Electronic Supplementary Information (ESI)

Photocatalyst- and transition-metal-free α-allylation of *N*-aryl tetrahydroisoquinolines mediated by visible light

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Abstract: A convenient and efficient α-allylation of tetrahydroisoquinolines has been achieved. This transformation can be realized under only visible light irradiation without the aid of transition metals or photocatalysts. The mechanism involves a novel in situ-generated electron-donor-acceptor (EDA) complex between the tetrahydroisoquinolines and an allyl or a benzyl bromide. Irradiation with purple light triggered single-electron transfer (SET) from the tetrahydroisoquinolines to the allyl or benzyl bromide of the EDA complex, inducing the formation of the corresponding allyl or benzyl radical and the subsequent radical-radical coupling. This approach represents the first example of a photocatalyst- and transition-metal-free α-allylic and benzylic functionalization of tetrahydroisoquinolines.

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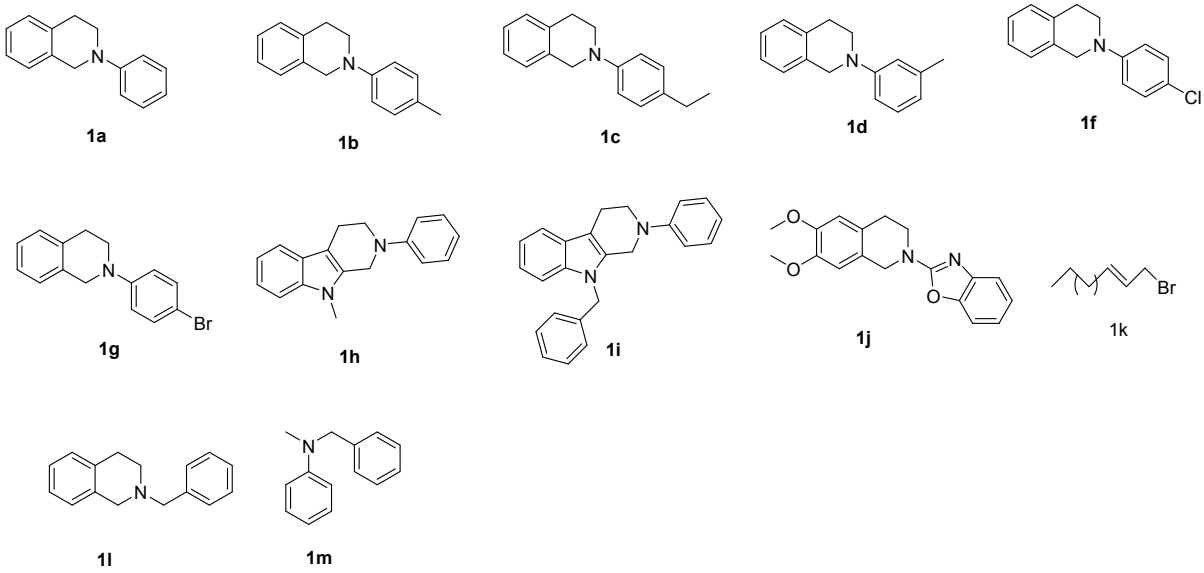
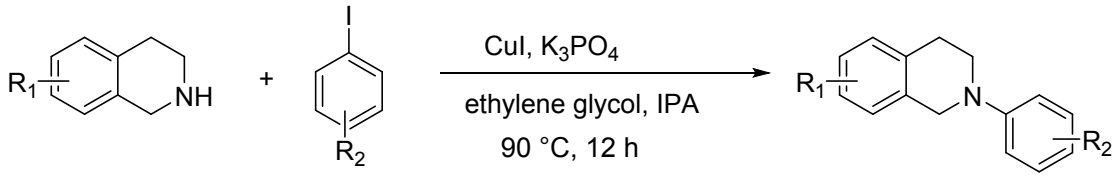
1. General Information

Starting materials were purchased from commercial suppliers (Adamas-beta, Aladdin, TCI, J&K, bidepharm etc.) and used as supplied unless otherwise stated. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. All reactions were performed under argon atmosphere using Schlenk techniques. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Ascend 500 MHz (^{13}C NMR at 125 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (TMS, δ 0.0 ppm) or chloroform (δ = 7.260, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). GC-MS was obtained using electron ionization (TRACE 1310 Mainframe MS). The reaction was monitored by TLC（GF-254） under UV light or treated with aqueous phosphomolybdic acid or $KMnO_4$ followed by heating. Blue (450 nm) and purple (400 nm) LED was purchased from CREE.

2. Preparation of Substrates



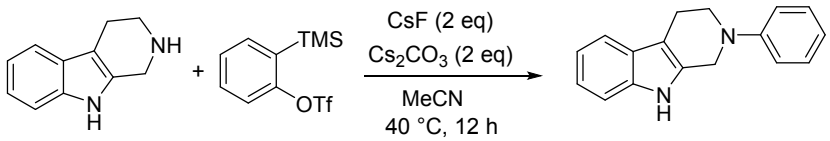
2.1 Procedure for the Preparation of *N*-aryl 1,2,3,4-tetrahydroisoquinoline (1a-1g) [S1]



The substrates **1a**-**1g** were synthesized according to literature procedures. A typical procedure is described as following for the synthesis of **1a**: To a two-neck round bottom flask, 400 mg cuprous iodide and 8.5 g anhydrous

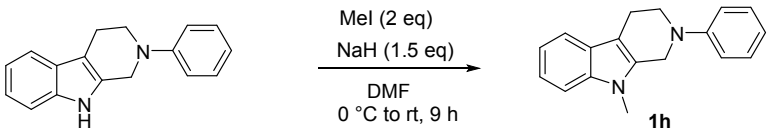
potassium phosphate was added. The flask was then connected with a condenser tube and the system was put into vacuum and recharged with argon. A nitrogen balloon was added to keep the system under inert atmosphere. 20 mL 2-propanol, 2.2 mL ethylene glycol, 4 mL 1,2,3,4-tetrahydroisoquinoline, and 2.6 mL iodine benzene was added into the flask via syringe. The mixture was refluxed for 24 h under 85℃ and then left to cool to room temperature to pass a celite pad. The filtrate was mixed with 20 mL water and then extracted with ethyl acetate. The organic phase was collected and dried over sodium sulphate. The solvent was removed via rotary evaporation, and the remaining residue was purified by flash column chromatography on silica gel (petroleum ether/DCM (100:1~100:10)) to afford the target compound. Compounds **1b**-**1g** were also synthesized according to the similar method.

2.2 Procedure for the preparation of 9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b] indole (1h)[S2]



***N*-phenyltetrahydro-β-carboline**

To a stirred solution of tetrahydro-β-carboline (1.00 g, 5.81 mmol) in MeCN (29 mL) were added silyl triflate (2.25 g, 7.55 mmol), Cs_2CO_3 (3.79 g, 11.6 mmol), and CsF (1.41 g, 9.29 mmol) at room temperature. The reaction mixture was stirred at 40 ºC for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was poured into H_2O, and the resulting mixture was extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (toluene-EtOAc = 100:0 to 95:5, gradient) to afford 567 mg (39%) of *N*-phenyltetrahydro-β-carboline as a pale yellow solid.

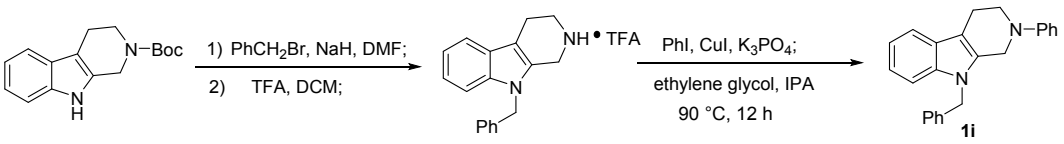


9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b] indole (1h)

To a stirred solution of *N*-phenyltetrahydro-β-carboline (300 mg, 1.21 mmol) in DMF (4 mL) were added MeI (90.0 μL, 1.45 mmol), NaH (72.5 mg, 1.81 mmol, 60 % dispersion in mineral oil) at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred for 9 h. The reaction mixture was poured into saturated aqueous NH_4Cl, and the resulting mixture was extracted with EtOAc three times. The combined

organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (toluene-hexanes = 9:1) to afford **1h** (268 mg, 1.02 mmol, 85%) as a pale yellow solid.

2.3 Procedure for the preparation of 9-Benzyl-2-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (1i)[S3]



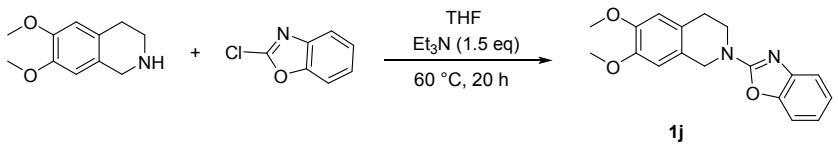
9-Benzyl-1,2,3,4-tetrahydro-β-carboline trifluoroacetic acid salt

In a flamed flask NaH (60%, 1.18 g, 29.5 mmol) was suspended in dried DMF (15mL). 2-Boc-1,2,3,4-tetrahydro-β-carboline (4.0 g, 14.7 mmol) was added at 0 °C portion-wise and the mixture was stirred at 0 °C for 30 min before the corresponding benzyl bromide (22.1 mmol) was introduced slowly. The reaction was warmed to rt and stirred overnight. The mixture was diluted with DCM (50 mL) and then washed with water (3 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4. After filtration and solvent evaporation, the crude product was dissolved into DCM (50 mL) and TFA (30 mL) and stirred at rt till complete conversion. The solvents was mostly removed in vacuo before water (50 mL) was added. The solid was filtered out and dried to give the title compound as yellow solid, which could be further purified by recrystallization from ethanol and water.

9-Benzyl-2-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (1i)

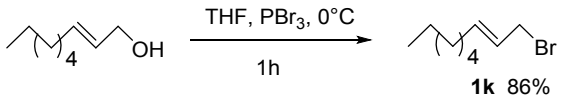
9-Benzyl-1,2,3,4-tetrahydro-β-carboline trifluoroacetic acid salt (195.2 mg, 0.5 mmol), iodobenzene (1.0 mmol), CuI (20 mg, 0.1 mmol) and anhydrous K_3PO_4 (638 mg, 3.0 mmol) were added into a mixed solvent of ethylene glycol (1.0 mL) and isopropyl alcohol (2.0 mL) in a dried schlenk tube. The mixture was stirred at 90 °C under the protection of N_2 for 12 h. Then water (10 mL) was added and the aqueous suspension was extracted with DCM (3 x 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and the product was purified by flash silica chromatography (petroleum ether /AcOEt, from 20 :1 to 5:1).

2.4 Procedure for the preparation of 2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)benzo[d]oxazole (1j)[S4]



To a mixture of 2-chlorobenzoxazole (350 mg, 3.6 mmol) in dry THF (15 mL) was added 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (16: 1.03 g, 5.3 mmol, 1.5 equiv) and Et_3N (0.69 g, 5.3 mmol, 1.5 equiv) under an argon atmosphere. The reaction mixture was stirred for 20 h at 60 °C . Then the mixture was cooled to room temperature and quenched by the addition of water (30 mL). The mixture was extracted with DCM (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether /AcOEt = 2/1) to afforded the title compound (1.10 g, 96%) as a pale yellow solid.

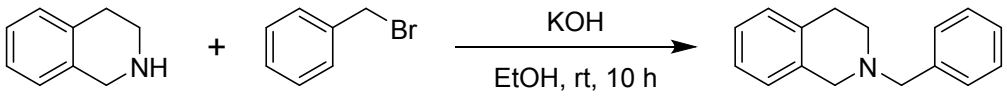
2.5 Procedure for the preparation of (E)-1-bromonon-2-ene (1k)[S5]



1k 86%

To a stirred solution of (*E*)-Non-2-en-1-ol (284 mg, 2.0 mmol, 1.0 equiv) in THF (20 mL) at 0 ˚C, PBr_3 (0.2 mL, 2.4 mmol, 1.2 equiv) was added dropwise. The reaction was stirred for 1 h at 0 ˚C, and quenched by the addition of saturated $NaHCO_3$ solution. The reaction mixture was allowed to warm to room temperature. The residue was then extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$.The residue was purified by flash column chromatography (petroleum ether) to afforded the title compound **1k** (350 mg, 86%) as a colorless oil.

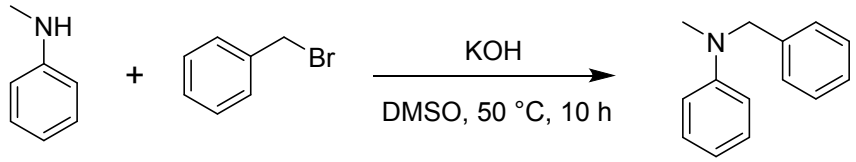
2.6 Procedure for the preparation of 2- benzyl-1,2,3,4-tetrahydroisoquinoline (1l)[S6]



1l

Based on a literature procedure, the solution of 1,2,3,4-tetrahydroisoquinoline (625 µL, 5.0 mmol, 1.0 equiv.) and benzyl bromide (595 µL, 5.0 mmol, 1.0 equiv.) in EtOH (10 mL) was added KOH (308 mg, 5.5 mmol, 1.1 equiv.). The mixture was stirred at room temperature for 24 hours, after which the solvent was removed in vacuo. The residue was partitioned between EtOAc and H_2O and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated to afford crude title compound. Flash column chromatography (n-hexane/EtOAc/Et_3N 95:4:1) afforded 2- benzyl-1,2,3,4-tetrahydroisoquinoline (1l).

2.7 Procedure for the preparation of N-benzyl-N-methylaniline (1m)[S7]

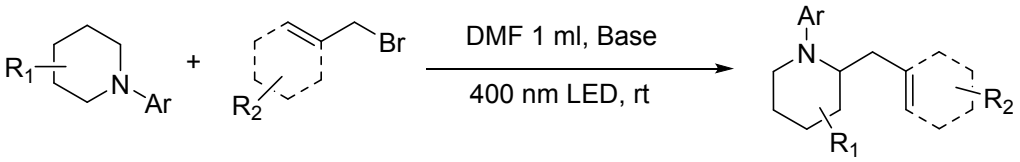


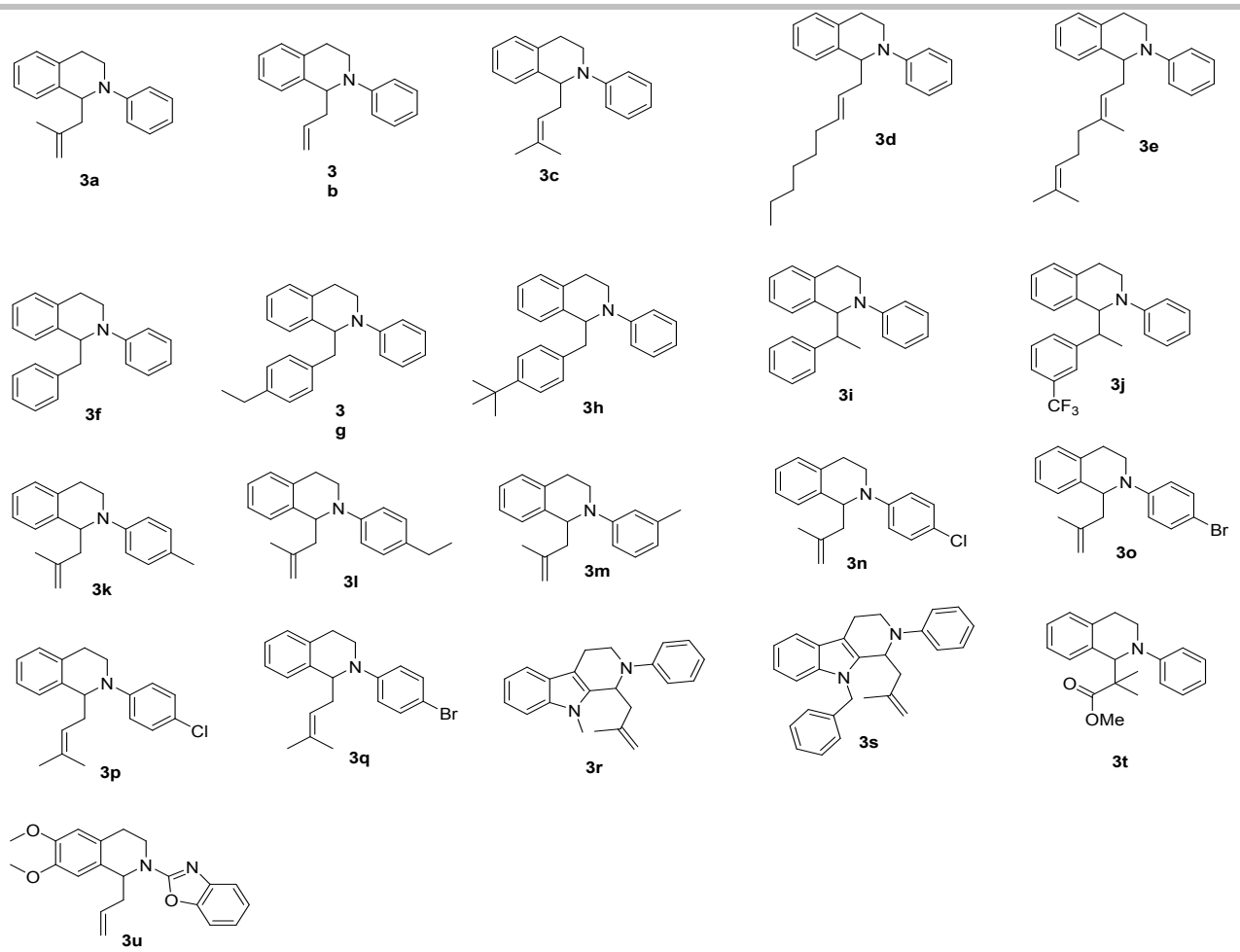
1m

A 50 mL flask equipped with a stir-bar was charged with N-methylaniline (5 mmol) and KOH (10.0 mmol). 20 mL of DMSO was added to the flask and the solution was stirred under room temperature. Followed alkyl bromides (2.0 equiv) was added. The reaction mixture was stirred at 50 °C and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and extracted by ethyl acetate (3×30 mL). Organic phase were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane) to afford the title compound **1m**.

3. General Procedure and Spectral Data of Products

3.1 General Procedure for α-Allylation of *N*-Aryl Tetrahydroisoquinolines





3.1.1 General Procedure A:

The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with 2-aryl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1.0 equiv.) and Cs_2CO_3 (0.40 mmol, 2.0 equiv.) was added followed by anhydrous *N*,*N*-dimethylformamide (1 mL) and alkyl bromide (0.6 mmol, 3 equiv) under nitrogen. The resulting mixture was degassed by using a "freeze–pump–thaw" procedure for 3 times. Afterwards, the solution was placed at a distance of 1 cm from a 3 W or 10 W purple (400 nm) LED and stirred at room temperature for the appropriate time. After the starting material has disappeared monitor by TLC, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel to give the desired product

3.1.2 General Procedure B:

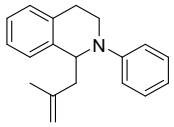
The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with 2-aryl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1.0 equiv.) and Cs_2CO_3 (0.40 mmol, 2.0 equiv.) was added followed by anhydrous *N*,*N*-dimethylformamide (1 mL) and alkyl bromide (0.7 mmol, 3.5 equiv.) under nitrogen. The resulting mixture was degassed by using a "freeze–pump–thaw" procedure for 3 times. Afterwards, the solution was placed at a distance of 1 cm from a 10 W purple (400 nm) LED and stirred at room temperature for the

appropriate time. After the starting material has disappeared monitor by TLC, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel to give the desired product

3.1.3 General Procedure C:

The oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with 2-aryl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1.0 equiv.), alkyl bromide (0.7 mmol, 3.5 equiv.), anhydrous *N*,*N*-dimethylformamide (1 mL) and 2,4,6-collidine (0.40 mmol, 2.0 equiv.) was added via syringe under nitrogen. The resulting mixture was degassed by using a "freeze–pump–thaw" procedure for 3 times. Afterwards, the solution was placed at a distance of 1 cm from a 3 W purple (400 nm) LED and stirred at room temperature for the appropriate time. After the starting material has disappeared monitor by TLC, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel to give the desired product

3.2 Spectral Data of Products



3a

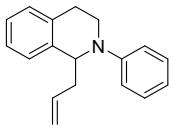
1-(2-methylallyl) -2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a): known compound[S8]

Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 43.6 mg (83% yield) of the title compound **3a**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14–7.11 (m, 2H), 7.06–6.97 (m, 4H), 6.81–6.79 (m, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 4.75 (t, *J* = 7.2 Hz, 1H), 4.71–4.67 (m, 1H), 4.58–4.53 (m, 1H), 3.52 (dd, *J* = 7.0, 5.5 Hz, 2H), 2.94–2.88 (m, 1H), 2.73 (dt, *J* = 16.0, 5.0 Hz, 1H), 2.59 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.29 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.68 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 143.0, 138.6, 134.9, 129.3, 128.7, 127.6, 125.6, 125.7, 117.5, 114.4, 113.6, 58.3, 44.7, 41.8, 27.1, 23.1.



3b

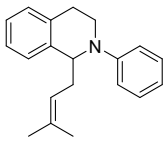
1-allyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3b): known compound[S8]

Following General Procedure C, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 33.9 mg (68% yield) of the title compound **3b**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21–7.12 (m, 2H), 7.08–7.02 (m, 3H), 7.00–6.97 (m, 1H), 6.64–6.61 (m, 2H), 5.10–5.06 (m, 1H), 4.49 (t, *J* = 7.5 Hz, 1H), 3.52–3.47 (m, 1H), 3.41–3.36 (m, 1H), 2.93–2.87 (m, 1H), 2.84–2.79 (m, 1H), 2.51–2.45 (m, 1H), 2.35–2.29 (m, 1H), 1.56 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.5, 138.1, 134.7, 134.0, 131.8, 128.3, 127.3, 125.6, 125.8, 120.8, 115.1, 108.7, 59.6, 42.4, 34.97, 27.5, 25.9, 17.8.



