Supporting Information

Radical Alkylation of C(sp^3)–H Bonds with Diacyl Peroxides under Catalyst-Free Conditions

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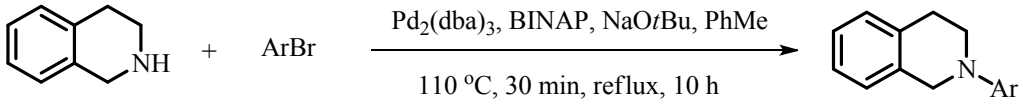
1. General Information

All commercially available reagents were used without further purification unless otherwise stated. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMs) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).

2. Preparation of Substrates.

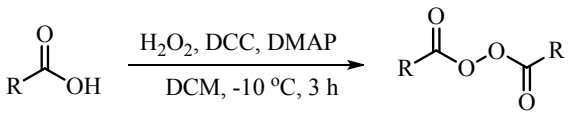
2.1 Preparation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a-1g**).



According to literature reports,[1] The **1a-1g** can be synthesized by the methods below:

An oven-dried round bottom flask (50 mL) was cooled down to room temperature under Ar, $Pd_2(dba)_3$ (115 mg, 0.2 mmol), BINAP (249 mg, 0.4 mmol) were introduced into the flask and degassed three time with Ar, then fresh distilled toluene (15 mL) was added into the flask through a syringe. The suspension was subsequently stirred at 110 °C for 30 min. After cooled down to room temperature, NaO*t*Bu (912 mg, 9.5 mmol), bromobenzene (5 mmol) and 1,2,3,4-tetrahydroisoquinoline (1.33 g, 10 mmol) were added into the solution. The mixture was then degassed three times with Ar and stirred under reflux for 10 h. The mixture was then cooled down to the room temperature and filtered through celite. The celite was washed with CH_2Cl_2 (5 x 3 mL), the combined organic layer was evaporated to remove the solvent and the crude product was then purified by column. The pure product was obtained as solid or liquid.

2.2 Preparation of diacyl peroxides.



According to literature reports,[2] the diacyl peroxides **2b-2v** can be synthesized by the methods below:

A solution of DMAP (0.6 mmol), 30% hydrogen peroxide (8 mmol), and acid (6 mmol) in DCM (8 mL) was cooled to -10 °C for about 10 min, then DCC (6.72 mmol) was added. After stirring at -10 °C for 3 h, the solution was filtered through a short pad of silica gel. Then washed the pad of silica gel by additional 20 mL of DCM. The combined solution was concentrated on a rotary evaporator under vacuum at 20 °C and then purified by flash column chromatography on silica gel to give the alkyl diacyl peroxide.

1a, white solid, 89% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.20 (m, 4H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 4.48 (s, 2H), 3.63 (t, *J* = 5.4 Hz, 2H), 3.06 (t, *J* = 5.4 Hz, 2H).
1b, white solid, 72% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.31 (m, 2H), 6.95 – 7.02 (m, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 4.3 Hz, 1H), 4.33 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.55 (t, *J* = 5.8 Hz, 2H), 2.90 (t, *J* = 5.7 Hz, 2H).
1c, white solid, 74% yield.
^{1}H NMR (400MHz, CDCl3) δ = 7.23-7.13 (m, 4H), 7.11-6.83 (m, 4H), 4.34 (s, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 2.99 (t, *J* = 5.9 Hz, 2H).
1d, yellow solid, 70% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 9.0 Hz, 2H), 7.10 – 7.22 (m, 4H), 6.82 (d, *J* = 9.0 Hz, 2H), 4.36 (s, 2H), 3.52 (t, *J* = 5.9 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H).
1e, white solid, 54% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.20 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.35 (s, 2H), 3.50 (t, *J* = 5.9 Hz, 2H), 2.98 (t, *J* = 5.8 Hz, 2H), 2.28 (s, 3H).
1f, white solid, 74% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.20 – 7.12 (m, 4H), 6.97 – 6.92 (m, 2H), 4.38 (s, 2H), 3.53 (t, *J* = 5.8 Hz, 2H), 2.98 (t, *J* = 5.8 Hz, 2H), 1.30 (s, 9H).
1g, white solid, 77% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 4H), 7.05 – 6.97 (m, 2H), 6.94 – 6.85 (m, 2H), 4.33 (s, 2H), 3.81 (s, 3H), 3.48 (t, *J* = 5.9 Hz, 2H), 3.02 (t, *J* = 5.9 Hz, 2H).
1h, colorless oil, 67% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 5H), 6.60 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.51 (t, *J* = 2.4 Hz, 1H), 6.39 (dd, *J* = 8.1, 2.4 Hz, 1H), 4.41 (s, 2H), 3.81 (s, 3H), 3.56 (t, *J* = 5.8 Hz, 2H), 2.98 (t, *J* = 5.8 Hz, 2H).
1i, colorless oil, 64% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.94 – 6.88 (m, 2H), 4.29 (s, 2H), 3.89 (s, 3H), 3.41 (t, *J* = 5.9 Hz, 2H), 2.98 (t, *J* = 5.9 Hz, 2H).
1j, white solid, 88% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.37 – 7.43 (m, 1H), 7.35 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.14 – 7.30 (m, 6H), 4.51 (s, 2H), 3.67 (t, *J* = 5.9 Hz, 2H), 3.04 (t, *J* = 5.8 Hz, 2H).
1k, white solid, 64% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.60 (m, 4H), 7.37 – 7.48 (m, 2H), 7.23 – 7.32 (m, 1H), 7.14 – 7.23 (m, 4H), 7.01 – 7.07 (m, 2H), 4.46 (s, 2H), 3.61 (t, *J* = 5.9 Hz, 2H), 3.01 (t, *J* = 5.8 Hz, 2H).
2b, colorless oil, 56% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26(t, *J* =7.6Hz,6H),2.47(q, *J* =7.6Hz,4H).
2c, colorless oil, 63% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.44 Hz, 4H), 1.72-1.60 (m, 4H), 1.36-1.20 (m, 8H), 0.83 (t, *J* = 7.72 Hz, 6H).
2d, colorless oil, 77% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (t, *J* = 7.40 Hz, 4H), 1.80-1.66 (m, 4H), 1.41-1.20 (m, 16H), 0.88 (t, *J* = 6.40 Hz, 6H).

2e, colorless oil, 87% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (t, *J* = 7.5 Hz, 4H), 1.78 – 1.66 (m, 12H), 1.44 – 1.17 (m, 20H), 0.95 – 0.81 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 37.4, 36.9, 33.3, 30.1, 26.7, 26.4, 26.2, 25.1.
2f, colorless oil, 84% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (t, *J* = 7.60 Hz, 4H), 1.86-1.69 (m, 10H), 1.65-1.49 (m, 8H), 1.12-1.09 (m, 4H).
2g, colorless oil, 77% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 4H), 1.10 (s, 18H).
2h, colorless oil, 67% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, J = 6.6 Hz, 4H), 2.69 (t, J = 6.7 Hz, 4H), 2.21 (d, J = 3.7 Hz, 6H).
2i, white solid, 58% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 2.81 – 2.69 (m, 8H).
2j, white solid, 68% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.04 Hz, 4H), 7.2m 7-7.17 (m, 6H), 3.03 (t, *J* = 7.64 Hz, 4H), 2.74 (t, *J* = 8.20 Hz, 4H).
2k, white solid, 73% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 2H), 7.05 – 6.94 (m, 2H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.21, 161.72 (d, *J* = 244.7 Hz), 134.9, 129.8 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.7 Hz), 31.8, 29.9.
2l, white solid, 58% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 138.3, 133.3, 130.3, 129.5, 32.2, 30.7.
2m, white solid, 62% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 4H), 7.59 – 7.53 (m, 2H), 7.49 – 7.43 (m, 4H), 3.14 (t, *J* = 7.0 Hz, 4H), 2.60 (t, *J* = 7.0 Hz, 4H), 2.18 (p, *J* = 7.0 Hz, 4H).
2n, colorless oil, 41% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89-5.79 (m, 2H), 5.14-5.06 (m, 4H), 2.56 (dd, *J* = 1.84 Hz, J2 = 8.52 Hz, 4H), 2.49 (dd, J1 = 6.32 Hz, J2 = 13.48 Hz, 4H).
2o, colorless oil, 53% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.1 Hz, 1H), 7.00 – 6.93 (m, 1H), 6.86 (d, *J* = 3.4 Hz, 1H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.23 – 2.02 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.2, 126.9, 125.0, 123.5, 29.0, 28.8, 26.7.
2p, white solid, 52% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76-1.70 (m, 2H), 1.18-1.14 (m, 4H), 1.08-1.03 (m, 4H).
2q, colorless oil, 47% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 – 3.21 (m, 2H), 2.55 – 2.37 (m, 4H), 2.37 – 2.22 (m, 4H), 2.15 – 1.92 (m, 4H).
2r, colorless oil, 53% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 – 2.80 (m, 2H), 2.06 – 1.87 (m, 8H), 1.84 – 1.70 (m, 4H), 1.69 – 1.56 (m, 4H).

2s, colorless oil, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 – 2.47 (m, 2H), 2.03 – 1.92 (m, 4H), 1.85 – 1.75 (m, 4H), 1.70 – 1.60 (m, 4H), 1.35 – 1.26 (m, 8H).

2t, colorless oil, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 – 2.48 (m, 2H), 1.81 – 1.72 (m, 2H), 1.63 – 1.54 (m, 2H), 1.30 – 1.25 (m, 6H), 1.03 – 0.96 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 110.0, 38.0, 27.0, 27.0, 16.9, 16.9, 11.5.

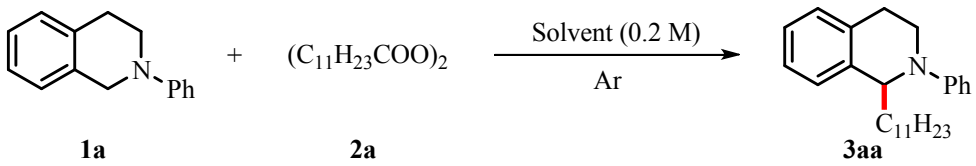
2u, colorless oil, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (m, 2H), 1.76 – 1.58 (m, 4H), 0.99 (t, J = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 45.8, 25.4, 11.7.

3. Investigation of the Key Reaction Parameters.

Table S1. Screening of solvent.[a]

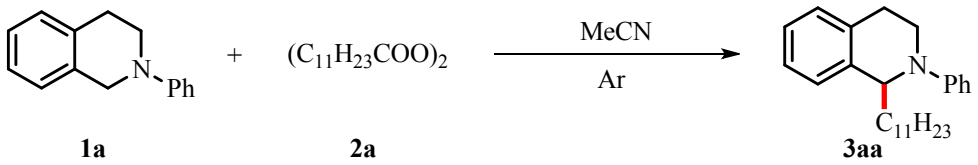


1a **2a** **3aa**

entry	solvent	yield[b] (%)
1	DMF	trace
2	DMSO	trace
3	DMA	trace
4	ether	trace
5	1,4-dioxane	trace
6	acetone	trace
7	DCM	37%
8	EtOH	36%
9	PhMe	trace
10	DCE	67%
11	IPA	trace
12	*n*-BuOH	trace
13	1,2-PG	40%
14	EG	trace
15	MeOH	76%
16	MeCN	84%
17	MeCN with 10 mol % CuI	81%
18	MeCN with air condition	none

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (0.2 mmol) in solvent (1 mL) were stirred in an 8 mL bottle at rt under Ar for 24 h. [b]Isolated yields are given.

Table S2. Screening of concentration.[a]

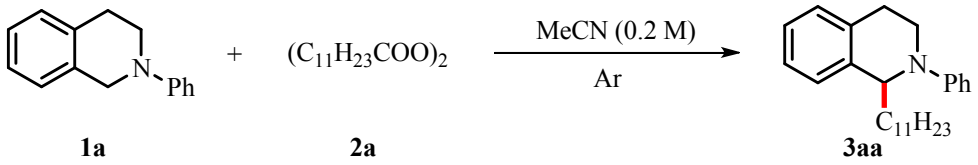


1a **2a** **3aa**

entry	concentration	yield[b] (%)
1	0.05M	47%
2	0.1M	74%
3	0.2M	91%
4	0.4M	90%

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (0.2 mmol) in MeCN were stirred in an 8 mL bottle at rt under Ar for 24 h. [b]Isolated yields are given.

Table S3. Screening of ratio of **1a** to **2a**.[a]



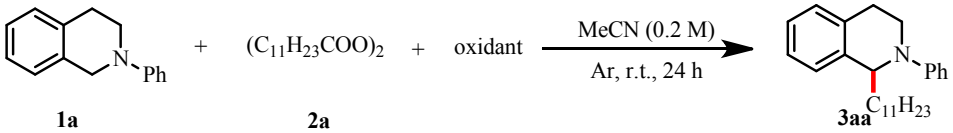
1a **2a** **3aa**

entry	ratio (**1a**:**2a**)	yield[b] (%)
1	1:1	89%
2	1:1.1	92%
3	1:1.5	89%

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** in MeCN (1 ml) were stirred in an 8 mL bottle at rt under Ar for 24 h. [b]Isolated yields are given.

Table S4. Screening of oxidant.[a]

If we ues 0.5 equivalent of diacyl peroxides, we assumed there should be an oxidant in the reaction system. The results are as follows.



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

entry	oxidant	yield
1	*t*-BPA	31%
2	*t*-BHP	none

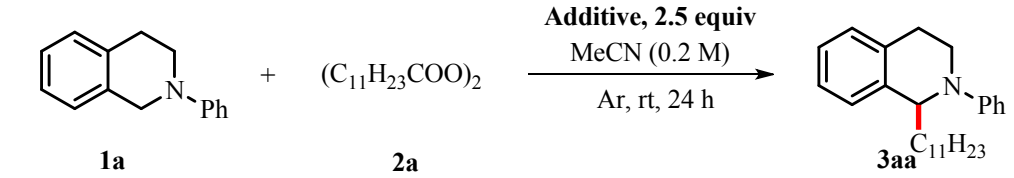
3	*t*-BPB	24%
4	H_2O_2	none
5	$Na_2S_2O_8$	45%
6	$K_2S_2O_8$	57%
7	$(NH_4)_2S_2O_8$	42%
8	DDQ	none
9	$NaClO_2$	none
10	DCP	trace

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol) and oxidant (0.1 mmol) in MeCN (1 mL) were stirred in an 8 mL bottle at rt under Ar for 24 h. Isolated yields are given.

4. Investigation of the mechamism.

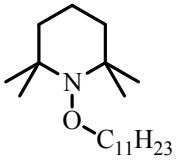
4.1 Radical trapping experiment

Radical trapping

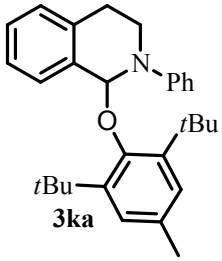


1a **2a** **3aa**

Additive	Yield of 3ab
TEMPO	trace
1,1-Diphenylethylene	trace
BHT	trace



Detected by HRMs
$[M+H]^+$ = 312.3270
Found = 312.3261



3ka

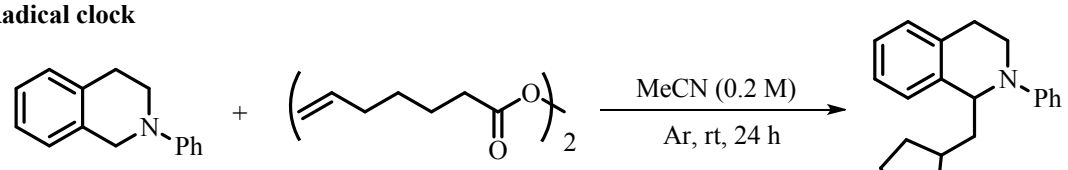
Detected by HRMs
$[M+H]^+$ = 428.2948
Found = 428.2948

Scheme S1

To a 8 mL glass vial was added **1a** (0.2 mmol), **2a** (0.22 mmol), MeCN (1 ml) and additive (TEMPO (0.5 mmol), 1,1-diphenylethylene (0.5 mmol) or BHT (0.5 mmol)). The reaction mixture was degassed by bubbling with argon for 15-20 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred at room temperature for 24 h.

4.2 Radical clock experiment

Radical clock



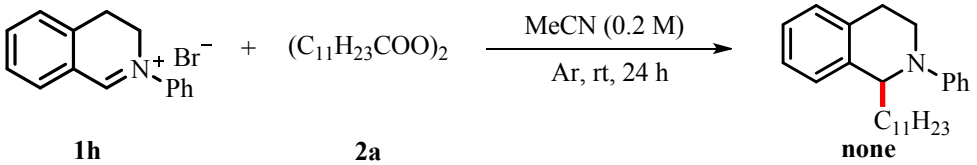
1a **2u** **3au** 45%

Scheme S2

To a 8 mL glass vial was added **1a** (0.2 mmol), **2u** (0.22 mmol) and MeCN (1 ml). The reaction mixture was degassed by bubbling with argon for 15-20 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred at room temperature for 24 h. Isolated yield is given.

4.3 Radical addition exclusion experiment

Radical addition exclusion experiment



1h **2a** **none**

Scheme S3

To a 8 mL glass vial was added **1h** (0.2 mmol)[3], **2a** (0.22 mmol) and MeCN (1 ml). The reaction mixture was degassed by bubbling with argon for 15-20 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred at room temperature for 24 h. No target product was obtained.

5. Experimental Procedures and Product Characterization.

General Procedure for the α–aminoalkylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline:

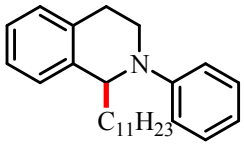
To a 8 mL glass vial was added **1h** (0.2 mmol), **2a** (0.22 mmol) and MeCN (1 ml). The reaction mixtures were degassed by bubbling with argon for 15-20 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the solvent. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product ((Petroleum ether/EtOAc from 4/1 to 100/1).

References

(1) Jiang, J. X.; Li, Y.; Wu, X.; Xiao, J.; Adams, D. J.; Cooper, A. I. *Macromolecules*, **2013**, *46*, 8779.

(2) Li, Y.; Han, Y.; Xiong, H.; Zhu, N.; Qian, B.; Ye, C.; Kantchev, E. A. B.; Bao, H. *Org. Lett.* **2016**, *18*, 392.

2-phenyl-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3aa)



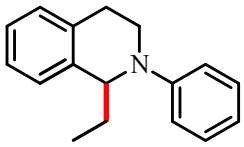
Yield (66 mg, 91%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 2H), 7.17-7.07 (m, 4H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.63 (t, *J* = 7.0 Hz, 1H), 3.66-3.51 (m, 1H), 3.06-2.93 (m, 1H), 2.90-2.77 (m, 1H), 2.01-1.86 (m, 1H), 1.75-1.62 (m, 1H), 1.53-1.35 (m, 2H), 1.35-1.18 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 135.0, 129.2, 128.5, 127.3, 126.4, 125.7, 116.9, 113.7, 59.2, 41.8, 36.8, 32.0, 29.7, 29.7, 29.7, 29.4, 27.1, 26.9, 22.7, 14.2.

HRMS (ESI) calcd for $C_{26}H_{37}N$ $[M + H]^+$ 364.2999, found 364.3006.

1-ethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ab)



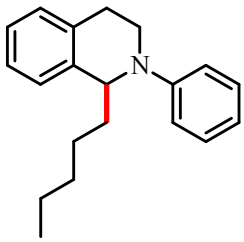
Yield (32 mg, 68%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 7.20 – 7.07 (m, 4H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 4.55 (t, *J* = 7.0 Hz, 1H), 3.68 – 3.49 (m, 2H), 3.10 – 2.96 (m, 1H), 2.91 – 2.79 (m, 1H), 2.05 – 1.89 (m, 1H), 1.82 – 1.67 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 138.9, 135.1, 129.3, 128.5, 127.5, 126.5, 125.7, 116.9, 113.6, 60.7, 42.0, 29.6, 27.3, 11.5.

HRMS (ESI) calcd for $C_{17}H_{19}N$ $[M + H]^+$ 238.1590, found 238.1597.

1-pentyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ac)



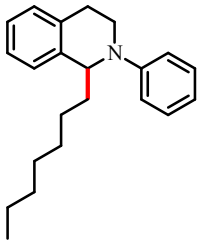
Yield (41 mg, 74%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.7 Hz, 2H), 7.18-7.04 (m, 4H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.63 (d, *J* = 7.0 Hz, 1H), 3.68-3.36 (m, 2H), 3.09-2.92 (m, 1H), 2.91-2.73 (m, 1H), 2.07-1.84 (m, 1H) , 1.77-1.58 (m, 1H) , 1.57-1.34 (m, 2H) , 1.34-1.15 (m, 4H), 0.97-0.76 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 135.0, 129.2, 128.5, 127.3, 126.4, 125.7, 116.9, 113.7, 59.3, 41.8, 36.8, 31.9, 27.1, 26.6, 22.7, 14.1.

HRMS (ESI) calcd for $C_{20}H_{25}N$ $[M + H]^+$ 280.2060, found 280.2064.

(1-octyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ad)



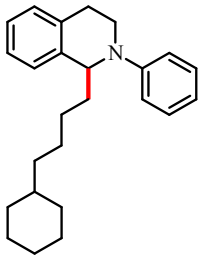
Yield (42 mg, 69%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 2H), 7.17-7.05 (m, 4H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.62 (t, *J* = 7.0 Hz, 1H), 3.68-3.49 (m, 2H), 3.06-2.94 (m, 1H), 2.89-2.77 (m, 1H), 2.01-1.87 (m, 1H), 1.75-1.61 (m, 1H) , 1.54-1.33 (m, 2H) , 1.33-1.14 (m, 8H) , 0.86 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 135.0, 129.3, 128.5, 127.4, 126.4, 125.7, 116.9, 113.7, 59.8, 41.8, 36.9, 31.9, 29.7, 29.4, 27.1, 27.0, 22.7, 14.16.

HRMS (ESI) calcd for $C_{22}H_{29}N$ $[M + H]^+$ 308.2373, found 308.2380.

1-(4-cyclohexylbutyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ae)



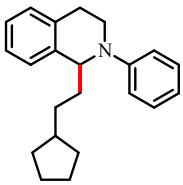
Yield (64 mg, 92%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.19-7.05 (m, 4H), 6.86 (t, *J* = 8.1 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 4.63 (t, *J* = 7.1 Hz, 1H), 3.68-3.51 (m, 2H), 3.10-2.94 (m, 1H), 2.89-2.75 (m, 1H), 2.07-1.85 (m, 1H), 1.82-1.52 (m, 6H) , 1.51-1.05 (m, 10H) , 0.94-0.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 135.0, 129.3, 128.5, 127.4, 126.4, 125.8, 116.9, 113.6, 59.3, 41.8, 37.7, 37.6, 36.9, 33.5, 27.3, 27.1, 27.0, 26.8, 26.5.

HRMS (ESI) calcd for $C_{25}H_{33}N$ $[M + H]^+$ 348.2686, found 348.2698.

1-(2-cyclopentylethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3af)



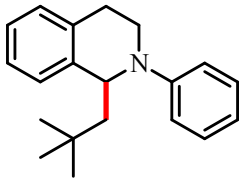
Yield (54 mg, 88%). Colorless oil.

^{1}H NMR (400 MHz, CDCl3) δ 7.22 (t, *J* = 7.8 Hz, 2H), 7.17-7.05 (m, 4H), 6.86 (t, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.61 (t, *J* = 7.1 Hz, 1H), 3.71-3.46 (m, 2H), 3.10-2.92 (m, 1H), 2.89-2.76 (m, 1H), 2.11-1.85 (m, 1H), 1.82-1.65 (m, 4H) , 1.63-1.37 (m, 6H) , 1.18-0.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 134.9, 129.2, 128.5, 127.3, 126.3, 125.7, 116.9, 113.7, 59.5, 41.7, 40.2, 36.1, 33.4, 32.8, 32.7, 27.0, 25.3.

HRMS (ESI) calcd for $C_{22}H_{27}N$ $[M + H]^+$ 306.2216, found 306.2221.

1-neopentyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ag)



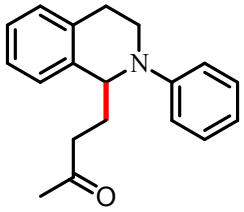
Yield (46 mg, 82%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.16 (m, 2H), 7.16-7.05 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 4.83 (d, *J* = 9.9 Hz, 1H), 3.84-3.73 (m, 1H), 3.73-3.60 (m, 1H), 3.00-2.85 (m, 1H), 2.61-2.47 (m, 1H), 2.10-1.98 (m, 1H), 1.60-1.48 (m, 1H), 1.06-0.95 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 140.3, 135.0, 129.2, 129.1, 127.5, 126.0, 125.8, 117.9, 116.1, 55.5, 50.3, 41.3, 31.3, 30.0, 25.0.

HRMS (ESI) calcd for $C_{20}H_{25}N$ $[M + H]^+$ 280.2060, found 280.2060.

4-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (3ah)



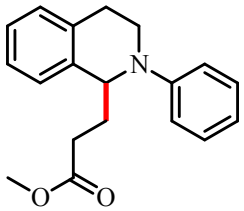
Yield (35 mg, 62%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.08 (m, 4H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 4.82 – 4.70 (m, 1H), 3.75 – 3.51 (m, 2H), 3.10 – 2.94 (m, 1H), 2.85 – 2.71 (m, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.30 – 2.19 (m, 1H), 2.17 – 2.00 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 149.9, 138.4, 134.9, 129.4, 128.8, 127.3, 126.6, 126.0, 117.7, 114.6, 58.0, 41.5, 40.4, 30.4, 30.4, 30.3, 26.4.

HRMS (ESI) calcd for $C_{19}H_{21}NO$ $[M + H]^+$ 280.1696, found 280.1701.

methyl 3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanoate (3ai)



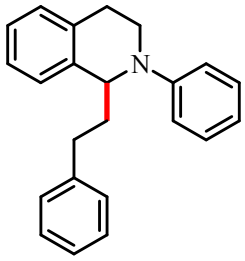
Yield (46 mg, 78%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.1 Hz, 2H), 7.18-7.07 (m, 4H), 6.88 (d, *J* = 9.1 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 4.73 (d, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 3.62-3.56(m, 2H), 3.05-2.92 (m, 1H), 2.82-2.72 (m, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.34-2.22 (m, 1H), 2.14-2.00 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 149.8, 138.1, 135.0, 129.3, 128.8, 127.3, 126.6, 126.0, 117.8, 114.6, 58.2, 51.6, 41.8, 31.5, 31.2, 26.5.

HRMS (ESI) calcd for $C_{19}H_{21}NO_2$ $[M + H]^+$ 296.1645, found 296.1649.

1-phenethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aj)



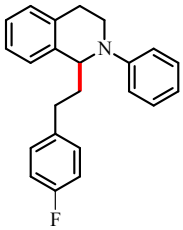
Yield (46 mg, 74%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.07 (m, 10H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 7.1 Hz, 1H), 3.63 (d, *J* = 6.1 Hz, 1H), 3.10-2.91 (m, 1H), 2.87-2.63 (m, 3H), 2.36-2.19 (m, 1H), 2.11-1.96 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 142.0, 138.8, 135.1, 129.3, 128.7, 128.5, 128.5, 128.4, 127.3, 126.5, 125.9, 117.4, 114.2, 58.5, 41.9, 38.4, 33.0, 26.9.

HRMS (ESI) calcd for $C_{23}H_{23}N$ $[M + H]^+$ 314.1903, found 314.1900.

1-(4-fluorophenethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ak)



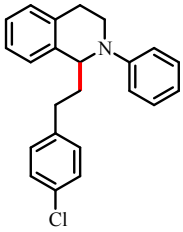
Yield (47 mg, 71%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 2.5 Hz, 2H), 7.25-7.18 (m, 2H), 7.18-7.07 (m, 4H), 6.94 (td, *J* = 8.7, 2.5 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.74 (t, *J* = 6.3 Hz, 1H), 4.66 (t, *J* = 6.0 Hz, 1H), 3.65 (t, *J* = 6.1 Hz, 1H), 3.10-2.91 (m, 1H), 2.87-2.65 (m, 3H), 2.32-2.19 (m, 1H), 2.13-1.96 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.0 Hz), 149.73, 138.73, 137.6 (d, *J* = 3.8 Hz), 135.05, 129.9 (d, *J* = 7.7 Hz), 129.30, 128.78, 127.26, 126.58, 125.92, 117.54, 115.22, 115.00, 114.41, 58.30, 41.91, 38.57, 32.15, 26.78.

HRMS (ESI) calcd for $C_{23}H_{22}FN$ $[M + H]^+$ 332.1809, found 332.1816.

