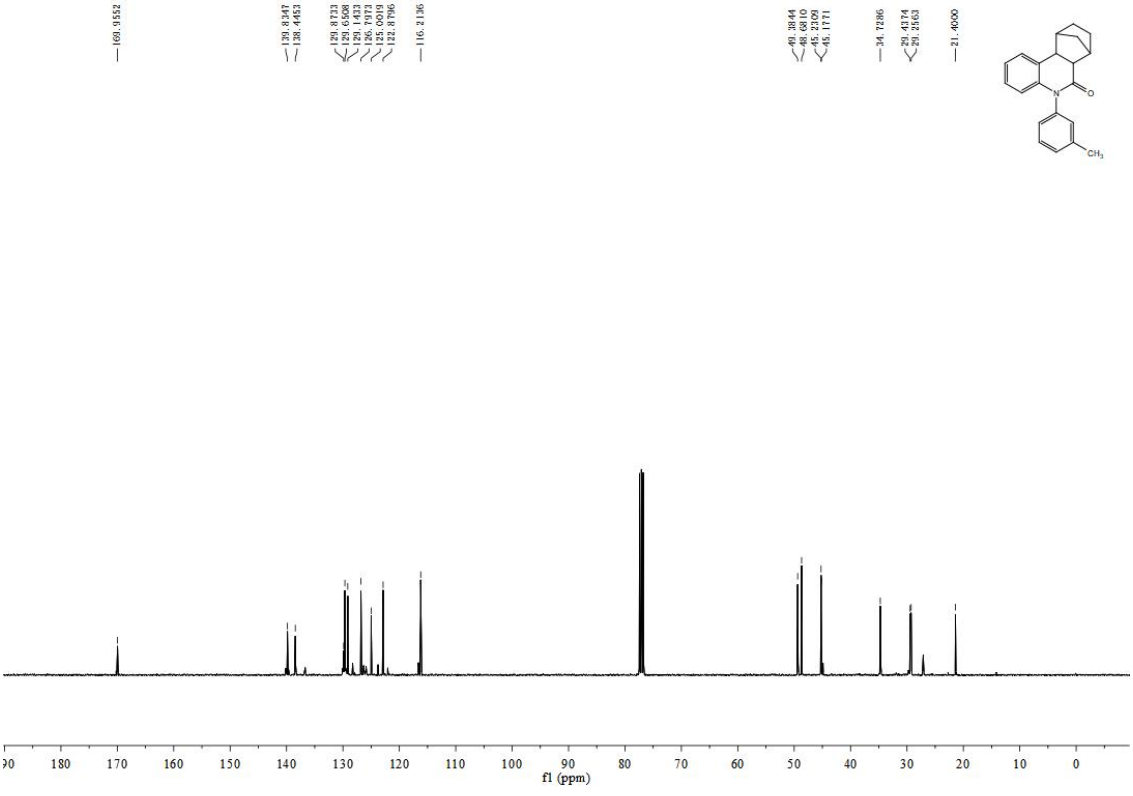
^{13}C NMR spectrum of 5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**2c**)



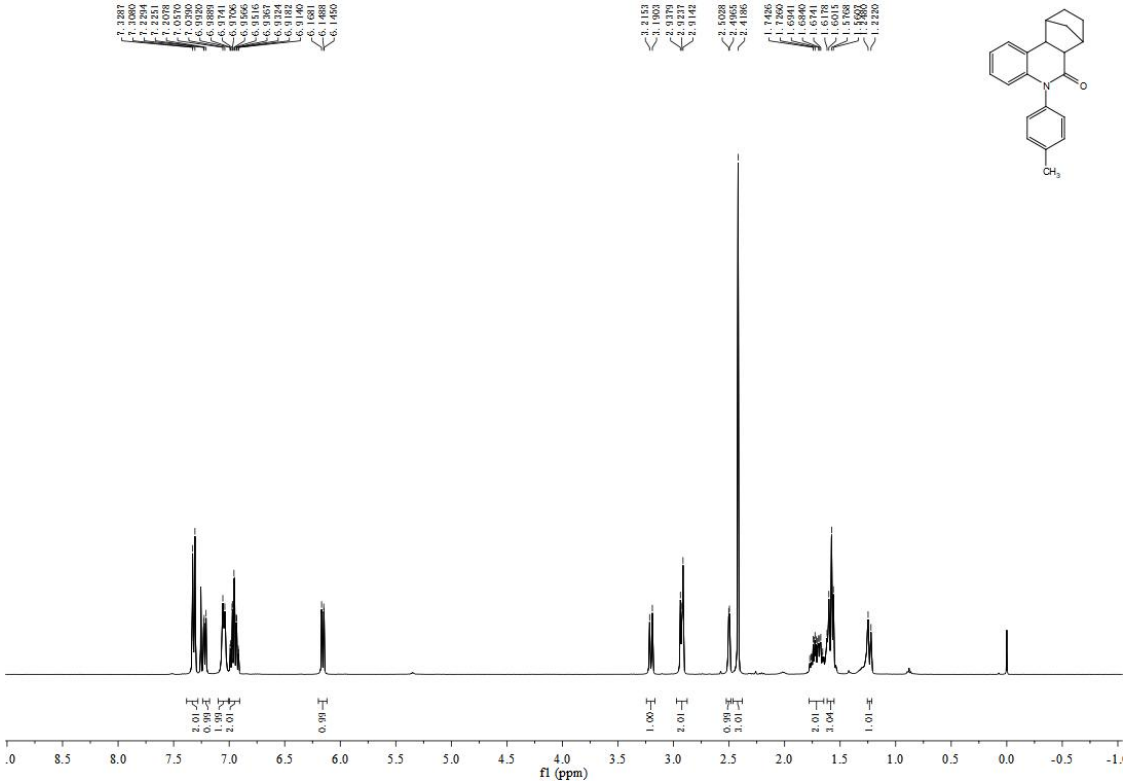
^{1}H NMR spectrum of 5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**3c**)



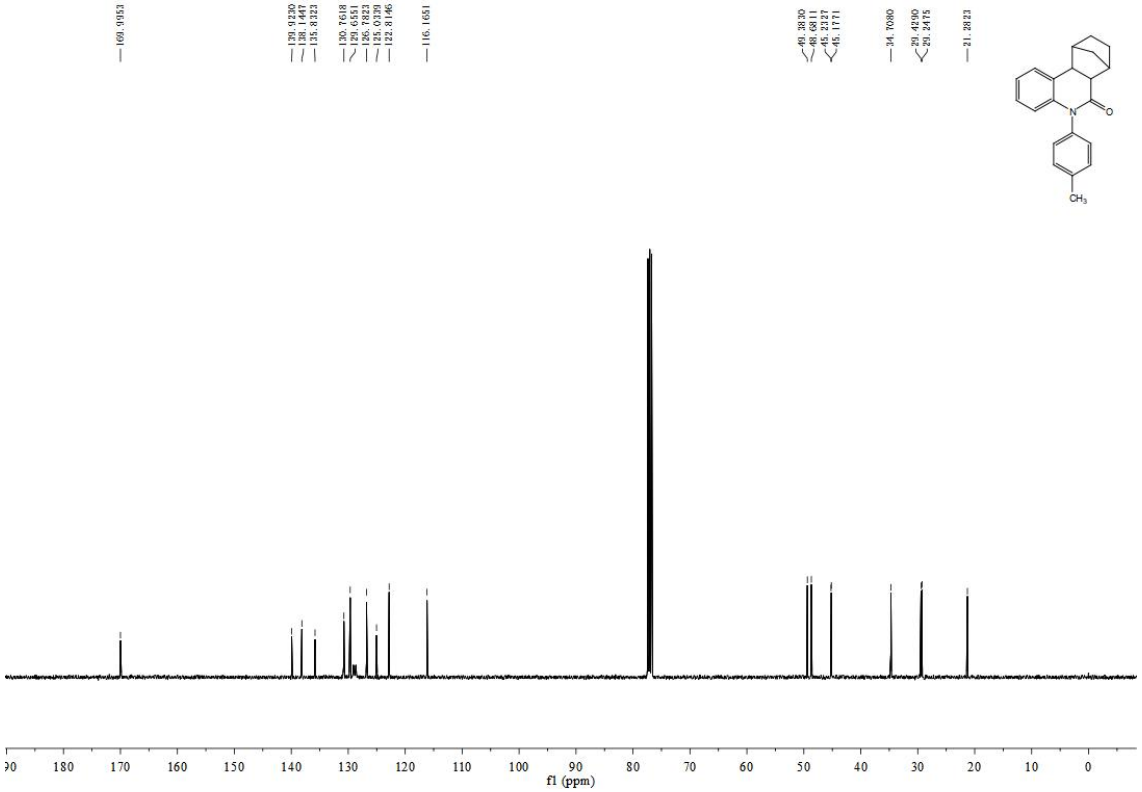
^{13}C NMR spectrum of 5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**3c**)



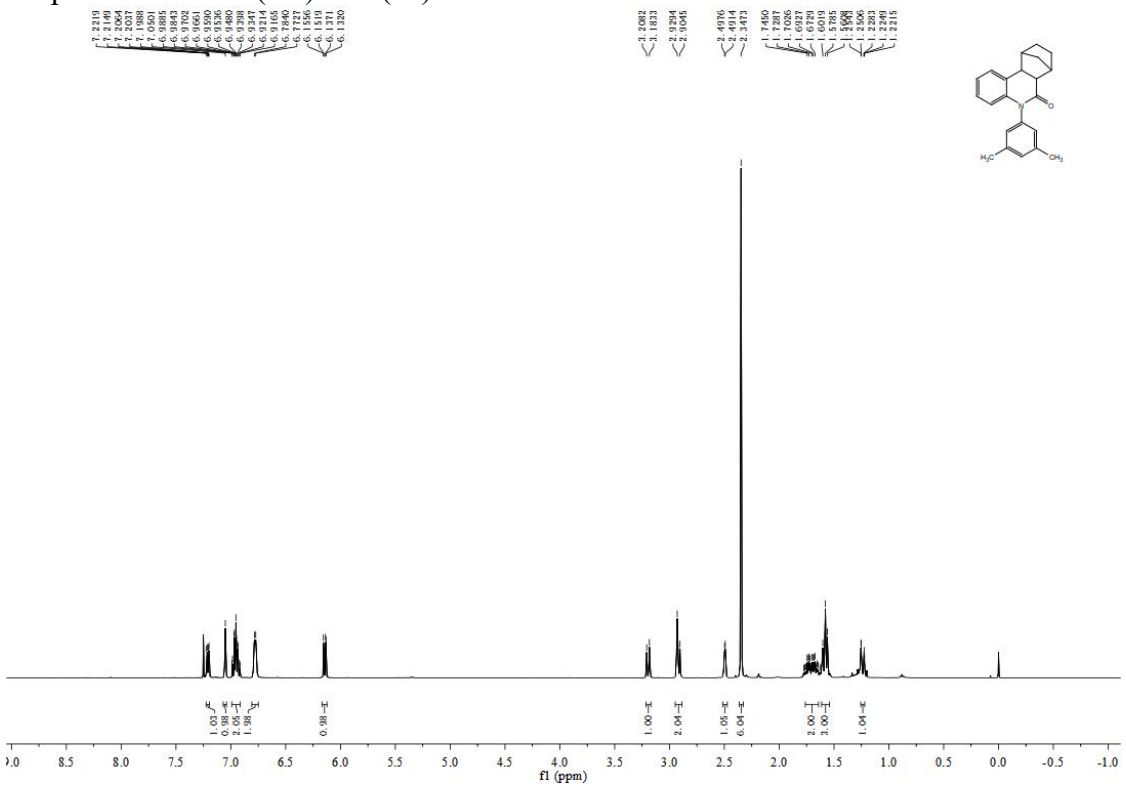
^{1}H NMR spectrum of 5-(*p*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**4c**)



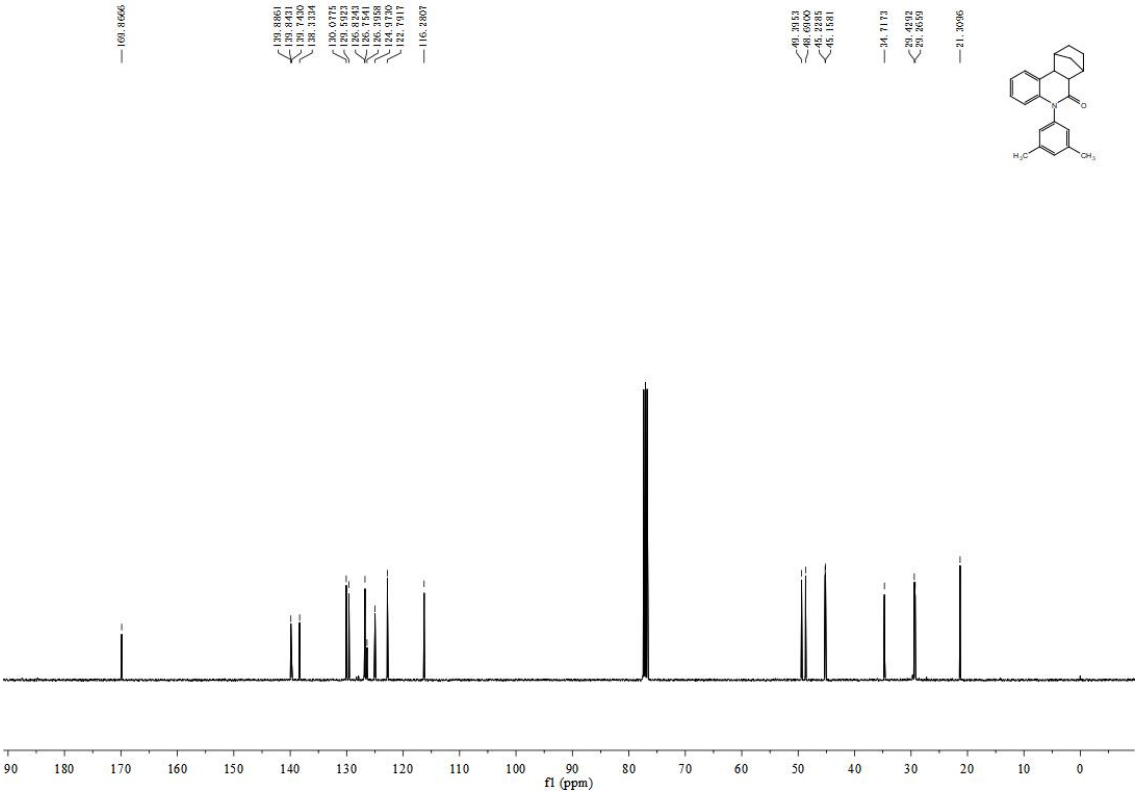
^{13}C NMR spectrum of 5-(*p*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**4c**)



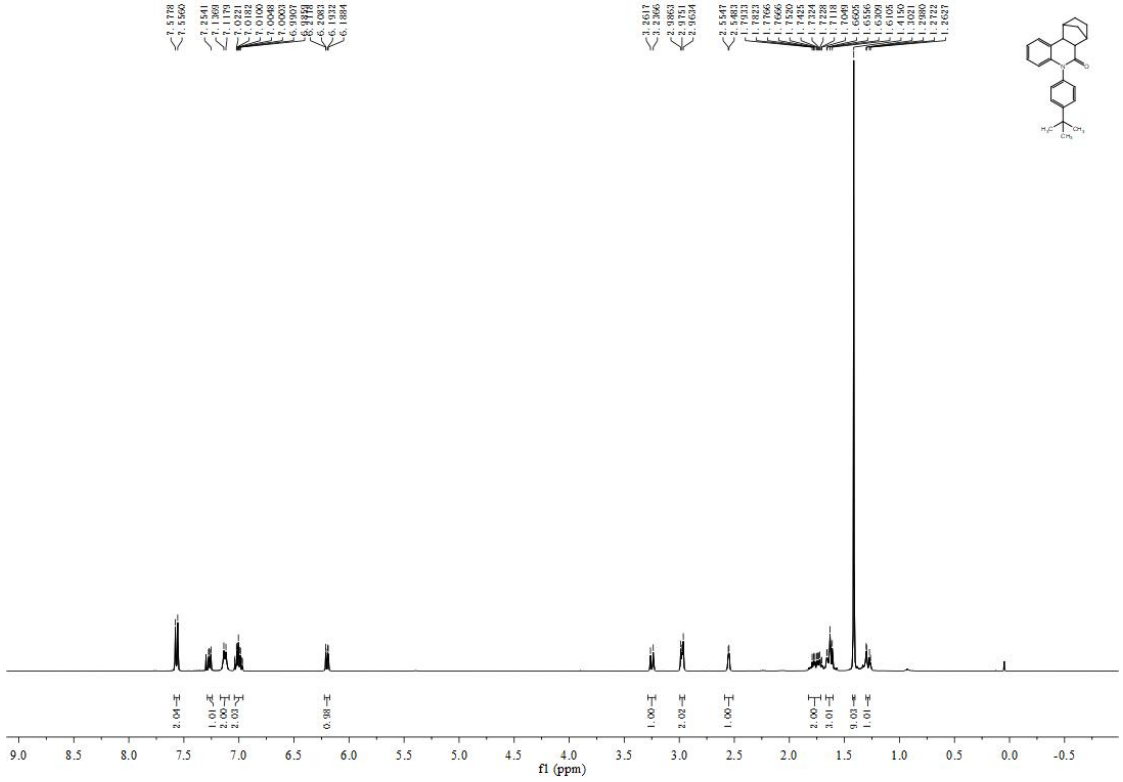
^{1}H NMR spectrum of 5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**5c**)



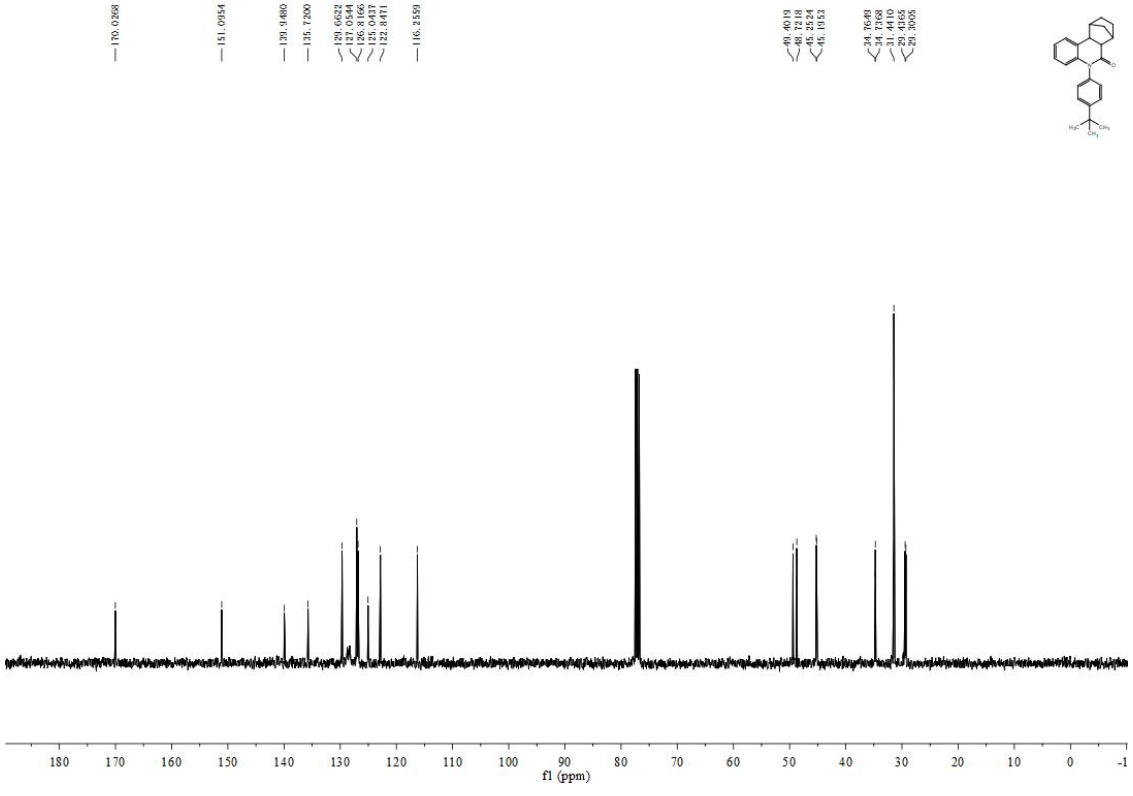
^{13}C NMR spectrum of 5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**5c**)



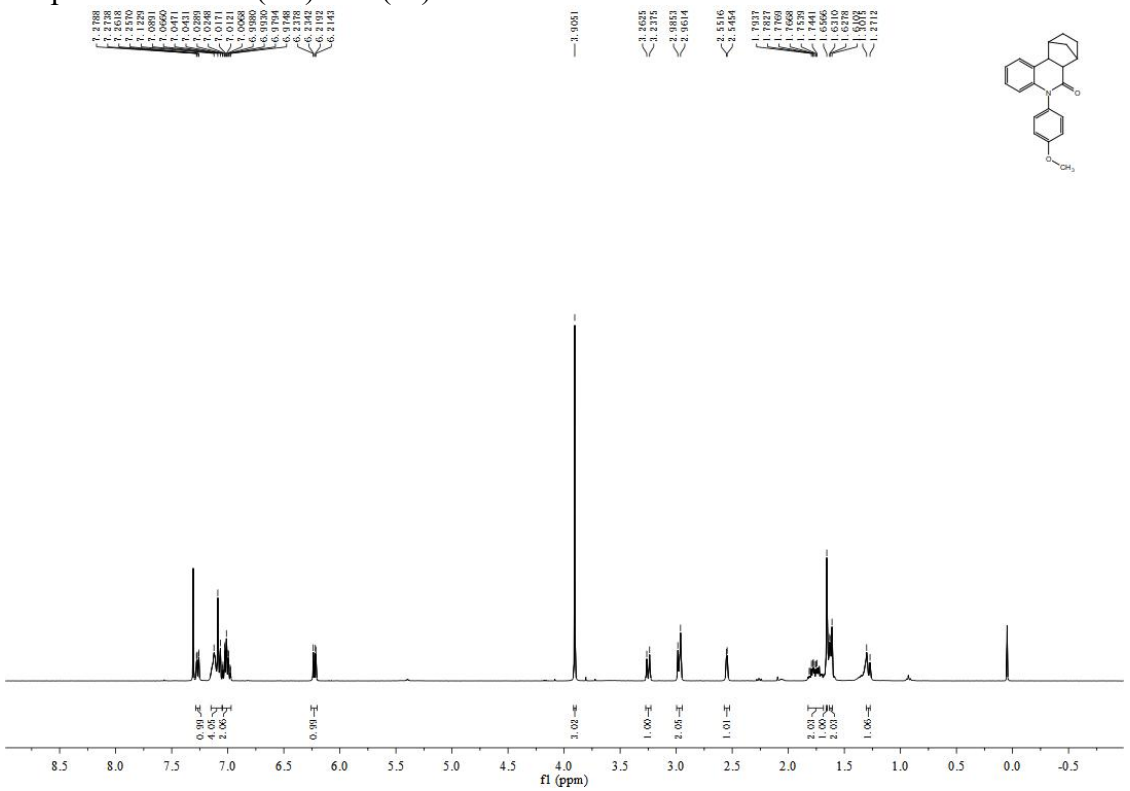
^{1}H NMR spectrum of 5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**6c**)



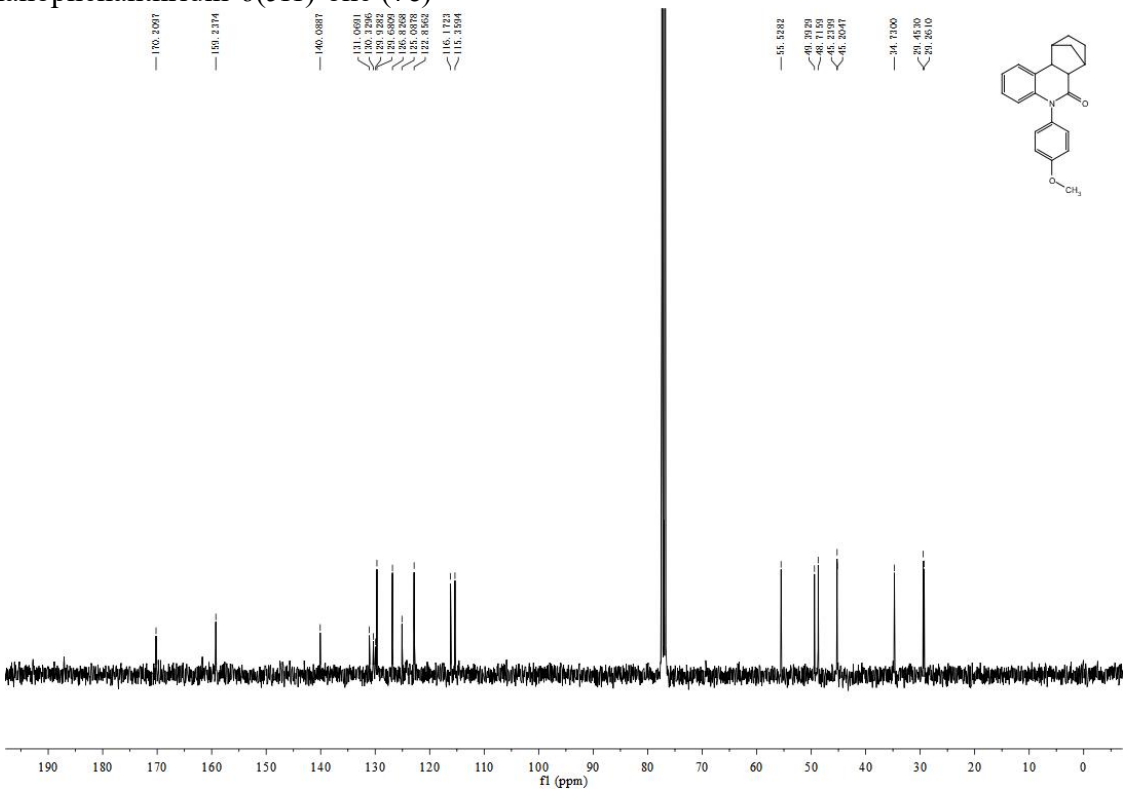
^{13}C NMR spectrum of 5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**6c**)



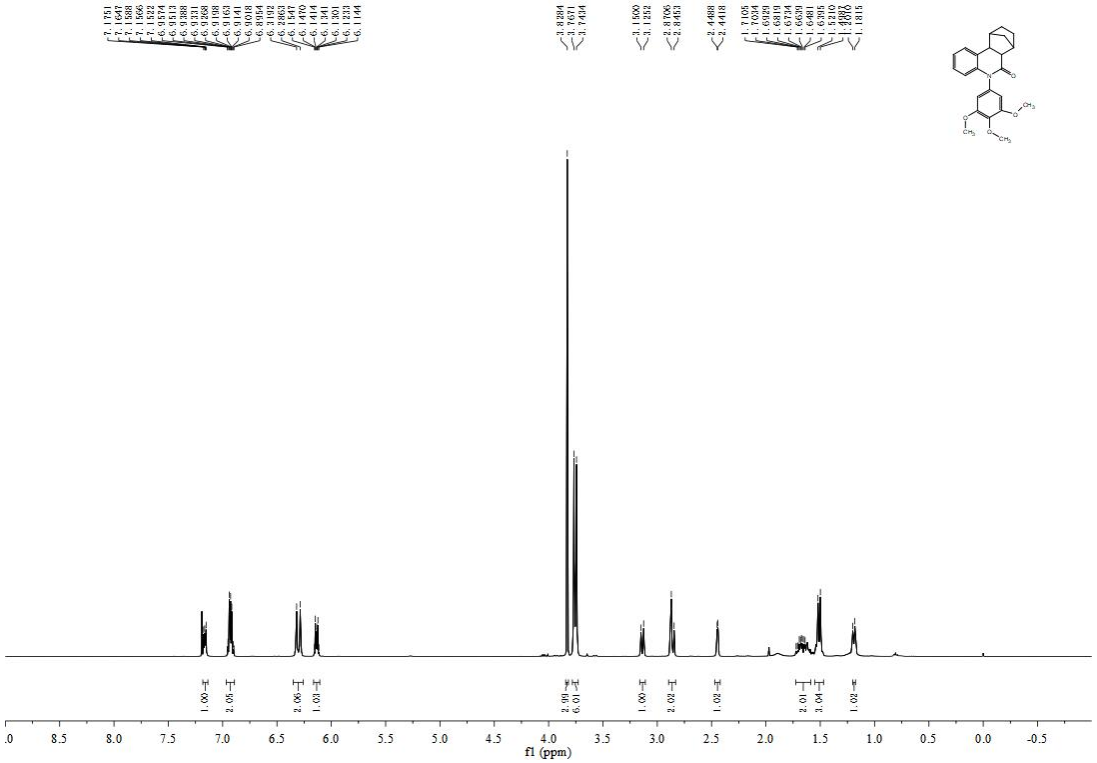
^{1}H NMR spectrum of 5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**7c**)



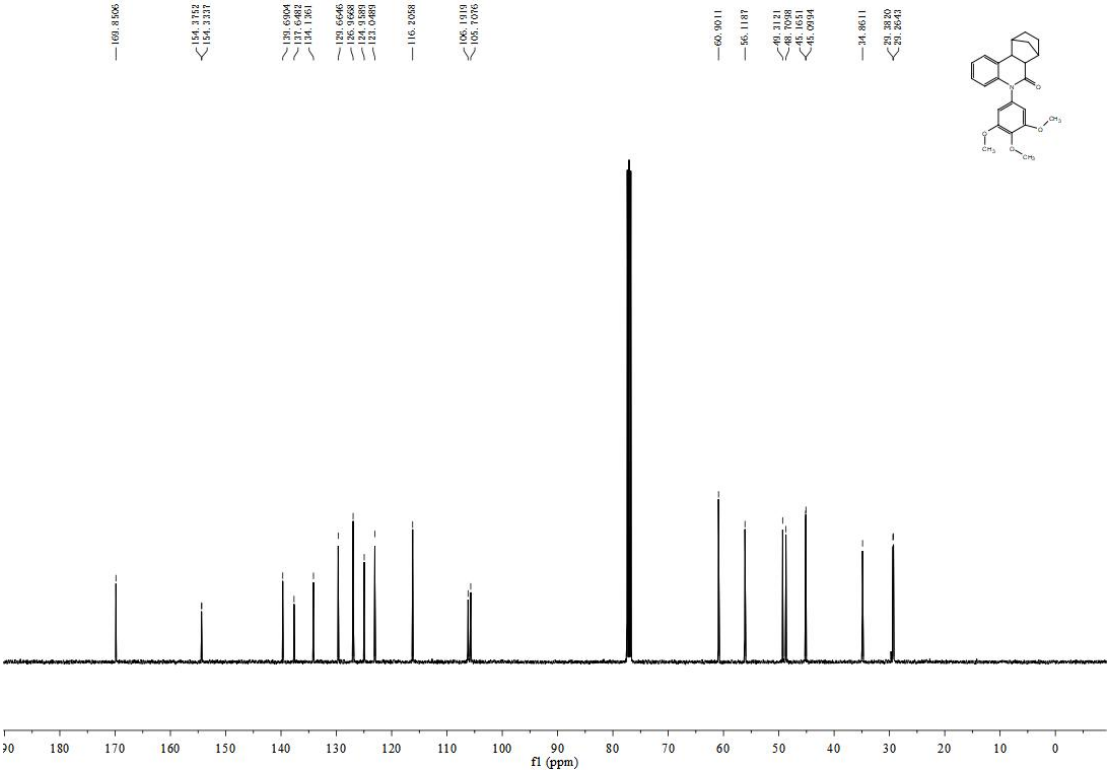
^{13}C NMR spectrum of 5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**7c**)



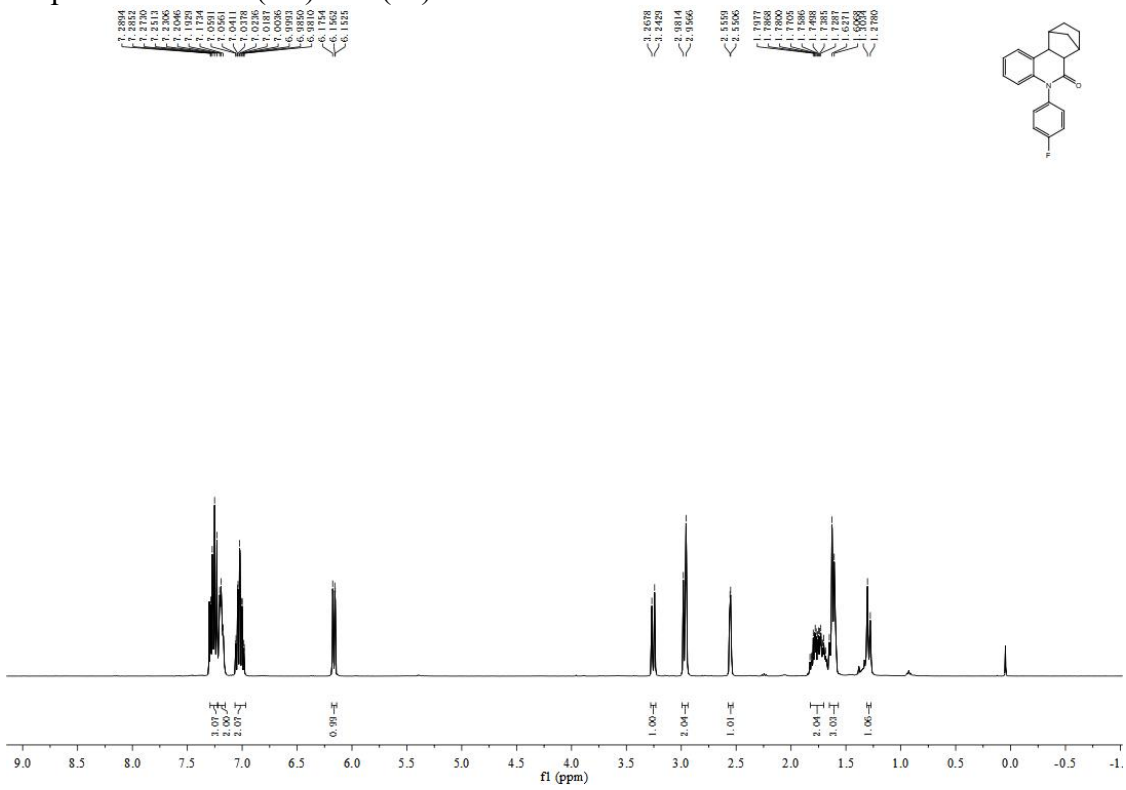
^{1}H NMR spectrum of 5-(3,4,5-trimethoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**8c**)



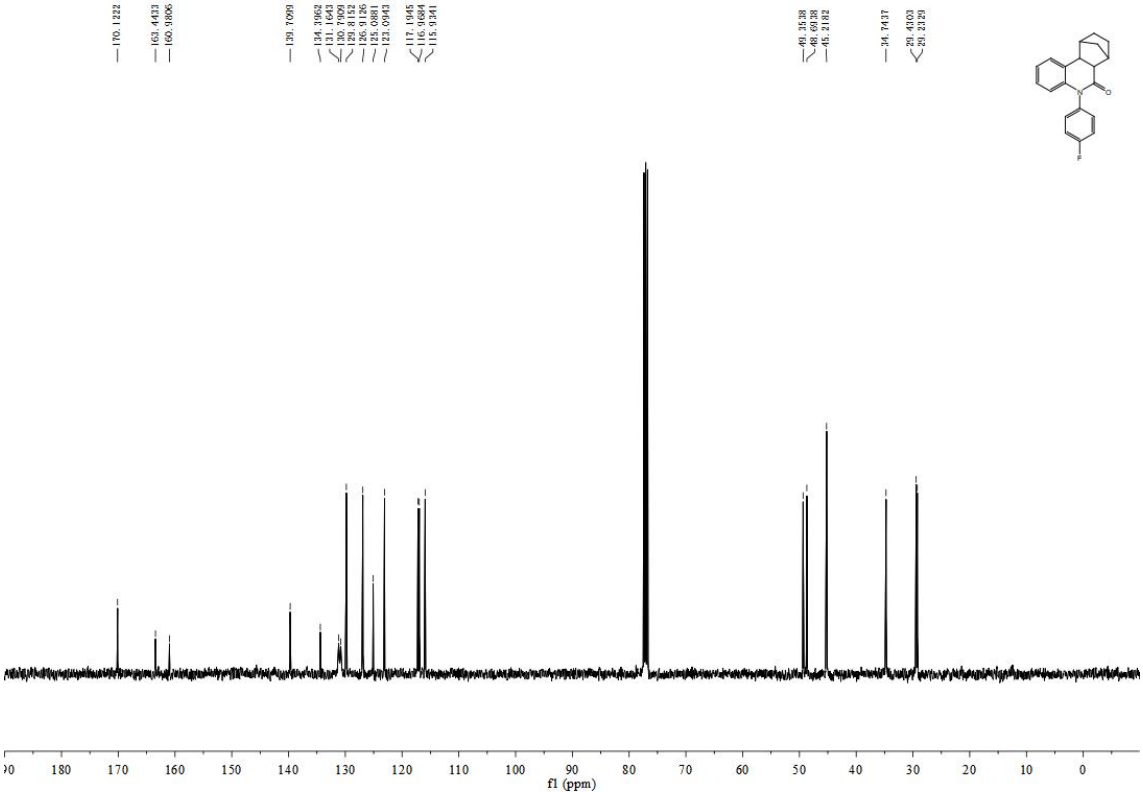
^{13}C NMR spectrum of 5-(3,4,5-trimethoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**8c**)



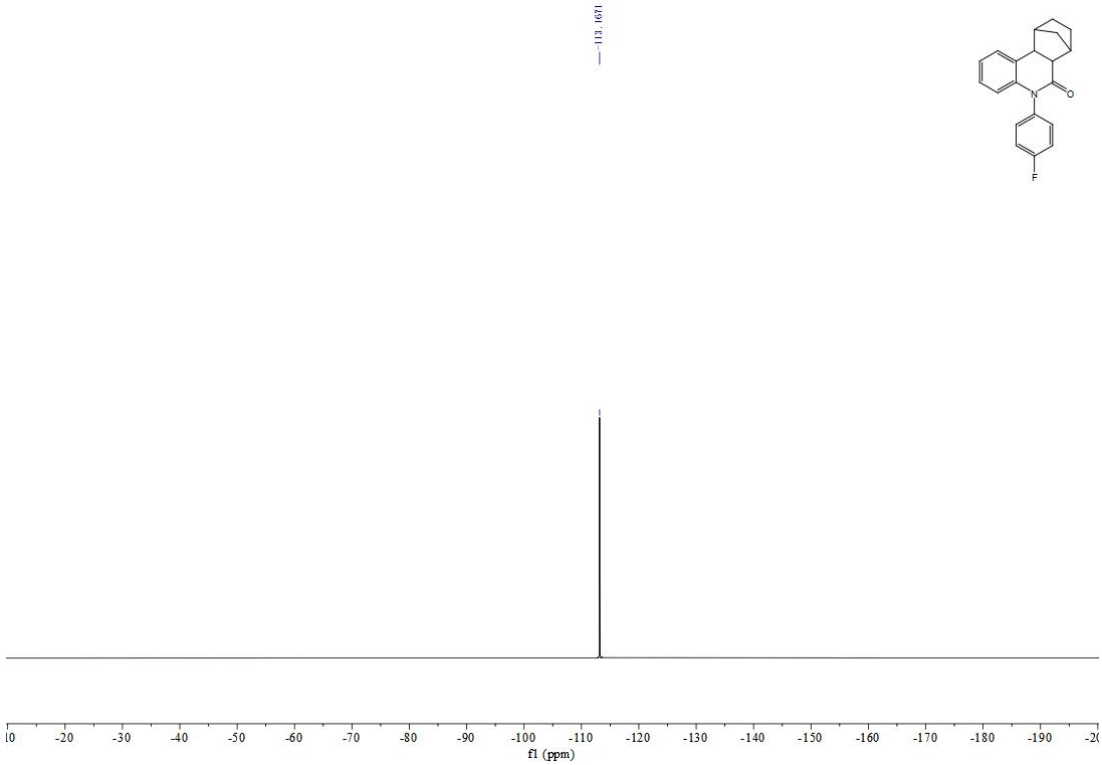
^{1}H NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**9c**)



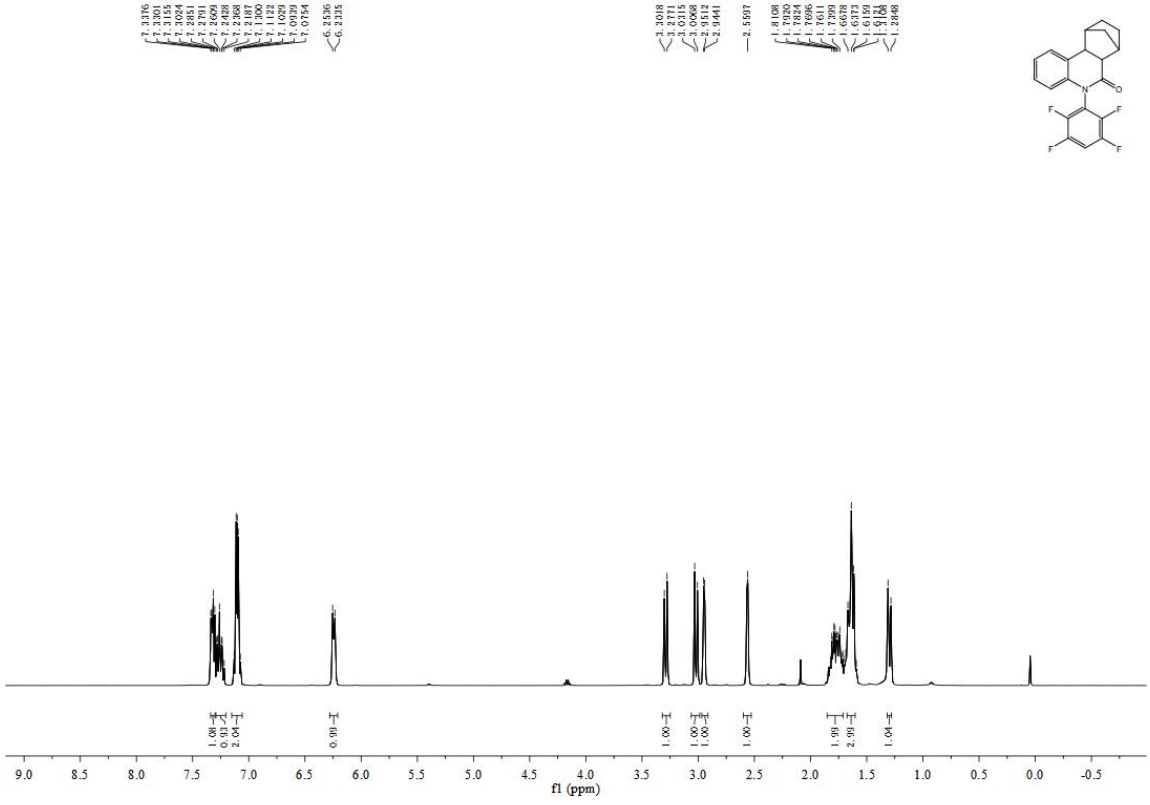
^{13}C NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**9c**)



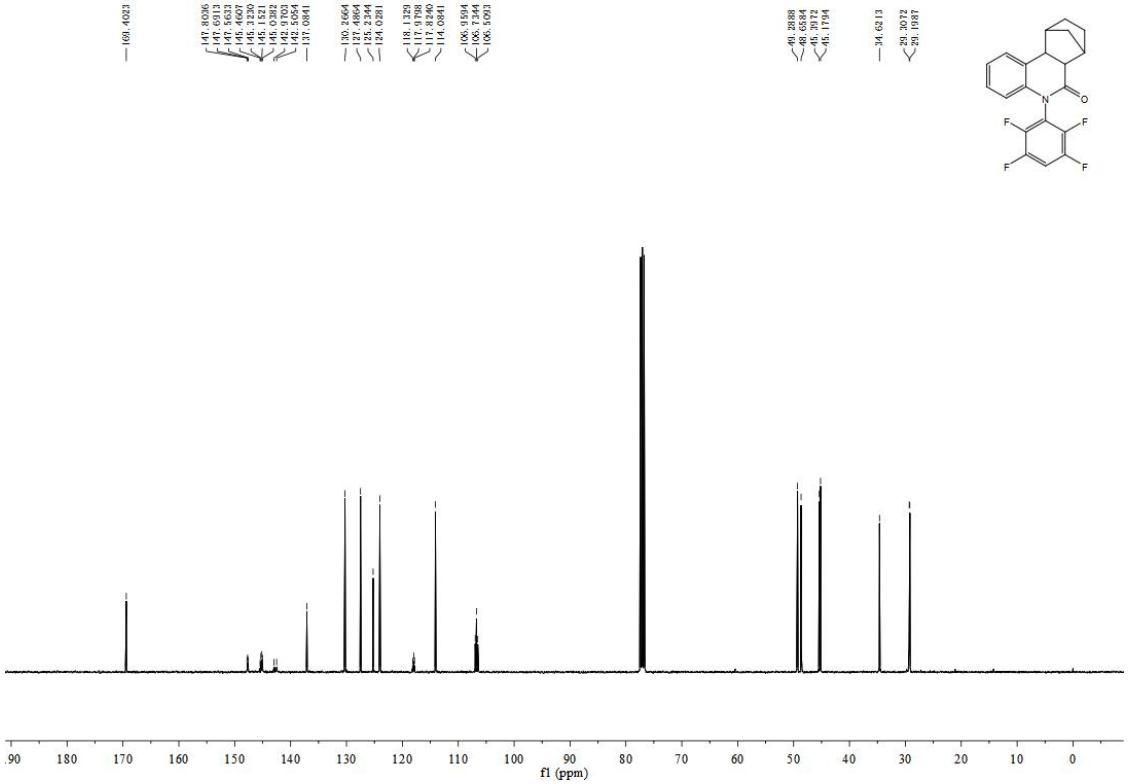
^{19}F NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**9c**)



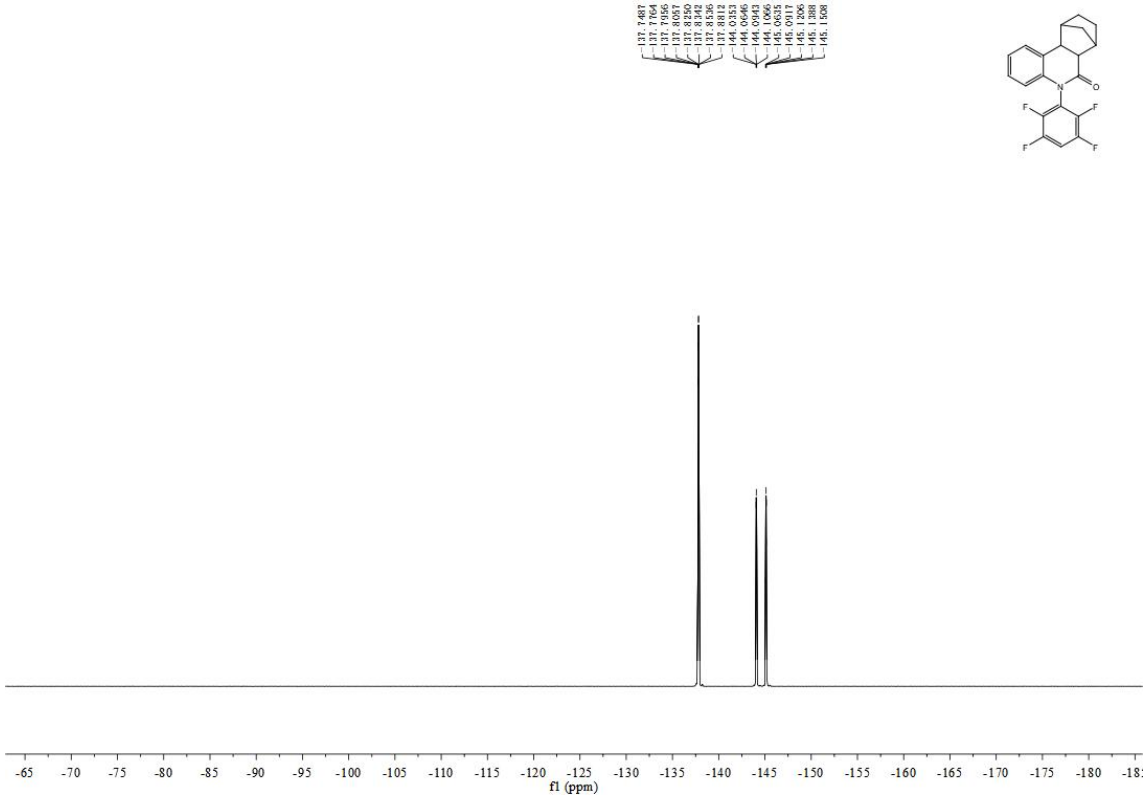
^{1}H NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**10c**)



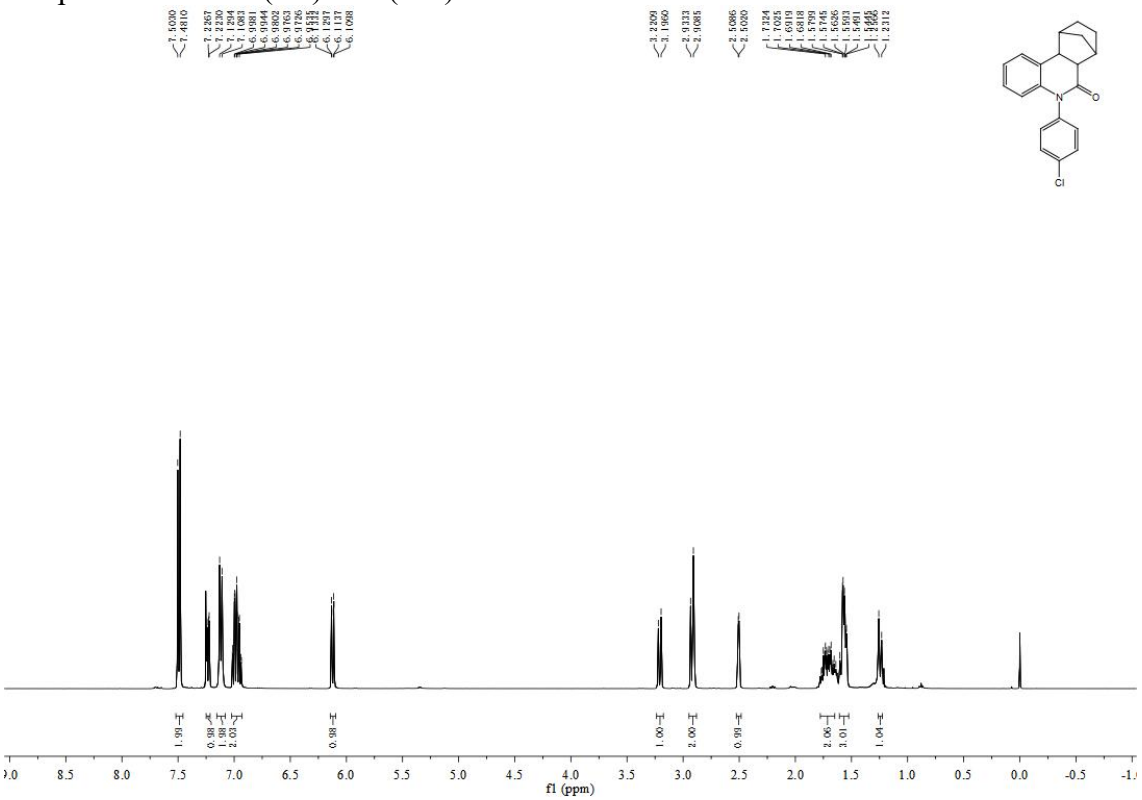
^{13}C NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**10c**)



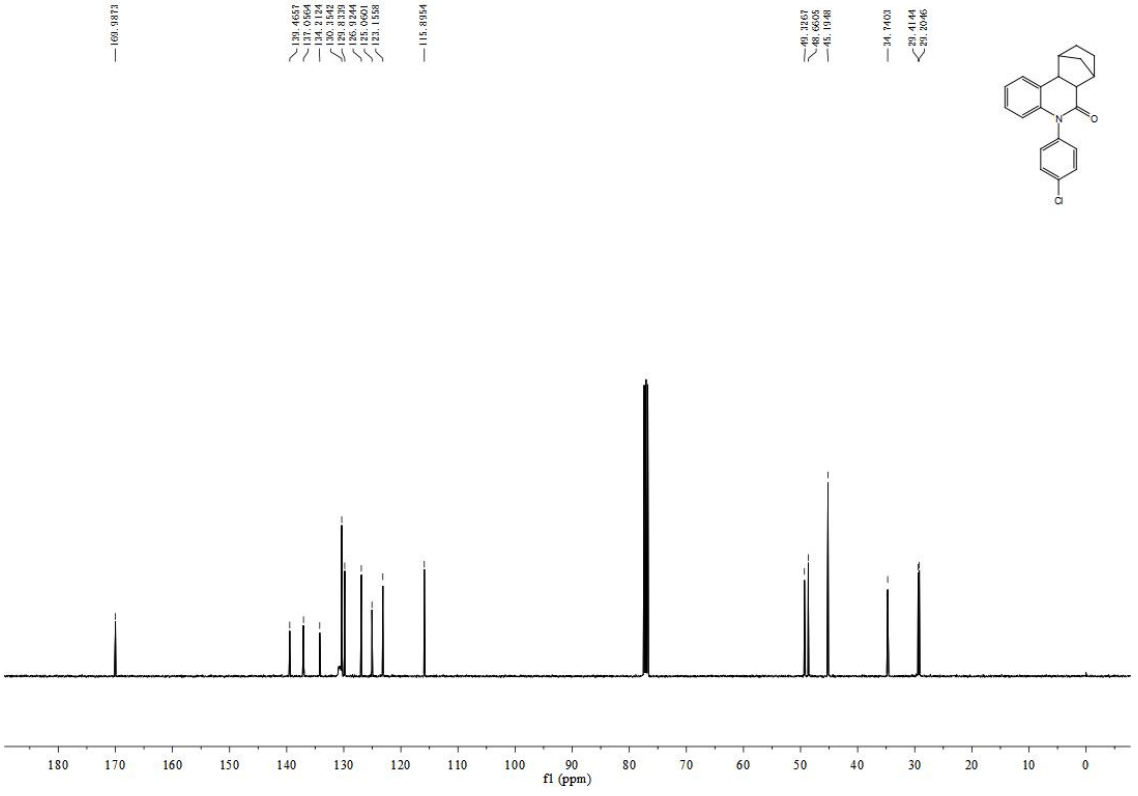
^{19}F NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**10c**)



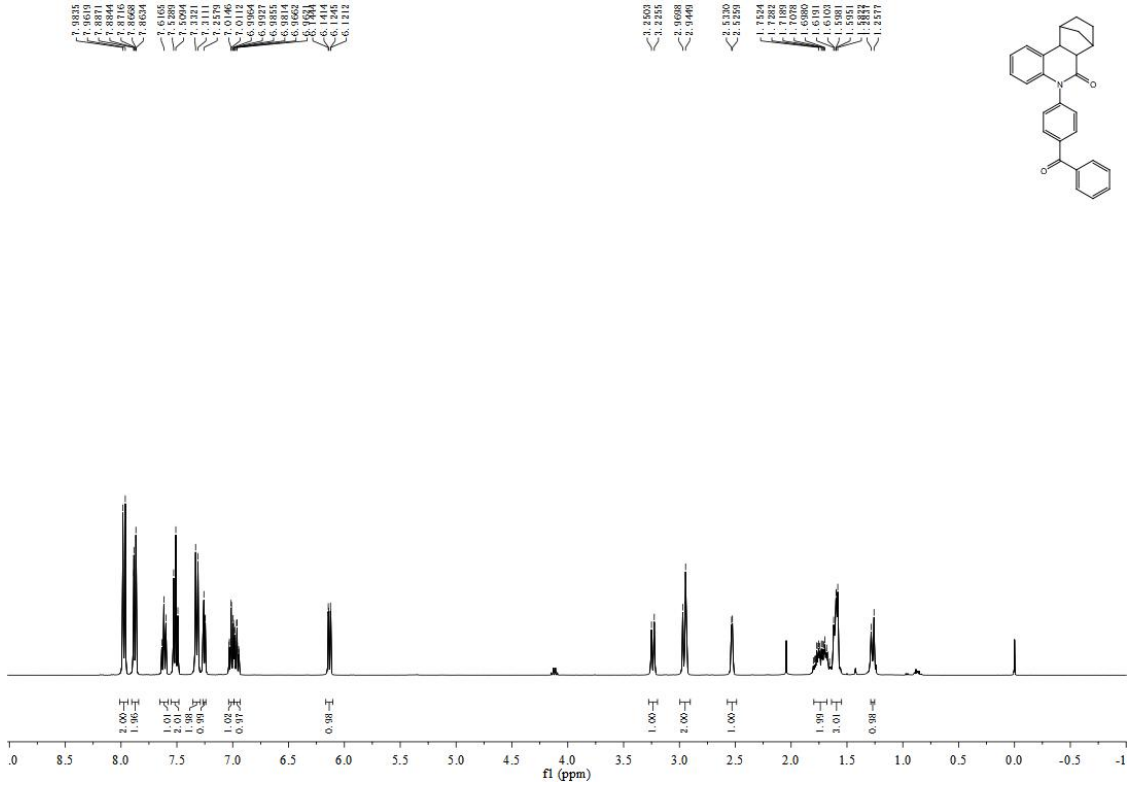
^{1}H NMR spectrum of 5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**11c**)



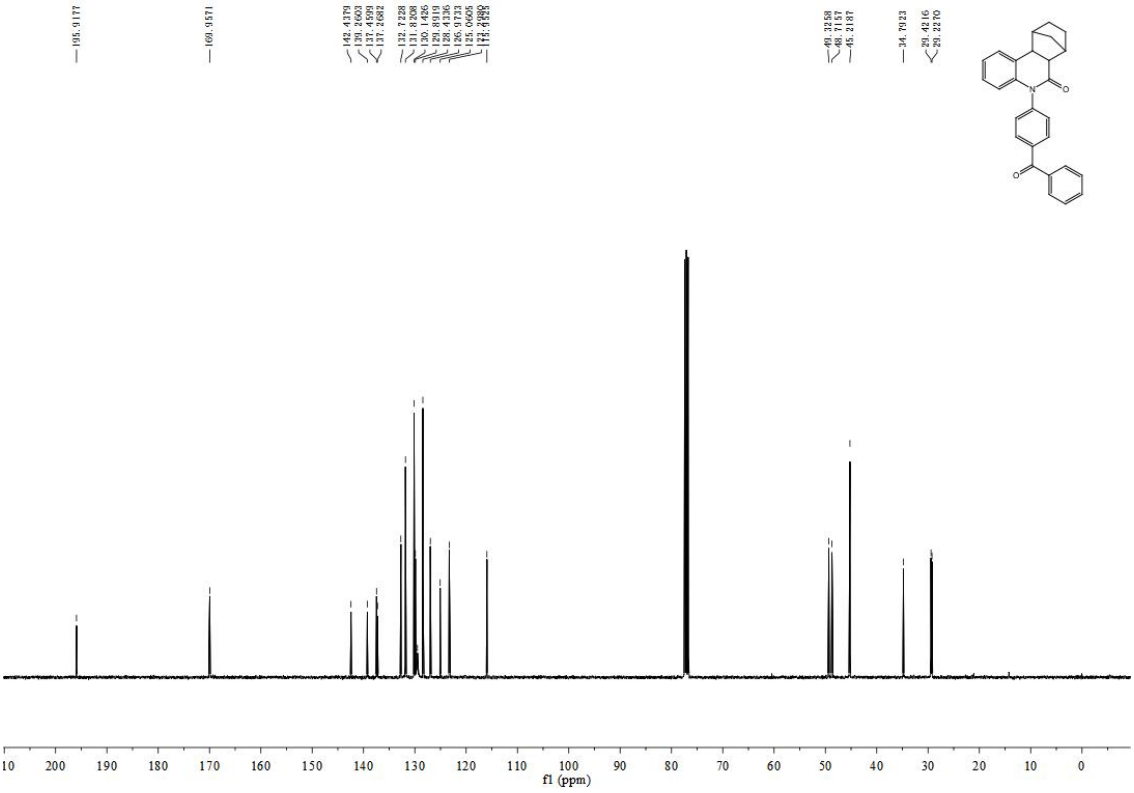
^{13}C NMR spectrum of 5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**11c**)



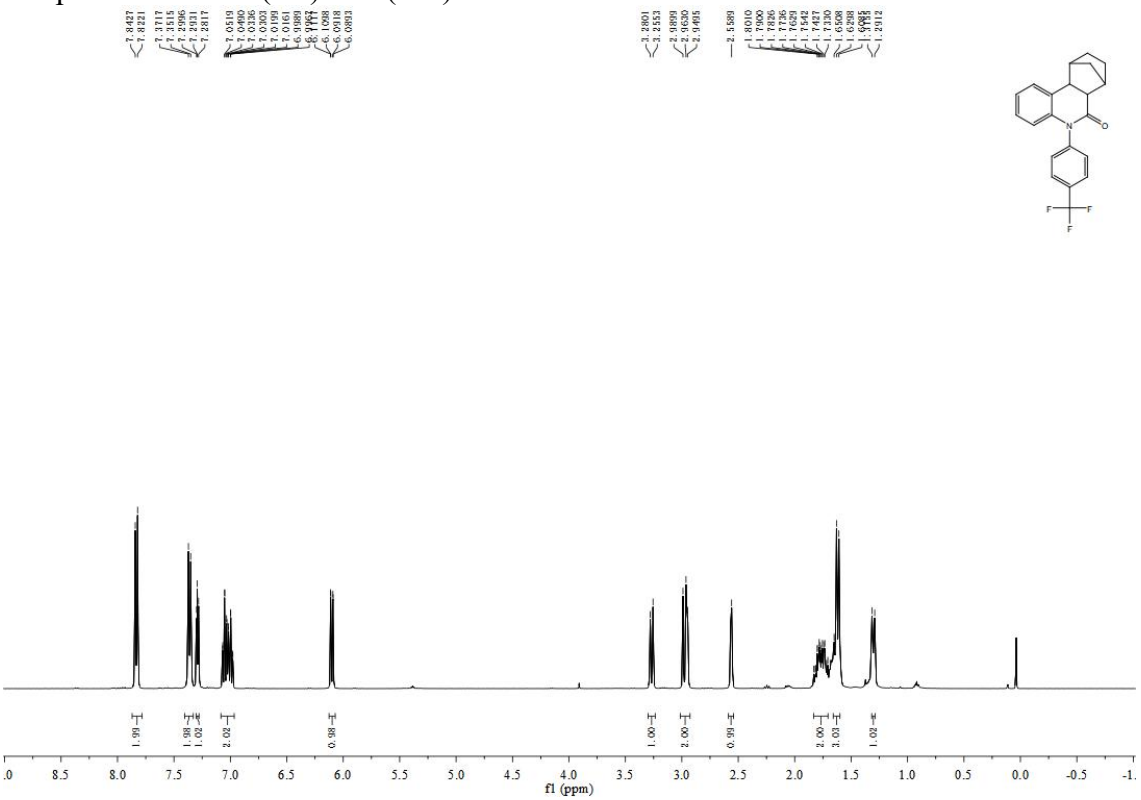
^{1}H NMR spectrum of 5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**12c**)



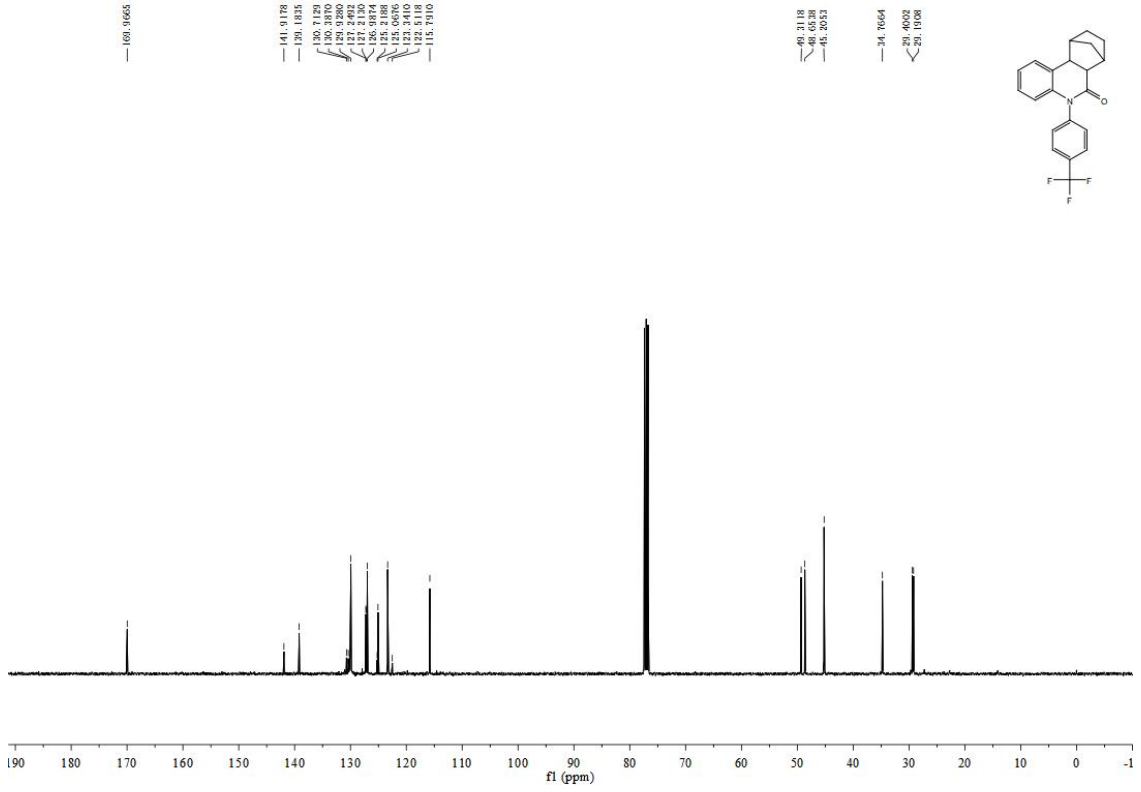
^{13}C NMR spectrum of 5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**12c**)



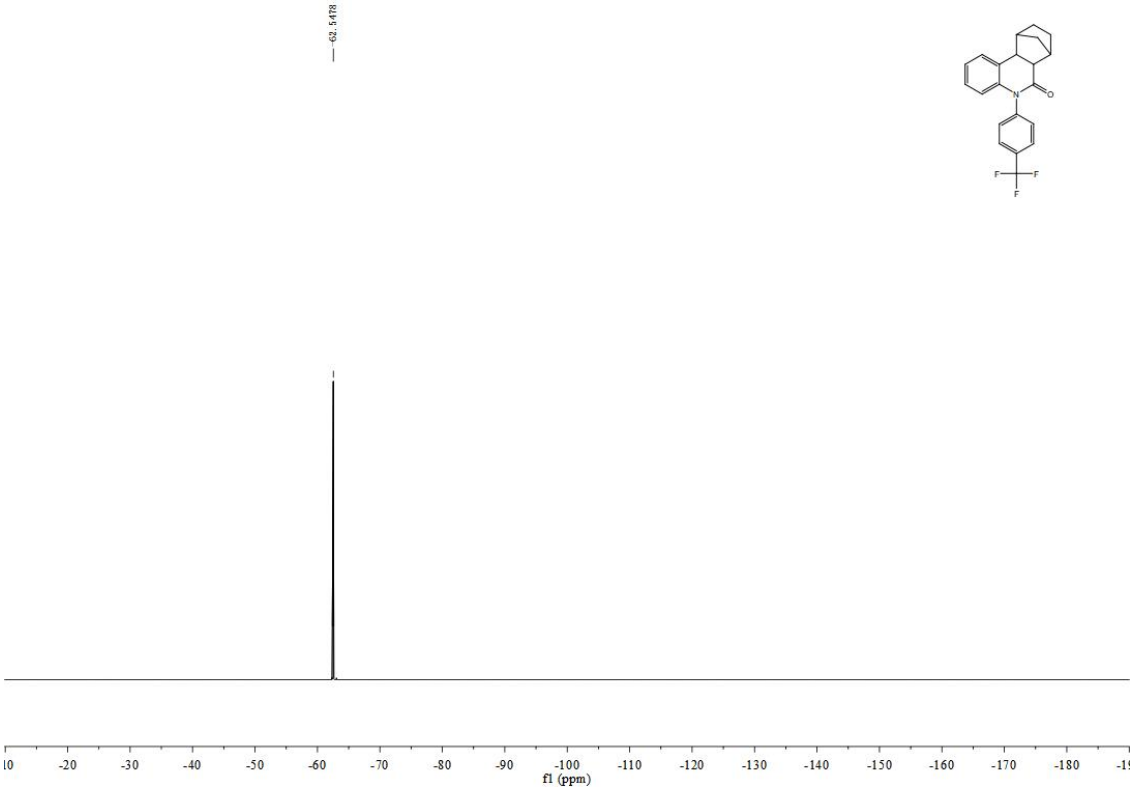
^{1}H NMR spectrum of 5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**13c**)



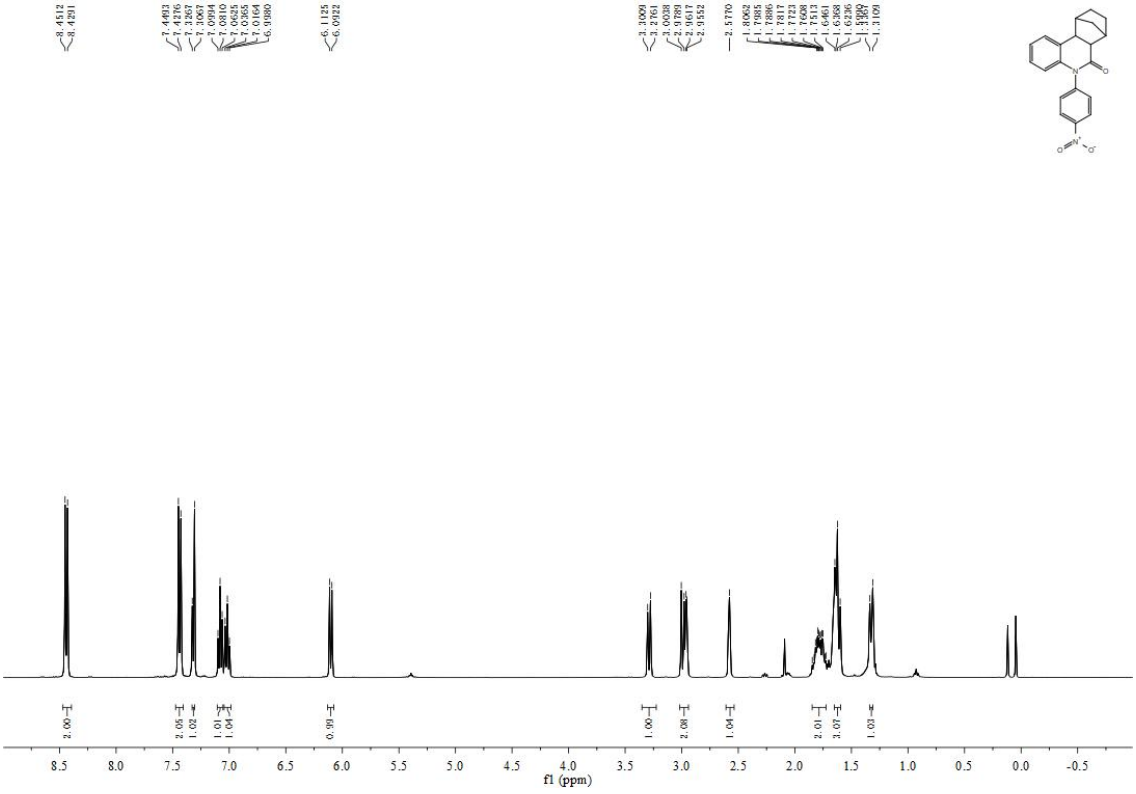
^{13}C NMR spectrum of 5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**13c**)



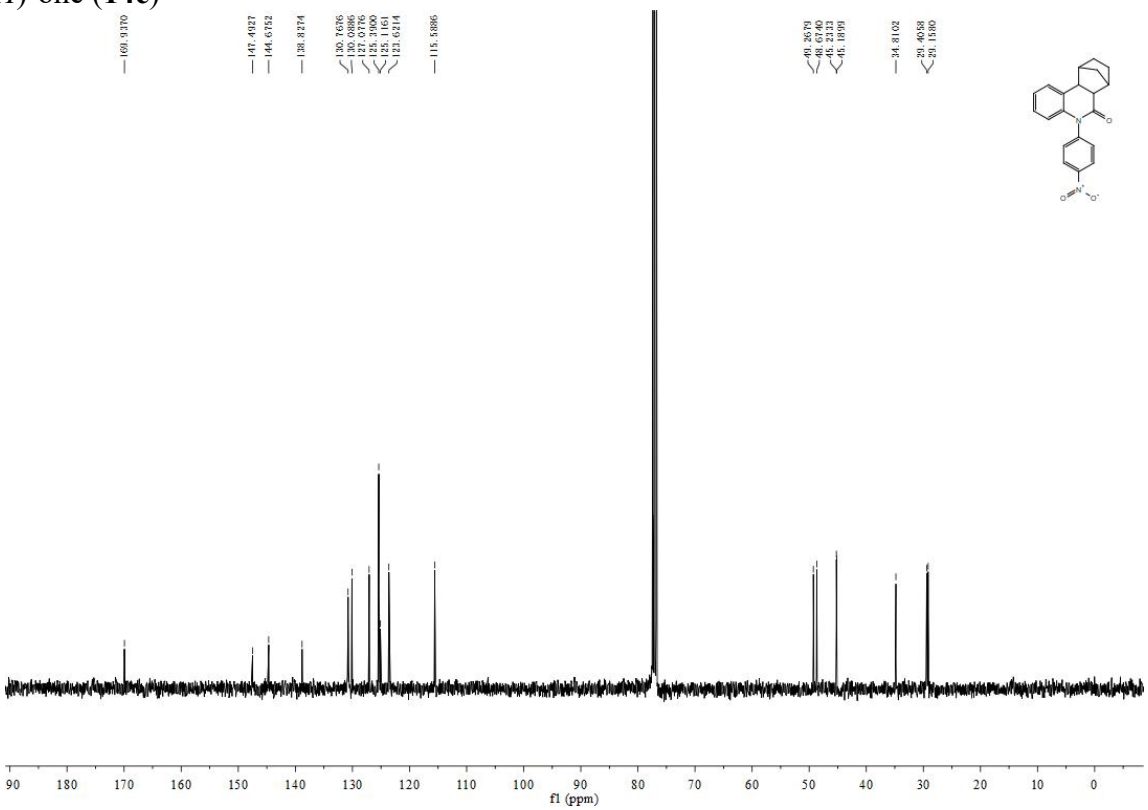
^{19}F NMR spectrum of 5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**13c**)



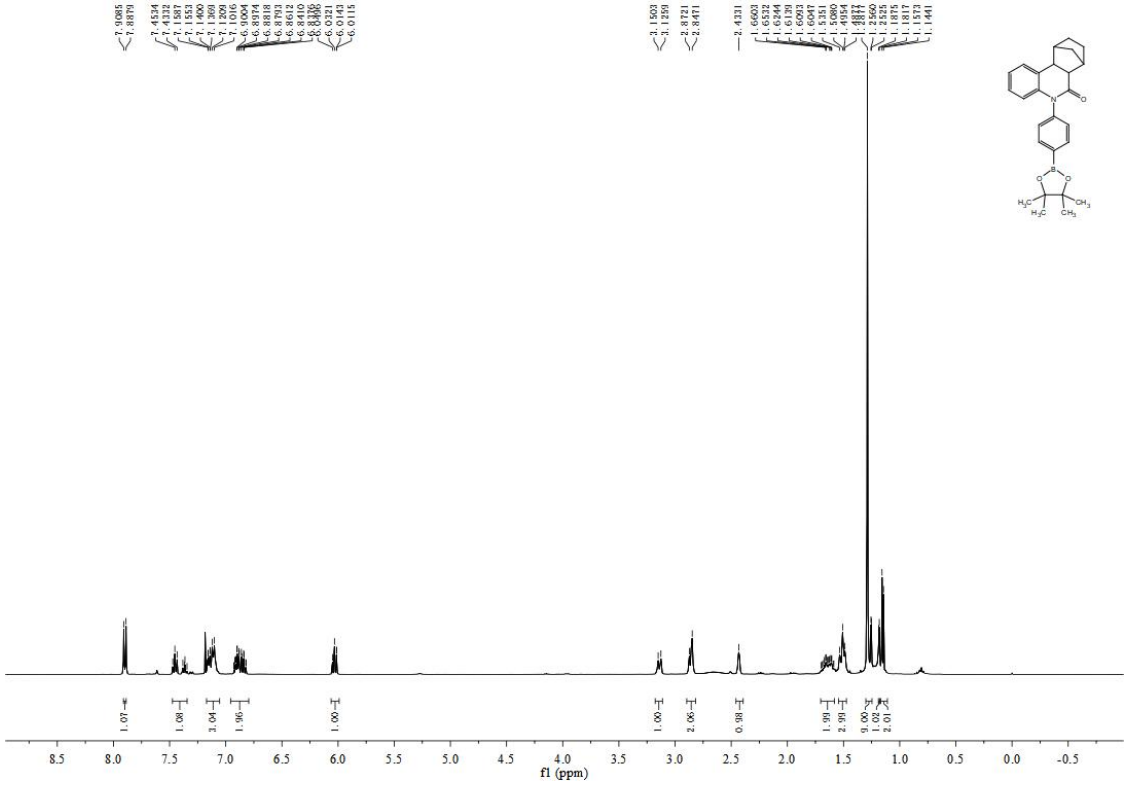
^{1}H NMR spectrum of 5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**14c**)



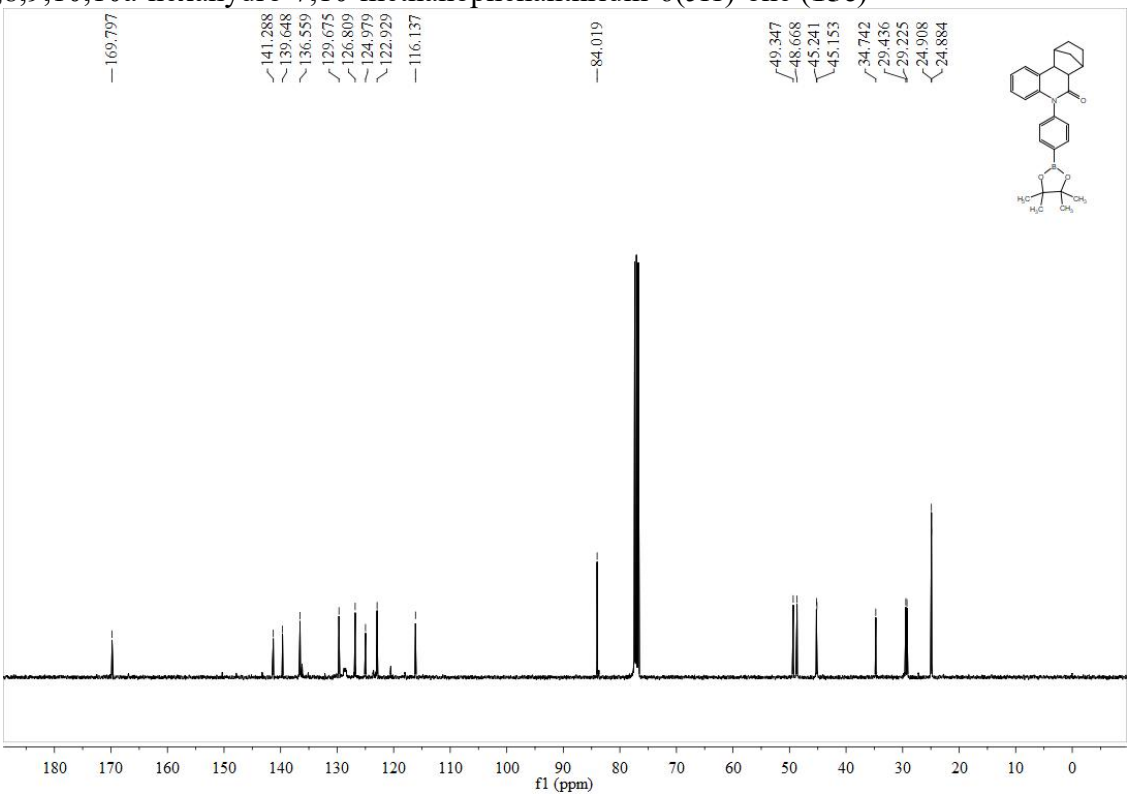
^{13}C NMR spectrum of 5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**14c**)



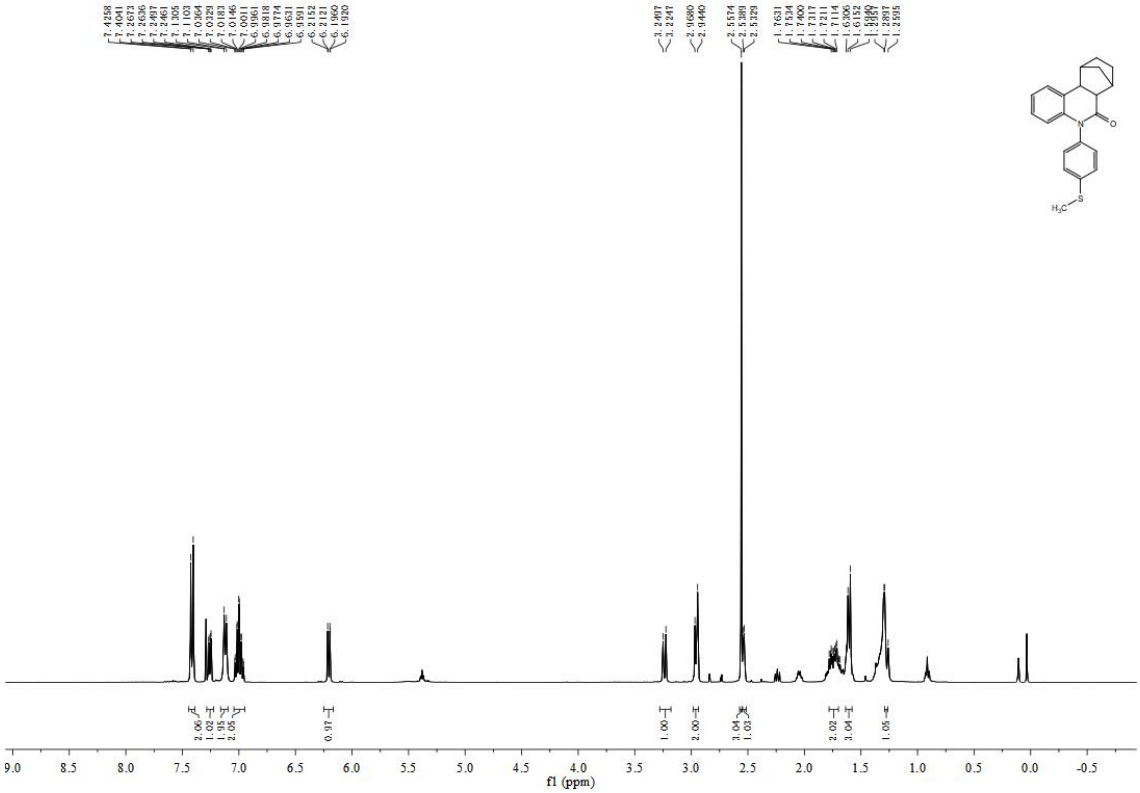
^{1}H NMR spectrum of 5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**15c**)



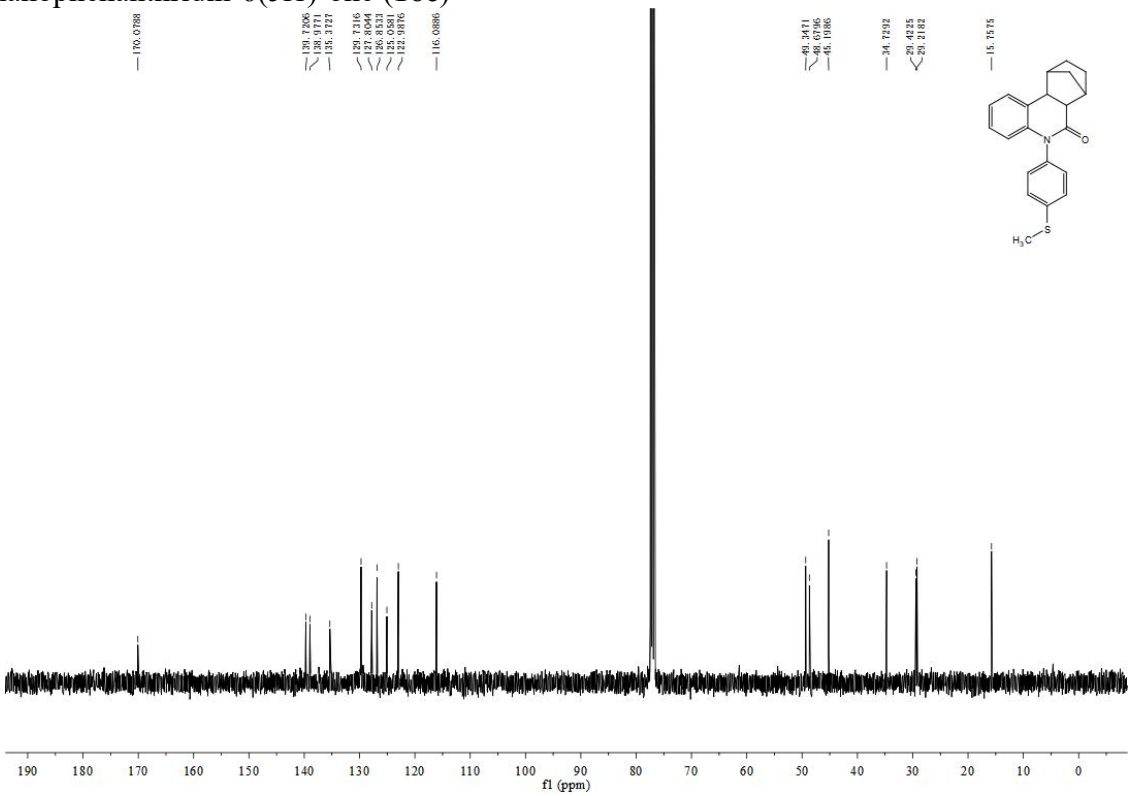
^{13}C NMR spectrum of 5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**15c**)



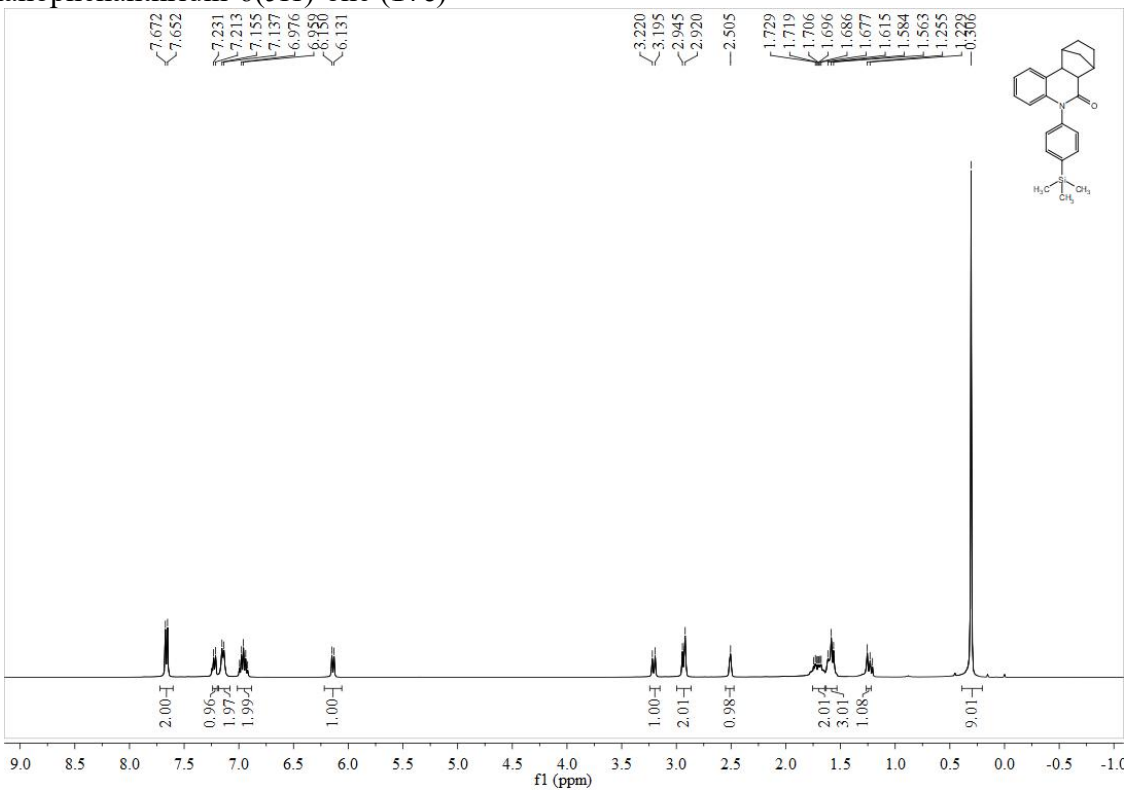
^{1}H NMR spectrum of 5-(4-(methylthio)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**16c**)



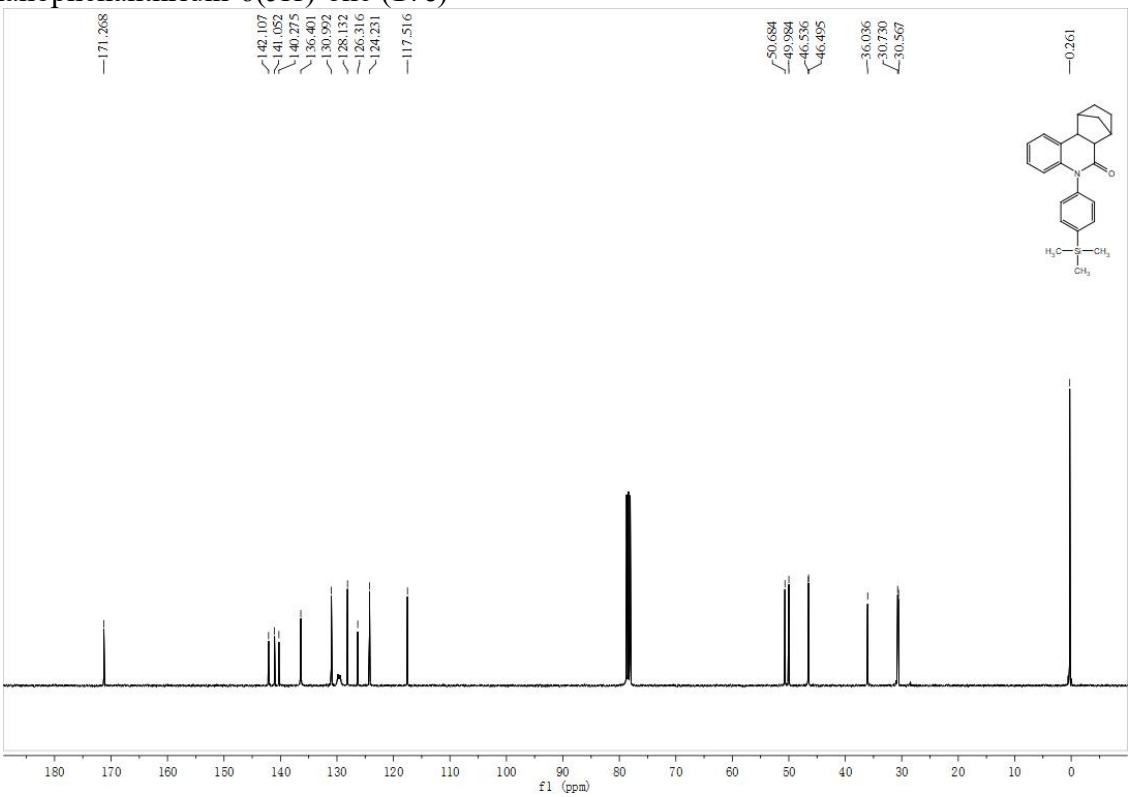
^{13}C NMR spectrum of 5-(4-(methylthio)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**16c**)



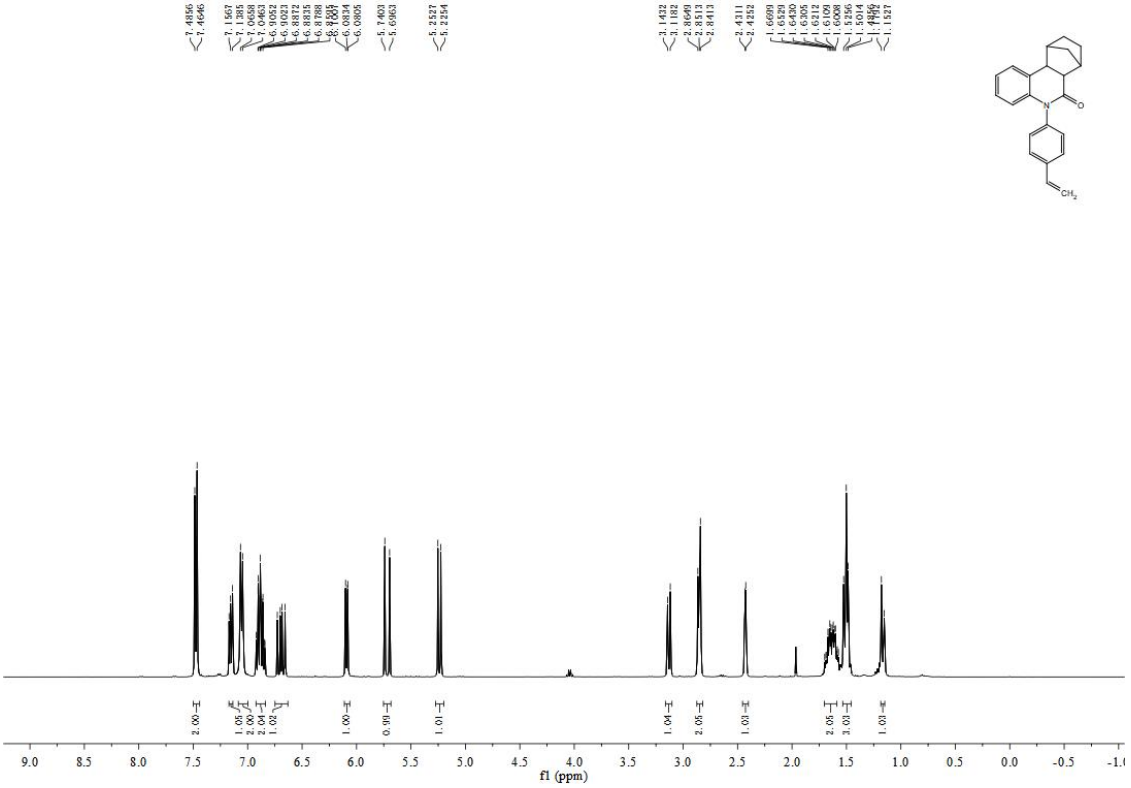
^{1}H NMR spectrum of 5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**17c**)



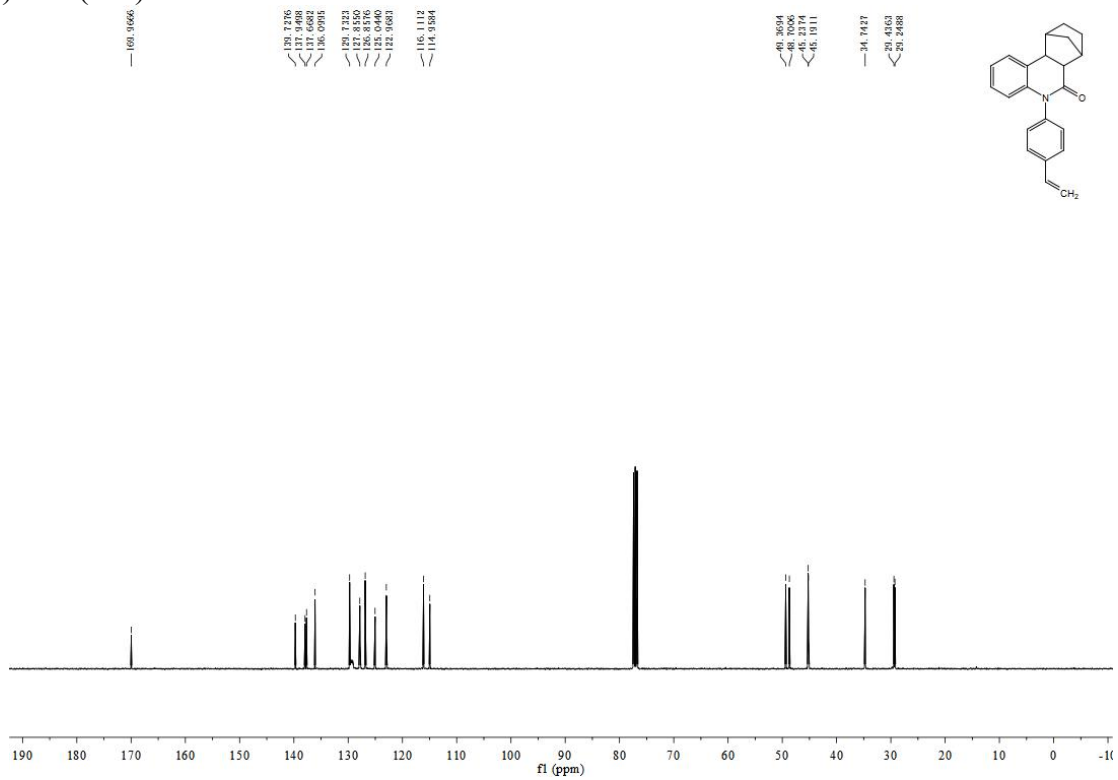
^{13}C NMR spectrum of 5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**17c**)



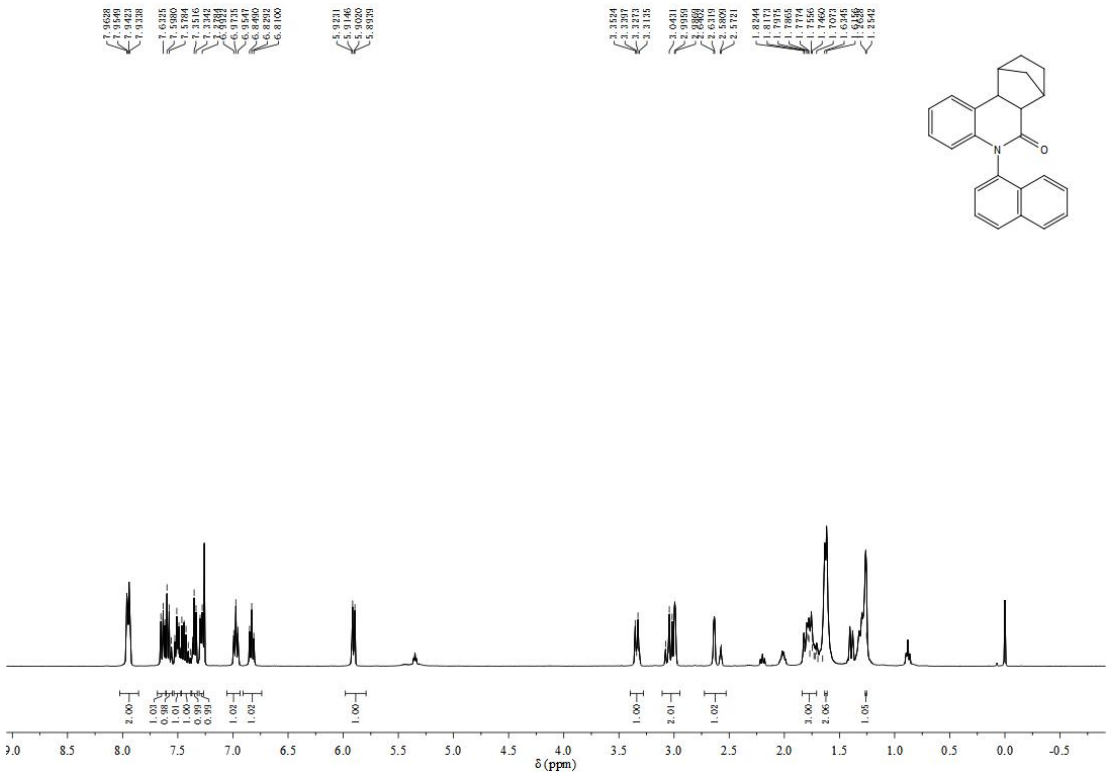
^{1}H NMR spectrum of 5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**18c**)



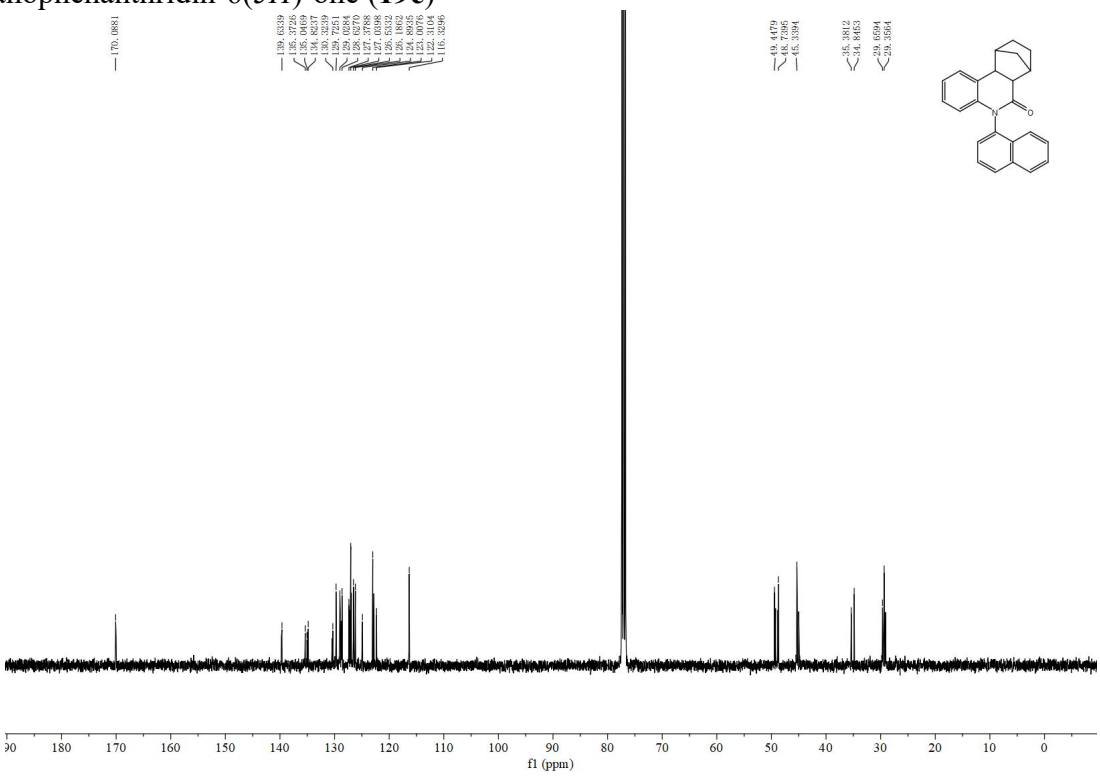
^{13}C NMR spectrum of 5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**18c**)



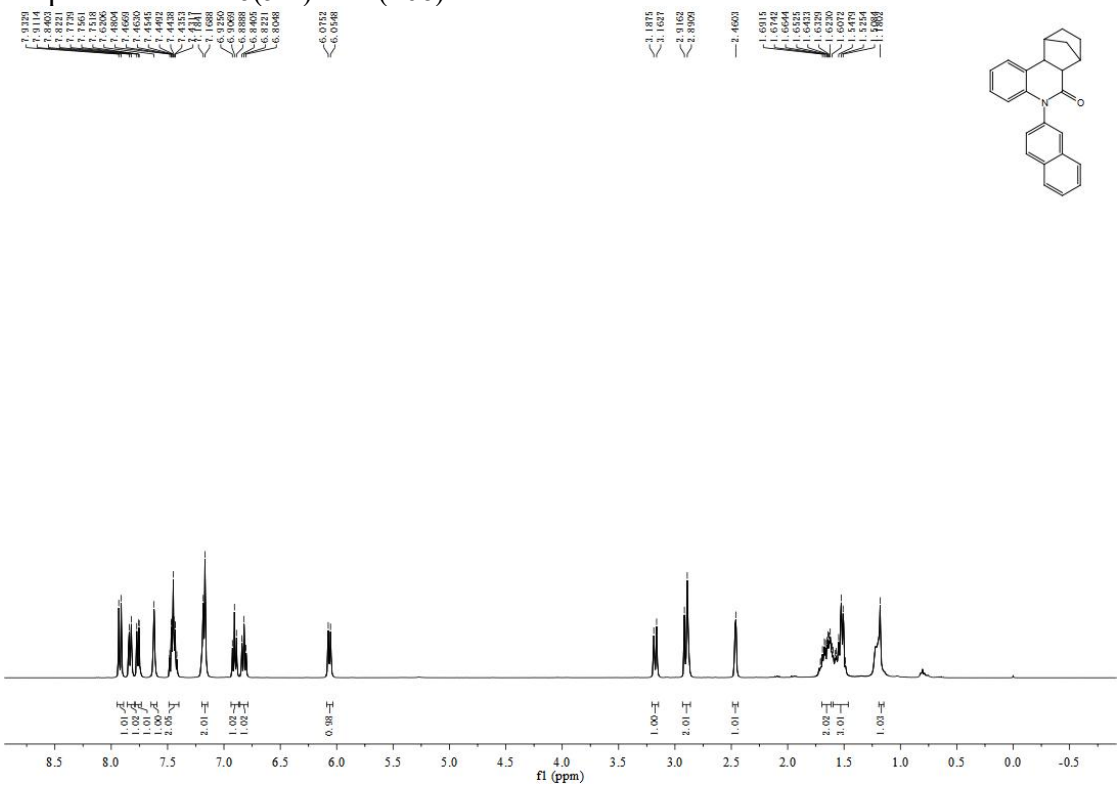
^{1}H NMR spectrum of 5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**19c**)



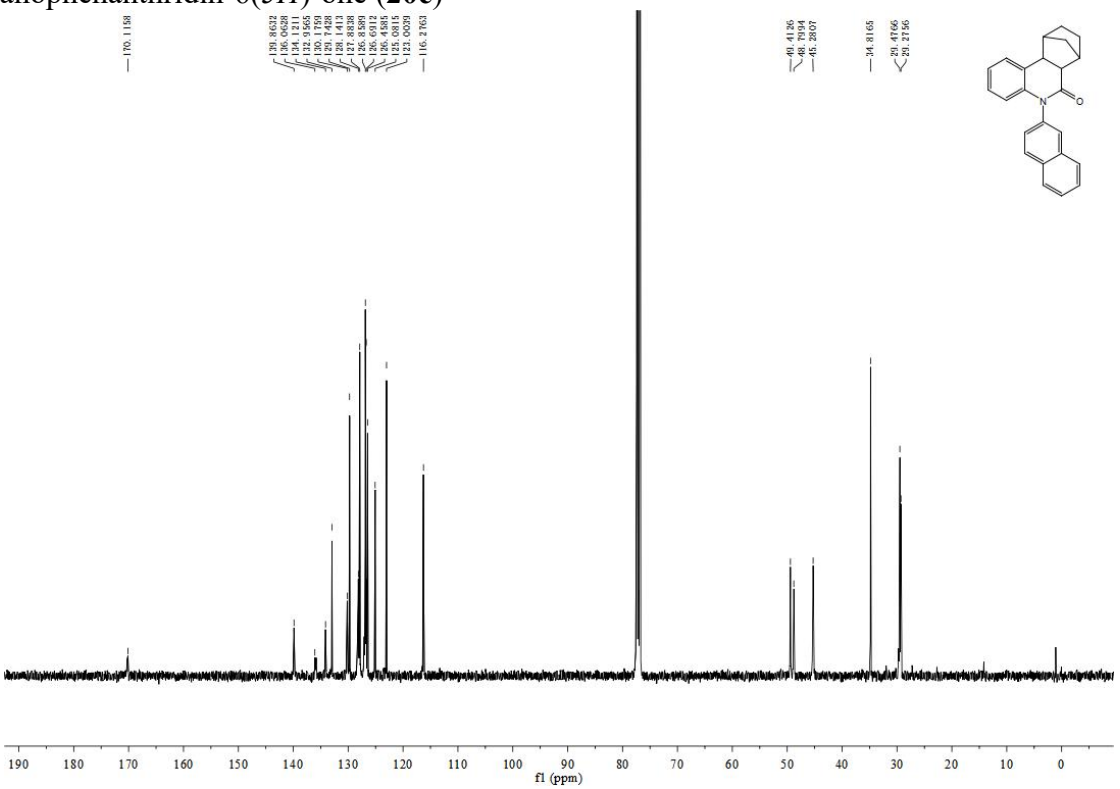
^{13}C NMR spectrum of 5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**19c**)



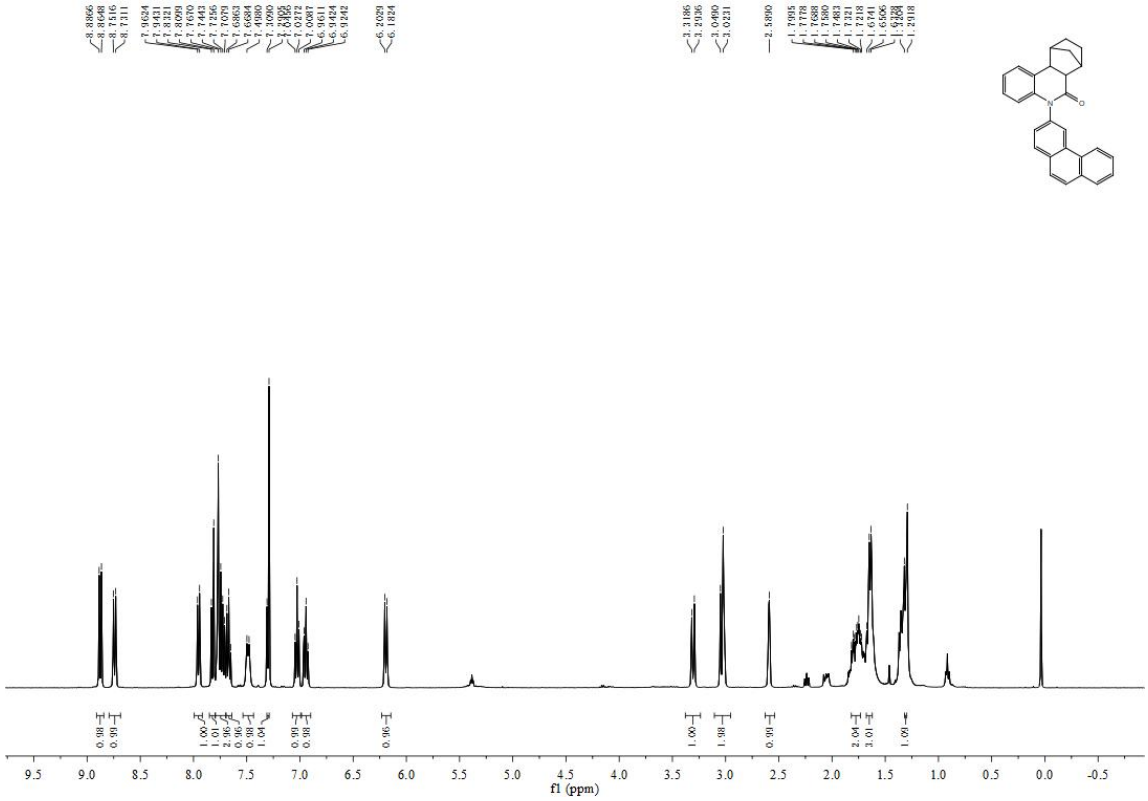
^{1}H NMR spectrum of 5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**20c**)



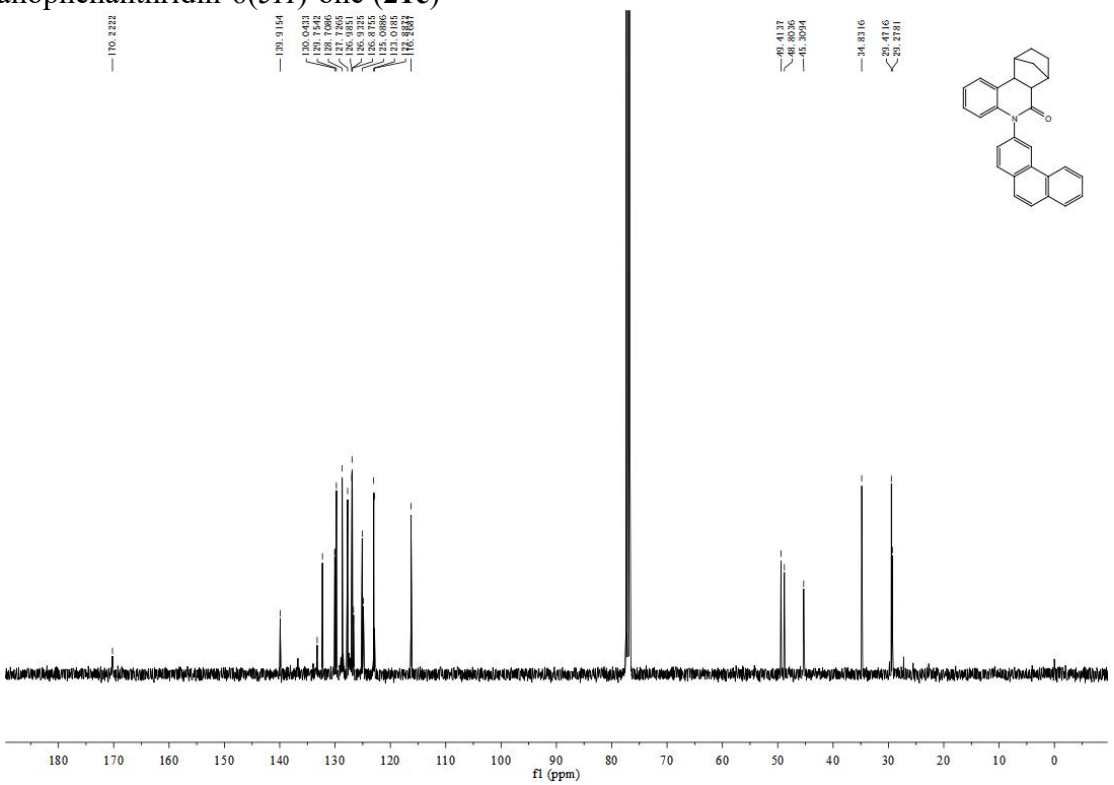
^{13}C NMR spectrum of 5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**20c**)



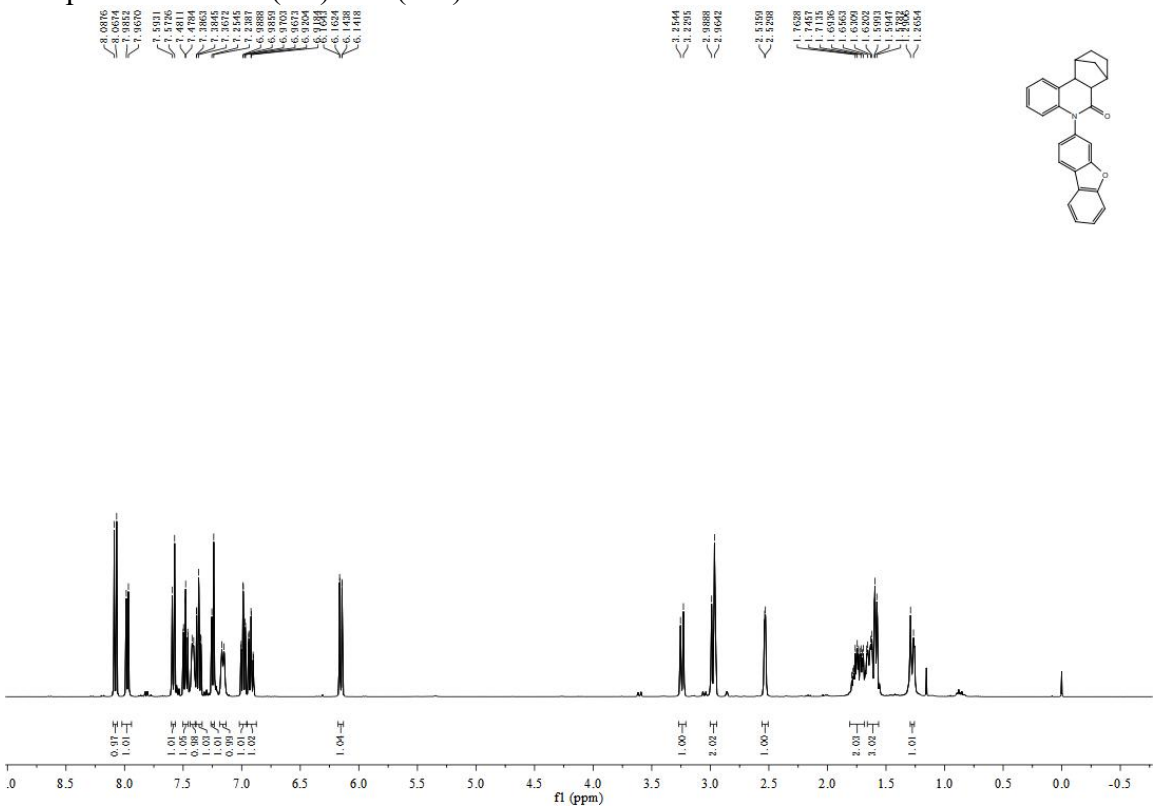
^{1}H NMR spectrum of 5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**21c**)



