Supporting Information

for

Zn-mediated electrochemical α-alkylation of amines with halogenated alkanes through convergent paired electrolysis

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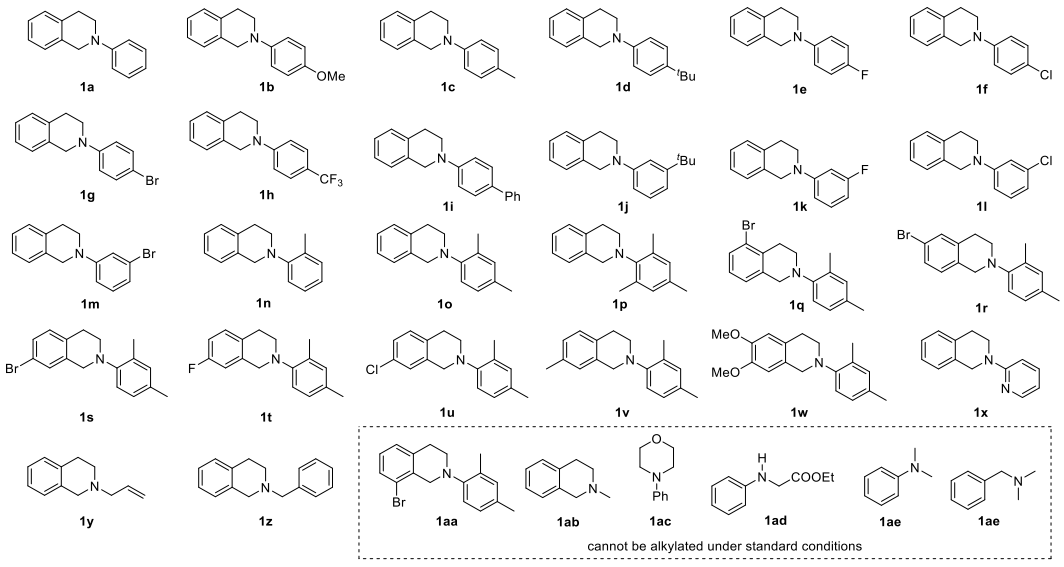
1. General information

All reagents and solvents were purchased from Adamas Reagent, Chendu Huaxia Chemical Reagent, Energy chemical, Alfa Aesa chemical company, Aladin Industrial Crporation, Macklin Biochemical Company, Acros Organics, Bide Pharmatech Ltd, and so forth. All chemicals are without purified unless otherwise stated. Petroleum ether (PE) and ethyl acetate (EA) for flash column chromatography were distilled before use. Thin layer chromatography (TLC) for analysis was performed on Schleicher & Schuell F1400/LS 254 silica gel plates, and observation under UV light (λ = 254 nm). ^{1}H NMR spectra recorded at 600 MHz, and ^{13}C NMR were recorded at 151 MHz. Use $CDCl_3$ as solvent and tetramethyl silane as internal standard (0.00 ppm) unless otherwise stated. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz). Flash chromatography was performed with Qingdao Haiyang flash silica gel (300–400 mesh). The substrates amine could be prepared according to literature.[1,2] Benzyl bromide could be easily prepared according to literature.[3]

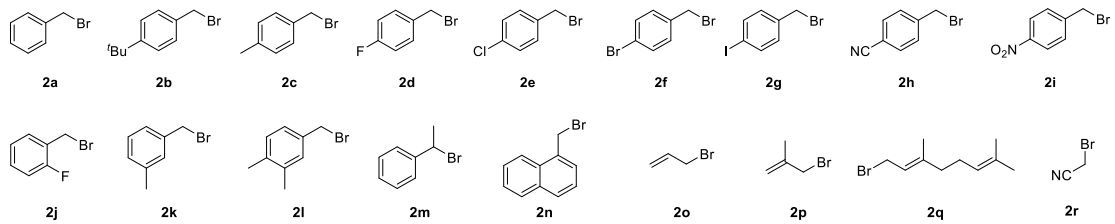
Abbreviated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); THF (Tetrahydrofuran); DMF (Dimethylformamide); SDS (Sodium dodecyl sulfonate); FE (Faraday efficiency).

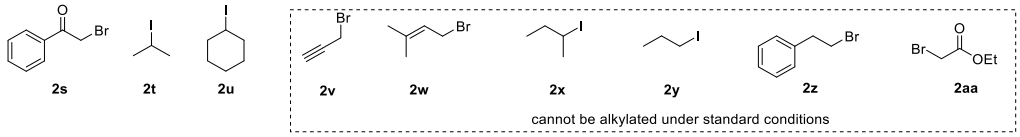
2. Structures of starting materials

2.1 Various amines used in this reaction

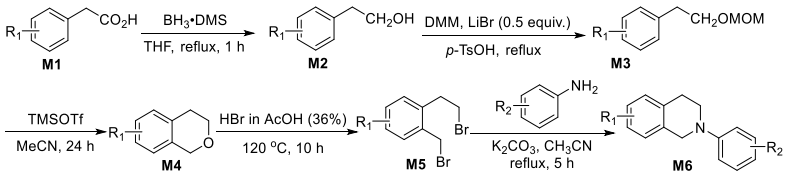


2.1 Various haloalkanes used in this reaction





3. Synthetic routes for 1,2,3,4-tetrahydroisoquinolines[1,2]



To a solution of phenylacetic acid (**M1**, 20 mmol, 1.0 equiv.) in THF (50 mL), BH_3·DMS (8 mL, 100 mmol, 5 equiv.) was added dropwise at room temperature. The solution was refluxed for 1 h and then cooled to room temperature. The reaction was quenched by adding MeOH (40 mL) dropwise. The mixture was concentrated, and the resulting residue was purified by silica gel chromatography to give alcohol **M2** as oil.

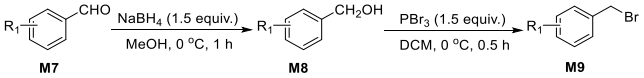
LiBr (1 g, 10 mmol, 0.5 equiv.) was added to a solution of phenylethyl alcohol (**M2**, 20 mmol, 1.0 equiv.) in dimethoxymethane (40 mL, 400 mol, 20 equiv.). In the catalysis of a spatula tip of *p*-TsOH, the reaction mixture was refluxed for 1 day. The reaction mixture was cooled to room temperature and concentrated. Then the resulted crude residue was purified by silica gel chromatography to give compound **M3**.

TMSOTf (0.35 mL, 1.95 mmol, 0.25 equiv.) was added drop wise to the solution of compound **M3** (10 mmol, 1.0 equiv.) in MeCN (40 mL) at 0 °C. The reaction mixture was warmed to room temperature, stirred for an additional 10 h, and then quenched by addition of saturated $NaHCO_3$ (15 mL). The MeCN was removed under reduced pressure, and the resulting aqueous layer was extracted with Et_2O (3 x 20 mL). Combined the ethereal layers and dried with Na_2SO_4, filtered, and concentrated to give the crude products, then, purified by silica gel chromatography furnished compound **M4.**

A mixture of **M4** (10 mol, 1.0 equiv.) and 33% HBr in AcOH (10 mL) was heated in a sealed tube at 110 °C for 18 h. After cooling to rt, and then poured into water (100 mL) and extracted with diethyl ether (3 × 100 mL). The organic phase was washed with 1 M NaOH (200 mL) and brine (100 mL), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by silica gel chromatography to give compound **M5.**

To a solution of **M5** (10 mmol, 1.0 equiv.) in CH_3CN (50 mL) was added aniline (10.0 mmol, 1.0 equiv.) and K_2CO_3 (20 mmol, 2.0 equiv.). The solution was refluxed for 5 h and then cooled to room temperature. The MeCN was removed under reduced pressure, and the resulting mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 100 mL). The ethereal layer was dried (Na_2SO_4), filtered, and concentrated to give the crude products. The crude products were purified by silica gel chromatography to give compound **M6.**

4. Synthetic routes for benzyl bromide



A solution of benzaldehyde (**M7**, 20 mmol, 1.0 equiv.) in MeOH (50 mL), $NaBH_4$ (750 mg, 30 mmol, 1.5 equiv.) was added at 0 °C. The reaction mixture was stirred at 0 °C for1 h, and then MeOH was removed under reduced pressure, the resulting mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 100 mL). The ethereal layer was dried (Na_2SO_4), filtered, and concentrated to give the crude products. The crude products were purified by silica gel chromatography to give compound **M8**.

A solution of benzyl alcohol **M8** in DCM (20 mL), PBr_3 (1.8 mL, 5.4 g, 30 mmol, 1.5 equiv.) was added at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. The reaction was quenched by adding water (10 mL) dropwise. Then the mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 100 mL). The ethereal layer was dried (Na_2SO_4), filtered, and concentrated to give the crude products. The crude products were purified by silica gel chromatography to give compound **M9**.

5. General procedure of alkylation reaction

5. 1 General procedure A of alkylation reaction

An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate amine (0.3 mmol), haloalkane (0.9 mmol), $ZnCl_2$ (0.6 mmol), $^nBu_4NI$ (0.3 mmol) was added to the cosolvent DMF (1.5 mL) and THF (1.5 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 1.7 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel or aluminum oxide to afford the desired product.

5.2 General procedure B of alkylation reaction

An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate amine (0.3 mmol), haloalkane (0.9 mmol), $ZnCl_2$ (0.6 mmol), NH_4I (0.3 mmol) and sodium dodecyl sulfonate (SDS, 20 mol%) was added to the cosolvent THF (2.7 mL) and H_2O (0.3 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 2 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel or aluminum oxide to afford the desired product.

5.3 General procedure C of alkylation reaction

An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate amine (0.3 mmol), haloalkane (1 mmol), $ZnCl_2$ (0.6 mmol), NH_4I (0.3 mmol) and Na_2SO_3 (0.75 mmol) was added to the cosolvent DMF (1.5 mL), THF (1.5 mL) and H_2O (0.3 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 4 hours. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and then extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in

vacuo. The residue was purified by column chromatography on silica gel or aluminum oxide to afford the desired product.

6. Procedure for gram scale alkylation reaction

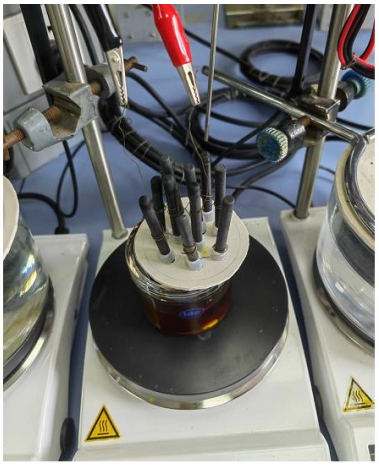
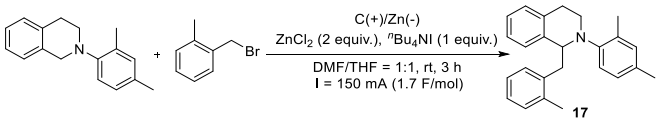
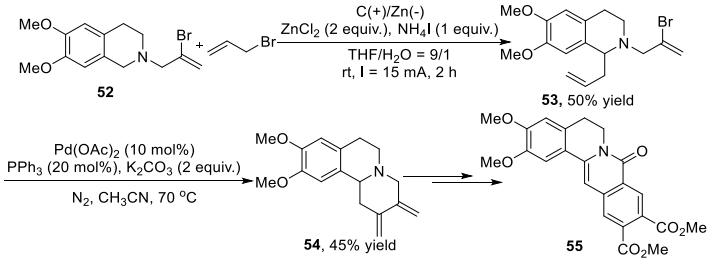


Figure S1. Gram-scale electrolysis setup



An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc plate (8*10 cm^2) as cathode (the electrolysis setup is shown in Fig. S1). The substrate amine (5 mmol), haloalkane (15 mmol), $ZnCl_2$ (10 mmol), $^nBu_4NI$ (5 mmol) was added to the cosolvent DMF (25 mL) and THF (25 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (150 mA) at room temperature for 3 h. After the reaction is complete, triethylamine (10 mL) was added to quench the reaction. Then the reaction mixture was poured into water (150 mL) and then extracted with ethyl acetate (3 × 30 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **17** (1.4 g, 82% yield, FE = 49%).

7. Formal synthesis of the 8-oxoprotoberberine derivative 55[3]

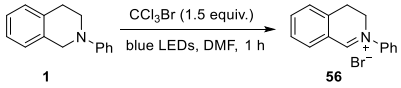


Step I: An undivided cell was equipped with a magnet stirrer; carbon rob as anode and zinc rob as cathode. The substrate amine **52** (0.3 mmol), allyl bromide (0.9 mmol), $ZnCl_2$ (0.6 mmol), NH_4I (0.3 mmol) and sodium dodecyl sulfonate (SDS, 20 mol%) was added to the cosolvent THF (2.7 mL) and H_2O (0.3 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 2 h. After the reaction is complete,

triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and then extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **53** (52 mg, 50% yield, FE = 26%).

Step II: A solution of amine **53** (0.1 mmol), $Pd(OAc)_2$ (10 mol%) and PPh_3 (20 mol%), K_2CO_3 (0.2 mmol), in dried CH_3CN (2 mL) at 70 °C under argon atmosphere for 12 h. Then, the reaction mixture was cooled to rt. The solid was removed and washed with ethyl acetate. Combined the organic solution together and the solvent was removed by vacuum to give the crude product, which was purified by flash chromatography on silica gel to provide pure product **54** as light-yellow oil in 45% yield.

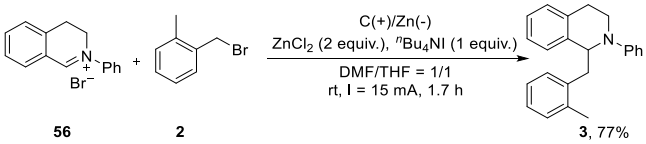
8. Synthetic routes for benzyl bromide[4]



1 **56**

In an oven-dried Schlenk tube equipped with a magnetic stir bar the amine (0.5 mmol, 1.0 equivalent.) was dissolved in DMF (1 mL). $CBrCl_3$ (0.75 mmol, 1.5 equiv.) was added under nitrogen and the tube was then irradiated with blue LEDs for 30 min at room temperature. After the reaction is complete, ethyl acetate was dropped slowly into the mixture of reaction with vigorous stirring. After a few minutes the brown precipitate emerged, filtered and washed three times with ethyl acetate to obtain the brown solid, which is iminium ion **56**.

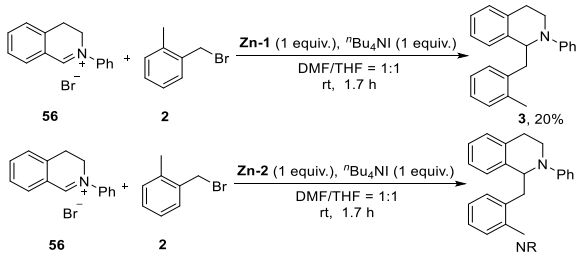
9. Procedure for control experiments



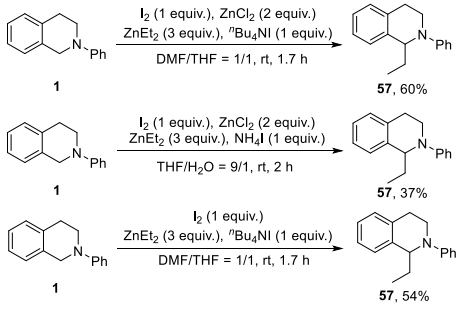
56 **2** **3**, 77%

Iminium ion **56** was prepared according to literature[4]. An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate haloalkane (0.9 mmol), iminium ion **56** (0.3 mmol), $ZnCl_2$ (0.6 mmol), $^nBu_4NI$ (0.3 mmol) was added to the cosolvent DMF (1.5 mL) and THF (1.5 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 1.7 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **3** in 77% yield.

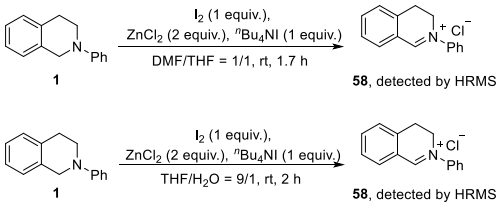
Figure S2. Zinc deposition (**Zn-1**) on the front side of zinc plate (left picture) and Zinc deposition (**Zn-2**) on the back side of zinc plate (right picture).



The Iminium ion **56** (0.3 mmol), haloalkane (0.9 mmol), $^{n}Bu_4NI$ (0.3 mmol), **Zn-1** (0.3 mmol) or **Zn-2** (0.3 mmol) was added to the cosolvent DMF (1.5 mL) and THF (1.5 mL). The resulting mixture was allowed to stir for 1.7 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product.

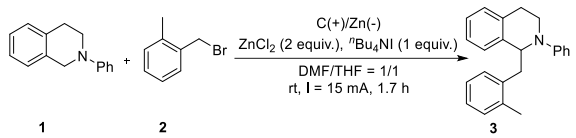


An oven-dried Schlenk tube was equipped with a magnet stirrer, the amine **1** (0.3 mmol), $ZnCl_2$ (0.6 mmol) or not, $^{n}Bu_4NI$ (0.3 mmol), $\mathbf{I_2}$ (0.3 mmol) were added to the cosolvent DMF/THF or amine **1** (0.3 mmol), $ZnCl_2$ (0.6 mmol), NH_4I (0.3 mmol), SDS (0.06 mmol), $\mathbf{I_2}$ (0.3 mmol) were added to the cosolvent THF/H_2O and stir for a few minutes, then the $ZnEt_2$ (1 mol/L, 0.9 ml) was added. The resulting mixture was allowed to stir for 1.7 h or 2 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product.



An oven-dried Schlenk tube was equipped with a magnet stirrer, the amine **1** (0.3 mmol), $ZnCl_2$ (0.6 mmol), $^{n}Bu_4NI$ (0.3 mmol), $\mathbf{I_2}$ (0.3 mmol) were added to the cosolvent DMF/THF or amine **1** (0.3 mmol), $ZnCl_2$ (0.6 mmol), NH_4I (0.3 mmol), SDS (0.06 mmol), $\mathbf{I_2}$ (0.3 mmol) were added to the cosolvent THF/H_2O. The resulting mixture was allowed to stir for 1.7 h or 2h. triethylamine (3 mL) was added to quench the reaction. The Iminium ion **58** was detected by HRMS.

Table S1 Radical capture experiments

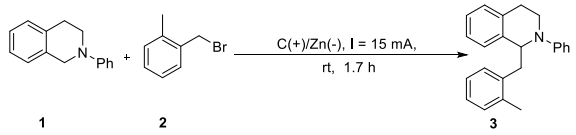


1 2 3

entry	radical scavenger	yield
1	TEMPO (2 equiv.)	78%
2	TEMPO (1 equiv.)	76%
3	TEMPO (0.5 equiv.)	78%
4	TEMPO (0.1 equiv.)	75%
5	BHT (2 equiv.)	80%

An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate haloalkane (0.9 mmol), amine **1** (0.3 mmol), $ZnCl_2$ (0.6 mmol), $^{n}Bu_4NI$ (0.3 mmol) and radical scavenger was added to the cosolvent DMF (1.5 mL) and THF (1.5 mL). The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 1.7 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **3** (Table S1).

Table S2 Effect of Zn^{2+} salts on the reaction



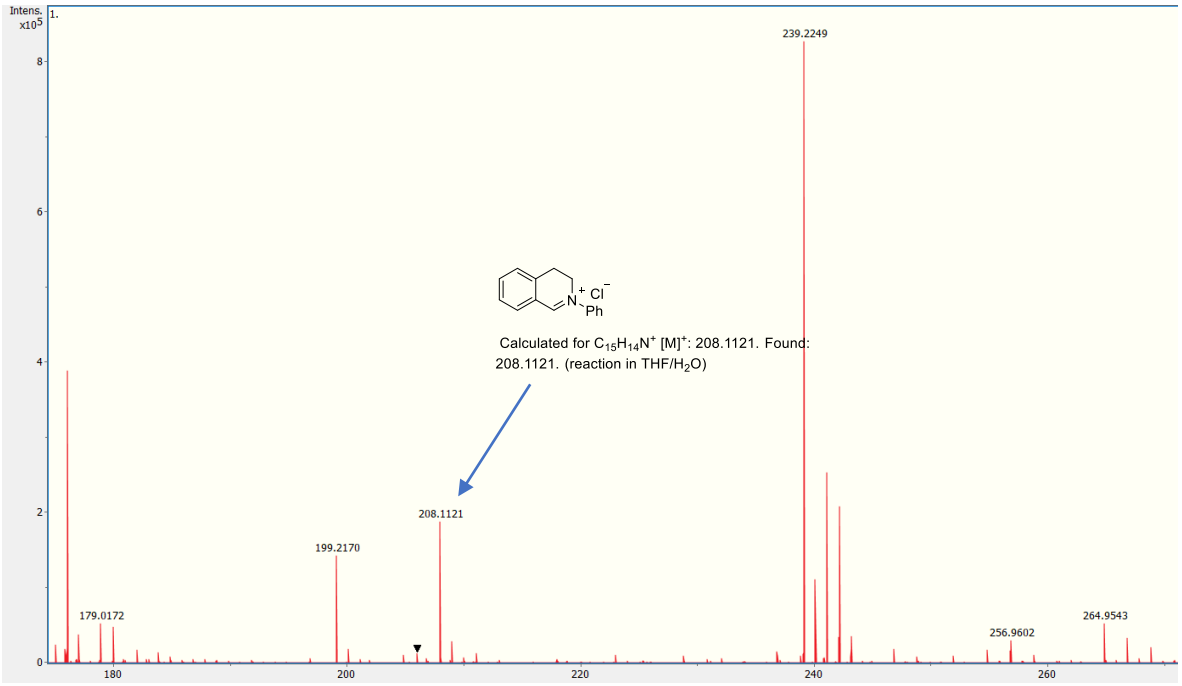
1 2 3

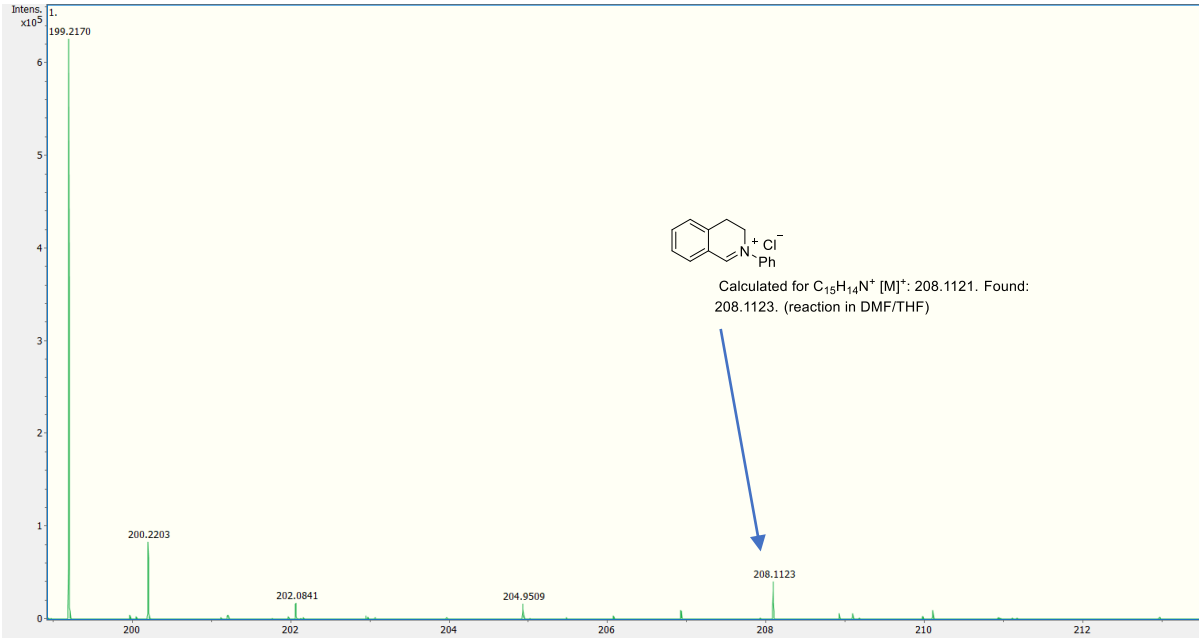
entry	Zn^{2+} salts	Yield[a]	yield[b]
1	$ZnBr_2$ (2 equiv.)	76%	56%
2	ZnI_2 (2 equiv.)	ND	37%
3	$Zn(OAc)_2$ (2 equiv.)	30%	race
4	$Zn(OTf)_2$ (2 equiv.)	ND	55%
5	$ZnCl_2$ (1 equiv.)	38%	--
6	$ZnCl_2$ (0.5 equiv.)	20%	--
7	$ZnCl_2$ (0.2 equiv.)	14%	--

[a] THF (1.5 mL), DMF (1.5 mL), $^{n}Bu_4NI$ (1 equiv.)
[b] THF (2.7 mL), H_2O (0.3 mL), NH_4I (1 equiv.), SDS (20 mol%)

An undivided cell was equipped with a magnet stirrer, carbon rob as anode and zinc rob as cathode. The substrate haloalkane (0.9 mmol), amine **1** (0.3 mmol), Zn^{2+} salts (0.6 mmol), $^{n}Bu_4NI$ or NH_4I (0.3 mmol) was added to the cosolvent DMF/THF or THF/H_2O. The resulting mixture was allowed to stir and electrolyze at constant current conditions (15 mA) at room temperature for 1.7 h. After the reaction is complete, triethylamine (3 mL) was added to quench the reaction. Then the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **3** (Table S2).

10. HRMS data of Iminium ion 58





11. Cyclic voltammetric experiments

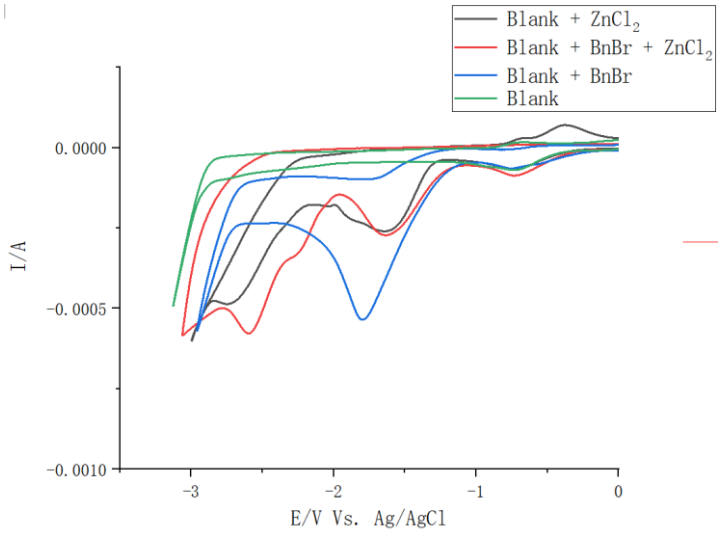


Figure S3. Cyclic voltammograms of substrates in 10 mL DMF-THF cosolvent (0.1 M $^{n}Bu_4NBF_4$, DMF/THF = 1/1), using a glassy carbon as working electrode, Pt wire as counter and Ag/AgCl as reference electrodes, scan rate: 150 mV/s; **Blank:** no substrate; **Blank + $ZnCl_2$**: 1 M $ZnCl_2$ in THF (200 µL); **Blank + $ZnCl_2$ + BnBr**: 1 M $ZnCl_2$ in THF (200 µL), 1-(bromomethyl)-2-methylbenzene (300 µmol); **Blank + BnBr**: 1-(bromomethyl)-2-methylbenzene (300 µmol).

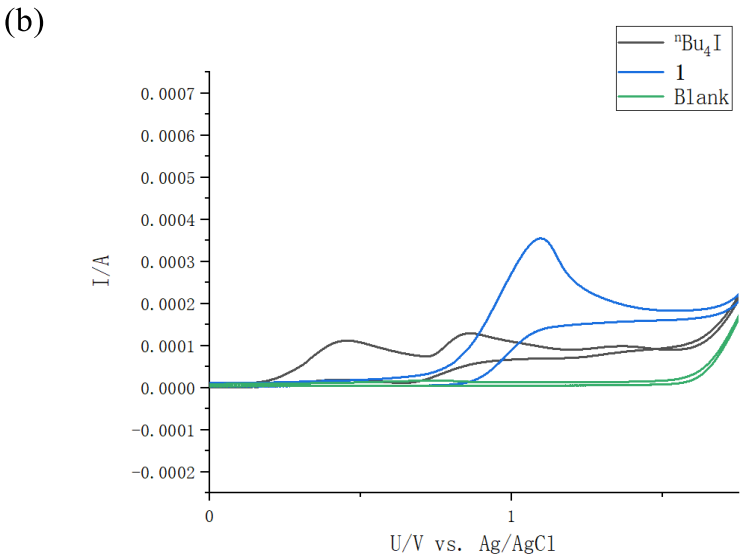
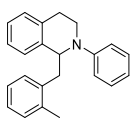


Figure S4. Cyclic voltammograms of substrates in 10 mL DMF-THF cosolvent (0.1 M $^{n}Bu_4NBF_4$, DMF/THF = 1/1), using a glassy carbon as working electrode, Pt wire as counter and Ag/AgCl as reference electrodes, scan rate: 100 mV/s; **Blank**: no substrate; **$^{n}Bu_4NI$**: $^{n}Bu_4NI$ (200 µmol); **1**: amine **1** (200 µmol)

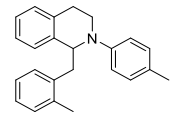
12. Characterization data for products

1-(2-methylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3)



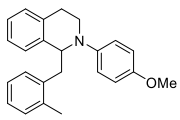
Target compound was obtained according to general procedure A giving pure product (73.3 mg, 78% yield, FE = 49%) or general procedure B giving pure product (70.5 mg, 75% yield, FE = 39%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, J = 7.8 Hz, 2H), 7.08–7.03 (m, 2H), 7.02–6.95 (m, 4H), 6.92 (s, 1H), 6.76 (s, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.7 Hz, 1H), 4.81 (t, J = 7.0 Hz, 1H), 3.65 (p, J = 6.0 Hz, 1H), 3.50 (dt, J = 12.1, 6.0 Hz, 1H), 3.14 (s, 1H), 3.02 (dd, J = 13.6, 7.6 Hz, 1H), 2.95 (dt, J = 14.0, 6.0 Hz, 1H), 2.75 (d, J = 16.2 Hz, 1H). 1.90 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 136.5, 136.1, 135.8, 133.9, 129.5, 129.08, 128.2, 127.1, 126.4, 125.6, 125.3, 124.8, 124.5, 116.4, 112.8, 60.3, 41.1, 37.7, 26.3, 18.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{23}H_{23}KN$: 352.1468; Found: 352.1455.

1-(2-methylbenzyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4)



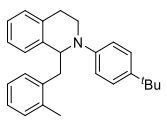
Target compound was obtained according to general procedure A giving pure product (78.5 mg, 80% yield, FE = 50%) or general procedure B giving pure product (77.5 mg, 79% yield, FE = 41%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 2H), 7.02 – 6.99 (m, 2H), 6.98 (d, J = 4.6 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.91 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.1 Hz, 2H), 6.55 (d, J = 7.6 Hz, 1H), 4.76 (t, J = 6.9 Hz, 1H), 3.49 (dt, J = 12.0, 5.6 Hz, 1H), 3.11 (dd, J = 13.7, 6.3 Hz, 1H), 2.99 (dd, J = 13.5, 7.5 Hz, 1H), 2.94 (dt, J = 14.8, 7.0 Hz, 1H), 2.16 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 136.7, 136.4, 135.8, 134.0, 129.5, 129.0, 128.7, 127.2, 126.4, 125.8, 125.5, 125.2, 124.7, 124.4, 113.4, 60.4, 41.1, 37.7, 26.2, 19.2, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}N$: 328.2065; Found: 328.2058.

2-(4-methoxyphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (5)



Target compound was obtained according to general procedure A giving pure product (74.1 mg, 72% yield, FE = 45%) or general procedure B giving pure product (72.1 mg, 70% yield, FE = 37%), purification by flash chromatography on silica gel (PE : EA = 20 : 1); colorless liquid; R_f: 0.5 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 3.1 Hz, 1H), 7.01 (td, J = 7.7, 6.9, 2.7 Hz, 3H), 6.96 (d, J = 6.7 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.72 (s, 4H), 6.53 (d, J = 7.7 Hz, 1H), 4.67 (t, J = 6.9 Hz, 1H), 3.67 (s, 3H), 3.62 (dq, J = 9.4, 4.7 Hz, 1H), 3.47 (dt, J = 12.4, 5.2 Hz, 1H), 3.08 (dd, J = 13.6, 6.4 Hz, 1H), 2.99 – 2.91 (m, 2H), 2.69 (dt, J = 16.1, 4.6 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6, 143.4, 136.9, 136.6, 135.8, 133.8, 129.6, 129.1, 127.5, 126.5, 125.5, 125.3, 124.7, 124.4, 115.9, 113.7, 61.0, 54.7, 41.5, 37.2, 26.1, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}NO$: 344.2014; Found: 344.2011.

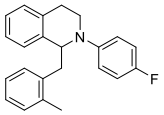
2-(4-(tert-butyl)phenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (6)



Target compound was obtained according to general procedure A giving pure product (84.2 mg, 76% yield, FE = 48%) or general procedure B giving pure product (79.8 mg, 72% yield, FE = 38%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, J

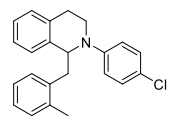
= 8.8 Hz, 2H), 7.16 – 7.08 (m, 5H), 7.06 (d, *J* = 5.2 Hz, 1H), 6.98 (t, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.86 (t, *J* = 7.0 Hz, 1H), 3.74 (p, *J* = 5.6 Hz, 1H), 3.58 (dt, *J* = 12.0, 5.9 Hz, 1H), 3.23 (t, *J* = 10.0 Hz, 1H), 3.10 – 3.01 (m, 2H), 2.82 (d, *J* = 15.1 Hz, 1H), 1.99 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 136.5, 135.8, 134.1, 129.6, 129.1, 127.2, 126.5, 125.5, 125.3, 124.9, 124.8, 124.5, 112.7, 60.6, 41.2, 38. 0, 32.8, 30.5, 26.3, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{32}N$: 370.2535; Found: 370.2529.

2-(4-fluorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (7)



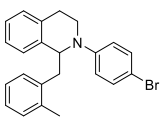
Target compound was obtained according to general procedure A giving pure product (79.5 mg, 80% yield, FE = 50%) or general procedure B giving pure product (76.5 mg, 77% yield, FE = 40%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.19 – 7.12 (m, 2H), 7.12 – 7.07 (m, 3H), 7.04 (dd, *J* = 16.0, 7.0 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.79 – 6.71 (m, 2H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.79 (t, *J* = 6.9 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.56 (dt, *J* = 11.9, 5.5 Hz, 1H), 3.18 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.06 (ddd, *J* = 36.5, 14.4, 6.4 Hz, 2H), 2.89 (d, *J* = 16.2 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 155.0 (d, $J_{C\text{-}F}$ = 236.6 Hz), 145.3, 136.6, 136.3, 135.7, 133.7, 129.5, 129.1, 127.4, 126.4, 125.7, 125.4, 124.8, 124.6, 114.8 (d, *J* = 6.8 Hz), 114.5 (d, *J* = 22.0 Hz), 60.9, 41.5, 37.8, 26.1, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}NF$: 354.1636; Found: 354.1648.

