
Supporting Information

**Light-driven redox deracemization of indolines and tetrahydroquinolines
using a photocatalyst coupled with chiral phosphoric acid**

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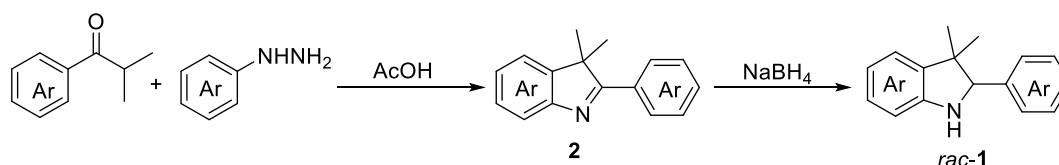
Experimental

1. General:

All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or Schlenk techniques. Deuterated solvents were purchased commercially and were degassed and stored over activated 4 Å molecular sieves. Photocatalysts, chiral phosphoric acids ((*R,R*)-CPA-1-(*R,R*)-CPA-4), and α -cyclodextrin, β -cyclodextrin, γ -cyclodextrin were purchased from Sigma–Aldrich Company Ltd and used as received. The racemic indolines or tetrahydroquinolines were prepared according to the published procedures (*J. Am. Chem. Soc.* **2013**, *135*, 14090-14093). All other reagents were obtained from commercial sources and used without further purification. The ^1H NMR spectra were performed on a Bruker Avance DPX-400 spectrometer in CDCl_3 solutions. Chemical shifts are given in parts per million (δ units) downfield from tetramethylsilane using the residual solvent signal (CHCl_3 , δ 7.26) as an internal standard. ^1H NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), the number of protons. The prefix app is occasionally applied when the true signal multiplicity was unresolved and br indicates the signal in question broadened. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are reported in ppm (δ) relative to residual CHCl_3 (δ 77.36) unless otherwise noted. The enantiomeric excesses (*ee*) were determined using a Daicel Chiralcel column IC–H or OD–H or AD–H with the above HPLC setup.

2. General procedure for the synthesis of starting materials.

2.1 General procedure for the synthesis of racemic indolines:

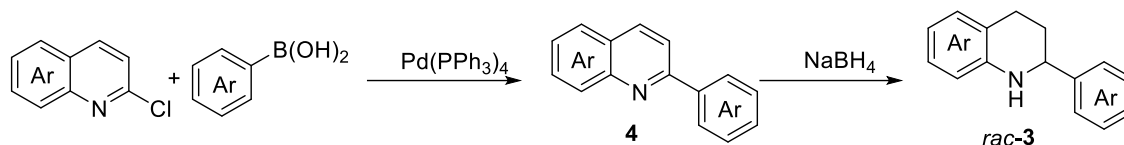


General procedure for the synthesis of **2:** In a typical synthetic route, the ketone (2.0 mmol, 1.0 eq) and arylhydrazine (3.0 mmol, 1.50 eq) were suspended in 10.0 mL of glacial acetic acid at 25 °C and the resulting mixture was heated to 120 °C for 16 h. The reaction mixture was poured onto saturated aqueous Na_2CO_3 and the crude product was extracted with CH_2Cl_2 (3 $\times$ 5.0 mL). The combined organic layers were dried with Na_2SO_4 , filtered, concentrated, and purified by flash column chromatography to give the responding imines (**2a-2z'**) in 65%-91% yields.

General procedure for the synthesis of *rac*-1: In a typical synthetic route, to a solution of the imine (1.0 mmol, 1.0 eq) in 10 mL of MeOH was added NaBH_4 (5.0 g, 5.0 eq) at 0 °C. The resulting mixture was allowed to warm to 25 °C and stirred for a further 5 h. Upon completion, the solvent was removed by evaporation, and 5.0 mL of water was added. The mixture was extracted with CH_2Cl_2 (3 $\times$ 5.0 mL). The combined extracts were washed with the saturated NaCl solution and then dehydrated with Na_2SO_4 .

After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford the racemic amine (*rac-1a-rac-1z'*) in 48%-86% yields.

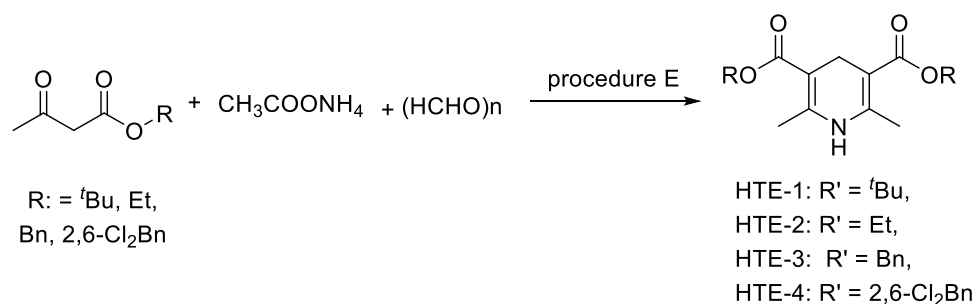
2.2 General procedure for the synthesis of racemic tetrahydroquinolines:



General procedure for the synthesis of **4**: In a typical synthetic route, to this suspension of tetrakis(triphenylphosphine)palladium (0.03 mmol, 1 mol%) was added 2-chloroquinoline (3.0 mmol, 1 equiv), arylboronic acid (3.9 mmol, 1.3 equiv) and anhydrous sodium carbonate (15 mmol, 5 equiv) in 30 mL of dioxane/water (v/v = 4/1). The resulting mixture was stirred at reflux for 12 h. The reaction mixture was then allowed to cool to room temperature and filtered through Celite. The filter cake was washed with ethyl acetate, and the organic layer of the filtrate was separated, washed with brine, dried (NaSO₄), and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to afford the responding imines (**4a-4r**) in 51%-87% yields.

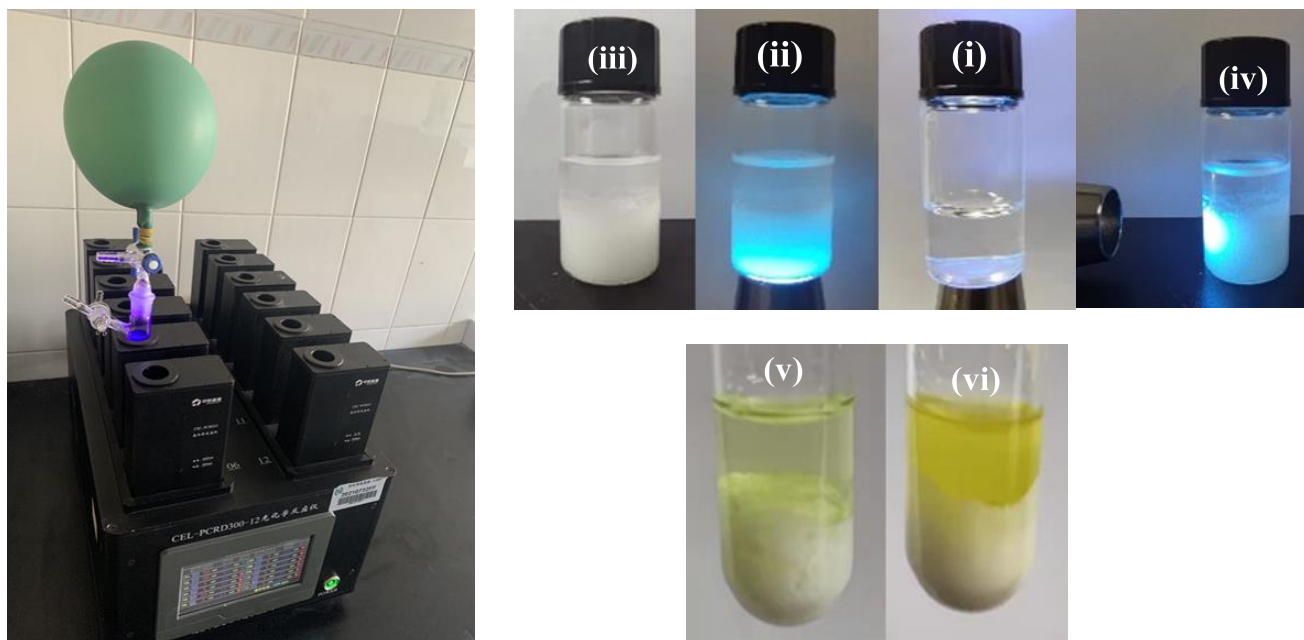
General procedure for the synthesis of *rac-3*: In a typical synthetic route, to a solution of the imine (1.0 mmol, 1.0 eq) in 15 mL of glacial acetic acid was added sodium cyanoborohydride (5.0 eq) at 0 °C. The reaction mixture was stirred overnight at room temperature, poured into saturated aqueous sodium carbonate, stirred for 15 min, and diluted with CH₂Cl₂. The organic layer was separated and the aqueous layer was extracted twice more with CH₂Cl₂ (3 × 5.0 mL). The combined organic extracts were dried (NaSO₄), concentrated under reduced pressure, and purified by column chromatography to afford the racemic amine (*rac-3a-rac-3r*) in 54%-89% yields.

2.3 General procedure for the synthesis of Hantzsch esters (HTE):

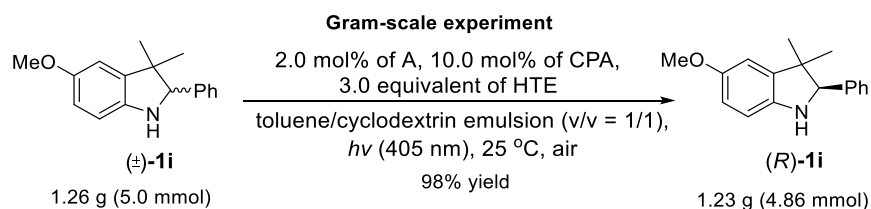


In a typical synthetic route, to a solution of ammonium acetate (10 mmol) and paraformaldehyde (10 mmol) was added ester (10 mmol) was added and the resulting mixture was stirred at 80 °C for 30 minutes under an argon atmosphere. A pale yellow precipitate formed through the course of the reaction, and the crude mixture was allowed to cool to room temperature and filtered through filter paper. The precipitate was washed with ethanol and diethyl ether and purified by column chromatography to afford the Hantzsch esters (HTE-1—THE-4) in 58%-73% yields.

2.4. A schematic illustration of the reaction system of the light-driven redox deracemization of substrates (i) a saturated β -cyclodextrin emulsion, (ii-iv) a mixture of toluene and aqueous β -cyclodextrin emulsion containing HTE with and without the light irradiation, and (v-vi) the mixture before and after the reaction.



