

Supporting Information

Asymmetric Aerobic Oxidative Cross-Coupling of
Tetrahydroisoquinolines with Alkynes

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(A) General

¹H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ¹³C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis in comparison with the authentic racemates. Details of the chiral column is as follows: Daicel Chiralcel OD-H (Cellulose tris(3,5-dimethylphenylcarbamate) coated on a silica support), AD-H (Amylose tris(3,5-dimethylphenylcarbamate) coated on a silica support), AS-H (Amylose tris[(S)- α -methylphenylcarbamate] coated on a silica support), OJ-H (Cellulose tris(4-methylbenzoate) coated on a silica support), OB-H (Cellulose triacetate coated on a silica support), IA (Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μ m/3 μ m silica support), IB (Cellulose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μ m/3 μ m silica support), IC (Cellulose tris(3,5-dichlorophenylcarbamate) immobilized on 5 μ m/3 μ m silica support) and ID (Amylose tris(3-chlorophenylcarbamate) immobilized on 5 μ m/3 μ m silica support). Optical rotations were reported as follows: $[\alpha]_D^{25}$ (c: g/100 mL, in solvent). CD spectra (MeOH as the solvent) were determined by Chirascan CD which was purchased from Applied photophysics Ltd. HRMS was recorded on a commercial apparatus (ESI source). All the solvents were purified by usual methods before use. All alkynes were commercial available. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

(B) General procedure for the preparation of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline¹

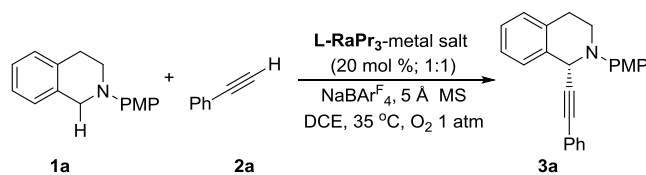
A Schlenk tube containing copper(I) iodide (1.0 mmol) and potassium phosphate (20.0 mmol) was evacuated and back filled with nitrogen. 2-Propanol (10 mL), ethylene glycol (20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (15.0 mmol) and 1-iodo-4-methoxybenzene (15.0 mmol) were added successively at room temperature. The reaction mixture was heated at 85-90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The aqueous layer was extracted with diethyl ether (2 $\times$ 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent. A white solid was obtained.

(C) General procedure for the catalytic asymmetric reaction

In a dry reaction tube I with a magnetic stirring bar, **L-RaPr₃** (0.01 mmol), Zn(NTf₂)₂ (0.01 mmol), and the 5 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 0.5 h under N₂ atmosphere. Next, alkyne **2** (0.06 mmol) were added, and the mixture continued stirring at 35 °C for 0.5 h. After the solvent was removed in vacuo, amines **1** (0.05 mmol) and NaBARF₄ (0.02 mmol) were added to the reaction mixture. Meanwhile, to a dry volumetric flask II, **L-RaPr₃** (0.01 mmol), Fe(OTf)₂ (0.01 mmol) and DCE (0.5 mL) were added and stirred at 35 °C for 2 h. Then the catalyst solution of **L-RaPr₃**/Fe(OTf)₂ (75 μ L) was added to the reaction tube I. Then, DCE (0.1 mL) was added and the reaction was stirred at 35 °C under O₂ (1 atm) for the indicated time. The residue was purified by flash chromatography on silica gel saturated by Et₃N quickly to afford the corresponding products.

(D) Optimization of the reaction conditions

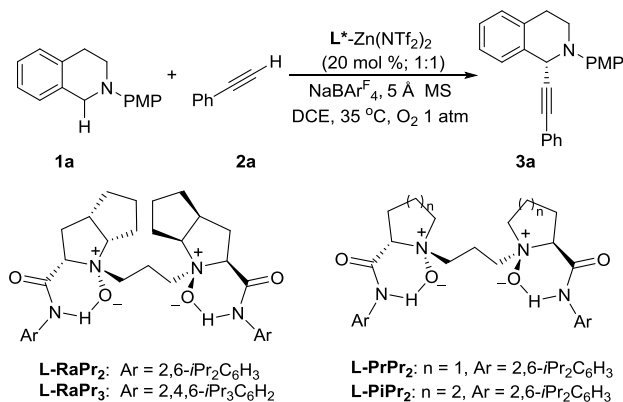
Table S1. Screen of chiral Ligand **L-RaPr₃** with different metal salts.^[a]



entry	metal salt	yield (%) ^[b]	ee (%) ^[c]
1	Cu(OTf) ₂	59	0
2	Ni(OTf) ₂	NR	/
3	In(OTf) ₃	NR	/
4	Fe(OTf) ₂	NR	/
5	Fe(OTf) ₃	NR	/
6	Co(BF ₄) ₂ 6H ₂ O	trace	ND
7	Zn(OTf) ₂	30	88
8	ZnBr ₂	24	0
9	Zn(NTf ₂) ₂	35	95

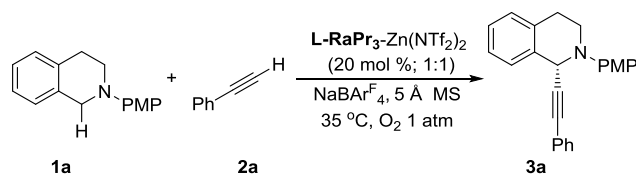
[a] Unless otherwise noted, all reaction were performed with **L-RaPr₃**-metal salt (20 mol %, 1:1), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH.

Table S2. Screen of chiral Ligands.^[a]



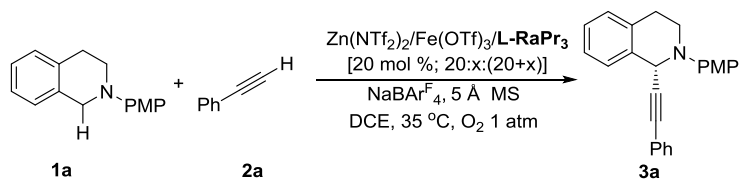
entry	ligand	yield (%) ^[b]	ee (%) ^[c]
1	L-RaPr₃	35	95
2	L-RaPr₂	33	90
3	L-PiPr₂	32	80
4	L-PrPr₂	21	70

[a] Unless otherwise noted, all reaction were performed with **L*-Zn(NTf₂)₂** (20 mol %, 1:1), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH.

Table S3. Screen of reaction solvents.^[a]

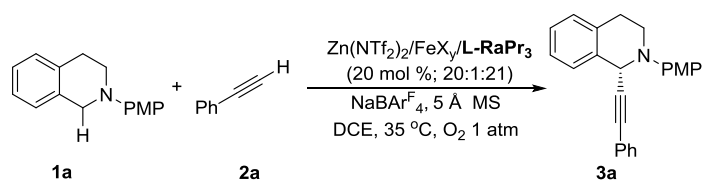
entry	solvent	yield (%) ^[b]	ee (%) ^[c]
1	CH ₂ Cl ₂	30	85
2	CH ₂ ClCH ₂ Cl	35	95
3	CHCl ₂ CHCl ₂	31	89
4	EtOAc	30	61
5	Toluene	35	83
6	THF	12	33

[a] Unless otherwise noted, all reaction were performed with **L-RaPr**₃-Zn(NTf₂)₂ (20 mol %, 1:1), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in solvent (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH.

Table S4. Screen of the Fe(OTf)₃ amount.^[a]

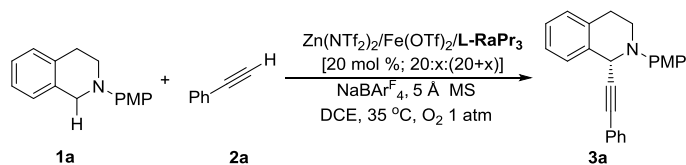
entry	x	yield (%) ^[b]	ee (%) ^[c]
1	20	77	41
2	10	74	50
3	5	75	68
4	2	72	80
5	1	40	90

[a] Unless otherwise noted, all reaction were performed with Zn(NTf₂)₂/Fe(OTf)₃/**L-RaPr**₃ (20 mol %, 20:x:20+x), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH.

Table S5. Screen of the kinds of [Fe].^[a]

entry	FeX _y	yield (%) ^[b]	ee (%) ^[c]
1	Fe(OTf) ₃	40	90
2	FeCl ₃	32	91
3	Fe(OTf) ₂	48	95
4	FeCl ₂	40	95
5	Fe(BF ₄) ₂ · 6H ₂ O	41	94
6	Fe(ClO ₄) ₂ · 6H ₂ O	42	93

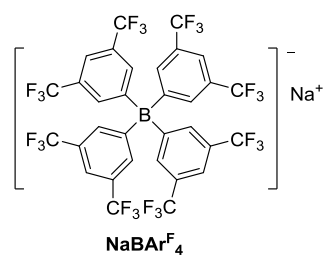
[a] Unless otherwise noted, all reaction were performed with Zn(NTf₂)₂/FeX_y/L-RaPr₃ (20 mol %, 20:1:21), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH.

Table S6. Screen of the reaction details.^[a]

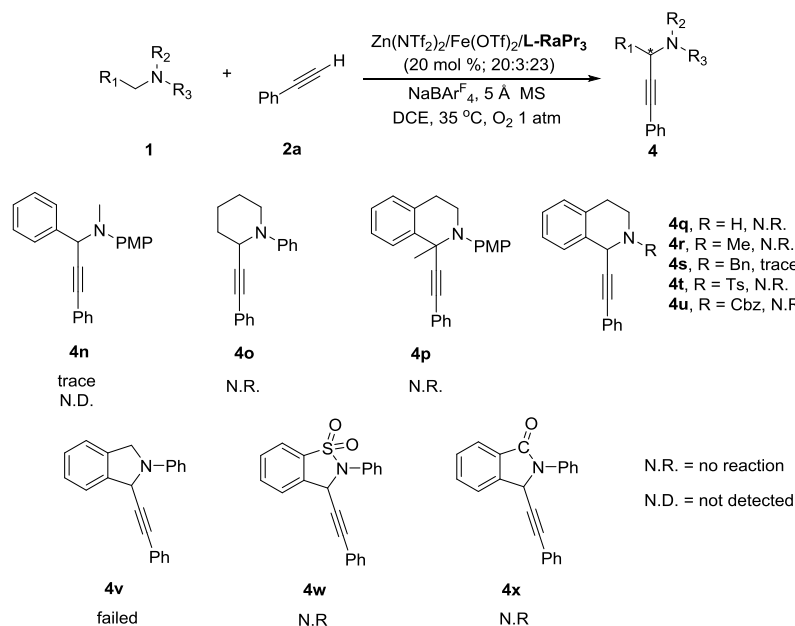
entry	x	yield (%) ^[b]	ee (%) ^[c]
1	1	48	95
2	2	70	88
3	3	78	80
4 ^[d]	2	54	70
5 ^[e]	2	76	67
6 ^[f]	2	68	97
7 ^[f]	3	78	96

[a] Unless otherwise noted, all reaction were performed with Zn(NTf₂)₂/Fe(OTf)₂/L-RaPr₃ (20 mol %, 20:x:20+x), **1a** (0.05 mmol), **2a** (0.06 mmol), NaBARF₄ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.5 mL) at 35 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on Daicel Chiralcel ODH. [d] Without 5 Å MS. [e] Without NaBARF₄. [f] 0.1 mL DCE.

The Structure of NaBARF₄



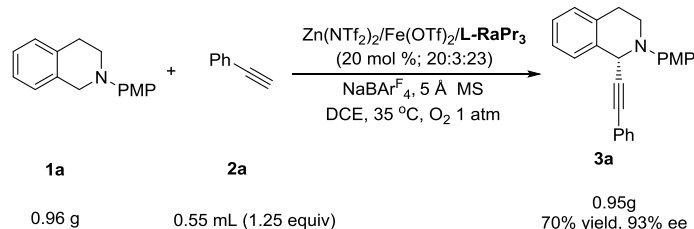
Scheme S1. Unsuccessful substrate scope.^[a]



[a] Unless otherwise noted, all reaction were performed with $\text{Zn}(\text{NTf}_2)_2/\text{Fe}(\text{OTf})_2/\text{L-RaPr}_3$ (20 mol %, 20:3:23), **1** (0.05 mmol), **2a** (0.06 mmol), $\text{NaBAr}^{\text{F}}_4$ (17.6 mg) and molecular sieves (5 Å MS 30 mg) with oxygen balloon (1 atm) in DCE (0.10 mL) at 35 °C for 72 h.

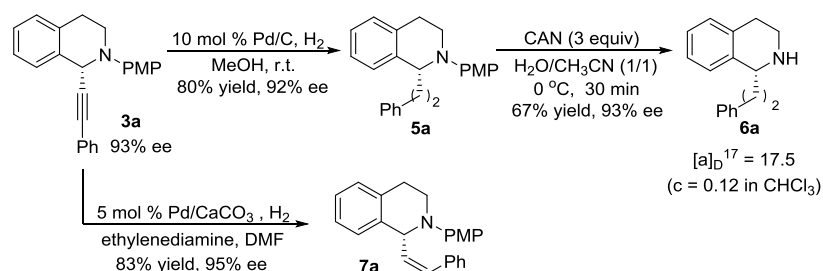
(E) Scaled-Up Version of the Reaction and Synthetic Transformation of the Product

1. Scaled-Up Version of the Reaction



In a dry reaction tube with a magnetic stirring bar, **L-RaPr**₃ (0.80 mmol), $\text{Zn}(\text{NTf}_2)_2$ (0.8 mmol), and the 5 Å MS (2.0 g) in CH_2Cl_2 (5.0 mL) were stirred at 35 °C for 90 min under N_2 atmosphere. Next, alkyne **2a** (5 mmol) were added, and the mixture continued stirring at 35 °C for 1 h. After the solvent was removed in vacuo, amines **1a** (4 mmol) and $\text{NaBAr}^{\text{F}}_4$ (1.408 g) were added to the reaction mixture. Meanwhile, to a dry volumetric flask, **L-RaPr**₃ (0.12 mmol), $\text{Fe}(\text{OTf})_2$ (0.12 mmol) and DCE (0.5 mL) were added and stirred at 35 °C for 2 h. Then the catalyst solution was added to the reaction tube. Then, $\text{CH}_2\text{ClCH}_2\text{Cl}$ (8.0 mL) was added and the reaction was stirred at 35 °C under O_2 (1 atm) for 24 h. The residue was purified by flash chromatography on silica gel saturated by Et_3N quickly to afford the corresponding products.

2. Synthetic Transformation of the Product.



The 1-phenylethynyl substituted THIQs could undergo useful transformations. Reduction of **3a** gave phenethyl substituted **5a** in 80% yield and (Z)-styryl substituted **7a** in 83% yield without loss of enantioselectivity. N-PMP group of tetrahydroisoquinoline derivative could be easily removed by using CAN (ceric ammonium nitrate) in aqueous acetonitrile,² giving the N-protected tetrahydroisoquinoline derivative **6a** in good yield with excellent ee value, which is a valuable and versatile intermediate in organic synthesis.³ The absolute configuration of **6a** was determined to be *R* by comparison the optical rotatory with the previous report.⁴ Thus, it allowed assignment of the absolute configuration of **3a** as *R*-isomer.

Experiments detail:

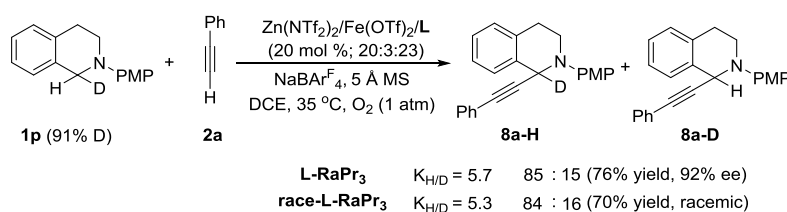
To a solution of alkyne **3a** (0.2 mmol, 93% ee) in MeOH (4 mL), 10 mol % Pd/C (7 mg) was added. The reaction mixture was stirred under H₂ (1 atm) for 4 h. After consumption of **3a** as determined by TLC analysis, the mixture was filtered through a small pad of Celite, which was then washed with ether (20 mL). The filtrate was concentrated, and the crude material was purified by silica gel chromatography to give the compound **5a** (54.9 mg, 80% yield, 92% ee) as colorless oil.

To **5a** (0.1 mmol) in acetonitrile/water (1/1, 2.0 mL) at 0 °C was added ceric ammonium nitrate (0.3 mmol, 3.0 equiv) in acetonitrile/water (1/1, 2.0 mL), and the reaction stirred at 0 °C for 5 min. The reaction mixture was diluted with water (10 mL) and ethyl acetate (10 mL). The aqueous phase was extracted with ethyl acetate (2 × 10 mL), diluted with saturated sodium hydrogen carbonate solution (10 mL) and further extracted with ethyl acetate (2 × 10 mL). The combined organic phases were dried (MgSO₄), concentrated under reduced pressure and the residue purified by flash column chromatography to give the product **6a** (15.9 mg, 67% yield, 93% ee) as a brown oil.

To a solution of **3a** (0.15 mmol) in DMF (1.0 mL) was added ethylenediamine (0.18 mmol) and 5 mol % palladium on calcium carbonate (4.6 mg). The reaction flask was evacuated, purged with H₂ five times, and then stirred under H₂ atmosphere for 1 h. The catalyst was filtered off, and the filtrate was diluted with ethyl acetate. The resulting solution was washed with 2 wt % NH₄Cl and brine and dried over anhydrous Na₂SO₄. The organic solution was concentrated to afford **7a** as a pale yellow oil (42.3 mg, 83% yield, 95% ee).

(F) Study of the mechanism.

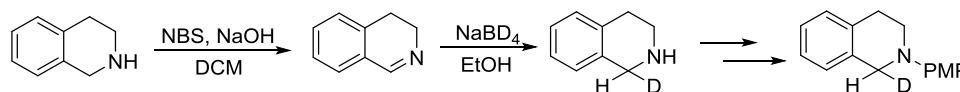
1. Reaction KIE experiments:



To clarify the detailed reaction course, a kinetic isotope effect (KIE) experiment was then conducted. Racemic

monodeuterated substrate **1p** was subjected to the enantiomerically enriched or racemic *N,N'*-dioxide/Zn(II)/Fe(II) catalytic system. Primary KIE value k_H/k_D of 5.7 and 5.3 were calculated for the two cases.

The synthesis of **1p**^{5, 6}



NBS (0.11 mol) was added to a methylene chloride (150 mL) solution containing 1,2,3,4-tetrahydroisoquinoline (0.1 mol) under ice-cooling over 20 minutes. After stirring for 40 minutes, an aqueous 30% sodium hydroxide (65 mL) solution was added to the reaction solution. The organic layer was washed with water and then extracted with a 10% aqueous hydrochloric acid (100 mL). The aqueous layer was washed with methylene chloride, basified with an aqueous ammonia chloride, and then extracted with methylene chloride. The extract was dried over magnesium sulfate and then evaporated. The resulting residue was distilled, to give 3,4-dihydroisoquinoline as an oil. NaBD₄ (55 mmol) was suspended in ethanol (100 mL), and 3,4-dihydroisoquinoline (55 mmol) was added slowly. The resulted reaction mixture was stirred at ambient temperature for an hour and was cooled to below 5 °C, which was then acidified by hydrochloric acid (1 M). After making the solution alkaline by adding sodium hydroxide, it was dried over sodium sulfate and concentrated under a reduced pressure to give 1-deuterated 1,2,3,4-tetrahydroisoquinoline (91% deuteration).

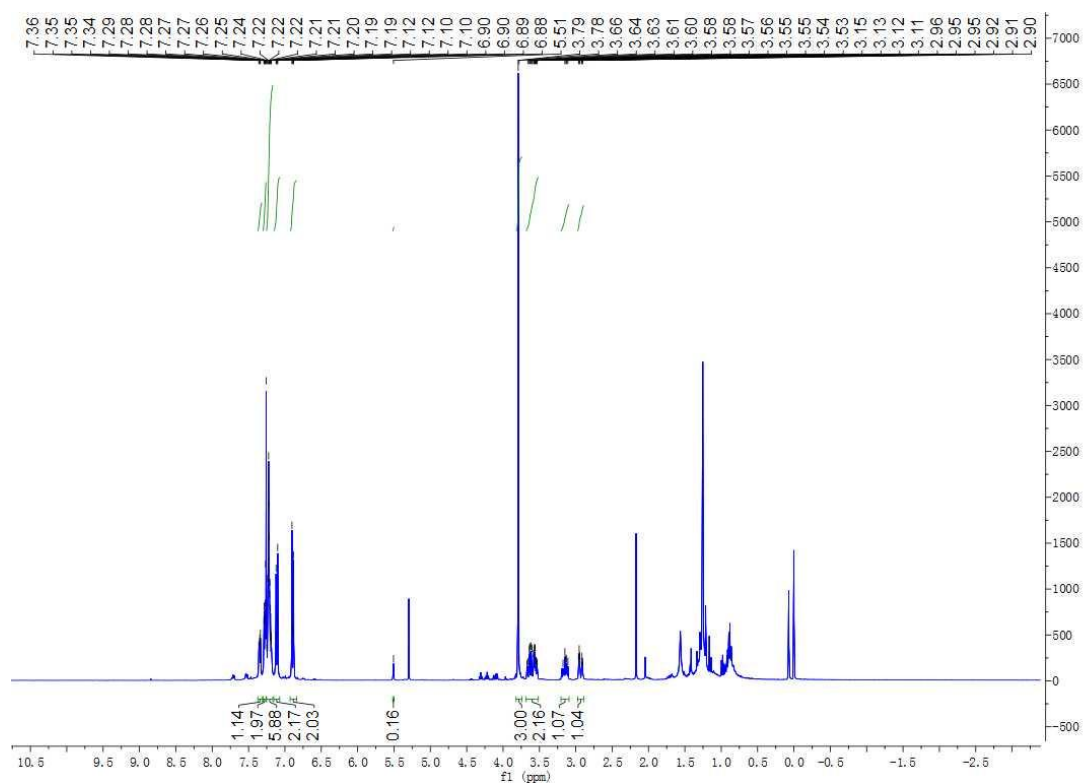
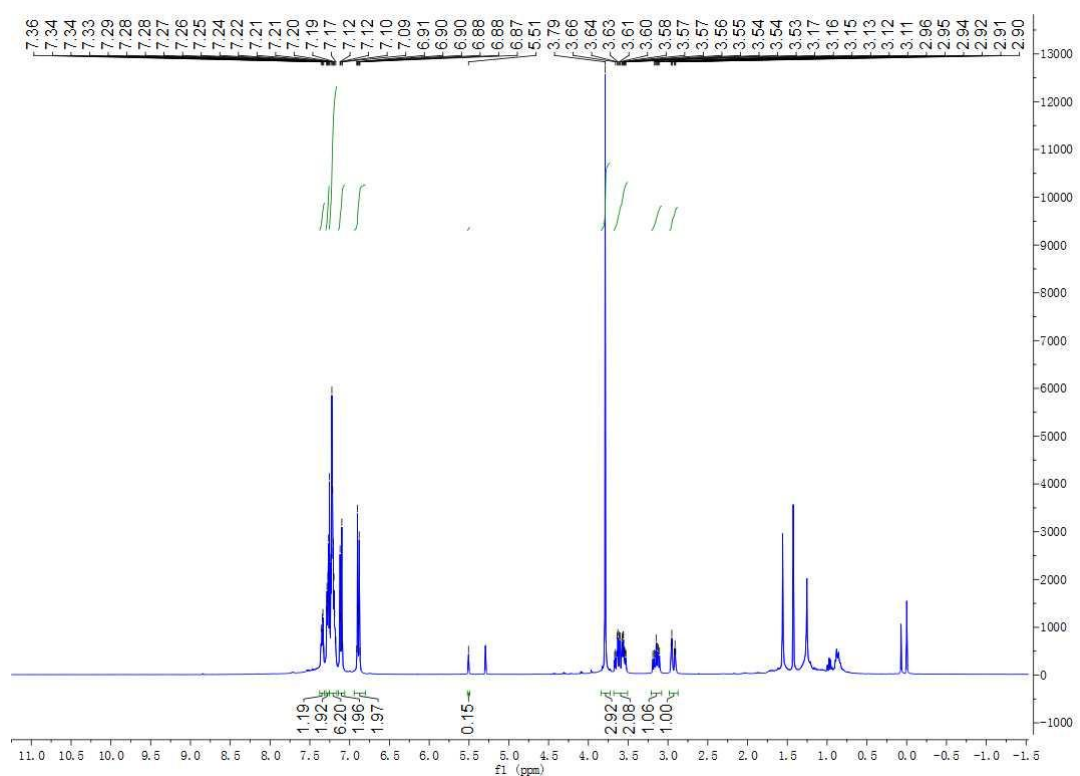
The experimental step

L-RaPr₃ as the ligand: In a dry reaction tube with a magnetic stirring bar, **L-RaPr₃** (20 mol %, 0.01 mmol), Zn(NTf₂)₂ (20 mol %, 0.01 mmol), and the 5 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 30 min under N₂ atmosphere. Next, alkyne **2a** (0.06 mmol) were added, and the mixture continued stirring at 35 °C for 0.5 h. After the solvent was removed in vacuo, amine **1p** (0.05 mmol) and NaBAR^F₄ (40 mol %, 17.6 mg) were added to the reaction mixture. Meanwhile, to a dry volumetric flask, **L-RaPr₃** (0.01 mmol), Fe(OTf)₂ (0.01 mmol) and DCE (0.5 mL) were added and stirred at 35 °C for 2 h. Then the catalyst solution (75 µL) was added to the reaction tube. Then, CH₂ClCH₂Cl (0.1 mL) was added and the reaction was stirred at 35 °C under O₂ (1 atm) for 24h. The residue was purified by flash chromatography on silica gel saturated by Et₃N quickly to afford the corresponding products in 76% yield and 92% ee.

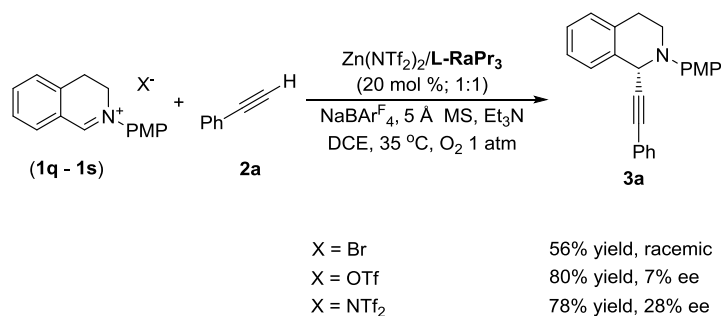
race-L-RaPr₃ as the ligand: The reaction procedure is the same as the above except that racemic ligand as used instead of **L-RaPr₃**.

The $K_{H/D}$ is calculated according to the NMR data.

The NMR data



2. Control experiments⁷

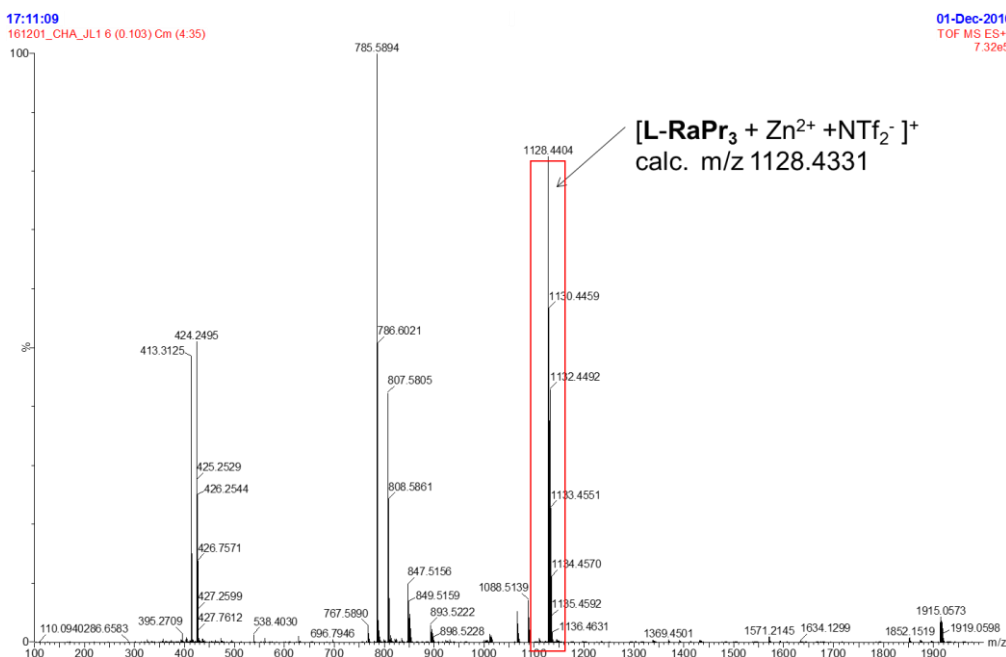


In a dry reaction tube with a magnetic stirring bar, **L-RaPr₃** (0.01 mmol), $\text{Zn}(\text{NTf}_2)_2$ (0.01 mmol), and the 5 Å MS (30 mg) in CH_2Cl_2 (0.5 mL) were stirred at 35 °C for 30 min under N_2 atmosphere. Next, alkyne **2a** (0.06 mmol) were added, and the mixture continued stirring at 35 °C for 0.5 h. After the solvent was removed in vacuo, **1q-1s** (0.05 mmol), NaBARF_4 (0.02 mmol, 17.6 mg) and Et_3N (0.06 mmol) were added to the reaction mixture. Then, $\text{CH}_2\text{ClCH}_2\text{Cl}$ (0.1 mL) was added and the reaction was stirred at 35 °C for 24h. The residue was purified by flash chromatography on silica gel saturated by Et_3N quickly to afford the corresponding products.

3. HRMS analysis

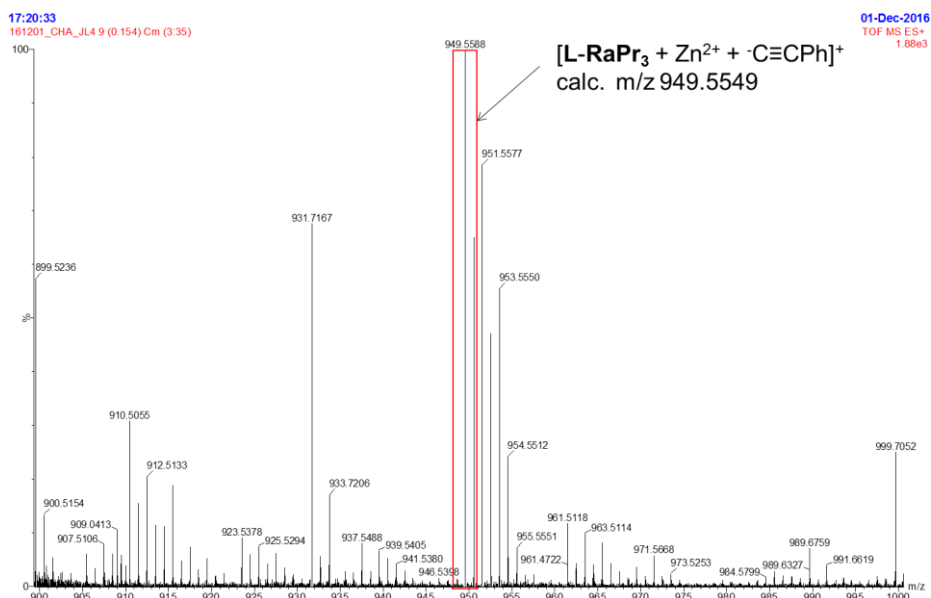
a) The catalyst $\text{L-RaPr}_3\text{-Zn}(\text{NTf}_2)_2$ complex in DCE

$[\text{L-RaPr}_3\text{-Zn}^{2+}\text{-(NTf}_2)_2]^{+}$



b) The intermediate (phenylethynyl)zinc (**II**) coordinate with **L-RaPr₃** in DCE

$[\text{L-RaPr}_3\text{-Zn-C}\equiv\text{CPh}]^{+}$



4. EPR investigations^{8,9}

In order to investigate the involved active oxygen species EPR measurements were performed. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) was used as probe for superoxide radical anion.

For EPR measurements concentrations: THIQ **1a** (0.1 mol L⁻¹), DMPO (1.33 mol L⁻¹), and Zn(NTf₂)₂ (0.02 mol L⁻¹) in DCE. The samples were saturated with oxygen before measuring. The samples were measured at room temperature.

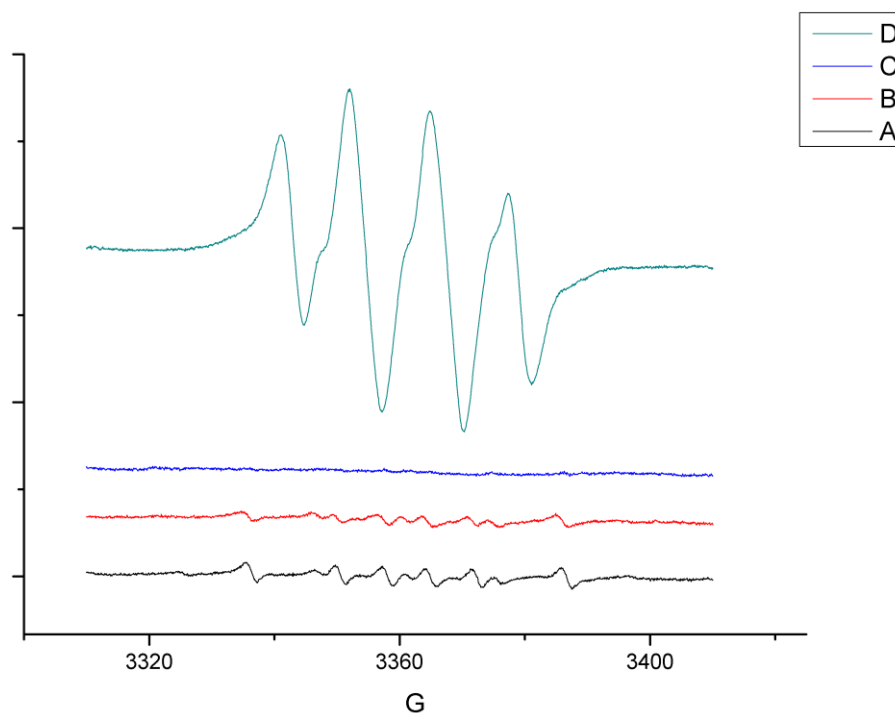


Figure S1. A): EPR spectra of a solution of Zn(NTf₂)₂ (0.02 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; B): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; C): EPR spectra of a solution of DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; D): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), Zn(NTf₂)₂ (0.02 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE.

The superoxide radical anion $O_2^{\cdot-}$ is formed in the presence of **1a** and $Zn(NTf_2)_2$. No $O_2^{\cdot-}$ is generated in the absence of one of them. (**Figure S1. A**)

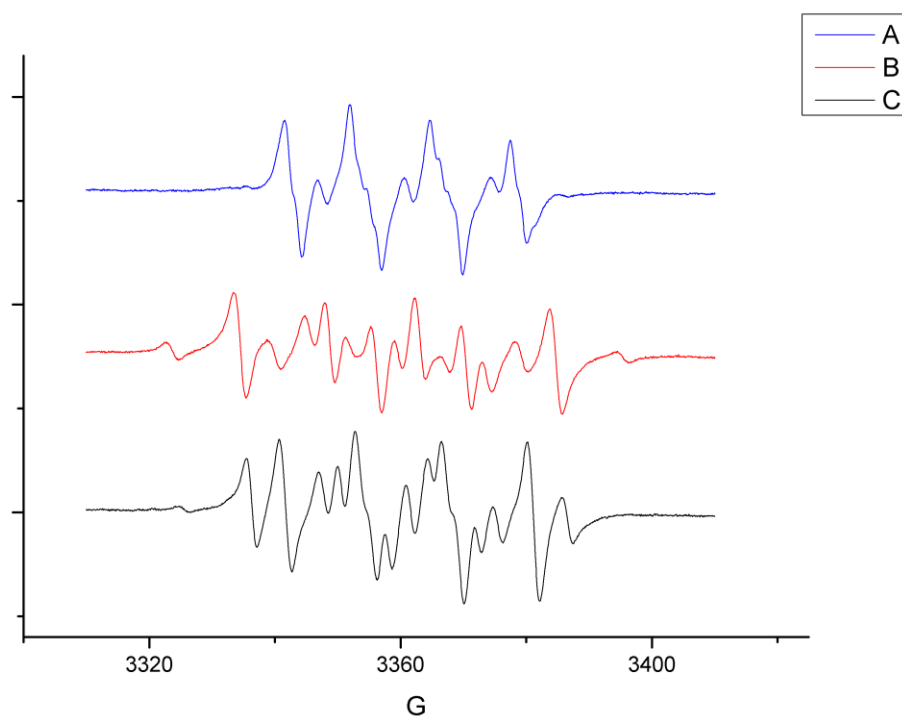


Figure S2. A); EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), $Zn(NTf_2)_2$ (0.02 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; B); EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), $Fe(OTf)_2$ (0.003 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; C); EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), $Zn(NTf_2)_2$ (0.02 mol L⁻¹) $Fe(OTf)_2$ (0.003 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE.

EPR signals appeared if $Fe(OTf)_2$ was added (**Figure S2, B and C**), although the fine structure related to which is not identified, it indicates that iron accelerates the oxidation process.

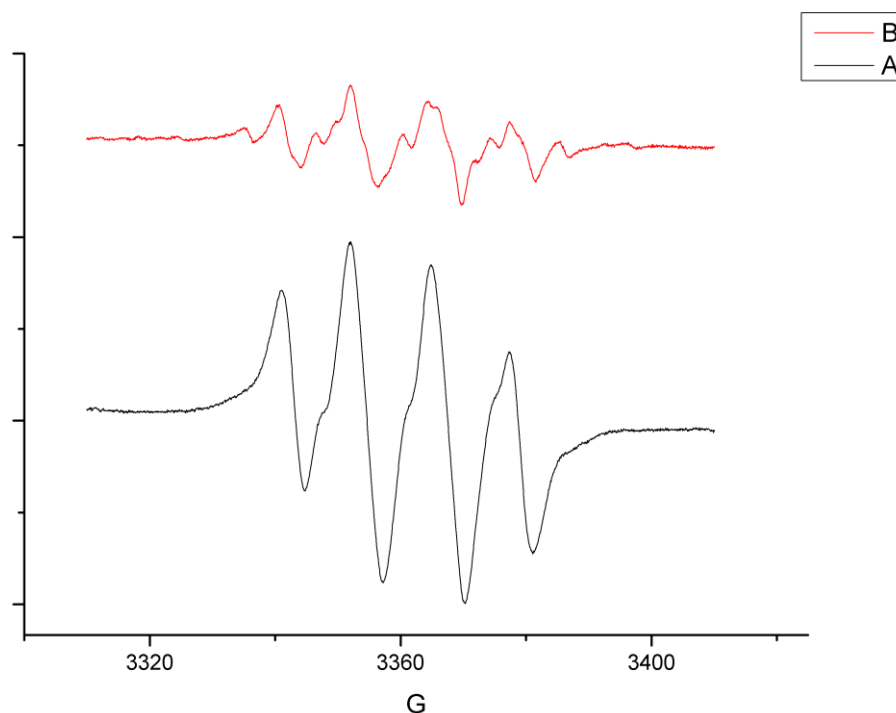


Figure S3. A): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), Zn(NTf₂)₂ (0.02 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE; B): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), Zn(NTf₂)₂ (0.02 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE in the dark.

The samples were kept in the dark and saturated with oxygen before measuring. The samples were measured at room temperature in the dark and during in situ irradiation in the EPR device with natural light.

The formation of O₂⁻ could be confirmed by EPR measurements using the radical trap DMPO. Control experiments showed that O₂⁻ could be formed when both reaction partner are present in the solution upon irradiation with natural light and even in the dark. (**Figure S3.** A and B)

In order to investigate the Fenton-type free-radical pathway HO[•] radical and HOO[•] radical species EPR measurements were performed, DMPO was used as probe for HO[•] radical and HOO[•] radical.

The samples were saturated with oxygen before measuring. The samples were measured at room temperature.

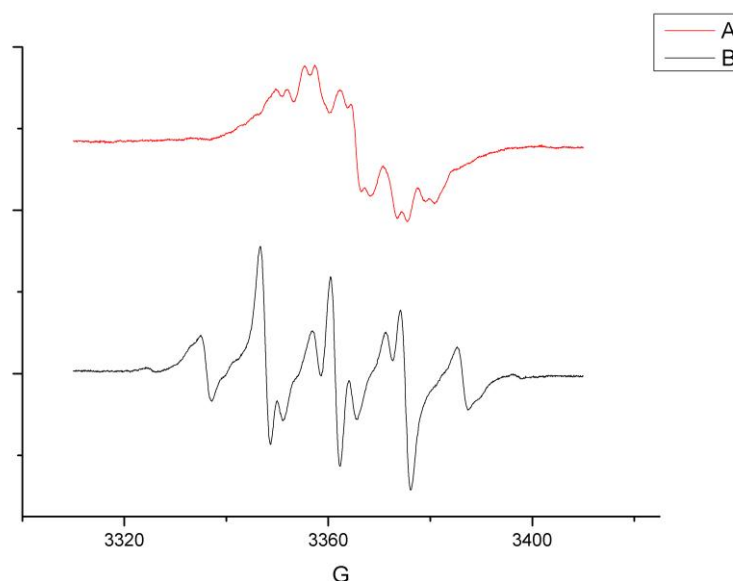
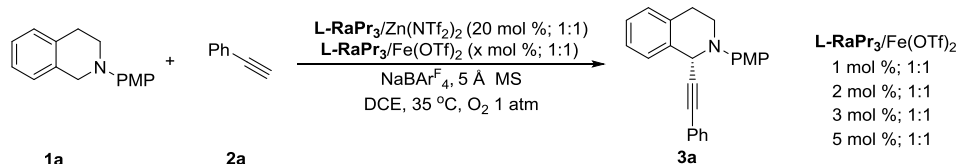


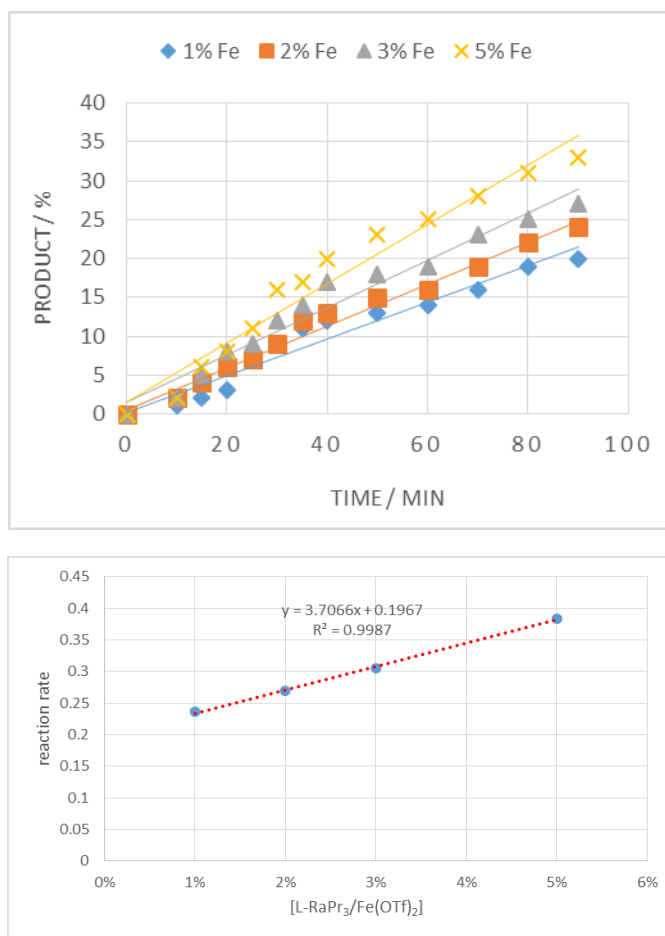
Figure S4. A): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), phenylacetylene **2a** (0.1 mol L⁻¹), Zn(NTf₂)₂ (0.02 mol L⁻¹), Fe(OTf)₂ (0.003 mol L⁻¹), **L-RaPr₃** (0.023 mol L⁻¹) in oxygen-saturated DCE; B): EPR spectra of a solution of THIQ **1a** (0.1 mol L⁻¹), phenylacetylene **2a** (0.1 mol L⁻¹), Zn(NTf₂)₂ (0.02 mol L⁻¹), Fe(OTf)₂ (0.003 mol L⁻¹), **L-RaPr₃** (0.023 mol L⁻¹) and DMPO (1.33 mol L⁻¹) in oxygen-saturated DCE.

5. Kinetic Studies

5.1 Dependence of the reaction rate on the concentration of **L-RaPr₃**/Fe(OTf)₂

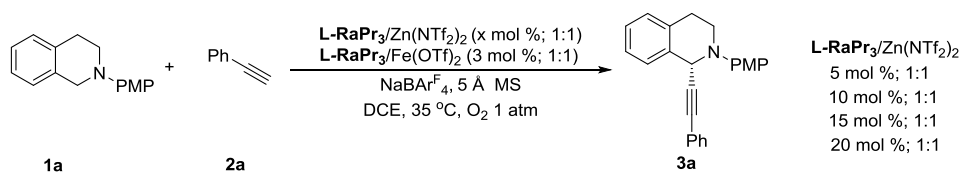


In a dry reaction tube I with a magnetic stirring bar, **L-RaPr₃** (0.01 mmol), Zn(NTf₂)₂ (0.01 mmol), and the 5 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 0.5 h under N₂ atmosphere. Next, alkyne **2** (0.06 mmol) were added, and the mixture continued stirring at 35 °C for 0.5 h. After the solvent was removed in vacuo, amines **1** (0.05 mmol) and NaBARF₄ (0.02 mmol) were added to the reaction mixture. Meanwhile, to a dry volumetric flask II, **L-RaPr₃** (0.01 mmol), Fe(OTf)₂ (0.01 mmol) and DCE (0.5 mL) were added and stirred at 35 °C for 2 h. Then the catalyst solution of **L-RaPr₃**/Fe(OTf)₂ was added to the reaction tube I. Then, DCE (0.5 mL) was added and the reaction was stirred at 35 °C under O₂ (1 atm) for the indicated time. Pass the reaction solution through a small silica gel plug, eluting with ethyl acetate. After removing ethyl acetate, the product yield was confirmed by ¹H NMR using CH₂Br₂ as an internal standard. Kinetic profiles of different initial concentration of **L-RaPr₃**/Fe(OTf)₂ (from 1 mol % to 5 mol %), The plot of *k*_{obs} vs [L-RaPr₃/Fe(OTf)₂] displayed a liner relationship in [L-RaPr₃/Fe(OTf)₂], which indicates a first-order kinetic dependence on [L-RaPr₃/Fe(OTf)₂].



L-RaPr₃/Fe(OTf)₂	reaction rate
1 mol %	0.2359
2 mol %	0.2697
3 mol %	0.3053
5 mol %	0.3836

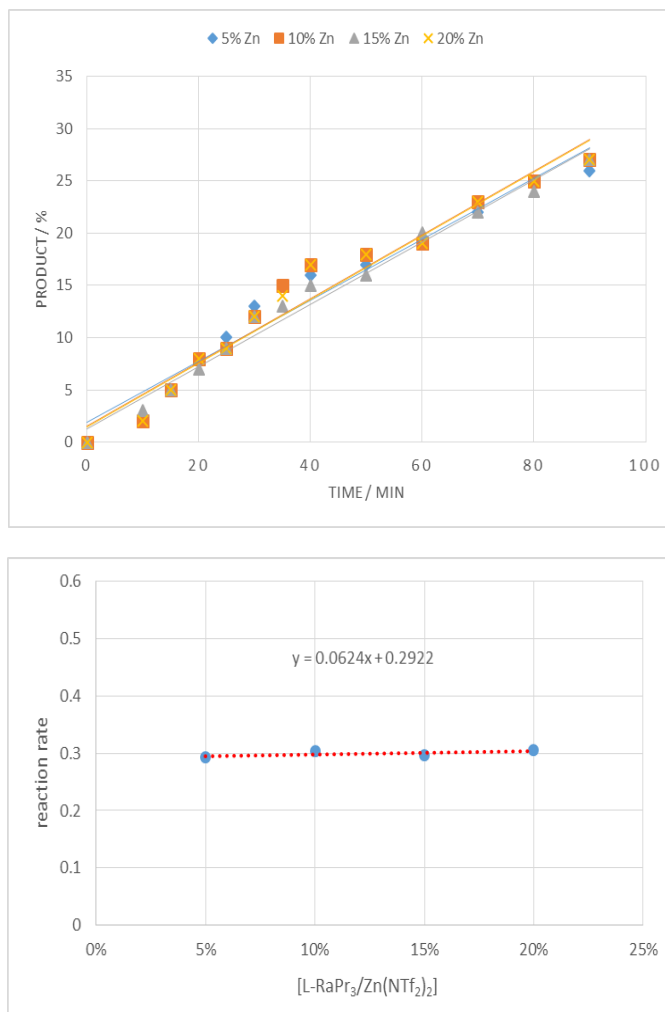
5.2 Dependence of the reaction rate on the concentration of **L-RaPr₃/Zn(NTf₂)₂**



In a dry reaction tube I with a magnetic stirring bar, **L-RaPr₃**, Zn(NTf₂)₂, and the 5 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 0.5 h under N₂ atmosphere. Next, alkyne **2** (0.06 mmol) were added, and the mixture continued stirring at 35 °C for 0.5 h. After the solvent was removed in vacuo, amines **1** (0.05 mmol) and NaBARF₄ (0.02 mmol) were added to the reaction mixture. Meanwhile, to a dry volumetric flask II, **L-RaPr₃** (0.01 mmol), Fe(OTf)₂ (0.01 mmol) and DCE (0.5 mL) were added and stirred at 35 °C for 2 h. Then the catalyst solution of **L-RaPr₃/Fe(OTf)₂** (75uL) was added to the reaction tube I. Then, DCE (0.5 mL) was added and the reaction was stirred at 35 °C under O₂ (1 atm) for the indicated time. Pass the reaction solution through a small silica gel plug, eluting with ethyl acetate. After removing ethyl acetate, the product yield was confirmed by ¹H NMR using CH₂Br₂ as an internal standard.