2-(4-chlorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (8)



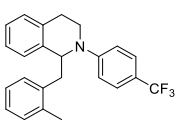
Target compound was obtained according to general procedure A giving pure product (79.1 mg, 76% yield, FE = 48%) or general procedure B giving pure product (79.1 mg, 76% yield, FE = 40%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.08 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 6.7 Hz, 3H), 7.03 – 6.99 (m, 2H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.64 – 6.59 (m, 3H), 4.75 (t, *J* = 6.9 Hz, 1H), 3.65 – 3.60 (m, 1H), 3.46 (dt, *J* = 12.1, 5.9 Hz, 1H), 3.11 (dd, *J* = 13.7, 6.5 Hz, 1H), 3.02 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.72 (d, *J* = 16.0 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 146.9, 136.4, 136.0, 135.7, 133.8, 129.5, 129.2, 128.0, 127.3, 126.4, 125.8, 125.5, 124.9, 124.8, 113.9, 60.4, 41.4, 37.9, 26.2, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}ClN$: 348.1519; Found: 348.1512.

2-(4-bromophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (9)



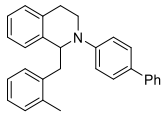
Target compound was obtained according to general procedure A giving pure product (91.5 mg, 78% yield, FE = 49%) or general procedure B giving pure product (92.7 mg, 79% yield, FE = 41%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.17 (d, *J* = 8.6 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.85 (m, 5H), 6.63 (d, *J* = 6.9 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 4.74 (t, *J* = 6.9 Hz, 1H), 3.65 – 3.57 (m, 1H), 3.45 (dt, *J* = 12.2, 5.9 Hz, 1H), 3.10 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.02 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.92 (dt, *J* = 13.7, 6.6 Hz, 1H), 2.71 (d, *J* = 16.0 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 147.4, 136.4, 136.0, 135.7, 133.8, 130.8, 129.5, 129.2, 127.3, 126.3, 125.8, 125.5, 124.9, 124.8, 114.2, 108.1, 60.3, 41.2, 37.9, 26.2, 26.2, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}BrN$: 392.1014; Found: 392.1006.

1-(2-methylbenzyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (10)



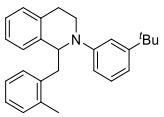
Target compound was obtained according to general procedure A giving pure product (83.5 mg, 73% yield, FE = 46%) or general procedure B giving pure product (86.9 mg, 76% yield, FE = 40%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.6 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.32 (d, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 6.1 Hz, 1H), 7.00 (t, *J* = 6.7 Hz, 2H), 6.97 (d, *J* = 6.9 Hz, 3H), 6.66 (t, *J* = 8.3 Hz, 3H), 4.85 (t, *J* = 6.9 Hz, 1H), 3.65 (ddd, *J* = 12.1, 7.0, 5.1 Hz, 1H), 3.49 (ddd, *J* = 12.3, 7.5, 5.1 Hz, 1H), 3.12 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.05 (dd, *J* = 13.7, 7.1 Hz, 1H), 2.92 (ddd, *J* = 15.6, 6.9, 5.0 Hz, 1H), 2.79 – 2.71 (m, 1H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.29, 136.18, 135.70, 133.83, 129.45, 129.24, 126.35, 125.99, 125.65, 125.46 (q, *J* = 3.8 Hz), 125.0, 124.1 (d, *J* = 269.9 Hz) 123.2, 121.4, 117.2 (q, *J* = 32.8 Hz), 112.0, 110.9, 59.9, 41.3, 37.9, 26.4, 18.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}F_3N$: 382.1783; Found: 382.1776.

2-([1,1'-biphenyl]-4-yl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (11)



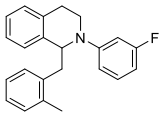
Target compound was obtained according to general procedure A giving pure product (82.9 mg, 71% yield, FE = 44%) or general procedure B giving pure product (91.1 mg, 78% yield, FE = 41%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.45 (d, *J* = 6.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 7.01 (d, *J* = 2.9 Hz, 3H), 6.97 (s, 1H), 6.92 (td, *J* = 7.3, 1.8 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 4.85 (t, *J* = 6.9 Hz, 1H), 3.66 (ddd, *J* = 12.5, 7.7, 5.0 Hz, 1H), 3.52 (dt, *J* = 12.2, 6.0 Hz, 1H), 3.15 (dd, *J* = 13.7, 6.4 Hz, 1H), 3.04 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.95 (ddd, *J* = 15.7, 7.7, 5.3 Hz, 1H), 2.73 (dt, *J* = 15.8, 5.8 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 147.7, 140.1, 136.6, 136.2, 135.8, 134.0, 129.6, 129.2, 128.9, 127.6, 127.2, 126.8, 126.4, 125.7, 125.4, 125.2, 125.0, 124.9, 124.7, 112.7, 60.2, 41.2, 38.0, 26.4, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{28}N$: 390.2222; Found: 390.2216.

2-(3-(tert-butyl)phenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (12)



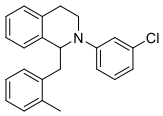
Target compound was obtained according to general procedure A giving pure product (61.9 mg, 56% yield, FE = 35%) or general procedure B giving pure product (58.6 mg, 53% yield, FE = 27%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.17 (d, *J* = 2.6 Hz, 1H), 7.16 (s, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 2.9 Hz, 3H), 7.00 – 6.97 (m, 1H), 6.90 (td, *J* = 7.2, 2.0 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 1H), 4.77 (t, *J* = 7.0 Hz, 1H), 3.49 (dt, *J* = 12.0, 5.9 Hz, 1H), 2.99 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.74 (d, *J* = 12.8 Hz, 1H), 1.90 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 139.1, 136.8, 136.5, 135.8, 134.1, 129.6, 129.1, 127.2, 126.5, 125.5, 125.3, 124.9, 124.8, 124.5, 112.7, 60.5, 41.2, 38.1, 32.8, 30.5, 26.4, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}N$: 370.2535; Found: 370.2530.

2-(3-fluorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (13)



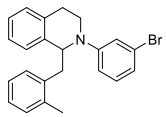
Target compound was obtained according to general procedure A giving pure product (49.6 mg, 50% yield, FE = 31%) or general procedure B giving pure product (50.6 mg, 51% yield, FE = 27%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.02 (m, 3H), 7.02 – 6.99 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 13.1 Hz, 1H), 6.30 (t, *J* = 8.2 Hz, 1H), 4.77 (t, *J* = 6.9 Hz, 1H), 3.60 (ddd, *J* = 12.2, 7.2, 5.0 Hz, 1H), 3.43 (ddd, *J* = 12.3, 7.3, 5.3 Hz, 1H), 3.11 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.91 (ddd, *J* = 15.8, 7.2, 5.2 Hz, 1H), 2.72 (ddd, *J* = 15.8, 7.2, 5.1 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2 (d, *J* = 242.1 Hz), 151.0 (d, *J* = 10.5 Hz), 137.30, 136.920, 136.800, 135.0, 130.5, 130.1 (d, *J* = 10.2 Hz), 130.1, 128.1, 127.4, 126.9, 126.5, 125.9, 125.8, 108.7 (d, *J* = 2.2 Hz), 103.5 (d, *J* = 21.7 Hz), 100.2 (d, *J* = 25.9 Hz), 61.3, 42.5, 38.9, 27.4, 19.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}FN$: 332.1815; Found: 332.1807.

2-(3-chlorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (14)



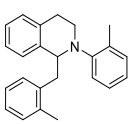
Target compound was obtained according to general procedure A giving pure product (51 mg, 49% yield, FE = 31%) or general procedure B giving pure product (54.1 mg, 52% yield, FE = 27%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.03 – 6.80 (m, 6H), 6.66 (s, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.57 (dd, *J* = 16.6, 8.1 Hz, 2H), 4.77 (t, *J* = 6.9 Hz, 1H), 3.65 – 3.56 (m, 1H), 3.47 – 3.39 (m, 1H), 3.11 (dd, *J* = 13.7, 6.5 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.77 – 2.68 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 135.9, 135.7, 134.1, 133.9, 129.5, 129.2, 129.0, 127.2, 126.4, 125.9, 125.5, 124.9, 124.8, 115.9, 112.2, 110.4, 60.2, 41.3, 37.9, 26.3, 18.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{22}NaClN$: 348.1519; Found: 348.1513.

2-(3-bromophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (15)



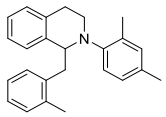
Target compound was obtained according to general procedure A giving pure product (63.3 mg, 54% yield, FE = 33%) or general procedure B giving pure product (66.8 mg, 57% yield, FE = 30%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 – 7.06 (m, 1H), 7.05 (d, *J* = 6.7 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.81 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 11.0 Hz, 1H), 4.77 (t, *J* = 6.9 Hz, 1H), 3.61 (ddd, *J* = 12.4, 7.4, 5.1 Hz, 1H), 3.44 (ddd, *J* = 12.3, 7.0, 5.3 Hz, 1H), 3.11 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.02 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.92 (ddd, *J* = 15.8, 7.5, 5.3 Hz, 1H), 2.74 (ddd, *J* = 15.9, 6.9, 5.0 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.5, 136.3, 135.9, 135.7, 133.9, 129.5, 129.3, 129.2, 127.2, 126.4, 125.9, 125.6, 124.1, 124.8, 122.5, 118.8, 115.1, 110.7, 60.1, 41.3, 37.9, 26.4, 18.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}BrN$: 392.1014; Found: 392.1008.

1-(2-methylbenzyl)-2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline (16)



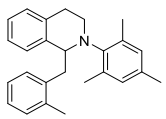
Target compound was obtained according to general procedure A giving pure product (76.6 mg, 78% yield, FE = 49%) or general procedure B giving pure product (70.7 mg, 72% yield, FE = 24%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, J = 6.0 Hz, 1H), 7.05 (d, J = 4.4 Hz, 1H), 7.04 (d, J = 5.6 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.98 (t, J = 2.7 Hz, 2H), 6.97 (d, J = 3.8 Hz, 1H), 6.94 (dd, J = 7.9, 2.5 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 4.35 (t, J = 7.2 Hz, 1H), 3.65 (td, J = 12.5, 4.1 Hz, 1H), 3.16 (dd, J = 13.4, 6.0 Hz, 1H), 3.06 (dd, J = 14.0, 8.0 Hz, 1H), 2.93 (dd, J = 14.0, 6.4 Hz, 1H), 2.80 (td, J = 11.5, 5.9 Hz, 1H), 2.57 (d, J = 16.5 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 138.0, 137.1, 135.4, 134.1, 132.5, 130.0, 129.6, 129.0, 128.1, 126.2, 125.3, 125.2, 125.0, 124.5, 124.5, 122.2, 121.7, 60.6, 42.1, 38.2, 25.2, 18.2, 17.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}N$: 328.2065; Found: 328.2051.

2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (17)



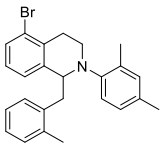
Target compound was obtained according to general procedure A giving pure product (87.0 mg, 85% yield, FE = 53%) or general procedure B giving pure product (83.9 mg, 82% yield, FE = 43%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (td, J = 7.4, 1.4 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.99 – 6.88 (m, 4H), 6.86 (s, 1H), 6.72 (t, J = 8.5 Hz, 2H), 6.63 (d, J = 8.1 Hz, 1H), 4.31 (t, J = 7.2 Hz, 1H), 3.66 – 3.57 (m, 1H), 3.11 (dd, J = 13.3, 5.9 Hz, 1H), 3.05 (dd, J = 14.1, 8.1 Hz, 1H), 2.91 (dd, J = 14.0, 6.2 Hz, 1H), 2.79 (ddd, J = 17.3, 11.7, 6.1 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 138.2, 137.2, 135.4, 134.2, 132.4, 131.5, 130.7, 129.6, 129.0, 128.0, 126.2, 125.7, 125.2, 124.9, 124.5, 124.5, 121.7, 60.7, 42.2, 38.3, 25.0, 19.6, 18.4, 16.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{28}N$: 342.2222; Found: 342.2203.

2-mesityl-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (18)



Target compound was obtained according to general procedure A giving pure product (99.1 mg, 93% yield, FE = 58%) or general procedure B giving pure product (95.9 mg, 90% yield, FE = 47%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 6.91 (d, J = 7.5 Hz, 2H), 6.85 (s, 1H), 6.81 (s, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.71 – 6.61 (m, 1H), 6.01 (d, J = 7.6 Hz, 1H), 4.27 (dd, J = 10.2, 4.3 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.12 (td, J = 9.8, 3.1 Hz, 1H), 3.09 – 3.04 (m, 1H), 3.02 (dd, J = 13.1, 4.5 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.32 (s, 3H), 2.21 (s, 3H), 2.01 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.2, 137.0, 136.5, 136.4, 135.9, 135.8, 135.1, 133.4, 129.6, 129.2, 128.9, 128.8, 127.1, 126.7, 125.0, 124.9, 124.4, 123.8, 62.5, 46.2, 41.4, 30.3, 19.8, 18.1, 18.0, 17.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{30}N$ 356.2378; Found: 356.2367.

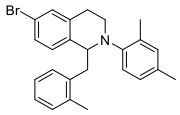
5-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (19)



Target compound was obtained according to general procedure A giving pure product (100.6 mg, 80% yield, FE = 50%) or general procedure B giving pure

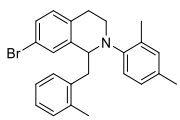
product (94.3 mg, 75% yield, FE = 39%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.09 (d, J = 10.4 Hz, 1H), 6.98 (d, J = 7.1 Hz, 3H), 6.90 (d, J = 6.9 Hz, 1H), 6.88 (s, 1H), 6.74 (d, J = 9.6 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 8.2 Hz, 1H), 4.24 (t, J = 7.2 Hz, 1H), 3.63 – 3.51 (m, 1H), 3.10 (dd, J = 13.4, 5.9 Hz, 1H), 3.02 (dd, J = 13.9, 7.5 Hz, 1H), 2.86 (dd, J = 13.9, 6.8 Hz, 1H), 2.79 (ddd, J = 17.4, 11.3, 6.0 Hz, 1H), 2.55 (d, J = 16.9 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 137.1, 136.7, 136.6, 135.4, 132.4, 131.8, 130.8, 130.8, 129.6, 129.1, 127.9, 127.5, 125.7, 125.1, 124.6, 121.6, 118.9, 60.4, 41.9, 37.9, 25.2, 19.7, 18.3, 16.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}BrN$ 420.1327; Found 420.1318.

6-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (20)



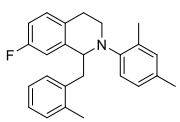
Target compound was obtained according to general procedure A giving pure product (96.8 mg, 77% yield, FE = 48%) or general procedure B giving pure product (99.3 mg, 79% yield, FE = 41%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 4.7 Hz, 3H), 6.90 (d, J = 6.8 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 6.8 Hz, 2H), 4.26 (t, J = 7.1 Hz, 1H), 3.63 (ddd, J = 13.1, 11.3, 4.6 Hz, 1H), 3.20 (dd, J = 13.5, 6.4 Hz, 1H), 3.05 (dd, J = 13.9, 7.5 Hz, 1H), 2.89 (dd, J = 13.9, 6.8 Hz, 1H), 2.72 (d, J = 16.3 Hz, 1H), 2.64 (ddd, J = 17.5, 11.3, 6.5 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 140.7, 136.7, 135.4, 133.7, 132.3, 131.7, 130.8, 129.6, 129.4, 129.1, 125.7, 125.6, 125.4, 125.1, 124.6, 124.5, 121.3, 60.8, 42.0, 37.7, 26.2, 19.7, 18.3, 16.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}BrN$ 420.1327; Found 420.1319.

7-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (21)



Target compound was obtained according to general procedure A giving pure product (99.3 mg, 79% yield, FE = 49%) or general procedure B giving pure product (104.4 mg, 83% yield, FE = 44%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 6.7 Hz, 3H), 6.91 (d, J = 8.3 Hz, 2H), 6.87 (s, 1H), 6.78 (s, 1H), 6.72 (d, J = 10.3 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 4.24 (t, J = 7.3 Hz, 1H), 3.60 – 3.53 (m, 1H), 3.10 (dd, J = 13.4, 6.0 Hz, 1H), 3.03 (dd, J = 14.0, 8.0 Hz, 1H), 2.88 (dd, J = 13.9, 6.5 Hz, 1H), 2.70 (ddd, J = 17.4, 11.7, 6.1 Hz, 1H), 2.48 (d, J = 16.2 Hz, 1H), 2.15 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 140.3, 136.6, 135.3, 133.1, 132.4, 131.8, 130.8, 129.7, 129.5, 129.1, 129.1, 128.2, 125.7, 125.2, 124.6, 121.5, 117.9, 60.5, 42.0, 38.1, 24.6, 19.7, 18.3, 16.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}BrN$ 420.1327; Found 420.1321.

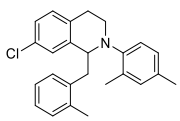
2-(2,4-dimethylphenyl)-7-fluoro-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (22)



Target compound was obtained according to general procedure A giving pure product (83.0 mg, 77% yield, FE = 48%) or general procedure B giving pure product (86.2 mg, 80% yield, FE = 42%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (q, J = 5.3, 4.2 Hz, 4H), 6.94 (d, J = 5.2 Hz, 1H), 6.86 (s, 1H), 6.79 (td, J = 8.4, 2.7 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H), 4.26 (t, J = 7.2 Hz, 1H), 3.57 (dd, J = 14.7, 10.4 Hz, 1H), 3.10 (dd, J = 13.8, 5.5 Hz, 1H), 3.04 (dd, J = 14.0, 8.0 Hz, 1H), 2.89 (dd, J = 14.0,

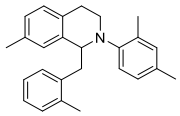
6.4 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.49 (s, 1H), 2.15 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6 (d, *J* = 243.9 Hz), 146.7, 140.0 (d, *J* = 6.1 Hz), 136.8, 135.3, 132.4, 131.7, 130.8, 129.7 (d, *J* = 2.8 Hz), 129.5, 129.3 (d, *J* = 7.4 Hz), 129.1, 125.7, 125.2, 124.6, 121.6, 112.5 (d, *J* = 21.0 Hz), 112.3 (d, *J* = 21.3 Hz), 60.7, 42.3, 38.1, 24.3, 19.6, 18.3, 16.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}FN$ 360.2128; Found 360.2111.

7-chloro-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (23)



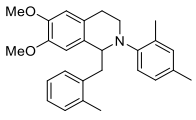
Target compound was obtained according to general procedure A giving pure product (84.4 mg, 75% yield, FE = 47%) or general procedure B giving pure product (84.4 mg, 75% yield, FE = 40%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.1 Hz, 1H), 7.03 – 6.98 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 6.6 Hz, 1H), 6.86 (s, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.64 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.25 (t, *J* = 7.3 Hz, 1H), 3.57 (td, *J* = 12.5, 4.1 Hz, 1H), 3.10 (dd, *J* = 13.5, 6.0 Hz, 1H), 3.03 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.73 (ddd, *J* = 17.4, 11.6, 6.1 Hz, 1H), 2.51 (d, *J* = 13.7 Hz, 1H), 2.15 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 139.9, 136.7, 135.3, 132.6, 132.4, 131.8, 130.8, 129.9, 129.5, 129.3, 129.1, 126.1, 125.7, 125.4, 125.2, 124.6, 121.6, 60.5, 42.1, 38.1, 24.5, 19.6, 18.3, 16.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}ClN$ 376.1832; Found 376.1824.

2-(2,4-dimethylphenyl)-7-methyl-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (24)



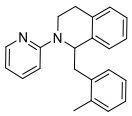
Target compound was obtained according to general procedure A giving pure product (82.1 mg, 77% yield, FE = 48%) or general procedure B giving pure product (77.8 mg, 73% yield, FE = 38%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 – 6.94 (m, 4H), 6.91 (q, *J* = 7.8 Hz, 2H), 6.85 (s, 1H), 6.70 (d, *J* = 10.3 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.51 (s, 1H), 4.29 – 4.23 (m, 1H), 3.63 – 3.53 (m, 1H), 3.13 – 3.00 (m, 2H), 2.89 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.48 (d, *J* = 21.3 Hz, 1H), 2.15 (d, *J* = 10.7 Hz, 6H), 2.04 (d, *J* = 10.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 138.9, 138.40, 136.4, 134.8, 133.4, 132.4, 132.1, 131.7, 130.6, 129.9, 128.9, 127.8, 127.0, 126.7, 125.9, 125.4, 122.8, 61.7, 43.4, 39.4, 25.7, 21.1, 20.7, 19.4, 17.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{30}N$ 356.2378; Found 356.2378.

2-(2,4-dimethylphenyl)-6,7-dimethoxy-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (25)



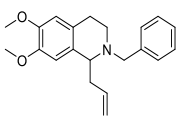
Target compound was obtained according to general procedure A giving pure product (81.8 mg, 68% yield, FE = 43%) or general procedure B giving pure product (85.5 mg, 71% yield, FE = 37%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (s, 3H), 6.91 (s, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.53 (s, 1H), 5.89 (s, 1H), 4.21 (t, *J* = 7.3 Hz, 1H), 3.78 (s, 3H), 3.60 (t, *J* = 12.3 Hz, 1H), 3.46 (s, 3H), 3.13 (dd, *J* = 13.4, 5.8 Hz, 1H), 3.01 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.91 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.76 (ddd, *J* = 16.9, 11.4, 6.1 Hz, 1H), 2.52 (d, *J* = 16.0 Hz, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 146.5, 145.4, 137.2, 135.8, 132.3, 131.5, 130.8, 129.7, 129.5, 129.1, 125.8, 125.7, 125.0, 124.6, 121.6, 110.6, 109.5, 60.4, 54.8, 54.5, 42.5, 37.5, 25.5, 19.7, 18.3, 17.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{32}NO_2$ 402.2433; Found 402.2432.

1-(2-methylbenzyl)-2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (26)



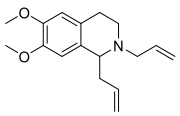
Target compound was obtained according to general procedure A giving pure product (65.0 mg, 69% yield, FE = 43%) or general procedure B giving pure product (62.2 mg, 66% yield, FE = 35%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.48 (t, J = 6.8 Hz, 1H), 3.79 (p, J = 6.3 Hz, 1H), 3.62 (dt, J = 11.9, 5.9 Hz, 1H), 3.20 (dd, J = 13.3, 6.1 Hz, 1H), 3.04 (dd, J = 13.3, 7.7 Hz, 1H), 2.90 (dt, J = 15.7, 5.9 Hz, 1H), 2.79 (ddd, J = 15.7, 7.9, 5.2 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 146.7, 136.5, 136.2, 135.9, 134.3, 129.9, 128.9, 127.0, 126.6, 125.7, 125.3, 124.7, 124.6, 110.8, 105.1, 56.7, 39.9, 38.2, 27.04, 18.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1861; Found 315.1859.

1-allyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (27)[5]



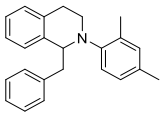
Target compound was obtained according to general procedure A giving pure product (30.0 mg, 31% yield, FE = 19%) or general procedure B giving pure product (27.0 mg, 28% yield, FE = 15%), purification by flash chromatography on aluminum trioxide (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 7.5 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.19 – 7.16 (m, 1H), 6.51 (s, 1H), 6.46 (s, 1H), 5.86 – 5.76 (m, 1H), 4.97 – 4.91 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 3.72 (s, 1H), 3.64 (d, J = 13.8 Hz, 1H), 3.58 (t, J = 6.5 Hz, 1H), 3.11 (ddd, J = 14.2, 9.5, 4.8 Hz, 1H), 2.76 (ddd, J = 15.7, 9.6, 5.7 Hz, 1H), 2.70 (dt, J = 13.4, 4.3 Hz, 1H), 2.52 (dt, J = 14.6, 7.0 Hz, 1H), 2.44 (dt, J = 16.2, 4.4 Hz, 1H), 2.41 – 2.35 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 147.2, 139.7, 136.9, 130.1, 128.8, 128.2, 126.9, 126.6, 115.7, 111.6, 111.0, 60.7, 57.9, 56.0, 55.9, 43.7, 40.4, 24.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{26}NO_2$ 324.1964; Found 324.1963.

1-(2-methylbenzyl)-2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (28)[5]



Target compound was obtained according to general procedure A giving pure product (43.1 mg, 53% yield, FE = 33%) or general procedure B giving pure product (45.0 mg, 55% yield, FE = 29%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 2:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.56 (s, 1H), 5.86-6.00 (m, 2H), 5.15-5.23 (m, 2H), 5.06-5.09 (m, 1H), 5.04 (t, J = 1.23 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.71 (t, J = 6.40 Hz, 1H), 3.28 (s, 1H), 3.26 (s, 1H), 3.18-3.25 (m, 1H), 2.79-2.91 (m, 2H), 2.52-2.63 (m, 2H), 2.41-2.48 (m, 1H). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}N$ 274.1807; Found 274.1802.

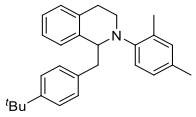
1-benzyl-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (29)



Target compound was obtained according to general procedure A giving pure product (78.5 mg, 80% yield, FE = 50%) or general procedure B giving pure product (71.6 mg, 73% yield, FE = 38%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.02 (m, 6H), 6.99 (d, J = 7.4 Hz, 2H), 6.91 (d, J = 7.4 Hz, 1H), 6.86 (s, 1H), 6.72 (d, J = 10.3 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H), 4.42 (t, J = 7.0 Hz, 1H), 3.47 (t, J = 12.2 Hz, 1H), 3.08 (dd, J = 14.2, 8.0 Hz, 2H), 2.91 (dd, J = 14.1, 5.6 Hz, 1H), 2.74 (dd, J = 16.4, 11.0 Hz, 1H), 2.51 (d, J = 16.4 Hz, 1H), 2.15 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 139.1, 138.3, 134.4, 132.5, 131.5, 130.8, 128.5, 128.1, 126.9, 126.2, 125.7, 125.1, 124.8, 124.6, 121.1, 61.5, 42.7, 41.6, 25.1, 19.7, 16.8. HRMS (ESI) *m/z*: [M +

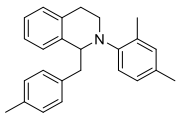
H]$^+$ Calcd for $C_{24}H_{26}N$ 328.2065; Found 328.2058.

1-(4-(tert-butyl)benzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (30)



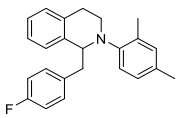
Target compound was obtained according to general procedure A giving pure product (92.0 mg, 80% yield, FE = 50%) or general procedure B giving pure product (86.2 mg, 75% yield, FE = 39%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.3 Hz, 2H), 7.08 (q, *J* = 7.3, 6.1 Hz, 2H), 7.03 (d, *J* = 6.3 Hz, 1H), 6.96 (d, *J* = 5.8 Hz, 2H), 6.94 (s, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 4.38 (d, *J* = 3.2 Hz, 1H), 3.49 (ddd, *J* = 13.3, 11.3, 4.0 Hz, 1H), 3.10 – 2.99 (m, 2H), 2.88 (dd, *J* = 14.2, 5.4 Hz, 1H), 2.73 (ddd, *J* = 16.8, 11.3, 5.8 Hz, 1H), 2.15 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 147.1, 138.6, 136.1, 134.4, 132.5, 131.4, 130.7, 128.1, 128.0, 126.1, 125.6, 125.1, 124.6, 123.8, 121.7, 61.5, 42.4, 41.3, 33.3, 30.4, 24.9, 19.7, 16.7. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{28}H_{34}N$ 384.2691; Found 384.2688.

2-(2,4-dimethylphenyl)-1-(4-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (31)



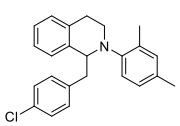
Target compound was obtained according to general procedure A giving pure product (80.9 mg, 79% yield, FE = 79%) or general procedure B giving pure product (74.7 mg, 73% yield, FE = 73%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.89 – 6.84 (m, 3H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.37 (t, *J* = 7.0 Hz, 1H), 3.47 (td, *J* = 12.6, 11.6, 4.1 Hz, 1H), 3.05 (dt, *J* = 14.0, 7.7 Hz, 2H), 2.86 (dd, *J* = 14.1, 5.6 Hz, 1H), 2.73 (ddd, *J* = 16.8, 11.2, 5.8 Hz, 1H), 2.50 (d, *J* = 16.3 Hz, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 138.4, 136.0, 134.4, 134.1, 132.4, 131.4, 130.7, 128.3, 128.0, 127.6, 126.2, 125.7, 125.1, 124.6, 121.6, 61.6, 42.7, 41.2, 25.1, 20.0, 19.7, 16.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{25}H_{28}NO$ 342.2222; Found 342.2221.

2-(2,4-dimethylphenyl)-1-(4-fluorobenzyl)-1,2,3,4-tetrahydroisoquinoline (32)



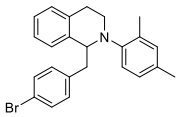
Target compound was obtained according to general procedure A giving pure product (75.6 mg, 73% yield, FE = 46%) or general procedure B giving pure product (81.8 mg, 79% yield, FE = 42%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 8.3, 5.6 Hz, 3H), 6.87 (s, 1H), 6.80 (t, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 10.3 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 4.40 (t, *J* = 6.9 Hz, 1H), 3.46 – 3.39 (m, 1H), 3.10 – 3.00 (m, 2H), 2.89 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.51 (d, *J* = 16.4 Hz, 1H), 2.16 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4 (d, *J* = 243.2 Hz), 146.8, 137.9, 134.7, 134.5, 132.4, 131.7, 130.8, 129.8 (d, *J* = 7.7 Hz), 128.1, 126.1, 125.7, 125.2, 124.7, 121.5, 113.6 (d, *J* = 20.9 Hz), 61.5, 43.0, 40.7, 25.1, 19.7, 16.8. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{24}H_{25}FN$ 346.1971; Found 346.1972.

1-(4-chlorobenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (33)



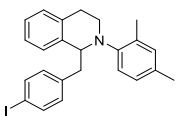
Target compound was obtained according to general procedure A giving pure product (75.8 mg, 70% yield, FE = 44%) or general procedure B giving pure product (79.1 mg, 73% yield, FE = 38%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 4H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.87 (s, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.40 (dd, *J* = 8.2, 5.4 Hz, 1H), 3.41 (ddd, *J* = 13.4, 10.8, 4.1 Hz, 1H), 3.03 (dd, *J* = 14.3, 7.7 Hz, 2H), 2.89 (dd, *J* = 14.1, 5.3 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.50 (d, *J* = 12.8 Hz, 1H), 2.16 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 138.9, 138.6, 135.5, 133.4, 132.7, 131.8, 131.6, 130.8, 129.1, 128.0, 126.7, 126.2, 125.7, 122.5, 62.3, 43.9, 41.9, 26.1, 20.6, 17.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}ClN$ 362.1676; Found 362.1660.

1-(4-bromobenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (34)



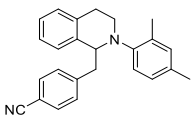
Target compound was obtained according to general procedure A giving pure product (89.9 mg, 74% yield, FE = 46%) or general procedure B giving pure product (91.1 mg, 75% yield, FE = 39%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.08 (td, *J* = 6.7, 6.1, 3.8 Hz, 2H), 7.02 (d, *J* = 5.5 Hz, 1H), 6.93 (d, *J* = 5.6 Hz, 1H), 6.86 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.39 (dd, *J* = 8.1, 5.5 Hz, 1H), 3.43 – 3.36 (m, 1H), 3.06 – 2.97 (m, 2H), 2.86 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.70 (ddd, *J* = 16.4, 10.8, 5.5 Hz, 1H), 2.49 (dt, *J* = 16.5, 3.6 Hz, 1H), 2.15 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 139.1, 138.9, 135.6, 133.4, 132.7, 131.9, 131.2, 131.0, 129.2, 127.1, 126.8, 126.3, 125.8, 122.5, 119.6, 62.3, 44.0, 42.0, 26.1, 20.7, 17.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}BrN$ 406.1170; Found 406.1160.

2-(2,4-dimethylphenyl)-1-(4-iodobenzyl)-1,2,3,4-tetrahydroisoquinoline (35)



Target compound was obtained according to general procedure A giving pure product (99.2 mg, 73% yield, FE = 46%) or general procedure B giving pure product (81.6 mg, 60% yield, FE = 26%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.09 (t, *J* = 5.9 Hz, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 6.1 Hz, 1H), 6.87 (s, 1H), 6.72 (d, *J* = 8.3 Hz, 3H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.39 (dd, *J* = 8.2, 5.4 Hz, 1H), 3.40 (ddd, *J* = 13.2, 10.8, 4.1 Hz, 1H), 3.03 (d, *J* = 11.3 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.85 (dd, *J* = 14.1, 5.3 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.49 (d, *J* = 16.4 Hz, 1H), 2.15 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 138.8, 137.8, 136.3, 135.9, 134.5, 132.4, 131.7, 130.8, 130.6, 128.1, 126.8, 126.1, 125.7, 125.2, 124.9, 124.7, 121.5, 89.9, 61.2, 42.9, 41.1, 25.1, 19.8, 197, 16.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}IN$ 454.1032; Found 454.1031.

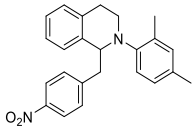
4-((2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)methyl)benzonitrile (36)



Target compound was obtained according to general procedure A giving pure product (42.3 mg, 40% yield, FE = 25%) or general procedure B giving pure product (74.0 mg, 70% yield, FE = 37%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 4.9 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 9.1 Hz,

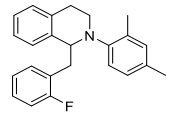
1H), 7.01 – 6.95 (m, 1H), 6.86 (s, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.48 (dd, *J* = 8.5, 5.1 Hz, 1H), 3.43 – 3.36 (m, 1H), 3.12 (dd, *J* = 14.2, 8.5 Hz, 1H), 3.02 (td, *J* = 14.0, 4.3 Hz, 2H), 2.70 (ddd, *J* = 16.1, 10.5, 5.4 Hz, 1H), 2.50 (d, *J* = 16.4 Hz, 1H), 2.16 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 146.4, 144.8, 137.4, 134.6, 132.3, 132.0, 130.92, 130.7, 129.2, 128.3, 125.9, 125.8, 125.5, 124.9, 121.4, 118.1, 108.7, 61.0, 43.1, 41.7, 25.0, 19.7, 16.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{25}N$ 353.2018; Found 353.2012.