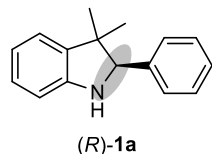
2.5. General procedure for the gram-scale preparation of (*R*)-**1i**.



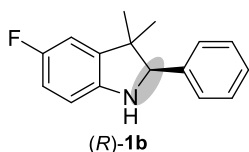
In an open-to-air test tube, to a suspension of di-*tert*-butyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HTE-1) (3.0 equiv.) in 15.0 mL of the aqueous β -cyclodextrin emulsion was added slowly a solution of photocatalyst (2.0 mol%), chiral phosphoric acid (10.0 mol%) and racemic 5-methoxy-3,3-dimethyl-2-phenylindoline (1.26 g, 5.0 mmol) in 15.0 mL of toluene at room temperature. The resulting mixture under the light irradiations was then stirred at 25 $^{\circ}\text{C}$ for the first 2.5 h. Upon completion, the organic layers were collected and the aqueous solution was extracted with toluene (3×10.0 mL). After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 10:1) to afford (*R*)-**1i** (1.23 g, 98% yield) as a white solid.

3. Data of chiral products.

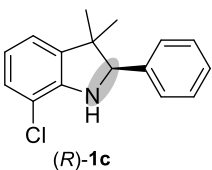
(R)-1a: (R)-3,3-dimethyl-2-phenylindoline. White solid, 99% yield, 98% *ee*. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.30 (m, 2H), 7.29 – 7.20 (m, 3H), 7.02 – 6.96 (m, 2H), 6.73 – 6.68 (m, 1H), 6.66 – 6.64 (m, 1H), 4.52 (s, 1H), 1.35 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.39, 140.01, 138.14, 128.18, 127.58, 122.57, 119.04, 109.26, 74.58, 45.42, 26.58, 24.61. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).



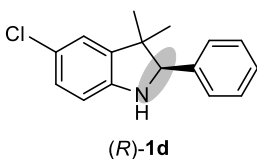
(R)-1b: (R)-5-fluoro-3,3-dimethyl-2-phenylindoline. White solid, 99% yield, 97% *ee*. ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.34 (m, 2H), 7.29 – 7.21 (m, 3H), 6.71 – 6.66 (m, 2H), 6.55 – 6.52 (dd, J = 9.1, 4.3 Hz, 1H), 4.52 (s, 1H), 1.33 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.62, 156.27, 144.85, 140.05, 139.98, 139.38, 128.17, 127.68, 127.45, 113.43, 113.20, 110.17, 109.93, 109.65, 109.58, 75.04, 45.71, 26.25, 24.24. ^{19}F NMR (376 MHz, CDCl_3) δ -125.62. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).



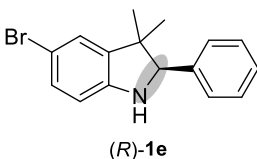
(R)-1c: (R)-4-chloro-3,3-dimethyl-2-phenylindoline. Yellow solid, 95% yield, 90% *ee*. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.36 (m, 2H), 7.30 – 7.23 (m, 3H), 7.01 – 6.98 (dd, J = 8.0, 1.1 Hz, 1H), 6.86 – 6.84 (dd, J = 7.3, 1.1 Hz, 1H), 6.65 – 6.61 (dd, J = 8.0, 7.3 Hz, 1H), 4.56 (s, 1H), 1.35 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.36, 139.59, 139.18, 128.21, 127.74, 127.40, 127.13, 120.70, 119.75, 114.62, 74.32, 46.58, 26.62, 24.51. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).



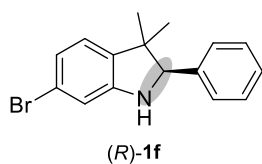
(R)-1d: (R)-5-chloro-3,3-dimethyl-2-phenylindoline. White solid, 98% yield, 95% *ee*. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.33 (m, 2H), 7.30 – 7.23 (m, 3H), 6.96 – 6.91 (m, 2H), 6.58 – 6.56 (d, J = 8.2 Hz, 1H), 4.53 (s, 1H), 1.33 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.81, 140.04, 139.36, 128.19, 127.71, 127.36, 127.12, 123.48, 122.91, 109.98, 74.78, 45.66, 26.46, 24.37. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).



(R)-1e: (R)-5-bromo-3,3-dimethyl-2-phenylindoline. White solid, 97% yield, 94% *ee*. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.23 (m, 5H), 7.10 – 7.04 (m, 2H), 6.52 – 6.50 (d, J = 8.2 Hz, 1H), 4.52 (s, 1H), 1.33 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.35, 140.48, 139.35, 130.01, 128.20, 127.72, 127.35, 125.73, 110.53, 74.71, 45.67, 26.52, 24.41. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).



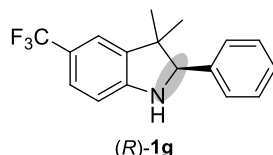
(R)-1f: (R)-6-bromo-3,3-dimethyl-2-phenylindoline. White solid, 99% yield, 98% *ee*. ¹H NMR (400



MHz, CDCl₃) δ 7.34 – 7.23 (m, 5H), 6.81 (d, *J* = 1.0 Hz, 2H), 6.77 – 6.76 (d, *J* = 1.1 Hz, 1H), 4.52 (s, 1H), 1.33 (s, 3H), 0.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.69, 139.35, 137.19, 128.21, 127.72, 127.30, 123.77, 121.63, 120.80, 112.12, 74.60, 45.08, 26.61, 24.43. HPLC (Chiralpak IC-H, elute:

Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

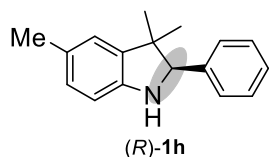
(R)-1g: (R)-3,3-dimethyl-2-phenyl-5-(trifluoromethyl)indoline. White solid, 97% yield, 96% *ee*. ¹H



NMR (400 MHz, CDCl₃) δ 7.32 – 7.22 (m, 6H), 7.15 – 7.14 (d, *J* = 2.1 Hz, 1H), 6.61 – 6.59 (d, *J* = 8.2 Hz, 1H), 4.56 (s, 1H), 1.35 (s, 3H), 0.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.15, 139.14, 138.22, 128.27, 127.82, 127.23, 125.40, 119.69, 108.04, 74.59, 45.28, 26.76, 24.55. ¹⁹F NMR (376

MHz, CDCl₃) δ -60.63. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

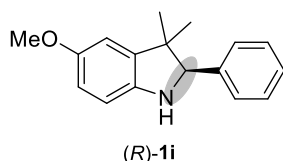
(R)-1h: (R)-3,3,5-trimethyl-2-phenylindoline. White solid, 99% yield, 98% *ee*. ¹H NMR (400 MHz,



CDCl₃) δ 7.42 – 7.39 (m, 2H), 7.32 – 7.23 (m, 3H), 6.85 – 6.82 (m, 2H), 6.60 – 6.58 (d, *J* = 7.7 Hz, 1H), 4.52 (s, 1H), 2.25 (s, 3H), 1.37 (s, 3H), 0.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 146.79, 139.97, 138.40, 128.08, 127.74, 127.51, 127.48, 123.28, 109.22, 74.78, 45.38, 26.44, 24.47, 21.01. HPLC (Chiralpak

IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

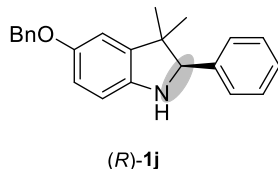
(R)-1i: (R)-5-methoxy-3,3-dimethyl-2-phenylindoline. White solid, 99% yield, 98% *ee*. ¹H NMR



(400 MHz, CDCl₃) δ 7.38 – 7.35 (m, 2H), 7.27 – 7.18 (m, 3H), 6.59 – 6.55 (m, 3H), 4.47 (s, 1H), 3.68 (s, 3H), 1.32 (s, 3H), 0.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.77, 142.96, 139.87, 128.09, 127.54, 111.92, 109.73, 75.02, 55.99, 45.71, 26.26, 24.28. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH =

97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

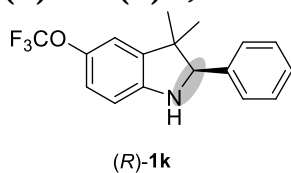
(R)-1j: (R)-5-(benzyloxy)-3,3-dimethyl-2-phenylindoline. White solid, 99% yield, 97% *ee*. ¹H NMR



(400 MHz, CDCl₃) δ 7.38 – 7.35 (m, 4H), 7.32 – 7.21 (m, 6H), 6.68 – 6.55 (m, 3H), 4.92 (s, 2H), 4.49 (s, 1H), 1.32 (s, 3H), 0.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.97, 143.32, 139.89, 137.60, 128.66, 128.63, 128.54, 128.09, 127.85, 127.66, 127.53, 113.05, 110.97, 109.57, 75.00, 71.07, 45.71, 26.28,

24.31. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

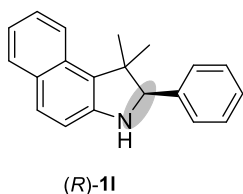
(R)-1k: (R)-3,3-dimethyl-2-phenyl-5-(trifluoromethoxy)indoline. White solid, 98% yield, 96%



ee. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.33 (m, 2H), 7.30 – 7.21 (m, 3H), 6.86 – 6.80 (m, 2H), 6.57 – 6.55 (d, J = 8.2 Hz, 1H), 4.58 (s, 1H), 1.36 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.88, 142.05, 139.57, 139.25, 128.78, 128.43, 128.21, 127.74, 127.36, 120.46, 116.38, 109.01, 74.92, 45.59,

26.32, 24.68, 24.39. ^{19}F NMR (376 MHz, CDCl_3) δ -58.34. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).

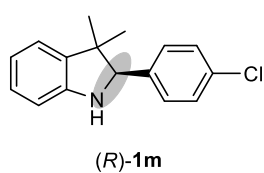
(R)-1l: (R)-1,1-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[e]indole. White solid, 97% yield, 94%



ee. ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.85 (dd, J = 8.7, 1.1 Hz, 1H), 7.70 – 7.68 (dd, J = 8.3, 1.4 Hz, 1H), 7.56 – 7.54 (d, J = 8.5 Hz, 1H), 7.46 – 7.44 (m, 2H), 7.32 – 7.23 (m, 4H), 7.15 – 7.11 (m, 1H), 6.97 – 6.95 (d, J = 8.5 Hz, 1H), 4.61 (s, 1H), 1.67 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.93, 139.50, 131.06, 129.75, 129.52, 128.96, 128.18, 128.10, 127.72, 126.75, 126.20, 121.62, 112.94,

75.18, 47.19, 27.41, 23.05. HPLC (Chiracel OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 $^\circ\text{C}$)

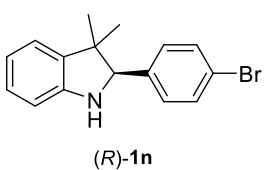
(R)-1m: (R)-2-(4-chlorophenyl)-3,3-dimethylindoline. White solid, 99% yield, 98% *ee.* ^1H NMR



(400 MHz, CDCl_3) δ 7.34 (d, J = 8.2 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.06 – 6.96 (m, 2H), 6.78 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 4.52 (s, 1H), 1.34 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.70, 138.22, 137.96, 133.19, 128.78, 128.29, 127.52, 122.54, 119.48, 109.58, 73.86, 45.40, 26.38,

24.54. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).