Kinetic profiles of different initial concentration of **L-RaPr₃/Zn(NTf₂)₂** (from 5 mol % to 20 mol %), The plot of k_{obs} vs

[L-RaPr₃/Zn(NTf₂)₂] displayed a linear relationship in [L-RaPr₃/Zn(NTf₂)₂], which indicates a zero-order kinetic dependence on [L-RaPr₃/Zn(NTf₂)₂].



L-RaPr ₃ /Zn(NTf ₂) ₂	reaction rate
5 mol %	0.2925
10 mol %	0.3047
15 mol %	0.2975
20 mol %	0.3053

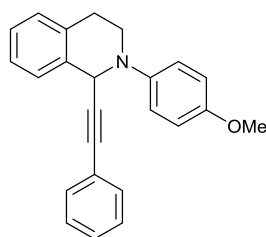
(G) References

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- (4). Xie, J.-H.; Yan, P.-C.; Zhang, Q.-Q.; Yuan, K.-X.; Zhou, Q.-L. *ACS Catal.* **2012**, *2*, 561-564.

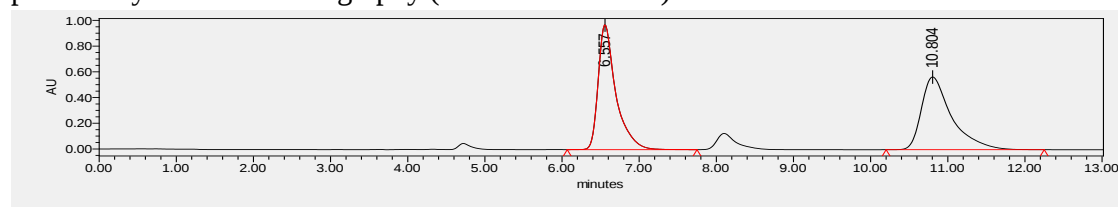
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(H) The analytical and spectral characterization data of the products

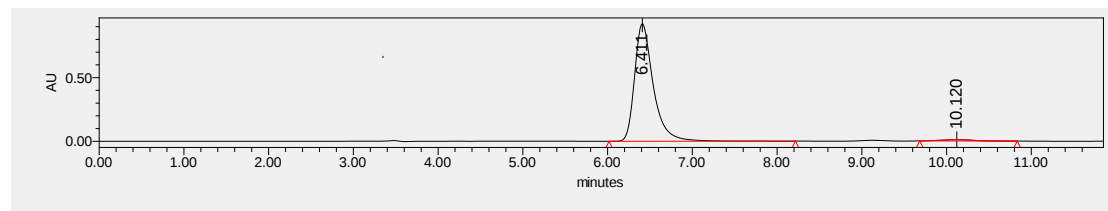
2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (3a)



Colorless oil; 78% yield, 96 ee. $[\alpha]_D^{26} = -183.5$ ($c = 0.18$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.41 min (major), 10.12 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 1H), 7.27 (m, 2H), 7.23 – 7.16 (m, 6H), 7.13 – 7.07 (m, 2H), 6.91 – 6.85 (m, 2H), 5.50 (s, 1H), 3.78 (s, 3H), 3.67 – 3.50 (m, 2H), 3.14 (m, 1H), 2.97 – 2.87 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.29, 144.19, 135.48, 134.08, 131.73, 129.11, 128.11, 128.01, 127.54, 127.18, 126.16, 123.10, 120.23, 114.40, 88.50, 85.54, 55.60, 54.44, 44.26, 29.08. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{22}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 340.1696, Found: 340.1703. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

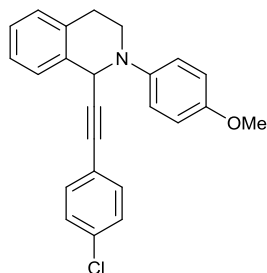


	Retention Time	Area	% Area
1	6.557	15389957	50.38
2	10.804	15157189	49.62



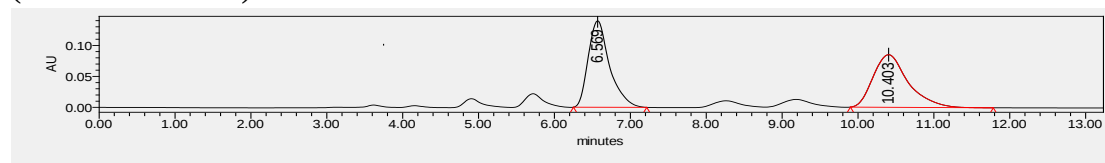
	Retention Time	Area	% Area
1	6.411	14101804	98.37
2	10.120	233364	1.63

1-((4-chlorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3b)

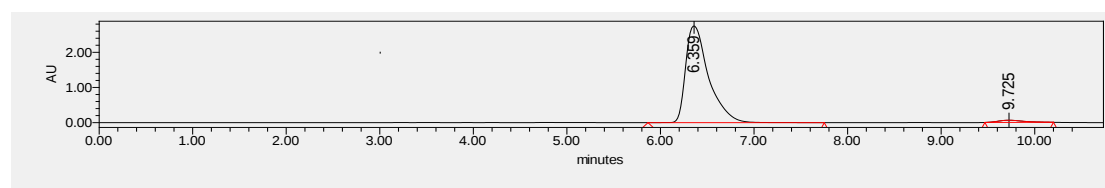


Colorless oil; 74% yield, 96 ee. $[\alpha]_D^{26} = -179.8$ ($c = 0.11$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.36 min (major), 9.73 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.32 (m, 1H), 7.25 – 7.16 (m, 7H), 7.09 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 5.49 (s, 1H), 3.79 (s, 3H), 3.66 – 3.50 (m, 2H), 3.14 (m, 1H), 2.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.34, 144.08, 135.19, 134.08, 133.97, 132.93, 129.11, 128.40, 127.46, 127.23, 126.17, 121.56, 120.16, 114.41, 89.56,

84.38, 55.59, 54.42, 44.24, 29.01. HRMS (ESI-TOF) calcd for $C_{24}H_{21}^{35}ClNO$ ($[M+H]^+$) = 374.1307, Found: 374.1310, HRMS (ESI-TOF) calcd for $C_{24}H_{21}^{37}ClNO$ ($[M+H]^+$) = 376.1277, Found: 376.1302. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

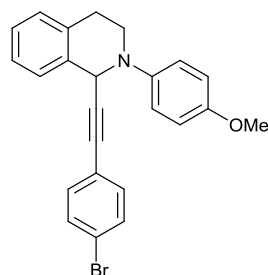


	Retention Time	Area	% Area
1	6.569	2789526	50.89
2	10.403	2692322	49.11



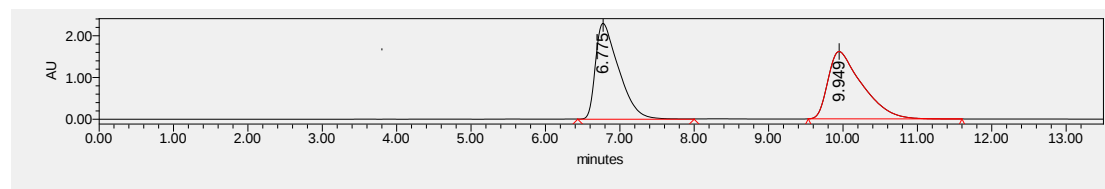
	Retention Time	Area	% Area
1	6.359	46478614	98.34
2	9.725	783068	1.66

1-((4-bromophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3c)

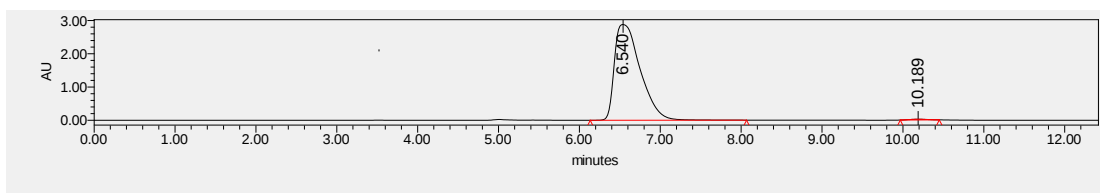


Colorless oil; 73% yield, 99 ee. $[\alpha]_D^{26} = -130.4$ ($c = 0.17$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.54 min (minor), 10.19 min (major). 1H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, $J = 6.8$ Hz, 3H), 7.26 – 7.18 (m, 3H), 7.10 (m, 4H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.48 (s, 1H), 3.78 (s, 3H), 3.65 – 3.49 (m, 2H), 3.14 (m, 1H), 2.98 – 2.87 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.35, 144.07, 135.15, 134.08, 133.16, 131.33, 129.12, 127.46, 127.24, 126.17, 122.17, 122.03, 120.17, 114.42, 89.77, 84.44, 55.60, 54.45, 44.25, 29.01. HRMS (ESI-TOF) calcd for $C_{24}H_{21}^{79}BrNO$ ($[M+H]^+$) = 418.0802, Found: 418.0803, $C_{24}H_{21}^{81}BrNO$ ($[M+H]^+$) = 420.0781, Found: 420.0789. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

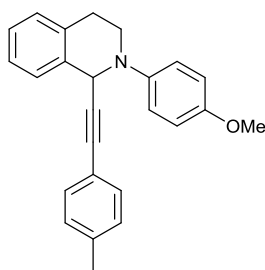


	Retention Time	Area	% Area
1	6.775	50171936	48.76
2	9.949	52721880	51.24

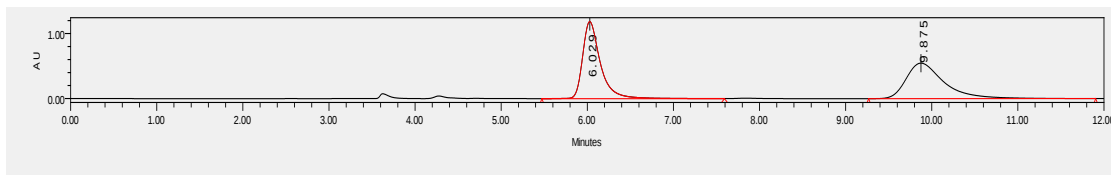


	Retention Time	Area	% Area
1	6.540	63776281	99.42
2	10.189	371738	0.58

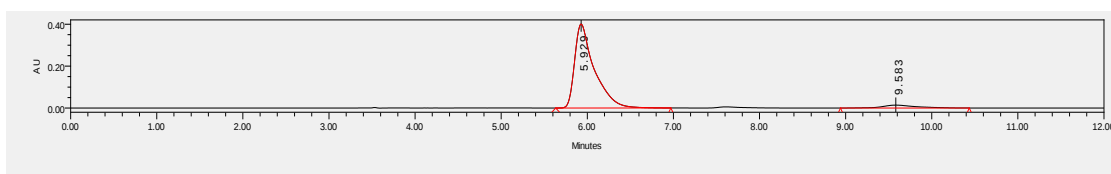
2-(4-methoxyphenyl)-1-(p-tolylethynyl)-1,2,3,4-tetrahydroisoquinoline (3d)



Yellow oil; 74% yield, 92 ee. $[\alpha]_D^{25} = -169.5$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.93 min (major), 9.58 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.31 (m, 1H), 7.25 – 7.14 (m, 5H), 7.13 – 7.08 (m, 2H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.89 (m, 2H), 5.49 (s, 1H), 3.78 (s, 3H), 3.69 – 3.59 (m, 1H), 3.55 (m, 1H), 3.11 (m, 1H), 2.92 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.25, 144.22, 138.01, 135.63, 134.06, 131.59, 129.05, 128.82, 127.52, 127.09, 126.10, 120.20, 120.03, 114.38, 87.72, 85.60, 55.59, 54.42, 44.26, 29.06, 21.41. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 354.1853, Found: 354.1864. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

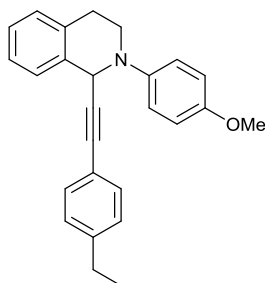


	Retention Time	Area	% Area
1	6.029	16935119	50.32
2	9.875	16719434	49.68



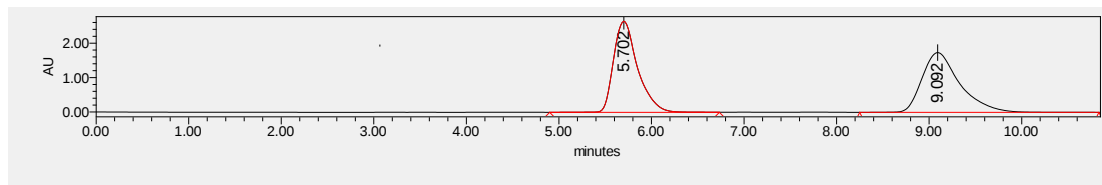
	Retention Time	Area	% Area
1	5.929	6343980	95.79
2	9.583	278947	4.21

1-((4-ethylphenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3e)

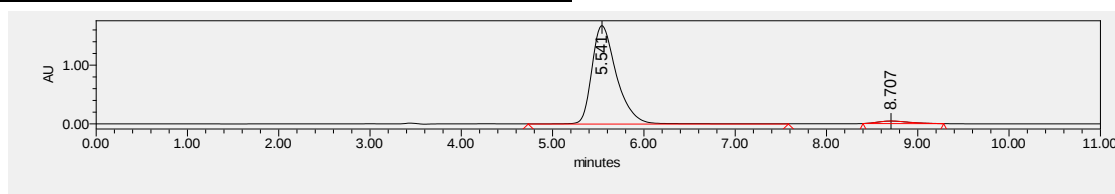


Yellow oil; 76% yield, 95 ee. $[\alpha]_D^{26} = -101.9$ ($c = 0.16$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.54 min (major), 8.71 min (minor). ^1H NMR (400 MHz, CDCl_3) δ

7.34 (m, 1H), 7.18 (m, 5H), 7.13 – 7.07 (m, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 6.91 – 6.84 (m, 2H), 5.49 (s, 1H), 3.76 (s, 3H), 3.67 – 3.58 (m, 1H), 3.57 – 3.48 (m, 1H), 3.13 (m, 1H), 2.95 – 2.86 (m, 1H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.16 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.27, 144.40, 144.25, 135.65, 134.08, 131.73, 129.10, 127.69, 127.58, 127.14, 126.15, 120.29, 120.26, 114.39, 87.77, 85.68, 55.60, 54.47, 44.28, 29.11, 28.81, 15.46. HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{26}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 368.2009, Found: 368.2008; The product was purified by flash chromatography (Pet/EtOAc = 20:1).

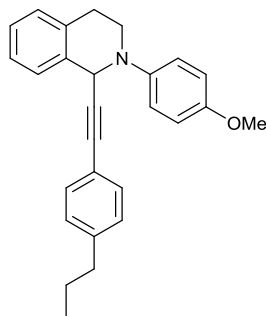


	Retention Time	Area	% Area
1	5.702	47693382	49.27
2	9.092	49112739	50.73

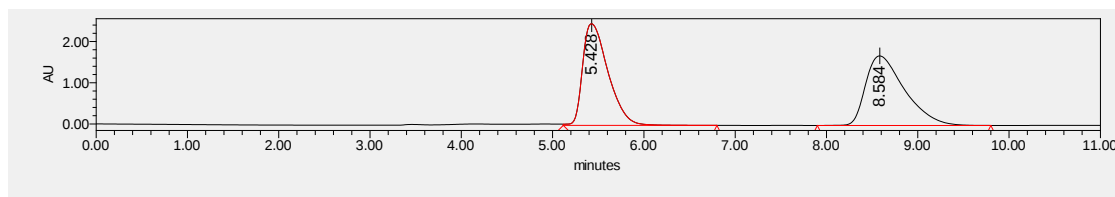


	Retention Time	Area	% Area
1	5.541	31764558	97.44
2	8.707	835007	2.56

2-(4-methoxyphenyl)-1-((4-propylphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3f)

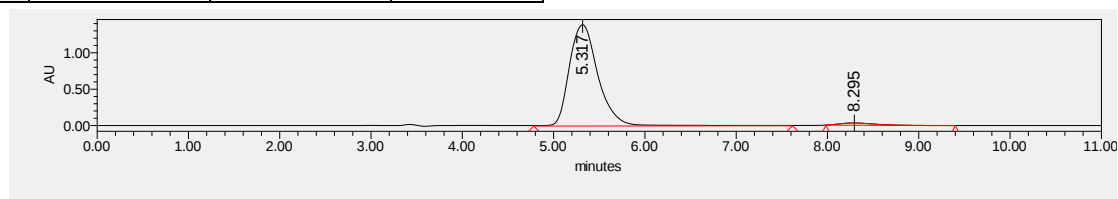


Yellow oil; 72% yield, 95 ee. $[\alpha]_{\text{D}}^{25} = -126.7$ ($c = 0.18$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.32 min (minor), 8.30 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 1H), 7.23 – 7.13 (m, 5H), 7.10 (d, $J = 8.9$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 5.49 (s, 1H), 3.75 (d, $J = 3.2$ Hz, 3H), 3.62 (m, 1H), 3.52 (m, 1H), 3.12 (m, 1H), 2.92 (t, $J = 16.0$ Hz, 1H), 2.49 (t, $J = 7.6$ Hz, 2H), 1.55 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.23, 144.22, 142.81, 135.63, 134.03, 131.58, 129.03, 128.23, 127.51, 127.07, 126.08, 120.18, 114.37, 87.72, 85.65, 55.59, 54.40, 44.24, 37.88, 29.06, 24.33, 13.69. HRMS (ESI-TOF) calcd for $\text{C}_{27}\text{H}_{28}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 382.2166, Found: 382.2170. The product was purified by flash chromatography (Pet/EtOAc = 20:1).



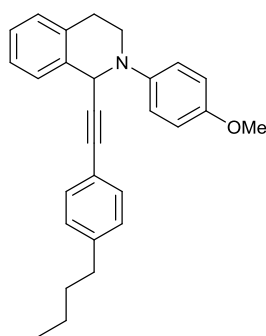
	Retention Time	Area	% Area
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1	5.428	47613434	48.85
2	8.584	49850888	51.15

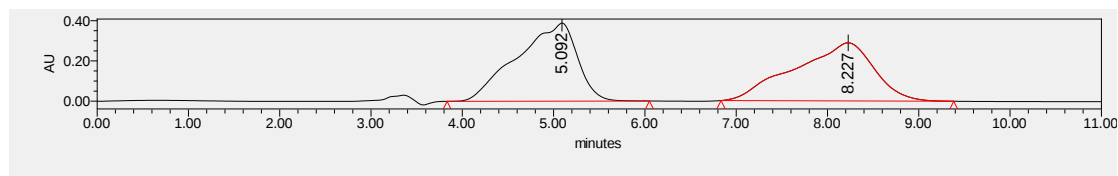


	Retention Time	Area	% Area
1	5.317	29702139	97.84
2	8.295	656543	2.16

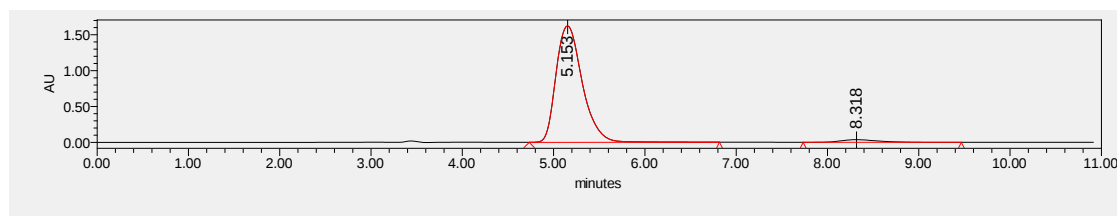
1-((4-butylphenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3g)



Colorless oil; 73% yield, 96 ee. $[\alpha]_D^{25} = -229.8$ ($c = 0.09$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.15 min (major), 8.32 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.31 (m, 1H), 7.27 – 7.16 (m, 5H), 7.10 (t, $J = 6.4$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 9.2$ Hz, 2H), 5.49 (s, 1H), 3.78 (s, 3H), 3.69 – 3.50 (m, 2H), 3.20 – 3.08 (m, 1H), 2.98 – 2.87 (m, 1H), 2.60 – 2.49 (m, 2H), 1.54 (m, 2H), 1.30 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.24, 144.23, 143.05, 135.64, 134.04, 131.60, 129.04, 128.19, 127.52, 127.07, 126.09, 120.18, 114.38, 87.72, 85.66, 55.59, 54.41, 44.25, 35.51, 33.39, 29.07, 22.25, 13.90. HRMS (ESI-TOF) calcd for $\text{C}_{28}\text{H}_{30}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 396.2322, Found: 396.2321. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

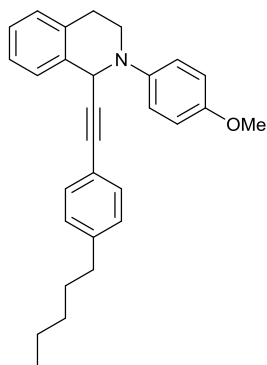


	Retention Time	Area	% Area
1	5.092	17742016	50.34
2	8.227	17505843	49.66

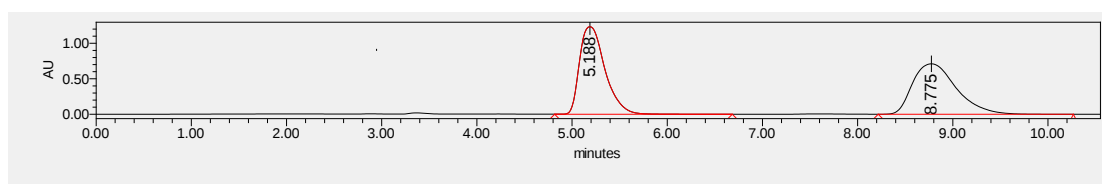


	Retention Time	Area	% Area
1	5.153	32212579	98.09
2	8.318	627753	1.91

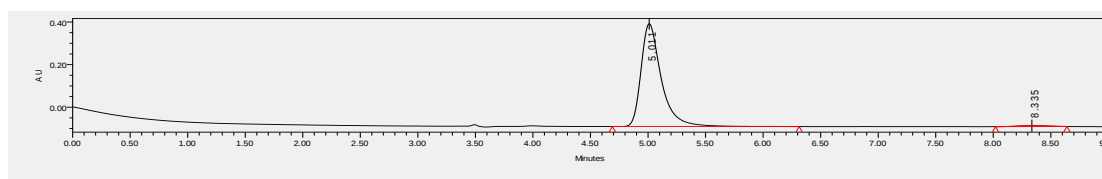
2-(4-methoxyphenyl)-1-((4-pentylphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3h)



Yellow oil; 68% yield, 96 ee. $[\alpha]_D^{21} = -83.3$ ($c = 0.14$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.01 min (major), 8.34 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.31 (m, 1H), 7.24 – 7.15 (m, 5H), 7.13 – 7.08 (m, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.89 (m, 2H), 5.49 (s, 1H), 3.79 (s, 3H), 3.68 – 3.59 (m, 1H), 3.55 (m, 1H), 3.12 (m, 1H), 2.93 (m, 1H), 2.58 – 2.49 (m, 2H), 1.57 (d, $J = 7.6$ Hz, 2H), 1.30 – 1.24 (m, 4H), 0.86 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.23, 144.22, 143.07, 135.64, 134.03, 131.58, 129.02, 128.17, 127.51, 127.06, 126.08, 120.16, 114.37, 87.71, 85.65, 55.59, 54.39, 44.24, 35.78, 31.37, 30.90, 29.06, 22.48, 13.98. HRMS (ESI-TOF) calcd for $\text{C}_{29}\text{H}_{32}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 410.2479, Found: 410.2486. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

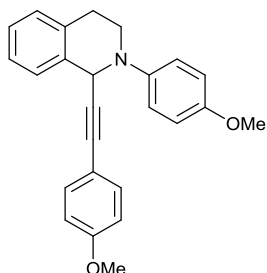


	Retention Time	Area	% Area
1	5.188	22832126	50.12
2	8.775	22718829	49.88

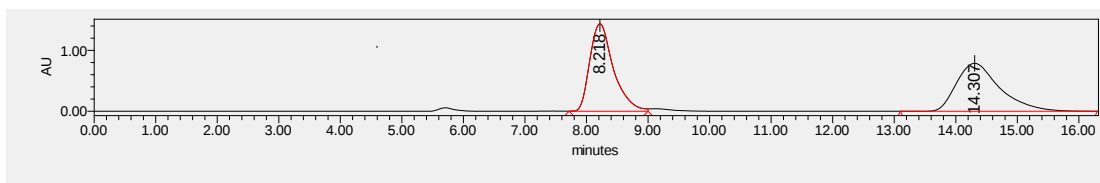


	Retention Time	Area	% Area
1	5.011	5903147	98.69
2	8.335	78342	1.31

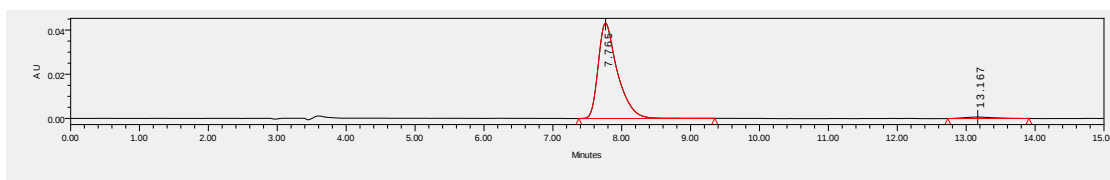
2-(4-methoxyphenyl)-1-((4-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3i)



Colorless oil; 75% yield, 96 ee. $[\alpha]_D^{18} = -103.6$ ($c = 0.14$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.77 min (minor), 13.17 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 1H), 7.24 – 7.15 (m, 5H), 7.14 – 7.07 (m, 2H), 6.92 – 6.85 (m, 2H), 6.78 – 6.69 (m, 2H), 5.49 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.67 – 3.58 (m, 1H), 3.57 – 3.50 (m, 1H), 3.13 (m, 1H), 2.97 – 2.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.36, 154.21, 144.23, 135.70, 134.05, 133.13, 129.08, 127.54, 127.09, 126.12, 120.18, 115.23, 114.36, 113.71, 86.97, 85.35, 55.59, 55.25, 54.40, 44.24, 29.06. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}^+]$) = 370.1802, Found: 370.1808. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

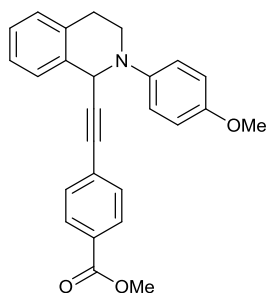


	Retention Time	Area	% Area
1	8.218	38424823	49.97
2	14.307	38470103	50.03

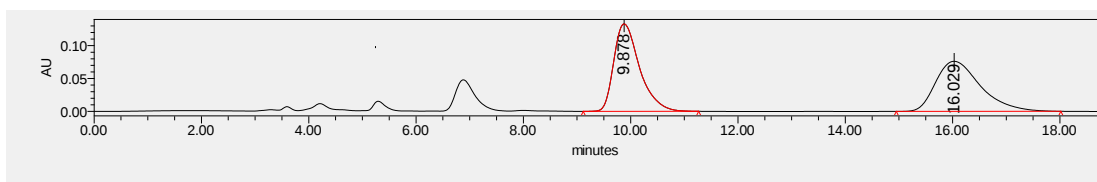


	Retention Time	Area	% Area
1	7.765	826608	97.94
2	13.167	17414	2.06

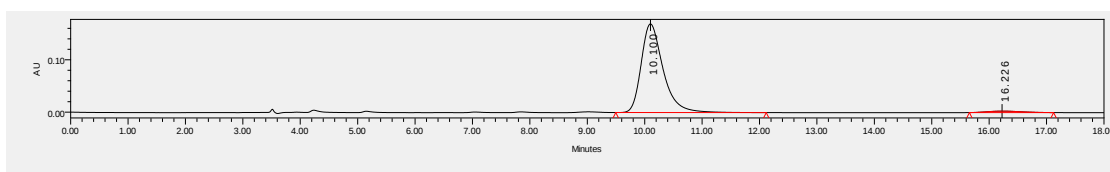
methyl 4-((2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)ethynyl)benzoate (3j)



Colorless oil; 50% yield, 95 ee. $[\alpha]_D^{25} = -82.1$ ($c = 0.16$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.10 min (major), 16.23 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.83 (m, 2H), 7.38 – 7.30 (m, 3H), 7.26 – 7.17 (m, 3H), 7.14 – 7.06 (m, 2H), 6.94 – 6.85 (m, 2H), 5.52 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.65 – 3.52 (m, 2H), 3.15 (m, 1H), 2.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.56, 154.38, 144.01, 134.97, 134.11, 131.64, 129.28, 129.16, 127.80, 127.48, 127.32, 126.22, 120.19, 114.42, 91.76, 84.87, 55.58, 54.51, 52.20, 44.24, 29.02. HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_3$ ($[\text{M}+\text{H}^+]$) = 398.1751, Found: 398.1751. The product was purified by flash chromatography (Pet/EtOAc = 5:1).

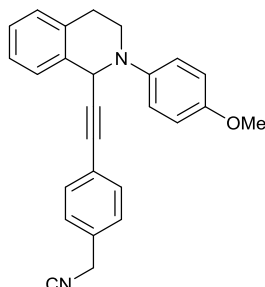


	Retention Time	Area	% Area
1	9.878	4429662	50.27
2	16.029	4382409	49.73

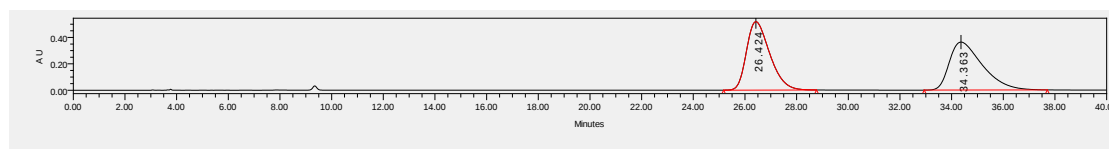


	Retention Time	Area	% Area
1	10.100	4492309	97.55
2	16.226	112773	2.45

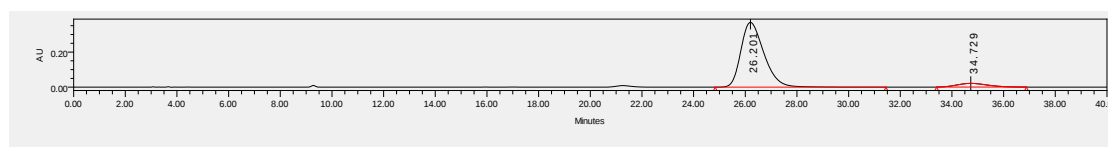
1-((4-(isocyanomethyl)phenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3k)



Yellow oil; 72% yield, 86 ee. $[\alpha]_D^{26} = -118.4$ ($c = 0.16$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 26.42 min (major), 34.36 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.21 (m, 5H), 7.09 (t, $J = 6.0$ Hz, 2H), 6.90 (t, $J = 6.0$ Hz, 2H), 5.50 (s, 1H), 3.79 (s, 3H), 3.67 (s, 2H), 3.64 – 3.50 (m, 2H), 3.14 (m, 1H), 2.97 – 2.88 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.34, 144.08, 135.20, 134.09, 132.39, 129.56, 129.12, 127.69, 127.48, 127.24, 126.17, 123.09, 120.18, 117.43, 114.41, 89.51, 84.61, 55.59, 54.42, 44.25, 29.02, 23.48. HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}$ ($[\text{M}+\text{H}^+]$) = 379.1805, Found: 379.1815. The product was purified by flash chromatography (Pet/EtOAc = 5:1).

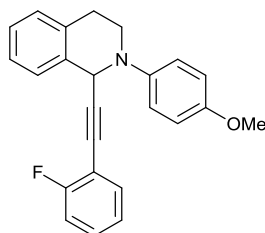


	Retention Time	Area	% Area
1	26.424	32423301	50.12
2	34.363	32273912	49.88



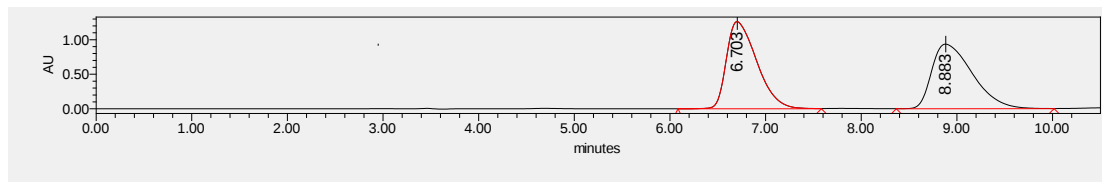
	Retention Time	Area	% Area
1	26.201	22856950	92.97
2	34.729	1728604	7.03

1-((2-fluorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3l)

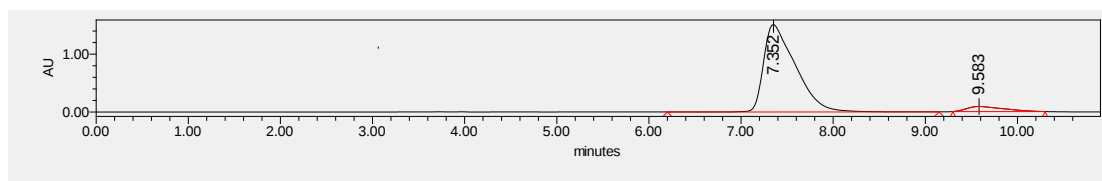


White solid; 65% yield, 90 ee. $[\alpha]_D^{27} = -85.1$ ($c = 0.19$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.35 min (major), 9.58 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 1H), 7.29 – 7.16 (m, 5H), 7.15 – 7.09 (m, 2H), 7.01 – 6.94 (m, 2H), 6.91 – 6.85 (m, 2H), 5.52 (s, 1H), 3.78 (s, 3H), 3.70 – 3.61 (m, 1H), 3.59 – 3.51 (m, 1H), 3.23 – 3.09 (m, 1H), 3.00 – 2.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.73 (d, $J = 125$ Hz), 154.35, 144.07, 135.17, 134.11, 133.54, 129.68, 129.60, 129.12, 127.50, 127.24, 126.17, 123.69, 123.65, 120.34, 115.32 (d, $J =$

10.50 Hz), 114.39, 111.68 (d, $J = 8.00$ Hz), 93.79 (d, $J = 1.50$ Hz), 79.01, 55.57, 54.61, 44.29, 29.07. HRMS (ESI-TOF) calcd for $C_{24}H_{21}FNO$ ($[M+H]^+$) = 358.1602, Found: 358.1600. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

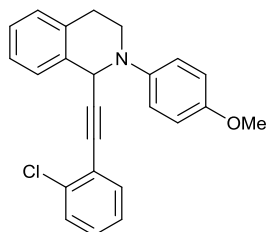


	Retention Time	Area	% Area
1	6.703	27782936	50.11
2	8.883	27662813	49.89

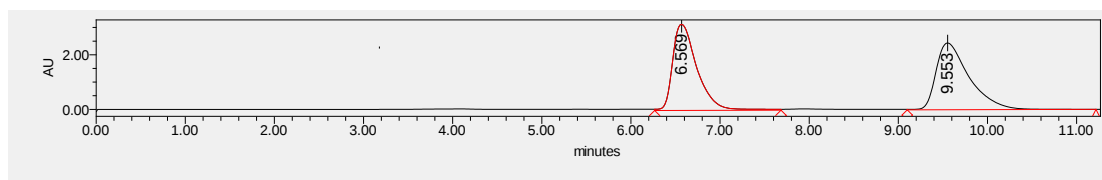


	Retention Time	Area	% Area
1	7.352	36223302	95.14
2	9.583	1851686	4.86

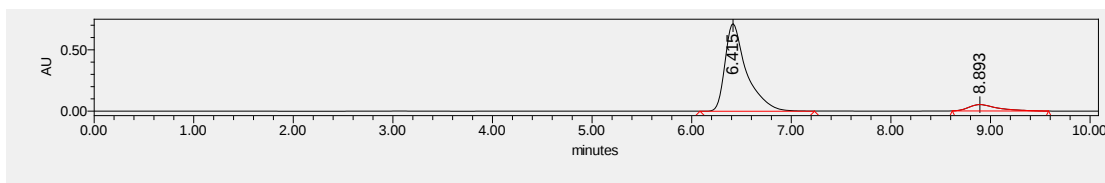
1-((2-chlorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3m)



White solid; 68% yield, 85 ee. $[\alpha]_D^{26} = -207.1$ ($c = 0.07$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.42 min (major), 8.90 min (minor). 1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.26 – 7.07 (m, 7H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.56 (s, 1H), 3.78 (s, 3H), 3.68 (m, 1H), 3.61 – 3.53 (m, 1H), 3.16 (m, 1H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.32, 144.09, 135.94, 135.18, 134.11, 133.32, 129.06, 128.94, 127.53, 127.20, 126.16, 126.13, 123.04, 120.27, 114.41, 93.97, 82.44, 55.60, 54.52, 44.33, 29.10. HRMS (ESI-TOF) calcd for $C_{24}H_{21}^{35}ClNO$ ($[M+H]^+$) = 374.1307, Found: 374.1307, HRMS (ESI-TOF) calcd for $C_{24}H_{21}^{37}ClNO$ ($[M+H]^+$) = 376.1277, Found: 376.1302. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

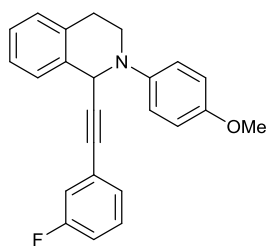


	Retention Time	Area	% Area
1	6.569	60085241	48.85
2	9.553	62926343	51.15

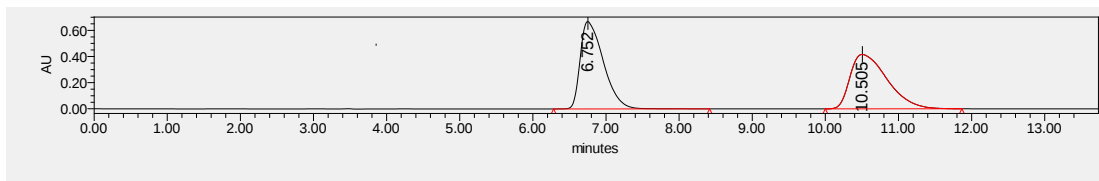


	Retention Time	Area	% Area
1	6.415	10712283	92.69
2	8.893	844317	7.31

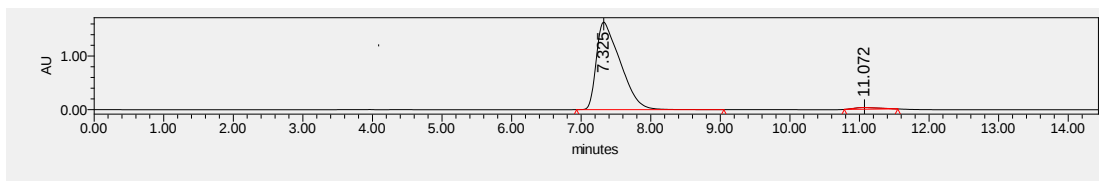
1-((3-fluorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3n)



White solid; 71% yield, 96 ee. $[\alpha]_D^{18} = -62.1$ ($c = 0.28$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.75 min (major), 10.50 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.28 (m, 1H), 7.24 – 7.07 (m, 6H), 7.04 (d, $J = 7.2$ Hz, 1H), 6.99 – 6.85 (m, 4H), 5.50 (s, 1H), 3.77 (d, $J = 1.2$ Hz, 3H), 3.56 (m, 2H), 3.14 (m, 1H), 2.91 (d, $J = 16.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.23 (d, $J = 122.00$ Hz), 154.40, 144.08, 135.12, 134.11, 129.68 (d, $J = 4.00$ Hz), 129.17, 127.62 (d, $J = 1.50$ Hz), 127.51, 127.31, 126.23, 124.92 (d, $J = 4.50$ Hz), 120.25, 118.65, 118.42, 115.48, 115.27, 114.44, 89.59, 84.37 (d, $J = 1.50$ Hz), 55.60, 54.47, 44.25, 29.06. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}\text{FNO}$ ($[\text{M}+\text{H}^+]$) = 358.1602, Found: 358.1609. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

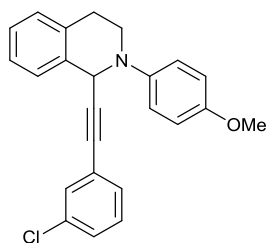


	Retention Time	Area	% Area
1	6.752	14614453	49.92
2	10.505	14660949	50.08



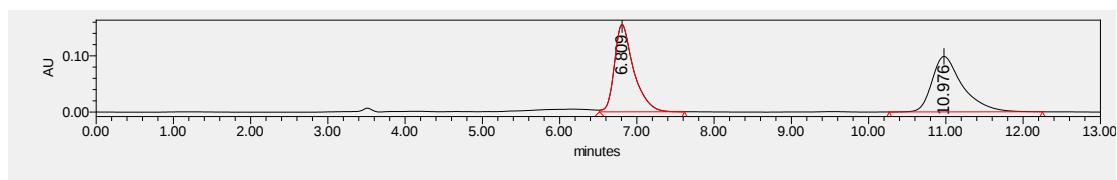
	Retention Time	Area	% Area
1	7.325	38962680	98.03
2	11.072	784530	1.97

1-((3-chlorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3o)

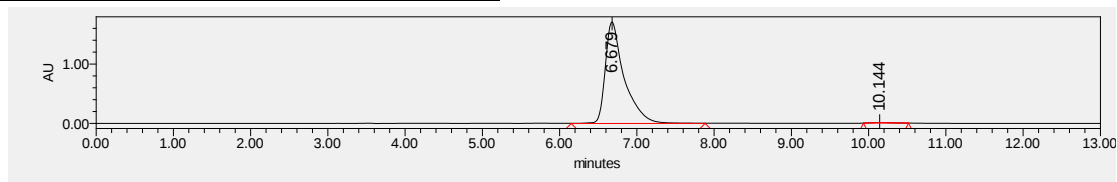


Yellow oil; 72% yield, 99 ee. $[\alpha]_D^{18} = -221.3$ ($c = 0.16$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.81

min (major), 10.98 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 1H), 7.22 (m, 5H), 7.13 (d, J = 6.0 Hz, 2H), 7.09 (d, J = 9.2 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.49 (s, 1H), 3.79 (s, 3H), 3.65 – 3.50 (m, 2H), 3.14 (m, 1H), 2.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.39, 144.05, 135.08, 134.08, 133.90, 131.58, 129.82, 129.30, 129.12, 128.26, 127.45, 127.27, 126.19, 124.77, 120.17, 114.44, 89.87, 84.16, 55.60, 54.42, 44.24, 29.03. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{35}\text{ClNO}$ ($[\text{M}+\text{H}^+]$) = 374.1307, Found: 374.1306, HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{37}\text{ClNO}$ ($[\text{M}+\text{H}^+]$) = 376.1277, Found: 376.1295. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

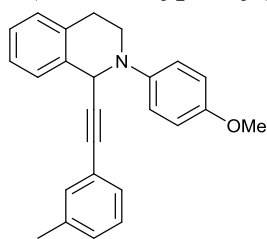


	Retention Time	Area	% Area
1	6.809	2668573	49.55
2	10.976	2717453	50.45

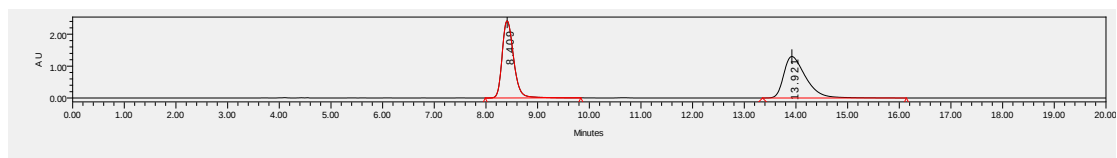


	Retention Time	Area	% Area
1	6.679	28647081	99.58
2	10.143	121596	0.42

2-(4-methoxyphenyl)-1-(m-tolyethynyl)-1,2,3,4-tetrahydroisoquinoline (3p)

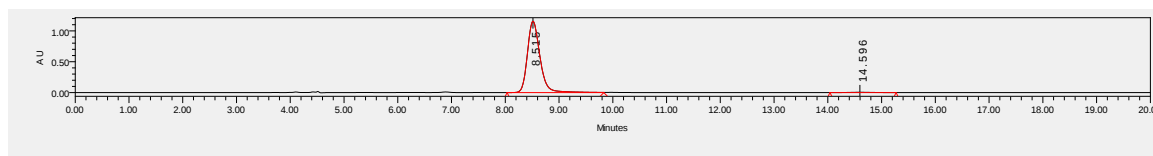


Yellow oil; 76% yield, 98 ee. $[\alpha]_{\text{D}}^{25}$ = -228.6 (c = 0.07 in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n -hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.52 min (major), 14.60 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (s, 1H), 7.21 (m, 3H), 7.16 – 6.98 (m, 6H), 6.89 (d, J = 8.0 Hz, 2H), 5.50 (s, 1H), 3.79 (s, 3H), 3.69 – 3.51 (m, 2H), 3.15 (m, 1H), 2.93 (d, J = 16.4 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.23, 144.18, 137.73, 135.54, 134.04, 132.29, 129.07, 128.87, 128.77, 127.98, 127.51, 127.12, 126.12, 122.86, 120.17, 114.37, 88.05, 85.68, 55.60, 54.38, 44.23, 29.06, 21.15. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 354.1853, Found: 354.1852. The product was purified by flash chromatography (Pet/EtOAc = 20:1).



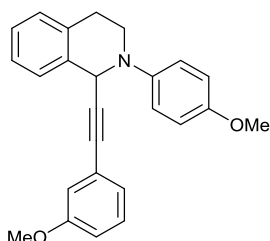
	Retention Time	Area	% Area
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1	8.409	37259075	49.30
2	13.921	38314864	50.70

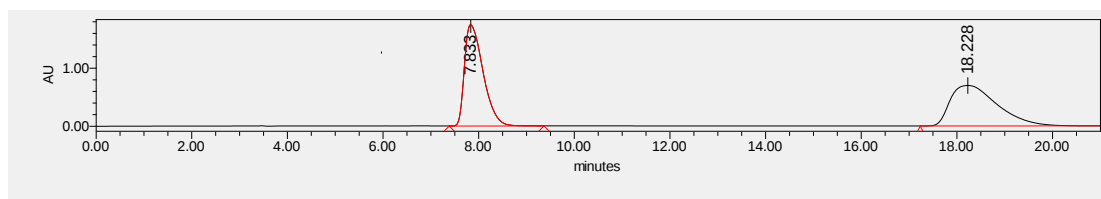


	Retention Time	Area	% Area
1	8.515	18769820	99.05
2	14.596	179975	0.95

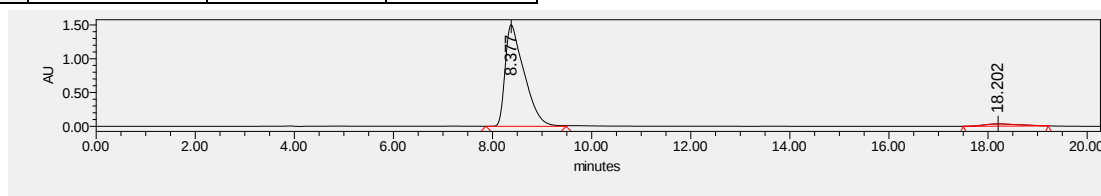
2-(4-methoxyphenyl)-1-((3-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3q)



Colorless oil; 82% yield, 93 ee. $[\alpha]_D^{27} = -52.4$ ($c = 0.21$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 8.34 min (major), 18.20 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 1H), 7.26 – 7.16 (m, 3H), 7.15 – 7.08 (m, 3H), 6.93 – 6.85 (m, 3H), 6.82 – 6.74 (m, 2H), 5.50 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.67 – 3.50 (m, 2H), 3.14 (m, 1H), 2.97 – 2.88 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.14, 154.30, 144.16, 135.39, 134.08, 129.15, 129.10, 127.54, 127.18, 126.15, 124.29, 124.07, 120.25, 116.54, 114.62, 114.38, 88.35, 85.42, 55.59, 55.25, 54.45, 44.25, 29.05. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}^+]$) = 370.1802, Found: 370.1803. The product was purified by flash chromatography (Pet/EtOAc = 15:1).