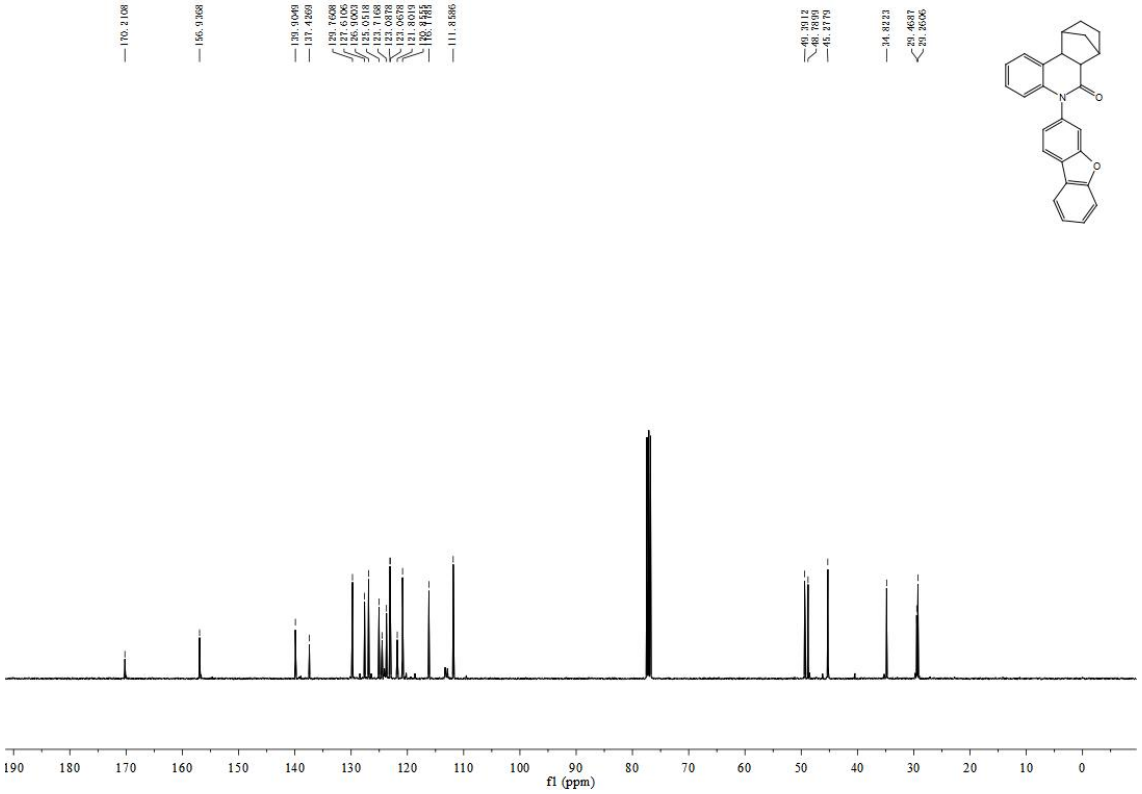
^{13}C NMR spectrum of 5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**21c**)



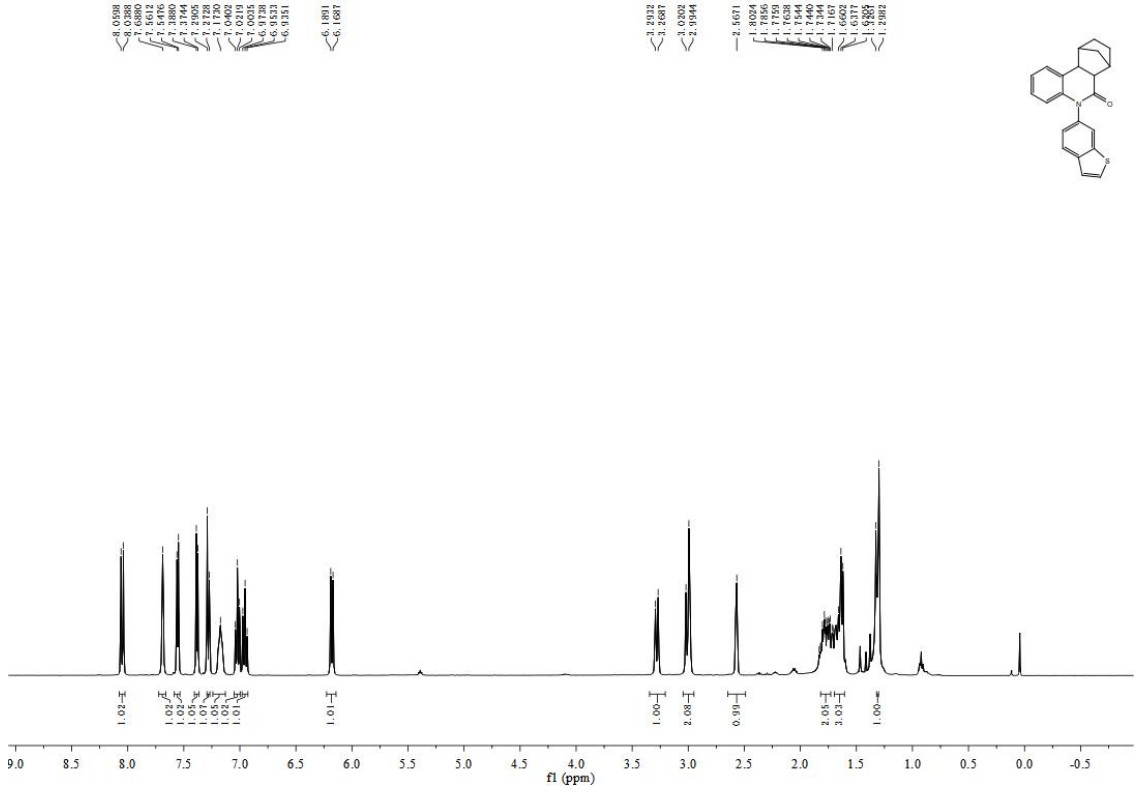
^{1}H NMR spectrum of 5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**22c**)



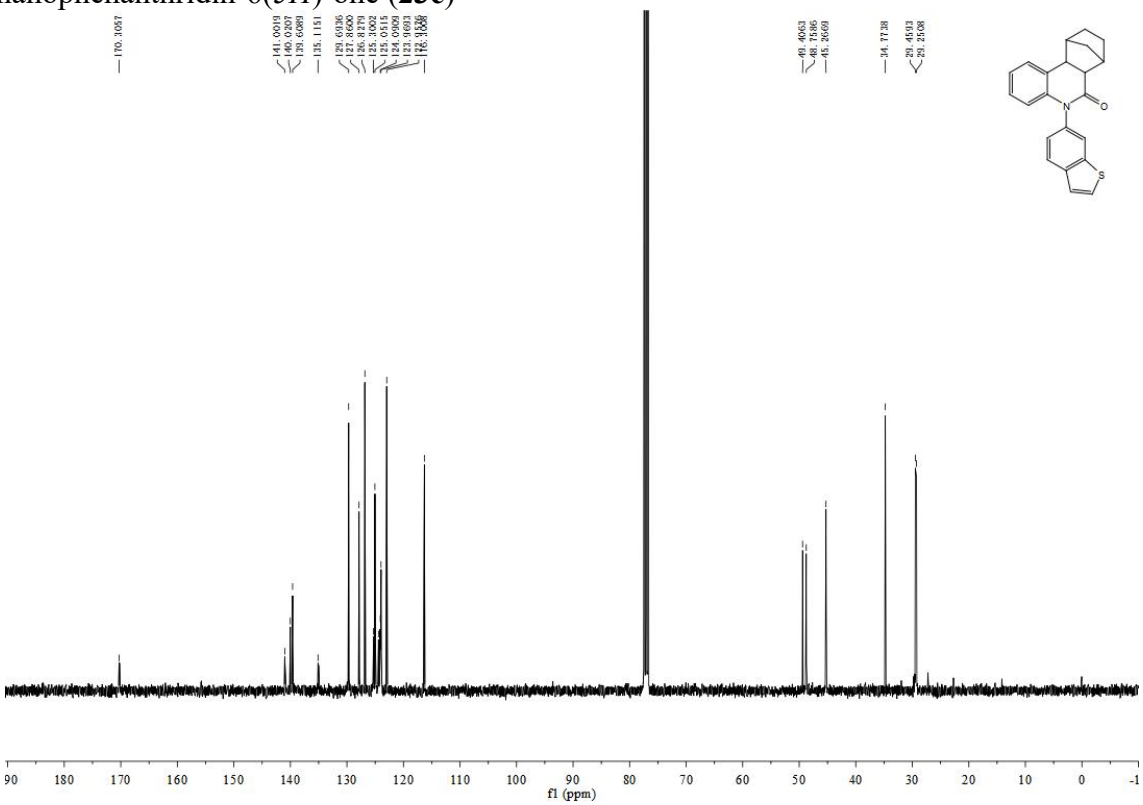
^{13}C NMR spectrum of 5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**22c**)



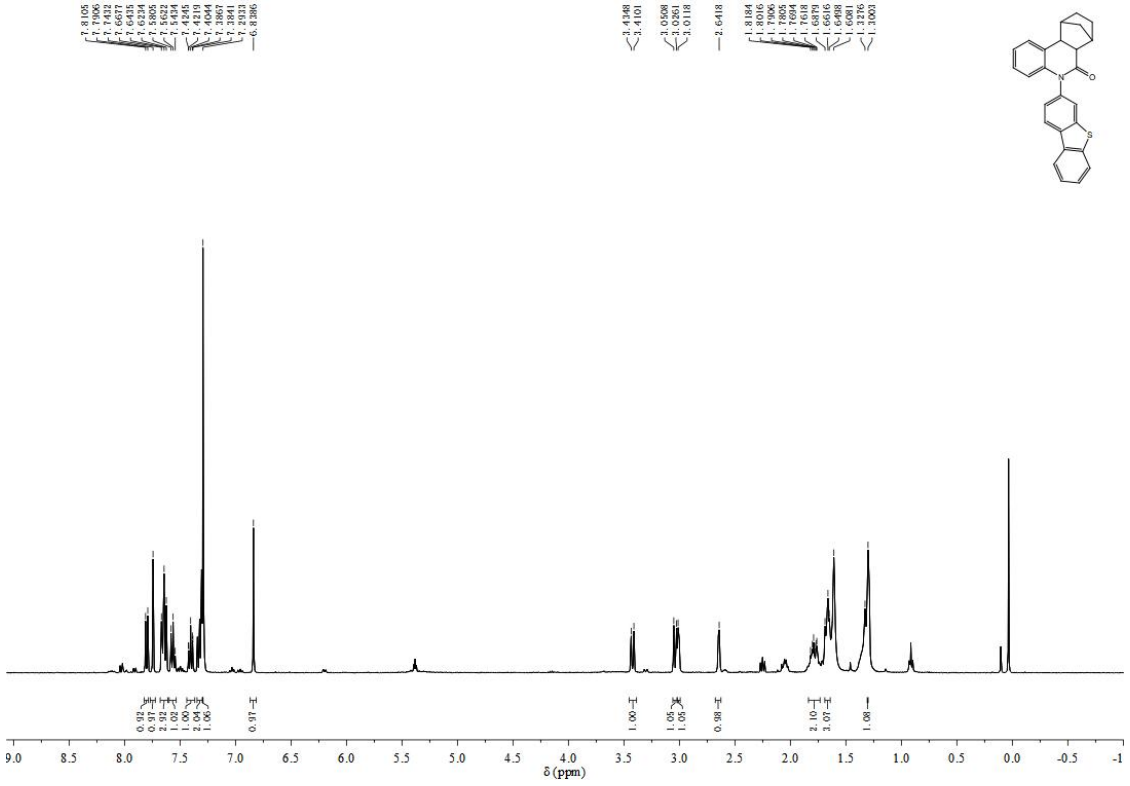
^{1}H NMR spectrum of 5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**23c**)



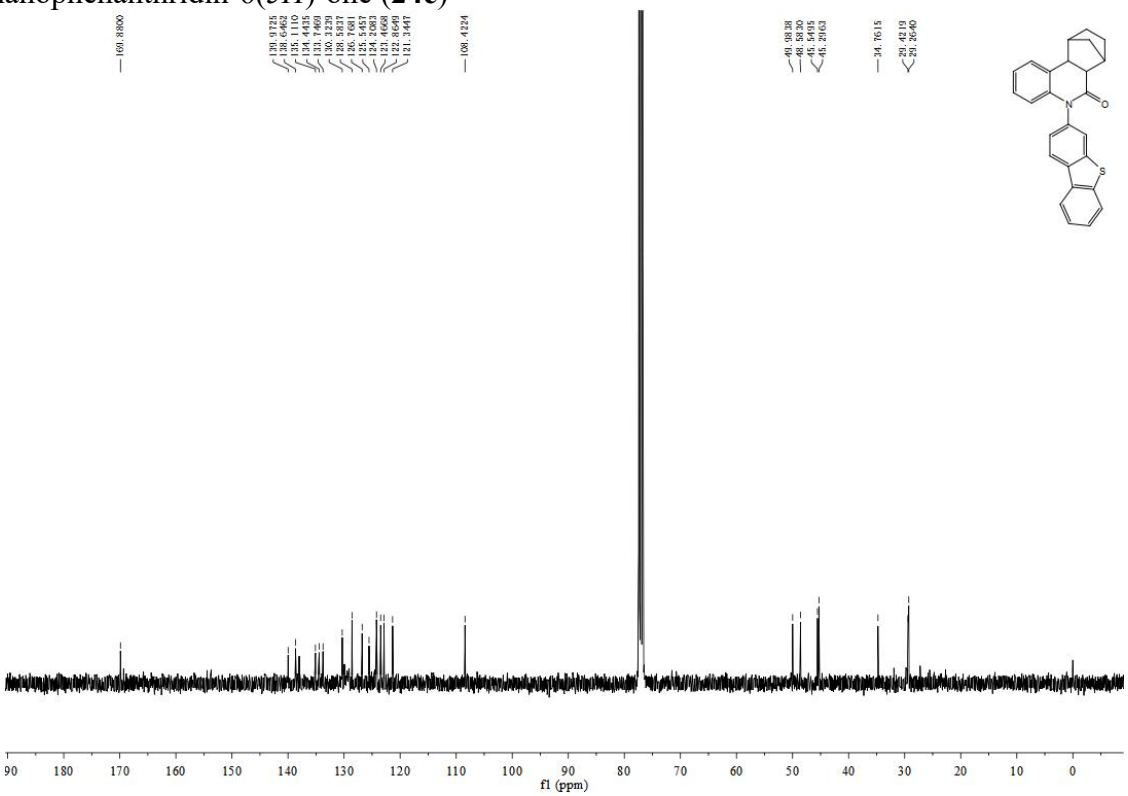
^{13}C NMR spectrum of 5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**23c**)



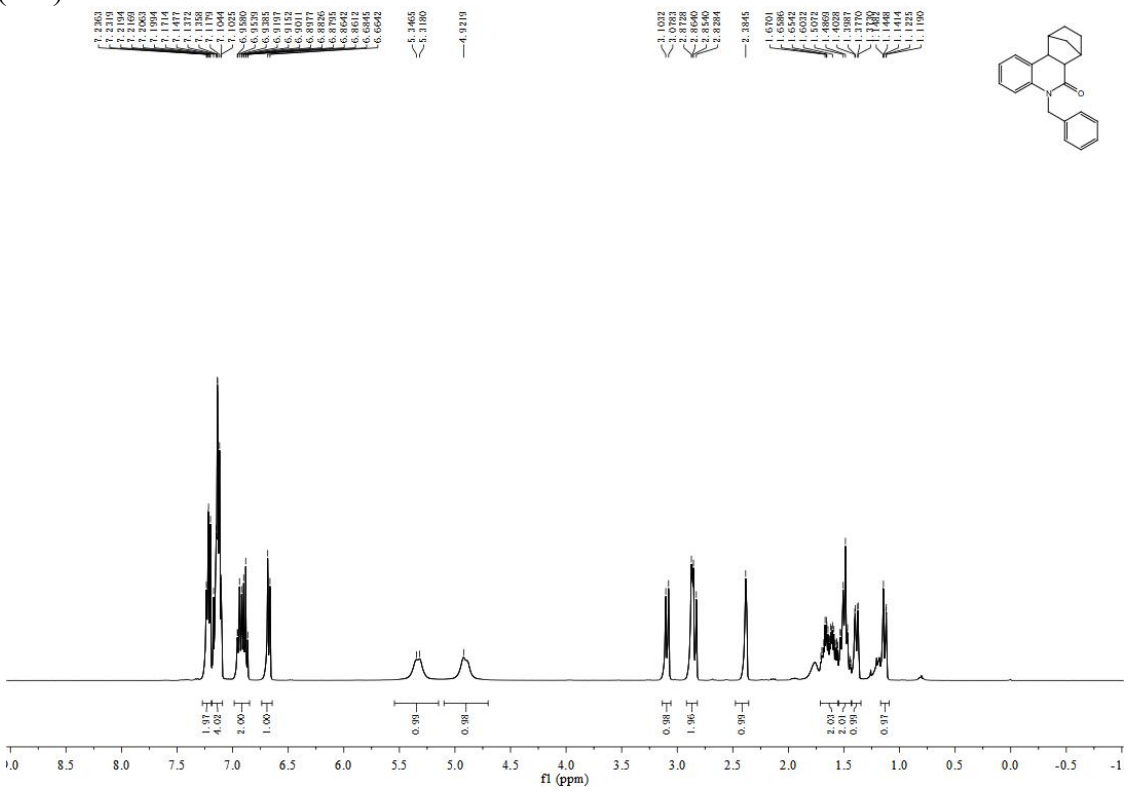
^{1}H NMR spectrum of 5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**24c**)



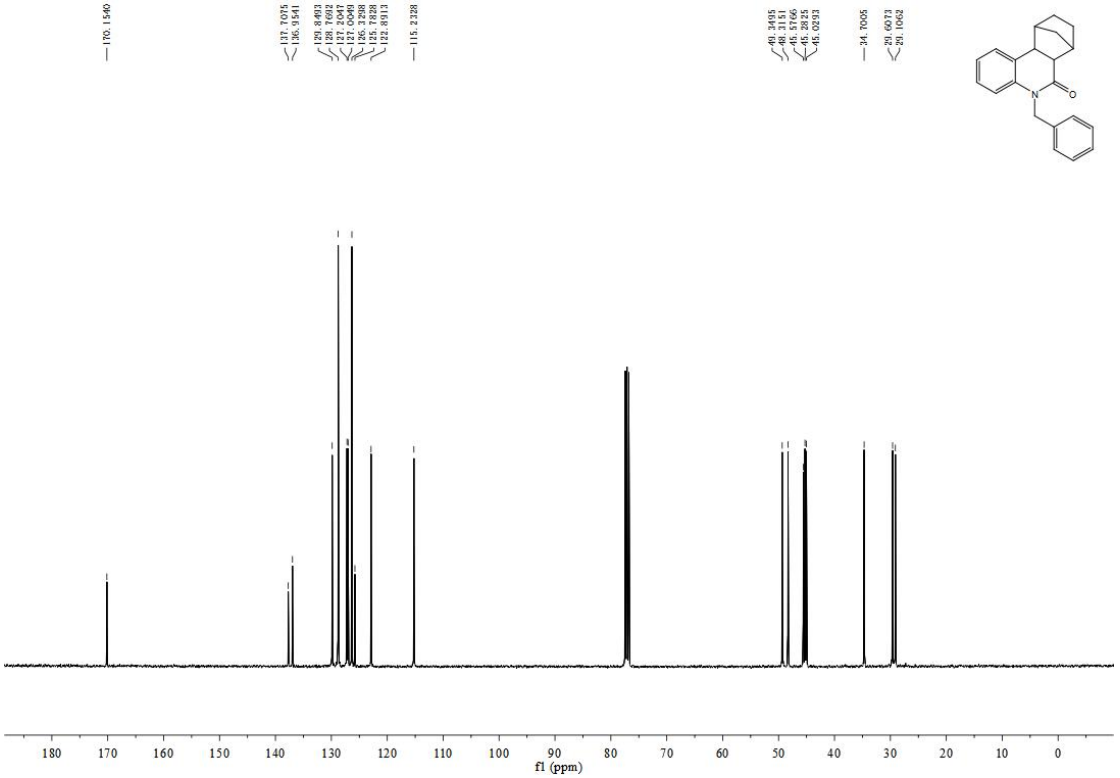
^{13}C NMR spectrum of 5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**24c**)



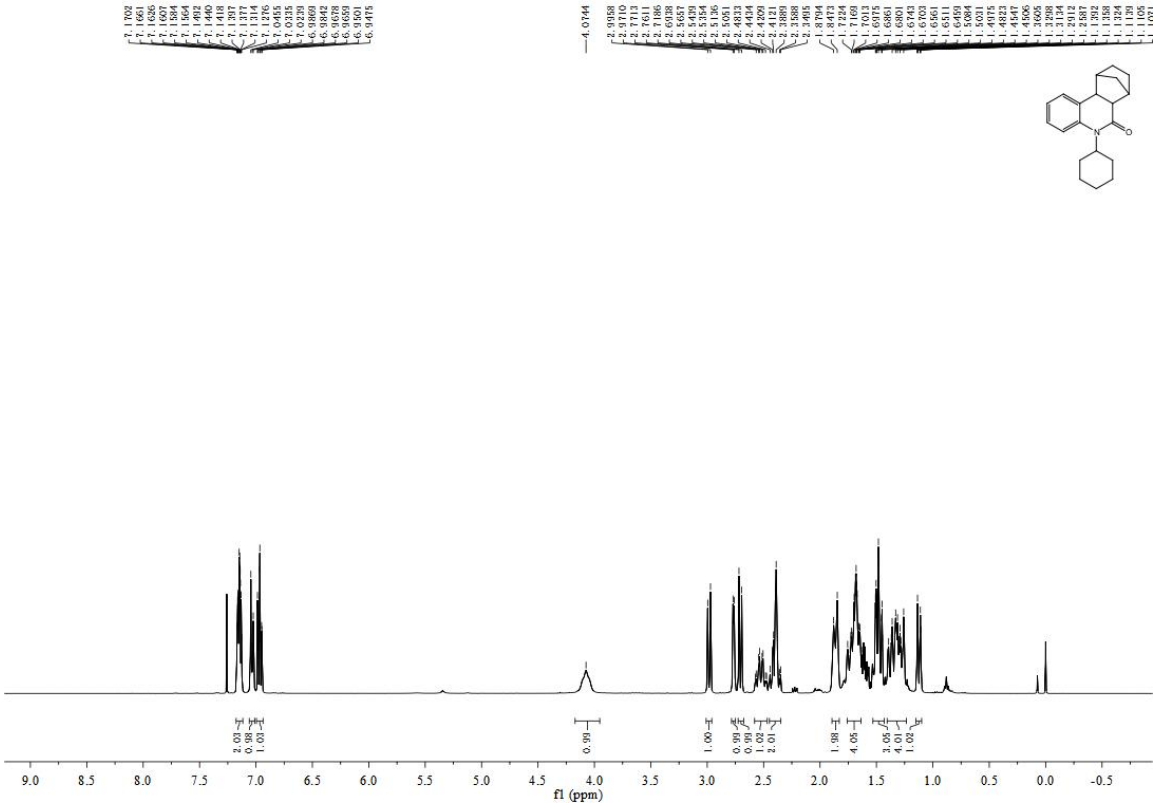
^{1}H NMR spectrum of 5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**25c**)



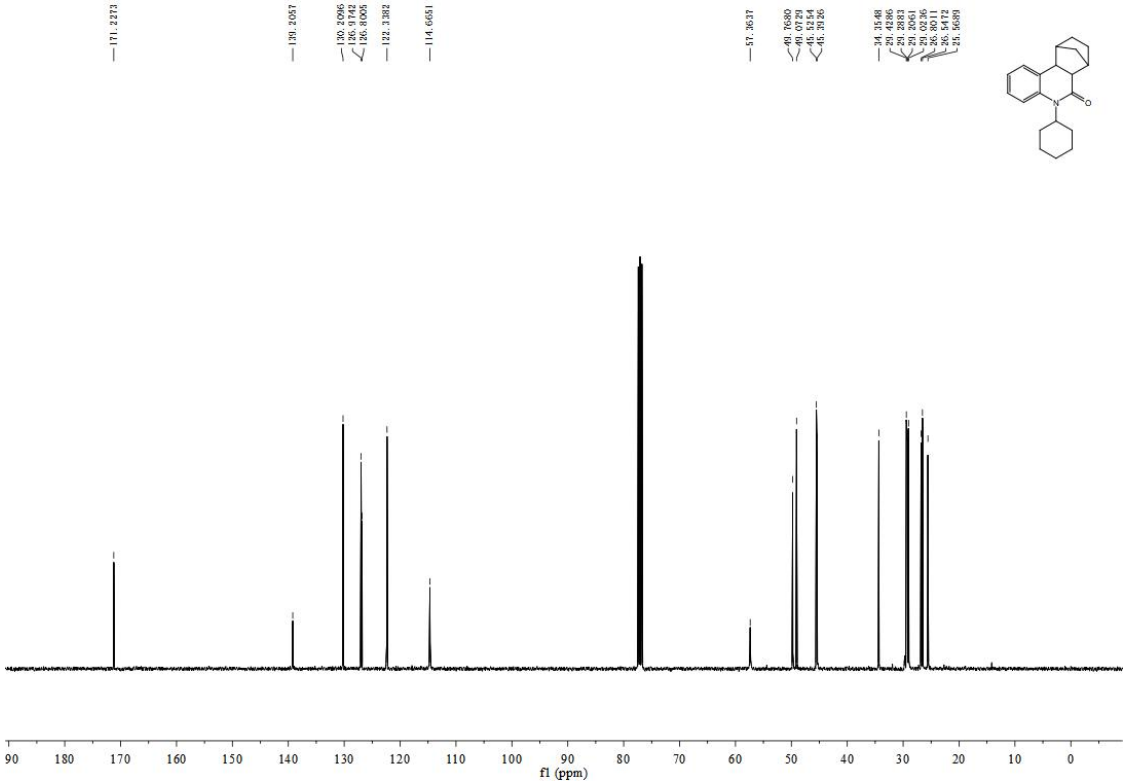
^{13}C NMR spectrum of 5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**25c**)



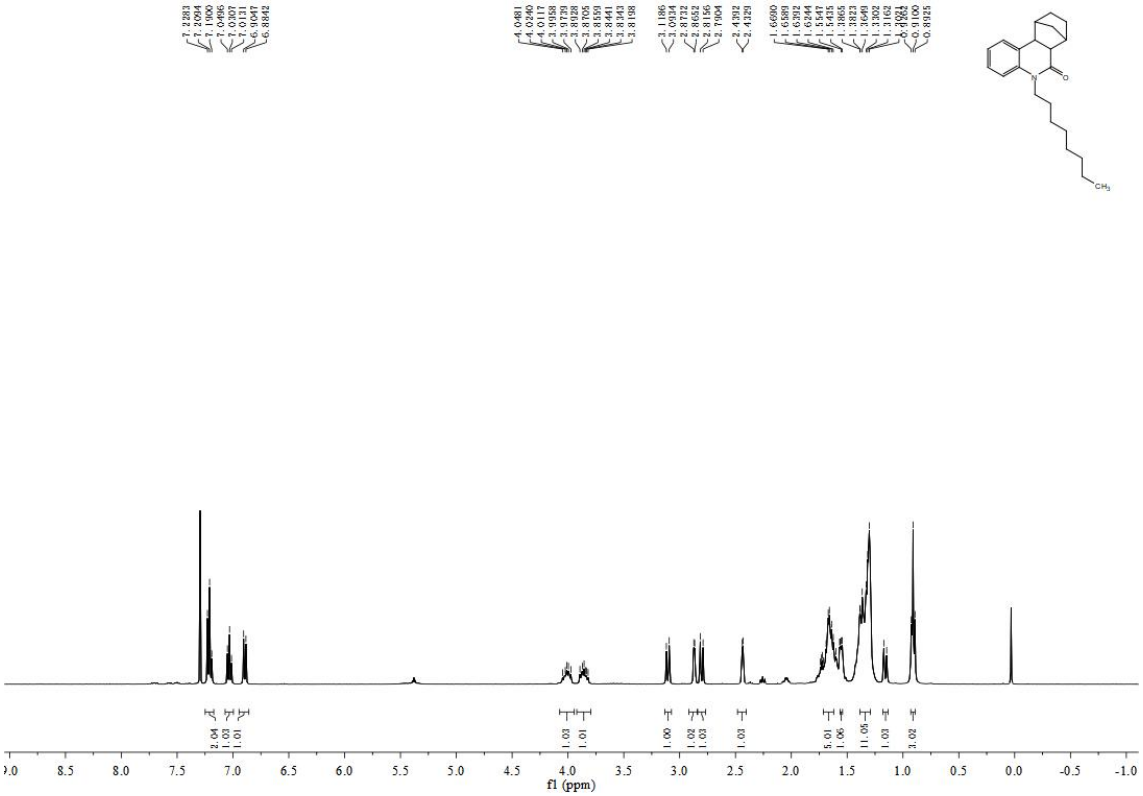
^{1}H NMR spectrum of 5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**26c**)



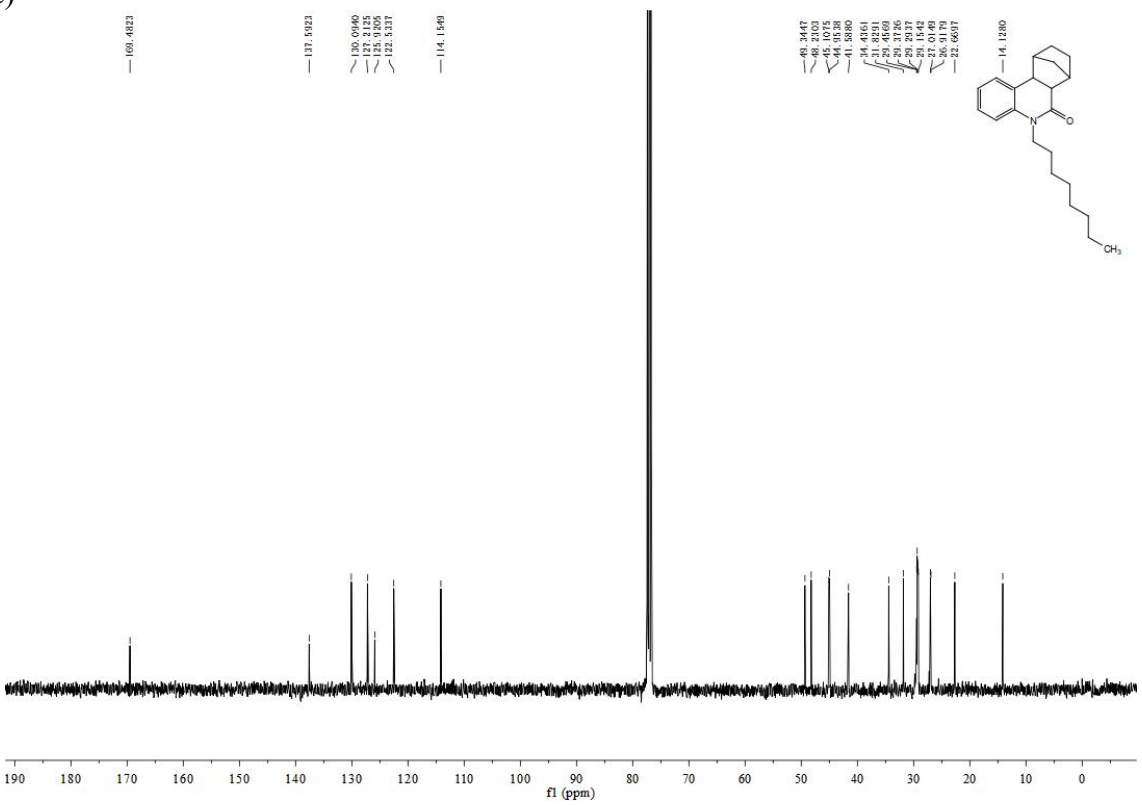
^{13}C NMR spectrum of 5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**26c**)



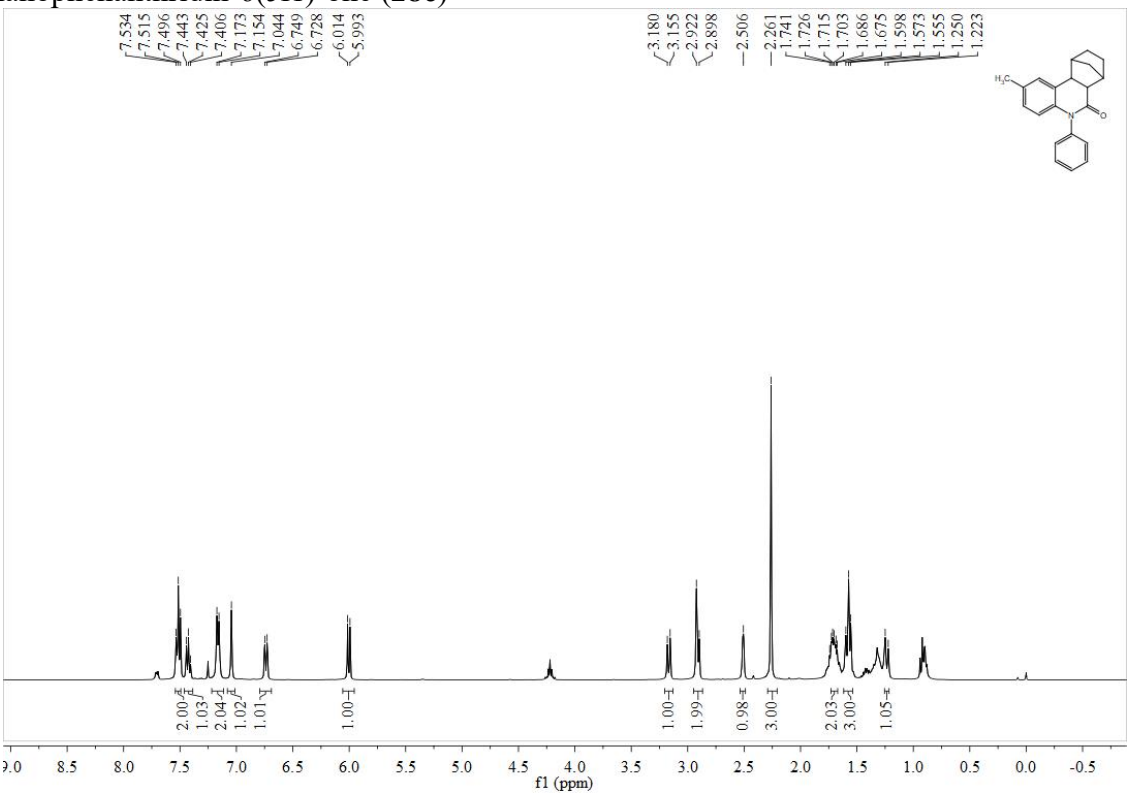
^{1}H NMR spectrum of 5-octyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**27c**)



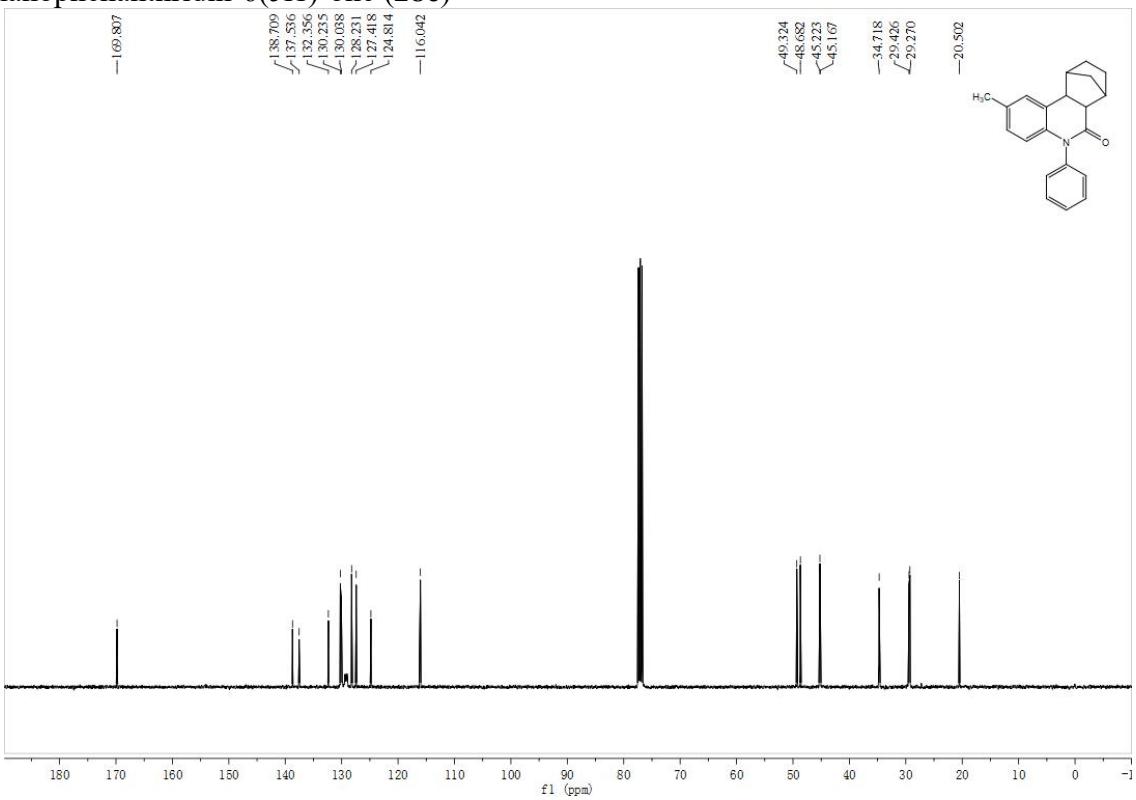
^{13}C NMR spectrum of 5-octyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**27c**)



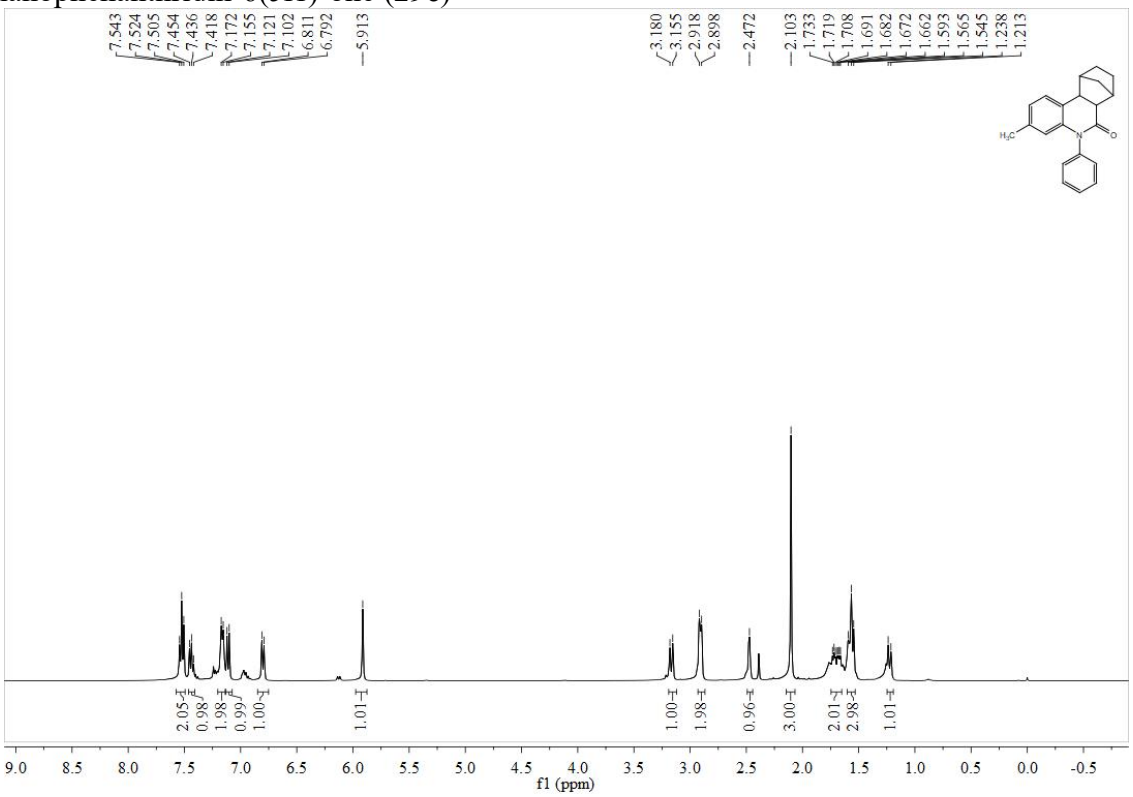
^{1}H NMR spectrum of 2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**28c**)



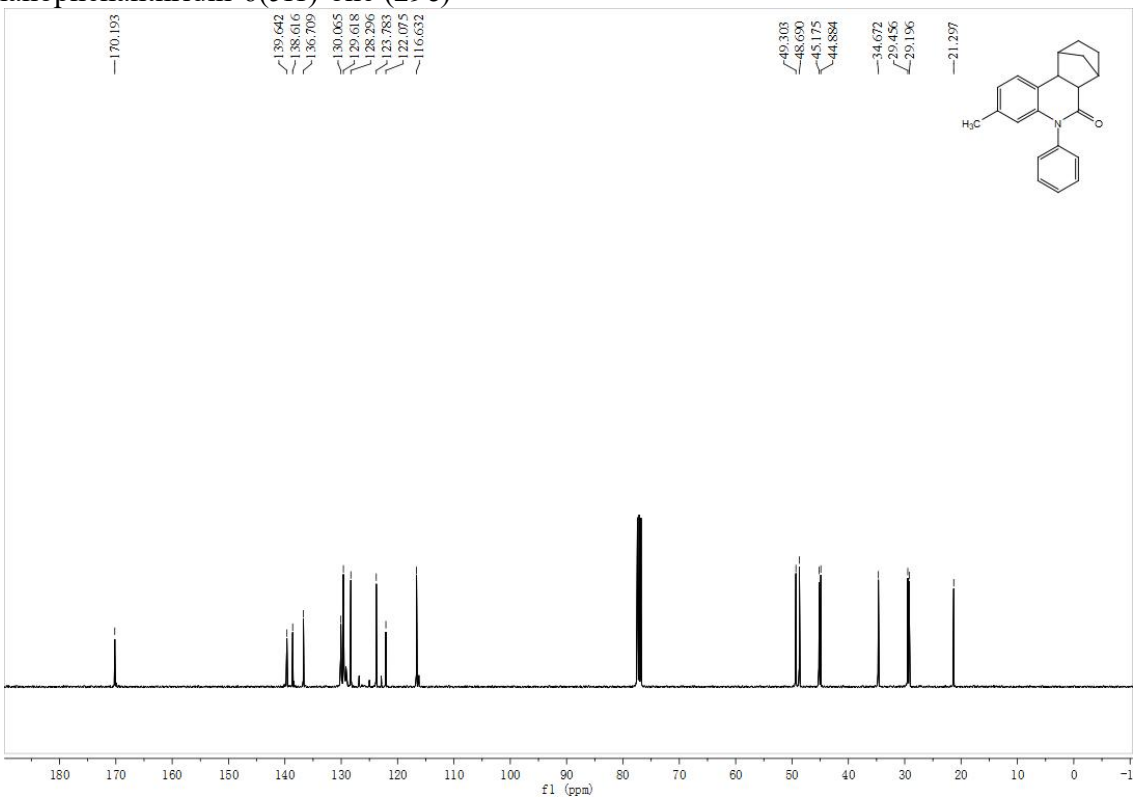
^{13}C NMR spectrum of 2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**28c**)



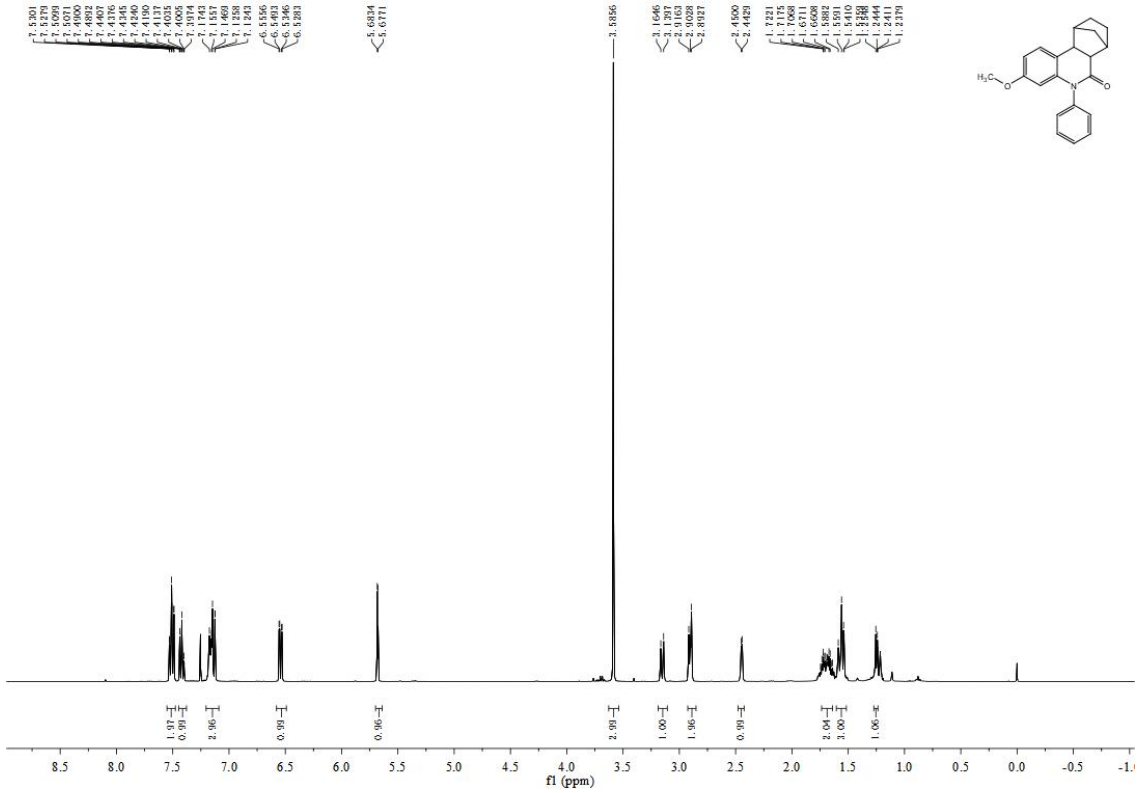
^{1}H NMR spectrum of 3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**29c**)



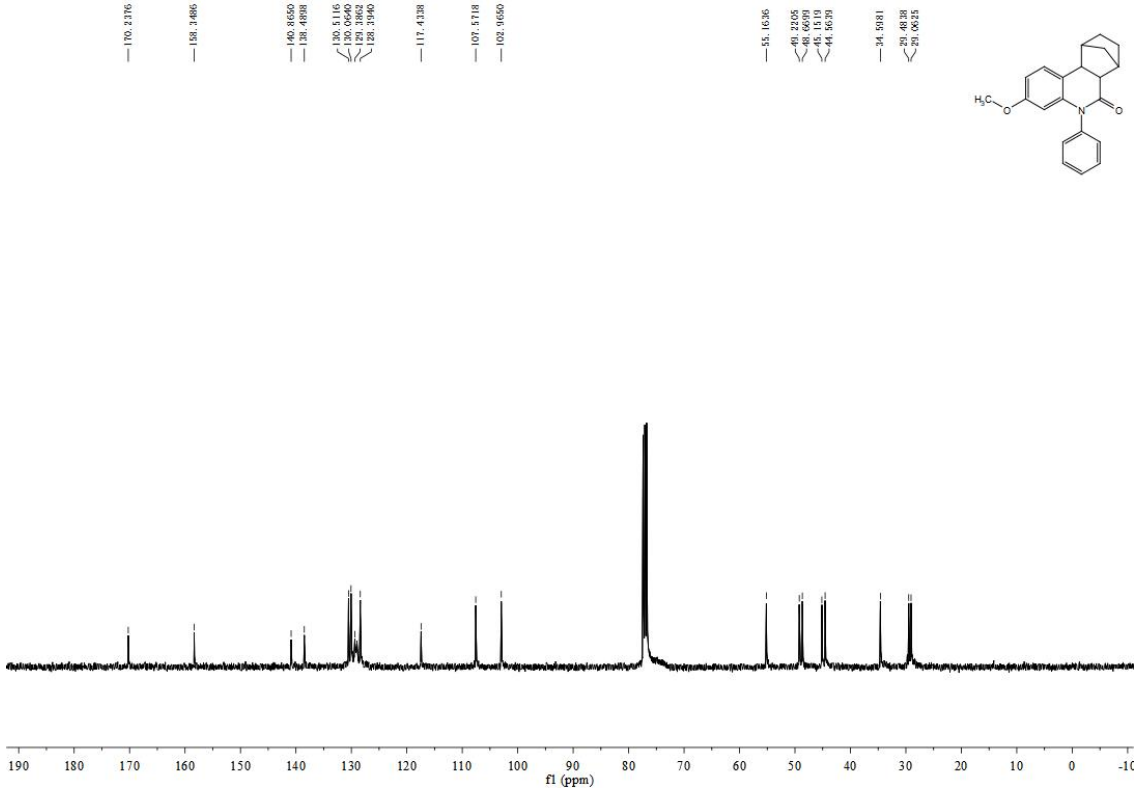
^{13}C NMR spectrum of 3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**29c**)



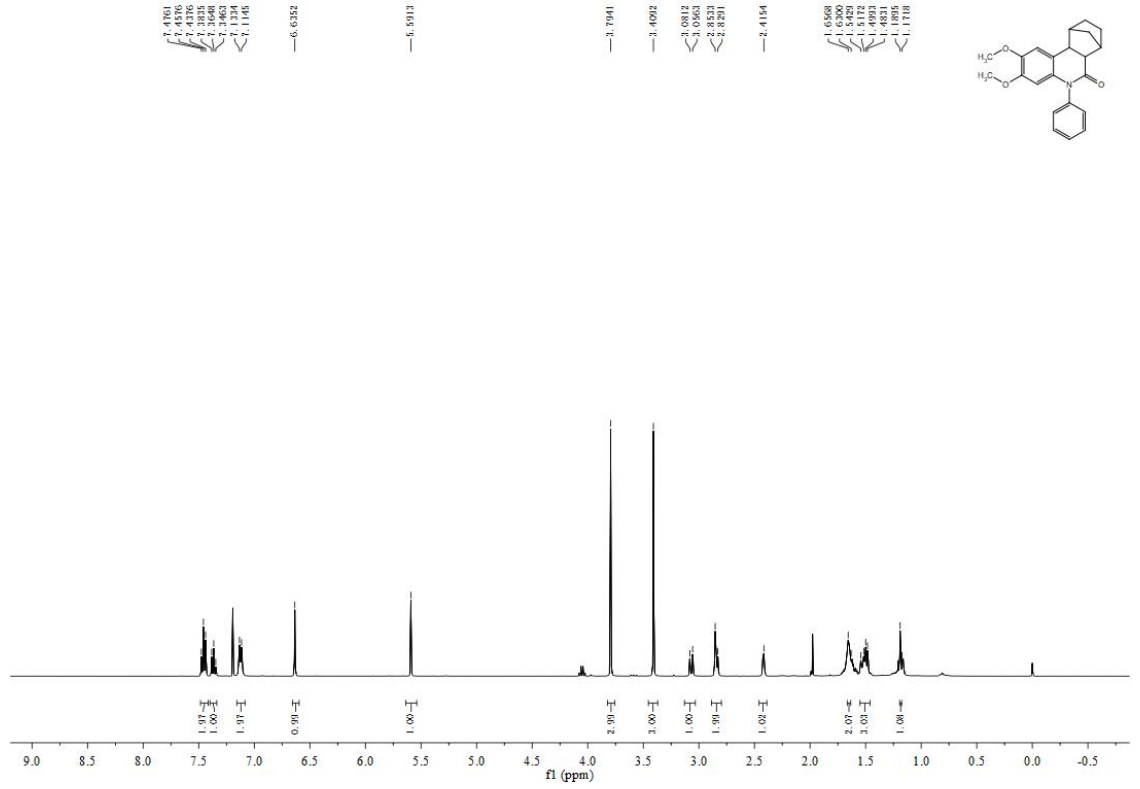
^{1}H NMR spectrum of 3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**30c**)



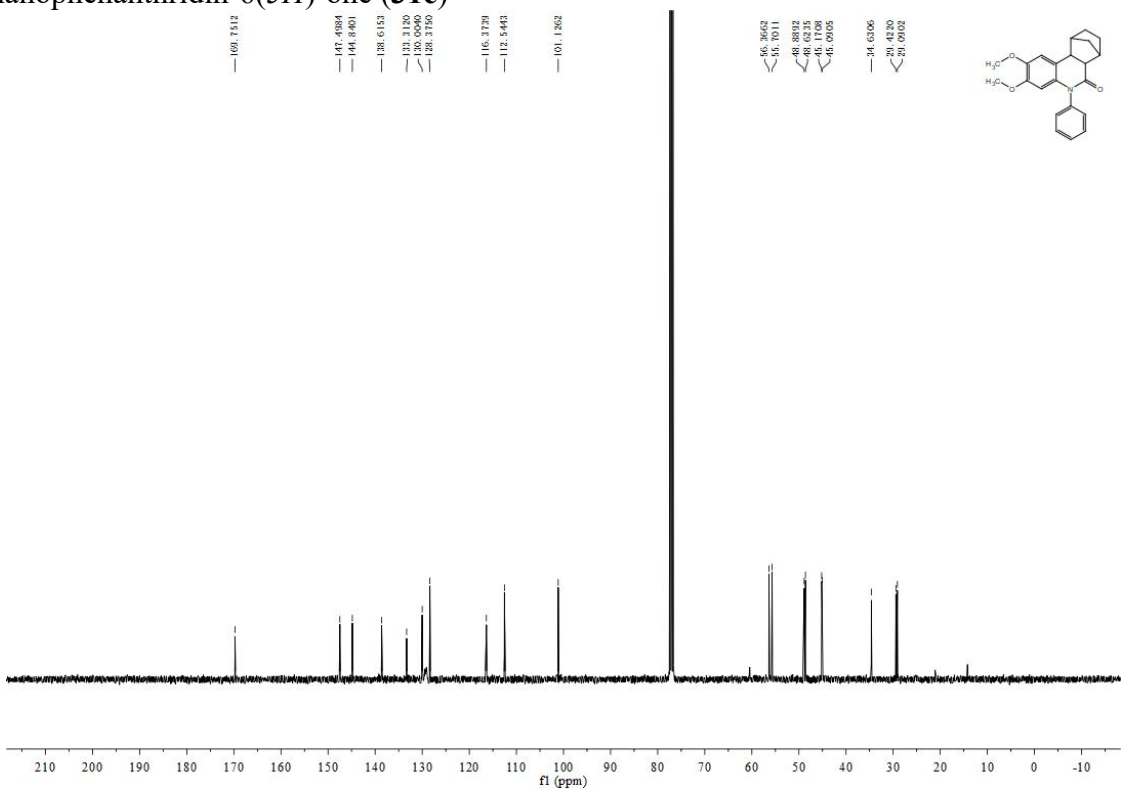
^{13}C NMR spectrum of 3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**30c**)



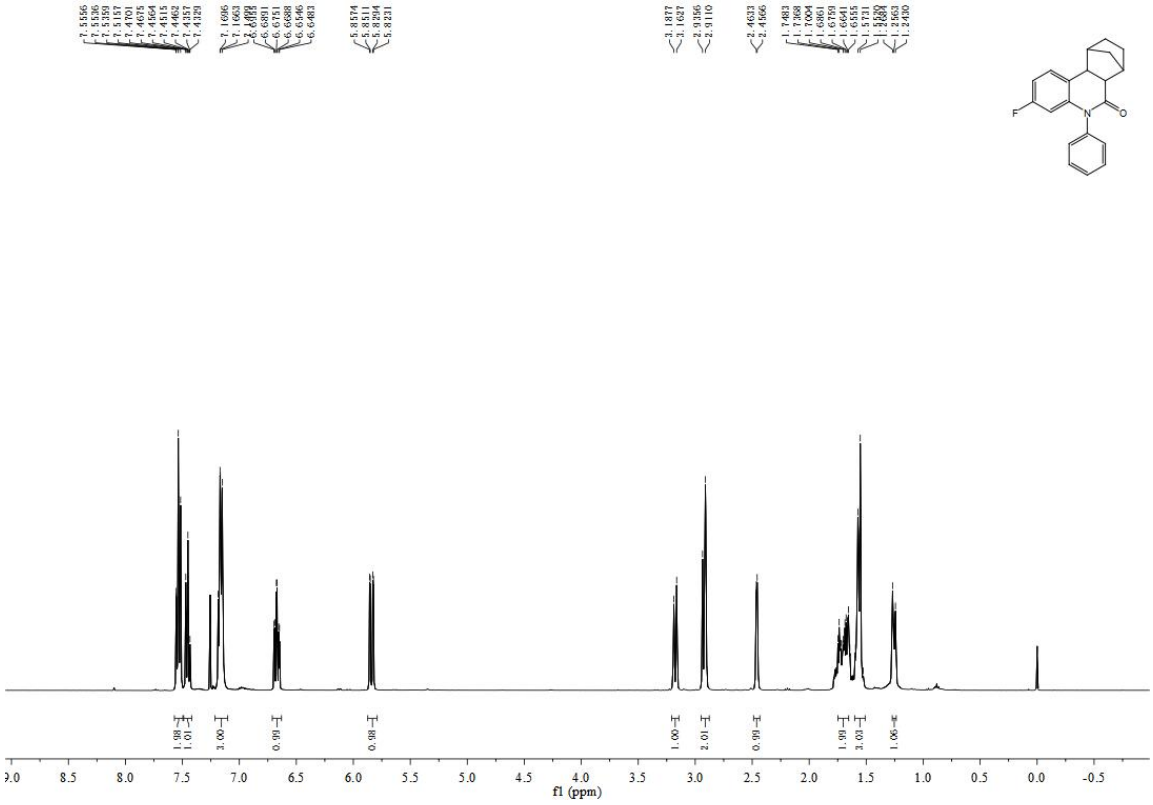
^{1}H NMR spectrum of 2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**31c**)



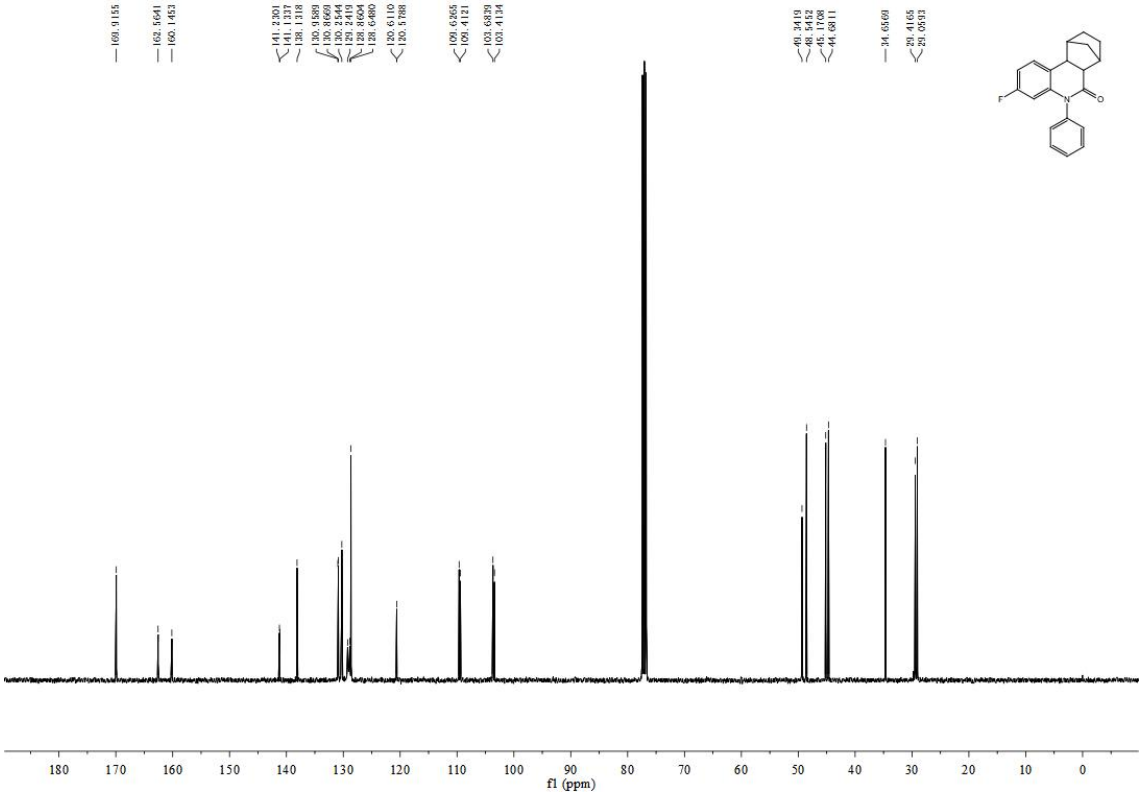
^{13}C NMR spectrum of 2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**31c**)



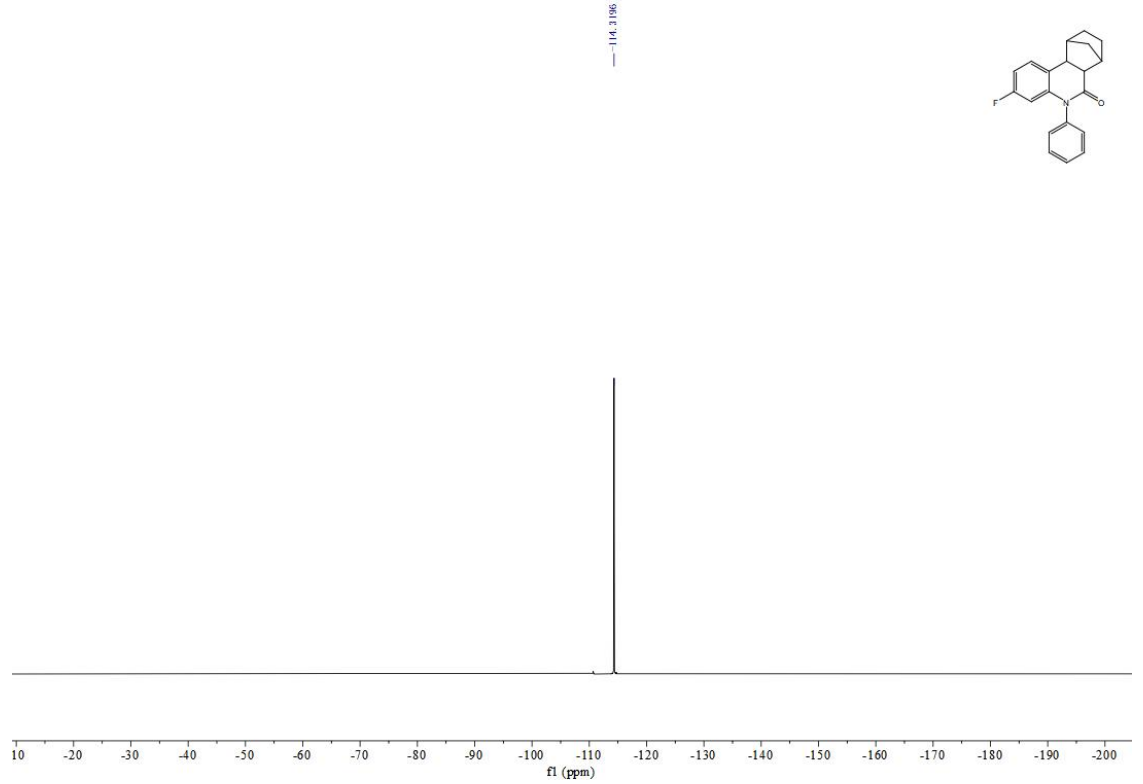
^{1}H NMR spectrum of 3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**32c**)



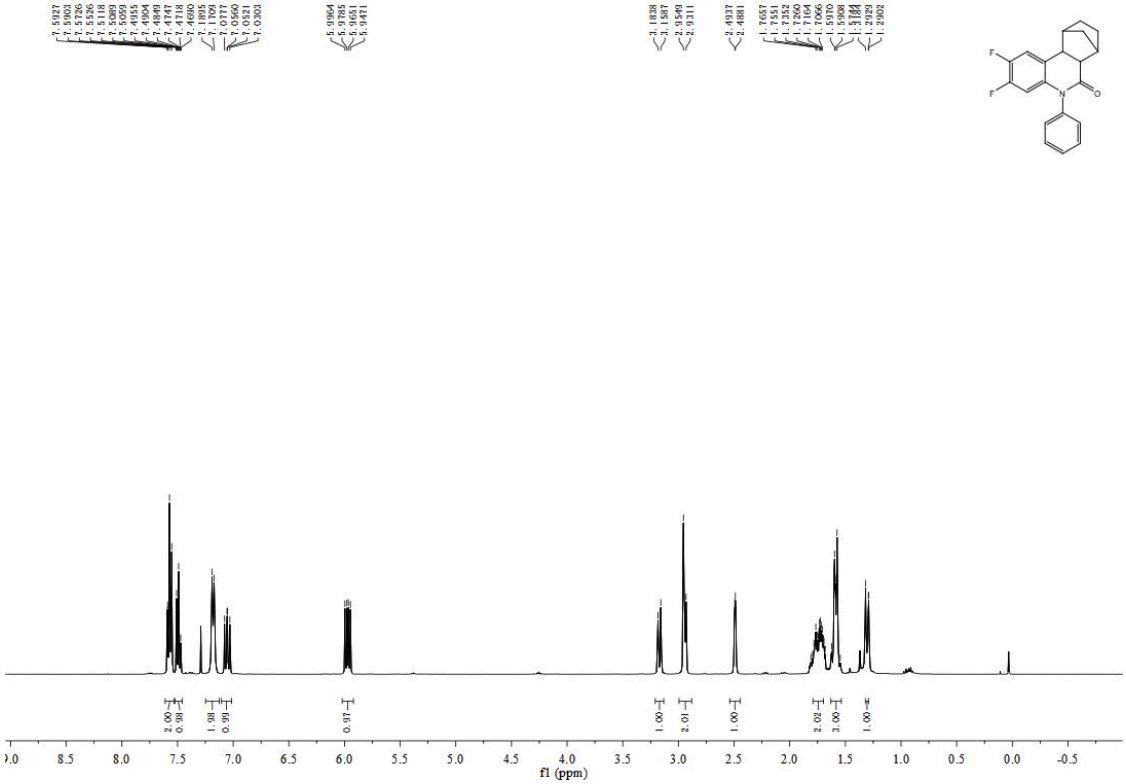
^{13}C NMR spectrum of 3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**32c**)



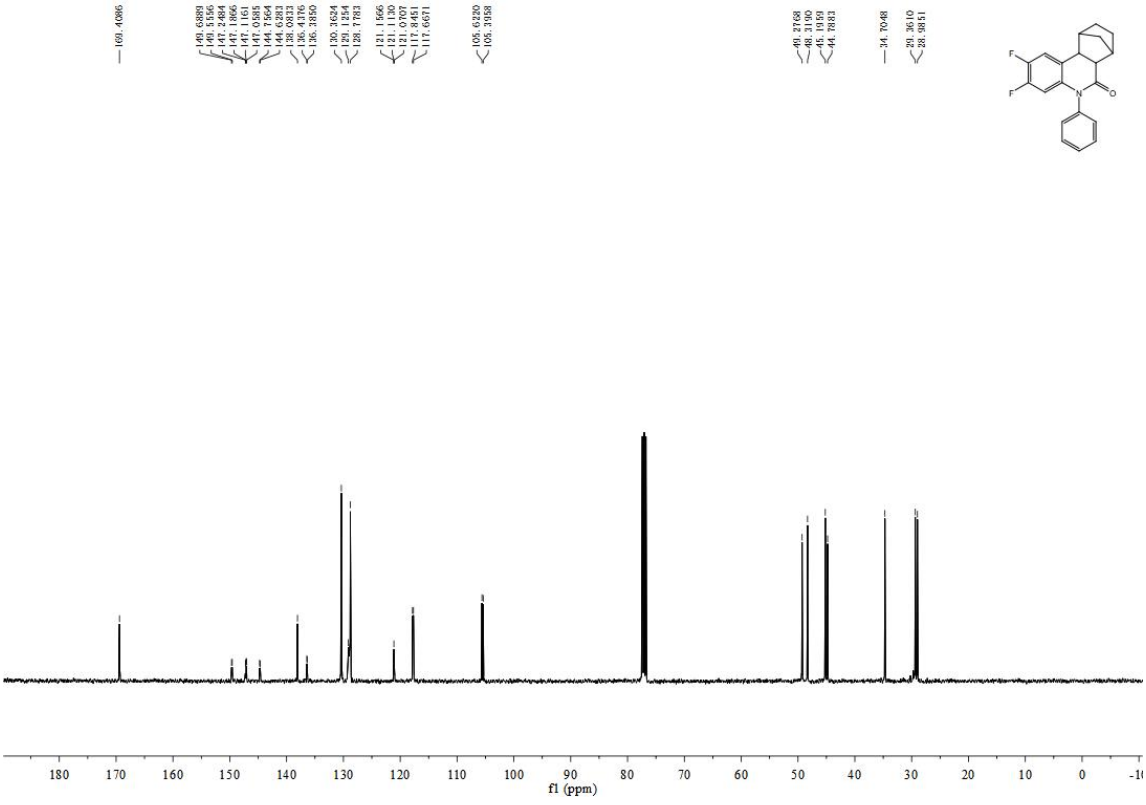
^{19}F NMR spectrum of 3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**32c**)



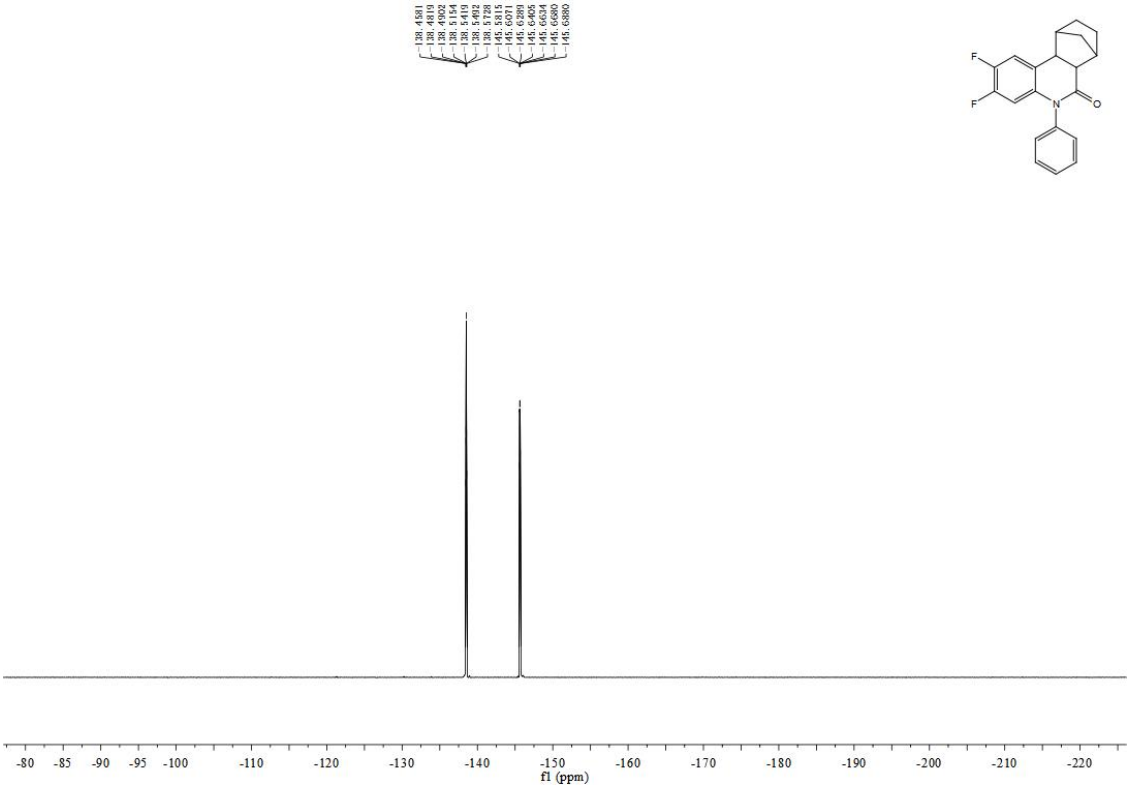
^{1}H NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**33c**)



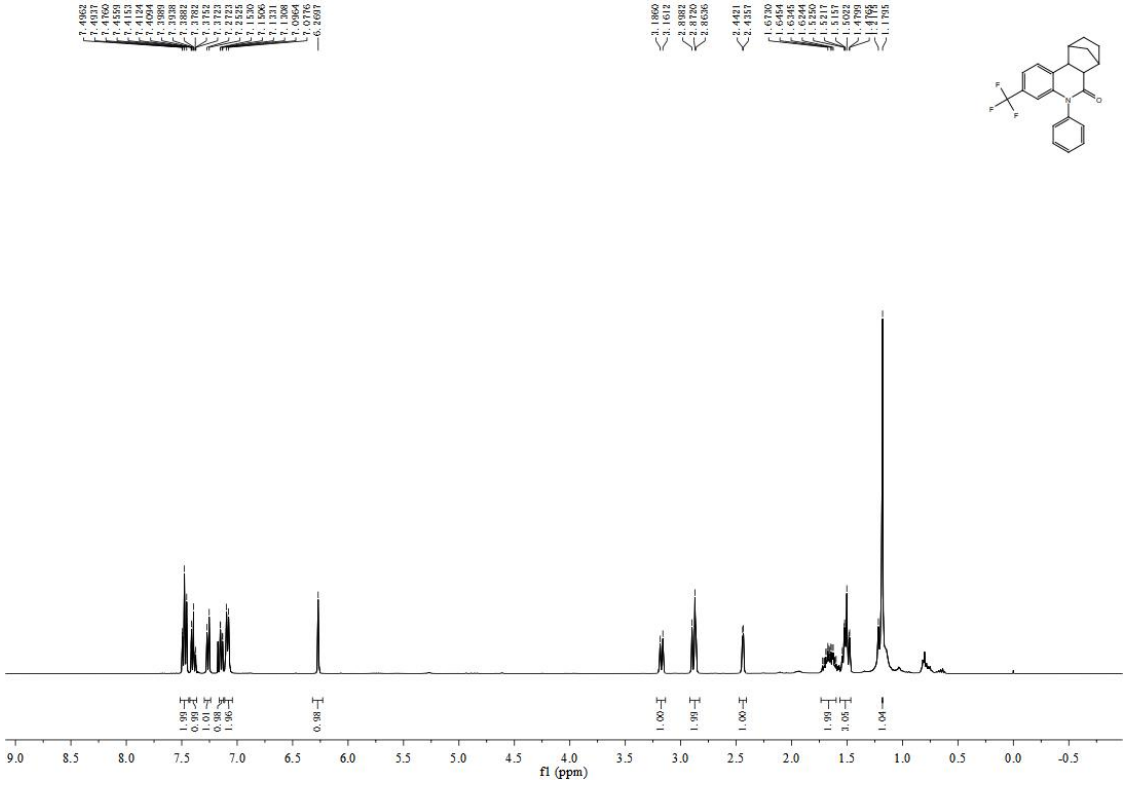
^{13}C NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**33c**)



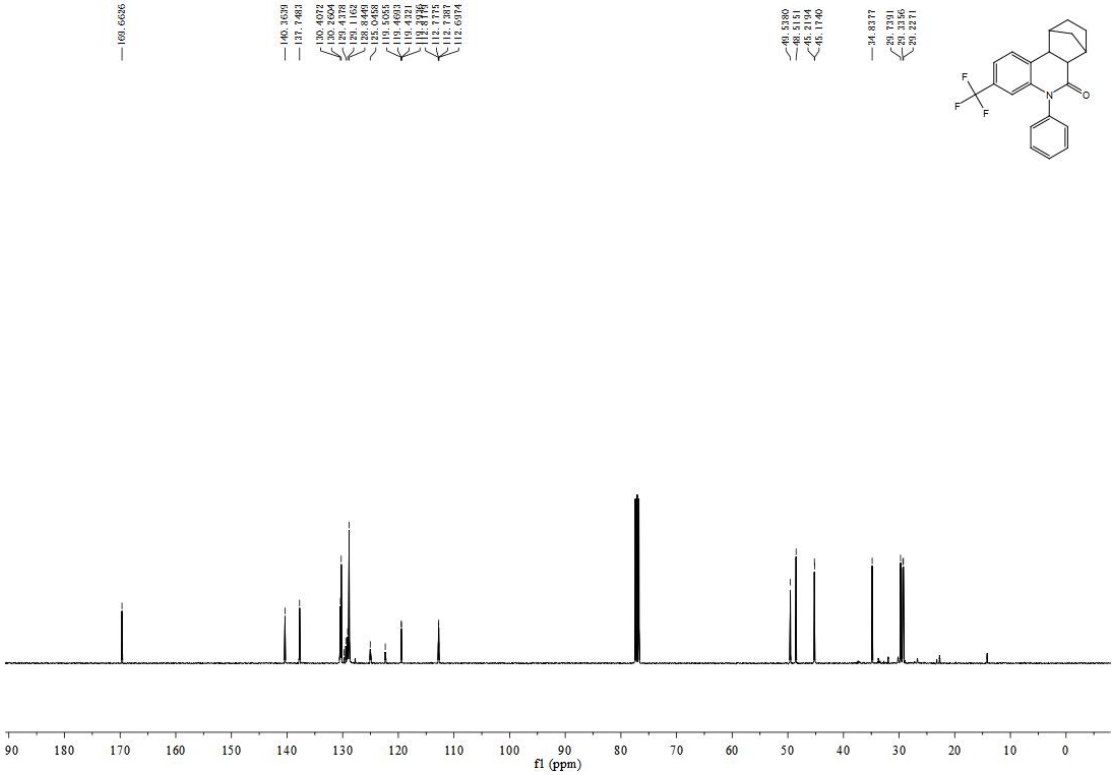
^{19}F NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**33c**)



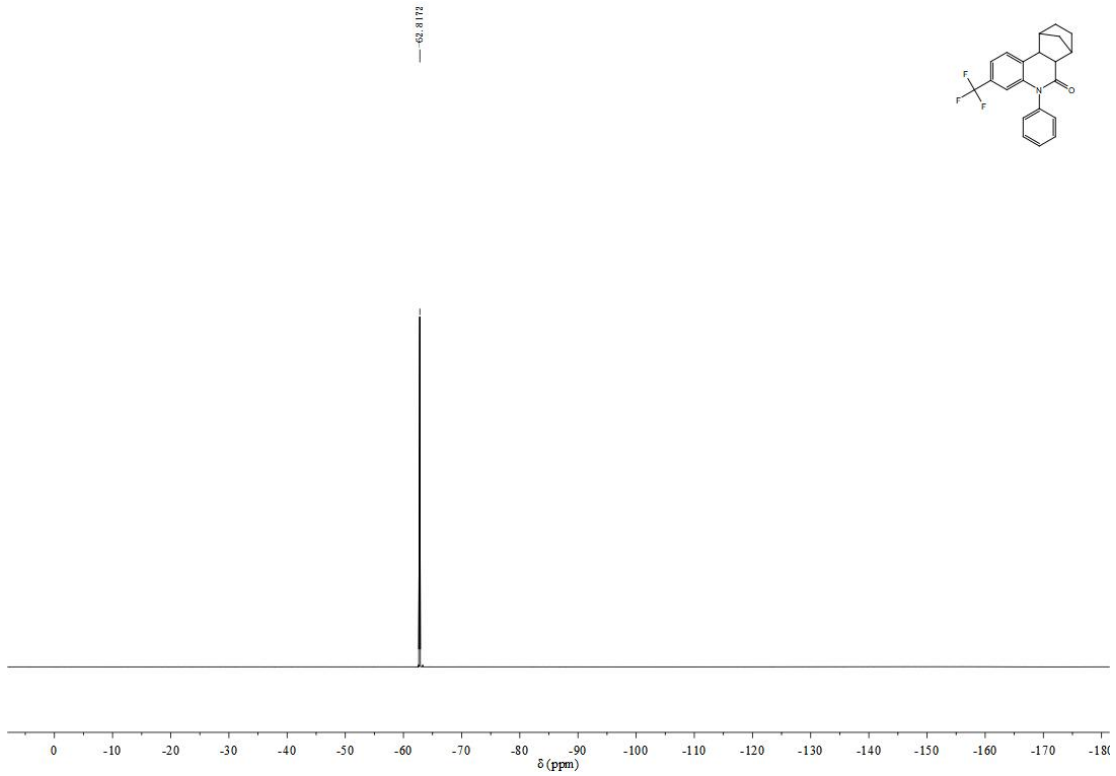
^{1}H NMR spectrum of 5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**34c**)



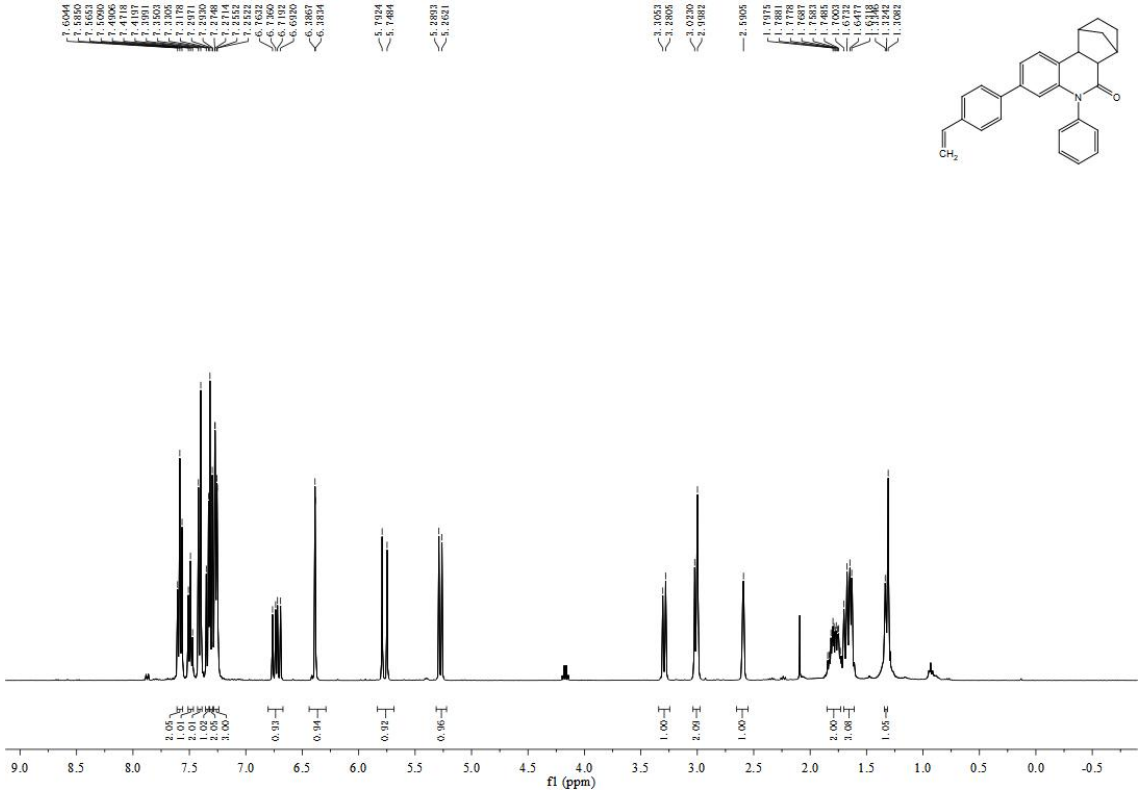
^{13}C NMR spectrum of 5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**34c**)



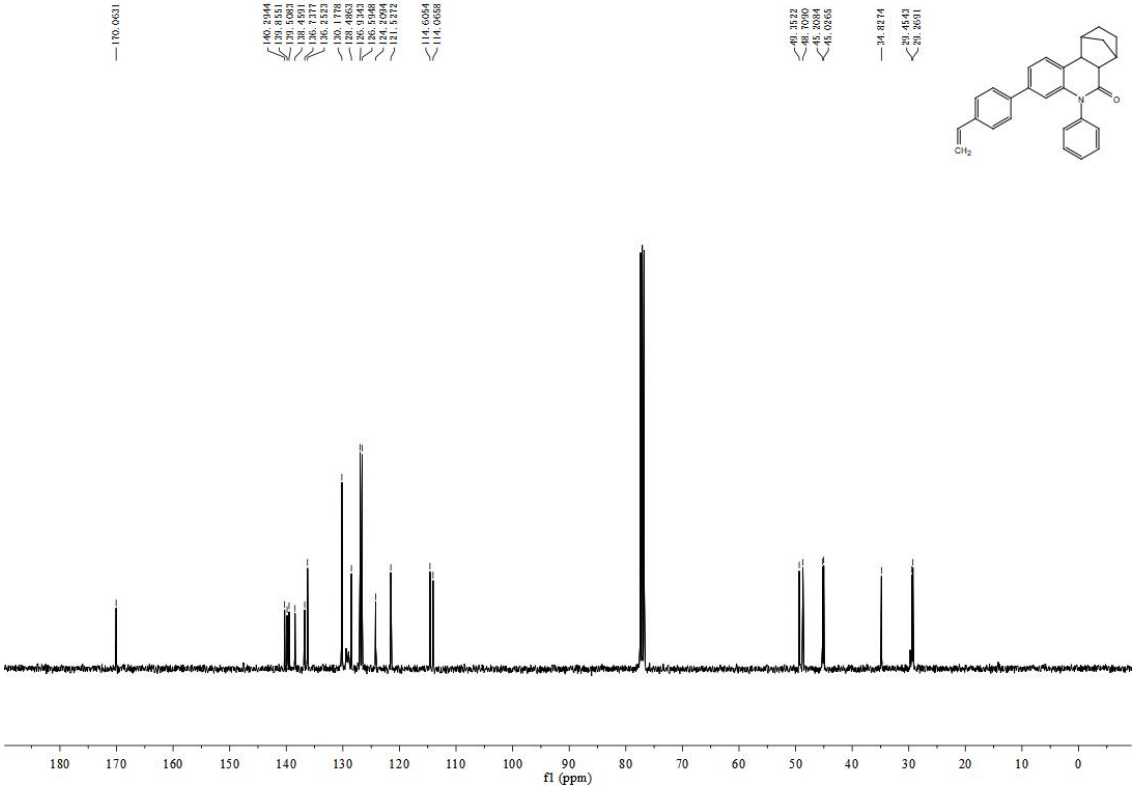
^{19}F NMR spectrum of 5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**34c**)



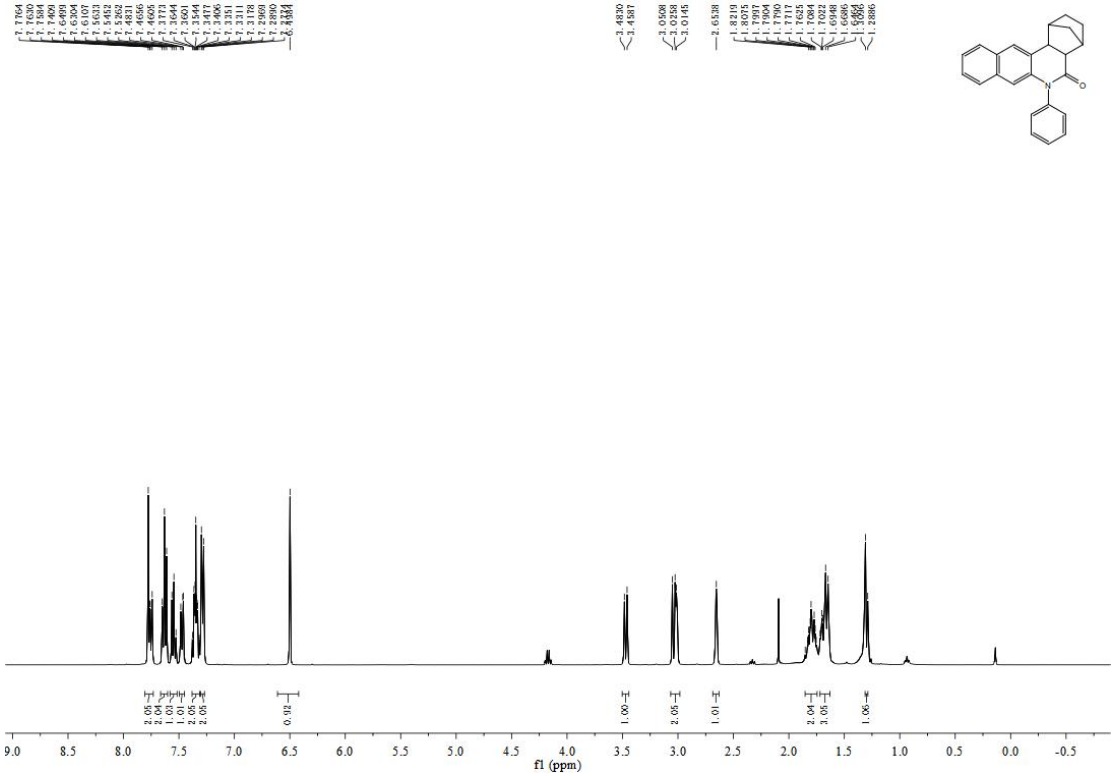
^{1}H NMR spectrum of 5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**35c**)



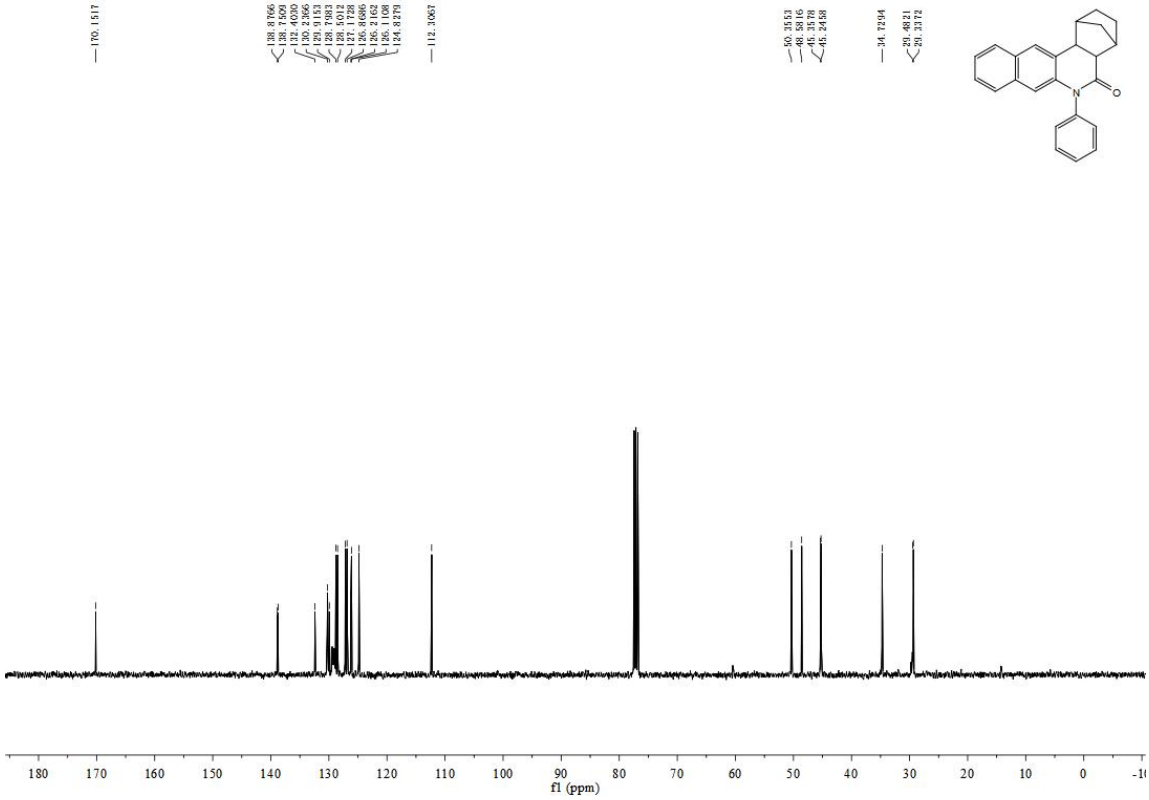
^{13}C NMR spectrum of 5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**35c**)



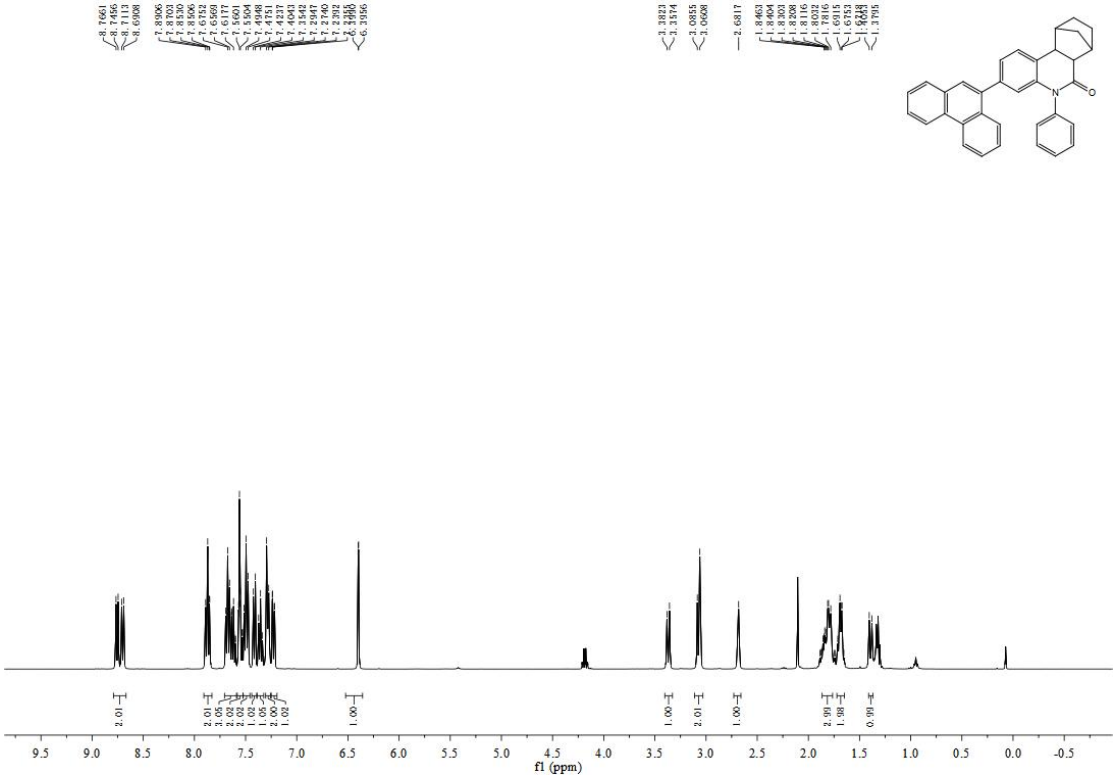
^{1}H NMR spectrum of 6-phenyl-2,3,4,4a,6,12b-hexahydro-1,4-methanobenzo[b]phenanthridin-5(*1H*)-one (**36c**)



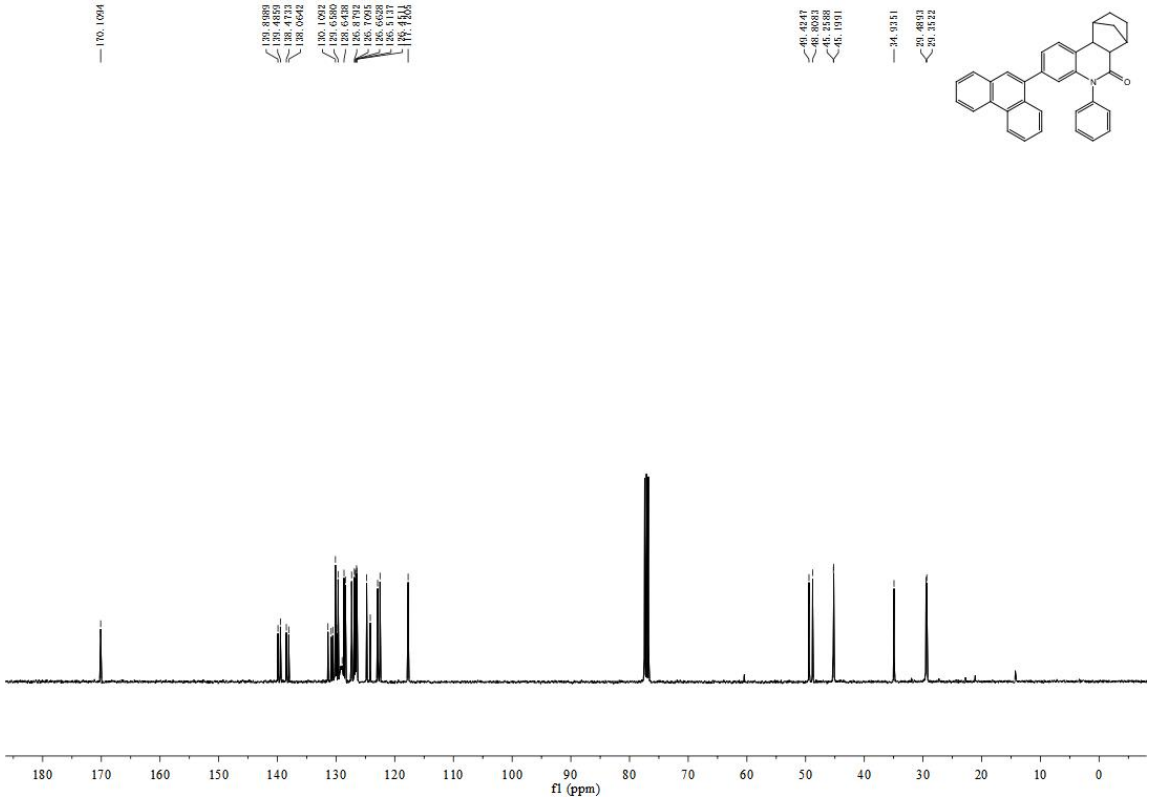
^{13}C NMR spectrum of 6-phenyl-2,3,4,4a,6,12b-hexahydro-1,4-methanobenzo[b]phenanthridin-5(*1H*)-one (**36c**)



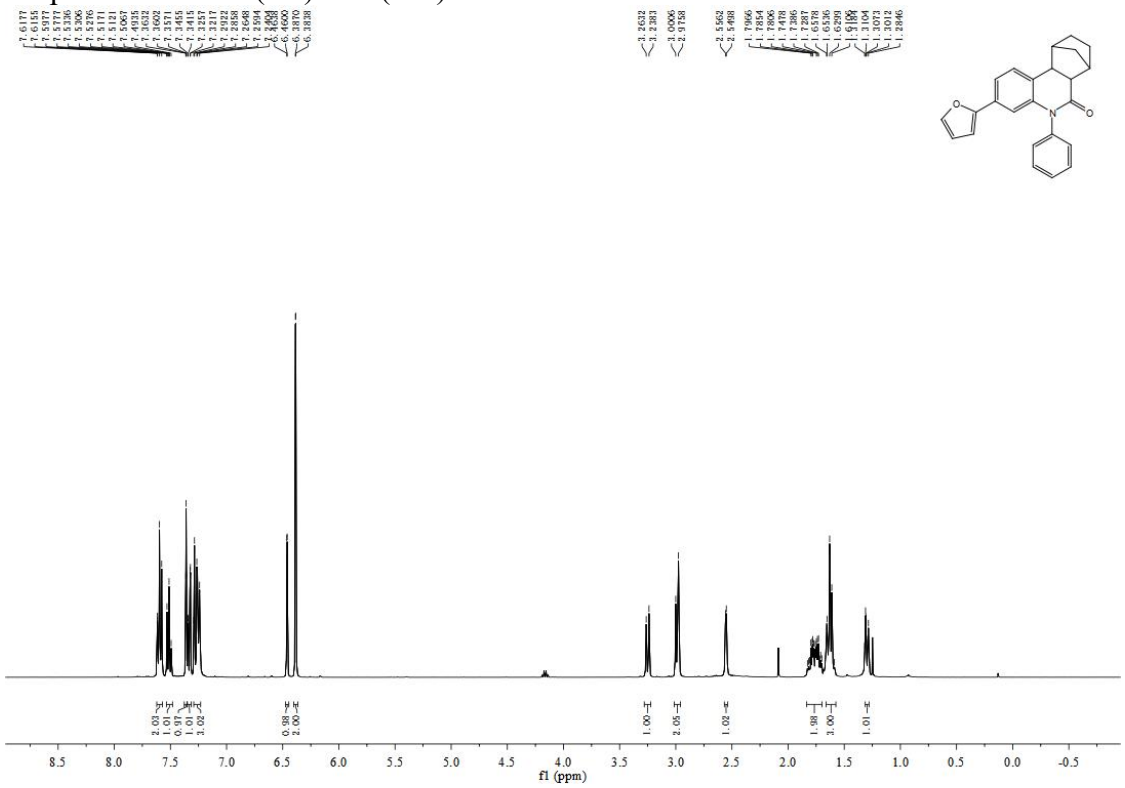
^{1}H NMR spectrum of 3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**37c**)



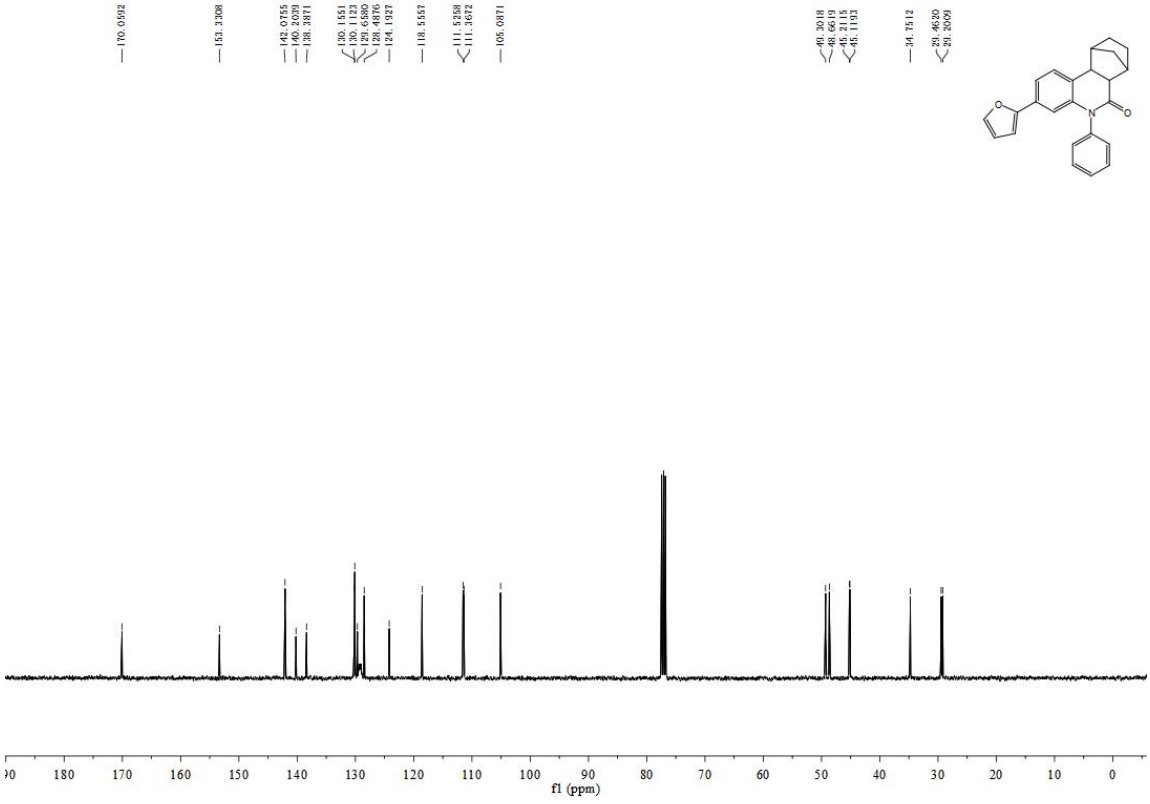
^{13}C NMR spectrum of 3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**37c**)



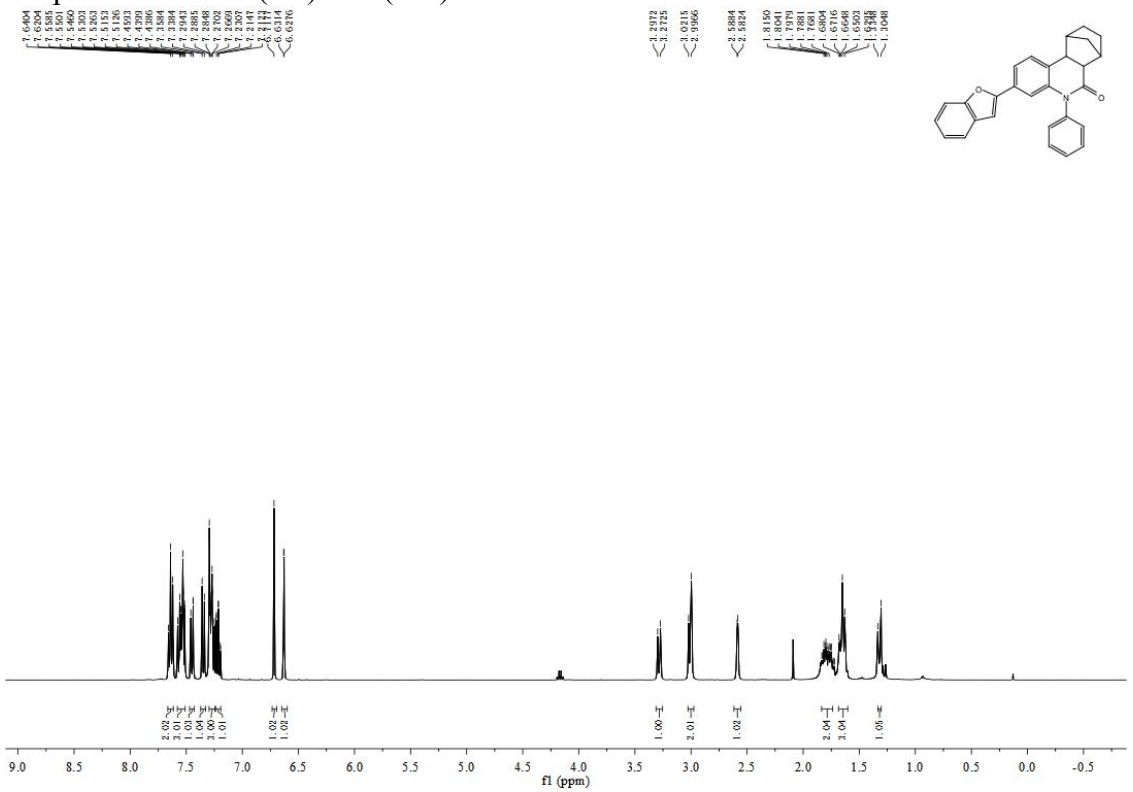
^{1}H NMR spectrum of 3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**38c**)



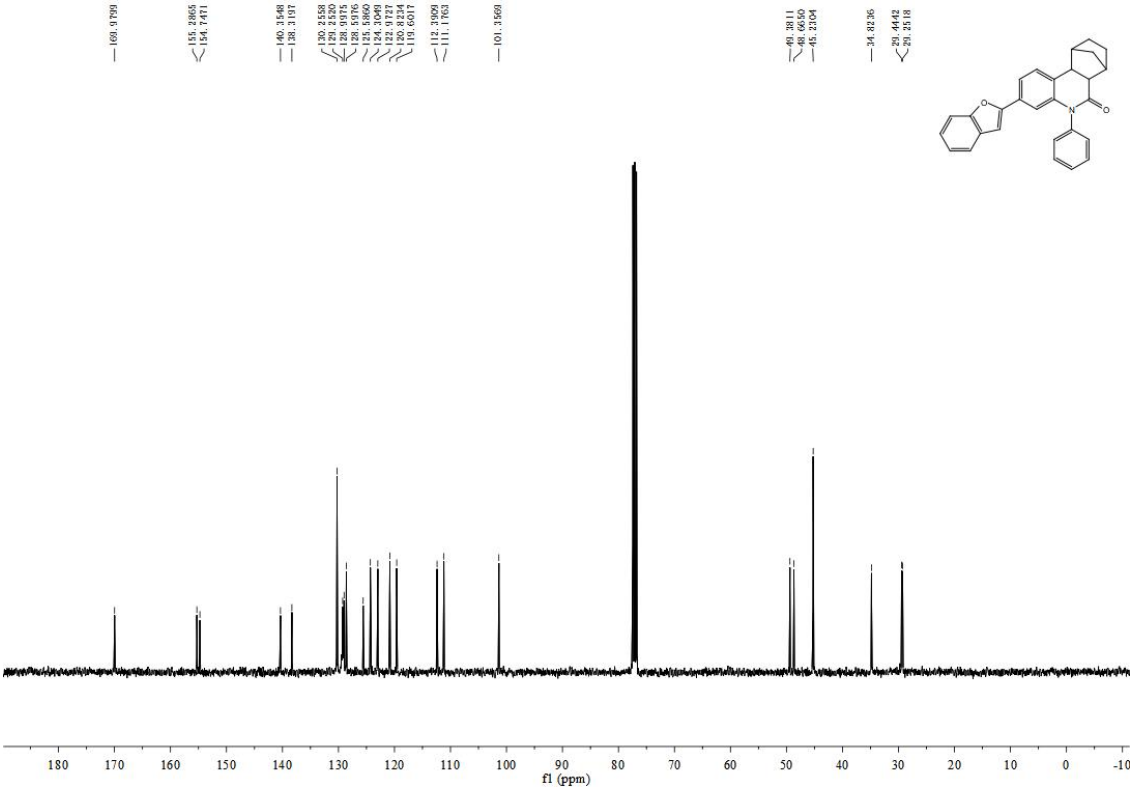
^{13}C NMR spectrum of 3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**38c**)



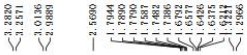
^{1}H NMR spectrum of 3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**39c**)

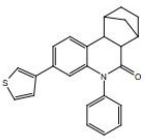


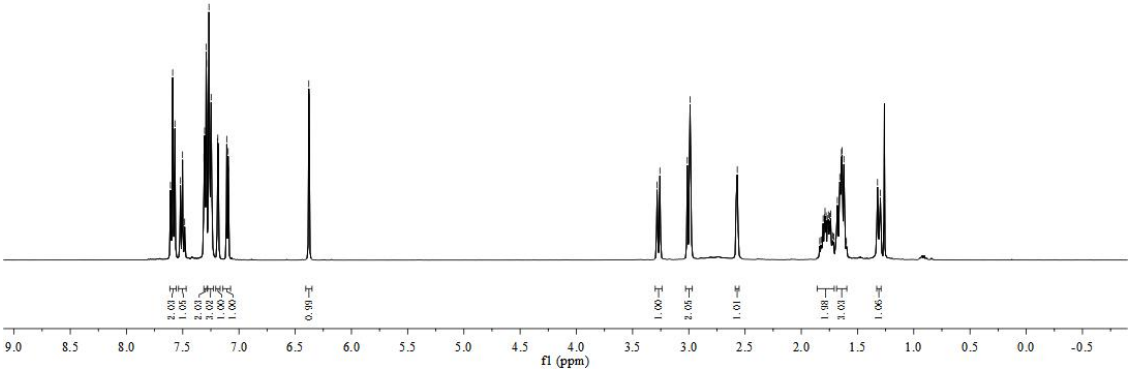
^{13}C NMR spectrum of 3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**39c**)



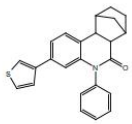
^{1}H NMR spectrum of 5-phenyl-3-(thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**40c**)

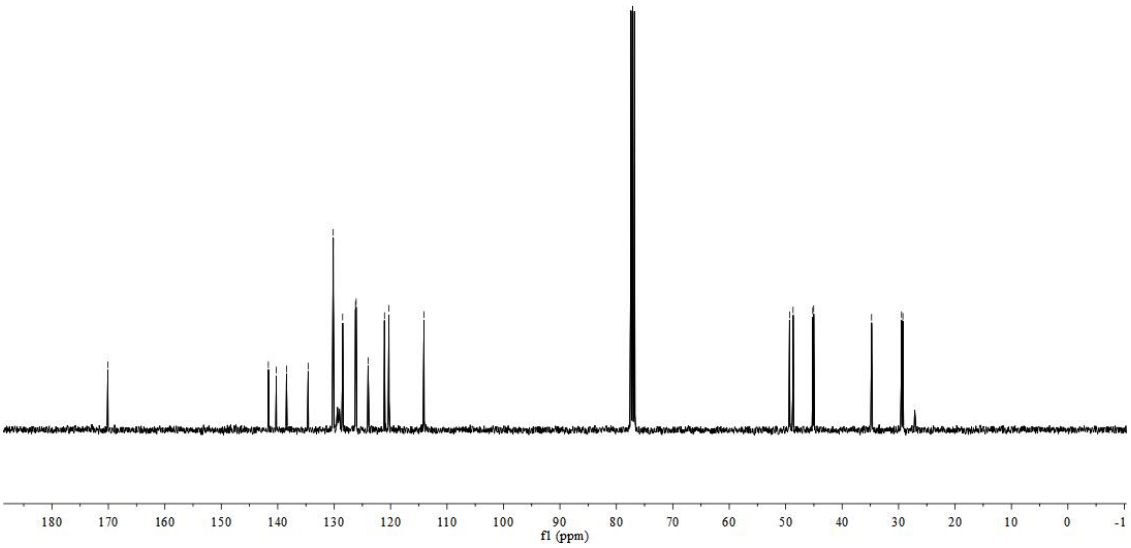




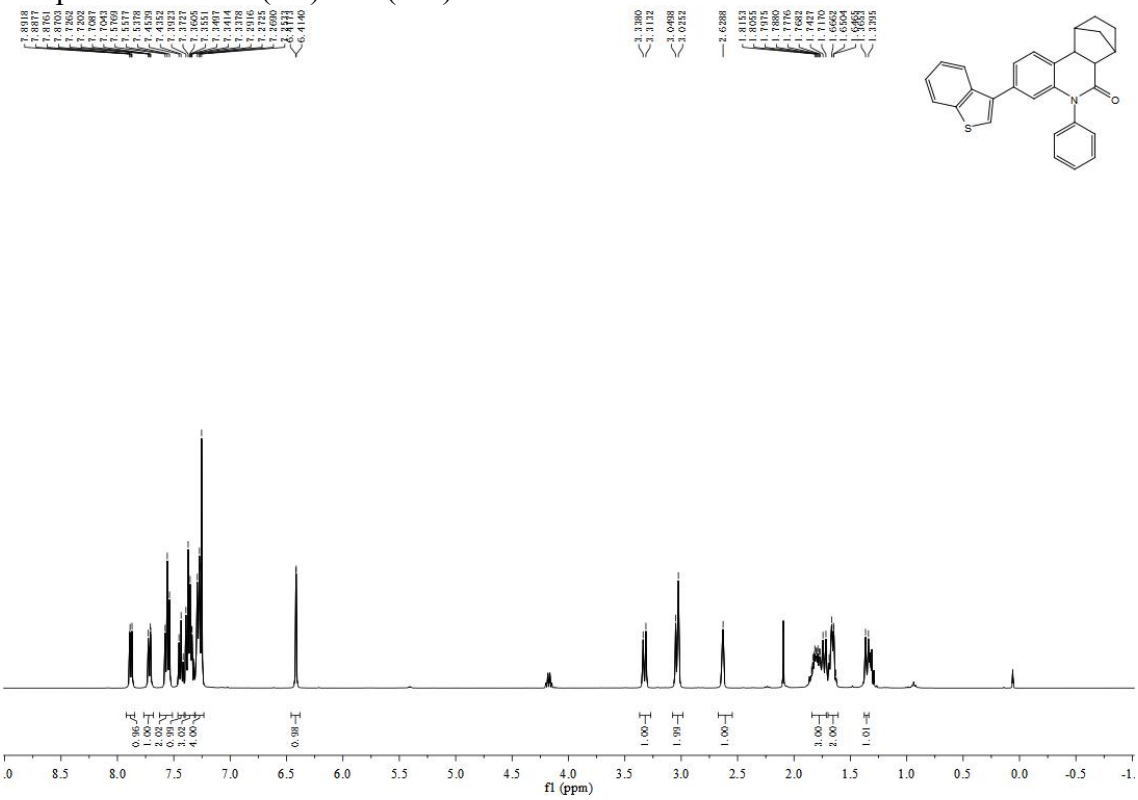


^{13}C NMR spectrum of 5-phenyl-3-(thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**40c**)

