Electronic Supplementary Information

Palladium-Catalyzed Ring-Expansion Reaction of Cyclobutanols with 2-Haloanilines Leading to Benzazepines and Quinolines

Xiao-Qin Shen,[a] Xiao-Wei Yan,[b] Xing-Guo Zhang*[a, b]

[a]*College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China;*

[b]*Guangxi Key Laboratory of Calcium Carbonate Resources Comprehensive Utilization, Hezhou University, Hezhou 542899, China*

E-mail: zxg@wzu.edu.cn

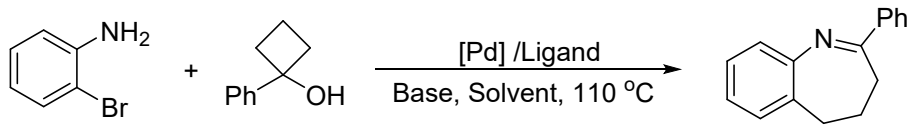
Supplementary data

List of Contents

Contents:

1. Investigation of the Reaction Parameters

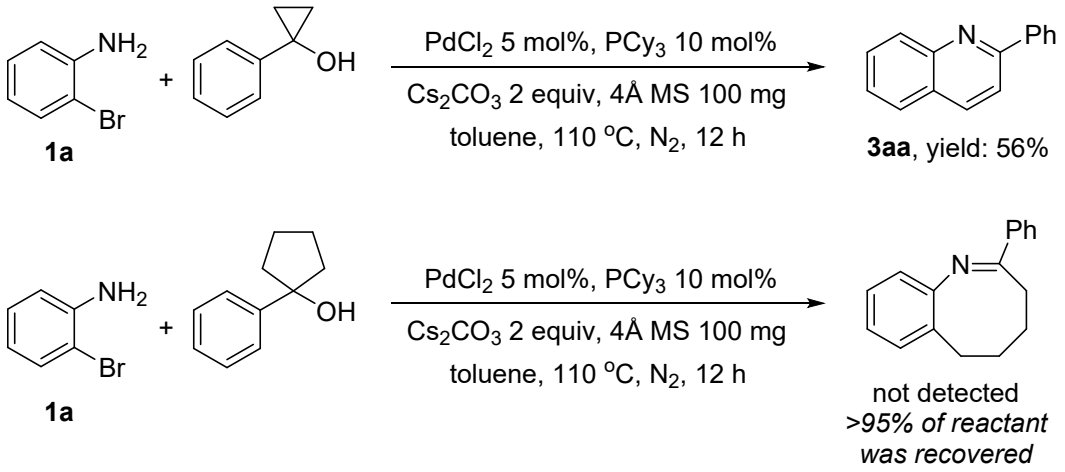
Table S1 Screening conditions [a]



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

Entry	Pd	Ligand	Base	Solvent	Yield
1	$Pd(OAc)_2$	PCy_3	K_3PO_4	Toluene	55
2	$Pd(acac)_2$	PCy_3	K_3PO_4	Toluene	35
3	$Pd(TFA)_2$	PCy_3	K_3PO_4	Toluene	51
4	$Pd(MeCN)_2Cl_2$	PCy_3	K_3PO_4	Toluene	58
5	$PdCl_2$	PCy_3	K_3PO_4	Toluene	67
6	$PdCl_2$	PCy_3	K_2CO_3	Toluene	28
7	$PdCl_2$	PCy_3	Na_2CO_3	Toluene	23
8	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	87
9	$PdCl_2$	PCy_3	*t*-BuOK	Toluene	76
10	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	85[b]
11	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	79[c]
12	$PdCl_2$	PCy_3	Cs_2CO_3	THF	75
13	$PdCl_2$	PCy_3	Cs_2CO_3	DMF	69
14	$PdCl_2$	PCy_3	Cs_2CO_3	DMSO	50
15	$PdCl_2$	PCy_3	Cs_2CO_3	NMP	71
16	$PdCl_2$	PCy_3	Cs_2CO_3	DCE	75
17	$PdCl_2$	PPh_3	Cs_2CO_3	Toluene	45
18	$PdCl_2$	X-Phos	Cs_2CO_3	Toluene	Trace
19	$PdCl_2$	S-Phos	Cs_2CO_3	Toluene	Trace
20	$PdCl_2$	DPPP	Cs_2CO_3	Toluene	48
21	-	PCy_3	Cs_2CO_3	Toluene	0
22	$PdCl_2$	-	Cs_2CO_3	Toluene	0
23	$PdCl_2$	PCy_3	-	Toluene	0
24	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	49[d]
25	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	73[e], 54[f]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.22 mmol), Pd salts (5 mol %), PCy_3 (10 mol %), bases (0.4 mmol) in solvent (2 mL) at 110 °C under N_2 atmosphere for 12 h, isolated yields. [b] Cs_2CO_3 (1.5 eq.) [c] Cs_2CO_3 (1.0 eq.) [d] under air atmosphere. [e] 120 °C. [f] 100 °C.



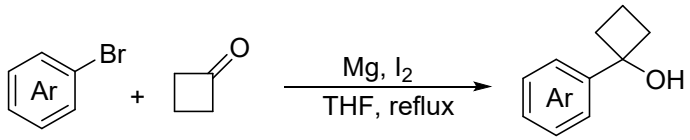
Scheme S1 Reactions of 3- and 5-Membered Cycloalkanols with **1a**[1]

2. General Information

Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were measured on a 500 MHz spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a 400 MHz spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C), using $CDCl_3$ or Acetone-d_6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions under air atmosphere were conducted using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus and uncorrected. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

3. Experimental procedures

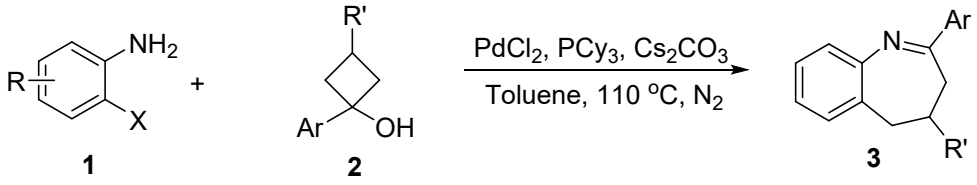
3.1 General Procedure for the Synthesis of Cyclobutanols 2:[2]



A dried two-neck round-bottomed flask equipped with a condenser and a magnetic stir bar was charged with Mg turnings (291.7 mg, 12 mmol, 2.0 equiv) under argon atmosphere. Anhydrous THF (0.5 mmol/mL) were added gradually. Then iodine (76.1 mg, 0.3 mmol, 0.05 equiv) was added under N_2. After stirring at room temperature for 10 min, bromobenzene (6.6 mmol, 1.1 equiv) in anhydrous THF (1

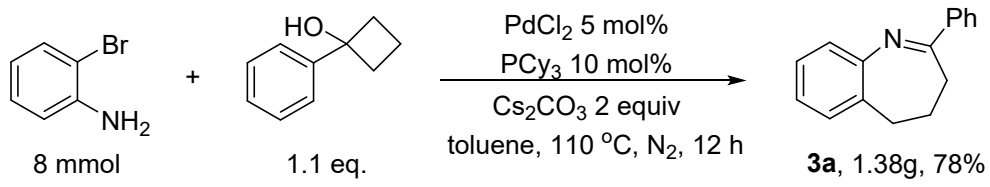
mmol/mL) was then added dropwise. The reaction was then placed in an oil bath and heated at reflux for 3 h. After cooling to room temperature, cyclobutanone (420.5 mg, 6.0 mmol, 1.0 equiv) was added. After stirring for 8 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) to give corresponding 1-substituted cyclobutanols **2**.

3.2 General Procedure for the Synthesis of Benzazepines 3:



A Schlenk tube with a magnetic stirring bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (0.22 mmol, 1.1 equiv), $PdCl_2$ (1.7 mg, 0.01 mmol, 5 mol%), PCy_3 (5.6 mg, 0.02 mmol, 10 mol%), Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv), and 4Å MS (100.0 mg) in anhydrous toluene (2 mL). The mixture was stirred under N_2 atmosphere and heated at 110 °C. After 12 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired products **3a-3z**.

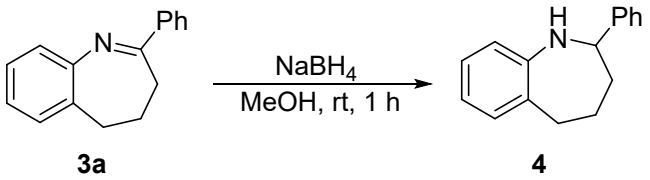
3.3 Gram Scale Reaction of Product 3a:



A Schlenk tube with a magnetic stirring bar was charged with **1a** (1.38 g, 8.0 mmol, 1.0 equiv), **2a** (1.30 g, 8.8 mmol, 1.1 equiv), $PdCl_2$ (70.9 mg, 0.4 mmol, 5 mol%), PCy_3 (224.3 mg, 0.8 mmol, 10 mol%), Cs_2CO_3 (5.21 g, 16.0 mmol, 2.0 equiv) in anhydrous toluene (80 mL). The mixture was stirred under N_2 atmosphere and heated at 110 °C. After 12 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum

ether/ethyl acetate as the eluent to afford the desired products **3a** (1.38 g, 78% yield).

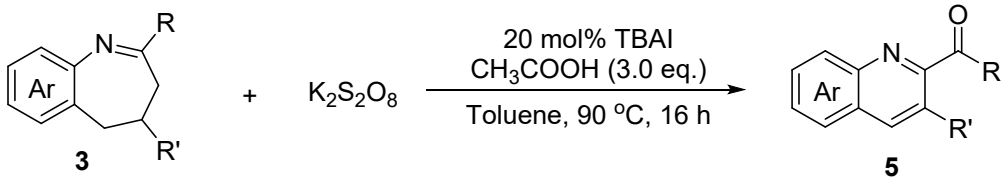
3.4 General Procedure for the Synthesis of Tetrahydrobenzazepine 4:[3]



3a **4**

A mixture of benzo[*b*]azepine **3a** (66.3 mg, 0.3 mmol) and $NaBH_4$ (17.0 mg, 0.45 mmol, 1.5 equiv) in MeOH (2 mL) was stirred at room temperature for 1 h. The reaction mixture was cooled to the room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **4** (40.1 mg, 60% yield).

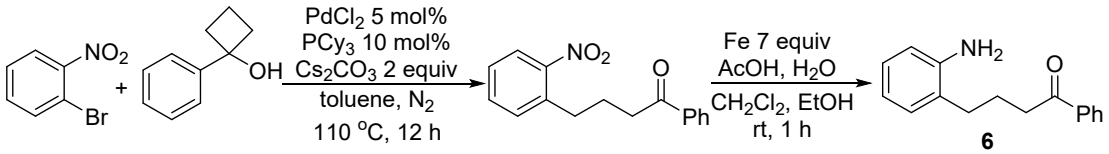
3.5 General Procedure for the Synthesis of Quinoline 5:[4]



3 **5**

A mixture of benzo[*b*]azepine **3** (0.1 mmol), *n*-Bu_4NI (7.4 mg, 0.02 mmol, 20 mol%), $K_2S_2O_8$ (108.1 mg, 0.4 mmol, 4.0 equiv) and acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) in 1 mL toluene was stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the quinoline **5**.

3.6 General Procedure for the Synthesis of intermediate 6:[5]



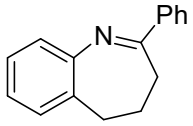
6

A Schlenk tube with a magnetic stirring bar was charged with 1-bromo-2-nitrobenzene1 (2.02 g, 10 mmol, 1.0 equiv), 1-phenylcyclobutan-1-ol (1.63 g, 11 mmol, 1.1 equiv), $PdCl_2$ (88.7 mg, 0.5 mmol, 5 mol%), PCy_3 (280.4 mg, 1 mmol, 10 mol%) and Cs_2CO_3 (6.52 g, 20 mmol, 2.0 equiv) in anhydrous toluene (20 mL). The mixture was stirred under N_2 atmosphere and heated at 110 °C. After 12 h, the

reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford 4-(2-nitrophenyl)-1-phenylbutan-1-one.

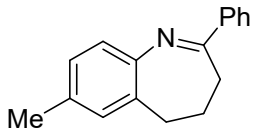
To a round flask were added 4-(2-nitrophenyl)-1-phenylbutan-1-one (1.35 g, 5 mmol), Fe powder (1.96 g, 35 mmol), AcOH (5 mL), CH_2Cl_2: EtOH (1:1, 15 mL), and H_2O (5 mL) subsequently, and the mixture continued stirring for 1 h at room temperature. After filtration, saturated $NaHCO_3$ solution was added to the mother liquor. The water layer was extracted CH_2Cl_2 (3×20 mL) and combined organic layer were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford 4-(2-aminophenyl)-1-phenylbutan-1-one.

4. Analytical Data for All Compounds.



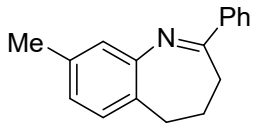
2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3a)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 38.4 mg, yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.48-7.47 (m, 3H), 7.34-7.31 (m, 1H), 7.20-7.18 (m, 2H), 7.10-7.07 (m, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.42-2.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 149.9, 139.2, 131.3, 130.4, 128.8, 128.5, 127.2, 124.5, 123.8, 34.5, 30.3, 28.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N^+$: 222.1277; Found 222.1271.



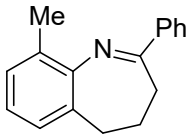
7-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3b)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 33.8 mg, yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.43-7.42 (m, 3H), 7.11-7.06 (m, 2H), 6.98 (s, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.37-2.31 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 147.3, 139.3, 134.0, 131.2, 130.2, 129.4, 128.4, 127.7, 127.1, 123.8, 34.5, 30.3, 28.8, 20.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N^+$: 236.1434; Found 236.1424.



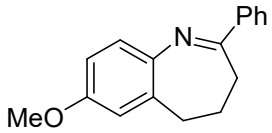
8-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3c)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 40.9 mg, yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.48-7.46 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.40-2.34 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 149.7, 139.2, 136.8, 130.3, 128.6, 128.5, 128.3, 127.2, 125.3, 124.5, 34.5, 29.9, 28.9, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N^+$: 236.1434; Found 236.1427.



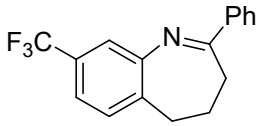
9-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3d)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 27.2 mg, yield: 58%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.37-7.35 (m, 3H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.93-6.87 (m, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.29-2.23 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 148.0, 139.2, 131.7, 130.7, 130.2, 128.6, 128.5, 127.1, 126.2, 124.3, 34.4, 30.4, 28.8, 17.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N^+$: 236.1434; Found 236.1426.



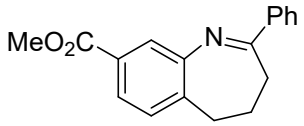
7-methoxy-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3e)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 27.7 mg, yield: 55%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.47-7.45 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.87 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.77(d, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.41-2.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 156.5, 143.2, 139.4, 132.8, 130.1, 128.4, 127.0, 125.1, 114.4, 112.0, 55.3, 34.2, 30.8, 28.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO^+$: 252.1383; Found 252.1385.



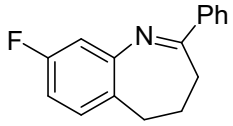
2-phenyl-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[*b*]azepine (3f)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 40.5 mg, yield: 70%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.52-7.46 (m, 3H), 7.44 (s, 1H), 7.33-7.28 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.45-2.39 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 150.3, 138.6, 135.1, 130.9, 129.8 (^{2}J = 32.1 Hz), 129.2, 128.6, 127.3, 124.3 (^{1}J = 270.4 Hz), 121.1 (^{3}J = 3.6 Hz), 120.7 (^{3}J = 3.6 Hz), 34.3, 30.2, 28.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.403(s, 3F). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3N^+$: 290.1151; Found 290.1150.



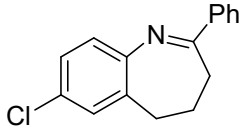
methyl 2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine-8-carboxylate (3g)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 44.1 mg, yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-8.00 (m, 2H), 7.84 (s, 1H), 7.75 (dd, *J* = 7.5, 1.0 Hz,1H), 7.48-7.47 (m, 3H), 7.25 (d, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 2.65-2.58 (m, 4H), 2.44-2.38 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 167.1, 150.0, 138.8, 136.6, 130.7, 129.4, 128.9, 128.6, 127.2, 125.7, 124.9, 52.0, 34.2, 30.4, 28.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2^+$: 280.1332; Found 280.1325.



8-fluoro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3h)[6]

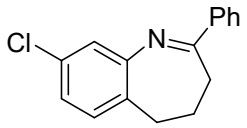
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 36.3 mg, yield: 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.51-7.45 (m, 3H), 7.12 (dd, *J* = 8.0, 6.5 Hz, 1H), 6.90 (dd, *J* = 10.0, 2.5 Hz, 1H), 6.77 (td, *J* = 8.5, 2.5 Hz 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.40-2.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 162.3 (^{1}J = 241.9 Hz), 151.3 (^{3}J = 10.0 Hz), 138.8, 130.7, 129.6(^{3}J = 8.9 Hz), 128.6, 127.3, 127.0 (^{4}J = 3.0 Hz), 111.0 (^{2}J = 21.1 Hz), 110.7 (^{2}J = 22.5 Hz), 34.5, 29.6, 28.9. ^{19}F NMR (470 MHz, Acetone-d_6) δ -59.464 (s, 1F). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}FN^+$: 240.1183; Found 240.1178.



7-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3i)

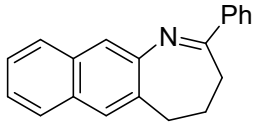
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 39.8 mg, yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.49-7.44 (m, 3H), 7.27-7.25 (m, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.40-2.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 148.4, 138.8, 133.1, 130.6, 129.4, 128.64, 128.59, 127.21, 127.18, 125.2, 34.2, 30.2, 28.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}ClN^+$:

256.0888; Found 256.0877.



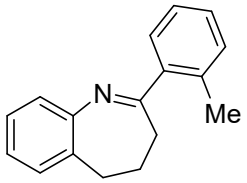
8-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3j)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 39.8 mg, yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.49-7.46 (m, 3H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.04 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.40-2.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 151.1, 138.7, 132.7, 130.7, 129.8, 128.6, 127.3, 124.4, 123.8, 34.3, 29.8, 28.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}ClN^+$: 256.0888; Found 256.0884.



2-phenyl-4,5-dihydro-3H-naphtho[1,2-*b*]azepine (3k)

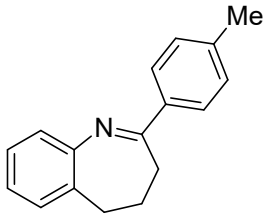
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 28.2 mg, yield: 52%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 1H), 8.19-8.18 (m, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53-7.48 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 1H), 2.72-2.68 (m, 4H), 2.58-2.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 144.8, 139.3, 133.2, 130.4, 129.0, 128.6, 127.7, 127.5, 127.3, 126.7, 125.45, 125.37, 124.4, 124.0, 36.5, 30.7, 29.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}N^+$: 272.1434; Found 272.1428.



2-(o-tolyl)-4,5-dihydro-3H-benzo[b]azepine (3l)

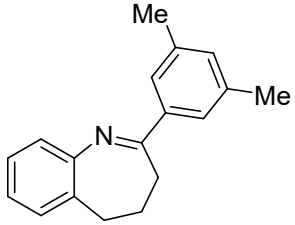
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 35.7 mg, yield: 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.31-7.23 (m, 4H), 7.20-7.16 (m, 2H), 7.08 (t, *J* = 7.0 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.53-2.50 (m, 5H), 2.40-2.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 149.3, 141.4, 135.3, 131.2, 131.0, 128.8, 128.7, 127.9, 127.2, 125.8, 124.7, 124.0, 34.6, 32.6, 30.5, 20.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N^+$: 236.1434; Found

236.1433.



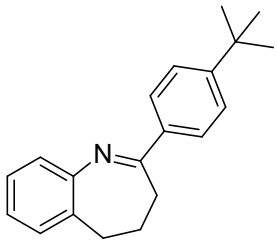
2-(p-tolyl)-4,5-dihydro-3H-benzo[*b*]azepine (3m)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 40.4 mg, yield: 86%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.31-7.25 (m, 3H), 7.18-7.15 (m, 2H), 7.07-7.03 (m, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.39-2.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 150.0, 140.7, 136.4, 131.4, 129.2, 128.7, 127.19, 127.15, 124.4, 123.8, 34.5, 30.3, 28.7, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N^+$: 236.1434; Found 236.1424.



2-(3,5-dimethylphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3n)

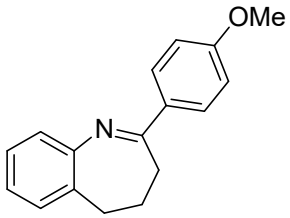
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 36.9 mg, yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.33-7.30 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 7.09-7.06 (m, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.41-2.36 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 149.9, 139.2, 138.0, 132.1, 131.3, 128.7, 127.1, 125.0, 124.4, 123.8, 34.6, 30.3, 28.9, 21.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}N^+$: 250.1590; Found 250.1583.



2-(4-(tert-butyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3o)

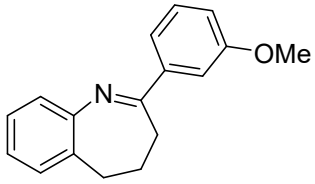
Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 41.0 mg, yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.08 (t, *J* =

7.5 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.41-2.36 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 153.9, 150.0, 136.2, 131.4, 128.7, 127.2, 127.0, 125.5, 124.4, 123.9, 34.8, 34.5, 31.2, 30.3, 28.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}N^+$: 278.1903; Found 278.1906.



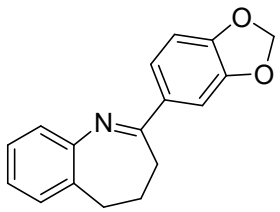
2-(4-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepin (3p)[7]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 33.1 mg, yield: 66%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99-6.97 (m, 2H), 3.87 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.39-2.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 161.6, 150.1, 131.7, 131.3, 128.9, 128.7, 127.1, 124.2, 123.8, 113.8, 55.4, 34.3, 30.3, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO^+$: 252.1383; Found 252.1378.



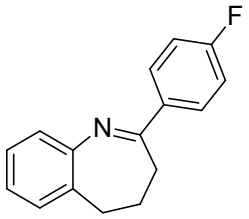
2-(3-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3q)[6]

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 30.1 mg, yield: 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.20-7.17 (m, 2H), 7.09-7.02 (m, 2H), 3.90 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.41-2.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 159.9, 149.8, 140.6, 131.3, 129.4, 128.8, 127.2, 124.6, 123.8, 119.8, 116.6, 112.0, 55.4, 34.6, 30.3, 28.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO^+$: 252.1383; Found 252.1386.



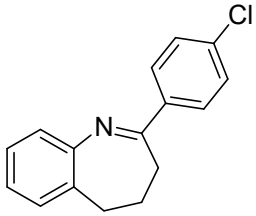
2-(benzo[d][1,3]dioxol-5-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3r)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 39.2 mg, yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.47 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18-7.13 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.38-2.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 149.9, 149.7, 148.2, 133.7, 131.3, 128.7, 127.2, 124.4, 123.8, 122.1, 107.9, 107.3, 101.5, 34.4, 30.3, 28.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_2^+$: 266.1176; Found 266.1168.



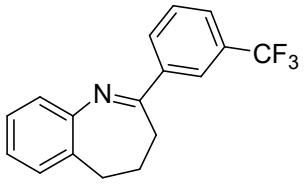
2-(4-fluorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3s)[6]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 33.5 mg, yield: 70%; m.p.: 117.5-118.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.32 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20-7.13 (m, 4H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.41-2.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 164.3 (^1J = 249.3 Hz), 149.7, 135.3 (^4J = 3.0 Hz), 131.2, 129.3 (^3J = 8.5 Hz), 128.8, 127.2, 124.6, 123.8, 115.4 (^2J = 21.5 Hz), 34.4, 30.3, 28.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -110.384 (s, 1F). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}FN^+$: 240.1183; Found 240.1181.



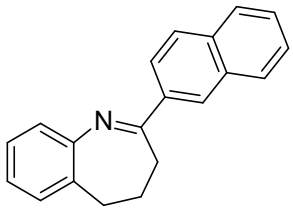
2-(4-chlorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3t)[6]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 29.1 mg, yield: 57%; m.p.: 116.4-118.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.32 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20-7.15 (m, 2H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.41-2.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 149.6, 137.5, 136.6, 131.2, 128.8, 128.7, 128.5, 127.3, 124.7, 123.8, 34.5, 30.3, 28.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}ClN^+$: 256.0888; Found 256.0887.



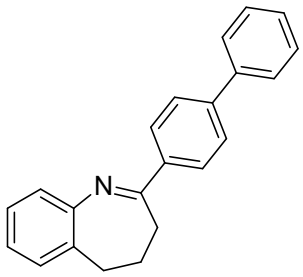
2-(3-(trifluoromethyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3u)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 49.7 mg, yield: 86%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22-7.19 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.45-2.39 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 149.4, 139.9, 131.2, 131.1 (^{2}J = 32.3 Hz), 130.4, 129.0, 128.9, 127.3, 126.9 (^{3}J = 3.7 Hz), 125.0, 124.1 (^{1}J = 270.8 Hz), 124.0 (^{3}J = 3.9 Hz), 123.9, 34.6, 30.3, 28.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.599 (s, 3F). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3N^+$: 290.1151; Found 290.1153.



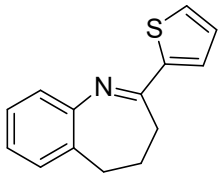
2-(naphthalen-2-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3v)

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 51.5 mg, yield: 95%; m.p.: 95.8-99.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.16 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.84-7.76 (m, 3H), 7.44-7.40 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.14-7.10 (m, 2H), 6.99 (t, *J* = 7.0 Hz,1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.37-2.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 150.0, 136.4, 134.4, 133.1, 131.3, 128.85, 128.79, 128.2, 127.7, 127.5, 127.2, 127.1, 126.4, 124.6, 124.3, 123.9, 34.6, 30.4, 28.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}N^+$: 272.1434; Found 272.1428.



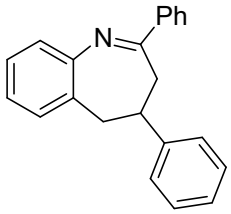
2-([1,1'-biphenyl]-4-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3w)

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 27.9 mg, yield: 47%; m.p.: 115.9-117.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.62-7.56 (m, 4H), 7.40-7.37 (m, 2H), 7.31-7.28 (m, 1H), 7.25-7.22 (m, 1H), 7.12-7.10 (m, 2H), 7.01-6.97 (m, 1H), 2.60-2.57 (m, 2H), 2.50-2.46 (m, 2H), 2.34-2.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 150.0, 143.2, 140.4, 137.9, 131.3, 128.9, 128.8, 127.73, 127.71, 127.2, 127.1, 124.6, 123.9, 34.6, 30.4, 28.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N^+$: 298.1590; Found 298.1598.



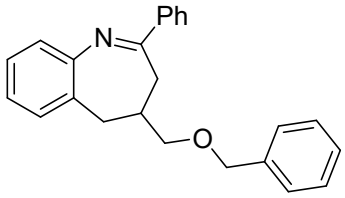
2-(thiophen-2-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3x)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 27.2mg, yield: 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.18-7.15 (m, 2H), 7.12-7.10 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.40-2.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 149.3, 145.8, 131.6, 130.4, 128.8, 128.3, 127.6, 127.2, 124.6, 124.2, 34.1, 30.3, 29.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NS^+$: 228.0841; Found 228.0831.



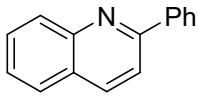
2,4-diphenyl-4,5-dihydro-3H-benzo[*b*]azepine (3y)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 53.5 mg, yield: 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.45-7.39 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.27-7.18 (m, 6H), 7.13-7.07 (m, 2H), 3.88-3.84 (m, 1H), 3.01-2.96 (m, 2H), 2.83-2.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 149.6, 144.8, 139.0, 130.5, 129.9, 129.7, 128.6, 128.5, 127.5, 127.4, 126.9, 126.8, 124.8, 124.3, 52.6, 37.5, 36.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N^+$: 298.1590; Found 298.1583.



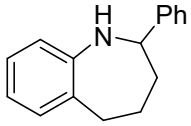
4-((benzyloxy)methyl)-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3z)

Yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 53.7 mg, yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.09 (m, 2H), 7.52-7.46 (m, 3H), 7.42-7.33 (m, 6H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 6.5 Hz, 1H), 7.09 (td, *J* = 7.0, 1.0 Hz, 1H), 4.57-4.50 (q, *J* = 10.0 Hz, 2H), 3.49-3.38 (m, 2H), 3.02-2.94 (m, 1H), 2.73-2.56 (m, 3H), 2.44-2.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 149.6, 139.4, 138.2, 130.4, 129.5, 129.4, 128.5, 128.4, 127.7, 127.6, 127.3, 127.2, 124.5, 124.0, 73.2, 72.7, 47.2, 32.9, 31.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO^+$: 342.1852; Found 342.1853.



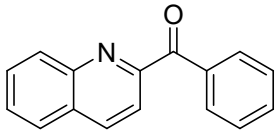
2-phenylquinoline (3aa)[8]

White solid obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 23.1 mg, yield: 56%; m.p.: 85.2-86.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.22-8.17 (m, 3H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.58-7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 148.2, 139.6, 136.6, 129.6, 129.5, 129.2, 128.7, 127.5, 127.4, 127.1, 126.2, 118.9.



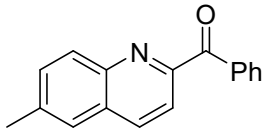
2-phenyl-2,3,4,5-tetrahydro-1H-benzo[*b*]azepine (4)[9]

Light yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 60:1), 40.1 mg, yield: 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.31 (m, 5H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.84 (d, *J* = 10.5 Hz, 1H), 3.71 (brs, 1H), 2.93-2.83 (m, 2H), 2.07-1.91 (m, 3H), 1.53-1.46 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 146.1, 133.8, 130.6, 128.8, 127.4, 126.7, 126.5, 121.3, 120.0, 63.9, 40.0, 35.5, 26.6. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{16}H_{18}N^+$: 224.1434; Found 224.1434.



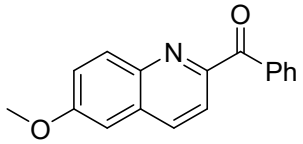
phenyl(quinolin-2-yl)methanone (5a)[10]

Light yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 17.1 mg, yield: 73%; m.p.: 105.3-106.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 1H), 8.25-8.23 (m, 2H), 8.21-8.20 (m, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.80-7.77 (m, 1H), 7.68-7.61(m, 2H), 7.53-7.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 154.7, 146.8, 137.0, 136.2, 133.0, 131.4, 130.5, 130.0, 128.9, 128.4, 128.1, 127.6, 120.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{11}NONa^+$: 256.0733; Found 256.0734.



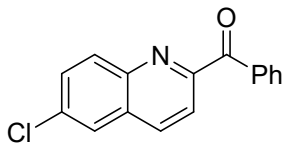
(6-methylquinolin-2-yl)(phenyl)methanone (5b)[11]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 18.5 mg, yield: 75%; m.p.: 76.8-78.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.23 (m, 3H), 8.10-8.08 (m, 2H), 7.66 (s, 1H), 7.62-7.60 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 153.8, 145.3, 138.7, 136.29, 136.27, 132.9, 132.4, 131.4, 130.2, 129.0, 128.1, 126.4, 120.8, 21.8.



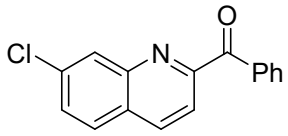
(6-methoxyquinolin-2-yl)(phenyl)methanone (5c)[12]

Gray solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 16.8 mg, yield: 64%; m.p.: 112.8-113.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.20 (m, 3H), 8.13-8.07 (m, 2H), 7.62-7.60 (m, 1H), 7.53-7.51 (m, 2H), 7.44-7.41 (m, 1H), 7.14 (s, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 159.4, 152.3, 142.8, 136.4, 135.5, 132.8, 132.0, 131.4, 130.3, 128.0, 123.1, 121.3, 104.8, 55.6.



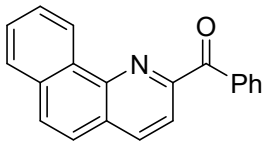
(6-chloroquinolin-2-yl)(phenyl)methanone (5d)[12]

Light yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 18.2 mg, yield: 68%; m.p.: 145.2-146.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 154.8, 145.1, 136.2, 136.0, 134.4, 133.2, 132.1, 131.4, 131.2, 129.5, 128.2, 126.3, 121.7.



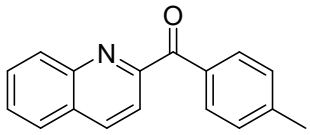
(7-chloroquinolin-2-yl)(phenyl)methanone (5e)[12]

White solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 15.0 mg, yield: 56%; m.p.: 89.7-90.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.22-8.21 (m, 3H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.52 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 155.5, 147.0, 137.0, 136.1, 135.9, 133.2, 131.4, 129.44, 129.38, 128.8, 128.2, 127.2, 121.0.



benzo[*h*]quinolin-2-yl(phenyl)methanone (5f)[12]

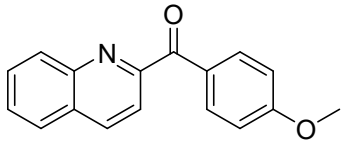
Red solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 11.3 mg, yield: 40%; m.p.: 108.3-109.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17-9.15 (m, 1H), 8.39-8.30 (m, 4H), 7.95-7.91 (m, 2H), 7.78-7.65 (m, 4H), 7.57 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 152.8, 145.0, 136.73, 136.70, 133.8, 132.7, 131.8, 131.6, 130.0, 128.6, 128.0, 127.9, 127.7, 127.6, 124.9, 124.8, 121.9.



quinolin-2-yl(p-tolyl)methanone (5g)[10]

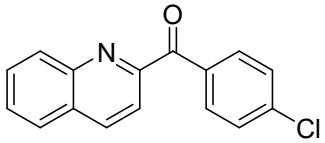
Brown solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 14.1 mg, yield: 57%; m.p.: 62.2-63.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 155.0, 146.7,

143.9, 137.0, 133.5, 131.5, 130.4, 130.0, 128.9, 128.8, 128.2, 127.6, 120.8, 21.7.



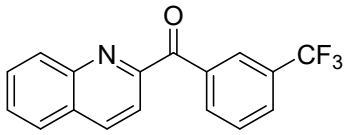
(4-methoxyphenyl)(quinolin-2-yl)methanone (5h)[10]

White solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 17.1 mg, yield: 65%; m.p.: 66.8-67.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.30-8.27 (m, 2H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.80-7.76 m, 1H), 7.67-7.63 (m, 1H), 7.01-6.98 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 163.7, 155.3, 146.6, 137.0, 133.8, 130.3, 130.0, 128.9, 128.7, 128.1, 127.6, 120.8, 113.5, 55.4.



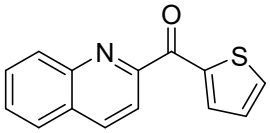
(4-chlorophenyl)(quinolin-2-yl)methanone (5i)[10]

Brown solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 16.5 mg, yield: 62%; m.p.: 105.2-106.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 154.2, 146.6, 139.5, 137.2, 134.5, 132.9, 130.5, 130.2, 129.0, 128.6, 128.4, 127.7, 120.7.



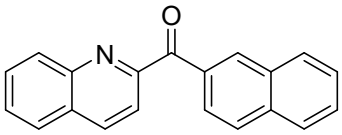
quinolin-2-yl(3-(trifluoromethyl)phenyl)methanone (5j)[13]

Light yellow oil obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 16.9 mg, yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.46 (d, *J* = 7.6 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 8.21-8.17 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.71-7.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 153.6, 146.7, 137.4, 136.8, 134.6, 130.60 (^{2}J = 32.6 Hz), 130.55, 130.3, 129.2 (^{3}J = 3.5 Hz), 129.1, 128.8, 128.6, 128.5 (^{3}J = 3.8 Hz), 127.7, 123.9 (^{1}J = 270.7 Hz), 120.6.