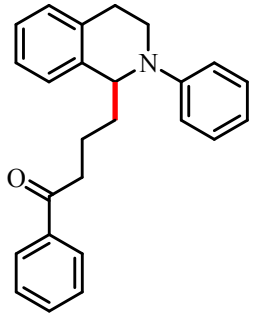
1-(4-chlorophenethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3al)



Yield (46 mg, 67%). Colorless oil.

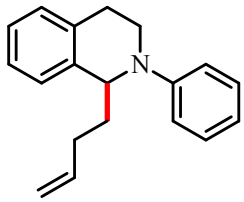
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.05 (m, 10H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.66 (t, *J* = 7.1 Hz, 1H), 3.71-3.57 (m, 2H), 3.10-2.96 (m, 1H), 2.85-2.63 (m, 3H), 2.33-2.19 (m, 1H), 2.12-1.96 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 140.4, 138.6, 135.0, 131.5, 129.9, 129.3, 128.8, 128.5, 127.2, 126.6, 125.9, 117.6, 114.5, 58.3, 41.9, 38.3, 32.3, 26.7.
HRMS (ESI) calcd for $C_{23}H_{22}ClN$ $[M + H]^+$ 348.1514, found 348.1515.

1-phenyl-4-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-1-one (3am)



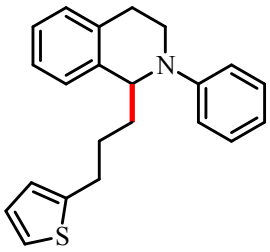
Yield (36 mg, 50%). Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.27-7.18 (m, 2H), 7.18-1.06 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 1H), 3.66-3.55 (m, 2H), 3.05-2.90 (m, 3H), 2.88-2.74 (m, 1H), 2.11-1.72 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 149.7, 138.8, 137.0, 134.9, 133.0, 129.3, 128.6, 128.6, 128.0, 127.3, 126.5, 125.9, 117.3, 114.2, 59.0, 41.9, 38.3, 36.3, 26.9, 21.7.
HRMS (ESI) calcd for $C_{25}H_{25}NO$ $[M + H]^+$ 356.2009, found 356.2016.

1-(but-3-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3an)



Yield (32 mg, 60%). Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.18 (m, 2H), 7.18-7.08 (m, 4H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.93-5.77 (m, 1H), 5.09-5.01 (m, 1H), 5.01-4.95 (m, 1H), 4.68 (d, *J* = 7.0 Hz, 1H), 3.64-3.55 (m, 2H), 3.08-2.94 (m, 1H), 2.88-2.76 (m, 1H), 2.30-2.11 (m, 2H), 2.11-1.98 (m, 1H), 1.87-1.74 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 138.9, 138.3, 135.1, 129.3, 128.6, 127.3, 126.5, 125.8, 117.2, 115.0, 114.0, 58.5, 41.8, 35.8, 30.9, 26.9.
HRMS (ESI) calcd for $C_{19}H_{21}N$ $[M + H]^+$ 264.1747, found 264.1746.

2-phenyl-1-(3-(thiophen-2-yl)propyl)-1,2,3,4-tetrahydroisoquinoline (3ao)



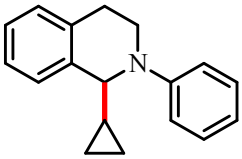
Yield (49 mg, 74%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 7.17-7.11 (m, 2H), 7.11-7.06 (m, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 4.66 (t, *J* = 7.1 Hz, 1H), 3.71-3.55 (m, 2H), 3.10-2.94 (m, 1H), 2.90-2.64 (m, 3H), 2.36-2.13 (m, 1H), 2.11-1.91 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 140.4, 138.6, 135.0, 131.5, 129.8, 129.3, 128.8, 128.5, 127.2, 126.6, 125.9, 117.6, 114.4, 58.3, 41.9, 38.3, 32.3, 26.7.

HRMS (ESI) calcd for $C_{22}H_{23}NS$ $[M + H]^+$ 334.1624, found 334.1626.

1-cyclopropyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ap)



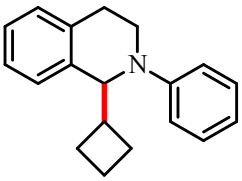
Yield (23 mg, 47%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.19 (m, 2H), 7.19–7.05 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 4.42 (d, *J* = 6.3 Hz, 1H), 3.82–3.70 (m, 1H), 3.66–3.55 (m, 1H), 3.08–2.95 (m, 1H), 2.95–2.80 (m, 1H), 1.39–1.16 (m, 2H), 0.60–0.38 (m, 2H), 0.35–0.17 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 137.4, 135.1, 129.2, 128.5, 127.4, 126.7, 125.6, 117.7, 114.9, 61.9, 42.3, 27.4, 16.5, 3.8, 2.9.

HRMS (ESI) calcd for $C_{18}H_{19}N$ $[M + H]^+$ 250.1590, found 250.1596.

1-cyclobutyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aq)



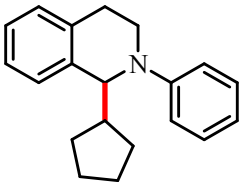
Yield (46 mg, 88%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.23-7.13 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 3.75-3.55 (m, 2H), 3.15-3.00 (m, 1H), 2.95-2.72 (m, 2H), 2.08-1.87 (m, 4H), 1.87-1.68 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 137.6, 134.8, 129.2, 128.7, 127.2, 126.5, 125.6, 117.3, 114.5, 63.3, 42.0, 41.7, 27.5, 27.0, 26.7, 18.1.

HRMS (ESI) calcd for $C_{19}H_{21}N$ $[M + H]^+$ 264.1747, found 264.1749.

1-cyclopentyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ar)



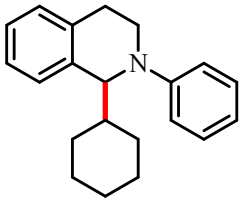
Yield (24 mg, 43%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.03 (m, 6H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 8.7 Hz, 1H), 3.80-3.55 (m, 2H), 3.01-2.94 (m, 1H), 2.95-2.79(m, 1H), 2.42-2.21 (m, 1H), 1.89-1.77 (m, 1H), 1.75-1.57 (m, 3H), 1.54-1.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 138.9, 134.9, 129.1, 128.6, 127.7, 126.5, 125.3, 116.8, 113.8, 62.8, 47.2, 42.0, 31.1, 30.6, 26.7, 25.2, 24.4.

HRMS (ESI) calcd for $C_{20}H_{23}N$ $[M + H]^+$ 278.1903, found 278.1912.

1-cyclohexyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3as)



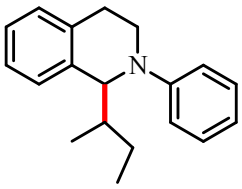
Yield (46 mg, 79%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 2H), 7.17-7.03 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 8.1 Hz, 1H), 3.77-3.66 (m, 1H), 3.51-3.39 (m, 1H), 3.09-2.91 (m, 2H), 1.97 (d, *J* = 10.0 Hz, 1H), 1.86-1.65 (m, 5H), 1.20-0.96 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 137.9, 135.3, 129.1, 128.4, 128.2, 126.6, 125.2, 116.3, 112.9, 63.8, 44.1, 43.0, 30.9, 30.7, 27.4, 26.7, 26.5, 26.4.

HRMS (ESI) calcd for $C_{21}H_{25}N$ $[M + H]^+$ 292.2060, found 292.2060.

1-(sec-butyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3at)



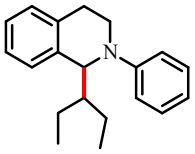
Yield (33 mg, 62%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 2H), 7.17-7.04 (m, 4H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 4.45 (t, *J* = 9.0 Hz, 1H), 3.78-3.64 (m, 1H), 3.53-3.37 (m, 1H), 3.09-2.86 (m, 2H), 1.94-1.80 (m, 1H), 1.80-1.50 (m, 1H), 1.23-1.07 (m, 1H) , 1.06-0.90 (m, 3H) , 0.90-0.82 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 150.1, 138.3, 138.0, 135.4, 129.1, 128.3, 128.2, 128.2, 126.6, 125.3, 125.3, 116.5, 116.5, 113.2, 113.2, 63.8, 63.3, 43.3, 43.2, 41.3, 41.2, 27.5, 26.7, 26.3, 16.5, 16.4, 12.2, 11.8.

HRMS (ESI) calcd for $C_{19}H_{23}N$ $[M + H]^+$ 266.1903, found 266.1909.

1-(pentan-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3au)



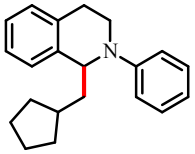
Yield (42 mg, 77%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.16 (m, 1H), 7.16-7.07 (m, 4H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 4.60 (d, *J* = 8.9 Hz, 1H), 3.75-3.65 (m, 2H), 3.56-3.47 (m, 1H), 2.97 (t, *J* = 6.6 Hz, 2H), 1.78-1.68 (m, 1H), 1.65-1.53 (m, 1H) , 1.53-1.40 (m, 2H) , 1.38-1.23 (m, 1H) , 0.92-0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 138.6, 135.3, 129.1, 128.4, 128.0, 126.5, 125.3, 116.6, 113.6, 60.3, 46.2, 43.1, 26.9, 21.9, 21.9, 11.4, 10.5.

HRMS (ESI) calcd for $C_{20}H_{25}N$ $[M + H]^+$ 280.2060, found 280.2064.

1-(cyclopentylmethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3av)



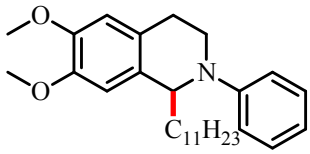
Yield (26 mg, 45%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.22 – 7.09 (m, 4H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 4.76 (t, *J* = 7.3 Hz, 1H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.15 – 2.97 (m, 1H), 2.93 – 2.79 (m, 1H), 2.15 – 1.87 (m, 3H), 1.88 – 1.61 (m, 4H), 1.59 – 1.49 (m, 2H), 1.36 – 1.15 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.3, 134.9, 129.3, 128.6, 127.3, 126.4, 125.7, 116.9, 113.8, 58.2, 43.0, 41.5, 37.1, 33.2, 32.8, 26.7, 25.4, 25.0.

HRMS (ESI) calcd for $C_{21}H_{25}N$ $[M + H]^+$ 292.2060, found 292.2062.

6,7-dimethoxy-2-phenyl-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ba)



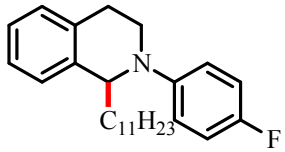
Yield (74 mg, 88%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 2H), 4.56 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.68-3.52 (m, 2H), 3.00-2.85 (m, 1H), 2.74-2.64 (m, 1H), 2.00-1.85 (m, 1H), 1.77-1.55 (m, 2H), 1.55-1.37 (m, 1H), 1.37-1.25 (m, 15H), 0.88-0.85 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 131.3, 129.2, 126.9, 117.1, 114.2, 111.5, 110.6, 58.9, 41.6, 36.9, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 27.0, 26.3, 24.7, 22.7, 14.2.

HRMS (ESI) calcd for $C_{28}H_{41}NO_2$ $[M + H]^+$ 424.3210, found 424.3221.

2-(4-fluorophenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ca)



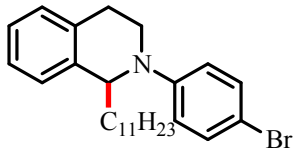
Yield (68 mg, 90%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.05 (m, 4H), 6.96-6.87 (m, 2H), 6.83-6.75 (m, 2H), 4.50 (t, *J* = 7.0 Hz, 1H), 3.66-3.45 (m, 2H), 3.02-2.88 (m, 1H), 2.83-2.72 (m, 1H), 2.01-1.80 (m, 1H), 1.75-1.60 (m, 1H), 1.55-1.34 (m, 2H), 1.34-1.18 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ155.75 (d, *J* = 236.2 Hz), 146.66, 139.10, 134.74, 128.64, 127.30, 126.36, 125.77, 115.83, 115.75, 115.62, 115.39, 59.79, 42.52, 36.82, 31.94, 29.68, 29.64, 29.37, 26.92, 26.70, 22.72, 14.14.

HRMS (ESI) calcd for $C_{26}H_{36}FN$ $[M + H]^+$ 382.2905, found 382.2911.

2-(4-bromophenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3da)



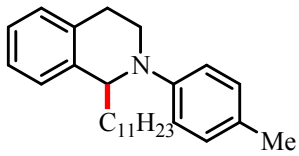
Yield (80 mg, 91%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.19-7.05 (m, 4H), 6.75-6.68 (m, 2H), 4.56 (t, *J* = 7.0 Hz, 1H), 3.66-3.45 (m, 2H), 3.06-2.93 (m, 1H), 2.91-2.80 (m, 1H), 1.98-1.84 (m, 1H), 1.73-1.60 (m, 1H), 1.50-1.34 (m, 2H), 1.34-1.18 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.61, 138.77, 134.68, 131.86, 128.48, 127.28, 126.54, 125.84, 115.16, 108.60, 59.24, 41.99, 36.66, 31.93, 29.65, 29.62, 29.35, 27.02, 26.83, 22.70, 14.14.

HRMS (ESI) calcd for $C_{26}H_{36}BrN$ $[M + H]^+$ 442.2104, found 442.2090.

2-(*p*-tolyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ea)



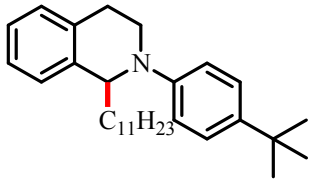
Yield (67 mg, 89%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.06 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.57 (t, *J* = 7.0 Hz, 1H), 3.63-3.52 (m, 2H), 3.05-2.93 (m, 1H), 2.84-2.73 (m, 1H), 2.23 (s, 3H), 1.96-1.85 (m, 1H), 1.73-1.62 (m, 1H), 1.47-1.25 (m, 2H), 1.33-1.15(m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 139.4, 135.0, 129.7, 128.6, 127.3, 126.4, 126.2, 125.6, 114.4, 59.4, 42.0, 36.8, 32.0, 29.7, 29.7, 29.7, 29.4, 26.9, 26.8, 22.7, 20.3, 14.2.

HRMS (ESI) calcd for $C_{27}H_{39}N$ $[M + H]^+$ 378.3155, found 378.3169.

2-(4-(tert-butyl)phenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3fa)



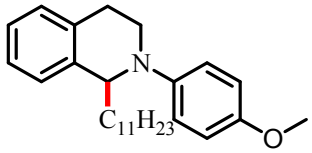
Yield (77 mg, 92%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.24 – 7.11 (m, 4H), 6.93 – 6.84 (m, 2H), 4.67 (t, *J* = 7.0 Hz, 1H), 3.74 – 3.57 (m, 2H), 3.14 – 3.02 (m, 1H), 2.93 – 2.81 (m, 1H), 2.08 – 1.94 (m, 1H), 1.82 – 1.68 (m, 1H), 1.63 – 1.41 (m, 2H), 1.40 – 1.28 (m, 25H), 0.95 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 139.5, 139.4, 135.1, 128.5, 127.3, 126.3, 126.0, 125.7, 113.4, 59.5, 41.8, 37.0, 33.8, 32.0, 31.6, 29.8, 29.7, 29.7, 29.7, 29.4, 27.0, 27.0, 22.8, 14.2.

HRMS (ESI) calcd for $C_{30}H_{45}N$ $[M + H]^+$ 420.3625, found 420.3625.

2-(4-methoxyphenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ga)



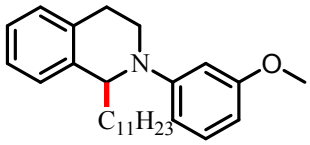
Yield (71 mg, 92%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 4H), 6.95 – 6.81 (m, 4H), 4.53 (t, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 3.67 – 3.52 (m, 2H), 3.07 – 2.94 (m, 1H), 2.84 – 2.72 (m, 1H), 2.02 – 1.87 (m, 1H), 1.79 – 1.67 (m, 1H), 1.58 – 1.41 (m, 2H), 1.40 – 1.24 (m, 16H), 0.93 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 144.8, 139.5, 134.9, 128.7, 127.3, 126.2, 125.7, 117.0, 114.7, 59.9, 55.7, 36.8, 32.0, 29.8, 29.7, 29.7, 29.4, 27.0, 26.6, 22.8, 14.2.

HRMS (ESI) calcd for $C_{27}H_{39}NO$ $[M + H]^+$ 94.3104, found 394.3104.

2-(3-methoxyphenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ha)



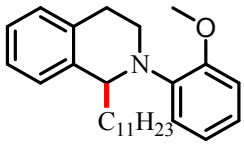
Yield (68 mg, 88%). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 5H), 6.48 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.40 (t, *J* = 2.4 Hz, 1H), 6.28 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.61 (t, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 3.65 – 3.49 (m, 2H), 3.08 – 2.95 (m, 1H), 2.91 – 2.77 (m, 1H), 2.04 – 1.87 (m, 1H), 1.77 – 1.58 (m, 1H), 1.53 – 1.35 (m, 2H), 1.34 – 1.19 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 151.0, 139.1, 135.0, 129.9, 128.5, 127.3, 126.4, 125.7, 106.6, 101.4, 100.1, 59.4, 55.1, 41.9, 36.8, 31.9, 29.7, 29.7, 29.7, 29.7, 29.6, 29.4, 27.2, 26.9, 22.7, 14.2.

HRMS (ESI) calcd for $C_{27}H_{39}NO$ $[M + H]^+$ 94.3104, found 394.3107.

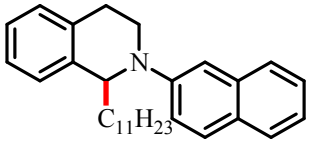
2-(2-methoxyphenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ia)



Yield (70 mg, 91%). Colorless oil.

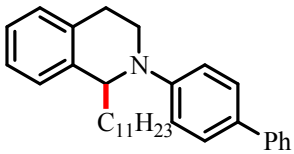
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.03 (m, 4H), 6.97 – 6.90 (m, 1H), 6.89 – 6.75 (m, 3H), 4.46 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.86 (s, 3H), 3.63 – 3.47 (m, 2H), 2.92 – 2.77 (m, 1H), 2.68 – 2.56 (m, 1H), 1.90 – 1.78 (m, 1H), 1.72 – 1.58 (m, 1H), 1.49 – 1.33 (m, 2H), 1.29 – 1.15 (m, 16H), 0.87 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 141.0, 140.1, 134.8, 129.0, 127.1, 125.9, 125.5, 122.3, 121.6, 120.9, 112.2, 59.5, 55.7, 42.3, 36.4, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 27.1, 26.8, 22.7, 14.2.
HRMS (ESI) calcd for $C_{27}H_{39}NO$ $[M + H]^+$ 94.3104, found 394.3107.

2-(4-fluorophenyl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ja)



Yield (45 mg, 55%). Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.23-7.09 (m, 5H), 7.05 (d, *J* = 2.5 Hz, 1H), 4.79 (t, *J* = 7.0 Hz, 1H), 3.83-3.60 (m, 2H), 3.14-2.99 (m, 1H), 2.94-2.75 (m, 1H), 2.06-1.91 (m, 1H), 1.81-1.67 (m, 1H), 1.55-1.36 (m, 2H), 1.31-1.20 (m, 16H), 0.87 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.63, 139.15, 135.03, 134.81, 128.81, 128.61, 127.34, 127.15, 126.40, 126.22, 126.13, 125.77, 122.19, 117.57, 107.91, 59.21, 41.95, 36.84, 31.93, 29.70, 29.66, 29.62, 29.35, 27.07, 26.95, 22.70, 14.14.
HRMS (ESI) calcd for $C_{30}H_{39}N$ $[M + H]^+$ 414.3155, found 414.3154.

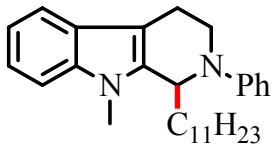
2-([1,1'-biphenyl]-4-yl)-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3ka)



Yield (60 mg, 67%). Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 3H), 7.24 (d, *J* = 4.7 Hz, 1H), 7.19 – 7.07 (m, 4H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.68 (t, *J* = 7.0 Hz, 1H), 3.71 – 3.55 (m, 2H), 3.10 – 2.98 (m, 1H), 2.94 – 2.82 (m, 1H), 2.05 – 1.89 (m, 1H), 1.78 – 1.65 (m, 1H), 1.52 – 1.37 (m, 1H), 1.35 – 1.19 (m, 17H), 0.87 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.2, 139.1, 134.9, 129.5, 128.7, 128.5, 127.9, 127.4, 126.5, 126.3, 126.0, 125.8, 113.6, 59.3, 41.9, 36.8, 32.0, 29.7, 29.7, 29.7, 29.4, 27.2, 26.9, 22.7, 14.2.

HRMS (ESI) calcd for $C_{32}H_{34}N$ $[M + H]^+$ 440.3312, found 440.3302.

9-methyl-2-phenyl-1-undecyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3na)



Yield (52 mg, 63%). Colorless oil.

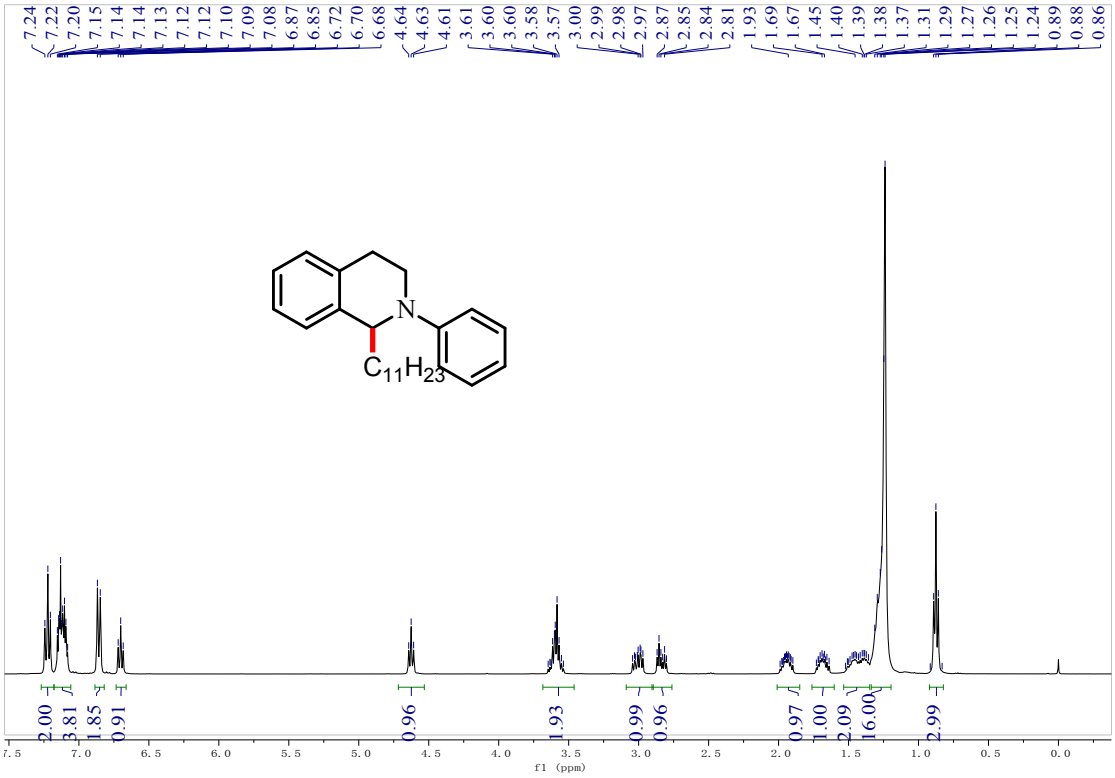
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 1H), 6.22-7.13 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 8.1 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 3.99-3.85 (m, 1H), 3.72-3.55 (m, 4H), 3.04-2.92 (m, 1H), 2.68-2.52 (m, 1H), 2.05-1.87 (m, 1H), 1.85-1.72 (m, 1H), 1.72-1.60 (m, 1H), 1.60-1.47 (m, 1H), 1.35-1.18(m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H),

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 137.3, 137.1, 129.2, 126.9, 121.1, 119.0, 118.4, 118.0, 116.3, 108.7, 107.6, 55.2, 42.0, 34.6, 32.0, 29.8, 29.7, 29.4, 27.1, 22.7, 19.1, 14.2.

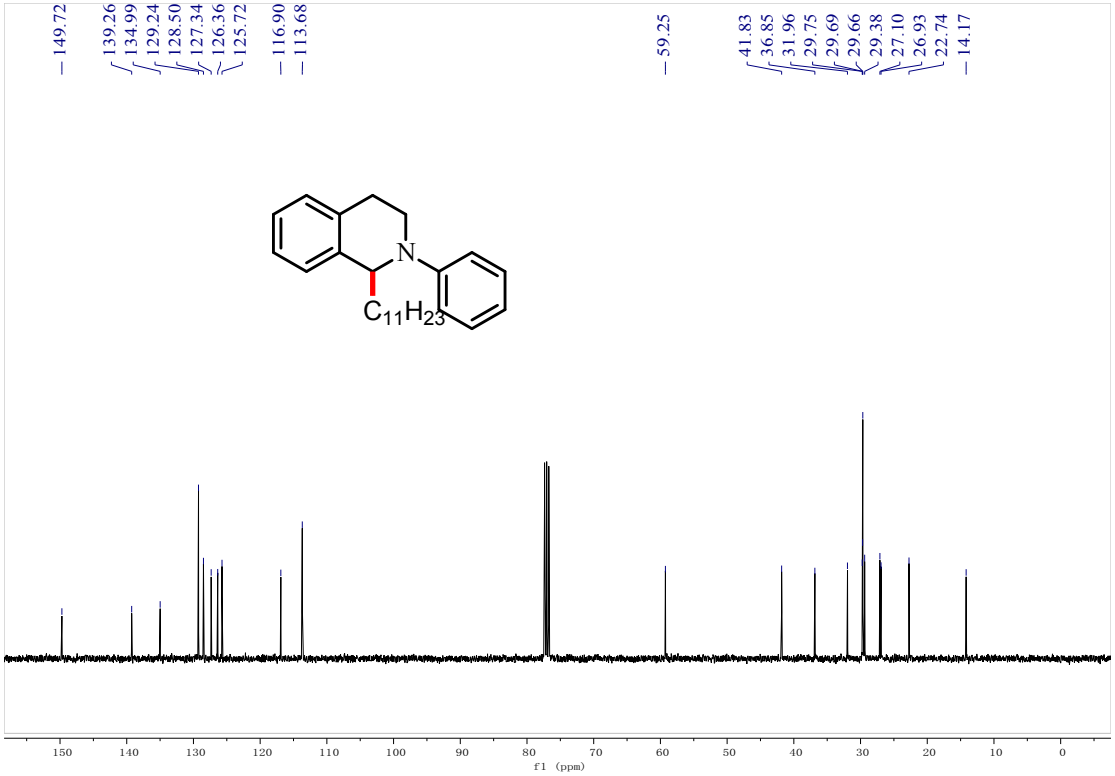
HRMS (ESI) calcd for $C_{29}H_{40}N_2$ $[M + H]^+$ 417.3264, found 417.3266.