2-(2,4-dimethylphenyl)-1-(4-nitrobenzyl)-1,2,3,4-tetrahydroisoquinoline (37)



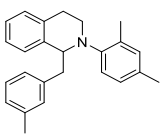
Target compound was obtained according to general procedure A giving pure product (60.5mg, 54% yield, FE = 33%) or general procedure B giving pure product (70.5 mg, 63% yield, FE = 33%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.97 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 9.1 Hz, 4H), 7.09 – 7.03 (m, 1H), 7.02 – 6.95 (m, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.74 (d, *J* = 10.3 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 4.54 (t, *J* = 6.7 Hz, 1H), 3.40 (ddd, *J* = 14.0, 10.4, 4.1 Hz, 1H), 3.18 (dd, *J* = 14.2, 8.4 Hz, 1H), 3.06 (dd, *J* = 14.1, 5.1 Hz, 2H), 2.71 (ddd, *J* = 16.0, 10.4, 5.3 Hz, 1H), 2.53 (d, *J* = 16.4 Hz, 1H), 2.16 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 147.1, 146.4, 145.4, 137.3, 134.7, 132.3, 132.1, 130.9, 129.2, 128.3, 125.9, 125.9, 125.5, 125.0, 122.1, 121.4, 61.0, 43.3, 41.4, 25.1, 19.7, 16.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_2$ 373.1916; Found 373.1910.

2-(2,4-dimethylphenyl)-1-(2-fluorobenzyl)-1,2,3,4-tetrahydroisoquinoline (38)



Target compound was obtained according to general procedure A giving pure product (72.5 mg, 70% yield, FE = 44%) or general procedure B giving pure product (65.2 mg, 63% yield, FE = 33%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.11 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 1H), 7.06 – 7.01 (m, 3H), 6.93 – 6.84 (m, 2H), 6.81 (s, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 4.39 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.56 (ddd, *J* = 13.7, 11.8, 3.9 Hz, 1H), 3.15 – 3.03 (m, 2H), 2.97 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.79 – 2.66 (m, 1H), 2.46 (d, *J* = 18.5 Hz, 1H), 2.12 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 161.4, 159.7, 147.0, 138.3, 134.5, 132.4, 131.5, 130.8, 130.8, 130.6, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 125.6, 125.2, 124.8, 122.5, 122.5, 121.7, 114.0, 113.9, 60.7, 42.0, 35.3, 24.2, 19.6, 16.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}NF$ 346.1971; Found 346.1962.

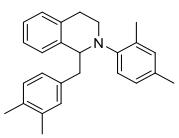
2-(2,4-dimethylphenyl)-1-(3-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (39)



Target compound was obtained according to general procedure A giving pure product (76.8 mg, 75% yield, FE = 47%) or general procedure B giving pure product (71.7 mg, 70% yield, FE = 37%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.08 (p, *J* = 7.3 Hz, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 10.0 Hz, 2H), 6.80 (d, *J* = 11.1 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.38 (t, *J* = 6.7 Hz, 1H), 3.49 (t, *J* = 10.3 Hz, 1H), 3.13 – 2.96 (m, 2H), 2.86 (dd, *J* = 14.0, 5.5 Hz, 1H), 2.73 (ddd, *J* = 16.8, 11.1, 5.8 Hz, 1H), 2.50 (d, *J* = 16.4 Hz, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 148.2, 140.0, 139.4, 137.3, 135.4, 133.4, 132.5, 131.8, 130.4, 129.0, 127.8, 127.2, 126.7, 126.5, 126.1, 125.6, 122.6, 62.7, 43.7, 42.6, 26.1, 21.3, 20.7, 17.8. HRMS (ESI) *m/z*: [M +

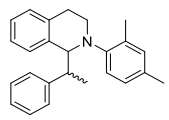
H]$^+$ Calcd for $C_{25}H_{28}N$ 342.2222; Found 342.2213.

1-(3,4-dimethylbenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (40)



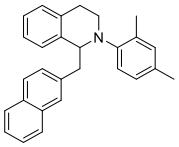
Target compound was obtained according to general procedure A giving pure product (82.1 mg, 77% yield, FE = 48%) or general procedure B giving pure product (79.9 mg, 75% yield, FE = 40%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.77 (s, 1H), 6.75 – 6.69 (m, 2H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.35 (t, *J* = 6.9 Hz, 1H), 3.49 (td, *J* = 12.4, 10.9, 4.0 Hz, 1H), 3.08 (d, *J* = 12.9 Hz, 1H), 3.02 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.82 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.73 (ddd, *J* = 16.6, 11.2, 5.6 Hz, 1H), 2.50 (d, *J* = 16.4 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 137.5, 135.8, 135.4, 133.7, 133.4, 132.4, 131.7, 130.9, 129.2, 129.0, 127.3, 126.8, 126.7, 126.0, 125.6, 122.6, 62.7, 43.7, 42.3, 26.1, 20.6, 19.5, 19.2, 17.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{26}H_{30}NO$ 356.2378; Found 356.2370.

2-(2,4-dimethylphenyl)-1-(1-phenylethyl)-1,2,3,4-tetrahydroisoquinoline (41)



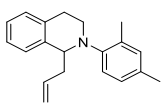
Target compound was obtained according to general procedure B giving pure product trace or general procedure B giving pure product (67.6 mg, 66% yield, FE = 35%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 5H), 6.98 – 6.91 (m, 4H), 6.87 (s, 1H), 6.74 (q, *J* = 8.3 Hz, 2H), 4.45 (d, *J* = 5.8 Hz, 1H), 3.18 (t, *J* = 6.7 Hz, 1H), 2.98 (ddd, *J* = 13.2, 8.7, 4.6 Hz, 1H), 2.74 (dt, *J* = 13.0, 5.0 Hz, 1H), 2.55 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.49 (d, *J* = 16.2 Hz, 1H), 2.16 (s, 3H), 1.95 (s, 3H), 1.20 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.7, 144.3, 144.1, 137.1, 136.8, 135.6, 134.5, 133.1, 132.0, 131.7, 131.2, 130.81, 130.70, 127.80, 127.76, 127.59, 127.12, 126.97, 126.88, 125.89, 125.84, 125.13, 125.08, 124.9, 124.7, 124.1, 123.6, 122.2, 121.6, 65.9, 65.8, 46.0, 45.1, 44.4, 42.8, 25.8, 24.3, 19.7, 19.6, 18.7, 17.4, 16.9, 16.6, 16.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{25}H_{28}NO$ 342.2222; Found 342.2217.

2-(2,4-dimethylphenyl)-1-(naphthalen-2-ylmethyl)-1,2,3,4-tetrahydroisoquinoline (42)



Target compound was obtained according to general procedure A giving pure product (82.5 mg, 73% yield, FE = 46%) or general procedure B giving pure product (76.8 mg, 68% yield, FE = 36%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.9 Hz, 2H), 7.41 (s, 1H), 7.34 – 7.26 (m, 2H), 7.13 – 7.07 (m, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 6.73 – 6.64 (m, 2H), 4.50 (d, *J* = 7.1 Hz, 1H), 3.51 (ddd, *J* = 14.3, 11.0, 3.9 Hz, 1H), 3.23 (dd, *J* = 14.1, 8.0 Hz, 1H), 3.07 (dt, *J* = 14.1, 7.1 Hz, 2H), 2.73 (ddd, *J* = 16.6, 10.9, 5.6 Hz, 1H), 2.59 – 2.46 (m, 1H), 2.13 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 138.2, 136.7, 134.5, 132.5, 132.4, 131.5, 131.0, 130.8, 128.1, 127.1, 126.9, 126.5, 126.4, 126.3, 126.2, 125.7, 125.1, 124.6, 124.6, 124.0, 121.5, 61.4, 42.9, 41.7, 25.2, 19.6, 16.8. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{28}H_{28}N$ 378.2222; Found 378.2207.

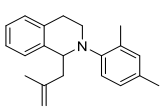
1-allyl-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (43)



Target compound was obtained according to general procedure A giving pure product (69.0 mg, 83% yield, FE = 52%) or general procedure B giving pure

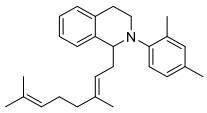
product (68.2 mg, 82% yield, FE = 43%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, J = 7.4 Hz, 2H), 7.10 – 7.06 (m, 1H), 7.03 (d, J = 7.4 Hz, 1H), 6.94 (s, 1H), 6.77 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 5.74 (td, J = 17.1, 6.9 Hz, 1H), 4.87 (d, J = 10.2 Hz, 1H), 4.85 (s, 1H), 4.29 (dd, J = 7.8, 4.6 Hz, 1H), 3.38 – 3.29 (m, 1H), 3.02 (d, J = 13.2 Hz, 1H), 2.78 – 2.65 (m, 1H), 2.60 (d, J = 16.3 Hz, 1H), 2.56 – 2.49 (m, 1H), 2.42 – 2.36 (m, 1H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 138.1, 135.7, 134.6, 132.8, 131.7, 130.7, 128.0, 126.0, 125.8, 124.9, 124.7, 121.6, 114.7, 59.7, 44.0, 39.54, 25.9, 19.7, 16.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}N$ 278.1909; Found 278.1901.

2-(2,4-dimethylphenyl)-1-(2-methylallyl)-1,2,3,4-tetrahydroisoquinoline (44)



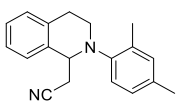
Target compound was obtained according to general procedure A giving pure product (68.1 mg, 78% yield, FE = 49%) or general procedure B giving pure product (62.9 mg, 72% yield, FE = 38%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 3H), 7.01 (d, J = 8.6 Hz, 1H), 6.91 (s, 1H), 6.71 (d, J = 8.1 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 4.68 (s, 1H), 4.60 (s, 1H), 4.35 – 4.26 (m, 1H), 3.44 – 3.34 (m, 1H), 3.05 (d, J = 13.0 Hz, 1H), 2.70 (t, J = 16.8 Hz, 1H), 2.54 (dd, J = 14.4, 9.2 Hz, 1H), 2.45 (d, J = 16.5 Hz, 1H), 2.33 (d, J = 14.4 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 142.9, 139.0, 134.4, 132.4, 131.4, 130.7, 128.1, 125.9, 125.7, 124.9, 124.7, 121.6, 111.2, 58.1, 44.3, 42.2, 24.5, 21.1, 19.7, 16.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{26}N$ 292.2065; Found 292.2059.

(E)-1-(3,8-dimethylnona-2,7-dien-1-yl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydro isoquinoline (45)



Target compound was obtained according to general procedure A giving pure product (42.5 mg, 38% yield, FE = 24%) or general procedure B giving pure product (35.8 mg, 32% yield, FE = 17%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, J = 10.2 Hz, 3H), 7.03 (d, J = 6.9 Hz, 1H), 6.93 (s, 1H), 6.77 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 5.13 (s, 1H), 5.03 – 4.93 (m, 1H), 4.21 (s, 1H), 3.37 (s, 1H), 3.04 (s, 1H), 2.73 (s, 1H), 2.60 (d, J = 14.6 Hz, 1H), 2.44 (d, J = 8.2 Hz, 1H), 2.33 (s, 1H), 2.23 (s, 3H), 2.18 (s, 3H), 2.01 – 1.89 (m, 2H), 1.86 (d, J = 7.9 Hz, 2H), 1.66 (m, 3H), 1.58 (m, 3H), 1.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.7, 130.7, 130.2, 127.9, 126.0, 125.7, 124.9, 124.7, 123.5, 121.7, 60.0, 38.8, 38.4, 36.4, 33.7, 28.7, 25.9, 25.6, 25.5, 24.9, 24.6, 22.4, 21.4, 19.7, 17.0, 16.6, 15.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{27}H_{35}NNa$ 396.2667; Found 396.2672.

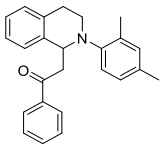
2-(2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile (46)



Target compound was obtained according to general procedure A giving pure product (33.9 mg, 41% yield, FE = 26%) or general procedure B giving pure product (29.0 mg, 35% yield, FE = 18%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 2H), 7.14 (d, J = 9.0 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.99 (s, 1H), 6.85 (dd, J = 8.1, 2.1 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.60 (t, J = 5.7 Hz, 1H), 3.28 (ddd, J = 12.7, 8.1, 4.6 Hz, 1H), 3.06 (dt, J = 12.8, 5.1 Hz, 1H), 2.79 (dtt, J = 21.1, 13.0, 4.8 Hz, 2H), 2.69 (dd, J = 16.7, 6.2 Hz, 1H), 2.62 (dd, J = 16.8, 5.3 Hz, 1H), 2.30 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 135.8, 135.6, 134.9,

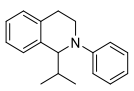
134.3, 132.2, 129.4, 127.3, 127.2, 126.5, 126.4, 122.5, 118.3, 57.7, 46.2, 27.8, 24.8, 20.8, 17.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2$ 277.1705; Found 277.1703.

2-(2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethan-1-one (47)



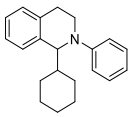
Target compound was obtained according to general procedure A giving pure product (67 mg, 63% yield, FE = 39%) or general procedure B giving pure product (51.1 mg, 48% yield, FE = 25%), purification by flash chromatography on aluminum trioxide (PE : EA = 200 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 2.9 Hz, 3H), 7.06 – 7.02 (m, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.70 – 6.62 (m, 2H), 5.05 (t, *J* = 6.2 Hz, 1H), 3.54 (dd, *J* = 15.7, 7.3 Hz, 1H), 3.46 – 3.36 (m, 1H), 3.05 (dt, *J* = 14.9, 4.7 Hz, 2H), 2.80 (ddd, *J* = 16.3, 10.7, 5.6 Hz, 1H), 2.61 (dt, *J* = 16.5, 3.6 Hz, 1H), 2.12 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.8, 147.3, 139.2, 137.6, 135.1, 133.5, 132.9, 132.8, 131.8, 129.2, 128.4, 128.1, 126.8, 126.8, 126.4, 126.1, 122.4, 57.5, 45.0, 44.5, 35.5, 26.9, 20.7, 17.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}NO$ 356.2014; Found 356.2008.

1-isopropyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (50)[6]



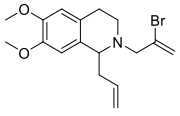
Target compound was obtained according to general procedure C giving pure product (46.1 mg, 55% yield, FE = 15%) purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 6.9 Hz, 1H), 7.06 (d, *J* = 6.1 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 7.4 Hz, 1H), 4.31 (d, *J* = 8.1 Hz, 1H), 3.67 (p, *J* = 6.0 Hz, 1H), 3.40 (dt, *J* = 12.0, 7.0 Hz, 1H), 2.96 – 2.87 (m, 2H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1, 136.8, 134.3, 128.1, 127.3, 127.2, 125.6, 124.3, 115.6, 112.4, 63.7, 42.1, 33.4, 26.4, 19.6, 19.1.

1-cyclohexyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (51)[6]



Target compound was obtained according to general procedure C giving pure product (59.9 mg, 68% yield, FE = 18%) purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 7.10 – 7.01 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 4.34 (d, *J* = 8.2 Hz, 1H), 3.65 (dt, *J* = 12.0, 6.1 Hz, 1H), 3.39 (ddd, *J* = 11.9, 7.8, 6.2 Hz, 1H), 3.00 – 2.86 (m, 2H), 1.89 (d, *J* = 14.1 Hz, 1H), 1.66 (t, *J* = 14.6 Hz, 4H), 1.59 – 1.50 (m, 1H), 1.14 – 0.88 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1, 136.9, 134.3, 128.1, 127.3, 127.2, 125.5, 124.2, 115.4, 112.1, 62.8, 43.1, 42.0, 30.0, 29.7, 26.4, 25.7, 25.4, 25.4.

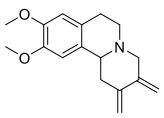
1-allyl-2-(2-bromoallyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (53)



Target compound was obtained according to general procedure A giving pure product (61.1 mg, 50% yield, FE = 26%), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.48 (d, *J* = 14.0 Hz, 2H), 5.98 – 5.79 (m, 2H), 5.50 (s, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.95 – 4.88 (m, 1H), 3.77 (d, *J* = 6.9 Hz, 6H), 3.59 (t, *J* = 6.4 Hz, 1H), 3.34 (s, 2H), 3.16 (ddd, *J* = 13.2, 10.3, 7.3 Hz, 1H), 2.75 (ddt, *J* = 22.1, 15.9, 5.6 Hz, 2H), 2.51 – 2.42 (m, 2H), 2.36 (dddd, *J* = 14.6, 8.6, 4.0, 2.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 146.3, 135.7, 131.3,

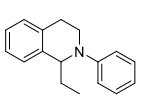
128.7, 125.3, 116.7, 115.0, 110.7, 109.9, 61.1, 59.9, 55.0, 54.9, 42.8, 39.8, 23.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{23}BrNO_2$ 352.0912; Found 352.0905.

9,10-dimethoxy-2,3-dimethylene-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinoline (54)[7]



Target compound was obtained according to general procedure A giving pure product (12.5 mg, 45% yield), purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; R_f: 0.4 (PE : EA = 3 : 1). 1H NMR (600 MHz, $CDCl_3$) *δ* 6.67 (s, 1H), 6.58 (s, 1H), 5.15 (d, *J* = 2.6 Hz, 2H), 4.88 (d, *J* = 2.4 Hz, 1H), 4.83 (s, 1H), 3.85 (d, *J* = 16.4 Hz, 6H), 3.47 (d, *J* = 12.7 Hz, 1H), 3.35 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.13 (d, *J* = 12.7 Hz, 1H), 3.07 (ddd, *J* = 15.6, 10.2, 5.4 Hz, 1H), 3.01 (ddd, *J* = 11.4, 5.7, 2.9 Hz, 1H), 2.86 (dd, *J* = 14.0, 3.1 Hz, 1H), 2.67 (dt, *J* = 15.7, 3.6 Hz, 1H), 2.53 (td, *J* = 10.8, 4.1 Hz, 1H), 2.35 (td, *J* = 12.7, 11.3, 2.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 147.3, 145.44, 144.1, 129.5, 126.7, 111.5, 109.7, 109.3, 108.6, 62.0, 61.9, 56.1, 55.8, 50.8, 40.1, 29.2.

1-ethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (57)[8]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 2H), 7.09 – 7.01 (m, 4H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.63 (t, *J* = 7.1 Hz, 1H), 4.48 (t, *J* = 7.0 Hz, 1H), 3.57 – 3.45 (m, 2H), 2.93 (ddd, *J* = 15.9, 7.9, 5.4 Hz, 1H), 2.78 (dt, *J* = 15.8, 5.6 Hz, 1H), 1.89 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.68 (dq, *J* = 14.2, 7.2 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H).

13. References

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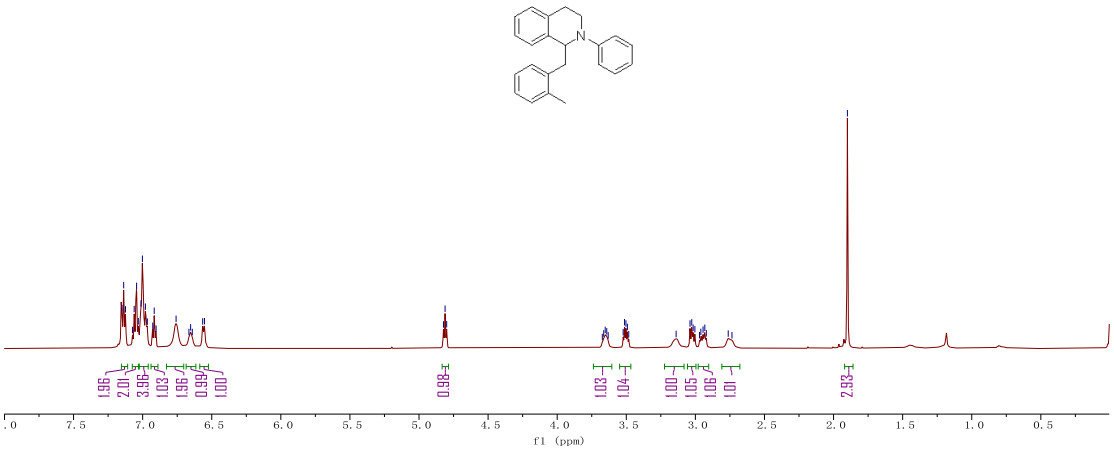
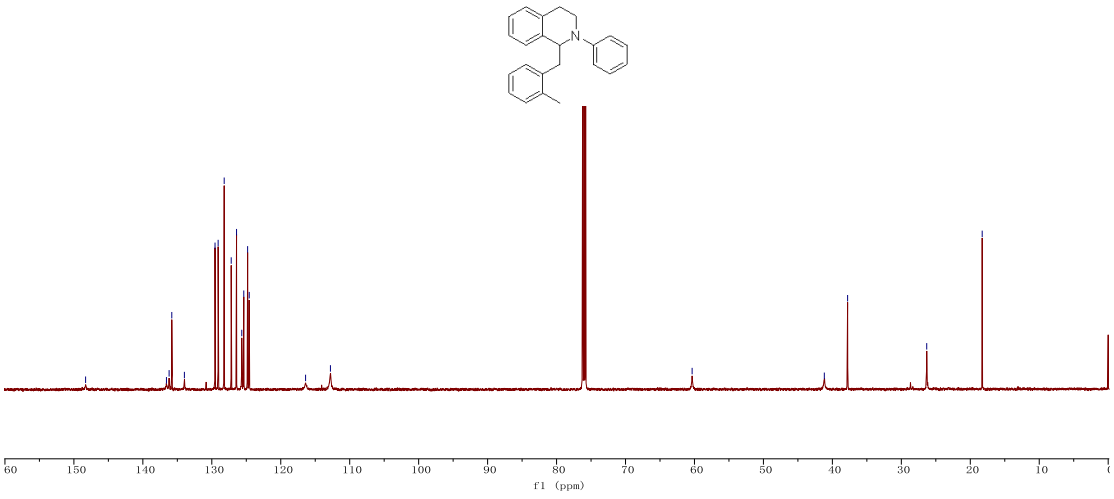
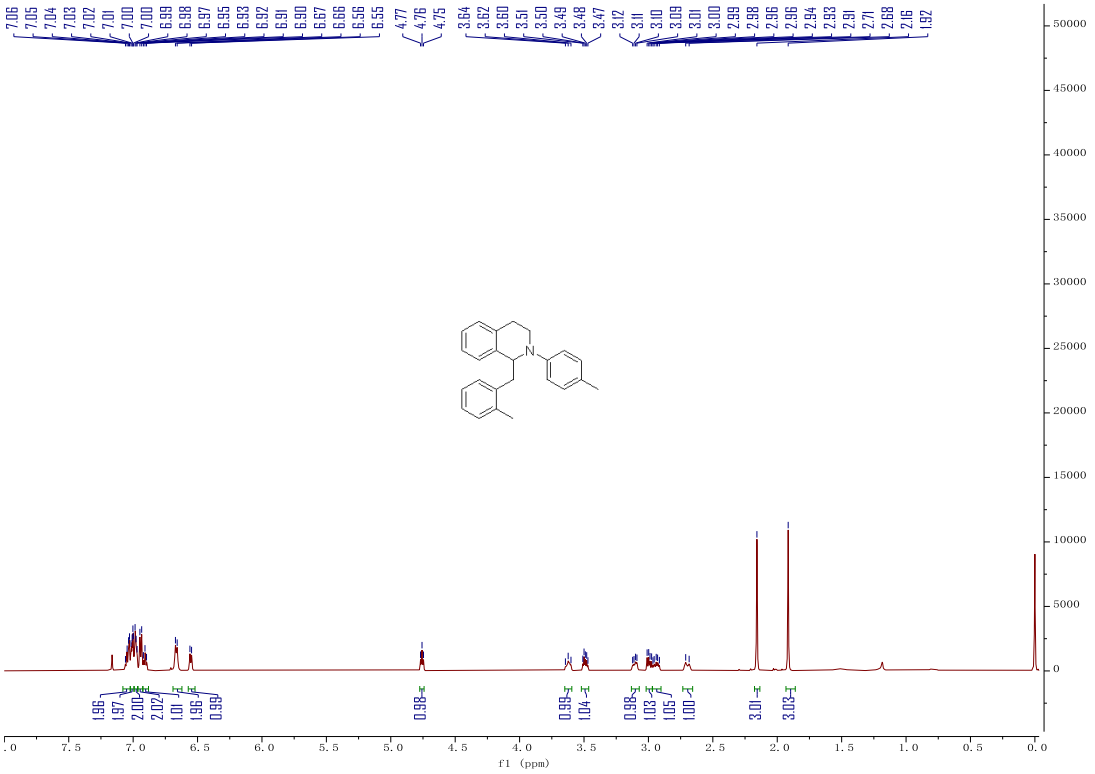
14. The spectra of NMR

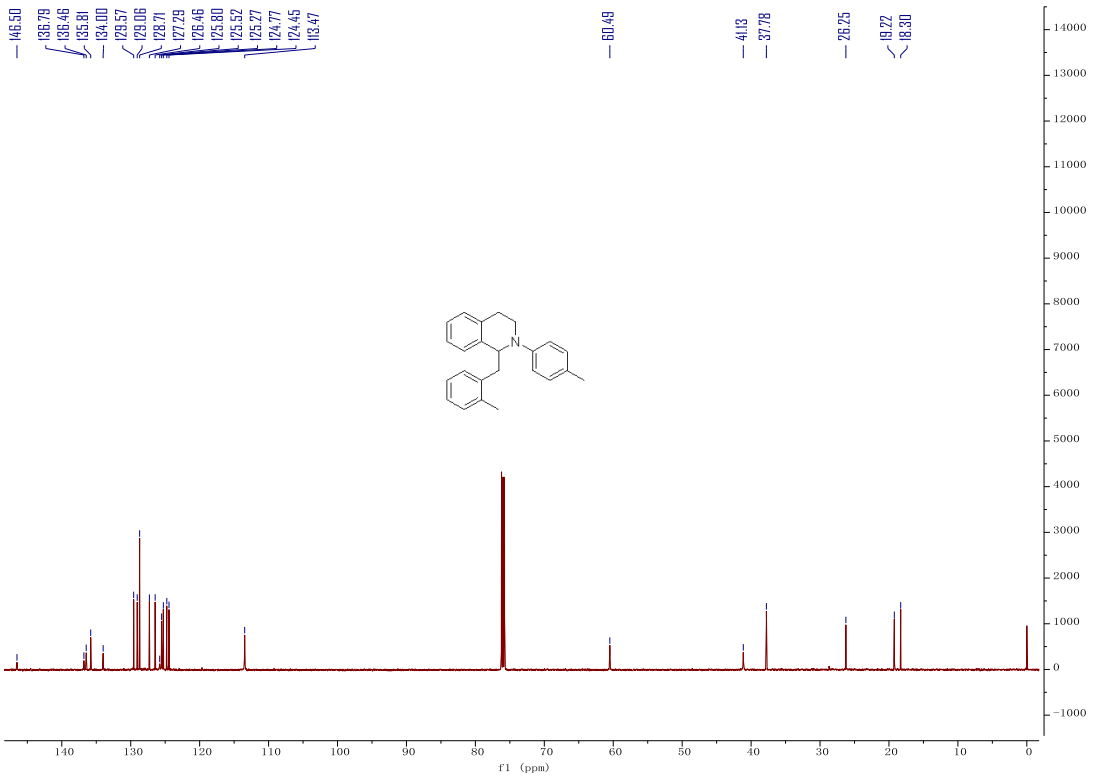
1-(2-methylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3)



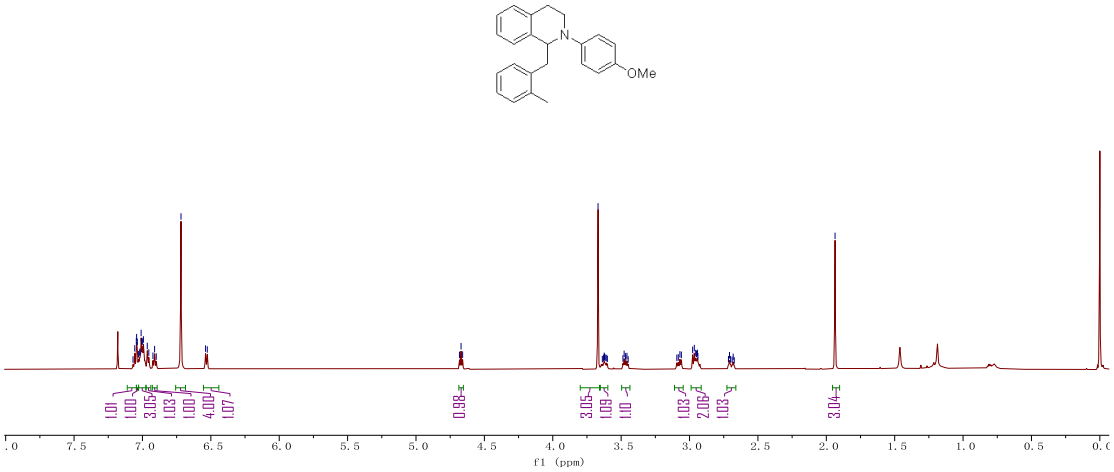


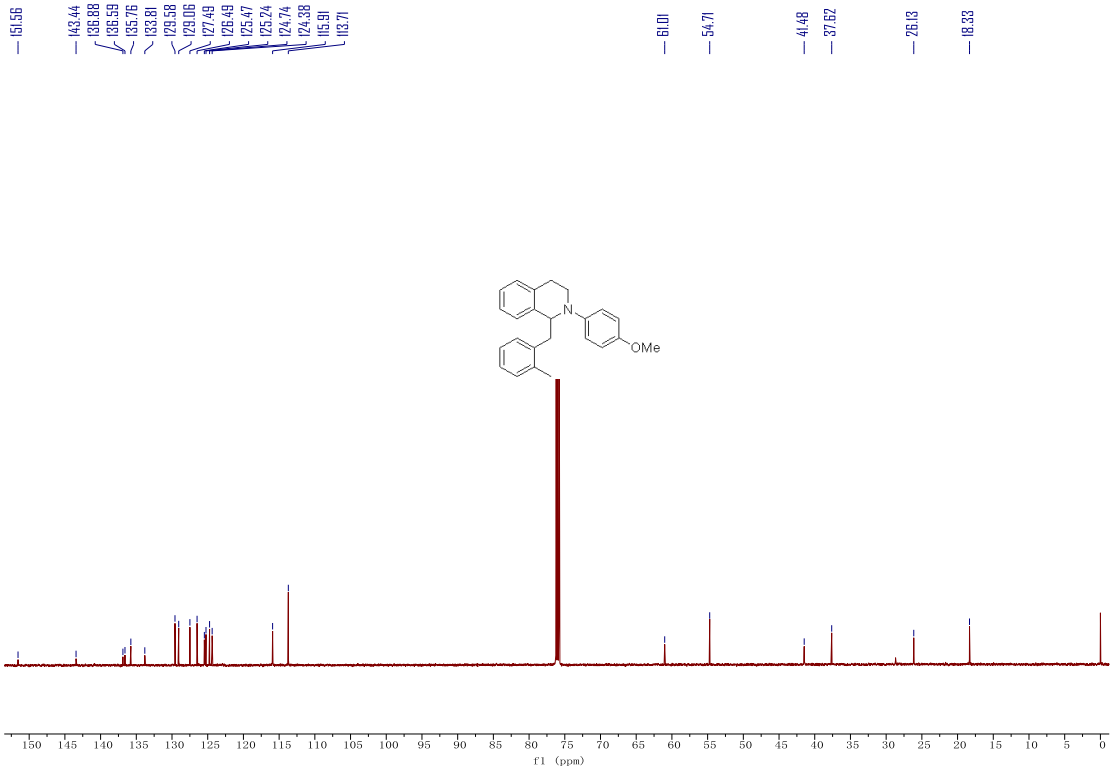
1-(2-methylbenzyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4)



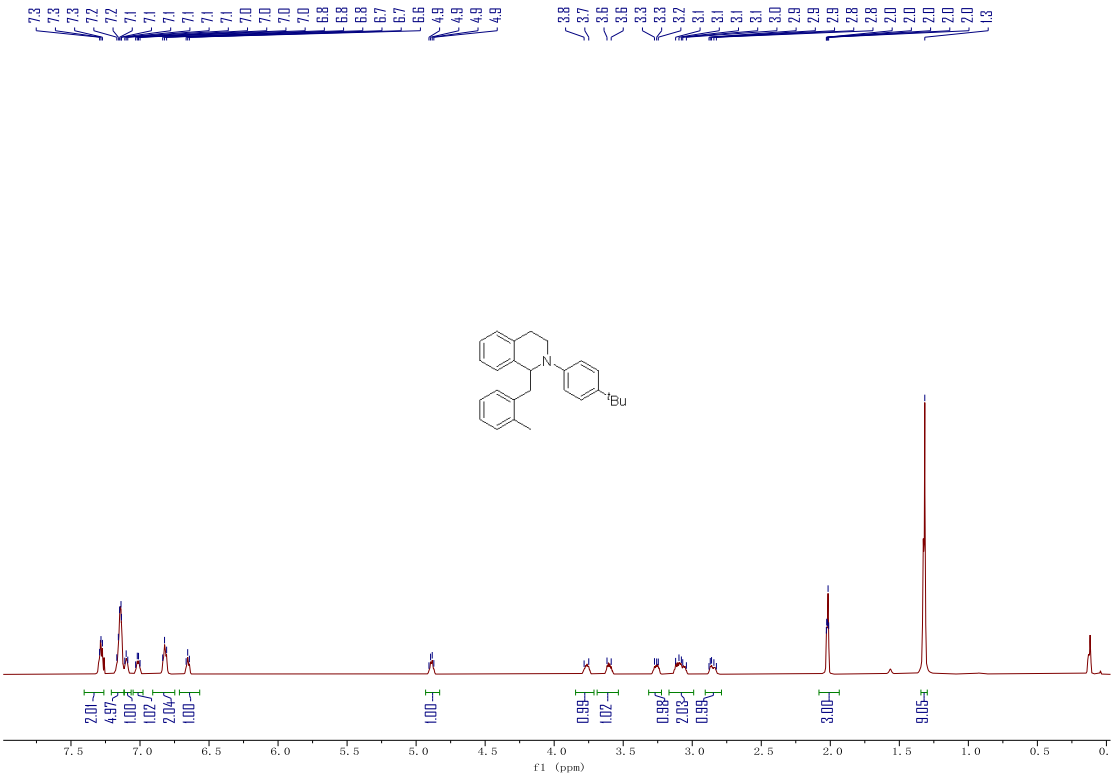


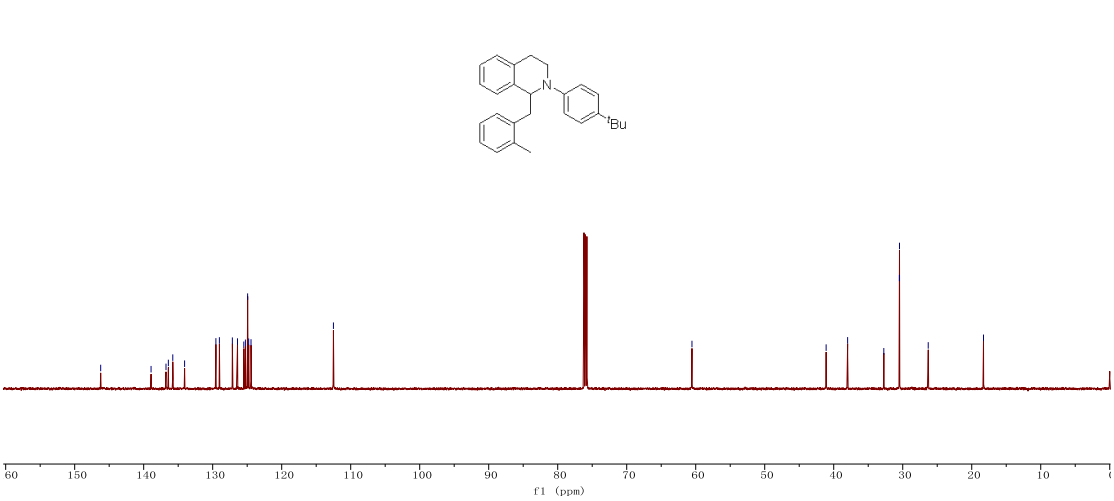
2-(4-methoxyphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (5)