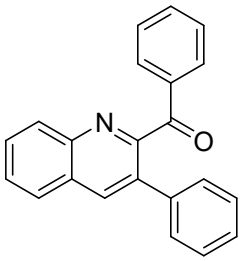
quinolin-2-yl(thiophen-2-yl)methanone (5k)[14]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 9.6 mg, yield: 40%; m.p.: 96.8-97.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51-8.50 (m, 1H), 8.35-8.25 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.84-7.80 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 153.4, 146.7, 139.7, 137.2, 136.8, 130.3, 130.1, 129.3, 128.6, 127.7, 127.5, 119.8.



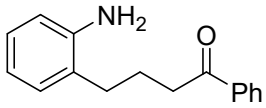
naphthalen-2-yl(quinolin-2-yl)methanone (5l)[14]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 14.4 mg, yield: 51%; m.p.: 135.1-136.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.97-7.90 (m, 4H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 155.0, 146.8, 137.1, 135.6, 134.1, 133.4, 132.4, 130.5, 130.1, 129.9, 128.9, 128.5, 128.4, 127.9, 127.72, 127.66, 126.5, 126.4, 120.9.



phenyl(3-phenylquinolin-2-yl)methanone (5m)[15]

Yellow solid obtained by column chromatography (Petroleum ether/ethyl acetate = 30:1), 7.7 mg, yield: 25%; m.p.: 113.2-114.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.42-7.39 (m, 4H), 7.34-7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 156.3, 146.0, 137.7, 137.2, 136.2, 134.0, 133.5, 130.5, 130.1, 129.7, 129.0, 128.6, 128.4, 128.1, 128.0, 127.9, 127.7.



4-(2-aminophenyl)-1-phenylbutan-1-one (6)

Colourless oil obtained by column chromatography (Petroleum ether/ethyl acetate = 10:1), 980.1mg, yield: 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.06-7.03 (m, 2H), 6.72-6.68 (m, 2H), 4.03 (s, 2H), 3.09 (t, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.08-2.01 (m, 2H).

5. References

(1) A. Nikolaev, N. Nithiy and A. Orellana, *Synlett*, 2014, **25**, 2301-2305.

(2) Y. Y. Hu, H. G. Luo, X. T. Tu, H. Xue, H. W. Jin, Y. K. Liu and B. W. Zhou, *Chem. Commun.,* 2021, **57**, 4686–4689.

(3) Q.-W. Song, B. Yu, X.-D. Li, R. Ma, Z.-F. Diao, R.-G. Li, W. Li, L.-N. He, *Green Chem.,* 2014, **16**, 1633-1638.

(4) D. Zhao, T. Wang, Q. Shen, J.-X. Li, *Chem. Commun.,* 2014, **50**, 4302-4304.

(5) J. Yang, C.-Q. Ke, D. Zhang, X.-H. Liu, X.-M Feng, *Org. Lett.* 2018, **20**, 4536-4539.

(6) R.-L. Yan and D.-J. Zhuang, CN 112574108 A, 2021.

(7) G. Dyker and H. Markwitz, *Synthesis* 1998; **1998**, 1750-1754.

(8) S. Y. Lee and C.-H. Cheon, *J. Org. Chem*. 2018, **83**, 13036-13044.

(9) O. Villanueva, N. M. Weldy, S. B. Blakey and C. E. MacBeth, *Chem. Sci.*, 2015, **6**, 6672-6675.

(10) W. Ali, A. Behera, S. Guin, and B. K. Patel, *J. Org. Chem.* 2015, **80**, 5625-5632.

(11) X. Wu, X. Geng, P. Zhao, J. J. Zhang, X. X. Gong, Y. D. Wu and A. X. Wu, *Org. Lett.* 2017, **19**, 1550-1553.

(12) Z. J. Mao, H. J. Qu, Y. Y. Zhao and X. F. Lin, *Chem. Commun.*, 2012, **48**, 9927-9929.

(13) B. Reux, T. Nevalainen, K. H. Raitio, A. M. P. Koskinen, *Bioorg. Med. Chem.* 2009, **17**, 4441.

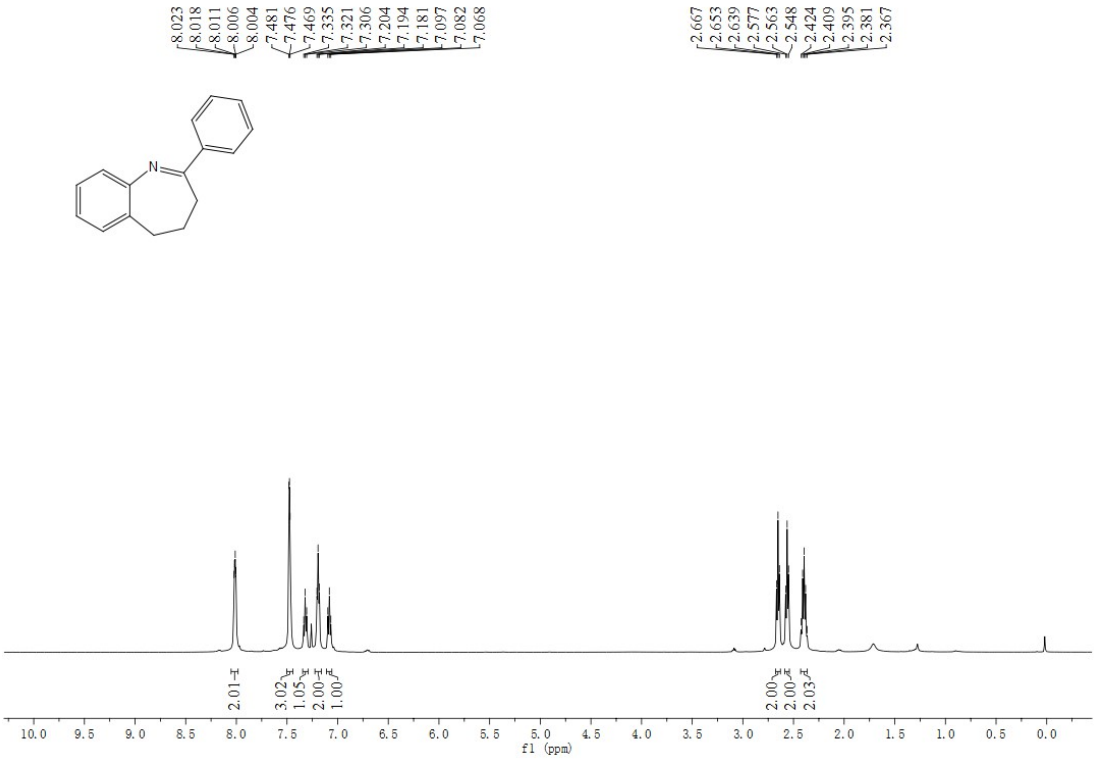
(14) T. J. Shao, Y. J. Li, N. N. Ma, C. Y. Li, G. B. Chai, X. W. Zhao, B. K. Qiao, Z. Y. Jiang, *iScience,* 2019, **16**, 410–419.

(15) S. Karimi, S. Ma, K. Ramig, E. M. Greer, D. J. Szalda, G. Subramaniam, *Tetrahedron Letters*, 2015, **56**, 6886-6889.

6. NMR Spectra for All Compounds

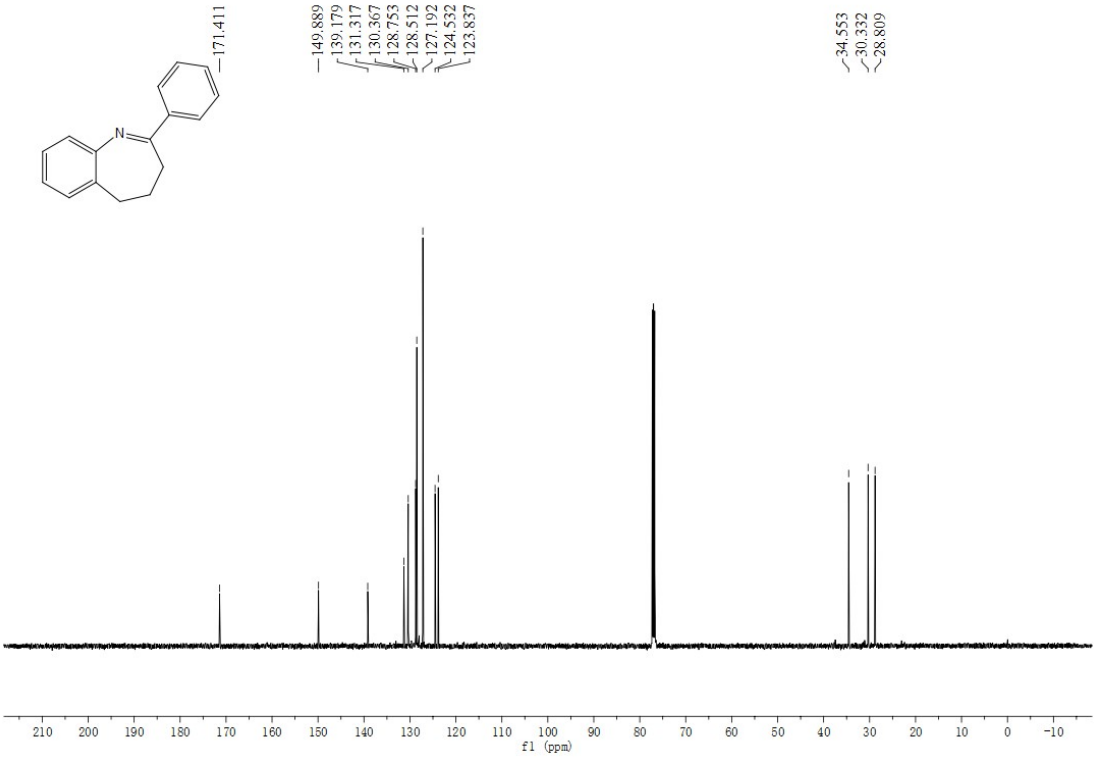
^{1}H NMR (500 MHz, $CDCl_3$)

2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3a)

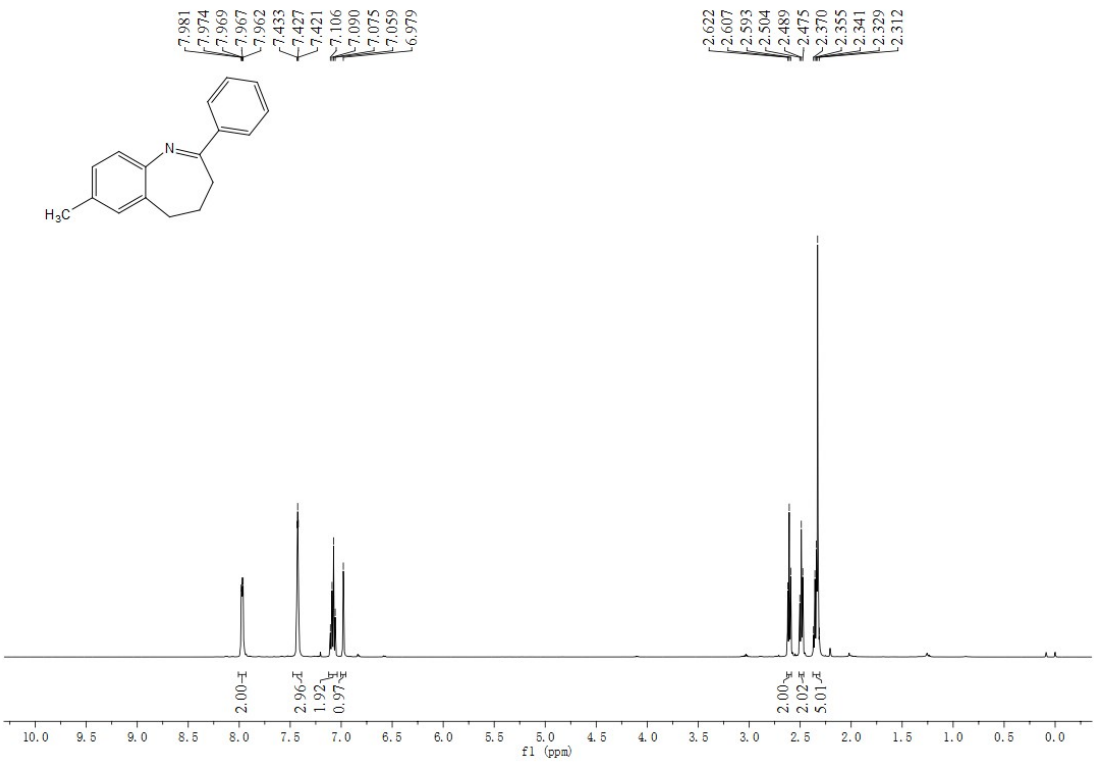


^{13}C NMR (125 MHz, $CDCl_3$)

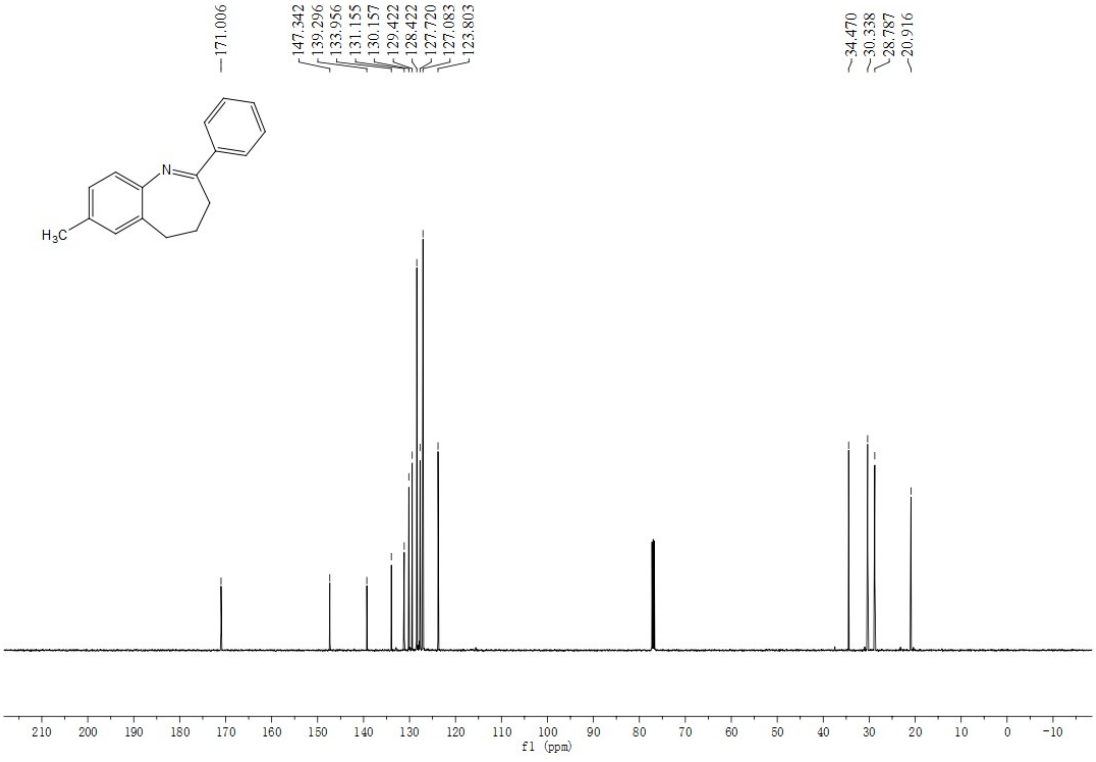
2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3a)



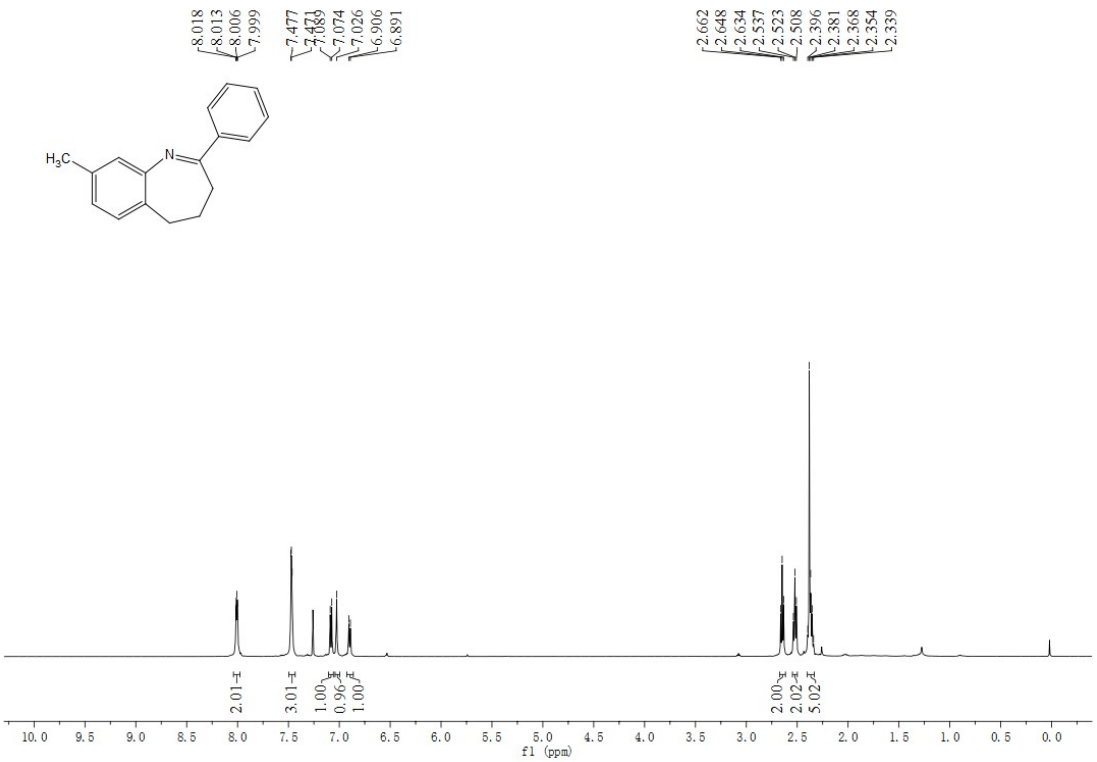
^{1}H NMR (500 MHz, $CDCl_3$)
7-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3b)



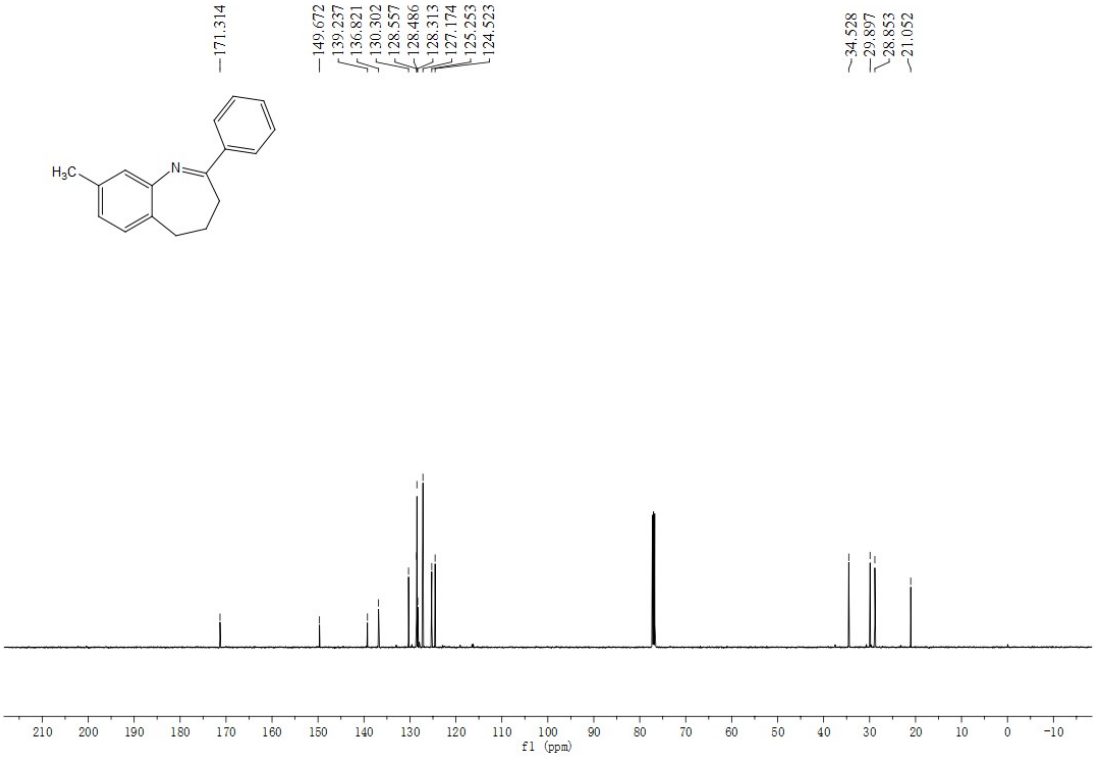
^{13}C NMR (125 MHz, $CDCl_3$)
7-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3b)



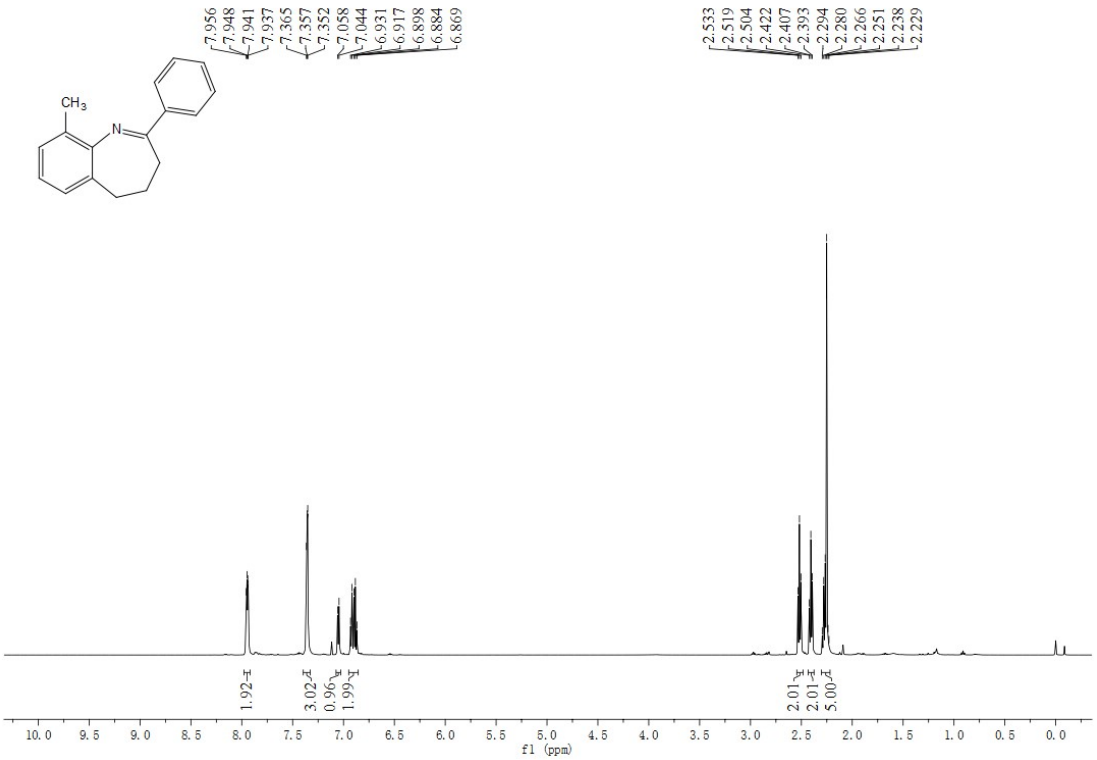
^{1}H NMR (500 MHz, $CDCl_3$)
8-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3c)



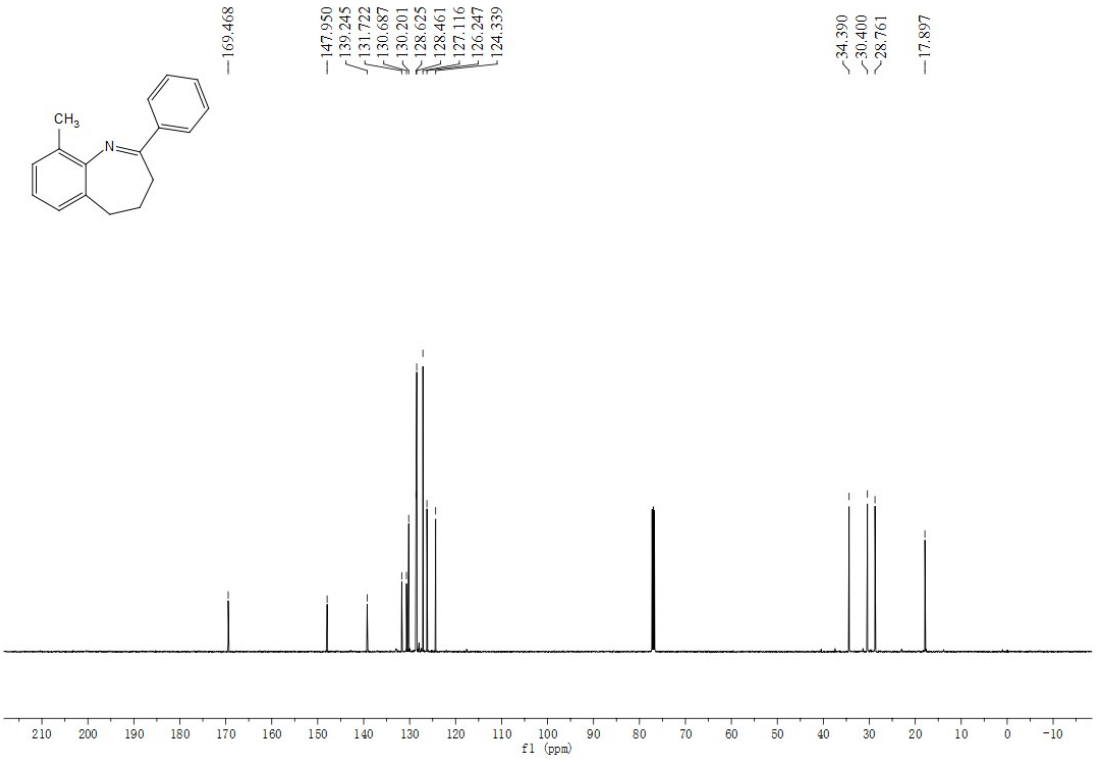
^{13}C NMR (125 MHz, $CDCl_3$)
8-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3c)



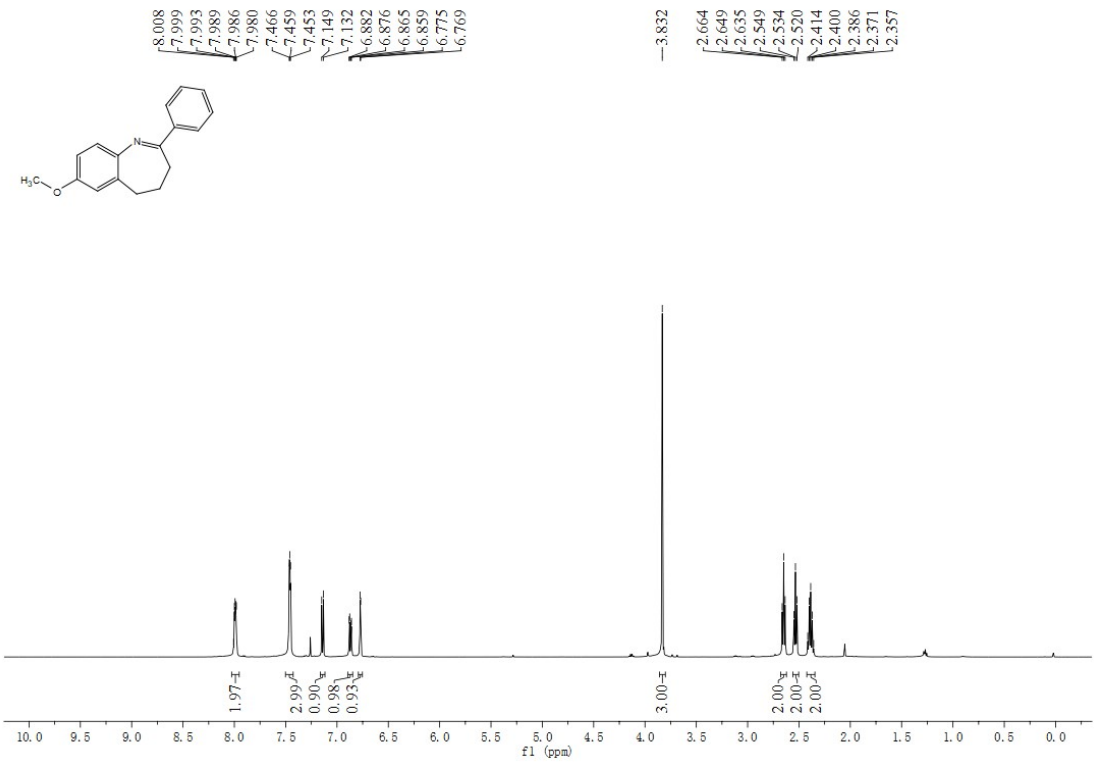
^{1}H NMR (500 MHz, $CDCl_3$)
9-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3d)



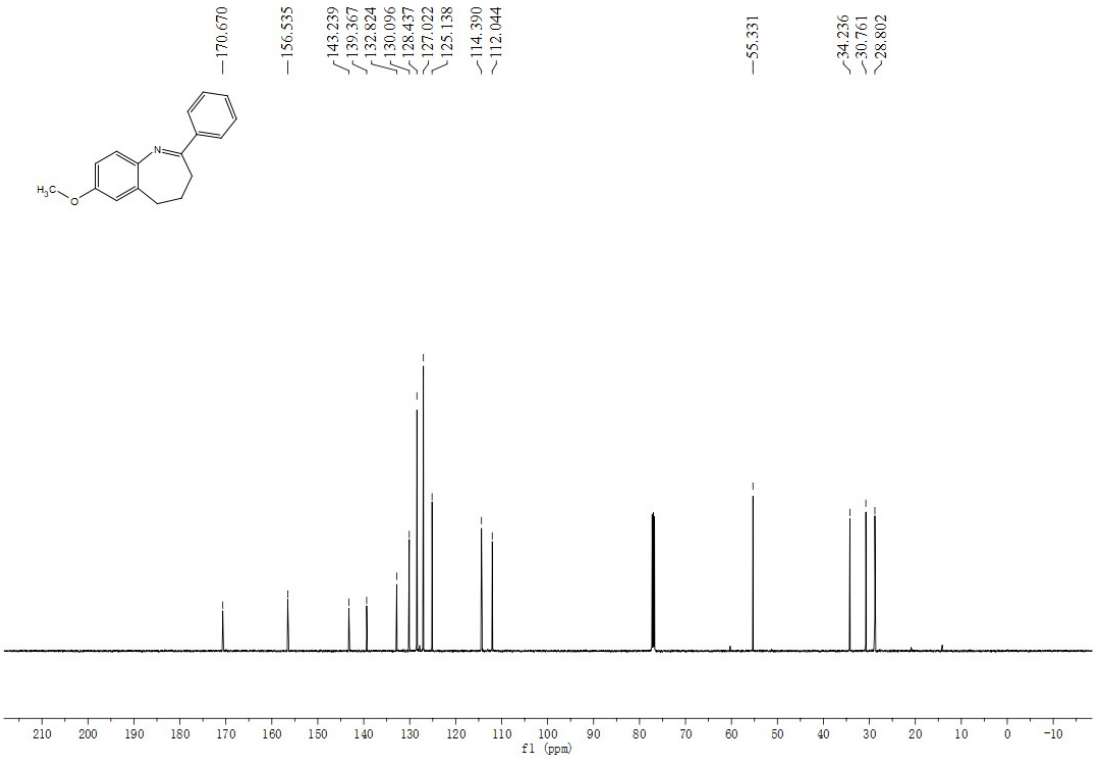
^{13}C NMR (125 MHz, $CDCl_3$)
9-methyl-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3d)



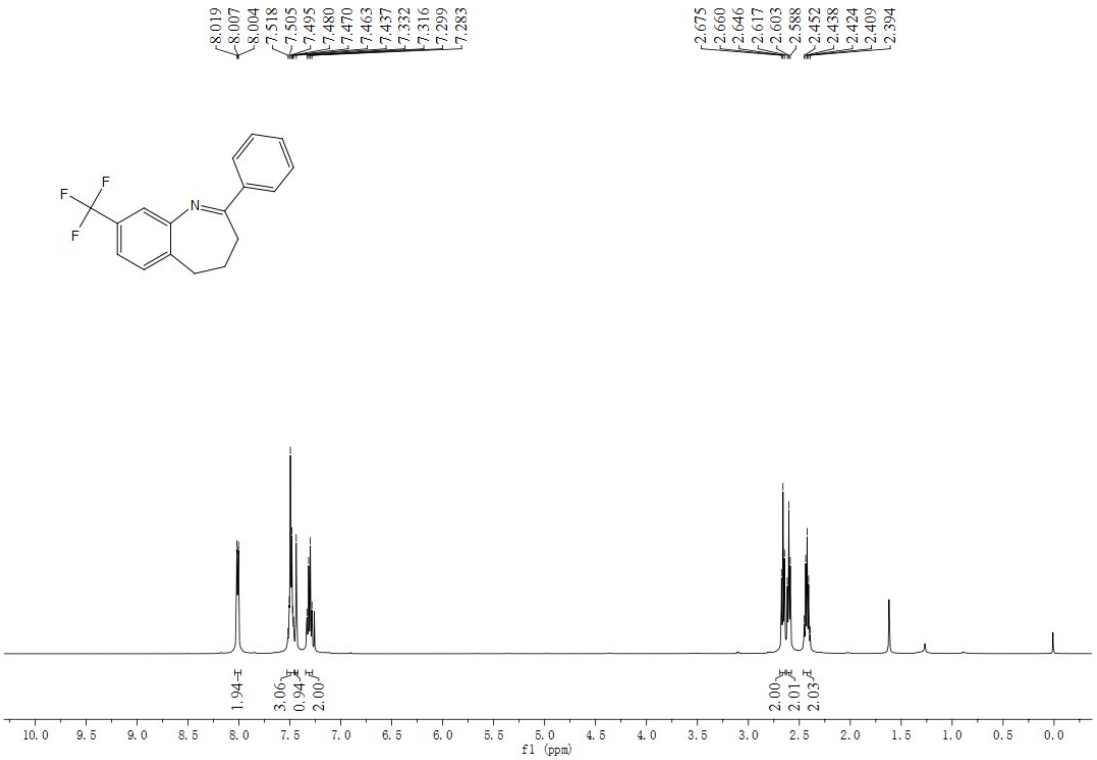
^{1}H NMR (500 MHz, $CDCl_3$)
7-methoxy-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3e)



