Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photo-Driven Traceless Directed Electron-Donor-Acceptor (EDA) Complex Initiated Radical Coupling/Dehydrogenation Tandem Reaction: Access to 1-Allyl/Benzyl-3,4-dihydroisoquinoline

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial sources (Adamas-beta, Energy Chemical) and used without further purification.

NMR spectrum

^{1}H and ^{13}C NMR spectra were collected on 400 or 600 MHz NMR spectrometers (Varian Inova-400 or Bruker Avance NEO 600). Chemical shifts for protons were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to residual protium in the NMR solvents ($CDCl_3$ = δ 7.26). Chemical shifts for carbon resonances were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the carbon resonances of the solvents ($CDCl_3$ = δ 77.16). The following abbreviations were used to describe peak splitting patterns when appropriate: s=singlet, d=doublet, t=triplet, q=quartet, sept=septet, m=multiplet, dd=doublet of doublets, dt=doublet of triplet, ddd=doublet of doublets of doublets, Coupling constants *J* were reported in hertz unit (Hz).

Melting point

Melting point (M.P.) was recorded on BÜCHI (M-560).

HRMS

High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Scientific QExactive.

Column Chromatography

Analytical thin layer chromatography (TLC) was performed on 0.20 mm silica gel $60F_{254}$ plates. Column chromatography was undertaken on silica gel (300-400 mesh)using a proper eluent.

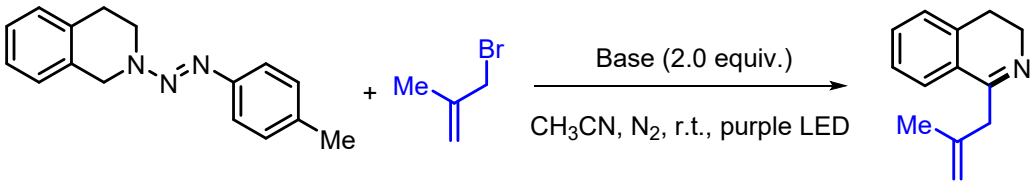
UV light

Visualization on TLC was achieved by the use of UV light (254 nm).

2. Experimental procedures

2.1 Optimization of reaction conditions

2.1.1 Table S1. Base screening[a]

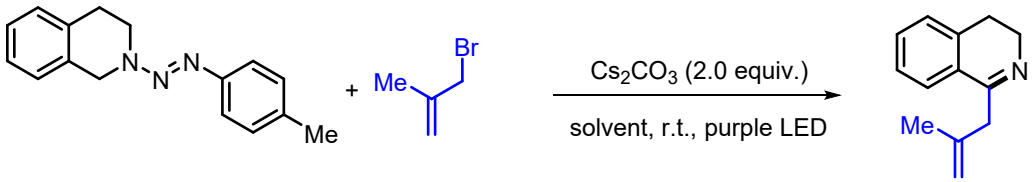


1a **2a** **3a**

Entry	Base	Yield/%[b]
1	**Cs_2CO_3**	**23**
2	K_2CO_3	20
3	Na_2CO_3	12
4	KOH	trace
5	NaOAc	trace
6	$NaHCO_3$	trace
7	DBU	trace
8	DABCO	trace
9	Et_3N	trace

[a]Reaction Conditions: **1a** (0. 2 mmol), **2a** (0.4 mmol), Base (2.0 equiv.), CH_3CN (2 mL), rt, 24 h, N_2, 10 W purple LED. [b]Yields of isolated products are reported.

2.1.2 Table S2. Solvent screening[a]

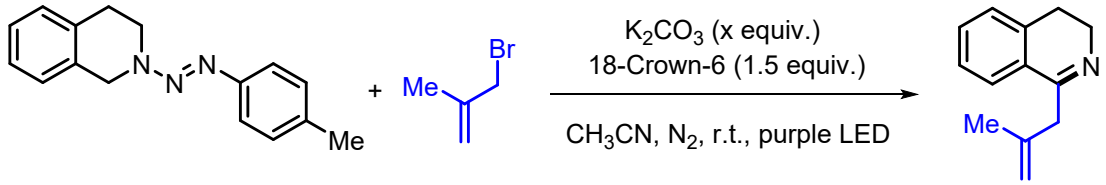


1a **2a** **3a**

Entry	Solvent	Yield/%[b]
1	DCM	N.D
2	1,4-Dioxane	trace
3	NMP	trace
4	EtOAc	trace
5	EtOH	trace
6	Toluene	trace
7	THF	trace
8	DMSO	trace
9	DMA	20
10	DMF	21
11	**CH_3CN**	**23**

[a]Reaction Conditions: **1a** (0. 2 mmol), **2a** (0.4 mmol), Cs_2CO_3 (2.0 equiv.), Solvent (2 mL), rt, 24 h, N_2, 10 W purple LED. [b]Yields of isolated products are reported.

2.1.3 Table S3. Screening of the amount of base[a]

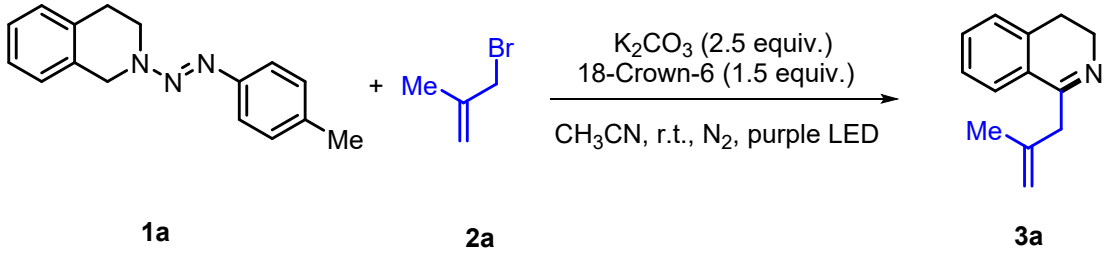


1a **2a** **3a**

Entry	Base	Solvent	Yield/%[b]
1	K_2CO_3(1.5 equiv.)	CH_3CN	45
2	K_2CO_3(2.0 equiv.)	CH_3CN	50
3	K_2CO_3(2.25 equiv.)	CH_3CN	41
4	**K_2CO_3(2.5 equiv.)**	**CH_3CN**	**63**
5	K_2CO_3(2.75 equiv.)	CH_3CN	56
6	K_2CO_3(3.0 equiv.)	CH_3CN	45

[a]Reaction Conditions: **1a** (0. 2 mmol), **2a** (0.4 mmol), K_2CO_3 (x equiv.), 18-crown-6 (1.5 equiv.), CH_3CN (2 mL), rt, 36 h, N_2, 10 W purple LED. [b]Yields of isolated products are reported.

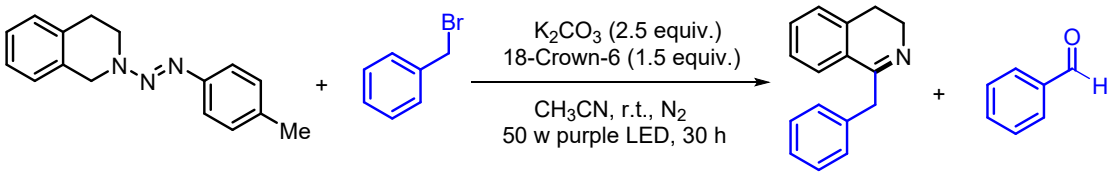
2.2 General procedure for the synthesis of products 3a-3y (taking 3a as an example)



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

(E)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (0.20 mmol, 1.0 equiv.), 3-bromomethylpropene **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.5 mmol, 2.5 equiv.) and 18-crown-6 (0.3 mmol, 1.5 equiv.), CH_3CN (2 mL), under N_2 atmosphere (1 atm) irradiated with 10 W purple LED (395 nm) at room temperature The reaction was carried out for 36 h. After the reaction is completed, the reaction mixture was filtered to remove inorganic salts, and wash with ethyl acetate three times. The filtrate was concentrated *in vacuo*, and the residue was purified by silica gel column chromatography eluting with a mixed solvent of petroleum ether and ethyl acetate (15:1-5:1, v/v) to afford the pure product **3a** with a yield of 63%.

2.3 Large-scale experiments



1a, 2.0 mmol **2c**, 4.0 mmol **3c**, 155 mg 35% yield **4a,** 50% yield

(*E*)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (2.0 mmol, 1.0 equiv.), benzyl bromide **2c** (4.0 mmol, 2.0 equiv.), K_2CO_3 (5 mmol, 2.5 equiv.) and 18-crown-6 (3 mmol, 1.5 equiv.), CH_3CN (10 mL), under N_2 atmosphere (1 atm) irradiated with 50 W purple LED (395 nm) at room temperature The reaction was carried out for 30 h. After the reaction is completed, the reaction mixture was filtered to remove inorganic salts, and wash with ethyl acetate three times. The filtrate was concentrated in *vacuo*, and the residue was purified by silica gel column chromatography eluting with a mixed solvent of petroleum ether and ethyl acetate (15:1-5:1, v/v) to afford the pure product **3c** and **4a** with yields of 35% and 50%, respectively. The pure product **4a** was consistent with previous reports[1-3].

3 Mechanistic studies

3.1 ON/OFF experiments

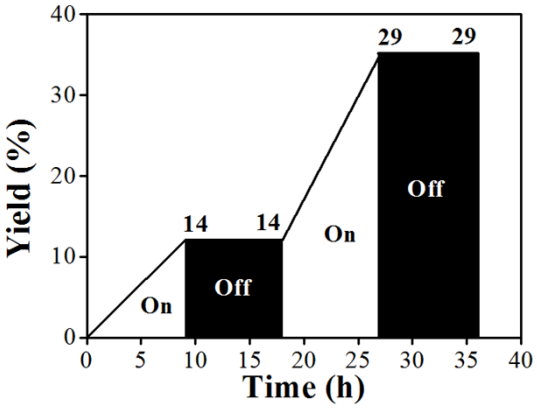


Figure S1. "ON/OFF" experiment

In order to further prove the effect of visible light irradiation, the "on/off" experiment by using model reaction was carried out. Under standard conditions, the reaction time is 9 h when the lamp is turned on and 9 h when the lamp is turned off. Loop twice. The results show that light plays an important role in the reaction system (Figure S1).

3.2 UV−vis spectroscopic measurements

The UV/vis absorption spectra of (*E*)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (0.02 M), 3-bromomethylpropene **2a** (0.04 M) in CH_3CN were recorded in 1 cm path quartz cuvettes by using a Thermo Nanodrop 2000c UV/Vis spectrophotometer, respectively (Figure S2-1).

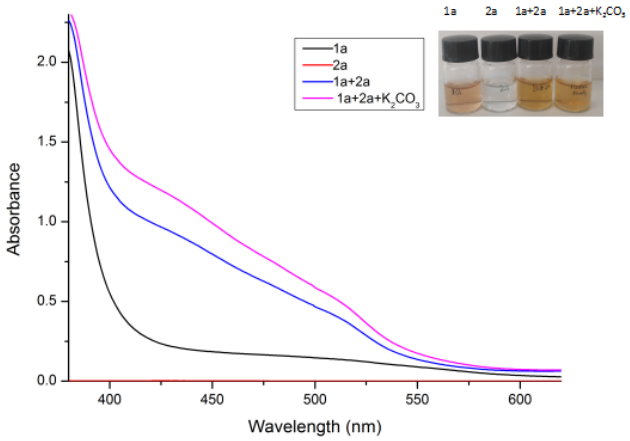


Figure S2-1. UV−vis spectroscopic measurements

Similarly, Figure S2-2 shows the light irradiation study for the mixture of **1a** and K_2CO_3 in CH_3CN. Thereafter, the quartz cuvette was kept under irradiation of 10 W

purple LEDs for 5 minutes and the absorption spectra were recorded immediately. This process was repeated for obtaining the absorption spectra after consecutive 5 min cycles of irradiation with the light source. As shown in Figure S2-2, although K_2CO_3 does not show significant UV-vis absorption alone in the visible light region, when **1a** and its mixture are not irradiation, UV-vis absorption occurs; And after irradiation, it shows a redshift. This indicates the possibility of interaction between carbonate and **1a**, leading to photoinduced cross-species SET[4].

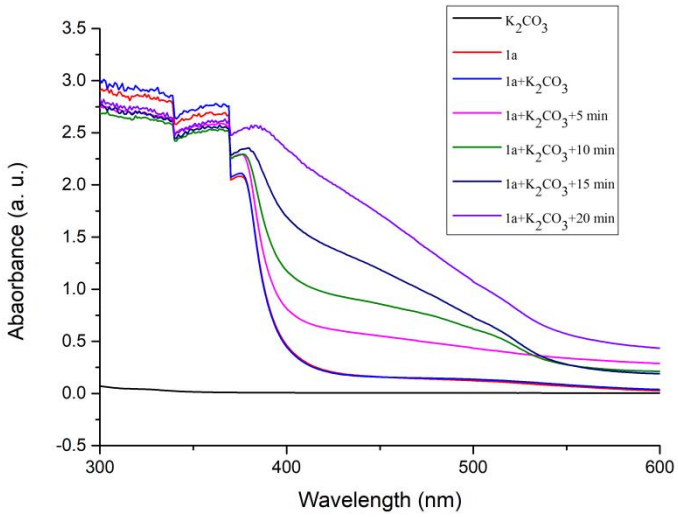
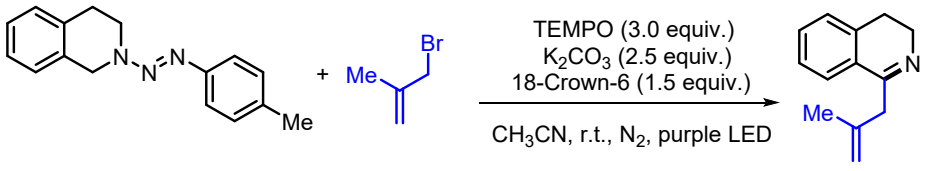


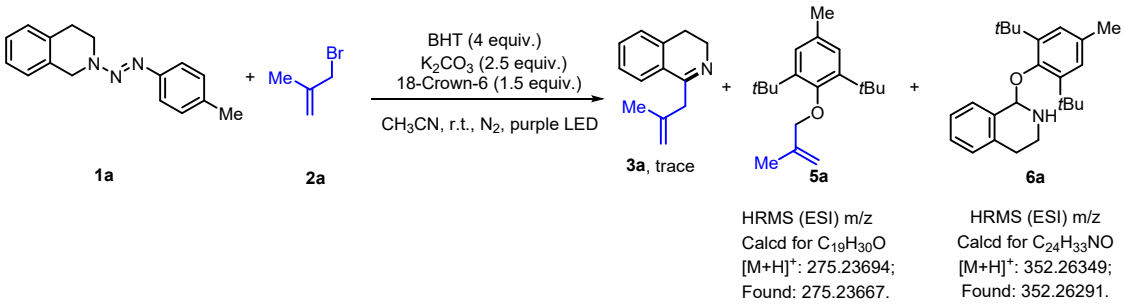
Figure S2-2. UV−vis spectroscopic measurements

3.3 Free radical trapping experiment

(*E*)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (0.20 mmol, 1.0 equiv.), 3-bromomethylpropene **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.5 mmol, 2.5 equiv.) and 18-crown-6 (0.3 mmol, 1.5 equiv.), TEMPO (0.6 mmol, 3.0 equiv.) or BHT(0.8 mmol, 4.0 equiv.), CH_3CN (2 mL), under N_2 atmosphere (1 atm) irradiated with 10 W purple LED (395 nm) at room temperature. The reaction was carried out for 36 h. The intermediates **5a** and **6a** were captured by free radical trapping agents and detected by high-resolution mass spectrometry (Figure S3).