NMR Spectra

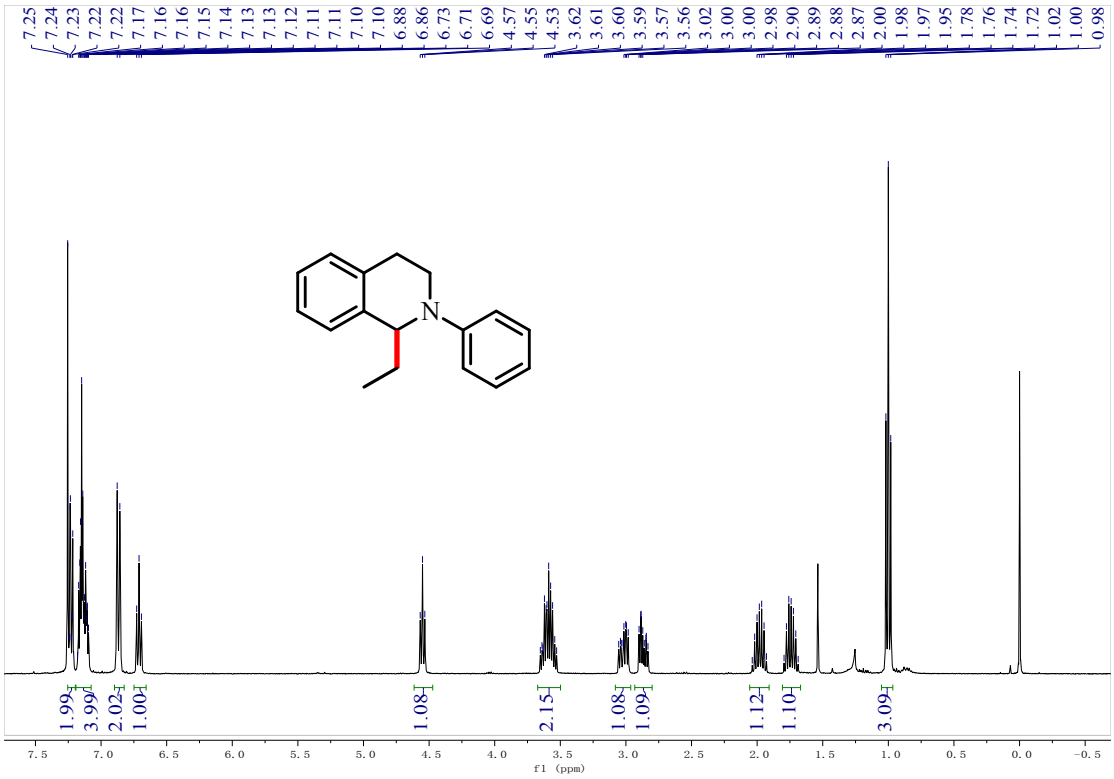
^{1}H NMR spectrum of compound **3aa**



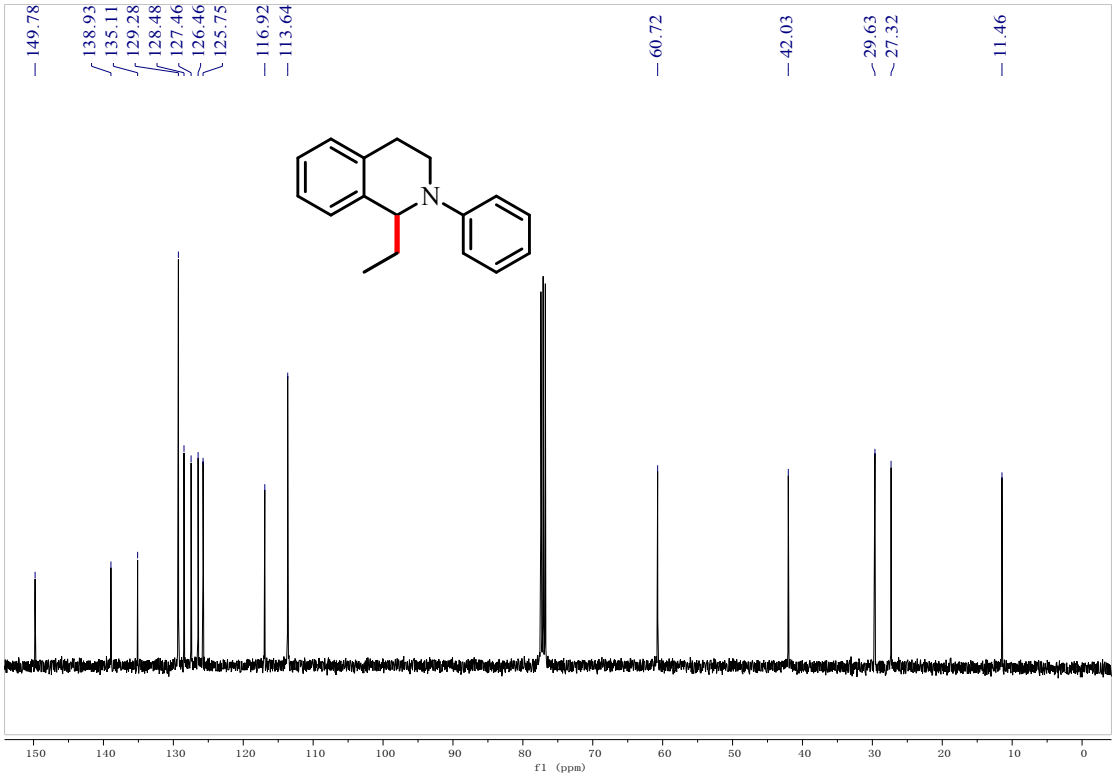
^{13}C NMR spectrum of compound **3aa**



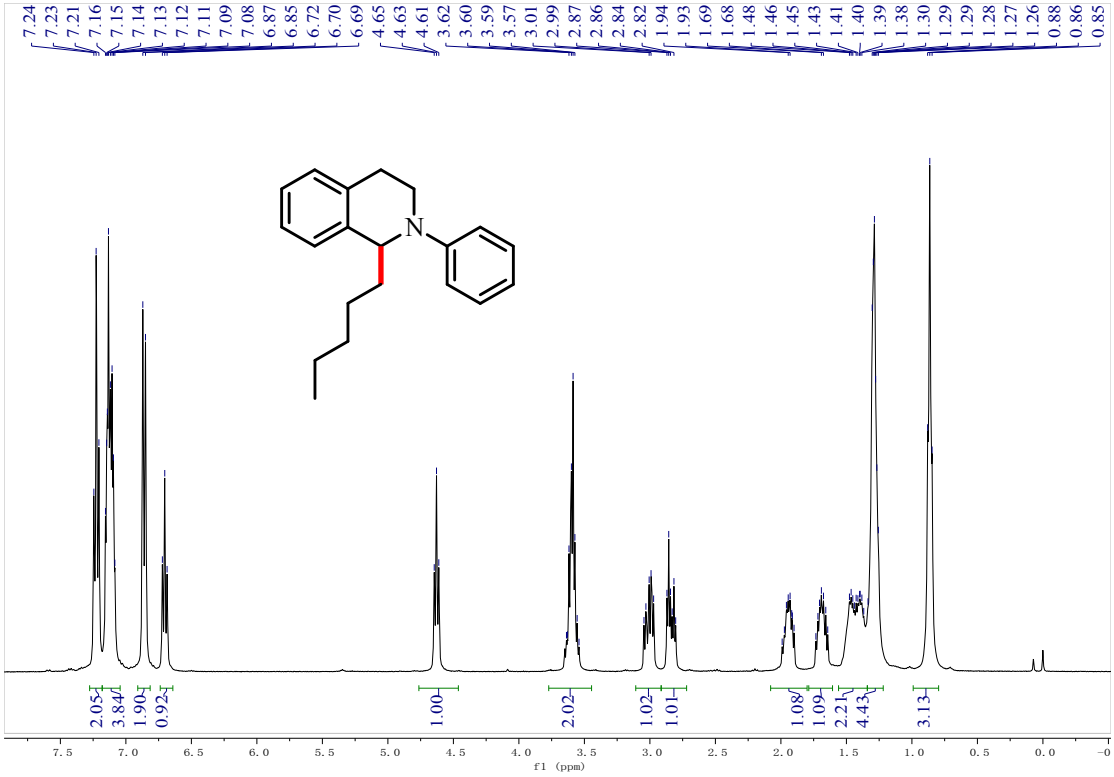
^{1}H NMR spectrum of compound **3ab**



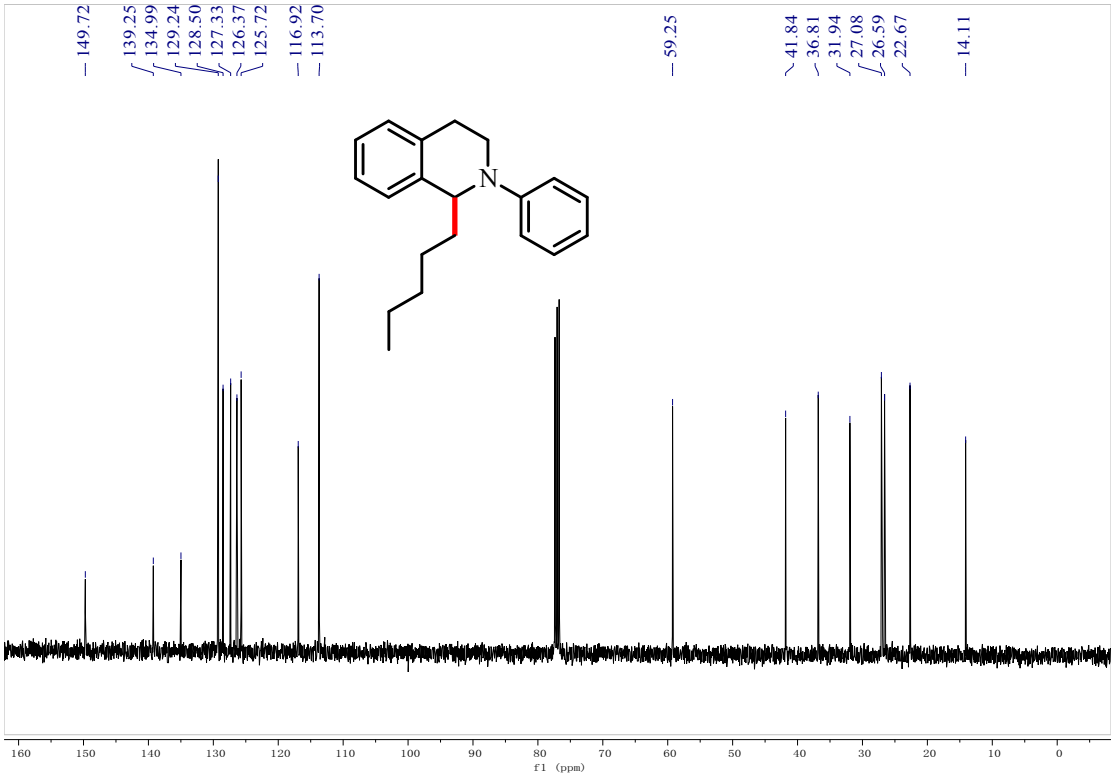
^{13}C NMR spectrum of compound **3ab**



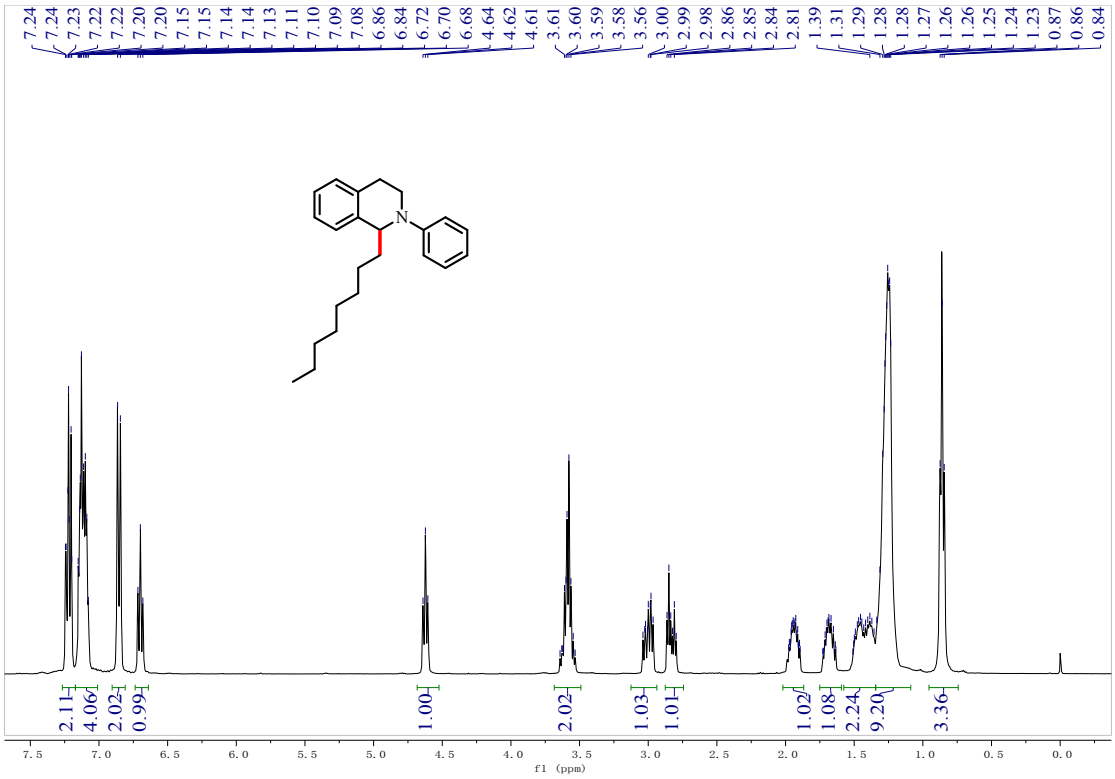
^{1}H NMR spectrum of compound **3ac**



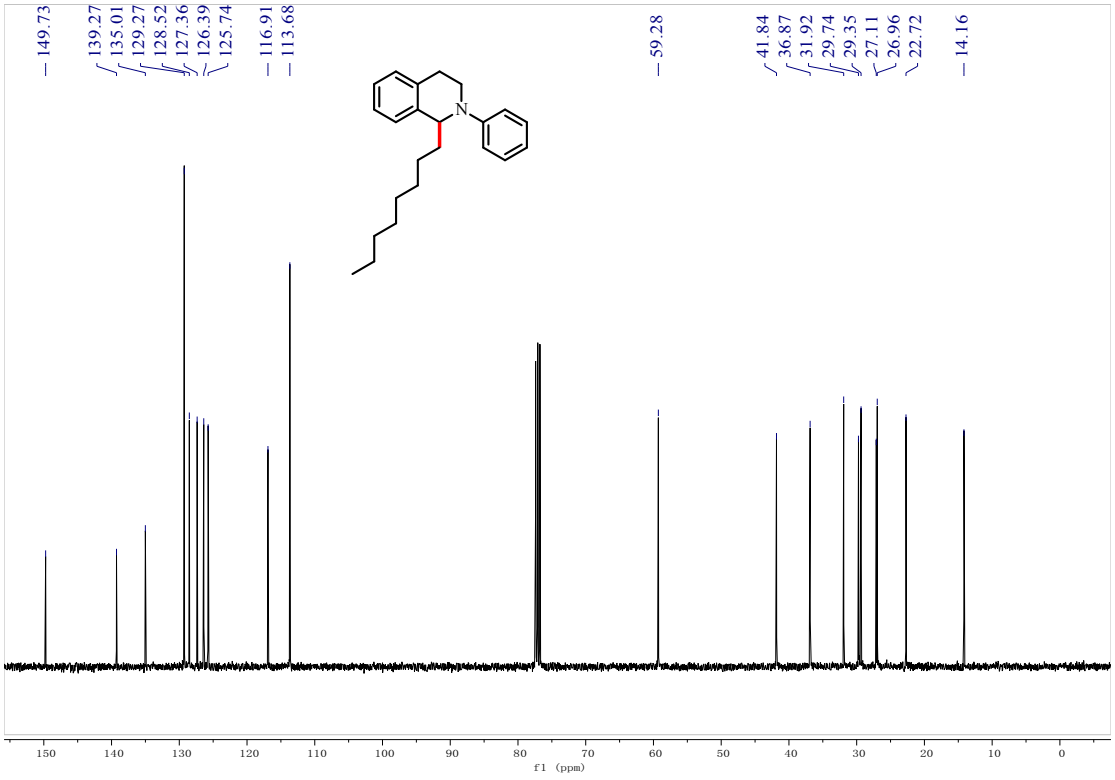
^{13}C NMR spectrum of compound **3ac**



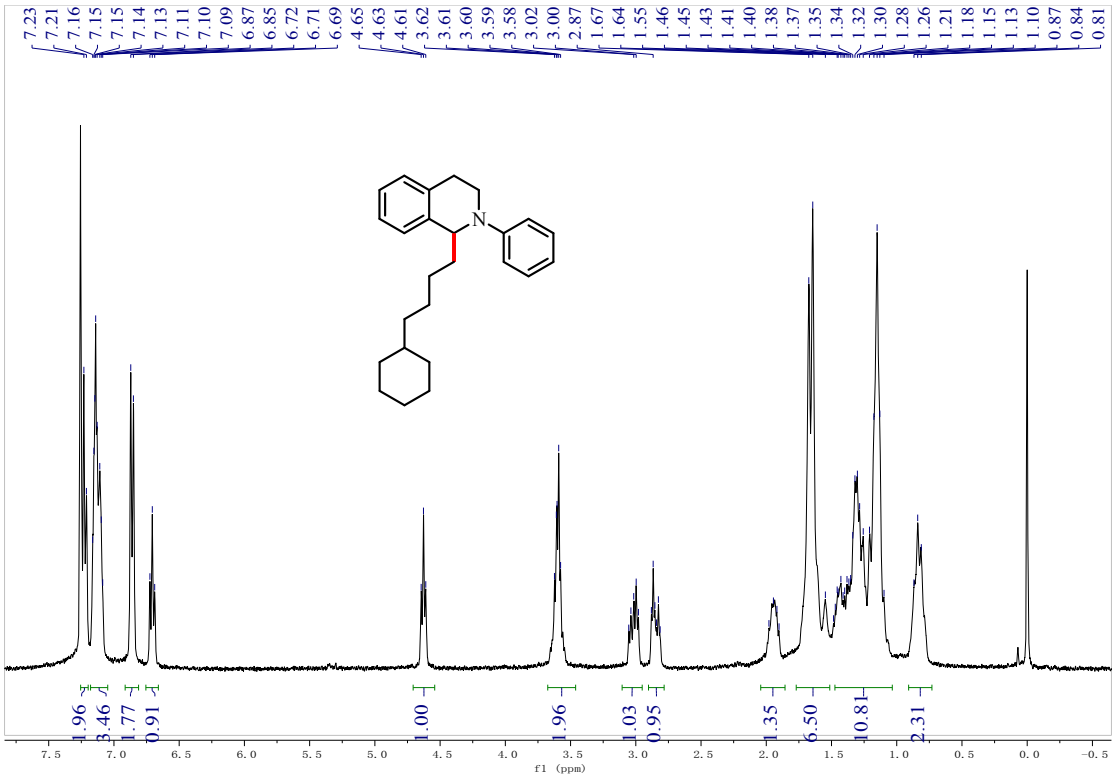
^{1}H NMR spectrum of compound **3ad**



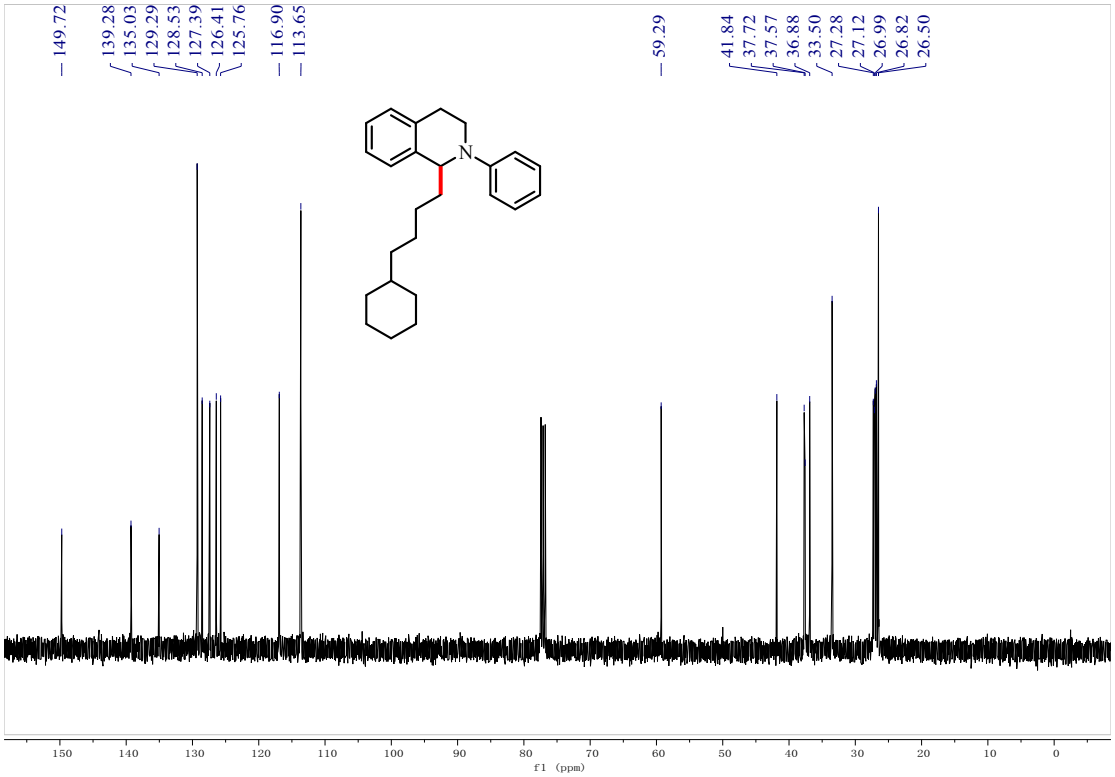
^{13}C NMR spectrum of compound **3ad**



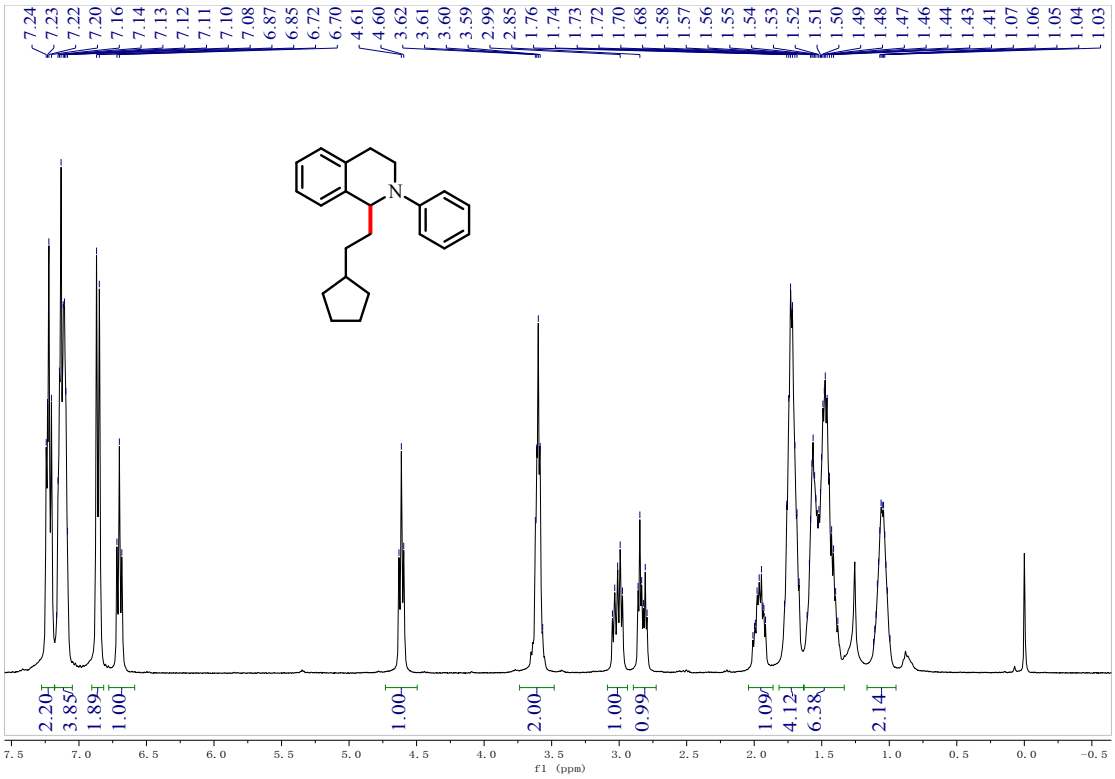
^{1}H NMR spectrum of compound **3ae**



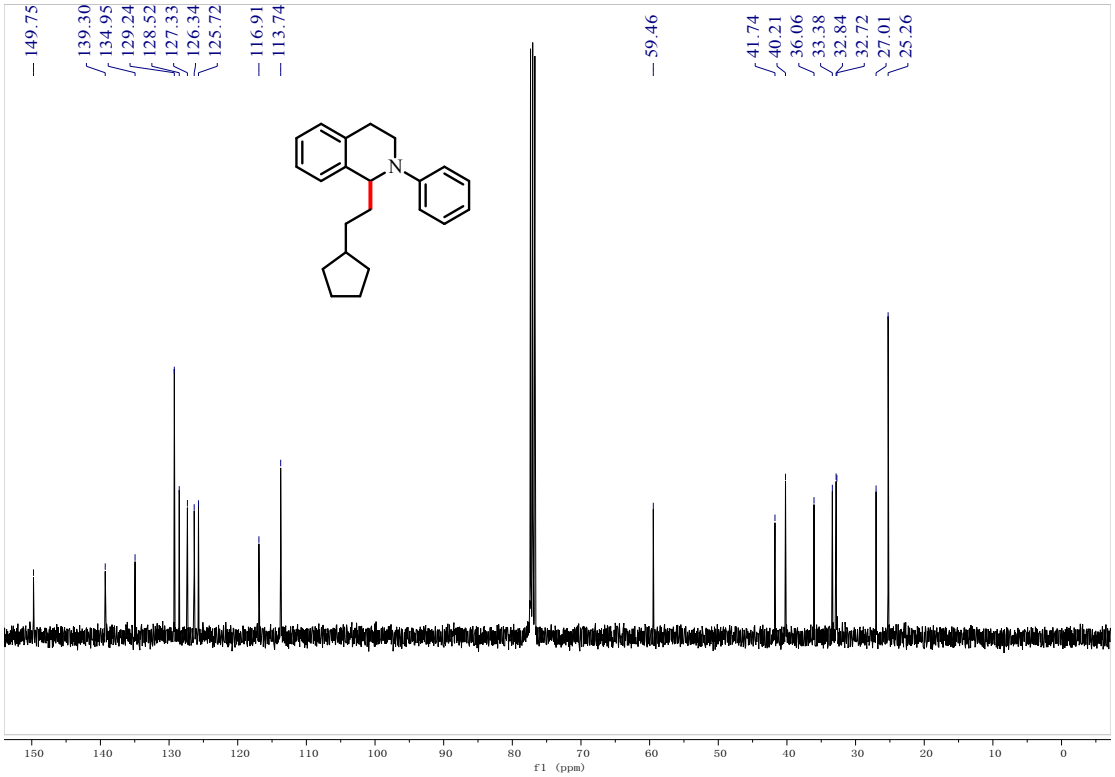
^{13}C NMR spectrum of compound **3ae**



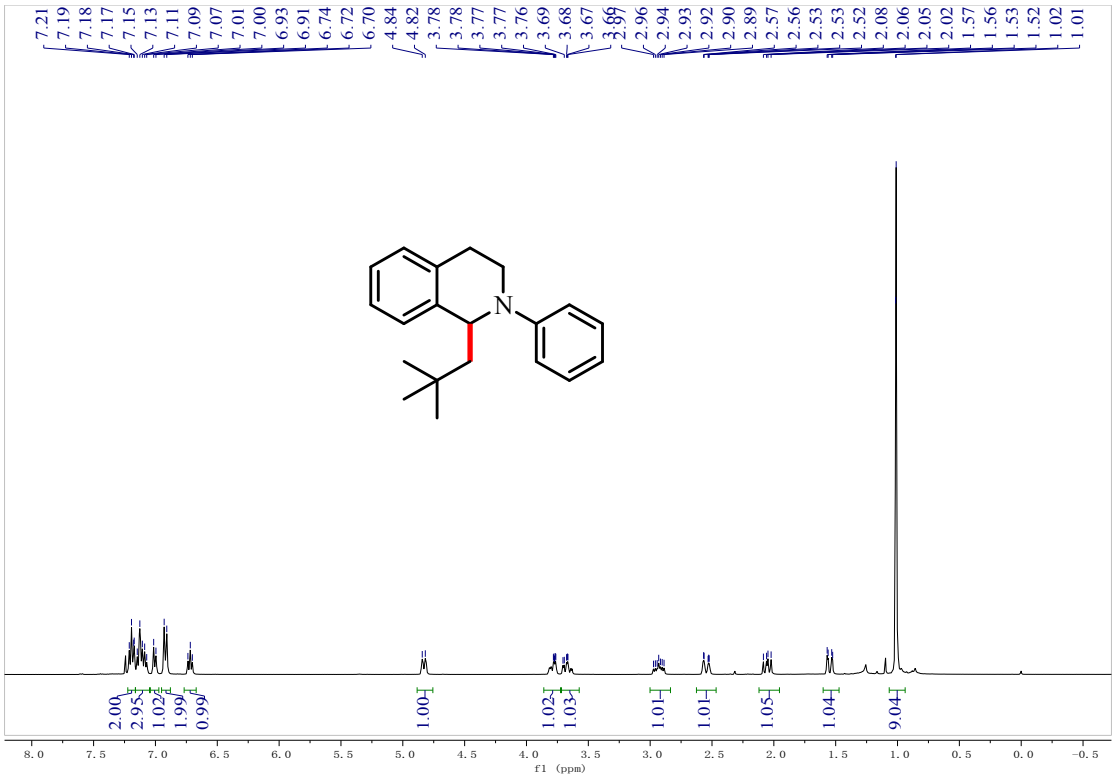