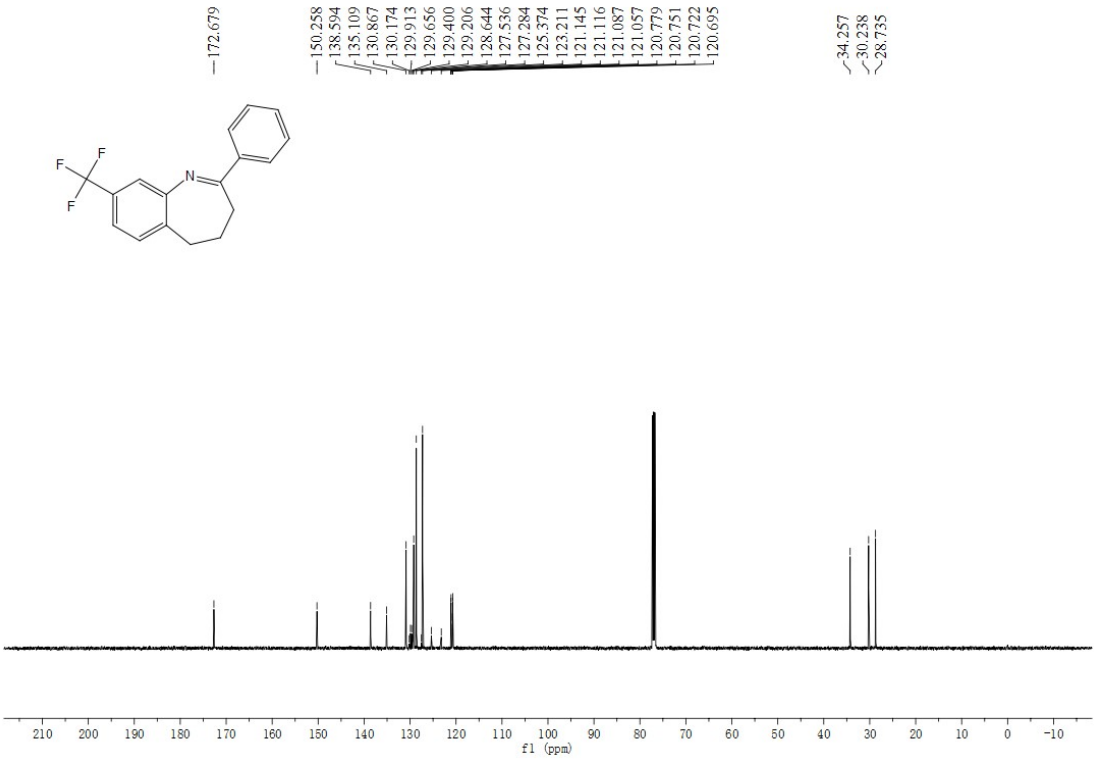
^{13}C NMR (125 MHz, $CDCl_3$)
7-methoxy-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3e)



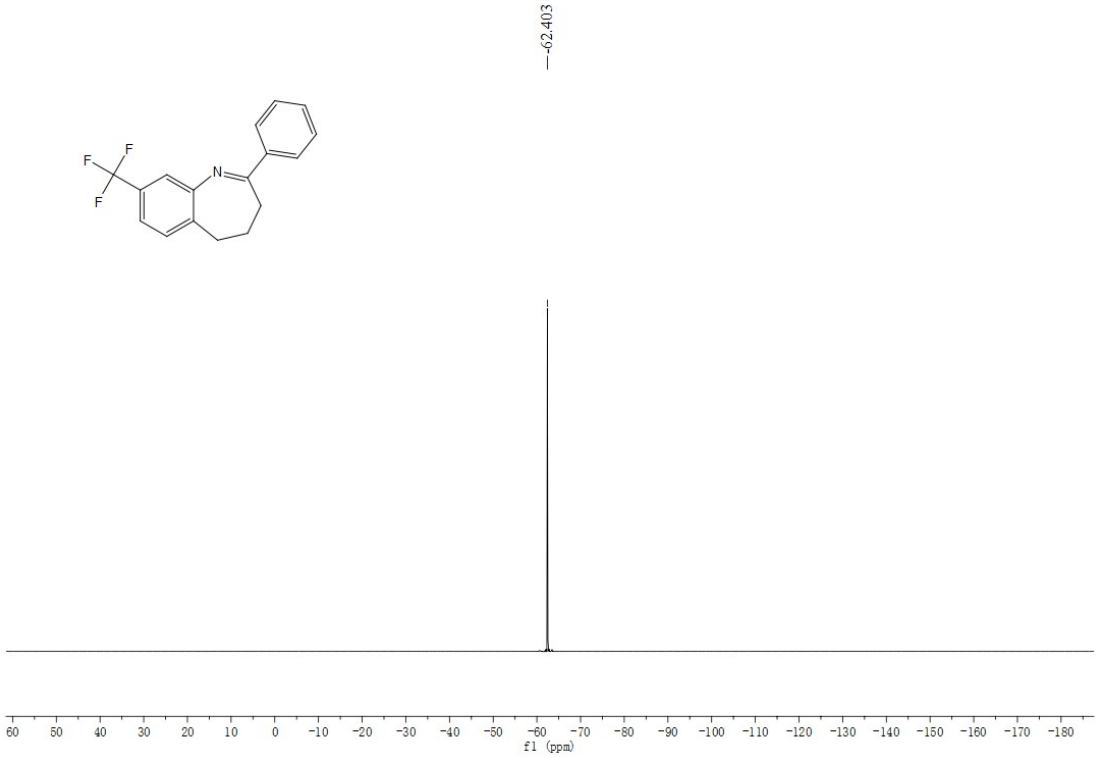
^{1}H NMR (500 MHz, $CDCl_3$)
2-phenyl-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[*b*]azepine (3f)



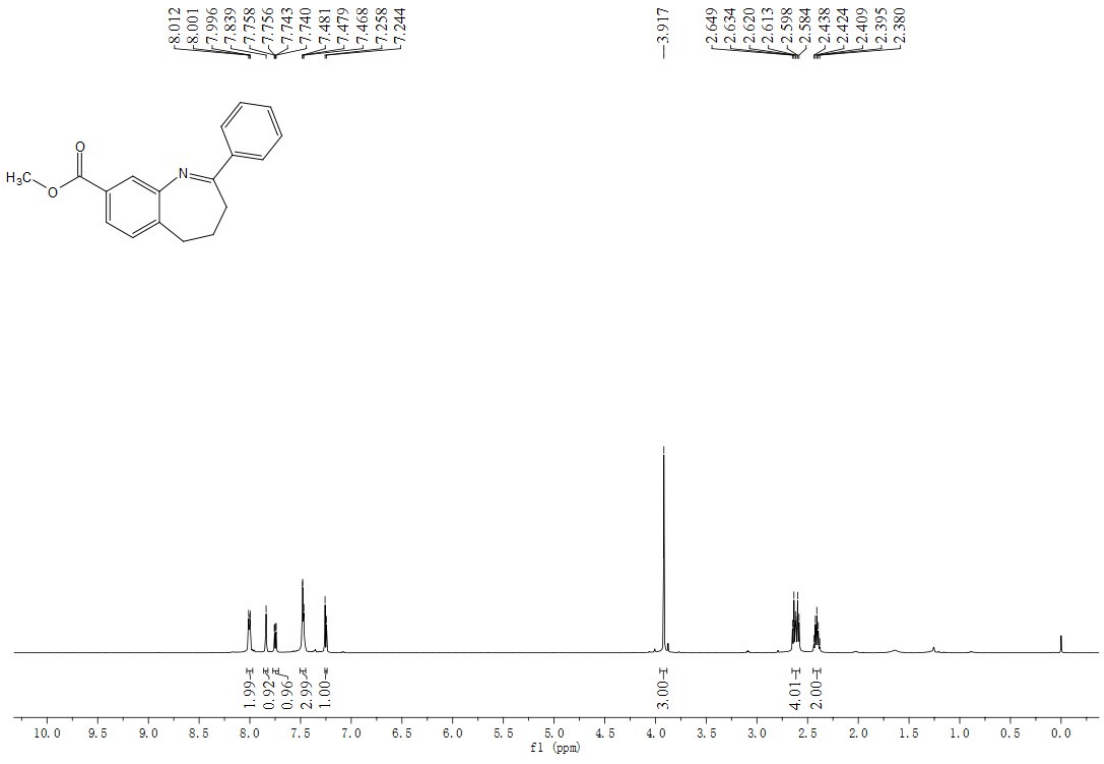
^{13}C NMR (125 MHz, $CDCl_3$)
2-phenyl-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[*b*]azepine (3f)



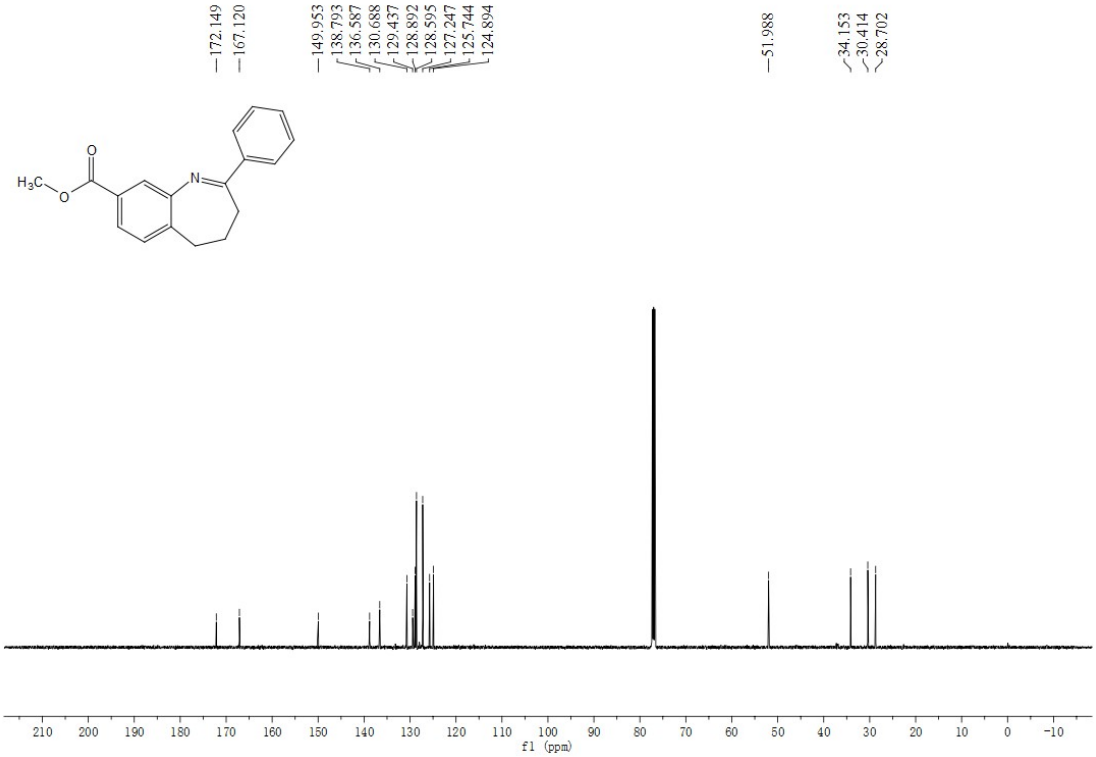
^{19}F NMR (470 MHz, $CDCl_3$)
2-phenyl-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[*b*]azepine (3f)



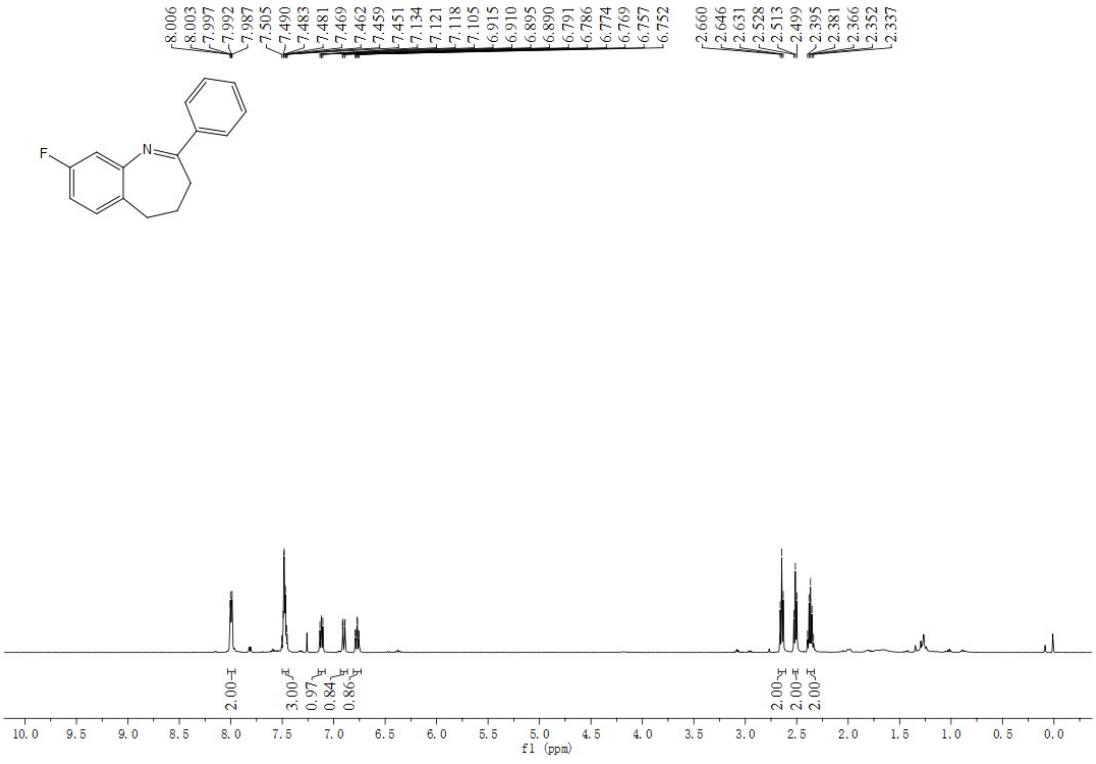
^{1}H NMR (500 MHz, $CDCl_3$)
methyl 2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine-8-carboxylate (3g)



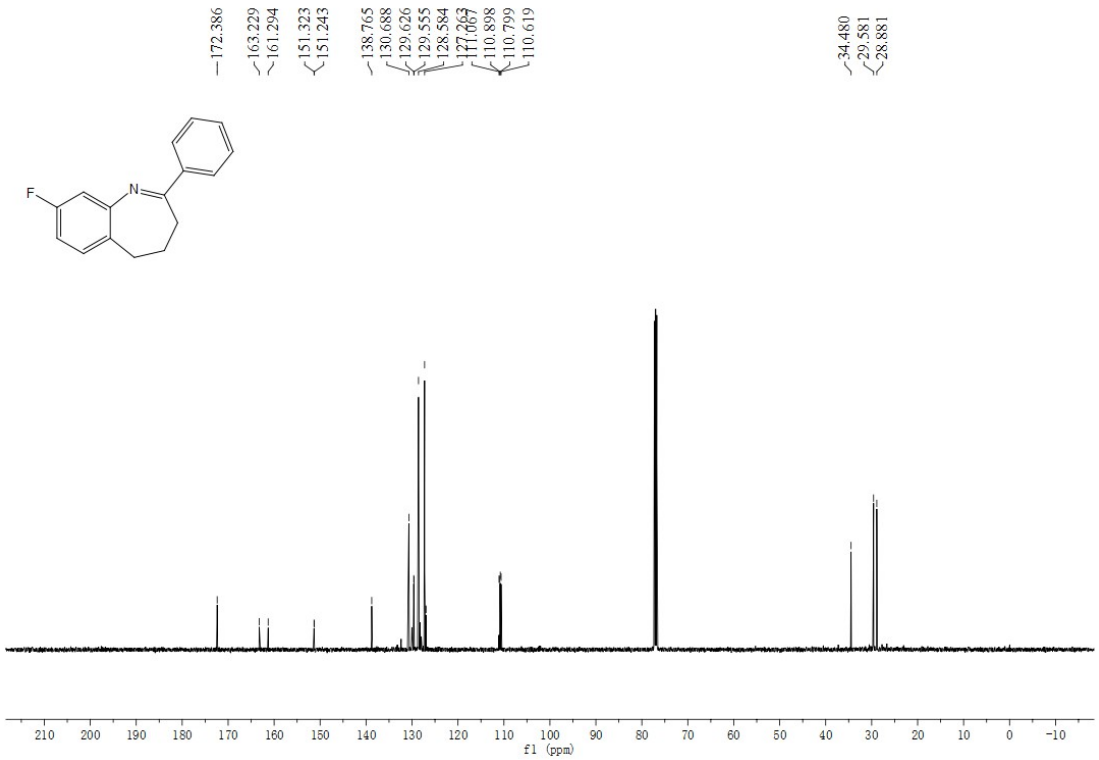
^{13}C NMR (125 MHz, $CDCl_3$)
methyl 2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine-8-carboxylate (3g)



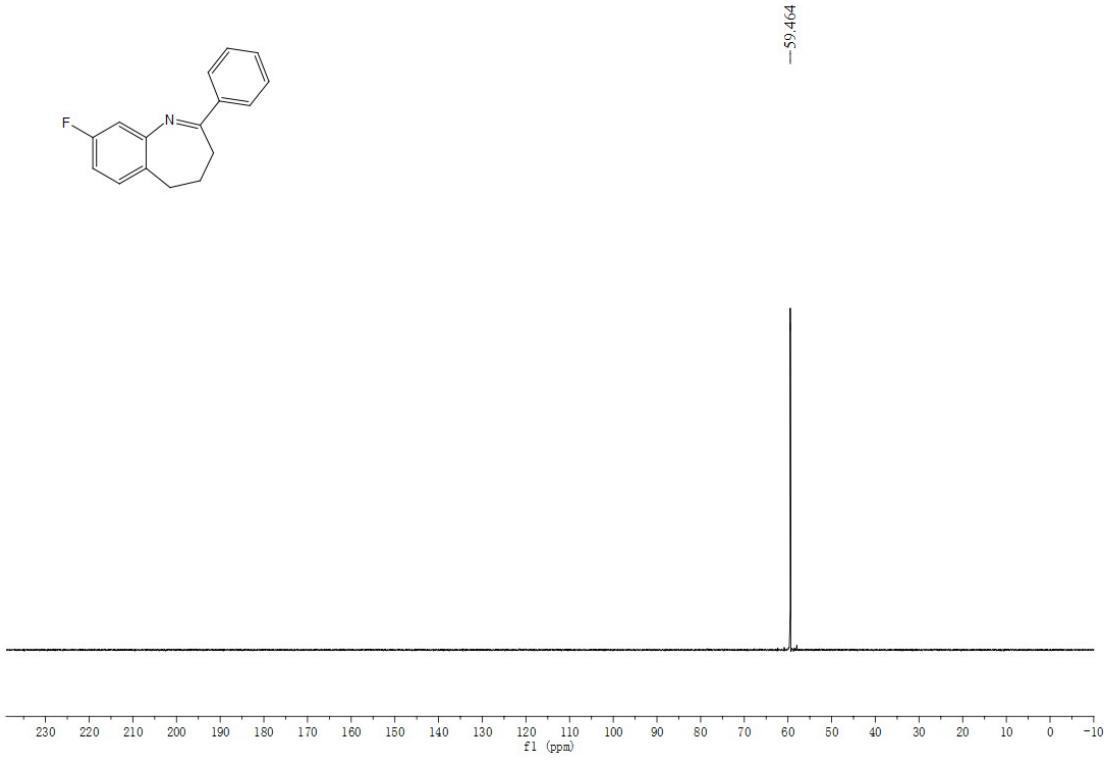
^{1}H NMR (500 MHz, $CDCl_3$)
8-fluoro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3h)



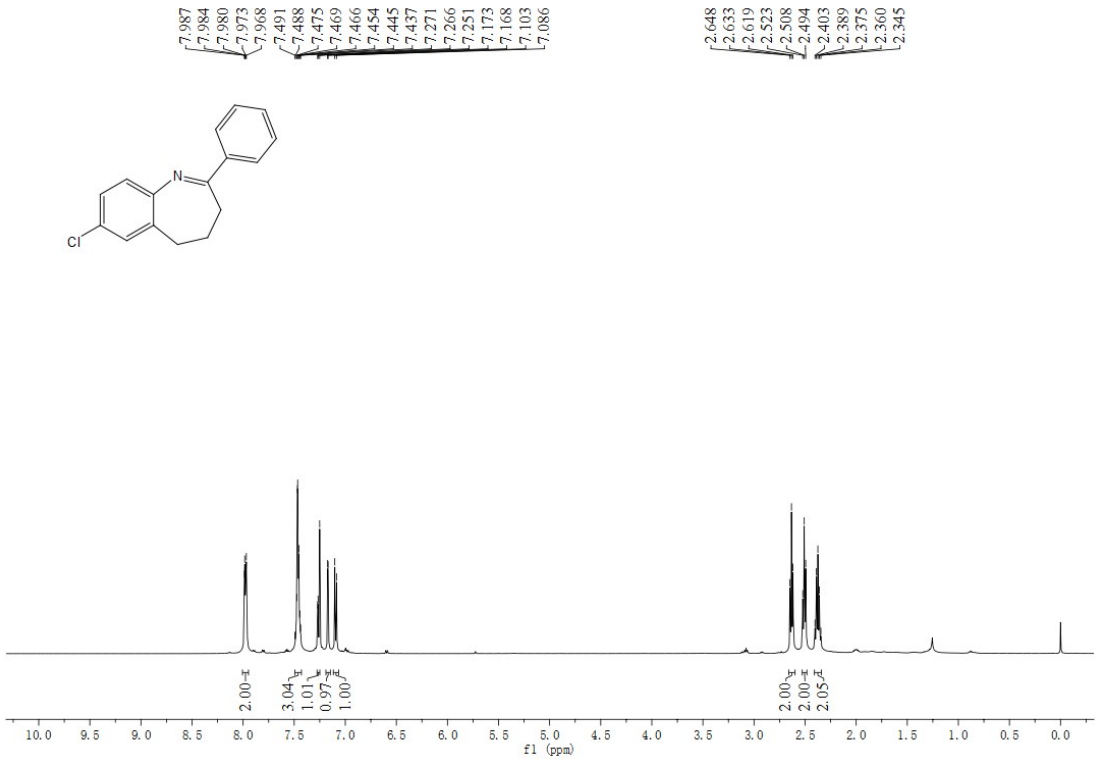
^{13}C NMR (125 MHz, $CDCl_3$)
8-fluoro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3h)



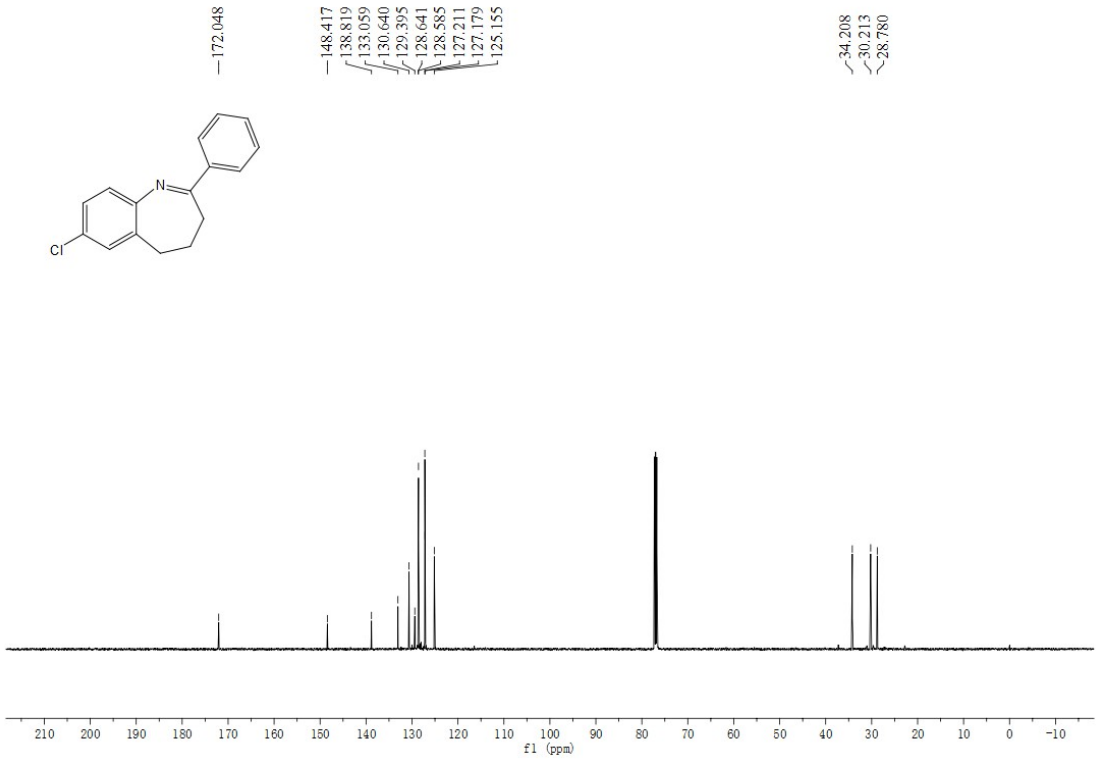
^{19}F NMR (470 MHz, Acetone-d_6)
8-fluoro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3h)



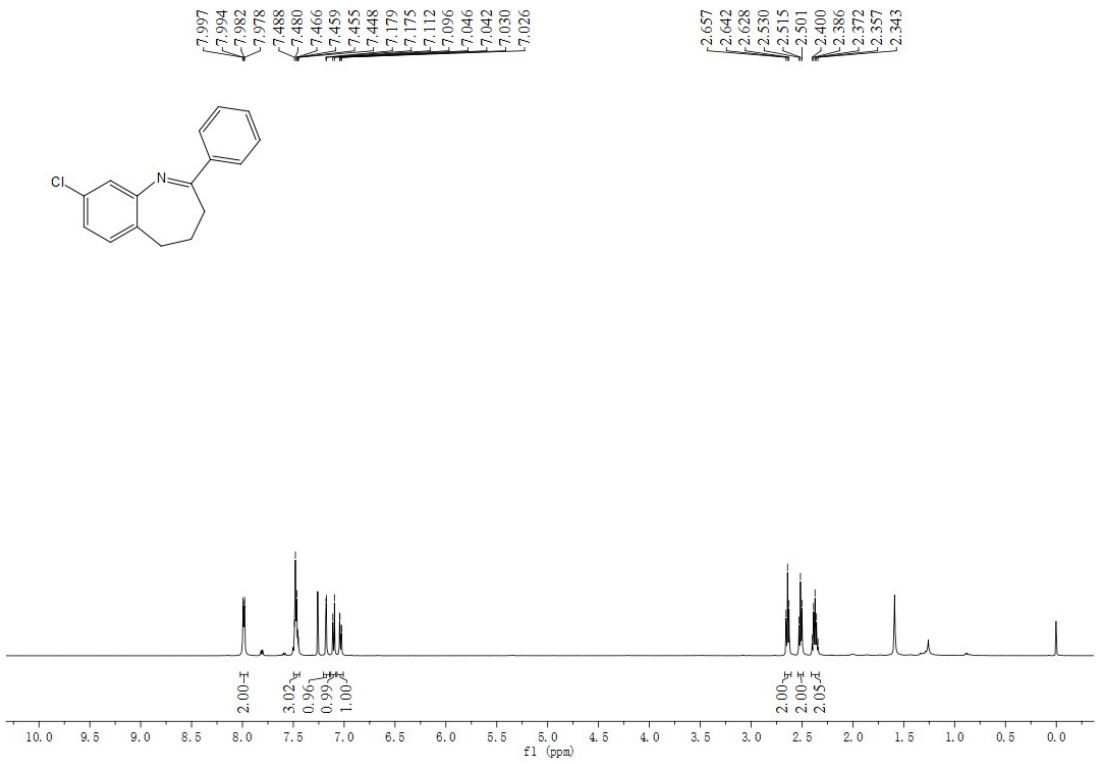
^{1}H NMR (500 MHz, $CDCl_3$)
7-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3i)



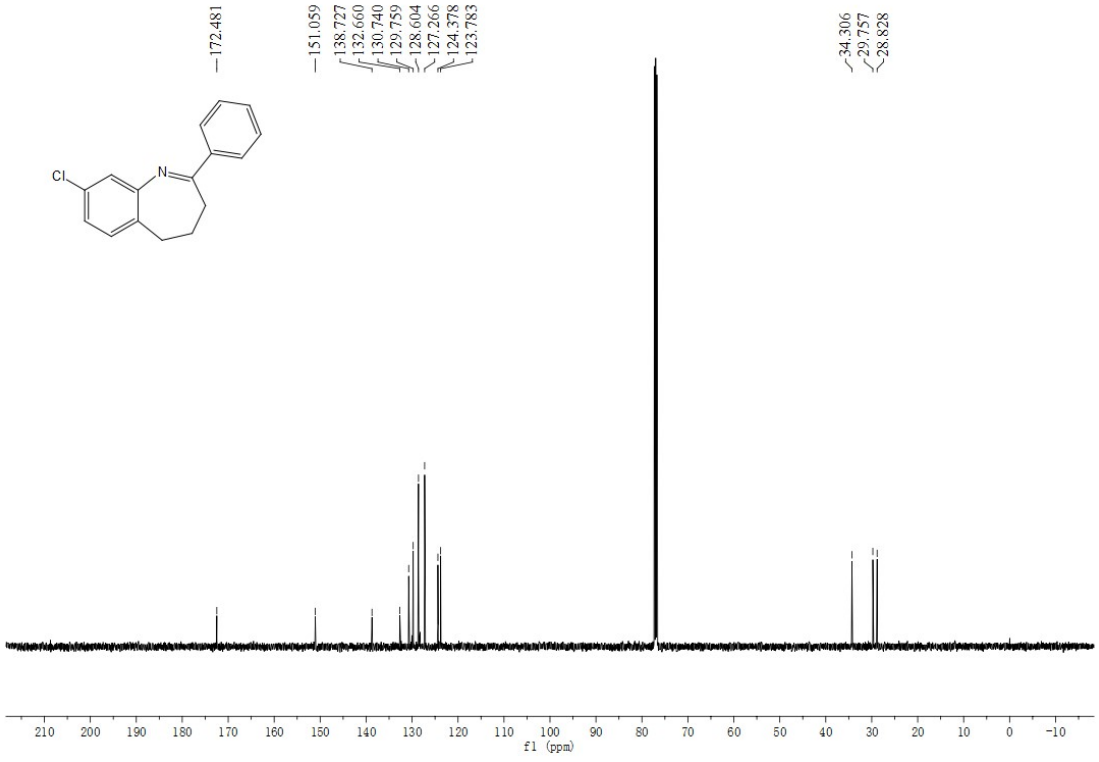
^{13}C NMR (125 MHz, $CDCl_3$)
7-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3i)



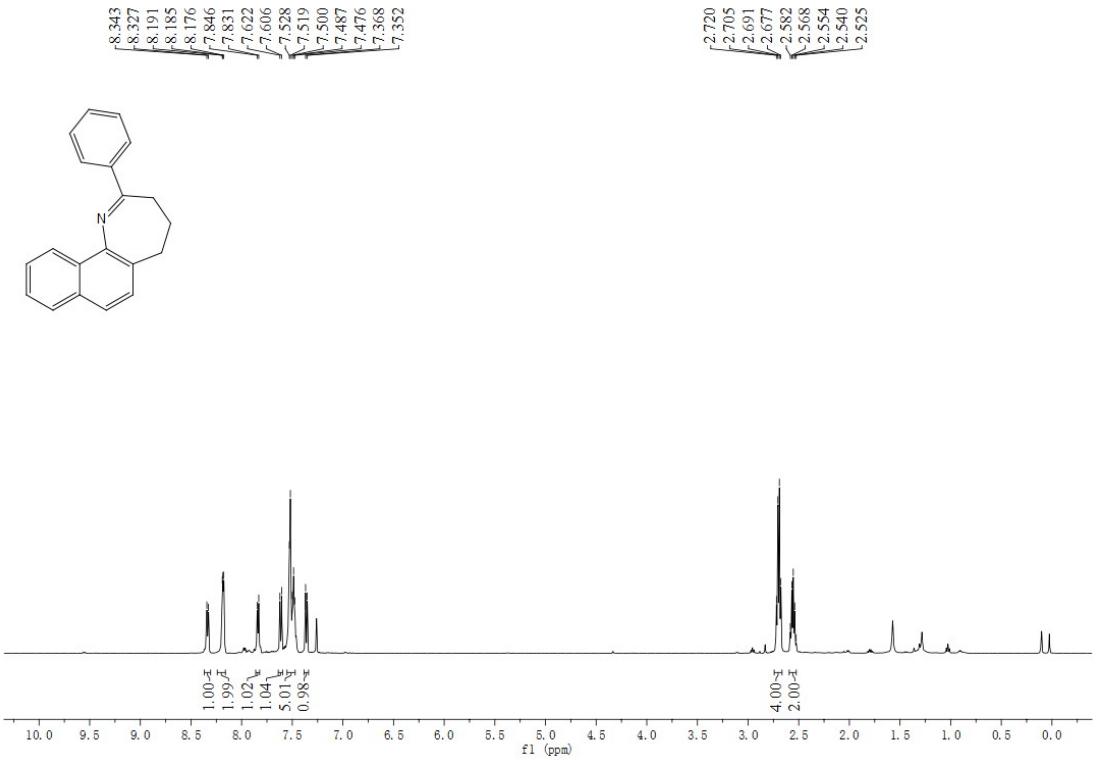
^{1}H NMR (500 MHz, $CDCl_3$)
8-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3j)



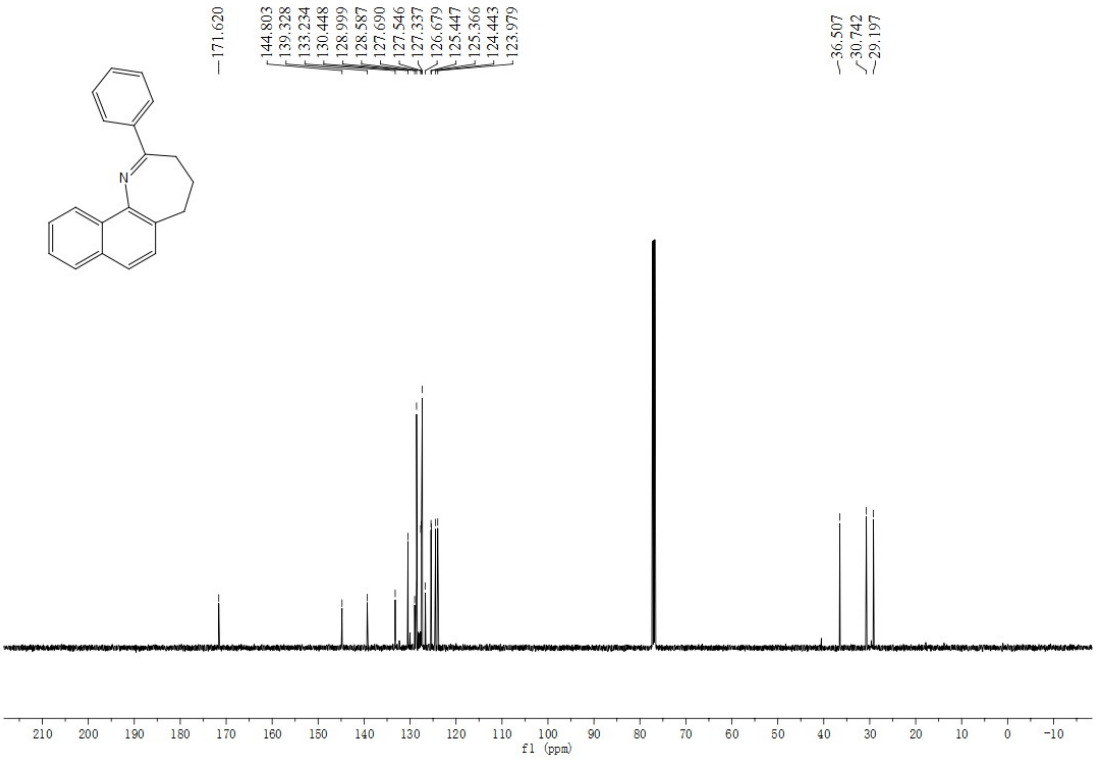
^{13}C NMR (125 MHz, $CDCl_3$)
8-chloro-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3j)