1a **2a** **3a**, 25%



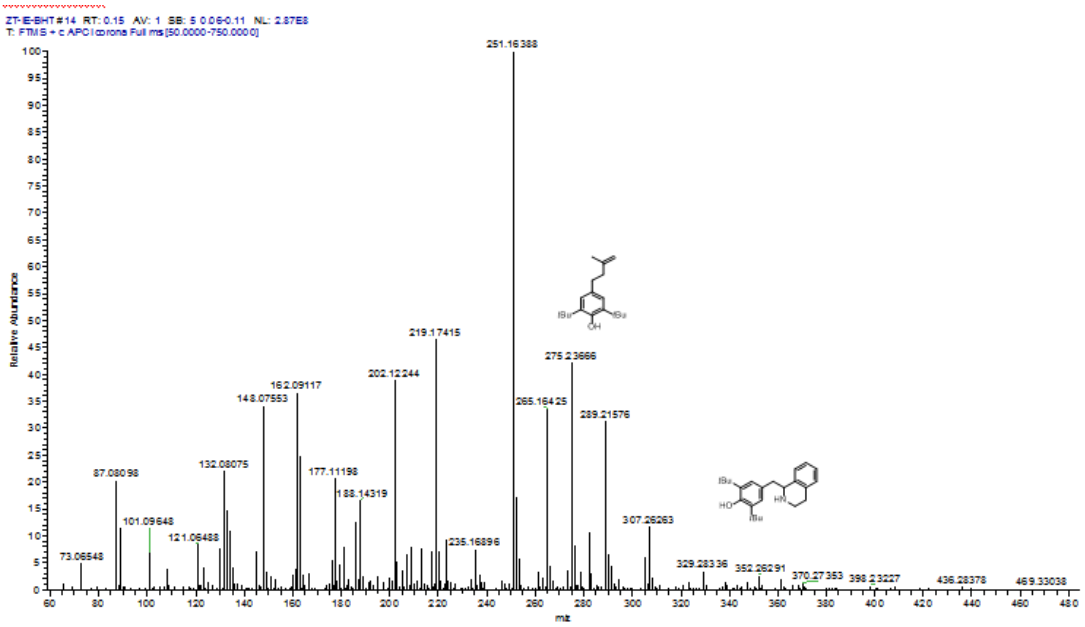
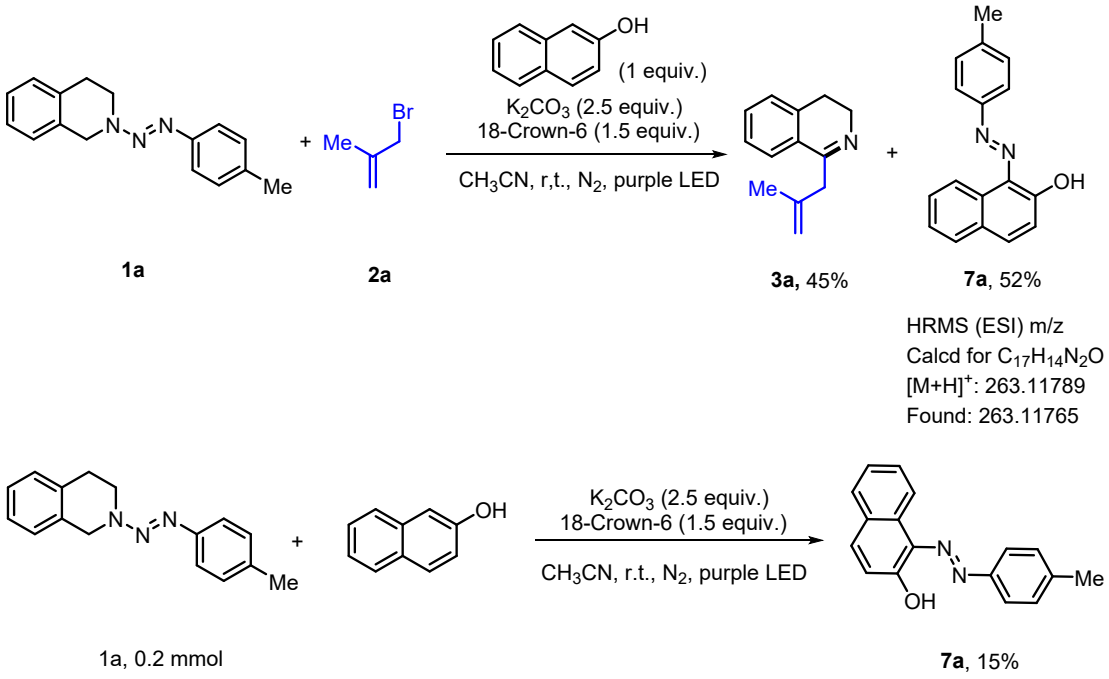


Figure S3. Free radical trapping experiment

3.4 Aryl diazo cation capture experiment

(*E*)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (0.20 mmol, 1.0 equiv.), 3-bromomethylpropene **2a** (0.4 mmol, 2.0 equiv.), *β*-naphthol (0.20 mmol, 1.0 equiv.), K_2CO_3 (0.5 mmol, 2.5 equiv.) and 18-crown-6 (0.3 mmol, 1.5 equiv.), CH_3CN (2 mL), under N_2 atmosphere (1 atm) irradiated with 10 W purple LED (395 nm) at room temperature. The reaction was carried out for 36 h. The desired product **3a** was obtained in 45% isolated yield and the captured diazo cation sideproduct (*E*)-1-(*p*-tolyldiazenyl)naphthalen-2-ol (**7a**) [5]was afforded in 52% isolated yield, and demonstrated through high-resolution mass spectrometry. In addition, in order to further prove that the diazo aryl group originates from the self-decomposition of 1a, we only added 1a and naphthol to the reaction system. In the end, we obtained the product of diazotization with a yield of 15%. Based on the above experiments, we believe that naphthol can be chosen as the capture agent for diazo aryl groups (Figure S4).



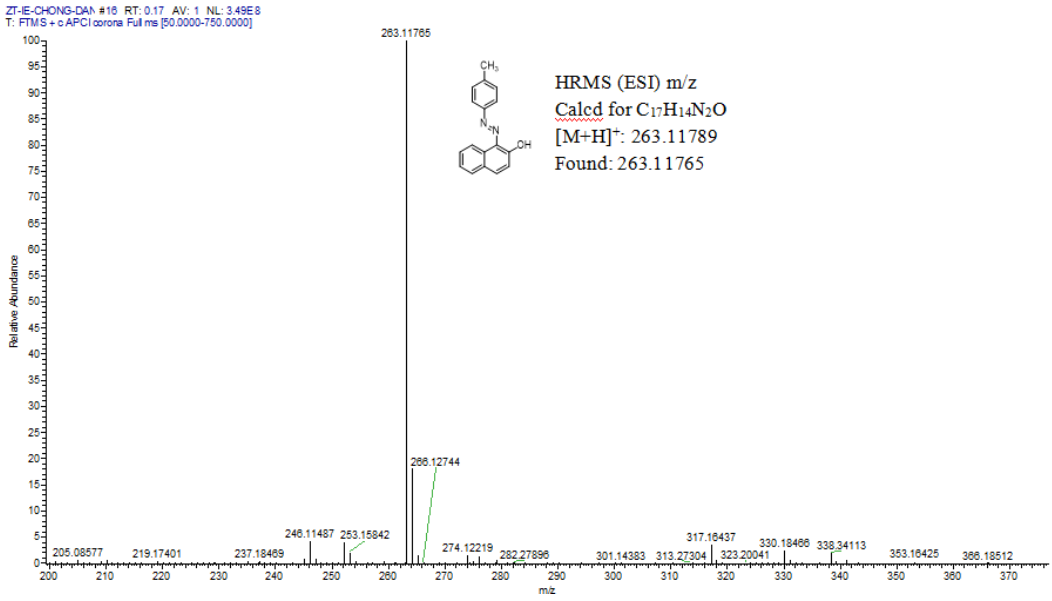
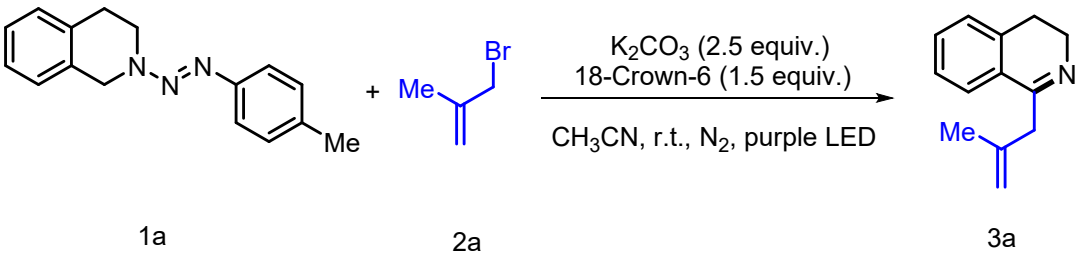


Figure S4. Aryl diazo cation capture experiment

3.5 H_2 detection experiments

In order to demonstrate the release of H_2 during this photochemical procedure, the model reaction of (*E*)-2-(*p*-toluenediazenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (0.20 mmol, 1.0 equiv.), 3-bromomethylpropene **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.5 mmol, 2.5 equiv.) and 18-crown-6 (0.3 mmol, 1.5 equiv.) was monitored by a H_2 detector under standard conditions. Just as shown in Figure S5, as the reaction proceeded, the H_2 was observed clearly and the concentration increased gradually.



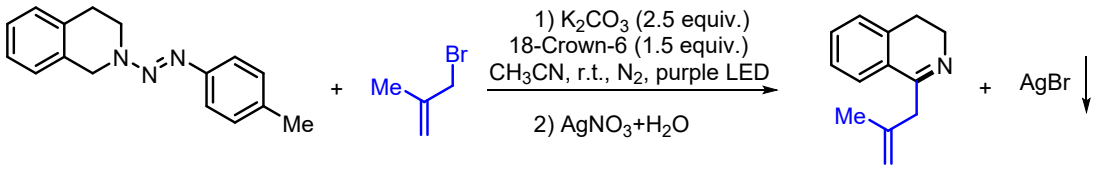
1a 2a 3a

0 min, 0 ppm | 360 min, 703 ppm | 24 h, 1000 ppm | 36 h, 1000 ppm | 48 h, 231 ppm

Figure S5. H_2 detection experiments

3.6 Br^- detection experiments

In order to demonstrate the generation of Br^- during the photocatalytic process, under standard conditions, after the reaction is completed, an aqueous solution of silver nitrate is added, and a light yellow sediment is observed, indicating the presence of Br^-(Figure S6).



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

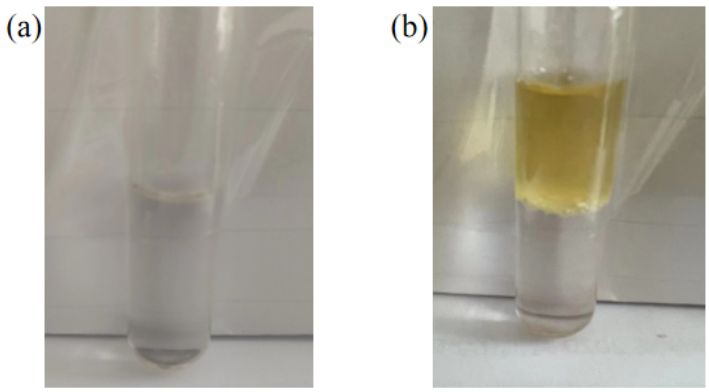
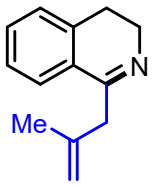
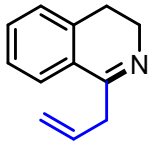


Figure S6. (a) Reaction mixture before the addition of Ag(I) solution; (b) Reaction mixture after the addition of Ag(I) solution.

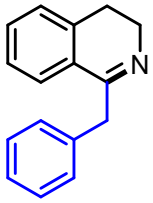
4. Analytical data



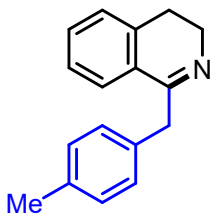
1-(2-methylallyl)-3,4-dihydroisoquinoline (3a): New compound, a yellow oil (23.3 mg, yield: 63%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 4.93 (s, 1H), 4.90 (s, 1H), 4.16 (s, 2H),3.48 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.6 Hz, 2H), 1.75 (s, 3H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.52, 141.12, 138.22, 131.75, 129.61, 128.58, 127.18, 127.00, 112.83, 52.73, 45.14, 28.26, 20.20 ppm. **HRMS (ESI) m/z** Calcd for $C_{13}H_{15}N$ $[M+H]^+$: 186.12773; Found: 186.12746.



1-allyl-3,4-dihydroisoquinoline (3b): New compound, a yellow oil (14.4 mg, yield: 42%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 5.86 (ddt, *J* = 16.1, 10.2, 5.9 Hz, 1H), 5.27-5.23 (m, 1H), 5.23-5.20 (m, 1H), 4.21 (t, *J* = 1.4 Hz, 1H), 4.20 (t, *J* = 1.4 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.40, 138.21, 133.30, 131.76, 129.58, 128.49, 127.17, 127.01, 117.58, 49.74, 45.46, 28.23 ppm. **HRMS (ESI) m/z** Calcd for $C_{12}H_{13}N$ $[M+H]^+$: 172.11208; Found: 172.11187.

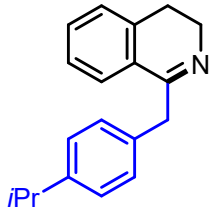


1-benzyl-3,4-dihydroisoquinoline (3c)[6]: Known compound, a yellow oil (24.3 mg, yield: 55%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.4 Hz, 1H), 7.44-7.41 (m, 1H), 7.30 -7.28 (m, 6H), 7.16 (d, *J* = 7.1 Hz, 1H), 4.80 (s, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.69, 138.17, 137.57, 131.81, 129.50, 129.50, 128.75, 128.57, 128.17, 127.56, 127.18, 127.02, 50.56, 45.47, 28.21 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.12773; Found: 222.12685.

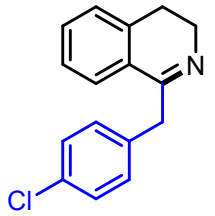


1-(4-methylbenzyl)-3,4-dihydroisoquinoline (3d): New compound, a yellow oil (25.4 mg, yield: 54%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H),

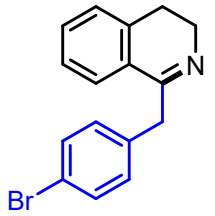
7.36 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.14 (t, J = 8.8 Hz, 3H), 4.76 (s, 2H), 3.47 (t, J = 6.6 Hz, 2H), 2.92 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.67, 138.20, 137.26, 134.55, 131.78, 129.61, 129.45, 128.60, 128.23, 127.19, 127.01, 50.28, 45.35, 28.25, 21.25 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{11}N$ $[M+H]^+$: 236.14338; Found: 236.14314.



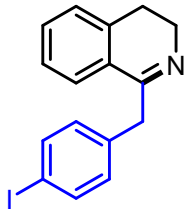
1-(4-isopropylbenzyl)-3,4-dihydroisoquinoline (3e): New compound, a yellow oil (22.1 mg, yield: 42%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (dd, J = 7.7, 1.0 Hz, 1H), 7.41 (td, J = 7.4, 1.4 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.4 Hz, 1H), 4.77 (s, 2H), 3.49 (t, J = 6.7 Hz, 2H), 2.94 (t, J = 6.7 Hz, 2H), 2.89 (sept, J = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.67, 148.25, 138.21, 134.89, 131.77, 129.62, 128.60, 128.21, 127.18, 127.01, 126.81, 50.35, 45.48, 33.93, 28.26, 24.13 ppm. **HRMS (ESI) m/z** Calcd for $C_{19}H_{21}N$ $[M+H]^+$: 264.17468; Found: 264.17435.



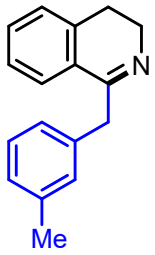
1-(4-chlorobenzyl)-3,4-dihydroisoquinoline (3f): New compound, a yellow oil (21.4 mg, yield: 42%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.31-7.28 (m, 4H), 7.16 (d, J = 7.3 Hz, 1H), 4.75 (s, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.94 (t, J = 6.6 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.73, 138.11, 136.15, 133.41, 131.96, 129.56, 129.32, 128.92, 128.58, 127.25, 127.08, 50.03, 45.59, 28.20 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{14}NCl$ $[M+H]^+$: 256.08875; Found: 256.08829.



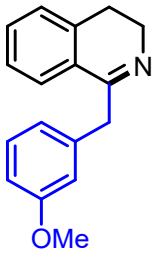
1-bromobenzyl)-3,4-dihydroisoquinoline (3g)[7]: Known compound, a yellow oil (29.9 mg, yield: 50%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (dd, J = 7.7, 1.1 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 7.5, 1.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.5 Hz, 1H), 4.74 (s, 2H), 3.47 (t, J = 6.6 Hz, 2H), 2.94 (t, J = 6.6 Hz, 2H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.77, 138.12, 136.70, 132.07, 131.99, 131.90, 129.93, 129.79, 129.33, 128.62, 127.29, 127.09, 121.52, 50.12, 45.62, 28.23 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{14}NBr$ $[M+H]^+$: 300.03824; Found: 300.03827.



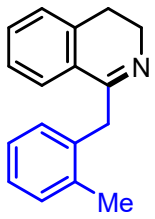
1-(4-iodobenzyl)-3,4-dihydroisoquinoline (3h): New compound, a yellow oil (39.6 mg, yield: 57%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.43 (td, *J* = 7.4, 1.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.73 (s, 2H), 3.47 (t, *J* = 6.7 Hz, 2H), 2.94 (t, *J* = 6.7 Hz, 2H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.78, 138.12, 137.88, 137.37, 131.99, 130.19, 129.32, 128.62, 127.29, 127.09, 93.03, 50.21, 45.63, 28.23 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{14}NI$ $[M+H]^+$: 348.02437; Found: 348.02332.



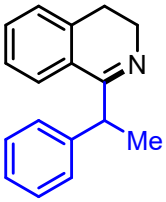
1-(3-methylbenzyl)-3,4-dihydroisoquinoline (3i): New compound, a yellow oil (24.9 mg, yield: 53%), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.4 Hz, 1H), 7.42 (td, *J* = 7.3, 1.0 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* =6.3 Hz, 3H), 7.13-7.07(m, 1H), 4.77 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.94 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.64, 138.45, 138.19, 137.48, 131.78, 129.54, 128.87, 128.60, 128.56, 128.32, 127.16, 127.01, 125.23, 50.46, 45.39, 28.20, 21.50 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{17}N$ $[M+H]^+$: 236.14338; Found: 236.14311.



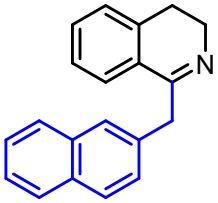
1-(3-methoxybenzyl)-3,4-dihydroisoquinoline (3j): New compound, a yellow oil (19.1 mg, yield: 38%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.77 (s, 2H), 3.78 (s, 3H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.94 (t, *J* = 6.3 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.46, 138.67, 137.26, 137.03, 134.74, 131.66, 131.43, 129.03, 128.88, 128.79, 128.59, 125.38, 121.16, 50.72, 45.33, 27.83, 21.63 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{17}NO$ $[M+H]^+$: 252.13829; Found: 252.13834.



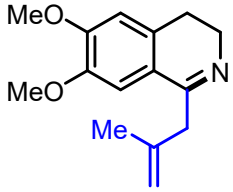
1-(2-methylbenzyl)-3,4-dihydroisoquinoline (3k): New compound, a yellow oil (25.4 mg, yield: 54%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.7 Hz, 1H), 7.43 (td, *J* = 7.4, 1.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.25-7.21 (m, 2H), 7.20-7.16 (m, 3H), 4.82 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.58, 138.15, 136.93, 135.01, 131.83, 130.71, 129.51, 128.62, 127.65, 127.21, 127.02, 126.18, 48.32, 44.98, 28.17, 19.41 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{17}N$ $[M+H]^+$: 236.14338; Found: 236.14305.



1-(1-phenylethyl)-3,4-dihydroisoquinoline (3l): New compound, a yellow oil (23.5 mg, yield: 50%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.41-7.38 (m, 3H), 7.37-7.32 (m, 3H), 7.30-7.27 (m, 1H), 7.13 (dd, *J* = 7.3, 0.6 Hz, 1H), 6.26 (q, *J* = 7.1 Hz, 1H), 3.42-3.35 (m, 1H), 3.14-3.08 (m, 1H), 2.82 (t, *J* = 6.5 Hz, 2H), 1.60 (d, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.36, 140.93, 138.14, 131.75, 129.87, 128.67, 128.59, 127.46, 127.44, 127.18, 126.93, 50.35, 40.24, 28.46, 15.81 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{17}N$ $[M+H]^+$: 236.14338; Found: 236.14304.