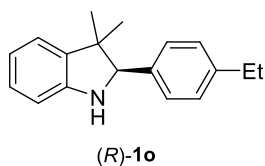
(R)-1n: (R)-2-(4-ethylphenyl)-3,3-dimethylindoline. White solid, 99% yield, 99% *ee.* ^1H NMR (400



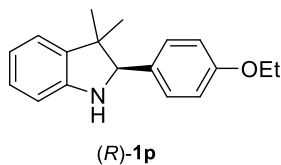
MHz, CDCl_3) δ 7.42 – 7.40 (m, 2H), 7.29 – 7.27 (m, 2H), 7.04 – 6.98 (m, 2H), 6.76 – 6.73 (t, J = 7.4 Hz, 1H), 6.68 – 6.66 (d, J = 7.7 Hz, 1H), 4.49 (s, 1H), 1.34 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.89, 138.89, 137.86, 131.23, 129.13, 127.51, 122.53, 121.27, 119.32, 109.41, 73.90, 45.36, 26.39,

24.55. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 $^\circ\text{C}$).

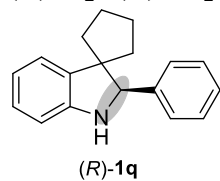
(R)-1o: (R)-2-(4-bromophenyl)-3,3-dimethylindoline. White solid, 99% yield, 98% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.27 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.09 (m, 2H), 7.02 – 6.96 (m, 2H), 6.72 – 6.68 (m, 1H), 6.65 – 6.62 (m, 1H), 4.49 (s, 1H), 2.61 – 2.56 (q, *J* = 7.6 Hz, 2H), 1.34 (s, 3H), 1.19 – 1.15 (t, *J* = 7.6 Hz, 3H), 0.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.40, 143.53, 138.19, 137.10, 127.58, 127.44, 127.35, 122.50, 118.89, 109.11, 74.37, 45.28, 28.57, 26.48, 24.51, 15.67. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).



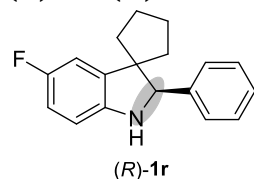
(R)-1p: (R)-3,3-dimethyl-2-(4-propoxyphenyl)indoline. White solid, 98% yield, 98% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.36 (d, *J* = 8.7 Hz, 2H), 7.12 – 7.06 (m, 2H), 6.91 – 6.89 (m, 2H), 6.82 – 6.79 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.73 (d, *J* = 7.7 Hz, 1H), 4.57 (s, 1H), 4.10 – 4.04 (q, *J* = 7.0 Hz, 2H), 1.47 – 1.43 (t, *J* = 7.1 Hz, 3H), 1.42 (s, 3H), 0.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.43, 149.26, 138.23, 131.68, 128.48, 127.33, 122.53, 118.97, 113.99, 109.18, 74.07, 63.42, 45.24, 26.43, 24.44, 14.92. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).



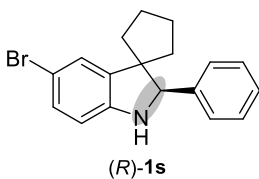
(R)-1q: (R)-2'-phenylspiro[cyclopentane-1,3'-indoline]. White solid, 97% yield, 93% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.20 (m, 5H), 7.02 – 7.68 (t, *J* = 7.5 Hz, 2H), 6.73 – 6.63 (m, 2H), 4.58 (s, 1H), 1.96 – 1.92 (m, 2H), 1.77 – 1.50 (m, 4H), 1.39 – 1.35 (t, *J* = 7.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.74, 141.10, 138.06, 128.21, 127.64, 127.31, 122.82, 119.08, 108.80, 73.70, 57.24, 39.60, 34.91, 24.57. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).



(R)-1r: (R)-5'-fluoro-2'-phenylspiro[cyclopentane-1,3'-indoline]. White solid, 98% yield, 96% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.30 (m, 5H), 6.85 – 6.74 (m, 2H), 6.62 (dd, *J* = 8.2, 4.4 Hz, 1H), 4.68 (s, 1H), 2.03 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.58 (m, 3H), 1.54 – 1.40 (m, 2H), 1.28 – 1.22 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.58, 156.24, 145.61, 140.76, 128.25, 127.76, 127.59, 113.23, 113.00, 110.40, 110.17, 74.27, 39.45, 34.78, 24.61, 24.53. ¹⁹F NMR (376 MHz, CDCl₃) δ -125.62. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

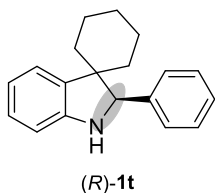


(R)-1s: 5'-bromo-2'-phenylspiro[cyclopentane-1,3'-indoline]. White solid, 95% yield, 93% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.19 (m, 5H), 7.10 – 7.05 (m, 2H), 6.50 – 6.48 (d, *J* = 8.1 Hz, 1H), 4.56 (s, 1H), 1.91 – 1.87 (m, 2H), 1.88 – 1.58 (m, 1H), 1.53 – 1.50 (m, 3H), 1.38 – 1.34 (m, 2H), 1.22 – 1.12 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 148.73, 140.52, 129.90, 128.30, 127.85, 127.51, 125.88, 110.58,

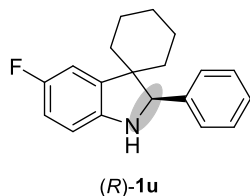


110.13, 73.96, 57.45, 39.77, 34.80, 24.57, 24.50. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

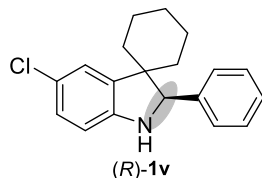
(R)-1t: (R)-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 95% yield, 95% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.15 (m, 6H), 7.02 – 6.98 (m, 1H), 6.71 – 6.67 (m, 1H), 6.60 – 6.58 (m, 1H), 4.48(s, 1H), 1.78 – 1.60(m,4H), 1.51 – 1.45 (m, 1H), 1.43 – 1.30 (m, 3H), 1.16 – 1.04(m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.93, 141.14, 137.26, 128.12, 127.95, 127.64, 127.49, 124.32, 118.61, 108.91, 72.98, 49.20, 37.32, 31.81, 25.76, 23.01, 22.18. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).



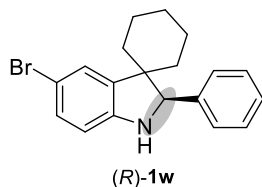
(R)-1u: (R)-5'-fluoro-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 93% yield, 94% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.19 (q, J = 2.3, 1.8 Hz, 5H), 6.93 – 6.90 (dd, J = 9.0, 2.6 Hz, 1H), 6.73 – 6.68 (m, 1H), 6.52 – 6.49 (dd, J = 8.4, 4.4 Hz, 1H), δ 4.50 (s, 1H), 1.79 – 1.57 (m, 4H), 1.48 – 1.29 (m, 4H), 1.18 – 1.03 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.13, 155.79, 145.93, 140.86, 138.99, 138.92, 128.18, 127.89, 127.77, 113.38, 113.15, 112.05, 111.81, 108.87, 108.79, 73.58, 49.45, 36.97, 31.62, 25.62, 22.90, 22.04. ¹⁹F NMR (376 MHz, CDCl₃) δ -126.06. HPLC (Chiracel OD-H, n-hexane/2-propanol = 90/10, detector: 254 nm, flow rate = 1.0 mL/min, 25 °C).



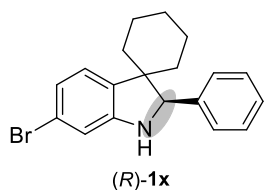
(R)-1v: (R)-5'-chloro-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 97% yield, 96% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.18 (dd, J = 8.9, 0.8 Hz, 5H), 7.11 (d, J = 2.1 Hz, 1H), 6.98 – 6.94 (d, J = 2.1 Hz, 1H), 6.53 – 6.51(m, 1H), 4.51 (s, 1H), 1.80 – 1.55 (m, 4H), 1.48 – 1.31 (m, 4H), 1.15 – 1.07 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.61, 140.71, 139.16, 128.21, 127.83, 127.18, 124.52, 122.99, 109.42, 73.17, 49.49, 37.22, 31.59, 25.60, 22.85, 22.09. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).



(R)-1w: (R)-5'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 96% yield, 95% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.19(m, 6H), 7.11 – 7.09 (dd, J = 8.2, 2.0 Hz, 1H), 6.49 – 6.47(d, J = 8.1 Hz, 1H), 1.81 – 1.55(m, 4H), 1.48 – 1.32 (m, 4H), 1.22 – 1.06 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.15, 140.73, 139.61, 130.08, 128.21, 127.83, 127.24, 110.00, 109.95, 73.06, 49.52, 37.29, 31.60, 25.60, 22.85, 22.12. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).



(R)-1x: (R)-6'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 97% yield, 96% *ee*. ¹H

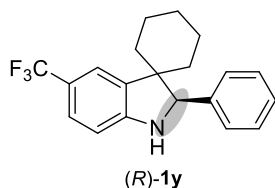


(R)-1x

NMR (400 MHz, CDCl₃) δ 7.21 – 7.18 (d, *J* = 8.5 Hz, 5H), 7.01 – 6.99 (d, *J* = 7.9 Hz, 1H), 6.80 – 6.78 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 4.50 (s, 1H), 1.78 – 1.53 (m, 4H), 1.46 – 1.30 (m, 4H), 1.12 – 1.03 (m, 2H). ¹³C NMR

(101 MHz, CDCl₃) δ 151.41, 140.59, 136.34, 128.22, 127.83, 125.39, 121.15, 120.99, 111.63, 73.00, 48.90, 37.37, 31.66, 25.62, 22.86, 22.13. HPLC (Chiralpak IC-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.5 mL/min, 25 °C).