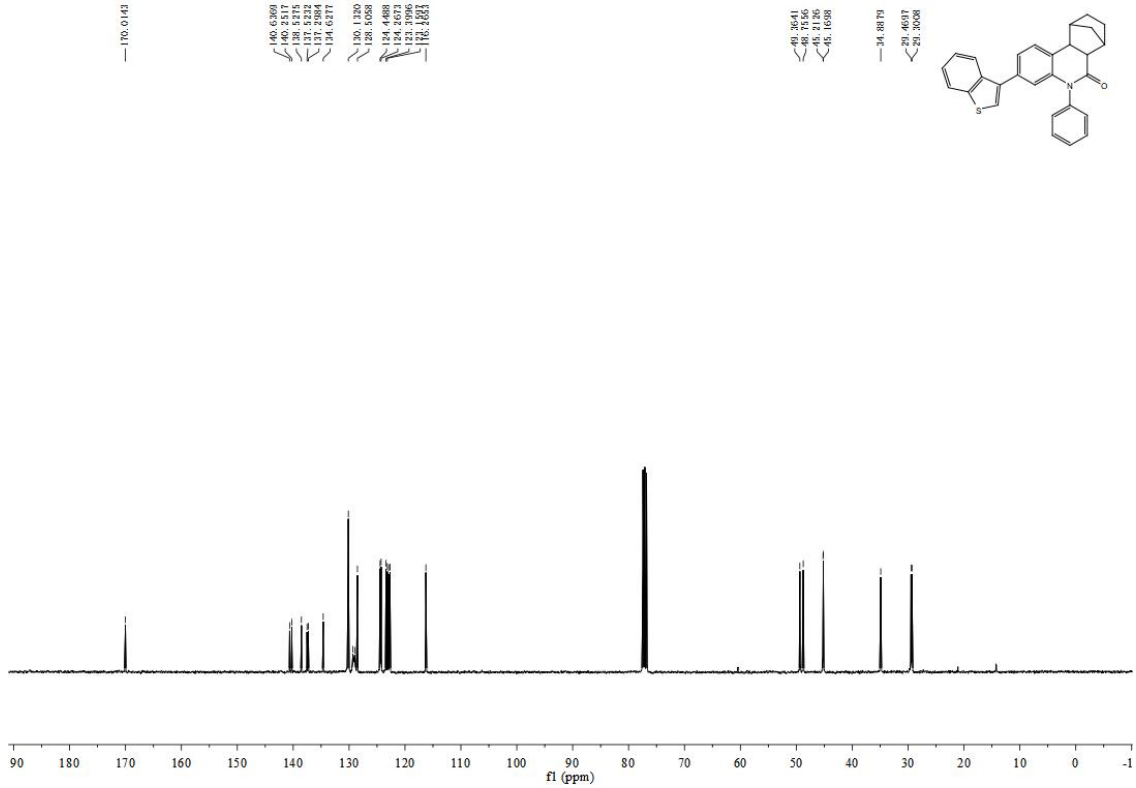




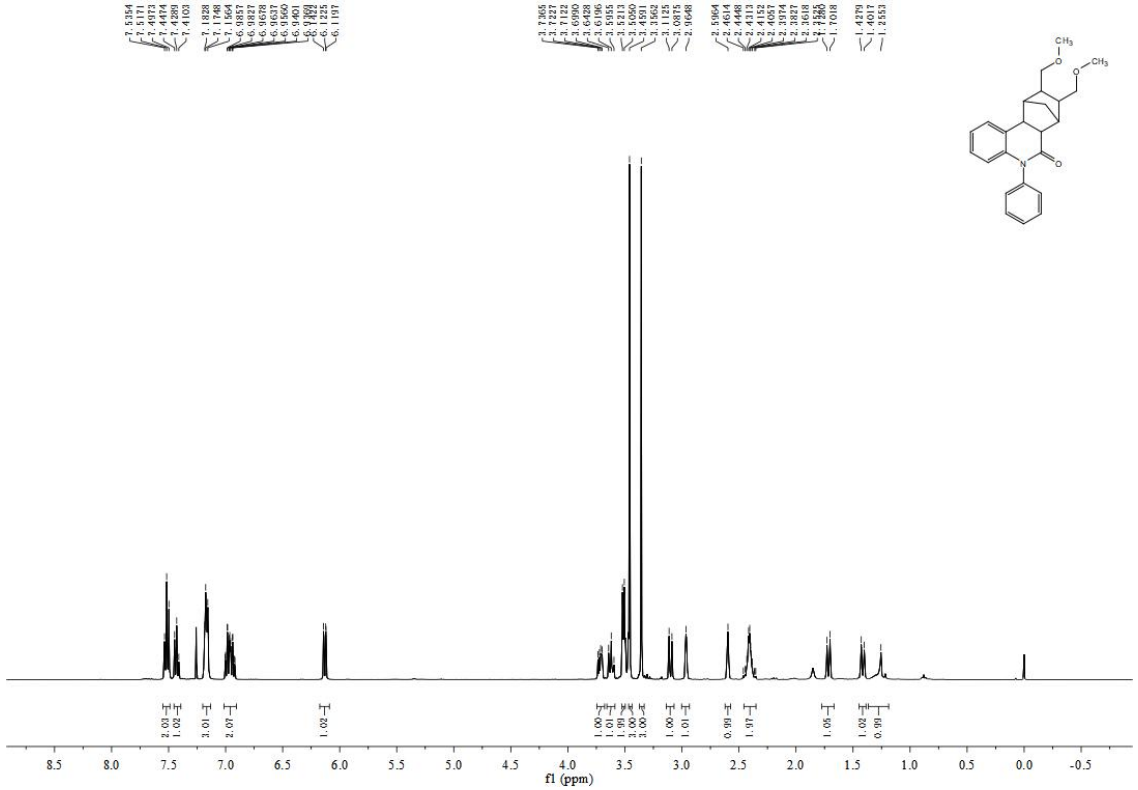
^{1}H NMR spectrum of 3-(benzo[*b*]thiophen-3-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**41c**)



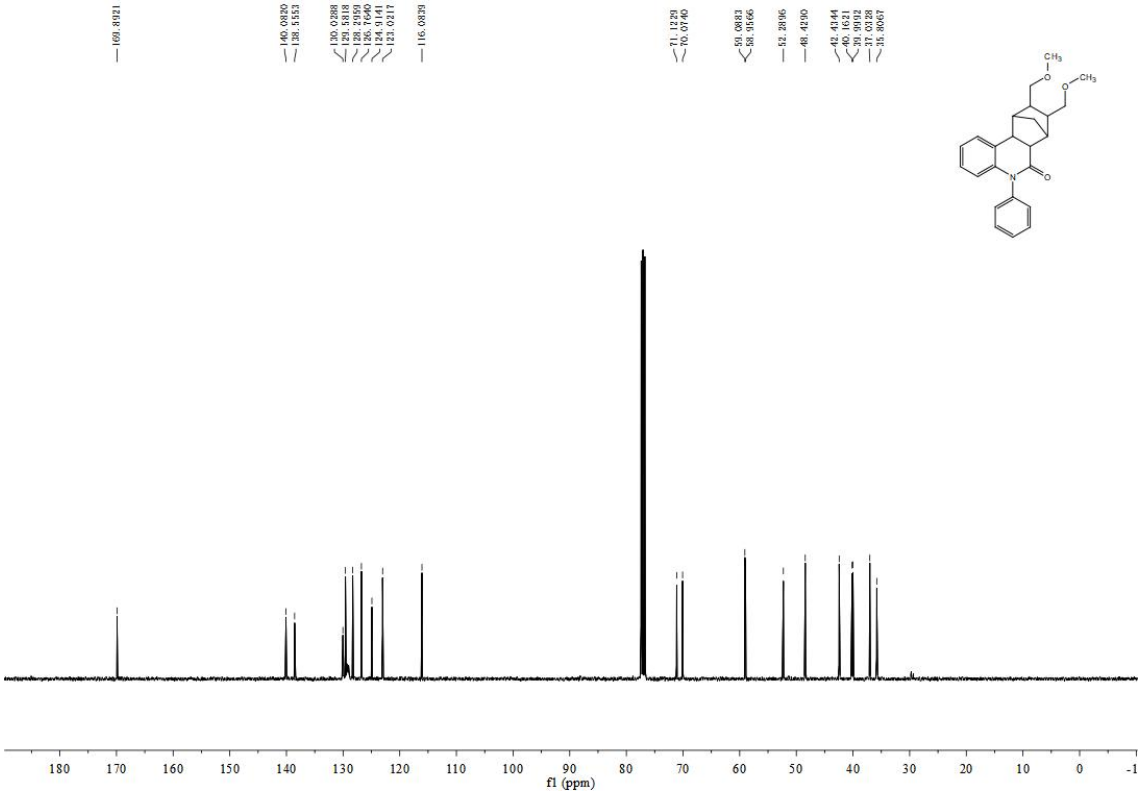
^{13}C NMR spectrum of 3-(benzo[*b*]thiophen-3-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**41c**)



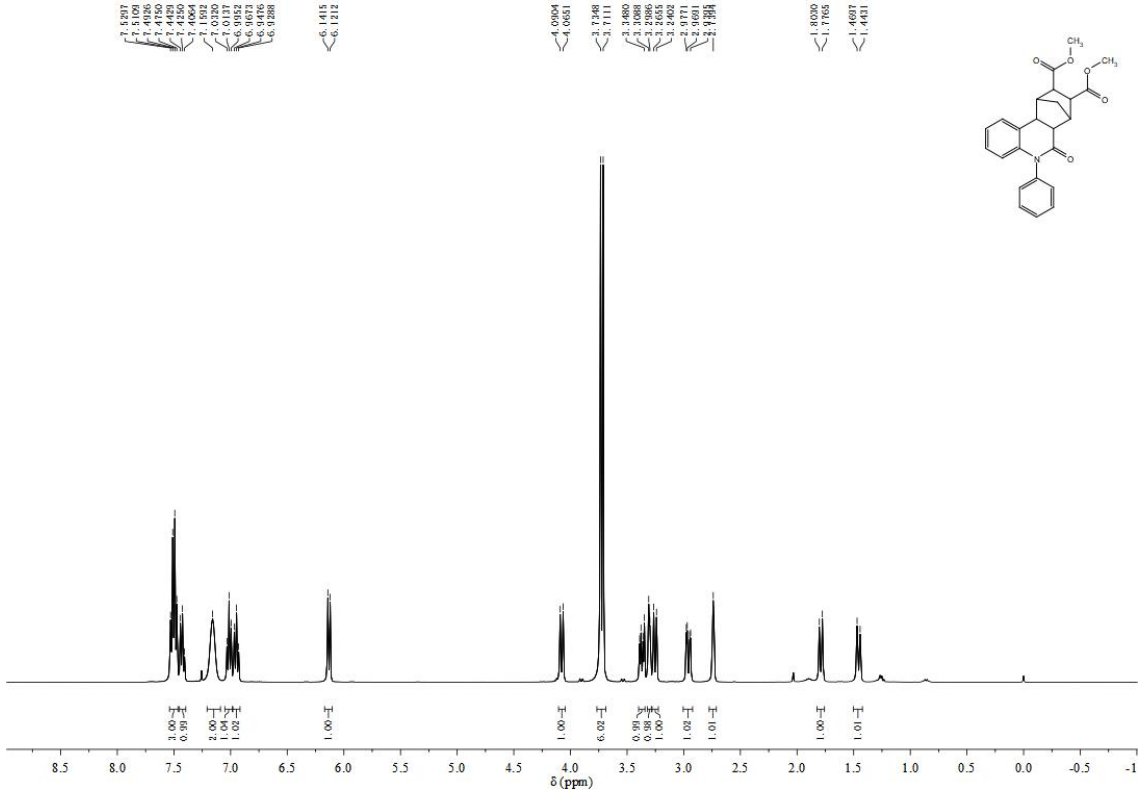
^{1}H NMR spectrum of 8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**42c**)



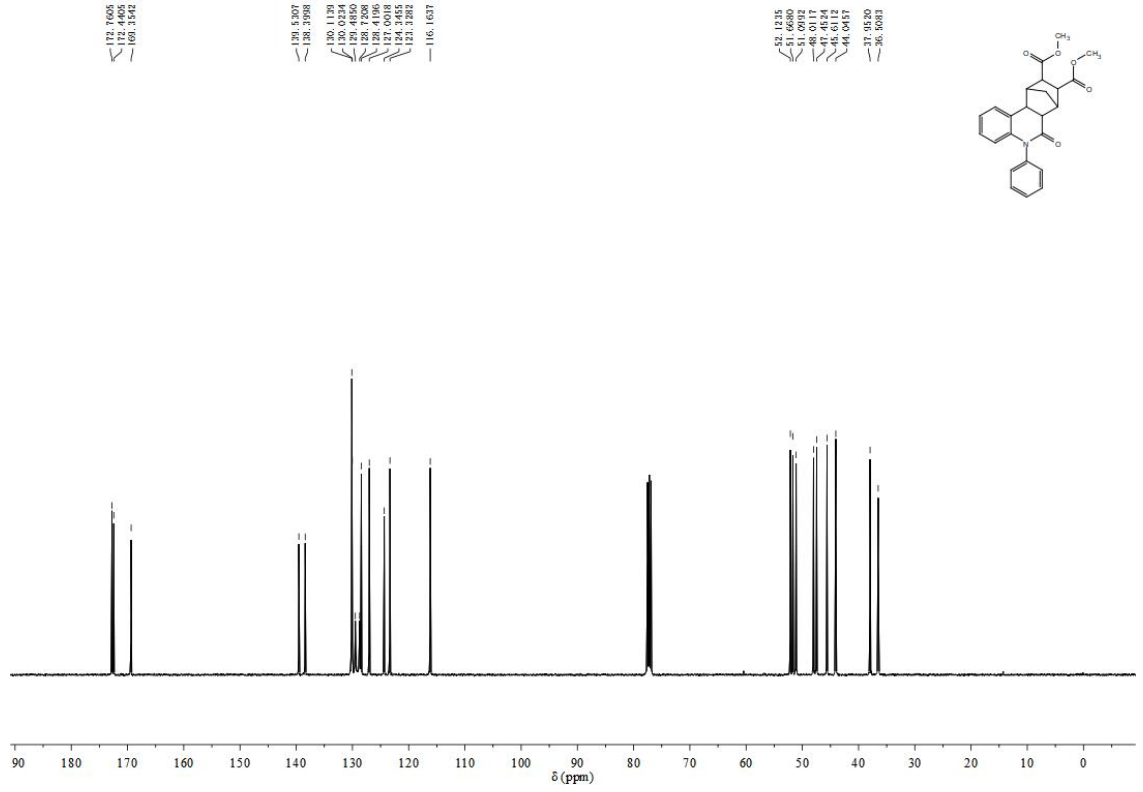
^{13}C NMR spectrum of 8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**42c**)



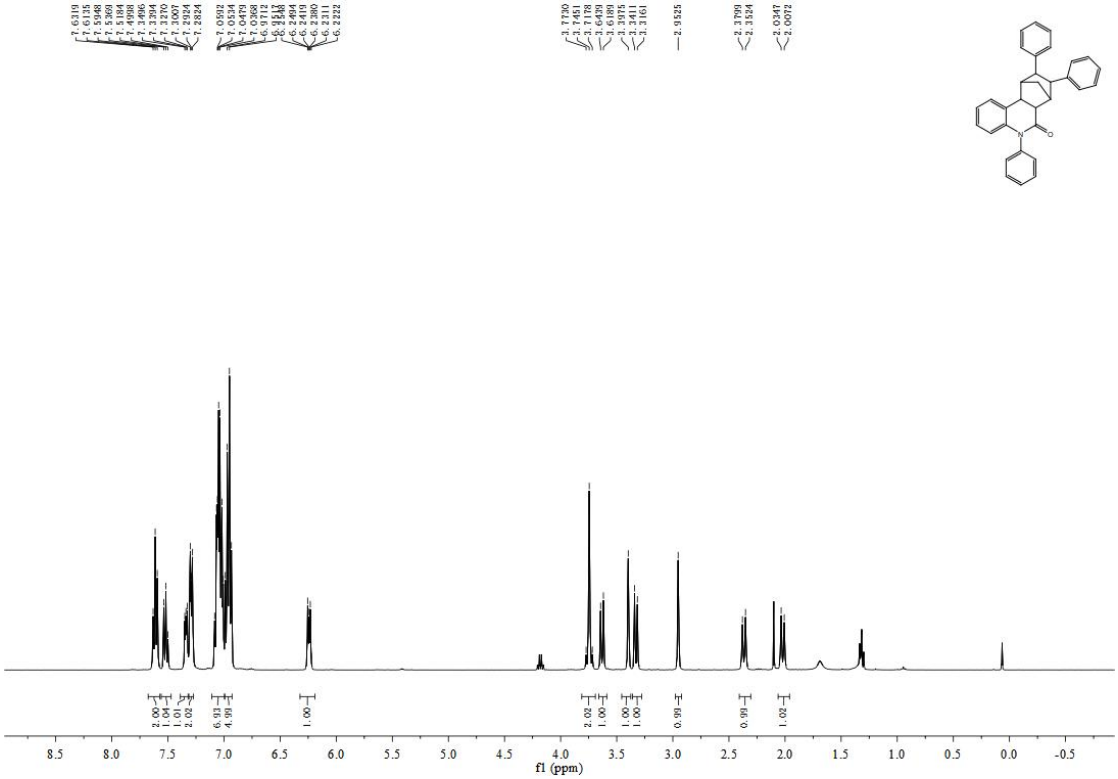
^{1}H NMR spectrum of dimethyl 6-oxo-5-phenyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydro-7, 10-methanophenanthridine-8, 9-dicarboxylate (**43c**)



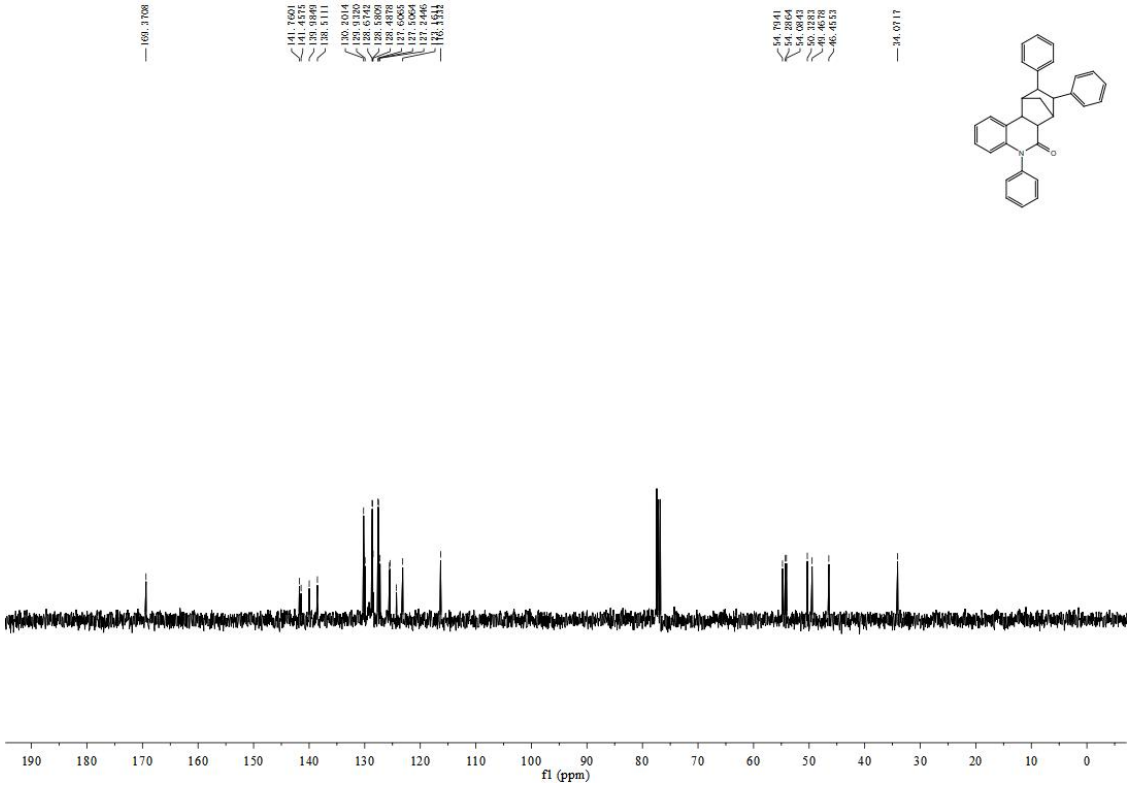
^{13}C NMR spectrum of dimethyl 6-oxo-5-phenyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydro-7, 10-methanophenanthridine-8, 9-dicarboxylate (**43c**)



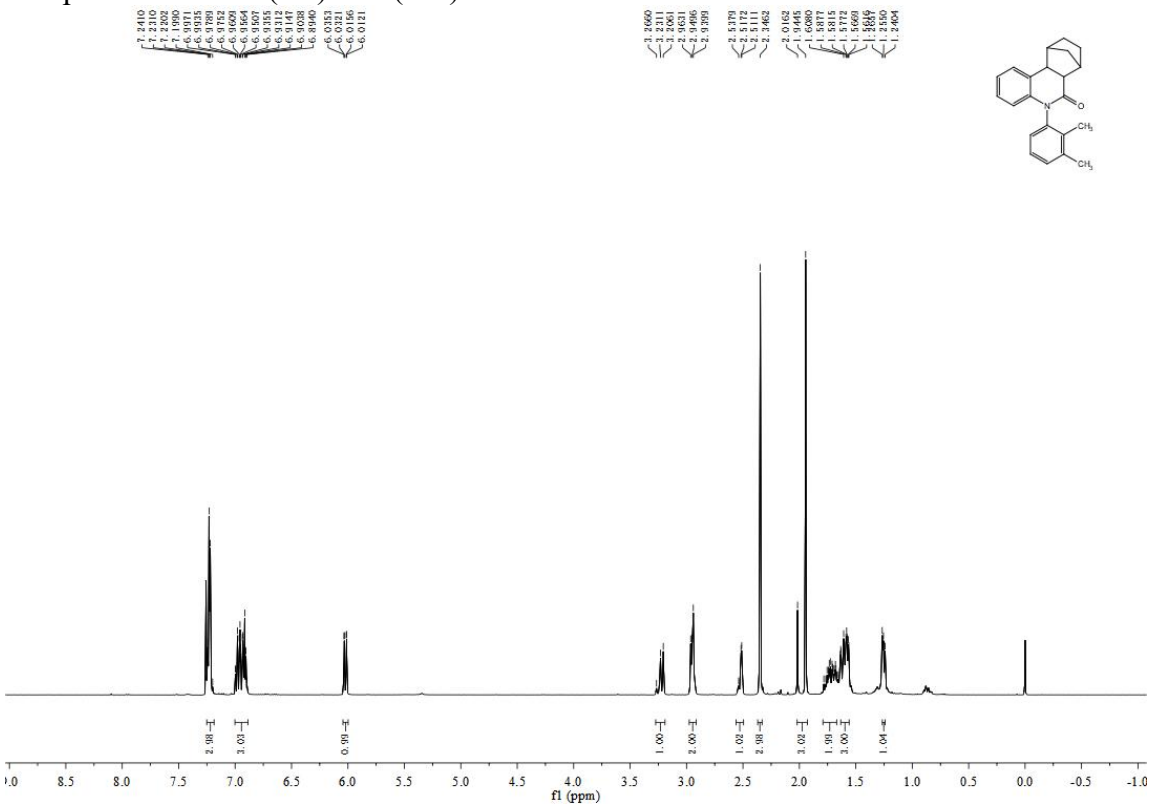
^{1}H NMR spectrum of 5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**44c**)



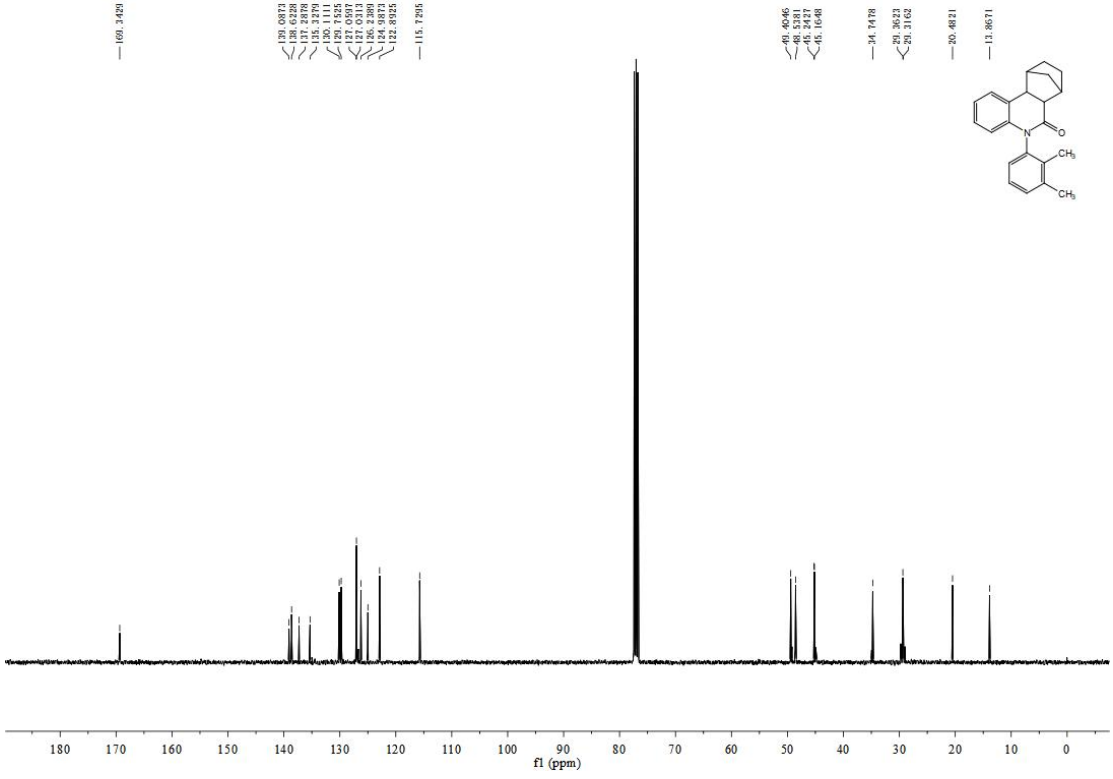
^{13}C NMR spectrum of 5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**44c**)



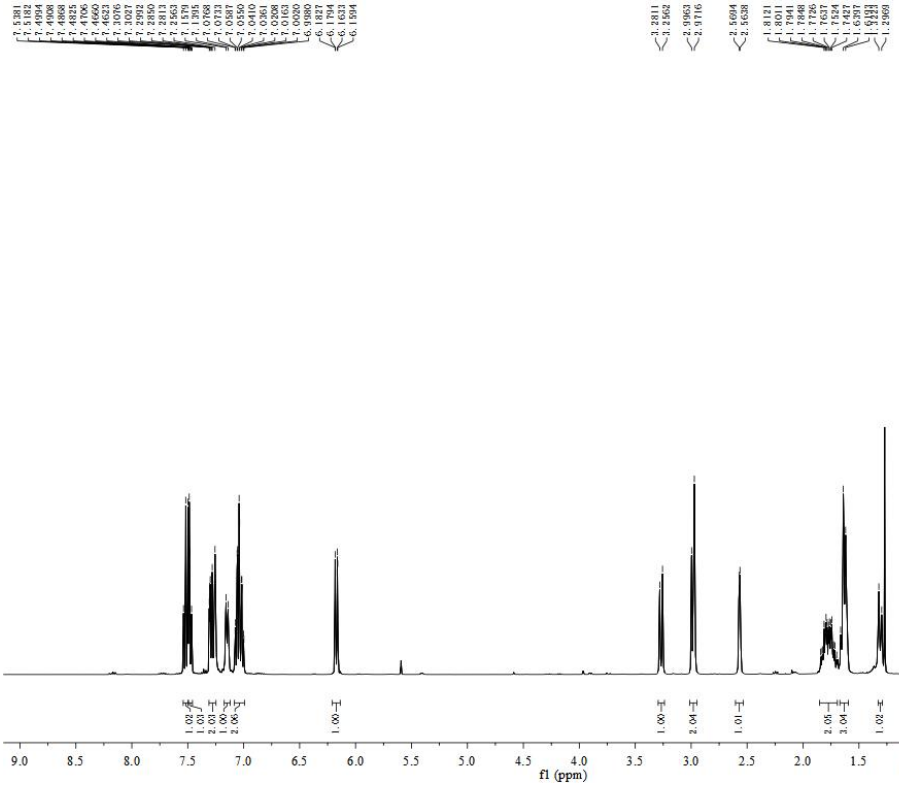
^{1}H NMR spectrum of 5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**45c**)



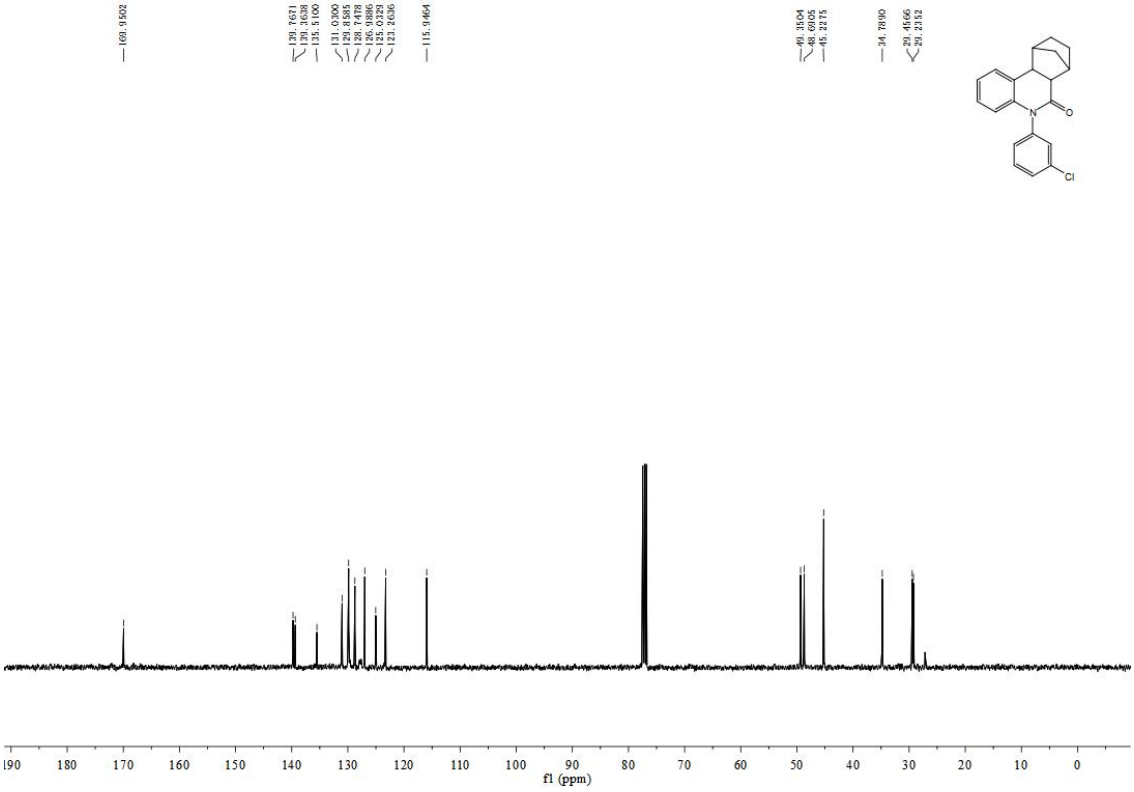
^{13}C NMR spectrum of 5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**45c**)



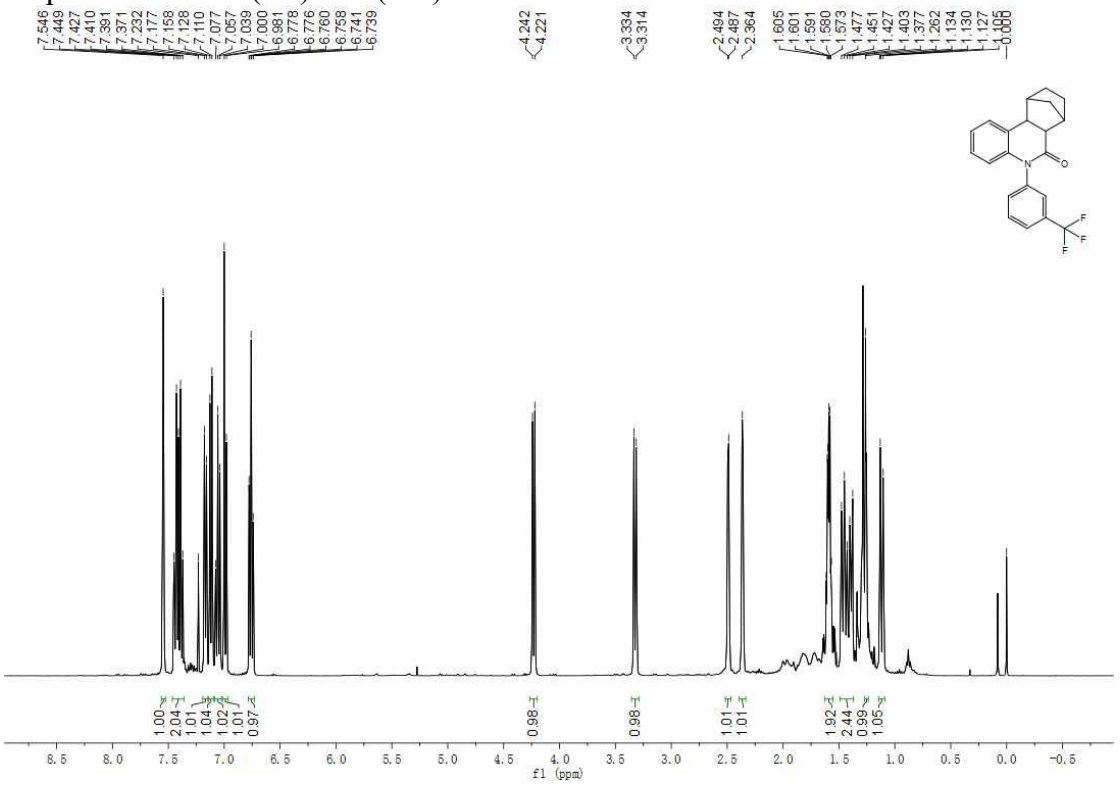
^{1}H NMR spectrum of 5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**46c**)



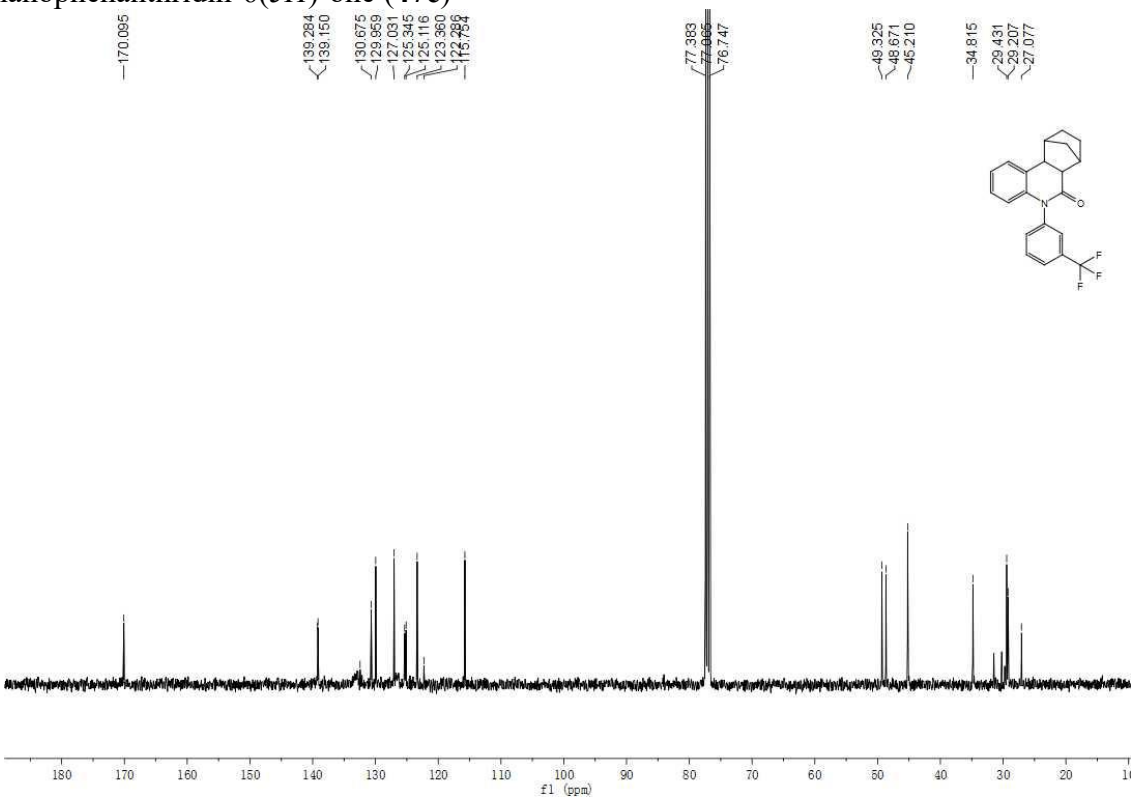
^{13}C NMR spectrum of 5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**46c**)



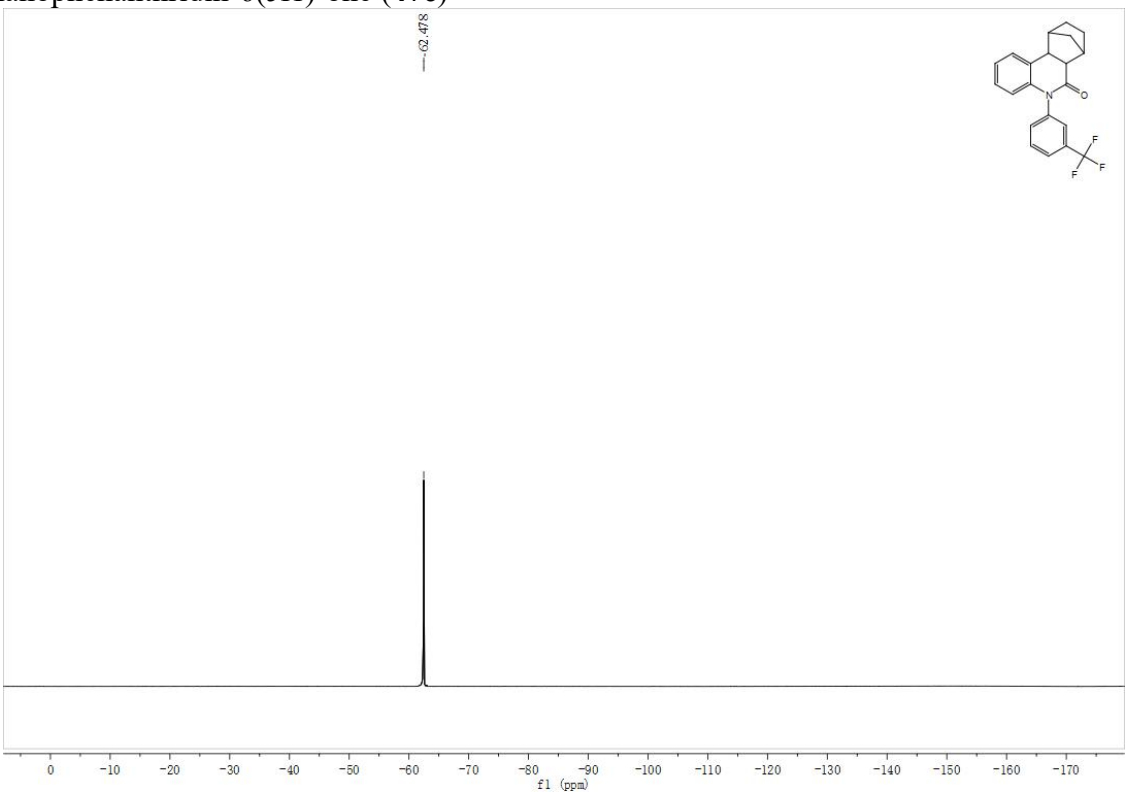
^{1}H NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**47c**)



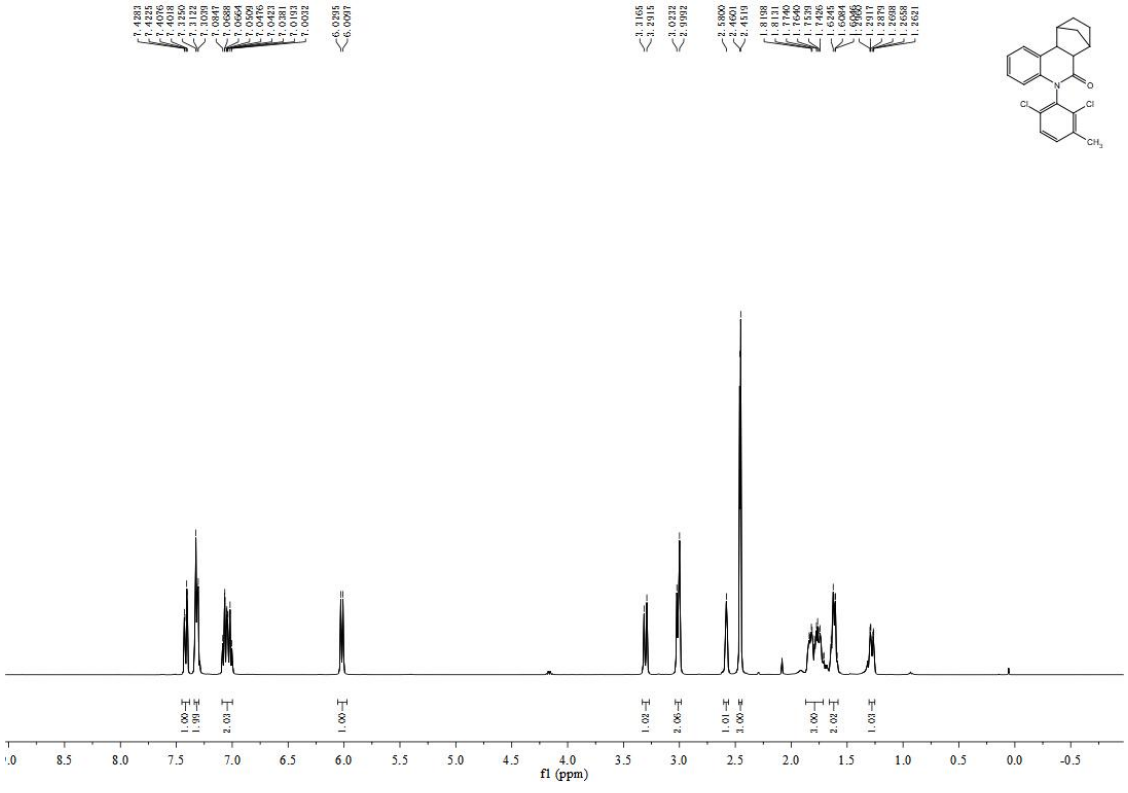
^{13}C NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**47c**)



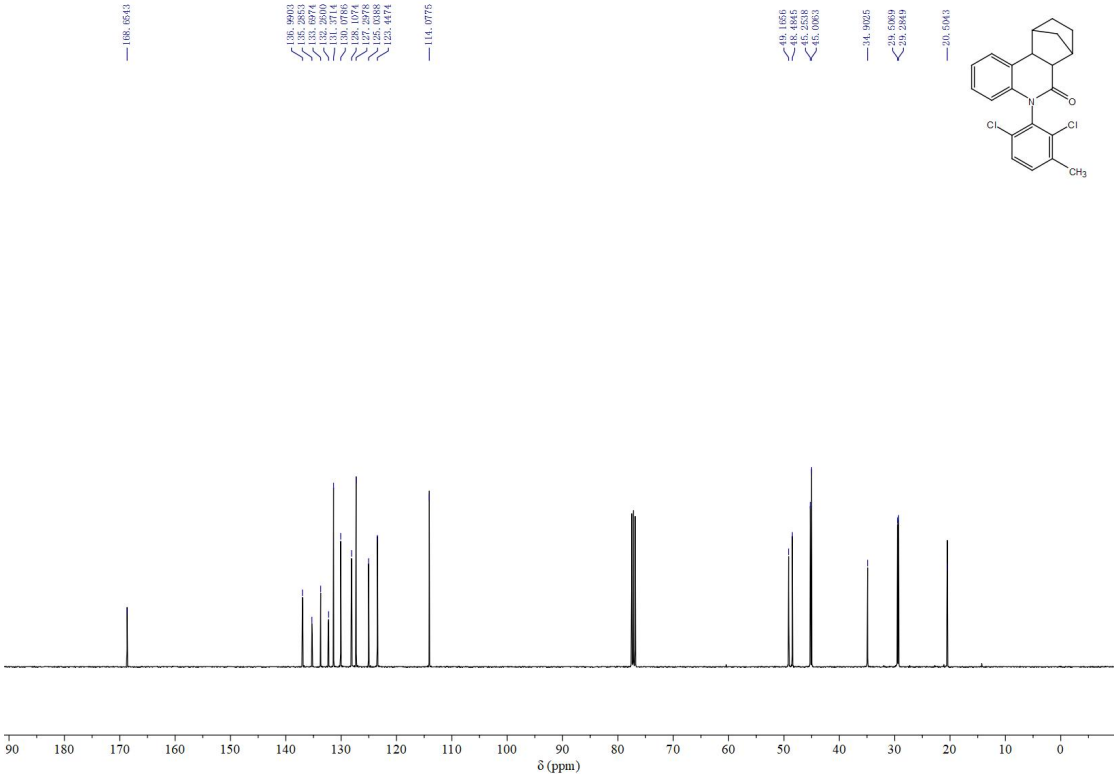
^{19}F NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**47c**)



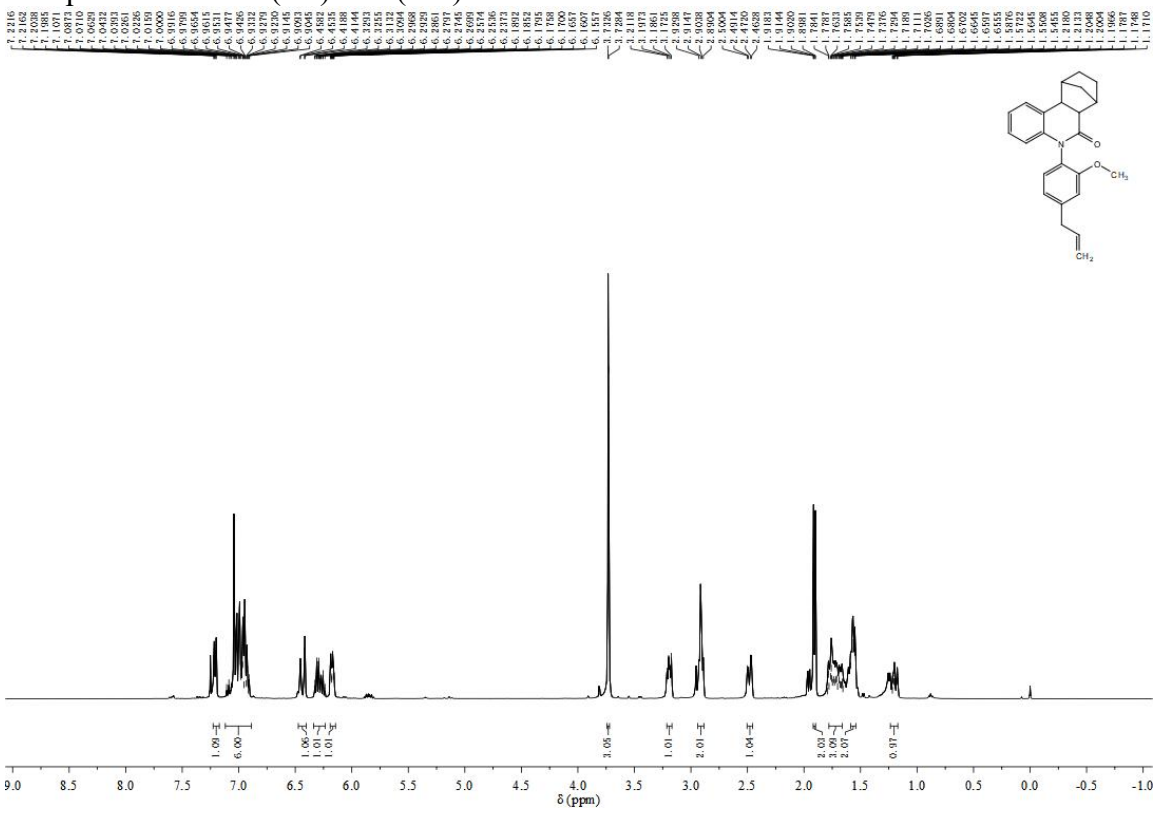
^{1}H NMR spectrum of 5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**48c**)



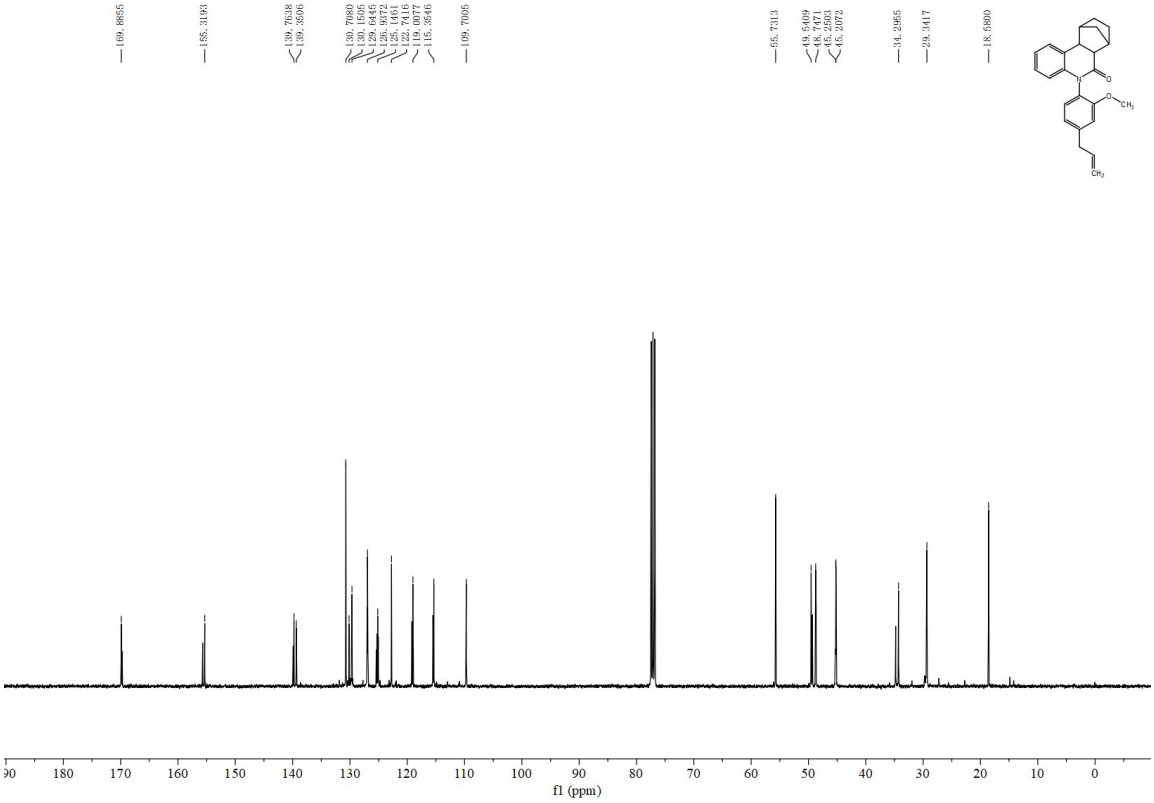
^{13}C NMR spectrum of 5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**48c**)



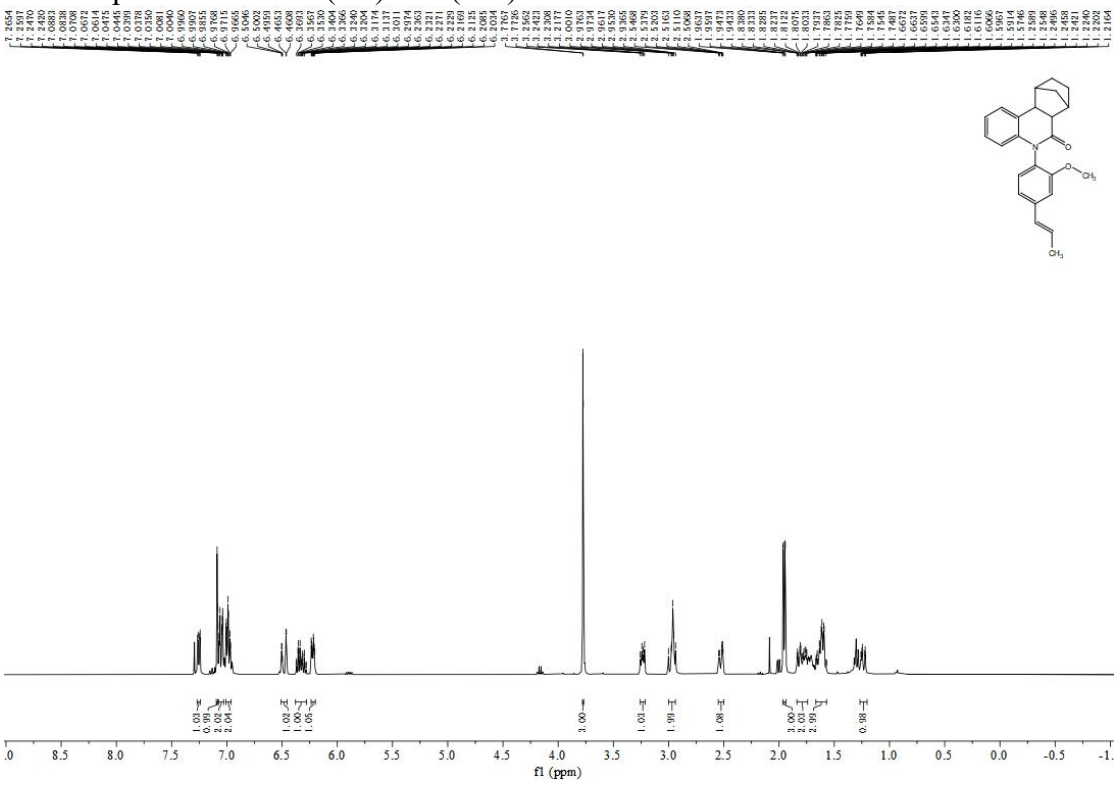
^{1}H NMR spectrum of 5-(4-allyl-2-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**49c**)



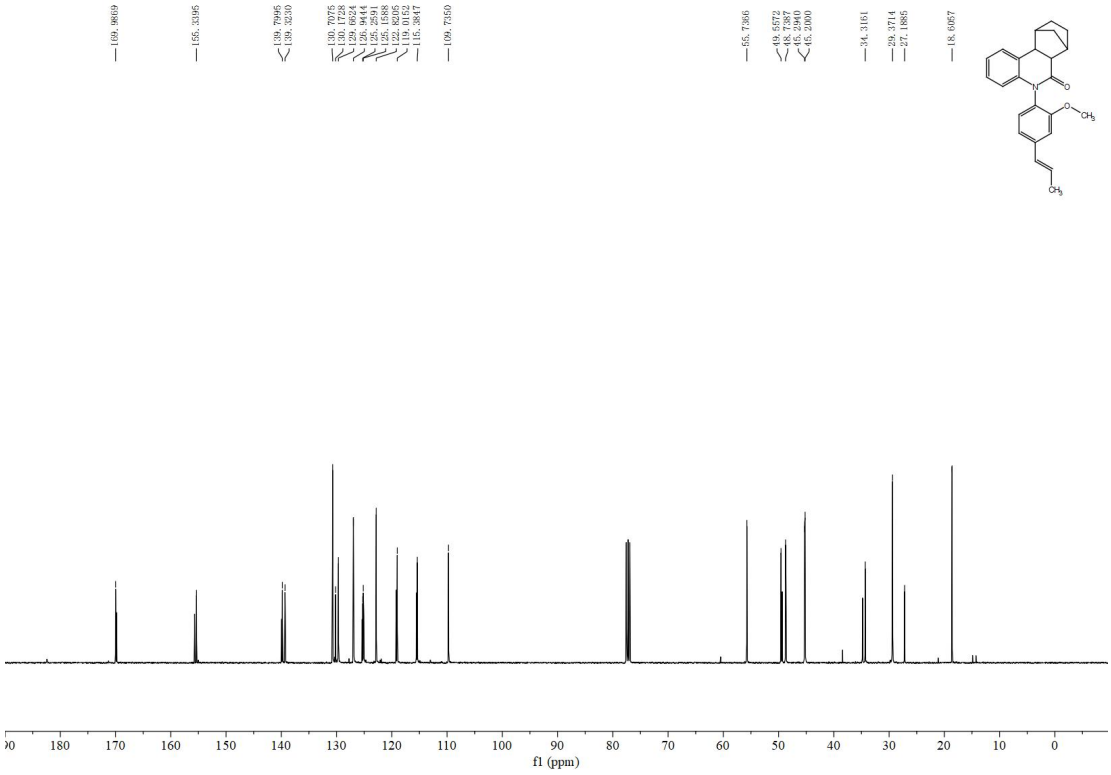
^{13}C NMR spectrum of 5-(4-allyl-2-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**49c**)



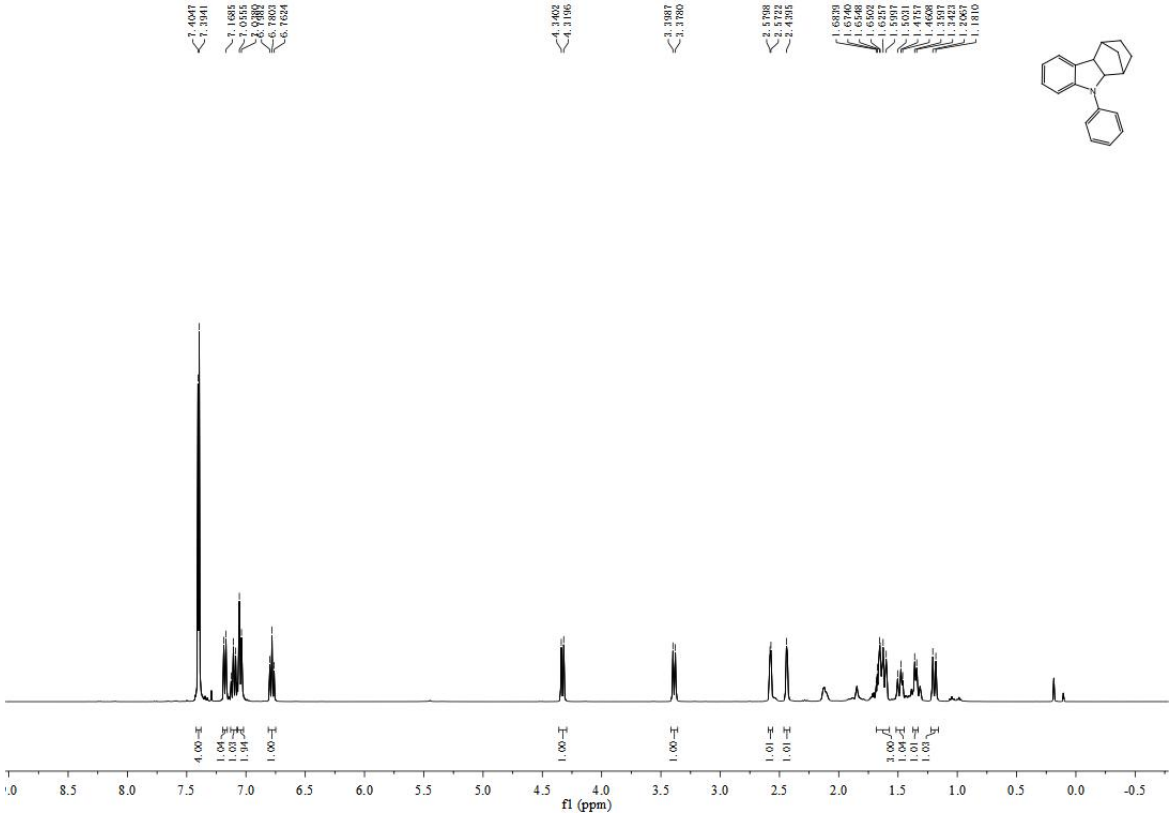
^{1}H NMR spectrum of (*E*)-5-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin -6(*5H*)-one (**50c**)



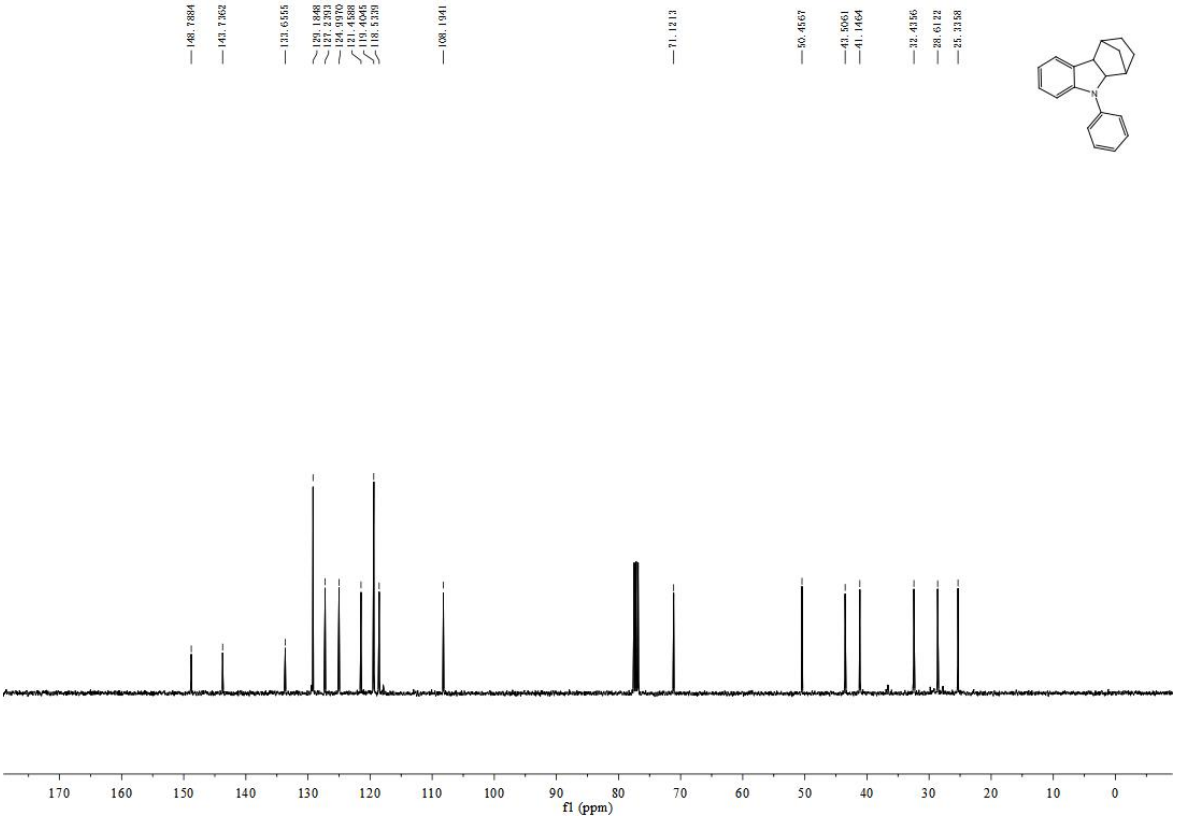
^{13}C NMR spectrum of (*E*)-5-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin -6(*5H*)-one (**50c**)



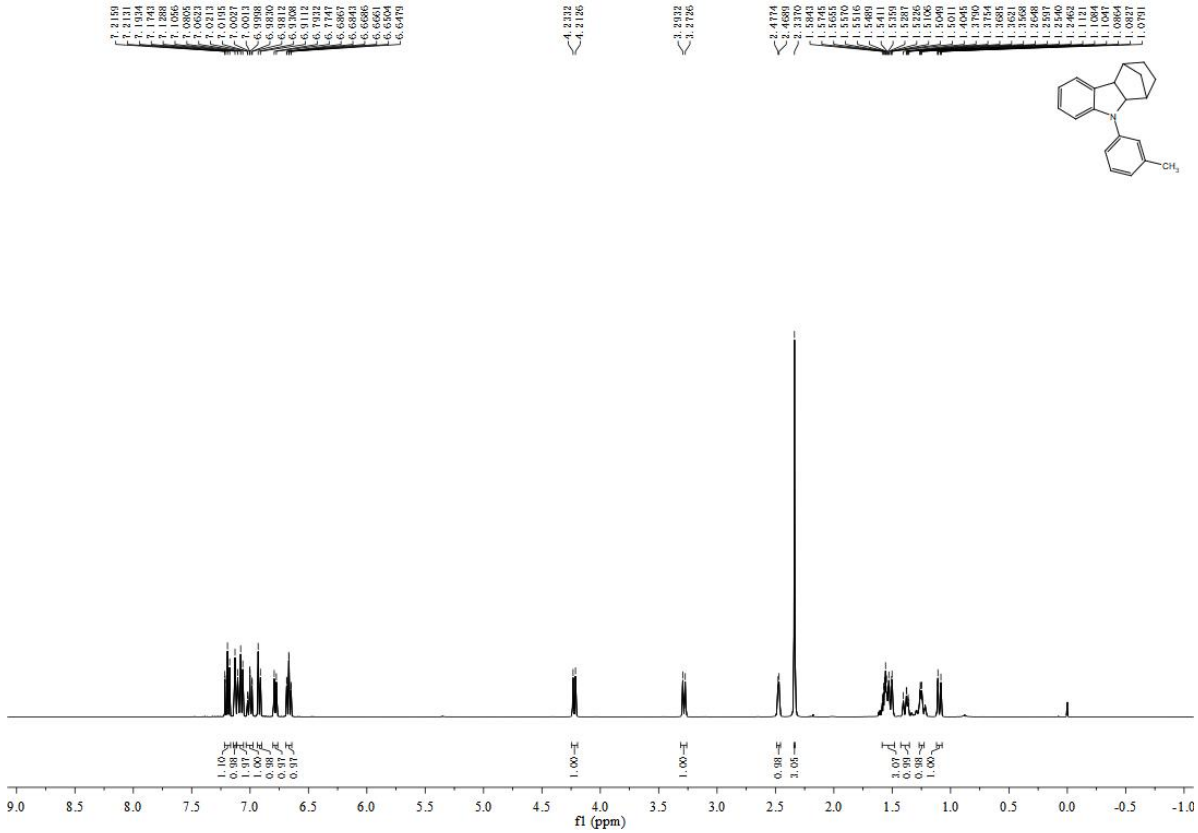
^{1}H NMR spectrum of 9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**1d**)



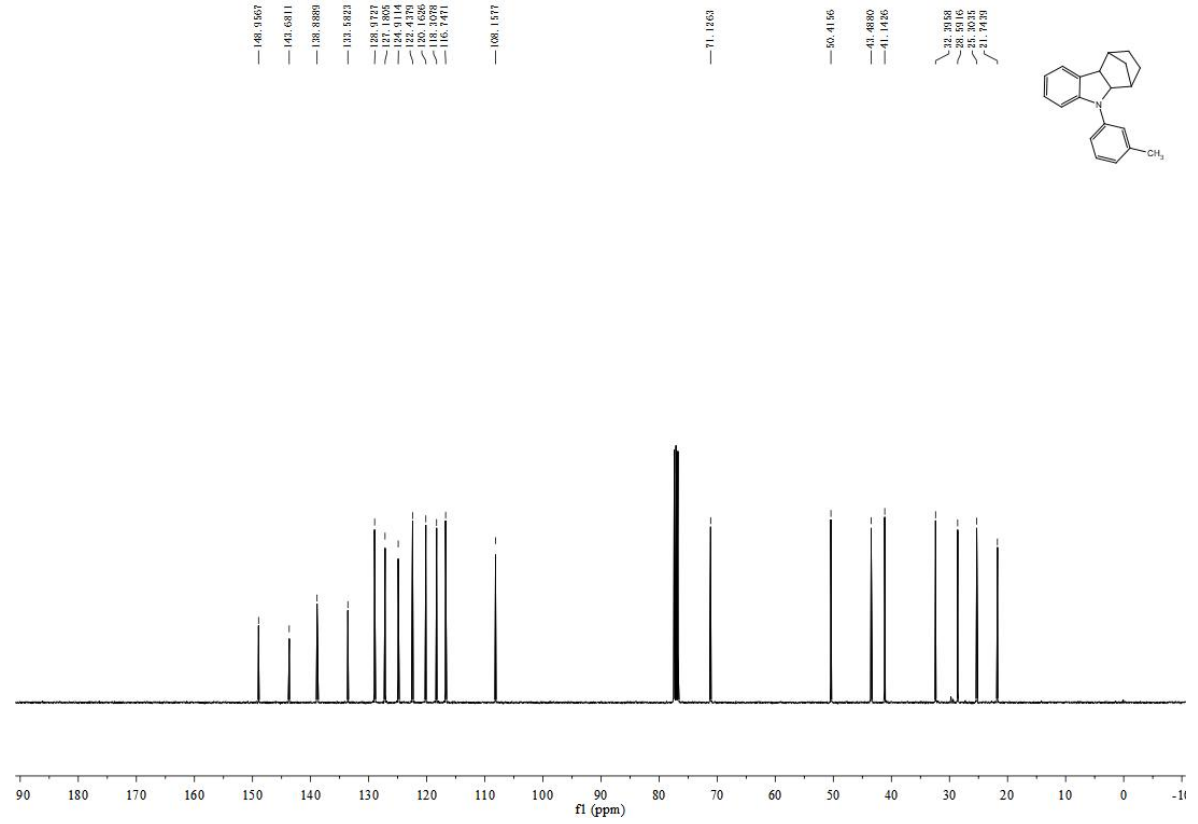
^{13}C NMR spectrum of 9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**1d**)



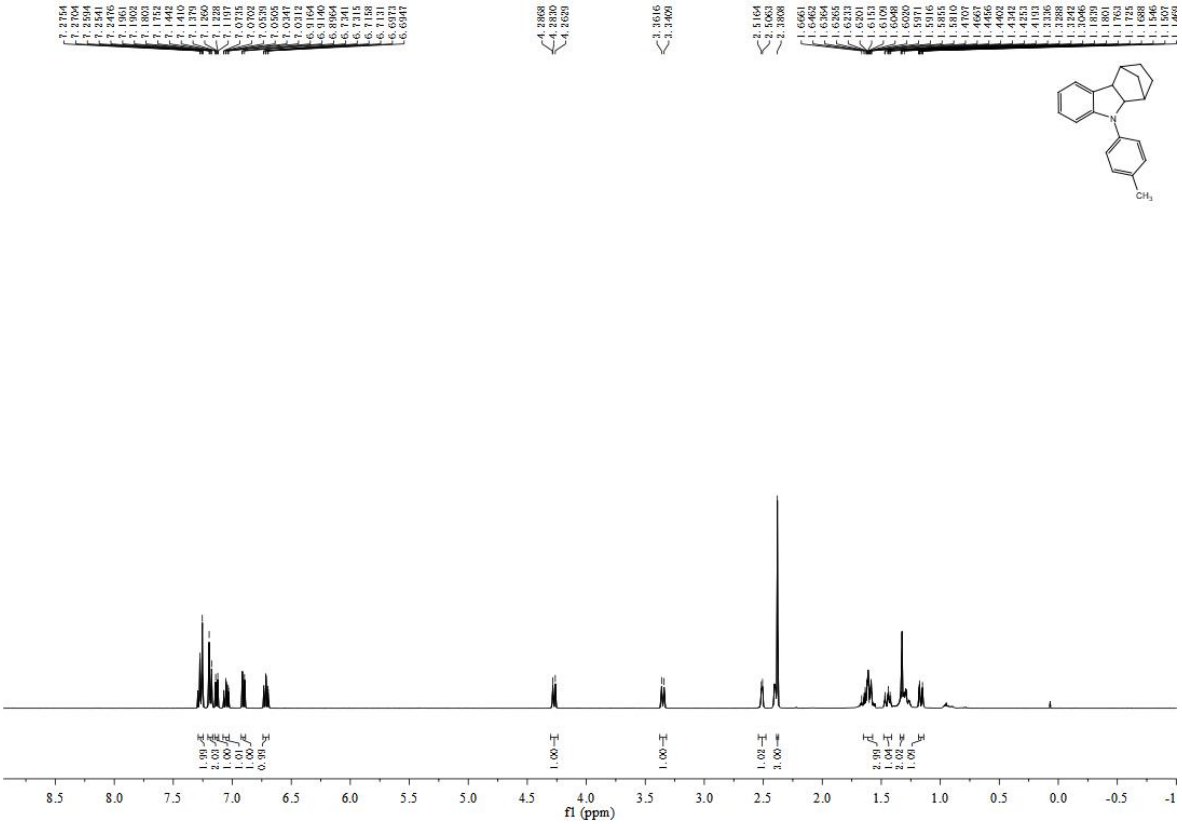
^{1}H NMR spectrum of 9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**2d**)



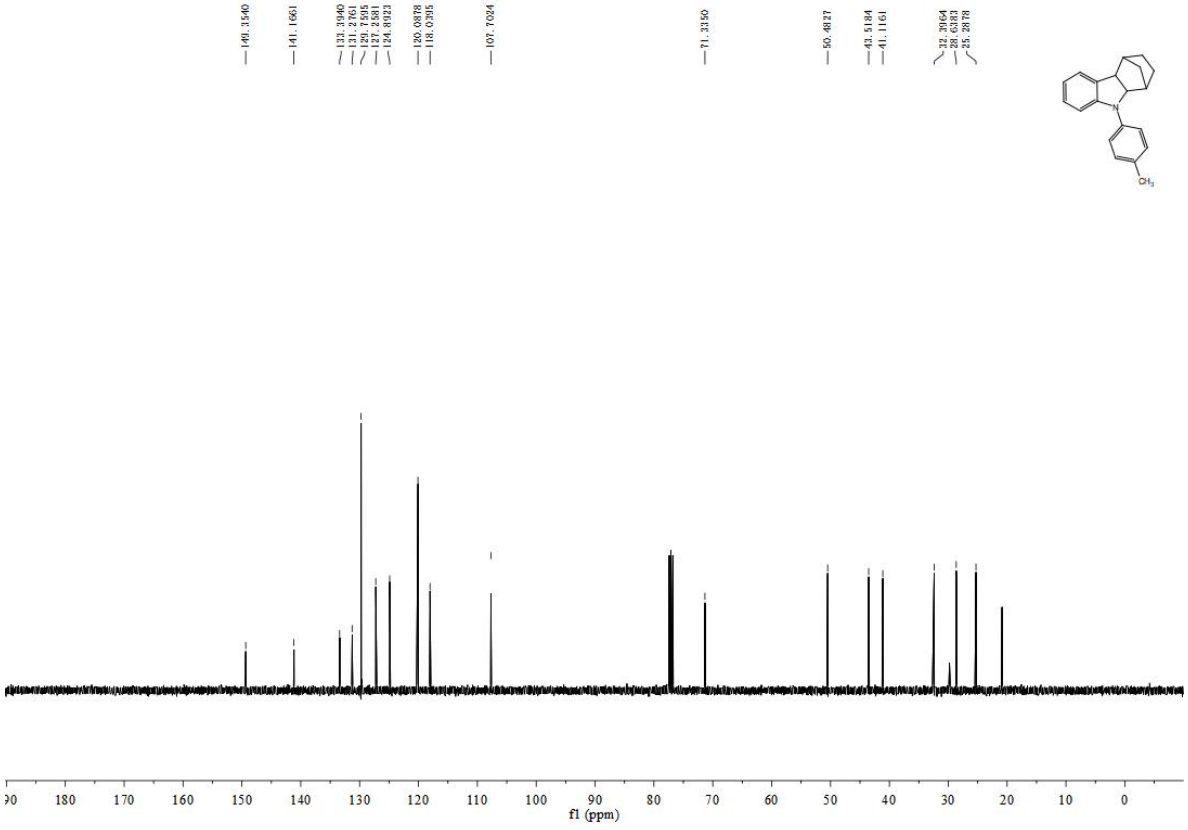
^{13}C NMR spectrum of 9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**2d**)



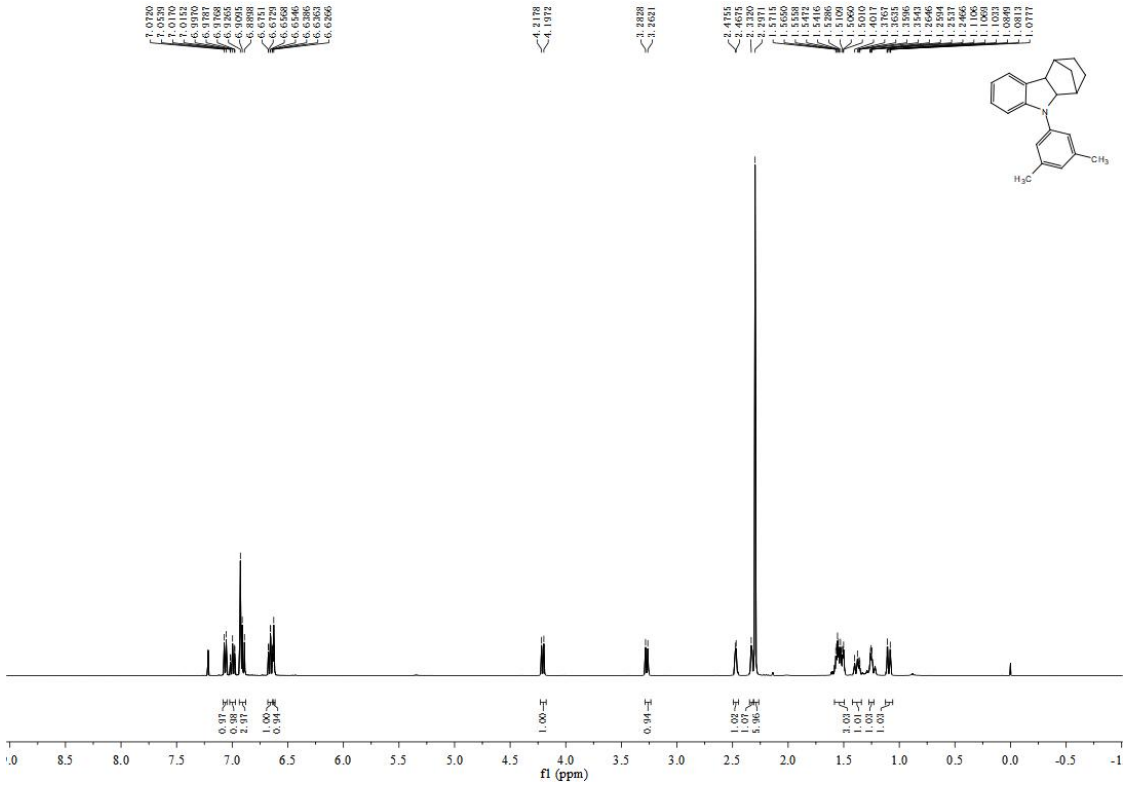
^{1}H NMR spectrum of 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**3d**)



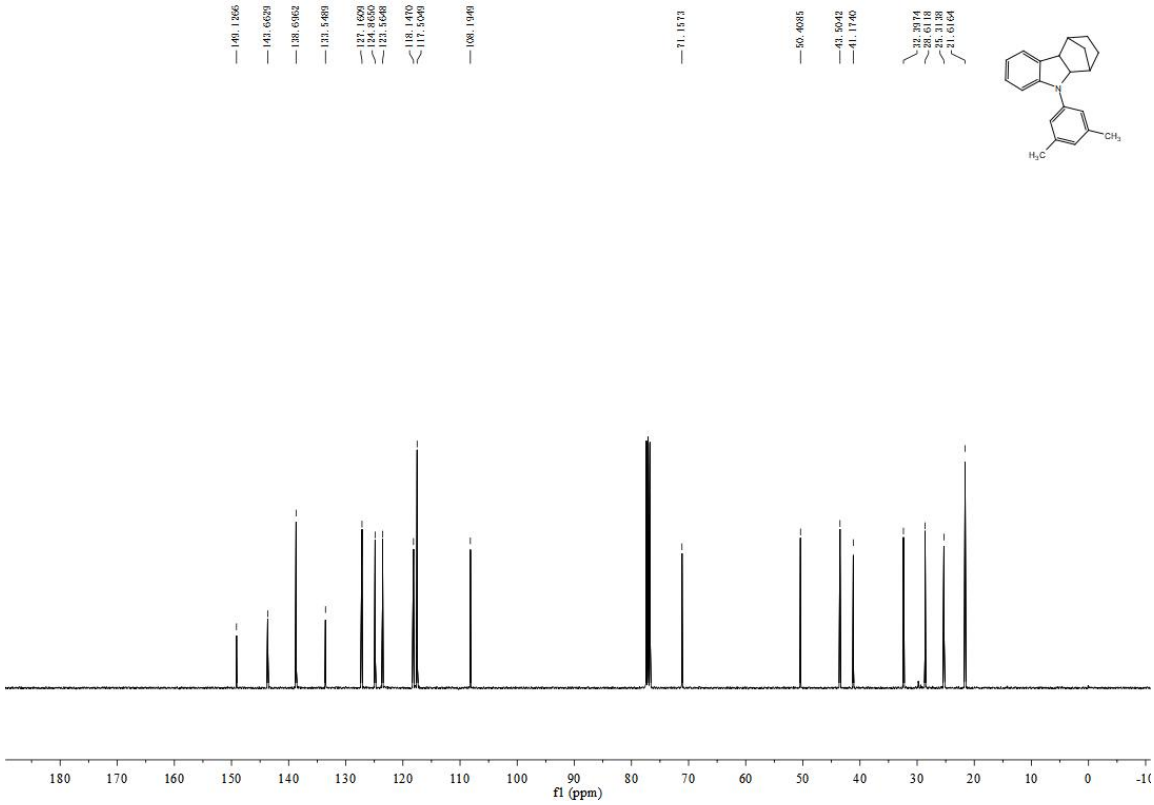
^{13}C NMR spectrum of 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**3d**)



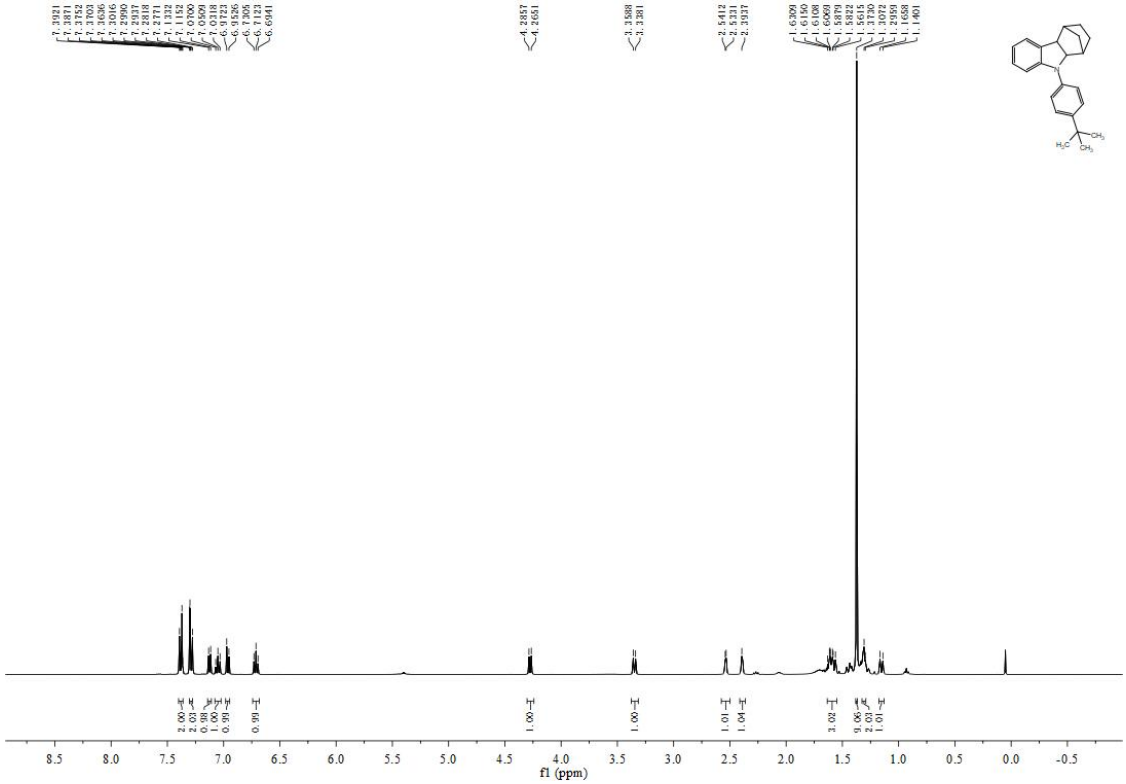
^{1}H NMR spectrum of 9-(3,5-dimethylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**4d**)



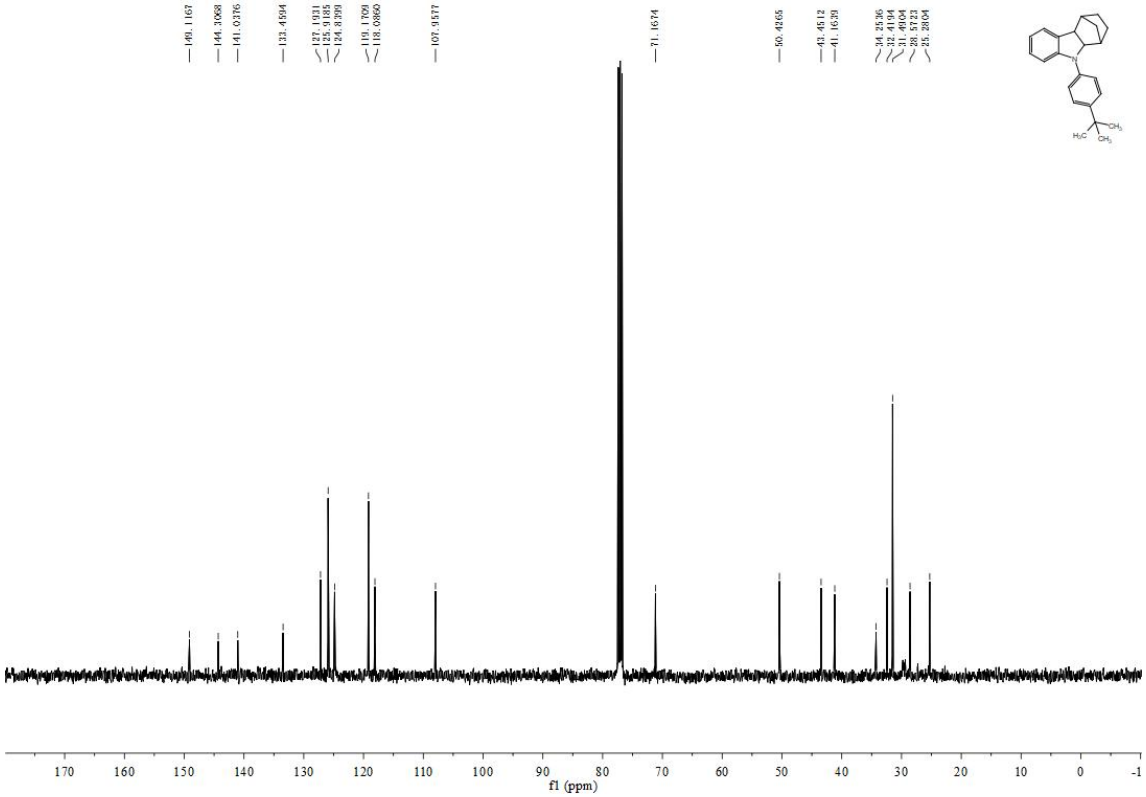
^{13}C NMR spectrum of 9-(3,5-dimethylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**4d**)



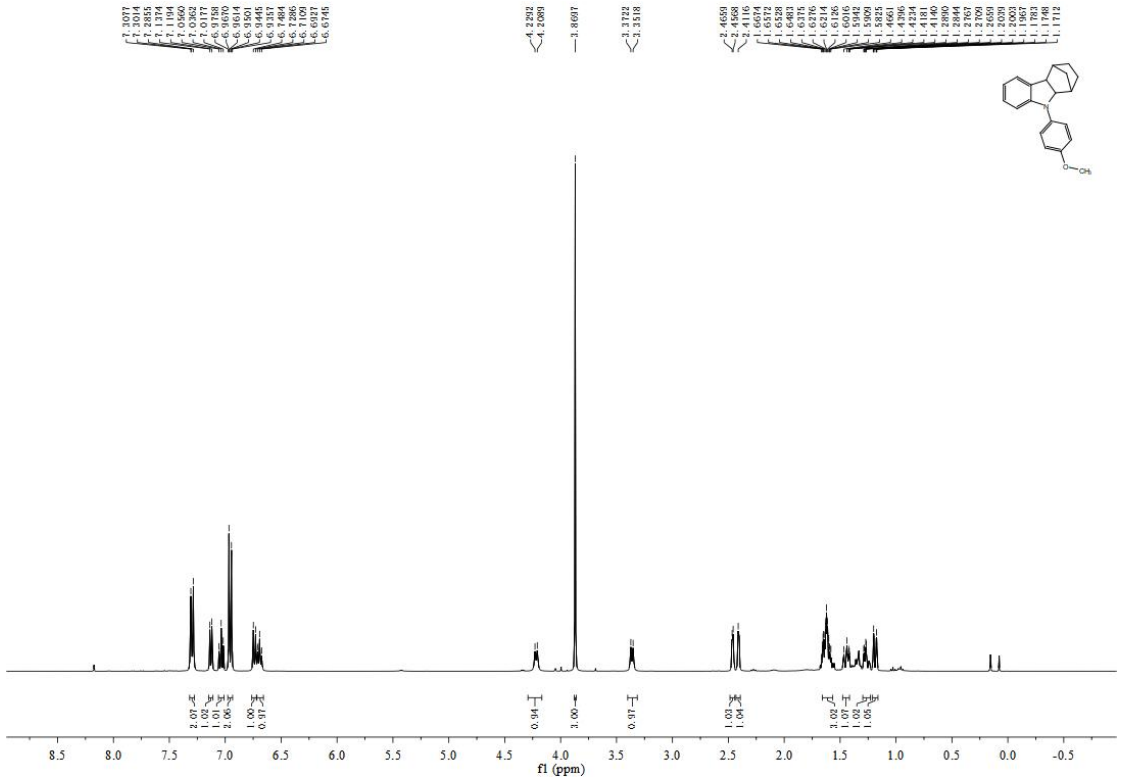
^{1}H NMR spectrum of 9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**5d**)



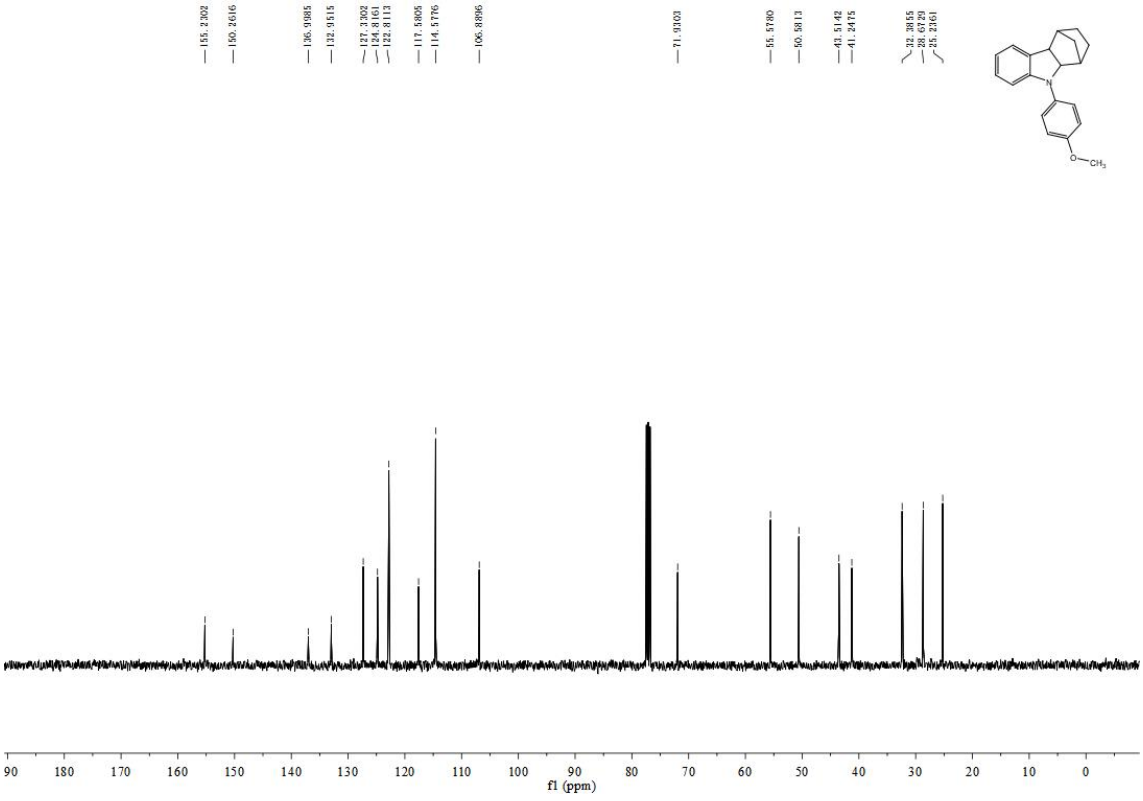
^{13}C NMR spectrum of 9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**5d**)



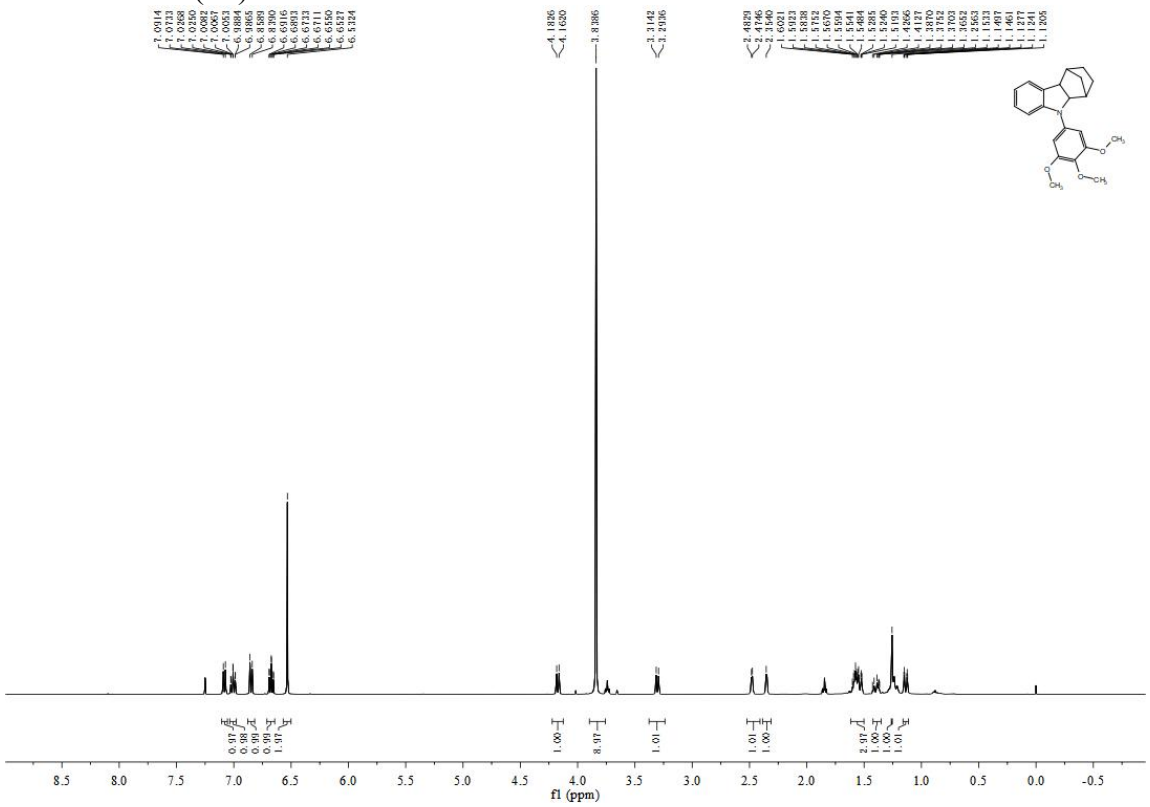
^{1}H NMR spectrum of 9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**6d**)



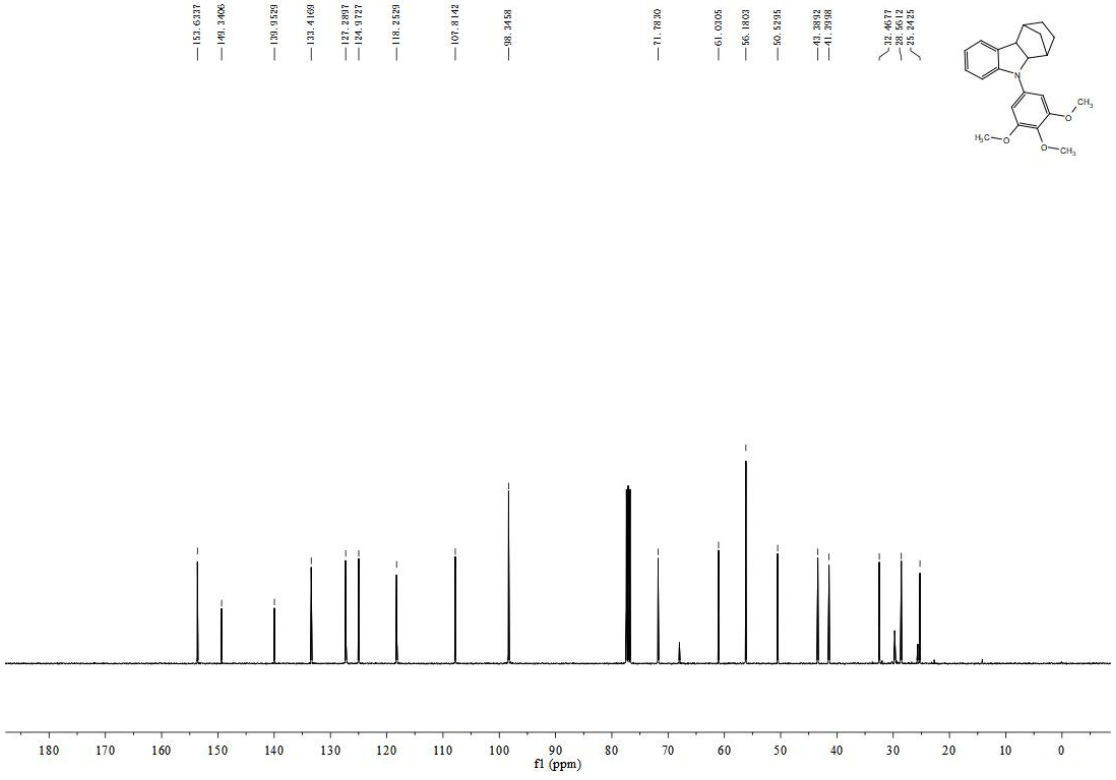
^{13}C NMR spectrum of 9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**6d**)



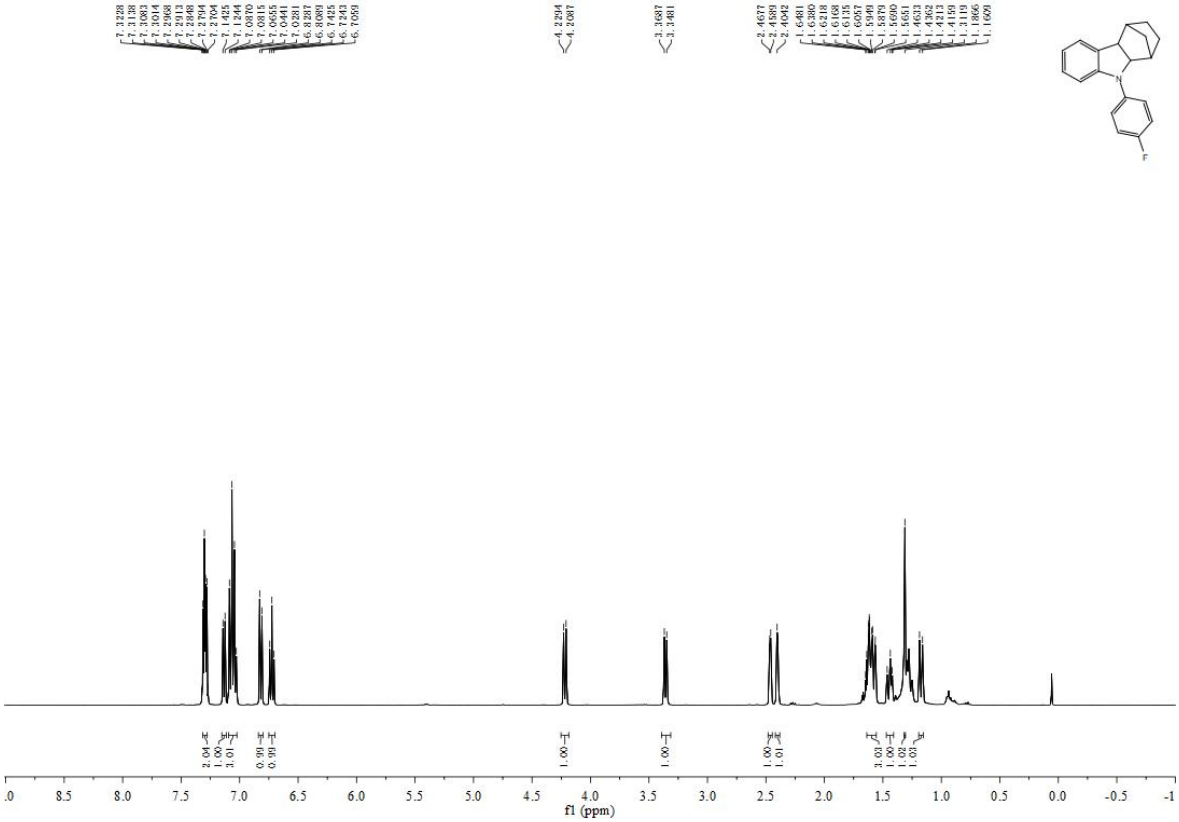
^{1}H NMR spectrum of 10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**7d**)



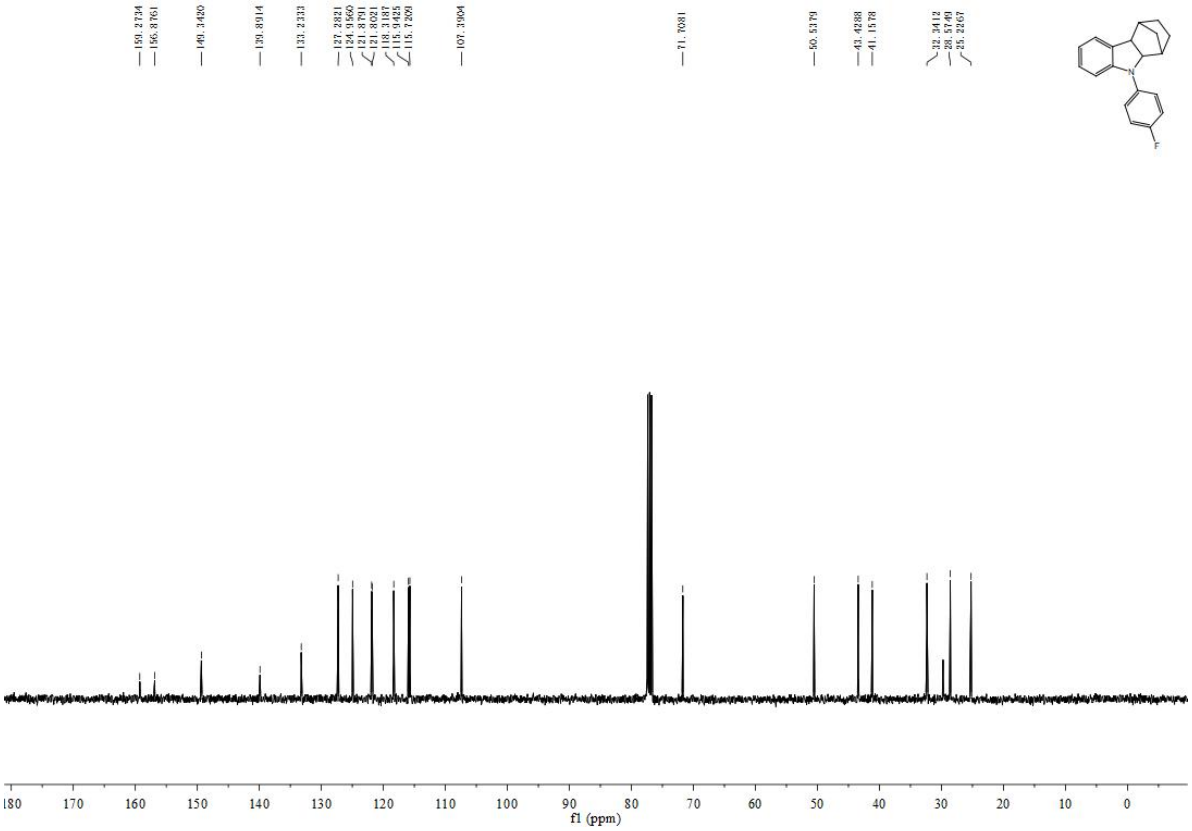
^{13}C NMR spectrum of 10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**7d**)



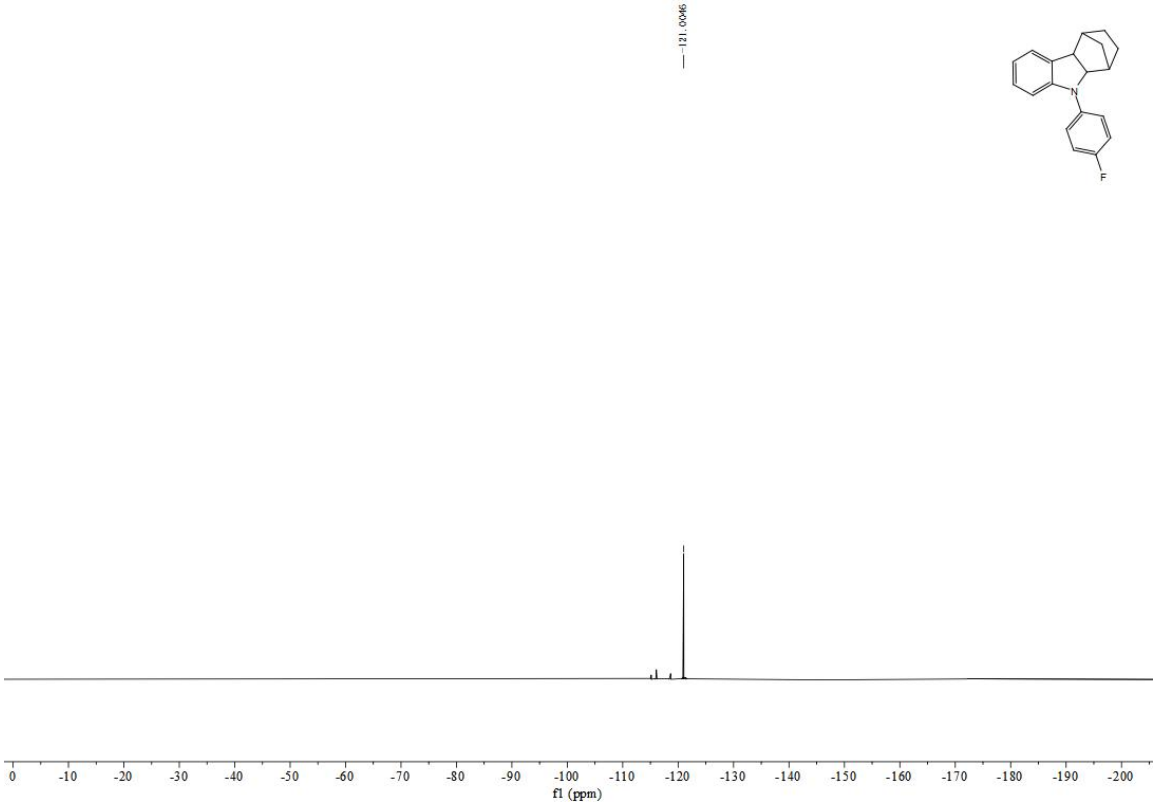
^{1}H NMR spectrum of 9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**8d**)



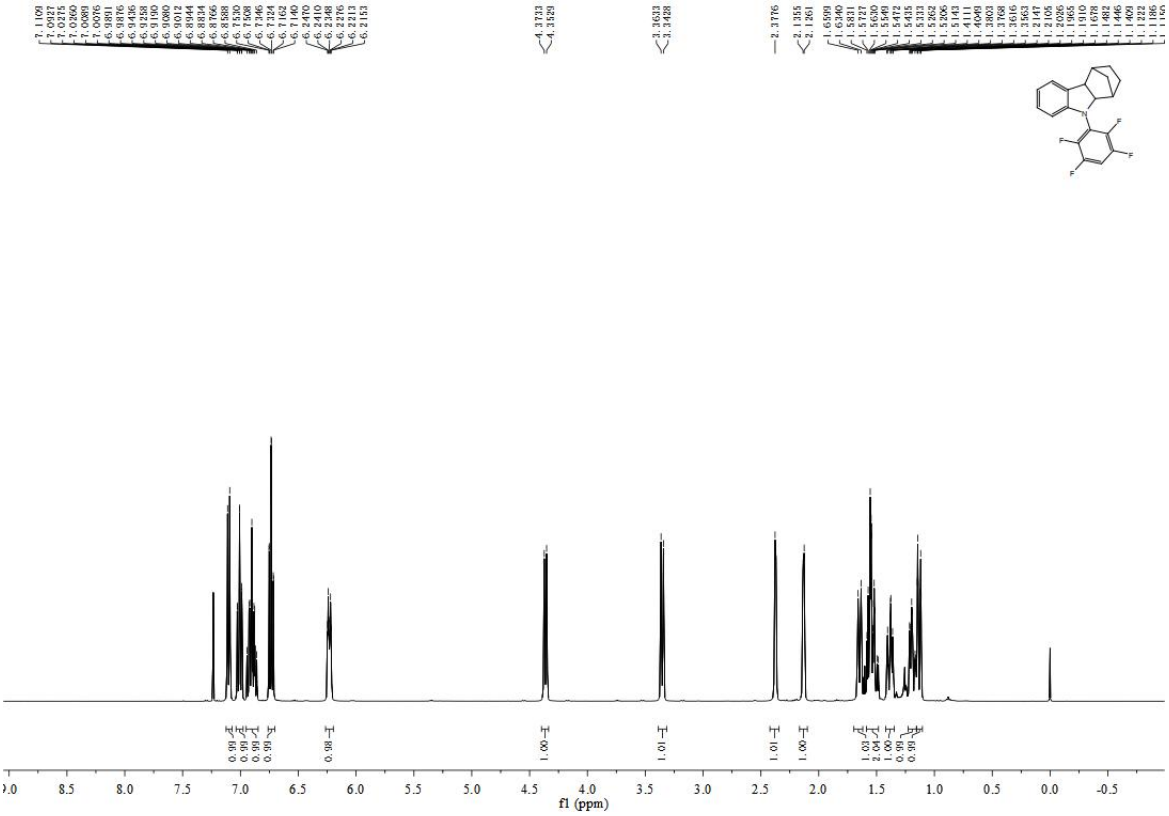
^{13}C NMR spectrum of 9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**8d**)



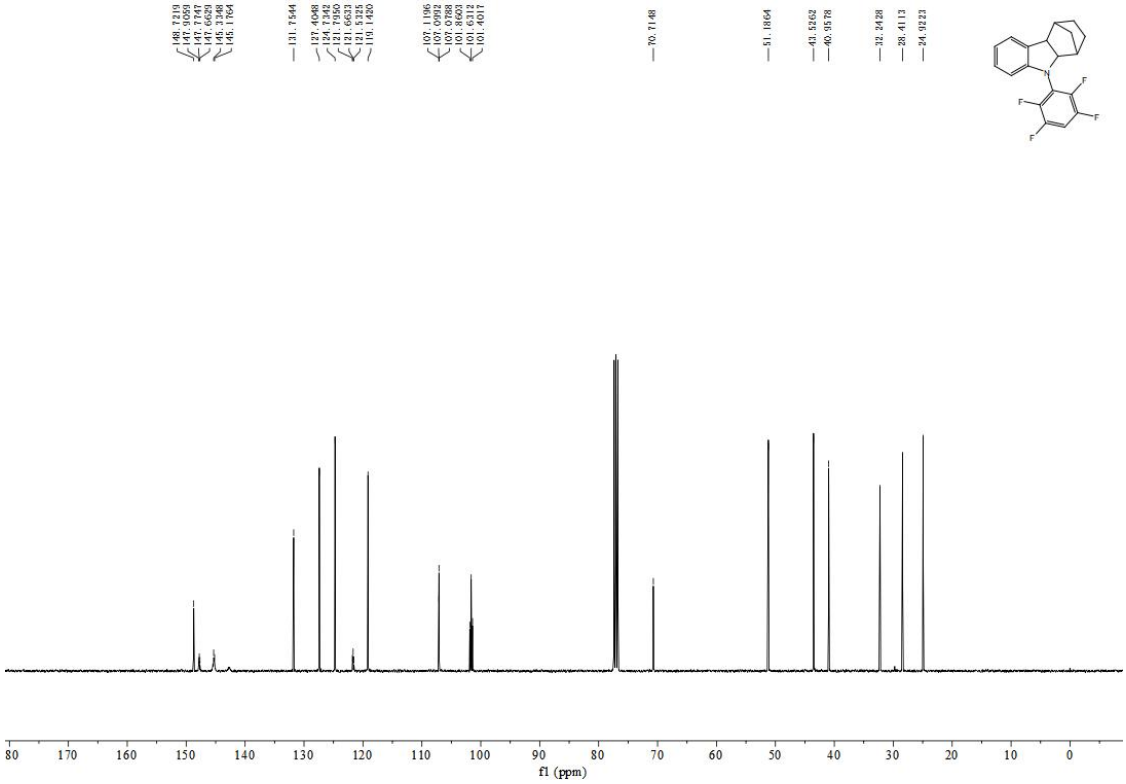
^{19}F NMR spectrum of 9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**8d**)



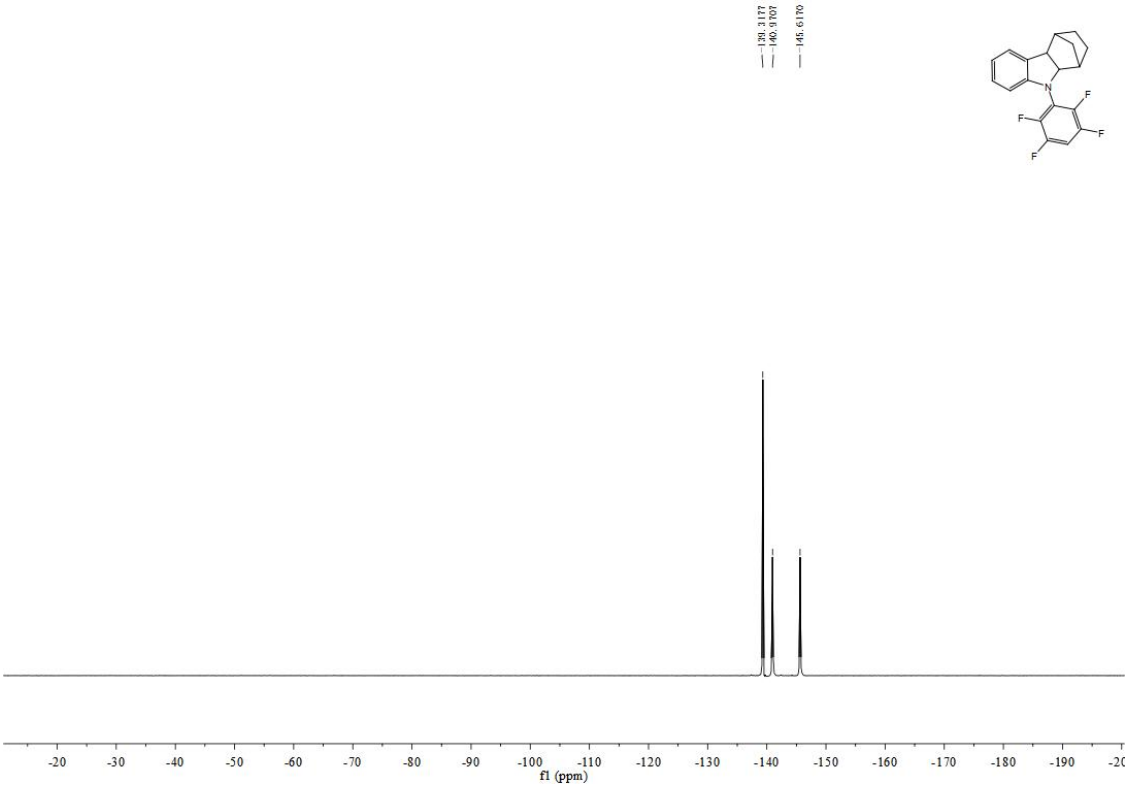
^{1}H NMR spectrum of 9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**9d**)