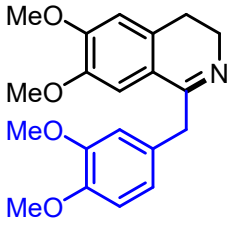


1-(naphthalen-2-ylmethyl)-3,4-dihydroisoquinoline (3m): New compound, a yellow oil (20.6 mg, yield: 38%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.84-7.81 (m, 3H), 7.77 (s, 1H), 7.51-7.44 (m, 3H), 7.42 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 4.96 (s, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.80, 138.21, 135.13, 133.44, 132.97, 131.89, 129.52, 128.71, 128.64, 127.84, 127.83, 127.24, 127.07, 127.00, 126.37, 126.31, 126.03, 50.64, 45.34, 28.24 ppm. **HRMS (ESI) m/z** Calcd for $C_{20}H_{17}N$ $[M+H]^+$: 272.14338; Found: 272.14255.

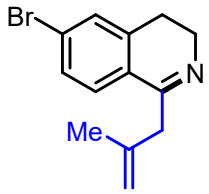


6,7-dimethoxy-1-(2-methylallyl)-3,4-dihydroisoquinoline (3n): New compound, a yellow oil (13.2 mg, yield: 27%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (s, 1H), 6.62 (s, 1H), 4.91 (s, 1H), 4.88 (s, 1H), 4.12 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.84 (t, *J* = 6.7 Hz,

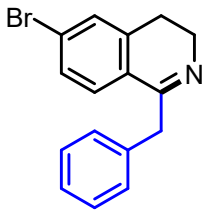
2H), 1.73 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.63, 151.97, 148.17, 141.36, 131.88, 122.20, 112.81, 110.91, 109.45, 56.27, 56.23, 52.78, 45.44, 27.92, 20.26 ppm. **HRMS (ESI) m/z** Calcd for $C_{15}H_{19}NO_2$ $[M+H]^+$: 246.14886; Found: 246.14926.



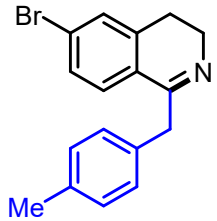
1-(3,4-dimethoxybenzyl)-6,7-dimethoxy-3,4-dihydroisoquinoline (3o)[8]: Known compound, a white soild (11.9 mg, yield: 35%), mp 98~100 °C. **^{1}H NMR (600 MHz, $CDCl_3$)** δ δ 7.65 (s, 1H), 6.87 (s, 1H), 6.86 (s, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.61 (s, 1H), 4.70 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.7 Hz, 2H) ppm. **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.70, 151.96, 149.35, 148.58, 148.13, 131.77, 130.39, 122.10, 120.63, 111.38, 111.12, 110.83, 109.40, 56.24, 56.16, 56.09, 56.04, 50.19, 45.40, 27.88 ppm. **HRMS (ESI) m/z** Calcd for $C_{20}H_{23}NO_4$ $[M+H]^+$: 342.16998; Found: 342.16965.



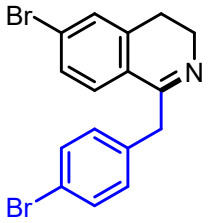
6-bromo-1-(2-methylallyl)-3,4-dihydroisoquinoline (3p): New compound, a yellow oil (21.0 mg, yield: 40%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 4.93 (s, 1H), 4.88 (s, 1H), 4.14 (s, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 1.74 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.20, 140.77, 136.95, 134.60, 131.51, 131.34, 128.76, 121.05, 113.06, 52.82, 44.95, 27.74, 20.16 ppm. **HRMS (ESI) m/z** Calcd for $C_{13}H_{14}BrN$ $[M+H]^+$: 264.03824; Found: 264.03816.



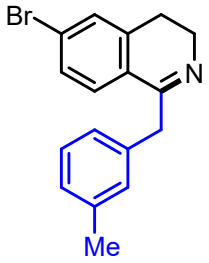
1-benzyl-6-bromo-3,4-dihydroisoquinoline (3q): New compound, a yellow oil (19.1 mg, yield: 32%), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.37-7.28 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.78 (s, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.88 (t, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.50, 137.33, 137.02, 134.77, 131.65, 131.36, 128.93, 128.89, 128.30, 127.82, 121.16, 50.79, 45.39, 27.82 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{14}BrN$ $[M+H]^+$: 300.03824; Found: 300.03857.



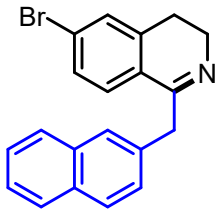
6-bromo-1-(4-methylbenzyl)-3,4-dihydroisoquinoline (3r): New compound, a yellow oil (23.8 mg, yield: 38%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 4.74 (s, 2H), 3.45 (t, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 6.1 Hz, 2H), 2.33 (s, 3H) ppm.**^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.33, 137.41, 136.92, 134.61, 134.17, 131.52, 129.49, 128.76, 128.22, 50.38, 45.14, 27.72, 21.24 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{16}BrN$ $[M+H]^+$: 314.05389; Found: 314.05469.



6-bromo-1-(4-bromobenzyl)-3,4-dihydroisoquinoline (3s): New compound, a yellow oil (26.4 mg, yield: 35%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 1.6 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.56, 136.93, 136.41, 134.93, 132.07, 131.81, 131.65, 131.14, 130.03, 128.94, 128.80, 121.78, 121.24, 50.31, 45.51, 27.80 ppm. **HRMS (ESI) m/z** Calcd for $C_{16}H_{13}Br_2N$ $[M+H]^+$: 377.94875; Found: 377.94797.



6-bromo-1-(3-methylbenzyl)-3,4-dihydroisoquinoline (3t): New compound, a yellow oil (26.3 mg, yield: 42%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13-7.09 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.88 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.46, 138.67, 137.26, 137.03, 134.74, 131.66, 131.43, 129.03, 128.88, 128.79, 128.59, 125.38, 121.16, 50.72, 45.33, 27.83, 21.63 ppm. **HRMS (ESI) m/z** Calcd for $C_{17}H_{16}BrN$ $[M+H]^+$: 314.05389; Found: 314.05408.



6-bromo-1-(naphthalen-2-ylmethyl)-3,4-dihydroisoquinoline (3u): New compound, a yellow oil (29.3 mg, yield: 42%).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 2.0 Hz, 1H), 7.83-7.81 (m, 3H), 7.75 (s, 1H), 7.53 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.49-7.43 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.93 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.47, 136.92, 134.73, 134.70, 133.40, 132.98, 131.55, 131.23, 128.81, 128.79, 127.83, 127.81, 127.08,

126.43, 126.20, 126.11, 121.06, 50.74, 45.13, 27.69 ppm. **HRMS (ESI) m/z** Calcd for $C_{20}H_{16}BrN$ $[M+H]^+$:350.05389; Found:350.05345.

5. References

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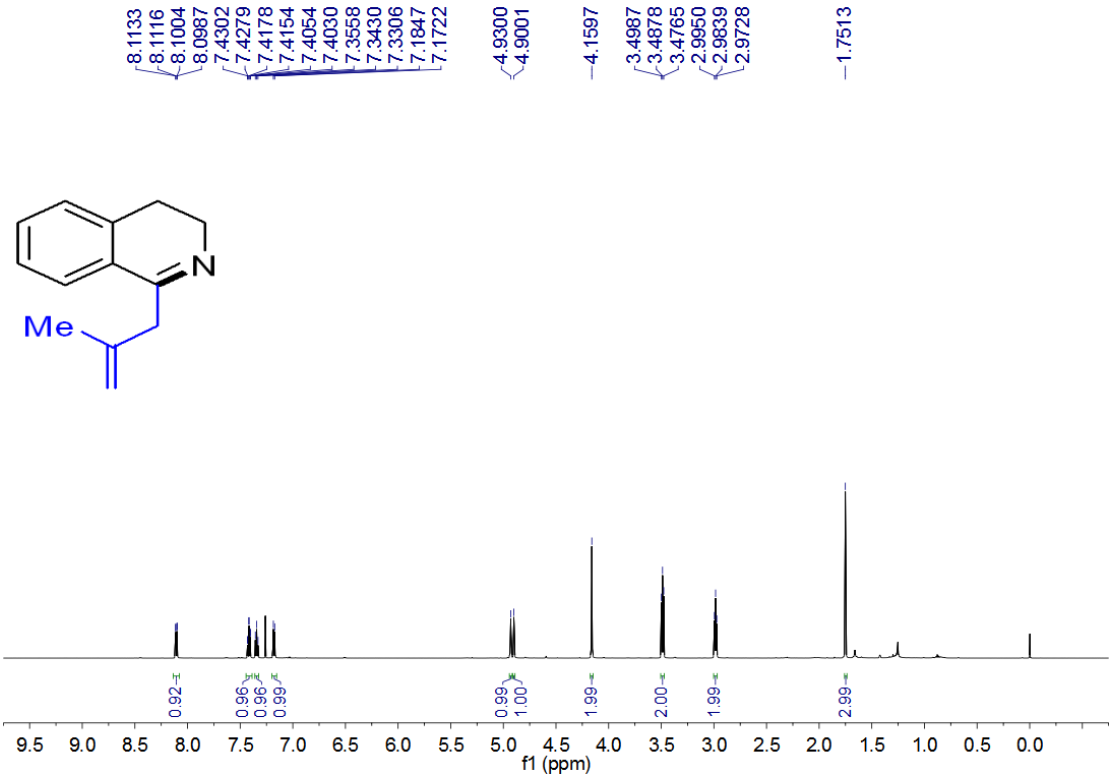
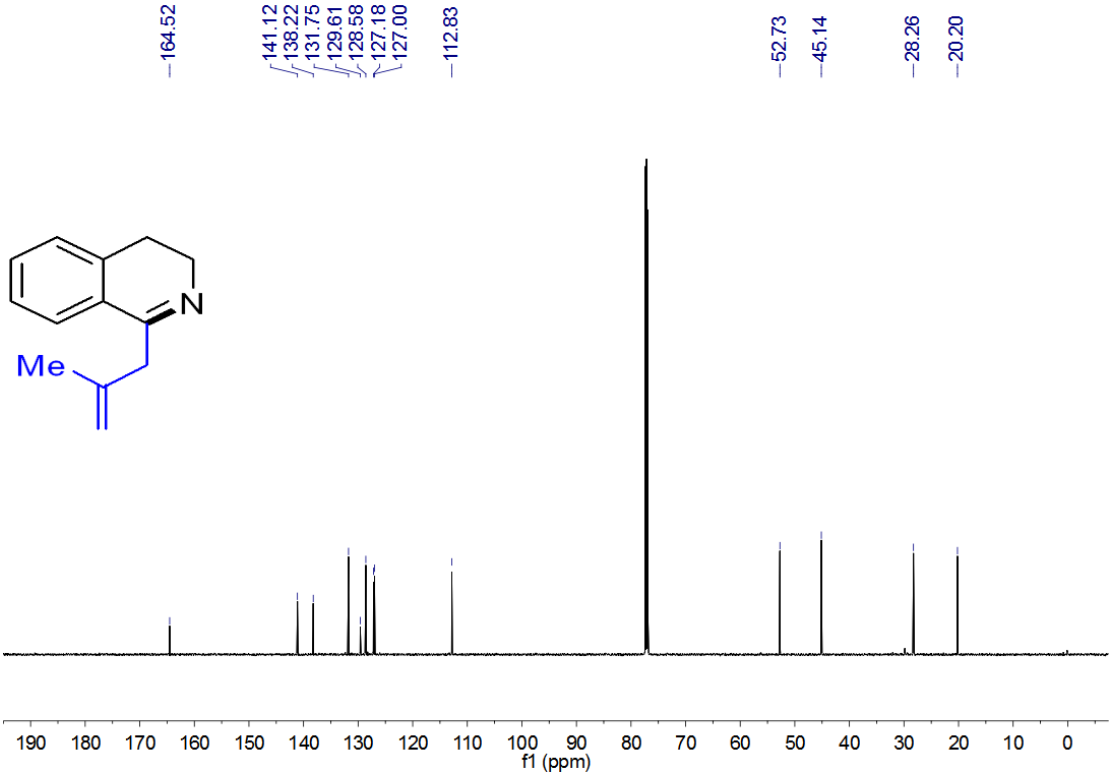
6. Copies of NMR spectra

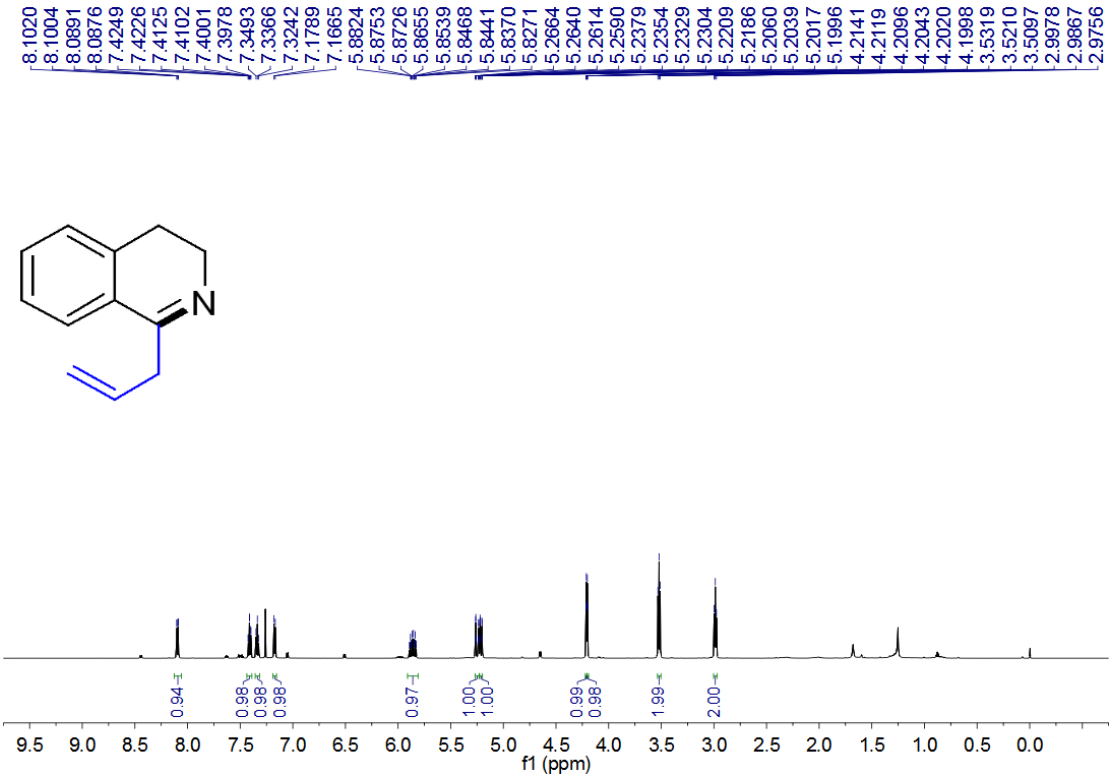
^{1}H NMR of product 3a in $CDCl_3$ (600 MHz)



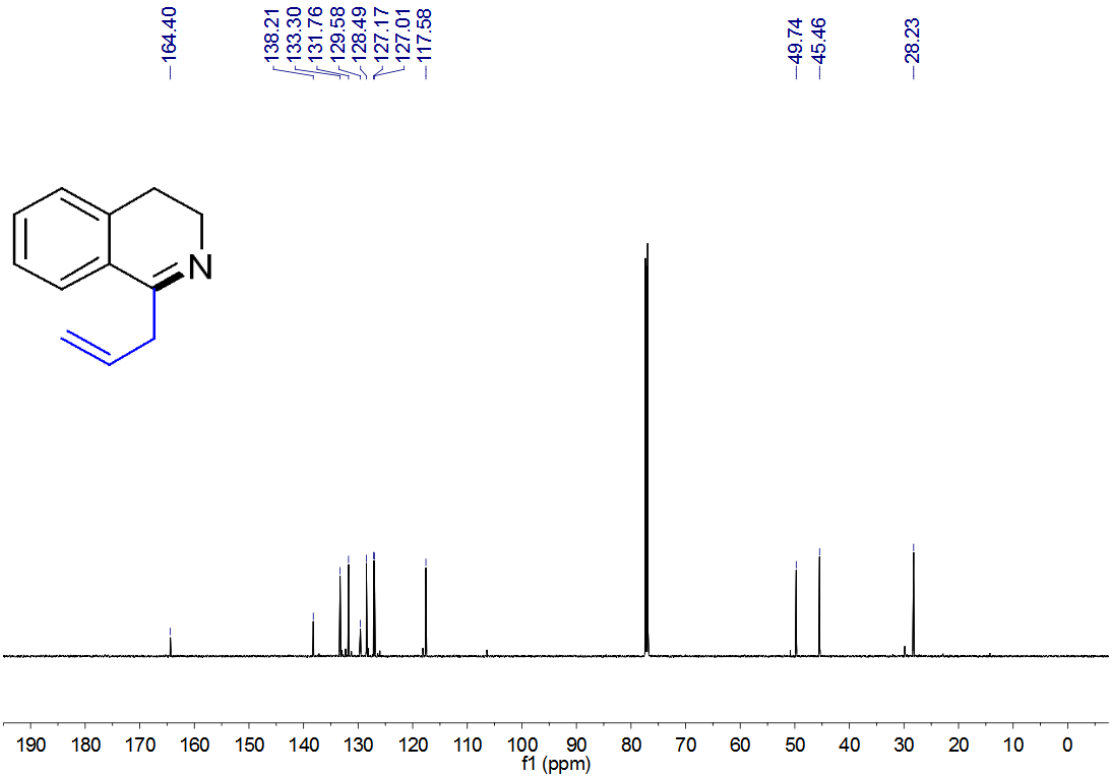
^{13}C NMR of product 3a in $CDCl_3$ (150 MHz)



