Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photo-induced two-carbon ring expansion of N-alkenyl lactams and N-alkenyl/phenyl benzoazetinones

Fayang Xie, Yi Chen, Yunshan Li, Zhiguo Wang, Jingyang Zhang and Yefeng Tang*

School of Pharmaceutical Sciences, MOE Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Tsinghua University, Beijing 100084, China.
*Email: yefengtang@tsinghua.edu.cn

Table of Contents

1. Materials and methods

Commercially available reagents were purchased from commercial sources and used as received without further purification. If no further details are given, the reaction was performed under ambient atmosphere and temperature. Analytical thin layer chromatography (TLC) was performed on silica gel-coated plates (Merck, 60 F_{254}) with the indicated solvent mixture, visualization was done using ultraviolet (UV) irradiation (λ = 254 nm) and/or staining with aqueous $KMnO_4$. Purification by column chromatography was carried out using silica gel 60 (Merck, 0.040-0.063 mm), reversed phase column chromatography was carried out using C_{18} Functional, Irregulair Silica (Screening Devices, 0.040-0.063 mm. 60Å, 12% functionalization).

^{1}H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer. TMS (δH 0.00) or the NMR solvent residual peak of $(CD_3)_2CO$ ((C_3HD_5O) δH 2.05), $CDCl_3$ (($CHCl_3$) δH 7.26), $(CD_3)_2SO$ ((C_2HD_5SO) δH 2.50), CD_3OD ((CHD_3O) δH 3.31) or D_2O ((HDO) δH 4.79) were used as the internal reference. ^{13}C NMR spectra were recorded on a Bruker Advance III 400 (100MHz) spectrometer in $(CD_3)_2CO$ (δC 29.8), $CDCl_3$ (δC 77.16), CD_3OD (δC 49.0) or $(CD_3)_2SO$ (δC 39.5) using their central resonance as the internal reference. All ^{13}C NMR spectra were proton decoupled. In ^{13}C NMR spectra the signal belonging to the carbon next to boron is broadened and as a result often becomes undetectable in the baseline. Absorbance measurements were performed at the Infinite M200 Pro plate reader (Tecan), if not stated otherwise. Lowresolution mass spectra (LRMS) were recorded on Thermo LCQ Advantage Max (Electrospray Ionization (ESI)). A Thermo Finnigan LCQ Fleet ESI ion-trap mass spectrometer, which is equipped with a Shimadzu HPLC (C18-column, 150 × 3 mm, particle size 3 μm, acetonitrile/water gradient 5-100%, 1-35 min and a flow of 0.2 mL/min) and a PDA detector, was used to separated organic compounds and record a low-resolution mass spectrum. High-resolution mass spectra (HRMS) of small molecules were recorded on a JEOL AccuTOF JMS-T100CS (ESI). Q-TOF mass spectrometry of proteins were recorded on a SYNAPTTM G2-Si HDMS (Waters). The commercially available UV lamp (model: Philips TUV 25W/G25 T8, emission wave-length range: 200-280 nm; λmax: 254 nm) was used as light resource.

2. Synthetic procedures and spectroscopic data

2.1 Irradiation system

The set-up below (UVC lamp, 254 nm, 25 W×4) has been used for the photo-induced two-carbon ring expansion of *N*-alkenyl lactams.

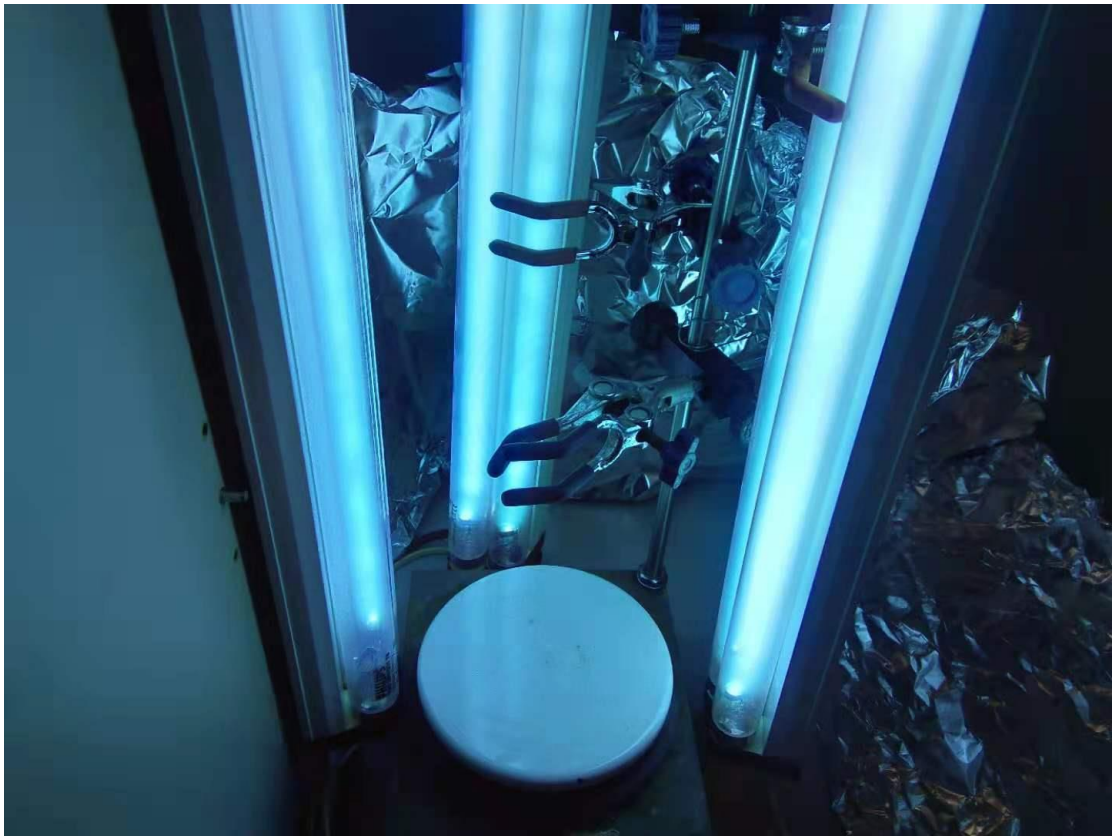


Figure S1. Photochemical Reactor Set-Up.

2.2 General procedure

General procedure A: preparation of *N*-alkenyl lactams

A modified procedure adopted from literature was used.[1] A resealable Schlenk tube was charged with CuI (5.0 mol%), K_2CO_3 (2.0 equiv) and amide (1.2 equiv), evacuated and backfilled with argon. *N*,*N*'-Dimethylethylenediamine (10 mol%) and vinyl bromide (1.0 equiv, 1 M in toluene) were added sequentially through a syringe. The Schlenk tube was sealed with a Teflon valve, immersed in a preheated oil bath. The reaction mixture was stirred at the 110 ℃ until the complete consumption of starting material was observed as indicated by GC analysis. The reaction vessel was removed from the oil bath and the resulting pale tan suspension was allowed to reach room temperature, and then it was filtered through a plug silica gel eluting with ethyl acetate. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (eluting with Petroleum ether/EtOAc) to provide the desired product. Of note, in some

cases, both (*Z*)- and (*E*)-*N*-alkenyl lactams could be identified. While both products were characterized in the current work, only the major component (*E*)-*N*-alkenyl lactams were used in the photo-induced ring-expansion reactions.

General procedure B: photo-induced ring expansion reaction of *N*-alkenyl lactams

Under the nitrogen atmosphere, a quartz tube was charged with a solution of *N*-alkenyl-lactams in anhydrous CH_3OH (or THF for substrate **1f**). Then the tube was irradiated with UVC lamps (254 nm, 25 W ×4, Philips TUV 25W/G25 T8) at 25 ℃. The progress of the reaction was monitored by TLC. After completion, the crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography (dichloromethane/methanol = 20 : 1 elution) to give the desired ring expansion product enaminone.

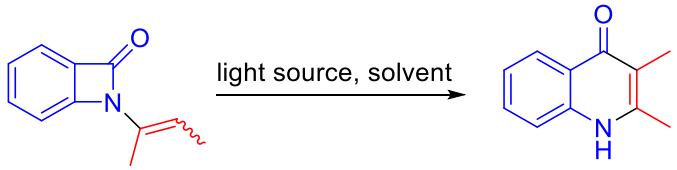
General Procedure C: photo-induced ring expansion reaction of *N*-alkenyl benzoazetinones and *N*-phenyl benzoazetinones

Under the nitrogen atmosphere, a quartz tube was charged with a solution of *N*-alkenyl-lactams in anhydrous THF and 4Å molecular sieve. Then the tube was irradiated with UVC lamps (254 nm, 25 W ×4, Philips TUV 25W/G25 T8) at 25 ℃. The progress of the reaction was monitored by TLC. After completion, the crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography (dichloromethane/methanol = 20 : 1 or ethyl acetate/petroleum ether = 2:1 elution) to give the desired ring expansion product enaminone.

General procedure D: imino ketene intermediate trapped by MeOH

Under the nitrogen atmosphere, a quartz tube was charged with a solution of *N*-alkenyl-lactams (30 mg) in anhydrous THF and MeOH (3 : 2, 1.8 mL and 1.2 mL) Then the tube was irradiated with UVC lamps (254 nm, 25 W ×4, Philips TUV 25W/G25 T8) at 25 ℃. The progress of the reaction was monitored by TLC. After completion, the crude reaction mixture was concentrated under reduced pressure and purified by preparatory TLC (ethyl acetate/petroleum ether = 2 : 1 elution).

Table S1. Optimization of reaction conditions of 5b[a,b]

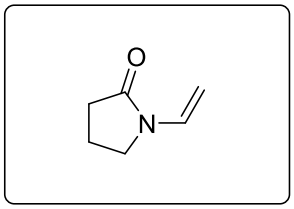


5b 6b

entry	substrate	solvent	light source	time	product: yield
1	**5b**	CH_3OH	365 nm	12 h	**6b**: 0%
2	**5b**	CH_3OH	254 nm	12 h	**6b**: 0%
3	**5b**	THF [c]	254 nm	12 h	**6b**: 0%
4	**5b**	THF [d]	254 nm	12 h	**6b**: 47%
5	**5b**	CH_3CN [c]	254 nm	12 h	**6b**: 0%
6	**5b**	CH_3CN [d]	254 nm	12 h	**6b**: 42%

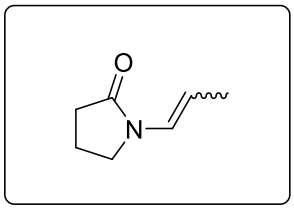
[a]Without special note, all reactions were conducted with a 0.5 mmol scale of substrates (C = 0.05 M) at 25 ℃ under nitrogen protection. [b]Isolated yield. [c]Analytical reagent. [d]Anhydrous reagent

2.3 Analysis data of *N*-alkenyl lactams



1-vinylpyrrolidin-2-one (1a):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.30 (dd, *J* = 16.7, 12.6 Hz, 2H), 3.45 – 3.36 (m, 2H), 2.37 (t, *J* = 8.2 Hz, 2H), 2.06 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 129.1, 94.1, 44.3, 31.1, 17.1. HRMS (ESI) *m/z* calcd for $C_6H_{10}NO$ $[M+H]^+$ 112.0762, found 112.0768.

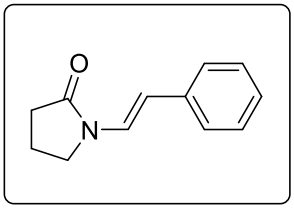


(*Z*)-1-(prop-1-en-1-yl)pyrrolidin-2-one (1b):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 – 6.30 (m, 1H), 4.97 (dq, *J* = 9.5, 7.3 Hz, 1H), 3.81 – 3.71 (m, 2H), 2.40 (t, *J* = 8.1 Hz, 2H), 2.13 – 2.00 (m, 2H), 1.74 (dd, *J* = 7.3, 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 123.7, 111.5, 48.7, 30.4, 18.8, 12.9.

(*E*)-1-(prop-1-en-1-yl)pyrrolidin-2-one (1b):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (dq, *J* = 14.4, 1.7 Hz, 1H), 4.92 – 4.77 (m, 1H), 3.42 – 3.35 (m, 2H), 2.35 (dd, *J* = 8.7, 7.6 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.62 (dd, *J* = 6.7, 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 124.3, 106.6, 45.1, 31.1, 17.3, 15.1. HRMS (ESI) *m/z* calcd for $C_7H_{12}NO$ $[M+H]^+$ 126.0919, found 126.0922.

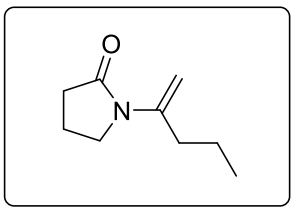


(*Z*)-1-styrylpyrrolidin-2-one (1c):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 9.9 Hz, 1H), 5.97 (d, *J* = 9.9 Hz, 1H), 3.18 (t, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.99 – 1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 136.3, 129.2, 127.9, 126.9, 123.9, 113.8, 48.1, 30.4, 18.9.

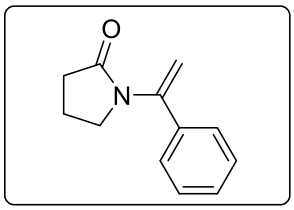
(*E*)-1-styrylpyrrolidin-2-one (1c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 14.9 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.24 (m, 2H), 7.21 – 7.13 (m, 1H), 5.88 (d, *J* = 14.8 Hz, 1H), 3.65 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 8.1 Hz, 2H), 2.21 – 2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 136.5, 128.8, 126.7, 125.7, 123.7, 111.9, 45.4, 31.4, 17.6. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1075.



1-(pent-1-en-2-yl)pyrrolidin-2-one (1d):

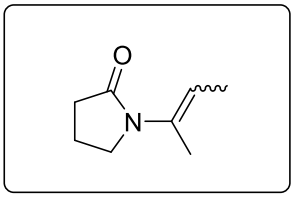
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (s, 1H), 4.53 (s, 1H), 3.56 (t, *J* = 7.0 Hz, 2H), 2.56 – 2.48 (m, 2H), 2.48 – 2.41 (m, 2H), 2.07 – 1.97 (m, 2H), 1.52 – 1.39 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 146.3, 100.7, 49.4, 35.5, 32.9, 21.3, 18.2, 13.7. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1231.



1-(1-phenylvinyl)pyrrolidin-2-one (1e):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 1H), 5.36 (s, 1H), 5.26 (s, 1H), 3.50 (t, *J* = 7.0 Hz, 1H), 2.52 (t, *J* = 8.0 Hz, 1H), 2.07 (dt, *J* = 10.5, 7.5 Hz, 1H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 174.5, 143.5, 136.1, 128.4, 126.3, 109.2, 49.4, 31.8, 18.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1075.

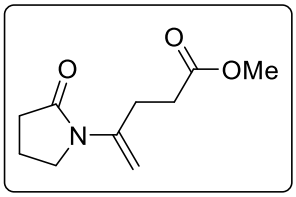


1-(but-2-en-2-yl)pyrrolidin-2-one (1g, isomer 1):

^1H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.21 (m, 1H), 3.52 – 3.43 (m, 2H), 2.37 (t, *J* = 8.1 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.89 – 1.86 (m, 3H), 1.61 (dd, *J* = 6.9, 1.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 134.0, 116.0, 49.3, 32.2, 18.3, 14.2, 12.5.

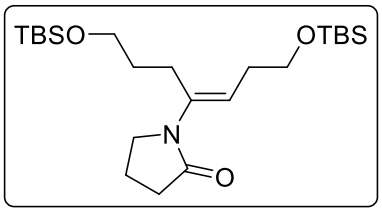
1-(but-2-en-2-yl)pyrrolidin-2-one (1g, isomer 2):

^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (qd, *J* = 6.8, 1.3 Hz, 1H), 3.35 (t, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 8.1 Hz, 2H), 1.98 (dq, *J* = 11.8, 7.4 Hz, 2H), 1.74 – 1.62 (m, 3H), 1.38 (ddd, *J* = 6.8, 3.0, 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 131.9, 121.4, 47.4, 30.9, 19.2, 18.6, 12.9. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1078.



methyl 4-(2-oxopyrrolidin-1-yl)pent-4-enoate (1f):

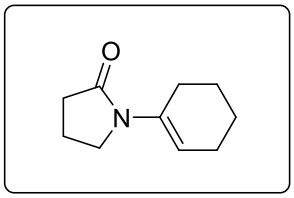
^1H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 1H), 3.64 (s, 1H), 3.55 (t, *J* = 7.1 Hz, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.47 (dt, *J* = 19.9, 7.9 Hz, 2H), 2.08 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.3, 144.9, 100.2, 51.6, 49.2, 33.1, 32.8, 28.9, 18.0. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO_3$ $[M+H]^+$ 198.1130, found 198.1133.



(*E*)-1-(2,2,3,3,13,13,14,14-octamethyl-4,12-dioxa-3,13-disilapentadec-7-en-8-yl)-pyrrolidin-2-one (1h):

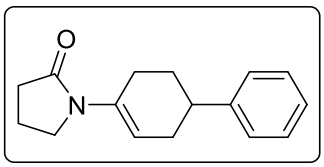
^1H NMR (400 MHz, $CDCl_3$) δ 5.26 (t, *J* = 7.3 Hz, 1H), 3.60 (dd, *J* = 14.8, 7.4 Hz, 4H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.9 Hz, 2H), 2.33 (q, *J* = 6.9 Hz, 2H), 2.02 (p, *J* = 7.4 Hz, 2H), 1.62 – 1.53 (m, 2H), 0.88 (s, 18H), 0.04 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 138.9, 118.6, 62.9, 62.6, 50.1, 32.4, 31.2, 30.9, 26.1, 24.3, 18.6, 18.5, 18.4, -5.1, -5.2. HRMS (ESI) *m/z* calcd for $C_{23}H_{48}NO_3Si_2$ $[M+H]^+$ 442.3173, found 442.3176.



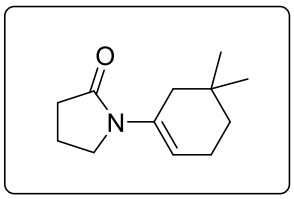
1-(cyclohex-1-en-1-yl)pyrrolidin-2-one (1i):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.32 (m, 1H), 3.49 – 3.37 (m, 2H), 2.38 – 2.27 (m, 4H), 2.07 – 1.97 (m, 2H), 1.92 (dq, *J* = 15.3, 7.5 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 136.3, 115.4, 48.7, 32.4, 26.3, 24.2, 22.5, 21.7, 18.1. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1217.



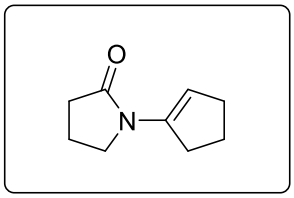
1-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)pyrrolidin-2-one (1j):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 1H), 7.25 – 7.17 (m, 1H), 5.55 (ddt, *J* = 5.5, 2.9, 1.5 Hz, 1H), 3.57 (qt, *J* = 9.7, 7.0 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.68 – 2.57 (m, 1H), 2.49 – 2.41 (m, 1H), 2.41 – 2.36 (m, 1H), 2.34 – 2.23 (m, 1H), 2.09 – 1.98 (m, 1H), 1.91 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 146.4, 136.4, 128.4, 126.8, 126.2, 114.6, 48.8, 39.5, 32.6, 32.6, 29.7, 27.1, 18.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}NO$ $[M+H]^+$ 242.1545, found 242.1539.



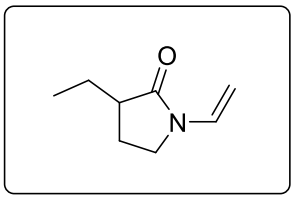
1-(5,5-dimethylcyclohex-1-en-1-yl)pyrrolidin-2-one (1k):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (t, *J* = 3.7 Hz, 1H), 3.52 (t, *J* = 7.0 Hz, 2H), 2.42 (t, *J* = 8.1 Hz, 2H), 2.19 (d, *J* = 1.2 Hz, 2H), 2.13 (tt, *J* = 6.2, 3.1 Hz, 2H), 2.05 – 1.96 (m, 2H), 1.32 (t, *J* = 6.4 Hz, 2H), 0.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 135.6, 114.5, 49.0, 40.3, 34.6, 32.7, 29.5, 28.2, 22.2, 18.4. $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1546.



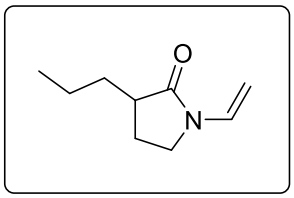
1-(cyclopent-1-en-1-yl)pyrrolidin-2-one (1l):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 – 5.12 (m, 1H), 3.61 – 3.52 (m, 2H), 2.86 (tdd, *J* = 6.7, 4.4, 2.1 Hz, 2H), 2.43 (m, 2H), 2.34 – 2.26 (m, 2H), 2.09 – 1.97 (m, 2H), 1.92 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.5, 110.0, 48.7, 32.4, 32.0, 29.6, 22.6, 18.0. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1077.



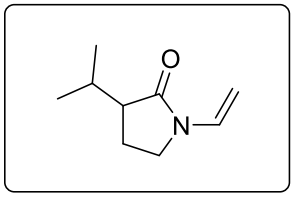
3-propyl-1-vinylpyrrolidin-2-one (1m):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.35 (dd, *J* = 14.0, 12.8 Hz, 2H), 3.44 (td, *J* = 9.6, 3.4 Hz, 1H), 3.33 (dt, *J* = 10.1, 7.9 Hz, 1H), 2.41 (qd, *J* = 8.8, 4.5 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.90 – 1.78 (m, 1H), 1.70 (ddd, *J* = 16.9, 12.8, 8.7 Hz, 1H), 1.46 – 1.33 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 129.5, 94.1, 43.8, 42.9, 24.1, 23.8, 11.4. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1075.



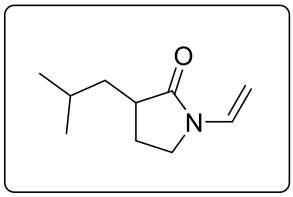
3-propyl-1-vinylpyrrolidin-2-one (1n):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.37 (dd, *J* = 15.2, 12.6 Hz, 2H), 3.46 (td, *J* = 9.6, 3.4 Hz, 1H), 3.35 (dt, *J* = 10.1, 7.9 Hz, 1H), 2.48 (qd, *J* = 8.8, 4.6 Hz, 1H), 2.30 – 2.20 (m, 1H), 1.88 – 1.77 (m, 1H), 1.71 (ddd, *J* = 16.8, 12.8, 8.8 Hz, 1H), 1.44 – 1.28 (m, 3H), 0.94 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 129.6, 94.0, 42.9, 42.3, 33.4, 24.5, 20.4, 14.0. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1232.



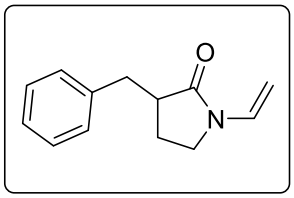
3-isopropyl-1-vinylpyrrolidin-2-one (1o):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.33 (dd, *J* = 15.7, 12.5 Hz, 2H), 3.40 (td, *J* = 9.7, 3.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 2.48 – 2.40 (m, 1H), 2.16 (dtd, *J* = 13.7, 6.9, 4.7 Hz, 1H), 2.10 – 1.99 (m, 1H), 1.81 (ddd, *J* = 16.4, 13.0, 8.6 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 129.4, 93.9, 48.2, 43.0, 28.4, 20.5, 19.3, 17.7. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1235.



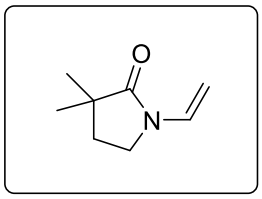
3-isobutyl-1-vinylpyrrolidin-2-one (1p):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.41 (dd, *J* = 15.5, 12.5 Hz, 2H), 3.51 (td, *J* = 9.6, 3.1 Hz, 1H), 3.38 (dt, *J* = 10.1, 8.1 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.37 – 2.24 (m, 1H), 1.84 – 1.65 (m, 3H), 1.32 – 1.21 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 129.7, 94.0, 42.9, 40.7, 40.4, 26.1, 25.1, 23.5, 21.5. HRMS (ESI) *m/z* calcd for $C_{10}H_{18}NO$ $[M+H]^+$ 168.1388, found 168.1389.



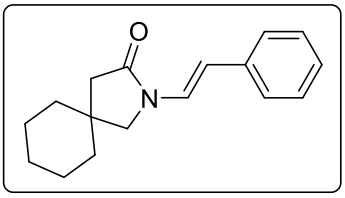
3-benzyl-1-vinylpyrrolidin-2-one (1q):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 7.10 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.39 (dd, *J* = 28.8, 12.5 Hz, 2H), 3.32 – 3.26 (m, 2H), 3.23 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.81 (ddd, *J* = 17.9, 8.8, 4.1 Hz, 1H), 2.68 (dd, *J* = 13.7, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 139.0, 129.4, 128.9, 128.4, 126.4, 94.3, 44.1, 42.7, 36.8, 23.7. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1232, found 202.1234.



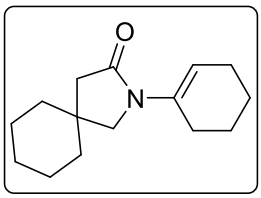
3,3-dimethyl-1-vinylpyrrolidin-2-one (1r):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.41 – 4.32 (m, 2H), 3.40 – 3.35 (m, 2H), 1.92 – 1.87 (m, 2H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 129.9, 94.0, 41.2, 33.6, 24.6. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1073.



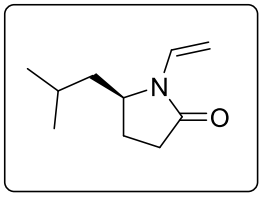
(*E*)-2-styryl-2-azaspiro[4.5]decan-3-one (1s):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 14.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 5.86 (d, *J* = 14.8 Hz, 1H), 3.39 (s, 2H), 2.40 (s, 2H), 1.62 – 1.39 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 136.5, 128.8, 126.6, 125.7, 123.8, 111.6, 56.8, 44.5, 37.2, 36.2, 25.6, 22.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1701, found 256.1697.



2-(cyclohex-1-en-1-yl)-2-azaspiro[4.5]decan-3-one (1t):

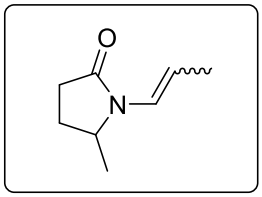
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 – 5.38 (m, 1H), 3.26 (s, 2H), 2.45 – 2.35 (m, 2H), 2.28 (s, 2H), 2.16 – 2.05 (m, 2H), 1.71 – 1.62 (m, 2H), 1.60 – 1.52 (m, 2H), 1.47 (s, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 136.7, 115.6, 60.2, 45.4, 36.9, 35.9, 26.6, 25.8, 24.4, 23.0, 22.8, 22.0. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1861.



5-isobutyl-1-vinylpyrrolidin-2-one (1u):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 16.3, 9.4 Hz, 1H), 4.44 – 4.29 (m, 2H), 3.92 – 3.81 (m, 1H), 2.48 (ddd, *J* = 17.4, 11.1, 9.1 Hz, 1H), 2.31 (ddd, *J* = 17.4, 9.6, 2.0 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.81 (ddt, *J* = 12.7, 9.1, 1.7 Hz, 1H), 1.67 – 1.54 (m, 2H), 1.26 – 1.16 (m, 1H), 0.97 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 128.0, 94.5, 54.7, 39.5, 29.8, 25.4, 23.9, 23.6, 21.5. HRMS (ESI) *m/z* calcd for $C_{10}H_{18}NO$

$[M+H]^+$ 168.1388, found 168.1374. Optical Rotation: $[\alpha]_D^{20}$ = +88.1 (c = 0.03, CH_2Cl_2)

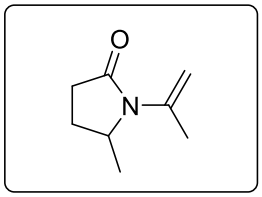


(*Z*)-5-methyl-1-(prop-1-en-1-yl)pyrrolidin-2-one (1v):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 8.8, 1.6 Hz, 1H), 5.26 (dq, *J* = 8.7, 7.1 Hz, 1H), 3.90 (dqd, *J* = 12.6, 6.3, 5.0 Hz, 1H), 2.45 – 2.29 (m, 2H), 2.19 (ddt, *J* = 12.7, 9.4, 7.3 Hz, 1H), 1.66 – 1.54 (m, 4H), 1.12 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 122.6, 119.3, 55.0, 29.9, 26.6, 20.0, 13.2.

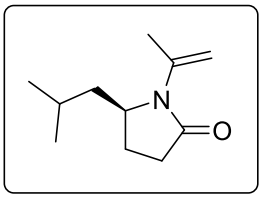
(*E*)-5-methyl-1-(prop-1-en-1-yl)pyrrolidin-2-one (1v):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (dd, *J* = 14.7, 1.6 Hz, 1H), 4.97 (dq, *J* = 13.3, 6.7 Hz, 1H), 4.01 – 3.90 (m, 1H), 2.54 – 2.43 (m, 1H), 2.31 (ddd, *J* = 17.2, 9.7, 2.5 Hz, 1H), 2.15 (ddt, *J* = 12.6, 9.7, 7.7 Hz, 1H), 1.75 – 1.61 (m, 4H), 1.18 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 123.0, 107.5, 52.4, 29.8, 26.1, 18.3, 15.4. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1079.



5-methyl-1-(prop-1-en-2-yl)pyrrolidin-2-one (1w):

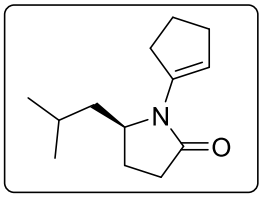
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (dd, *J* = 2.5, 1.2 Hz, 1H), 4.66 (s, 1H), 3.88 (dqd, *J* = 7.4, 6.2, 5.0 Hz, 1H), 2.40 (ddd, *J* = 16.6, 9.4, 7.1 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.14 (ddt, *J* = 12.6, 9.5, 7.3 Hz, 1H), 1.92 (d, *J* = 0.7 Hz, 3H), 1.54 (dddd, *J* = 12.6, 9.4, 6.1, 4.9 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 139.8, 106.7, 54.6, 31.1, 26.4, 20.7, 19.6. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1079.



5-isobutyl-1-(prop-1-en-2-yl)pyrrolidin-2-one (1x):

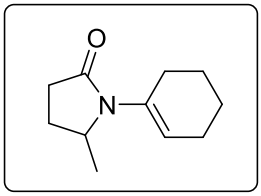
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (d, *J* = 1.4 Hz, 1H), 4.72 (s, 1H), 3.83 (dddd, *J* = 10.5, 7.4, 4.5, 2.8 Hz, 1H), 2.44 (ddd, *J* = 17.0, 9.4, 7.5 Hz, 1H), 2.31 (ddd, *J* = 17.1,

9.6, 5.8 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.95 (d, *J* = 1.2 Hz, 3H), 1.71 – 1.47 (m, 3H), 1.26 – 1.15 (m, 1H), 0.87 (dd, *J* = 9.8, 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 139.8, 106.9, 57.5, 42.2, 31.1, 24.9, 24.3, 24.0, 21.4, 20.9. HRMS (ESI) *m/z* calcd for $C_{11}H_{20}NO$ $[M+H]^+$ 182.1545, found 182.1541. Optical Rotation: $[\alpha]_D^{20}$ = +21.3 (c = 0.02, CH_2Cl_2)



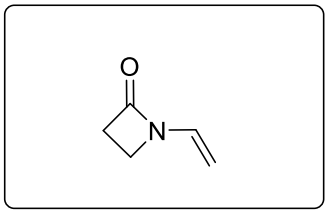
1-(cyclopent-1-en-1-yl)-5-isobutylpyrrolidin-2-one (1y):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 1H), 3.87 (dd, *J* = 10.5, 8.5 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.70 – 2.59 (m, 1H), 2.53 (dd, *J* = 18.1, 8.7 Hz, 1H), 2.46 – 2.28 (m, 3H), 2.21 – 2.08 (m, 1H), 1.95 – 1.85 (m, 2H), 1.79 (dd, *J* = 12.0, 9.8 Hz, 1H), 1.73 – 1.60 (m, 1H), 1.56 (t, *J* = 11.0 Hz, 1H), 1.38 – 1.28 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 138.5, 113.2, 58.2, 41.3, 32.2, 30.7, 30.0, 25.3, 23.9, 23.8, 22.2, 21.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1701, found 208.1699. Optical Rotation: $[\alpha]_D^{20}$ = +36.2. (c = 0.04, CH_2Cl_2)



1-(cyclohex-1-en-1-yl)-5-methylpyrrolidin-2-one (1z):

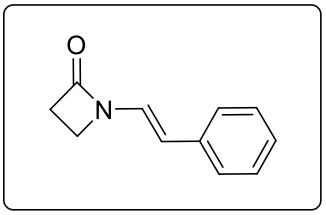
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (t, *J* = 3.7 Hz, 1H), 3.89 – 3.73 (m, 1H), 2.45 – 2.24 (m, 3H), 2.22 – 2.01 (m, 3H), 1.95 – 1.79 (m, 1H), 1.72 – 1.61 (m, 2H), 1.61 – 1.49 (m, 3H), 1.12 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 134.1, 123.6, 54.8, 31.1, 27.0, 26.9, 24.5, 22.6, 21.8, 20.3. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1388, found 180.1380.



1-vinylazetidin-2-one (2a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (dd, *J* = 15.7, 8.9 Hz, 1H), 4.39 (dd, *J* = 28.9, 12.3 Hz, 2H), 3.39 (t, *J* = 4.5 Hz, 2H), 2.98 (t, *J* = 4.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 164.2, 127.5, 93.7, 37.7, 36.1. HRMS (ESI) *m/z* calcd for C_5H_8NO $[M+H]^+$ 98.0606, found 98.0609.

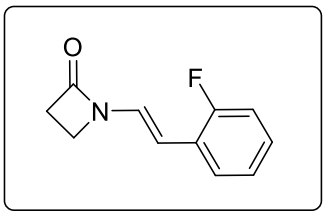


(*Z*)-1-styrylazetidin-2-one (2b)

^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 3H), 6.63 (d, *J* = 9.7 Hz, 1H), 5.84 (d, *J* = 9.7 Hz, 1H), 3.13 (t, *J* = 4.7 Hz, 2H), 2.96 (t, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 135.6, 129.2, 128.0, 127.1, 121.2, 111.2, 42.1, 37.5. HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0919, found 174.0913.

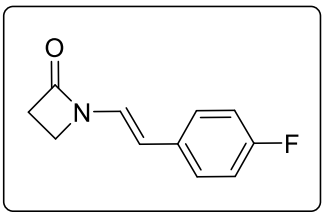
(*E*)-1-styrylazetidin-2-one (2b)

^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.4 Hz, 4H), 7.24 (d, *J* = 14.8 Hz, 1H), 7.19 (dt, *J* = 8.6, 4.2 Hz, 1H), 5.94 (d, *J* = 14.6 Hz, 1H), 3.53 (t, *J* = 4.6 Hz, 2H), 3.07 (t, *J* = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 135.7, 128.8, 126.9, 125.6, 121.4, 111.2, 38.5, 36.4. HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0919, found 174.0916.



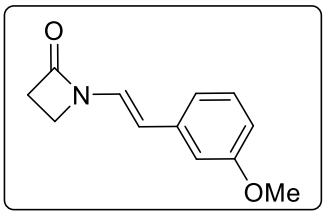
(*E*)-1-(2-fluorostyryl)azetidin-2-one (2c):

^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.14 (dd, *J* = 13.1, 7.2 Hz, 1H), 7.09 – 6.97 (m, 2H), 6.00 (d, *J* = 14.7 Hz, 1H), 3.54 (t, *J* = 4.1 Hz, 2H), 3.08 (t, *J* = 3.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δδ ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 159.9 (d, *J* = 248.3 Hz), 128.0 (d, *J* = 8.3 Hz), 126.7 (d, *J* = 3.8 Hz), 124.4 (d, *J* = 3.4 Hz), 123.6 (d, *J* = 12.5 Hz), 123.3 (d, *J* = 6.5 Hz), 115.8 (d, *J* = 22.0 Hz), 103.8 (d, *J* = 3.2 Hz), 38.5, 36.4. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NOF$ $[M+H]^+$ 192.0825, found 192.0805.



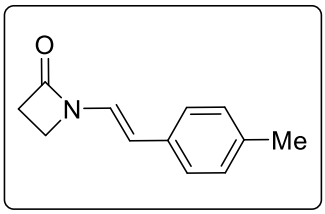
(*E*)-1-(4-fluorostyryl)azetidin-2-one (2d):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 14.6 Hz, 1H), 7.00 (t, *J* = 8.1 Hz, 2H), 5.93 (d, *J* = 14.6 Hz, 1H), 3.55 (s, 2H), 3.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.9 (d, *J* = 246.2 Hz), 131.8 (d, *J* = 3.2 Hz), 127.0 (d, *J* = 7.9 Hz), 121.2, 115.8 (d, *J* = 21.7 Hz), 110.2, 38.6, 36.5. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NOF$ $[M+H]^+$ 192.0825, found 192.0806.



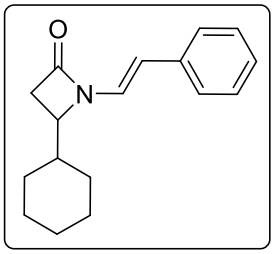
(*E*)-1-(3-methoxystyryl)azetidin-2-one (2e):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 19.9, 11.3 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.91 (d, *J* = 14.6 Hz, 1H), 3.80 (s, 3H), 3.54 (s, 2H), 3.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.33, 160.0, 137.2, 129.8, 121.6, 118.4, 112.8, 111.1, 110.7, 55.3, 38.6, 36.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1025, found 204.1022.



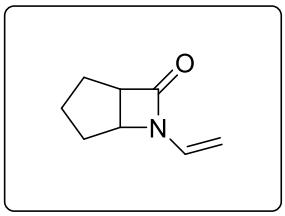
(*E*)-1-(4-methylstyryl)azetidin-2-one (2f):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 7.10 (d, *J* = 7.4 Hz, 2H), 5.93 (d, *J* = 14.6 Hz, 1H), 3.54 (s, 2H), 3.07 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 136.8, 132.8, 129.6, 125.6, 120.7, 111.3, 38.5, 36.4, 21.3. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1073.



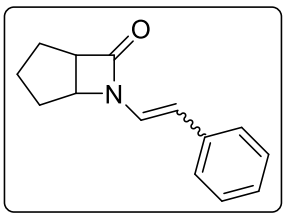
(*E*)-4-cyclohexyl-1-styrylazetidin-2-one (2g):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 4H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.07 (d, *J* = 14.8 Hz, 1H), 6.19 (d, *J* = 14.8 Hz, 1H), 3.86 (s, 1H), 2.97 (dd, *J* = 15.3, 5.3 Hz, 1H), 2.80 (d, *J* = 15.3 Hz, 1H), 1.94 (t, *J* = 10.4 Hz, 1H), 1.84 – 1.58 (m, 5H), 1.40 – 1.12 (m, 3H), 1.02 (dd, *J* = 24.4, 12.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 136.0, 128.7, 126.8, 125.4, 121.6, 112.6, 56.7, 38.8, 38.4, 29.4, 26.3, 26.0, 25.6, 25.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1701, found 256.1699.



6-vinyl-6-azabicyclo[3.2.0]heptan-7-one (2h):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 16.0, 9.0 Hz, 1H), 4.50 (dd, *J* = 16.0, 0.4 Hz, 1H), 4.40 – 4.32 (m, 1H), 4.22 (t, *J* = 4.4 Hz, 1H), 3.51 (dd, *J* = 8.0, 3.9 Hz, 1H), 2.16 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.04 (dd, *J* = 13.1, 6.1 Hz, 1H), 1.87 (dt, *J* = 13.0, 6.7 Hz, 1H), 1.66 – 1.52 (m, 1H), 1.49 – 1.39 (m, 1H), 1.37 – 1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 126.0, 94.3, 57.0, 54.6, 26.5, 24.8, 22.8. HRMS (ESI) *m/z* calcd for $C_8H_{12}NO$ $[M+H]^+$ 138.0919, found 138.0918.



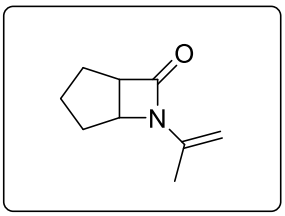
(*Z*)-6-styryl-6-azabicyclo[3.2.0]heptan-7-one (2j)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.22 (dd, *J* = 10.2, 4.3 Hz, 3H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.83 (d, *J* = 9.6 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.48 (dt, *J* = 12.4, 6.2 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.72 – 1.60 (m, 1H), 1.49 – 1.31 (m, 3H), 0.89 – 0.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.9, 129.1, 128.0, 127.0, 119.2,

112.3, 60.6, 55.0, 27.1, 26.3, 22.5.

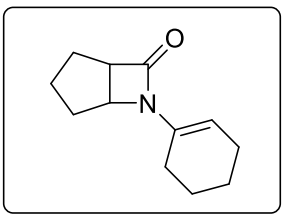
(*E*)-6-styryl-6-azabicyclo[3.2.0]heptan-7-one (2j)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 4H), 7.19 – 7.13 (m, 1H), 7.09 (d, *J* = 14.8 Hz, 1H), 5.99 (d, *J* = 14.8 Hz, 1H), 4.29 (t, *J* = 4.3 Hz, 1H), 3.55 (dd, *J* = 7.9, 3.9 Hz, 1H), 2.21 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.06 (dd, *J* = 13.1, 6.1 Hz, 1H), 1.87 (dt, *J* = 13.1, 6.7 Hz, 1H), 1.67 – 1.54 (m, 1H), 1.50 – 1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 135.8, 128.7, 126.7, 125.4, 119.8, 111.4, 57.6, 54.8, 26.8, 24.8, 22.8. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1075, found 214.1077.



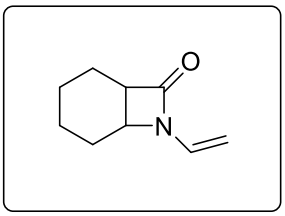
6-(prop-1-en-2-yl)-6-azabicyclo[3.2.0]heptan-7-one: (2k)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 1H), 4.09 (t, *J* = 4.4 Hz, 1H), 4.04 (d, *J* = 0.8 Hz, 1H), 3.37 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.08 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.03 (s, 3H), 1.97 (dd, *J* = 13.1, 6.3 Hz, 1H), 1.79 (dt, *J* = 13.2, 6.8 Hz, 1H), 1.55 (qt, *J* = 12.6, 6.2 Hz, 1H), 1.42 – 1.31 (m, 1H), 1.30 – 1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 139.1, 93.2, 56.8, 53.6, 26.9, 24.7, 22.7, 19.2. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1059.



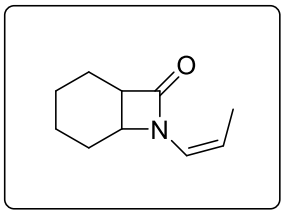
6-(cyclohex-1-en-1-yl)-6-azabicyclo[3.2.0]heptan-7-one (2l)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 – 5.11 (m, 1H), 4.11 (t, *J* = 4.4 Hz, 1H), 3.38 (dd, *J* = 8.0, 3.9 Hz, 1H), 2.55 (dtt, *J* = 16.5, 6.2, 2.0 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.12 – 1.99 (m, 4H), 1.83 (dt, *J* = 13.3, 6.8 Hz, 1H), 1.71 – 1.50 (m, 5H), 1.46 – 1.35 (m, 1H), 1.33 – 1.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 134.4, 106.8, 56.4, 53.2, 27.4, 25.7, 24.8, 23.6, 22.9, 22.10, 22.1. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1386.



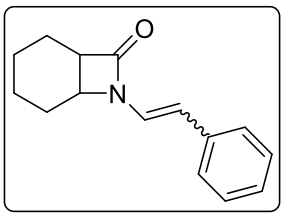
7-vinyl-7-azabicyclo[4.2.0]octan-8-one (2m)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.44 (d, *J* = 16.1 Hz, 1H), 4.33 (d, *J* = 9.1 Hz, 1H), 3.98 (dt, *J* = 5.7, 4.1 Hz, 1H), 3.24 (td, *J* = 6.2, 3.8 Hz, 1H), 1.94 (dtd, *J* = 8.8, 5.2, 2.7 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.80 – 1.62 (m, 2H), 1.60 – 1.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 126.6, 94.3, 50.2, 47.1, 22.5, 19.4, 18.7, 16.6. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1077.



(*Z*)-7-(prop-1-en-1-yl)-7-azabicyclo[4.2.0]octan-8-one (2n)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (dd, *J* = 9.2, 1.6 Hz, 1H), 4.67 (dq, *J* = 9.1, 7.2 Hz, 1H), 3.99 (dt, *J* = 5.5, 4.0 Hz, 1H), 3.13 (td, *J* = 6.2, 3.7 Hz, 1H), 1.75 – 1.63 (m, 3H), 1.55 (dd, *J* = 7.2, 1.7 Hz, 3H), 1.50 (dd, *J* = 7.9, 6.2 Hz, 1H), 1.46 – 1.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 119.7, 109.7, 52.5, 46.9, 23.8, 19.2, 18.4, 16.6, 12.6. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1234

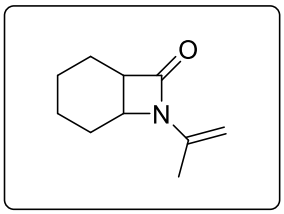


(*Z*)-7-styryl-7-azabicyclo[4.2.0]octan-8-one (2o)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.17 (m, 3H), 6.57 (d, *J* = 9.6 Hz, 1H), 5.83 (d, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 10.1, 4.3 Hz, 1H), 3.30 (td, *J* = 6.3, 3.6 Hz, 1H), 1.87 (ddt, *J* = 10.2, 8.5, 4.3 Hz, 1H), 1.64 – 1.38 (m, 3H), 1.36 – 1.16 (m, 2H), 1.04 (dt, *J* = 9.9, 3.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 136.1, 128.8, 128.0, 127.0, 119.9, 111.9, 53.0, 47.2, 22.9, 19.5, 18.8, 16.8.

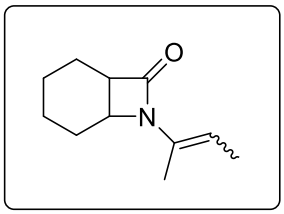
(*E*)-7-styryl-7-azabicyclo[4.2.0]octan-8-one (2o)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.5 Hz, 4H), 7.21 – 7.13 (m, 2H), 5.99 (d, *J* = 14.8 Hz, 1H), 4.13 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.35 (td, *J* = 6.2, 3.9 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.90 (dqd, *J* = 24.5, 9.8, 5.1 Hz, 2H), 1.79 – 1.69 (m, 1H), 1.67 – 1.44 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 136.0, 128.8, 126.8, 125.5, 120.5, 111.6, 50.9, 47.5, 22.8, 19.6, 18.7, 16.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1389. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1391.



7-(prop-1-en-2-yl)-7-azabicyclo[4.2.0]octan-8-one (2p)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 1H), 4.08 (d, *J* = 1.2 Hz, 1H), 3.91 (dt, *J* = 5.7, 4.3 Hz, 1H), 3.16 (td, *J* = 6.2, 4.0 Hz, 1H), 2.08 (d, *J* = 0.6 Hz, 3H), 1.94 – 1.81 (m, 2H), 1.73 (m, 1H), 1.68 – 1.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 139.6, 93.4, 50.0, 46.3, 23.0, 19.6, 19.5, 18.9. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1075. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1226.

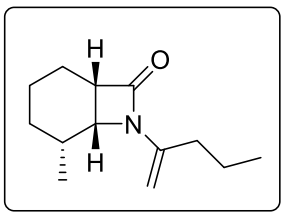


7-(but-2-en-2-yl)-7-azabicyclo[4.2.0]octan-8-one (2q, isomer 1)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (qd, *J* = 6.9, 0.9 Hz, 1H), 3.89 (dd, *J* = 9.8, 4.3 Hz, 1H), 3.10 (dt, *J* = 10.1, 5.0 Hz, 1H), 1.99 (s, 3H), 1.84 (tt, *J* = 7.5, 5.2 Hz, 2H), 1.76 (s, 1H), 1.75 – 1.31 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 132.6, 105.0, 49.8, 45.6, 23.2, 19.6, 18.9, 17.1, 13.4, 11.4.

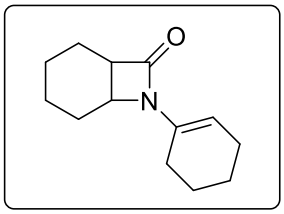
7-(but-2-en-2-yl)-7-azabicyclo[4.2.0]octan-8-one (2q, isomer 2)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (qd, *J* = 7.0, 1.2 Hz, 1H), 4.05 – 3.98 (m, 1H), 3.16 (td, *J* = 6.0, 4.0 Hz, 1H), 1.90 – 1.79 (m, 4H), 1.78 – 1.58 (m, 7H), 1.54 – 1.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 129.6, 115.4, 50.9, 45.6, 23.6, 20.0, 19.7, 19.0, 17.2, 13.5. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1388, found 180.1386.



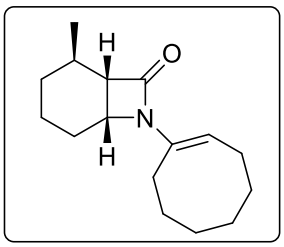
5-methyl-7-(pent-1-en-2-yl)-7-azabicyclo[4.2.0]octan-8-one (2r):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 1H), 4.31 (s, 1H), 3.99 (dd, *J* = 6.0, 2.2 Hz, 1H), 3.25 – 3.16 (m, 1H), 2.76 – 2.64 (m, 1H), 2.21 – 2.11 (m, 1H), 2.05 – 1.89 (m, 1H), 1.87 – 1.78 (m, 1H), 1.72 – 1.35 (m, 7H), 1.05 (d, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 145.2, 96.7, 55.1, 47.6, 35.6, 30.8, 24.1, 21.1, 20.8, 18.7, 17.7, 13.7. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1701, found 208.1697.



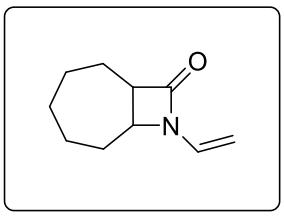
7-(cyclohex-1-en-1-yl)-7-azabicyclo[4.2.0]octan-8-one (2s)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 – 5.07 (m, 1H), 3.88 (dt, *J* = 5.6, 4.2 Hz, 1H), 3.11 (dt, *J* = 10.1, 5.0 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.40 – 2.29 (m, 1H), 2.10 – 1.93 (m, 2H), 1.90 – 1.80 (m, 2H), 1.72 (m, 1H), 1.67 – 1.46 (m, 8H), 1.44 – 1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 134.8, 107.0, 49.5, 45.8, 25.7, 23.6, 23.4, 22.2, 22.1, 19.6, 18.9, 17.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1545, found 206.1539.



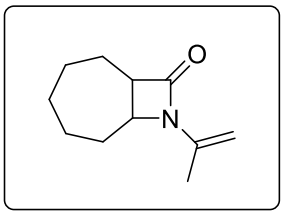
7-((E)-cyclooct-1-en-1-yl)-2-methyl-7-azabicyclo[4.2.0]octan-8-one (2t):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (t, *J* = 8.4 Hz, 1H), 3.85 (q, *J* = 5.6 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.51 (ddd, *J* = 13.7, 9.1, 4.3 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.12 – 1.98 (m, 3H), 1.87 – 1.37 (m, 16H), 1.10 – 0.95 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 137.0, 109.7, 52.3, 50.0, 30.7, 29.4, 28.4, 27.2, 26.7, 25.9, 25.2, 25.0, 23.9, 22.2, 17.6. $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2012.



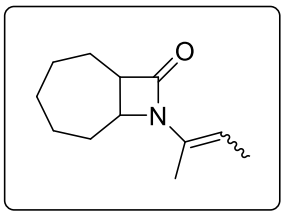
8-vinyl-8-azabicyclo[5.2.0]nonan-9-one (2u)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.45 (d, *J* = 16.1 Hz, 1H), 4.33 (d, *J* = 9.2 Hz, 1H), 3.96 (d, *J* = 3.1 Hz, 1H), 3.34 (dd, *J* = 13.2, 6.3 Hz, 1H), 2.15 – 1.25 (m, 10H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 126.9, 94.6, 56.6, 54.2, 31.4, 28.8, 27.8, 25.3, 24.6. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1232.



8-(prop-1-en-2-yl)-8-azabicyclo[5.2.0]nonan-9-one (2v)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 1H), 4.09 (d, *J* = 1.1 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.25 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.08 (s, 3H), 2.03 – 1.23 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 139.8, 93.8, 56.2, 53.2, 31.3, 28.6, 27.8, 25.2, 24.6, 19.7. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1393, found 180.1388.

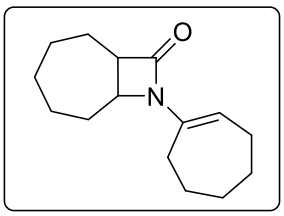


8-(but-2-en-2-yl)-8-azabicyclo[5.2.0]nonan-9-one (2w, isomer 1)：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (dt, *J* = 13.2, 6.6 Hz, 1H), 3.92 – 3.81 (m, 1H), 3.18 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.98 (s, 3H), 1.83 – 1.16 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 132.6, 105.3, 55.9, 52.5, 31.3, 28.8, 27.7, 25.2, 24.5, 13.5, 11.4.

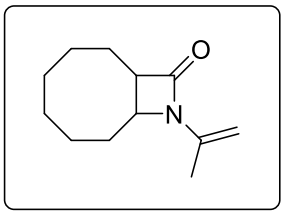
8-(but-2-en-2-yl)-8-azabicyclo[5.2.0]nonan-9-one (2w, isomer 2)：：

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (qd, *J* = 6.8, 1.1 Hz, 1H), 3.99 – 3.86 (m, 1H), 3.19 (dd, *J* = 13.6, 6.0 Hz, 1H), 1.83 – 1.20 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 129.3, 115.8, 56.8, 52.8, 31.4, 30.2, 27.8, 25.5, 24.5, 19.5, 13.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1552.



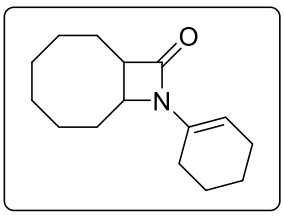
8-(cyclohept-1-en-1-yl)-8-azabicyclo[5.2.0]nonan-9-one (2x):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (t, *J* = 6.8 Hz, 1H), 3.92 – 3.78 (m, 1H), 3.18 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.64 – 2.55 (m, 1H), 2.11 – 2.04 (m, 2H), 1.84 – 1.20 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 140.8, 113.8, 56.1, 52.5, 32.0, 31.4, 29.1, 28.7, 27.8, 27.3, 26.3, 25.9, 25.3, 24.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1857.



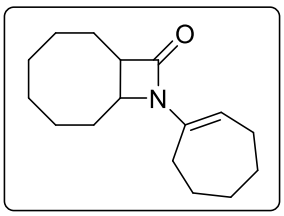
9-(prop-1-en-2-yl)-9-azabicyclo[6.2.0]decan-10-one (2y):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (s, 1H), 4.13 (d, *J* = 0.9 Hz, 1H), 3.74 (ddd, *J* = 11.4, 5.6, 1.7 Hz, 1H), 3.01 (ddd, *J* = 12.5, 5.6, 2.0 Hz, 1H), 2.22 – 2.15 (m, 1H), 2.08 (s, 3H), 1.97 (ddd, *J* = 15.5, 6.2, 4.3 Hz, 1H), 1.75 – 1.60 (m, 3H), 1.55 – 1.17 (m, 8H), 0.88 – 0.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 139.2, 94.0, 56.8, 52.9, 29.2, 27.5, 26.2, 25.6, 24.1, 21.7, 20.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1536.



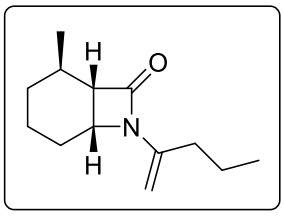
9-(cyclohex-1-en-1-yl)-9-azabicyclo[6.2.0]decan-10-one (2z):

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (t, *J* = 3.9 Hz, 1H), 3.73 (ddd, *J* = 11.3, 5.4, 1.7 Hz, 1H), 2.97 (ddd, *J* = 12.6, 5.4, 1.9 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.31 – 2.19 (m, 1H), 2.16 – 1.94 (m, 4H), 1.72 – 1.21 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 134.1, 108.2, 56.4, 52.4, 29.2, 27.6, 26.3, 26.2, 25.7, 24.7, 23.8, 22.3, 22.2, 21.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1845.



9-(cyclohept-1-en-1-yl)-9-azabicyclo[6.2.0]decan-10-one (2aa):

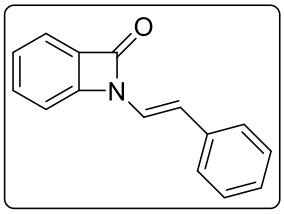
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (t, *J* = 6.8 Hz, 1H), 3.78 – 3.66 (m, 1H), 2.99 – 2.90 (m, 1H), 2.73 – 2.65 (m, 1H), 2.60 – 2.50 (m, 1H), 2.16 – 2.04 (m, 3H), 2.03 – 1.94 (m, 1H), 1.77 – 1.25 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 139.8, 114.5, 56.8, 52.0, 32.0, 29.4, 29.2, 27.6, 27.3, 26.4, 26.2, 25.9, 25.7 24.5, 21.8. HRMS (ESI) *m/z* calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2016.



2-methyl-7-(pent-1-en-2-yl)-7-azabicyclo[4.2.0]octan-8-one (14):

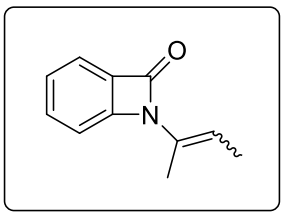
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 1H), 4.14 (s, 1H), 3.88 (q, *J* = 5.7 Hz, 1H), 2.70 (dd, *J* = 7.1, 6.0 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.32 – 2.20 (m, 1H), 2.08 – 1.96 (m, 1H), 1.87 – 1.69 (m, 3H), 1.61 – 1.39 (m, 4H), 1.11 – 0.96 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 143.7, 93.0, 52.6, 50.0, 34.7, 29.3, 27.3, 23.7, 22.2, 21.2, 17.7, 13.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1701, found 208.1702.

2.4 Analysis data of *N*-alkenyl benzoazetinones and *N*-phenyl benzoazetinones



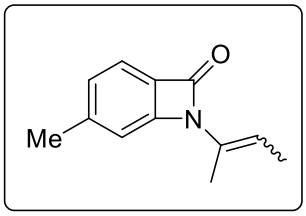
(*E*)-7-styryl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.25 – 8.18 (m, 2H), 8.00 – 7.93 (m, 1H), 7.85 – 7.79 (m, 1H), 7.62 – 7.53 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 143.4, 135.2, 135.1, 132.9, 129.0, 128.9, 128.4, 127.1, 125.8, 122.8, 121.7, 119.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0919, found 222.0917.



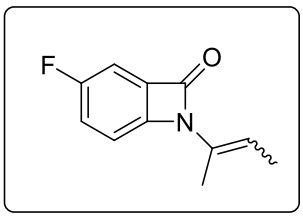
7-(but-2-en-2-yl)-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5b, isomer 1):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.90 (m, 1H), 7.83 – 7.76 (m, 1H), 5.85 (qd, *J* = 7.0, 1.1 Hz, 1H), 2.17 (d, *J* = 1.0 Hz, 3H), 1.90 (dd, *J* = 7.0, 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 144.1, 135.8, 134.9, 132.5, 128.4, 126.3, 125.4, 120.6, 15.8, 13.4. HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0919, found 174.0921.



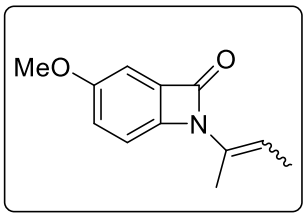
7-(but-2-en-2-yl)-4-methyl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 1.6 Hz, 1H), 7.61 (dd, J = 8.1, 1.7 Hz, 1H), 5.85 (tdt, J = 7.0, 5.7, 1.3 Hz, 1H), 2.61 (s, 3H), 2.17 (t, J = 1.3 Hz, 3H), 1.91 (dt, J = 7.0, 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 146.1, 144.2, 135.7, 133.8, 127.8, 126.0, 125.1, 118.1, 21.9, 15.7, 13.2. HRMS (ESI) m/z calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1088.



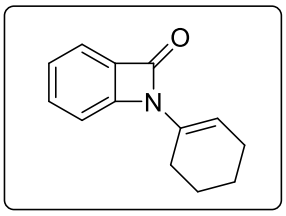
7-(but-2-en-2-yl)-3-fluoro-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 9.0, 4.8 Hz, 1H), 8.01 (dd, J = 7.9, 2.8 Hz, 1H), 7.66 (td, J = 8.5, 2.8 Hz, 1H), 5.88 (qd, J = 7.0, 1.4 Hz, 1H), 2.18 (t, J = 1.3 Hz, 3H), 1.93 (dd, J = 6.8, 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, J = 257.1 Hz), 154.2, 141.0, 135.4, 131.5 (d, J = 9.0 Hz), 126.4, 123.5 (d, J = 24.3 Hz), 122.7 (d, J = 9.3 Hz), 110.6 (d, J = 24.1 Hz), 15.6, 13.3. HRMS (ESI) m/z calcd for $C_{11}H_{11}FNO$ $[M+H]^+$ 192.0825, found 192.0822.



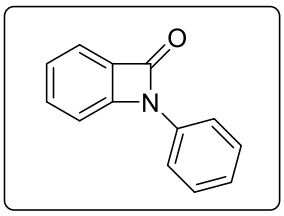
7-(but-2-en-2-yl)-3-methoxy-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 2.8 Hz, 1H), 7.48 (dd, J = 8.9, 2.8 Hz, 1H), 5.86 (dtt, J = 7.1, 5.7, 1.3 Hz, 1H), 4.00 (s, 3H), 2.20 – 2.16 (m, 3H), 1.92 (dt, J = 7.0, 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 155.0, 139.2, 135.7, 130.2, 126.0, 124.8, 122.3, 104.4, 56.2, 15.6, 13.3. HRMS (ESI) m/z calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1025, found 204.1025.



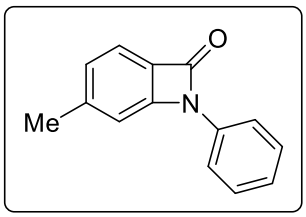
7-(cyclohex-1-en-1-yl)-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5f):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.84 (m, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 6.04 (dd, *J* = 4.5, 3.1 Hz, 1H), 2.45 (dd, *J* = 7.7, 6.0 Hz, 2H), 2.29 (tt, *J* = 6.0, 3.1 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.77 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 143.9, 137.9, 134.7, 132.3, 128.2, 127.9, 125.3, 120.4, 27.5, 24.7, 22.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1075, found 200.1076.



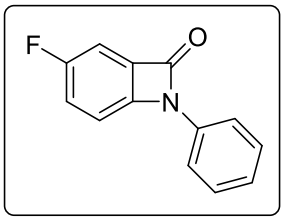
7-phenyl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5h):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.03 – 7.96 (m, 1H), 7.89 – 7.83 (m, 1H), 7.70 – 7.63 (m, 2H), 7.57 (dd, *J* = 10.2, 4.9 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 143.9, 139.0, 135.2, 132.9, 129.2, 129.1, 128.7, 126.2, 125.8, 120.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}NO$ $[M+H]^+$ 196.0762, found 196.0762.



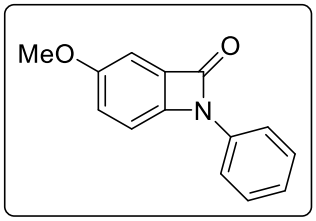
4-methyl-7-phenyl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.1 Hz, 1H), 8.02 (s, 1H), 7.68 (dd, J = 8.5, 1.3 Hz, 3H), 7.61 – 7.54 (m, 2H), 7.54 – 7.46 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 146.5, 143.9, 138.9, 134.2, 129.0, 128.8, 128.1, 126.1, 125.5, 118.0, 22.0. HRMS (ESI) m/z calcd for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0919, found 210.0909.



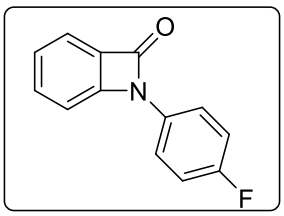
3-fluoro-7-phenyl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, J = 8.9, 4.8 Hz, 1H), 8.09 (dd, J = 7.9, 2.8 Hz, 1H), 7.76 – 7.48 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (d, J = 257.8 Hz), 154.5, 140.8, 138.6, 131.8 (d, J = 9.0 Hz), 129.2, 126.0, 123.8 (d, J = 24.3 Hz), 122.7 (d, J = 9.4 Hz), 111.1 (d, J = 24.2 Hz). HRMS (ESI) m/z calcd for $C_{13}H_9NOF$ $[M+H]^+$ 214.0668, found 214.0675.



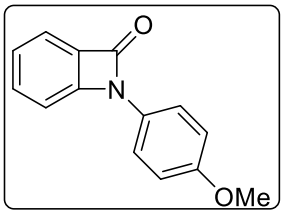
3-methoxy-7-phenyl-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 2.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.60 – 7.55 (m, 2H), 7.51 (tdd, J = 8.7, 4.0, 2.1 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 155.4, 139.0, 138.8, 130.5, 129.0, 128.8, 126.1, 124.9, 122.3, 105.0, 56.3. HRMS (ESI) m/z calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0868, found 226.0857.



7-(4-fluorophenyl)-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5l):

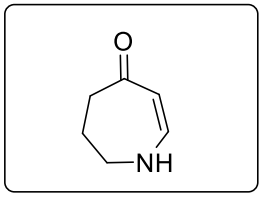
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.21 (dd, *J* = 8.1, 0.4 Hz, 1H), 8.02 – 7.96 (m, 1H), 7.87 – 7.81 (m, 1H), 7.68 – 7.60 (m, 2H), 7.27 – 7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 249.0 Hz), 155.4, 143.8, 135.3, 134.9 (d, *J* = 3.0 Hz), 133.0, 128.7, 128.0 (d, *J* = 8.8 Hz), 125.8, 120.4, 116.1 (d, *J* = 23.0 Hz). HRMS (ESI) *m/z* calcd for $C_{13}H_9NOF$ $[M+H]^+$ 214.0668, found 214.0670.



7-(4-methoxyphenyl)-7-azabicyclo[4.2.0]octa-1,3,5-trien-8-one (5m):

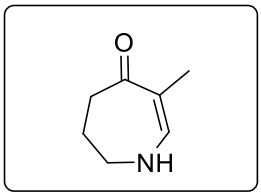
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.98 (t, *J* = 7.5 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 155.5, 143.9, 135.1, 132.8, 131.9, 128.6, 127.4, 125.7, 120.5, 114.4, 55.7. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0868, found 226.0869.

2.5 Analysis data of cycloenaminones



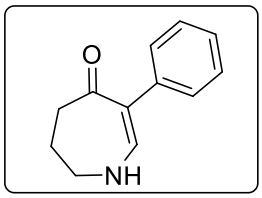
1,5,6,7-tetrahydro-4H-azepin-4-one (3a)：

Prepared according to the general procedure B. Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.56 (dd, *J* = 9.7, 7.9 Hz, 1H), 4.68 (dd, *J* = 9.7, 0.9 Hz, 1H), 3.45 – 3.38 (m, 2H), 2.61 – 2.47 (m, 2H), 1.95 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 146.2, 98.1, 46.9, 42.9, 21.5. HRMS (ESI) *m/z* calcd for $C_6H_{10}NO$ $[M+H]^+$ 112.0762, found 112.0752.



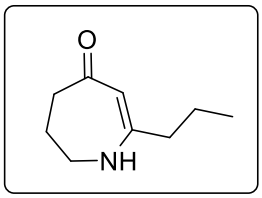
3-methyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3b)：

Prepared according to the general procedure B. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 3.39 – 3.24 (m, 2H), 2.72 – 2.48 (m, 2H), 1.95 – 1.84 (m, 2H), 1.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 146.7, 103.6, 46.7, 43.4, 23.1, 18.4. HRMS (ESI) *m/z* calcd for $C_7H_{12}NO$ $[M+H]^+$ 126.0919, found 126.0927.



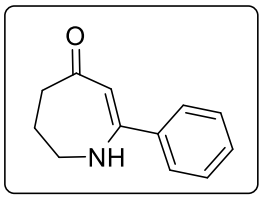
3-phenyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3c)：

Prepared according to the general procedure B. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 1H), 7.21 – 7.08 (m, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.16 (s, 1H), 3.34 – 3.19 (m, 1H), 2.82 – 2.71 (m, 1H), 2.09 – 1.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 149.1, 141.0, 130.1, 127.9, 125.7, 112.6, 47.0, 44.0, 24.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1083.



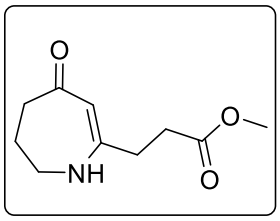
2-propyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3d)：

Prepared according to the general procedure B. Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 4.86 (d, *J* = 2.0 Hz, 1H), 3.44 – 3.37 (m, 2H), 2.61 – 2.55 (m, 2H), 2.06 (dd, *J* = 8.4, 6.8 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.60 – 1.49 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 160.3, 100.2, 46.8, 42.8, 40.9, 23.2, 22.4, 13.6. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1233.



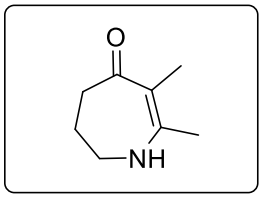
2-phenyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3e)：

Prepared according to the general procedure B. Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.45 – 7.33 (m, 3H), 5.43 (s, 1H), 5.25 (s, 1H), 3.60 (dd, *J* = 9.9, 4.7 Hz, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 2.09 (dt, *J* = 10.6, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 157.6, 139.8, 130.3, 128.9, 127.0, 102.1, 47.6, 42.9, 24.6. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1080.



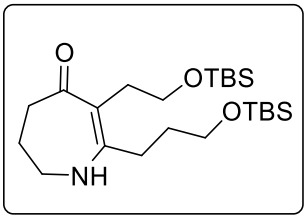
methyl 3-(4-oxo-4,5,6,7-tetrahydro-1H-azepin-2-yl)propanoate (3f):

Prepared according to the general procedure B (Reaction solvent: THF). Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (s, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 3.69 (s, 3H), 3.41 (dd, *J* = 9.6, 4.5 Hz, 2H), 2.61 (dd, *J* = 11.5, 6.2 Hz, 4H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.94 (dt, *J* = 10.2, 6.2 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 174.0, 158.0, 100.8, 52.2, 47.1, 42.9, 33.6, 33.5, 23.2. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO_3$ $[M+H]^+$ 198.1130, found 198.1124.



2,3-dimethyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3g):

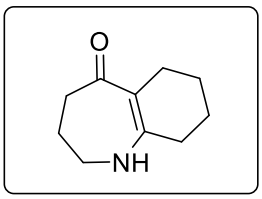
Prepared according to the general procedure B. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (s, 1H), 3.18 (dd, *J* = 12.0, 6.7 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.08 (p, *J* = 7.2 Hz, 2H), 1.97 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 161.9, 107.5, 48.6, 42.0, 33.5, 22.2, 13.6. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1075.



3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-(3-((tertbutyldimethylsilyl)oxy)-propyl)-1,5,6,7-tetrahydro-4H-azepin-4-one (3h):

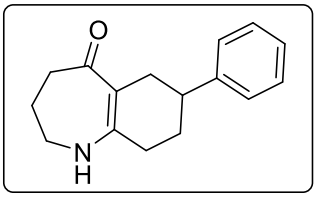
Prepared according to the general procedure B. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 5.42 (s, 1H), 3.64 (t, *J* = 5.5 Hz, 2H), 3.56 (t, *J* = 6.7 Hz, 2H), 3.16 (dd, *J* = 12.1, 5.9 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 6.7 Hz, 4H), 2.17 – 2.06 (m, 2H), 1.78 – 1.69 (m, 2H), 0.91 (s, 9H), 0.87 (s, 9H), 0.06 (s, 6H), 0.02 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 167.3, 109.4, 63.4, 62.1, 48.8, 42.1, 34.1, 31.5, 31.2, 31.1, 26.2, 26.1, 18.5, 18.4, -5.1, -5.2. HRMS (ESI) *m/z* calcd for $C_{23}H_{48}NO_3Si_2$ $[M+H]^+$ 442.3173, found 442.3175.



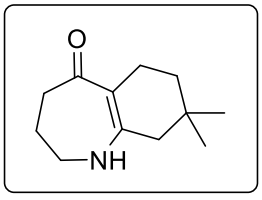
1,2,3,4,6,7,8,9-octahydro-5H-benzo[b]azepin-5-one (3i):

Prepared according to the general procedure B. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 3.61 (t, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.31 (t, *J* = 5.9 Hz, 4H), 2.05 – 1.94 (m, 2H), 1.77 – 1.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 167.5, 97.6, 47.8, 37.7, 31.1, 26.4, 24.0, 23.3, 21.3. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1235.



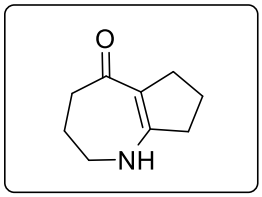
8-phenyl-1,2,3,4,6,7,8,9-octahydro-5H-benzo[b]azepin-5-one (3j):

Prepared according to the general procedure B. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.25 – 7.14 (m, 3H), 4.81 (s, 1H), 3.34 (dt, *J* = 10.9, 5.9 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.84 (dd, *J* = 16.3, 5.2 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.72 – 2.64 (m, 1H), 2.64 – 2.55 (m, 1H), 2.49 – 2.31 (m, 2H), 2.23 (dd, *J* = 16.3, 10.8 Hz, 1H), 2.17 – 2.00 (m, 2H), 1.99 – 1.90 (m, 1H), 1.78 (ddd, *J* = 23.6, 11.5, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 161.4, 146.2, 128.4, 127.0, 126.2, 110.1, 48.6, 42.4, 40.4, 32.7, 32.1, 31.9, 29.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}NO$ $[M+H]^+$ 242.1545, found 242.1549.



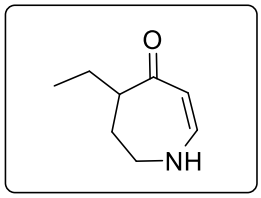
7,7-dimethyl-1,2,3,4,6,7,8,9-octahydro-5H-benzo[b]azepin-5-one (3k):

Prepared according to the general procedure B. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (s, 1H), 3.19 (td, *J* = 6.8, 4.8 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.31 (tt, *J* = 6.7, 1.2 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.32 (t, *J* = 6.7 Hz, 2H), 0.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 160.9, 108.9, 48.5, 45.3, 42.5, 35.6, 32.1, 30.2, 27.8, 22.2. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1555.



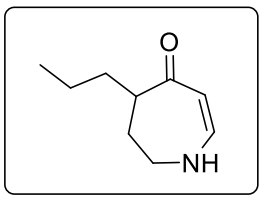
1,3,4,6,7,8-hexahydrocyclopenta[b]azepin-5(2H)-one (3l):

Prepared according to the general procedure B. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 3.42 (d, *J* = 4.7 Hz, 2H), 2.63 (t, *J* = 6.9 Hz, 4H), 2.59 – 2.46 (m, 2H), 1.96 (m, 2H), 1.82 – 1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 159.0, 108.4, 46.8, 43.2, 38.5, 32.6, 22.4, 21.0. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1080.



5-ethyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3m):

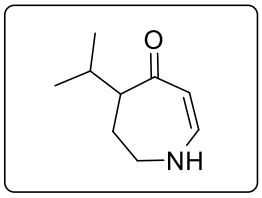
Prepared according to the general procedure B. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (dd, *J* = 9.8, 7.7 Hz, 1H), 5.82 (s, 1H), 4.74 (dd, *J* = 9.8, 1.4 Hz, 1H), 3.54 (dddd, *J* = 13.3, 9.3, 3.8, 2.0 Hz, 1H), 3.36 (dddd, *J* = 13.9, 8.0, 3.6, 2.2 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.09 – 2.02 (m, 1H), 1.94 – 1.77 (m, 2H), 1.62 – 1.48 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 144.6, 98.9, 52.5, 44.1, 26.5, 25.6, 11.5. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1072.



5-propyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3n):

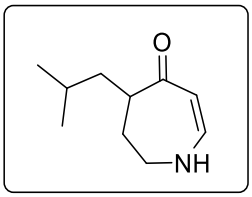
Prepared according to the general procedure B. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (dd, *J* = 9.9, 7.6 Hz, 1H), 5.19 (s, 1H), 4.79 (dd, *J* = 9.9, 1.2 Hz, 1H), 3.55 (dddd, *J* = 13.4, 9.5, 3.7, 2.0 Hz, 1H), 3.37 (dddd, *J* = 13.8, 7.8, 3.6, 2.3 Hz, 1H), 2.61 – 2.50

(m, 1H), 2.07 (dddd, J = 15.3, 9.5, 3.7, 2.3 Hz, 1H), 1.83 (dddd, J = 18.9, 15.8, 9.7, 3.7 Hz, 2H), 1.53 – 1.42 (m, 1H), 1.42 – 1.26 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 143.9, 99.5, 51.0, 44.2, 34.8, 27.1, 20.2, 14.3. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1233.



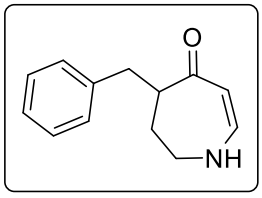
5-isopropyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3o)：

Prepared according to the general procedure B. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (dd, J = 9.7, 7.7 Hz, 1H), 5.96 (s, 1H), 4.75 (dd, J = 9.8, 1.3 Hz, 1H), 3.58 (dddd, J = 13.4, 8.5, 4.6, 2.2 Hz, 1H), 3.32 (ddt, J = 13.7, 8.4, 2.4 Hz, 1H), 2.39 – 2.26 (m, 2H), 2.01 – 1.92 (m, 1H), 1.92 – 1.82 (m, 1H), 0.95 (d, J = 6.6 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 144.4, 99.3, 57.5, 44.9, 29.2, 23.3, 21.1, 18.0. HRMS (ESI) *m/z* calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found 154.1230.



5-isobutyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3p)：

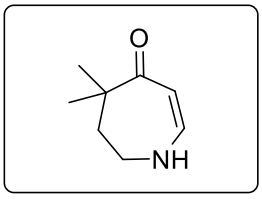
Prepared according to the general procedure B. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, J = 9.7, 7.8 Hz, 1H), 6.19 (s, 1H), 4.69 (dd, J = 9.7, 1.0 Hz, 1H), 3.56 – 3.45 (m, 1H), 3.40 – 3.30 (m, 1H), 2.63 – 2.54 (m, 1H), 2.04 (dddd, J = 15.7, 9.9, 3.4, 2.4 Hz, 1H), 1.79 (dtd, J = 9.4, 7.6, 1.8 Hz, 1H), 1.71 – 1.53 (m, 2H), 1.39 – 1.27 (m, 1H), 0.89 (d, J = 6.3 Hz, 3H), 0.86 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 144.9, 98.2, 48.8, 43.6, 41.6, 26.6, 25.0, 23.5, 21.7. HRMS (ESI) *m/z* calcd for $C_{10}H_{18}NO$ $[M+H]^+$ 168.1388, found 168.1391.



5-benzyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3q)：

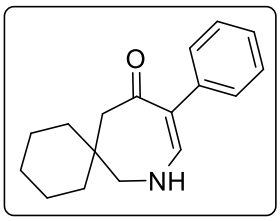
Prepared according to the general procedure B. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 8.5 Hz, 3H), 6.60 (dd, J = 9.5, 7.9 Hz, 1H), 4.84

(d, *J* = 9.7 Hz, 1H), 3.58 – 3.47 (m, 1H), 3.39 (dd, *J* = 13.7, 4.1 Hz, 1H), 3.27 (dd, *J* = 12.7, 10.4 Hz, 1H), 2.86 – 2.75 (m, 1H), 2.63 (dd, *J* = 13.7, 10.4 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.81 – 1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 145.1, 140.2, 129.2, 128.5, 126.2, 98.8, 52.9, 44.5, 38.6, 26.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1232, found 202.1242.



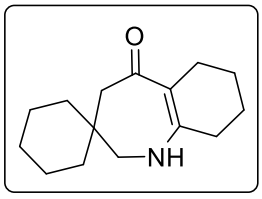
5,5-dimethyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3r):

Prepared according to the general procedure B. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (dd, *J* = 9.8, 7.6 Hz, 1H), 6.30 (s, 1H), 4.64 (dd, *J* = 9.9, 0.8 Hz, 1H), 3.47 – 3.35 (m, 2H), 1.90 – 1.80 (m, 2H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 144.6, 97.3, 46.0, 42.2, 36.9, 28.1. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1072



10-phenyl-8-azaspiro[5.6]dodec-9-en-11-one (3s):

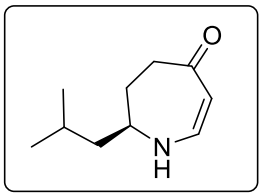
Prepared according to the general procedure B. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 5H), 7.19 – 7.13 (m, 1H), 5.45 (s, 1H), 3.12 (d, *J* = 5.1 Hz, 2H), 2.63 (s, 2H), 1.60 – 1.35 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 151.5, 138.5, 129.1, 128.1, 126.0, 116.7, 58.9, 54.9, 46.2, 35.2, 26.2, 22.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1701, found 256.1697.



1,2,6,7,8,9-hexahydrospiro[benzo[b]azepine-3,1'-cyclohexan]-5(4H)-one (3t):

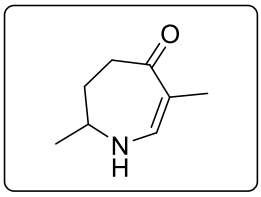
Prepared according to the general procedure B. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (s, 1H), 2.96 (d, *J* = 5.1 Hz, 2H), 2.45 (s, 2H), 2.29 (t, *J* = 6.2 Hz, 2H), 2.25 (t, *J* = 6.1 Hz, 2H), 1.66 – 1.36 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 162.8, 111.2, 59.9, 54.0, 47.4, 35.5, 31.2, 26.3, 24.0, 22.8, 22.6, 22.2. HRMS (ESI) *m/z* calcd for

$C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1859.



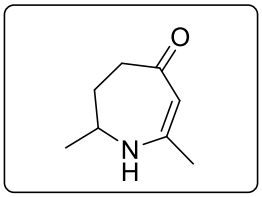
(*R*)-7-isobutyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3u):

Prepared according to the general procedure B. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 – 6.45 (m, 2H), 4.72 – 4.65 (m, 1H), 3.44 (q, *J* = 7.6 Hz, 1H), 2.56 – 2.49 (m, 2H), 1.92 – 1.83 (m, 1H), 1.82 – 1.72 (m, 1H), 1.70 – 1.58 (m, 1H), 1.51 – 1.41 (m, 1H), 1.32 (ddd, *J* = 13.8, 7.4, 6.7 Hz, 1H), 0.86 (dd, *J* = 6.6, 3.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 145.2, 98.4, 43.8, 40.3, 27.0, 24.5, 22.7, 22.3. HRMS (ESI) *m/z* calcd for $C_{10}H_{18}NO$ $[M+H]^+$ 168.1388, found 168.1388. Optical Rotation: $[\alpha]_D^{20}$ = -234.9 (c = 0.03, CH_2Cl_2)



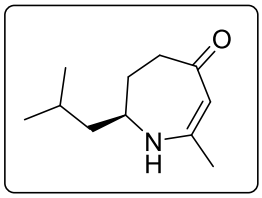
3,7-dimethyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3v):

Prepared according to the general procedure B. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.0 Hz, 1H), 4.82 (s, 1H), 3.55 – 3.44 (m, 1H), 2.75 – 2.58 (m, 2H), 1.96 – 1.78 (m, 2H), 1.72 (s, 3H), 1.25 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 144.7, 105.2, 53.2, 41.7, 31.0, 22.3, 18.1. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1073.



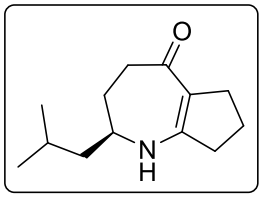
2,7-dimethyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3w):

Prepared according to the general procedure B. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 4.85 (d, *J* = 1.8 Hz, 1H), 3.53 (qd, *J* = 6.6, 3.5 Hz, 1H), 2.58 (dd, *J* = 7.4, 5.4 Hz, 2H), 1.92 (s, 3H), 1.89 – 1.82 (m, 2H), 1.28 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 154.7, 101.1, 53.0, 40.9, 30.2, 25.32, 22.21. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO$ $[M+H]^+$ 140.1075, found 140.1072.



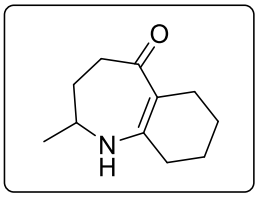
(*R*)-7-isobutyl-2-methyl-1,5,6,7-tetrahydro-4H-azepin-4-one (3x):

Prepared according to the general procedure B. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (s, 1H), 4.87 (d, *J* = 1.7 Hz, 1H), 3.46 – 3.36 (m, 1H), 2.66 – 2.50 (m, 2H), 1.92 (s, 3H), 1.90 – 1.75 (m, 2H), 1.70 – 1.59 (m, 1H), 1.52 – 1.35 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 154.9, 101.4, 55.2, 44.4, 40.7, 29.0, 25.3, 24.9, 22.8, 22.5. HRMS (ESI) *m/z* calcd for $C_{11}H_{20}NO$ $[M+H]^+$ 182.1545, found 182.1547. Optical Rotation: $[\alpha]_D^{20}$ = -416.6 (c = 0.01, CH_2Cl_2)



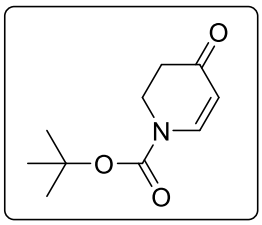
(*R*)-2-isobutyl-1,3,4,6,7,8-hexahydrocyclopenta[b]azepin-5(2H)-one (3y):

Prepared according to the general procedure B. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (s, 1H), 3.43 (q, *J* = 7.3 Hz, 1H), 2.62 (dd, *J* = 12.5, 6.7 Hz, 4H), 2.53 (t, *J* = 7.7 Hz, 2H), 1.94 – 1.85 (m, 1H), 1.85 – 1.78 (m, 1H), 1.78 – 1.68 (m, 2H), 1.63 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.49 – 1.34 (m, 2H), 0.91 (dd, *J* = 6.6, 2.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 157.9, 108.5, 54.5, 44.7, 40.8, 38.9, 32.6, 27.8, 24.8, 22.8, 22.6, 20.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1071, found 208.1075. Optical Rotation: $[\alpha]_D^{20}$ = -131.7 (c = 0.01, CH_2Cl_2)



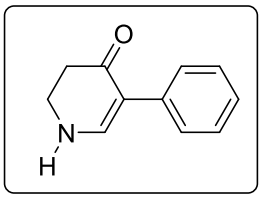
2-methyl-1,2,3,4,6,7,8,9-octahydro-5H-benzo[b]azepin-5-one (3z):

Prepared according to the general procedure B. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 1H), 3.36 – 3.19 (m, 1H), 2.84 (td, *J* = 12.0, 8.2 Hz, 1H), 2.58 – 2.41 (m, 2H), 2.31 (dd, *J* = 12.4, 4.9 Hz, 1H), 2.21 – 2.00 (m, 3H), 1.94 – 1.81 (m, 2H), 1.54 – 1.40 (m, 1H), 1.39 – 1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 160.5, 110.6, 55.6, 41.9, 40.0, 31.9, 24.2, 22.8, 22.6, 21.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1388, found 180.1402.



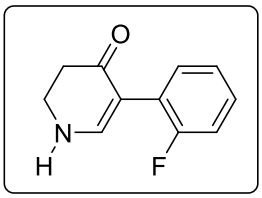
tert-butyl 4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (4a):

The NMR spectrums agree with the reported data[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 5.30 (d, *J* = 5.4 Hz, 1H), 3.97 (t, *J* = 7.1 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 144.2, 106.8, 83.6, 42.3, 41.2, 35.8, 28.2.



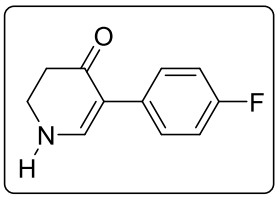
5-phenyl-2,3-dihydropyridin-4(1H)-one (4b):

Prepared according to the general procedure B. Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.29 (s, 1H), 3.63 (td, *J* = 7.8, 2.5 Hz, 2H), 2.69 – 2.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 150.6, 136.4, 128.3, 128.1, 125.9, 112.3, 42.2, 36.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0919, found 174.0919.



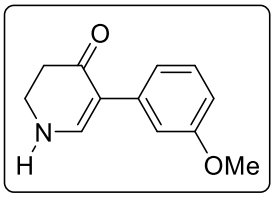
5-(2-fluorophenyl)-2,3-dihydropyridin-4(1H)-one (4c):

Prepared according to the general procedure B. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 6.98 (m, 2H), 5.72 (s, 1H), 3.62 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 160.2 (d, *J* = 244.8 Hz), 152.4 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 3.7 Hz), 127.8 (d, *J* = 8.3 Hz), 123.9, 123.8 (d, *J* = 3.4 Hz), 115.6 (d, *J* = 23.0 Hz), 105.8, 41.9, 36.3. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NOF$ $[M+H]^+$ 192.0825, found 192.0815.



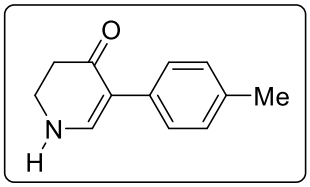
5-(4-fluorophenyl)-2,3-dihydropyridin-4(1H)-one (4d):

Prepared according to the general procedure B. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.2 Hz, 3H), 6.99 (t, *J* = 8.3 Hz, 2H), 5.32 (s, 1H), 3.64 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 161.2 (d, *J* = 244.3 Hz), 150.5, 132.3 (d, *J* = 3.0 Hz), 129.6 (d, *J* = 7.7 Hz), 115.0 (d, *J* = 21.1 Hz), 111.4, 42.2, 36.6. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NOF$ $[M+H]^+$ 192.0825, found 192.0831.



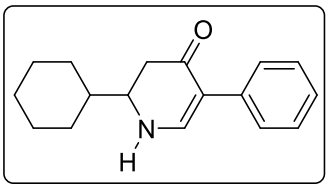
5-(3-methoxyphenyl)-2,3-dihydropyridin-4(1H)-one (4e)：

Prepared according to the general procedure B. Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.4 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.50 (s, 1H), 3.79 (s, 3H), 3.61 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 159.5, 150.7, 137.9, 129.2, 120.4, 113.7, 112.0, 111.6, 55.3, 42.1, 36.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1025, found 204.1025.



5-(p-tolyl)-2,3-dihydropyridin-4(1H)-one (4f)：

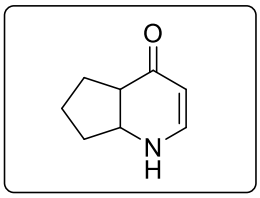
Prepared according to the general procedure B. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 5.57 (s, 1H), 3.57 (t, *J* = 7.6 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 150.6, 135.5, 133.5, 129.0, 128.0, 112.1, 42.2, 36.8, 21.2. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1076.



2-cyclohexyl-5-phenyl-2,3-dihydropyridin-4(1H)-one (4g)：

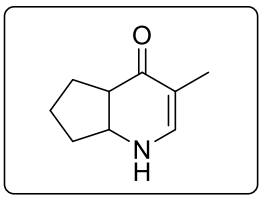
Prepared according to the general procedure B. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 3H), 7.17 (t, *J* = 7.0 Hz, 1H), 5.20 (s, 1H), 3.52 (dd, *J* = 16.4, 7.7 Hz, 1H), 2.55 (d, *J* = 9.1 Hz, 2H), 1.85 – 1.48 (m, 7H), 1.31

– 1.01 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 150.1, 136.3, 128.3, 127.9, 125.8, 111.9, 58.4, 41.2, 40.0, 29.0, 28.7, 26.4, 26.1, 26.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1701, found 256.1703.



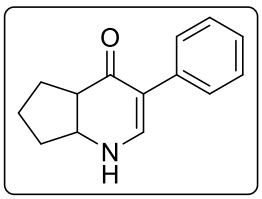
1,4a,5,6,7,7a-hexahydro-4H-cyclopenta[b]pyridin-4-one (4h):

Prepared according to the general procedure B. Yield: 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (t, *J* = 7.1 Hz, 1H), 4.90 (d, *J* = 7.5 Hz, 1H), 4.84 (s, 1H), 4.08 (t, *J* = 7.2 Hz, 1H), 2.58 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.12 – 1.89 (m, 3H), 1.88 – 1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 149.0, 96.1, 57.8, 49.5, 33.3, 29.4, 22.2. HRMS (ESI) *m/z* calcd for $C_8H_{12}NO$ $[M+H]^+$ 138.0919, found 138.0915.



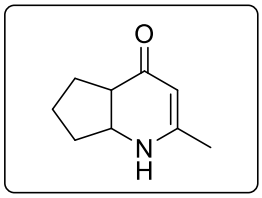
3-methyl-1,4a,5,6,7,7a-hexahydro-4H-cyclopenta[b]pyridin-4-one (4i):

Prepared according to the general procedure B. Yield: 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 6.5 Hz, 1H), 4.74 – 4.49 (m, 1H), 4.29 – 4.21 (m, 1H), 2.72 (dd, *J* = 15.7, 8.6 Hz, 1H), 2.28 – 1.78 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 147.2, 102.9, 58.4, 49.8, 33.4, 29.4, 22.3, 12.8. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1071.



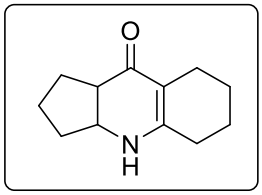
3-phenyl-1,4a,5,6,7,7a-hexahydro-4H-cyclopenta[b]pyridin-4-one (4j):

Prepared according to the general procedure B. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.16 (dd, *J* = 14.6, 7.1 Hz, 2H), 5.21 (s, 1H), 4.12 (s, 1H), 2.66 (dd, *J* = 15.9, 8.5 Hz, 1H), 2.18 – 2.07 (m, 1H), 2.07 – 1.99 (m, 1H), 1.99 – 1.91 (m, 1H), 1.89 – 1.78 (m, 2H), 1.76 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 149.0, 136.8, 128.2, 128.0, 125.6, 107.8, 57.9, 49.9, 33.4, 29.7, 22.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1232, found 214.1233.



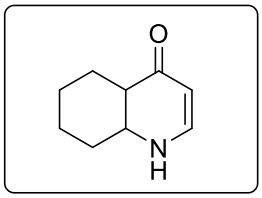
2-methyl-1,4a,5,6,7,7a-hexahydro-4H-cyclopenta[b]pyridin-4-one (4k):

Prepared according to the general procedure B. Yield: 38%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (s, 1H), 4.79 (d, *J* = 0.9 Hz, 1H), 4.06 – 4.00 (m, 1H), 2.47 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.09 – 1.98 (m, 1H), 1.97 – 1.86 (m, 5H), 1.85 – 1.72 (m, 2H), 1.71 – 1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 160.3, 95.7, 57.8, 48.1, 33.2, 29.4, 22.3, 21.4. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1075.



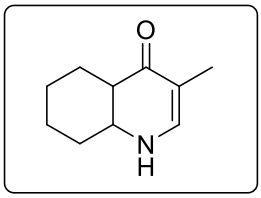
1,2,3,3a,4,5,6,7,8,9a-decahydro-9H-cyclopenta[b]quinolin-9-one (4l):

Prepared according to the general procedure B. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (s, 1H), 4.02 (s, 1H), 2.52 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.29 (dt, *J* = 15.5, 5.9 Hz, 1H), 2.20 (dt, *J* = 11.9, 6.5 Hz, 3H), 2.04 (tdd, *J* = 13.6, 8.9, 4.3 Hz, 1H), 1.97 – 1.51 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 157.0, 103.1, 57.4, 49.4, 33.5, 29.4, 29.3, 22.9, 22.4, 22.2, 21.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1373.



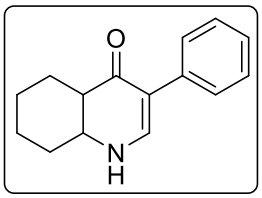
4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4m):

Prepared according to the general procedure B. Yield: 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.0 Hz, 1H), 4.95 (d, *J* = 7.4 Hz, 1H), 4.91 (s, 1H), 3.78 (s, 1H), 2.35 – 2.19 (m, 1H), 1.88 – 1.78 (m, 1H), 1.72 – 1.49 (m, 5H), 1.29 (dt, *J* = 22.6, 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 150.6, 97.8, 52.8, 47.3, 28.7, 24.7, 24.0, 21.5. HRMS (ESI) *m/z* calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found 152.1071.



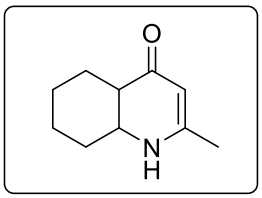
3-methyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4n):

Prepared according to the general procedure B. Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 6.4 Hz, 1H), 4.37 (s, 1H), 3.73 (d, *J* = 2.6 Hz, 1H), 2.24 (dd, *J* = 12.5, 6.8 Hz, 1H), 1.79 – 1.72 (m, 1H), 1.68 (s, 3H), 1.67 – 1.62 (m, 1H), 1.62 – 1.46 (m, 6H), 1.32 – 1.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 148.5, 105.0, 53.3, 47.5, 29.1, 24.6, 24.2, 21.4, 12.8.HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1234.



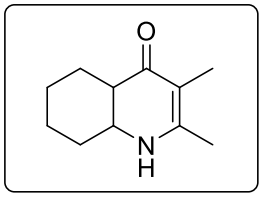
3-phenyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4o):

Prepared according to the general procedure B. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 5H), 7.16 (t, *J* = 7.1 Hz, 1H), 5.20 (s, 1H), 3.83 (s, 1H), 2.38 (s, 1H), 1.92 – 1.50 (m, 7H), 1.40 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (s), 149.6, 136.6, 128.2, 128.1, 125.8, 110.4, 52.8, 47.4, 28.7, 24.6, 24.0, 21.4. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1393.



2-methyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4p):

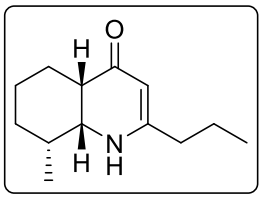
Prepared according to the general procedure B. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (s, 1H), 4.72 (s, 1H), 3.74 (s, 1H), 2.15 (m, 1H), 1.96 (s, 3H), 1.89 – 1.75 (m, 2H), 1.64 – 1.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 161.2, 97.9, 52.8, 46.2, 28.9, 24.7, 24.1, 21.4, 21.2. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1233.



2,3-dimethyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4q):

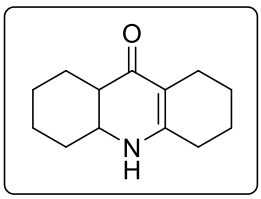
Prepared according to the general procedure B. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 1H), 3.68 (s, 1H), 1.99 (s, 3H), 1.78 – 1.45 (m, 12H).^{13}C NMR (100 MHz,

$CDCl_3$) δ 195.1, 158.0, 102.6, 52.1, 46.6, 29.1, 24.6, 24.2, 21.3, 19.9, 9.9. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1388, found 180.1387.



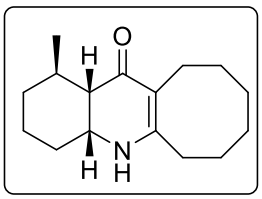
8-methyl-2-propyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (4r):

Prepared according to the general procedure B. Yield: 64%. **4s:** ^1H NMR (400 MHz, $CDCl_3$) δ 4.92 (s, 1H), 4.56 (s, 1H), 3.56 (s, 1H), 2.25 – 2.08 (m, 2H), 2.08 – 1.99 (m, 1H), 1.79 – 1.47 (m, 6H), 1.38 – 1.21 (m, 3H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 165.0, 97.6, 57.0, 48.3, 37.3, 33.3, 28.8, 24.8, 24.4, 21.4, 18.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1701, found 208.1698.



1,3,4,4a,5,6,7,8,9a,10-decahydroacridin-9(2H)-one (4s):

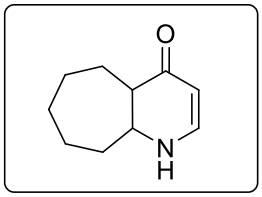
Prepared according to the general procedure B. Yield: 68%. ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 1H), 3.71 (d, *J* = 3.0 Hz, 1H), 2.40 – 2.12 (m, 5H), 1.84 – 1.46 (m, 11H), 1.36 – 1.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 158.6, 105.0 52.2, 47.2, 29.3, 29.1, 24.6, 24.2, 22.8, 22.3, 21.3, 21.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1245, found 206.1245.



(1R,4aR,12aS)-1-methyl-1,3,4,4a,5,6,7,8,9,10,11,12a-dodecahydrocycloocta-[b]-quinolin-12(2H)-one (4t):

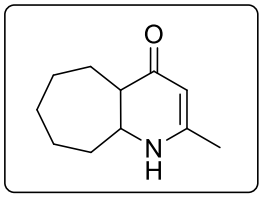
Prepared according to the general procedure B. Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 1H), 3.75 (d, *J* = 2.0 Hz, 1H), 2.63 – 2.50 (m, 1H), 2.50 – 2.36 (m, 1H), 2.22 (ddd, *J* = 20.3, 14.5, 4.7 Hz, 2H), 1.86 – 1.29 (m, 15H), 1.04 – 0.91 (m, 1H), 0.88 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 161.0, 107.6, 53.6, 52.6, 33.8, 32.7, 30.4, 29.8, 29.7, 28.7, 26.7, 26.5, 23.0, 21.0, 19.7. HRMS (ESI) *m/z* calcd for

$C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2012.



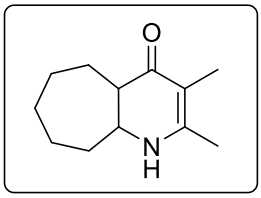
1,4a,5,6,7,8,9,9a-octahydro-4H-cyclohepta[b]pyridin-4-one (4u):

Prepared according to the general procedure B. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 6.9 Hz, 1H), 4.95 (d, *J* = 7.3 Hz, 1H), 4.78 (s, 1H), 3.93 (dd, *J* = 11.2, 5.4 Hz, 1H), 2.27 (dd, *J* = 10.2, 4.9 Hz, 1H), 1.98 – 1.66 (m, 6H), 1.61 – 1.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 150.5, 98.4, 55.7, 51.5, 32.6, 28.8, 27.4, 25.0, 22.1. HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1232, found 166.1236.



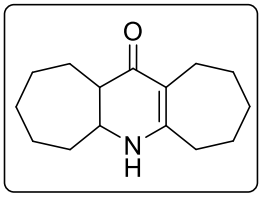
2-methyl-1,4a,5,6,7,8,9,9a-octahydro-4H-cyclohepta[b]pyridin-4-one (4v):

Prepared according to the general procedure B. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (s, 1H), 4.83 (s, 1H), 3.88 (dd, *J* = 11.3, 5.5 Hz, 1H), 2.17 (dd, *J* = 10.0, 4.9 Hz, 1H), 2.02 – 1.87 (m, 4H), 1.87 – 1.61 (m, 5H), 1.61 – 1.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 161.4, 98.0, 55.6, 50.4, 32.6, 29.0, 27.6, 25.0, 22.1, 21.7. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1388, found 180.1399.



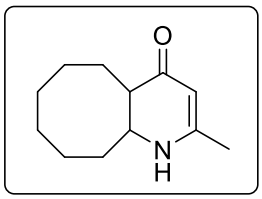
2,3-dimethyl-1,4a,5,6,7,8,9,9a-octahydro-4H-cyclohepta[b]pyridin-4-one (4w):

Prepared according to the general procedure B. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 3.79 (dd, *J* = 10.8, 5.3 Hz, 1H), 2.17 (dd, *J* = 10.3, 4.6 Hz, 1H), 1.96 (s, 3H), 1.91 – 1.81 (m, 1H), 1.80 – 1.63 (m, 8H), 1.54 – 1.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 158.5, 102.6, 54.9, 50.7, 32.8, 28.9, 27.6, 24.6, 22.0, 19.6, 10.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1531



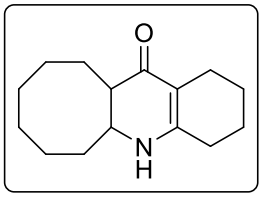
2,3,4,5,5a,6,7,8,9,10,11,12a-dodecahydrodicyclohepta[b,e]pyridin-12(1H)-one (4x):

Prepared according to the general procedure B. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (s, 1H), 3.84 (dd, *J* = 10.8, 5.4 Hz, 1H), 2.52 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.41 – 2.15 (m, 4H), 1.97 – 1.87 (m, 1H), 1.85 – 1.29 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 165.0, 109.6, 55.0, 50.2, 36.7, 33.0, 32.3, 29.0, 28.5, 27.5, 26.5, 24.7, 23.2, 22.1. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1846



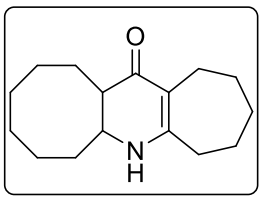
2-methyl-4a,5,6,7,8,9,10,10a-octahydrocycloocta[b]pyridin-4(1H)-one (4y):

Prepared according to the general procedure B. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (s, 1H), 4.83 (s, 1H), 3.67 (dd, *J* = 9.7, 4.5 Hz, 1H), 2.31 (s, 1H), 1.94 (s, 3H), 1.90 – 1.70 (m, 4H), 1.68 – 1.49 (m, 6H), 1.47 – 1.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 161.8, 97.7, 56.3, 46.2, 28.7, 28.3, 28.1, 24.5, 24.3, 22.7, 21.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1545, found 194.1549.



1,3,4,5,5a,6,7,8,9,10,11,11a-dodecahydrocycloocta[b]quinolin-12(2H)-one (4z):

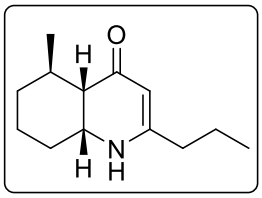
Prepared according to the general procedure B. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (d, *J* = 11.5 Hz, 1H), 3.69 – 3.55 (m, 1H), 2.45 – 2.05 (m, 5H), 1.88 – 1.30 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 158.5, 105.4, 55.8, 46.9, 29.2, 28.9, 28.3, 28.2, 24.5, 24.0, 22.9, 22.6, 22.3, 21.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1858, found 234.1842.



1,2,3,4,5,6,6a,7,8,9,10,11,12,12a-tetradecahydro-13H cyclohepta-[b]-cycloocta-[e]-pyridin-13-one (4aa):

Prepared according to the general procedure B. Yield: 74%. ^{1}H NMR (400 MHz, MeOD) δ 3.60 (dt, *J* = 10.0, 5.0 Hz, 1H), 2.58 – 2.36 (m, 3H), 2.32 – 2.20 (m, 2H), 1.96 – 1.73

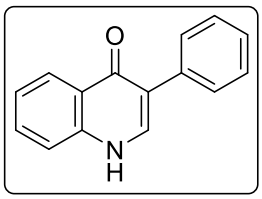
(m, 6H), 1.67 – 1.43 (m, 10H), 1.36 – 1.24 (m, 2H).^{13}C NMR (100 MHz, MeOD) δ 196.1, 171.2, 108.8, 56.6, 46.4, 35.7, 33.1, 29.8, 29.3, 29.3, 28.7, 27.6, 25.3, 25.1, 24.1, 23.6. HRMS (ESI) *m/z* calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.2007.



5-methyl-2-propyl-4a,5,6,7,8,8a-hexahydroquinolin-4(1H)-one (15)：

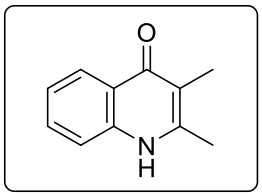
Prepared according to the general procedure B. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.44 (s, 1H), 3.79 (s, 1H), 2.22 – 2.06 (m, 2H), 1.83 – 1.51 (m, 9H), 0.99 – 0.90 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 164.4, 97.3, 53.4, 53.0, 37.0, 33.7, 29.5, 29.1, 21.2, 20.9, 19.8, 13.8. HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1701, found 208.1711.

2.6 Analysis data of 4-quinolone and acridone



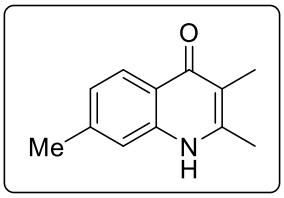
3-phenylquinolin-4(1H)-one (6a)

Prepared according to the general procedure C. Yield: 20%. ^{1}H NMR (400 MHz, MeOD) δ 8.39 – 8.35 (m, 1H), 8.09 (s, 1H), 7.74 – 7.69 (m, 1H), 7.67 – 7.63 (m, 2H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 178.2, 140.9, 140.1, 137.1, 133.3, 130.1, 129.3, 128.1, 126.8, 125.2, 123.1, 119.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0919, found 222.0918.



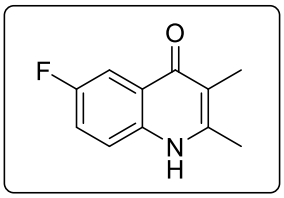
2,3-dimethylquinolin-4(1H)-one (6b)：

Prepared according to the general procedure C. Yield: 47%. ^{1}H NMR (400 MHz, MeOD) δ 8.22 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.31 (m, 1H), 2.50 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, MeOD) δ 179.0, 149.5, 140.4, 132.6, 126.2, 124.5, 118.6, 116.6, 18.5, 10.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0919, found 174.0925.



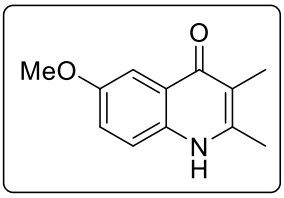
2,3,7-trimethylquinolin-4(1H)-one (6c)

Prepared according to the general procedure C. Yield: 42%. ^{1}H NMR (400 MHz, MeOD) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 1H), 7.18 (dd, *J* = 8.4, 1.1 Hz, 1H), 2.47 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 179.0, 149.1, 143.6, 140.7, 126.4, 126.1, 122.6, 117.9, 116.3, 21.7, 18.4, 10.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1075, found 188.1088.



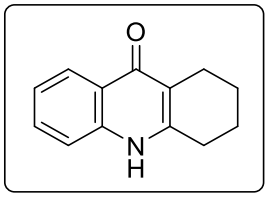
6-fluoro-2,3-dimethylquinolin-4(1H)-one (6d)

Prepared according to the general procedure C. Yield: 50%. ^{1}H NMR (400 MHz, MeOD) δ 7.82 (dd, *J* = 9.5, 2.8 Hz, 1H), 7.53 (dd, *J* = 9.1, 4.5 Hz, 1H), 7.44 – 7.37 (m, 1H), 2.48 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 178.1 (d, *J* = 3.0 Hz), 160.4 (d, *J* = 242.8 Hz), 149.6, 137.1, 125.5 (d, *J* = 7.2 Hz), 121.5 (d, *J* = 26.2 Hz), 121.2 (d, *J* = 8.2 Hz), 116.2, 110.0 (d, *J* = 22.8 Hz), 18.5, 10.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NOF$ $[M+H]^+$ 192.0825, found 192.0822.



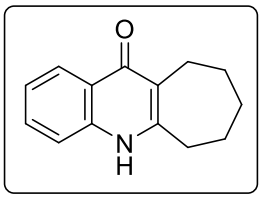
6-fluoro-2,3-dimethylquinolin-4(1H)-one (6e)

Prepared according to the general procedure C. Yield: 35%. ^{1}H NMR (400 MHz, DMSO-d6) δ 11.40 (s, 1H), 7.46 (d, *J* = 2.9 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.21 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.81 (s, 3H), 2.35 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 175.0, 154.8, 145.0, 133.7, 123.8, 121.3, 119.1, 113.0, 104.2, 55.2, 17.9, 10.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1025, found 204.1025.



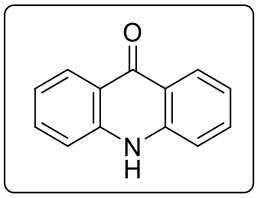
1,3,4,10-tetrahydroacridin-9(2H)-one (6f)

Prepared according to the general procedure C. Yield: 50%. ^{1}H NMR (400 MHz, MeOD) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 1.92 – 1.78 (m, 4H). ^{13}C NMR (101 MHz, MeOD) δ 179.3, 150.2, 140.7, 132.7, 126.0, 124.6, 124.2, 118.5, 117.9, 28.8, 23.3, 23.0, 22.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1075, found 200.1079.



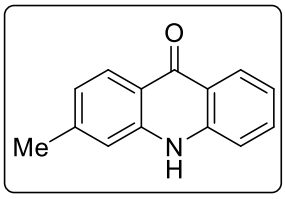
5,6,7,8,9,10-hexahydro-11H-cyclohepta[b]quinolin-11-one (6g):

Prepared according to the general procedure C. Yield: 55%. ^{1}H NMR (400 MHz, MeOD) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 3.00 – 2.91 (m, 4H), 1.97 – 1.88 (m, 2H), 1.82 – 1.75 (m, 2H), 1.65 – 1.57 (m, 2H). ^{13}C NMR (100 MHz, MeOD) δ 177.9, 156.8, 140.1, 132.6, 126.5, 125.0, 124.8, 123.1, 118.9, 35.4, 33.4, 28.5, 27.4, 24.8. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1232, found 214.1217.



acridin-9(10H)-one (6h):

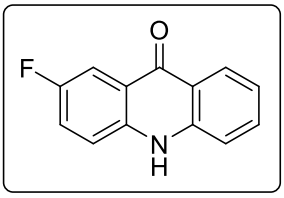
Prepared according to general procedure C. Yield: 51%. ^{1}H NMR (400 MHz, DMSO d6) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.21 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.7, 140.8, 133.4, 126.0, 121.0, 120.4, 117.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}NO$ $[M+H]^+$ 196.0762, found 196.0765.



3-methylacridin-9(10H)-one (6i):

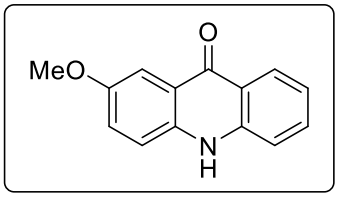
Prepared according to the general procedure C. Yield: 45%. ^{1}H NMR (400 MHz, DMSO-d6) δ 11.59 (s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd,

J = 8.4, 7.0, 1.5 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.20 (m, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.4, 143.8, 141.0, 140.8, 133.2, 126.0, 125.9, 122.8, 120.8, 120.5, 118.6, 117.2, 116.5, 21.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0919, found 210.0909.



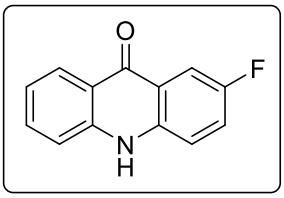
2-fluoroacridin-9(10H)-one (6j):

Prepared according to the general procedure C. Yield: 47%. ^{1}H NMR (400 MHz, DMSO-d6) δ 11.87 (s, 1H), 8.25 – 8.19 (m, 1H), 7.87 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.75 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.25 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.1, 156.8 (d, *J* = 239.7 Hz), 140.7, 137.6, 133.6, 125.8, 122.3 (d, *J* = 25.4 Hz), 121.2, 120.9 (d, *J* = 6.5 Hz), 119.9 (d, *J* = 7.8 Hz), 119.5, 117.4, 109.6 (d, *J* = 22.0 Hz). HRMS (ESI) *m/z* calcd for $C_{13}H_9NOF$ $[M+H]^+$ 214.0668, found 214.0665.



2-methoxyacridin-9(10H)-one (6k):

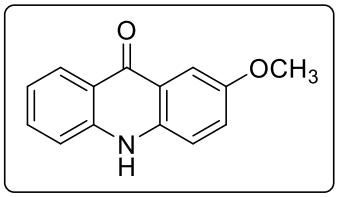
Prepared according to the general procedure C. Yield: 41%. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.22 (d, *J* = 7.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.63 (d, *J* = 2.9 Hz, 1H), 7.52 (dd, *J* = 8.7, 3.1 Hz, 2H), 7.40 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.22 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.0, 153.9, 140.4, 135.7, 133.0, 125.9, 124.2, 121.0, 120.6, 119.6, 119.1, 117.2, 104.9, 55.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0868, found 226.0851.



2-fluoroacridin-9(10H)-one (6l):

Prepared according to the general procedure C. Yield: 48%. ^{1}H NMR (400 MHz, DMSO-d6) δ 11.87 (s, 1H), 8.25 – 8.19 (m, 1H), 7.87 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.75

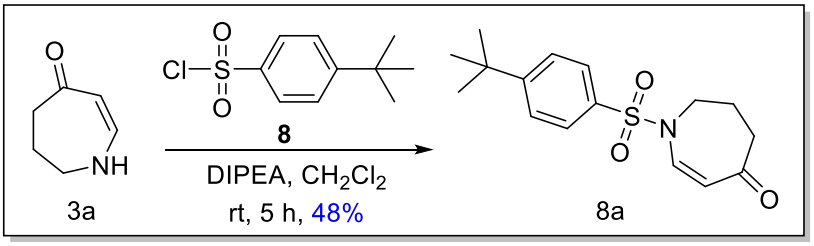
(ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.55 (d, J = 8.3 Hz, 1H), 7.30 – 7.25 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.1, 156.8 (d, J = 239.7 Hz), 140.7, 137.6, 133.6, 125.8, 122.3 (d, J = 25.4 Hz), 121.2, 120.9 (d, J = 6.5 Hz), 119.9 (d, J = 7.8 Hz), 119.5, 117.4, 109.6 (d, J = 22.0 Hz). HRMS (ESI) *m/z* calcd for $C_{13}H_9NOF$ $[M+H]^+$ 214.0668, found 214.0665.



2-methoxyacridin-9(10H)-one (6m):

Prepared according to the general procedure C. Yield: 56%. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.22 (d, J = 7.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.63 (d, J = 2.9 Hz, 1H), 7.52 (dd, J = 8.7, 3.1 Hz, 2H), 7.40 (dd, J = 9.0, 3.0 Hz, 1H), 7.22 (dd, J = 11.1, 3.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 176.0, 153.9, 140.4, 135.7, 133.0, 125.9, 124.2, 121.0, 120.6, 119.6, 119.1, 117.2, 104.9, 55.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0868, found 226.0851.

2.7 Late-stage transformations of the ring expansion products

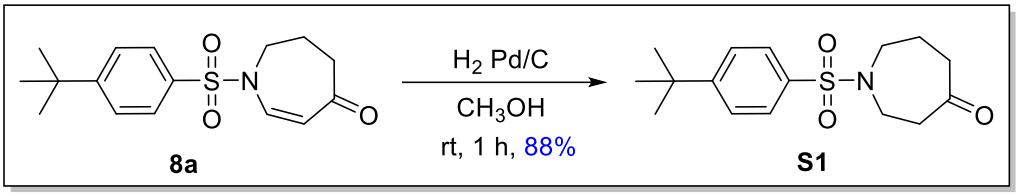


To a solution of enaminone product **3a** (111.1 mg, 1.00 mmol, 1.00 eq) and *N*, *N*-Diisopropylethylamine (DIPEA, 0.348 mL, 2.00 mmol, 2.00 eq) in CH_2Cl_2 (5 mL) was added 4-(tert-Butyl)benzenesulphonyl chloride (349.1 mg, 1.50 mmol, 1.50 eq). The reaction mixture was stirred for 5 h at room temperature and quenched with a saturated aqueous NH_4Cl solution (10 mL). After separation of the layers, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **8a** (146.3 mg, 0.476 mmol, 48% yield) as white solid.

1-((4-(tert-butyl)phenyl)sulfonyl)-1,5,6,7-tetrahydro-4H-azepin-4-one (8a):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.36

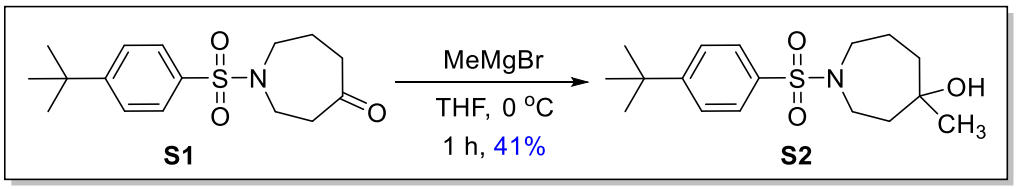
(d, J = 10.8 Hz, 1H), 5.29 (d, J = 10.7 Hz, 1H), 3.78 – 3.70 (m, 2H), 2.61 (t, J = 6.4 Hz, 2H), 2.00 (dt, J = 11.9, 6.1 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 158.2, 136.4, 134.7, 127.1, 126.8, 109.2, 49.1, 42.8, 35.5, 31.1, 22.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{22}NO_3S$ $[M+H]^+$ 308.1320, found 308.1322.



To a solution of **8a** (78.3 mg, 0.25 mmol, 1.00 eq) in CH_3OH (5 mL) was added 10% Pd/C (100 mg). The reaction mixture was stirred for 1 h at room temperature under 1 atm H_2 atmosphere. the reaction was filtered and concentrated under reduced pressure. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **S1** (69.0 mg, 0.223 mmol, 88% yield) as white solid.

1-((4-(tert-butyl)phenyl)sulfonyl)azepan-4-one (S1)：

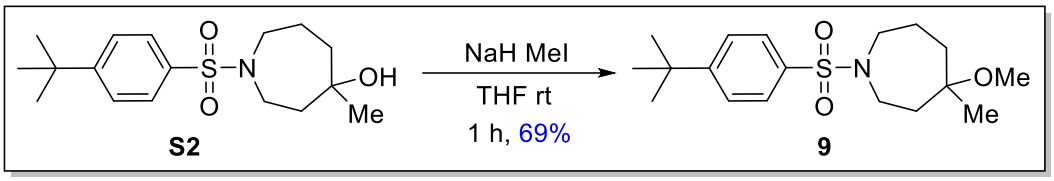
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H), 3.47 – 3.36 (m, 4H), 2.75 – 2.67 (m, 2H), 2.63 – 2.56 (m, 2H), 1.91 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 156.7, 135.8, 127.0, 126.4, 51.0, 45.0, 44.7, 42.7, 35.3, 31.2, 25.1. HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NO_3S$ $[M+H]^+$ 310.1477, found 310.1475.



A modified procedure adopted from literature was used[3]. **S1** (69.0 mg, 0.22 mmol, 1.00 eq) was dissolved in anhydrous Et_2O (5 mL) and cooled to 0 °C and MeMgBr (1.0 M in Et_2O, 0.44 mL; 0.44 mmol; 2.0 eq) was added dropwise and the obtained white suspension was stirred for 1 h. The reaction was quenched with concentrated aqueous NH_4Cl (10 mL) solution and extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure.. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **S2** (29.9 mg, 0.092 mmol, 41% yield) as colorless oil.

1-((4-(tert-butyl)phenyl)sulfonyl)-4-methylazepan-4-ol (S2)：

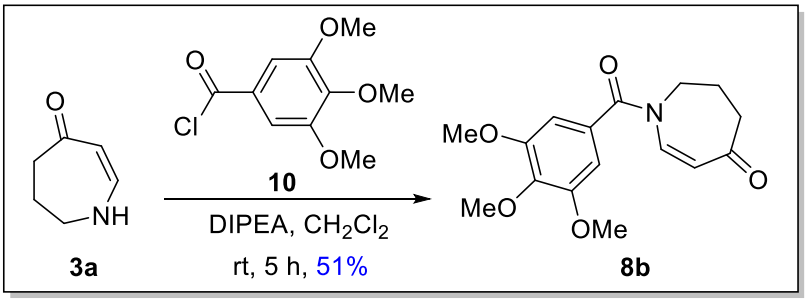
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 3.42 (t, *J* = 13.6 Hz, 2H), 3.14 (t, *J* = 9.6 Hz, 2H), 2.03 – 1.60 (m, 6H), 1.33 (s, 9H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.0, 127.0, 126.1, 71.6, 47.9, 43.5, 42.4, 39.7, 35.2, 31.6, 31.2, 21.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{28}NO_3S$ $[M+H]^+$ 326.1790, found 326.1791.



To a solution of enaminone product **S2** (41.3 mg, 0.13 mmol, 1.00 eq) in THF (5 mL) was added NaH (60% dispersion in mineral oil, 10.4 mg, 0.26 mmol, 2.00 eq) and Iodomethane (36.9 mg, 0.26 mmol, 2.00 eq). The reaction mixture was stirred for 1 h at room temperature and quenched with a saturated aqueous NH_4Cl solution (10 mL). After separation of the layers, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **9** (30.3 mg, 0.089 mmol, 69% yield) as white solid.

1-((4-(tert-butyl)phenyl)sulfonyl)-4-methoxy-4-methylazepane (9):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 3.58 – 3.44 (m, 2H), 3.10 (s, 3H), 3.06 – 2.94 (m, 2H), 1.94 – 1.75 (m, 3H), 1.72 – 1.53 (m, 3H), 1.32 (s, 9H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 136.2, 126.9, 126.0, 74.9, 48.8, 47.9, 41.8, 41.3, 35.4, 35.2, 31.2, 25.3, 20.8. HRMS (ESI) *m/z* calcd for $C_{18}H_{30}NO_3S$ $[M+H]^+$ 340.1946, found 340.1949.

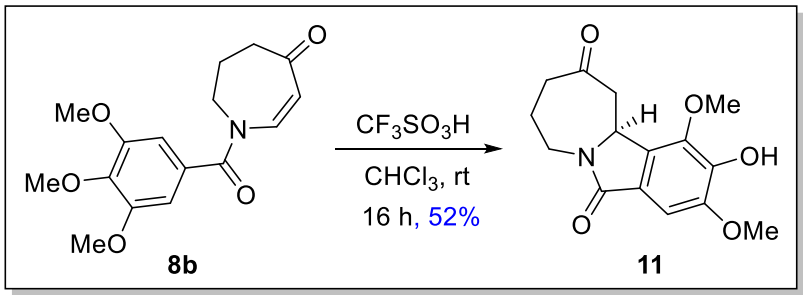


To a solution of enaminone product **3a** (222.3 mg, 2.00 mmol, 1.00 eq) and *N*, *N*-Diisopropylethylamine (DIPEA, 0.7 mL, 4.00 mmol, 2.00 eq) in CH_2Cl_2 (5 mL) was added 3,4,5-Trimethoxybenzoyl Chloride (691.9 mg, 3.00 mmol, 1.50 eq). The reaction mixture was stirred for 5 h at room temperature and quenched with a saturated aqueous

NH_4Cl solution (10 mL). After separation of the layers, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **8b** (311.4 mg, 1.021 mmol, 51% yield) as white solid.

1-(3,4,5-trimethoxyphenyl)-1,5,6,7-tetrahydro-4H-azepin-4-one (8b):

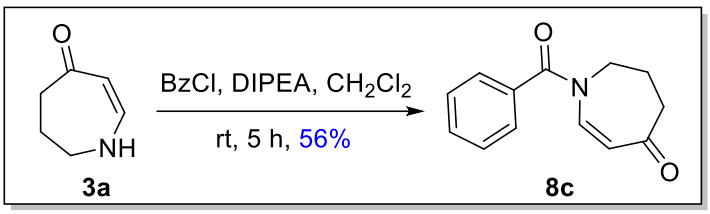
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 10.3 Hz, 1H), 6.71 (s, 2H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.05 (dd, *J* = 11.3, 7.0 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 6H), 2.72 (t, *J* = 6.5 Hz, 2H), 2.16 – 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 170.8, 153.4, 141.0, 139.6, 128.7, 110.4, 106.0, 61.0, 56.4, 47.8, 42.7, 23.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}NO_5$ $[M+H]^+$ 306.1341, found 306.1333.