3c

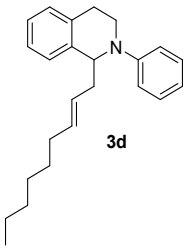
1-(3-methylbut-2-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3c): known compound[S11]

Following General Procedure C, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 42.1 mg (76% yield) of the title compound **3c**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.25 (m, 2H), 7.25 – 7.10 (m, 4H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 5.41 – 5.19 (m, 1H), 4.72 (t, *J* = 7 Hz, 1H), 3.72–3.68(m, 1H), 3.63–3.59(m, 1H), 3.14 – 3.02 (m, 1H), 2.99–2.94 (m, 1H), 2.68 (dt, *J* = 14.5, 6.5 Hz, 1H), 2.49 (dt, *J* = 14.5, 7.5 Hz, 1H), 1.73 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 138.5, 134.9, 133.8, 129.2, 128.3, 127.4, 125.4, 125.7, 121.1, 117.0, 113.7, 59.6, 42.1, 35.1, 27.6, 25.9, 17.8.



3d

(*E*)-1-(non-2-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3d)

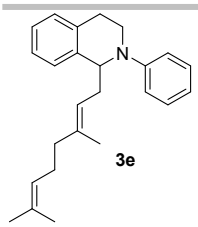
Following General Procedure C, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 28.2 mg (42% yield) of the title compound **3d**.

Physical State: light yellow solid

^{1}H NMR (500 MHz, $CDCl_3$) :δ 7.19 – 7.15 (m, 2H), 7.09–7.01 (m, 2H), 6.82–6.80 (m, 1H), 5.48 – 5.21 (m, 2H), 4.62 (q, *J* = 6.8 Hz, 1H), 3.56–3.52 (m, 1H), 3.52 – 3.47 (m, 1H), 2.99–2.92 (m, 1H), 2.87–2.79 (m, 1H), 2.63–2.56 (m, 1H), 2.45 – 2.30 (m, 1H), 1.98–1.73 (m, 2H), 1.97–1.71 (m, 2H), 1.25–1.10(m, 9H), 0.80 (td, *J* = 7.0, 4.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.44, 137.3, 133.93, 132.32, 131.17, 128.17, 127.33, 125.41, 125.45, 124.57, 116.04, 112.62, 58.80, 58.38, 38.66, 33.12, 31.60, 30.73, 28.34, 27.82, 21.60, 13.10.

HRMS: calcd for $C_{24}H_{31}N$ $[M+H]^+$: 334.2529, found: 334.2542.



3e

(*E*)-1-(3,7-dimethylocta-2,6-dien-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e)

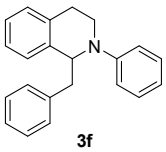
Following General Procedure B, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 59.5 mg (86% yield) of the title compound **3e**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 – 7.14 (m, 2H), 7.09 – 7.01 (m, 4H), 6.80 (d, *J* = 8. 5 Hz, 2H), 6.64 (t, *J* = 7.0 Hz, 1H), 5.18–5.15 (m, 1H), 5.03–4.96 (m, 1H), 4.61–4.54 (m, 1H), 3.58–3.42 (m, 1H), 3.49–3.42 (m, 1H), 2.98–2.91 (m, 1H), 2.87–2.77 (m, 1H), 2.55 (dt, *J* = 13.5, 6.5 Hz, 1H), 2.37 (dt, *J* = 22. 0, 8.0 Hz, 1H), 1.98 – 1.77 (m, 4H), 1.62 – 1.48 (m, 7H), 1.38–1.32 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 138.5, 137.3, 135.0, 131.4, 129.2, 128.3, 127.4,125.4, 125.6, 124.4, 120.9, 116.9, 113.6, 59.6, 42.0, 39.9, 34.9, 2.8, 26.6, 25.8, 17.7, 16.1.

HRMS: calcd for $C_{25}H_{31}N$ $[M+H]^+$: 346.2529, found: 346.2536



3f

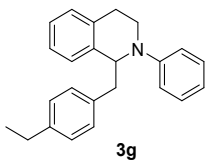
1-benzyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f): known compound[S9]

Following General Procedure A, Purification by preparative thin layer chromatography (petroleum ether/DCM (100:1~100:5)) afforded 21.6 mg (36% yield) of the title compound **3f**.

Physical State:light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.16 (m, 5H), 7.14 – 7.09 (m, 2H), 7.05 – 6.99 (m, 3H), 6.85 –6.83 (m, 2H), 6.74 – 6.71 (m, 2H), 4.89 (t, *J* = 6.5 Hz, 1H), 3.66 – 3.61 (m, 1H), 3.56 – 3.51 (m, 1H), 3.25 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.01 – 2.95 (m, 2H), 2.74 (dt, *J* = 16, 6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 138.8, 137.6, 135.1, 129.8, 129.2, 128., 128.2, 127.7, 125.6, 125.3, 125.5, 117.2, 113.7, 61.5, 42.4, 42.2, 27.5.



3g

1-(4-ethylbenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3g)

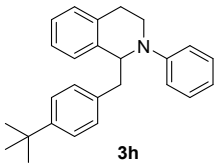
Following General Procedure A, Purification by preparative thin layer chromatography (petroleum ether/DCM (100:1~100:5)) afforded 30.6 mg (46% yield) of the title compound **3g**.

Physical State:light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.13 (m, 2H), 7.10–7.01 (m, 2H), 6.98–6.95 (t, *J* = 6.5 Hz, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.90–6.62 (d, *J* = 8.2 Hz, 2H), 6.71 – 6.59 (m, 2H), 4.80 (t, *J* = 6.5 Hz, 1H), 3.59 –3.54(m, 1H), 3.47 (m, 1H), 3.14 (dd, *J* = 13.5, 5.8 Hz, 1H), 2.94–2.87 (m, 2H), 2.67 (dt, *J* = 15.9, 5.8 Hz, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 142.2, 137.8, 136.0, 135.1, 129.7, 129.2, 128.2, 127.7, 127.6, 125.6, 125.5, 117.12, 113.7, 61.5, 42.1, 42.1, 28.5, 27.5, 15.7, 1.1.

HRMS: calcd for $C_{24}H_{25}N$ $[M+H]^+$: 328.2060, found: 328.2047.



3h

1-(4-(tert-butyl)benzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3h)

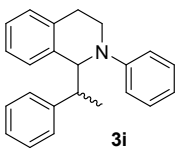
Following General Procedure A, Purification by preparative thin layer chromatography (petroleum ether/DCM (100:1~100:5)) afforded 37.2 mg (52% yield) of the title compound **3h**.

Physical State:light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 4H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 6.5 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 20.5, 7.7 Hz, 3H), 6.76 (t, *J* = 7.1 Hz, 1H), 4.92 (t, *J* = 6.5 Hz, 1H), 3.71 (ddd, *J* = 12.5, 7.9, 5.0 Hz, 1H), 3.61 (dt, *J* = 12.0, 5.8 Hz, 1H), 3.28 (dd, *J* = 13.3, 5.7 Hz, 1H), 3.12 – 2.92 (m, 2H), 2.81 (dd, *J* = 10.4, 5.4 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 149.2, 137.9, 135.8, 135.1, 129.4, 129.2, 128.3, 127.7, 125.6, 125.5, 125.1, 117.2, 113.8, 61.6, 42.1, 34.4, 31.4, 29.7, 27.4.

HRMS: calcd for $C_{24}H_{25}N$ $[M+H]^+$: 356.2372, found: 356.2365.



3i

2-phenyl-1-(1-phenylethyl)-1,2,3,4-tetrahydroisoquinoline (3i): known compound[S10]

Following General Procedure A, Purification by preparative thin layer chromatography (petroleum ether/DCM (100:1~100:5)) afforded 54.0 mg (86% yield) of the title compound **3i**.

3i (a) Physical State: light yellow oil

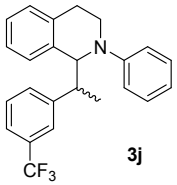
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.22 (m, 2H), 7.22–7.12 (m, 3H), 7.12–7.08 (m, 1H), 6.99 –6.94 (m, 2H), 6.92–6.90 (m, 2H), 6.86–6.84 (m, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.61–6.59 (m, 1H), 4.78 (d, *J* = 6.8 Hz, 1H), 3.62–3.58 (m, 1H), 3.41 – 3.20 (m, 2H), 2.65 (dt, *J* = 15, 5 Hz, 1H), 2.4-1.98 (m, 1H), 1.43 (d, *J* = 7 Hz, 3H).

^{13}C NMR (125 MHz,$CDCl_3$): δ 149.5, 143.6, 135.8, 135.9, 129.3, 128.8, 128.3, 127.9, 127.7, 125.7, 125.5, 124.9, 116.6, 112.7, 64.9, 45.6, 43.1, 27.1, 18.6.

3i (b) Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21–7.03 (m, 10H), 6.88–6.86 (m, 1H), 6.77–6.76 (m, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 7 Hz, 1H), 3.56–3.51 (m, 1H), 3.33–3.42 (m, 2H), 2.96–2.84 (m, 2H), 1.28 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.9, 144.2, 136.7, 135.5, 129.0, 128.7, 128.4, 127.99, 125.7, 125.3, 125.1, 117.1, 114.0, 64.9, 44.9, 42.8, 27.1, 18.4.



3j

2-phenyl-1-(1-(3-(trifluoromethyl)phenyl)ethyl)-1,2,3,4-tetrahydroisoquinoline (3j)

Following General Procedure A, Purification by preparative thin layer chromatography (petroleum ether/DCM (100:1~100:5)) afforded 54.1 mg (71% yield) of the title compound **3j**.

3j (a) Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.41 (m, 1H), 7.32–7.23 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.00 (dt, *J* = 15.0, 7.5 Hz, 3H), 6.95 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 3.59 (dt, *J* = 11.0, 5.5 Hz, 1H), 3.49–3.44 (m, 1H), 3.28–3.22 (m, 1H), 2.61 (dt, *J* = 16.0, 5.0 Hz, 1H), 1.84 (ddd, *J* = 16.0, 9.5, 6.0 Hz, 1H), 1.46 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 144.4, 135.2, 134.9, 132.3, 130.2, 129.9, 129.4, 127.9, 127.0, 125.6,125.2, 123.3, 116.9, 112.9, 65.0, 45.5, 43.3, 27.2, 18.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.59.

HRMS: calc'd for $C_{24}H_{22}NF_3$ $[M+H]^+$: 382.1777, found: 382.1771.

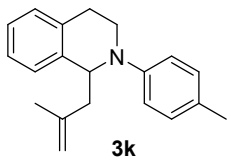
3j (b) Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.38 (m, 2H), 7.35 – 7.27 (m, 2H), 7.21 – 7.17 (m, 1H), 7.14 – 7.10 (m, 4H), 6.97 – 6.96 (m, 1H), 6.73 – 6.72 (m, 2H), 6.65 (t, *J* = 7.5, 1H), 4.84 (d, *J* = 7.5 Hz, 1H), 3.56–3.51 (m, 1H), 3.46–3.36 (m, 2H), 3.01–2.88 (m, 2H), 1.55 (s, 2H), 1.34 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 144.4, 135.9, 134.9, 132.3, 130.2, 129.9, 129.4, 127.9, 127.0, 125.6, 125.2, 123.3, 116.9, 112.9, 65.0, 45.5, 43.3, 27.2, 18.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.59.

HRMS: calcd for $C_{24}H_{22}NF_3$ $[M+H]^+$: 382.1777, found: 382.1776.



3k

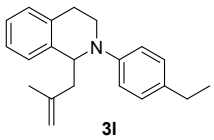
1-(2-methylallyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (3k): known compound[S8]

Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 44.8 mg (81% yield) of the title compound **3k**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17–7.13 (m, 2H), 7.13 – 7.08 (m, 2H), 7.12–7.02 (m, 2H), 7.07–7.05 (m, 2H), 6.86–6.84(m, 2H), 4.83 – 4.80 (m, 2H), 4.69 (s, 1H), 3.65 – 3.59 (m, 2H), 3.02–2.99 (m, 1H), 2.80 (dt, *J* = 16.1, 4.6 Hz, 1H), 2.69 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.42 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.26 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.6, 143.1, 138.6, 134.7, 129.7, 128.7, 127.5, 125.9, 125.4, 125.5, 115.0, 113.3, 58.3, 44.6, 26.7, 22.9, 20.3.



3l

2-(4-ethylphenyl)-1-(2-methylallyl)-1,2,3,4-tetrahydroisoquinoline (3l)

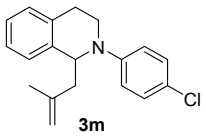
Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 45.0 mg (77% yield) of the title compound **3l**.

Physical State: light yellow solid

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17–7.08 (m, 6H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.84 – 4.81 (m, 2H), 4.68 (s, 1H), 3.64–3.62 (m, 2H), 3.06–3.0 (m, 1H), 2.81 (dt, *J* = 16.1, 4.6 Hz, 1H), 2.69 (dd, *J* = 14 Hz, 1H), 2.57 (dd, *J* = 15 Hz, 2H), 2.41 (dd, *J* = 13.5 Hz, 1H), 1.80 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.7, 143.1, 138.7, 134.8, 133.4, 128.6, 127.5, 125.4, 125.5, 113.3, 58.4, 44.7, 27.8, 26.8, 22.9, 15.9.

HRMS: calcd for $C_{21}H_{25}N$ $[M+H]^+$: 292.2060, found: 292.2057.



3m

2-(4-chlorophenyl)-1-(2-methylallyl)-1,2,3,4-tetrahydroisoquinoline (3m)

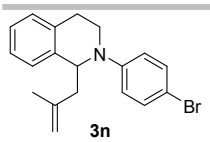
Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 28.6 mg (48% yield) of the title compound **3m**.

Physical State:light yellow solid

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19–7.13 (m, 5H), 7.10–7.08 (m, 1H), 6.83 – 6.73 (m, 2H), 5.21–5.18 (m, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.64–3.59 (m, 1H), 3.53–3.49 (m, 1H), 3.01–2.99 (m, 1H), 2.92 (dt, *J* = 15.9, 5.7 Hz, 1H), 2.56–2.52 (m, 1H), 2.46–2.40 (m, 1H), 1.67 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 138.2, 134.7, 133.9, 128.9, 128.3, 127.3, 125.6, 125.8, 121.6, 120.8, 114.7, 59.64, 42.2, 34.9, 27.5, 25.8, 17.8.

HRMS: calcd for $C_{19}H_{20}NCl$ $[M+H]^+$: 298.1357, found: 298.1349.



3n

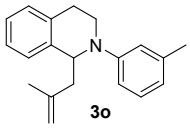
2-(4-bromophenyl)-1-(2-methylallyl)-1,2,3,4-tetrahydroisoquinoline (3n): known compound[S8]

Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 51.3 mg (75% yield) of the title compound **3n**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.16 (m, 2H), 7.07–6.93 (m, 4H), 6.67–6.65 (m, 2H), 4.72–4.69 (m, 1H), 4.68 (t, *J* = 7.2 Hz, 1H), 4.56 (s, 1H), 3.53–3.43 (m, 2H), 2.92–2.85 (m, 1H), 2.74 (dt, *J* = 16.0, 5.0 Hz, 1H), 2.55 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.29 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.66 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.5, 141.6, 137.0, 133.4, 130.8, 127.5, 125.3, 125.6, 124.7, 114.7, 112.7, 108.1, 57.2, 40.8, 25.8, 21.9.



3o

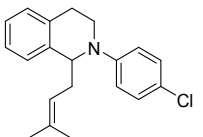
1-(2-methylallyl)-2-(*m*-tolyl)-1,2,3,4-tetrahydroisoquinoline (3o): known compound[S12]

Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 47.6 mg (86% yield) of the title compound **3o**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17–7.08 (m, 6H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.84 – 4.81 (m, 2H), 4.68 (s, 1H), 3.64–3.62 (m, 2H), 3.06–3.0 (m, 1H), 2.81 (dt, *J* = 16.1, 4.6 Hz, 1H), 2.69 (dd, *J* = 14 Hz, 1H), 2.57 (dd, *J* = 15 Hz, 2H), 2.41 (dd, *J* = 13.5 Hz, 1H), 1.80 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.7, 143.1, 138.7, 134.8, 133.4, 128.6, 127.5, 125.4, 125.5, 113.3, 58.4, 44.7, 27.8, 26.8, 22.9, 15.9.



3p

2-(4-chlorophenyl)-1-(3-methylbut-2-en-1-yl)-1,2,3,4-tetrahydroisoquinoline (3p)

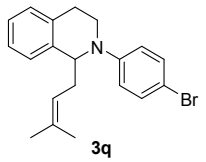
Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 25.6 mg (41% yield) of the title compound **3p**.

Physical State:light yellow solid

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19–7.13 (m, 5H), 7.10–7.08 (m, 1H), 6.83 – 6.73 (m, 2H), 5.21–5.18 (m, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.64–3.59 (m, 1H), 3.53–3.49 (m, 1H), 3.01–2.99 (m, 1H), 2.92 (dt, *J* = 15.9, 5.7 Hz, 1H), 2.56–2.52 (m, 1H), 2.46–2.40 (m, 1H), 1.67 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 138.2, 134.7, 133.9, 128.9, 128.3, 127.3, 125.6, 125.8, 121.6, 120.8, 114.7, 59.64, 42.2, 34.9, 27.5, 25.8, 17.8.

HRMS: calcd for $C_{20}H_{22}NCl$ $[M+H]^+$: 312.1514, found: 312.1509.



3q

2-(4-bromophenyl)-1-(3-methylbut-2-en-1-yl)-1,2,3,4-tetrahydroisoquinoline (3q)

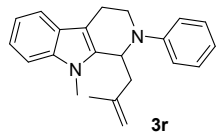
Following General Procedure B, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:5)) afforded 50.4 mg (71% yield) of the title compound **3q**.

Physical State:light yellow solid

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.14 (m, 5H), 7.11–7.09 (m, 1H), 6.81–6.78 (m, 2H), 5.21 – 5.18 (m, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.64–3.59 (m, 1H), 3.54–3.49 (m, 1H), 3.05–3.00 (m, 1H), 2.92 (dt, *J* = 15.9, 5.7 Hz, 1H), 2.62–2.57 (m, 1H), 2.46–2.40 (m, 1H), 1.68 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 138.2, 134.7, 134.0, 128.9 128.3, 127.3, 125.6, 125.8, 121.6, 120.8, 114.7, 59.7, 42.2, 34.9, 27.5, 17.8.

HRMS: calcd for $C_{20}H_{22}NBr$ $[M+H]^+$: 356.1008, found: 356.0994.



3r

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

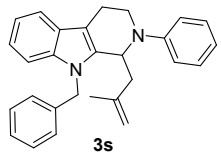
Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:10)) afforded 19.6 mg (31% yield) of the title compound **3r**.

Physical State:light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 3H), 7.07 (t, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 4.88 (d, *J* = 10.0 Hz, 3H), 3.94 (dd, *J* = 14.4, 5.5 Hz, 1H), 3.72 – 3.66 (m, 4H), 2.97 (ddd, *J* = 15.4, 11.9, 5.6 Hz, 1H), 2.71 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.63 (dd, *J* = 15.4, 4.4 Hz, 1H), 2.51 (dd, *J* = 14.5, 3.5 Hz, 1H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6, 143.2, 129.1, 125.9, 121.3, 119.0, 118.1, 116.8, 113.3, 108.8, 108.0, 54.7, 42.4, 41.2, 29.9, 23.0, 19.0.

HRMS: calcd for $C_{22}H_{24}N_2$ $[M+H]^+$: 317.2012, found: 317.2012.



3s

9-benzyl-1-(2-methylallyl)-2-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3s)

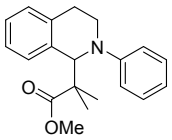
Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/DCM (100:1~100:10)) afforded 40.8 mg (52% yield) of the title compound **3s**.

Physical State: light yellow oil

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.44 (m, 1H), 7.31–7.27 (m, 3H), 7.25–7.22 (m, 1H), 7.17 – 6.96 (m, 6H), 6.70–6.62 (m, 3H), 5.51–5.43 (m, 1H), 5.28–5.21 (m, 1H), 4.81 – 4.75 (m, 3), 3.97 (dd, *J* = 14.5, 5.6 Hz, 1H), 3.72 – 3.66 (m, 1H), 2.99–2.92 (m, 1H), 2.72 – 2.62 (m, 2H), 2.44 (dd, *J* = 14.7, 3.2 Hz, 1H), 1.76 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 143.1, 137.6, 137.1, 128.9, 127.5, 127.1, 125.3, 121.6, 119.3, 118.7, 118.2, 116.6, 112.8, 109.4, 109.0, 53.5, 46.9, 42.6, 41.1, 22.7, 18.9.

HRMS: calcd for $C_{28}H_{28}N_2$ $[M+H]^+$: 393.2325, found: 393.2321.



3t

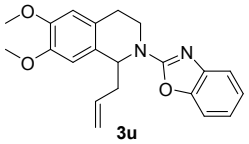
methyl 2-methyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanoate (3t)

Following General Procedure A, Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate (100:1~100:5)) afforded 37.1 mg (60 % yield) of the title compound **3t**.

1H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.09 (m, 5H), 7.07–7.06 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 7.0 Hz, 1H), 5.25 (s, 1H), 3.85–3.79 (m, 1H), 3.68–3.63 (m, 1H), 3.58 (s, 3H), 3.03–2.97 (m, 1H), 2.84 (dt, J = 16.5, 5.0 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H).

13C NMR (125 MHz, $CDCl_3$): δ 177.74, 150.94, 135.51, 135.35, 129.08, 128.94, 127.45, 126.94, 125.57, 118.22, 115.87, 64.15, 51.83, 50.25, 43.39, 26.23, 24.86, 24.00.

HRMS: calcd for $C_{20}H_{23}NO_2$ $[M+H]^+$ **:** 310.1801, found: 310.1802.



3u

2-(1-allyl-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)benzo[d]oxazole (3u): known compound[S11]

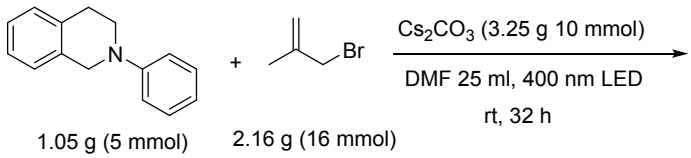
Following General Procedure C, Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate (100:5~100:20)) afforded 40.6 mg (58 % yield) of the title compound **3u**.

Physical State: light yellow oil

^{1}H NMR (500 MHz,$CDCl_3$): δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.17–7.14 (m, 1H), 7.02–6.98 (m, 1H), 6.65 (d, *J* = 25.2 Hz, 2H), 5.89 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.34 (t, *J* = 6.8 Hz, 1H), 5.03 – 5.01 (m, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 4.33–4.29 (m, 1H), 3.86 (d, *J* = 5.3 Hz, 6H), 3.69–3.64 (m, 1H), 3.07–3.0 (m, 1H), 2.78 (dt, *J* = 16.1, 3.9 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1, 148.6, 147.9, 147.5, 143.3, 134.3, 128.1, 125.7, 123.9, 120.3, 117.9, 116.1, 111.5, 109.9, 108.6, 56.0, 55.9, 55.9, 41.1, 39.8, 27.5.