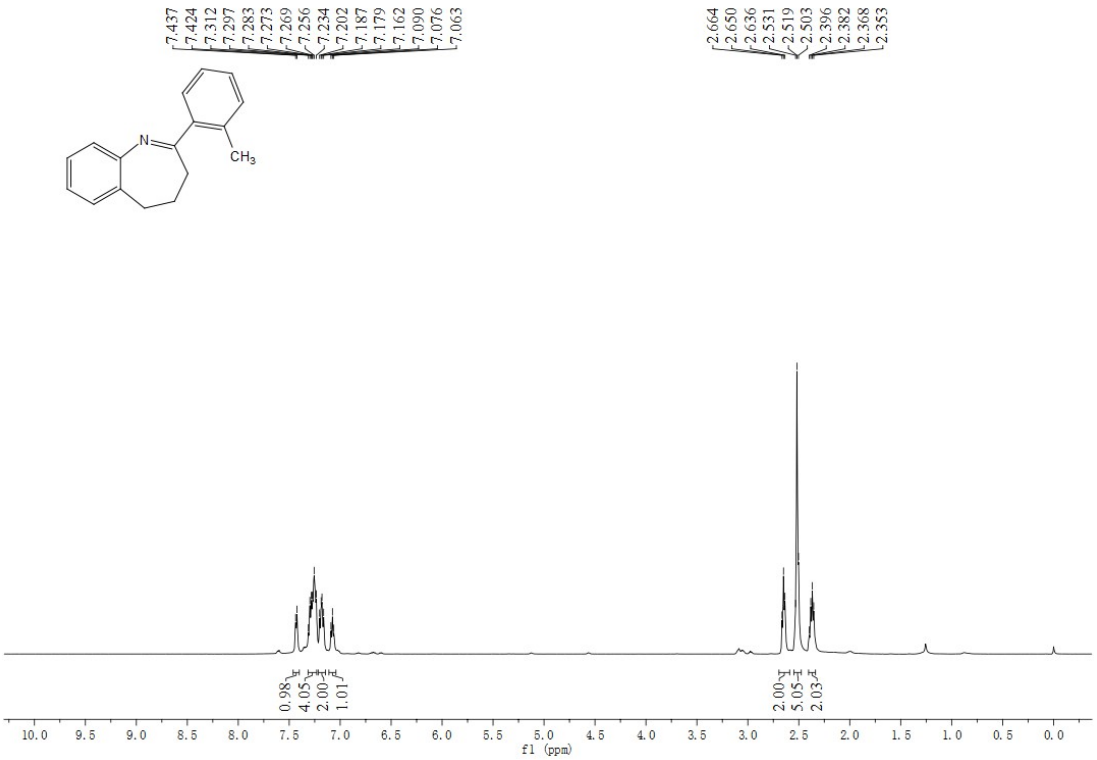
^{1}H NMR (500 MHz, $CDCl_3$)
2-phenyl-4,5-dihydro-3H-naphtho[1,2-*b*]azepine (3k)



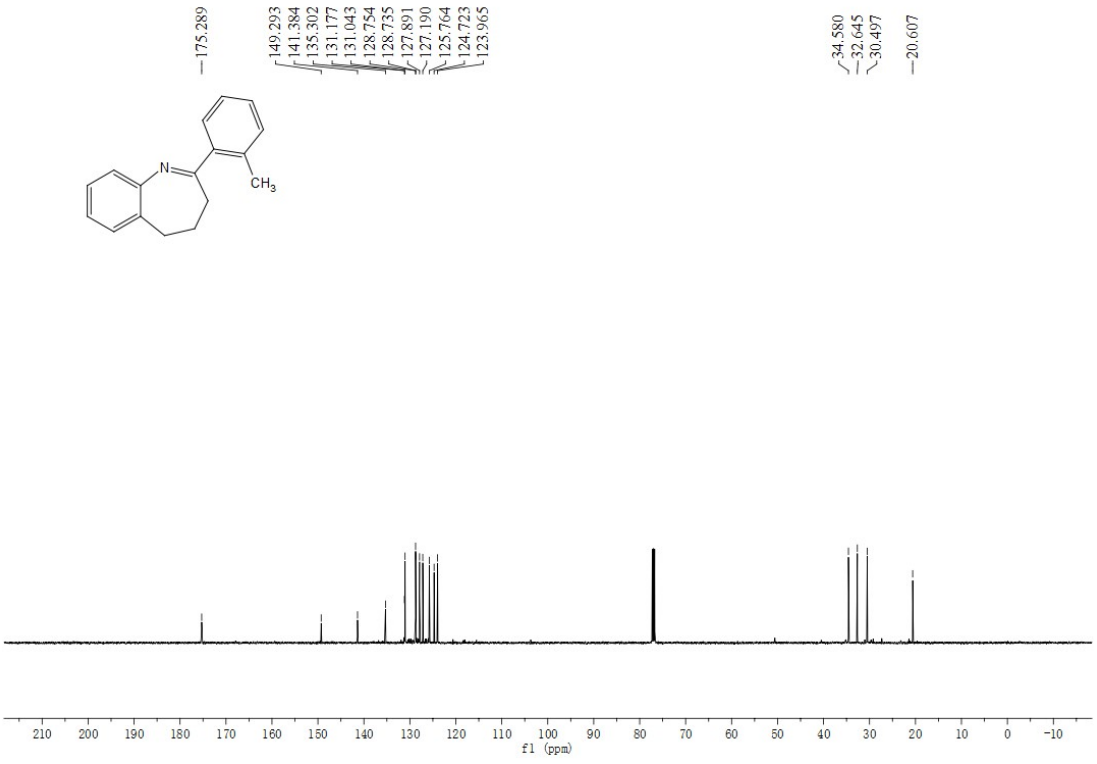
^{13}C NMR (125 MHz, $CDCl_3$)
2-phenyl-4,5-dihydro-3H-naphtho[1,2-*b*]azepine (3k)



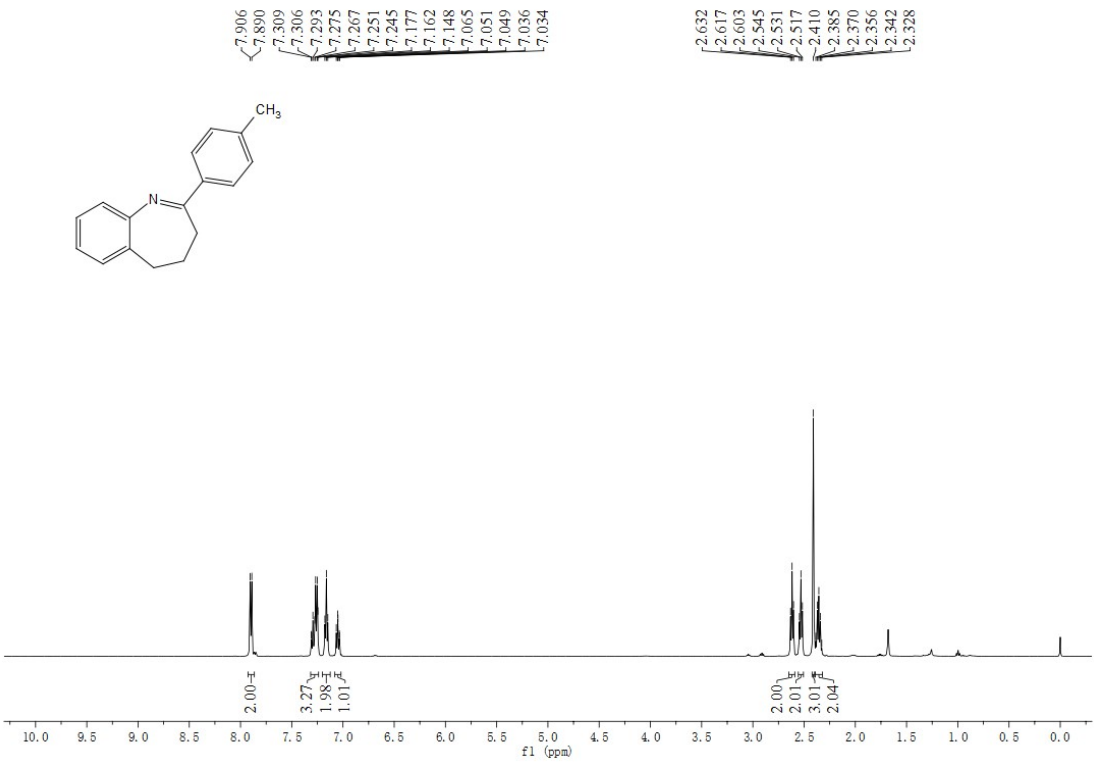
^{1}H NMR (500 MHz, $CDCl_3$)
2-(o-tolyl)-4,5-dihydro-3H-benzo[*b*]azepine (3l)



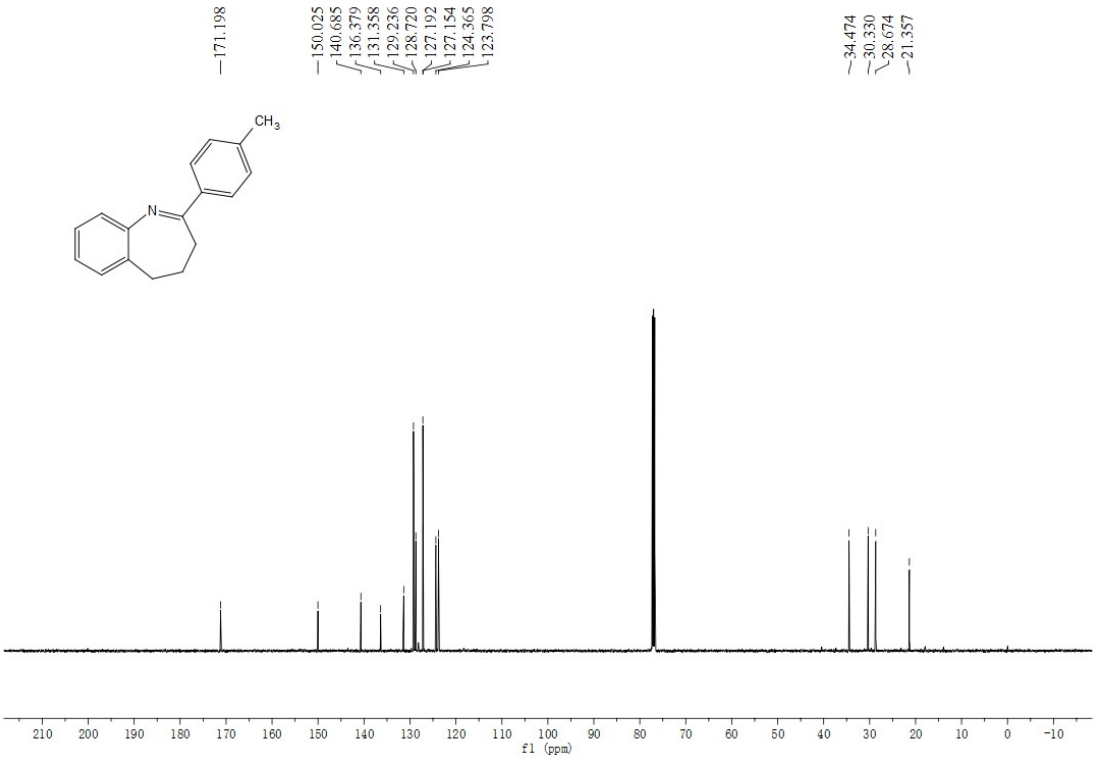
^{13}C NMR (125 MHz, $CDCl_3$)
2-(o-tolyl)-4,5-dihydro-3H-benzo[*b*]azepine (3l)



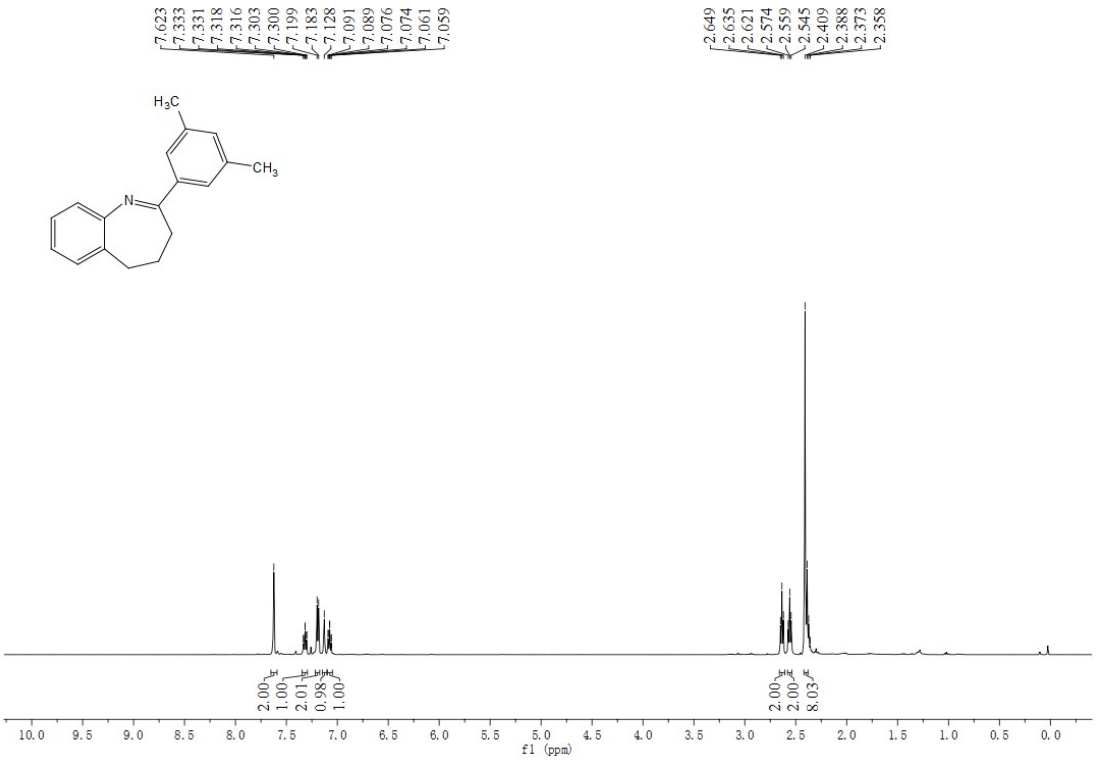
^{1}H NMR (500 MHz, $CDCl_3$)
2-(p-tolyl)-4,5-dihydro-3H-benzo[*b*]azepine (3m)



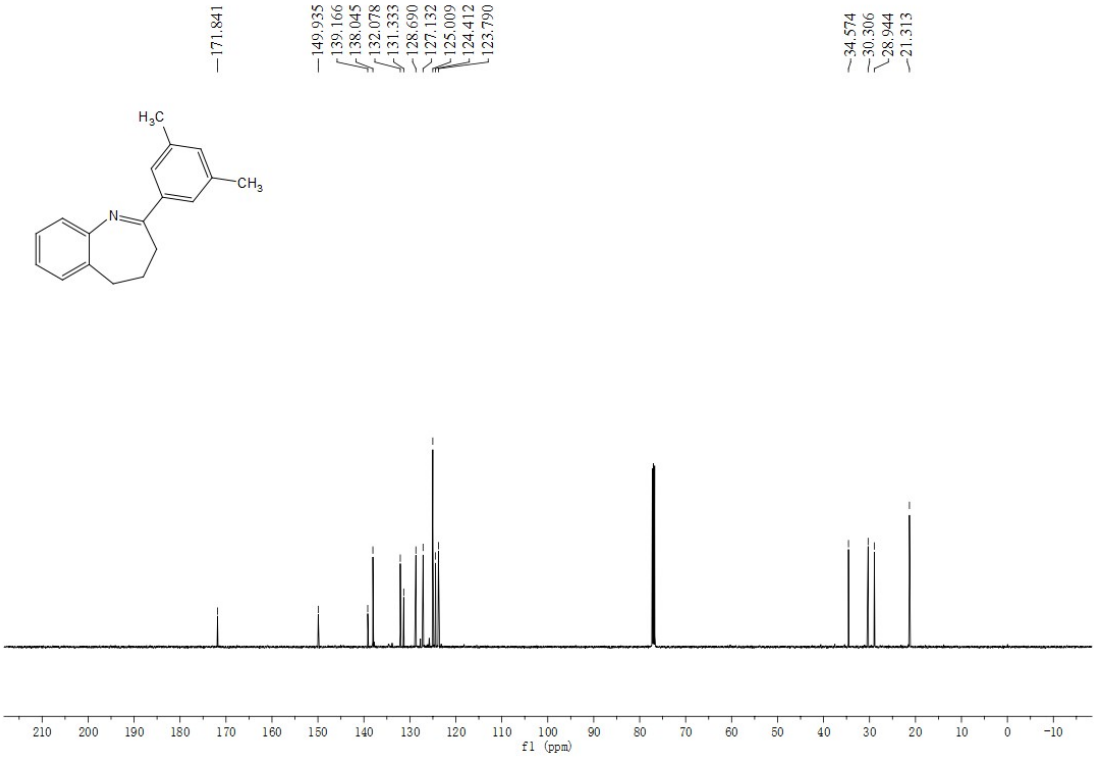
^{13}C NMR (125 MHz, $CDCl_3$)
2-(p-tolyl)-4,5-dihydro-3H-benzo[*b*]azepine (3m)



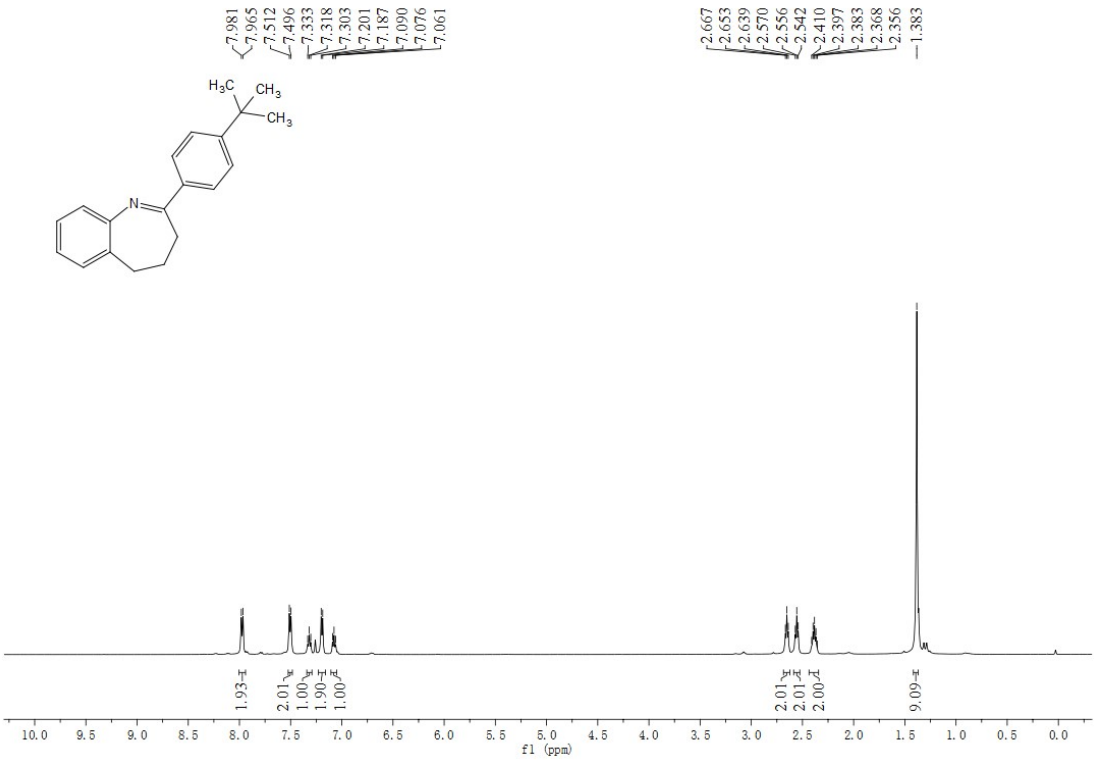
^{1}H NMR (500 MHz, $CDCl_3$)
2-(3,5-dimethylphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3n)



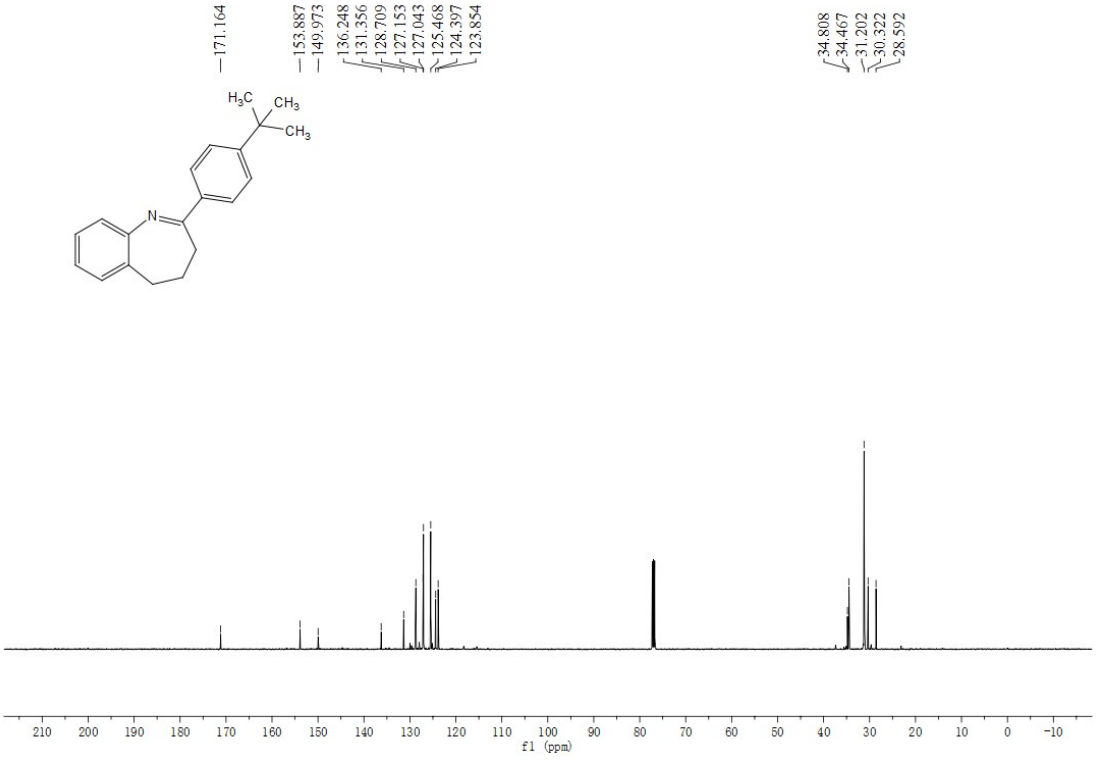
^{13}C NMR (125 MHz, $CDCl_3$)
2-(3,5-dimethylphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3n)



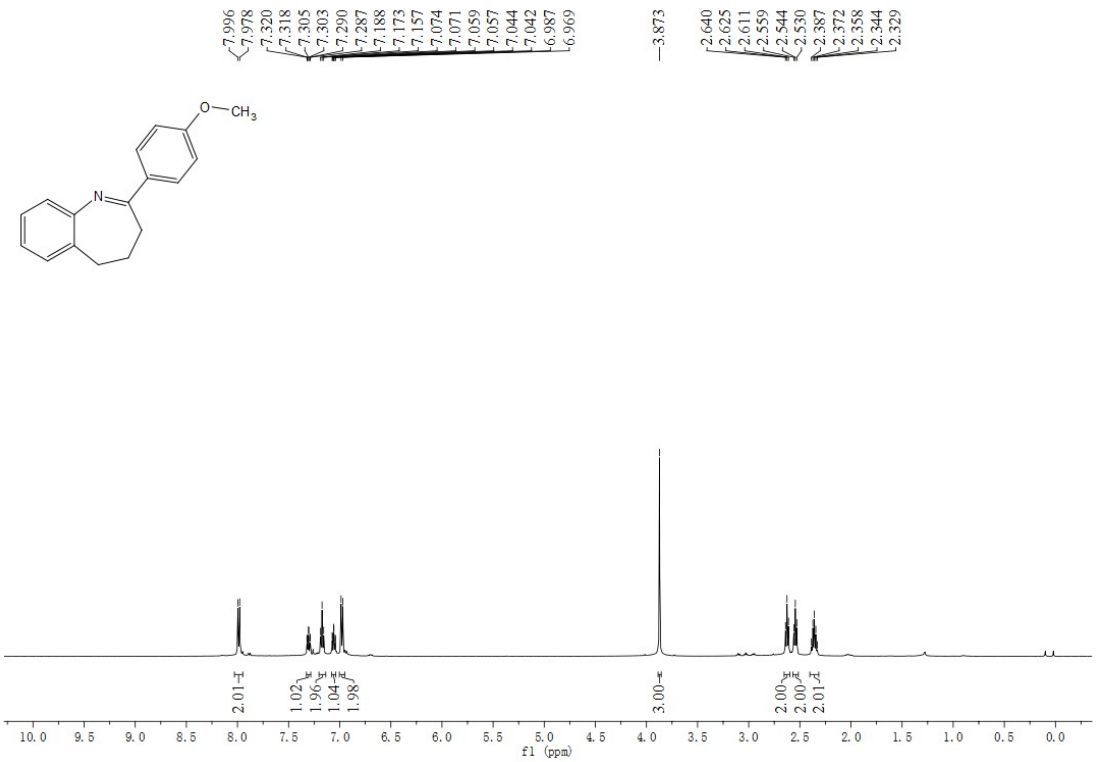
^{1}H NMR (500 MHz, $CDCl_3$)
2-(4-(tert-butyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3o)



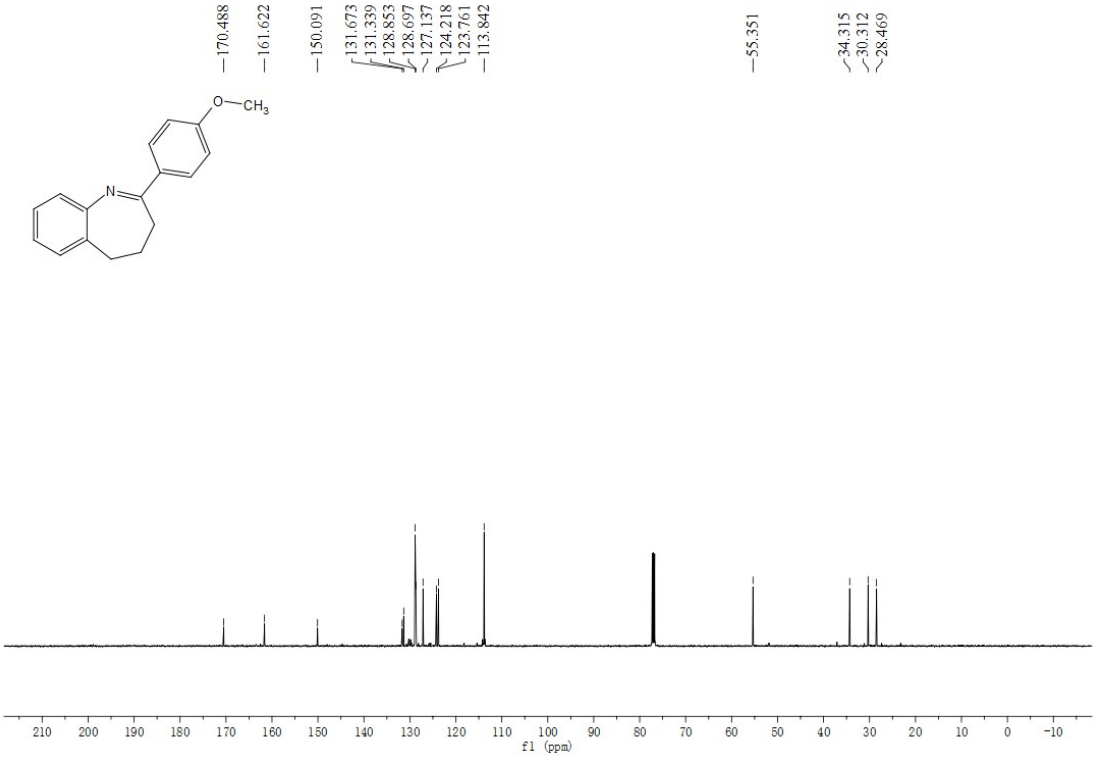
^{13}C NMR (125 MHz, $CDCl_3$)
2-(4-(tert-butyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3o)



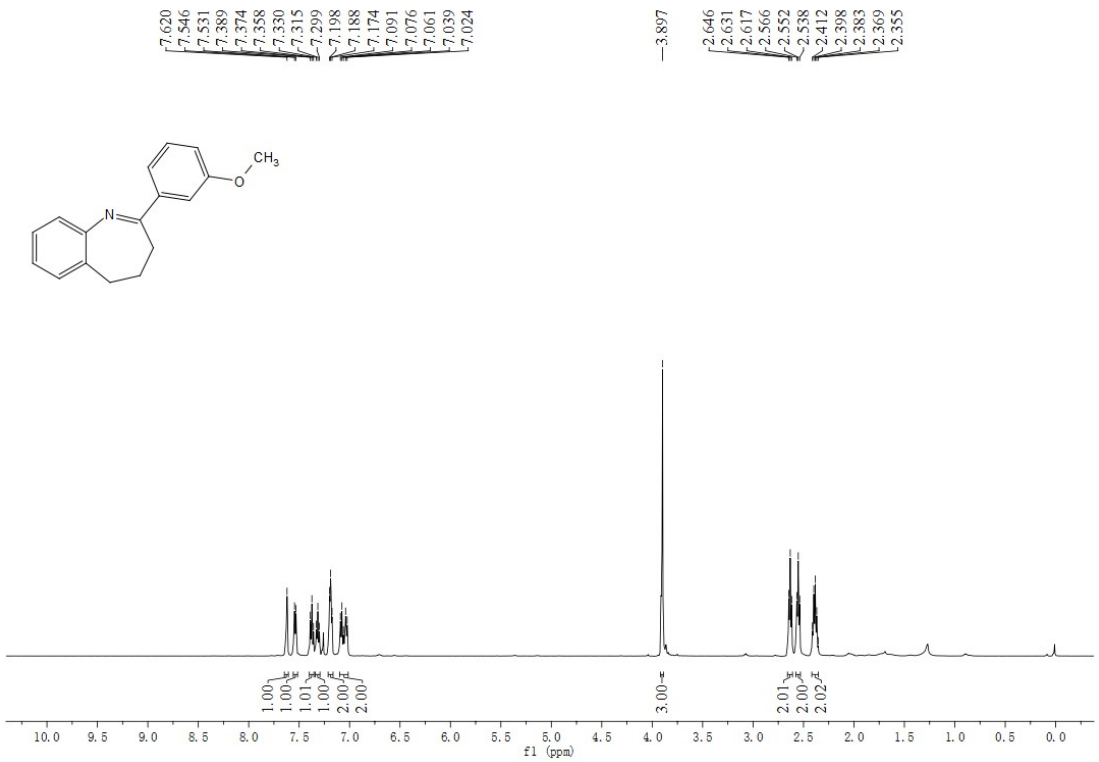
^{1}H NMR (500 MHz, $CDCl_3$)
2-(4-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepin (3p)



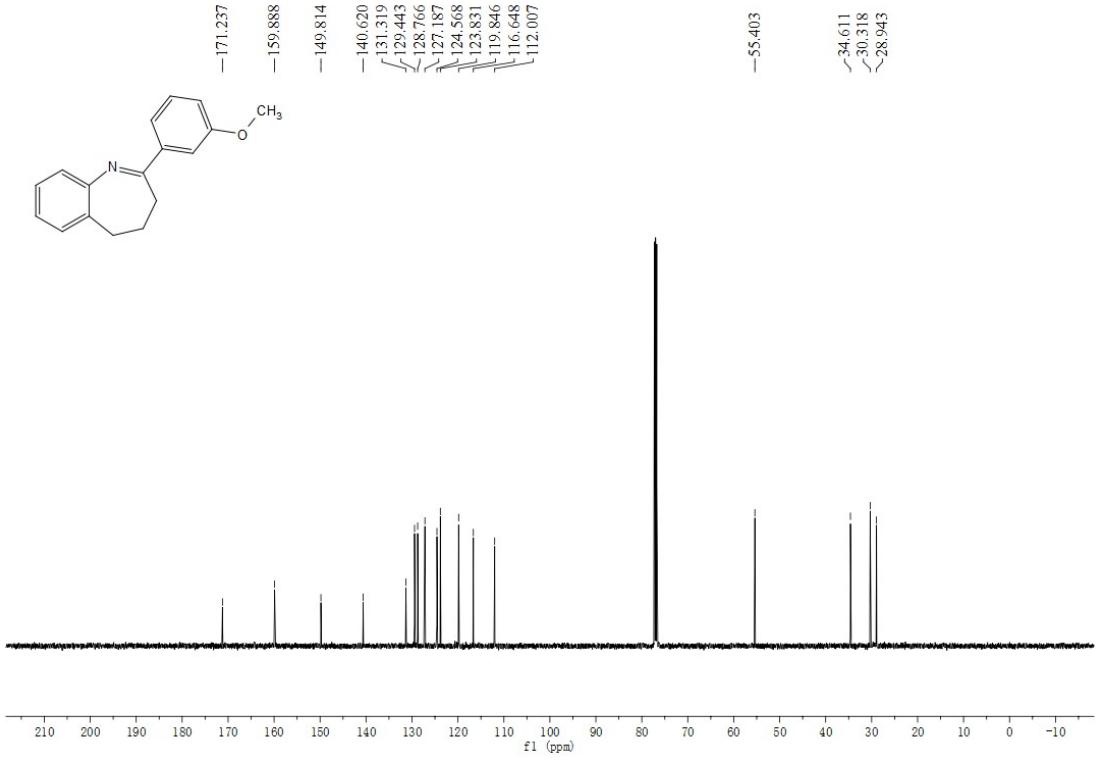
^{13}C NMR (125 MHz, $CDCl_3$)
2-(4-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepin (3p)



^{1}H NMR (500 MHz, $CDCl_3$)
2-(3-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3q)

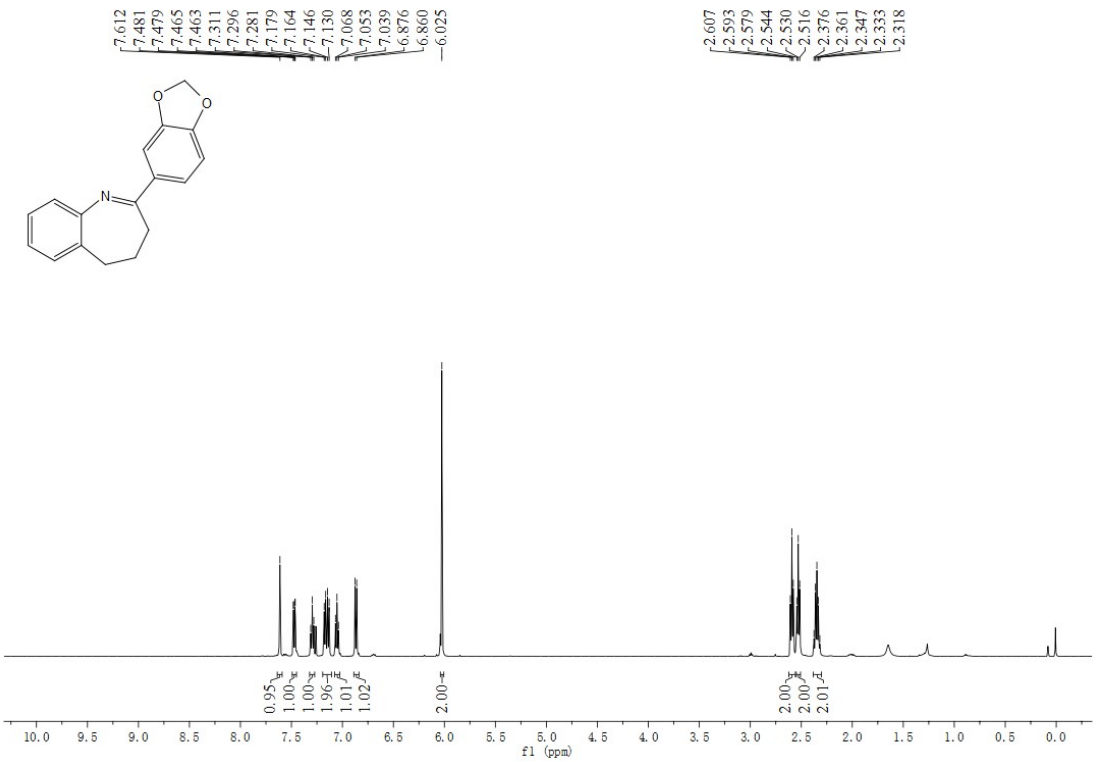


^{13}C NMR (125 MHz, $CDCl_3$)
2-(3-methoxyphenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3q)