^{1}H NMR spectrum of compound **3af**



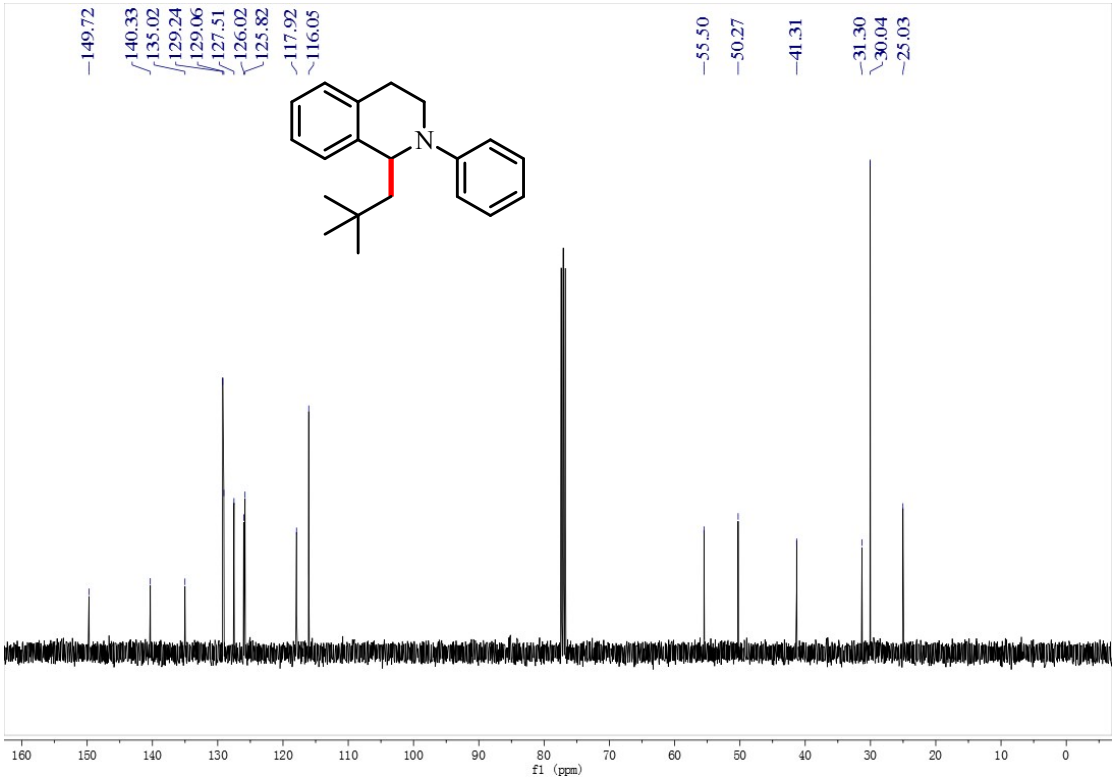
^{13}C NMR spectrum of compound **3af**



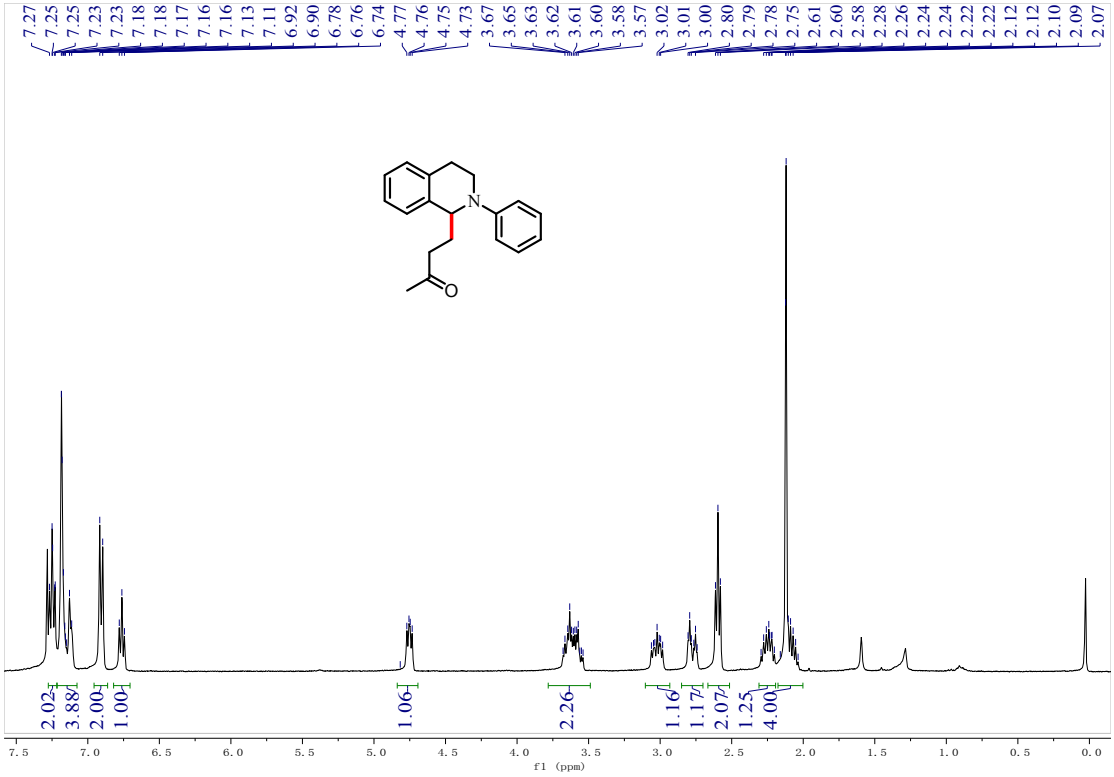
^{1}H NMR spectrum of compound **3ag**



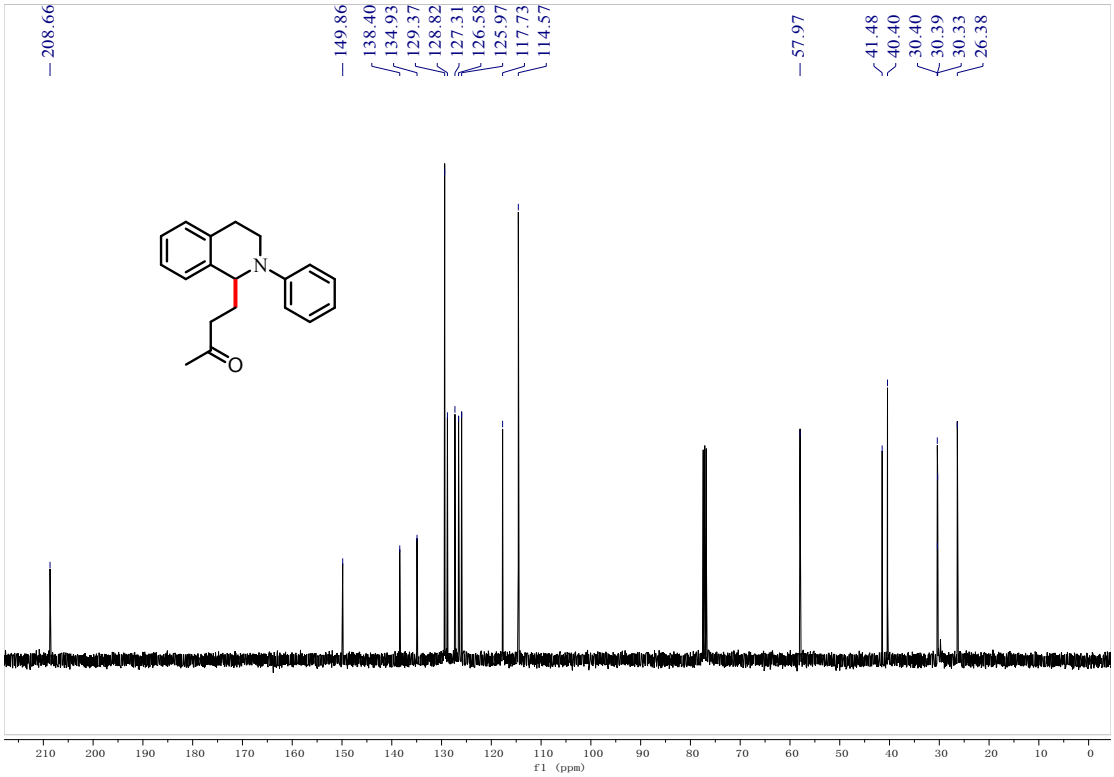
^{13}C NMR spectrum of compound **3ag**



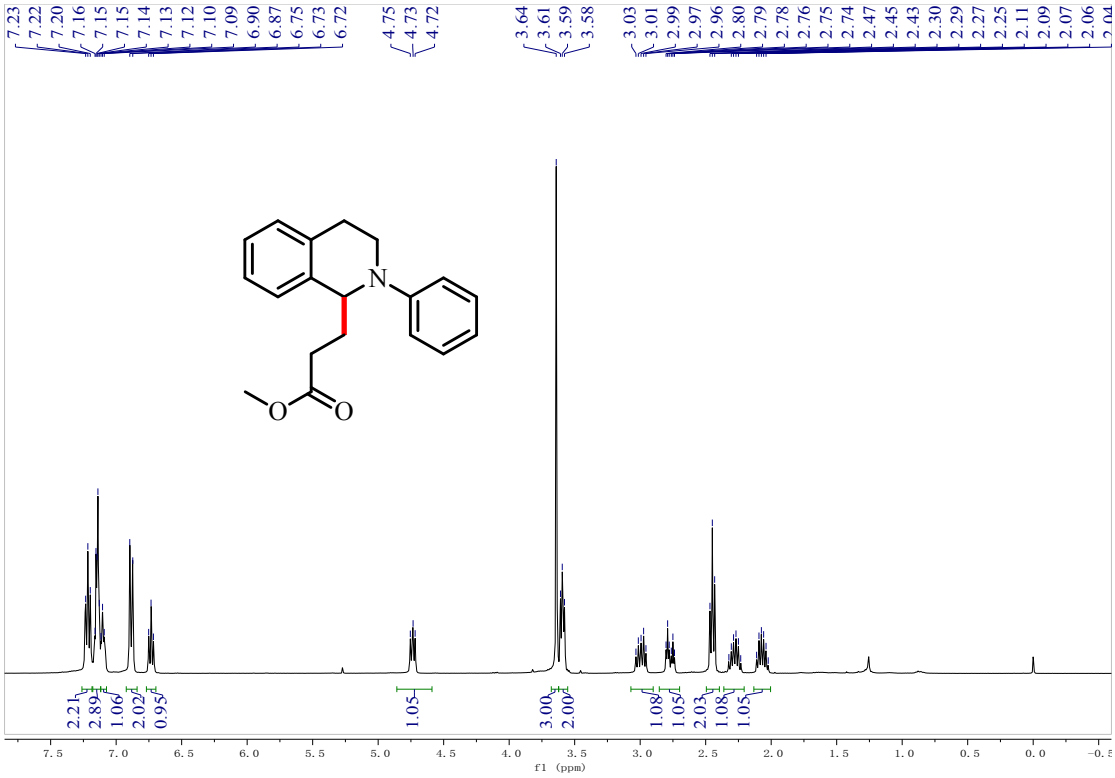
^{1}H NMR spectrum of compound **3ah**



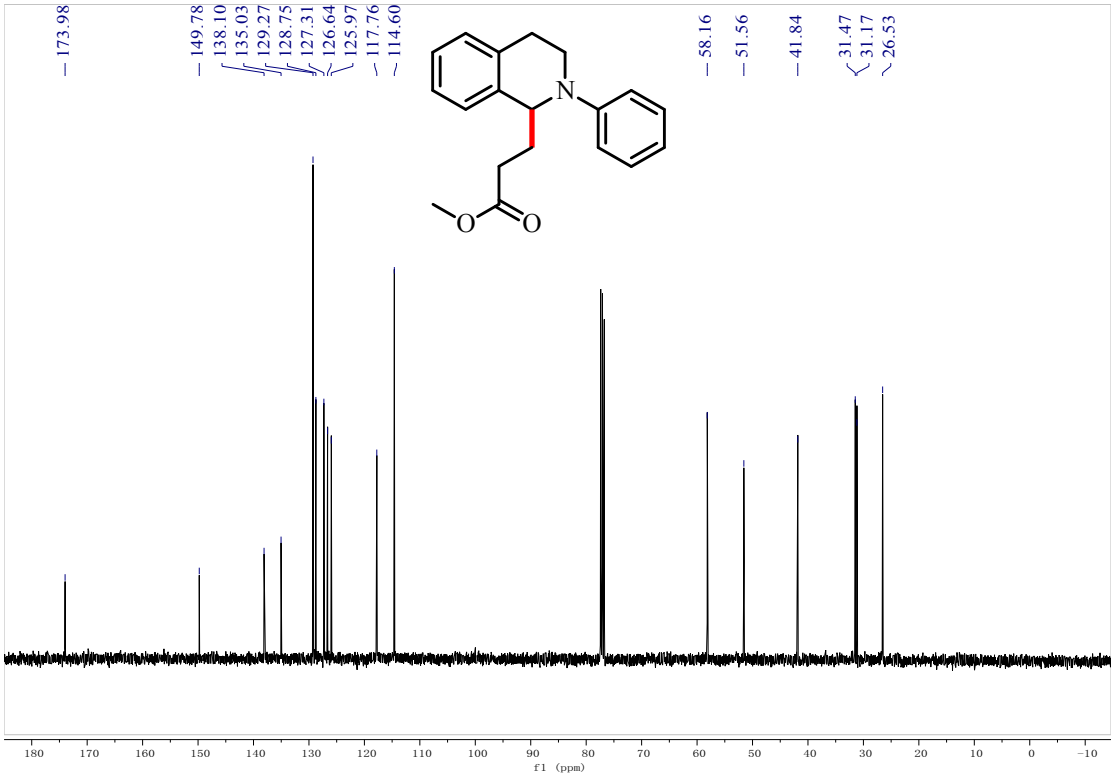
^{13}C NMR spectrum of compound **3ah**



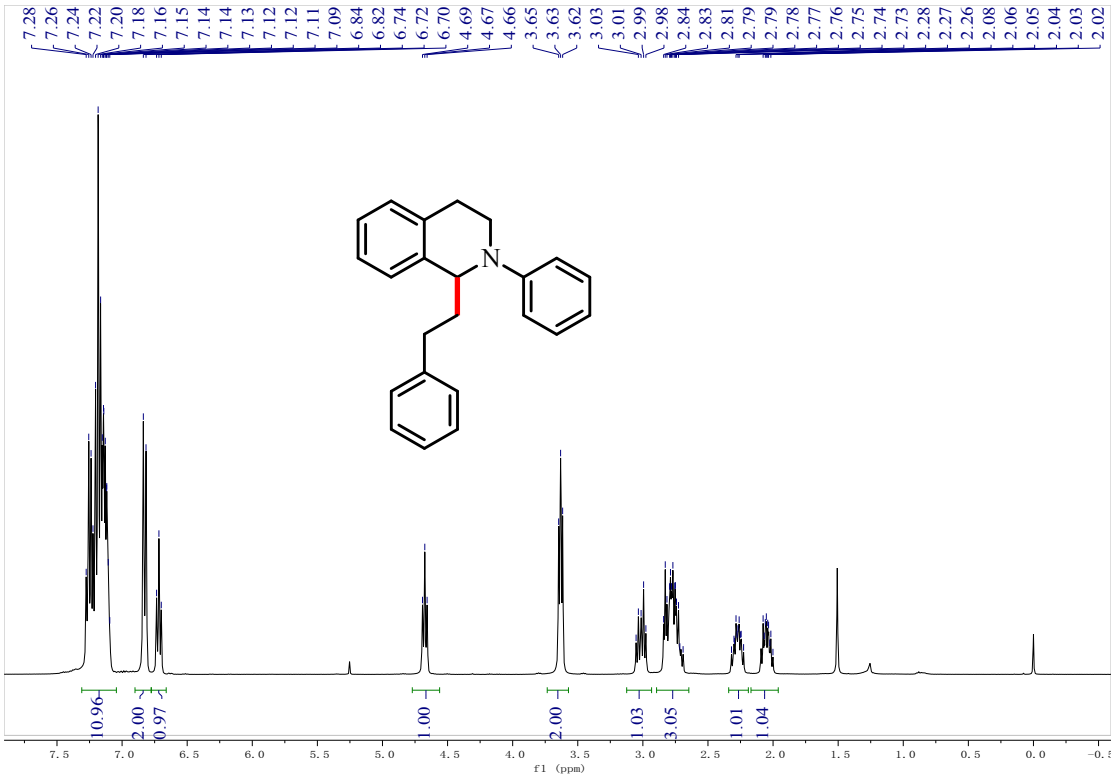
^{1}H NMR spectrum of compound **3ai**



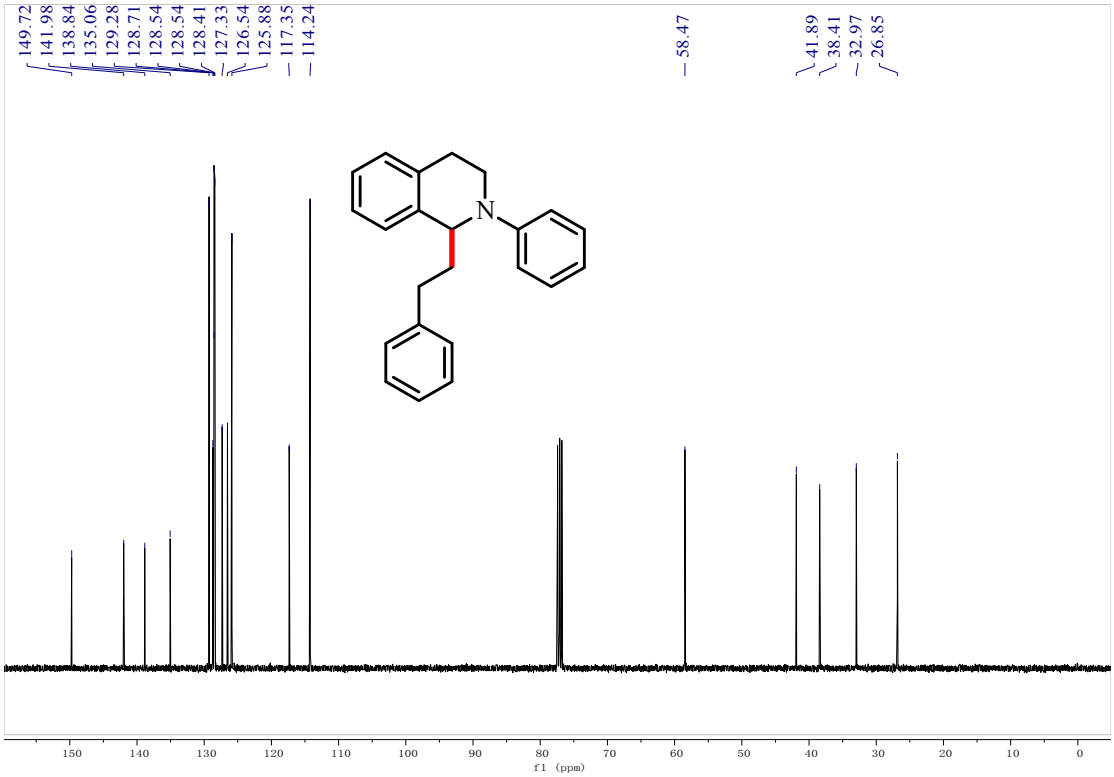
^{13}C NMR spectrum of compound **3ai**



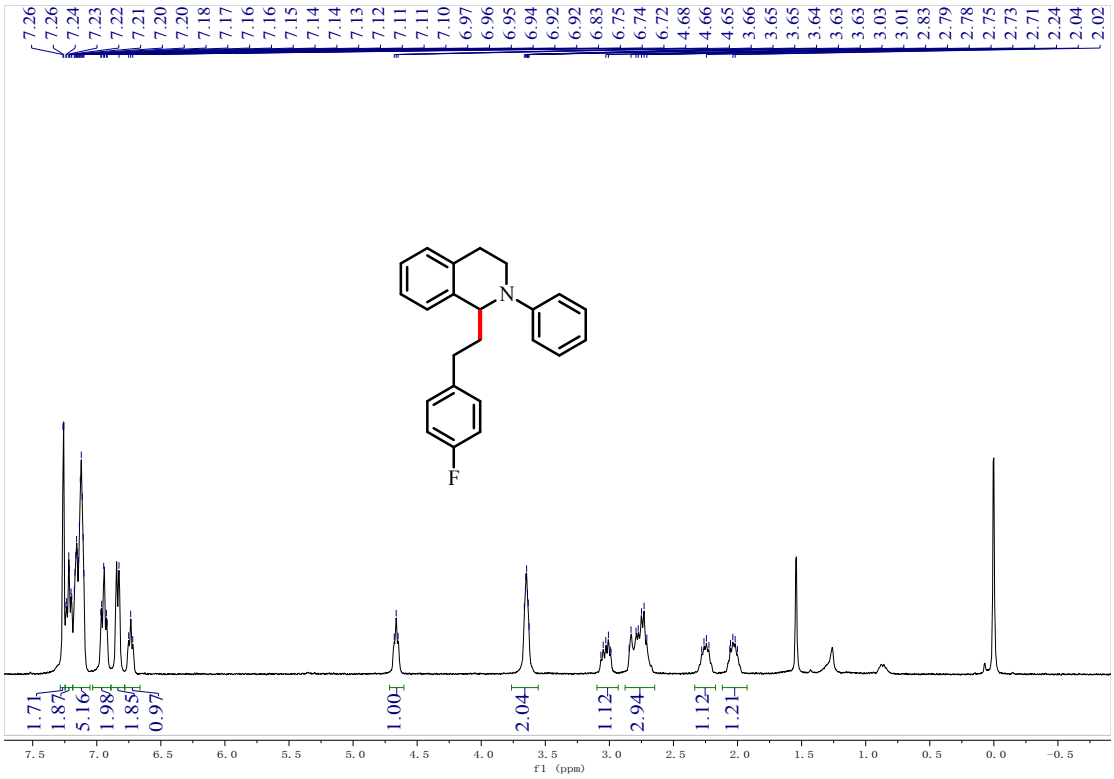
^{1}H NMR spectrum of compound **3aj**



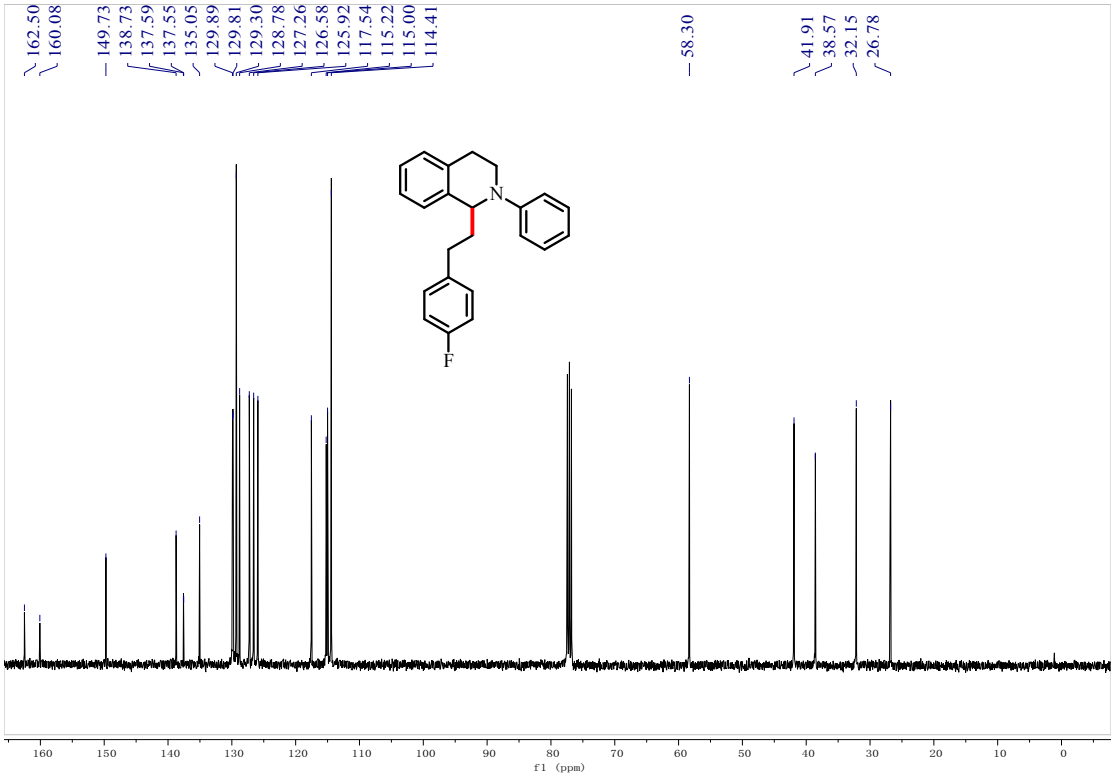
^{13}C NMR spectrum of compound **3aj**



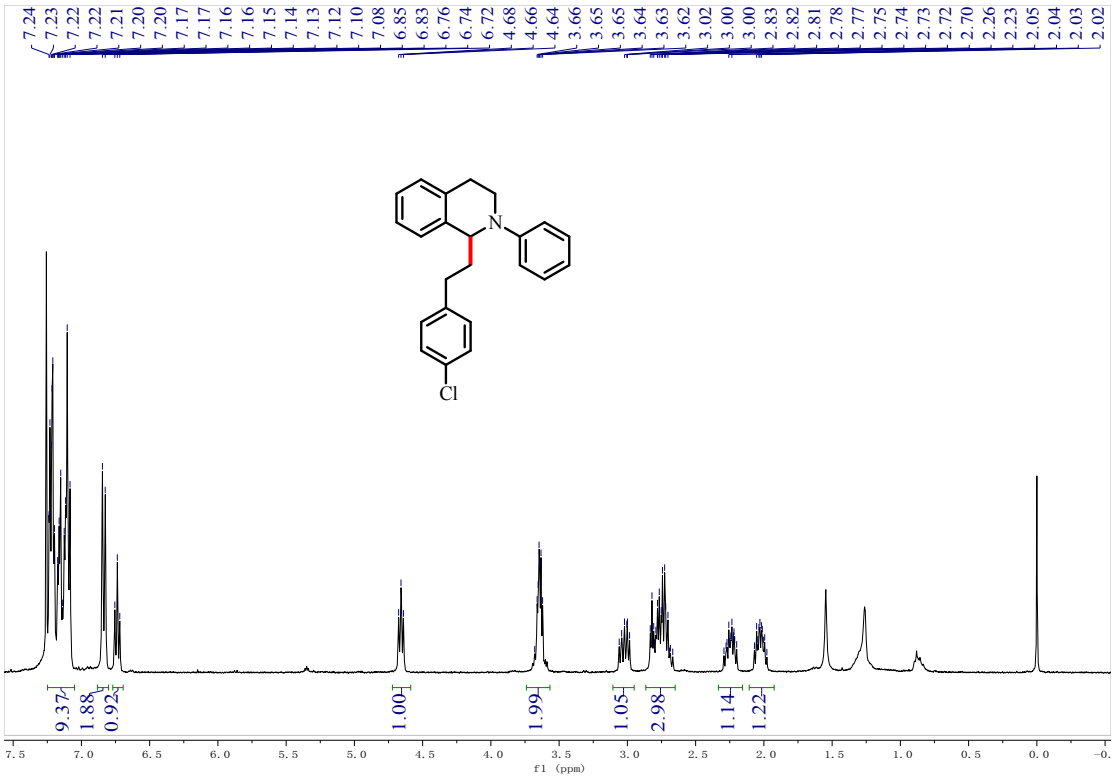
^{1}H NMR spectrum of compound **3ak**



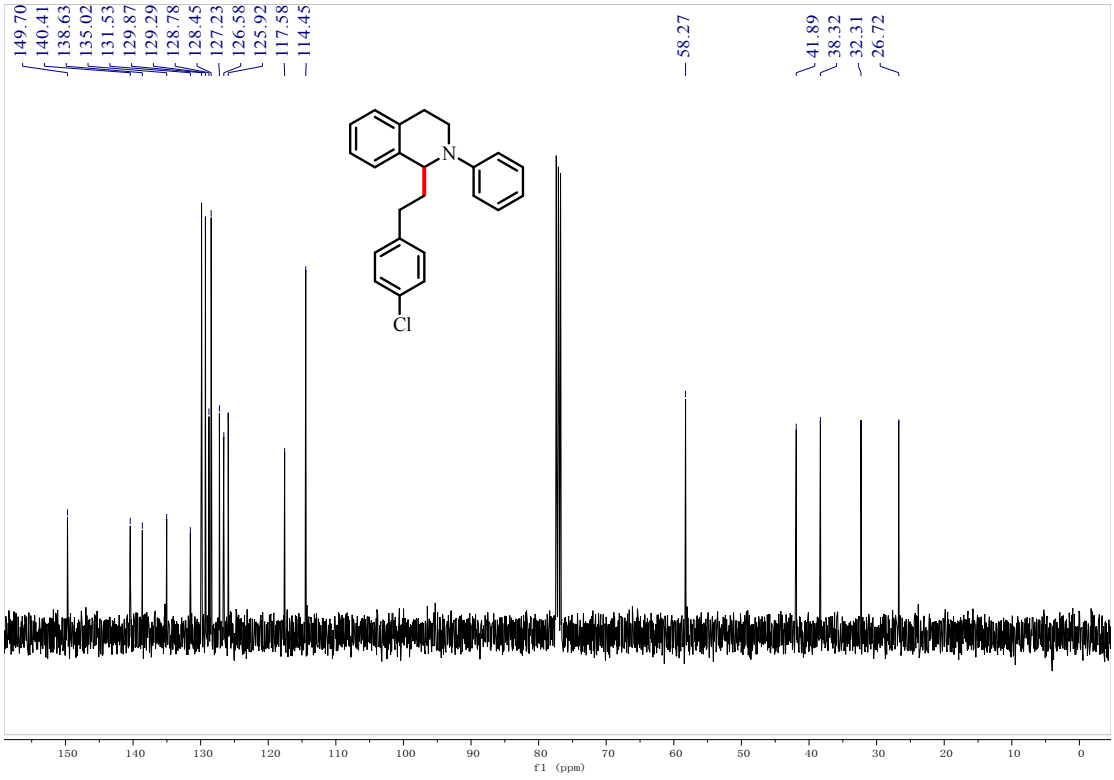