4. Gram Scale Reaction



1.05 g (5 mmol) 2.16 g (16 mmol) 0.89 g (68 % yield)

The oven-dried Schlenk tube (50 mL) containing a stirring bar was charged with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (1.05 g, 5 mmol) and Cs_2CO_3 (3.25 g, 10 mmol) was added followed by anhydrous *N*,*N*-dimethylformamide (25 mL) and 3-bromo-2-methylprop-1-ene (2.16 g, 16 mmol) under nitrogen. The resulting mixture was degassed by using a ‘‘freeze–pump–thaw’’ procedure for 3 times. Afterwards, the solution was stirred at a distance of 2 cm from a 24 W(3 W * 8) purple (400 nm) LED and stirred at room temperature for 32 h. After the starting material has disappeared monitor by TLC, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel to give the desired product

5. Mechanistic studies

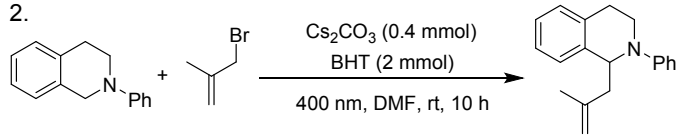
a) Control experiments

1.

1a (0.2 mmol) **2a** (0.6 mmol) **3a** n.d. **5**

HRMS: $(M+H^+)$
Calcd: 212.2009
Found: 212.2008

2.

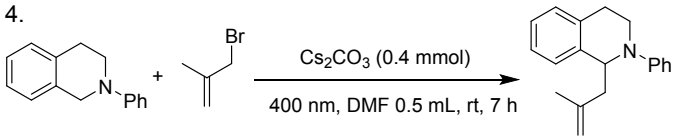


1a (0.2 mmol) **2a** (0.6 mmol) Trace

3.

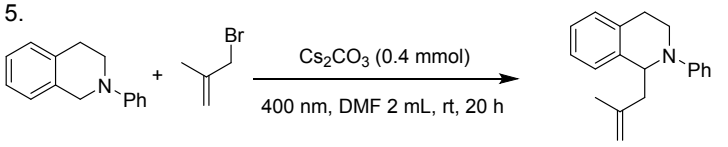
0.2 mmol 0.6 mmol Trace

4.



1a (0.2 mmol) **2a** (0.6 mmol) 72 %

5.



1a (0.2 mmol) **2a** (0.6 mmol) 60 % (62 % brsm)

The fact that the pyridinium salt replace the allyl bromide affording trace yield, which means that the pyridine acts only as a base in the reaction system.[S13]

We added this experiment and found that concentration has an effect on both reaction rate and yield. When reaction solution was reduced to 0.5 mL, the time was shortened to 7h affording 72% yield. When the reaction solution was raised to 2 ml, even if the reaction time was increased to 20 hours, N-phenyl-1,2,3,4-tetrahydroisoquinoline couldn't be completely converted.

b) Spectroscopic studies

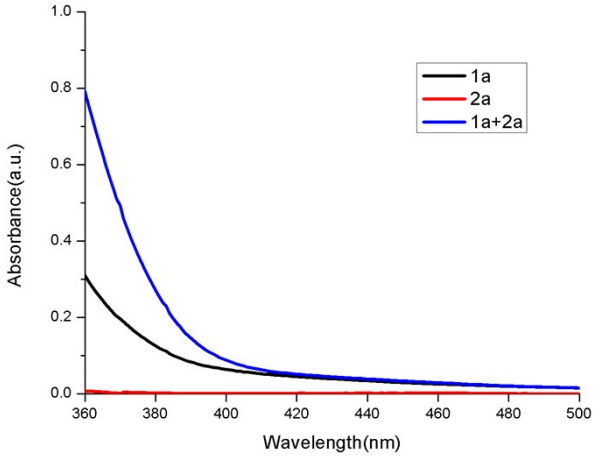


Figure 1.UV-Vis absorption spectra

c) Light/dark cycle experiments for the model reaction[S14]

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started a reaction with successive irradiation and black periods. We determined the GC yields directly from the crude mixture using n-dodecane as internal standard. These results demonstrated that light is necessary.

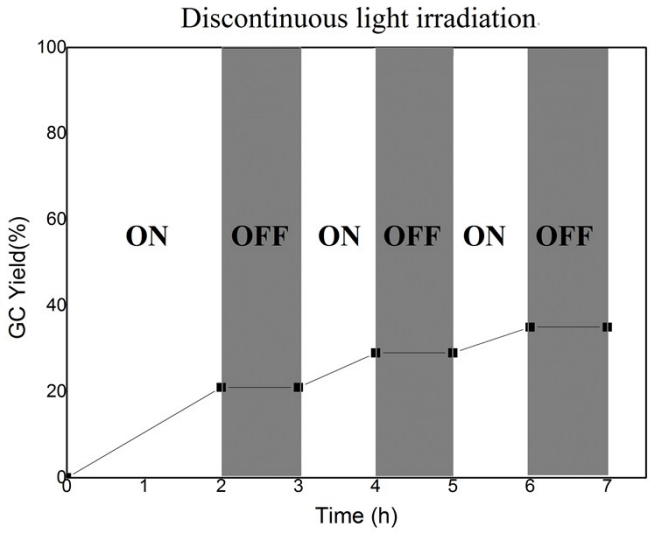


Figure S2. Each point of the graphic represents the GC yield, calculated from the relative amounts of an internal standard (n-dodecane). The grey boxes represent the periods in which the reaction vessels were covered (dark period). The reaction was done with: 0.2 mmol of **1a**, 0.6 mmol of 2a, 0.4 mmol of Cs_2CO_3 in 1 mL of DMF at 10W 400 nm.

6. References

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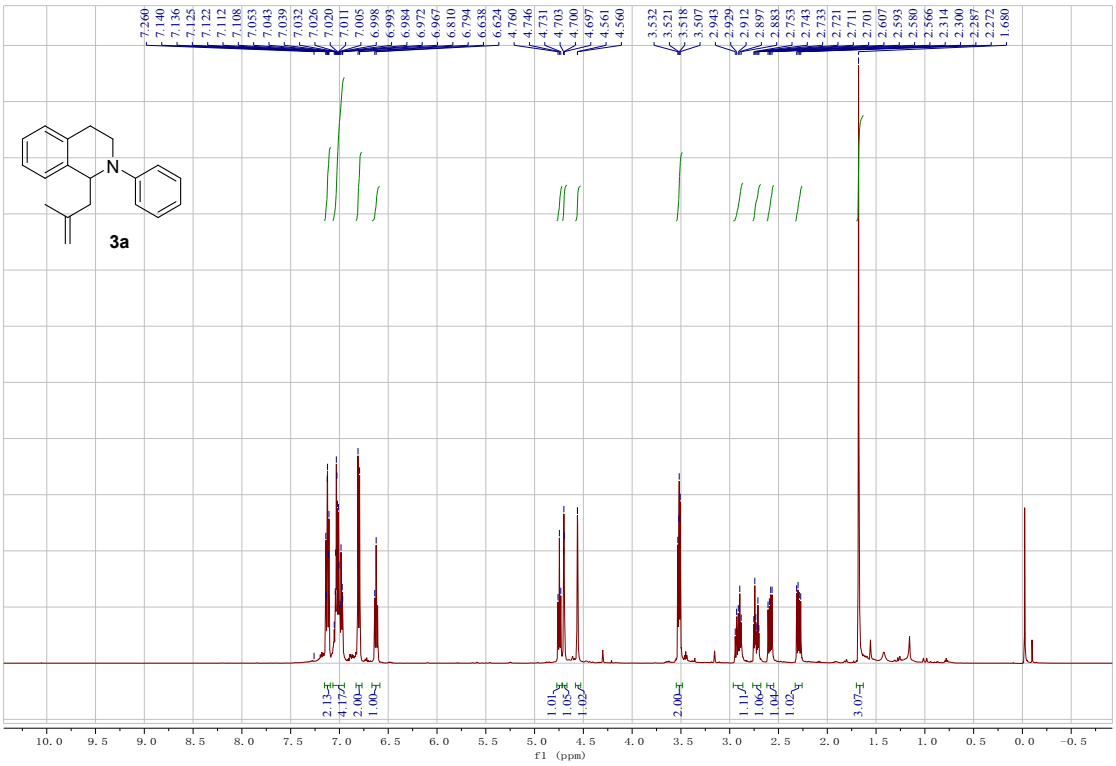
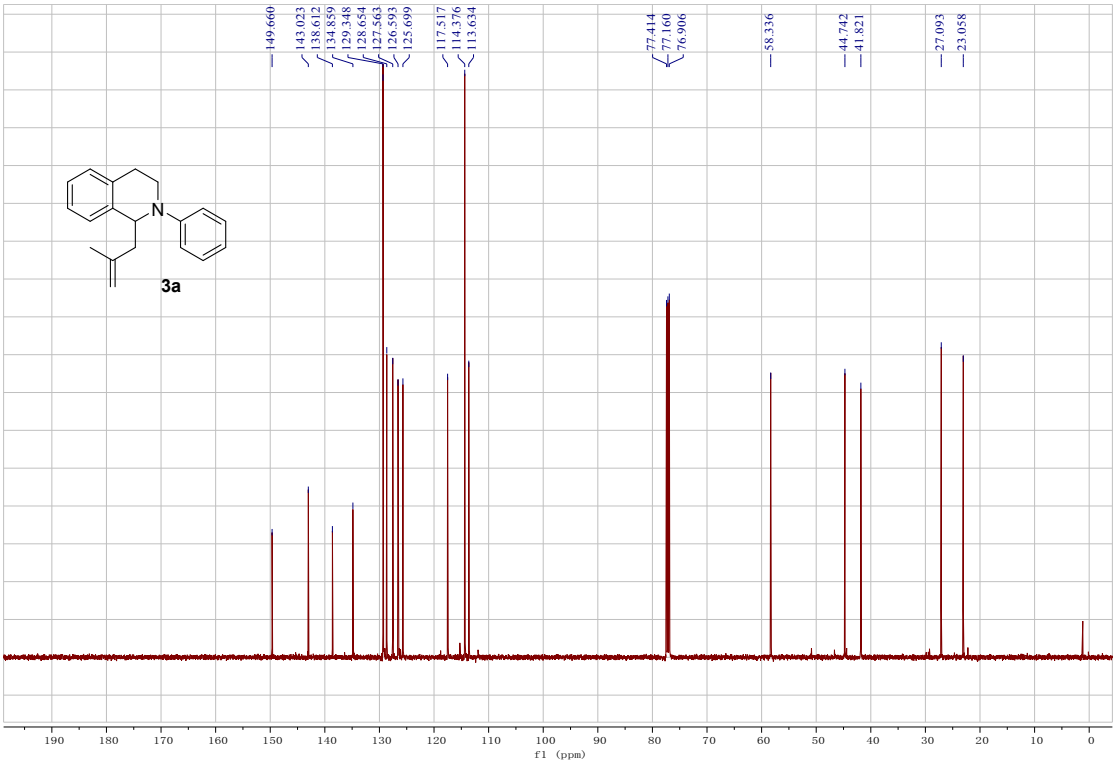
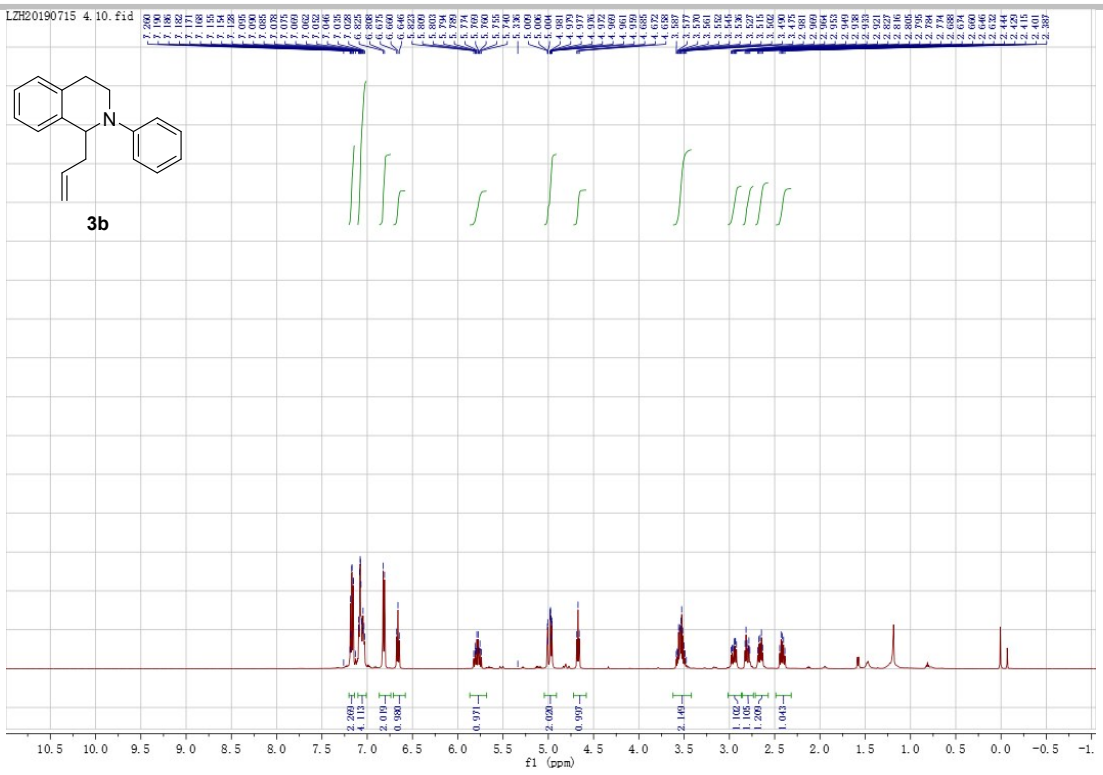
7. Copies of NMR Spectra