A modified procedure adopted from literature was used[4]. To a solution of the enaminone **8b** (122.1 mg, 0.40 mmol, 1.00 eq) dissolved in $CHCl_3$ (5 mL) trifluoromethanesulfonic acid (0.88 mL, 10.00 mmol, 25.0 eq) was added slowly. The reaction was stirred for 16 h before it was poured into ice water. The aqueous phase was extracted three times with EtOAc (50 mL), the organic phases were combined and dried over anhydrous $MgSO_4$. After concentration of the organic phase under reduced pressure, the crude material was subjected to flash column chromatography (Petroleum ether/EtOAc = 1 : 1) affording the cyclized product **11** (60.8 mg, 0.209 mmol, 52% yield) as white solid.

(S)-2-hydroxy-1,3-dimethoxy-8,9,11,11a-tetrahydro-5H-azepino[2,1-a]isoindole-5,10(7H)-dione (11):

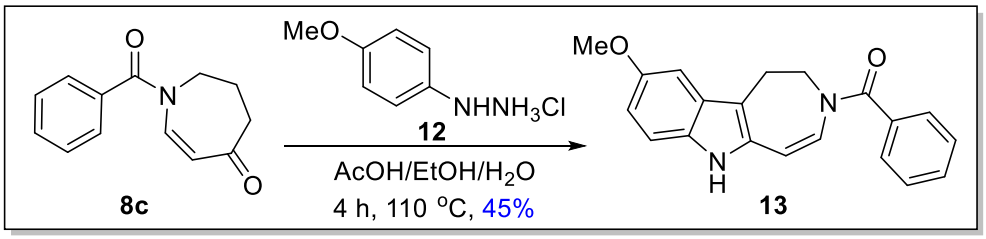
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.10 (s, 1H), 4.69 – 4.57 (m, 2H), 4.00 (s, 3H), 3.94 (s, 3H), 3.38 (dd, *J* = 14.8, 2.5 Hz, 1H), 3.09 (dd, *J* = 18.3, 6.7 Hz, 1H), 2.74 (dd, *J* = 9.2, 4.5 Hz, 2H), 2.51 (dd, *J* = 14.7, 10.7 Hz, 1H), 2.14 – 2.02 (m, 1H), 2.00 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.28, 168.0, 149.2, 141.8, 141.7, 129.5, 122.8, 100.8, 60.5, 56.8, 56.2, 47.7, 43.9, 43.0, 24.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NO_5$ $[M+H]^+$ 292.1185, found 292.1194.



To a solution of enaminone product **3a** (146.7 mg, 1.32 mmol, 1.00 eq) and *N*, *N*-Diisopropylethylamine (DIPEA, 0.46 mL, 2.64 mmol, 2.00 eq.) in CH_2Cl_2 (5 mL) was added Benzoyl chloride (0.23 mL, 1.98 mmol，1.50 eq). The reaction mixture was stirred for 5 h at room temperature and quenched with a saturated aqueous NH_4Cl solution (10 mL). After separation of the layers, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 1 : 1) affording product **8a** (158.6 mg, 0.737 mmol, 56% yield) as white solid.

1-benzoyl-1,5,6,7-tetrahydro-4H-azepin-4-one (8c):

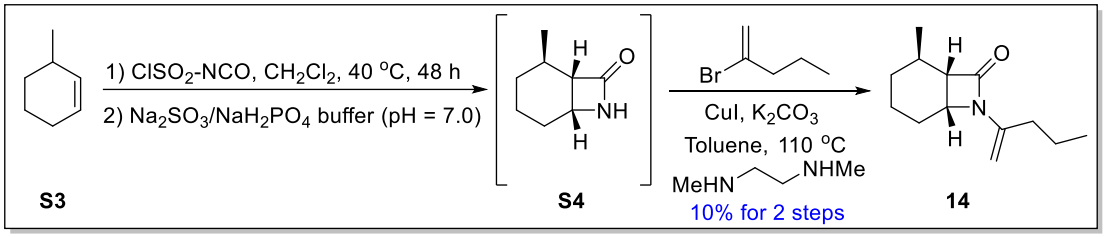
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.48 – 7.42 (m, 3H), 7.17 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.12 – 4.04 (m, 2H), 2.73 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 171.2, 139.6, 133.8, 131.6, 128.8, 128.5, 110.7, 47.7, 42.7, 23.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1025, found 216.1025.



A modified procedure adopted from literature was used[4]. An oven-dried screw-cap vial was loaded with **8c** (81.7 mg, 0.380 mmol, 1.00 eq.), (4-methoxyphenyl)hydrazine hydrochloride **12** (79.3 mg, 0.456 mmol, 1.20 eq.) and a solvent mixture of AcOH/EtOH/H_2O (4 : 3.5 : 2.5, 5 mL). The reaction mixture was heated at 110 ℃ for 4 h. After cooling to room temperature, EtOAc (10 mL) was added and the organic phase was washed with saturated aqueous $NaHCO_3$ (3 × 10mL), dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude material was subjected to flash column chromatography (eluting with Petroleum ether/EtOAc = 2 : 1) affording the title compound (54.4 mg, 0.171 mmol, 45%) as a yellow solid.

(9-methoxy-1,6-dihydroazepino[4,5-b]indol-3(2H)-yl)(phenyl)methanone (13):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.45 (dq, *J* = 14.2, 7.2 Hz, 3H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 5.68 (d, *J* = 6.6 Hz, 1H), 4.28 – 4.04 (m, 2H), 3.88 (s, 3H), 3.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 135.8, 131.6, 130.8, 130.7, 129.3, 128.5, 113.0, 111.6, 104.8, 100.1 (s), 56.0, 26.9. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.79 (s, 1H), 7.49 (s, 5H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 5.87 (s, 1H), 4.13 – 3.88 (m, 2H), 3.76 (s, 3H), 3.09 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d6) δ 153.3, 135.7, 131.8, 130.5, 130.3, 128.4, 112.3, 111.6, 105.0, 99.6, 55.3, 26.2. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}N_2O_2$ $[M+H]^+$ 319.1447, found 319.1448.



A modified procedure adopted from literature was used[5]. 3-methyl-1-cyclohexene **S3** (961.7 mg, 10.00 mmol, 1.00 eq) in a round bottom flask was cooled with an ice-water bath and then treated with chlorosulfonyl isocyanate (2122.9 mg, 15.00 mmol, 1.50 eq). The reaction mixture was heated at 40 °C for 48 h. After cooling, the mixture was diluted with CH_2Cl_2 (200 mL) and poured into a cold buffer solution (400 mL) containing Na_2SO_3 (58.1 g) and Na_2HPO_4 (52.1 g). The mixture was stirred at room temperature for 48 h. After phase separation, the organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated**,** the crude product was directly used for the next step without further purification

A resealable Schlenk tube was charged with CuI (95.2mg, 0.50 mmol, 5 mol%), K_2CO_3 (2764.2 mg, 20.00 mmol, 2.0 equiv) and crude product, evacuated and backfilled with argon. *N,N'*-Dimethylethylenediamine (88.15mg, 1.00mmol, 10 mol%), 2-bromo-1-pentene (1490.3 mg, 20.00 mmol, 1.0 equiv) and toluene (1 M of vinyl bromide, 10 mL) were added under argon atmosphere. The reaction mixture was stirred at the 110 ℃ until the complete consumption of starting material was observed as indicated by TLC analysis. The reaction was cooled to room temperature, and then filtered through a plug silica gel eluting with ethyl acetate. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (eluting with Petroleum ether/EtOAc = 5 : 1) to provide the desired product **14** (200.9 mg, 0.97mmol) as yellow oil.

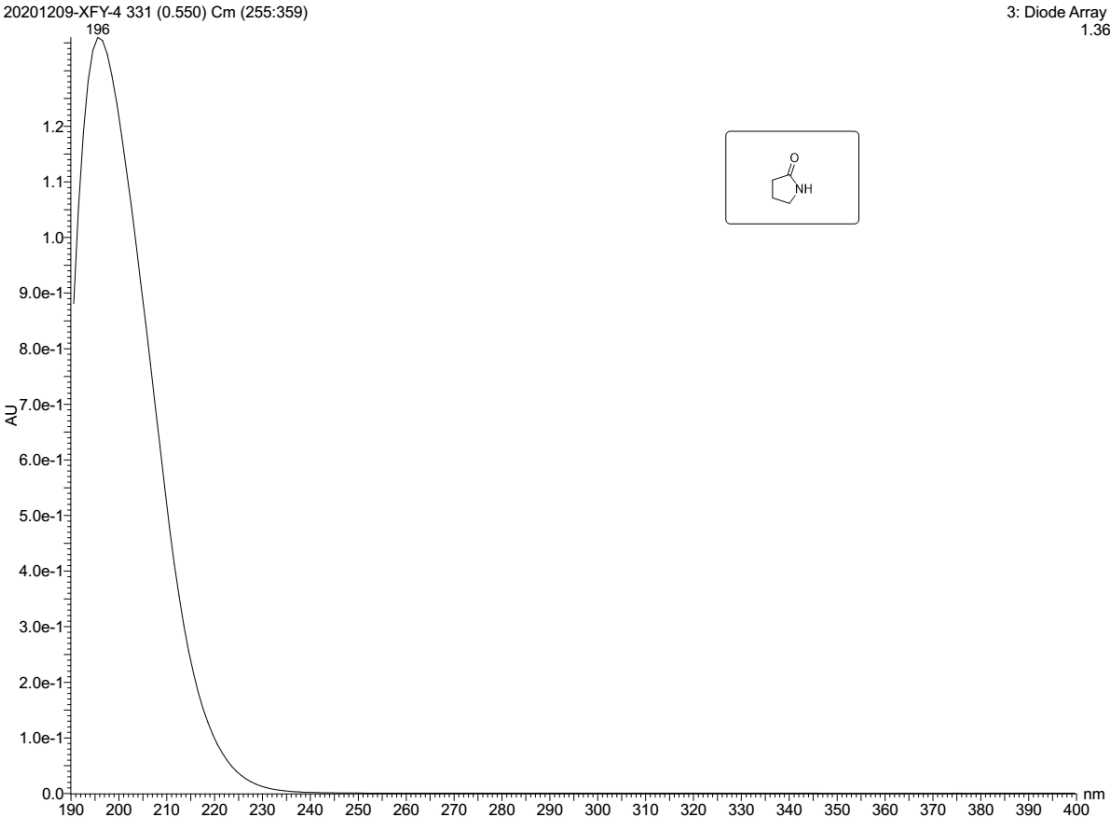
Reference

(1) L. Jiang, G. E. Job, A. Klapars and S. L. Buchwald, *Org. Lett.*, 2003, **5**, 3667-3669.
(2) R. Šebesta, M. G. Pizzuti, A. J. Boersma, A. J. Minnaard and B. L. Feringa, *Chem. Commun.*, 2005, 1711-1713.
(3) J. Zhao, X.-J. Zhao, P. Cao, J.-K. Liu and B. Wu, *Org. Lett.*, 2017, **19**, 4880-4883.
(4) P. Spieß, M. Berger, D. Kaiser and N. Maulide, *J. Am. Chem. Soc.*, 2021, **143**, 10524-10529.
(5) R. Liu, X. Chen, S. H. Gellman and K. S. Masters, *J. Am. Chem. Soc.*, 2013, **135**, 16296-16299.

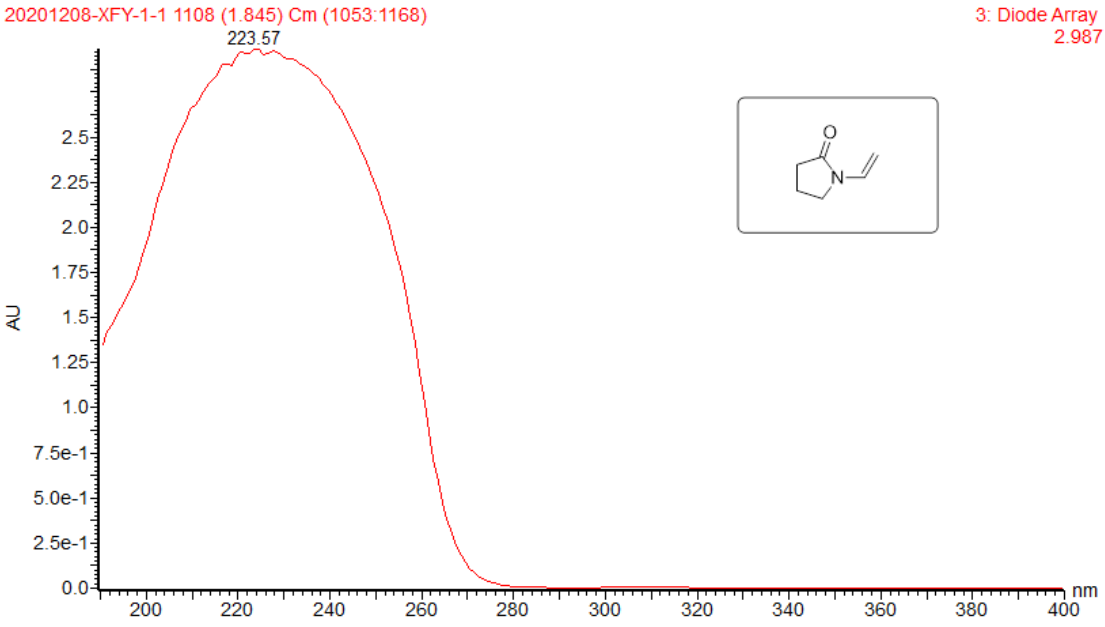
2.8 UV Spectra of Representative Compounds

The UV-Vis measurement was performed with a CH_3OH solution (0.05M) of 2-Pyrrolidinone, **1a**, **2a** and **3a**

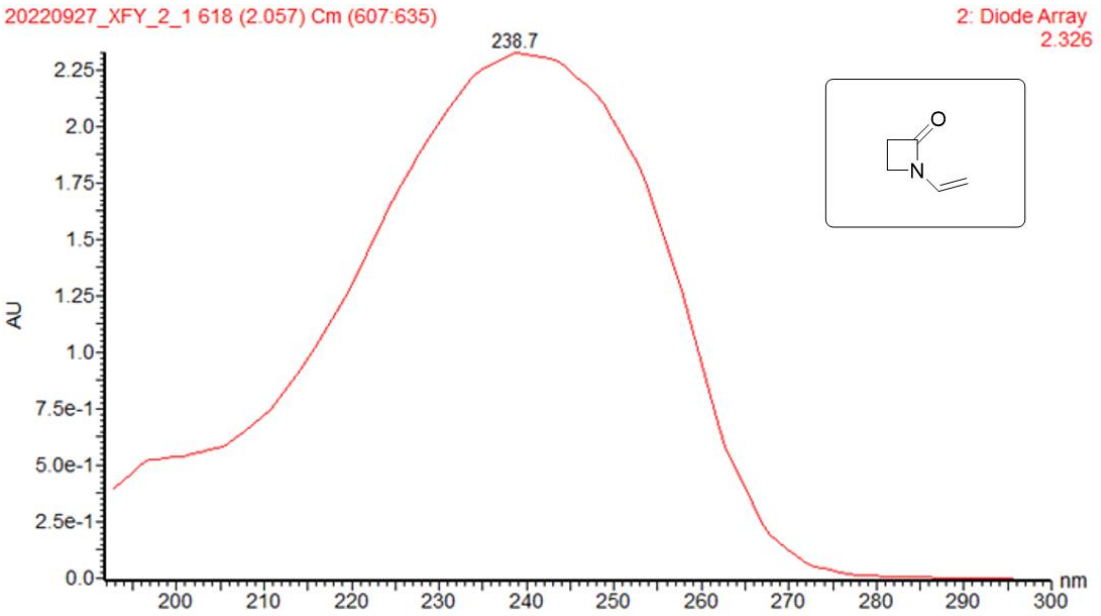
UV Spectra for 2-Pyrrolidinone



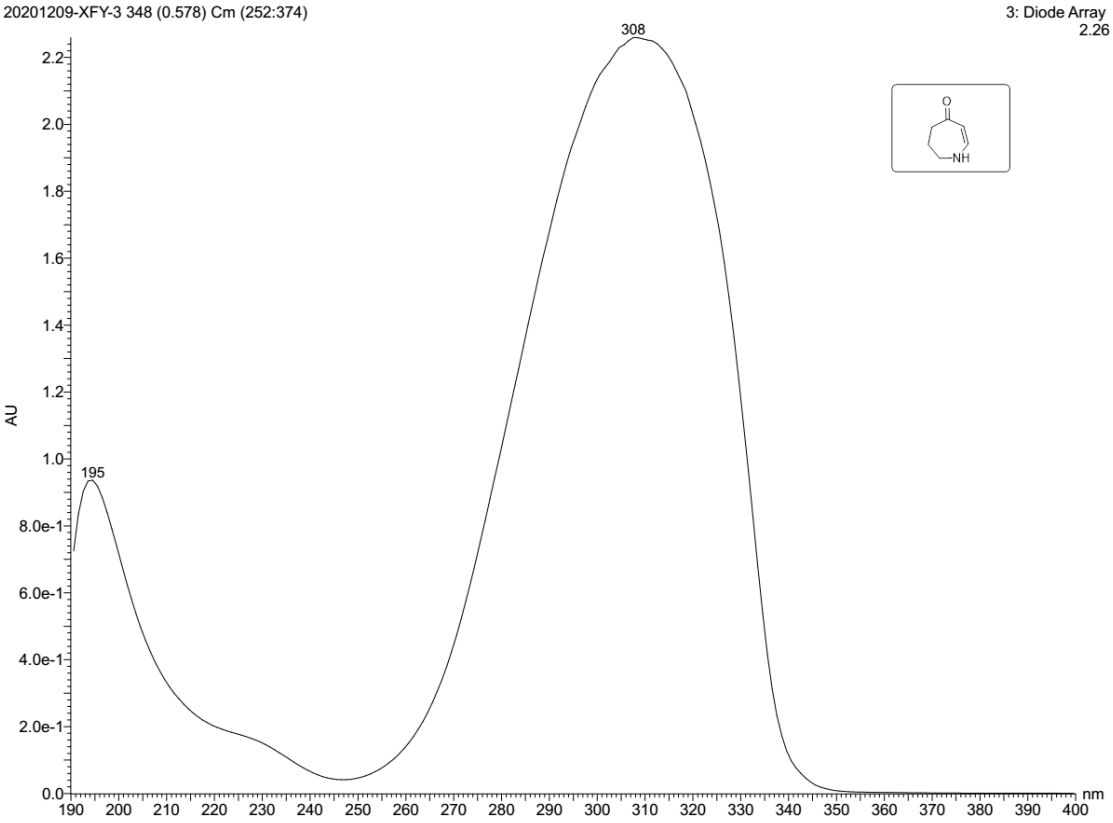
UV Spectra for 1a



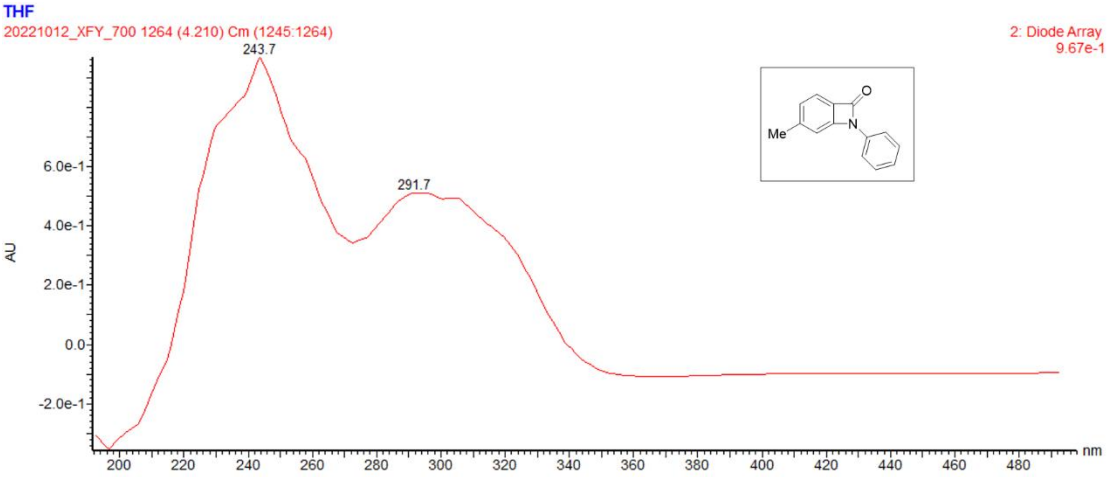
UV Spectra for 2a



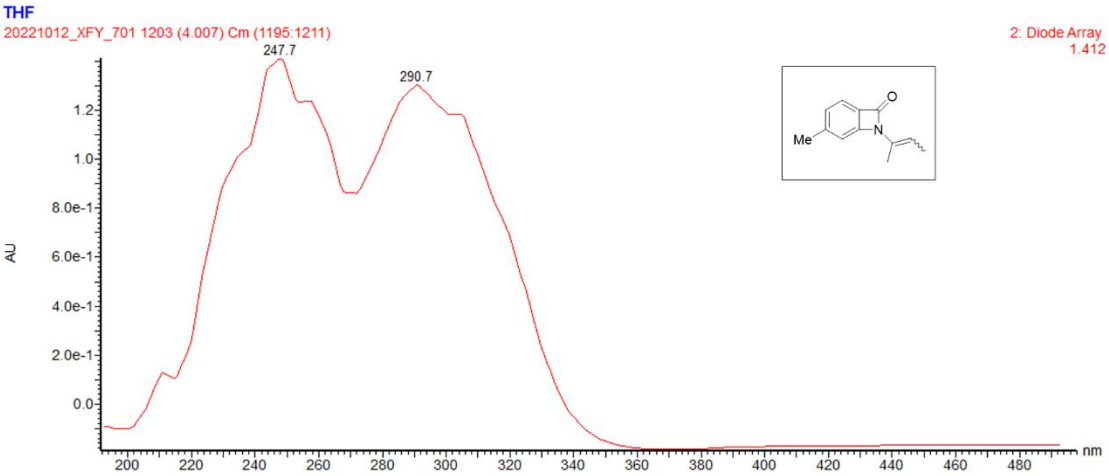
UV Spectra for 3a



UV Spectra for 5c

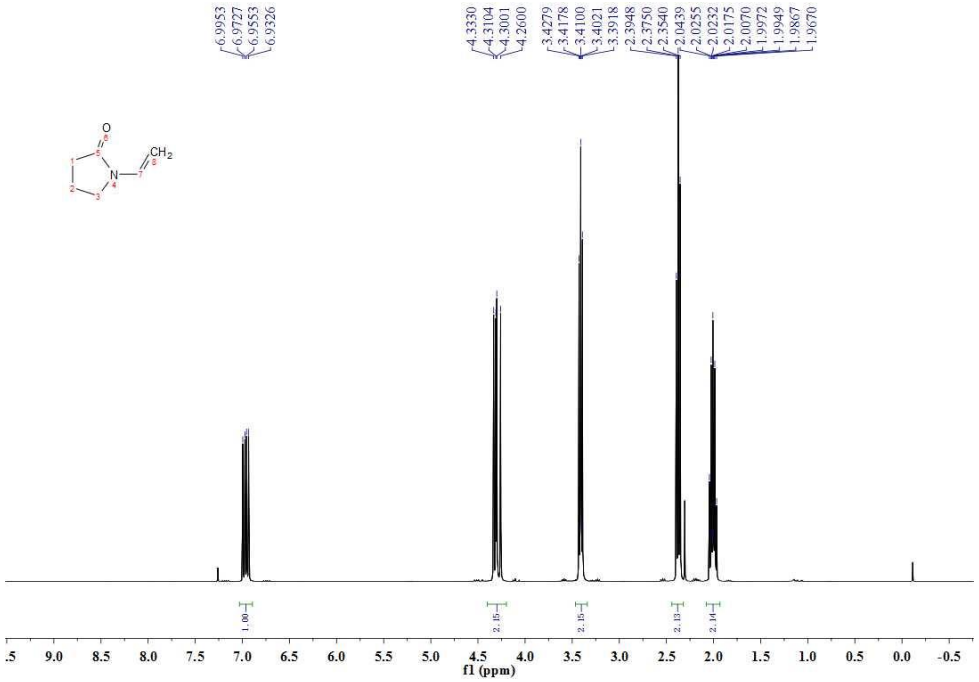


UV Spectra for 5i

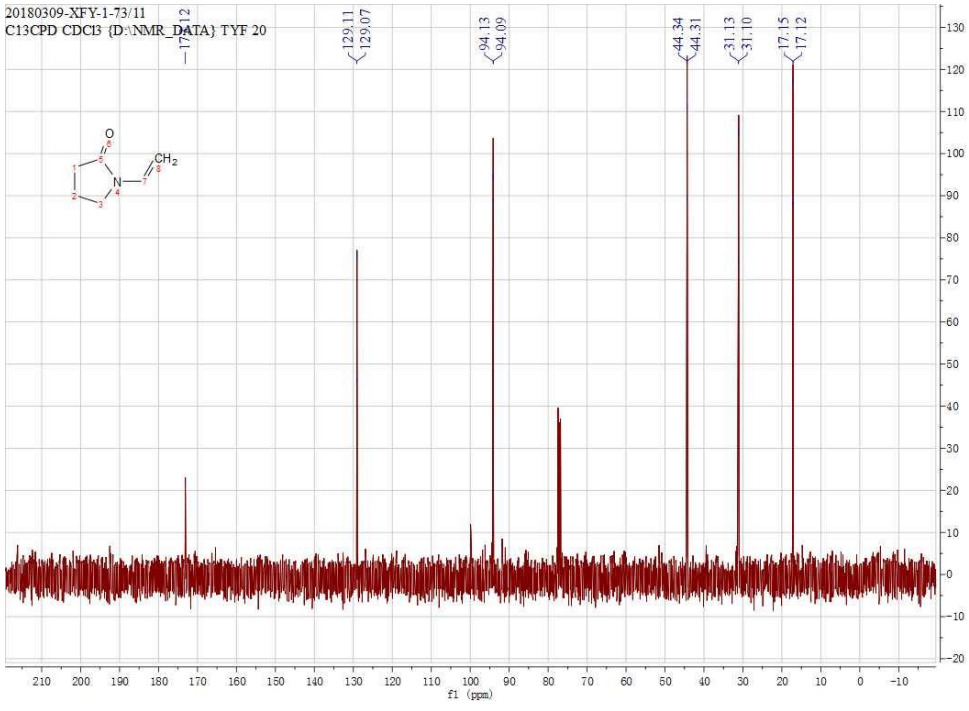


3. ^{1}H and ^{13}C NMR spectra

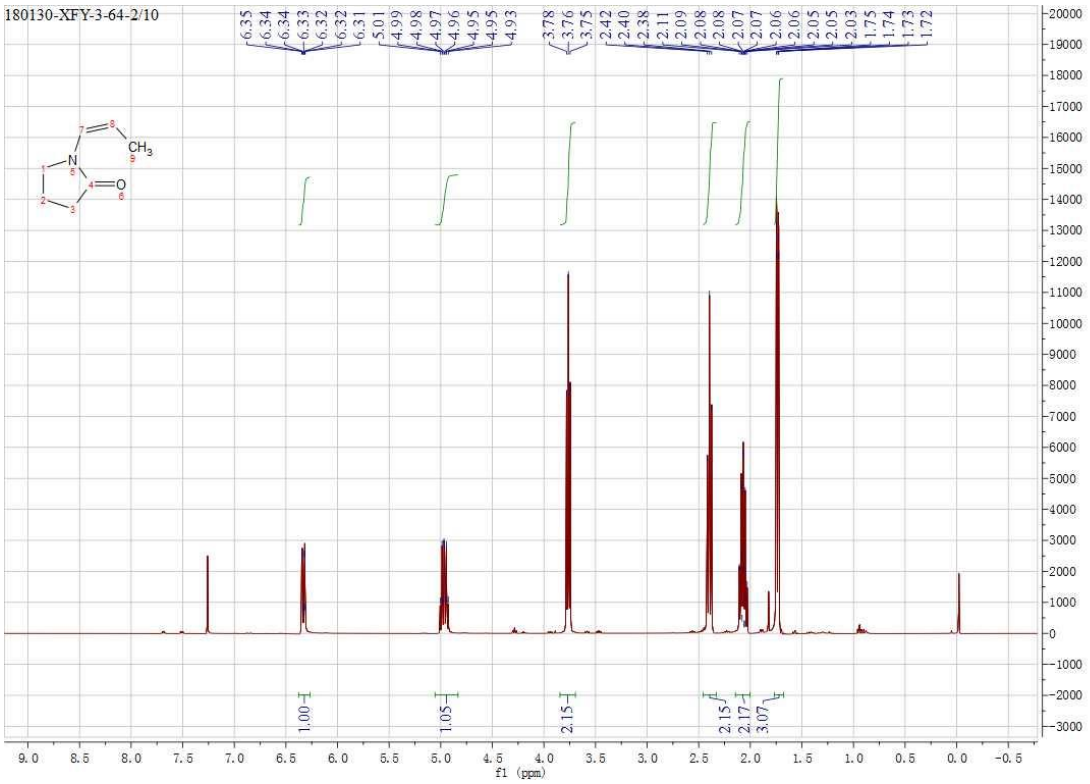
^{1}H NMR spectrum for **1a** ($CDCl_3$, 400 MHz)



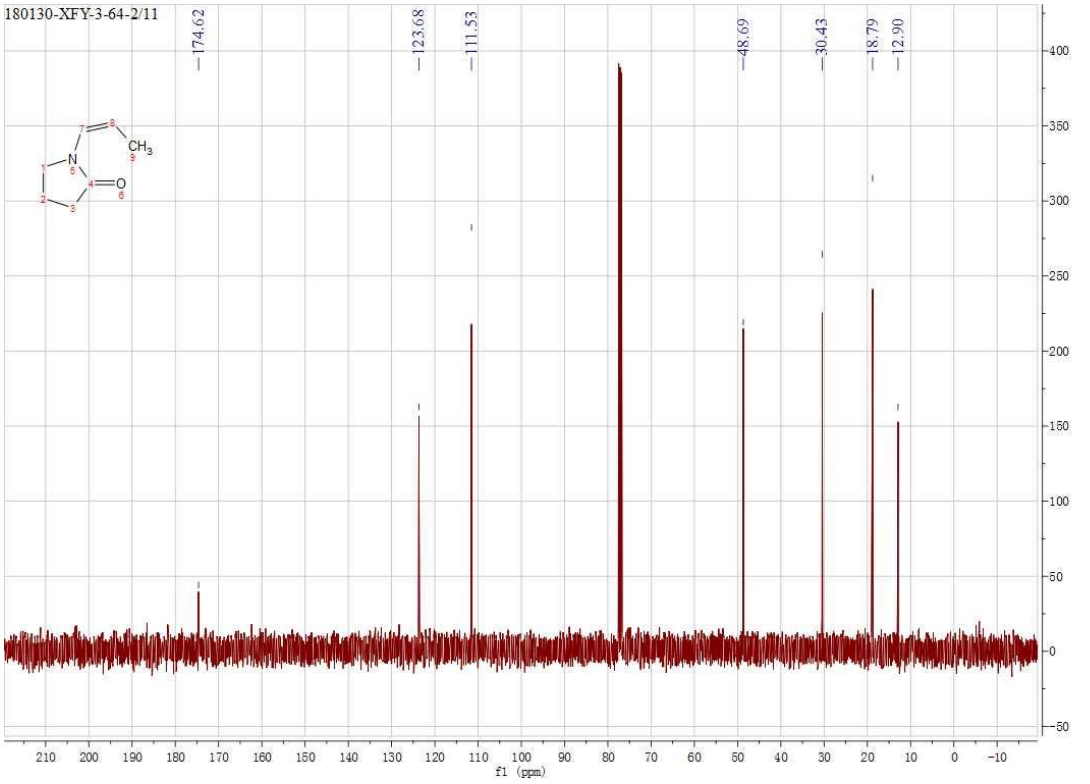
^{13}C NMR spectrum for **1a** ($CDCl_3$, 101 MHz)



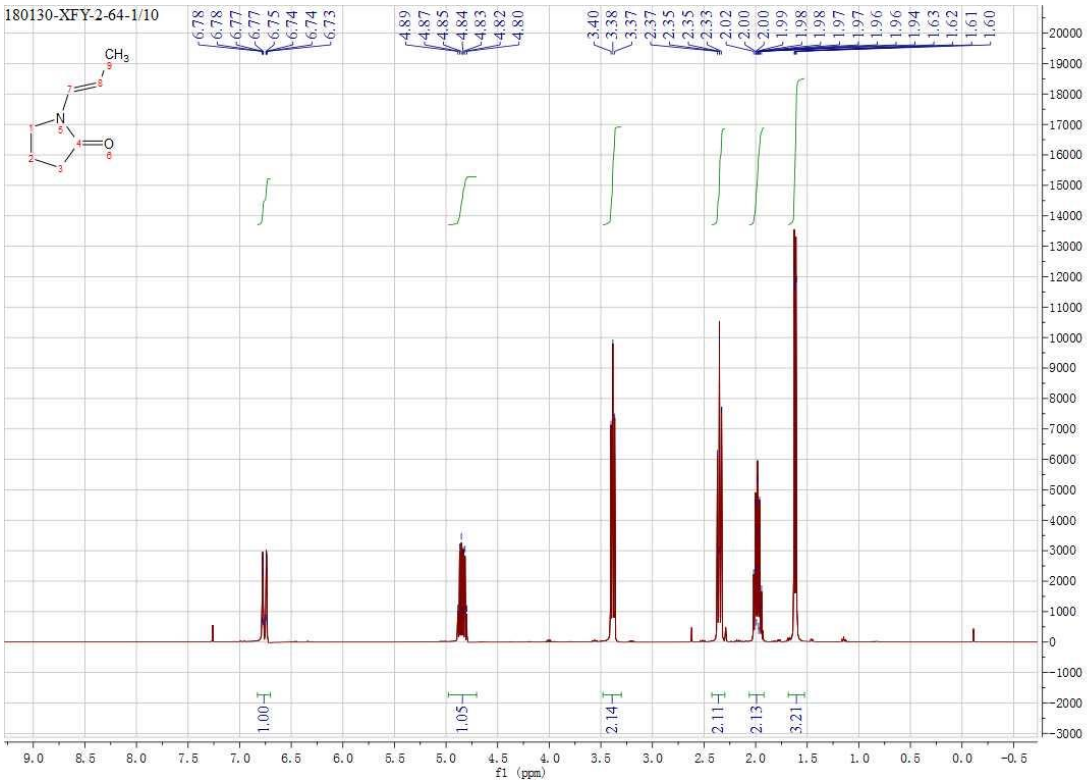
^{1}H NMR spectrum for **1b** (*cis*-isomer, $CDCl_3$, 400 MHz)



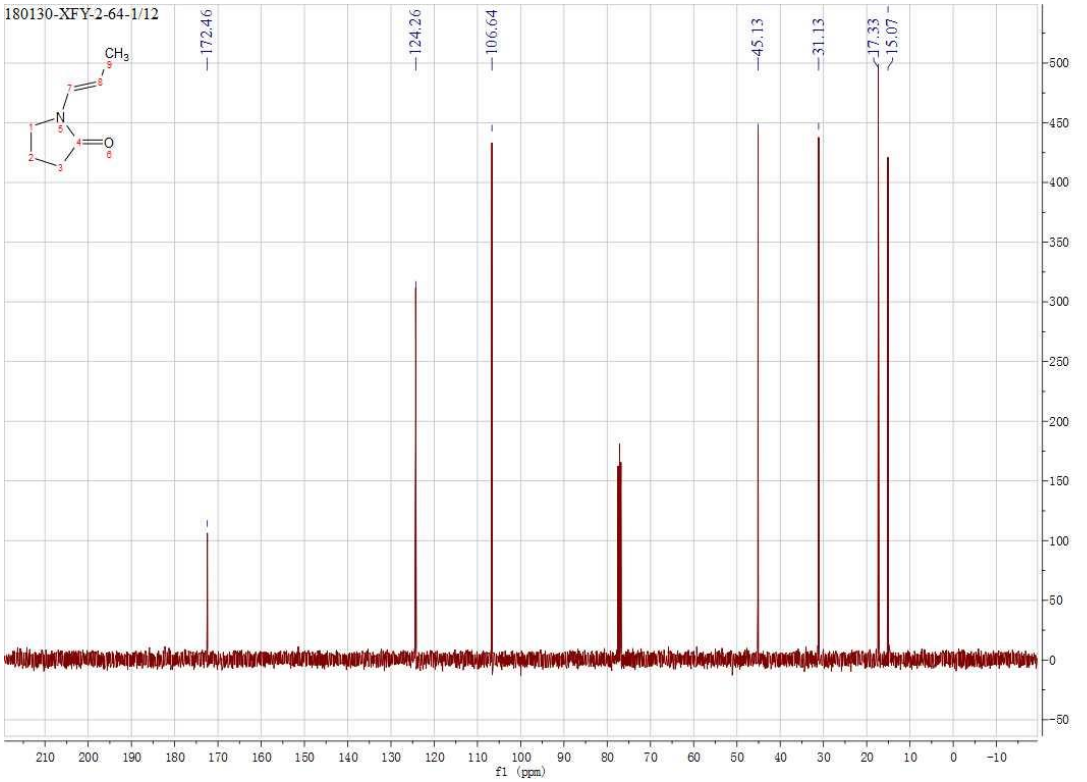
^{13}C NMR spectrum for **1b** (*cis*-isomer,$CDCl_3$, 101 MHz)



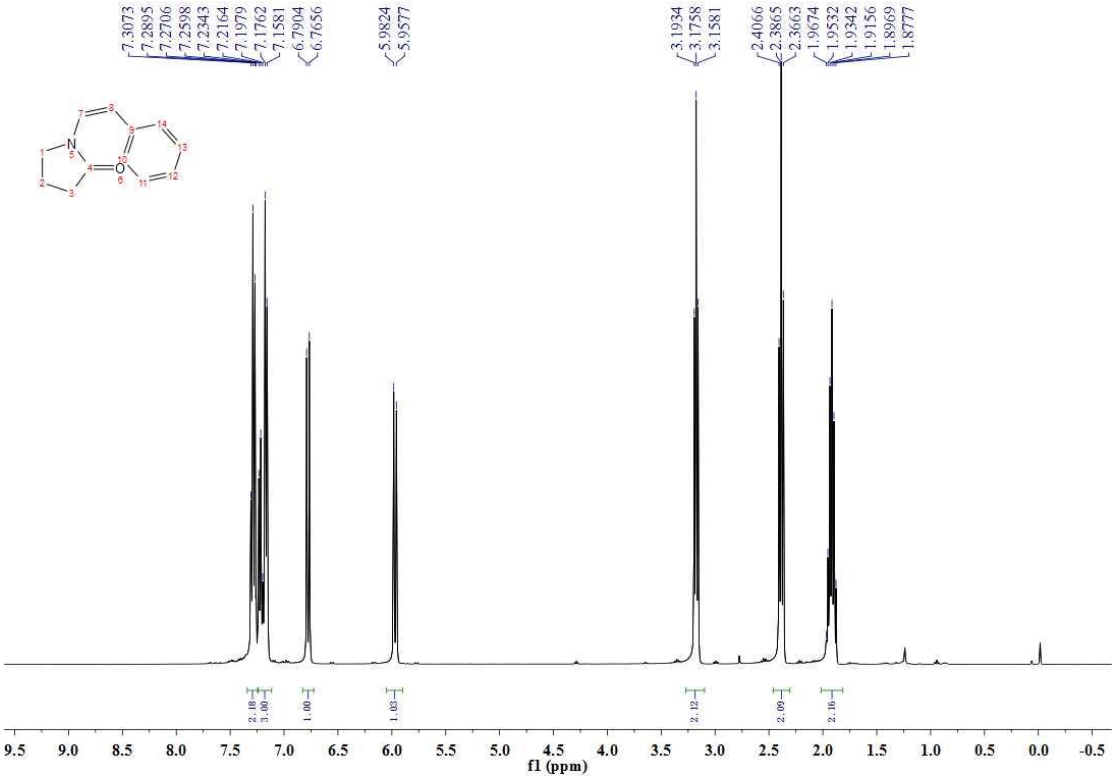
^{1}H NMR spectrum for **1b** (*trans*-isomer, $CDCl_3$, 400 MHz)



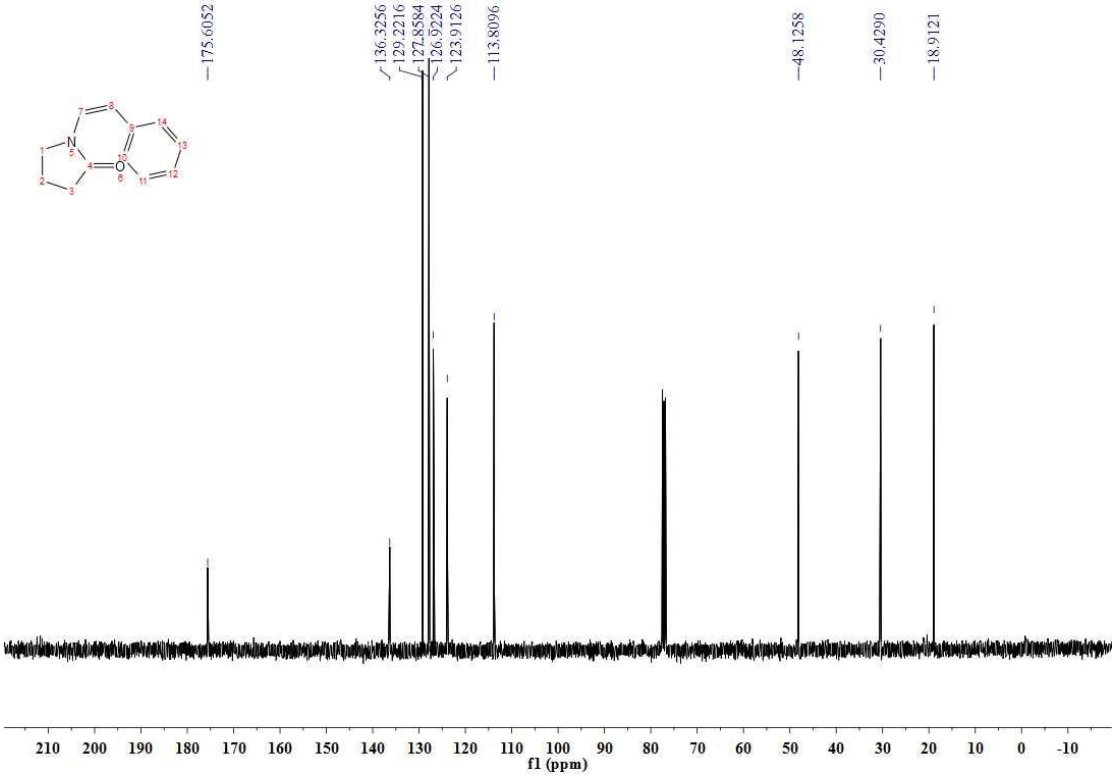
^{13}C NMR spectrum for **1b** (*trans*-isomer, $CDCl_3$, 101 MHz)



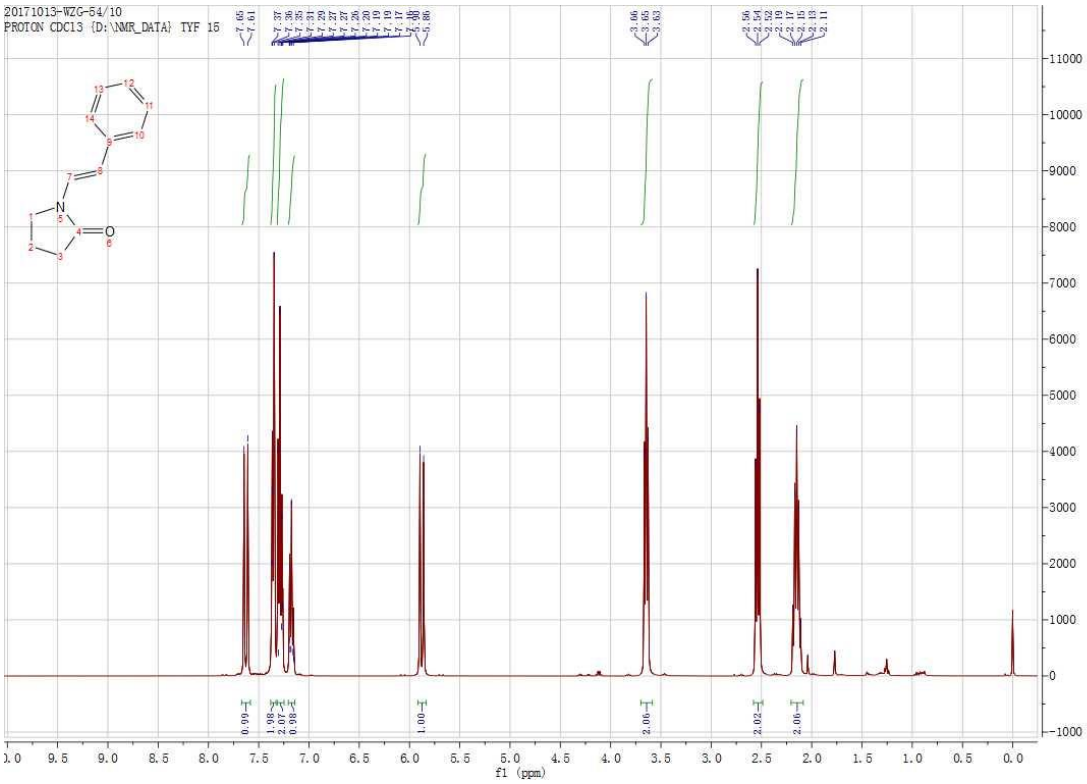
^{1}H NMR spectrum for **1c** (*cis*-isomer, $CDCl_3$, 400 MHz)



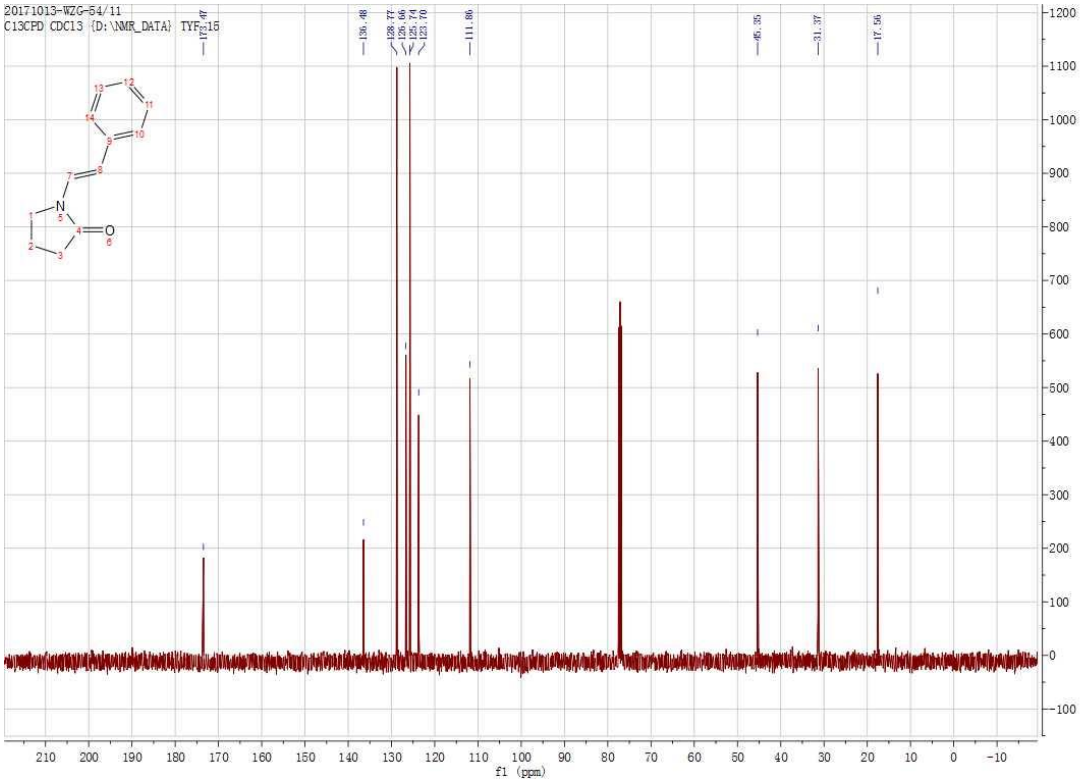
^{13}C NMR spectrum for **1c** (*cis*-isomer, $CDCl_3$, 101 MHz)



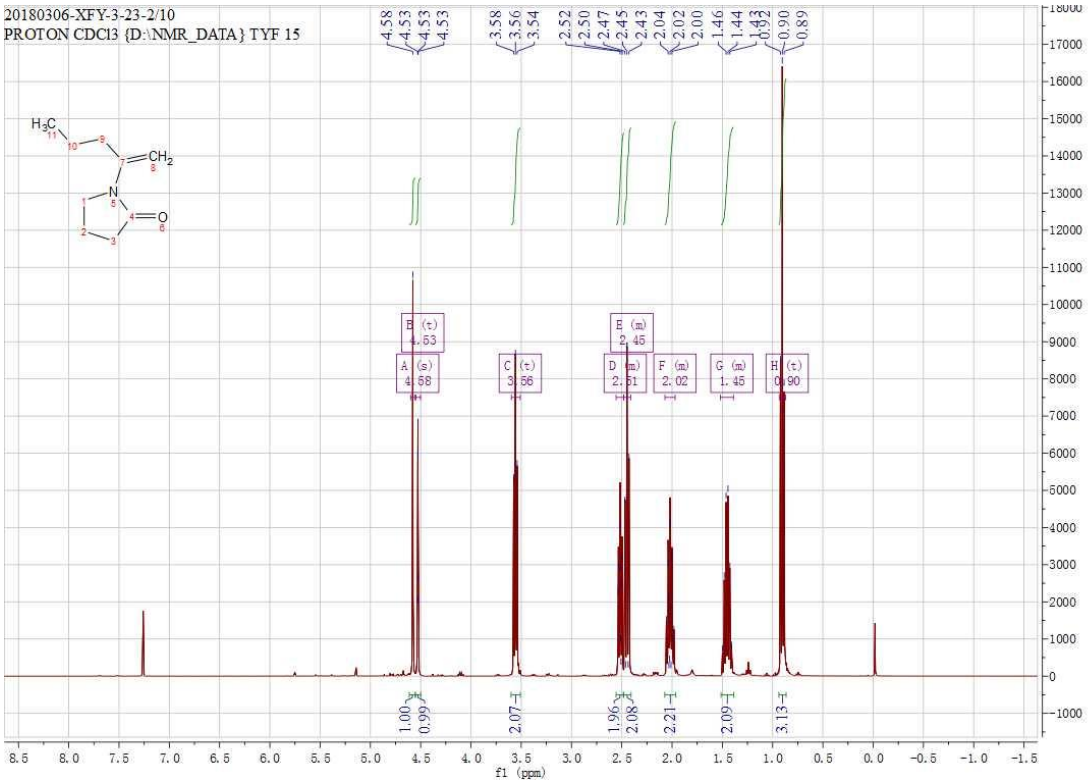
^{1}H NMR spectrum for **1c** (*trans*-isomer, $CDCl_3$, 400 MHz)



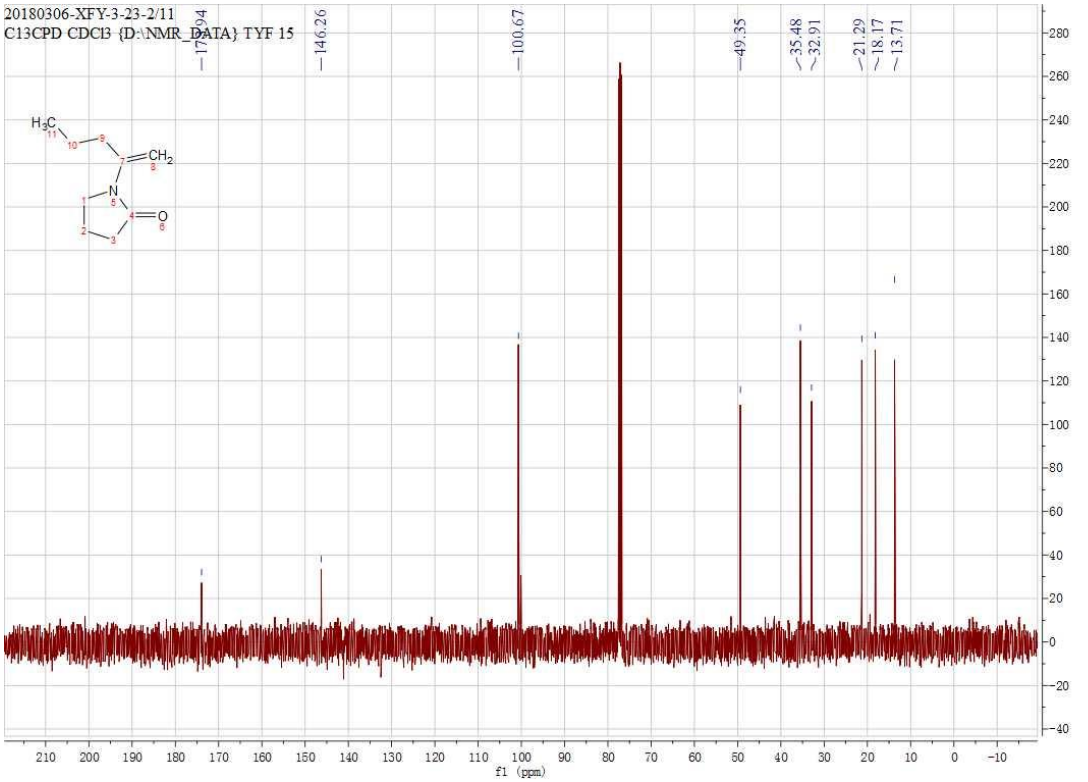
^{13}C NMR spectrum for **1c** (*trans*-isomer, $CDCl_3$, 101 MHz)



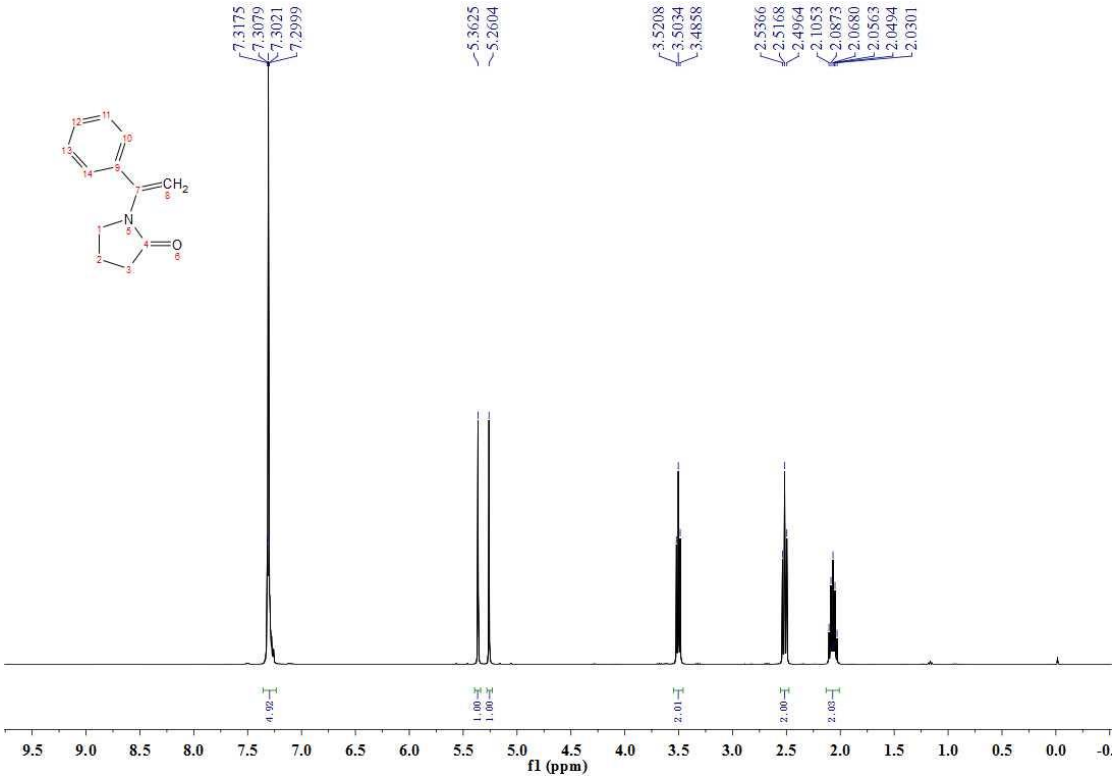
^{1}H NMR spectrum for **1d** ($CDCl_3$, 400 MHz)



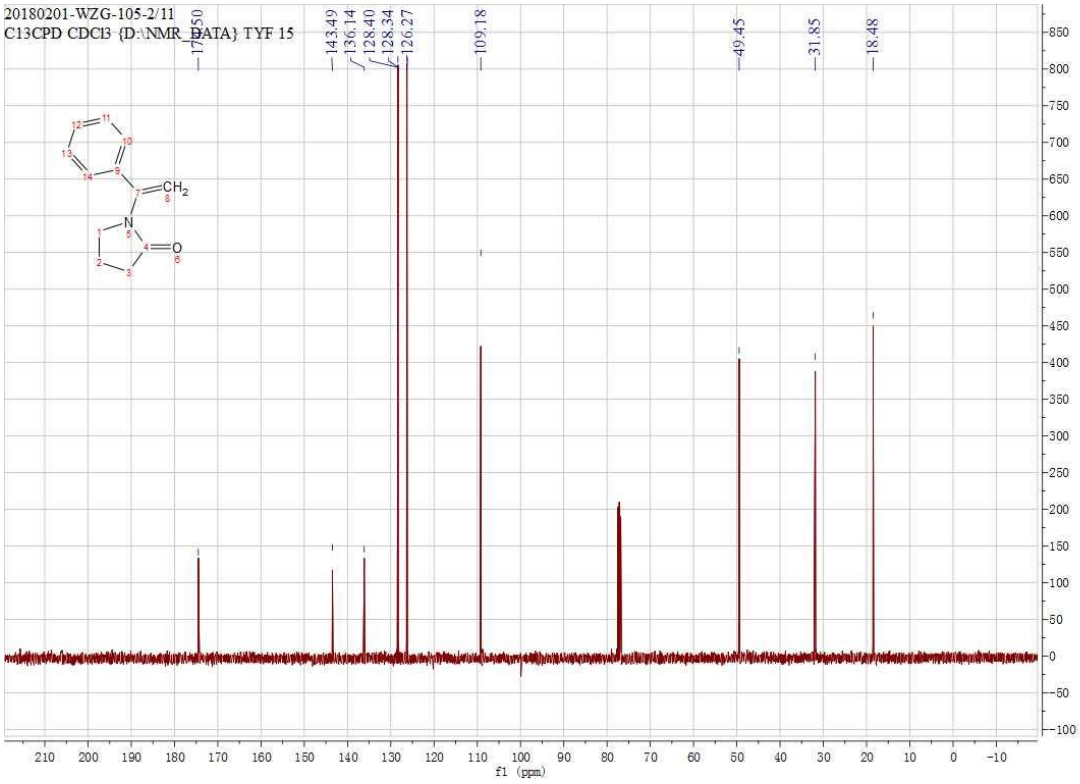
^{13}C NMR spectrum for **1d** ($CDCl_3$, 101 MHz)



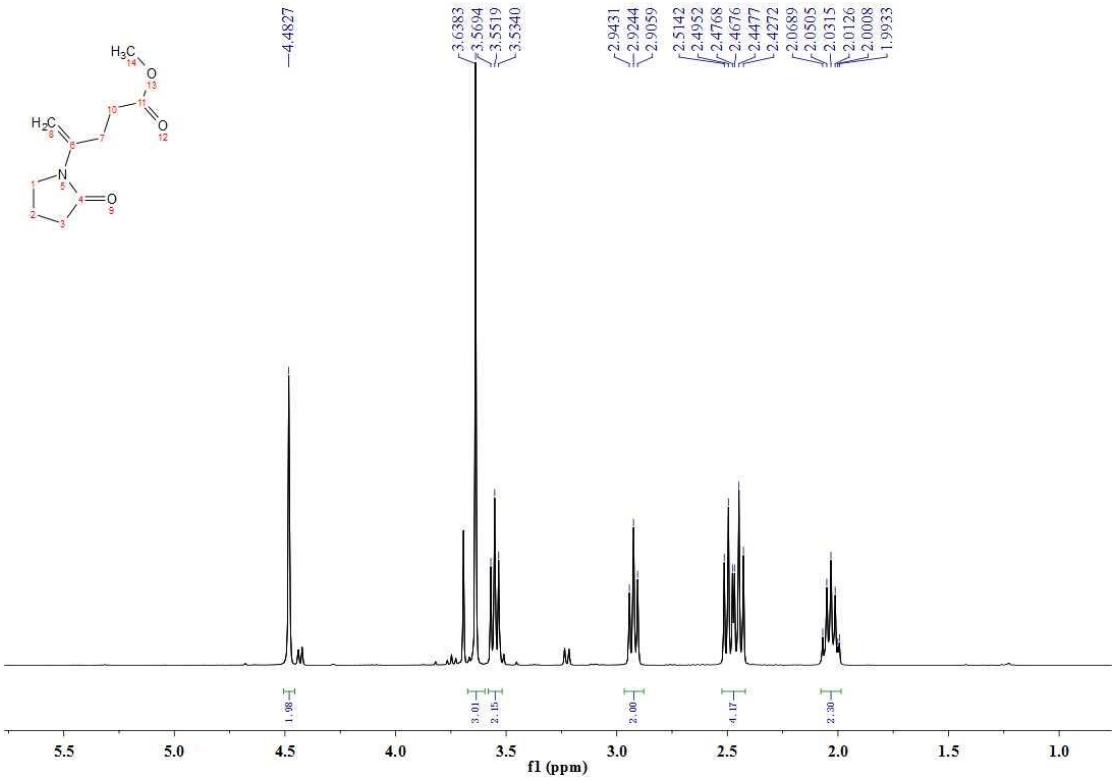
^{1}H NMR spectrum for **1e** ($CDCl_3$, 400 MHz)



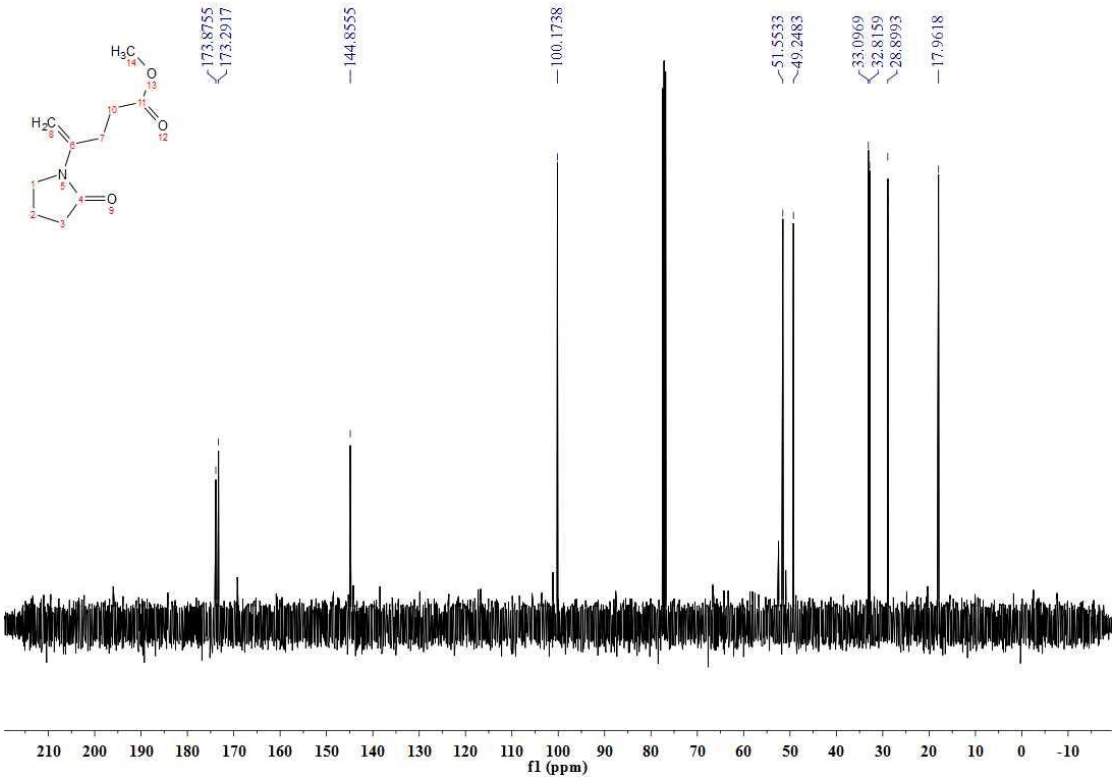
^{13}C NMR spectrum for **1e** ($CDCl_3$, 101 MHz)



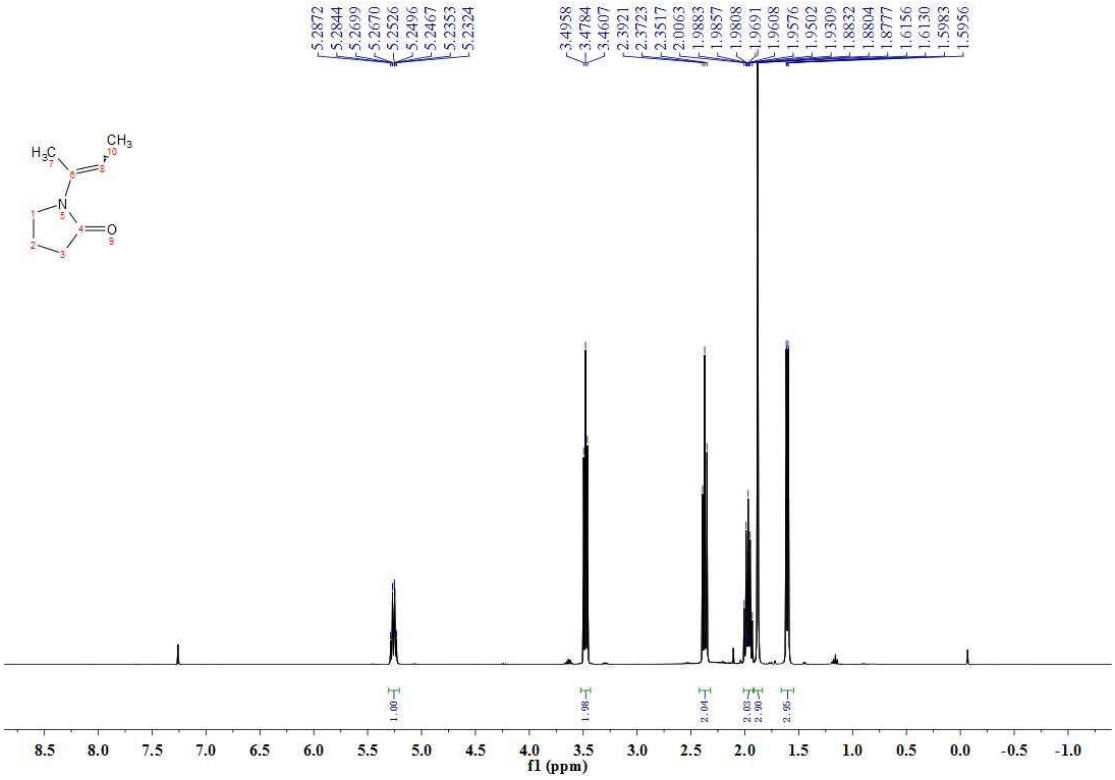
^{1}H NMR spectrum for **1f** ($CDCl_3$, 400 MHz)



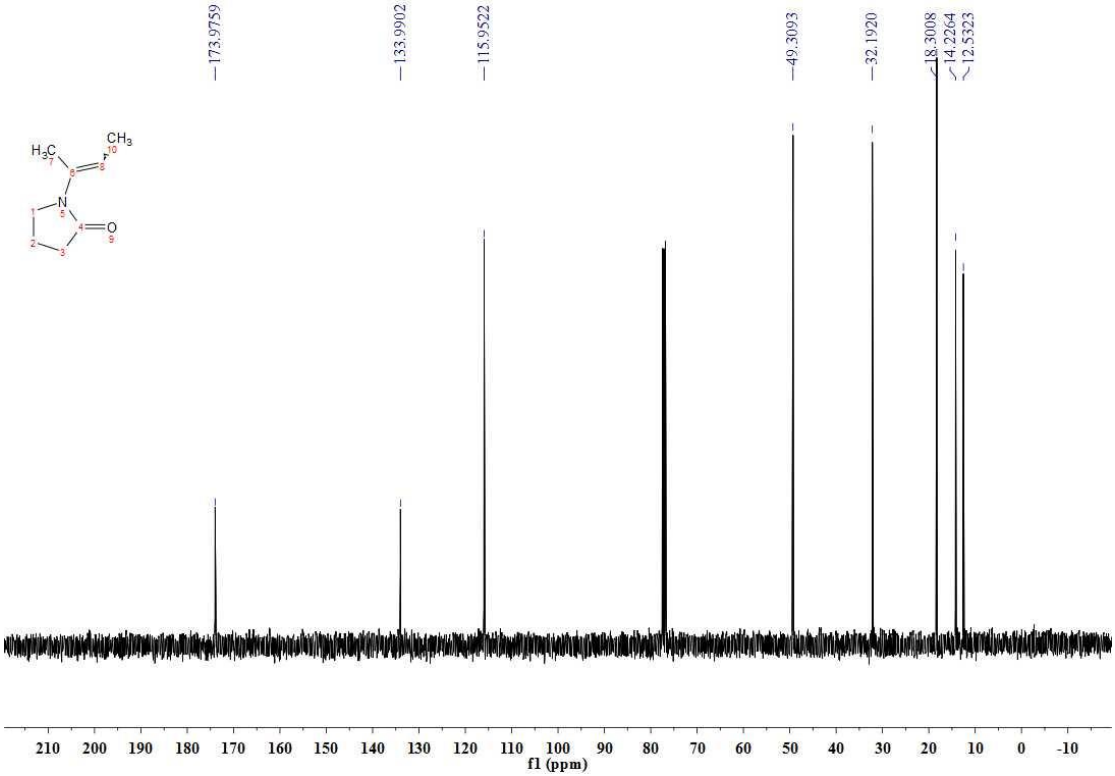
^{13}C NMR spectrum for **1f** ($CDCl_3$, 101 MHz)



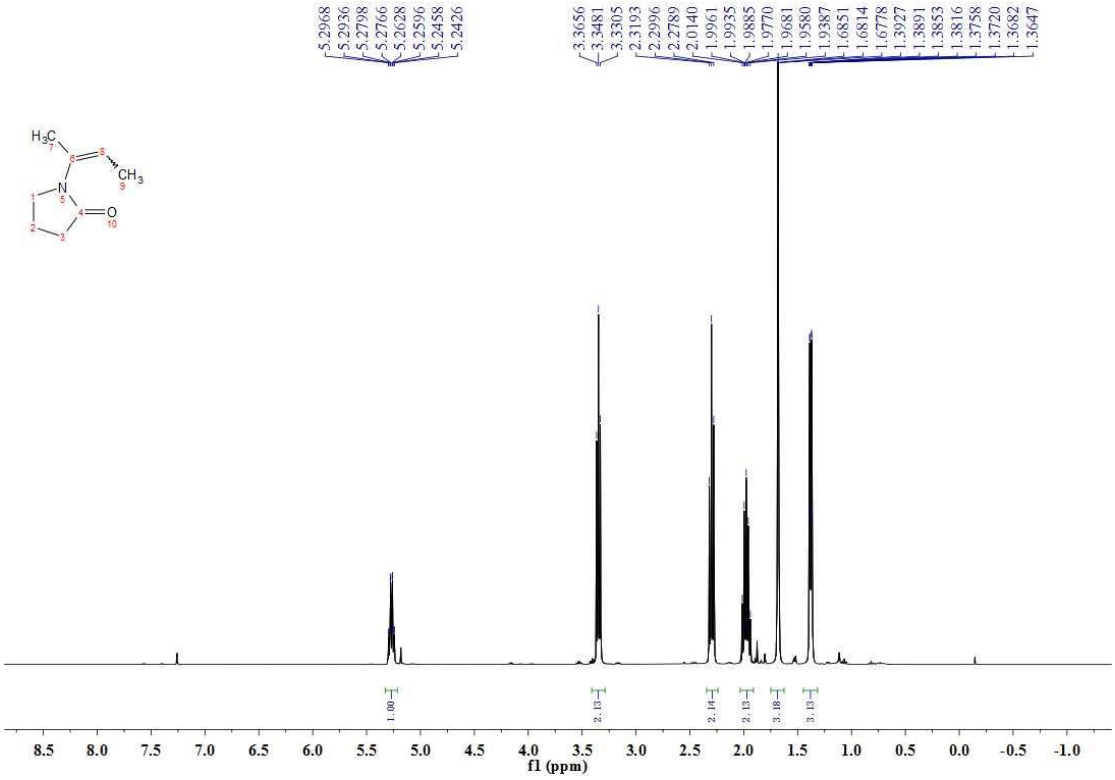
^{1}H NMR spectrum for **1g** (isomer 1, $CDCl_3$, 400 MHz)



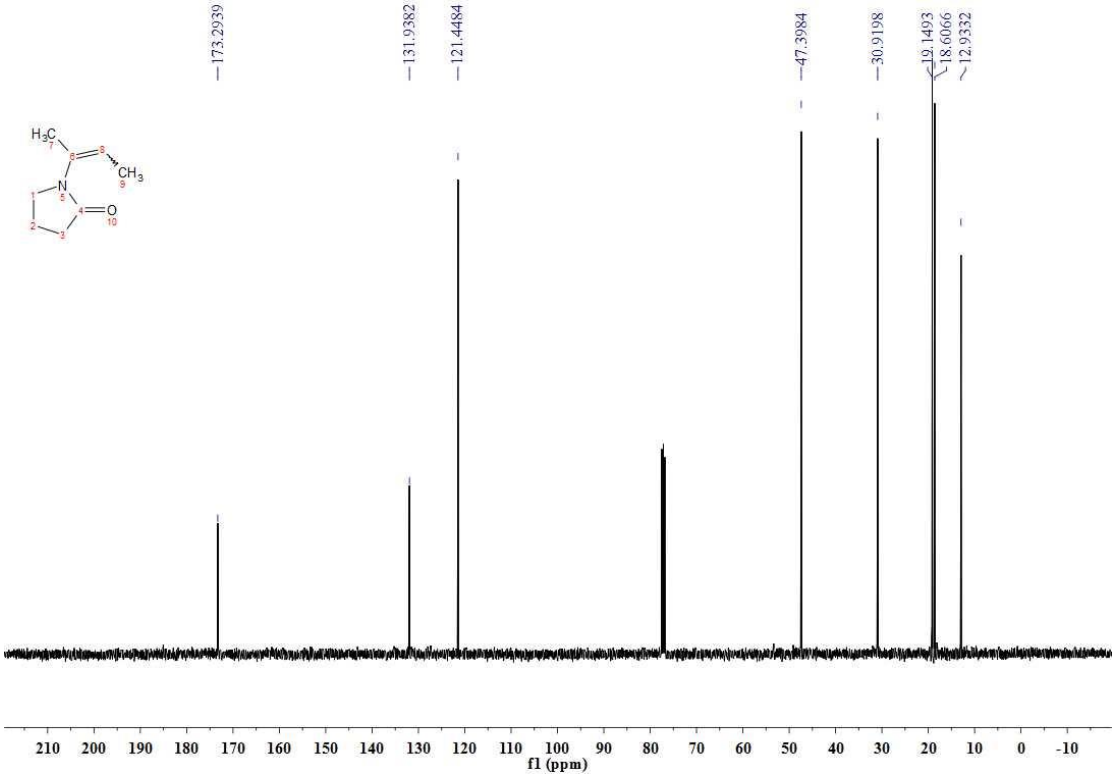
^{13}C NMR spectrum for **1g** (isomer 1, $CDCl_3$, 101 MHz)



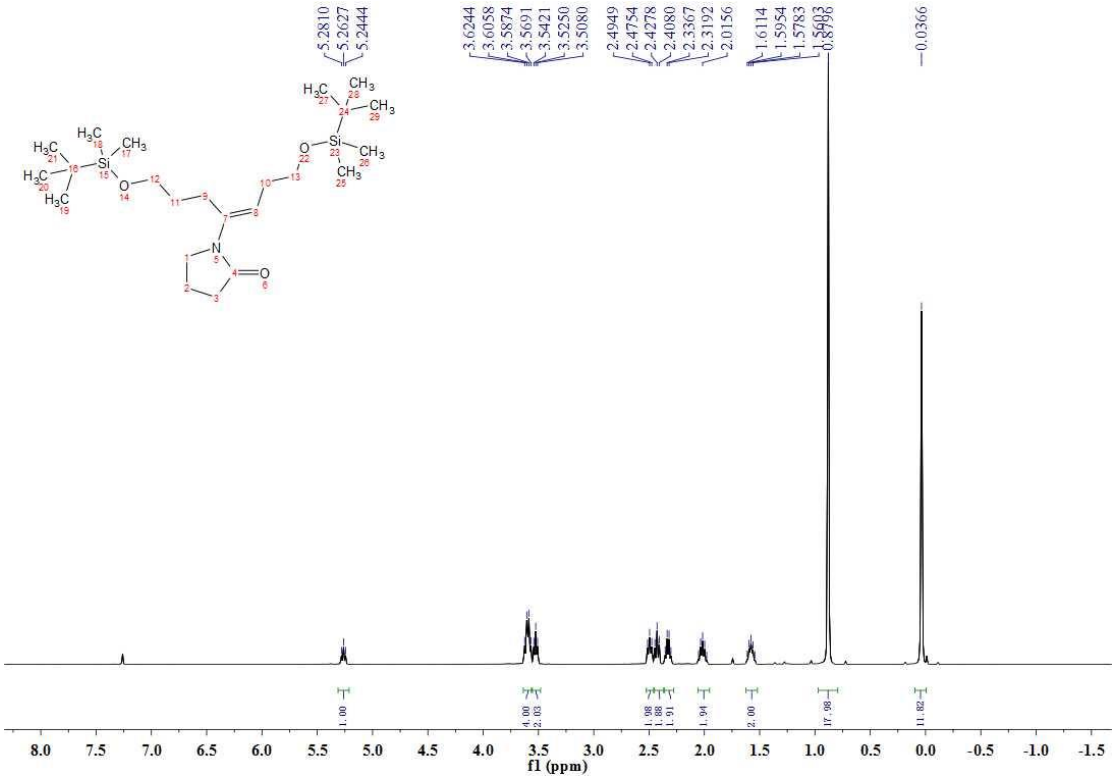
^{1}H NMR spectrum for **1g** (isomer 2, $CDCl_3$, 400 MHz)



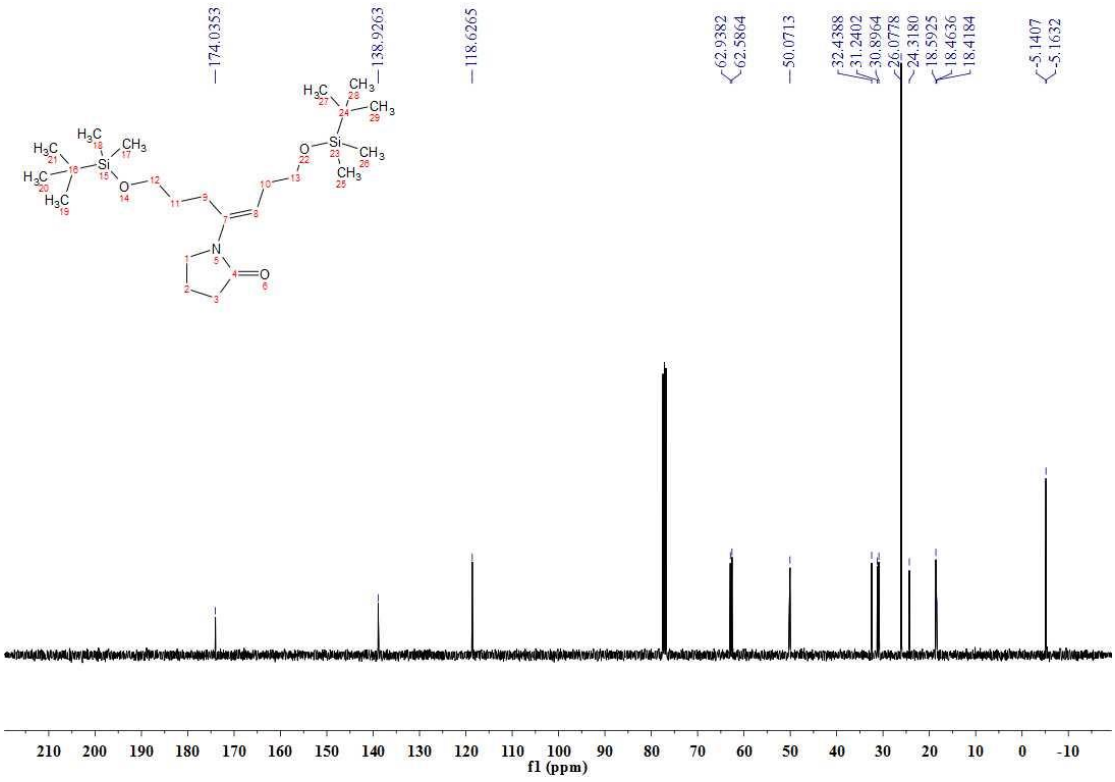
^{13}C NMR spectrum for **1g** (isomer 2, $CDCl_3$, 101 MHz)



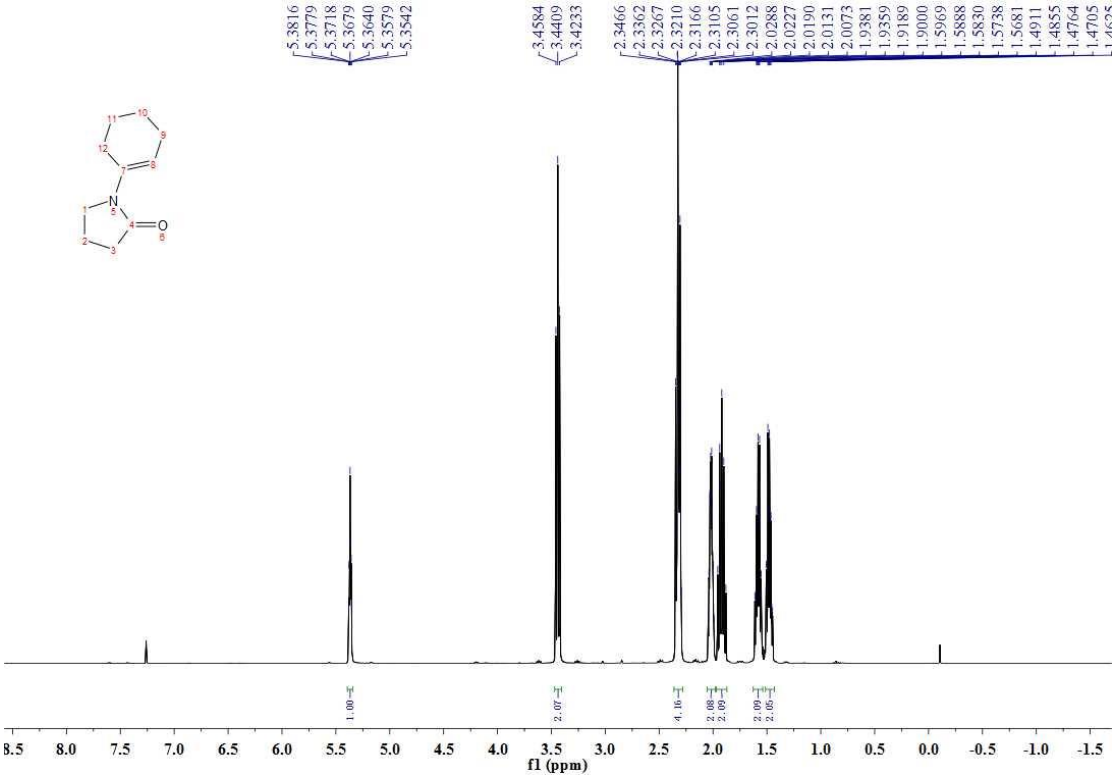
^{1}H NMR spectrum for **1h** ($CDCl_3$, 400 MHz)



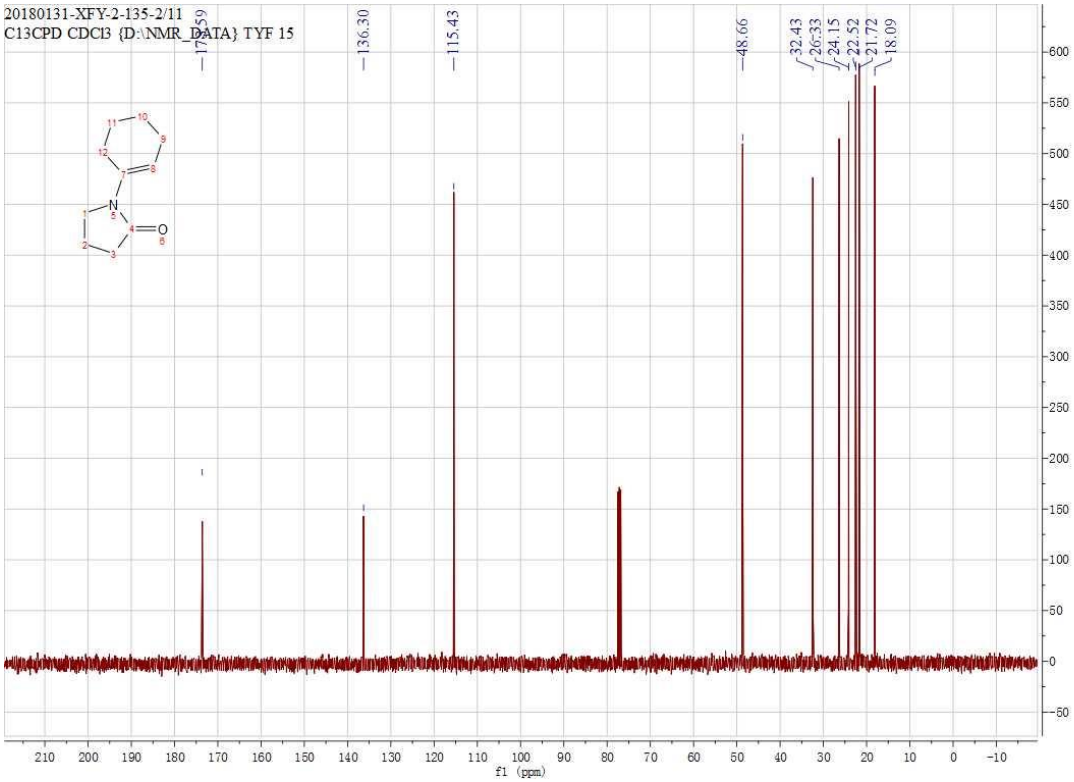
^{13}C NMR spectrum for **1h** ($CDCl_3$, 101 MHz)



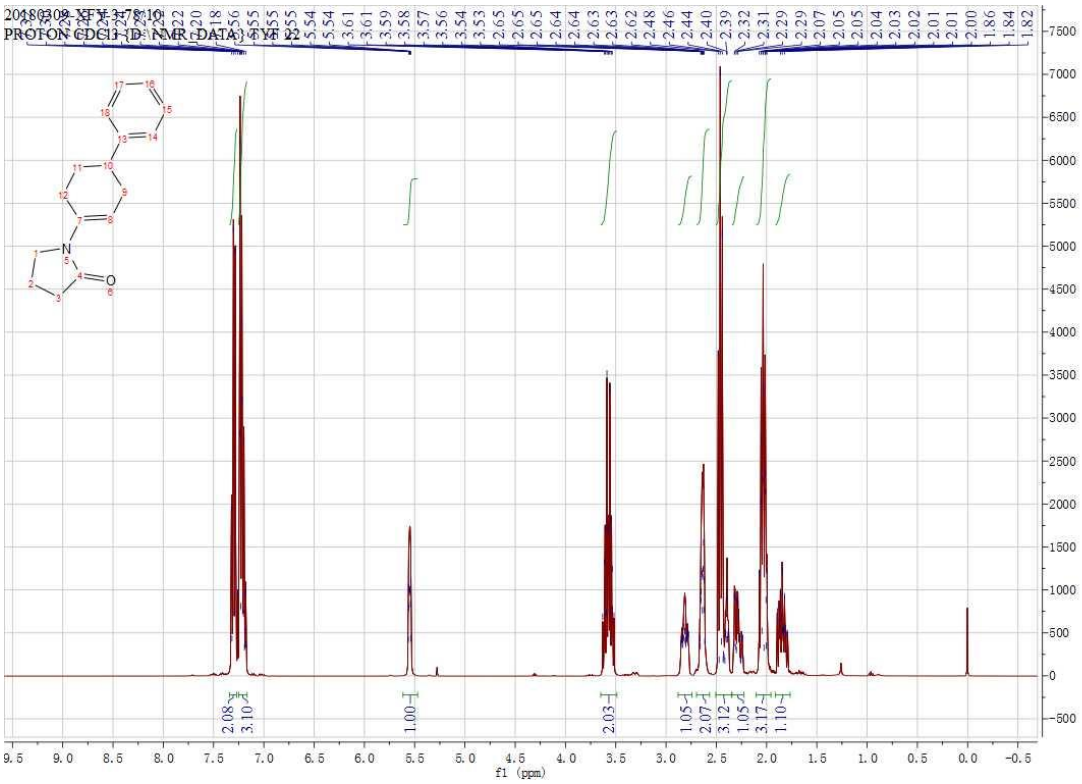
^{1}H NMR spectrum for **1i** ($CDCl_3$, 400 MHz)



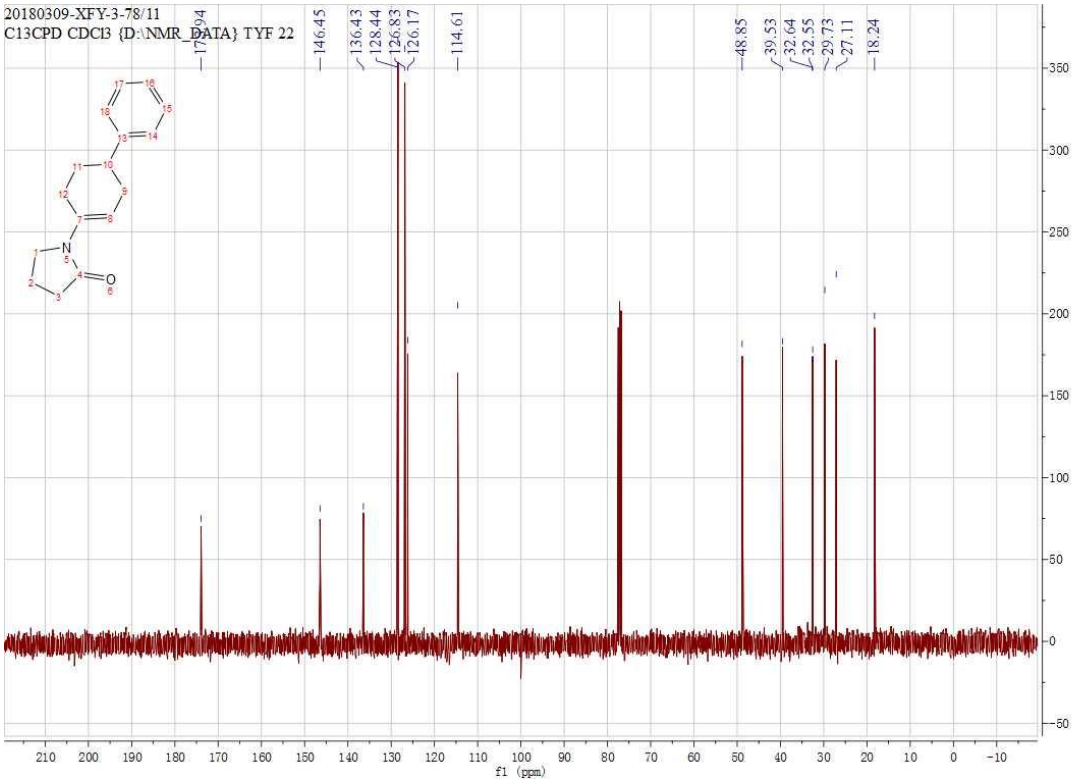
^{13}C NMR spectrum for **1i** ($CDCl_3$, 101 MHz)



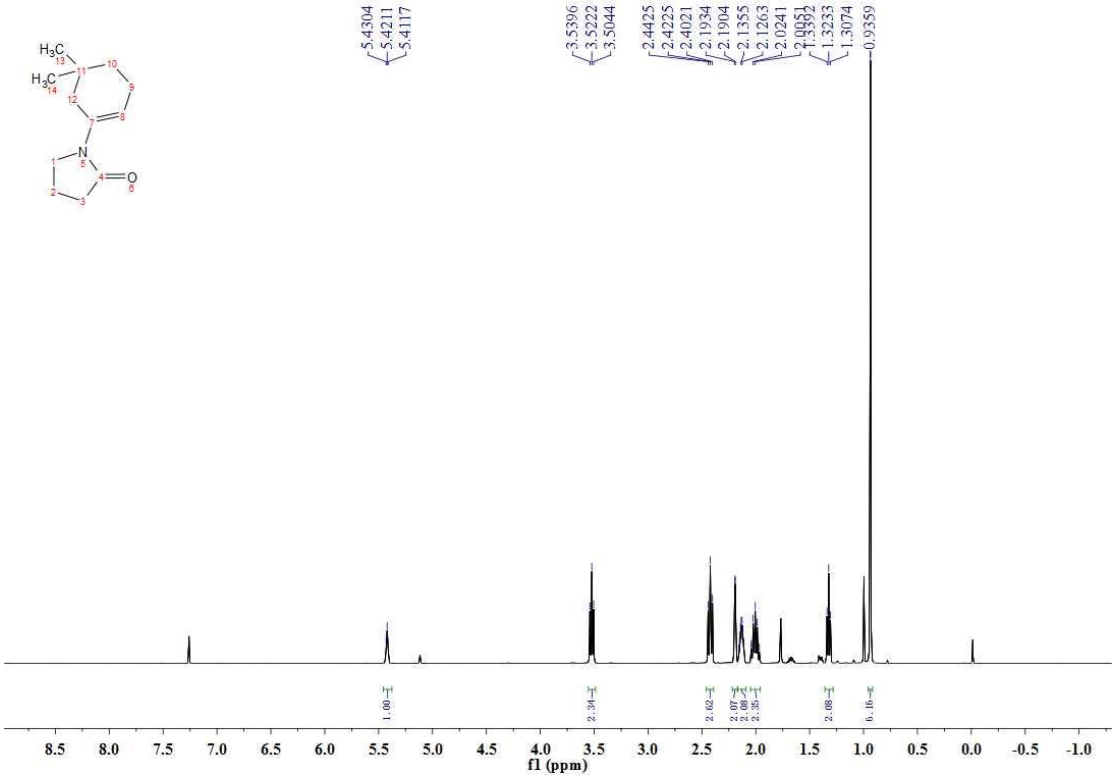
^{1}H NMR spectrum for **1j** ($CDCl_3$, 400 MHz)



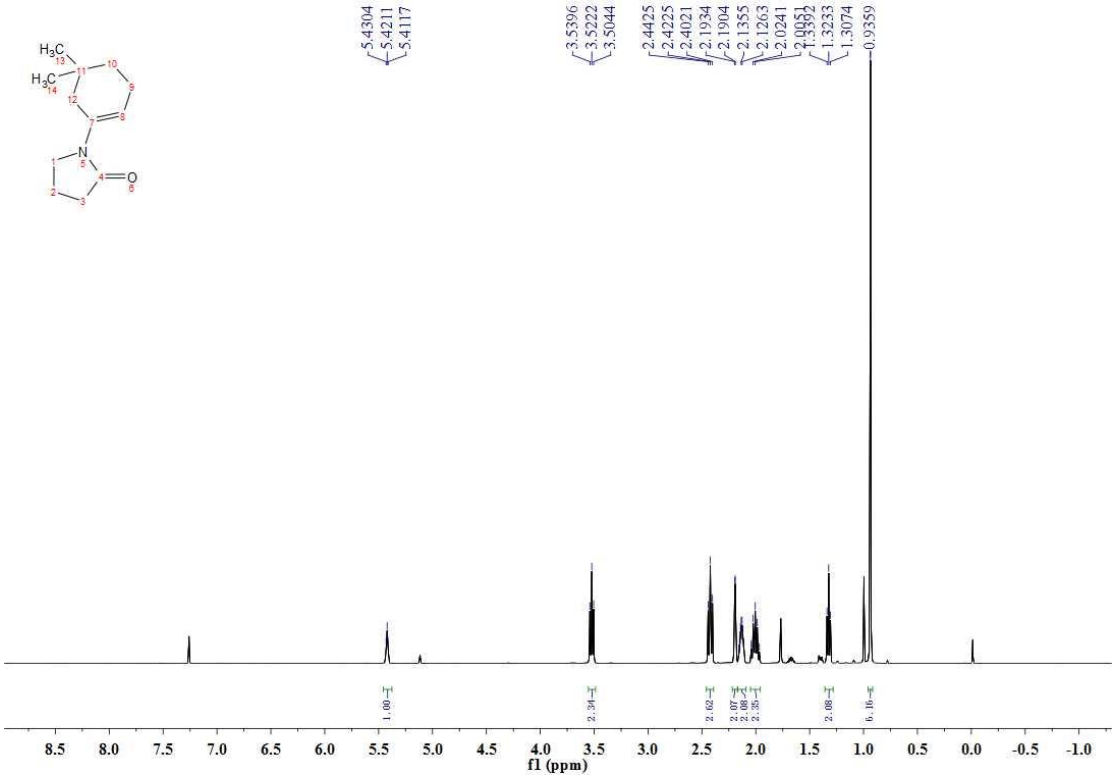
^{13}C NMR spectrum for **1j** ($CDCl_3$, 101 MHz)



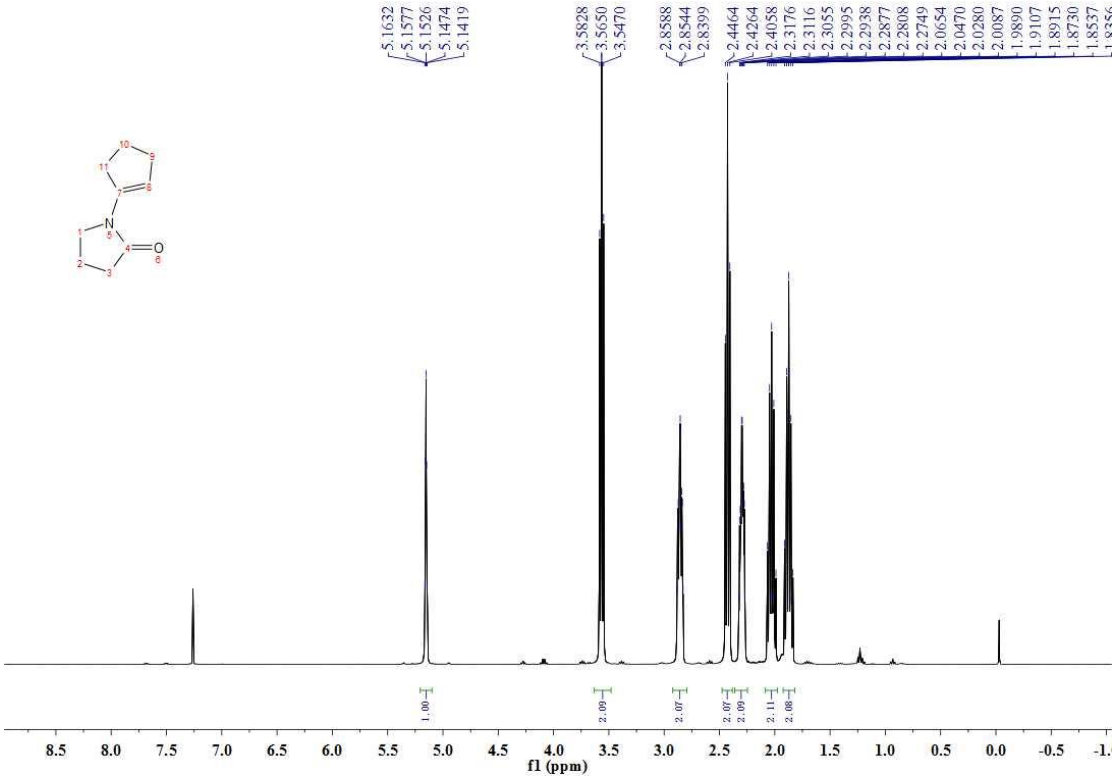
^{1}H NMR spectrum for **1k** ($CDCl_3$, 400 MHz)



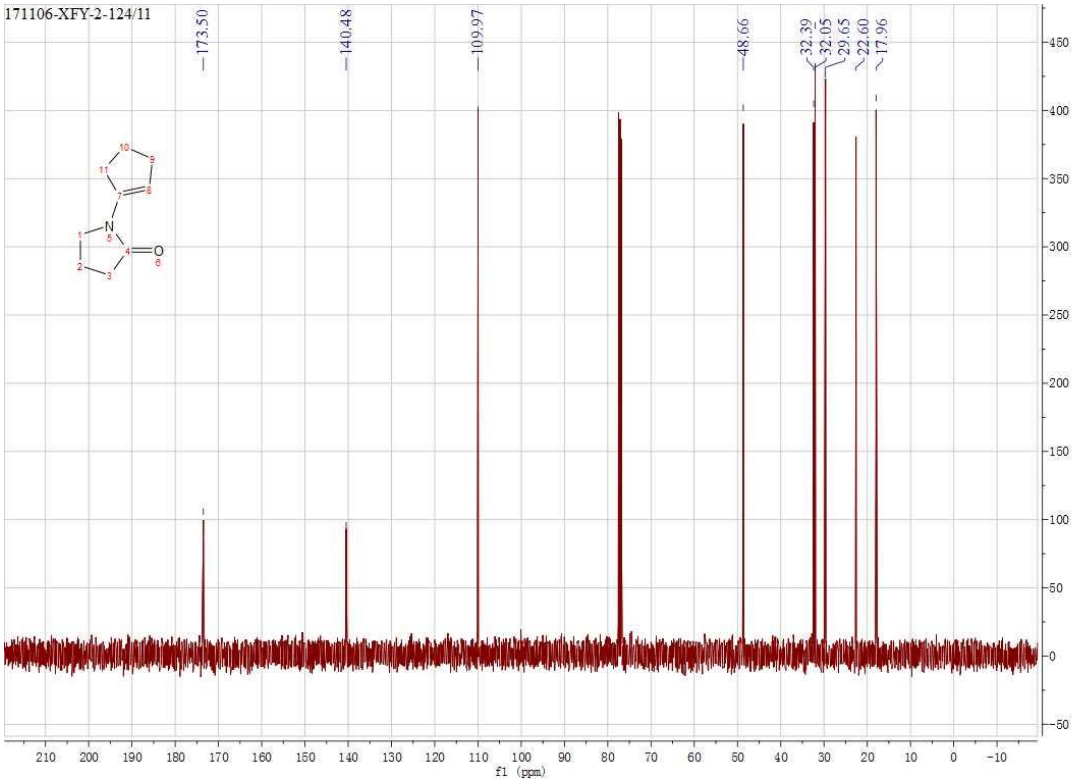
^{13}C NMR spectrum for **1k** ($CDCl_3$, 101 MHz)



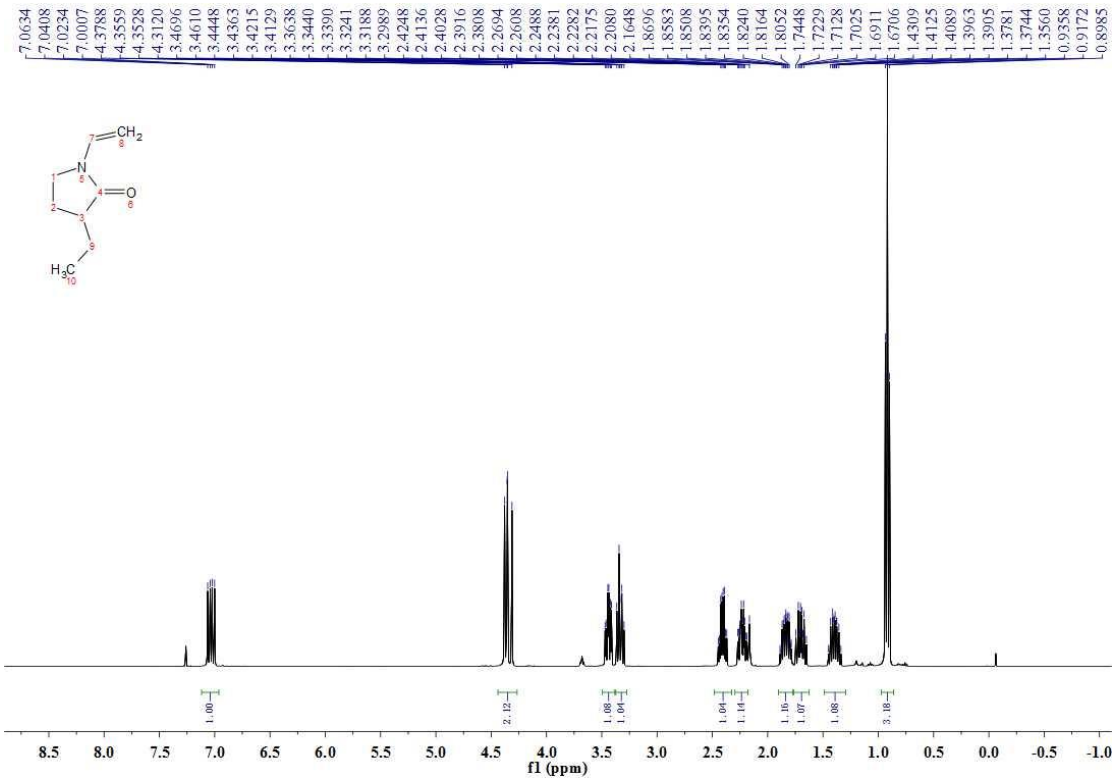
^{1}H NMR spectrum for **1l** ($CDCl_3$, 400 MHz)



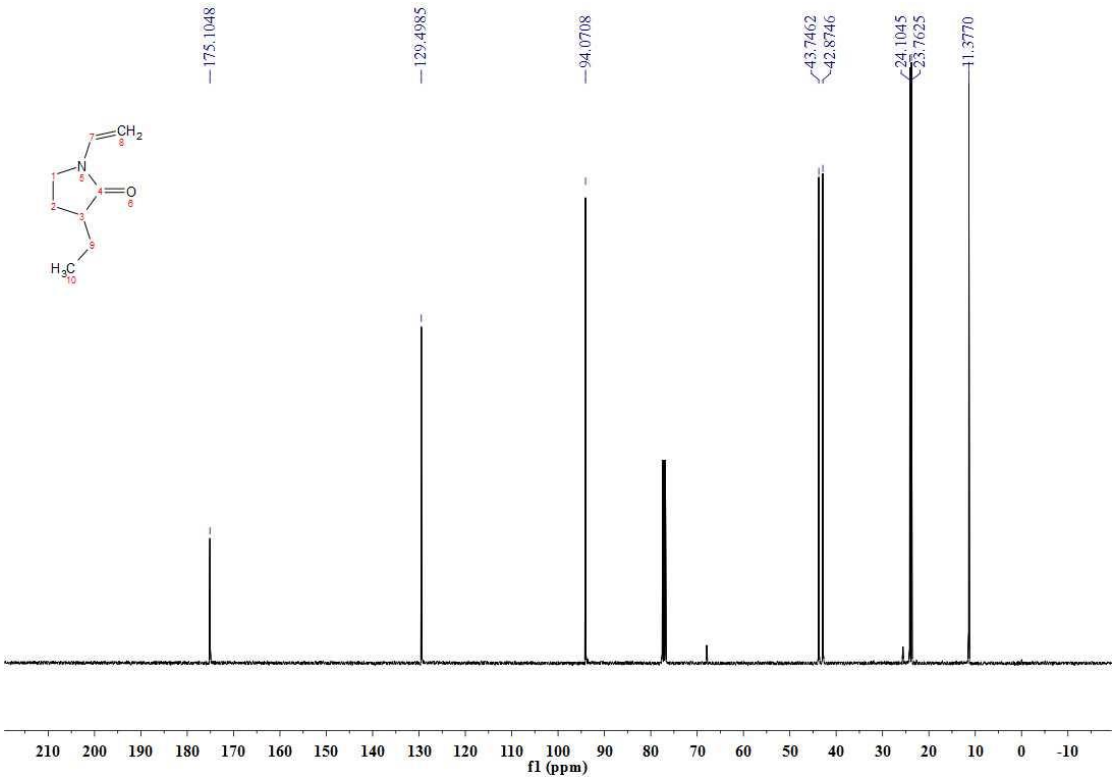
^{13}C NMR spectrum for **1l** ($CDCl_3$, 101 MHz)



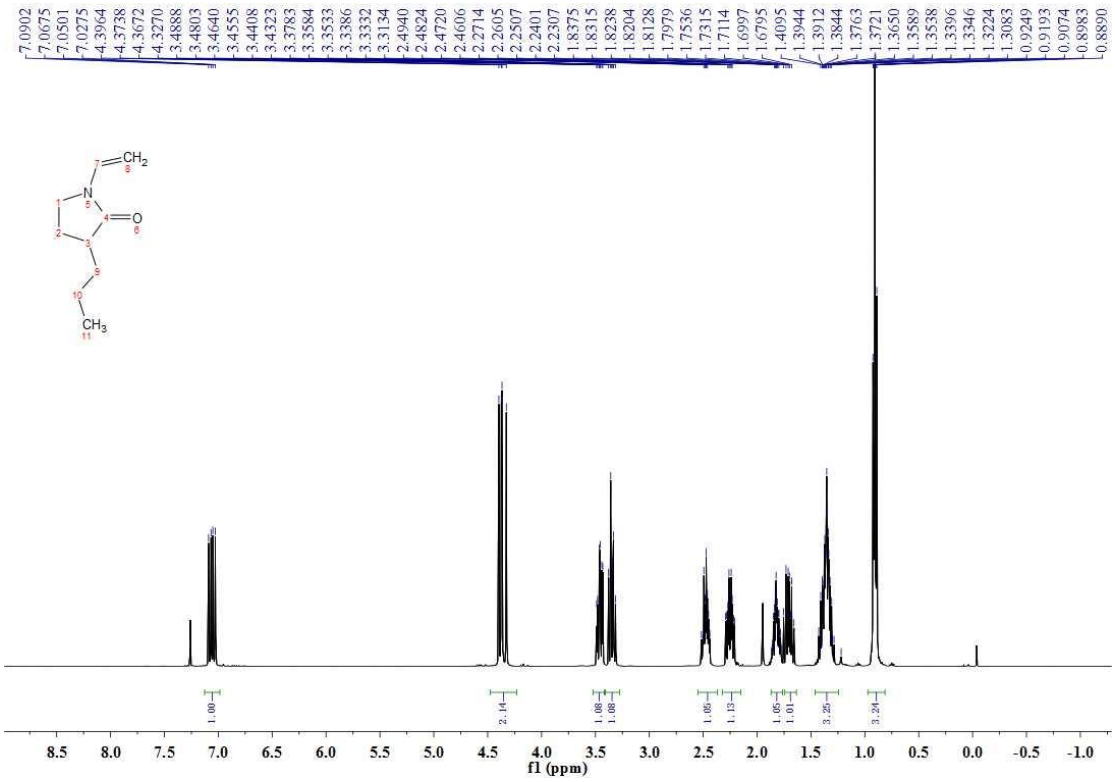
^{1}H NMR spectrum for **1m** ($CDCl_3$, 400 MHz)



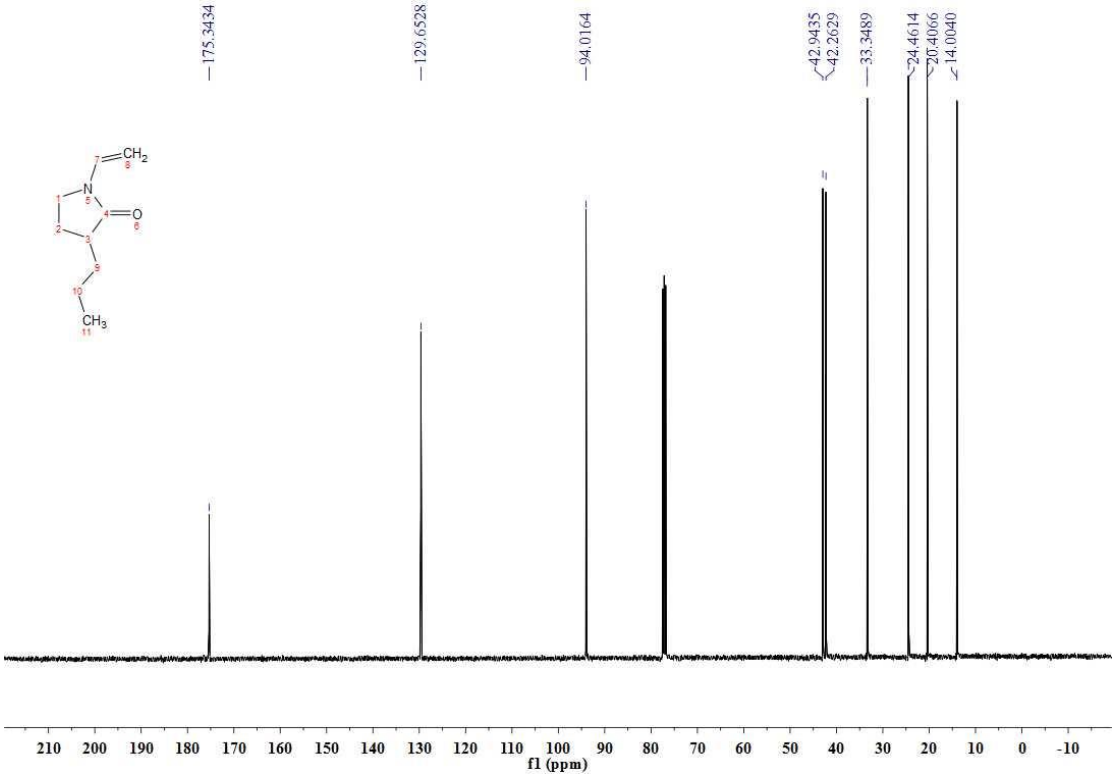
^{13}C NMR spectrum for **1m** ($CDCl_3$, 101 MHz)



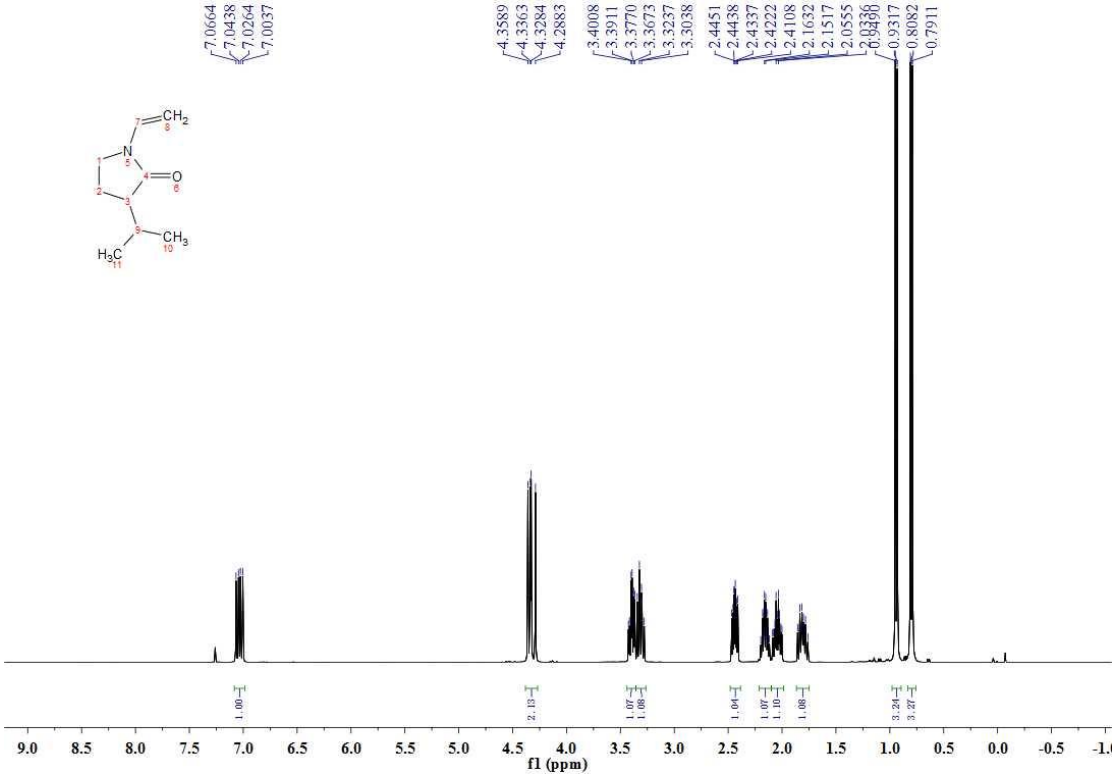
^{1}H NMR spectrum for **1n** ($CDCl_3$, 400 MHz)



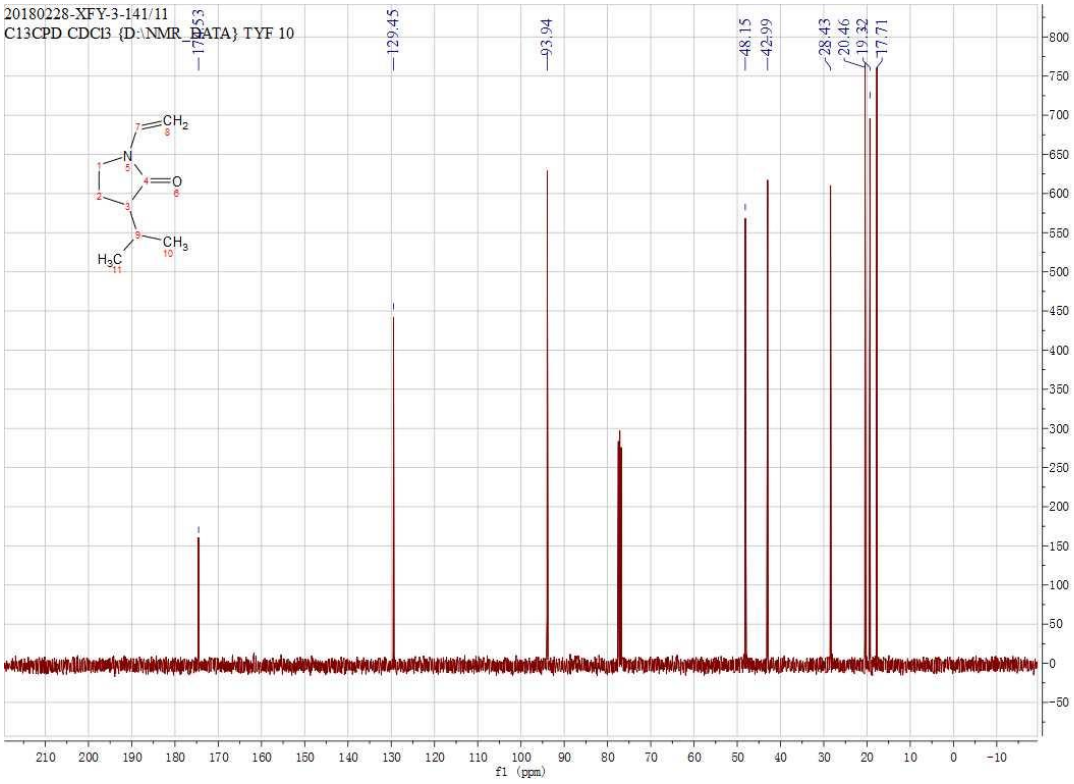
^{13}C NMR spectrum for **1n** ($CDCl_3$, 101 MHz)



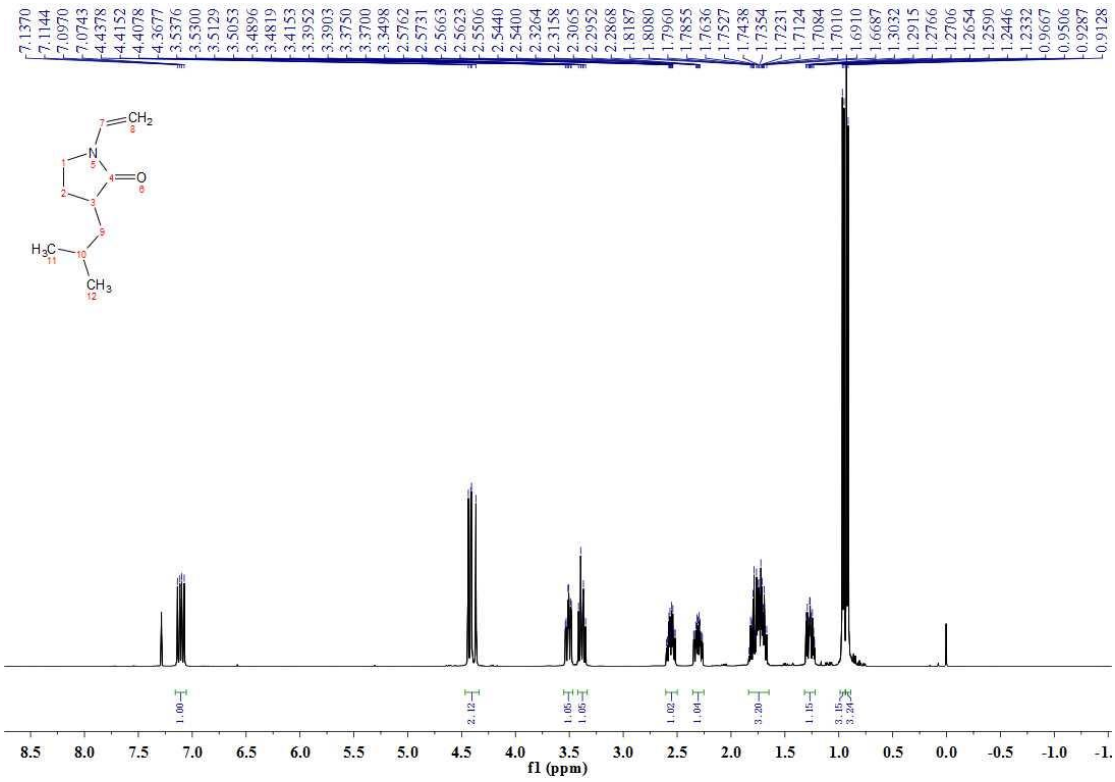
^{1}H NMR spectrum for **1o** ($CDCl_3$, 400 MHz)



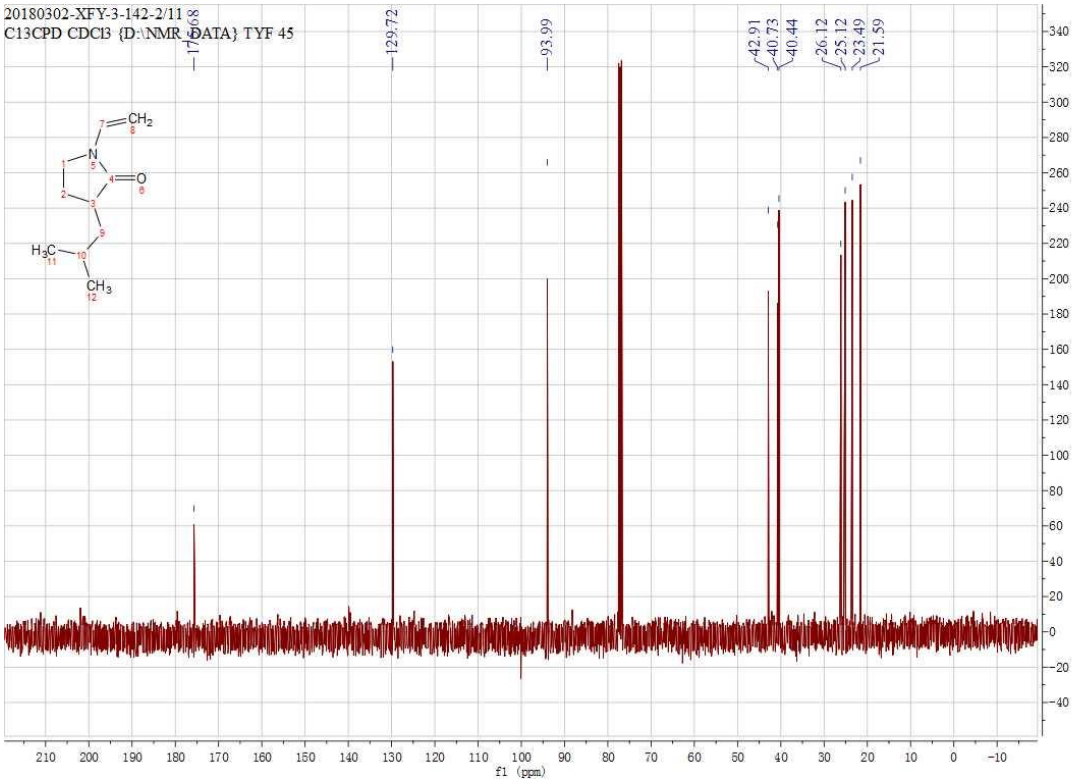
^{13}C NMR spectrum for **1o** ($CDCl_3$, 101 MHz)



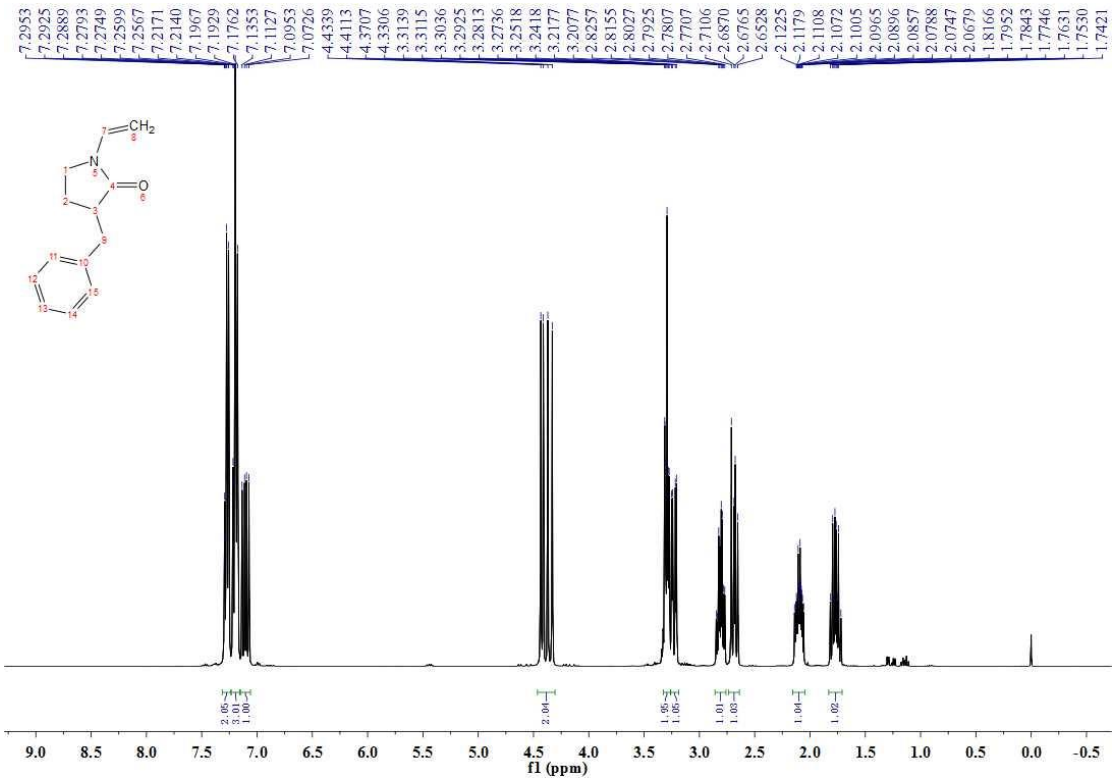
^{1}H NMR spectrum for **1p** ($CDCl_3$, 400 MHz)