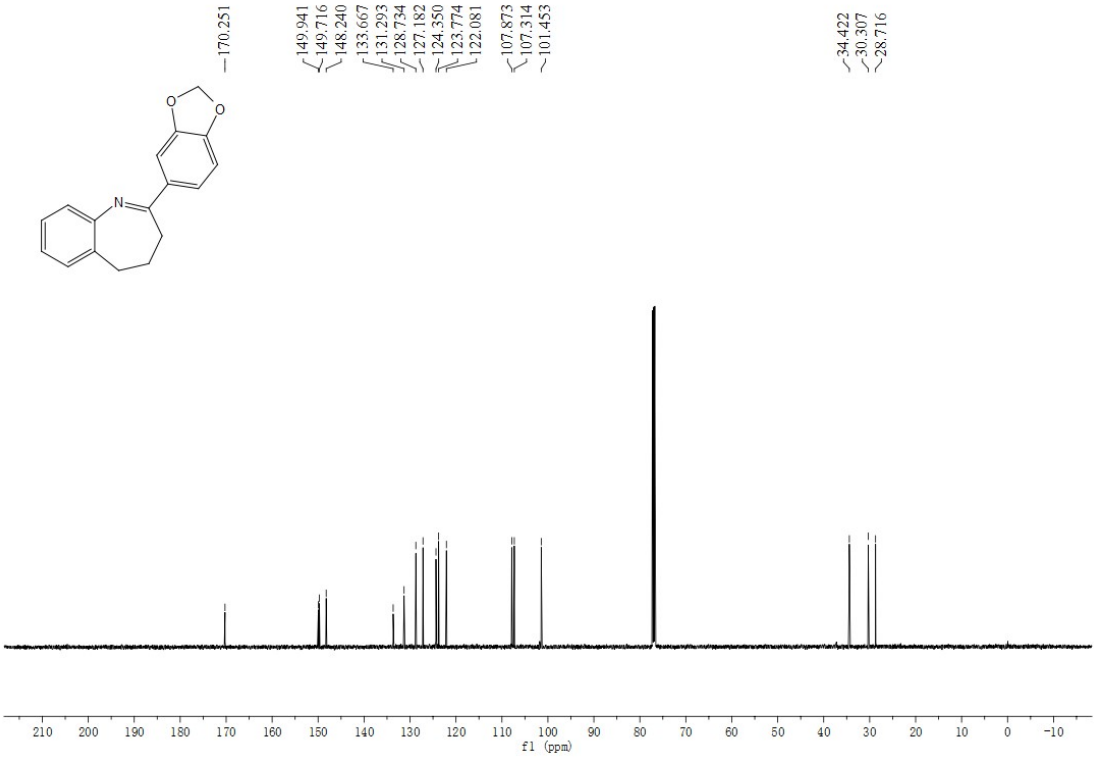
^{1}H NMR (500 MHz, $CDCl_3$)

2-(benzo[d][1,3]dioxol-5-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3r)

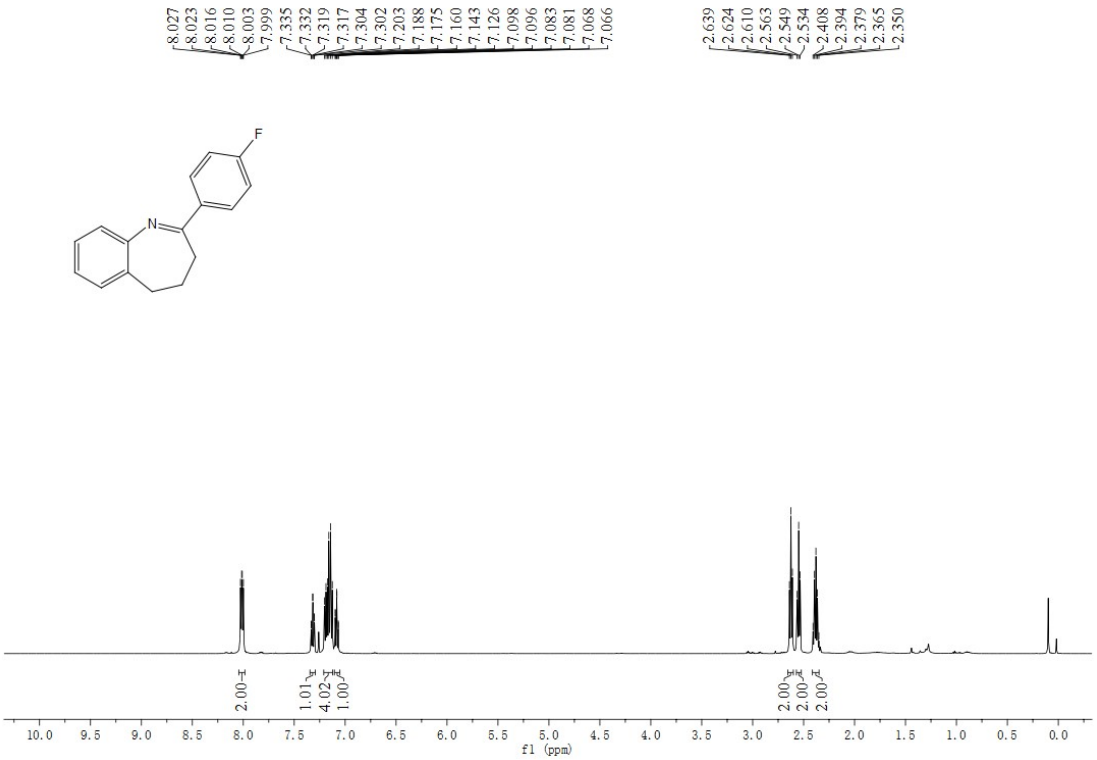


^{13}C NMR (125 MHz, $CDCl_3$)

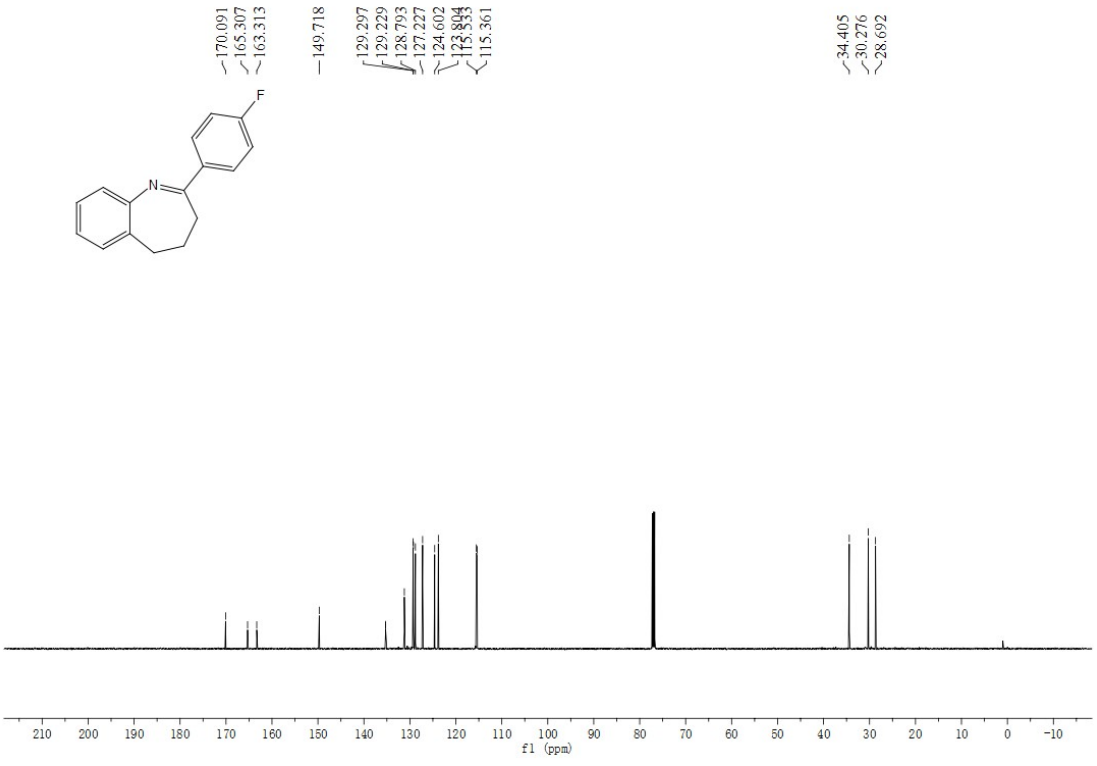
2-(benzo[d][1,3]dioxol-5-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3r)



^{1}H NMR (500 MHz, $CDCl_3$)
2-(4-fluorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3s)

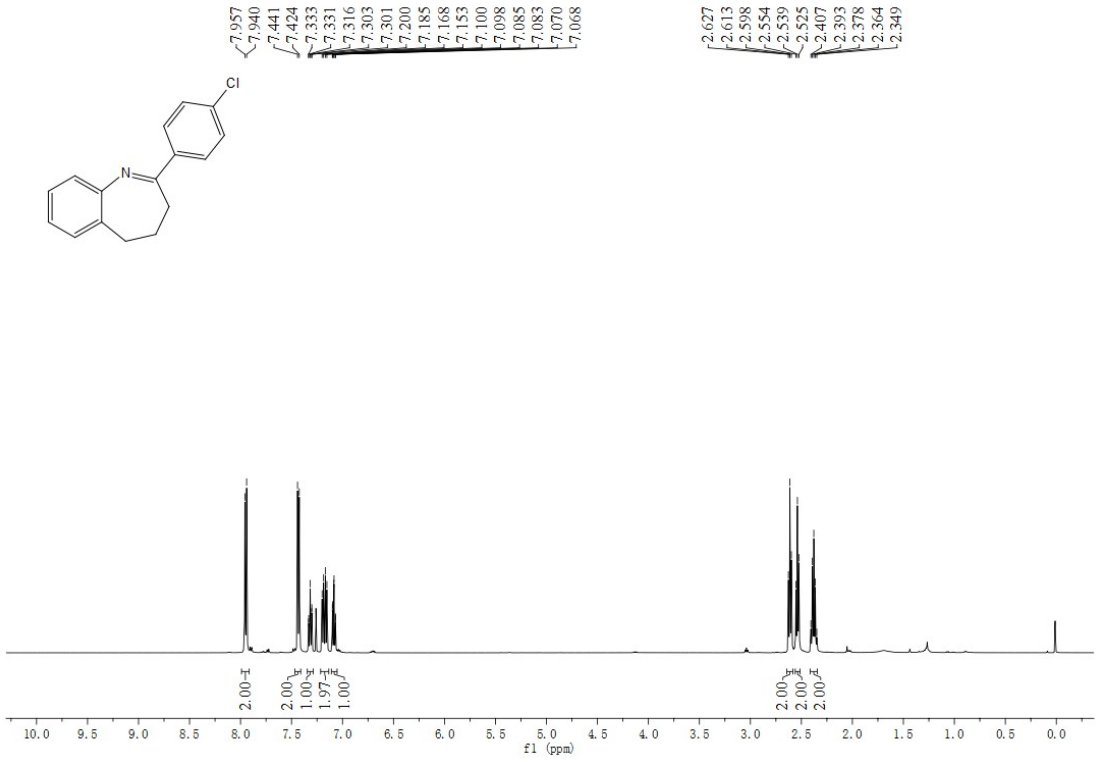


^{13}C NMR (125 MHz, $CDCl_3$)
2-(4-fluorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3s)

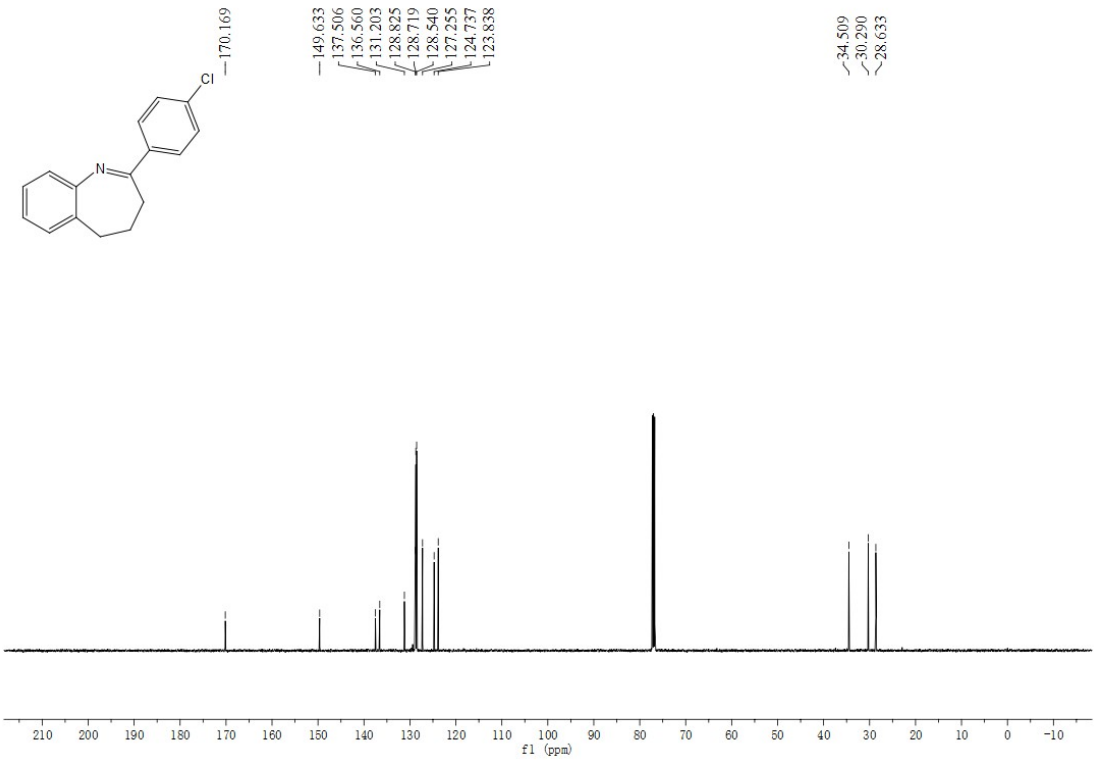


^{19}F NMR (470 MHz, $CDCl_3$)
2-(4-fluorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3s)

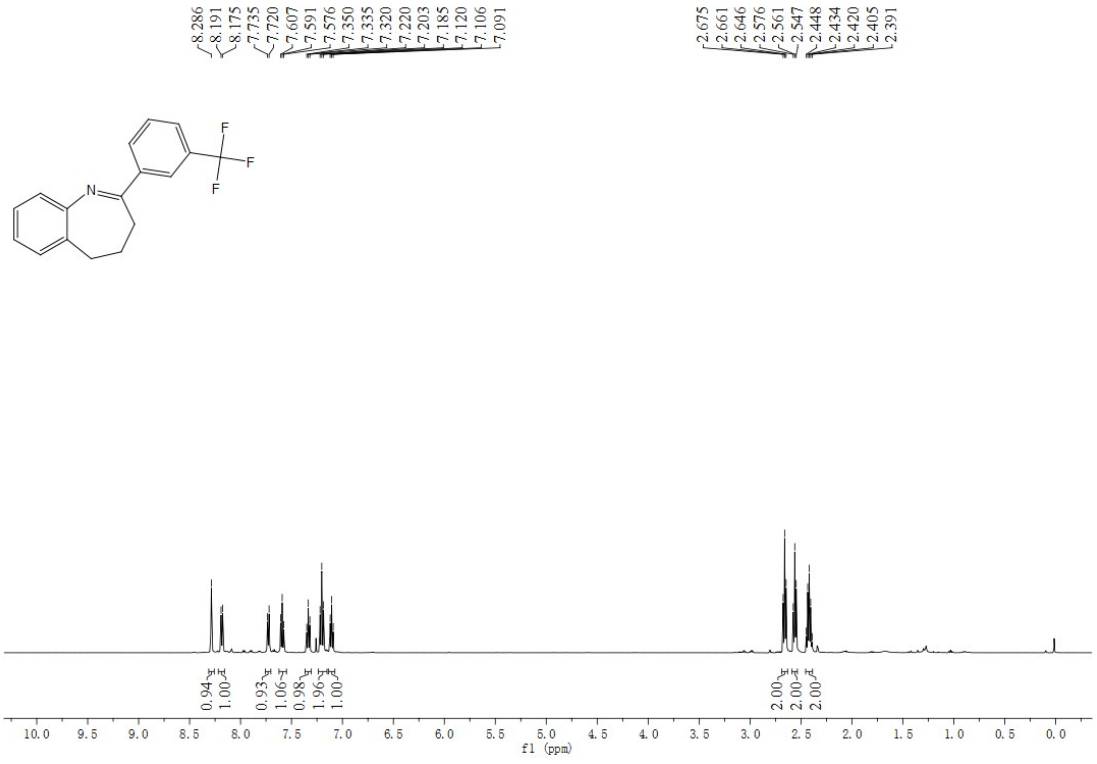
^{1}H NMR (500 MHz, $CDCl_3$)
2-(4-chlorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3t)



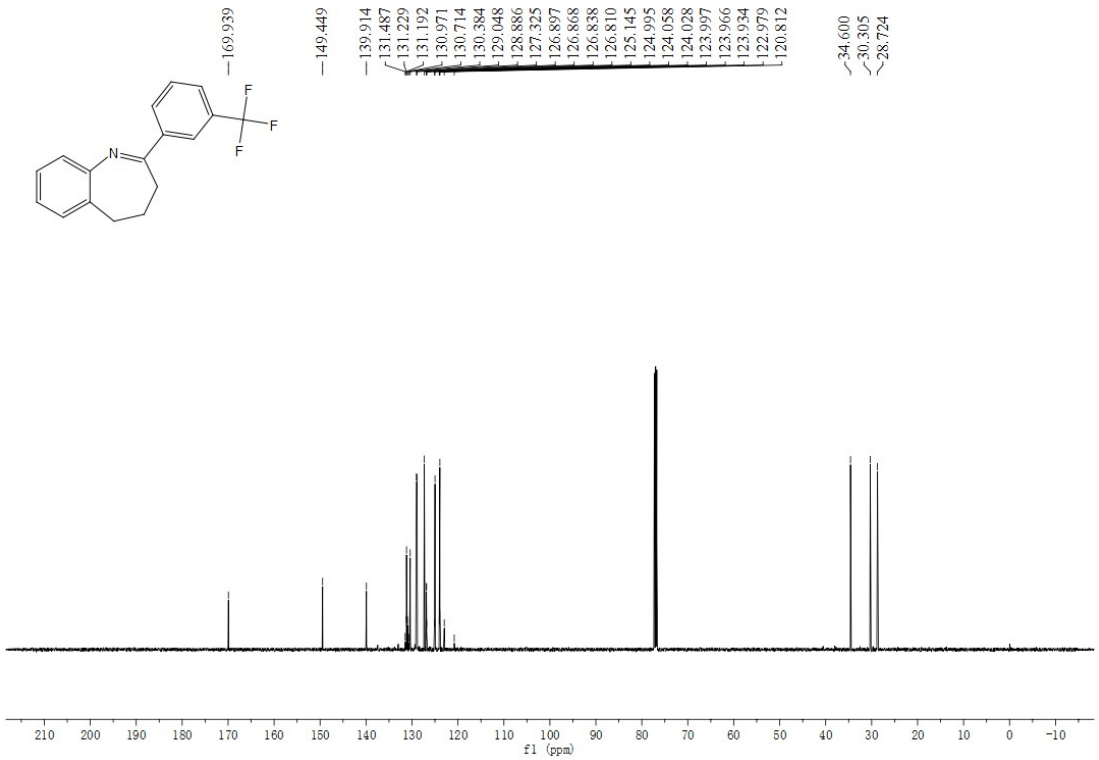
^{13}C NMR (125 MHz, $CDCl_3$)
2-(4-chlorophenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3t)



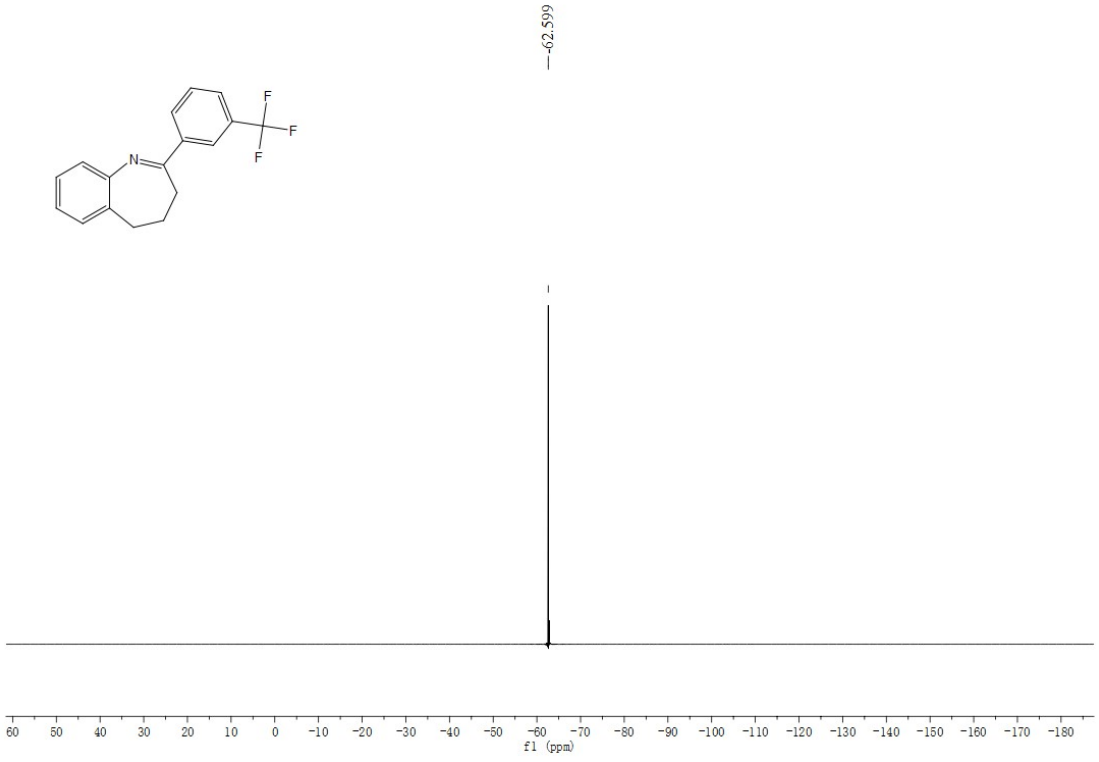
^{1}H NMR (500 MHz, $CDCl_3$)
2-(3-(trifluoromethyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3u)



^{13}C NMR (125 MHz, $CDCl_3$)
2-(3-(trifluoromethyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3u)

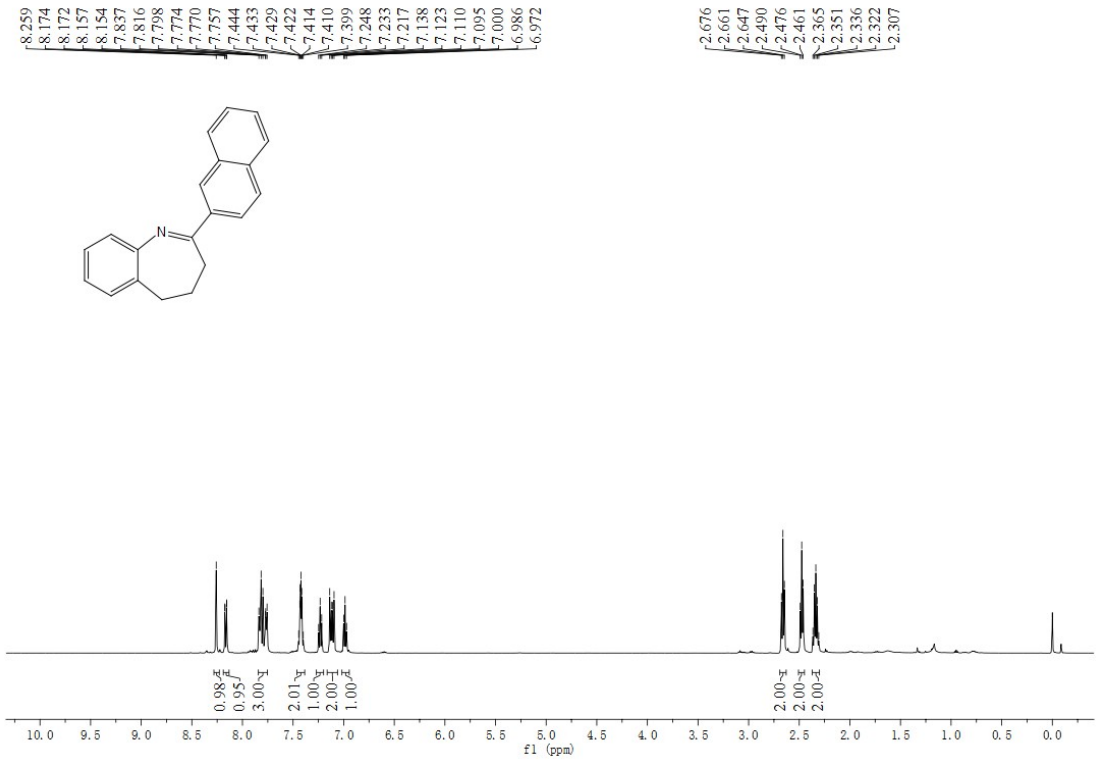


^{19}F NMR (470 MHz, $CDCl_3$)
2-(3-(trifluoromethyl)phenyl)-4,5-dihydro-3H-benzo[*b*]azepine (3u)



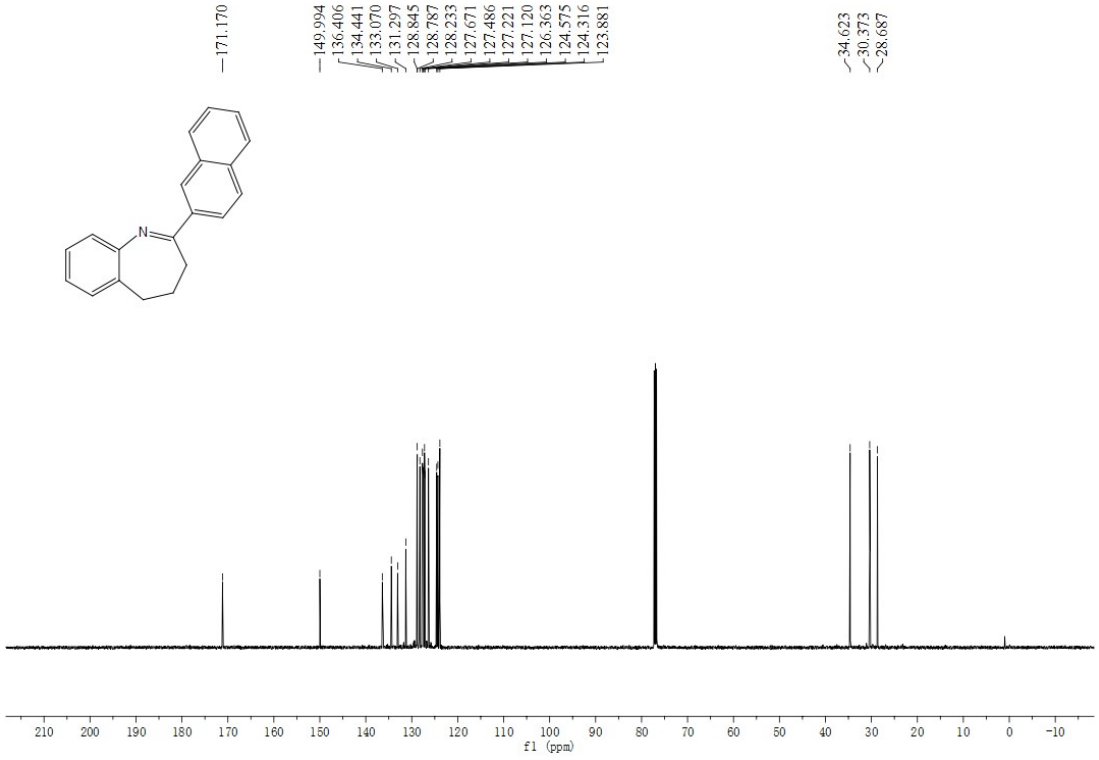
^{1}H NMR (500 MHz, $CDCl_3$)

2-([1,1'-biphenyl]-4-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3v)



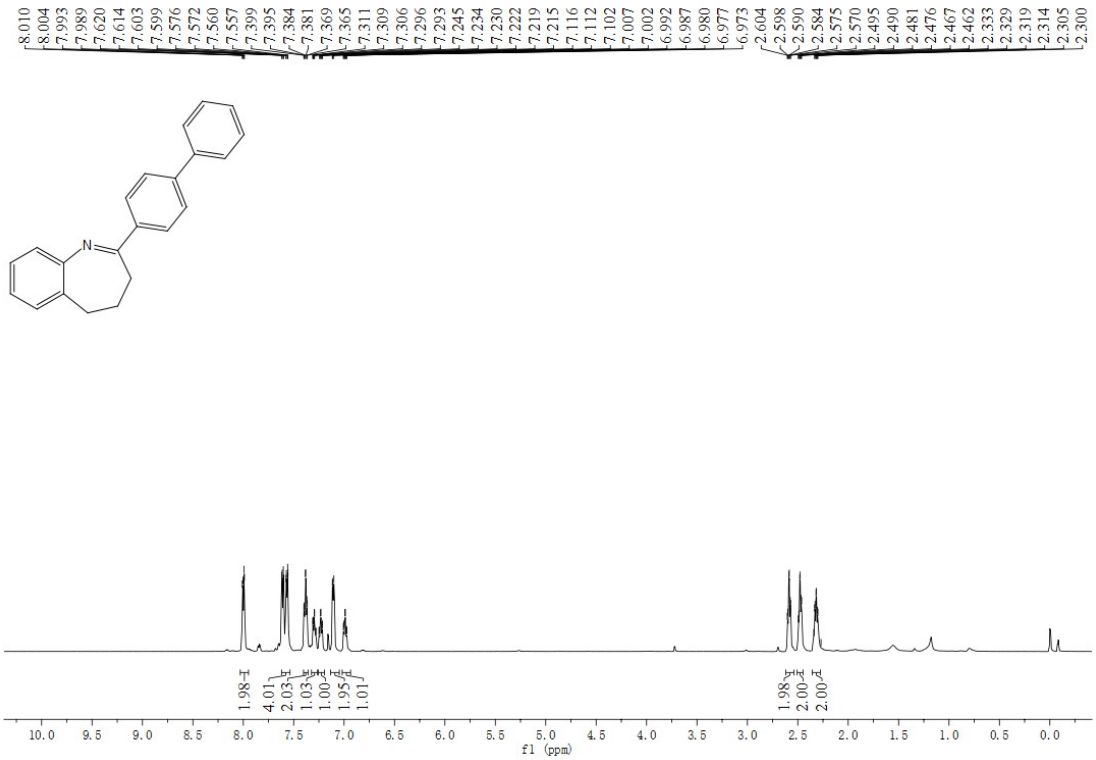
^{13}C NMR (125 MHz, $CDCl_3$)

2-([1,1'-biphenyl]-4-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3v)



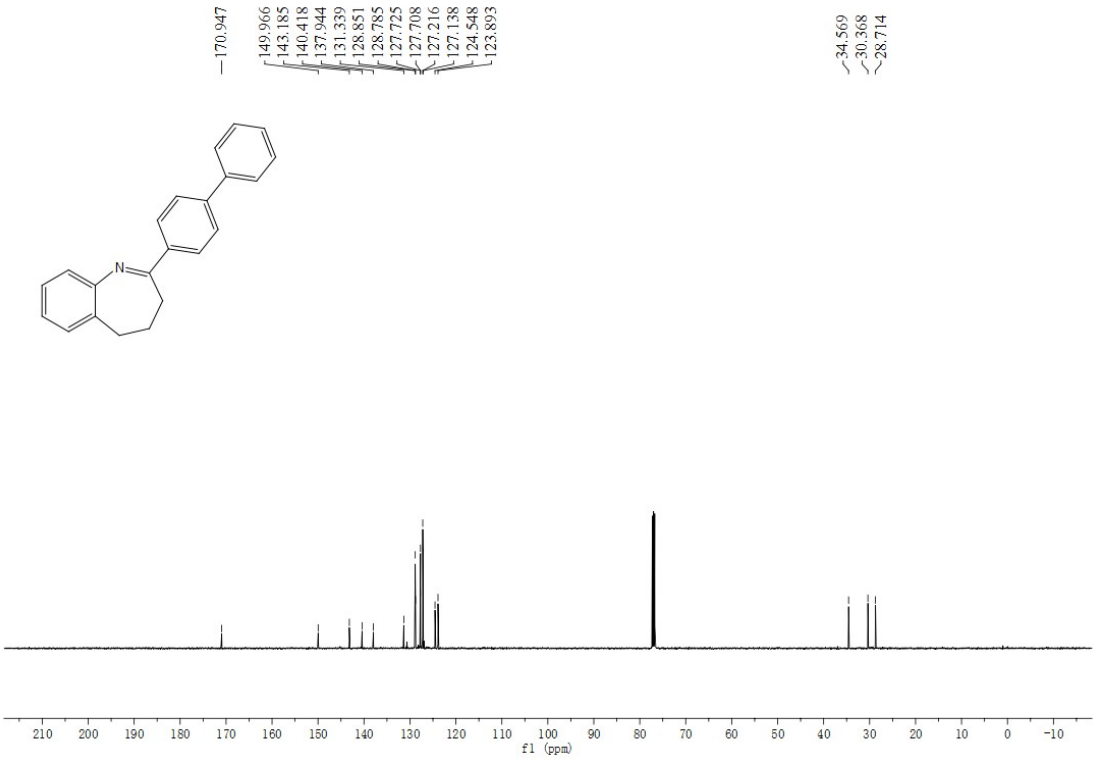
^{1}H NMR (500 MHz, $CDCl_3$)

2-([1,1'-biphenyl]-4-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3w)

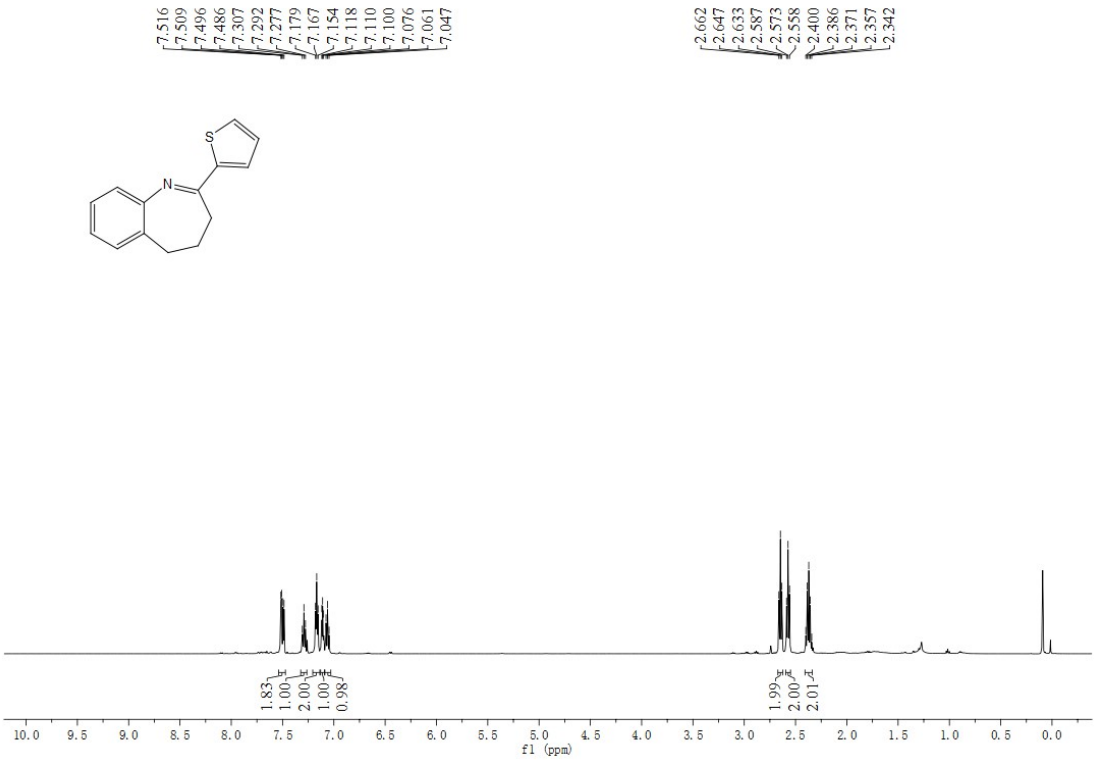


^{13}C NMR (125 MHz, $CDCl_3$)