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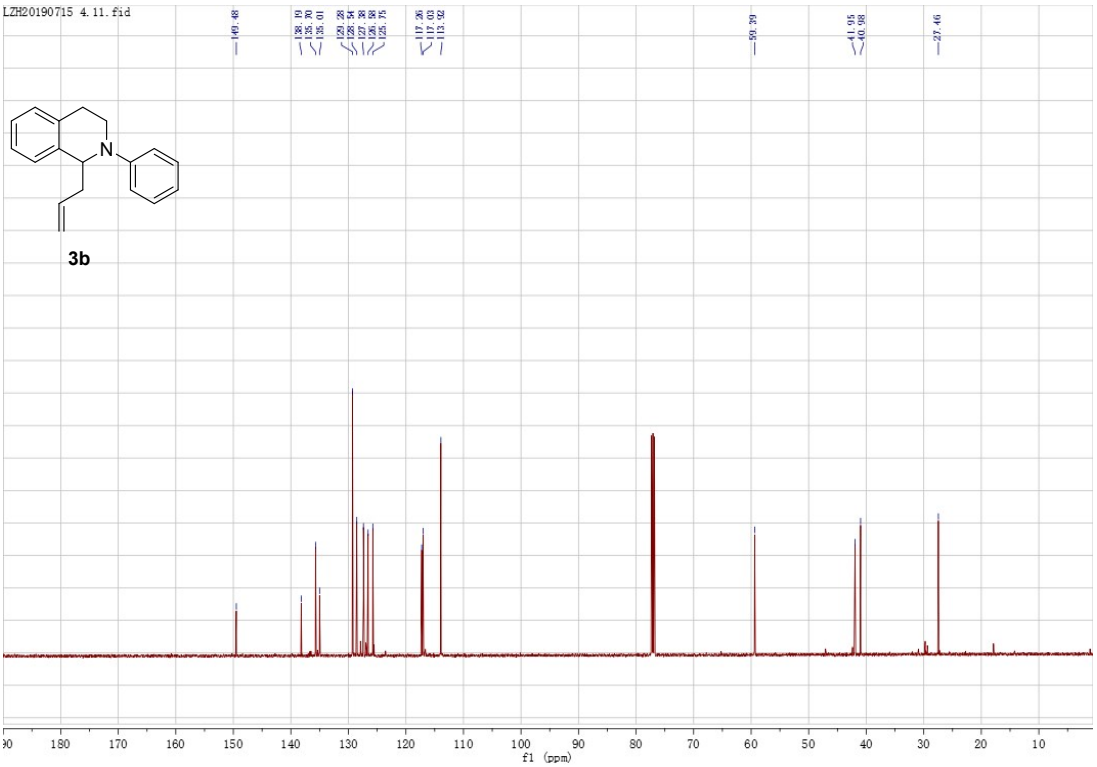
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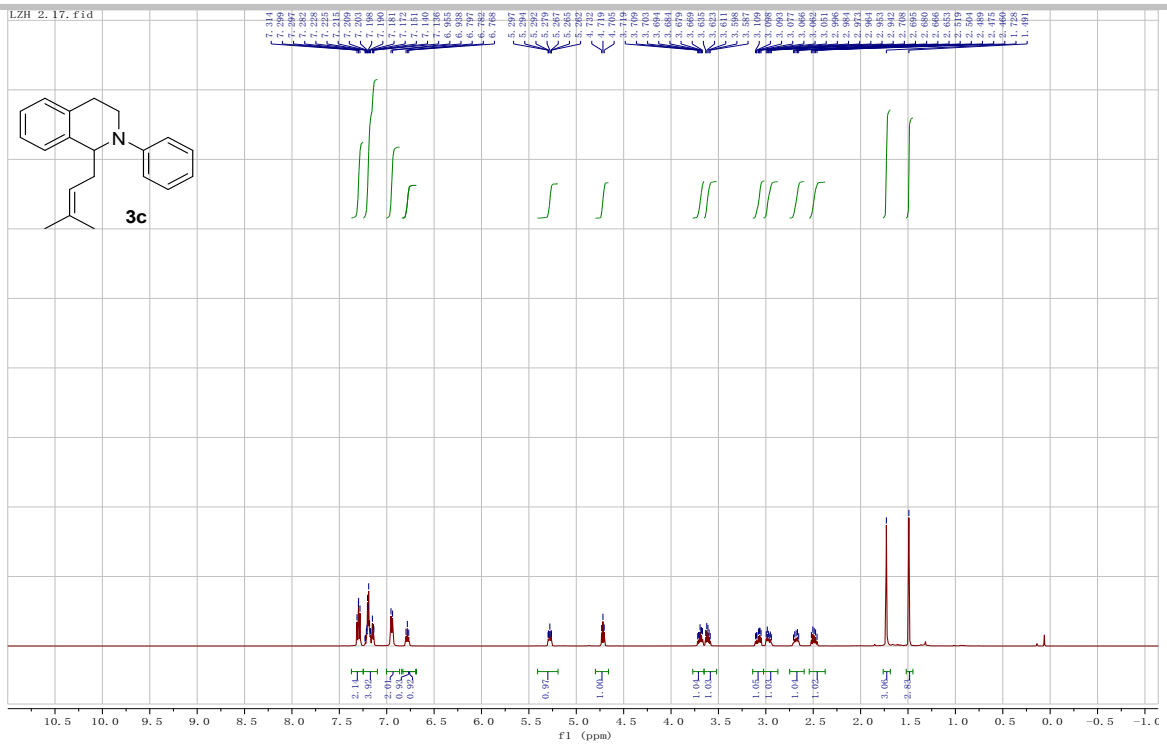
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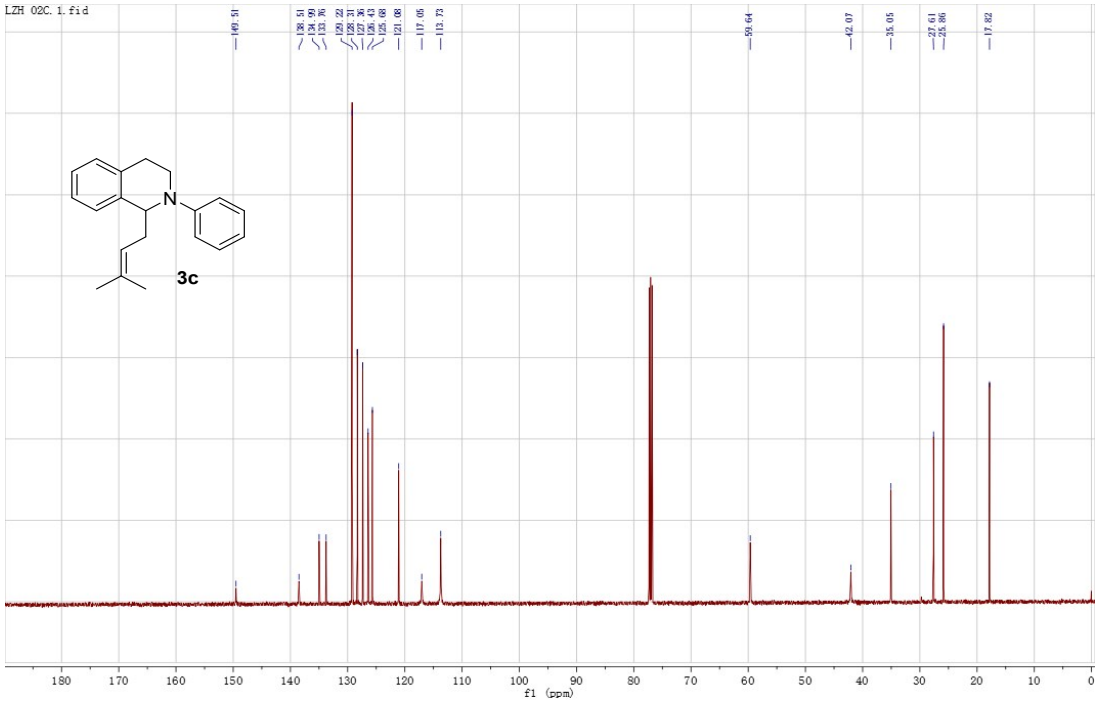
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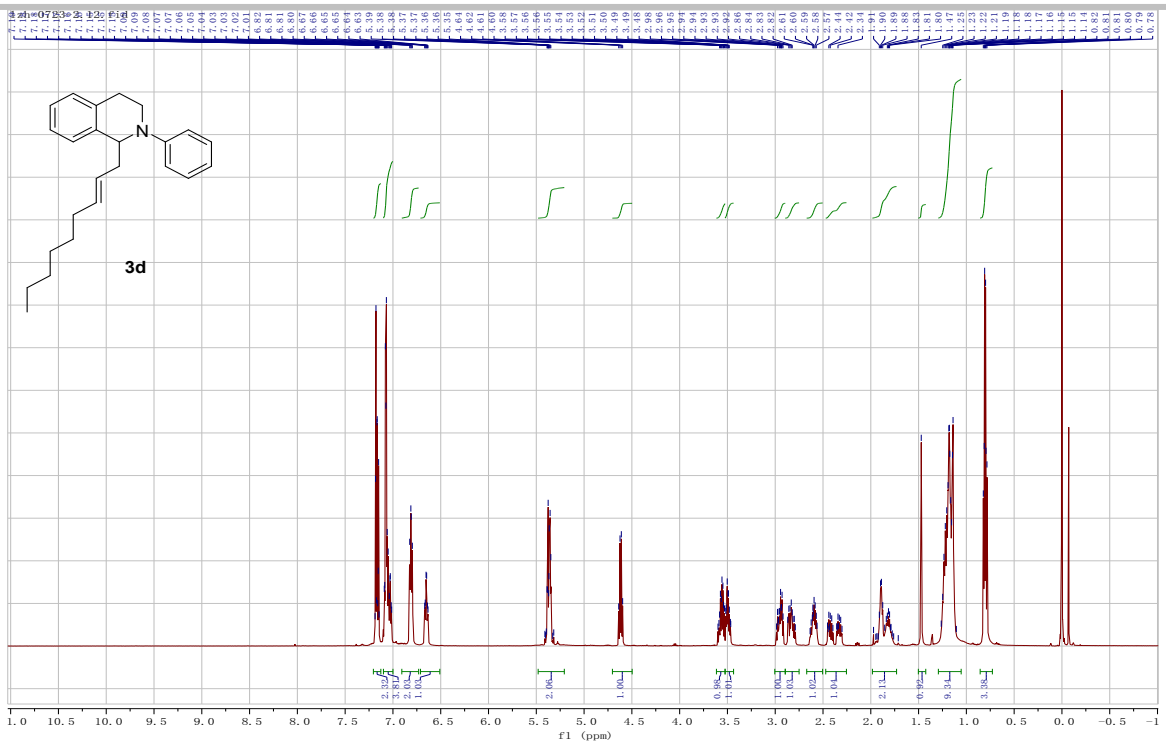
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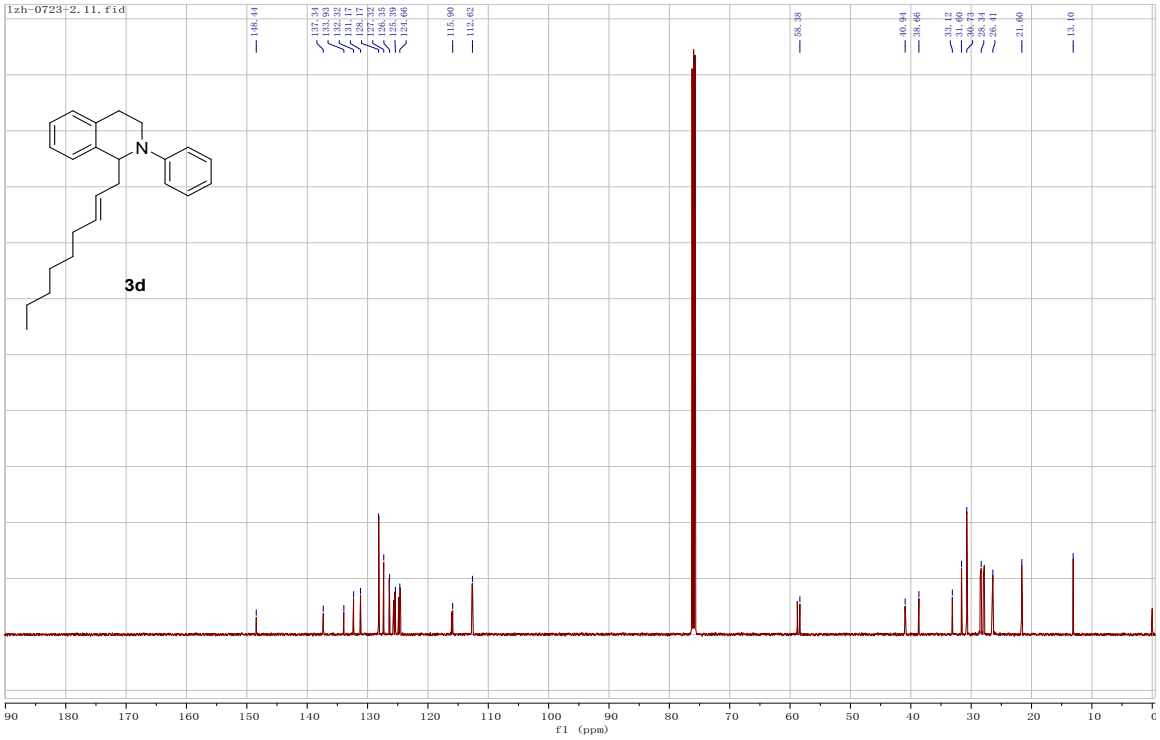
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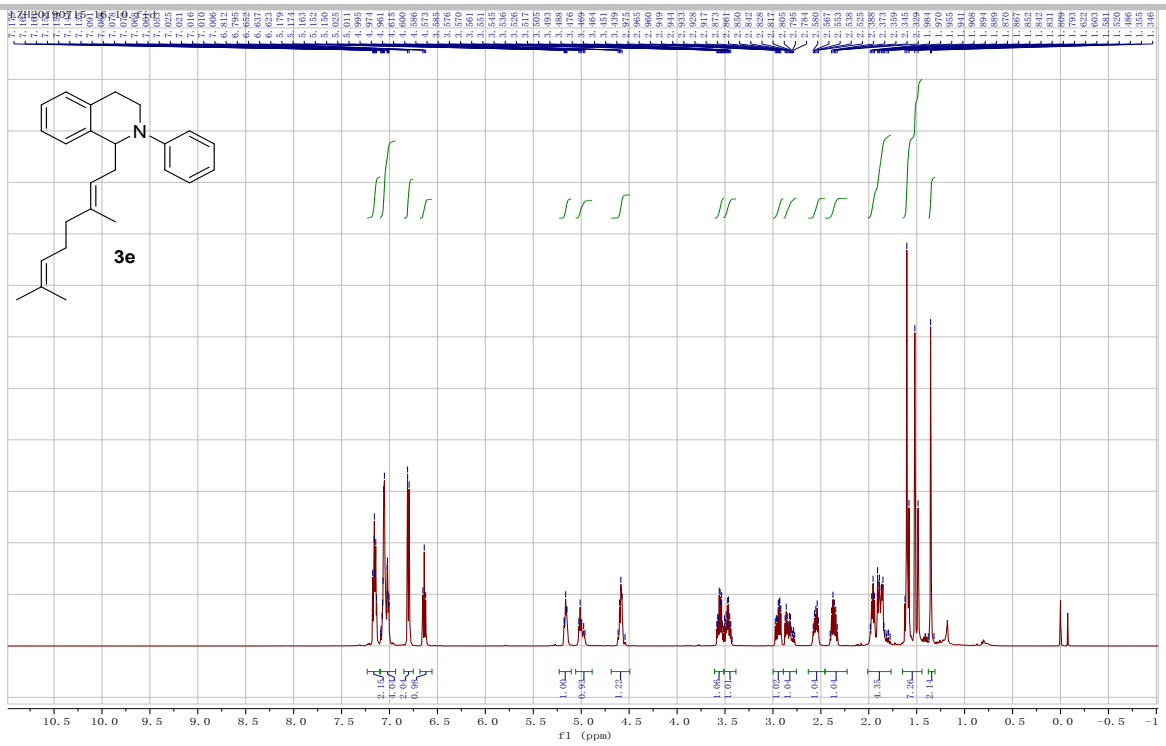
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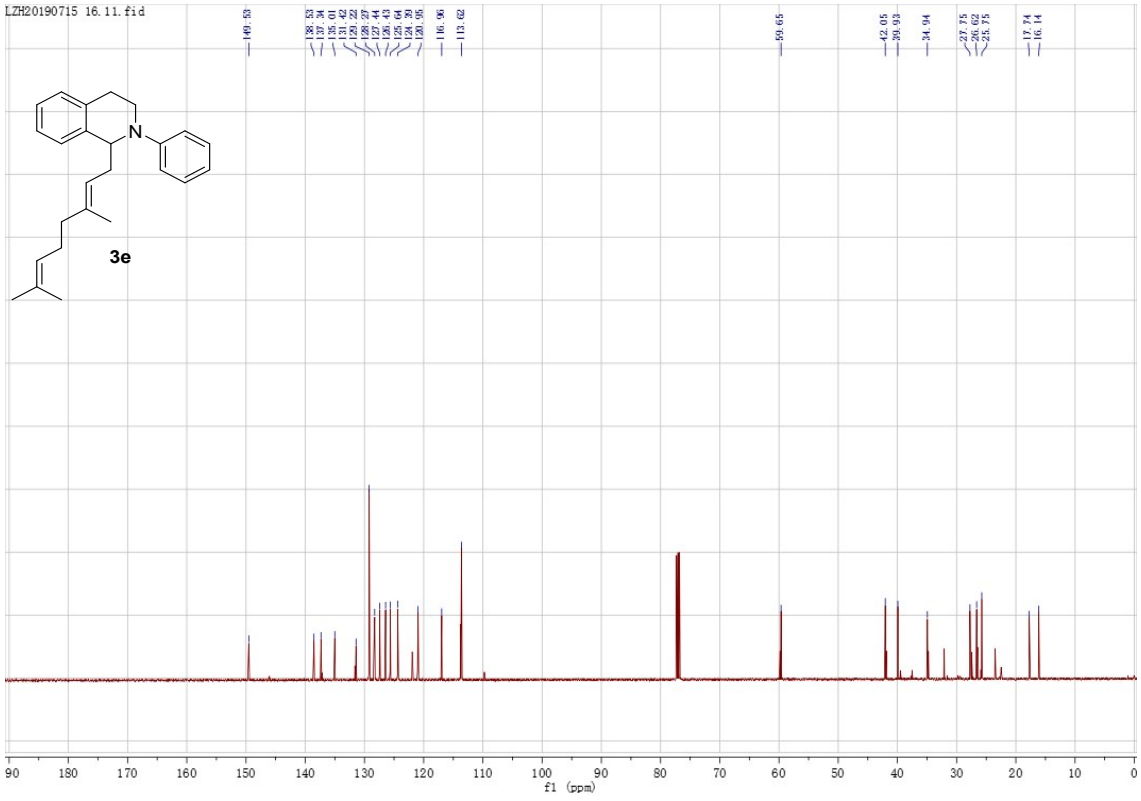
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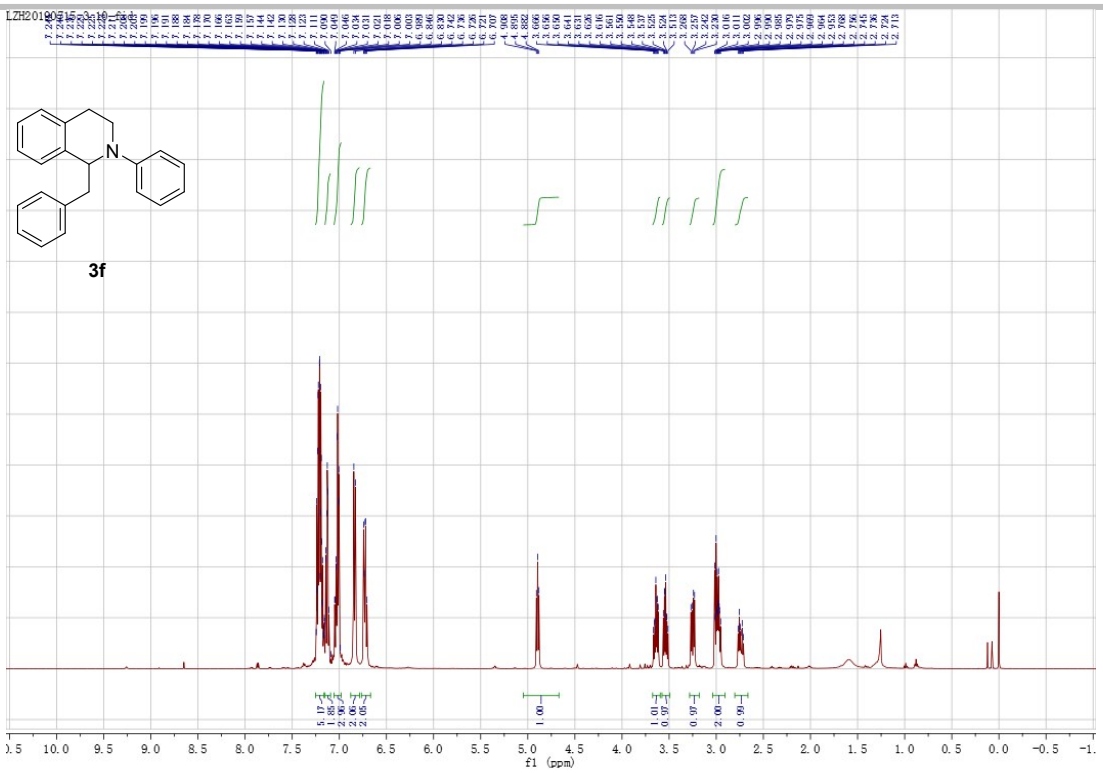
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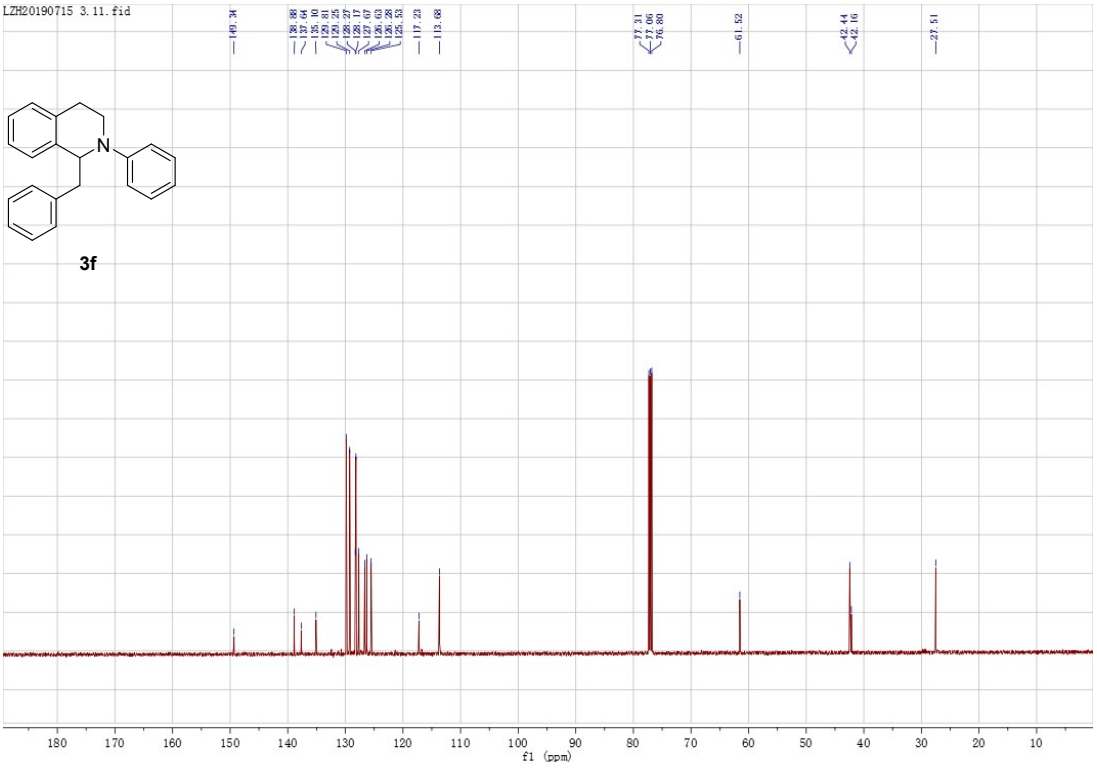