(R)-1y: (R)-2'-phenyl-5'-(trifluoromethyl)spiro[cyclohexane-1,3'-indoline]. White solid, 98% yield,

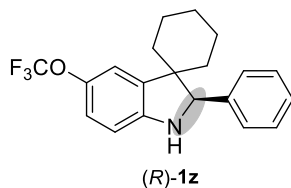


(R)-1y

97% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 1.8 Hz, 1H), 7.27 – 7.16 (m, 6H), 6.56 – 6.54 (d, *J* = 8.1 Hz, 1H), 4.56 (s, 1H), 1.81 – 1.45 (m, 5H), 1.40 – 1.30 (m, 3H), 1.16 – 1.06 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 152.70, 140.41, 137.39, 128.28, 127.96, 127.78, 125.56, 121.11, 107.51, 72.78, 49.13,

37.63, 31.62, 25.55, 22.77, 22.17. ¹⁹F NMR (376 MHz, CDCl₃) δ -60.45. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

(R)-1z: (R)-2'-phenyl-5'-(trifluoromethoxy)spiro[cyclohexane-1,3'-indoline]. White solid, 98%

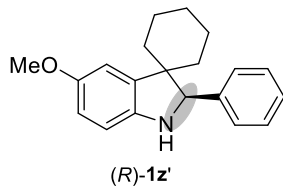


(R)-1z

yield, 96% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (s, 5H), 7.02 (s, 1H), 6.87 – 6.84 (m, 1H), 6.53 – 6.51 (d, *J* = 8.4 Hz, 1H), 4.53 (s, 1H), 1.79 – 1.58 (m, 4H), 1.48 – 1.26 (m, 4H), 1.13 – 1.05 (m, 2H). ¹³C NMR (101 MHz, CDCl₃)

δ 148.66, 141.57, 140.55, 138.55, 128.21, 127.86, 120.47, 118.24, 108.32, 73.50, 49.31, 37.07, 31.65, 25.56, 22.82, 21.97. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.31. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

(R)-1z': (R)-5'-methoxy-2'-phenylspiro[cyclohexane-1,3'-indoline]. White solid, 97% yield, 96%

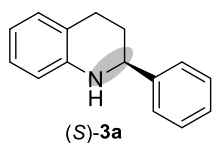


(R)-1z'

ee. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 5H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.59 – 6.52 (m, 2H), 4.48 (s, 1H), 3.71 (s, 3H), 1.78 – 1.59 (m, 4H), 1.50 – 1.26 (m, 4H), 1.26 – 1.04 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.36, 143.87, 141.32, 139.10, 128.10, 127.94, 127.60, 111.98, 111.60, 109.10, 73.41,

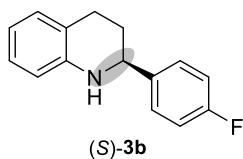
56.02, 49.51, 37.10, 31.66, 25.71, 23.03, 22.16. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

(S)-3a: (S)-2-phenyl-1,2,3,4-tetrahydroquinoline. White solid, 96% yield, 90% *ee*. ¹H NMR (400



MHz, CDCl₃) δ 7.34 – 7.15 (m, 5H), 6.95 – 6.91 (m, 2H), 6.64 – 6.60 (m, 1H), 6.51 – 6.48 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.37 – 4.33 (dd, *J* = 9.4, 3.3 Hz, 1H), 2.84 – 2.80 (m, 1H), 2.70 – 2.65 (m, 1H), 2.06 – 1.97 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 144.86, 144.77, 129.39, 128.65, 127.52, 126.98, 126.64, 120.95, 117.25, 114.08, 56.31, 31.05, 26.45. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

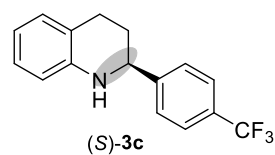
(S)-3b: (S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline. White solid, 96% yield, 94% *ee*. ¹H



NMR (400 MHz, CDCl₃) δ 7.31 – 7.28 (m, 2H), 6.99 – 6.93 (m, 4H), 6.63 – 6.59 (m, 1H), 6.50 – 6.48 (d, *J* = 7.8 Hz, 1H), 4.38 – 4.35 (dd, *J* = 9.4, 3.2 Hz, 1H), 2.90 – 2.82 (m, 1H), 2.70 – 2.63 (m, 1H), 2.07 – 1.86 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 163.35, 160.91, 144.51, 140.48, 129.36, 128.16, 128.08, 126.97, 120.89, 117.43, 115.48, 115.26, 114.12, 55.62, 31.13, 26.32. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.26.

HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

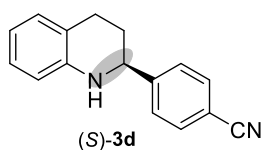
(S)-3c: (S)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline. White solid, 94% yield,



95% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.52 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.42 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.93 (m, 2H), 6.63 – 6.60 (m, 1H), 6.52 – 6.50 (d, *J* = 8.1 Hz, 1H), 4.47 – 4.44 (dd, *J* = 8.9, 3.4 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.67 – 2.60 (m, 1H), 2.10 – 1.87 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.91, 144.20, 129.40, 127.08, 126.92, 125.58, 125.54, 122.86, 120.85, 117.65, 114.21, 55.80, 30.86, 25.96.

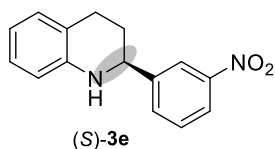
¹⁹F NMR (376 MHz, CDCl₃) δ -62.36. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

(S)-3d: (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzonitrile. White solid, 96% yield, 97% *ee*. ¹H



NMR (400 MHz, CDCl₃) δ 7.55 – 7.53 (m, 2H), 7.42 – 7.40 (m, 2H), 6.97 – 6.91 (m, 2H), 6.63 – 6.59 (m, 1H), 6.52 – 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.46 – 4.43 (dd, *J* = 8.6, 3.5 Hz, 1H), 2.85 – 2.77 (m, 1H), 2.63 – 2.56 (m, 1H), 2.08 – 2.02 (m, 1H), 1.93 – 1.83 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.39, 143.90, 132.47, 129.40, 127.34, 127.15, 120.76, 118.91, 117.81, 114.28, 111.16, 55.75, 30.67, 25.69. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

(S)-3e: (S)-2-(3-nitrophenyl)-1,2,3,4-tetrahydroquinoline. White solid, 96% yield, 90% *ee*. ¹H NMR

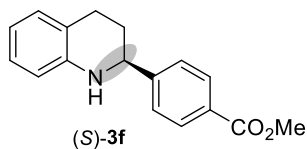


(400 MHz, CDCl₃) δ 8.19 – 8.18 (t, *J* = 2.0 Hz, 1H), 8.07 – 8.04 (m, 1H), 7.67 – 7.65 (m, 1H), 7.46 – 7.42 (t, *J* = 7.9 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.62 (td, *J* = 7.4, 1.2 Hz, 1H), 6.64 – 6.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.51 – 4.48 (dd, *J* = 9.0, 3.4 Hz, 1H), 2.89 – 2.81 (m, 1H), 2.67 – 2.60 (m, 1H), 2.11 – 1.88 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.51, 147.11, 143.94, 132.84, 129.59, 129.39, 127.15, 122.51, 121.63,

120.79, 117.92, 114.43, 55.57, 30.99, 25.94. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

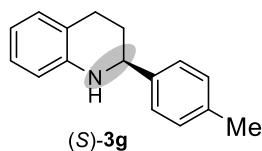
(S)-3f: methyl (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzoate. White solid, 99% yield, 98% *ee*. ¹H



NMR (400 MHz, CDCl₃) δ 7.94 – 7.92 (m, 2H), 7.39 – 7.37 (d, *J* = 8.3 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.61 – 6.57 (m, 1H), 6.51 – 6.48 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.45 – 4.41 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.83 (s, 3H), 2.87 – 2.79 (m, 1H), 2.66 – 2.59 (m, 1H), 2.08 – 2.02 (m, 1H), 1.95 – 1.85 (m, 1H). ¹³C NMR

(101 MHz, CDCl₃) δ 166.97, 150.10, 144.25, 129.95, 129.36, 129.29, 127.04, 126.55, 120.86, 117.52, 114.17, 55.94, 52.15, 30.81, 26.01. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

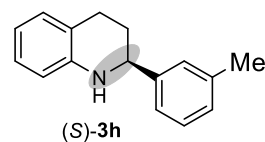
(S)-3g: (S)-2-(*p*-tolyl)-1,2,3,4-tetrahydroquinoline. White solid, 96% yield, 91% *ee*. ¹H NMR (400



MHz, CDCl₃) δ 7.28 – 7.26 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.14 (t, *J* = 9.4 Hz, 2H), 7.01 – 6.98 (t, *J* = 7.3 Hz, 2H), 6.66 – 6.62 (m, 1H), 6.52 – 6.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 4.40 – 4.36 (dd, *J* = 9.4, 3.3 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.75 – 2.69 (m, 1H), 2.34 (s, 3H), 2.12 – 2.05 (m, 1H), 2.01 – 1.91 (m, 1H). ¹³C NMR (101

MHz, CDCl₃) δ 144.83, 141.86, 137.15, 129.35, 129.30, 126.93, 126.53, 120.94, 117.16, 114.03, 56.06, 31.08, 26.55, 21.18. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

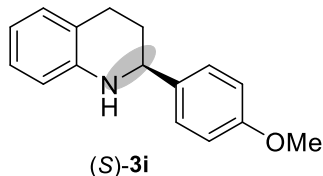
(S)-3h: (S)-2-(*m*-tolyl)-1,2,3,4-tetrahydroquinoline. White solid, 93% yield, 90% *ee*. ¹H NMR (400



MHz, CDCl₃) δ 7.13 (m, 3H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.61 – 6.53 (m, 1H), 6.49 – 6.42 (m, 1H), 4.31 (dd, *J* = 9.6, 3.3 Hz, 1H), 2.84 (m, 1H), 2.66 (m, 1H), 2.28 (s, 3H), 2.02 (m, 1H), 1.90 (m, 1H). ¹³C NMR (101

MHz, CDCl₃) δ 144.72, 138.29, 129.34, 128.53, 128.26, 127.31, 126.94, 123.70, 121.02, 117.25, 114.10, 56.36, 31.06, 26.59, 21.54. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

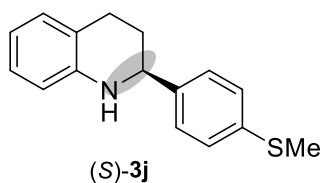
(S)-3i: (S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline. White solid, 95% yield, 92% *ee*. ¹H



NMR (400 MHz, CDCl₃) δ 7.26 – 7.24 (d, *J* = 8.5 Hz, 2H), 6.95 – 6.91 (p, *J* = 4.1, 3.3 Hz, 2H), 6.83 – 6.80 (m, 2H), 6.61 – 6.57 (t, *J* = 7.4 Hz, 1H), 6.47 – 6.45 (m, 1H), 4.32 – 4.29 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.74 (s, 3H), 2.90 – 2.81 (m, 1H), 2.71 – 2.64 (m, 1H), 2.05 – 1.87 (m, 2H). ¹³C NMR (101

MHz, CDCl₃) δ 158.97, 144.72, 136.81, 129.33, 127.69, 126.89, 120.98, 117.23, 114.08, 113.92, 55.76, 55.35, 31.08, 26.58. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

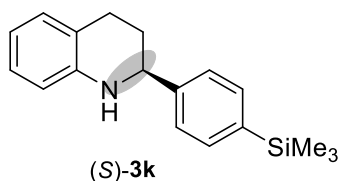
(S)-3j: (S)-2-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline. White solid, 96% yield, 93% *ee*.