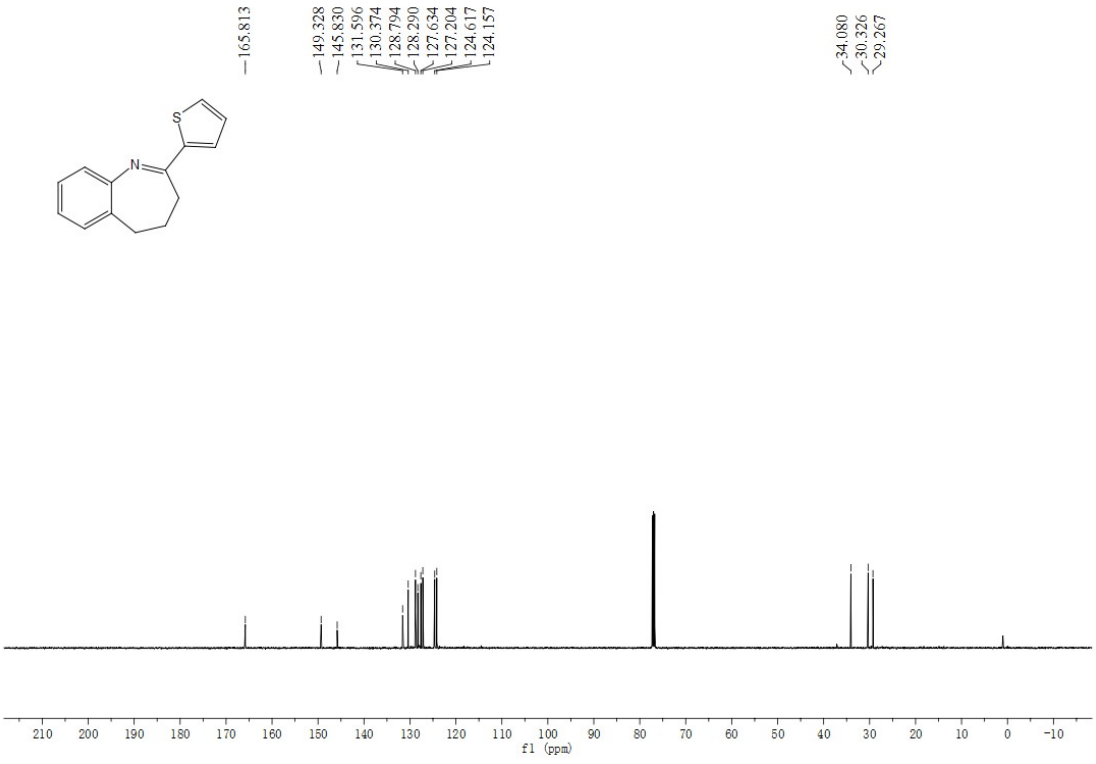
2-([1,1'-biphenyl]-4-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3w)



^{1}H NMR (500 MHz, $CDCl_3$)
2-(thiophen-2-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3x)

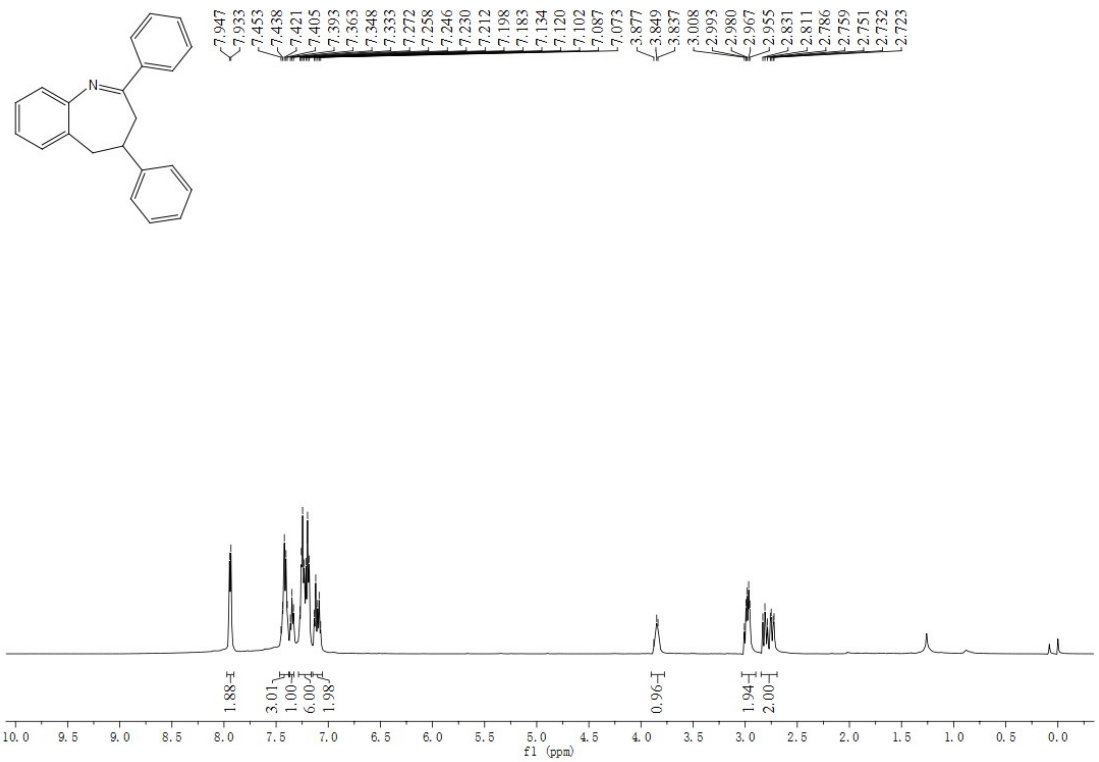


^{13}C NMR (125 MHz, $CDCl_3$)
2-(thiophen-2-yl)-4,5-dihydro-3H-benzo[*b*]azepine (3x)



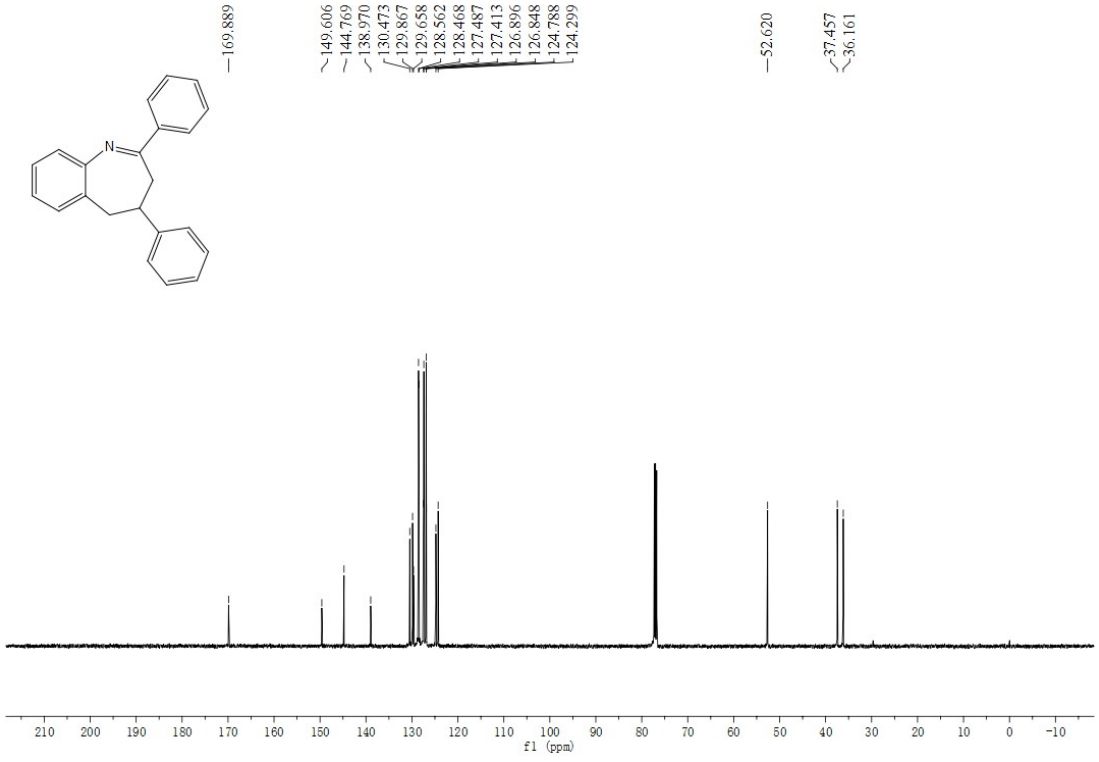
^{1}H NMR (500 MHz, $CDCl_3$)

2,4-diphenyl-4,5-dihydro-3H-benzo[*b*]azepine (3y)



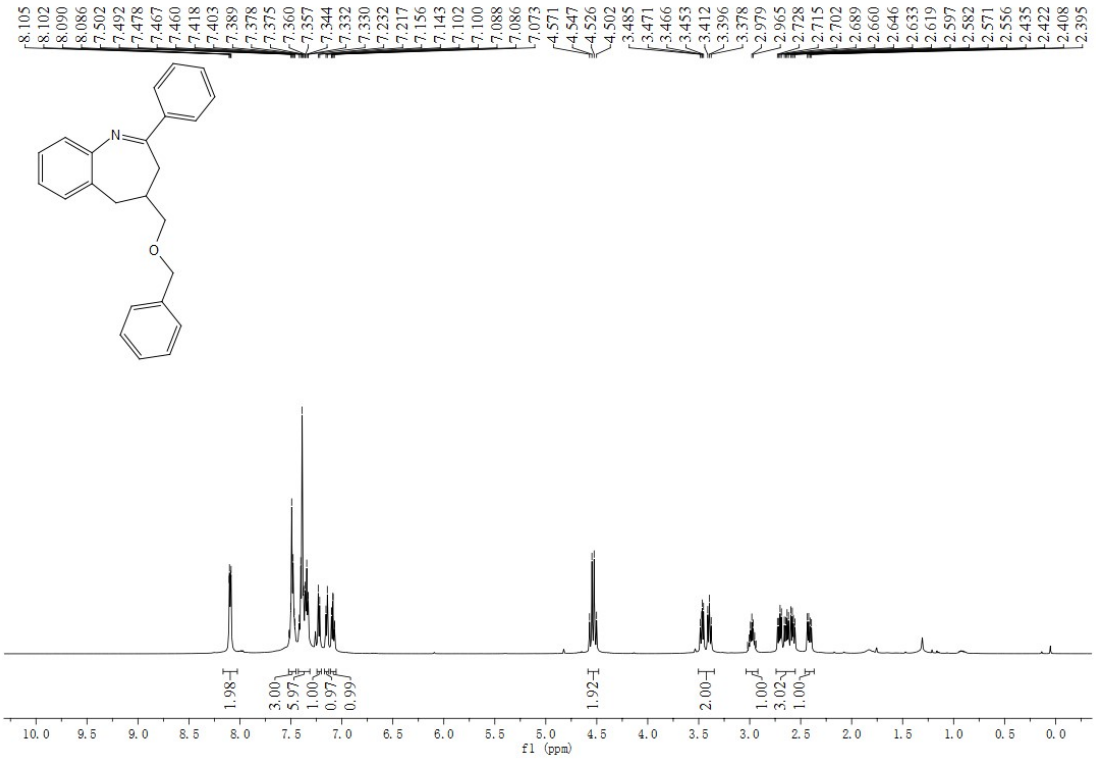
^{13}C NMR (125 MHz, $CDCl_3$)

2,4-diphenyl-4,5-dihydro-3H-benzo[*b*]azepine (3y)



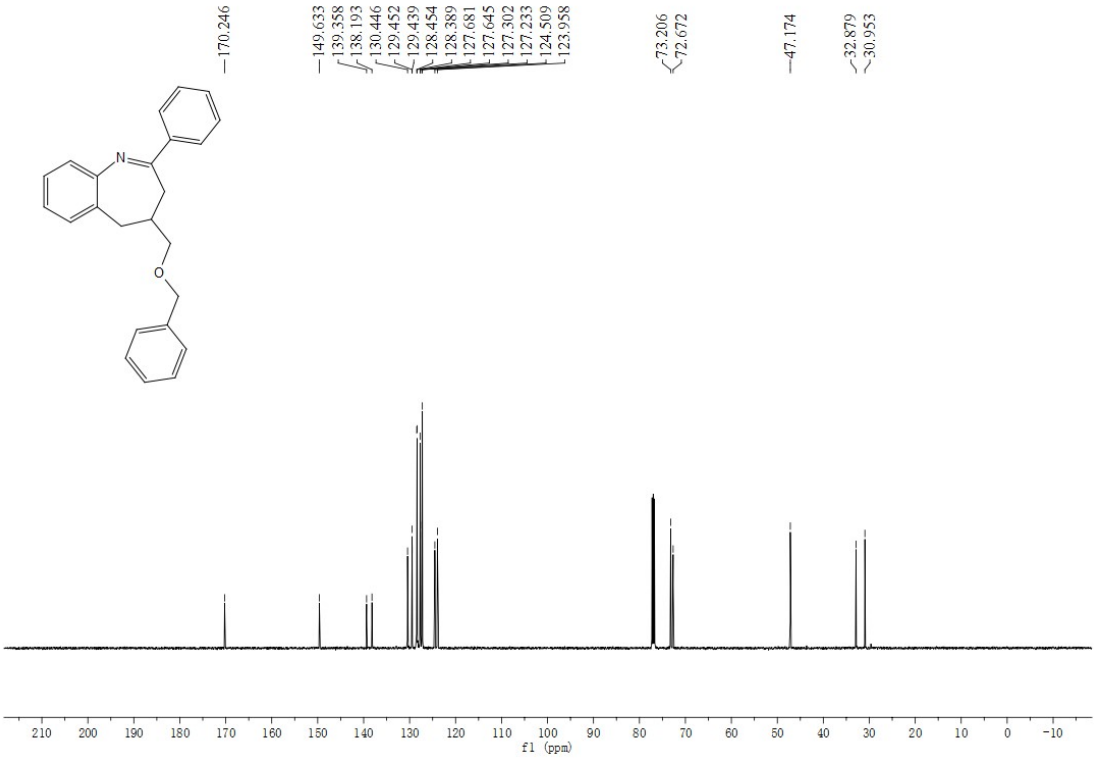
^{1}H NMR (500 MHz, $CDCl_3$)

4-((benzyloxy)methyl)-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3z)



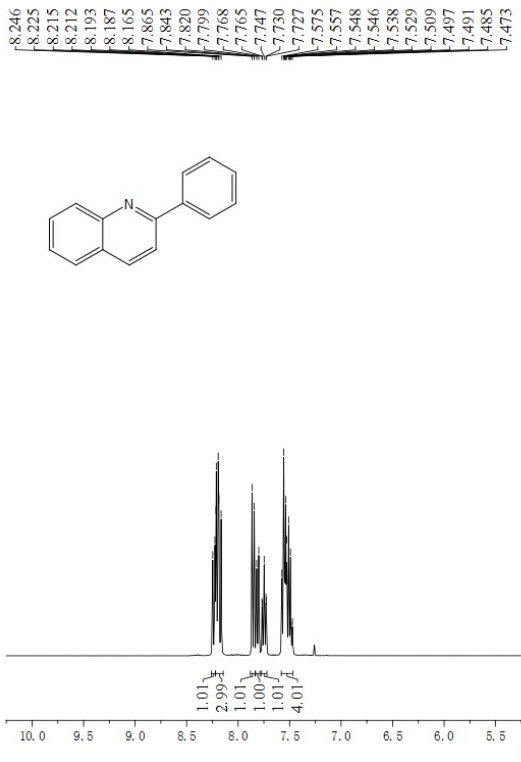
^{13}C NMR (125 MHz, $CDCl_3$)

4-((benzyloxy)methyl)-2-phenyl-4,5-dihydro-3H-benzo[*b*]azepine (3z)



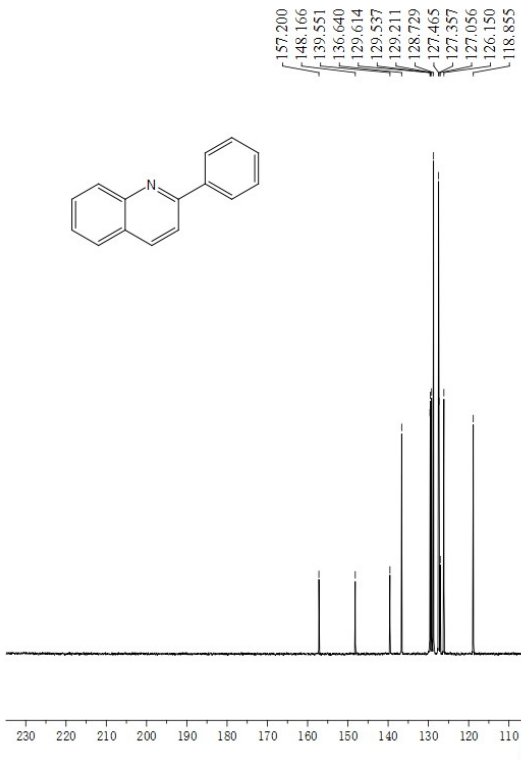
^{1}H NMR (400 MHz, $CDCl_3$)

2-phenylquinoline (3aa)



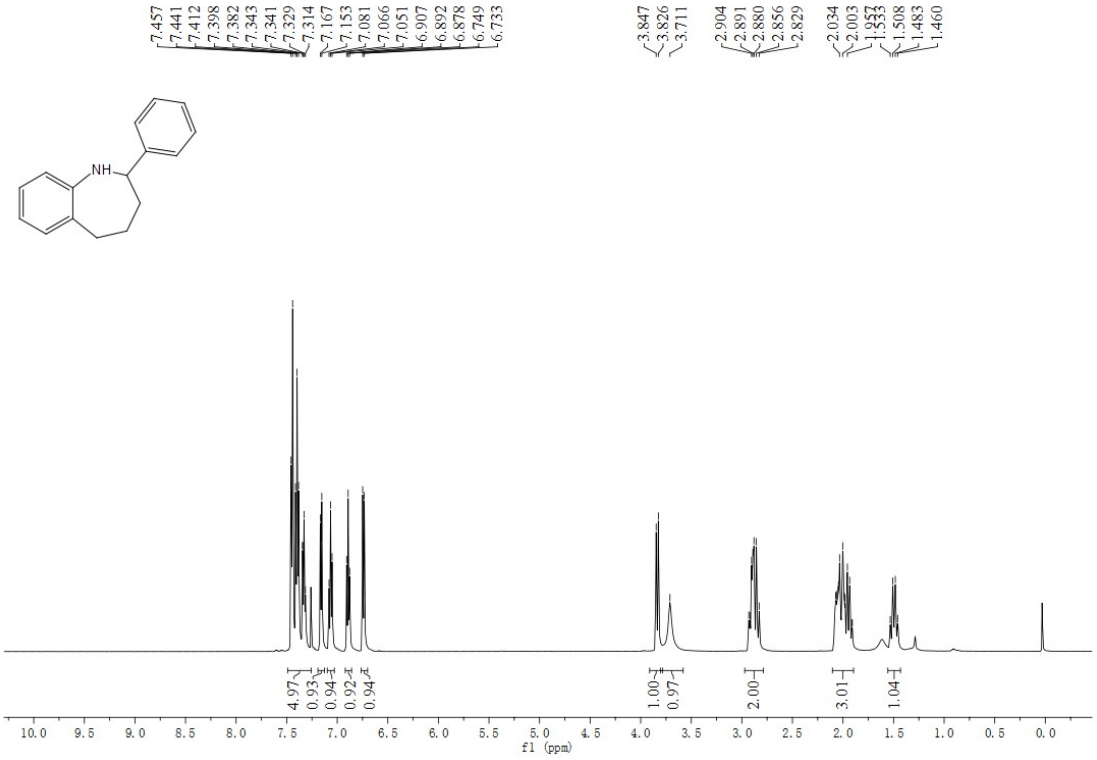
^{13}C NMR (100 MHz, $CDCl_3$)

2-phenylquinoline (3aa)



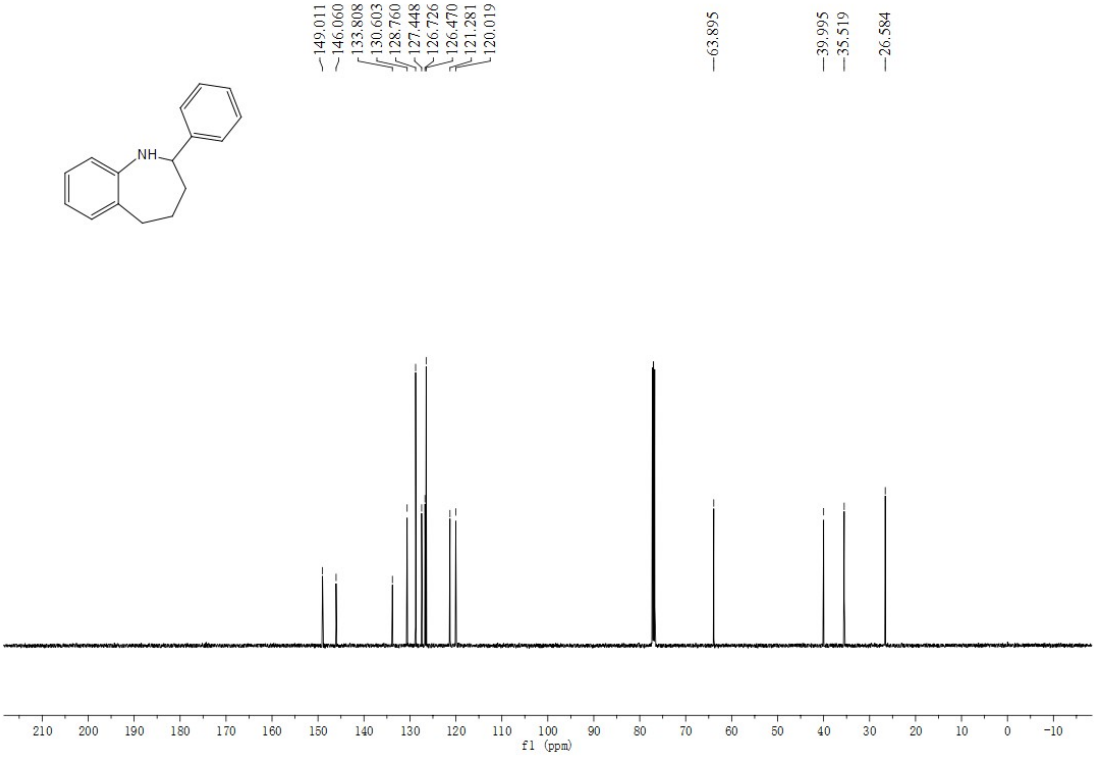
^{1}H NMR (500 MHz, $CDCl_3$)

2-phenyl-2,3,4,5-tetrahydro-1H-benzo[*b*]azepine (4)



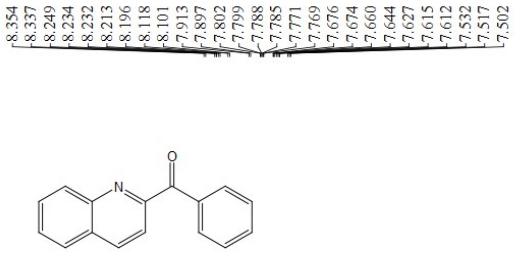
^{13}C NMR (125 MHz, $CDCl_3$)

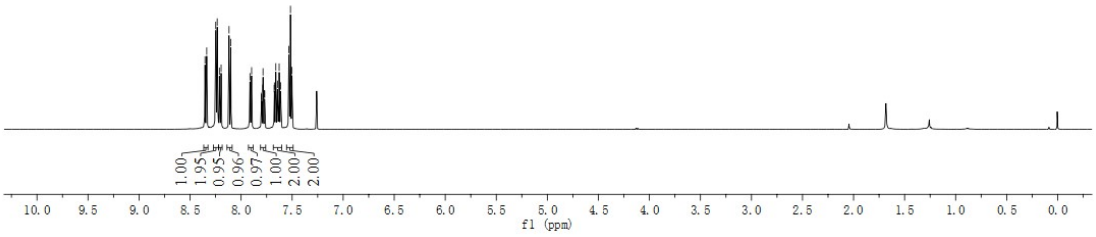
2-phenyl-2,3,4,5-tetrahydro-1H-benzo[*b*]azepine (4)



^{1}H NMR (500 MHz, $CDCl_3$)

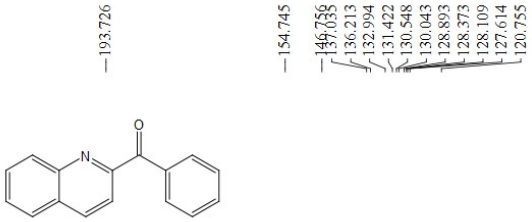
phenyl(quinolin-2-yl)methanone (5a)

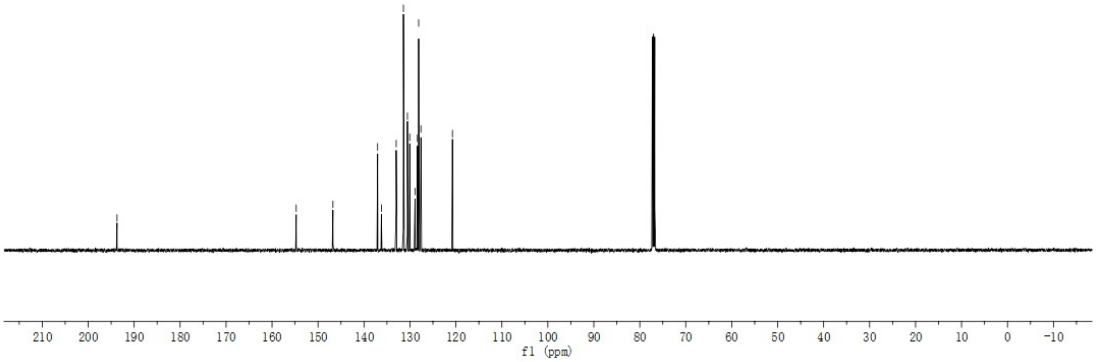




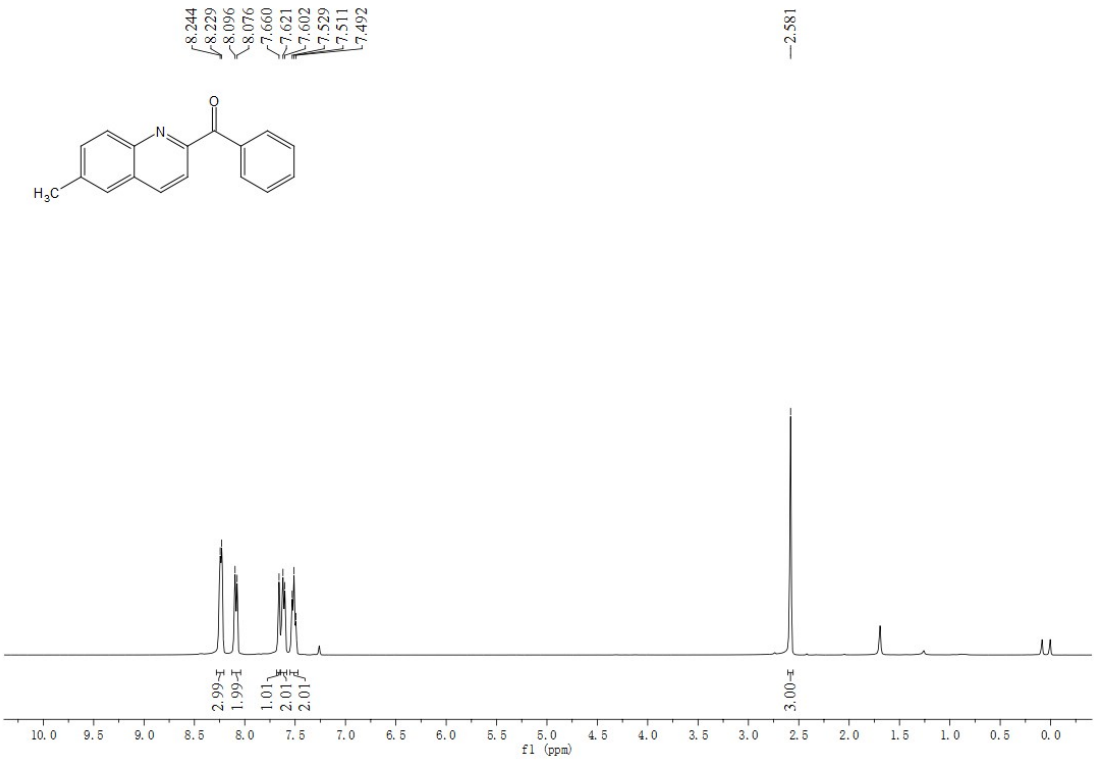
^{13}C NMR (125 MHz, $CDCl_3$)

phenyl(quinolin-2-yl)methanone (5a)

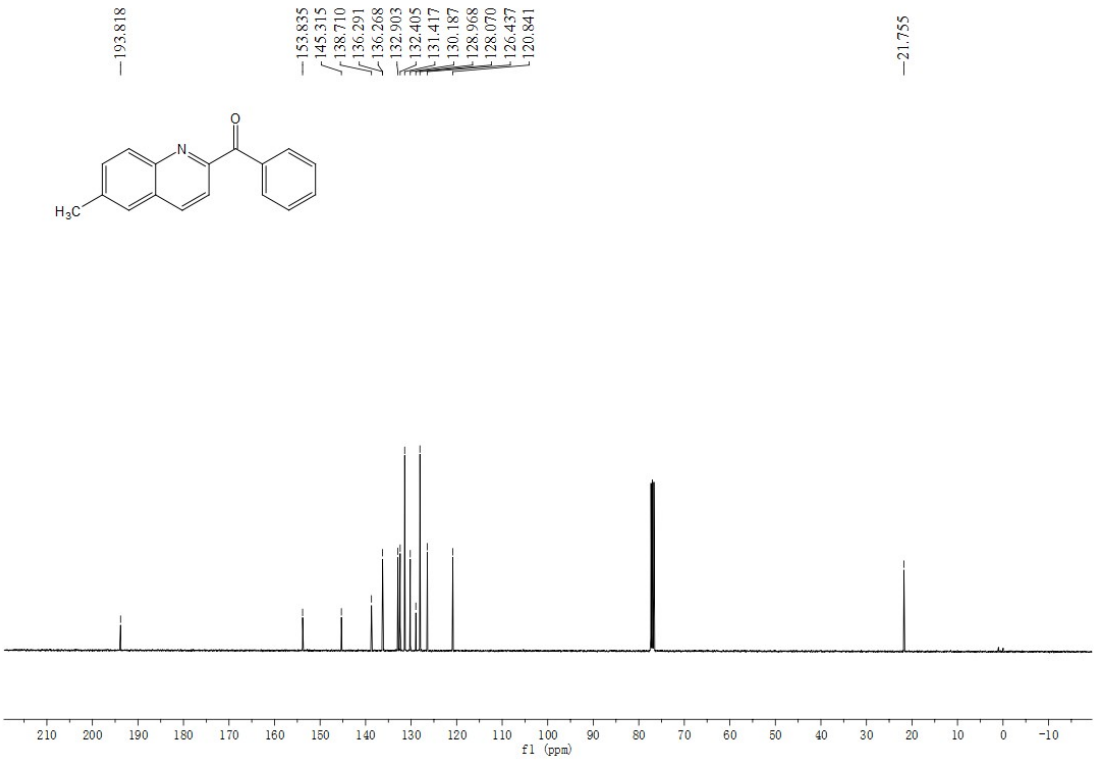




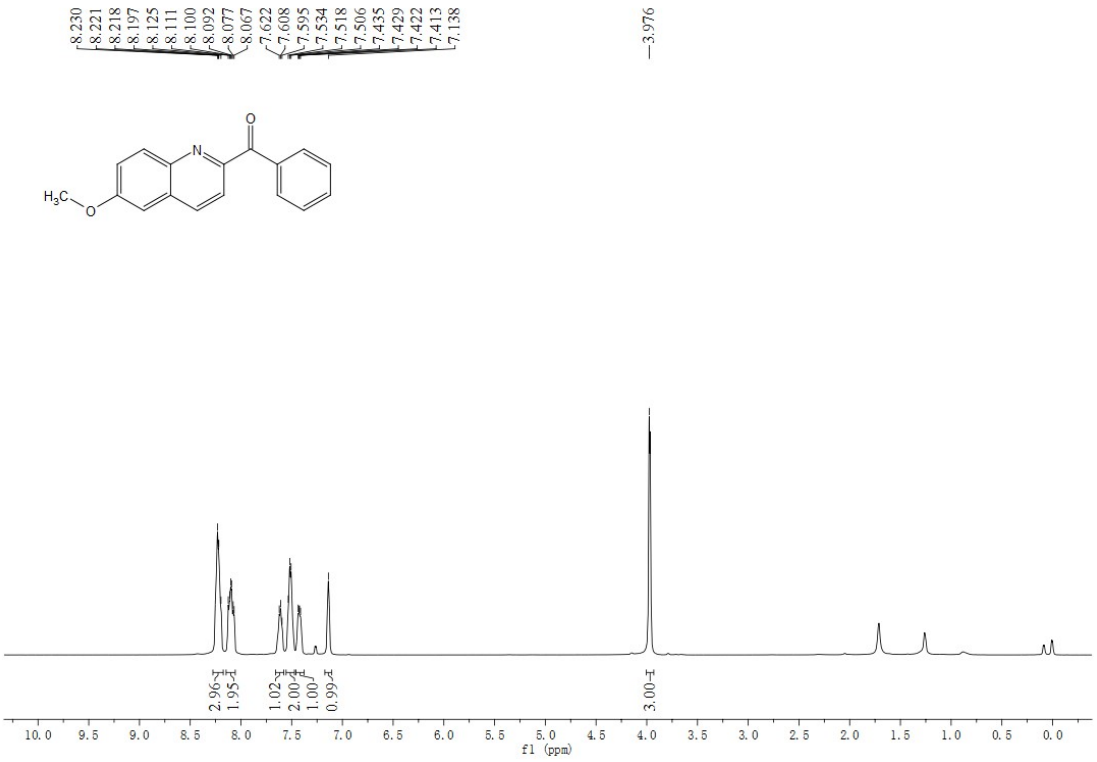
^{1}H NMR (400 MHz, $CDCl_3$)
(6-methylquinolin-2-yl)(phenyl)methanone (5b)