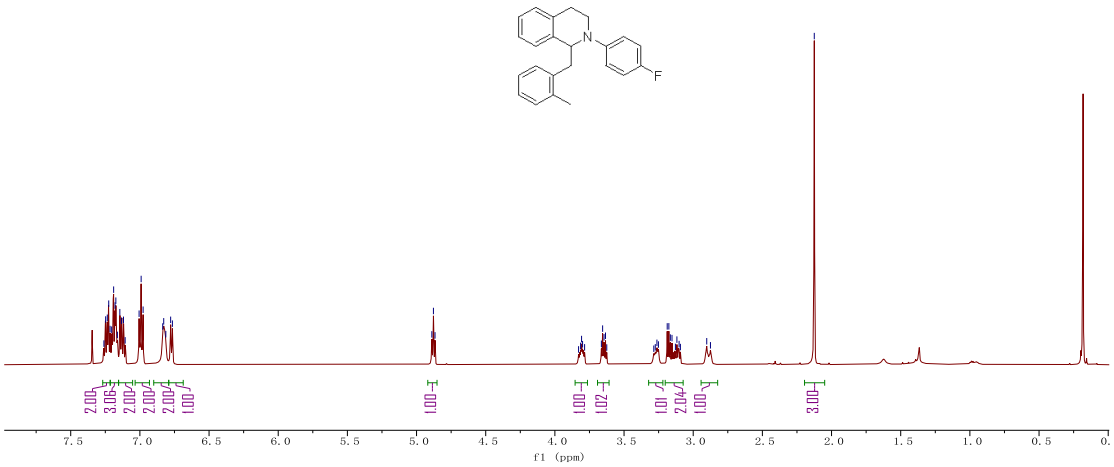


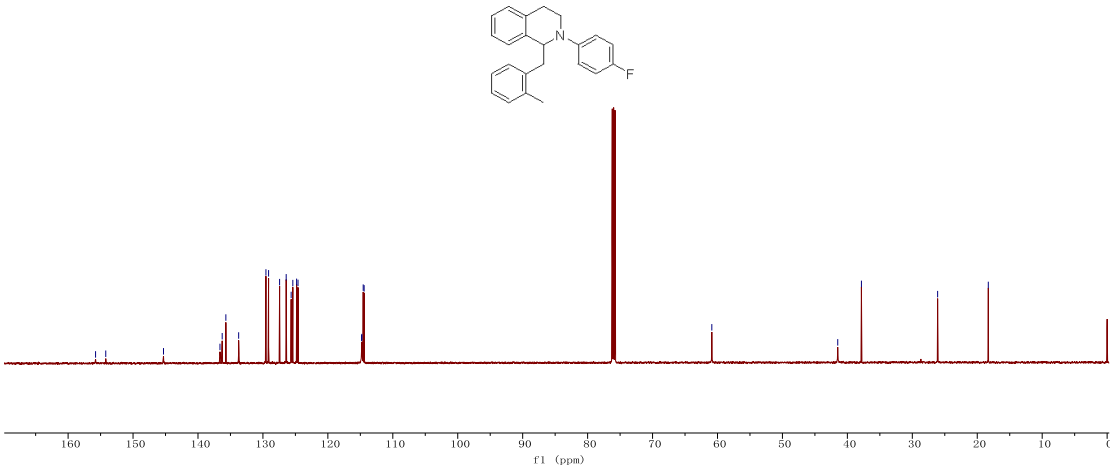
2-(4-(tert-butyl)phenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (6)



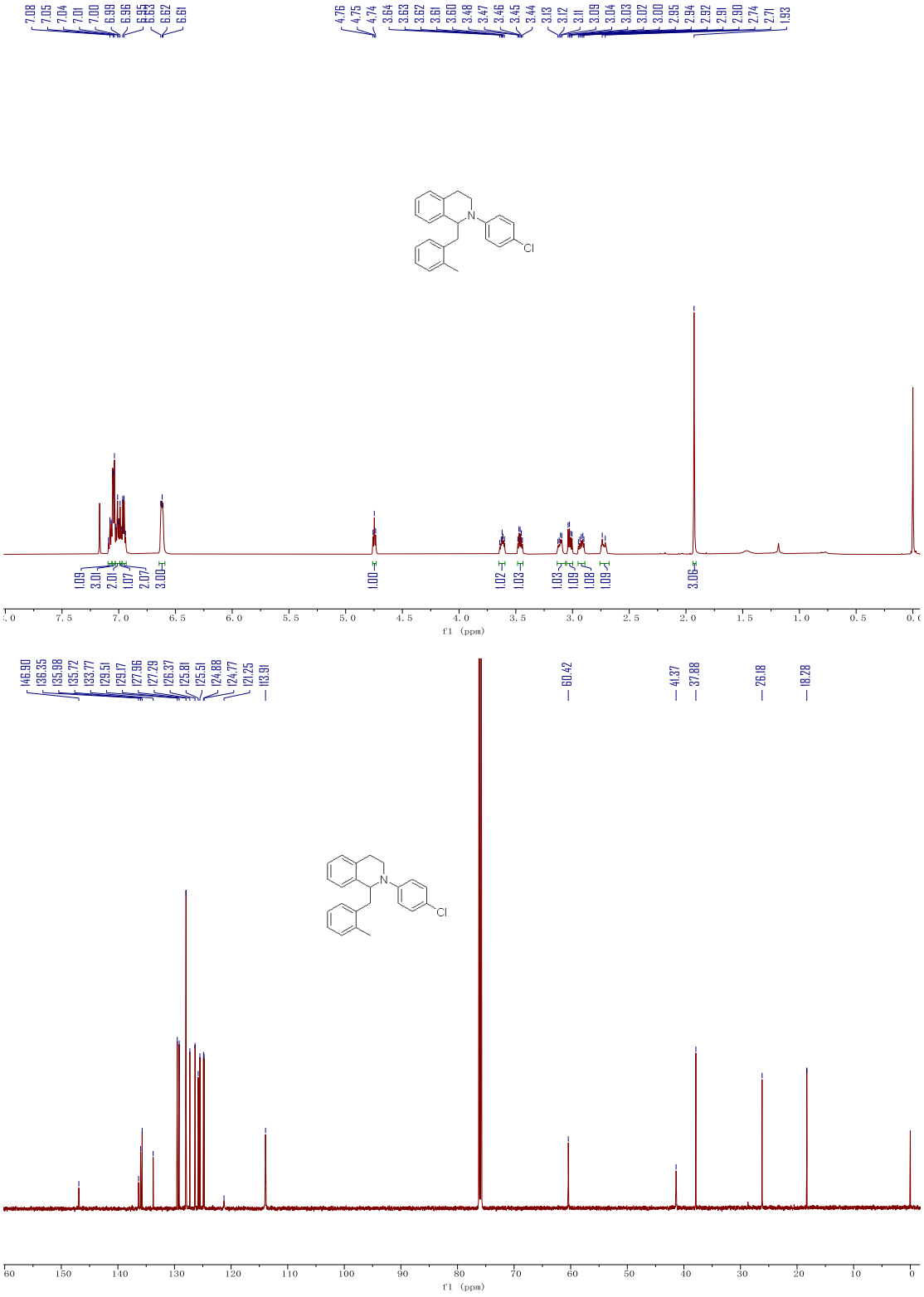


2-(4-fluorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (7)

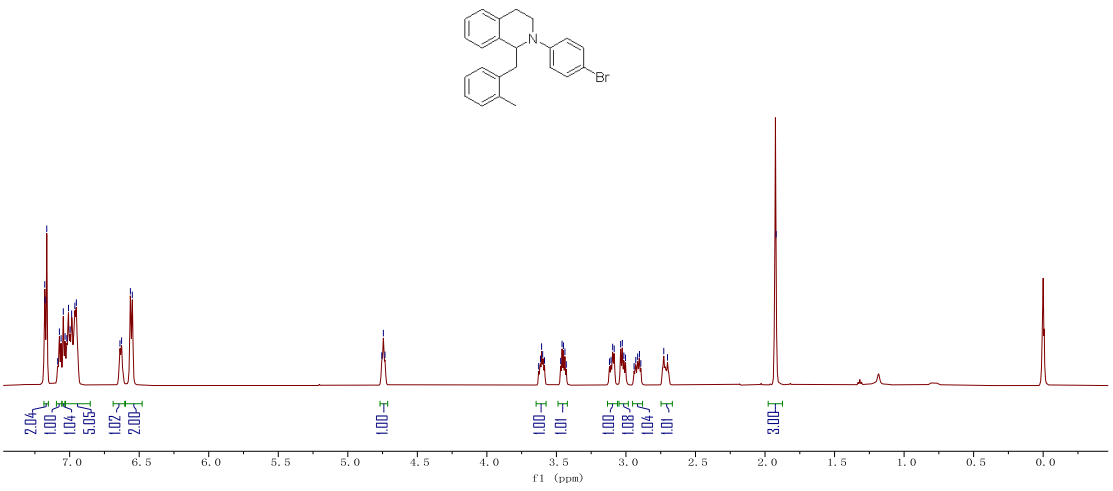


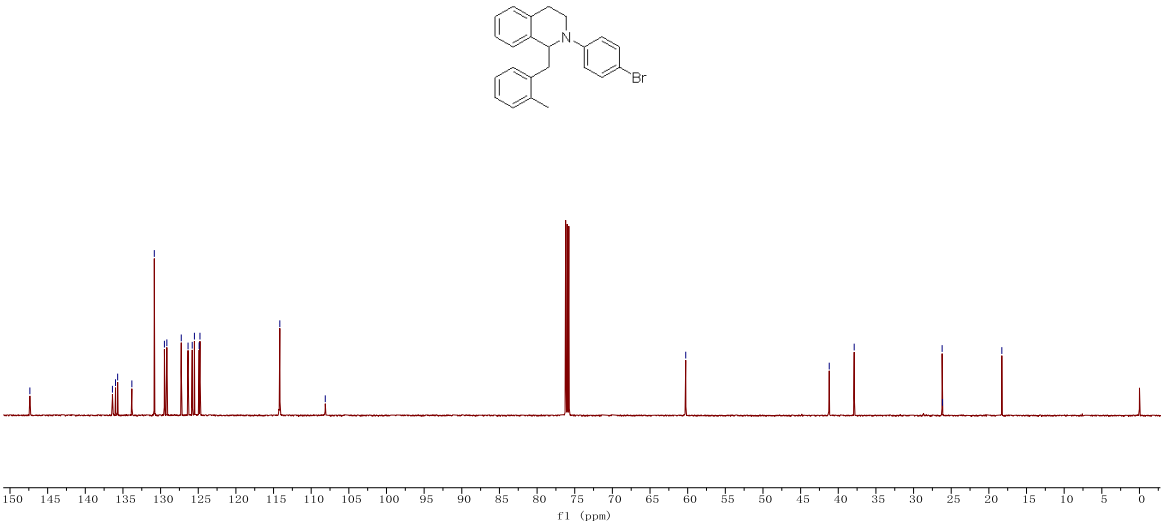


2-(4-chlorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (8)

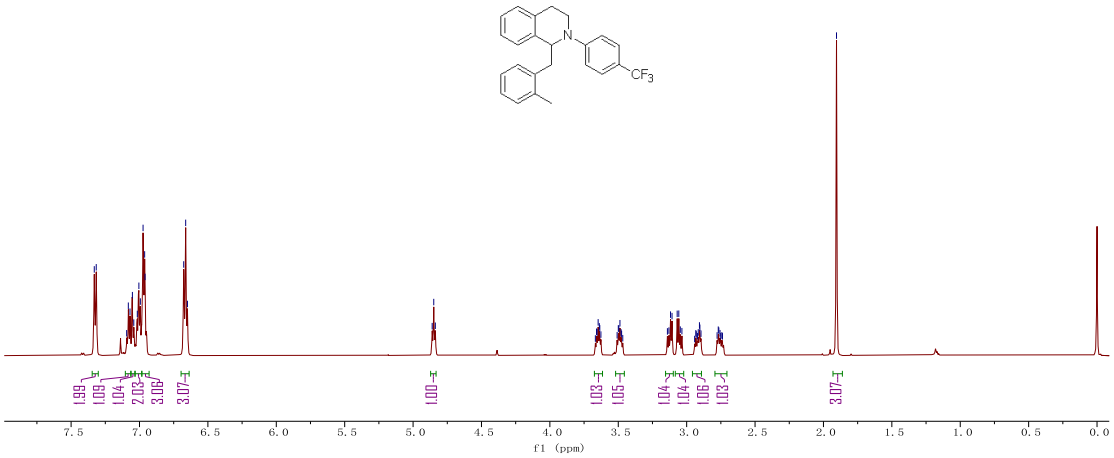


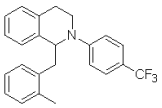
2-(4-bromophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (9)

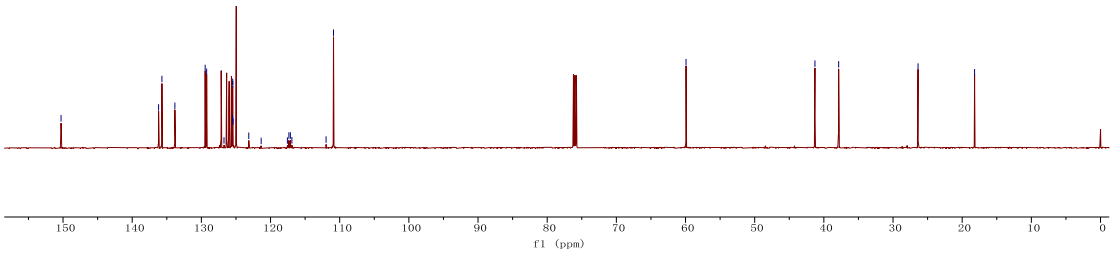




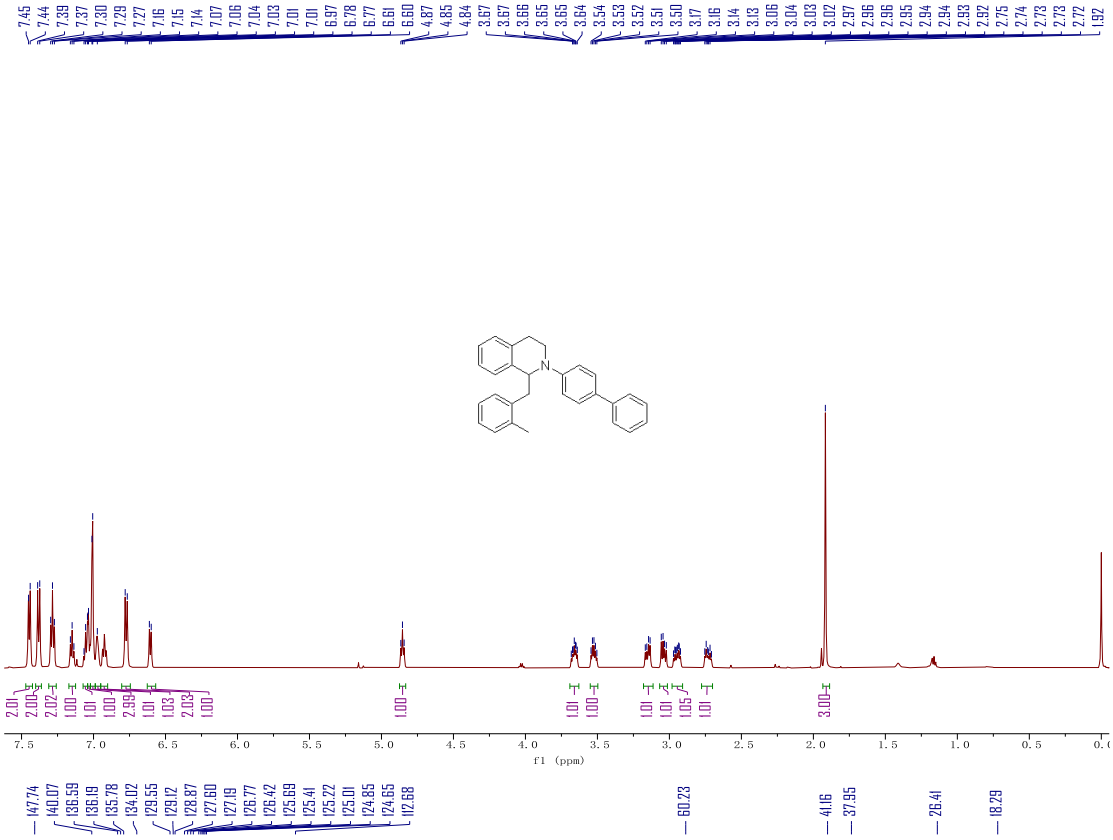
1-(2-methylbenzyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (10)

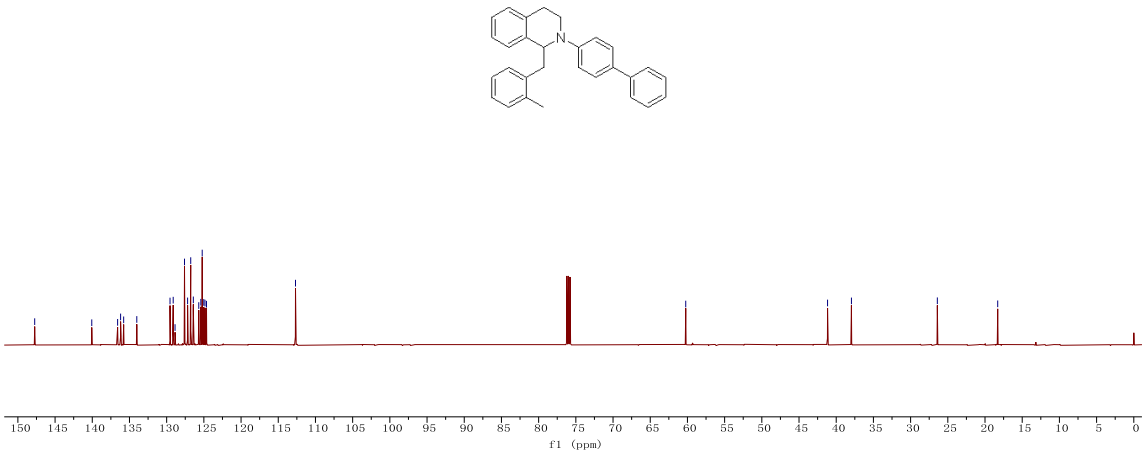




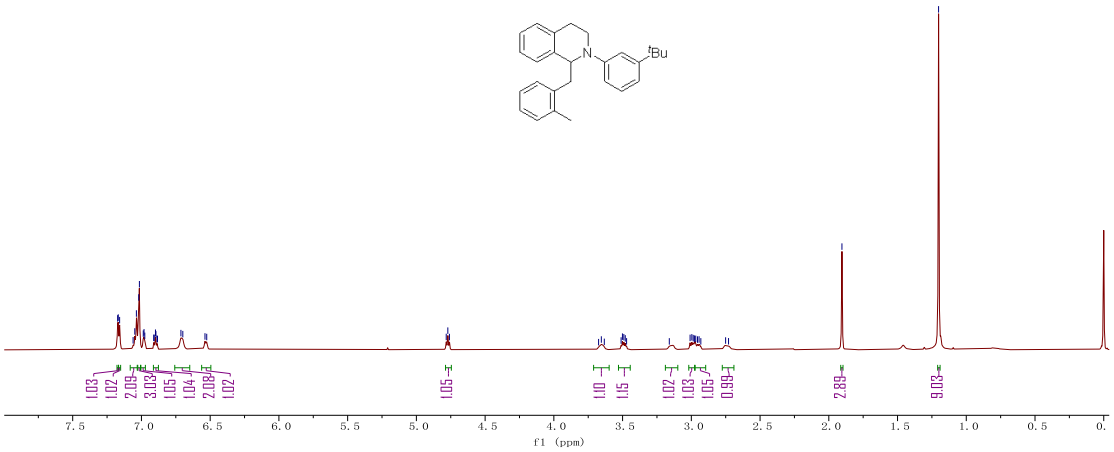


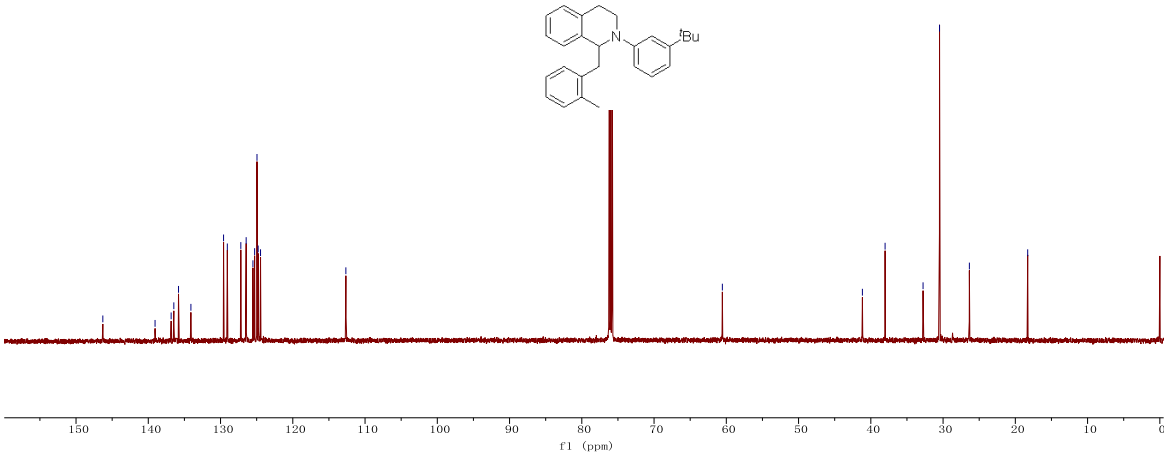
2-([1,1'-biphenyl]-4-yl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (11)



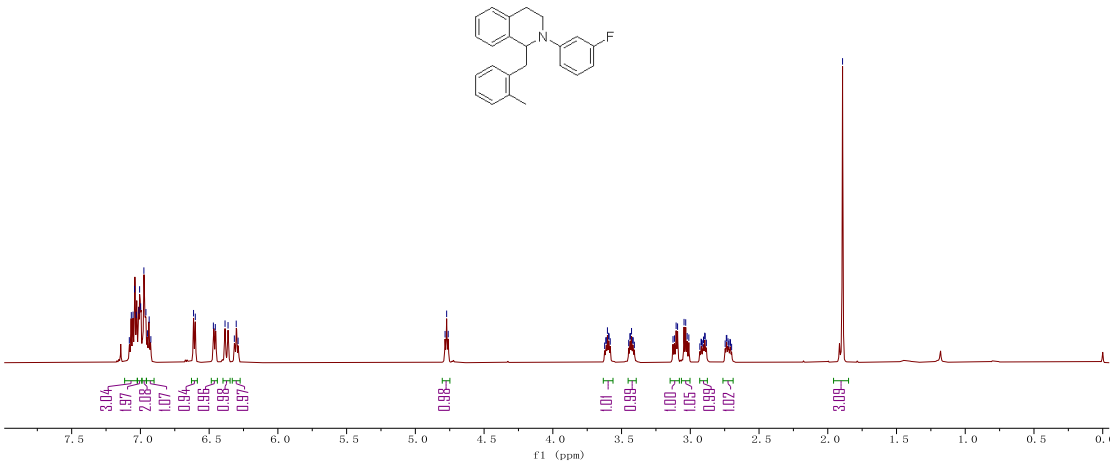


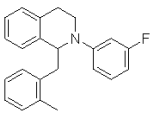
2-(3-(tert-butyl)phenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (12)

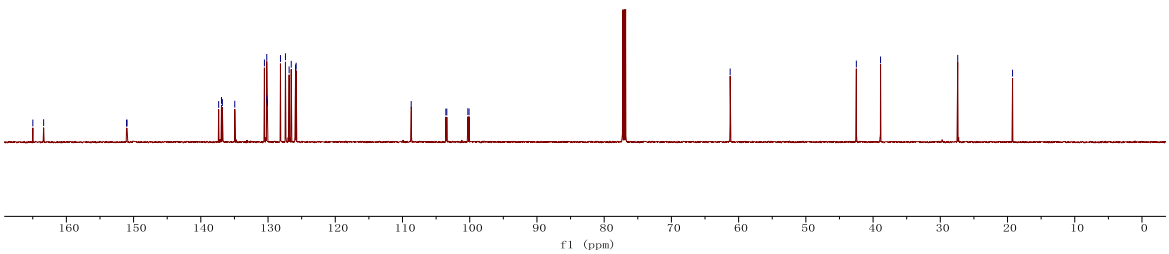




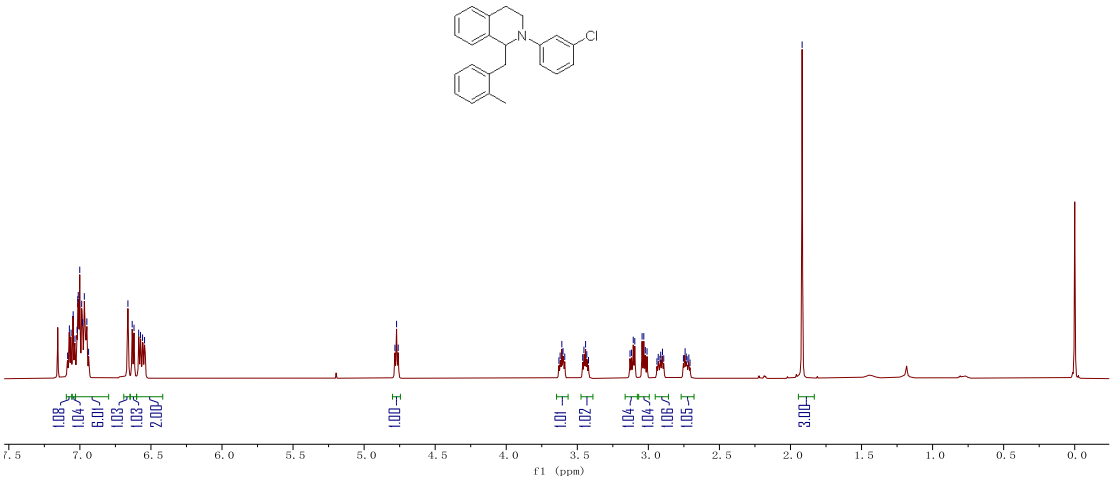
2-(3-fluorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (13)

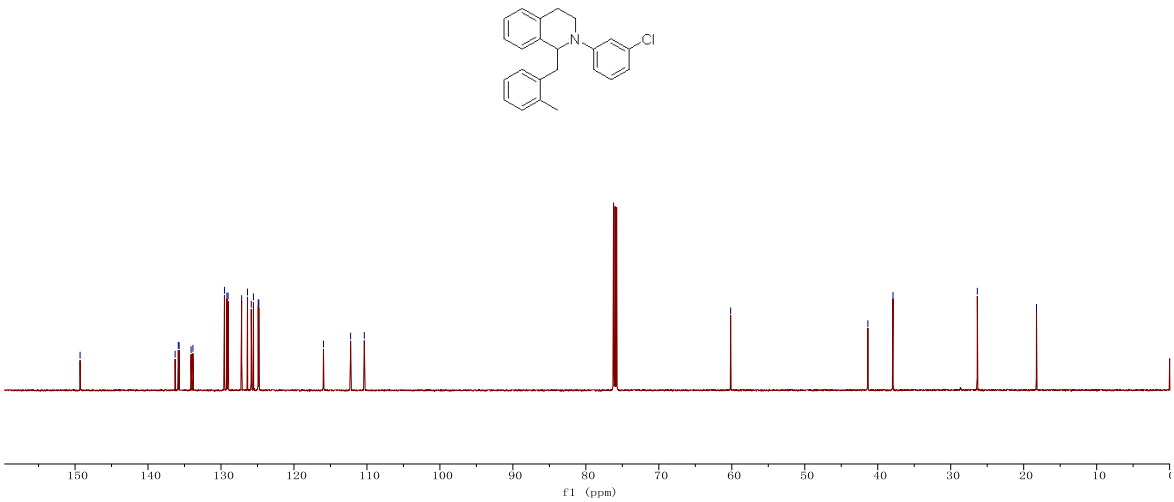




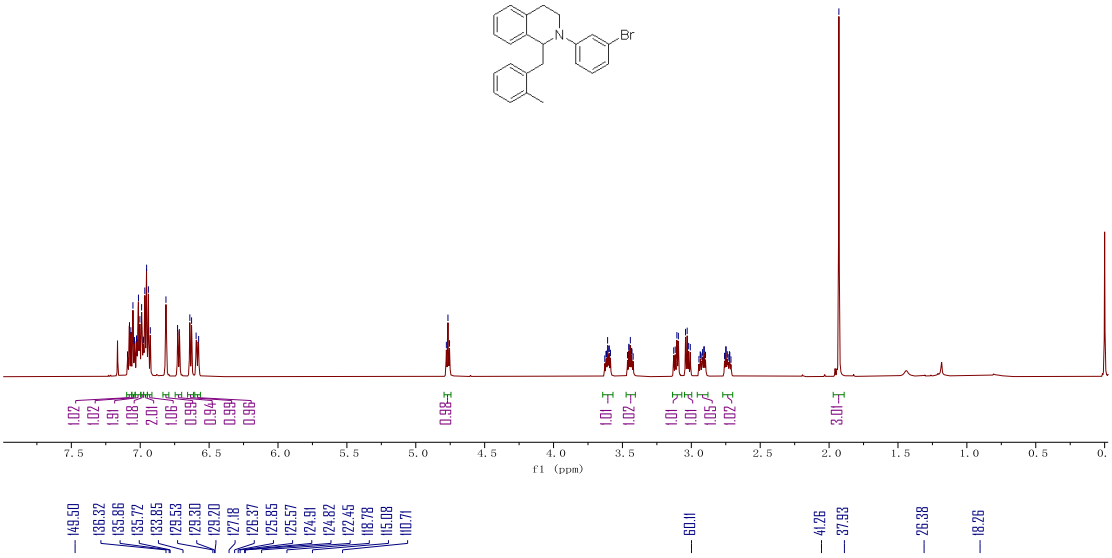


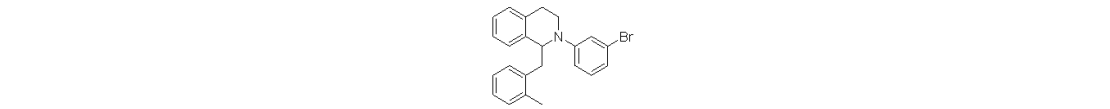
2-(3-chlorophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (14)

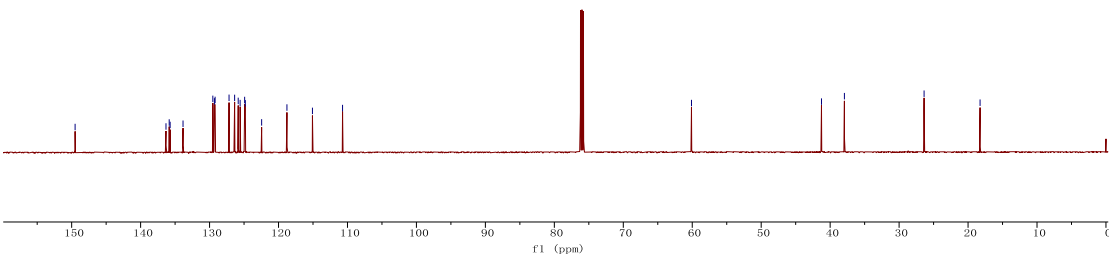




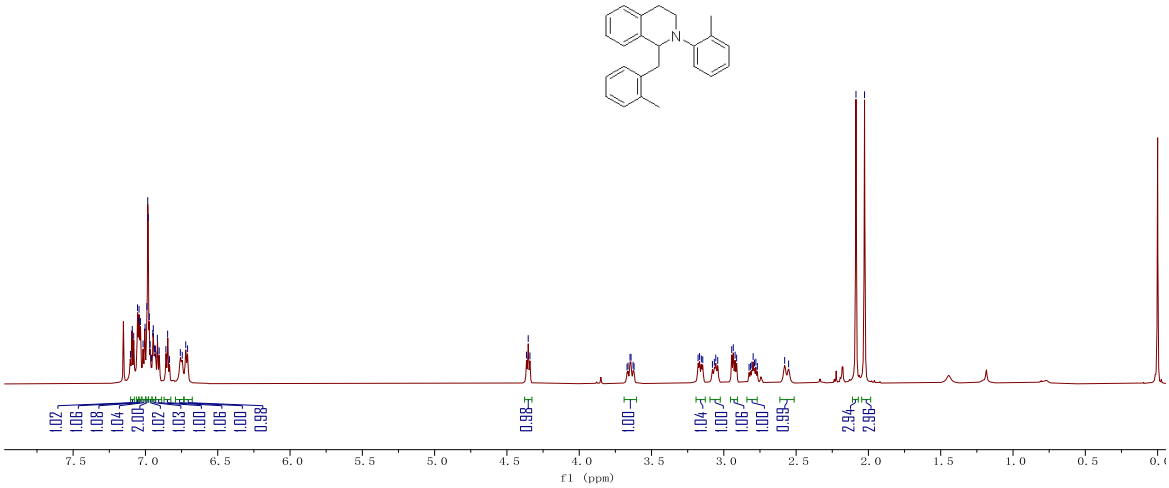
2-(3-bromophenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (15)