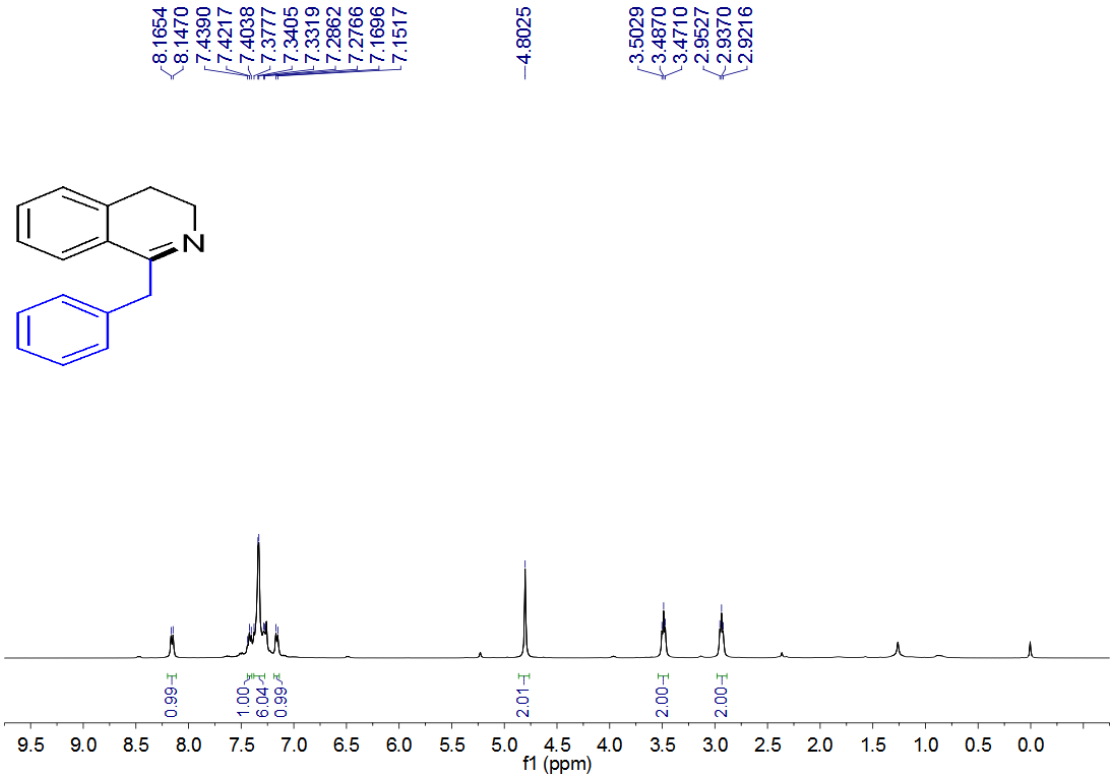
^{1}H NMR of product 3b in $CDCl_3$ (600 MHz)



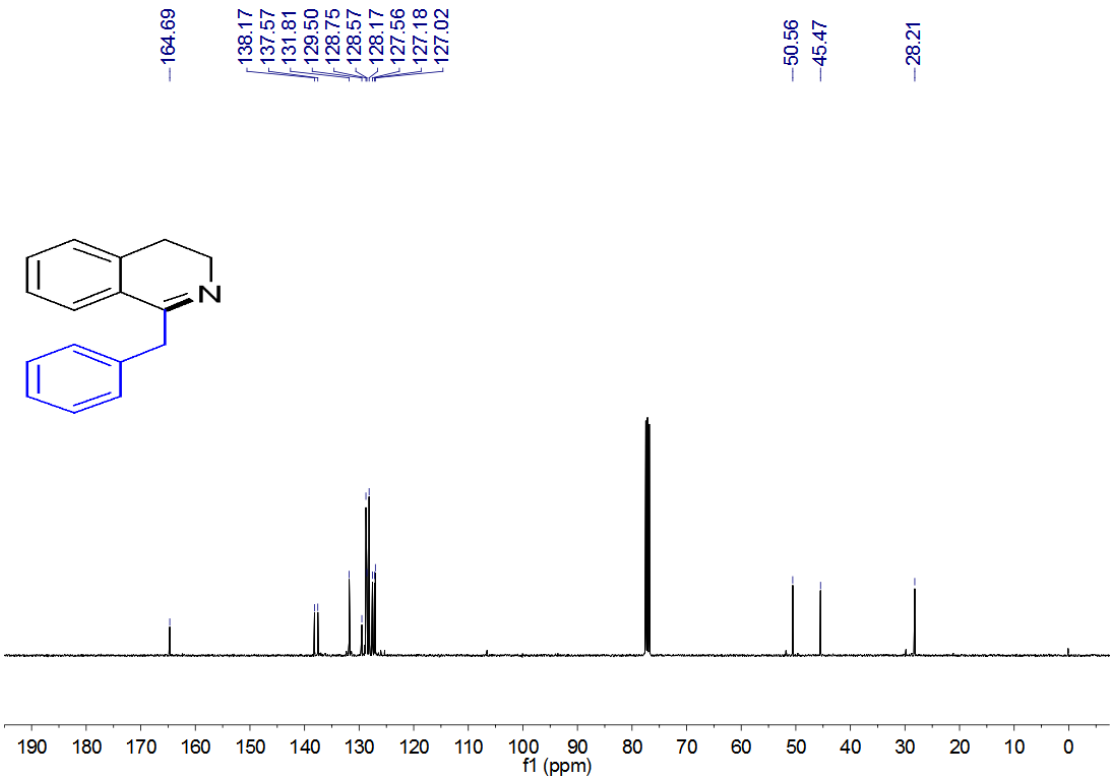
^{13}C NMR of product 3b in $CDCl_3$ (150 MHz)



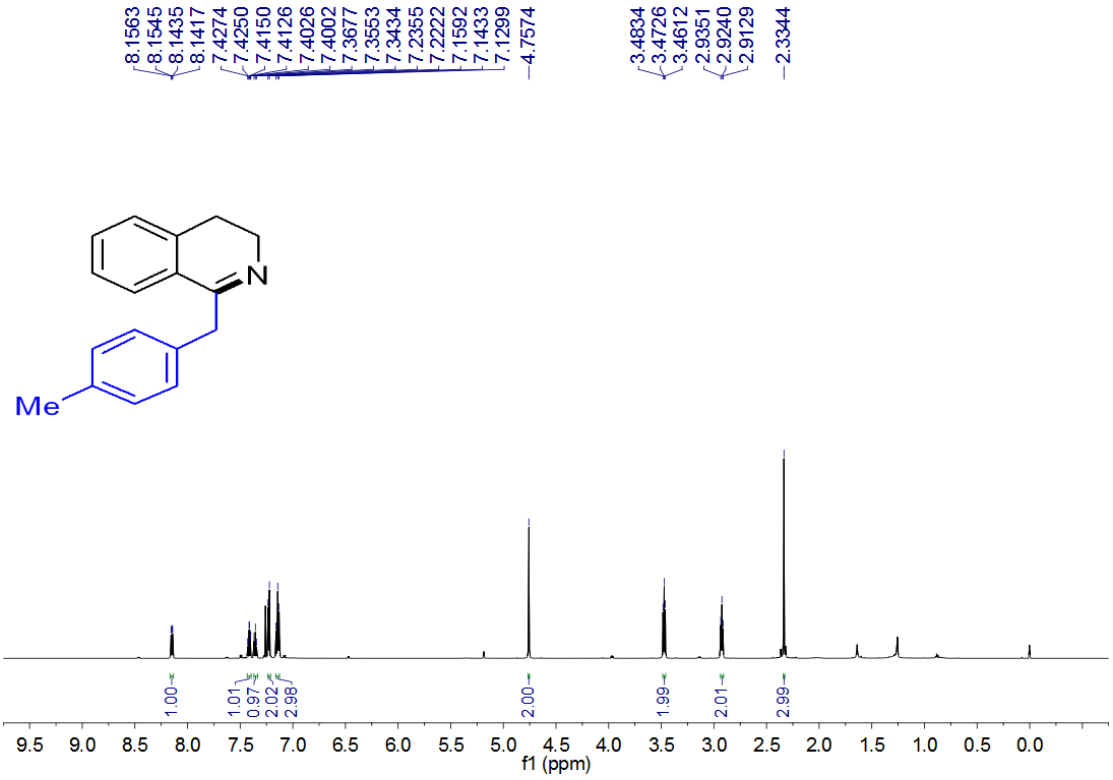
^{1}H NMR of product 3c in $CDCl_3$ (400 MHz)



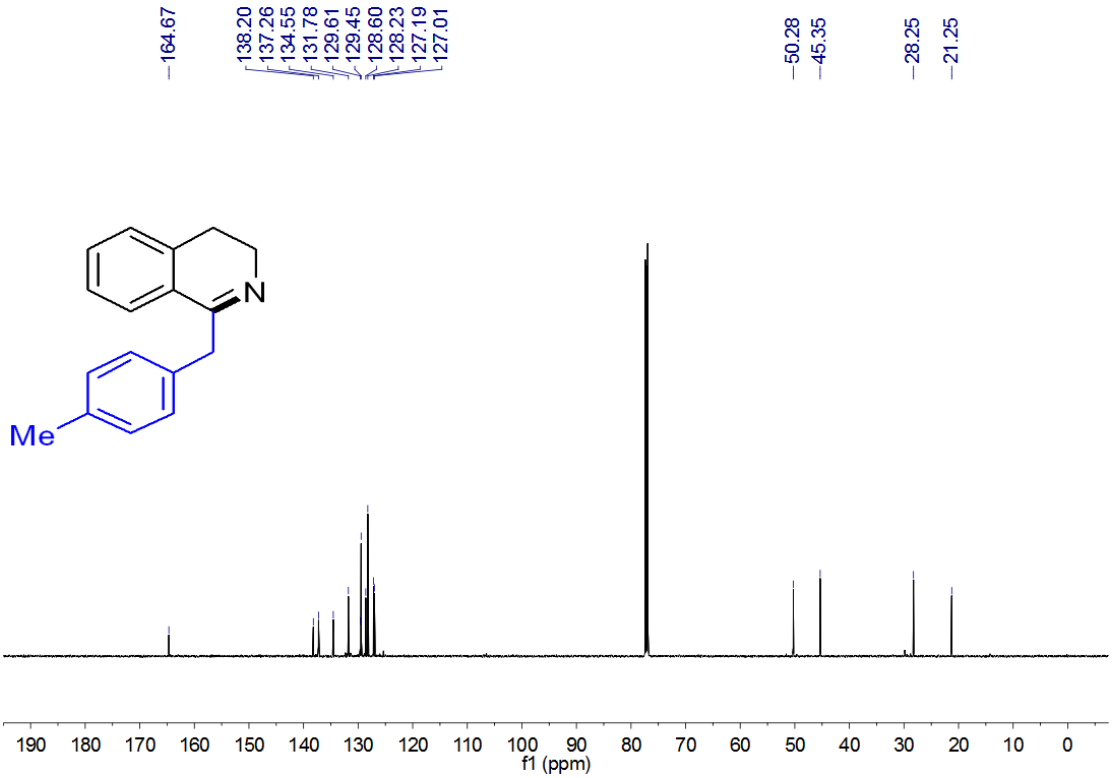
^{13}C NMR of product 3c in $CDCl_3$ (100 MHz)



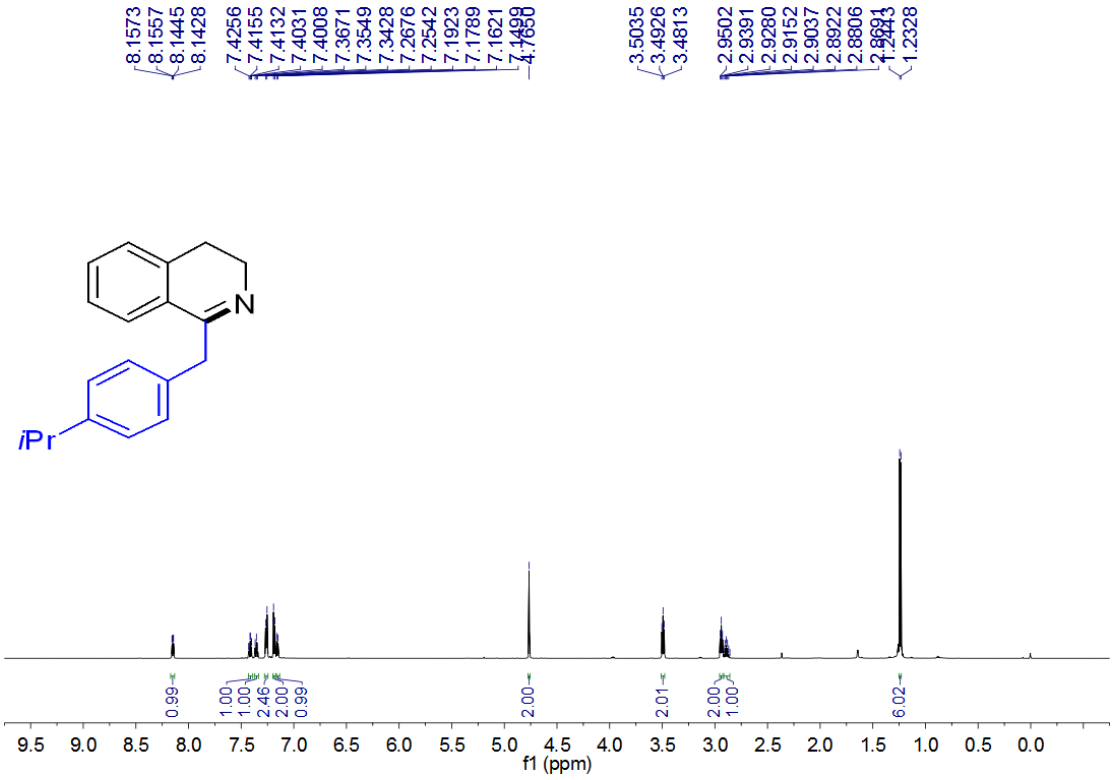
^{1}H NMR of product 3d in $CDCl_3$ (600 MHz)



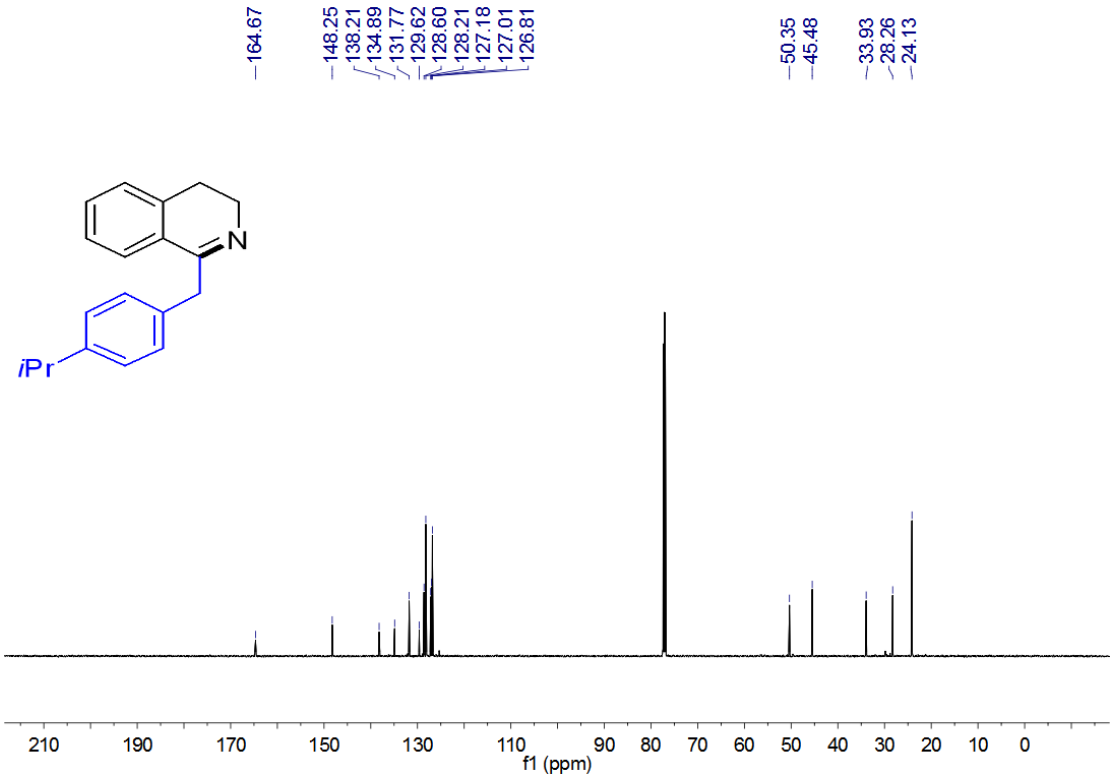
^{13}C NMR of product 3d in $CDCl_3$ (150 MHz)



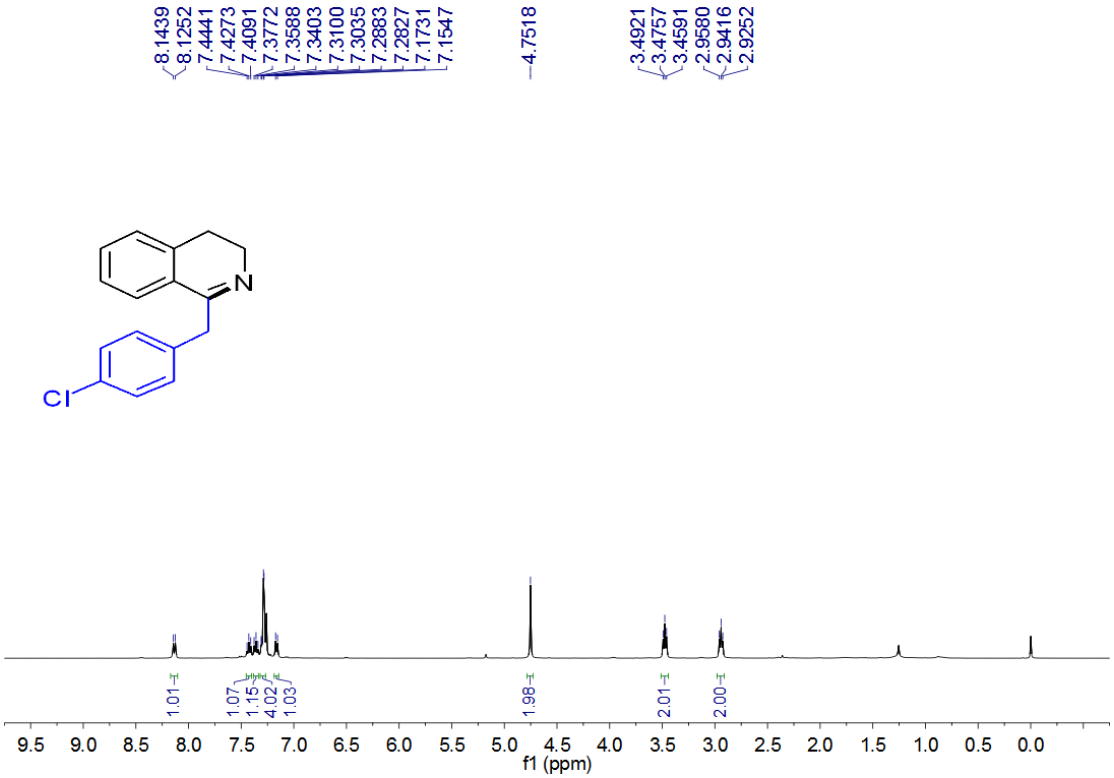
^{1}H NMR of product 3e in $CDCl_3$ (600 MHz)