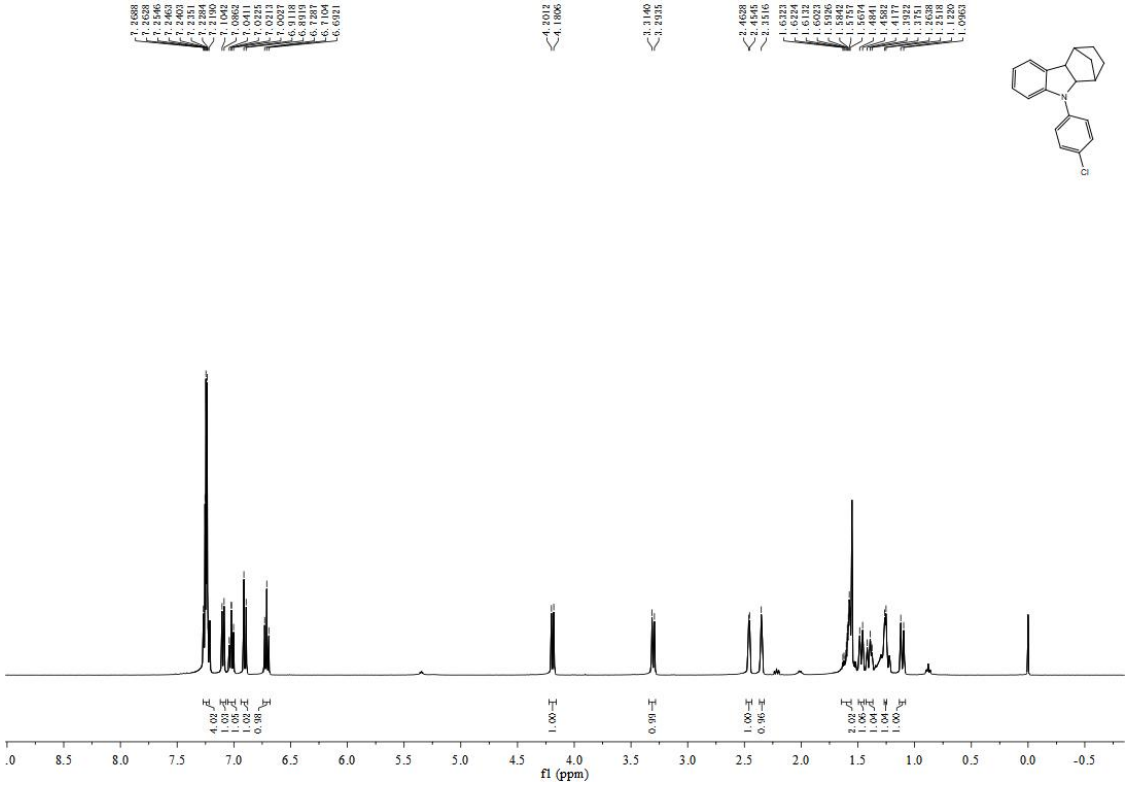
^{13}C NMR spectrum of 9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**9d**)



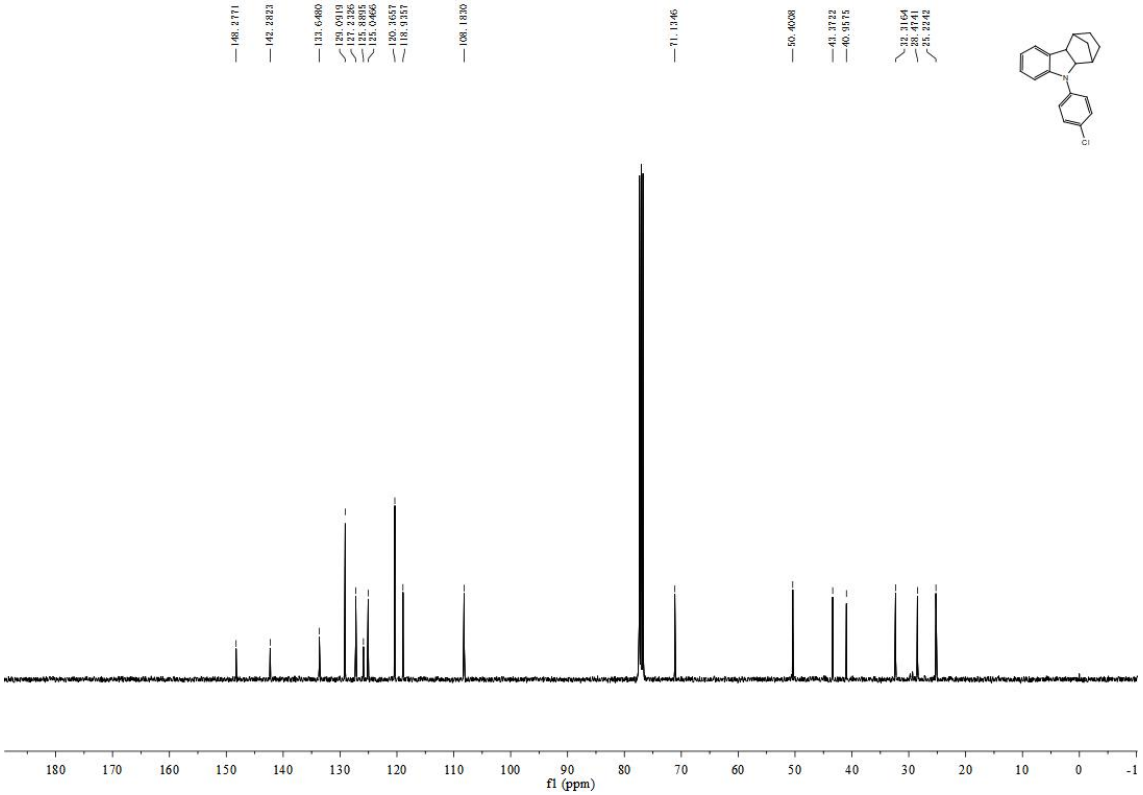
^{19}F NMR spectrum of 9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**9d**)



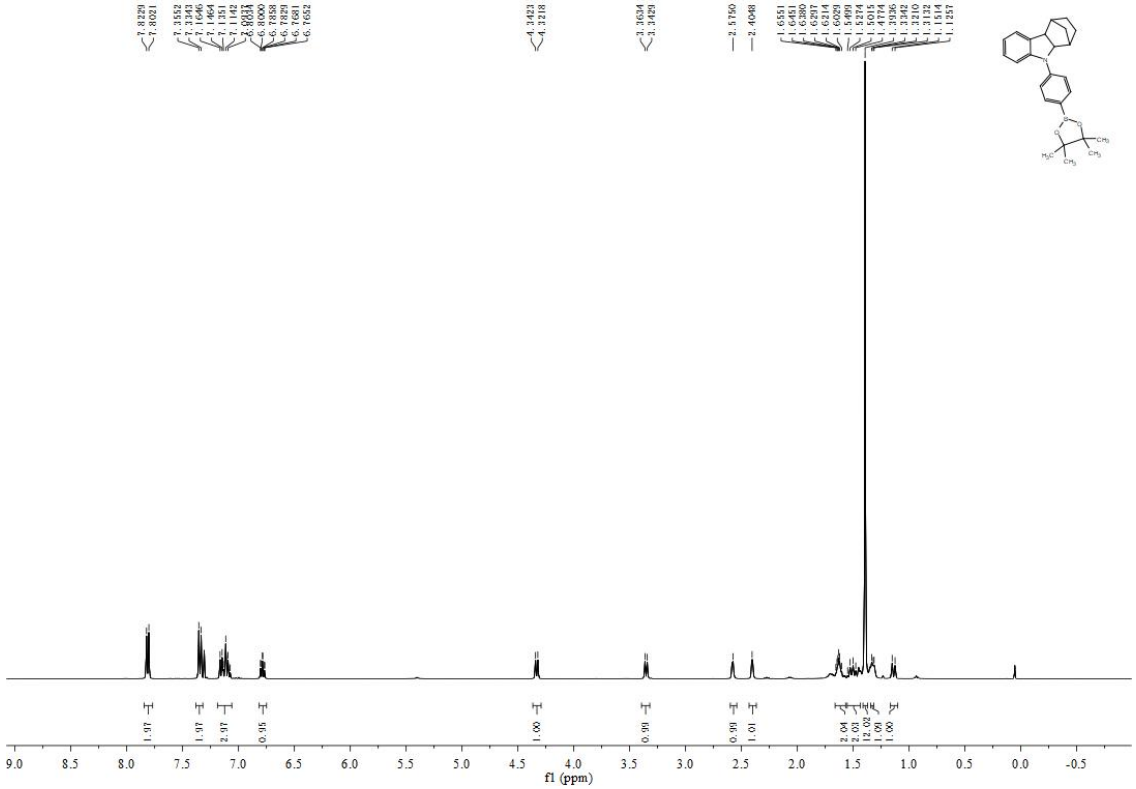
^{1}H NMR spectrum of 9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**10d**)



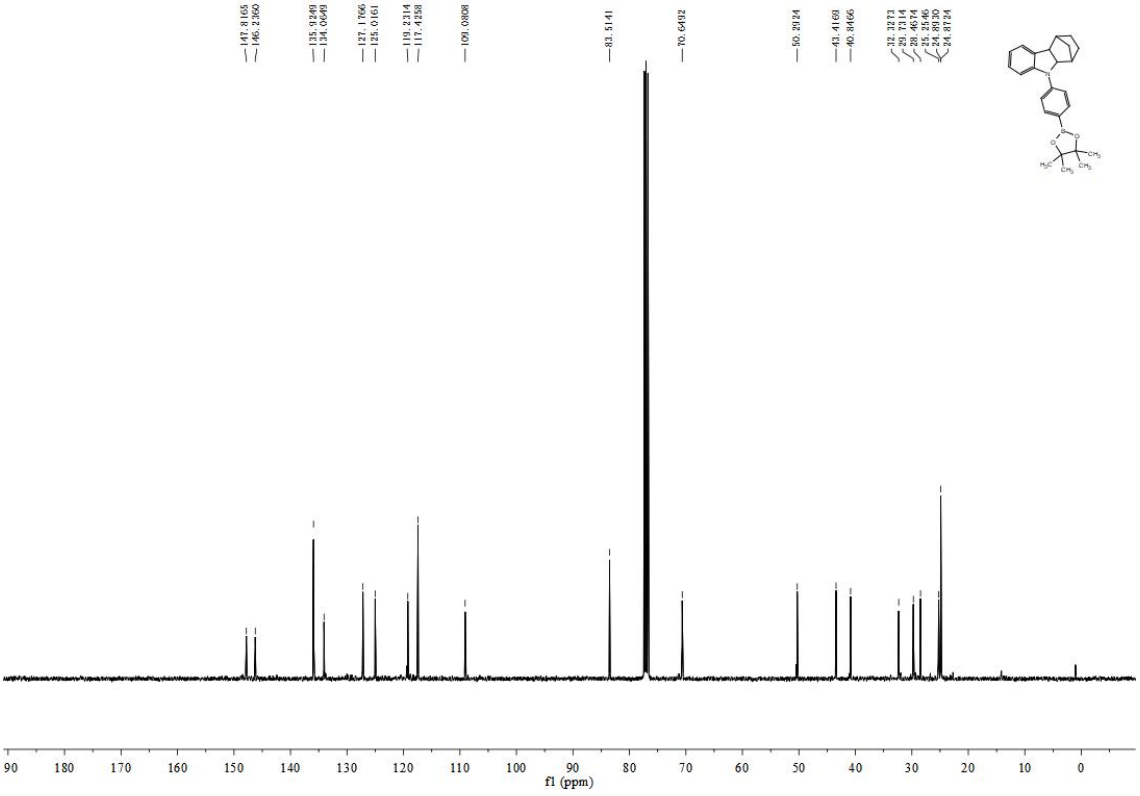
^{13}C NMR spectrum of 9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**10d**)



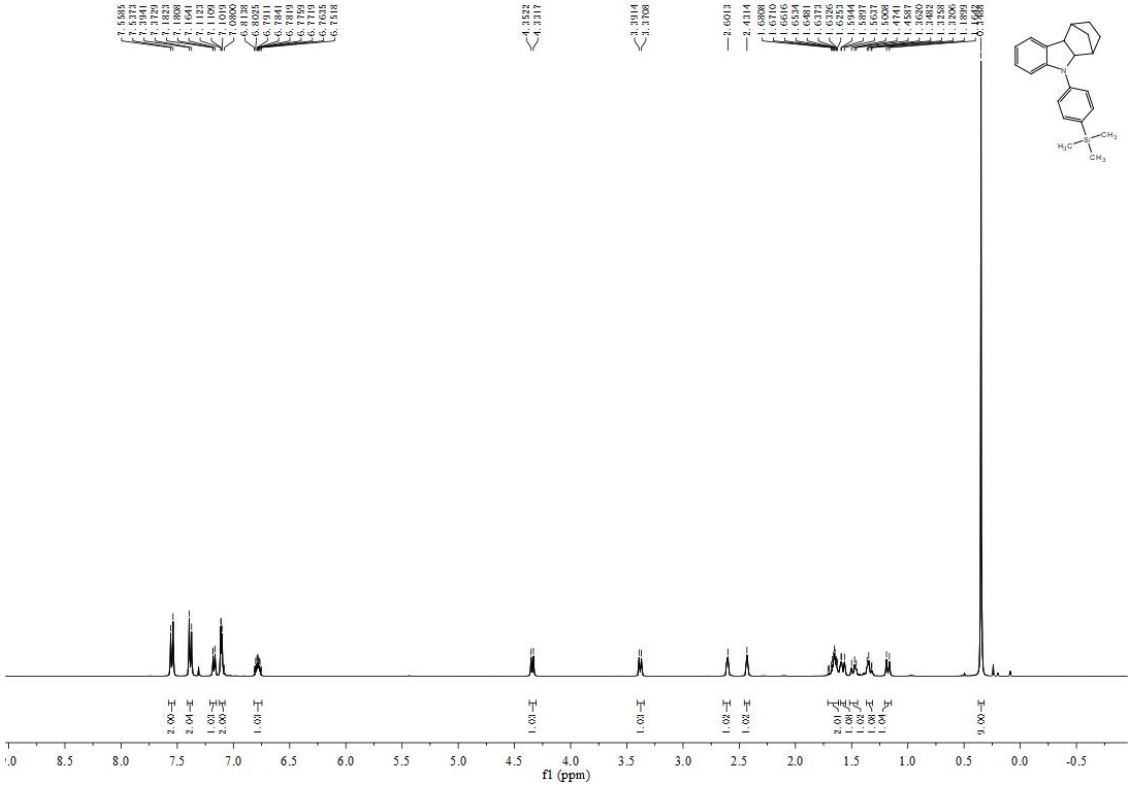
^{1}H NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**)



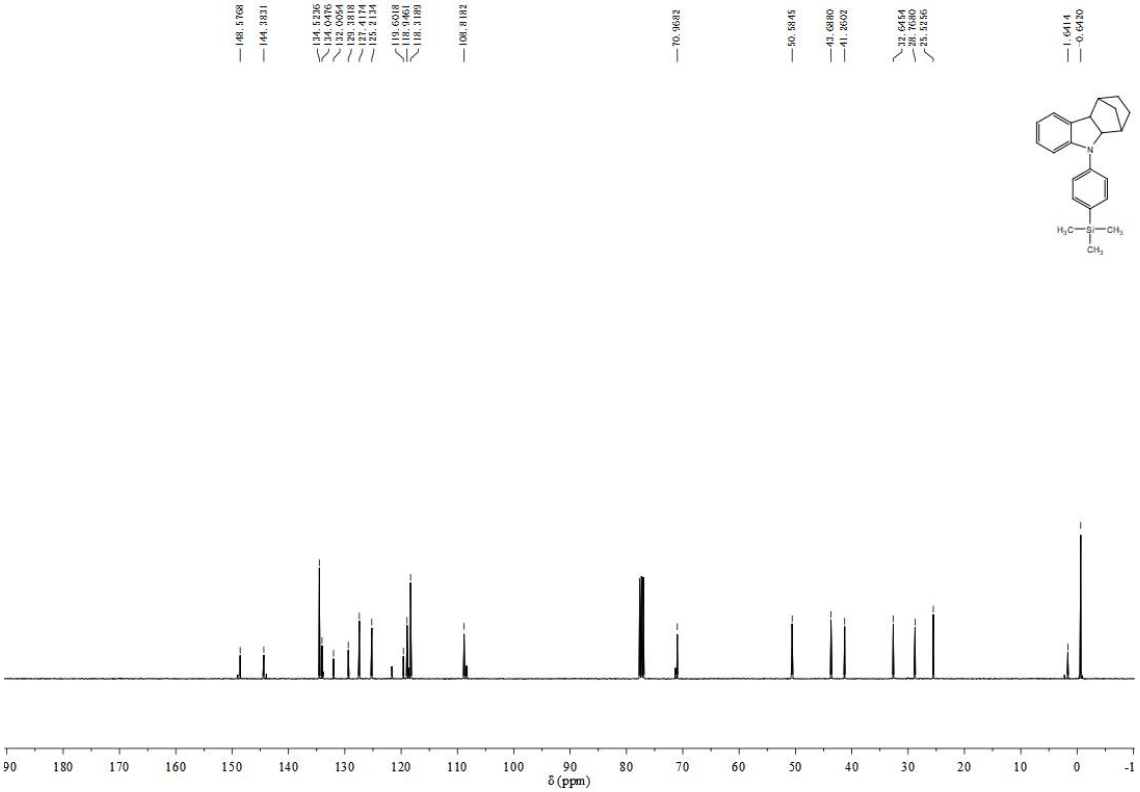
^{13}C NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**)



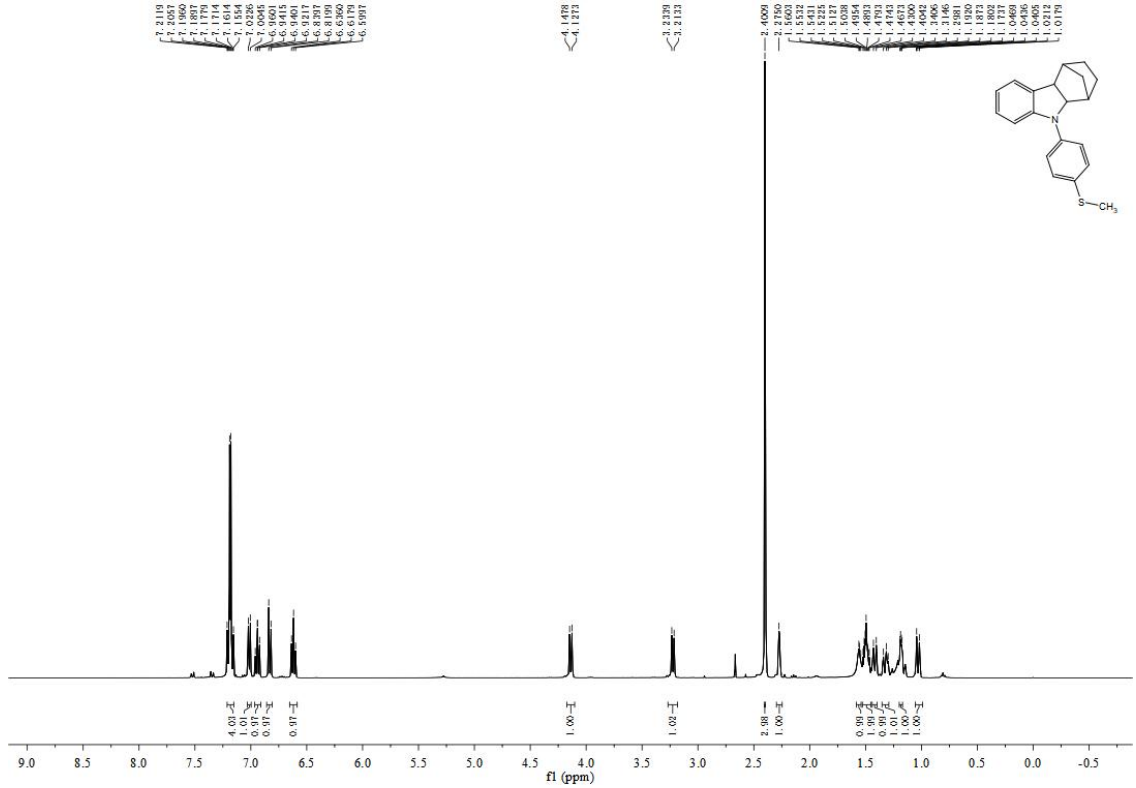
^{1}H NMR spectrum of 9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**12d**)



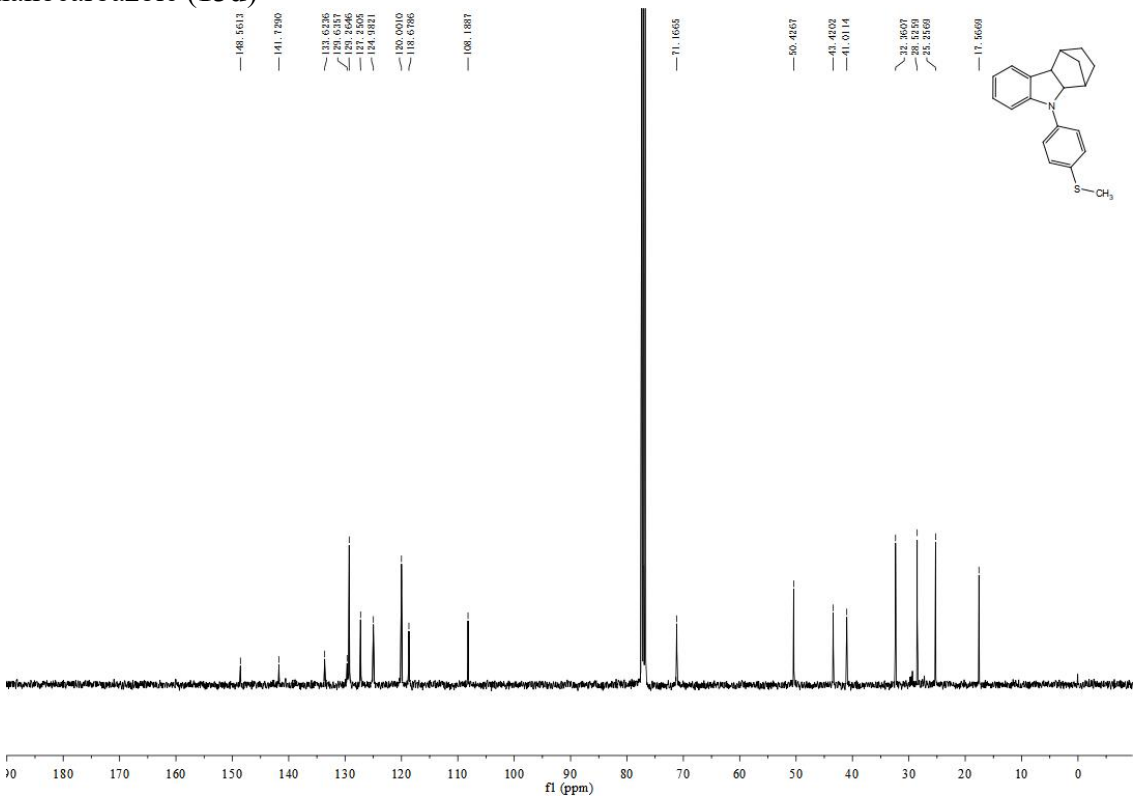
^{13}C NMR spectrum of 9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**12d**)



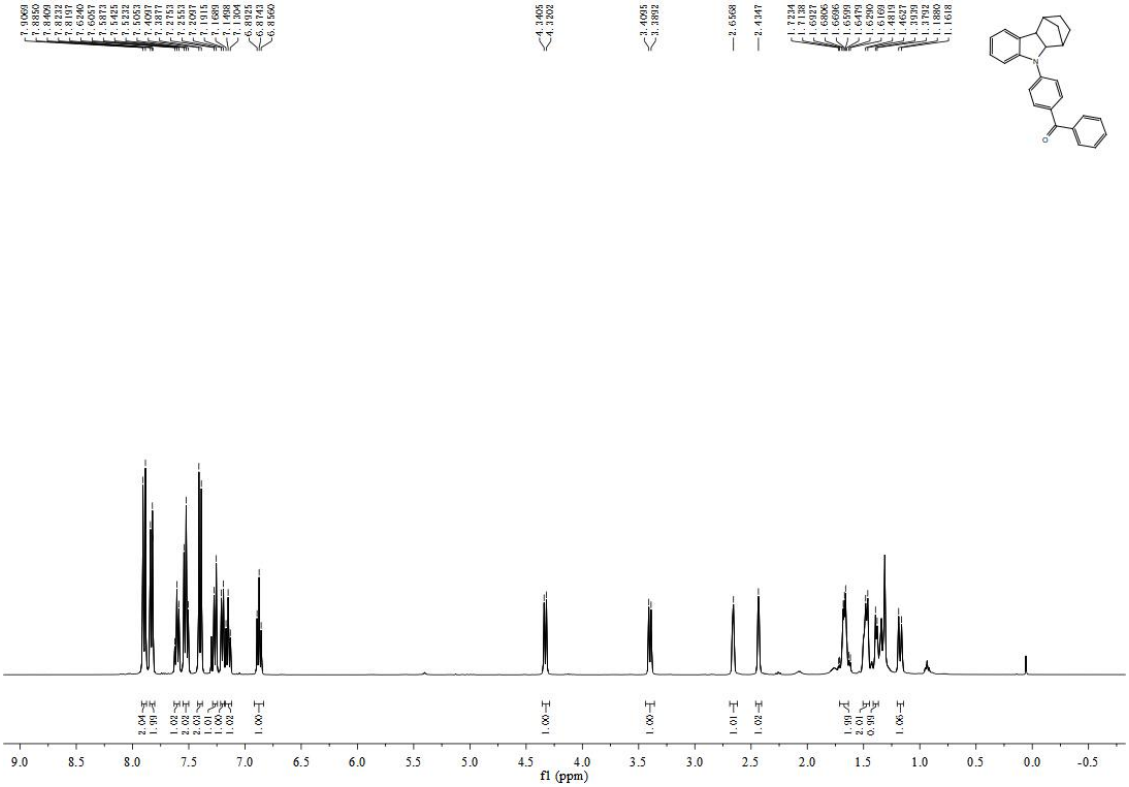
^{1}H NMR spectrum of 9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**13d**)



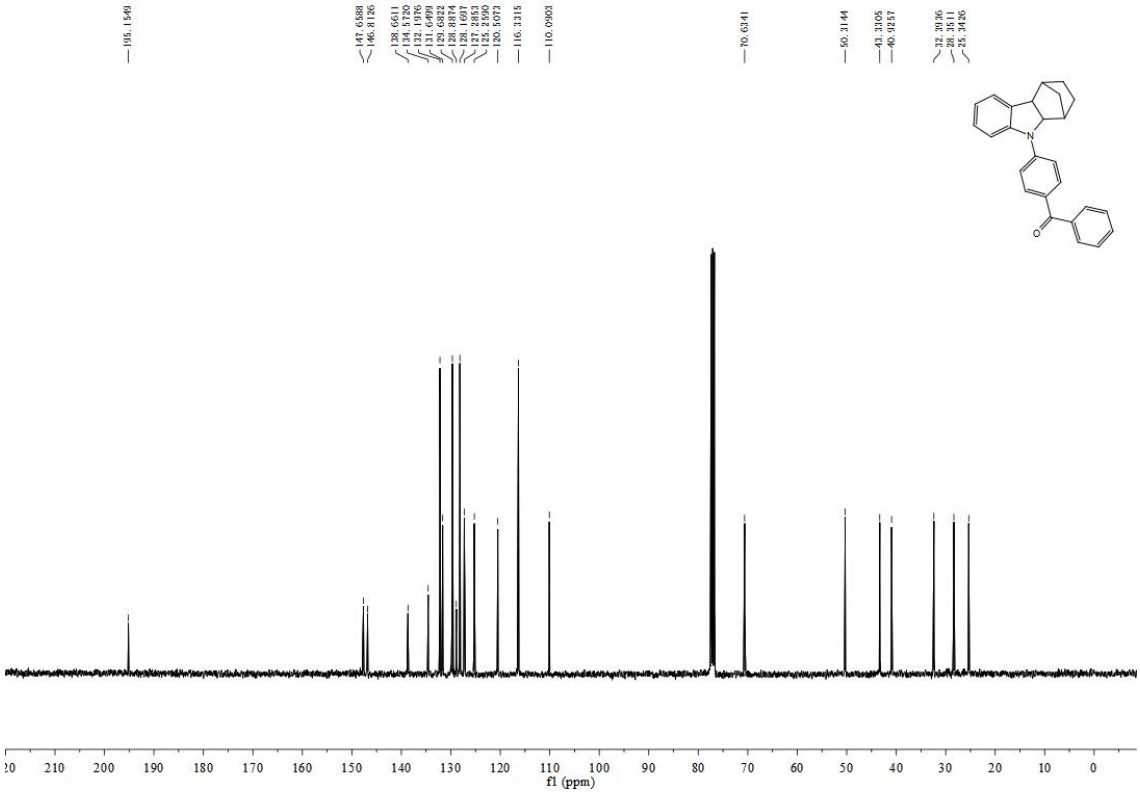
^{13}C NMR spectrum of 9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**13d**)



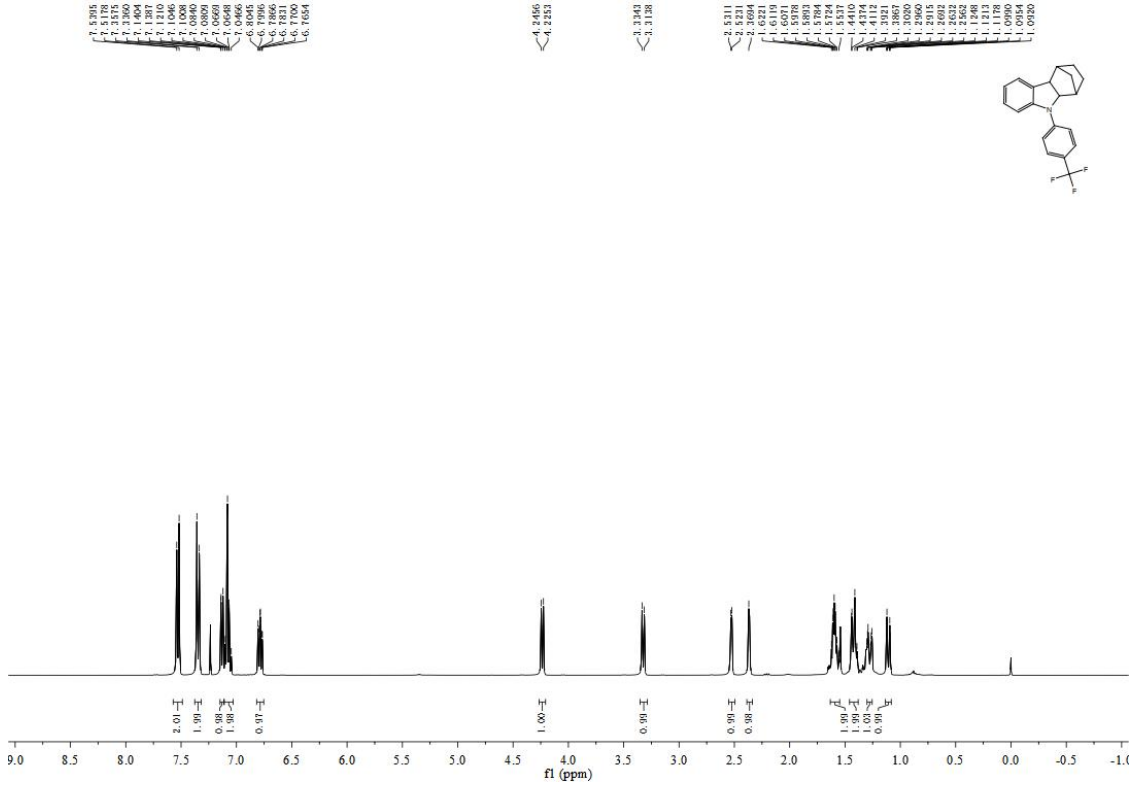
^{1}H NMR spectrum of (4-(1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazol-9-yl)phenyl)(phenyl)methanone (**14d**)



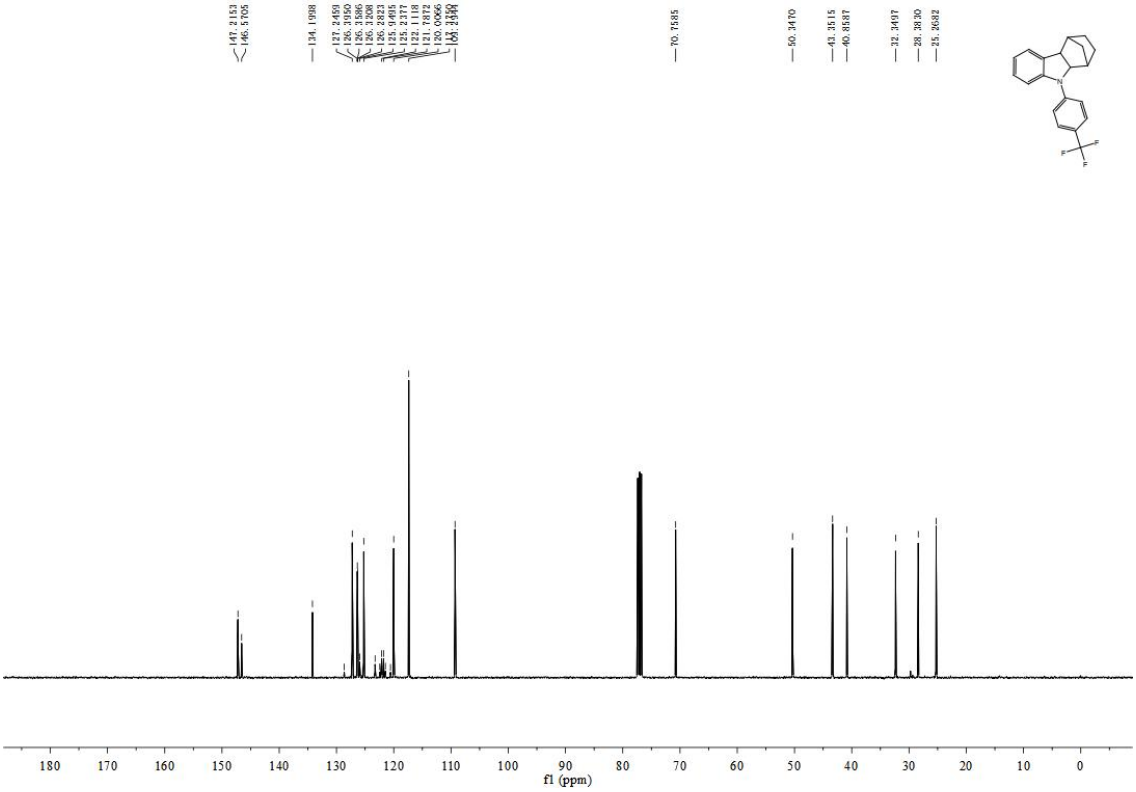
^{13}C NMR spectrum of (4-(1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazol-9-yl)phenyl)(phenyl)methanone (**14d**)



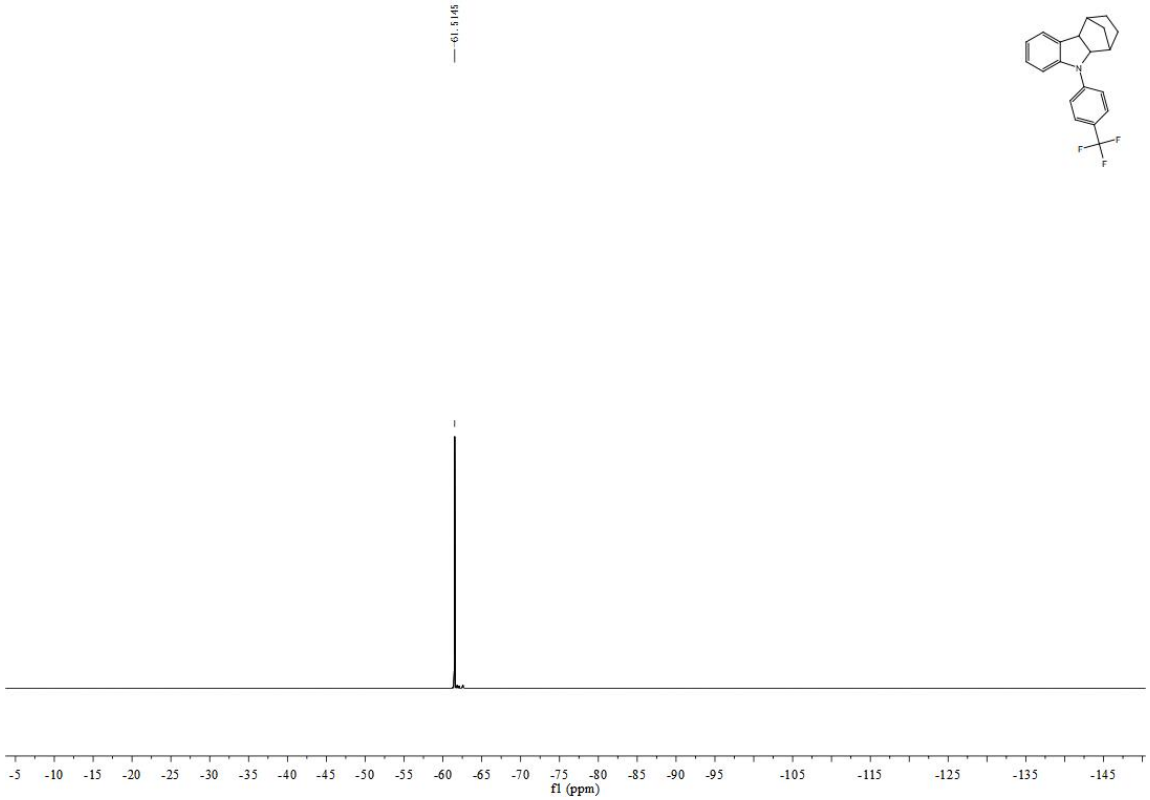
^{1}H NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**15d**)



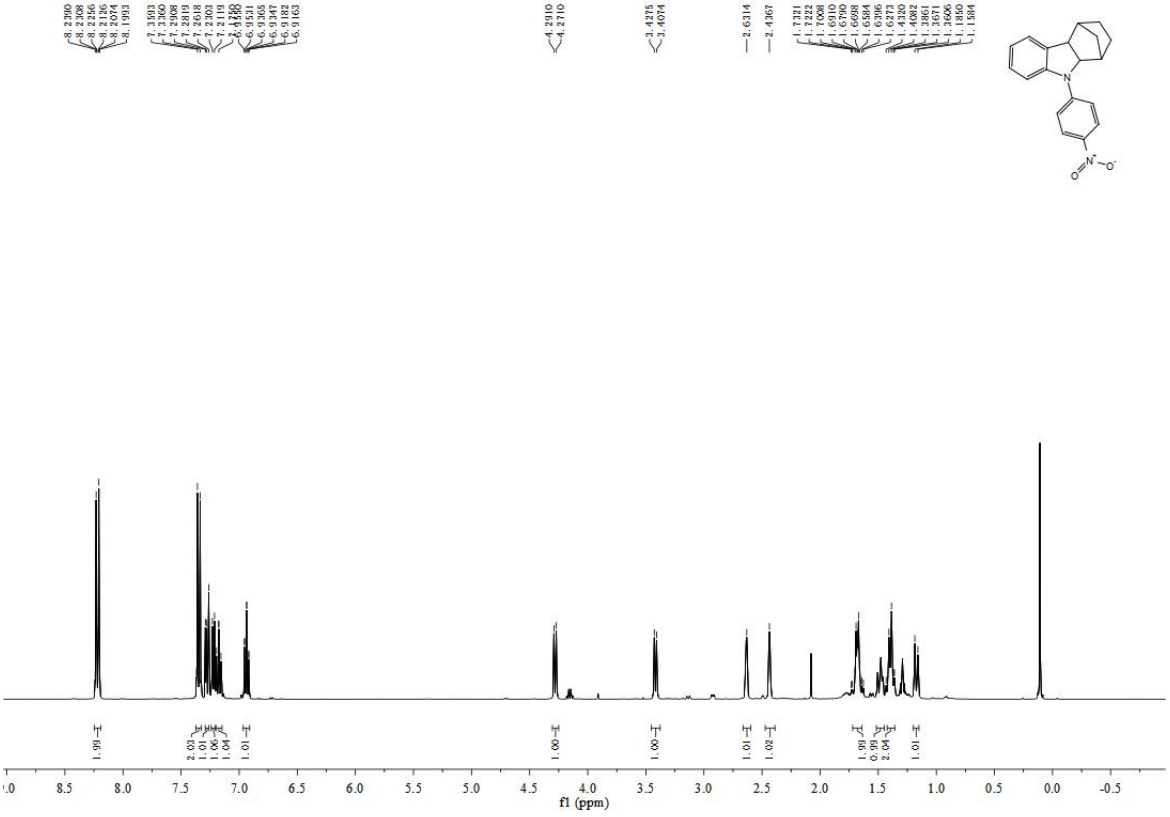
^{13}C NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**15d**)



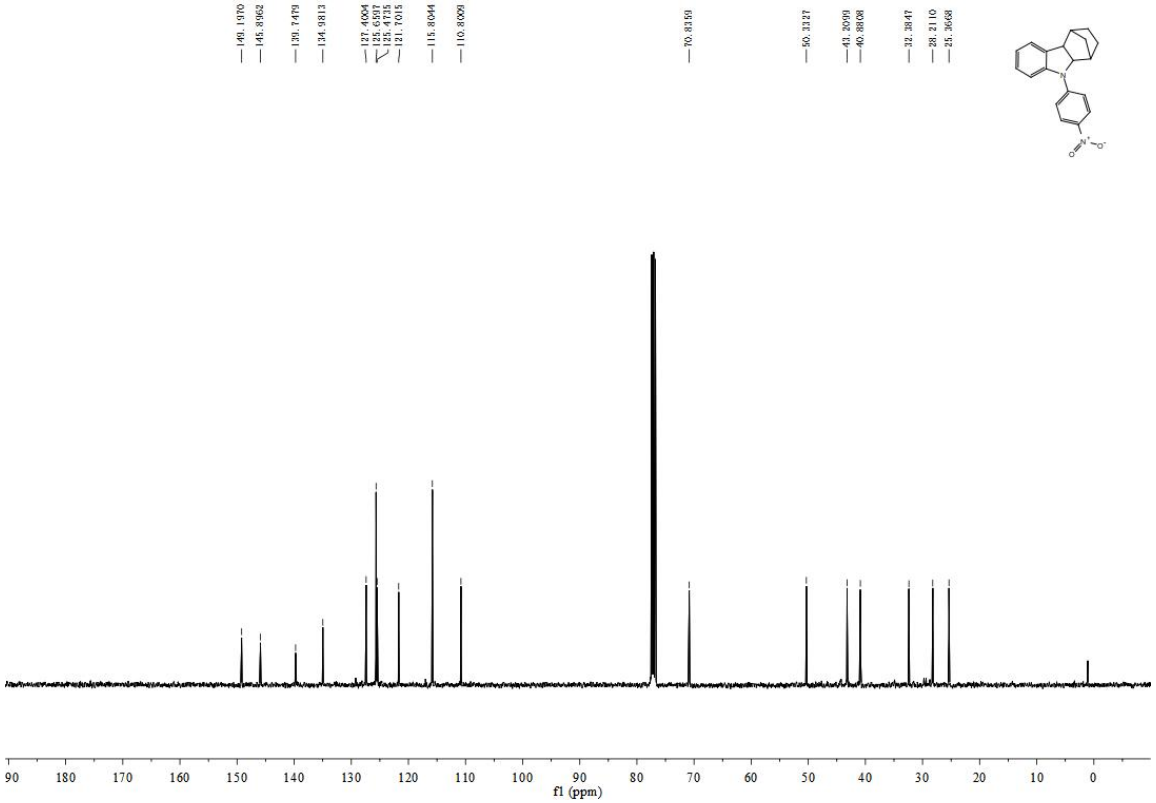
^{19}F NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**15d**)



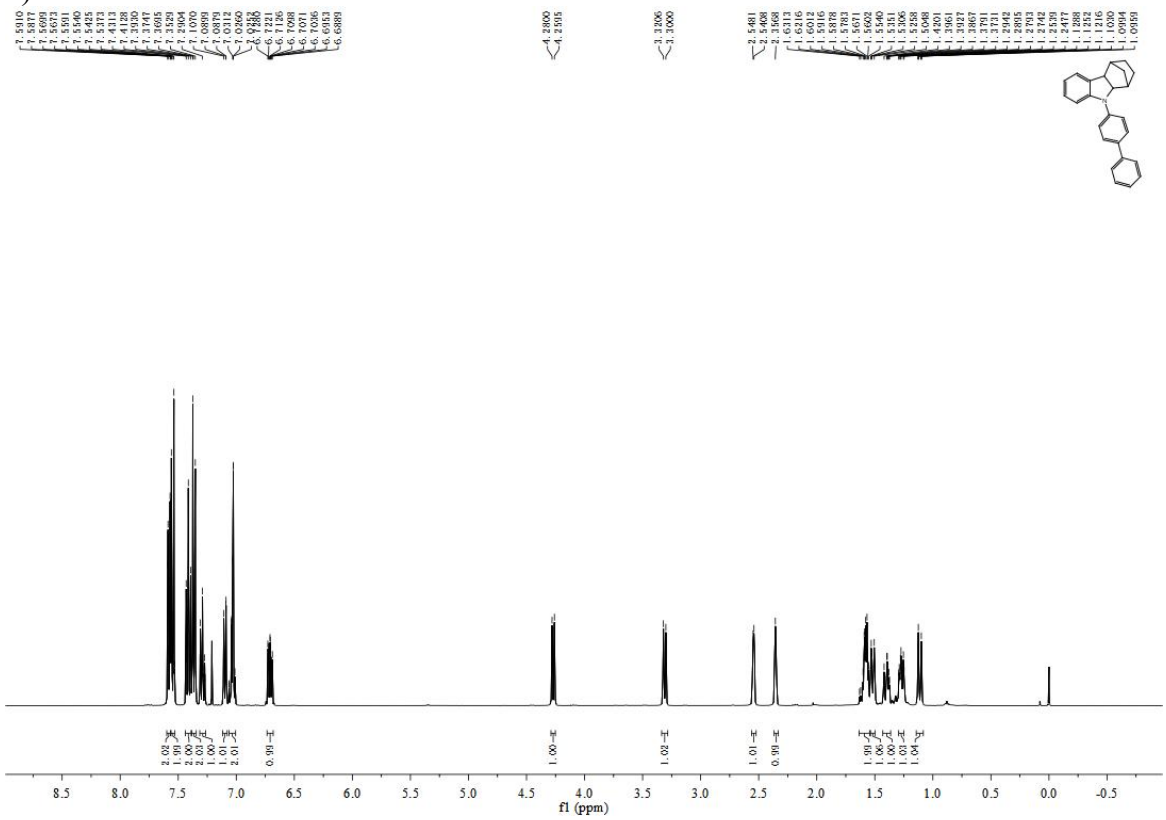
^{1}H NMR spectrum of 9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**16d**)



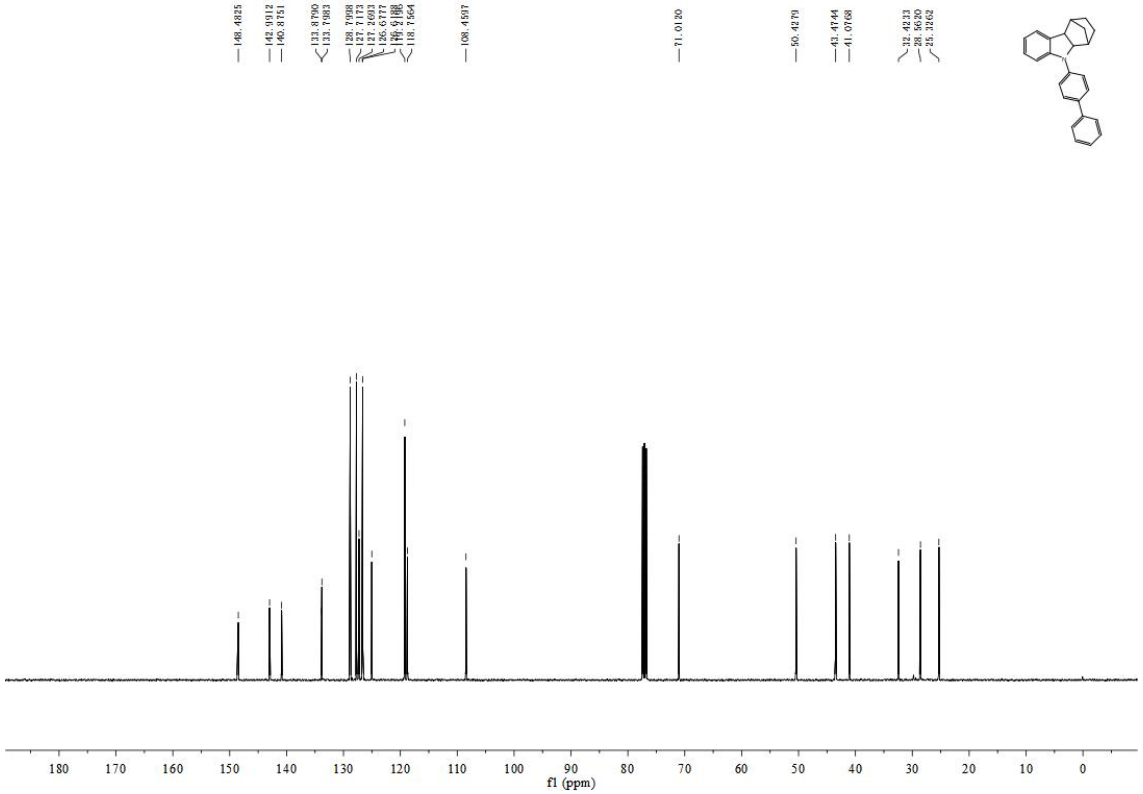
^{13}C NMR spectrum of 9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**16d**)



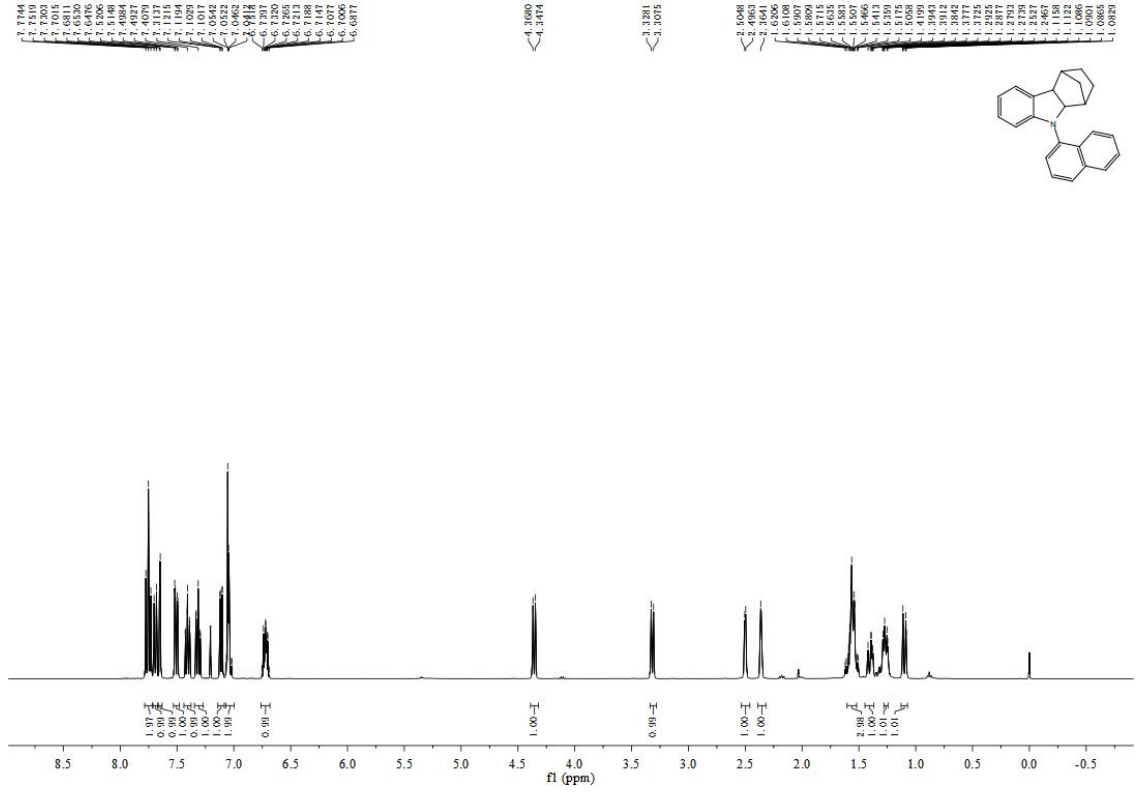
^{1}H NMR spectrum of 9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**17d**)



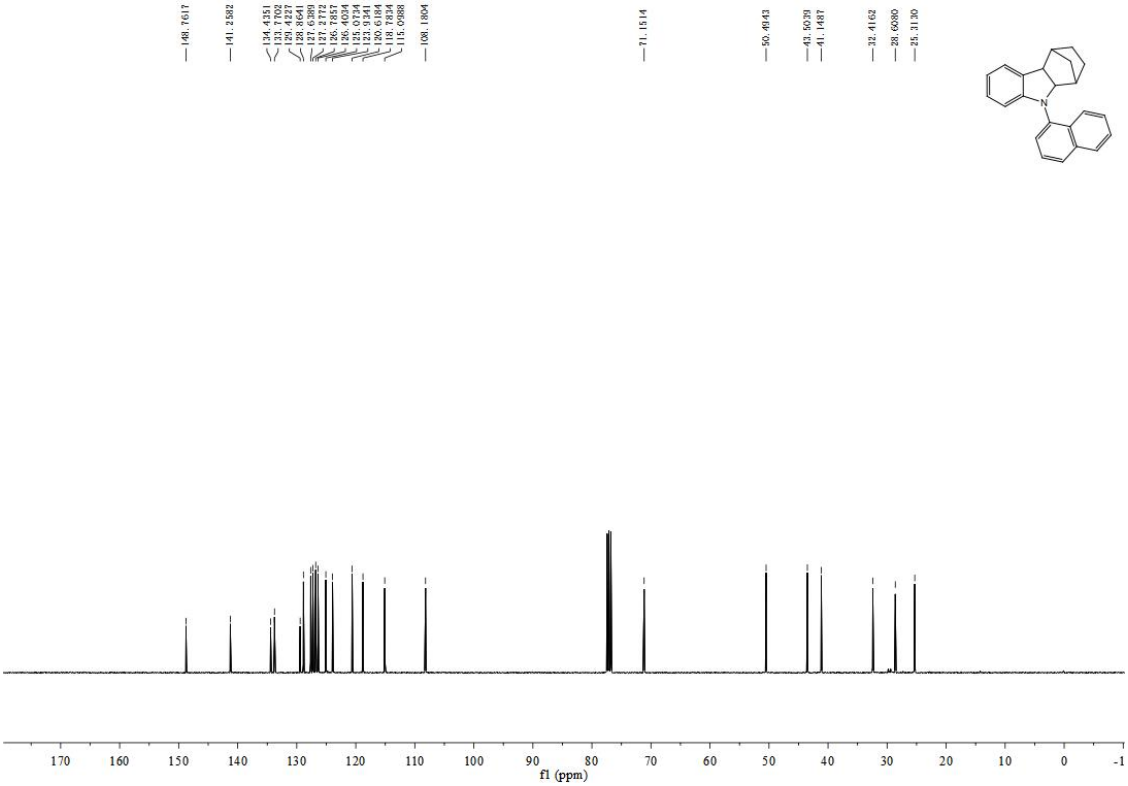
^{13}C NMR spectrum of 9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**17d**)



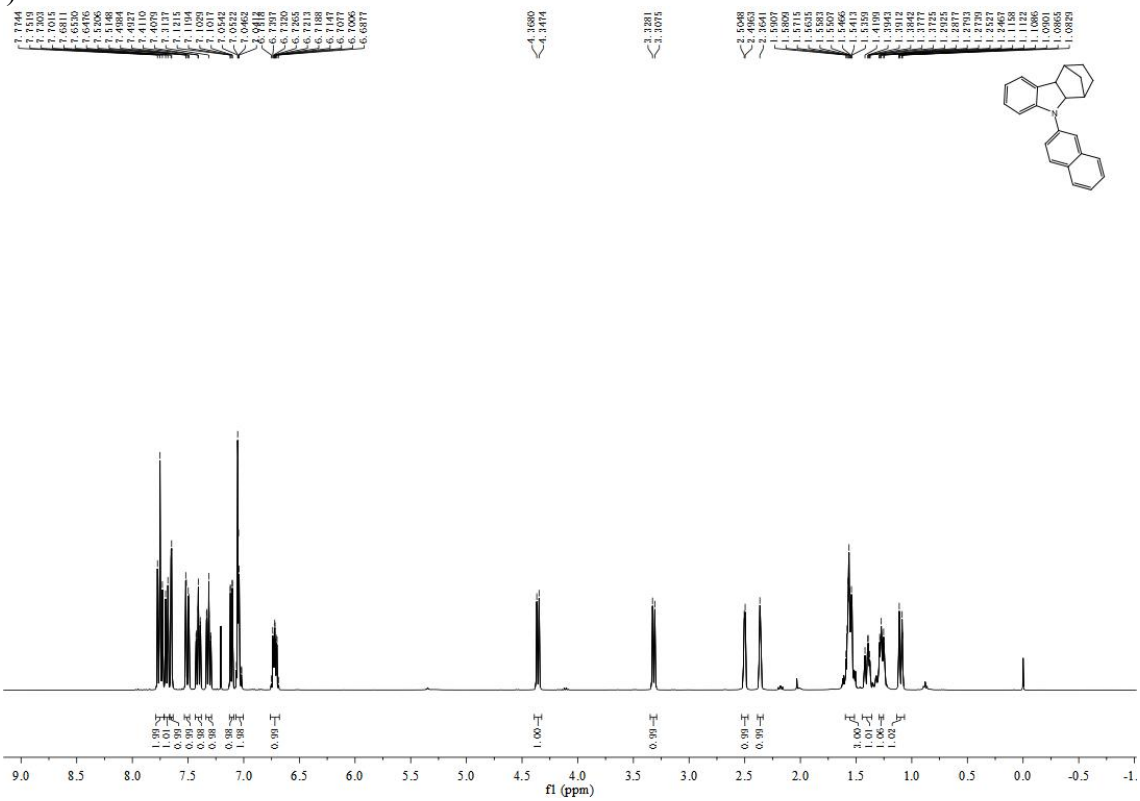
^{1}H NMR spectrum of 9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**18d**)



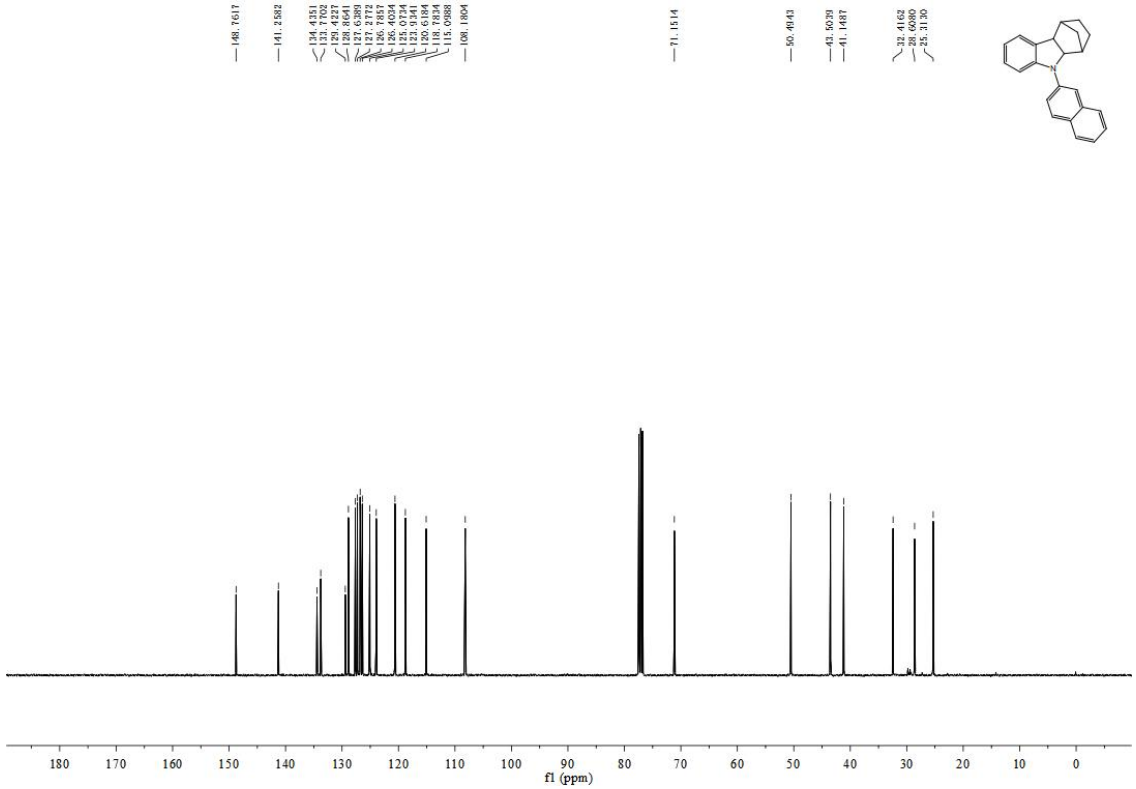
^{13}C NMR spectrum of 9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**18d**)



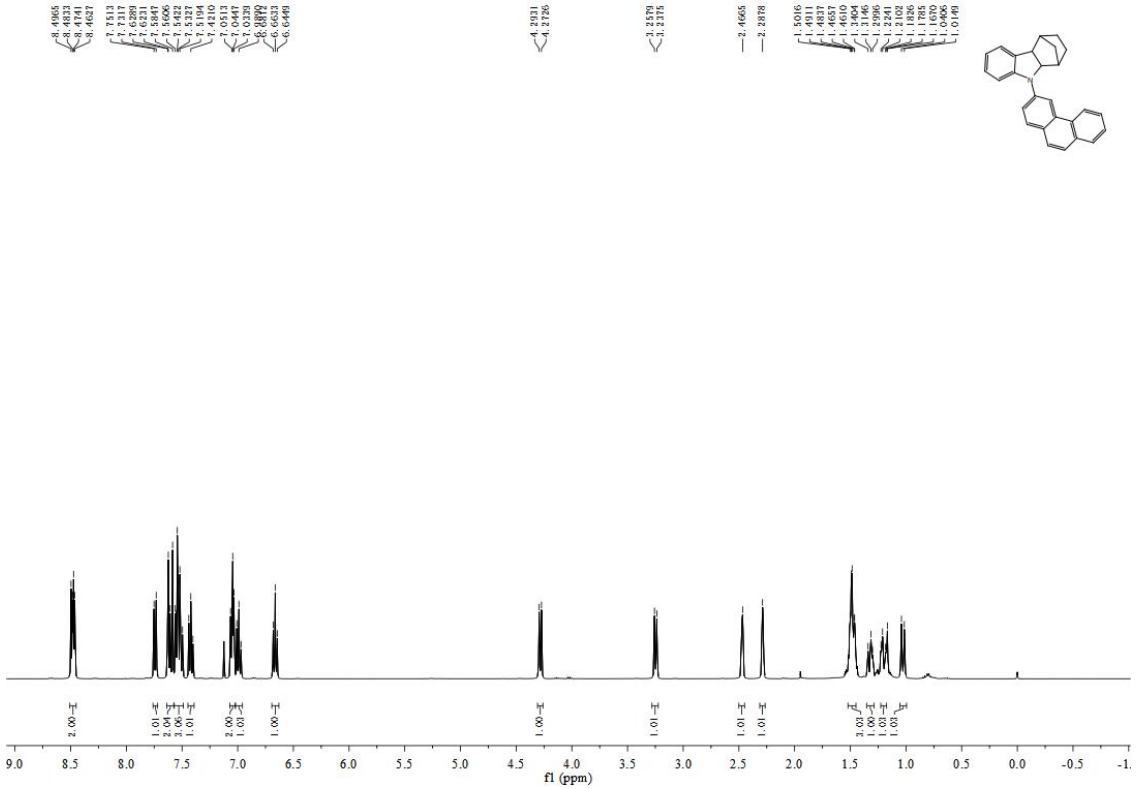
^{1}H NMR spectrum of 9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**19d**)



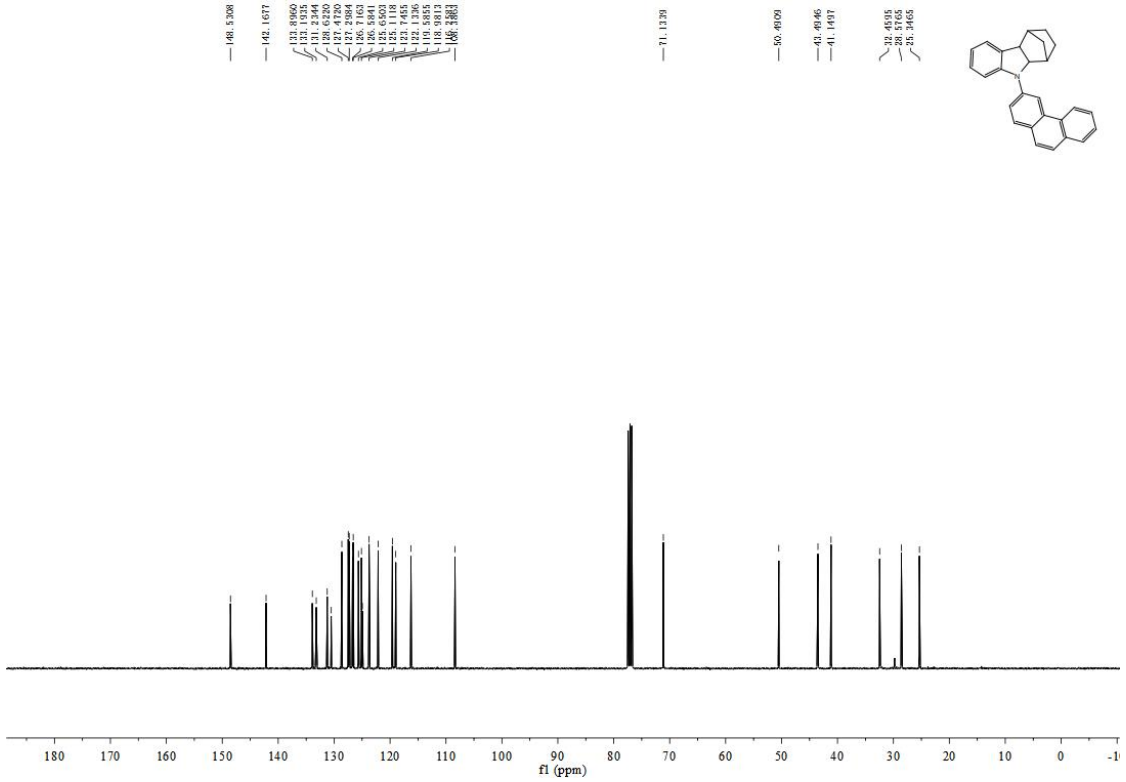
^{13}C NMR spectrum of 9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**19d**)



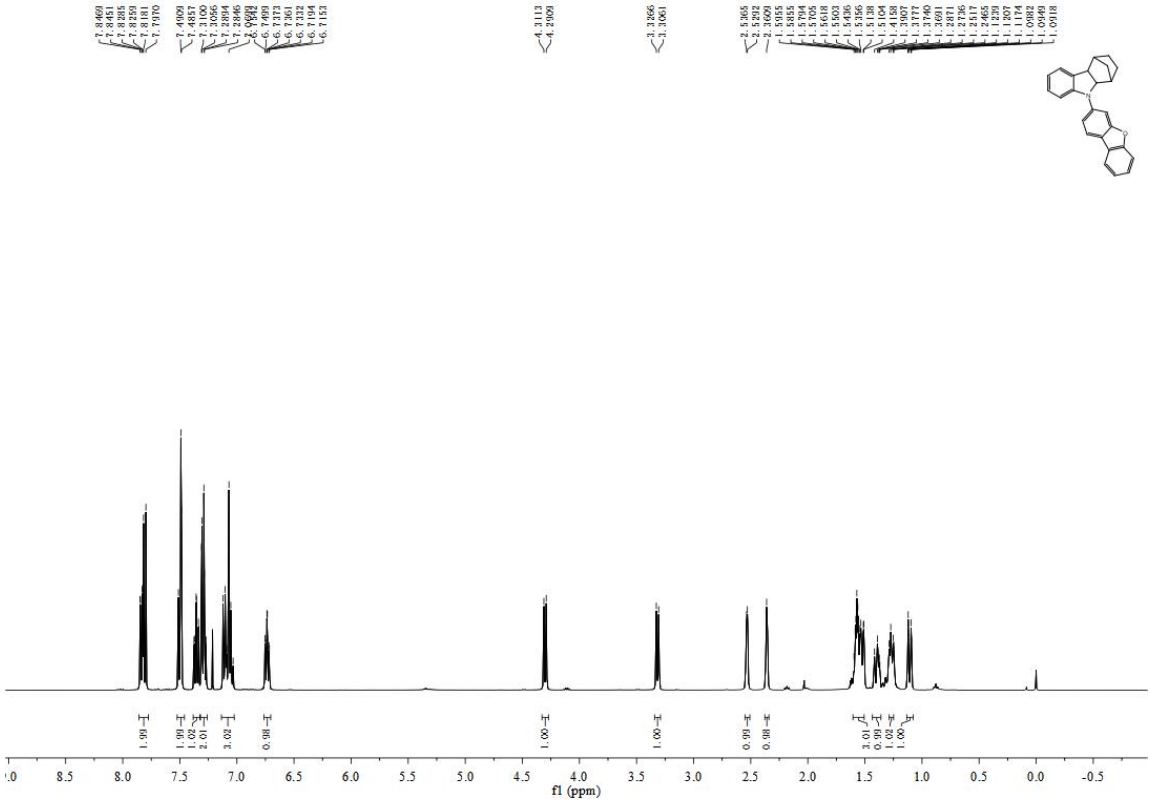
^{1}H NMR spectrum of 9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**20d**)



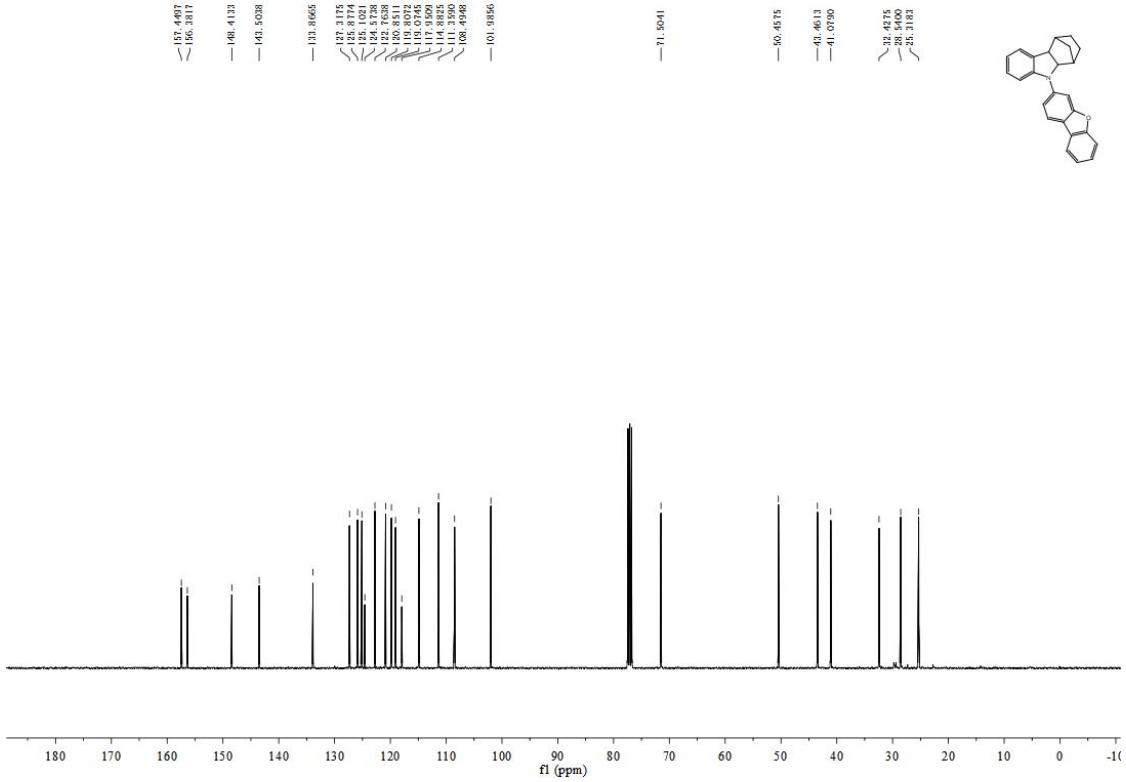
^{13}C NMR spectrum of 9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**20d**)



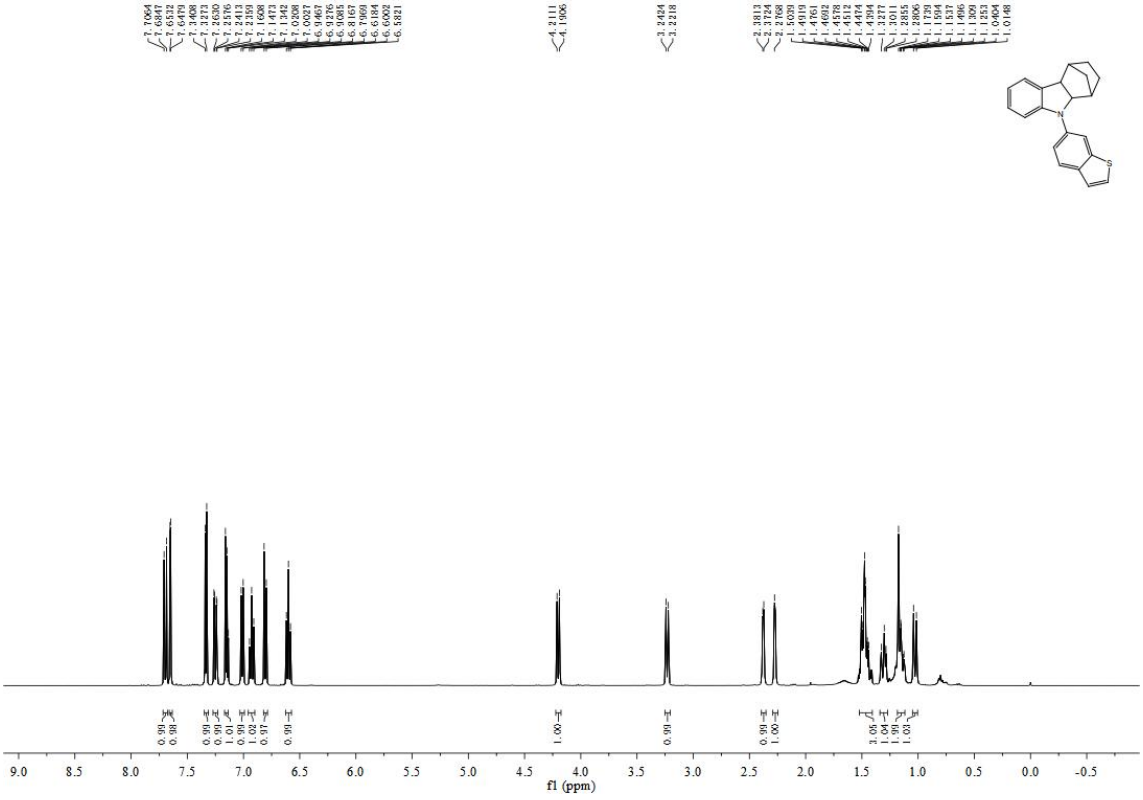
^{1}H NMR spectrum of 9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**21d**)



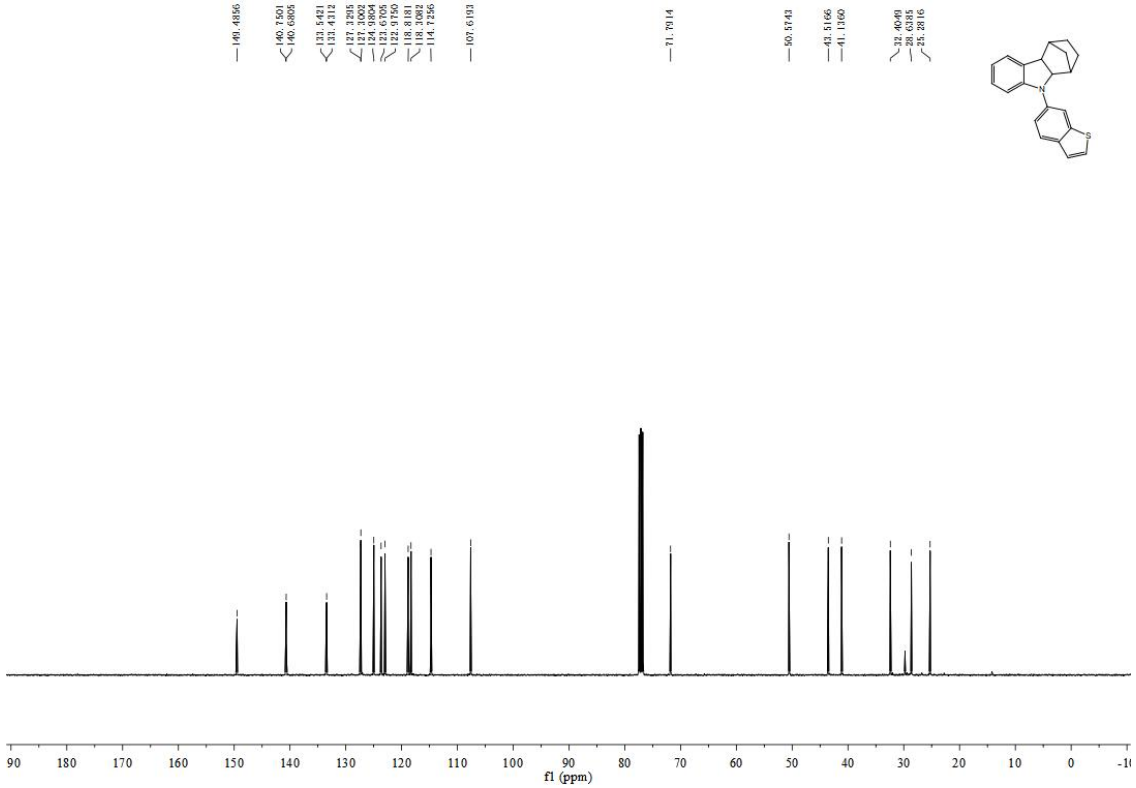
^{13}C NMR spectrum of 9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**21d**)



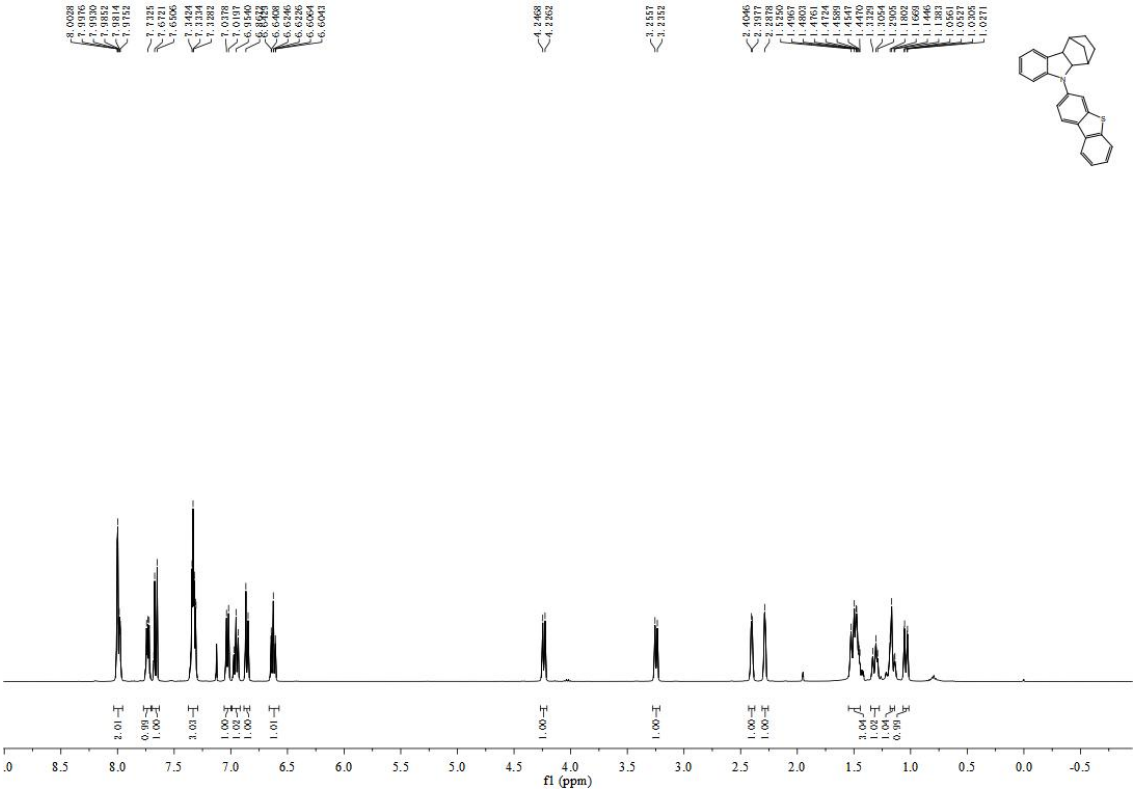
^{1}H NMR spectrum of 9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**22d**)



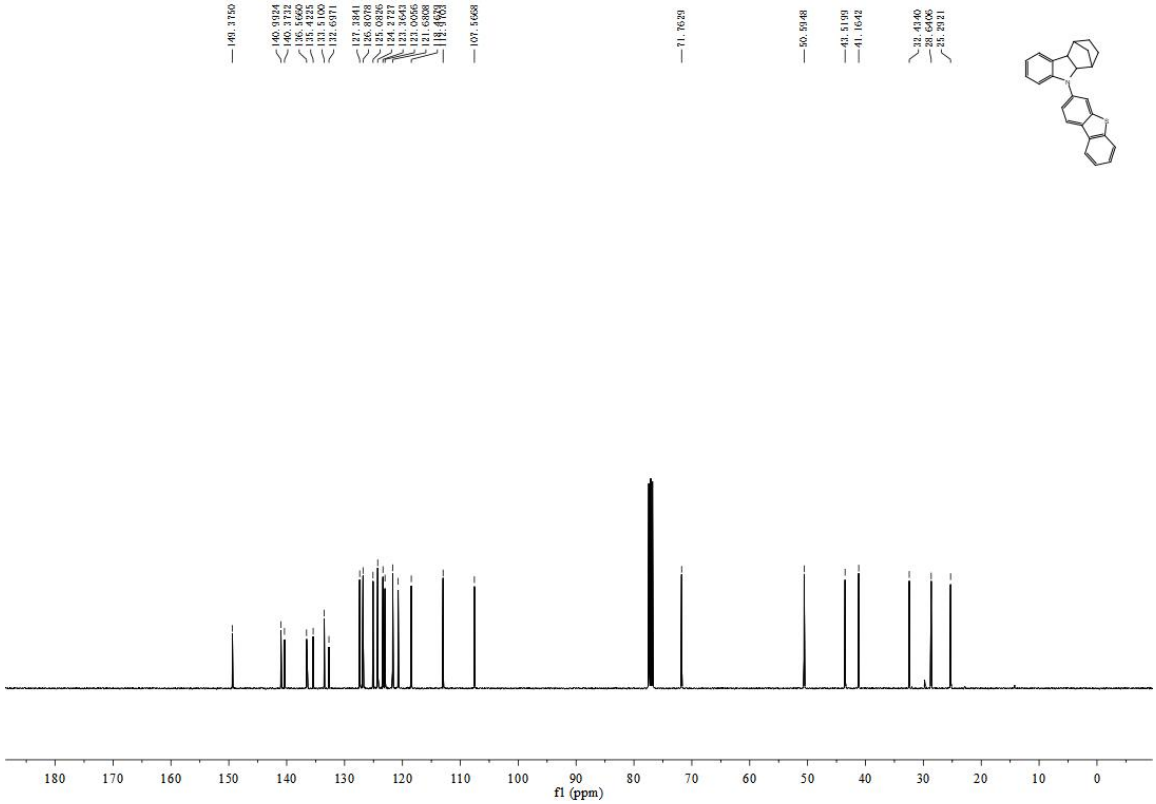
^{13}C NMR spectrum of 9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**22d**)



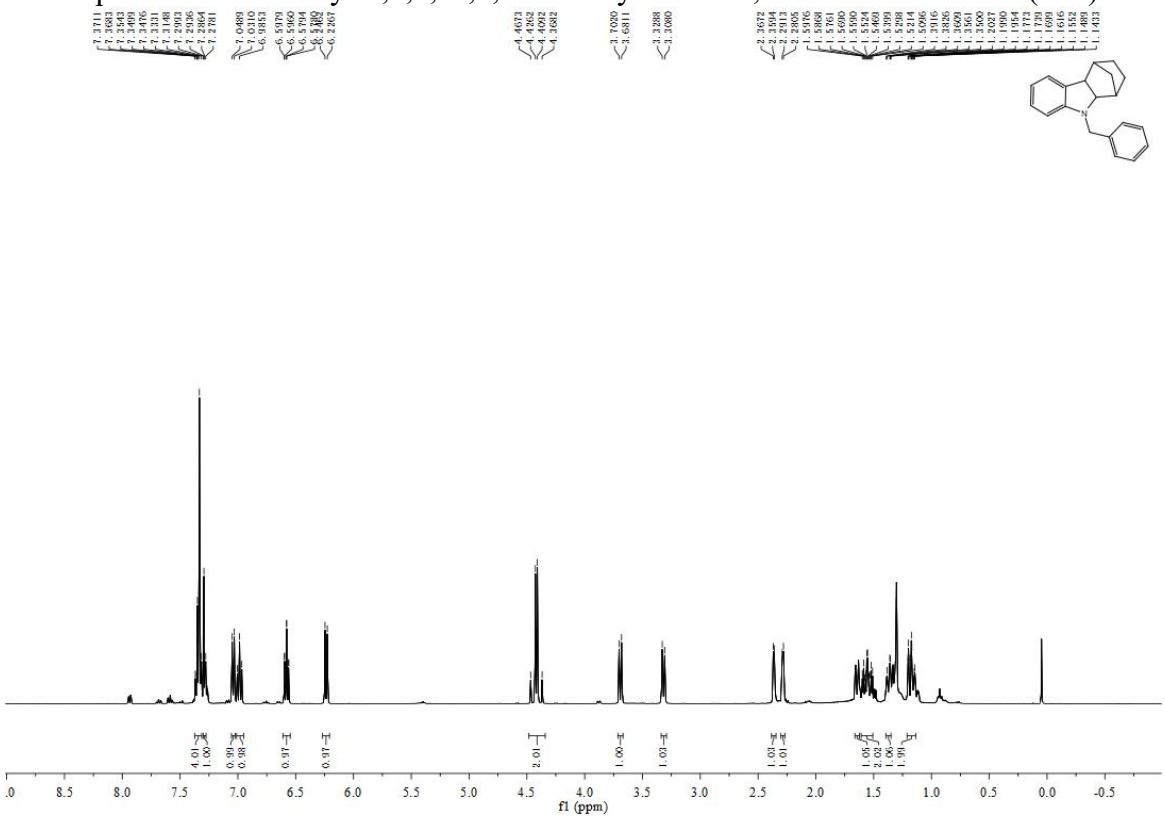
^{1}H NMR spectrum of 9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**23d**)



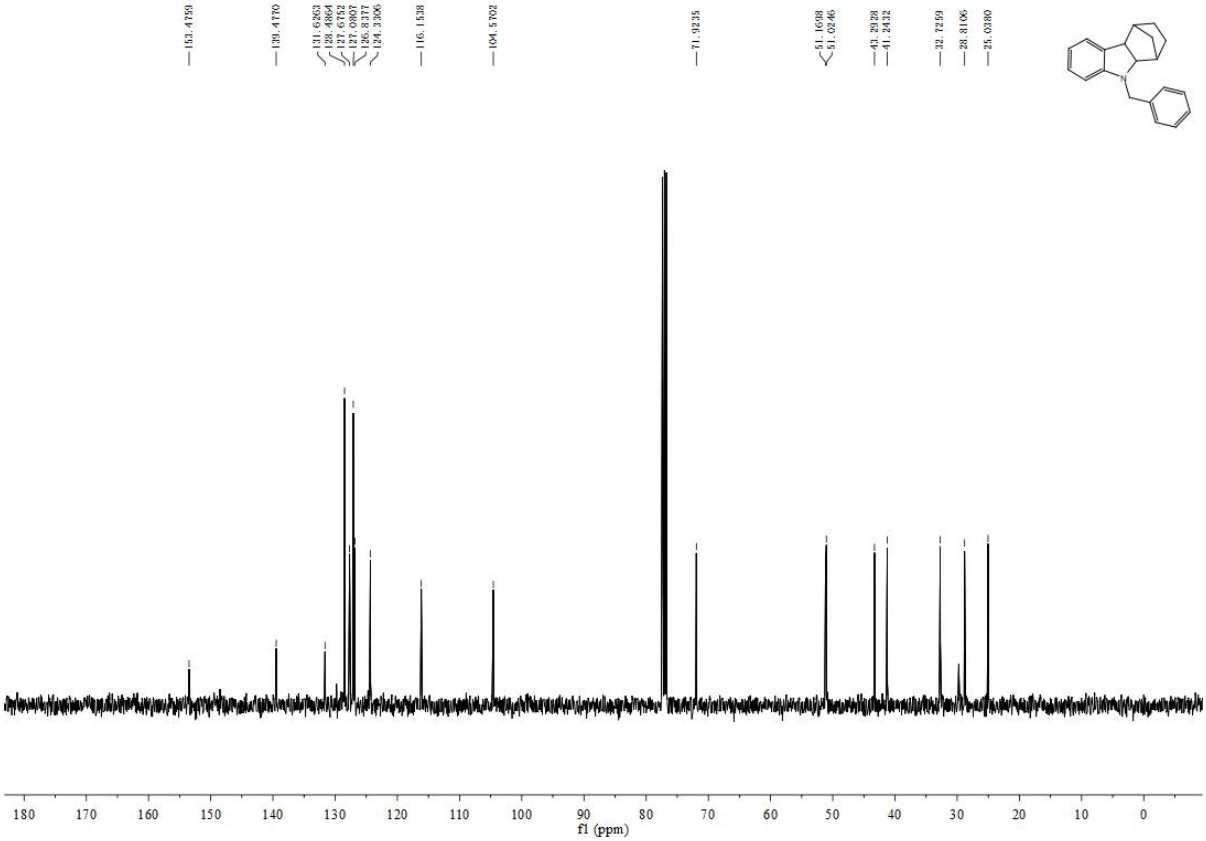
^{13}C NMR spectrum of 9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**23d**)



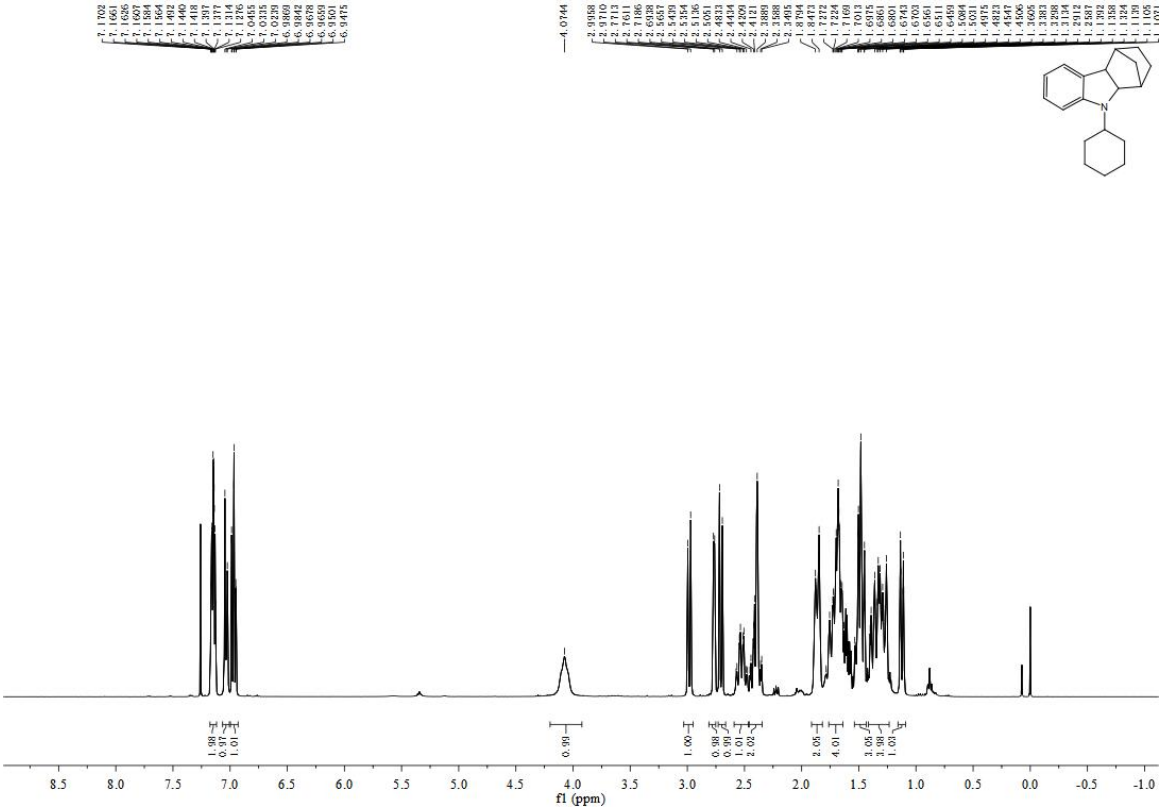
^{1}H NMR spectrum of 9-benzyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**24d**)



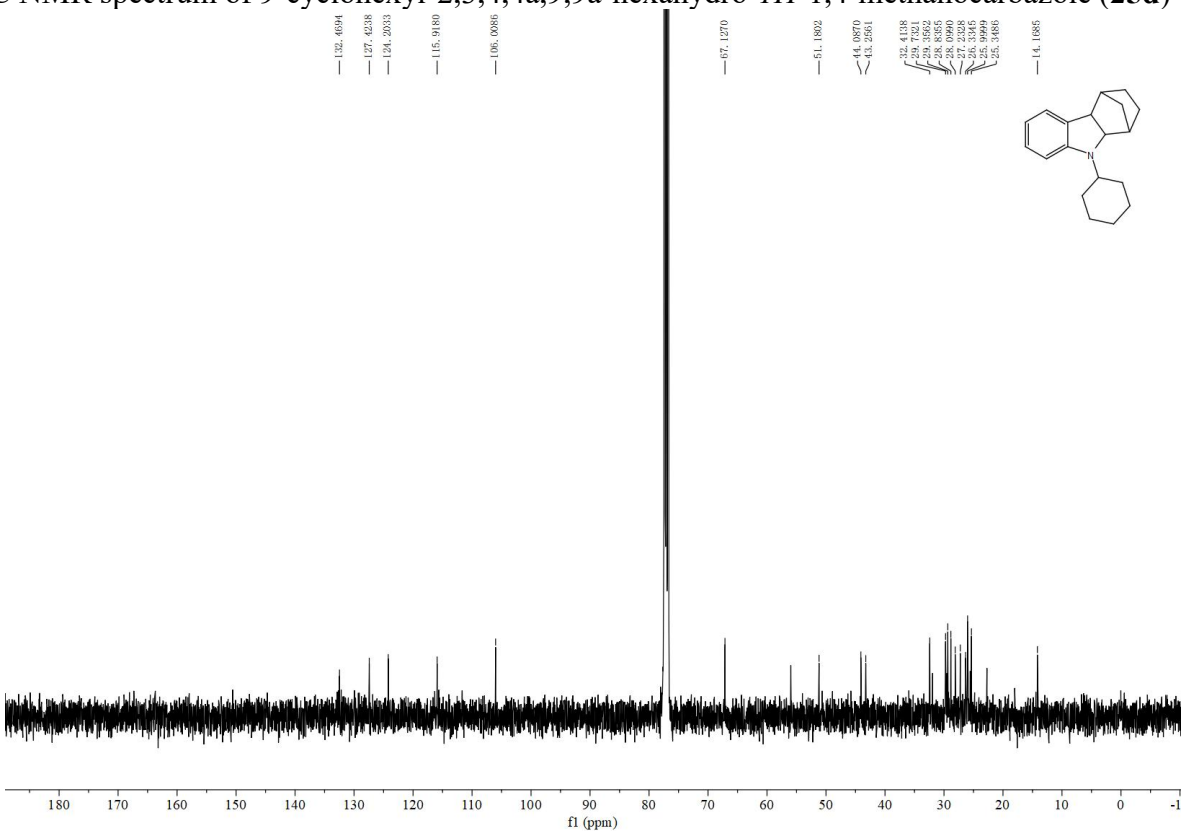
^{13}C NMR spectrum of 9-benzyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**24d**)



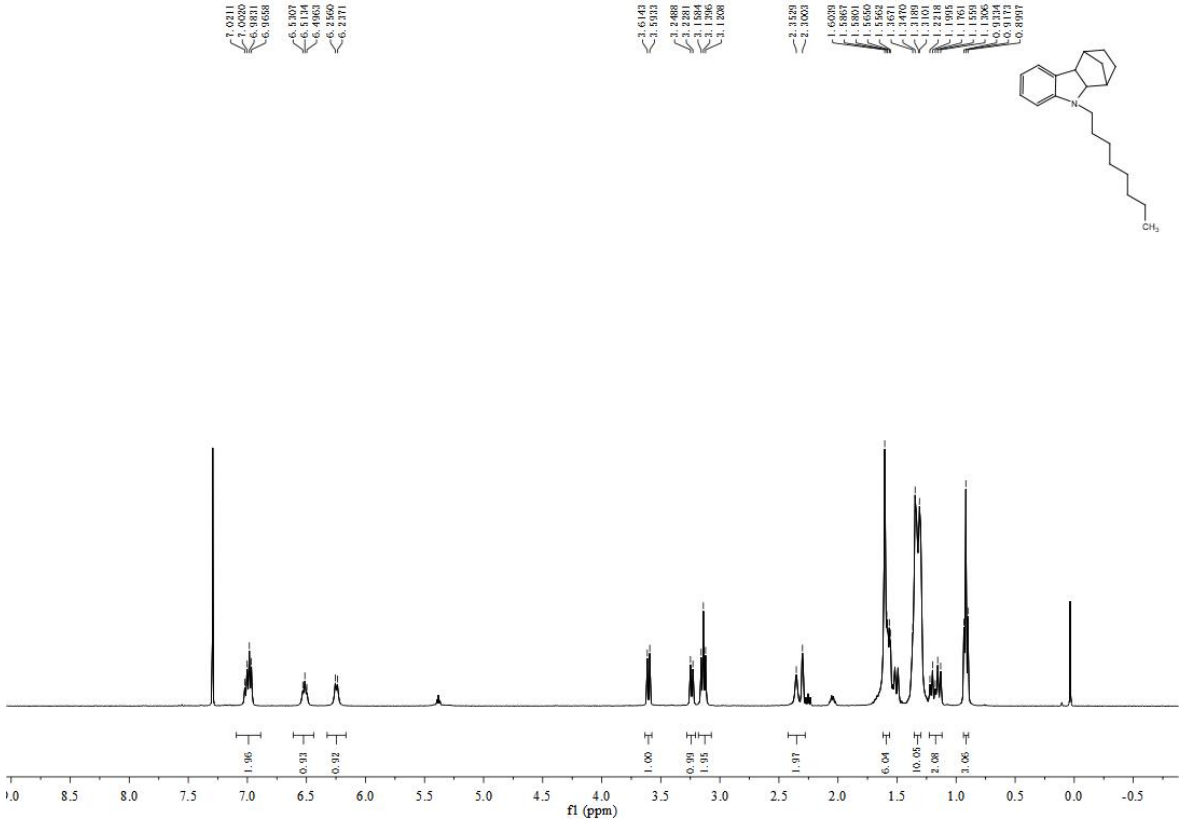
^{1}H NMR spectrum of 9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**25d**)



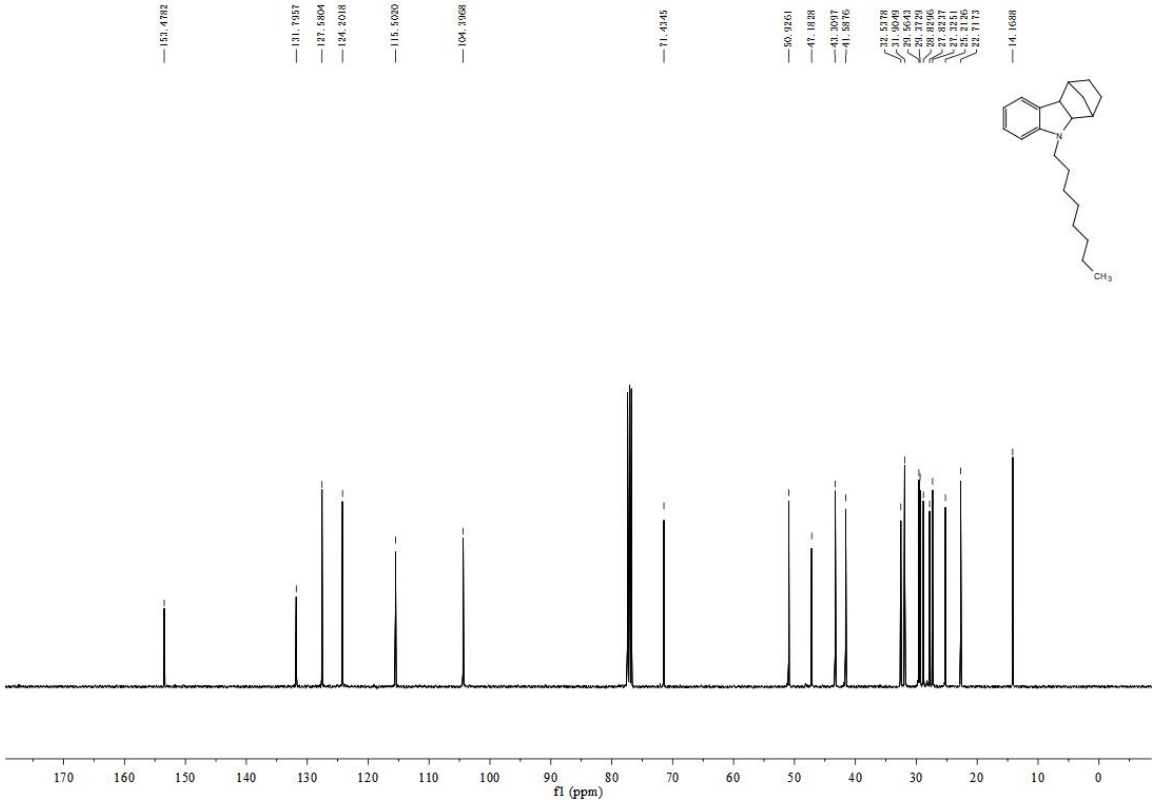
^{13}C NMR spectrum of 9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**25d**)



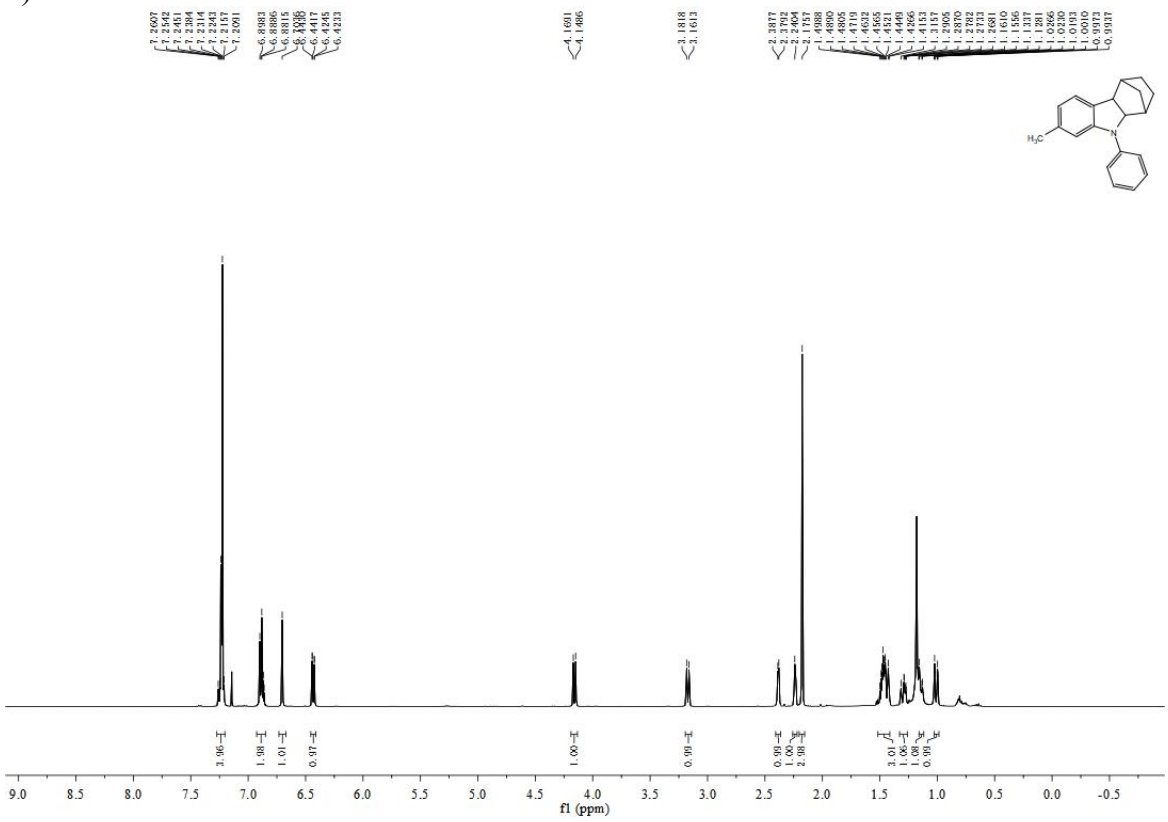
^{1}H NMR spectrum of 9-octyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**26d**)



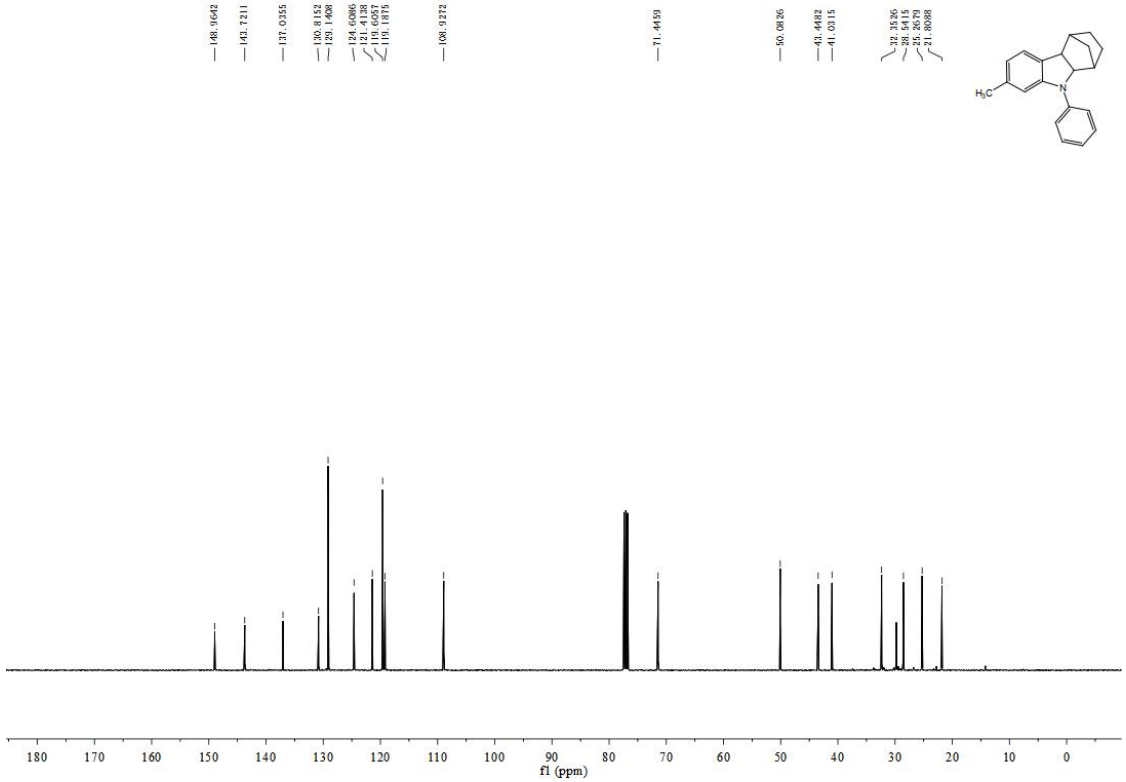
^{13}C NMR spectrum of 9-octyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**26d**)



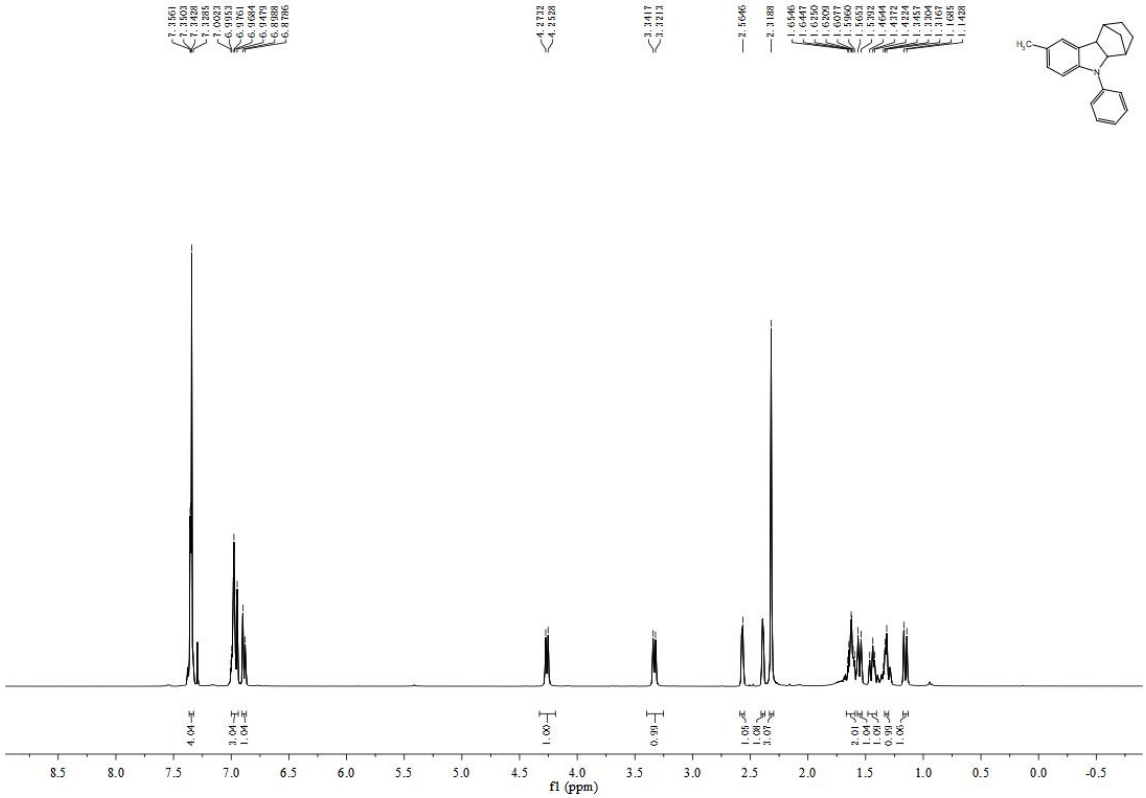
^{1}H NMR spectrum of 7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**27d**)



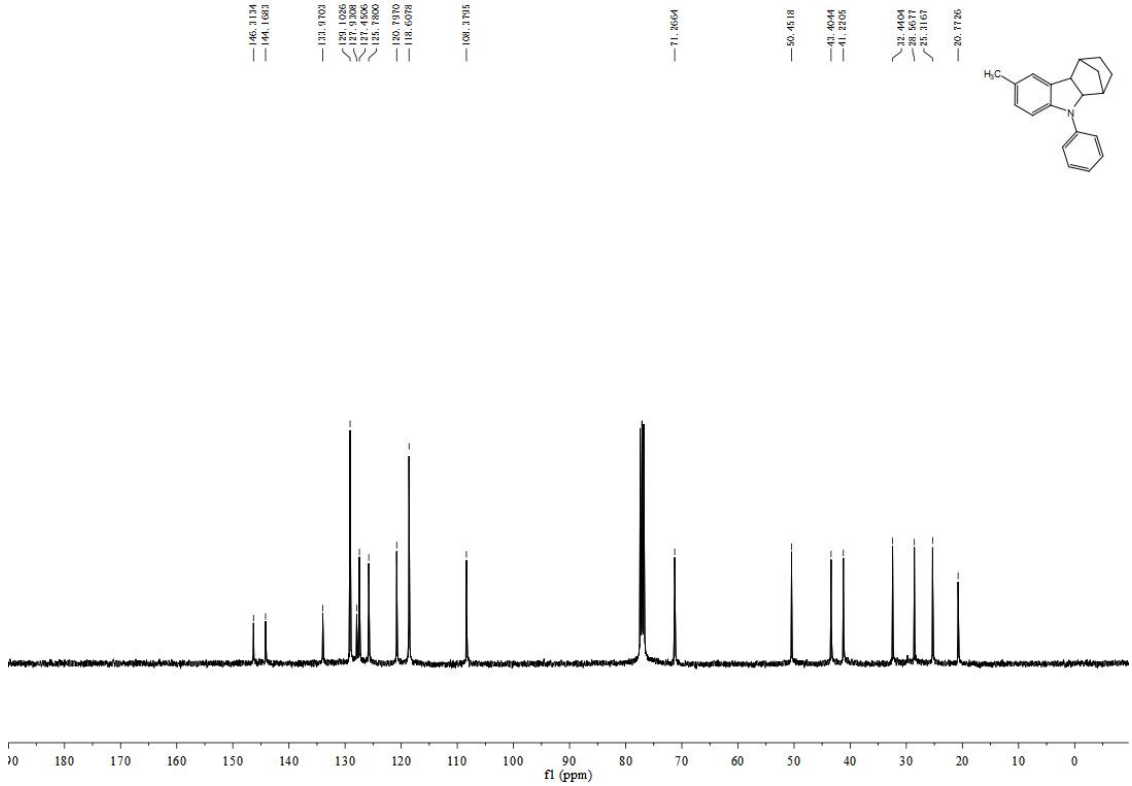
^{13}C NMR spectrum of 7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**27d**)



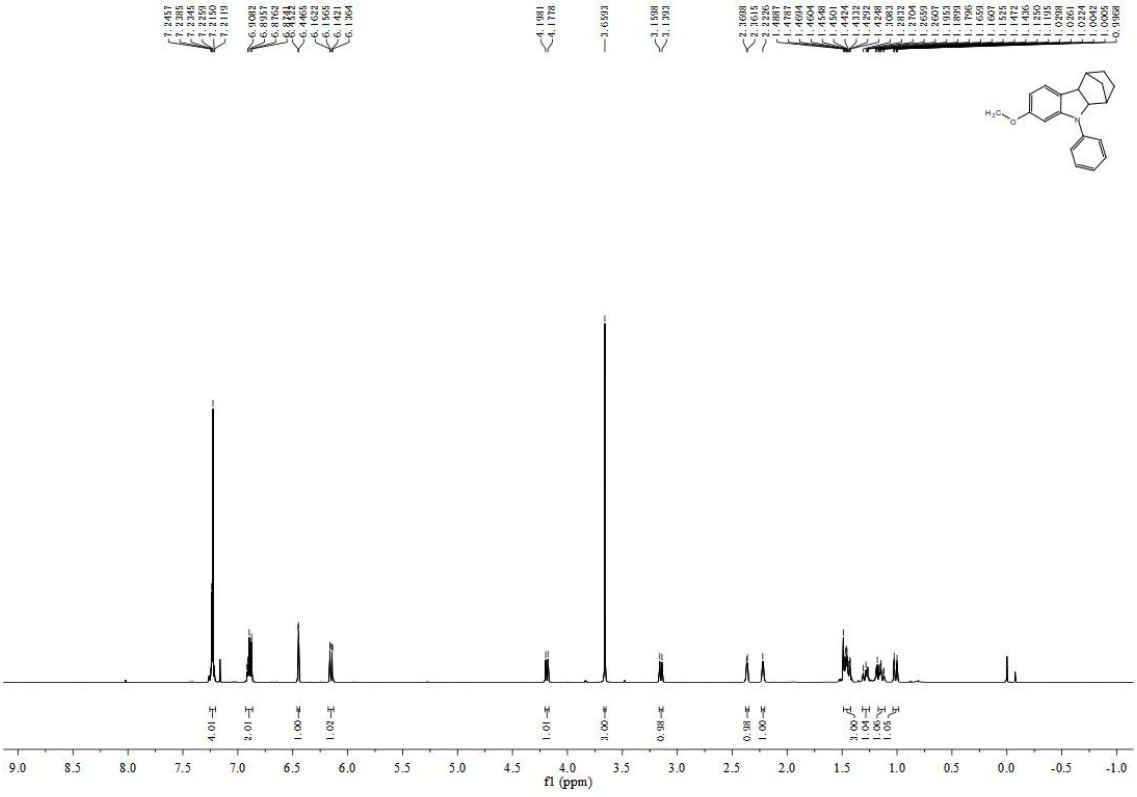
^{1}H NMR spectrum of 6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**28d**)