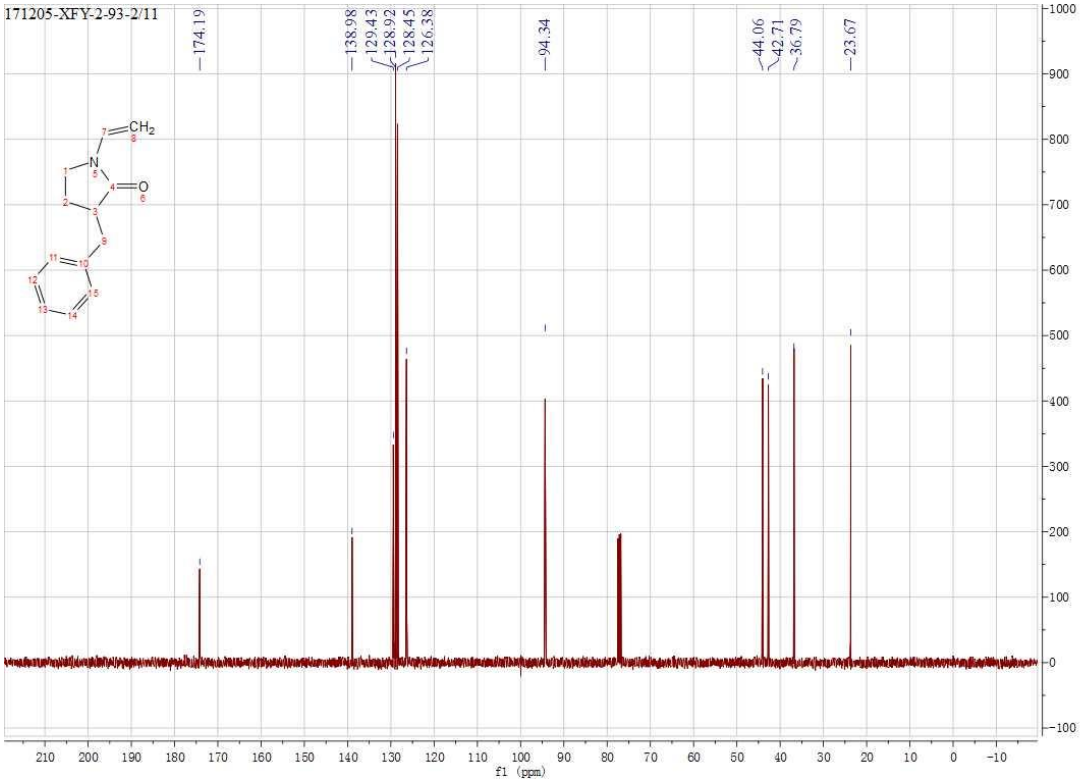
^{13}C NMR spectrum for **1p** ($CDCl_3$, 101 MHz)



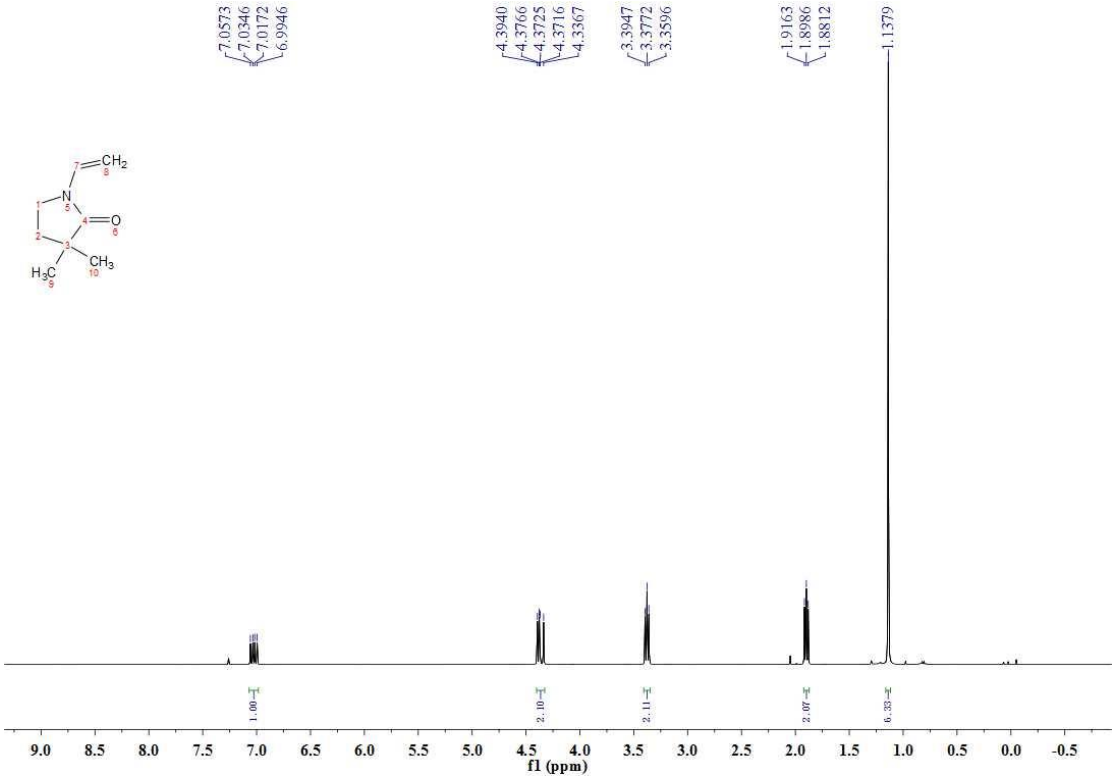
^{1}H NMR spectrum for **1q** ($CDCl_3$, 400 MHz)



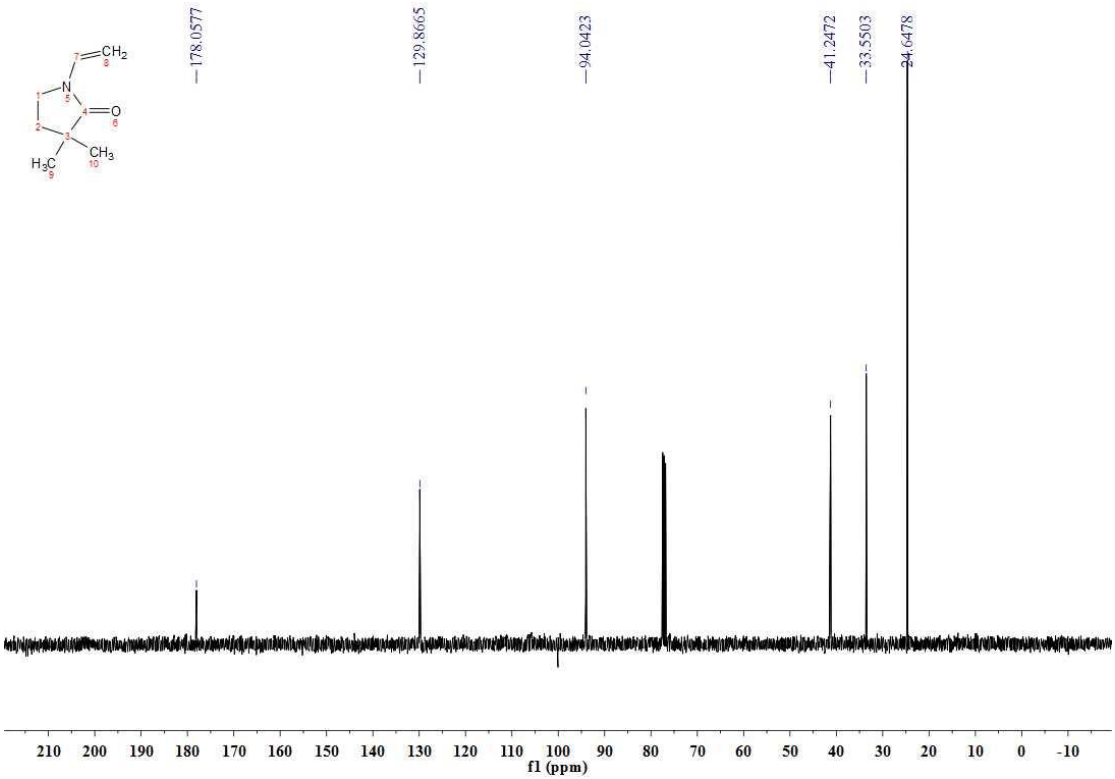
^{13}C NMR spectrum for **1q** ($CDCl_3$, 101 MHz)



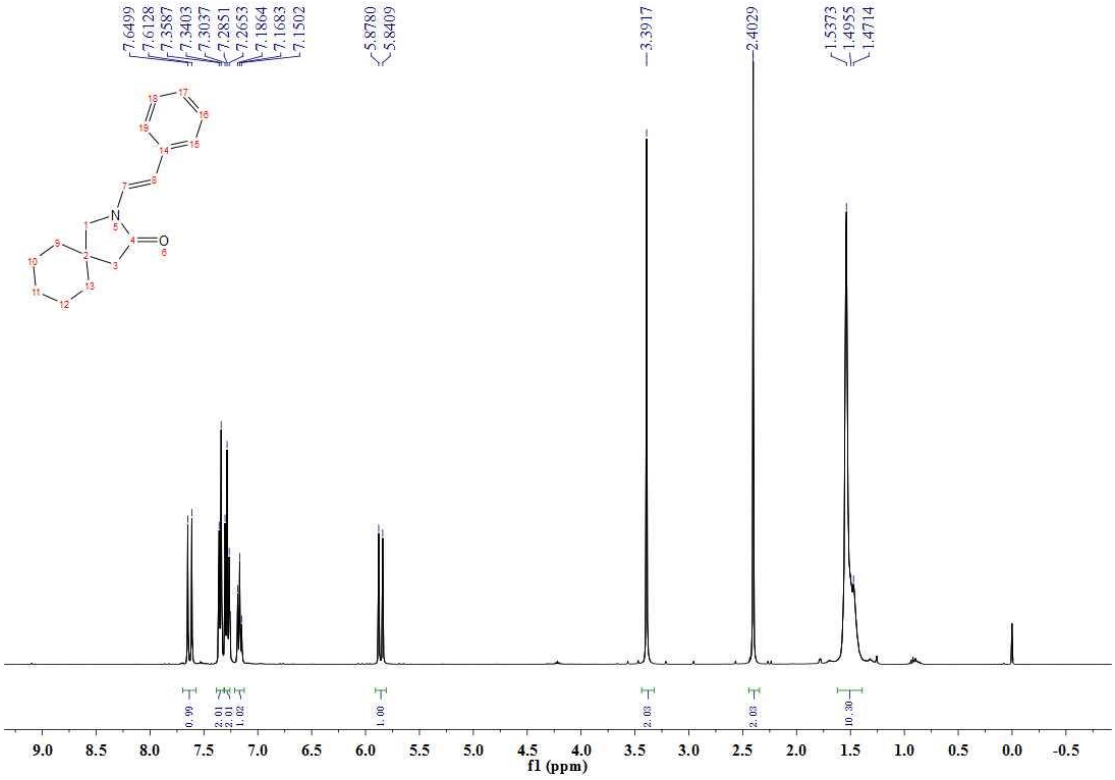
^{1}H NMR spectrum for **1r** ($CDCl_3$, 400 MHz)



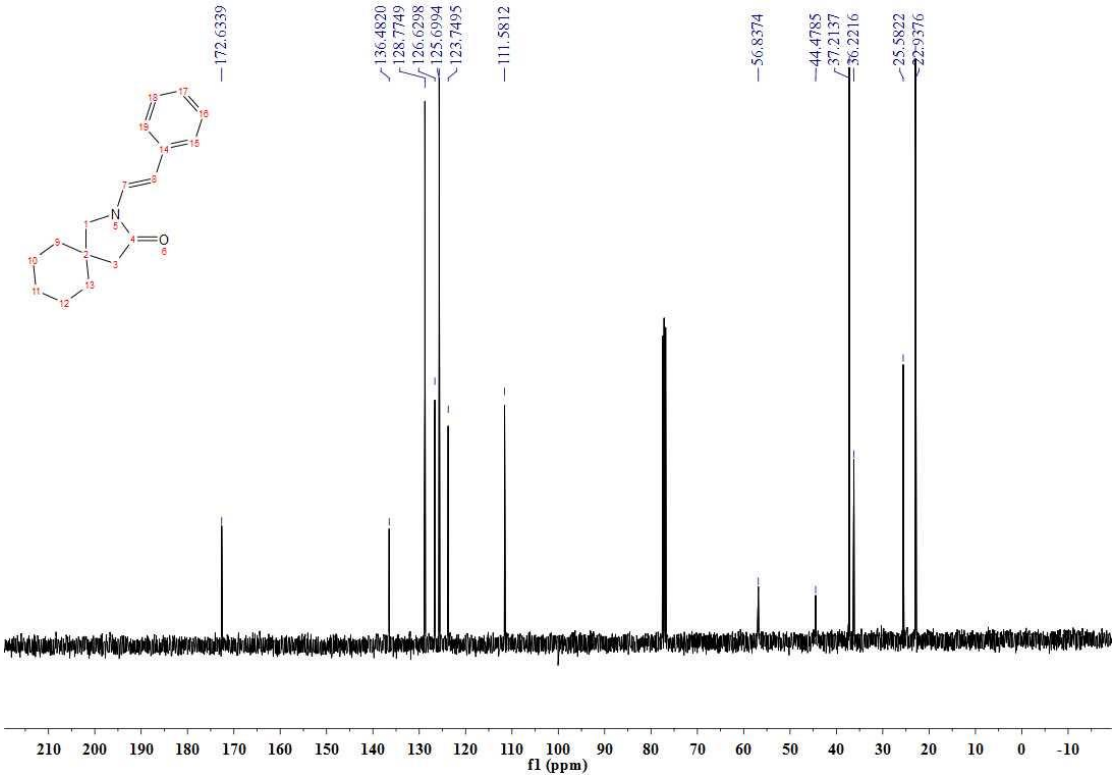
^{13}C NMR spectrum for **1r** ($CDCl_3$, 101 MHz)



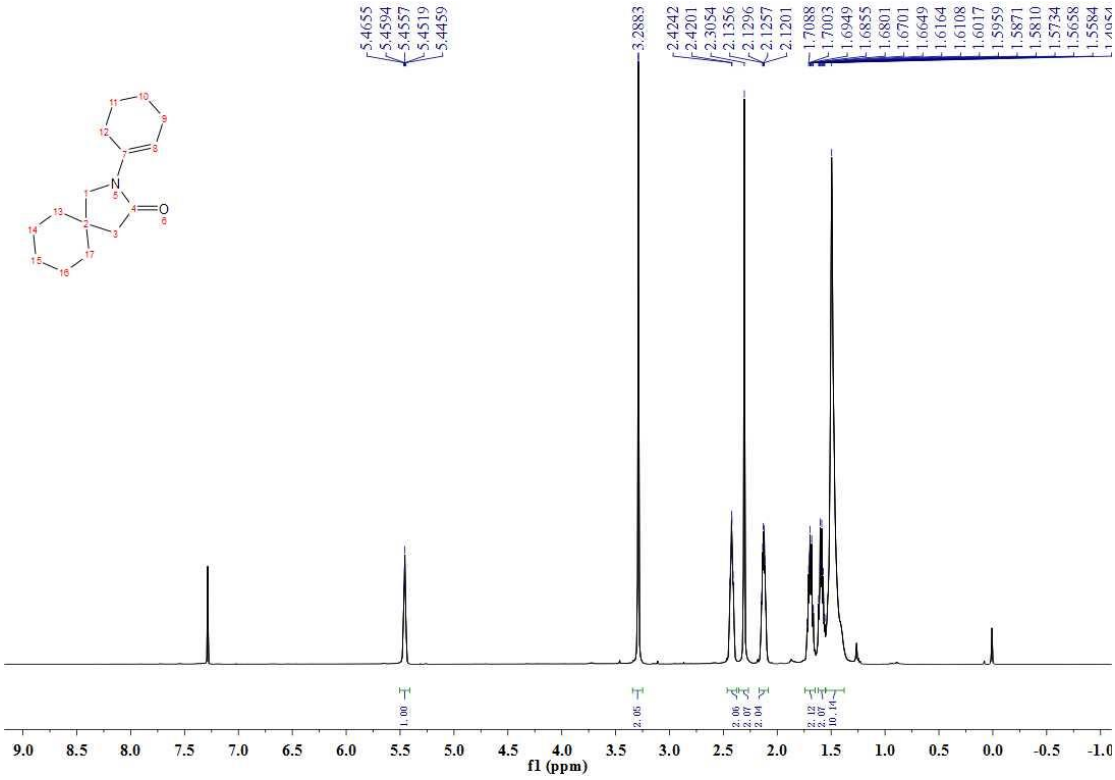
^{1}H NMR spectrum for **1s** ($CDCl_3$, 400 MHz)



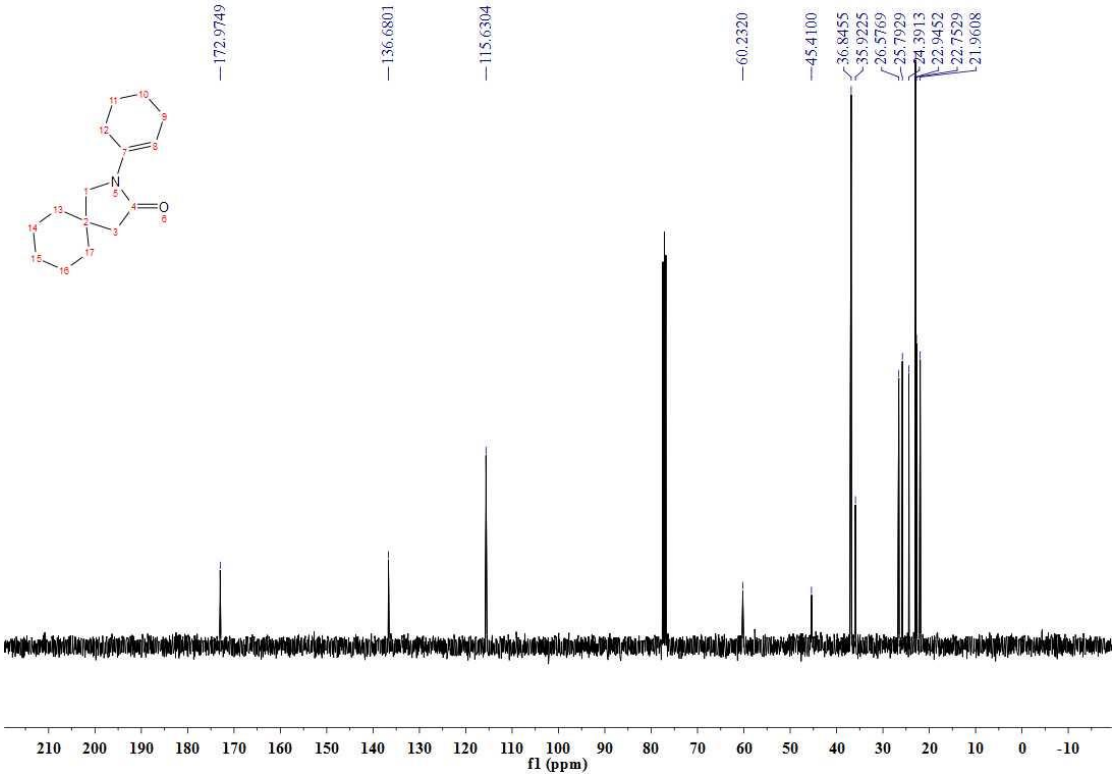
^{13}C NMR spectrum for **1s** ($CDCl_3$, 101 MHz)



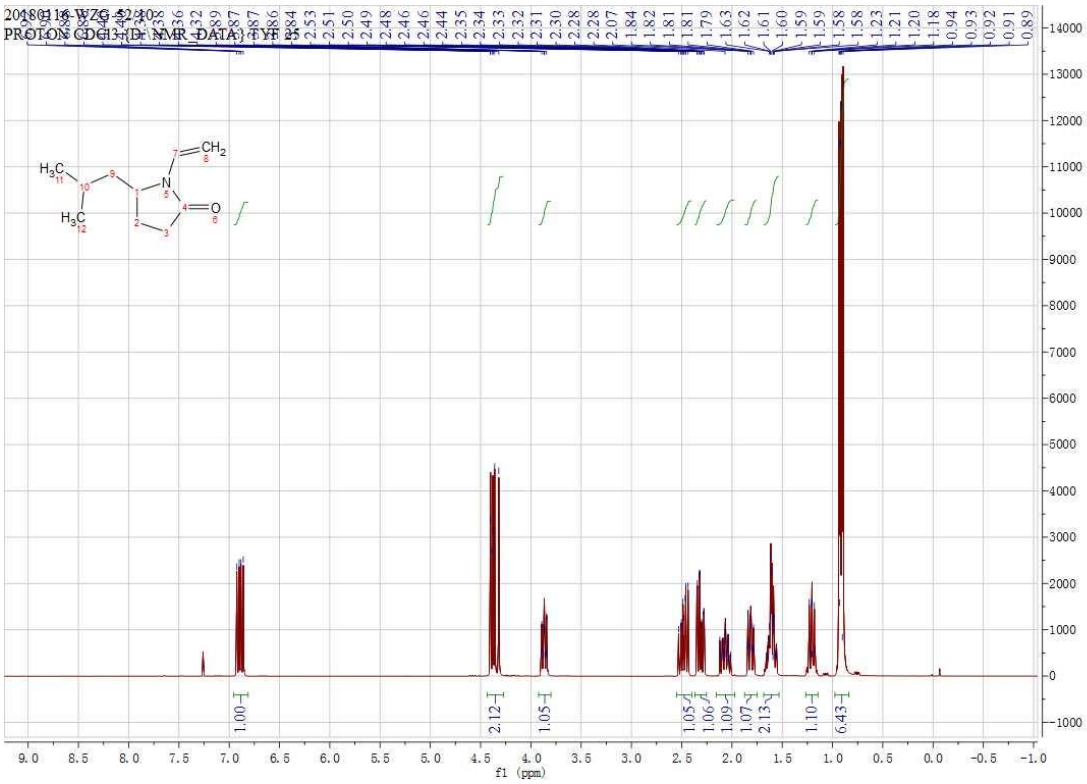
^{1}H NMR spectrum for **1t** ($CDCl_3$, 400 MHz)



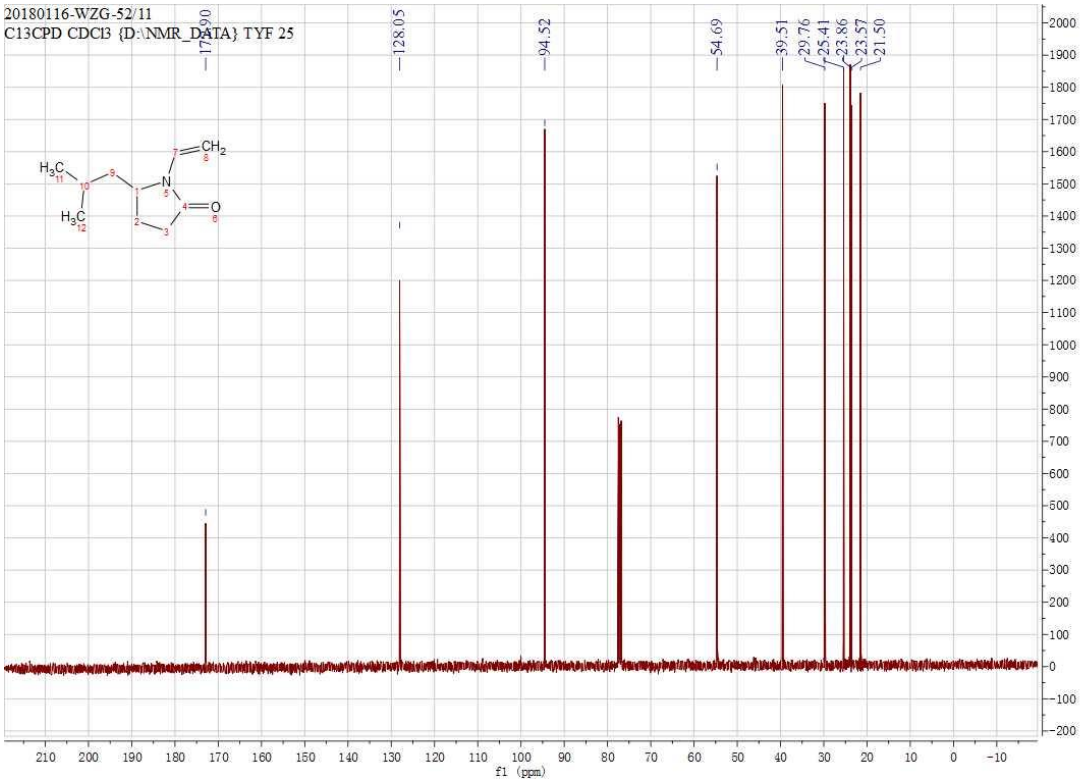
^{13}C NMR spectrum for **1t** ($CDCl_3$, 101 MHz)



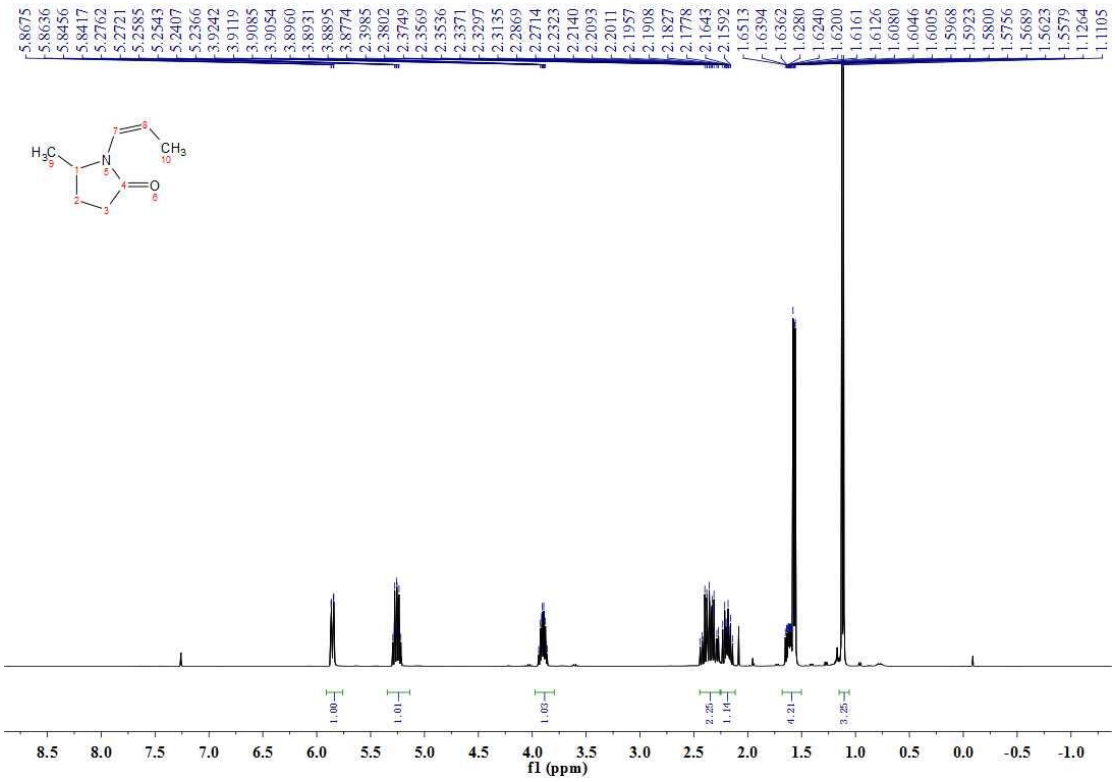
^{1}H NMR spectrum for **1u** ($CDCl_3$, 400 MHz)



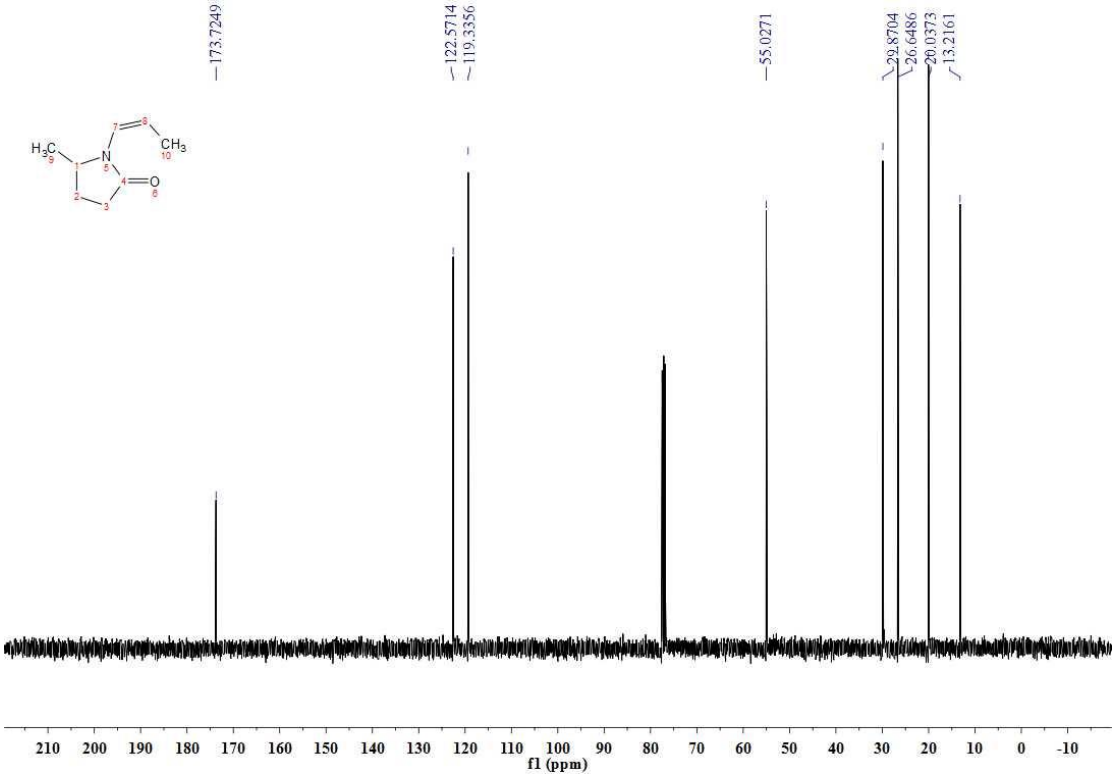
^{13}C NMR spectrum for **1u** ($CDCl_3$, 101 MHz)



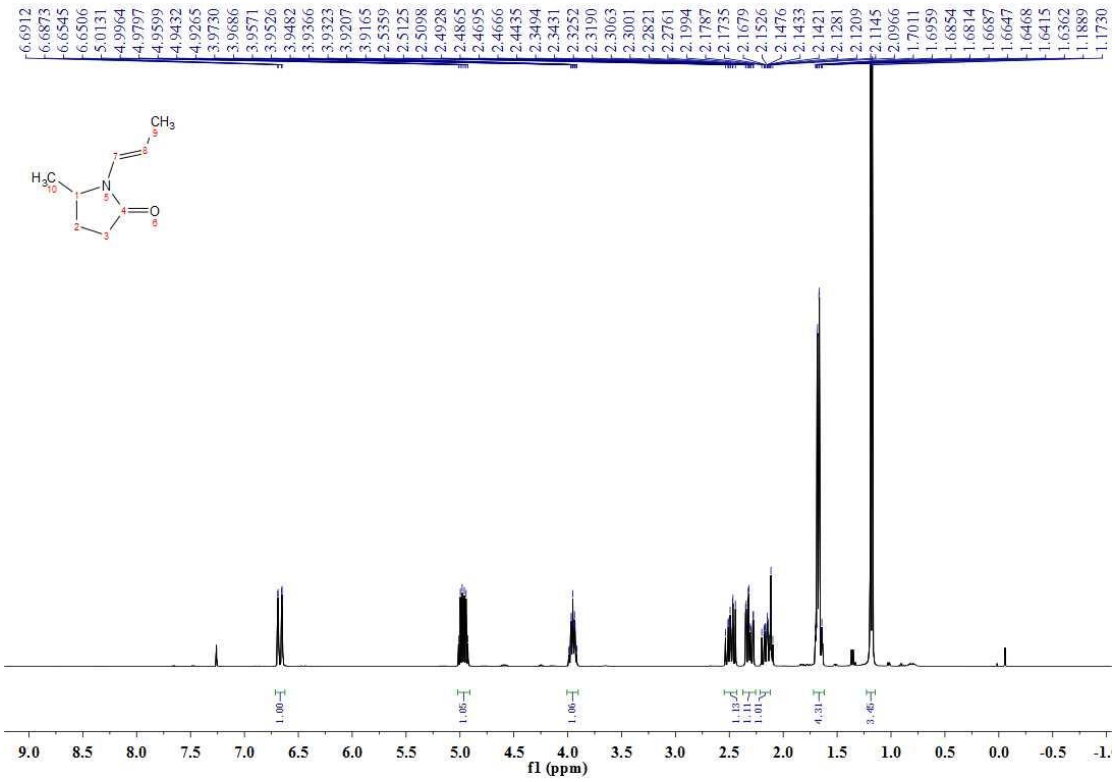
^{1}H NMR spectrum for **1v** (*cis*-isomer $CDCl_3$, 400 MHz)



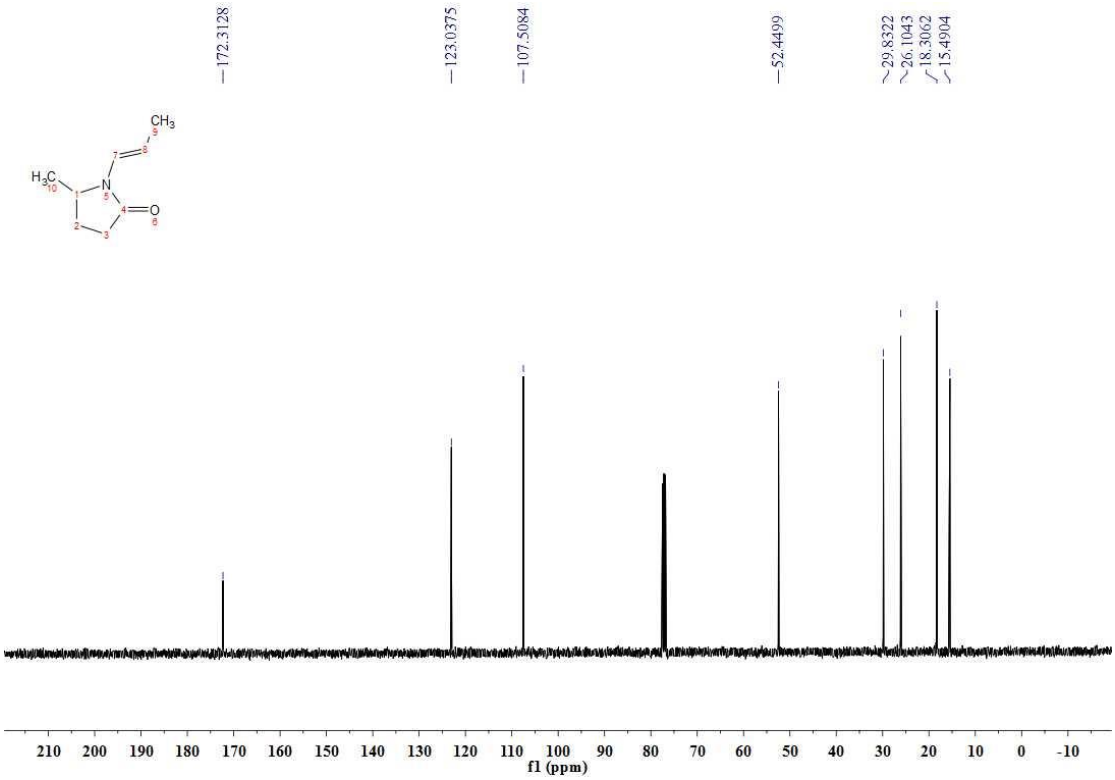
^{13}C NMR spectrum for **1v** (*cis*-isomer $CDCl_3$, 101 MHz)



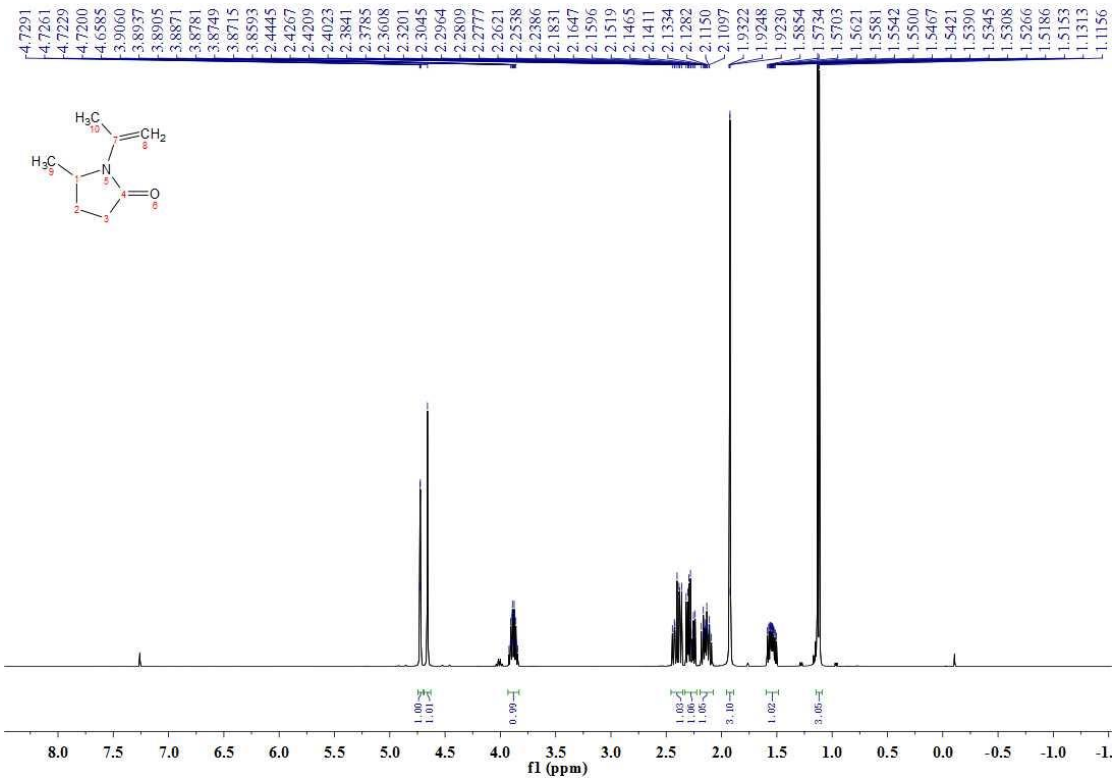
^{1}H NMR spectrum for **1v** (*trans*-isomer $CDCl_3$, 400 MHz)



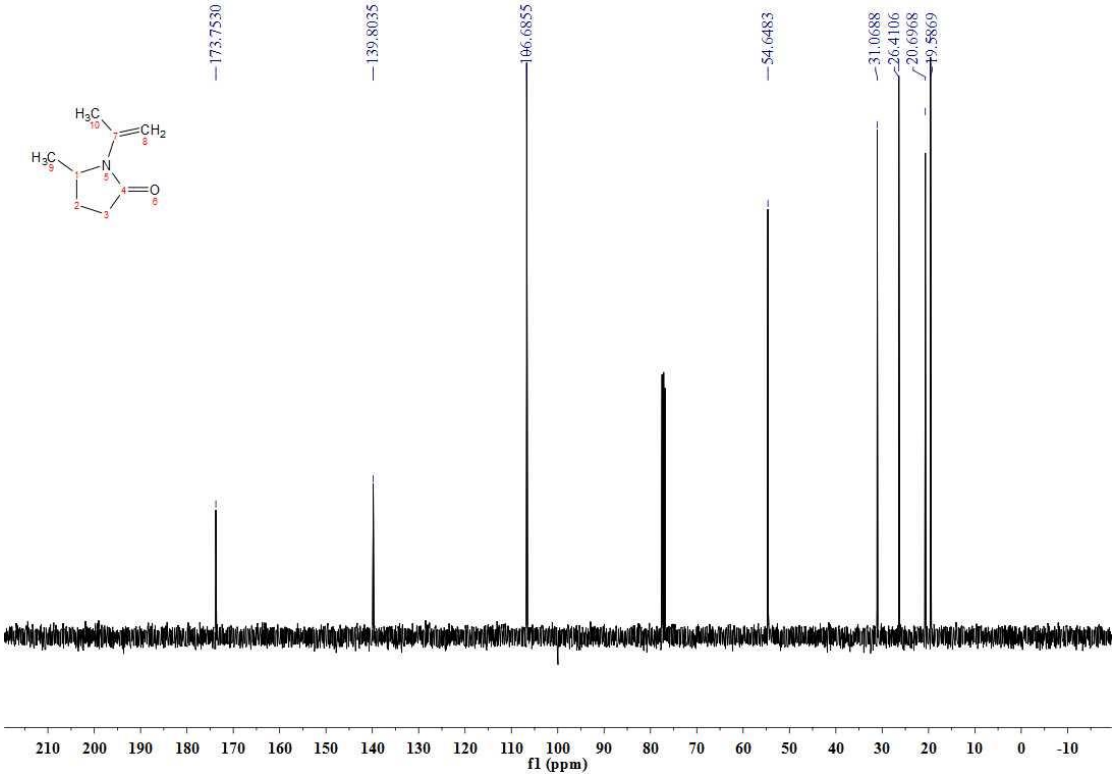
^{13}C NMR spectrum for **1v** (*trans*-isomer $CDCl_3$, 101 MHz)



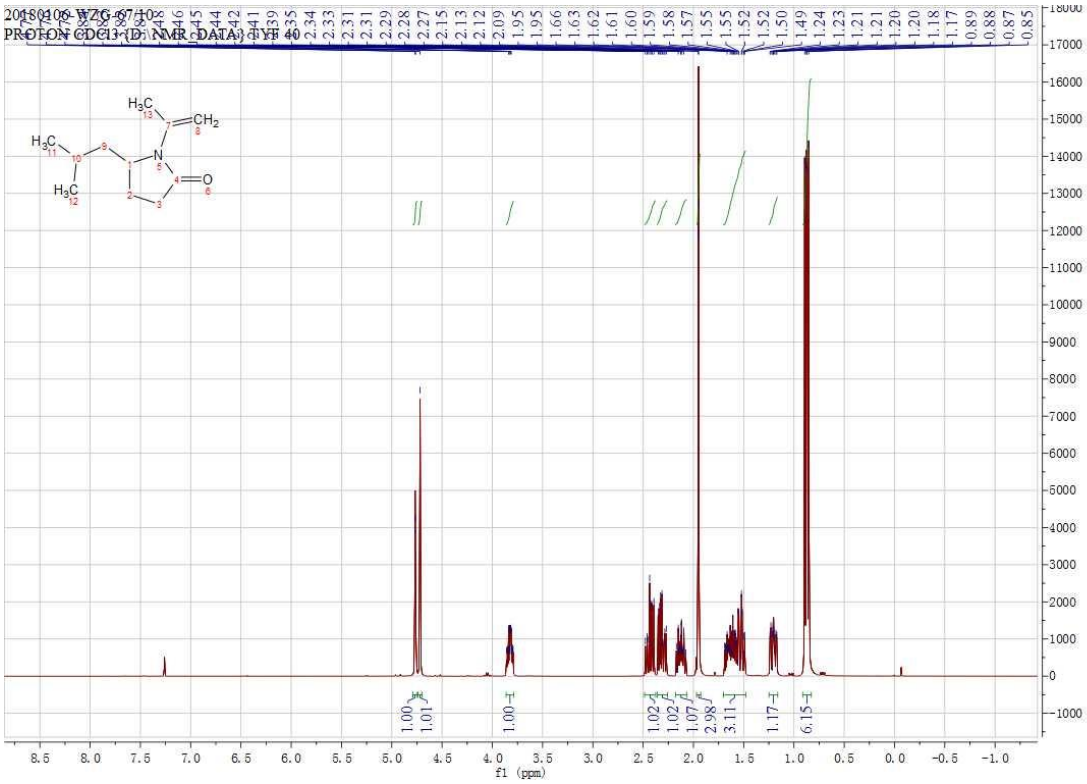
^{1}H NMR spectrum for **1w** ($CDCl_3$, 400 MHz)



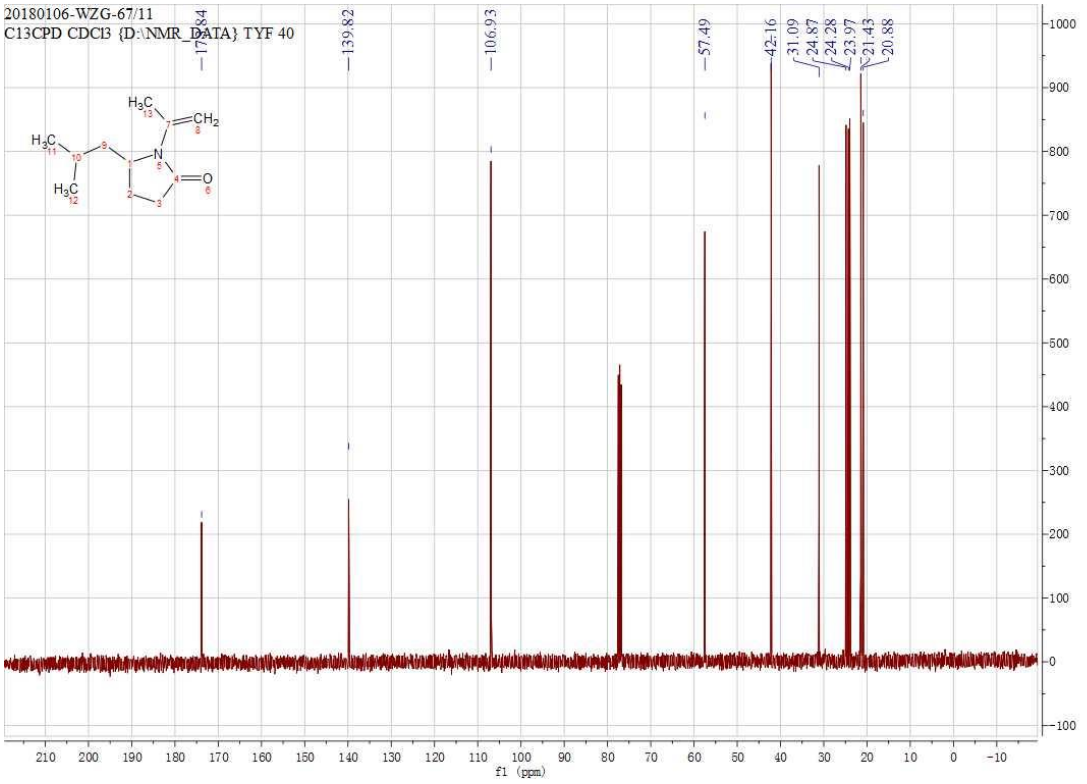
^{13}C NMR spectrum for **1w** ($CDCl_3$, 101 MHz)



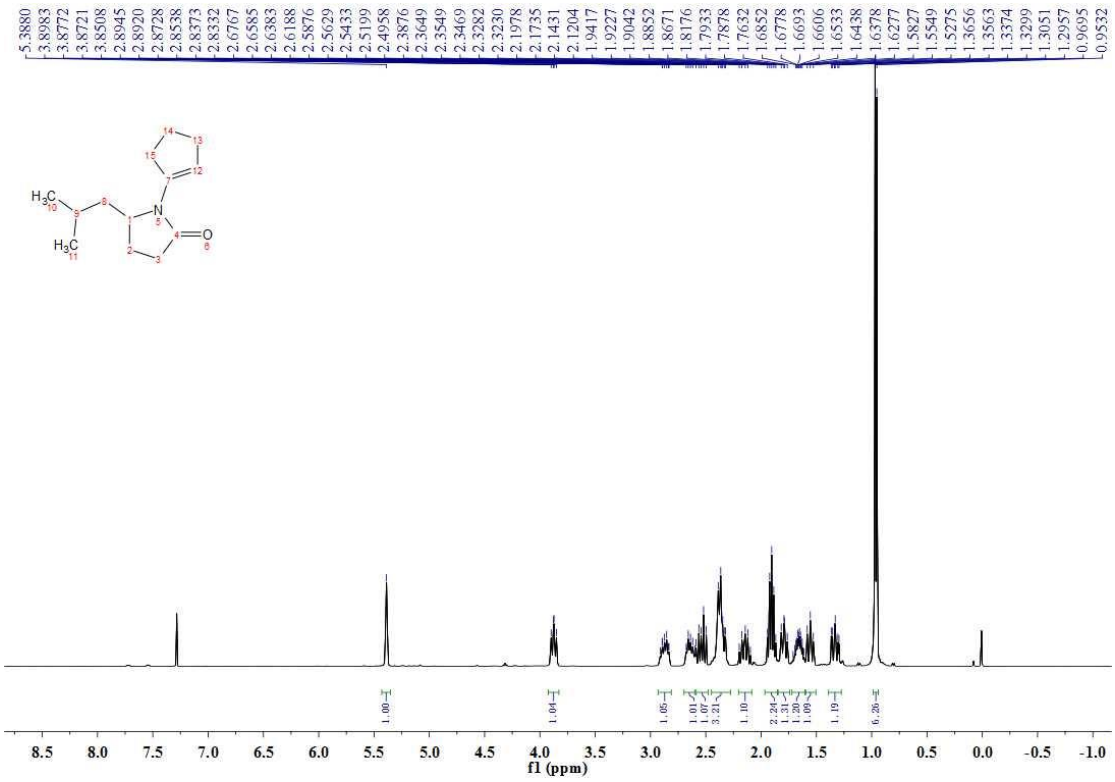
^{1}H NMR spectrum for **1x** ($CDCl_3$, 400 MHz)



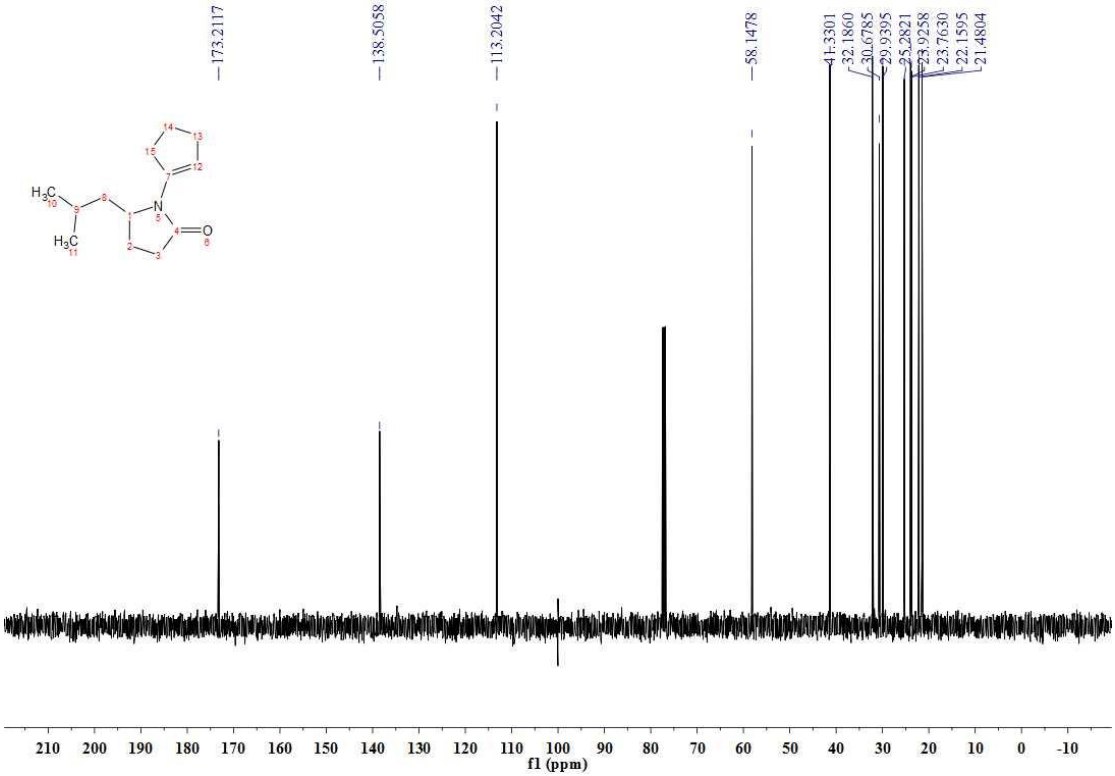
^{13}C NMR spectrum for **1x** ($CDCl_3$, 101 MHz)



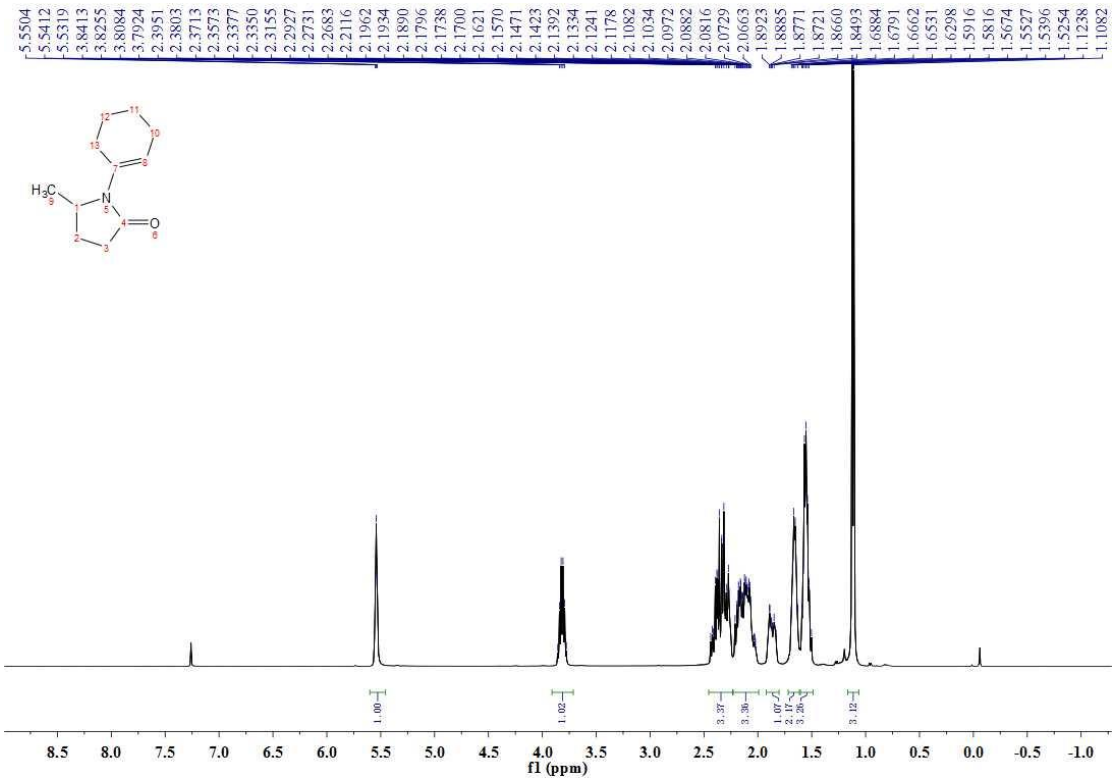
^{1}H NMR spectrum for **1y** ($CDCl_3$, 400 MHz)



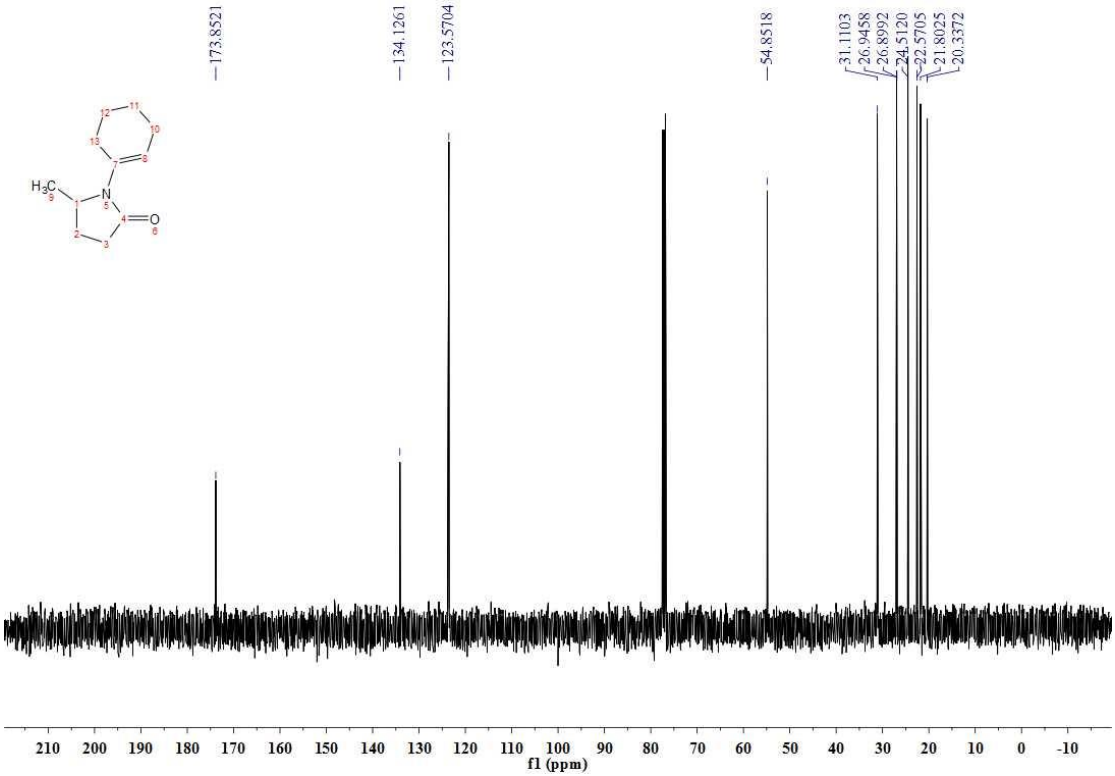
^{13}C NMR spectrum for **1y** ($CDCl_3$, 101 MHz)



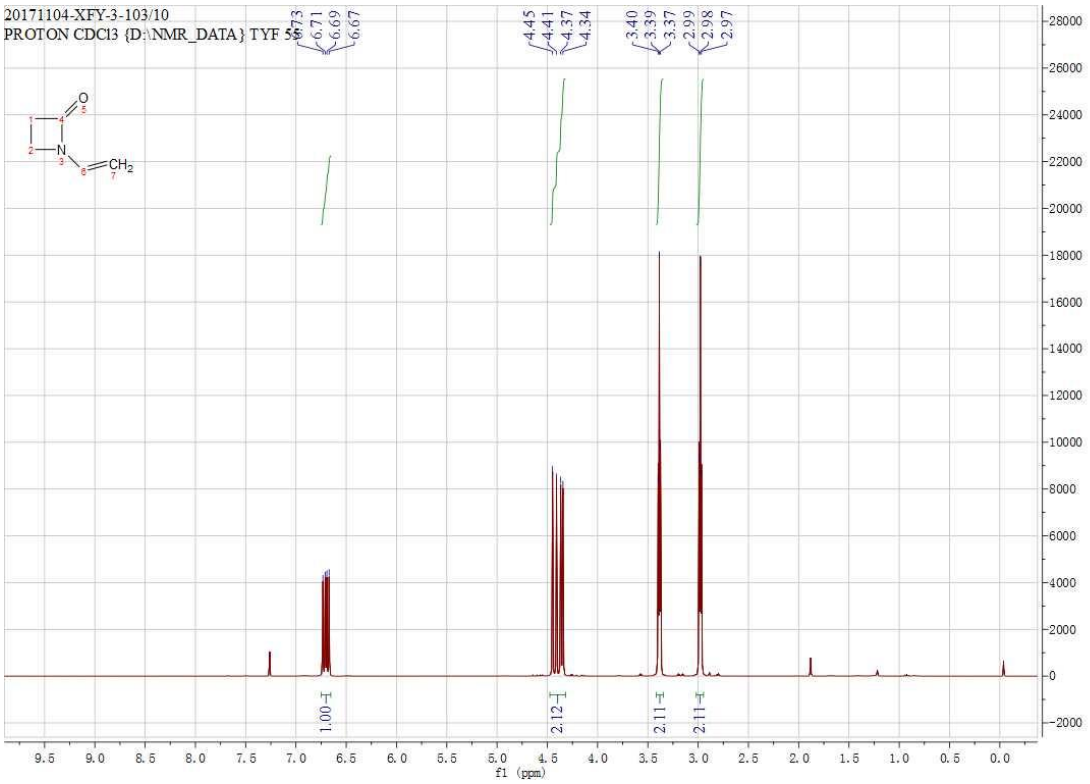
^{1}H NMR spectrum for **1z** ($CDCl_3$, 400 MHz)



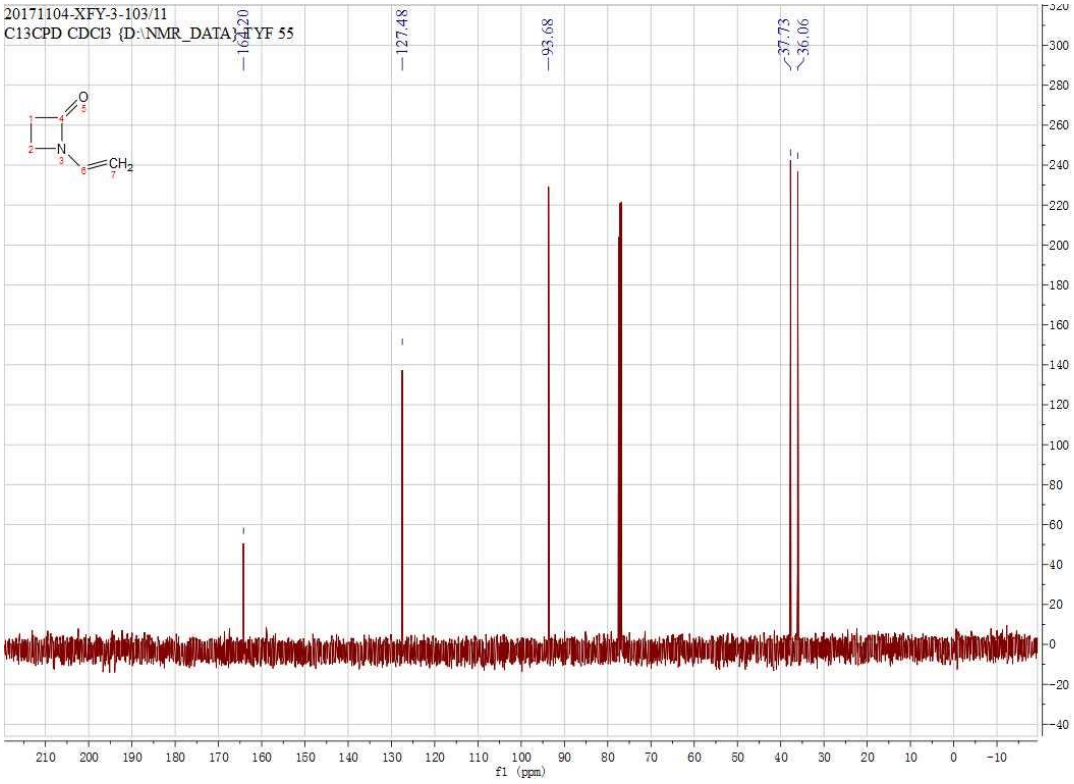
^{13}C NMR spectrum for **1z** ($CDCl_3$, 101 MHz)



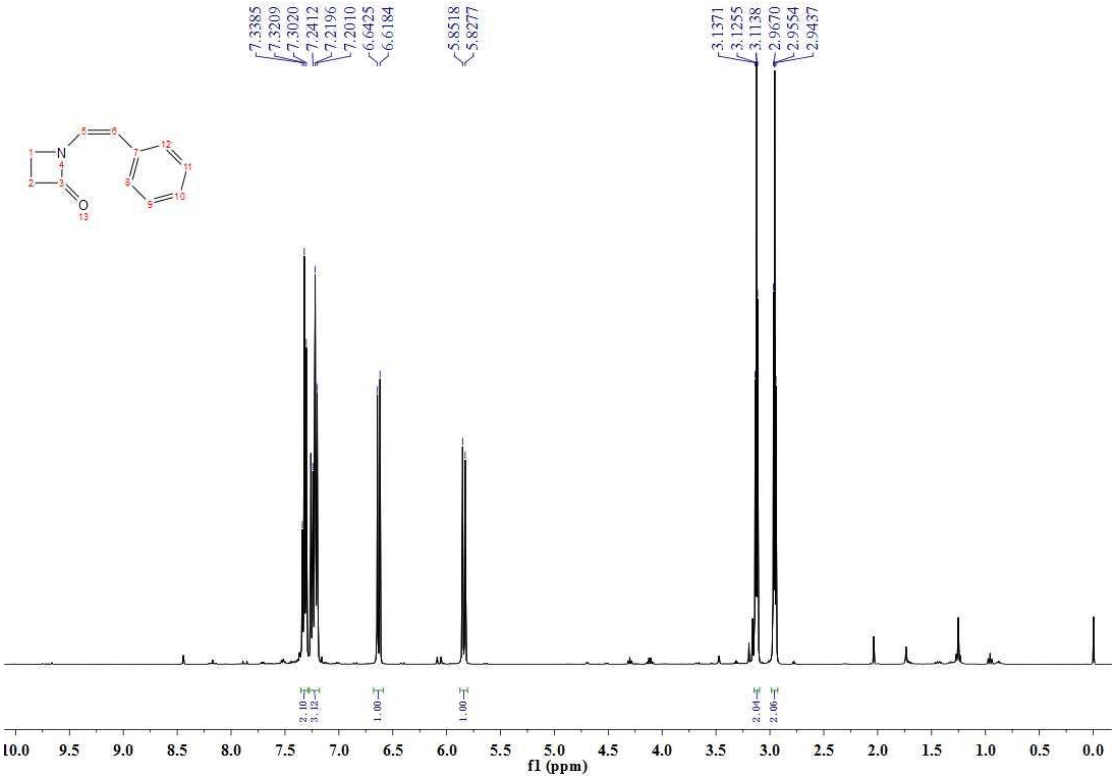
^{1}H NMR spectrum for **2a** ($CDCl_3$, 400 MHz)



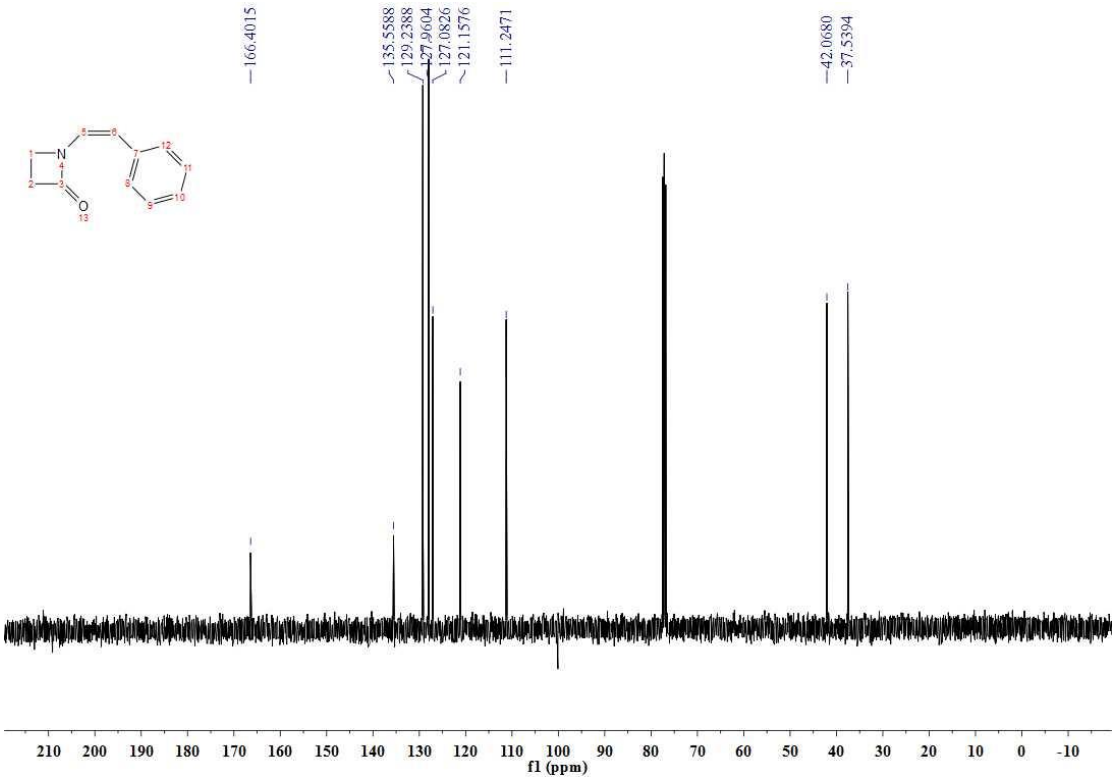
^{13}C NMR spectrum for **2a** ($CDCl_3$, 101 MHz)



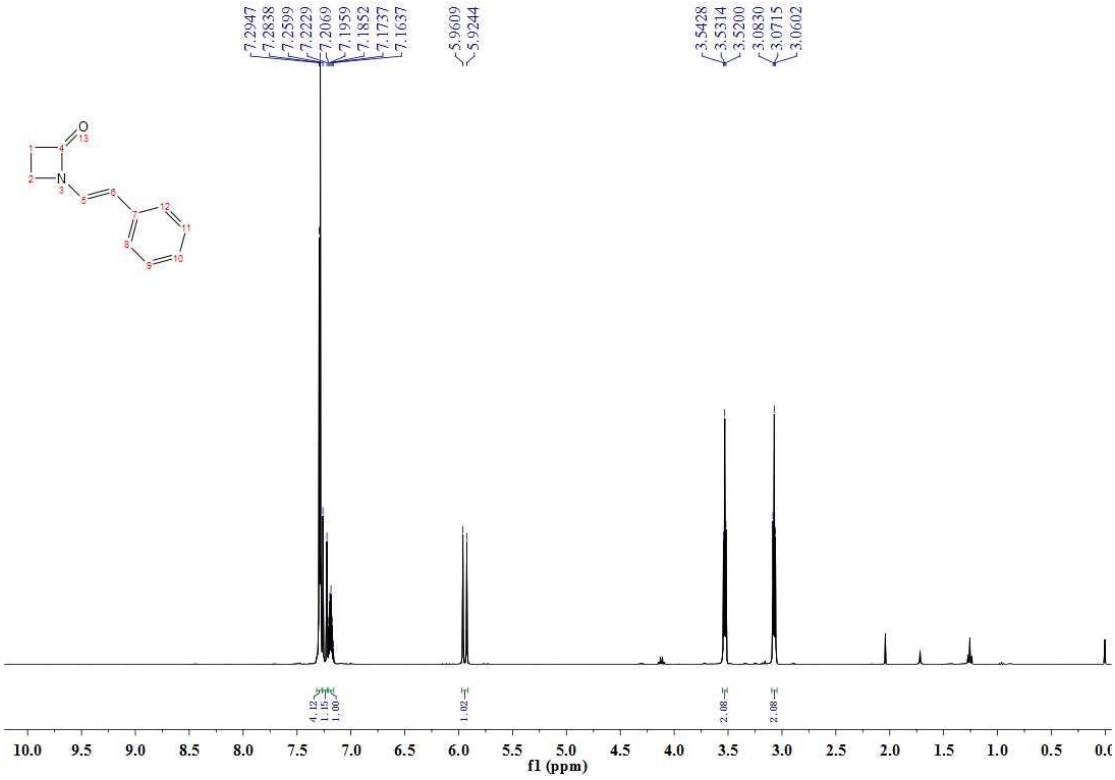
^{1}H NMR spectrum for **2b** (*cis*-isomer, $CDCl_3$, 400 MHz)



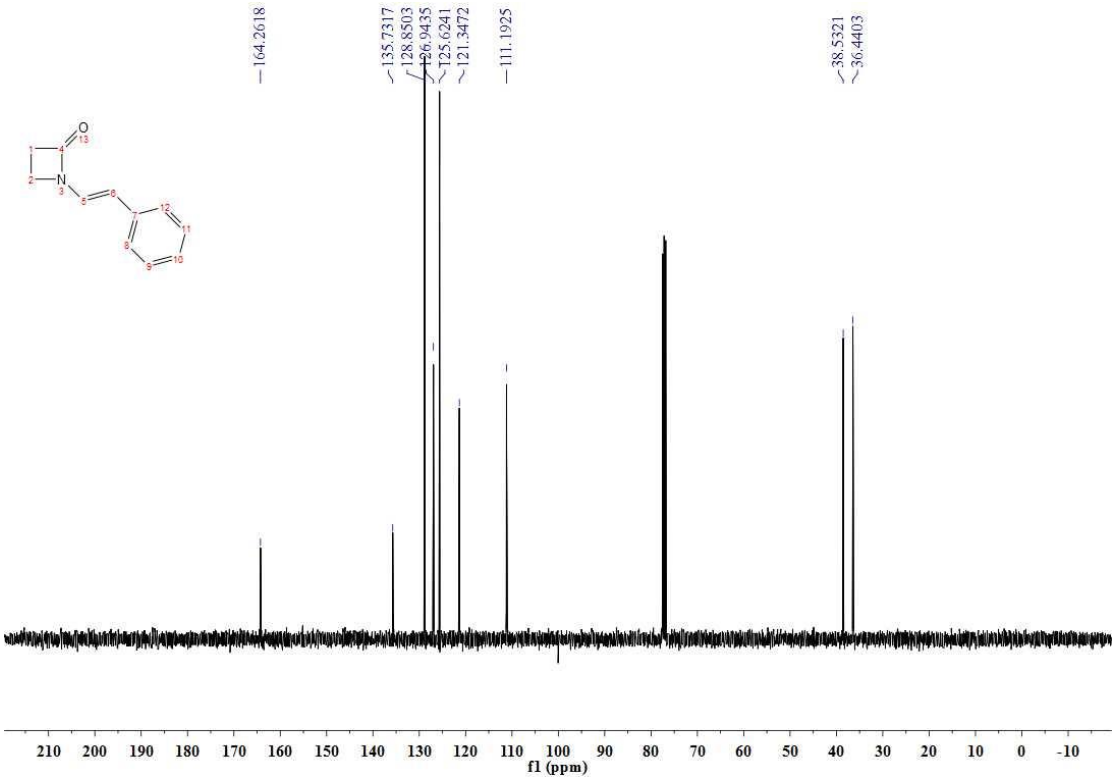
^{13}C NMR spectrum for **2b** (*cis*-isomer, $CDCl_3$, 101 MHz)



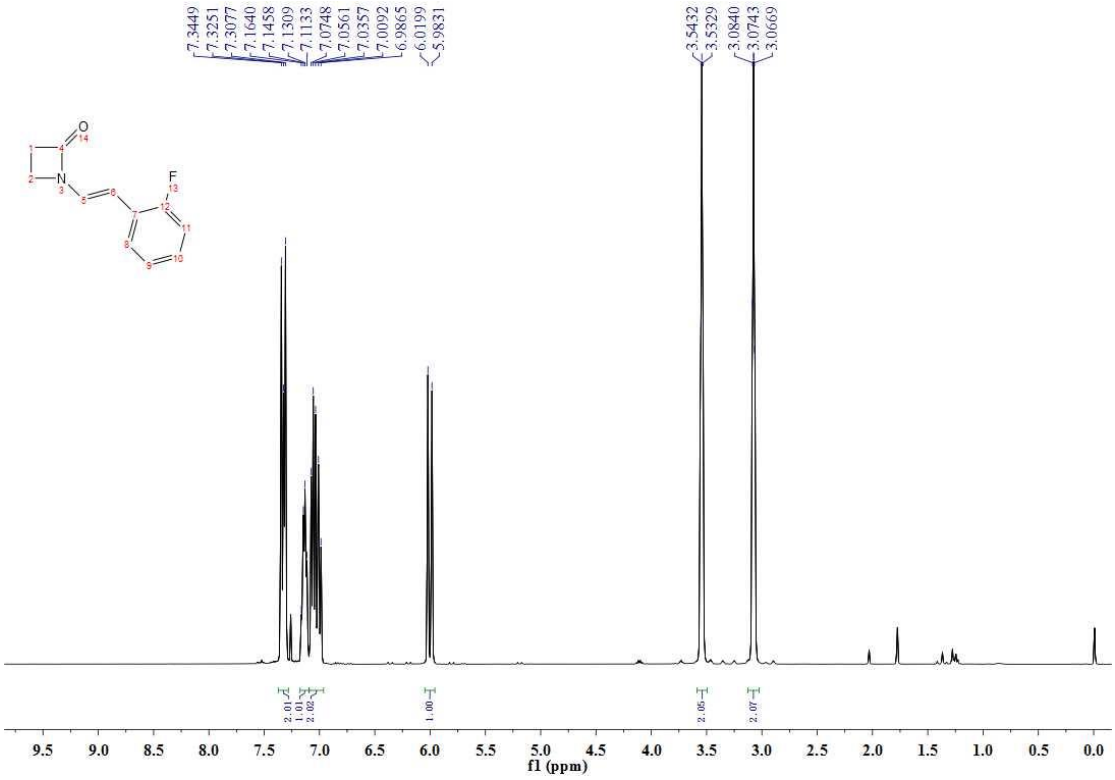
^{1}H NMR spectrum for **2b** (*trans*-isomer, $CDCl_3$, 400 MHz)



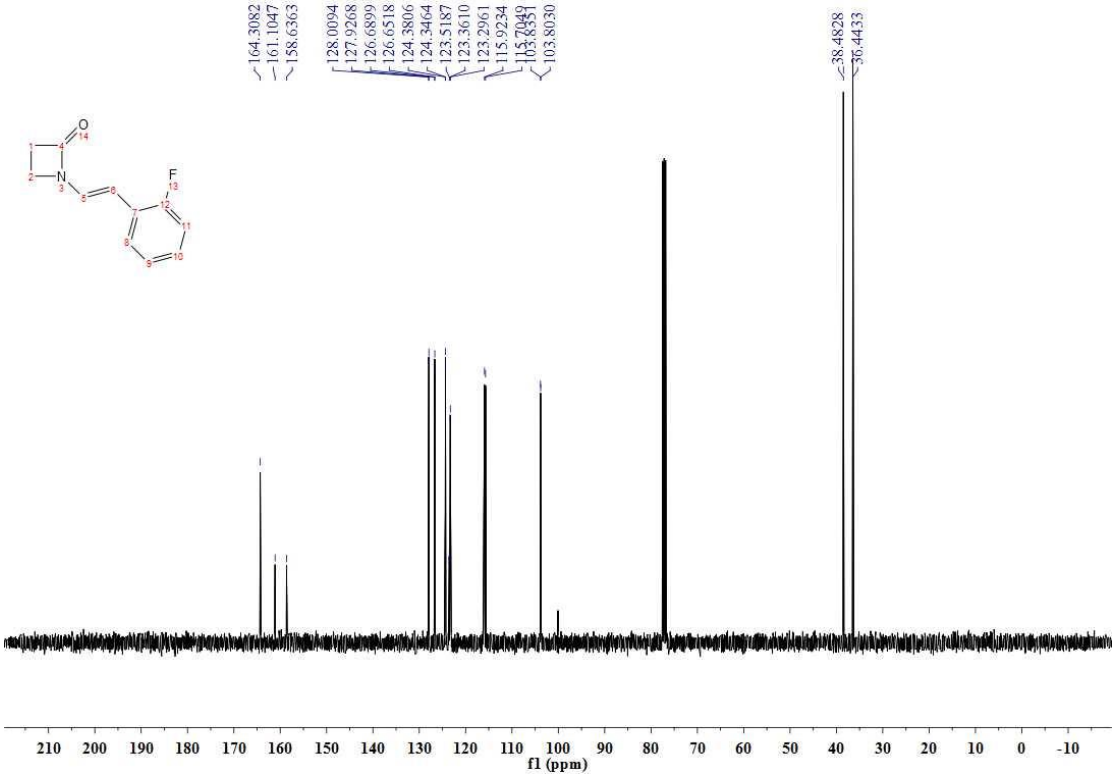
^{13}C NMR spectrum for **2b** (*trans*-isomer, $CDCl_3$, 101 MHz)



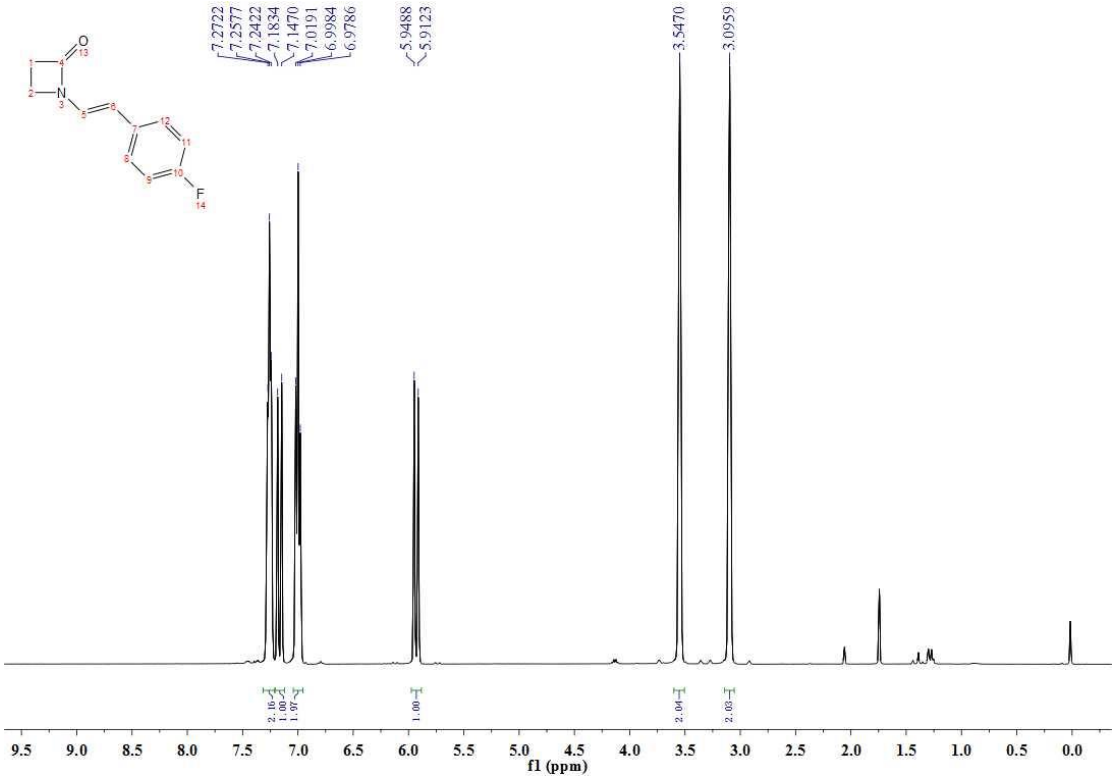
^{1}H NMR spectrum for **2c** ($CDCl_3$, 400 MHz)



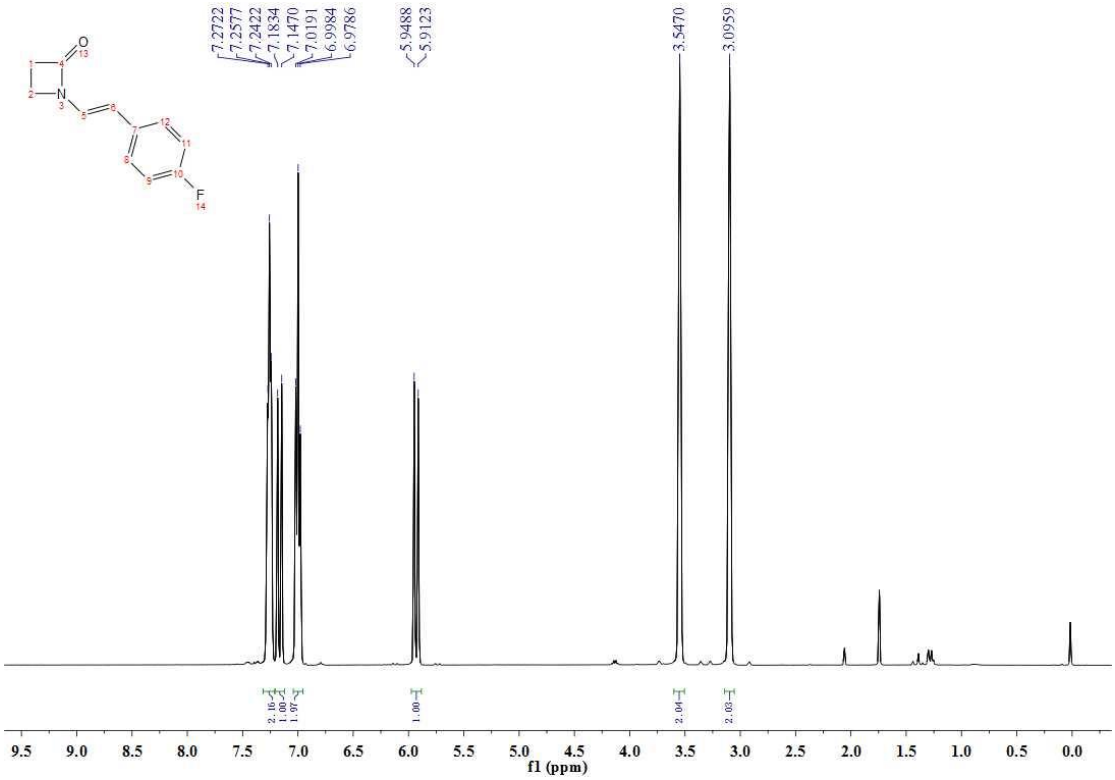
^{13}C NMR spectrum for **2c** ($CDCl_3$, 101 MHz)



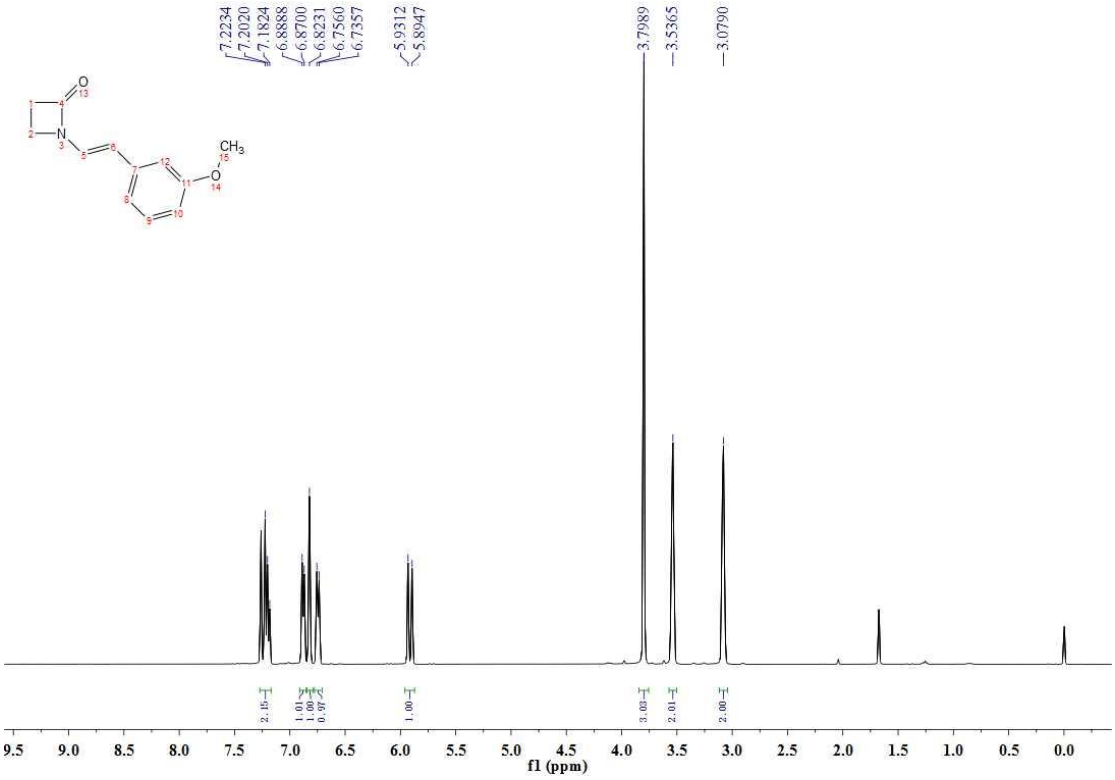
^{1}H NMR spectrum for **2d** ($CDCl_3$, 400 MHz)



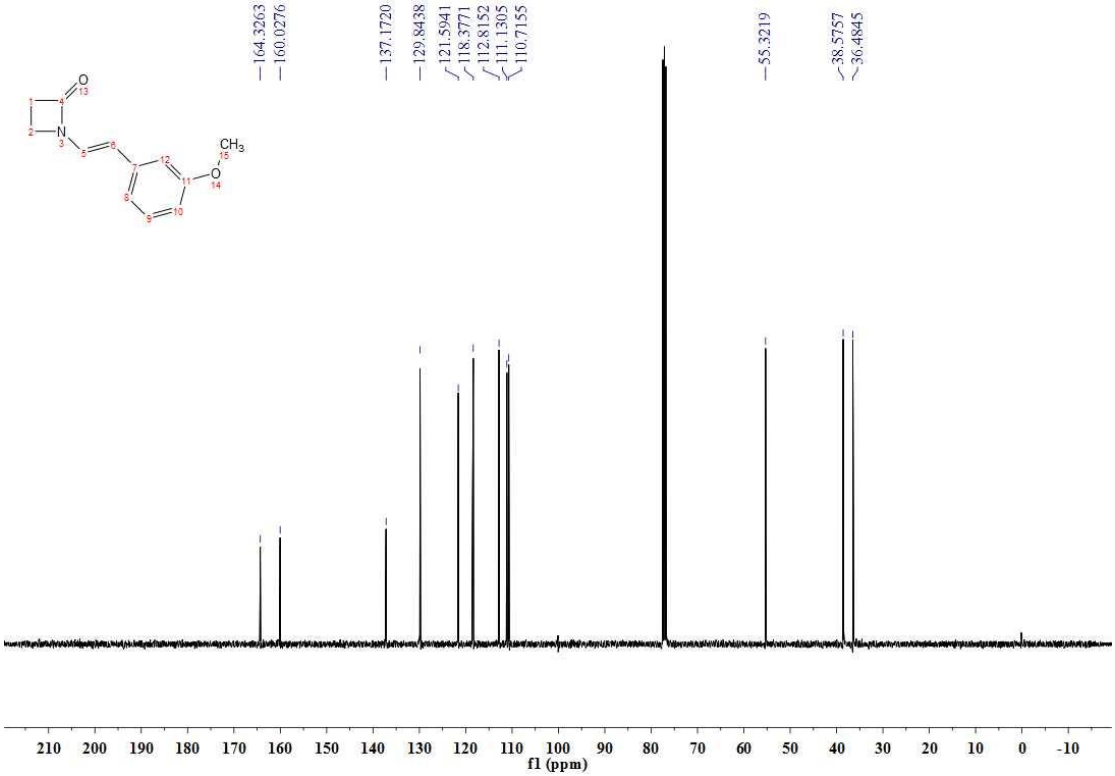
^{13}C NMR spectrum for **2d** ($CDCl_3$, 101 MHz)



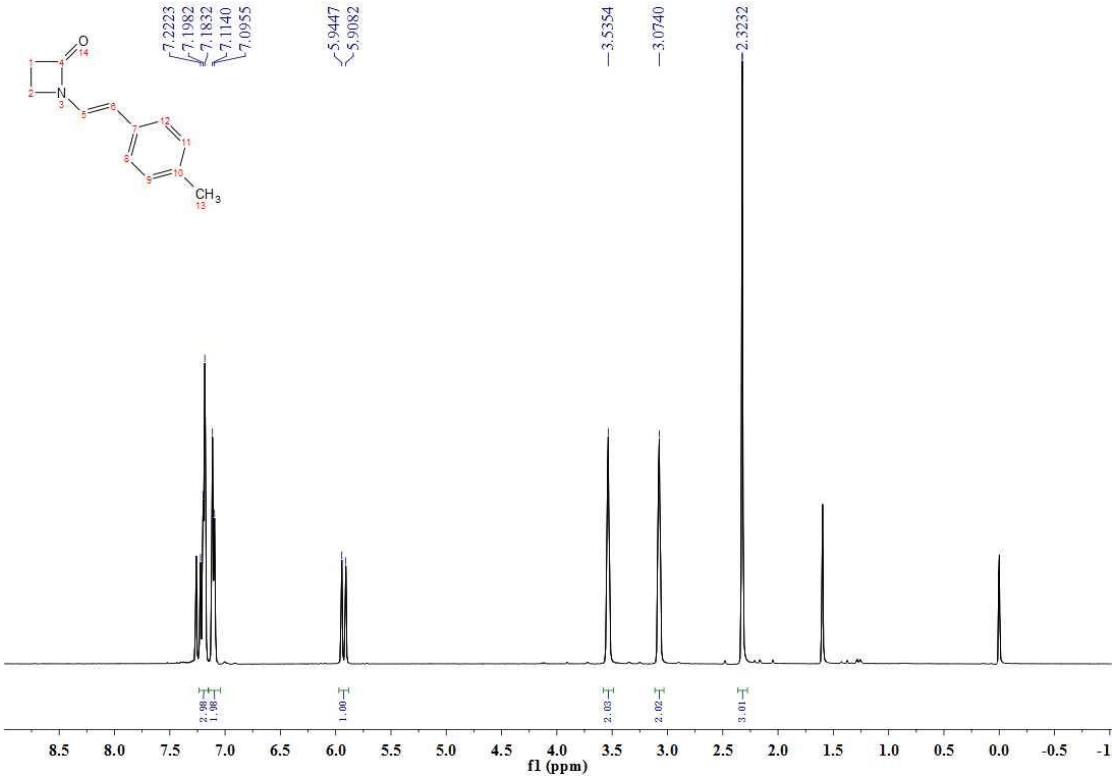
^{1}H NMR spectrum for **2e** ($CDCl_3$, 400 MHz)



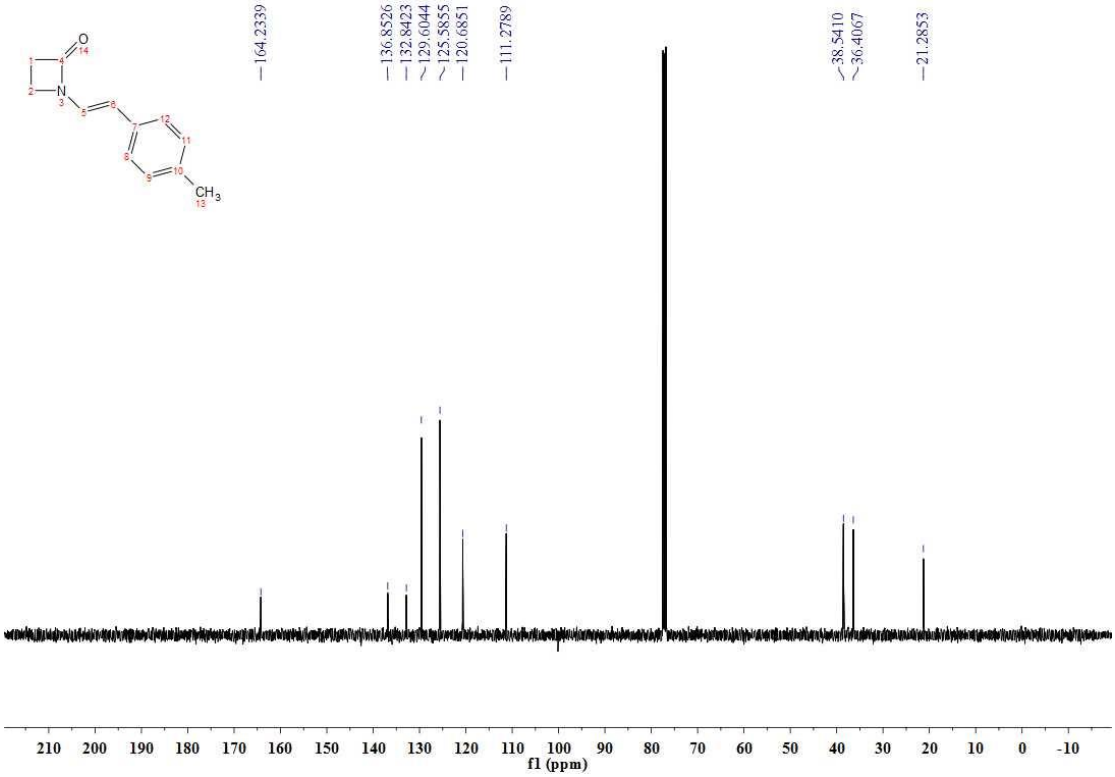
^{13}C NMR spectrum for **2e** ($CDCl_3$, 101 MHz)



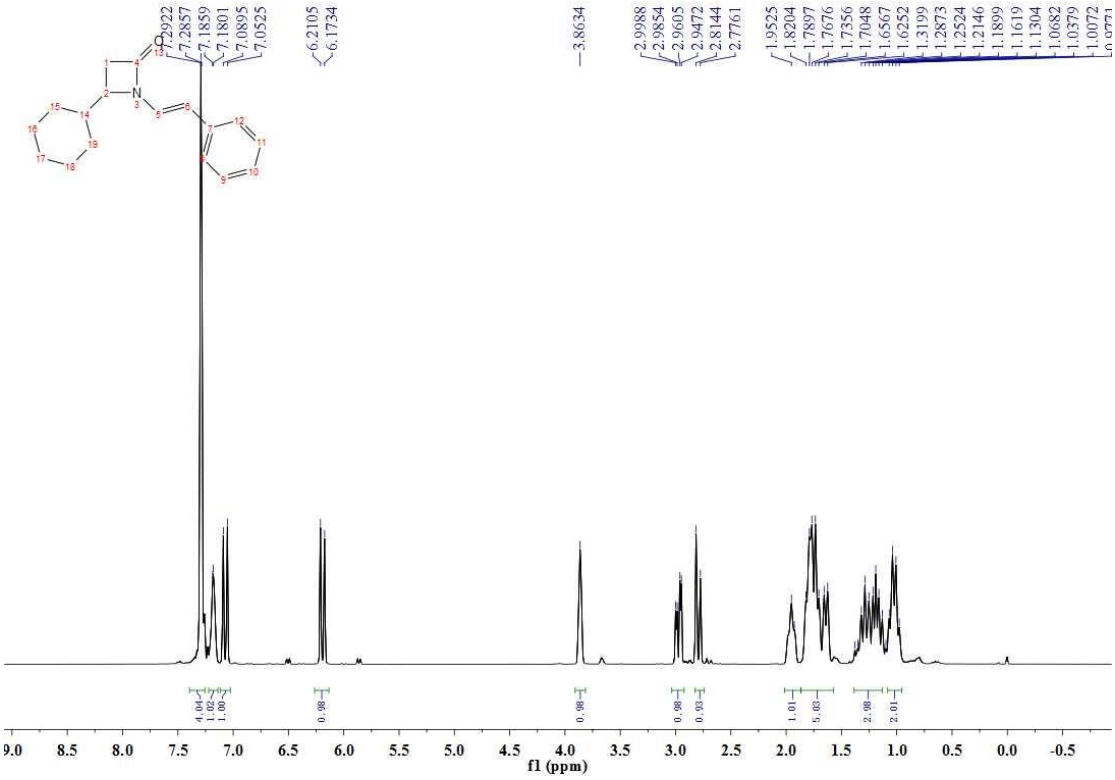
^{1}H NMR spectrum for **2f** ($CDCl_3$, 400 MHz)



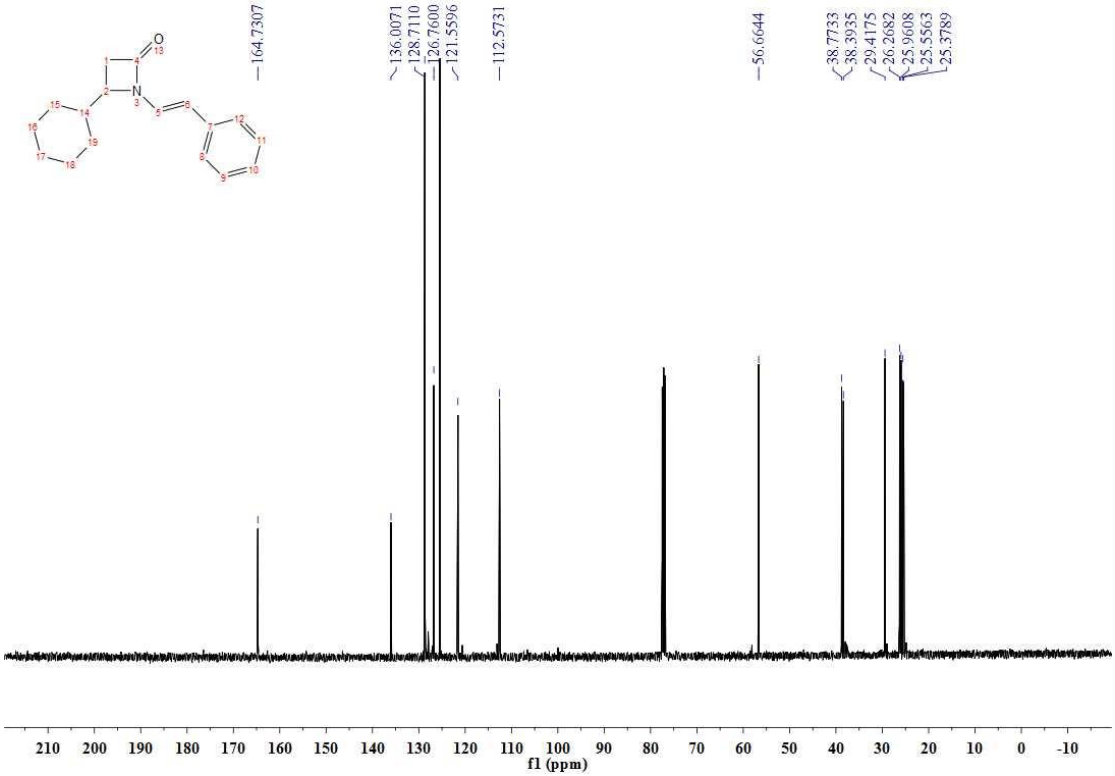
^{13}C NMR spectrum for **2f** ($CDCl_3$, 101 MHz)



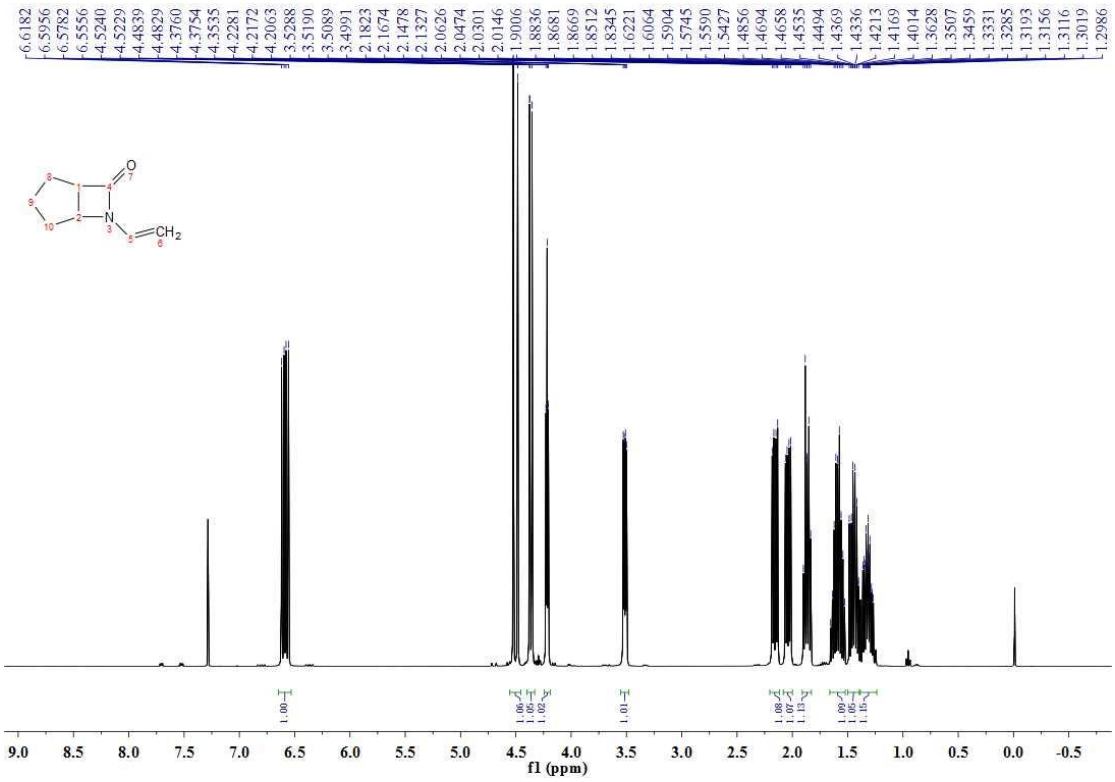
^{1}H NMR spectrum for **2g** ($CDCl_3$, 400 MHz)



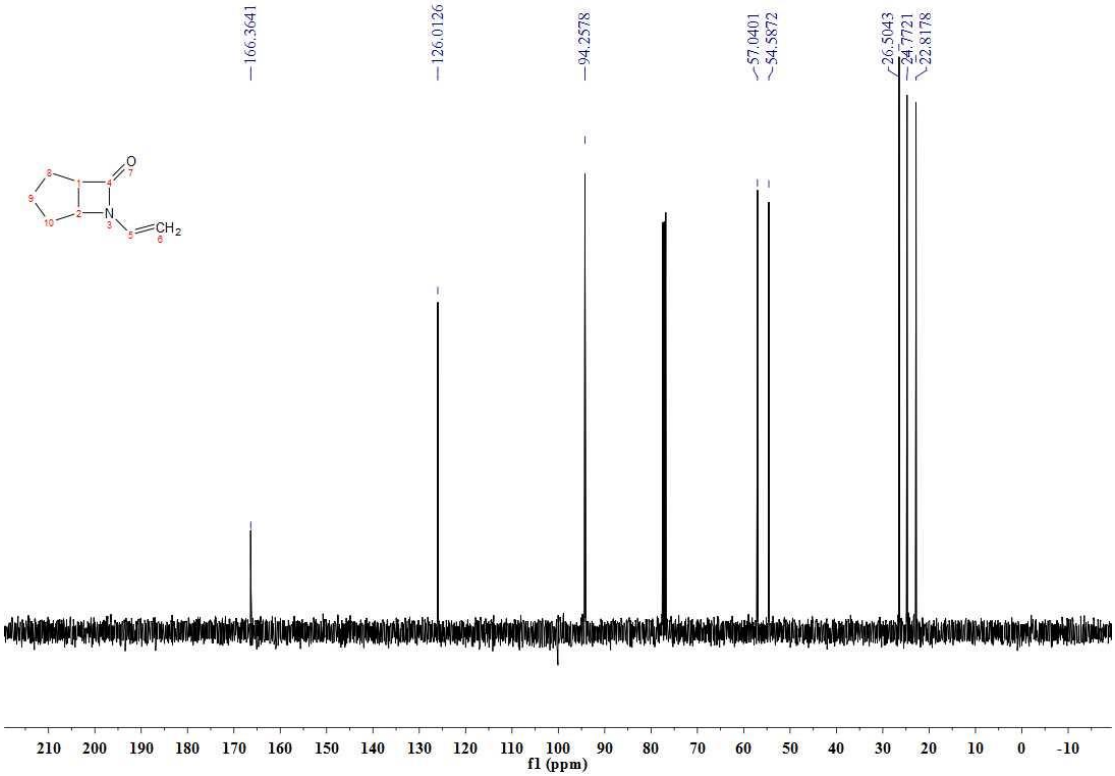
^{13}C NMR spectrum for **2g** ($CDCl_3$, 101 MHz)



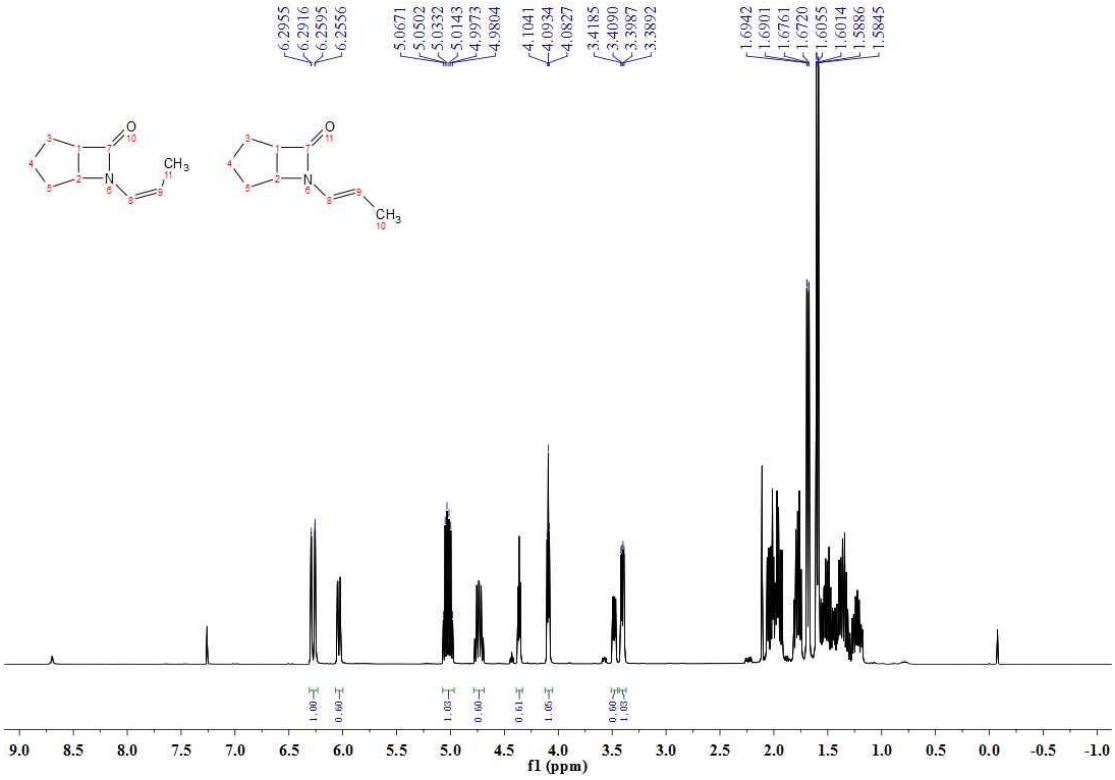
^{1}H NMR spectrum for **2h** ($CDCl_3$, 400 MHz)



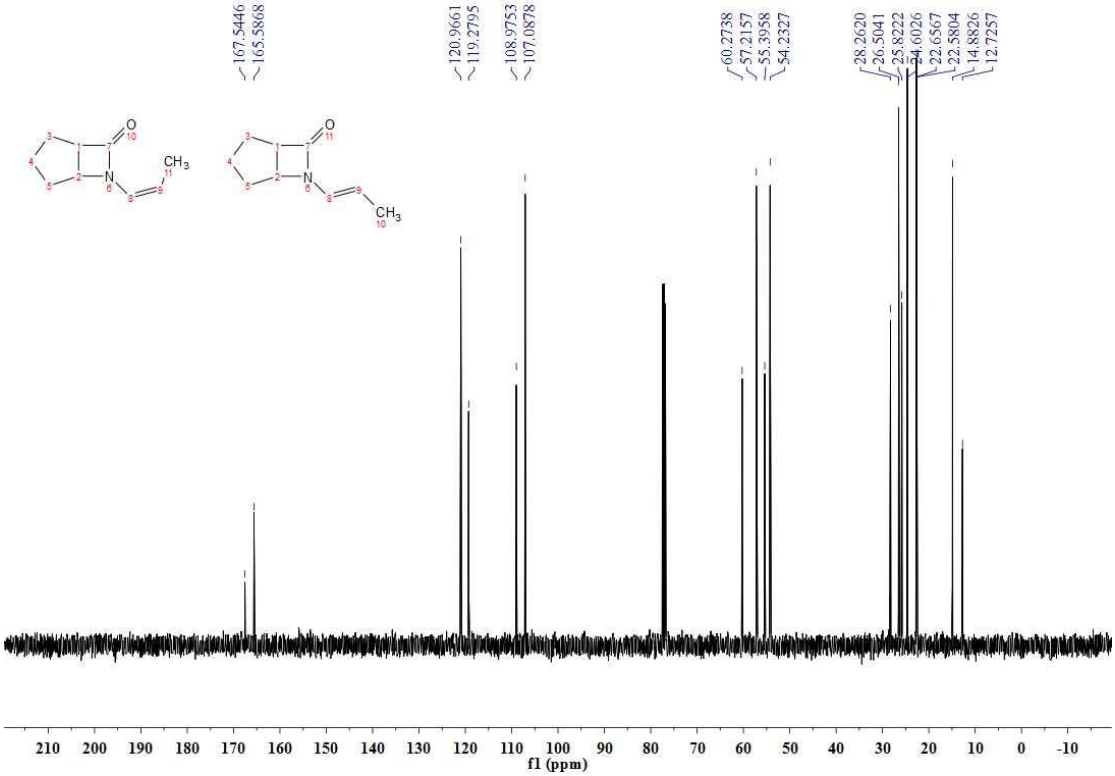
^{13}C NMR spectrum for **2h** ($CDCl_3$, 101 MHz)



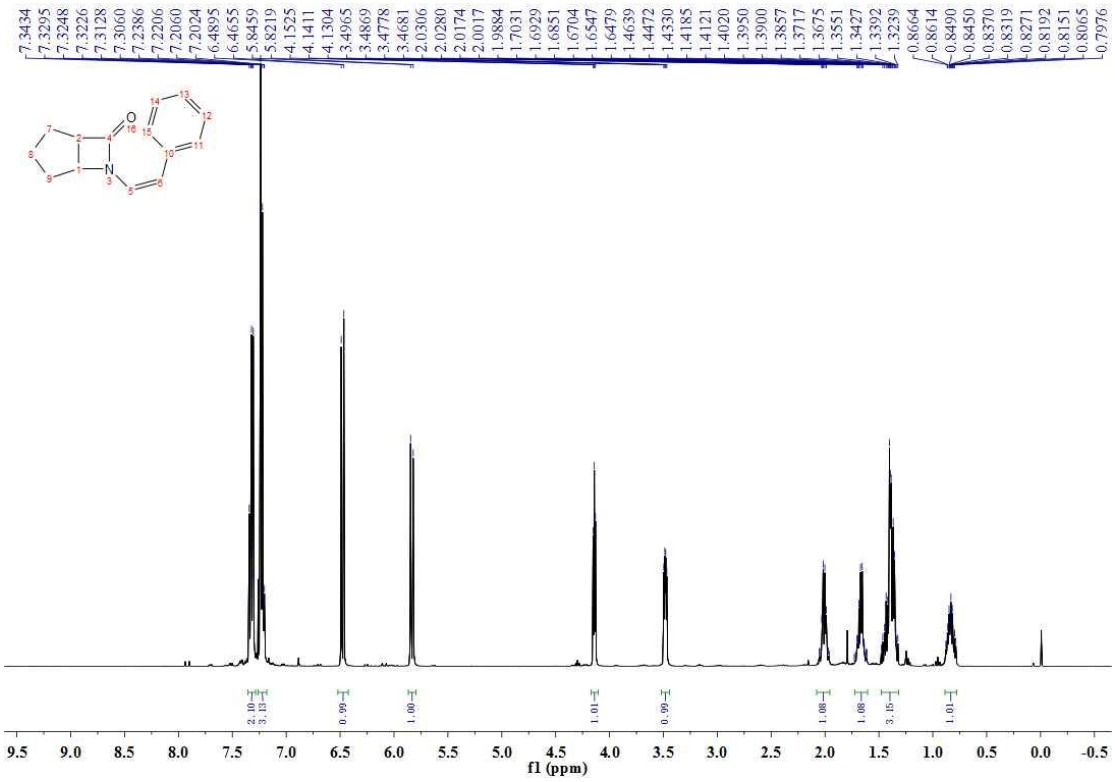
^{1}H NMR spectrum for **2i** ($CDCl_3$, 400 MHz)



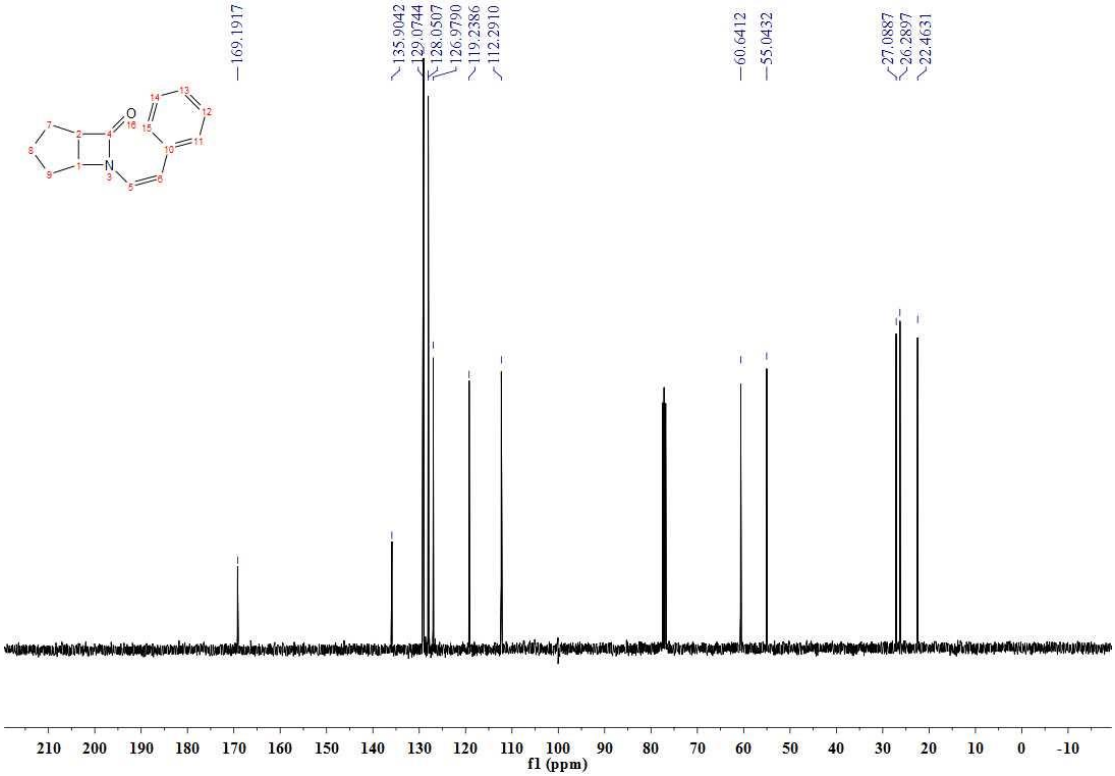
^{13}C NMR spectrum for **2i** ($CDCl_3$, 101 MHz)



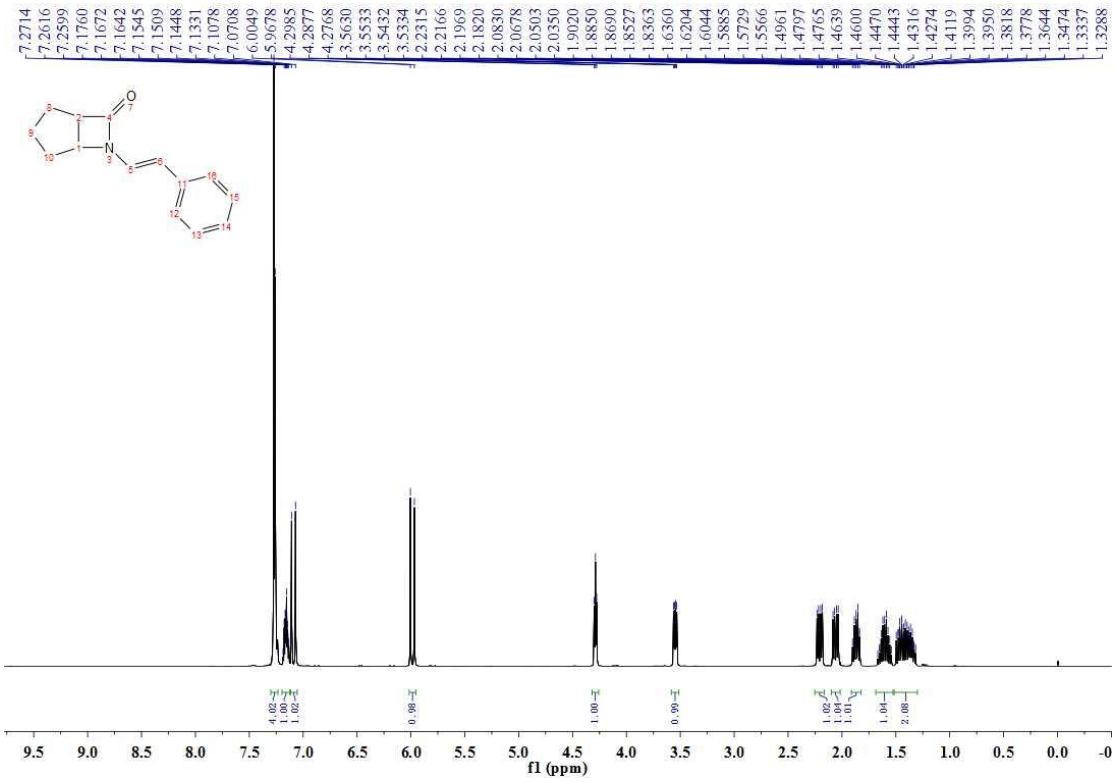
^{1}H NMR spectrum for **2j** (*cis*-isomer, $CDCl_3$, 400 MHz)



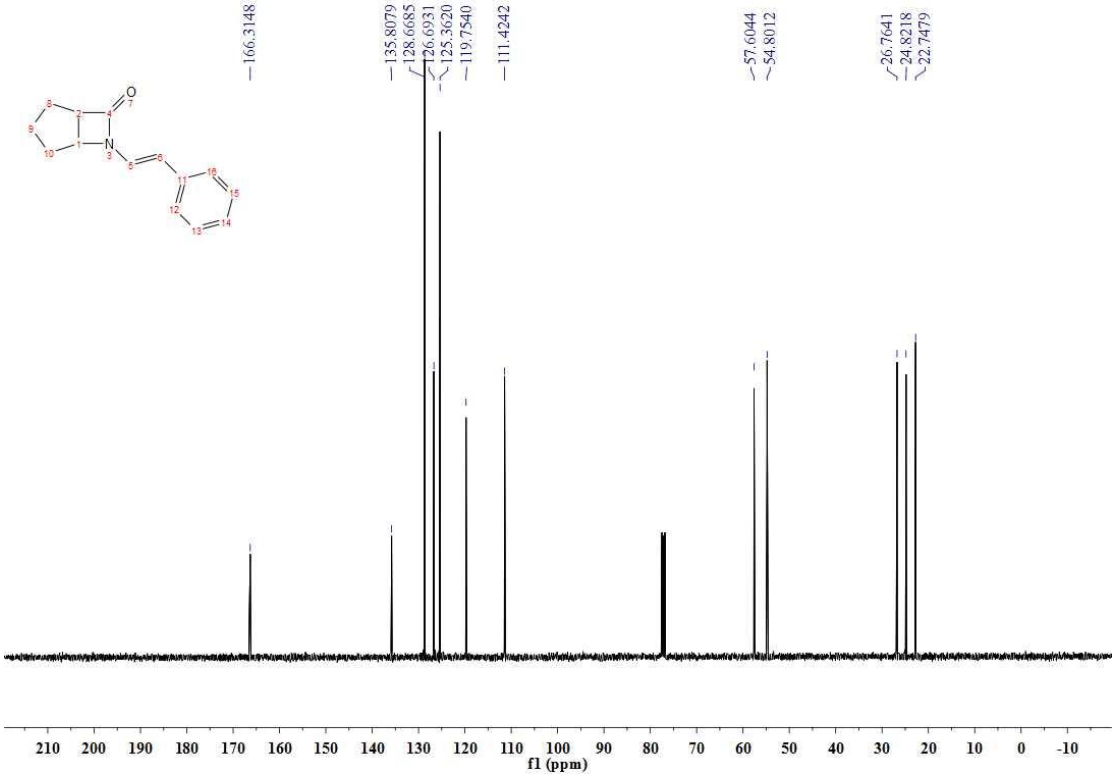
^{13}C NMR spectrum for **2j** (*cis*-isomer, $CDCl_3$, 101 MHz)



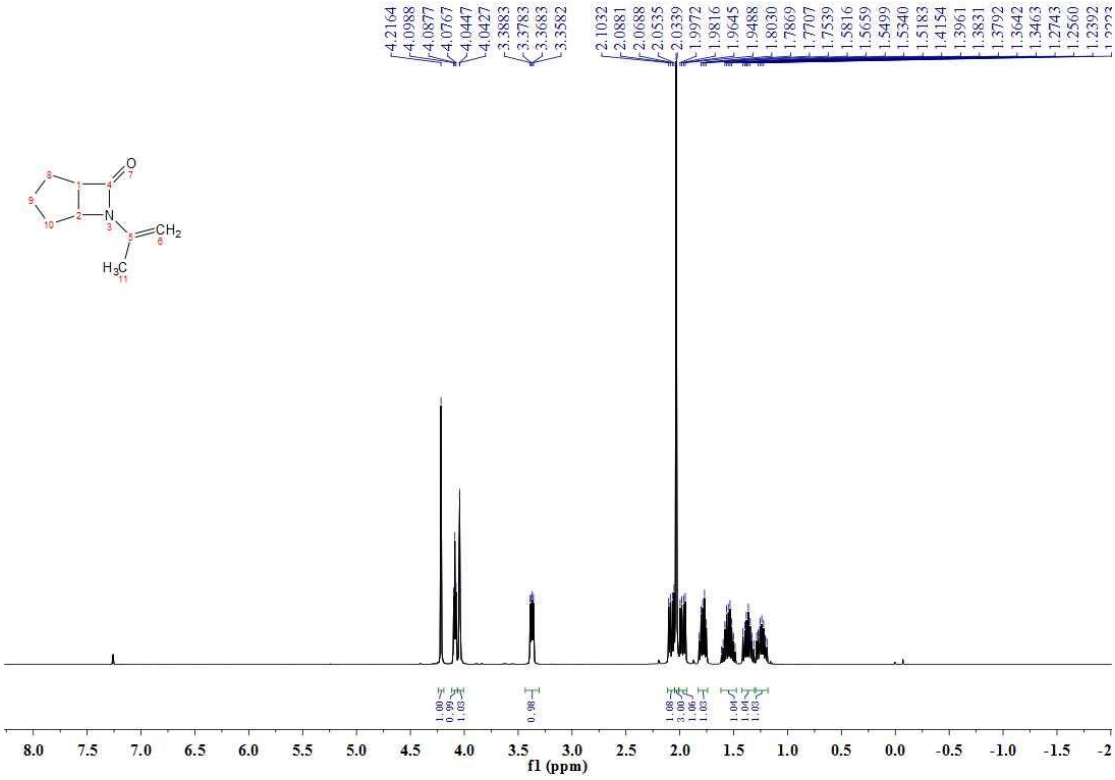
^{1}H NMR spectrum for **2j** (*trans*-isomer, $CDCl_3$, 400 MHz)