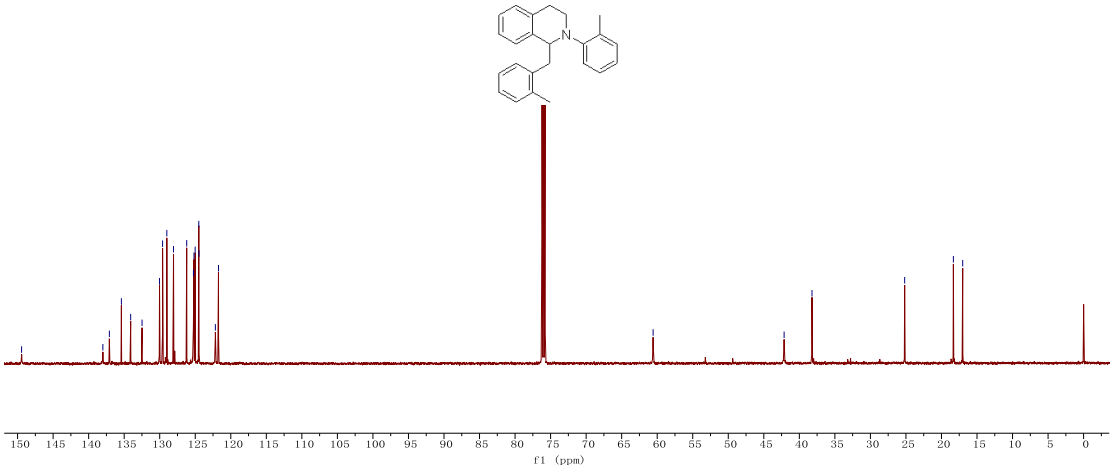




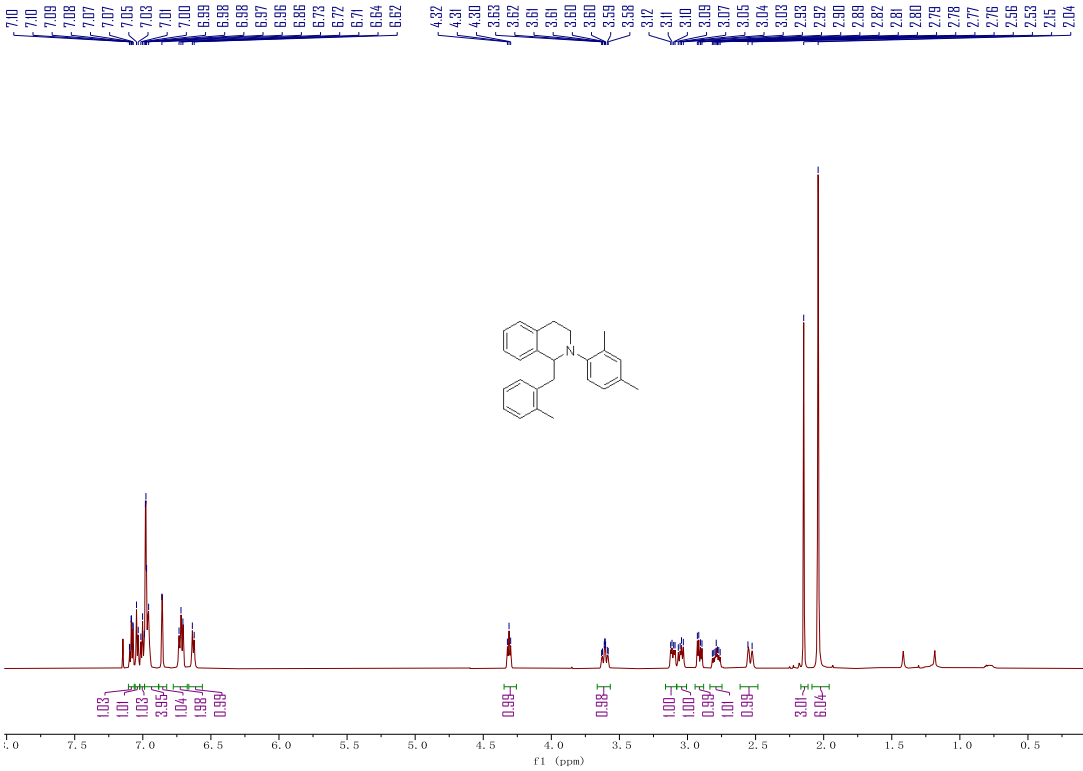


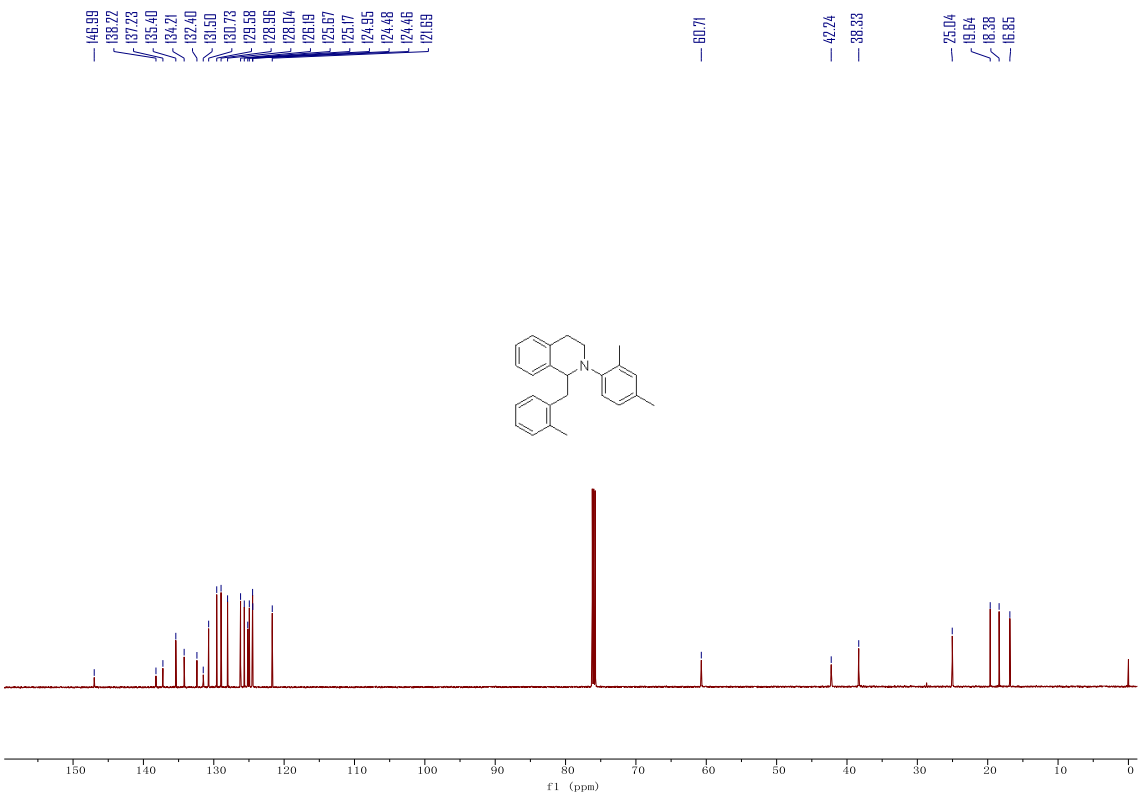
1-(2-methylbenzyl)-2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline (16)



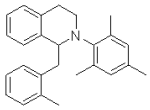


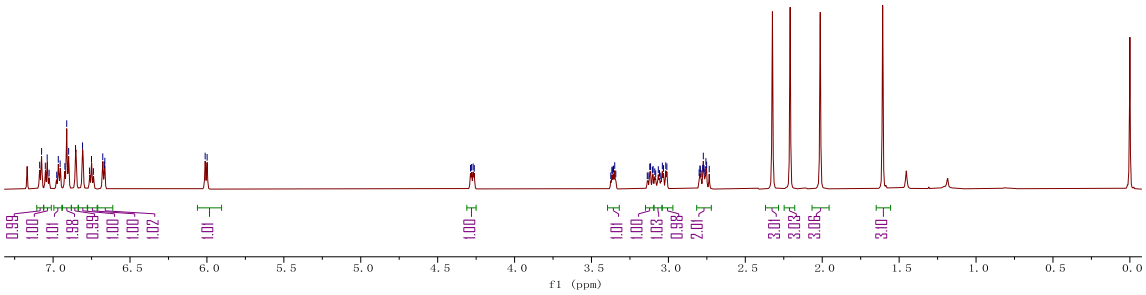
2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (17)

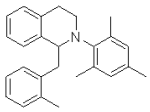


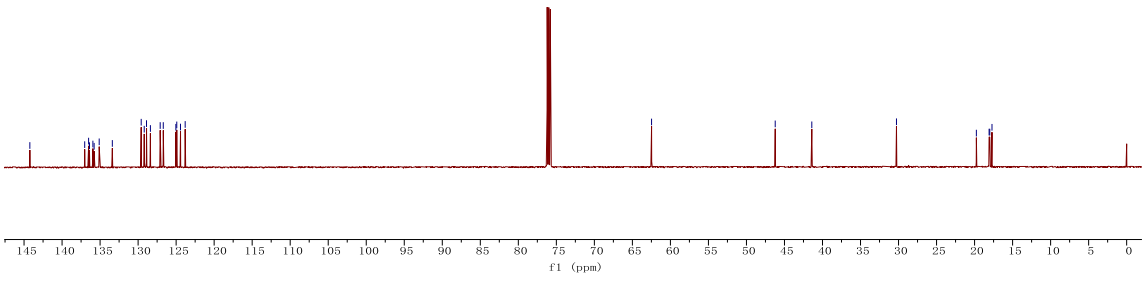


2-mesityl-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (18)

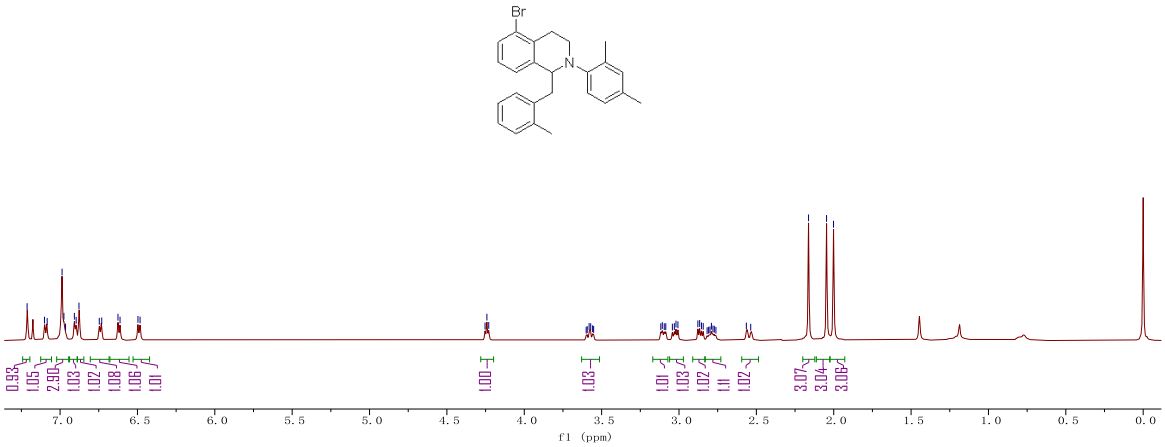


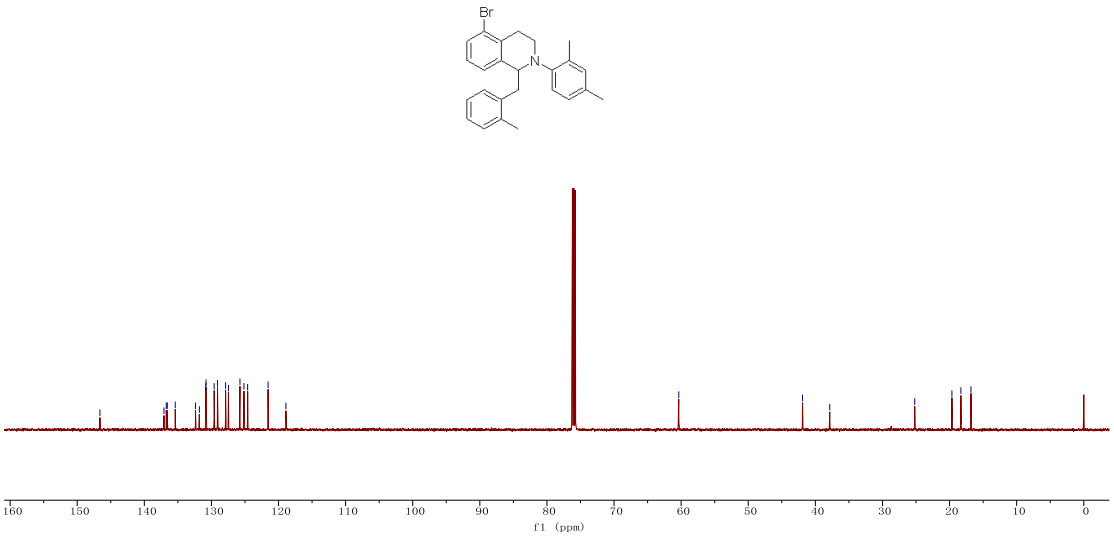




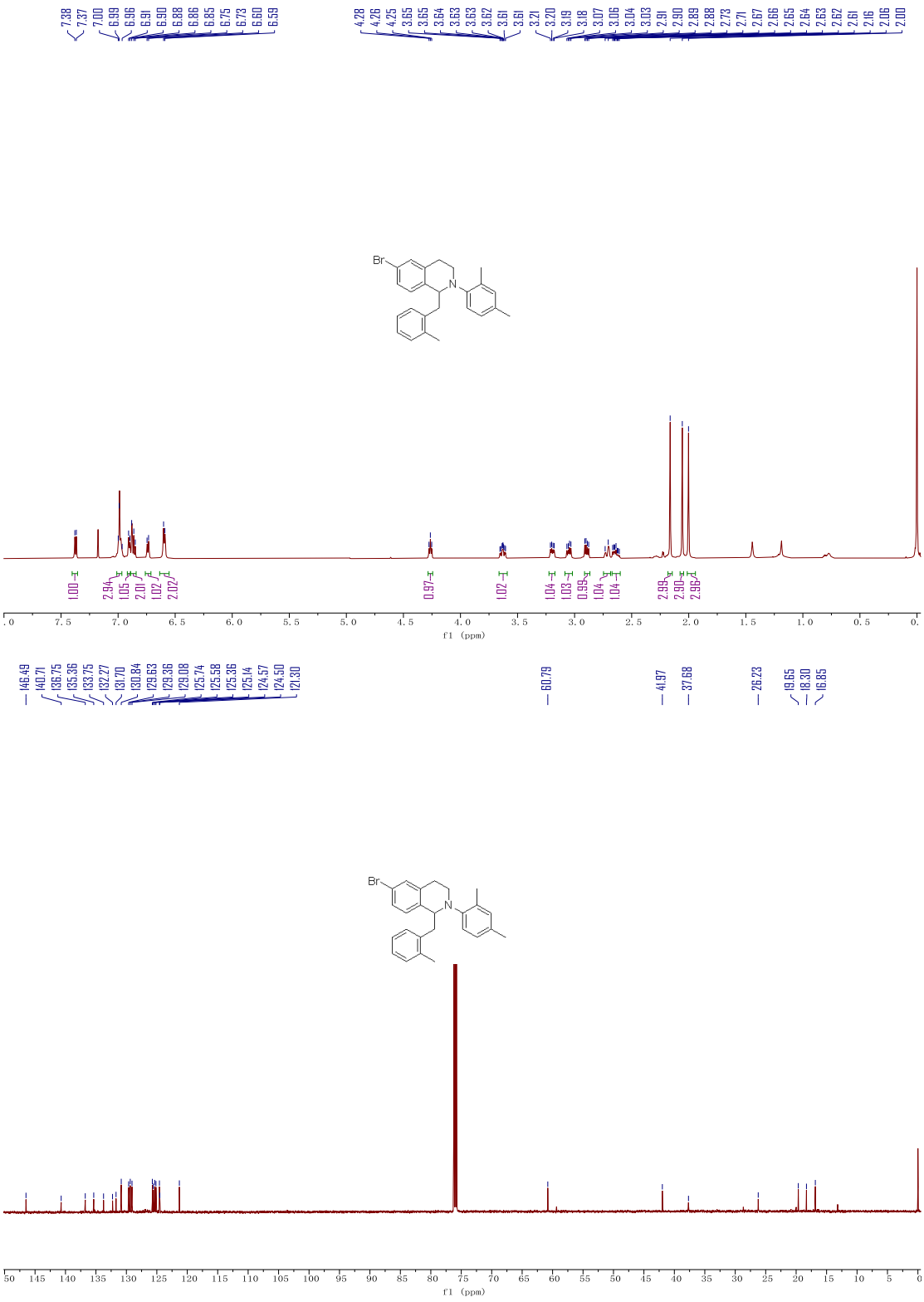


5-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (19)

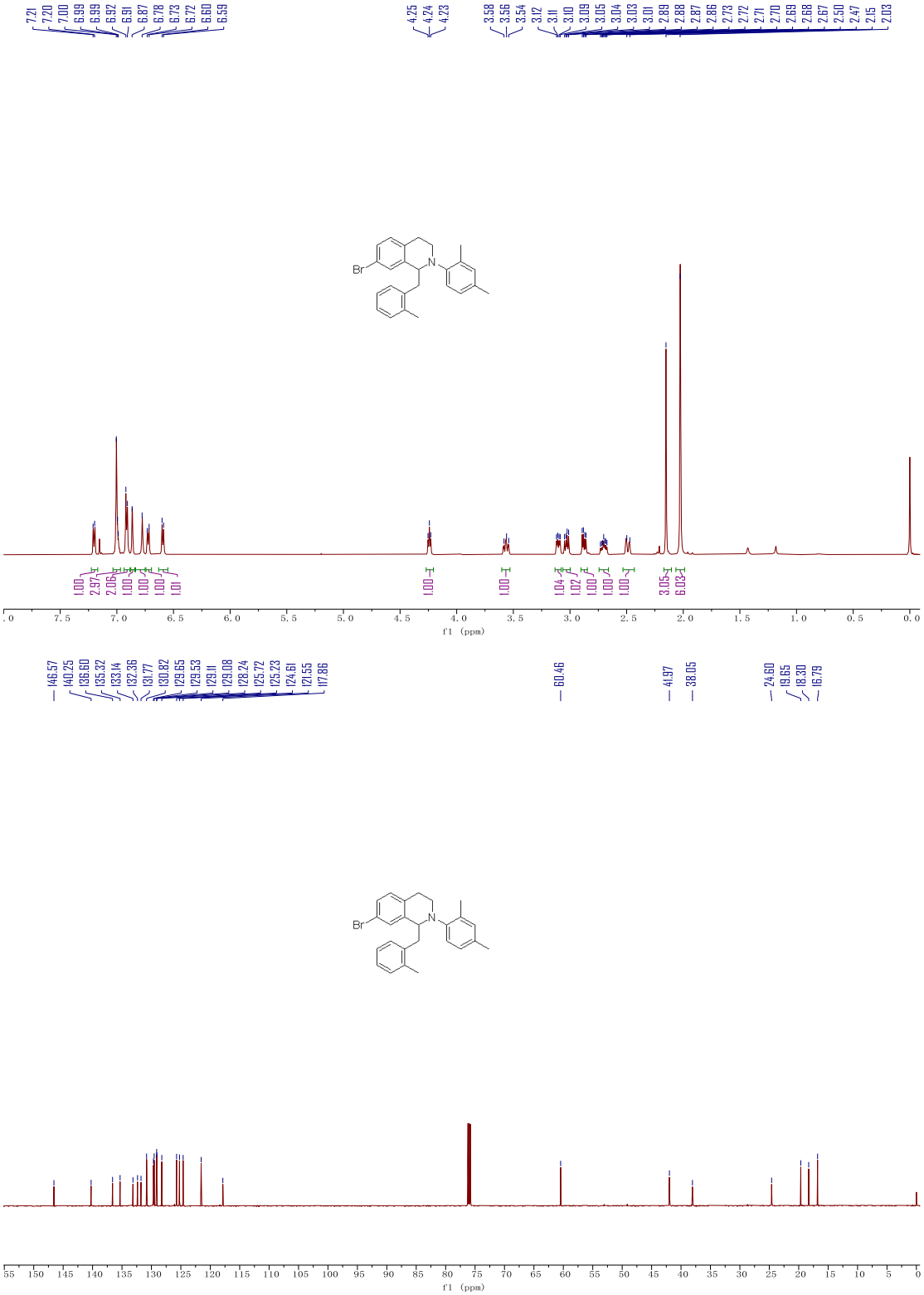




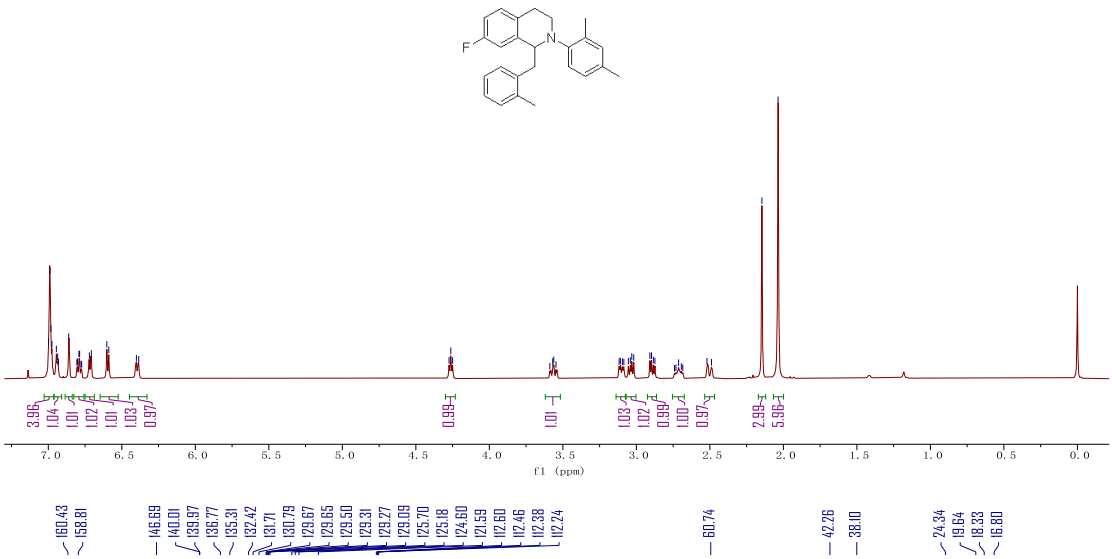
6-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (20)

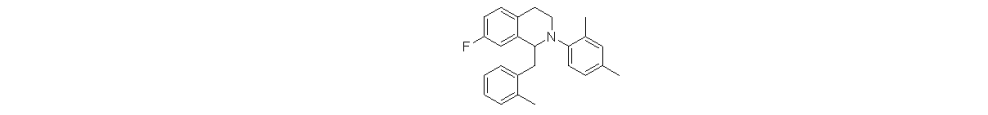


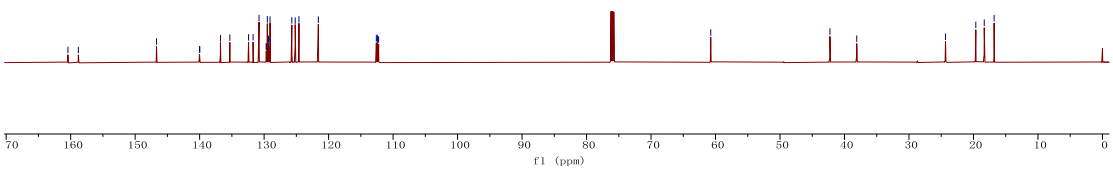
7-bromo-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (21)



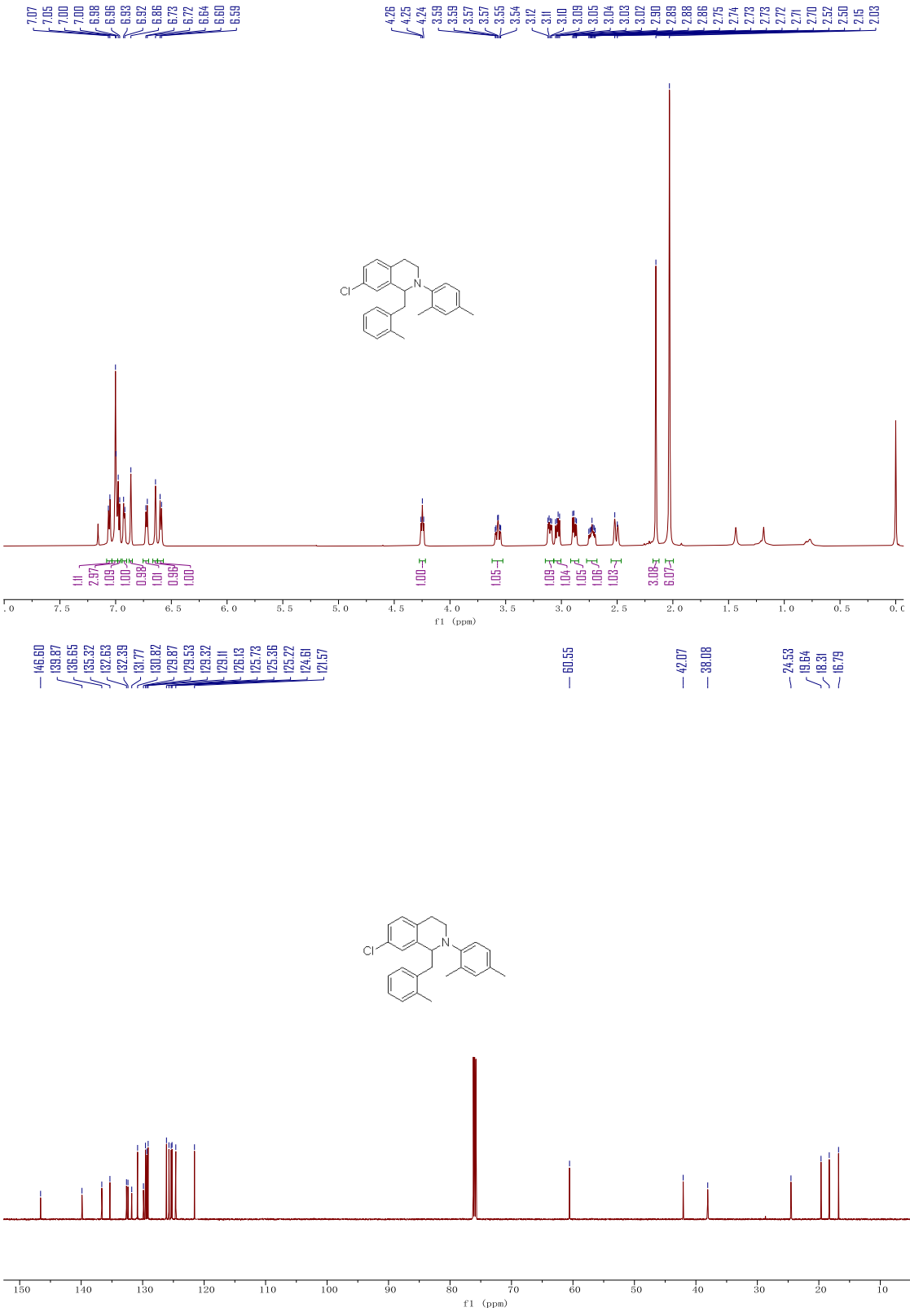
2-(2,4-dimethylphenyl)-7-fluoro-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (22)



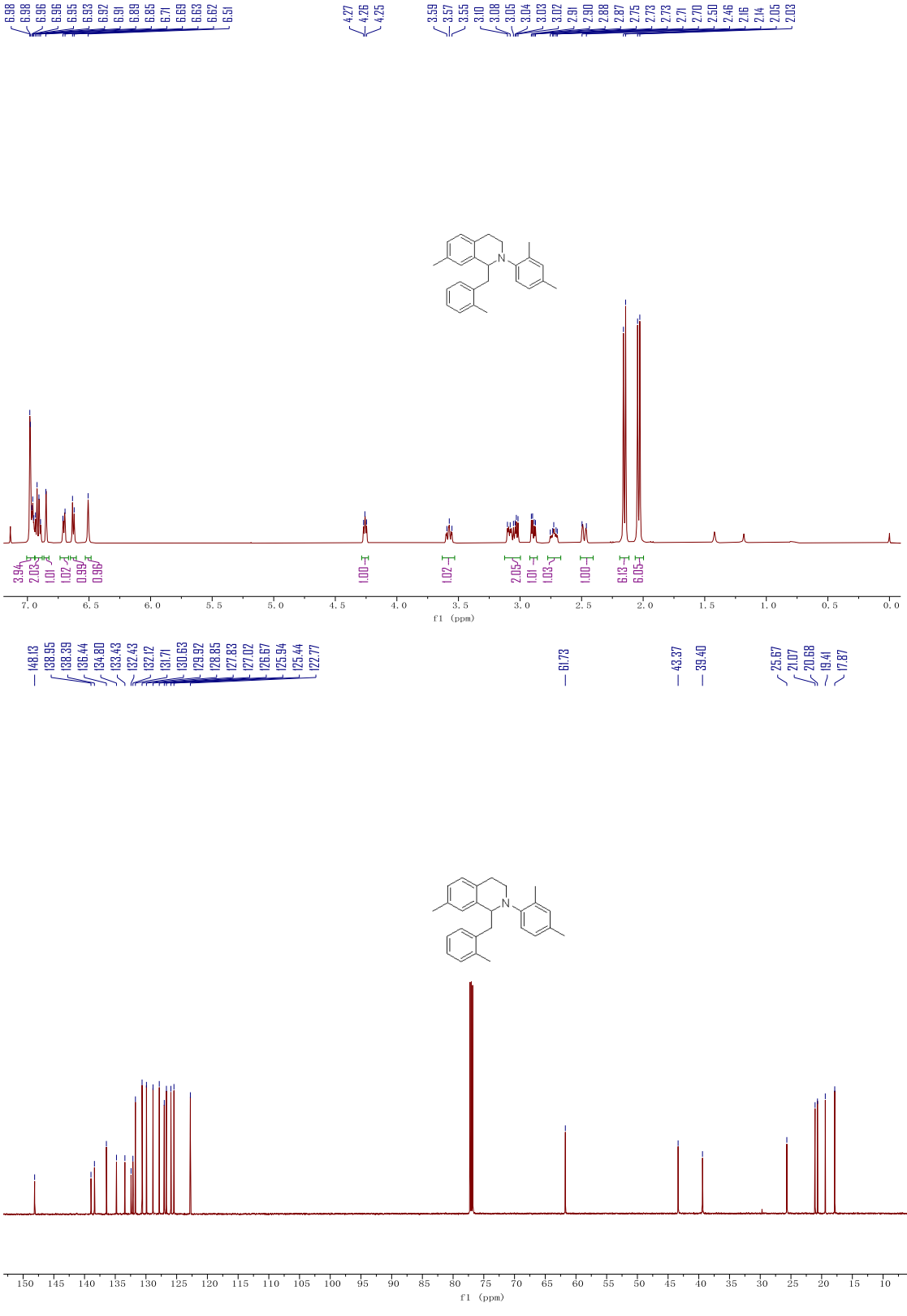




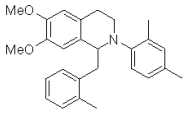
7-chloro-2-(2,4-dimethylphenyl)-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (23)

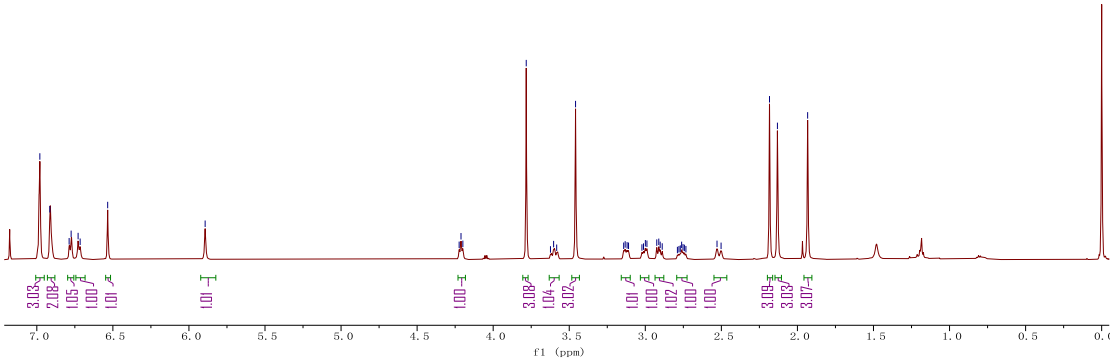


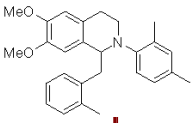
2-(2,4-dimethylphenyl)-7-methyl-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (24)

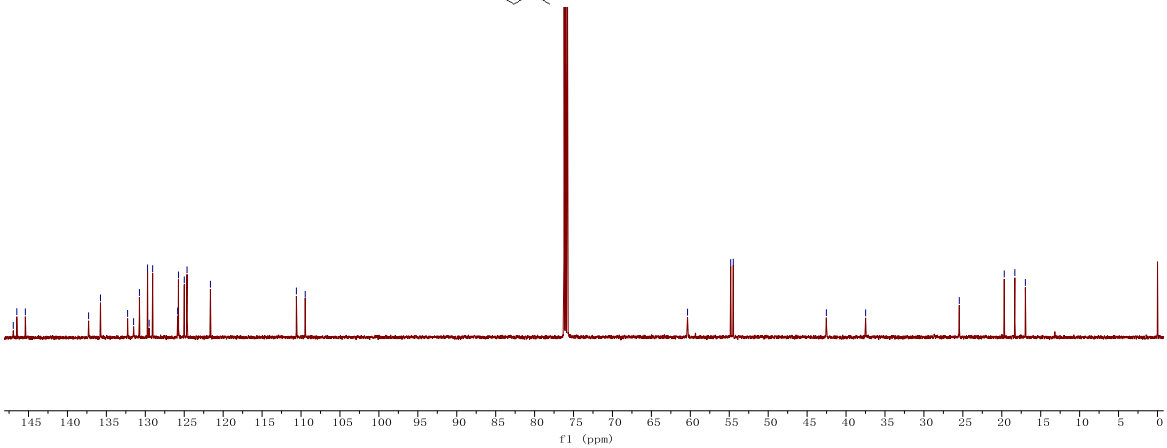


2-(2,4-dimethylphenyl)-6,7-dimethoxy-1-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (25)