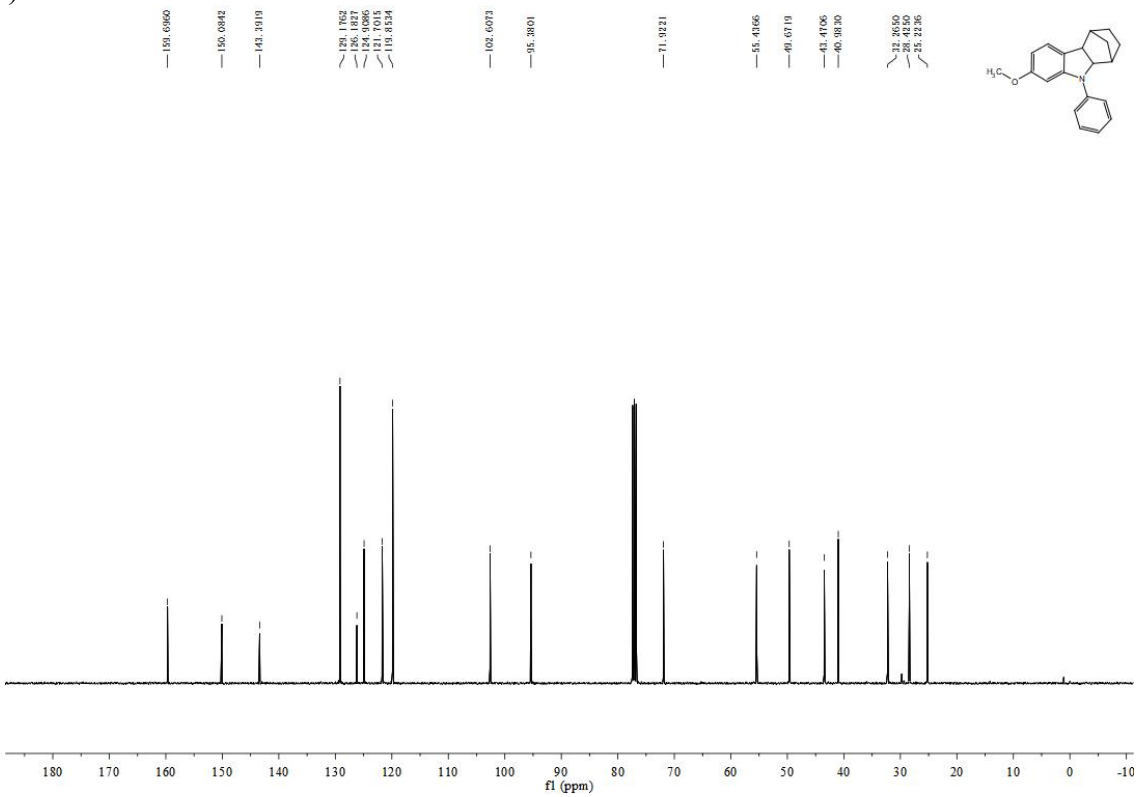
^{13}C NMR spectrum of 6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**28d**)



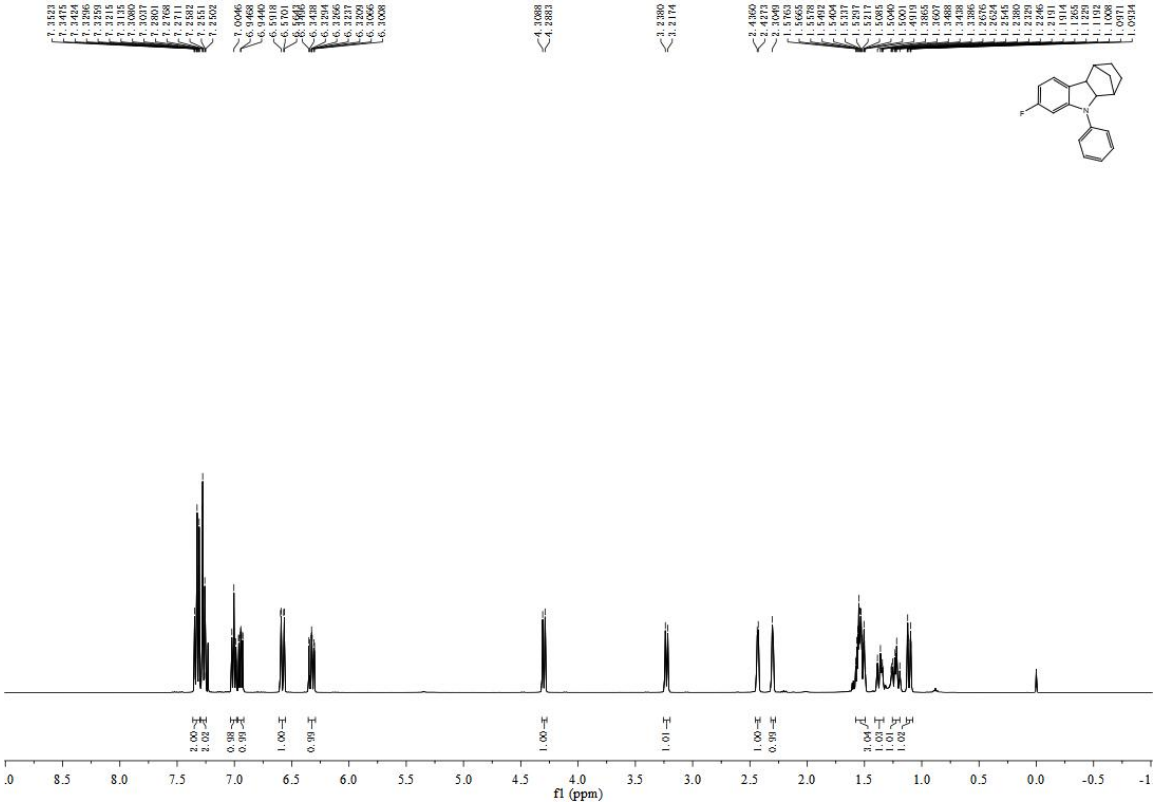
^{1}H NMR spectrum of 7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**29d**)



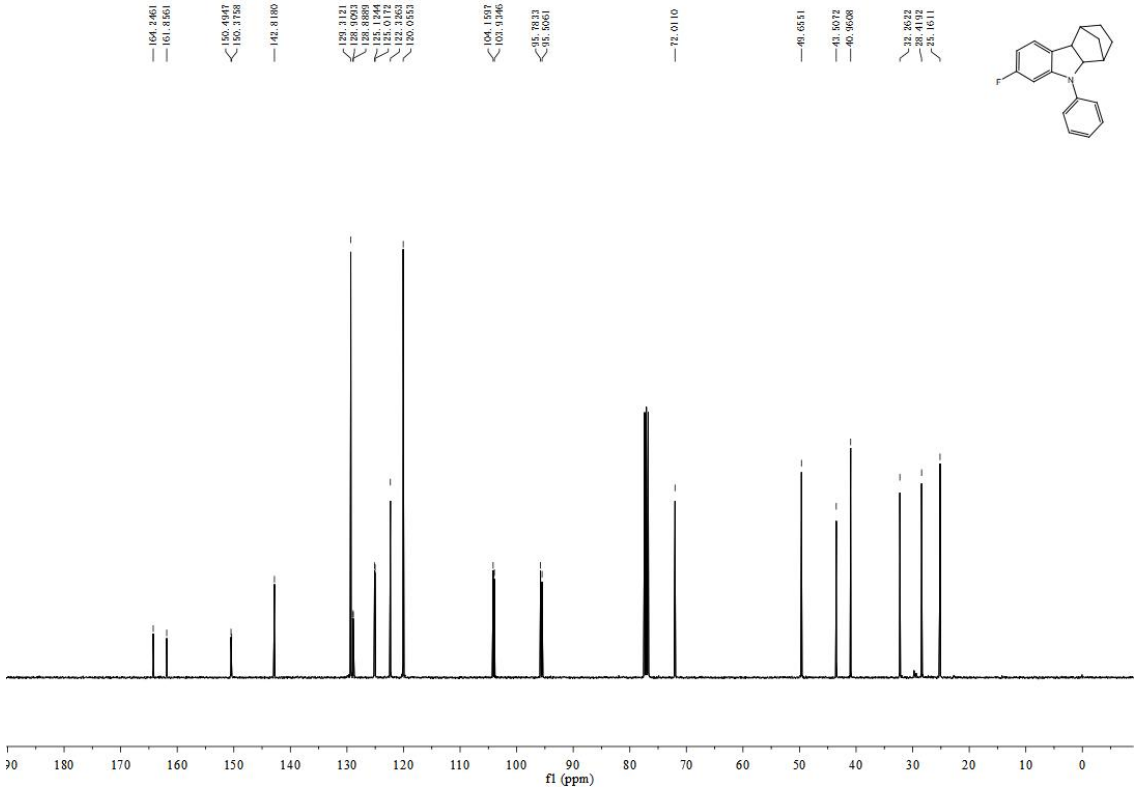
^{13}C NMR spectrum of 7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**29d**)



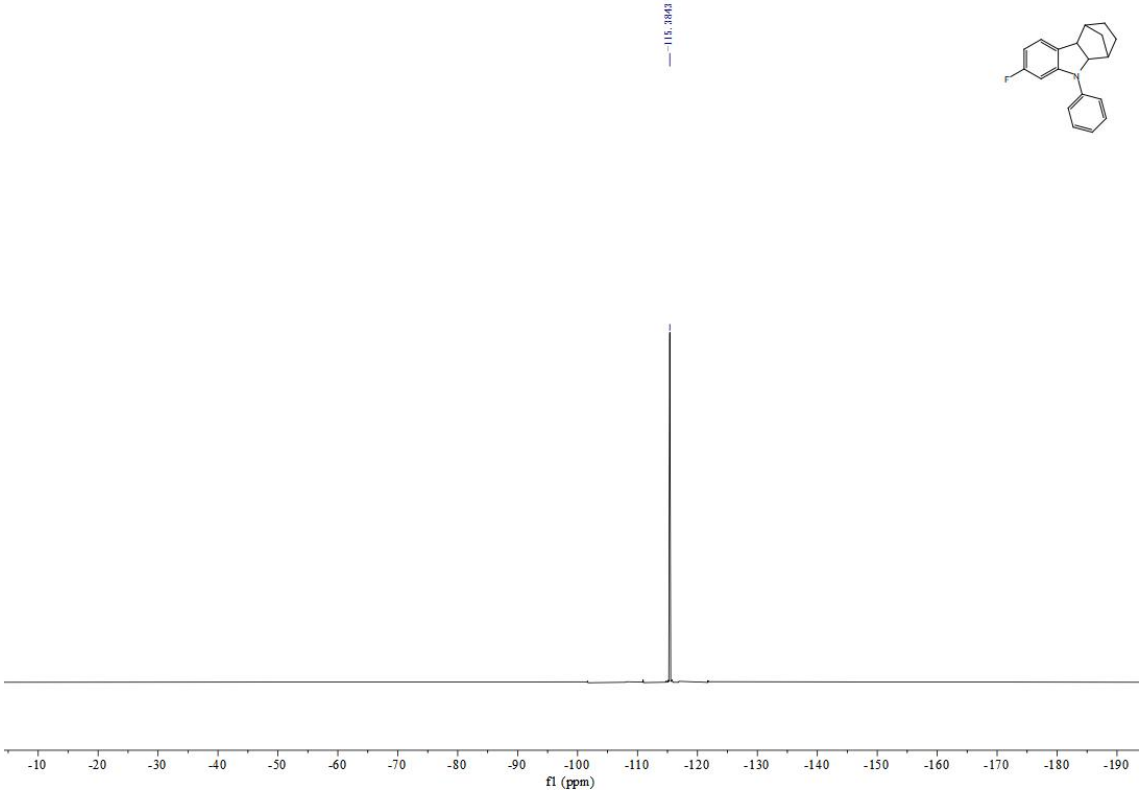
^{1}H NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**30d**)



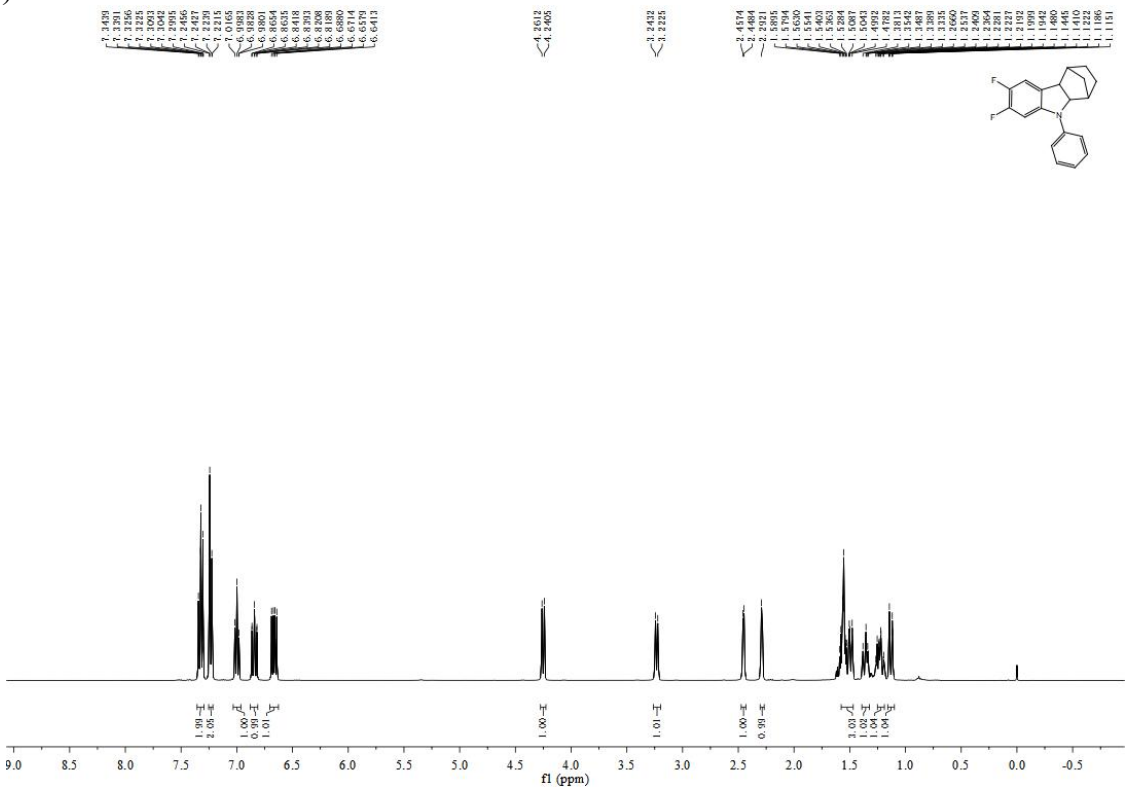
^{13}C NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**30d**)



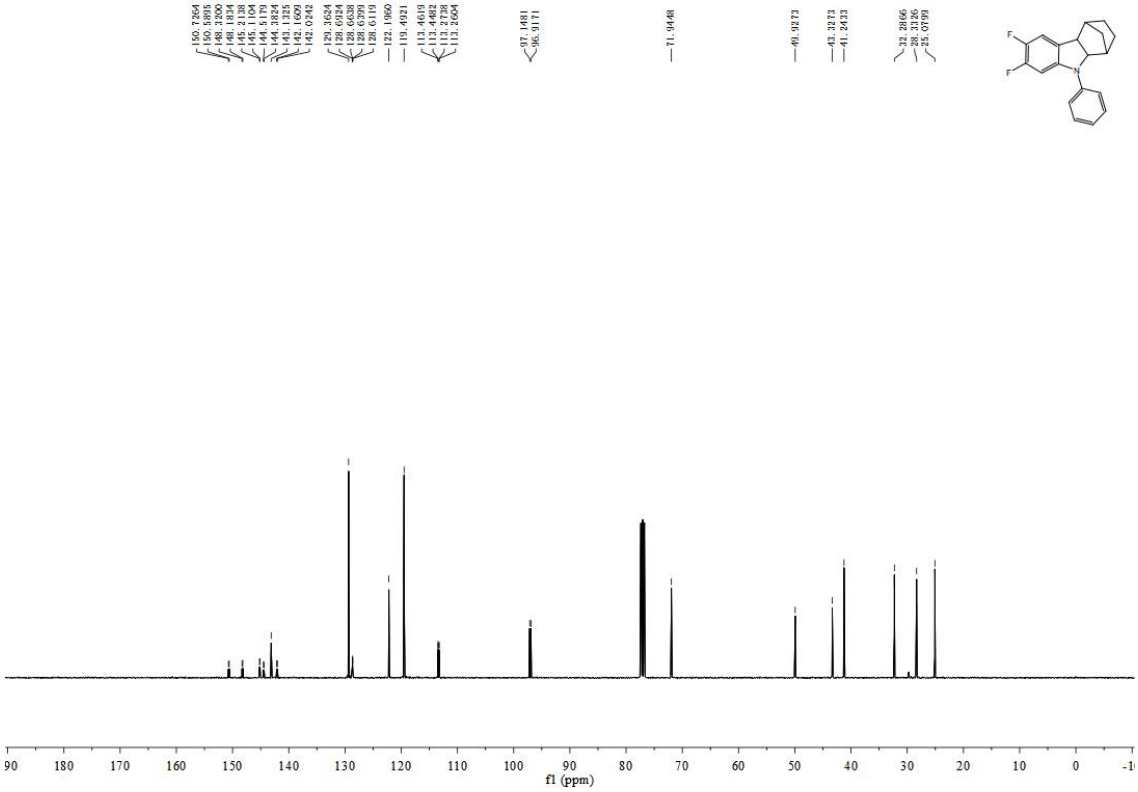
^{19}F NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**30d**)



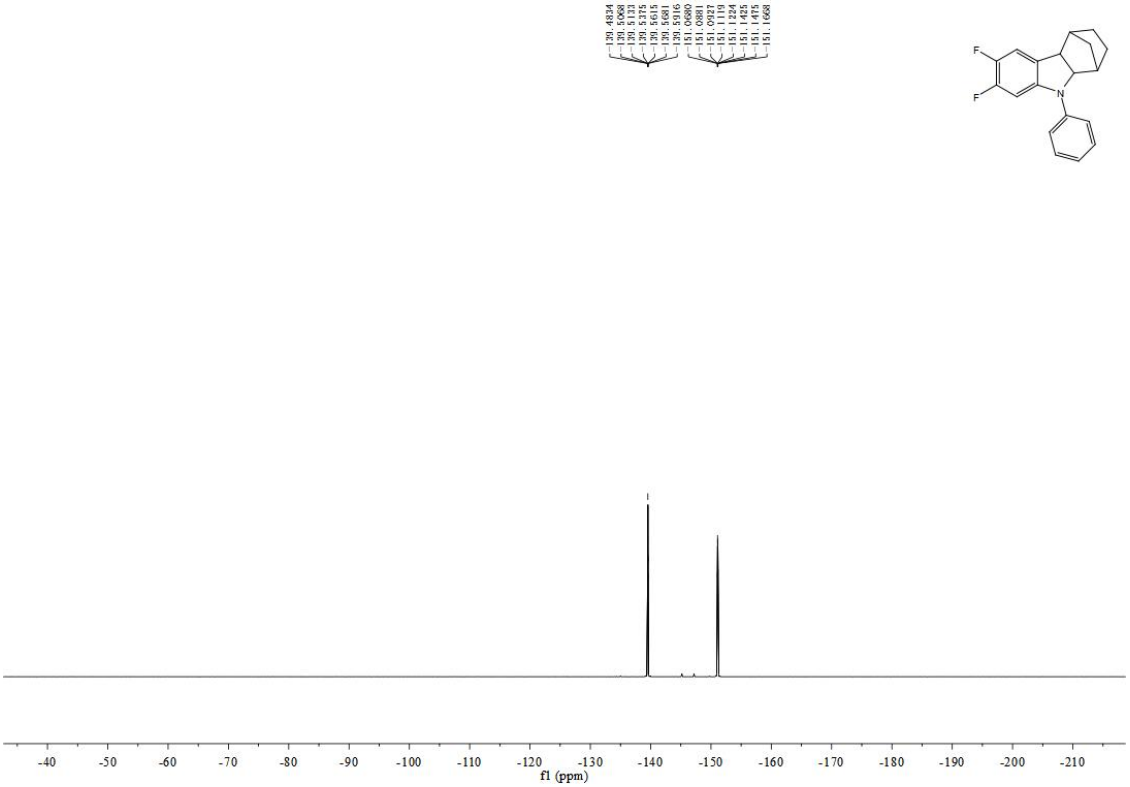
^{1}H NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**31d**)



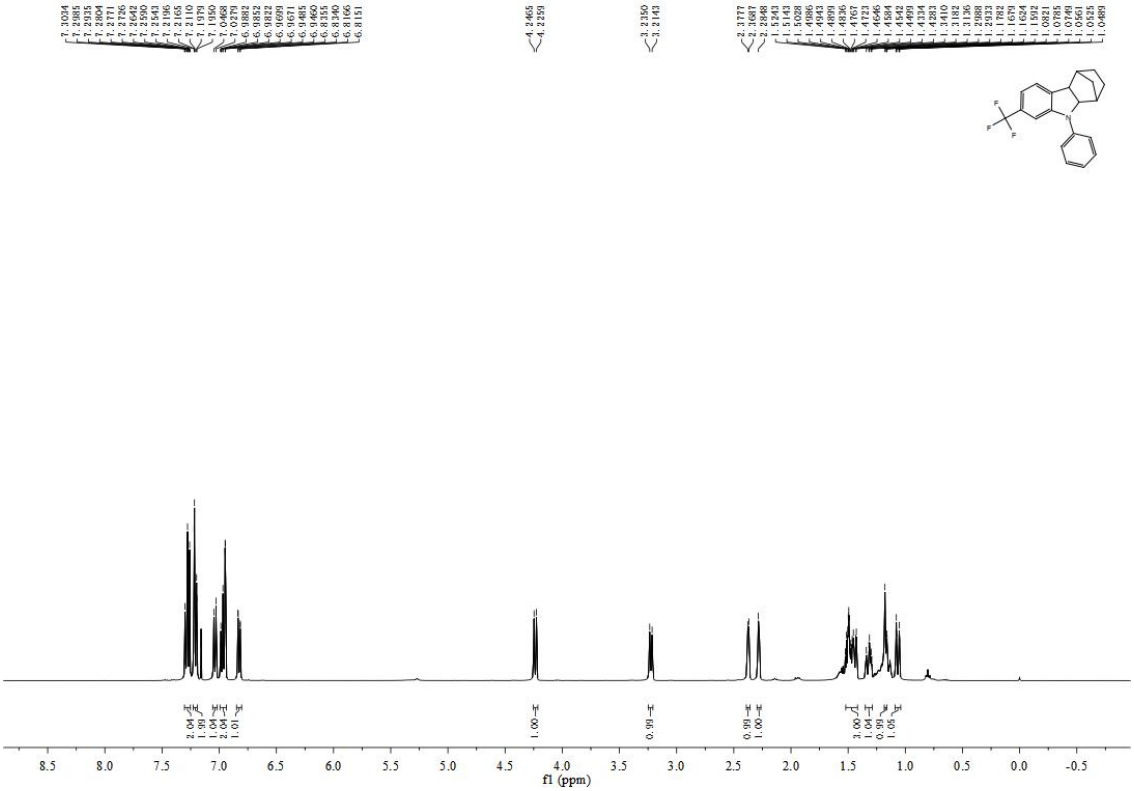
^{13}C NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**31d**)



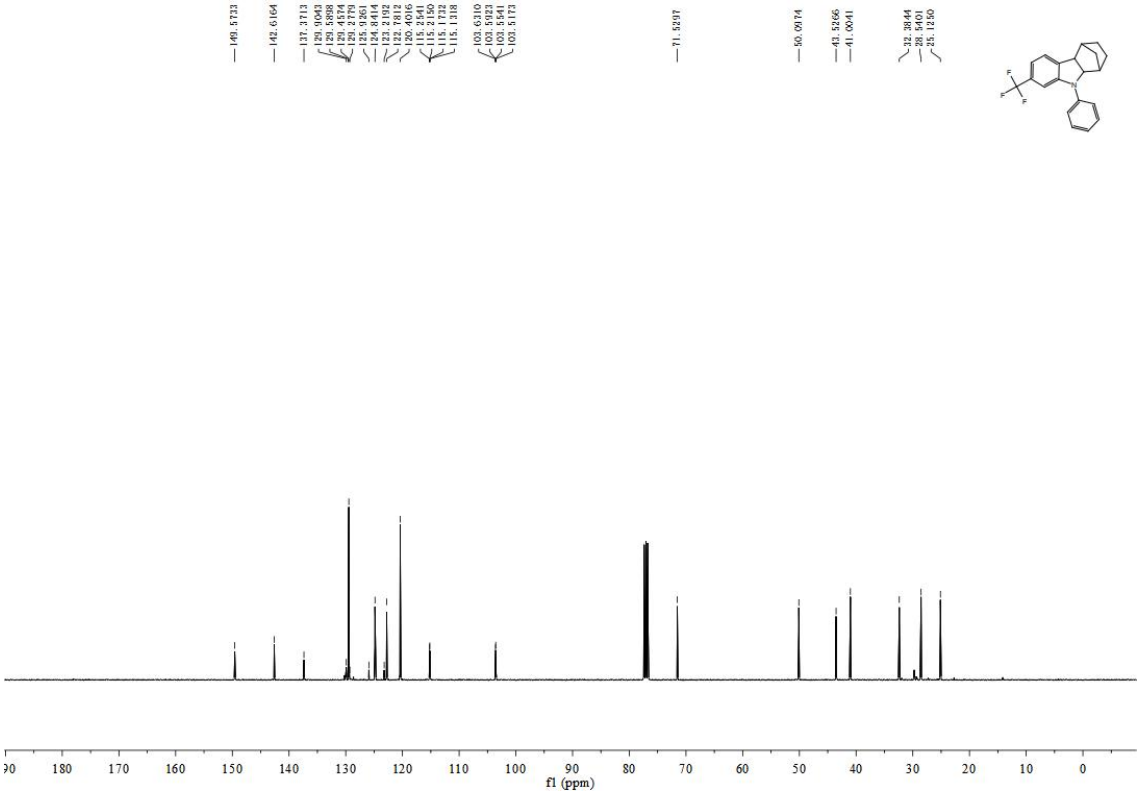
^{19}F NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**31d**)



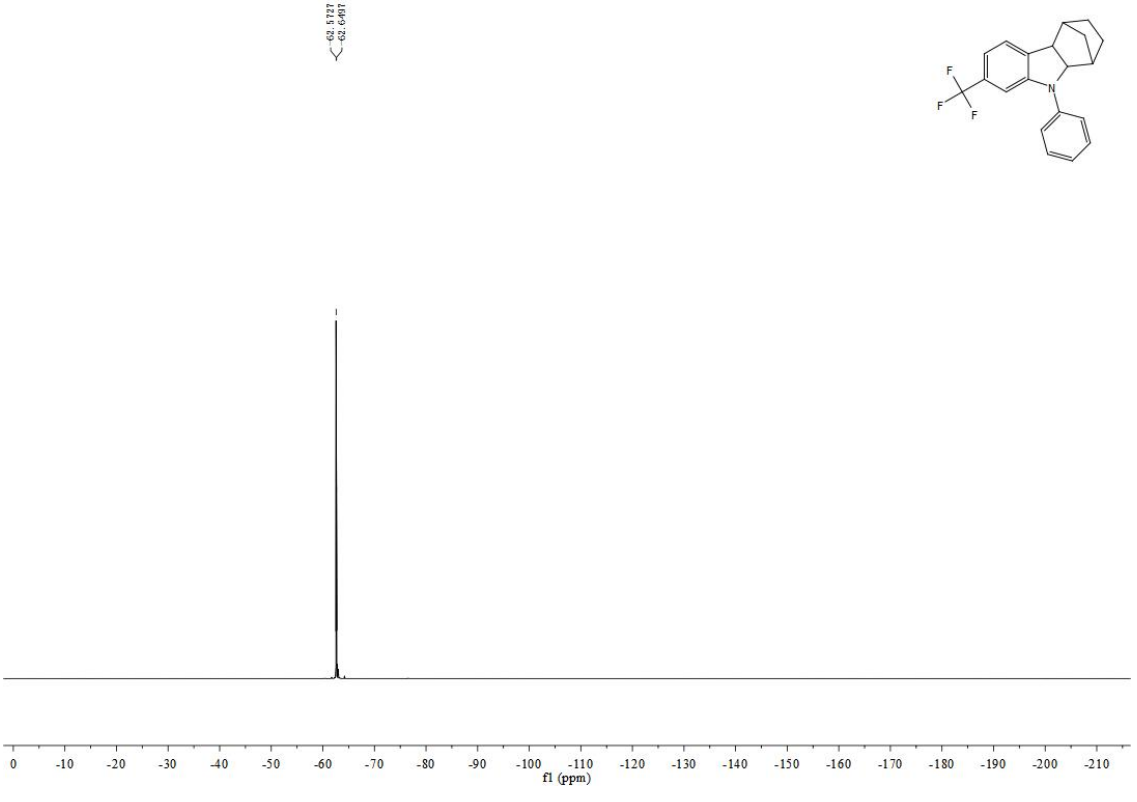
^{1}H NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**32d**)



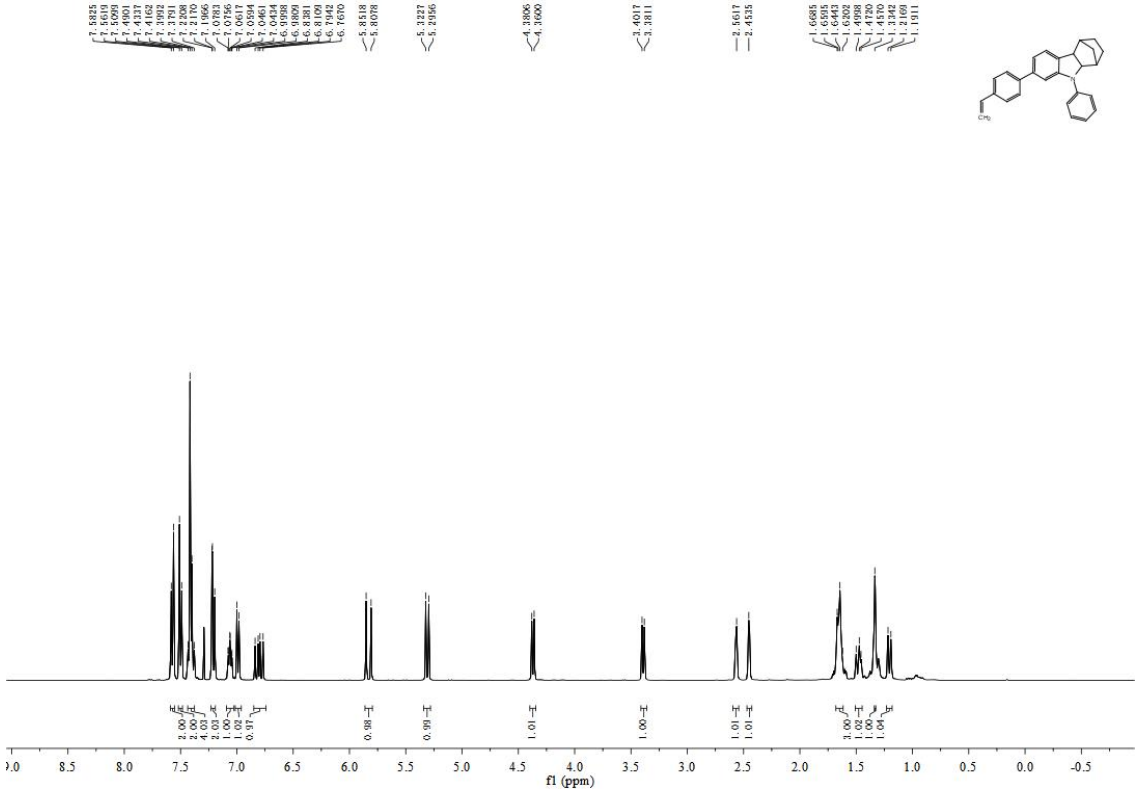
^{13}C NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**32d**)



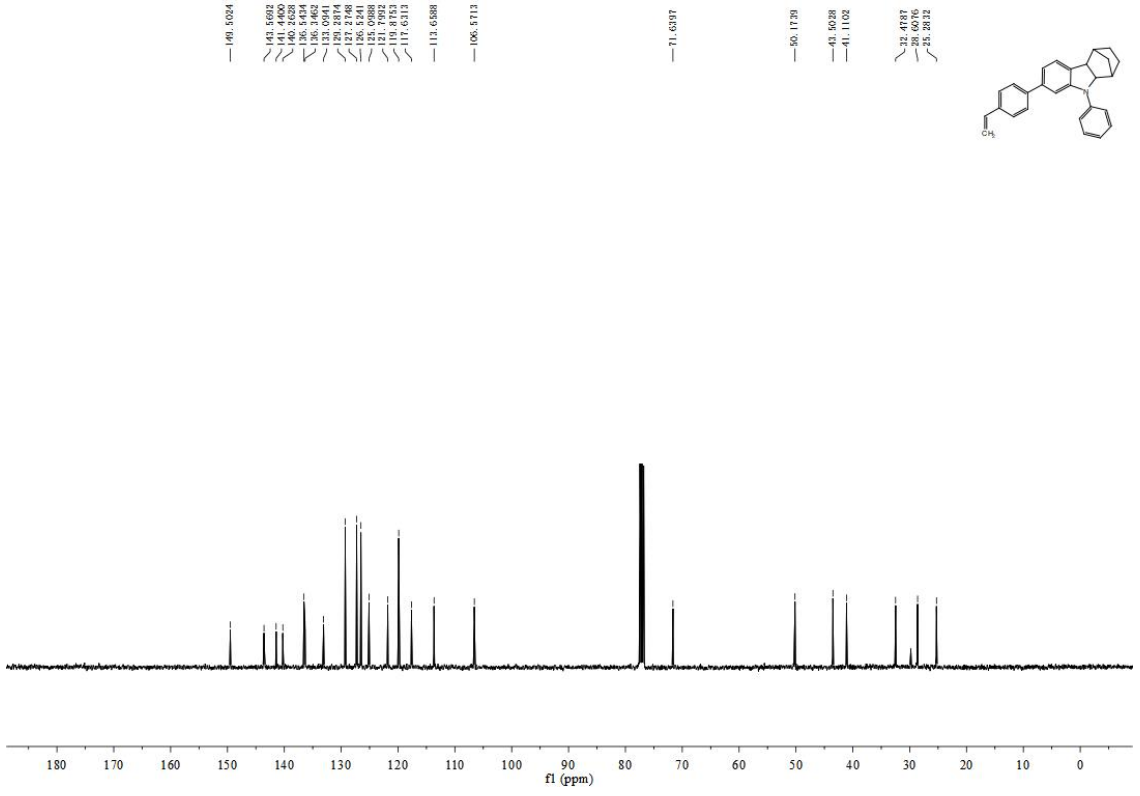
^{19}F NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**32d**)



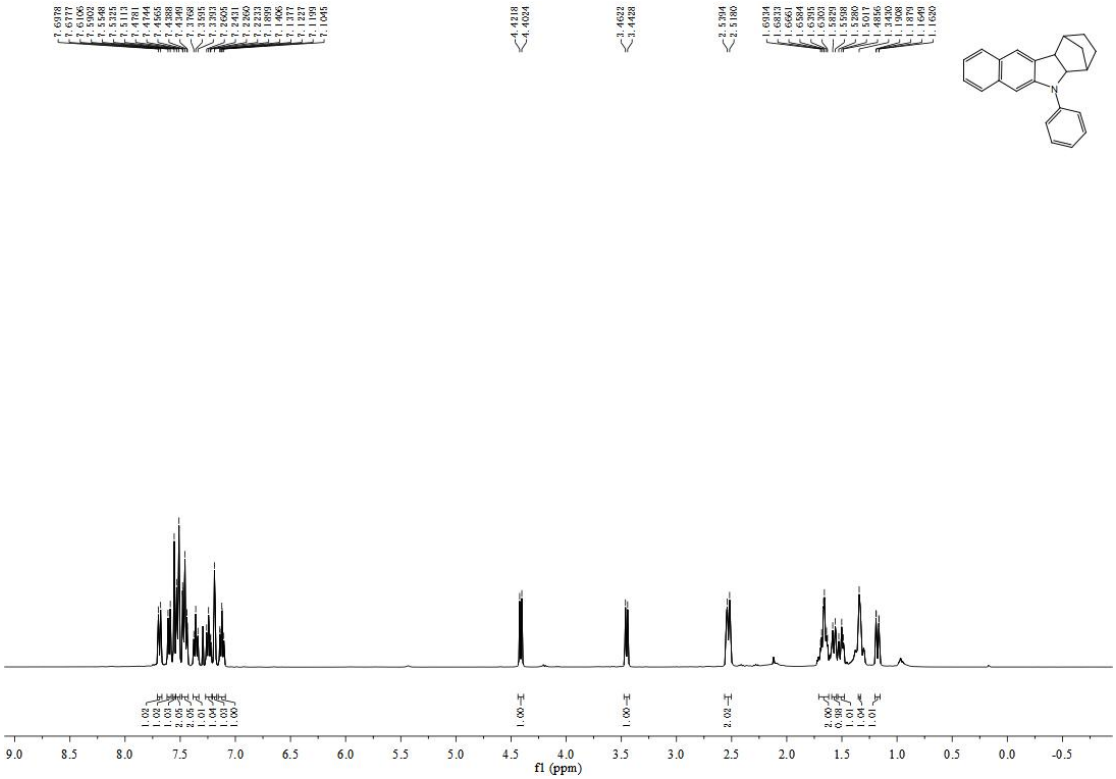
^{1}H NMR spectrum of 9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**33d**)



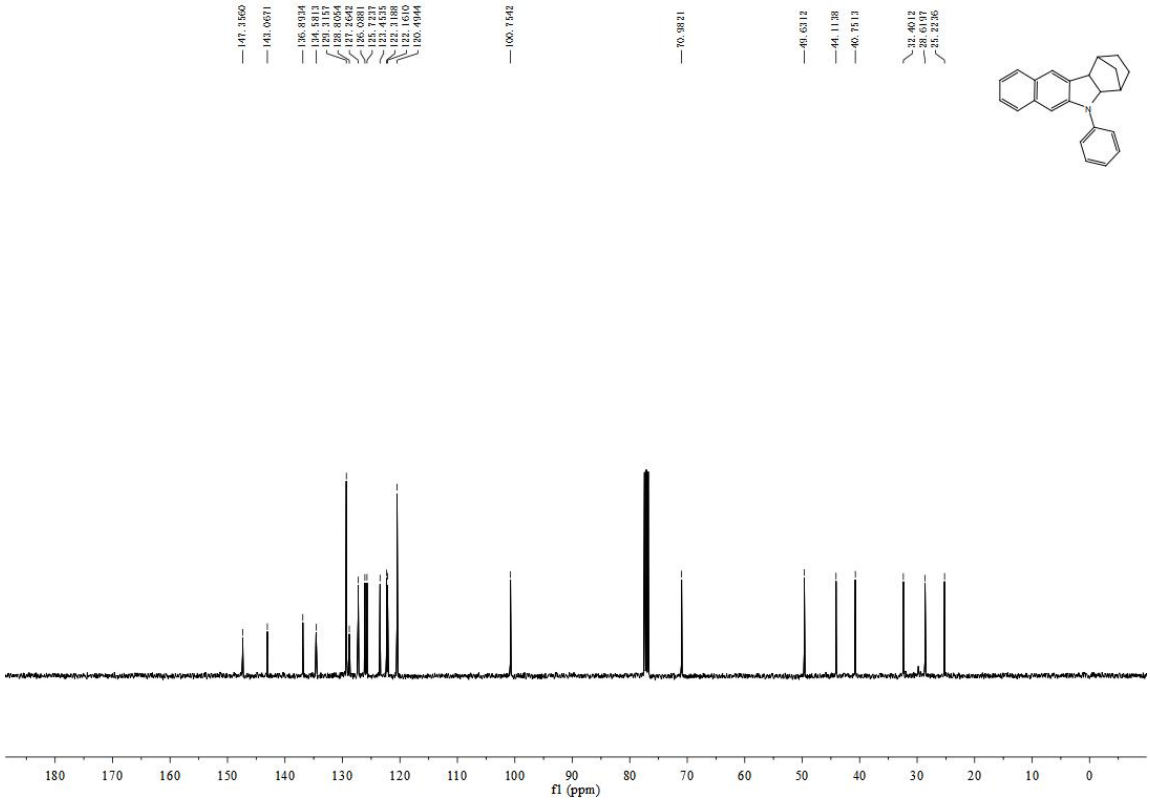
^{13}C NMR spectrum of 9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**33d**)



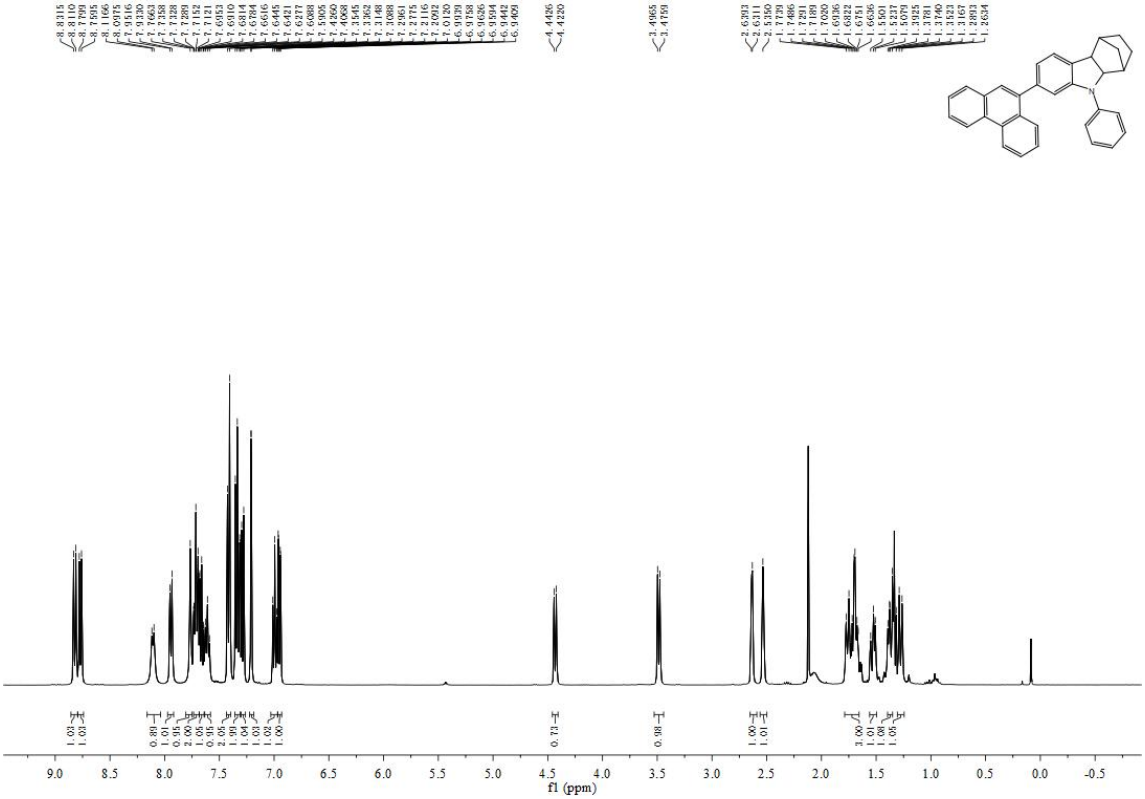
^{1}H NMR spectrum of 5-phenyl-2,3,4,4a,5,11b-hexahydro-*1H*-1,4-methanobenzo[*b*]carbazole (**34d**)



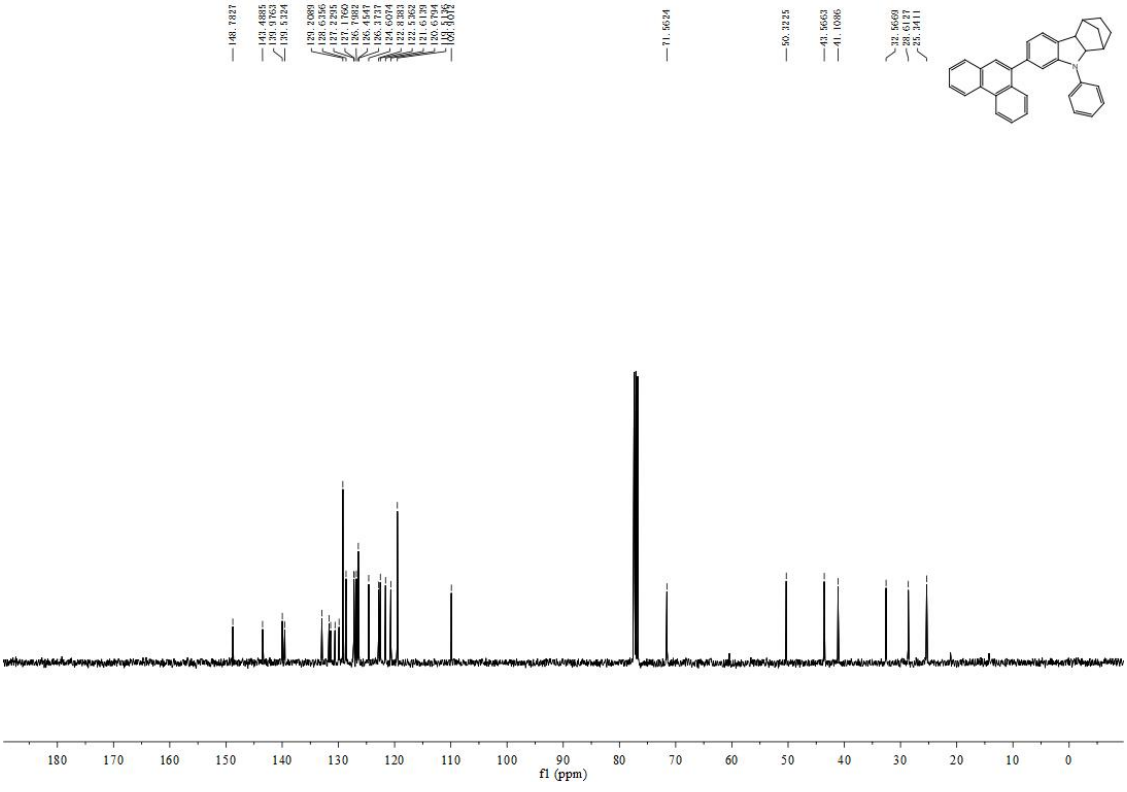
^{13}C NMR spectrum of 5-phenyl-2,3,4,4a,5,11b-hexahydro-*1H*-1,4-methanobenzo[*b*]carbazole (**34d**)



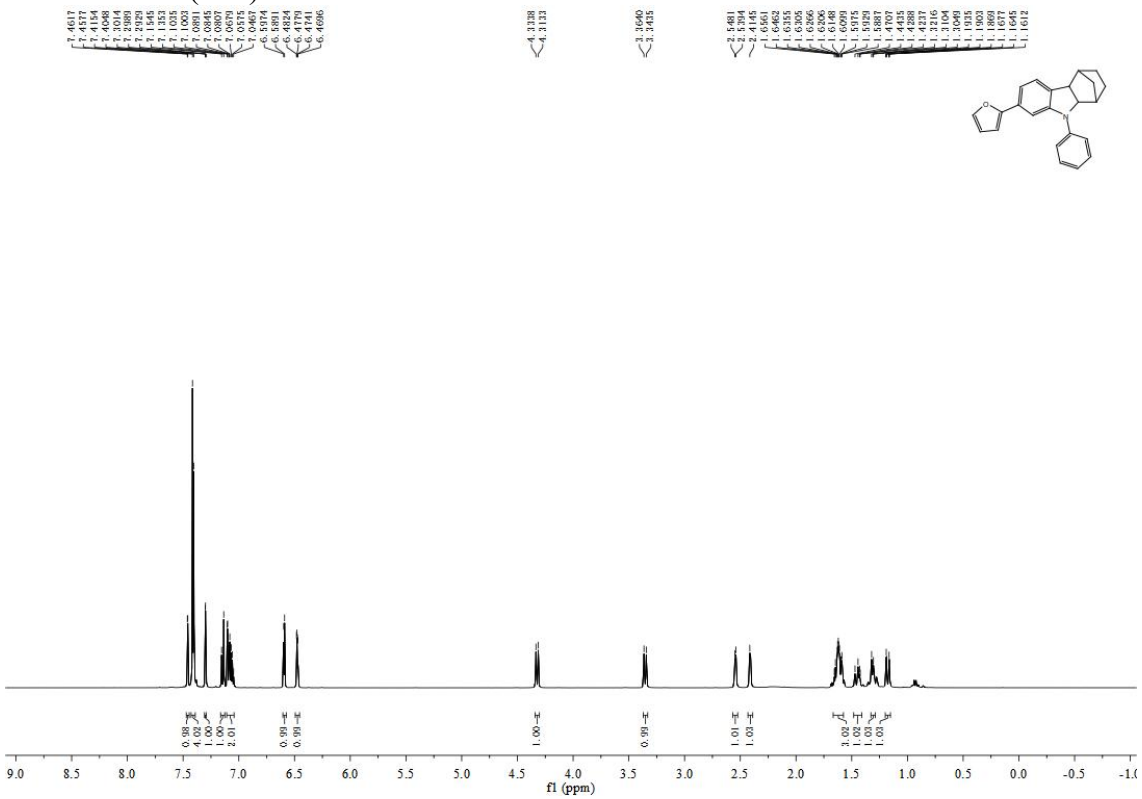
^{1}H NMR spectrum of 7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**35d)**



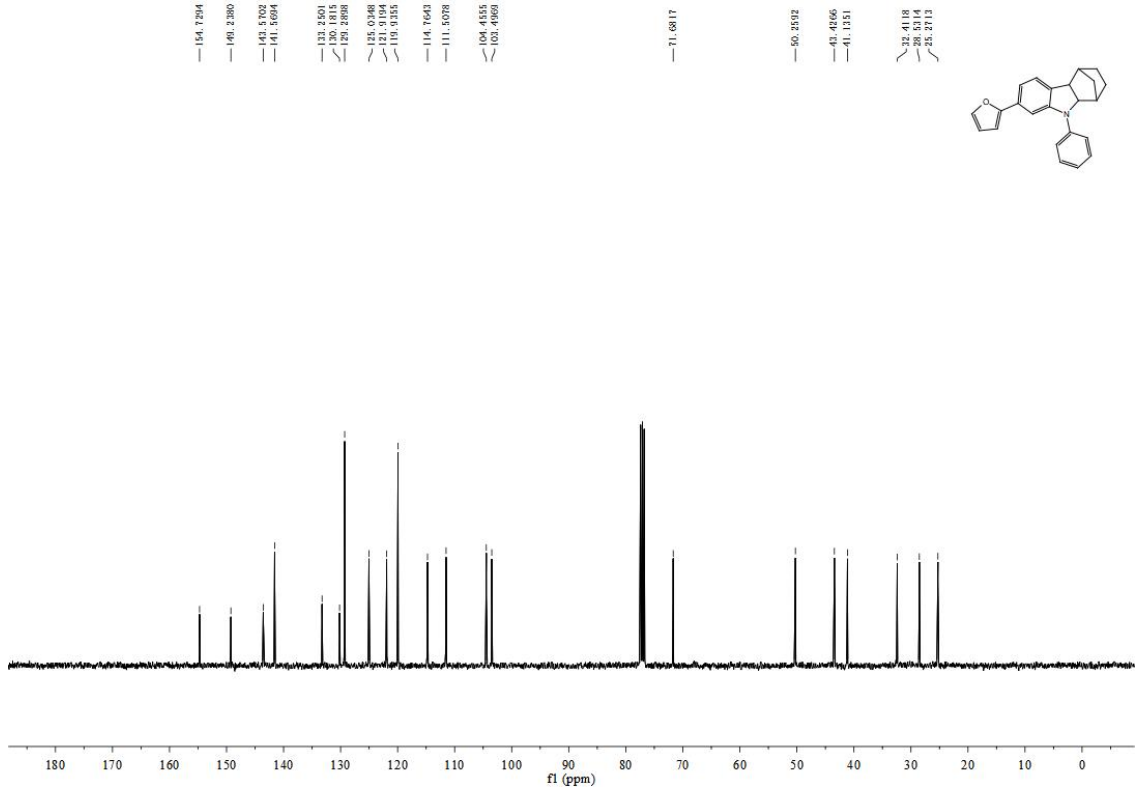
^{13}C NMR spectrum of 7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**35d)**



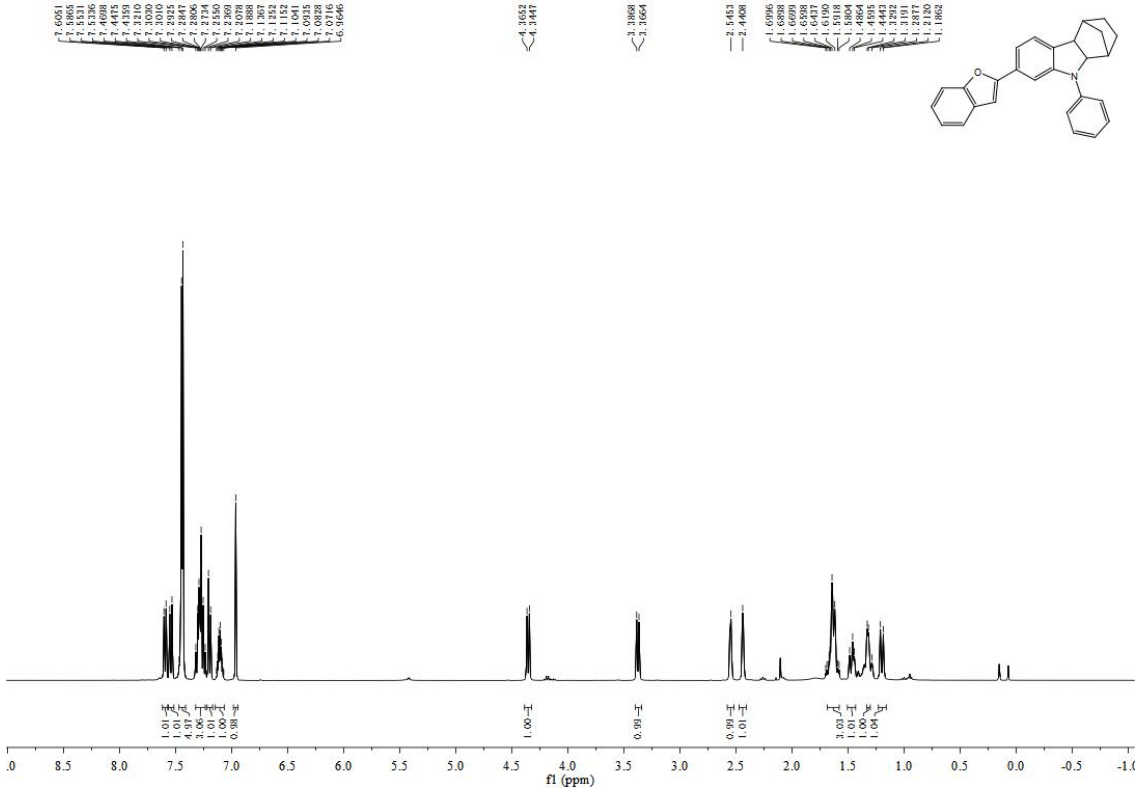
^{1}H NMR spectrum of 7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**36d**)



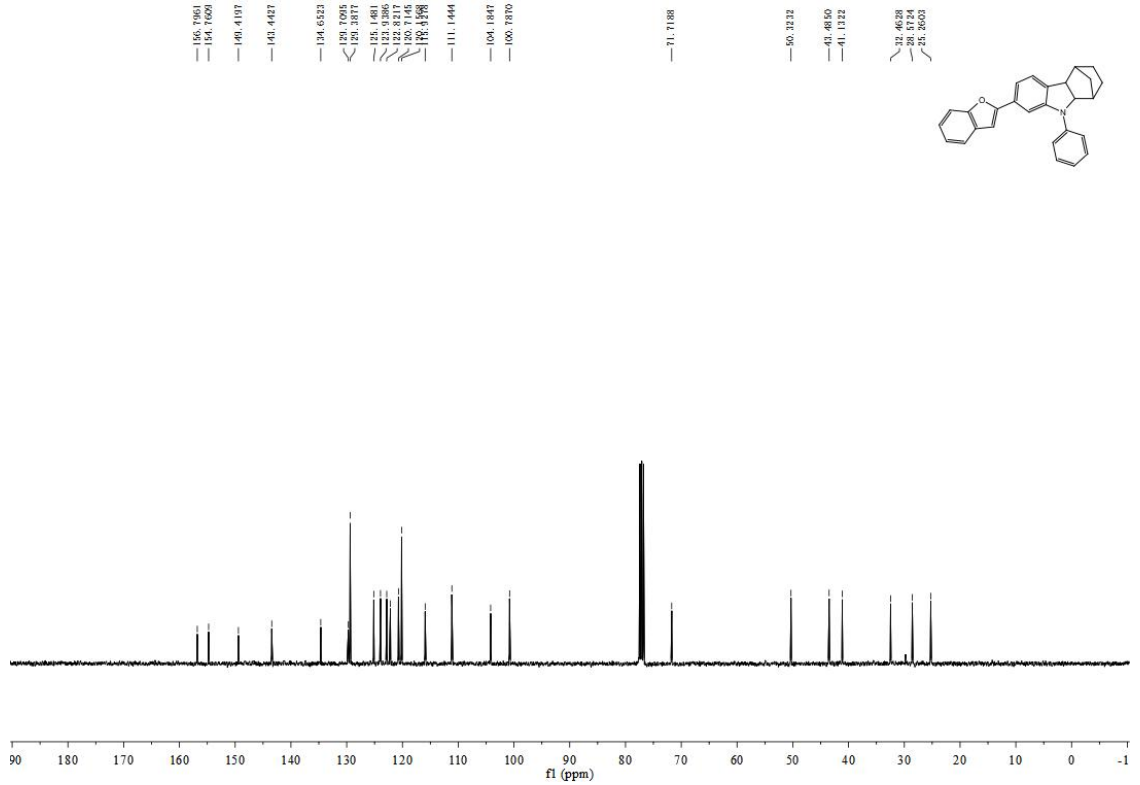
^{13}C NMR spectrum of 7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**36d**)



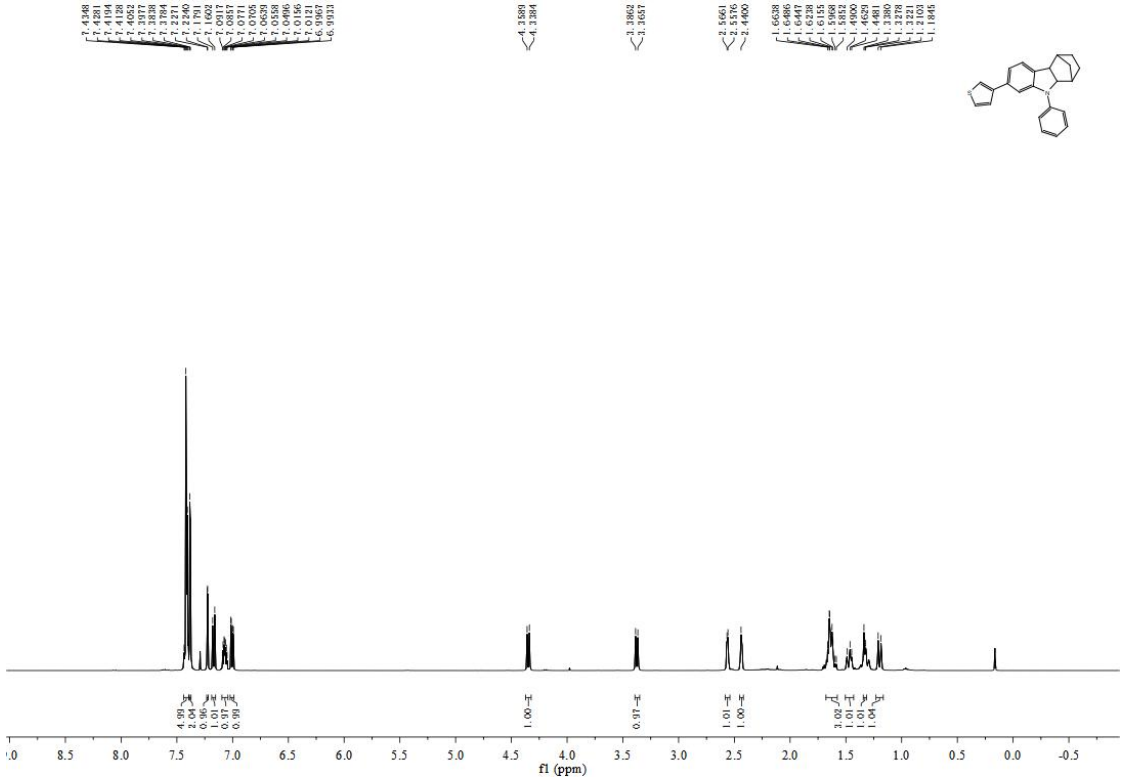
^{1}H NMR spectrum of 7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**37d**)



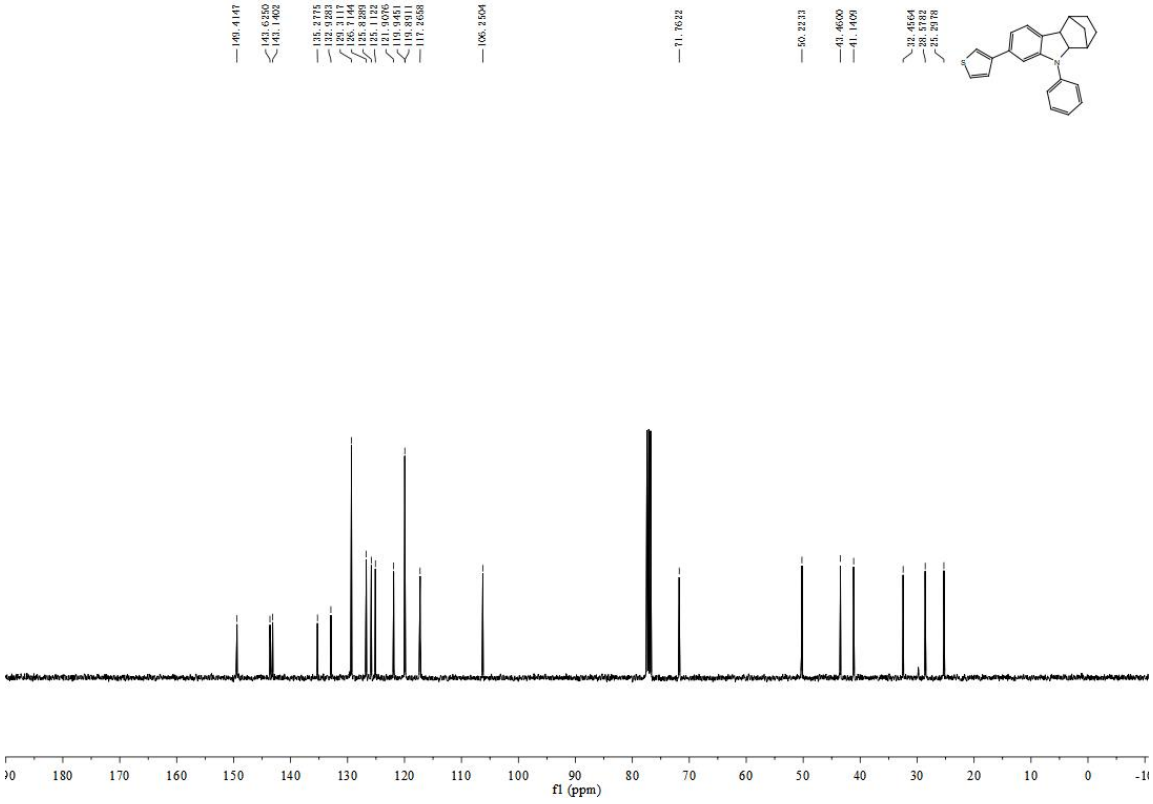
^{13}C NMR spectrum of 7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**37d**)



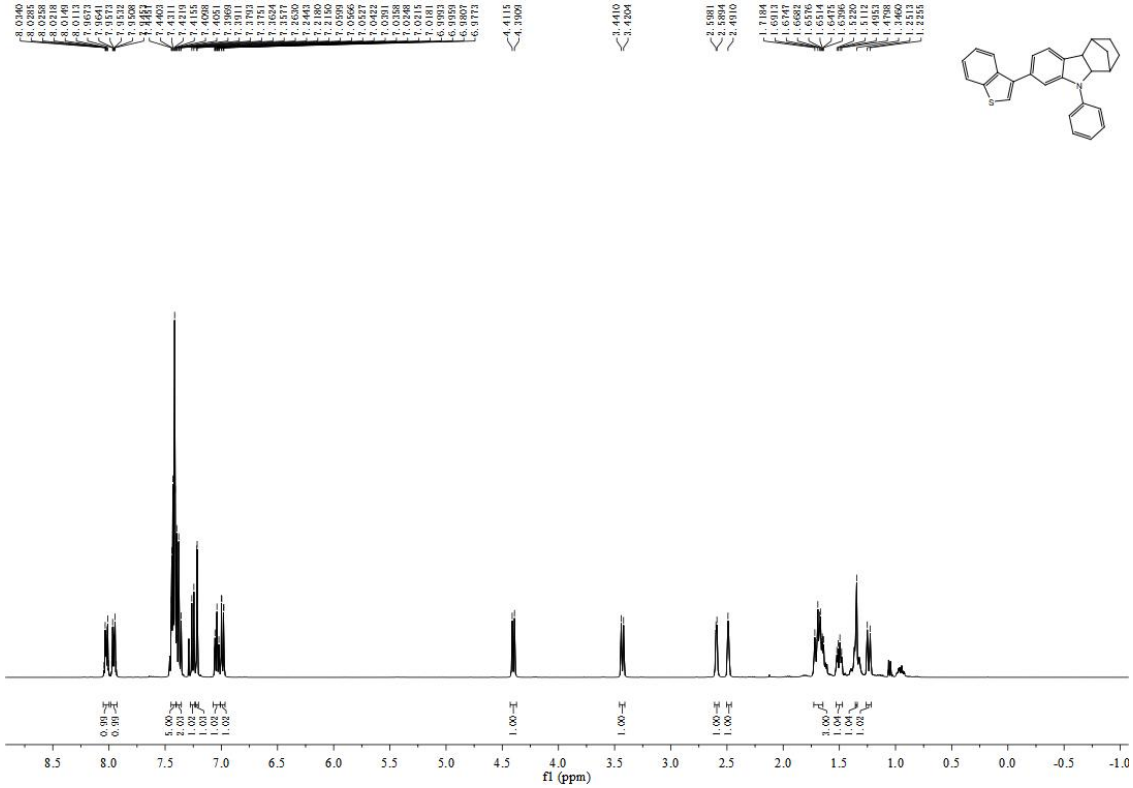
^{1}H NMR spectrum of 9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**38d**)



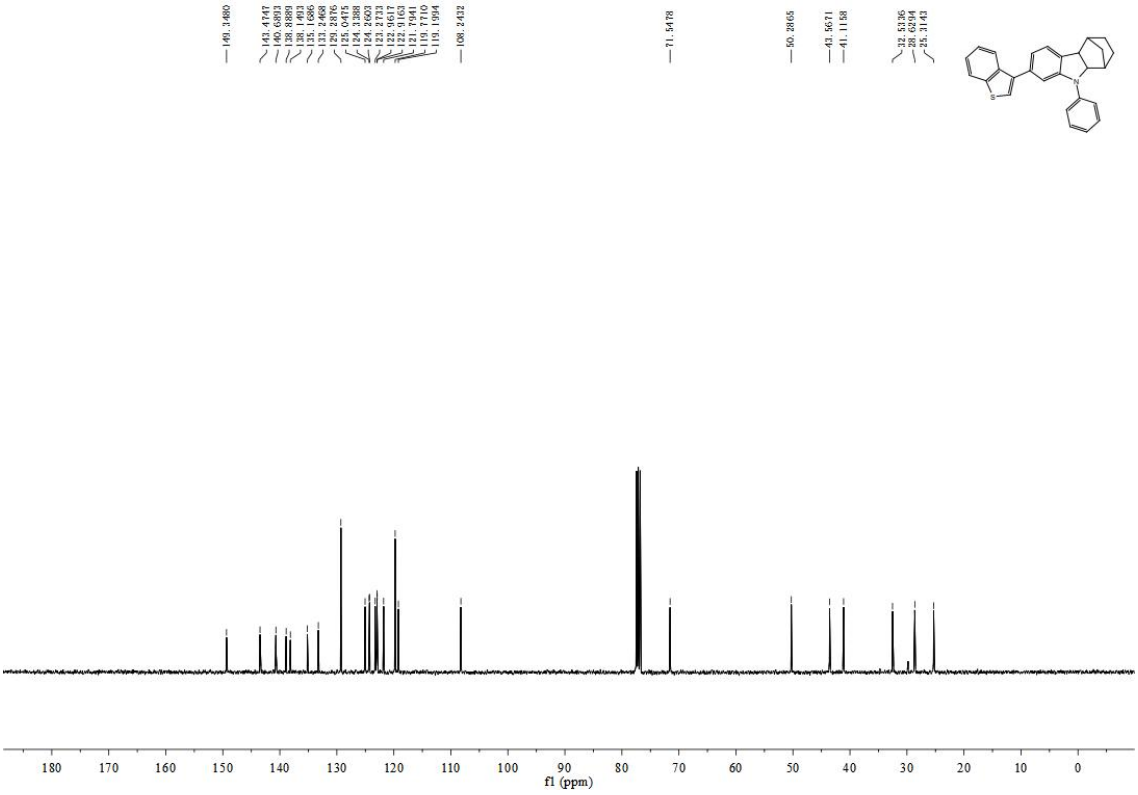
^{13}C NMR spectrum of 9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**38d**)



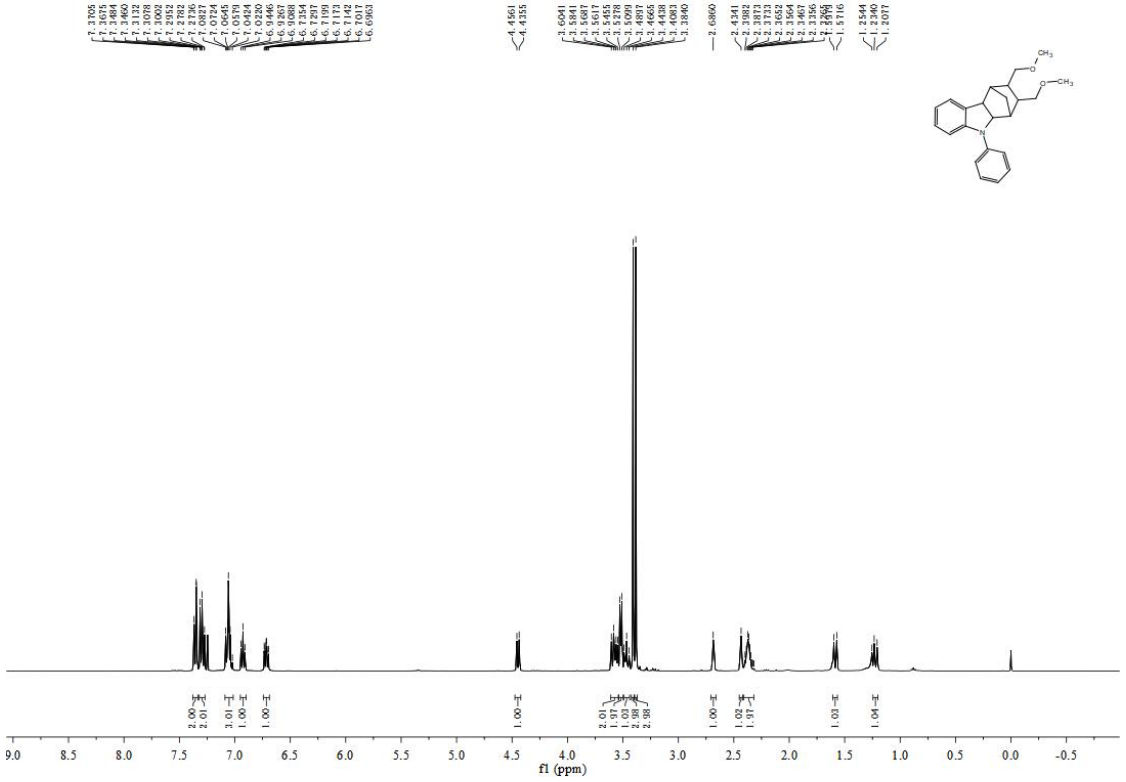
^{1}H NMR spectrum of 7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**39d**)



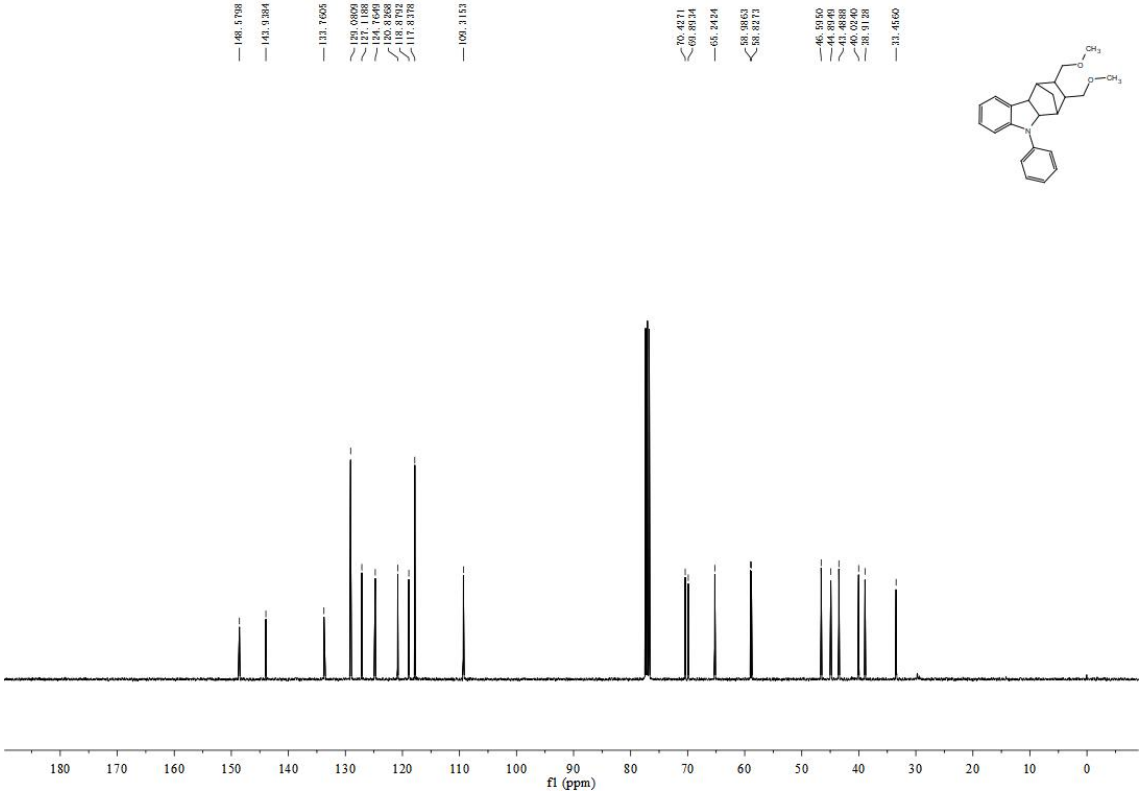
^{13}C NMR spectrum of 7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**39d**)



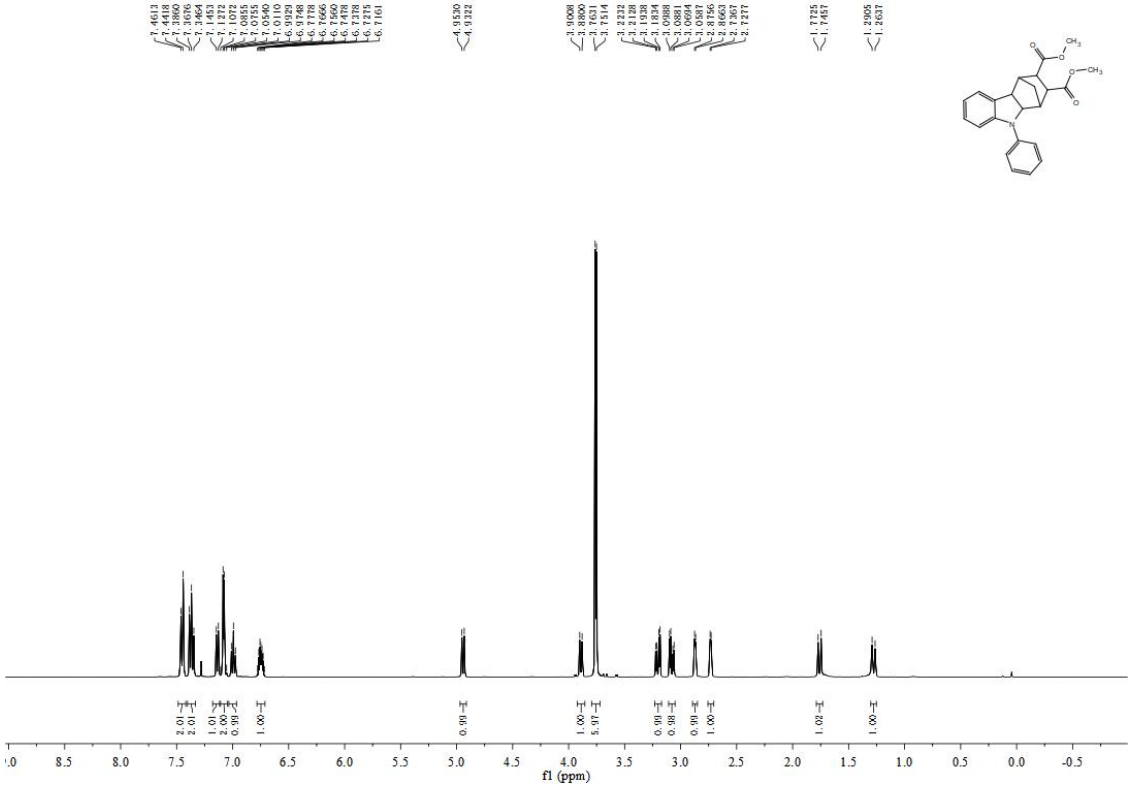
^{1}H NMR spectrum of 2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**40d**)



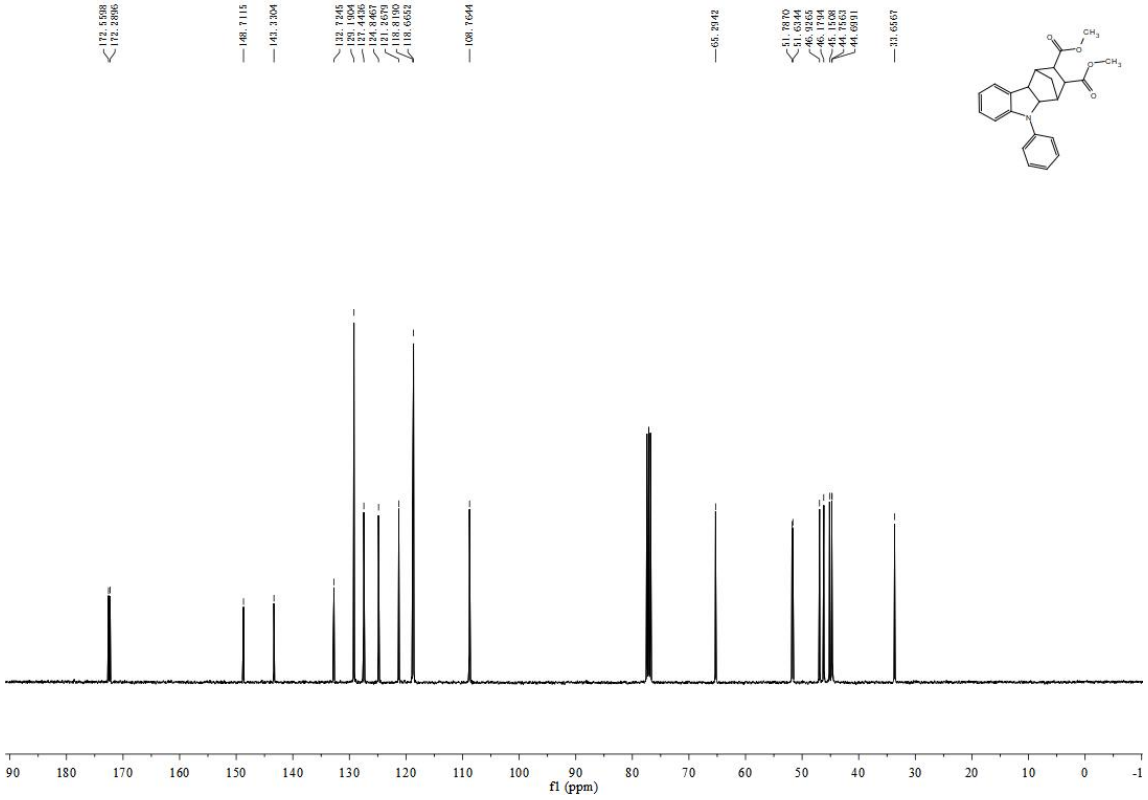
^{13}C NMR spectrum of 2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**40d**)



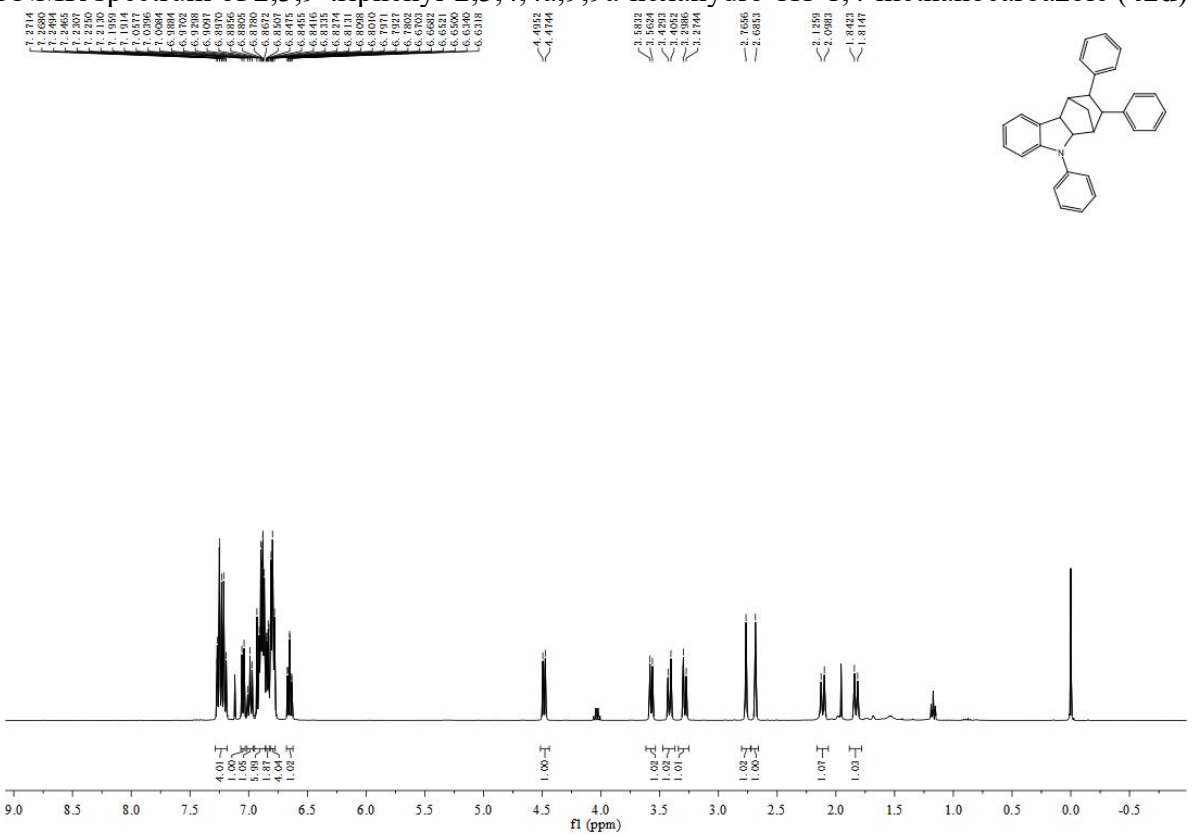
^{1}H NMR spectrum of dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole-2,3-dicarboxylate (**41d**)



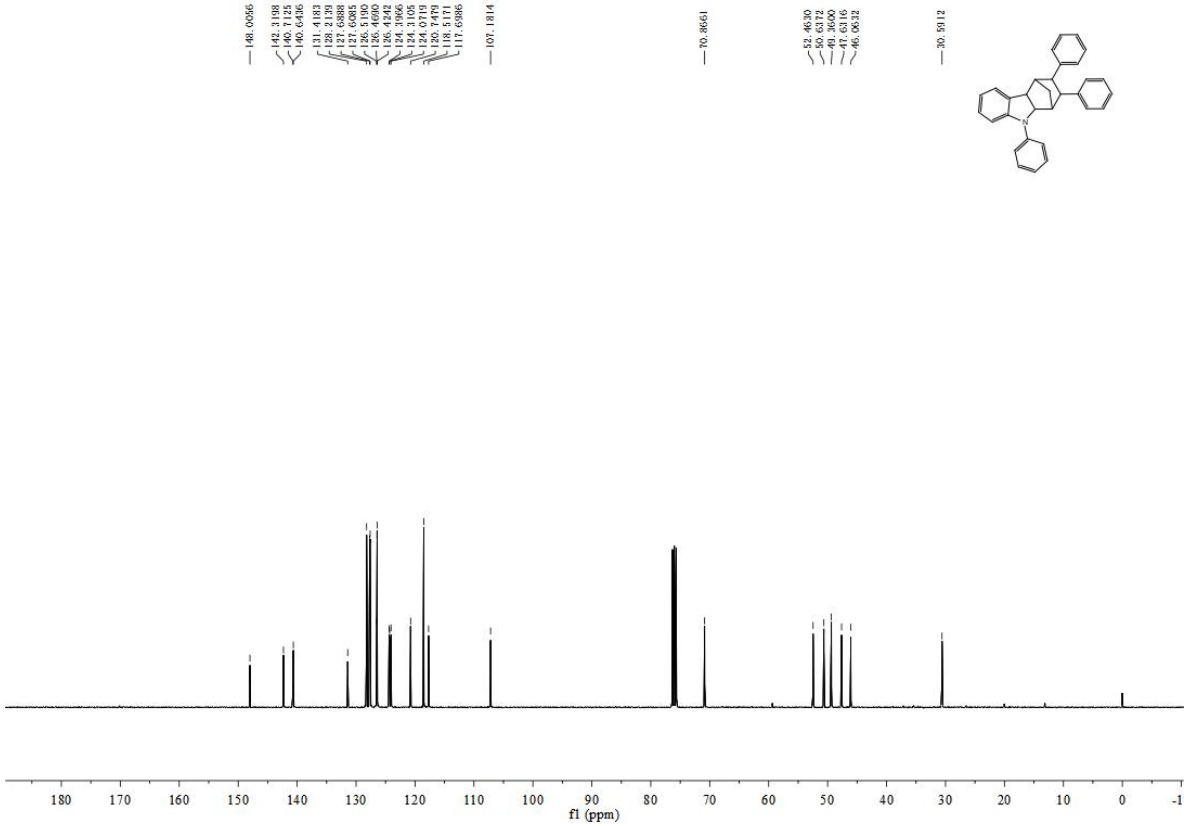
^{13}C NMR spectrum of dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole-2,3-dicarboxylate (**41d**)



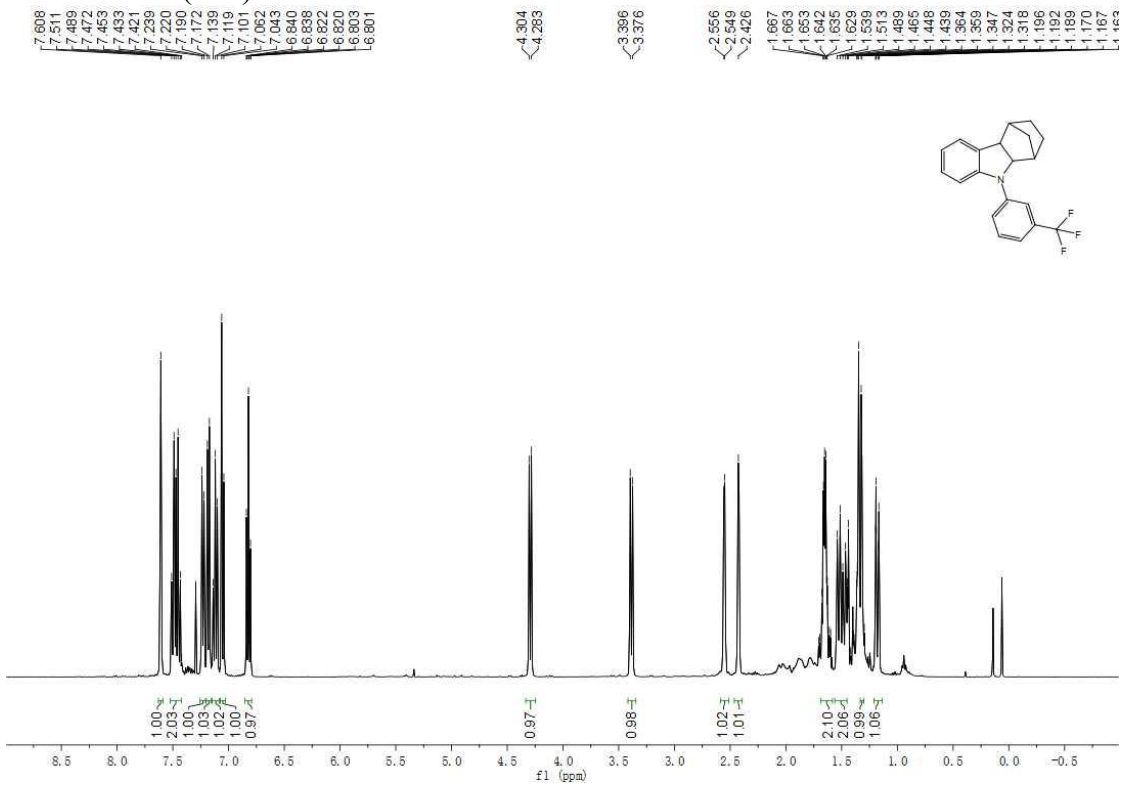
^{1}H NMR spectrum of 2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**42d**)



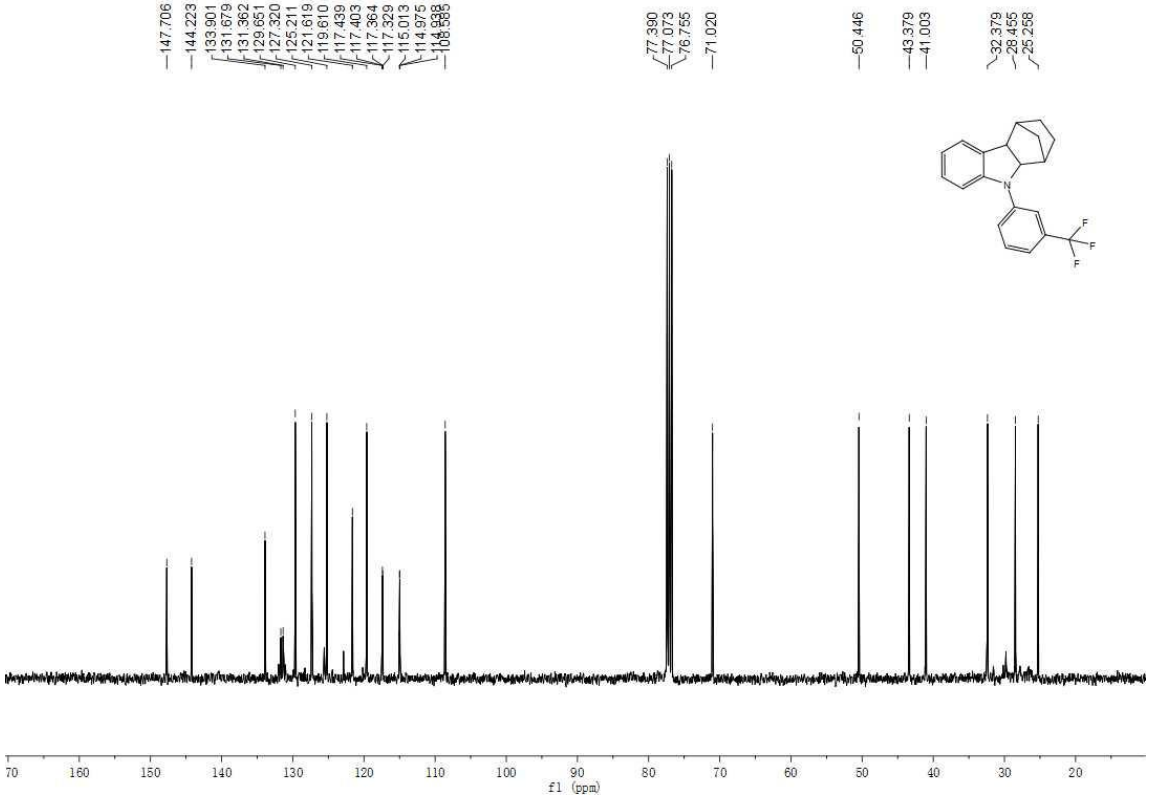
^{13}C NMR spectrum of 2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**42d**)



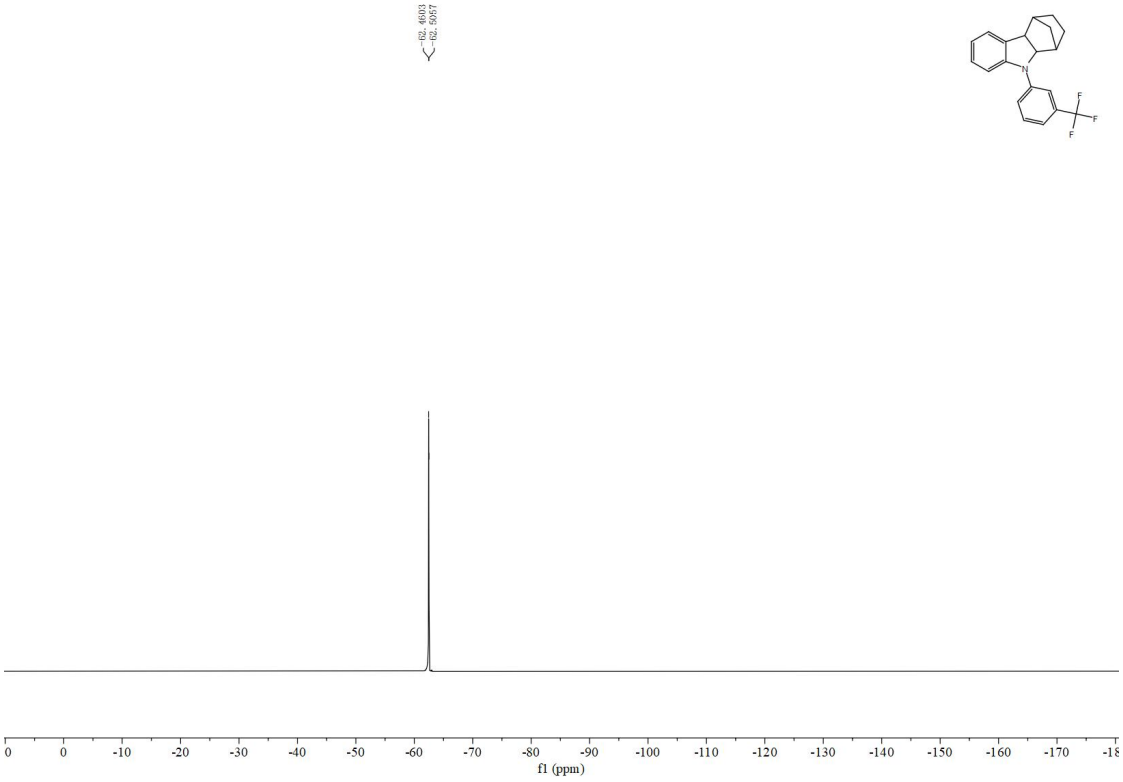
^{1}H NMR spectrum of 9-(3-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**43d**)



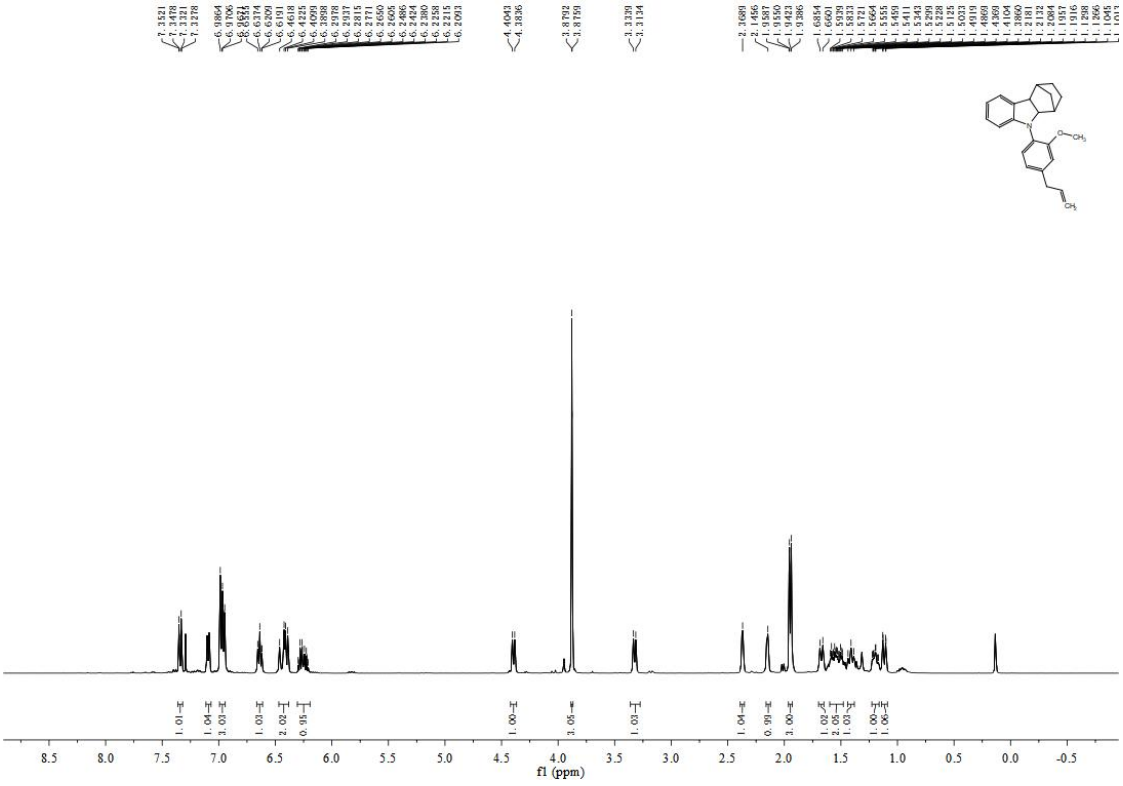
^{13}C NMR spectrum of 9-(3-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**43d**)



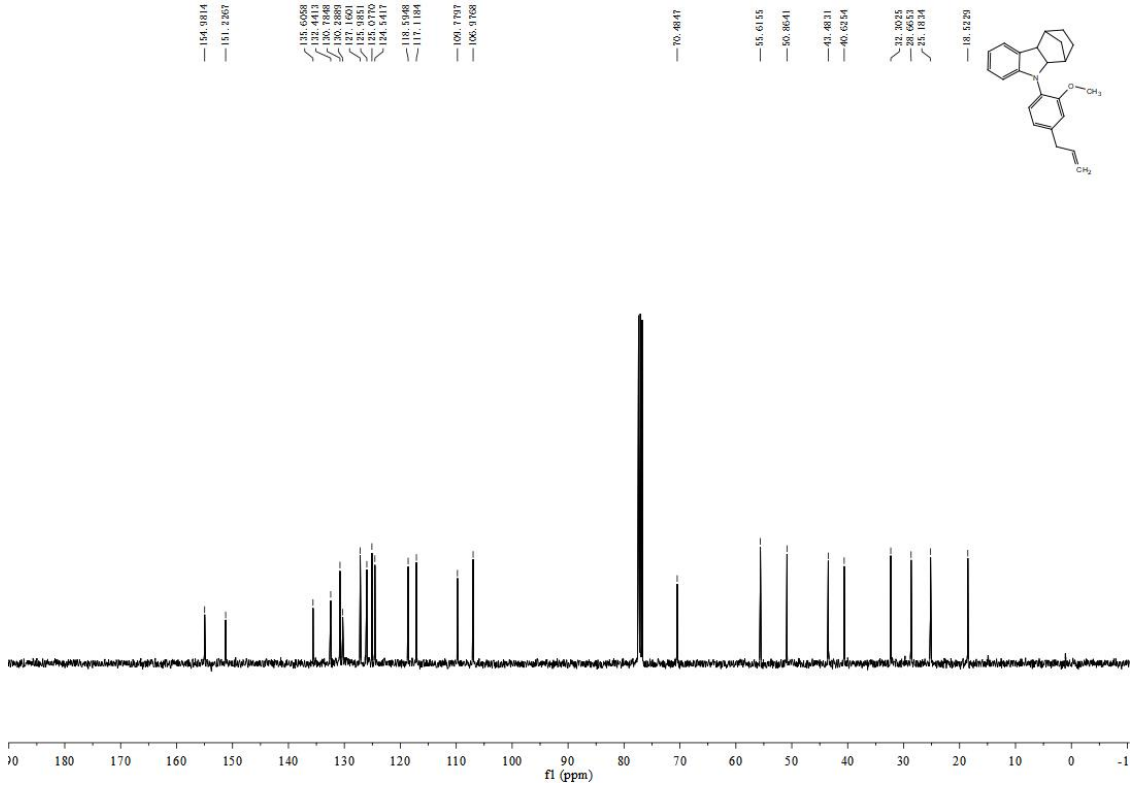
^{19}F NMR spectrum of 9-(3-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**43d**)



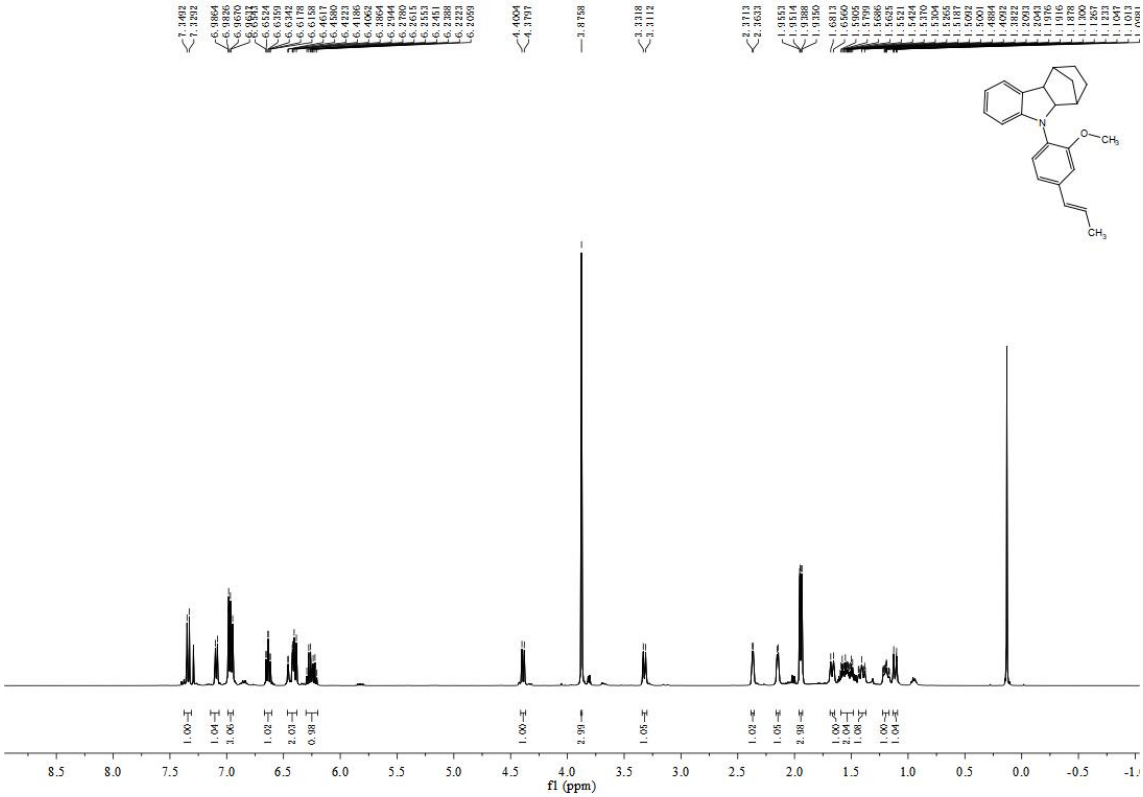
^{1}H NMR spectrum of 9-(4-allyl-2-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**44d**)



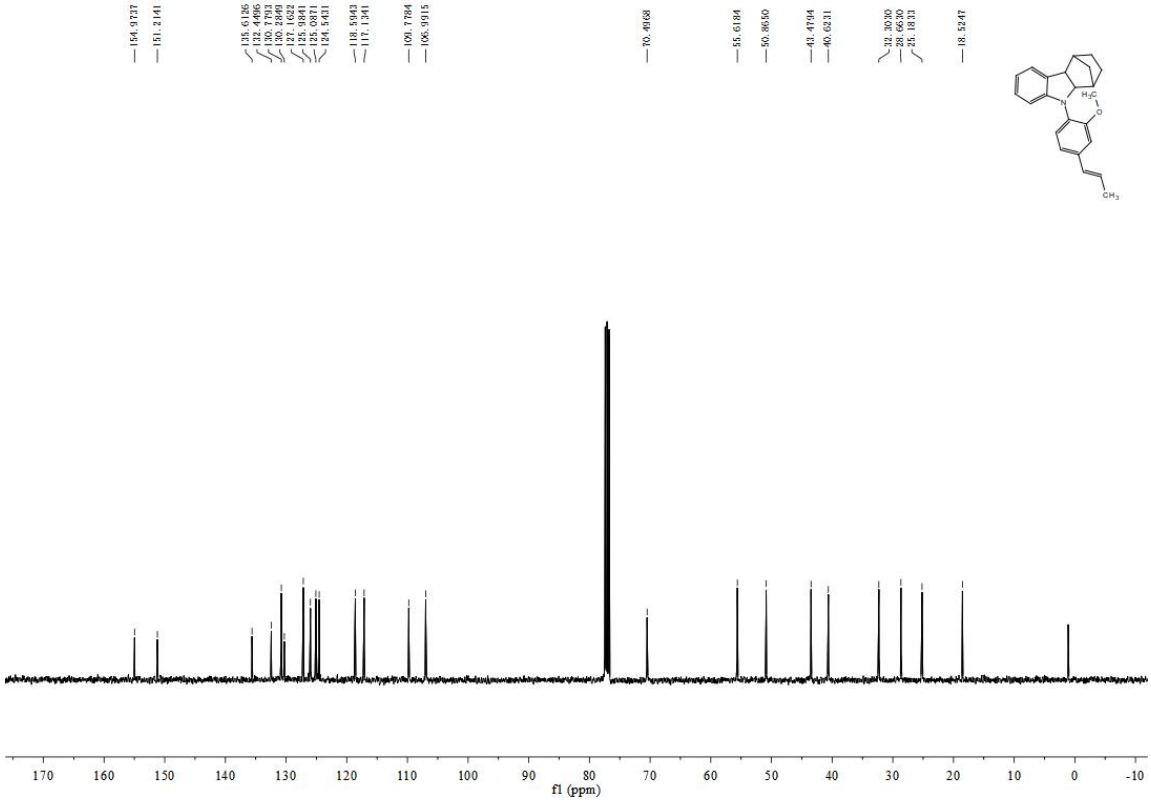
^{13}C NMR spectrum of 9-(4-allyl-2-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**44d**)



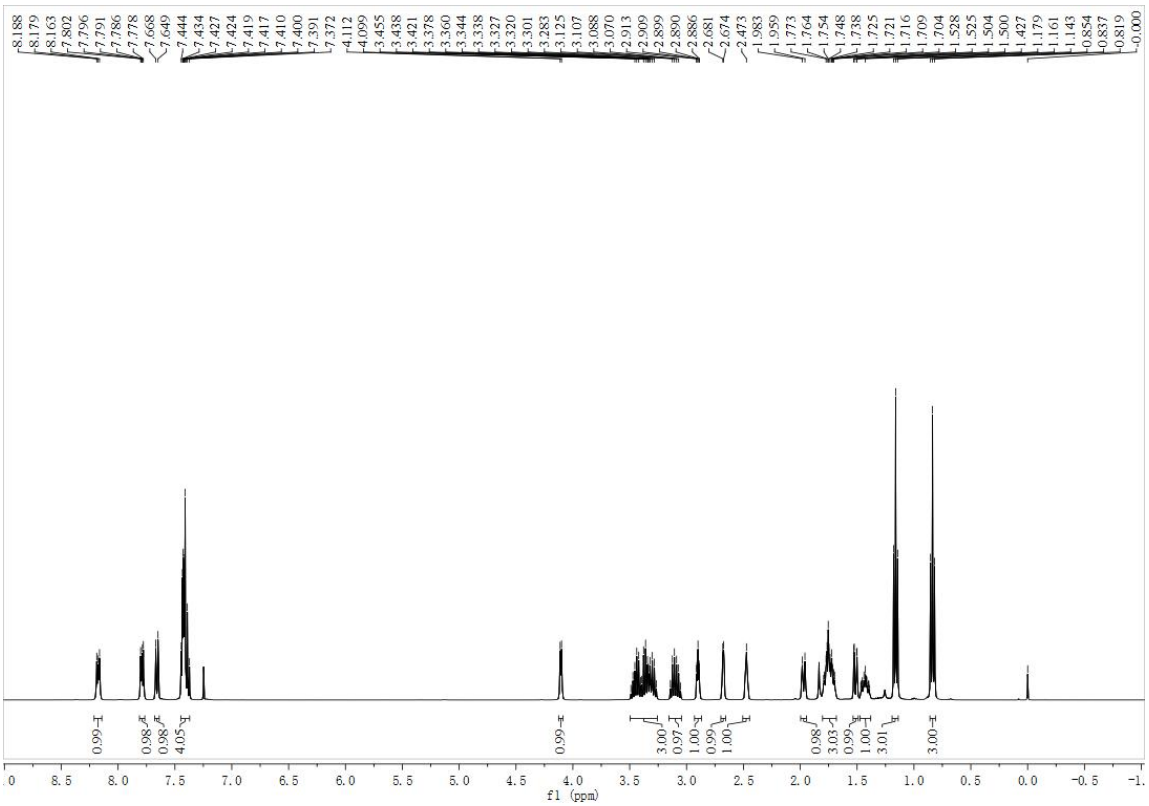
^{1}H NMR spectrum of (*E*)-9-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**45d**)



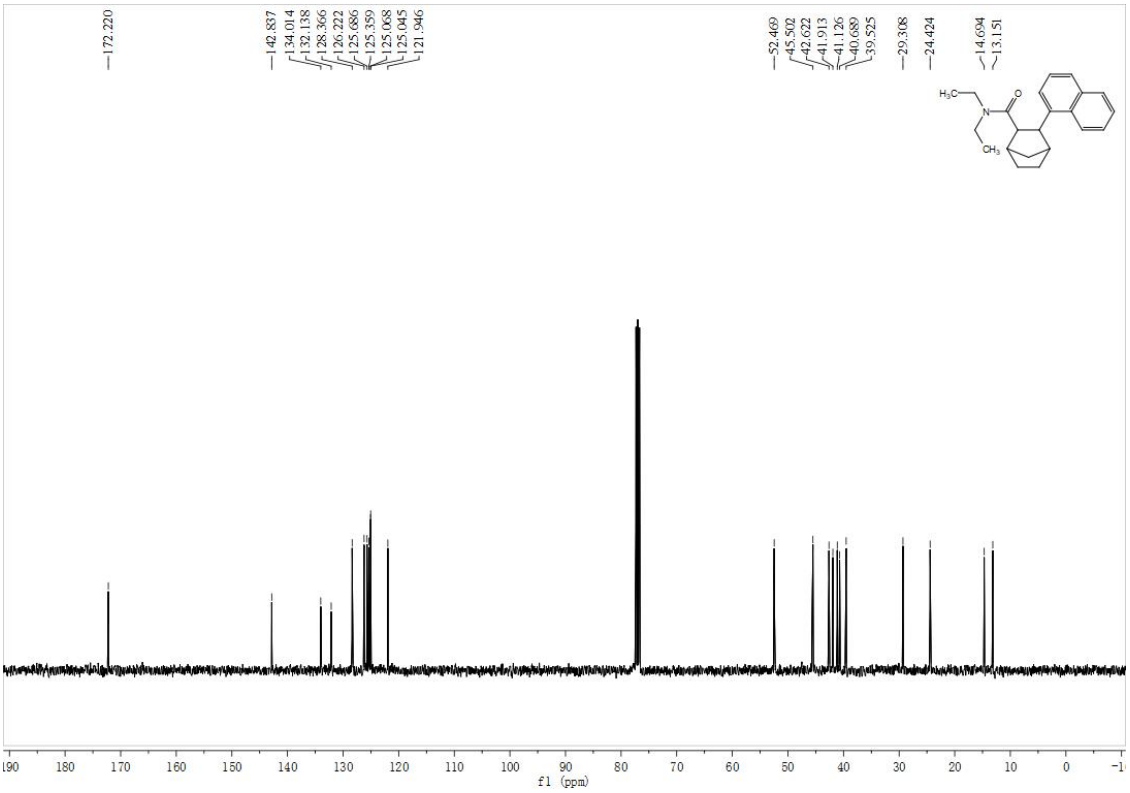
^{13}C NMR spectrum of (*E*)-9-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-*1H*-1,4-methanocarbazole (**45d**)



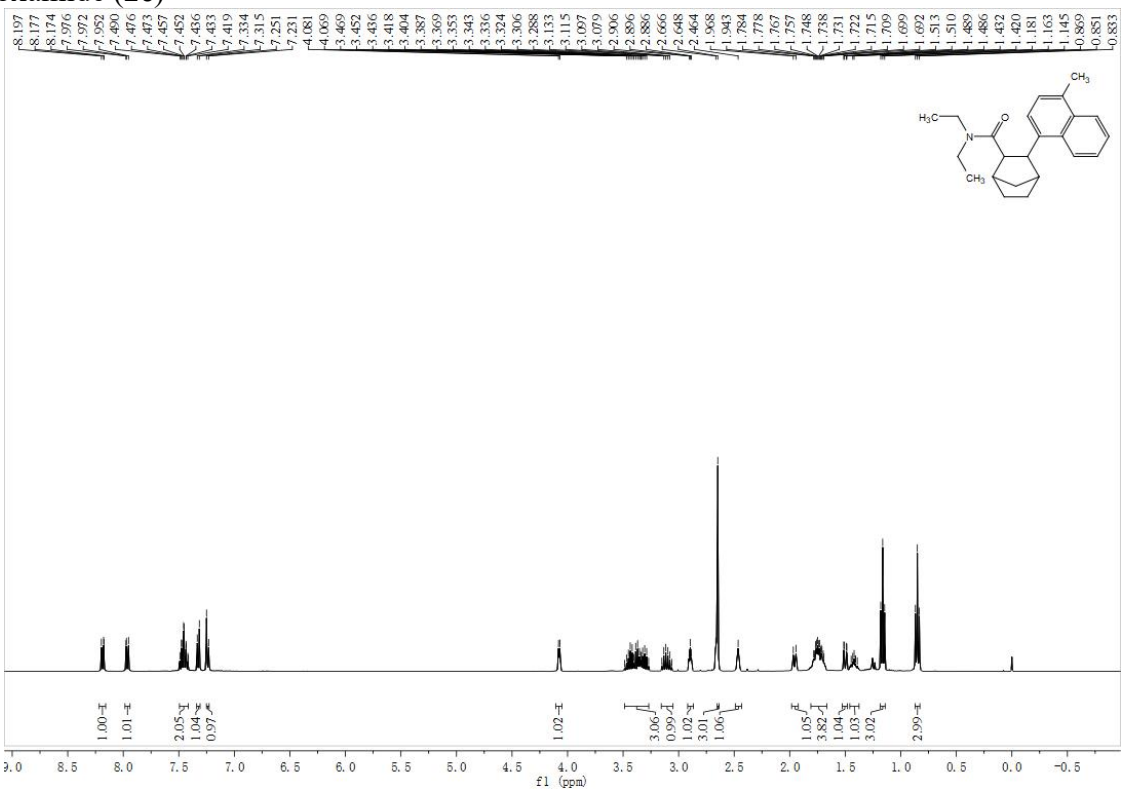
^{1}H NMR spectrum of *N,N*-diethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**1e**)