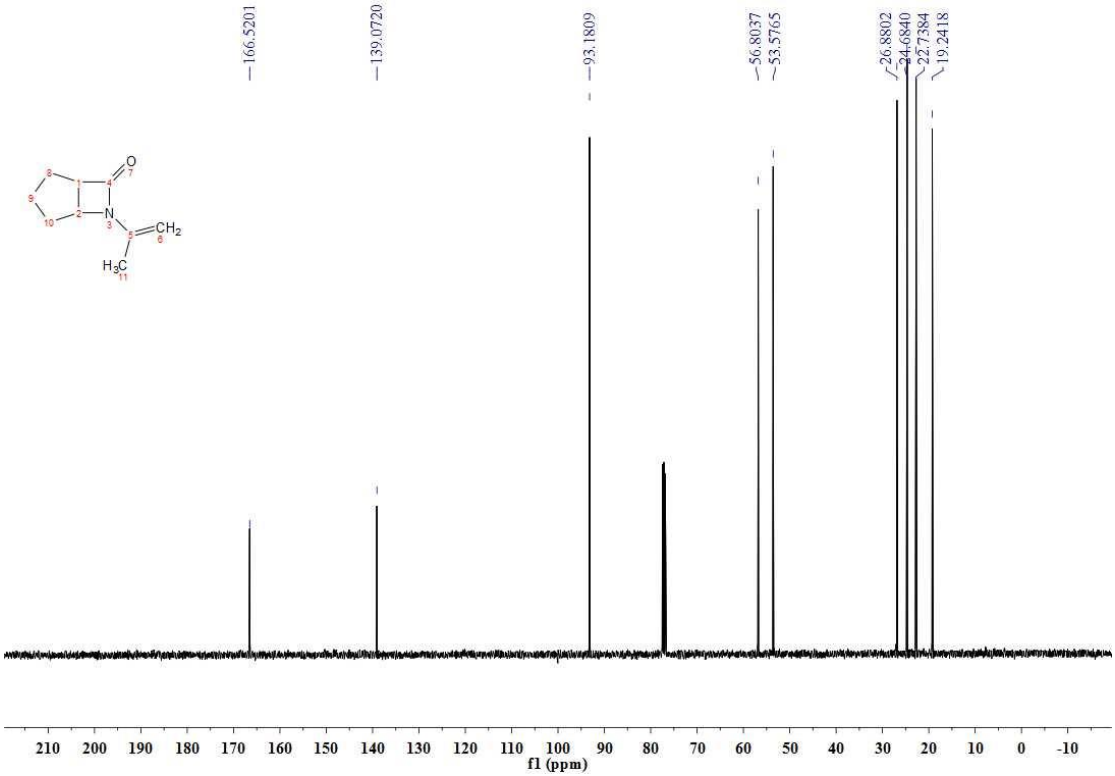
^{13}C NMR spectrum for **2j** (*trans*-isomer, $CDCl_3$, 101 MHz)



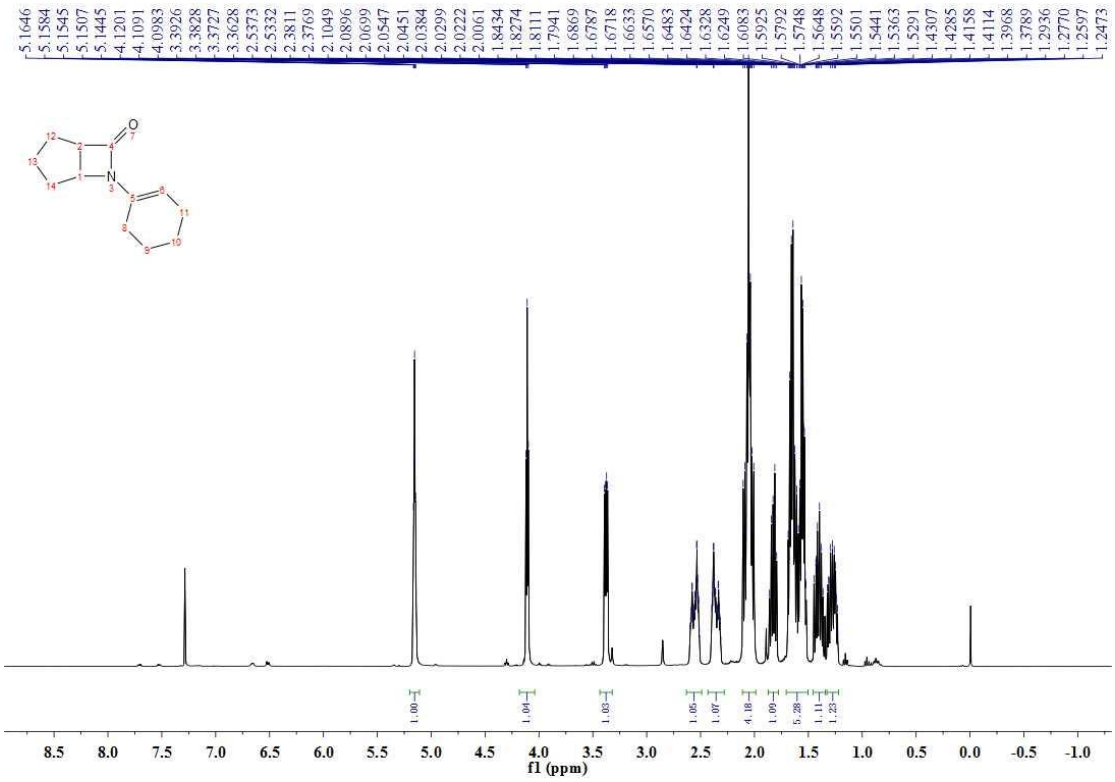
^{1}H NMR spectrum for **2k** ($CDCl_3$, 400 MHz)



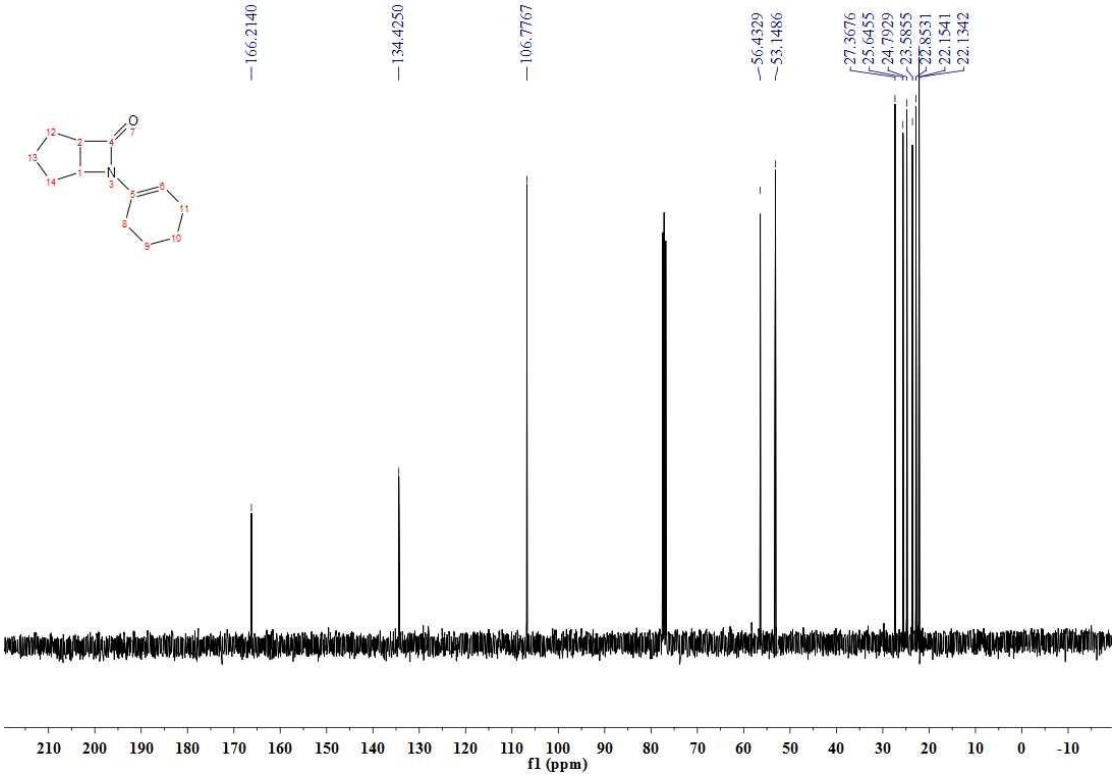
^{13}C NMR spectrum for **2k** ($CDCl_3$, 101 MHz)



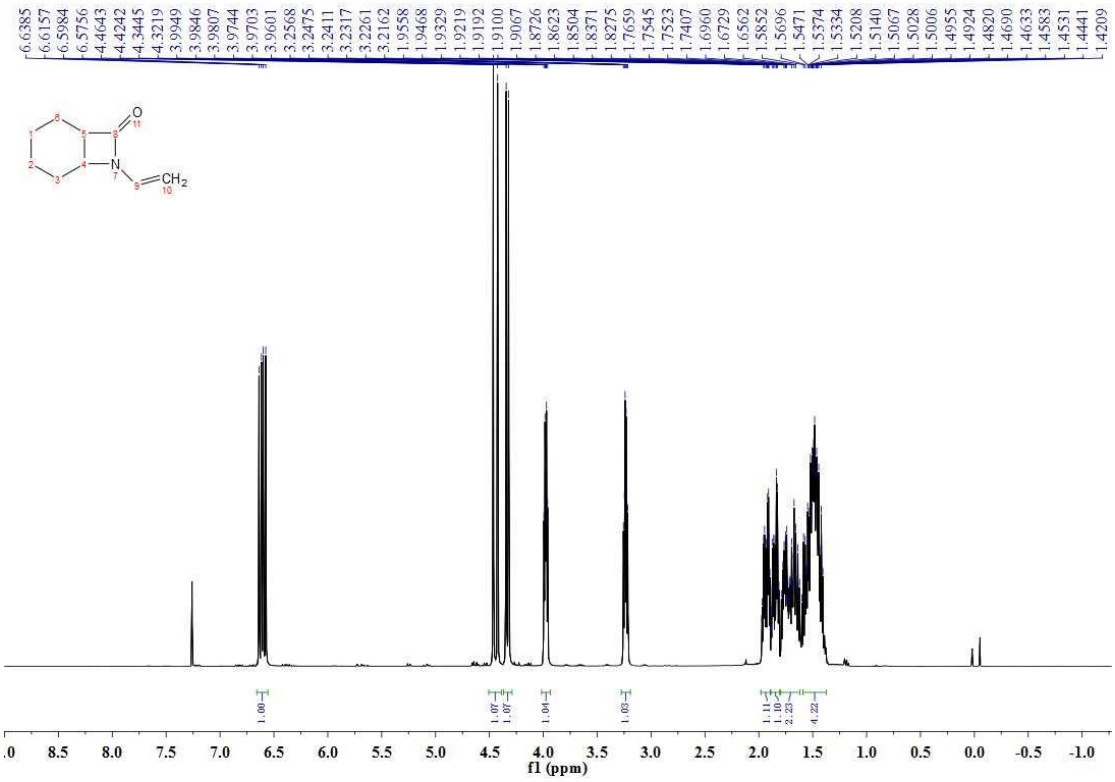
^{1}H NMR spectrum for **2l** ($CDCl_3$, 400 MHz)



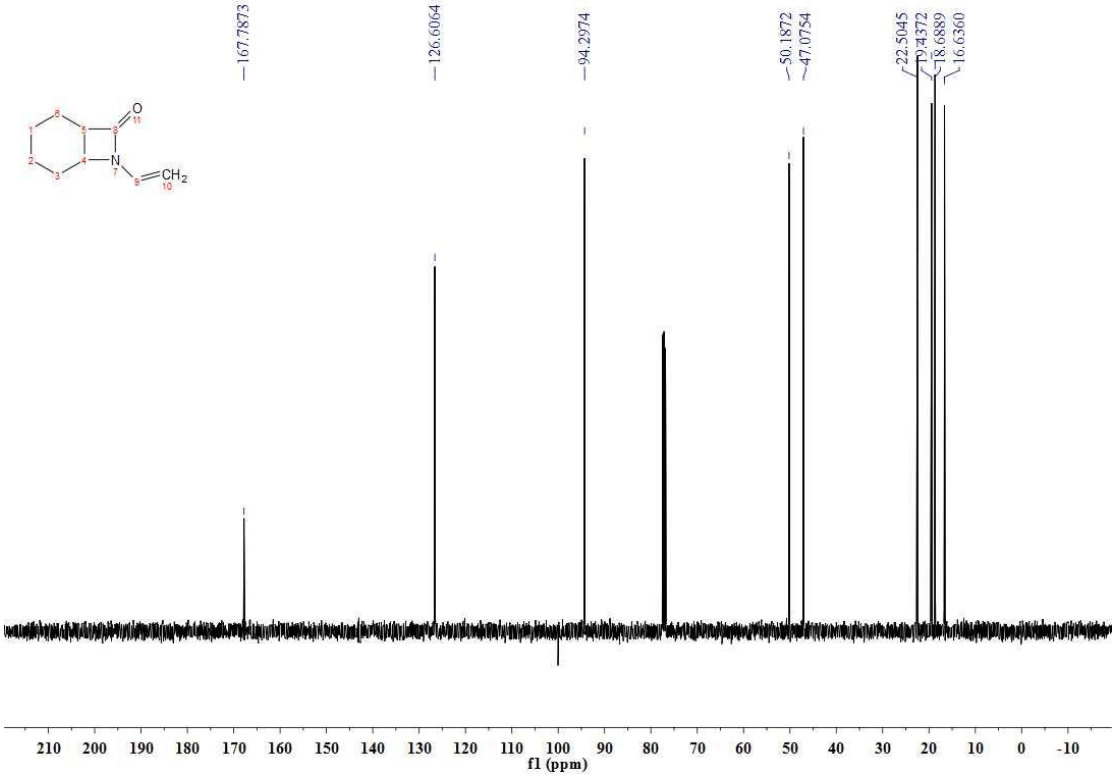
^{13}C NMR spectrum for **2l** ($CDCl_3$, 101 MHz)



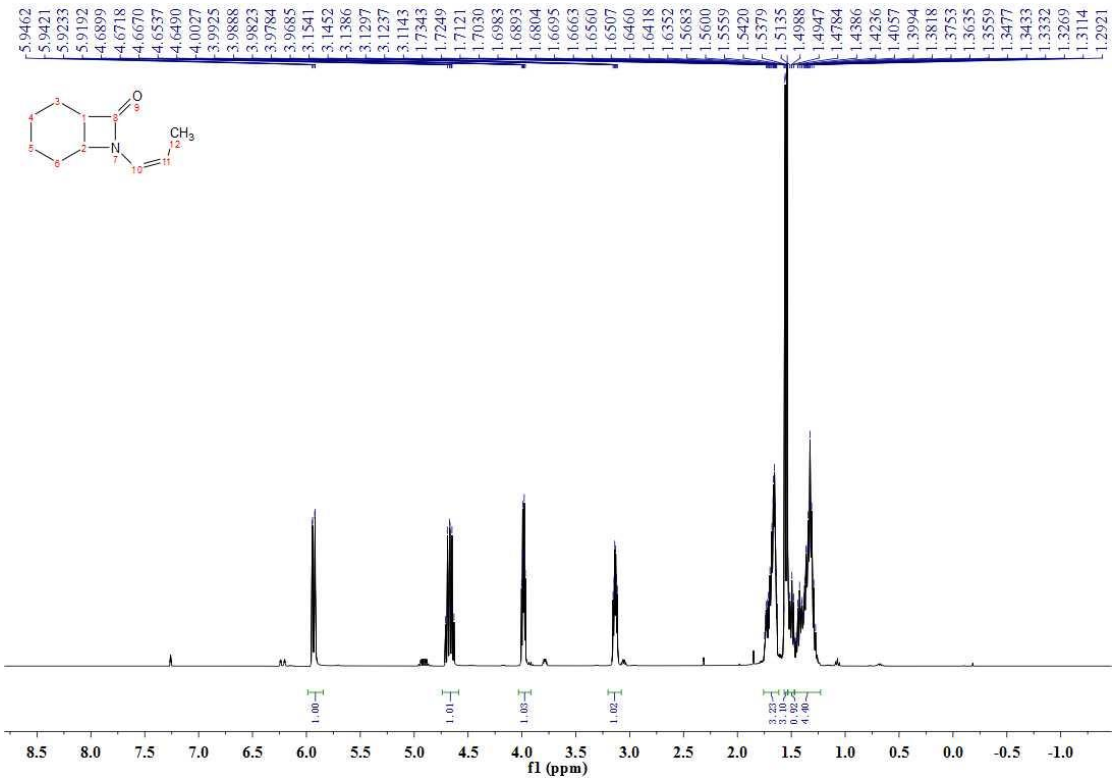
^{1}H NMR spectrum for **2m** ($CDCl_3$, 400 MHz)



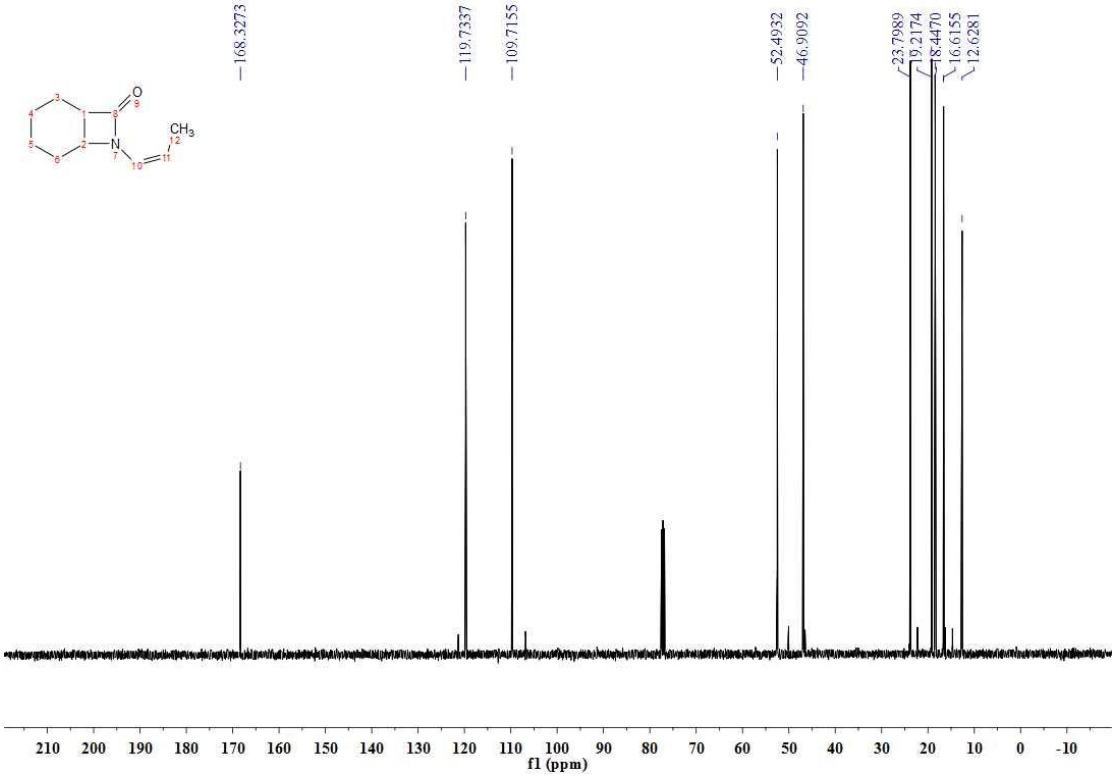
^{13}C NMR spectrum for **2m** ($CDCl_3$, 101 MHz)



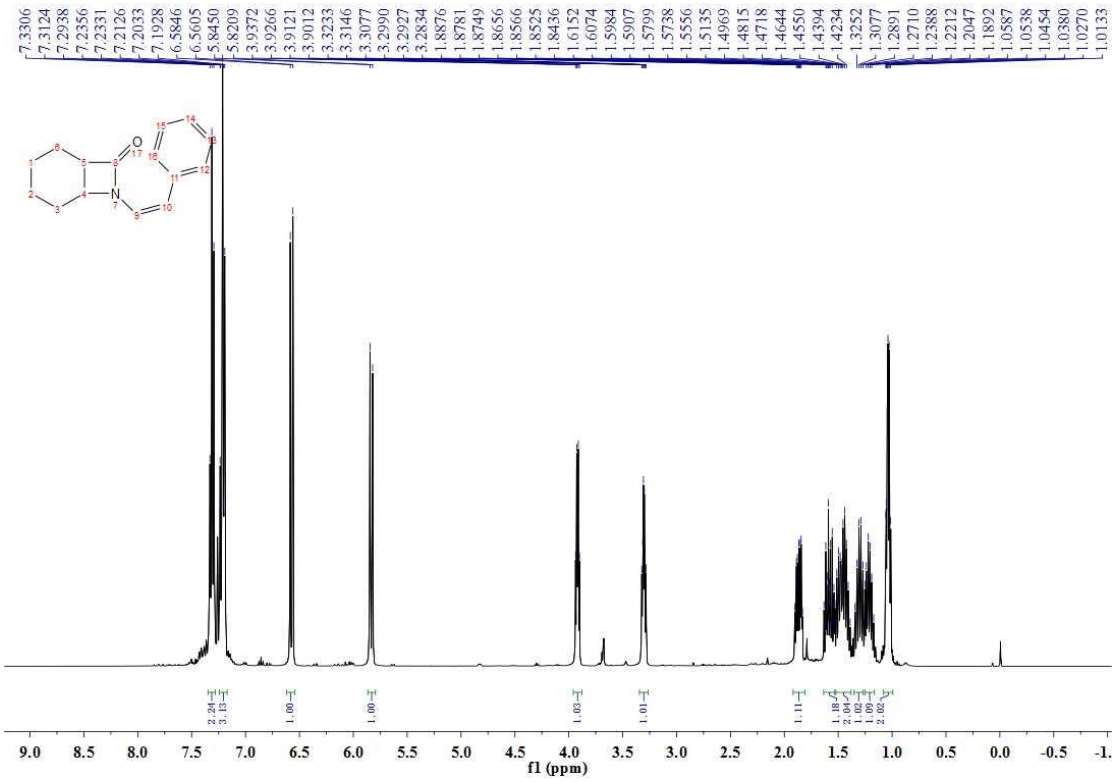
^{1}H NMR spectrum for **2n** (*cis*-isomer, $CDCl_3$, 400 MHz)



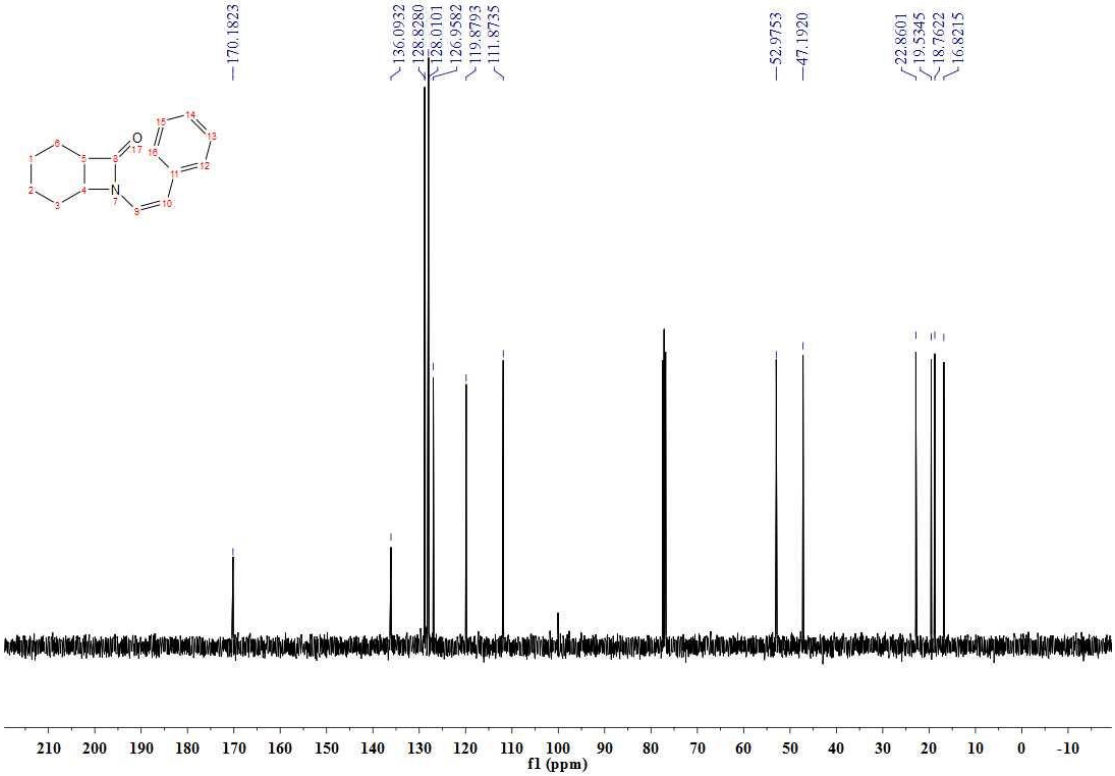
^{13}C NMR spectrum for **2n** (*cis*-isomer, $CDCl_3$, 101 MHz)



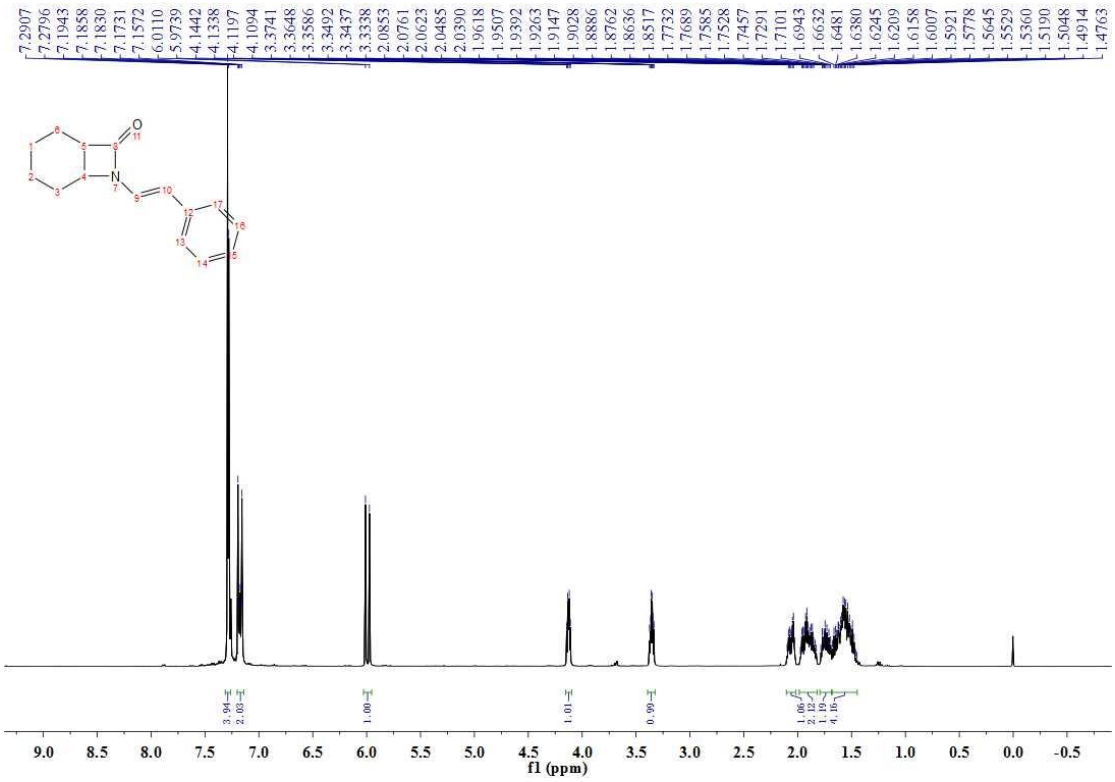
^{1}H NMR spectrum for **2o** (*cis*-isomer, $CDCl_3$, 400 MHz)



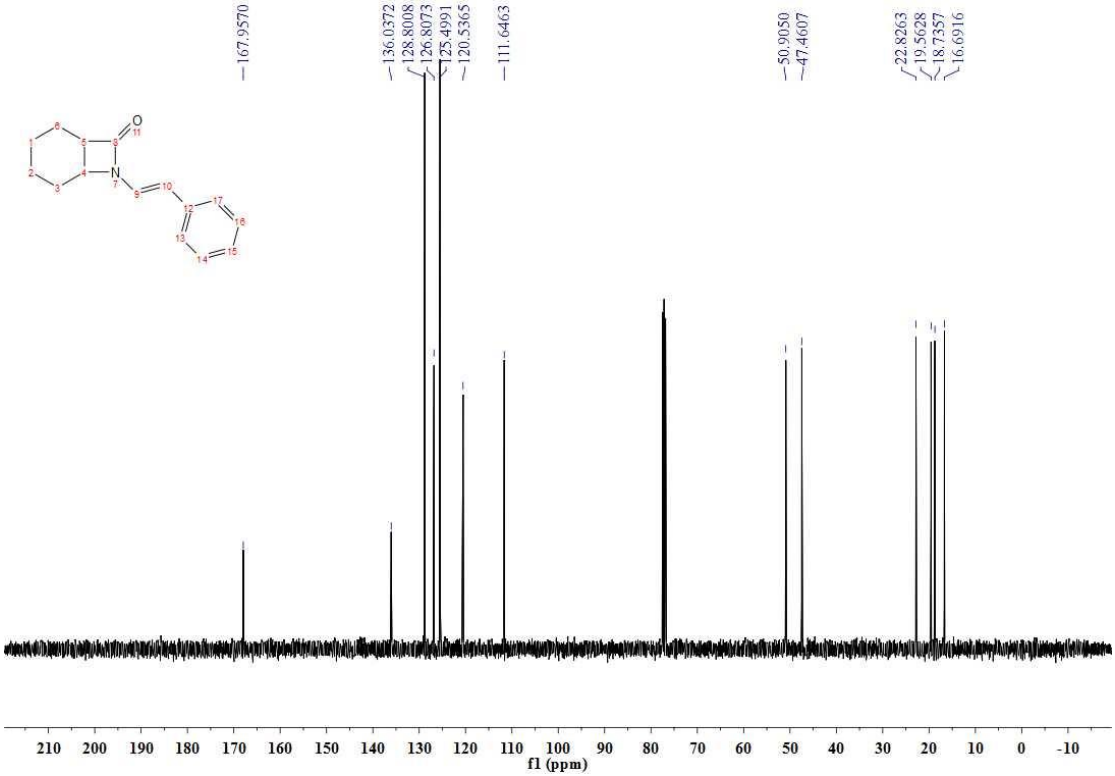
^{13}C NMR spectrum for **2o** (*cis*-isomer, $CDCl_3$, 101 MHz)



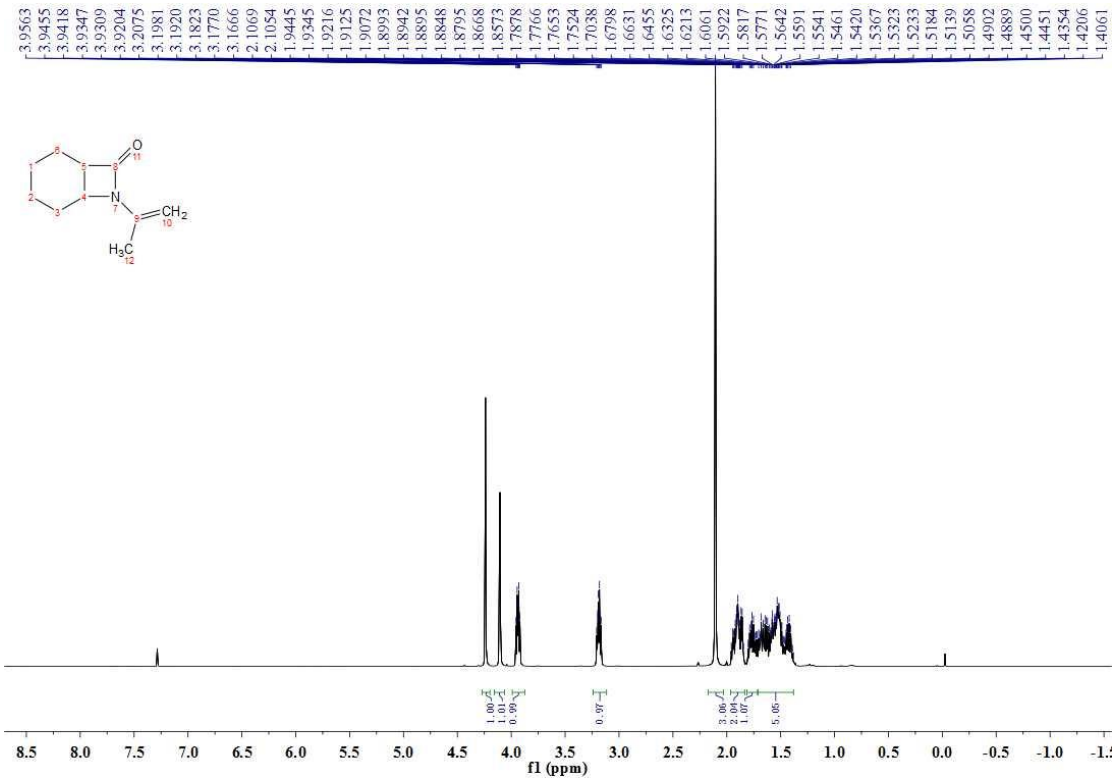
^{1}H NMR spectrum for **2o** (*trans*-isomer, $CDCl_3$, 400 MHz)



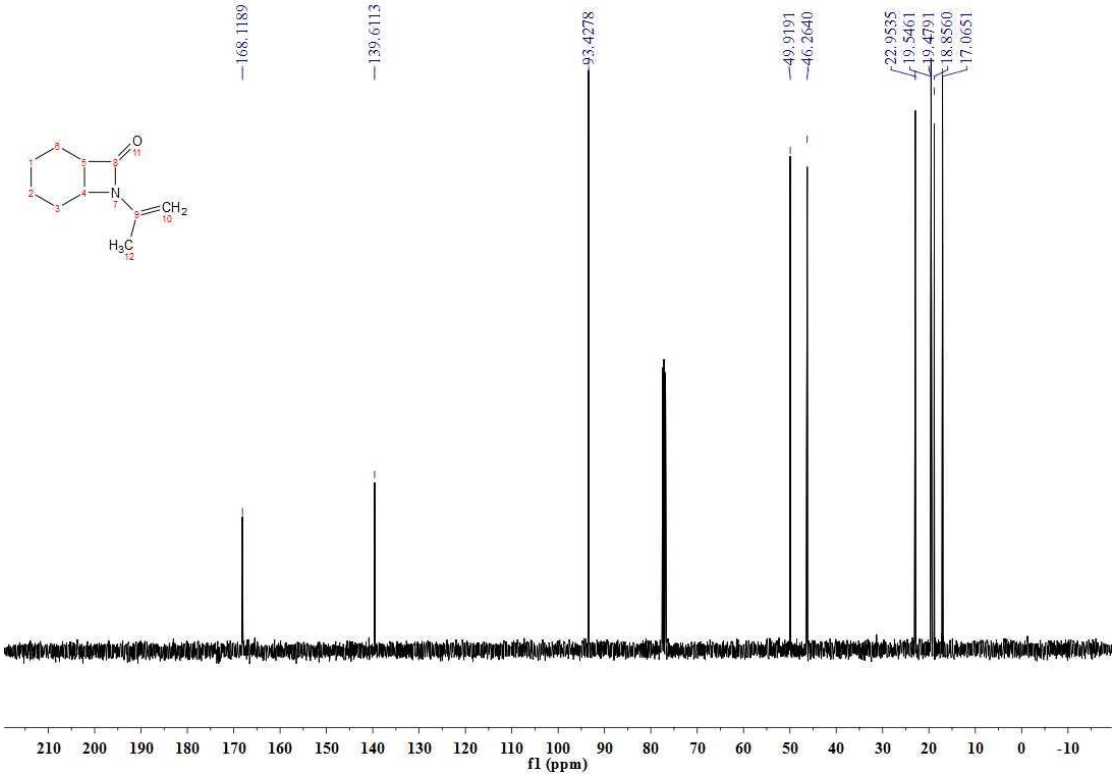
^{13}C NMR spectrum for **2o** (*trans*-isomer, $CDCl_3$, 101 MHz)



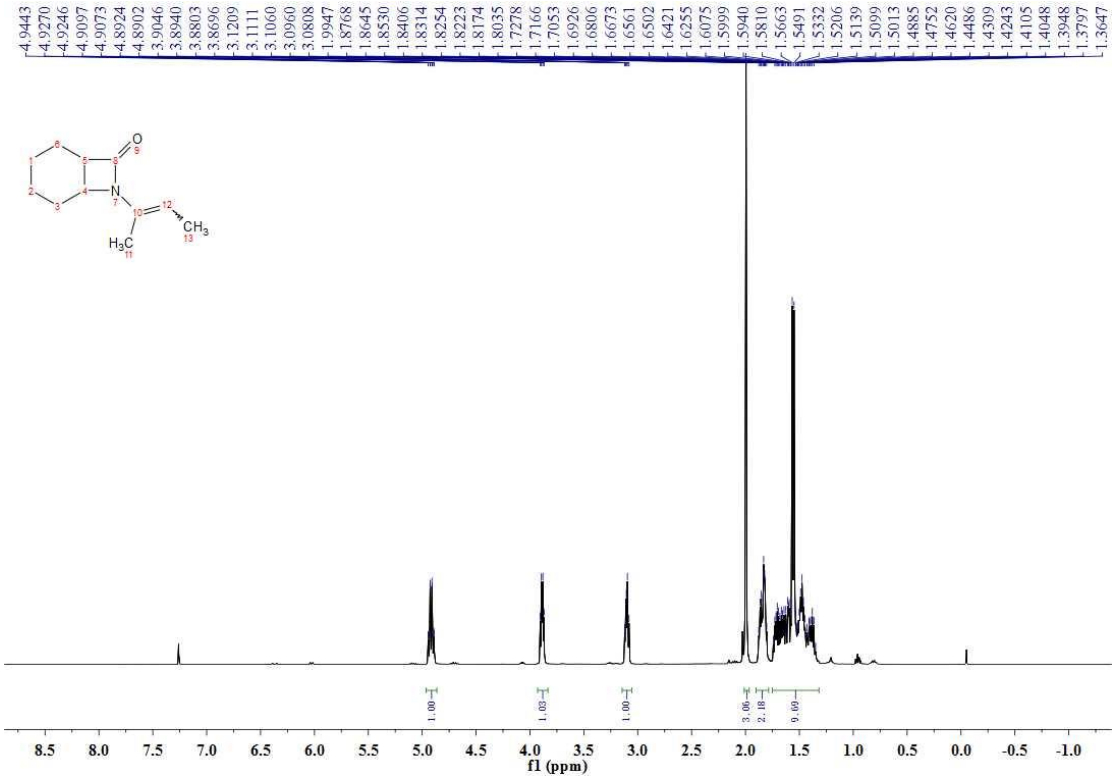
^{1}H NMR spectrum for **2p** ($CDCl_3$, 400 MHz)



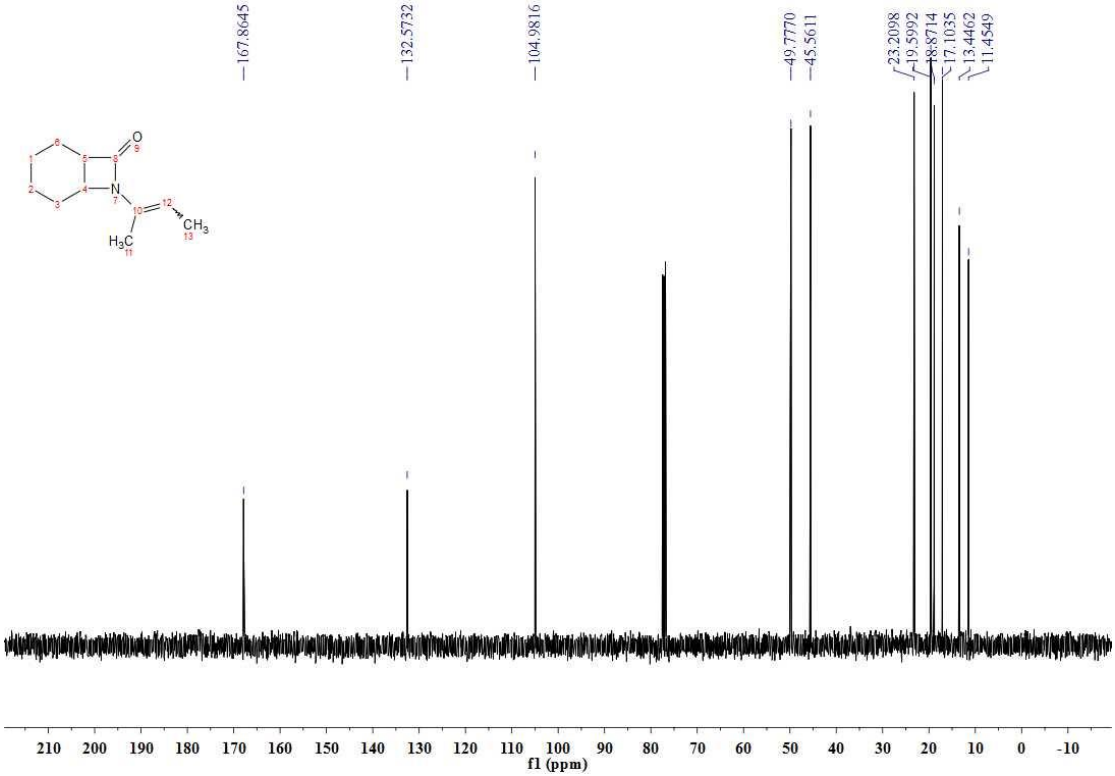
^{1}H NMR spectrum for **2p** ($CDCl_3$, 400 MHz)



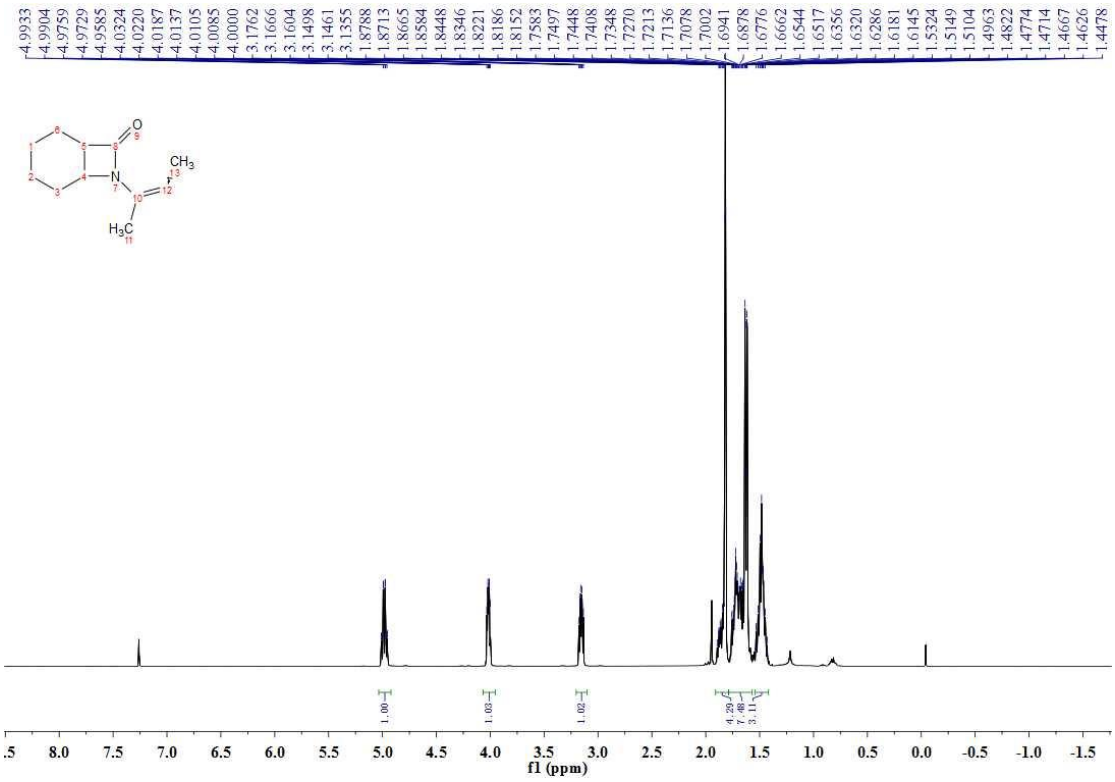
^{1}H NMR spectrum for **2q** (isomer 1, $CDCl_3$, 400 MHz)



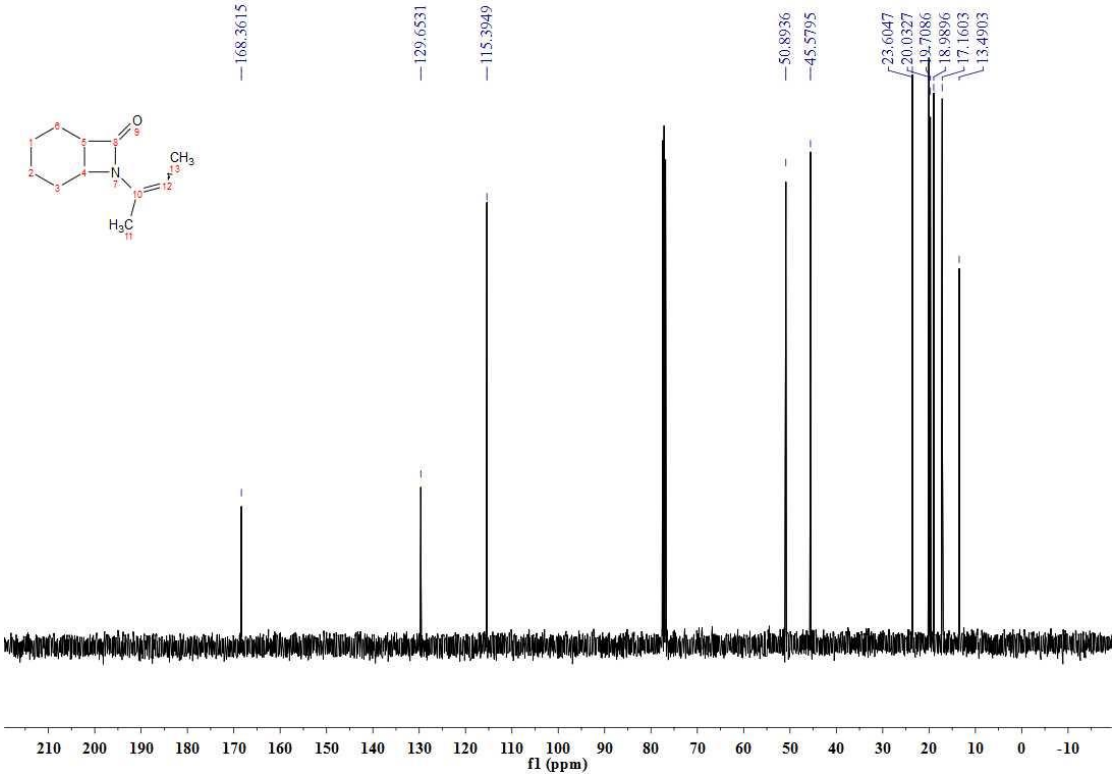
^{13}C NMR spectrum for **2q** (isomer 1, $CDCl_3$, 101 MHz)



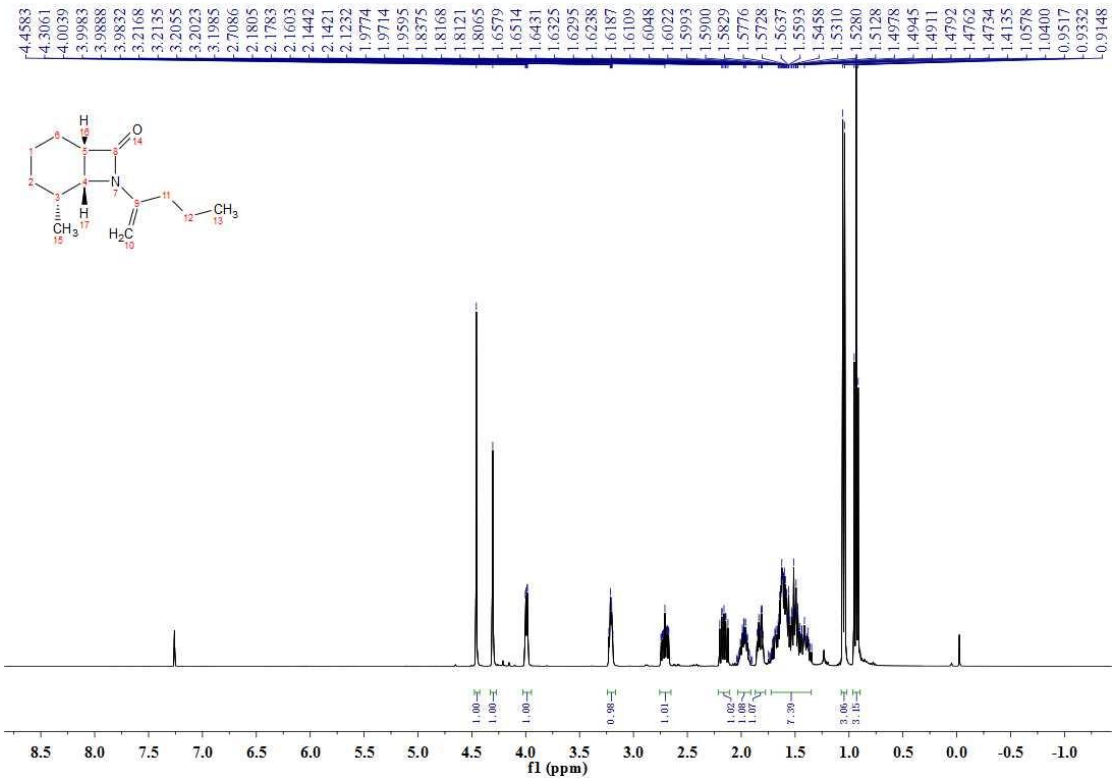
^{1}H NMR spectrum for **2q** ((isomer 2, $CDCl_3$, 400 MHz)



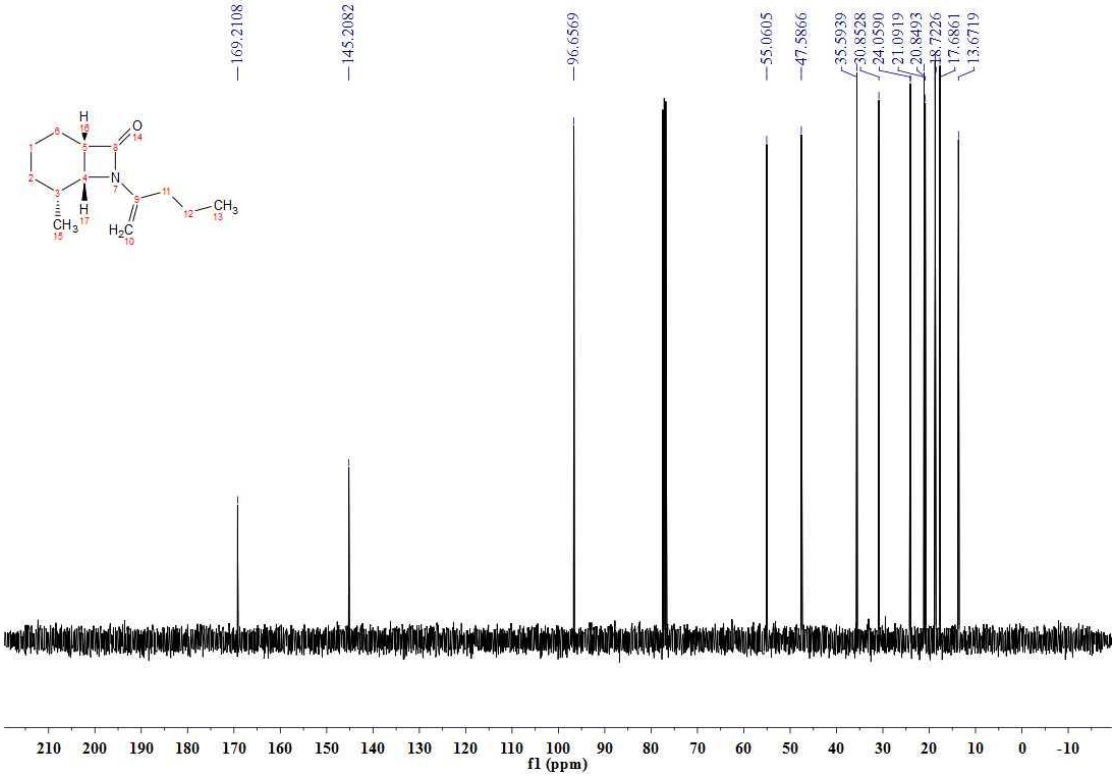
^{13}C NMR spectrum for **2q** ((isomer 2, $CDCl_3$, 101 MHz)



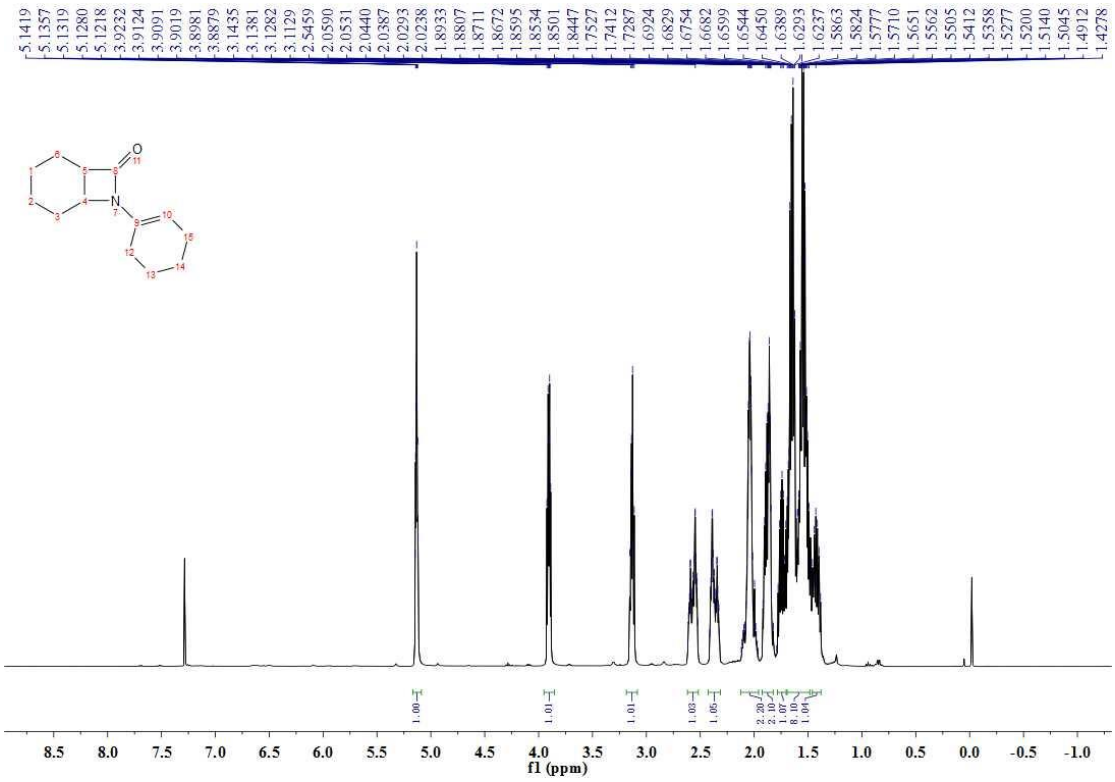
^{1}H NMR spectrum for **2r** ($CDCl_3$, 400 MHz)



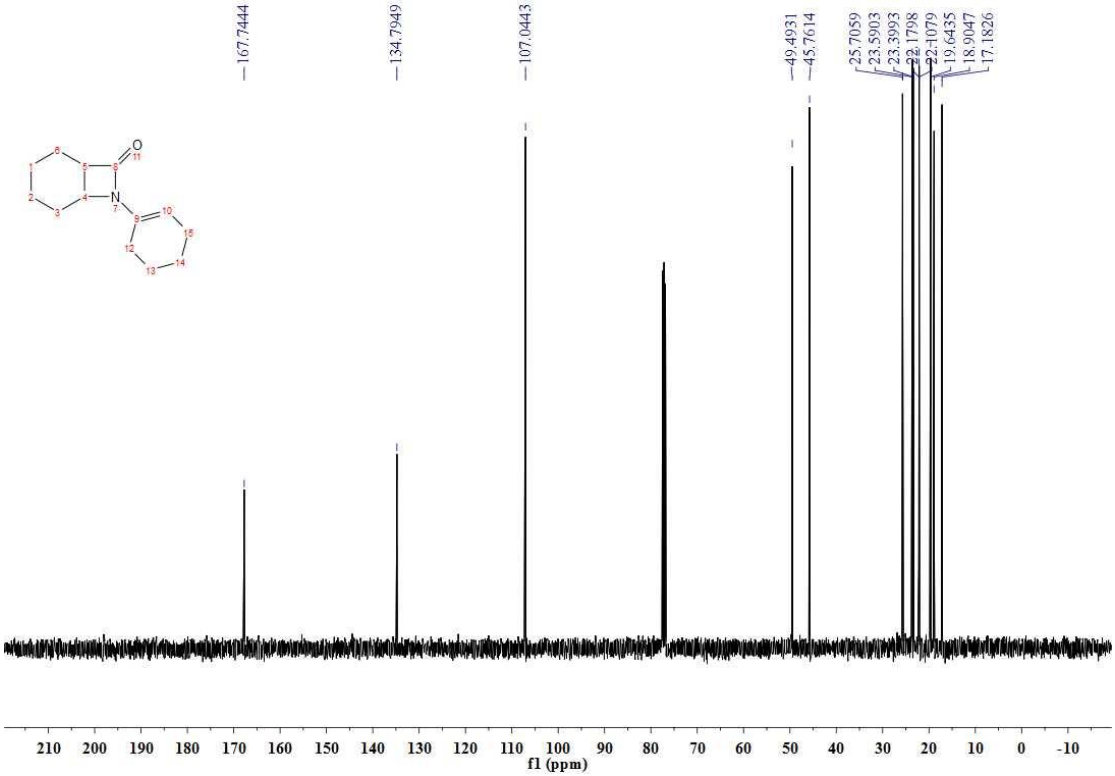
^{13}C NMR spectrum for **2r** ($CDCl_3$, 101 MHz)



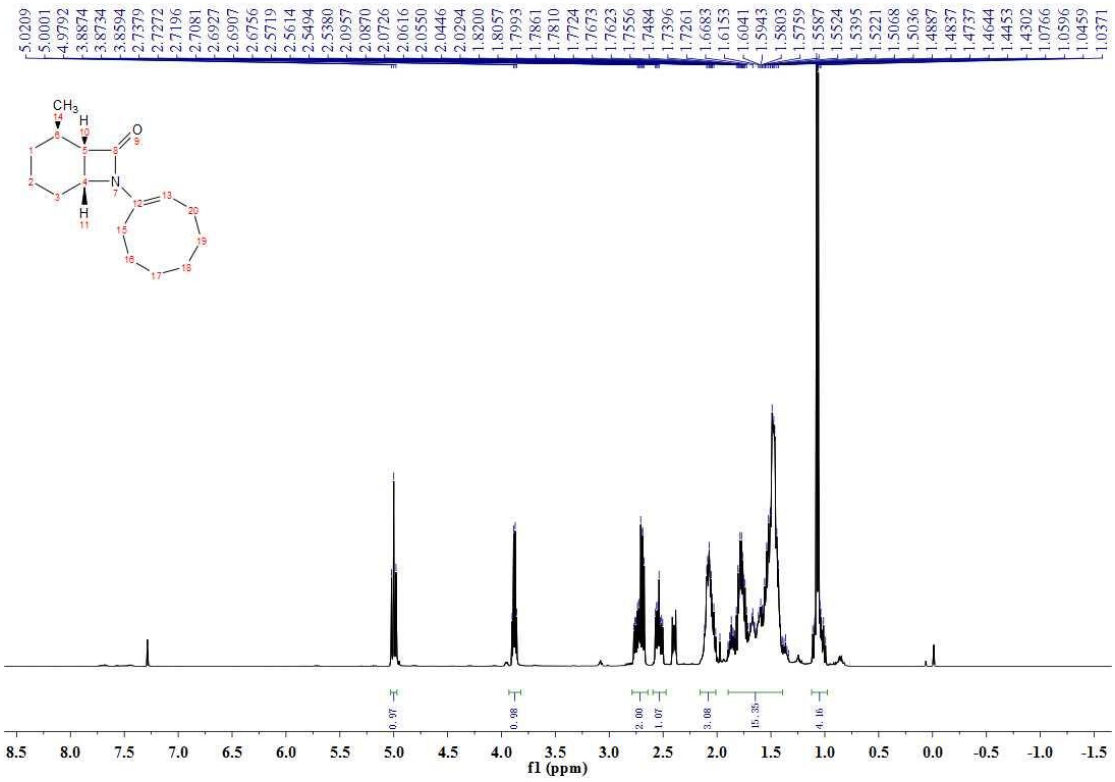
^{1}H NMR spectrum for **2s** ($CDCl_3$, 400 MHz)



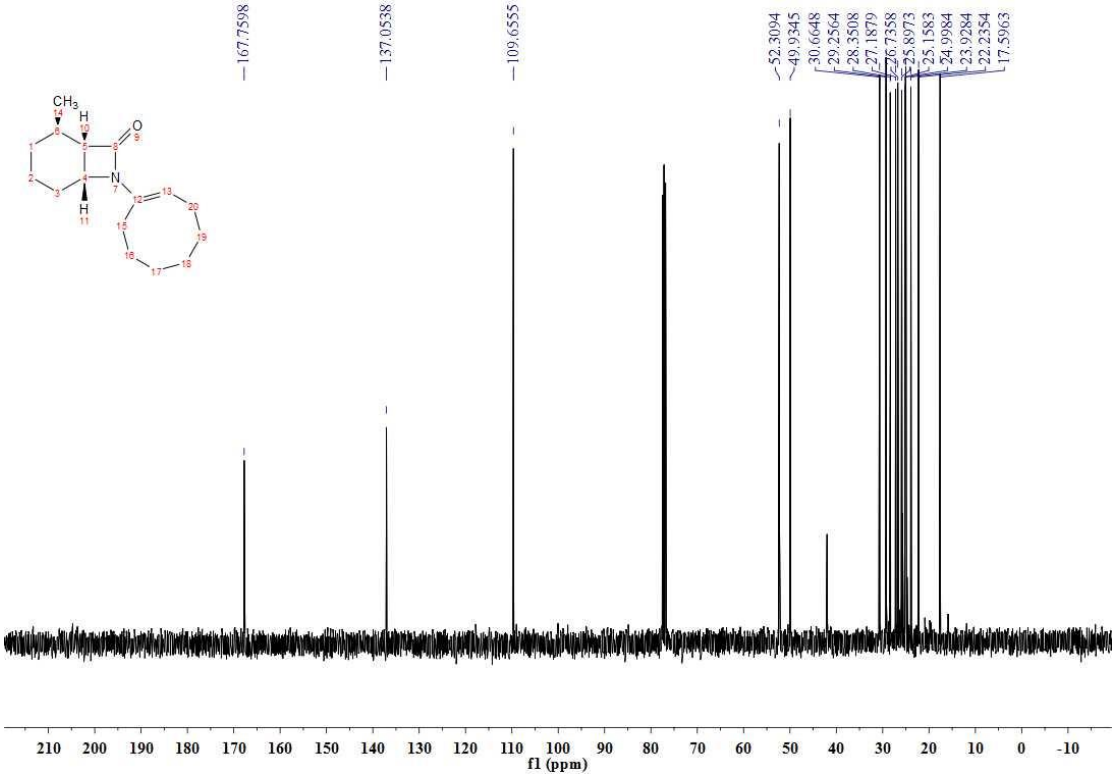
^{13}C NMR spectrum for **2s** ($CDCl_3$, 101 MHz)



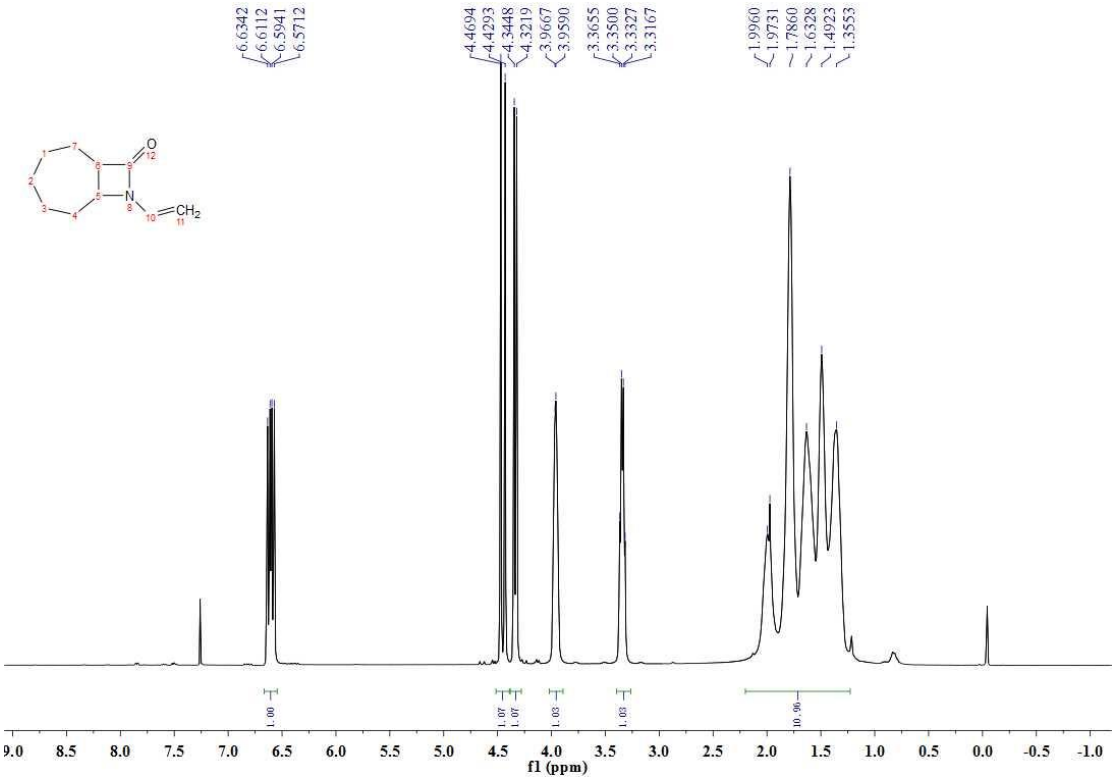
^{1}H NMR spectrum for **2t** ($CDCl_3$, 400 MHz)



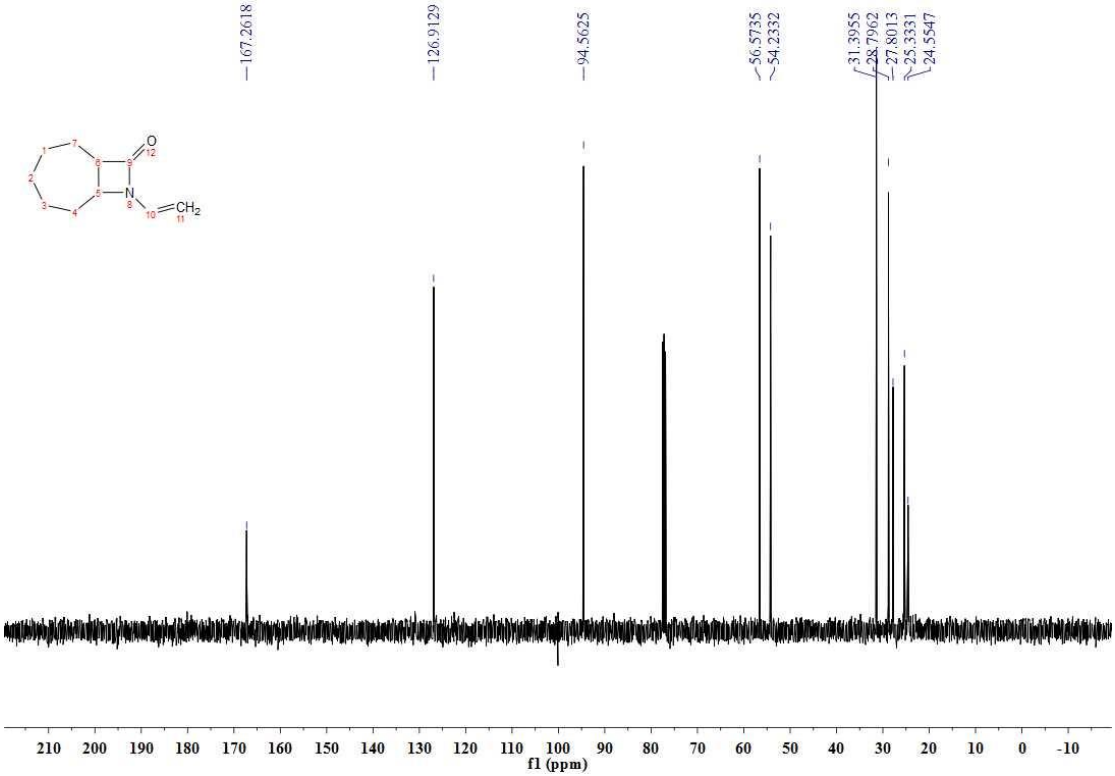
^{13}C NMR spectrum for **2t** ($CDCl_3$, 101 MHz)



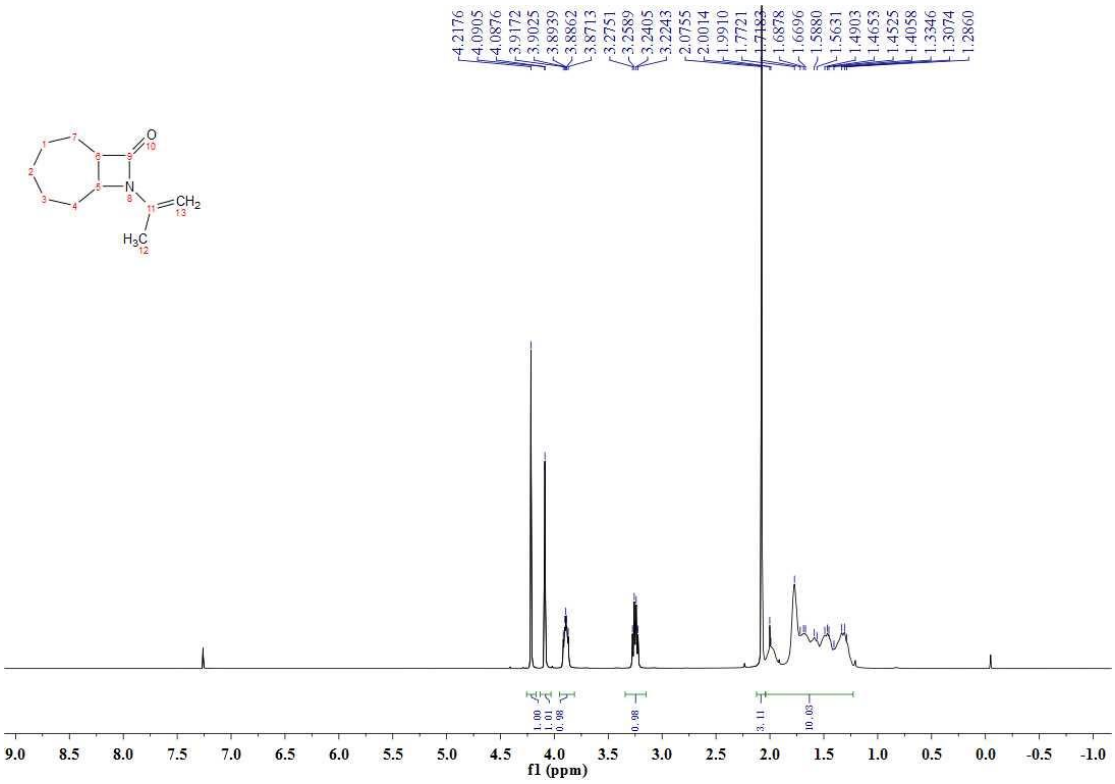
^{1}H NMR spectrum for **2u** ($CDCl_3$, 400 MHz)



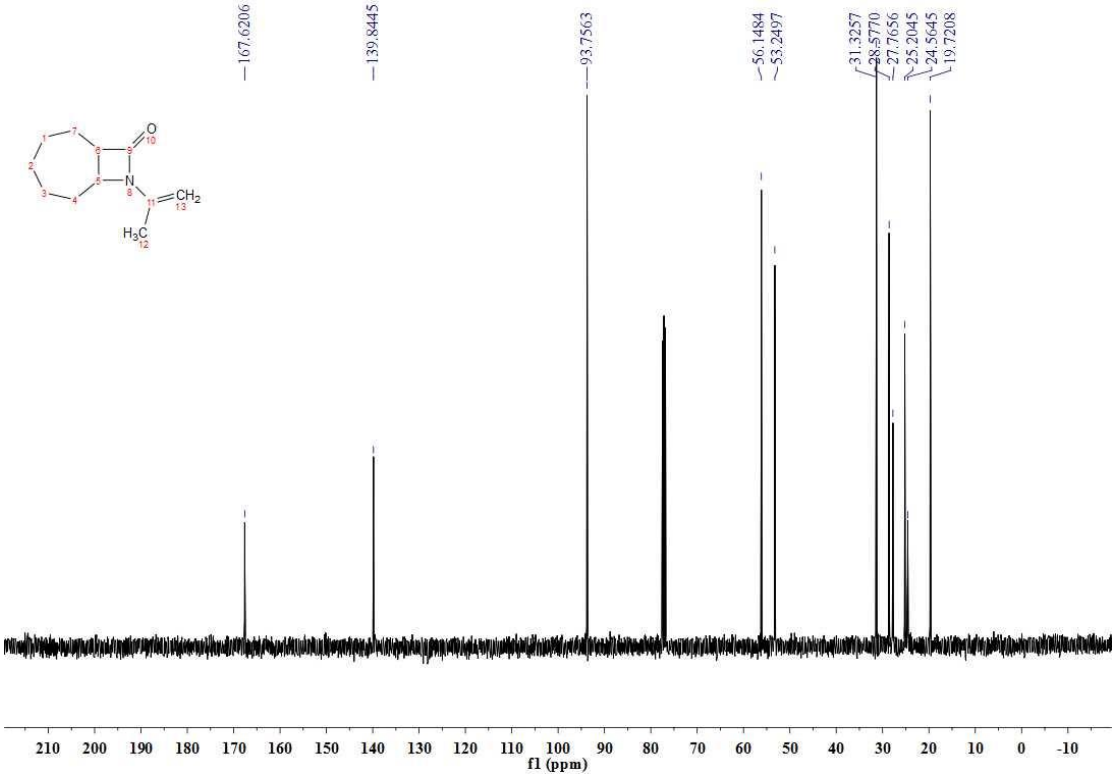
^{13}C NMR spectrum for **2u** ($CDCl_3$, 101 MHz)



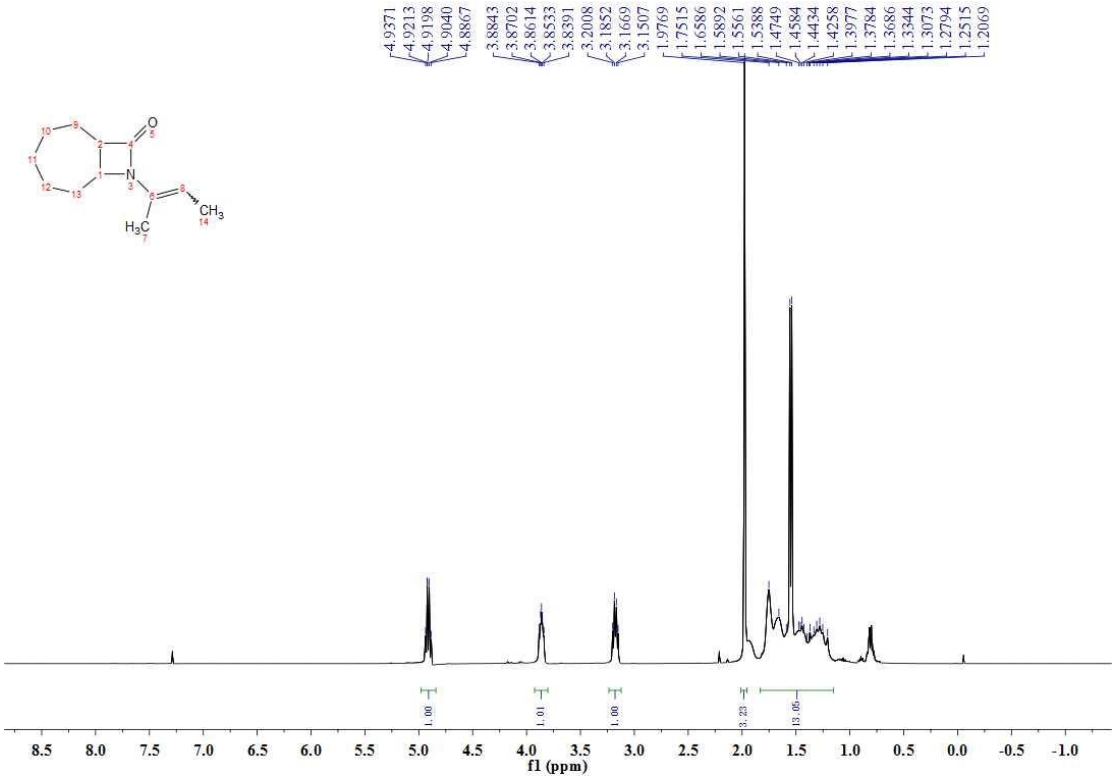
^{1}H NMR spectrum for **2v** ($CDCl_3$, 400 MHz)



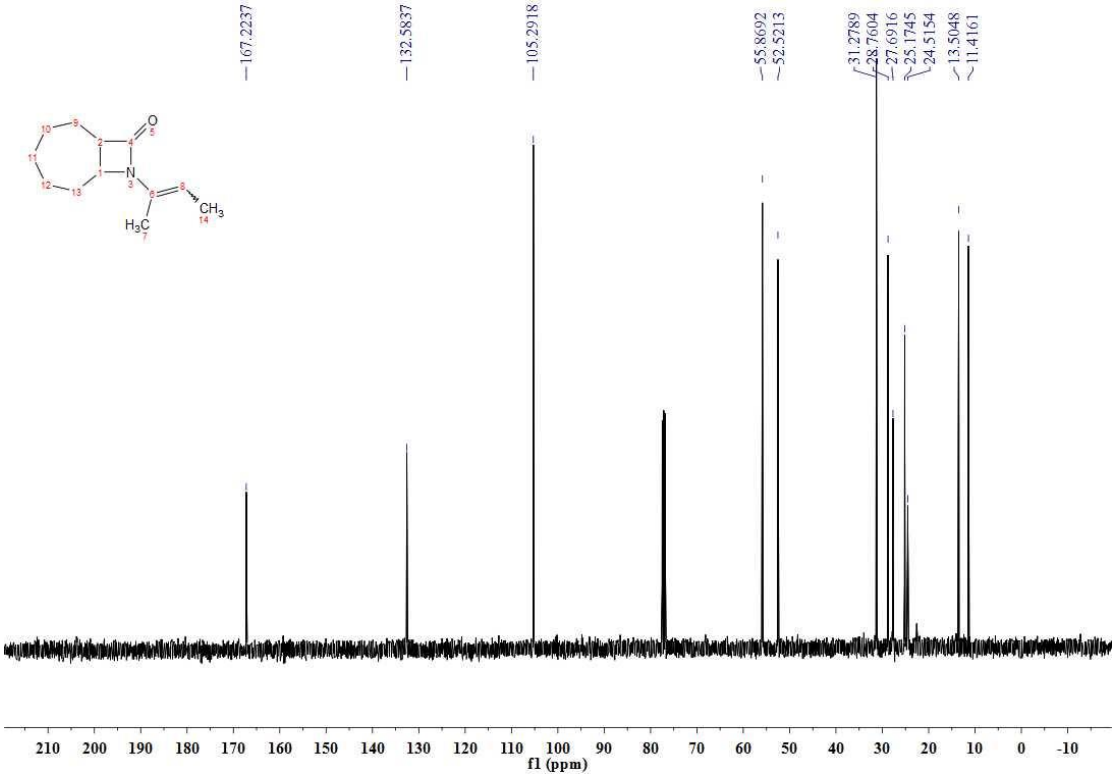
^{13}C NMR spectrum for **2v** ($CDCl_3$, 101 MHz)



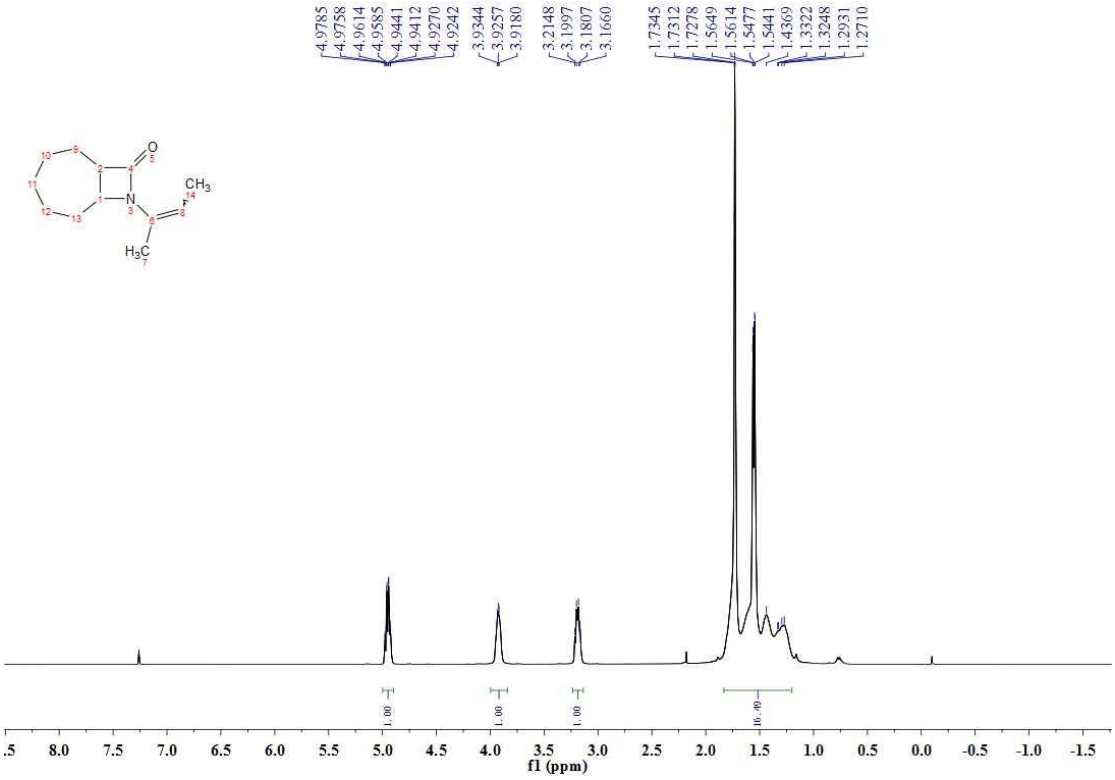
^{1}H NMR spectrum for **2w** (isomer 1, $CDCl_3$, 400 MHz)



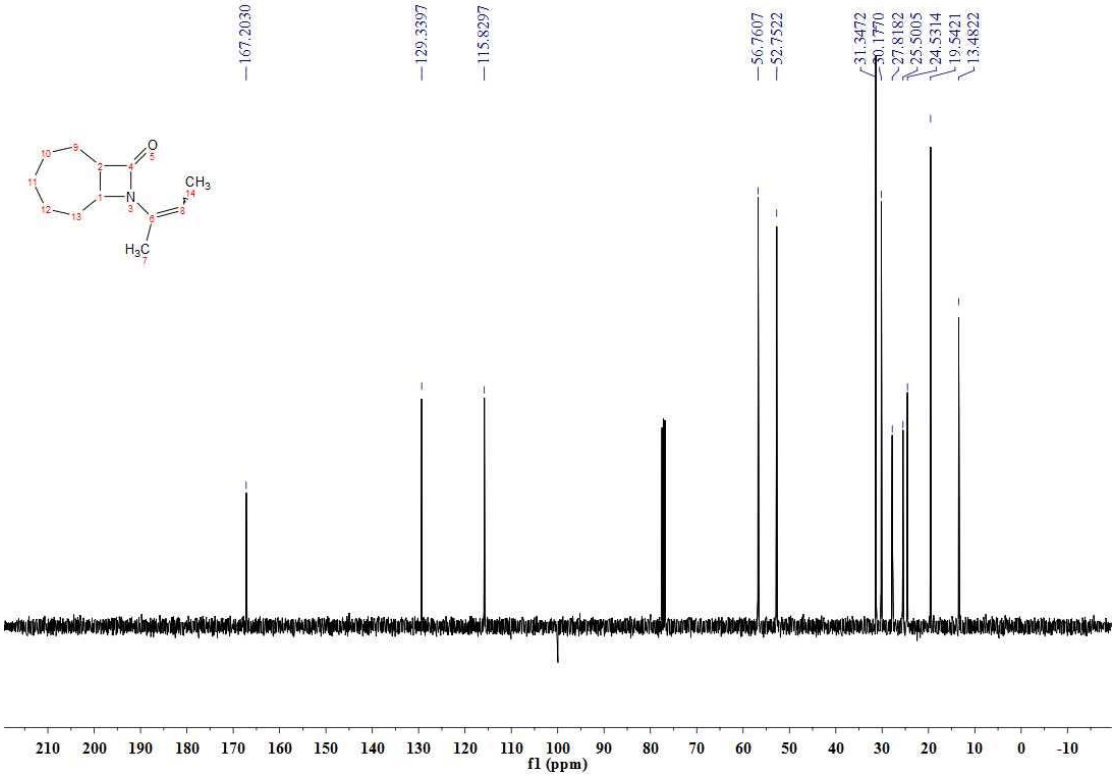
^{13}C NMR spectrum for **2w** (isomer 1, $CDCl_3$, 101 MHz)



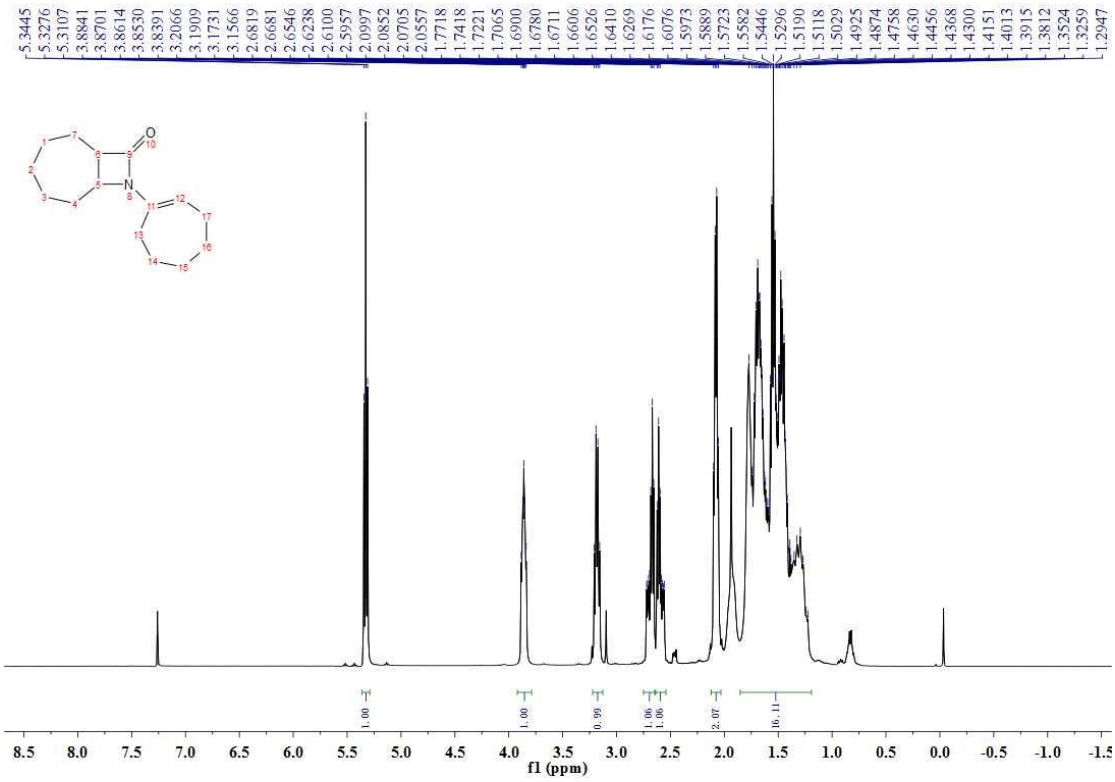
^{1}H NMR spectrum for **2w** (isomer 2, $CDCl_3$, 400 MHz)



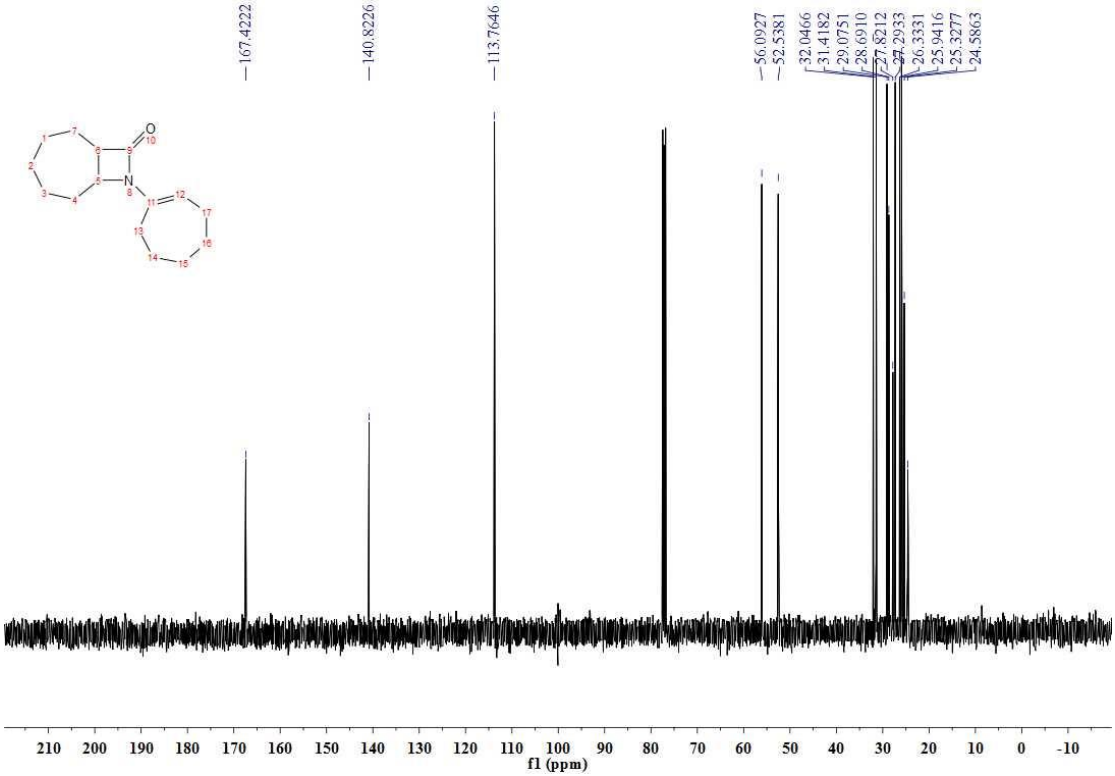
^{13}C NMR spectrum for **2w** (isomer 2, $CDCl_3$, 101 MHz)



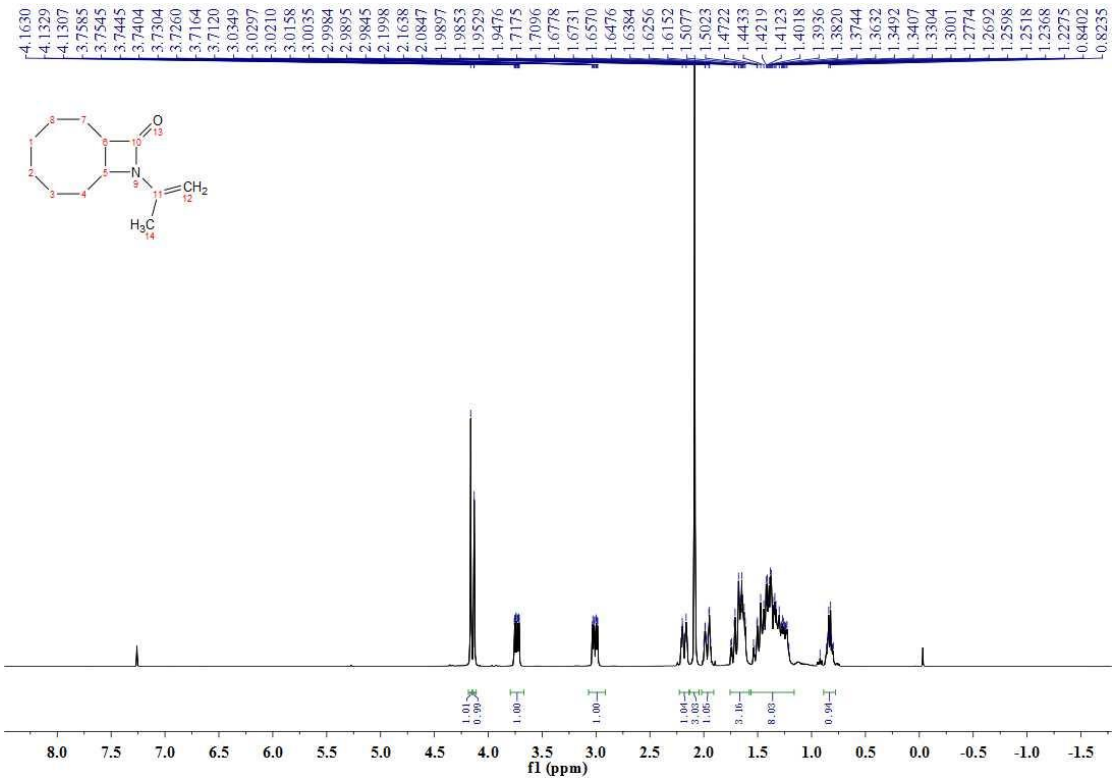
^{1}H NMR spectrum for **2x** ($CDCl_3$, 400 MHz)



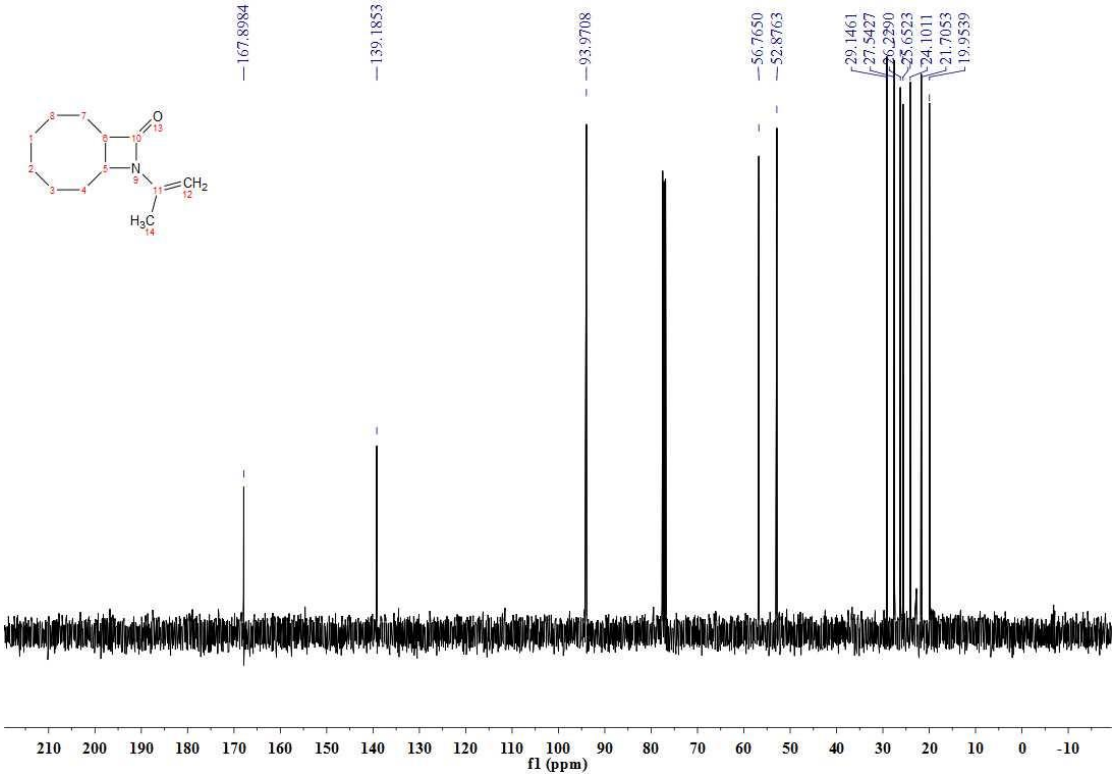
^{13}C NMR spectrum for **2x** ($CDCl_3$, 101 MHz)



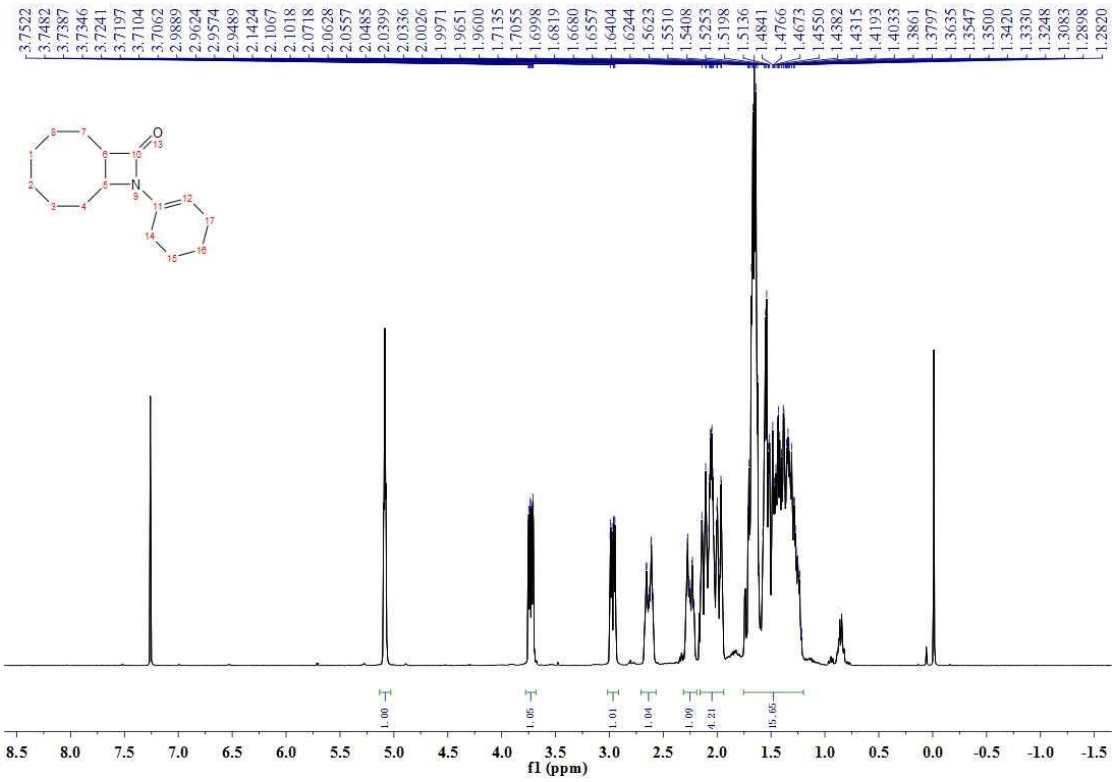
^{1}H NMR spectrum for **2y** ($CDCl_3$, 400 MHz)



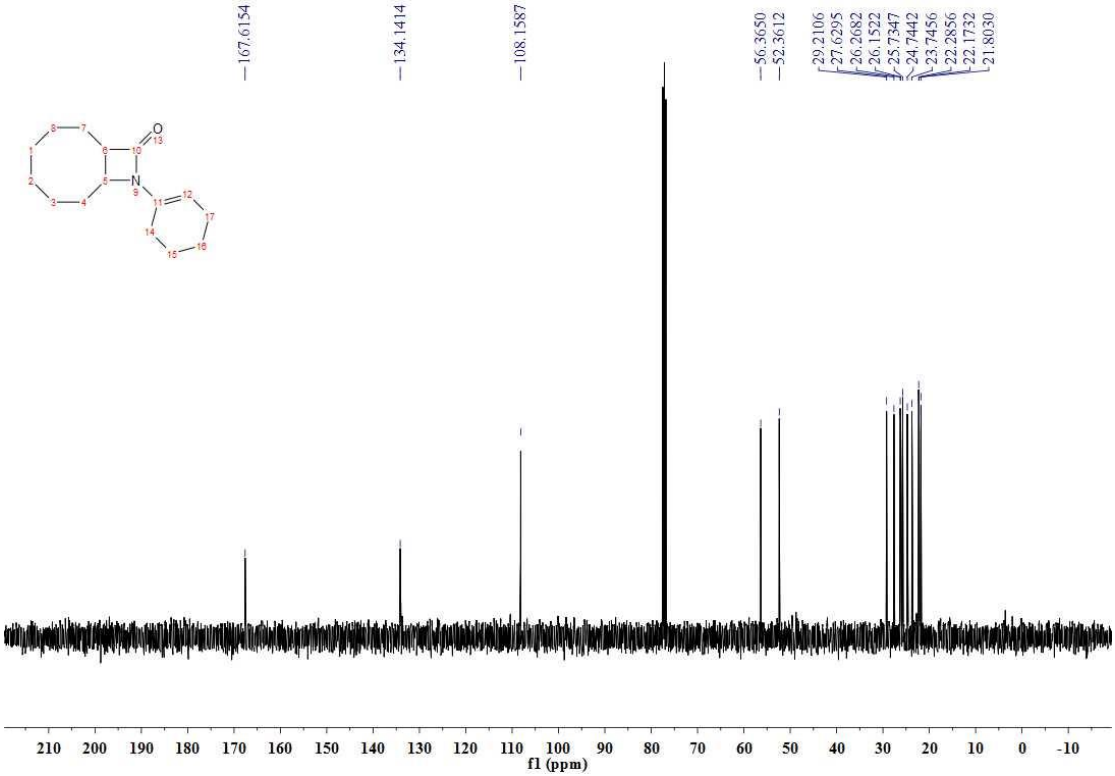
^{13}C NMR spectrum for **2y** ($CDCl_3$, 101 MHz)



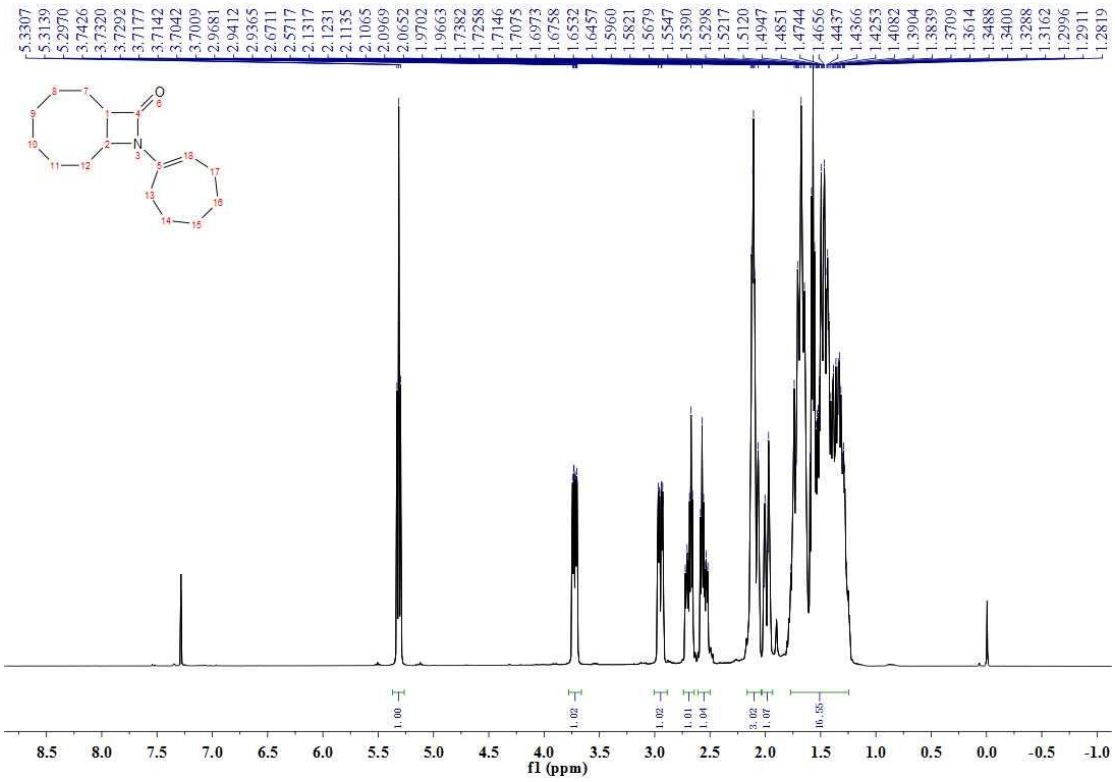
^{1}H NMR spectrum for **2z** ($CDCl_3$, 400 MHz)



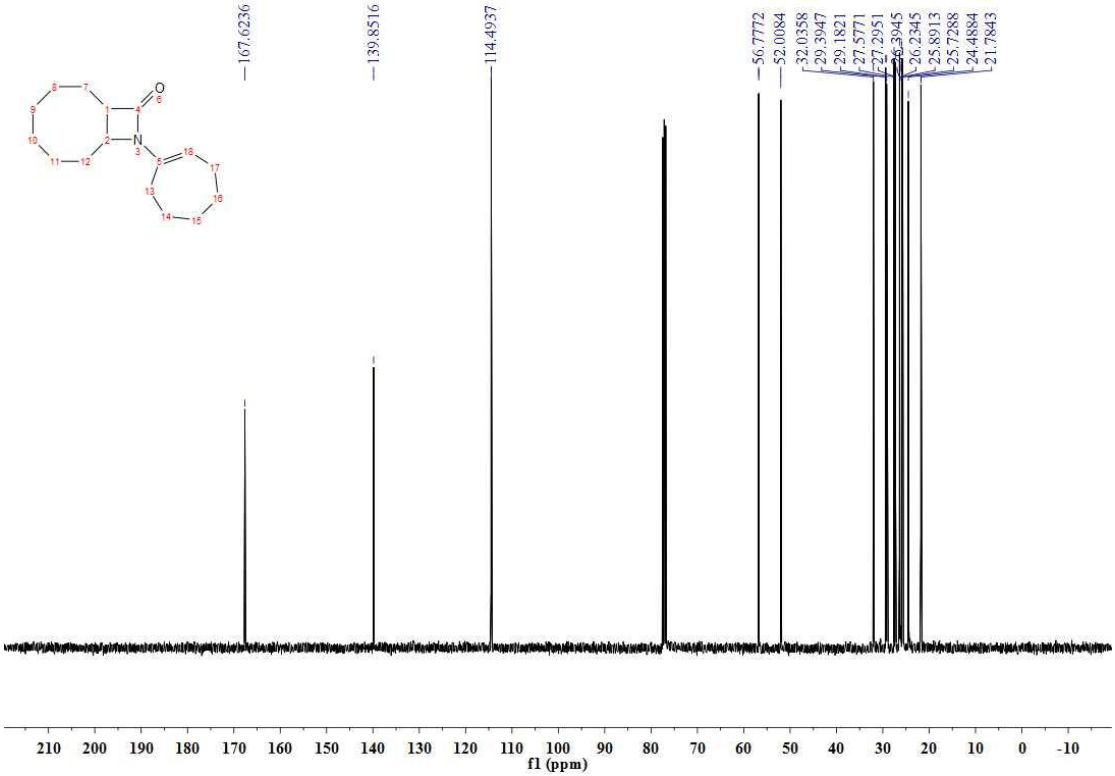
^{13}C NMR spectrum for **2z** ($CDCl_3$, 101 MHz)



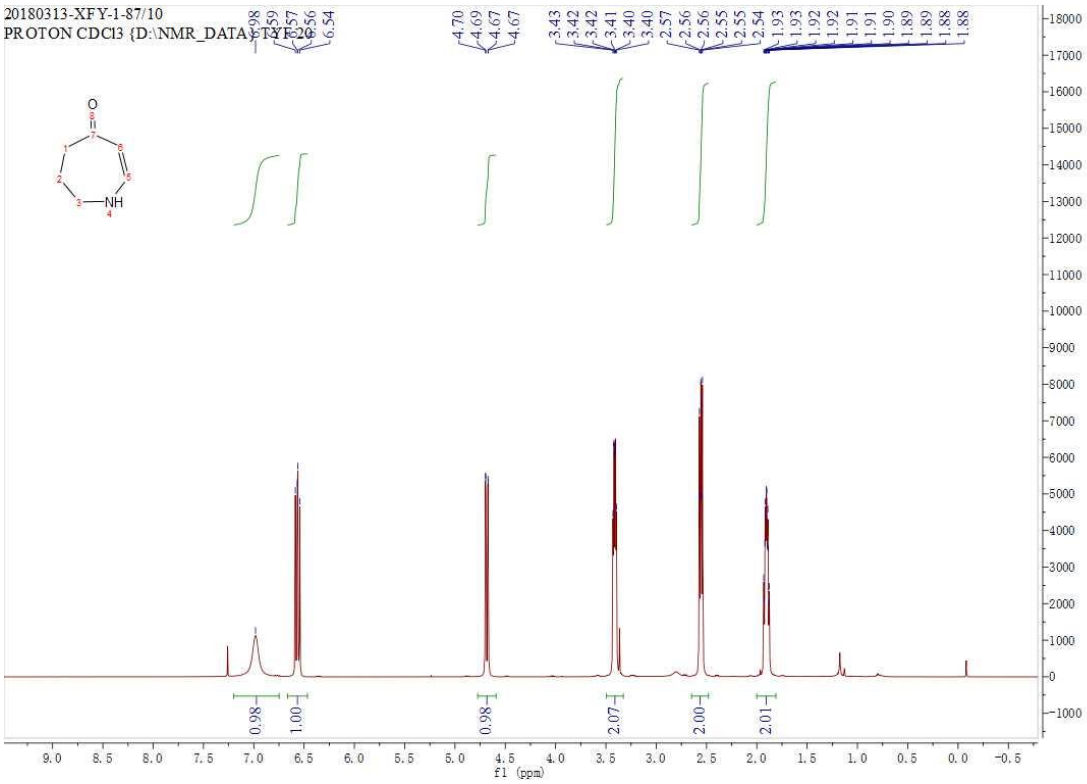
^{1}H NMR spectrum for **2aa** ($CDCl_3$, 400 MHz)



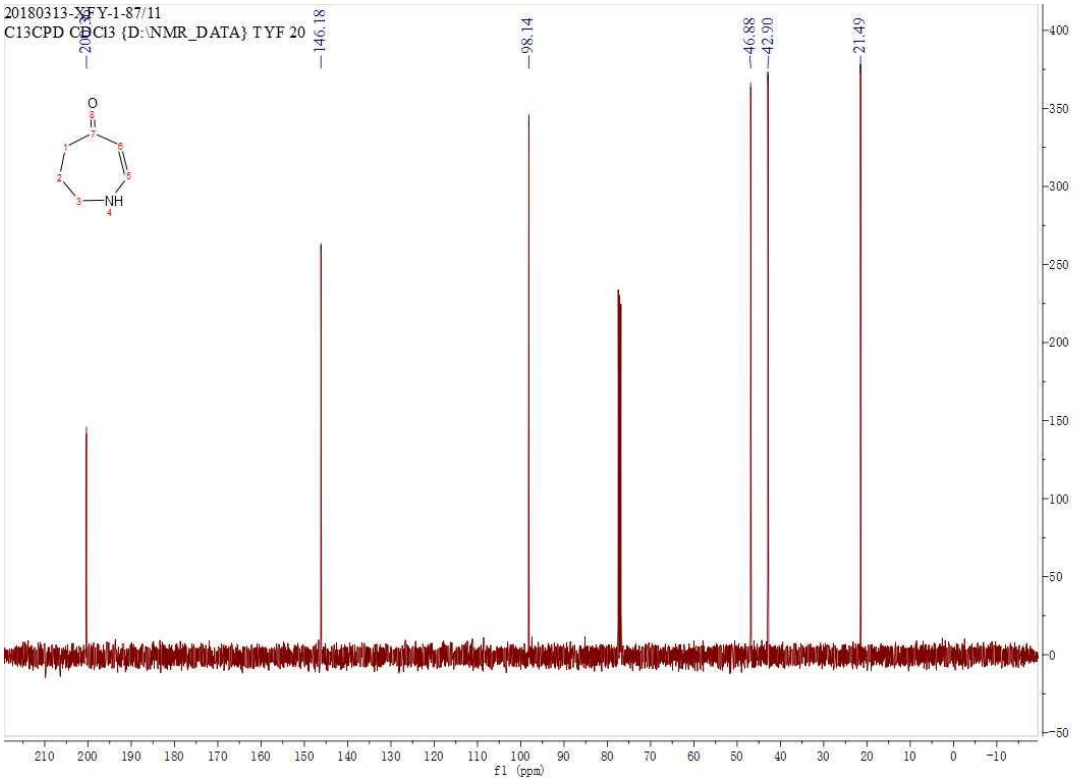
^{13}C NMR spectrum for **2aa** ($CDCl_3$, 101 MHz)



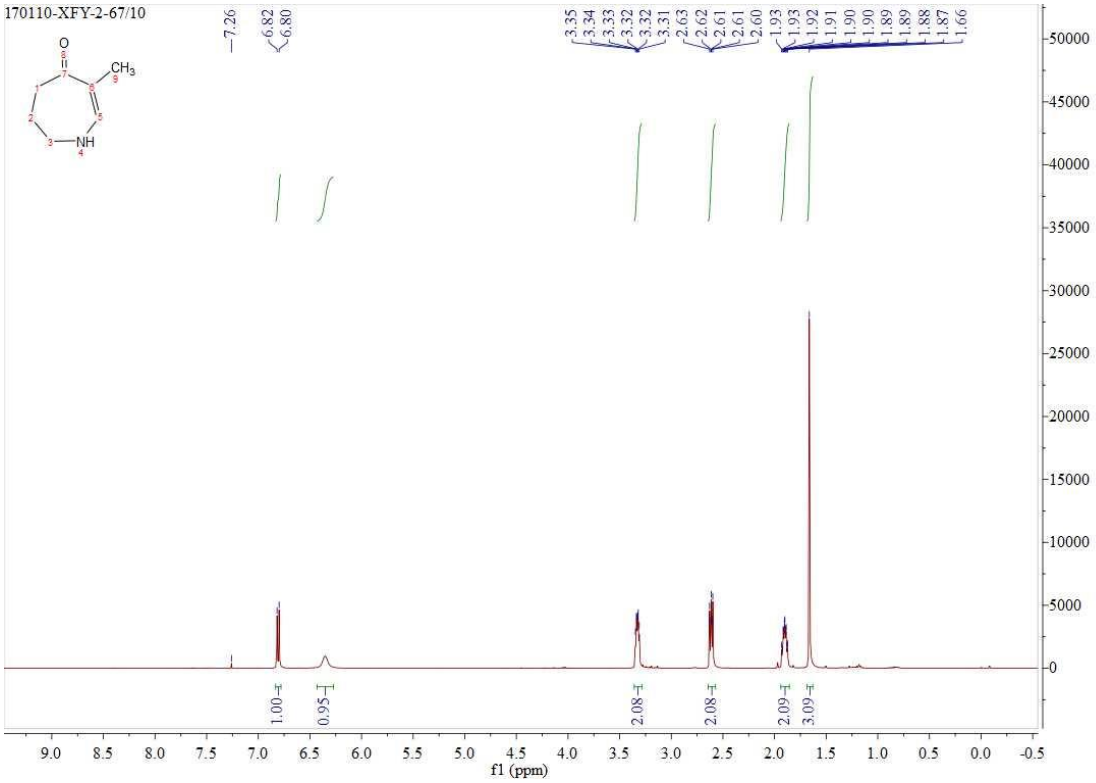
^{1}H NMR spectrum for **3a** ($CDCl_3$, 400 MHz)



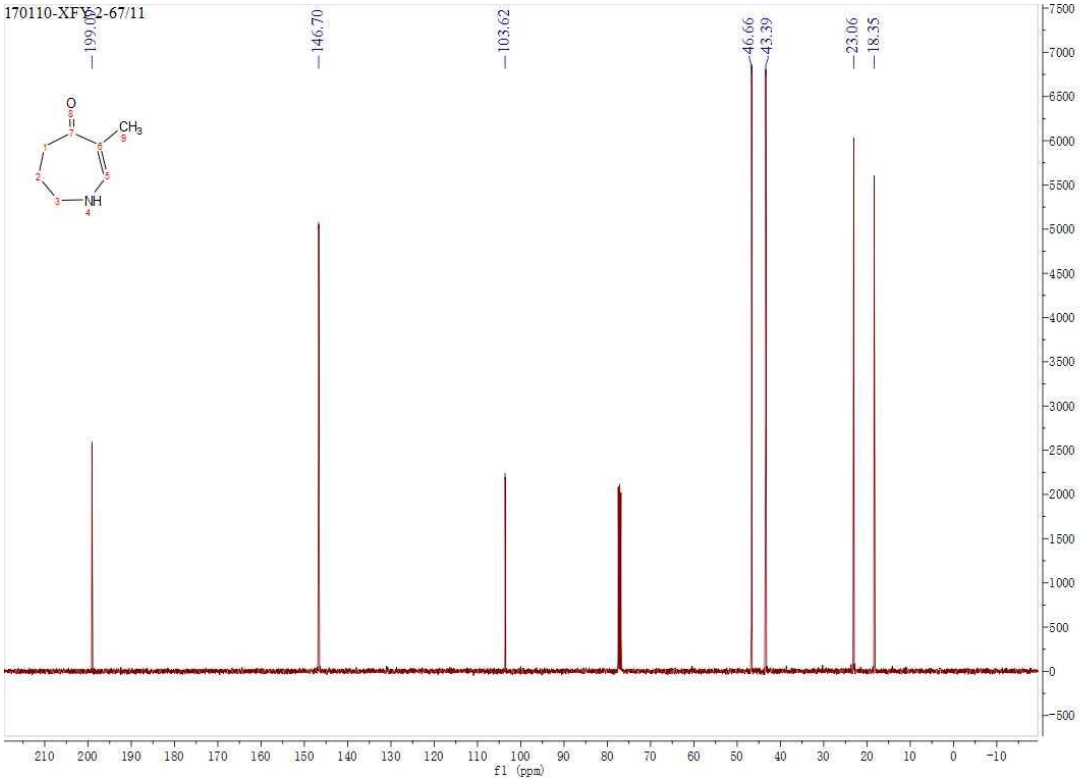
^{13}C NMR spectrum for **3a** ($CDCl_3$, 101 MHz)



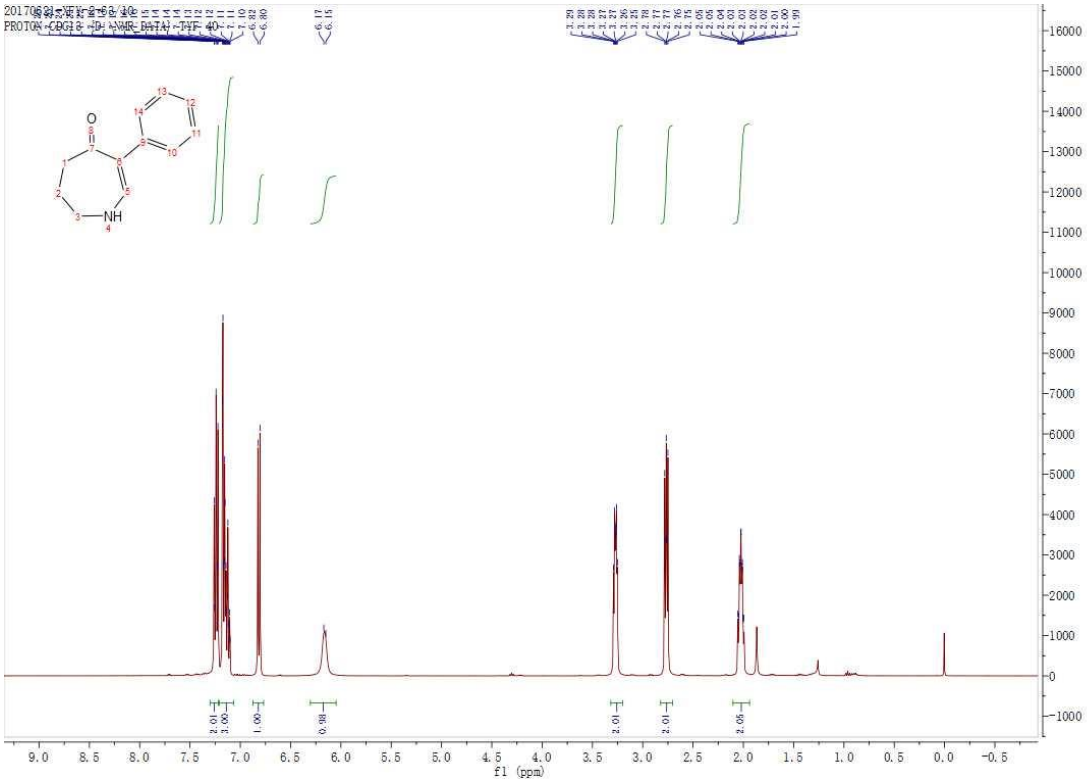
^{1}H NMR spectrum for **3b** ($CDCl_3$, 400 MHz)



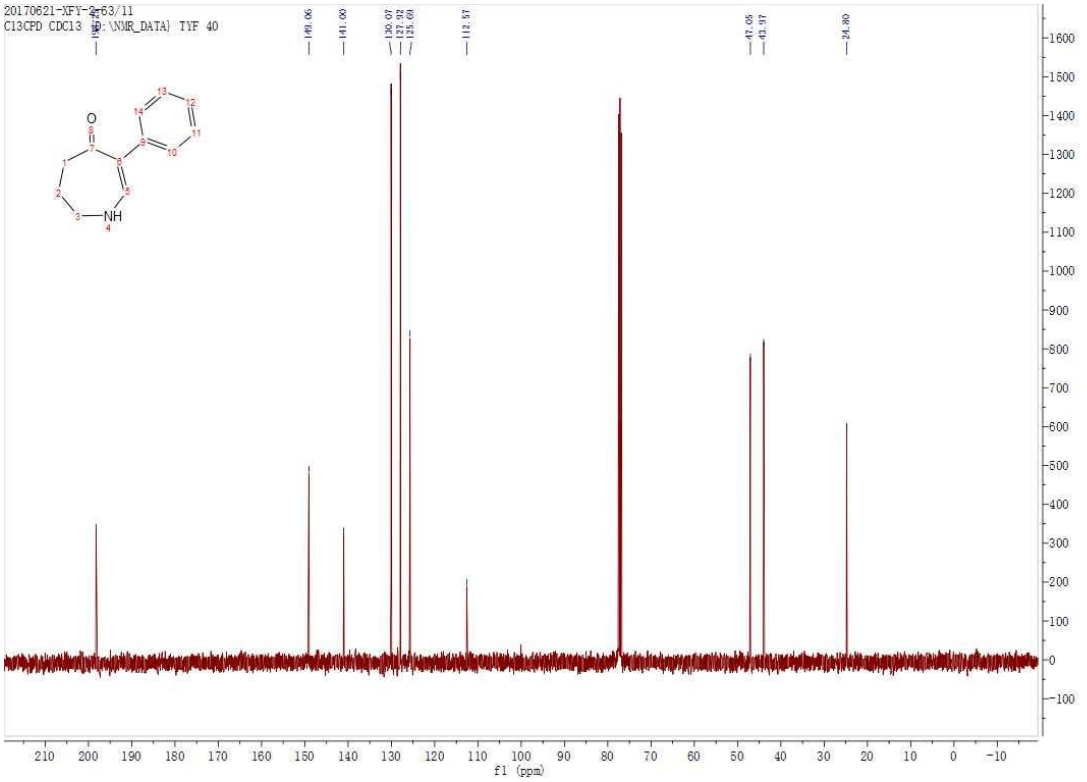
^{13}C NMR spectrum for **3b** ($CDCl_3$, 101 MHz)



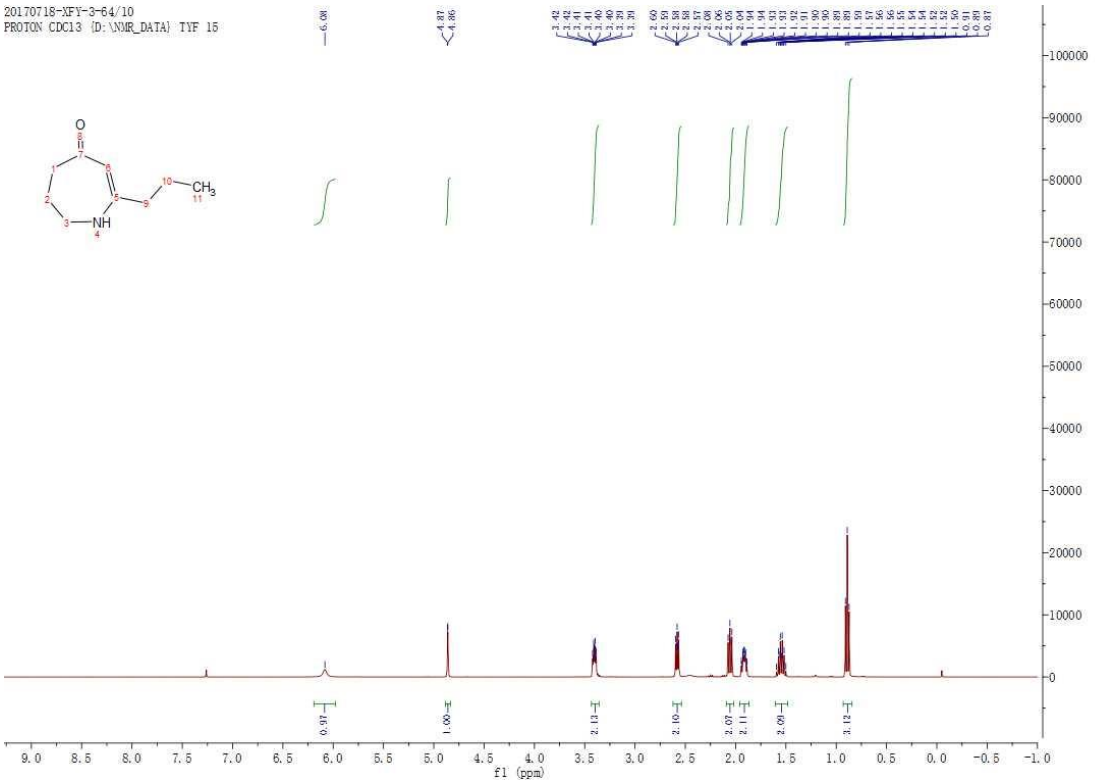
^{1}H NMR spectrum for **3c** ($CDCl_3$, 400 MHz)