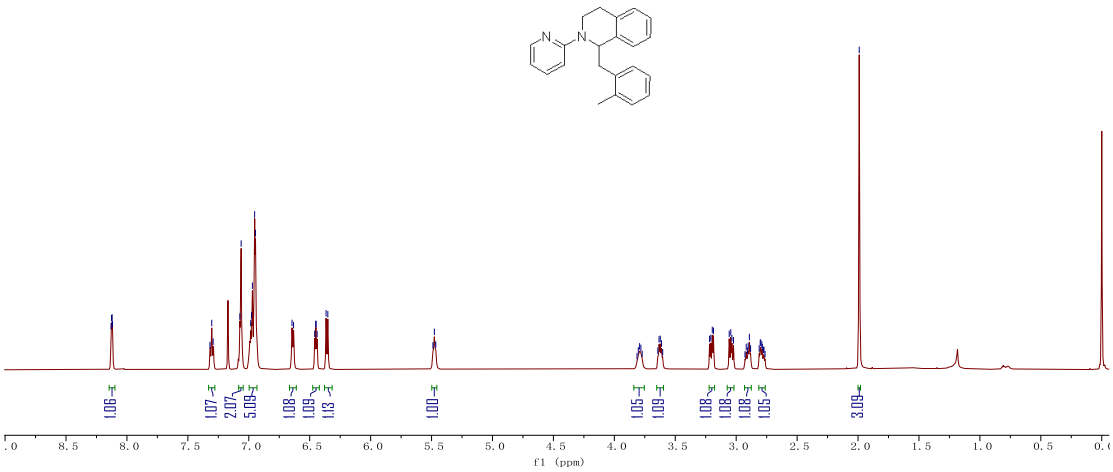


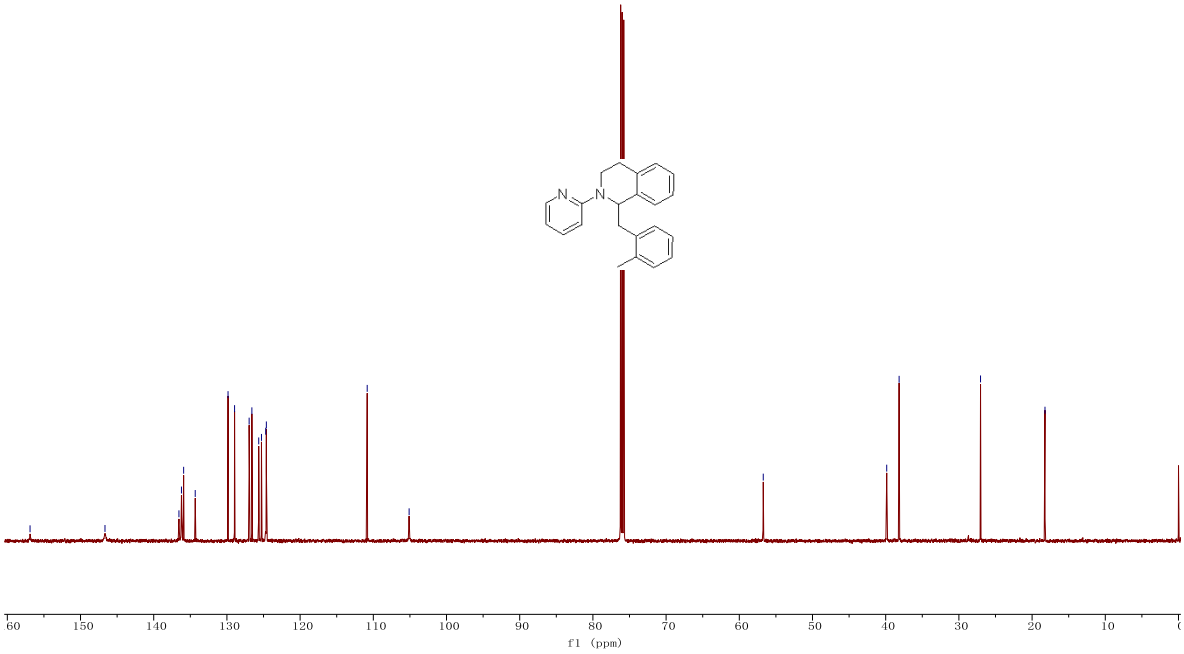




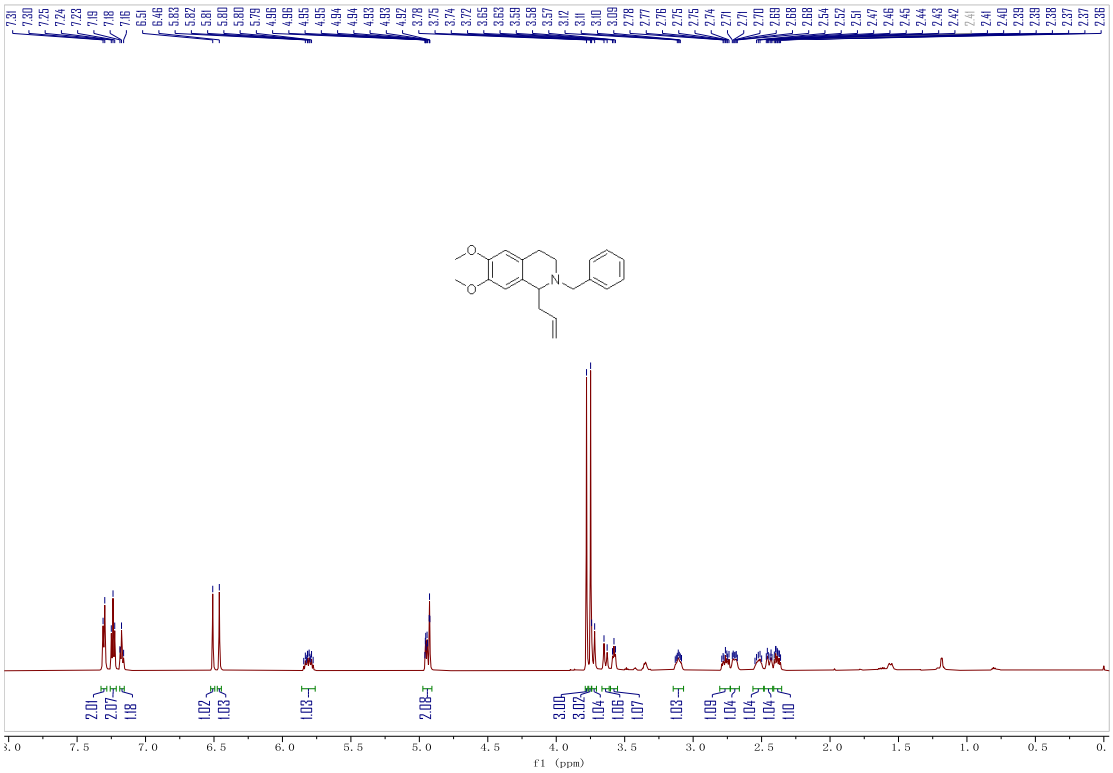


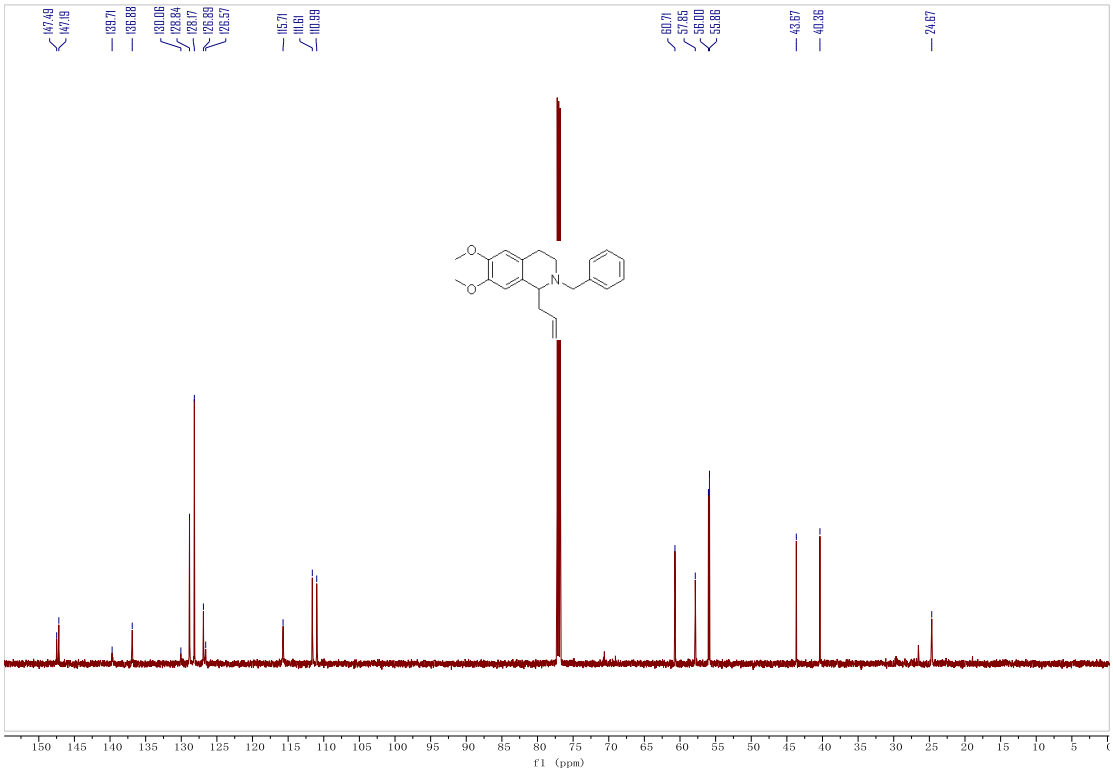
1-(2-methylbenzyl)-2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (26)



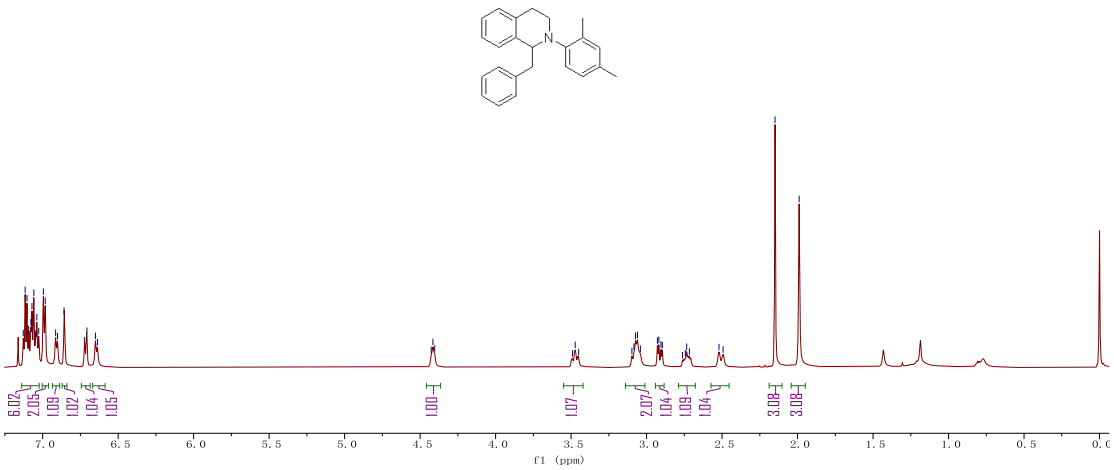


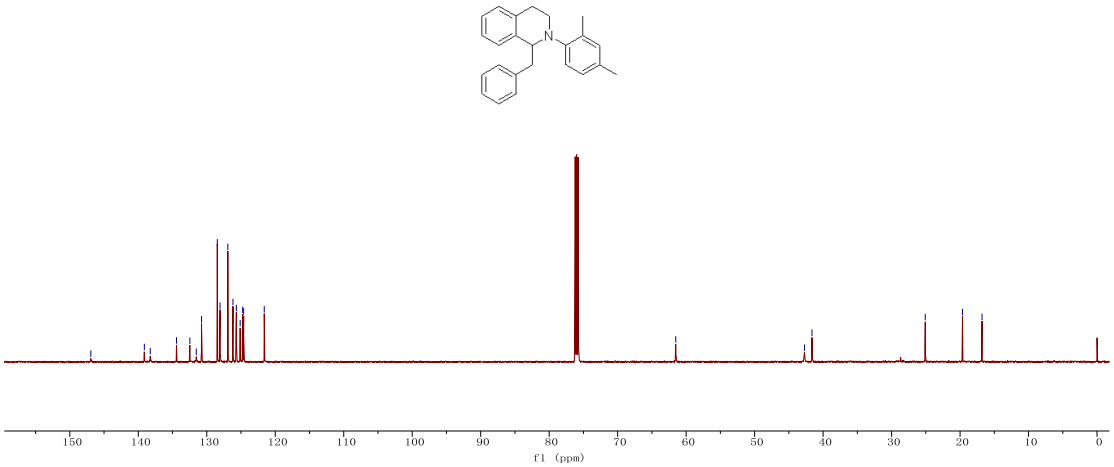
1-allyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (27)



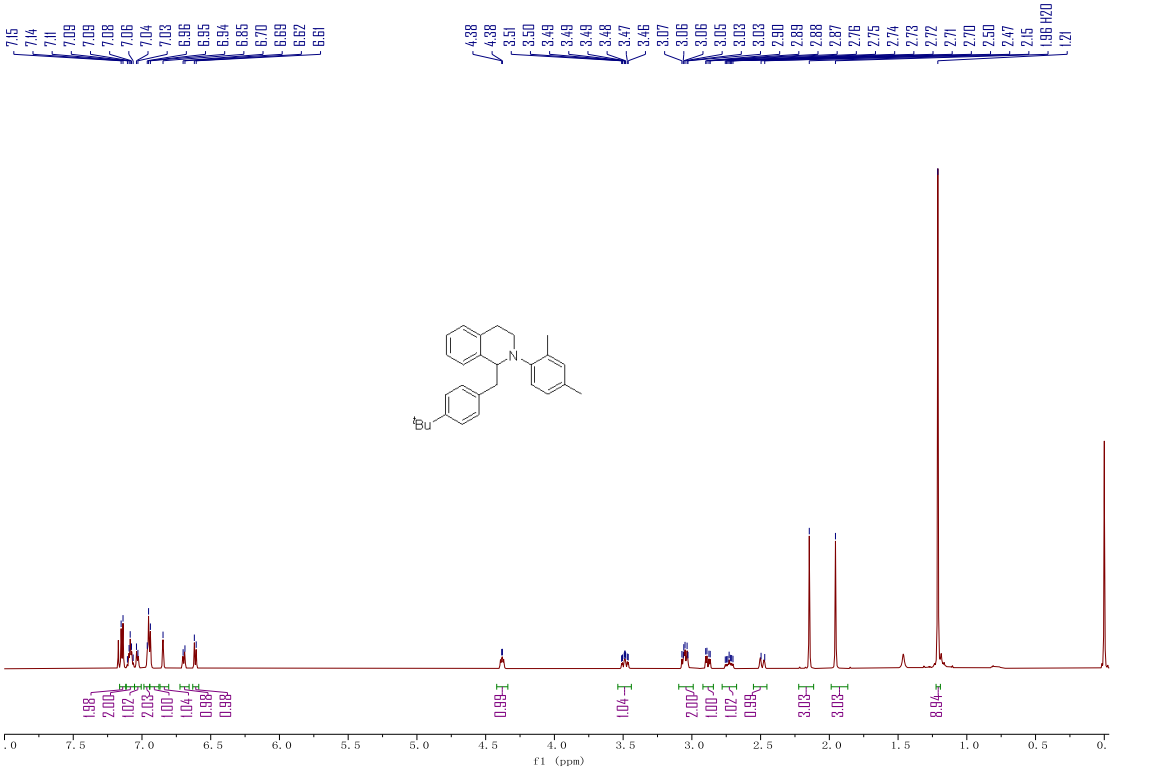


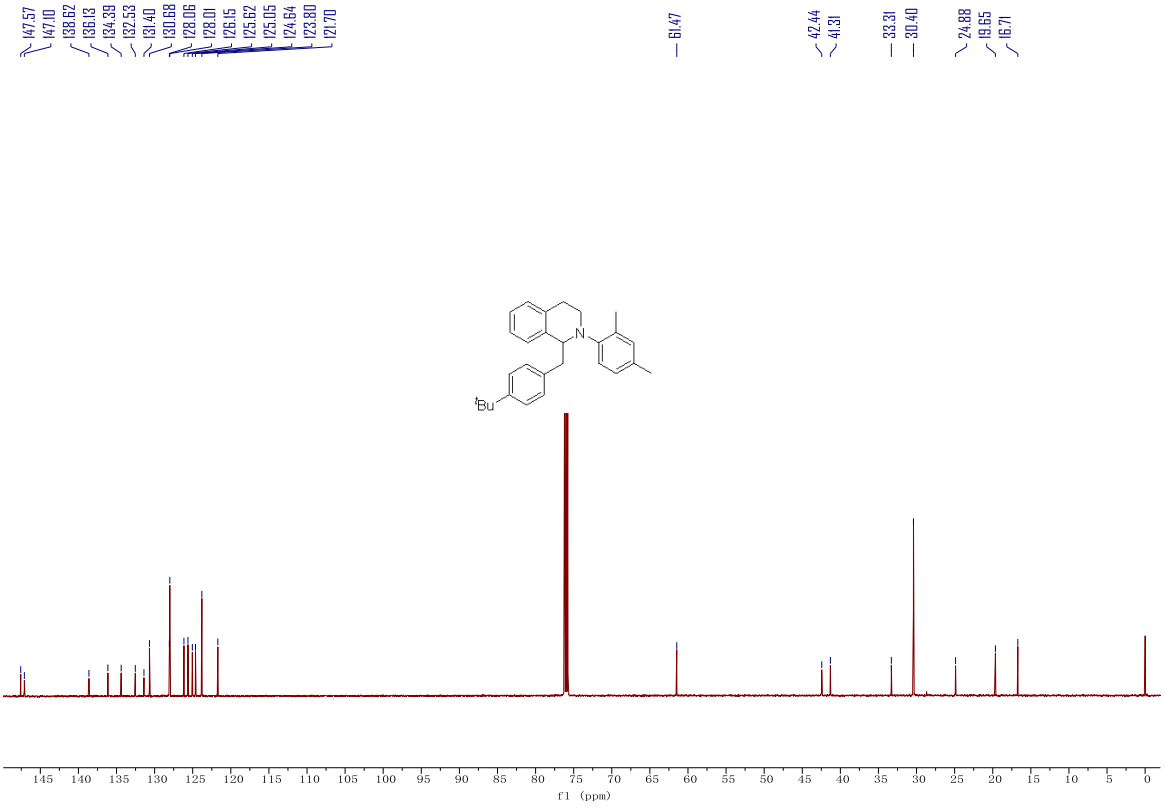
1-benzyl-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (29)



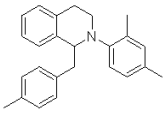


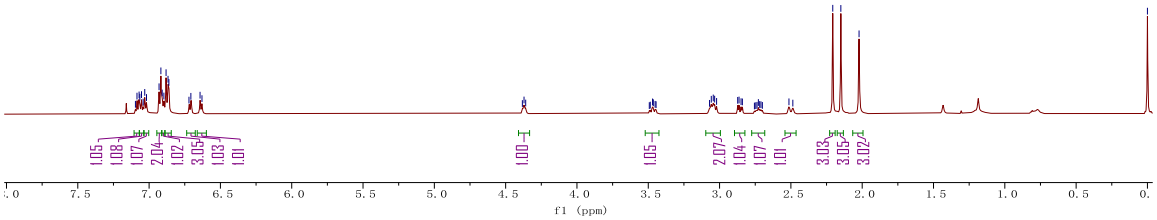
1-(4-(tert-butyl)benzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (30)

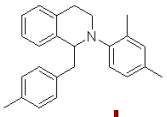


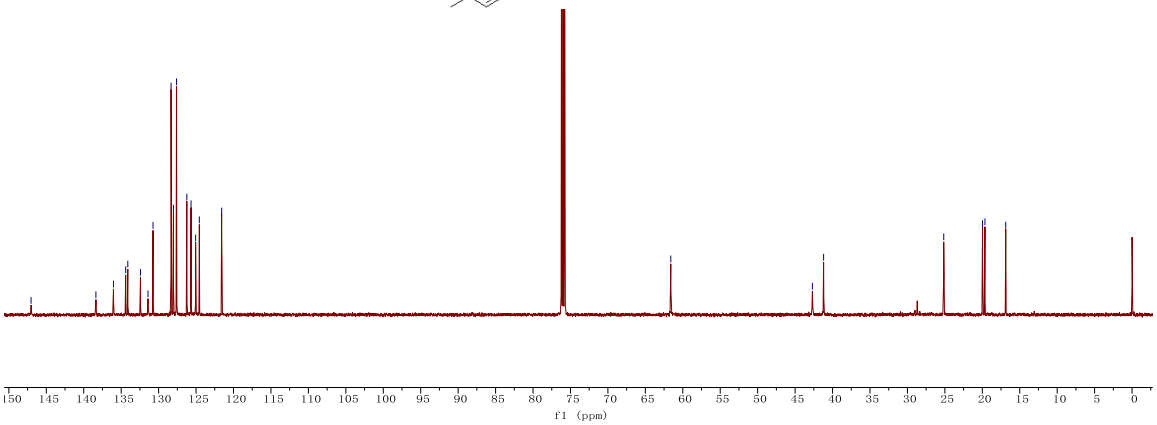


2-(2,4-dimethylphenyl)-1-(4-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (31)

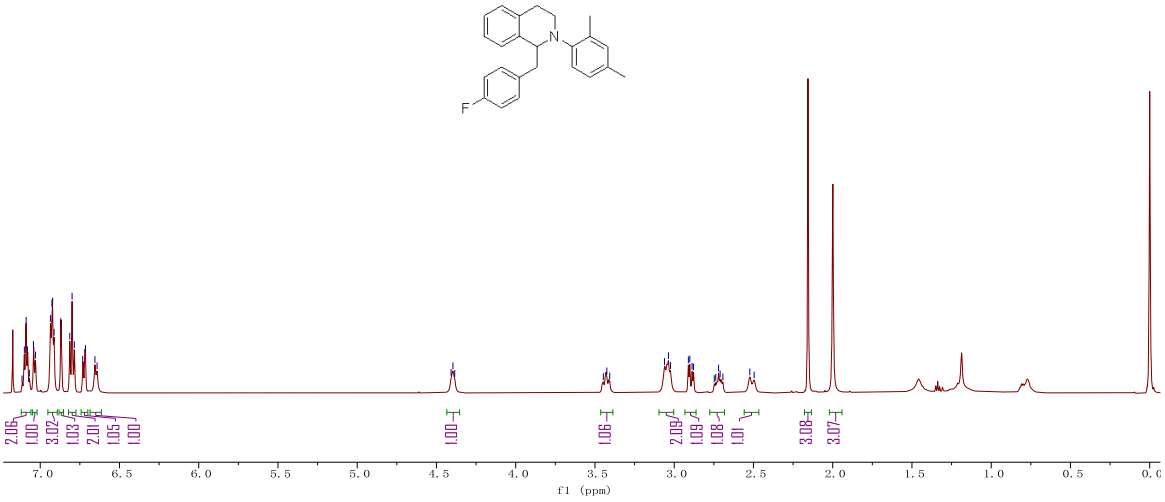


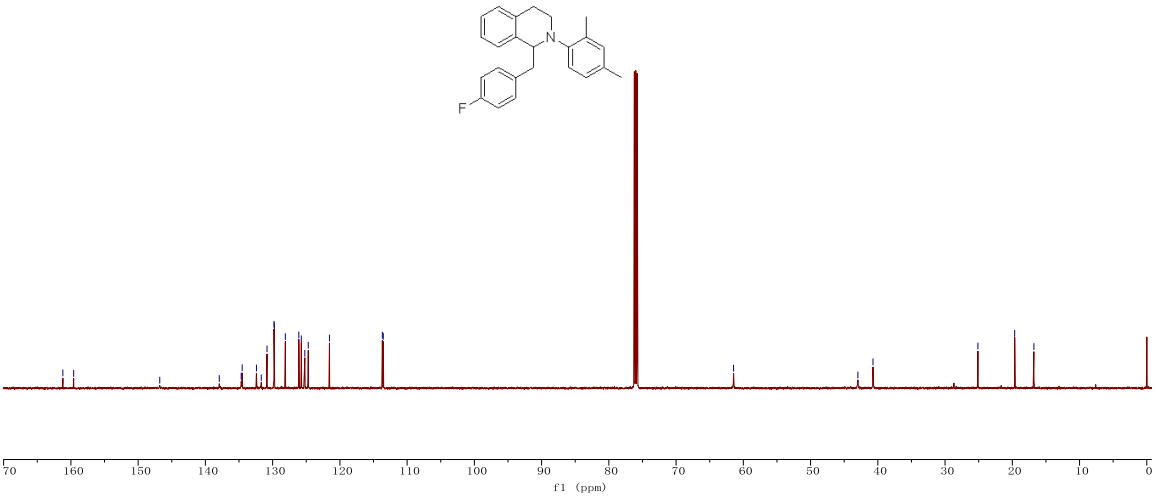




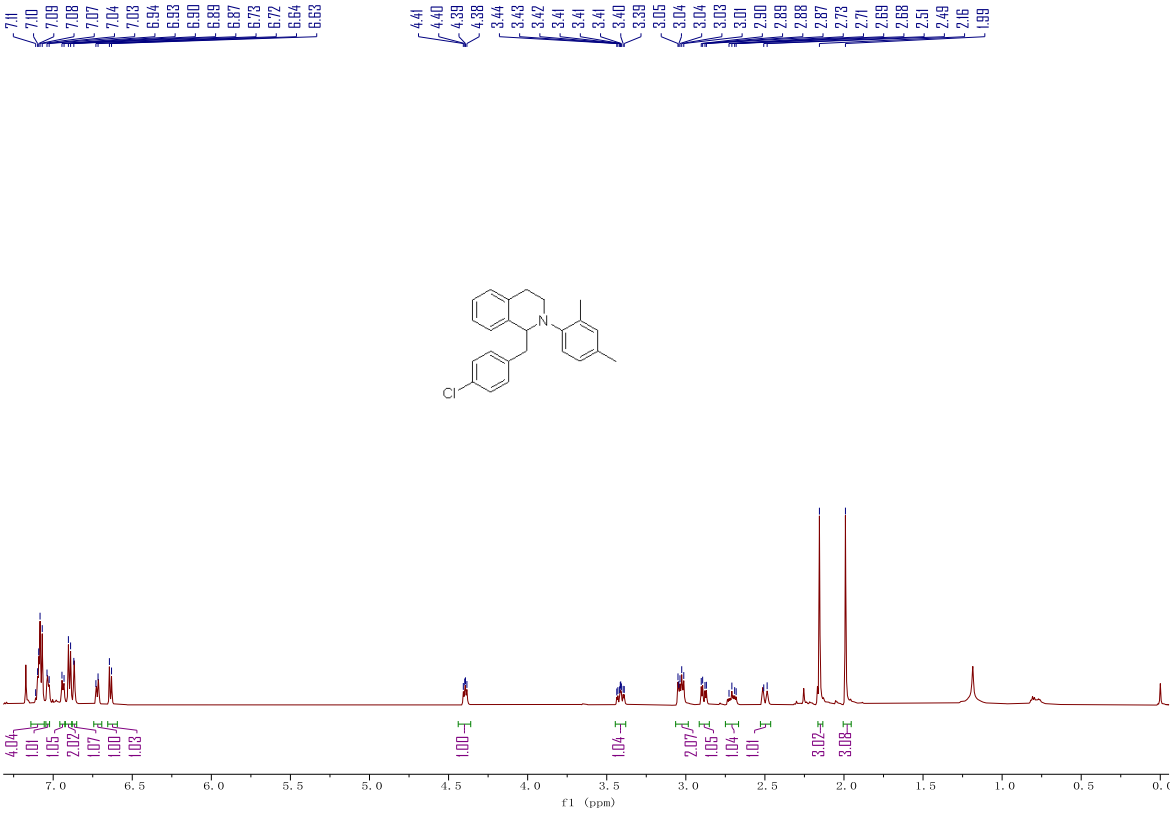


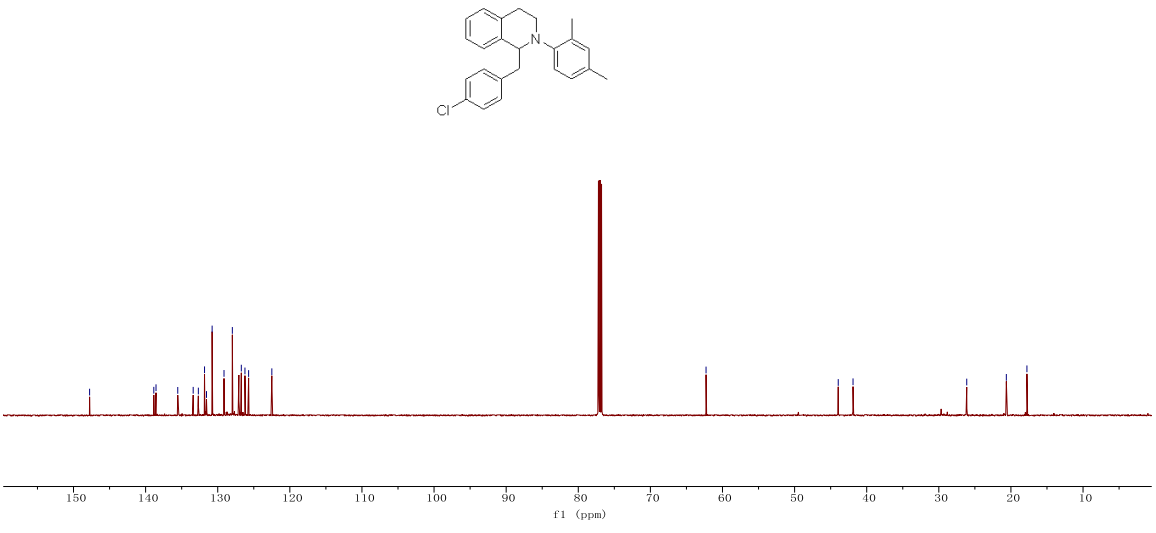
2-(2,4-dimethylphenyl)-1-(4-fluorobenzyl)-1,2,3,4-tetrahydroisoquinoline (32)



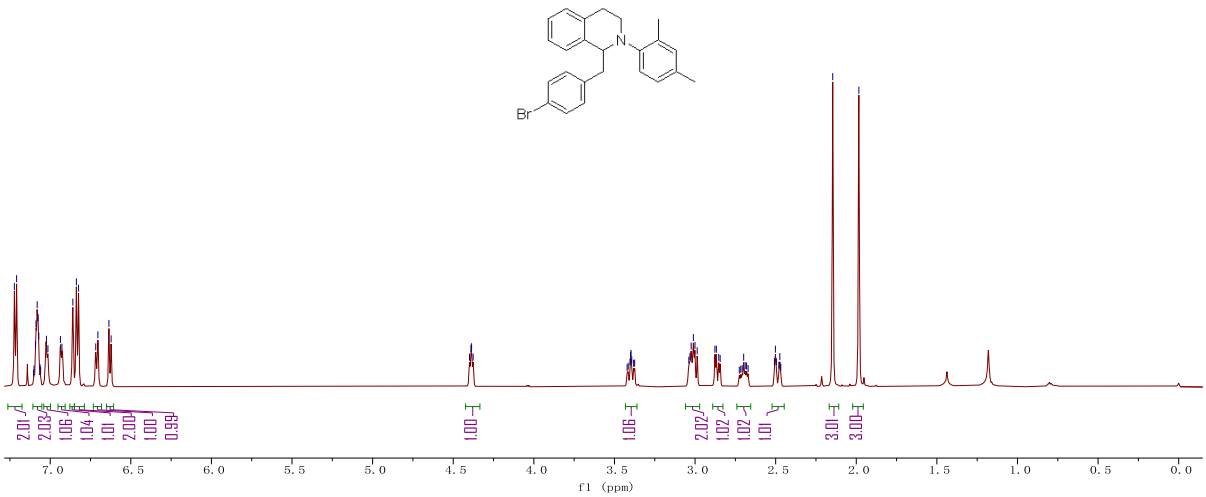


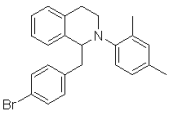
1-(4-chlorobenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (33)

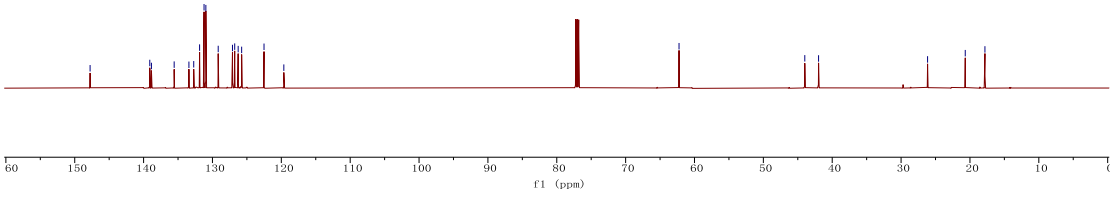




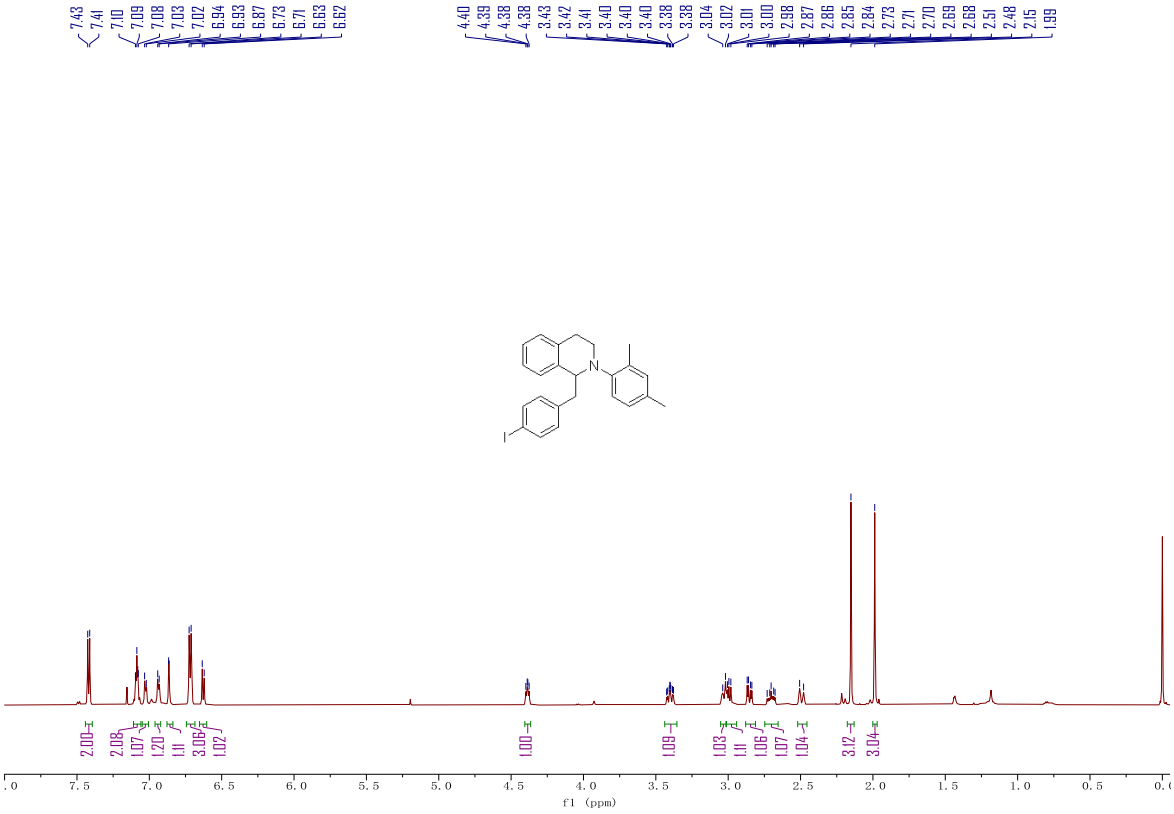
1-(4-bromobenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (34)