^{13}C NMR of product 3e in $CDCl_3$ (150 MHz)



^{1}H NMR of product 3f in $CDCl_3$ (400 MHz)



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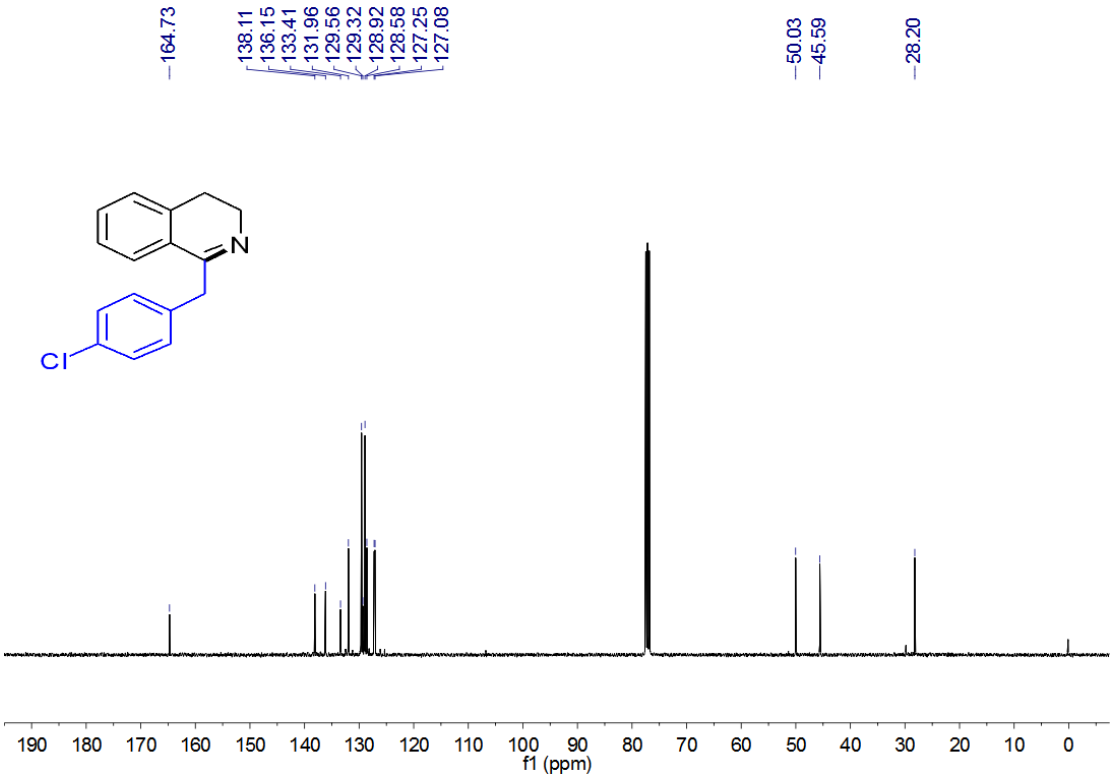

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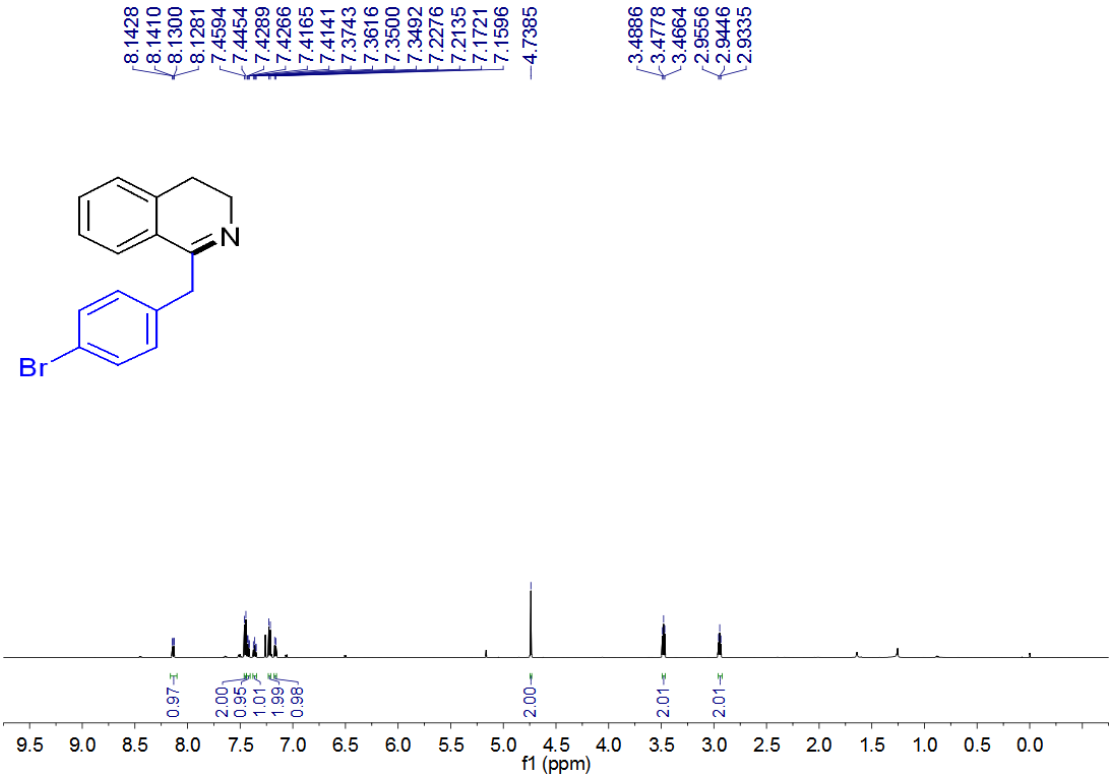
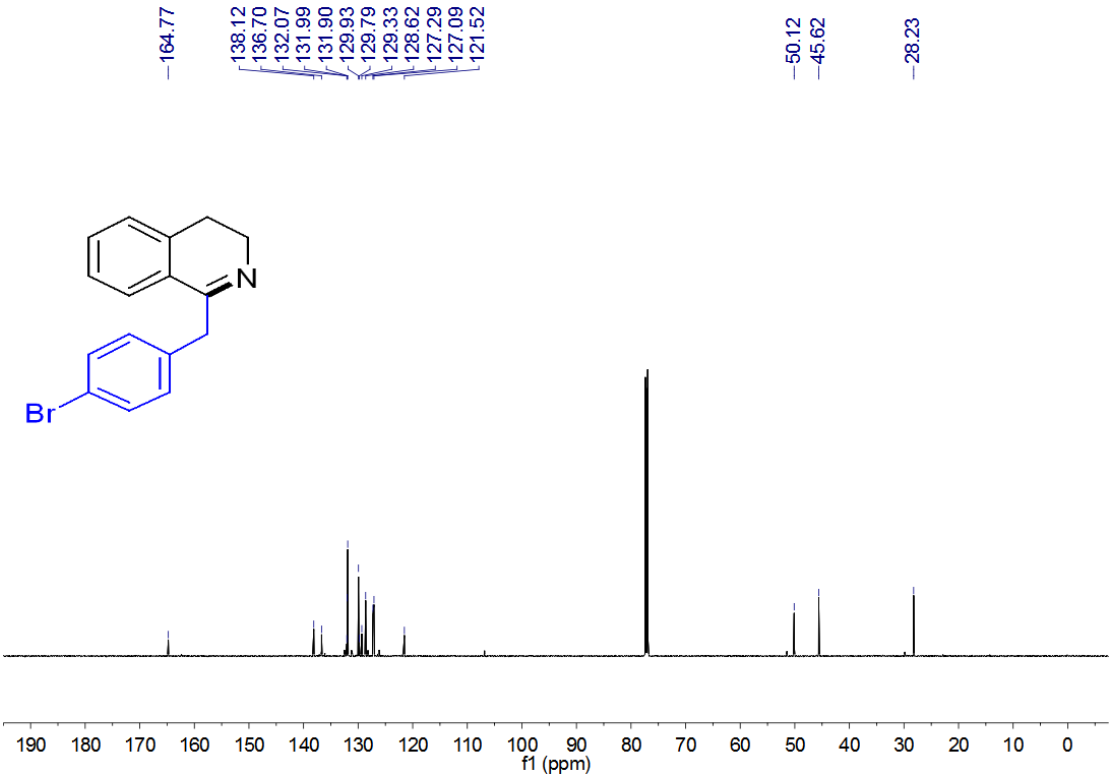
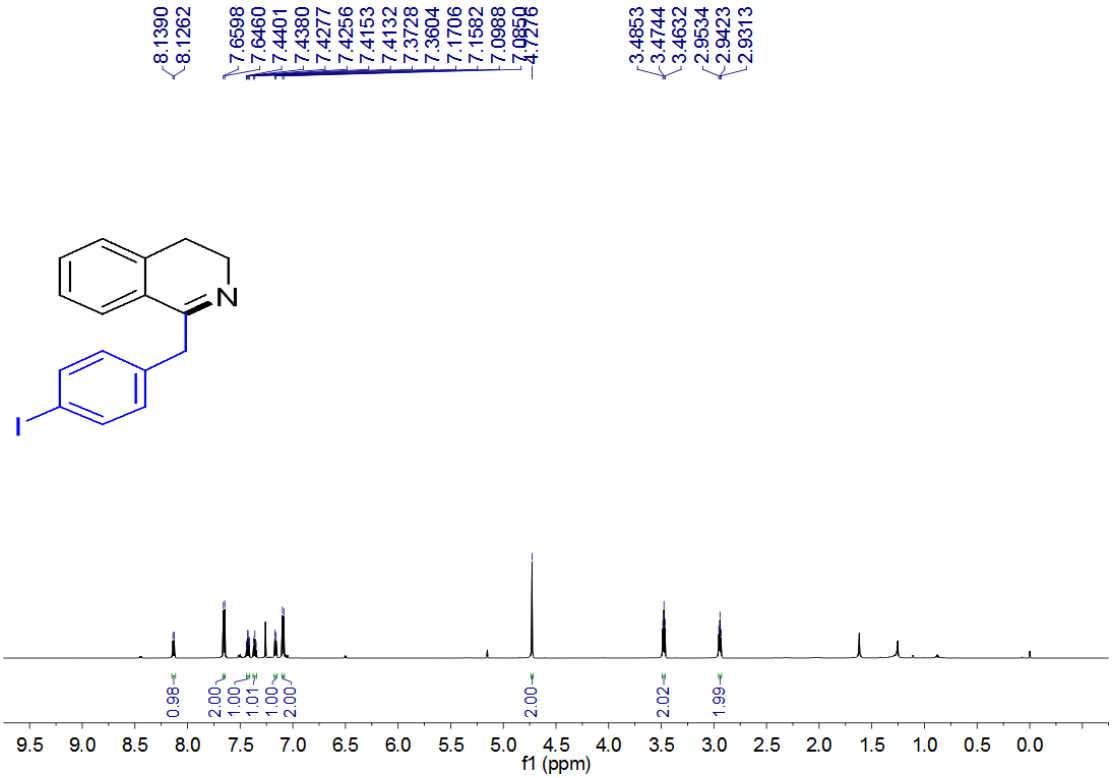


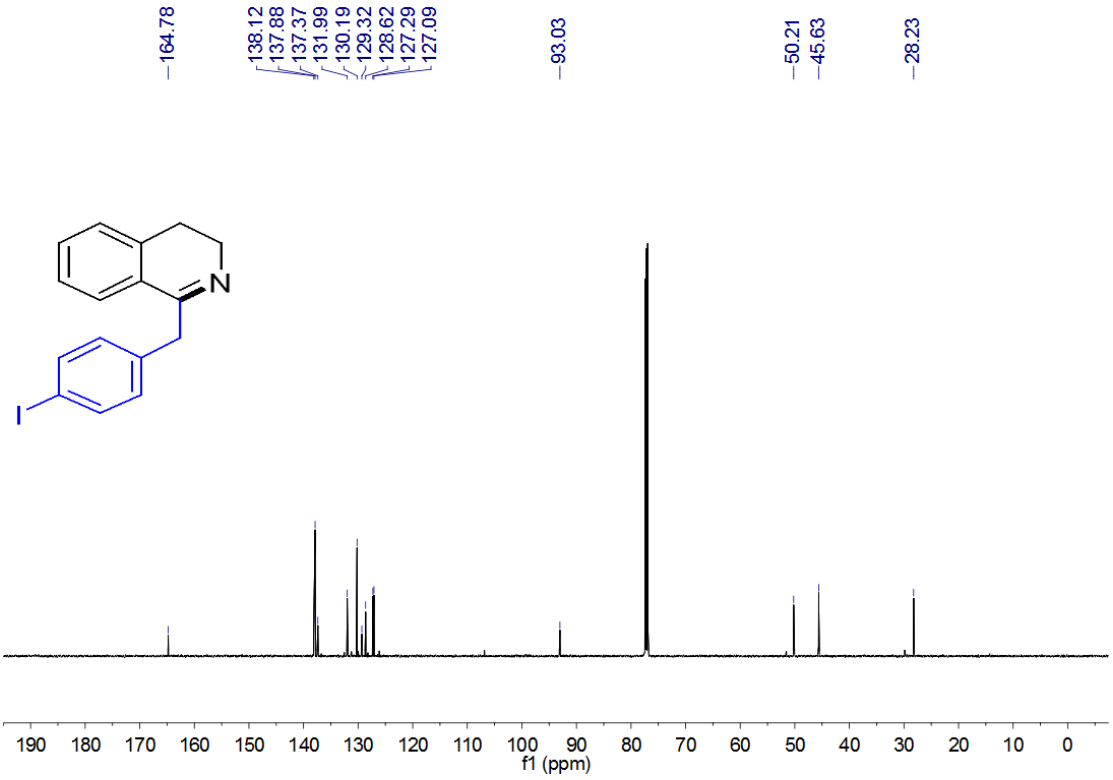
^{13}C NMR of product 3g in $CDCl_3$ (150 MHz)



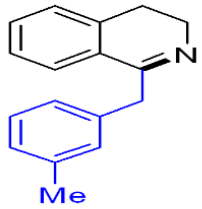
^{1}H NMR of product 3h in $CDCl_3$ (600 MHz)

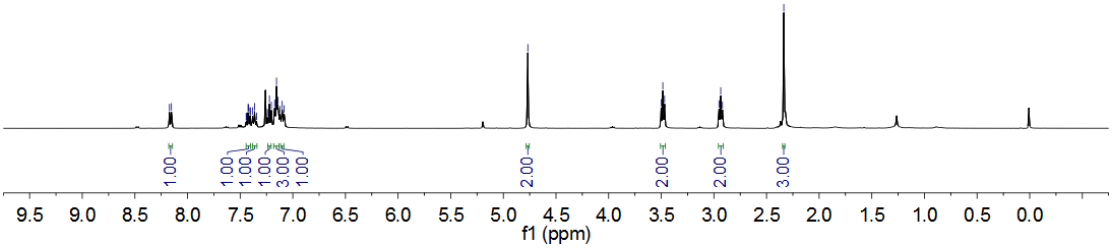


^{13}C NMR of product 3h in $CDCl_3$ (150 MHz)

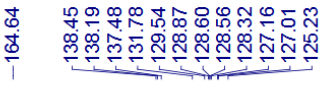


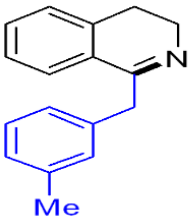
^{1}H NMR of product 3i in $CDCl_3$ (600 MHz)