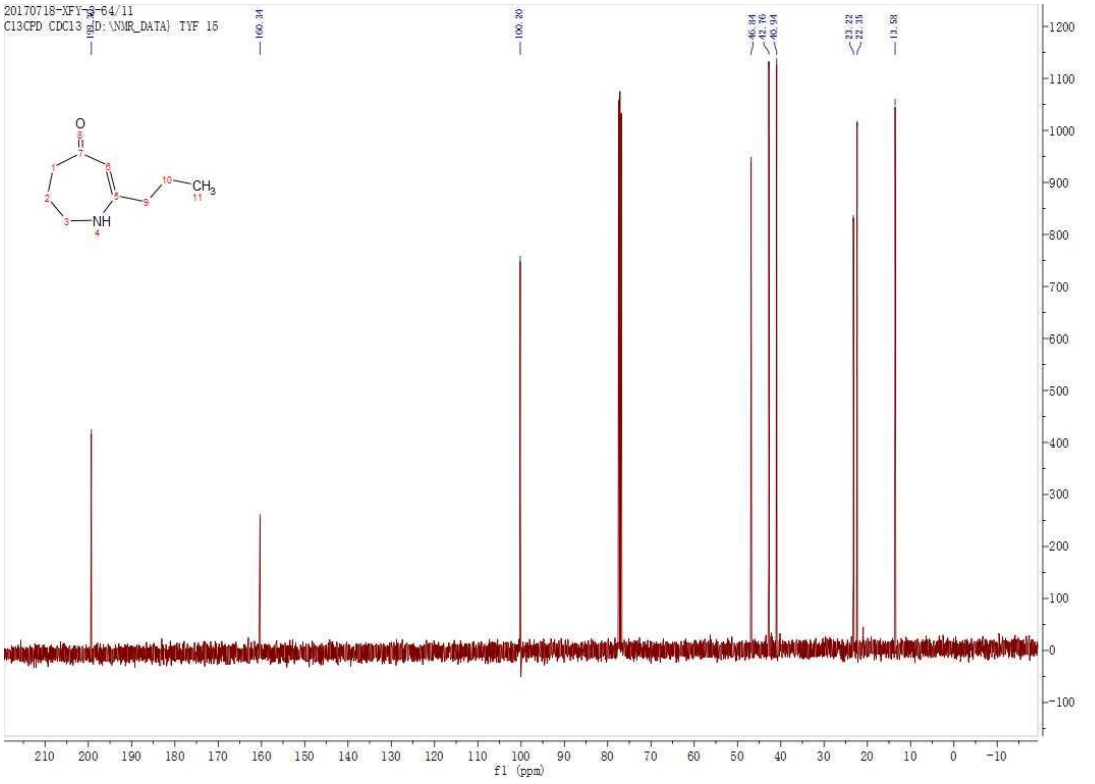
^{13}C NMR spectrum for **3c** ($CDCl_3$, 101 MHz)



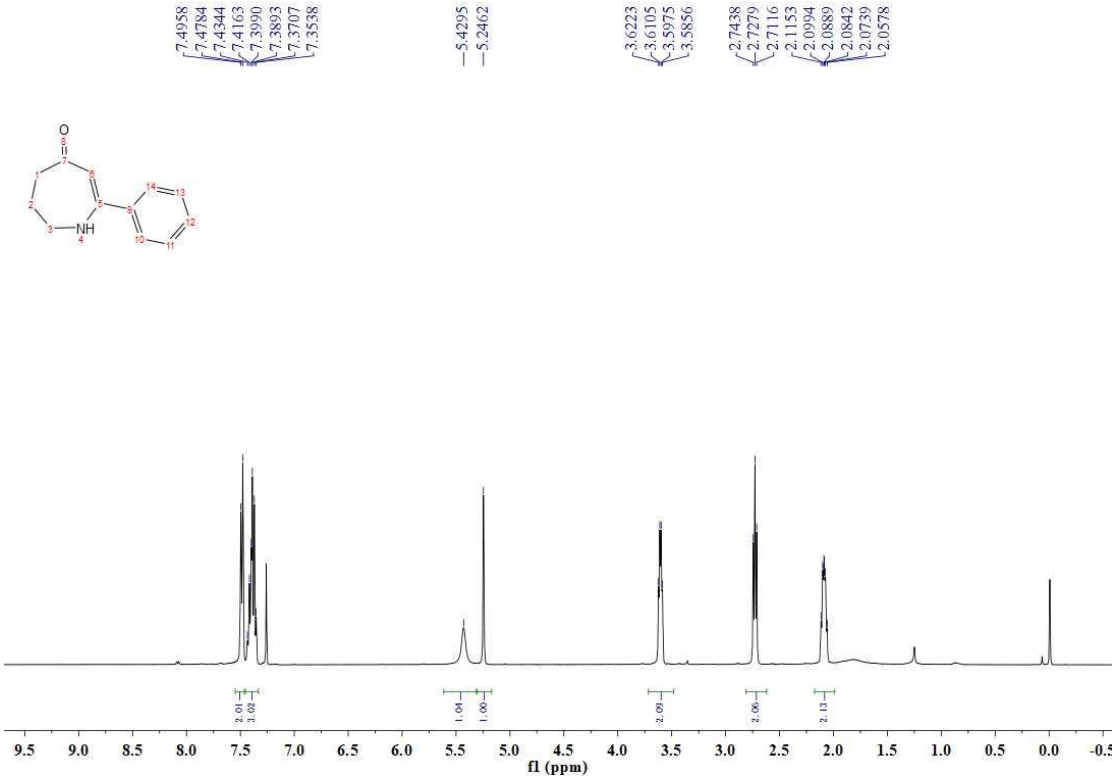
^{1}H NMR spectrum for **3d** ($CDCl_3$, 400 MHz)



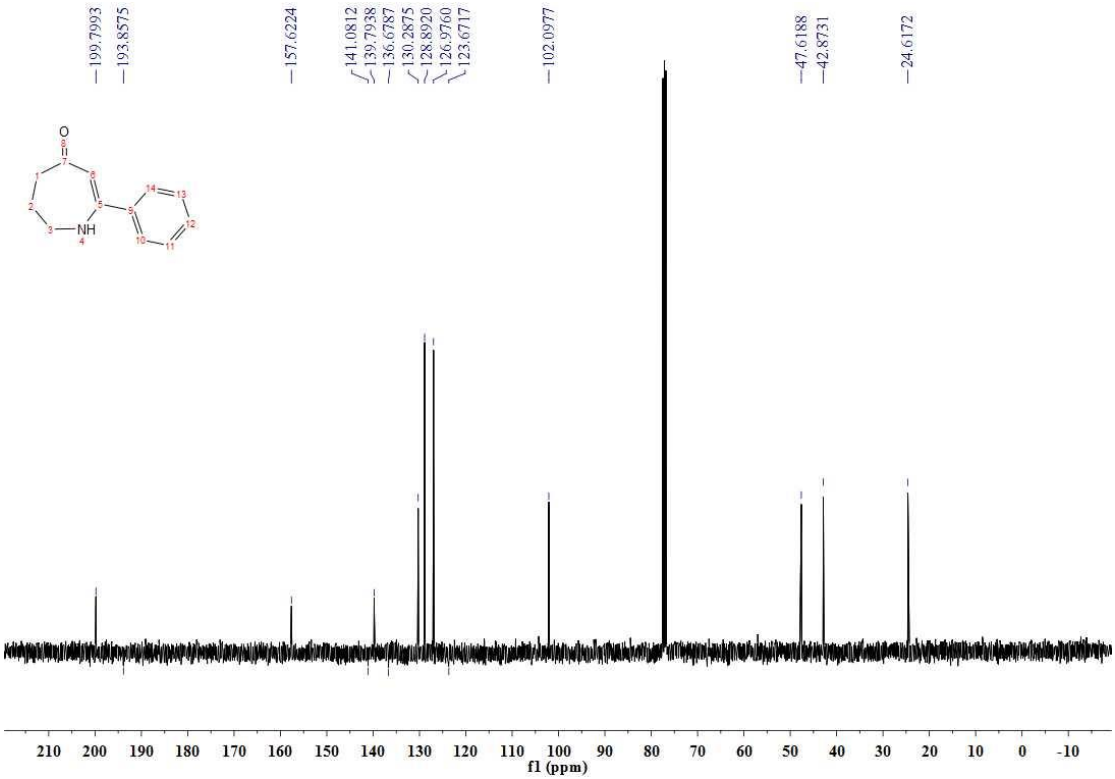
^{13}C NMR spectrum for **3d** ($CDCl_3$, 101 MHz)



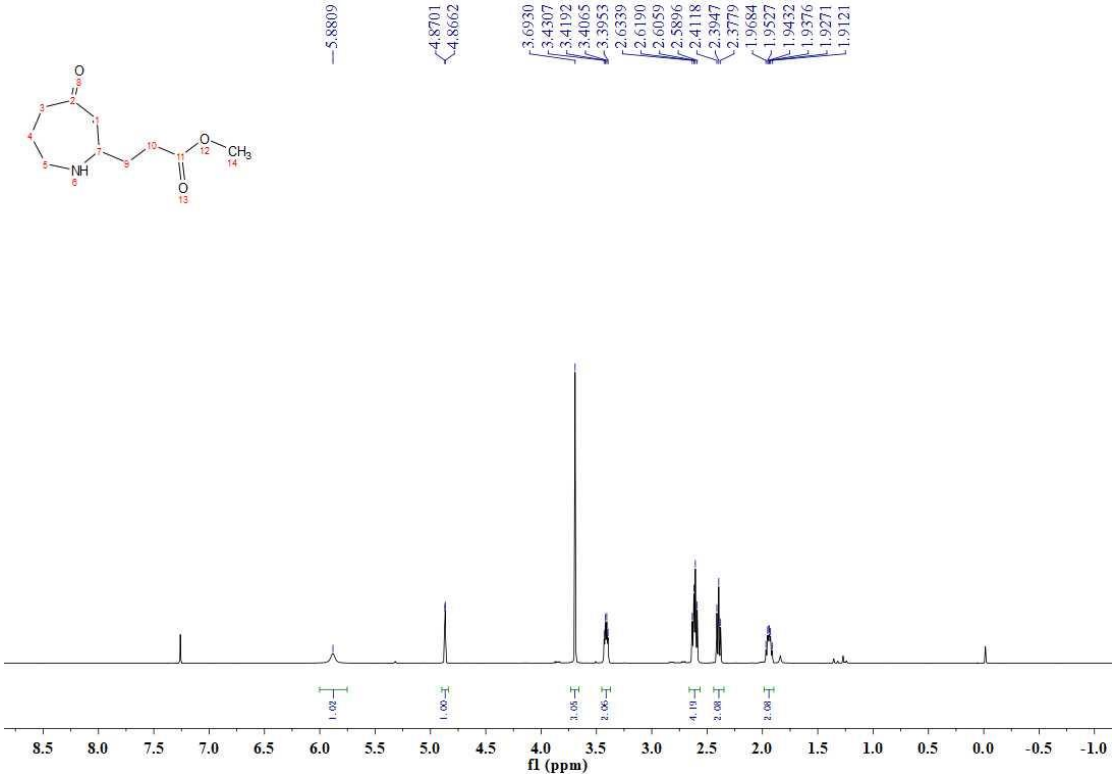
^{1}H NMR spectrum for **3e** ($CDCl_3$, 101 MHz)



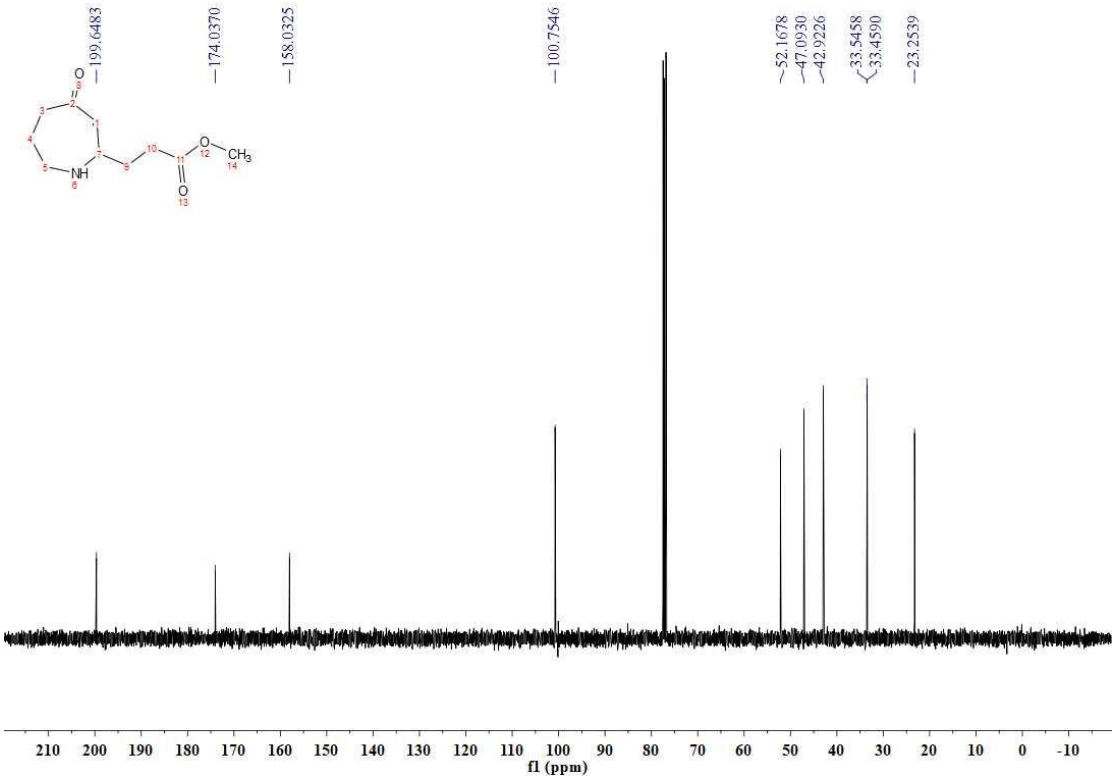
^{13}C NMR spectrum for **3e** ($CDCl_3$, 101 MHz)



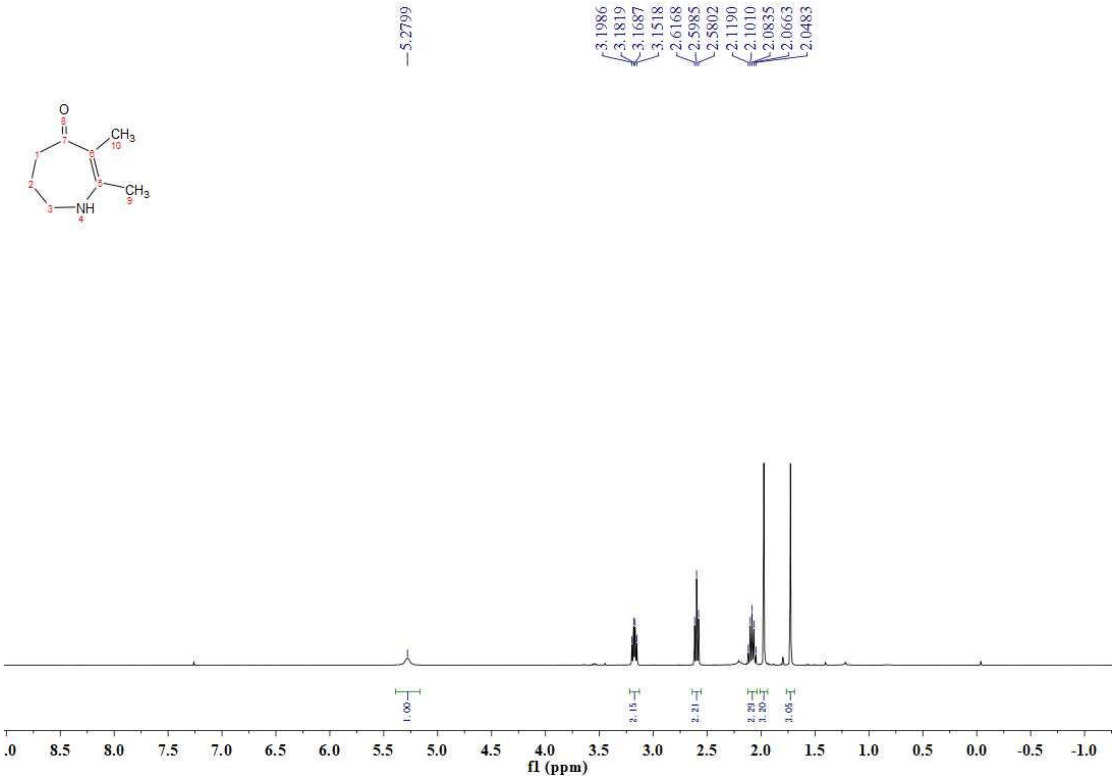
^{1}H NMR spectrum for **3f** ($CDCl_3$, 400 MHz)



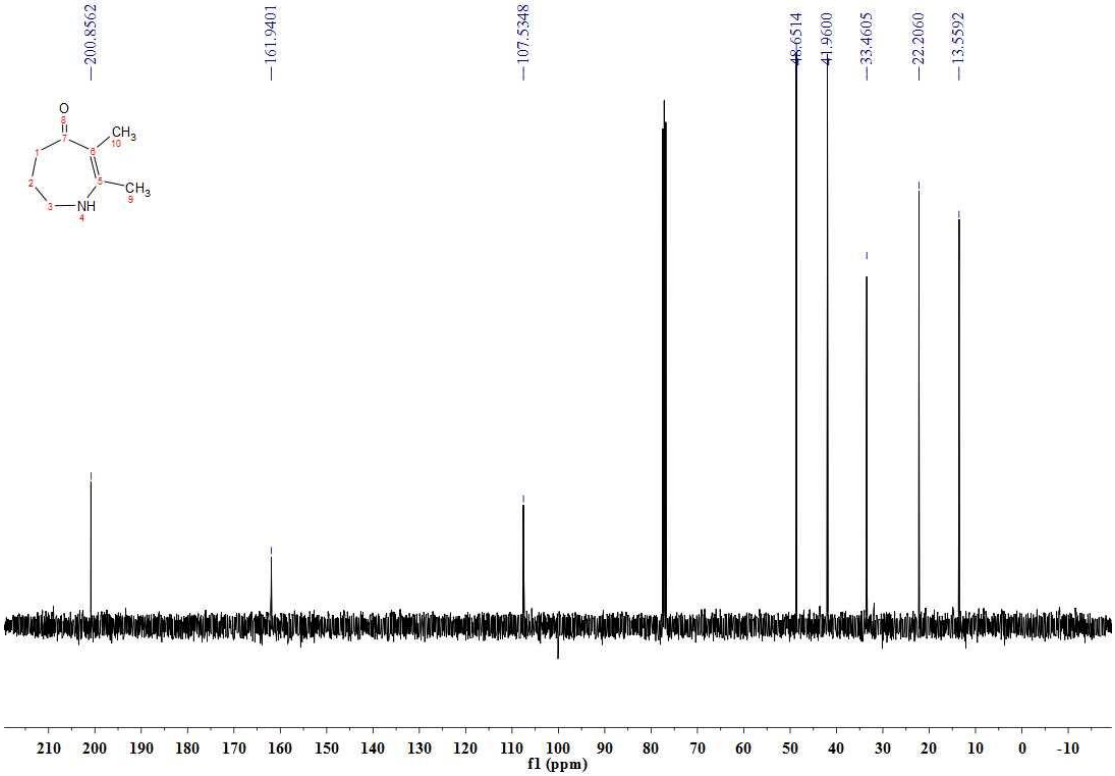
^{13}C NMR spectrum for **3f** ($CDCl_3$, 101 MHz)



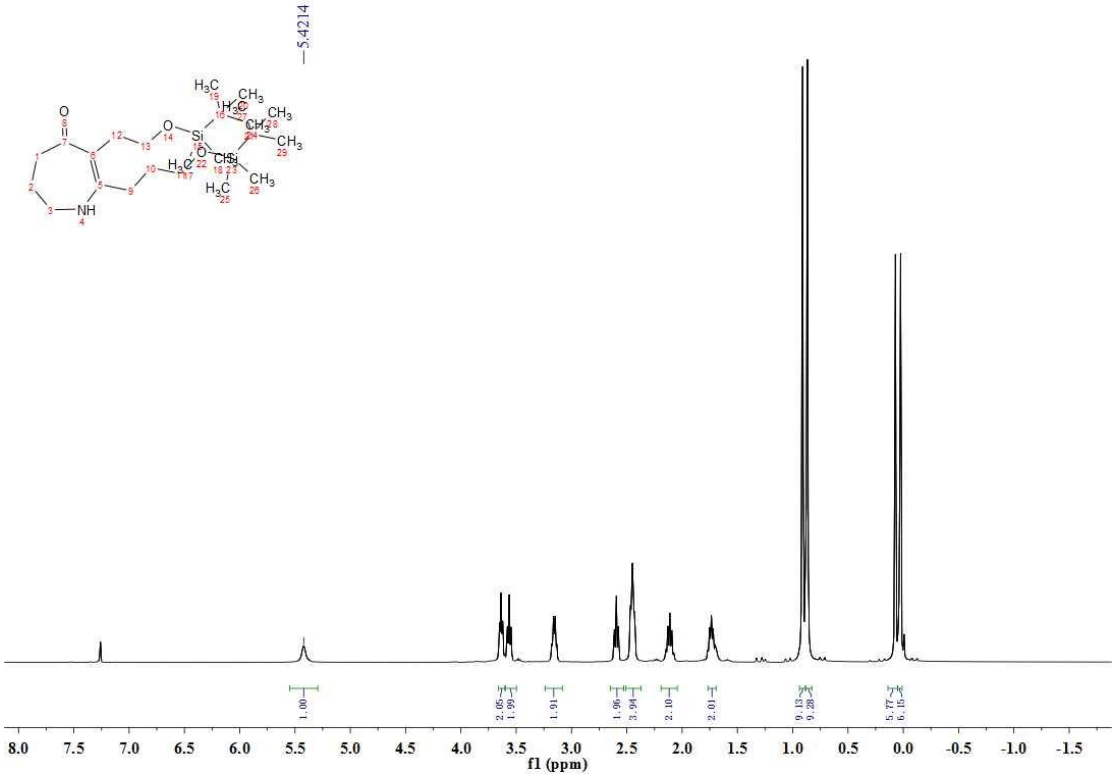
^{1}H NMR spectrum for **3g** ($CDCl_3$, 400 MHz)



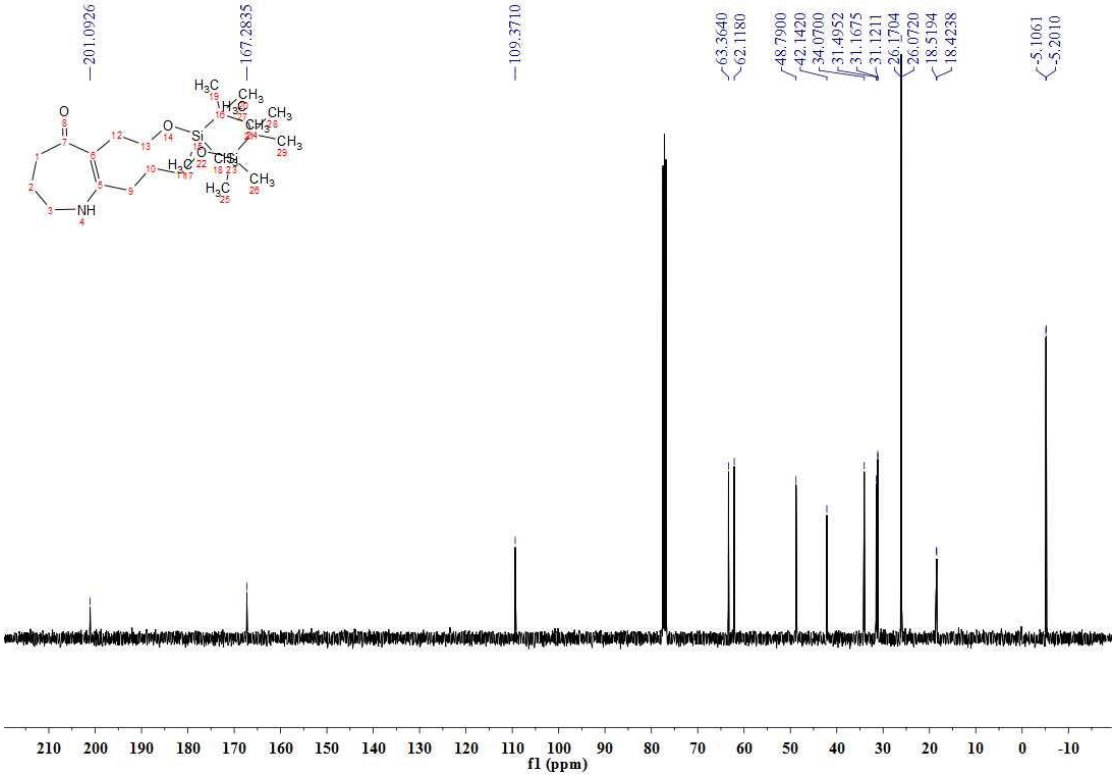
^{13}C NMR spectrum for **3g** ($CDCl_3$, 101 MHz)



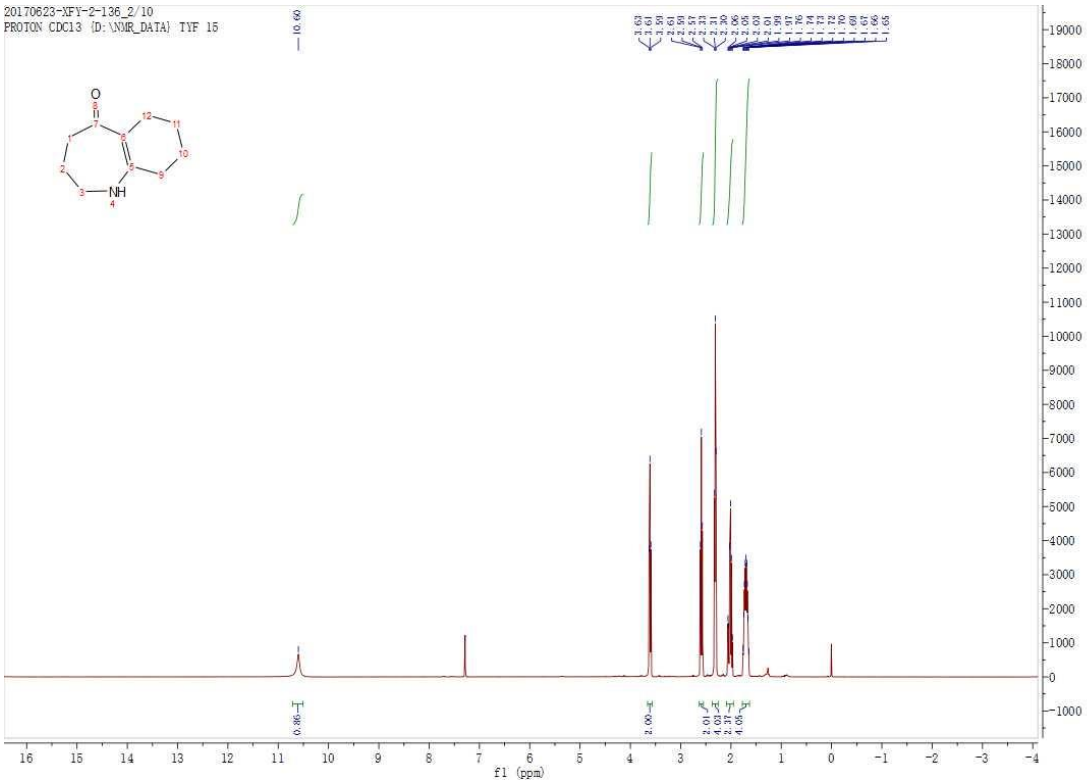
^{1}H NMR spectrum for **3h** ($CDCl_3$, 400 MHz)



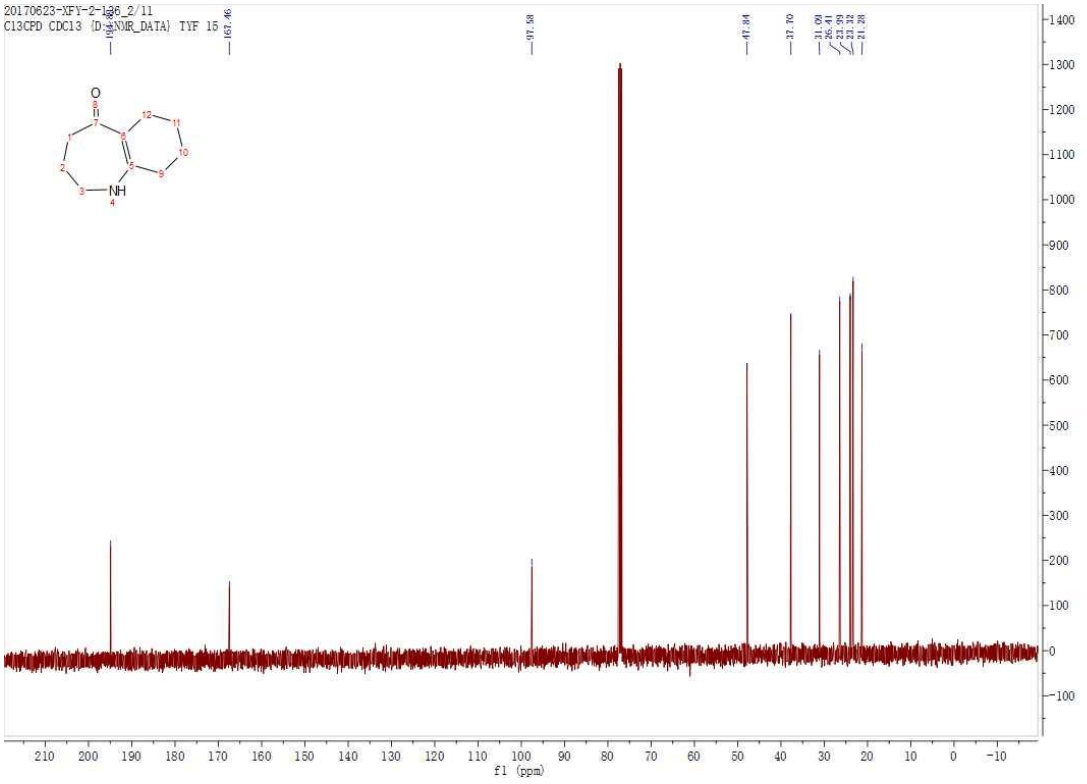
^{13}C NMR spectrum for **3h** ($CDCl_3$, 101 MHz)



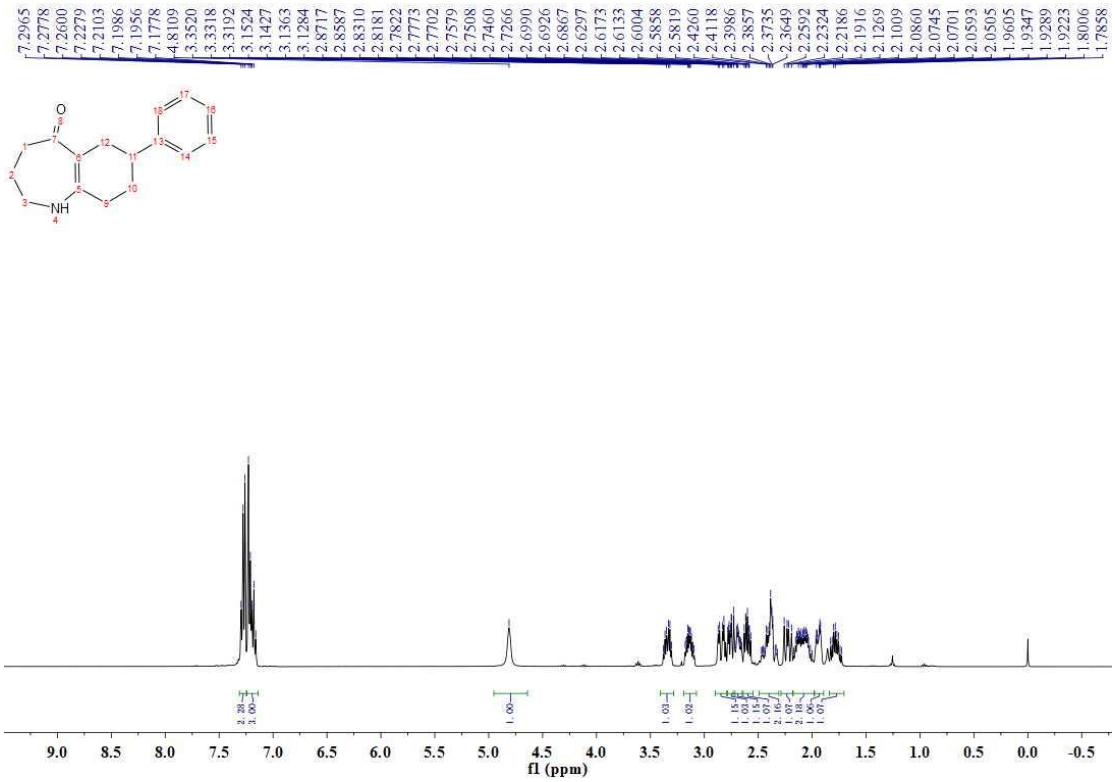
^{1}H NMR spectrum for **3i** ($CDCl_3$, 400 MHz)



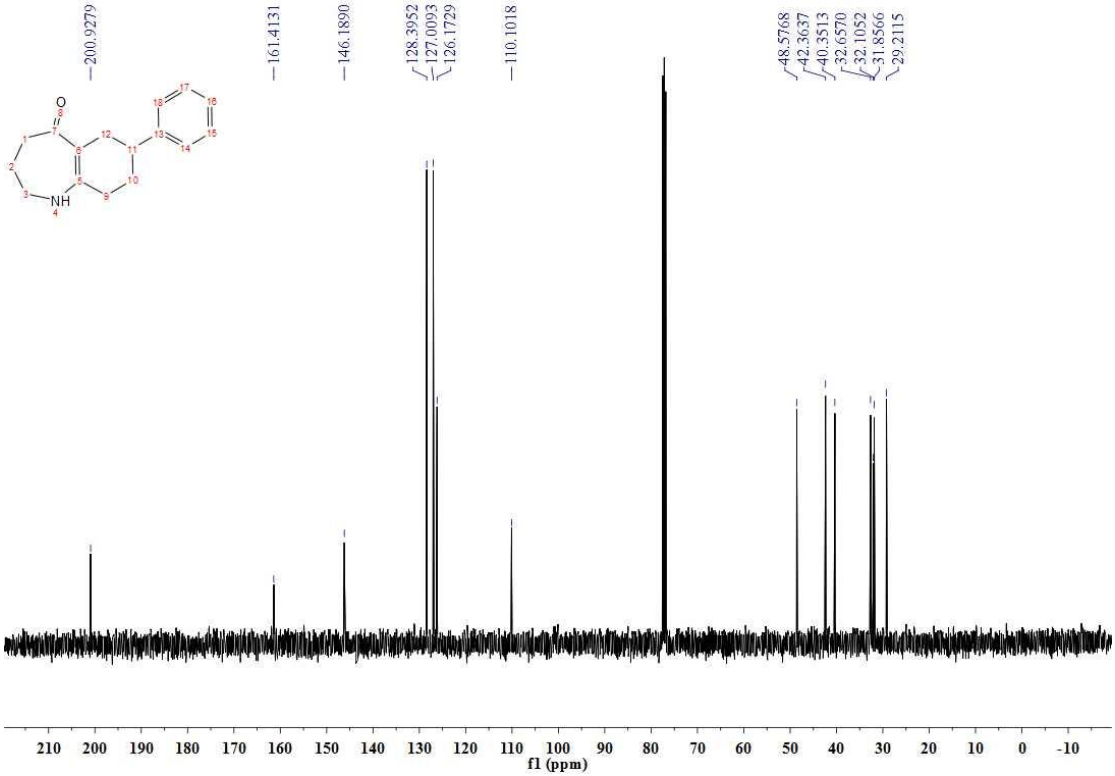
^{13}C NMR spectrum for **3i** ($CDCl_3$, 101 MHz)



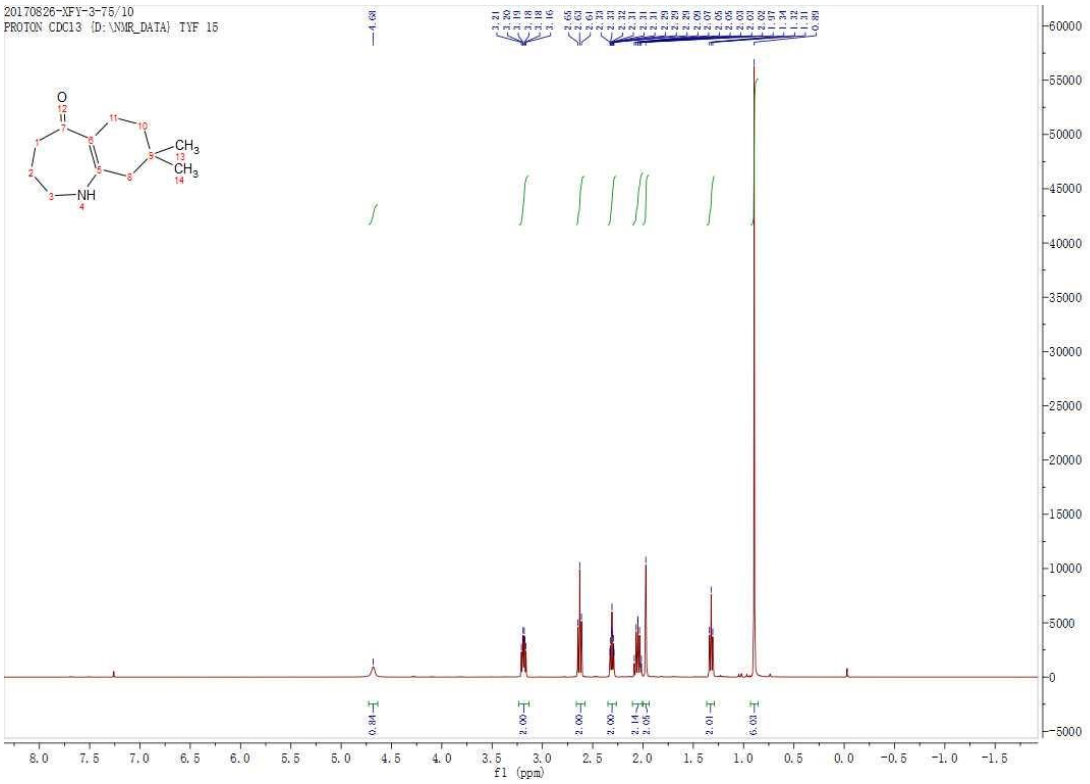
^{1}H NMR spectrum for **3j** ($CDCl_3$, 400 MHz)



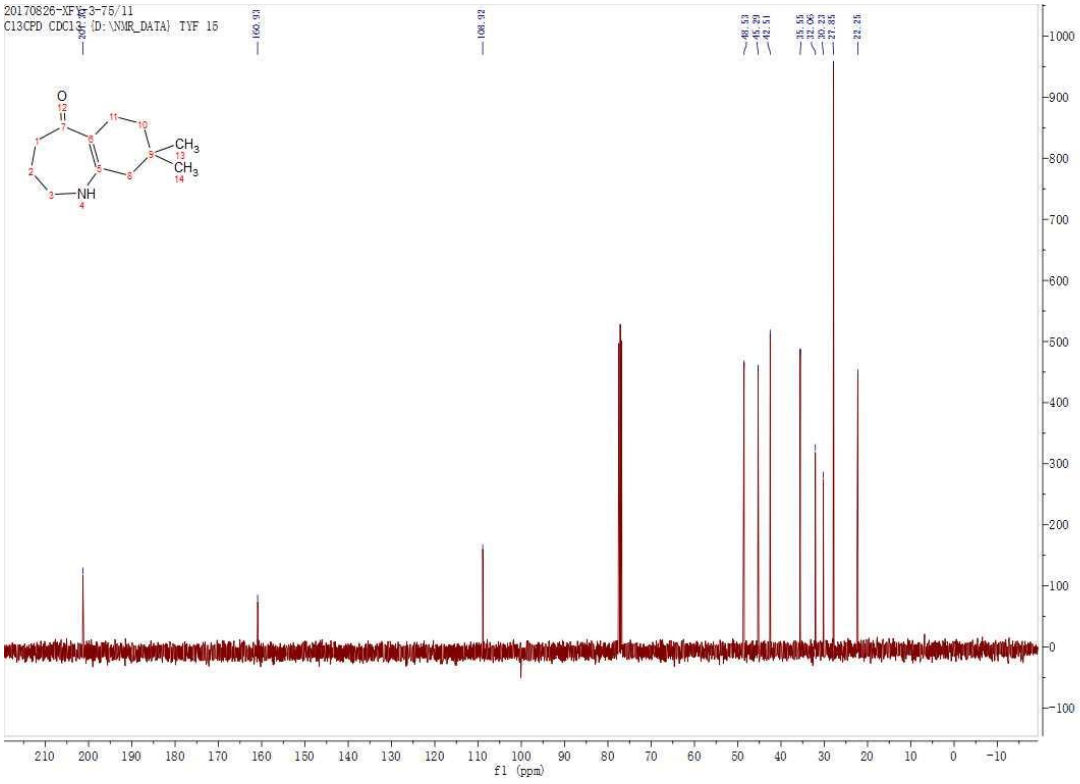
^{13}C NMR spectrum for **3j** ($CDCl_3$, 101 MHz)



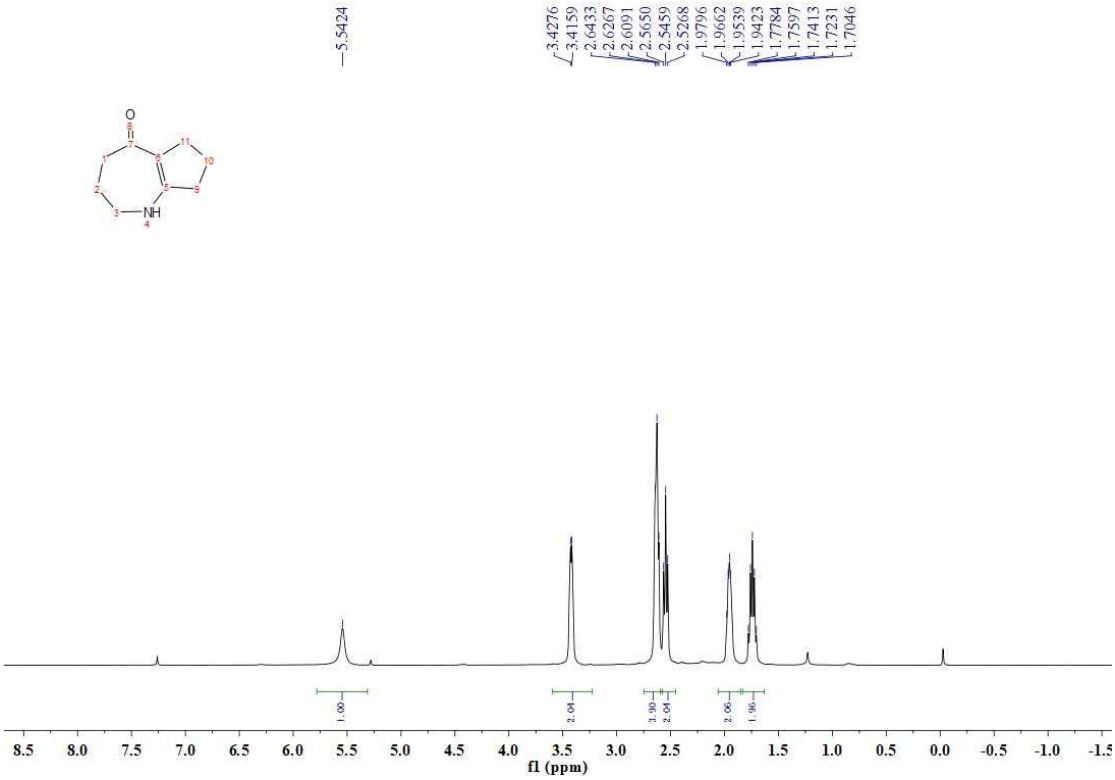
^{1}H NMR spectrum for **3k** ($CDCl_3$, 400 MHz)



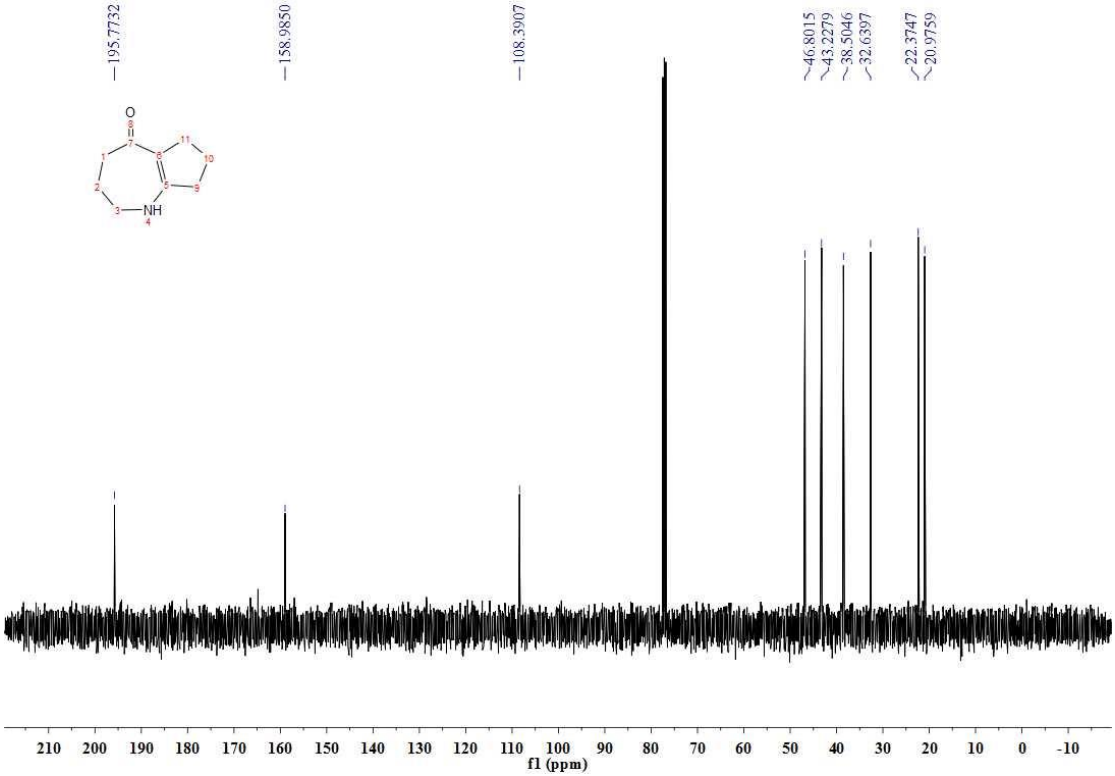
^{13}C NMR spectrum for **3k** ($CDCl_3$, 101 MHz)



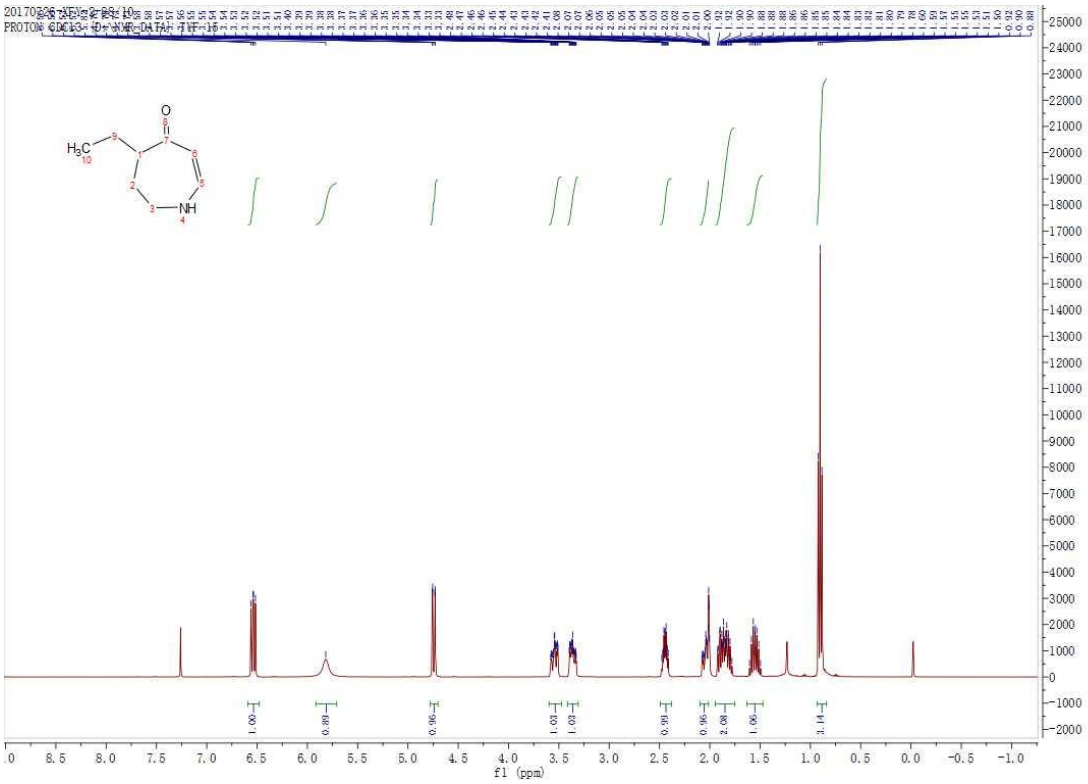
^{1}H NMR spectrum for **3l** ($CDCl_3$, 400 MHz)



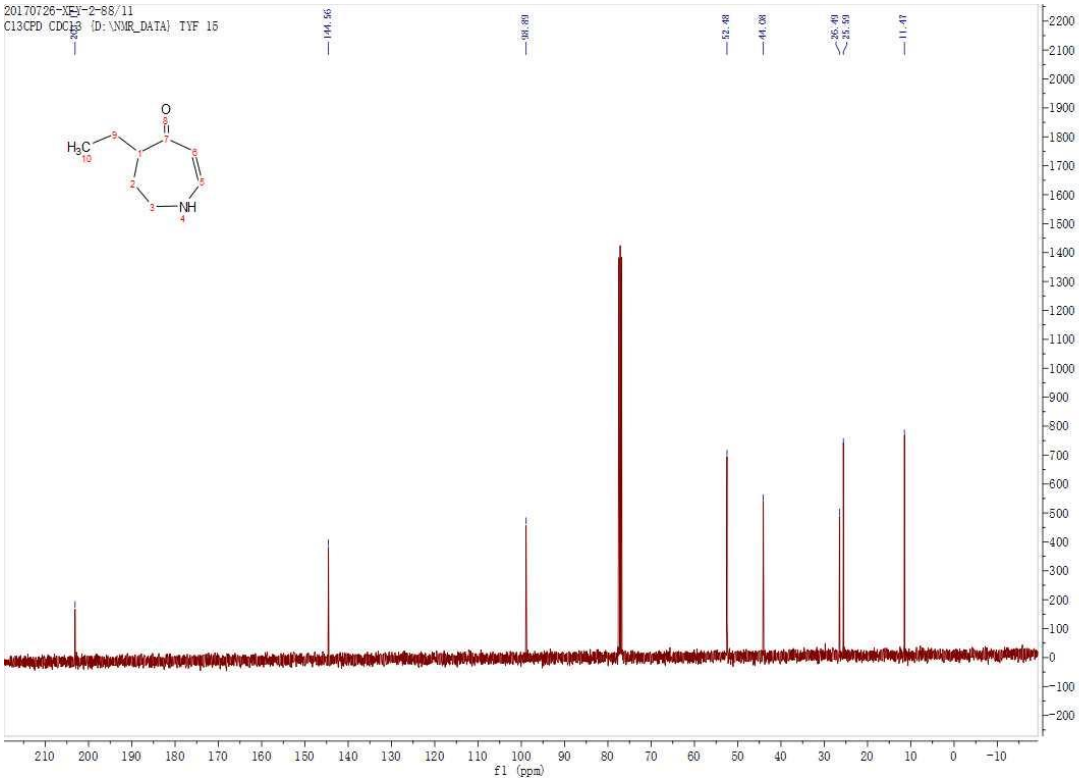
^{13}C NMR spectrum for **3l** ($CDCl_3$, 101 MHz)



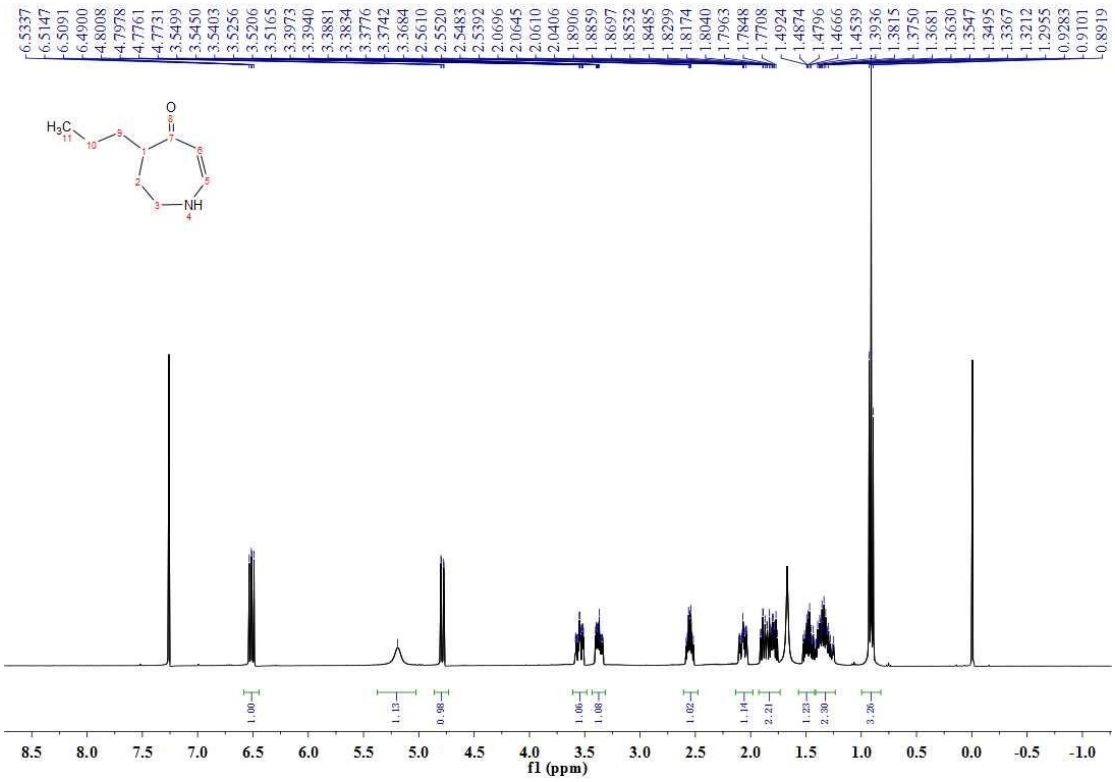
^{1}H NMR spectrum for **3m** ($CDCl_3$, 400 MHz)



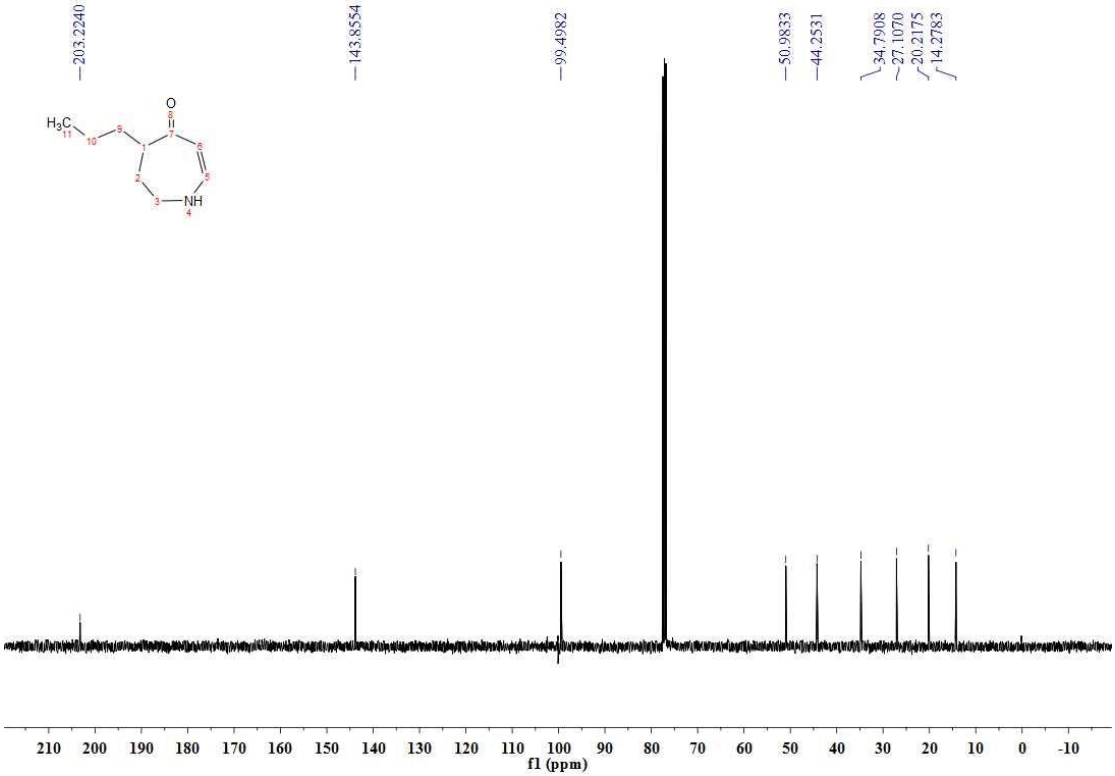
^{13}C NMR spectrum for **3m** ($CDCl_3$, 101 MHz)



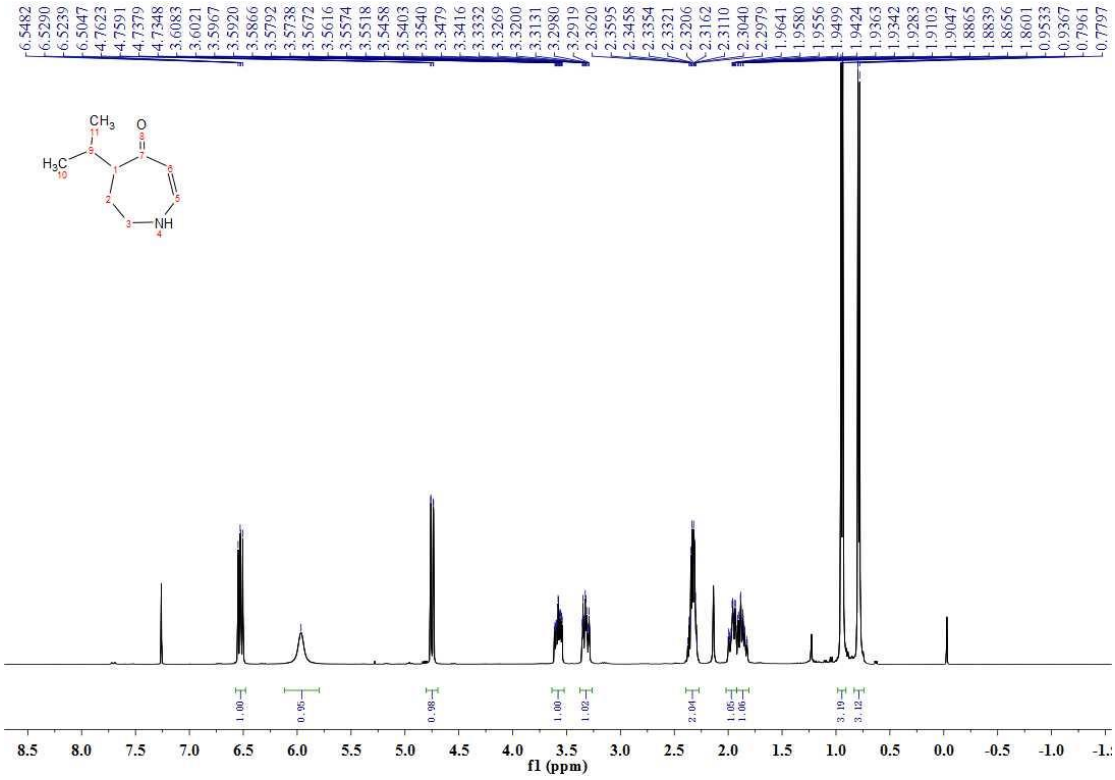
^{1}H NMR spectrum for **3n** ($CDCl_3$, 400 MHz)



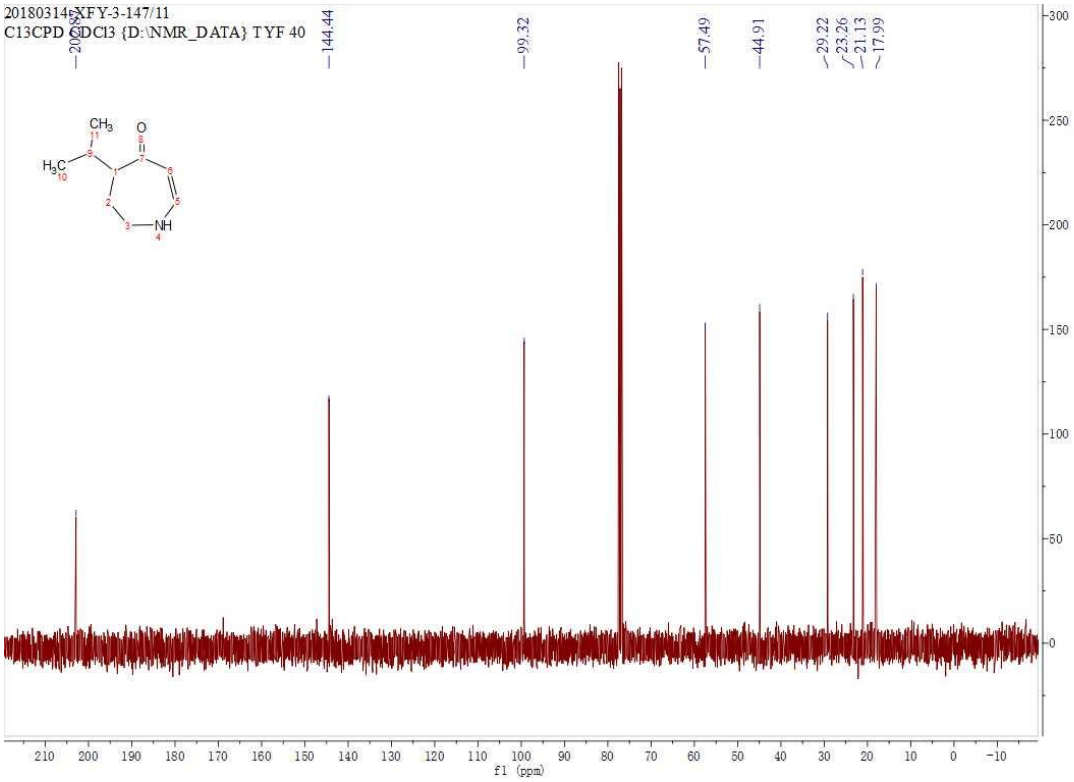
^{13}C NMR spectrum for **3n** ($CDCl_3$, 101 MHz)



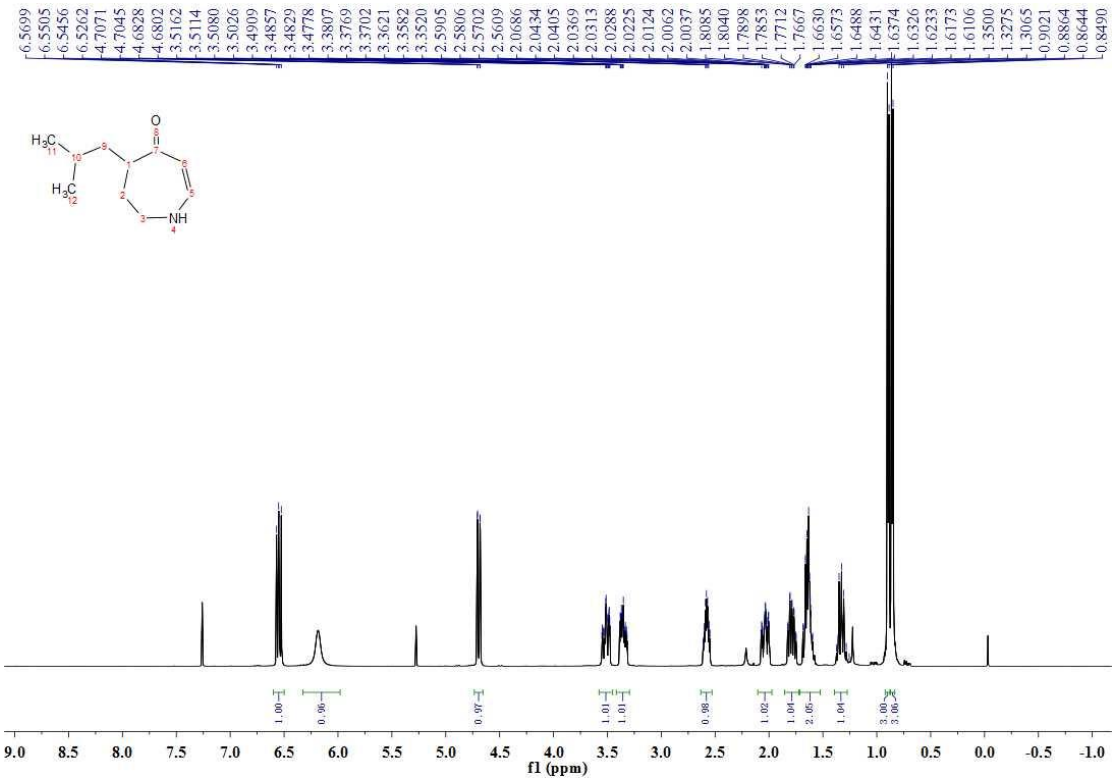
^{1}H NMR spectrum for **3o** ($CDCl_3$, 400 MHz)



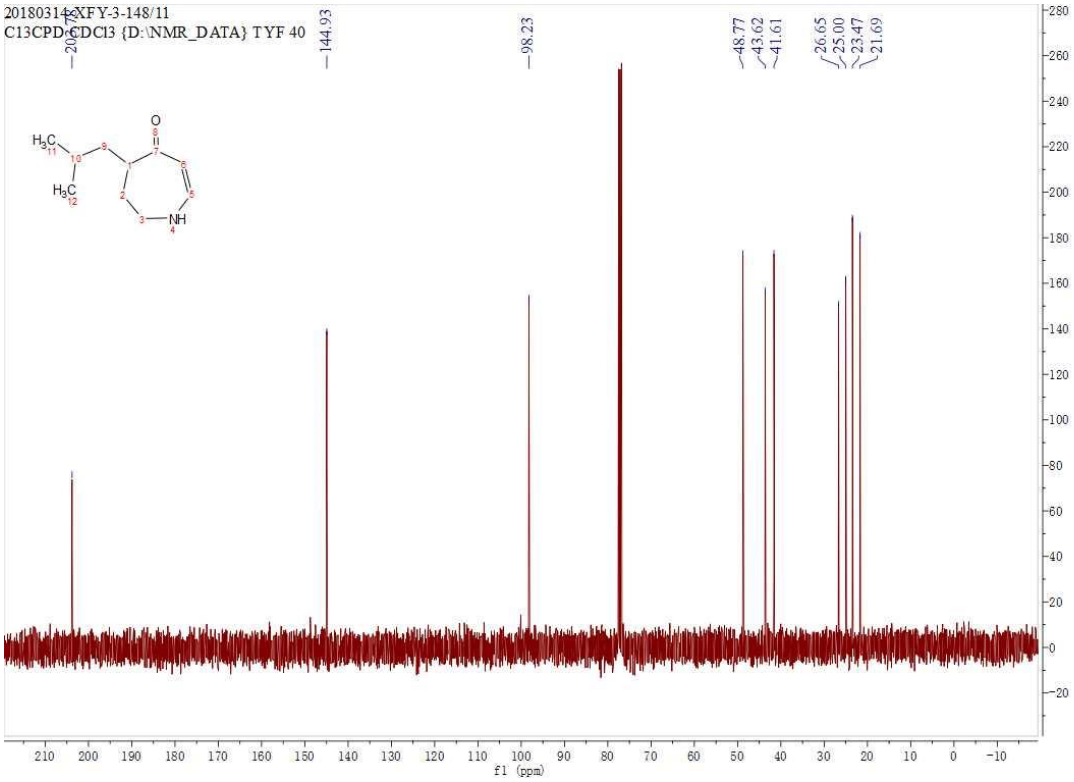
^{13}C NMR spectrum for **3o** ($CDCl_3$, 101 MHz)



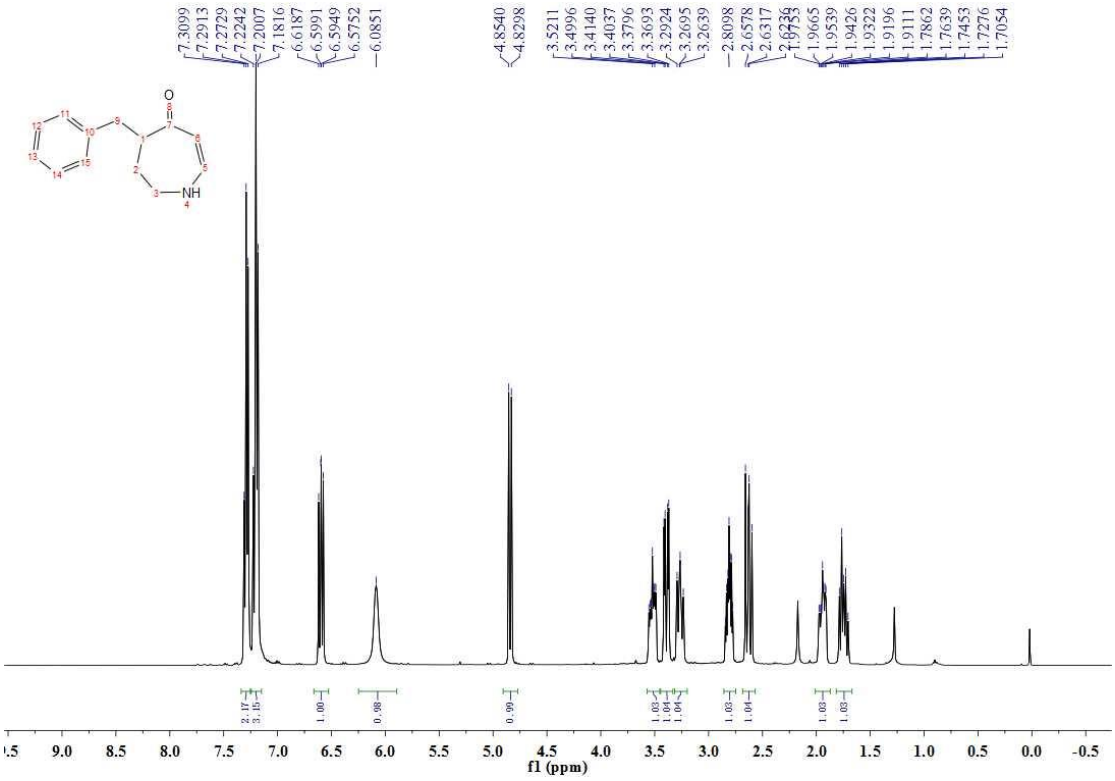
^{1}H NMR spectrum for **3p** ($CDCl_3$, 400 MHz)



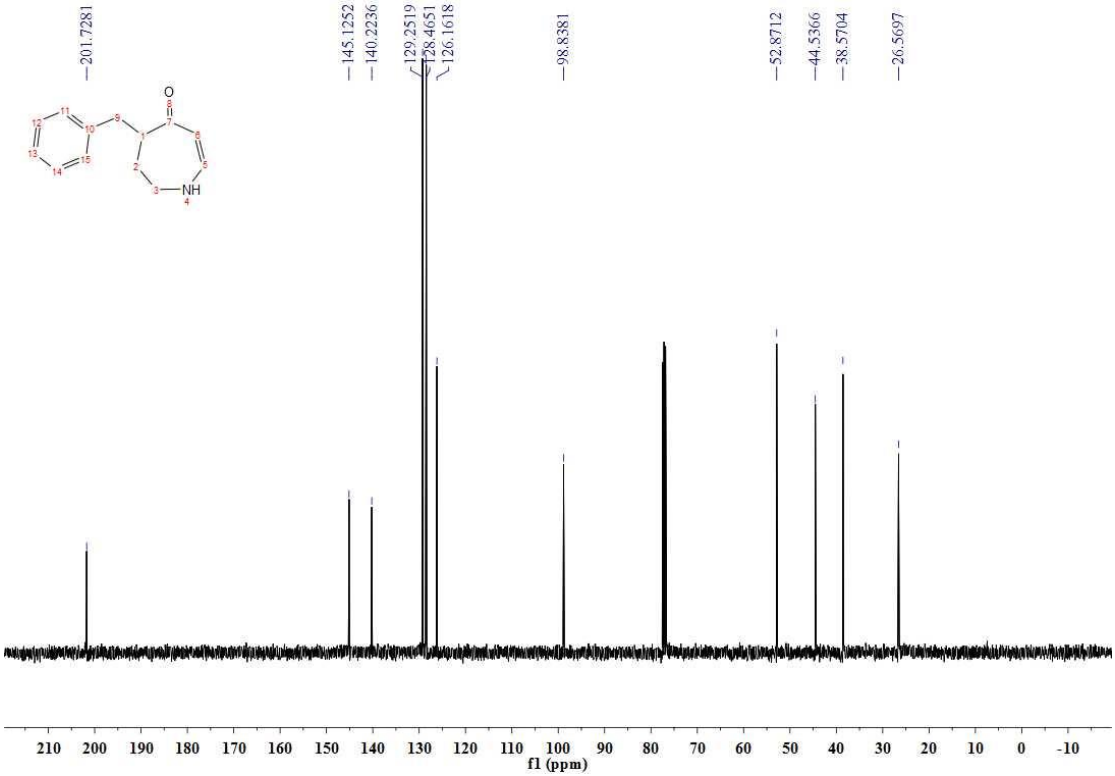
^{13}C NMR spectrum for **3p** ($CDCl_3$, 101 MHz)



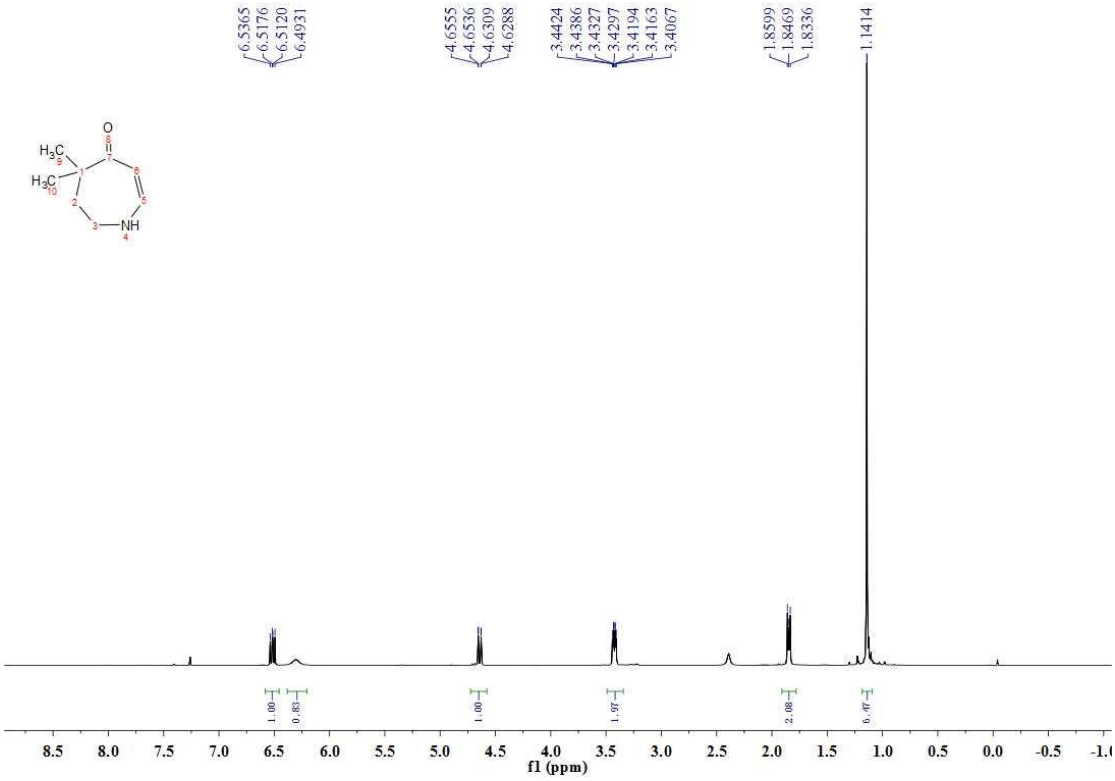
^{1}H NMR spectrum for **3q** ($CDCl_3$, 400 MHz)



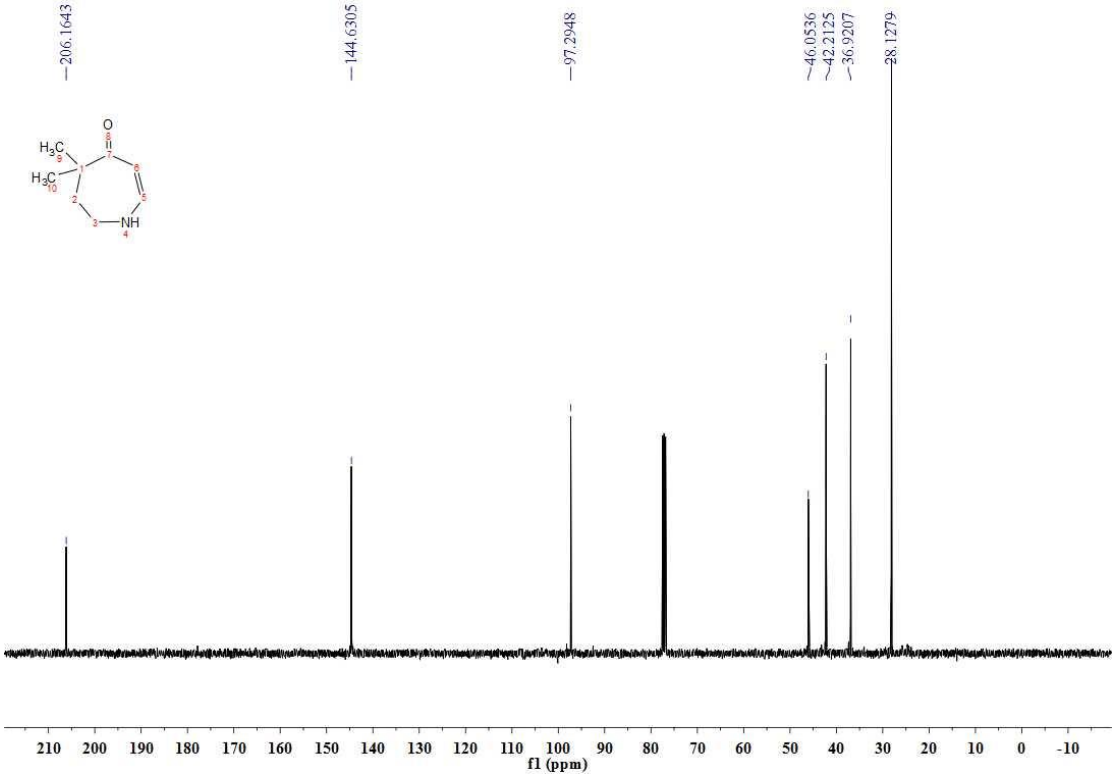
^{13}C NMR spectrum for **3q** ($CDCl_3$, 101 MHz)



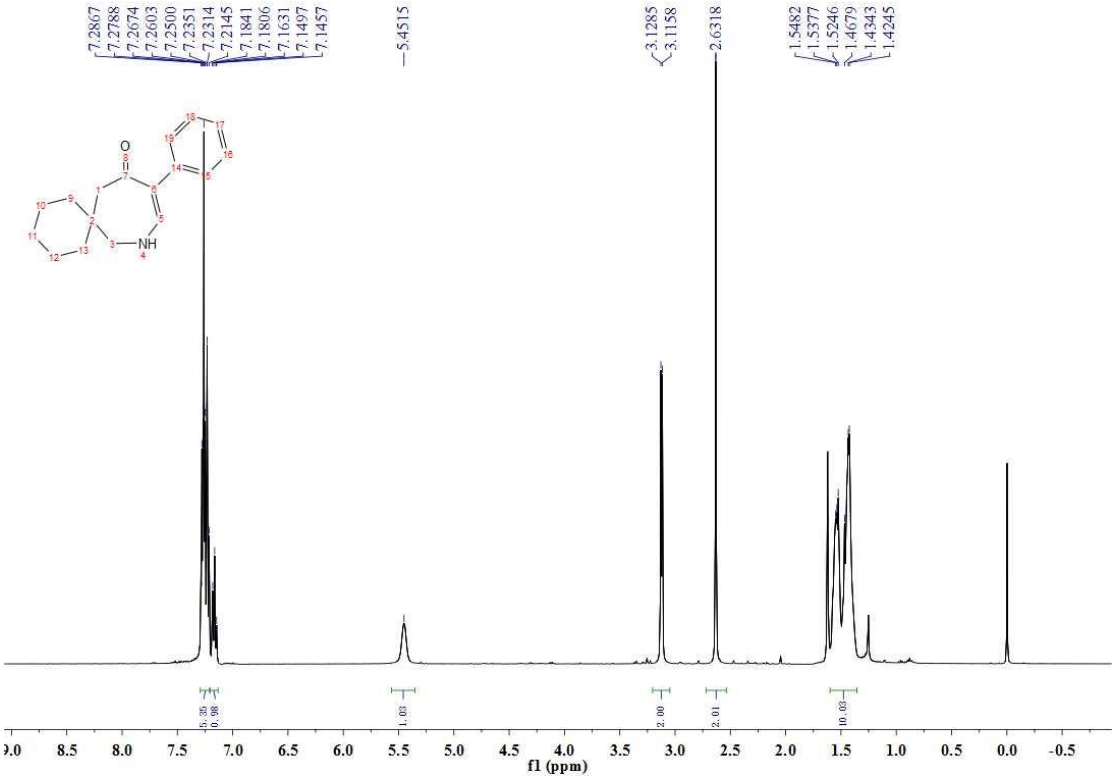
^{1}H NMR spectrum for **3r** ($CDCl_3$, 400 MHz)



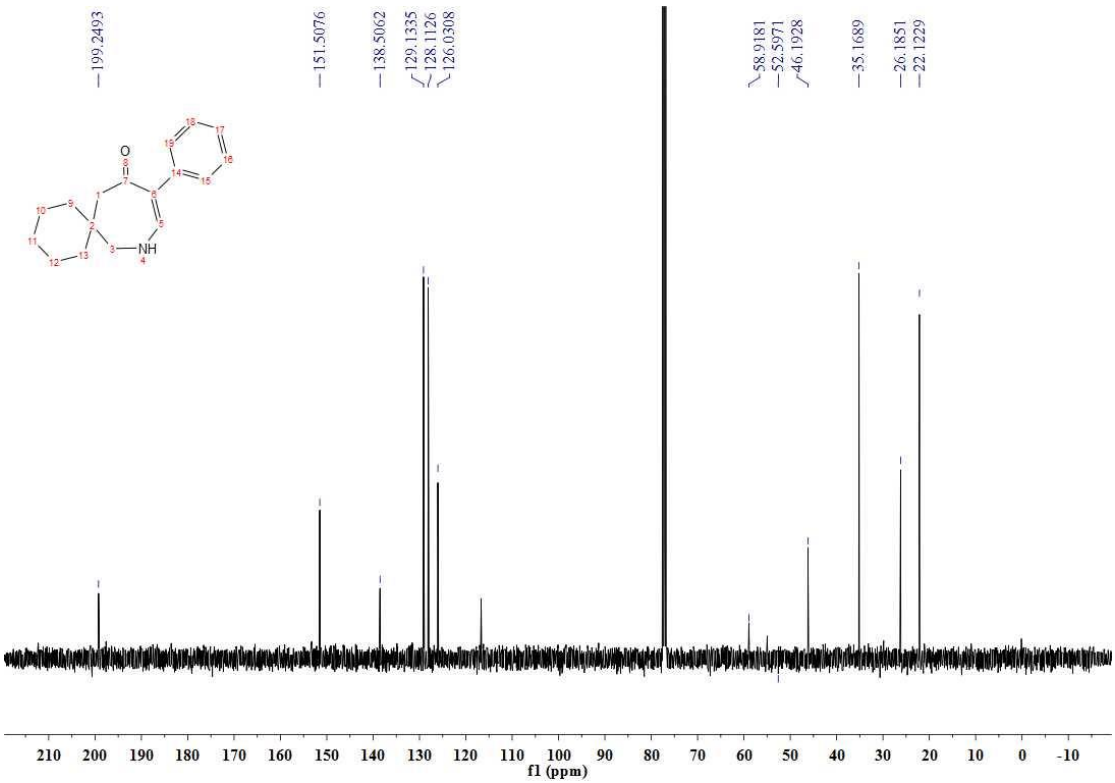
^{13}C NMR spectrum for **3r** ($CDCl_3$, 101 MHz)



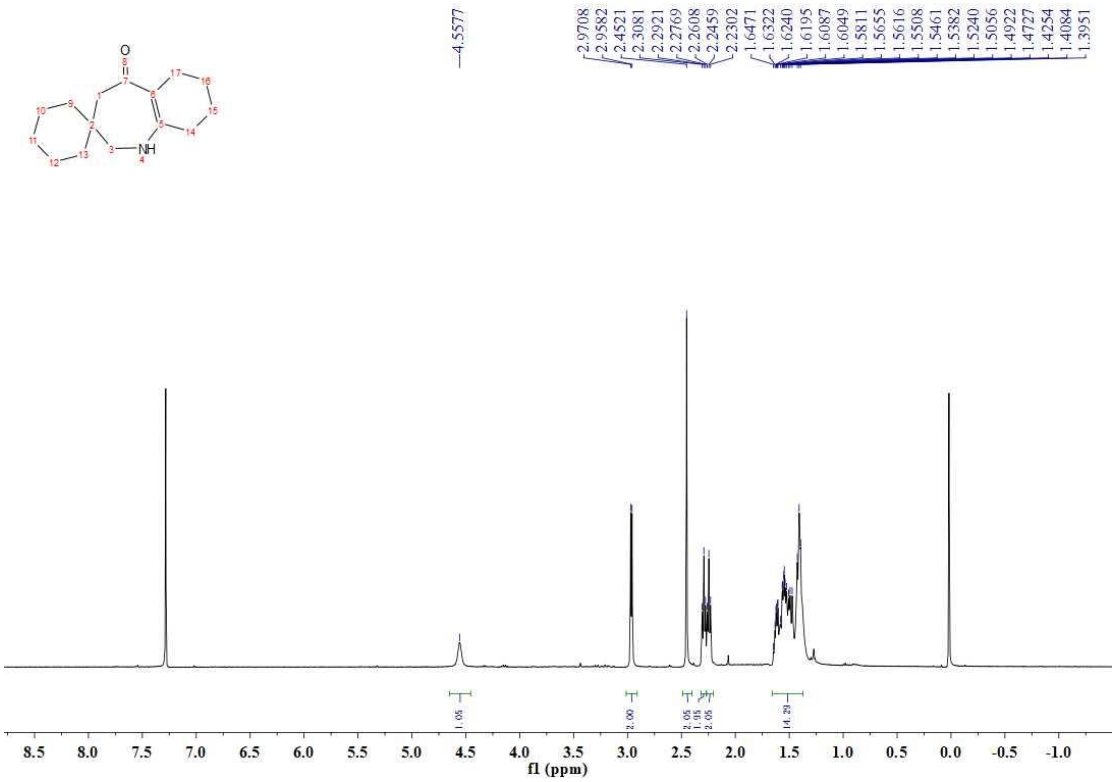
^{1}H NMR spectrum for **3s** ($CDCl_3$, 400 MHz)



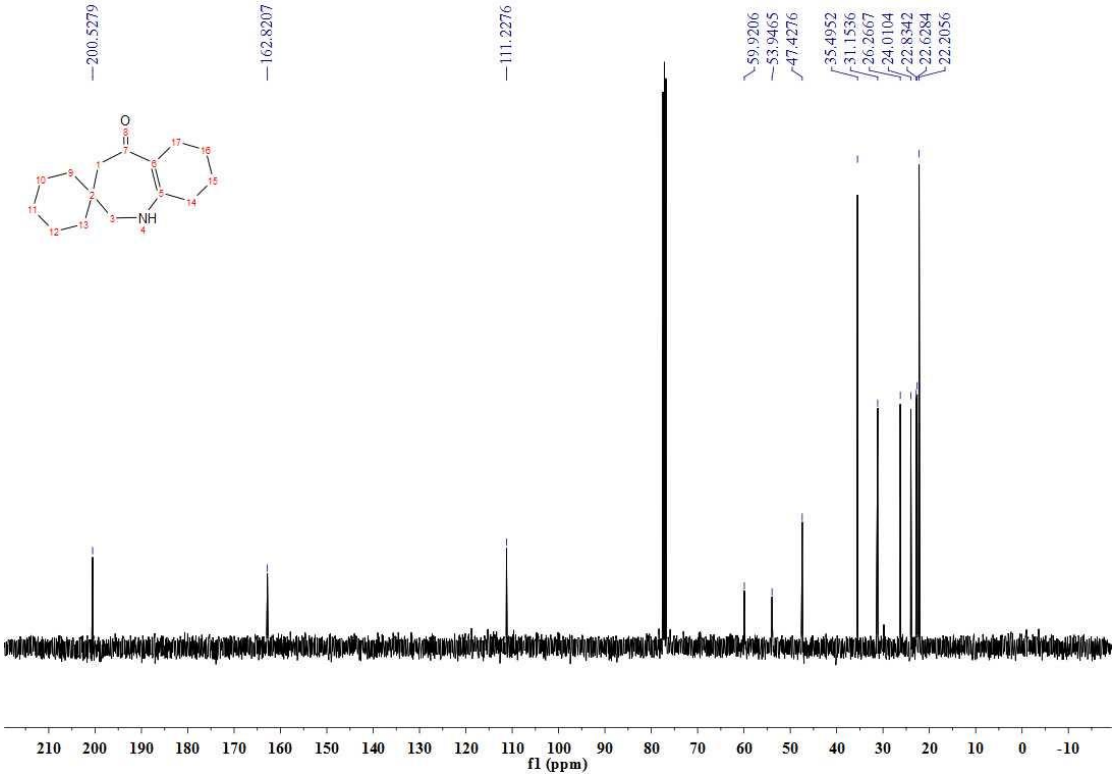
^{13}C NMR spectrum for **3s** ($CDCl_3$, 101 MHz)



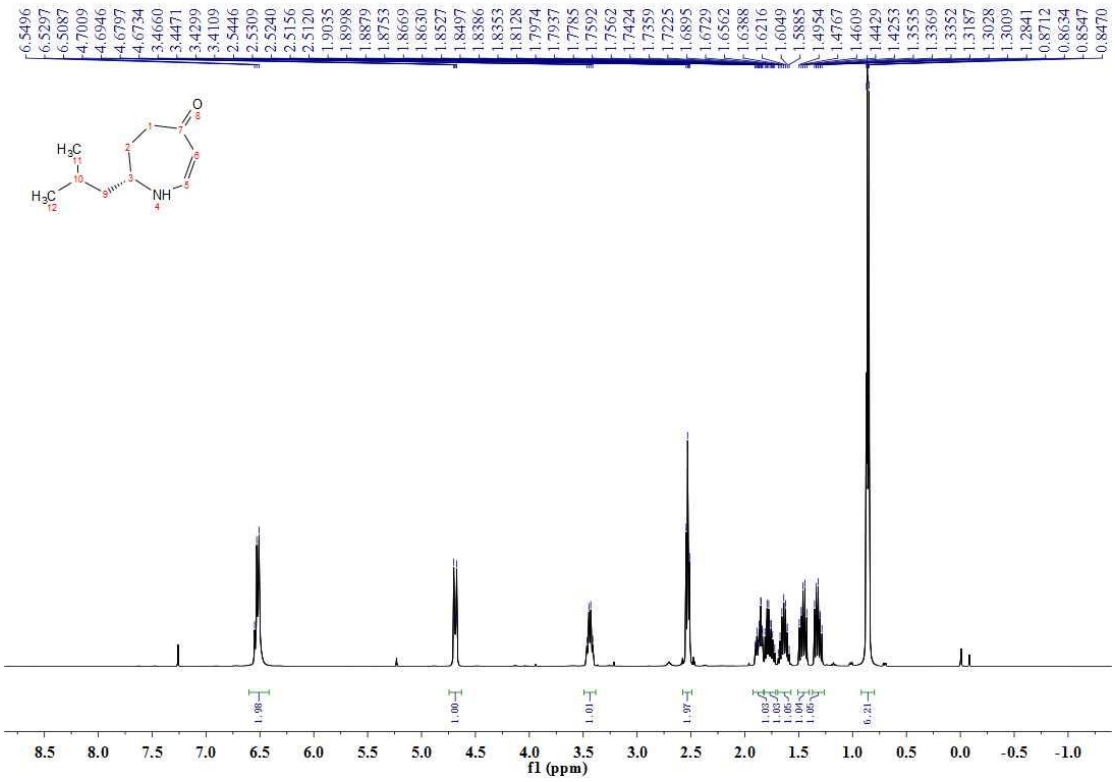
^{1}H NMR spectrum for **3t** ($CDCl_3$, 400 MHz)



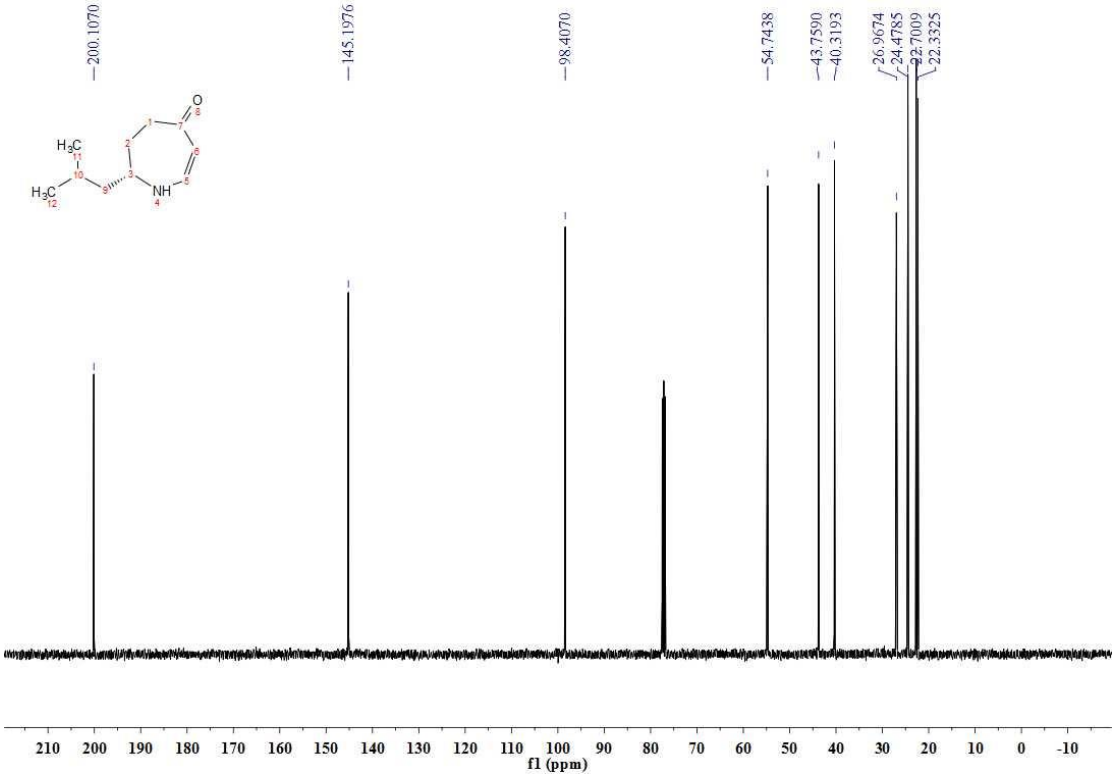
^{13}C NMR spectrum for **3t** ($CDCl_3$, 101 MHz)



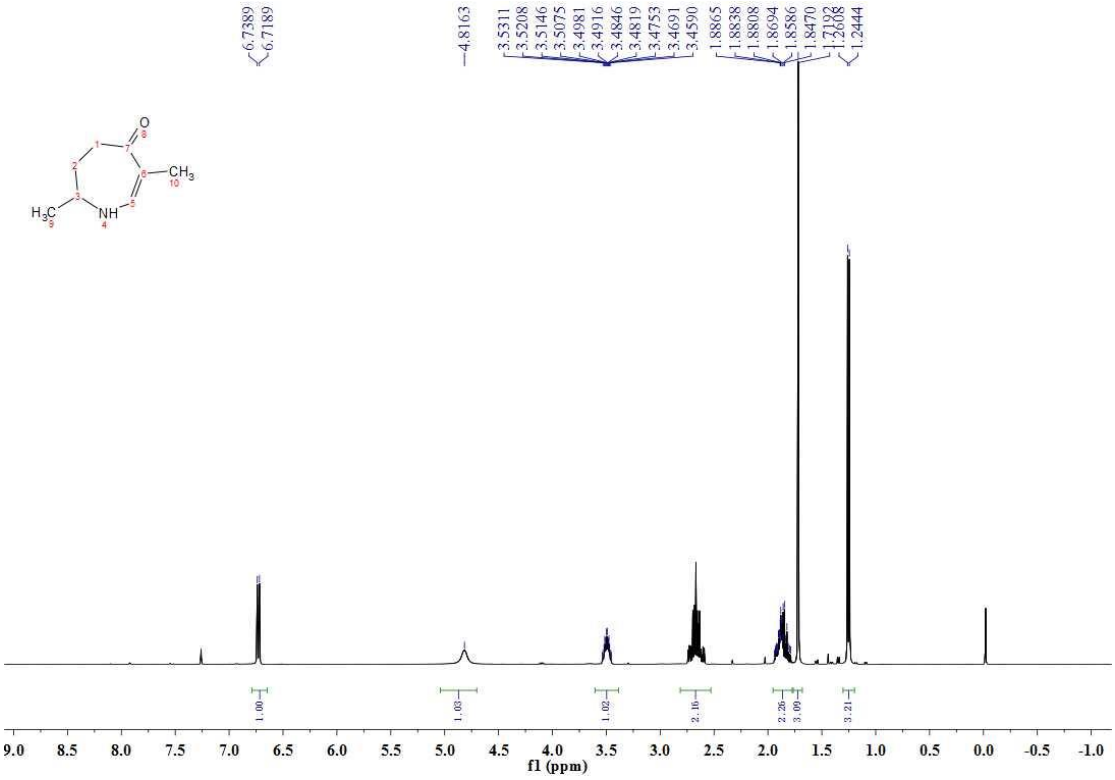
^{1}H NMR spectrum for **3u** ($CDCl_3$, 400 MHz)



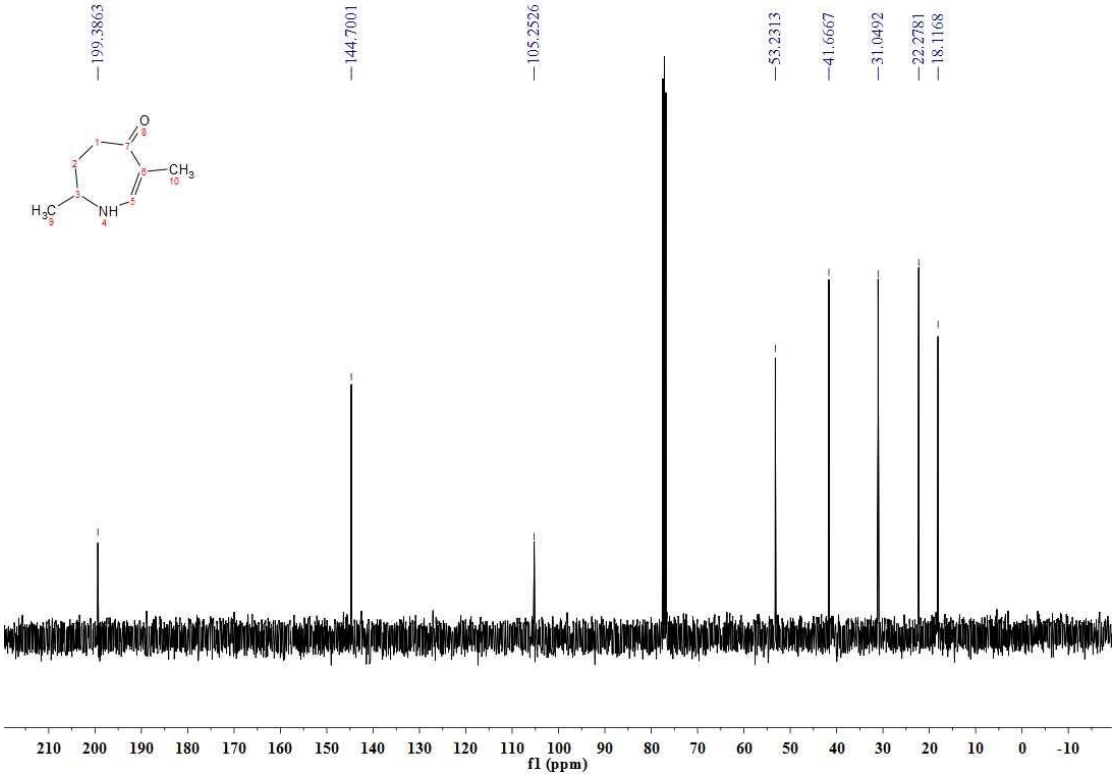
^{13}C NMR spectrum for **3u** ($CDCl_3$, 101 MHz)



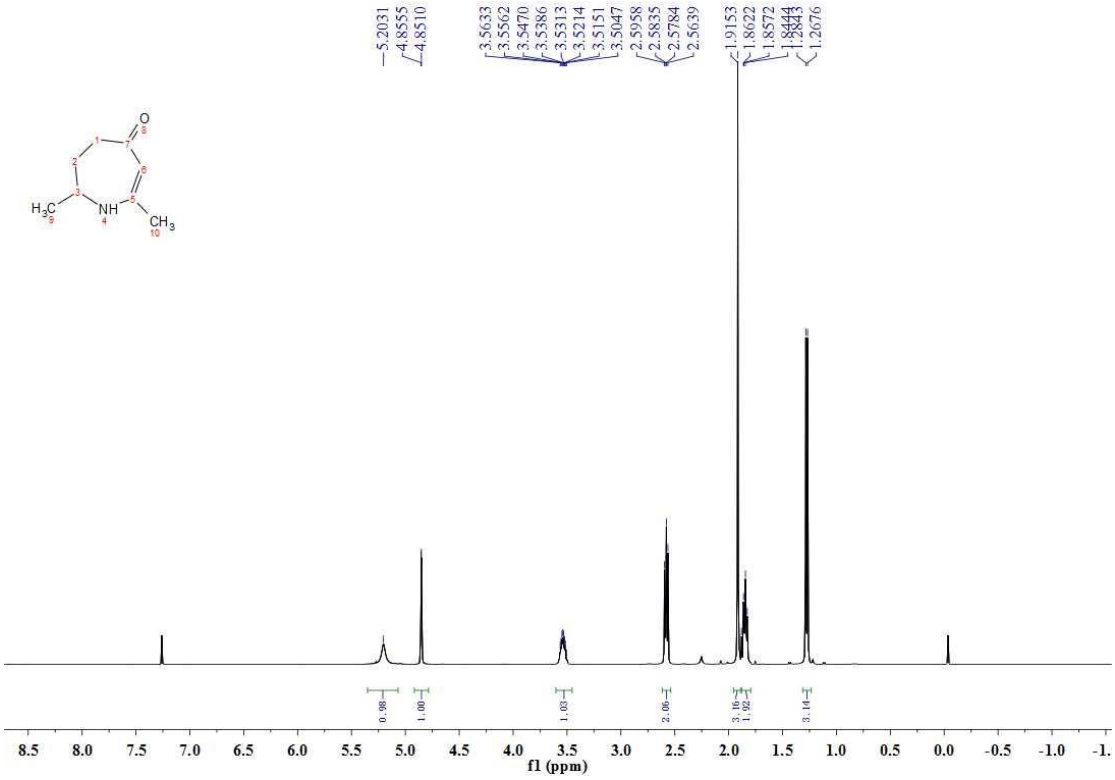
^{1}H NMR spectrum for **3v** ($CDCl_3$, 400 MHz)



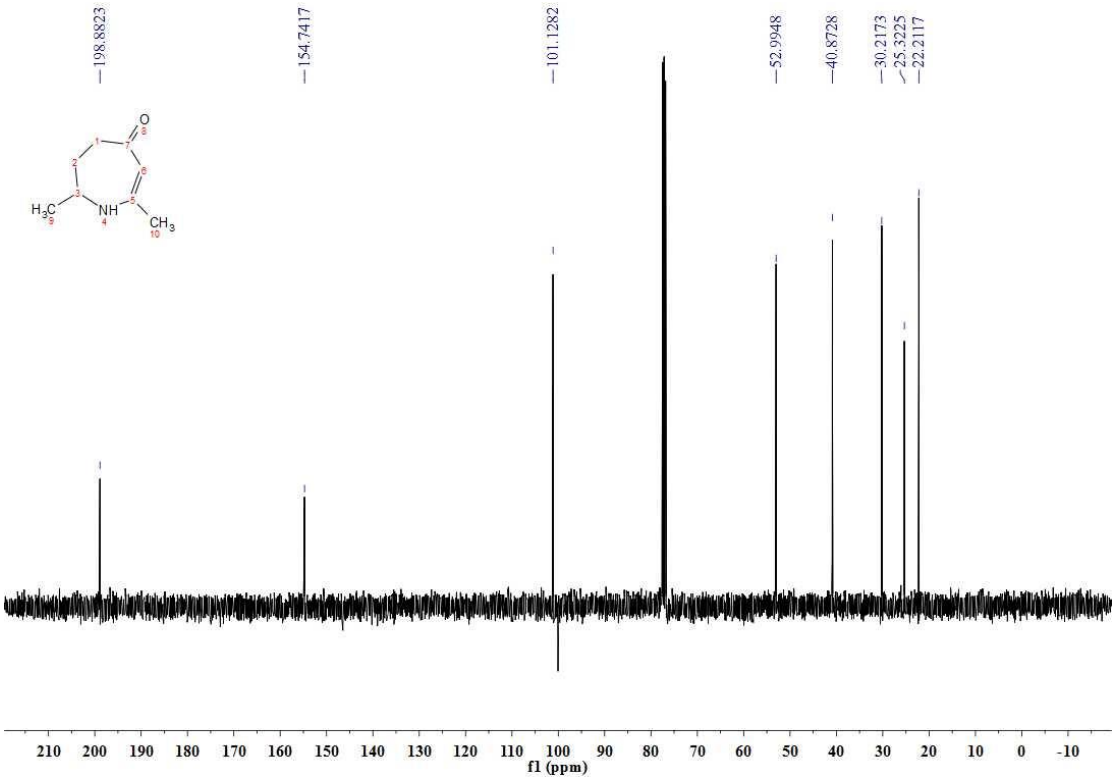
^{13}C NMR spectrum for **3v** ($CDCl_3$, 101 MHz)



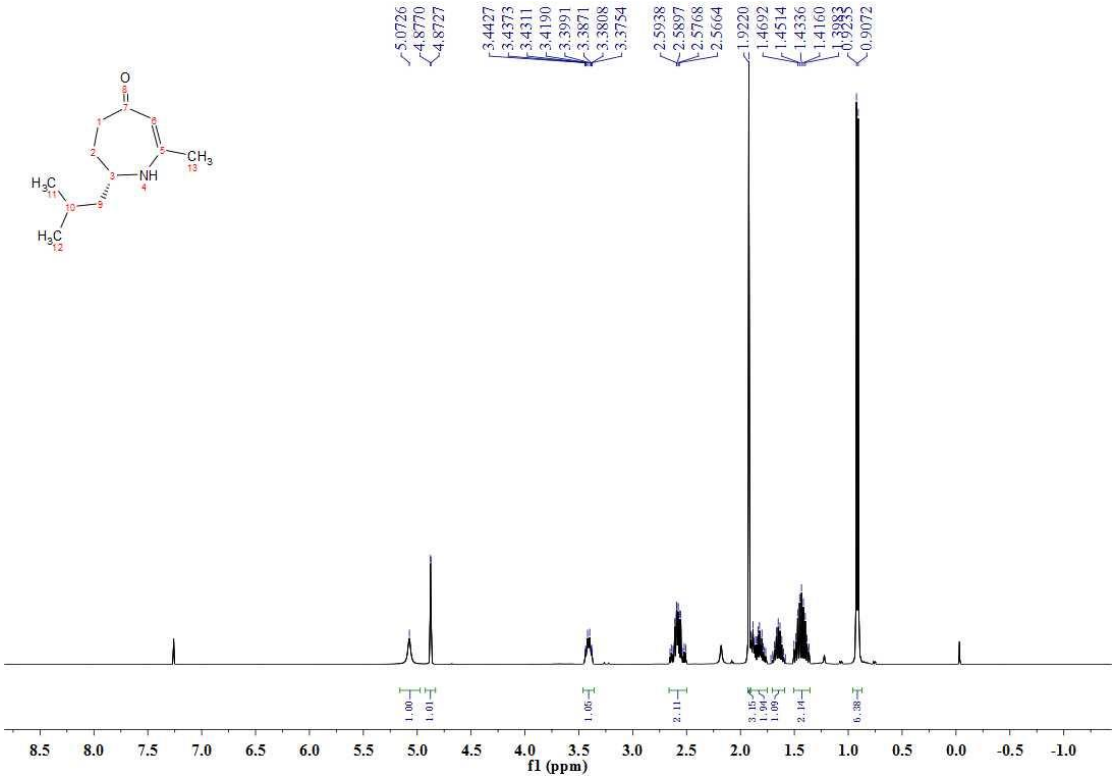
^{1}H NMR spectrum for **3w** ($CDCl_3$, 400 MHz)



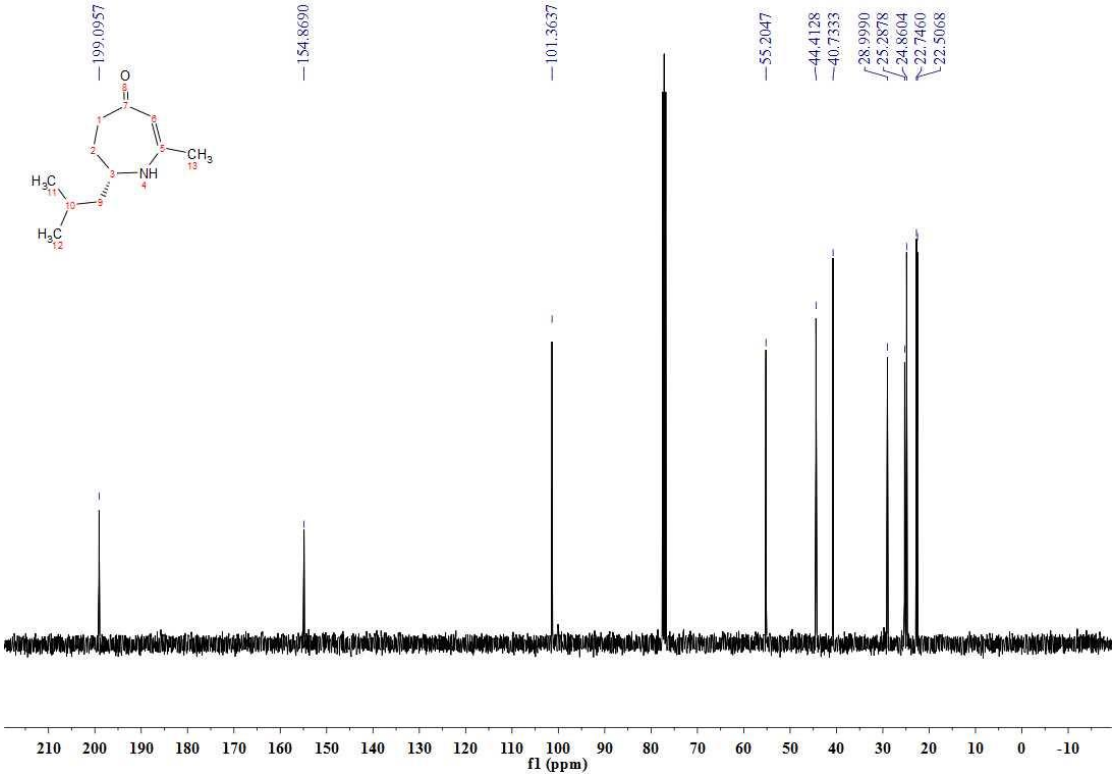
^{13}C NMR spectrum for **3w** ($CDCl_3$, 101 MHz)



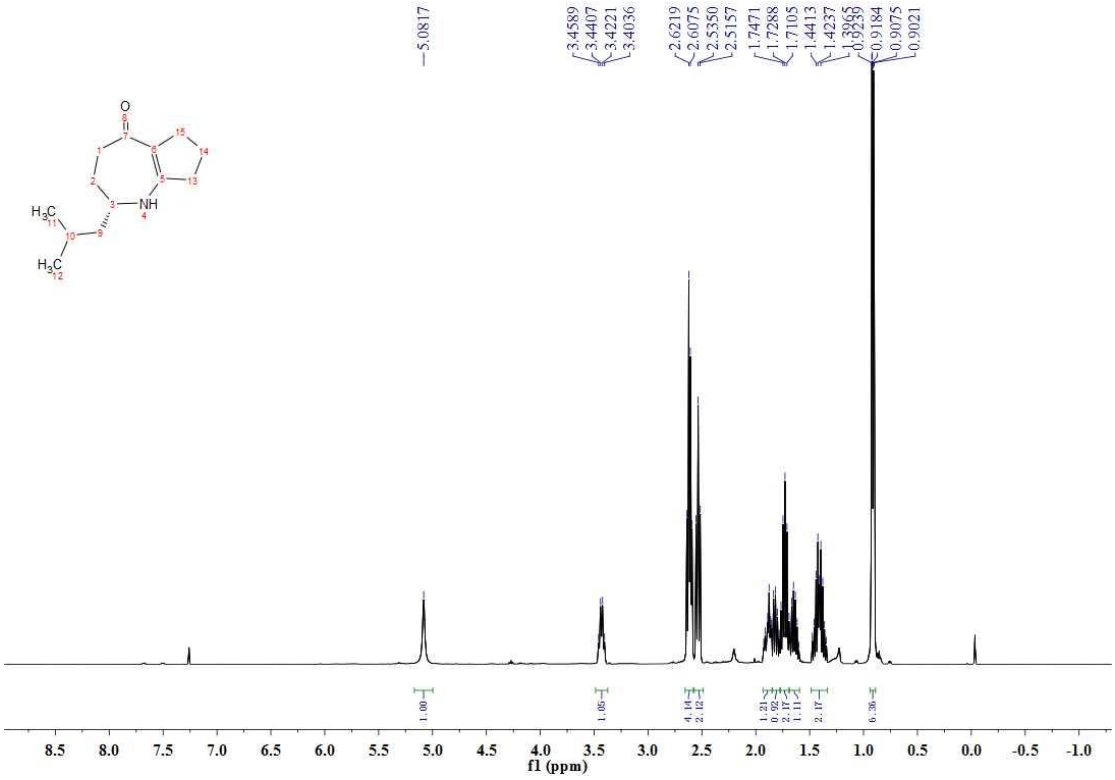
^{1}H NMR spectrum for **3x** ($CDCl_3$, 400 MHz)



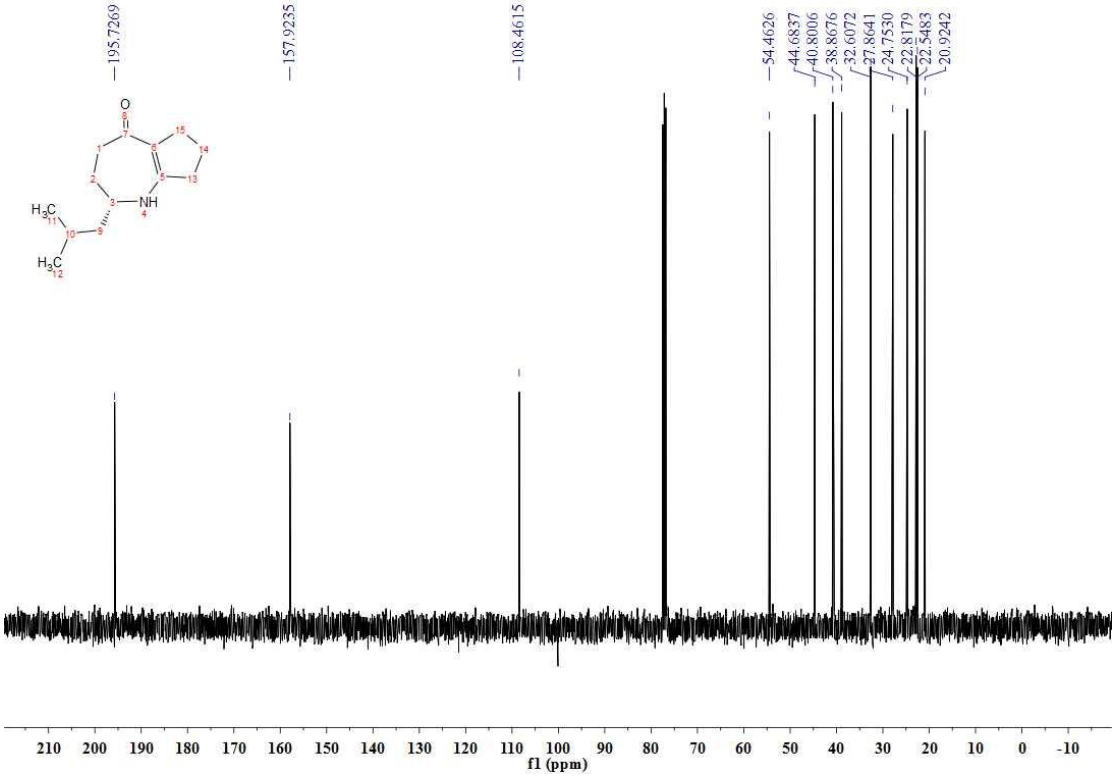
^{13}C NMR spectrum for **3x** ($CDCl_3$, 101 MHz)



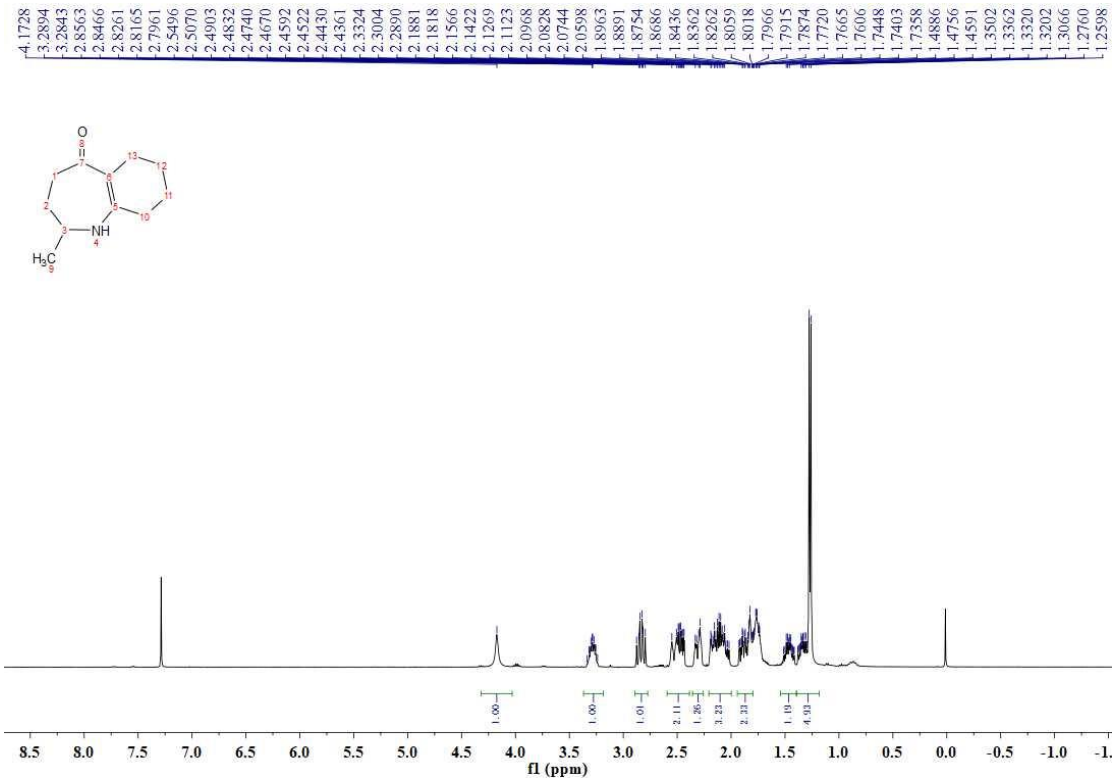
^{1}H NMR spectrum for **3y** ($CDCl_3$, 400 MHz)



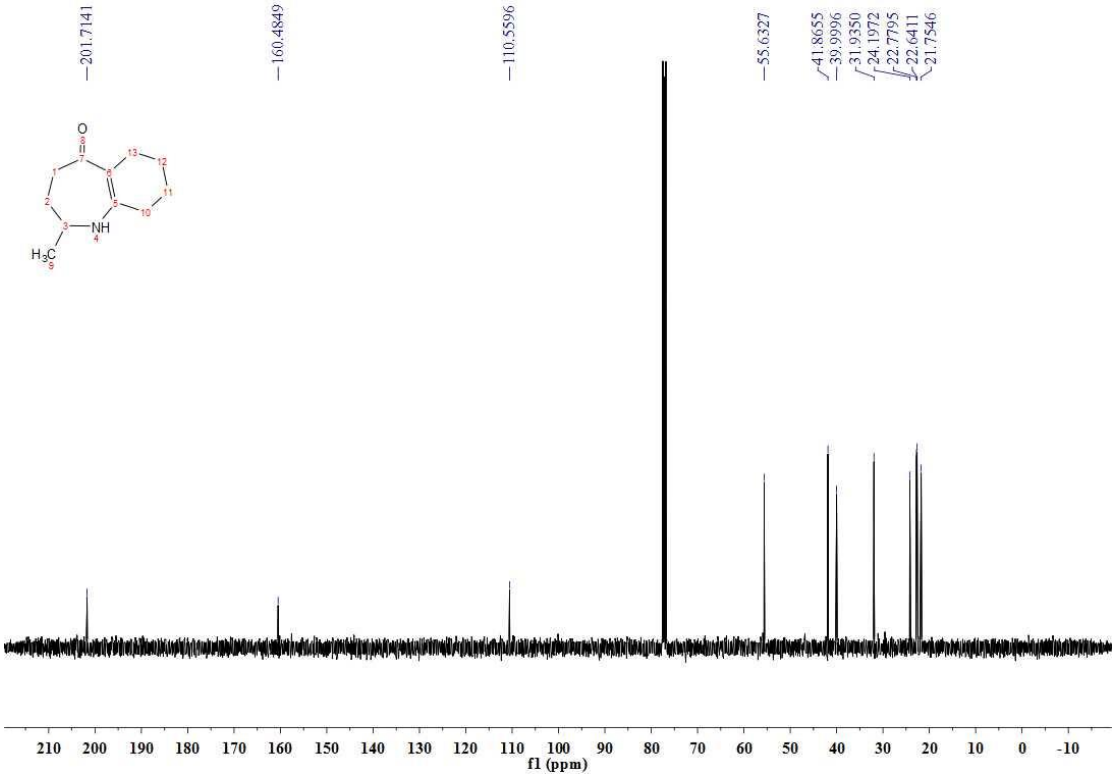
^{13}C NMR spectrum for **3y** ($CDCl_3$, 101 MHz)



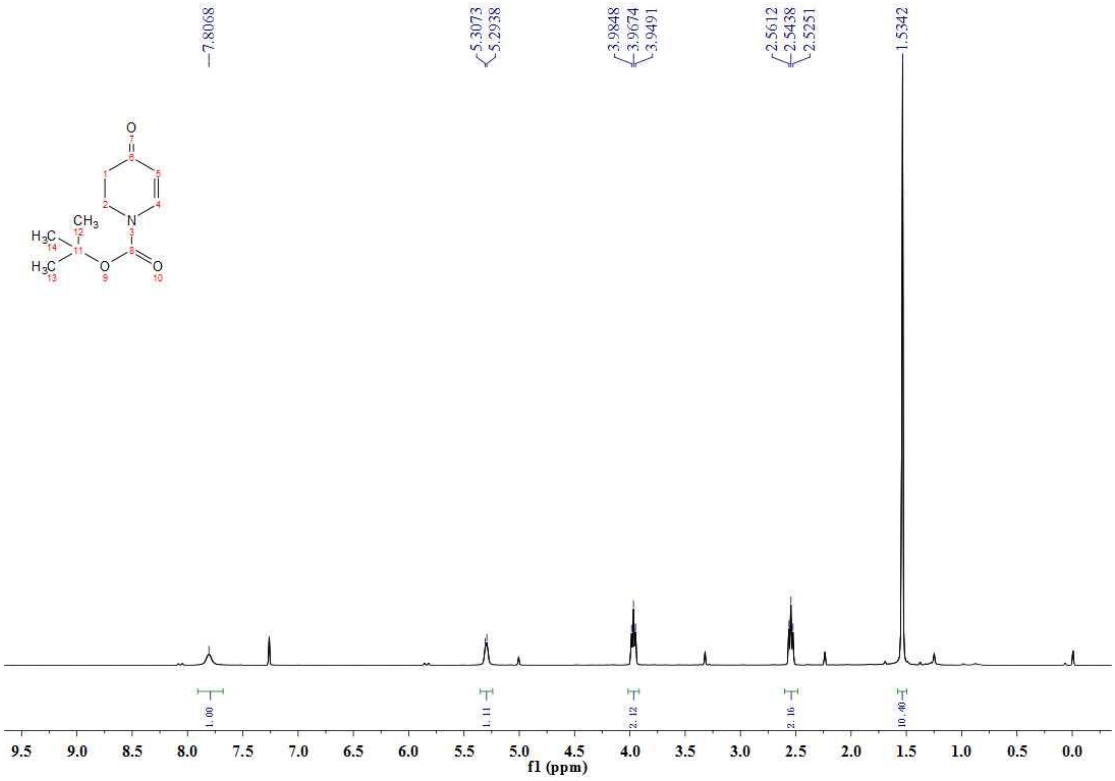
^{1}H NMR spectrum for **3z** ($CDCl_3$, 400 MHz)