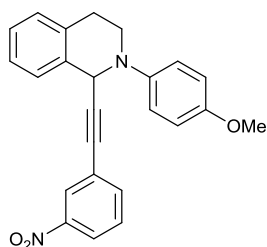


	Retention Time	Area	% Area
1	7.833	47208178	49.74
2	18.228	47705077	50.26

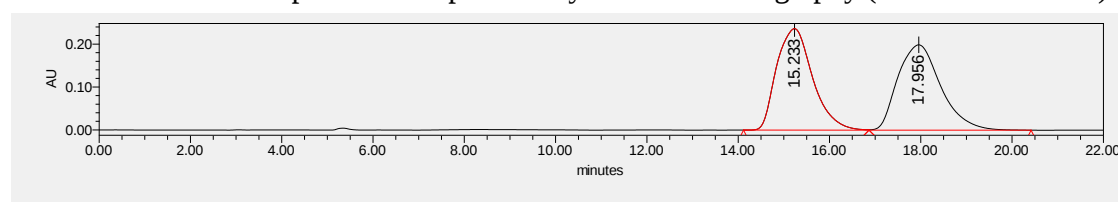


	Retention Time	Area	% Area
1	8.377	40026606	96.46
2	18.202	1469692	3.54

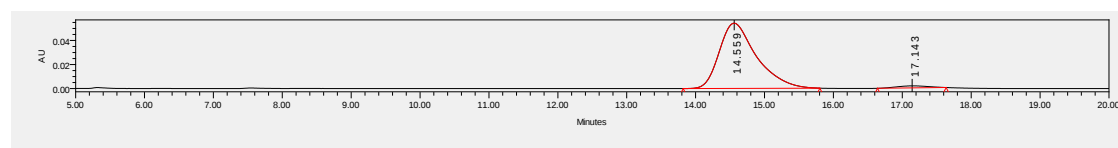
2-(4-methoxyphenyl)-1-((3-nitrophenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3r)



Red oil; 45% yield, 95 ee. $[\alpha]_D^{18} = -103.5$ ($c = 0.20$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 14.56 min (major), 17.16 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (m, 2H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.38 – 7.29 (m, 2H), 7.26 – 7.16 (m, 3H), 7.09 (t, $J = 6.4$ Hz, 2H), 6.94 – 6.86 (m, 2H), 5.52 (s, 1H), 3.77 (s, 3H), 3.64 – 3.51 (m, 2H), 3.14 (m, 1H), 2.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.53, 143.92, 137.37, 134.63, 134.12, 129.20, 129.09, 127.42, 126.55, 126.27, 124.86, 122.72, 120.20, 114.49, 91.50, 83.18, 55.57, 54.51, 44.24, 29.00. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}^+]$) = 385.1547, Found: 385.1549. The product was purified by flash chromatography (Pet/EtOAc = 10:1).

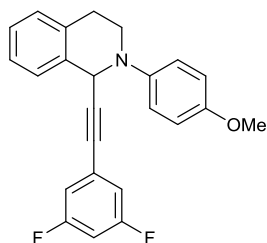


	Retention Time	Area	% Area
1	15.233	12951842	49.95
2	17.956	12975866	50.05

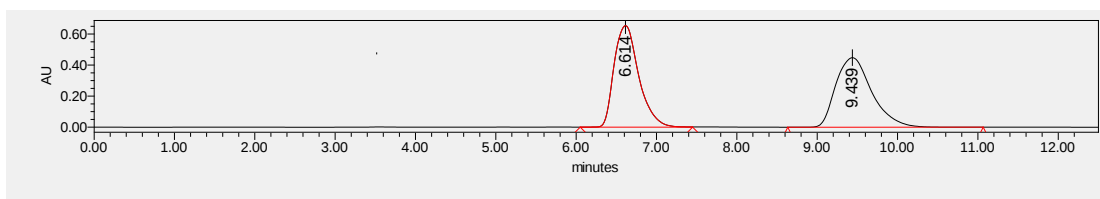


	Retention Time	Area	% Area
1	14.559	2048053	97.43
2	17.162	54117	2.57

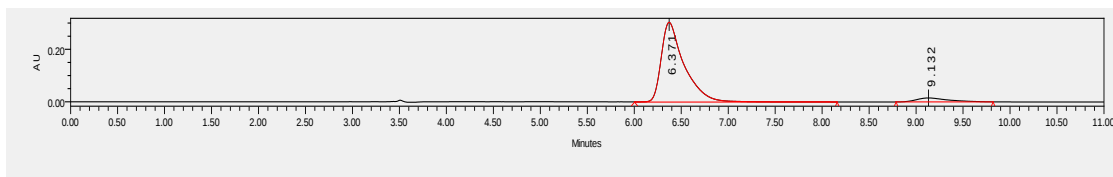
1-((3,5-difluorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3s)



White solid; 69% yield, 88 ee. $[\alpha]_D^{25} = -67.5$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.37 min (major), 9.13 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 1H), 7.26 – 7.17 (m, 3H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.81 – 6.74 (m, 2H), 6.70 (m, 1H), 5.49 (s, 1H), 3.79 (s, 3H), 3.56 (m, 2H), 3.21 – 3.09 (m, 1H), 2.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.75 (d, $J = 6.50$ Hz) 161.28 (d, $J = 6.50$ Hz), 154.48, 143.95, 134.74, 134.10, 129.16, 127.41, 127.36, 126.23, 120.20, 114.65 (d, $J = 6.57$ Hz, $J = 14.00$), 114.46, 104.18 (t, $J = 25.00$ Hz), 104.18, 90.80, 55.59, 54.45, 44.22, 29.00. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{NO}$ ($[\text{M}+\text{H}^+]$) = 376.1508, Found: 376.1516. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

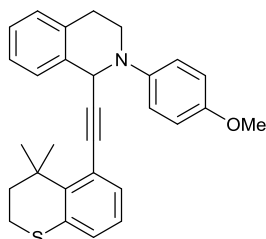


	Retention Time	Area	% Area
1	6.614	13899480	50.30
2	9.439	13733328	49.70

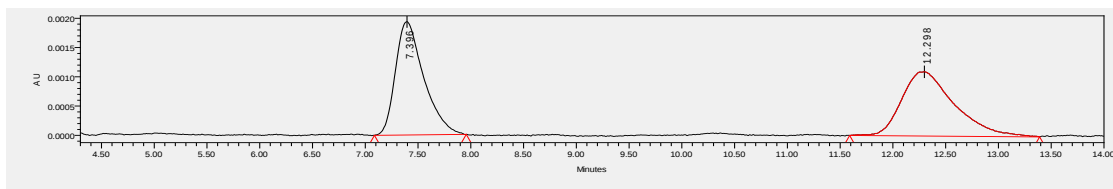


	Retention Time	Area	% Area
1	6.371	5095224	94.05
2	9.132	322288	5.95

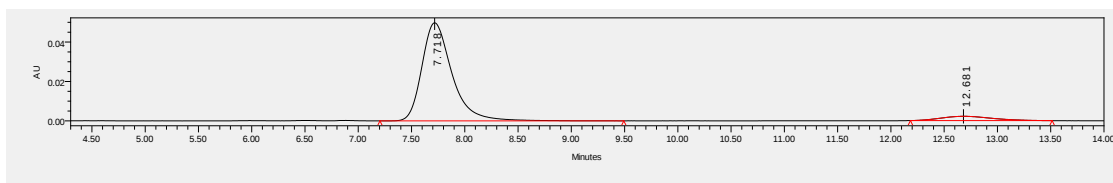
1-((4,4-dimethylthiochroman-5-yl)ethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisquinoline (3t)



Colorless oil; 75% yield, 88 ee. $[\alpha]_D^{21} = -24.0$ ($c = 0.15$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.72 min (minor), 12.68 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 1H), 7.25 – 7.15 (m, 4H), 7.13 – 7.07 (m, 2H), 6.89 (m, 4H), 5.50 (s, 1H), 3.79 (s, 3H), 3.69 – 3.58 (m, 1H), 3.57 – 3.49 (m, 1H), 3.13 (m, 1H), 3.02 – 2.96 (m, 2H), 2.96 – 2.89 (m, 1H), 1.89 (m, 2H), 1.25 (d, $J = 2.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.26, 144.22, 141.74, 135.56, 134.07, 132.47, 129.72, 129.15, 129.05, 127.55, 127.09, 126.24, 126.10, 120.24, 114.36, 87.62, 85.69, 55.57, 54.49, 44.24, 37.30, 32.87, 29.91, 29.00, 23.15. HRMS (ESI-TOF) calcd for $\text{C}_{29}\text{H}_{30}\text{NOS}$ ($[\text{M}+\text{H}^+]$) = 440.2043, Found: 440.2051. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

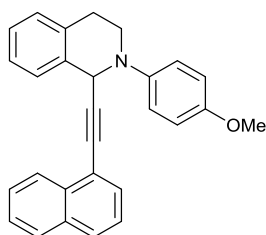


	Retention Time	Area	% Area
1	7.396	36107	48.65
2	12.298	38115	51.35

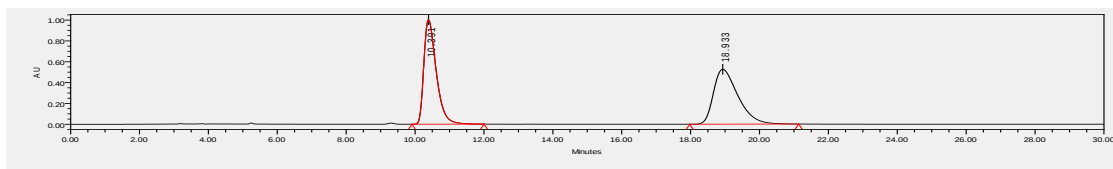


	Retention Time	Area	% Area
1	7.718	976241	94.26
2	12.681	59467	5.74

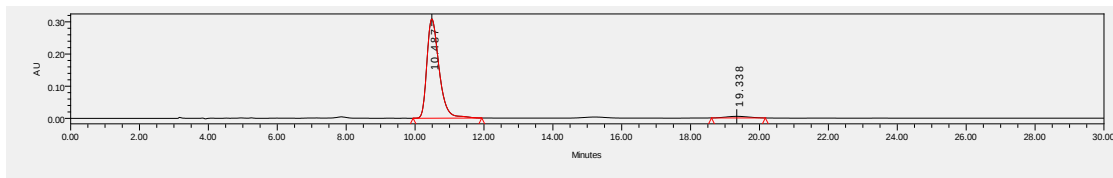
2-(4-methoxyphenyl)-1-(naphthalen-1-ylethynyl)-1,2,3,4-tetrahydroisoquinoline (3u)



Colorless oil; 75% yield, 95 ee. $[\alpha]_D^{21} = -86.7$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.49 min (major), 19.34 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.54 (m, 4H), 7.39 – 7.28 (m, 3H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.14 (m, 3H), 7.09 – 7.02 (m, 2H), 6.88 – 6.77 (m, 2H), 5.47 (s, 1H), 3.70 (d, $J = 1.2$ Hz, 3H), 3.60 (m, 1H), 3.49 (m, 1H), 3.08 (m, 1H), 2.87 (d, $J = 16.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.31, 144.20, 135.47, 134.12, 132.87, 132.66, 131.45, 129.14, 128.66, 127.71, 127.64, 127.57, 127.21, 126.49, 126.42, 126.20, 120.39, 120.23, 114.43, 88.87, 85.89, 55.61, 54.52, 44.31, 29.09. HRMS (ESI-TOF) calcd for $\text{C}_{27}\text{H}_{26}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 380.2009, Found: 380.2018. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

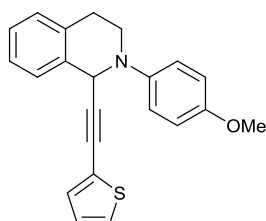


	Retention Time	Area	% Area
1	10.391	25001382	49.05
2	18.933	25967321	50.95



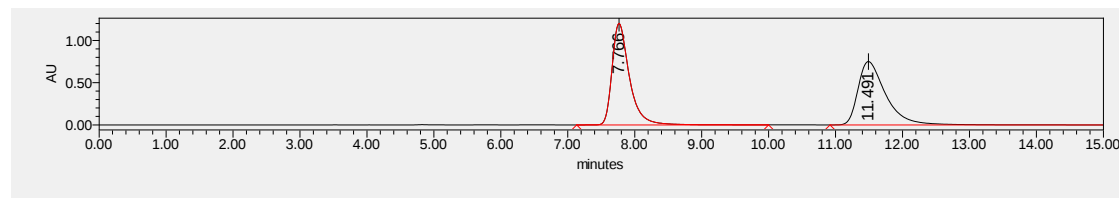
	Retention Time	Area	% Area
1	10.487	7578604	97.43
2	19.338	200013	2.57

2-(4-methoxyphenyl)-1-(thiophen-2-ylethynyl)-1,2,3,4-tetrahydroisoquinoline (3v)

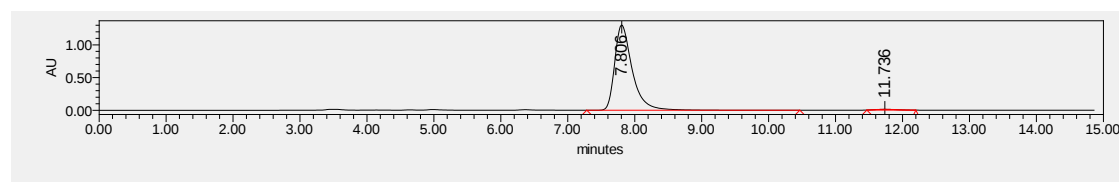


Brown solid; 70% yield, 98 ee. $[\alpha]_D^{21} = -125.2$ ($c = 0.26$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.81 min (major), 11.74 min (minor). ^1H

NMR (400 MHz, CDCl₃) δ 7.30 (m, 1H), 7.22 – 7.14 (m, 3H), 7.12 – 7.04 (m, 3H), 7.02 (m, 1H), 6.86 (m, 3H), 5.49 (s, 1H), 3.75 (s, 3H), 3.64 – 3.47 (m, 2H), 3.11 (m, 1H), 2.89 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.40, 144.07, 135.09, 134.17, 131.90, 129.18, 127.58, 127.31, 126.82, 126.76, 126.24, 123.08, 120.28, 114.48, 92.54, 78.77, 55.61, 54.71, 44.32, 29.04. HRMS (ESI-TOF) calcd for C₂₇H₂₆NO ([M+H]⁺) = 360.2339, Found: 360.2336 The product was purified by flash chromatography (Pet/EtOAc = 20:1).

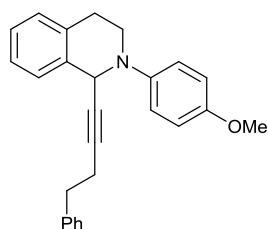


	Retention Time	Area	% Area
1	7.766	21632063	50.05
2	11.491	21592202	49.95

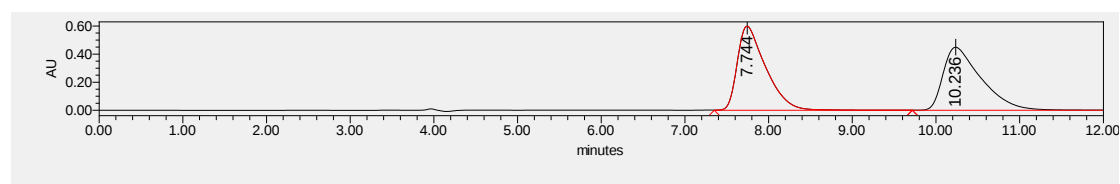


	Retention Time	Area	% Area
1	7.806	23688791	98.92
2	11.736	257854	1.08

2-(4-methoxyphenyl)-1-(4-phenylbut-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (3w)

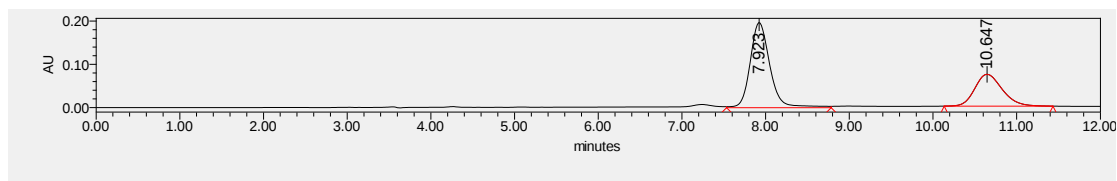


Colorless oil; 55% yield, 37 ee. $[\alpha]_D^{21} = -41.4$ (c = 0.16 in CH₂Cl₂). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.92 min (major), 10.65 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.13 (m, 7H), 7.07 – 7.02 (m, 2H), 7.02 – 6.96 (m, 2H), 6.88 – 6.81 (m, 2H), 5.25 (s, 1H), 3.78 (s, 3H), 3.46 (m, 2H), 3.07 (m, 1H), 2.85 (m, 1H), 2.67 (m, 2H), 2.38 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.96, 144.17, 140.68, 136.13, 133.87, 128.97, 128.54, 128.23, 127.40, 126.94, 126.09, 125.99, 119.77, 114.32, 85.17, 79.78, 55.58, 53.61, 43.94, 35.07, 28.96, 20.99. HRMS(ESI-TOF) calcd for C₂₆H₂₆NO ([M+H]⁺) = 368.2009, Found: 368.2007. The product was purified by flash chromatography (Pet/EtOAc = 30:1).



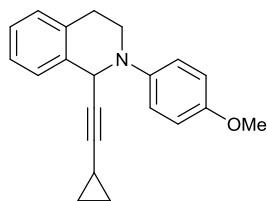
	Retention Time	Area	% Area
1	7.744	14092679	49.92

2	10.236	14138641	50.08
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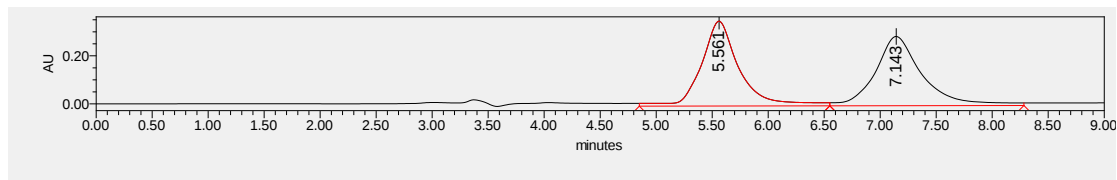


	Retention Time	Area	% Area
1	7.923	3232029	68.13
2	10.647	1512214	31.87

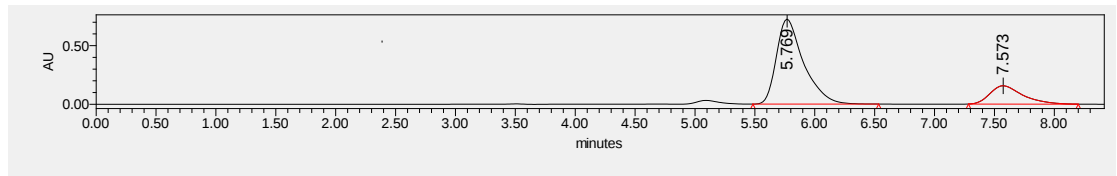
1-(cyclopropylethynyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3x)



Colorless oil; 60% yield, 61 ee. $[\alpha]_D^{21} = -90.8$ ($c = 0.20$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.77 min (major), 7.57 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.24 (m, 1H), 7.21 – 7.13 (m, 3H), 7.06 – 6.99 (m, 2H), 6.90 – 6.83 (m, 2H), 5.23 (s, 1H), 3.79 (s, 3H), 3.59 – 3.42 (m, 2H), 3.08 (m, 1H), 2.87 (m, 1H), 1.25 (s, 1H), 0.64 (m, 2H), 0.55 – 0.44 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.44, 144.65, 136.51, 134.27, 129.39, 127.80, 127.31, 126.41, 120.39, 114.67, 89.44, 74.45, 56.01, 54.19, 44.45, 29.35, 8.76. HRMS(ESI-TOF) calcd for $\text{C}_{21}\text{H}_{22}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 304.1696, Found: 304.1707. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

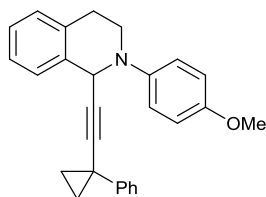


	Retention Time	Area	% Area
1	5.561	8406754	49.80
2	7.143	8474620	50.20

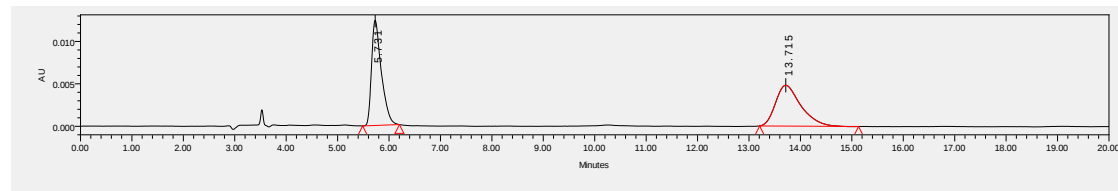


	Retention Time	Area	% Area
1	5.769	11582014	80.46
2	7.573	2812256	19.54

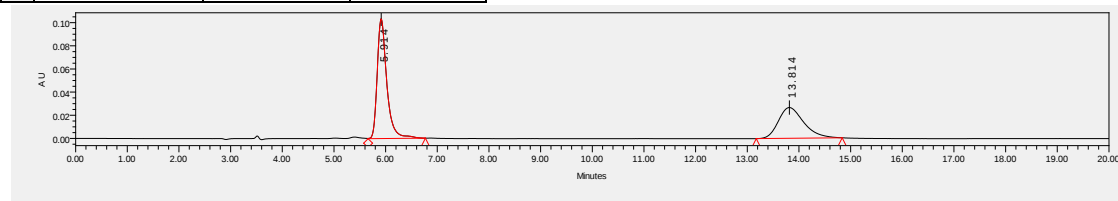
2-(4-methoxyphenyl)-1-((1-phenylcyclopropyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (3y)



Colorless oil; 77% yield, 20 ee. $[\alpha]_D^{21} = -151.7$ ($c = 0.24$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.91 min (major), 13.81 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 1H), 7.24 – 6.98 (m, 10H), 6.89 (m, 2H), 5.40 (s, 1H), 3.80 (s, 3H), 3.50 (m, 2H), 3.18 – 3.02 (m, 1H), 2.92 (m, 1H), 1.27 – 1.24 (m, 2H), 1.17 – 1.06 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.31, 144.43, 141.94, 135.80, 133.85, 128.95, 128.07, 127.49, 126.90, 125.98, 125.65, 125.00, 120.42, 114.35, 89.17, 77.25, 55.60, 54.30, 43.98, 29.16, 20.81. HRMS (ESI-TOF) calcd for $\text{C}_{27}\text{H}_{26}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 380.2009, Found: 380.2019. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

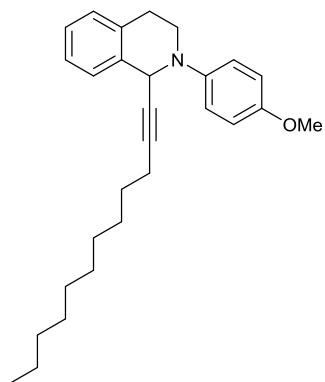


	Retention Time	Area	% Area
1	5.731	164342	52.35
2	13.715	149572	47.65

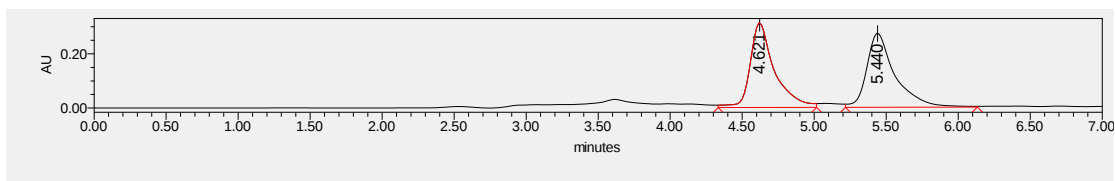


	Retention Time	Area	% Area
1	5.914	1333347	60.01
2	13.814	888365	39.99

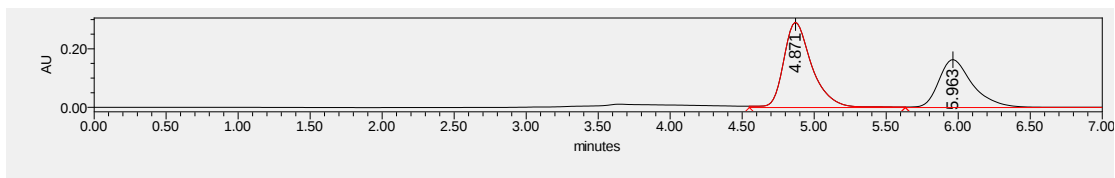
1-(dodec-1-yn-1-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (3z)



Colorless oil; 40% yield, 20 ee. $[\alpha]_D^{21} = -28.2$ ($c = 0.17$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 4.87 min (major), 5.96 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 5.6$ Hz, 1H), 7.22 – 7.12 (m, 3H), 7.05 (d, $J = 9.2$ Hz, 2H), 6.87 (d, $J = 9.2$ Hz, 2H), 5.28 (s, 1H), 3.79 (s, 3H), 3.57 – 3.42 (m, 2H), 3.09 (m, 1H), 2.89 (m, 1H), 2.08 (m, 2H), 1.31 – 1.17 (m, 16H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.00, 144.27, 136.30, 133.81, 128.96, 127.39, 126.88, 125.98, 119.93, 114.26, 86.04, 78.91, 55.54, 53.75, 44.02, 31.94, 29.61, 29.57, 29.37, 29.13, 29.01, 28.74, 28.72, 22.72, 18.77, 14.15. HRMS(ESI-TOF) calcd for $\text{C}_{28}\text{H}_{38}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 404.2948, Found: 404.2958. The product was purified by flash chromatography (Pet/EtOAc = 35:1).

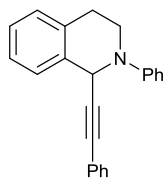


	Retention Time	Area	% Area
1	4.621	3666183	49.61
2	5.440	3723290	50.39

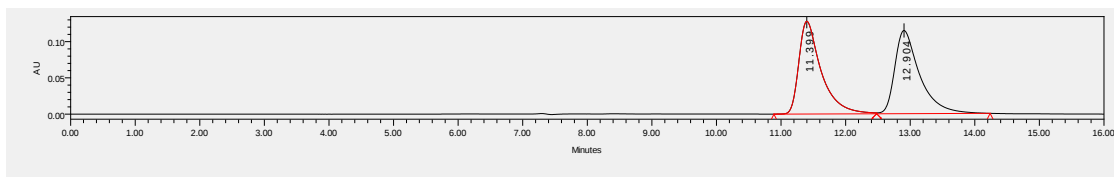


	Retention Time	Area	% Area
1	4.871	3765210	60.04
2	5.963	2505521	39.96

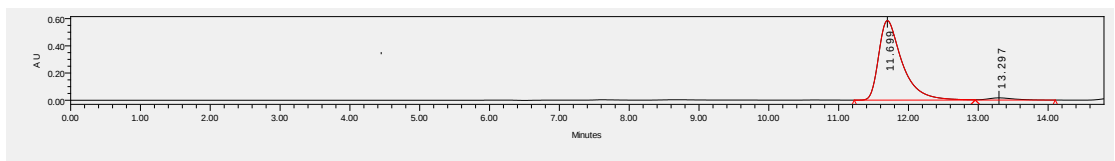
2-phenyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4a)



Colorless oil; 65% yield, 94 ee. $[\alpha]_D^{25} = -91.9$ ($c = 0.06$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 11.70 min (major), 13.30 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 1H), 7.34 – 7.26 (m, 4H), 7.25 – 7.16 (m, 6H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.88 (t, $J = 7.2$ Hz, 1H), 5.64 (s, 1H), 3.75 (m, 1H), 3.66 (m, 1H), 3.13 (m, 1H), 2.97 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.59, 135.44, 134.42, 131.77, 129.17, 128.96, 128.11, 128.05, 127.46, 127.25, 126.31, 123.04, 119.67, 116.74, 88.63, 84.81, 52.35, 43.47, 28.95. HRMS (ESI-TOF) calcd for $\text{C}_{23}\text{H}_{20}\text{N}$ ($[\text{M}+\text{H}^+]$) = 310.1591, Found: 310.1597. The product was purified by flash chromatography (Pet/EtOAc = 30:1).



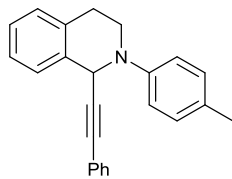
	Retention Time	Area	% Area
1	11.399	3067225	50.05
2	12.904	3061619	49.95



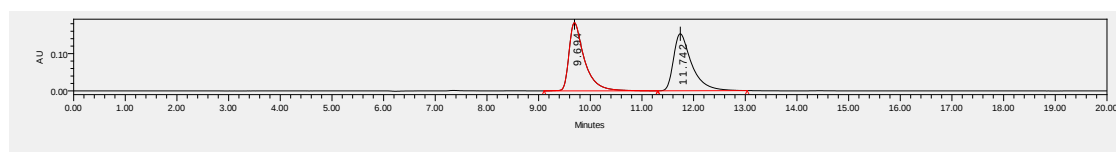
	Retention Time	Area	% Area
1	11.699	13706426	96.97

2	13.297	428873	3.03
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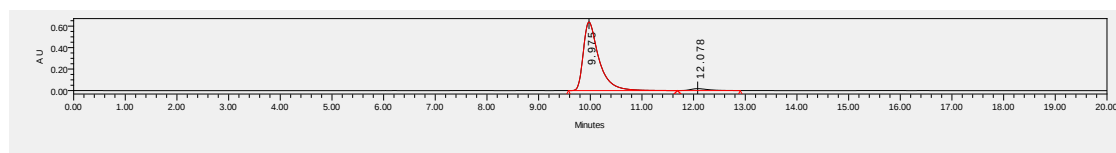
1-(phenylethynyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4b)



Yellow oil; 66% yield, 95 ee. $[\alpha]_D^{26} = -51.4$ ($c = 0.07$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 9.98 min (major), 12.08 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.32 (m, 1H), 7.29 – 7.25 (m, 2H), 7.23 – 7.13 (m, 6H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.05 – 6.99 (m, 2H), 5.58 (s, 1H), 3.71 – 3.55 (m, 2H), 3.11 (m, 1H), 2.90 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.62, 135.58, 134.38, 131.84, 129.77, 129.45, 129.11, 128.18, 128.08, 127.58, 127.27, 126.30, 123.18, 117.58, 88.76, 85.20, 53.05, 43.80, 29.05, 20.67. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{22}\text{N}$ ($[\text{M}+\text{H}^+]$) = 324.1747, Found: 324.1747. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

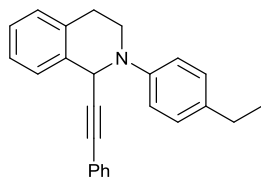


	Retention Time	Area	% Area
1	9.694	3789010	50.45
2	11.742	3721156	49.55

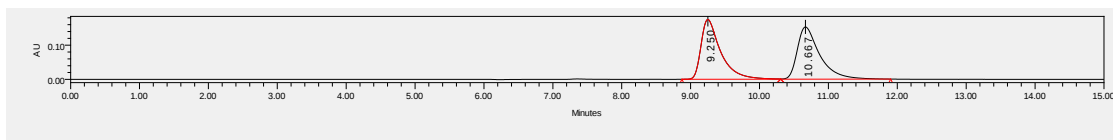


	Retention Time	Area	% Area
1	9.975	13362495	97.51
2	12.078	341908	2.49

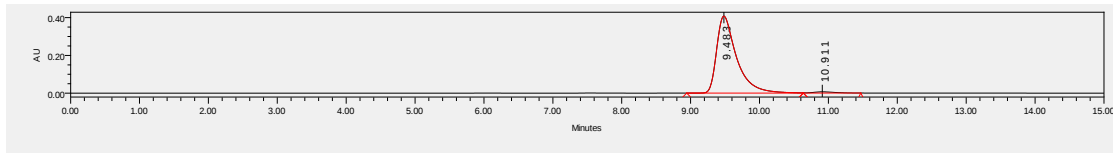
2-(4-ethylphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4c)



Yellow oil; 63% yield, 97 ee. $[\alpha]_D^{26} = -71.1$ ($c = 0.09$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 9.48 min (major), 10.91 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 1H), 7.27 (m, 2H), 7.23 – 7.11 (m, 8H), 7.06 (m, 2H), 5.59 (s, 1H), 3.76 – 3.56 (m, 2H), 3.12 (m, 1H), 2.92 (m, 1H), 2.59 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.74, 135.86, 135.59, 134.42, 131.82, 129.07, 128.54, 128.15, 128.06, 127.54, 127.24, 126.28, 123.17, 117.41, 88.80, 85.10, 52.91, 43.77, 29.05, 28.11, 15.95. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{N}$ ($[\text{M}+\text{H}^+]$) = 338.1904, Found: 338.1902. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

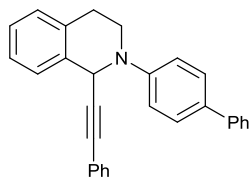


	Retention Time	Area	% Area
1	9.250	3456651	50.09
2	10.667	3444075	49.91

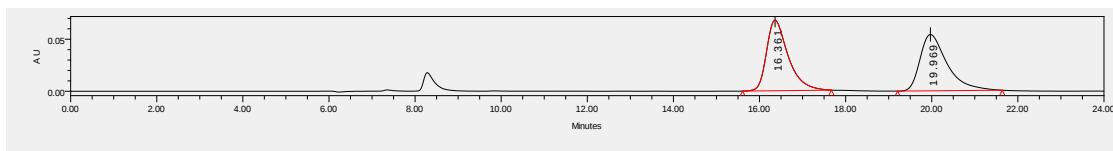


	Retention Time	Area	% Area
1	9.483	8138482	98.81
2	10.911	97862	1.19

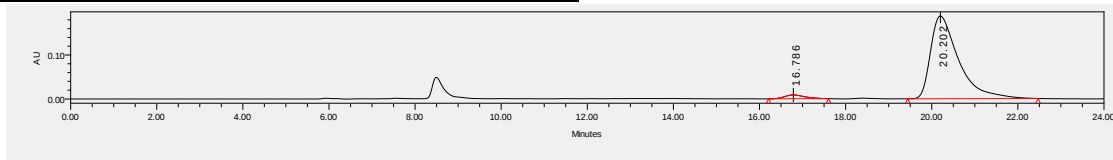
2-([1,1'-biphenyl]-4-yl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4d)



Colorless oil; 60% yield, 94 ee. $[\alpha]_D^{26} = -155.7$ ($c = 0.09$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 16.79 min (minor), 20.20 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.58 (m, 4H), 7.40 (m, 3H), 7.34 – 7.29 (m, 2H), 7.27 – 7.16 (m, 9H), 5.70 (s, 1H), 3.89 – 3.65 (m, 2H), 3.15 (m, 1H), 3.06 – 2.96 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.78, 141.01, 135.32, 134.42, 132.12, 131.80, 128.95, 128.73, 128.13, 127.80, 127.46, 127.32, 126.55, 126.42, 126.38, 122.95, 116.55, 88.55, 84.77, 52.01, 43.47, 28.93. HRMS (ESI-TOF) calcd for $\text{C}_{29}\text{H}_{24}\text{N}$ ($[\text{M}+\text{H}^+]$) = 386.1904, Found: 386.1907. The product was purified by flash chromatography (Pet/EtOAc = 50:1).

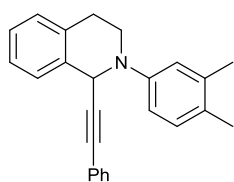


	Retention Time	Area	% Area
1	16.361	2361081	50.04
2	19.969	2357581	49.96

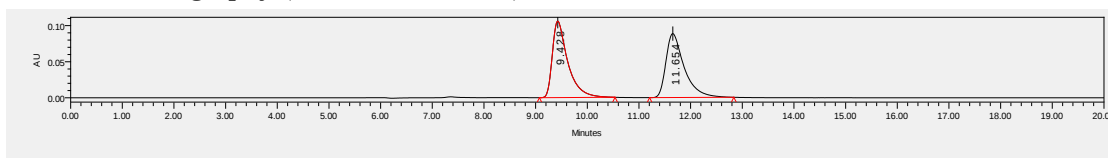


	Retention Time	Area	% Area
1	16.786	239593	2.74
2	20.202	8513330	97.26

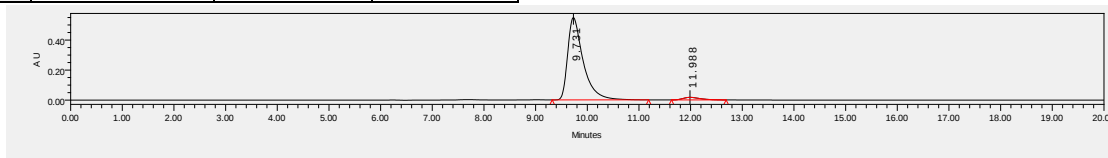
2-(3,4-dimethylphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4e)



Colorless oil; 63% yield, 94 ee. $[\alpha]_D^{20} = -54.0$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 9.73 min (major), 11.99 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 1H), 7.28 (m, 2H), 7.23 – 7.13 (m, 6H), 7.06 (d, $J = 8.4$ Hz, 1H), 6.94 (d, $J = 2.4$ Hz, 1H), 6.88 (m, 1H), 5.58 (s, 1H), 3.73 – 3.57 (m, 2H), 3.12 (m, 1H), 2.92 (m, 1H), 2.23 (d, $J = 26.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.95, 137.15, 135.65, 134.39, 131.80, 130.22, 129.07, 128.23, 128.12, 128.01, 127.53, 127.19, 126.22, 123.21, 119.20, 114.90, 88.83, 85.18, 53.03, 43.74, 29.04, 20.36, 18.96. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{N}$ ($[\text{M}+\text{H}^+]$) = 338.1904, Found: 338.1905. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

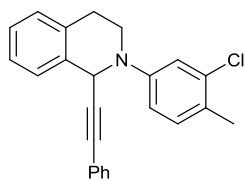


	Retention Time	Area	% Area
1	9.428	2197504	50.26
2	11.654	2174841	49.74

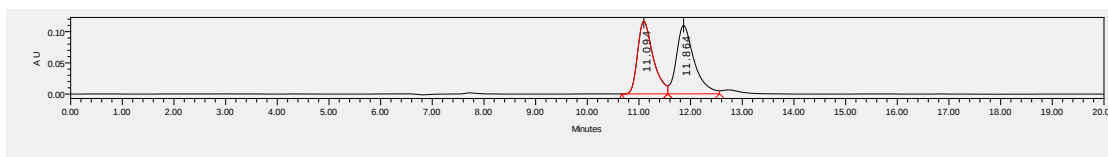


	Retention Time	Area	% Area
1	9.731	11476318	96.92
2	11.988	364894	3.08

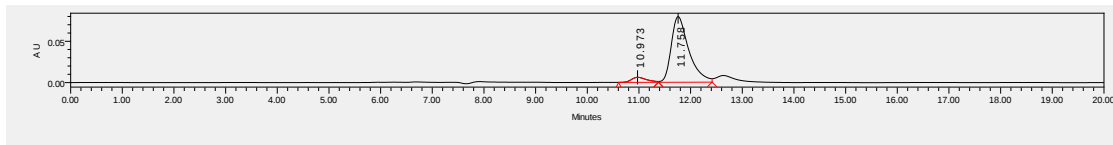
2-(3-chloro-4-methylphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4f)



Colorless oil; 61% yield, 89 ee. $[\alpha]_D^{26} = -50.0$ ($c = 0.04$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 10.97 min (major), 11.76 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.17 (m, 6H), 7.13 (t, $J = 5.6$ Hz, 2H), 6.92 (m, 1H), 5.57 (s, 1H), 3.64 (m, 2H), 3.13 (m, 1H), 2.97 (m, 1H), 2.29 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.70, 135.11, 134.76, 134.15, 131.77, 131.14, 128.93, 128.11, 127.43, 127.31, 126.75, 126.34, 122.87, 117.37, 115.29, 88.14, 85.06, 52.38, 43.51, 28.84, 19.05. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{35}\text{ClN}$ ($[\text{M}+\text{H}^+]$) = 358.1358, Found: 358.1360, HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{37}\text{ClN}$ ($[\text{M}+\text{H}^+]$) = 360.1328, Found: 360.1339. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

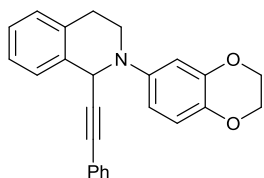


	Retention Time	Area	% Area
1	11.094	2439373	48.14
2	11.864	2627518	51.86

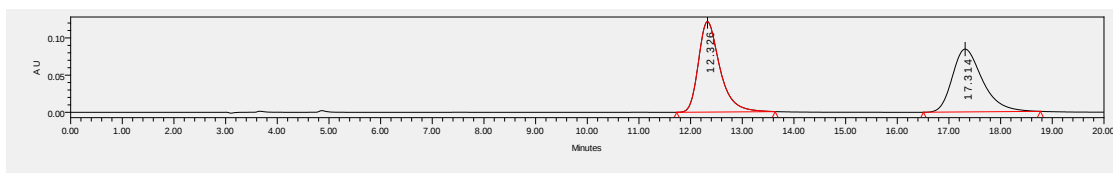


	Retention Time	Area	% Area
1	10.973	111074	5.59
2	11.758	1875668	94.41

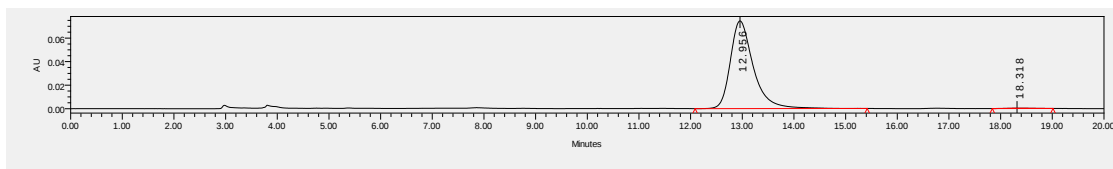
2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4g)



Colorless oil; 50% yield, 99 ee. $[\alpha]_D^{26} = -39.4$ ($c = 0.10$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 12.96 min (major), 18.32 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (m, 3H), 7.26 – 7.17 (m, 6H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.67 (m, 2H), 5.50 (s, 1H), 4.30 – 4.18 (m, 4H), 3.66 – 3.52 (m, 2H), 3.13 (m, 1H), 2.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.78, 143.70, 137.77, 135.43, 134.12, 131.74, 129.01, 128.06, 127.96, 127.47, 127.14, 126.15, 123.11, 117.30, 111.72, 107.35, 88.48, 85.34, 64.64, 64.30, 53.79, 43.99, 28.93. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{22}\text{NO}_2$ ($[\text{M}+\text{H}^+]$) = 368.1646, Found: 368.1646. The product was purified by flash chromatography (Pet/EtOAc = 5:1).

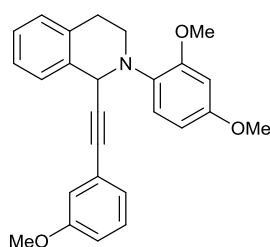


	Retention Time	Area	% Area
1	12.326	3502492	50.53
2	17.314	3428938	49.47

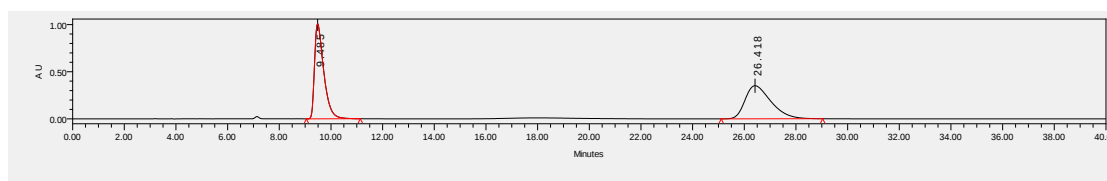


	Retention Time	Area	% Area
1	12.956	2296008	99.58
2	18.318	9591	0.42

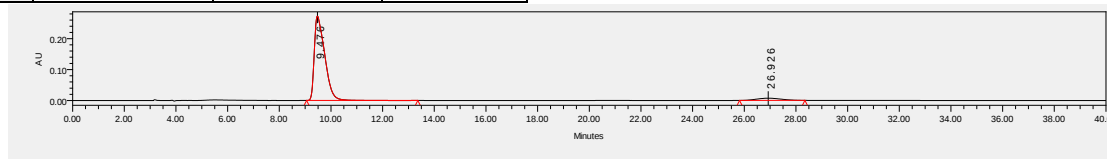
2-(2,4-dimethoxyphenyl)-1-((3-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (4h)



Colorless oil; 42% yield, 88 ee. $[\alpha]_D^{18} = -47.1$ ($c = 0.14$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 9.48 min (major), 26.41 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (m, 1H), 7.23 – 7.15 (m, 3H), 7.13 – 7.06 (m, 2H), 6.84 (m, 1H), 6.79 – 6.72 (m, 2H), 6.54 – 6.44 (m, 2H), 5.63 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.72 (s, 3H), 3.65 (m, 1H), 3.33 (m, 1H), 3.23 (m, 1H), 2.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.11, 156.67, 153.78, 135.70, 133.80, 133.43, 129.24, 129.11, 127.70, 126.97, 125.84, 124.33, 124.23, 121.97, 116.53, 114.41, 103.51, 99.49, 88.78, 85.55, 55.58, 55.51, 55.22, 53.40, 44.41, 29.29. HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_3$ ($[\text{M}+\text{H}^+]$) = 400.1908, Found: 400.1915. The product was purified by flash chromatography (Pet/EtOAc = 5:1).

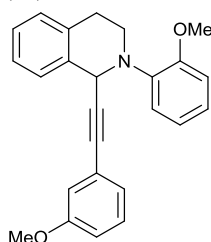


	Retention Time	Area	% Area
1	9.485	24952060	50.47
2	26.418	24485192	49.53

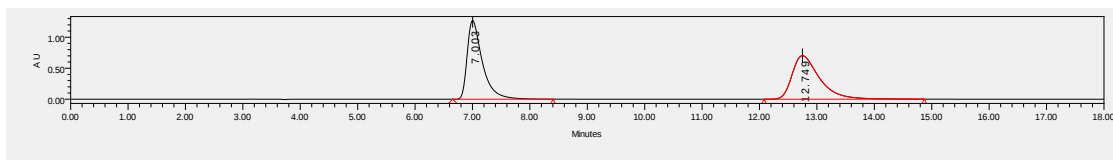


	Retention Time	Area	% Area
1	9.476	7626365	94.15
2	26.926	473701	5.85

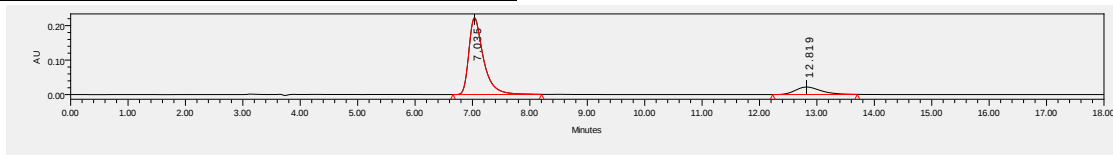
2-(2-methoxyphenyl)-1-((2-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (4i)



Colorless oil; 22% yield, 71 ee. $[\alpha]_D^{26} = -100.0$ ($c = 0.03$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 95/5, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 7.04 min (major), 12.82 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 1H), 7.24 – 7.17 (m, 4H), 7.12 – 7.03 (m, 2H), 6.97 (m, 1H), 6.90 (m, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.79 – 6.72 (m, 2H), 5.75 (s, 1H), 3.88 (d, $J = 10.0$ Hz, 3H), 3.71 (s, 3H), 3.66 (m, 1H), 3.44 (m, 1H), 3.29 – 3.18 (m, 1H), 2.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.12, 152.70, 139.77, 135.62, 133.83, 129.25, 129.11, 127.67, 127.00, 125.90, 124.26, 124.23, 123.67, 121.35, 120.81, 116.51, 114.49, 111.19, 88.73, 85.44, 55.54, 55.23, 52.88, 44.04, 29.21. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}^+]$) = 370.1802, Found: 370.1802. The product was purified by flash chromatography (Pet/EtOAc = 10:1).