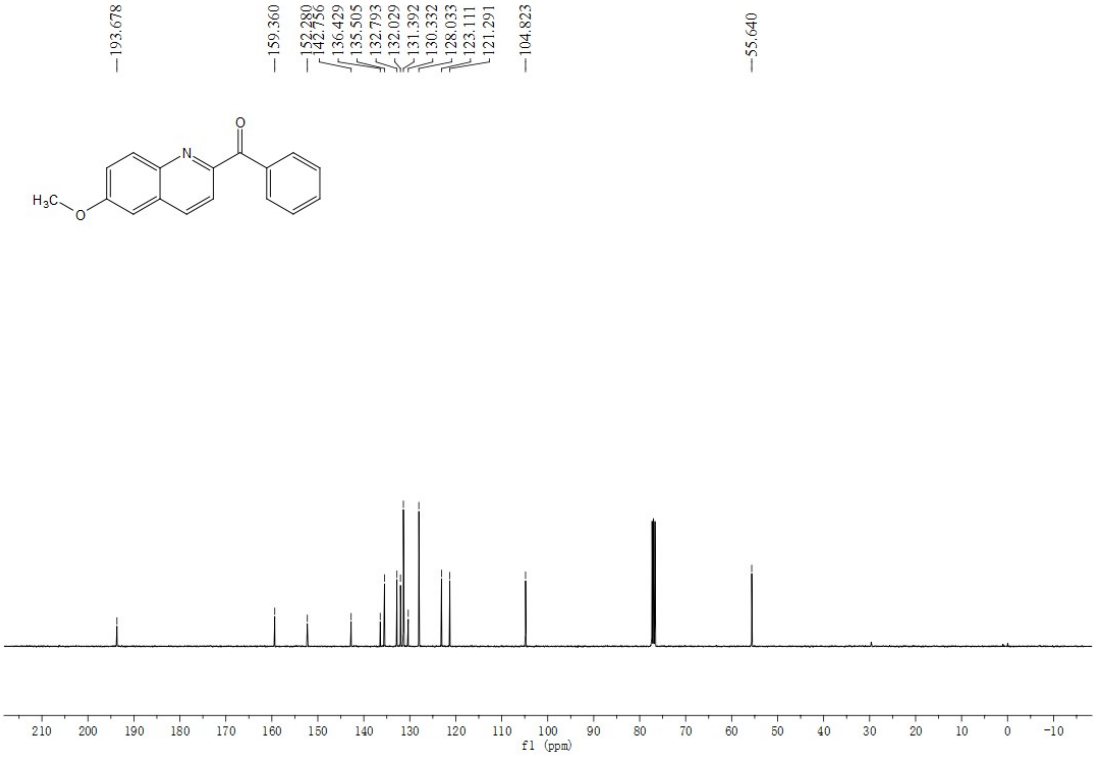
^{13}C NMR (100 MHz, $CDCl_3$)
(6-methylquinolin-2-yl)(phenyl)methanone (5b)



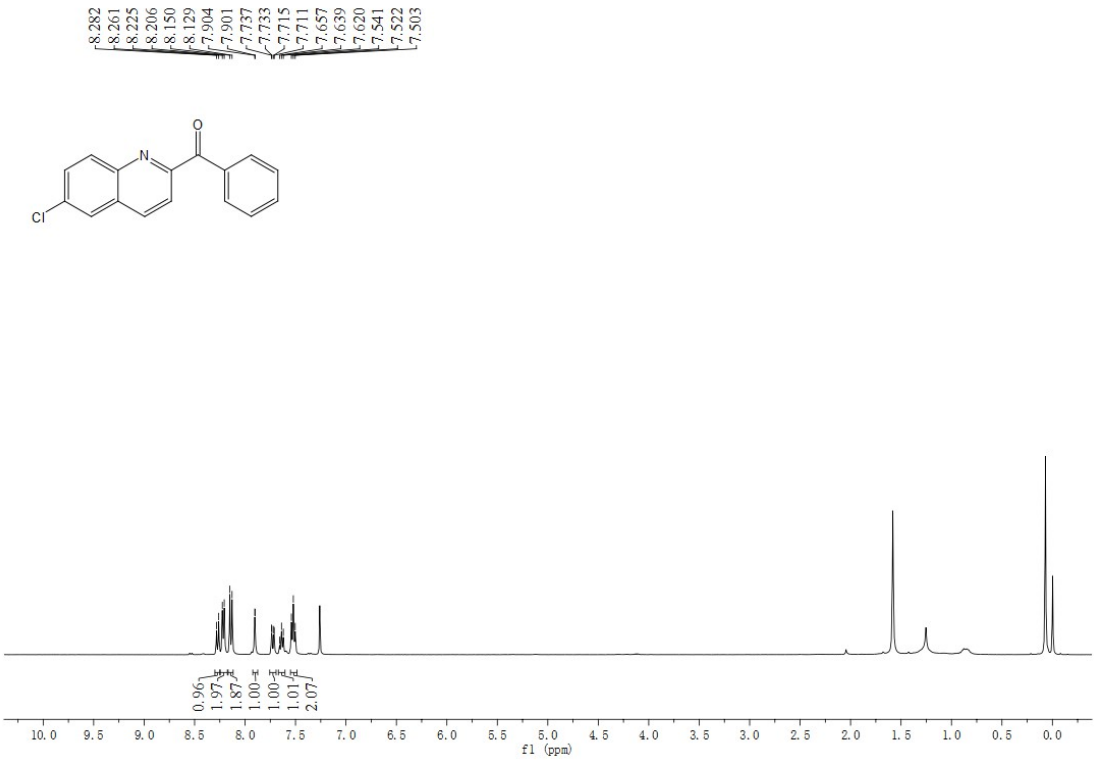
^{1}H NMR (400 MHz, $CDCl_3$)
(6-methoxyquinolin-2-yl)(phenyl)methanone (5c)



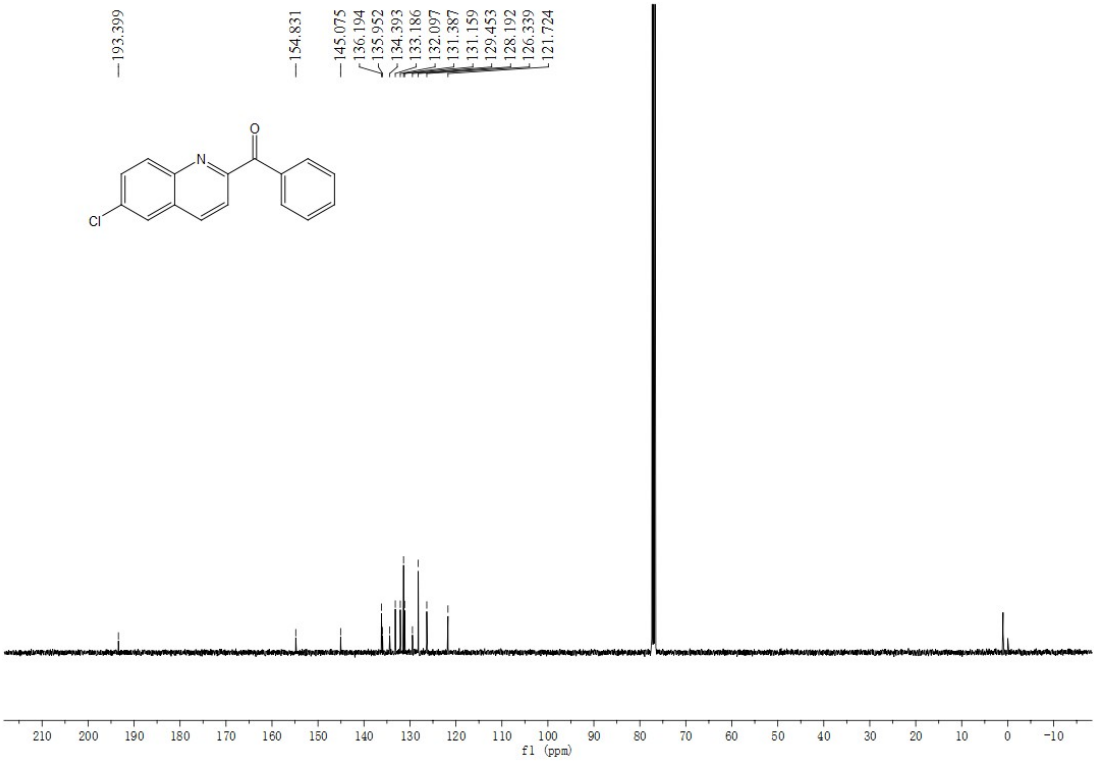
^{13}C NMR (100 MHz, $CDCl_3$)
(6-methoxyquinolin-2-yl)(phenyl)methanone (5c)



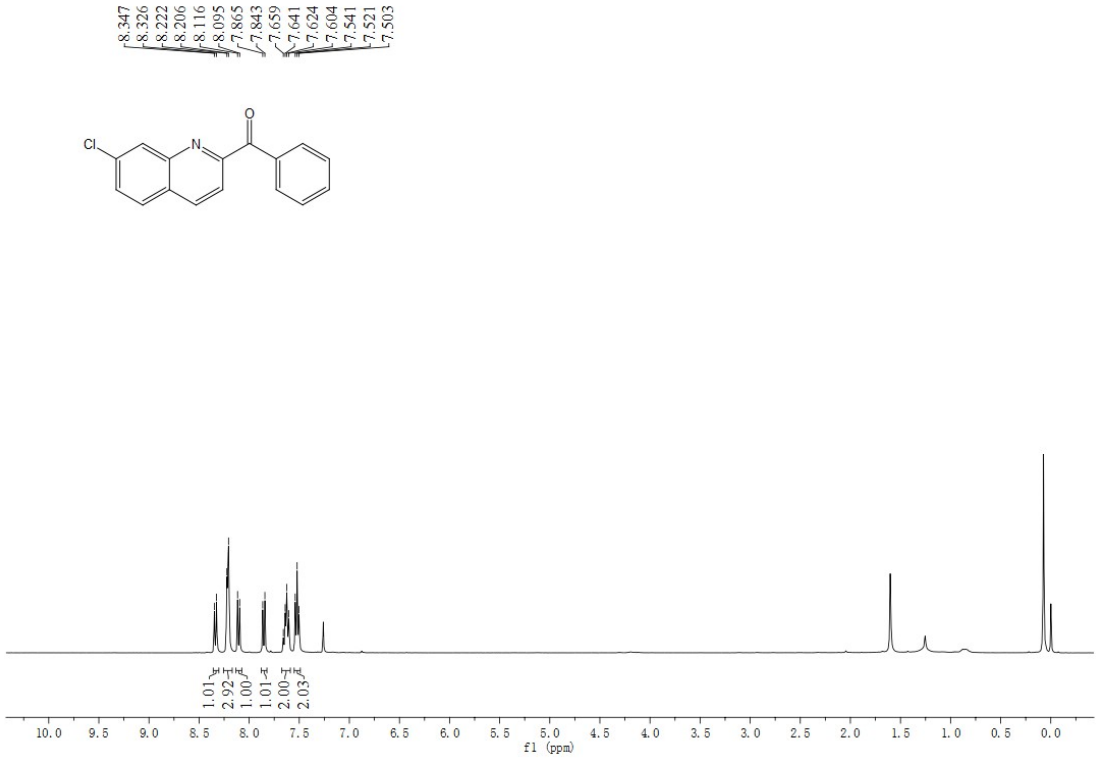
^{1}H NMR (400 MHz, $CDCl_3$)
(6-chloroquinolin-2-yl)(phenyl)methanone (5d)



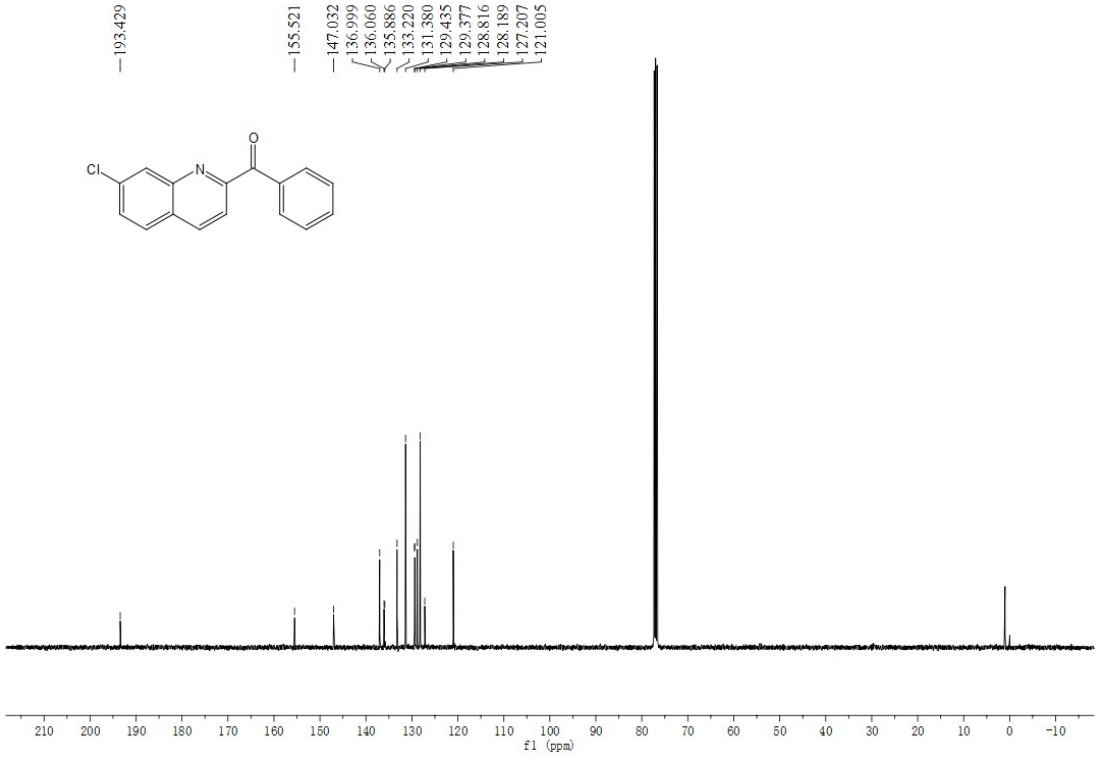
^{13}C NMR (100 MHz, $CDCl_3$)
(6-chloroquinolin-2-yl)(phenyl)methanone (5d)



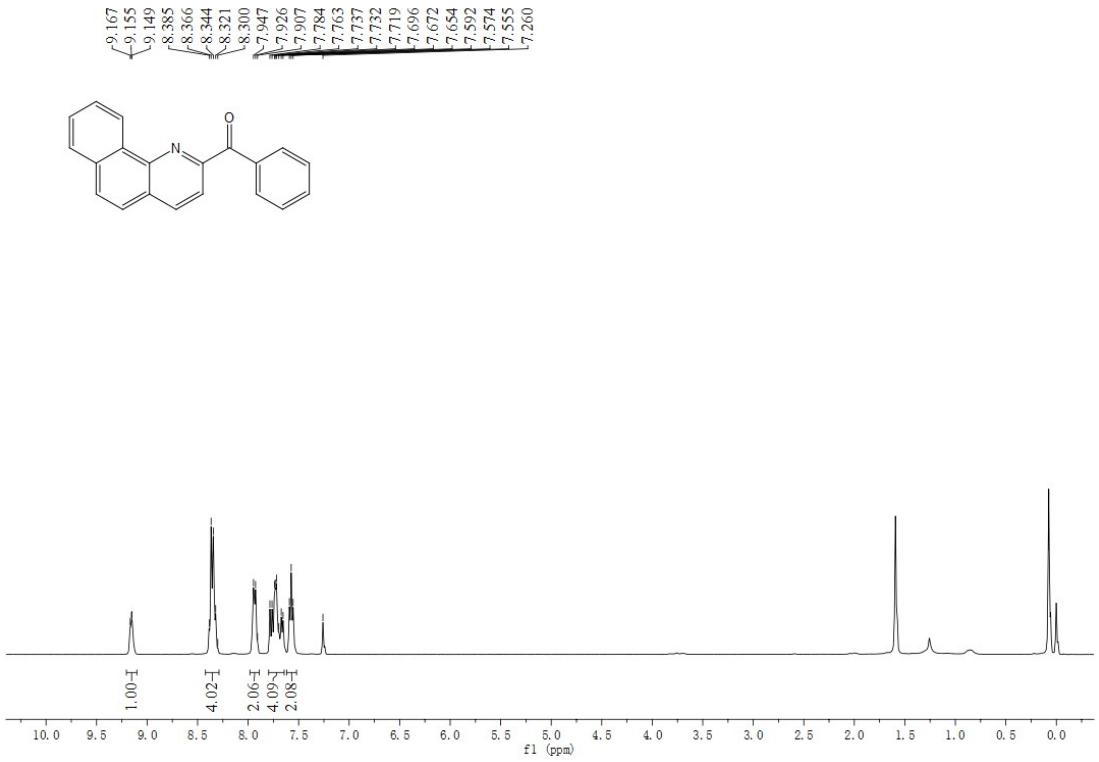
^{1}H NMR (400 MHz, $CDCl_3$)
(7-chloroquinolin-2-yl)(phenyl)methanone (5e)



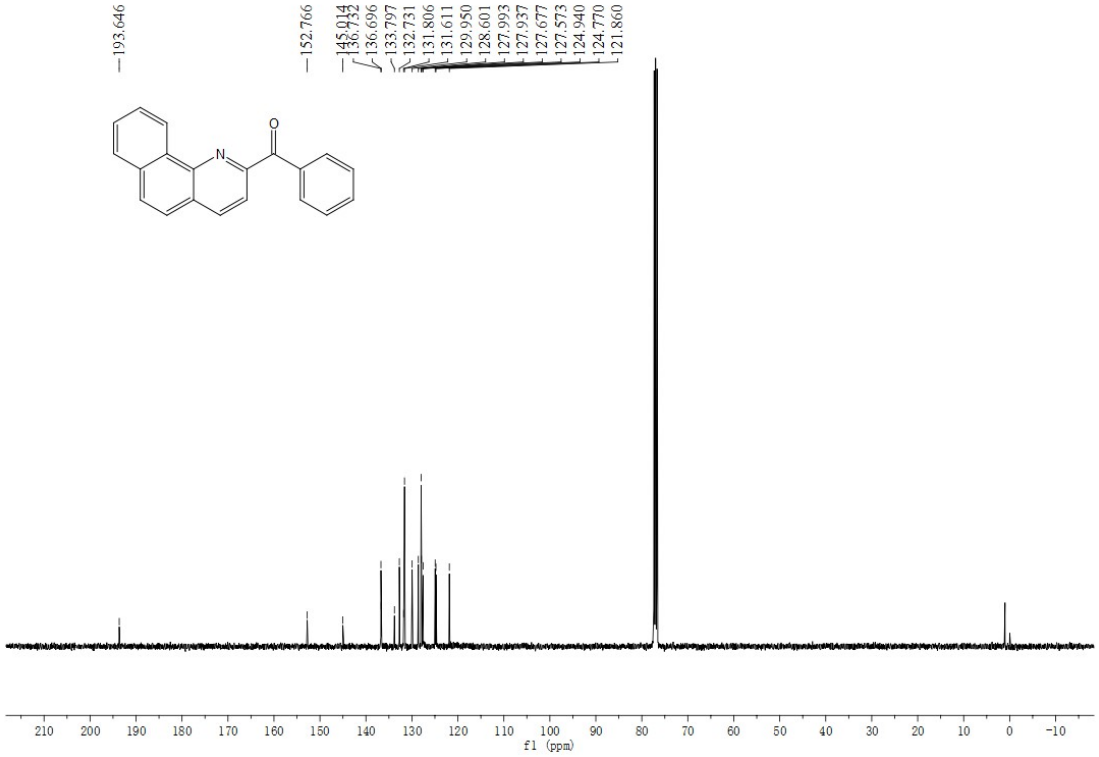
^{13}C NMR (100 MHz, $CDCl_3$)
(7-chloroquinolin-2-yl)(phenyl)methanone (5e)



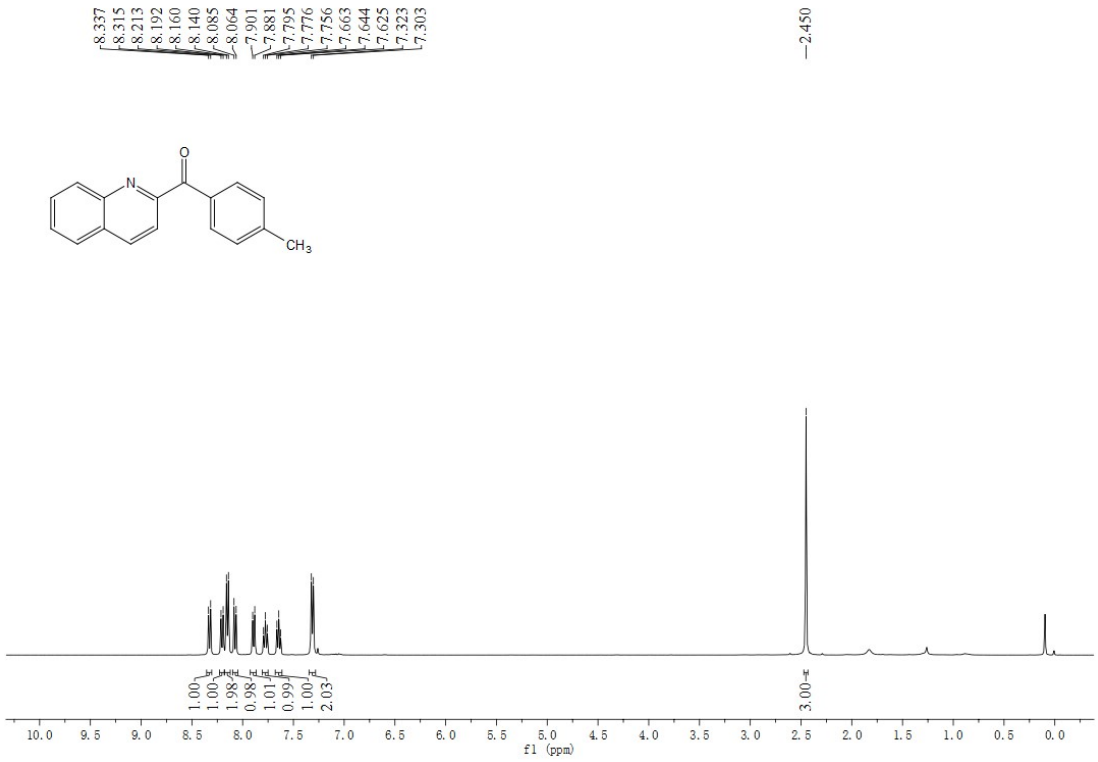
^{1}H NMR (400 MHz, $CDCl_3$)
benzo[*h*]quinolin-2-yl(phenyl)methanone (5f)



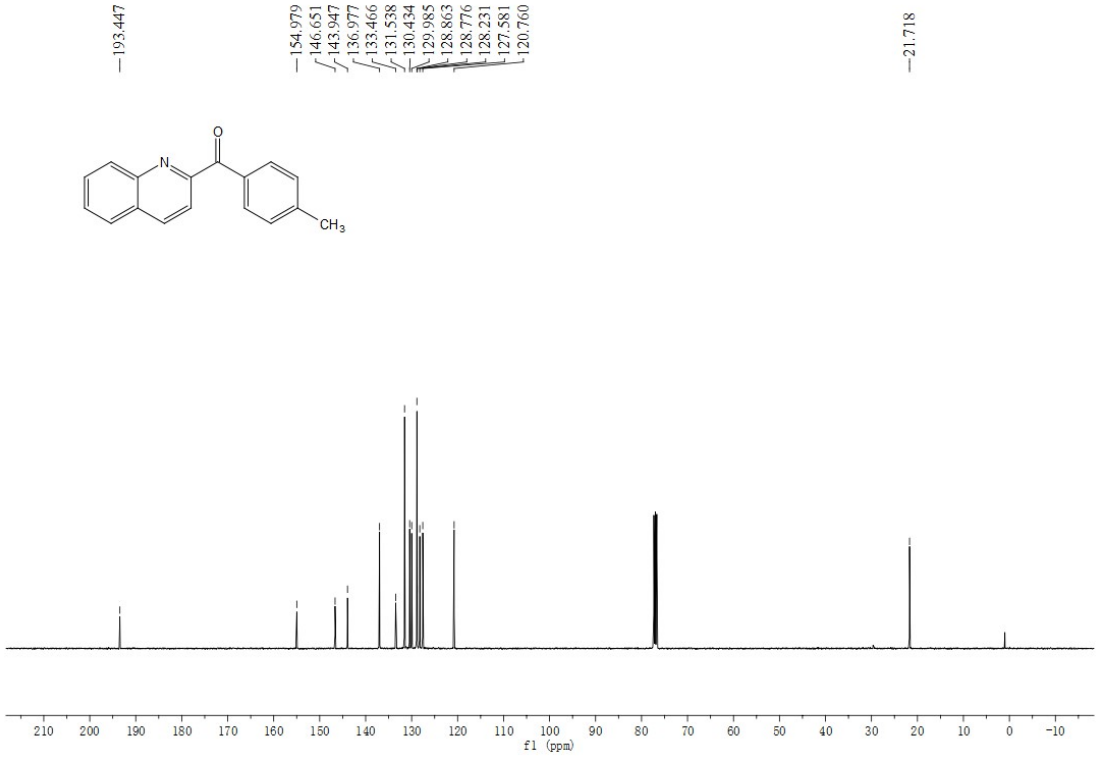
^{13}C NMR (100 MHz, $CDCl_3$)
benzo[*h*]quinolin-2-yl(phenyl)methanone (5f)



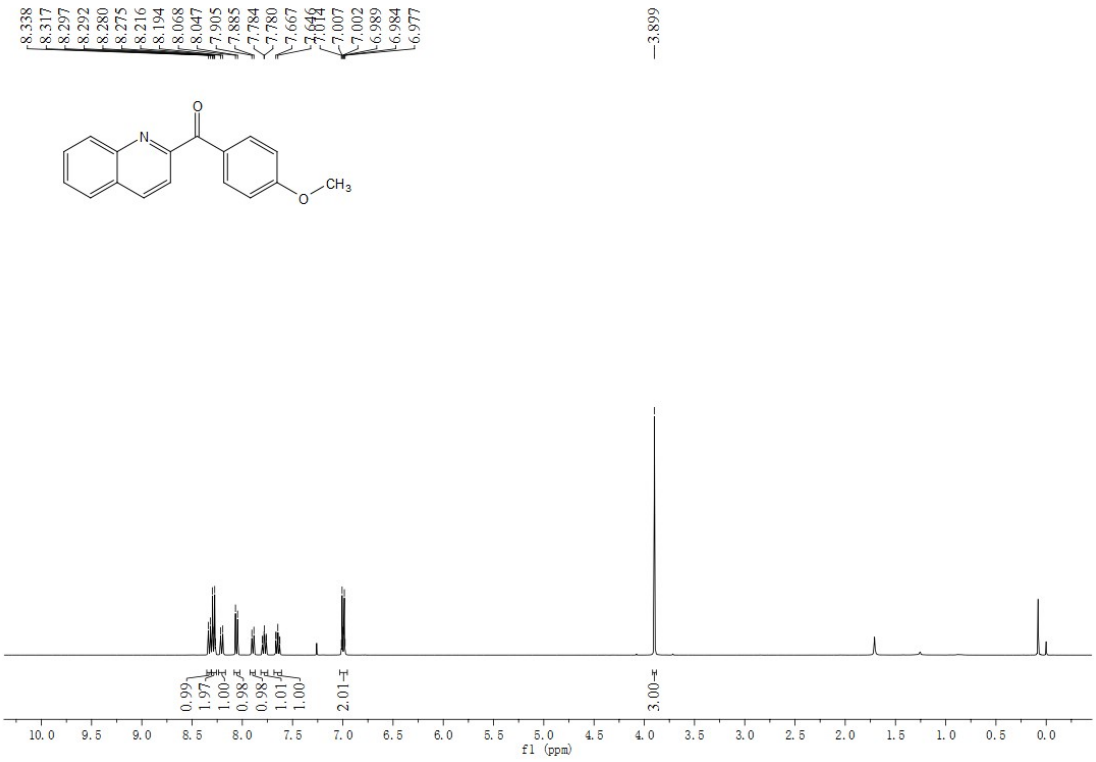
^{1}H NMR (400 MHz, $CDCl_3$)
quinolin-2-yl(p-tolyl)methanone (5g)



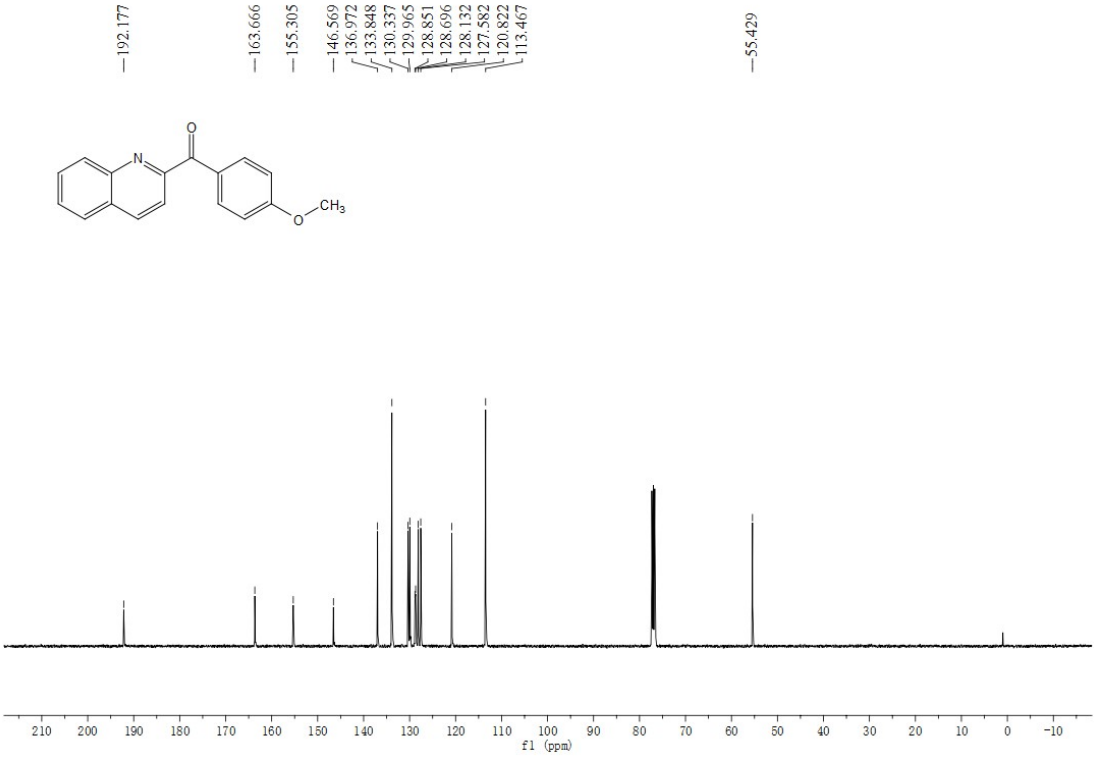
^{13}C NMR (100 MHz, $CDCl_3$)
quinolin-2-yl(p-tolyl)methanone (5g)



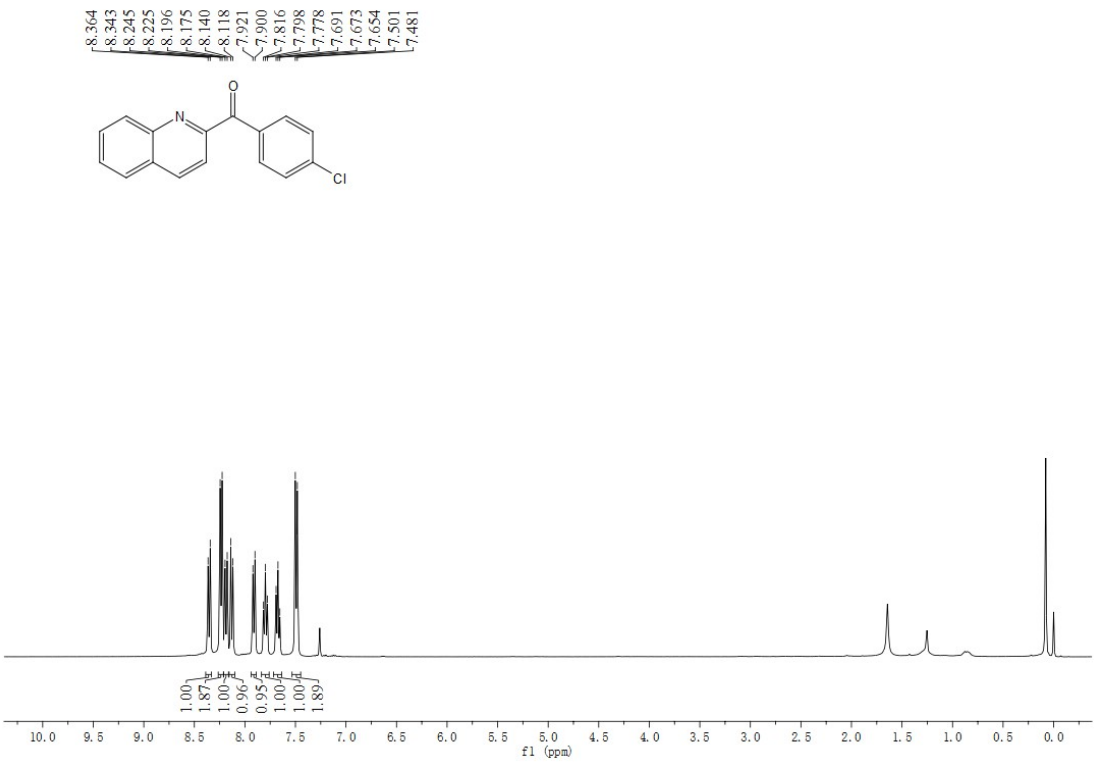
^{1}H NMR (400 MHz, $CDCl_3$)
(4-methoxyphenyl)(quinolin-2-yl)methanone (5h)



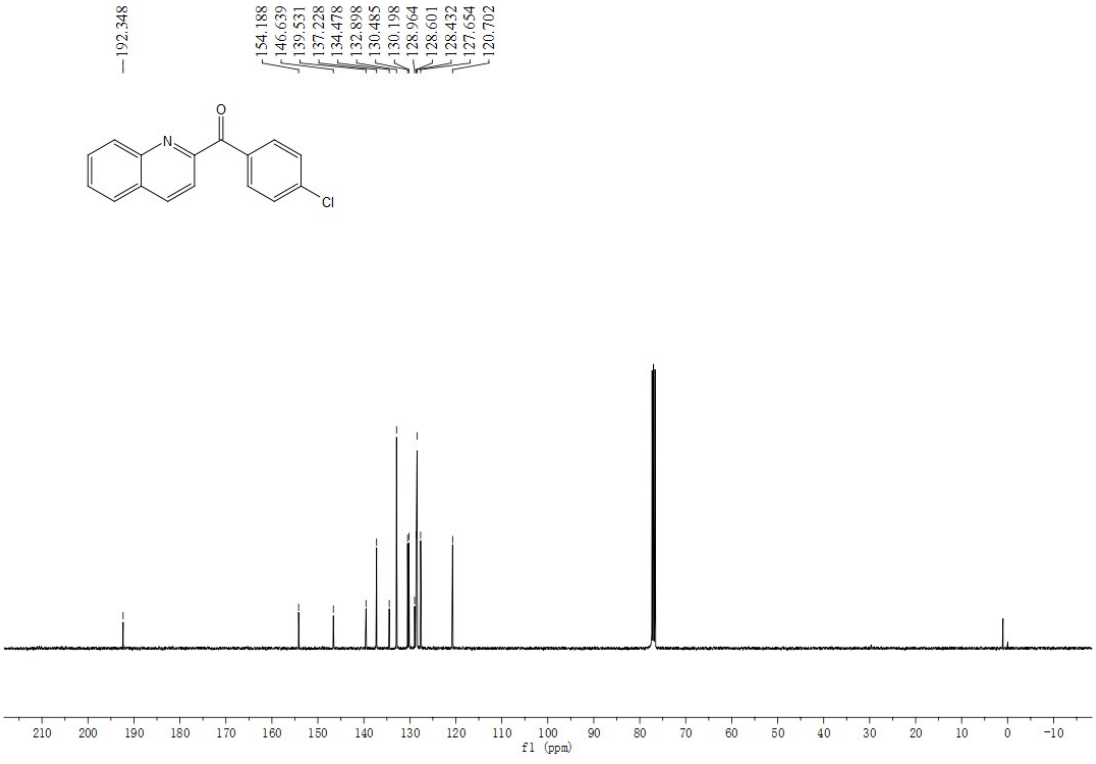
^{13}C NMR (100 MHz, $CDCl_3$)
(4-methoxyphenyl)(quinolin-2-yl)methanone (5h)