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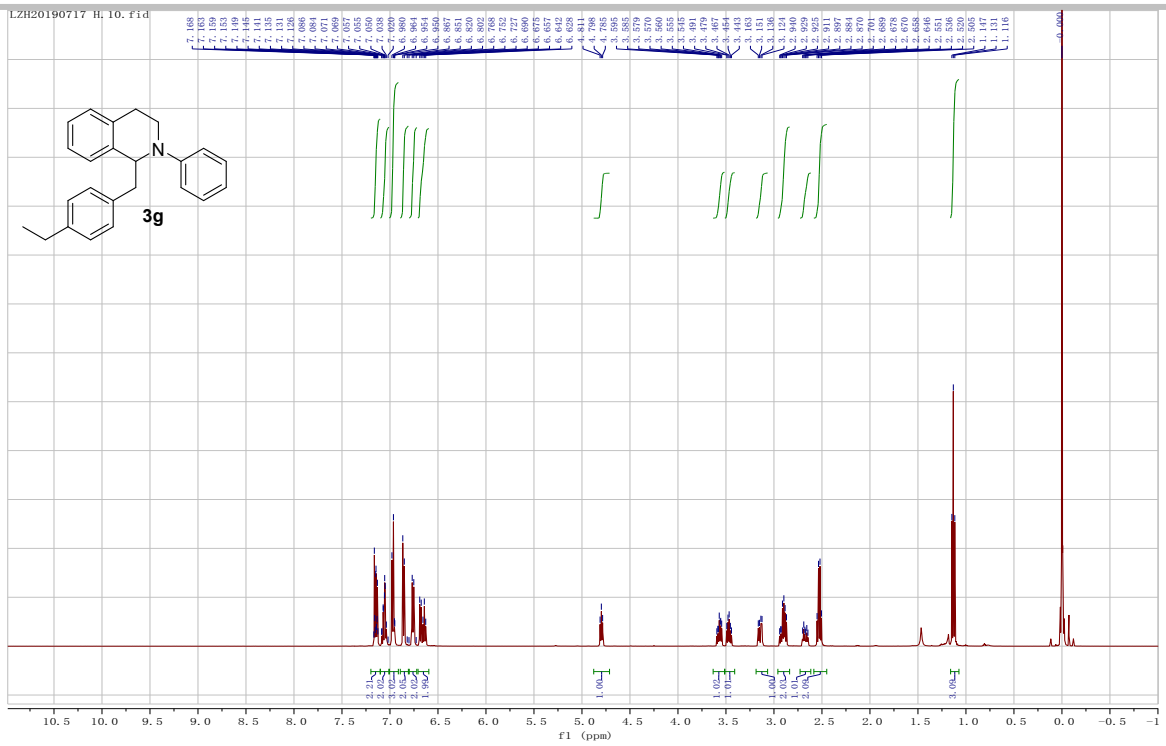
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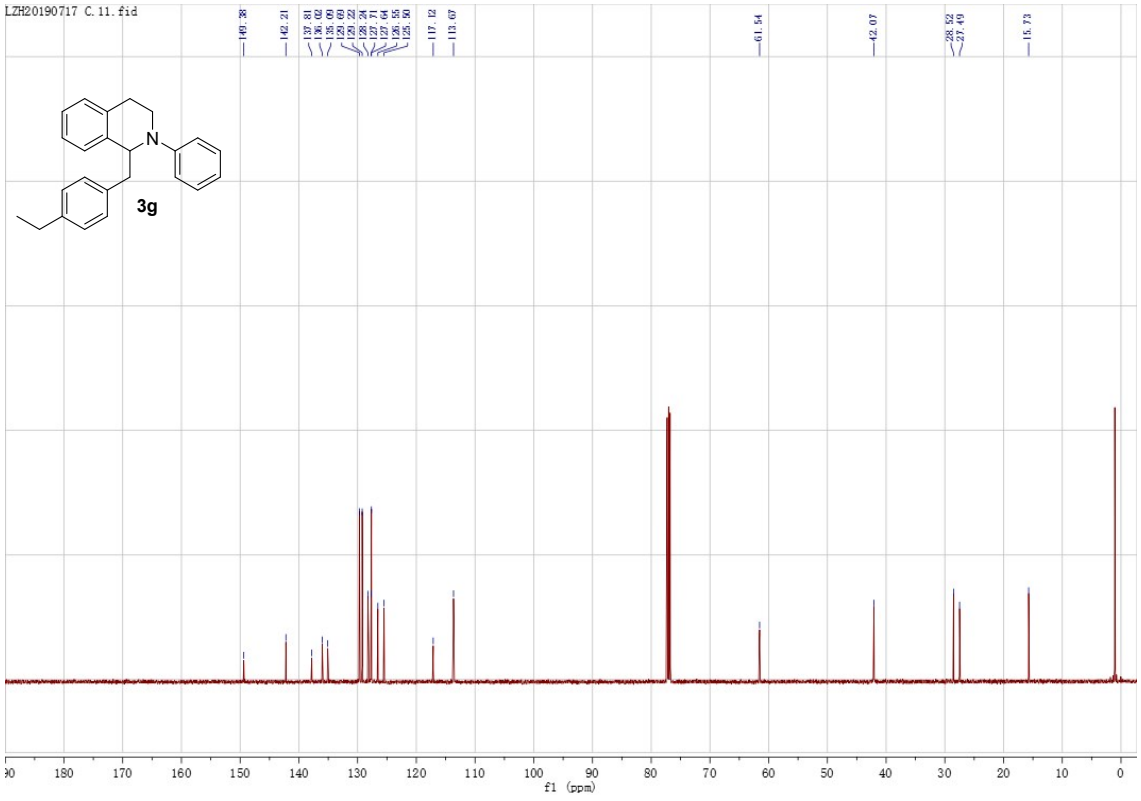
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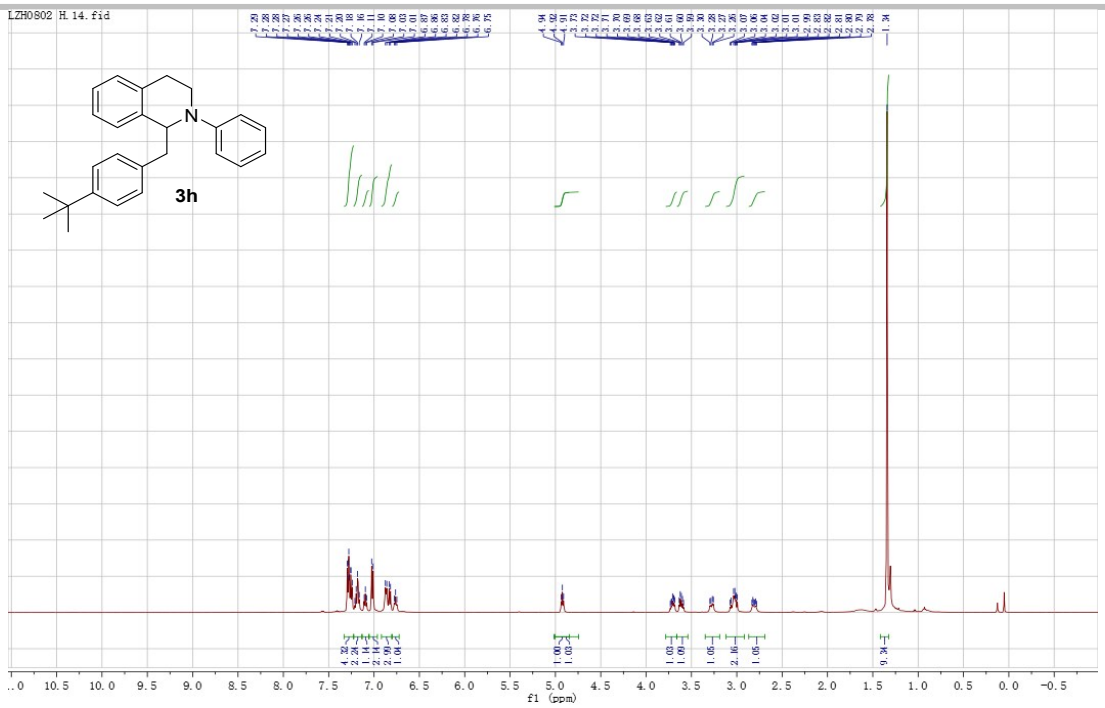
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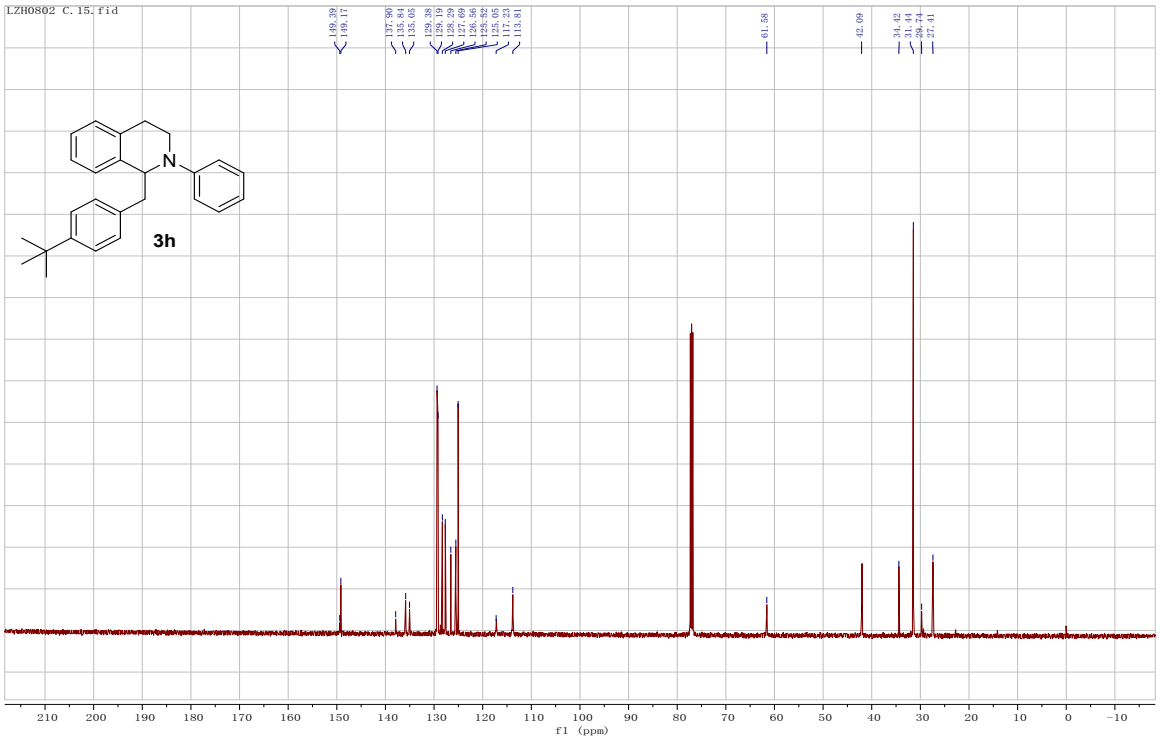
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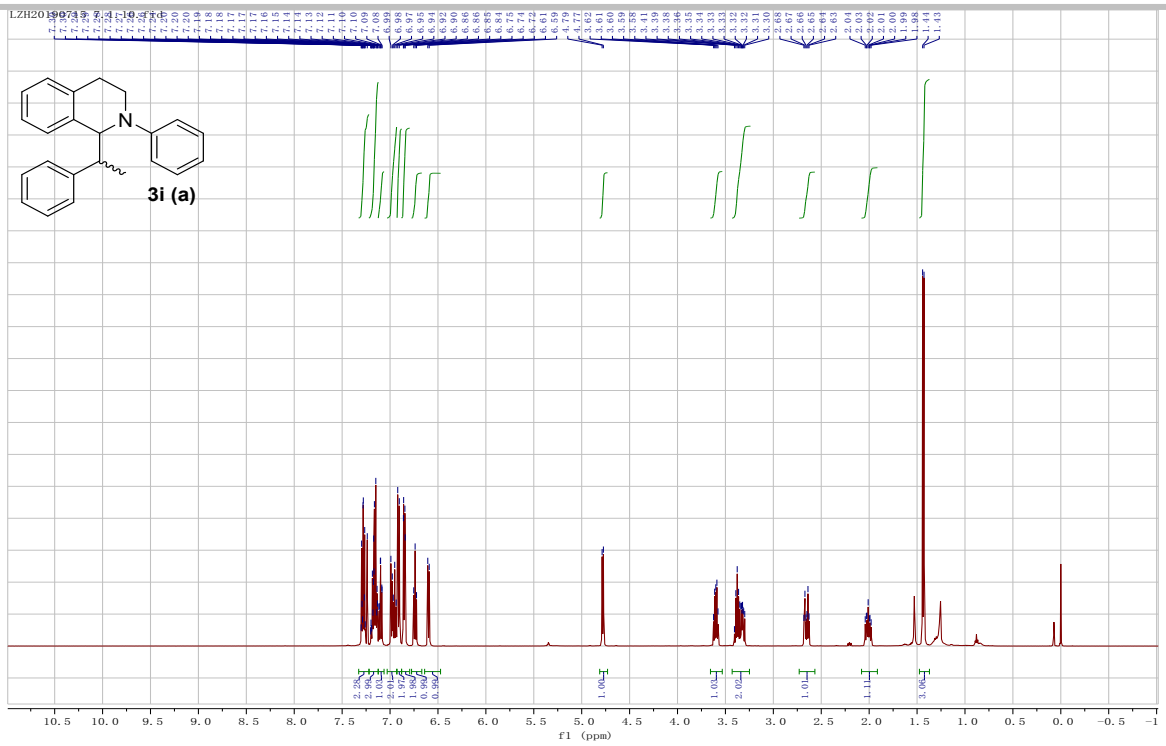
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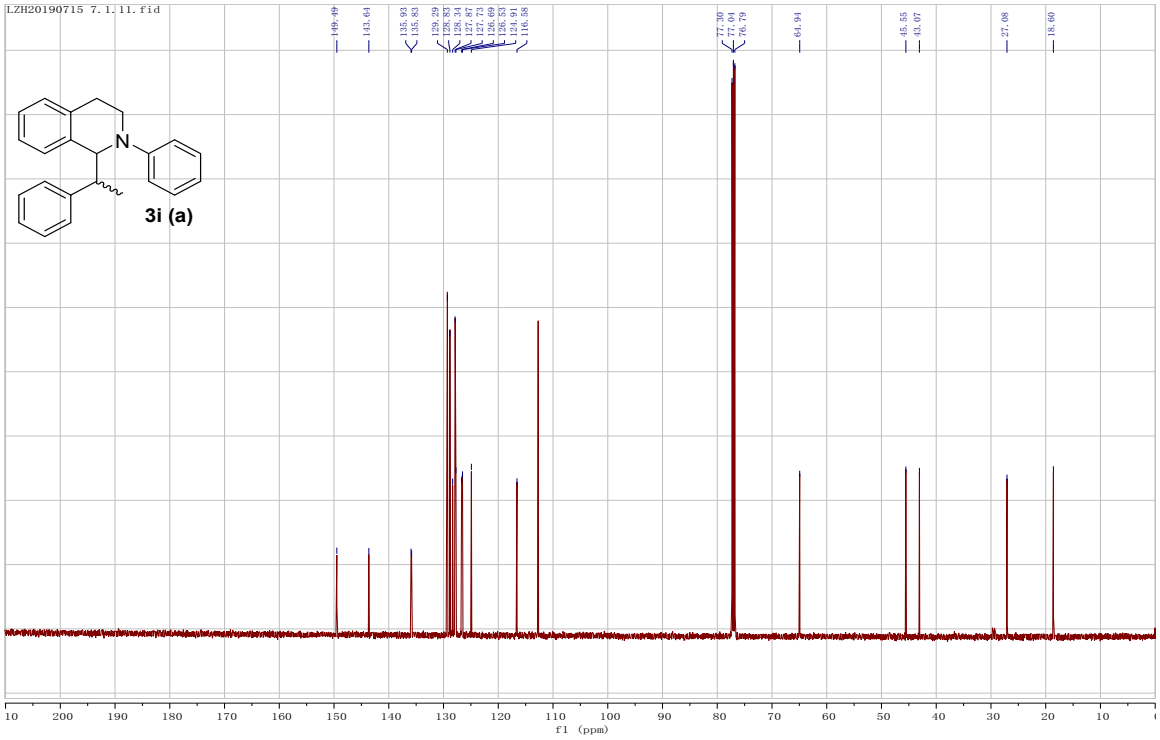
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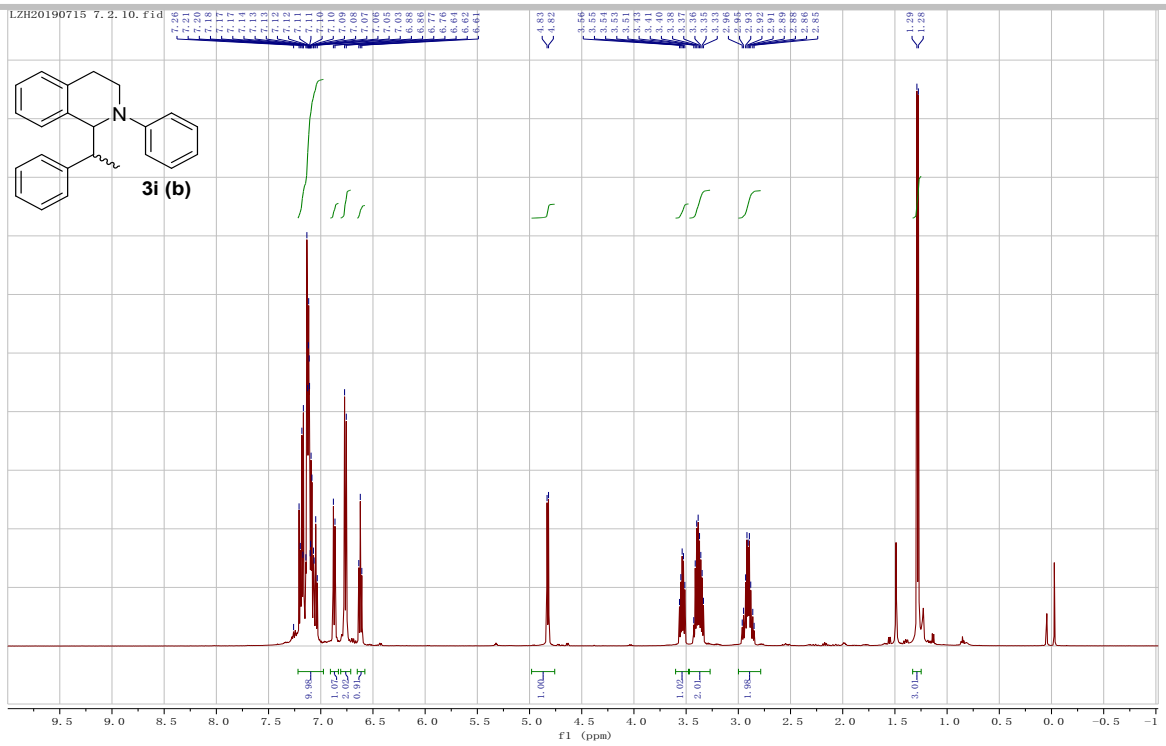
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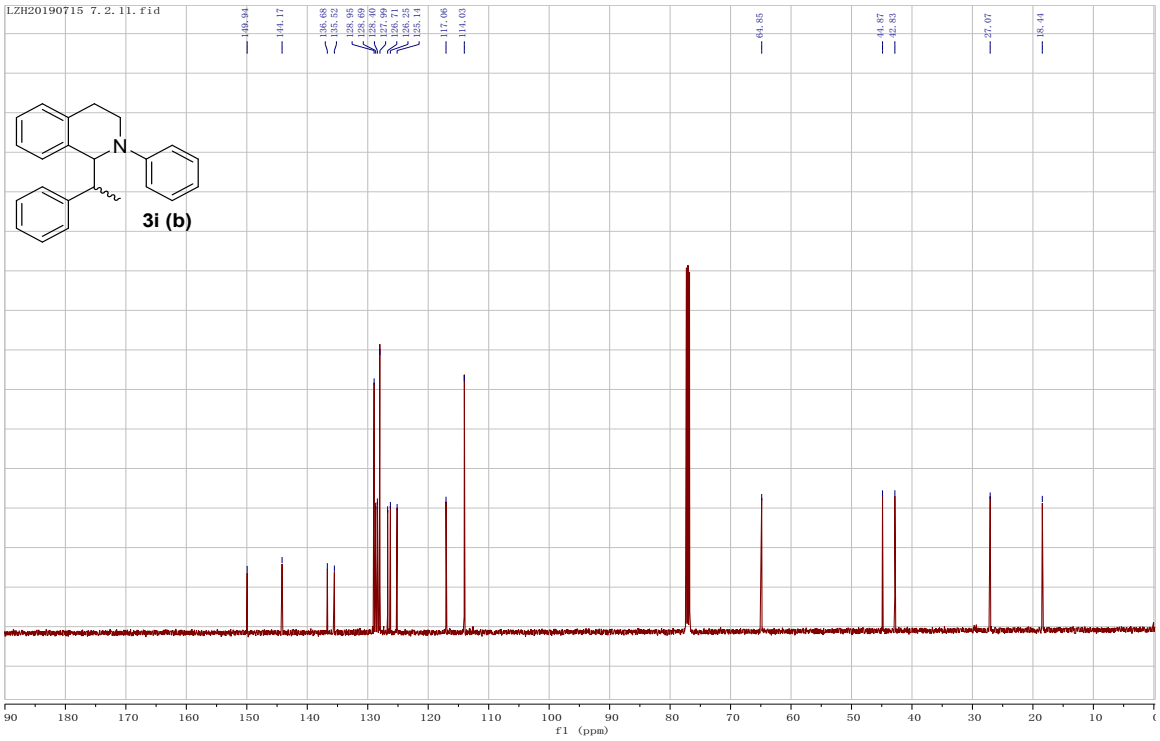
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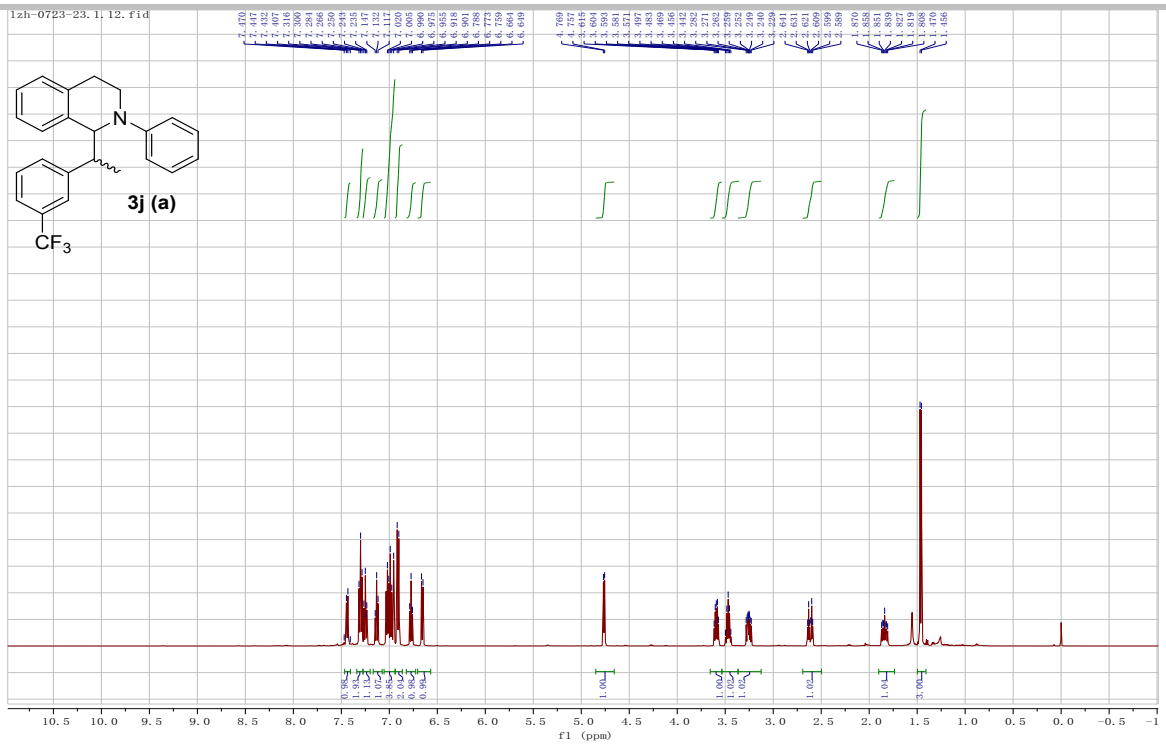