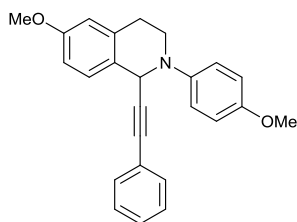


	Retention Time	Area	% Area
1	7.003	23367840	50.10
2	12.749	23277238	49.90

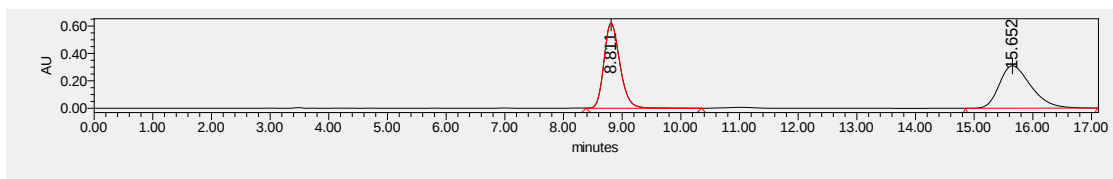


	Retention Time	Area	% Area
1	7.035	3913861	85.67
2	12.819	654891	14.33

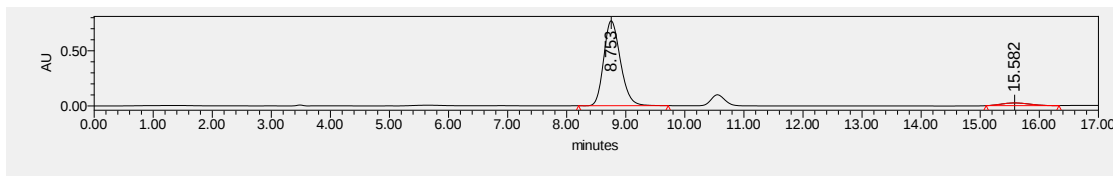
6-methoxy-2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4j)



White solid; 43% yield, 90 ee. $[\alpha]_D^{27} = -91.1$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n -hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 8.75 min (major), 15.58 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.27 (m, 3H), 7.24 – 7.18 (m, 3H), 7.13 – 7.07 (m, 2H), 6.91 – 6.86 (m, 2H), 6.80 (m, 1H), 6.71 (d, $J = 2.4$ Hz, 1H), 5.46 (s, 1H), 3.79 (d, $J = 6.8$ Hz, 6H), 3.66 – 3.49 (m, 2H), 3.12 (m, 1H), 2.90 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.58, 154.23, 144.20, 135.33, 131.70, 128.50, 128.06, 127.92, 127.82, 123.15, 120.17, 114.36, 113.42, 112.64, 88.69, 85.28, 55.58, 55.30, 53.90, 44.12, 29.35. HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}^+]$) = 370.1802, Found: 370.1806. The product was purified by flash chromatography (Pet/EtOAc = 20:1).



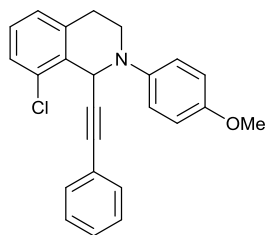
	Retention Time	Area	% Area
1	8.811	11605303	50.25
2	15.652	11489885	49.75



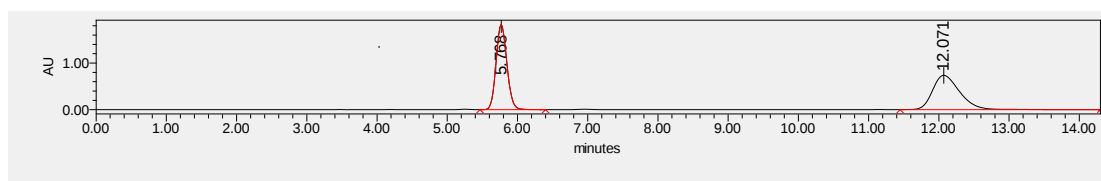
	Retention Time	Area	% Area
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1	8.753	15159393	94.96
2	15.582	805249	5.04

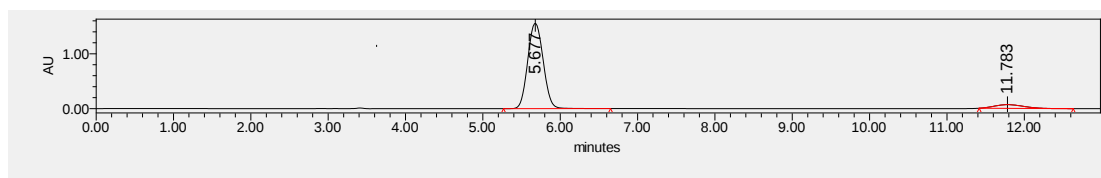
8-chloro-2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4k)



Colorless oil; 69% yield, 84 ee. $[\alpha]_D^{25} = -45.4$ ($c = 0.26$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 5.67 min (major), 11.78 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.29 (m, 2H), 7.26 – 7.16 (m, 5H), 7.16 – 7.08 (m, 3H), 6.92 – 6.85 (m, 2H), 5.65 (s, 1H), 3.79 (s, 3H), 3.70 (m, 1H), 3.59 – 3.51 (m, 1H), 3.22 – 3.11 (m, 1H), 2.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.58, 143.81, 136.50, 133.38, 132.67, 131.78, 128.08, 128.01, 127.72, 127.23, 123.06, 120.56, 114.42, 86.53, 85.43, 55.58, 52.76, 43.80, 28.93. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{35}\text{ClNO}$ ($[\text{M}+\text{H}^+]$) = 374.1307, Found: 374.1308, HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{21}^{37}\text{ClNO}$ ($[\text{M}+\text{H}^+]$) = 376.1277, Found: 376.1296. The product was purified by flash chromatography (Pet/EtOAc = 50:1).

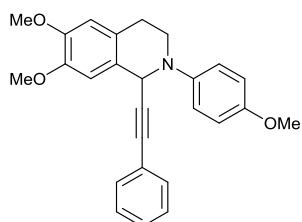


	Retention Time	Area	% Area
1	5.768	19583756	49.73
2	12.071	19798968	50.27



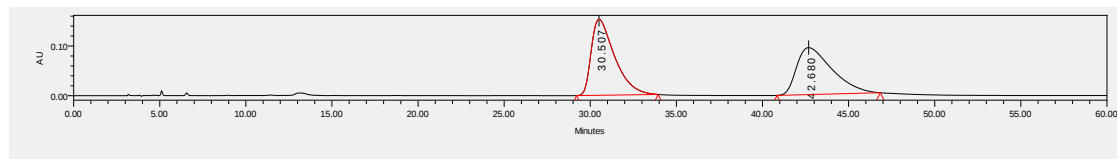
	Retention Time	Area	% Area
1	5.677	21562096	92.14
2	11.783	1838857	7.86

6,7-dimethoxy-2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4l)

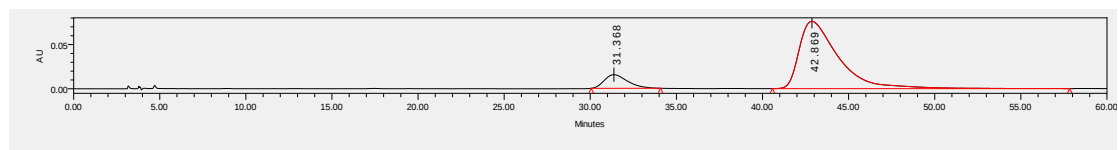


Colorless oil; 36% yield, 79 ee. $[\alpha]_D^{18} = -75.0$ ($c = 0.12$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 31.36 min (minor), 42.87 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 3H), 7.13 – 7.07 (m, 2H), 6.92 – 6.86 (m, 2H), 6.83 (s, 1H), 6.66 (s, 1H), 5.43 (s, 1H), 3.90 (s, 3H), 3.89 – 3.85 (m, 3H), 3.78 (d, $J = 5.2$ Hz, 3H), 3.57 (m, 2H), 3.07 (m, 1H), 2.88 – 2.75 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.28, 148.27, 147.57, 144.17, 131.72, 128.10, 127.99, 127.24, 126.10,

123.10, 120.32, 114.34, 111.41, 110.12, 88.56, 85.34, 56.09, 55.91, 55.57, 54.12, 44.29, 28.59. HRMS (ESI-TOF) calcd for C₂₆H₂₆NO₃ ([M+H⁺]) = 400.1908, Found: 400.1915. The product was purified by flash chromatography (Pet/EtOAc = 2:1).

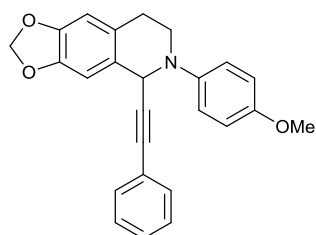


	Retention Time	Area	% Area
1	30.507	14416780	51.72
2	42.680	13459699	48.28

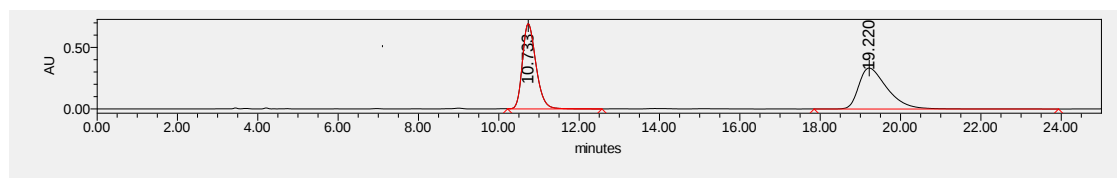


	Retention Time	Area	% Area
1	31.368	1440966	10.72
2	42.869	12002217	89.28

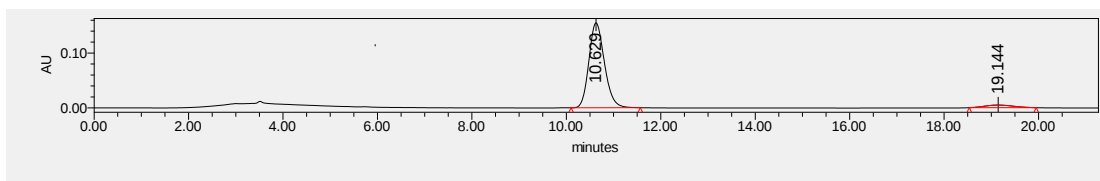
6-(4-methoxyphenyl)-5-(phenylethynyl)-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinoline (4m)



Colorless oil; 45% yield, 90 ee. $[\alpha]_D^{25} = -54.5$ (c = 0.13 in CH₂Cl₂). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 10.63 min (major), 19.14 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 7.11 – 7.02 (m, 2H), 6.93 – 6.85 (m, 2H), 6.80 (s, 1H), 6.62 (s, 1H), 5.93 (d, *J* = 2.0 Hz, 2H), 5.39 (s, 1H), 3.78 (s, 3H), 3.64 – 3.46 (m, 2H), 3.04 (m, 1H), 2.80 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.31, 146.87, 146.06, 144.03, 131.70, 128.30, 128.09, 128.00, 127.35, 123.03, 120.23, 114.37, 108.61, 107.31, 100.91, 88.38, 85.43, 55.59, 54.41, 44.21, 29.03. HRMS (ESI-TOF) calcd for C₂₅H₂₂NO₃ ([M+H⁺]) = 384.1595, Found: 384.1597. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

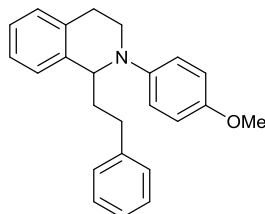


	Retention Time	Area	% Area
1	10.733	16294982	49.98
2	19.220	16307595	50.02

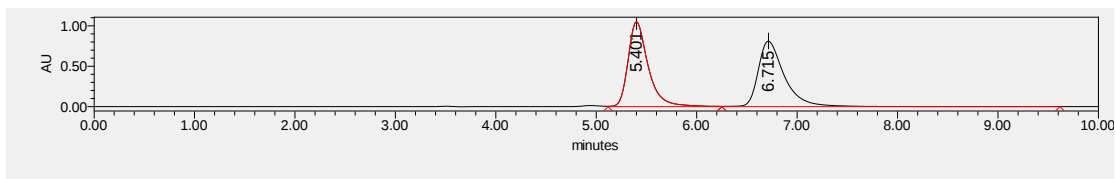


	Retention Time	Area	% Area
1	10.629	3583064	94.96
2	19.144	190162	5.04

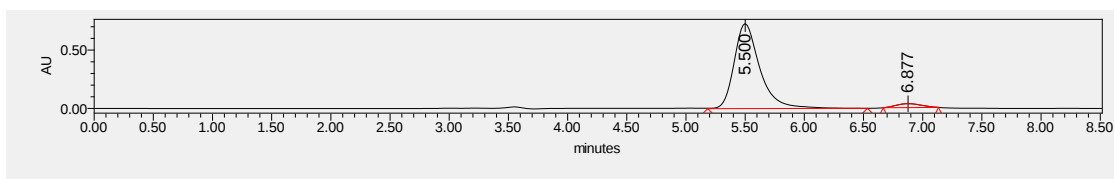
2-(4-methoxyphenyl)-1-phenethyl-1,2,3,4-tetrahydroisoquinoline (5a)



Colorless oil; 80% yield, 92 ee. $[\alpha]_D^{20} = -57.8$ ($c = 0.10$ in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 5.40 min (major), 6.72 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.18 (m, 2H), 7.16 – 7.11 (m, 5H), 7.10 – 7.08 (m, 1H), 7.05 (m, 1H), 6.85 – 6.74 (m, 4H), 4.49 (m, 1H), 3.70 (s, 3H), 3.54 (m, 2H), 2.92 (m, 1H), 2.80 – 2.62 (m, 3H), 2.29 – 2.13 (m, 1H), 2.07 – 1.94 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.70, 144.71, 142.27, 139.05, 135.03, 128.91, 128.58, 128.37, 127.27, 126.31, 125.86, 125.78, 117.86, 114.65, 59.02, 55.72, 43.10, 38.43, 32.96, 26.34. HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}$ ($[\text{M}+\text{H}^+]$) = 344.2009, Found: 344.2015. The product was purified by flash chromatography (Pet/EtOAc = 30:1).

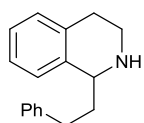


	Retention Time	Area	% Area
1	5.401	14617664	49.88
2	6.715	14688940	50.12



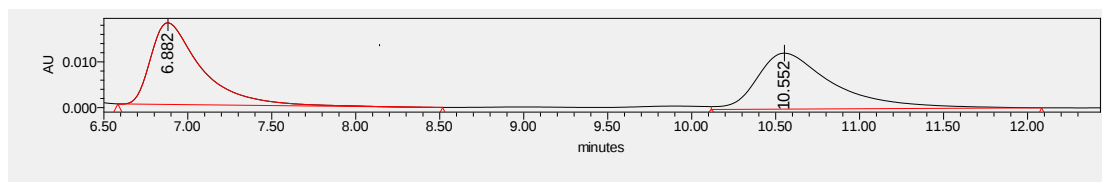
	Retention Time	Area	% Area
1	5.500	10682977	96.03
2	6.877	441830	3.97

1-phenethyl-1,2,3,4-tetrahydroisoquinoline (6a)

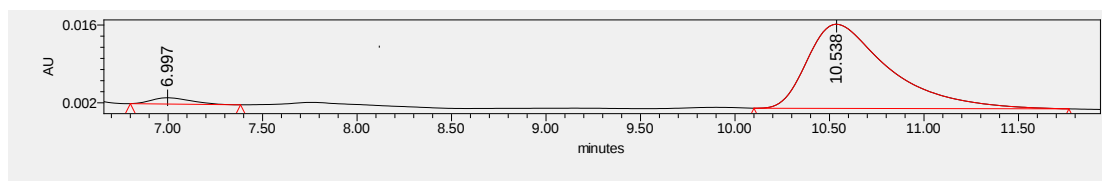


Brown oil; 67% yield, 93 ee. $[\alpha]_D^{17} = 17.5$ ($c = 0.12$ in CHCl_3). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 6.99 min (major), 10.54 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.04 (m, 9H), 4.02 (m, 1H), 3.26 (m, 1H), 3.02 (m, 1H), 2.79 (m, 4H), 2.23 – 1.97 (m, 2H), 1.79 (s, 1H). ^{13}C NMR (100 MHz,

CDCl₃) δ 142.32, 139.41, 135.24, 129.32, 128.44, 126.13, 125.94, 125.83, 55.36, 40.98, 38.15, 32.43, 29.99. HRMS (ESI-TOF) calcd for C₁₇H₂₀N ([M+H]⁺) = 238.1591, Found: 238.1591. The product was purified by flash chromatography (Pet/EtOAc = 2:1).

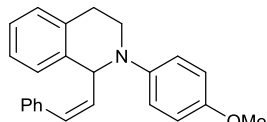


	Retention Time	Area	% Area
1	6.882	365192	51.23
2	10.552	347638	48.77

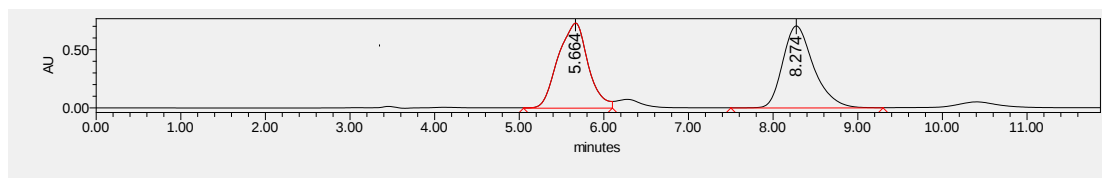


	Retention Time	Area	% Area
1	6.997	14847	3.17
2	10.538	453100	96.83

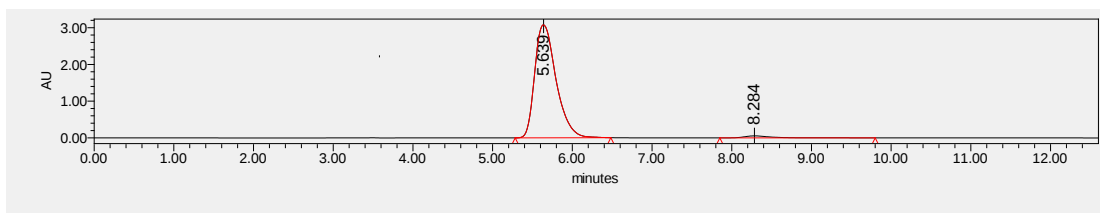
(Z)-2-(4-methoxyphenyl)-1-styryl-1,2,3,4-tetrahydroisoquinoline (7a)



Colorless oil; 83% yield, 95 ee. $[\alpha]_D^{20} = -106.2$ ($c = 0.50$ in CH₂Cl₂). HPLC DAICEL CHIRALCEL ODH, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 5.66 min (major), 8.27 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.14 (m, 6H), 7.09 (m, 3H), 6.75 – 6.68 (m, 2H), 6.66 – 6.58 (m, 2H), 6.48 (d, $J = 11.6$ Hz, 1H), 5.71 (m, 1H), 5.38 (d, $J = 10.0$ Hz, 1H), 3.67 (s, 3H), 3.40 (m, 2H), 2.88 (t, $J = 5.6$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 154.29, 144.44, 137.28, 137.02, 134.85, 132.55, 130.46, 129.05, 128.60, 128.30, 127.58, 127.14, 126.55, 126.03, 121.63, 114.08, 57.82, 55.54, 46.64, 28.77. HRMS (ESI-TOF) calcd for C₂₄H₂₄NO ([M+H]⁺) = 342.1853, Found: 342.1858. The product was purified by flash chromatography (Pet/EtOAc = 20:1).

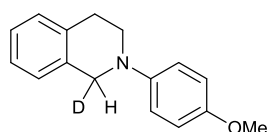


	Retention Time	Area	% Area
1	5.664	17992416	50.14
2	8.274	17890554	49.86



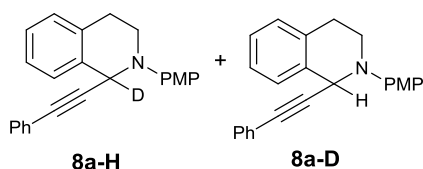
	Retention Time	Area	% Area
1	5.639	56867599	97.76
2	8.284	1301381	2.24

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-d (1p)



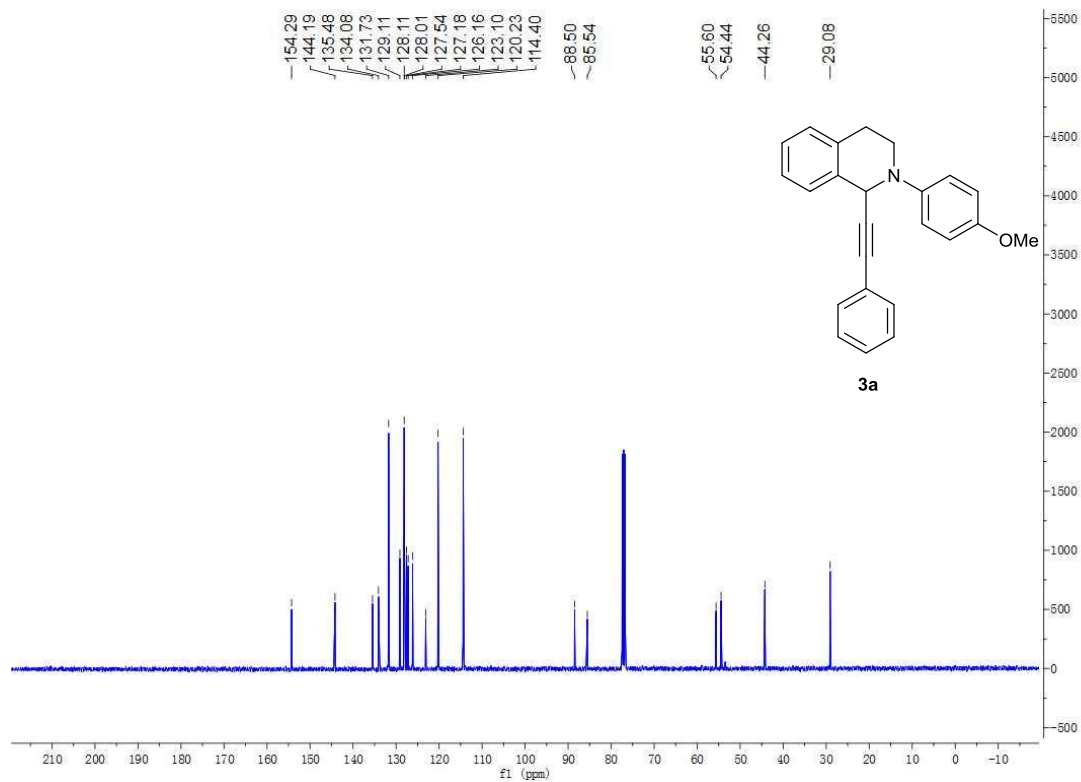
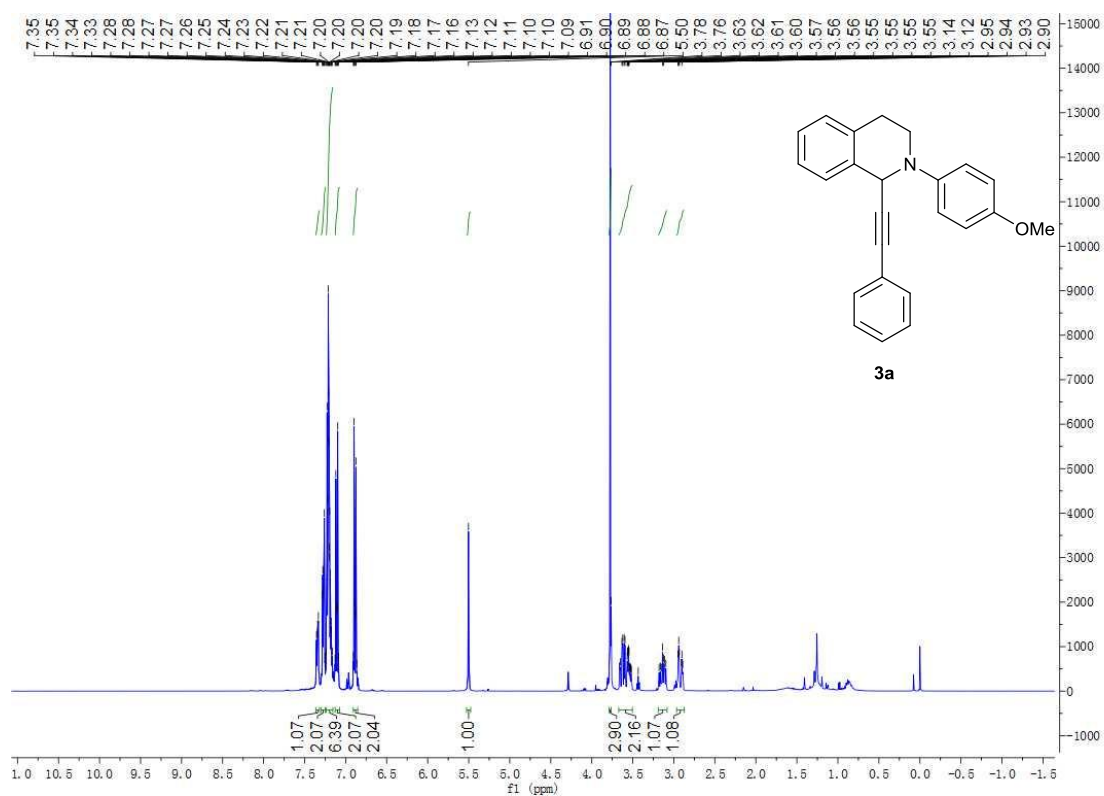
White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.20 – 7.10 (m, 4H), 7.01 – 6.95 (m, 2H), 6.90 – 6.84 (m, 2H), 4.27 (s, 0.91H), 3.78 (s, 3H), 3.45 (m, 2H), 2.98 (t, $J = 5.6$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.32, 139.41, 135.24, 129.32, 128.44, 126.13, 125.94, 125.83, 55.36, 40.98, 38.15, 32.43, 29.99.

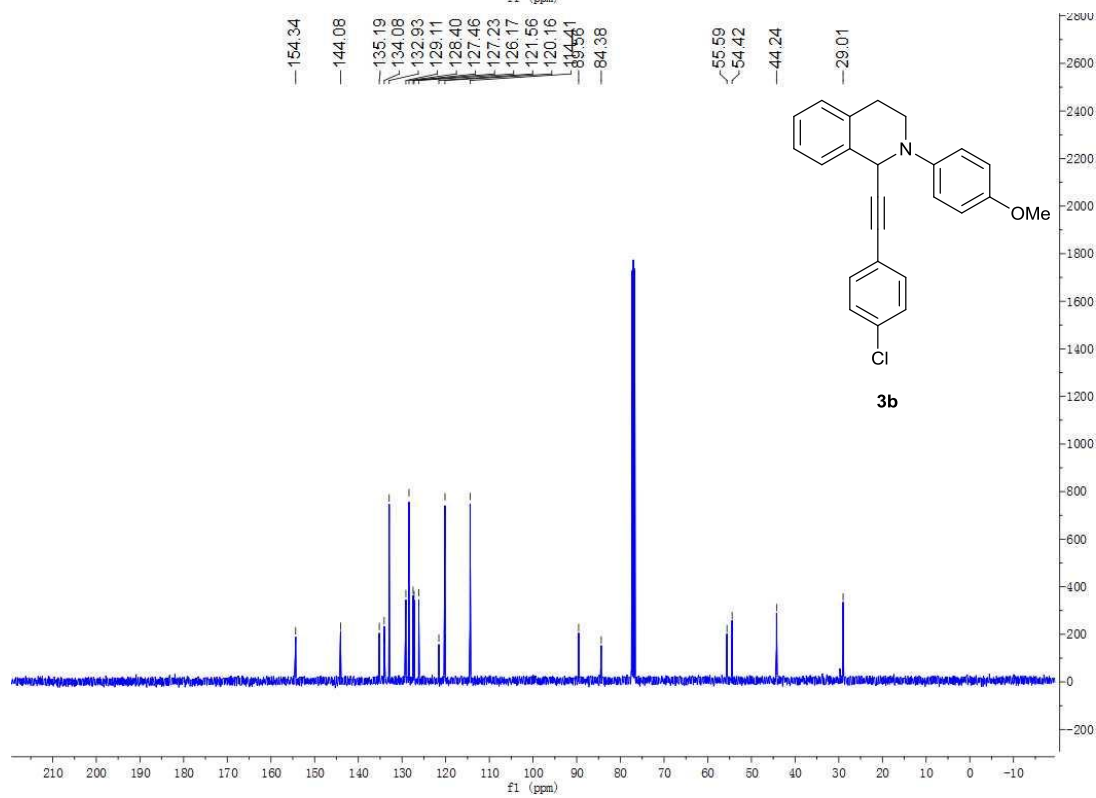
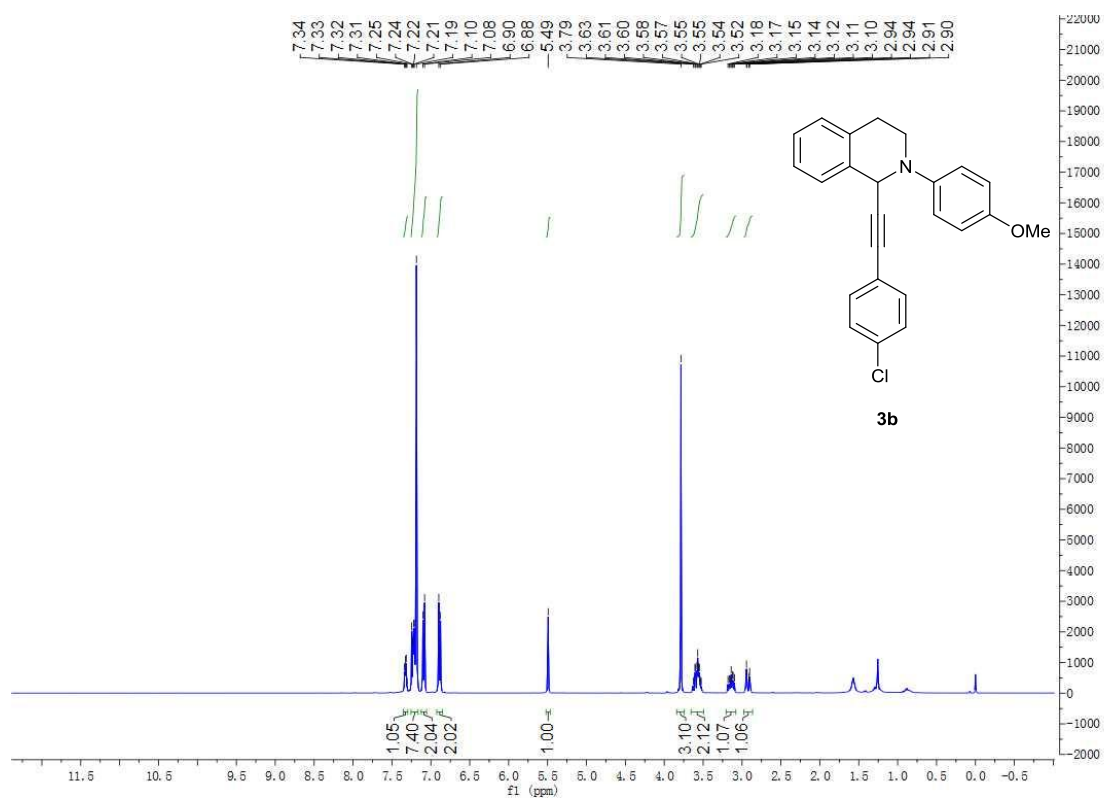
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-d (8a-H + 8a-D)

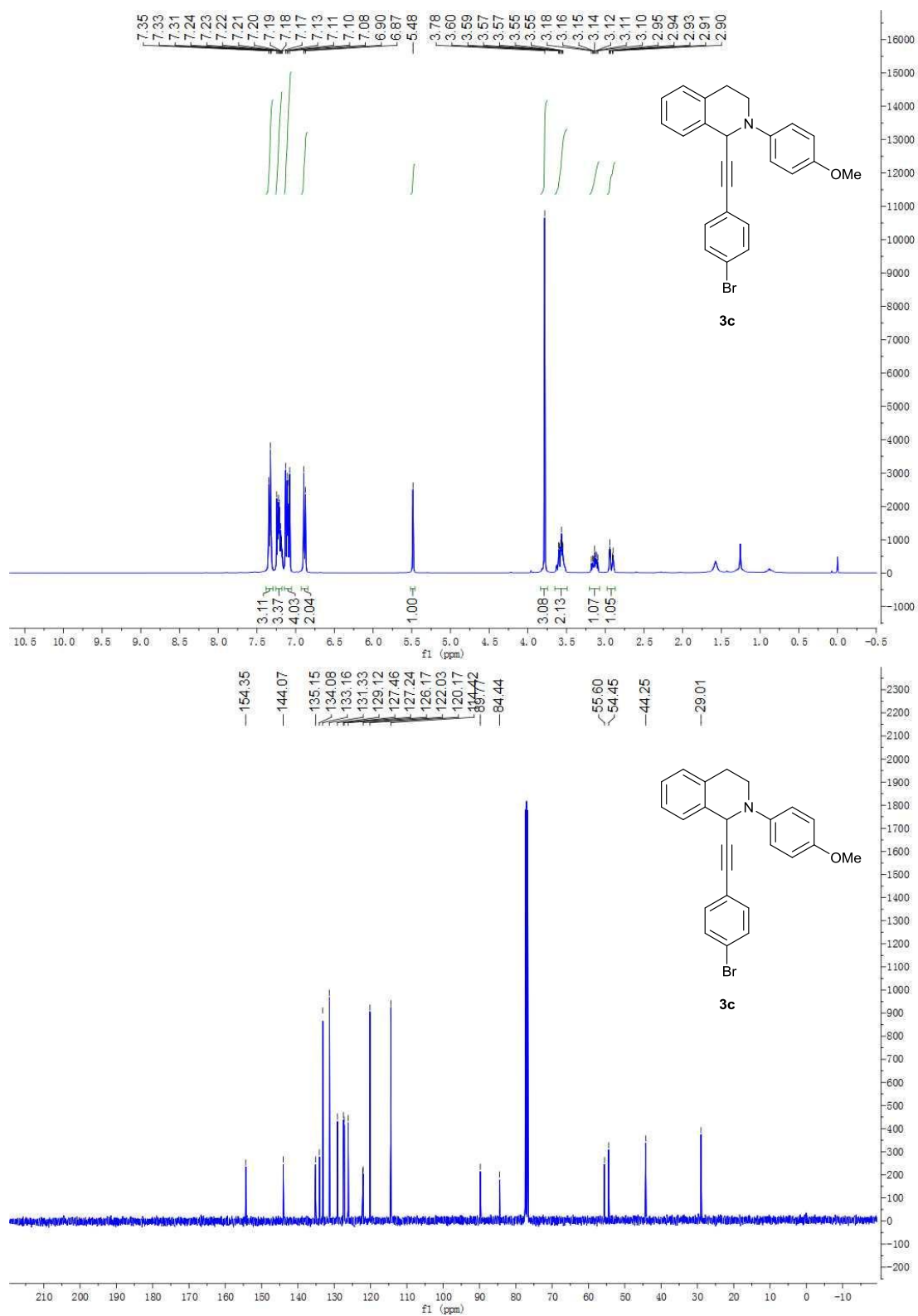


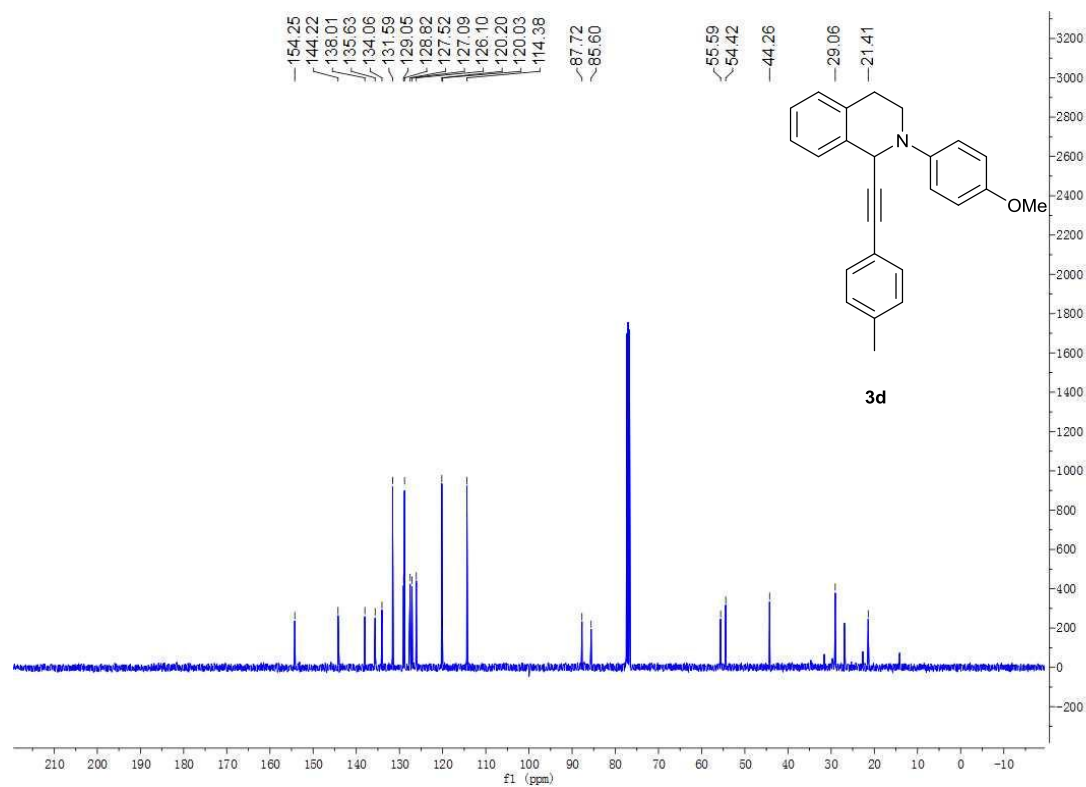
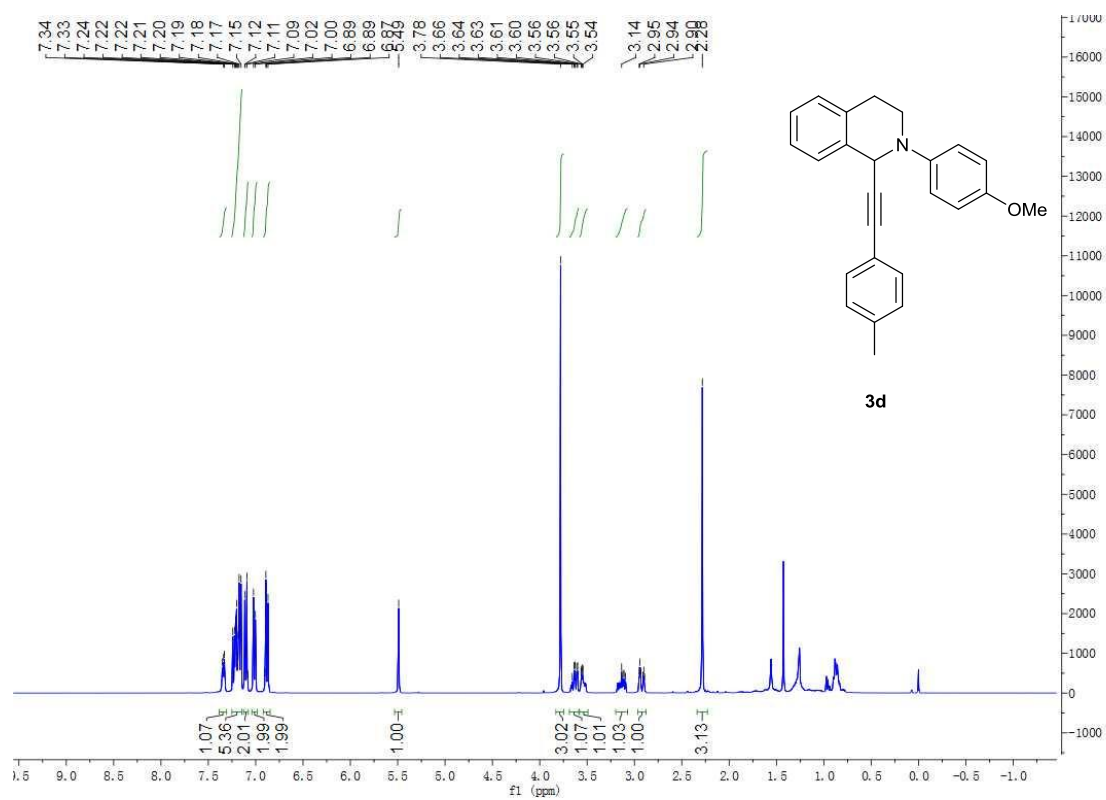
colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 1H), 7.30 – 7.26 (m, 2H), 7.21 (m, 6H), 7.11 (m, 2H), 6.94 – 6.80 (m, 2H), 5.51 (s, 0.15H), 3.79 (s, 3H), 3.68 – 3.51 (m, 2H), 3.15 (m, 1H), 2.98 – 2.87 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.24, 144.14, 135.39, 134.07, 131.71, 129.08, 128.07, 127.97, 127.48, 127.15, 126.12, 123.07, 120.14, 114.38, 88.42, 85.50, 55.58, 44.15, 29.03, 26.93.