^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.21 (m, 2H), 7.17 – 7.14 (m, 1H), 6.95 – 6.90 (t, J = 7.6 Hz, 2H), 6.59 – 6.55 (m, 1H), 6.46 – 6.44 (m, 1H), 4.32 – 4.29 (dd, J = 9.3, 3.3 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.67 – 2.61 (m, 1H), 2.40 (s, 3H), 2.04 – 1.97 (m, 1H), 1.92 – 1.83 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.60, 141.77, 137.38, 129.35, 127.14, 126.96, 126.89,

120.92, 117.32, 114.09, 55.82, 30.96, 26.36, 16.05. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

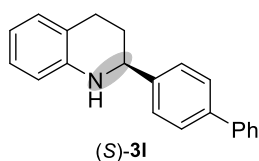
(S)-3k: (S)-2-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline. White solid, 95% yield, 91% *ee*.



^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.40 (m, 2H), 7.35 – 7.27 (m, 2H), 6.93 (t, J = 7.1 Hz, 2H), 6.57 (td, J = 7.4, 1.2 Hz, 1H), 6.48 – 6.42 (m, 1H), 4.35 (dd, J = 9.4, 3.3 Hz, 1H), 2.84 (ddd, J = 16.3, 10.7, 5.5 Hz, 1H), 2.66 (dt, J = 16.4, 4.8 Hz, 1H), 2.04 (dddd, J = 13.1, 5.4, 4.4, 3.3 Hz, 1H), 1.92 (dddd, J = 13.0, 10.7, 9.4, 5.1 Hz, 1H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.39, 145.72, 140.68, 134.72, 130.38, 127.98, 127.08, 121.98, 118.28, 115.09, 57.33,

31.93, 27.50, -0.00. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

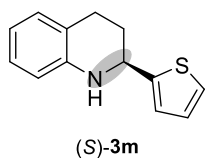
(S)-3l: (S)-2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline. White solid, 92% yield, 92% *ee*.



^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.50 (dd, J = 8.1, 4.3 Hz, 4H), 7.40 – 7.34 (dd, J = 15.3, 7.8 Hz, 4H), 7.29 – 7.25 (t, J = 7.4 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.63 – 6.51 (m, 2H), 4.43 – 4.39 (dd, J = 9.2, 3.3 Hz, 1H), 2.91 – 2.83 (m, 1H), 2.73 – 2.64 (m, 1H), 2.13 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.58, 143.80,

140.86, 140.45, 129.36, 128.82, 127.34, 127.31, 127.11, 127.04, 126.96, 120.99, 117.34, 114.13, 56.00, 30.94, 26.39. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

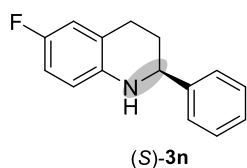
(S)-3m: (S)-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline. White solid, 93% yield, 90% *ee*.



^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.20 (dd, J = 5.0, 3.0 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.01 – 6.99 (dd, J = 5.0, 1.4 Hz, 1H), 6.94 – 6.89 (t, J = 7.7 Hz, 2H), 6.59 – 6.55 (m, 1H), 6.45 – 6.43 (d, J = 7.9 Hz, 1H), 4.48 – 4.45 (dd, J = 9.1, 3.2 Hz, 1H), 2.85 – 2.77 (m, 1H), 2.68 – 2.61 (m, 1H), 2.08 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3)

δ 146.01, 144.29, 129.36, 126.92, 126.14, 121.03, 120.83, 117.44, 114.20, 52.12, 30.22, 26.21. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

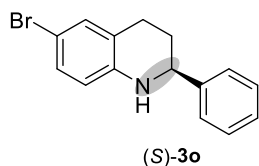
(S)-3n: (S)-6-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline. White solid, 91% yield, 87% *ee*.



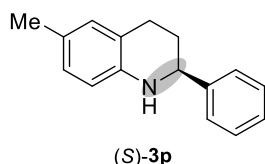
^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.19 (m, 5H), 6.66 – 6.62 (m, 2H), 6.39 – 6.36 (dd, J = 9.5, 4.8 Hz, 1H), 4.31 – 4.28 (dd, J = 9.5, 3.2 Hz, 1H), 2.87 – 2.79 (m, 1H), 2.66 – 2.60 (m, 1H), 2.05 – 1.99 (m, 1H), 1.94 – 1.84 (m, 1H). ^{13}C NMR

(101 MHz, CDCl₃) δ 156.75, 154.41, 144.52, 140.93, 128.64, 127.57, 126.57, 122.27, 122.21, 115.58, 115.37, 114.75, 114.68, 113.54, 113.32, 56.38, 30.71, 26.58. ¹⁹F NMR (376 MHz, CDCl₃) δ -127.97. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

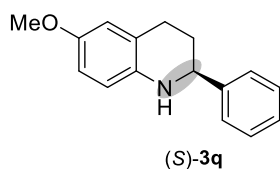
(S)-3o: (S)-6-bromo-2-phenyl-1,2,3,4-tetrahydroquinoline. White solid, 93% yield, 91% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.18 (m, 5H), 7.02 – 6.98 (m, 2H), 6.33 – 6.31 (d, *J* = 8.4 Hz, 1H), 4.34 – 4.31 (dd, *J* = 9.1, 3.4 Hz, 1H), 2.82 – 2.74 (m, 1H), 2.63 – 2.57 (m, 1H), 2.05 – 1.98 (m, 1H), 1.91 – 1.82 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.32, 143.68, 131.73, 129.58, 128.68, 127.63, 126.50, 122.97, 115.43, 108.56, 56.06, 30.40, 26.09. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).



(S)-3p: (S)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline. White solid, 95% yield, 90% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.17 (m, 5H), 6.75 – 6.73 (dd, *J* = 5.9, 2.3 Hz, 2H), 6.39 – 6.37 (d, *J* = 8.5 Hz, 1H), 4.32 – 4.29 (dd, *J* = 9.4, 3.2 Hz, 1H), 2.85 – 2.77 (m, 1H), 2.64 – 2.58 (m, 1H), 2.15 (s, 3H), 2.05 – 1.98 (m, 1H), 1.94 – 1.85 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.95, 142.37, 129.89, 128.59, 127.49, 127.44, 126.63, 126.49, 121.01, 114.23, 56.45, 31.19, 26.44, 20.51. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).



(S)-3q: (S)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline. White solid, 92% yield, 84% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.17 (m, 5H), 6.56 – 6.52 (m, 2H), 6.42 – 6.40 (d, *J* = 8.4 Hz, 1H), 4.29 – 4.25 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.65 (s, 3H), 2.89 – 2.80 (m, 1H), 2.67 – 2.60 (m, 1H), 2.05 – 1.98 (m, 1H), 1.95 – 1.85 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.93, 144.85, 138.90, 128.59, 127.45, 126.65, 122.22, 115.25, 114.68, 113.08, 56.62, 55.87, 31.15, 26.87. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).



(S)-3r: methyl (S)-4-(6-methoxy-1,2,3,4-tetrahydroquinolin-2-yl)benzoate. White solid, 99% yield, 99% *ee*. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.93 (m, 2H), 7.40 – 7.38 (d, *J* = 8.3 Hz, 2H), 6.59 – 6.53 (m, 2H), 6.48 – 6.46 (d, *J* = 8.5 Hz, 1H), 4.38 – 4.35 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 2.89 – 2.81 (m, 1H), 2.66 – 2.60 (m, 1H), 2.07 – 2.01 (m, 1H), 1.95 – 1.86 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.98, 152.13, 150.06, 138.28, 129.92, 129.26, 126.60, 122.17, 115.41, 114.63, 113.16, 56.30, 55.83, 52.14, 30.96, 26.49. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C).