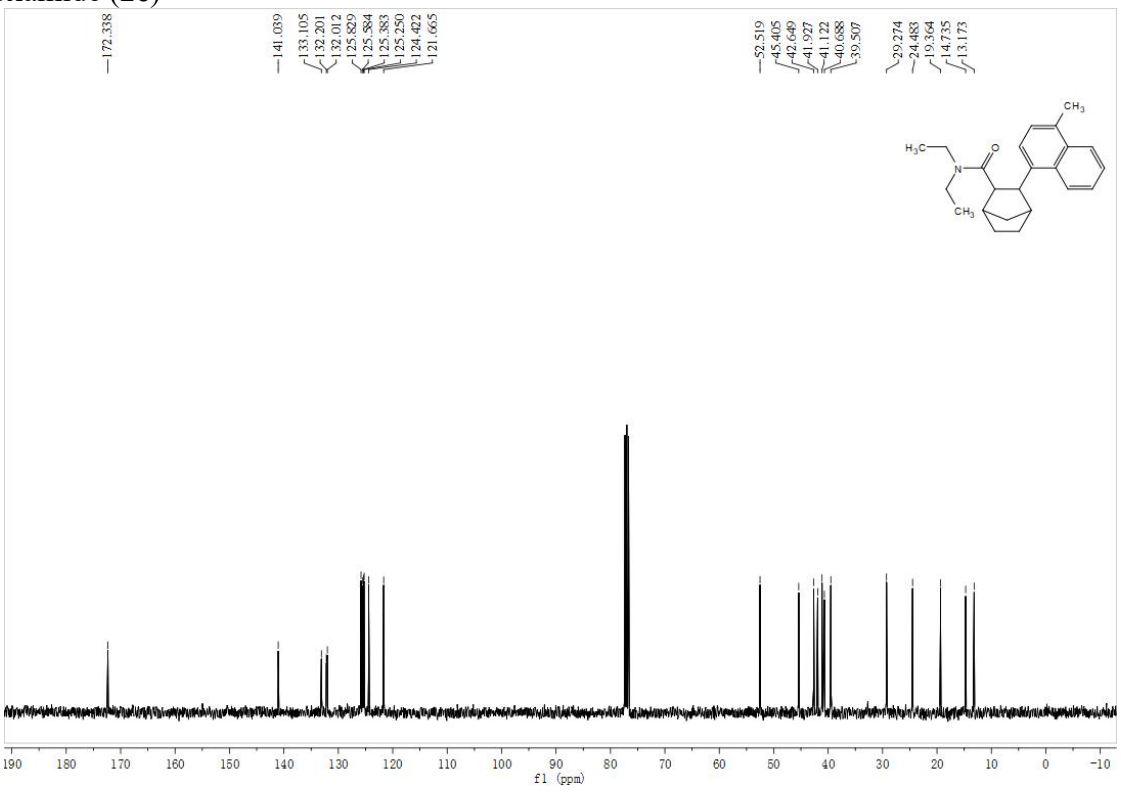
^{13}C NMR spectrum of *N,N*-diethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**1e**)



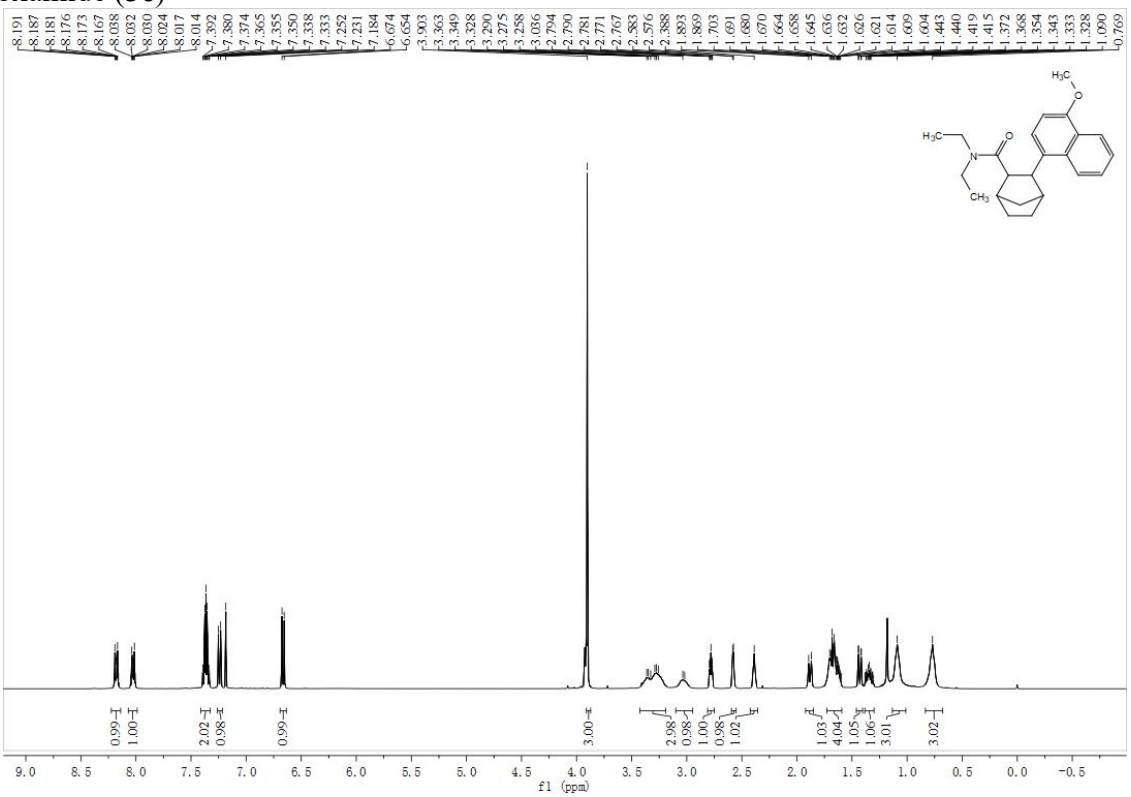
^{1}H NMR spectrum of *N,N*-diethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**2e**)



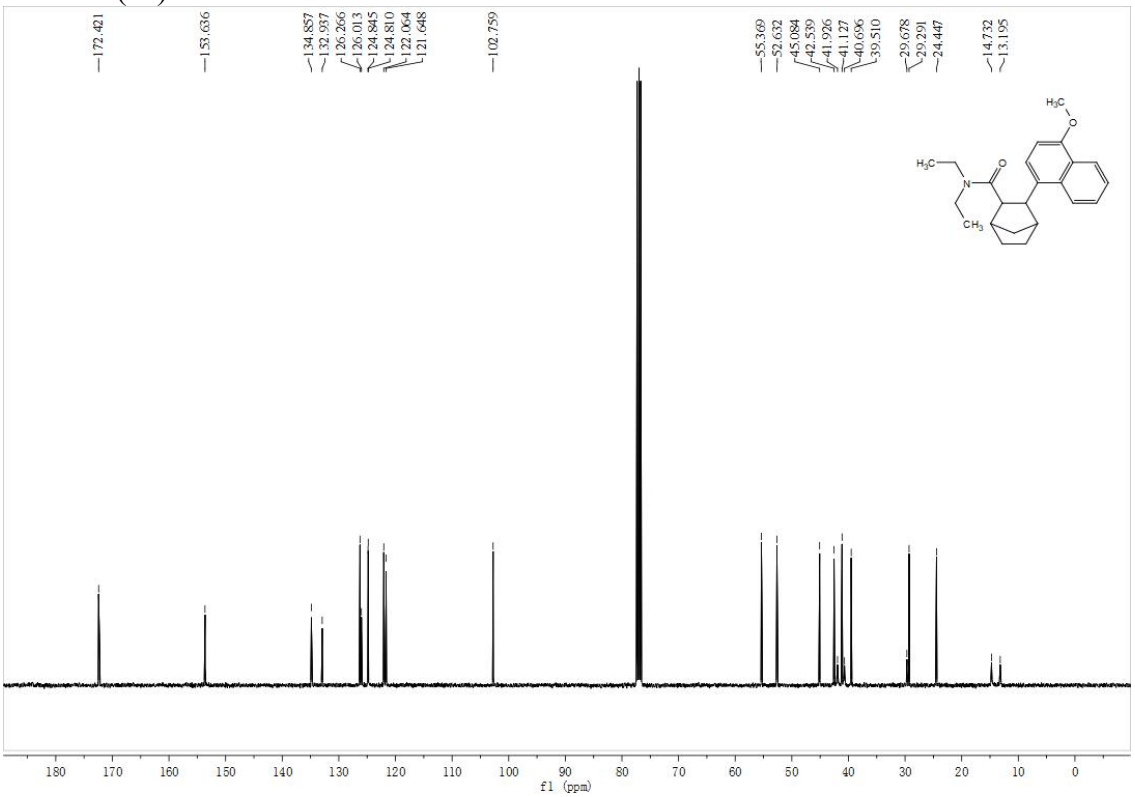
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**2e**)



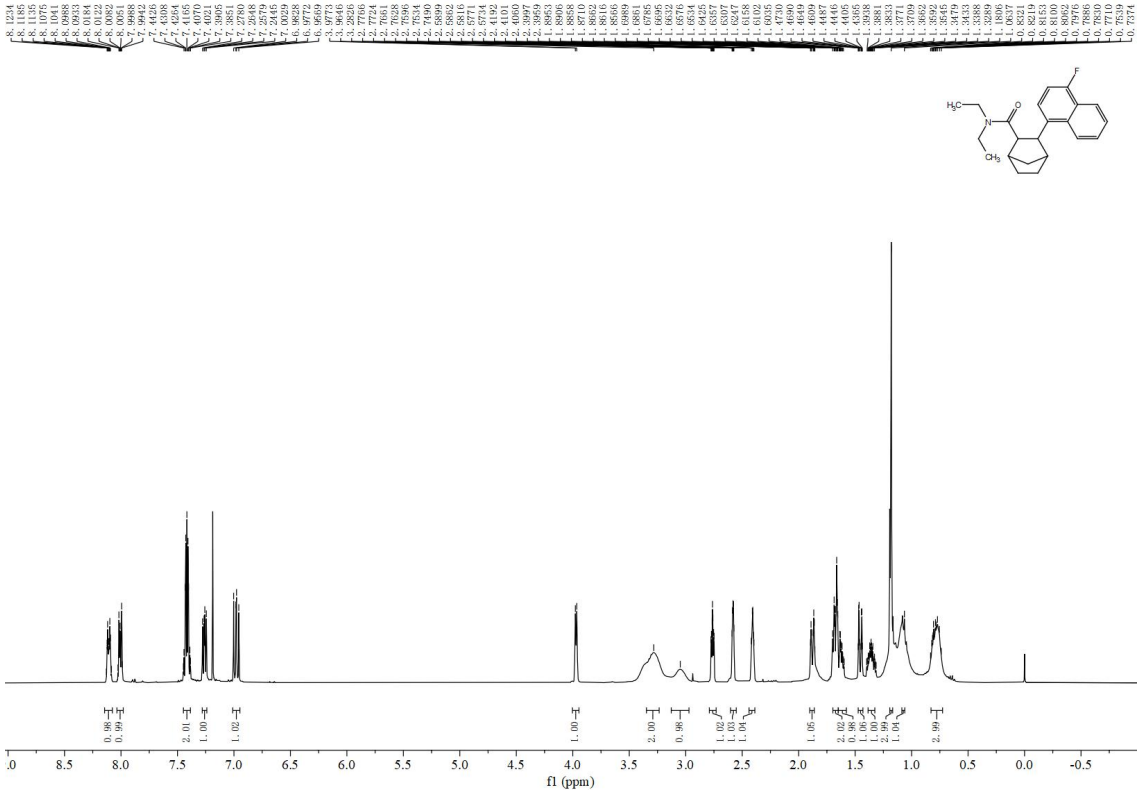
^{1}H NMR spectrum of *N,N*-diethyl-3-(4-methoxynaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**3e**)



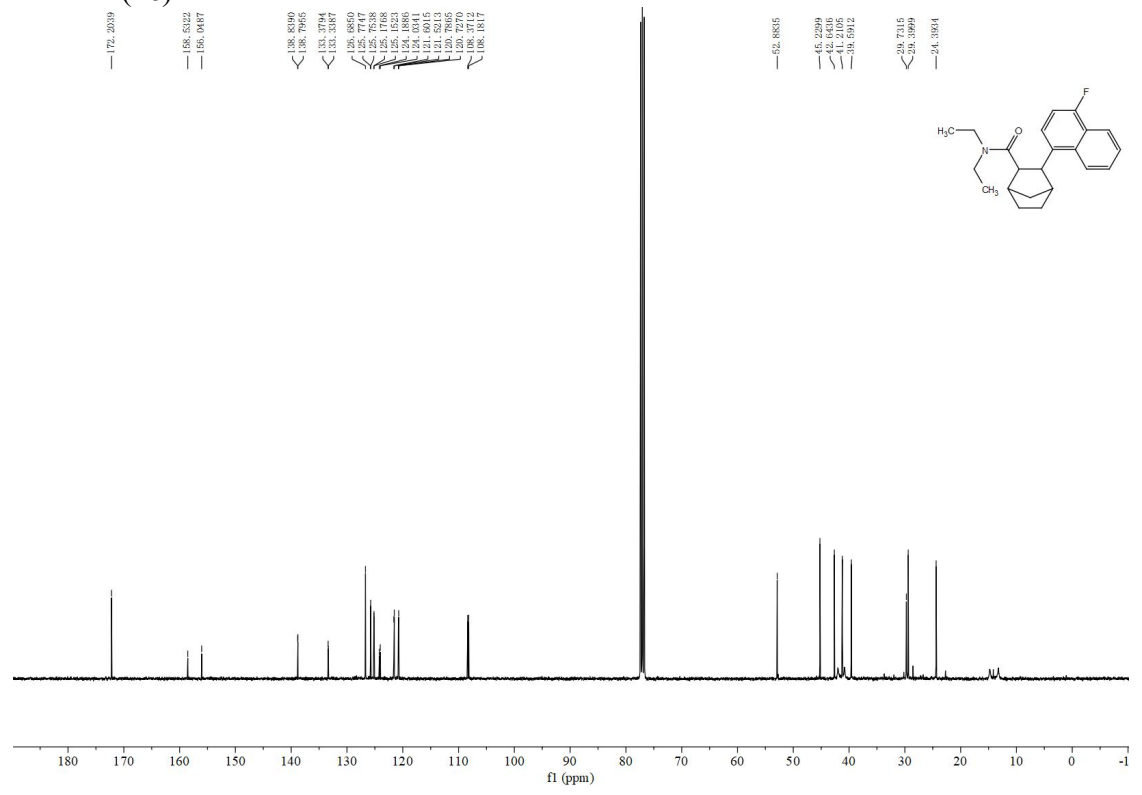
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-methoxynaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**3e**)



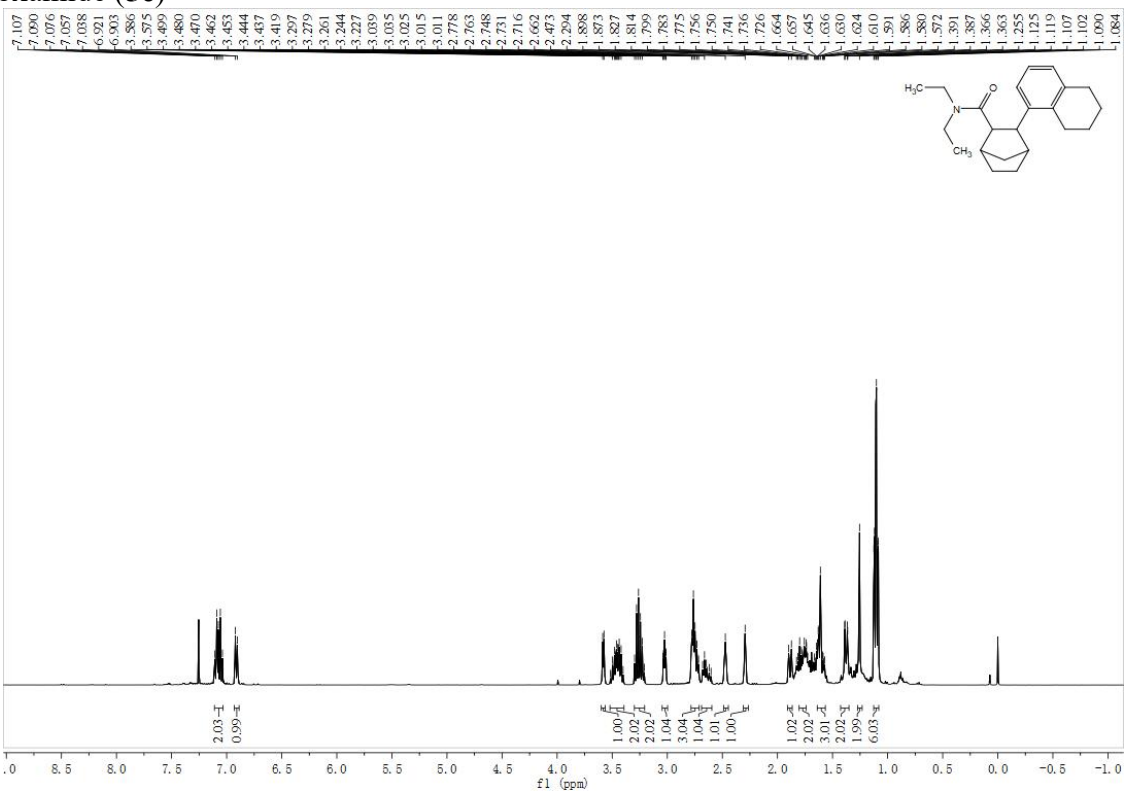
^{1}H NMR spectrum of *N,N*-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**)



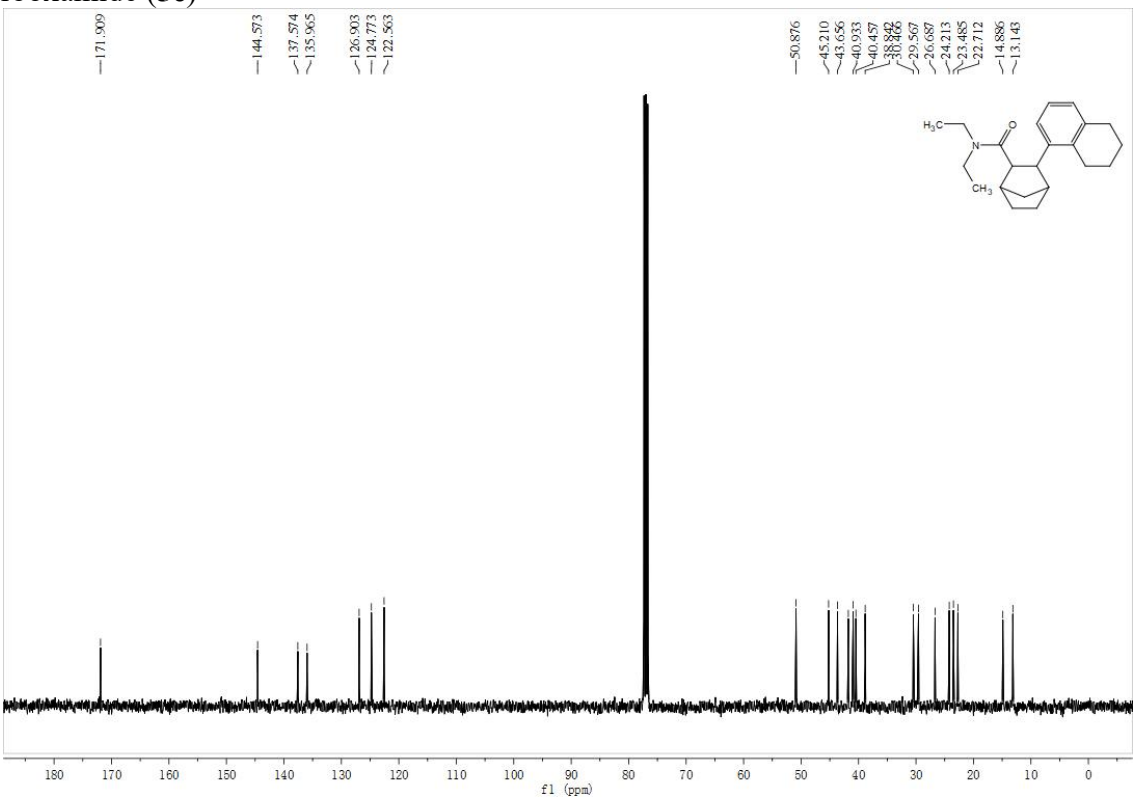
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**)



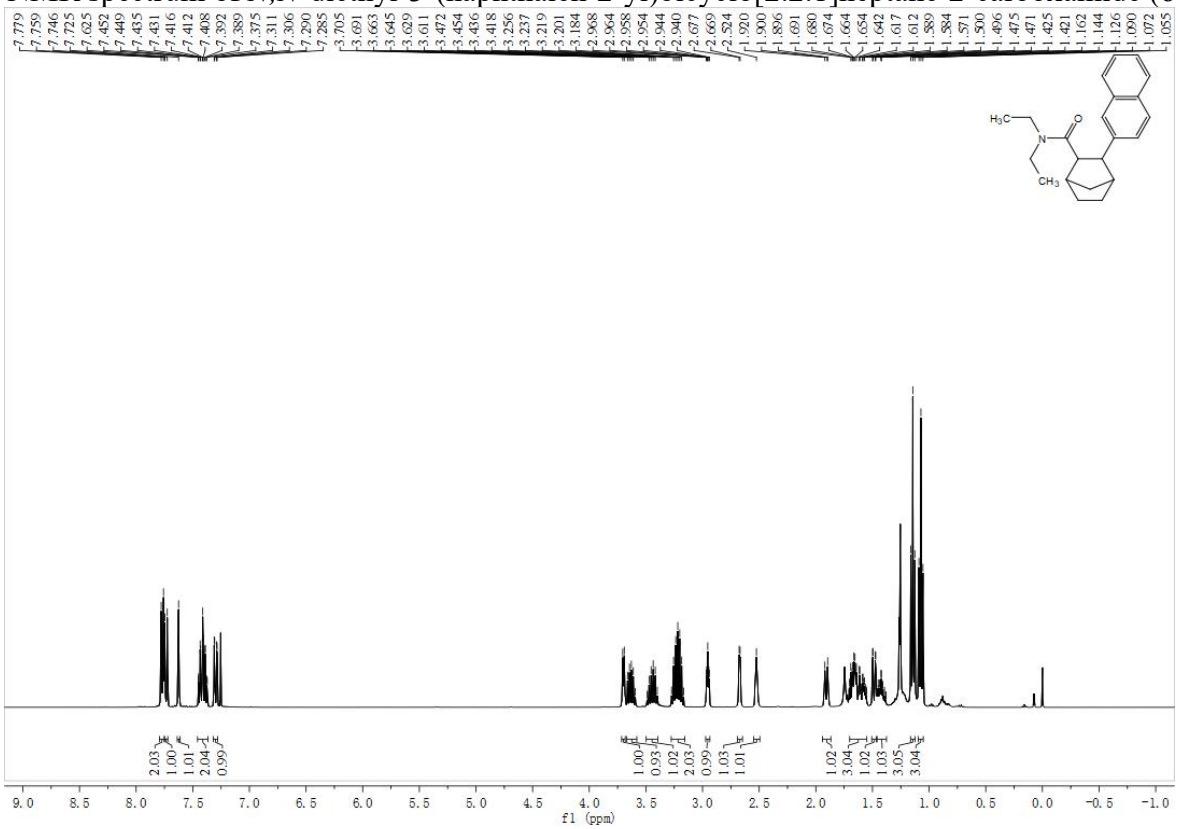
^{1}H NMR spectrum of *N,N*-diethyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**5e**)



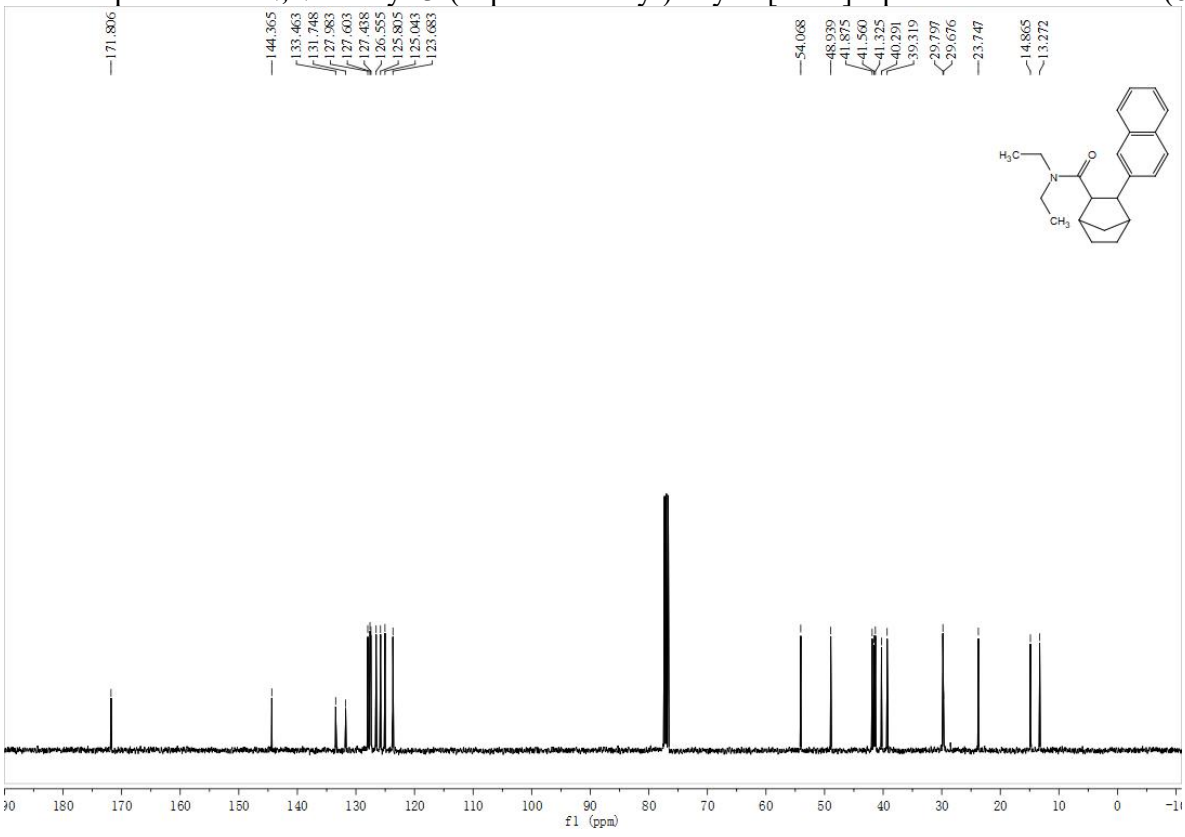
^{13}C NMR spectrum of *N,N*-diethyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**5e**)



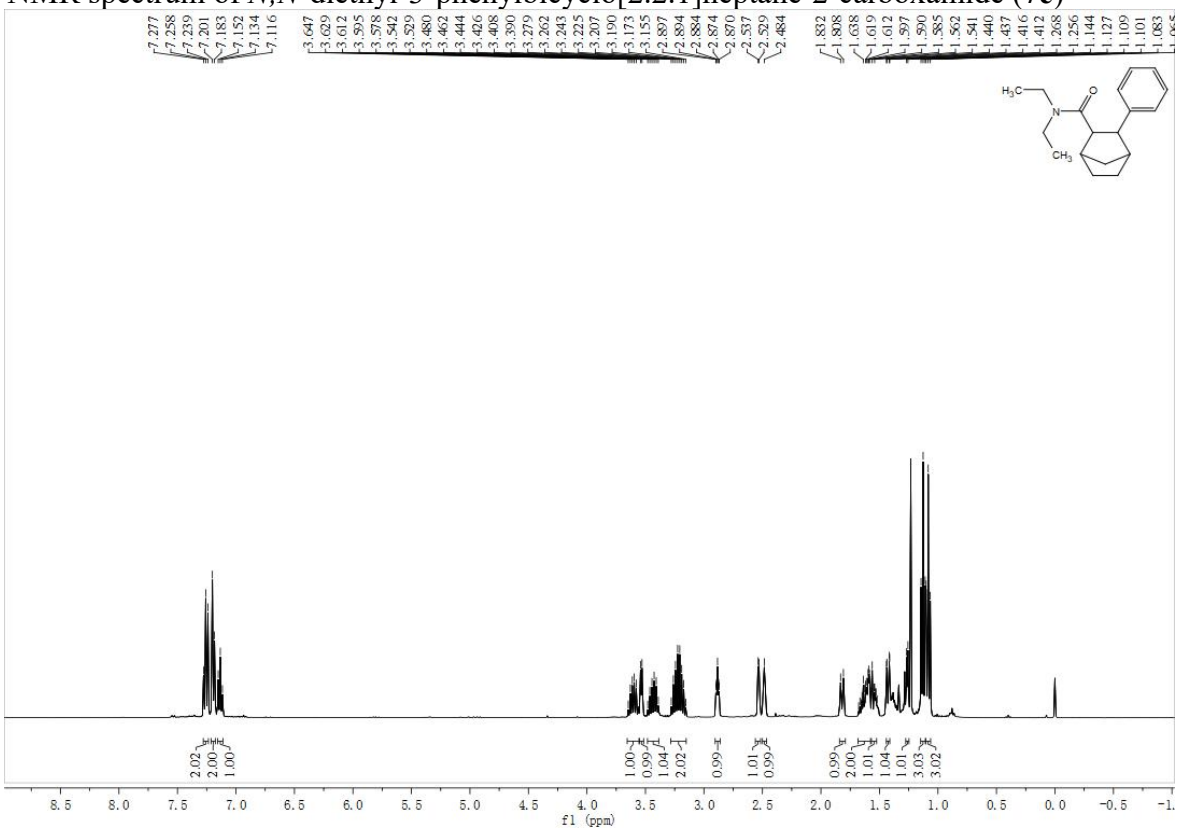
^{1}H NMR spectrum of *N,N*-diethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**6e**)



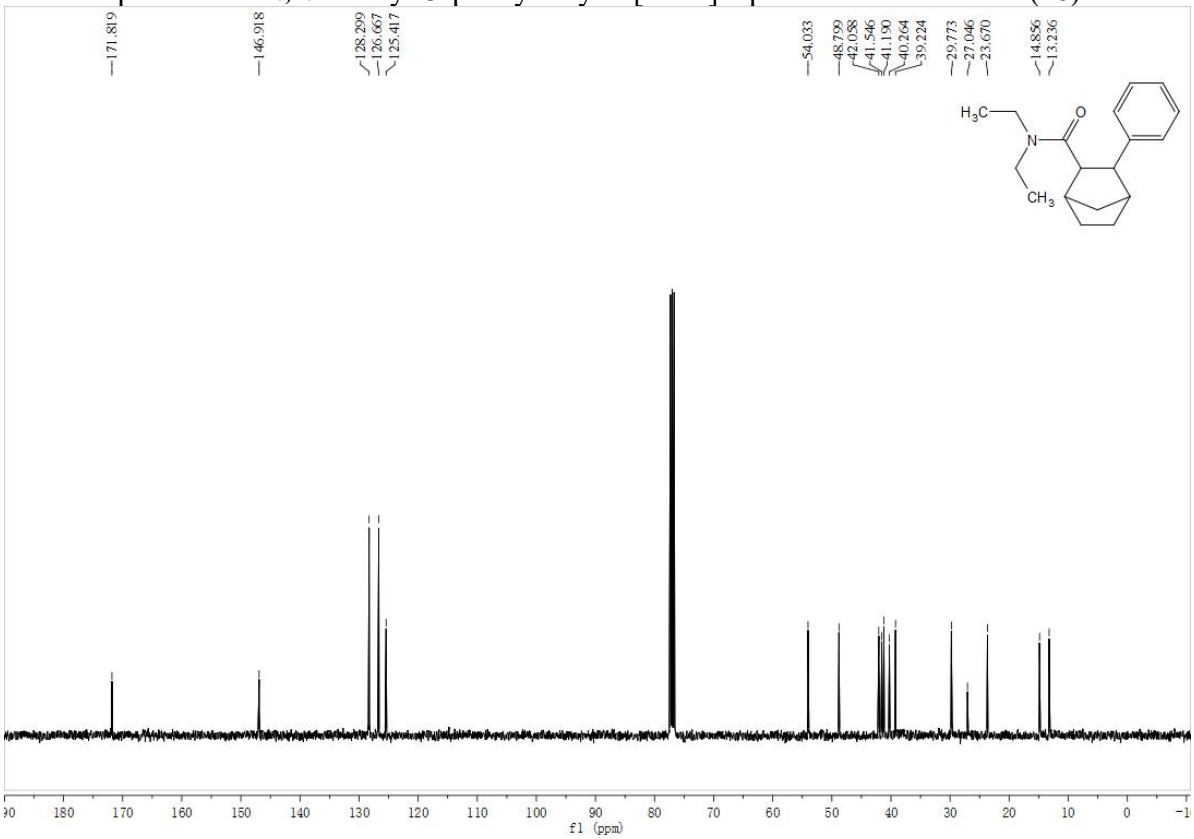
^{13}C NMR spectrum of *N,N*-diethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**6e**)



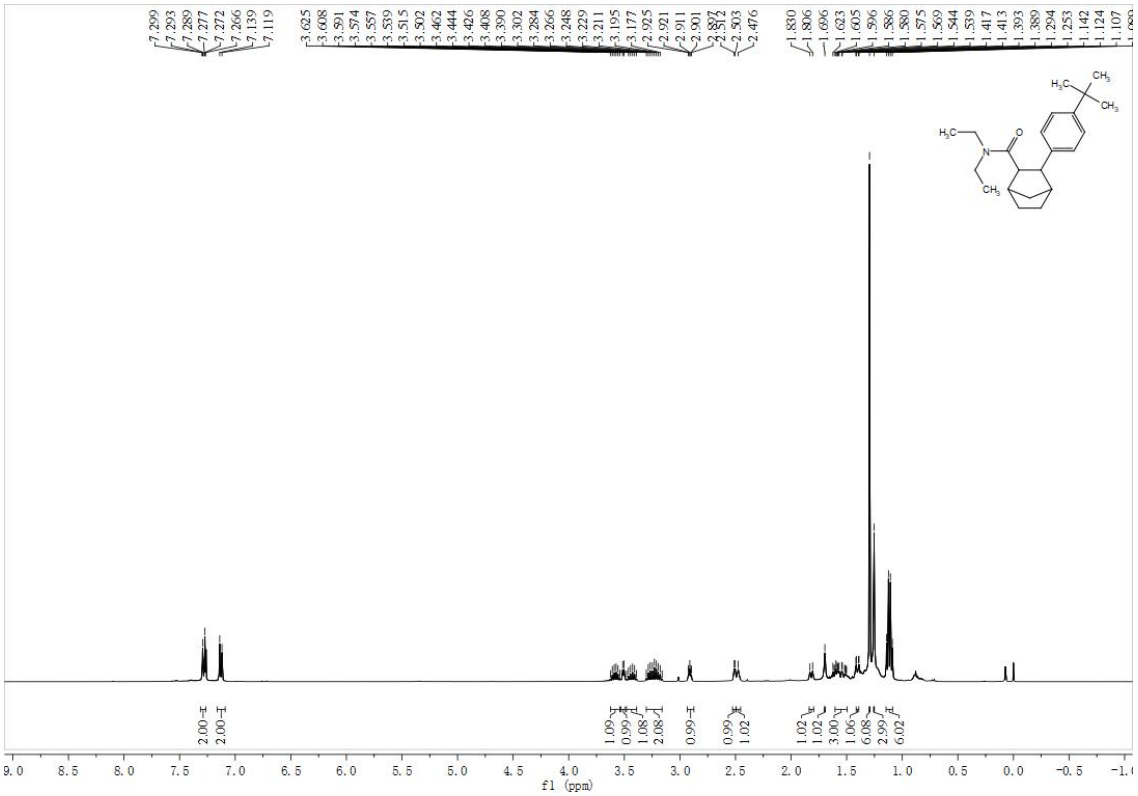
^{1}H NMR spectrum of *N,N*-diethyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (**7e**)



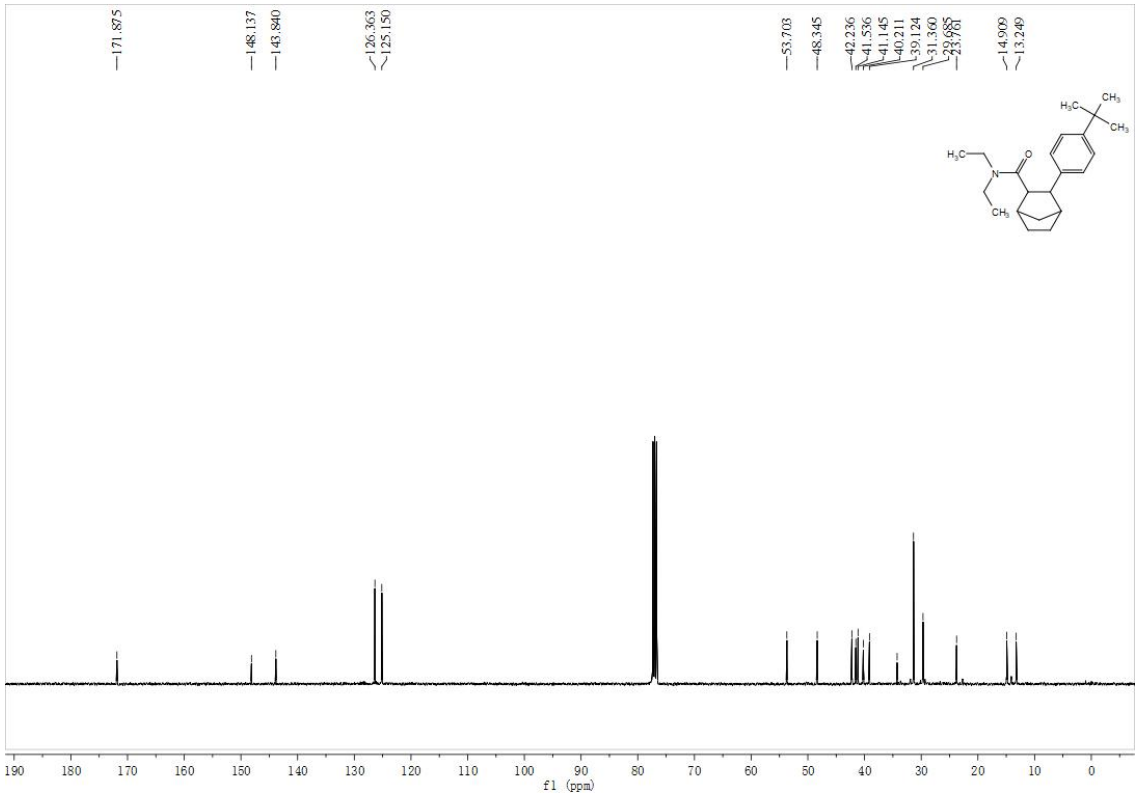
^{13}C NMR spectrum of *N,N*-diethyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (**7e**)



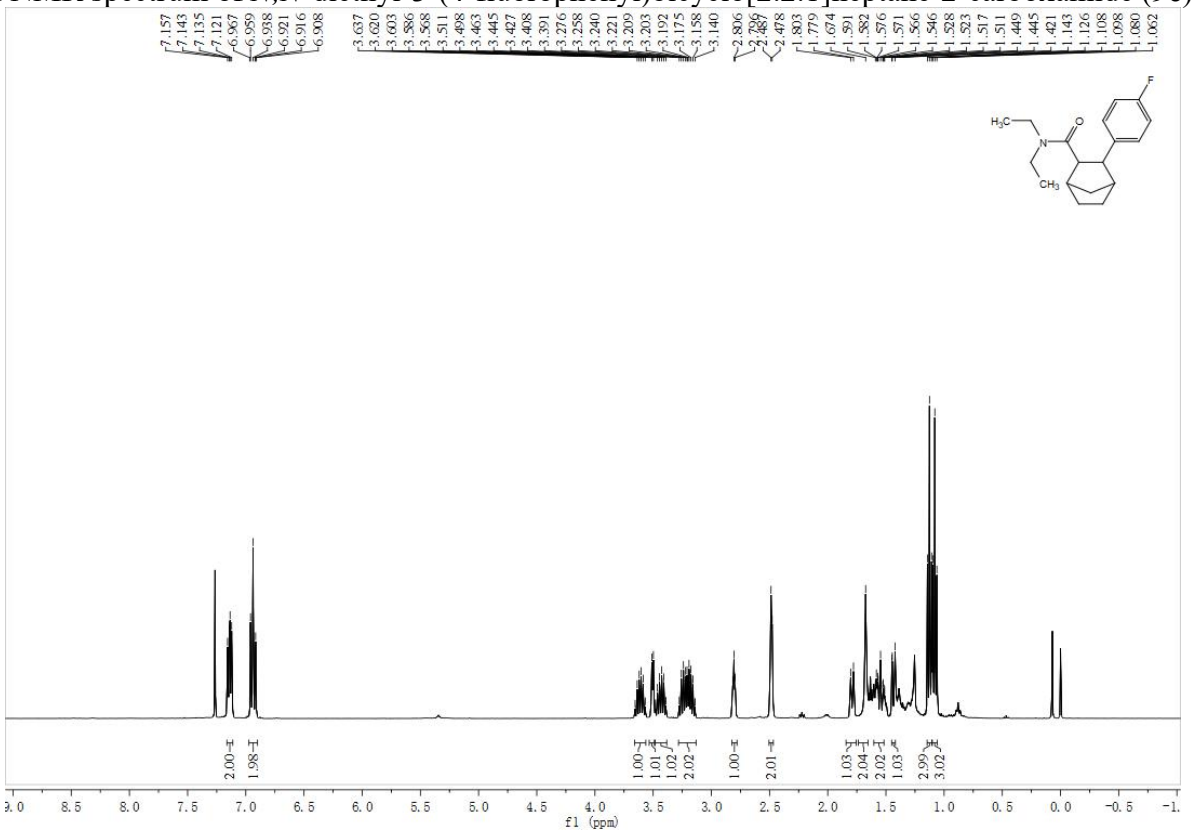
^{1}H NMR spectrum of 3-(4-(*tert*-butyl)phenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**8e**)



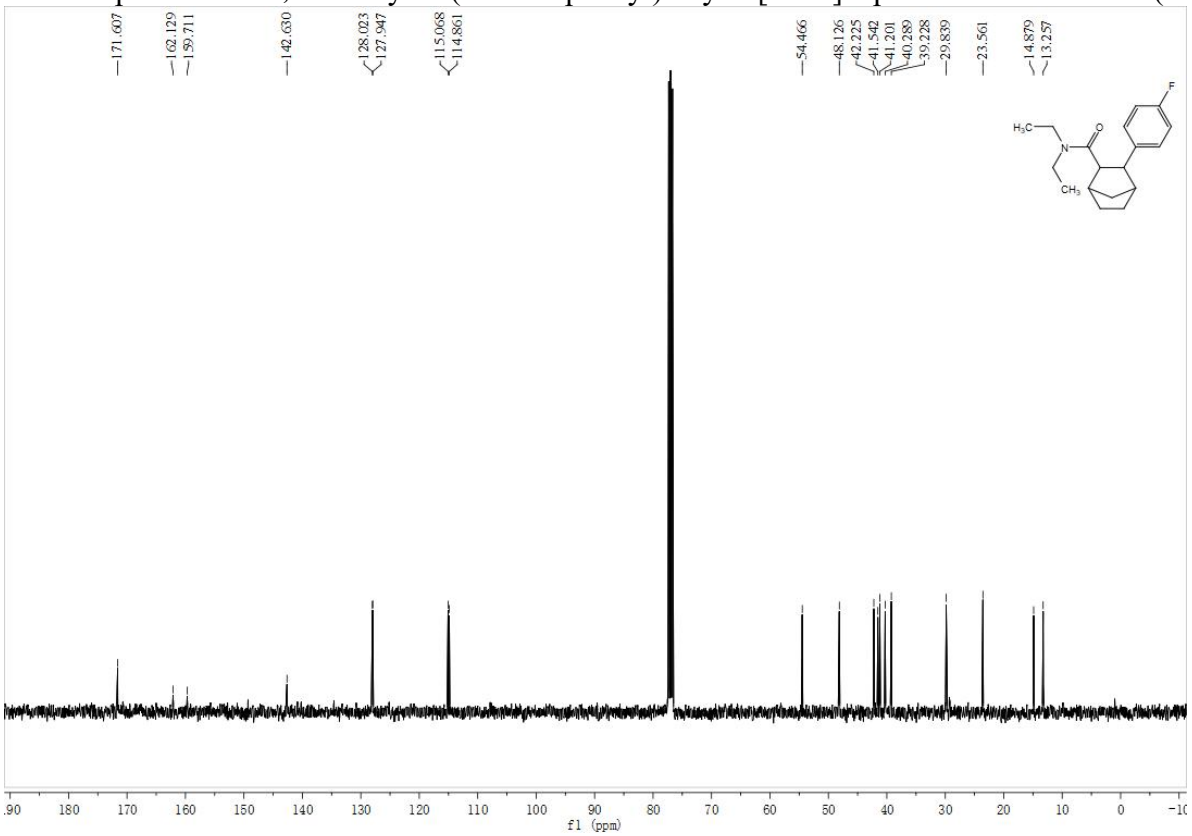
^{13}C NMR spectrum of 3-(4-(*tert*-butyl)phenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**8e**)



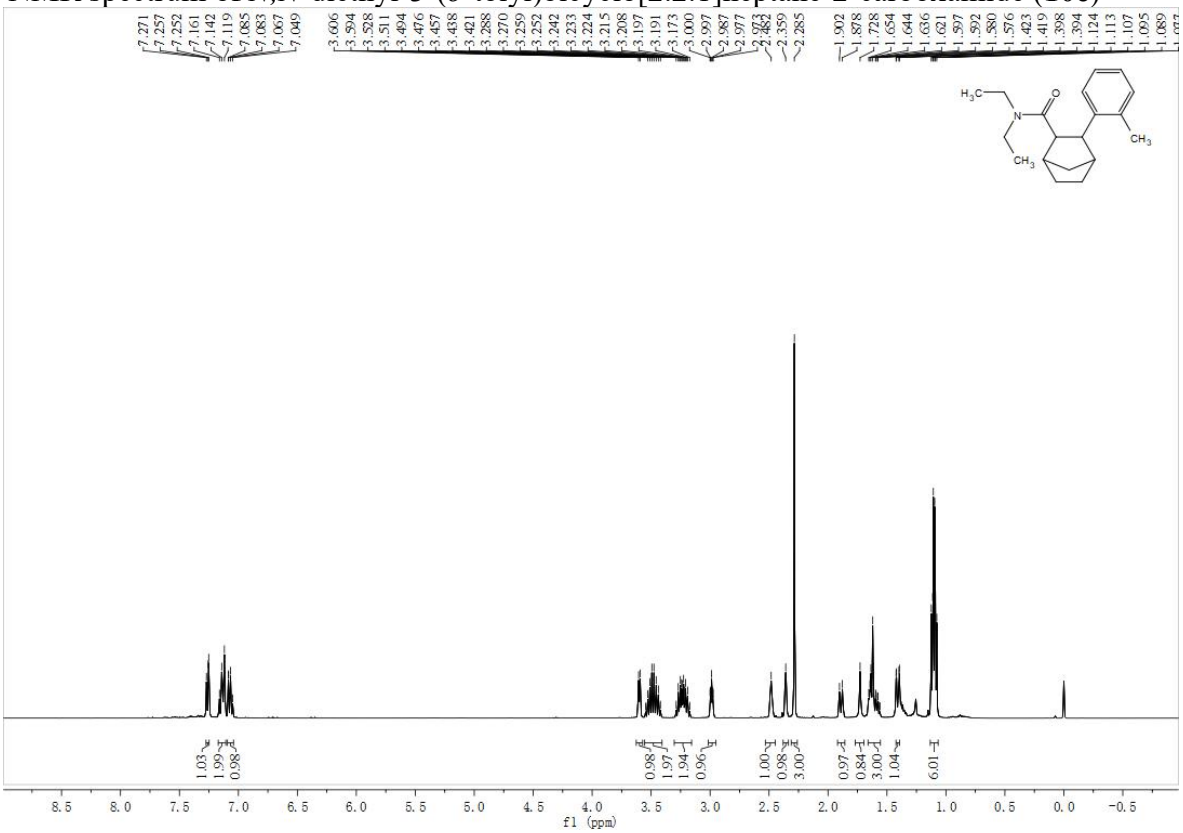
^{1}H NMR spectrum of *N,N*-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**)



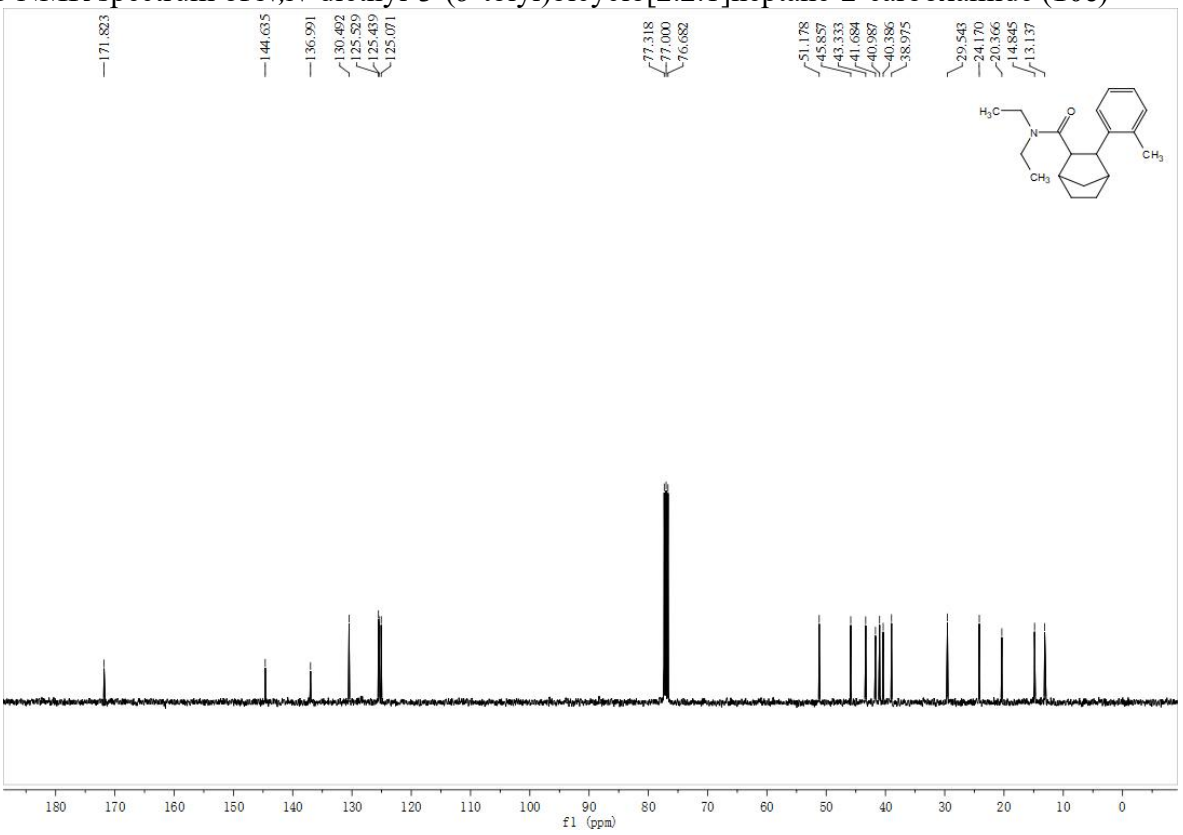
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**)



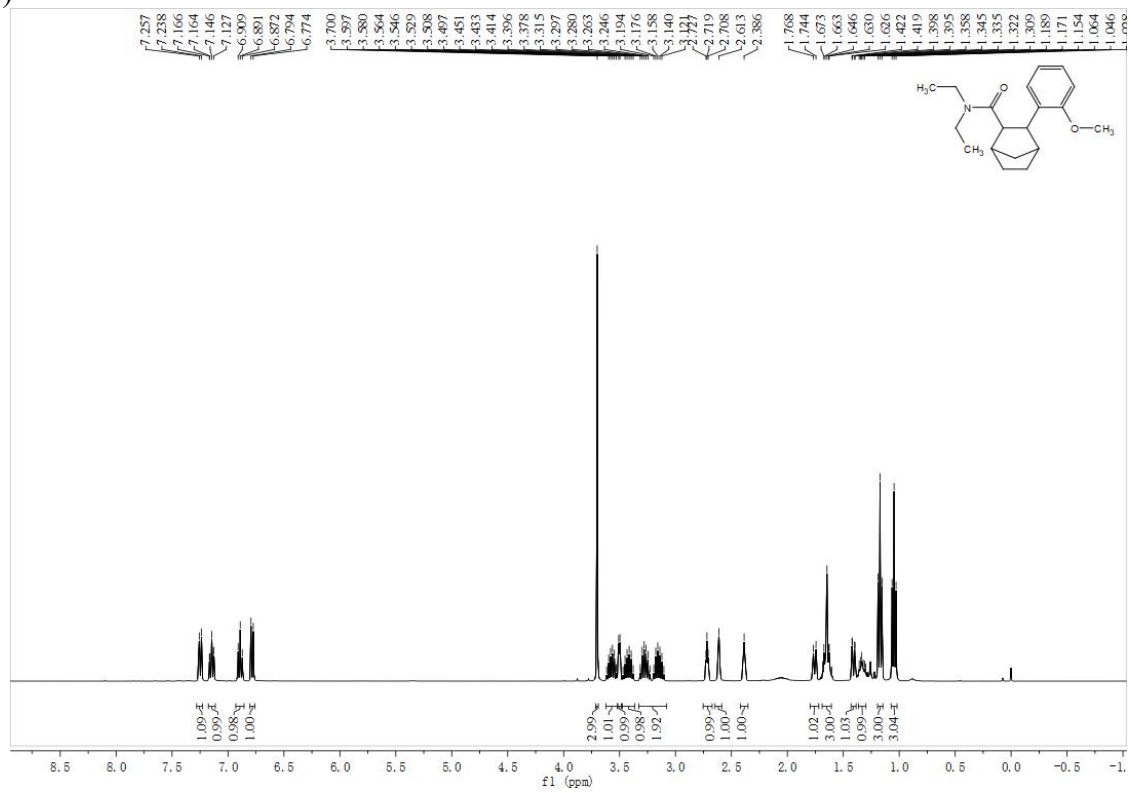
^{1}H NMR spectrum of *N,N*-diethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**10e**)



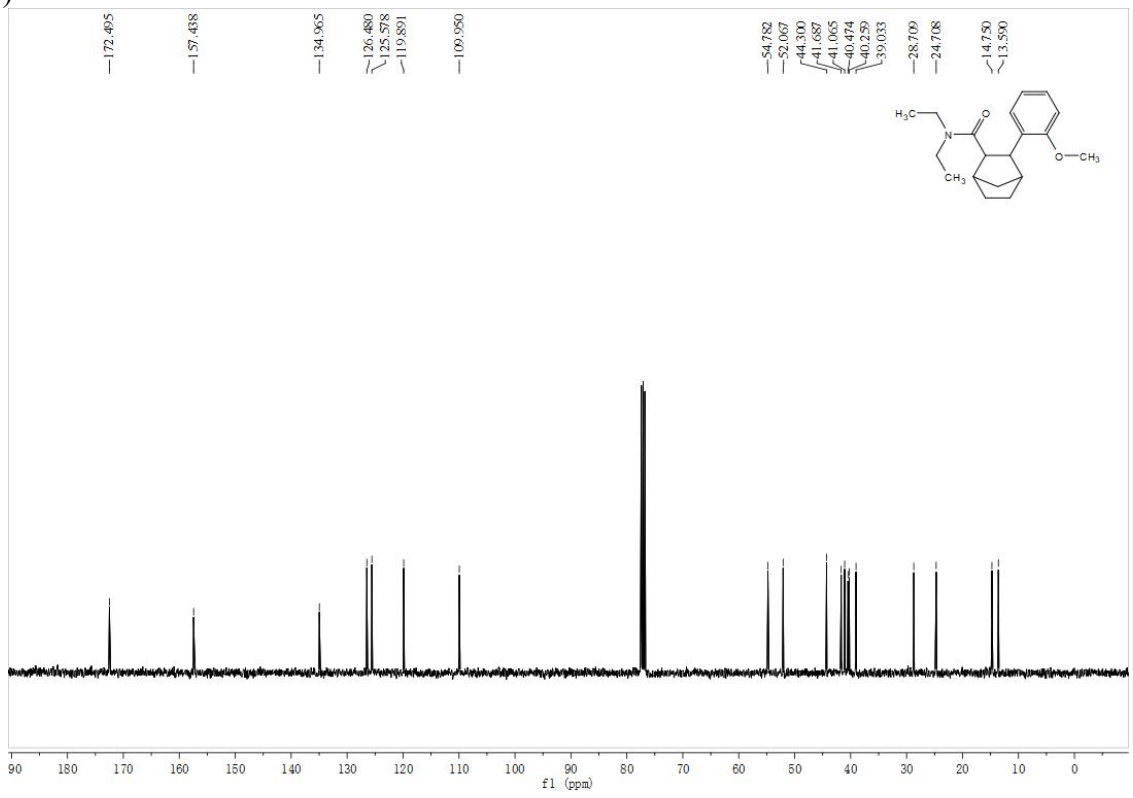
^{13}C NMR spectrum of *N,N*-diethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**10e**)



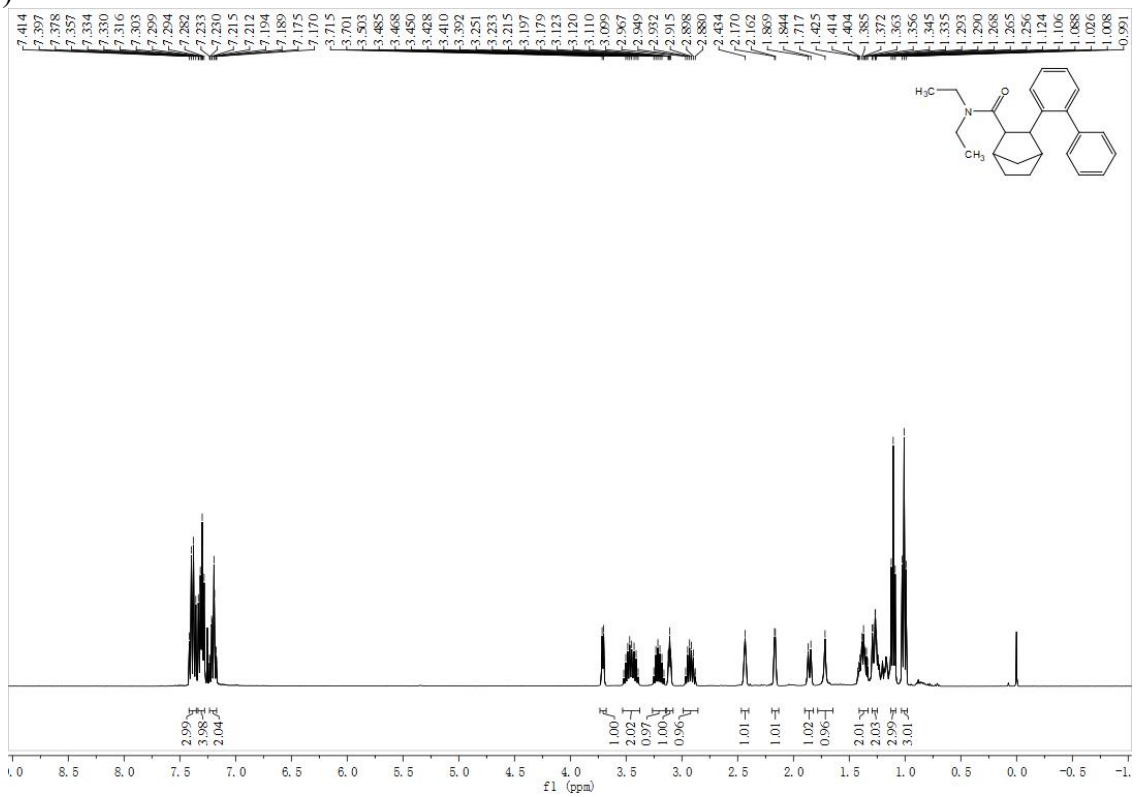
^{1}H NMR spectrum of *N,N*-diethyl-3-(2-methoxyphenyl)bicyclo[2.2.1]heptane-2-carboxamide (**11e**)



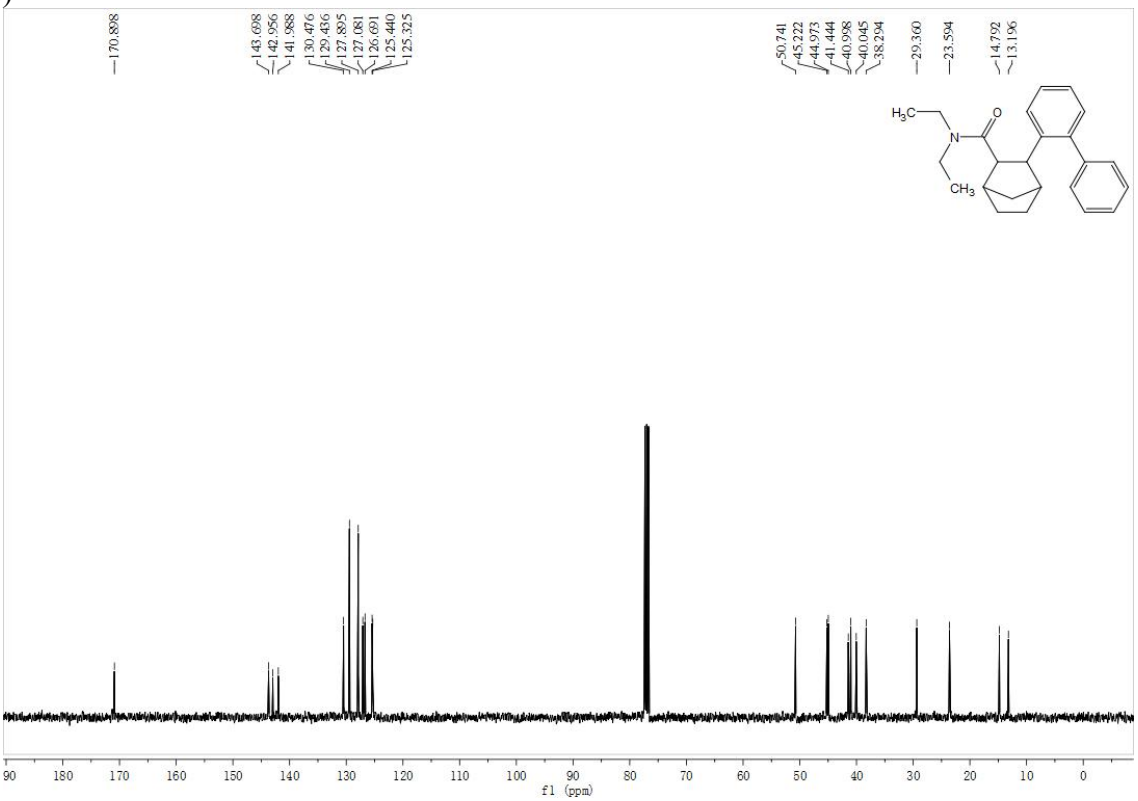
^{13}C NMR spectrum of *N,N*-diethyl-3-(2-methoxyphenyl)bicyclo[2.2.1]heptane-2-carboxamide (**11e**)



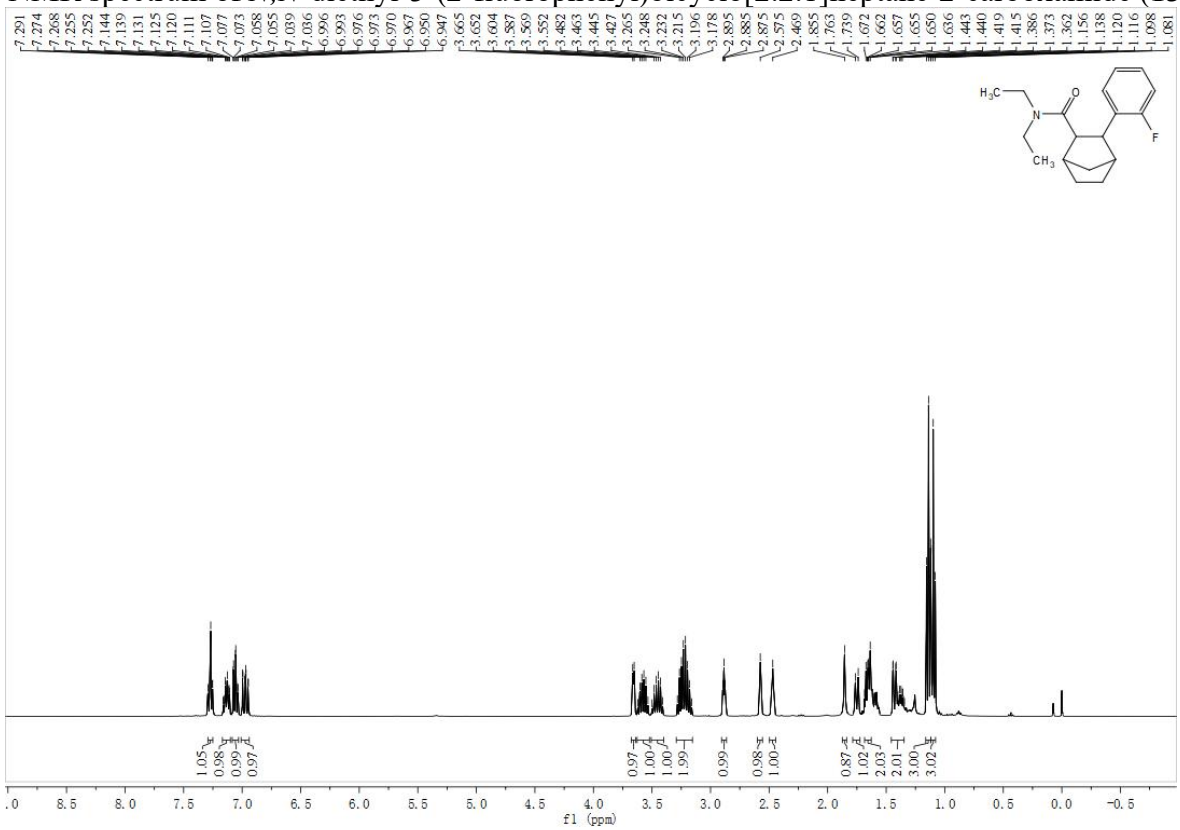
^{1}H NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-N,N-diethylbicyclo[2.2.1]heptane-2-carboxamide (**12e**)



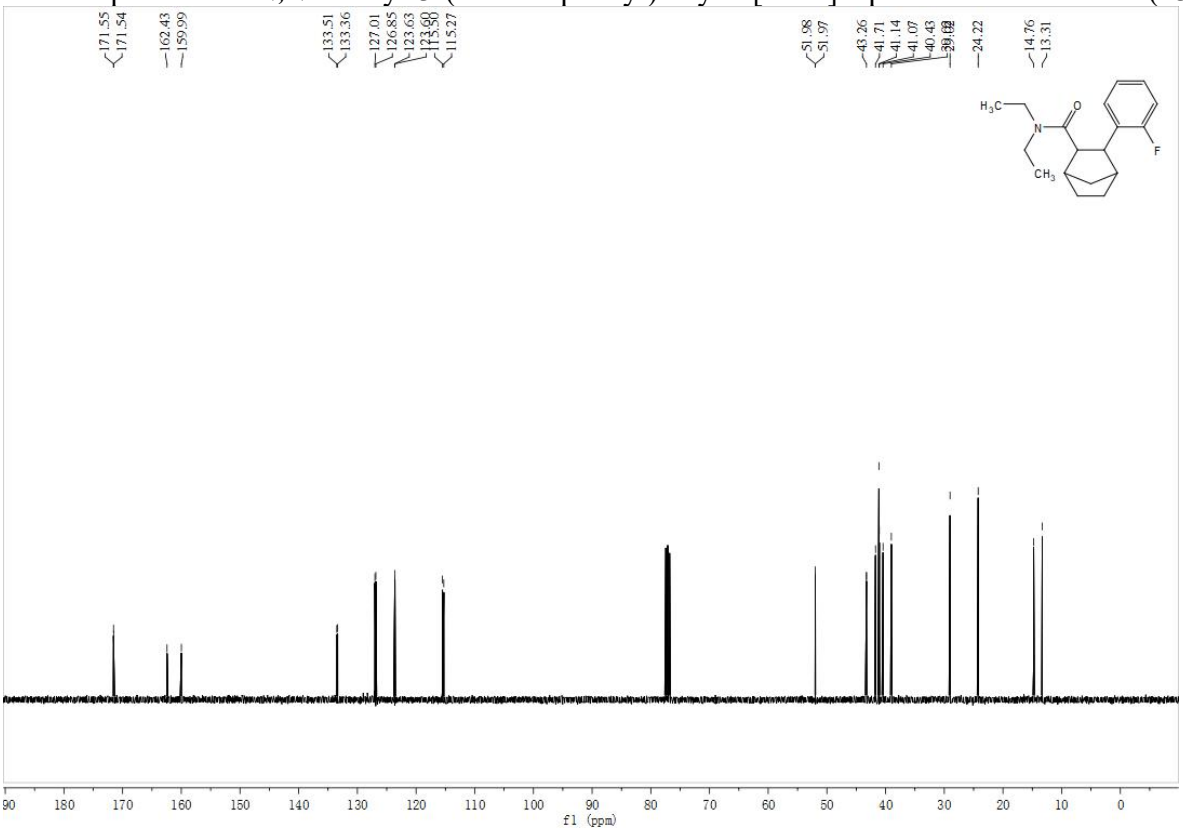
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-N,N-diethylbicyclo[2.2.1]heptane-2-carboxamide (**12e**)



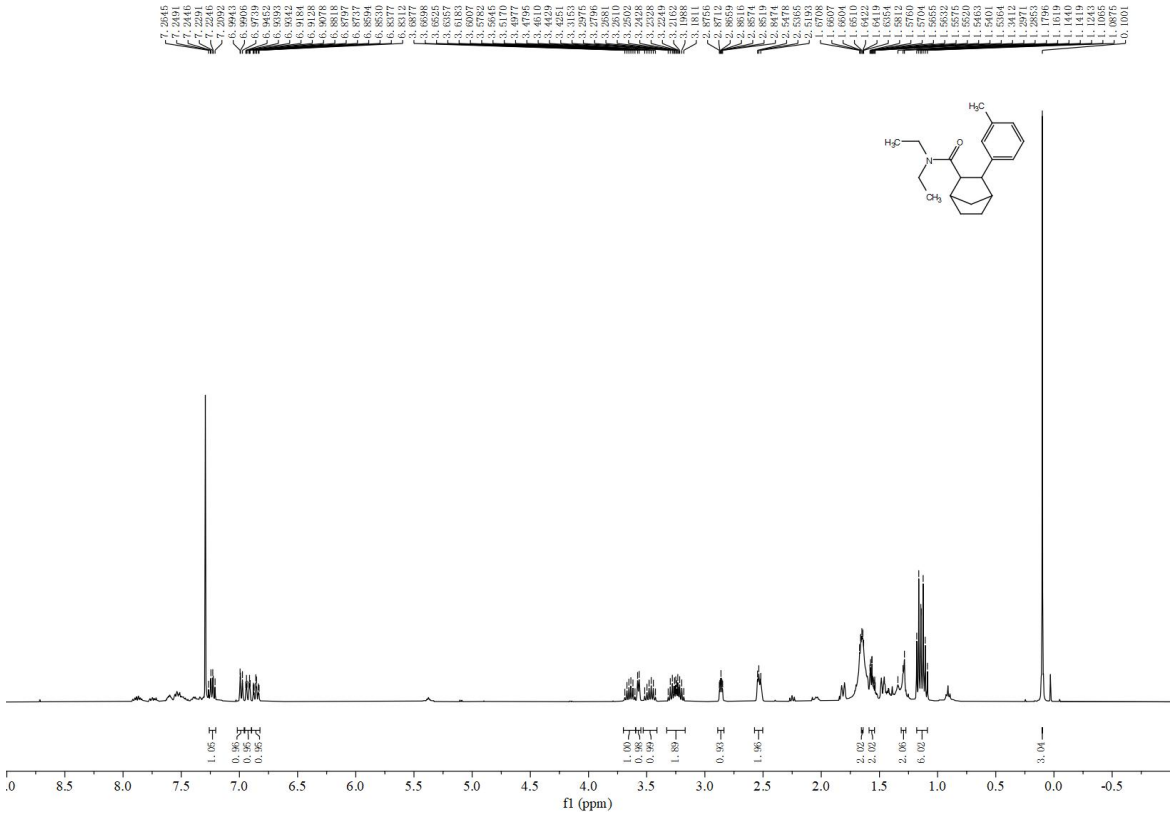
^{1}H NMR spectrum of *N,N*-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**)



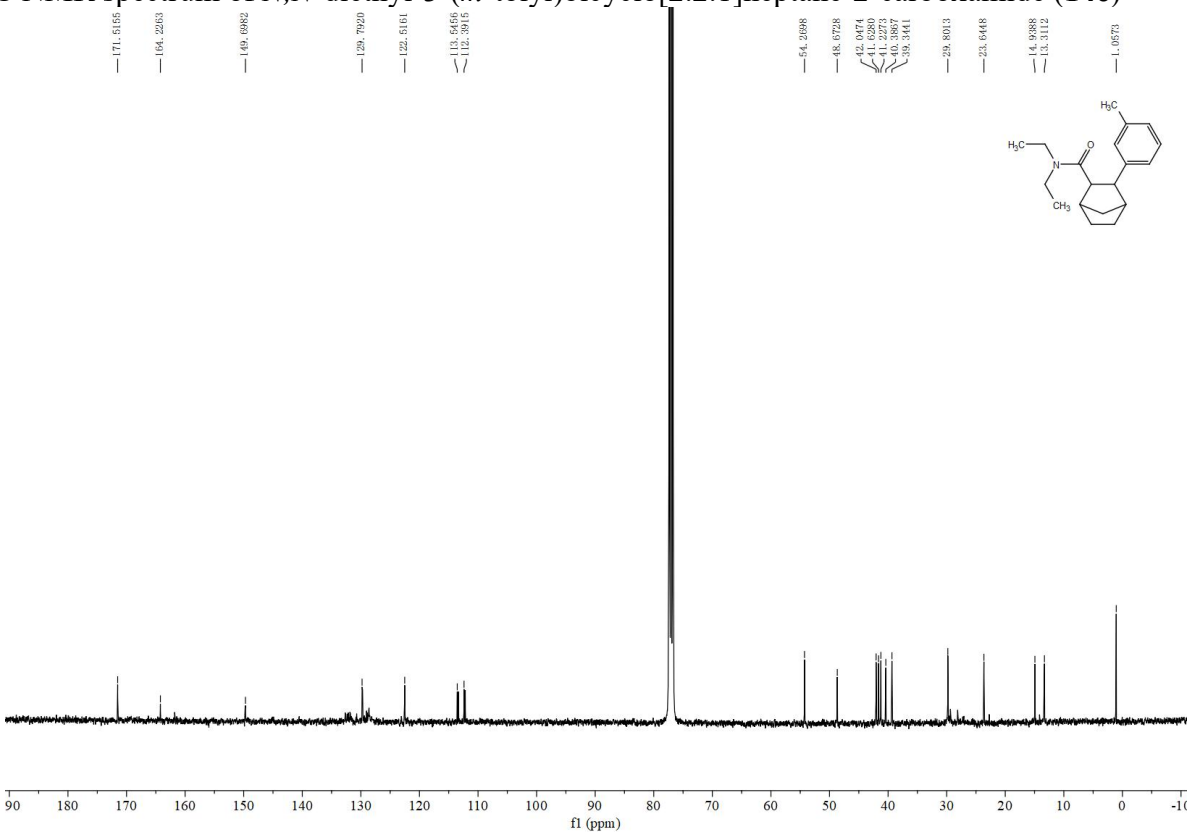
^{13}C NMR spectrum of *N,N*-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**)



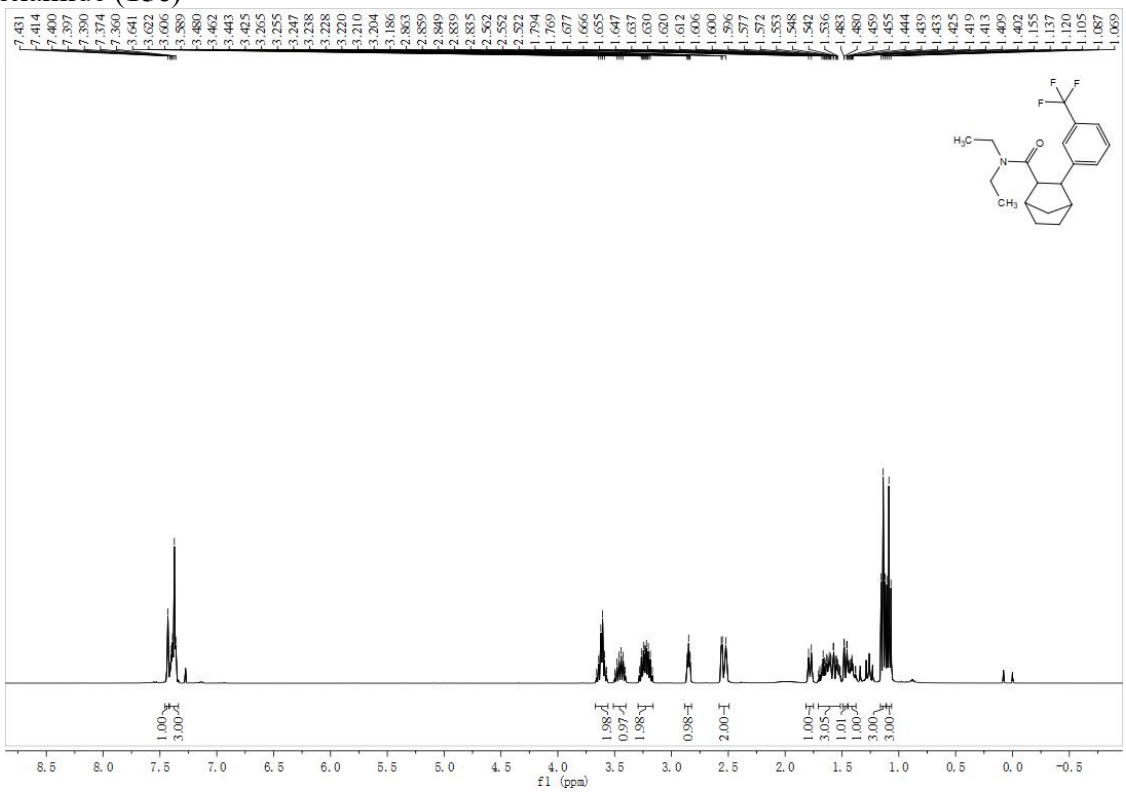
^{1}H NMR spectrum of *N,N*-diethyl-3-(*m*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**14e**)



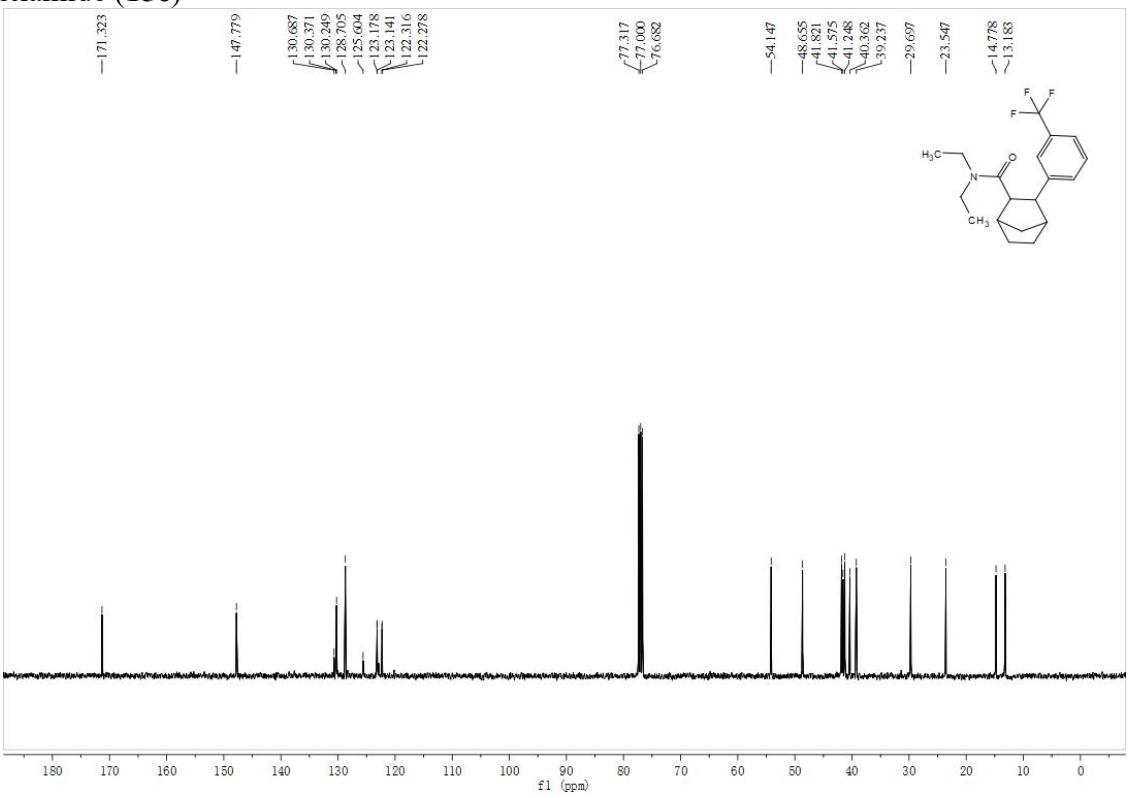
^{13}C NMR spectrum of *N,N*-diethyl-3-(*m*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**14e**)



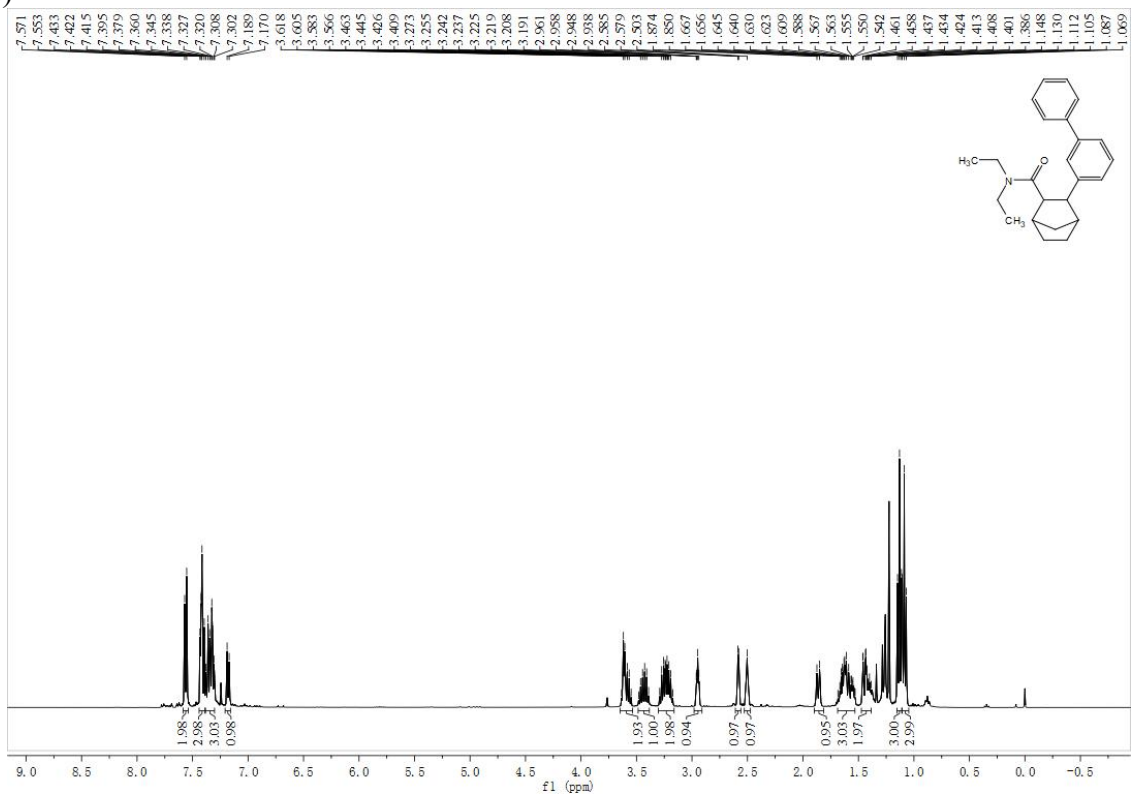
^{1}H NMR spectrum of *N,N*-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**)



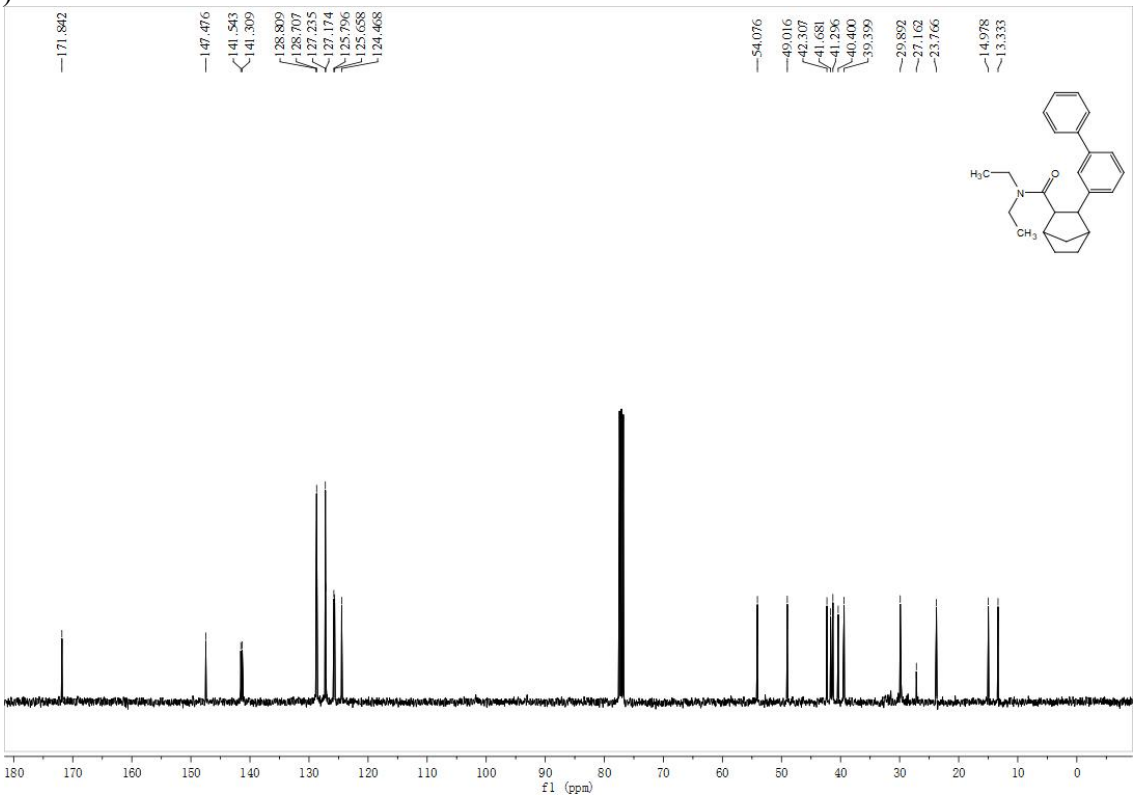
^{13}C NMR spectrum of *N,N*-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**)



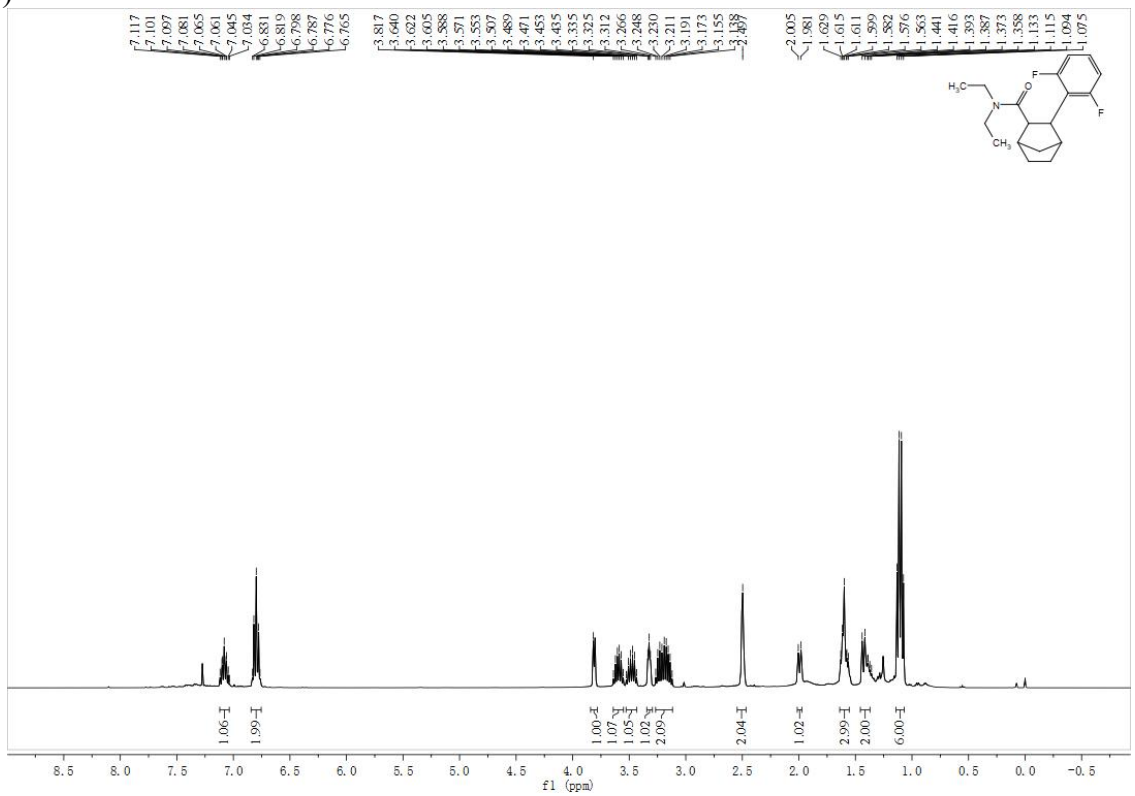
^{1}H NMR spectrum of 3-([1,1'-biphenyl]-3-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**16e**)



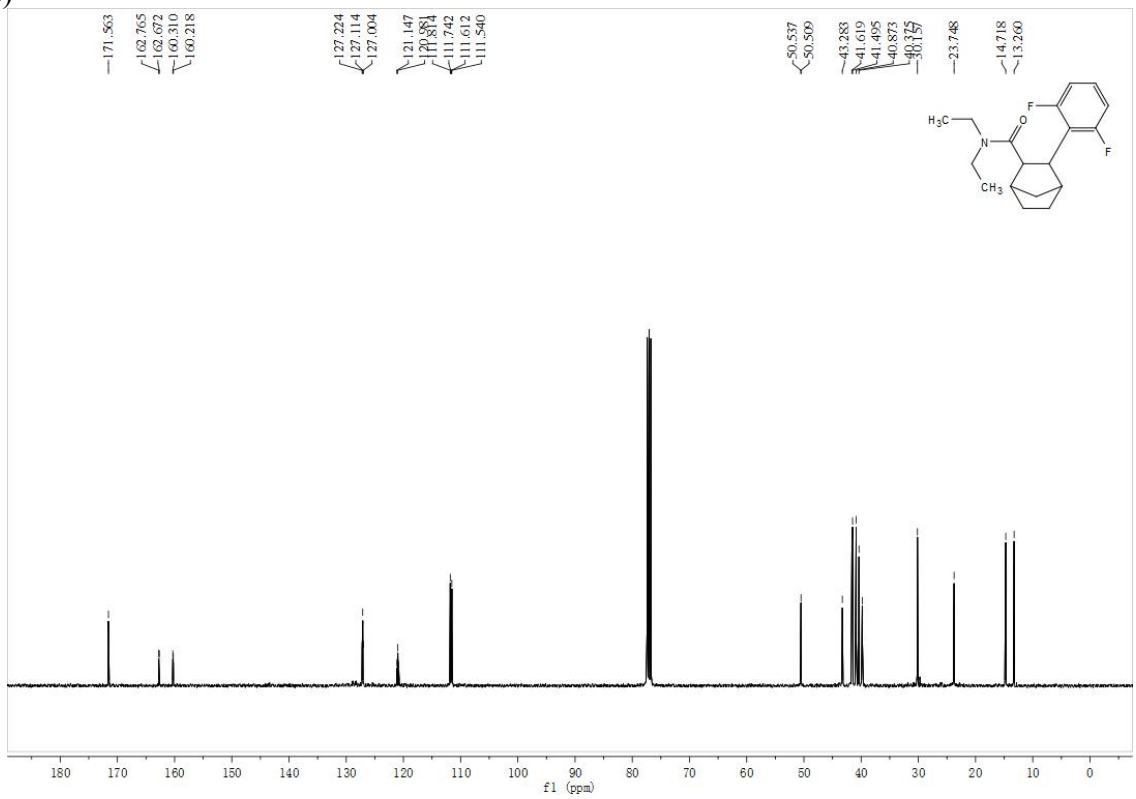
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-3-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**16e**)



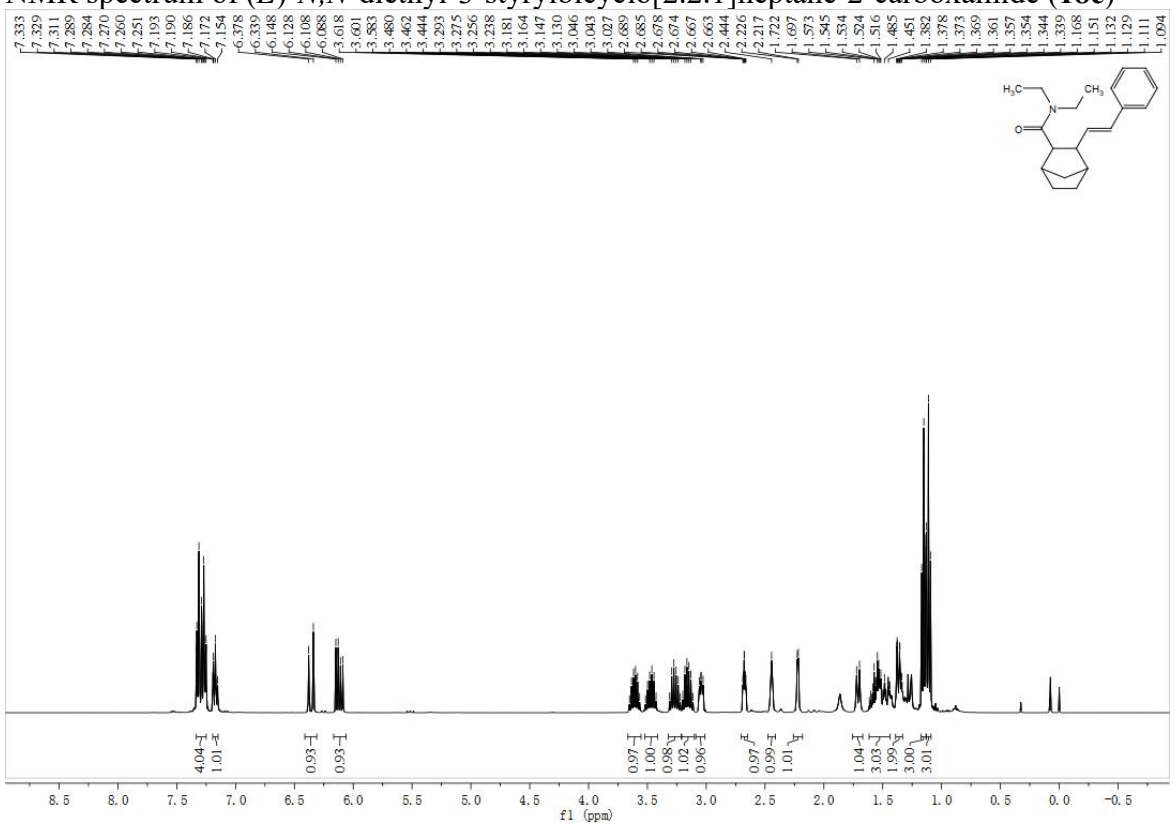
^{1}H NMR spectrum of 3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**)



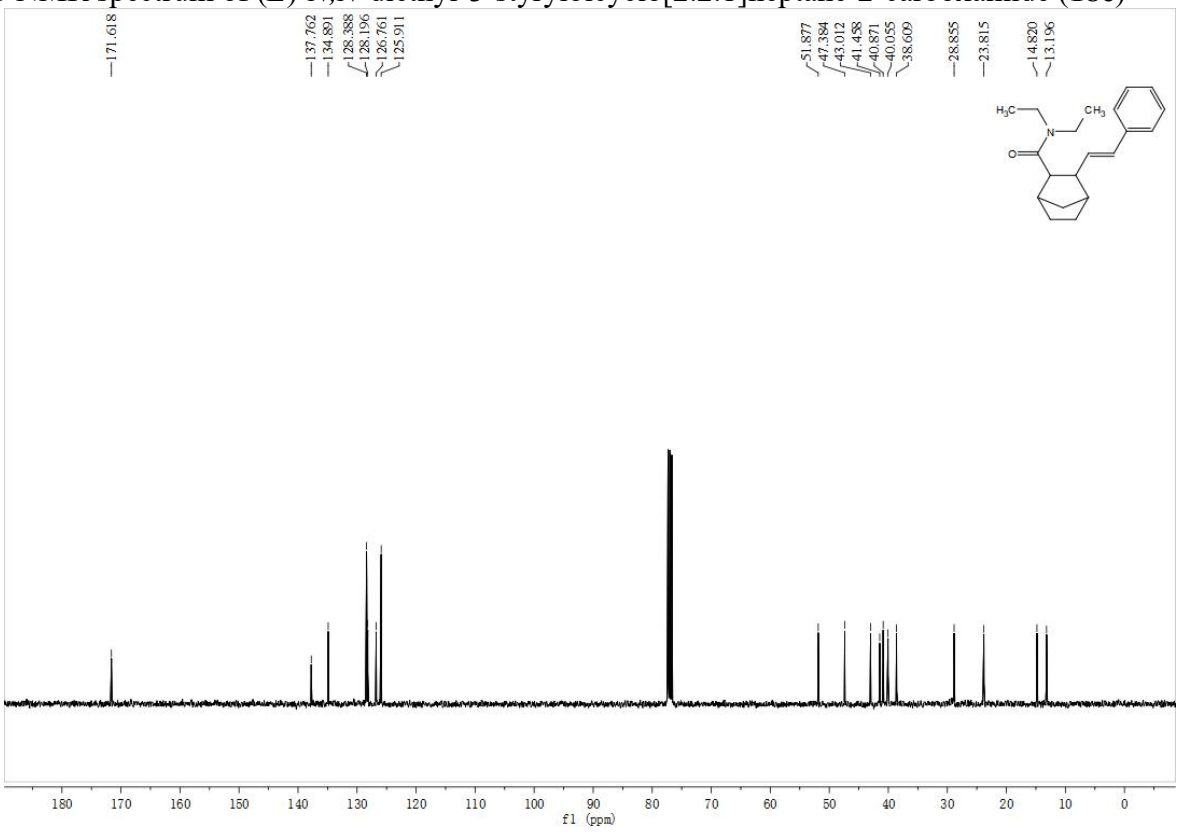
^{13}C NMR spectrum of 3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**)



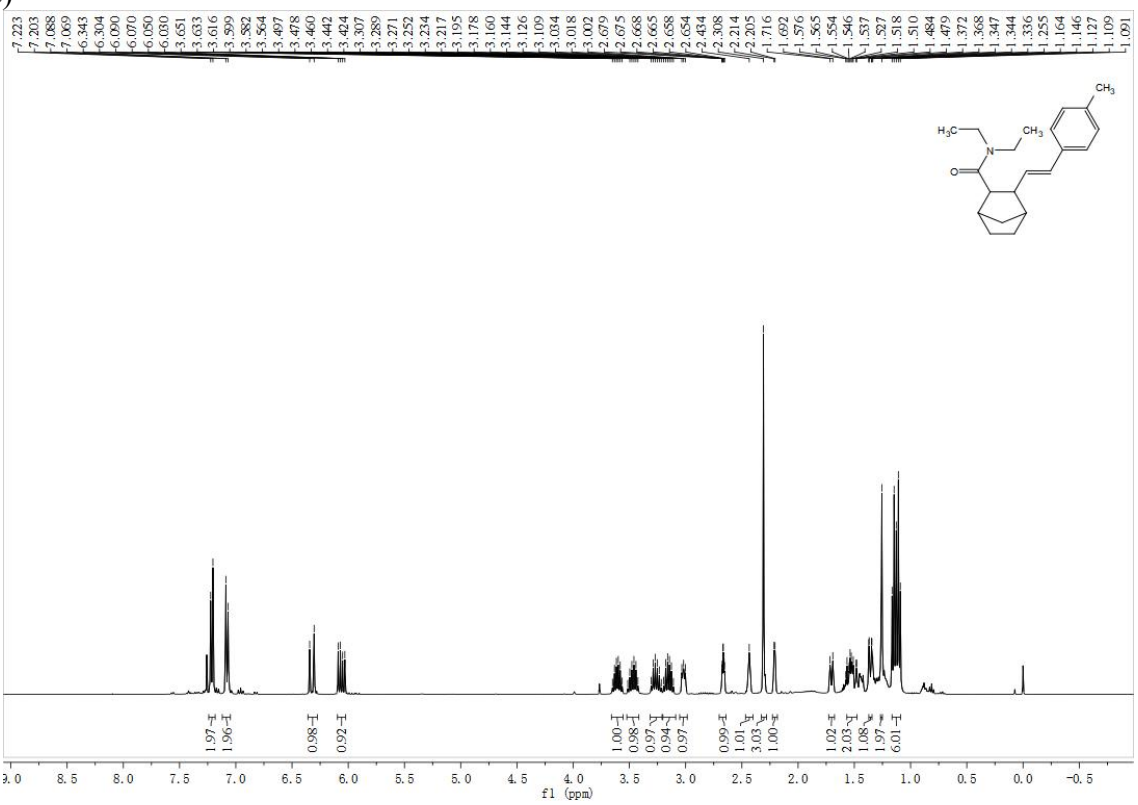
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**18e**)



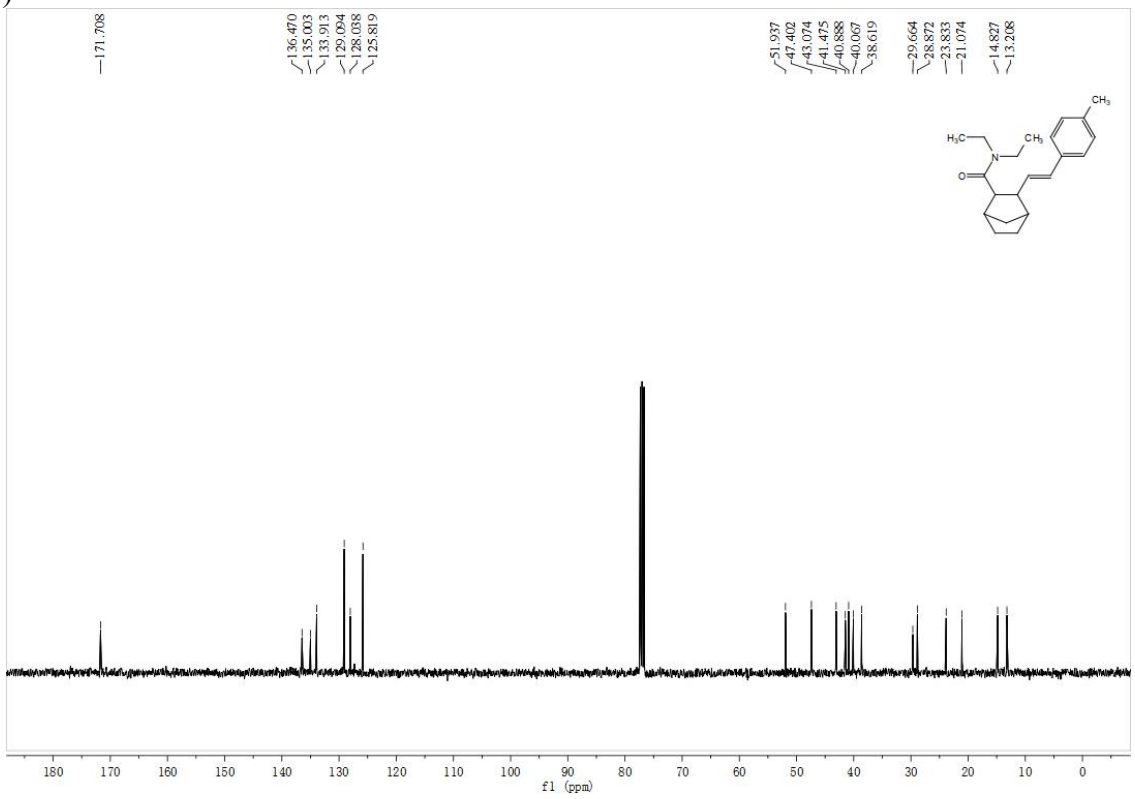
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**18e**)



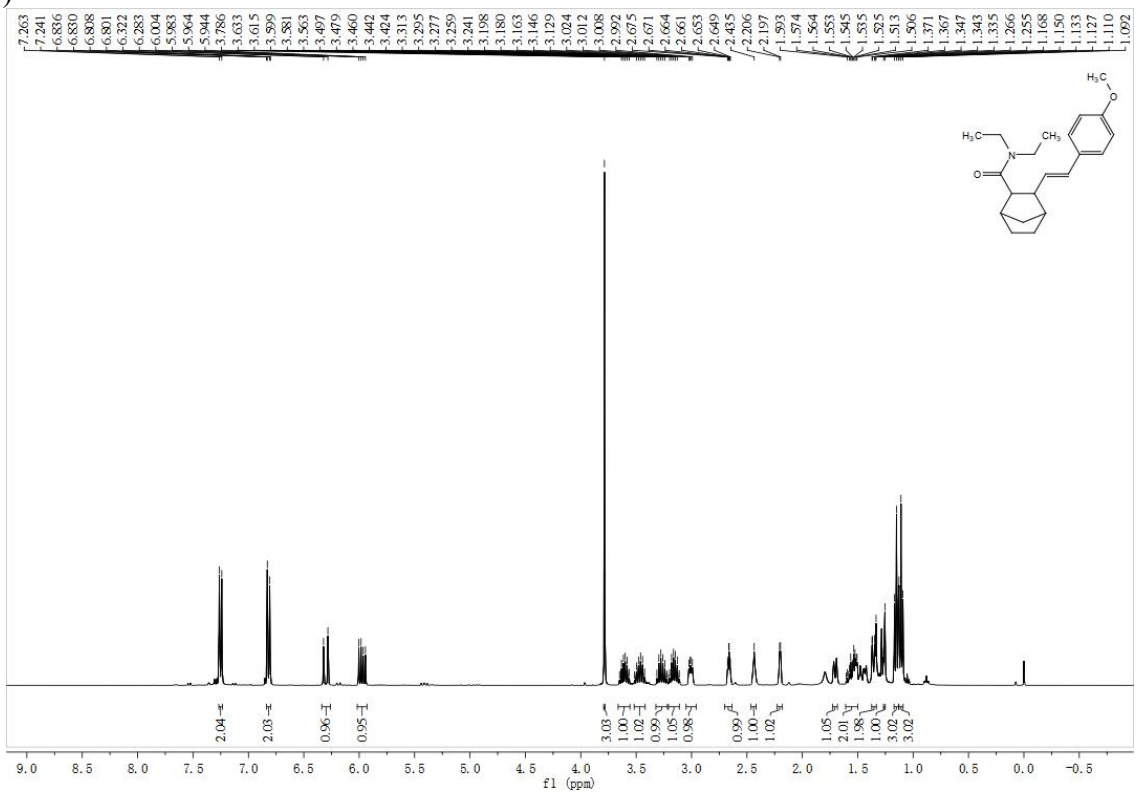
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**19e**)



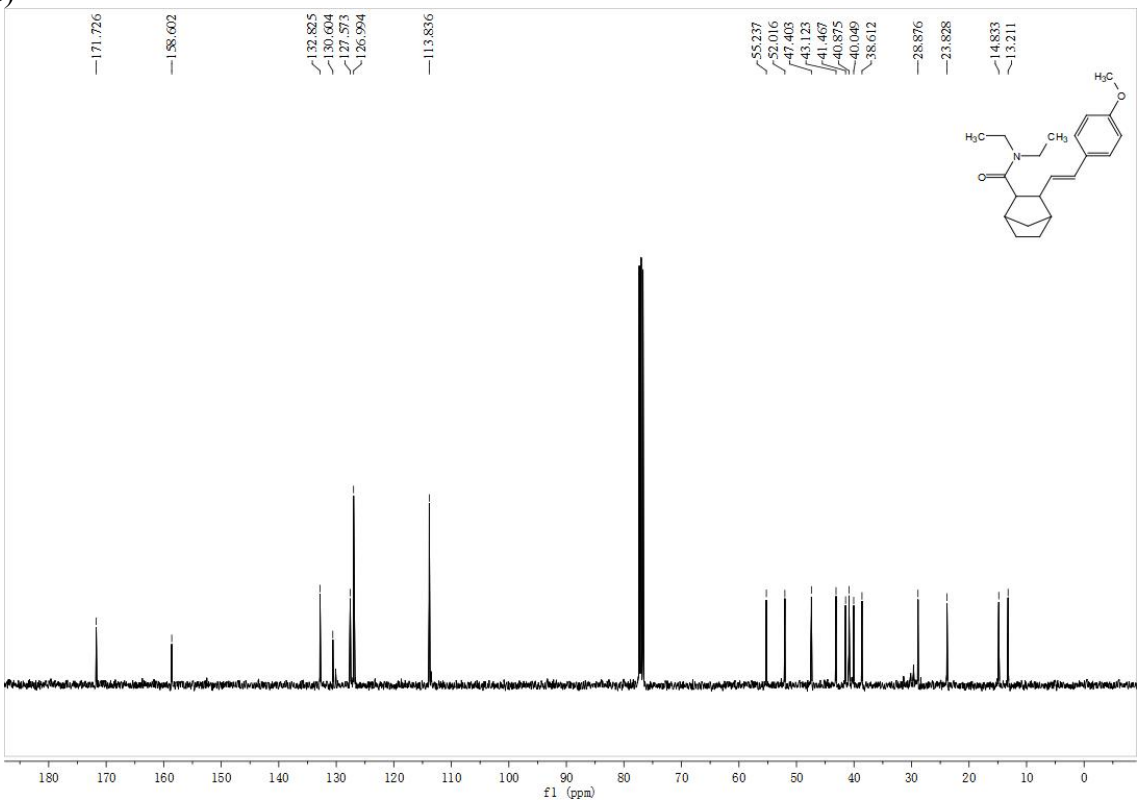
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**19e**)



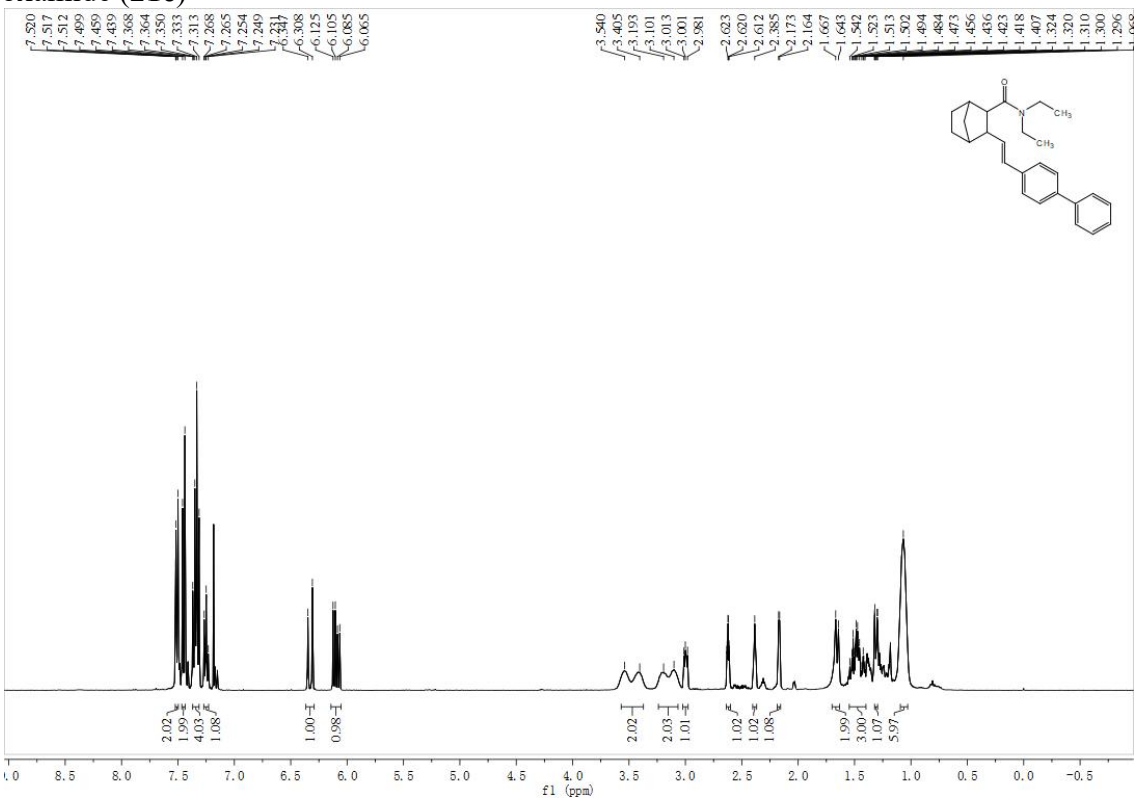
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**20e**)



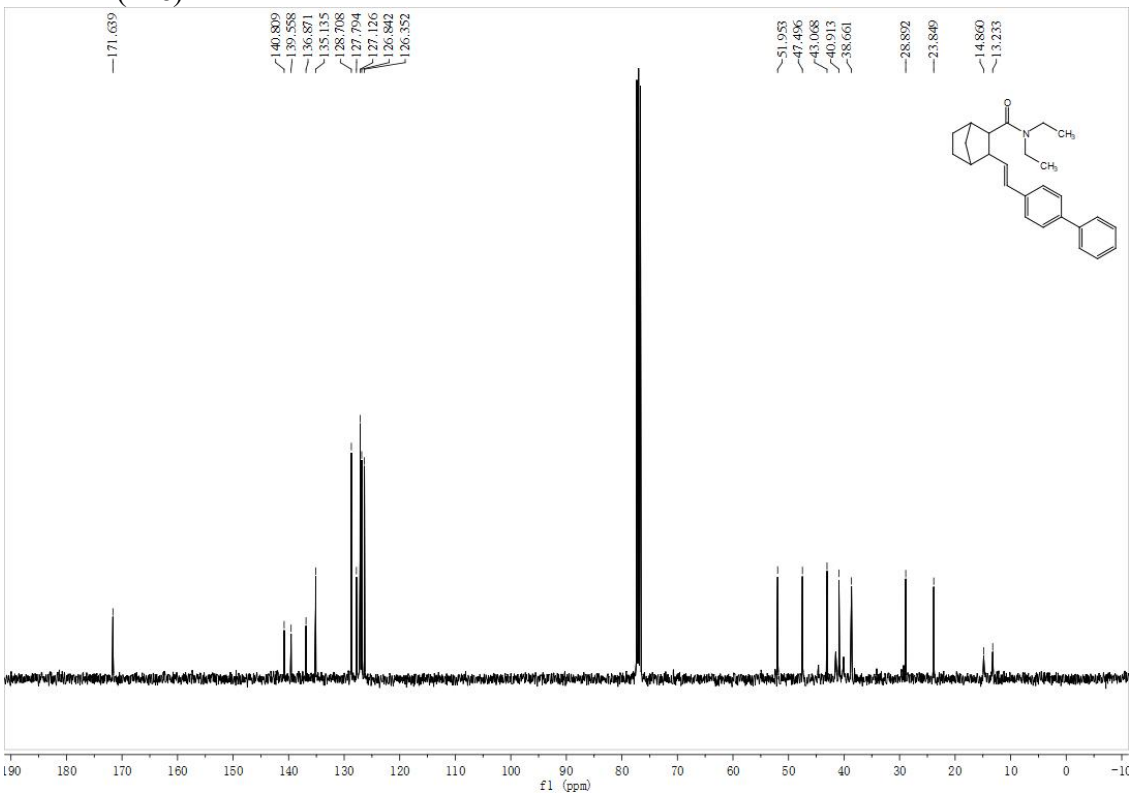
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**20e**)