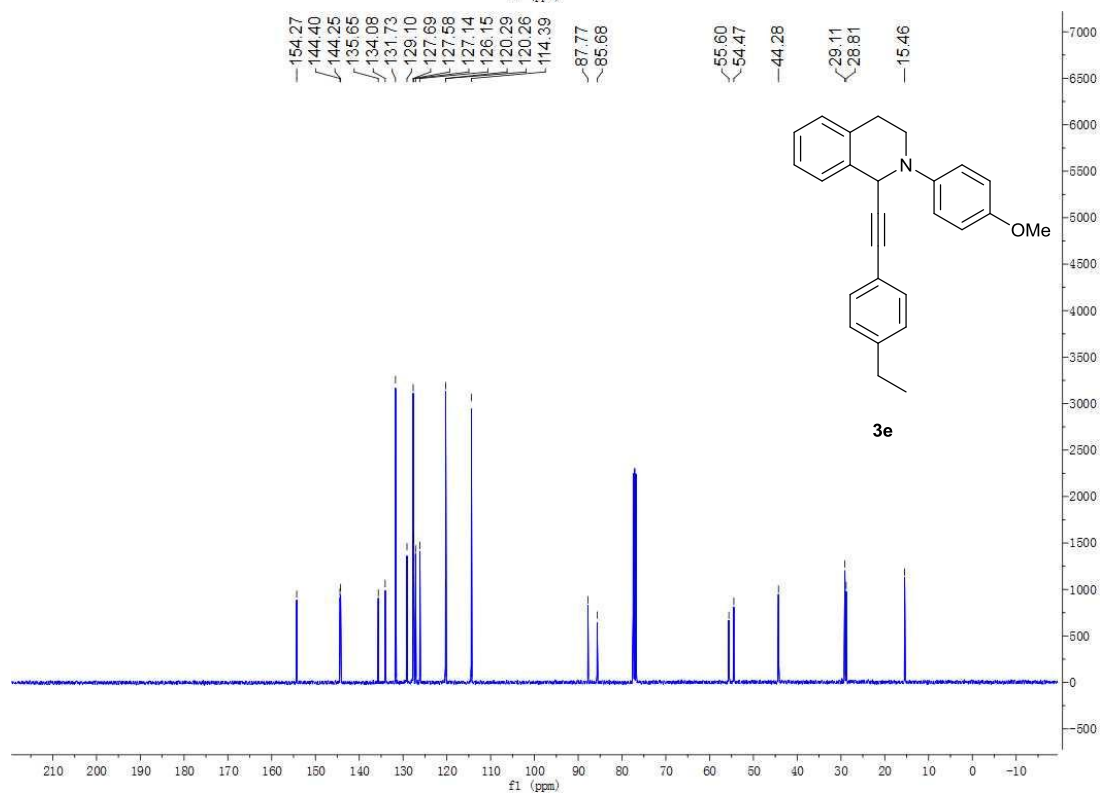
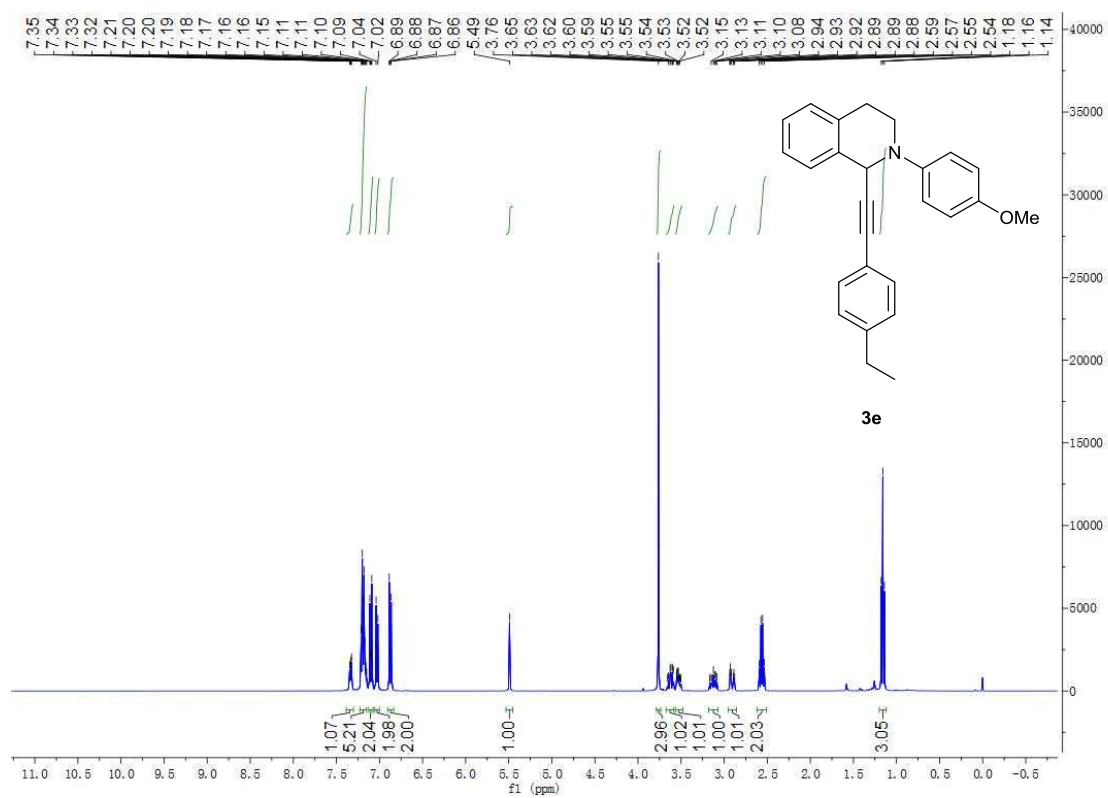
(I) Copies of NMR spectra

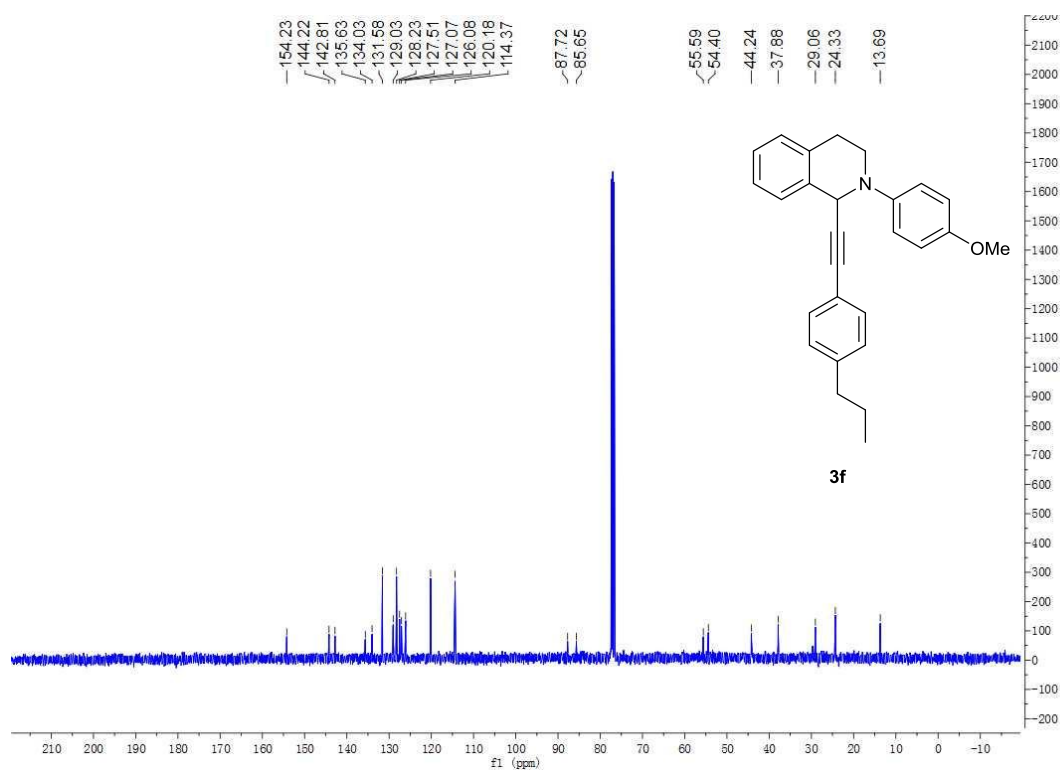
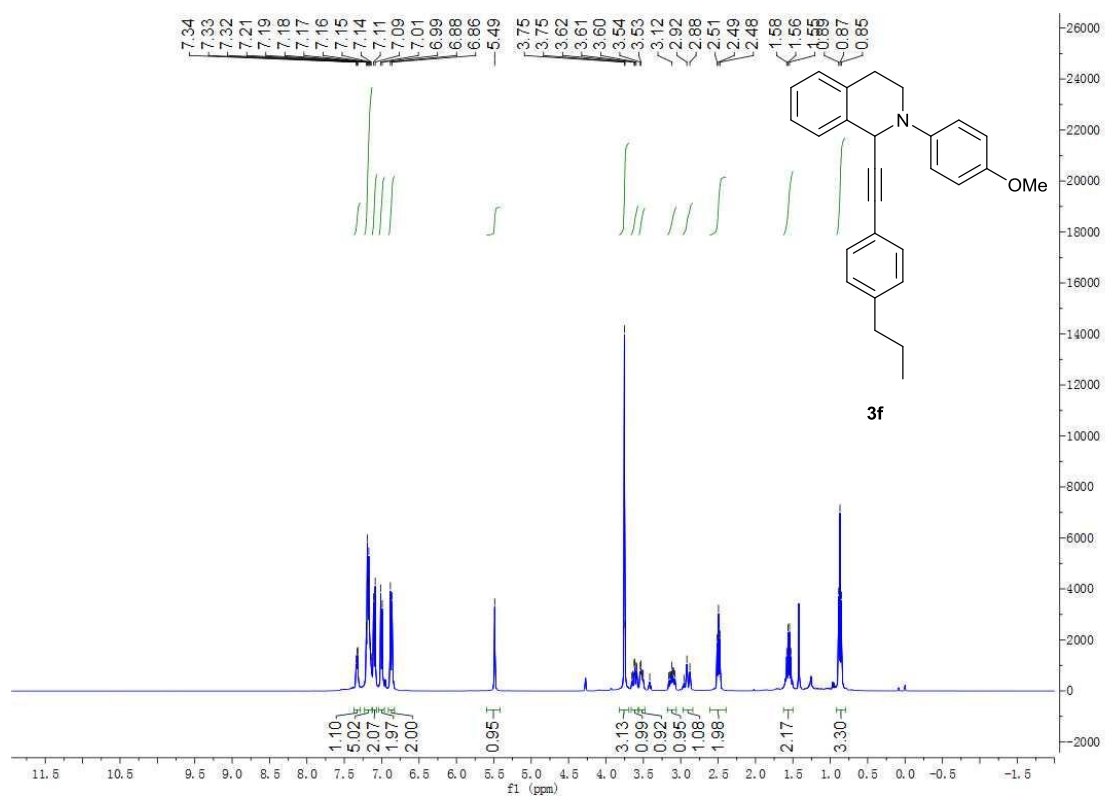


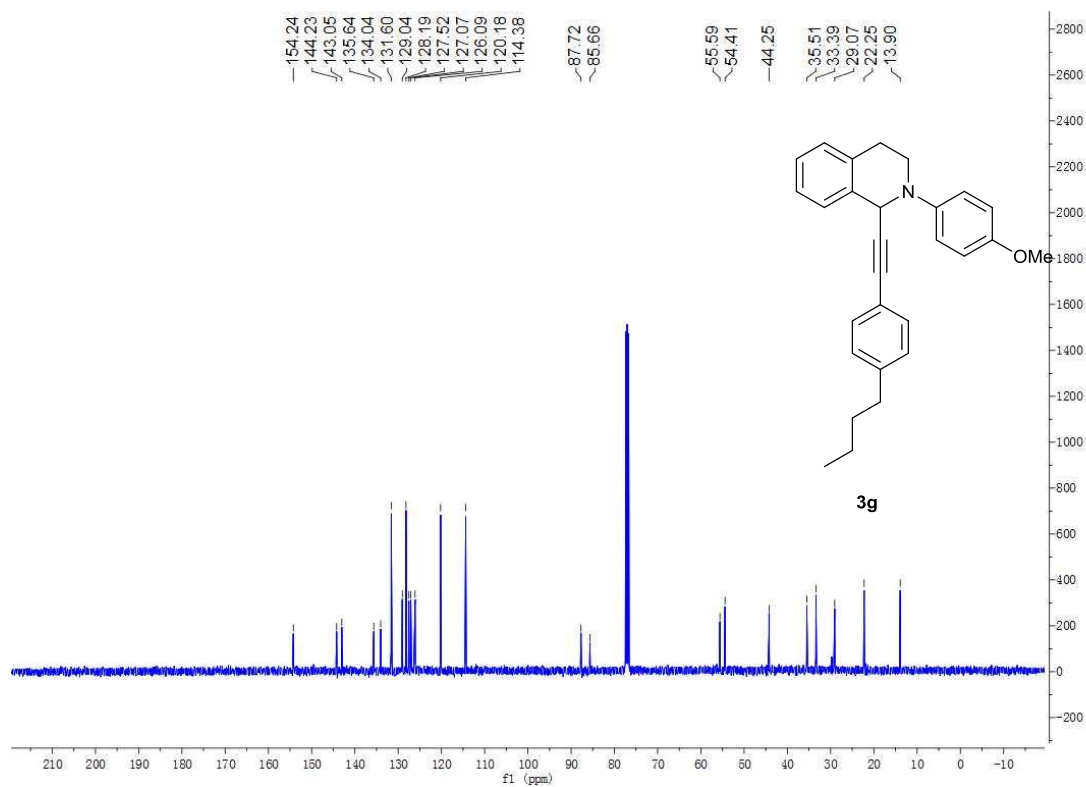
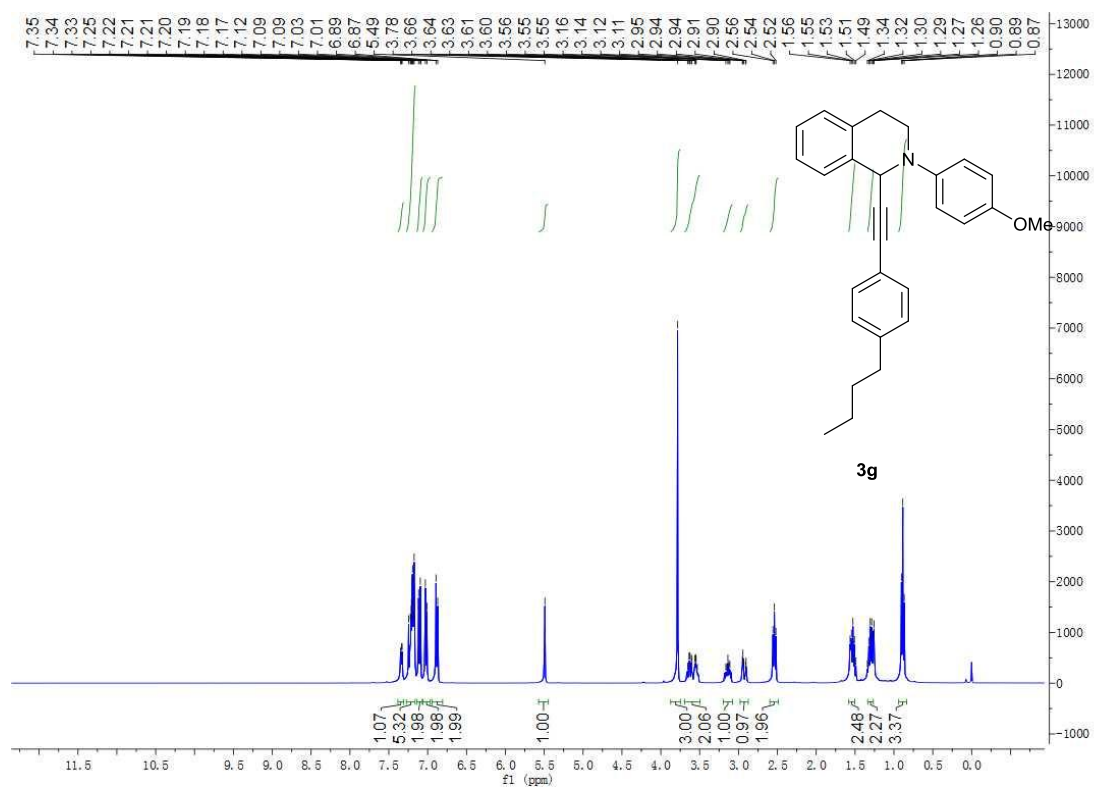


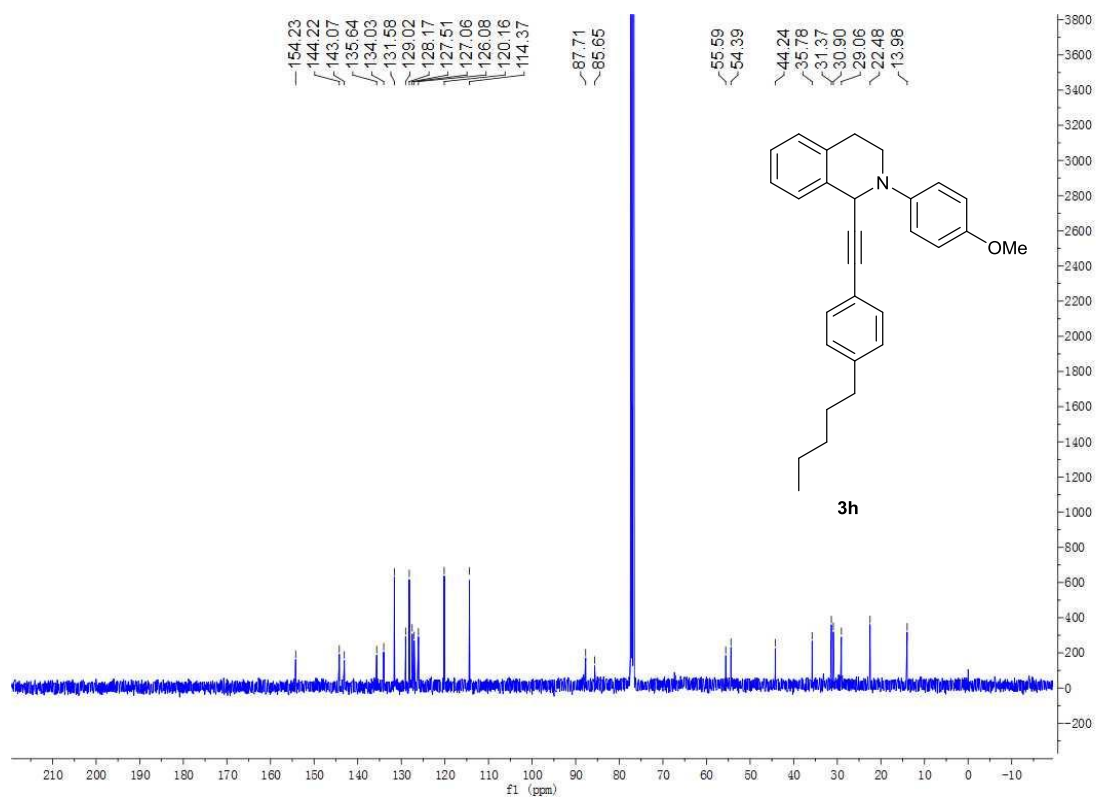
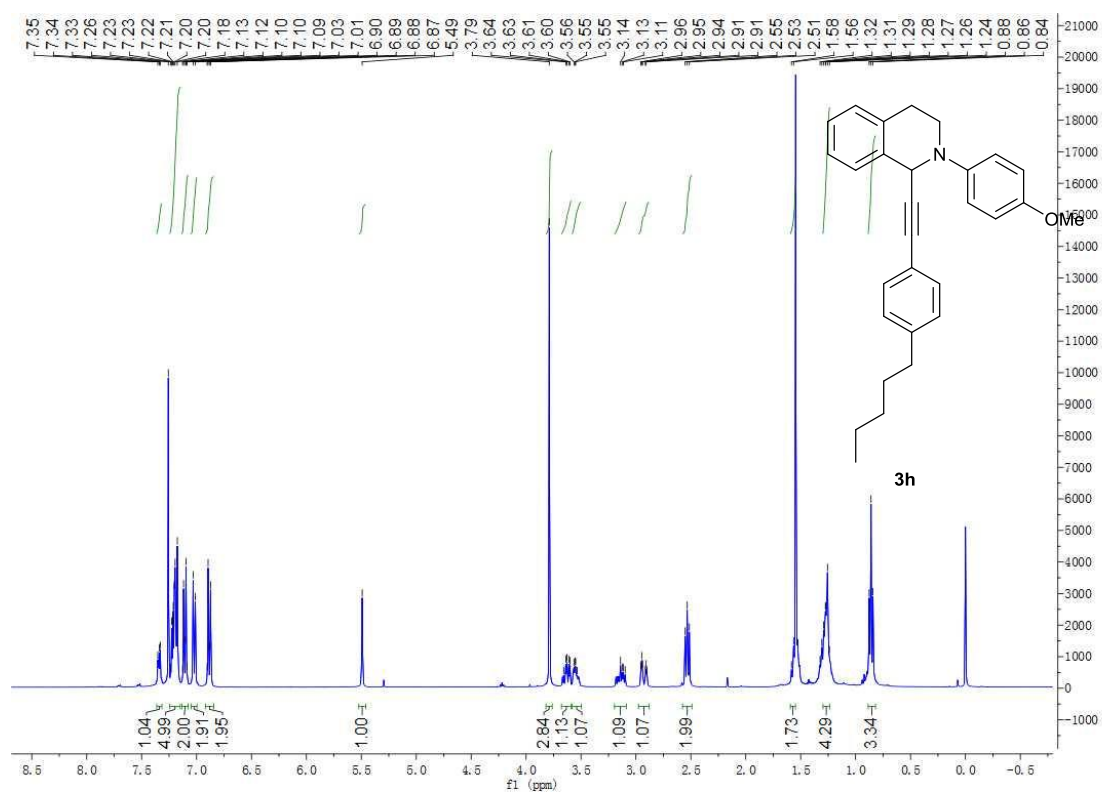


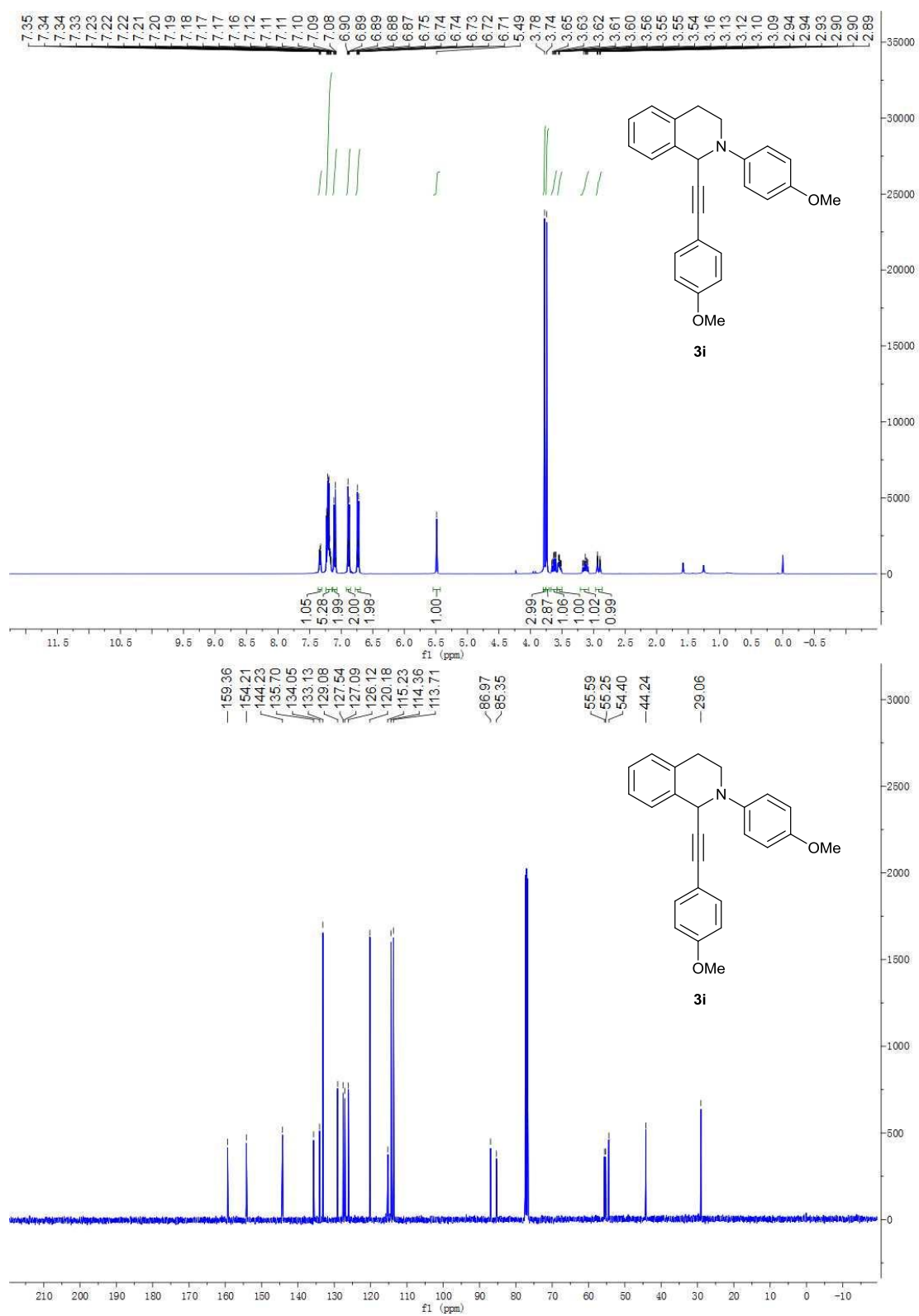


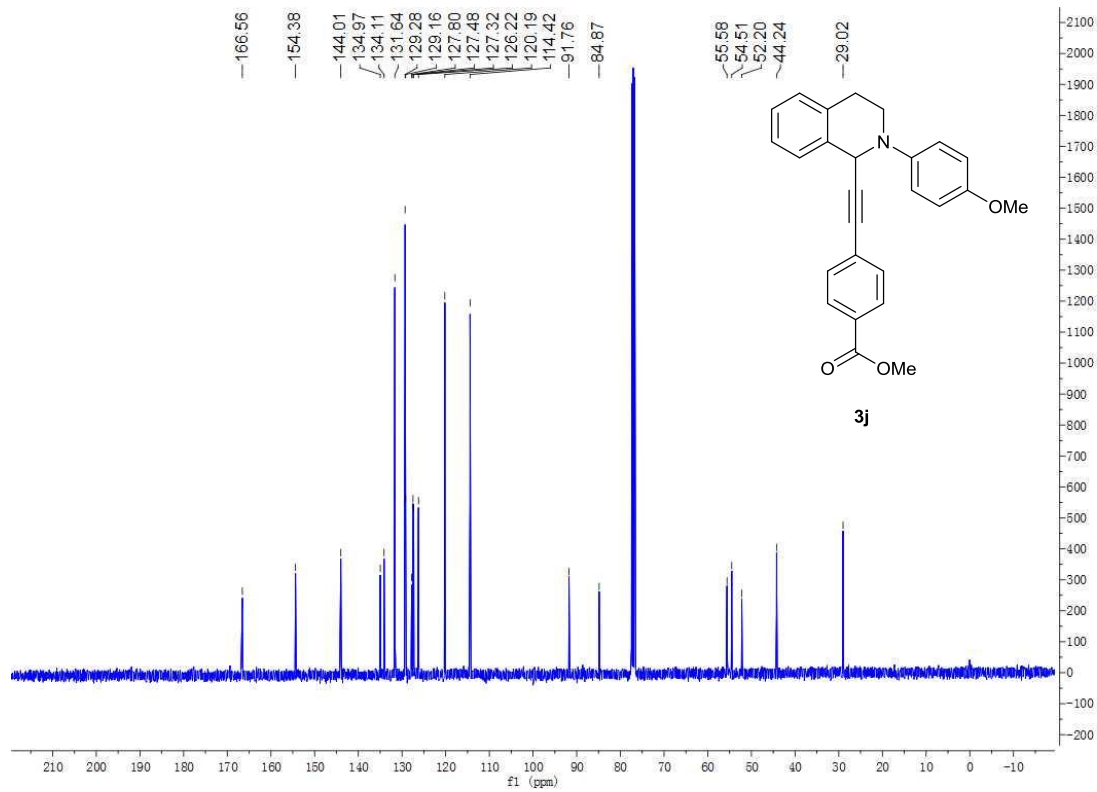
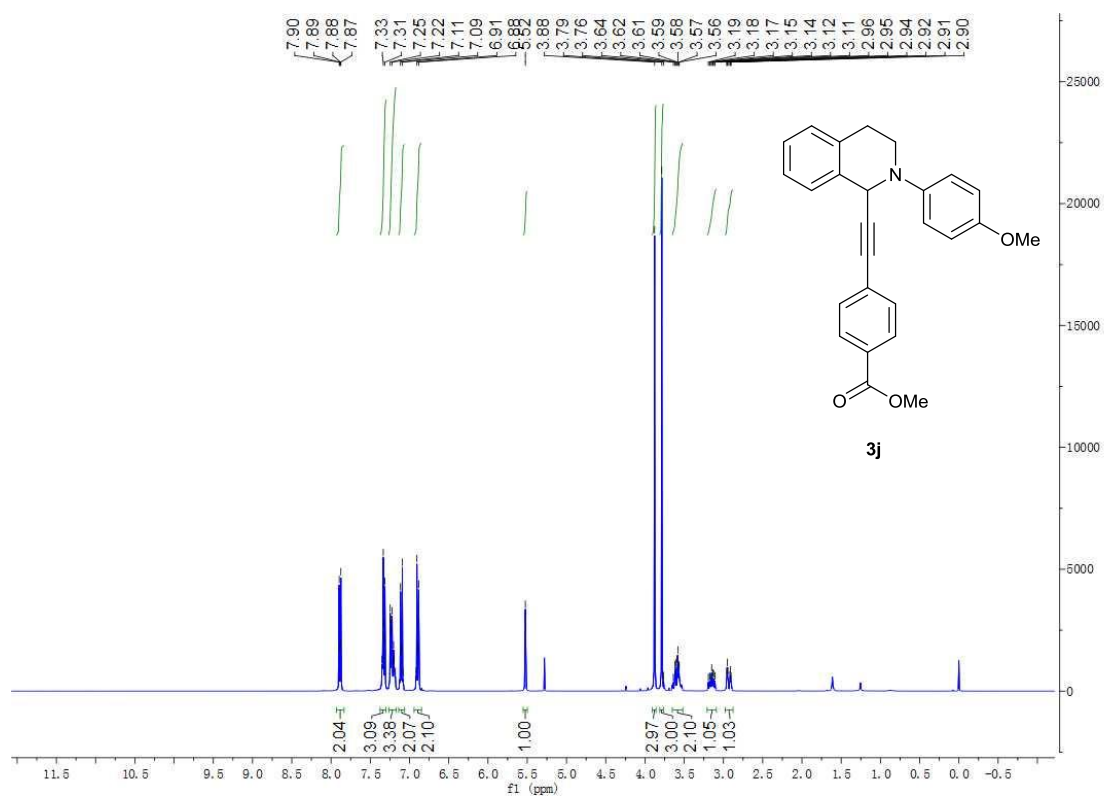


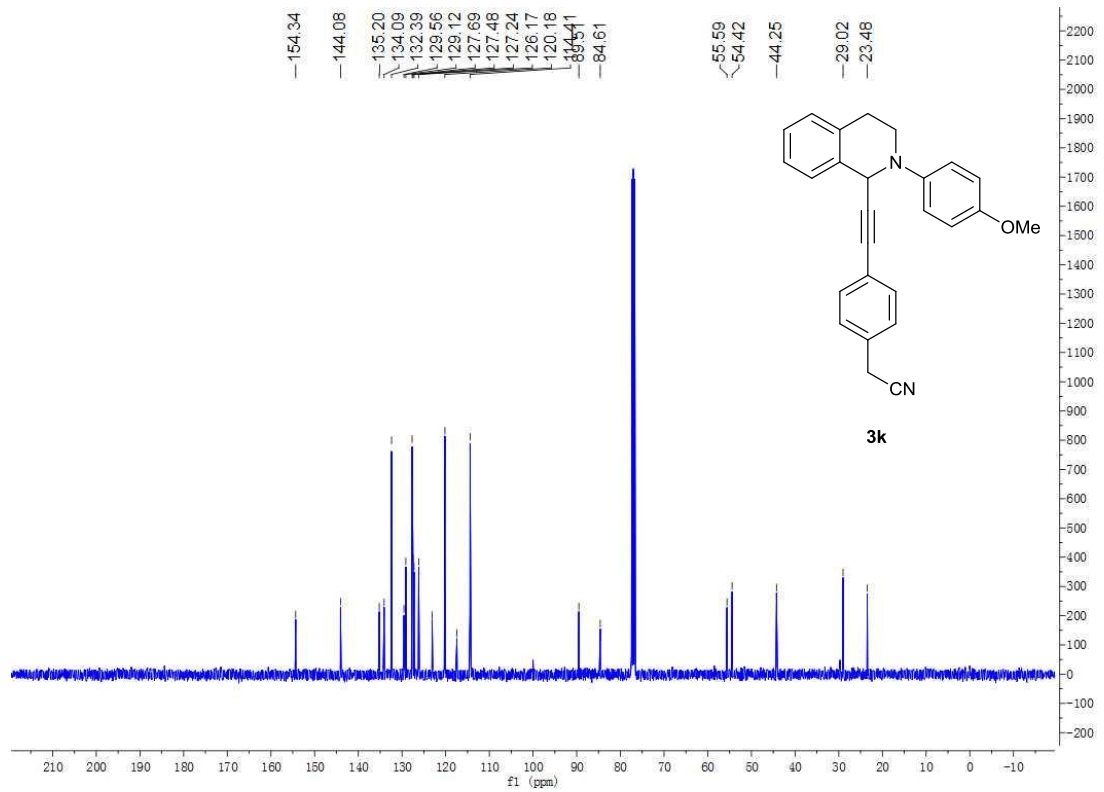
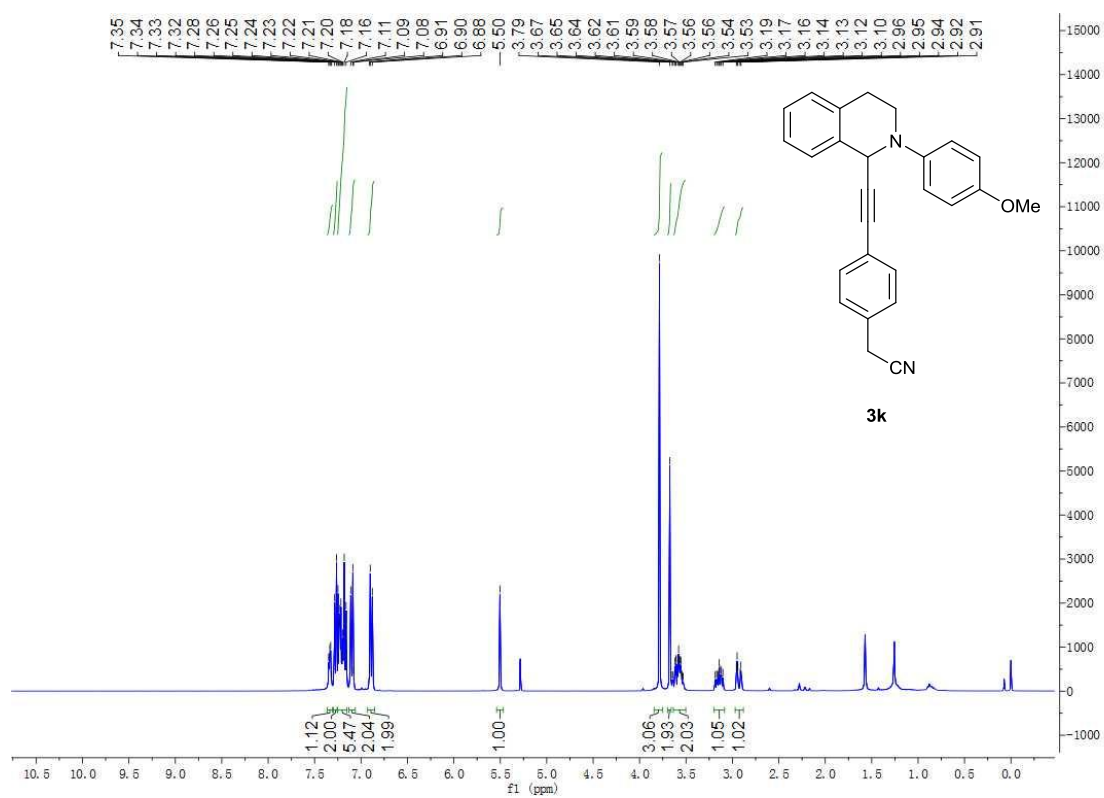


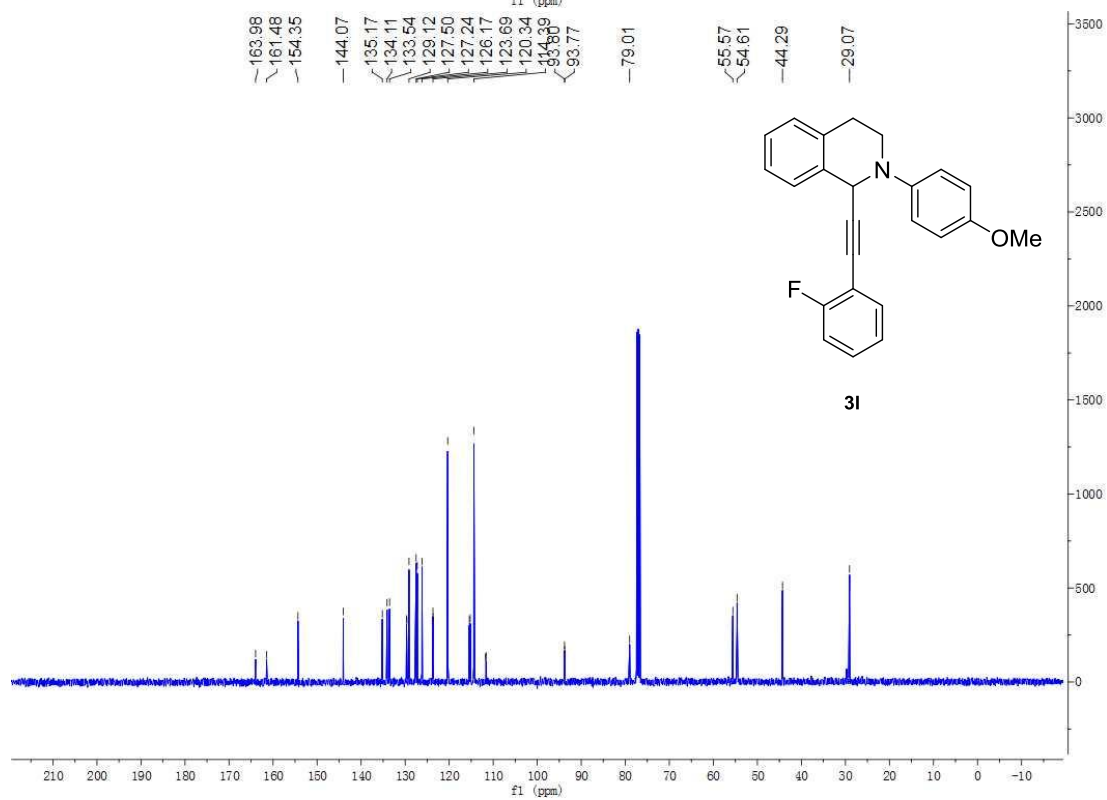
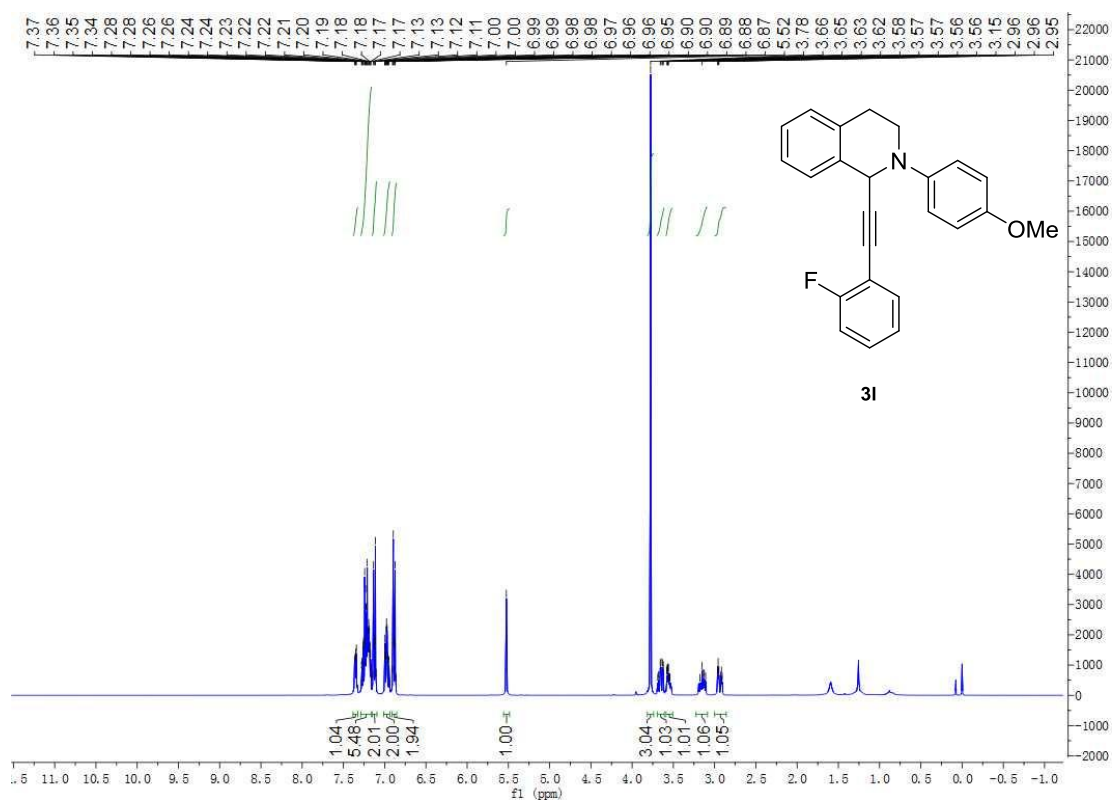


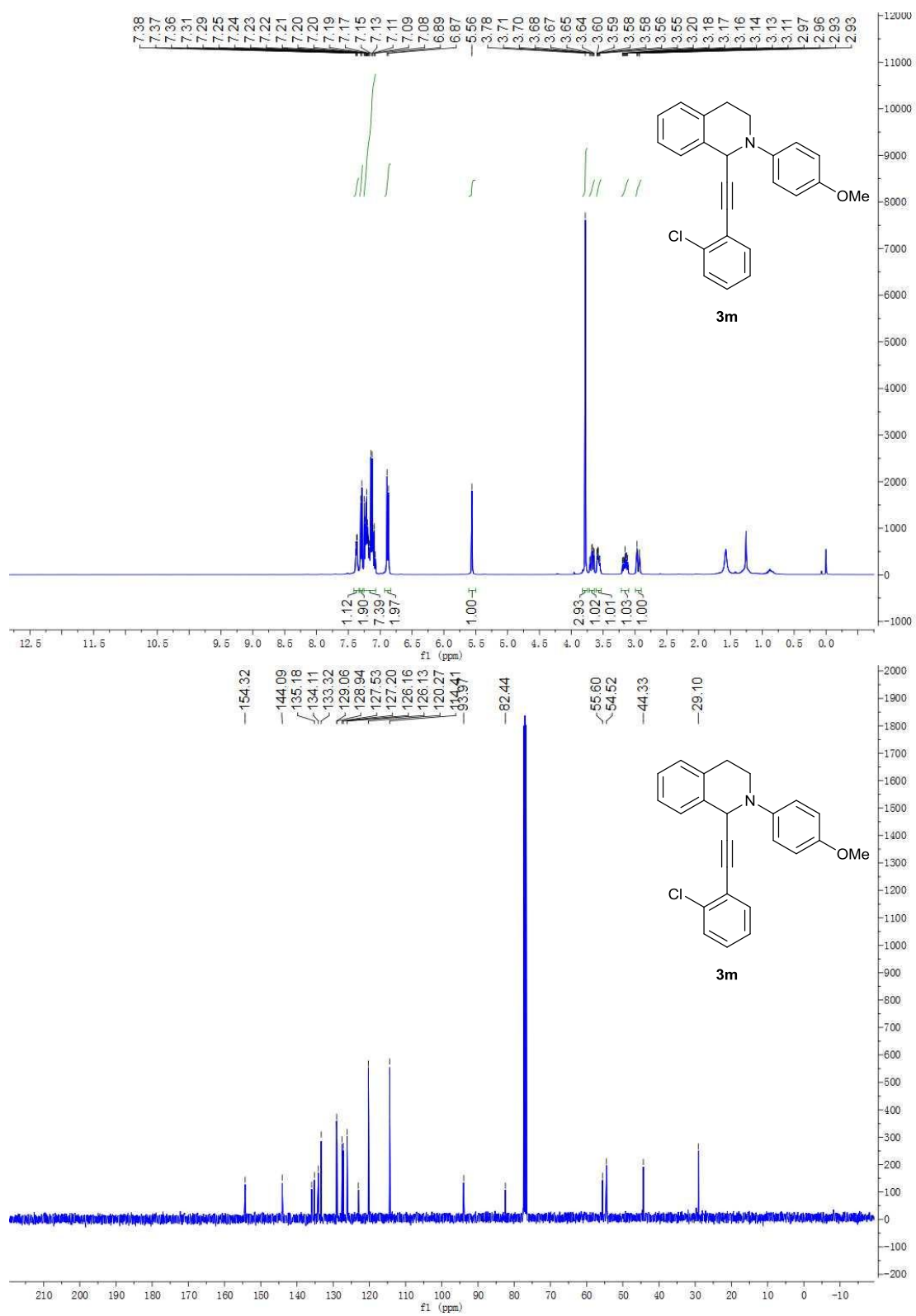


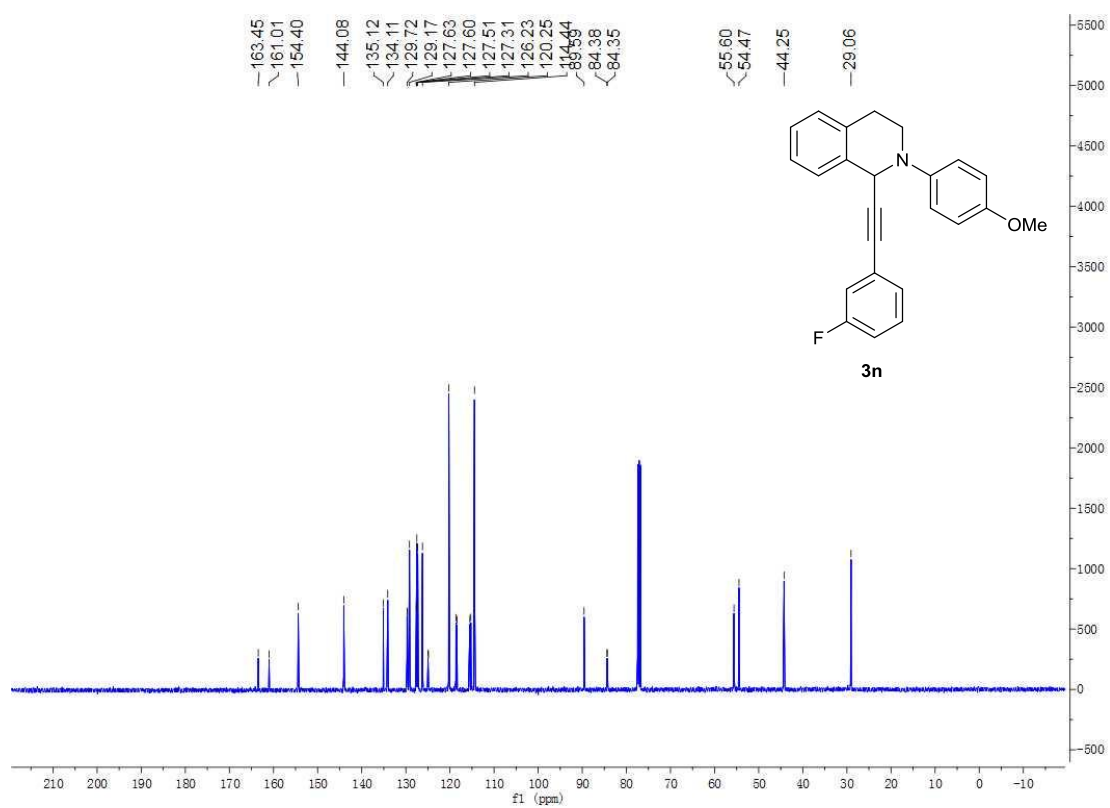
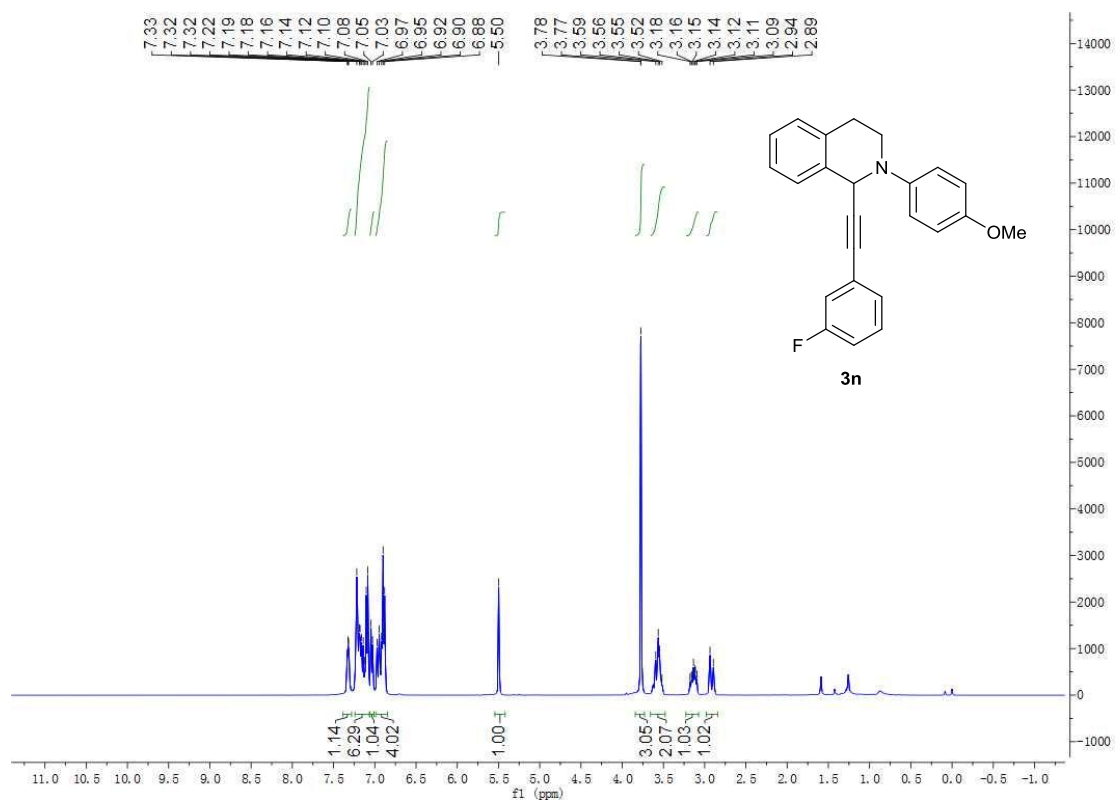