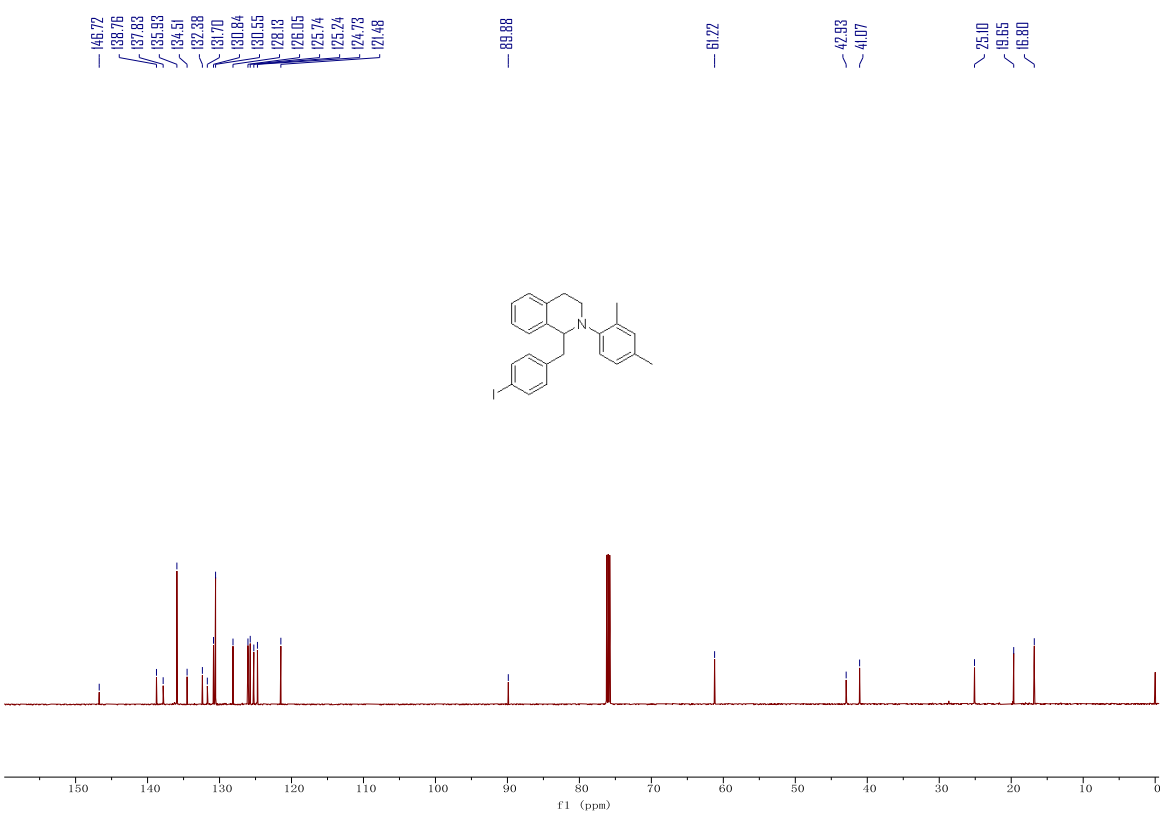




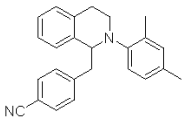


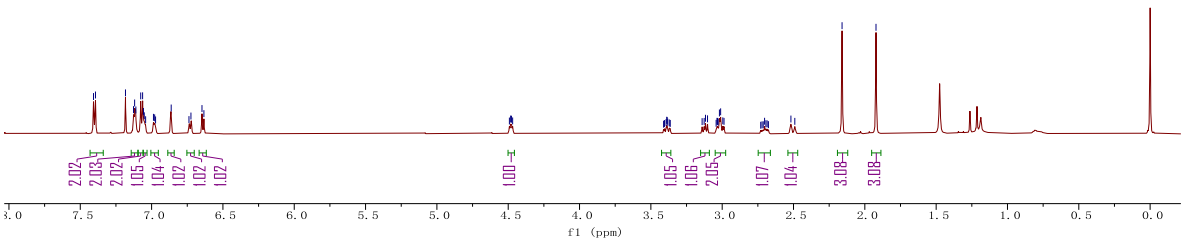
2-(2,4-dimethylphenyl)-1-(4-iodobenzyl)-1,2,3,4-tetrahydroisoquinoline (35)

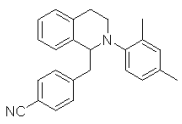


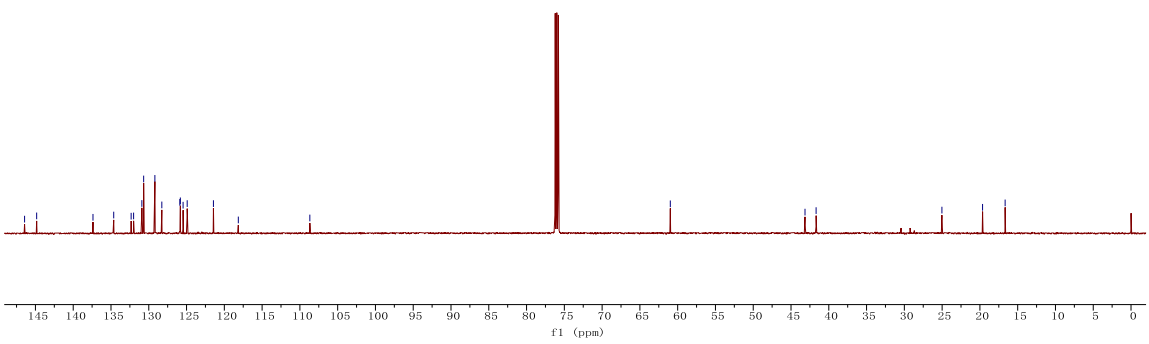


4-((2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)methyl)benzonitrile (36)

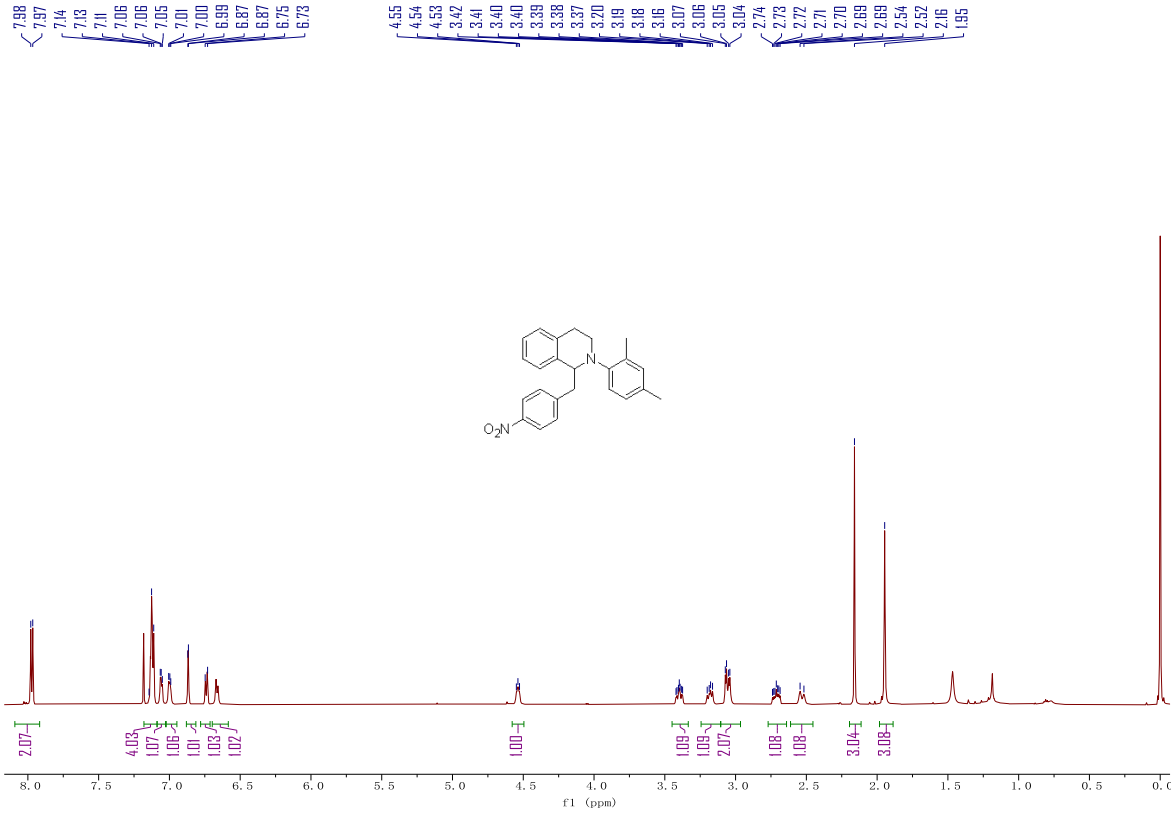


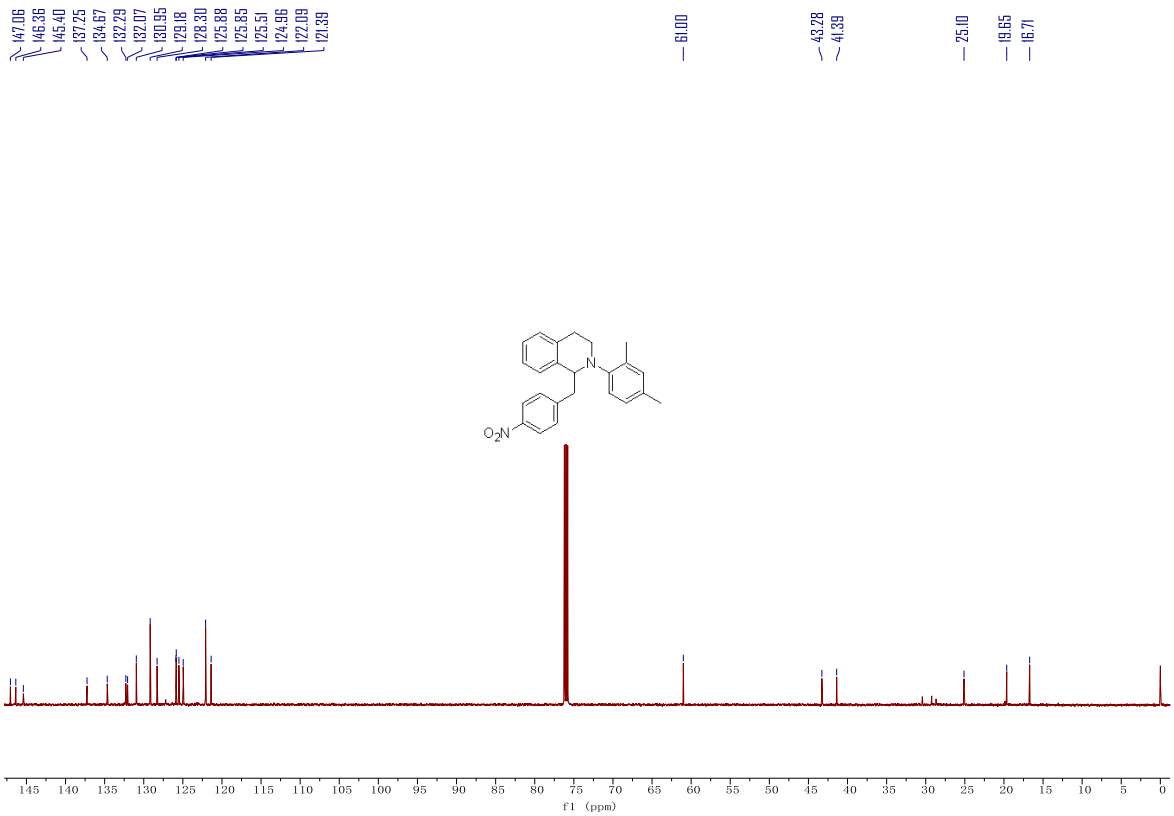




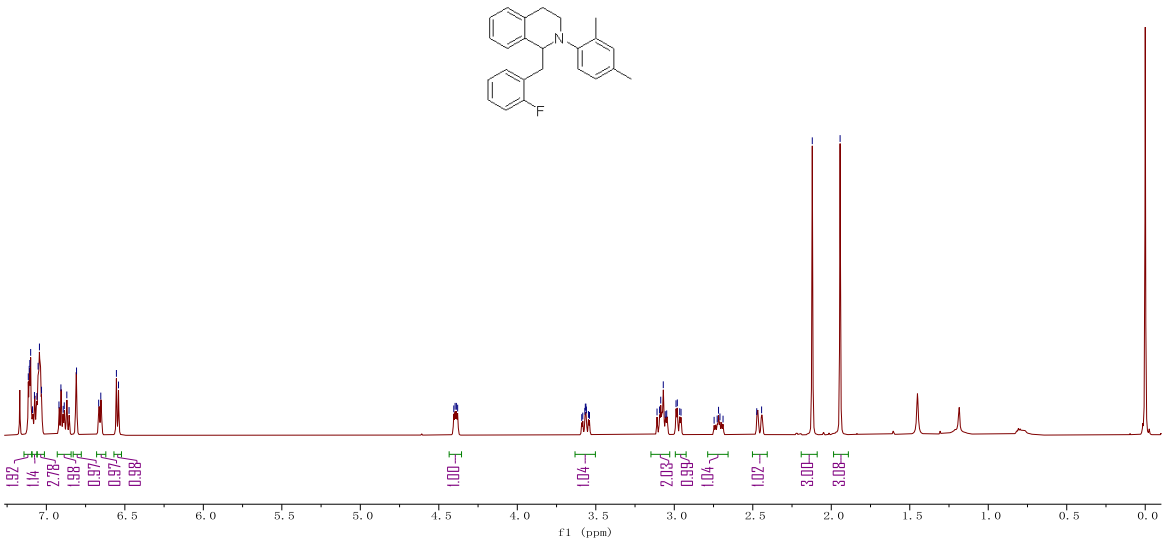


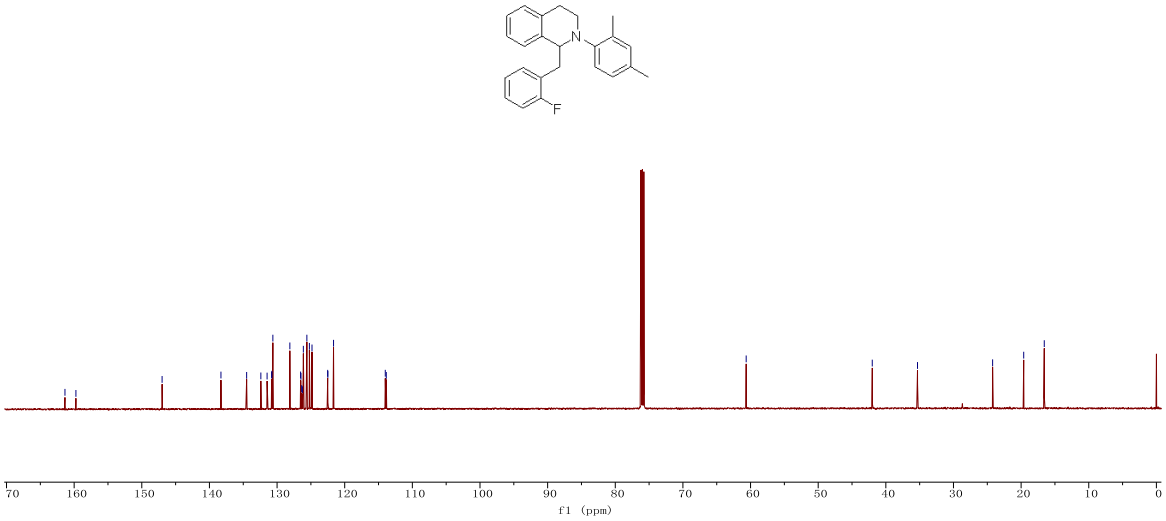
2-(2,4-dimethylphenyl)-1-(4-nitrobenzyl)-1,2,3,4-tetrahydroisoquinoline (37)



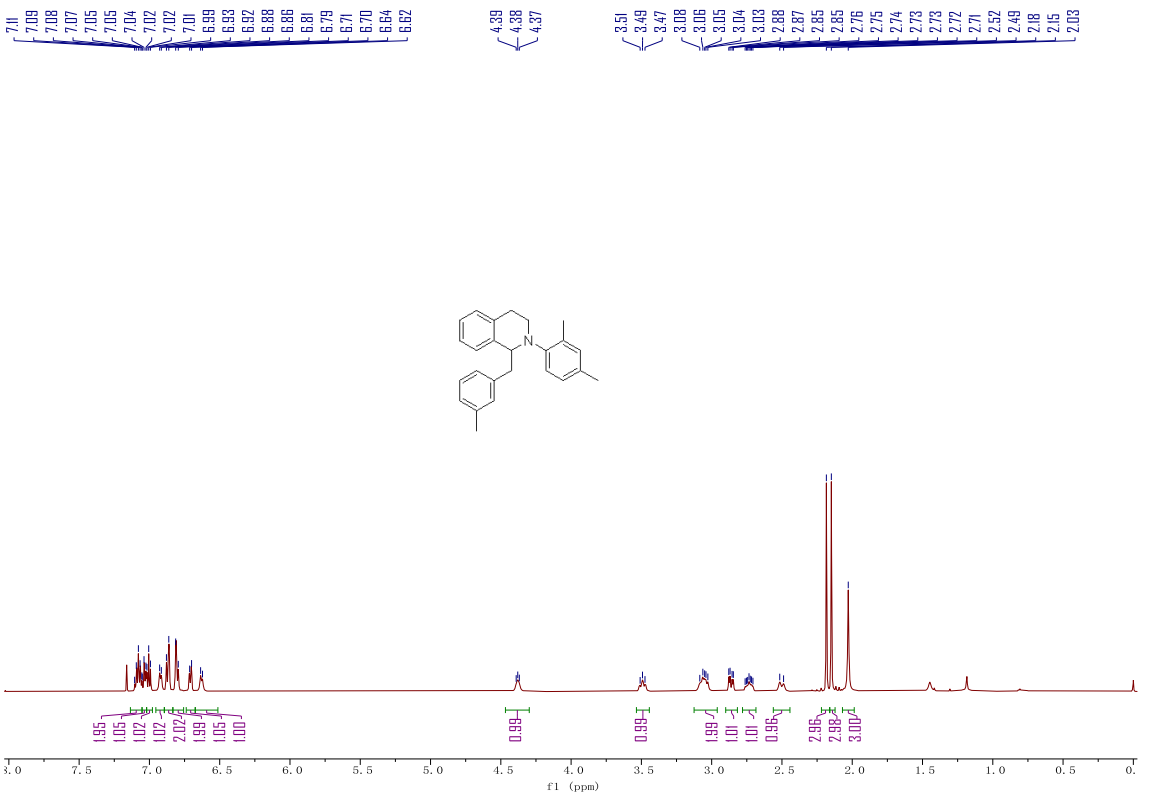


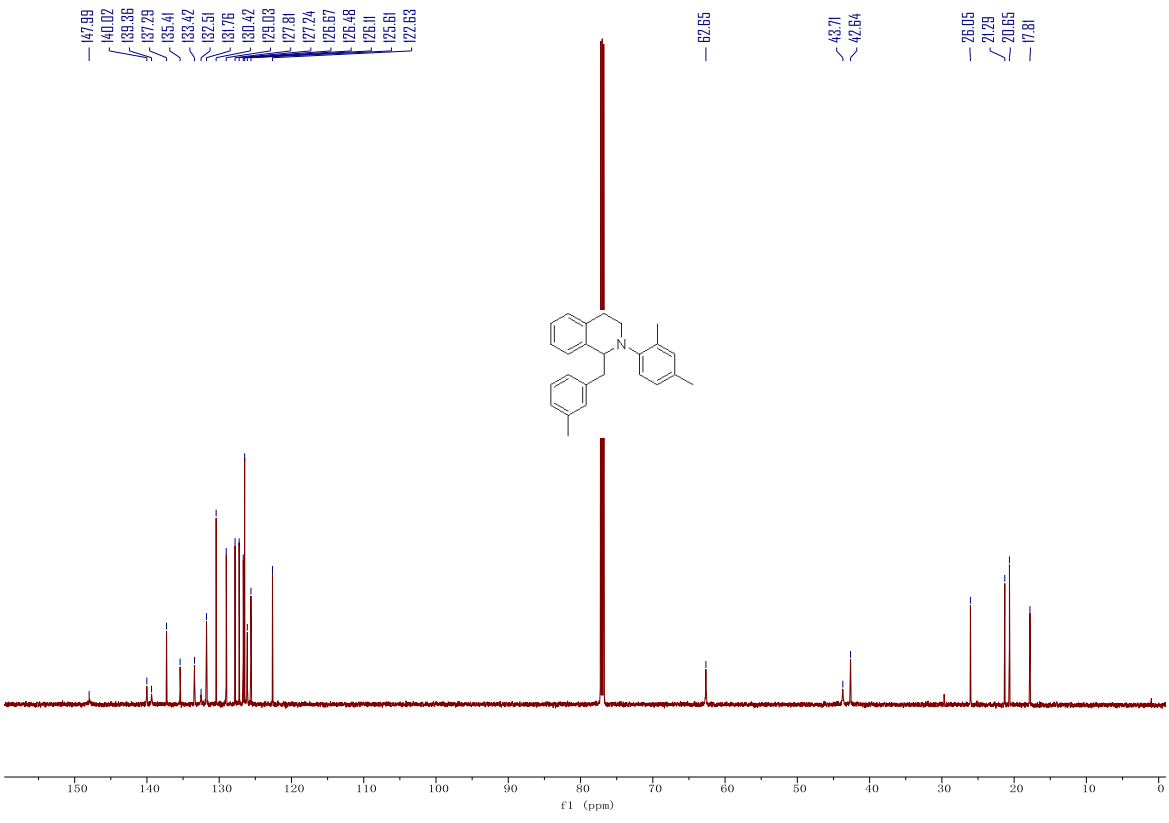
2-(2,4-dimethylphenyl)-1-(2-fluorobenzyl)-1,2,3,4-tetrahydroisoquinoline (38)



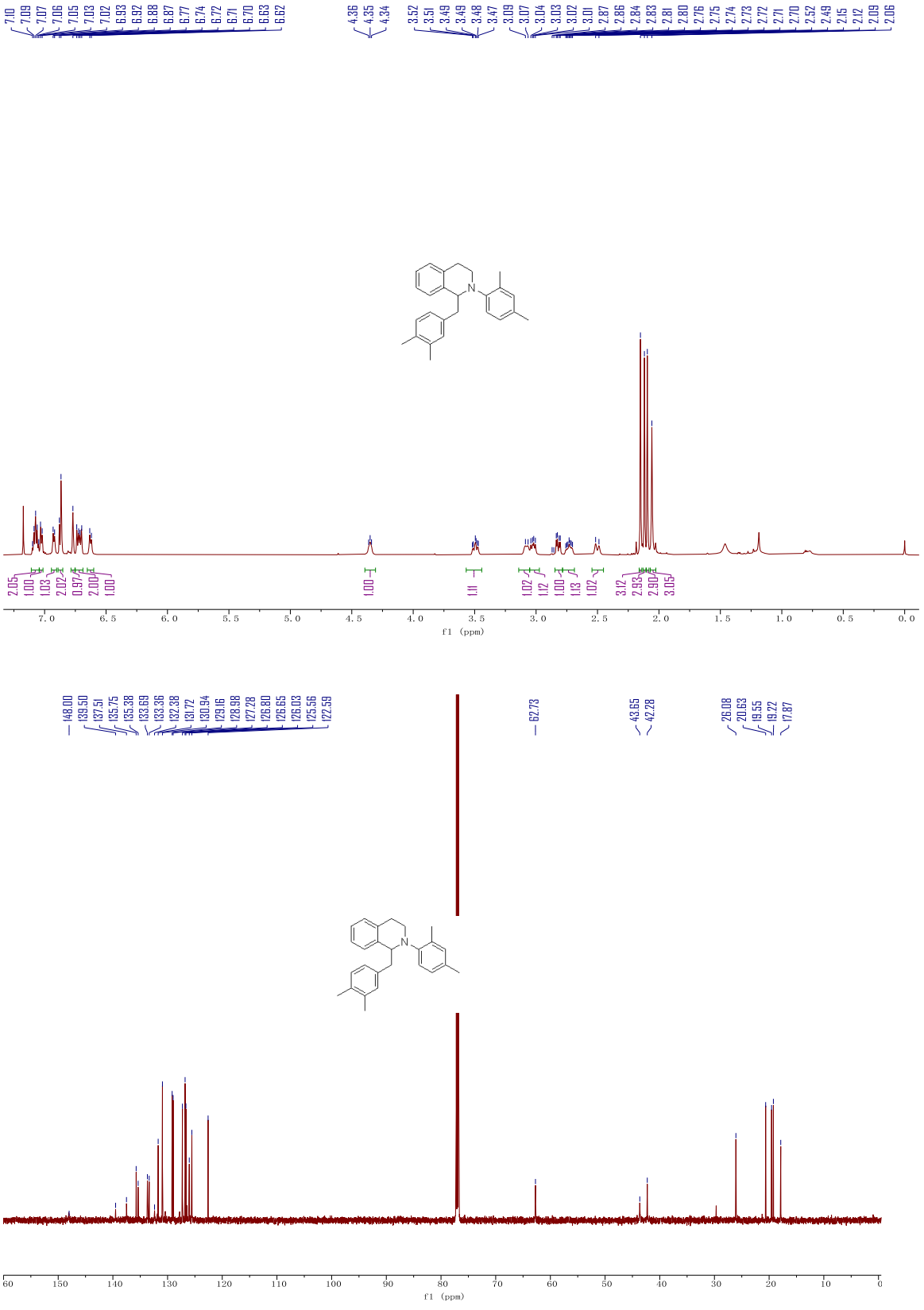


2-(2,4-dimethylphenyl)-1-(3-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (39)

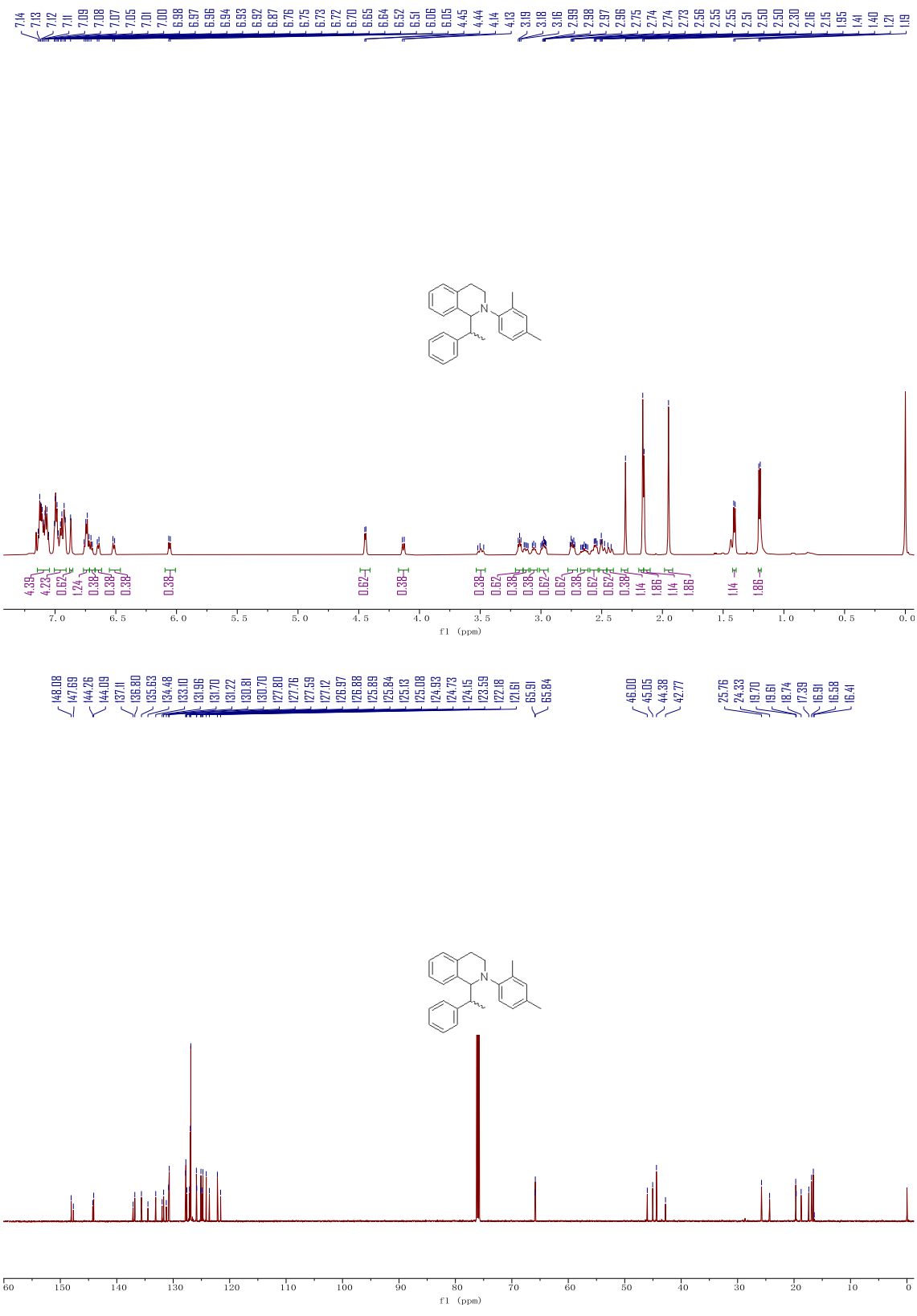




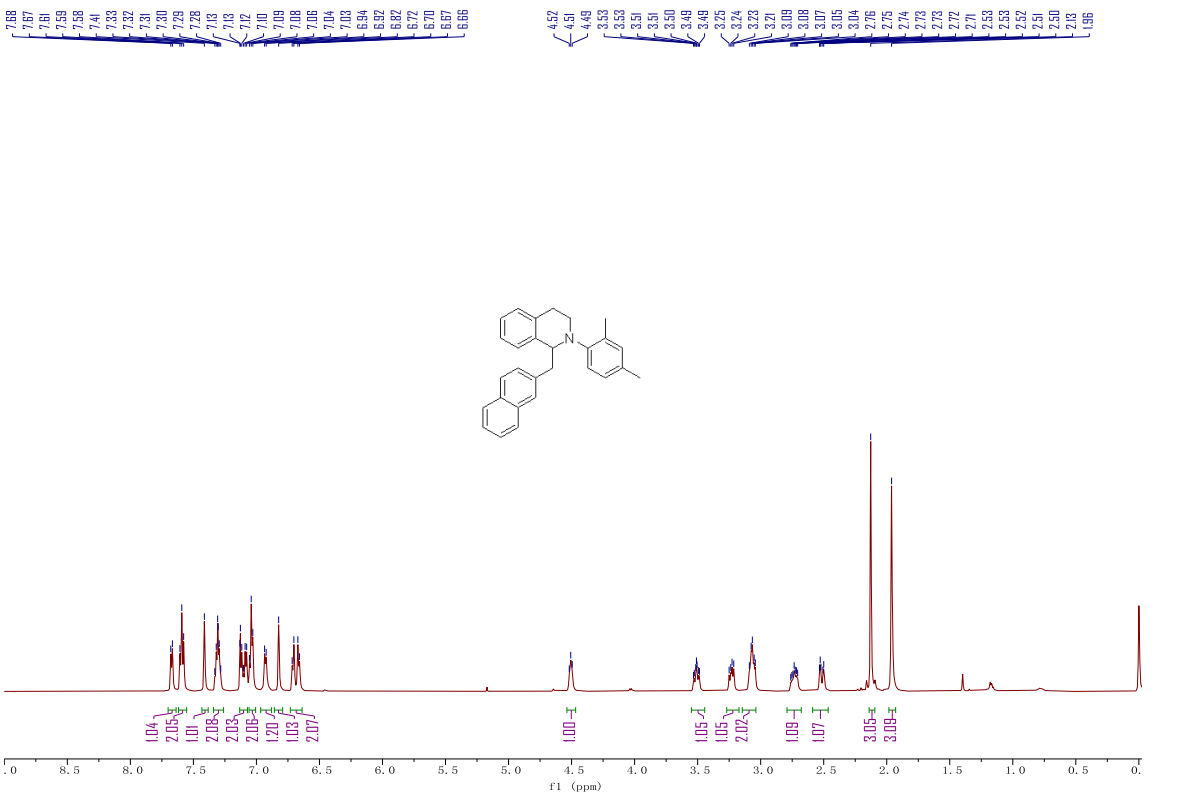
1-(3,4-dimethylbenzyl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (40)

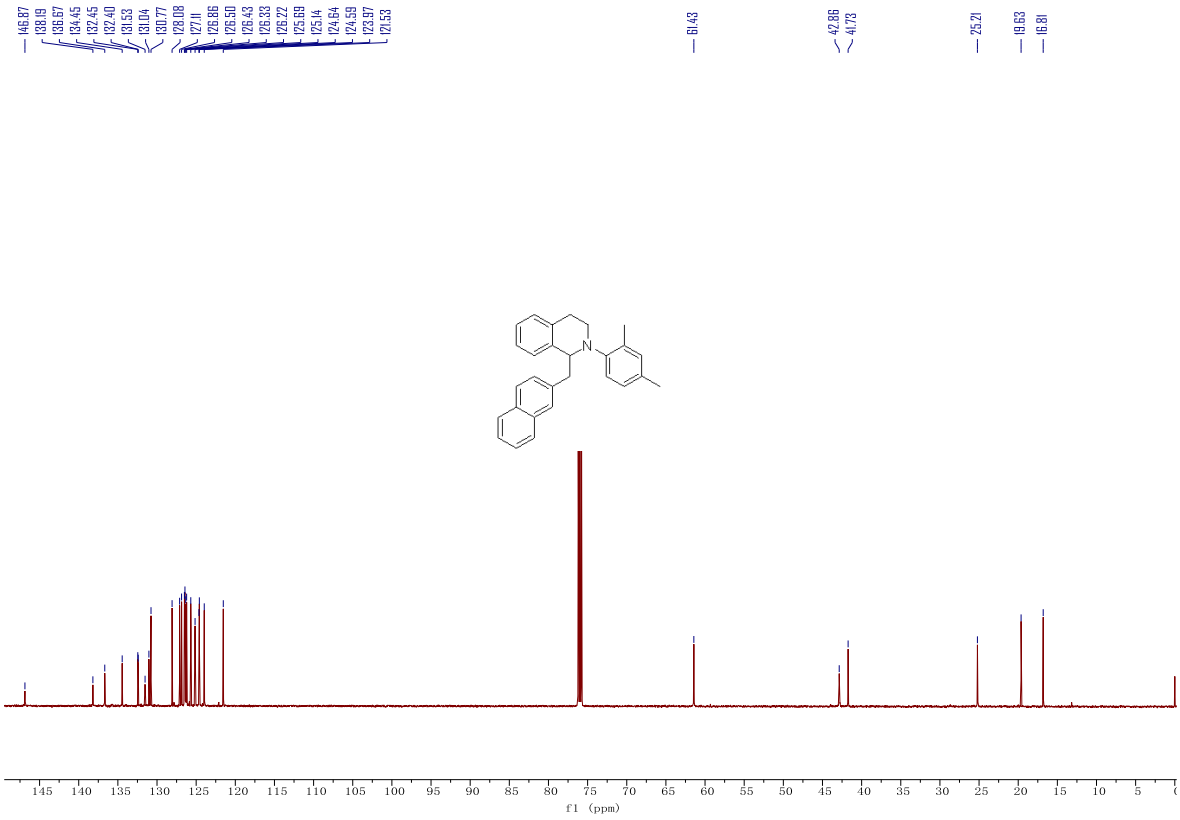


2-(2,4-dimethylphenyl)-1-(1-phenylethyl)-1,2,3,4-tetrahydroisoquinoline (41, dr=1.63)