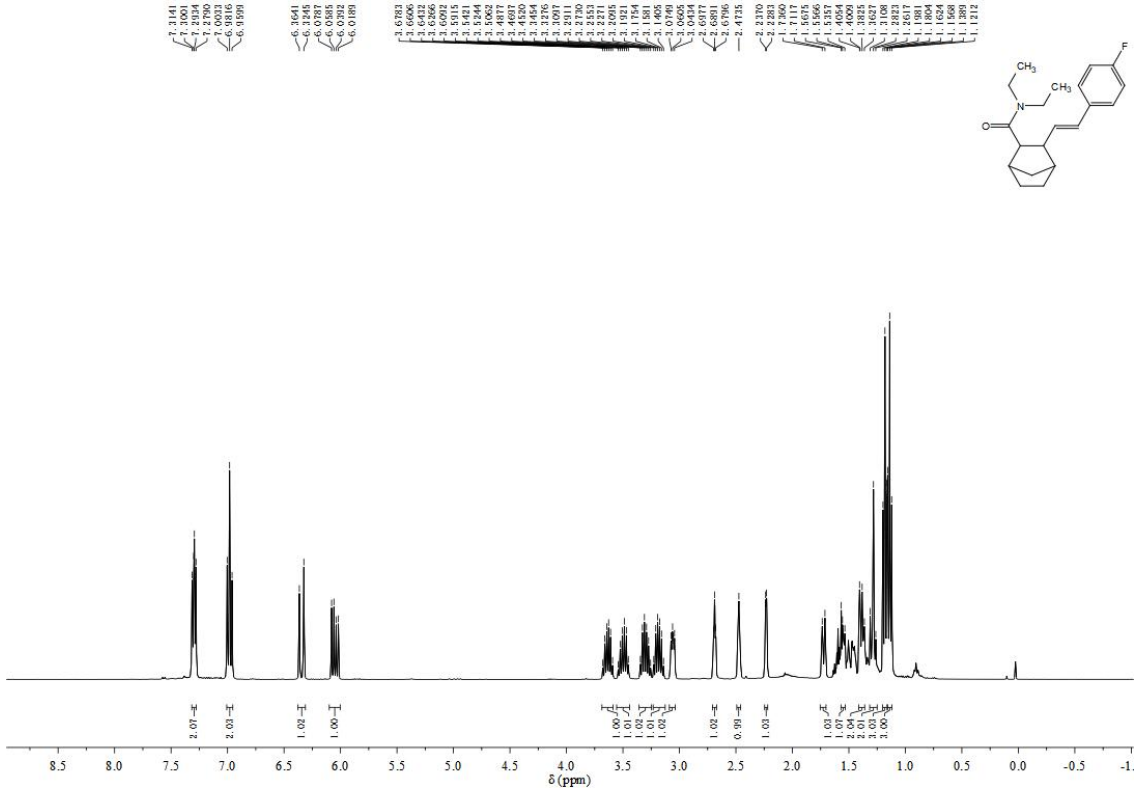
^{1}H NMR spectrum of (*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**21e**)



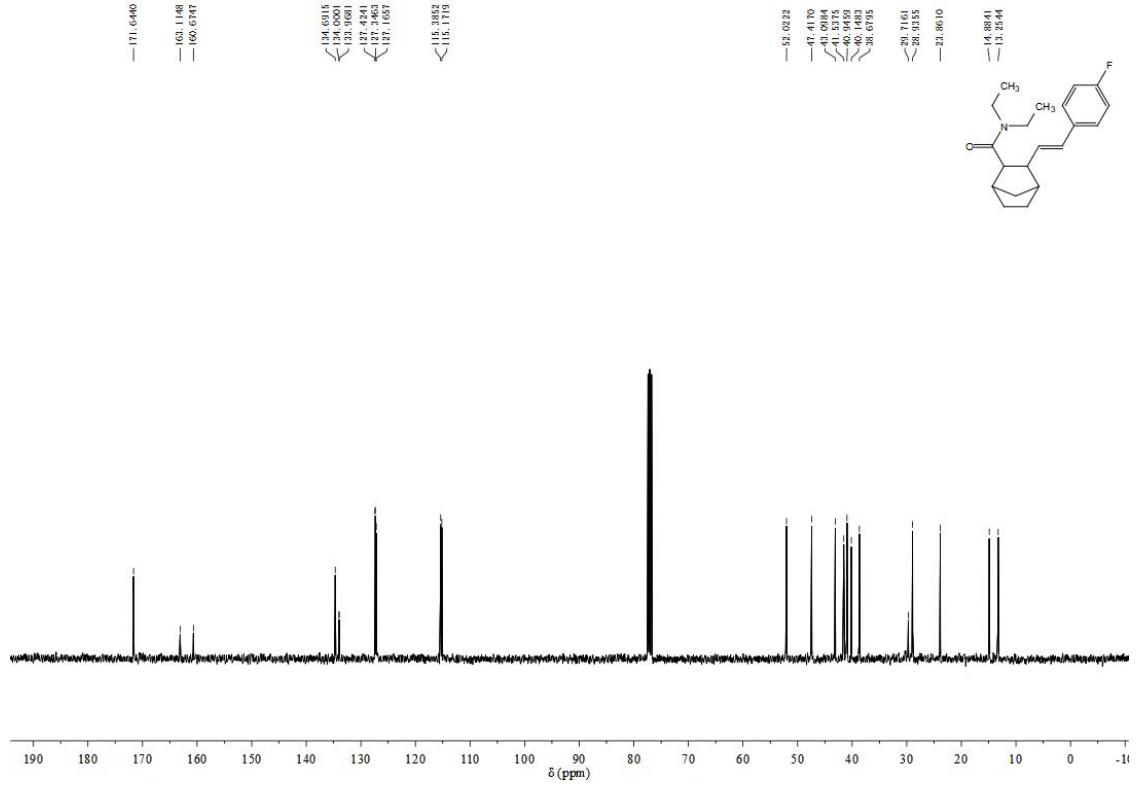
^{13}C NMR spectrum of (*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**21e**)



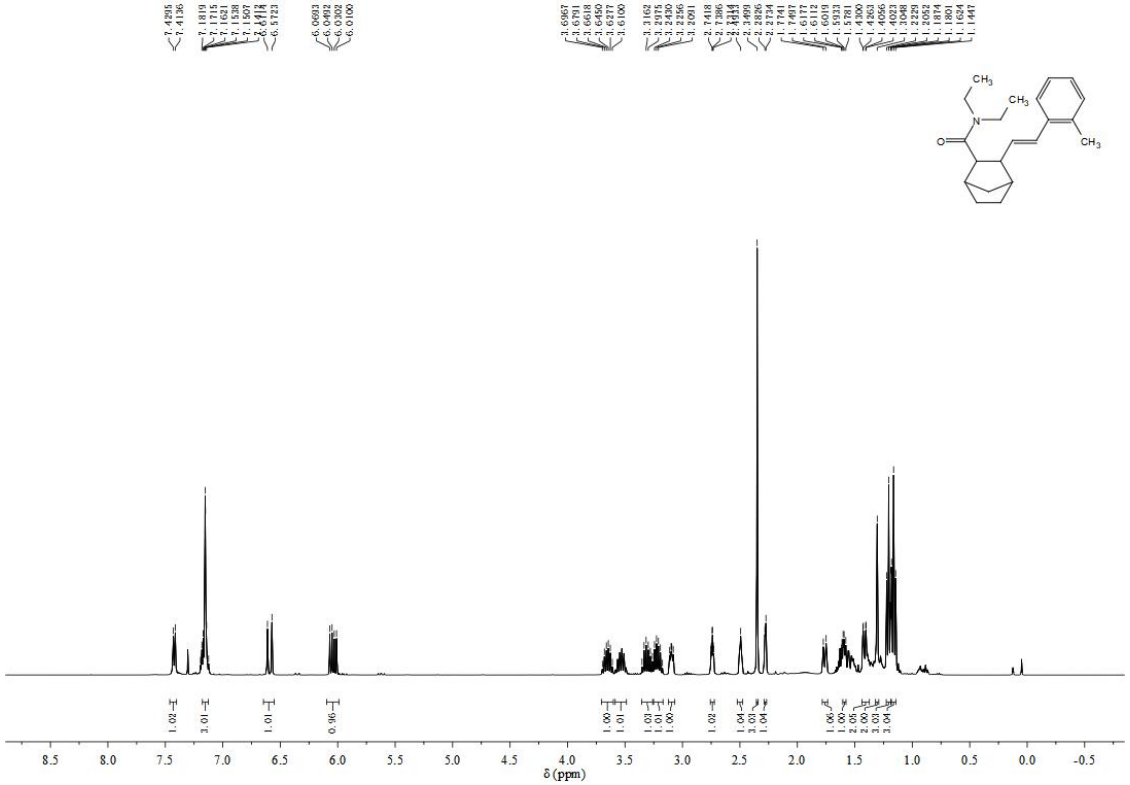
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**)



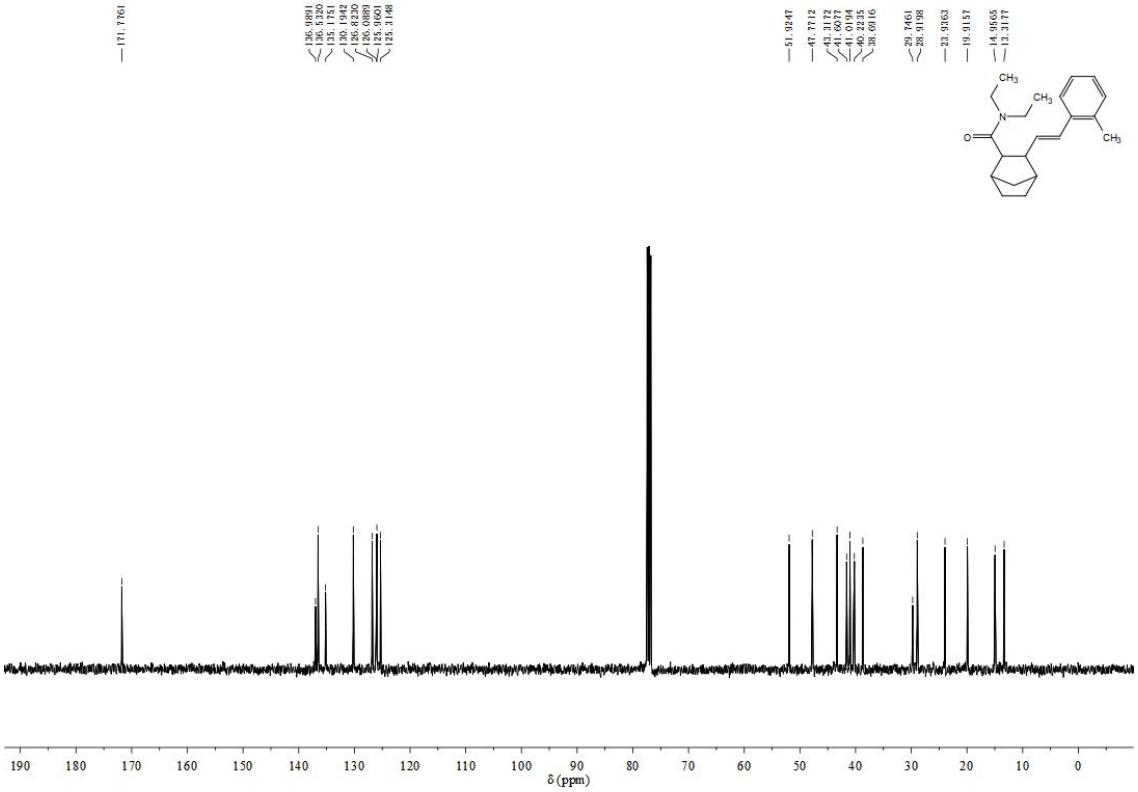
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**)



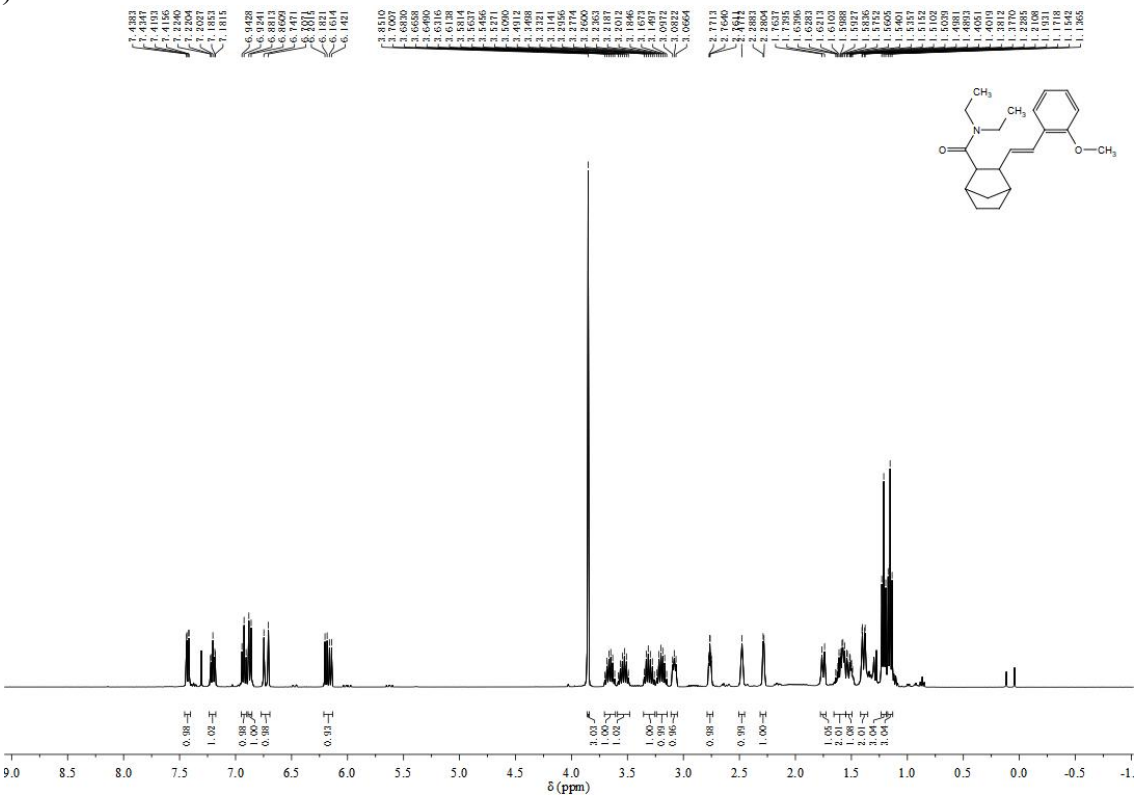
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**23e**)



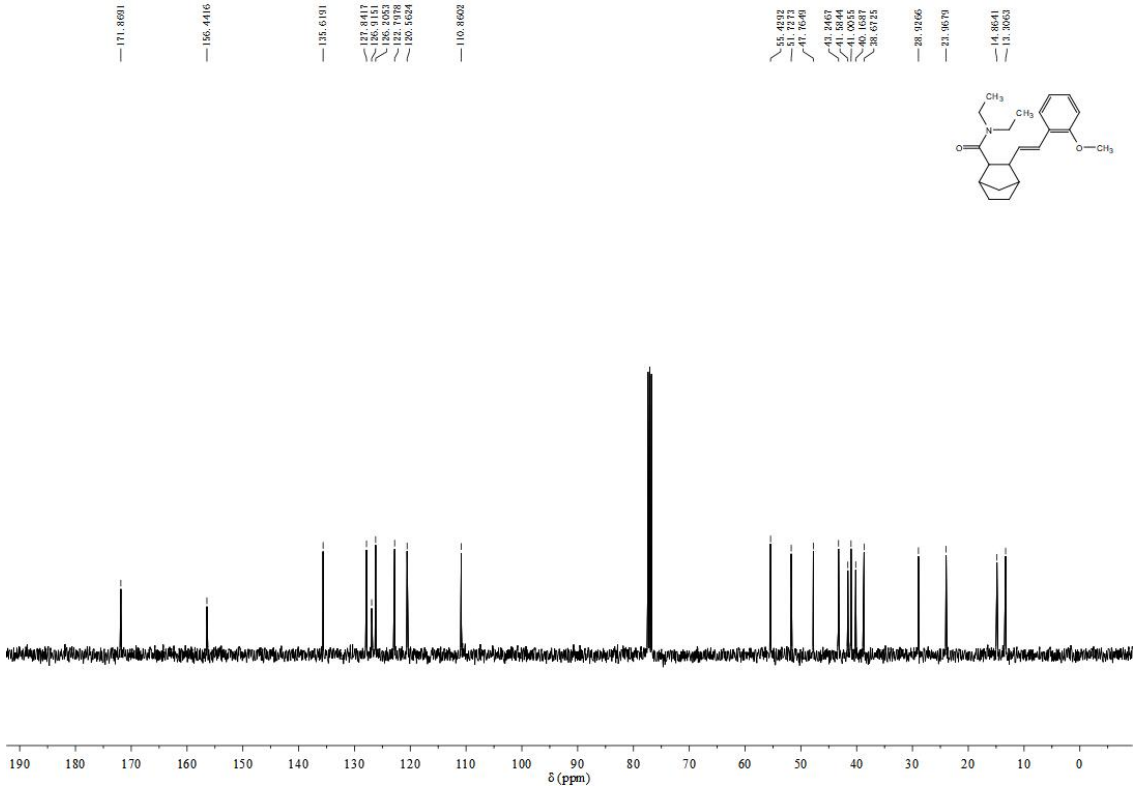
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**23e**)



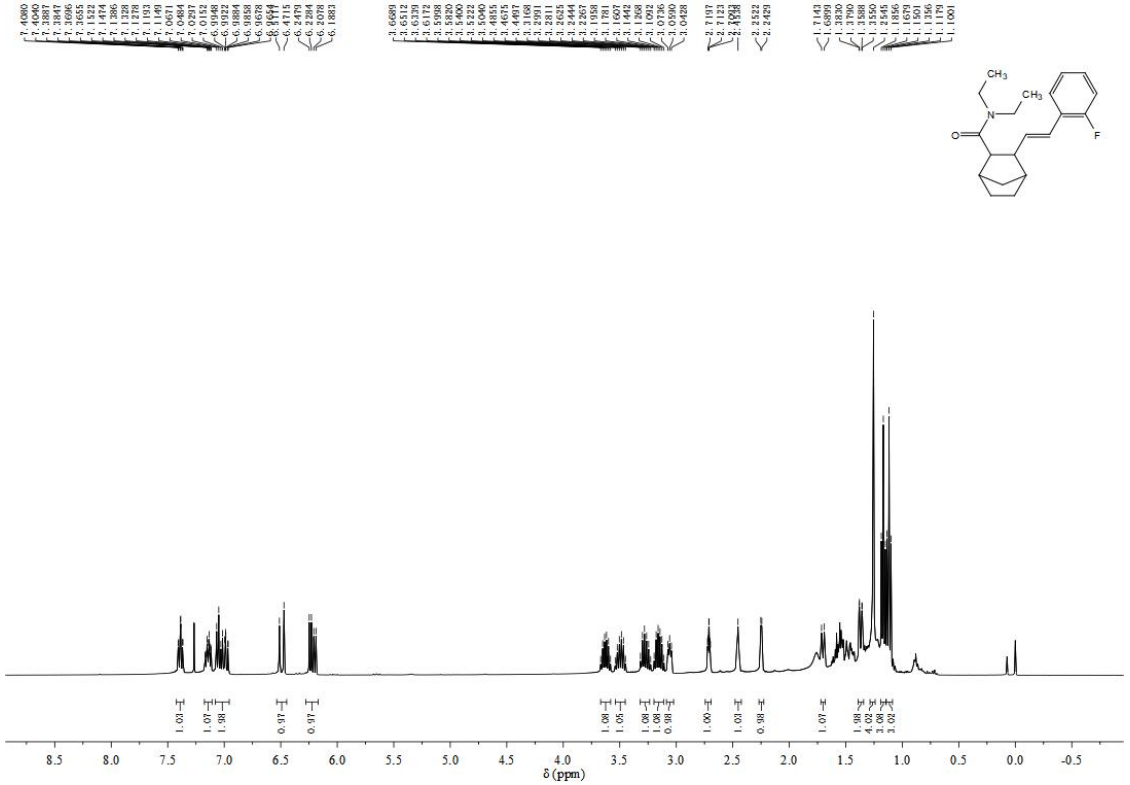
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**24e**)



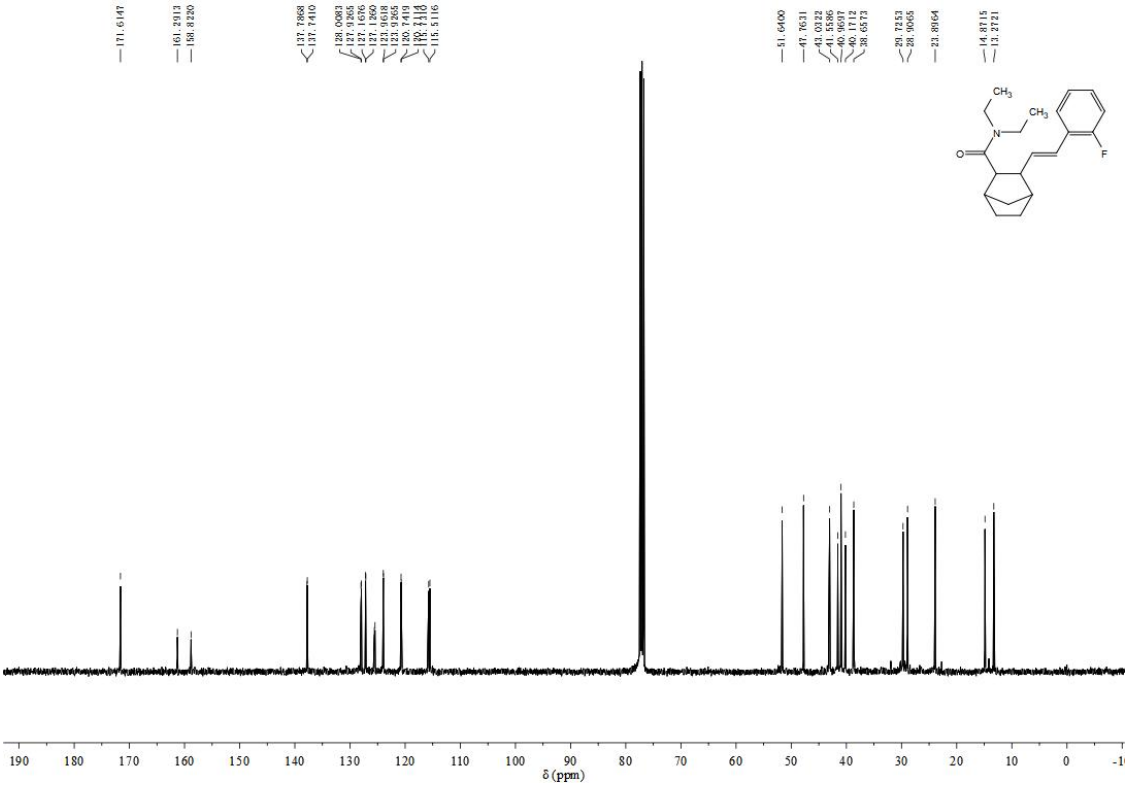
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**24e**)



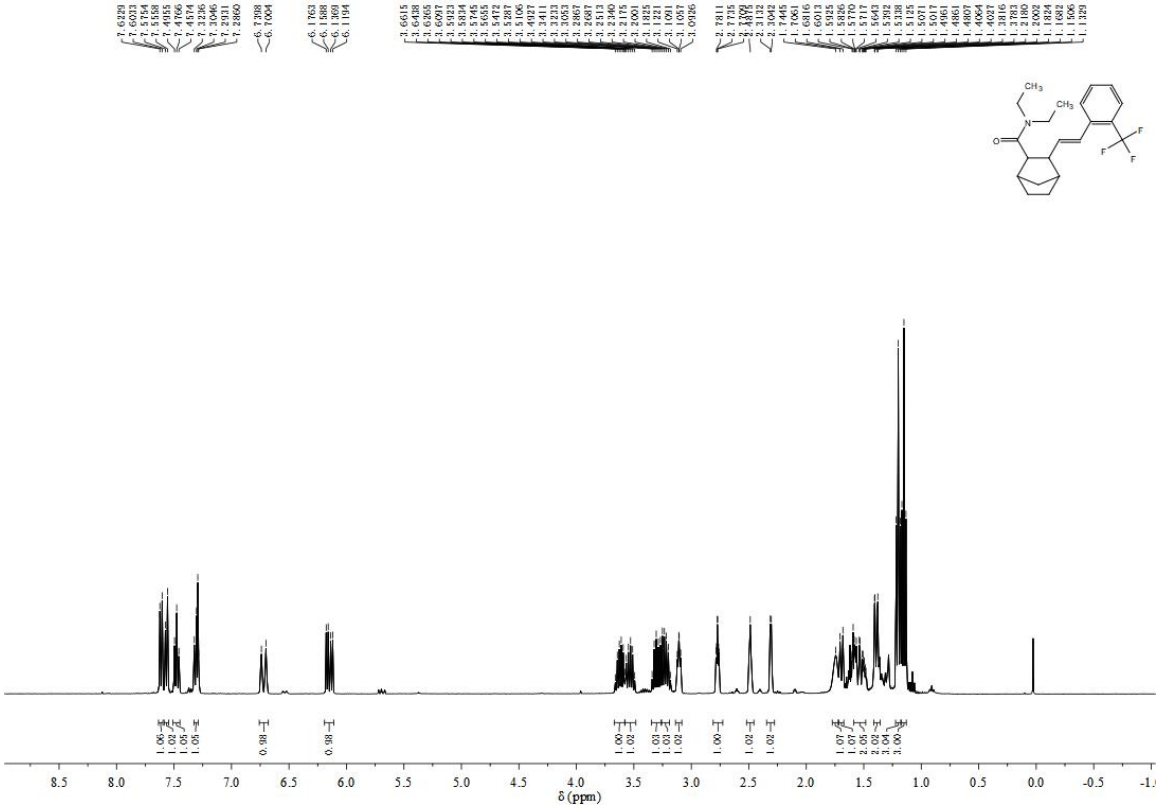
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**)



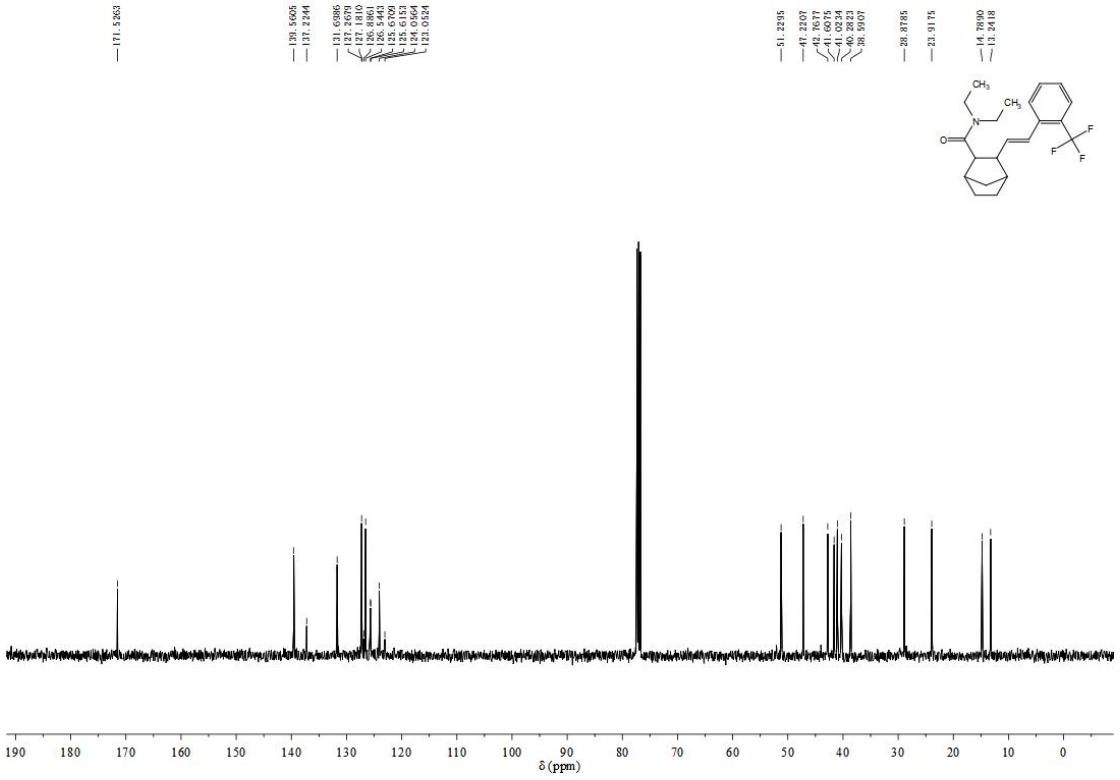
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**)



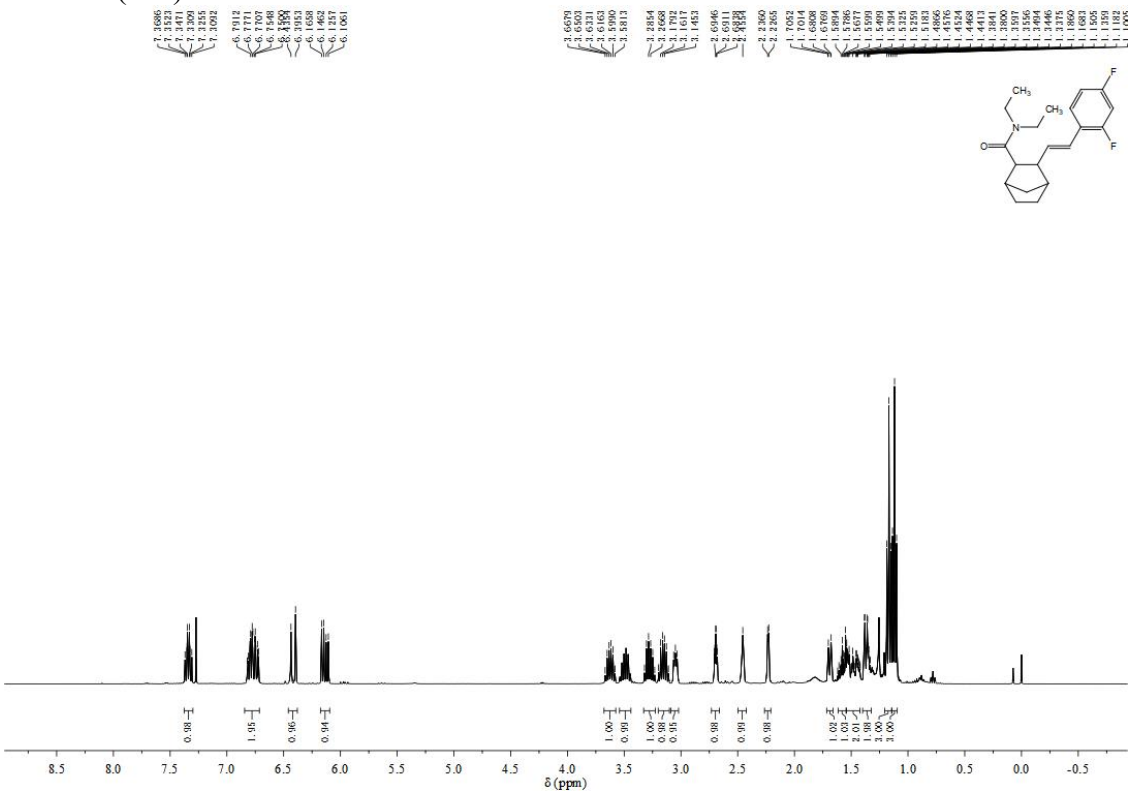
^{1}H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**)



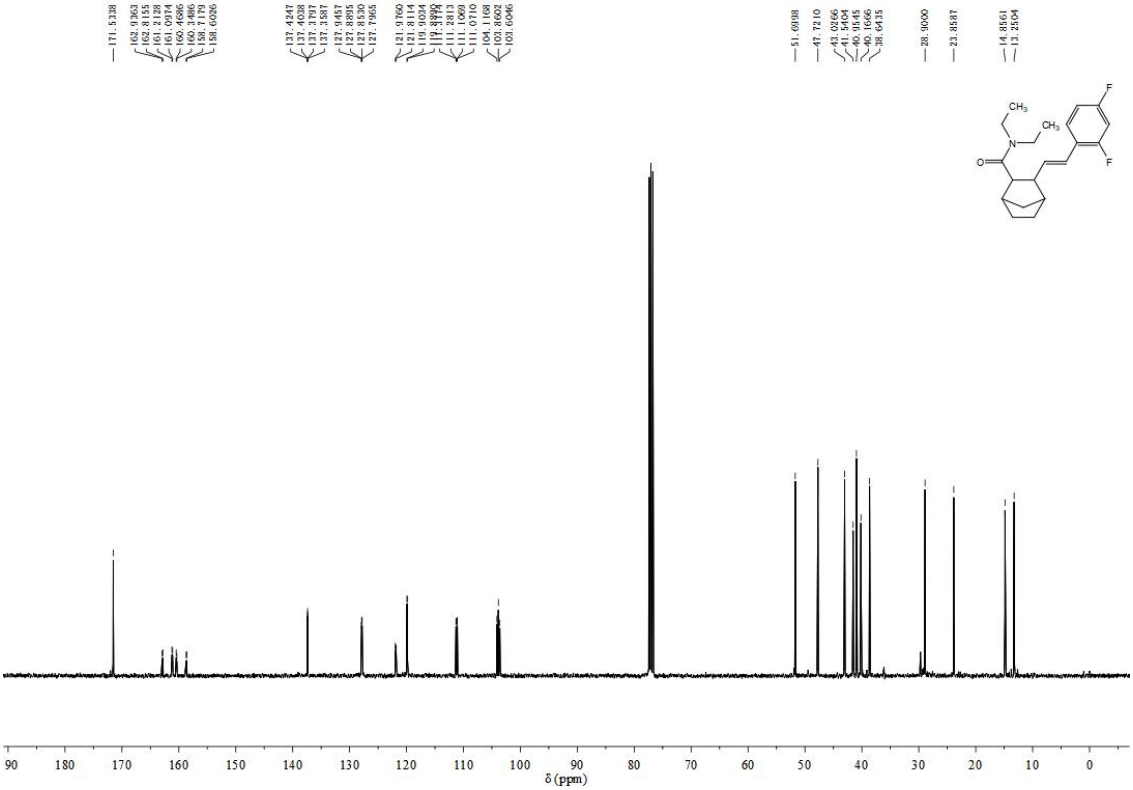
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**)



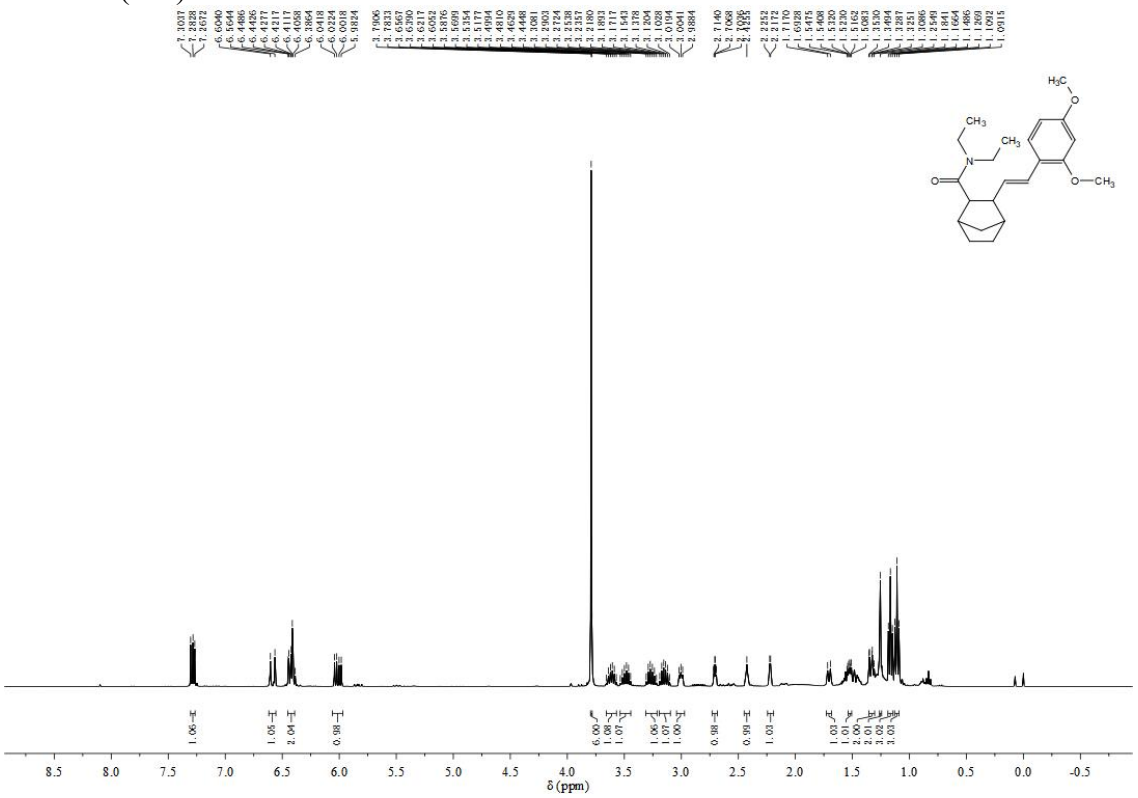
^{1}H NMR spectrum of (*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo [2.2.1] heptane-2-carboxamide (**27e**)



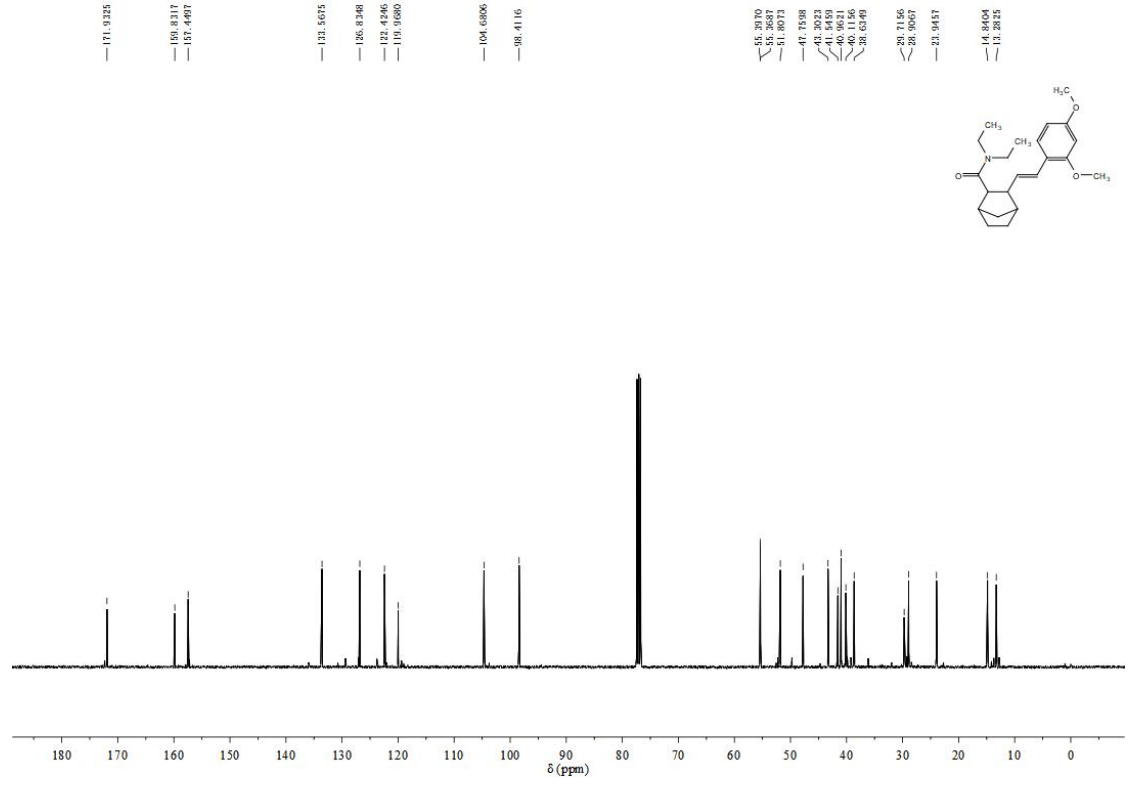
^{13}C NMR spectrum of (*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo [2.2.1] heptane-2-carboxamide (**27e**)



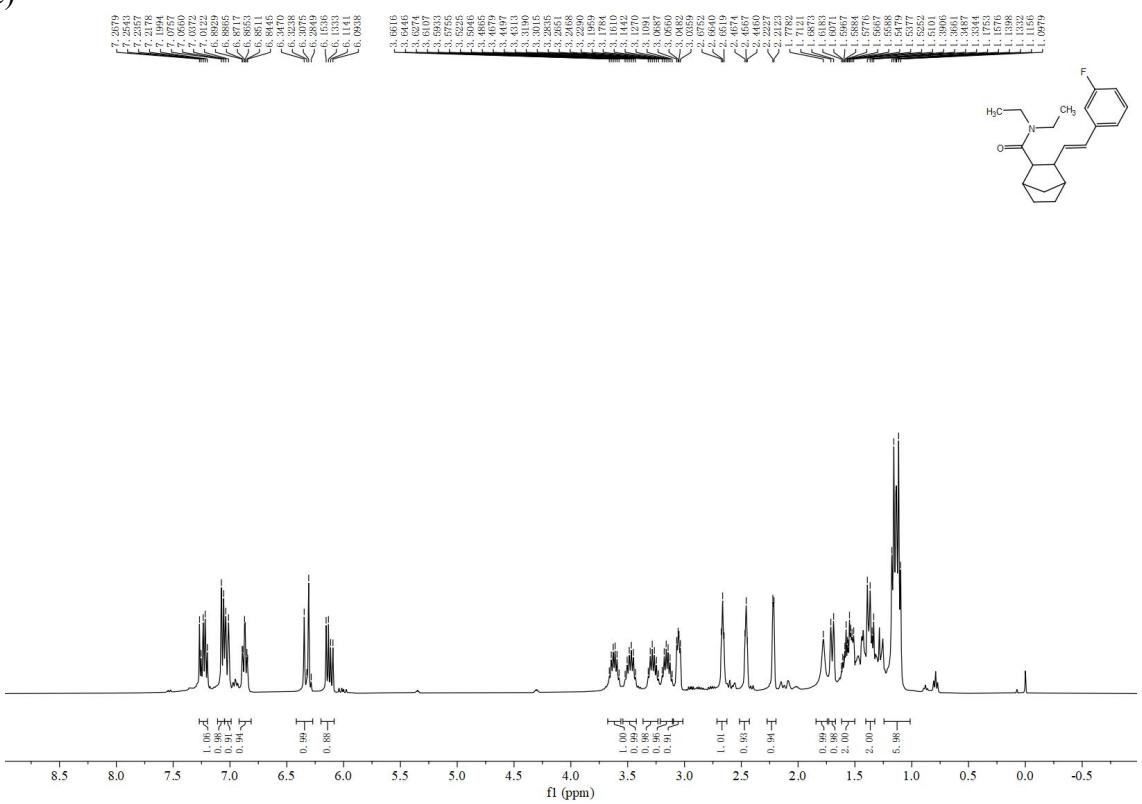
^{1}H NMR spectrum of (*E*)-3-(2,4-dimethoxystyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**28e**)



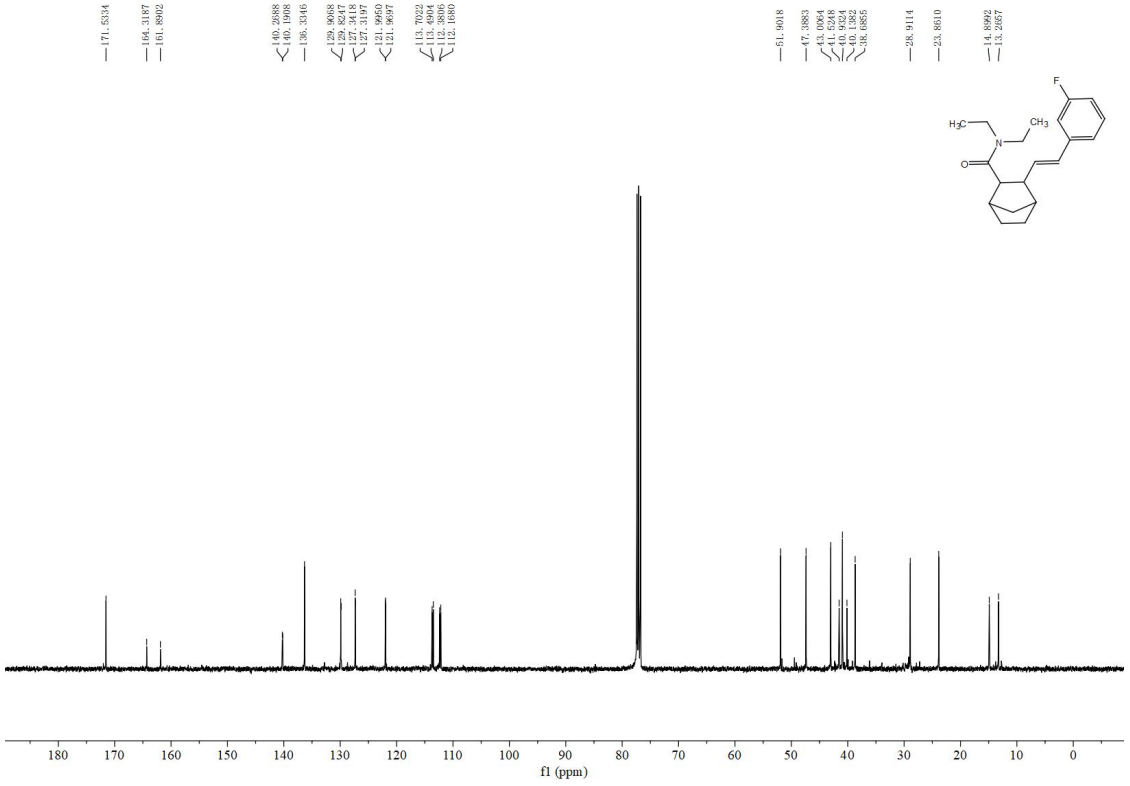
^{13}C NMR spectrum of (*E*)-3-(2,4-dimethoxystyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**28e**)



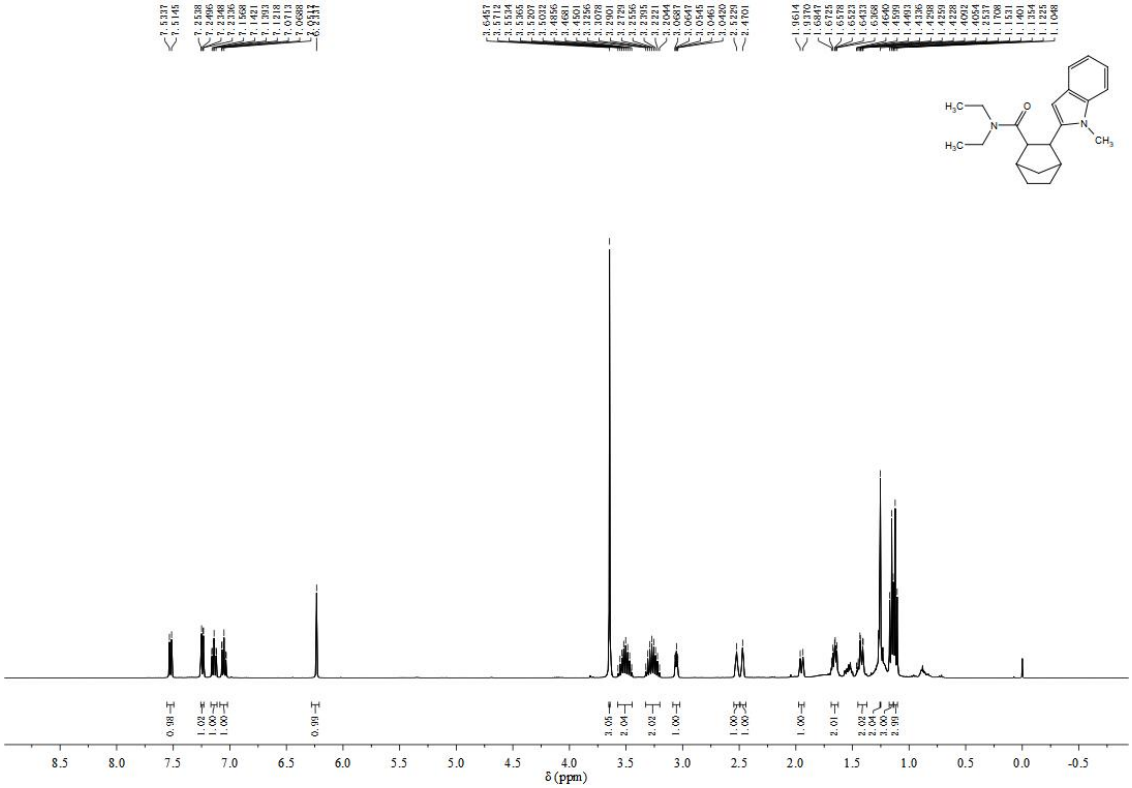
^{1}H NMR spectrum of (*E*)-*N,*N-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**)



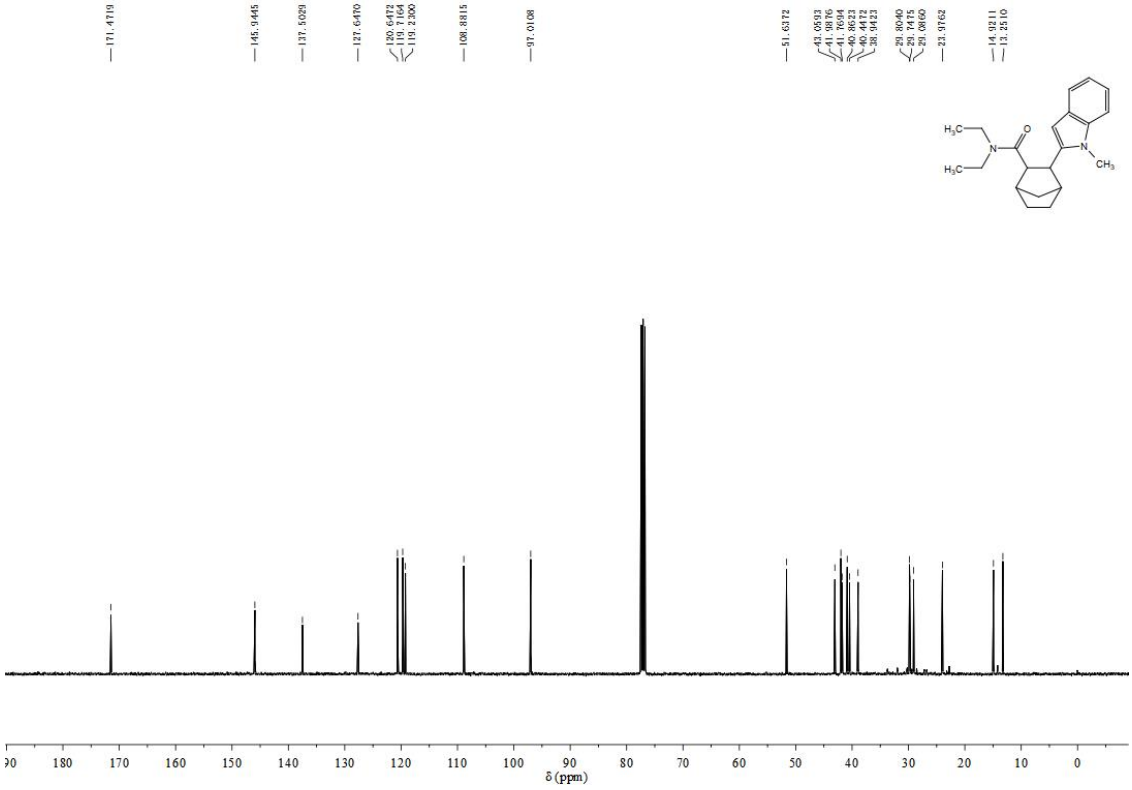
^{13}C NMR spectrum of (*E*)-*N,*N-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**)



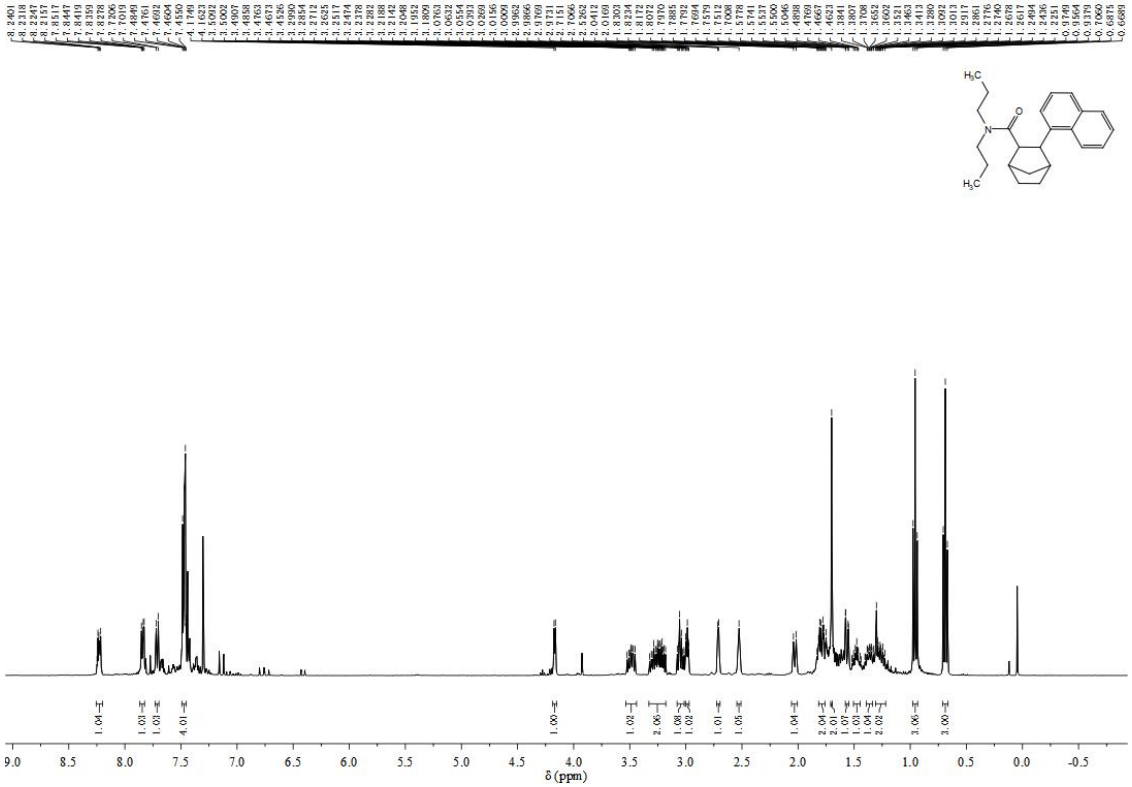
^{1}H NMR spectrum of *N,N*-diethyl-3-(1-methyl-1*H*-indol-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**30e**)



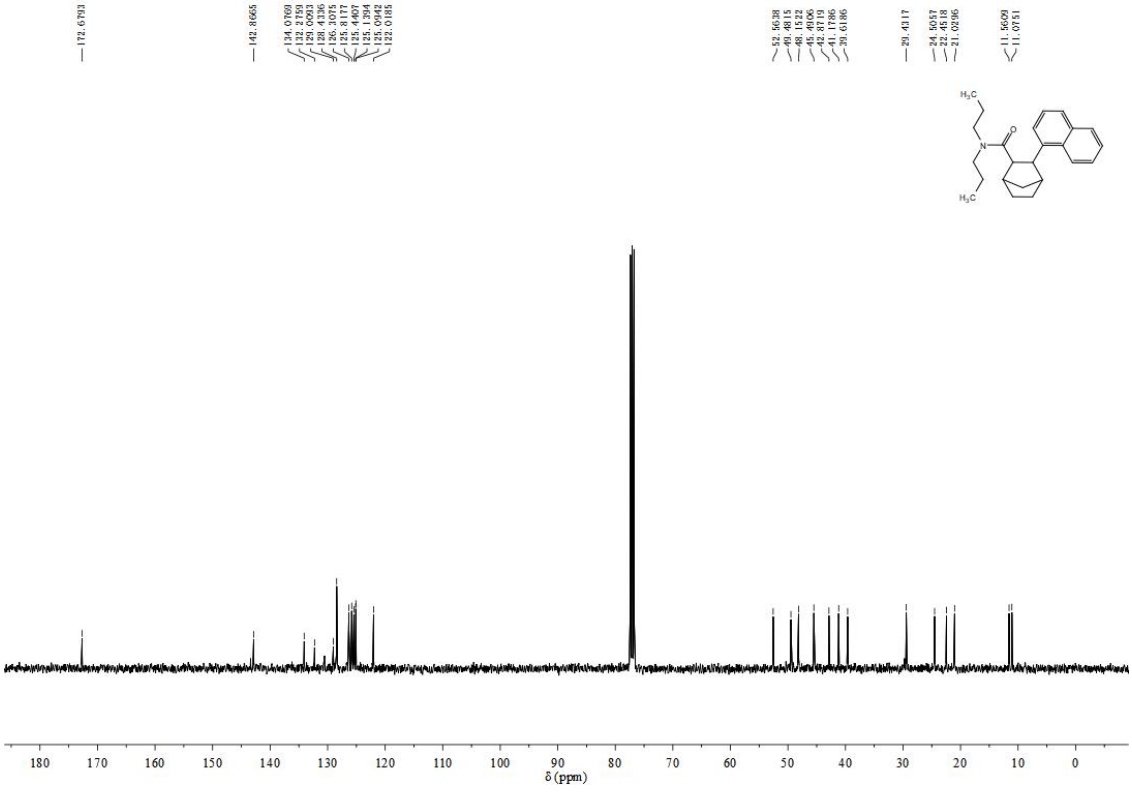
^{13}C NMR spectrum of *N,N*-diethyl-3-(1-methyl-1*H*-indol-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**30e**)



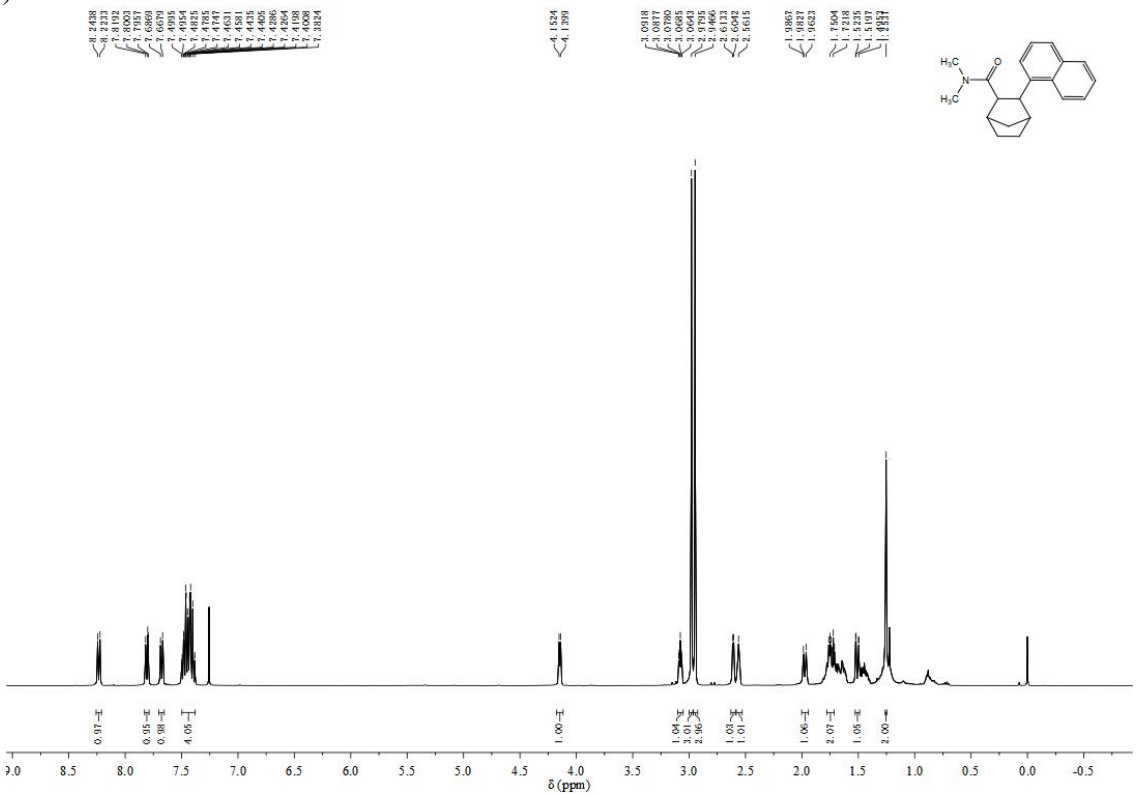
^{1}H NMR spectrum of 3-(naphthalen-1-yl)-*N,N*-dipropylbicyclo[2.2.1]heptane-2-carboxamide (**31e**)



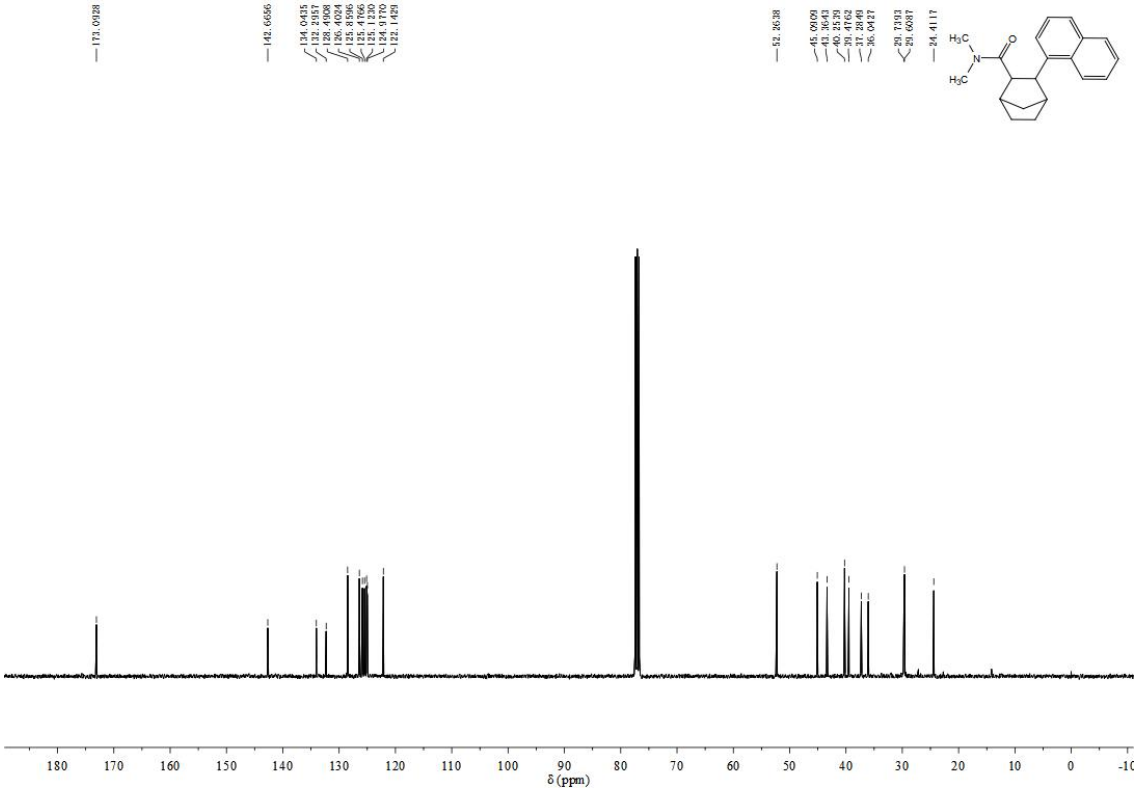
^{13}C NMR spectrum of 3-(naphthalen-1-yl)-*N,N*-dipropylbicyclo[2.2.1]heptane-2-carboxamide (**31e**)



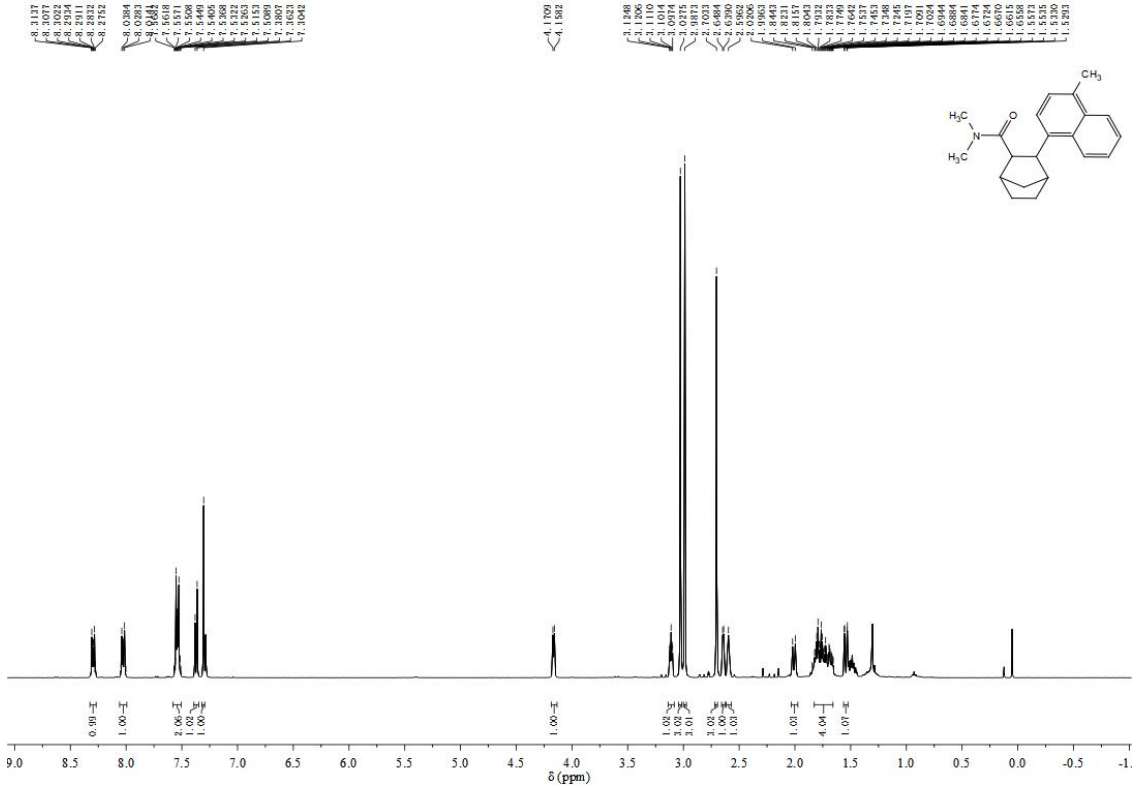
^{1}H NMR spectrum of *N,N*-dimethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**32e**)



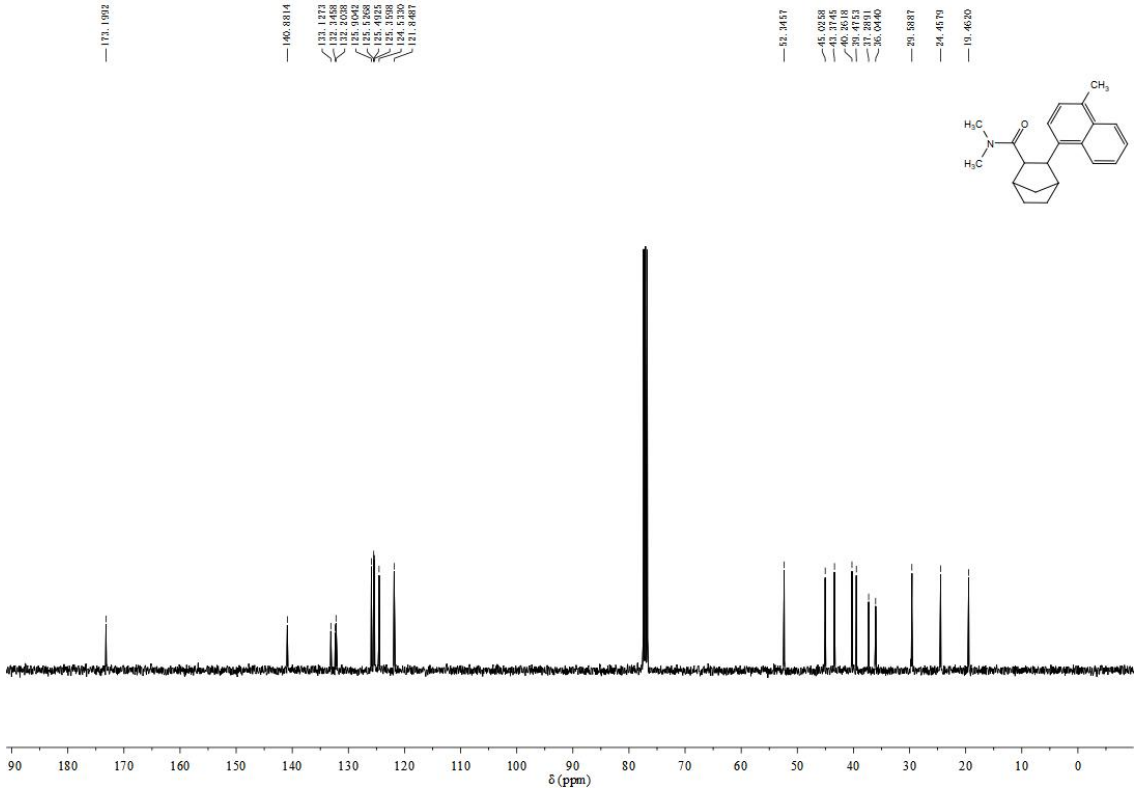
^{13}C NMR spectrum of *N,N*-dimethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**32e**)



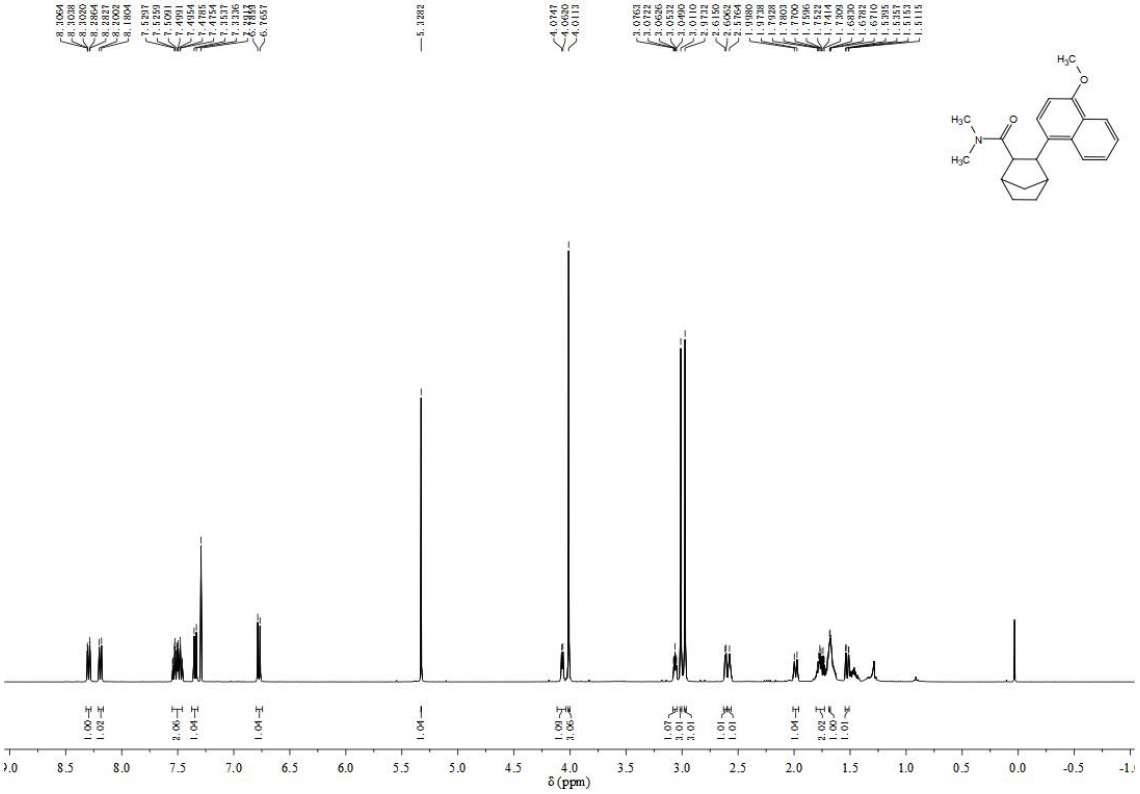
^{1}H NMR spectrum of *N,N*-dimethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**33e**)



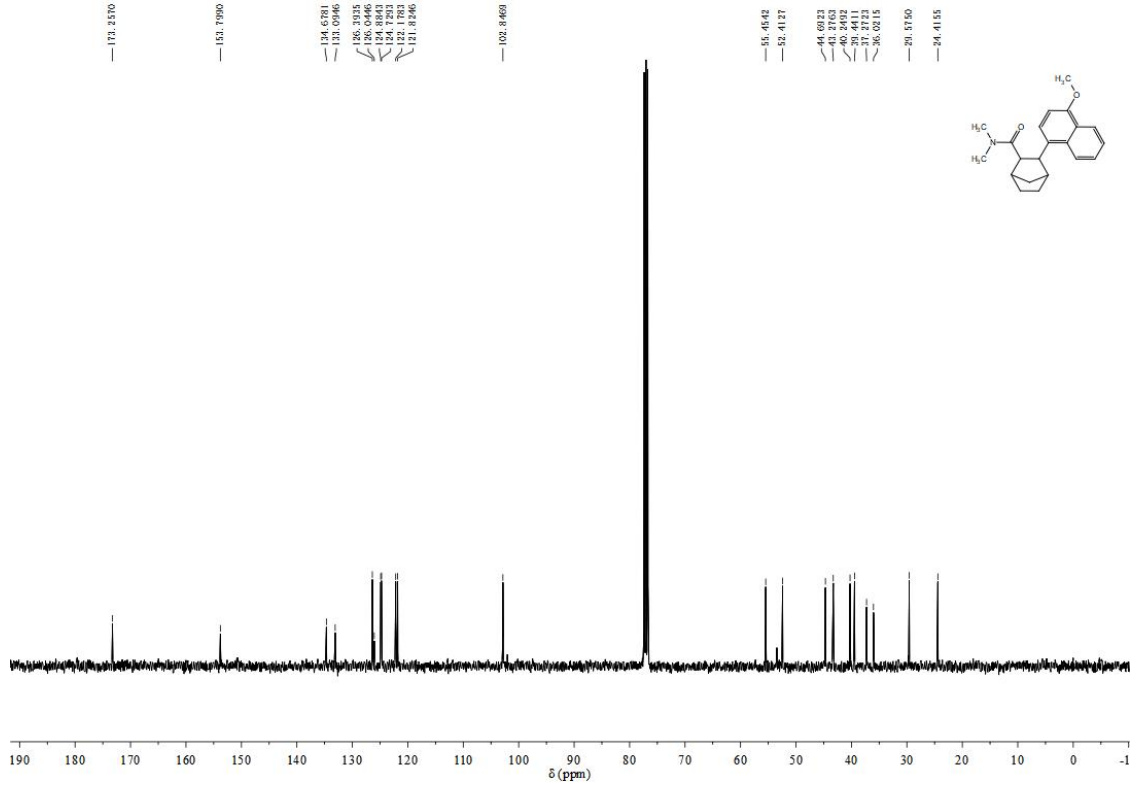
^{13}C NMR spectrum of *N,N*-dimethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**33e**)



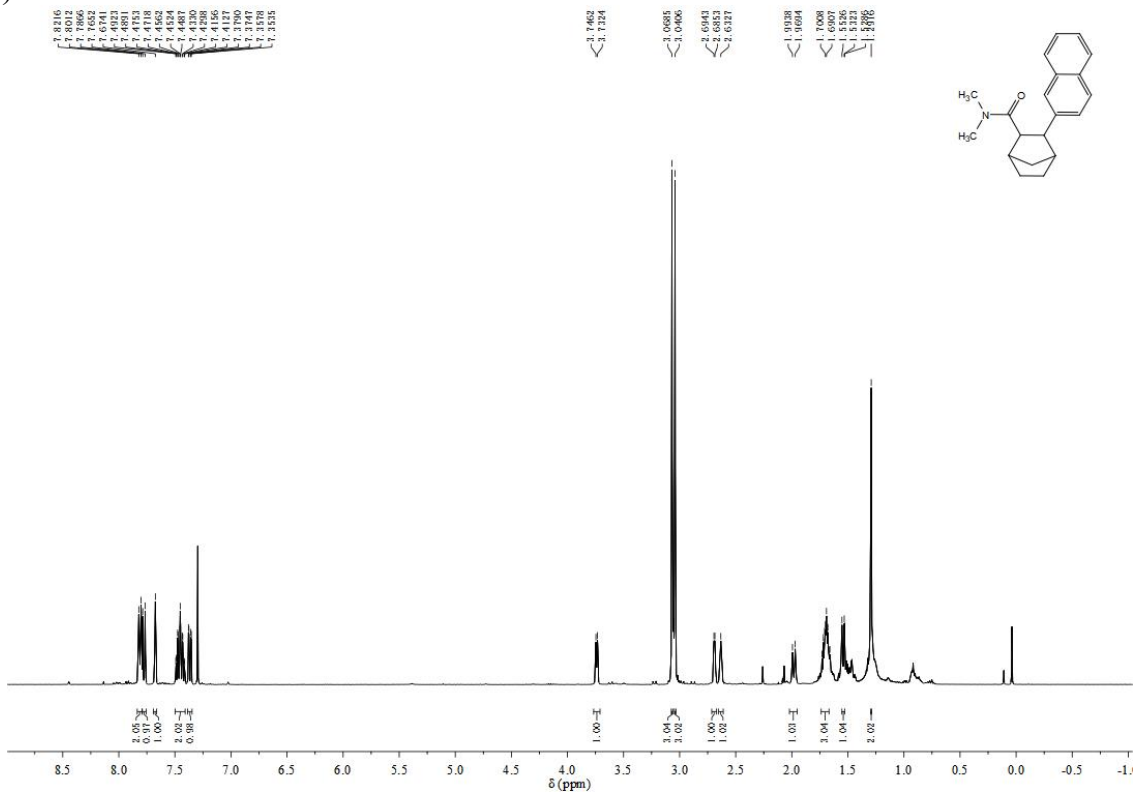
^{1}H NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**34e**)



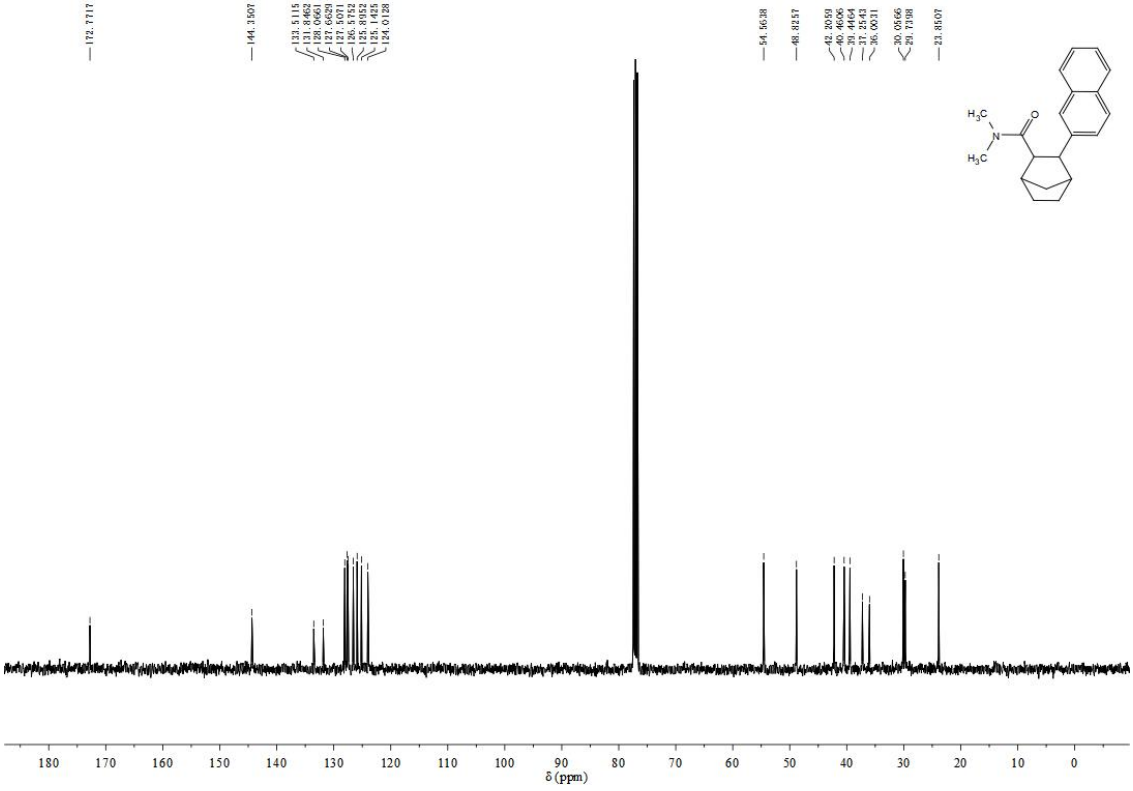
^{13}C NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**34e**)



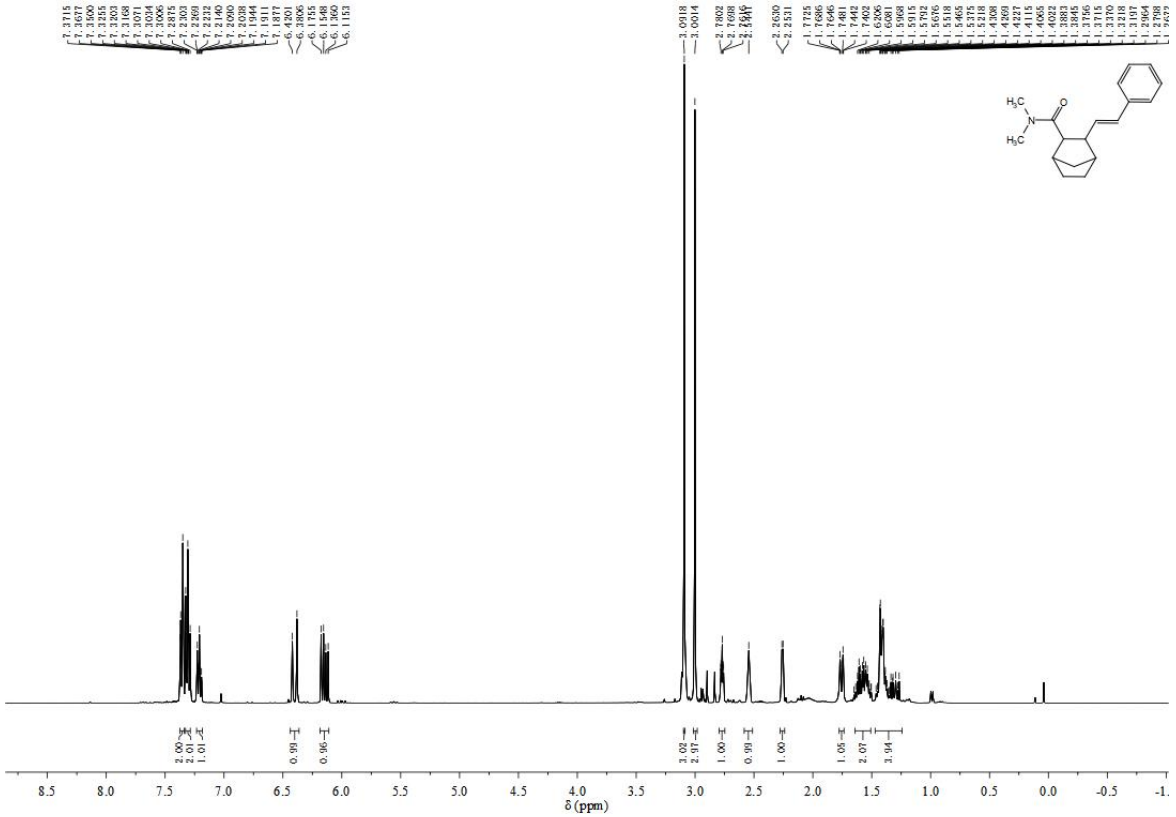
^{1}H NMR spectrum of *N,N*-dimethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**35e**)



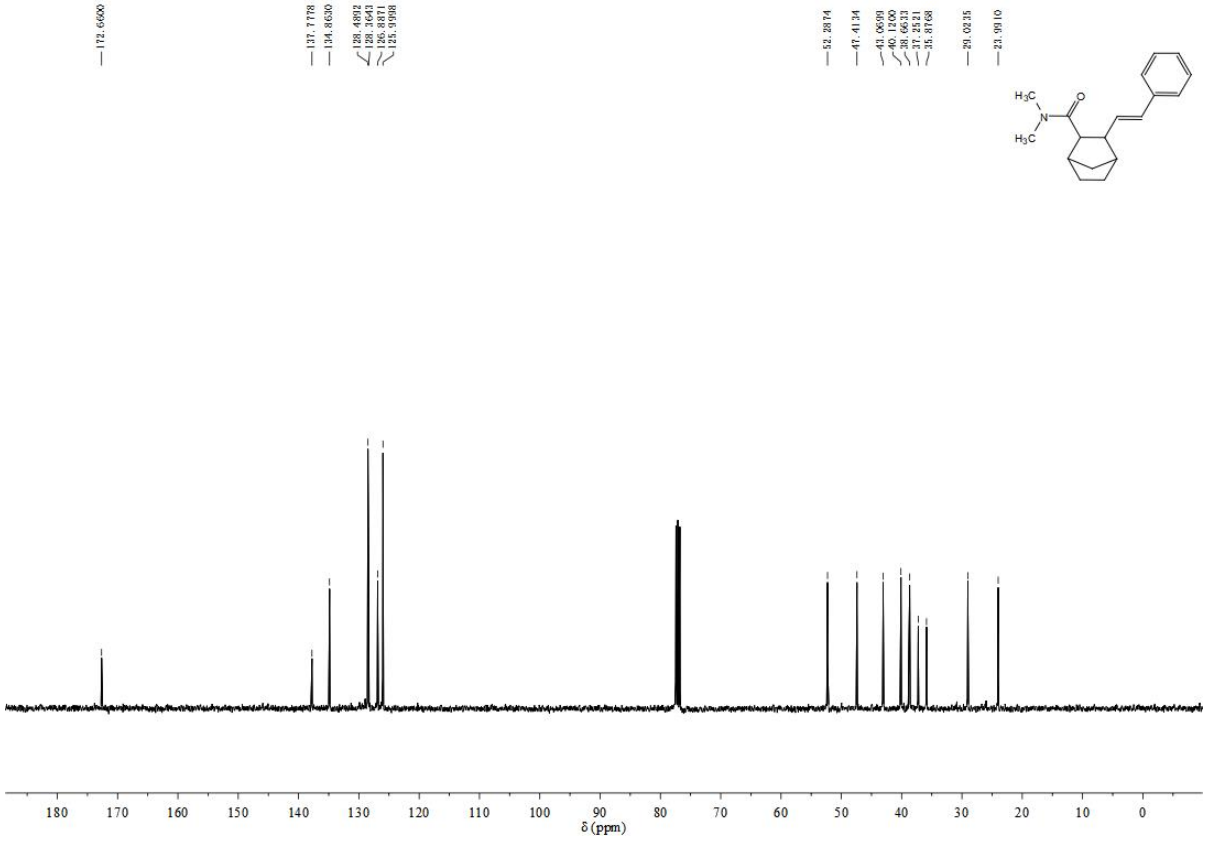
^{13}C NMR spectrum of *N,N*-dimethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**35e**)



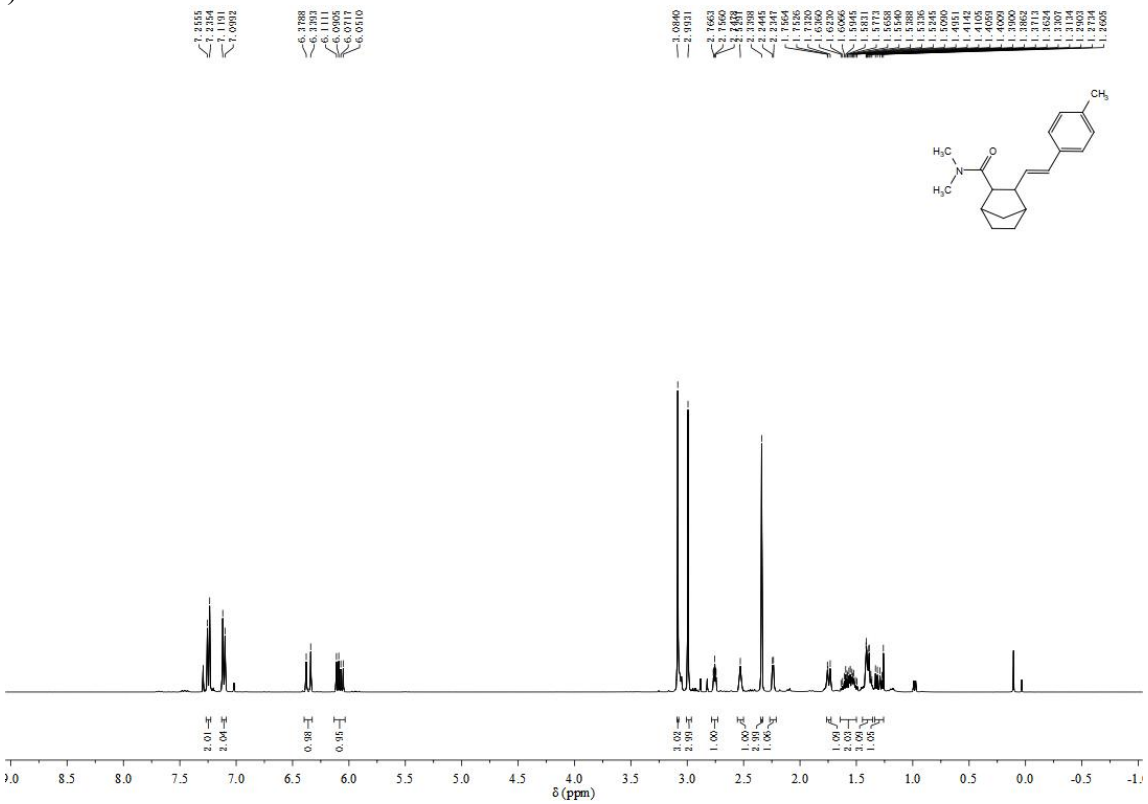
^{1}H NMR spectrum of (*E*)-*N,N*-dimethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**36e**)



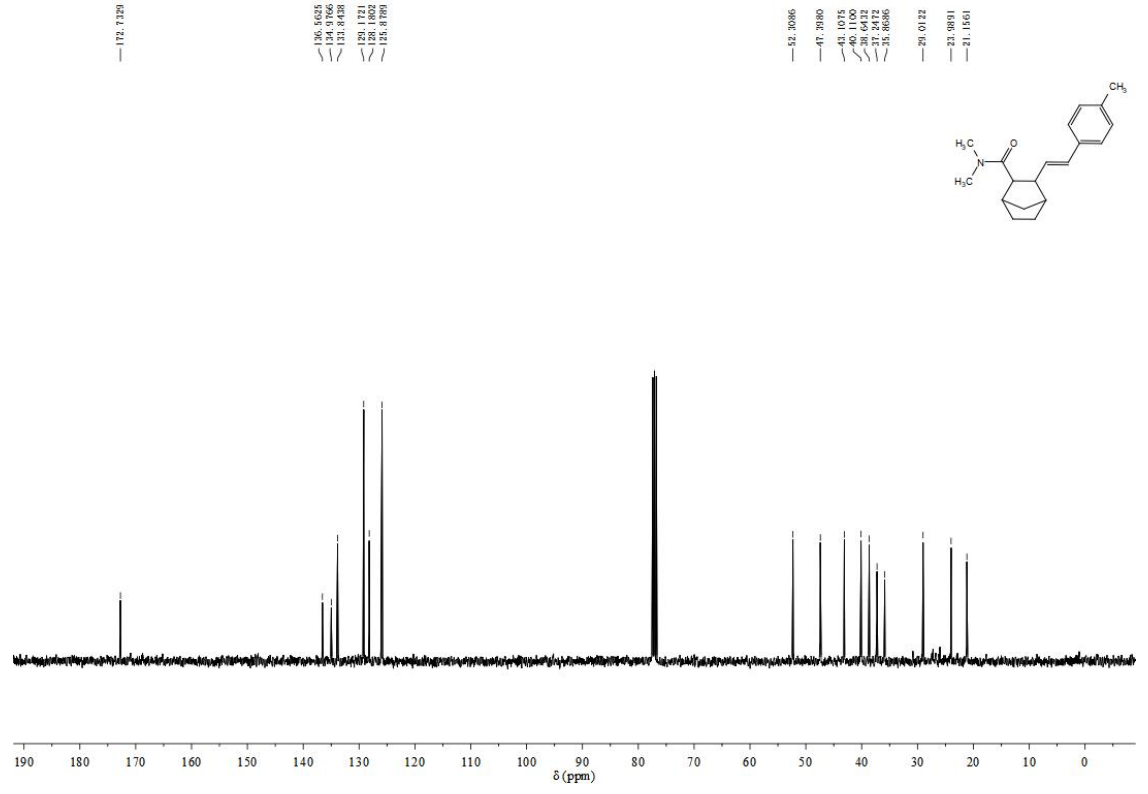
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**36e**)



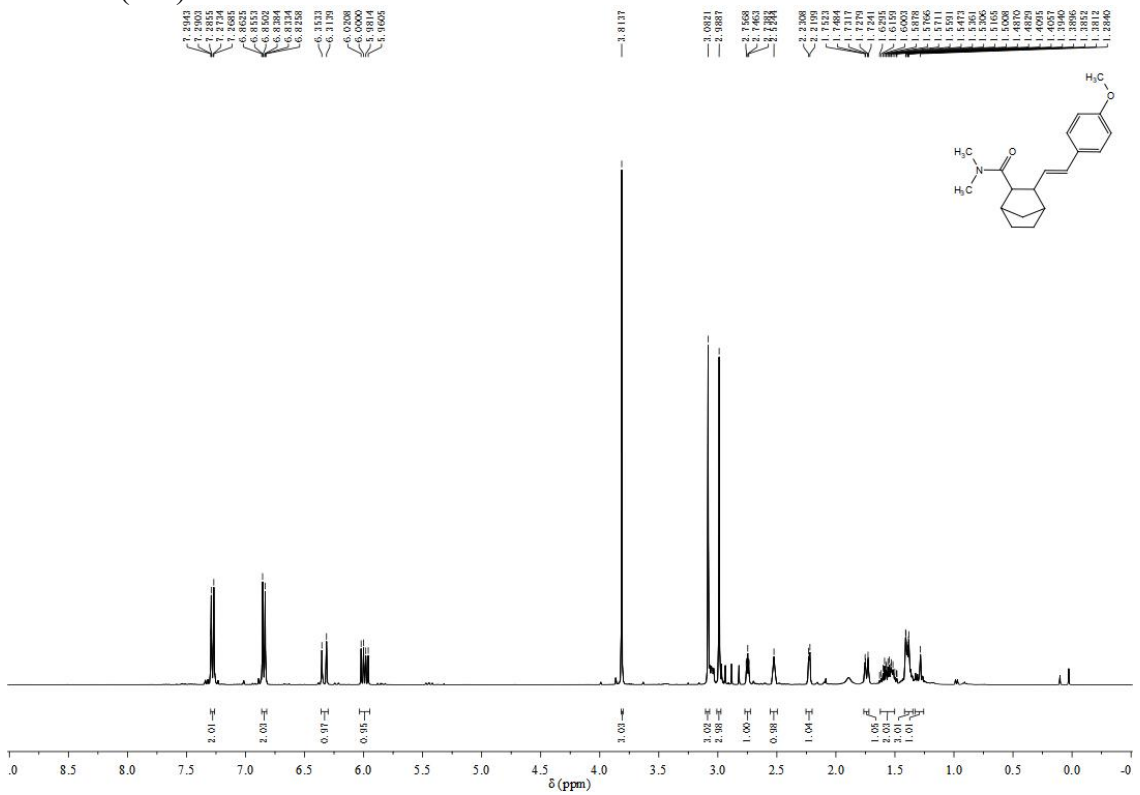
^{1}H NMR spectrum of (*E*)-*N,N*-dimethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**37e**)



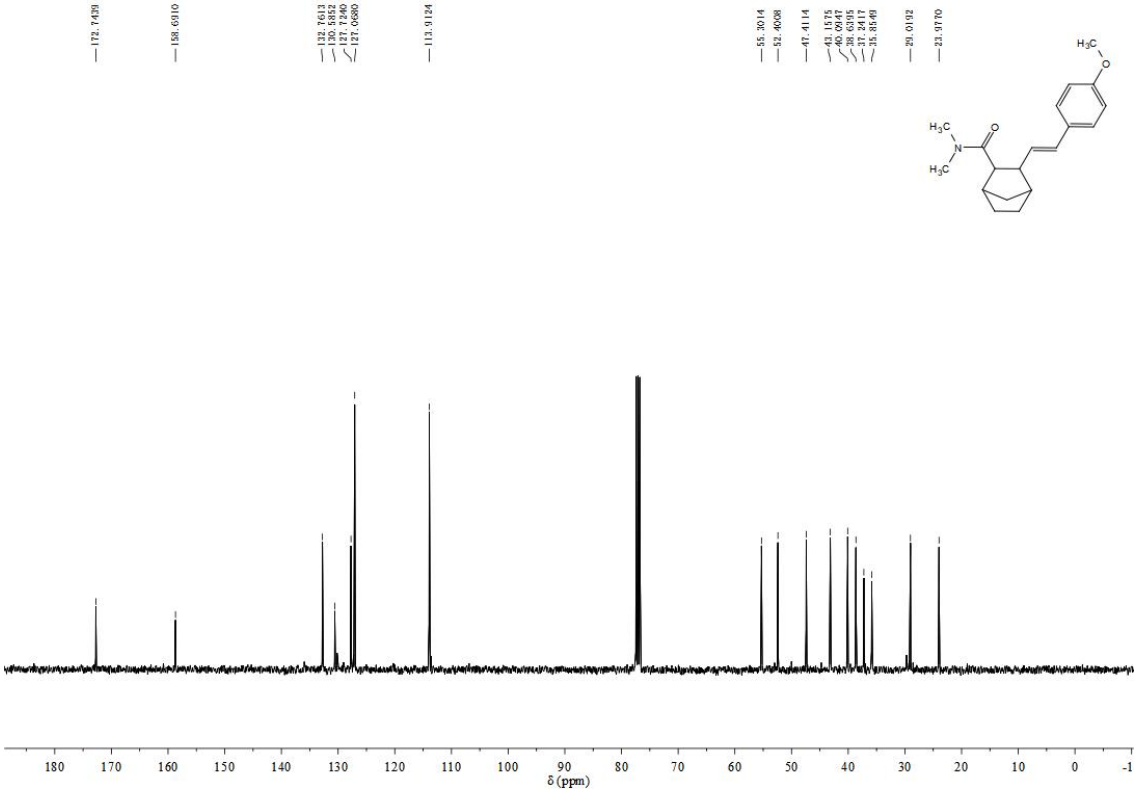
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**37e**)



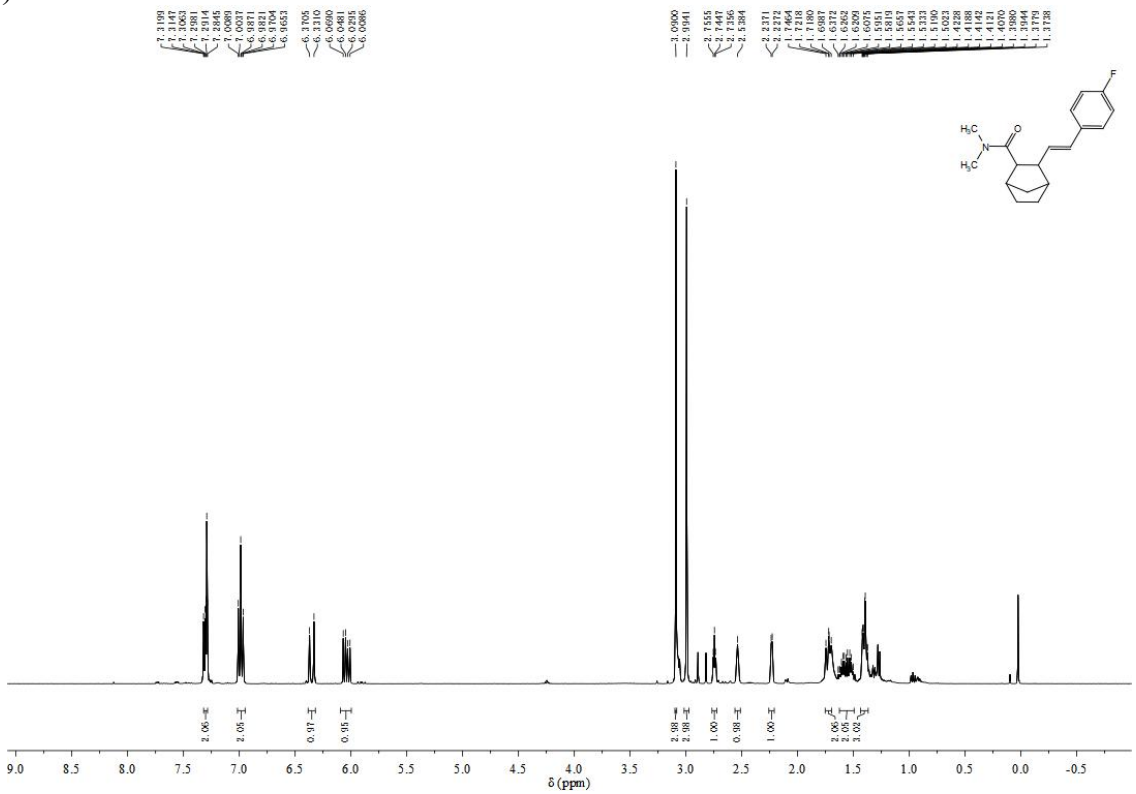
^{1}H NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**38e**)



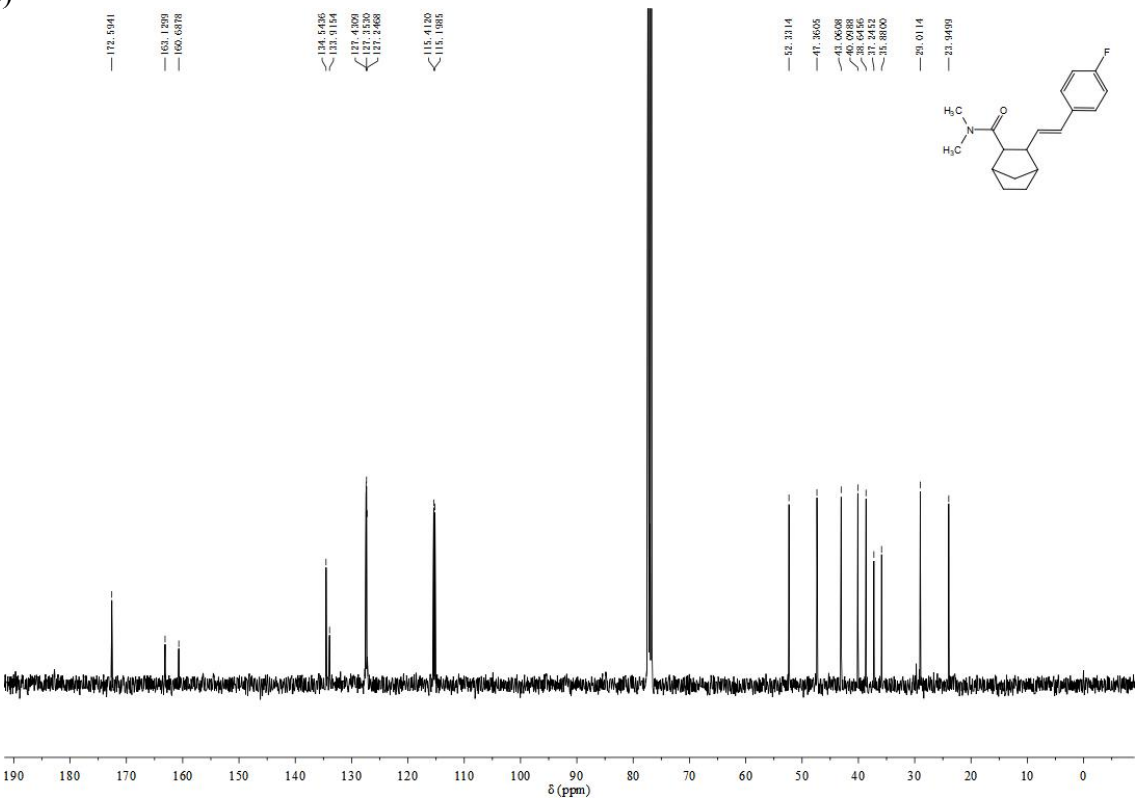
^{13}C NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**38e**)



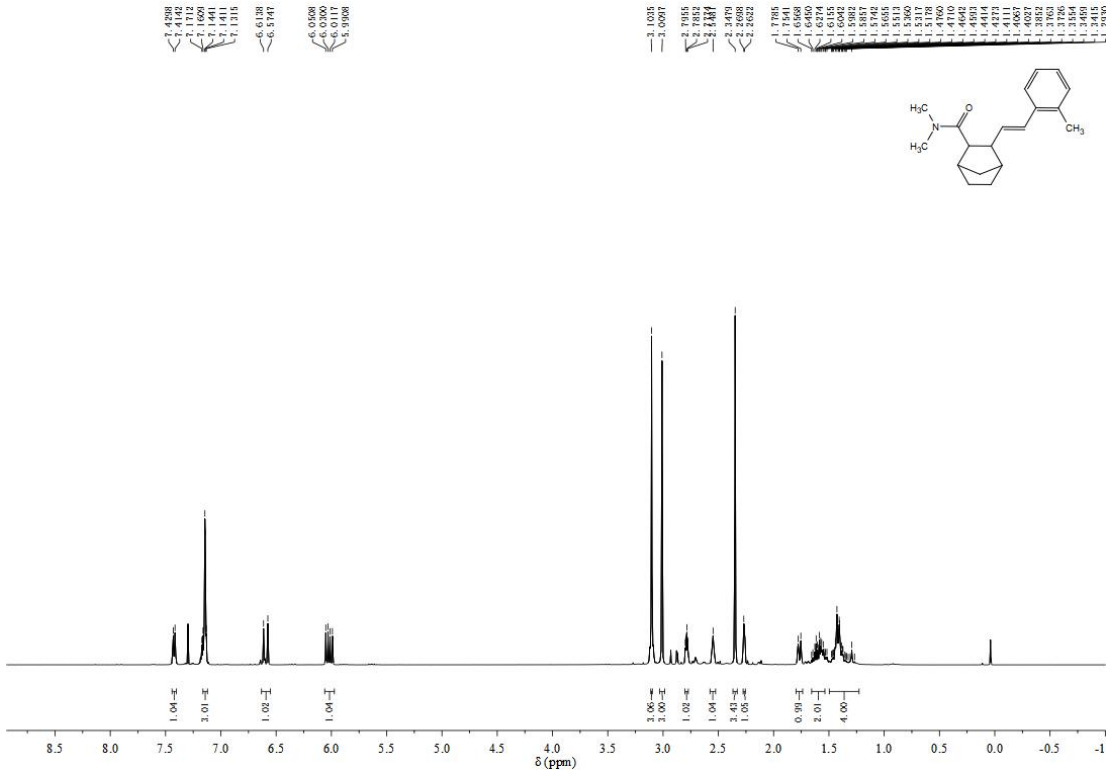
^{1}H NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**)



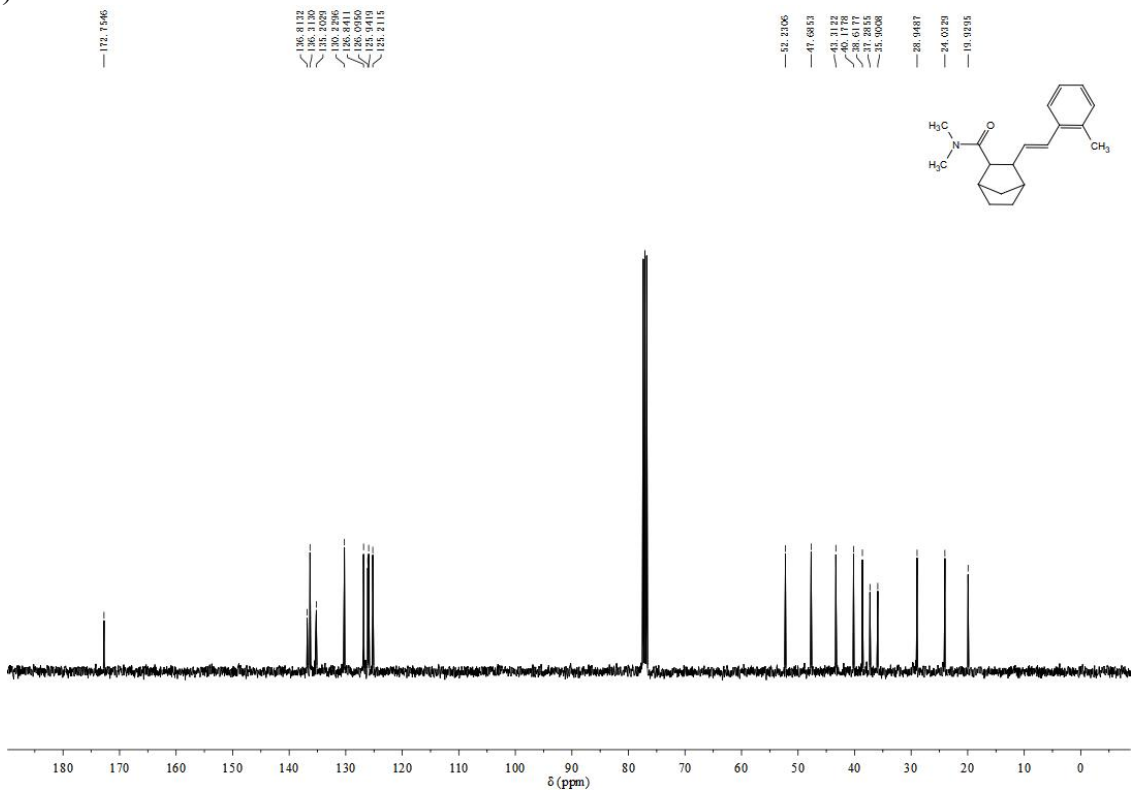
^{13}C NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**)



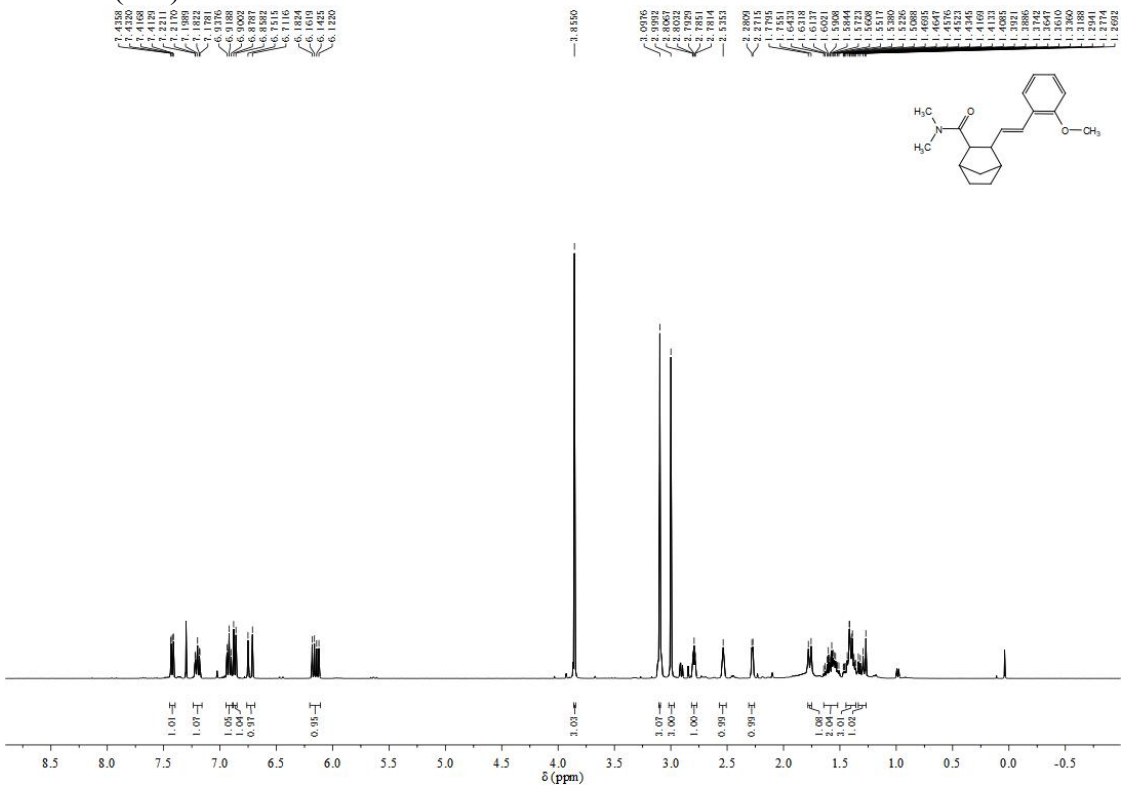
^{1}H NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**40e**)



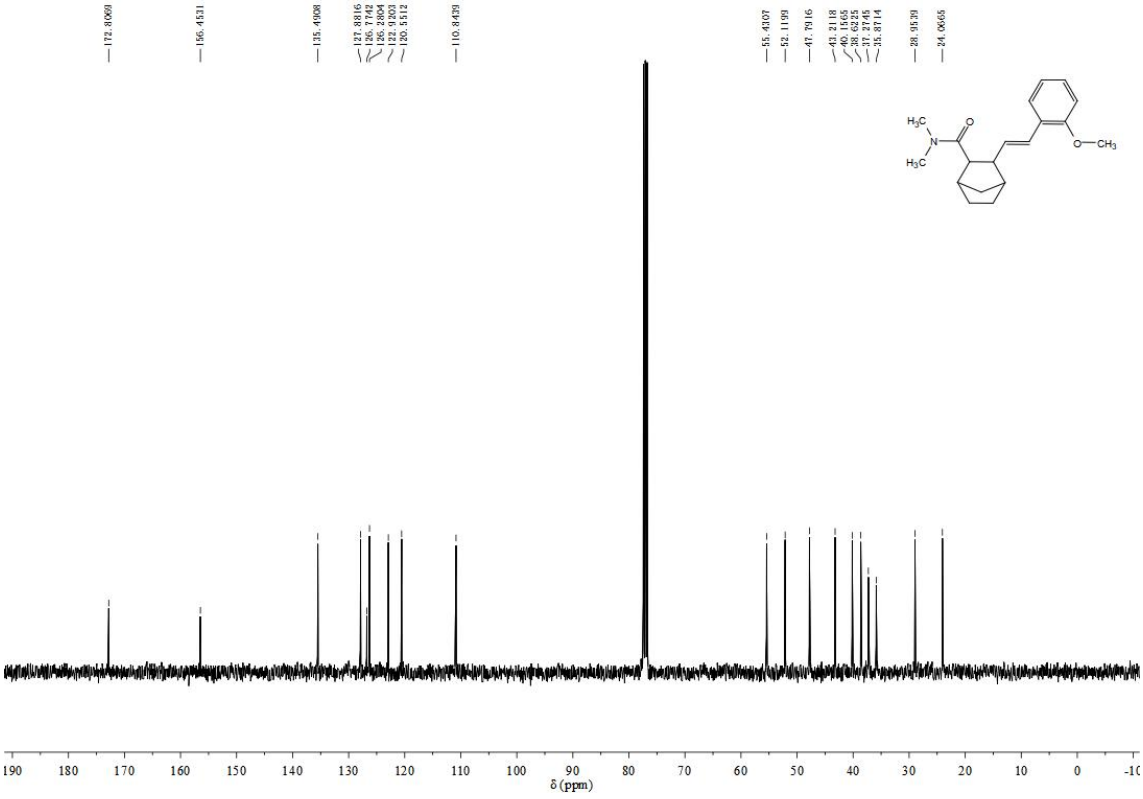
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**40e**)



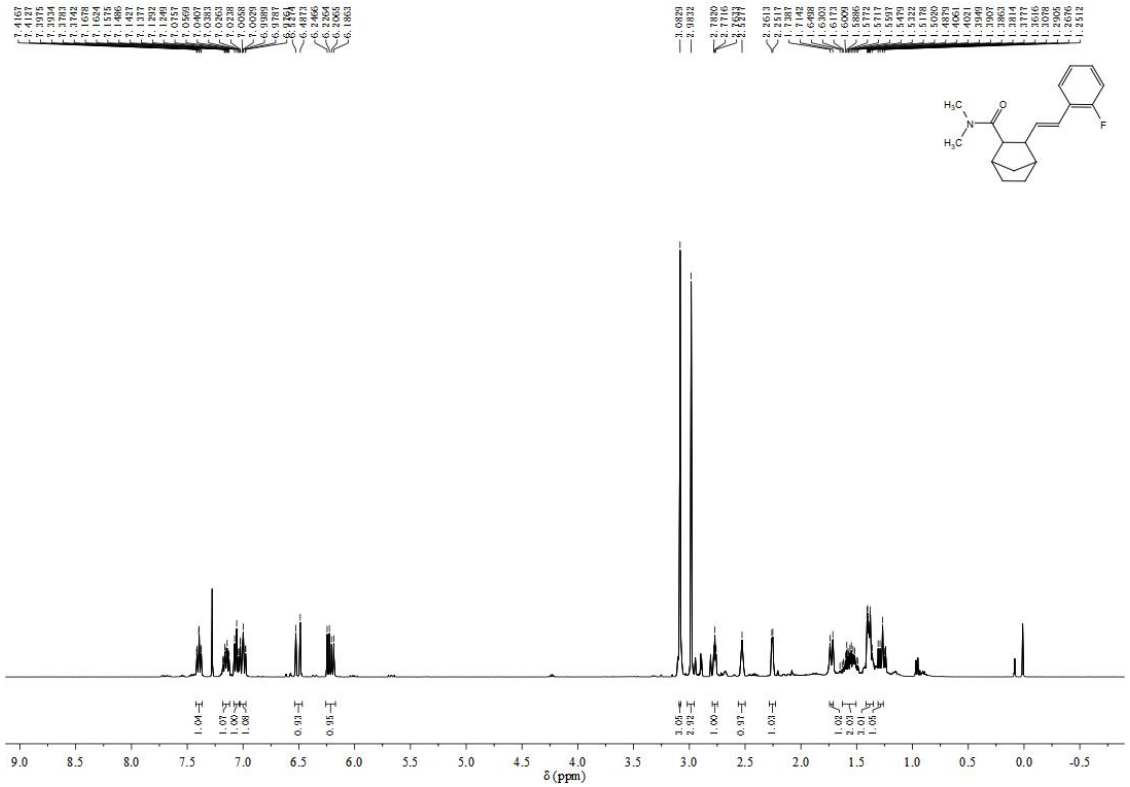
^{1}H NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**41e**)