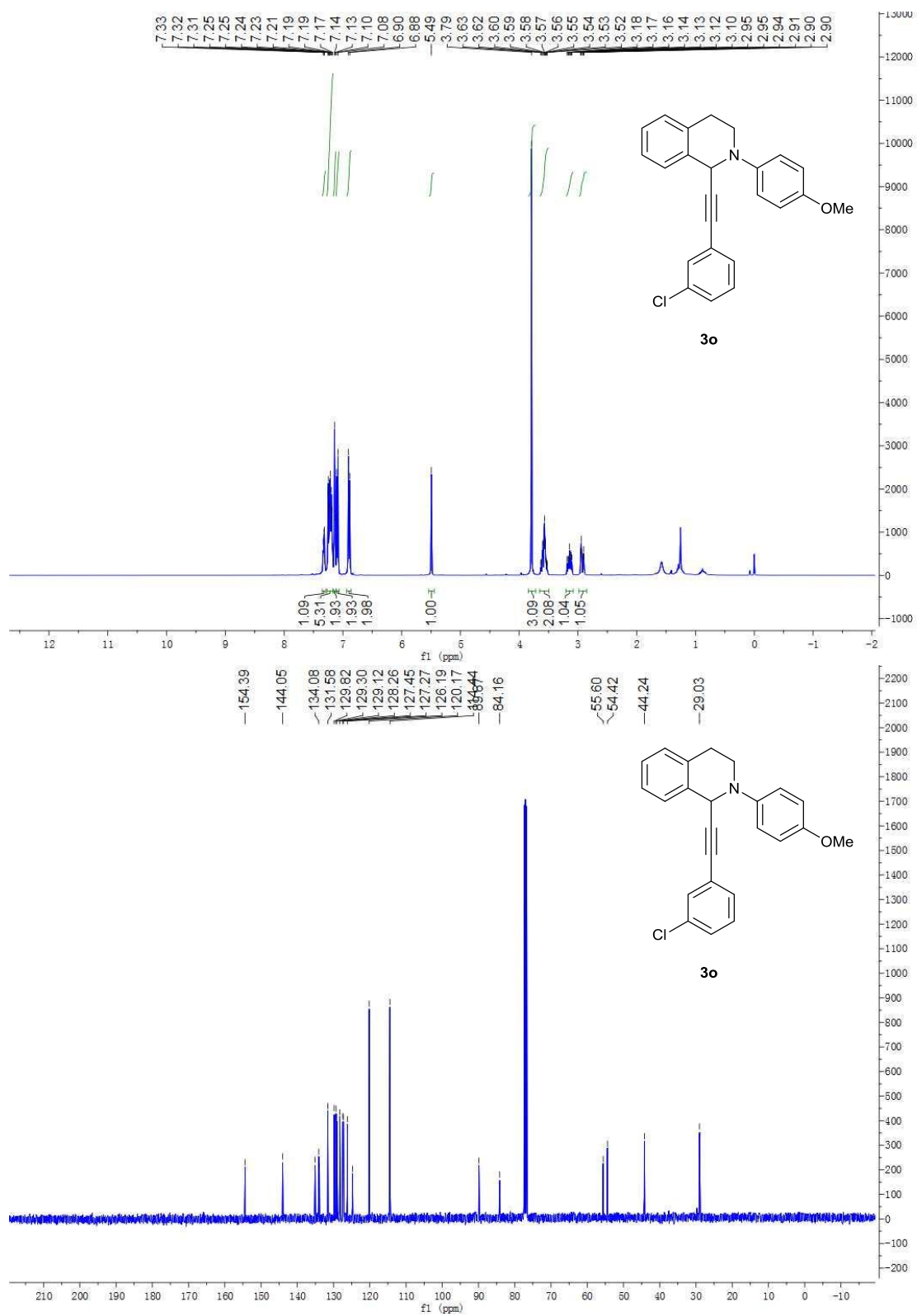


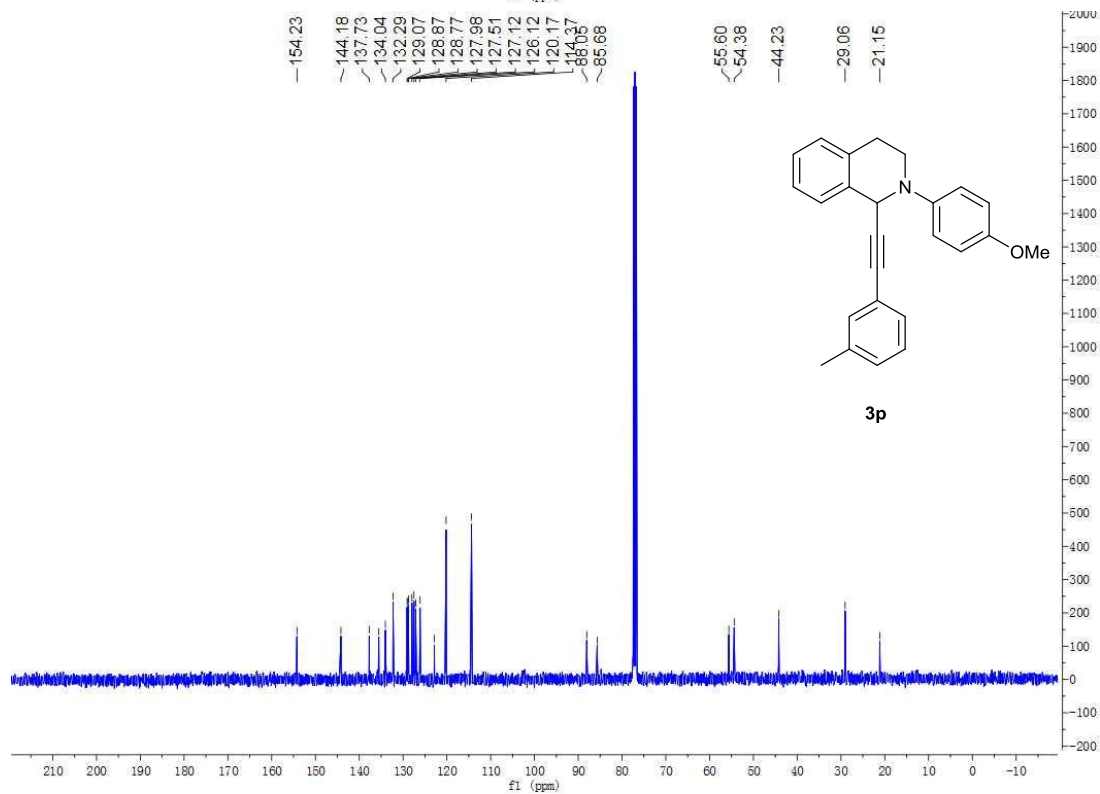
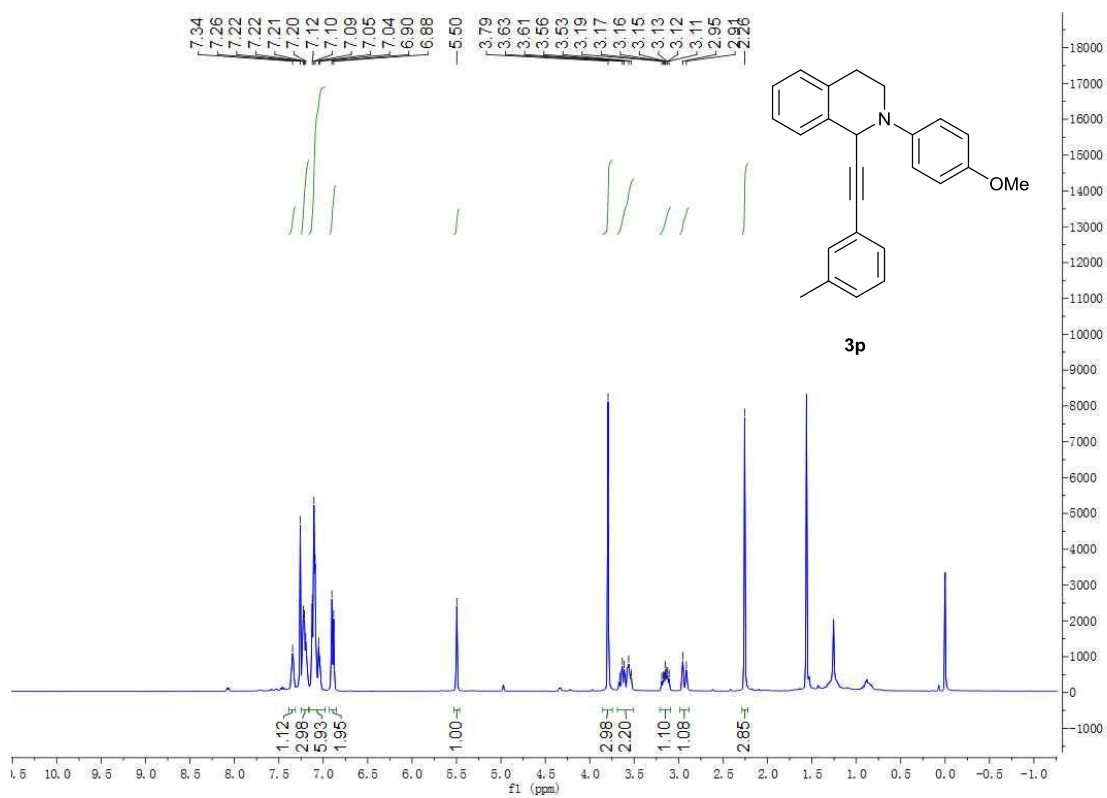


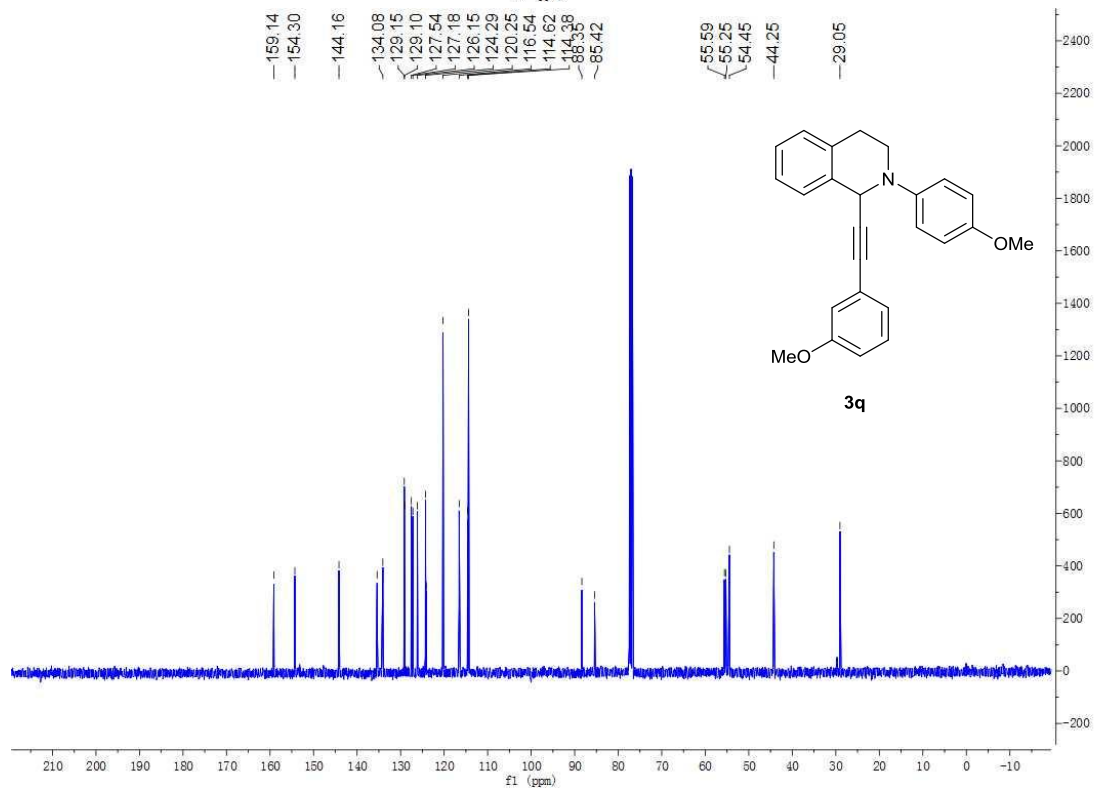
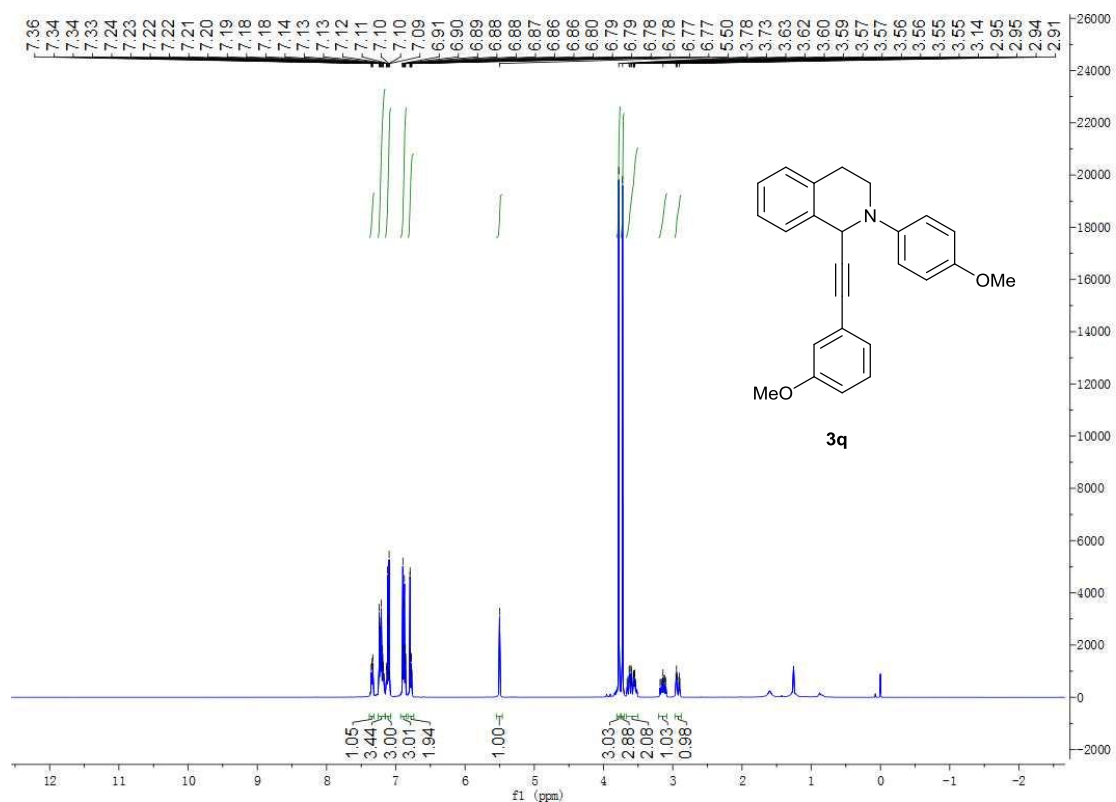


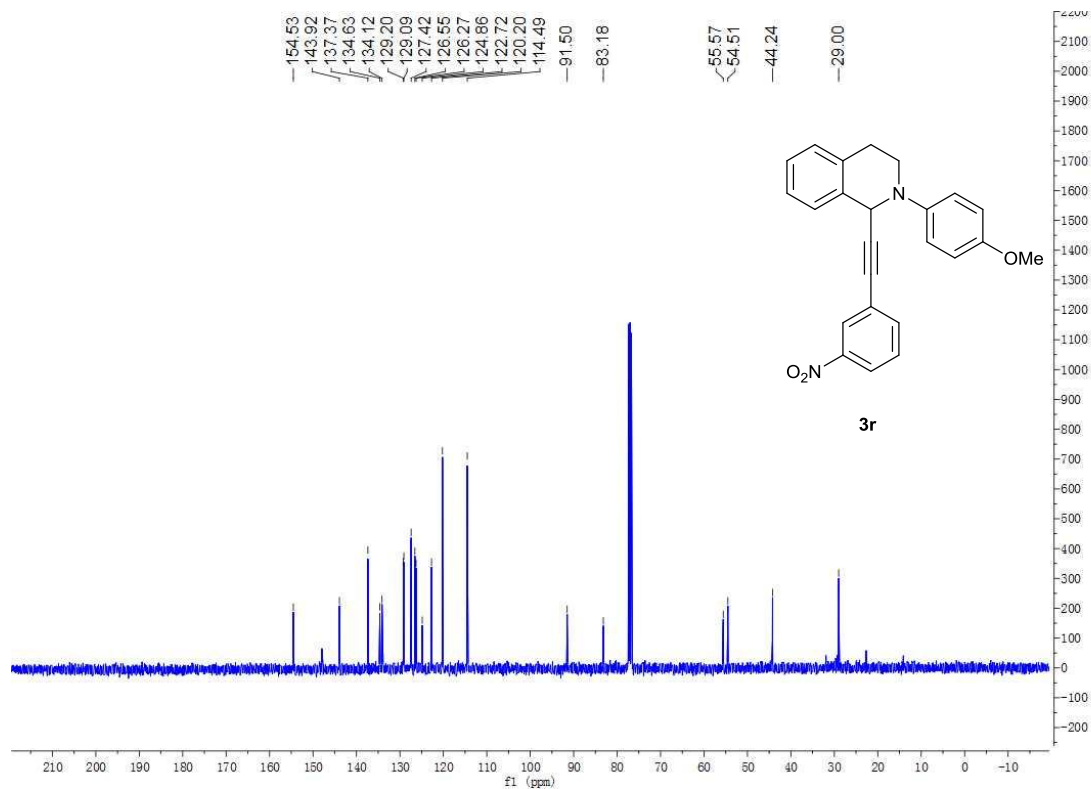
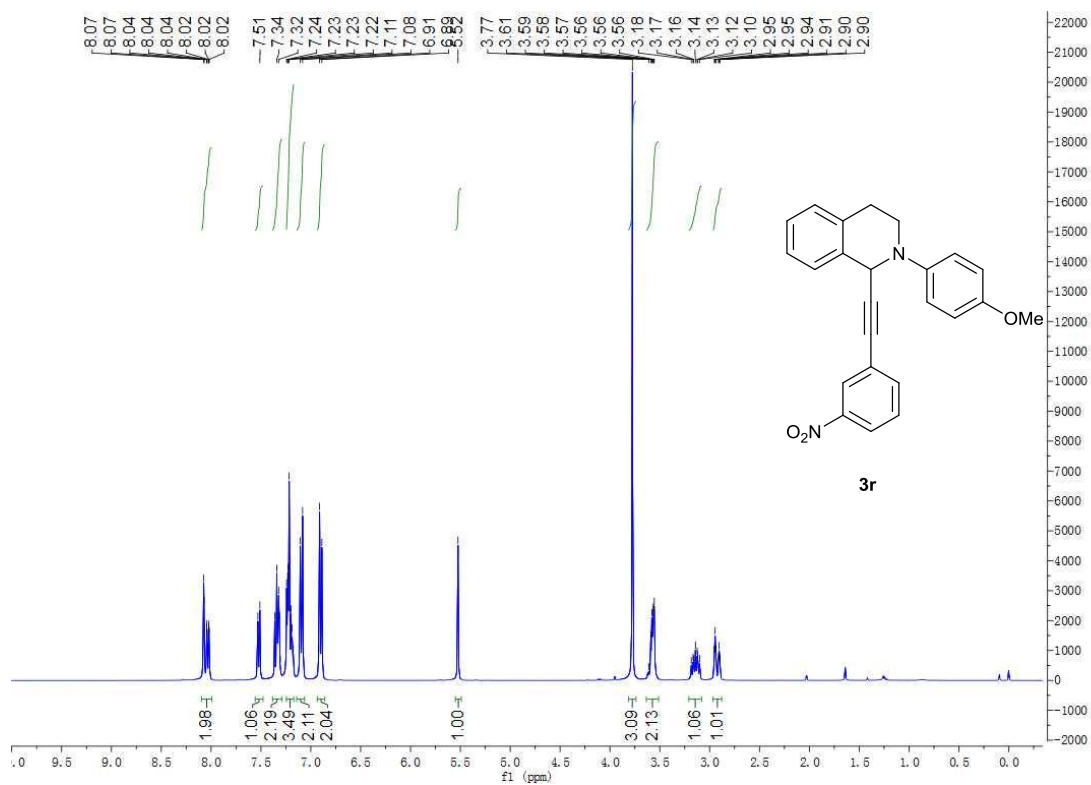


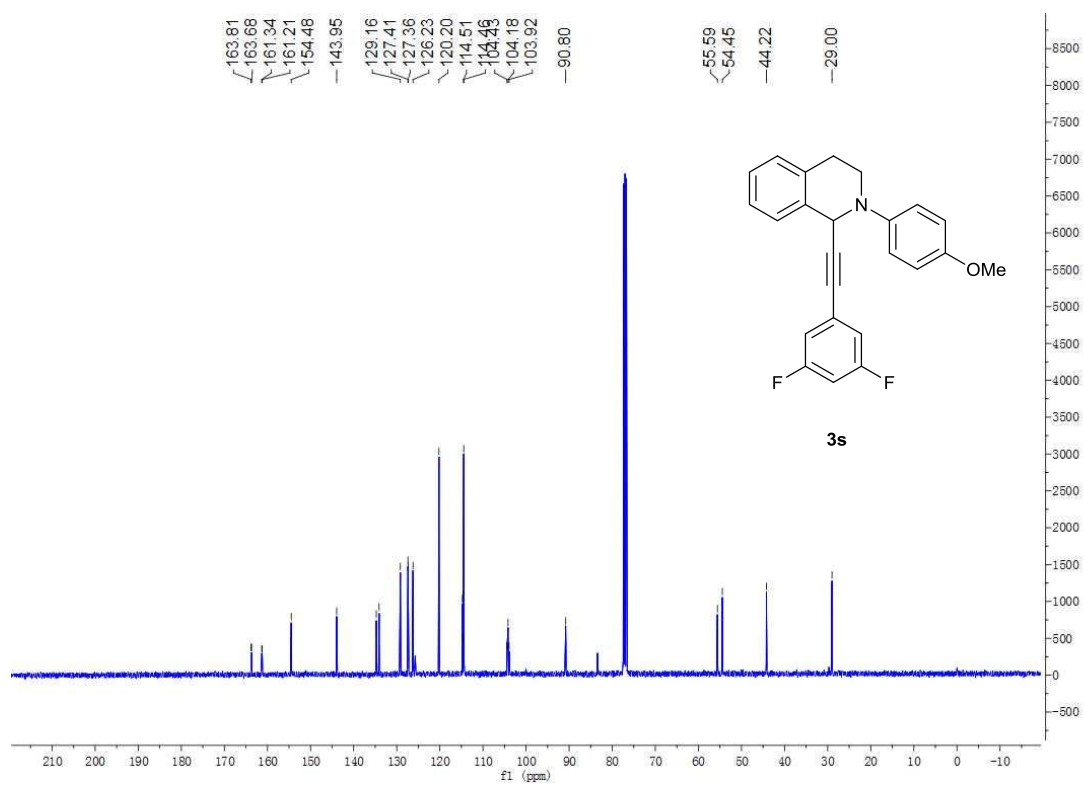
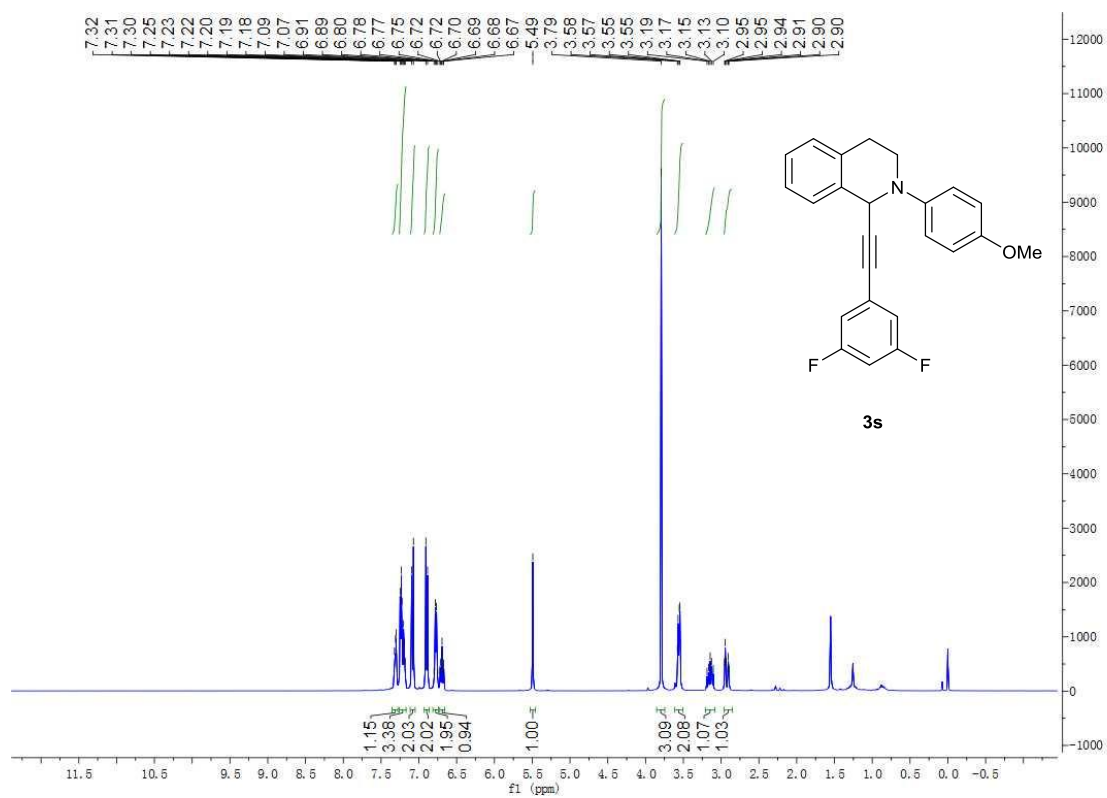


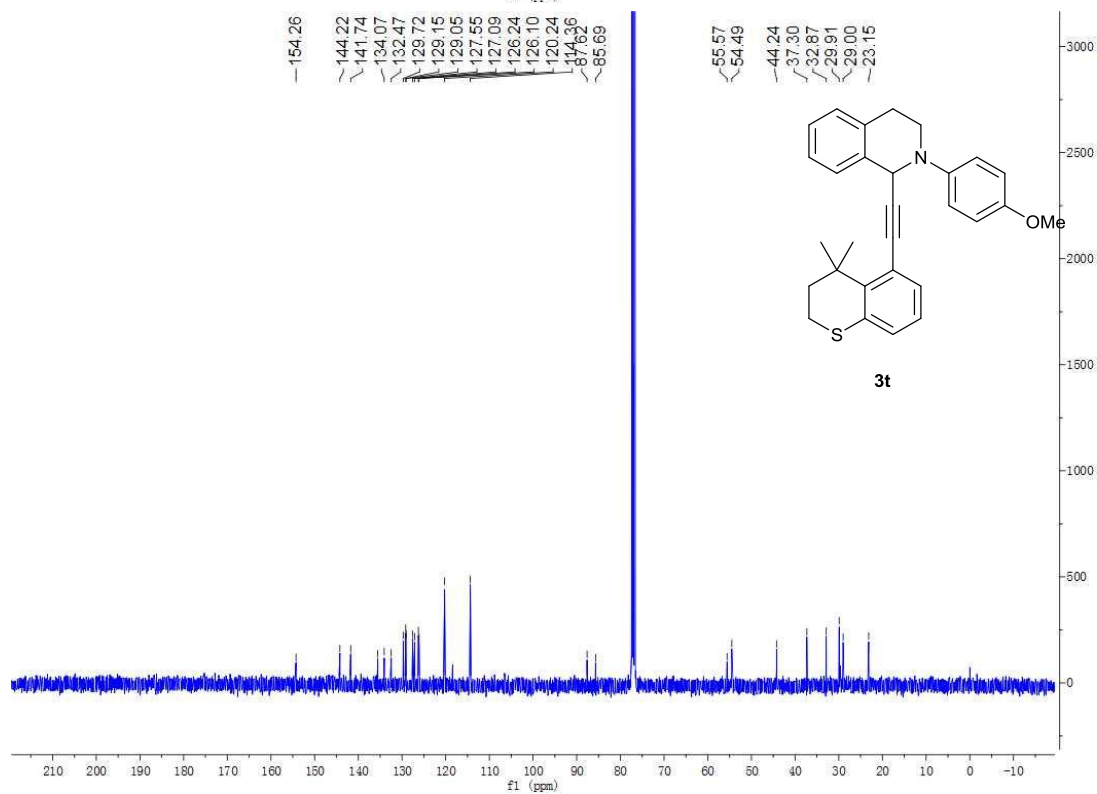
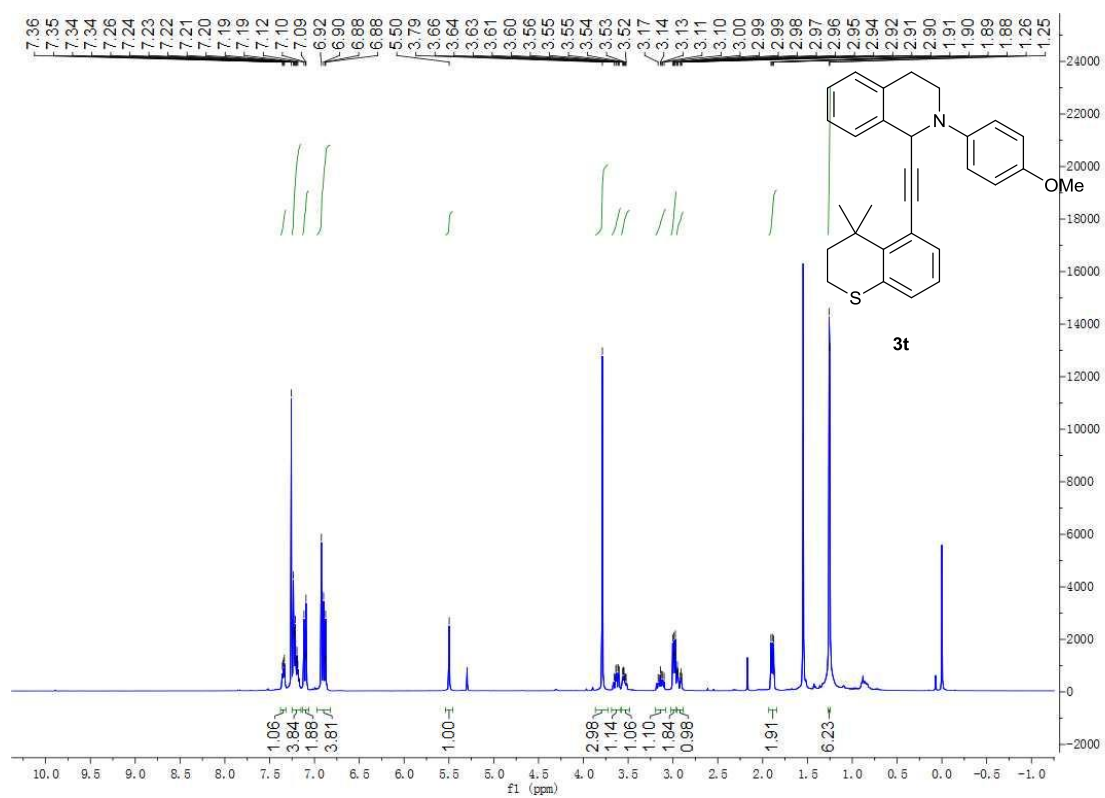


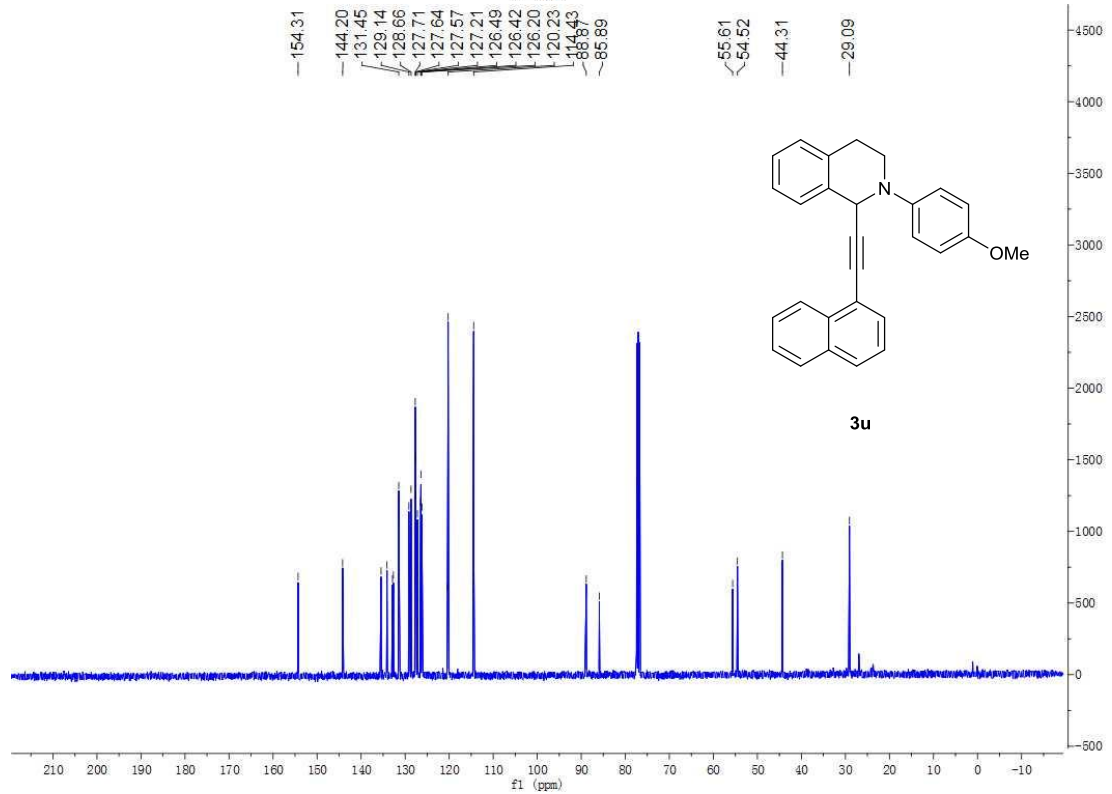
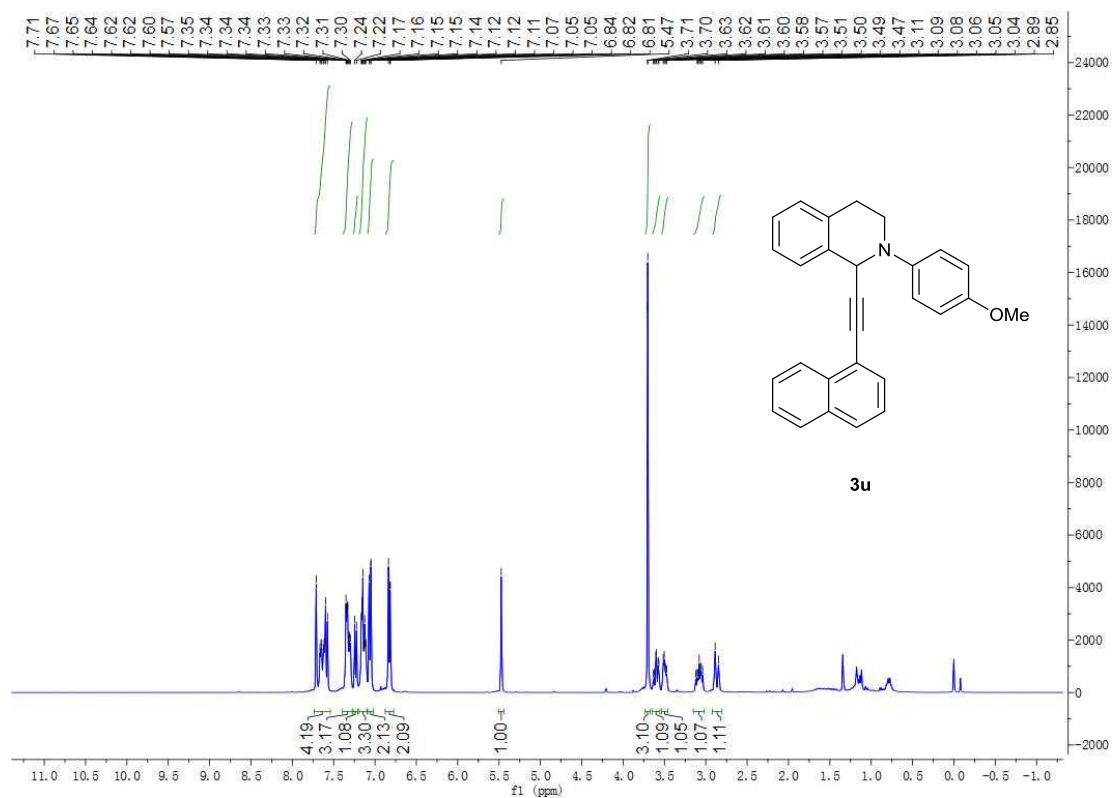


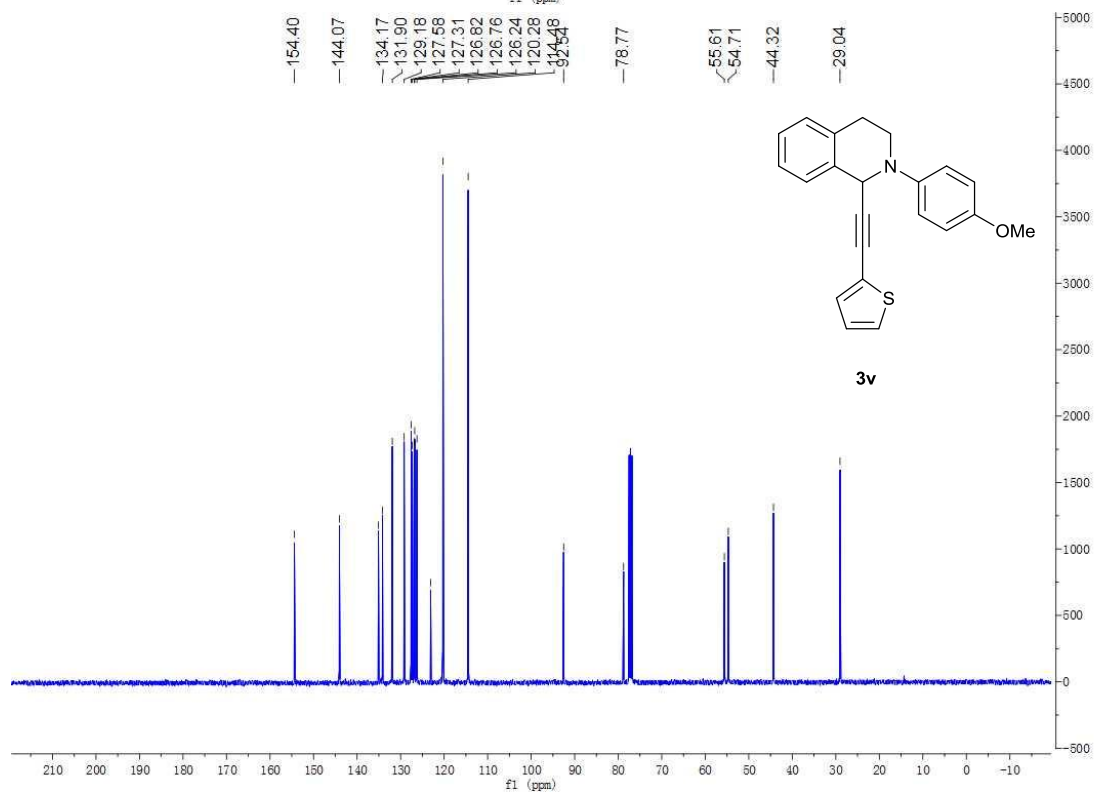
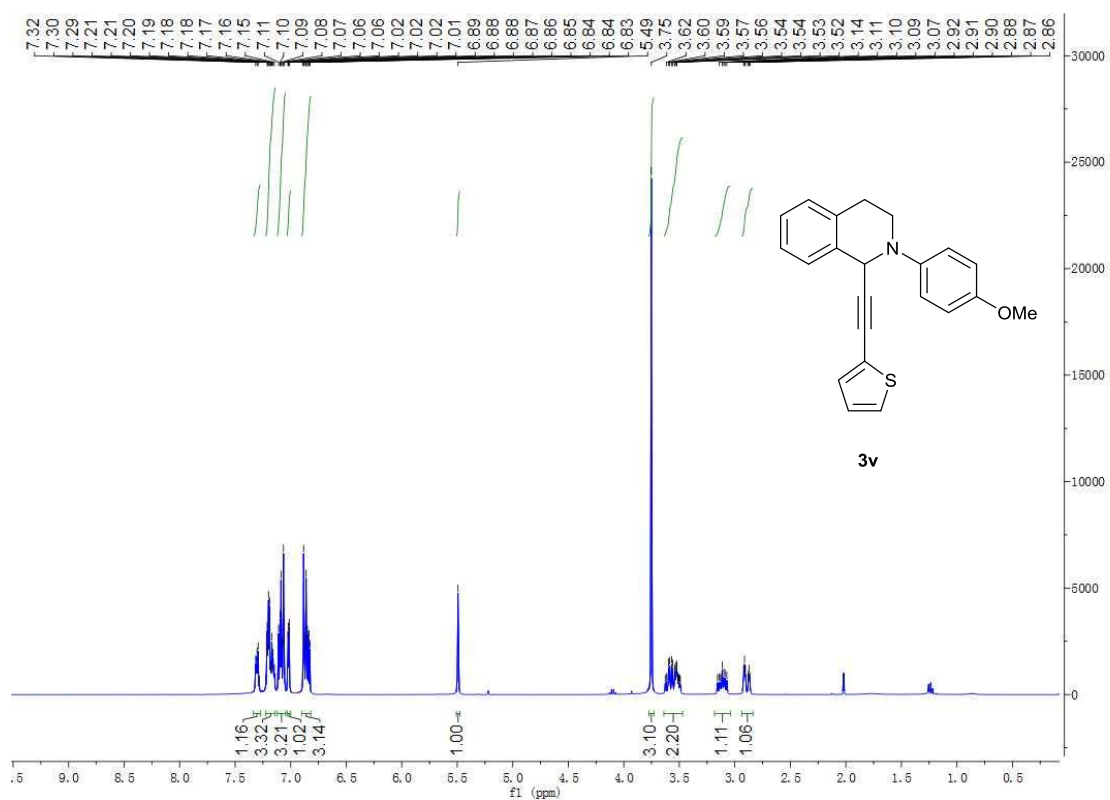


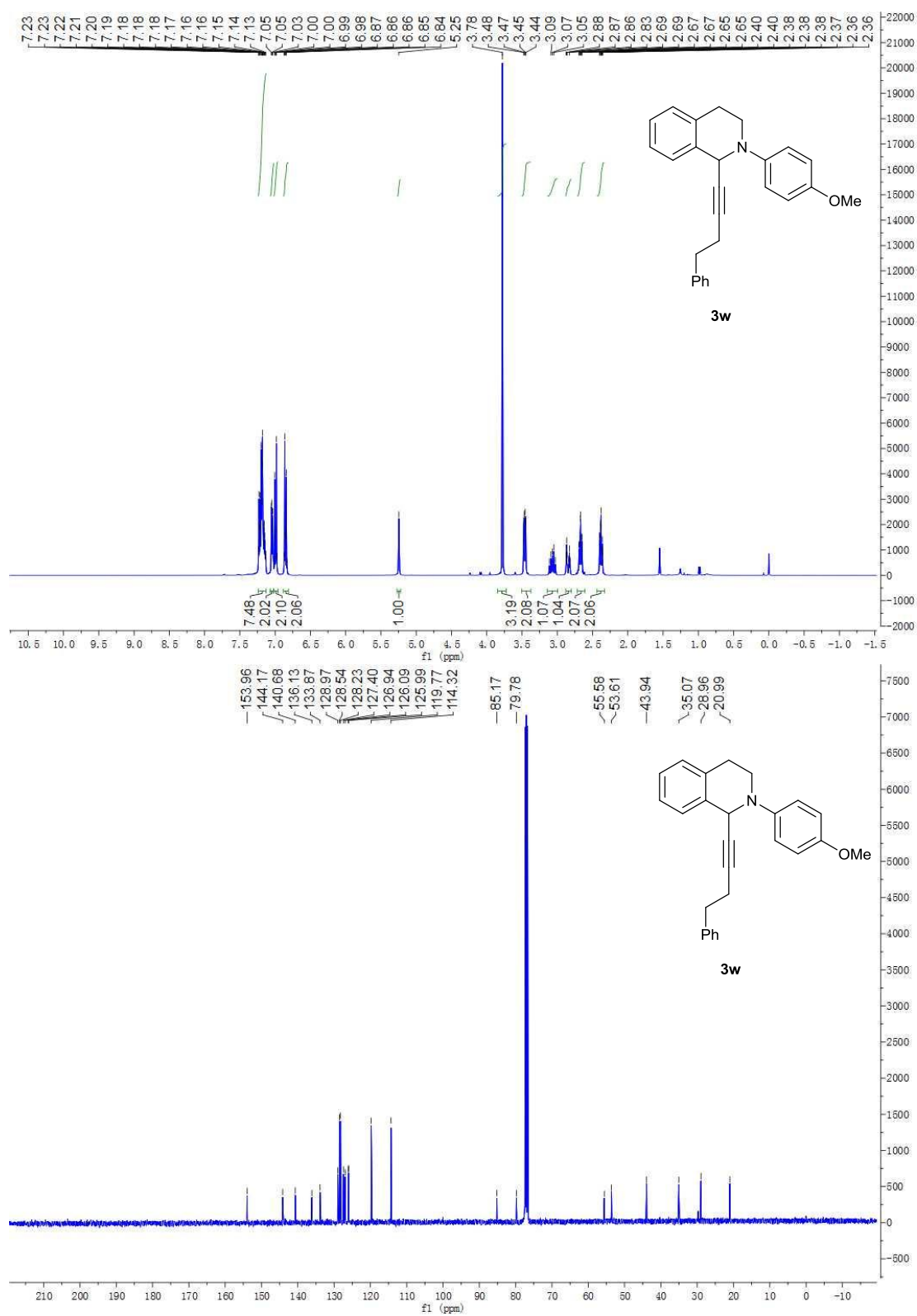


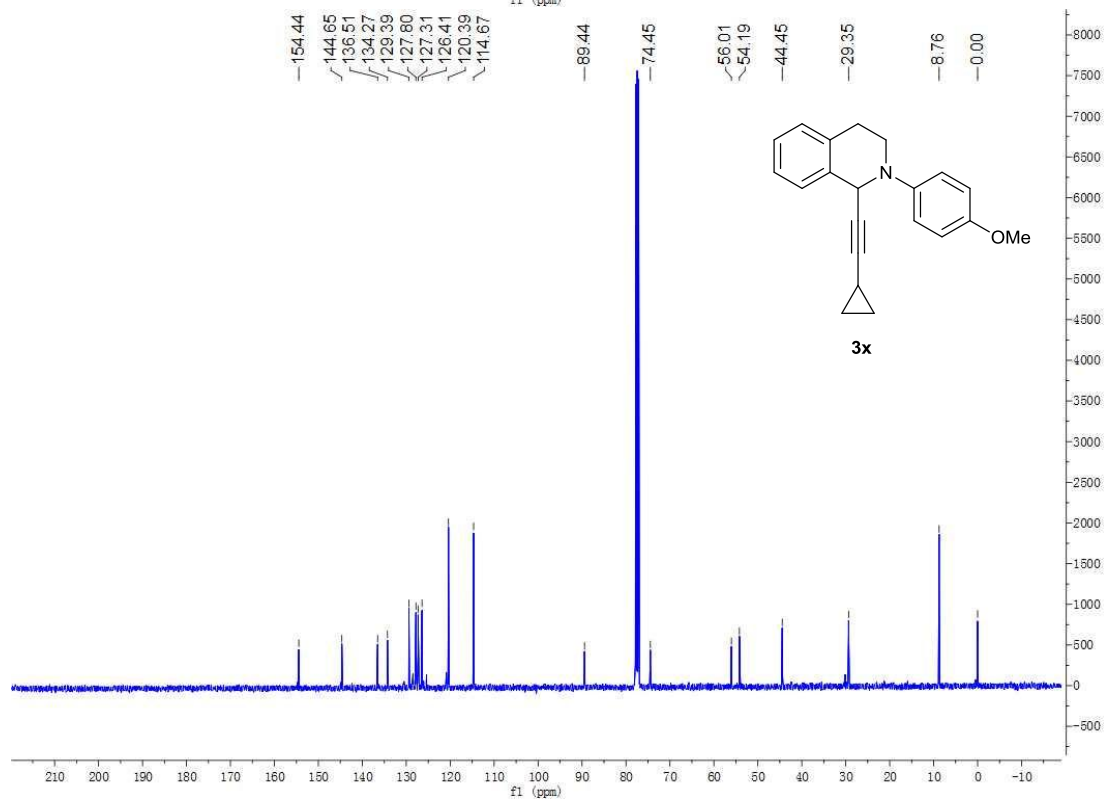
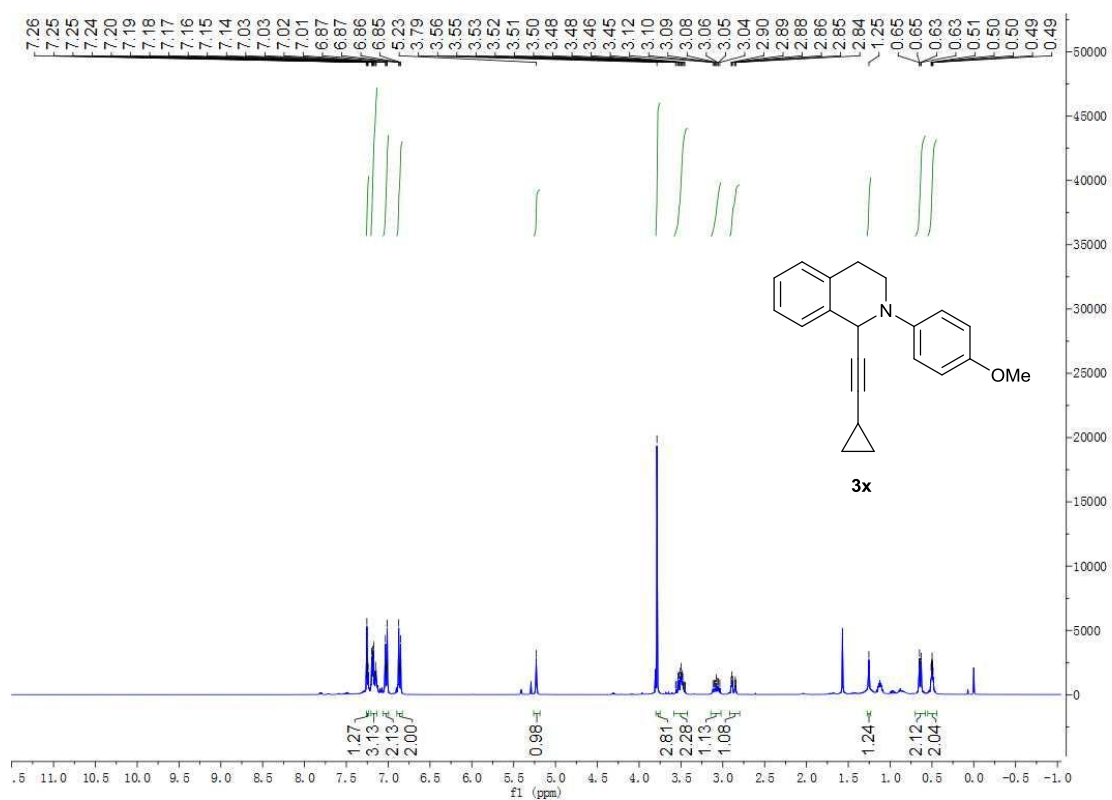