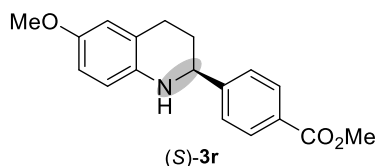
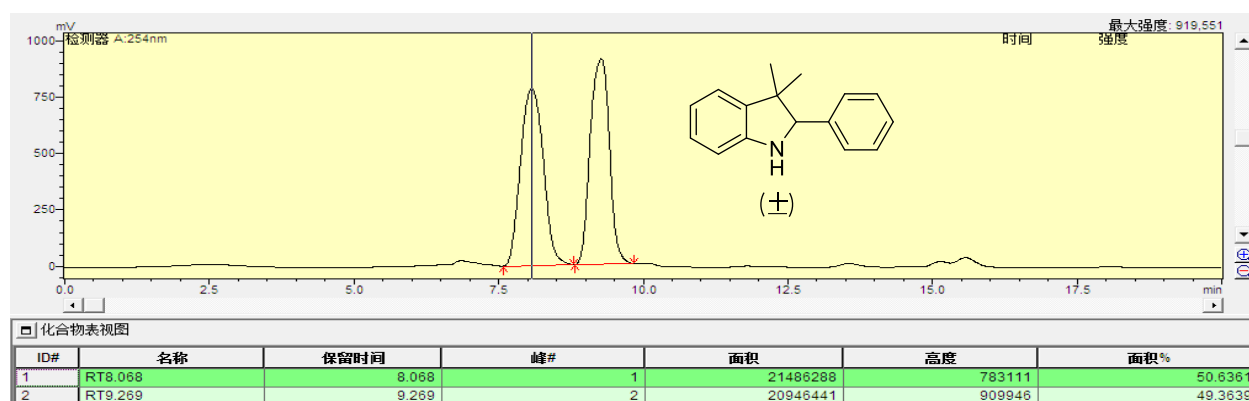
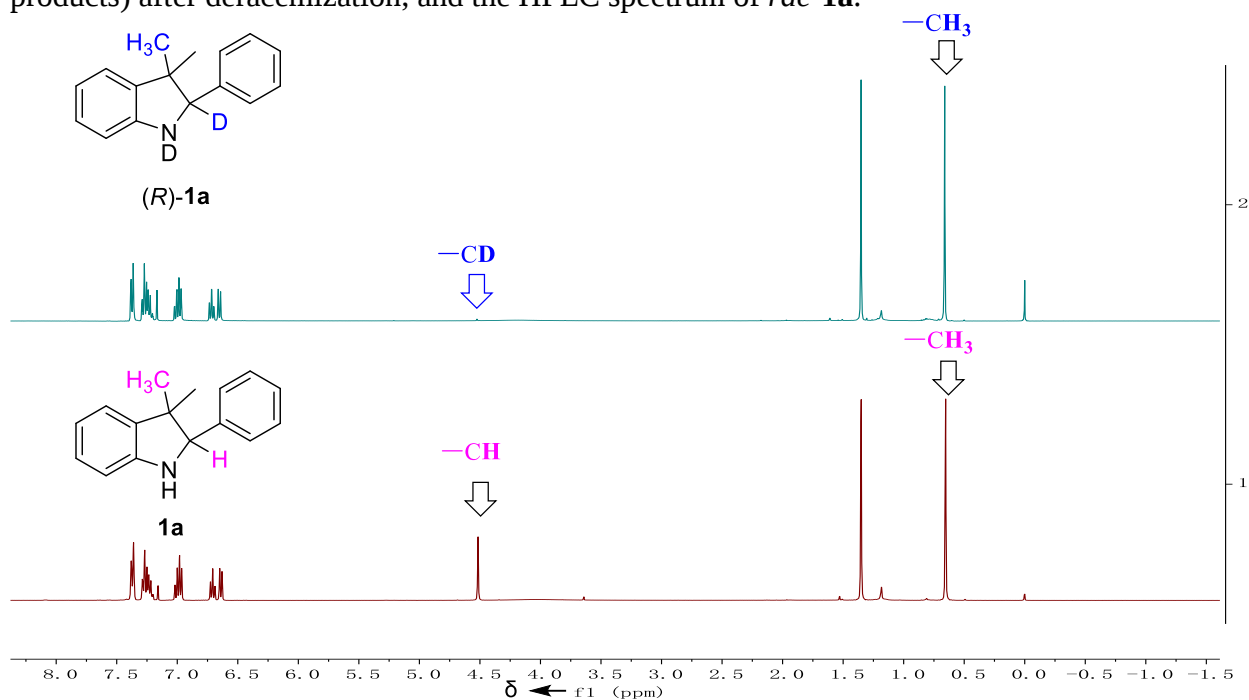
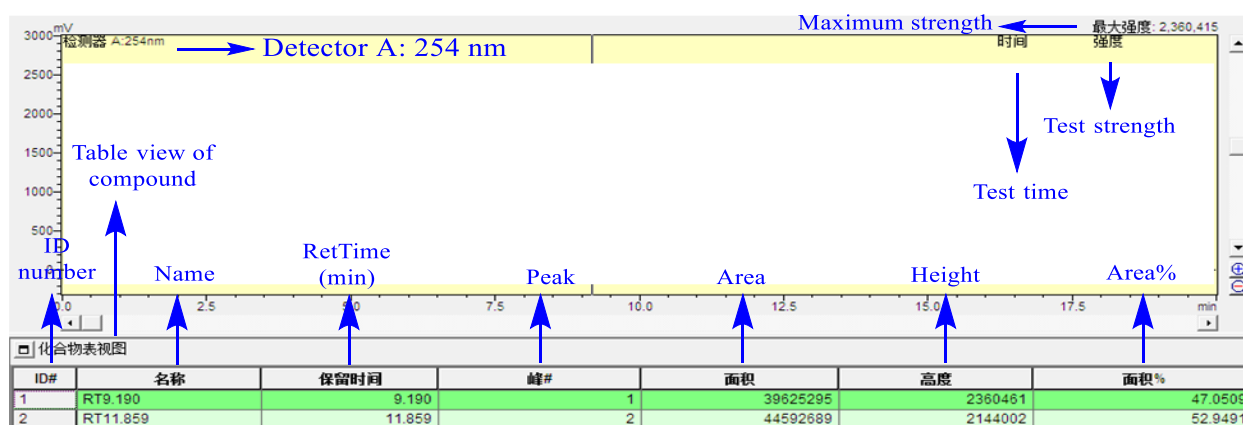


Figure S1. ^1H -NMR and HPLC spectra of (*R*)-**1a** in the reactions of *rac*-**1a-d**₁ in Table 2

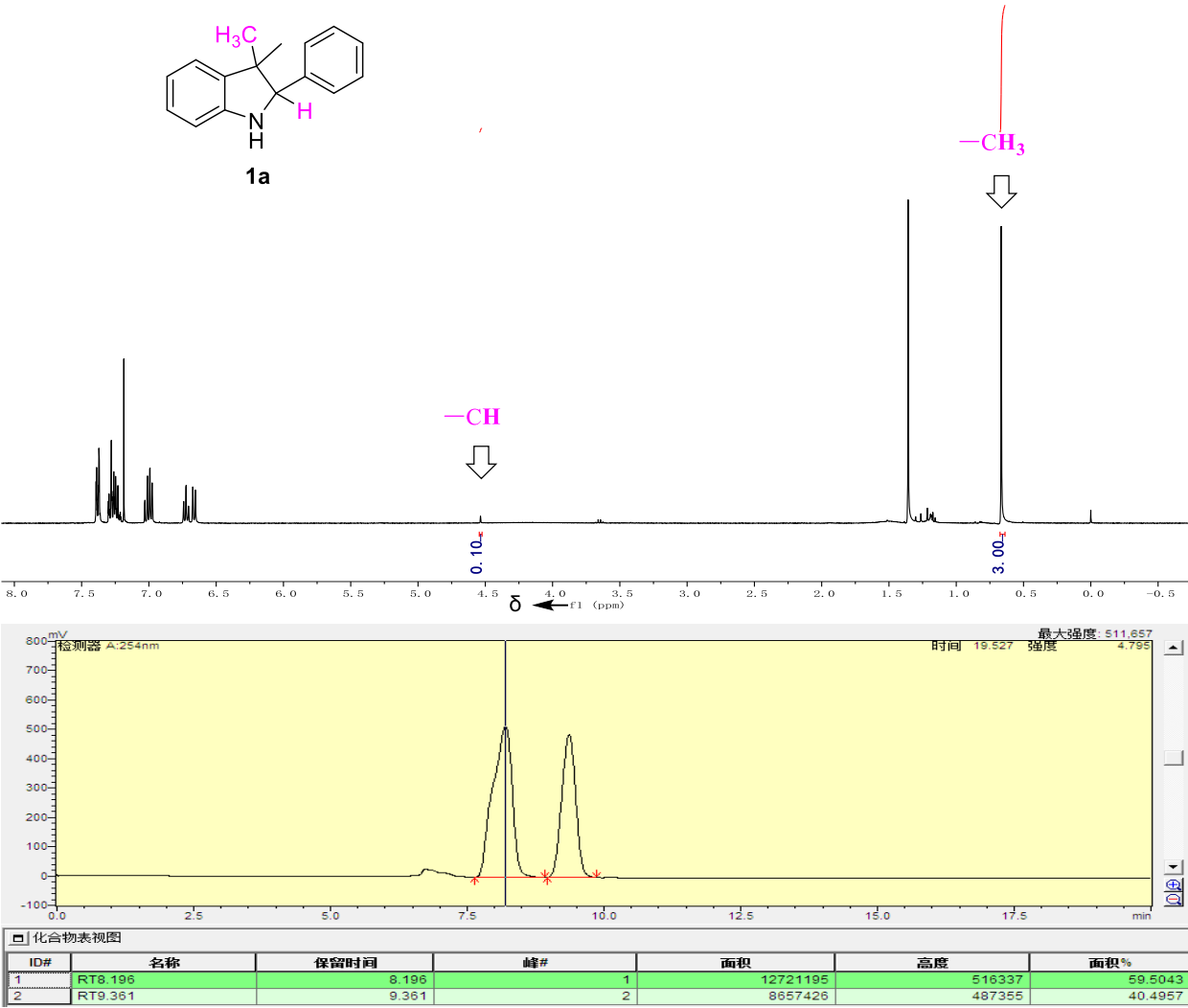
General Note. The ^1H -NMR spectra of *rac*-**1a-d** (starting material) before reaction *and* (*R*)-**1a** (chiral products) after deracemization, and the HPLC spectrum of *rac*-**1a**.



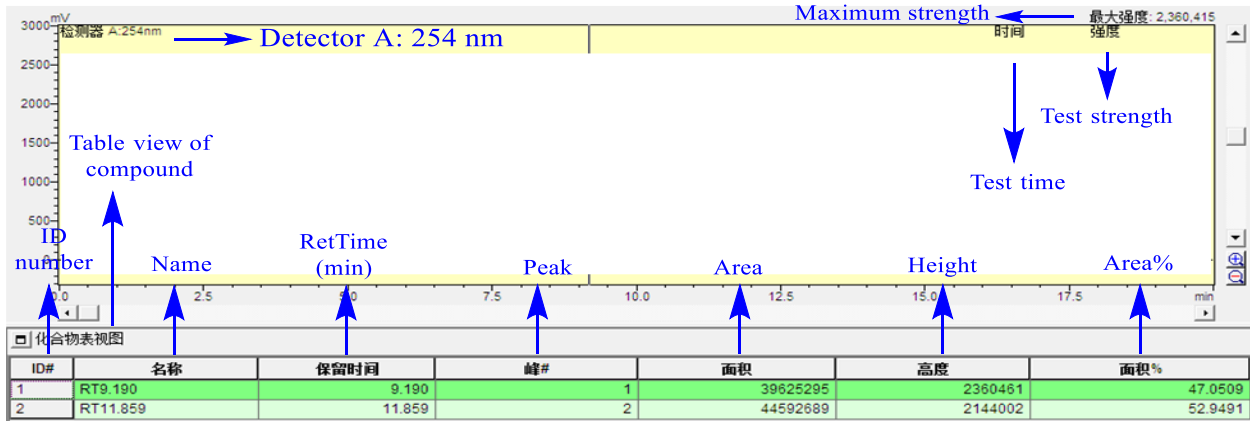
Translation of all characters (Chinese) in the above framework to English is as follows:



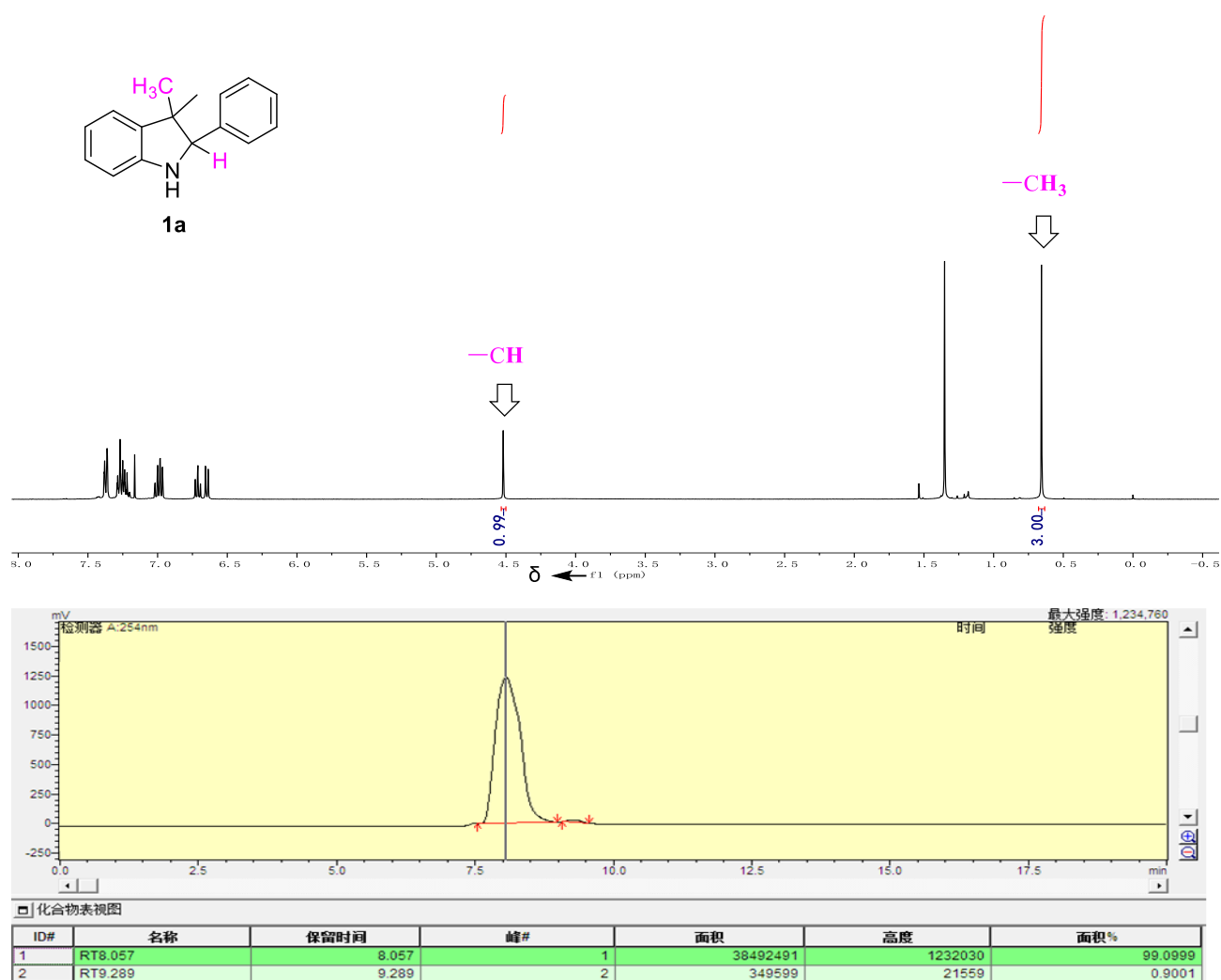
Entry 2 in Table 2 for **A** and **CPA-1** as catalysts and HTE-1 as an H-atom transfer reagent in the only aqueous β -cyclodextrin emulsion.



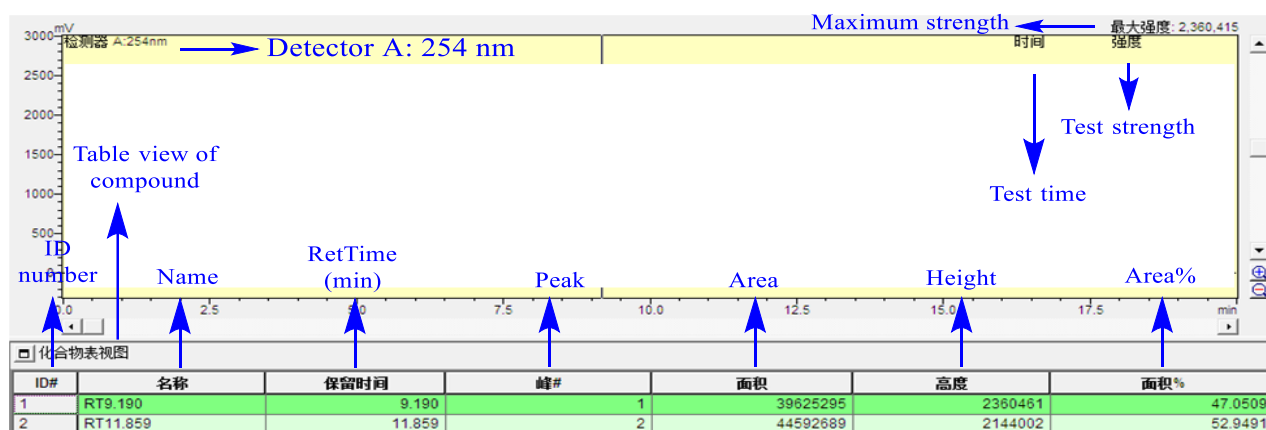
Translation of all characters (Chinese) in the above framework to English is as follows:



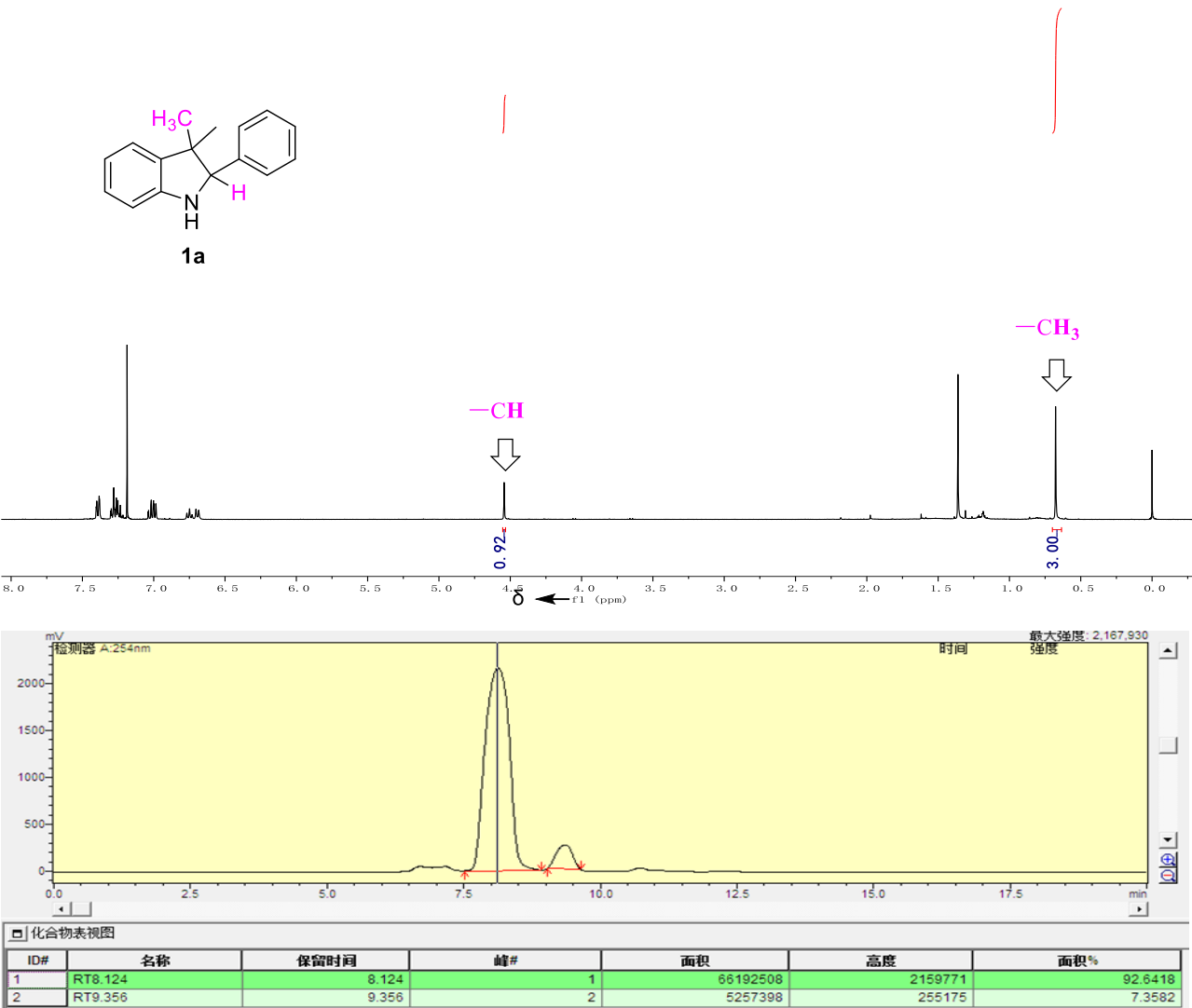
Entry 3 in Table 2 for **A** and **CPA-1** as catalysts and HTE-1 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent.