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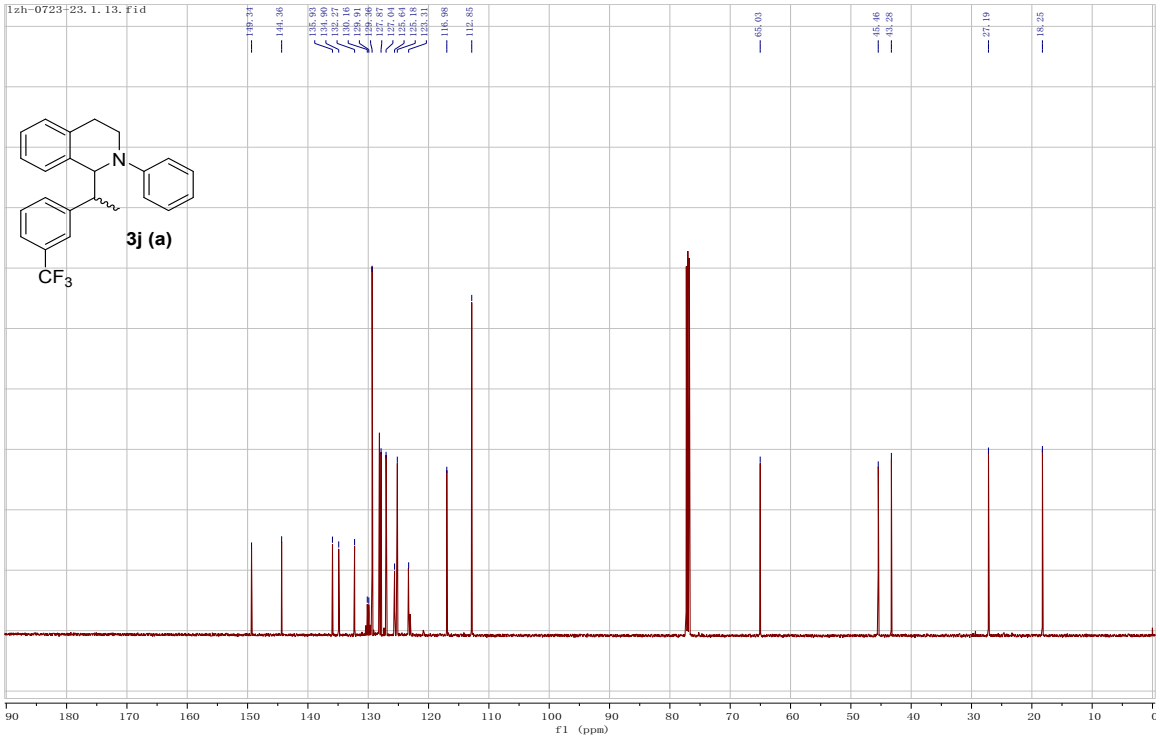
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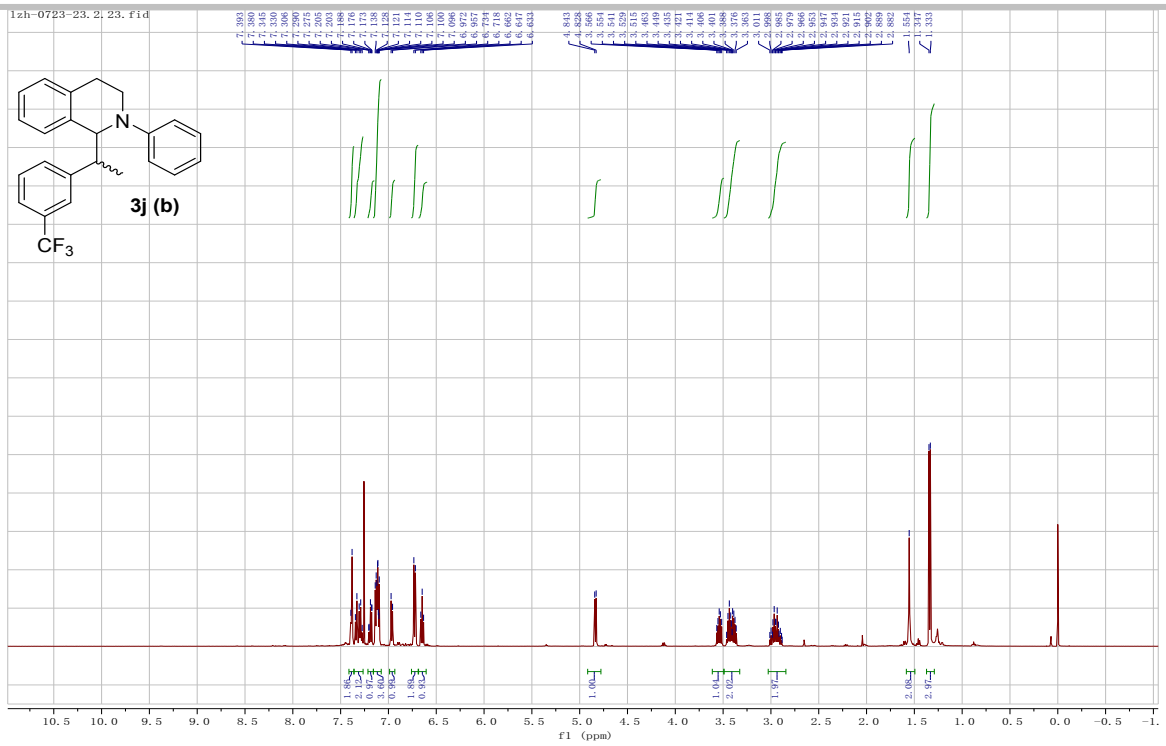
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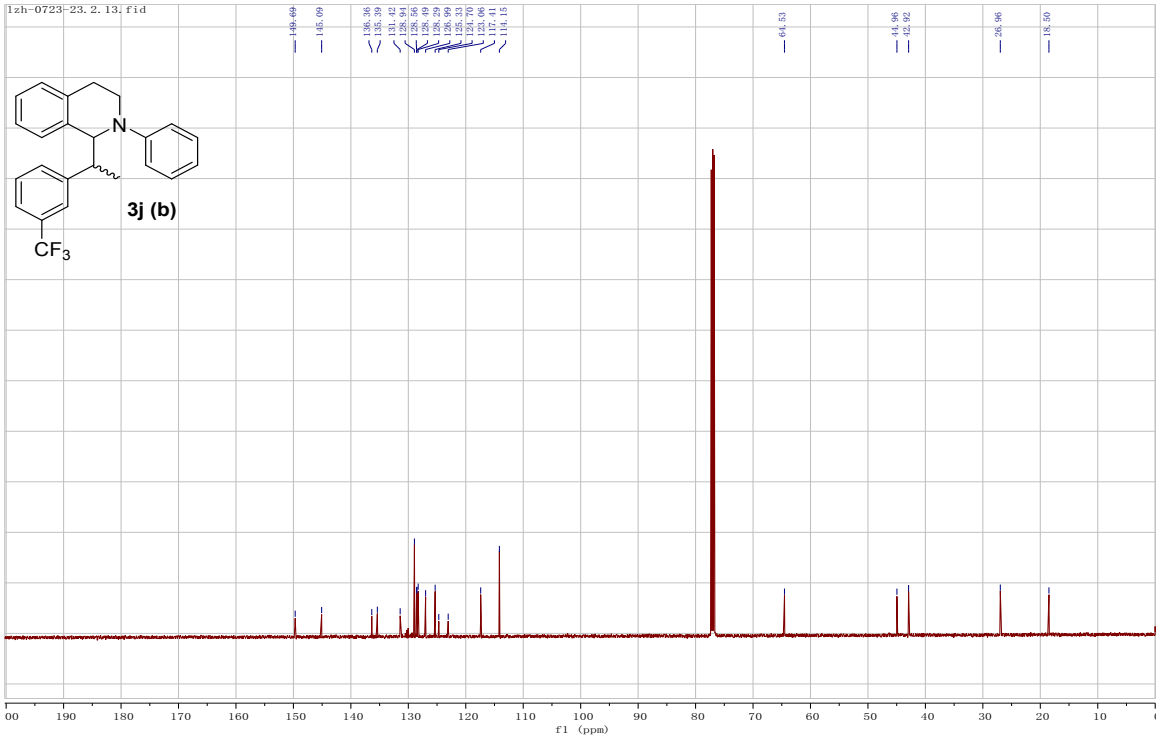
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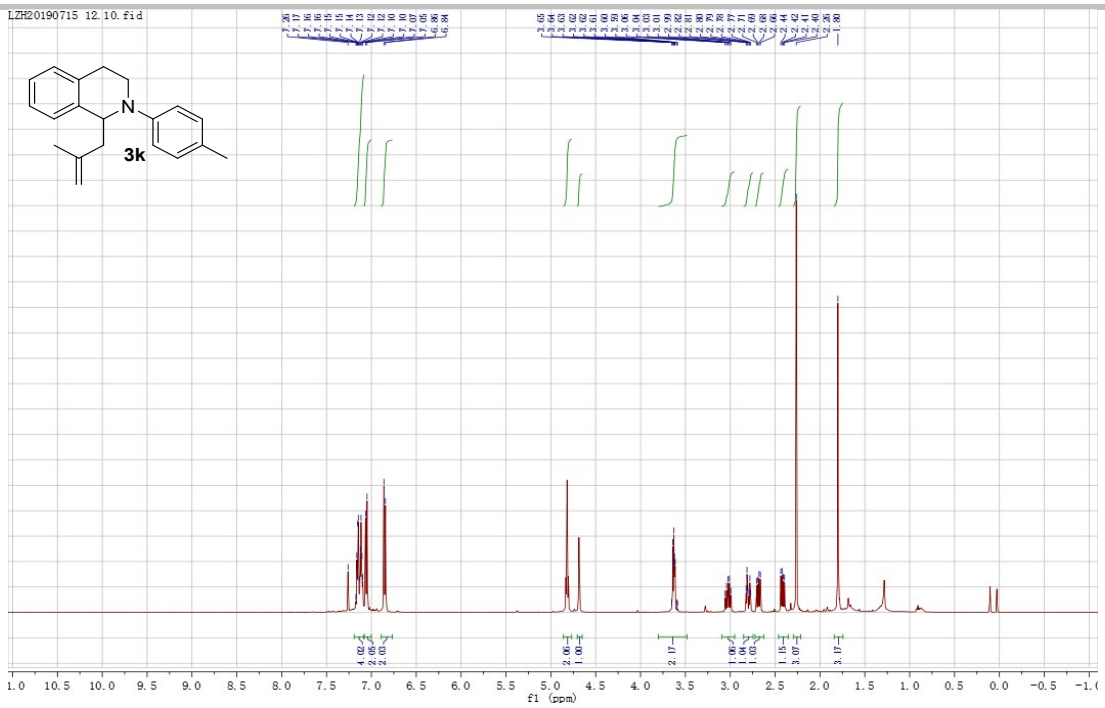
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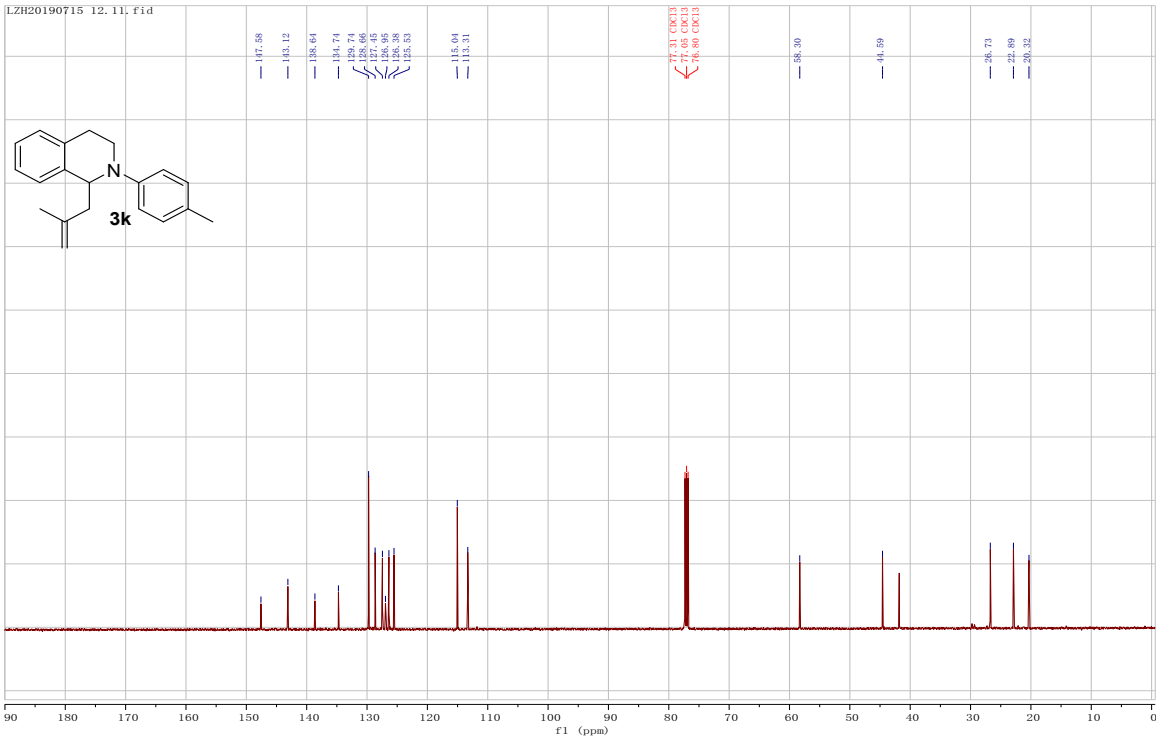
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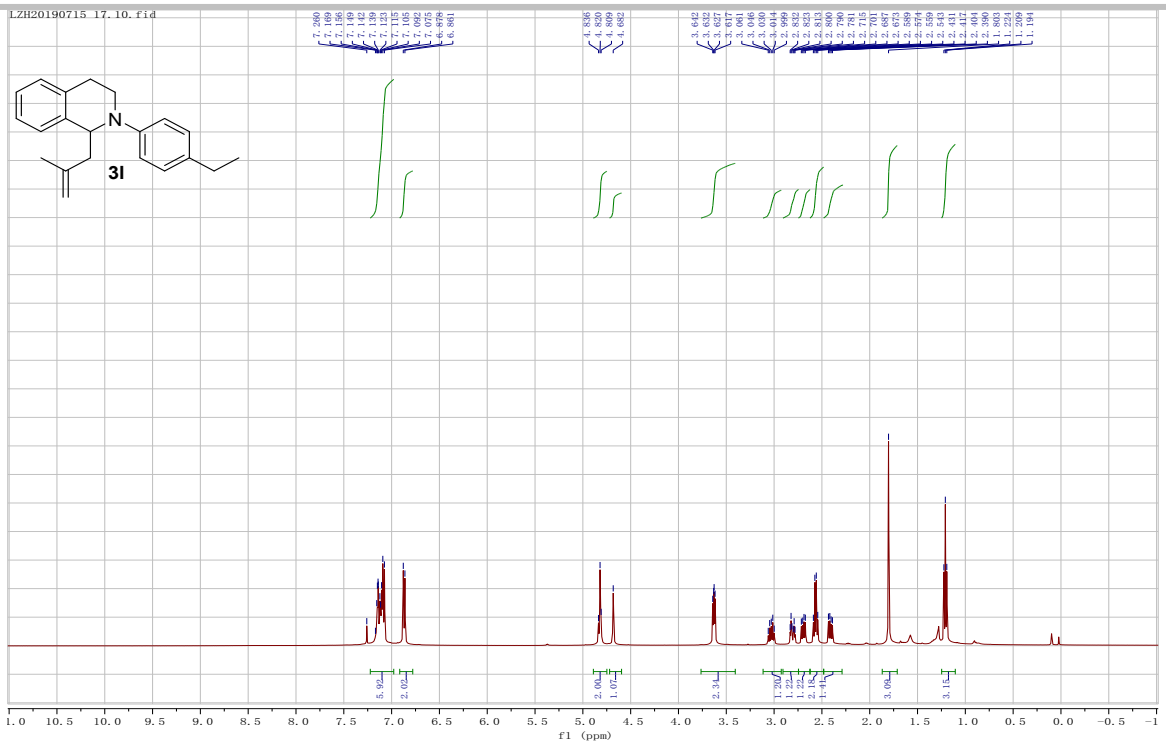
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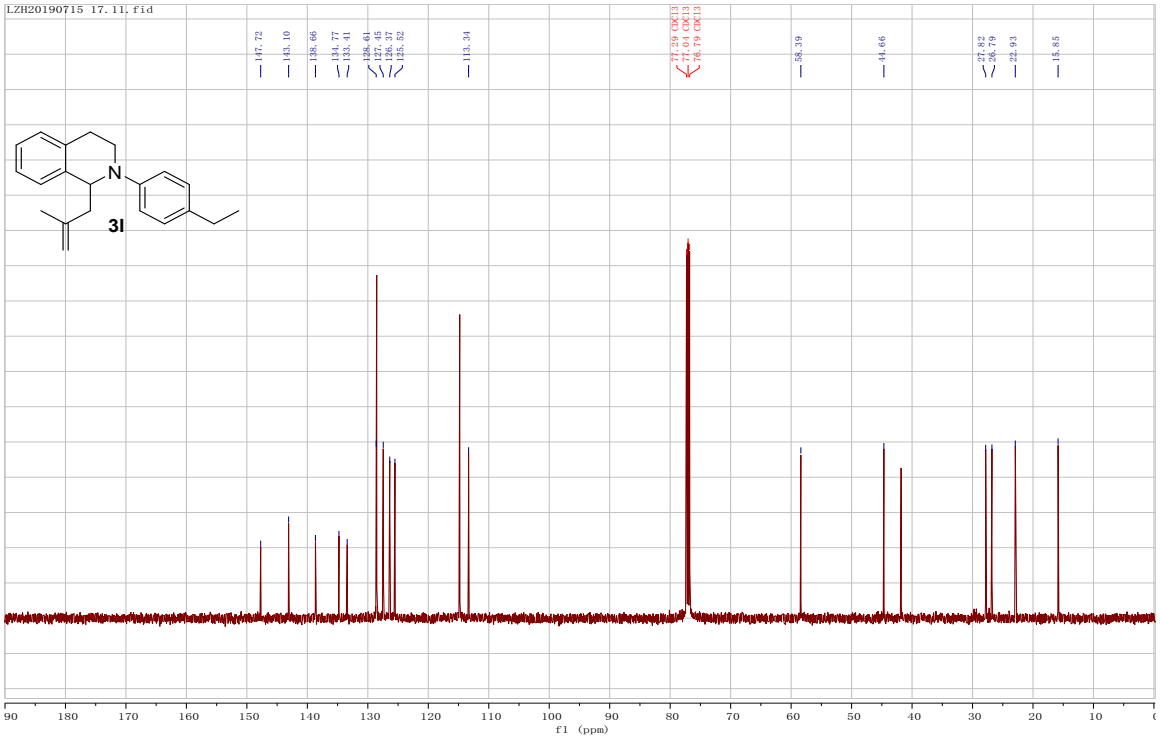
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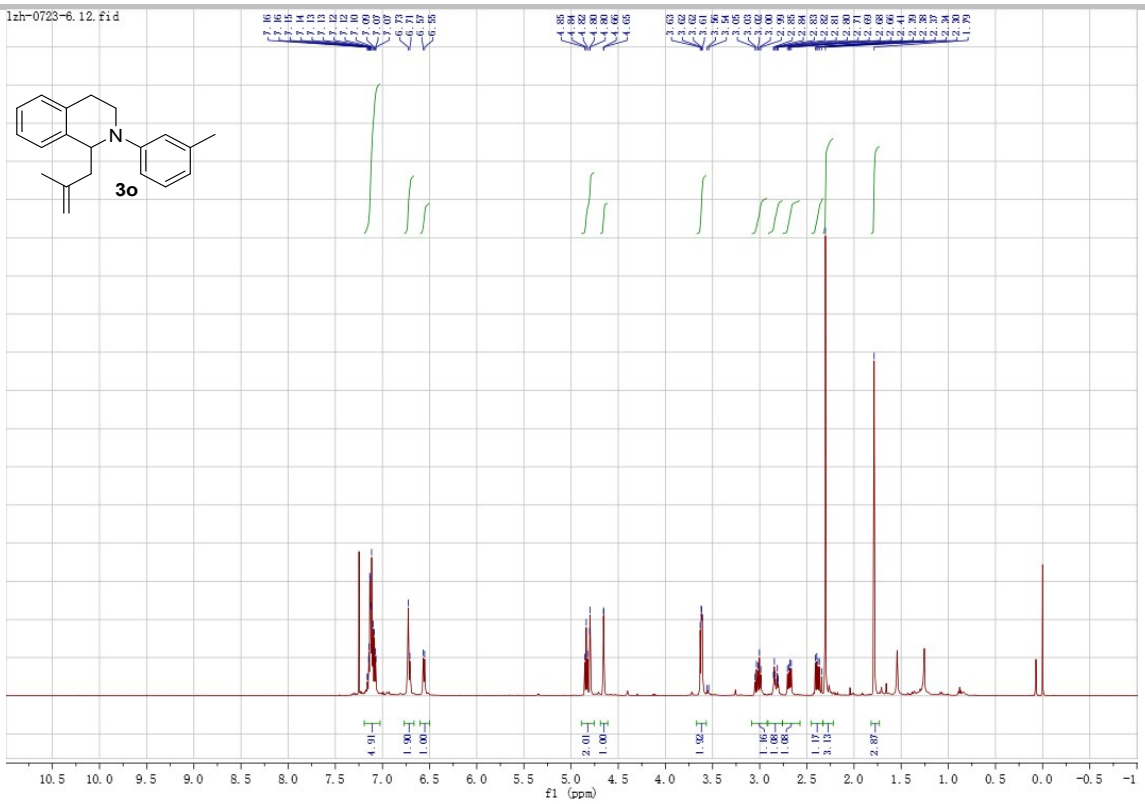
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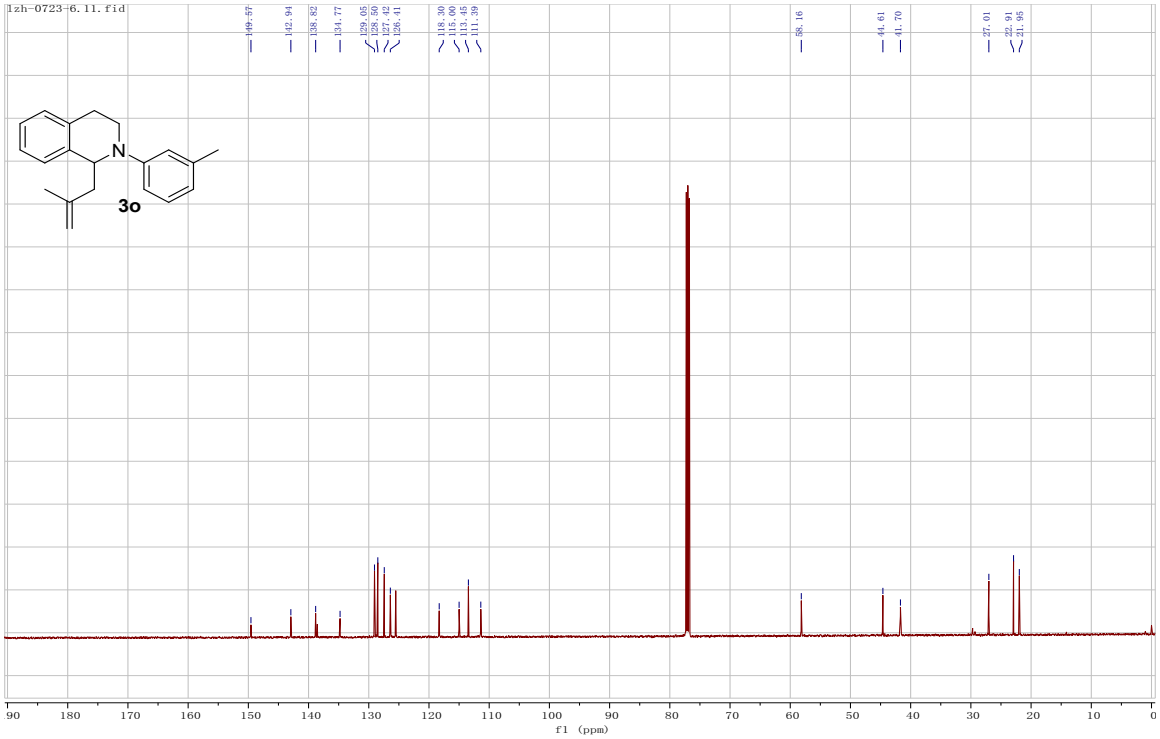