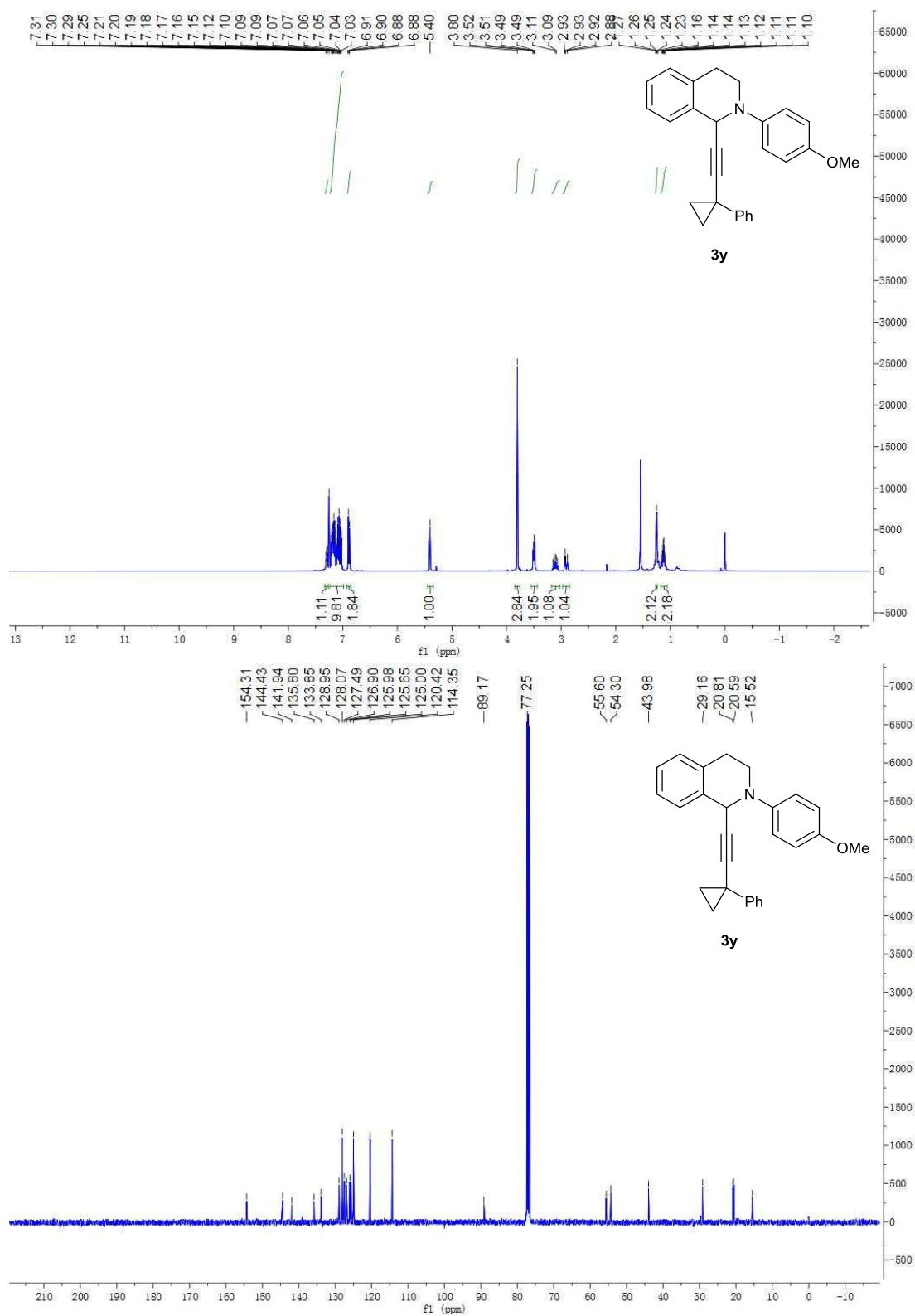


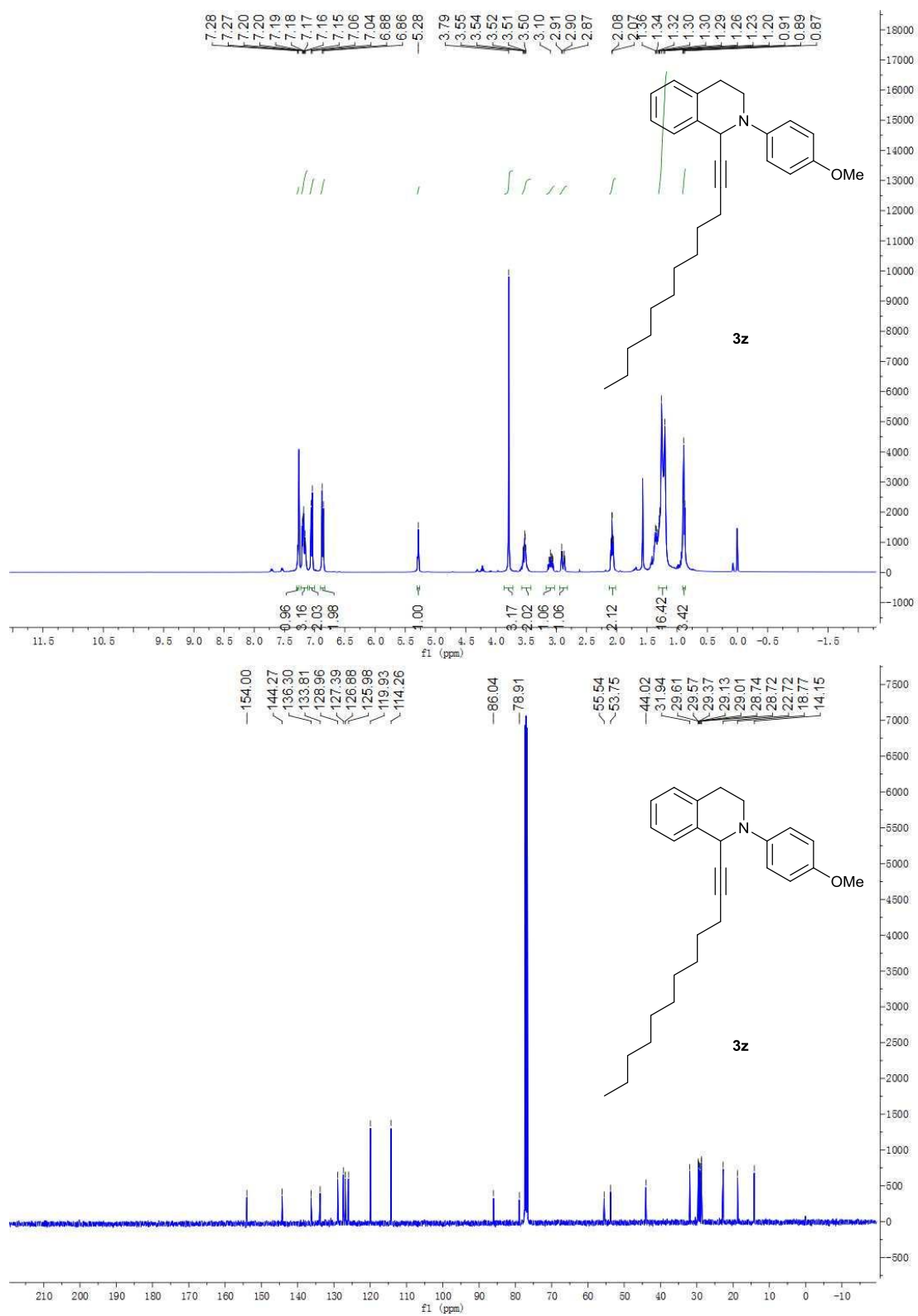


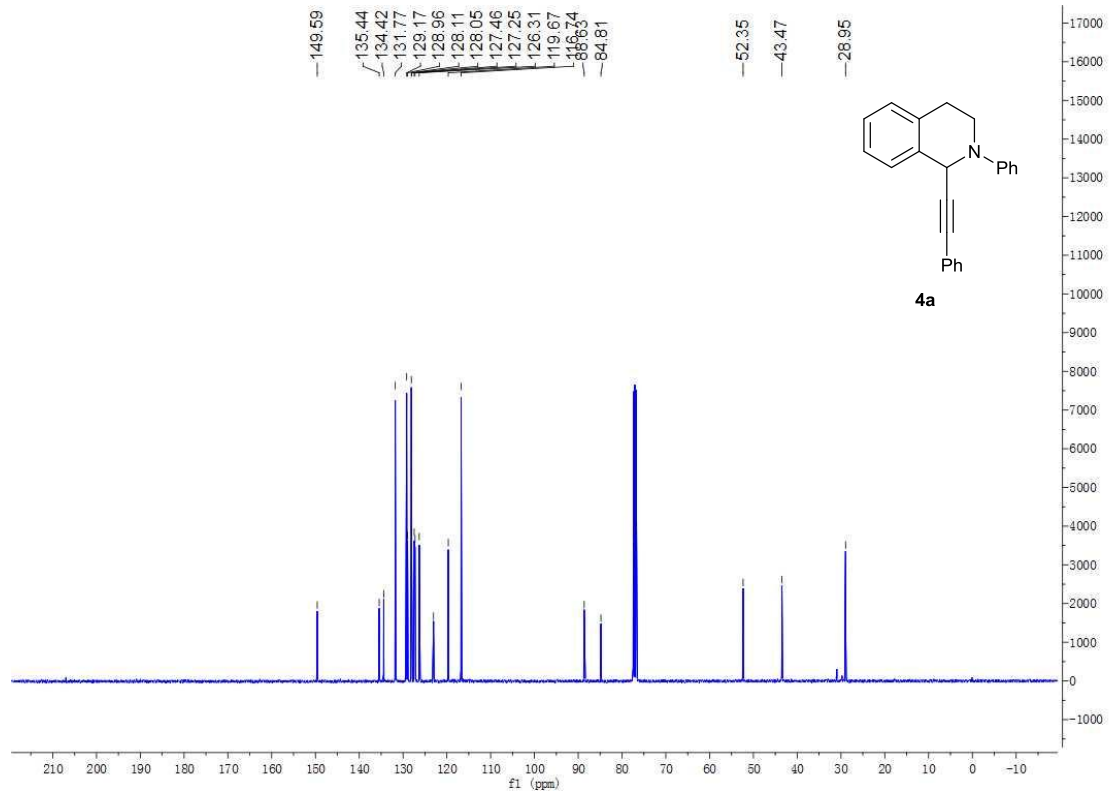
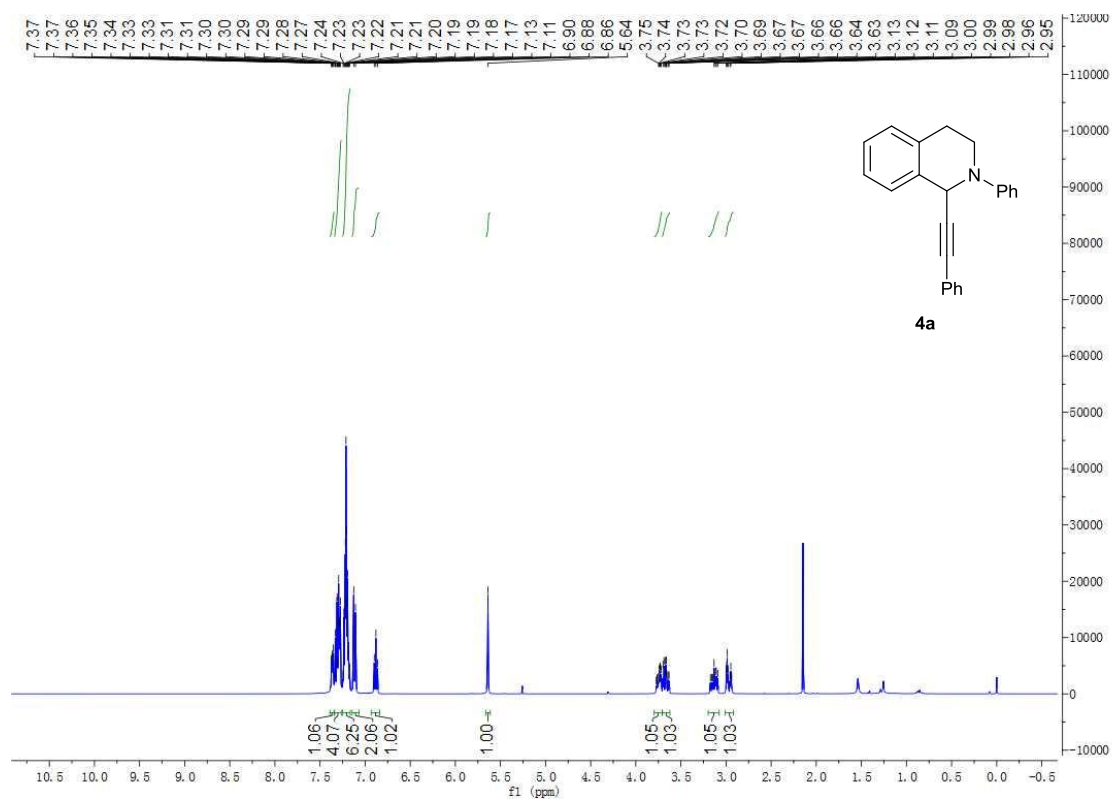


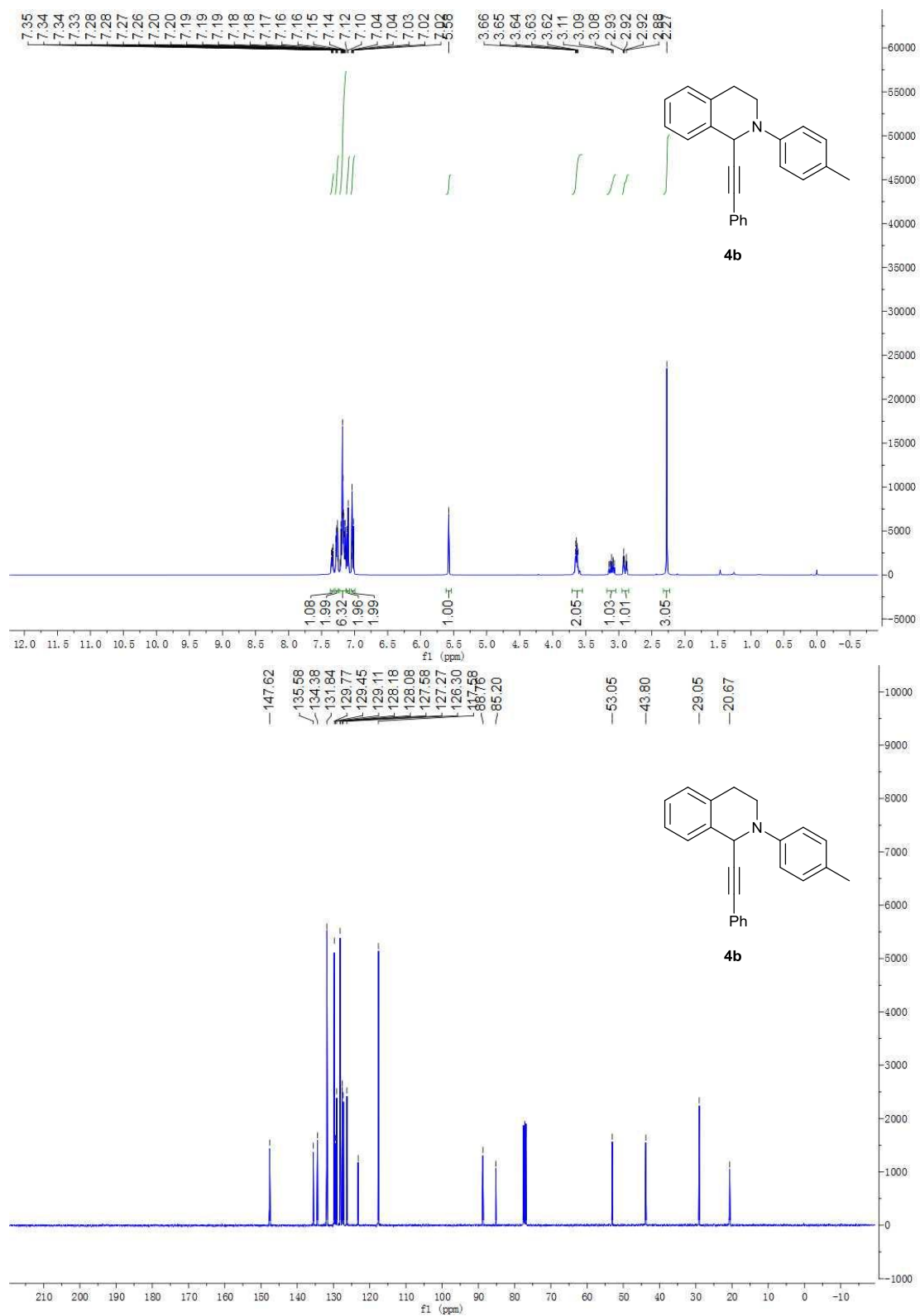


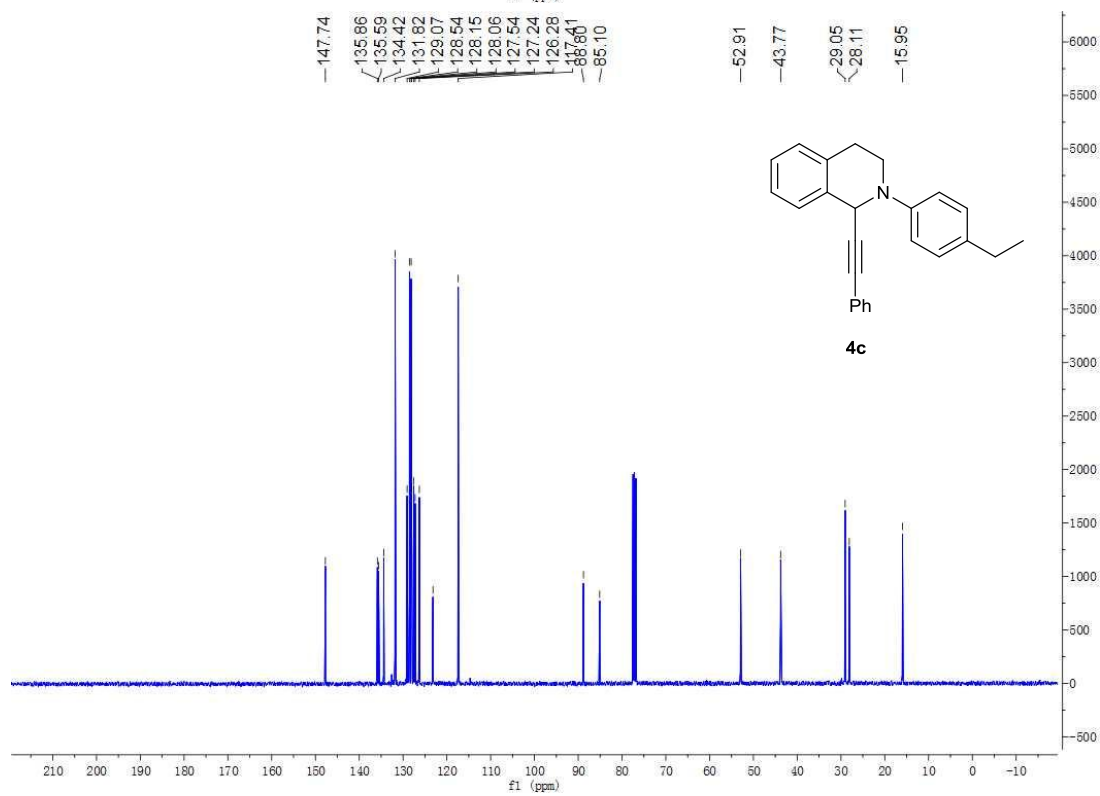
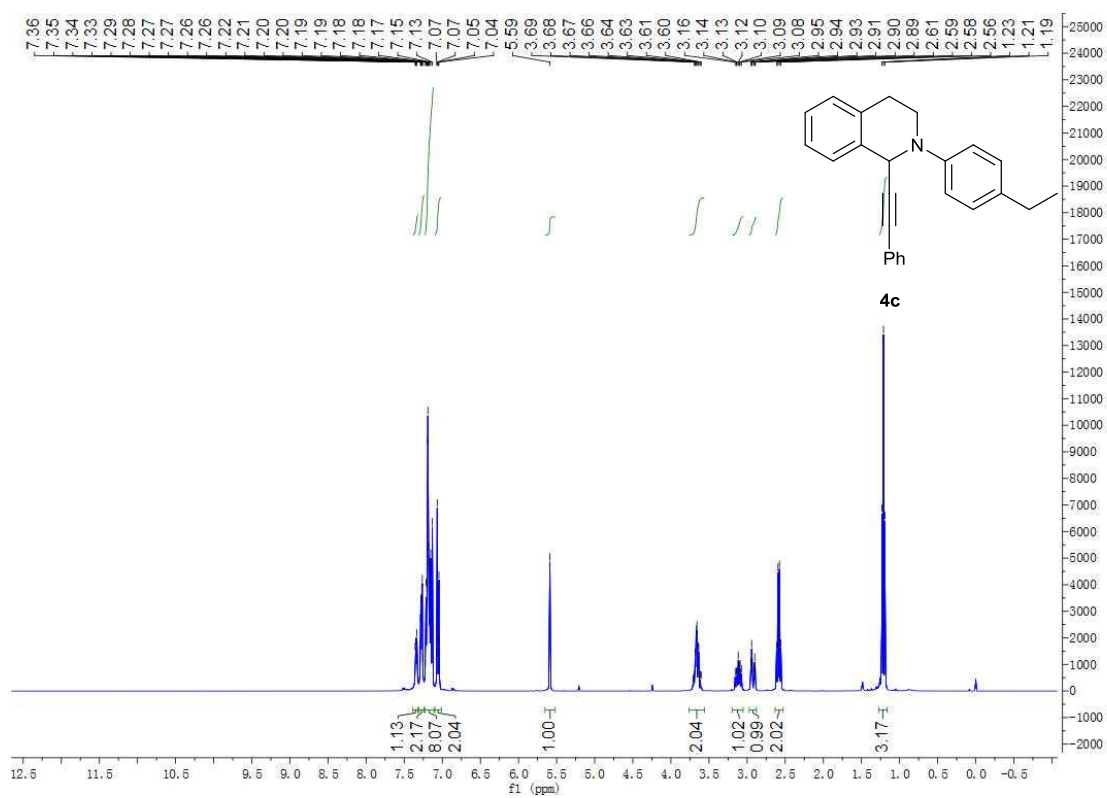


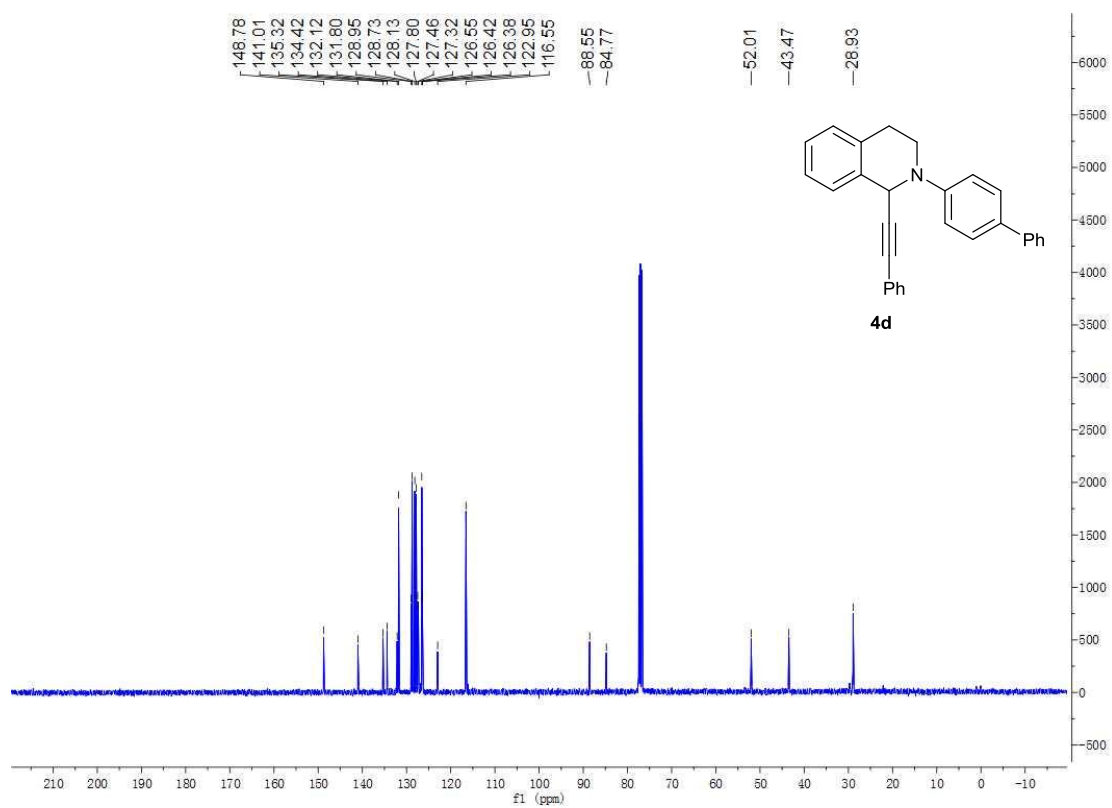
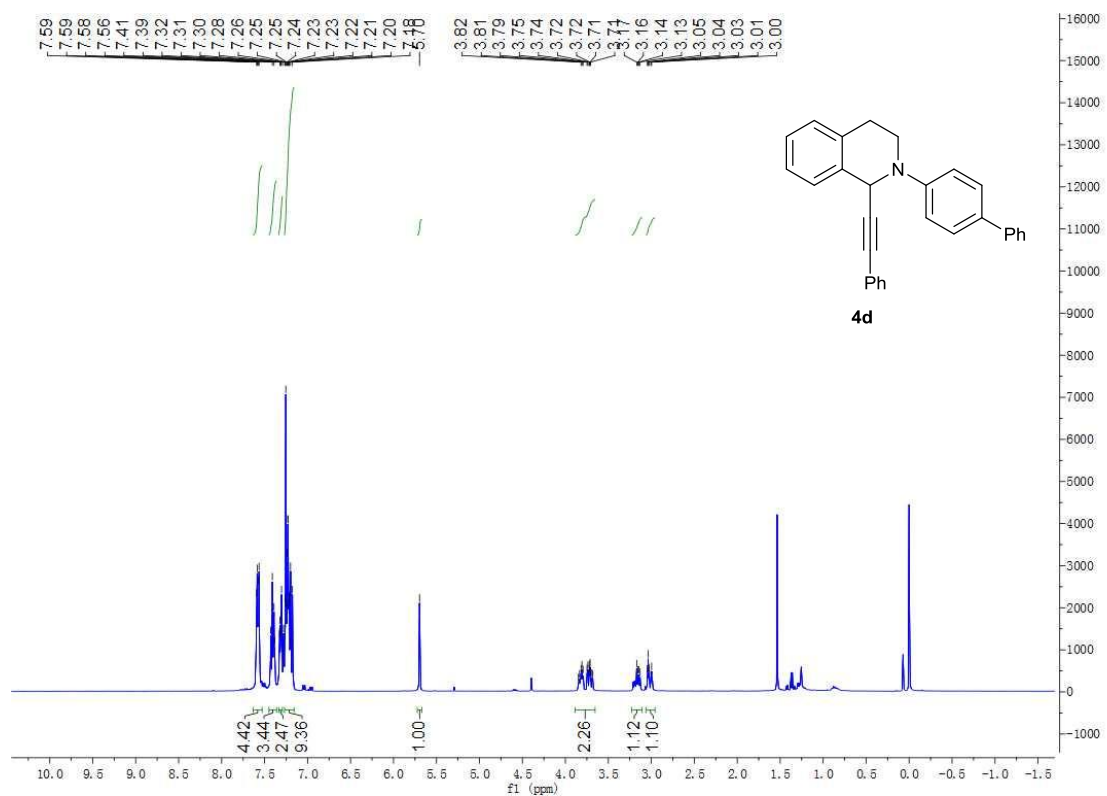


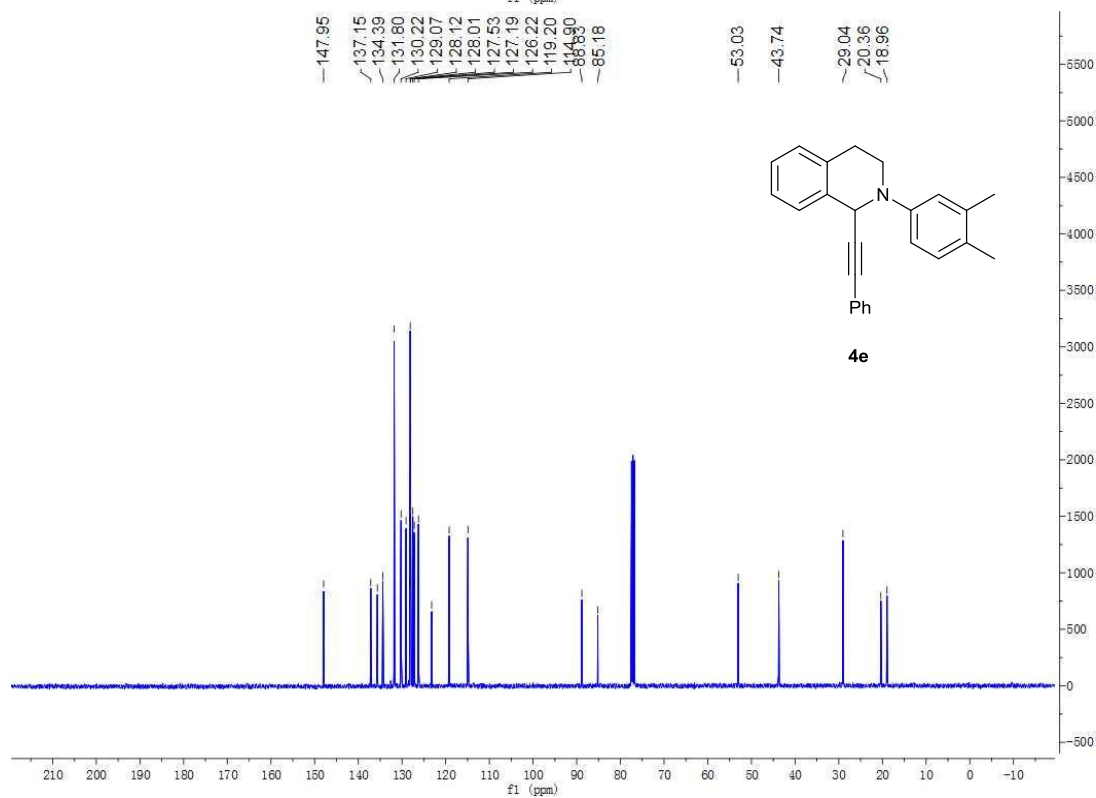
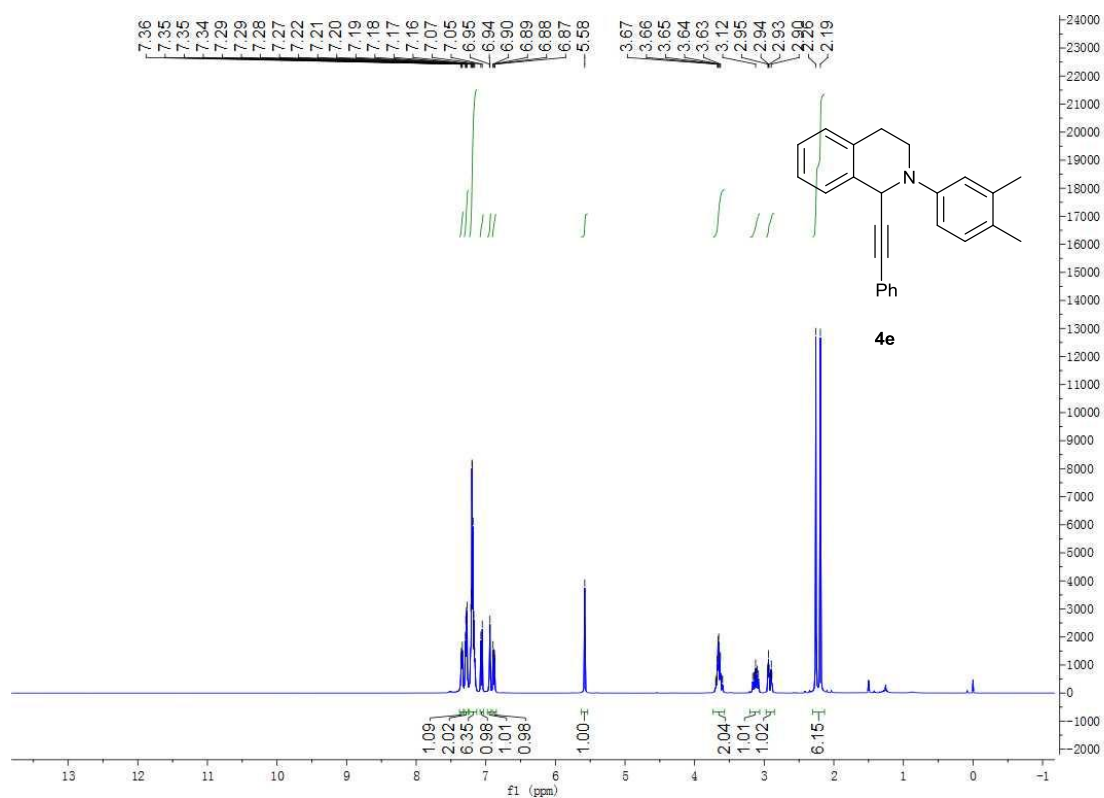


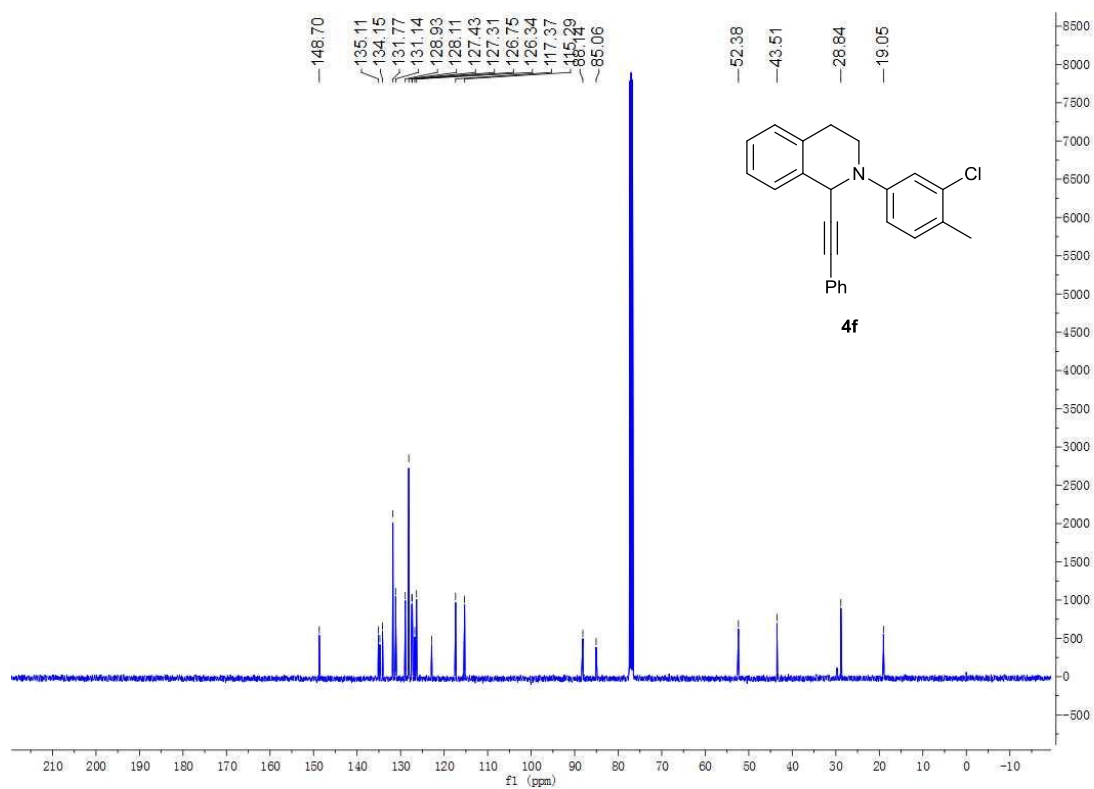
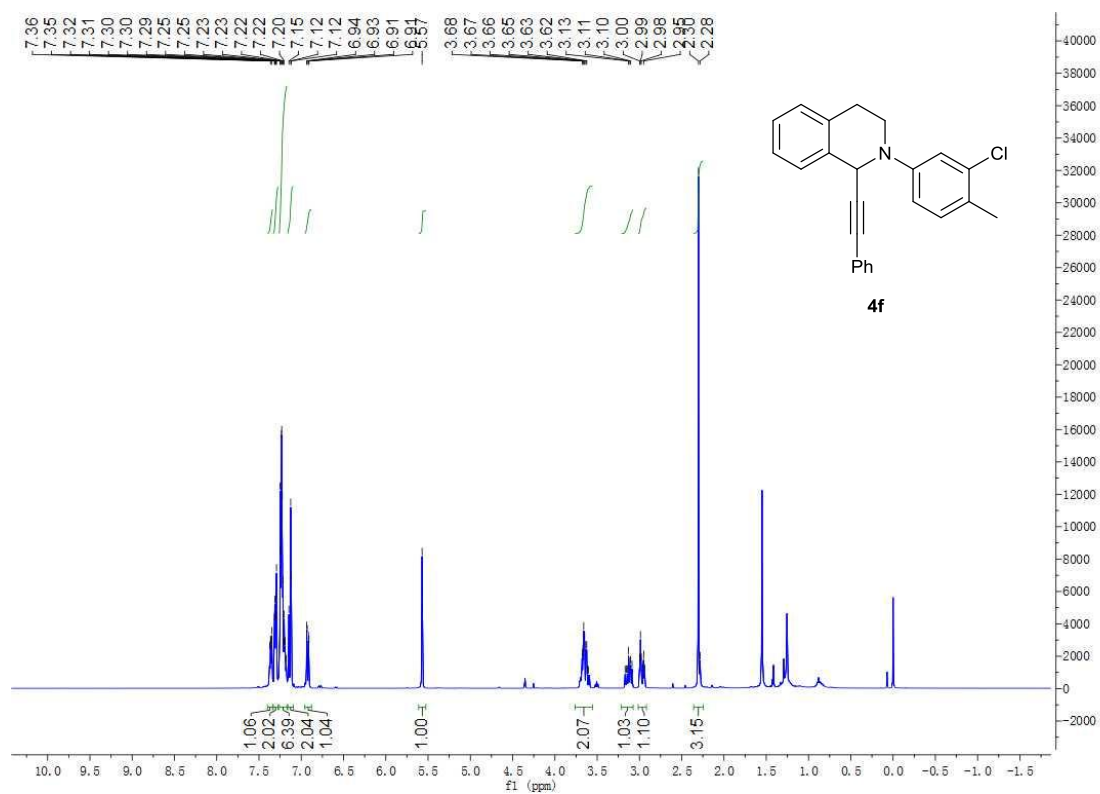


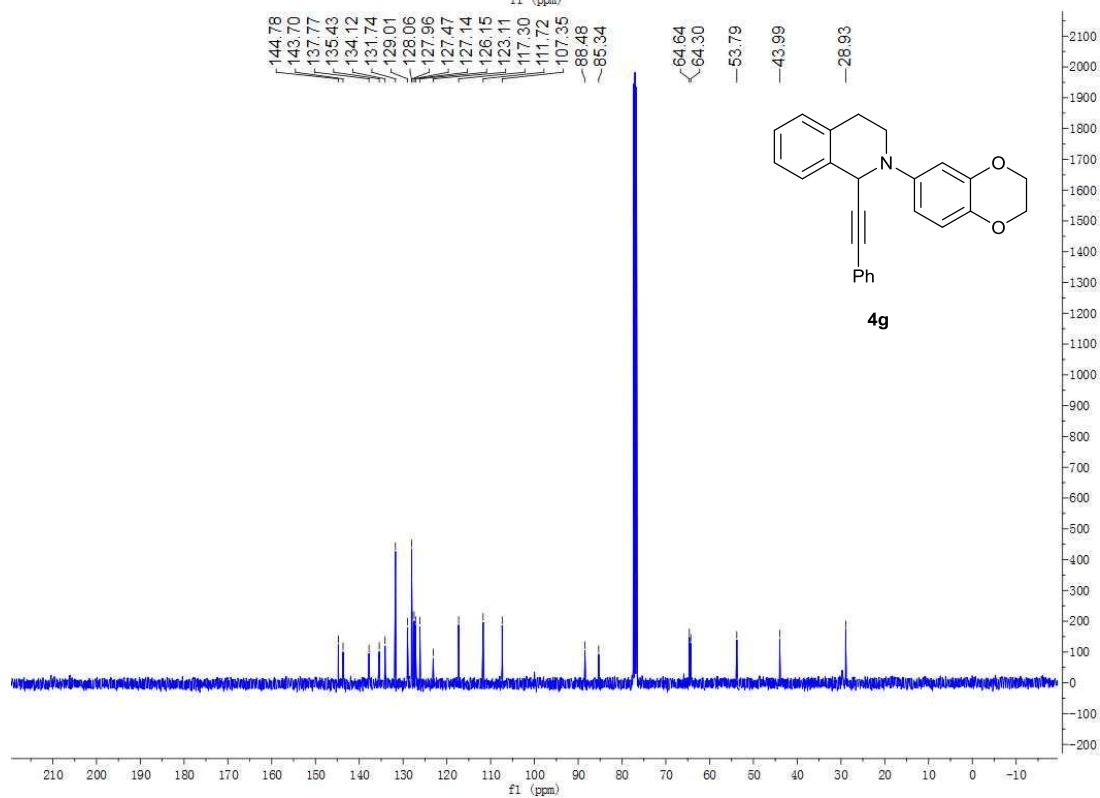
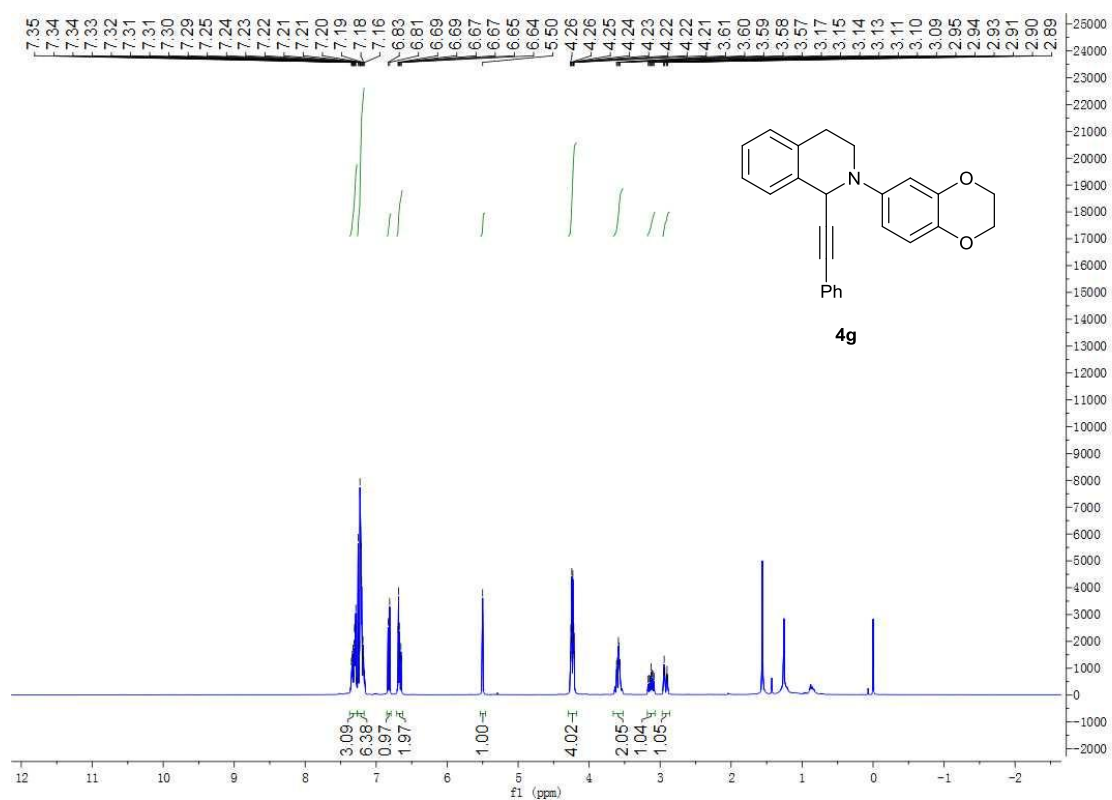


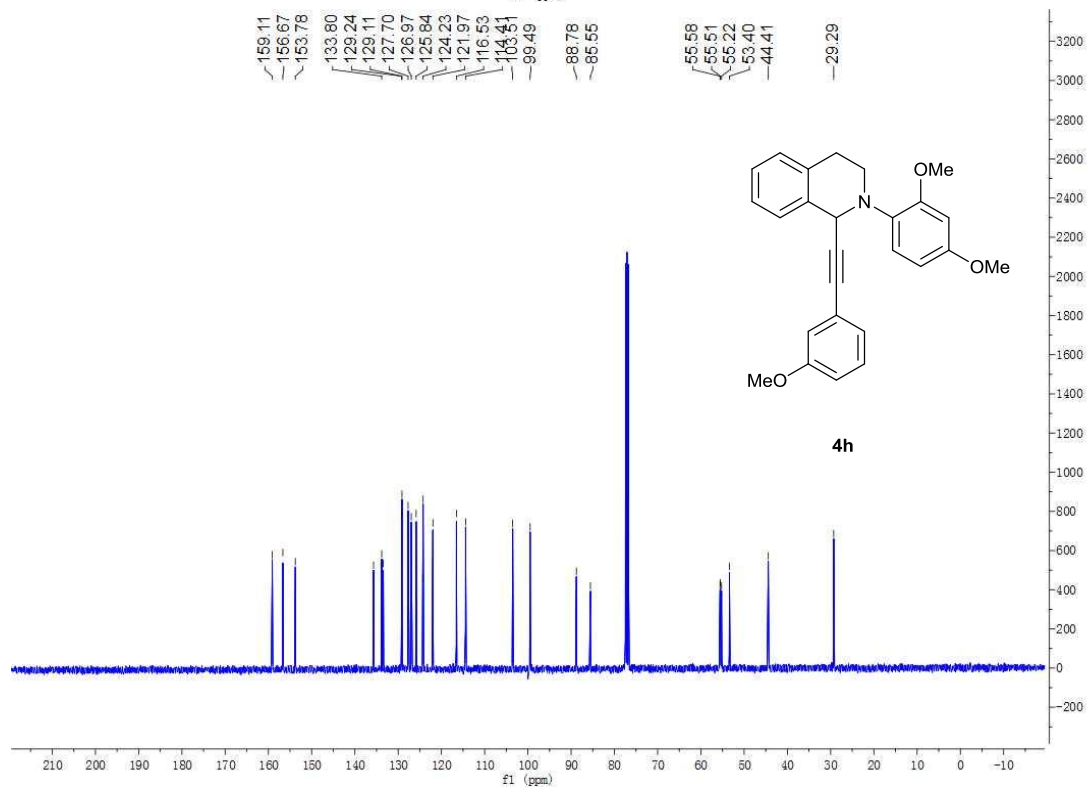
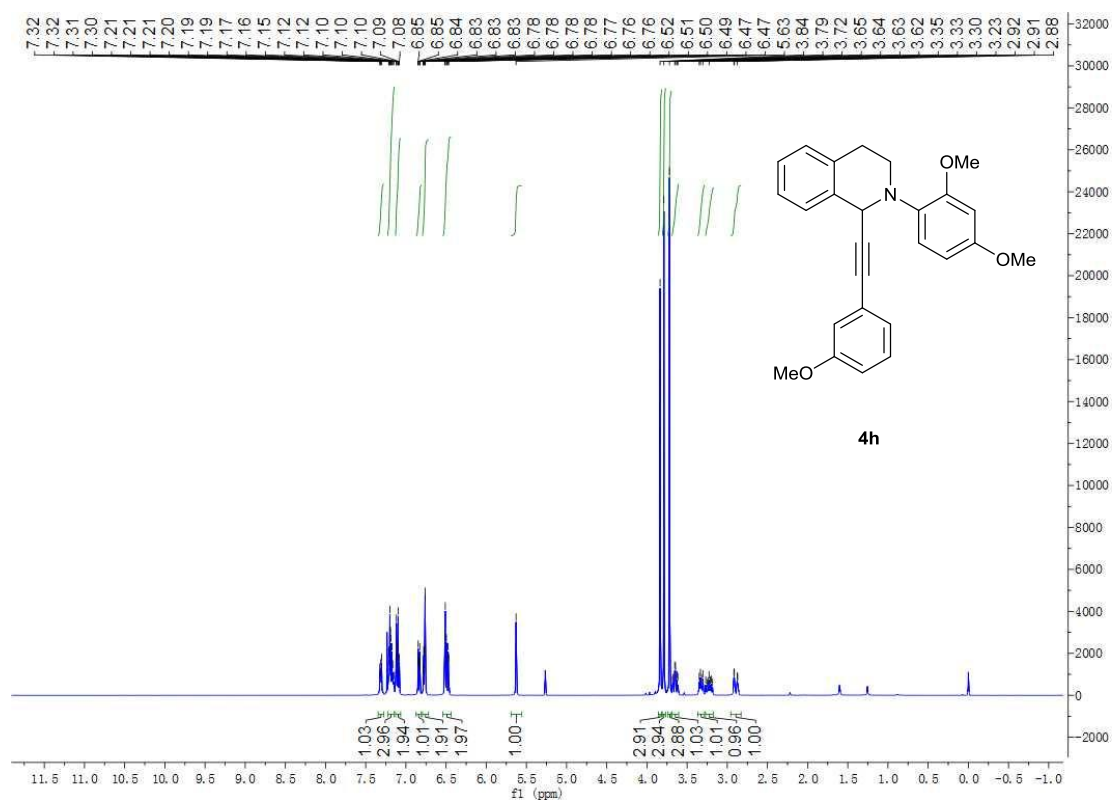