^{13}C NMR spectrum of compound **3ak**



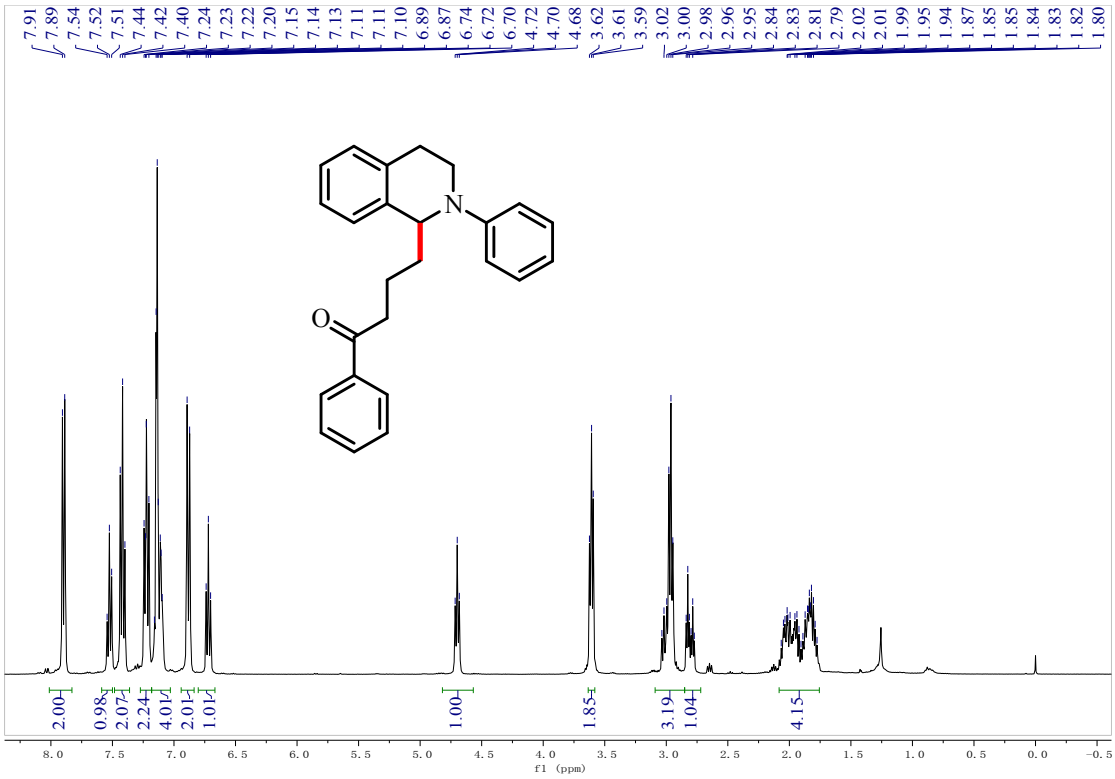
^{1}H NMR spectrum of compound **3al**



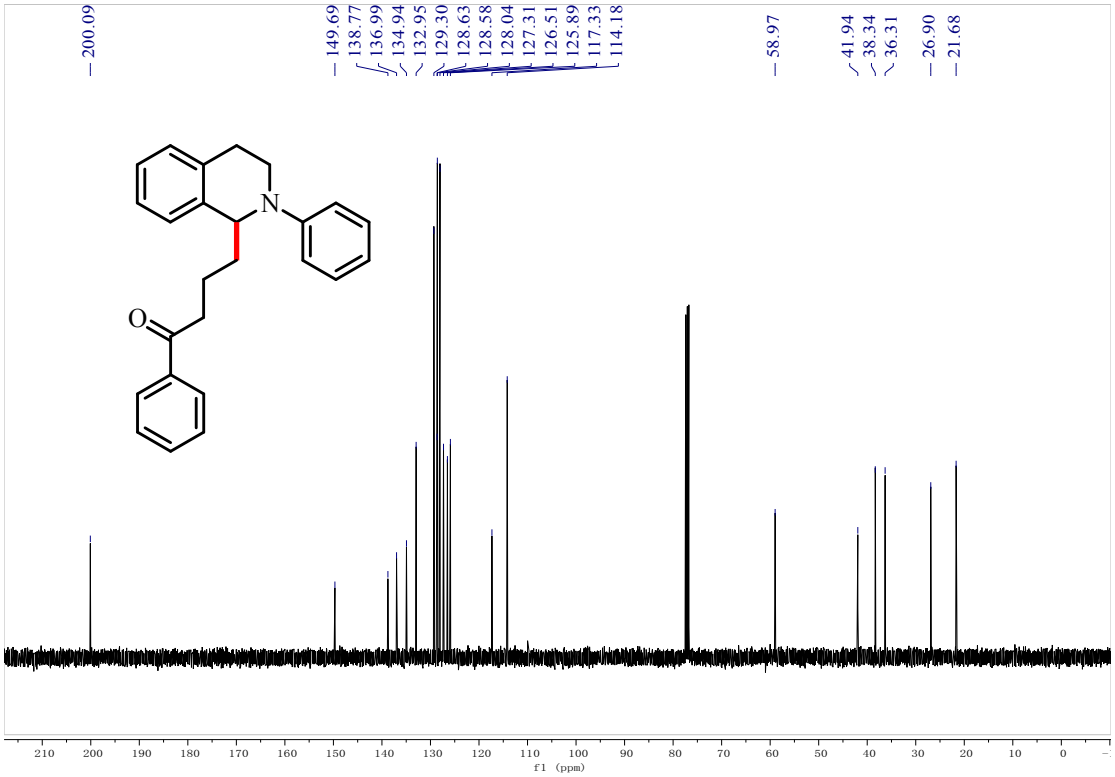
^{13}C NMR spectrum of compound **3al**



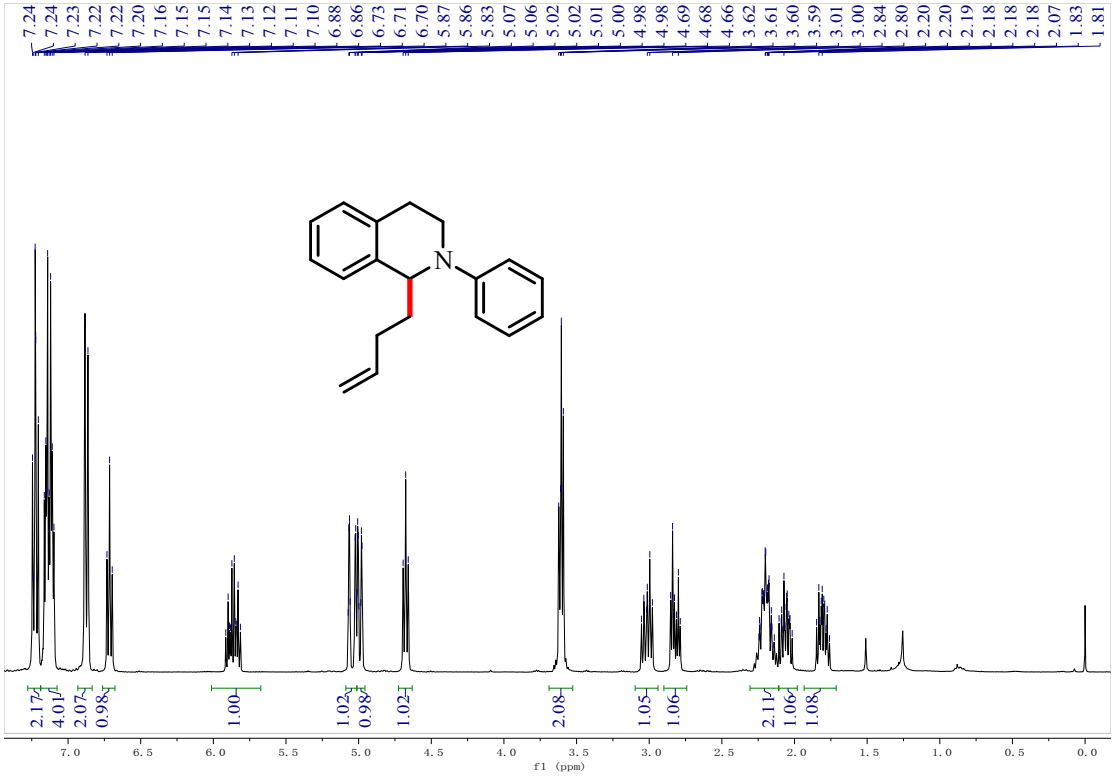
^{1}H NMR spectrum of compound **3am**



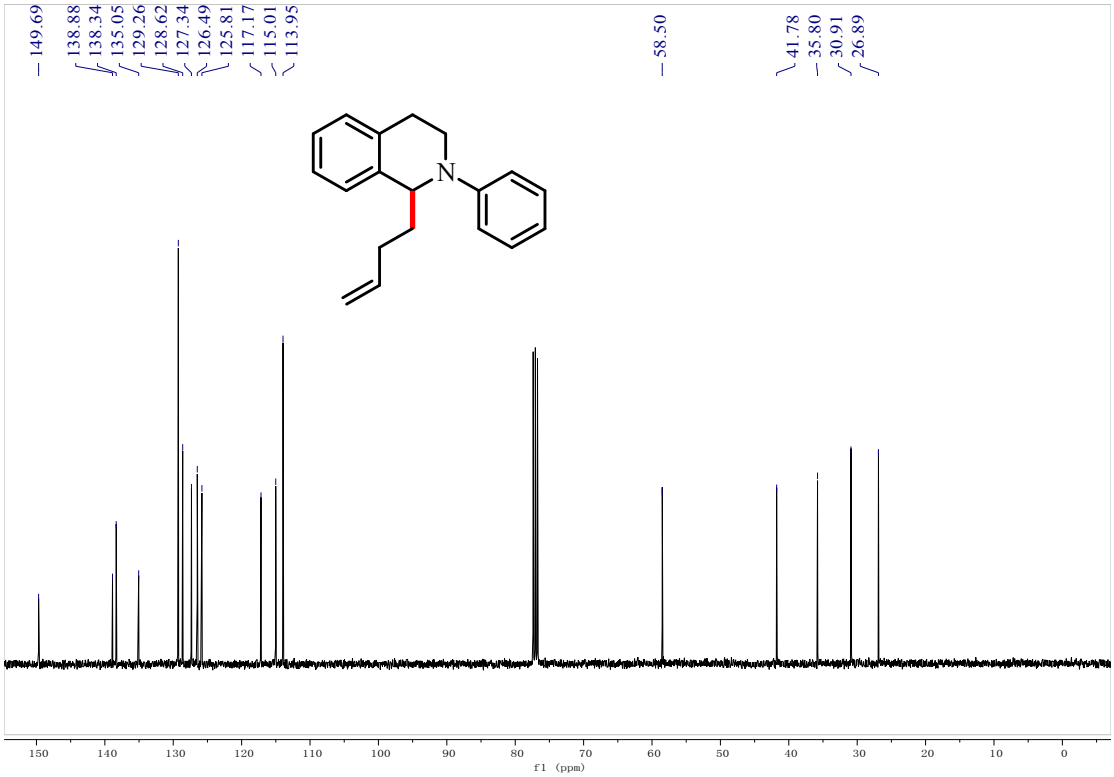
^{13}C NMR spectrum of compound **3am**



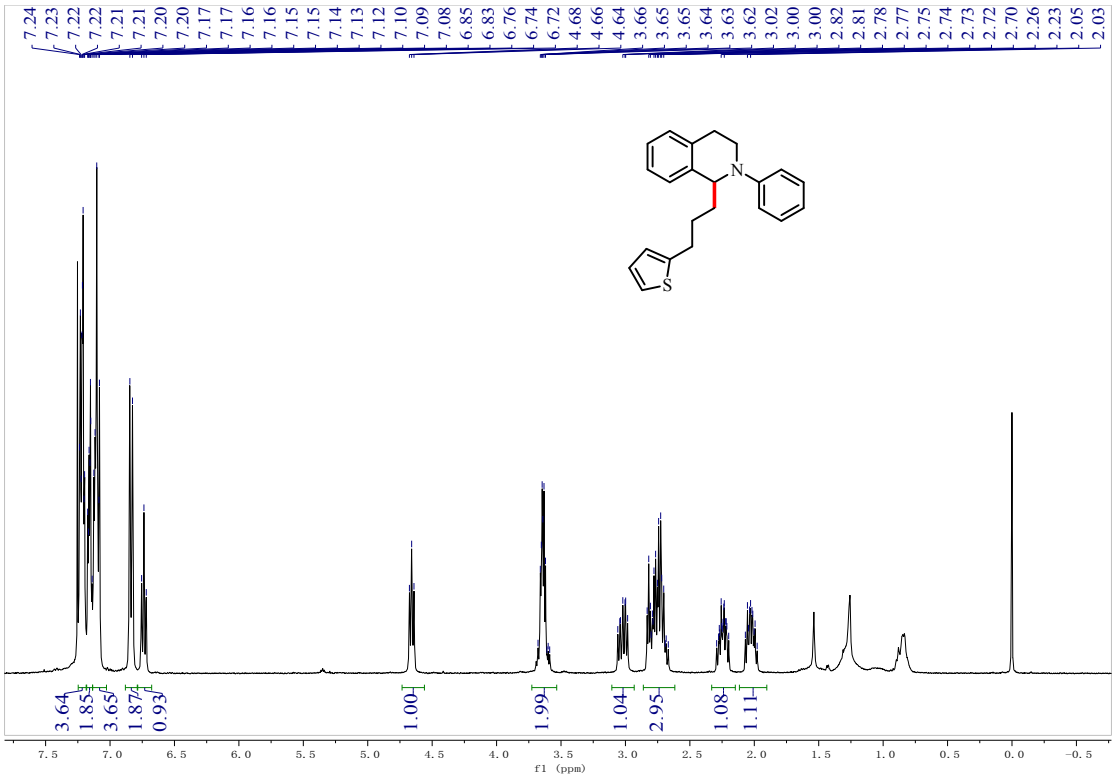
^{1}H NMR spectrum of compound **3an**



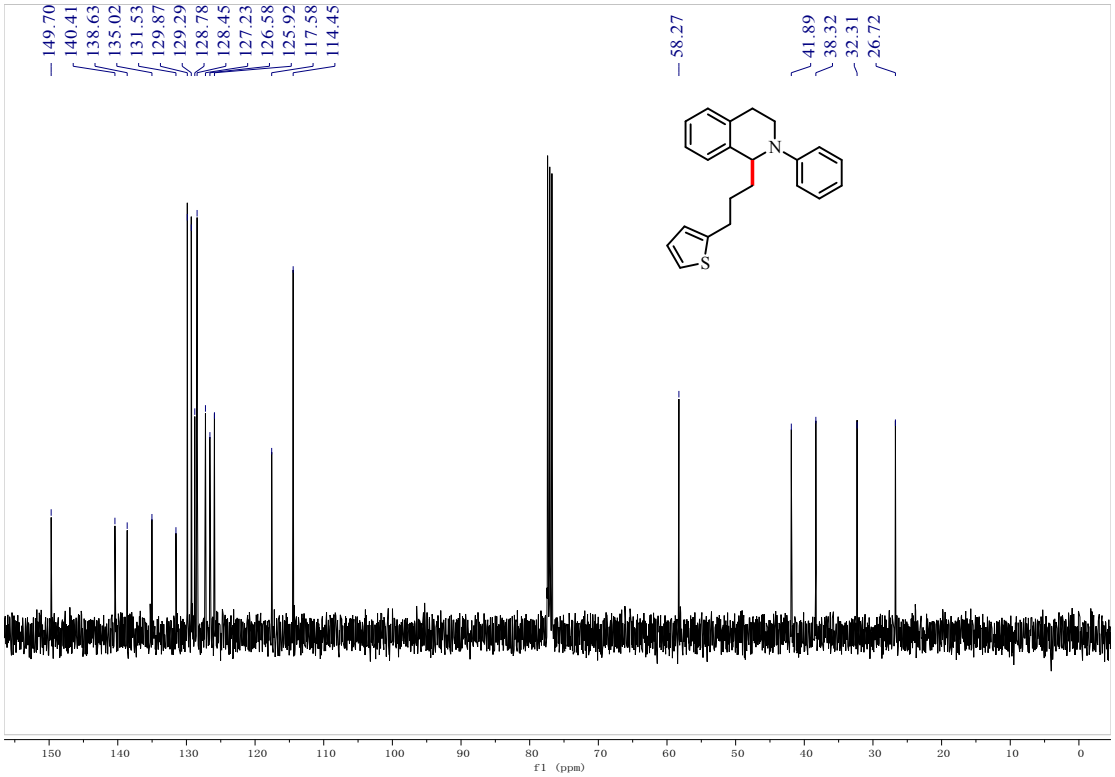
^{13}C NMR spectrum of compound **3an**



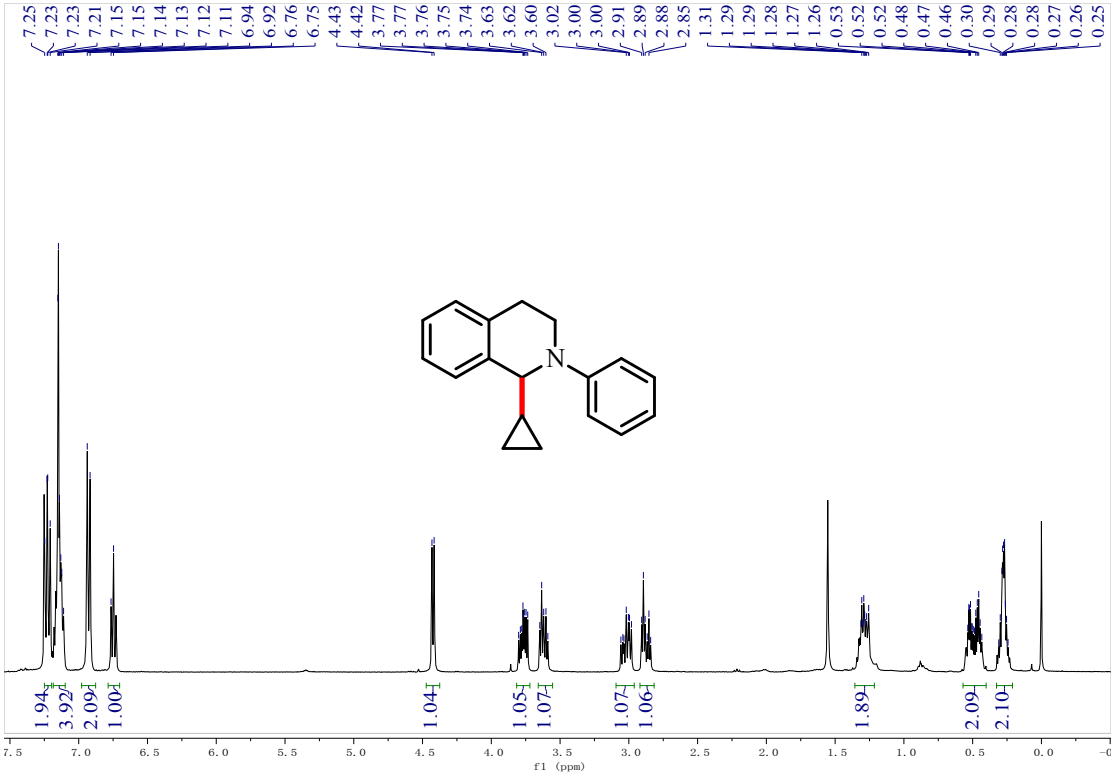
^{1}H NMR spectrum of compound **3ao**



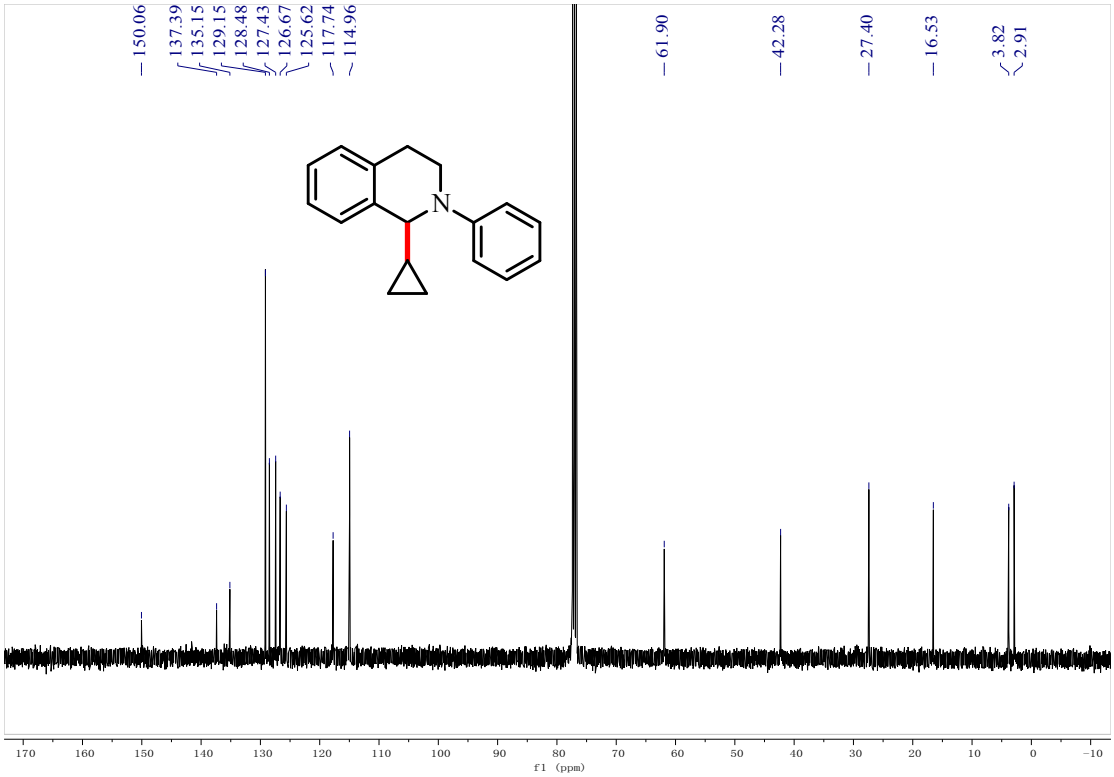
^{13}C NMR spectrum of compound **3ao**



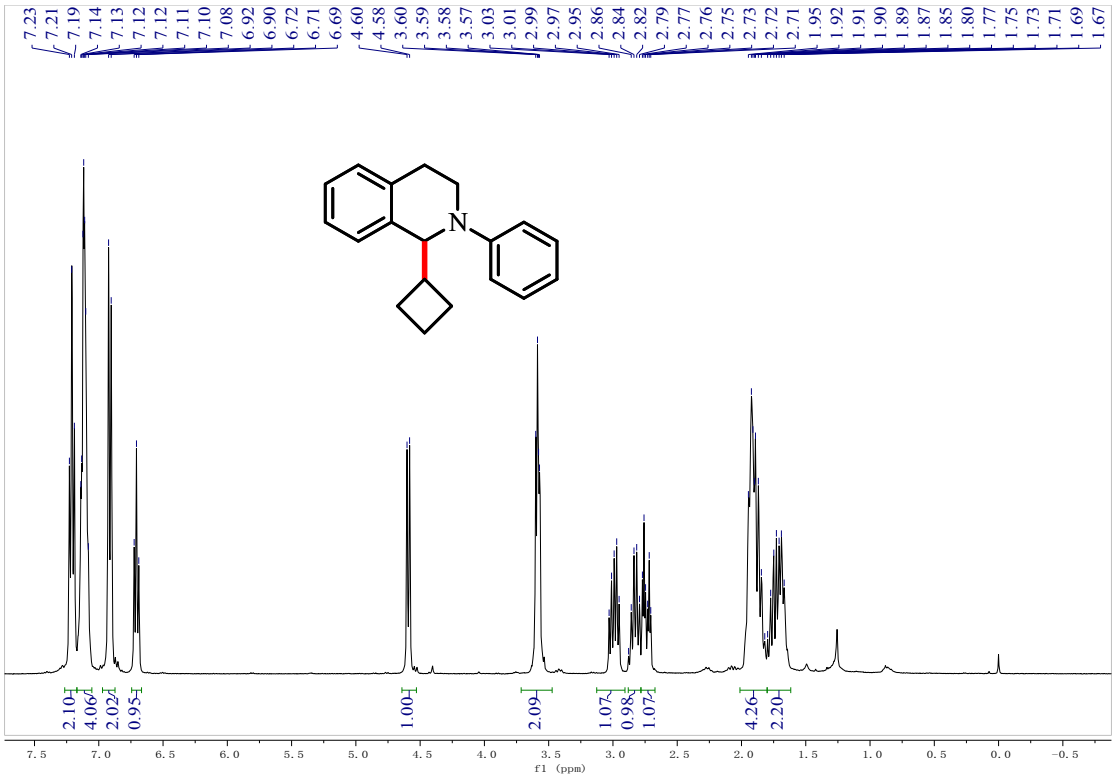
^{1}H NMR spectrum of compound **3ap**



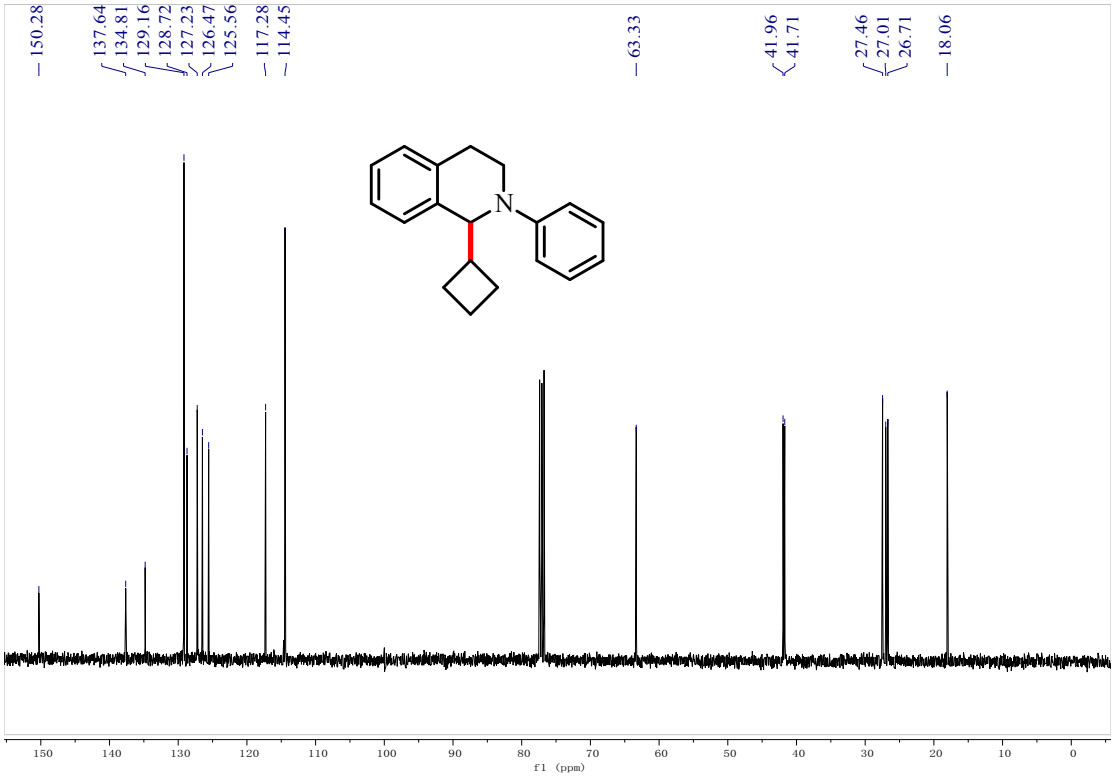
^{13}C NMR spectrum of compound **3ap**