f1 (ppm)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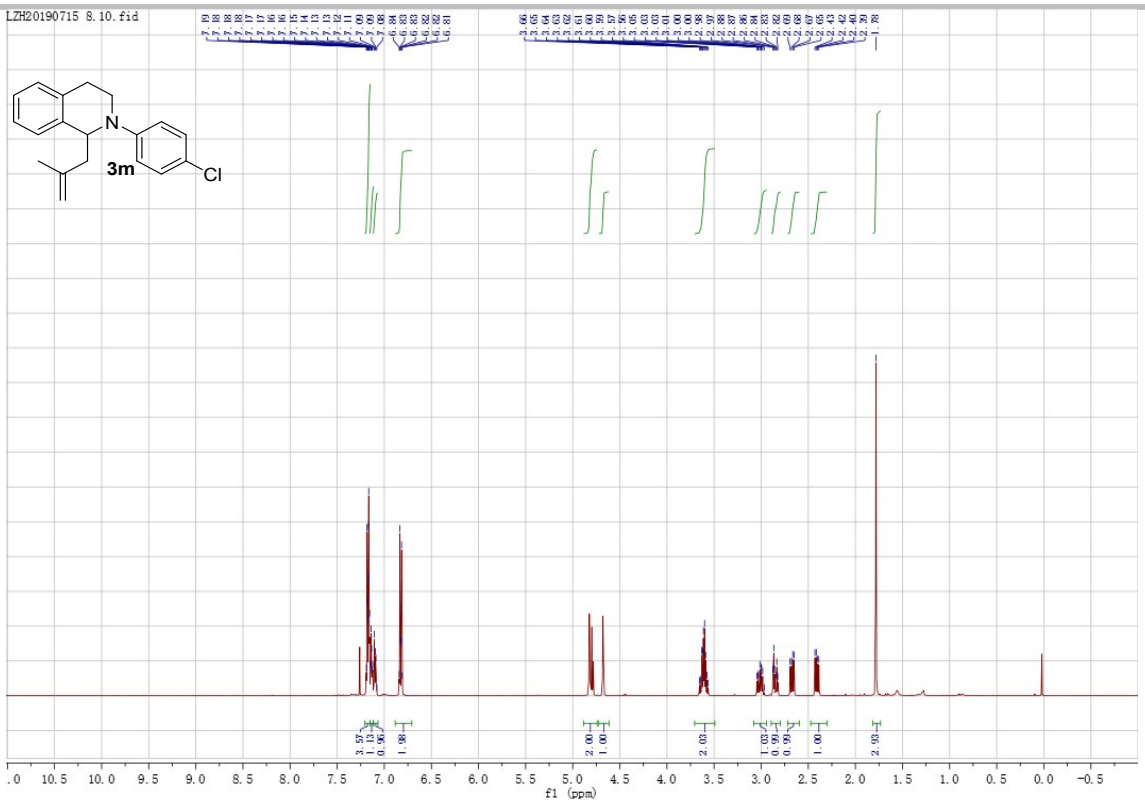
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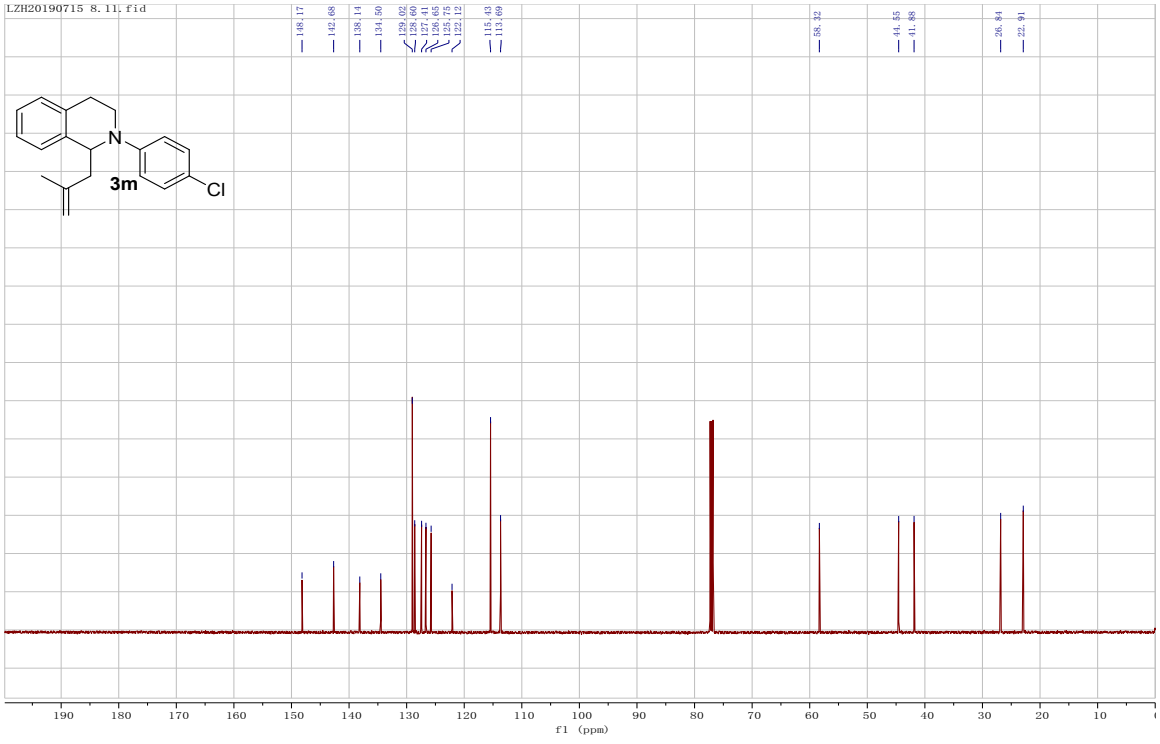
Cl
f1 (ppm)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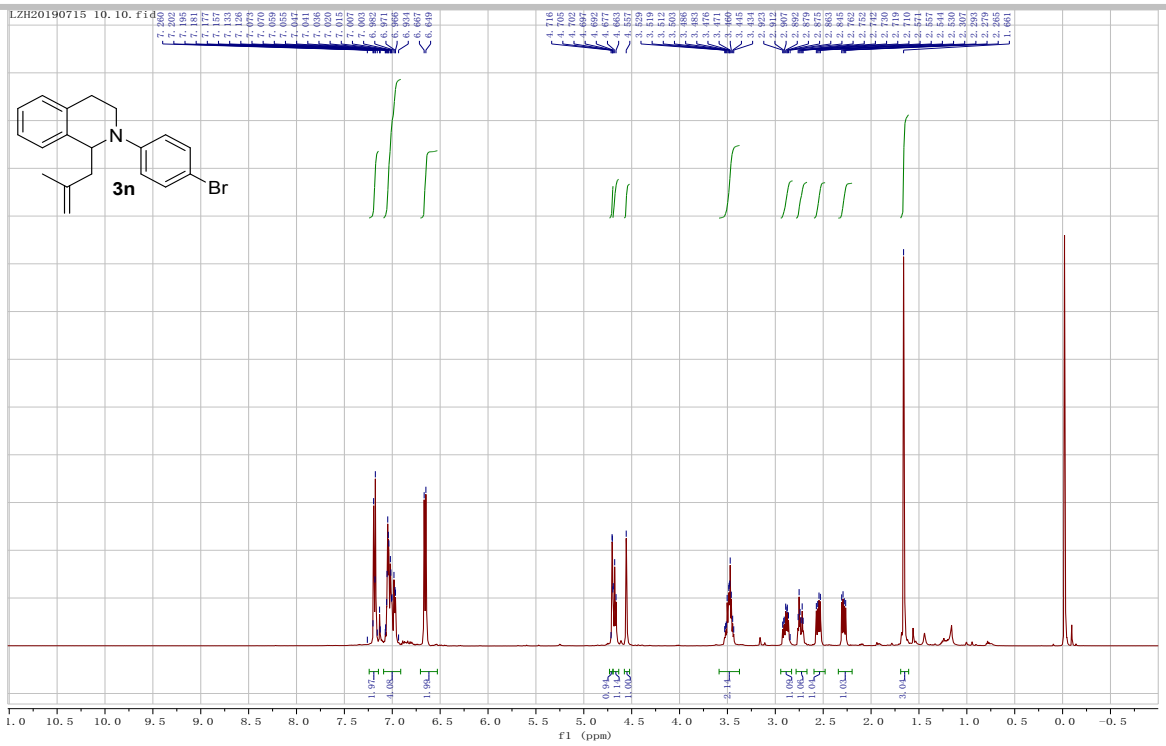
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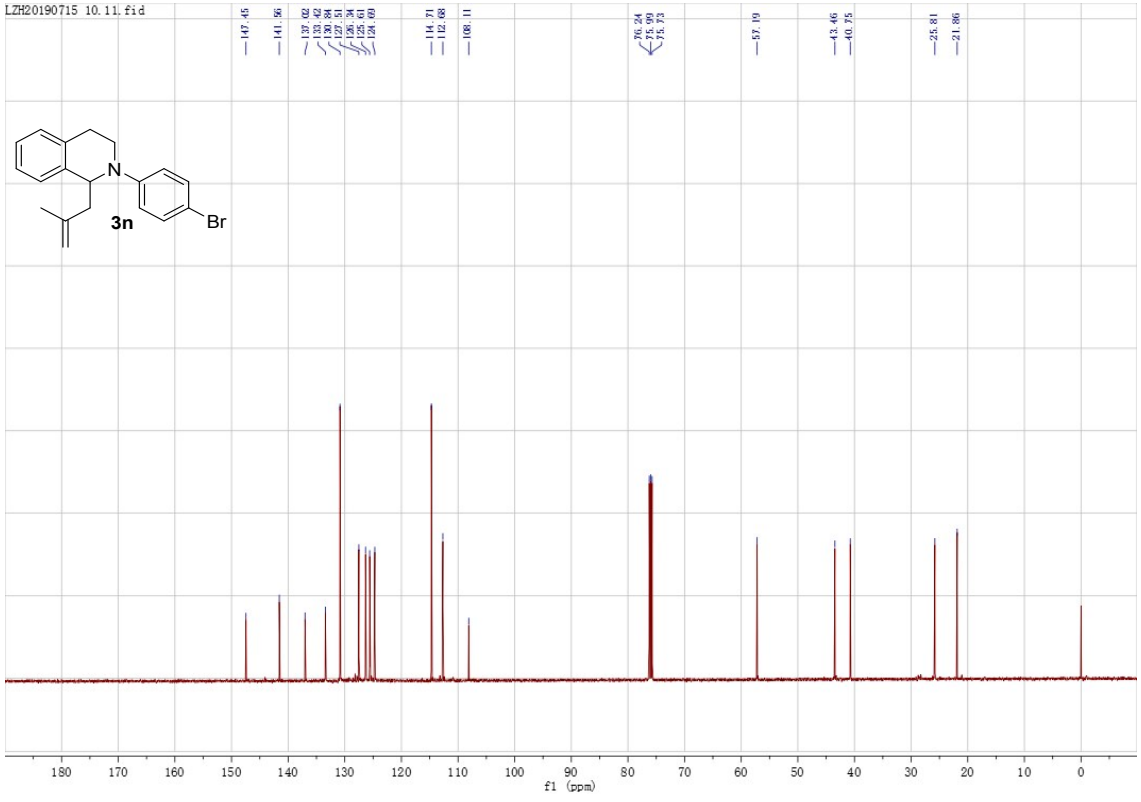
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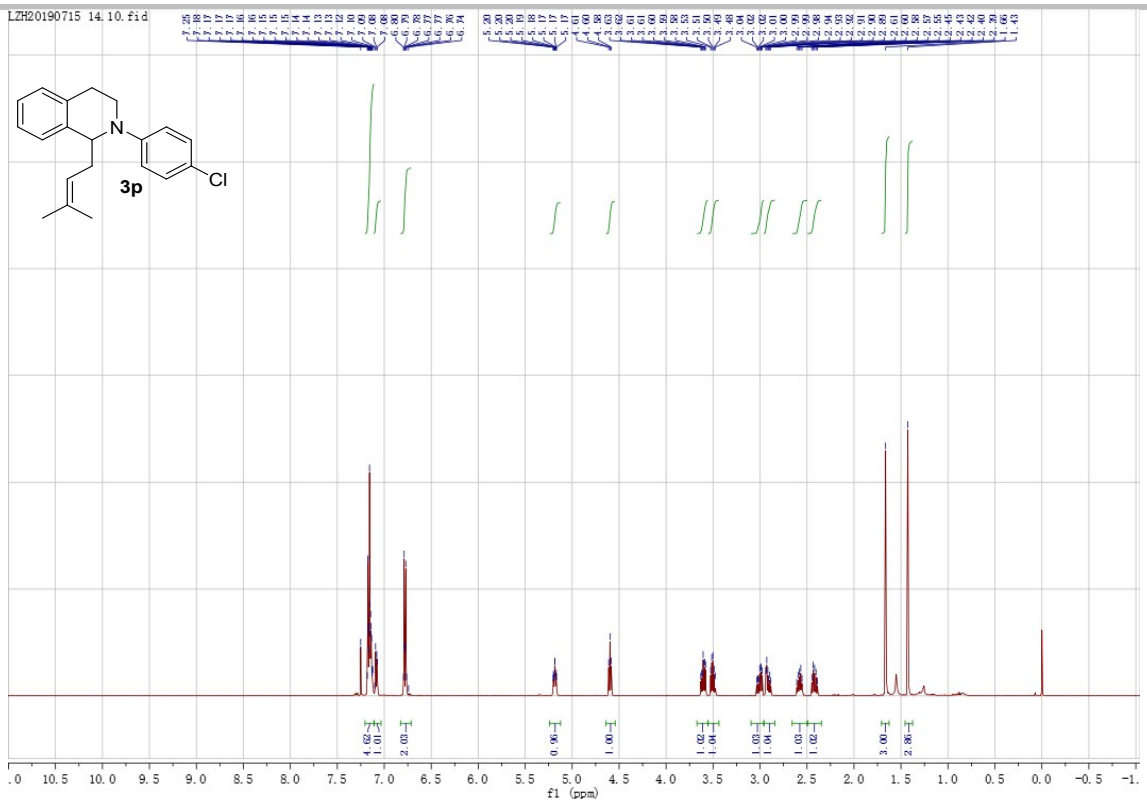
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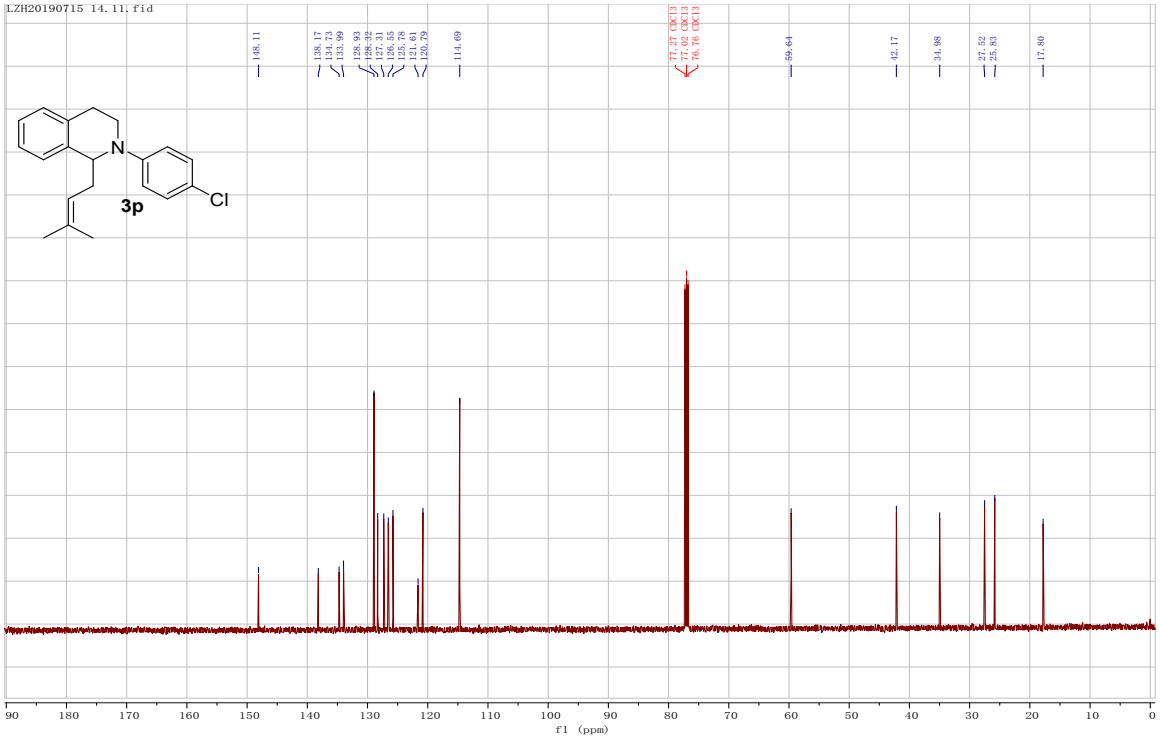
f1 (ppm)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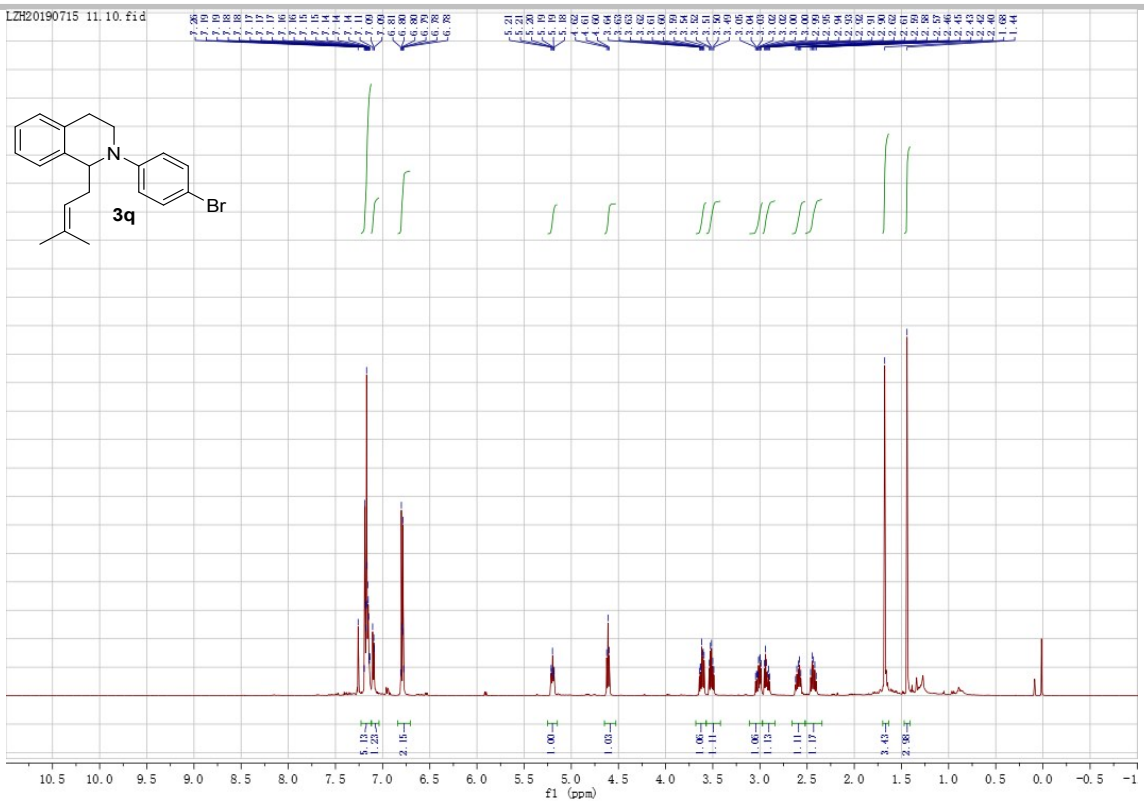
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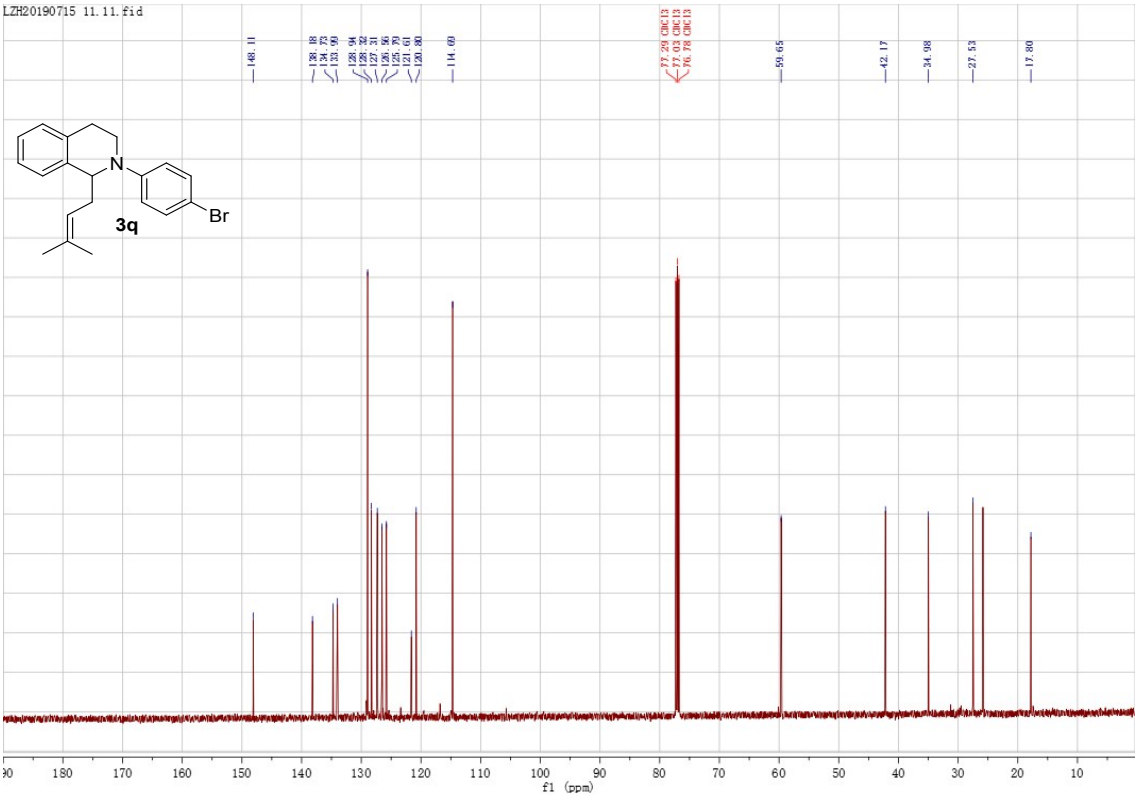