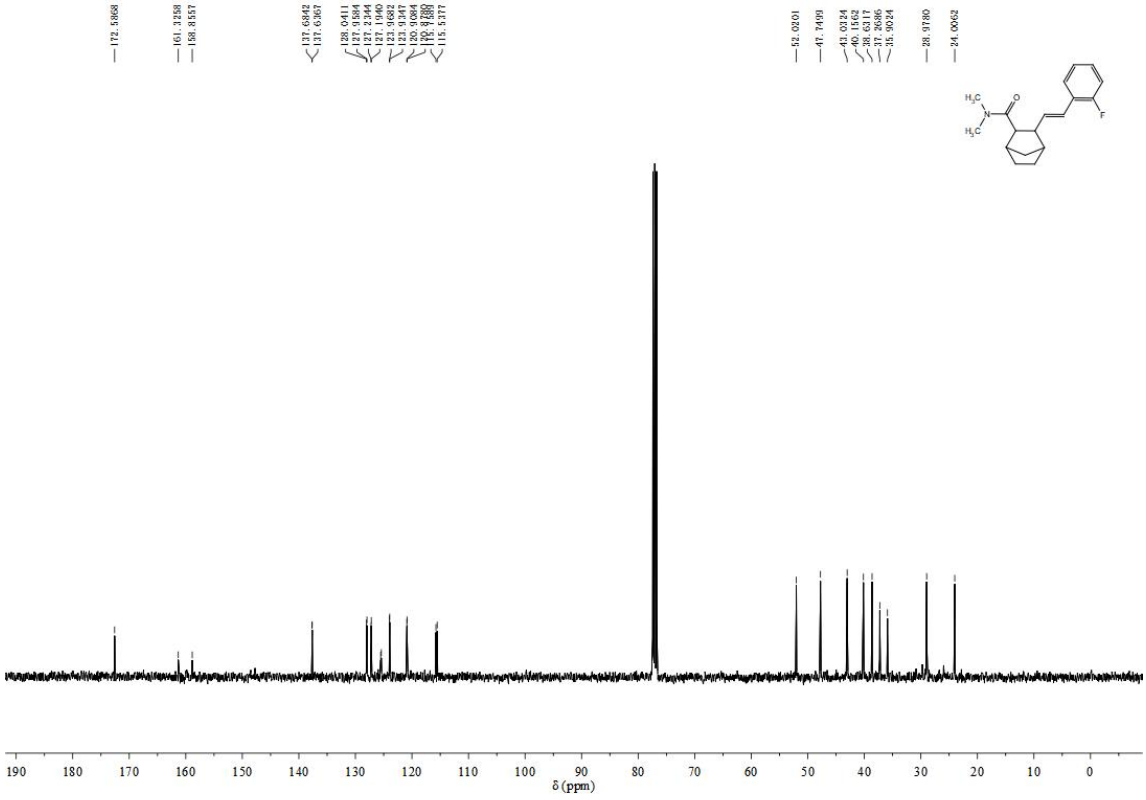
^{13}C NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**41e**)



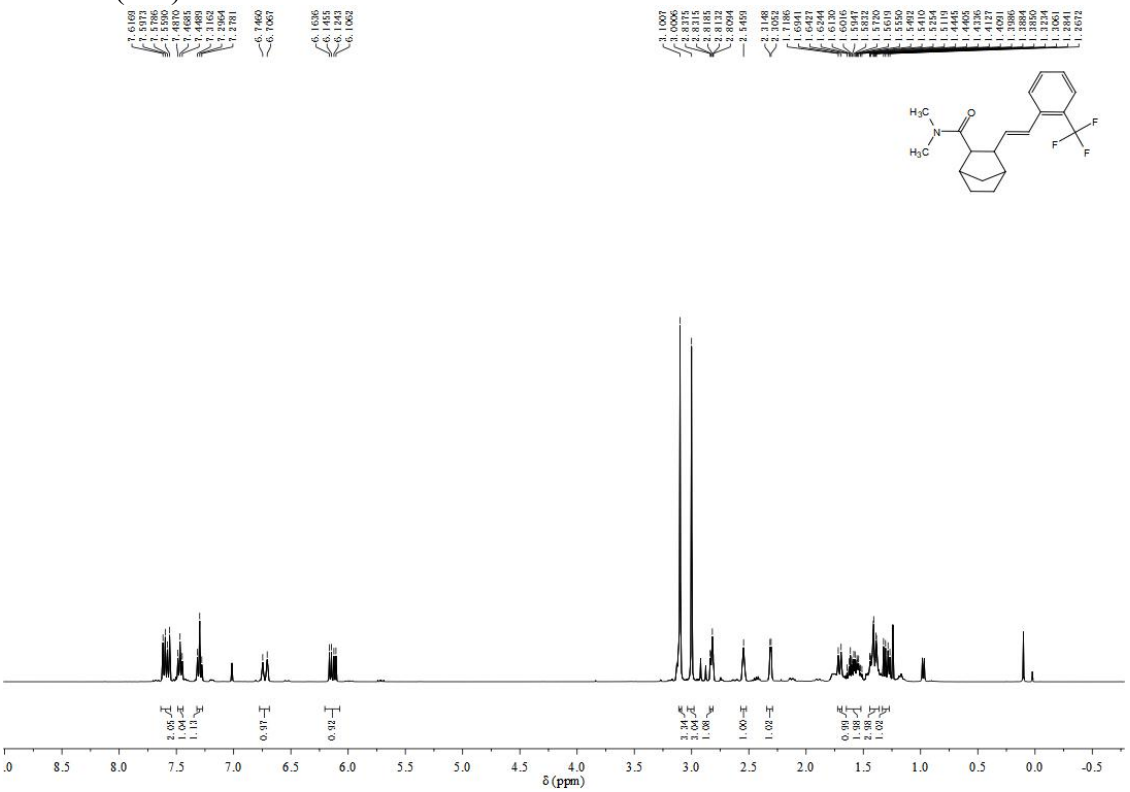
^{1}H NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**)



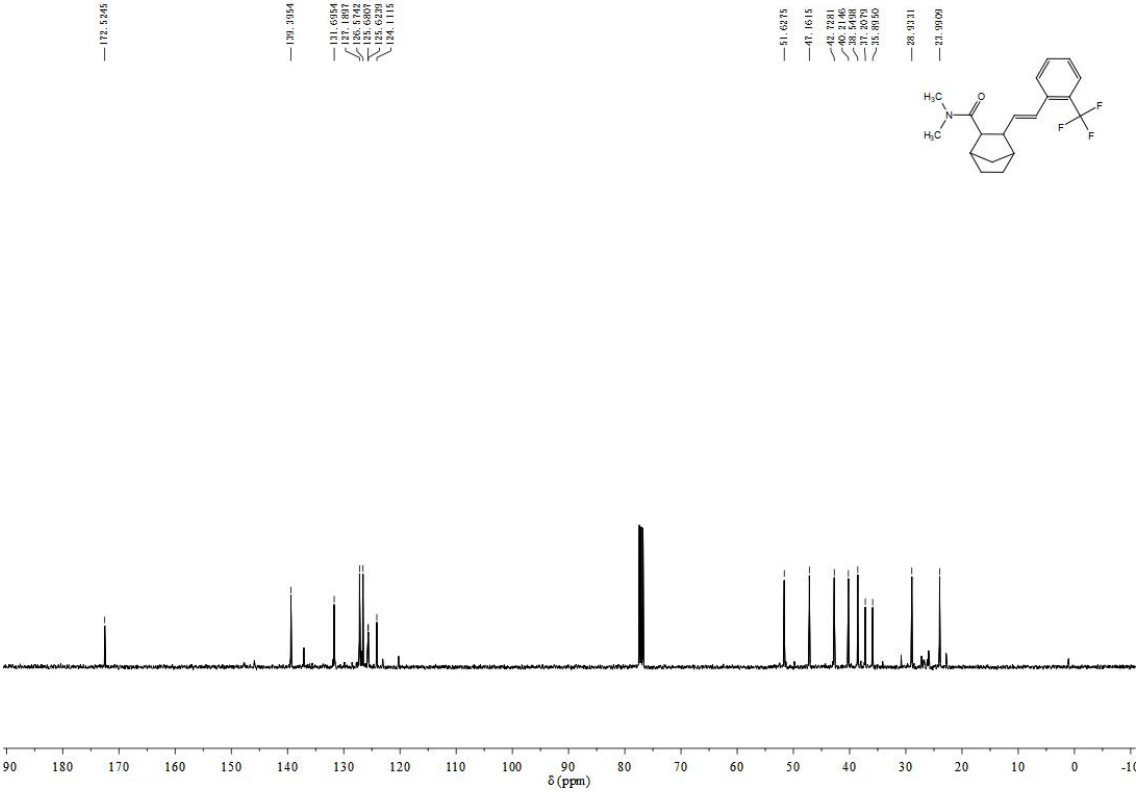
^{13}C NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**)



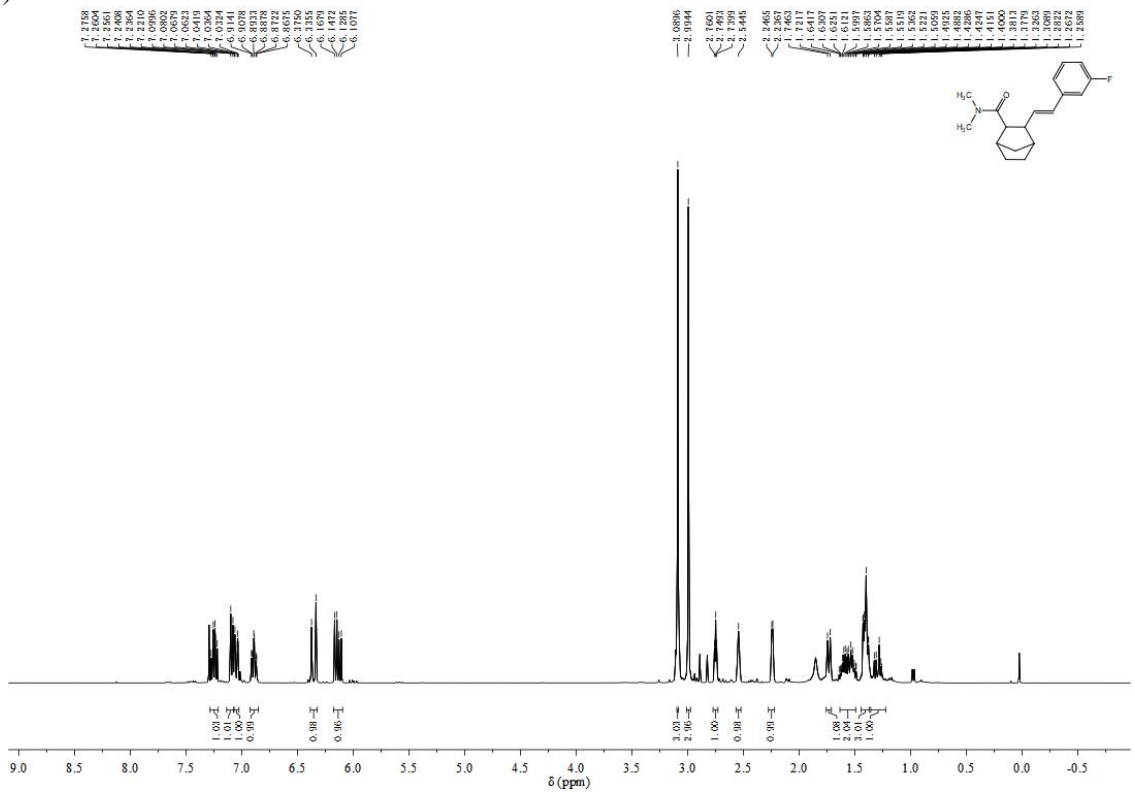
^{1}H NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**)



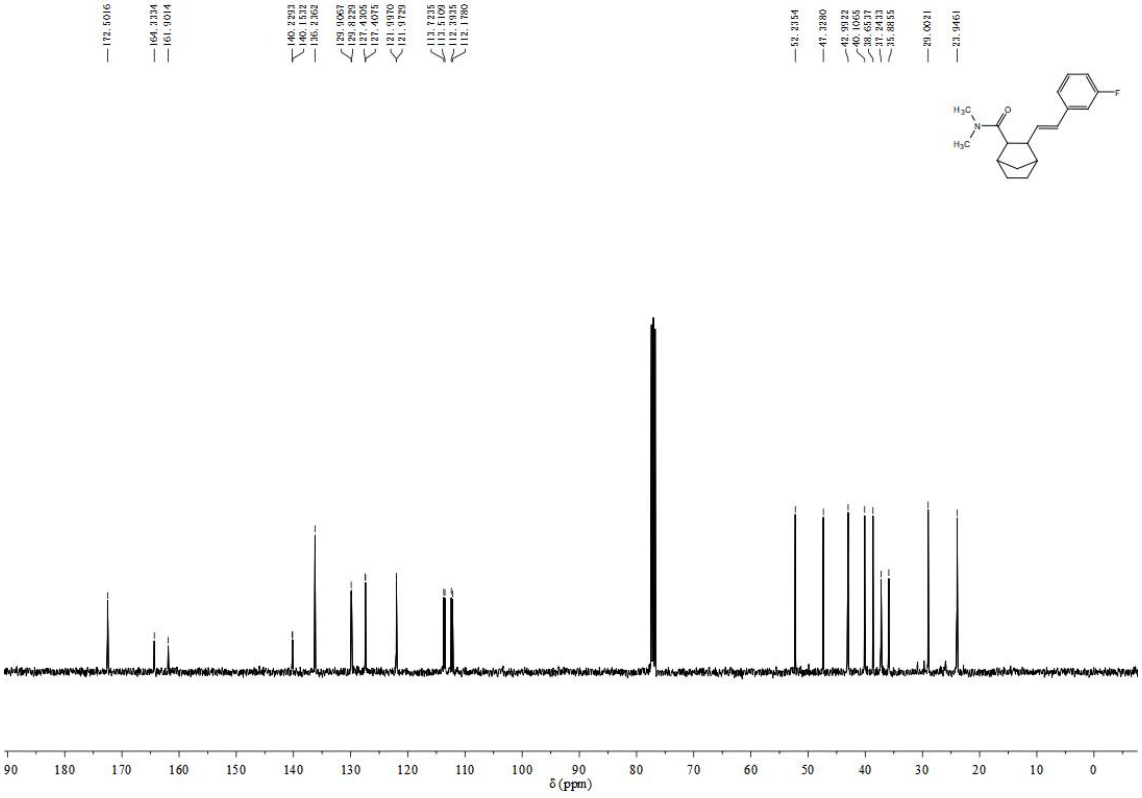
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**)



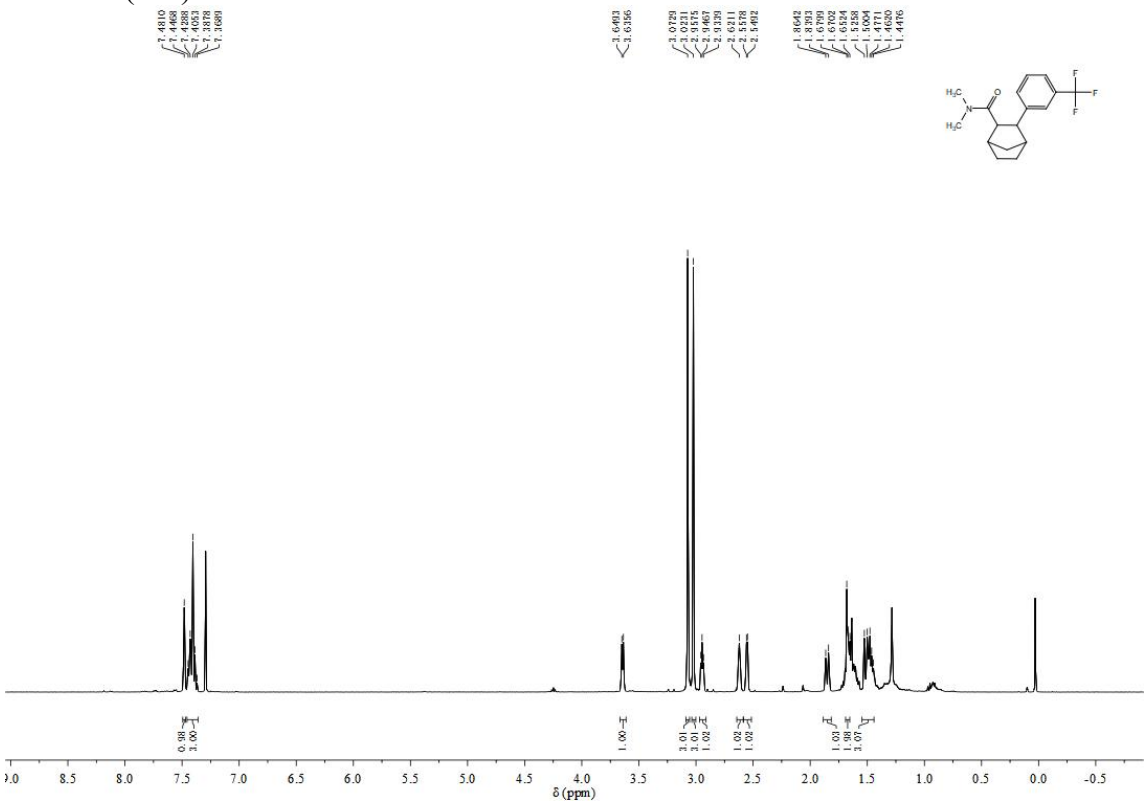
^{1}H NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**)



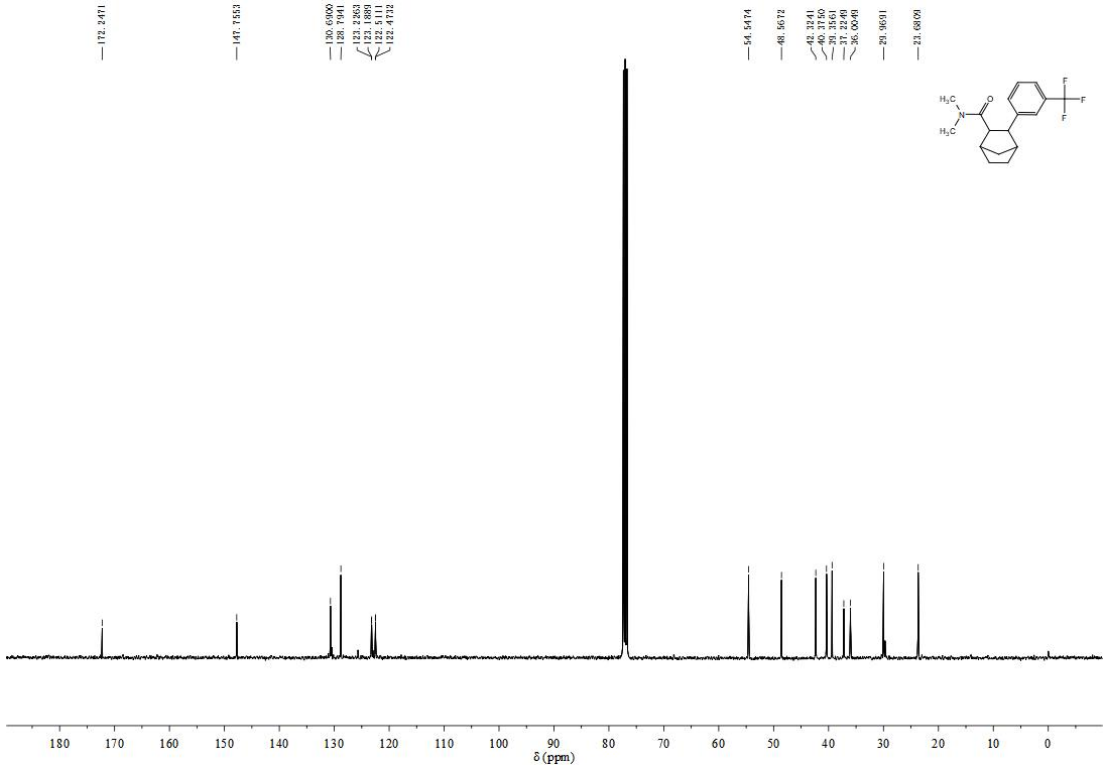
^{13}C NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**)



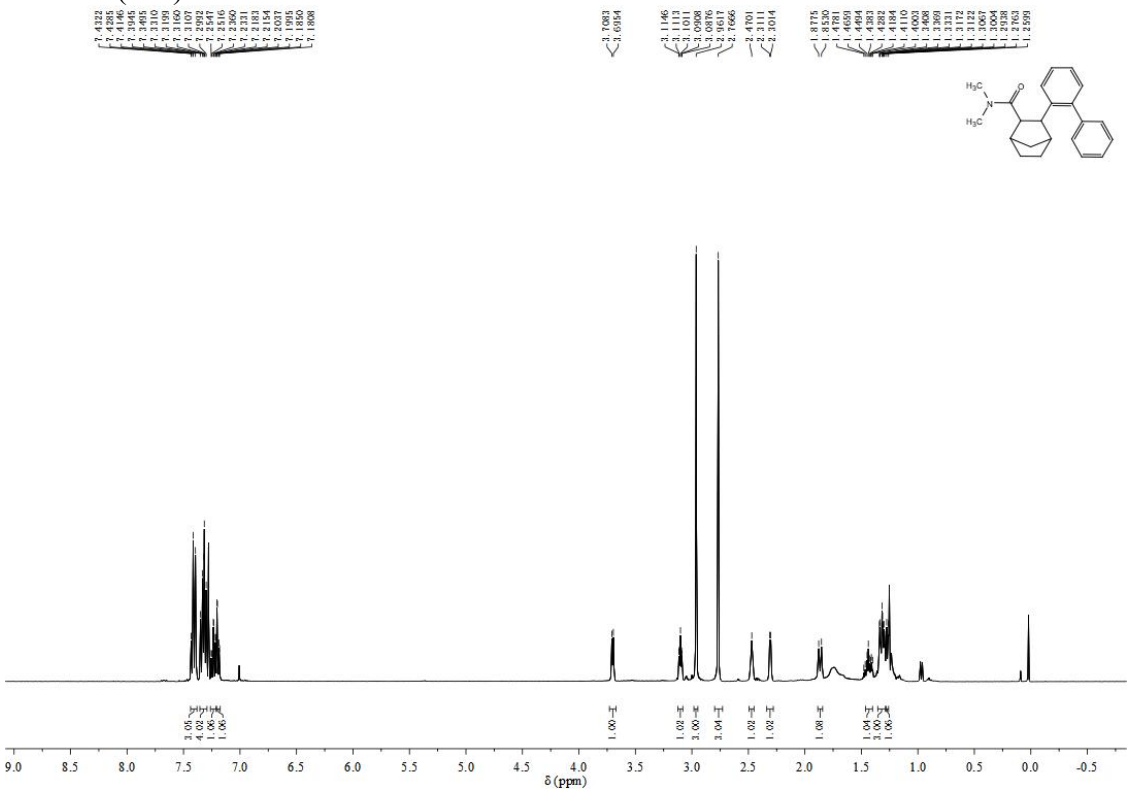
^{1}H NMR spectrum of *N,N*-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**)



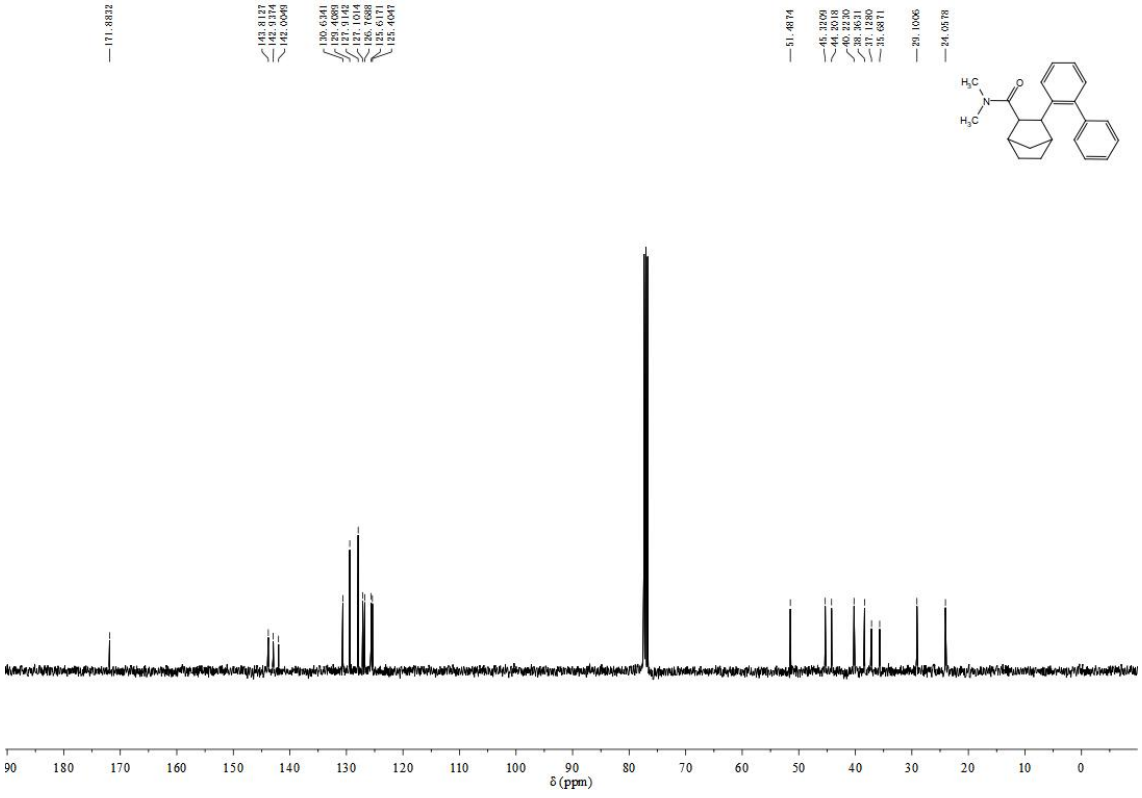
^{13}C NMR spectrum of *N,N*-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**)



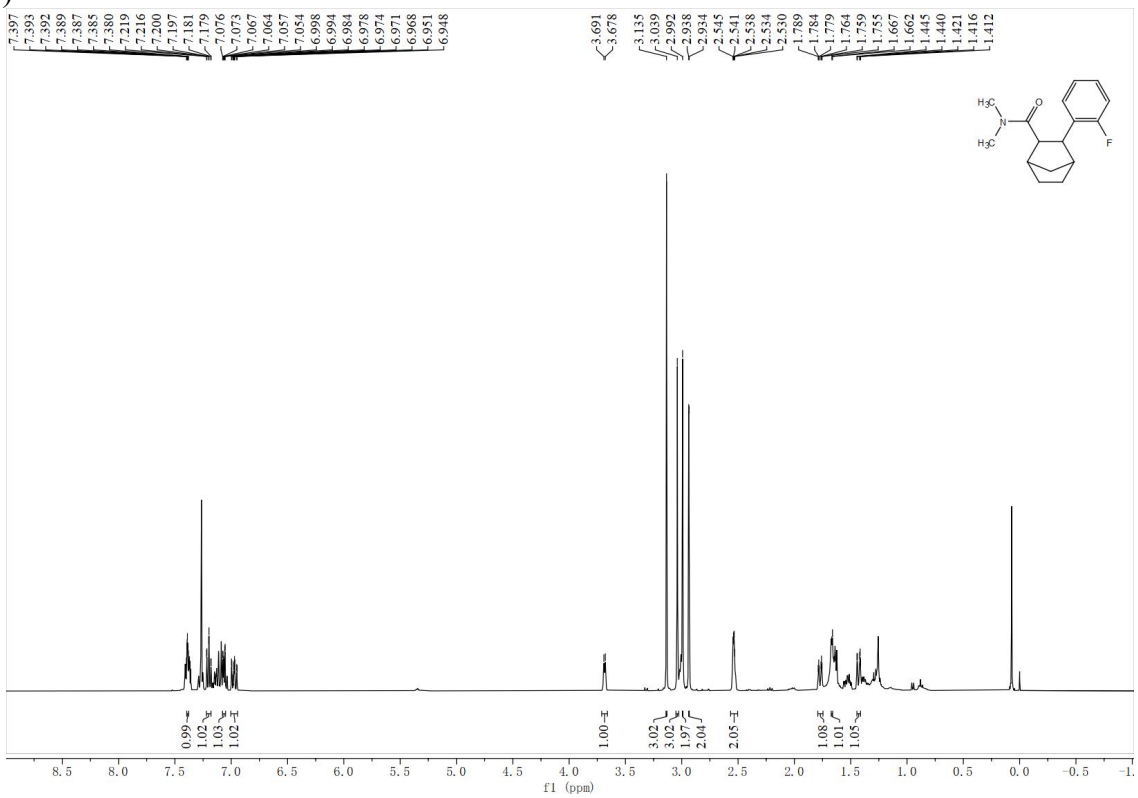
^{1}H NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**46e**)



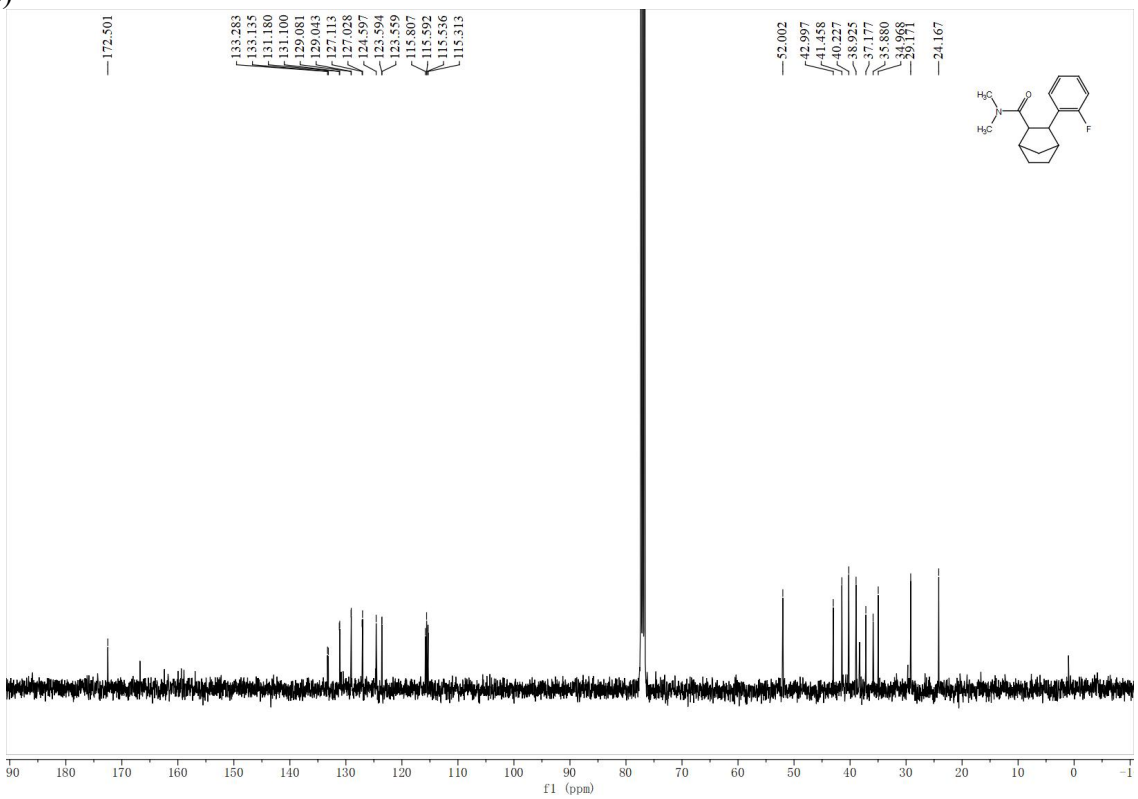
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**46e**)



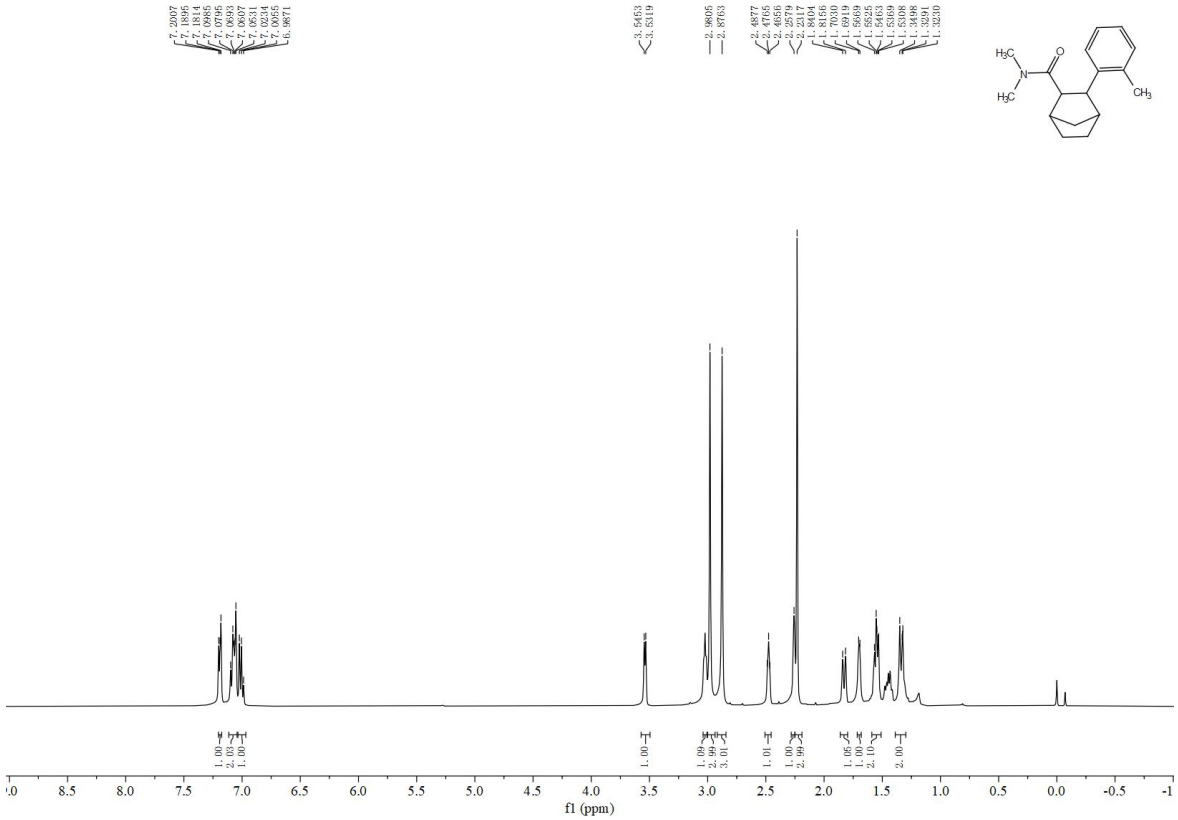
^{1}H NMR spectrum of 3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**)



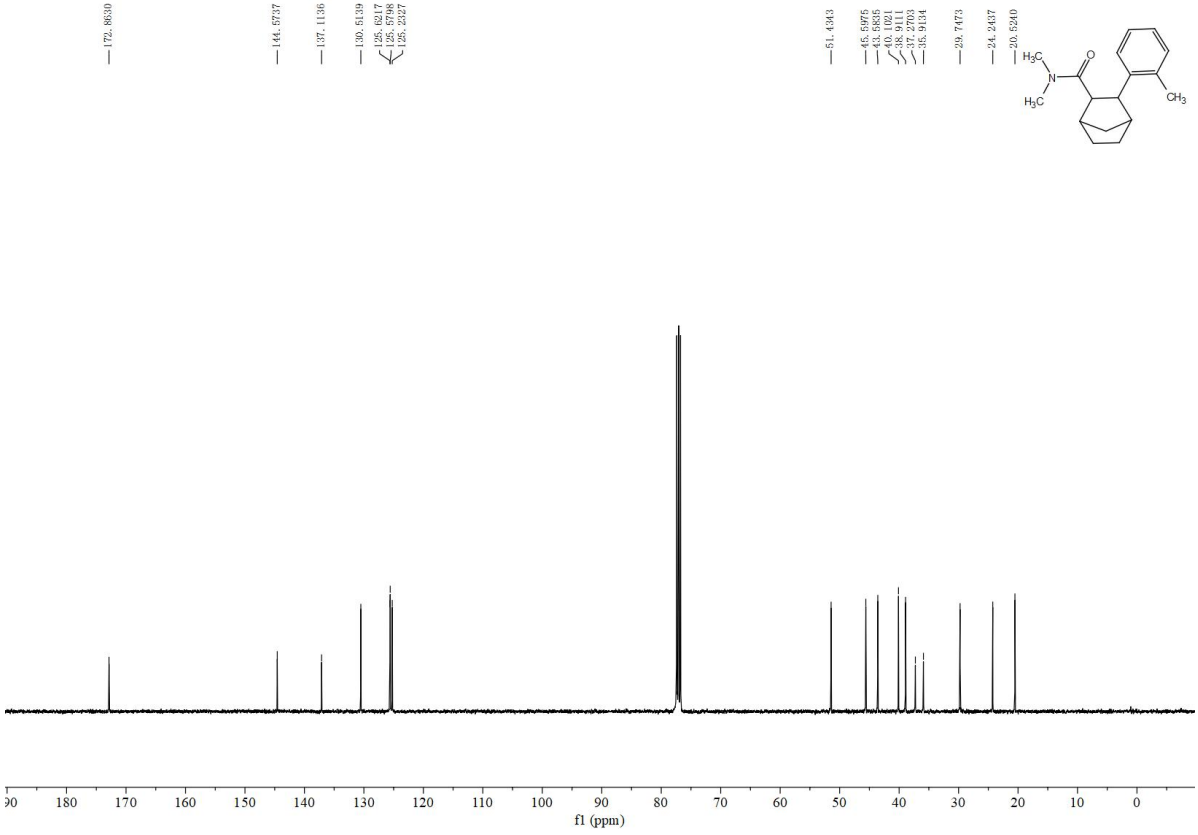
^{13}C NMR spectrum of 3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**)



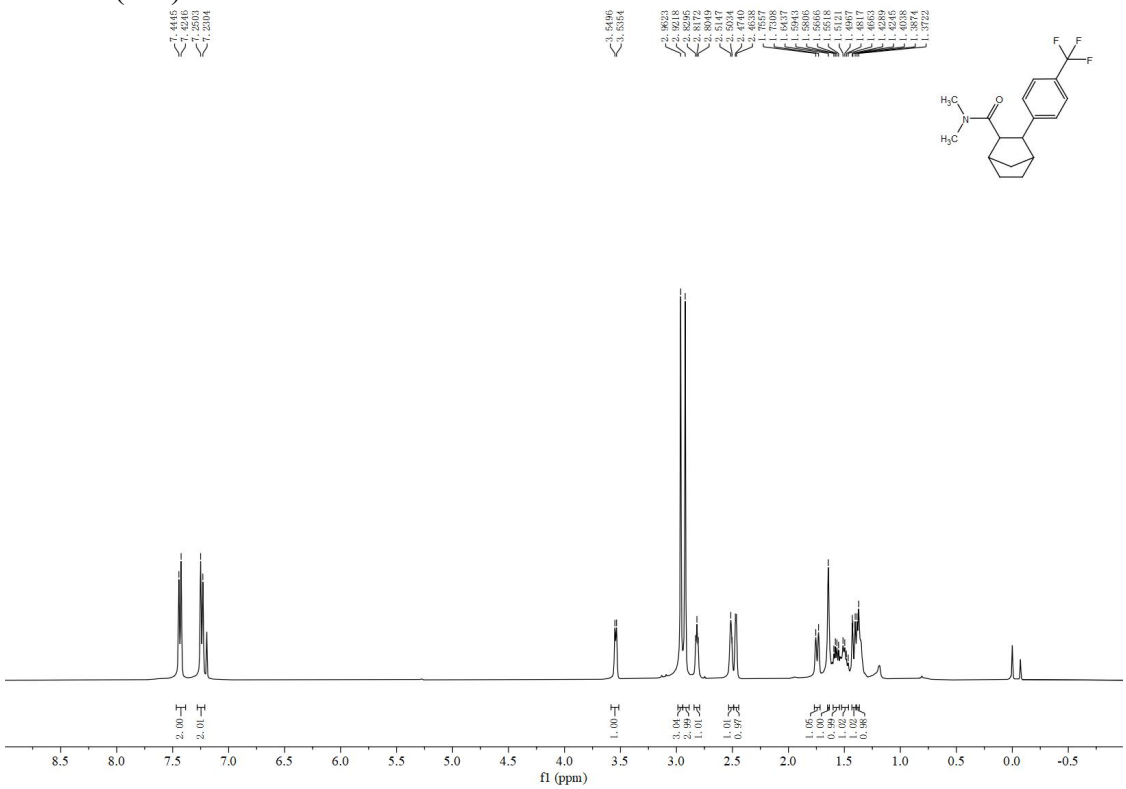
^{1}H NMR spectrum of *N,N*-dimethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**48e**)



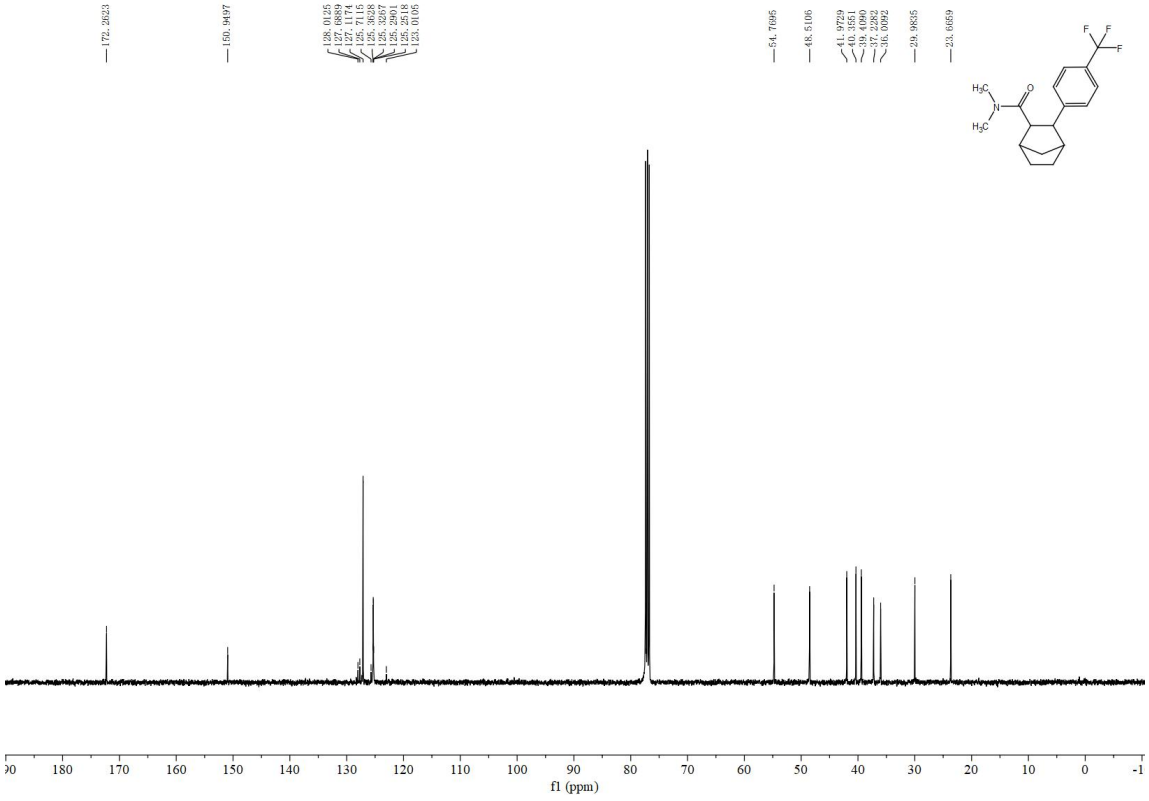
^{13}C NMR spectrum of *N,N*-dimethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**48e**)



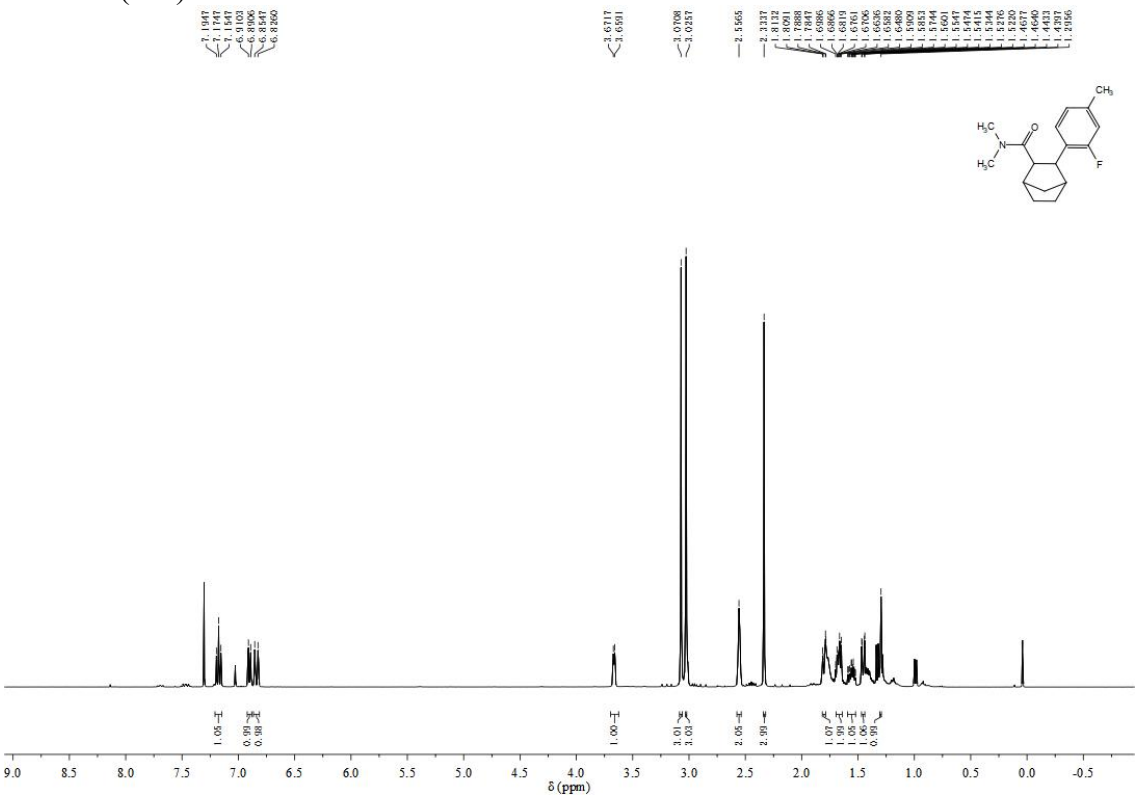
^{1}H NMR spectrum of *N,N*-dimethyl-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**49e**)



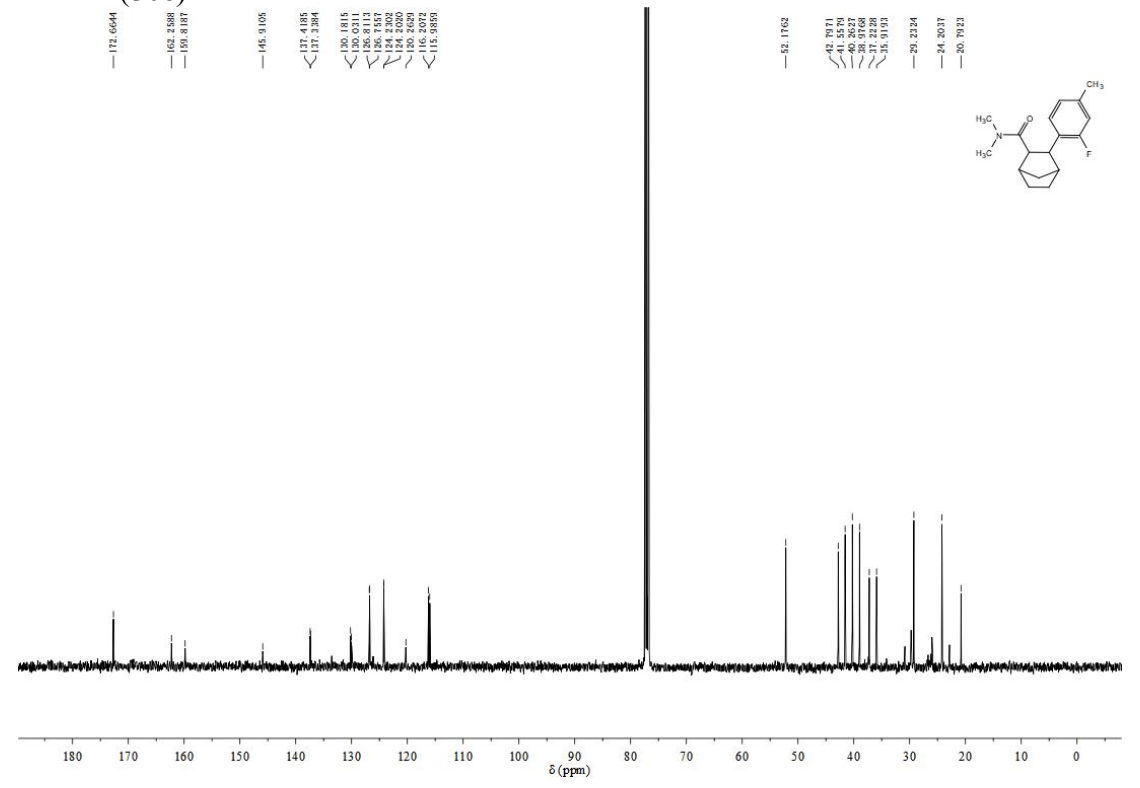
^{13}C NMR spectrum of *N,N*-dimethyl-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**49e**)



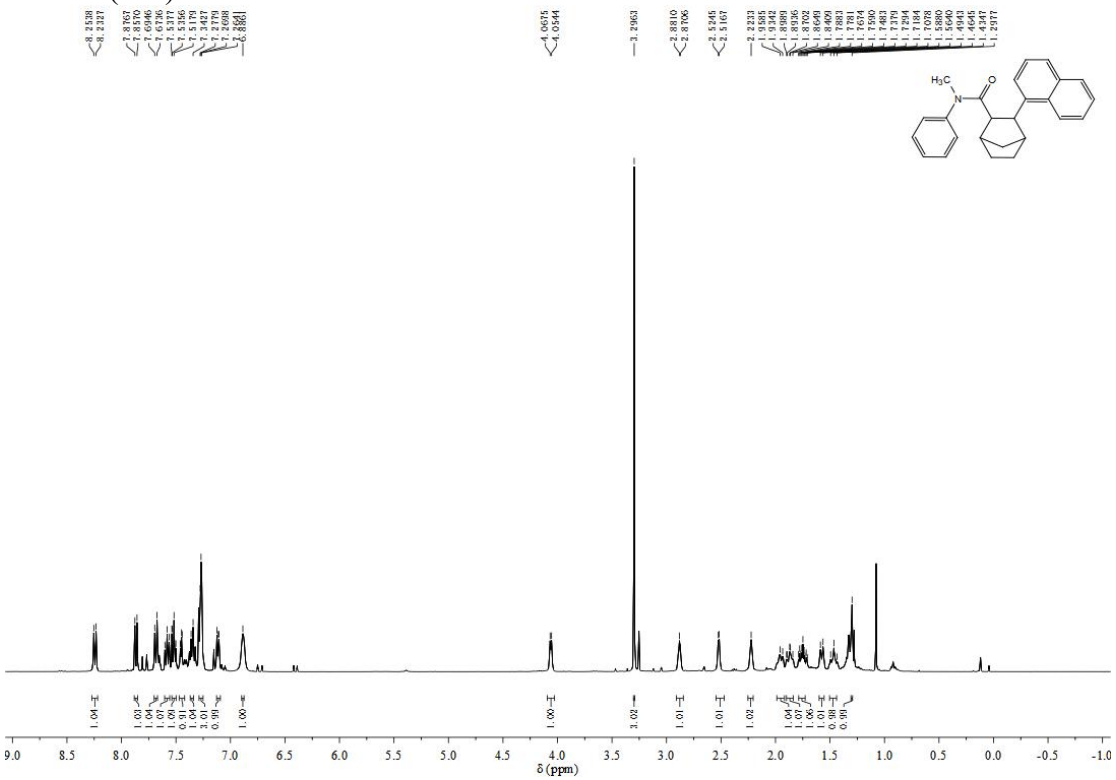
^{1}H NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**)



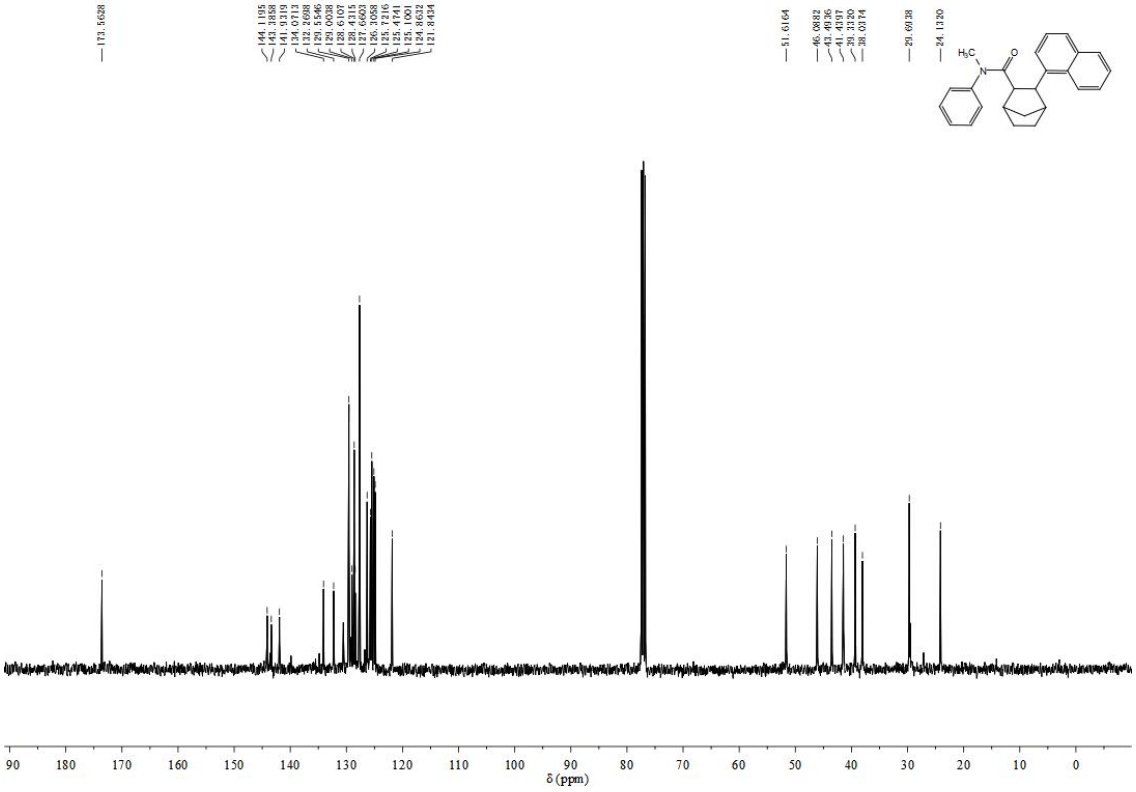
^{13}C NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**)



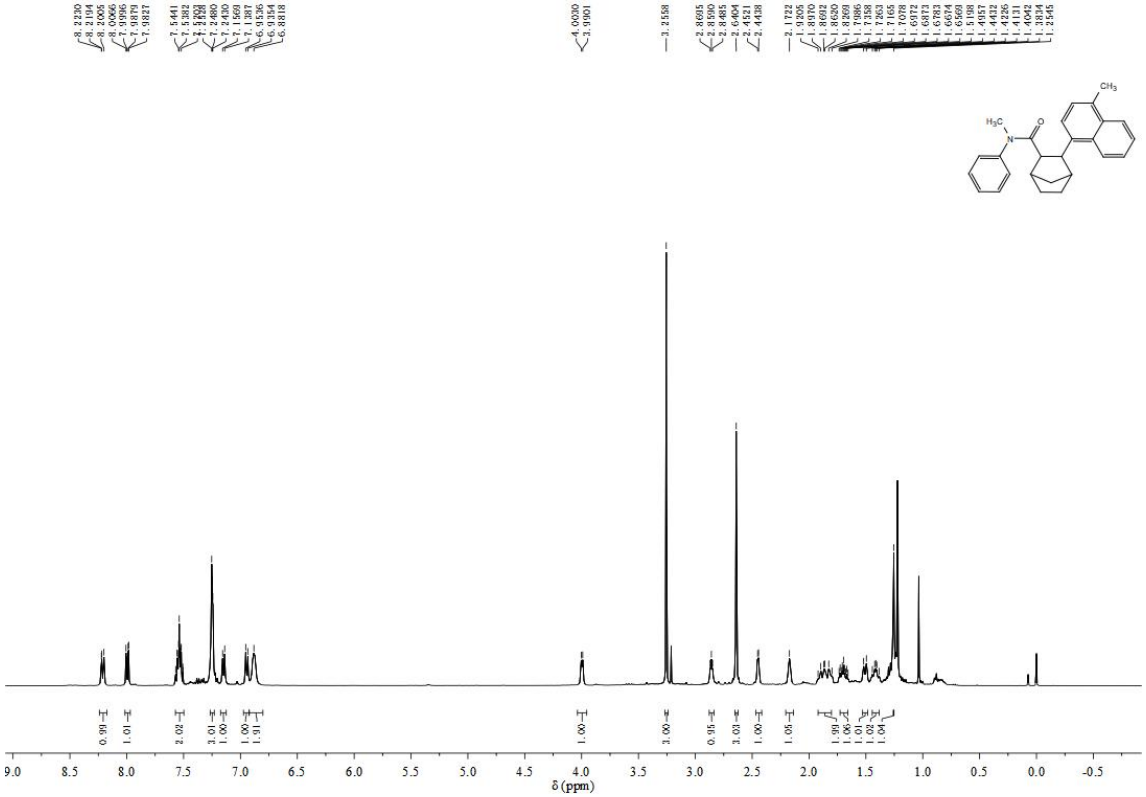
^{1}H NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**51e**)



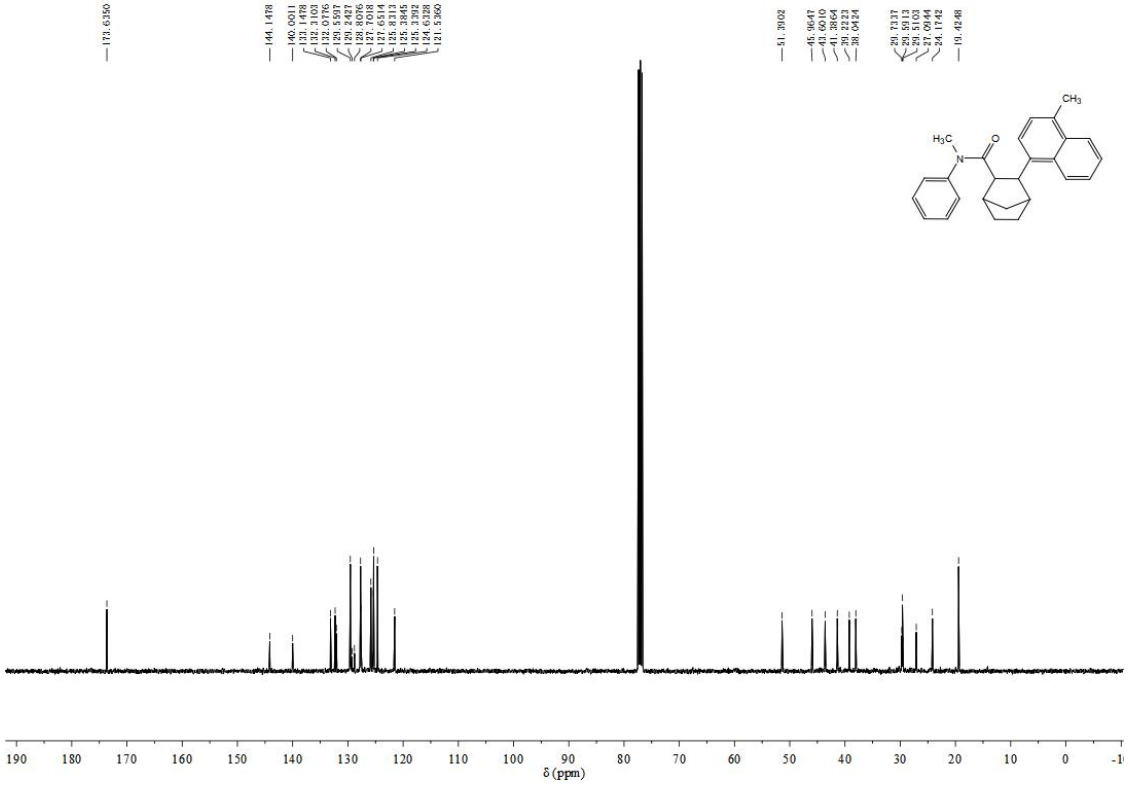
^{13}C NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**51e**)



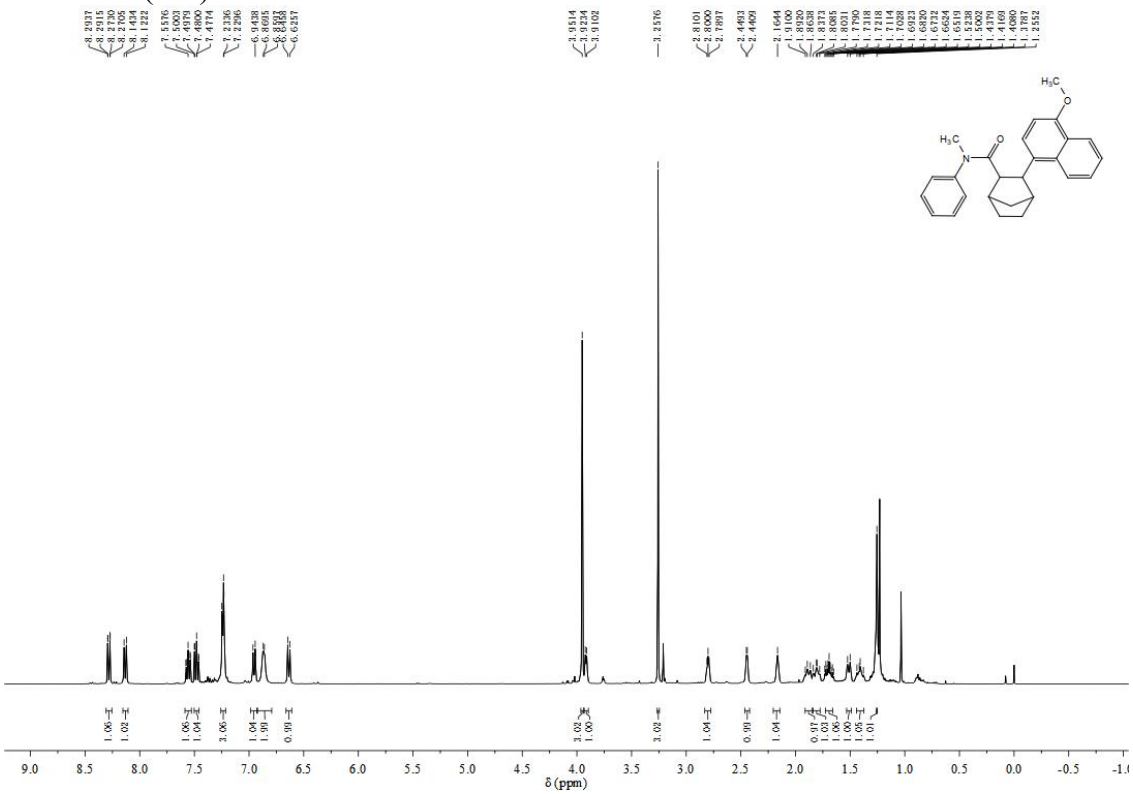
^{1}H NMR spectrum of *N*-methyl-3-(4-methylnaphthalen-1-yl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**52e**)



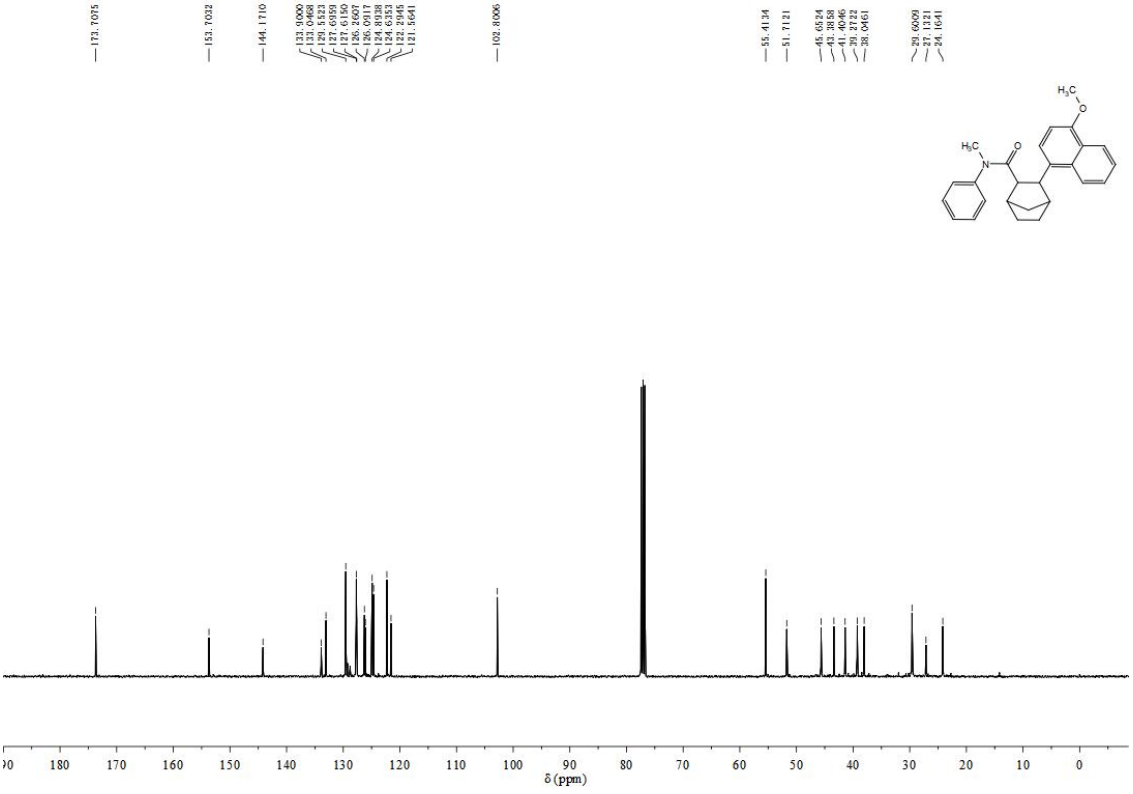
^{13}C NMR spectrum of *N*-methyl-3-(4-methylnaphthalen-1-yl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**52e**)



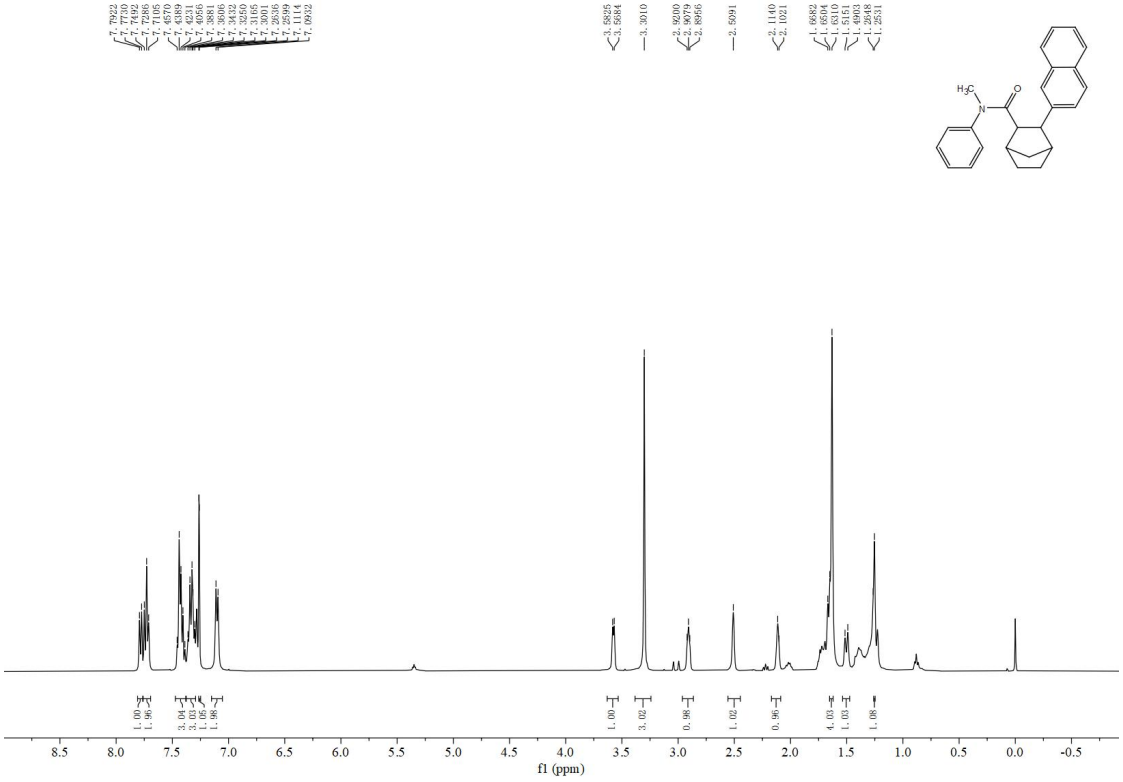
^{1}H NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**53e**)



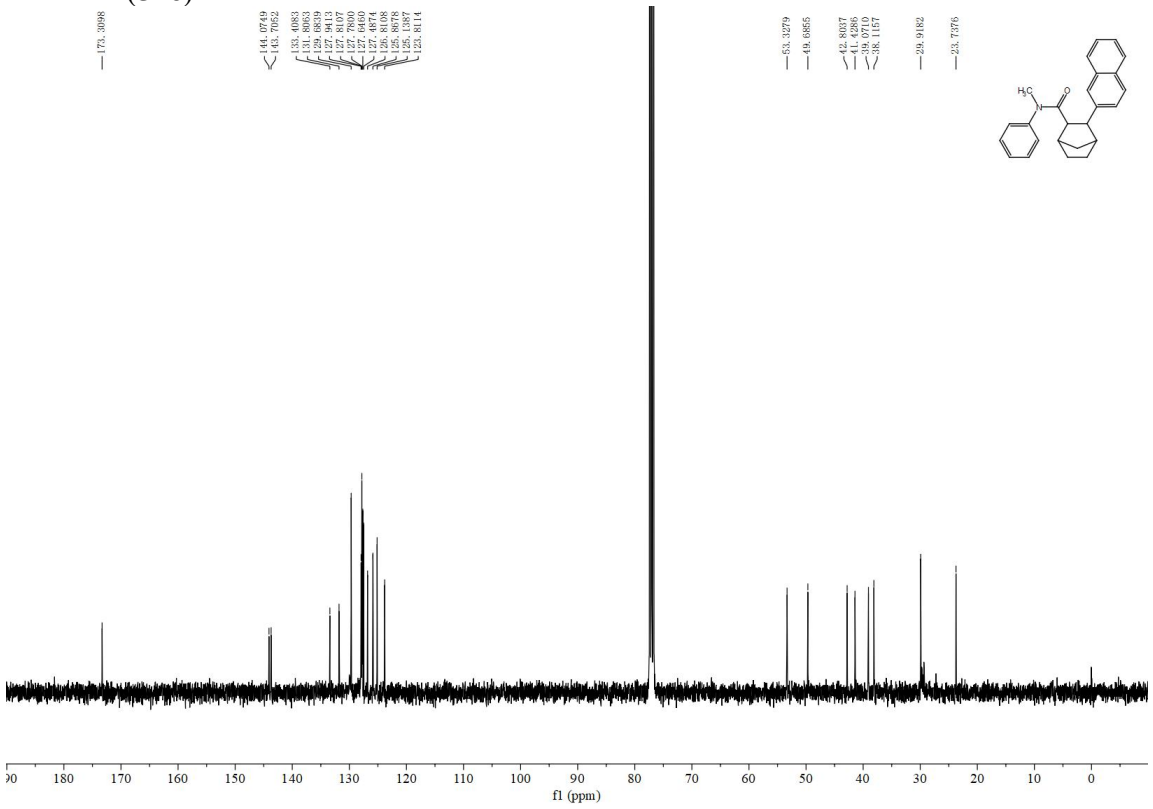
^{13}C NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**53e**)



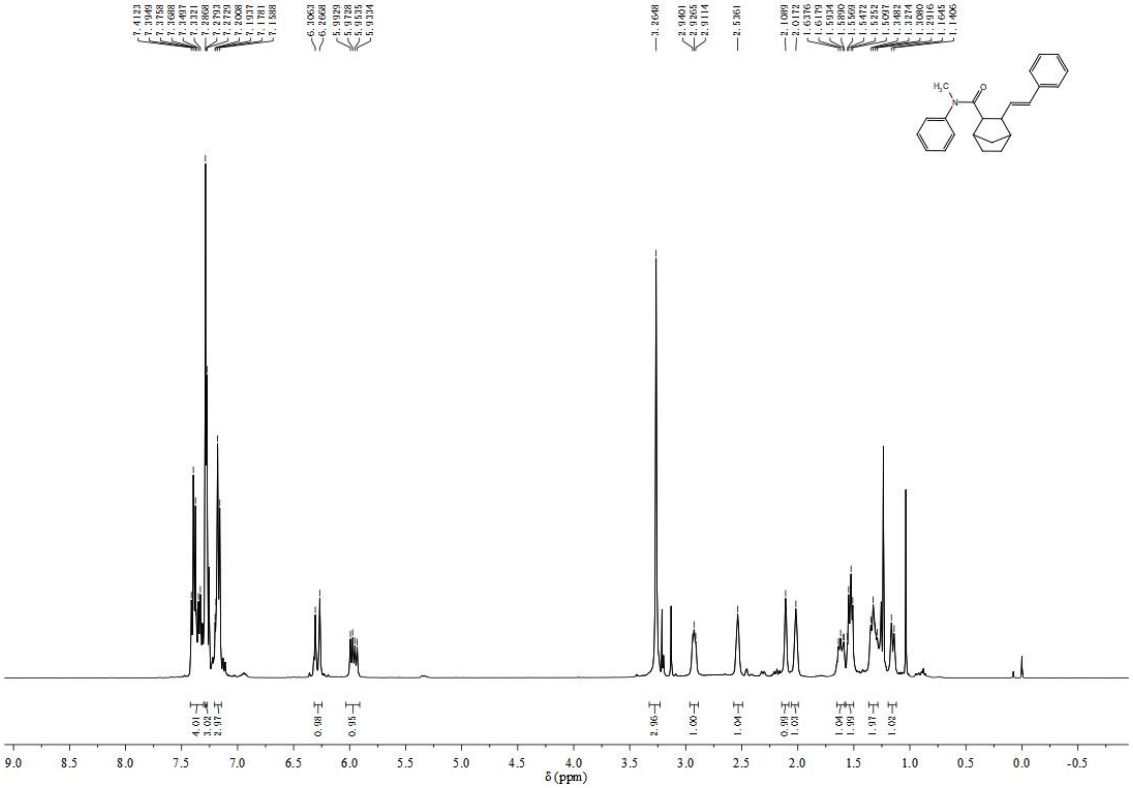
^{1}H NMR spectrum of *N*-methyl-3-(naphthalen-2-yl)-*N*-phenylbicyclo [2.2.1] heptane-2-carboxamide (**54e**)



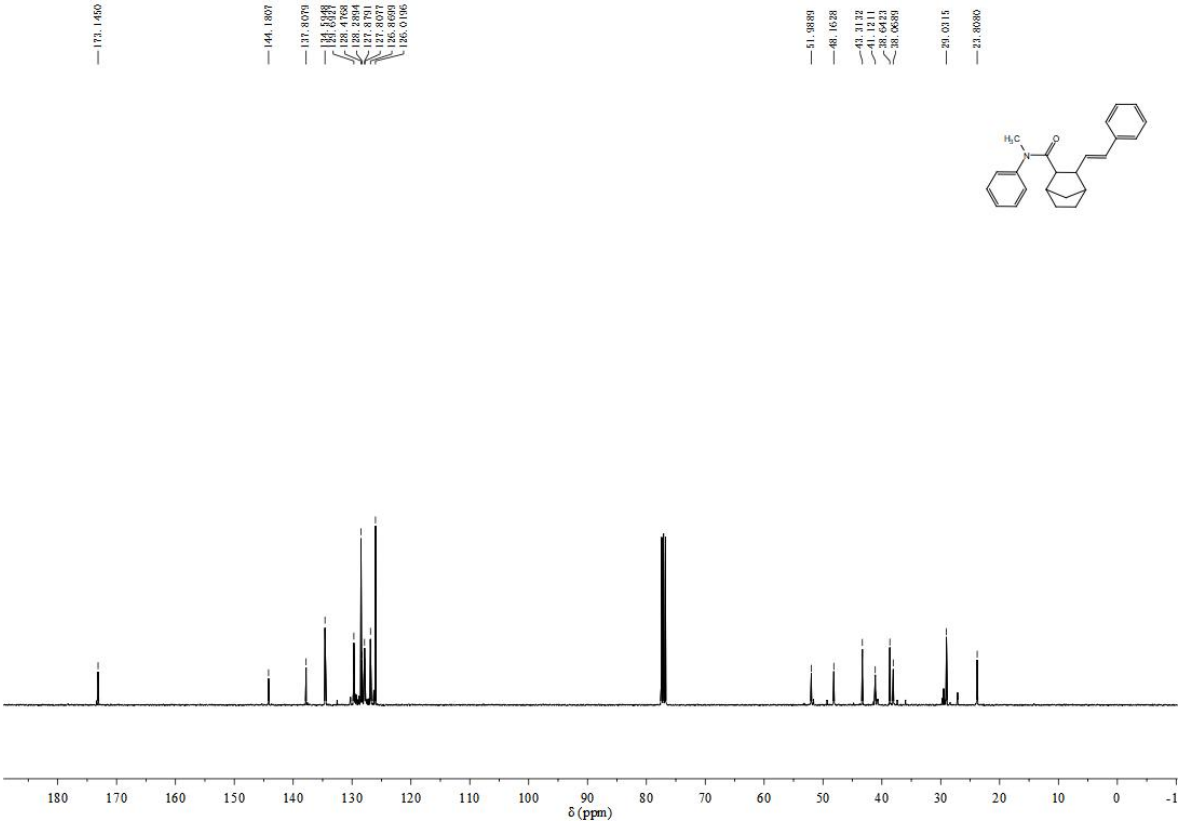
^{13}C NMR spectrum of *N*-methyl-3-(naphthalen-2-yl)-*N*-phenylbicyclo [2.2.1] heptane-2-carboxamide (**54e**)



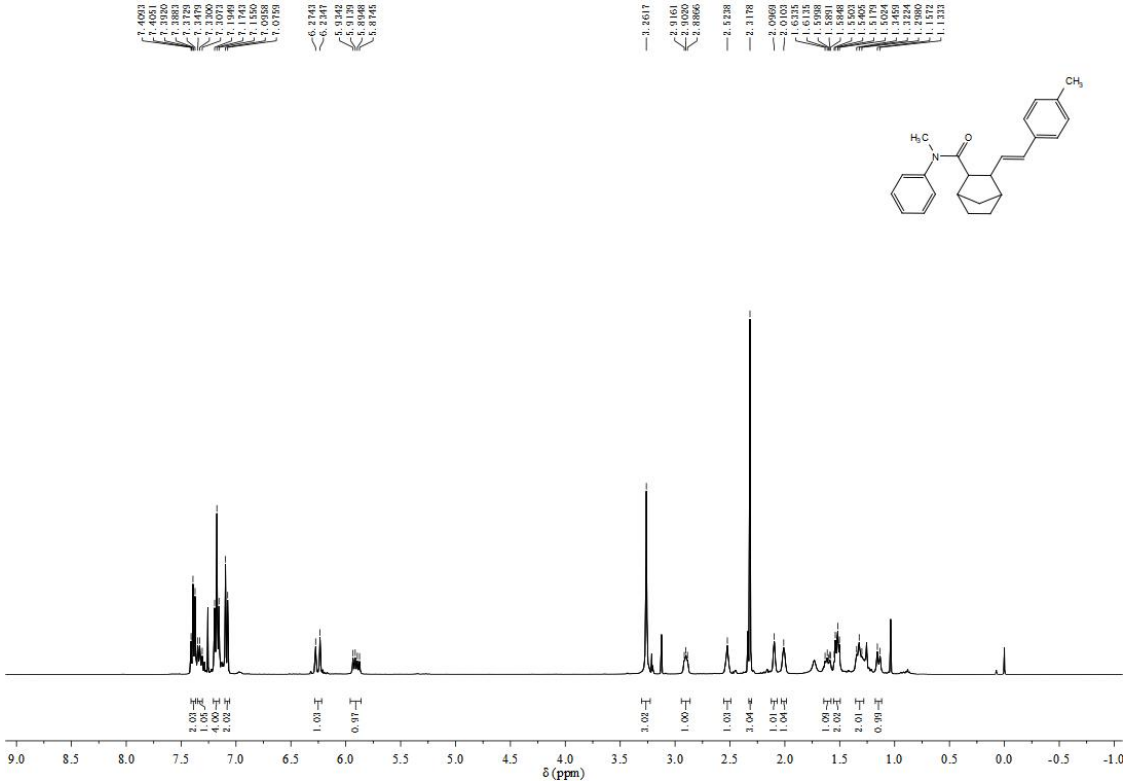
^{1}H NMR spectrum of (*E*)-*N*-methyl-*N*-phenyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**55e**)



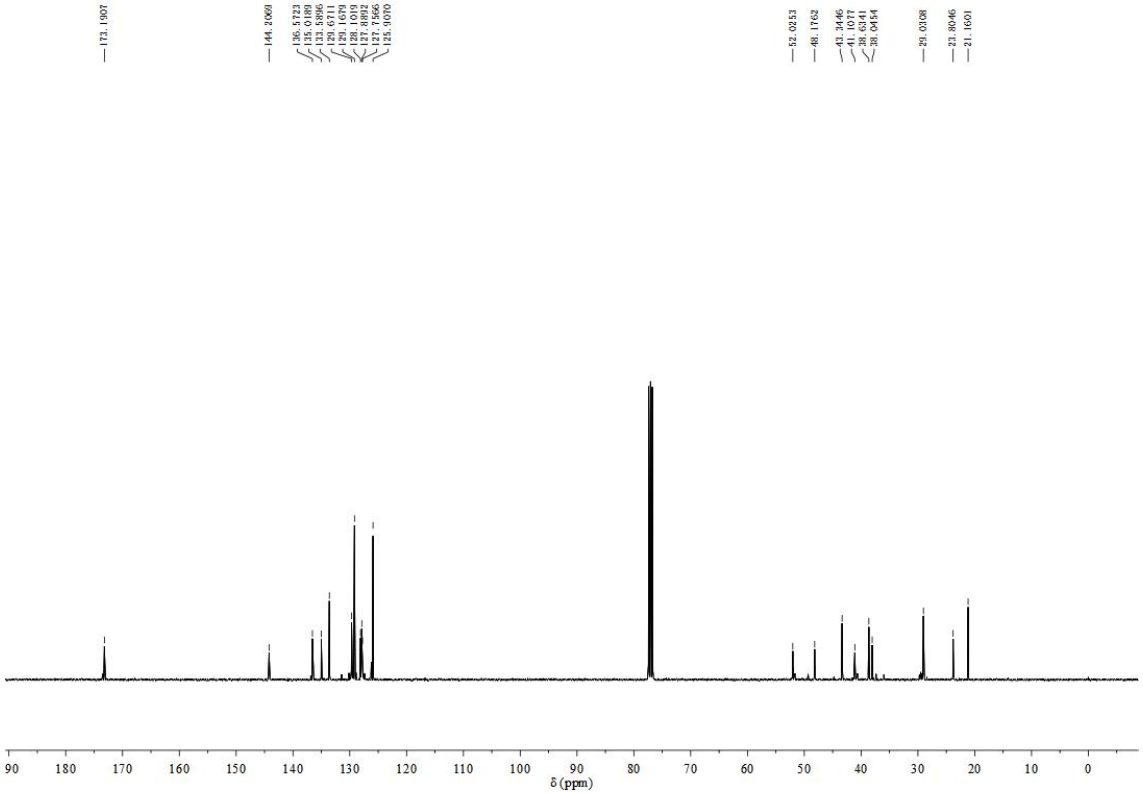
^{13}C NMR spectrum of (*E*)-*N*-methyl-*N*-phenyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**55e**)



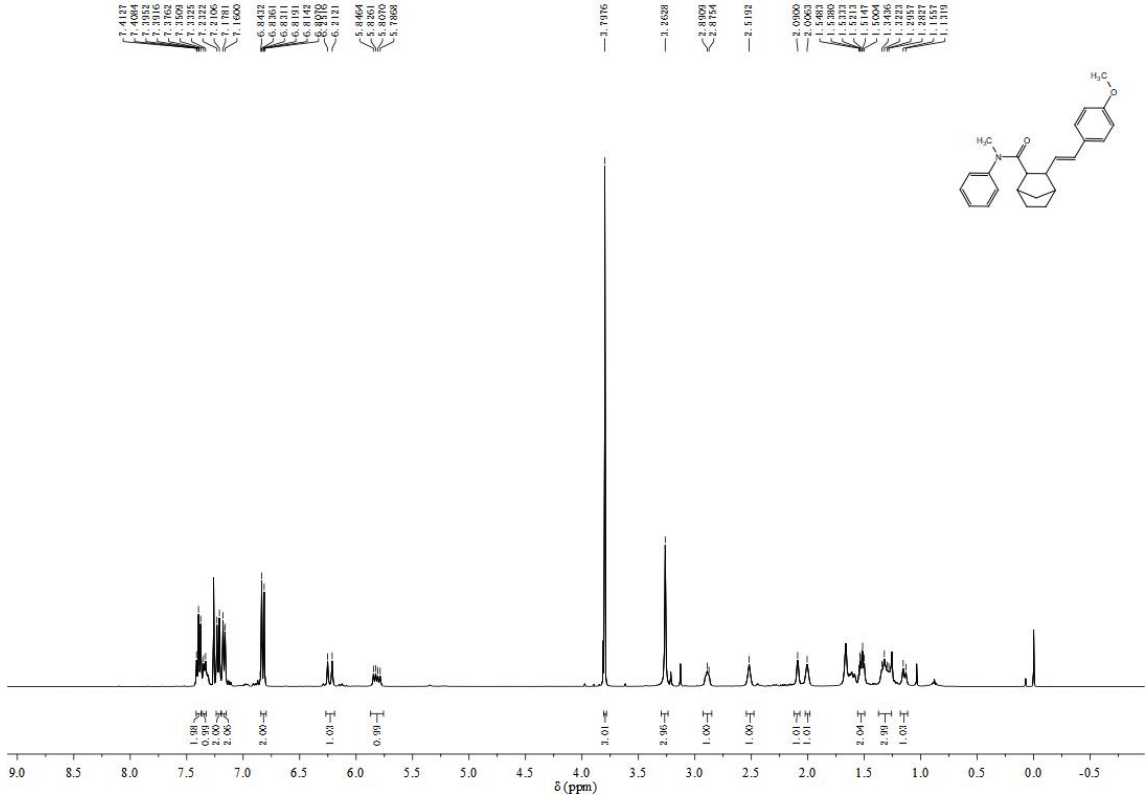
^{1}H NMR spectrum of (*E*)-*N*-methyl-3-(4-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**56e**)



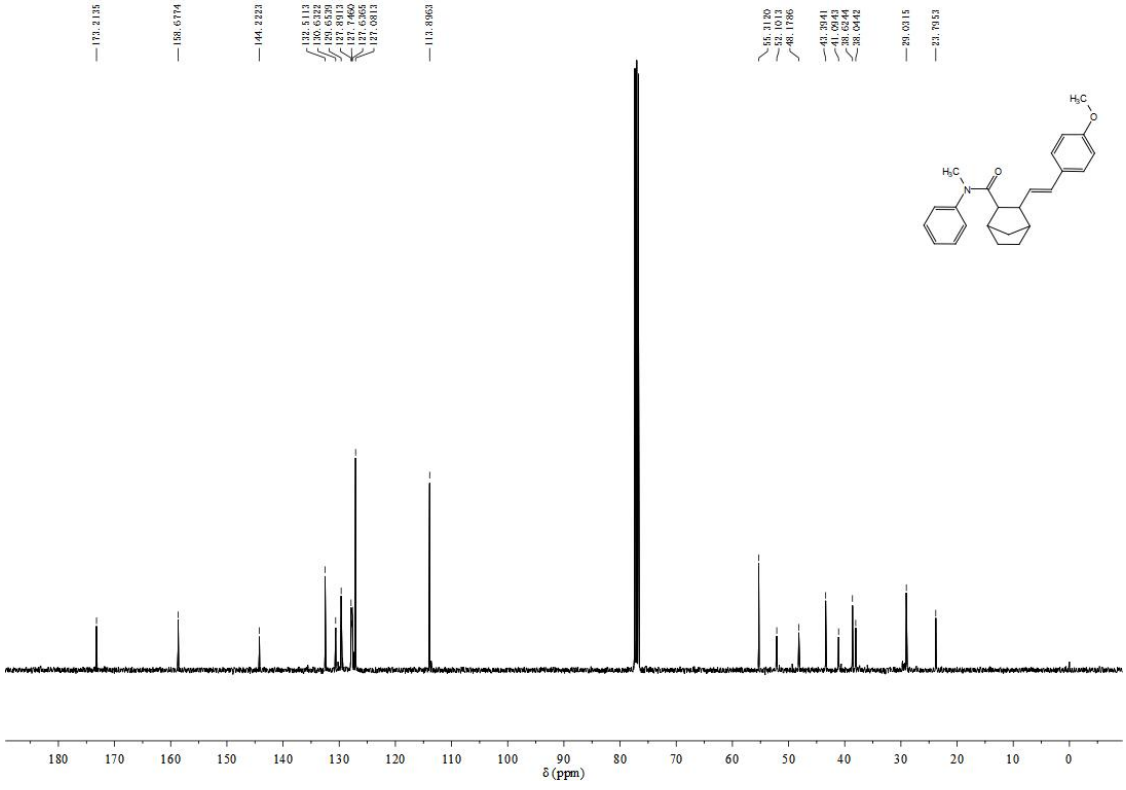
^{13}C NMR spectrum of (*E*)-*N*-methyl-3-(4-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**56e**)



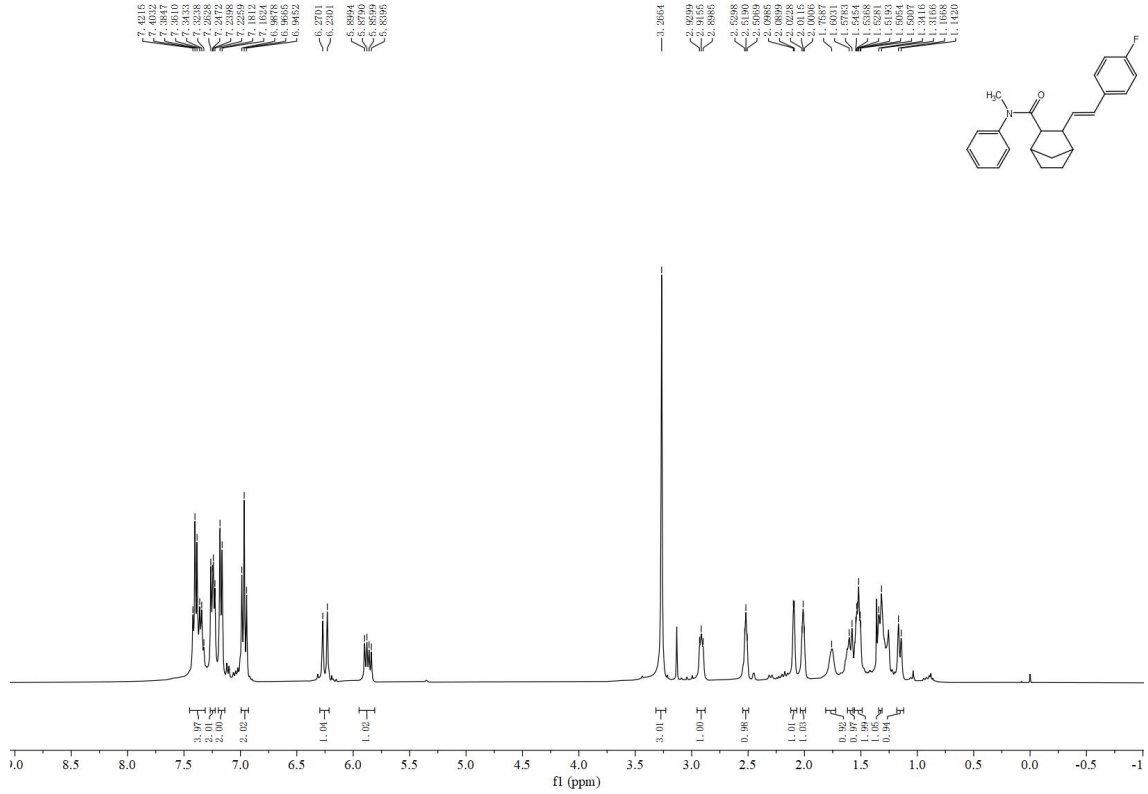
^{1}H NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**57e**)



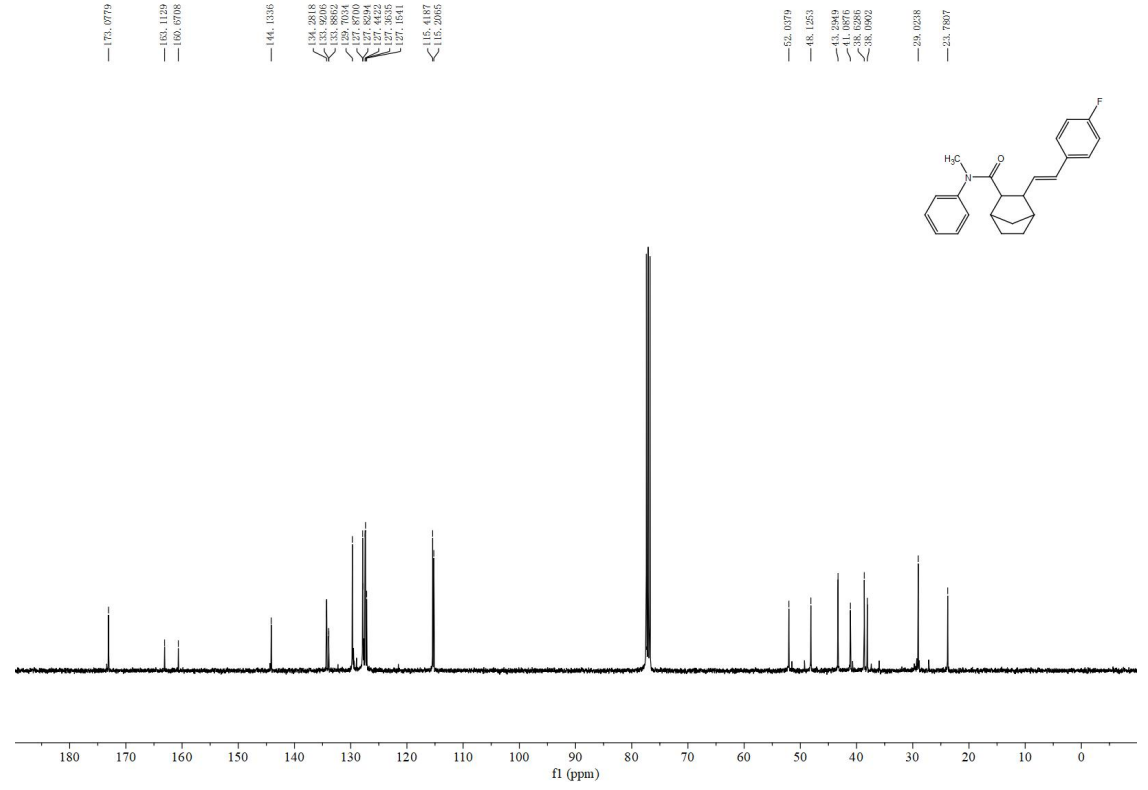
^{13}C NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**57e**)



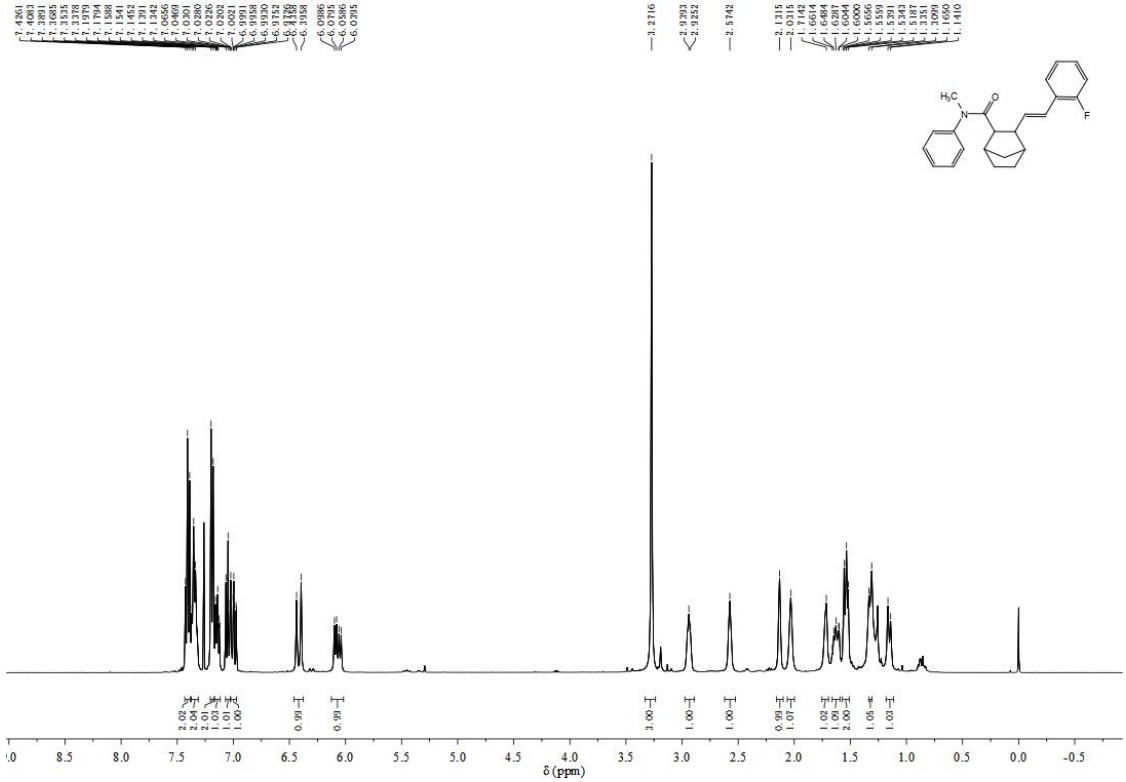
^{1}H NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**58e**)



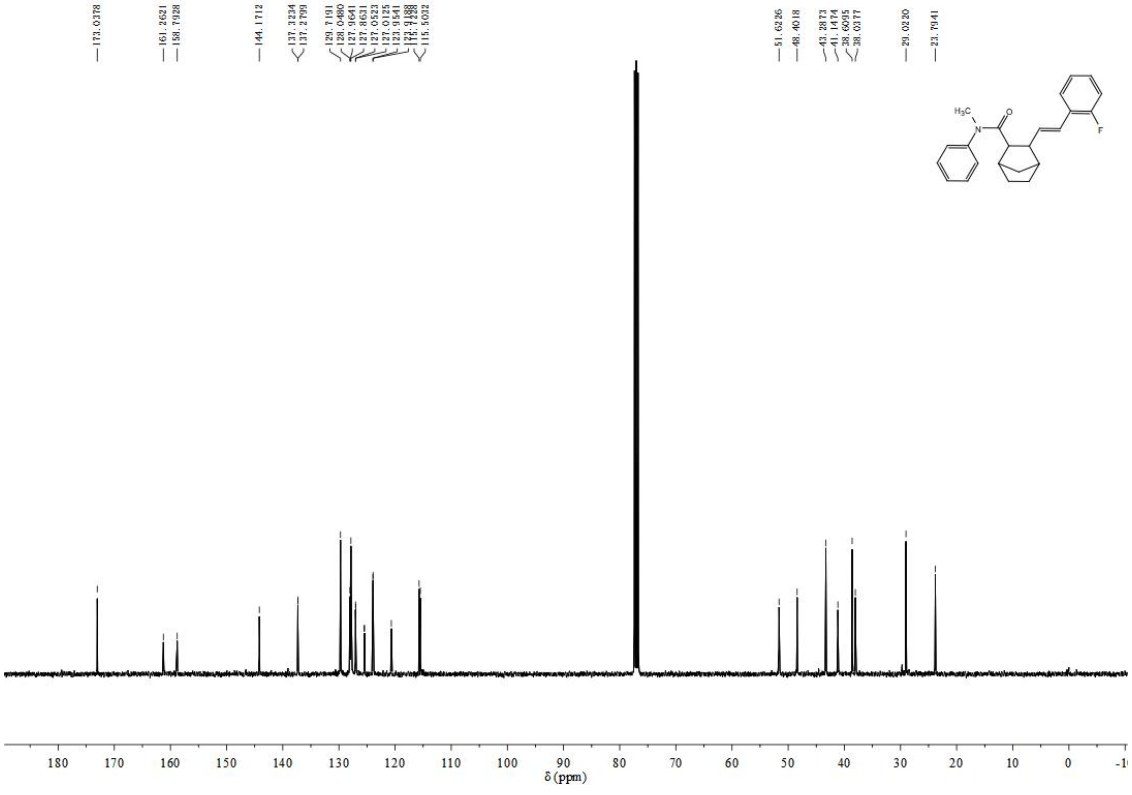
^{13}C NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**58e**)



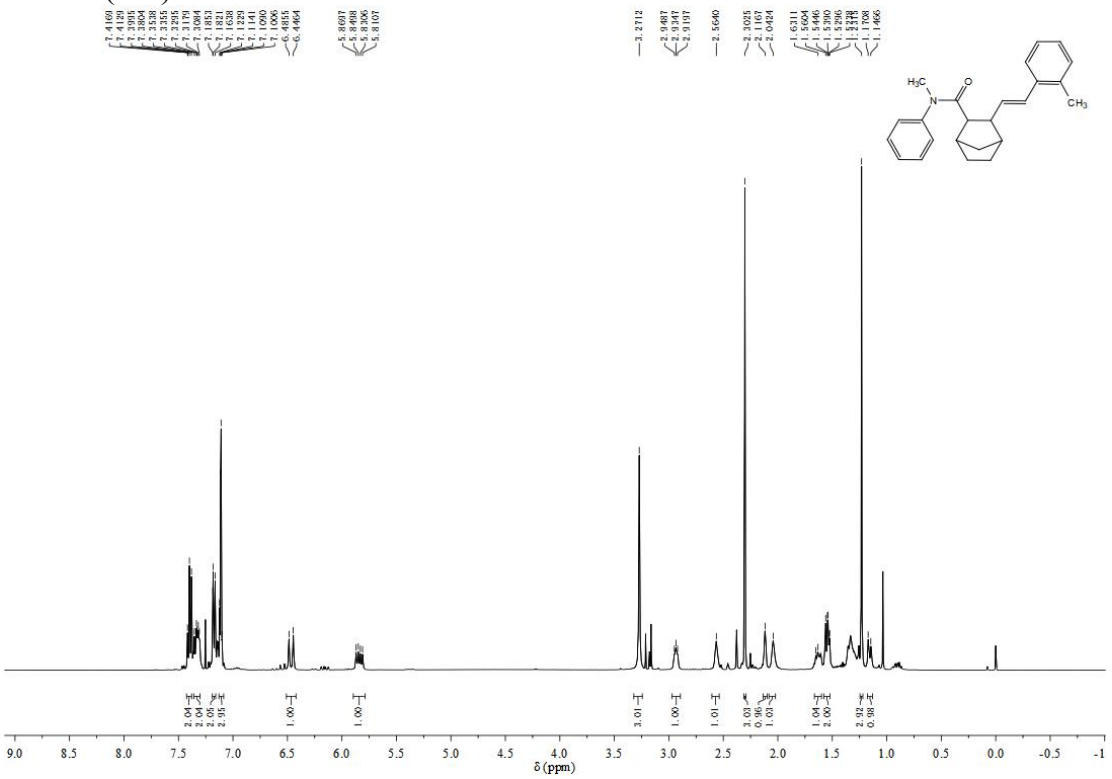
^{1}H NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**59e**)



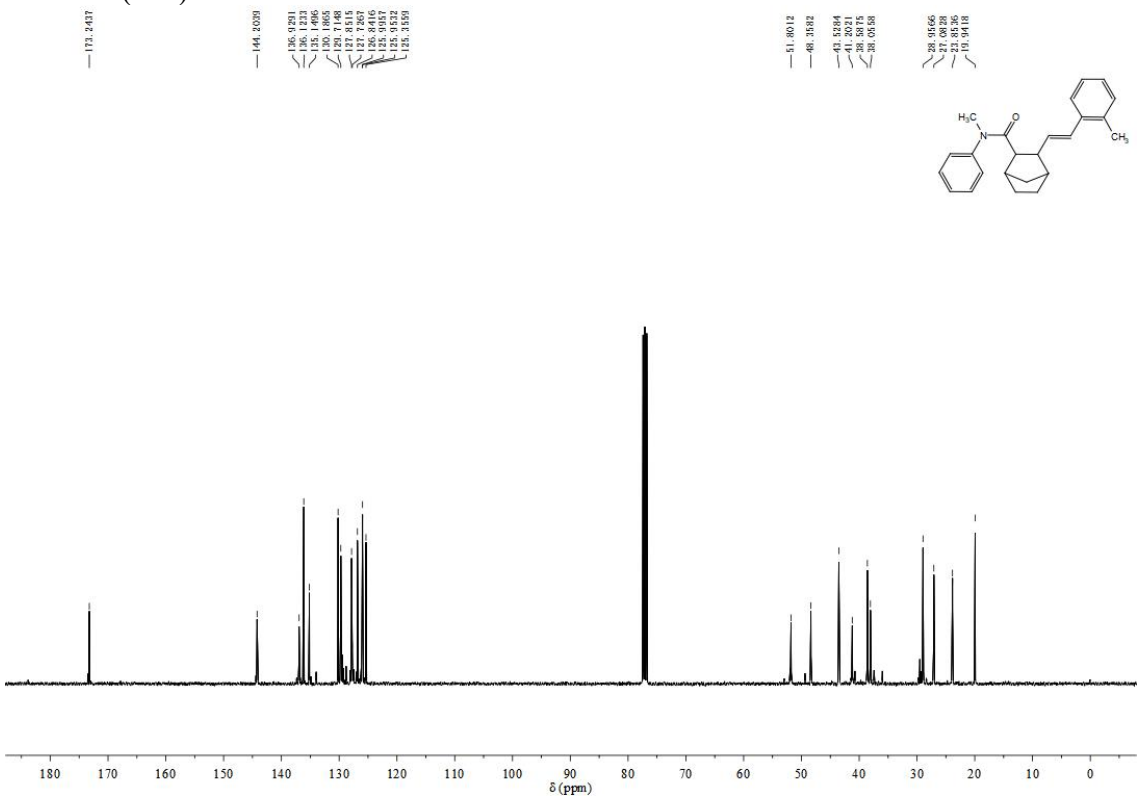
^{13}C NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**59e**)



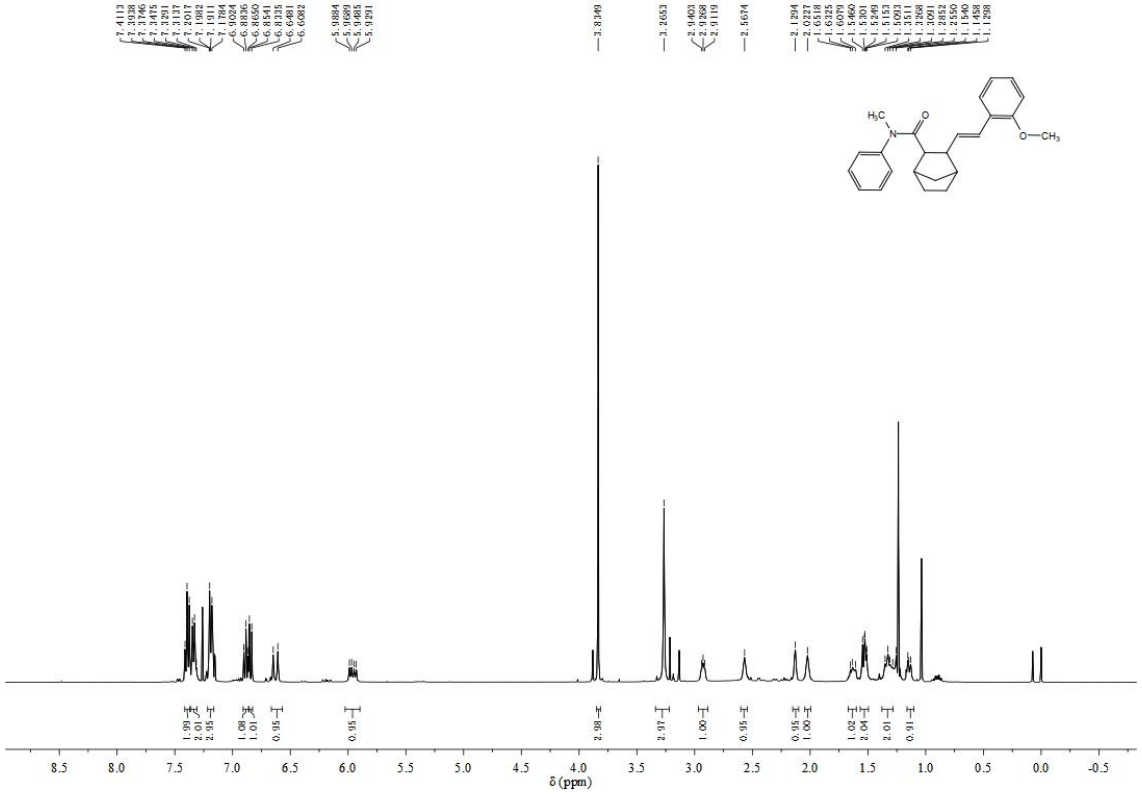
^{1}H NMR spectrum of (*E*)-*N*-methyl-3-(2-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**60e**)



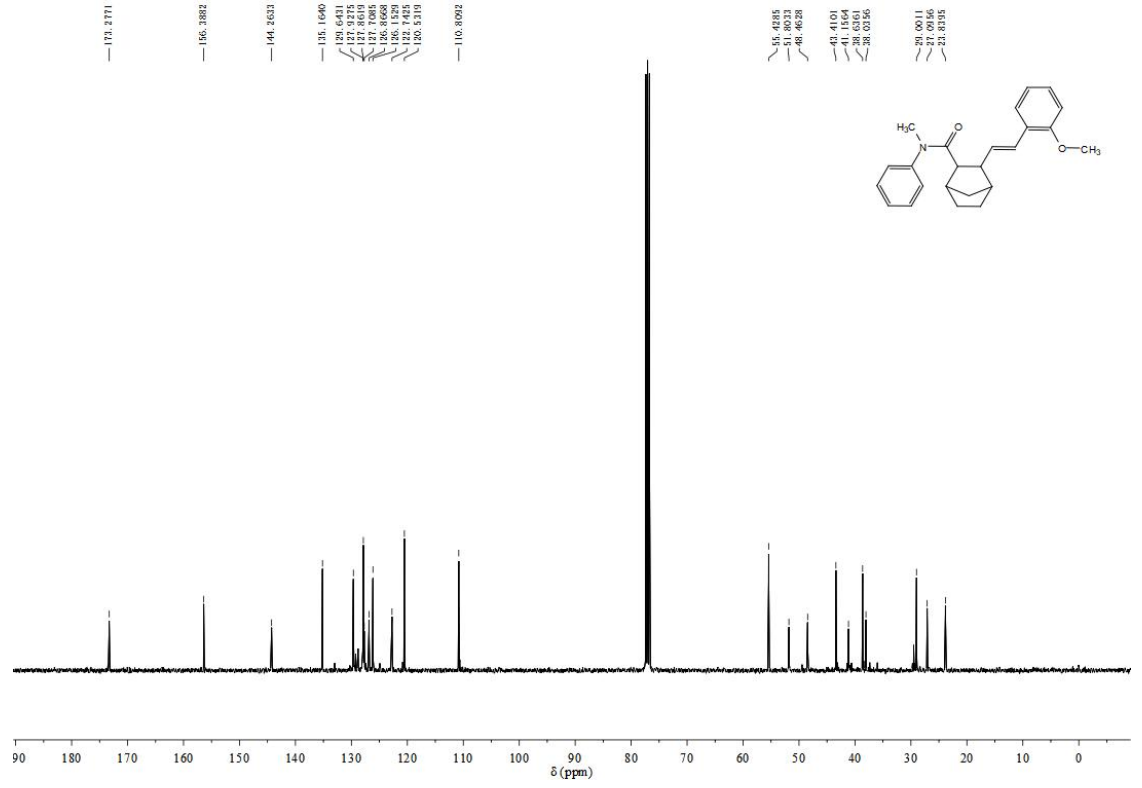
^{13}C NMR spectrum of (*E*)-*N*-methyl-3-(2-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**60e**)



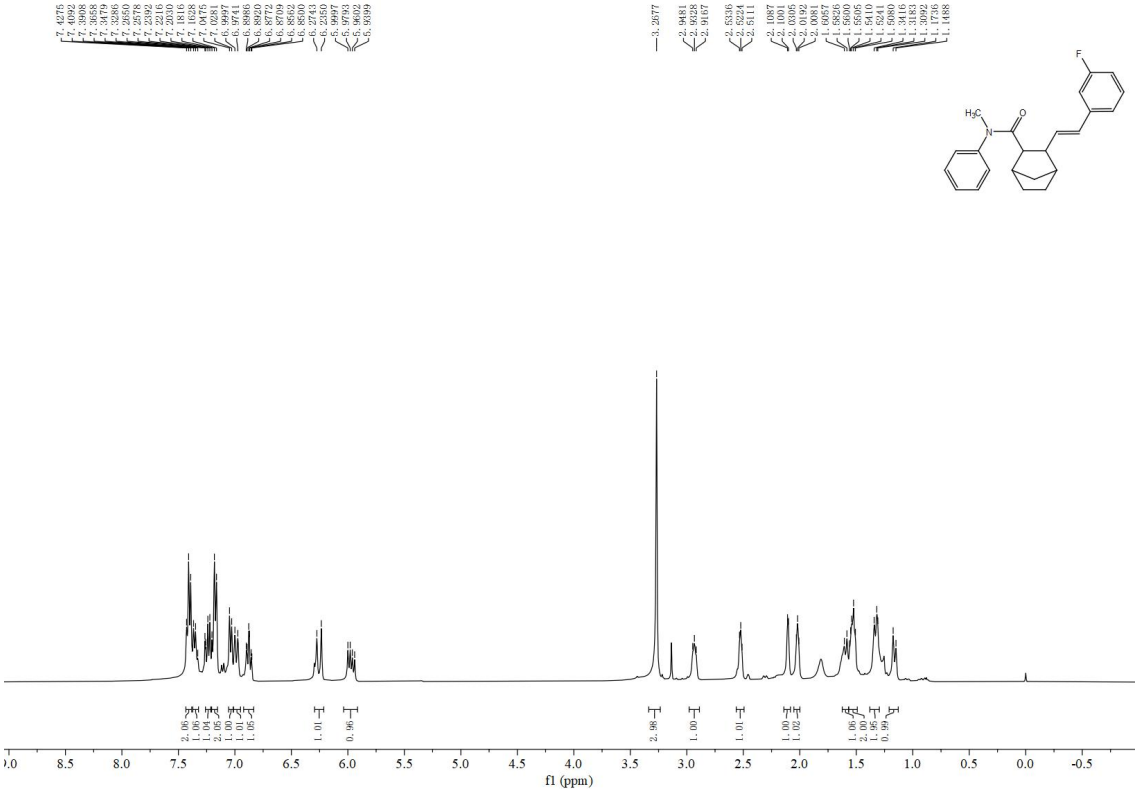
^{1}H NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**61e**)



^{13}C NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**61e**)



^{1}H NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**62e**)



^{13}C NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**62e**)