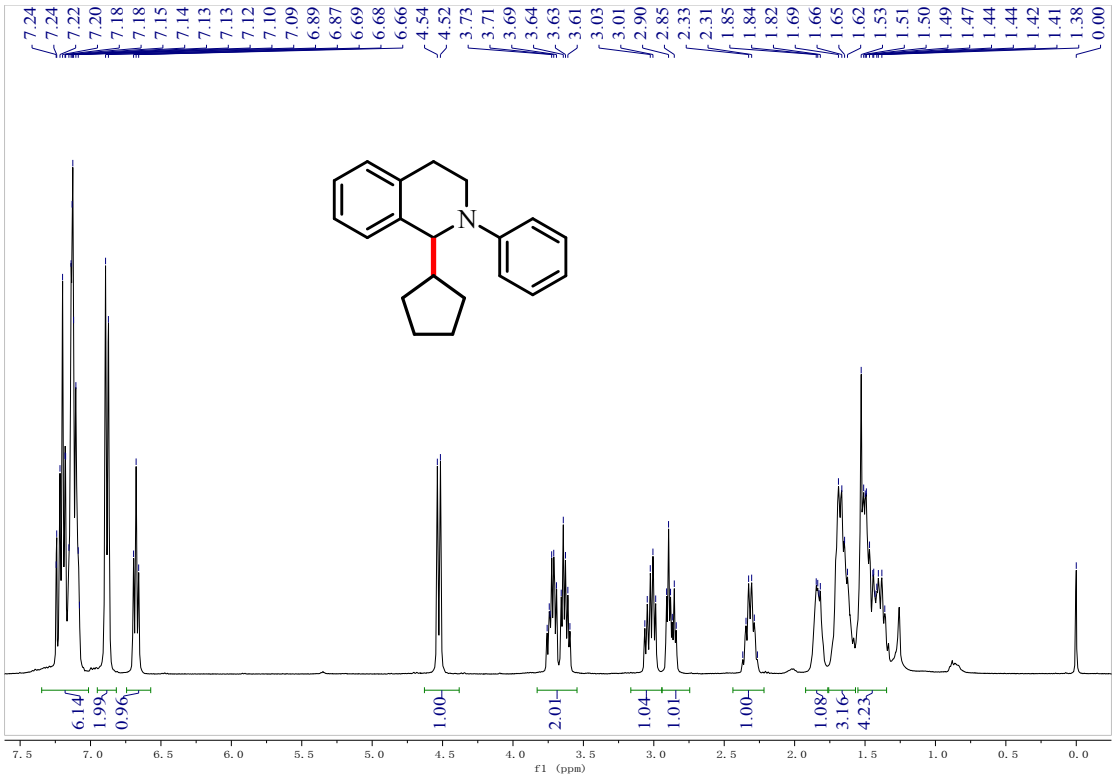
^{1}H NMR spectrum of compound **3aq**



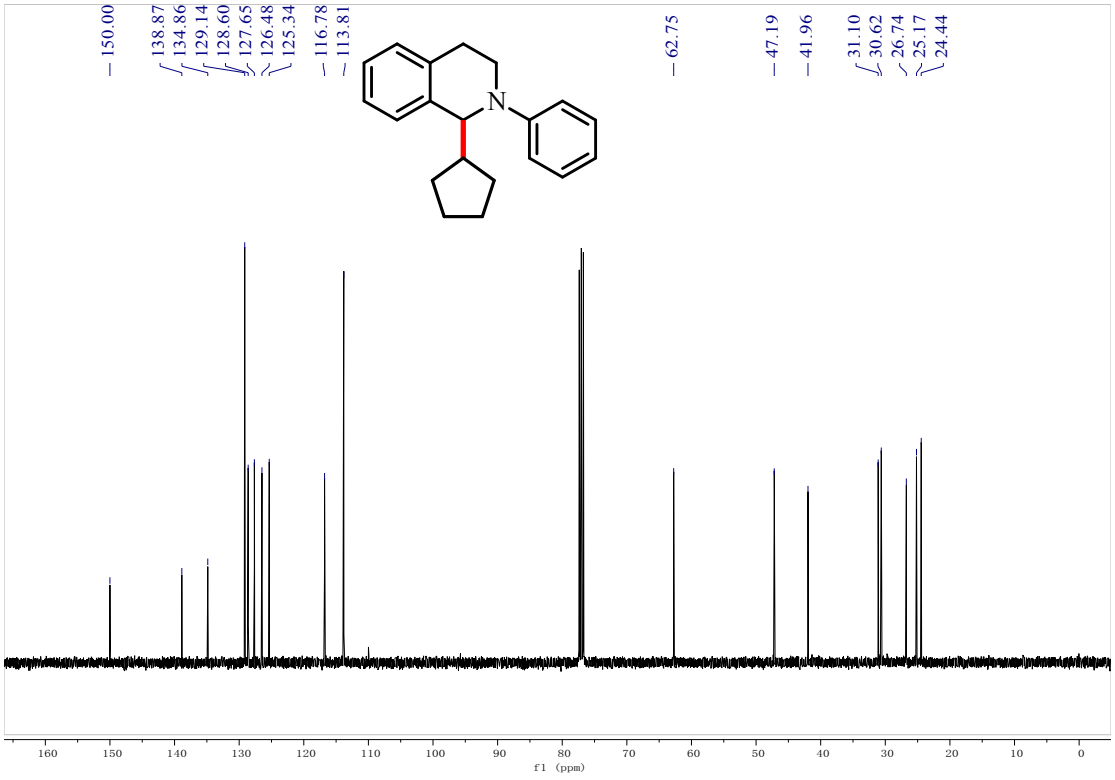
^{13}C NMR spectrum of compound **3aq**



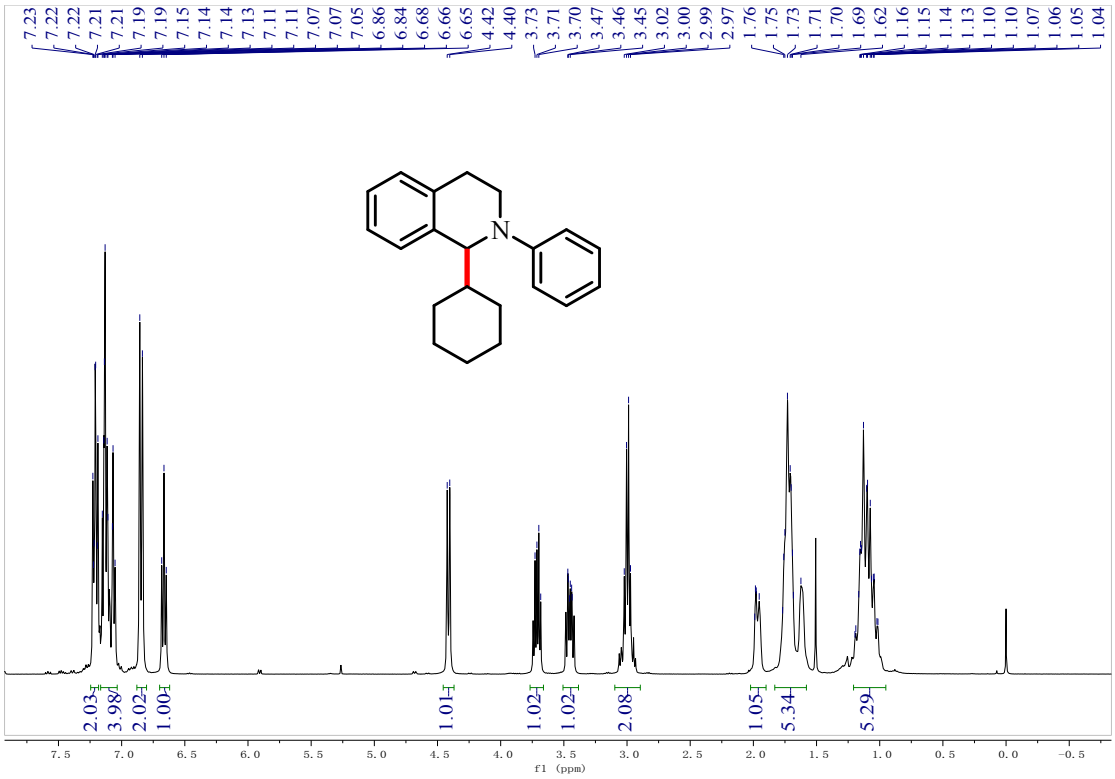
^{1}H NMR spectrum of compound **3ar**



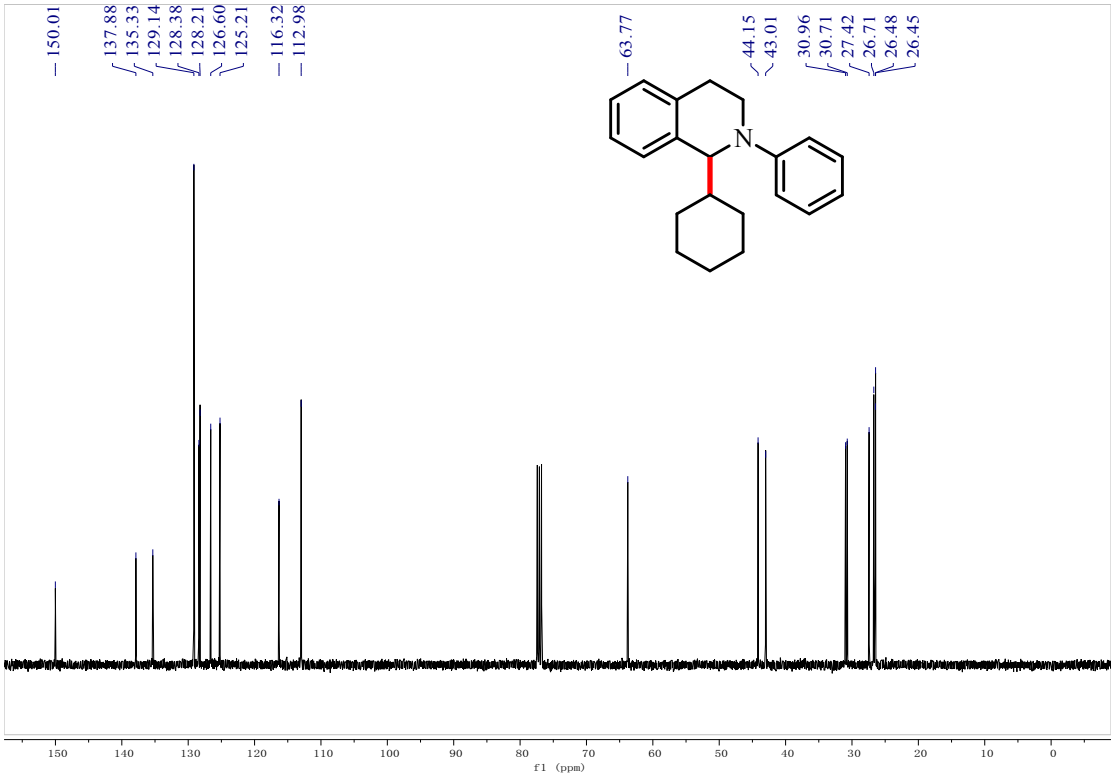
^{13}C NMR spectrum of compound **3ar**



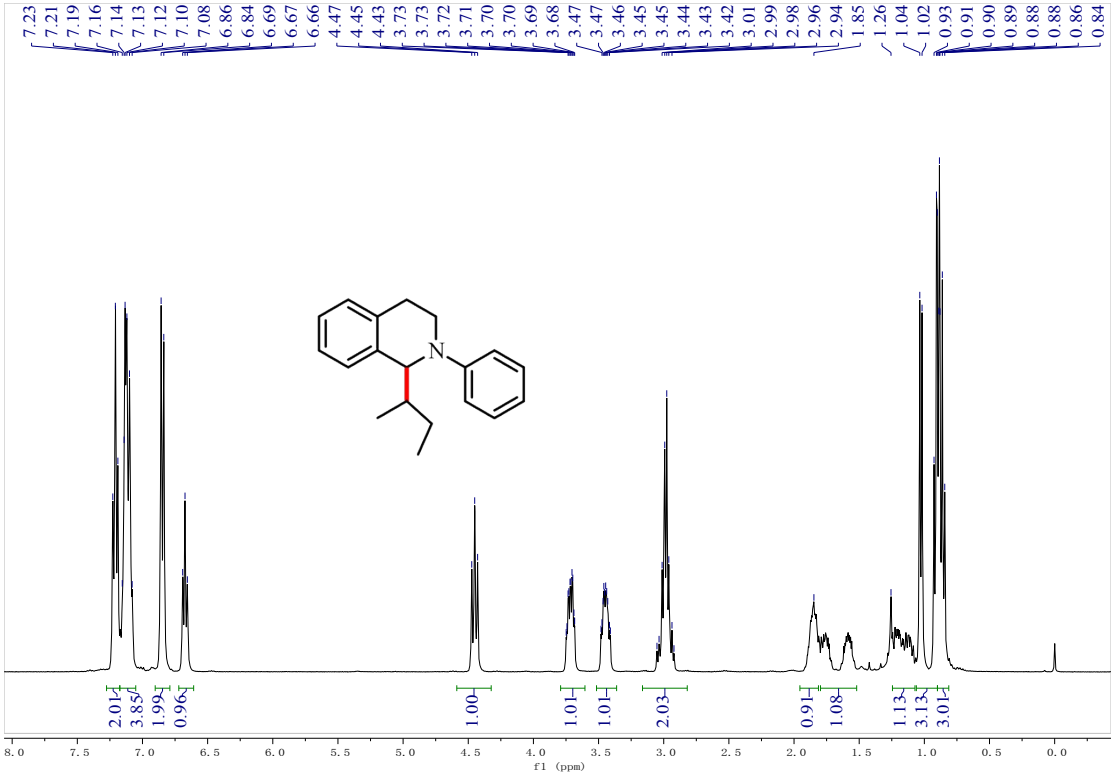
^{1}H NMR spectrum of compound **3as**



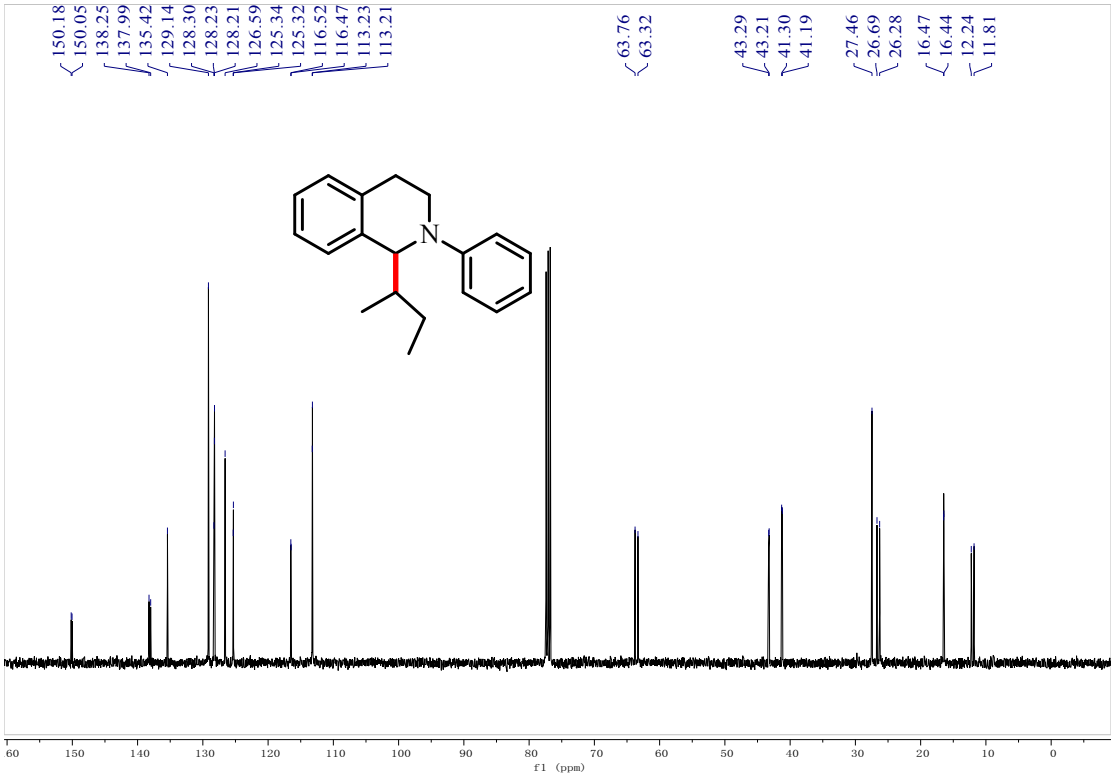
^{13}C NMR spectrum of compound **3as**



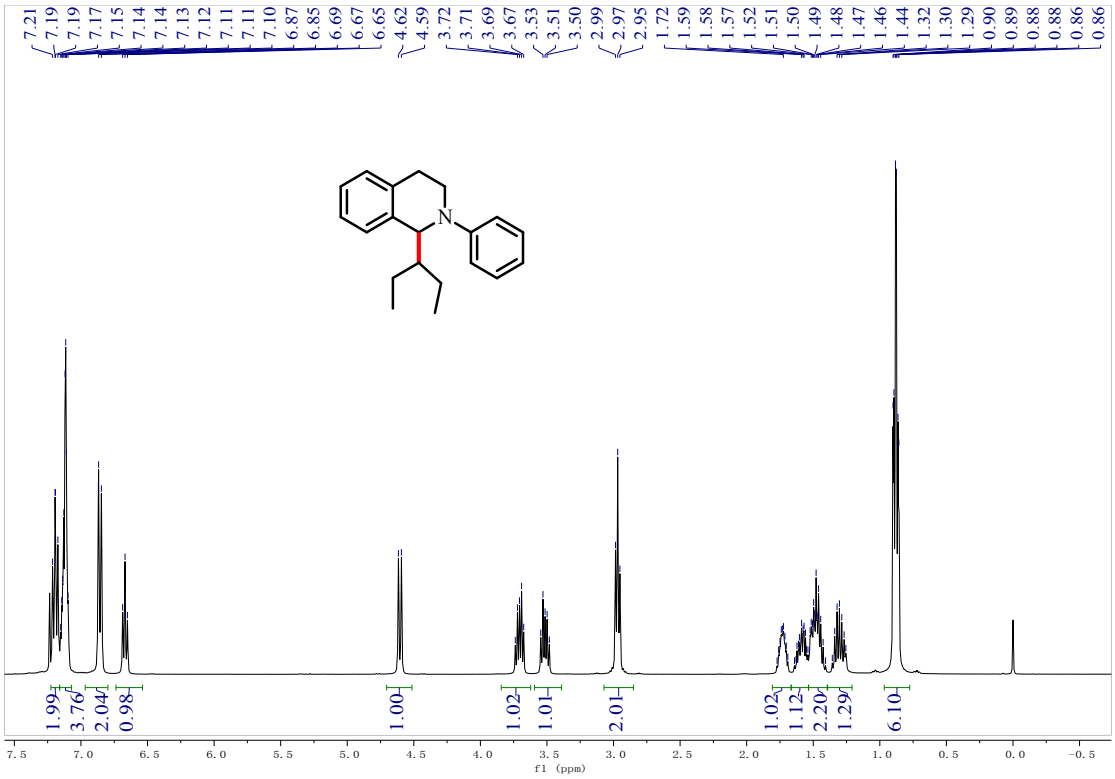
^{1}H NMR spectrum of compound **3at**



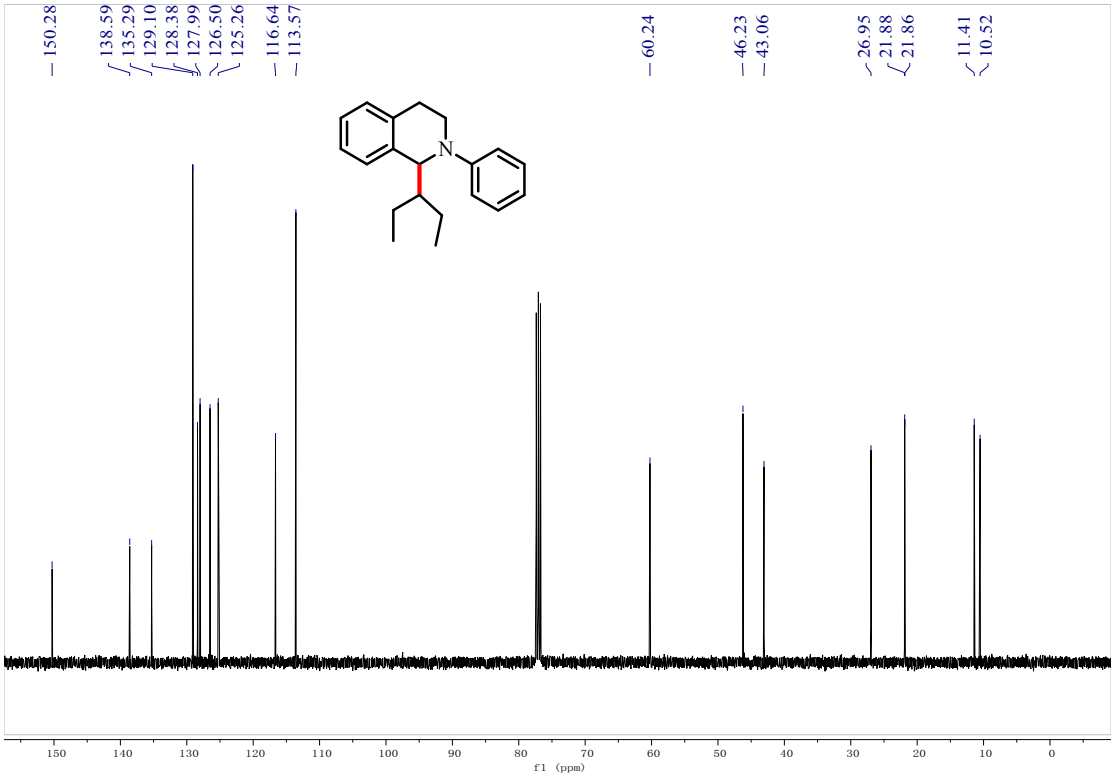
^{13}C NMR spectrum of compound **3at**



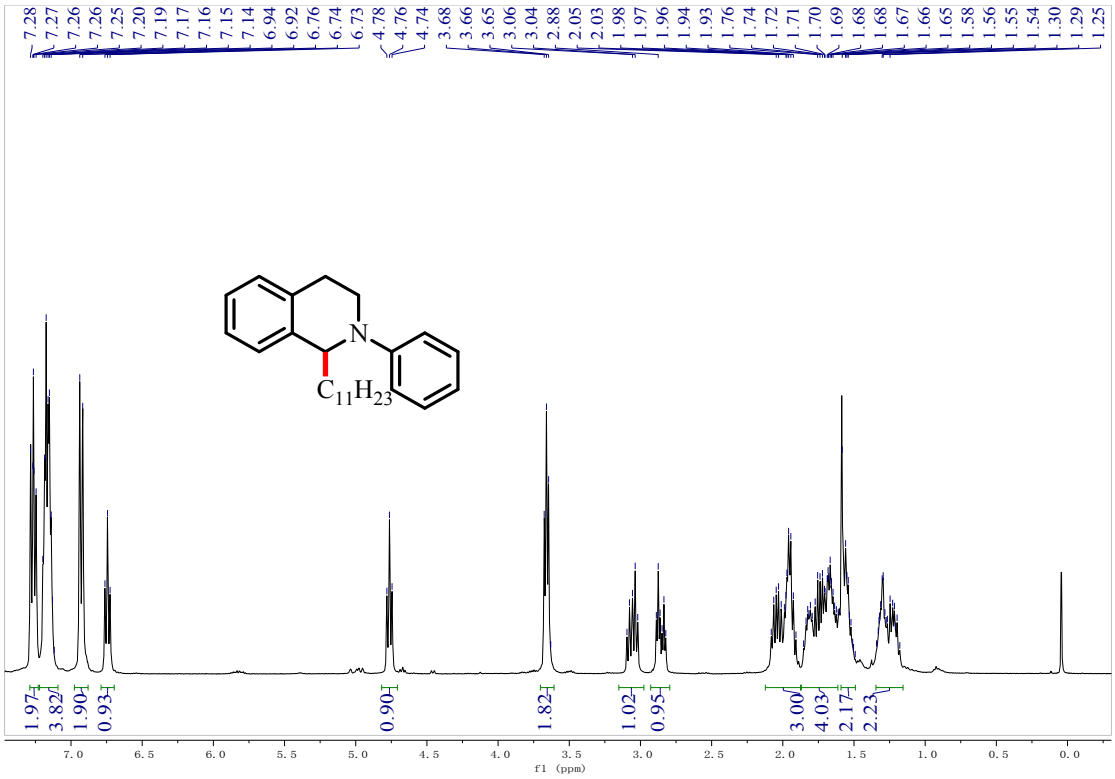
^{1}H NMR spectrum of compound **3au**



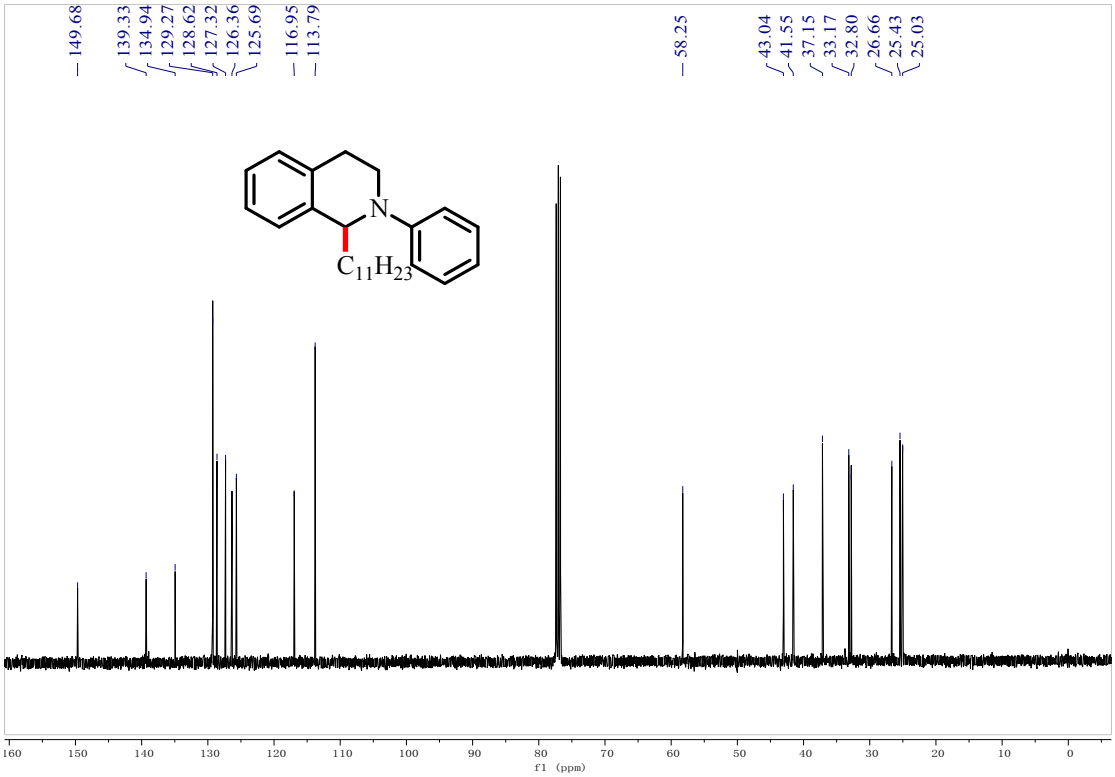
^{13}C NMR spectrum of compound **3au**



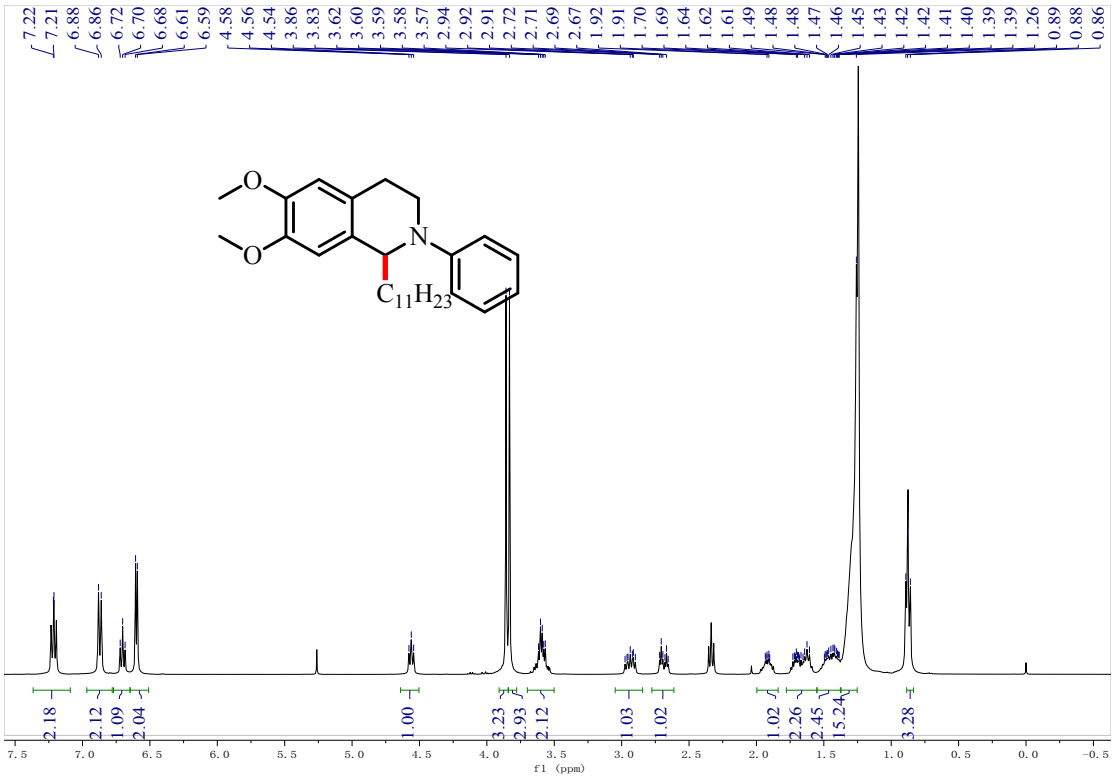
^{1}H NMR spectrum of compound **3av**