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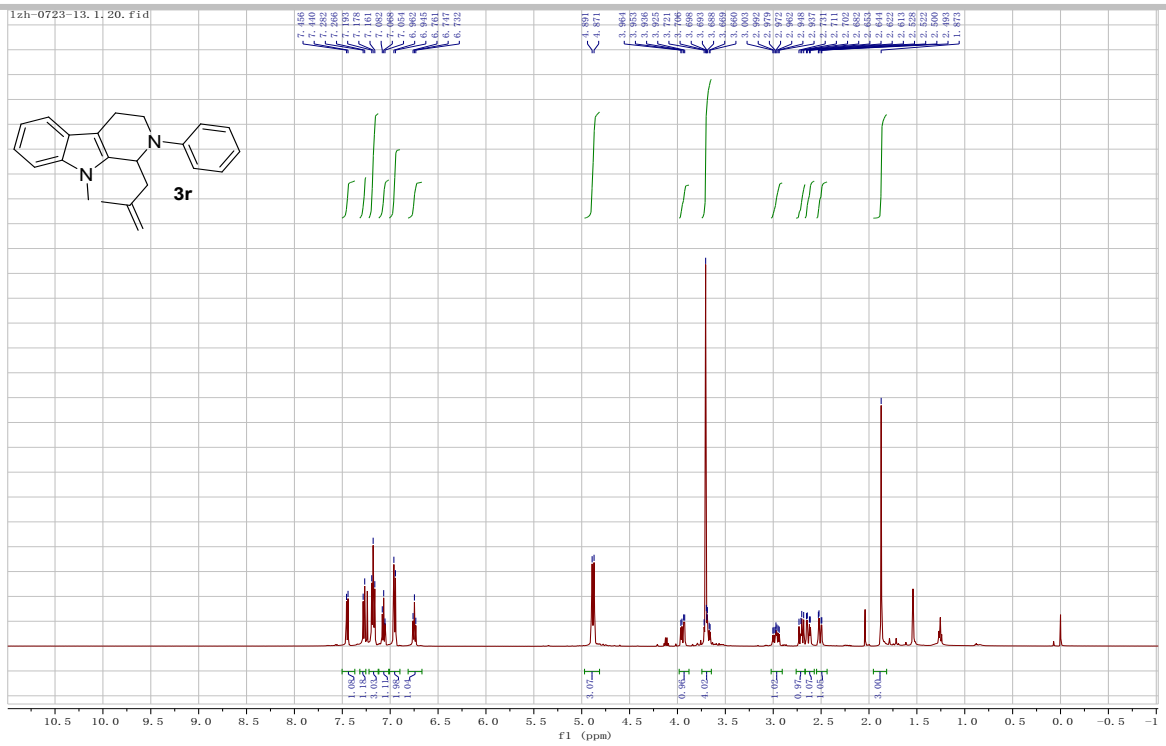
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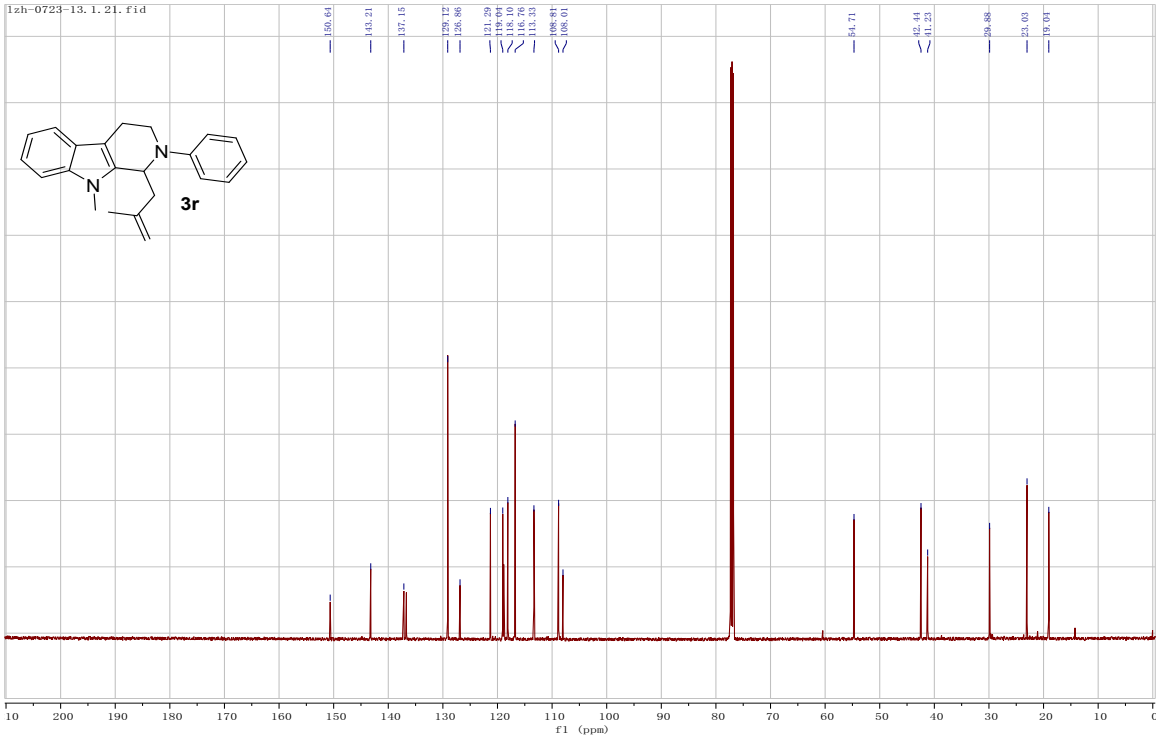
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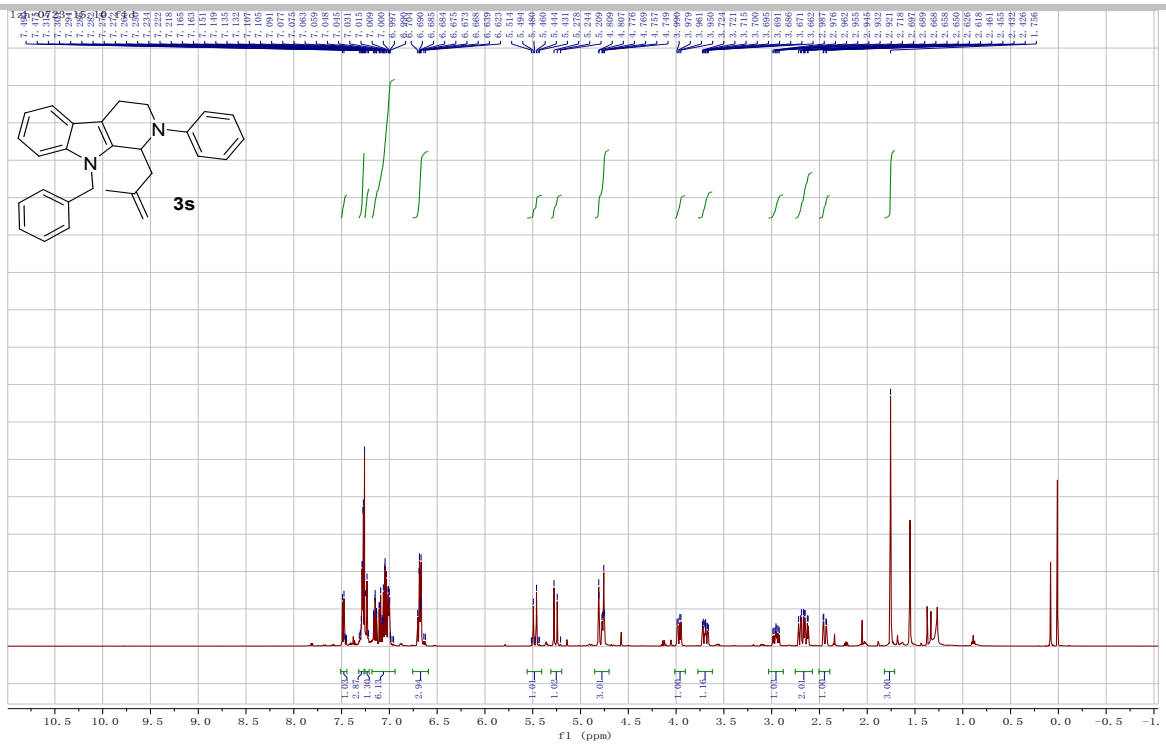
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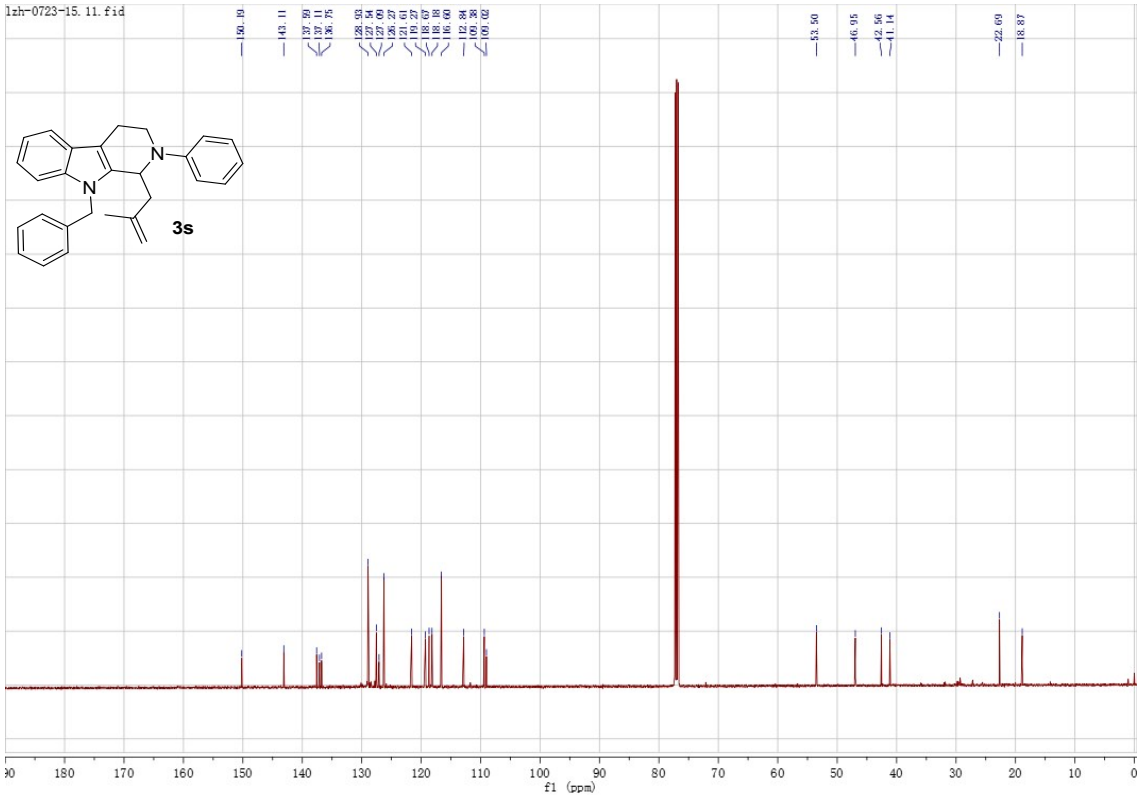
f1 (ppm)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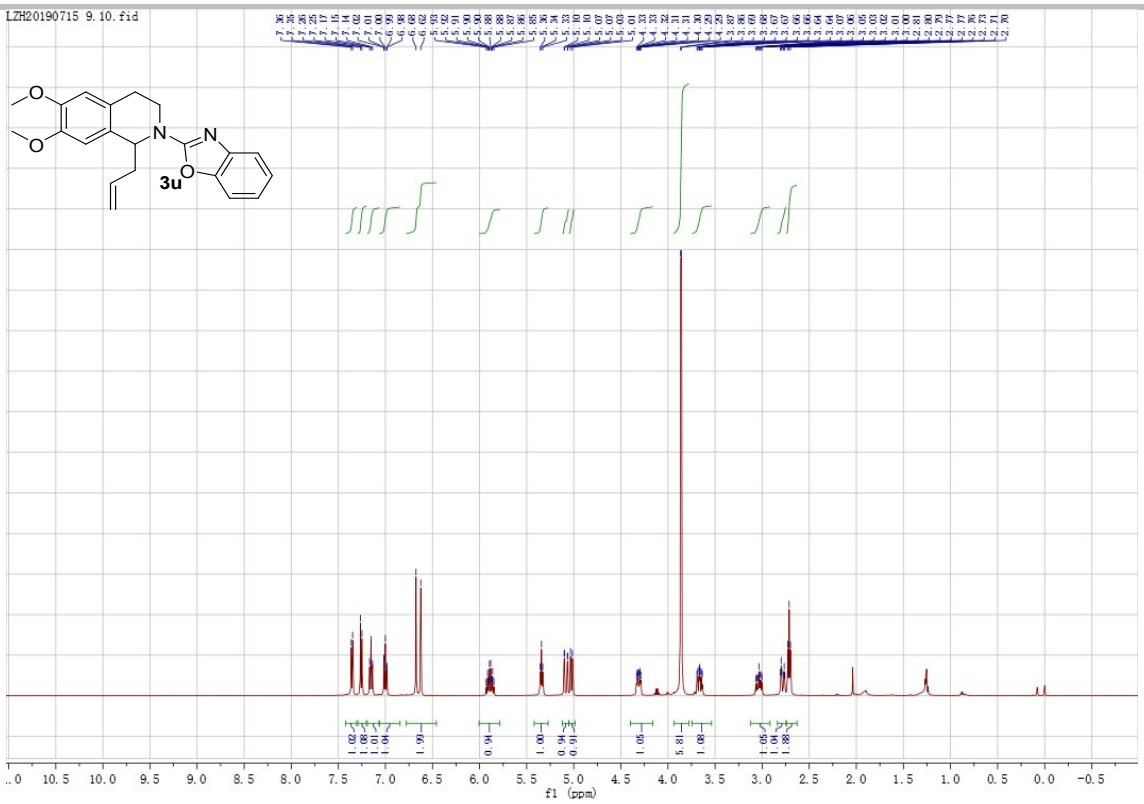
f1 (ppm)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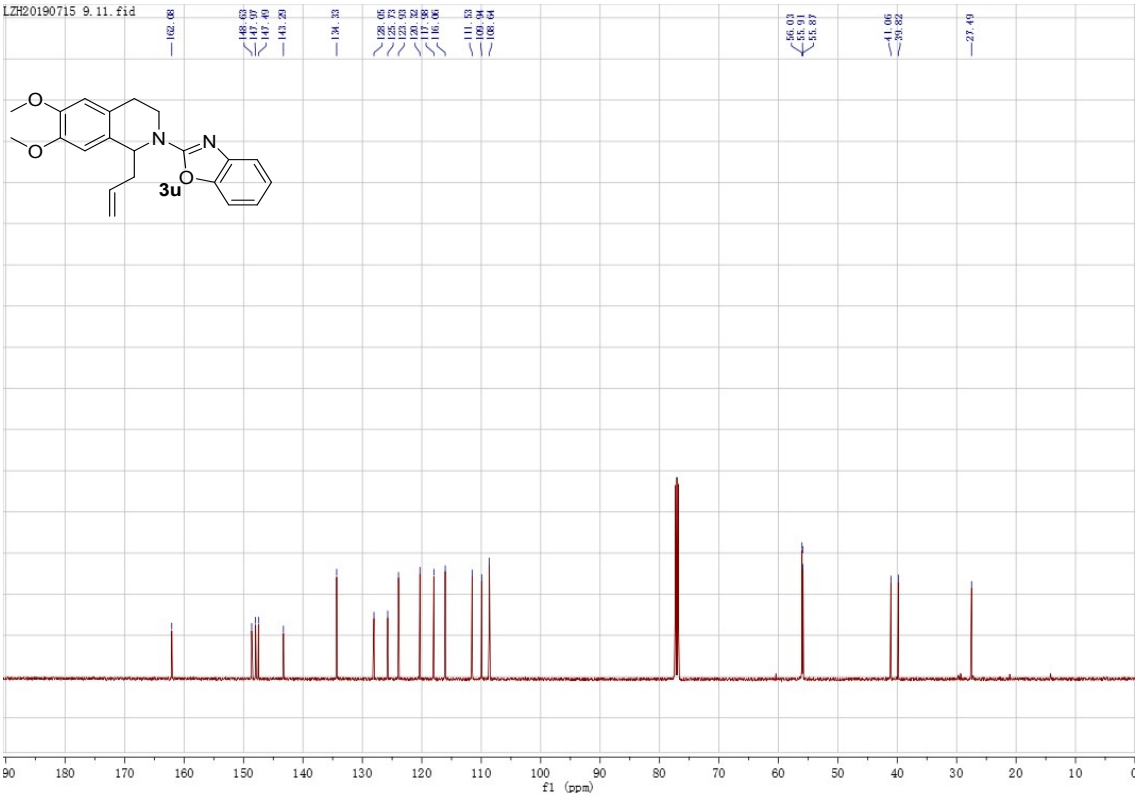
f1 (ppm)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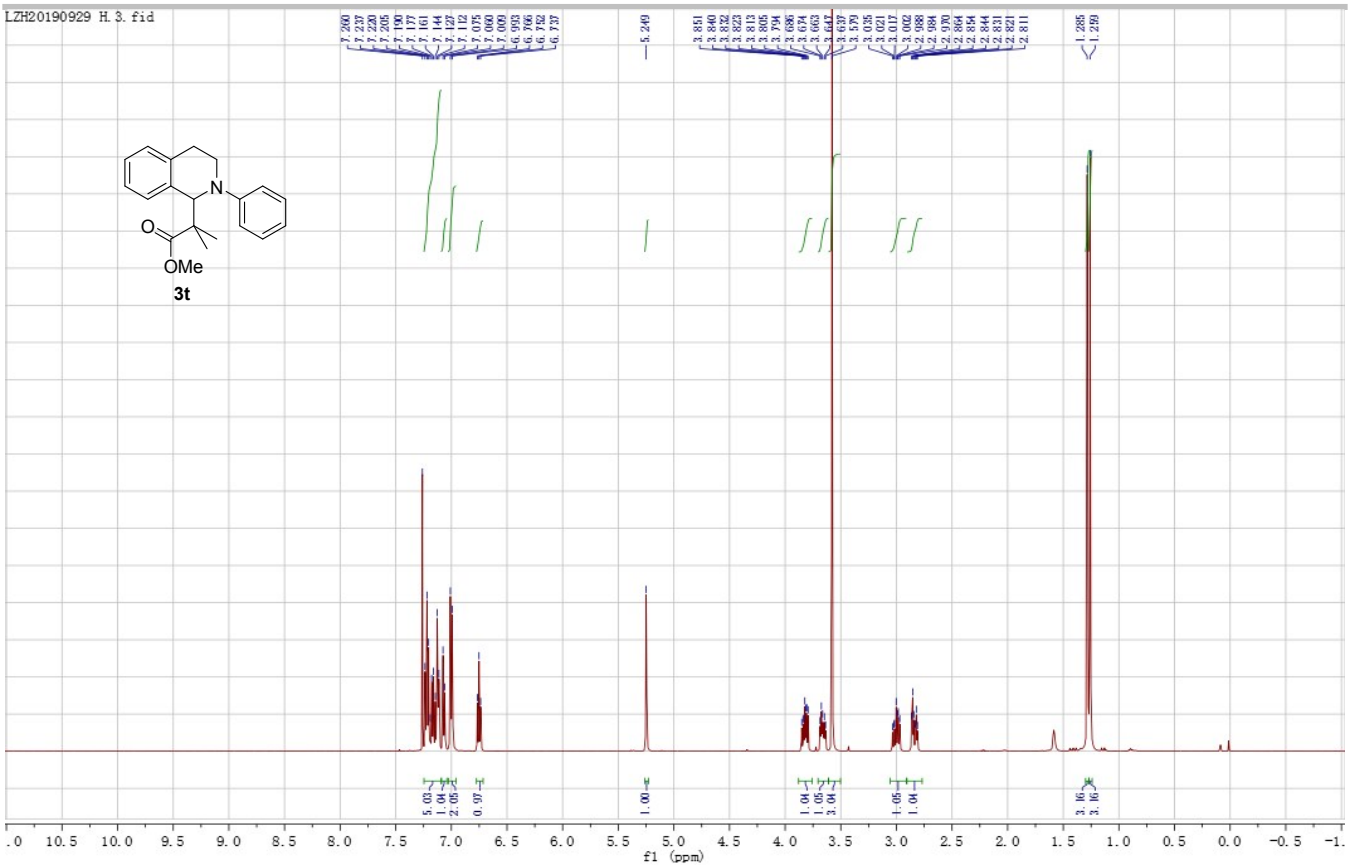
f1 (ppm)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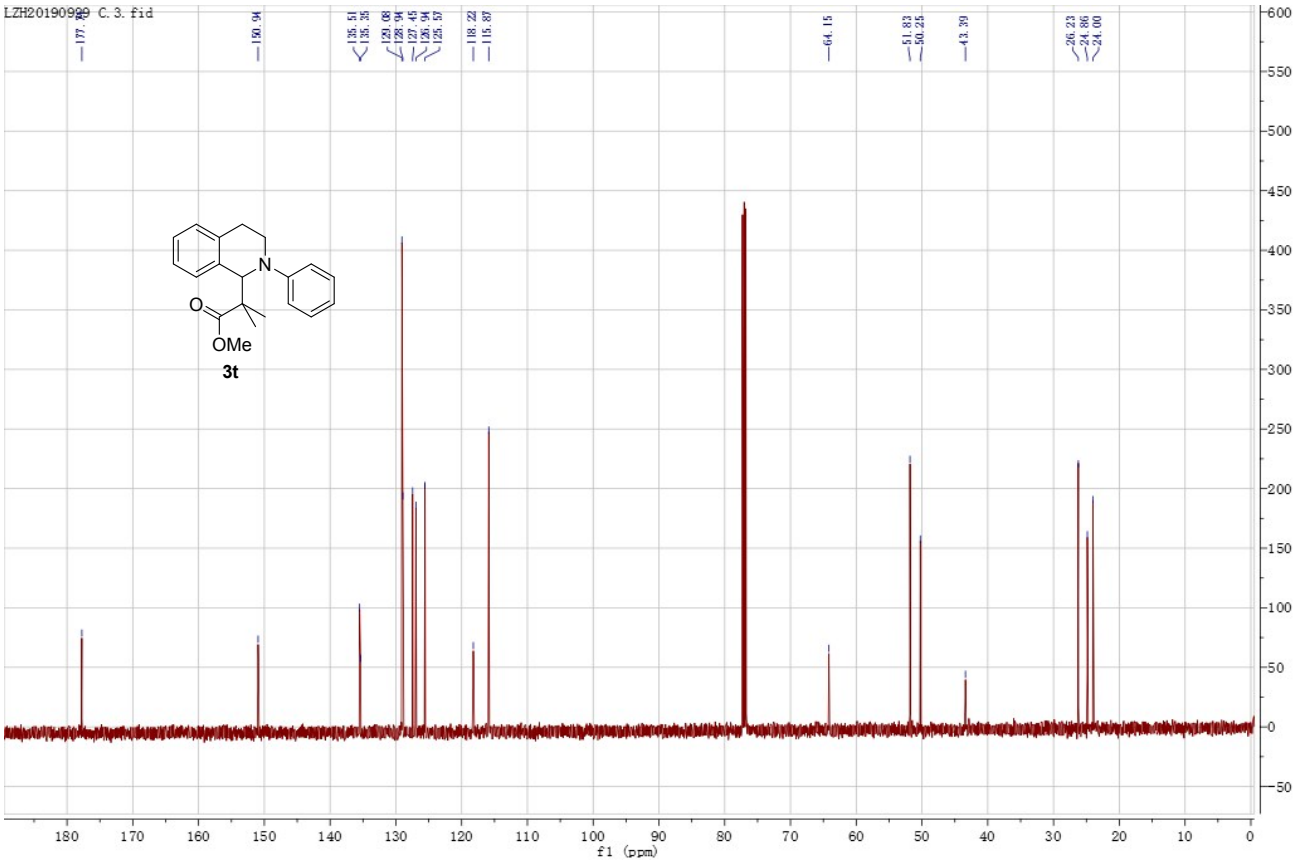
OMe
3t
f1 (ppm)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OMe
3t
f1 (ppm)