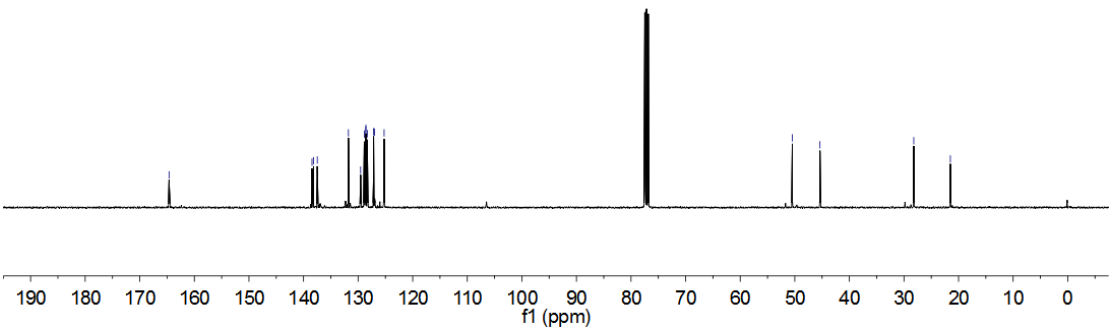




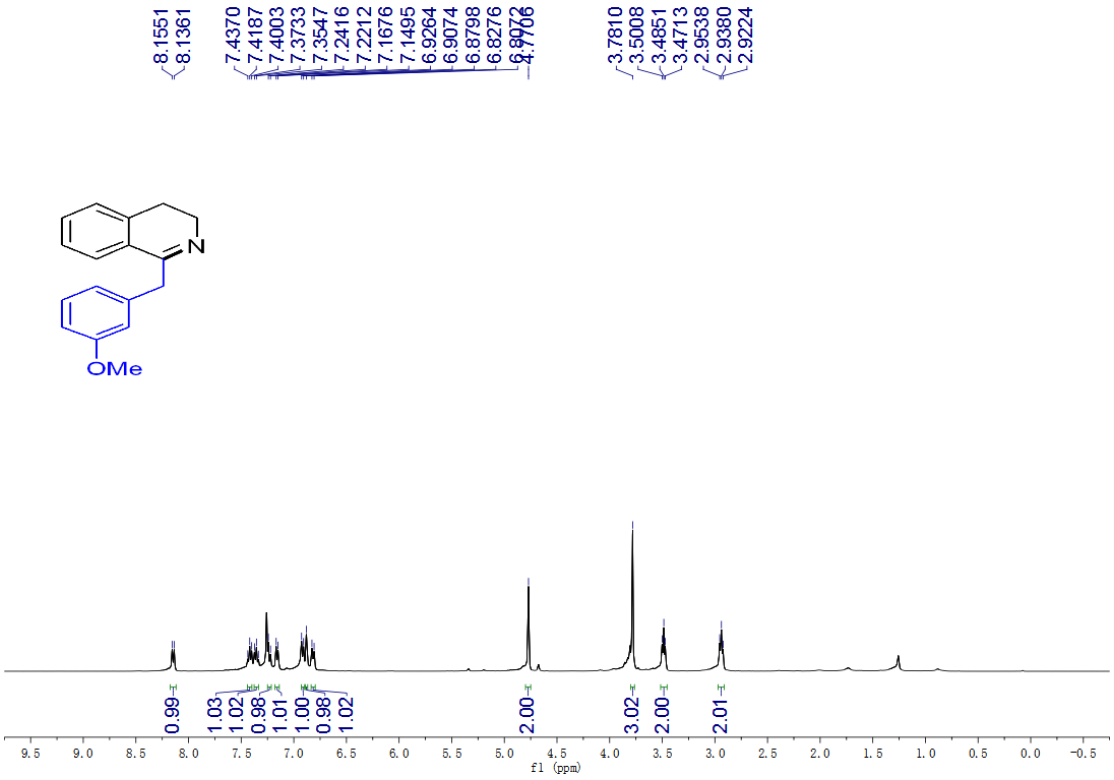
^{13}C NMR of product 3i in $CDCl_3$ (150 MHz)



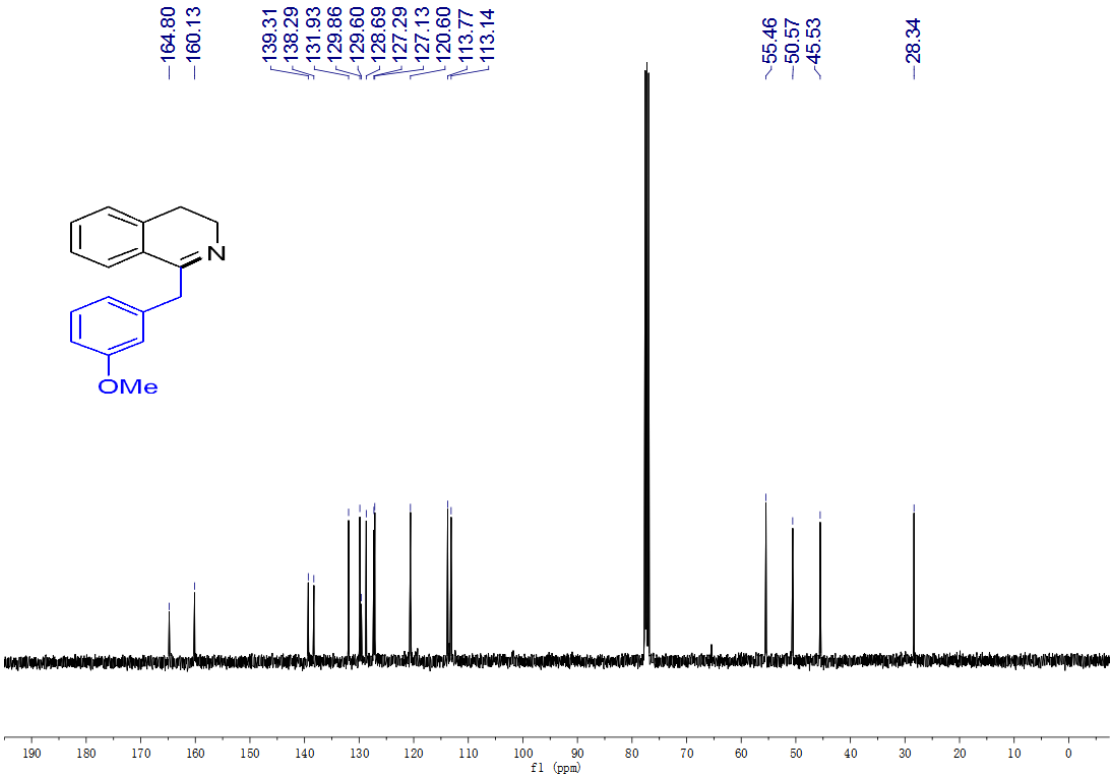




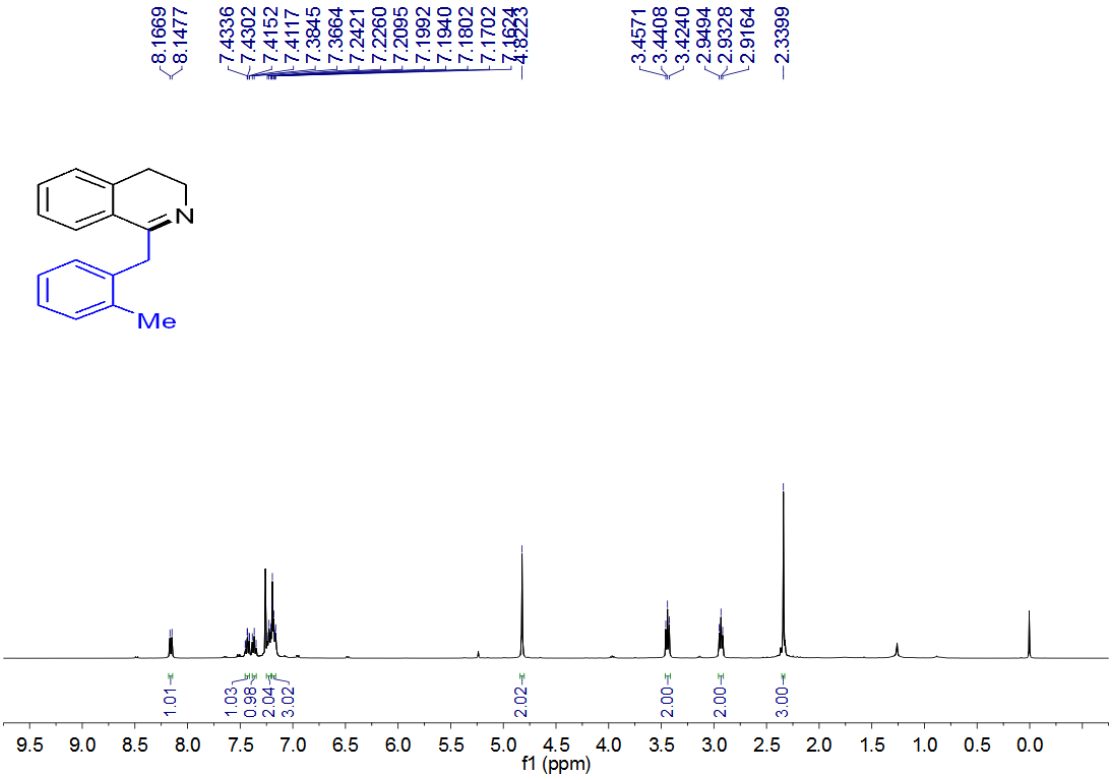
^{1}H NMR of product 3j in $CDCl_3$ (400 MHz)



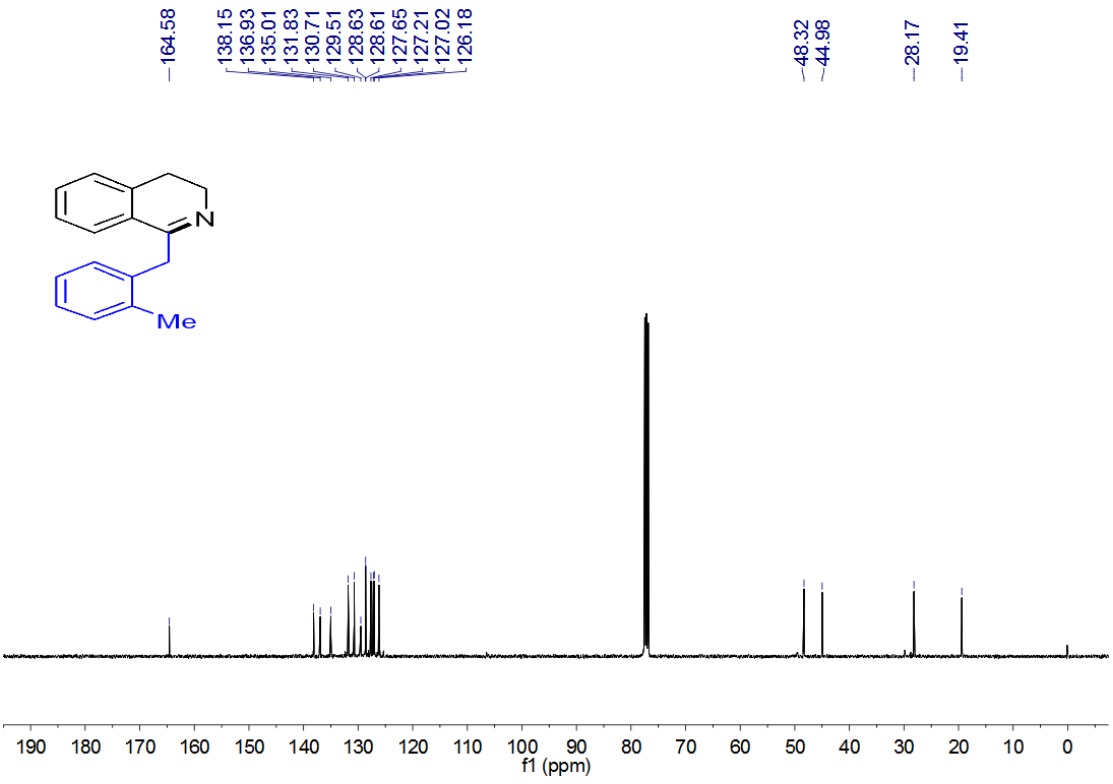
^{13}C NMR of product 3j in $CDCl_3$ (100 MHz)



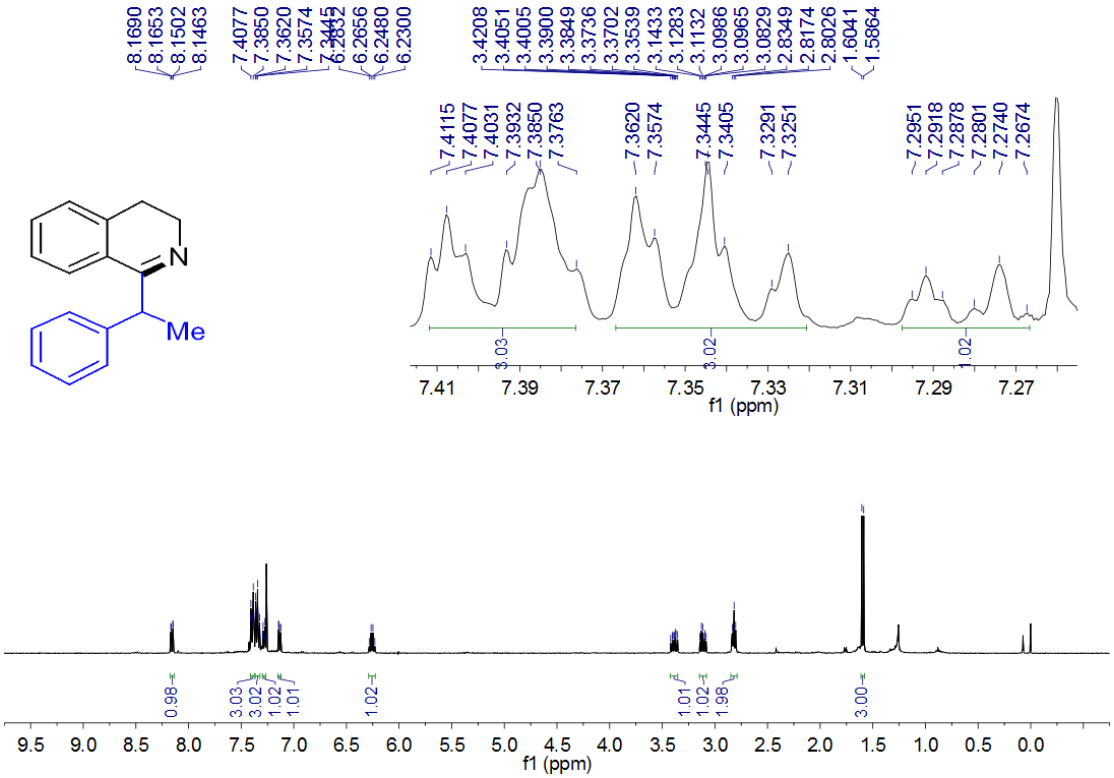
^{1}H NMR of product 3k in $CDCl_3$ (400 MHz)



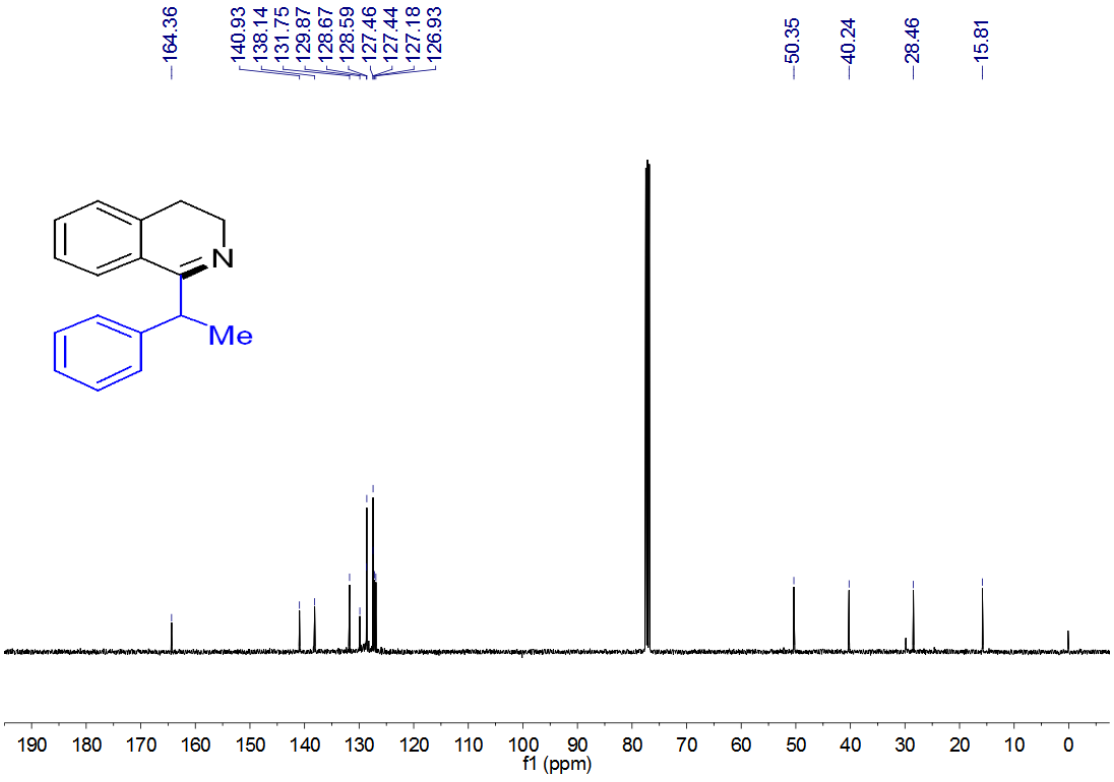
^{13}C NMR of product 3k in $CDCl_3$ (100 MHz)



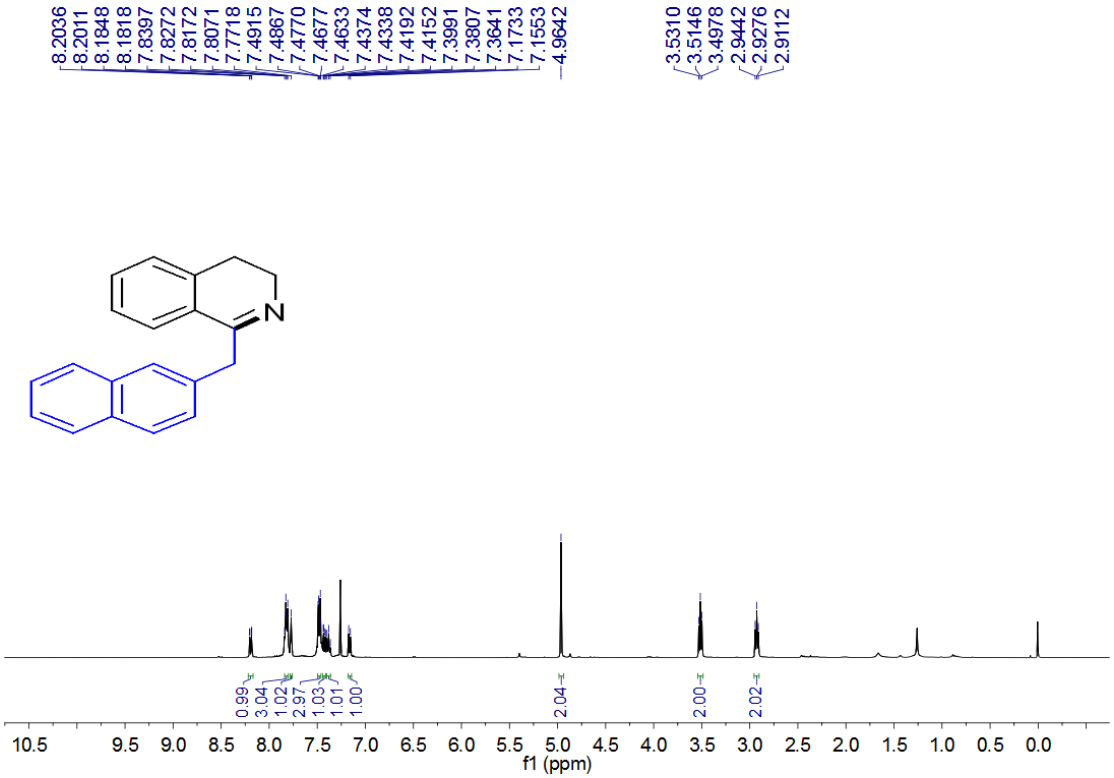
^{1}H NMR of product 3l in $CDCl_3$ (400 MHz)