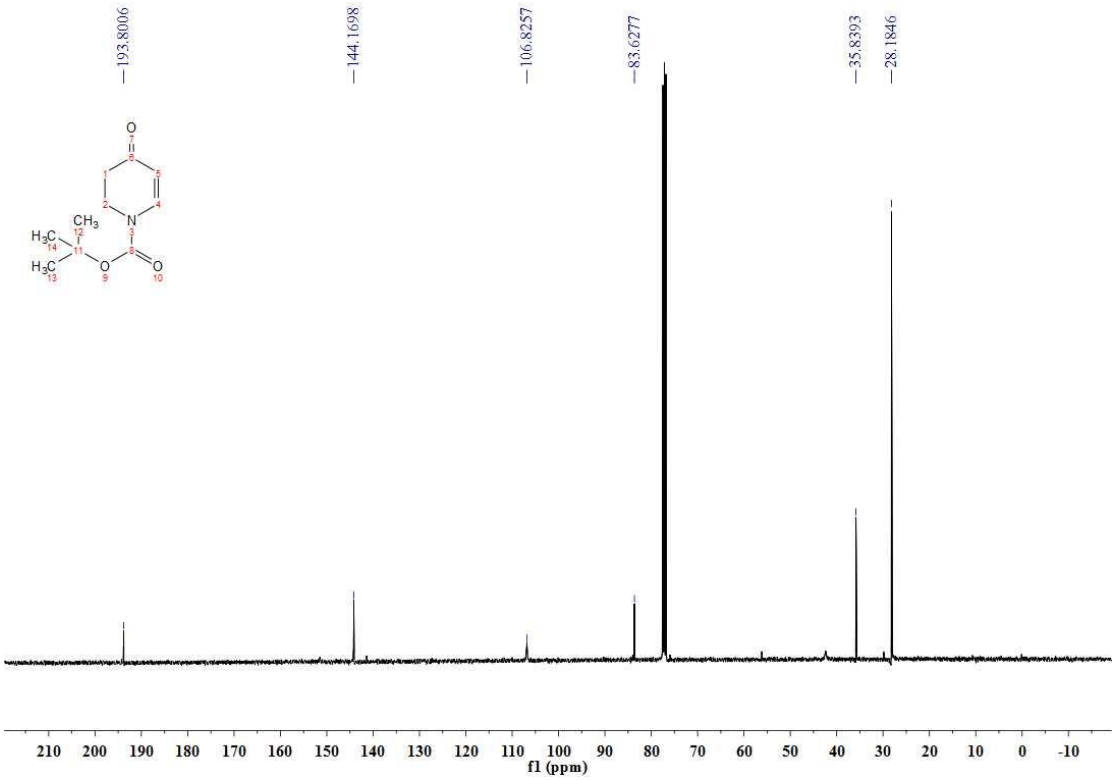
^{13}C NMR spectrum for **3z** ($CDCl_3$, 101 MHz)



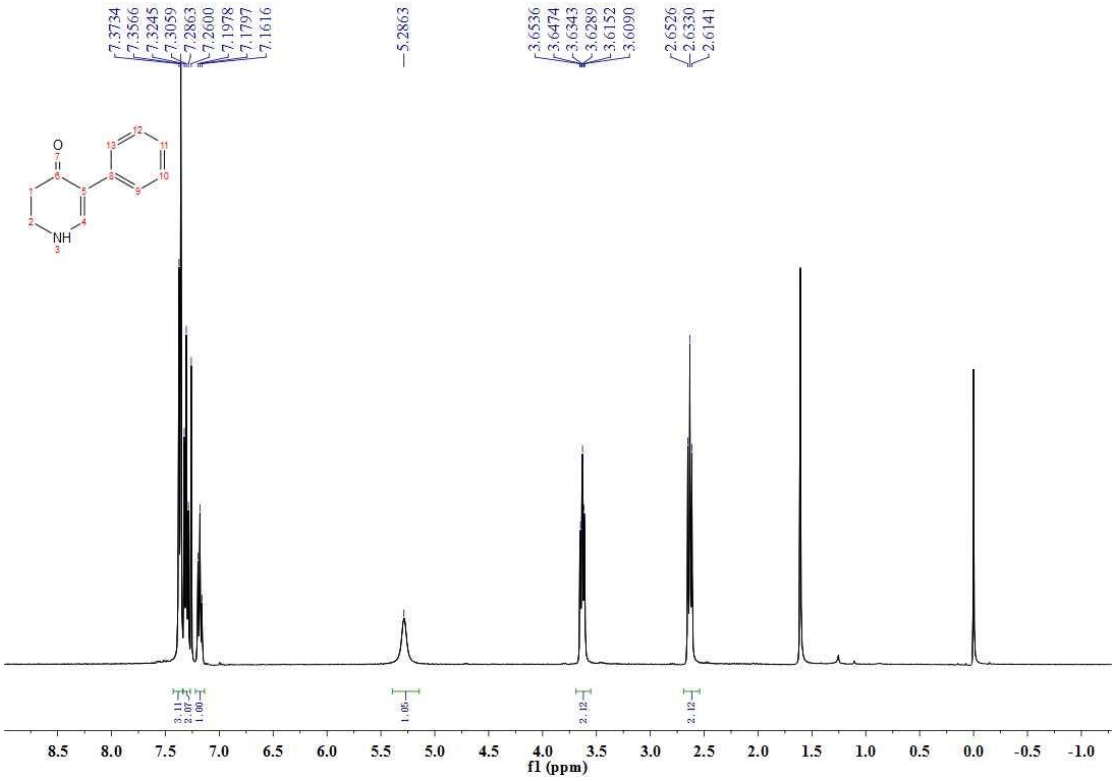
^{1}H NMR spectrum for **4a** ($CDCl_3$, 400 MHz)



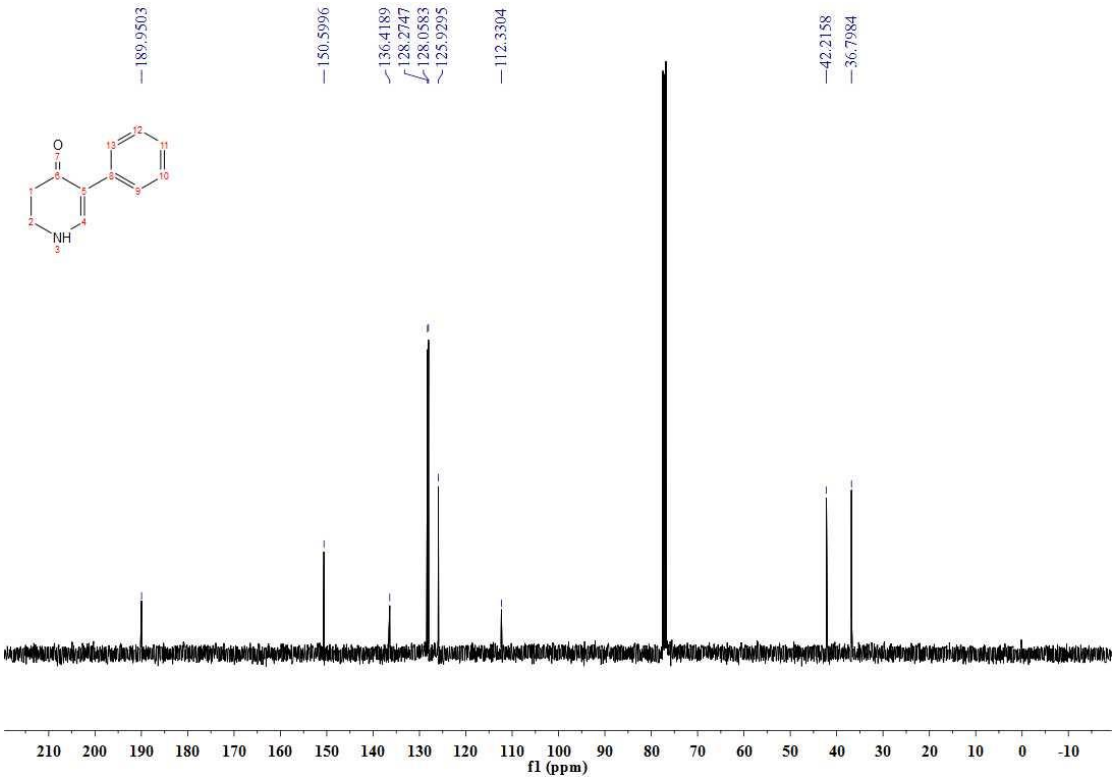
^{13}C NMR spectrum for **4a** ($CDCl_3$, 101 MHz)



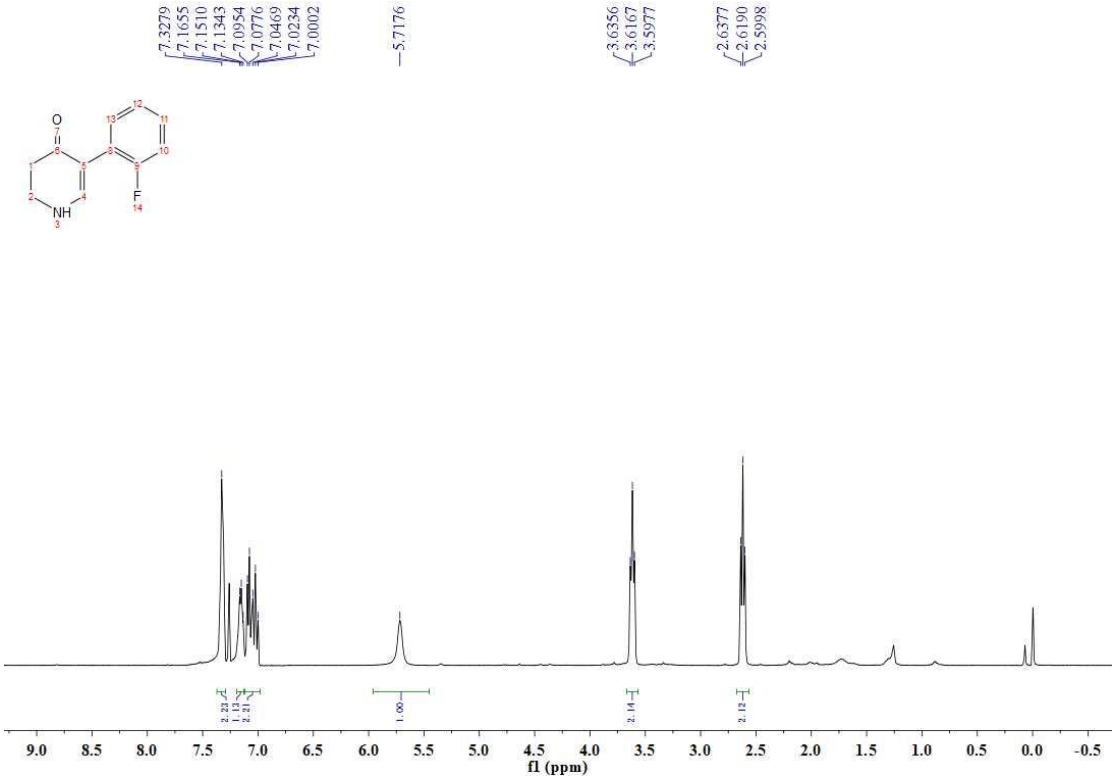
^{1}H NMR spectrum for **4b** ($CDCl_3$, 400 MHz)



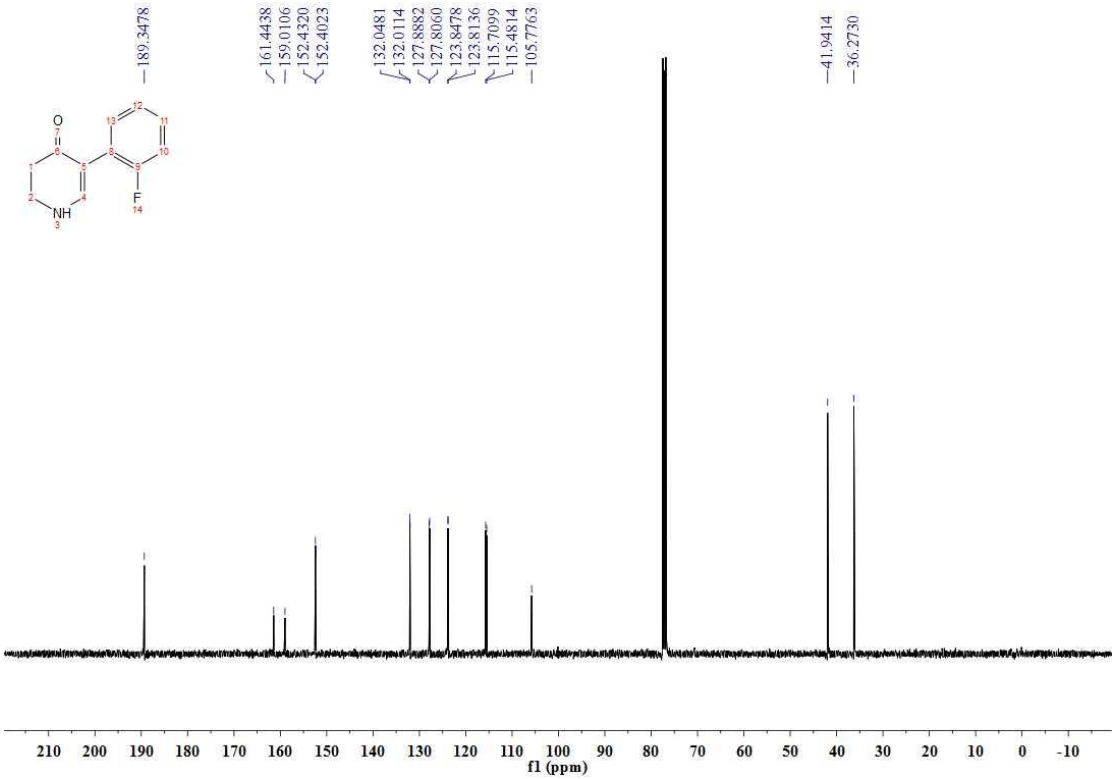
^{13}C NMR spectrum for **4b** ($CDCl_3$, 101 MHz)



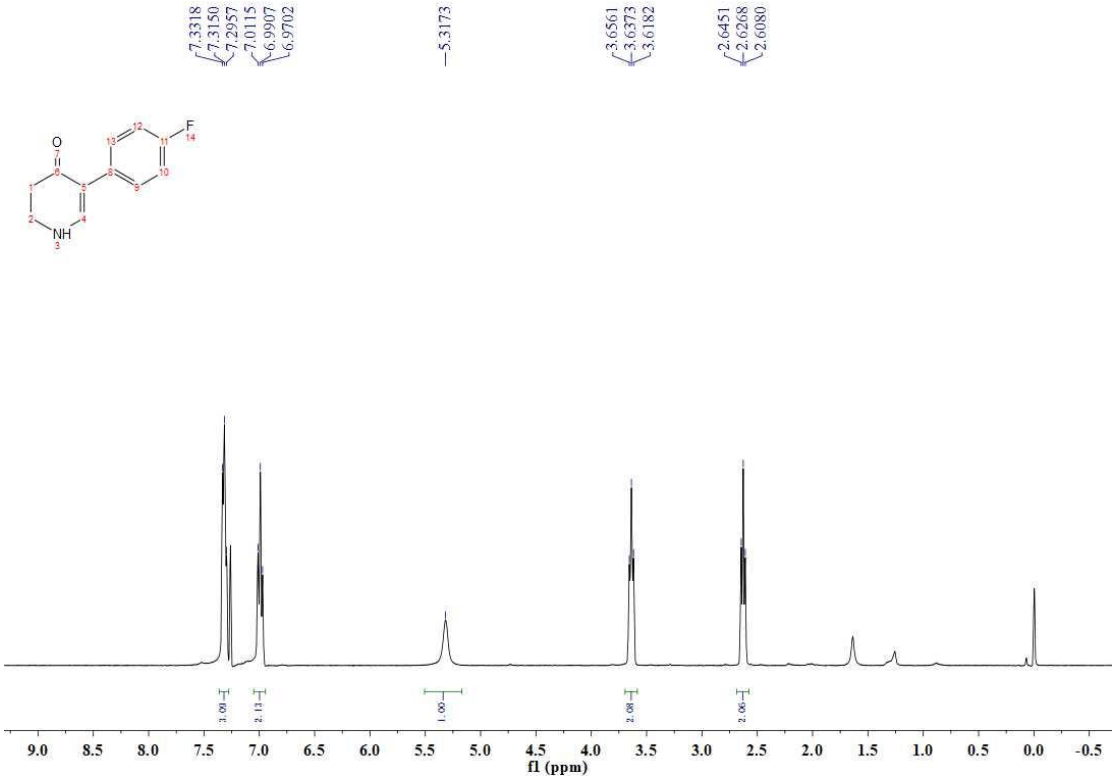
^{1}H NMR spectrum for **4c** ($CDCl_3$, 400 MHz)



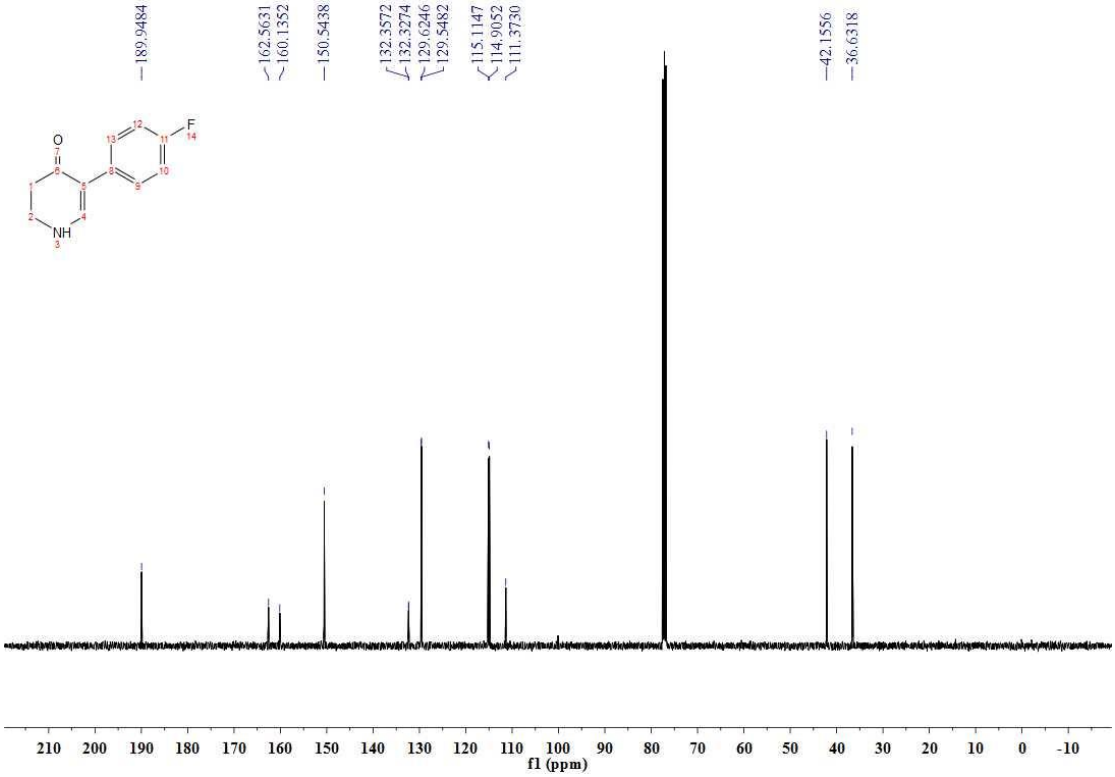
^{13}C NMR spectrum for **4c** ($CDCl_3$, 101 MHz)



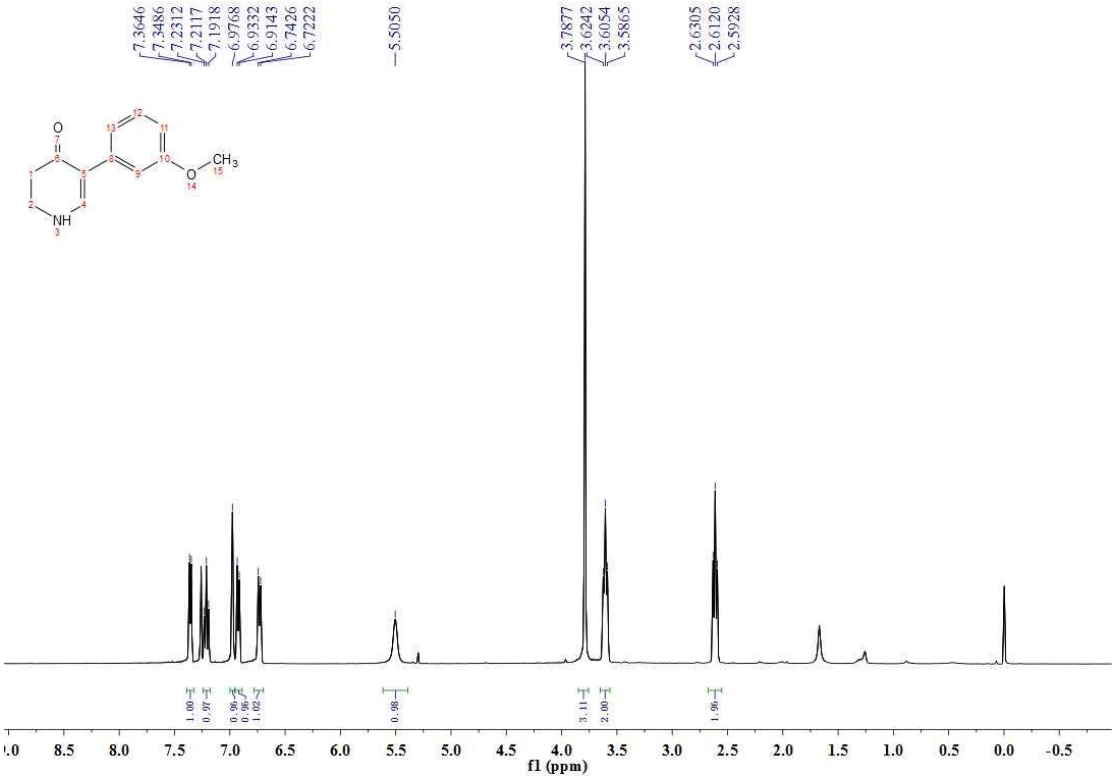
^{1}H NMR spectrum for **4d** ($CDCl_3$, 400 MHz)



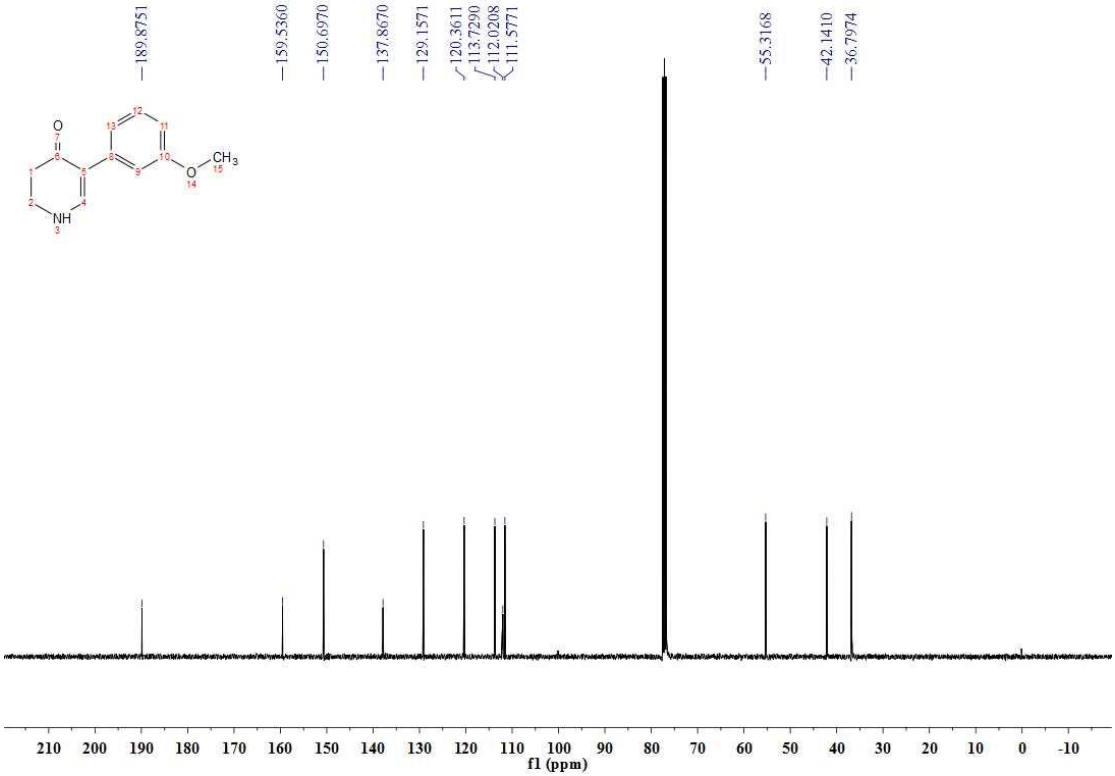
^{13}C NMR spectrum for **4d** ($CDCl_3$, 101 MHz)



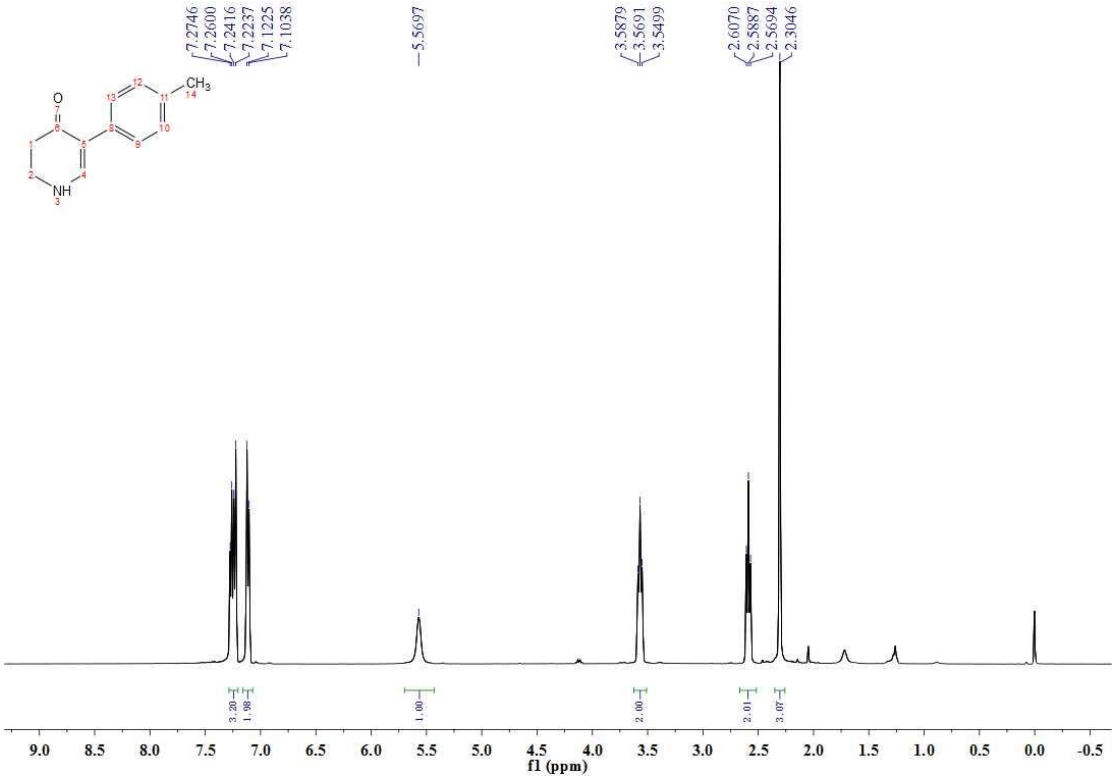
^{1}H NMR spectrum for **4e** ($CDCl_3$, 400 MHz)



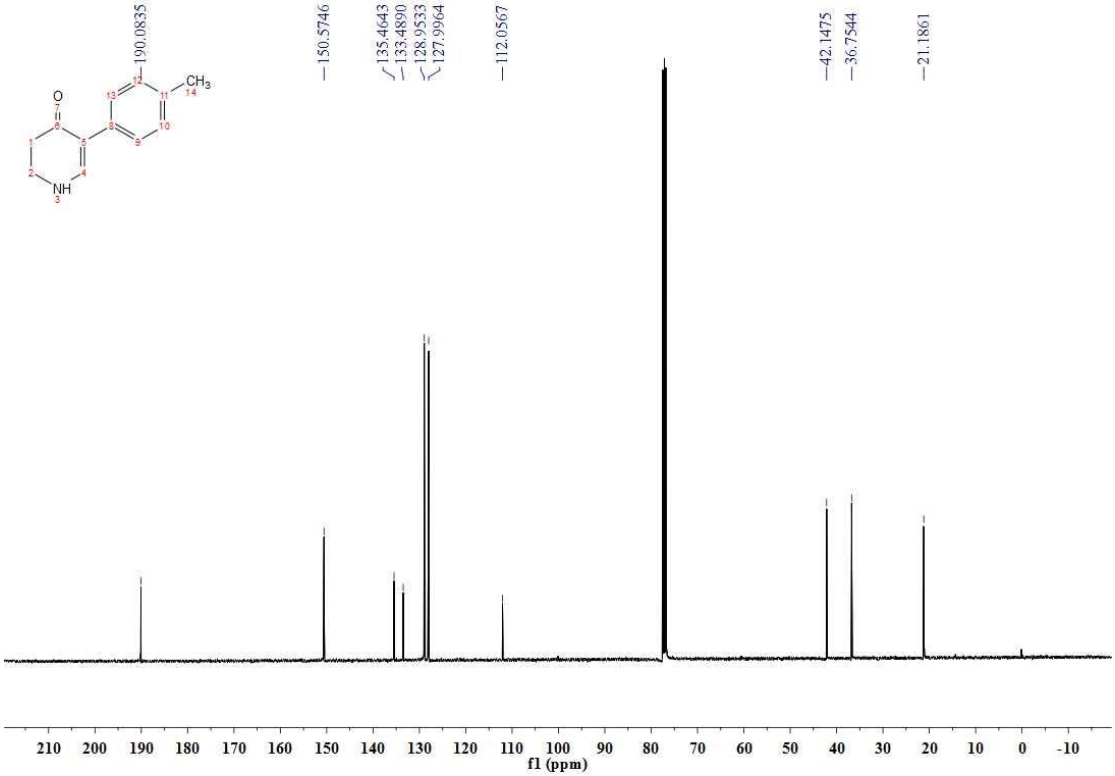
^{13}C NMR spectrum for **4e** ($CDCl_3$, 101 MHz)



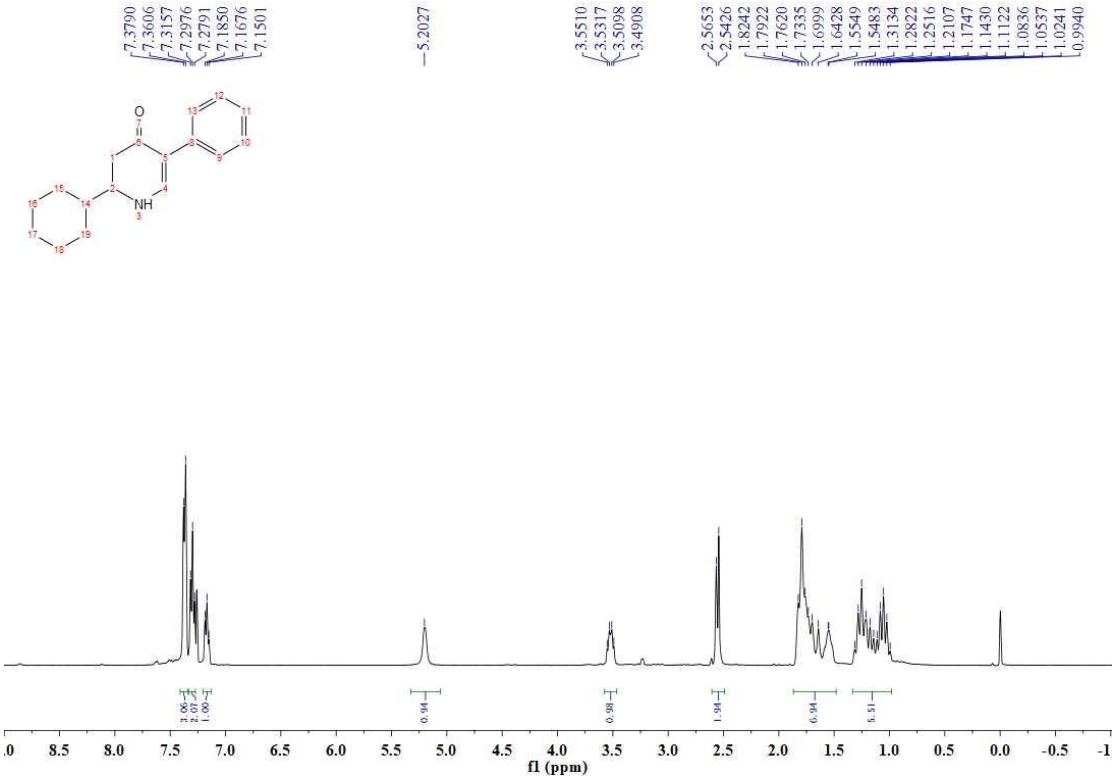
^{1}H NMR spectrum for **4f** ($CDCl_3$, 400 MHz)



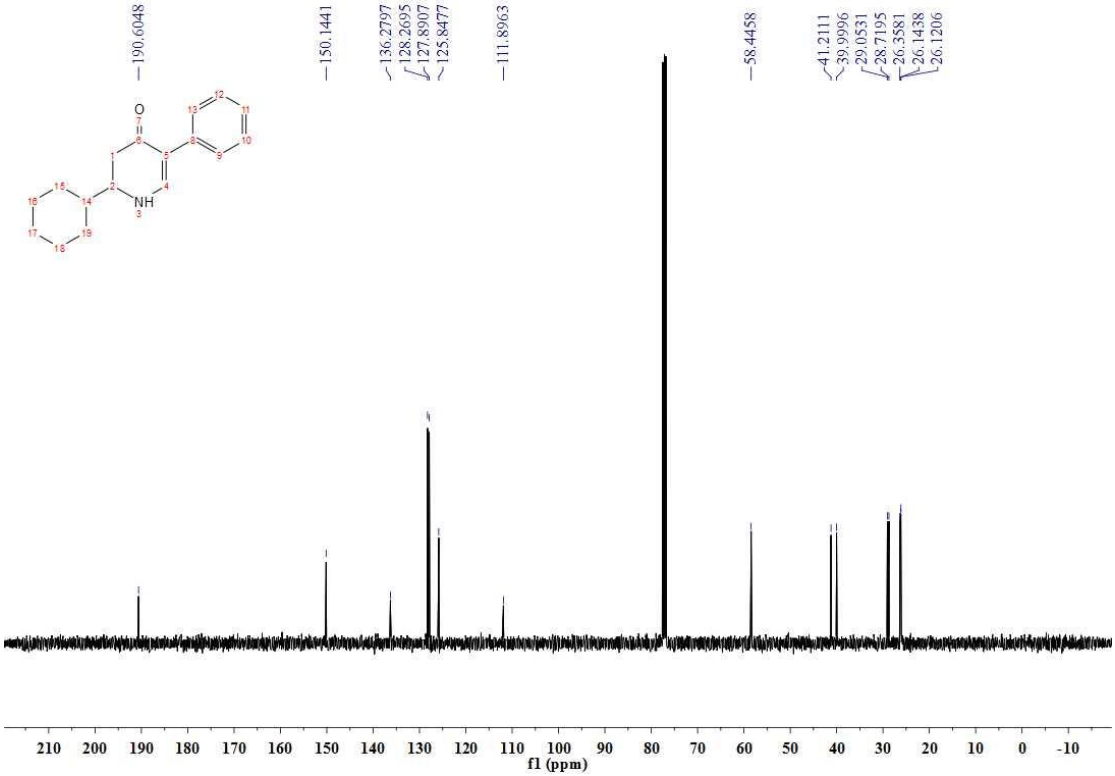
^{13}C NMR spectrum for **4f** ($CDCl_3$, 101 MHz)



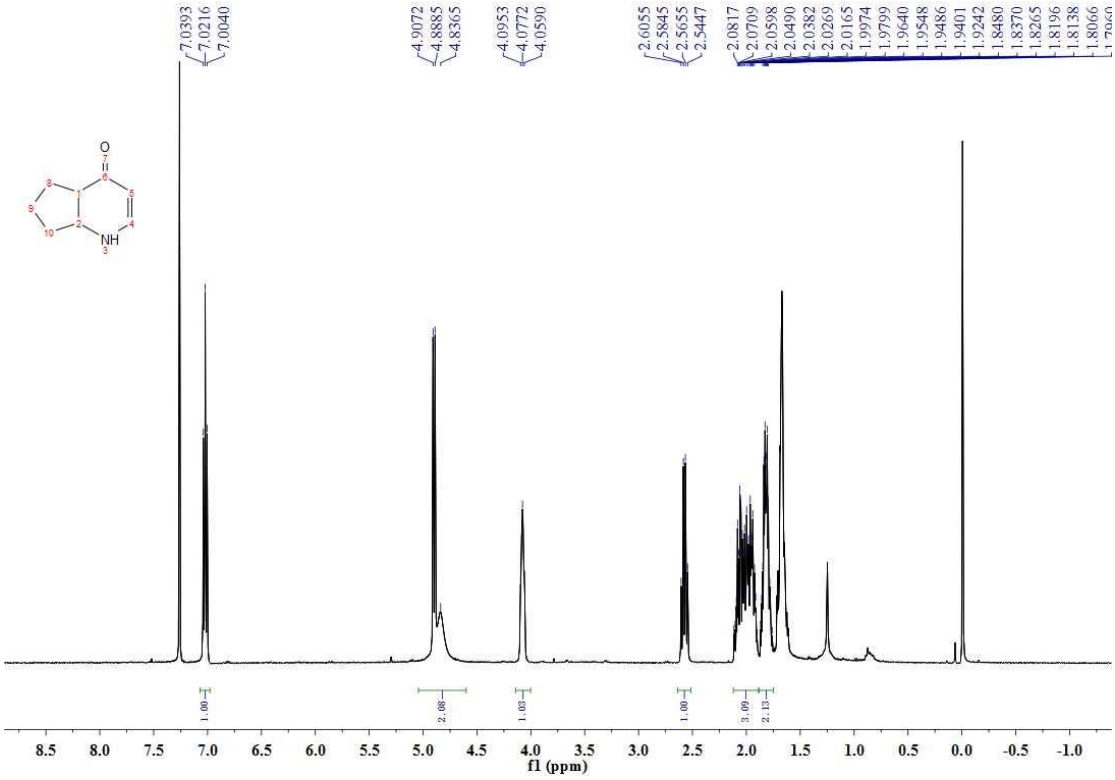
^{1}H NMR spectrum for **4g** (MeOD, 400 MHz)



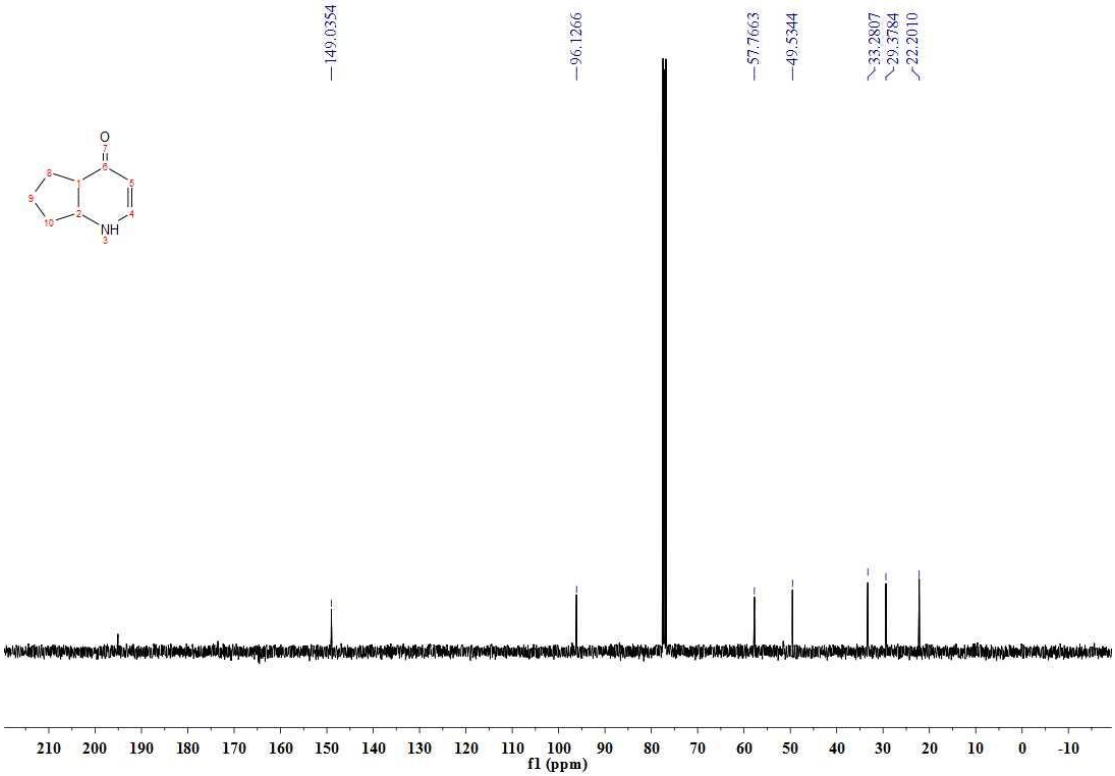
^{13}C NMR spectrum for **4g** ($CDCl_3$, 101 MHz)



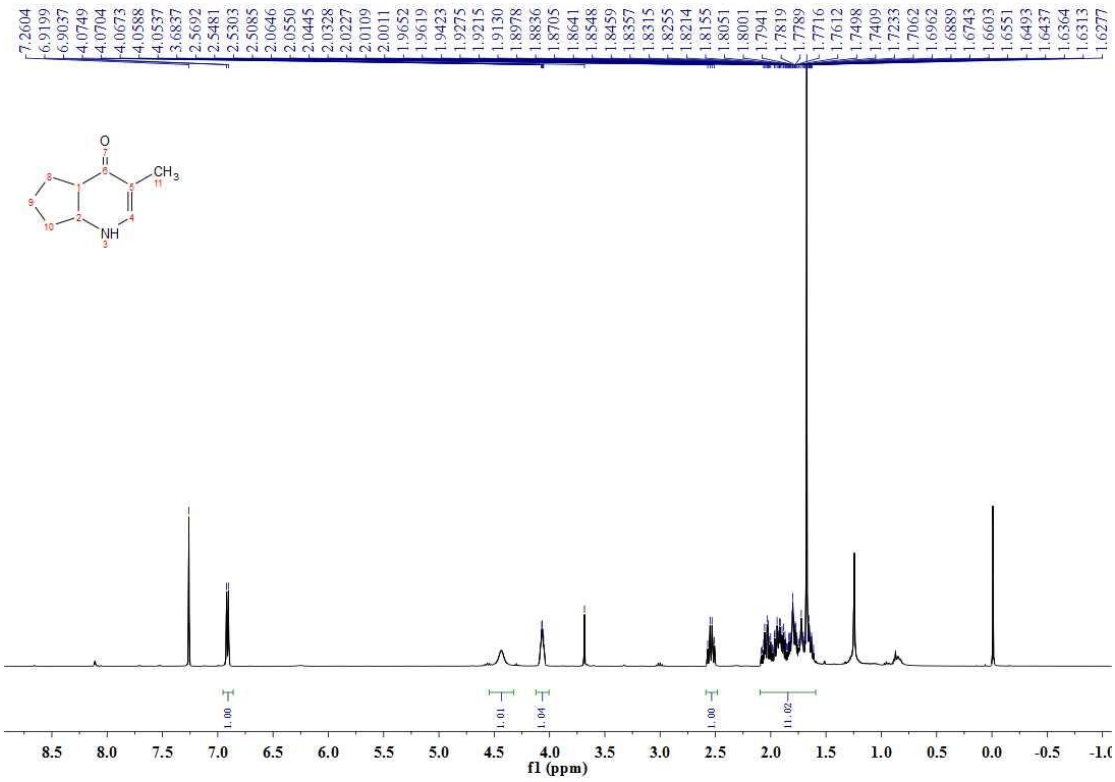
^{1}H NMR spectrum for **4h** ($CDCl_3$, 400 MHz)



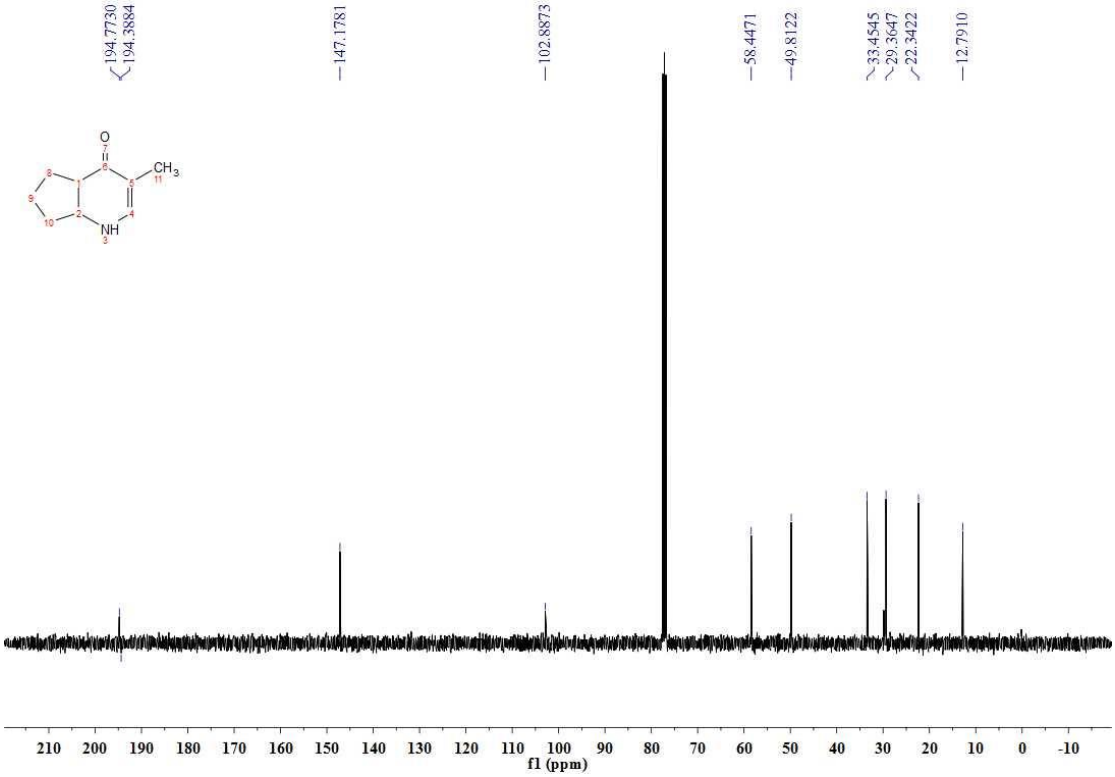
^{13}C NMR spectrum for **4h** ($CDCl_3$, 101 MHz)



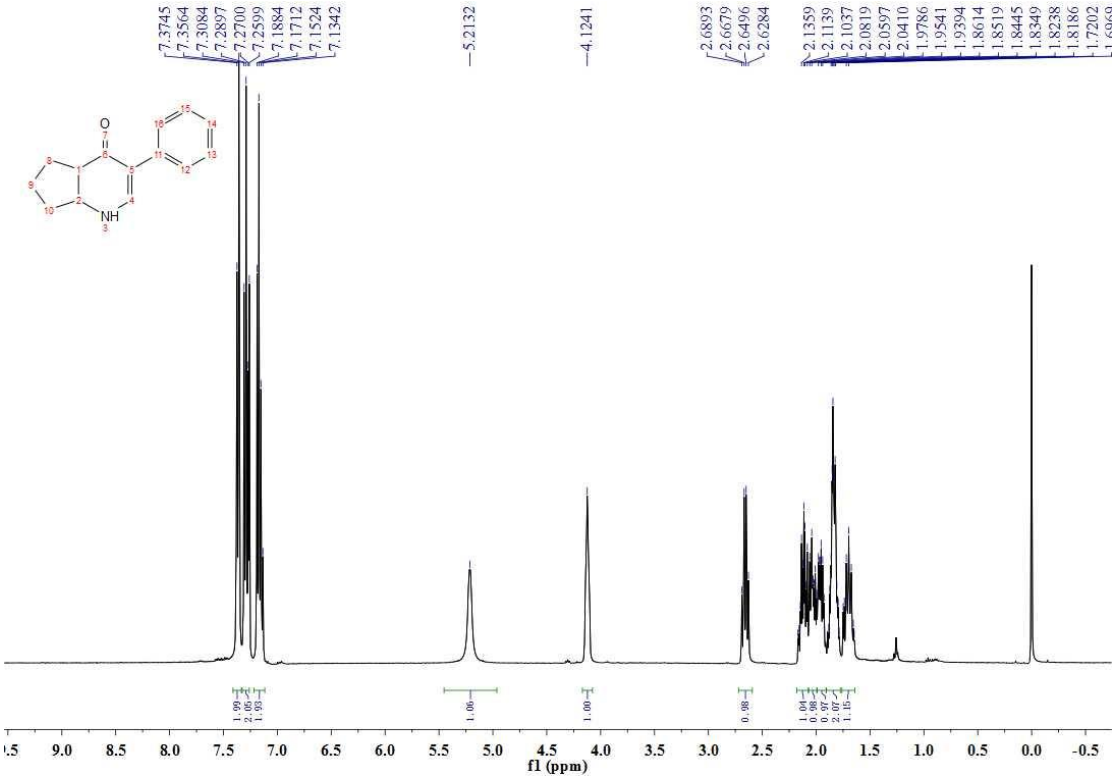
^{1}H NMR spectrum for **4i** ($CDCl_3$, 400 MHz)



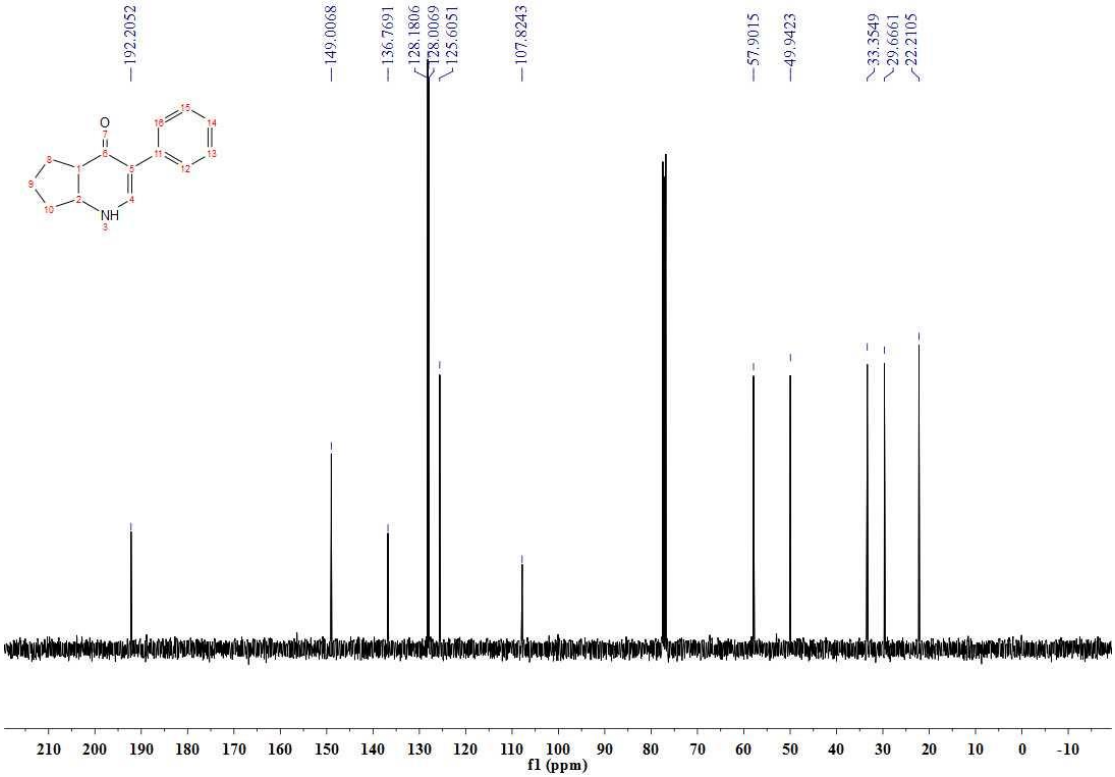
^{13}C NMR spectrum for **4i** ($CDCl_3$, 101 MHz)



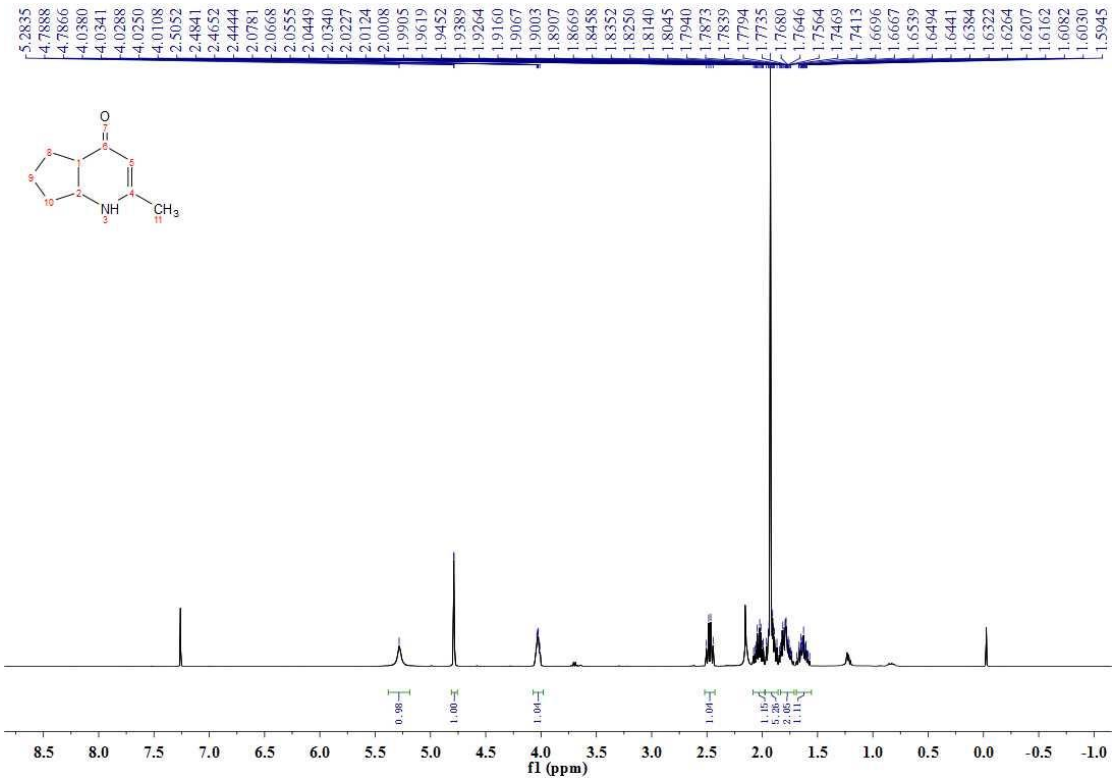
^{1}H NMR spectrum for **4j** ($CDCl_3$, 400 MHz)



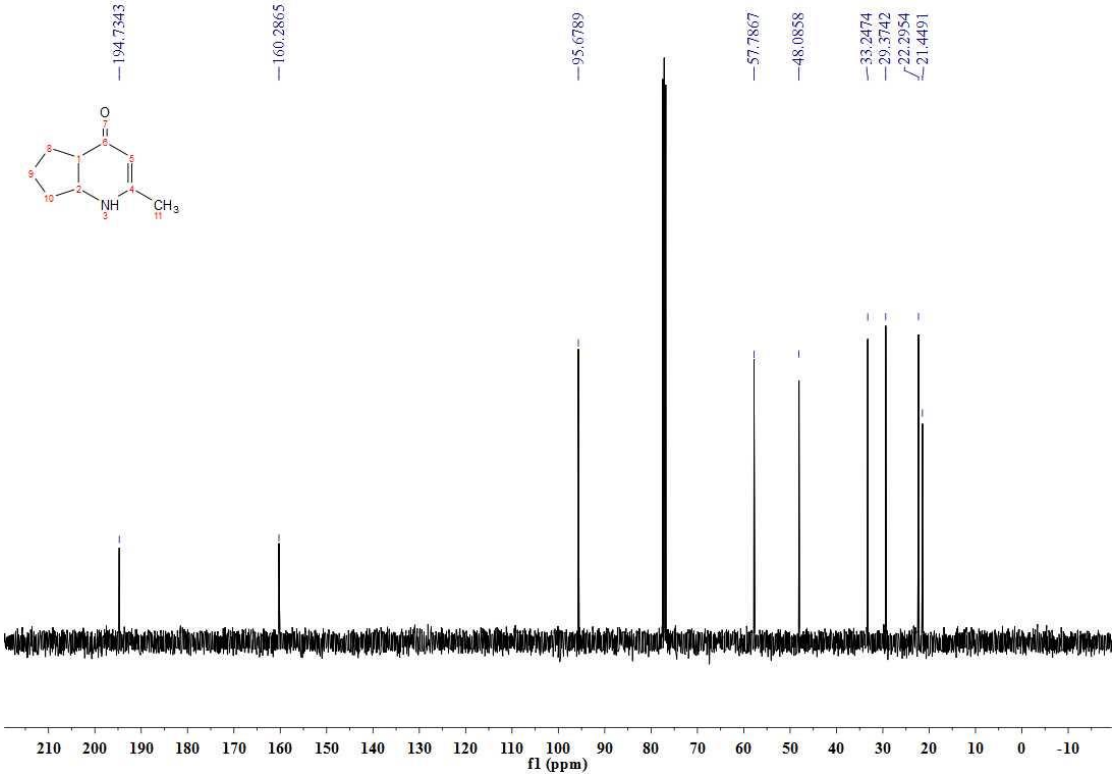
^{13}C NMR spectrum for **4j** ($CDCl_3$, 101 MHz)



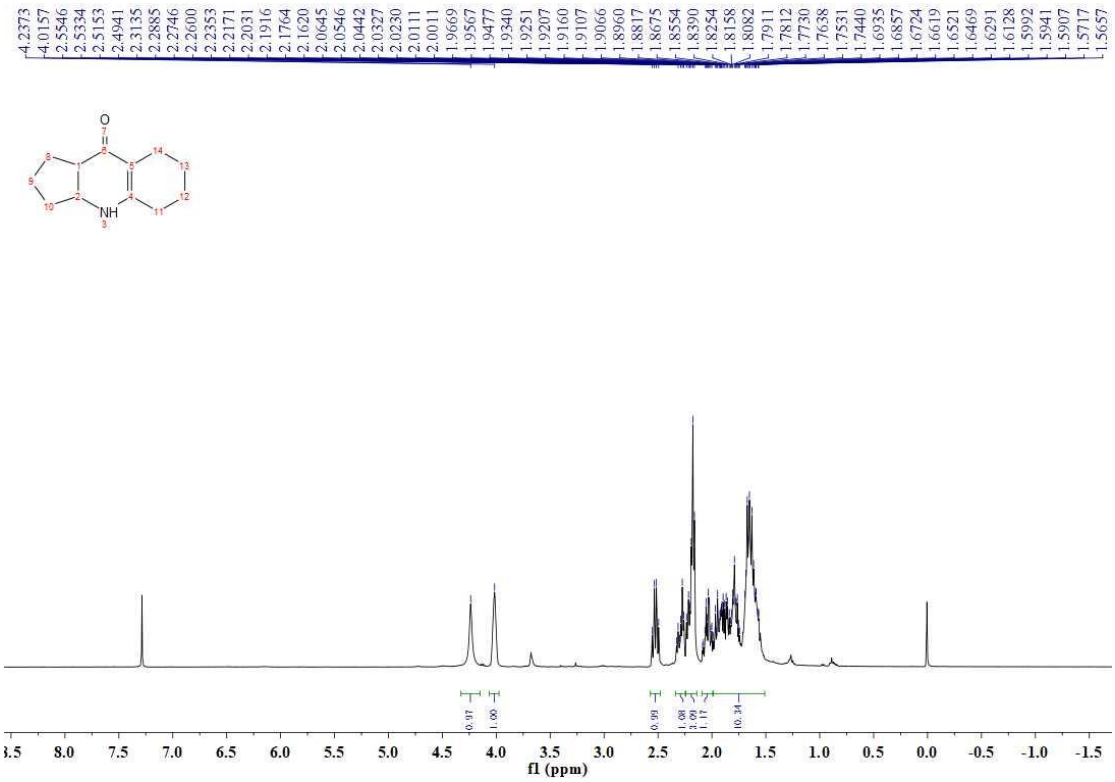
^{1}H NMR spectrum for **4k** ($CDCl_3$, 400 MHz)



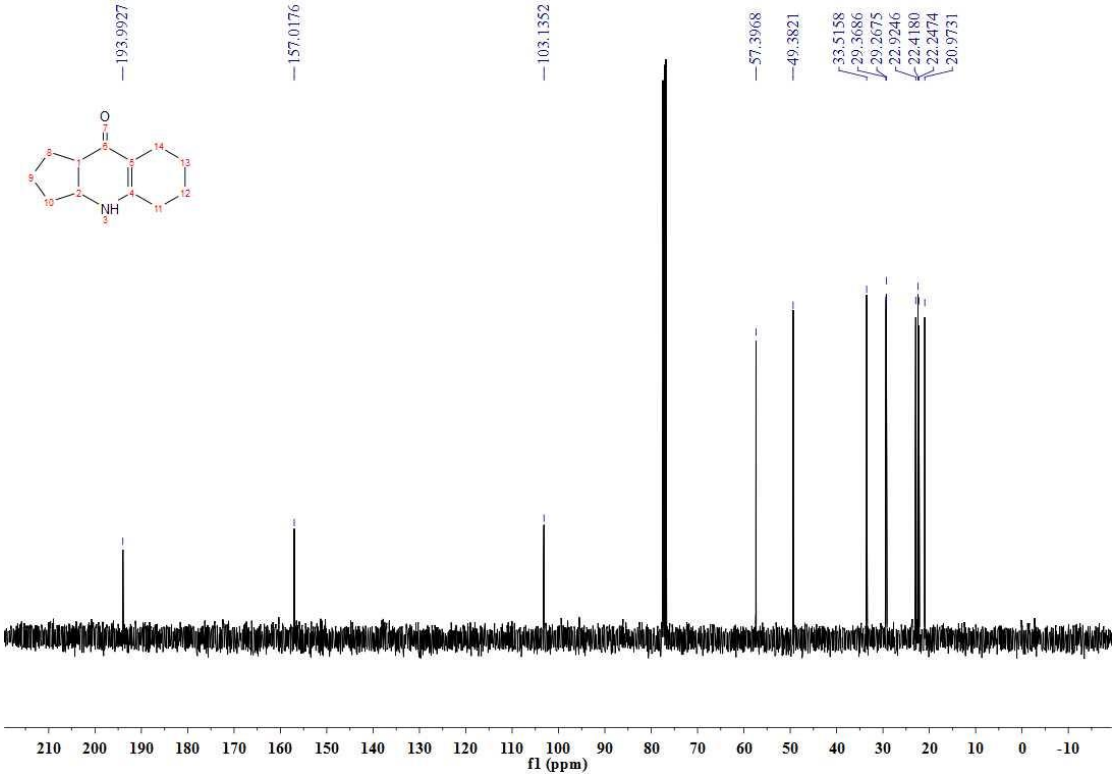
^{13}C NMR spectrum for **4k** ($CDCl_3$, 101 MHz)



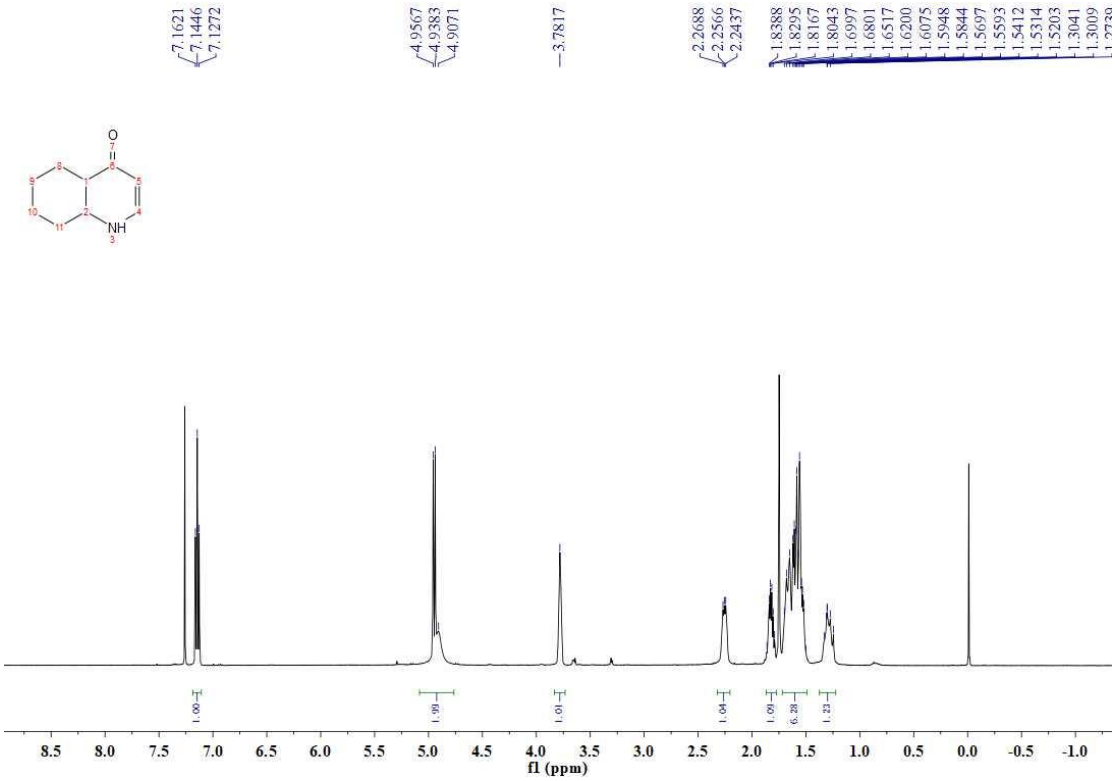
^{1}H NMR spectrum for **4l** ($CDCl_3$, 400 MHz)



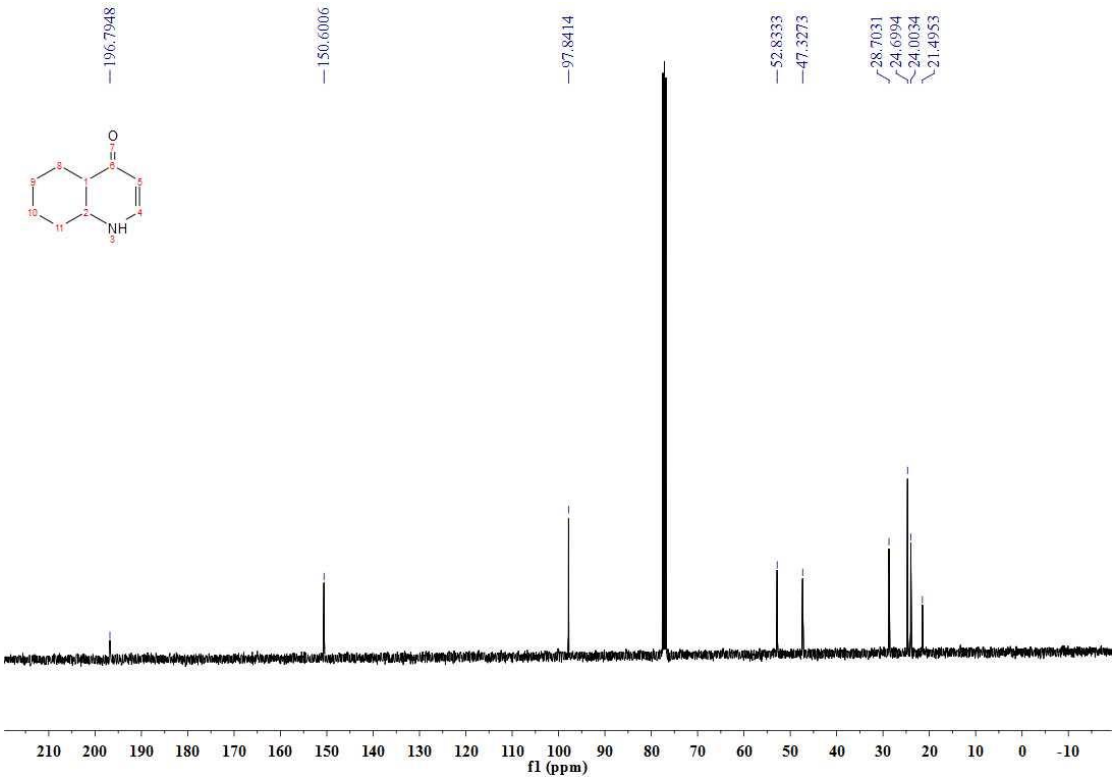
^{13}C NMR spectrum for **4l** ($CDCl_3$, 101 MHz)



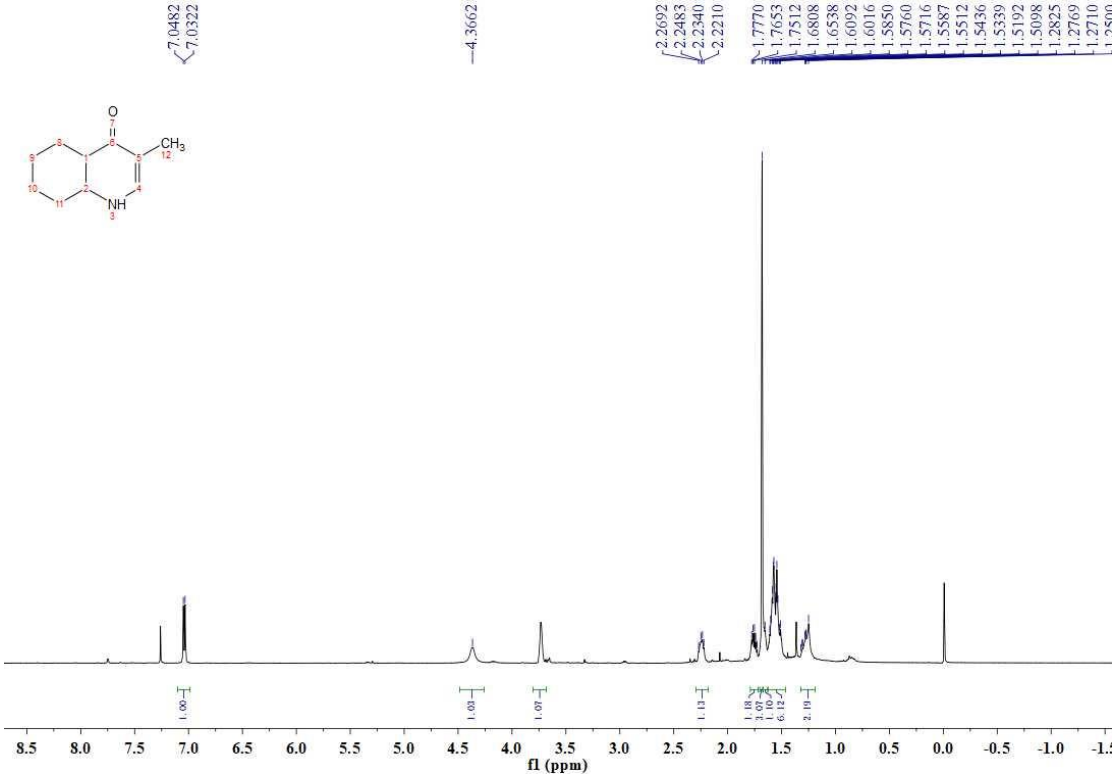
^{1}H NMR spectrum for **4m** ($CDCl_3$, 400 MHz)



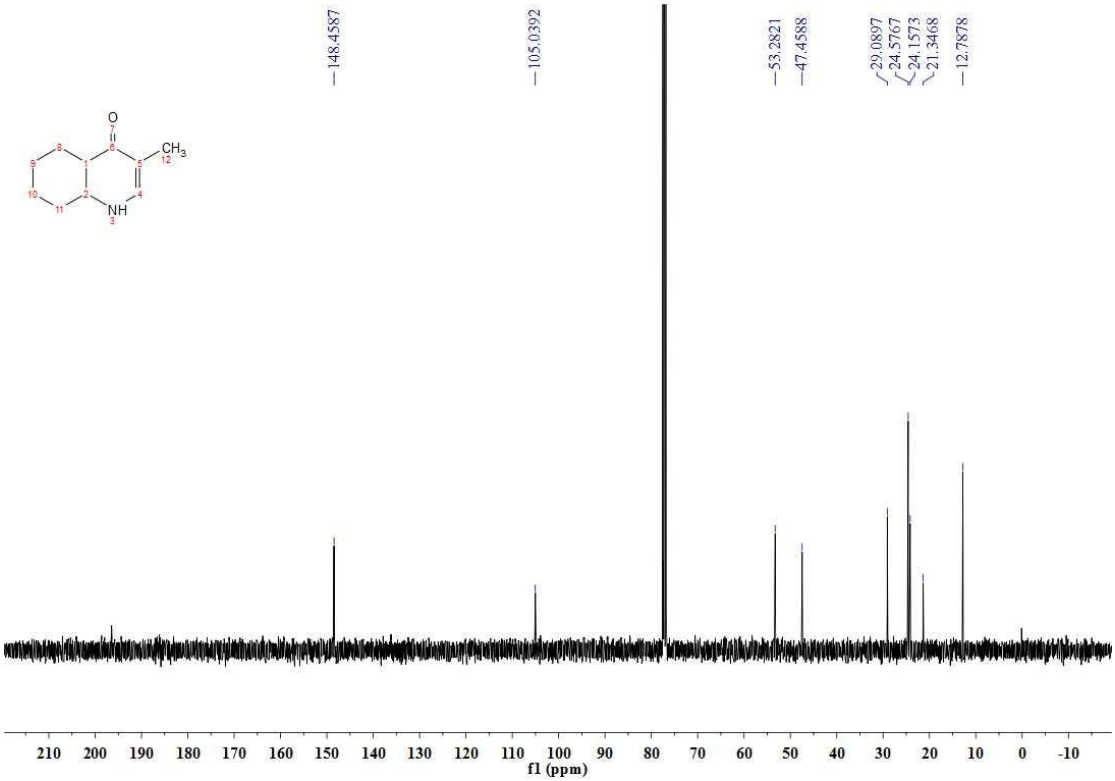
^{13}C NMR spectrum for **4m** ($CDCl_3$, 101 MHz)



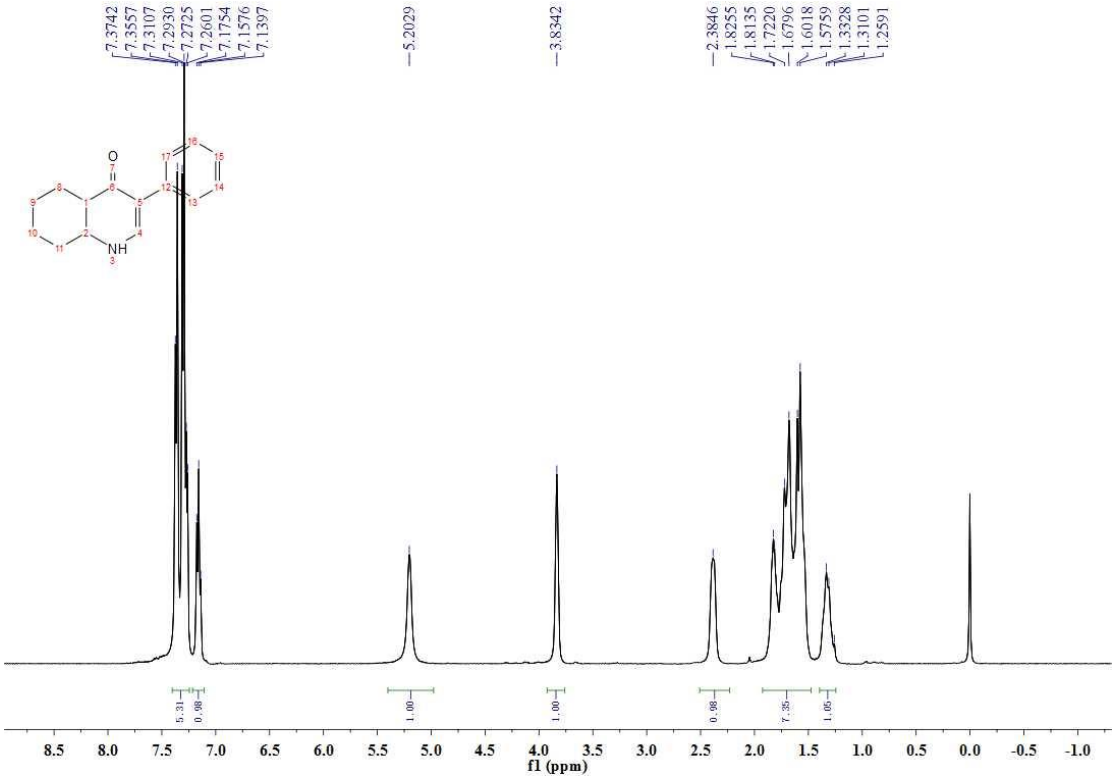
^{1}H NMR spectrum for **4n** ($CDCl_3$, 400 MHz)



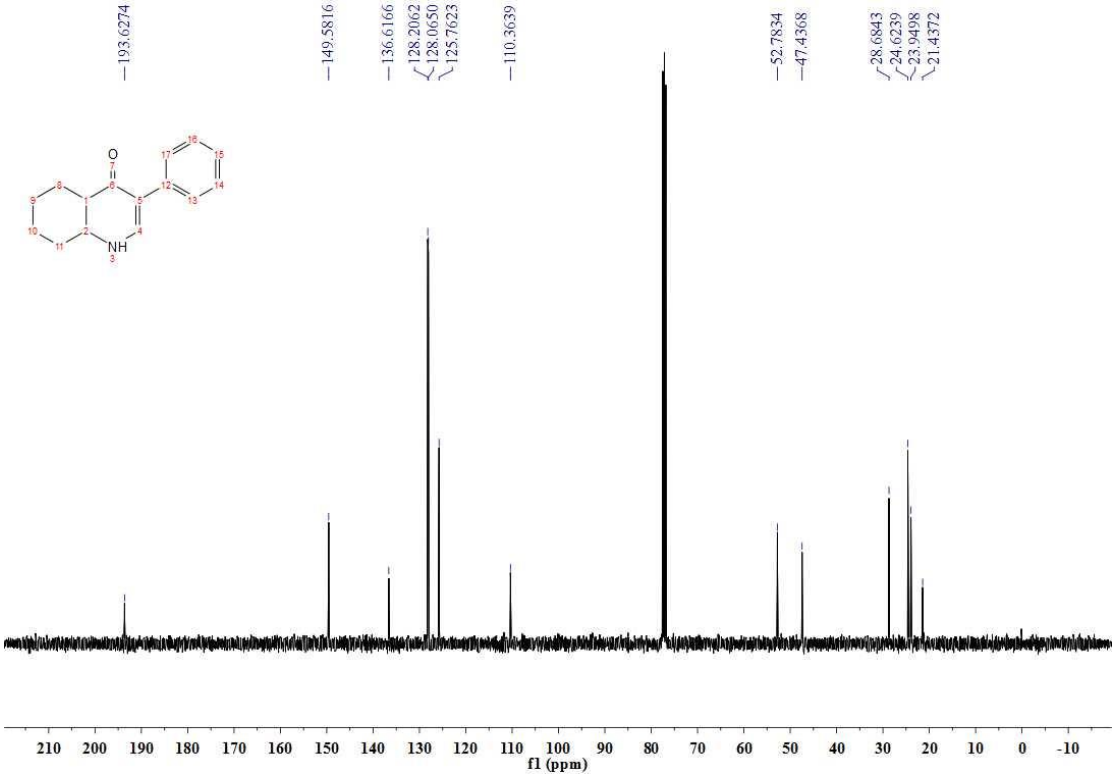
^{13}C NMR spectrum for **4n** ($CDCl_3$, 101 MHz)



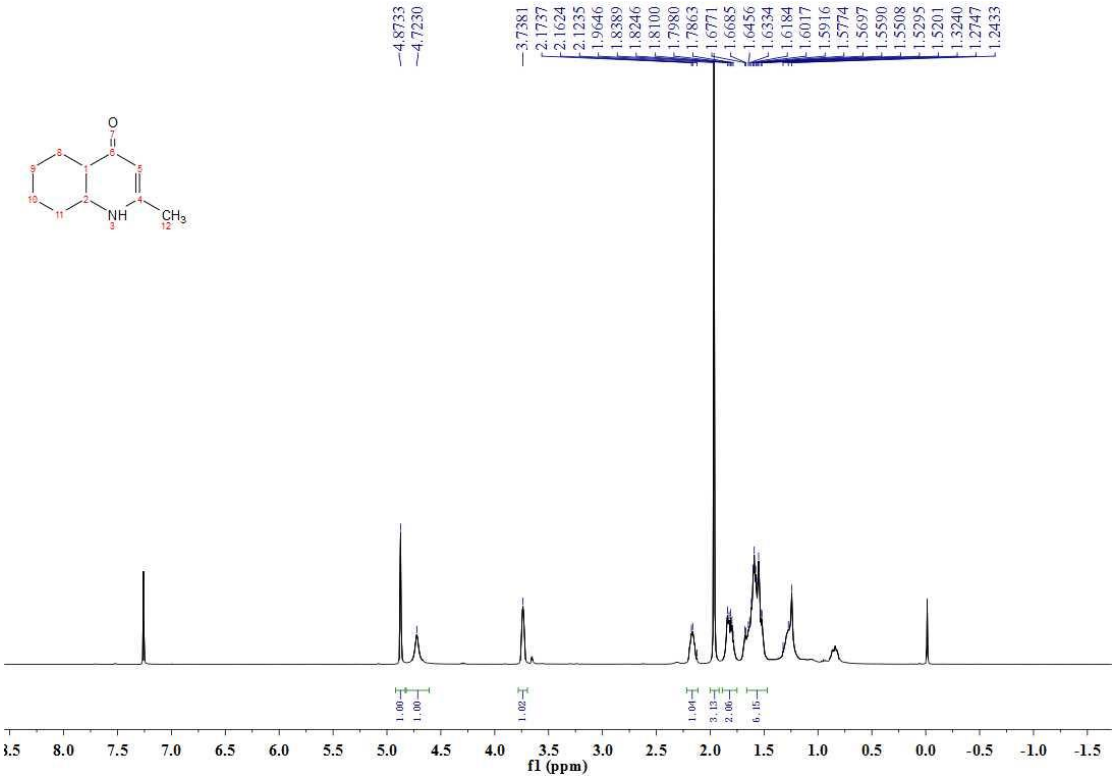
^{1}H NMR spectrum for **4o** ($CDCl_3$, 400 MHz)



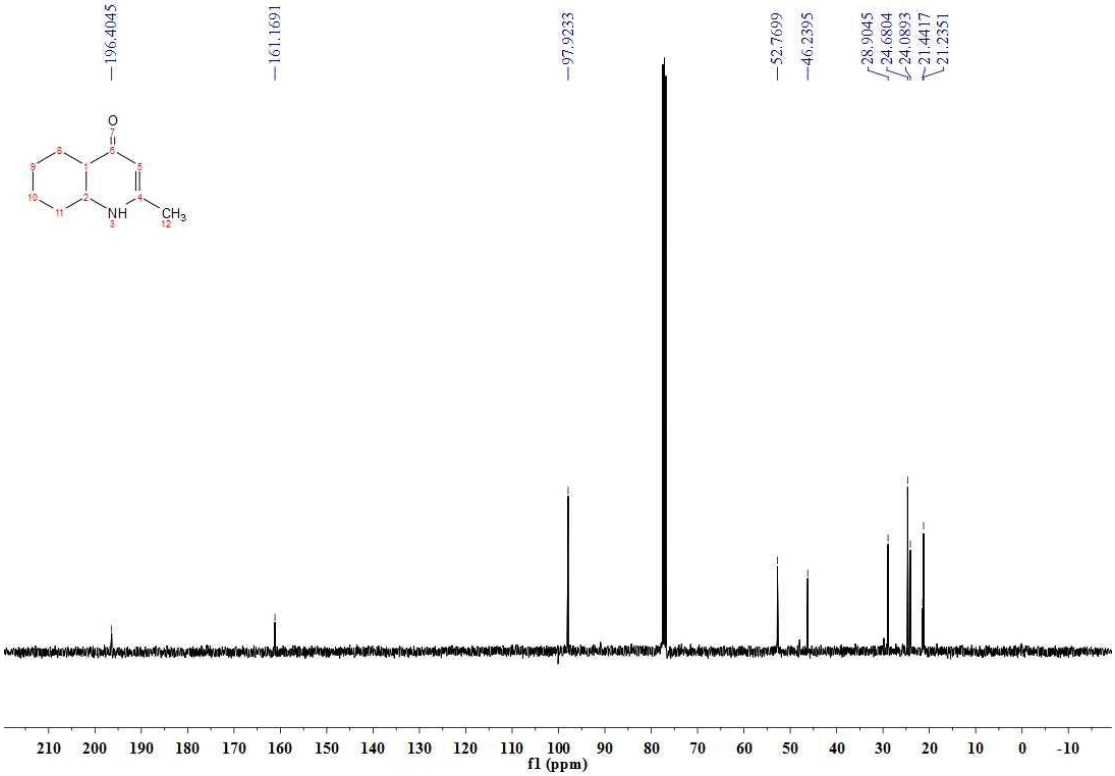
^{13}C NMR spectrum for **4o** ($CDCl_3$, 101 MHz)



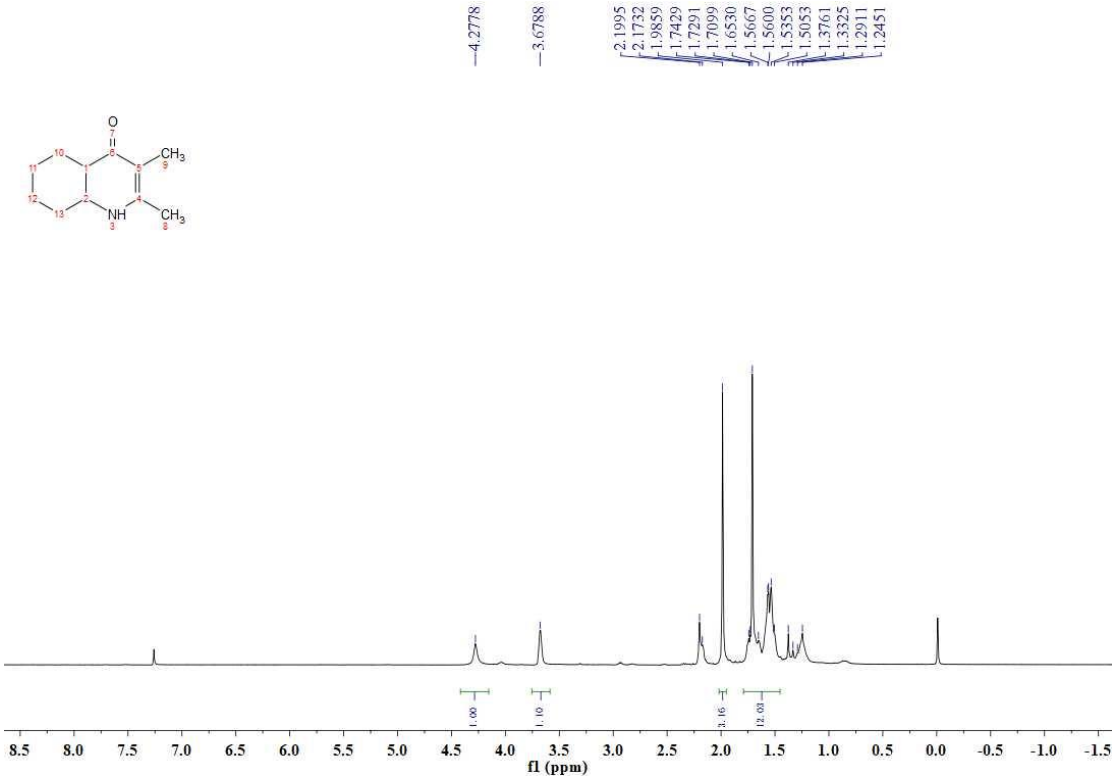
^{1}H NMR spectrum for **4p** ($CDCl_3$, 400 MHz)



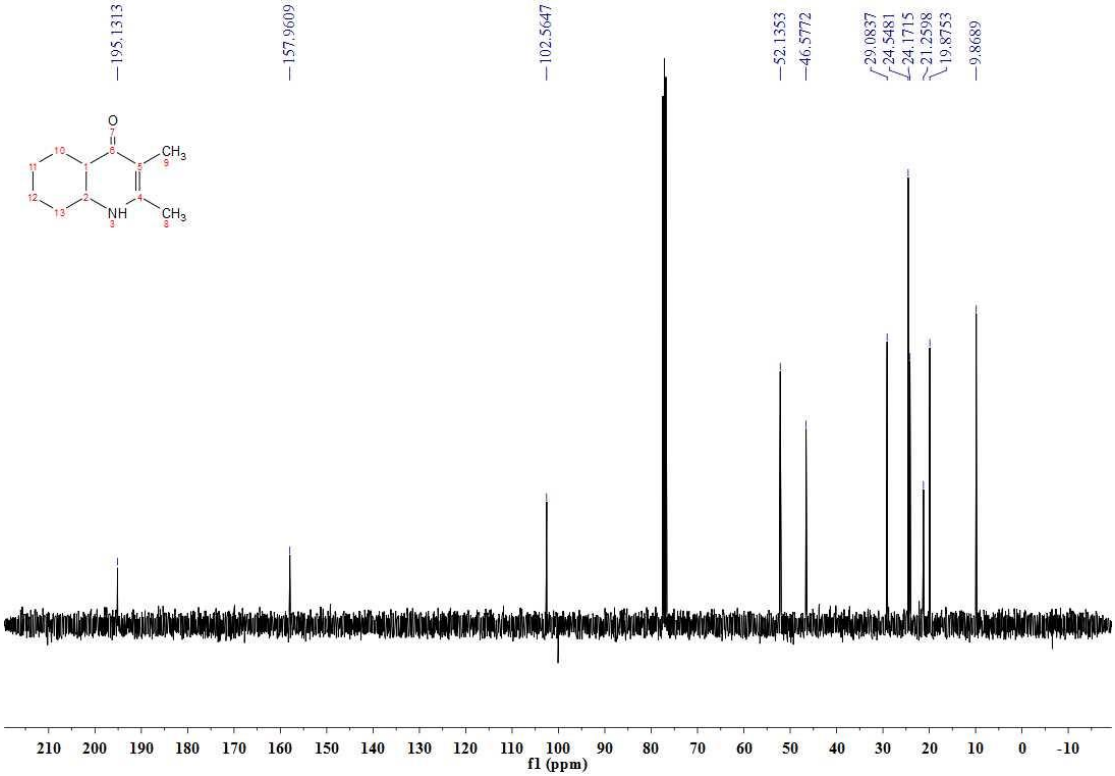
^{13}C NMR spectrum for **4p** ($CDCl_3$, 101 MHz)



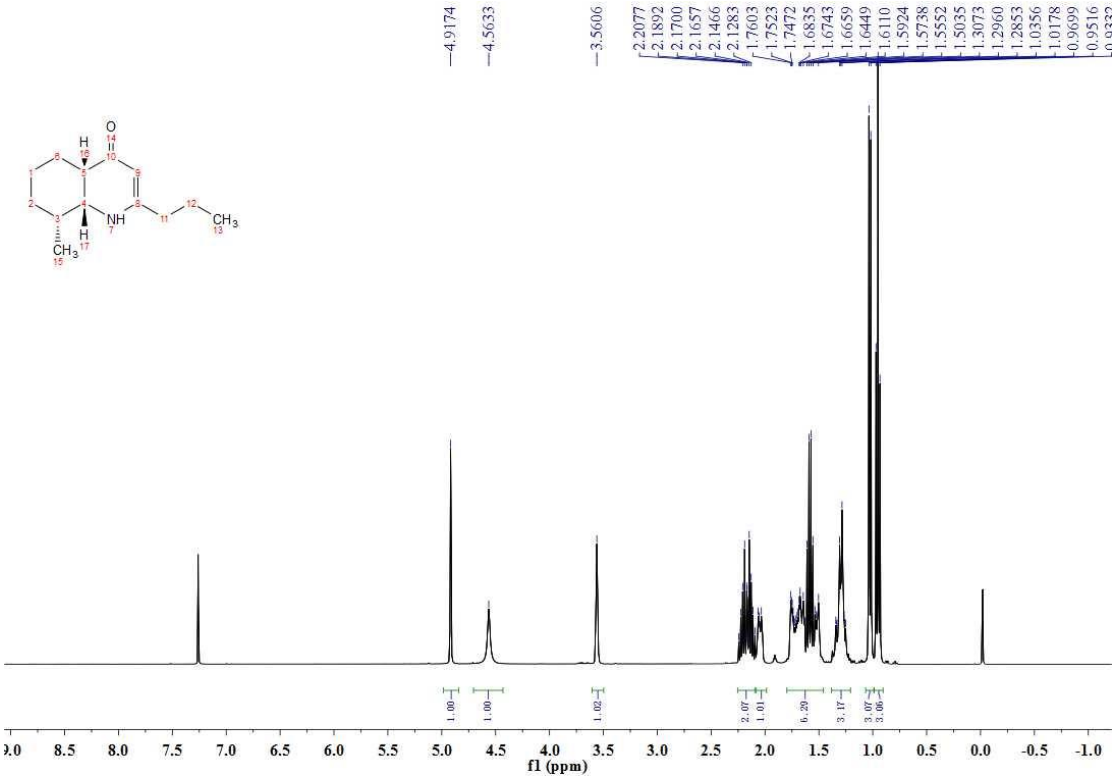
^{1}H NMR spectrum for **4q** ($CDCl_3$, 400 MHz)



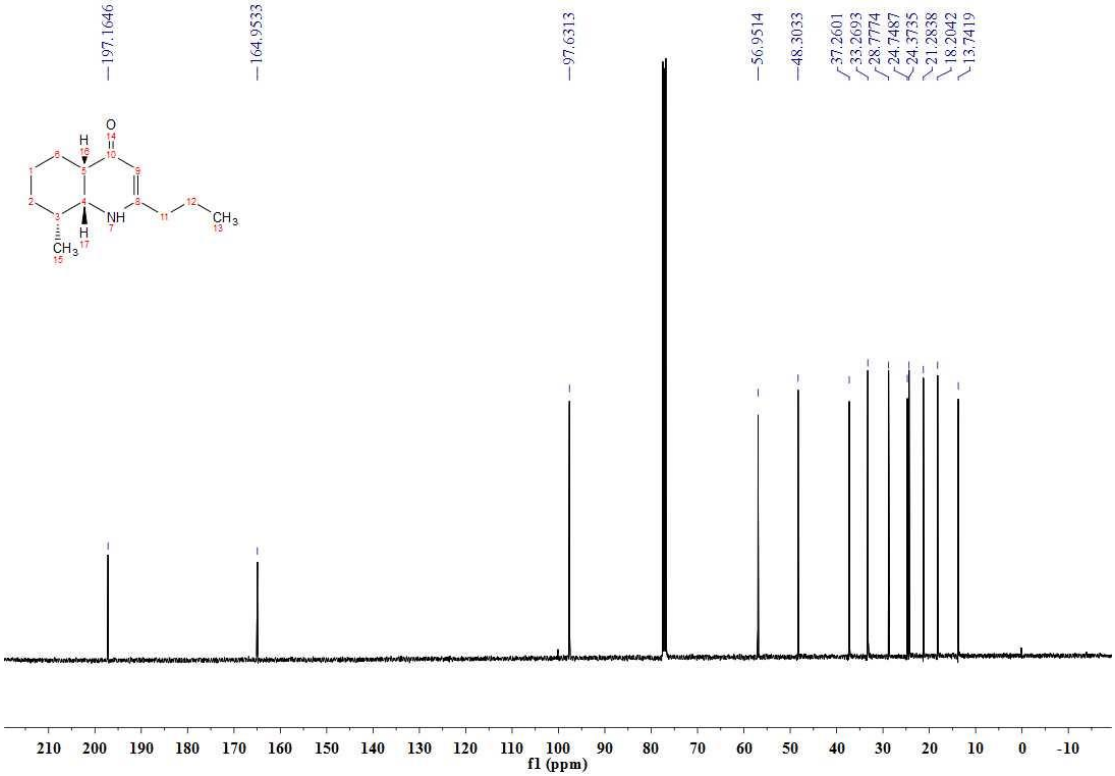
^{13}C NMR spectrum for **4q** ($CDCl_3$, 101 MHz)



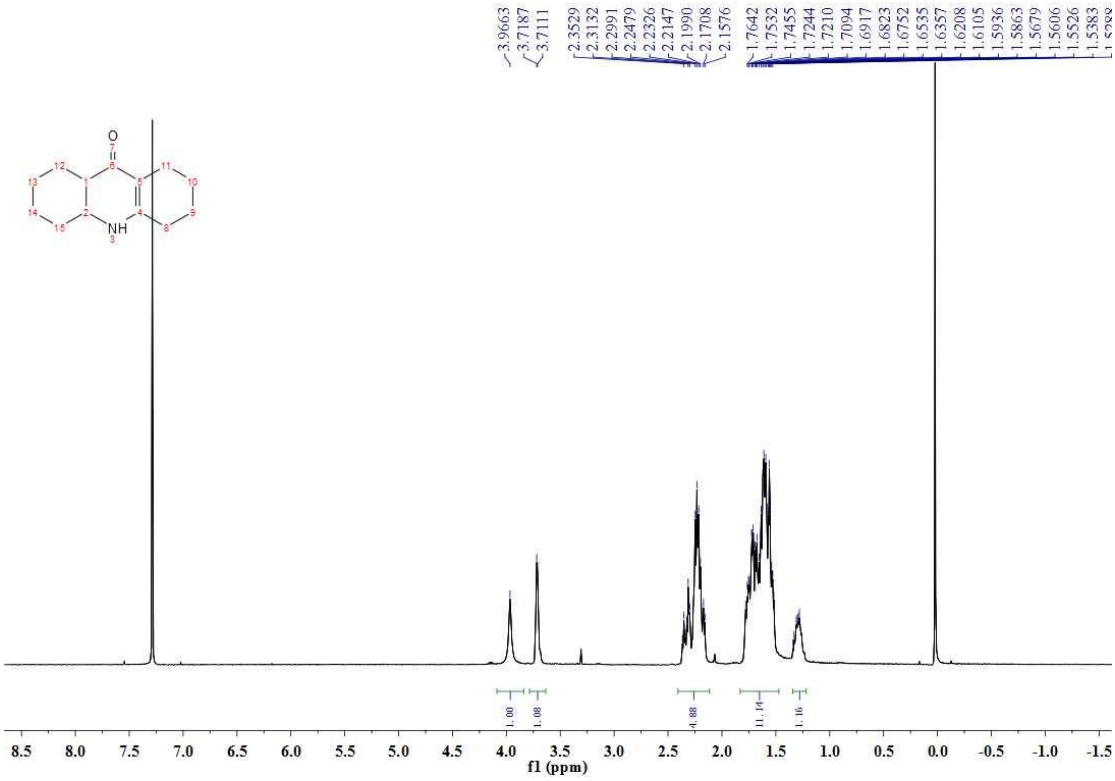
^{1}H NMR spectrum for **4r** ($CDCl_3$, 400 MHz)



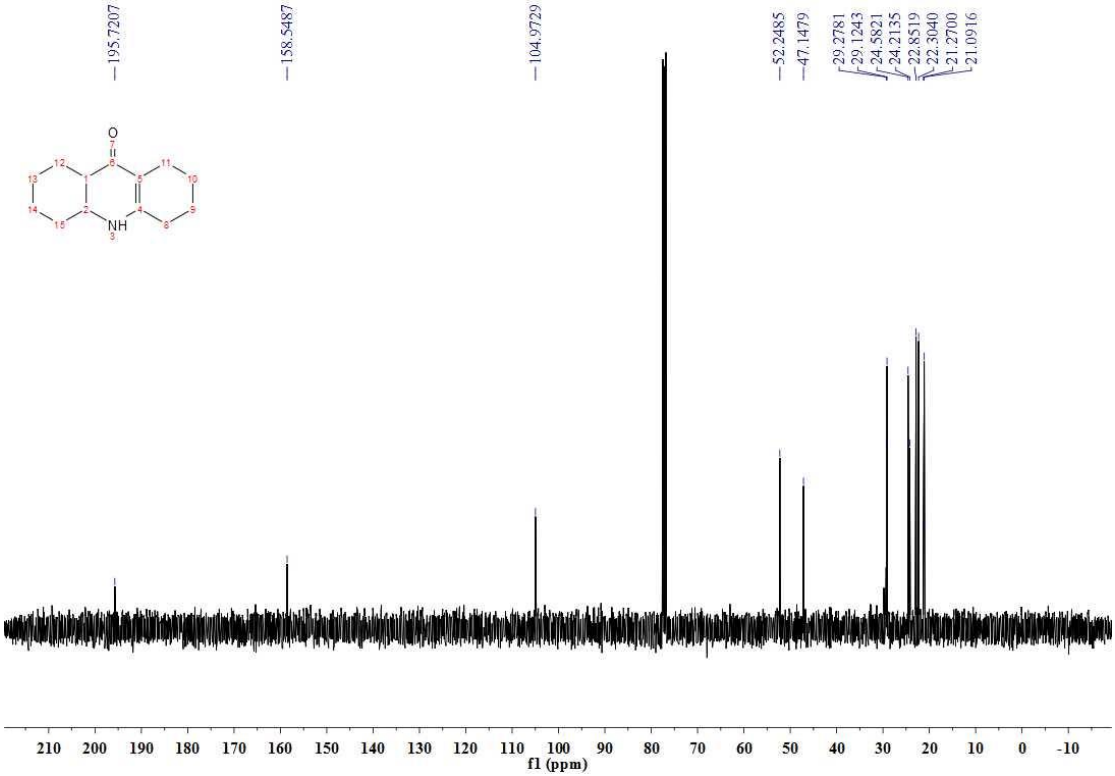
^{13}C NMR spectrum for **4r** ($CDCl_3$, 101 MHz)



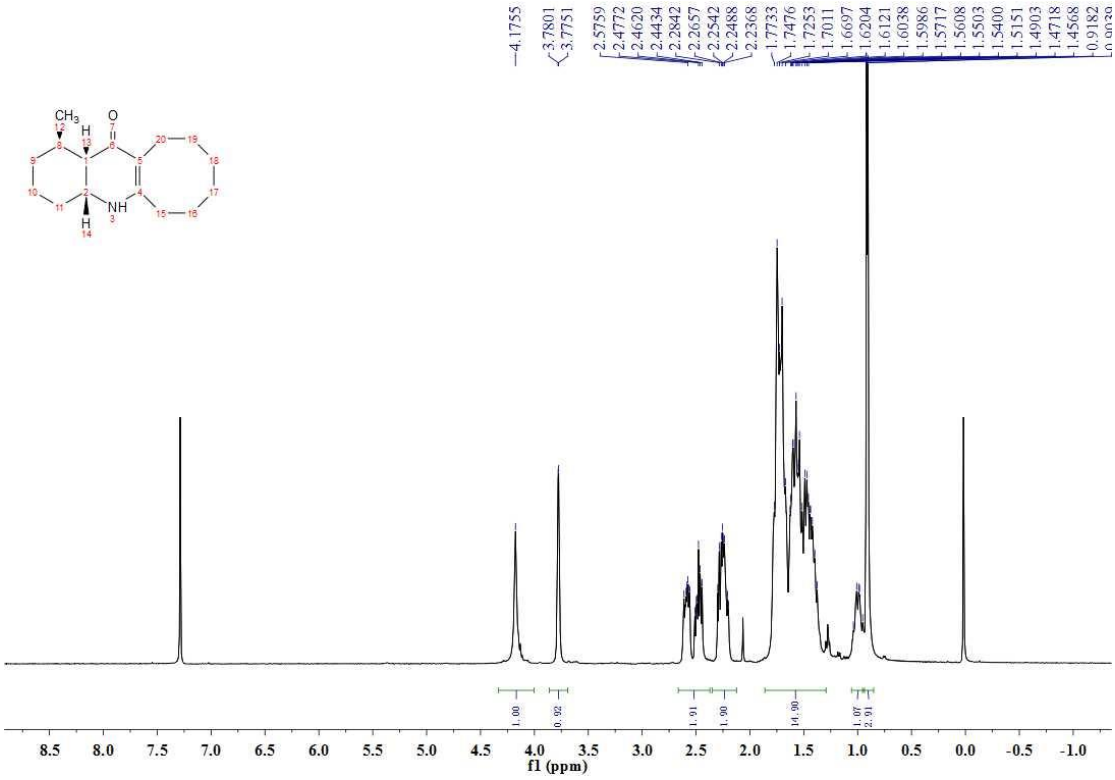
^{1}H NMR spectrum for **4s** ($CDCl_3$, 400 MHz)



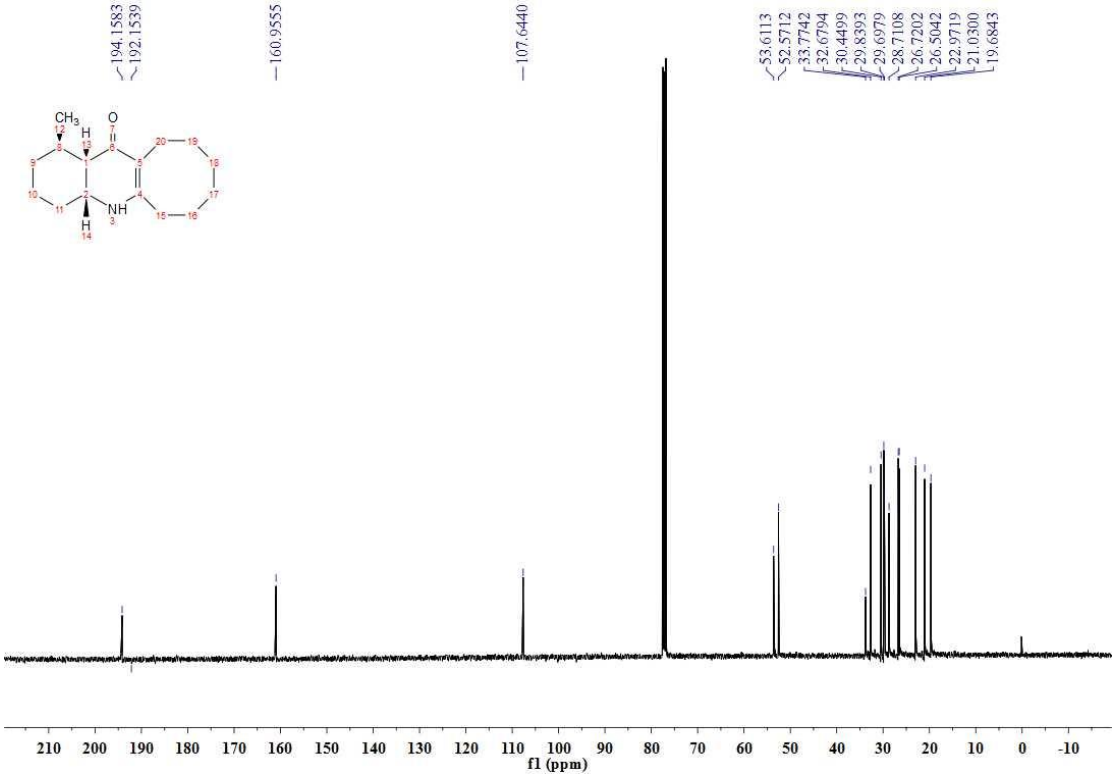
^{13}C NMR spectrum for **4s** ($CDCl_3$, 101 MHz)



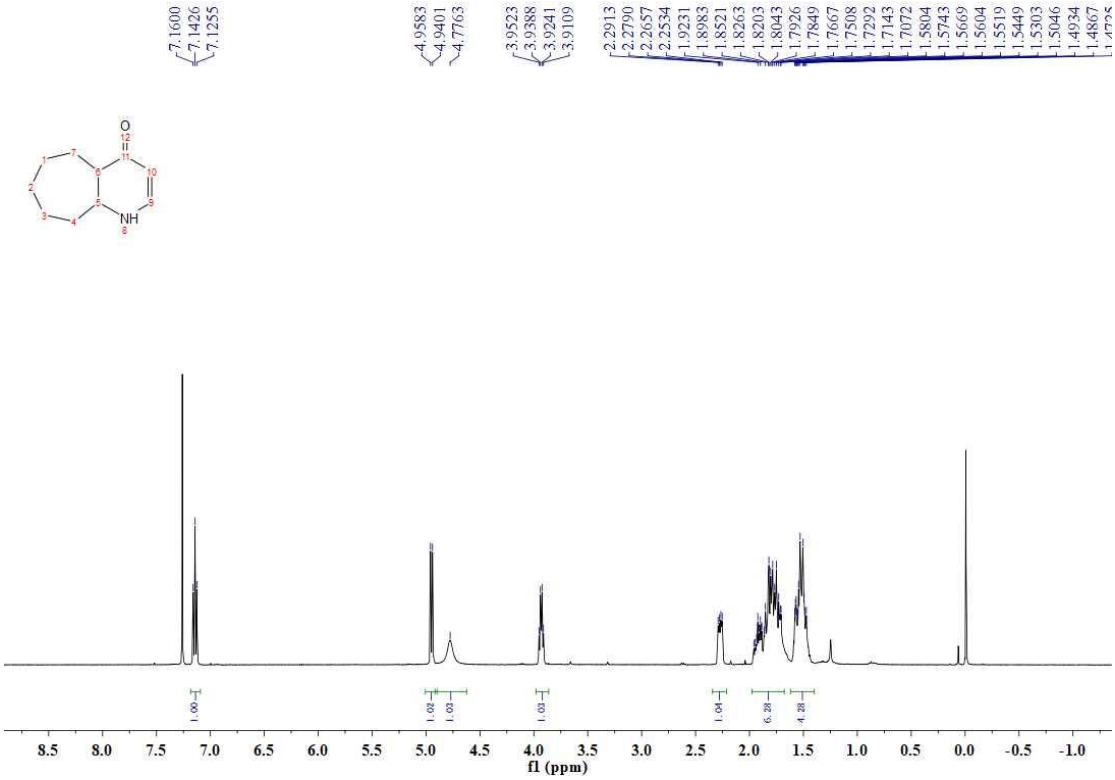
^{1}H NMR spectrum for **4t** ($CDCl_3$, 400 MHz)



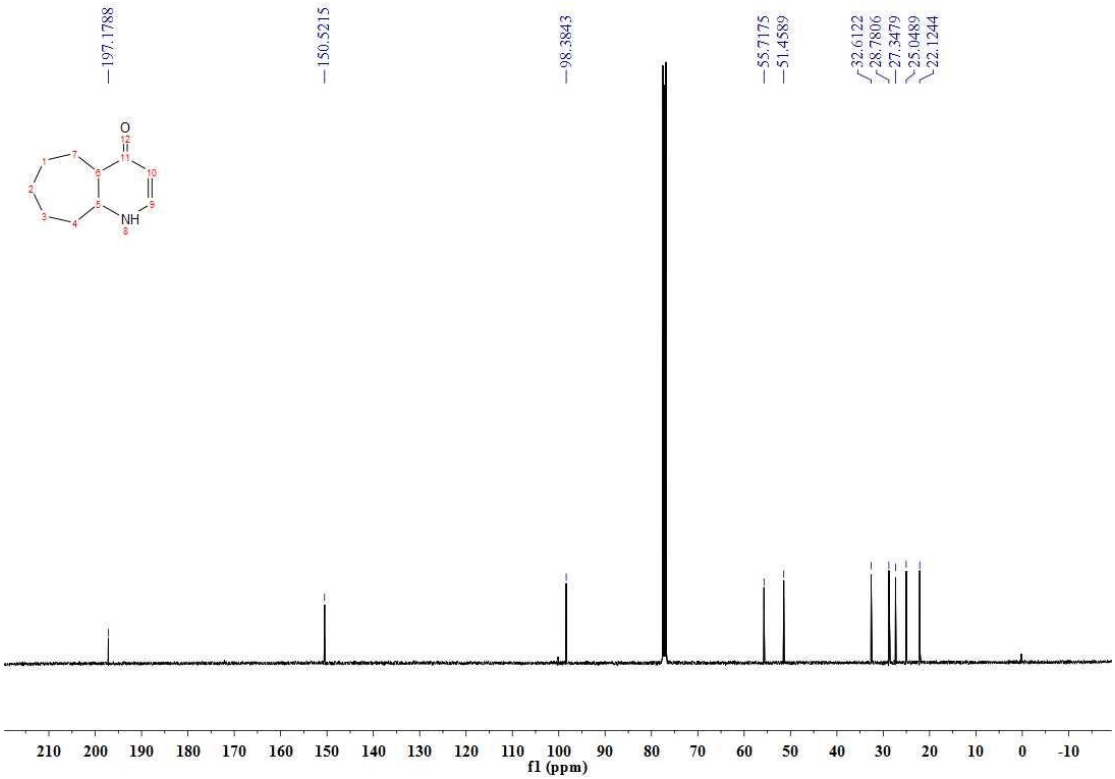
^{13}C NMR spectrum for **4t** ($CDCl_3$, 400 MHz)



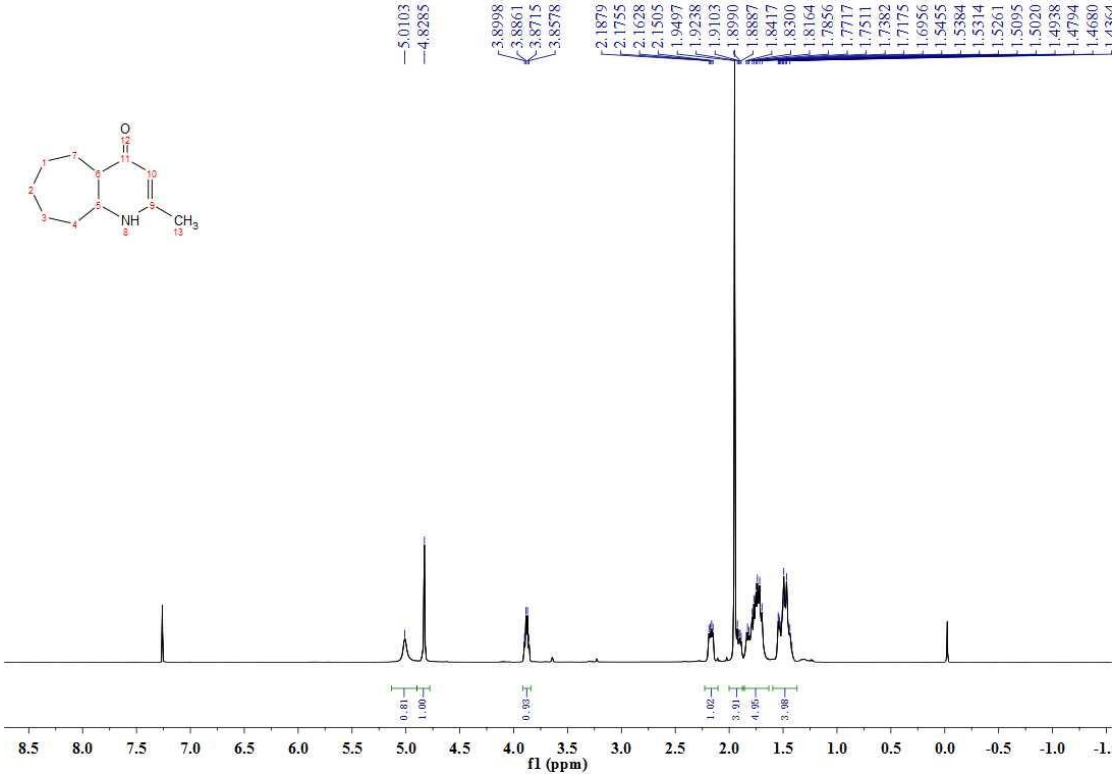
^{1}H NMR spectrum for **4u** ($CDCl_3$, 400 MHz)



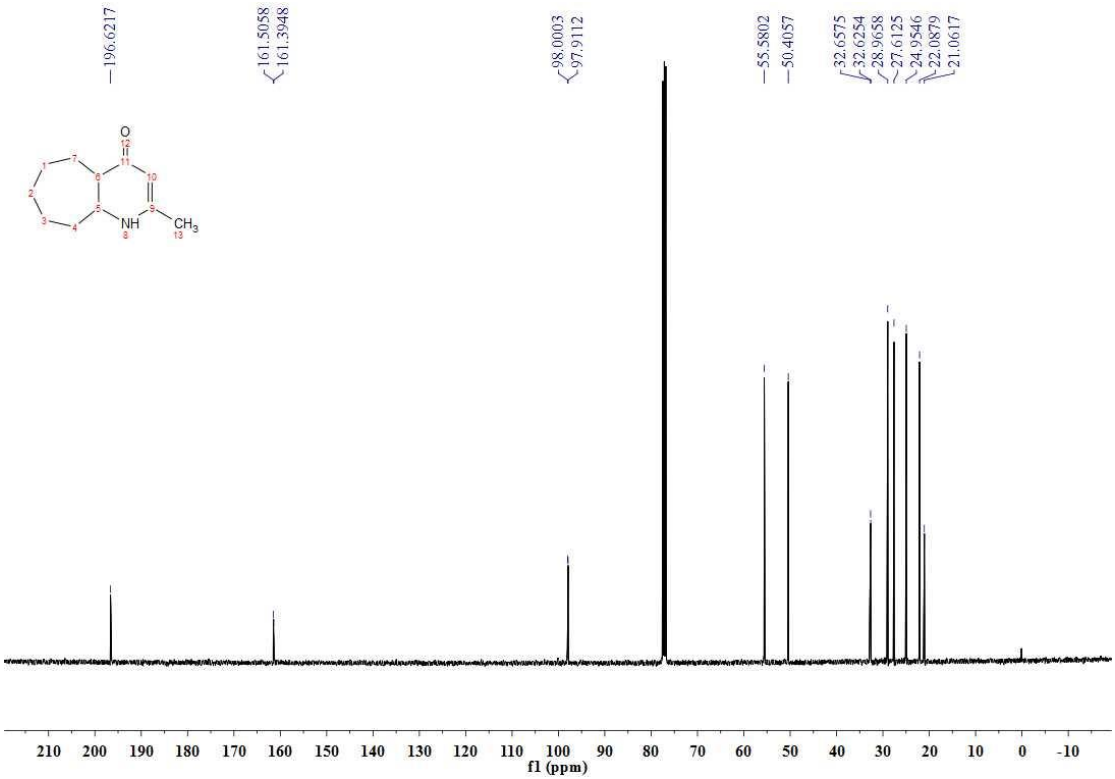
^{13}C NMR spectrum for **4u** ($CDCl_3$, 101 MHz)



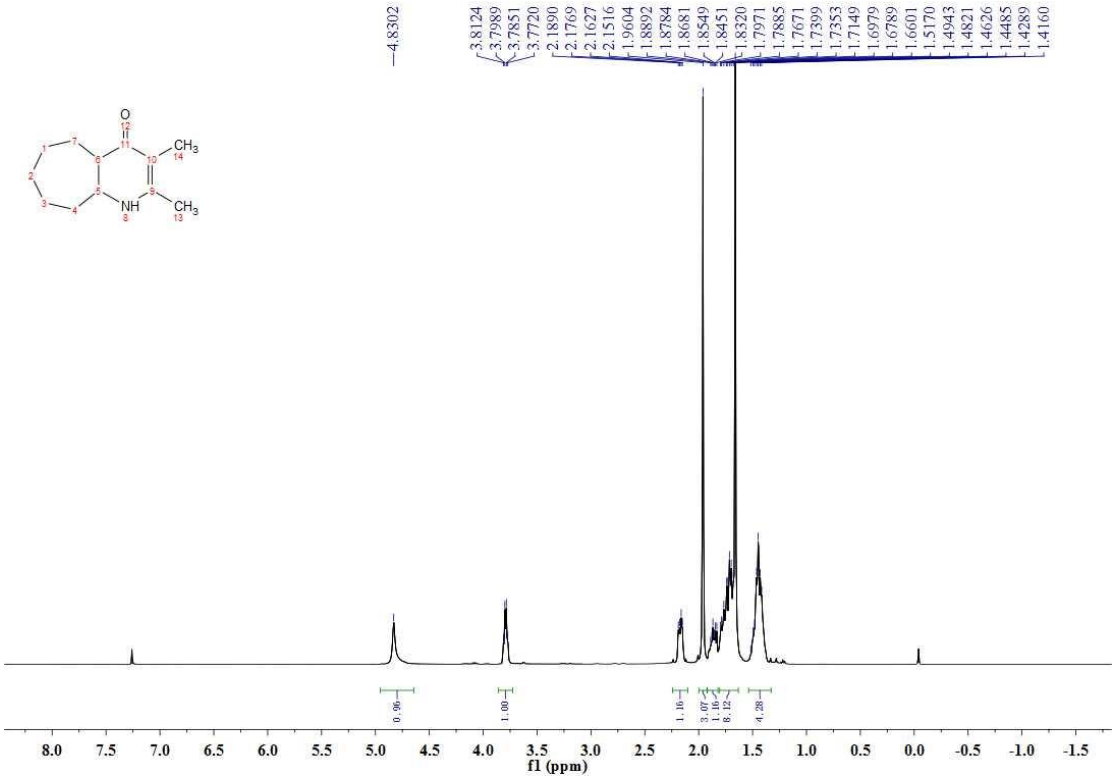
^{1}H NMR spectrum for **4v** ($CDCl_3$, 400 MHz)



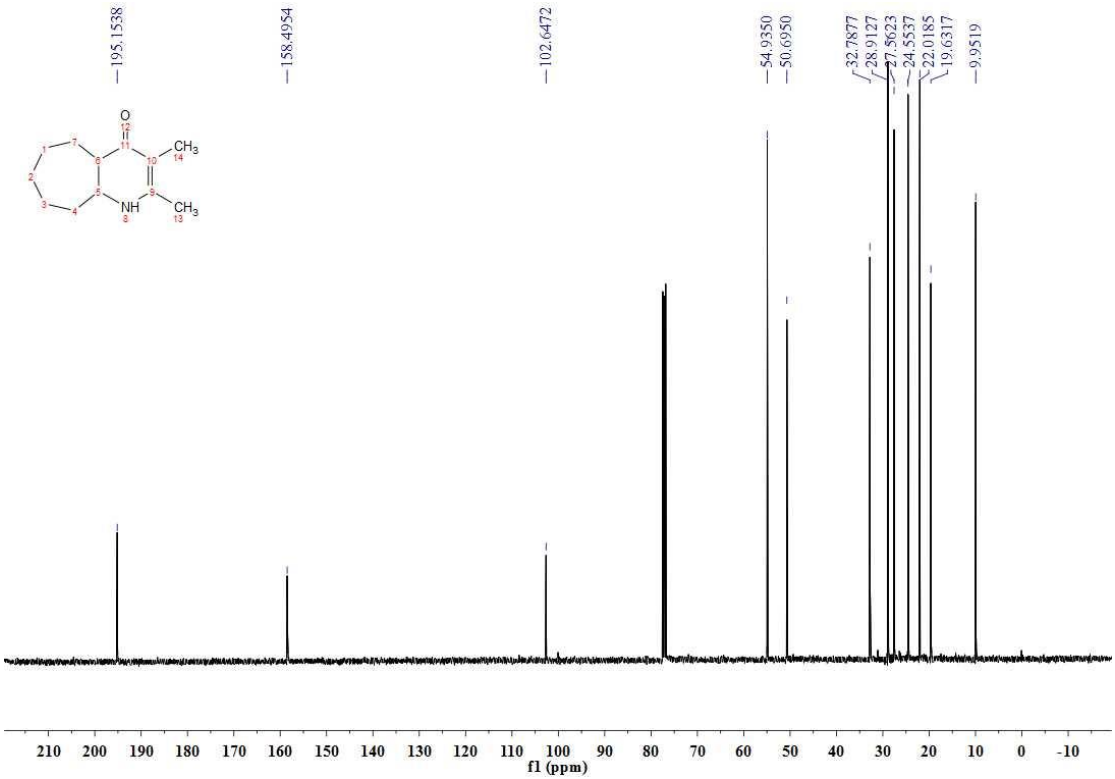
^{13}C NMR spectrum for **4v** ($CDCl_3$, 400 MHz)



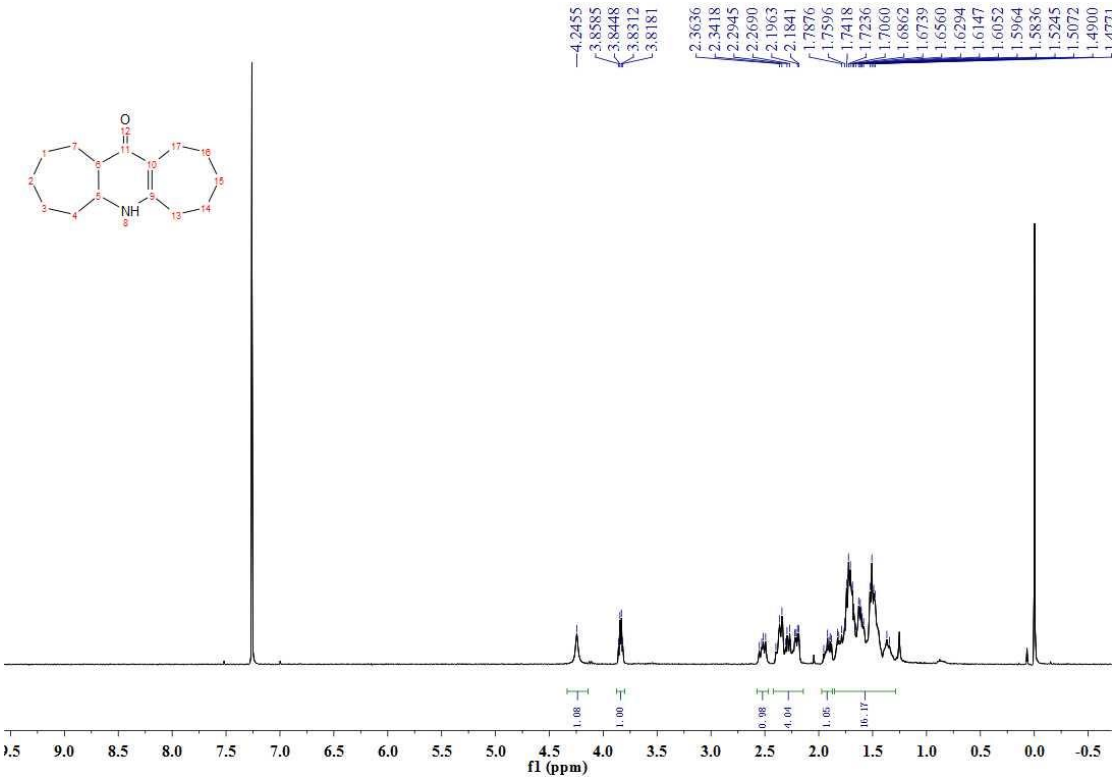
^{1}H NMR spectrum for **4w** ($CDCl_3$, 400 MHz)