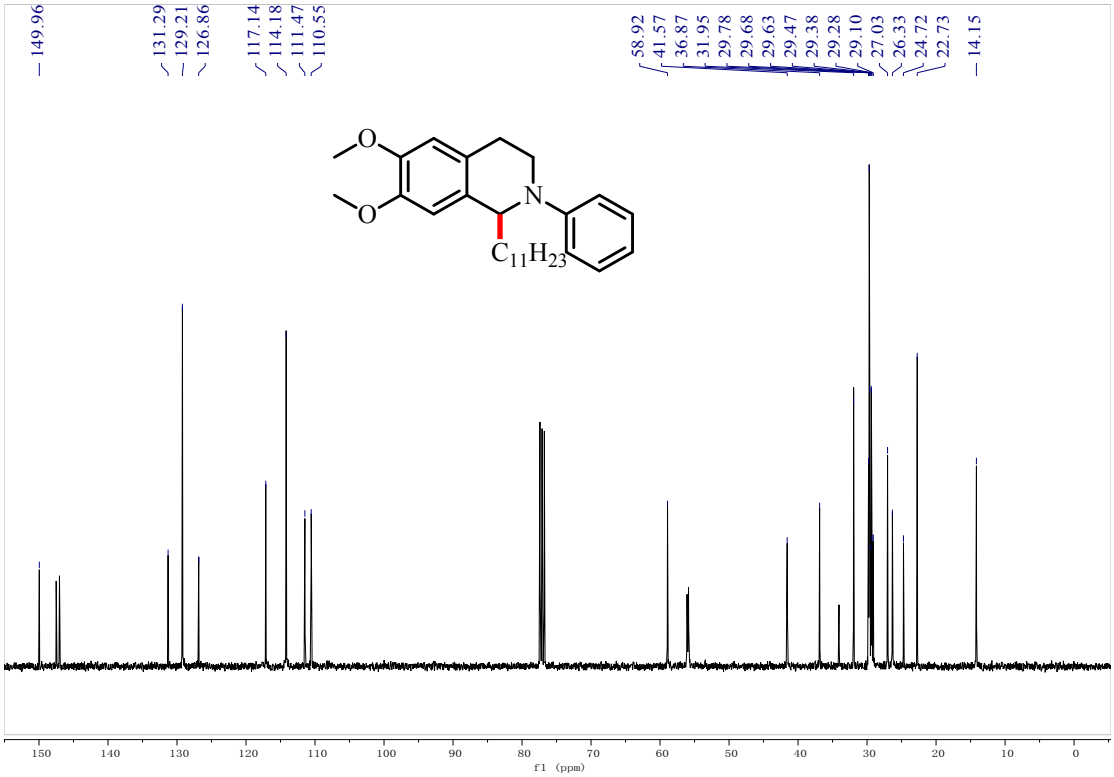
^{13}C NMR spectrum of compound **3av**



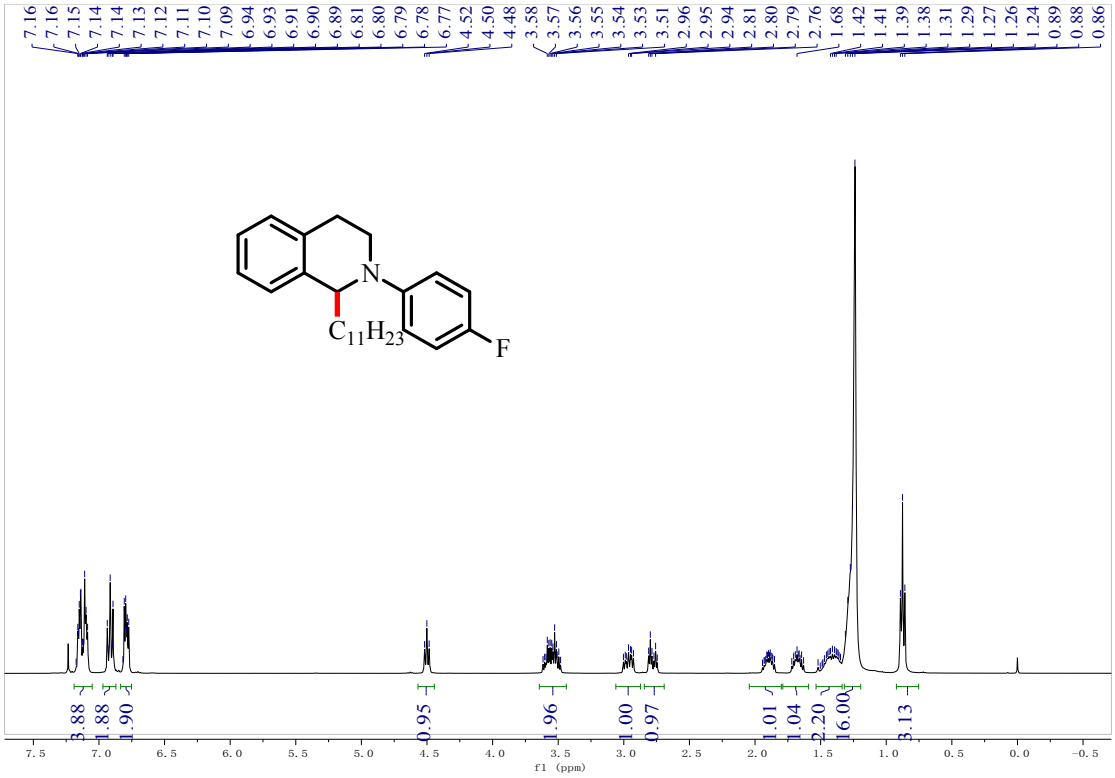
^{1}H NMR spectrum of compound **3ba**



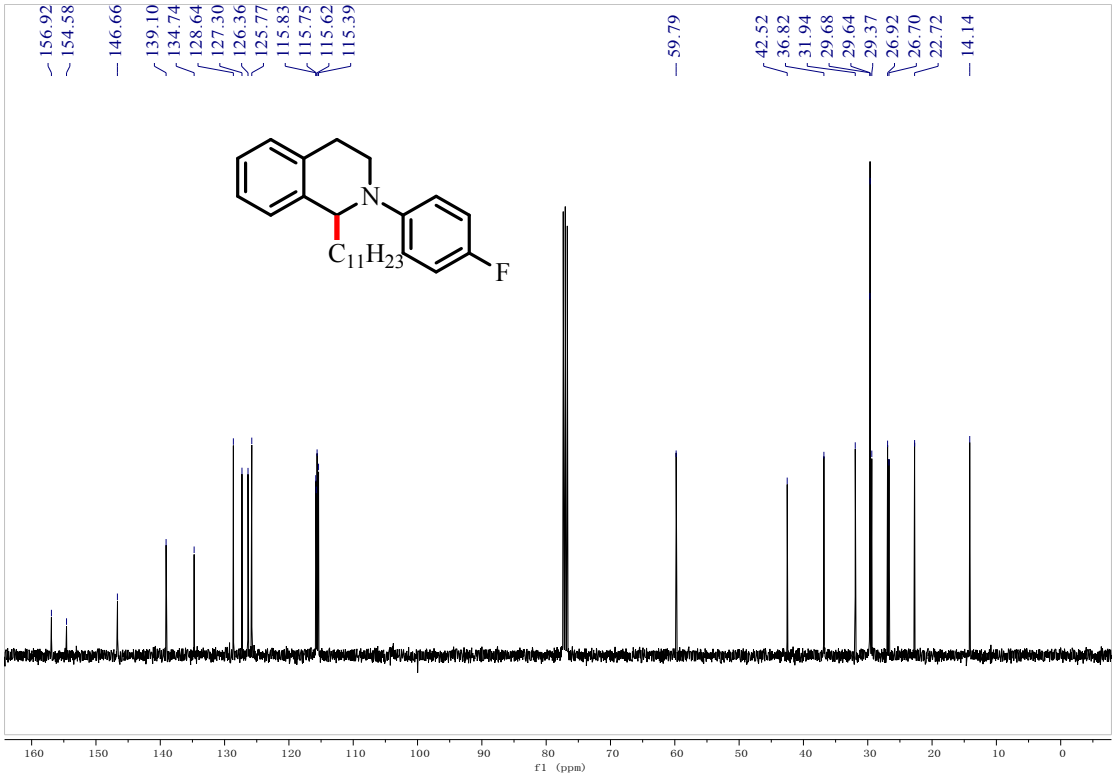
^{13}C NMR spectrum of compound **3ba**



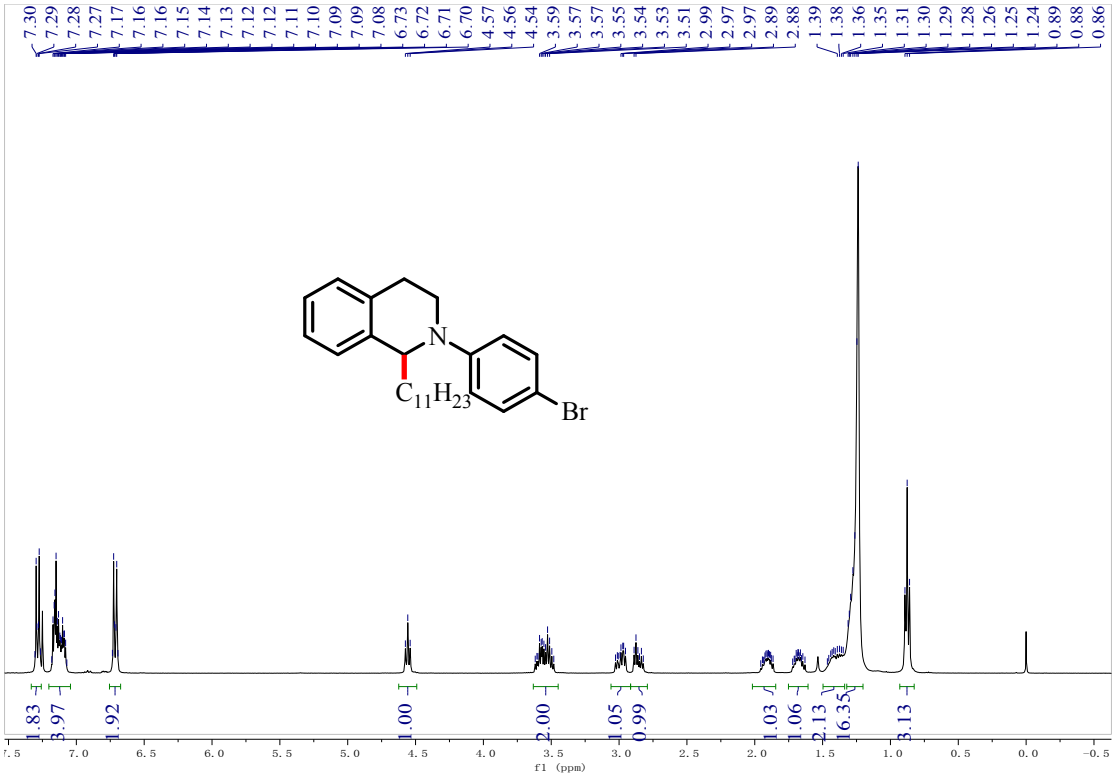
^{1}H NMR spectrum of compound **3ac**



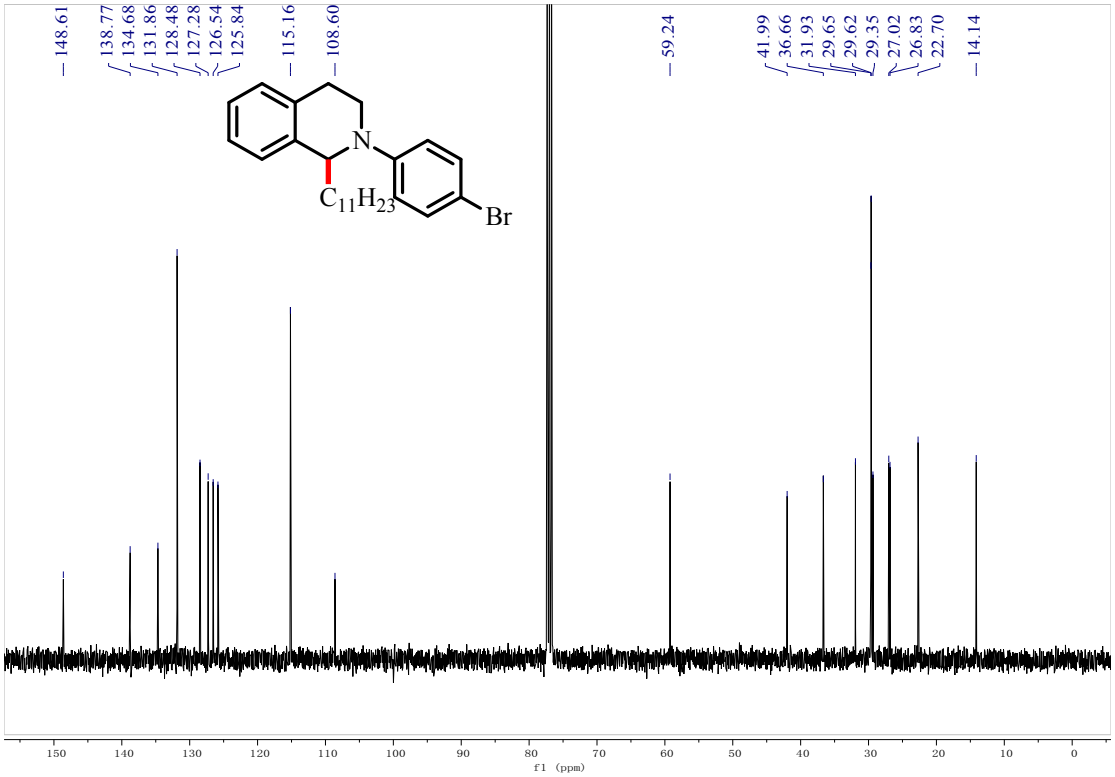
^{13}C NMR spectrum of compound **3ac**



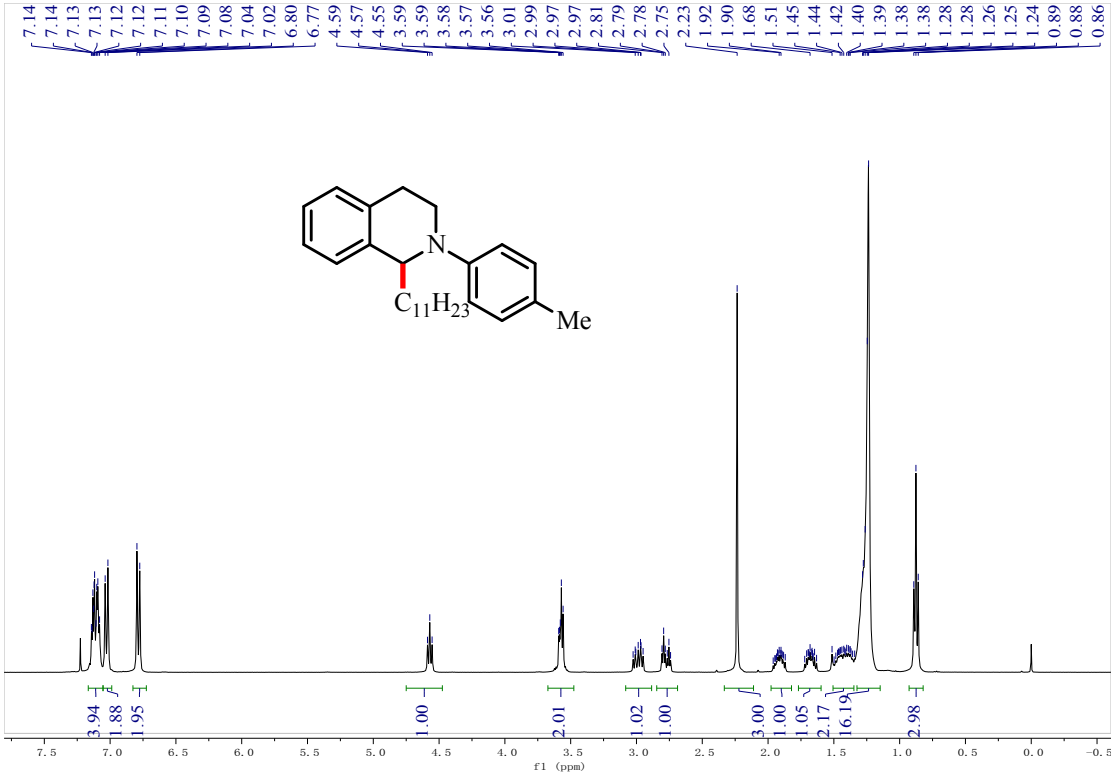
^{1}H NMR spectrum of compound **3da**



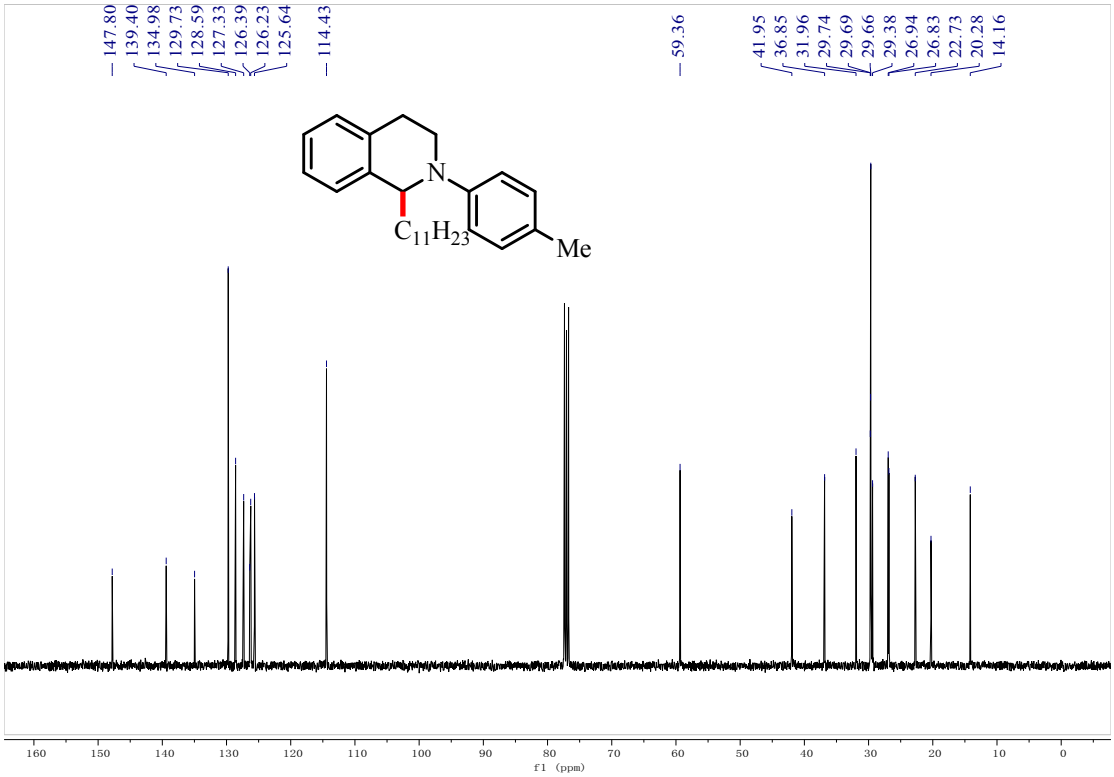
^{13}C NMR spectrum of compound **3da**



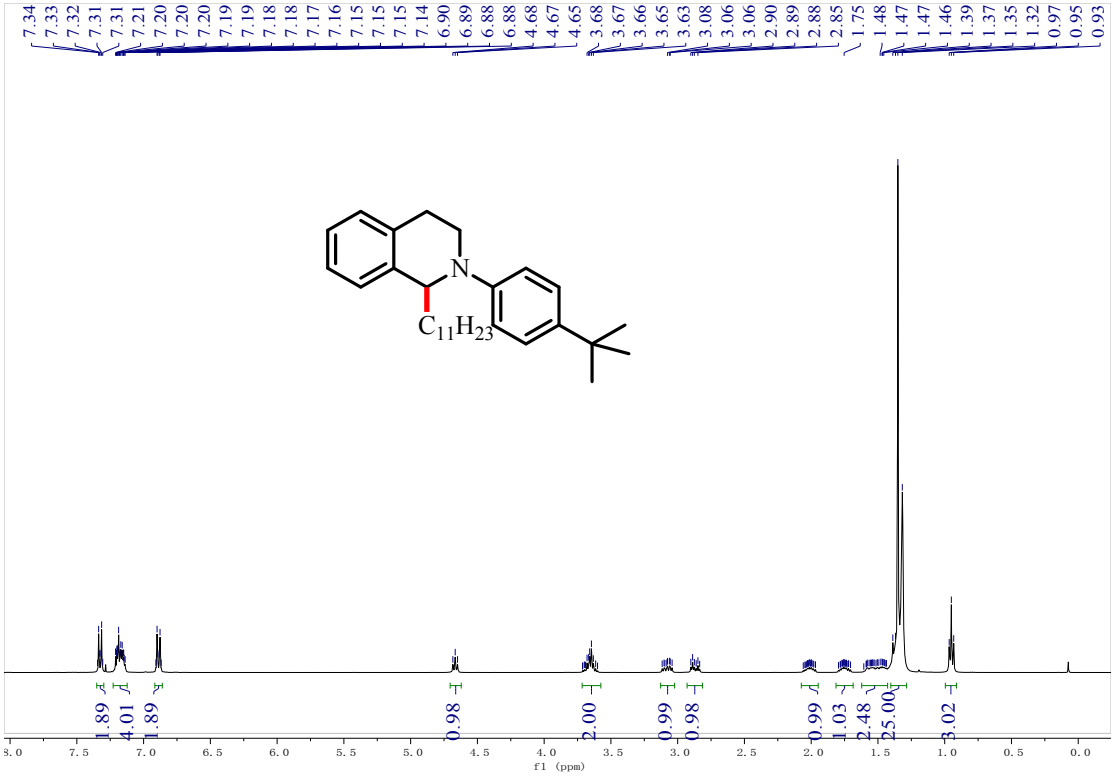
^{1}H NMR spectrum of compound **3ea**



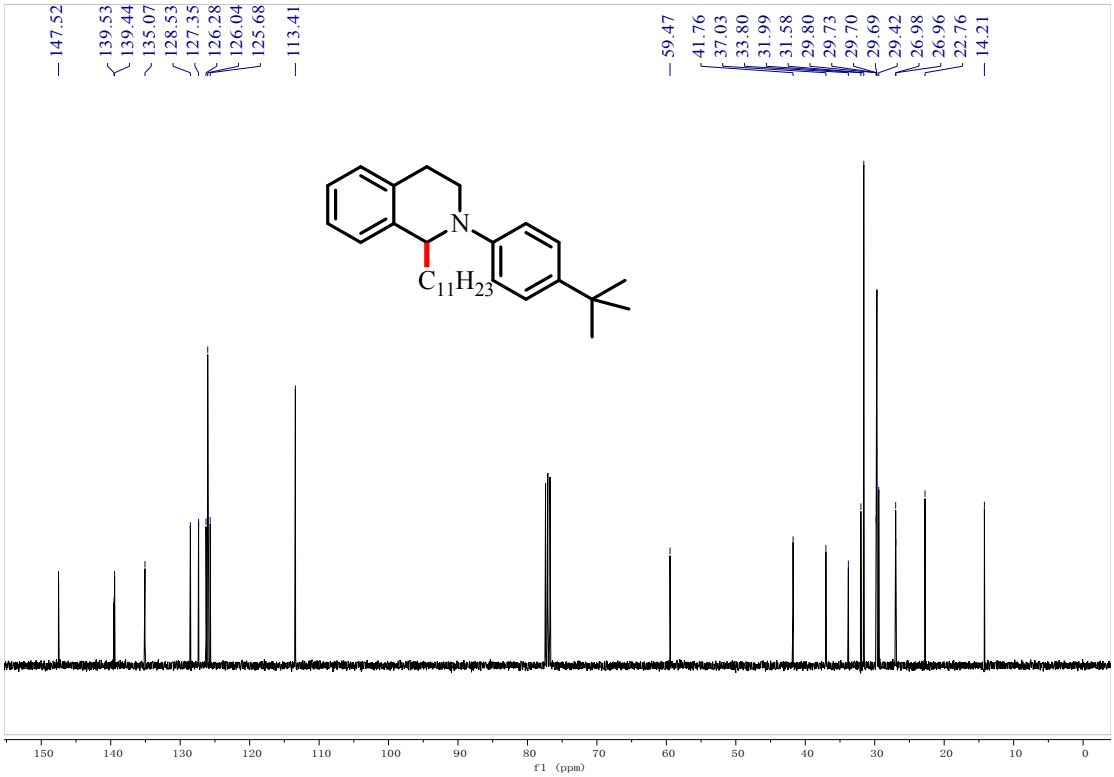
^{13}C NMR spectrum of compound **3ea**



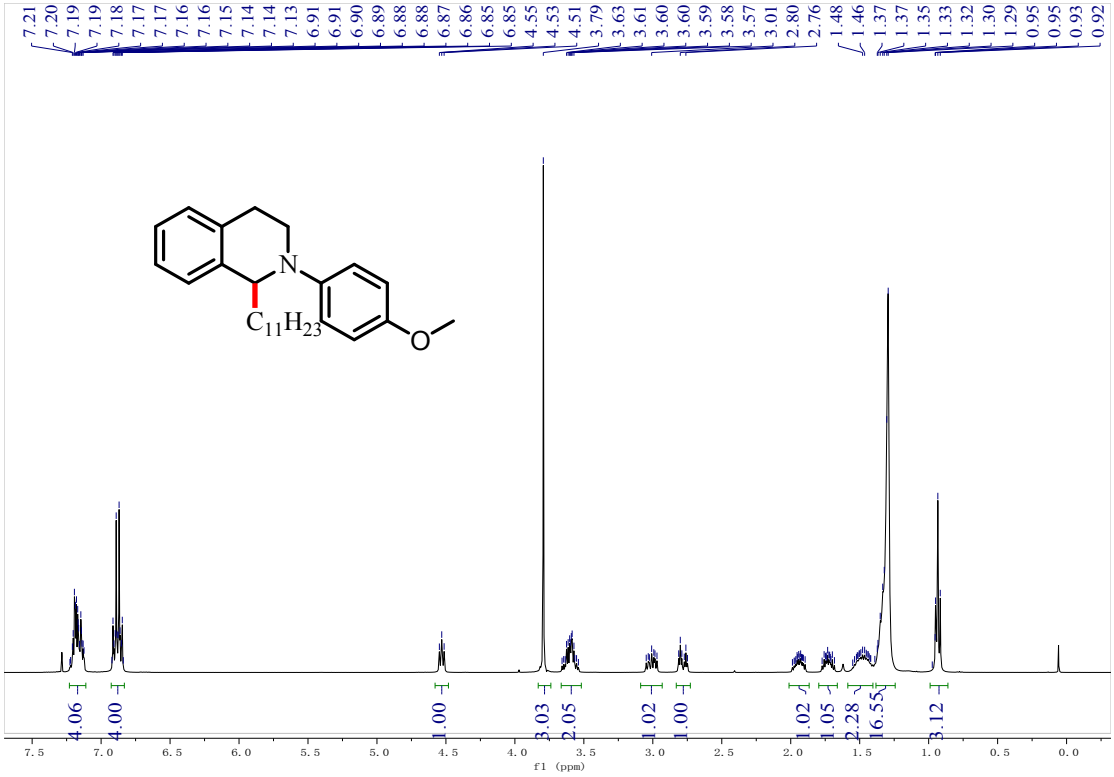
^{1}H NMR spectrum of compound **3fa**



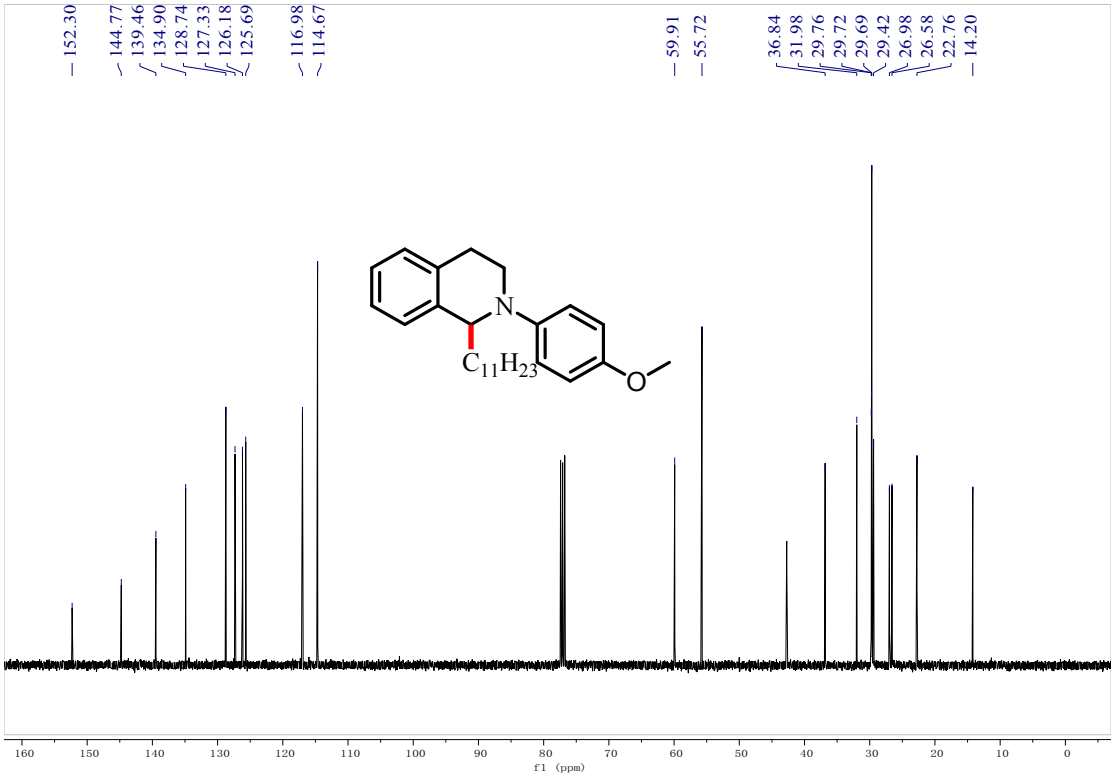