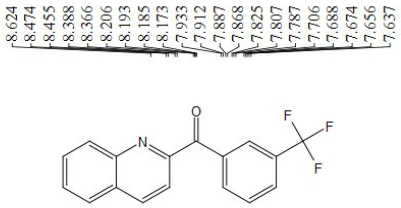
^{1}H NMR (400 MHz, $CDCl_3$)
(4-chlorophenyl)(quinolin-2-yl)methanone (5i)

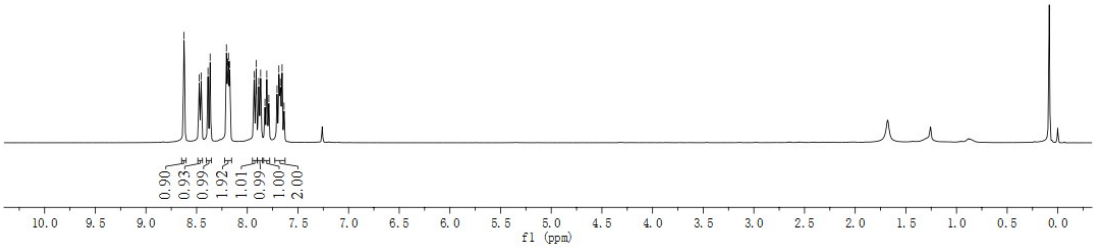


^{13}C NMR (100 MHz, $CDCl_3$)
(4-chlorophenyl)(quinolin-2-yl)methanone (5i)

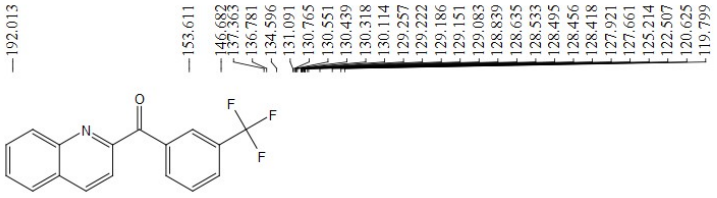


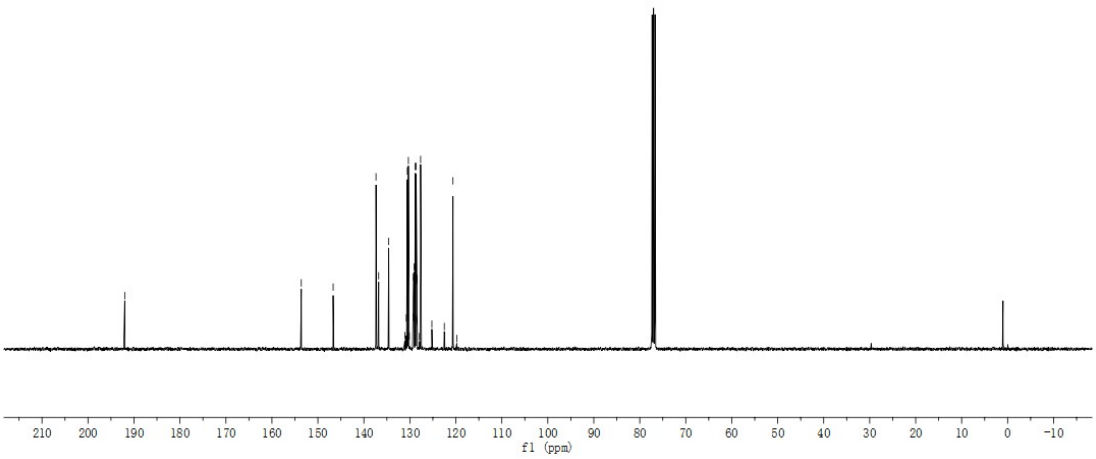
^{1}H NMR (400 MHz, $CDCl_3$)
quinolin-2-yl(3-(trifluoromethyl)phenyl)methanone (5j)



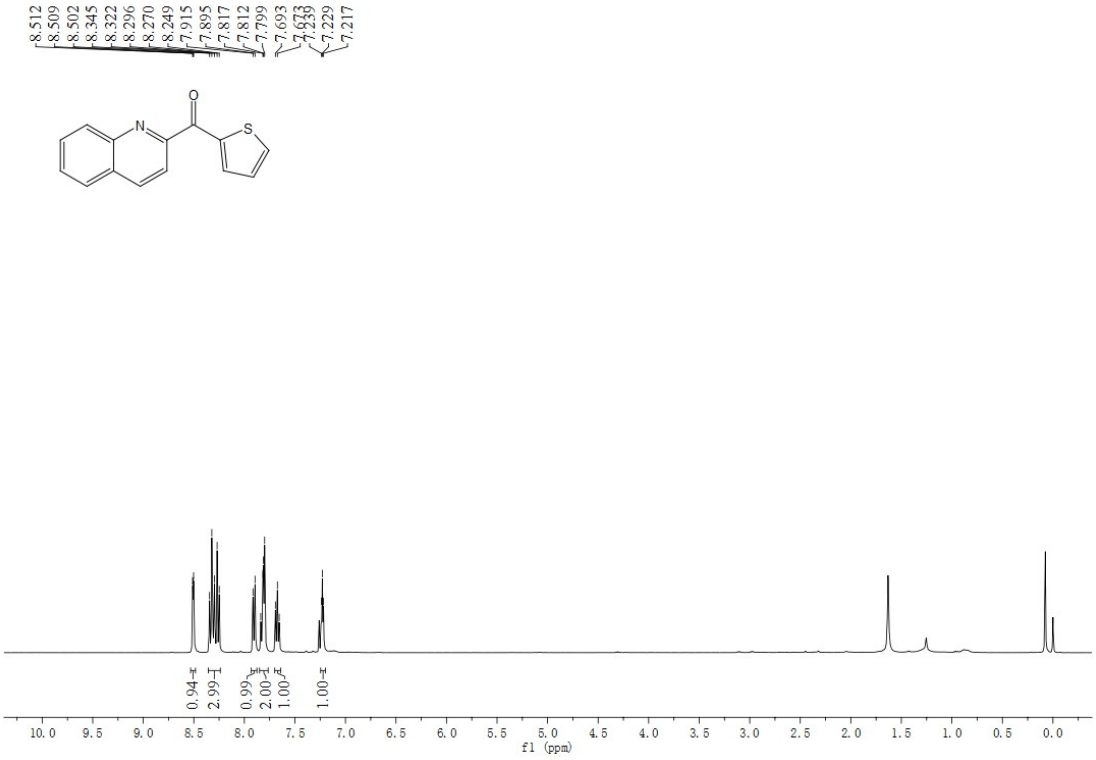


^{13}C NMR (100 MHz, $CDCl_3$)
quinolin-2-yl(3-(trifluoromethyl)phenyl)methanone (5j)

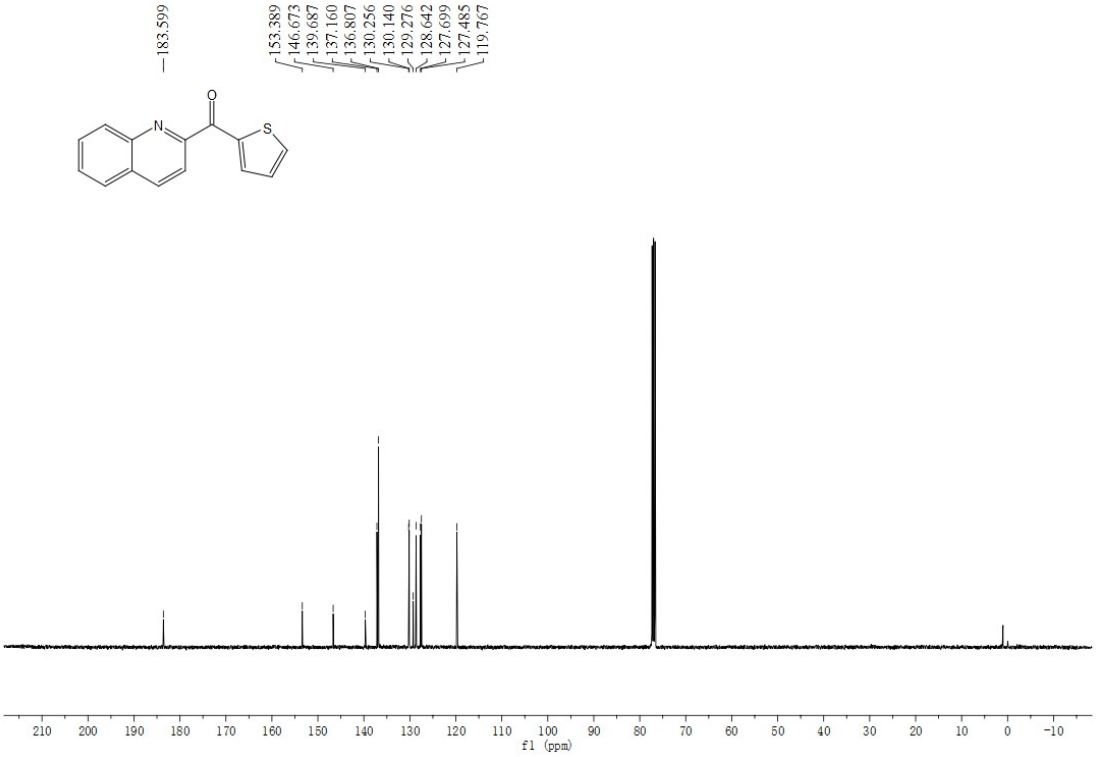




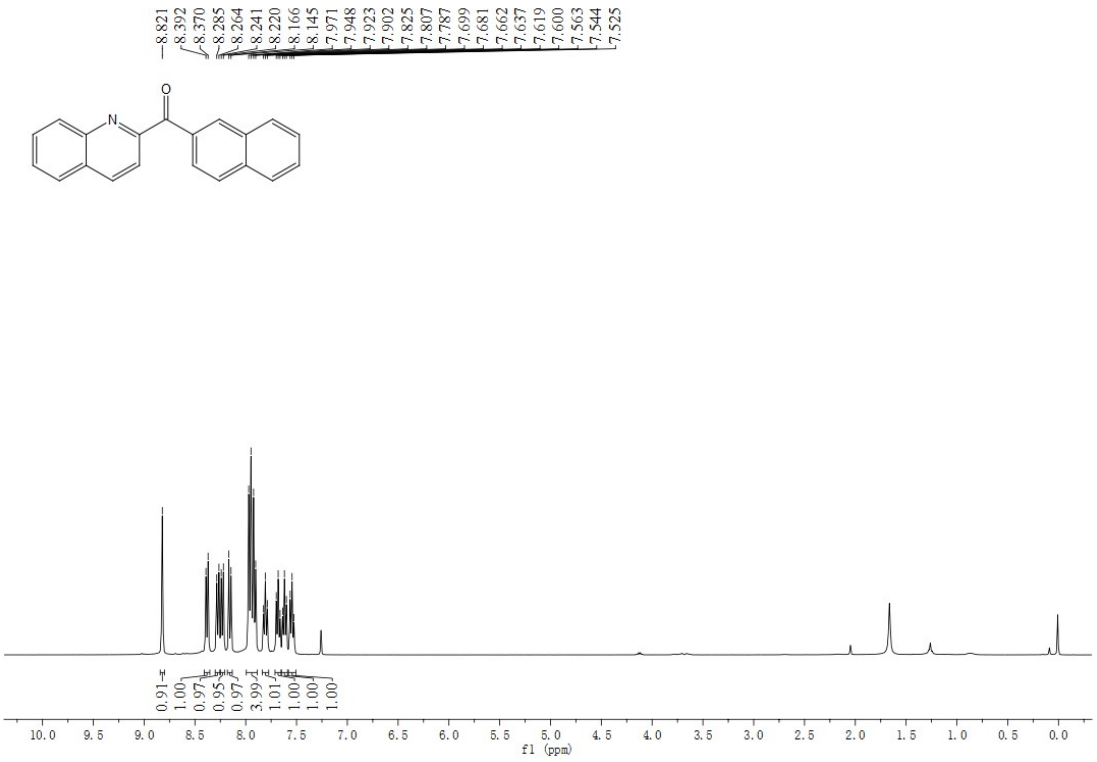
^{1}H NMR (400 MHz, $CDCl_3$)
quinolin-2-yl(thiophen-2-yl)methanone (5k)



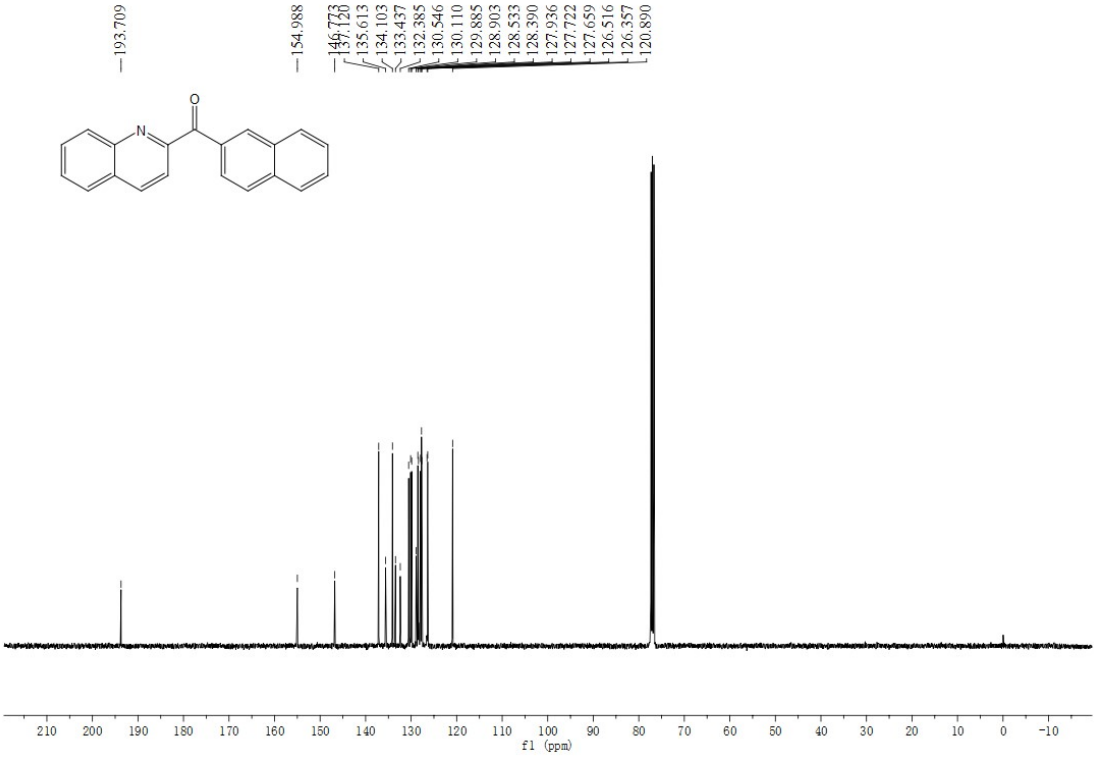
^{13}C NMR (100 MHz, $CDCl_3$)
quinolin-2-yl(thiophen-2-yl)methanone (5k)



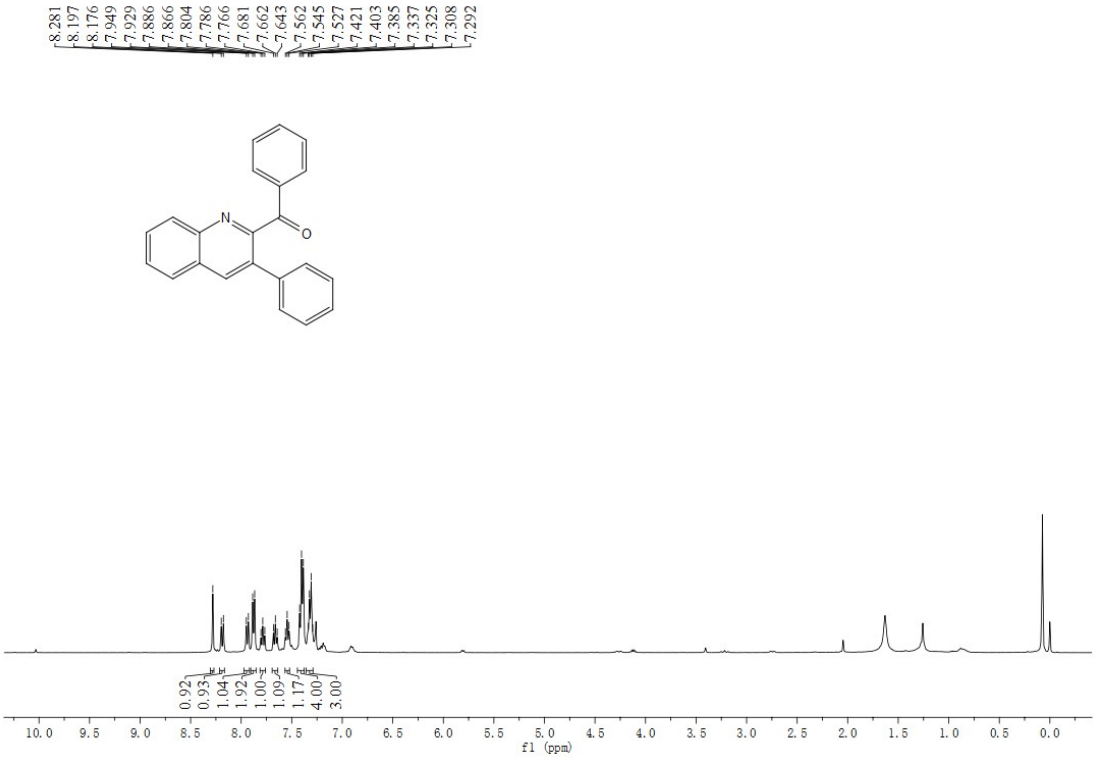
^{1}H NMR (400 MHz, $CDCl_3$)
naphthalen-2-yl(quinolin-2-yl)methanone (5l)



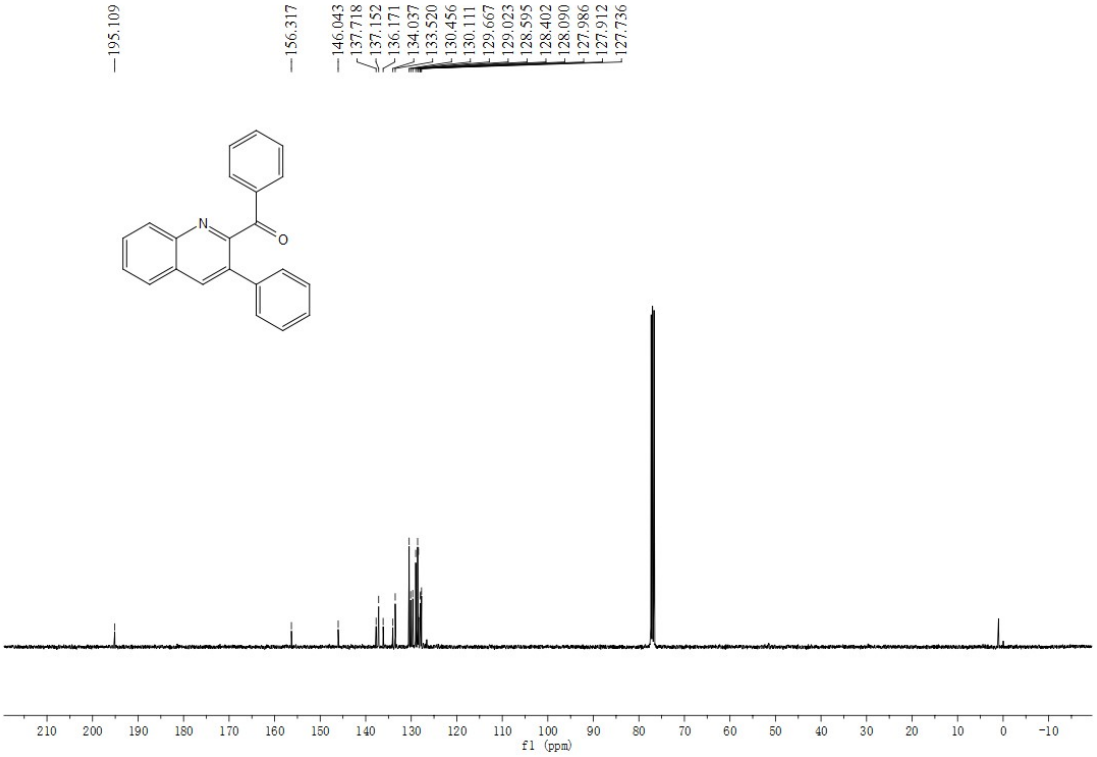
^{13}C NMR (100 MHz, $CDCl_3$)
naphthalen-2-yl(quinolin-2-yl)methanone (5l)



^{1}H NMR (400 MHz, $CDCl_3$)
phenyl(3-phenylquinolin-2-yl)methanone (5m)

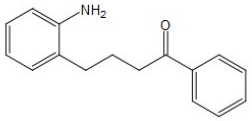


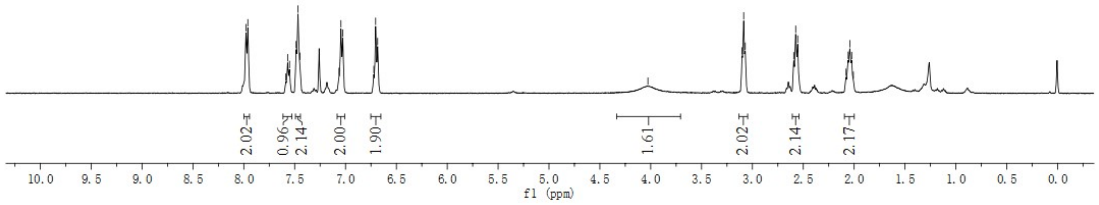
^{13}C NMR (100 MHz, $CDCl_3$)
phenyl(3-phenylquinolin-2-yl)methanone (5m)



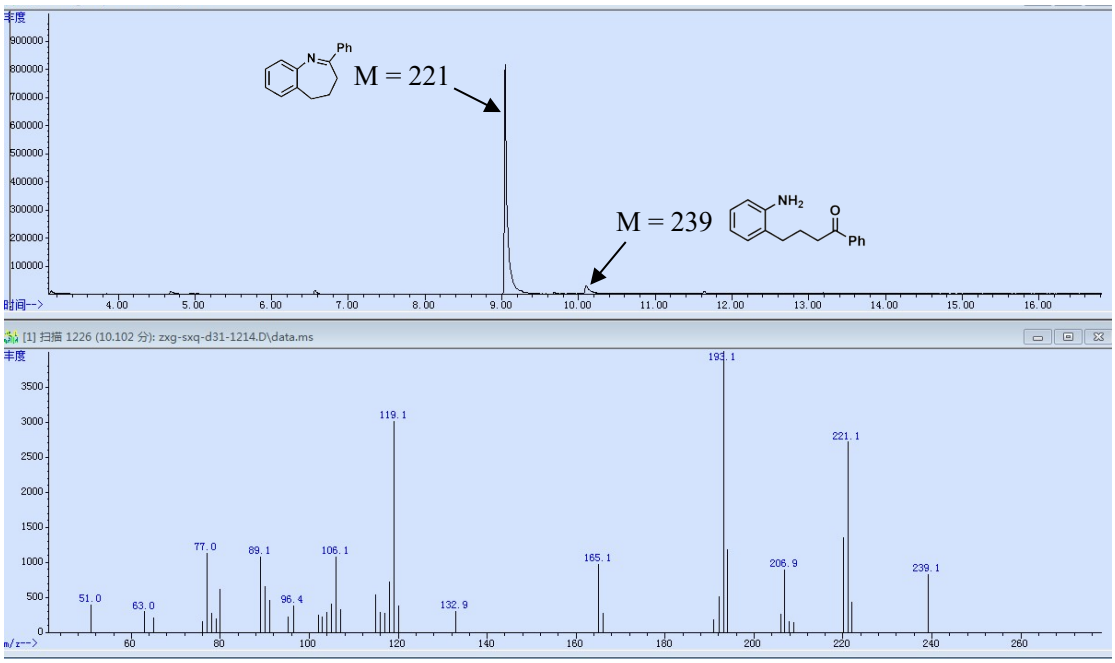
^{1}H NMR (400 MHz, $CDCl_3$)

4-(2-aminophenyl)-1-phenylbutan-1-one (6)



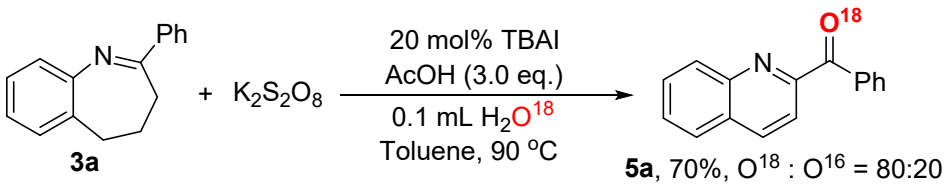


7. GC-MS Data of intermediate 6



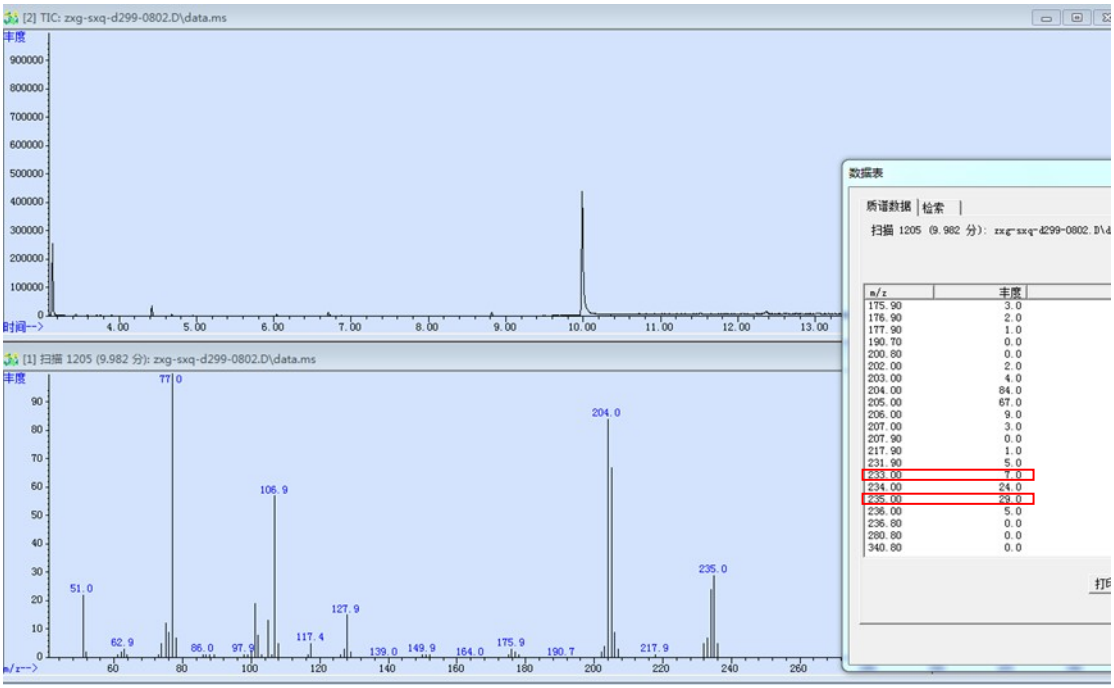
8. Control Experiments on the Reaction Mechanism

8.1 O^{18}-labeled experiment of benzazepine 3a

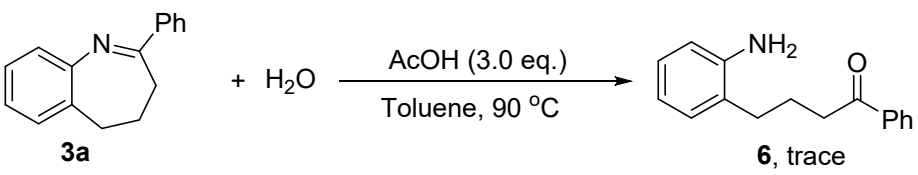


A mixture of benzo[*b*]azepine **3a** (22.1 mg, 0.1 mmol), *n*-Bu_4NI (7.4 mg, 0.02 mmol, 20 mol%), $K_2S_2O_8$ (108.1 mg, 0.4 mmol, 4.0 equiv), acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) and 0.1 mL H_2O^{18} in 1 mL anhydrous toluene was stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the quinoline **5a** (16.3 mg, 70% yield).

a) O^{18}:O^{16}-5a GC analysis

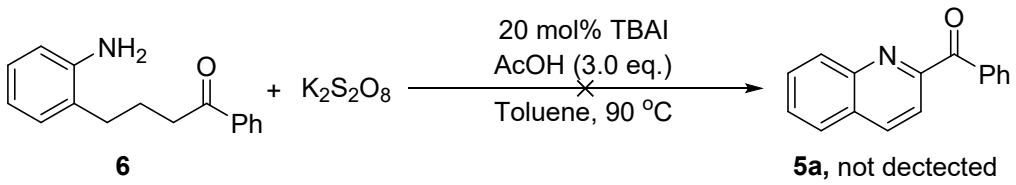


8.2 Reaction of 3a in the Presence of AcOH



A mixture of benzo[*b*]azepine **3a** (22.1 mg, 0.1 mmol), acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) and 0.1 mL H_2O in 1 mL anhydrous toluene was stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature and monitored by GC-MS and TLC.

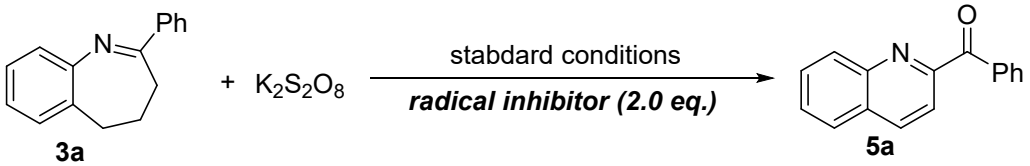
8.3 Oxidation Experiment of 6



6 **5a,** not dectected

A mixture of **6** (23.9 mg, 0.1 mmol), *n*-Bu_4NI (7.4 mg, 0.02 mmol, 20 mol%), $K_2S_2O_8$ (108.1 mg, 0.4 mmol, 4.0 equiv) and acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) in 1 mL toluene was stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature and monitored by GC-MS and TLC.

8.4 Radical Inhibition Experiments



3a **5a**

TEMPO	32%
1,1-diphenylethylene	trace

A mixture of benzo[*b*]azepine **3a** (22.1 mg, 0.1 mmol), *n*-Bu_4NI (7.4 mg, 0.02 mmol, 20 mol%), $K_2S_2O_8$ (108.1 mg, 0.4 mmol, 4.0 equiv), acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) and TEMPO (31.3 mg, 2.0 equiv) in 1 mL toluene was stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the quinoline **5a** (7.5 mg, 32% yield).

A mixture of benzo[*b*]azepine **3a** (22.1 mg, 0.1 mmol), *n*-Bu_4NI (7.4 mg, 0.02 mmol, 20 mol%), $K_2S_2O_8$ (108.1 mg, 0.4 mmol, 4.0 equiv), acetic acid (18.0 mg, 0.3 mmol, 3.0 equiv) and 1,1-diphenylethylene (36.1 mg, 2.0 equiv) in 1 mL toluene was

stirred in a Schlenk tube at 90 °C. After stirring for 16 h, the reaction mixture was cooled to the room temperature and monitored by GC-MS and TLC.

9. X-Ray Crystallographic Data (CCDC 2098117).

Method for crystal growth: Product **5a** (20 mg) was added into a clean tube, and dissolved by dichloromethane, then the mixture was evaporating slowly at room temperature under the air condition until the single crystal was obtained as a yellow crystal.

Crystal measurement: Sheldrick, G. M.; SHELXL-97, Program for X-ray Crystal Structure Solution and Refinement, University of Göttingen: Germany, 1997. Sheldrick, G. M. SHELXTL. Structure Determination Software Programs. Version 6.14. Bruker AXS. Madison, Wisconsin, USA 2000.

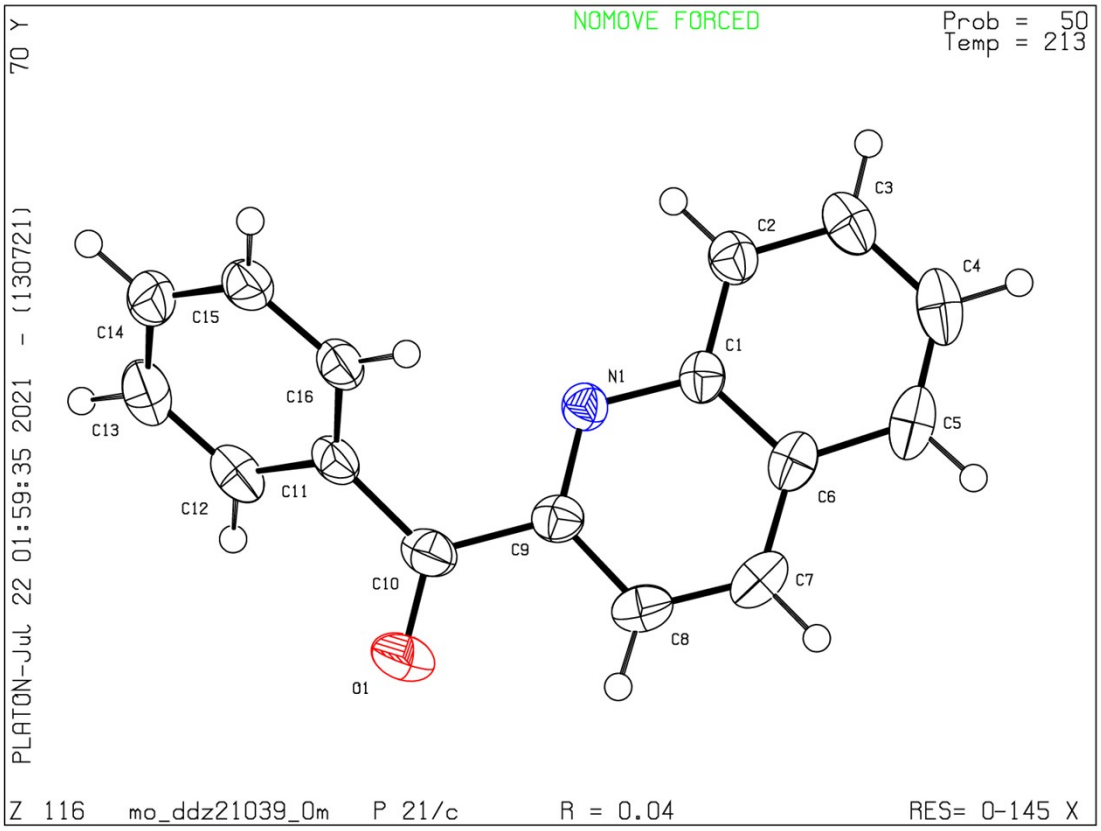


Figure S1. ORTEP diagram of compound **5a** (30% probability factor for thermal ellipsoids)

Bond precision: C-C = 0.0018 A Wavelength=0.71073

Cell: a=3.9127(1) b=28.5829(8) c=10.3664(3)
alpha=90 beta=92.863(1) gamma=90

Temperature: 213 K

	Calculated	Reported
Volume	1157.89(6)	1157.89(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H11 N O	?
Sum formula	C16 H11 N O	C16 H11 N O
Mr	233.26	233.26
Dx, g cm-3	1.338	1.338
Z	4	4
Mu (mm-1)	0.084	0.084
F000	488.0	488.0
F000'	488.20	
h, k, lmax	4, 35, 12	4, 35, 12
Nref	2276	2255
Tmin, Tmax	0.985, 0.990	0.632, 0.746
Tmin'	0.983	

Correction method= # Reported T Limits: Tmin=0.632 Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 25.995

R(reflections)= 0.0360(1933) wR2(reflections)= 0.0940(2255)

S = 1.050 Npar= 164