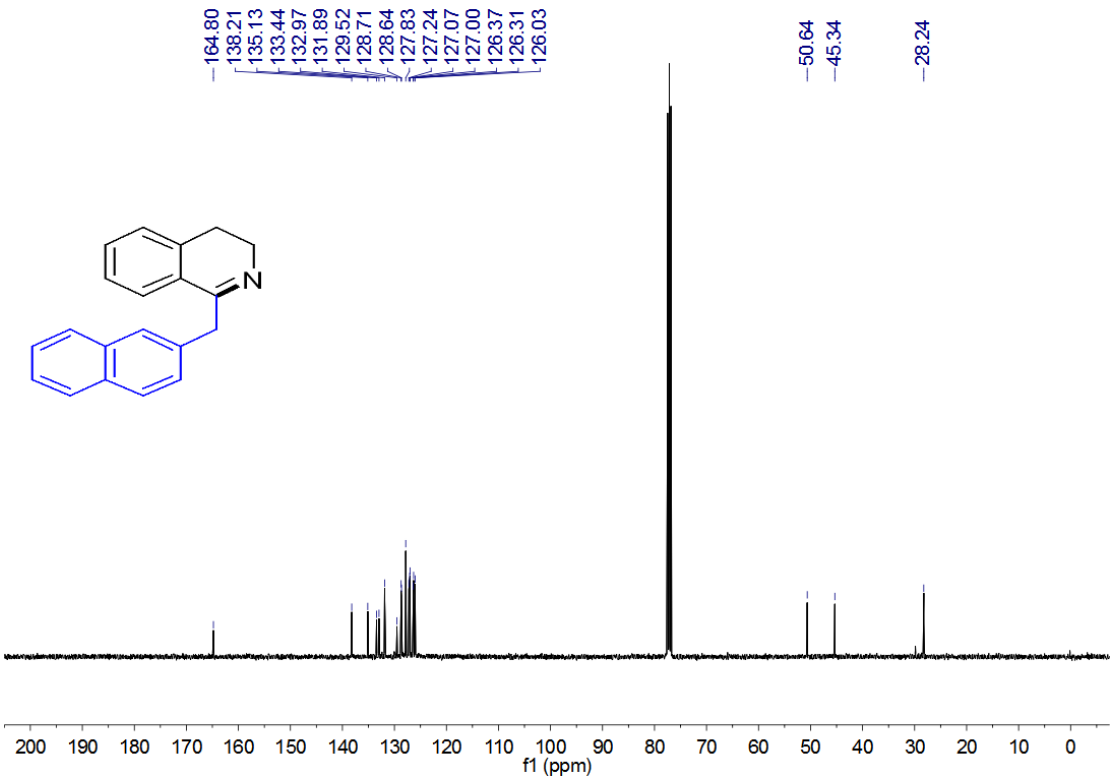
^{13}C NMR of product 3l in $CDCl_3$ (100 MHz)



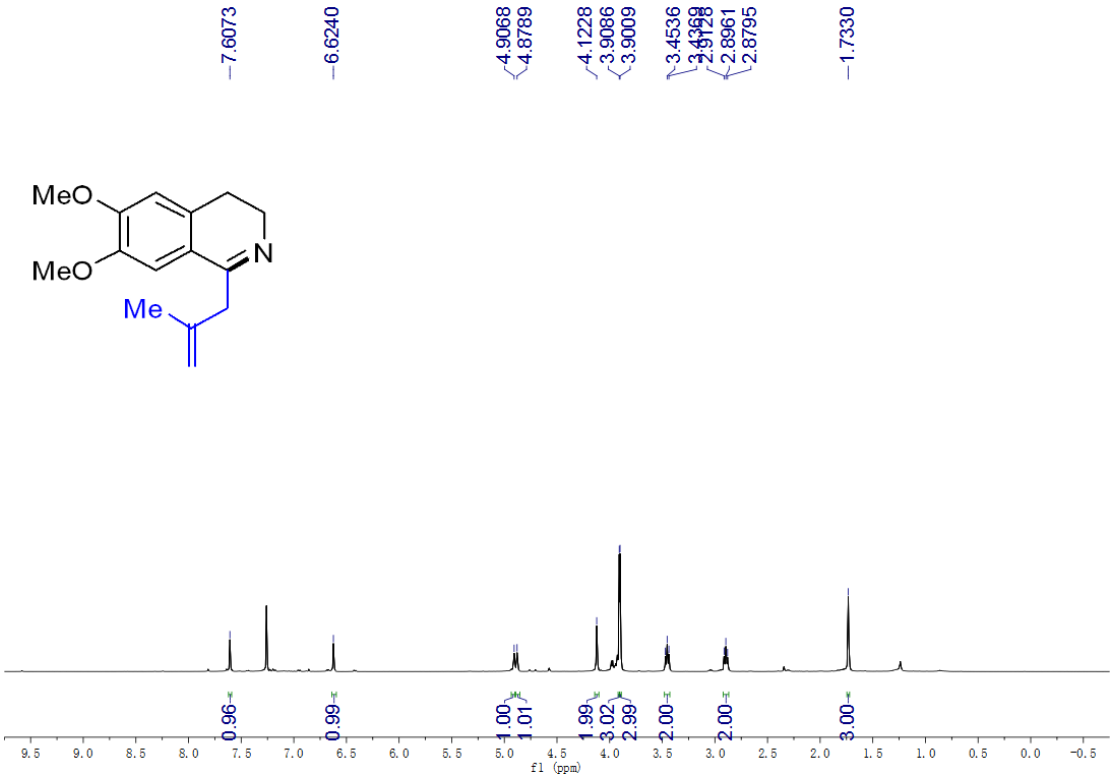
^{1}H NMR of product 3m in $CDCl_3$ (400 MHz)



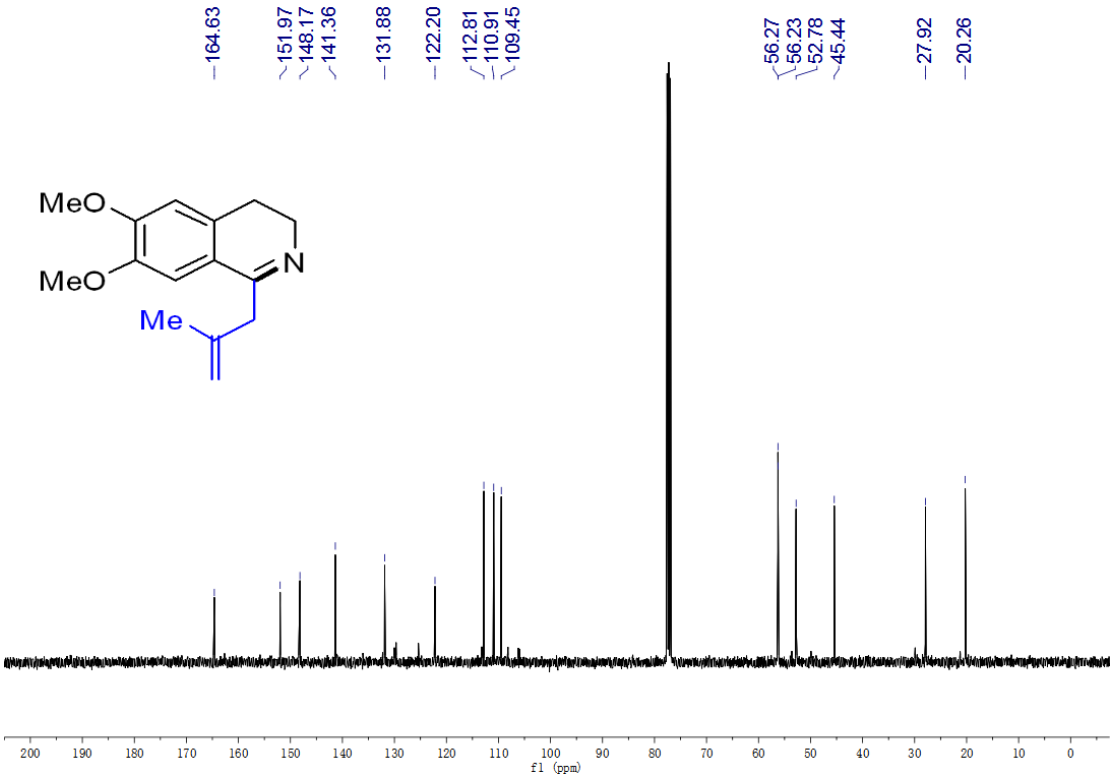
^{13}C NMR of product 3m in $CDCl_3$ (100 MHz)



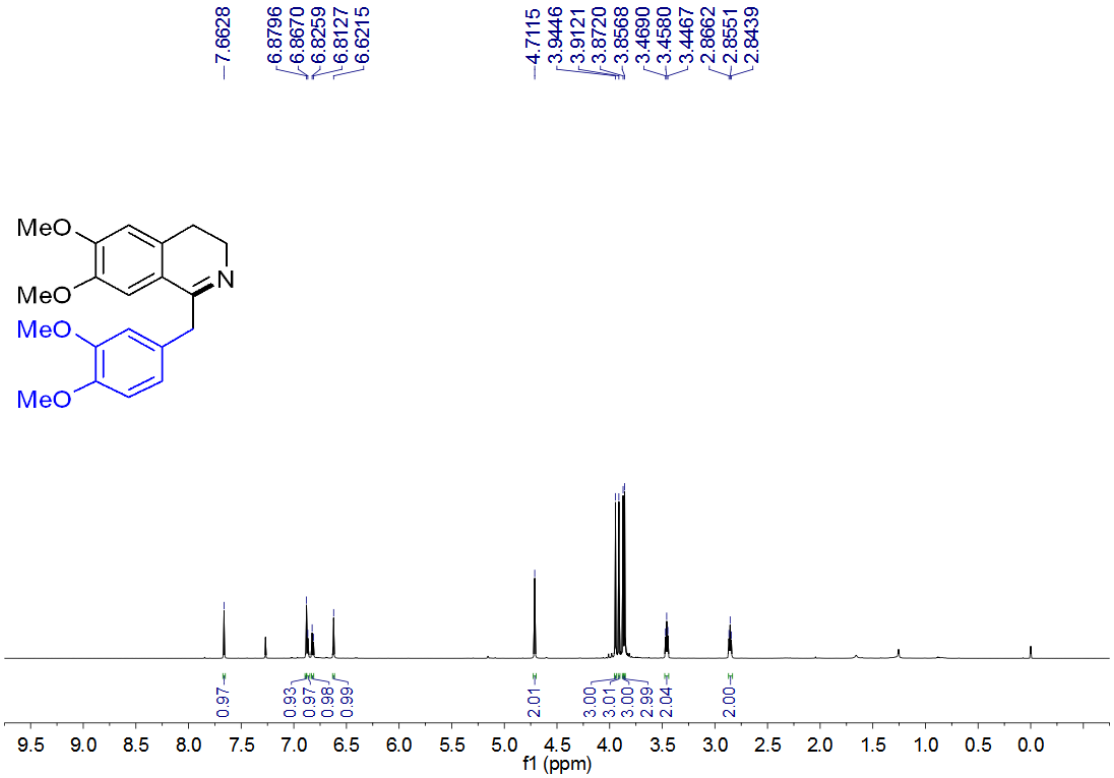
^{1}H NMR of product 3n in $CDCl_3$ (400 MHz)



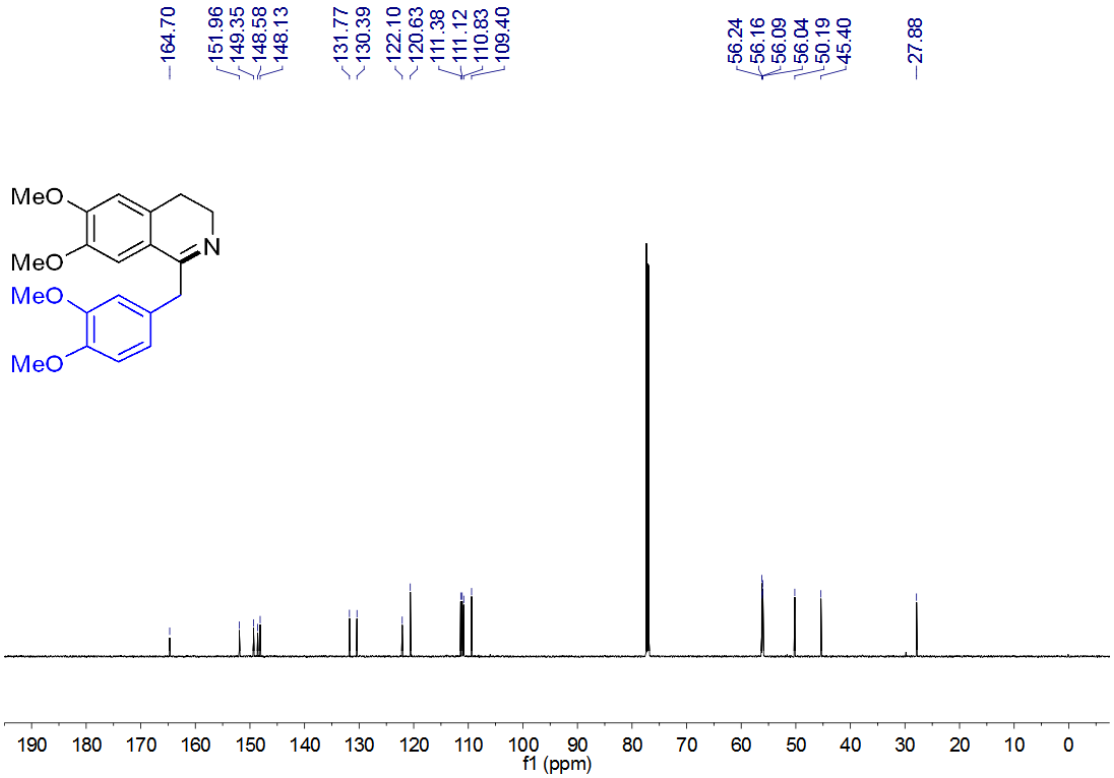
^{13}C NMR of product 3n in $CDCl_3$ (100 MHz)



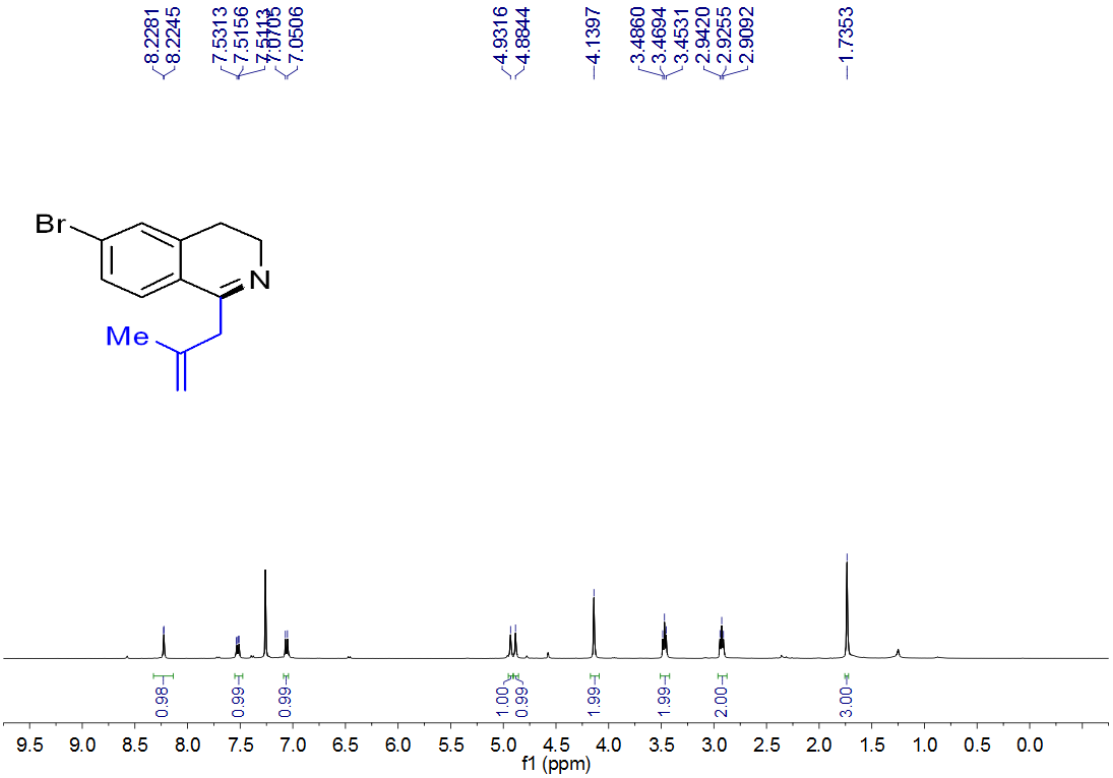
^{1}H NMR of product 3o in $CDCl_3$ (600 MHz)