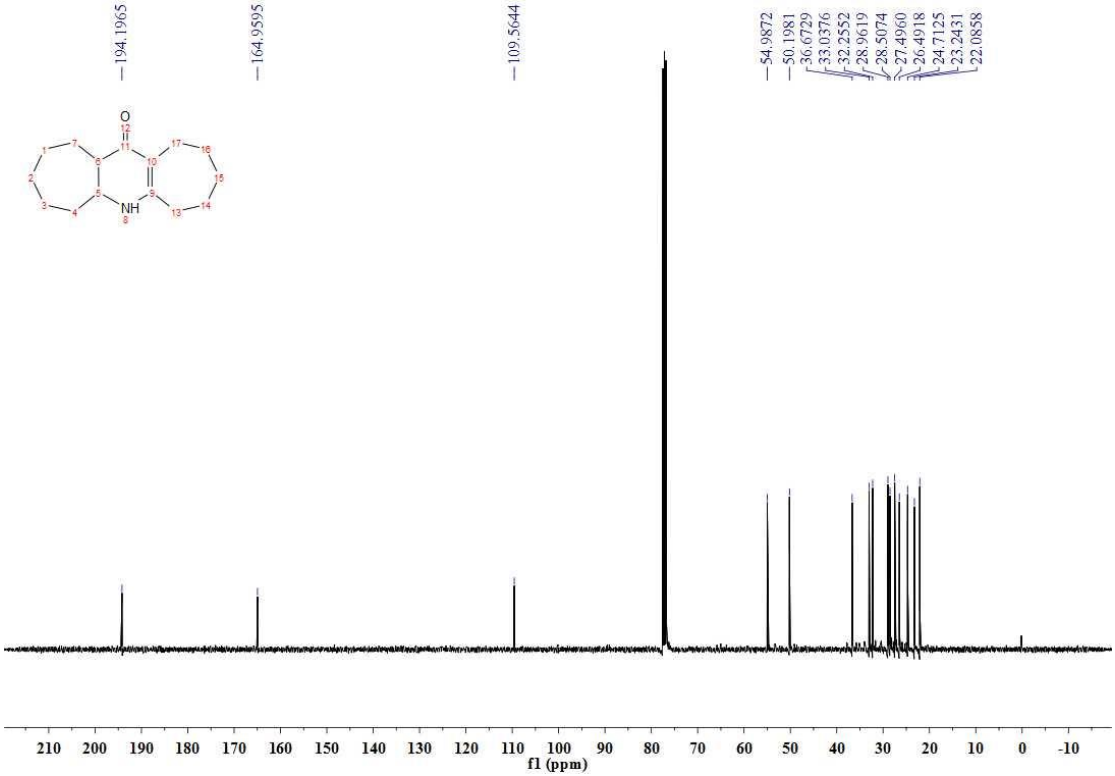
^{13}C NMR spectrum for **4w** ($CDCl_3$, 101 MHz)



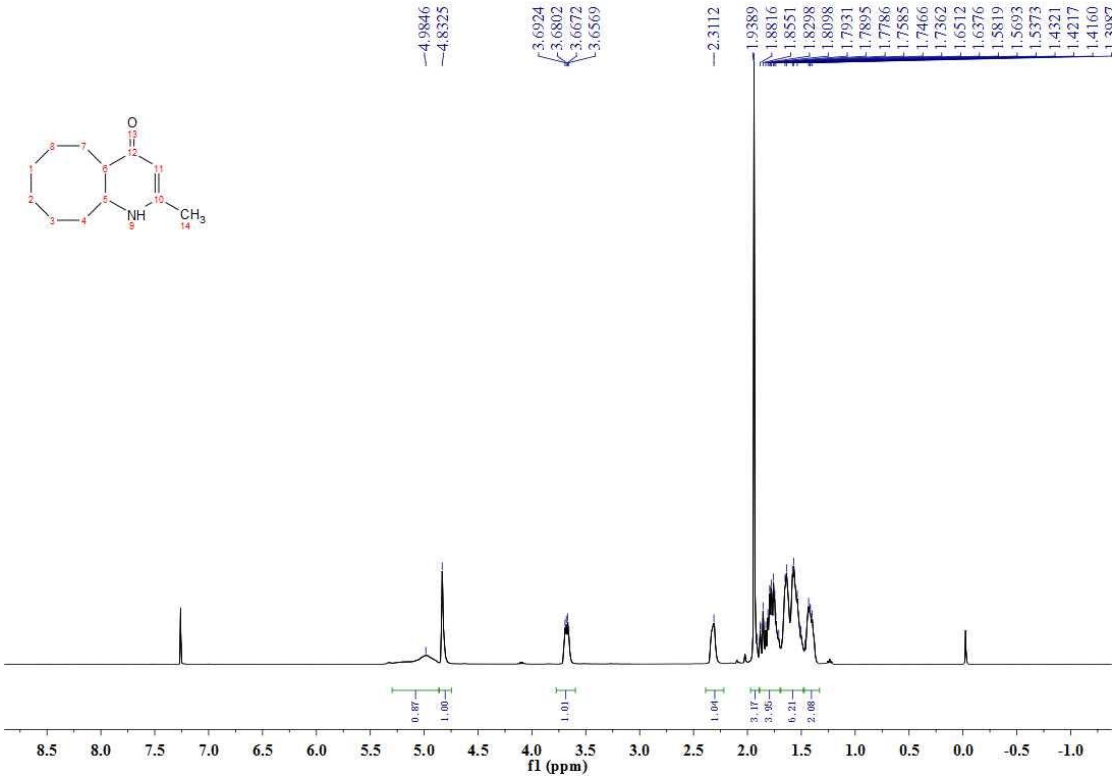
^{1}H NMR spectrum for **4x** ($CDCl_3$, 400 MHz)



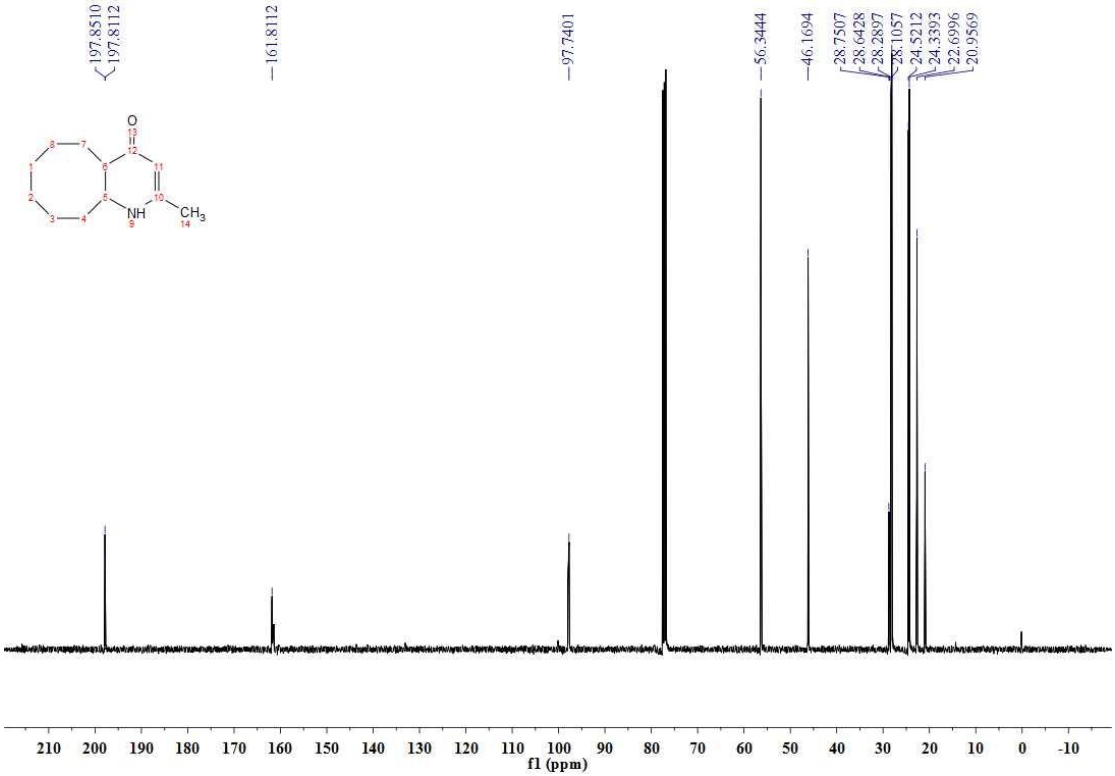
^{13}C NMR spectrum for **4x** ($CDCl_3$, 101 MHz)



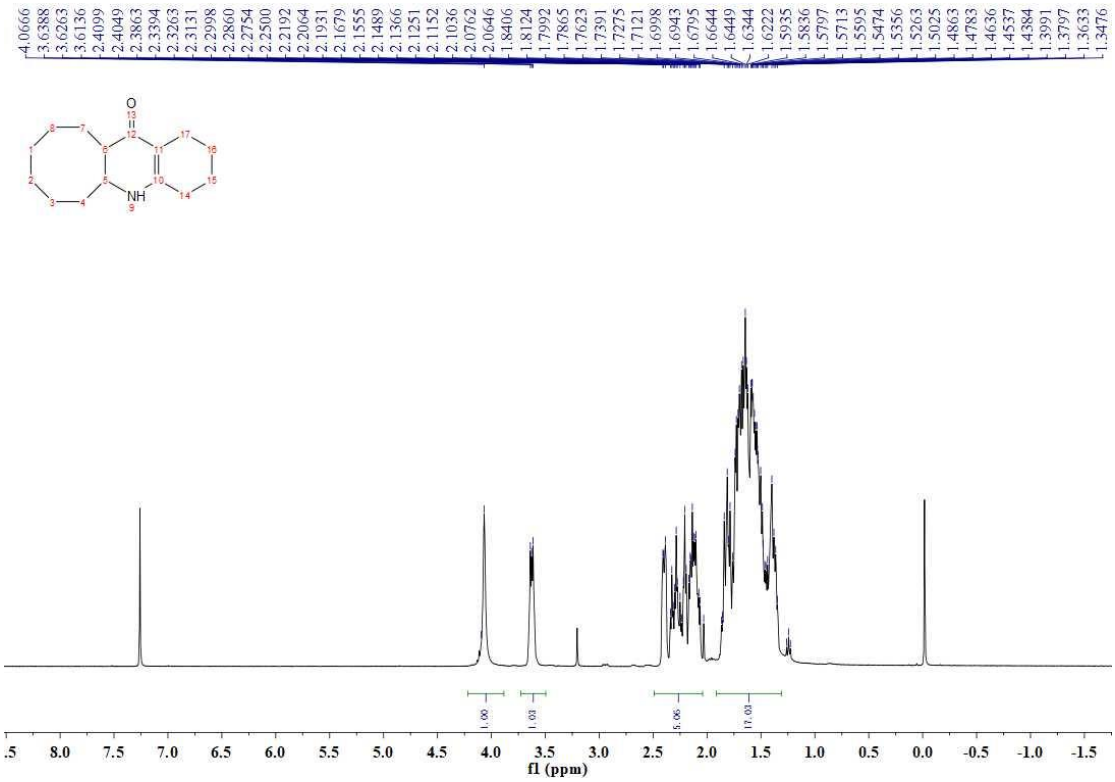
^{1}H NMR spectrum for **4y** ($CDCl_3$, 400 MHz)



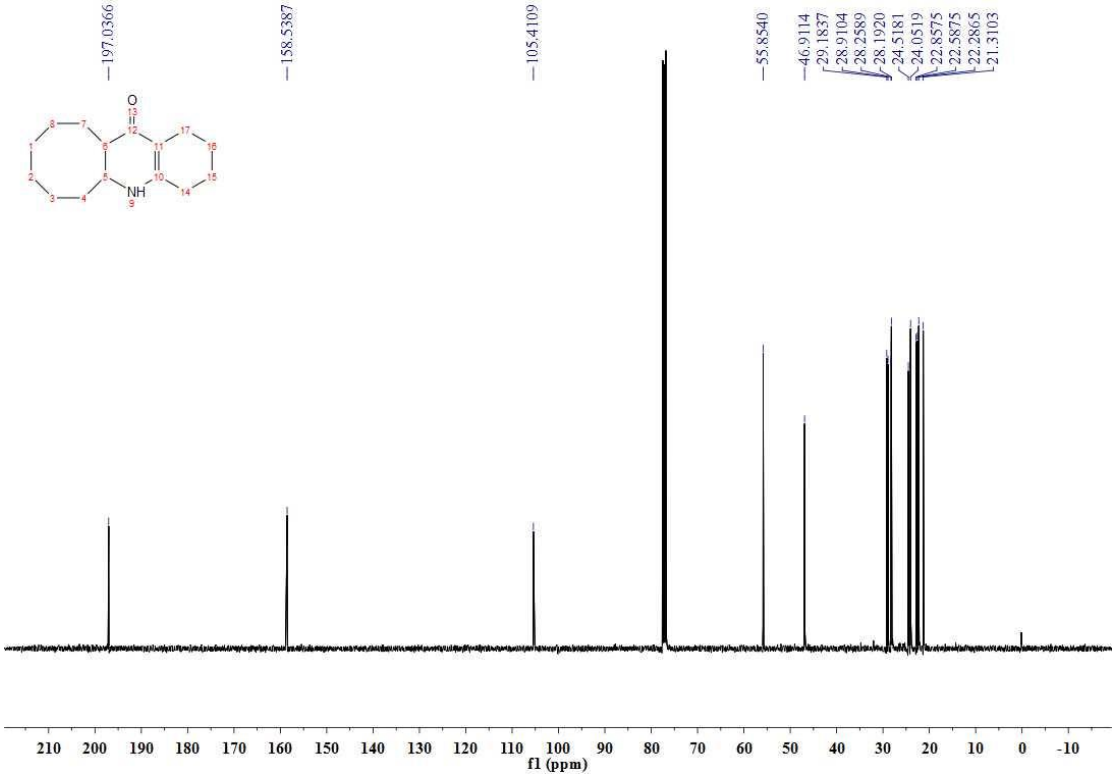
^{1}H NMR spectrum for **4y** ($CDCl_3$, 101 MHz)



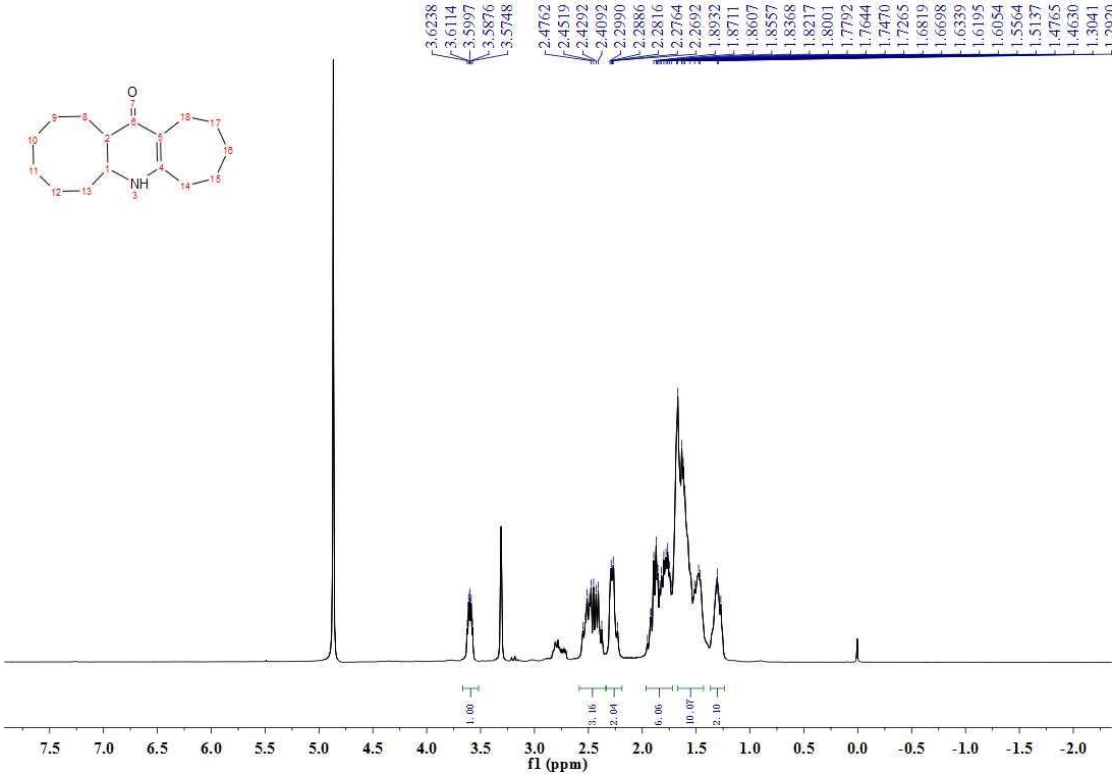
^{1}H NMR spectrum for **4z** ($CDCl_3$, 400 MHz)



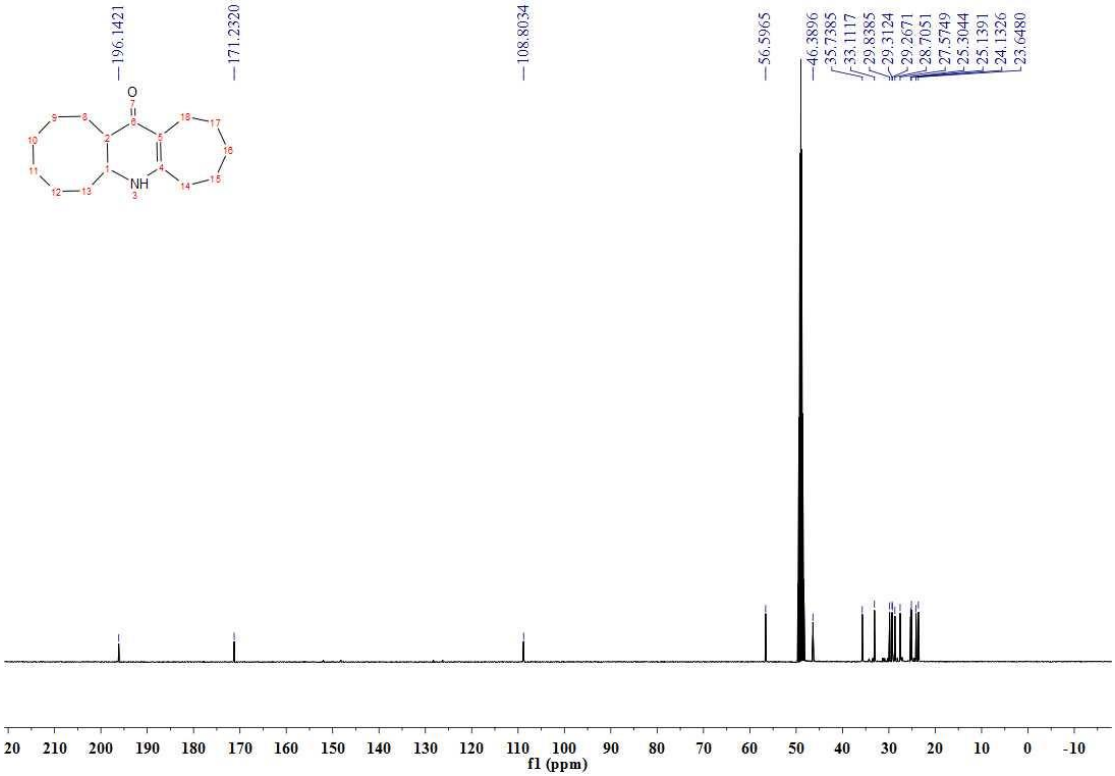
^{13}C NMR spectrum for **4z** ($CDCl_3$, 101 MHz)



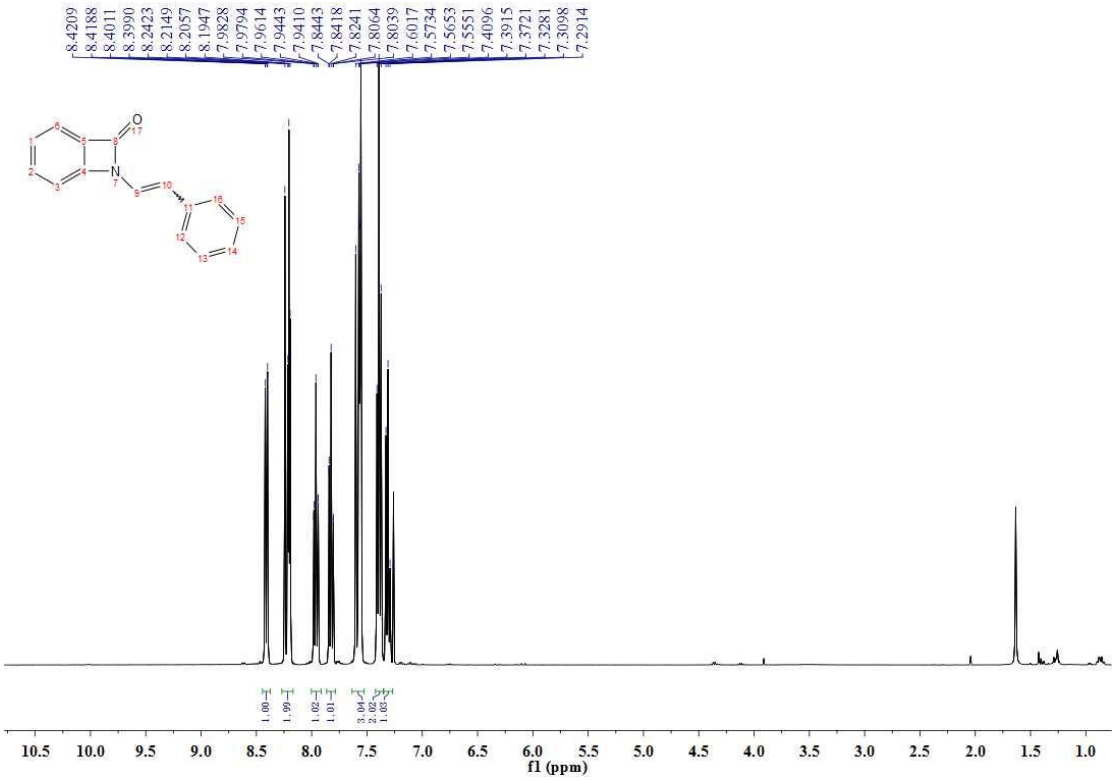
^{1}H NMR spectrum for **4aa** (MeOD, 400 MHz)



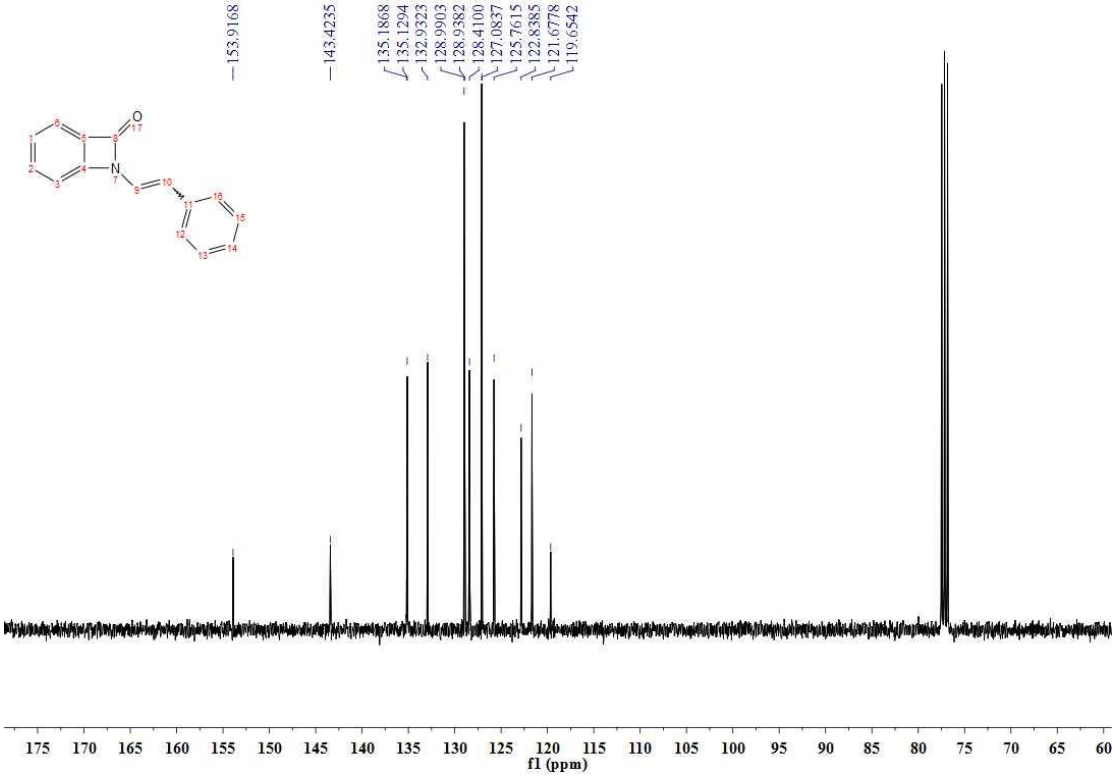
^{13}C NMR spectrum for **4aa** (MeOD, 101 MHz)



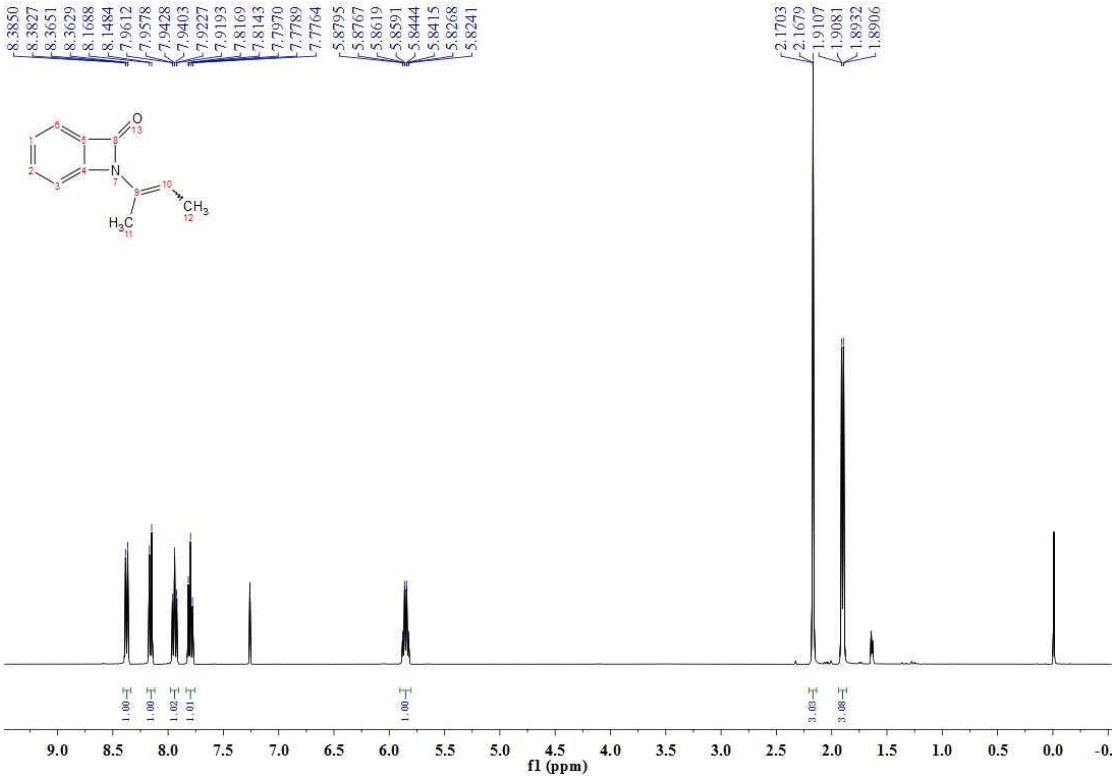
^{1}H NMR spectrum for **5a** (*trans*-isomer, $CDCl_3$, 400 MHz)



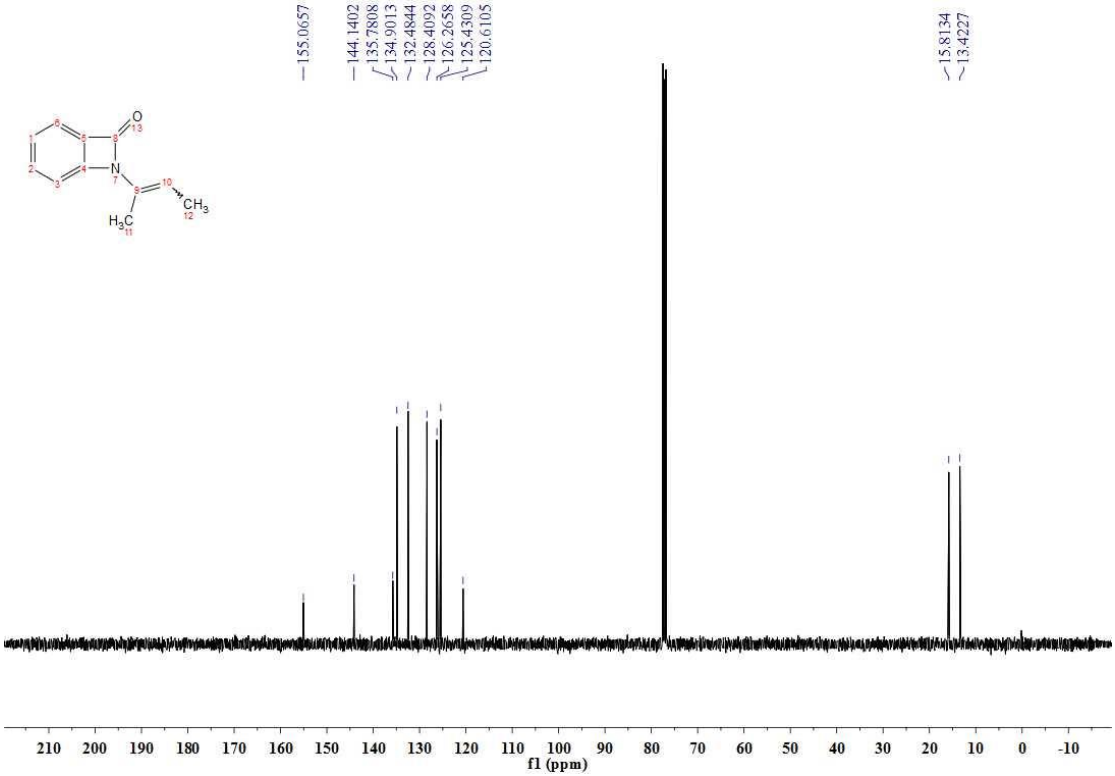
^{13}C NMR spectrum for **5a** (*trans*-isomer, $CDCl_3$, 101 MHz)



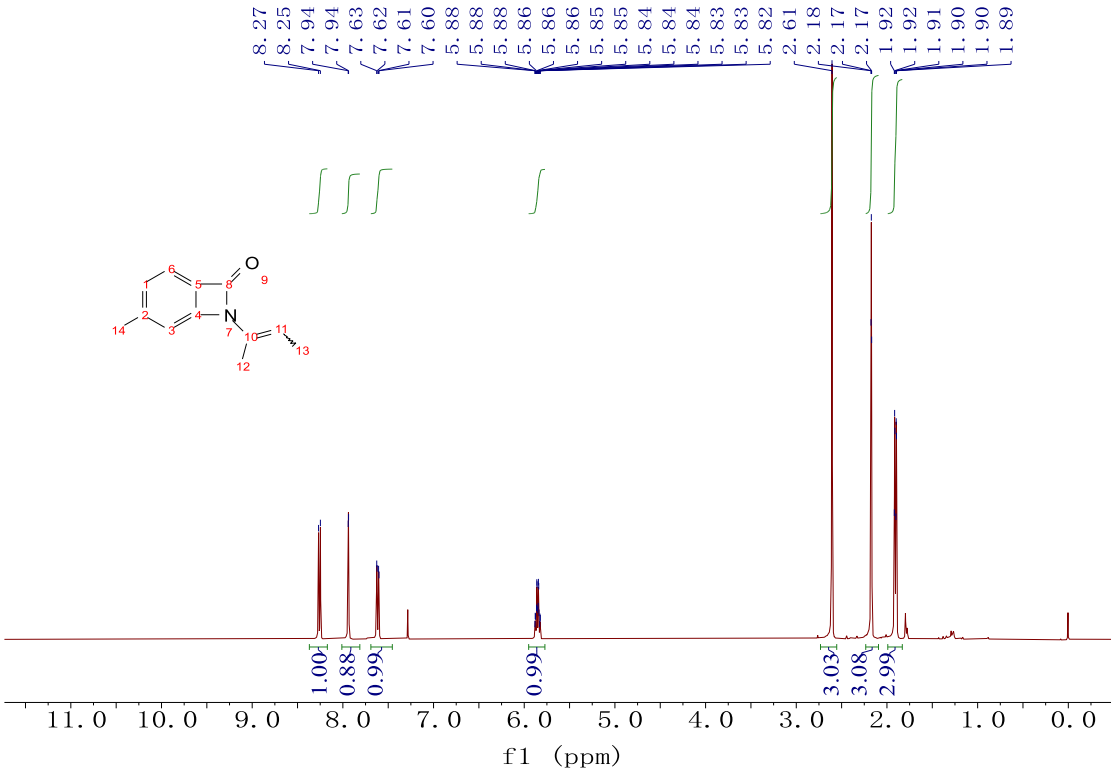
^{1}H NMR spectrum for **5b** (isomer 1, $CDCl_3$, 400 MHz)



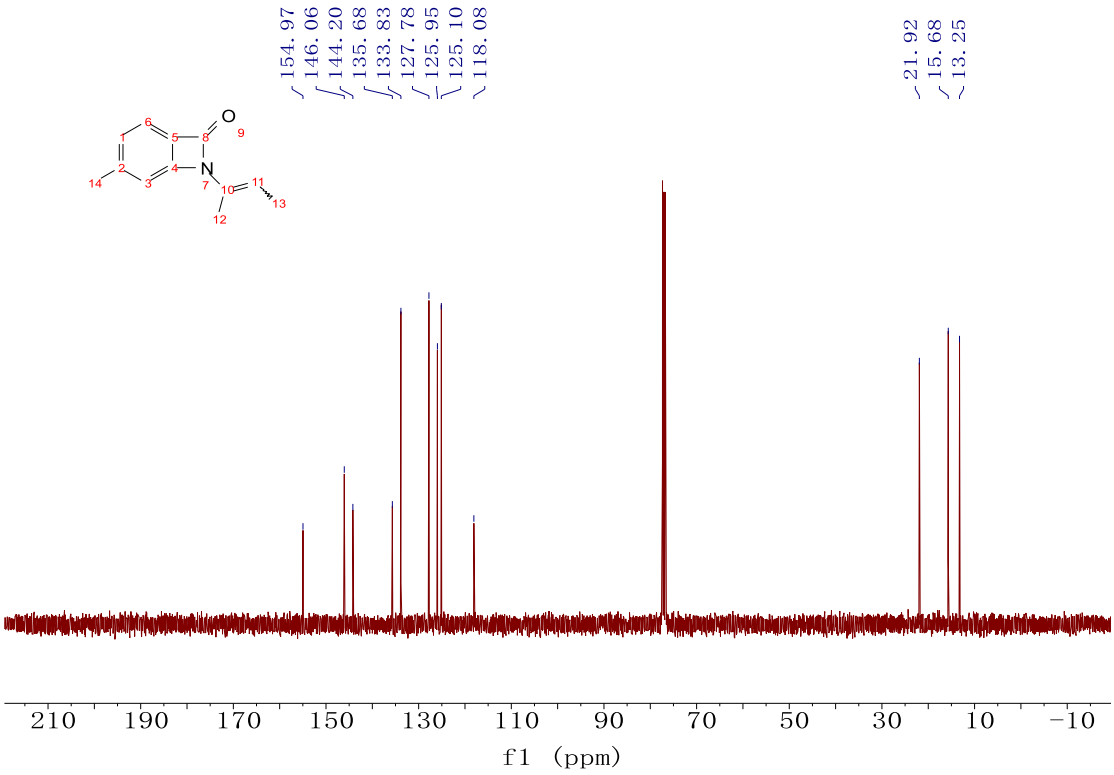
^{13}C NMR spectrum for **5b** (isomer 1, $CDCl_3$, 101 MHz)



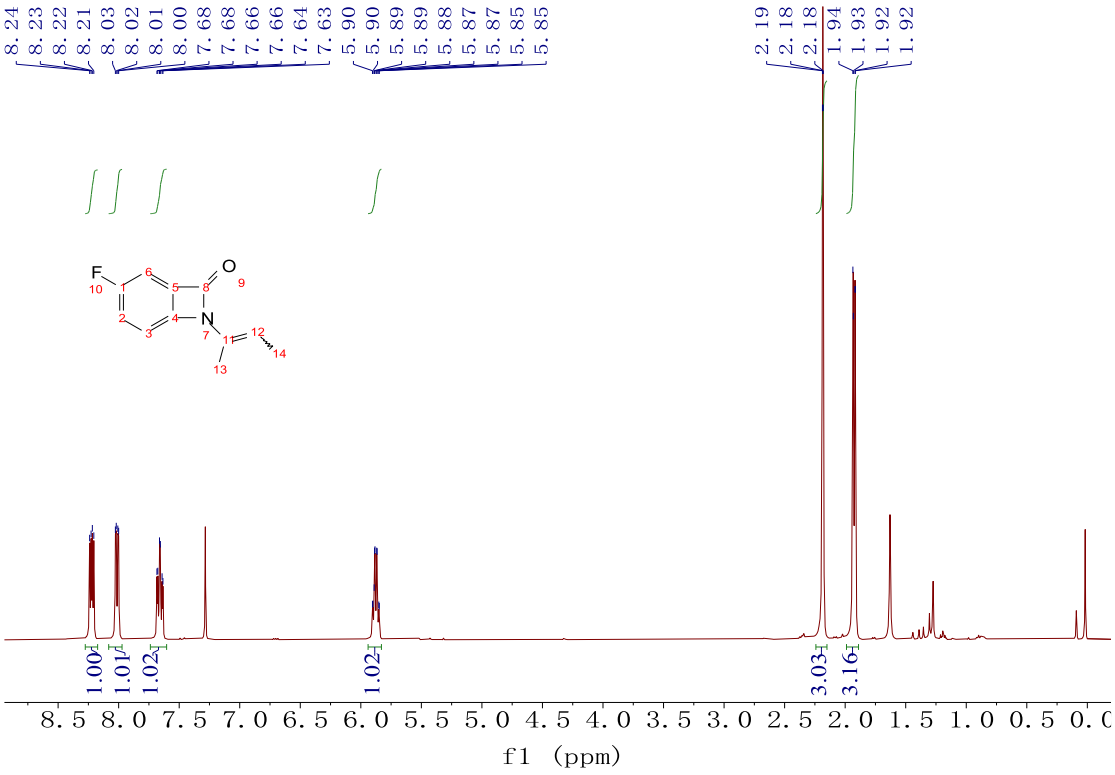
^{1}H NMR spectrum for **5c** ($CDCl_3$, 400 MHz)



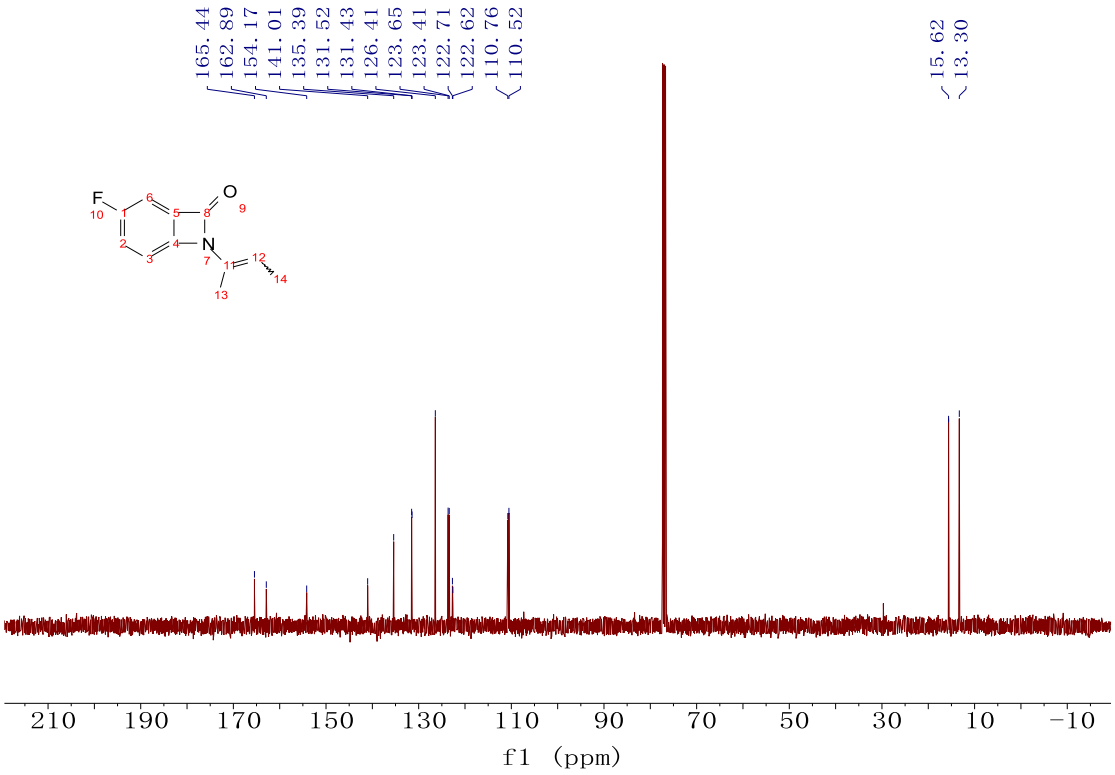
^{13}C NMR spectrum for **5c** ($CDCl_3$, 101 MHz)



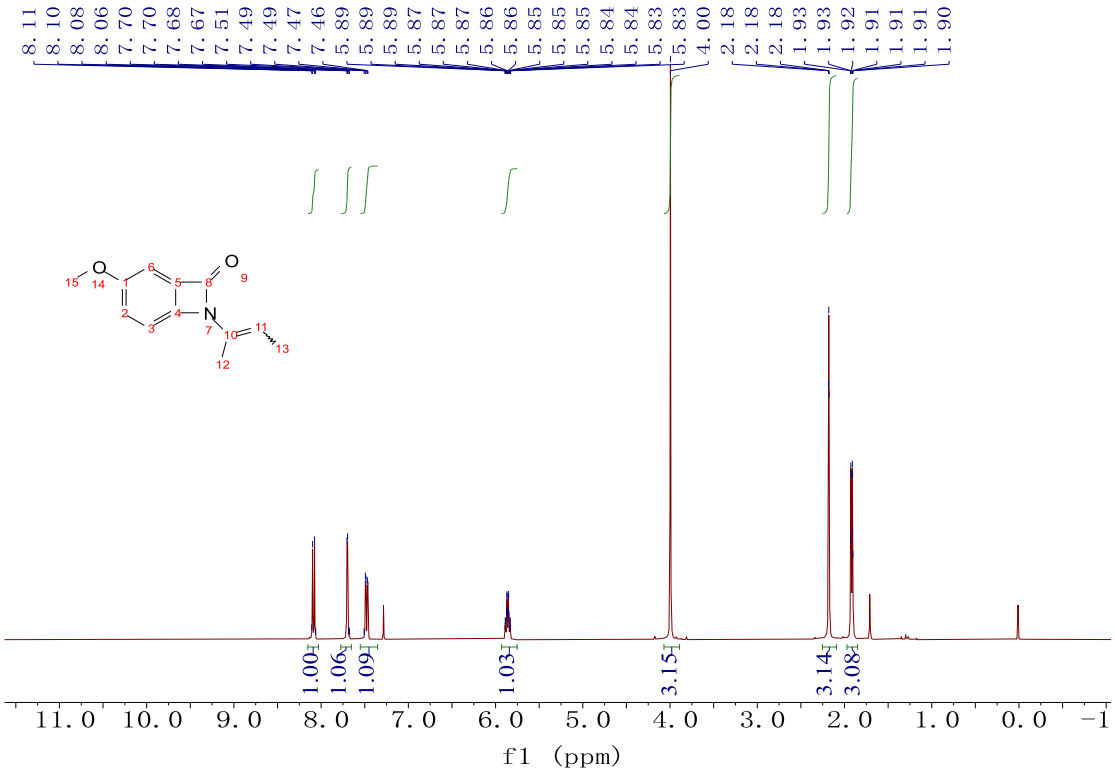
^{1}H NMR spectrum for **5d** ($CDCl_3$, 400 MHz)



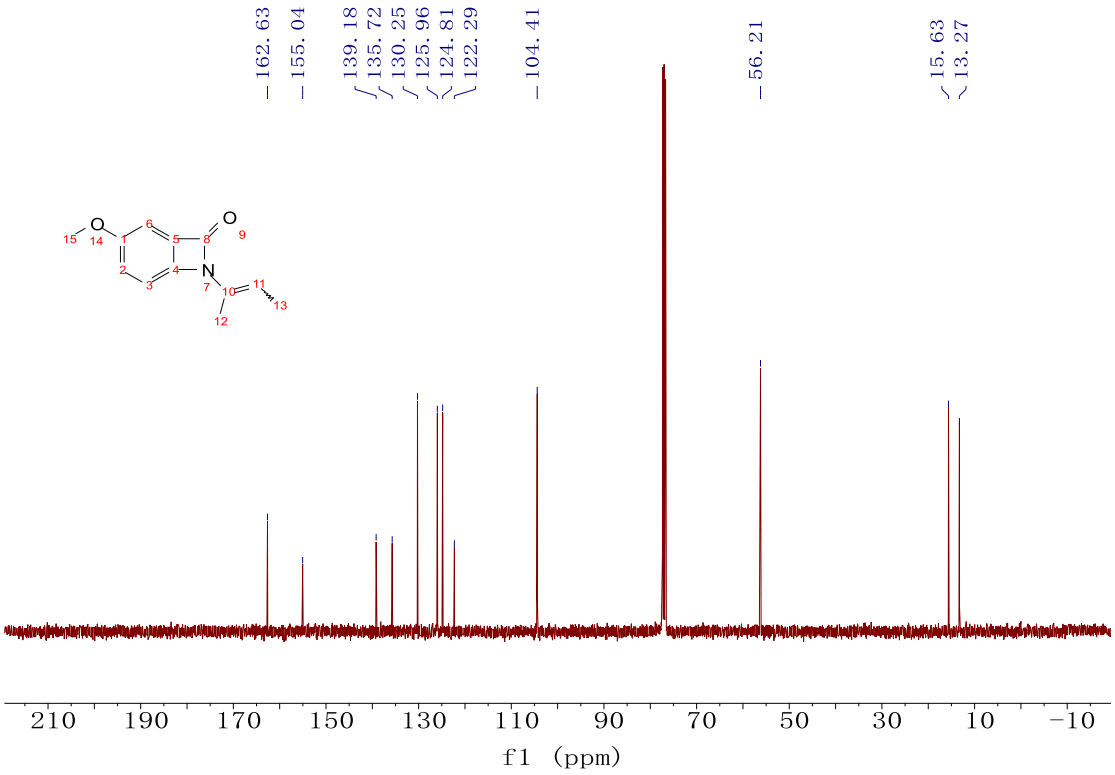
^{13}C NMR spectrum for **5d** ($CDCl_3$, 101 MHz)



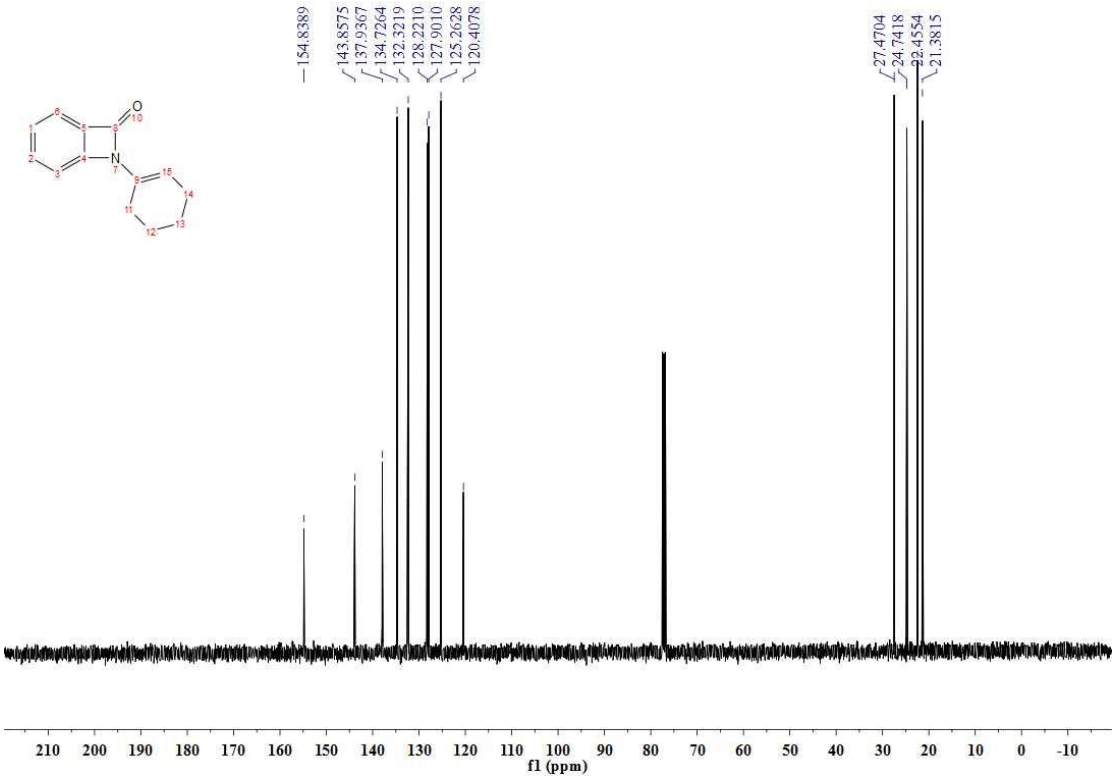
^{1}H NMR spectrum for **5e** ($CDCl_3$, 400 MHz)



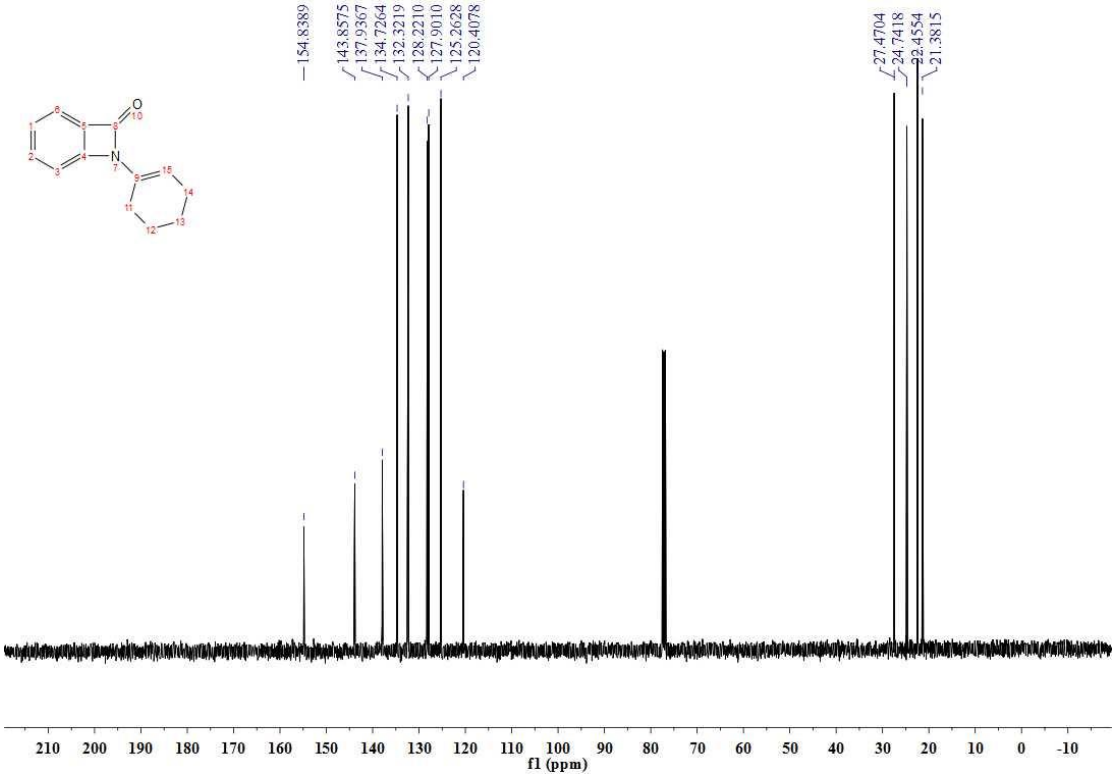
^{13}C NMR spectrum for **5e** ($CDCl_3$, 101 MHz)



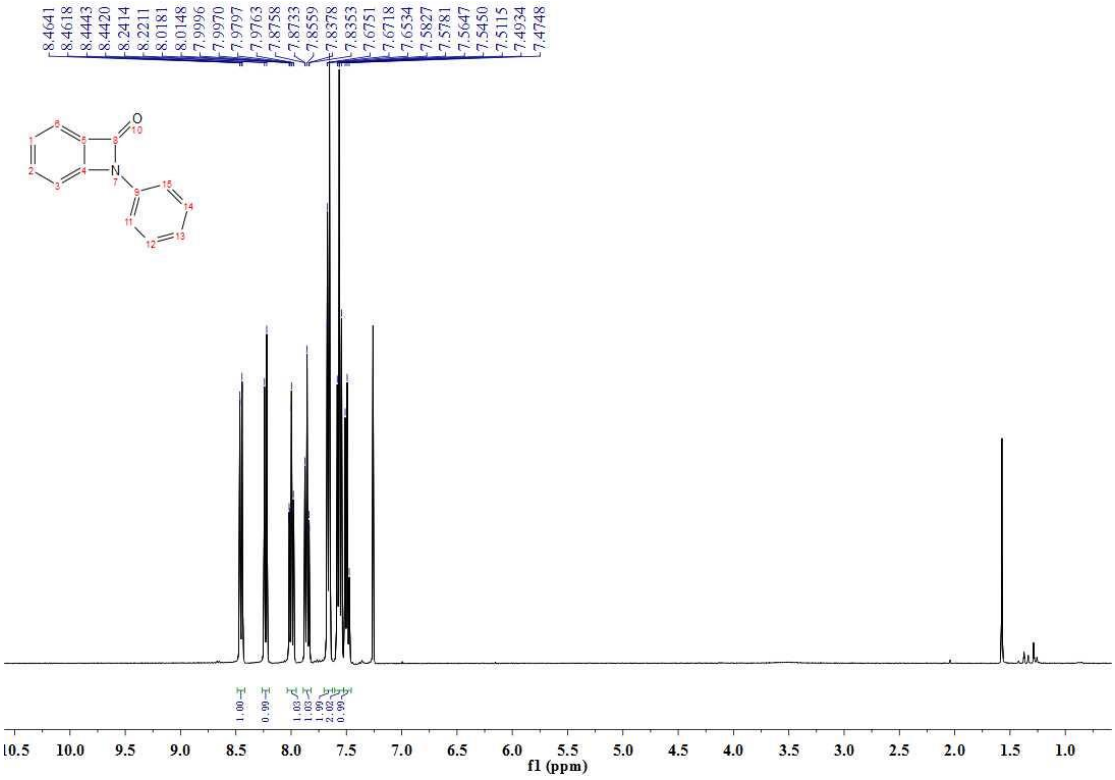
^{1}H NMR spectrum for **5f** ($CDCl_3$, 400 MHz)



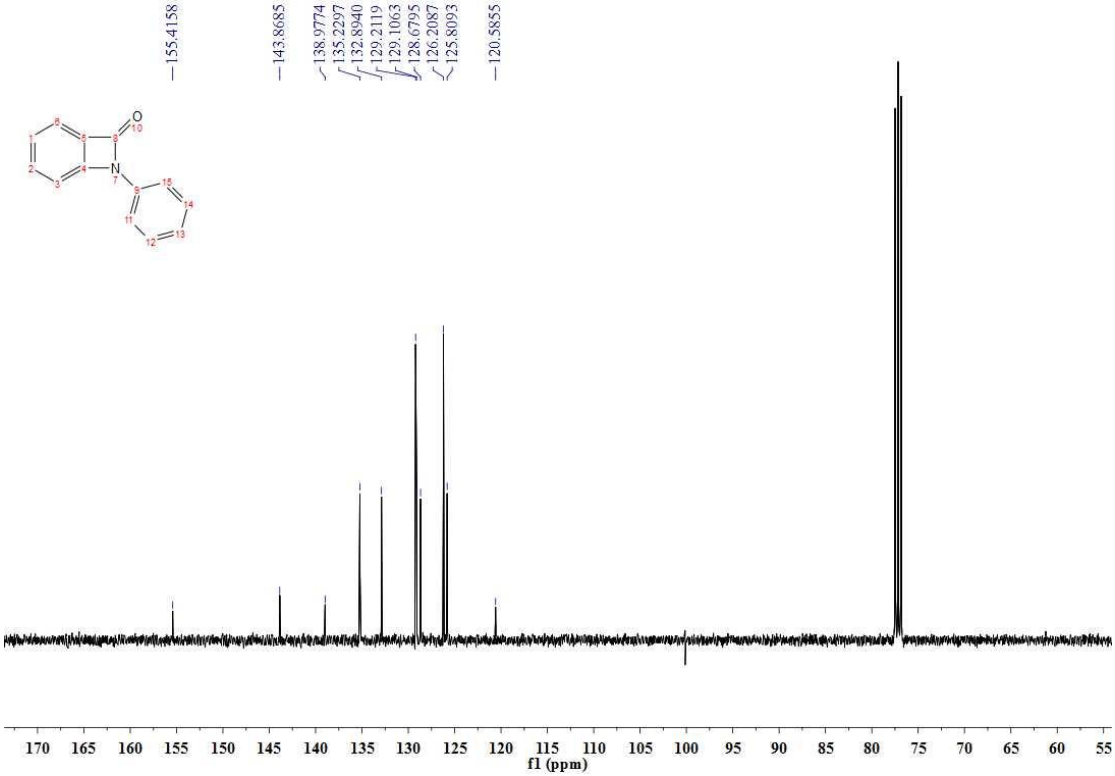
^{13}C NMR spectrum for **5f** ($CDCl_3$, 101 MHz)



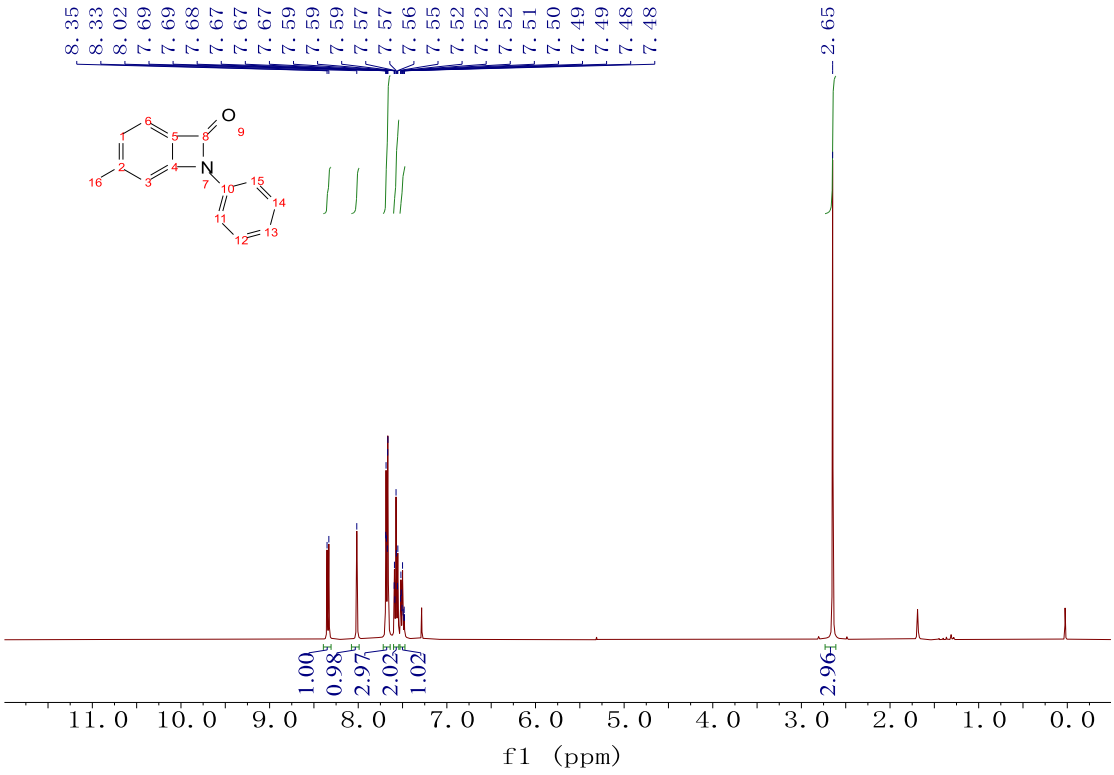
^{1}H NMR spectrum for **5h** ($CDCl_3$, 400 MHz)



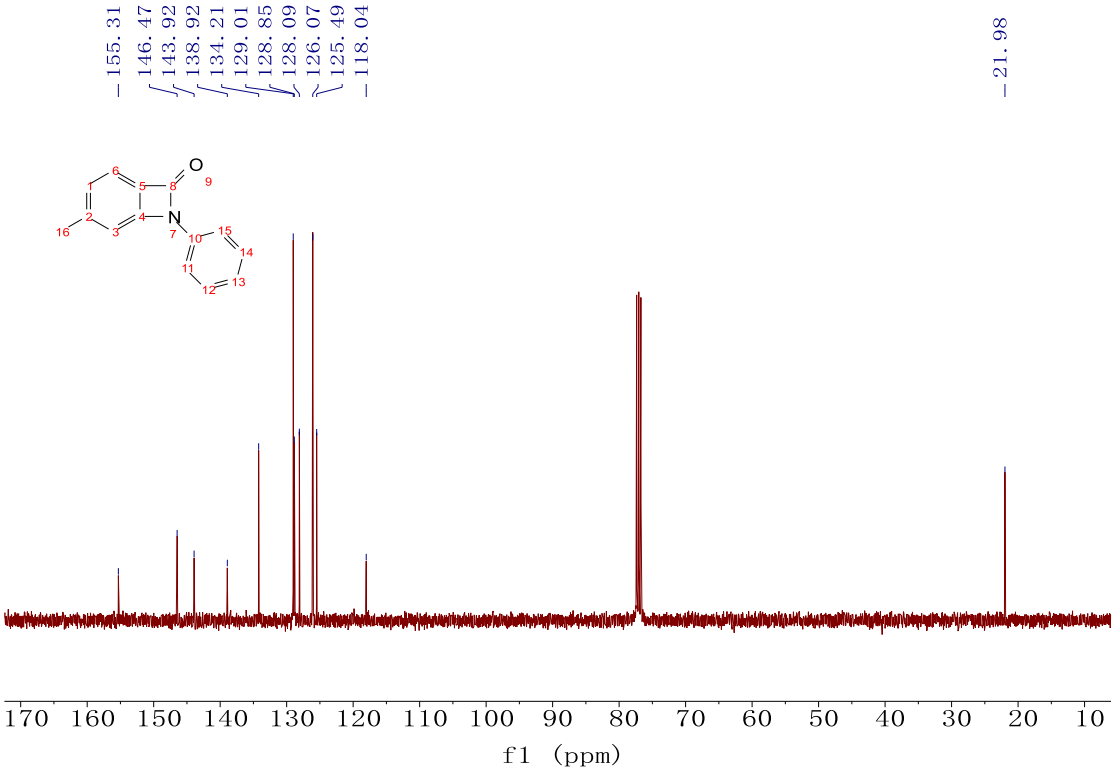
^{13}C NMR spectrum for **5h** ($CDCl_3$, 101 MHz)



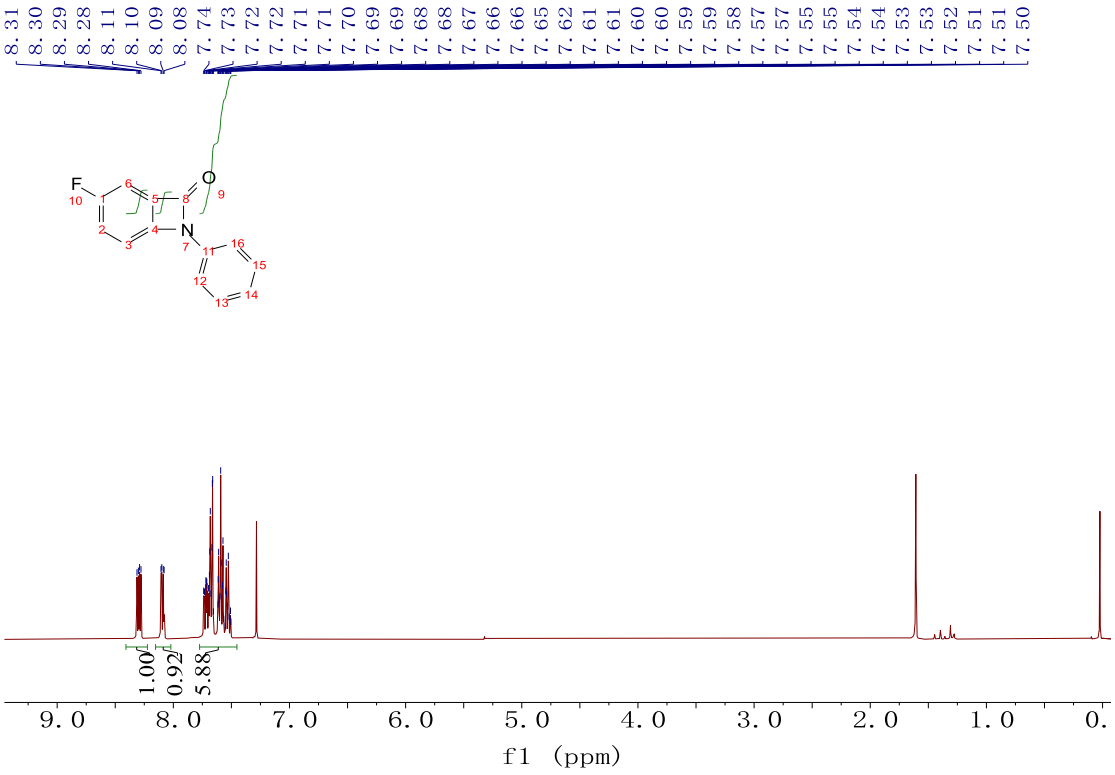
^{1}H NMR spectrum for **5i** ($CDCl_3$, 400 MHz)



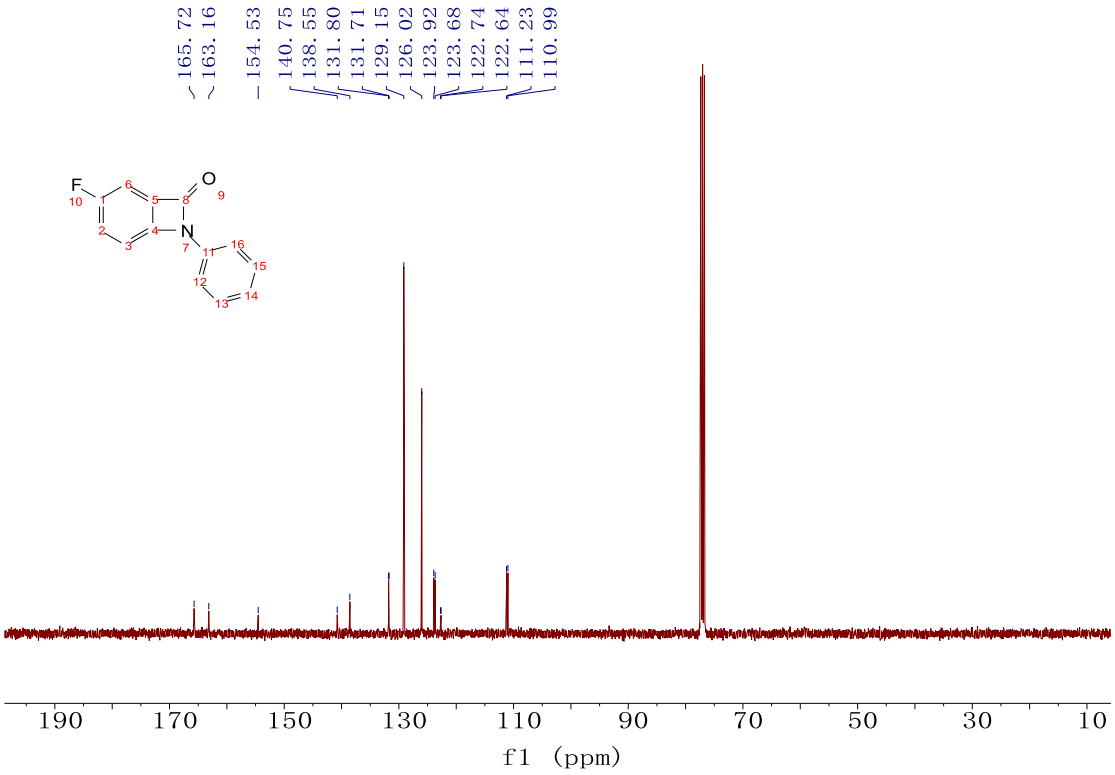
^{13}C NMR spectrum for **5i** ($CDCl_3$, 101 MHz)



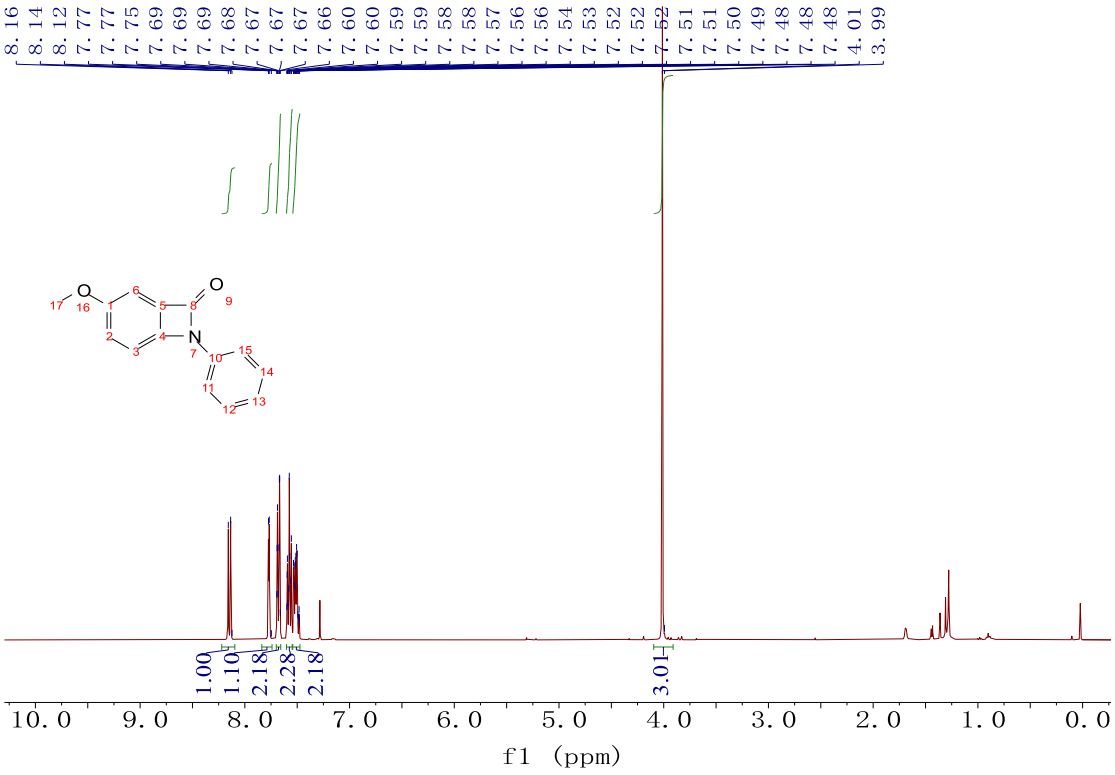
^{1}H NMR spectrum for **5j** ($CDCl_3$, 400 MHz)



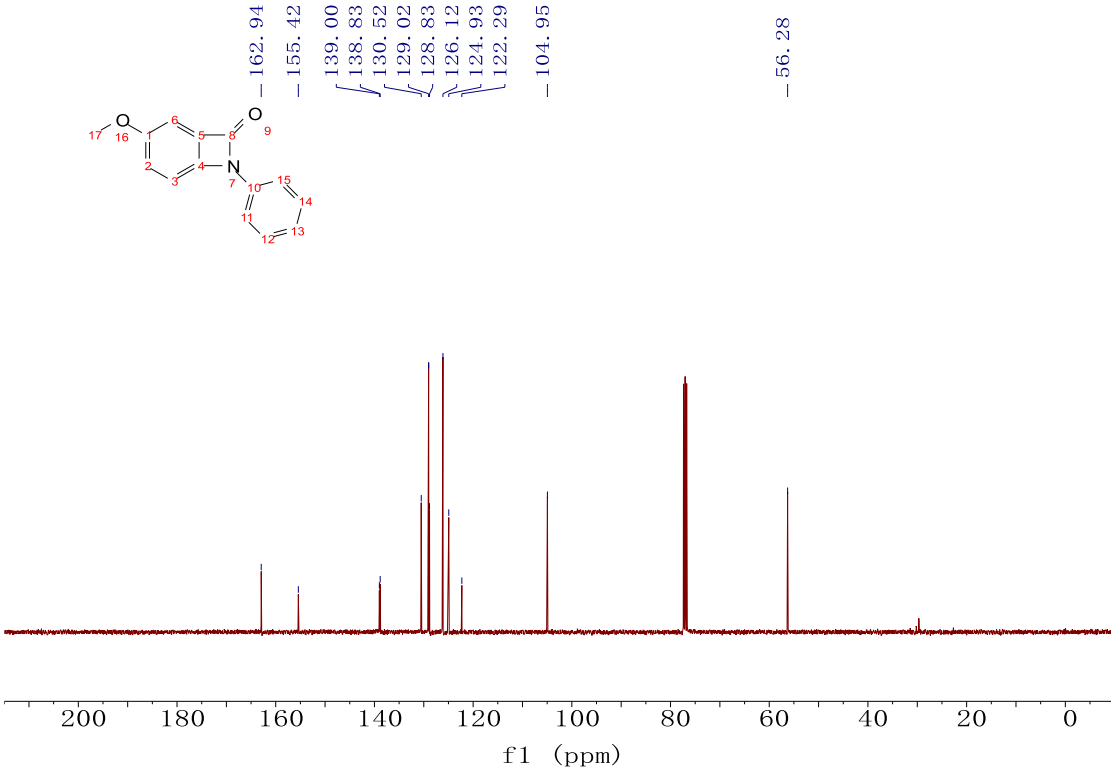
^{13}C NMR spectrum for **5j** ($CDCl_3$, 101 MHz)



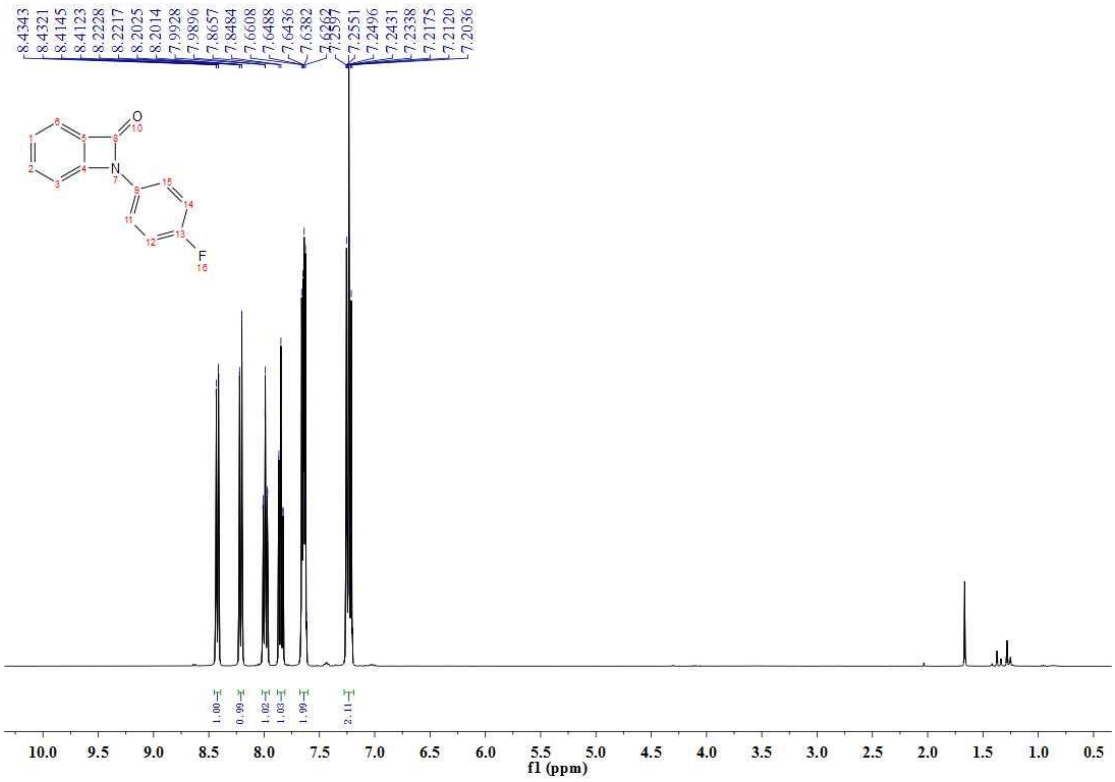
^{1}H NMR spectrum for **5k** ($CDCl_3$, 400 MHz)



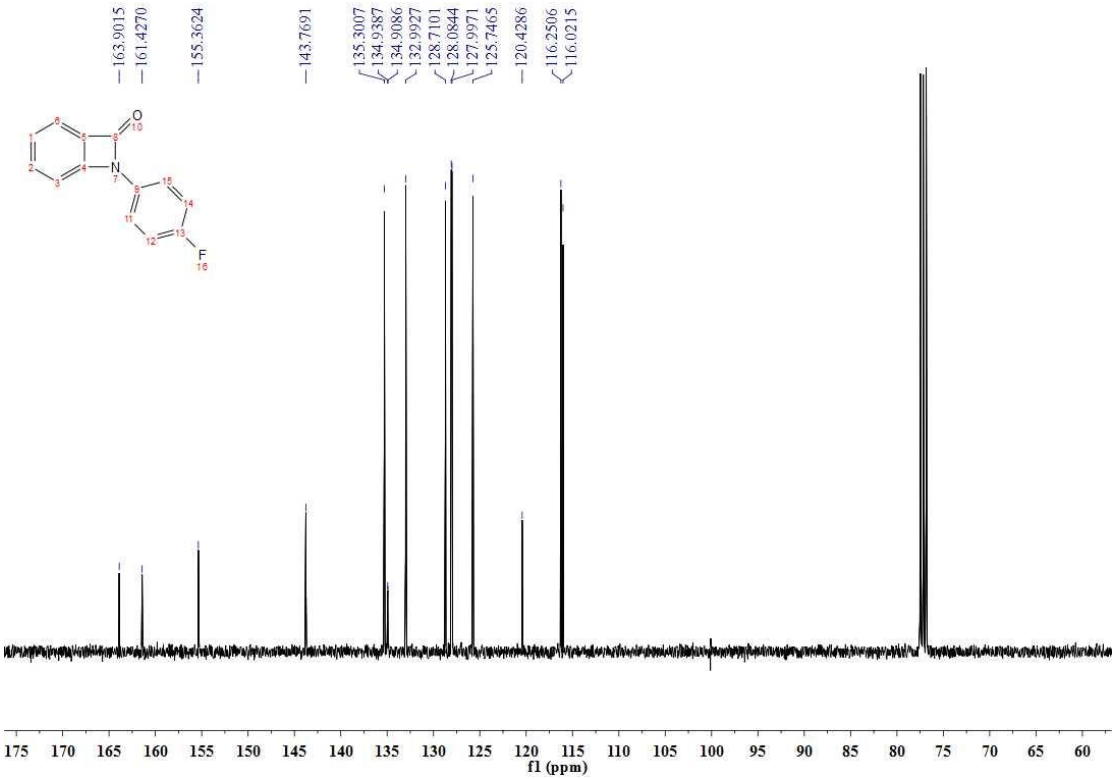
^{13}C NMR spectrum for **5k** ($CDCl_3$, 101 MHz)



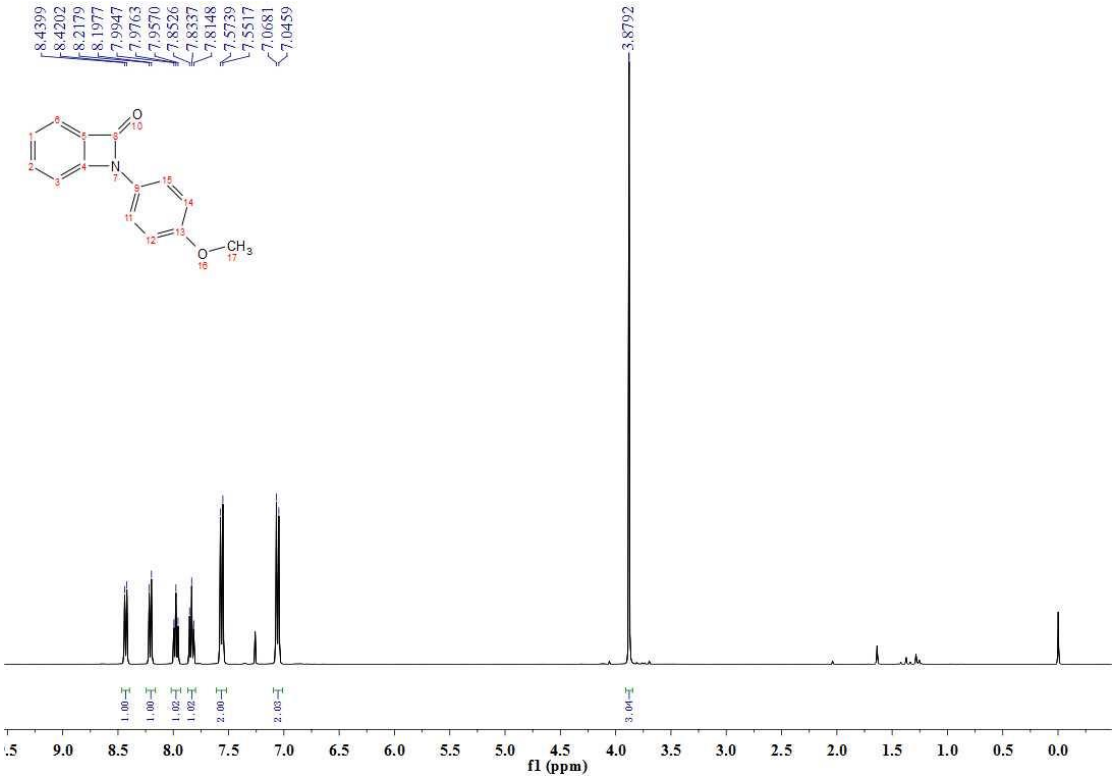
^{1}H NMR spectrum for **5l** ($CDCl_3$, 400 MHz)



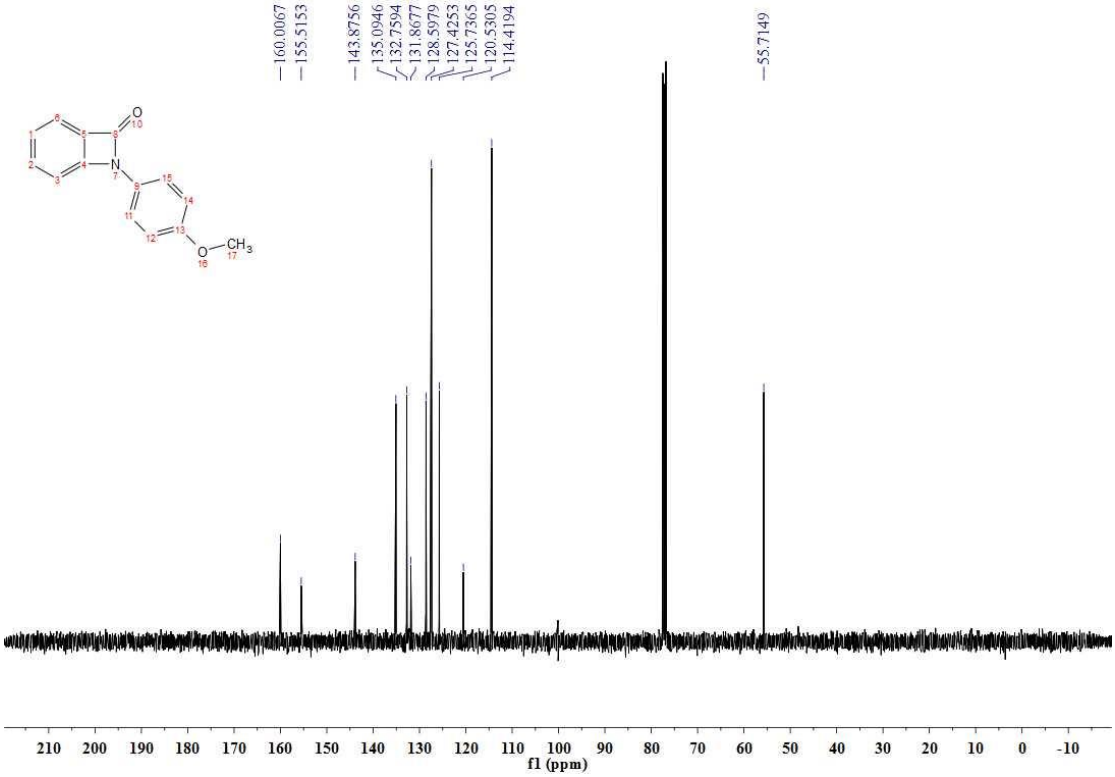
^{13}C NMR spectrum for **5l** ($CDCl_3$, 101 MHz)



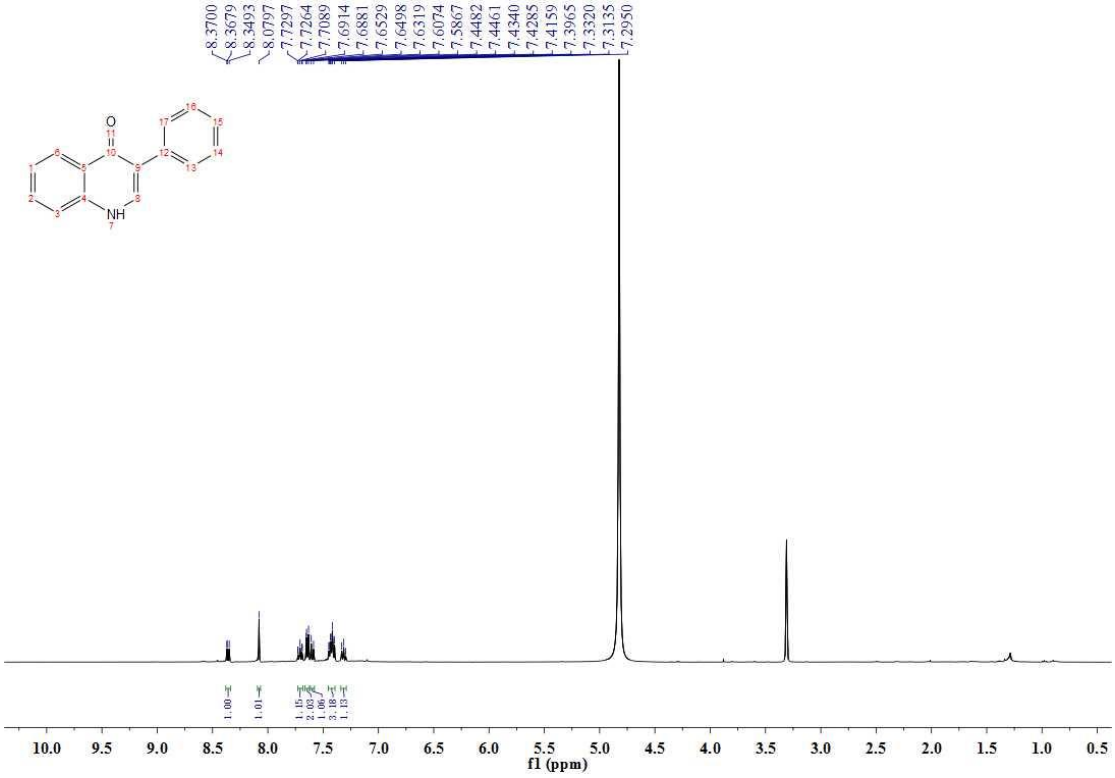
^{1}H NMR spectrum for **5m** ($CDCl_3$, 400 MHz)



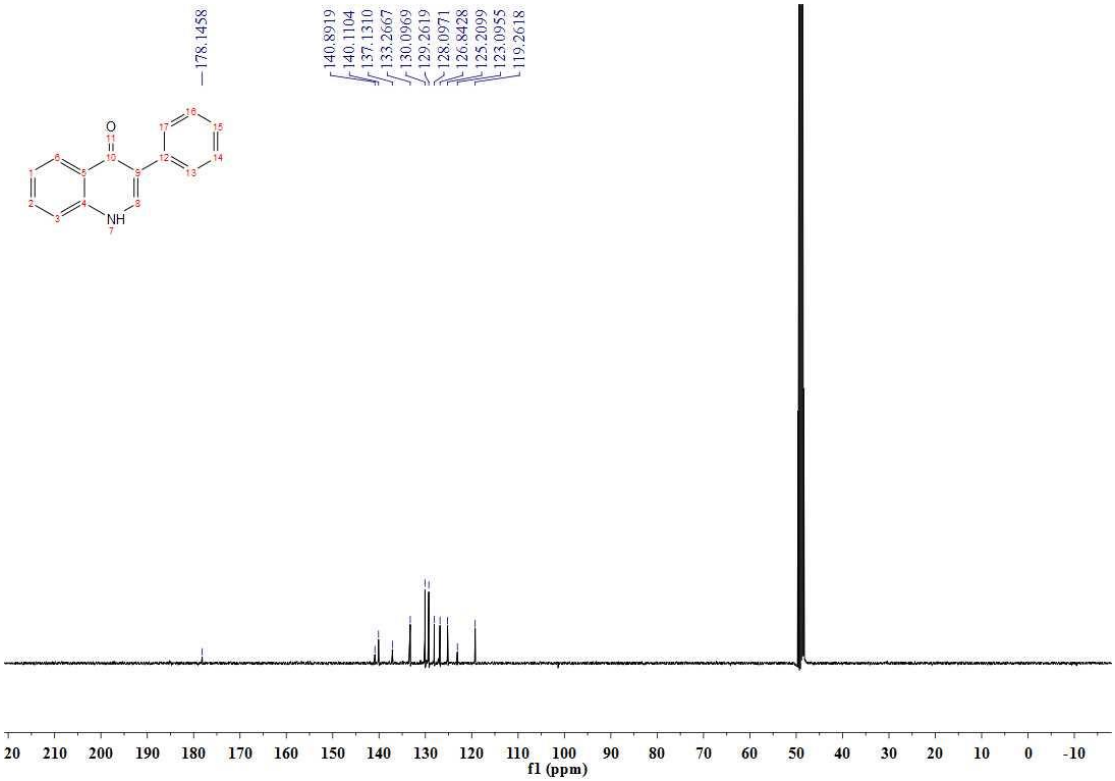
^{13}C NMR spectrum for **5m** ($CDCl_3$, 101 MHz)



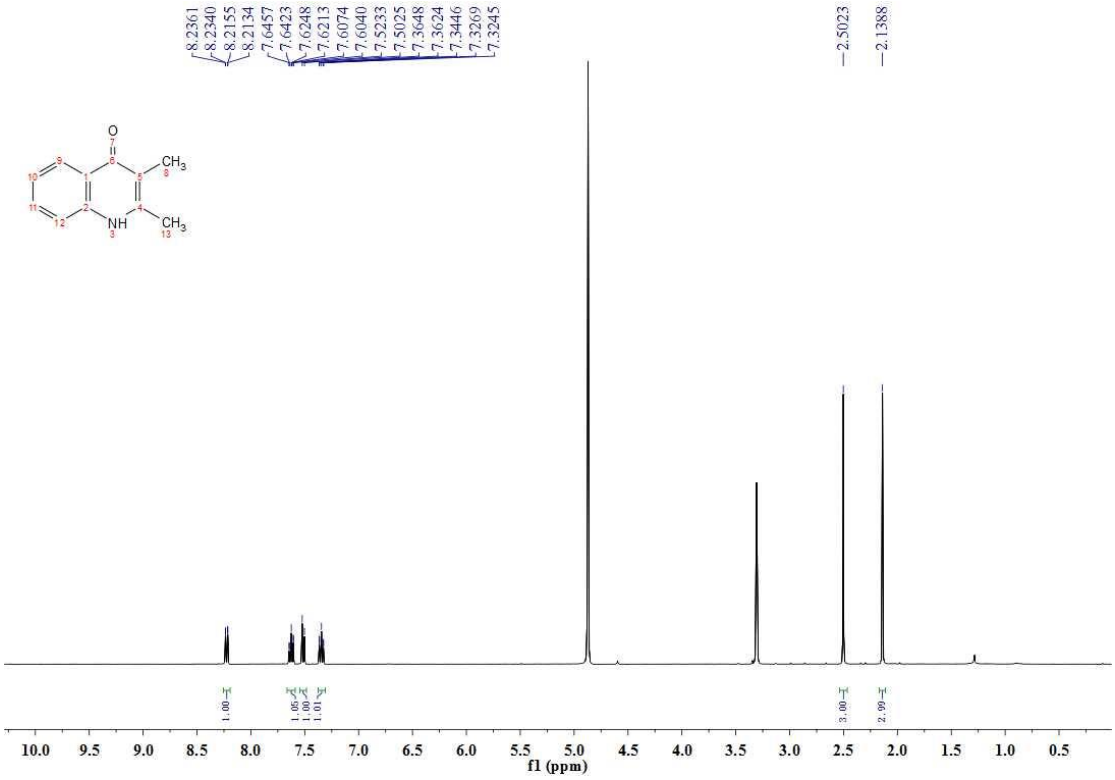
^{1}H NMR spectrum for **6a** (MeOD, 400 MHz)



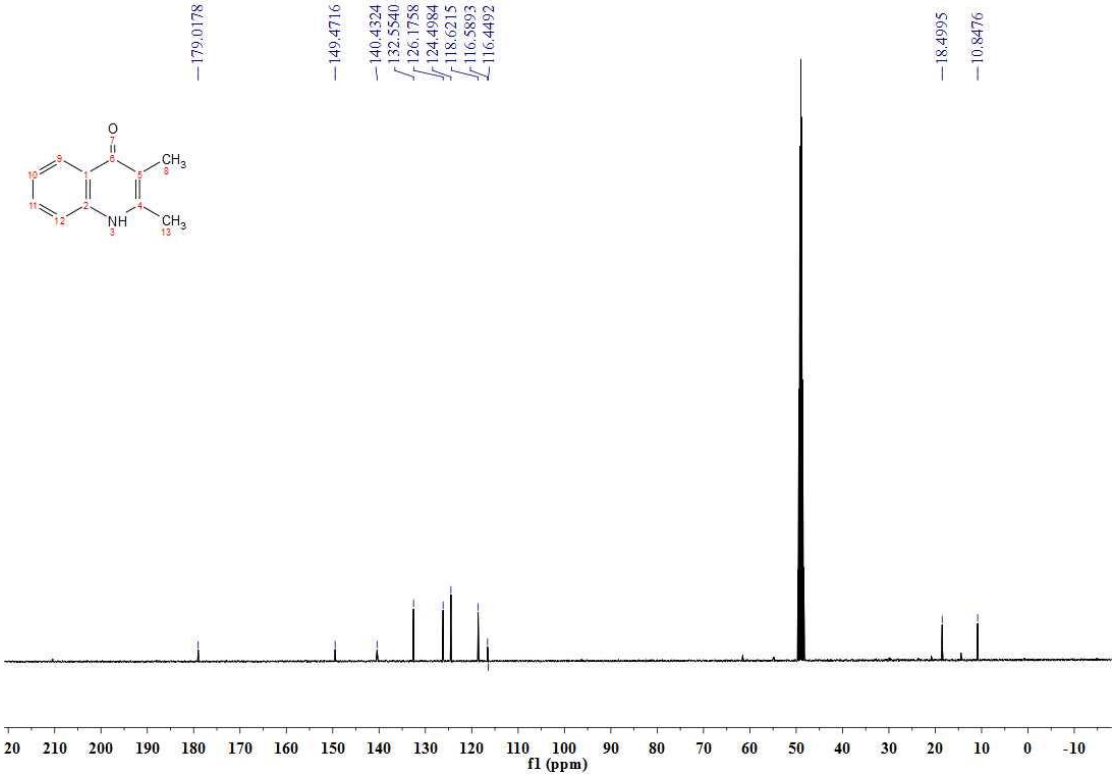
^{13}C NMR spectrum for **6a** (MeOD, 101 MHz)



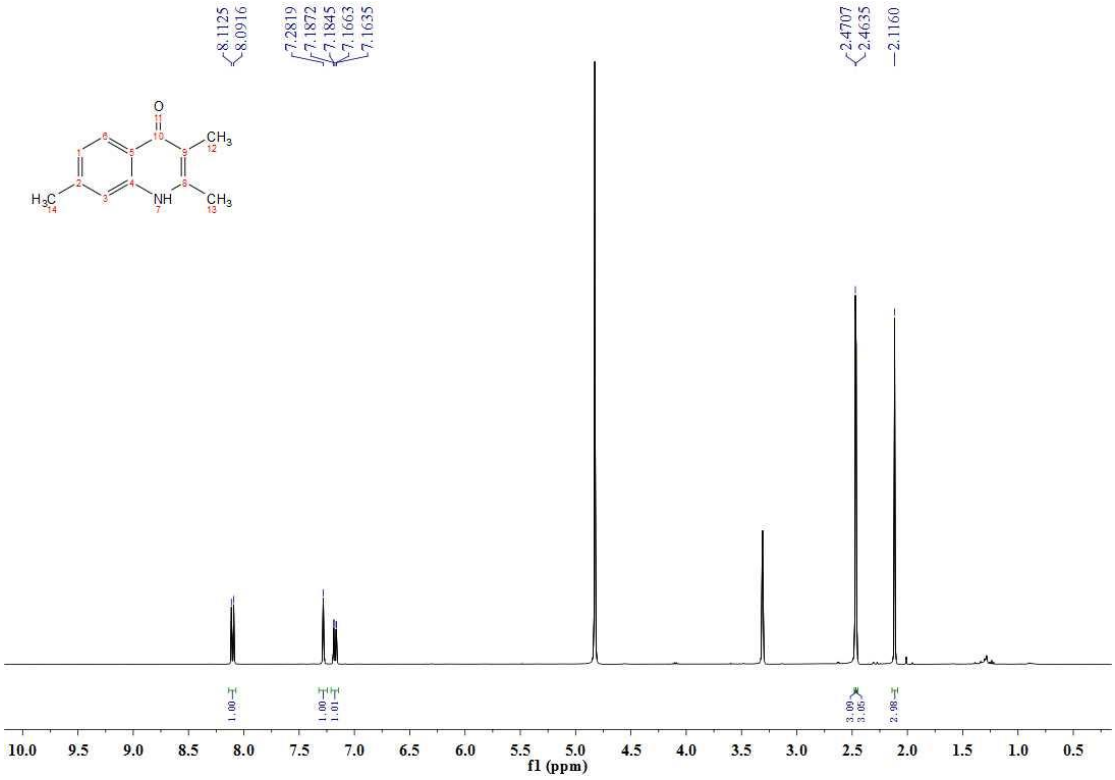
^{1}H NMR spectrum for **6b** (MeOD, 400 MHz)



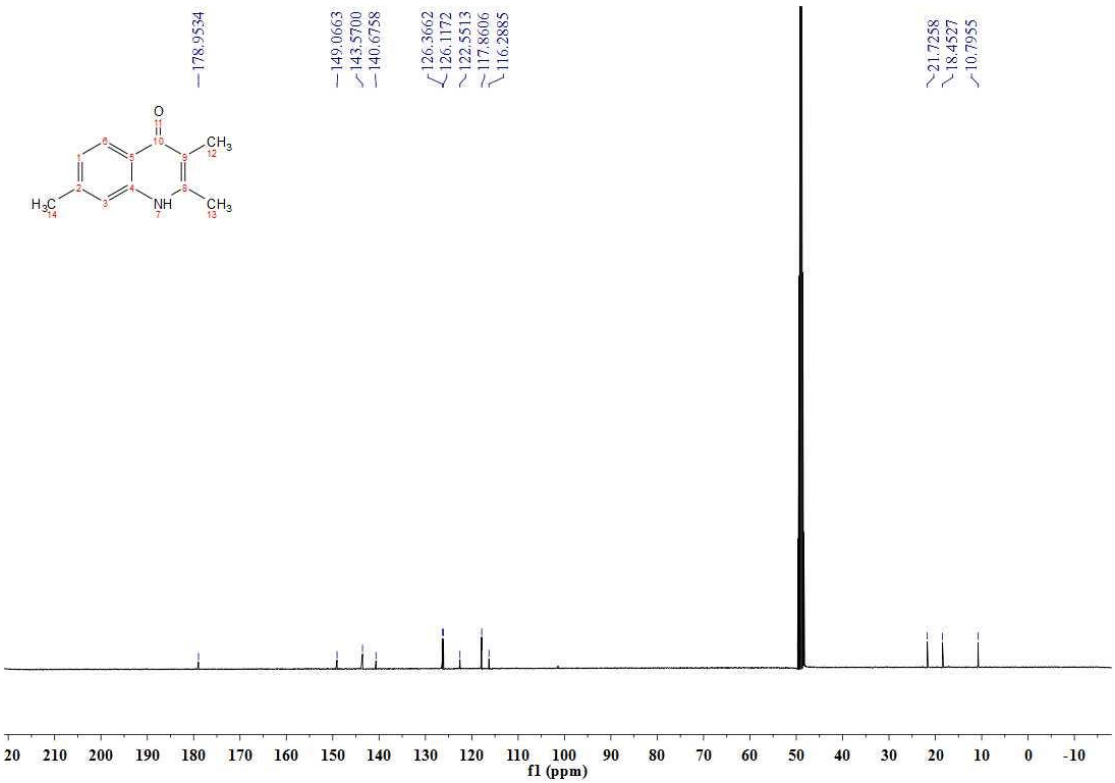
^{13}C NMR spectrum for **6b** (MeOD, 101 MHz)



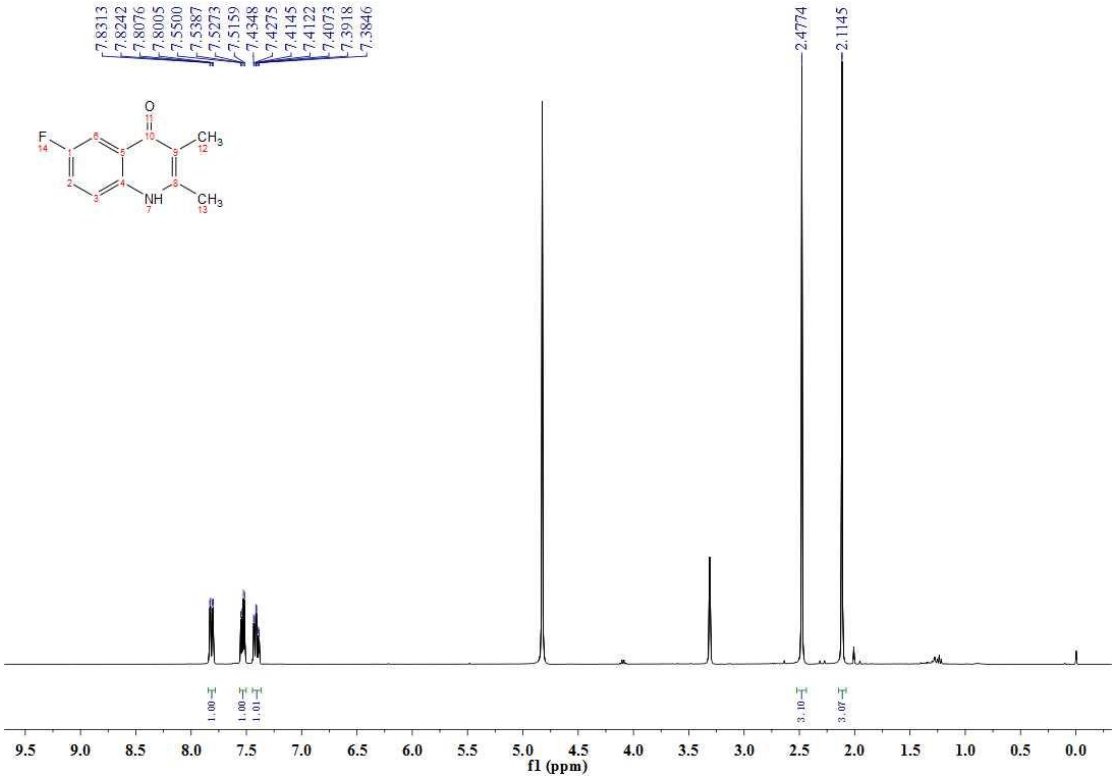
^{1}H NMR spectrum for **6c** (DMSO-d6, 400 MHz)



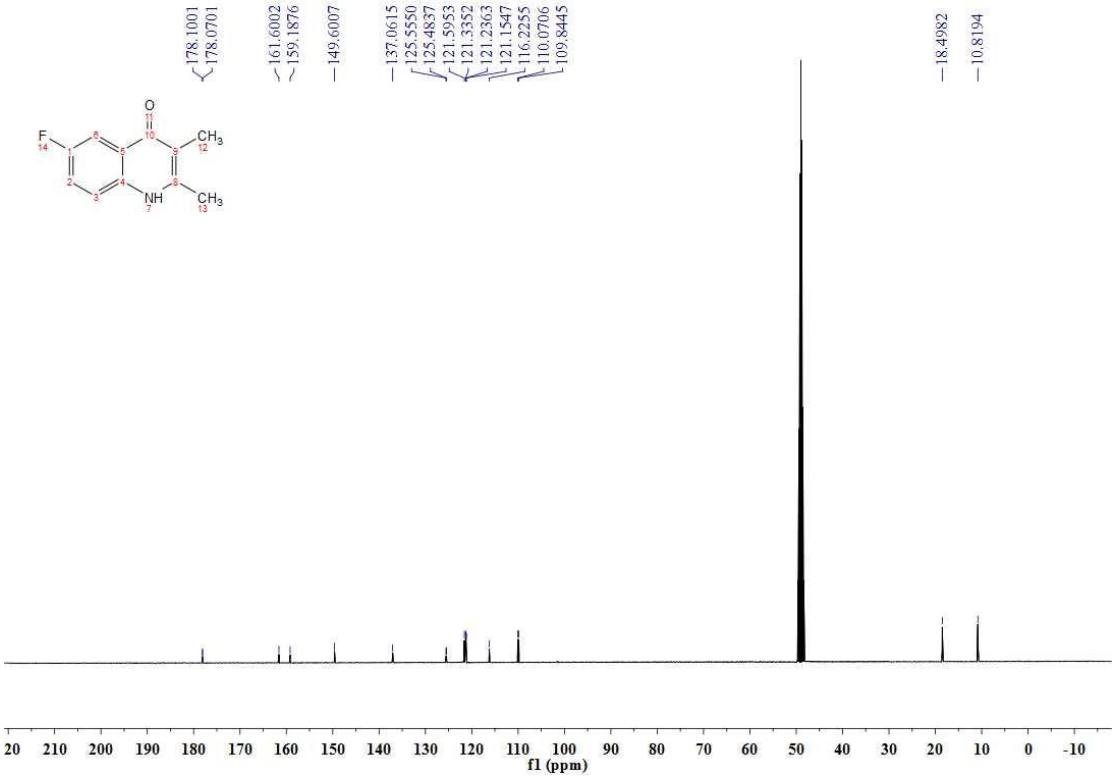
^{13}C NMR spectrum for **6c** (DMSO-d6, 101 MHz)



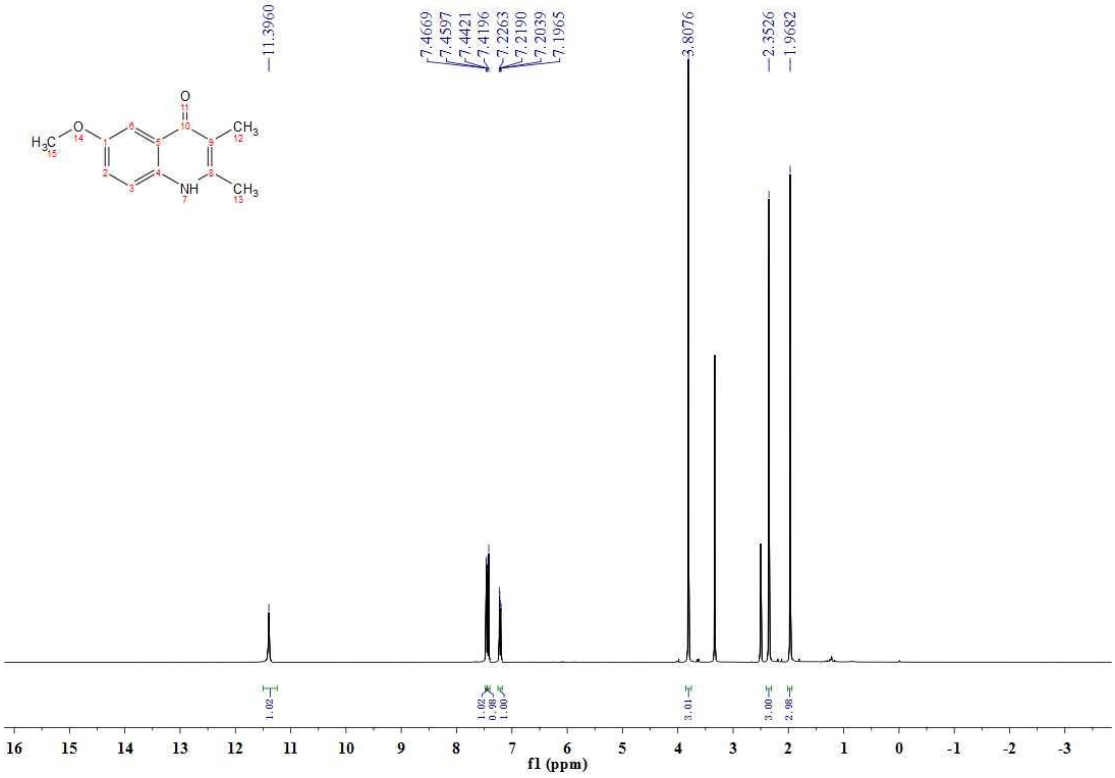
^{1}H NMR spectrum for **6d** (DMSO-d6, 400 MHz)



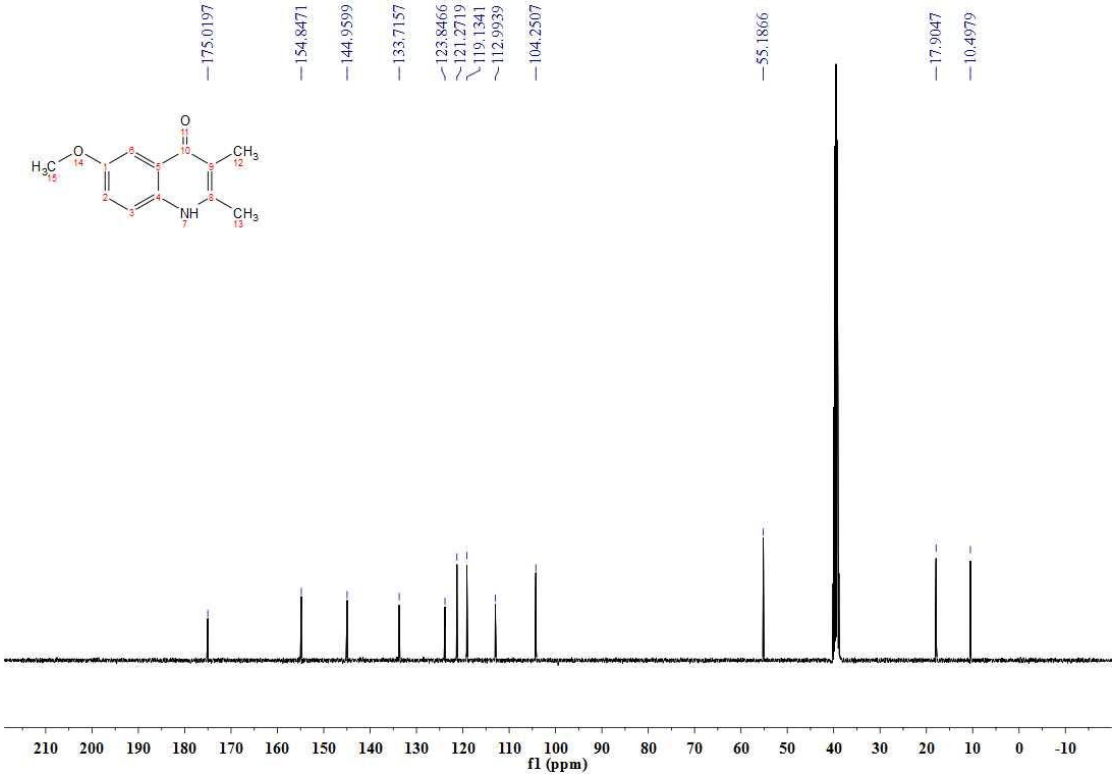
^{13}C NMR spectrum for **6d** (DMSO-d6, 101 MHz)



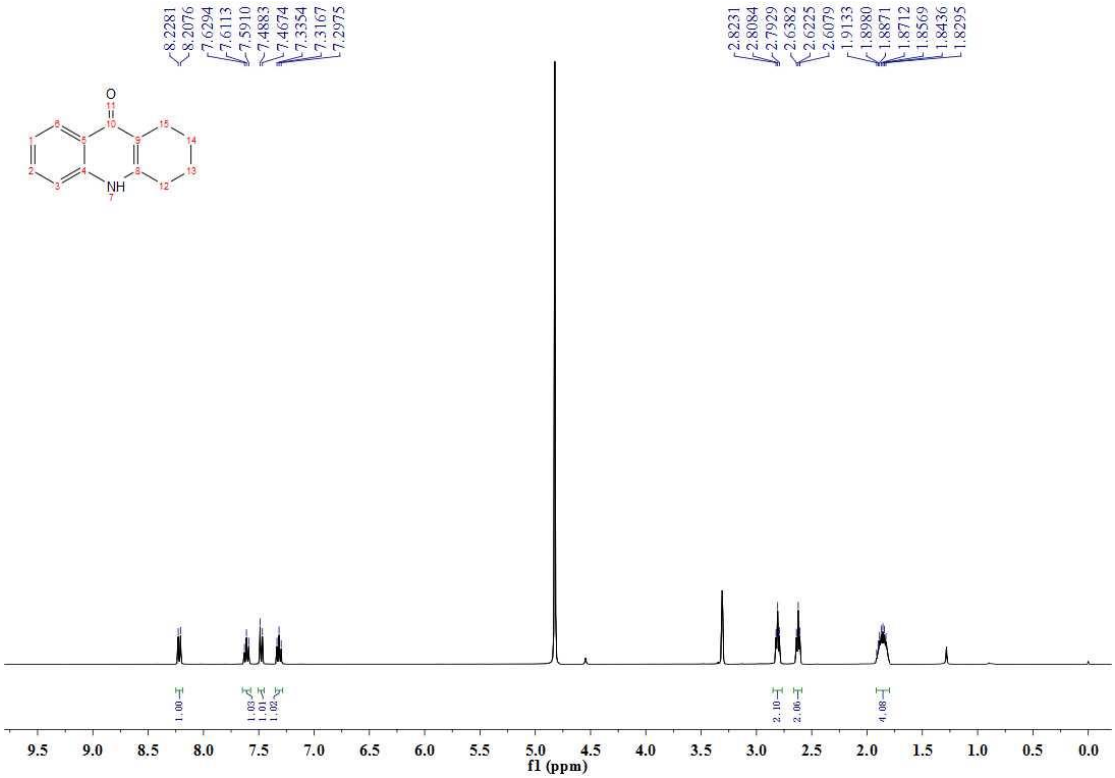
^{1}H NMR spectrum for **6e** (DMSO-d6, 400 MHz)



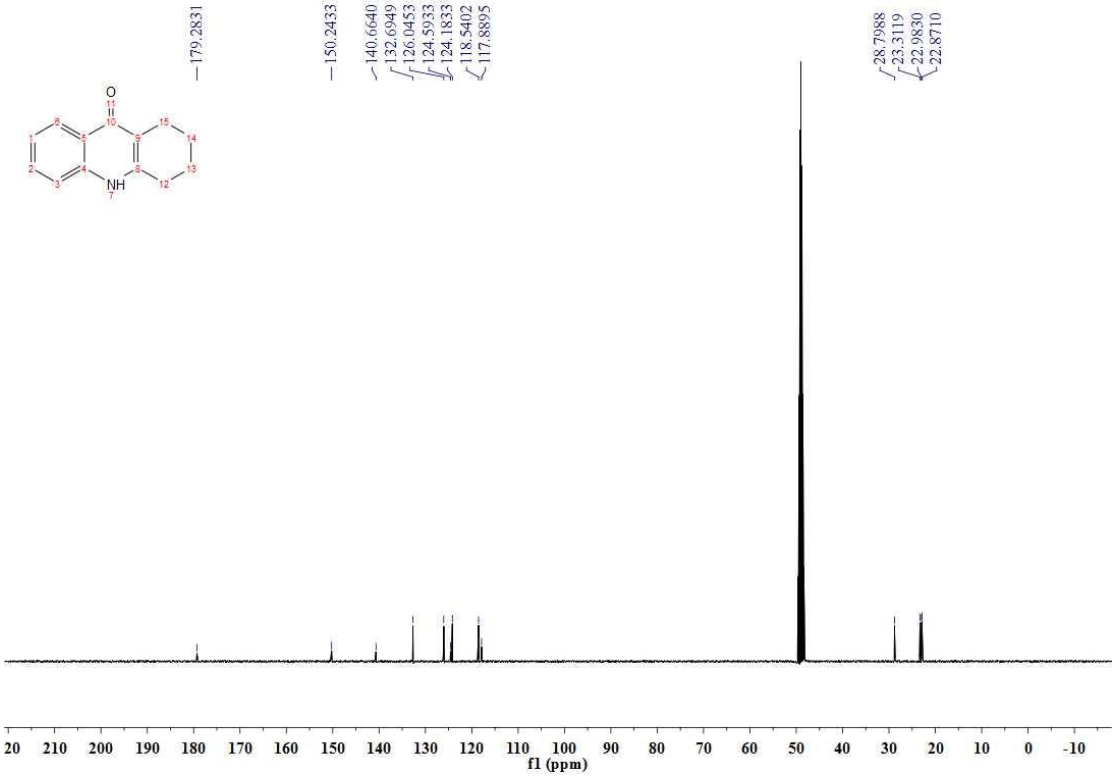
^{13}C NMR spectrum for **6e** (DMSO-d6, 101 MHz)



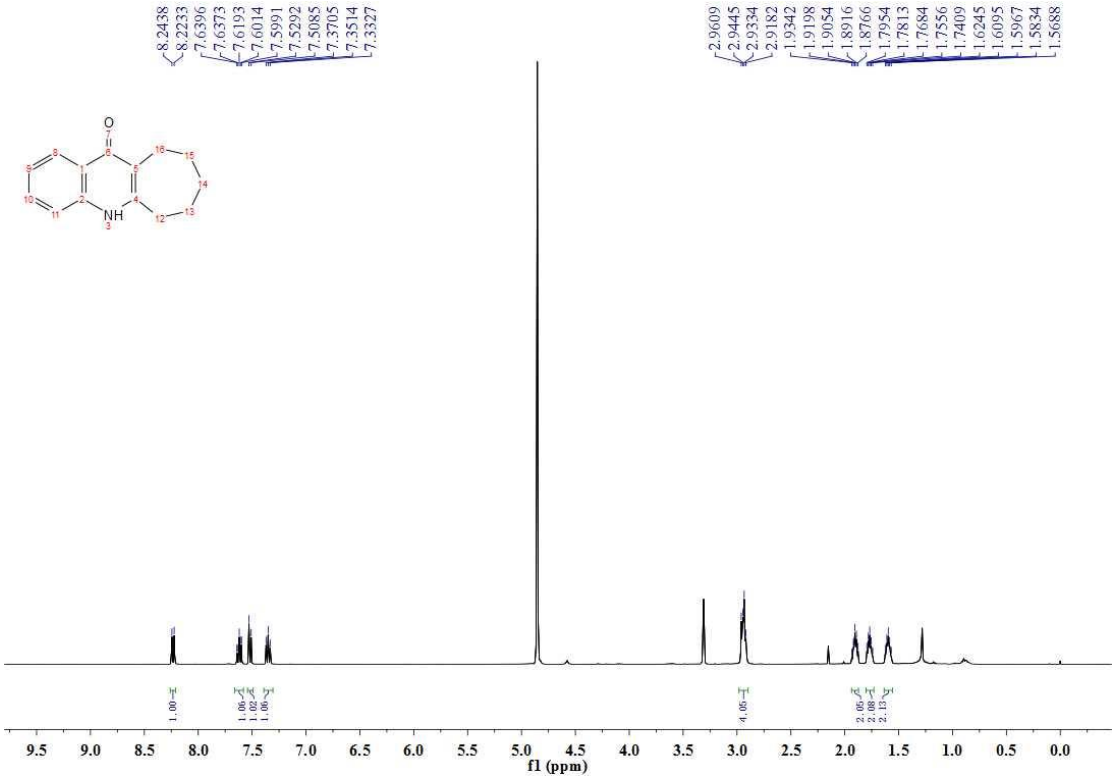
^{1}H NMR spectrum for **6f** (MeOD, 400 MHz)



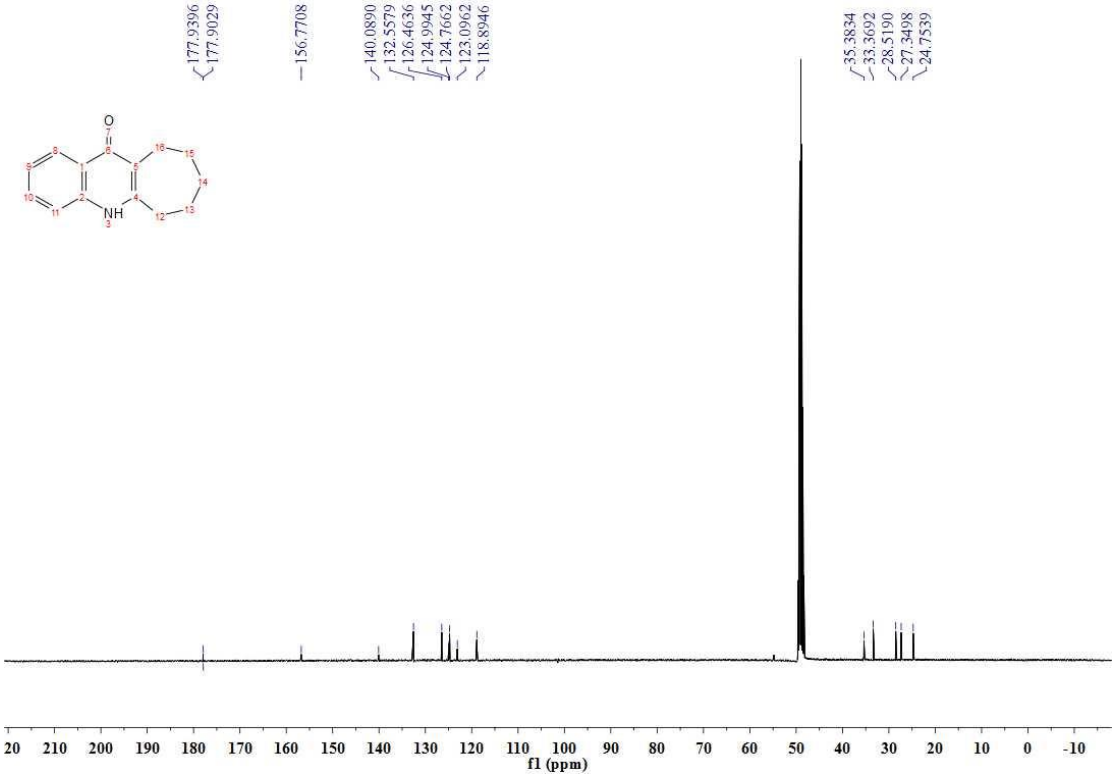
^{13}C NMR spectrum for **6f** (MeOD, 101 MHz)



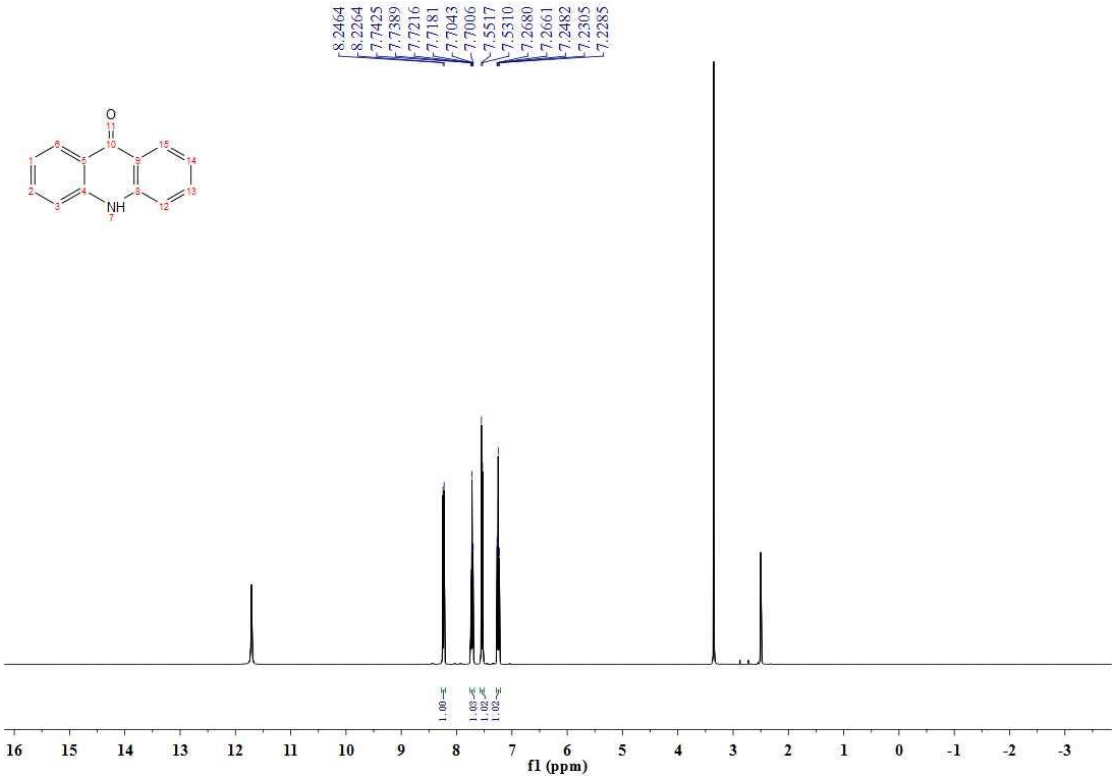
^{1}H NMR spectrum for **6g** (MeOD, 400 MHz)