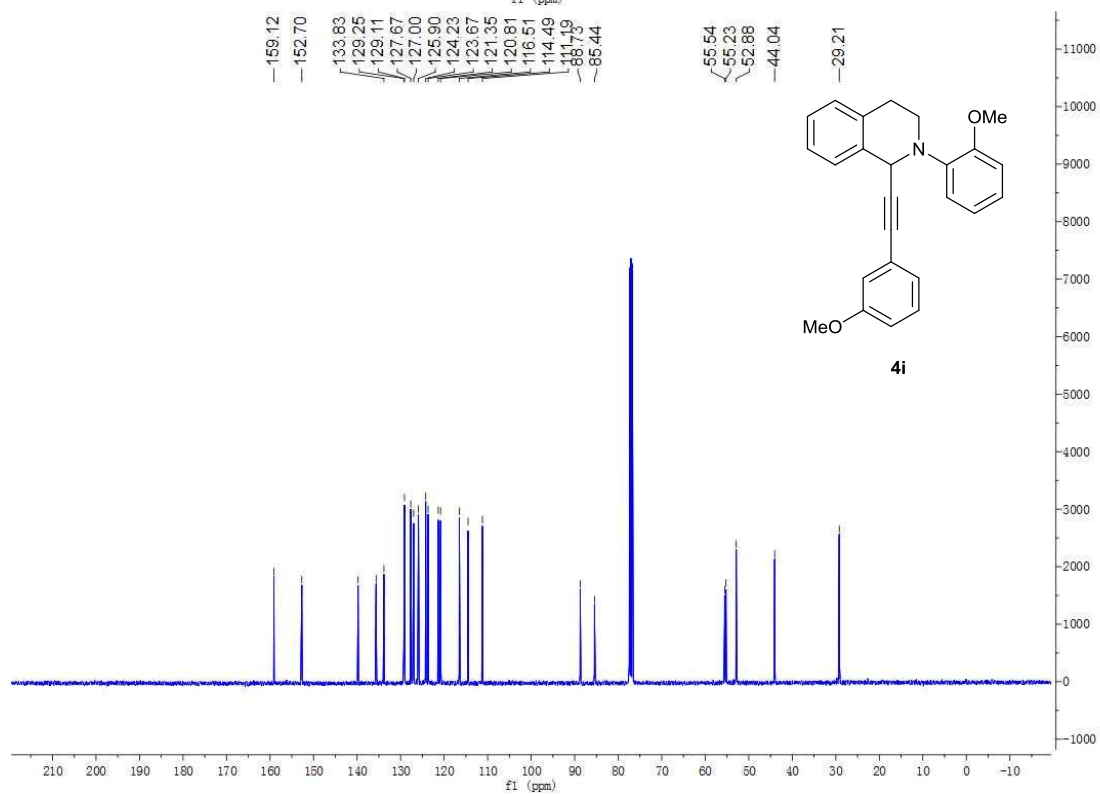
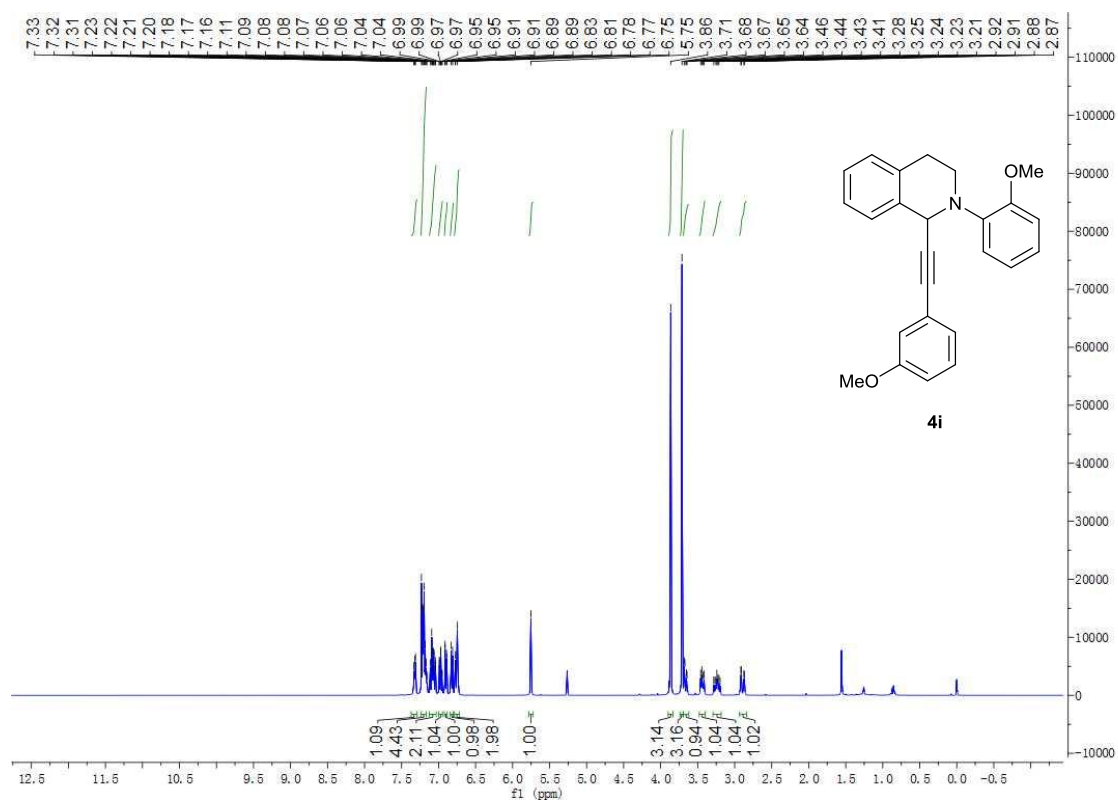


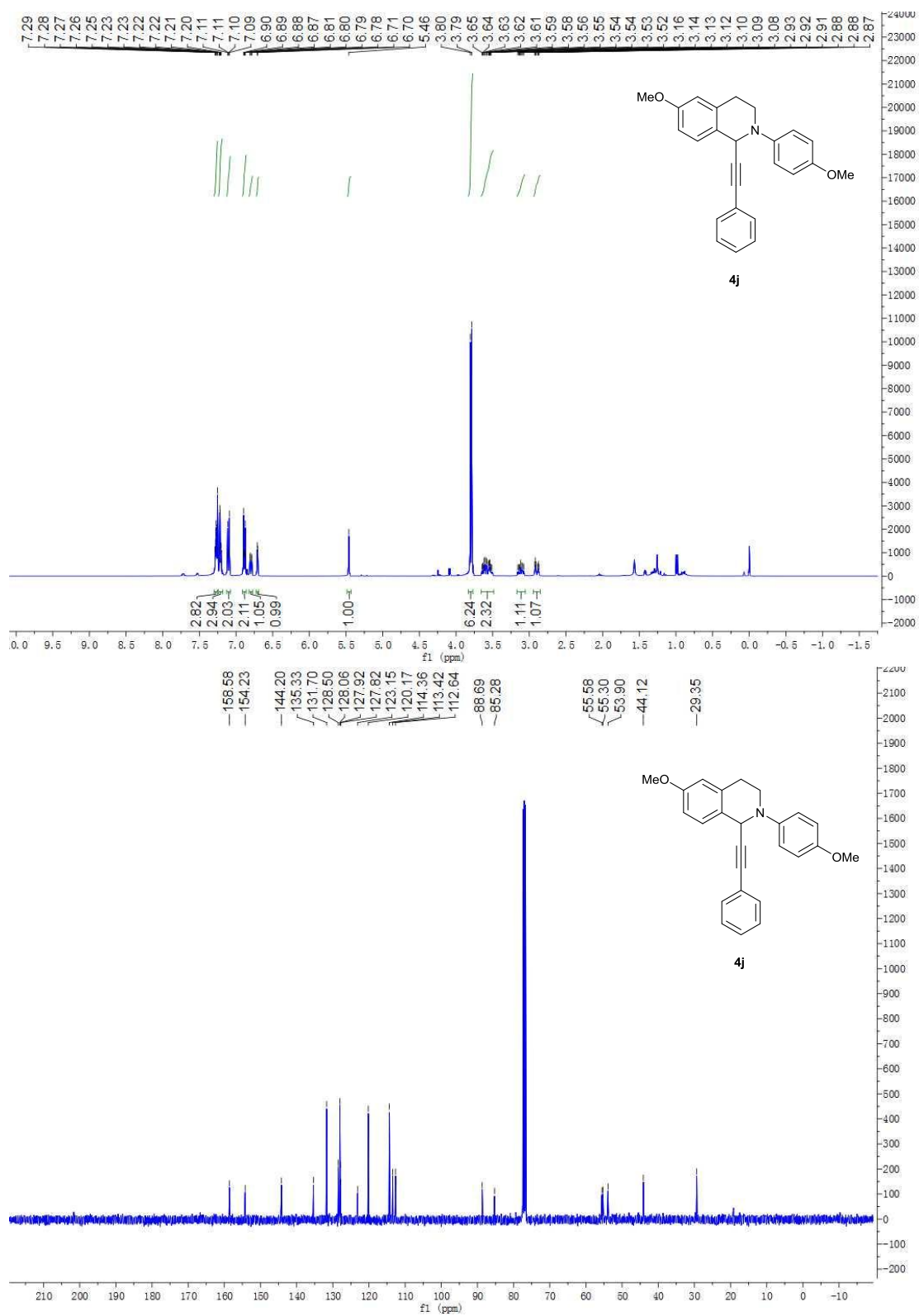


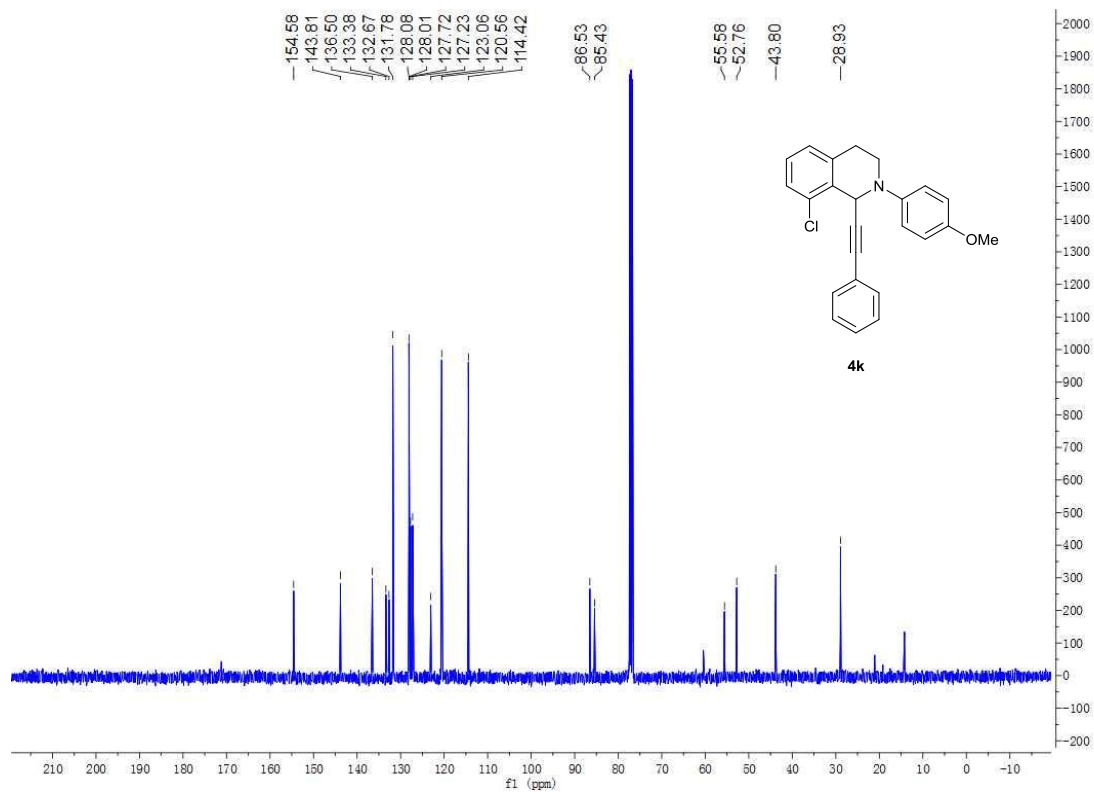
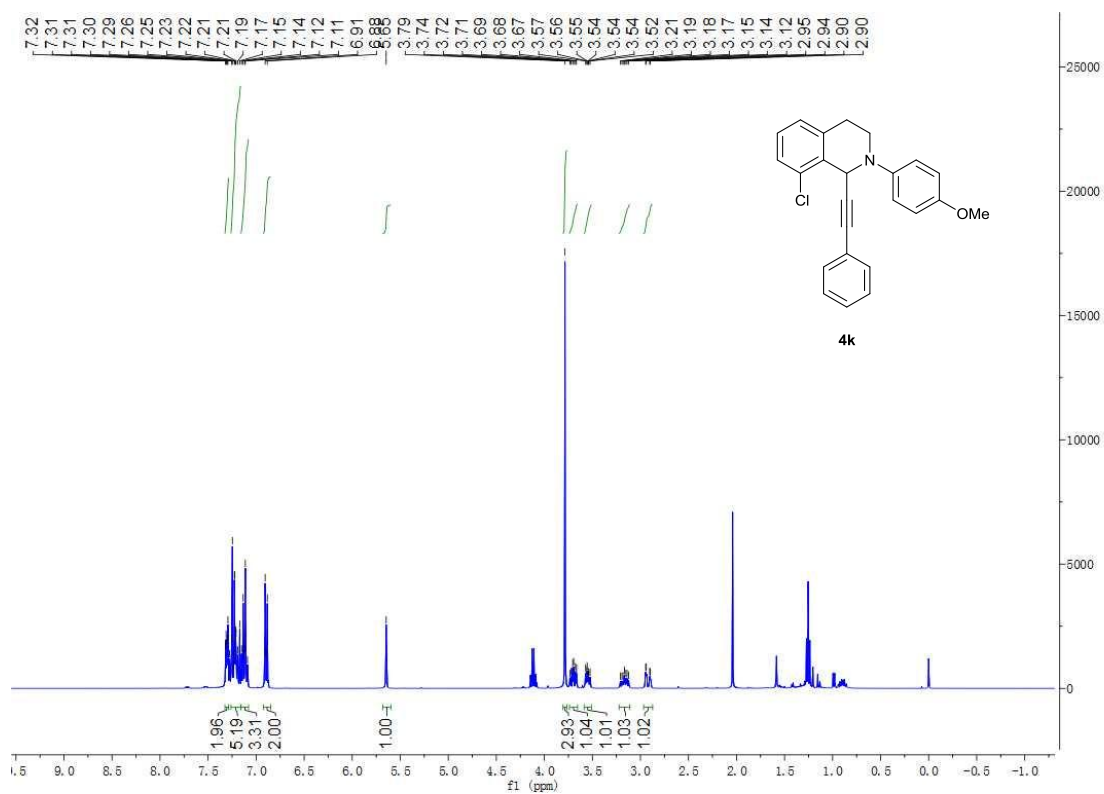


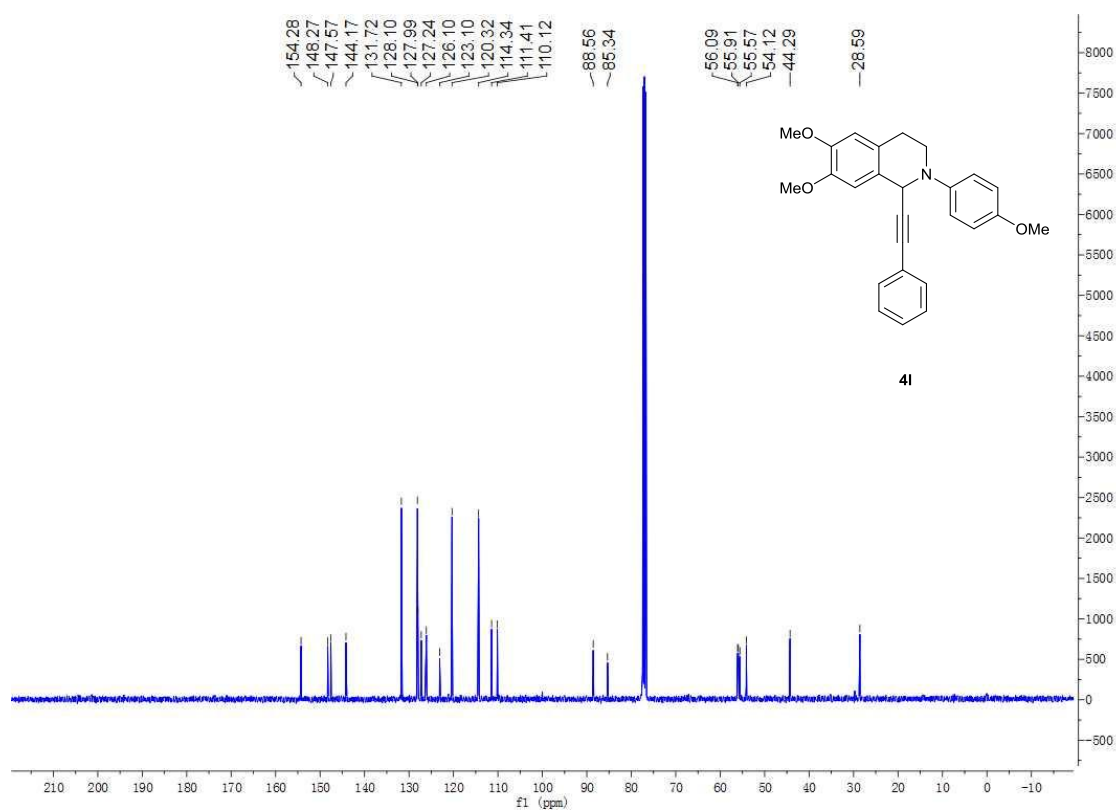
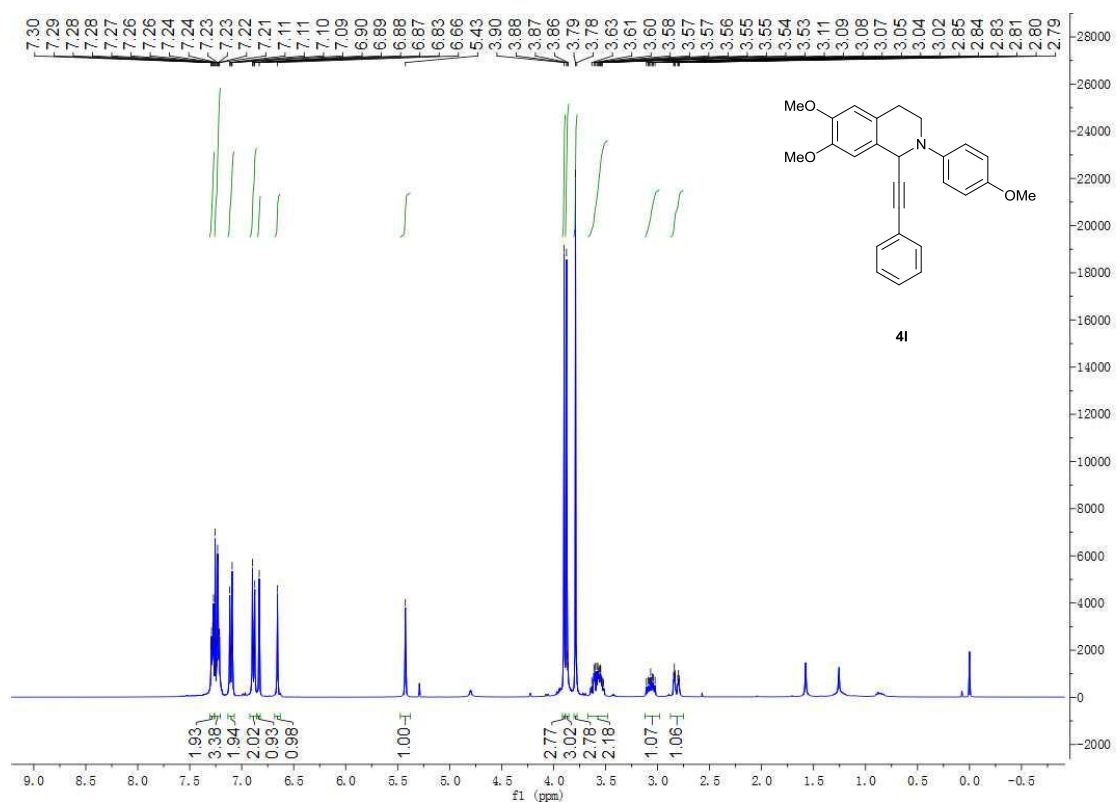


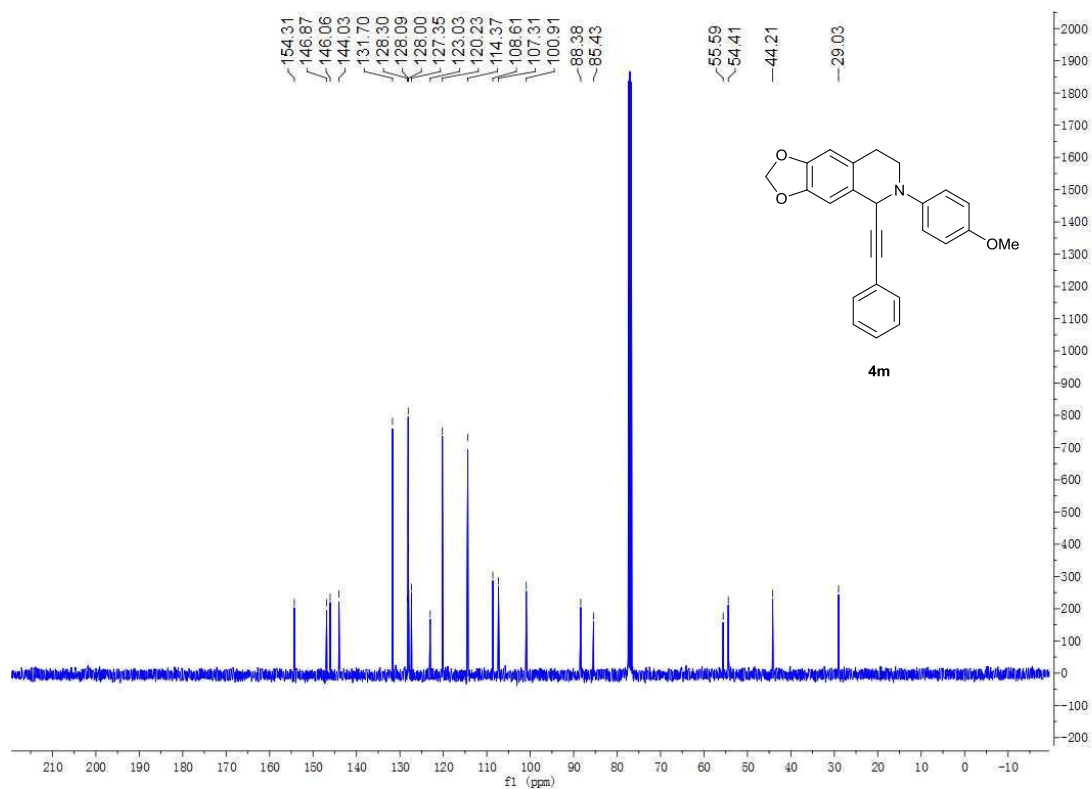
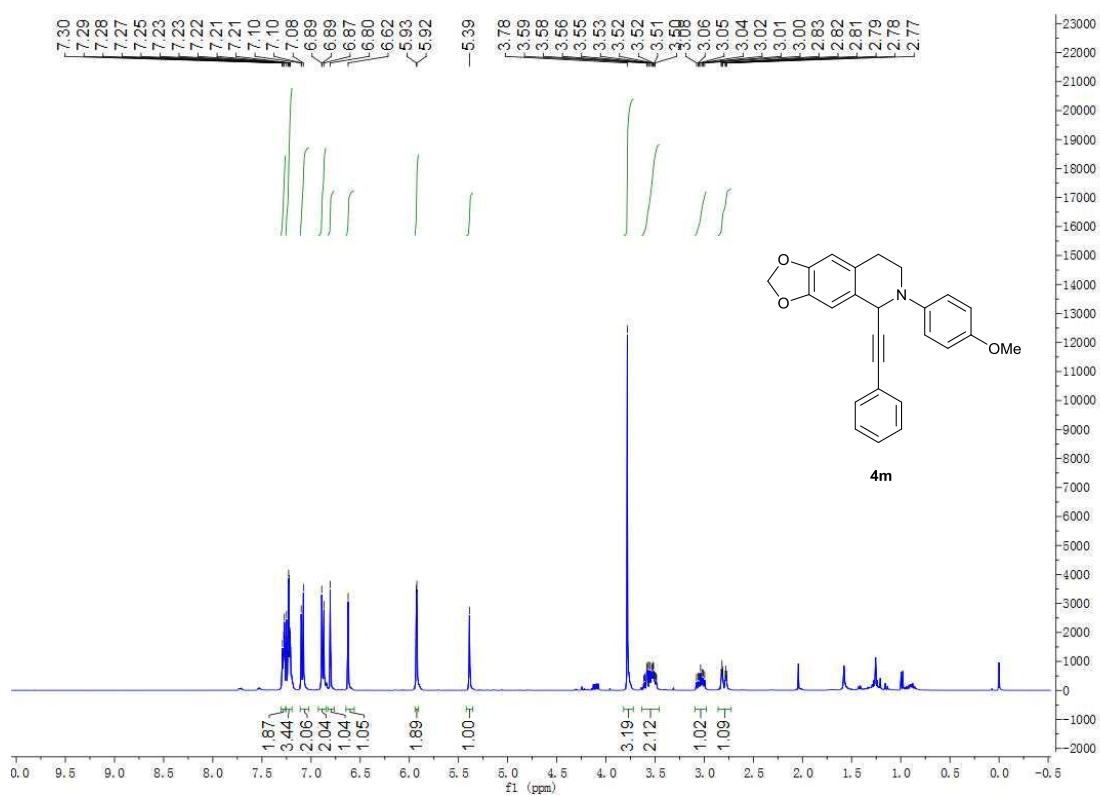


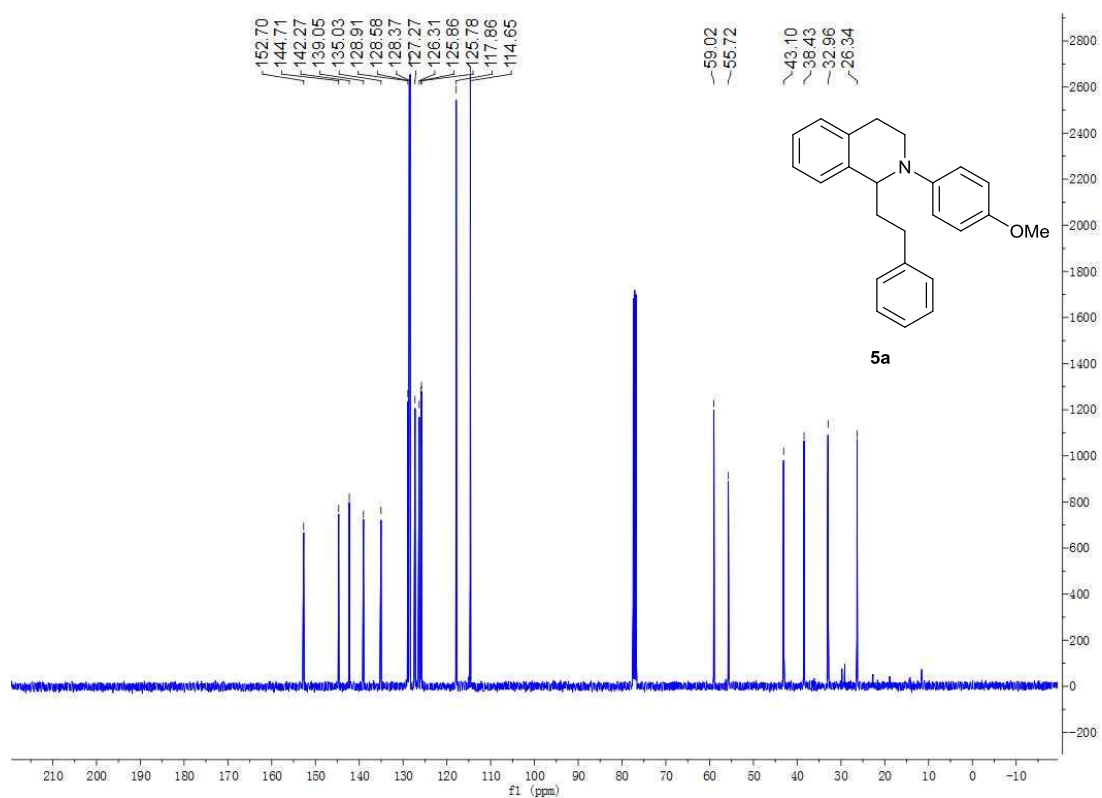
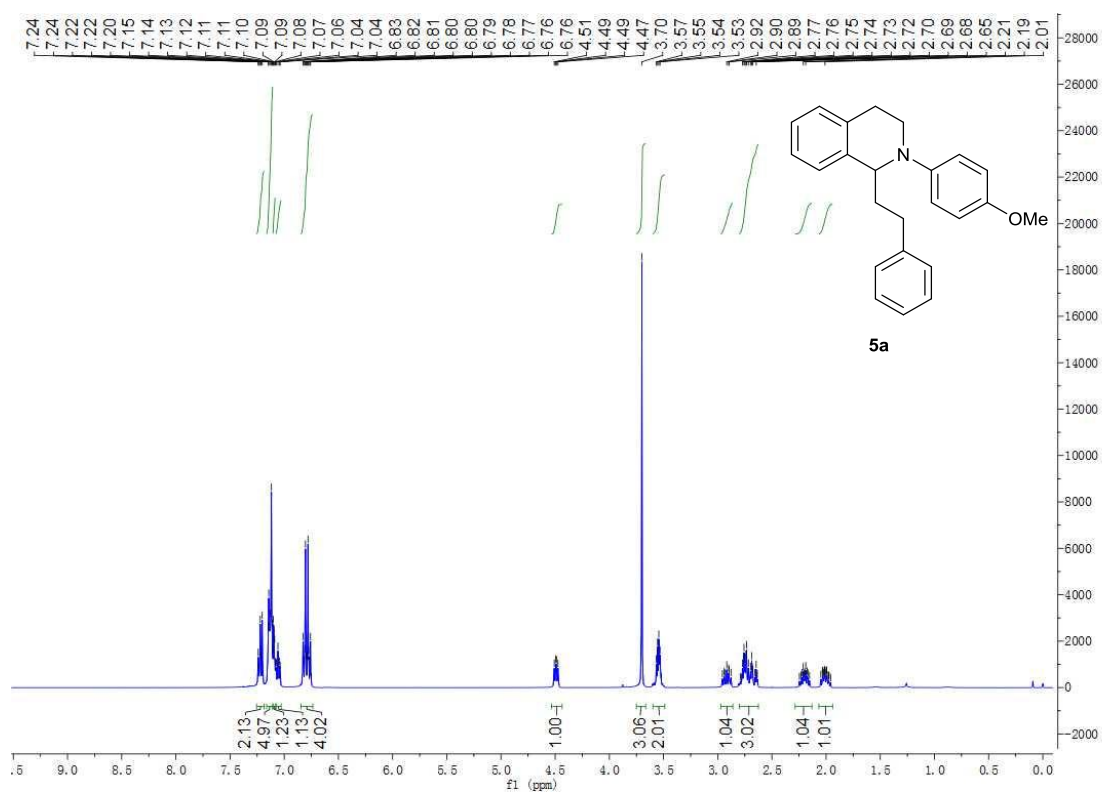


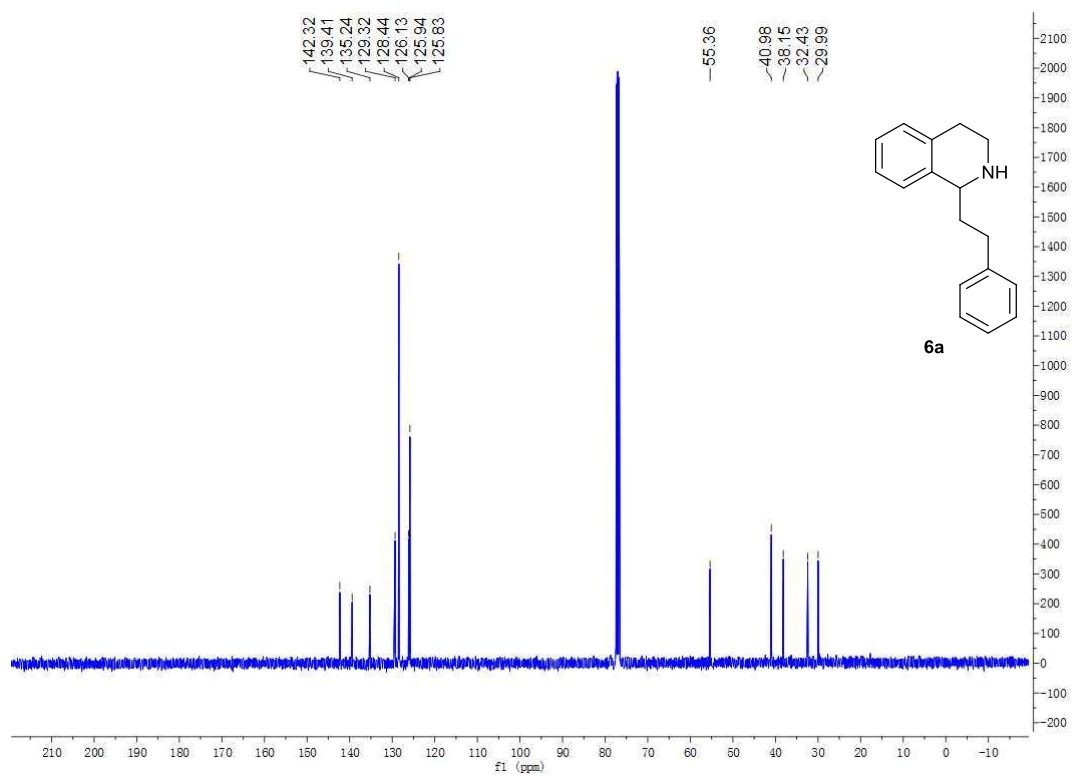
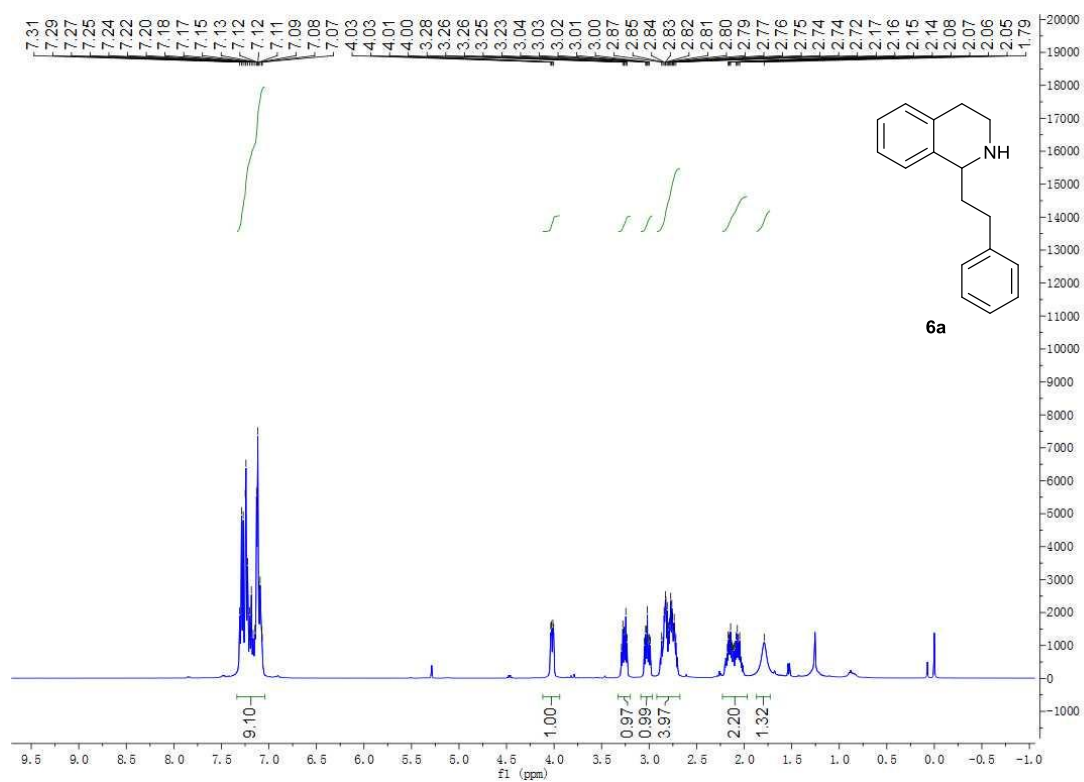


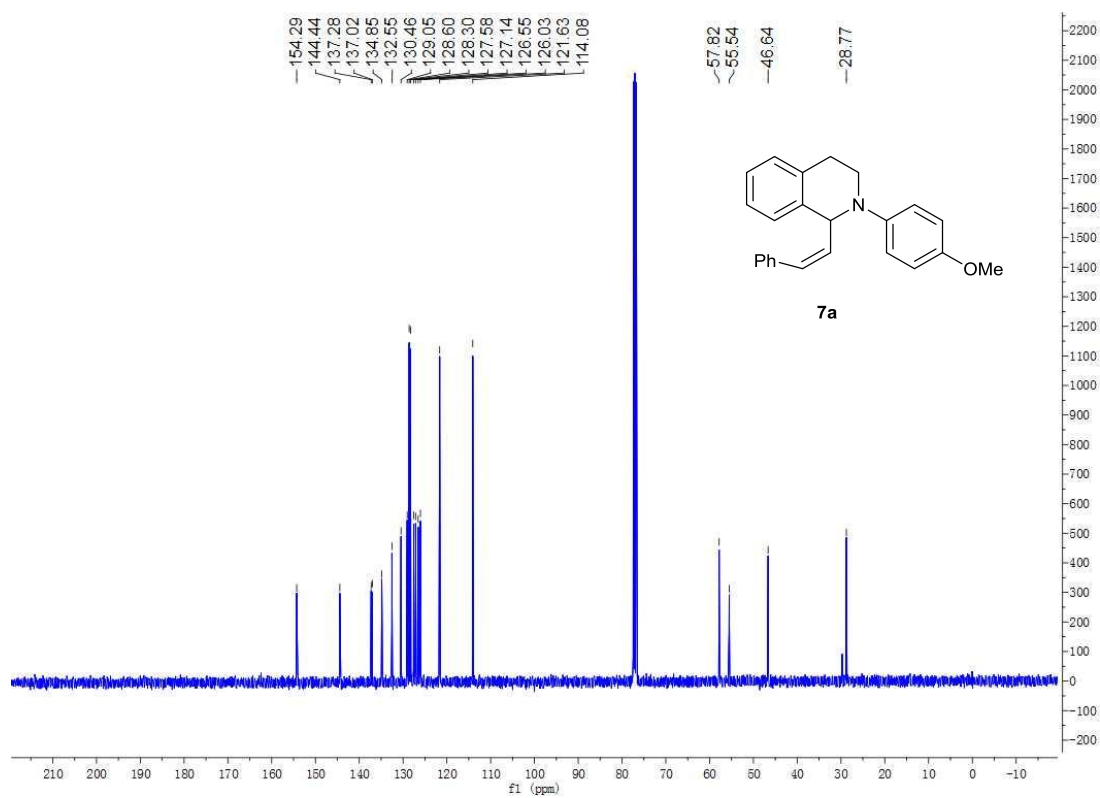
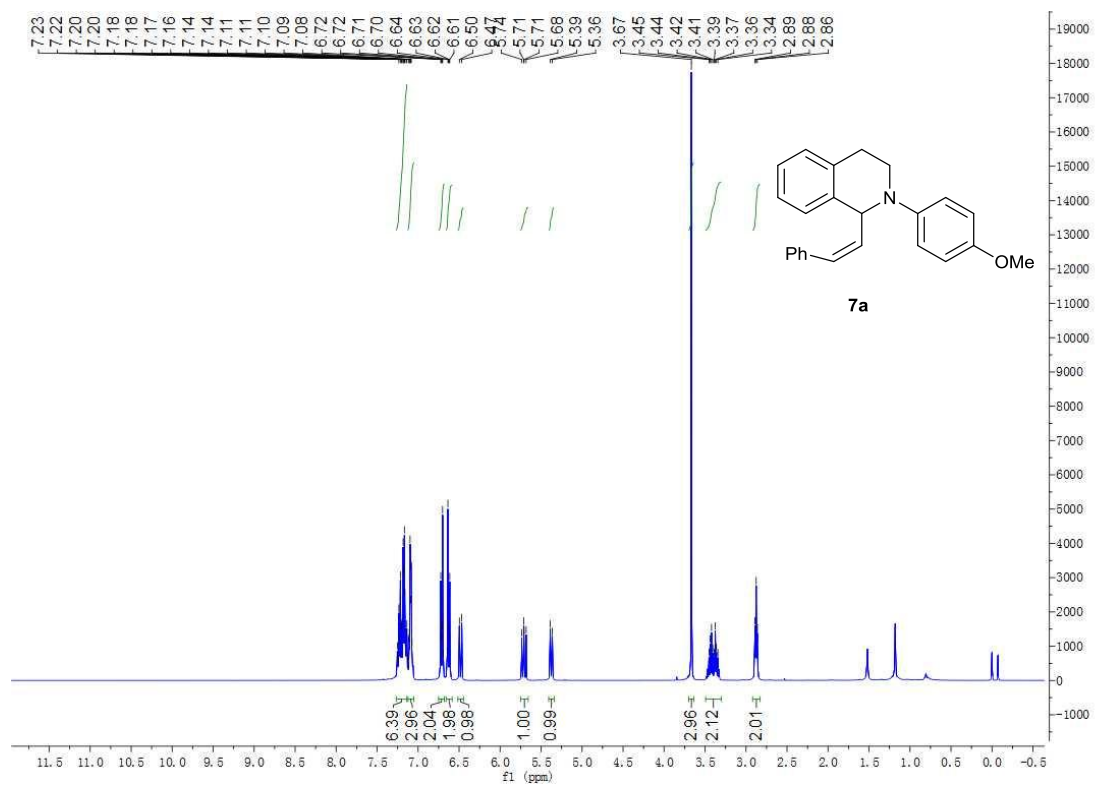


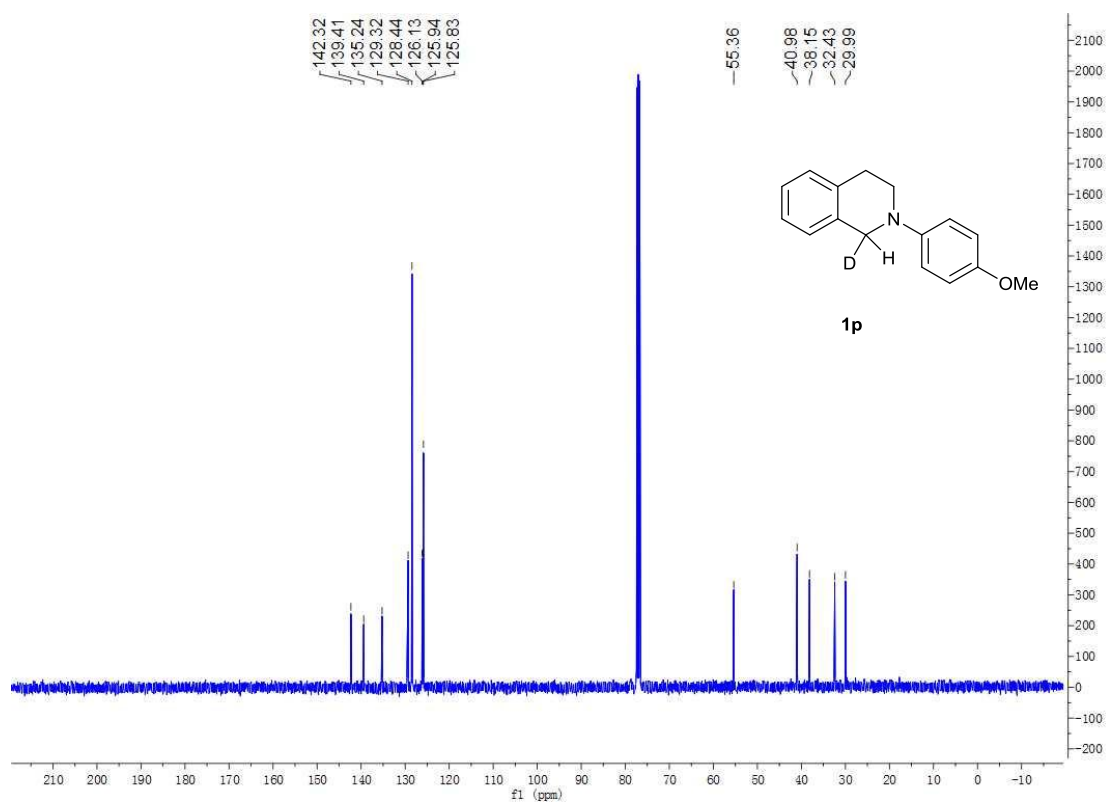
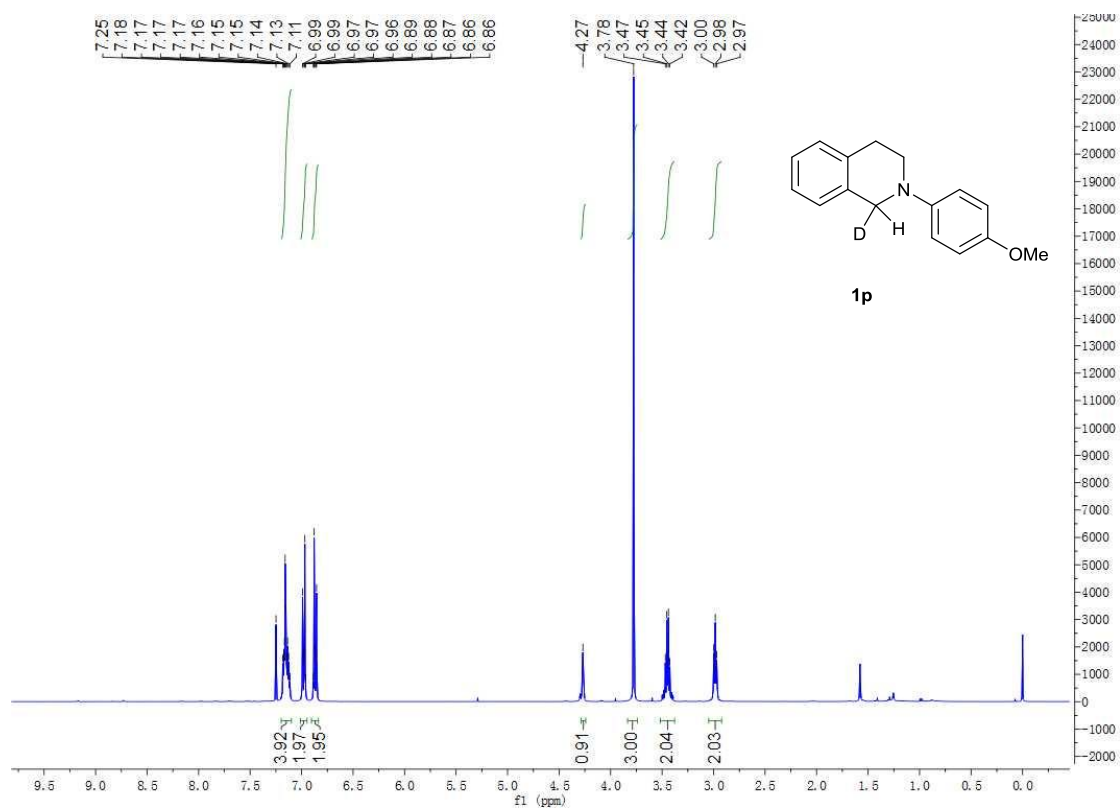












(J) Copies of CD spectra