^{13}C NMR spectrum of compound **3fa**



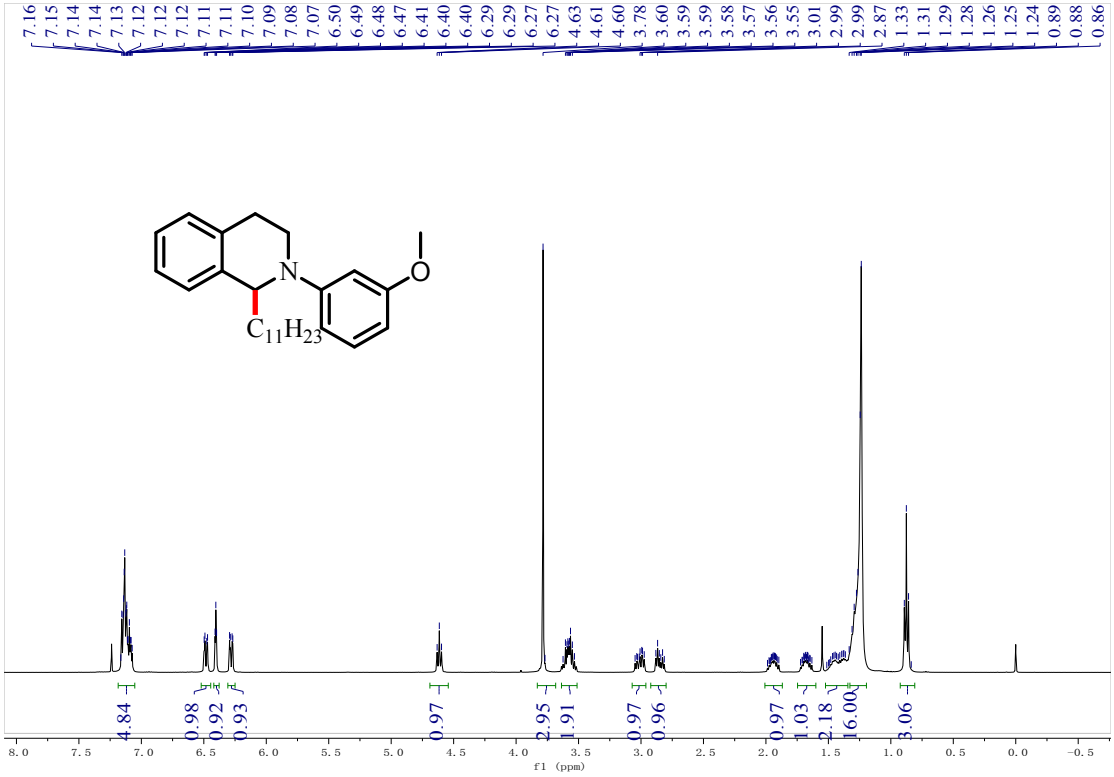
^{1}H NMR spectrum of compound **3ga**



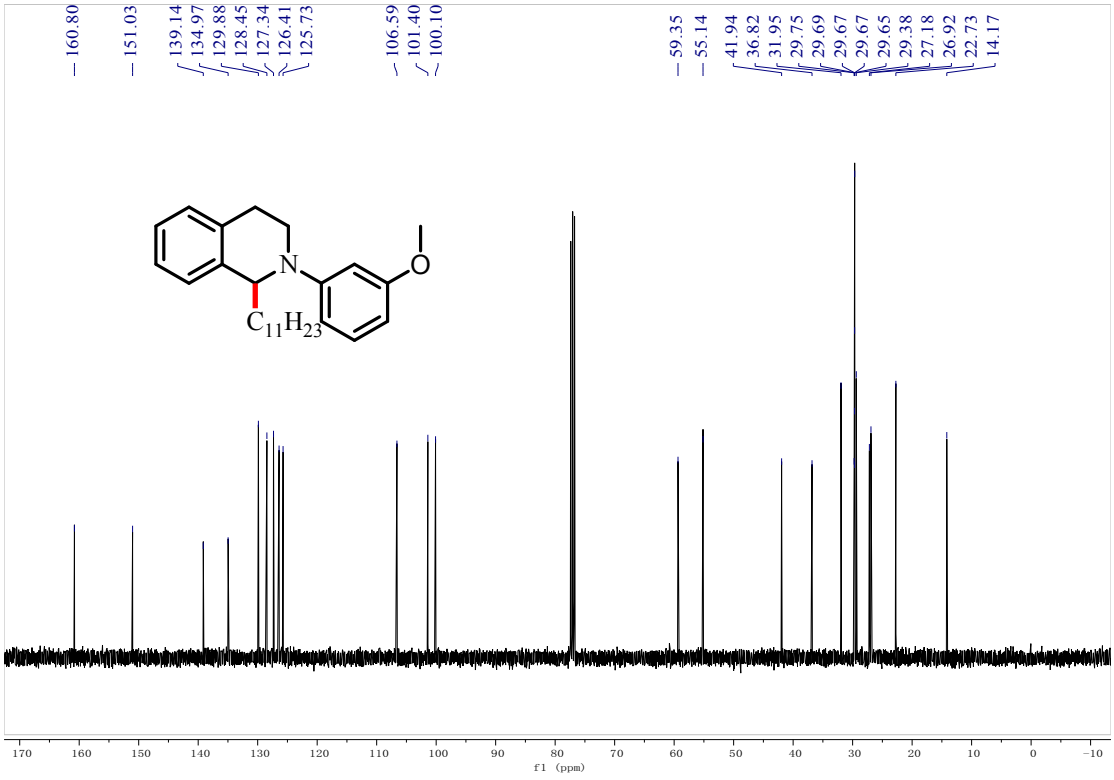
^{13}C NMR spectrum of compound **3ga**



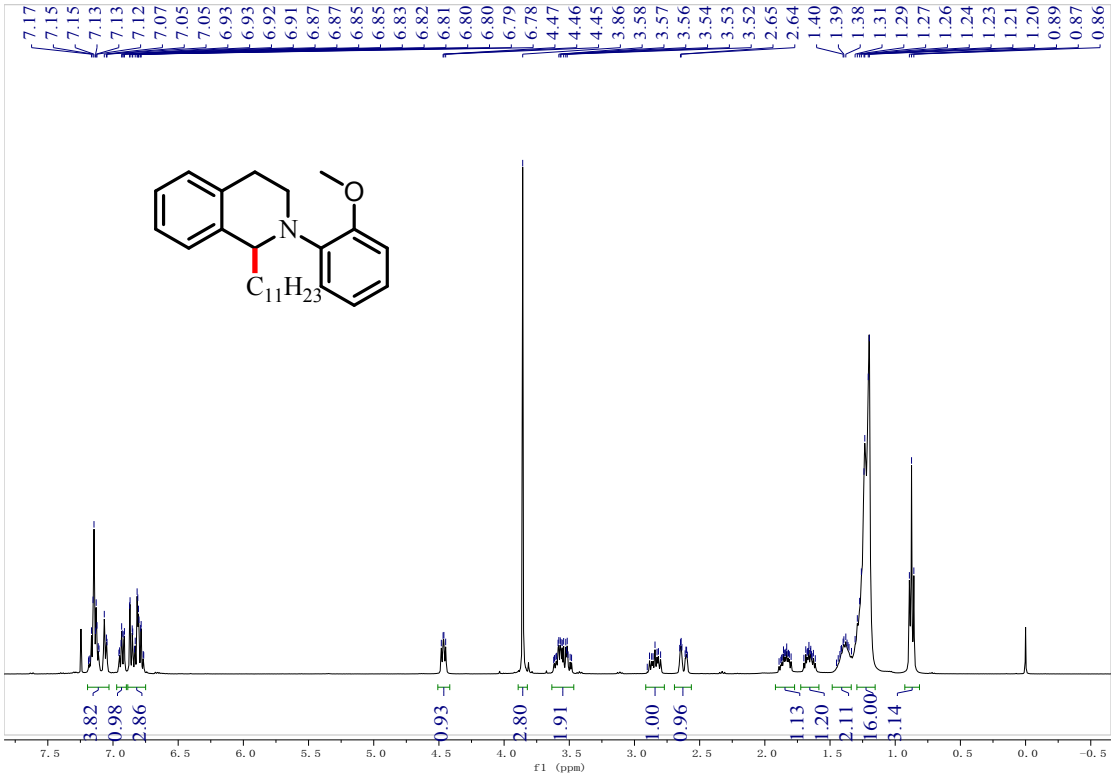
^{1}H NMR spectrum of compound **3ha**



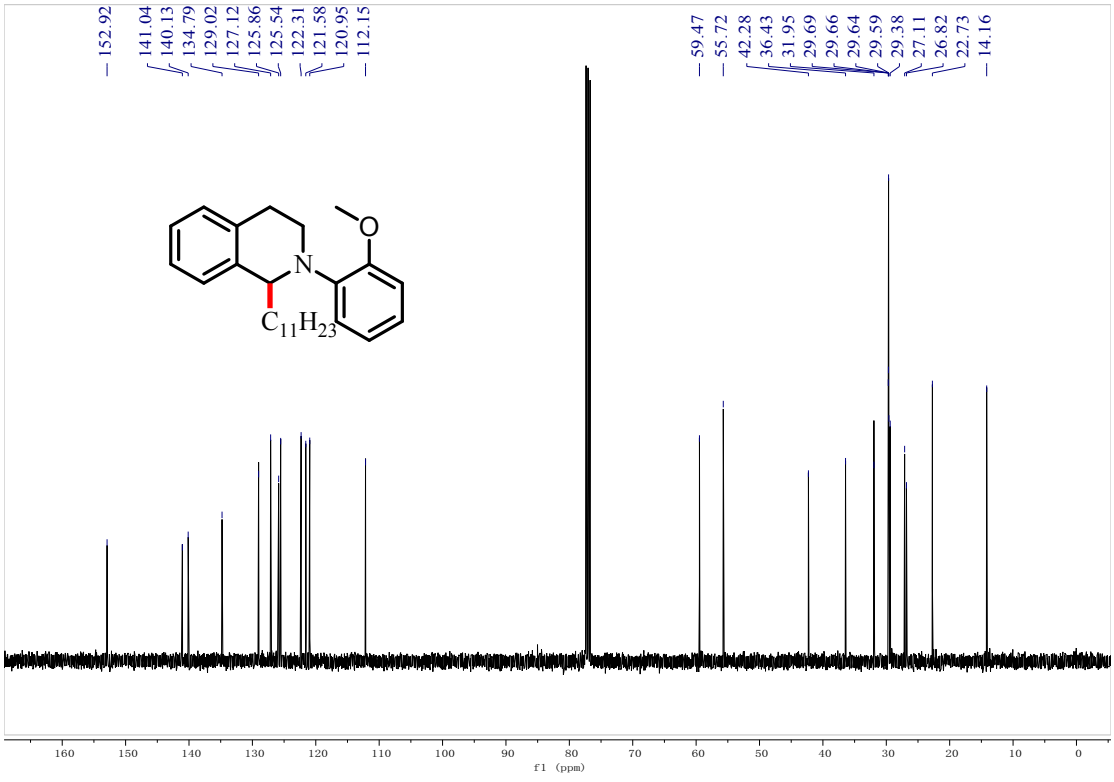
^{13}C NMR spectrum of compound **3ha**



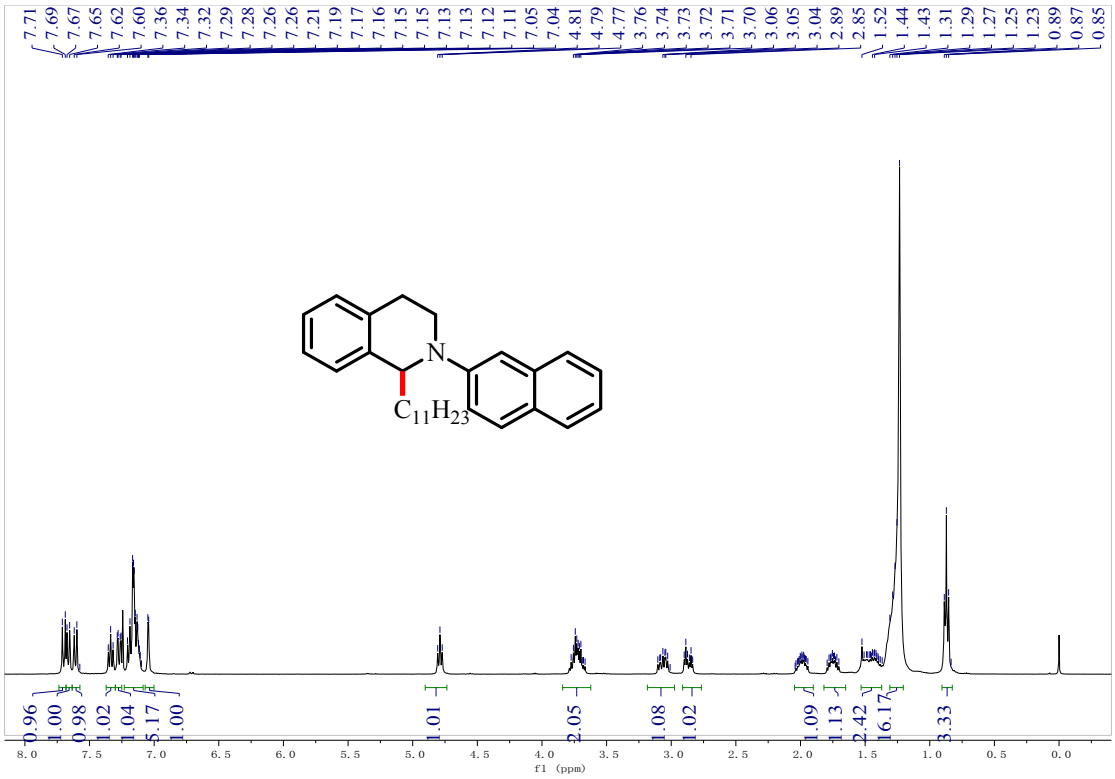
^{1}H NMR spectrum of compound **3ia**



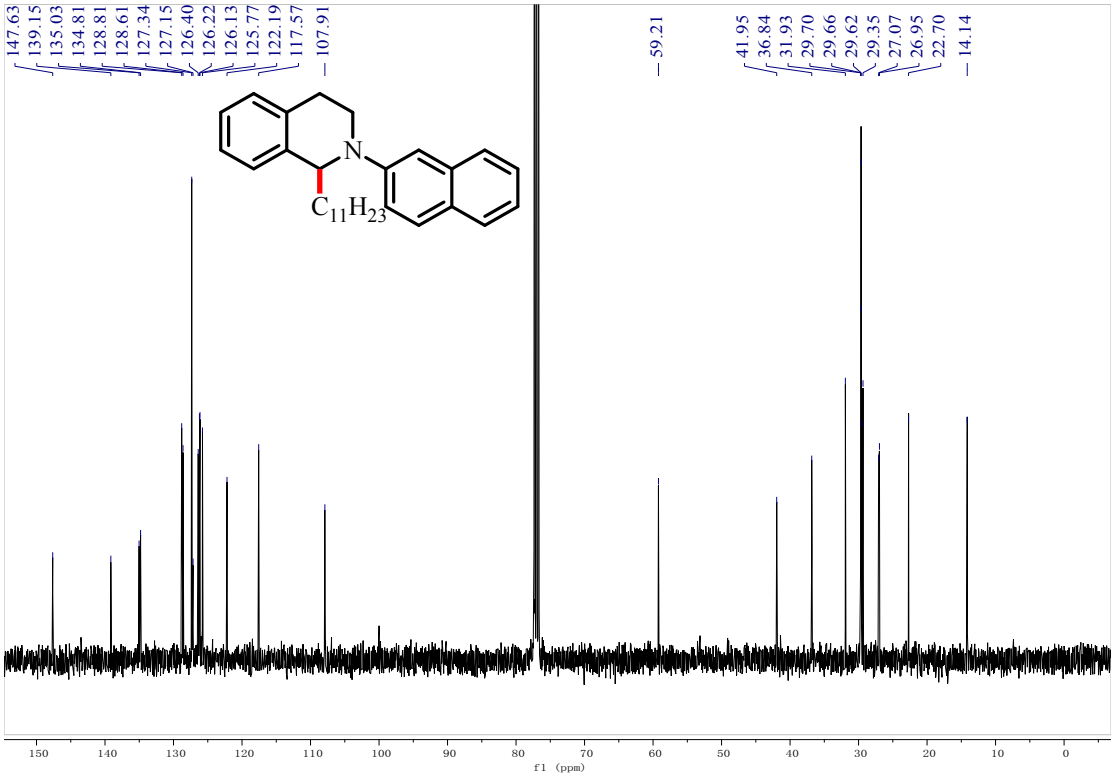
^{13}C NMR spectrum of compound **3ia**



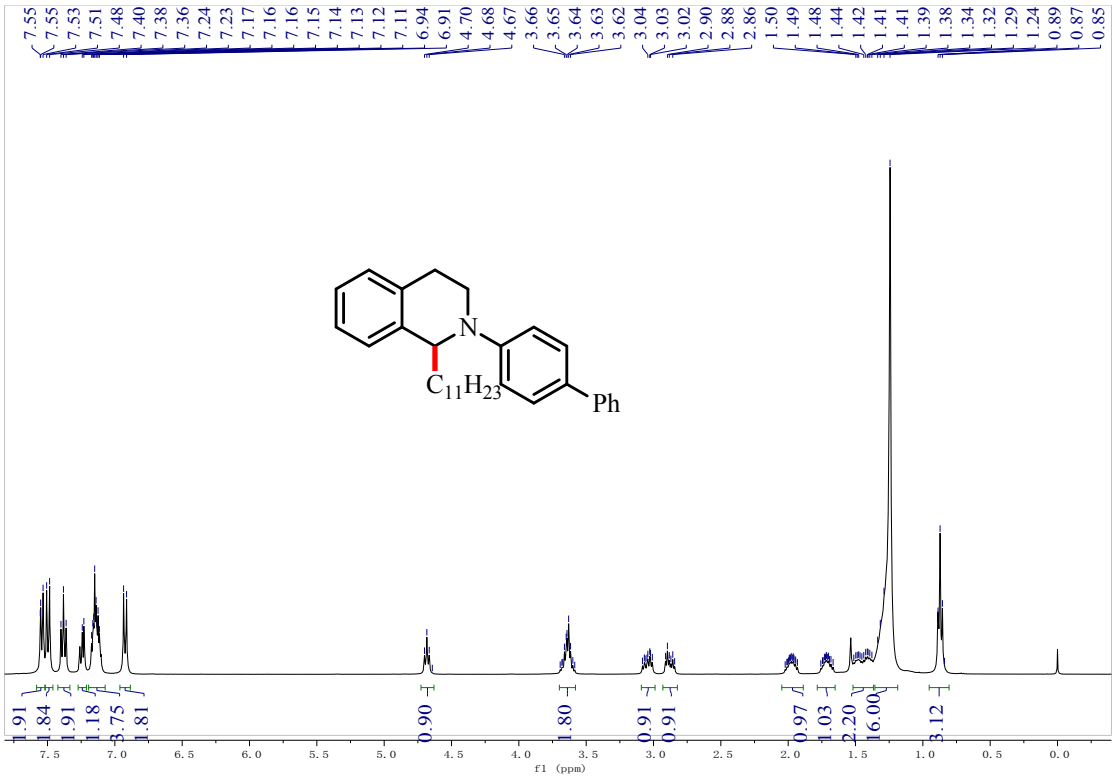
^{1}H NMR spectrum of compound **3ja**



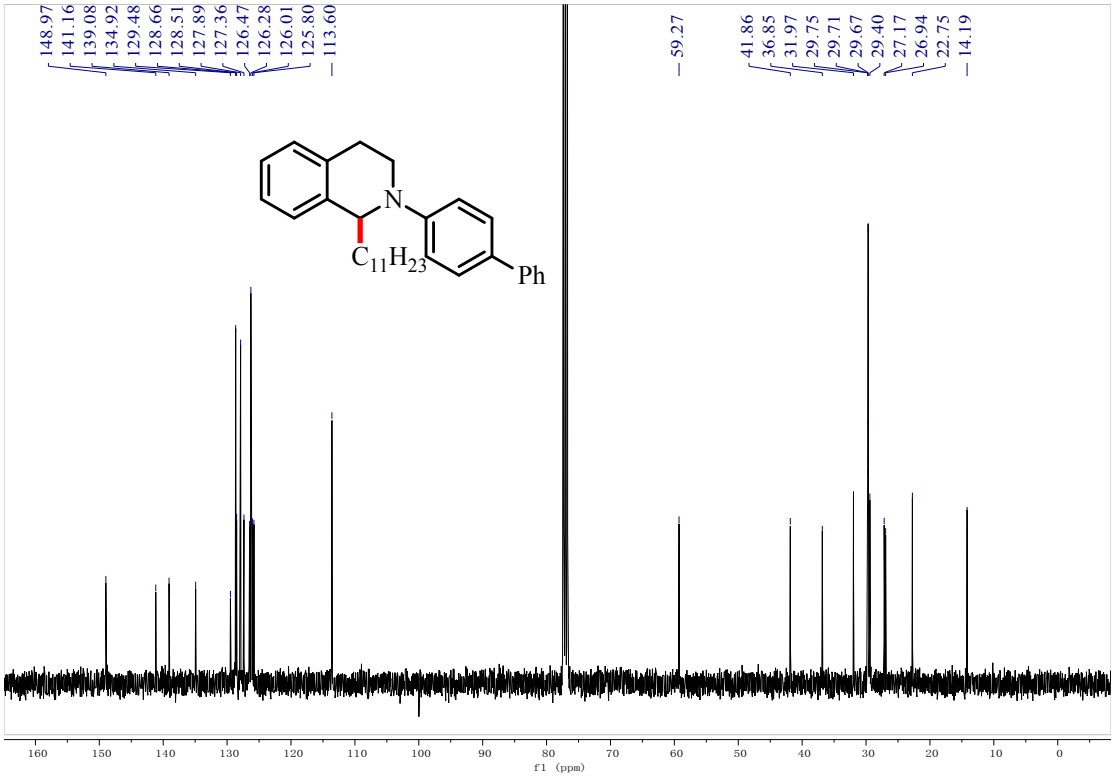
^{13}C NMR spectrum of compound **3ja**



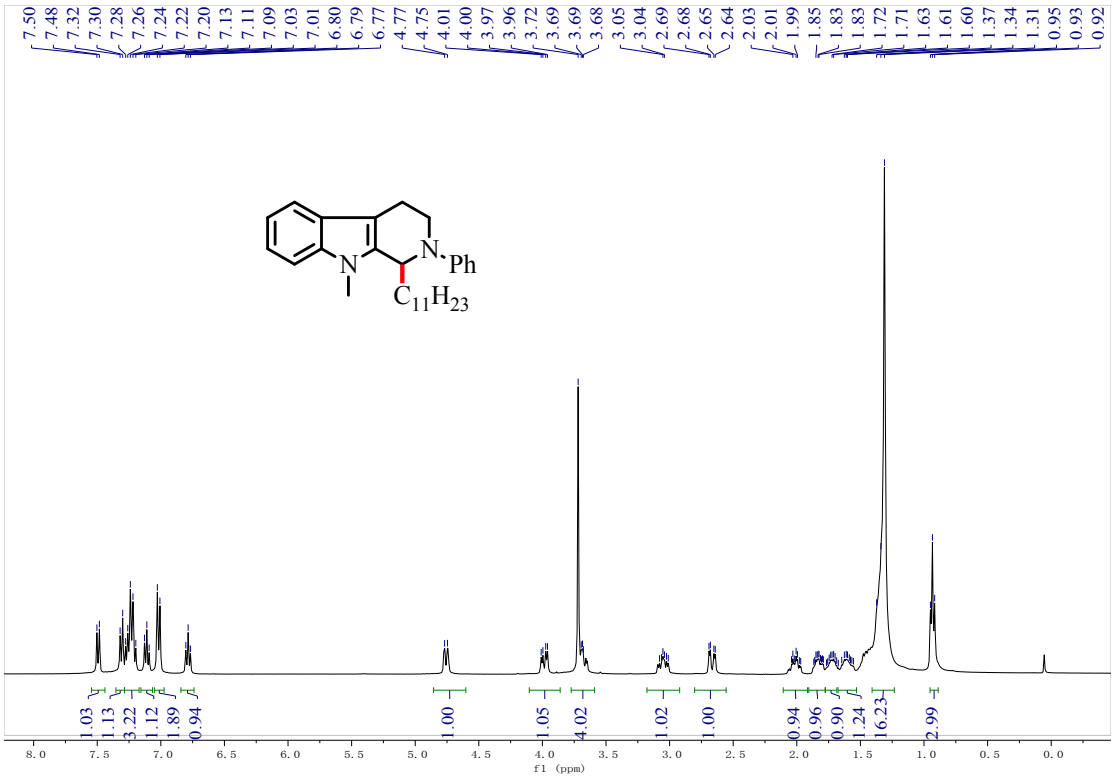
^{1}H NMR spectrum of compound **3ka**



^{13}C NMR spectrum of compound **3ka**



^{1}H NMR spectrum of compound **3na**



^{13}C NMR spectrum of compound **3na**