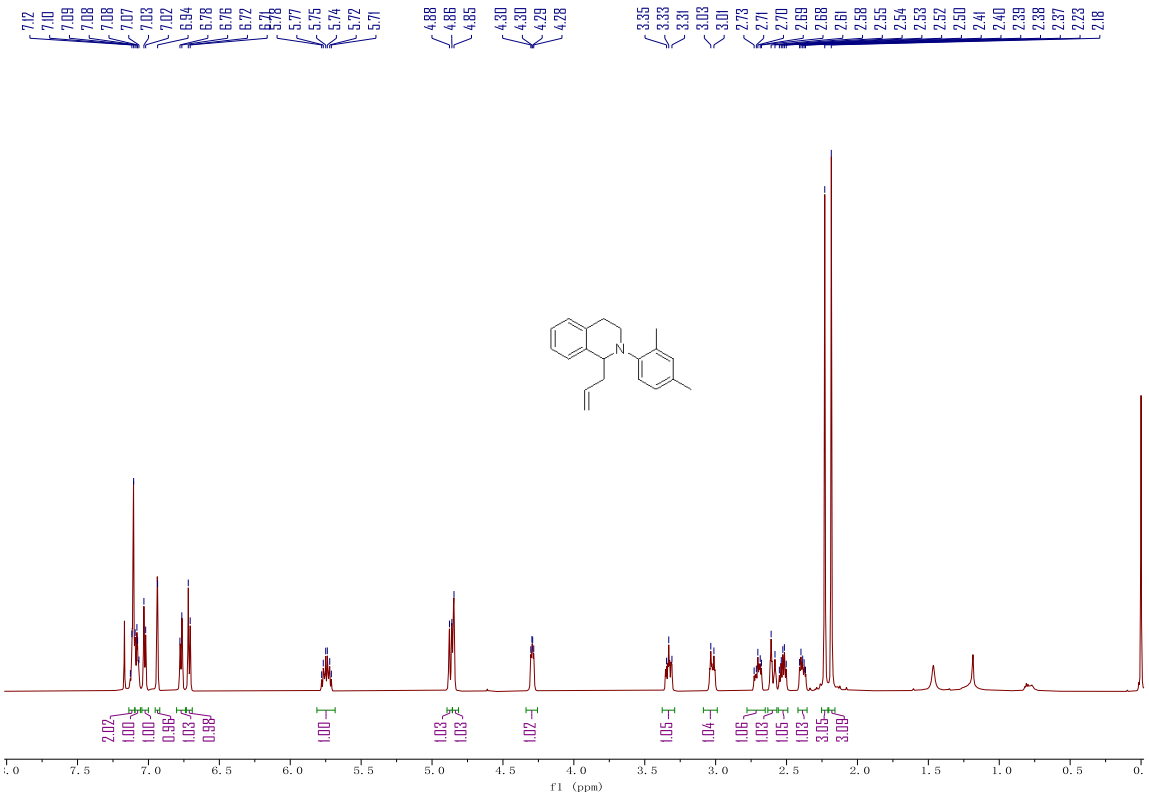


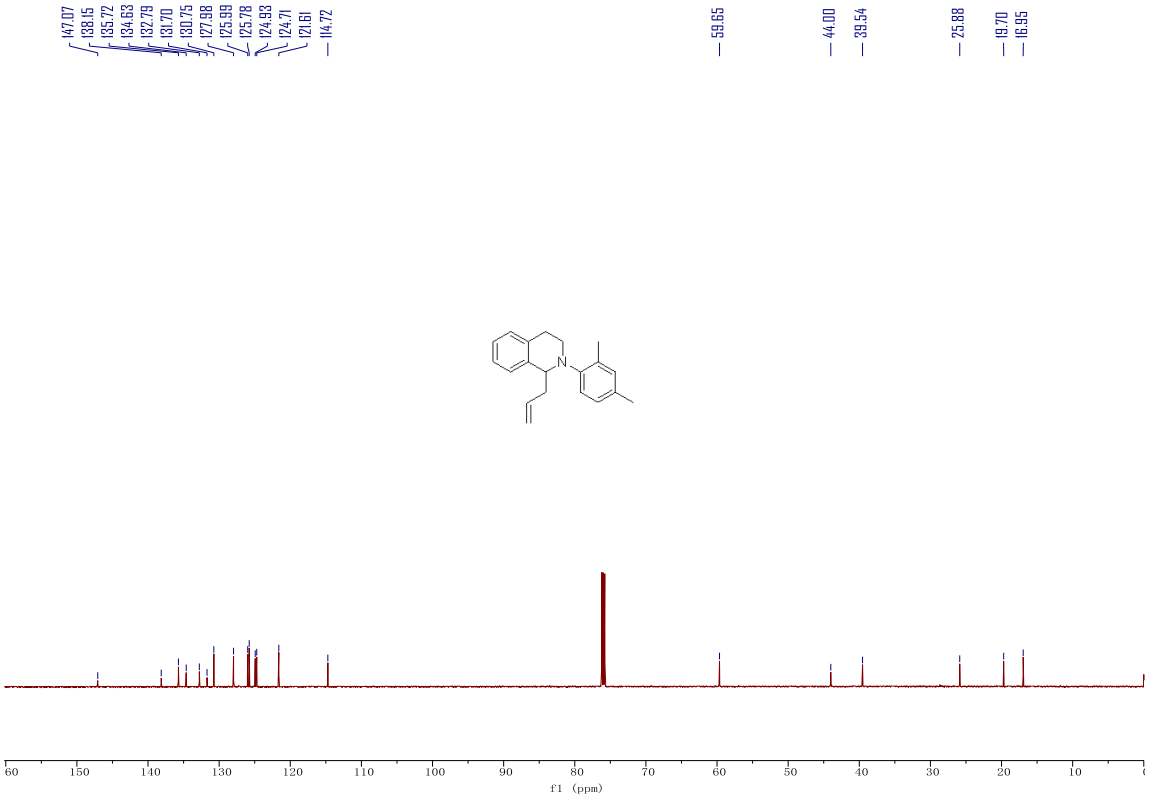
2-(2,4-dimethylphenyl)-1-(naphthalen-2-ylmethyl)-1,2,3,4-tetrahydroisoquinoline (42)



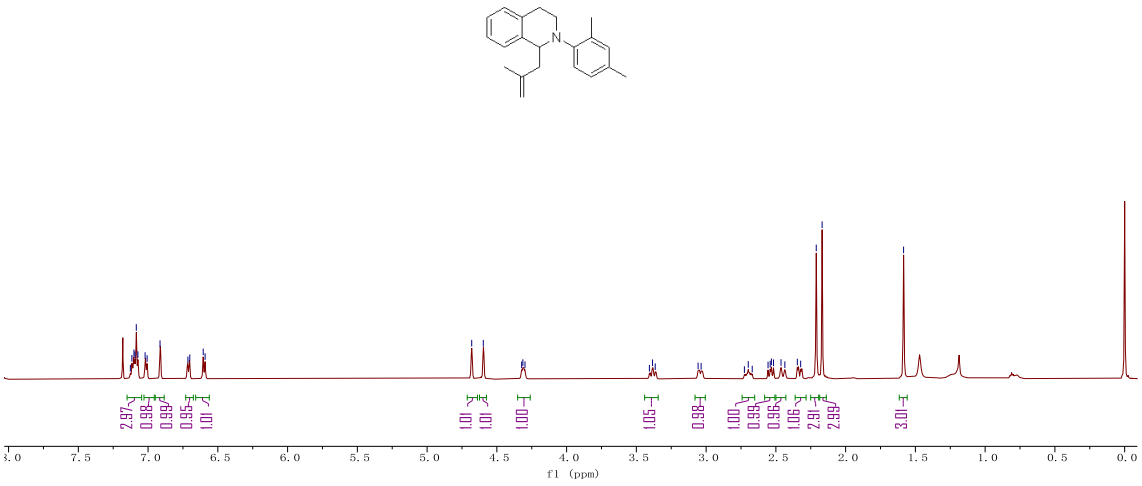


1-allyl-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (43)

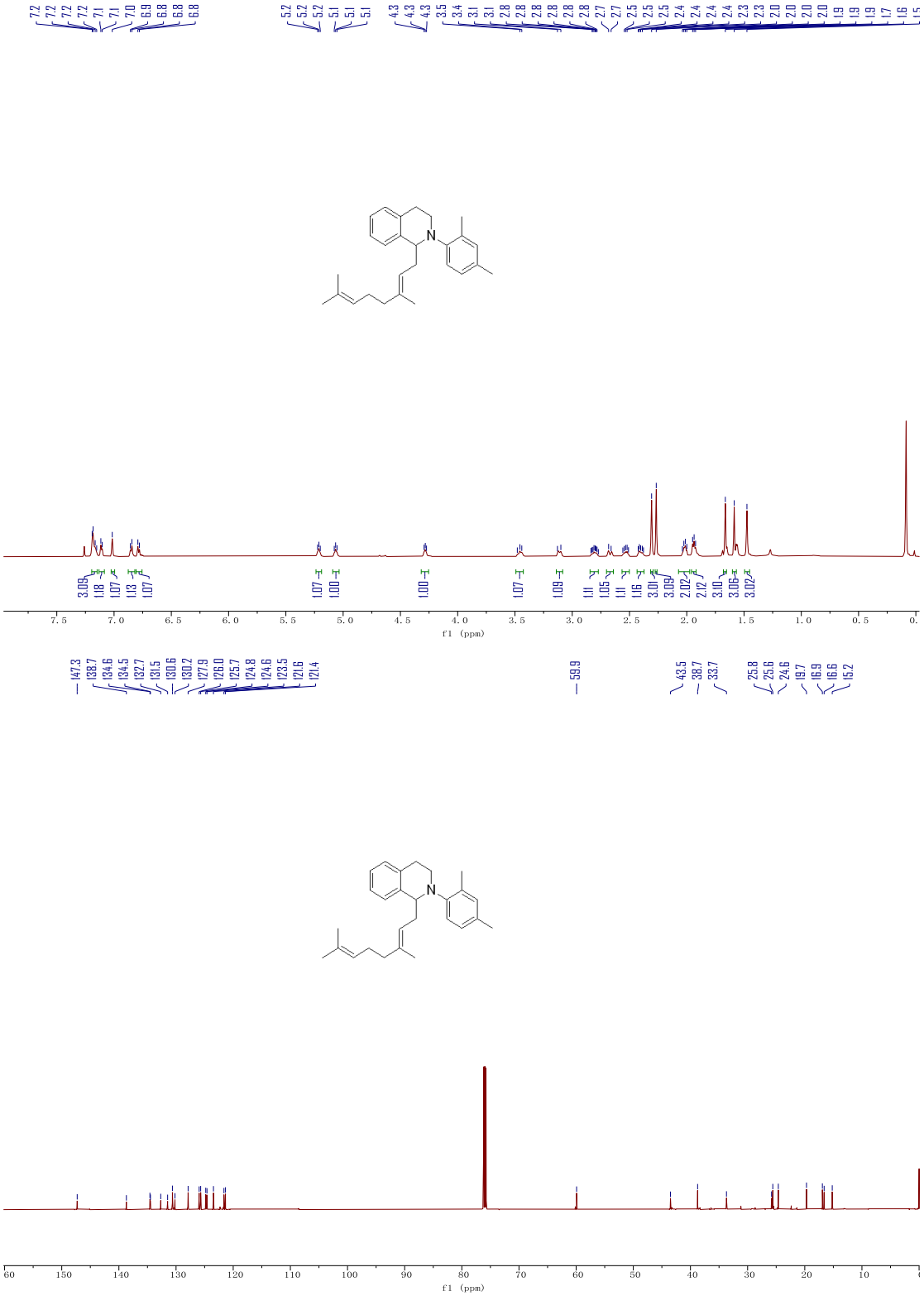




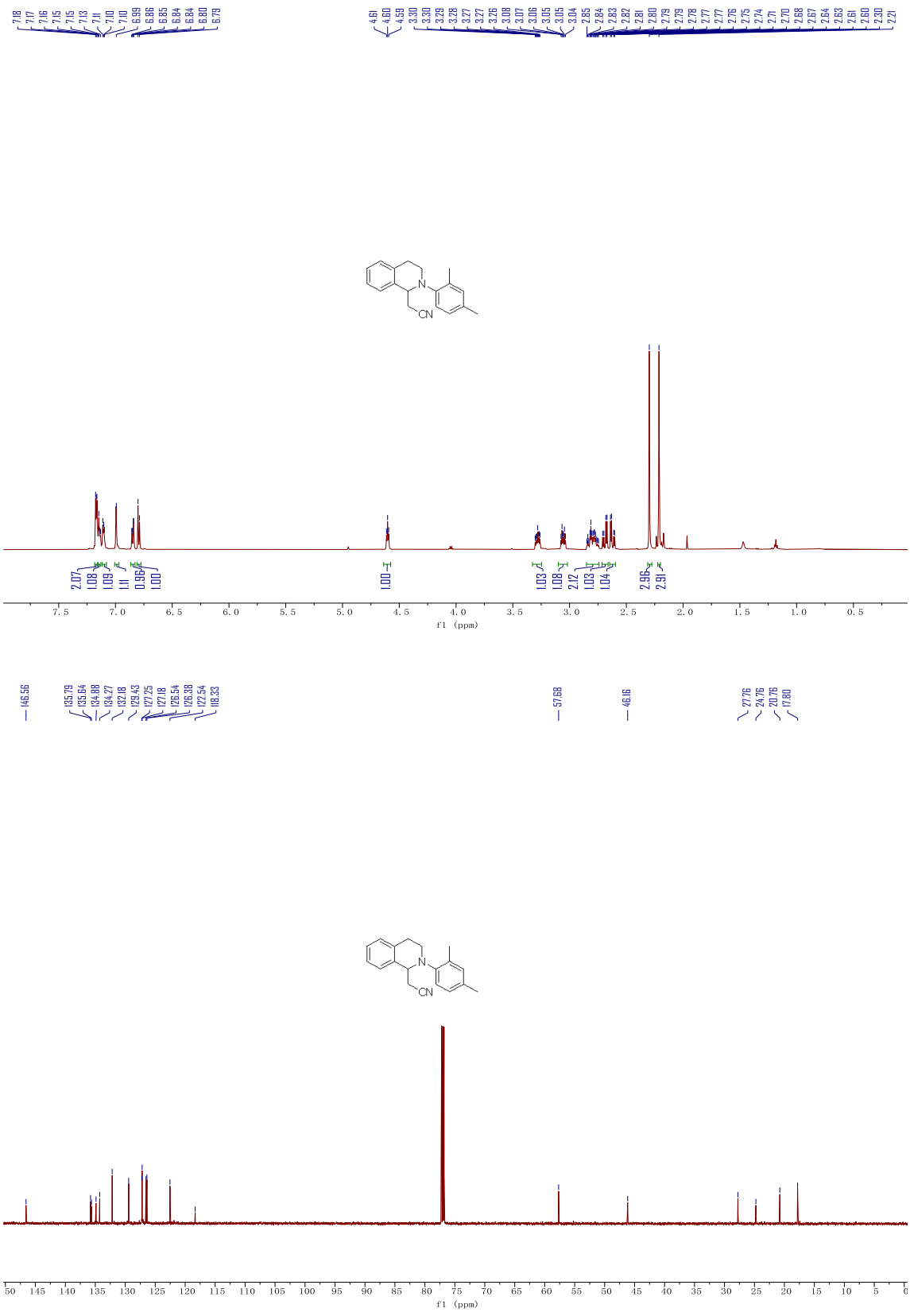
2-(2,4-dimethylphenyl)-1-(2-methylallyl)-1,2,3,4-tetrahydroisoquinoline (44)



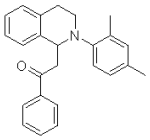
(E)-1-(3,8-dimethylnona-2,7-dien-1-yl)-2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (45)

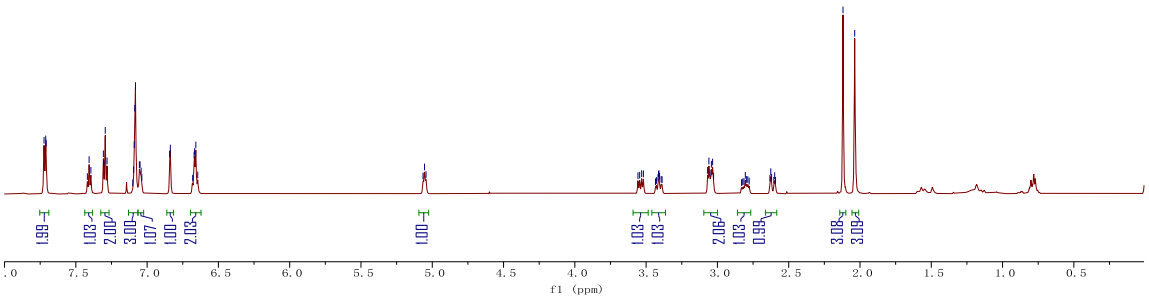


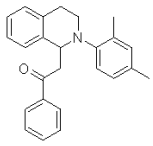
2-(2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile (46)

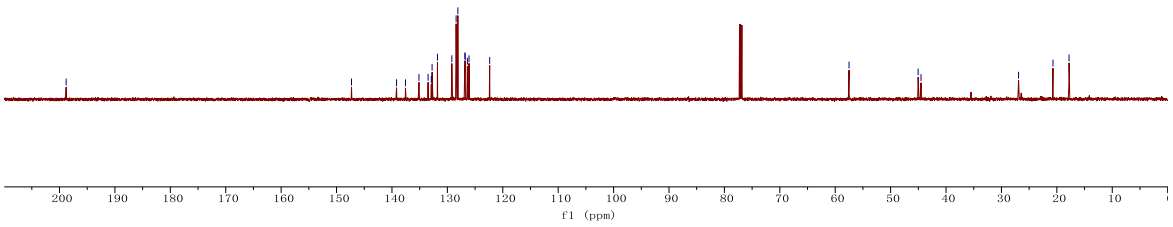


2-(2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethan-1-one (47)

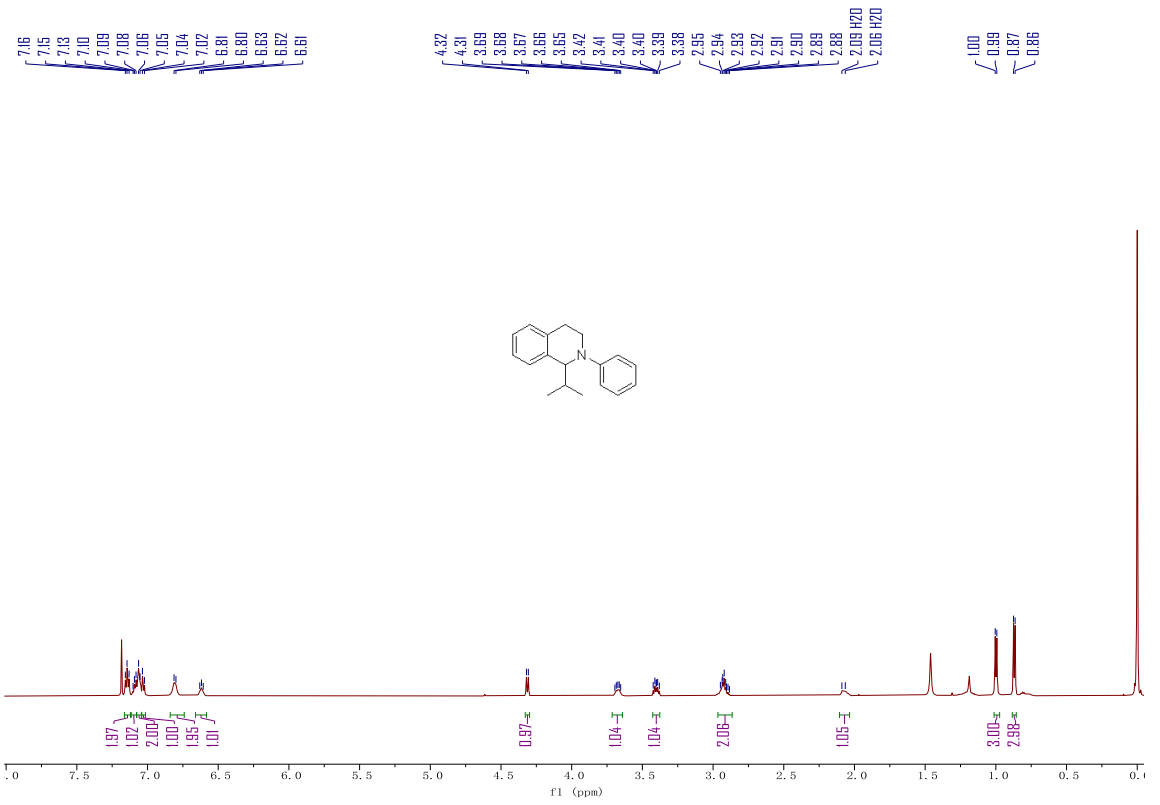


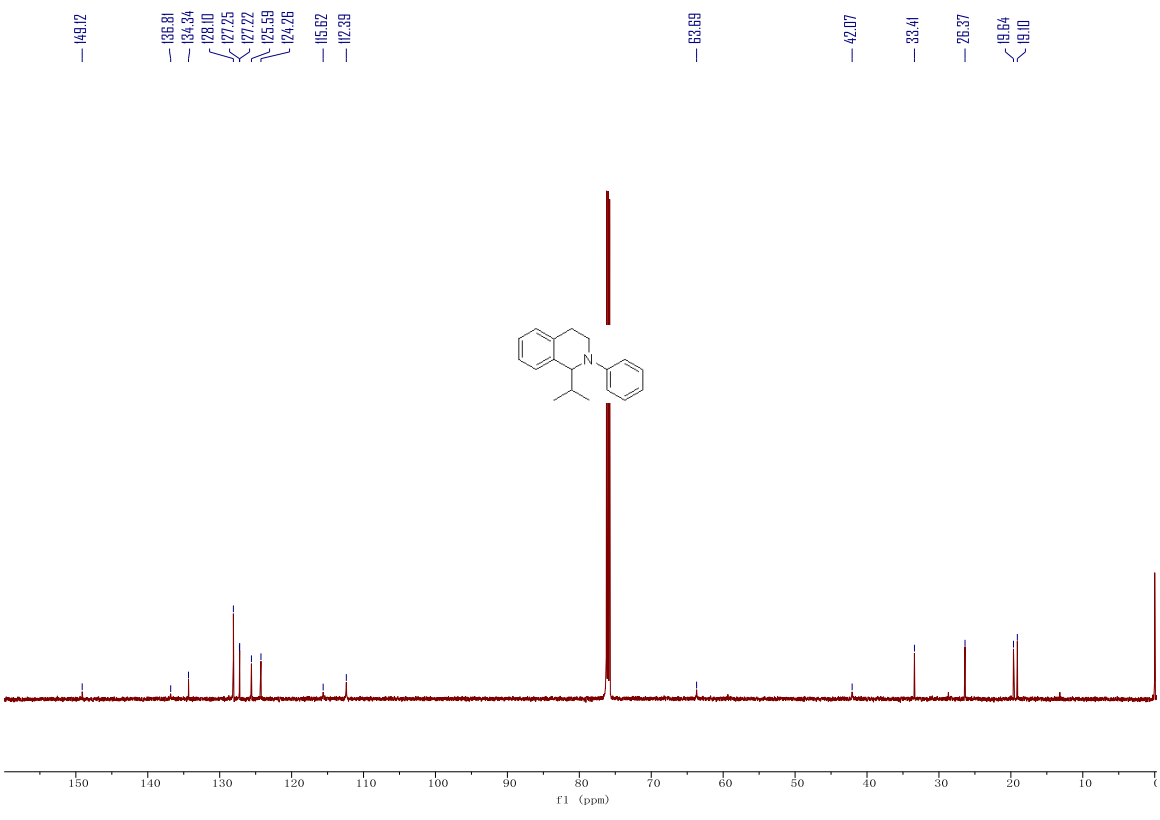




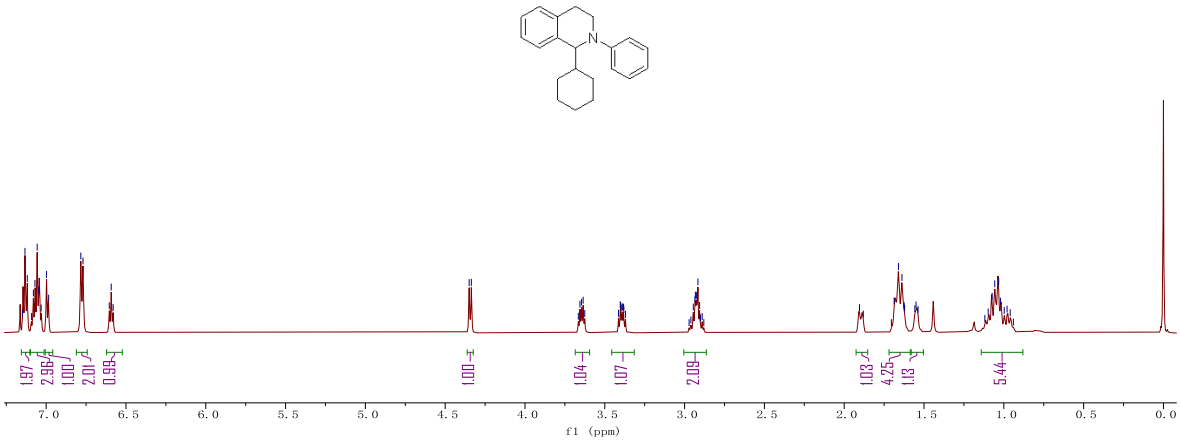


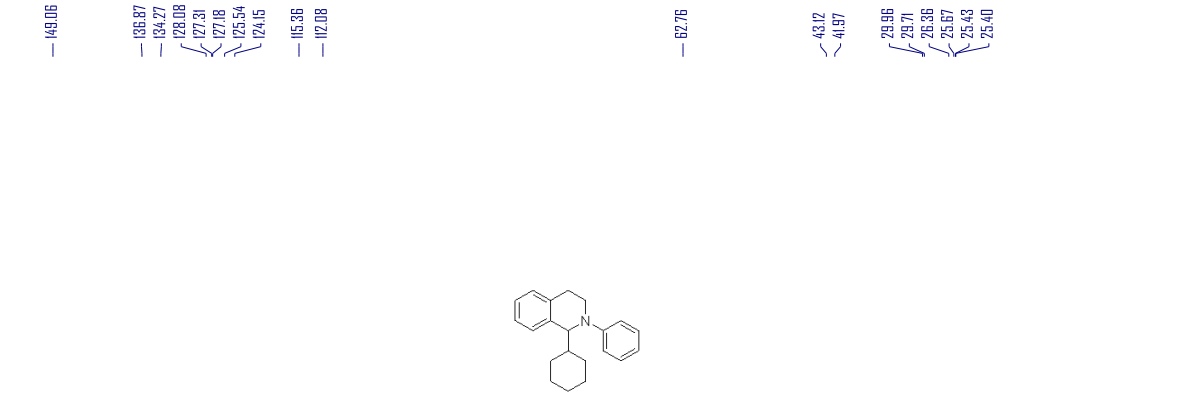
1-isopropyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (50)

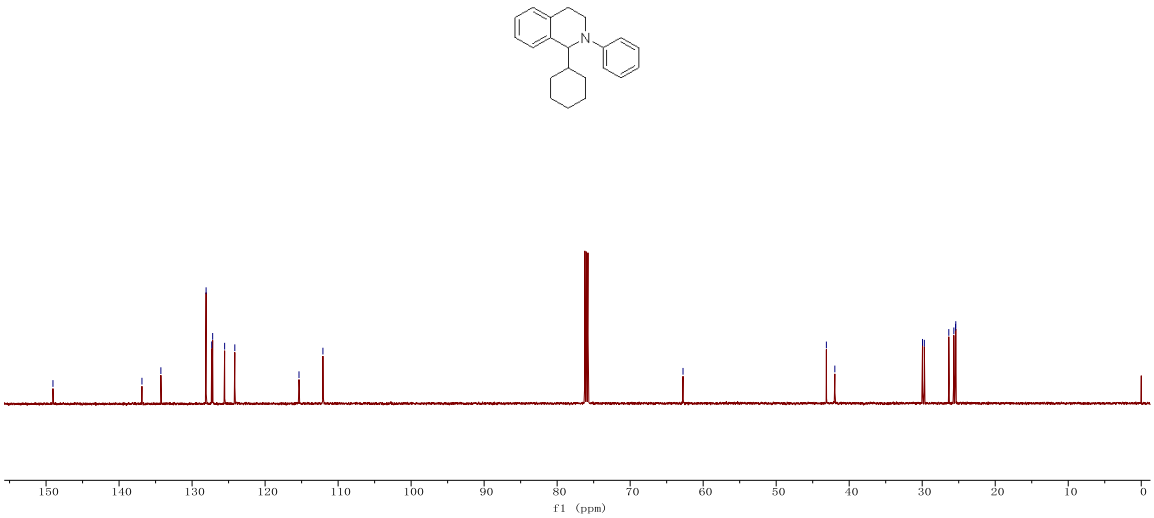




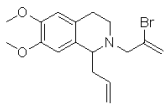
1-cyclohexyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (51)

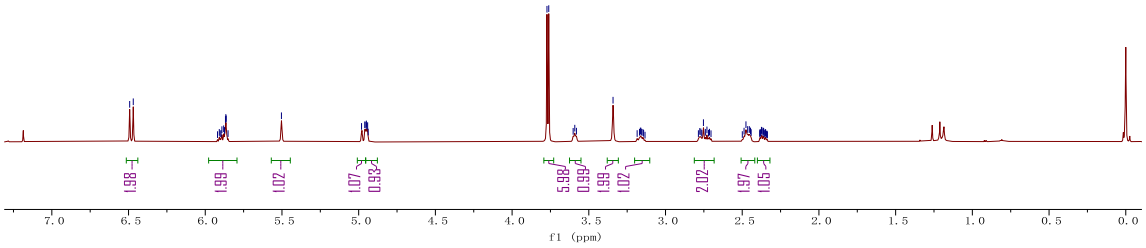


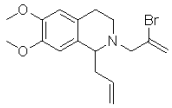


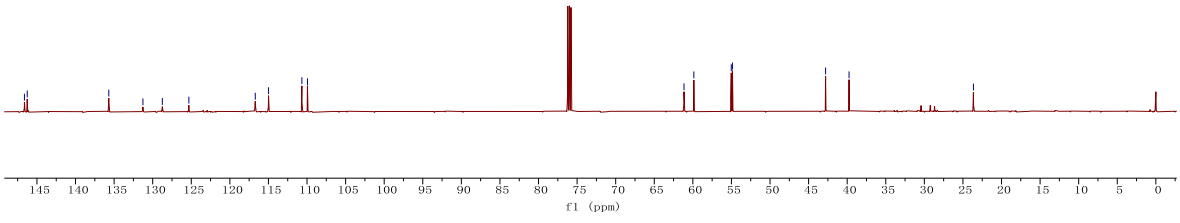


1-allyl-2-(2-bromoallyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (53)

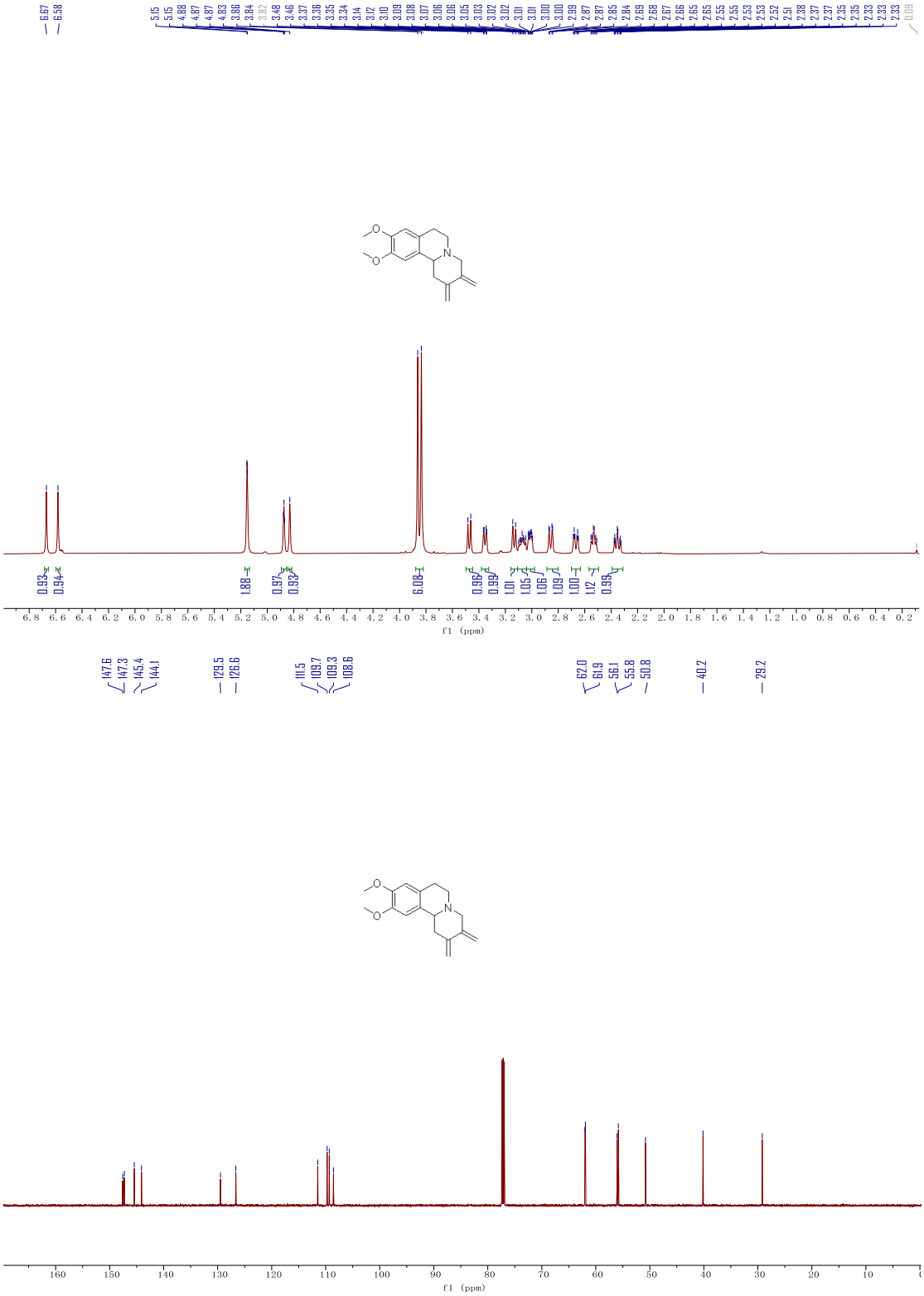








9,10-dimethoxy-2,3-dimethylene-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinoline (54)



1-ethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (57)