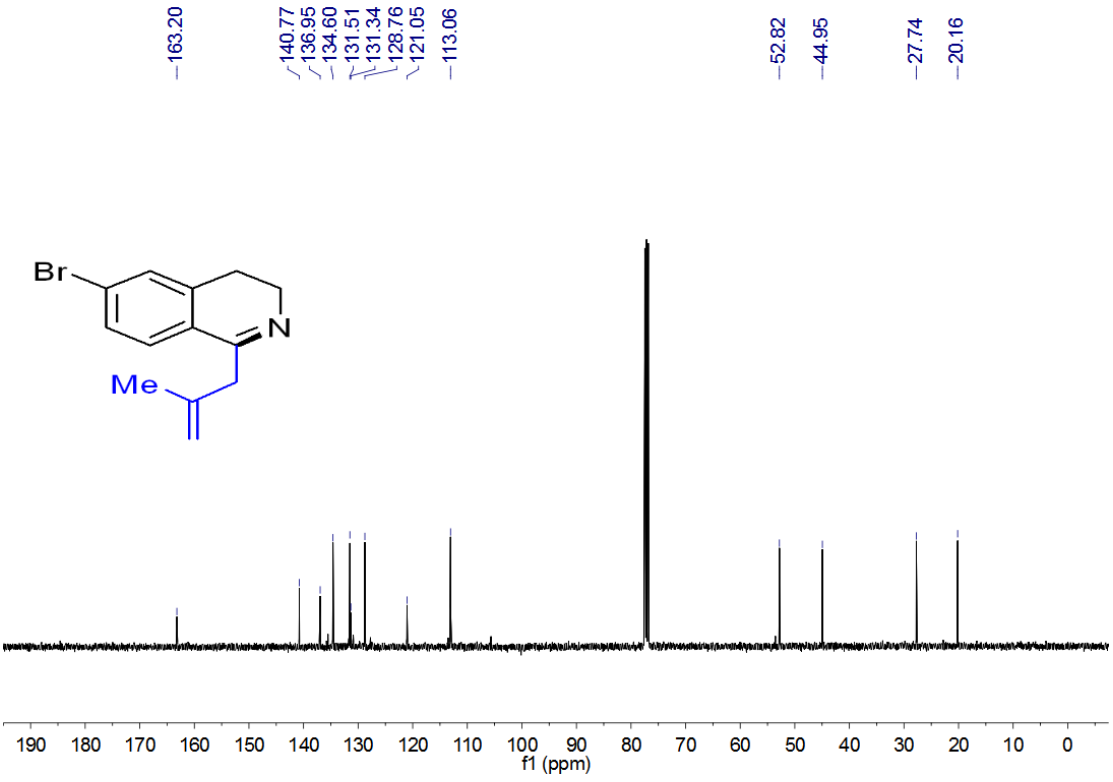
^{13}C NMR of product 3o in $CDCl_3$ (150 MHz)



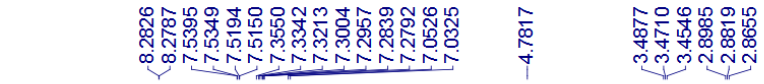
^{1}H NMR of product 3p in $CDCl_3$ (400 MHz)

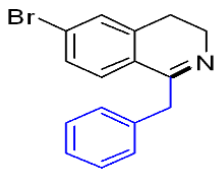


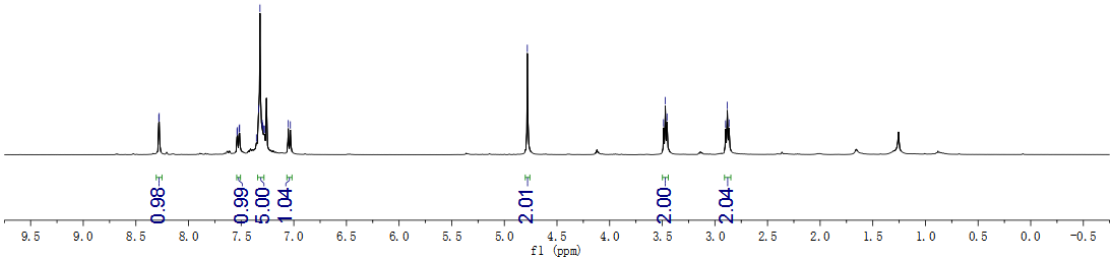
^{13}C NMR of product 3p in $CDCl_3$ (100 MHz)



^{1}H NMR of product 3q in $CDCl_3$ (400 MHz)







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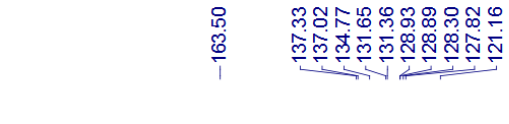
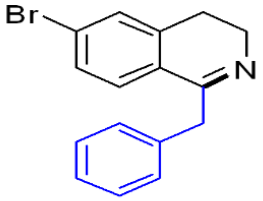
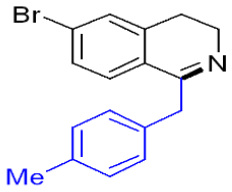
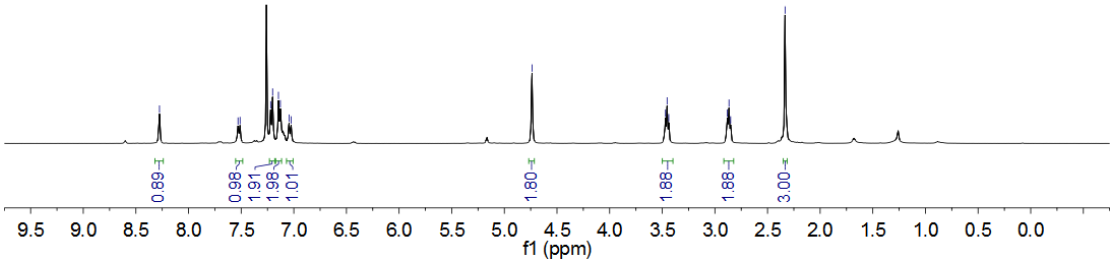




^{1}H NMR of product 3r in $CDCl_3$ (400 MHz)





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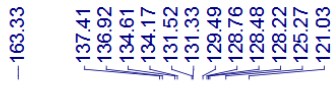
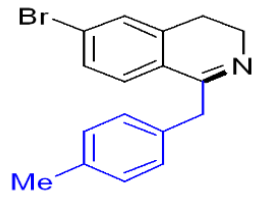
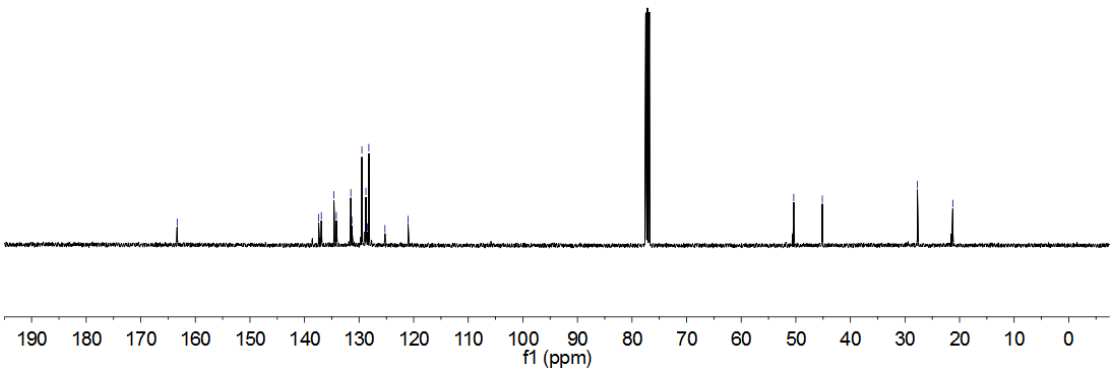
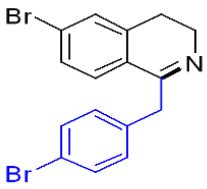
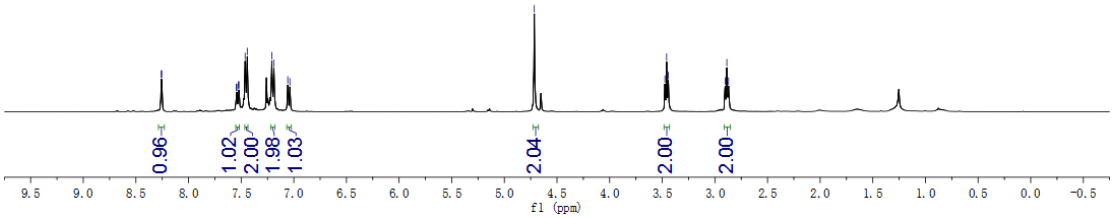




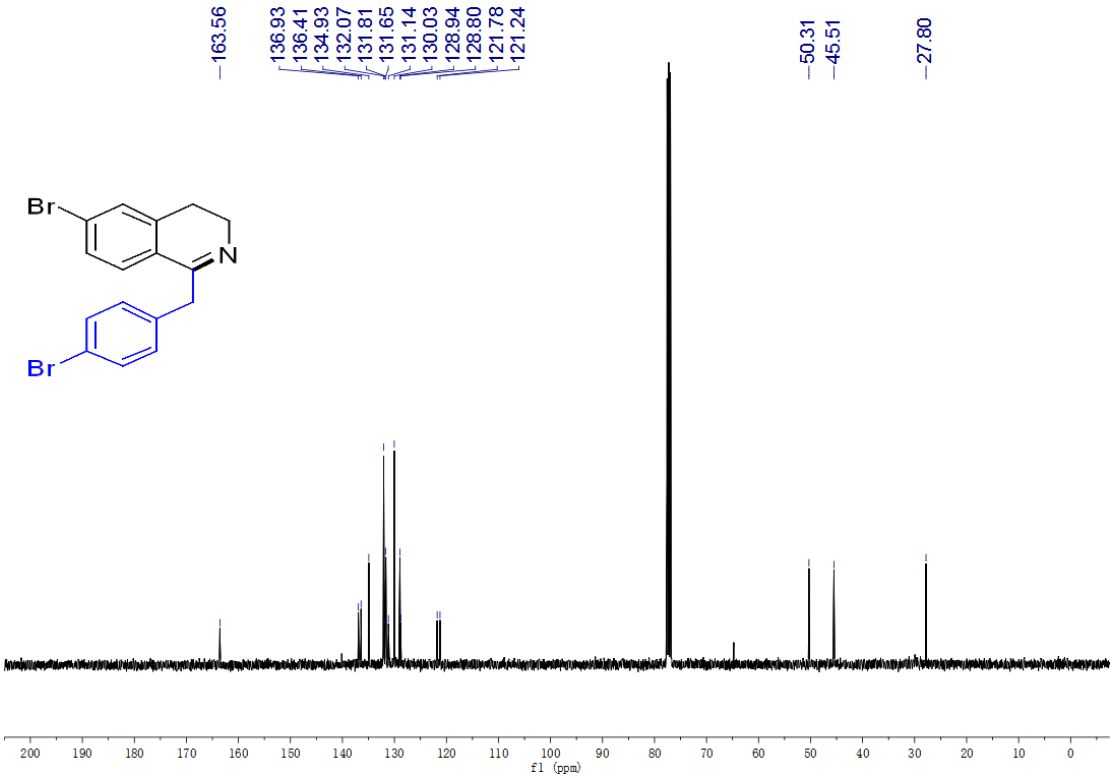


^{1}H NMR of product 3s in $CDCl_3$ (400 MHz)

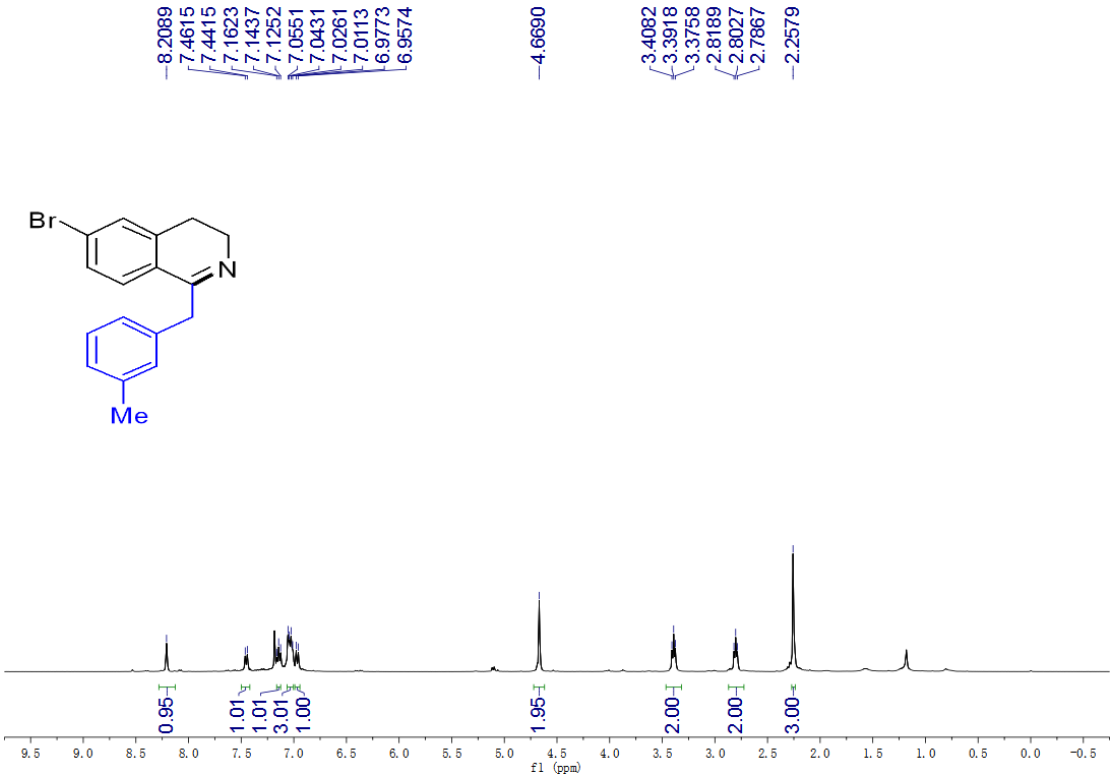




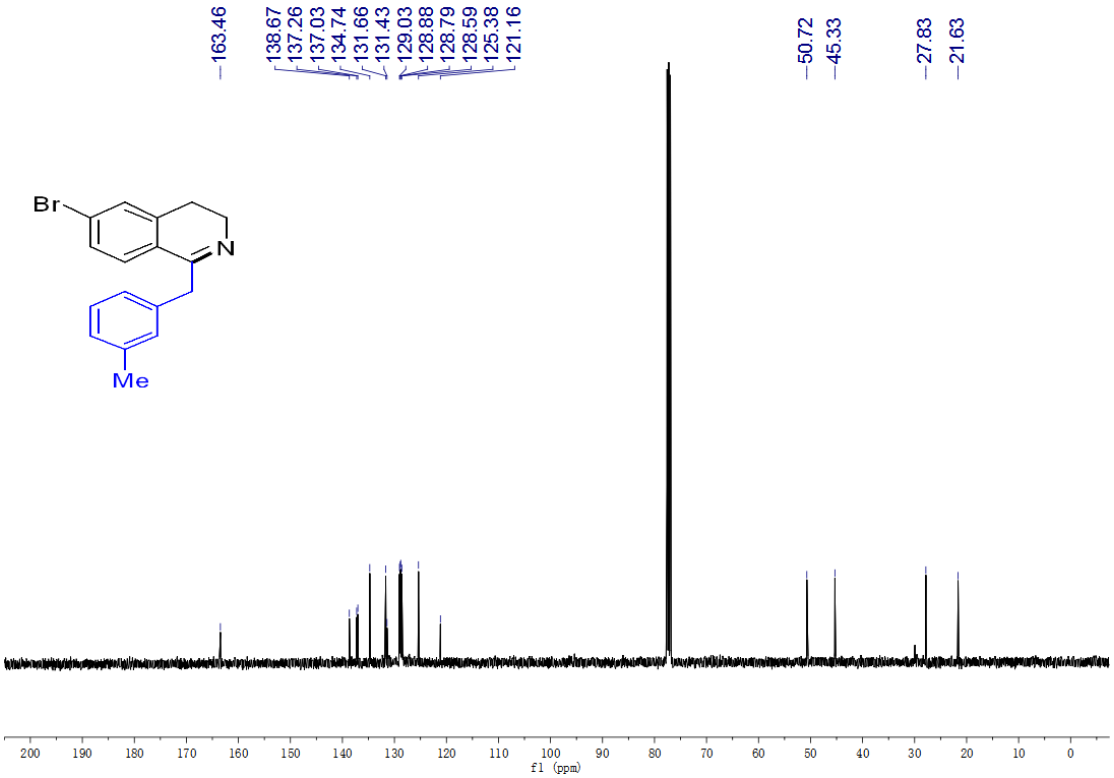
^{13}C NMR of product 3s in $CDCl_3$ (100 MHz)



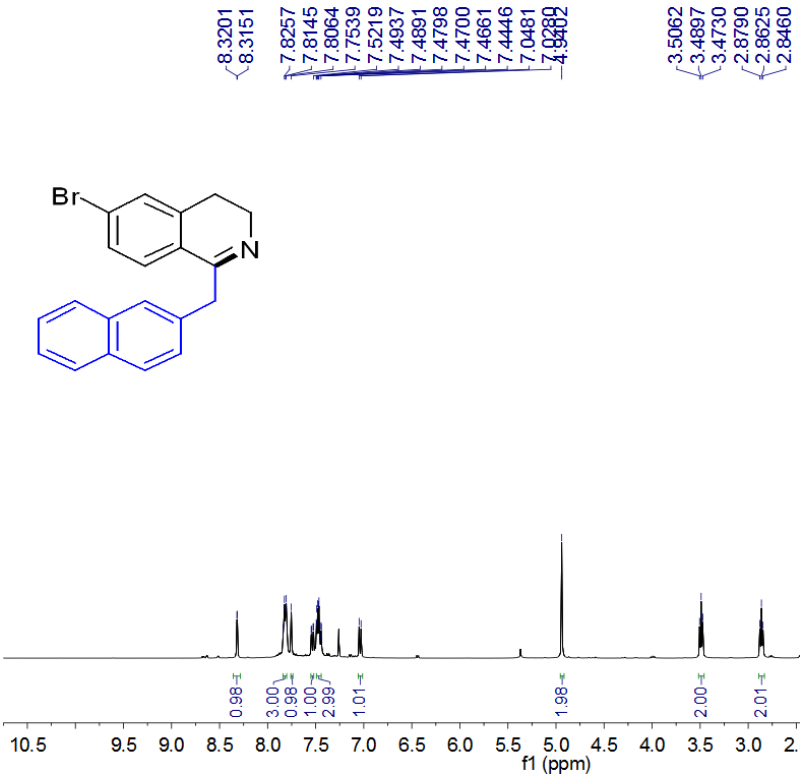
^{1}H NMR of product 3t in $CDCl_3$ (400 MHz)



^{13}C NMR of product 3t in $CDCl_3$ (100 MHz)



^{1}H NMR of product 3u in $CDCl_3$ (400 MHz)



^{13}C NMR of product 3u in $CDCl_3$ (100 MHz)