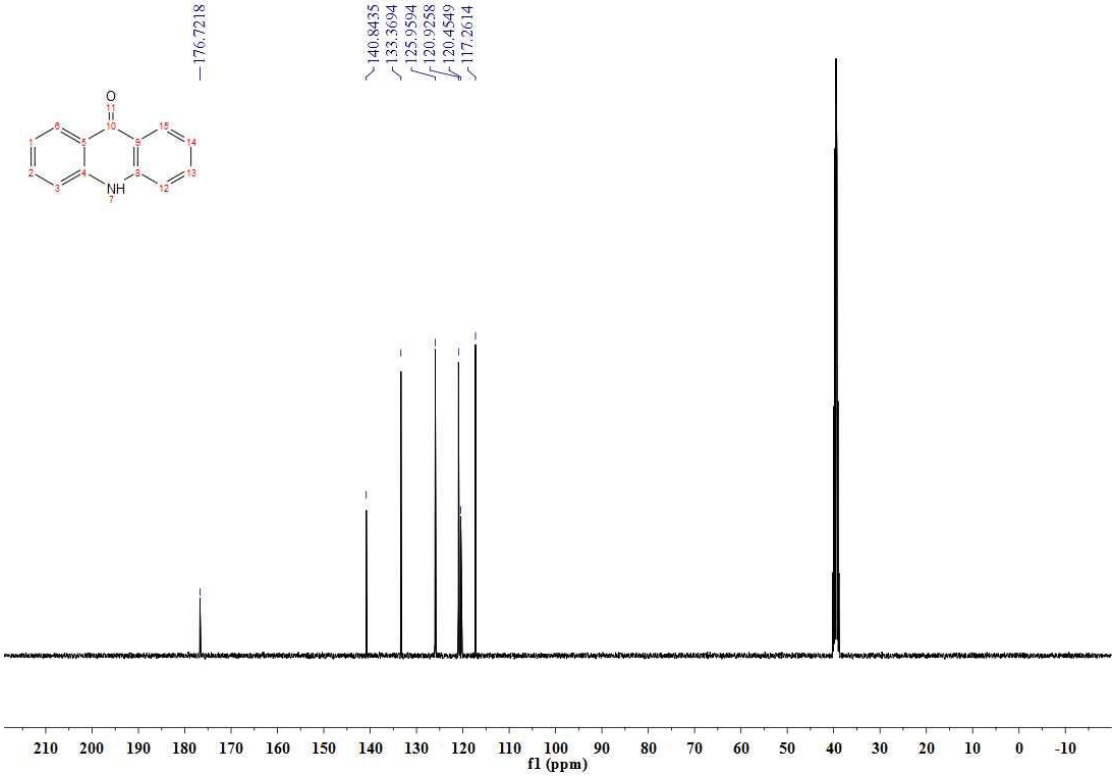
^{13}C NMR spectrum for **6g** (MeOD, 101 MHz)



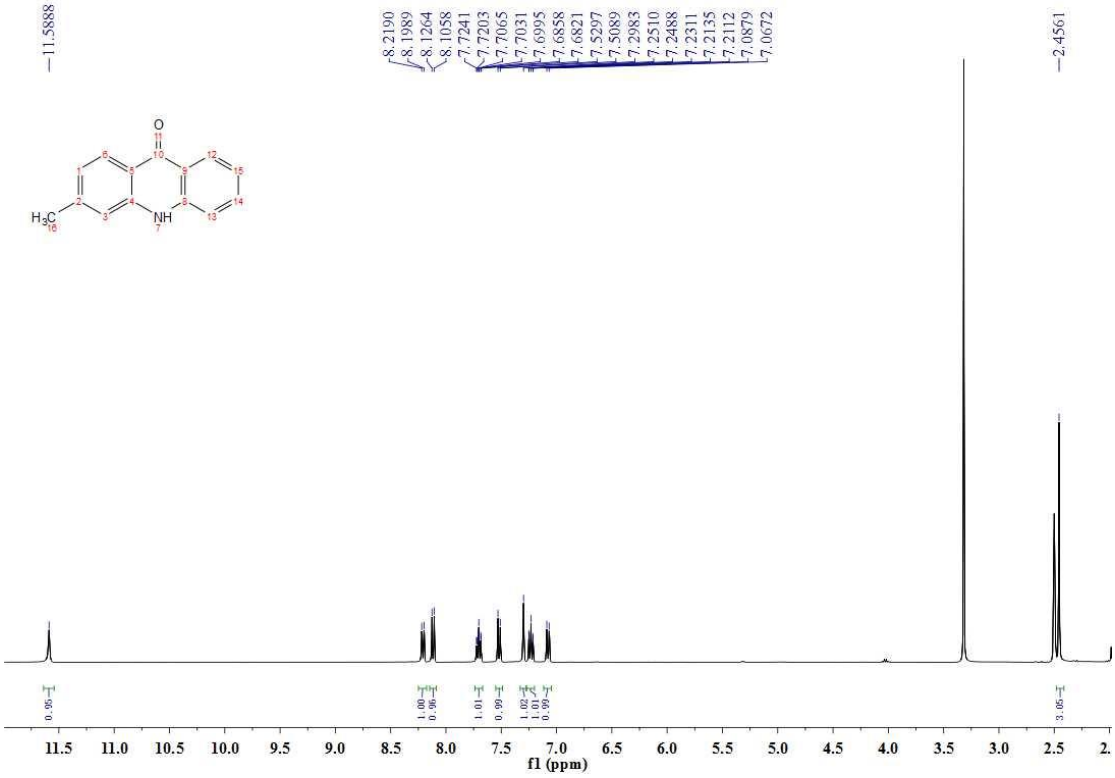
^{1}H NMR spectrum for **6h** (DMSO-d6, 400 MHz)



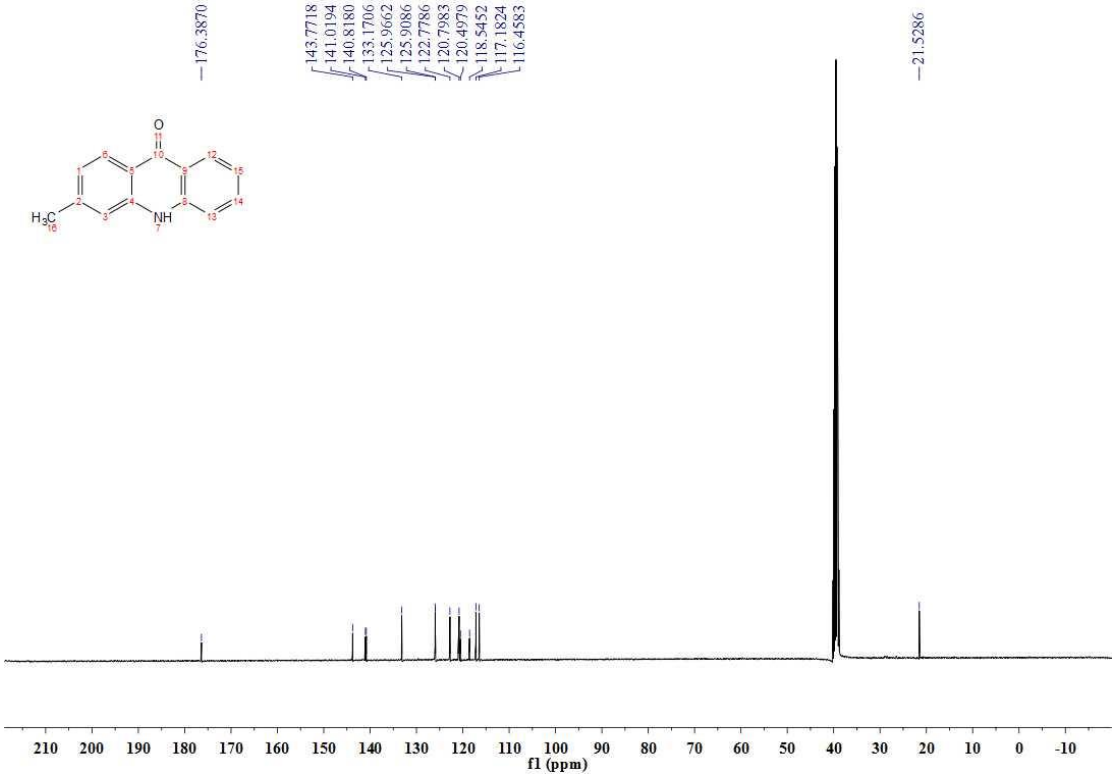
^{13}C NMR spectrum for **6h** (DMSO-d6, 101 MHz)



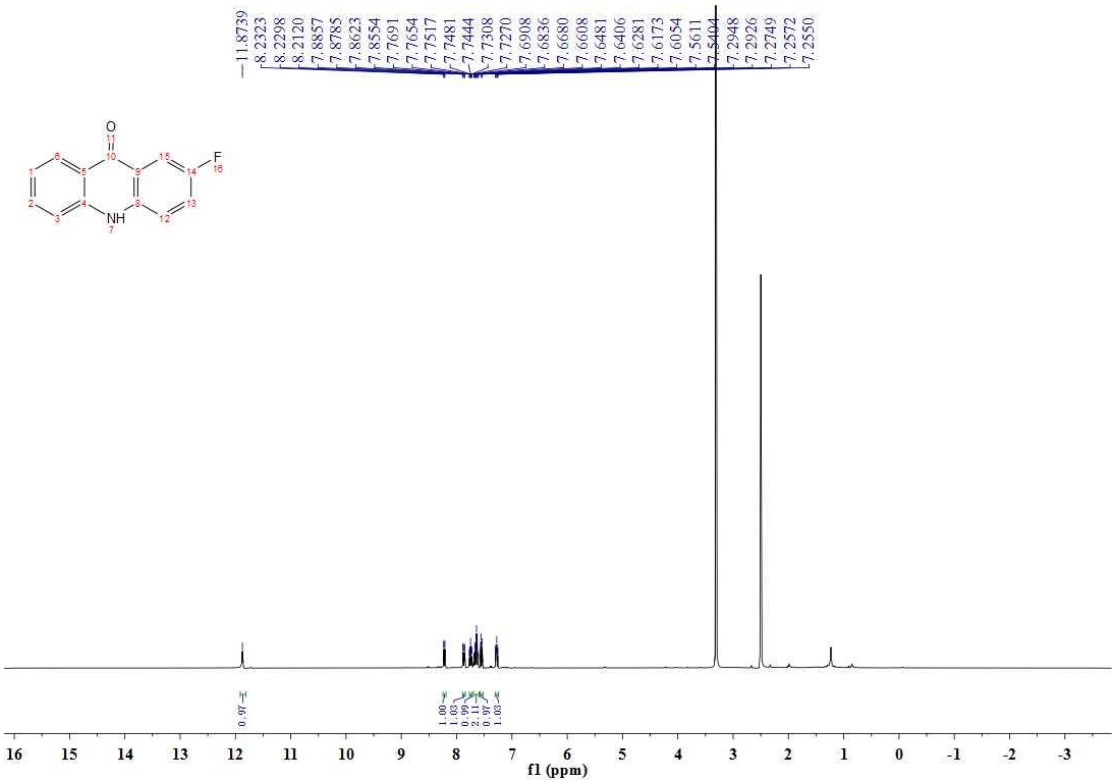
^{1}H NMR spectrum for **6i** (DMSO-d6, 400 MHz)



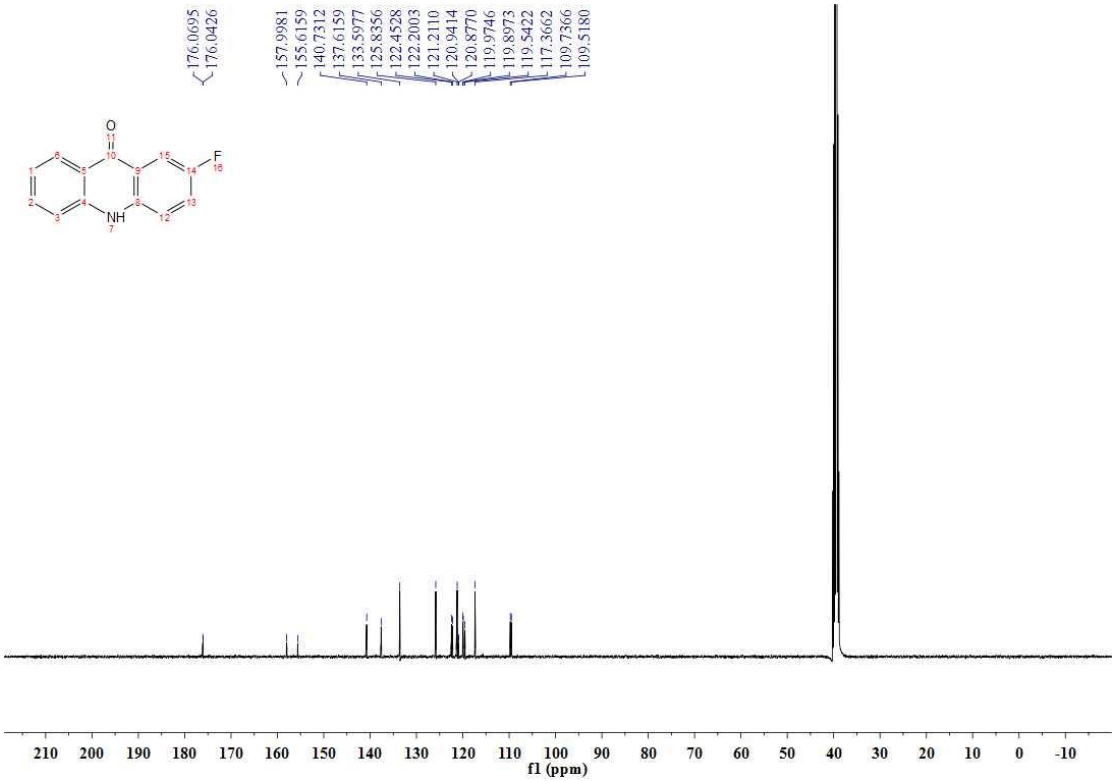
^{13}C NMR spectrum for **6i** (DMSO-d6, 101 MHz)



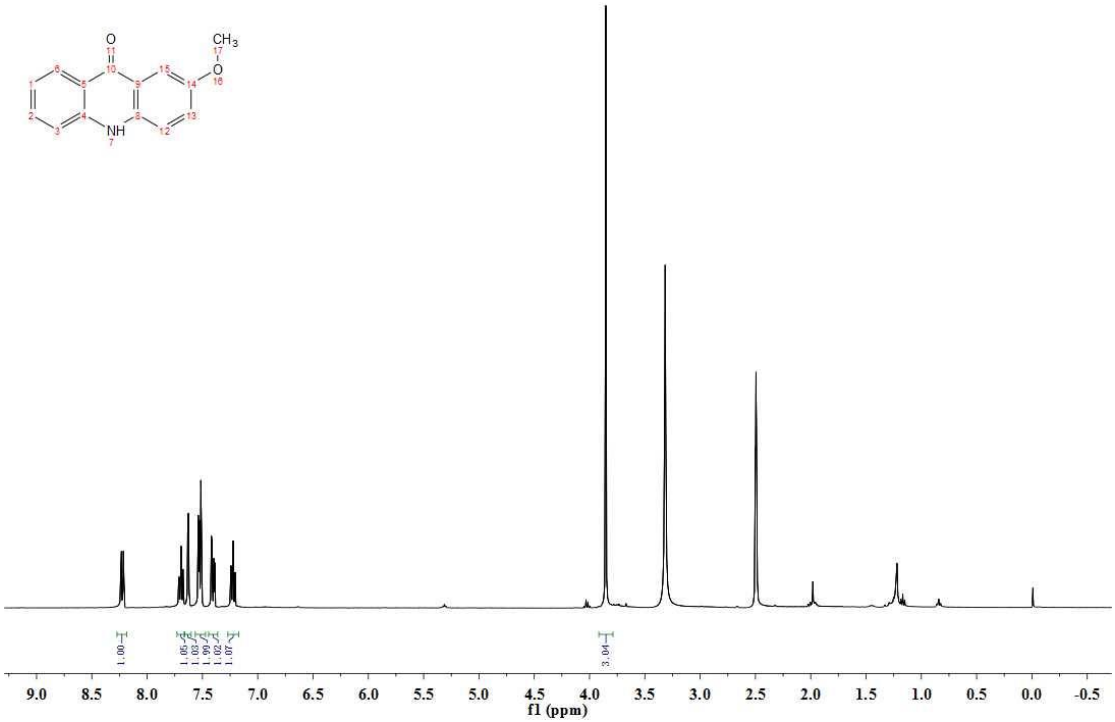
^{1}H NMR spectrum for **6j** (DMSO-d6, 400 MHz)



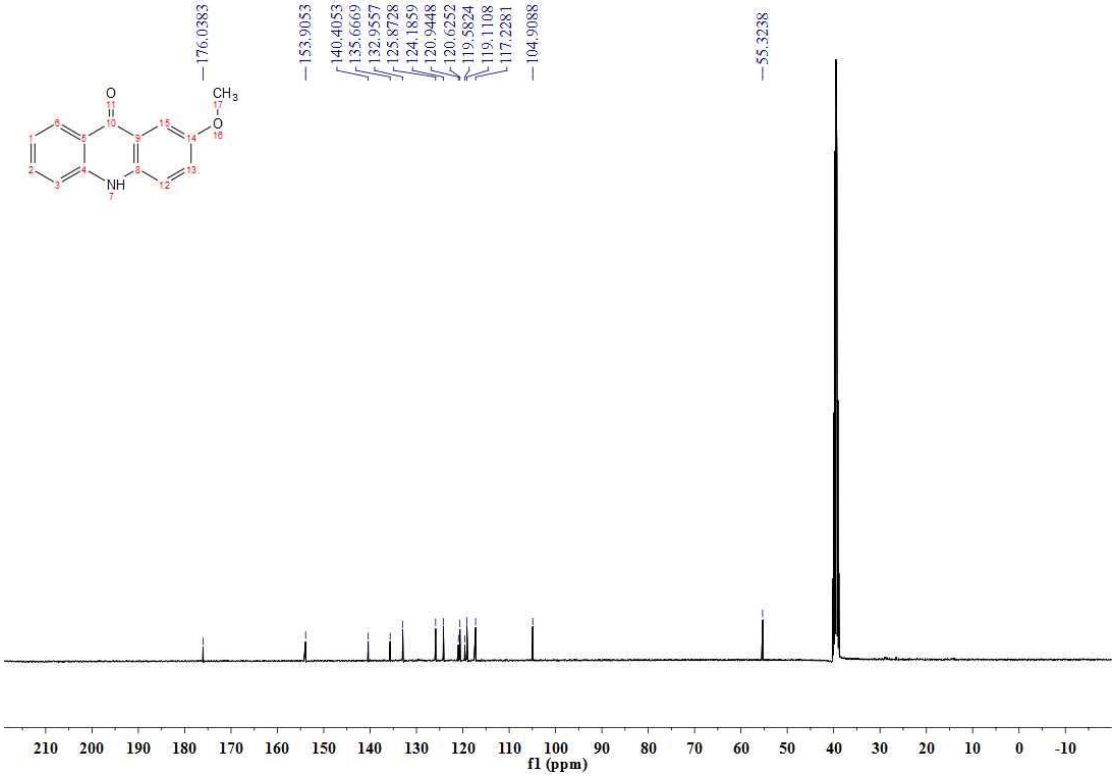
^{13}C NMR spectrum for **6j** (DMSO-d6, 101 MHz)



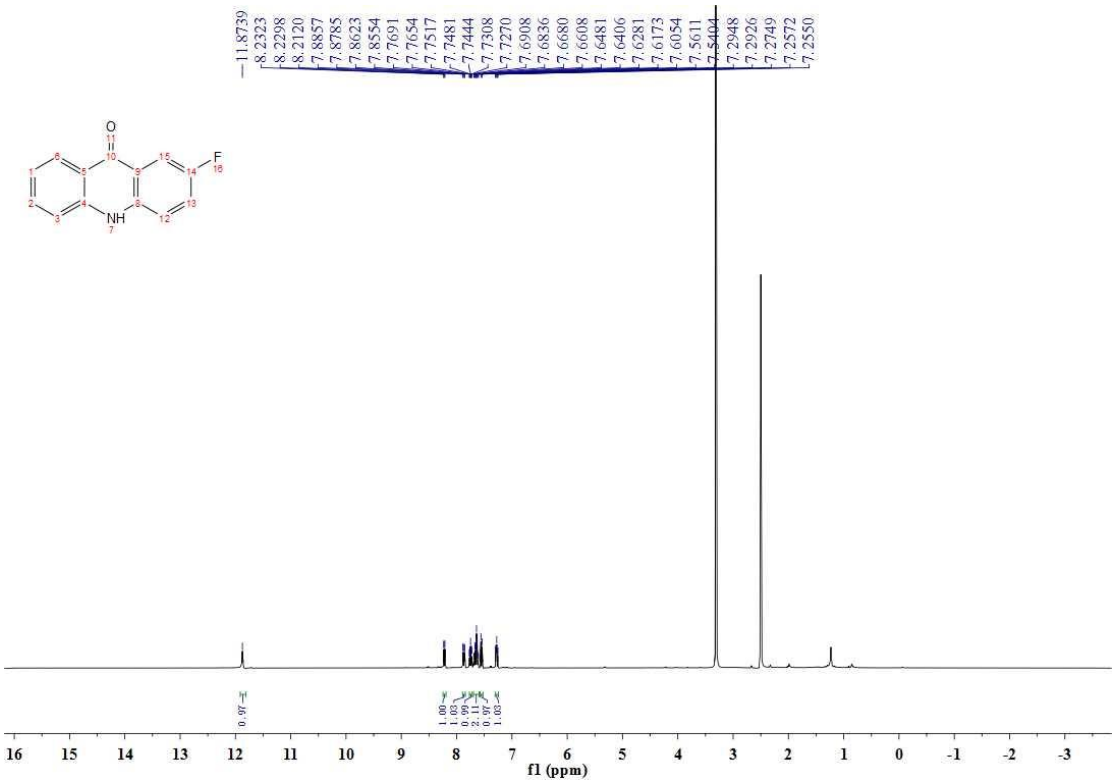
^{1}H NMR spectrum for **6k** (DMSO-d6, 400 MHz)



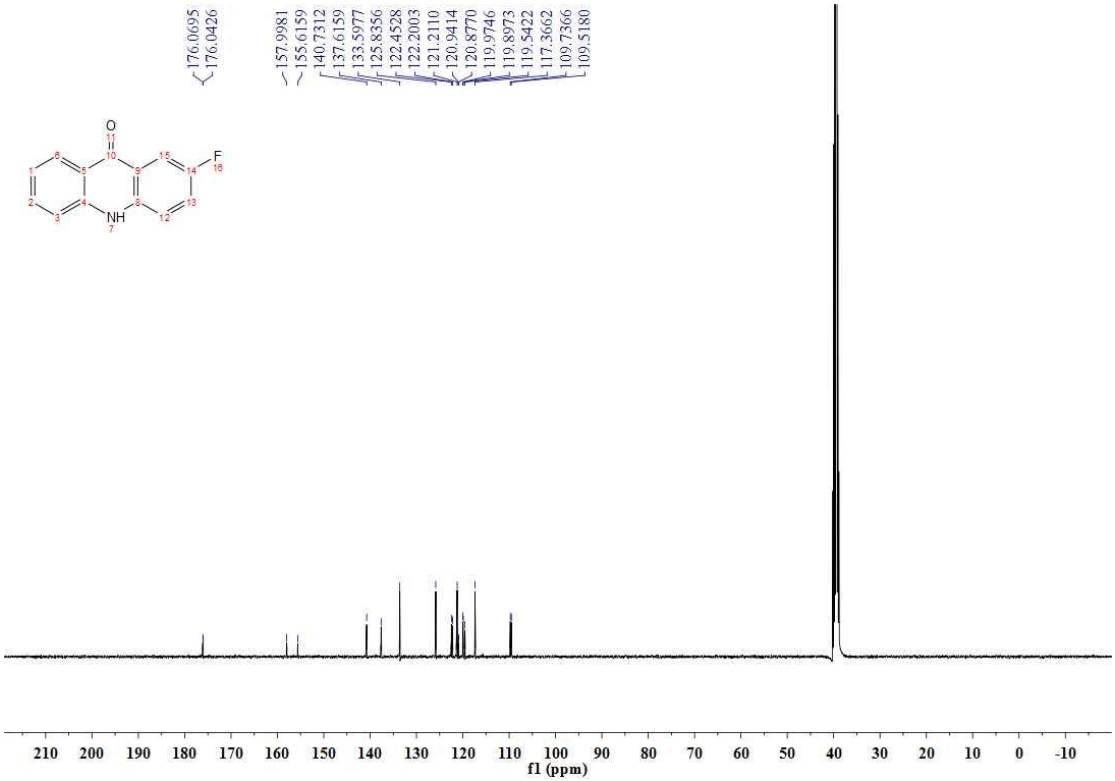
^{13}C NMR spectrum for **6k** (DMSO-d6, 101 MHz)



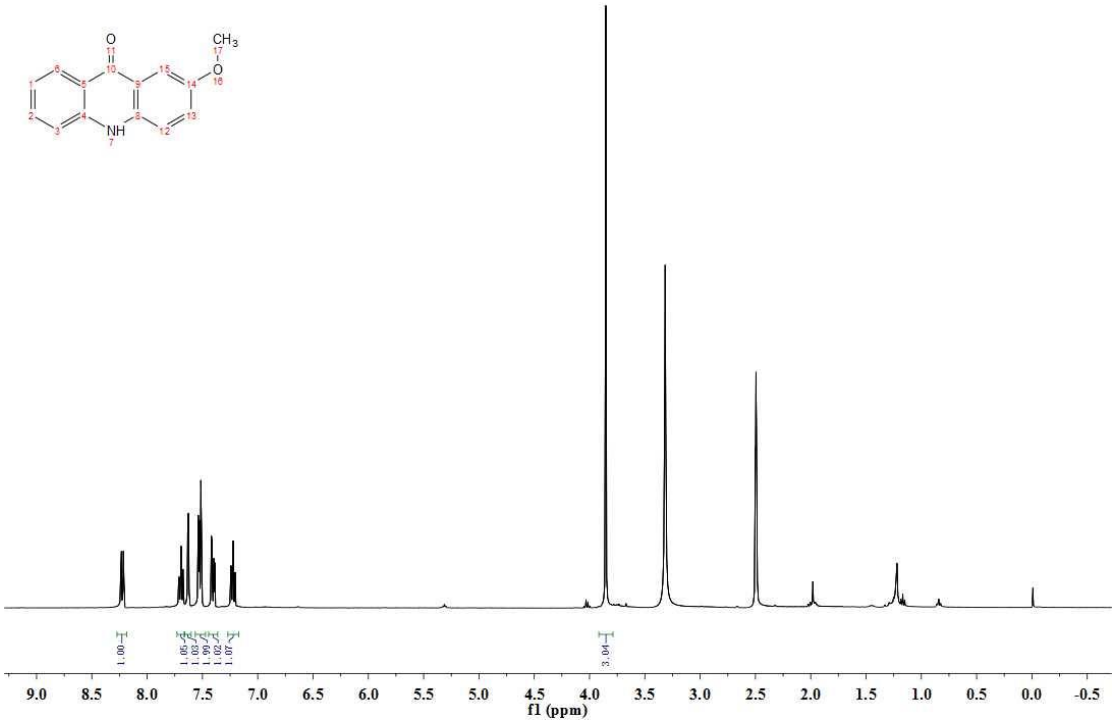
^{1}H NMR spectrum for **6l** (DMSO-d6, 400 MHz)



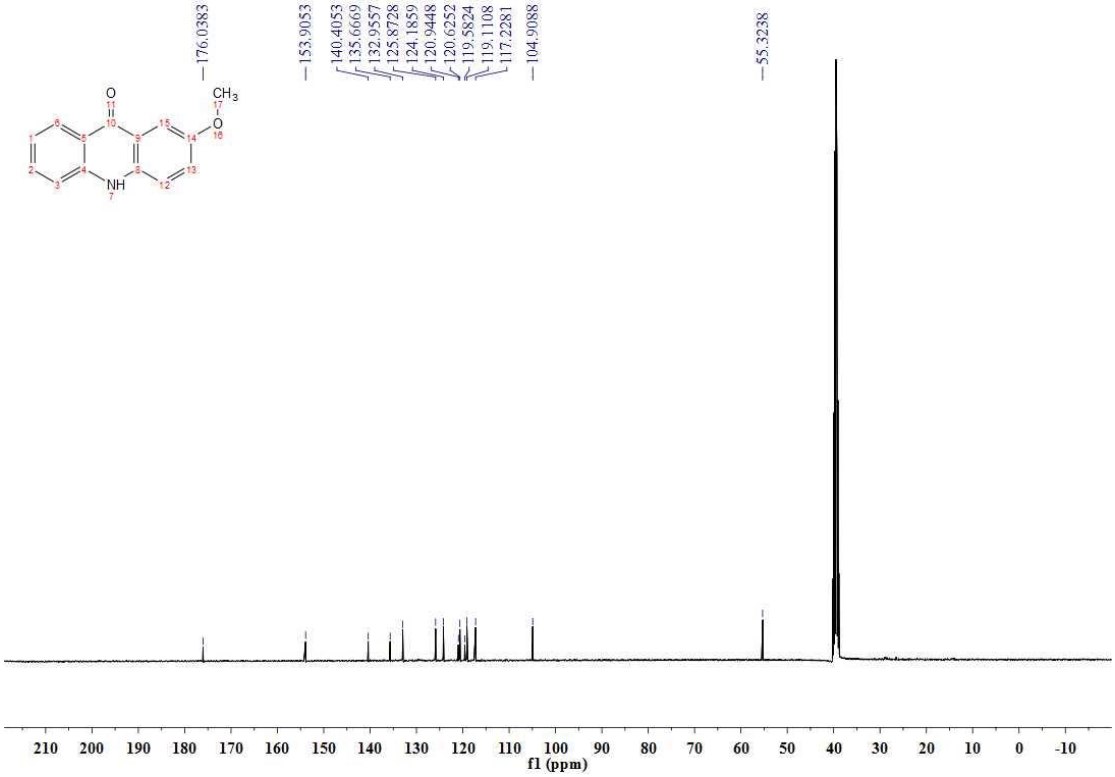
^{13}C NMR spectrum for **6l** (DMSO-d6, 101 MHz)



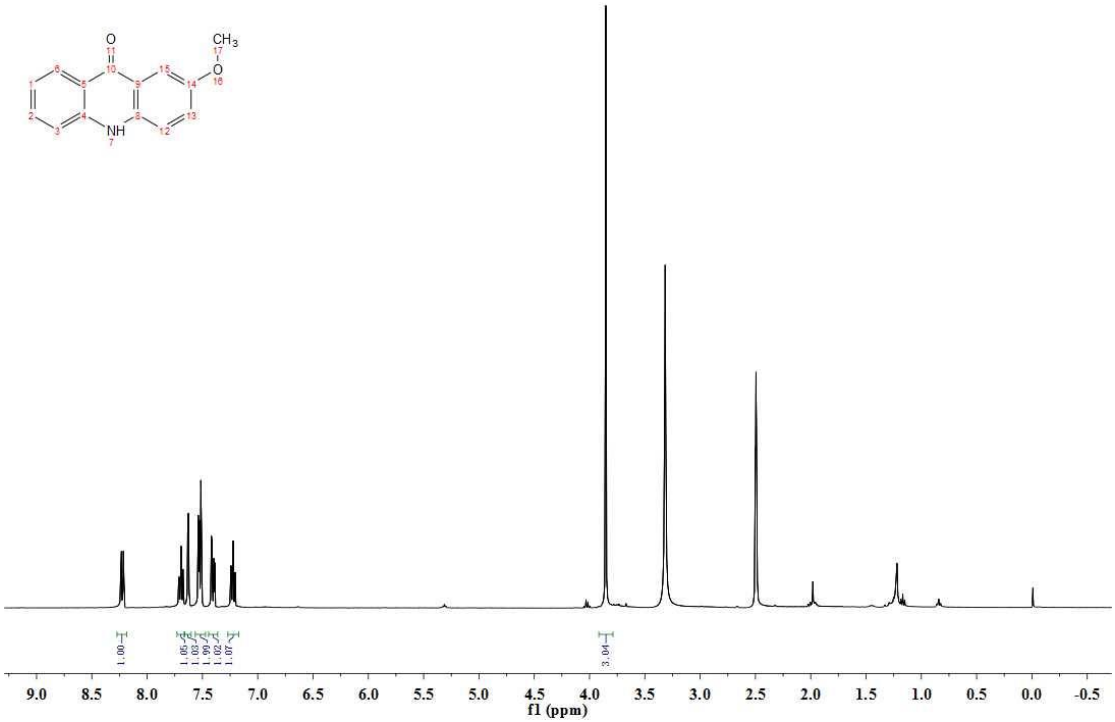
^{1}H NMR spectrum for **6m** (DMSO-d6, 400 MHz)



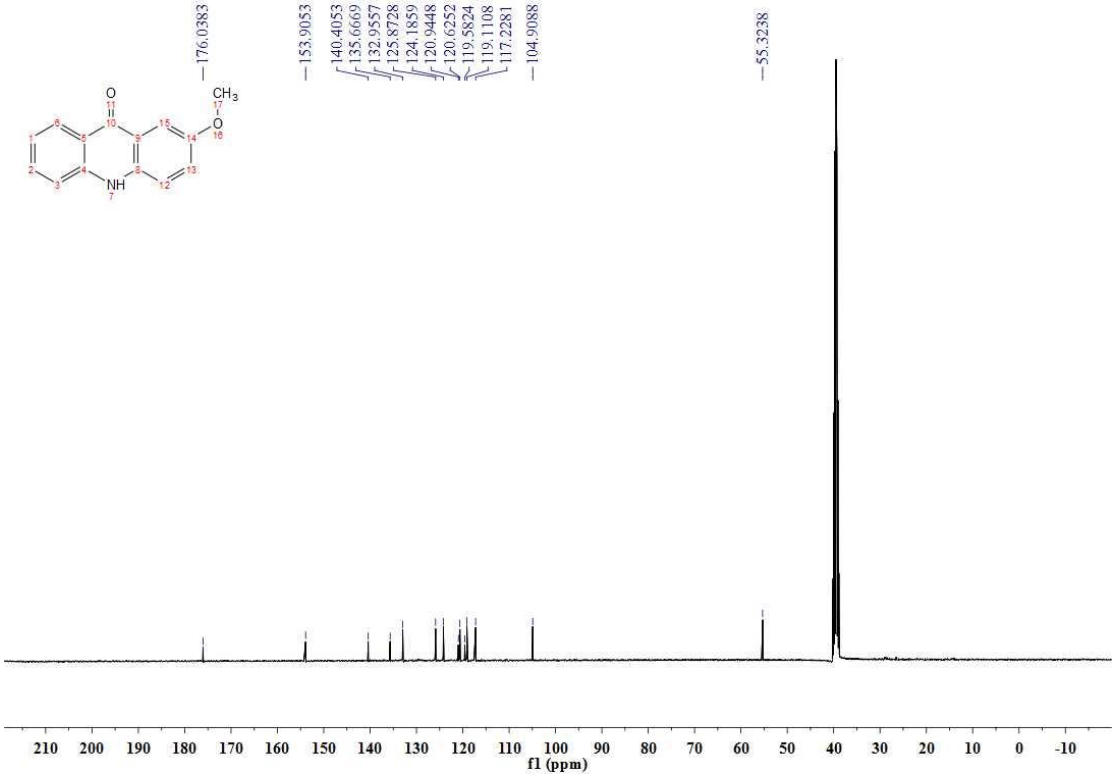
^{13}C NMR spectrum for **6m** (DMSO-d6, 101 MHz)



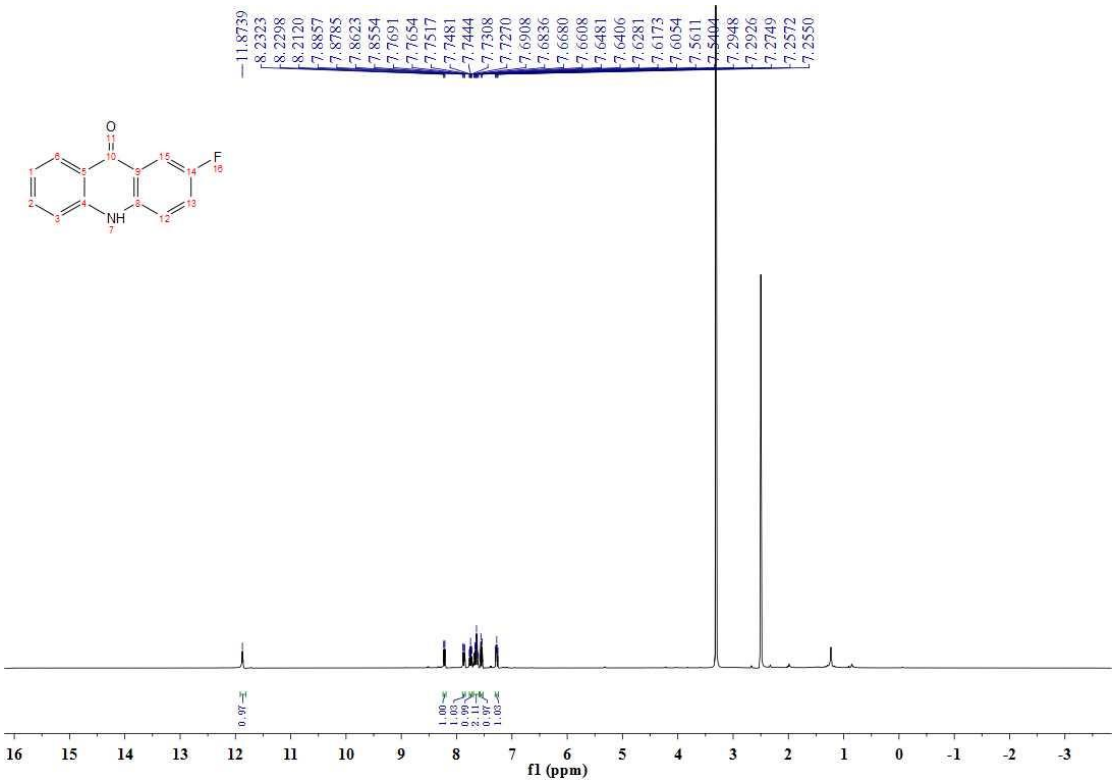
^{1}H NMR spectrum for **6l** (DMSO-d6, 400 MHz)



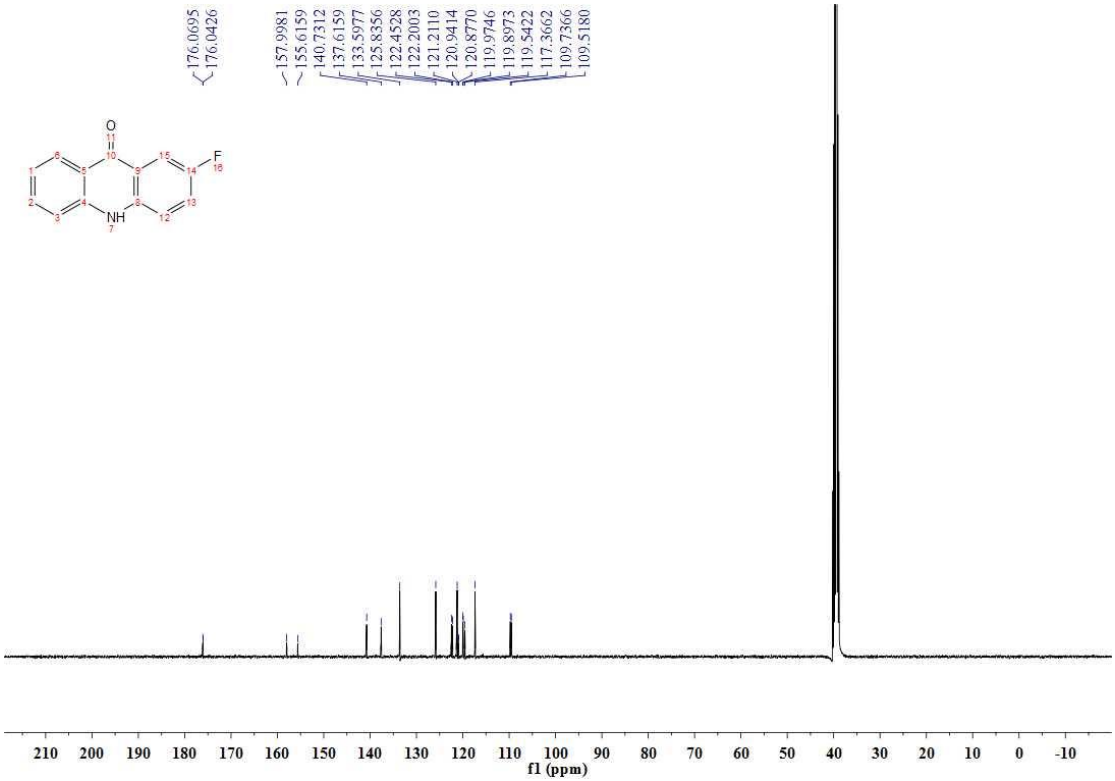
^{13}C NMR spectrum for **6l** (DMSO-d6, 101 MHz)



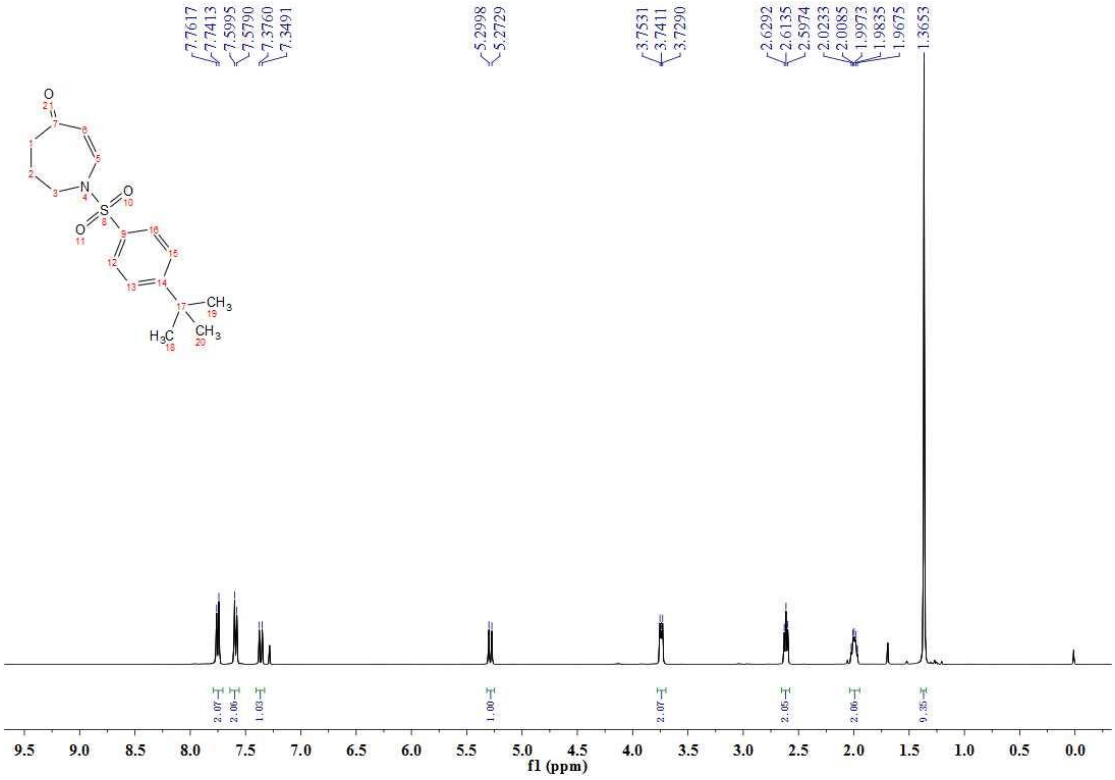
^{1}H NMR spectrum for **6m** (DMSO-d6, 400 MHz)



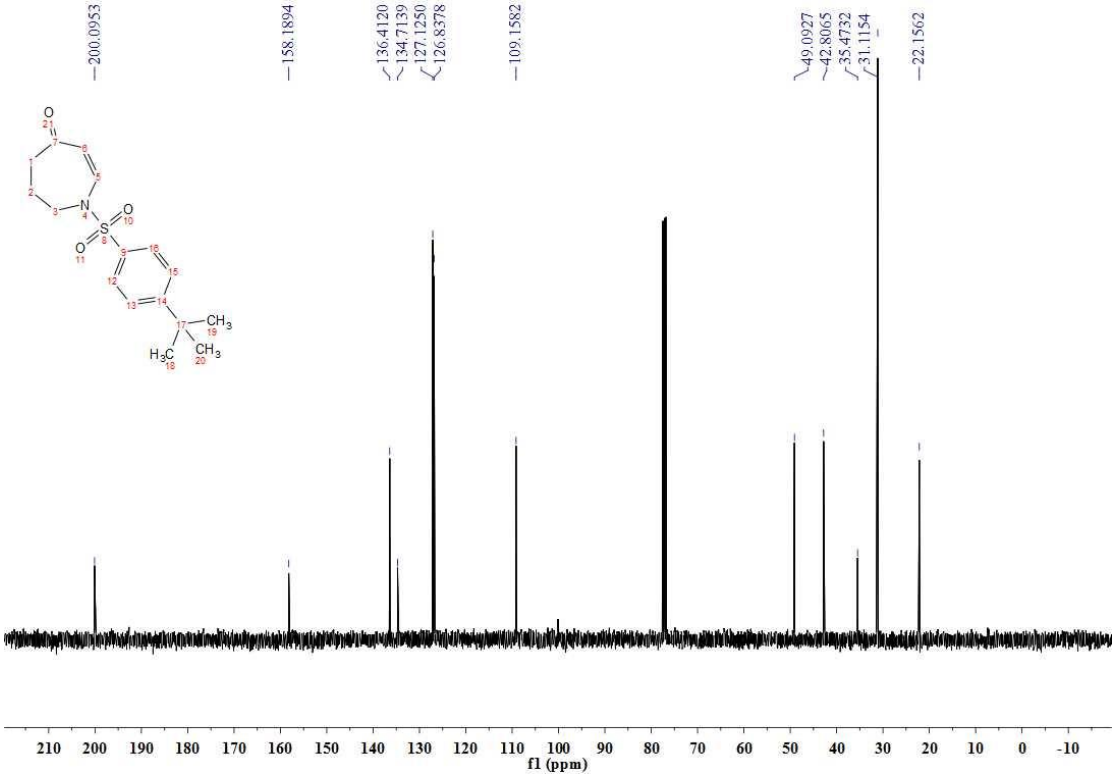
^{13}C NMR spectrum for **6m** (DMSO-d6, 101 MHz)



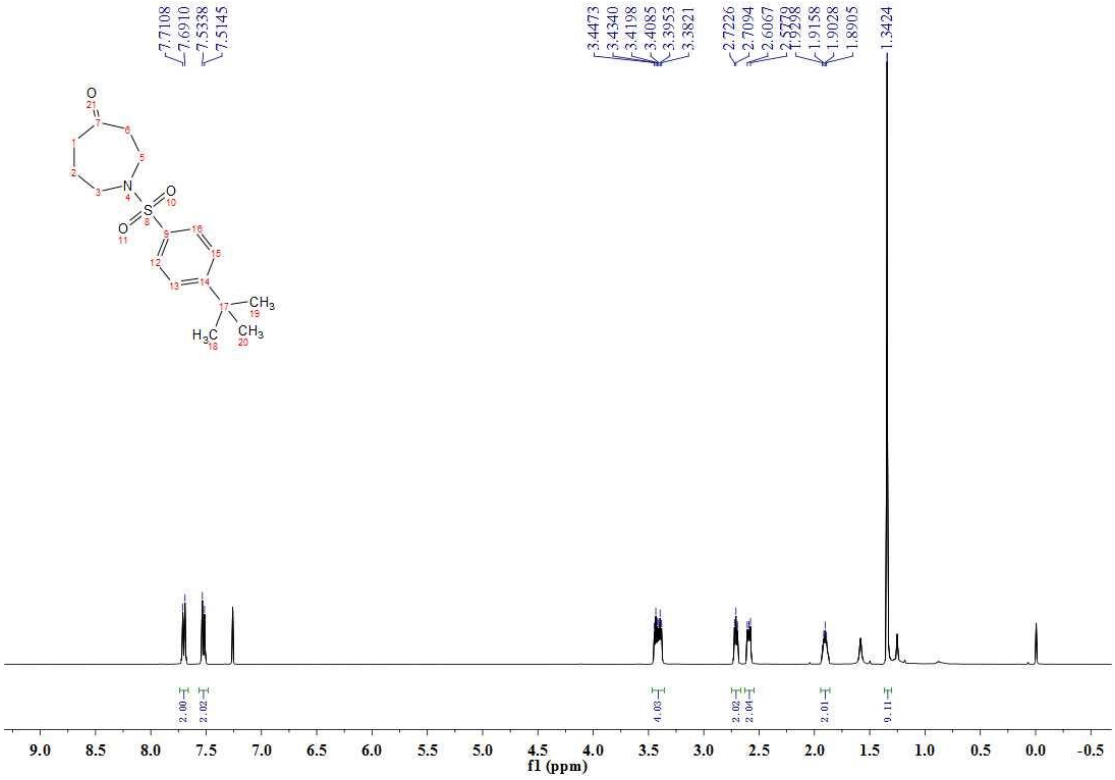
^{1}H NMR spectrum for **8a** ($CDCl_3$, 400 MHz)



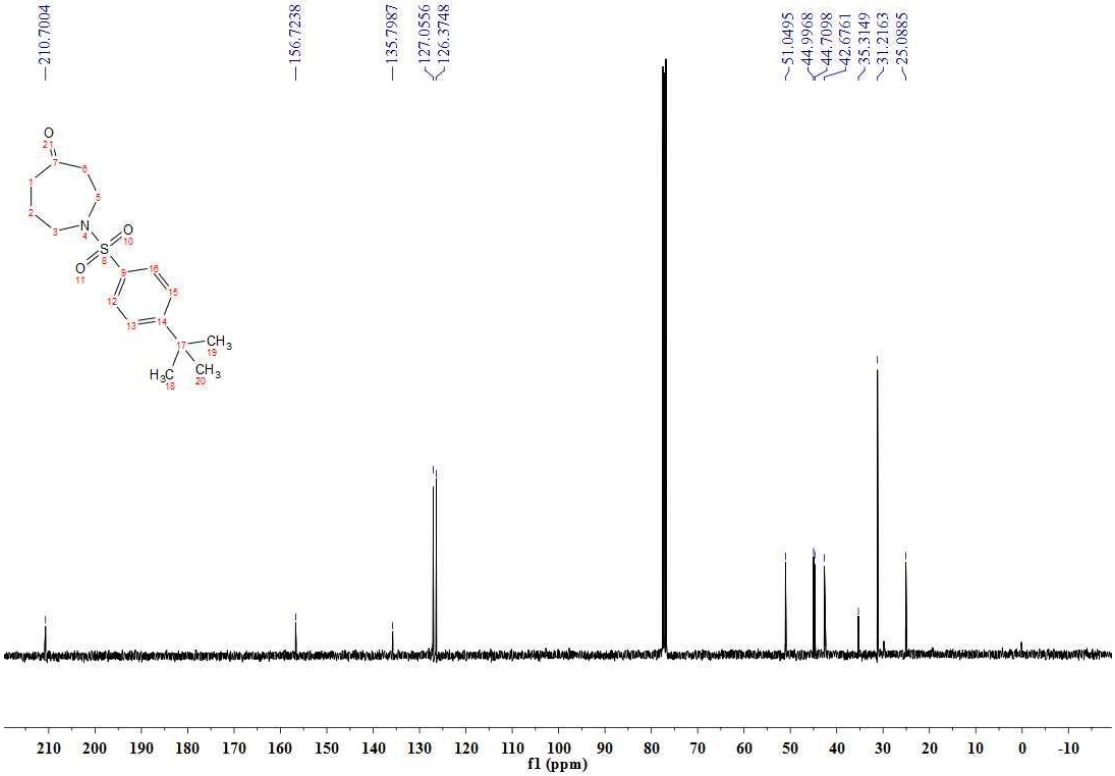
^{13}C NMR spectrum for **8a** ($CDCl_3$, 101 MHz)



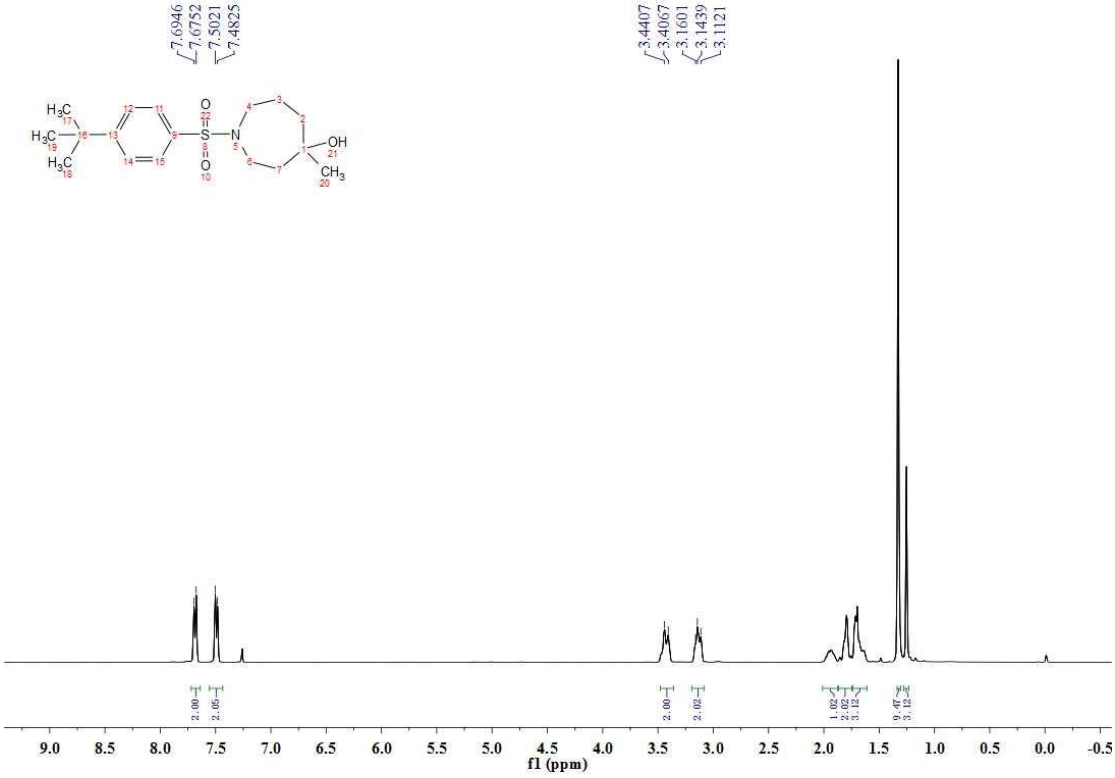
^{1}H NMR spectrum for **S1** ($CDCl_3$, 400 MHz)



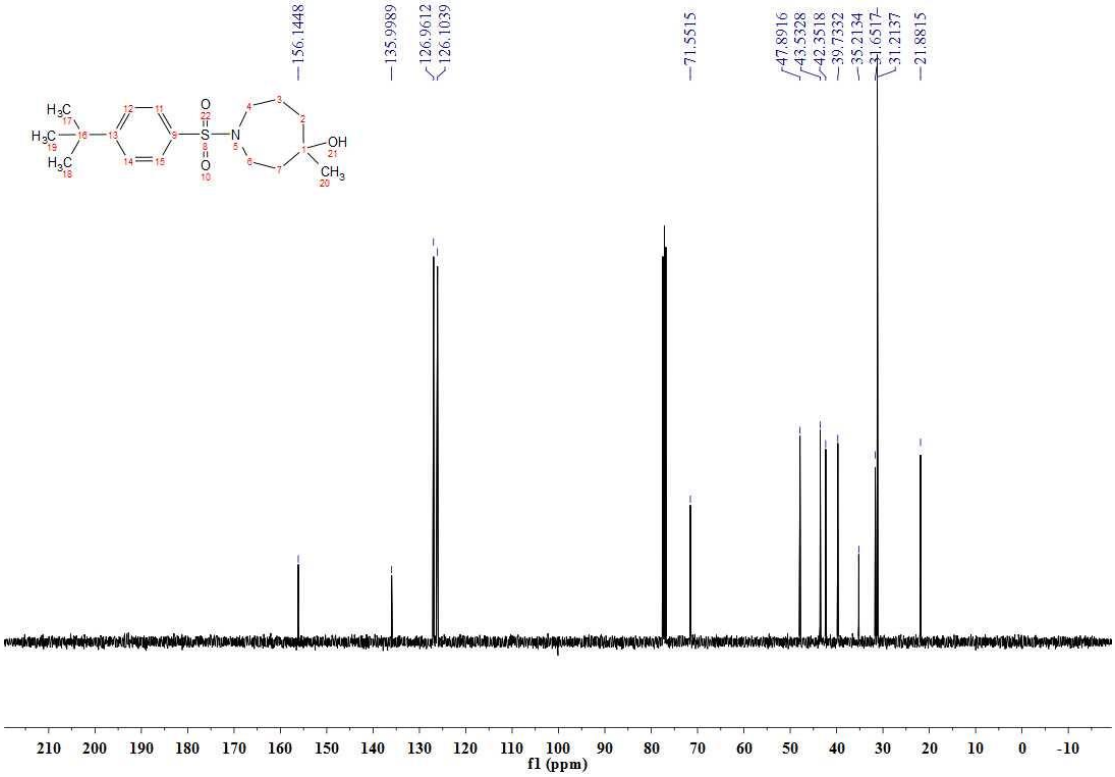
^{13}C NMR spectrum for **S1** ($CDCl_3$, 101 MHz)



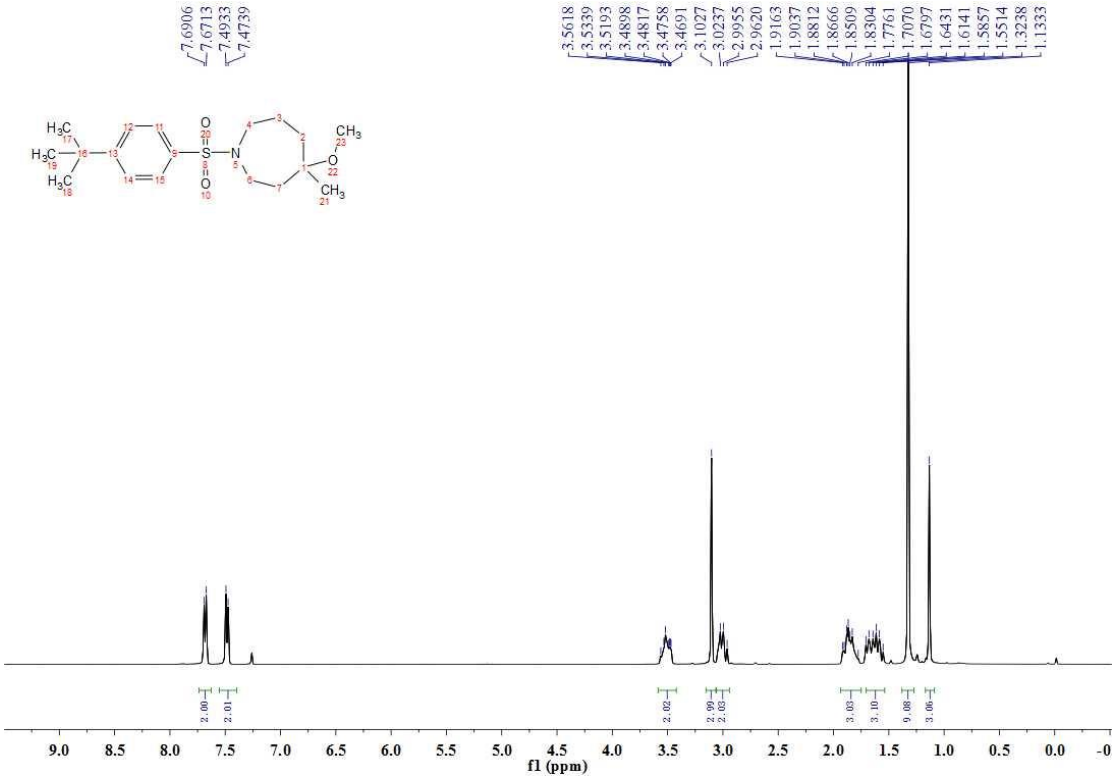
^{1}H NMR spectrum for **S2** ($CDCl_3$, 400 MHz)



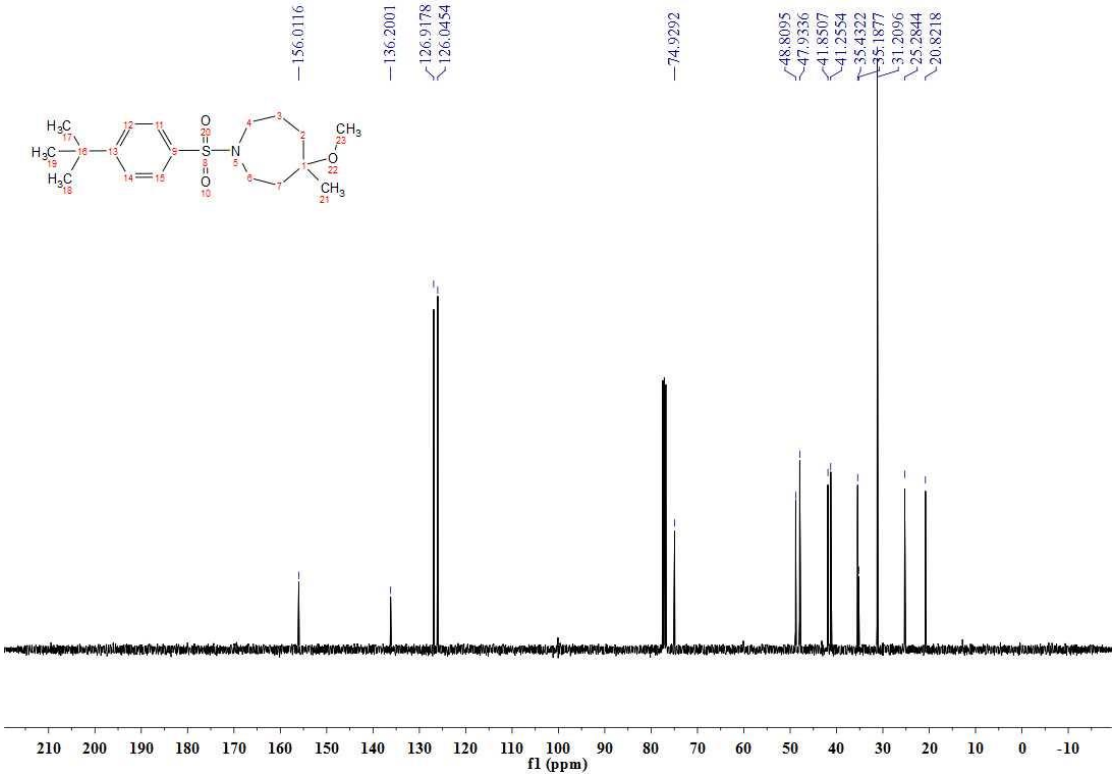
^{13}C NMR spectrum for **S2** ($CDCl_3$, 101 MHz)



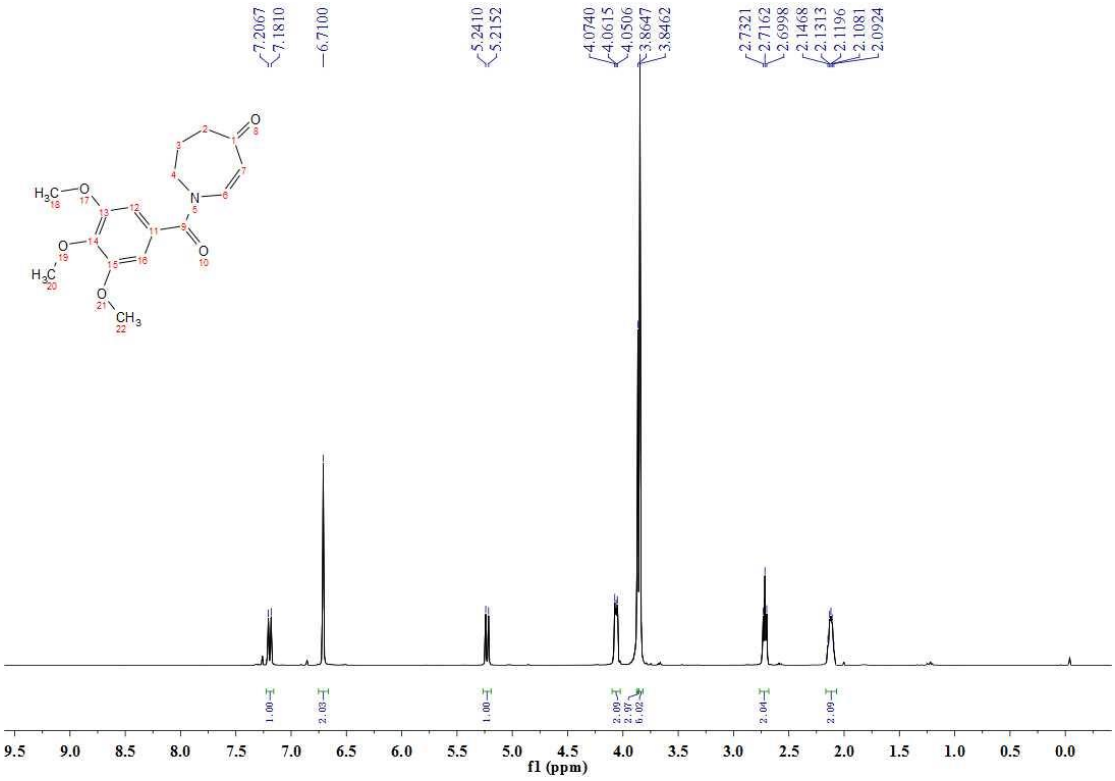
^{1}H NMR spectrum for **9** ($CDCl_3$, 400 MHz)



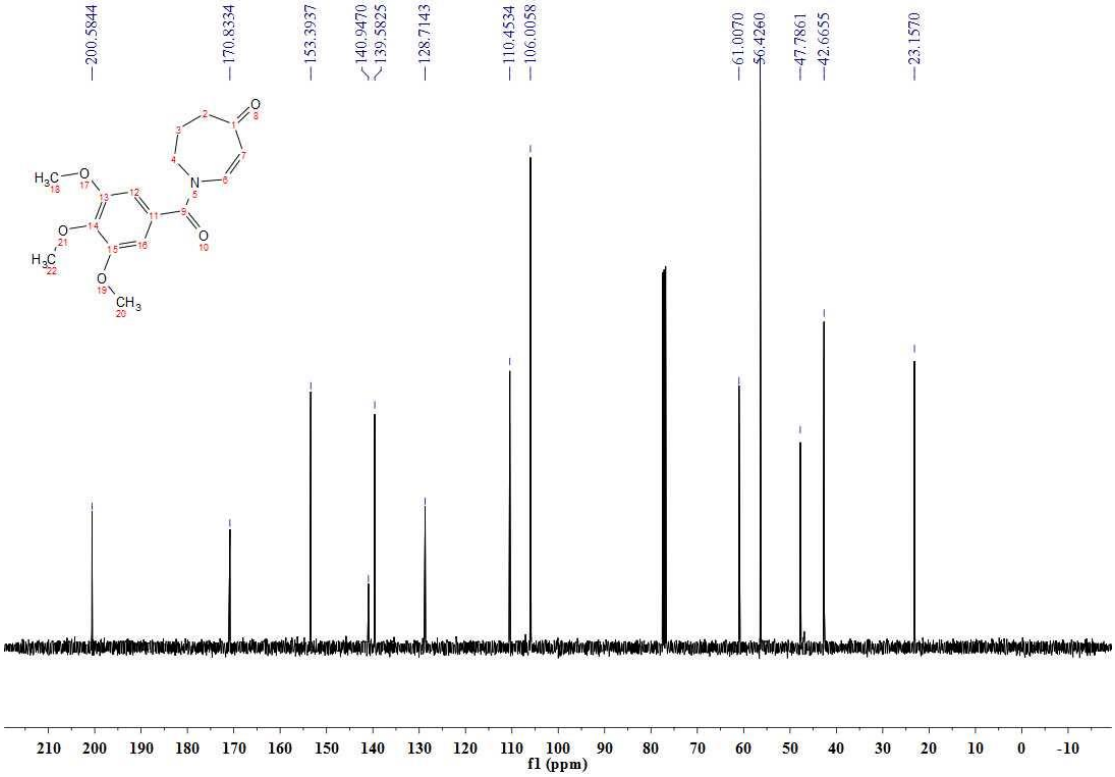
^{13}C NMR spectrum for **9** ($CDCl_3$, 101 MHz)



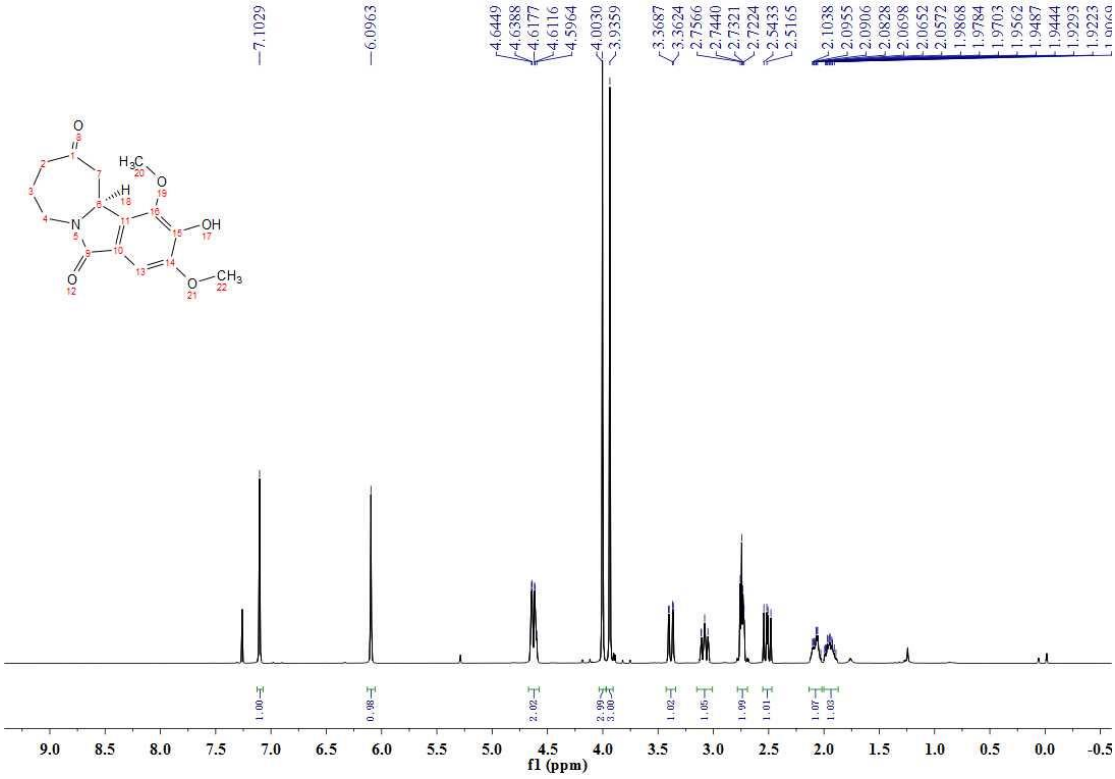
^{1}H NMR spectrum for **8b** ($CDCl_3$, 400 MHz)



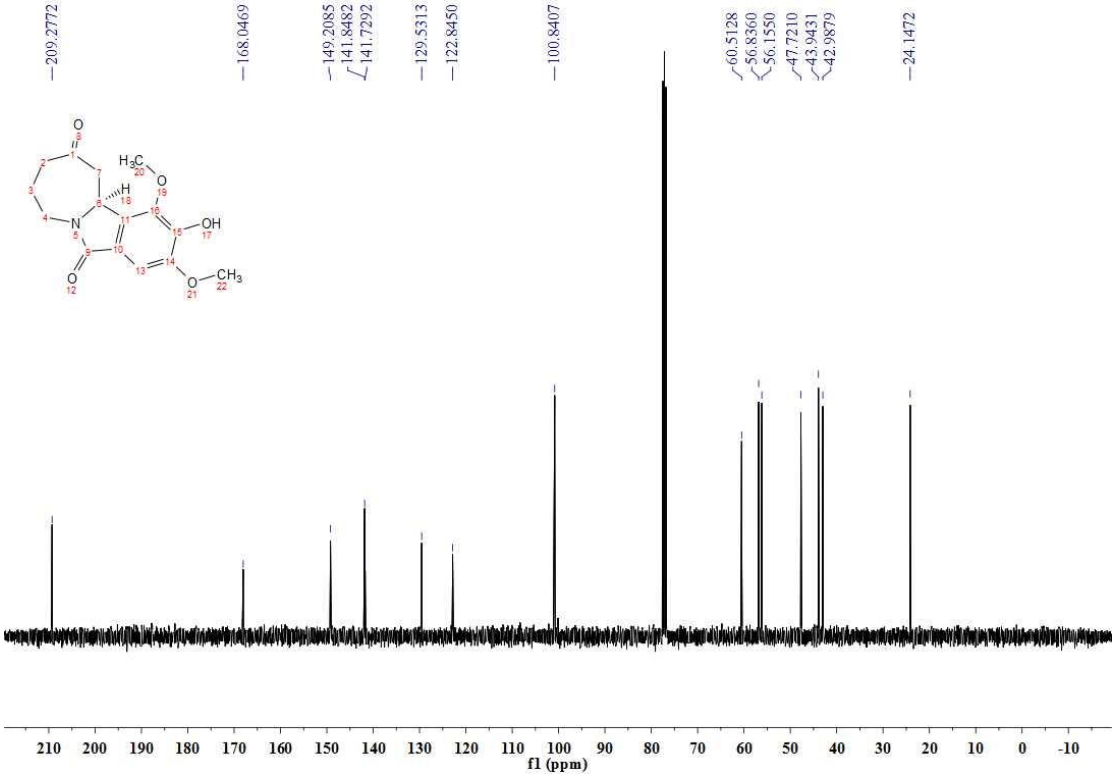
^{13}C NMR spectrum for **8b** ($CDCl_3$, 101 MHz)



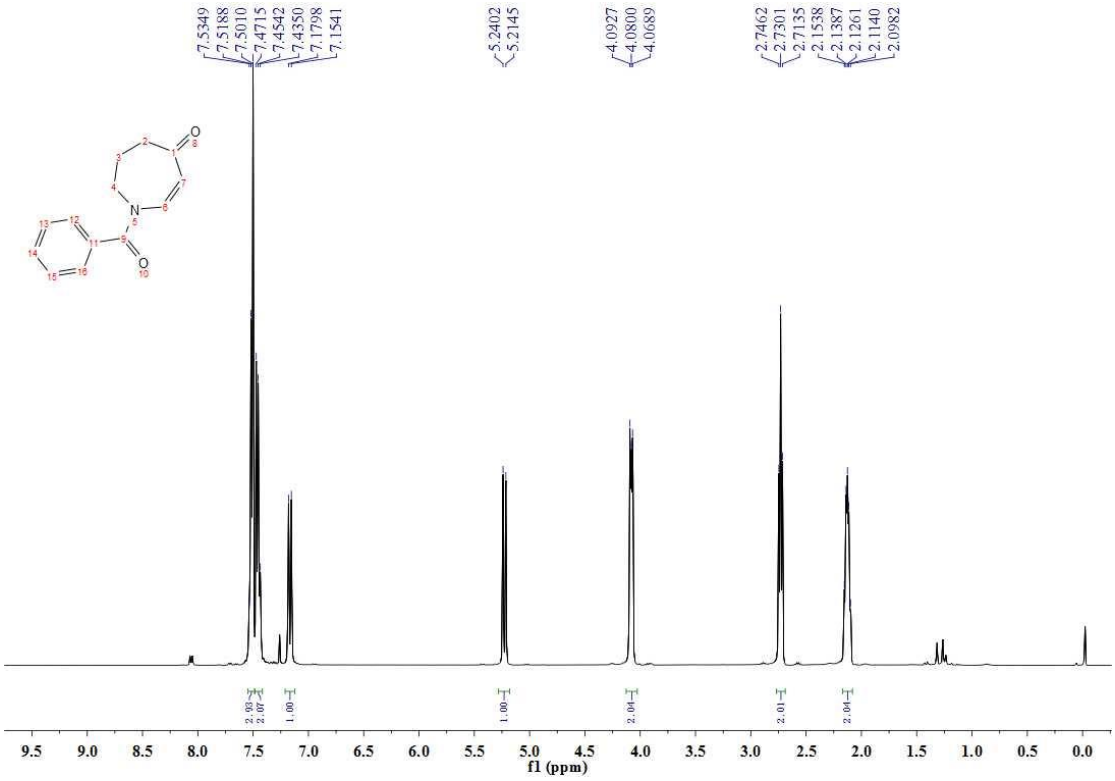
^{1}H NMR spectrum for **11** ($CDCl_3$, 400 MHz)



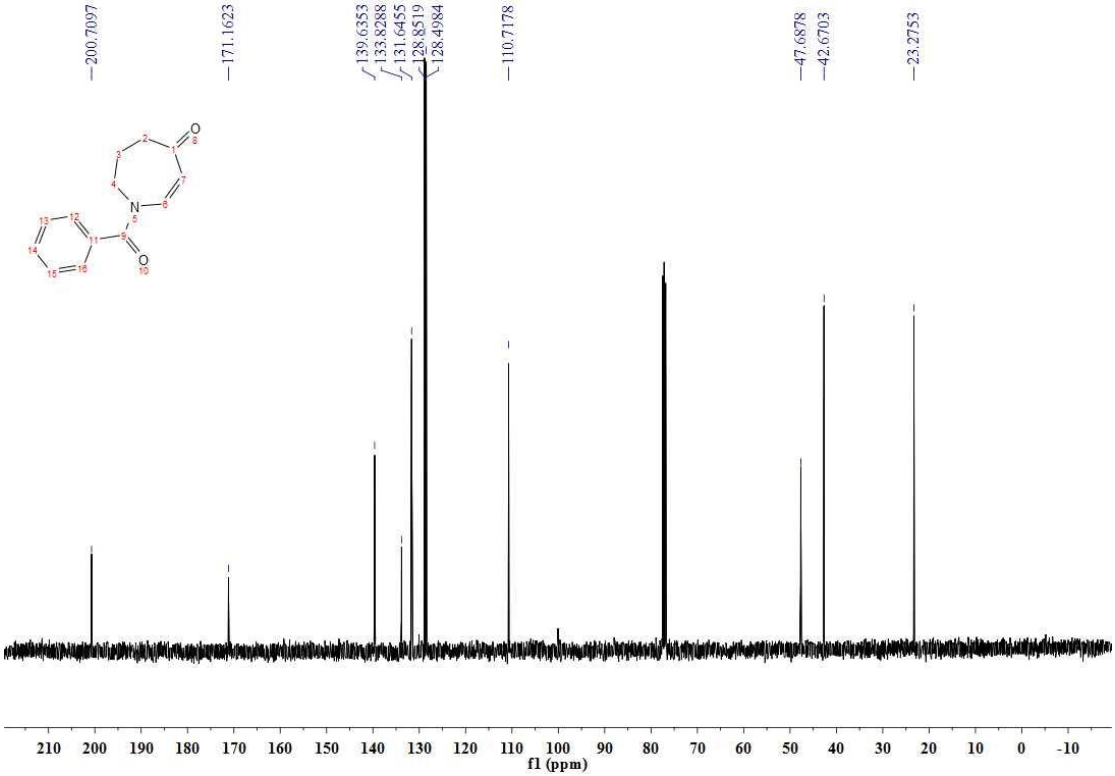
^{13}C NMR spectrum for **11** ($CDCl_3$, 101 MHz)



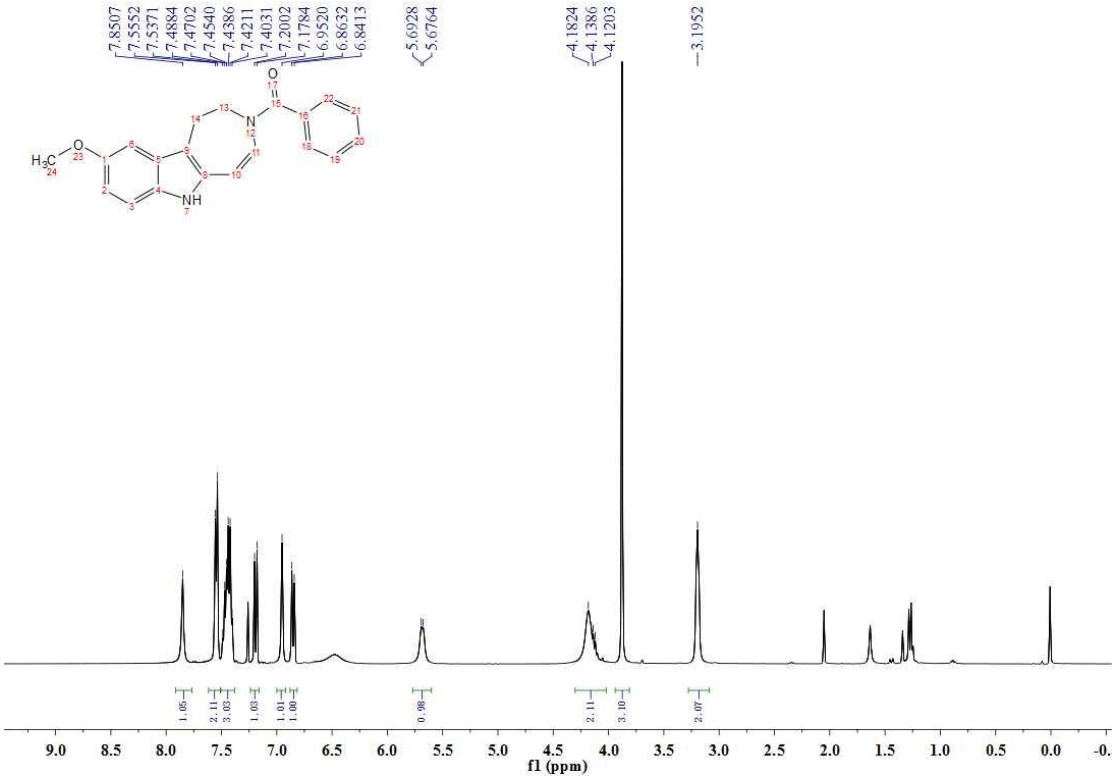
^{1}H NMR spectrum for **8c** ($CDCl_3$, 400 MHz)



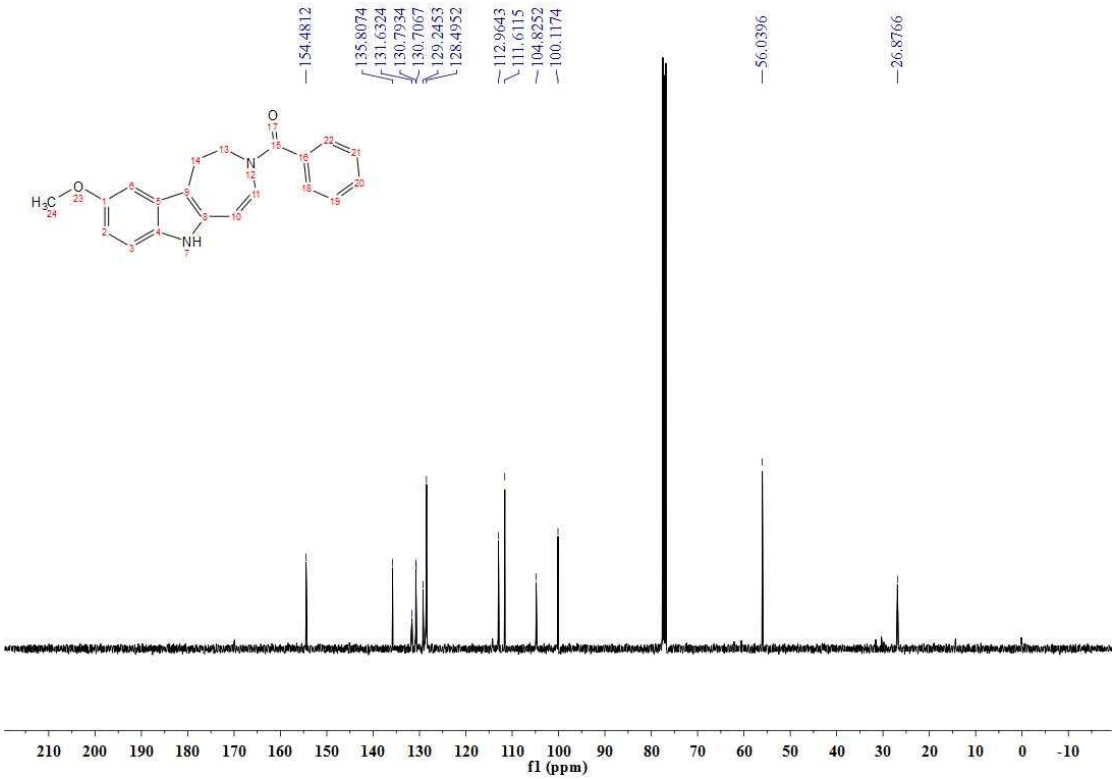
^{13}C NMR spectrum for **8c** ($CDCl_3$, 101 MHz)



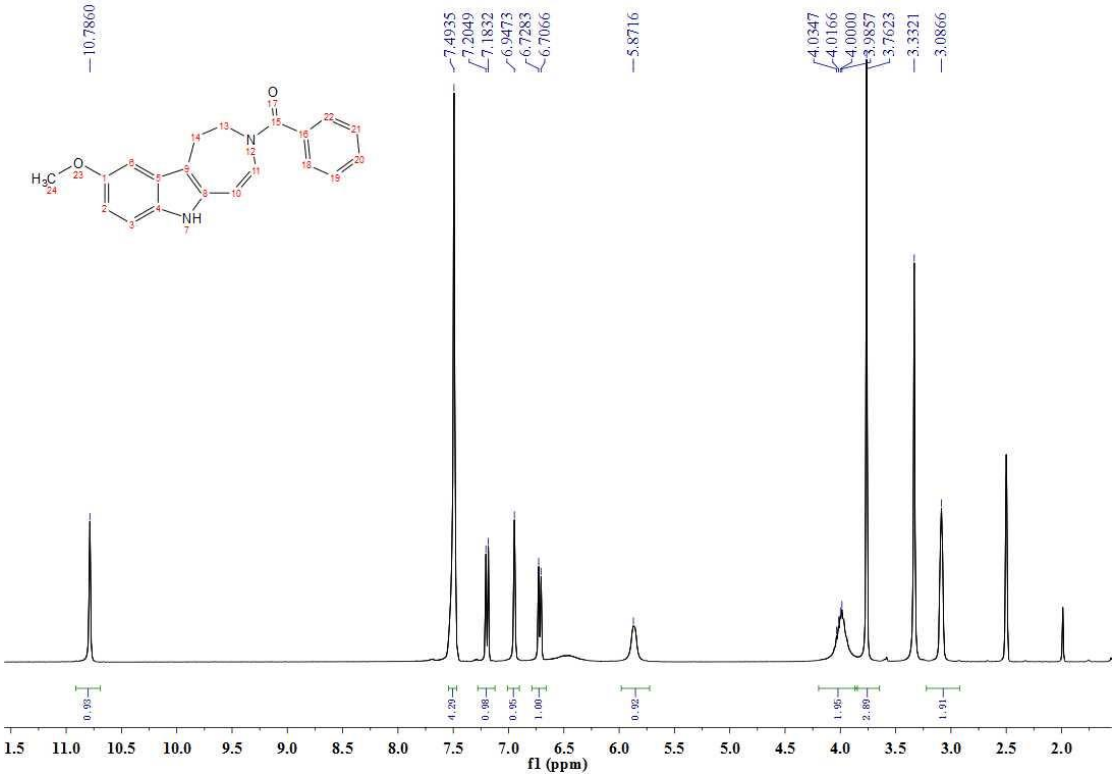
^{1}H NMR spectrum for **13** ($CDCl_3$, 400 MHz)



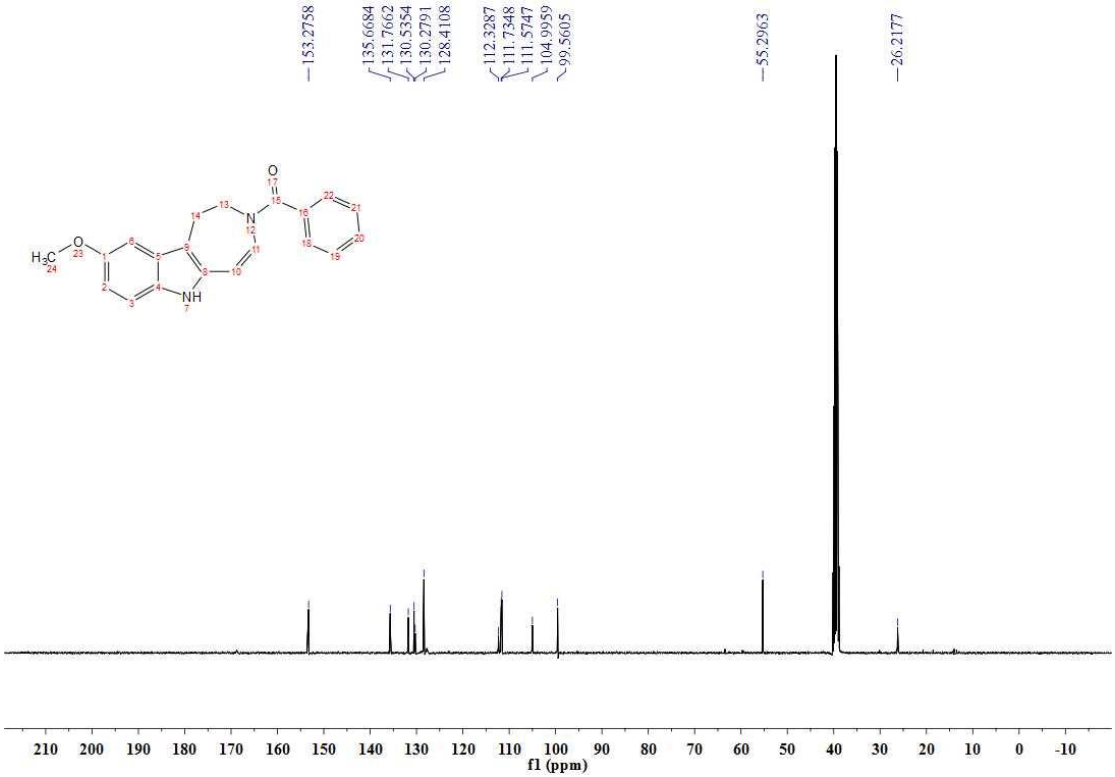
^{13}C NMR spectrum for **13** ($CDCl_3$, 101 MHz)



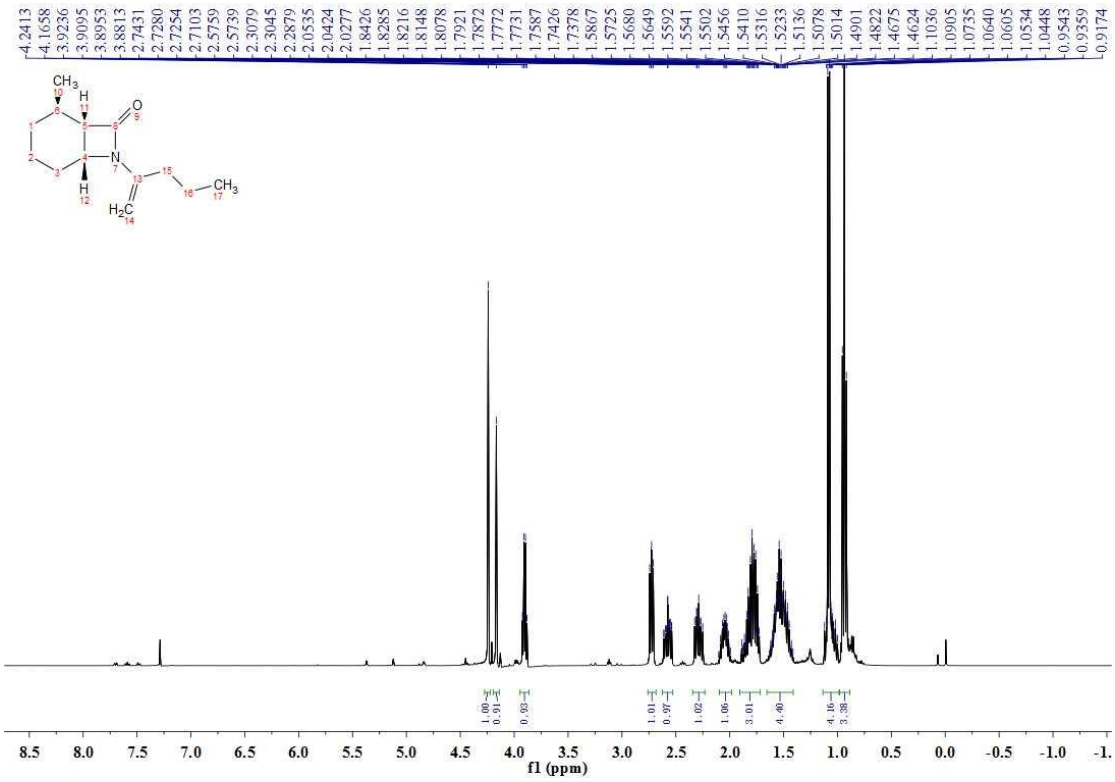
^{1}H NMR spectrum for **13** (DMSO-d6, 400 MHz)



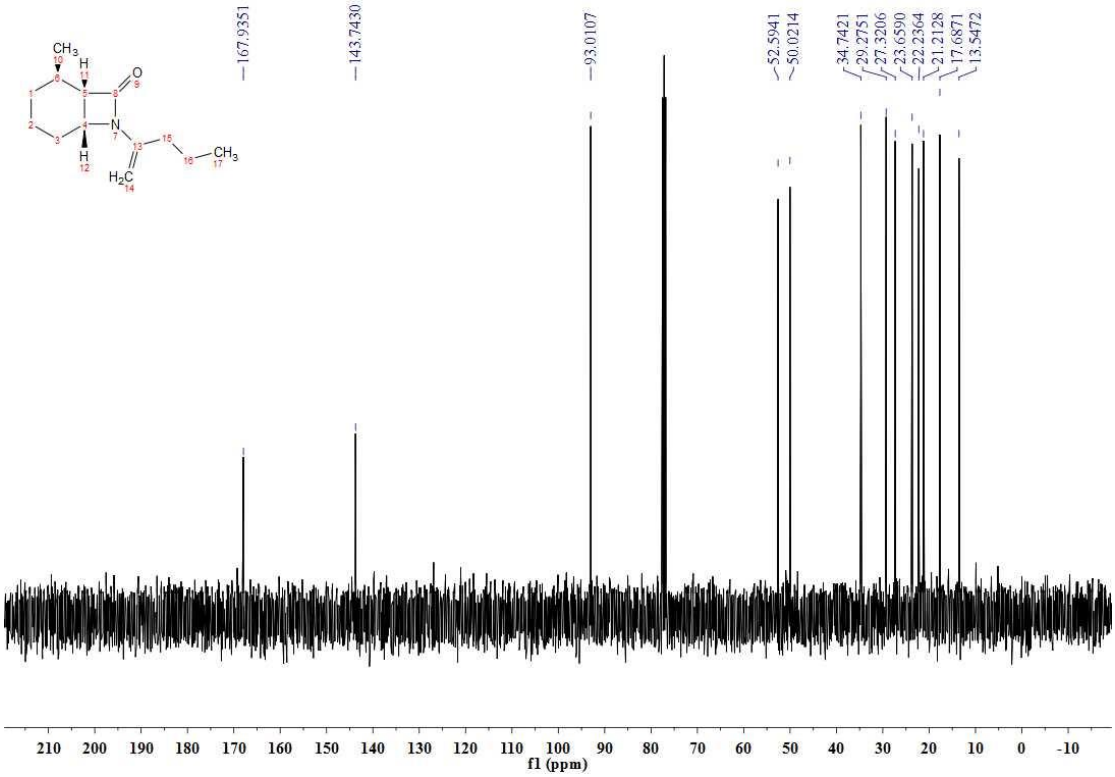
^{13}C NMR spectrum for **13** (DMSO-d6, 101 MHz)



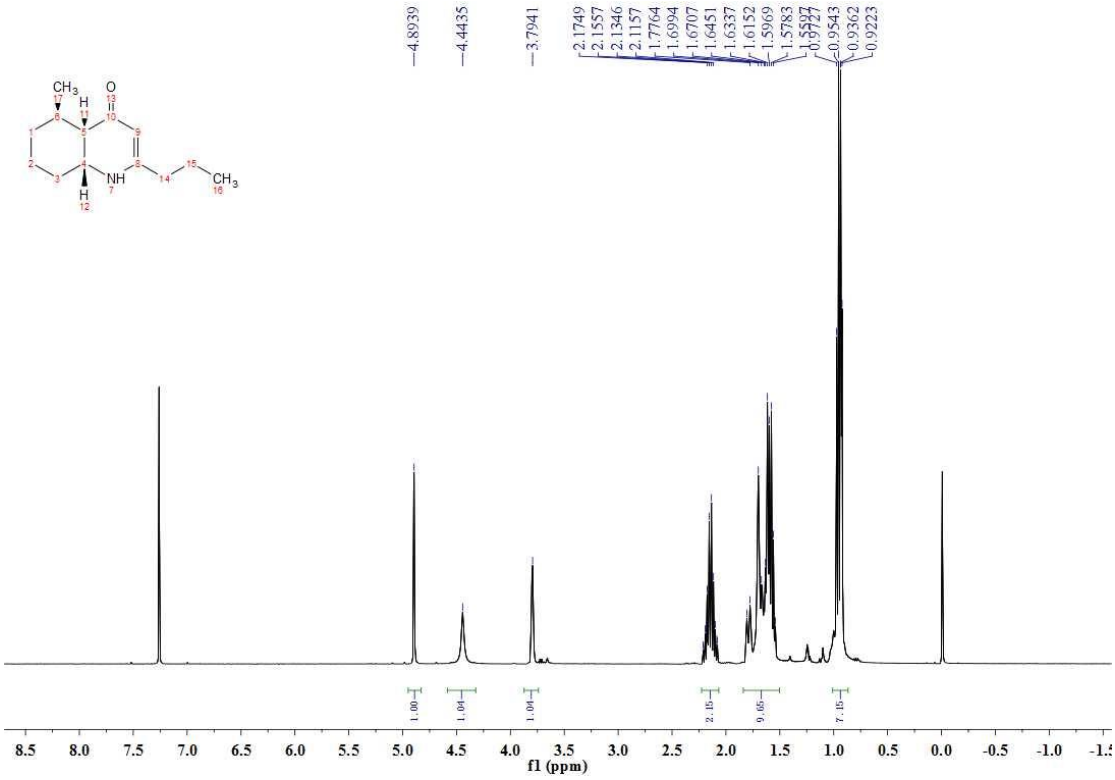
^{1}H NMR spectrum for **14** ($CDCl_3$, 400 MHz)



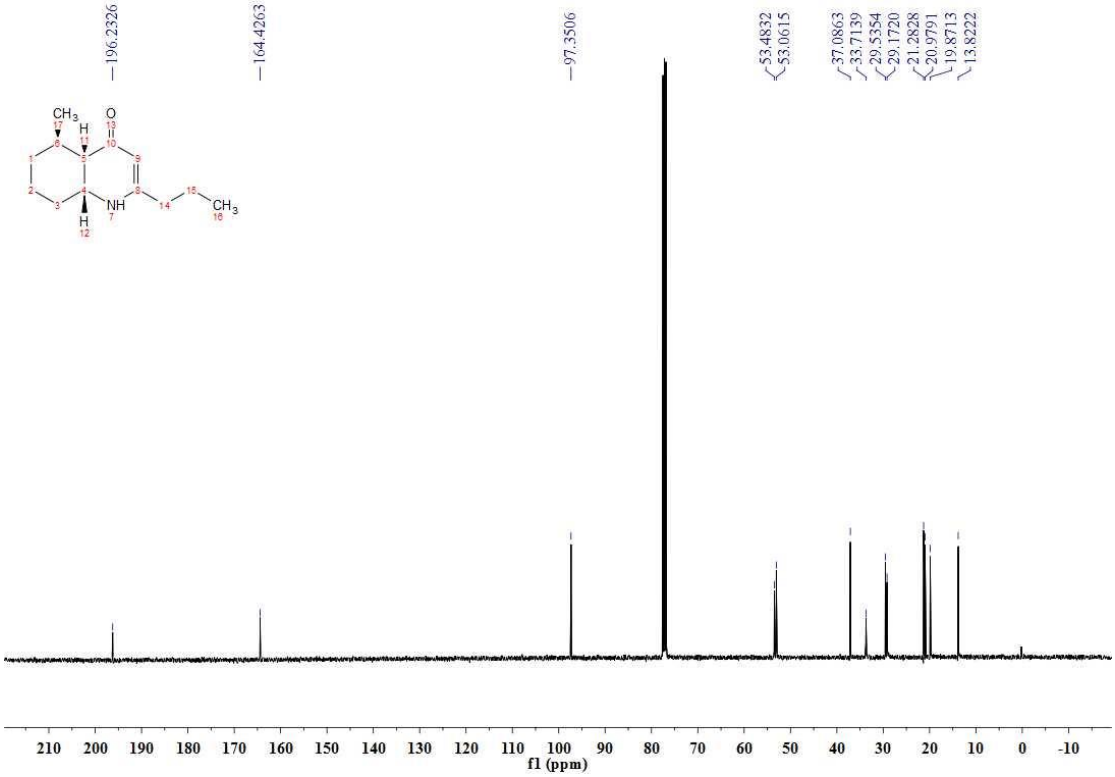
^{13}C NMR spectrum for **14** ($CDCl_3$, 101 MHz)



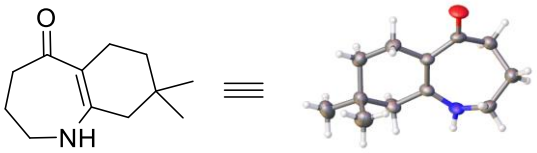
^{1}H NMR spectrum for **15** ($CDCl_3$, 400 MHz)



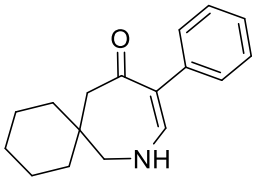
^{13}C NMR spectrum for **15** ($CDCl_3$, 101 MHz)

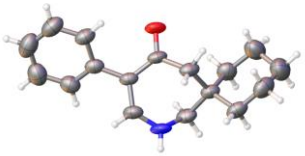


4. X-ray crystallographic structure

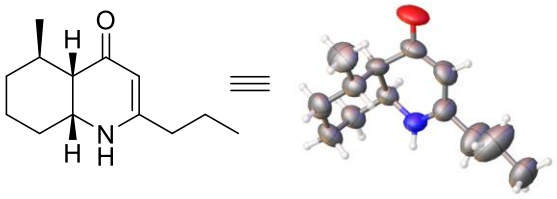


Compound	**3k**
CCDC	2179725
Formula	$C_{12}H_{19}NO$
Formula Weight	193.28
Crystal system	monoclinic
Space group	Pbca
a/Å	7.0479(5)
b/Å	10.5812(7)
c/Å	29.416(2)
α/deg	90
β/deg	90
γ/deg	90
Temperature/K	293(2)
Radiation	Mo Kα (λ = 0.71073)
Volume/Å^3	2193.7(3)
Z	8
D_x/g cm^{-3}	1.170
μ(mm^{-1})	0.074
F(000)	848.0
$R1^a$ ($I > 2\sigma$)	0.0508(1867)
w$R2^b$ (all data)	0.1253(2156)
GOF	1.078

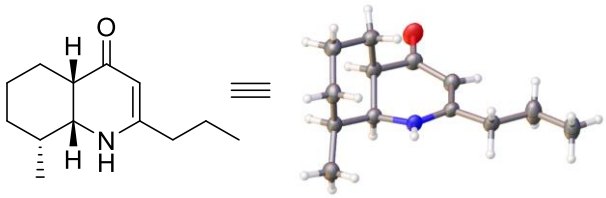




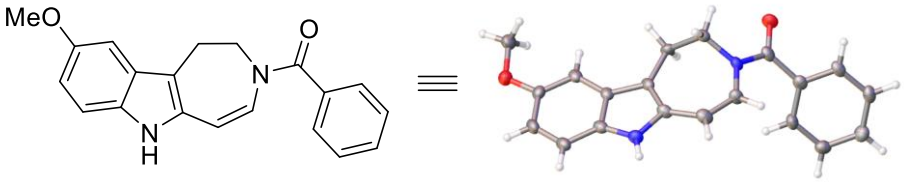
Compound	**3s**
CCDC	2179723
Formula	$C_{17}H_{21}NO$
Formula Weight	255.35
Crystal system	orthorhombic
Space group	Iba2
a/Å	24.820(3)
b/Å	16.9474(15)
c/Å	6.8317(5)
α/deg	90
β/deg	90
γ/deg	90
Temperature/K	293(2)
Radiation	Mo Kα (λ = 0.71073)
Volume/Å^3	2873.7(4)
Z	8
D_x/g cm^{-3}	1.180
μ(mm^{-1})	0.073
F(000)	1104.0
$R1^a$ ($I > 2\sigma$)	0.0362(2292)
w$R2^b$ (all data)	0.0909(2647)
GOF	1.040



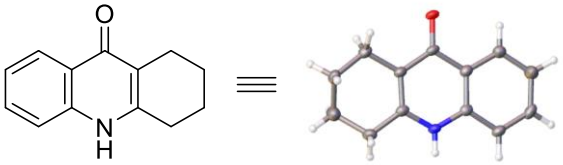
Compound	**15**
CCDC	2179726
Formula	$C_{13}H_{21}NO$
Formula Weight	207.31
Crystal system	monoclinic
Space group	P 1 21/n 1
a/Å	5.3301(2)
b/Å	19.5449(6)
c/Å	12.1194(3)
α/deg	90
β/deg	94.176(2)
γ/deg	90
Temperature/K	273
Radiation	Cu Kα (λ = 1.54184)
Volume/Å^3	1259.20(7)
Z	4
D_X/g cm^{-3}	1.094
μ(mm^{-1})	0.527
F(000)	456.0
*R*1a ($I > 2\sigma$)	0.0839(1887)
w*R*2b (all data)	0.2552(2413)
GOF	1.087



Compound	**4r**
CCDC	2179728
Formula	$C_{13}H_{21}NO$
Formula Weight	207.31
Crystal system	monoclinic
Space group	P 1 21/n 1
a/Å	9.1335(7)
b/Å	6.9499(4)
c/Å	19.3720(11)
α/deg	90
β/deg	97.031(6)
γ/deg	90
Temperature/K	173
Radiation	Cu Kα (λ = 1.54184)
Volume/Å^3	1220.44(13)
Z	4
D_X/g cm^{-3}	1.095
μ(mm^{-1})	0.544
F(000)	456.0
$R1^a$ ($I > 2\sigma$)	0.0616(1650)
w$R2^b$ (all data)	0.1873(2299)
GOF	1.059



Compound	**13**
CCDC	2179669
Formula	$C_{20}H_{18}N_2O_2$
Formula Weight	318.36
Crystal system	monoclinic
Space group	P 21 21 21
a/Å	8.7961(2)
b/Å	14.7189(3)
c/Å	12.7861(3)
α/deg	90
β/deg	90
γ/deg	90
Temperature/K	173
Radiation	Cu Kα (λ = 1.54184)
Volume/Å^3	1655.40(6)
Z	4
D_X/g cm^{-3}	1.277
μ(mm^{-1})	0.668
F(000)	672.0
$R1^a$ ($I > 2\sigma$)	0.0628(3038)
w$R2^b$ (all data)	0.1452(3117)
GOF	1.184



Compound	**6f**
CCDC	2182442
Formula	$C_{13}H_{13}NO$
Formula Weight	199.24
Crystal system	monoclinic
Space group	P 1 21/c 1
a/Å	5.0081(1)
b/Å	15.7243(2)
c/Å	12.7801(2)
α/deg	90
β/deg	100.522(2)
γ/deg	90
Temperature/K	293
Radiation	Cu Kα (λ = 1.54184)
Volume/Å^3	989.50(3)
Z	4
D_X/g cm^{-3}	1.337
μ(mm^{-1})	0.669
F(000)	424.0
$R1^a$ ($I > 2\sigma$)	0.0679(1553)
w$R2^b$ (all data)	0.1792(1619)
GOF	1.051

5. Computational study

(1) Computational methods

The calculations were performed with the Gaussian 16 C01 program package.[1] The geometry optimizations of the substrates and transition states were performed using the Time dependent(TD)[2]-M06-2X functional[3] with def-TZVP basis set[4] for all atoms, solving for the 6 lowest excited states. Higher level of single point electronic energies were calculated at def2-TZVP level[4] with the same functional. The solvent effect in CH_3OH was evaluated with the Universal Solvation Model Based on Solute Electron Density (SMD)[5] method. Geometry optimization, Vibration analysis and electronic energies are all computed with SMD model. Intrinsic reaction coordinate (IRC) calculations were performed for the identified transition states to confirm the reaction path proceeding in both directions (reactant and product). The structure is created with CYLview[6].

(2) Energy of the excitation light source (254 nm)

$$E = N_A h \frac{c}{\lambda}$$

$$= 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times \frac{3 \times 10^8}{254 \times 10^{-9}}$$

$$= 472440\ J$$

$$= 472.44\ kJ$$

(3) Geometries and original energies

Species	**1a-S0**	**1a-S1**	**1a-T1**
Optimization Level	SMD-(TD)-M06-2X/def-TZVP		
Electronic Energy Level	SMD-(TD)-M06-2X/def2-TZVP		
G Correction (au)	0.113217	0.110510	0.106494
Electronic Energy (au)	-364.027508	-363.856707	-363.922975
Imaginaries	/		
G_{sol}(au)	-363.914291	-363.746197	-363.816481

Species	TS-S1	TS-T1
Optimization Level	SMD-(TD)-M06-2X/def-TZVP	
Electronic Energy Level	SMD-(TD)-M06-2X/def2-TZVP	
G Correction (au)	0.107808	0.105665
Electronic Energy (au)	-363.832848	-363.877663
Imaginaries	83.72i	172.38i
G_{sol}(au)	-363.725040	-363.771998

Species	S(5j)	Int1	Int2	Int3
Optimization Level	SMD-M06-2X/def-TZVP			
Electronic Energy Level	SMD-M06-2X/def2-TZVP			
G Correction (au)	0.135797	0.135086	0.136210	0.140202
Electronic Energy (au)	-729.98537	-729.961651	-729.9636910	-729.996794
Imaginaries	/			
G_{sol}(au)	-729.849573	-729.826565	-729.827481	-729.856592

Species	TS1	TS2	TS3
Optimization Level	SMD-M06-2X/def-TZVP		
Electronic Energy Level	SMD-M06-2X/def2-TZVP		
G Correction (au)	0.135607	0.131619	0.137642
Electronic Energy (au)	-729.945672	-729.930397	-729.946630
Imaginaries	337.60i	220.00i	409.60i
G_{sol}(au)	-729.810065	-729.798778	-729.808988

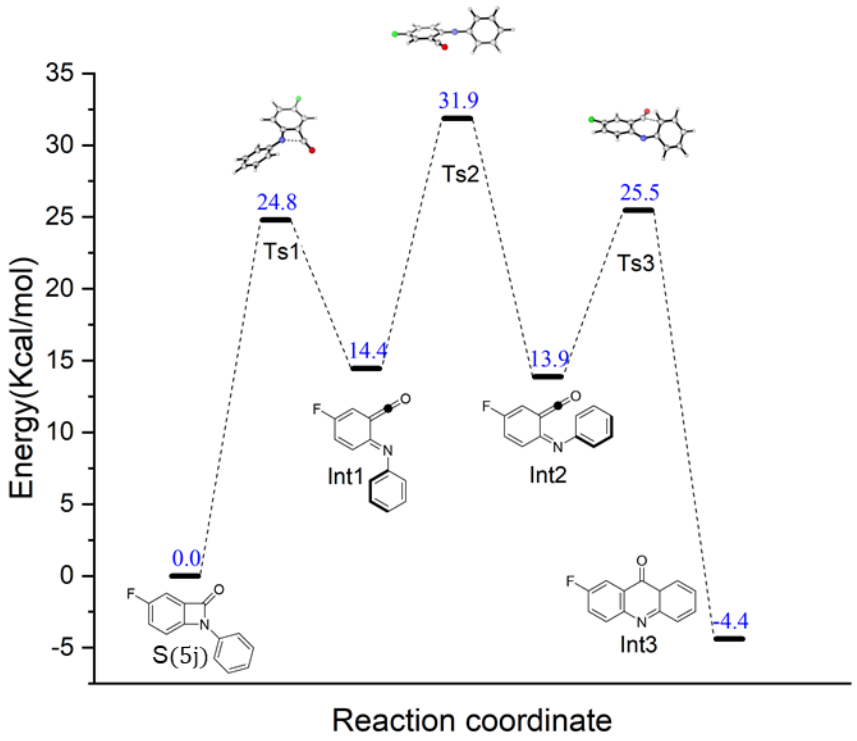


Figure S2. Computational study of proposed mechanism in ground state

1a-S0

C	0.682901	0.873786	0.006850
C	1.941847	0.057409	0.166399
C	1.511156	-1.361940	-0.204256
C	0.007824	-1.383563	0.096056
H	2.241420	0.134526	1.215722
H	2.743227	0.464698	-0.447108
H	1.670440	-1.529929	-1.269395
H	2.044470	-2.129621	0.351231
H	-0.553181	-1.995344	-0.609647
H	-0.213078	-1.725586	1.110797
O	0.600854	2.095174	-0.043043
N	-0.378028	0.020358	-0.041415
C	-1.700287	0.451110	-0.057635
H	-1.802470	1.524916	-0.157155
C	-2.755784	-0.352634	0.039154

H	-2.668225	-1.426515	0.146958
H	-3.749187	0.073950	0.013435

1a-S1

C	-0.722705	-0.967861	-0.306164
C	-1.831016	-0.022652	-0.694764
C	-1.533820	1.175478	0.238135
C	0.001549	1.239627	0.315287
H	-2.812687	-0.460411	-0.524730
H	-1.737254	0.270160	-1.742314
H	-1.951174	2.112907	-0.124232
H	-1.943554	0.970167	1.227043
H	0.417591	1.991056	-0.361011
H	0.381843	1.432592	1.319965
O	-0.787879	-1.617687	0.805286
N	0.437290	-0.067674	-0.185681
C	1.727326	-0.475949	-0.309883
H	1.834557	-1.469285	-0.730563
C	2.788975	0.282682	0.011977
H	2.685254	1.266836	0.450724
H	3.785565	-0.086761	-0.184929

1a-T1

C	0.744790	0.846289	0.004221
C	1.953198	-0.045346	0.144394
C	1.423113	-1.433440	-0.216575
C	-0.065577	-1.361751	0.134977
H	2.285869	0.007988	1.185559
H	2.765647	0.305403	-0.489914
H	1.535440	-1.604834	-1.287347
H	1.924055	-2.236992	0.318287
H	-0.692932	-1.948381	-0.534078
H	-0.265308	-1.666704	1.164931
O	0.727983	2.076602	-0.054081
N	-0.374329	0.068114	-0.010755

C	-1.654014	0.570715	-0.026383
H	-1.728908	1.649534	-0.076041
C	-2.811272	-0.304611	-0.004064
H	-3.291043	-0.580198	0.929756
H	-3.277811	-0.646563	-0.922644

TS-S1

C	1.606387	-0.867524	0.380240
C	1.861844	0.621182	0.529659
C	0.949836	1.370732	-0.439528
C	-0.511555	1.124639	-0.074022
H	2.916533	0.784449	0.297367
H	1.664468	0.920436	1.558158
H	1.168708	2.438538	-0.403097
H	1.141494	1.023529	-1.457748
H	-0.739220	1.663861	0.857918
H	-1.177385	1.520079	-0.846868
O	1.961433	-1.566754	-0.505078
N	-0.689215	-0.283644	0.168888
C	-1.923100	-0.806531	0.121812
H	-1.958726	-1.882624	0.275286
C	-3.099950	-0.141043	-0.051817
H	-3.151186	0.931548	-0.183045
H	-4.032423	-0.688998	-0.037629

TS-T1

C	1.295863	0.958791	0.372435
C	1.867712	-0.437775	0.528199
C	1.120433	-1.384047	-0.412481
C	-0.368689	-1.261209	-0.088531
H	1.751993	-0.764436	1.563024
H	2.931665	-0.379813	0.290279
H	1.300042	-1.081865	-1.446826
H	1.461709	-2.412278	-0.292137
H	-0.994685	-1.638793	-0.900437

H	-0.606631	-1.828986	0.818542
O	1.513623	1.712616	-0.549170
N	-0.596670	0.142313	0.173603
C	-1.766167	0.711101	0.165064
H	-1.767657	1.781458	0.363341
C	-2.990483	0.074460	-0.055793
H	-3.906306	0.647339	-0.022590
H	-3.054435	-0.987675	-0.248409

S(5j)

C	-3.54312500	-0.36402100	-0.00114400
C	-2.83151200	-1.54015200	0.00216000
C	-1.41771300	-1.54417100	0.00453900
C	-0.84708700	-0.30274300	0.00315800
C	-1.59238500	0.88006300	-0.00022200
C	-2.95476200	0.91104700	-0.00257700
F	-4.89227400	-0.42804200	-0.00326100
N	0.40699900	0.39089900	0.00485700
C	-0.27164500	1.63264700	0.00025700
O	0.12173500	2.75620800	-0.00261300
C	1.74418400	0.01221800	0.00204400
C	2.08362500	-1.34138500	-0.00226800
C	3.42046000	-1.71395100	-0.00479000
C	4.42401500	-0.75366600	-0.00317900
C	4.07685600	0.59342300	0.00113300
C	2.74777500	0.98644500	0.00393800
H	-3.37697000	-2.47526400	0.00300000
H	-0.87246200	-2.47591800	0.00709700
H	-3.55709700	1.80960900	-0.00522500
H	1.30957700	-2.09675600	-0.00367800
H	3.67477700	-2.76674100	-0.00811100
H	5.46494300	-1.05006700	-0.00521900
H	4.84969200	1.35235200	0.00254000
H	2.48301200	2.03467400	0.00755900

TS1

C	3.36263800	-0.66335700	-0.04689800
C	2.39863000	-1.67485700	-0.27995900
C	1.05764600	-1.40552800	-0.34832500
C	0.65357100	-0.04474900	-0.23106300
C	1.65817700	0.90830500	0.07016200
C	3.04134300	0.64488300	0.12983400
F	4.65616400	-1.04983500	0.00681900
N	-0.49061000	0.62438100	-0.38175400
C	0.89217900	2.05947100	0.25211800
O	0.59709900	3.12223600	0.55545200
C	-1.76074000	0.10296700	-0.16955800
C	-2.85087300	0.78539300	-0.72838600
C	-4.14498700	0.32868900	-0.53855700
C	-4.38587600	-0.81926400	0.21140400
C	-3.31301100	-1.49447500	0.78231600
C	-2.01408300	-1.03689500	0.60839200
H	2.76032800	-2.68854300	-0.40831300
H	0.34613200	-2.19371300	-0.54957400
H	3.78524500	1.40494700	0.32486500
H	-2.65554600	1.67418200	-1.31656200
H	-4.97255100	0.86980200	-0.98161900
H	-5.39728900	-1.17793300	0.35481300
H	-3.48834600	-2.37913500	1.38315100
H	-1.19364900	-1.55314100	1.09165300

Int1

C	3.06292400	-1.12150600	-0.13453900
C	1.83924500	-1.85734600	-0.26227900
C	0.64279700	-1.23977100	-0.20597100
C	0.53510000	0.20667400	-0.03770200
C	1.83067800	0.89680200	0.06778100
C	3.09888600	0.20668200	0.01584500
F	4.20642500	-1.83711100	-0.19083300
N	-0.54314900	0.91295900	-0.01608300

C	1.77944300	2.22257000	0.23435400
O	1.72759100	3.35300700	0.38357700
C	-1.81469900	0.32229500	0.00124900
C	-2.19595400	-0.60030700	0.98186900
C	-3.48791700	-1.10746600	1.00314400
C	-4.41912700	-0.70562000	0.05188000
C	-4.04837700	0.22070700	-0.91721500
C	-2.76203200	0.74060600	-0.93738100
H	1.90626900	-2.92805500	-0.41589300
H	-0.26804000	-1.80924000	-0.32703200
H	4.03097300	0.74918800	0.09682800
H	-1.47676500	-0.90144700	1.73496500
H	-3.76950300	-1.81661000	1.77240700
H	-5.42629400	-1.10252200	0.07163700
H	-4.76813200	0.54810600	-1.65787900
H	-2.47081300	1.47388000	-1.67976800

TS2

C	3.60313500	-0.38718300	0.00009500
C	2.86182400	-1.61707300	-0.00043400
C	1.51710100	-1.61736000	-0.00070200
C	0.73168400	-0.37523400	-0.00038400
C	1.57594000	0.85488300	0.00008600
C	3.02246900	0.81598100	0.00036100
F	4.94854400	-0.49876100	0.00032000
N	-0.51994400	-0.35375400	-0.00054700
C	0.91260100	2.01111400	0.00024500
O	0.29857400	2.97458000	0.00033600
C	-1.85797500	-0.32113800	-0.00024800
C	-2.58146600	-0.30360500	1.21054000
C	-3.96606800	-0.26628300	1.19677200
C	-4.67664100	-0.24671600	0.00039600
C	-3.96657800	-0.26496000	-1.19630400
C	-2.58198200	-0.30224200	-1.21070400
H	3.42139500	-2.54520100	-0.00063300

H	0.95414700	-2.54171000	-0.00110000
H	3.60172500	1.72950800	0.00072800
H	-2.03610200	-0.31842100	2.14574400
H	-4.49753000	-0.25289200	2.14148400
H	-5.75832900	-0.21738800	0.00064300
H	-4.49844400	-0.25051900	-2.14077300
H	-2.03701400	-0.31599600	-2.14615500

Int2

C	3.60313500	-0.38718300	0.00009500
C	2.86182400	-1.61707300	-0.00043400
C	1.51710100	-1.61736000	-0.00070200
C	0.73168400	-0.37523400	-0.00038400
C	1.57594000	0.85488300	0.00008600
C	3.02246900	0.81598100	0.00036100
F	4.94854400	-0.49876100	0.00032000
N	-0.51994400	-0.35375400	-0.00054700
C	0.91260100	2.01111400	0.00024500
O	0.29857400	2.97458000	0.00033600
C	-1.85797500	-0.32113800	-0.00024800
C	-2.58146600	-0.30360500	1.21054000
C	-3.96606800	-0.26628300	1.19677200
C	-4.67664100	-0.24671600	0.00039600
C	-3.96657800	-0.26496000	-1.19630400
C	-2.58198200	-0.30224200	-1.21070400
H	3.42139500	-2.54520100	-0.00063300
H	0.95414700	-2.54171000	-0.00110000
H	3.60172500	1.72950800	0.00072800
H	-2.03610200	-0.31842100	2.14574400
H	-4.49753000	-0.25289200	2.14148400
H	-5.75832900	-0.21738800	0.00064300
H	-4.49844400	-0.25051900	-2.14077300
H	-2.03701400	-0.31599600	-2.14615500

TS3

C	-3.27663900	0.19112000	-0.21097800
C	-3.17526800	-1.17616700	0.15933000
C	-1.96150500	-1.71715400	0.41595100
C	-0.74047700	-0.95741100	0.29489700
C	-0.91150100	0.45999000	0.05254400
C	-2.20370200	0.99827600	-0.28441800
F	-4.51356100	0.67734600	-0.45795000
N	0.39570000	-1.61966400	0.29522200
C	0.11576200	1.38487100	0.01072600
O	0.41604400	2.50113000	-0.09999400
C	1.56257000	-0.92658200	0.18000000
C	2.58968000	-1.43507700	-0.64841000
C	3.74486600	-0.71862100	-0.83217000
C	3.94743400	0.52143400	-0.18760300
C	2.98215800	1.01217500	0.64973800
C	1.77059800	0.30671000	0.83153100
H	-4.08079100	-1.76723400	0.22353400
H	-1.85935700	-2.76573400	0.66335000
H	-2.31341400	2.04695300	-0.53023500
H	2.42971100	-2.38659100	-1.13972100
H	4.51619800	-1.10802500	-1.48598300
H	4.87017500	1.06475900	-0.34436900
H	3.13252400	1.94713000	1.17586600
H	1.16490000	0.53986000	1.70567800

Int3

C	-3.29887200	0.13572500	-0.03843400
C	-3.17479200	-1.24717800	-0.01756700
C	-1.91064500	-1.80144300	0.00945300
C	-0.77128800	-0.98731600	0.03030600
C	-0.93931500	0.40810900	0.02424300
C	-2.21190300	0.97490100	-0.03124500
F	-4.53657600	0.66803300	-0.06484300
C	0.25414900	1.27779400	0.03325200

N	0.47305700	-1.62078700	-0.01261700
C	1.54015800	-0.90960100	0.08799100
C	2.83650000	-1.54497400	-0.05422100
C	3.95615600	-0.80926800	-0.17025500
C	3.92719100	0.64599800	-0.15430700
C	2.79030900	1.30326200	0.08658800
C	1.53554900	0.56435400	0.41102700
O	0.21194600	2.46922800	-0.17122400
H	-4.06416200	-1.86433600	-0.02852500
H	-1.77749900	-2.87558000	0.00350400
H	-2.33614100	2.05033500	-0.04963100
H	2.84920500	-2.62531900	-0.12825000
H	4.90952000	-1.30260700	-0.31745400
H	4.84470700	1.18466100	-0.35455700
H	2.74131600	2.38465000	0.09573500
H	1.45608200	0.56540700	1.51989800

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J., Gaussian 16, Revision. C.01, Wallingford, CT, 2016.

(2) Gross, Eberhard KU, and Neepa T. Maitra. "Introduction to TDDFT." Fundamentals of time-dependent density functional theory. Springer, Berlin, Heidelberg, 2012. 53-99.

(3) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

(4) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829-5835.

(5) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Chem. Phys*., 2009, **113**, 6378-6396.
(6) “CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)”.