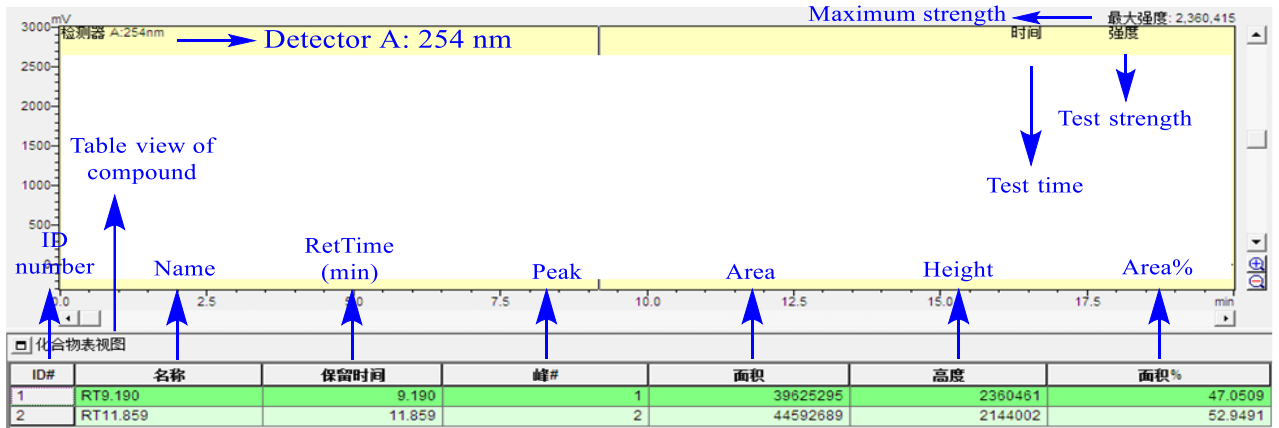
Translation of all characters (Chinese) in the above framework to English is as follows:



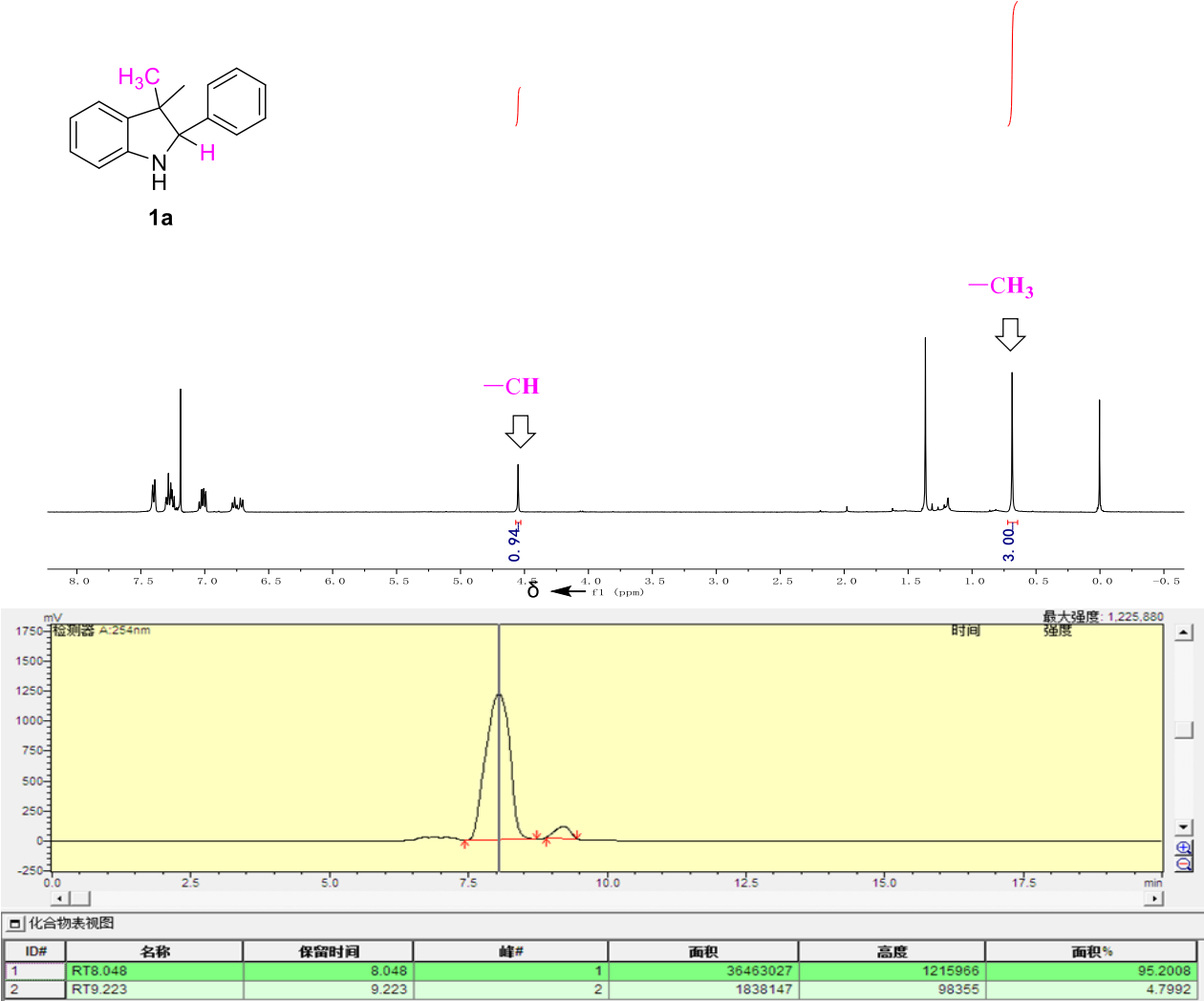
Entry 4 in Table 2 for **A** and **CPA-1** as catalysts and HTE-2 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent.



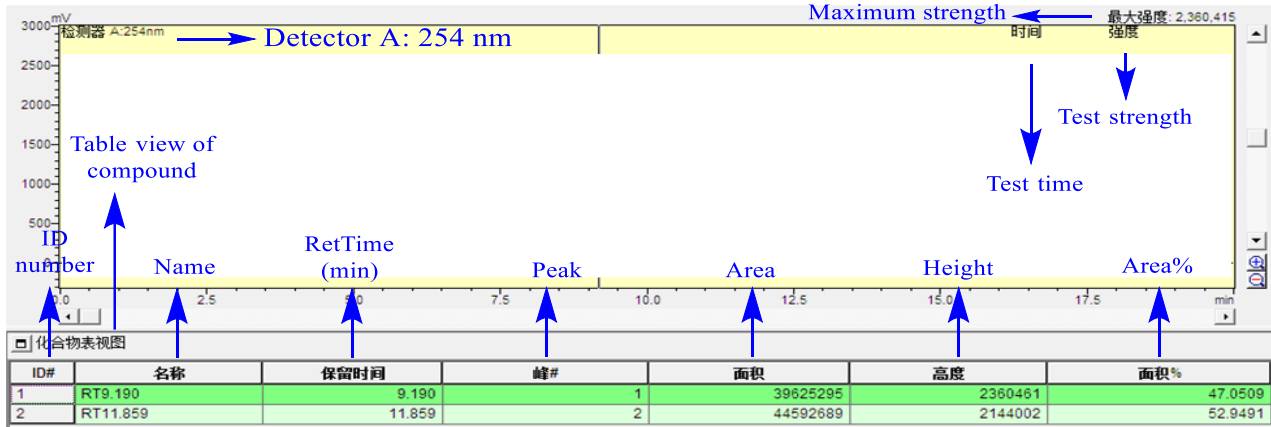
Translation of all characters (Chinese) in the above framework to English is as follows:



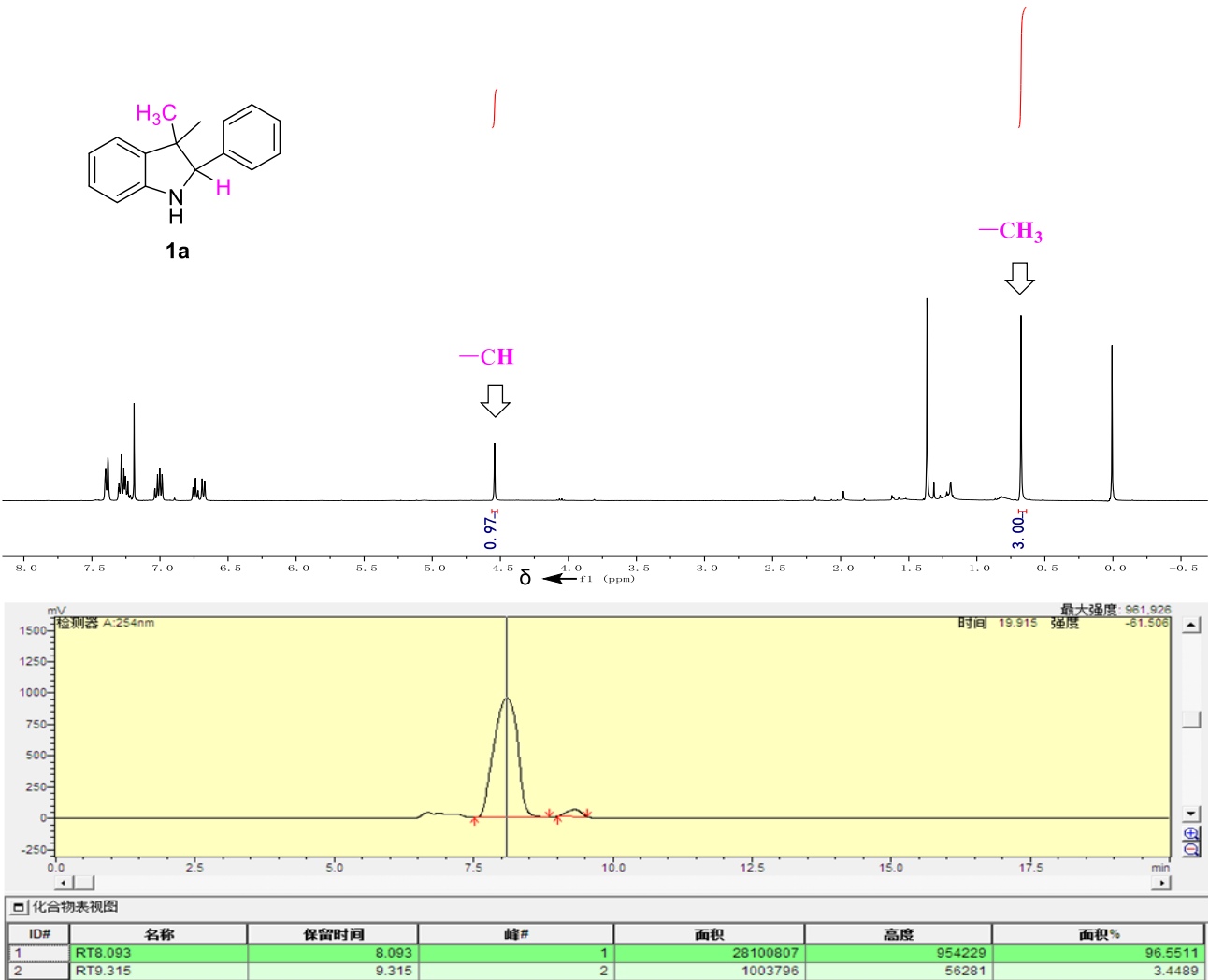
Entry 5 in Table 2 for **A** and **CPA-1** as catalysts and HTE-3 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent.



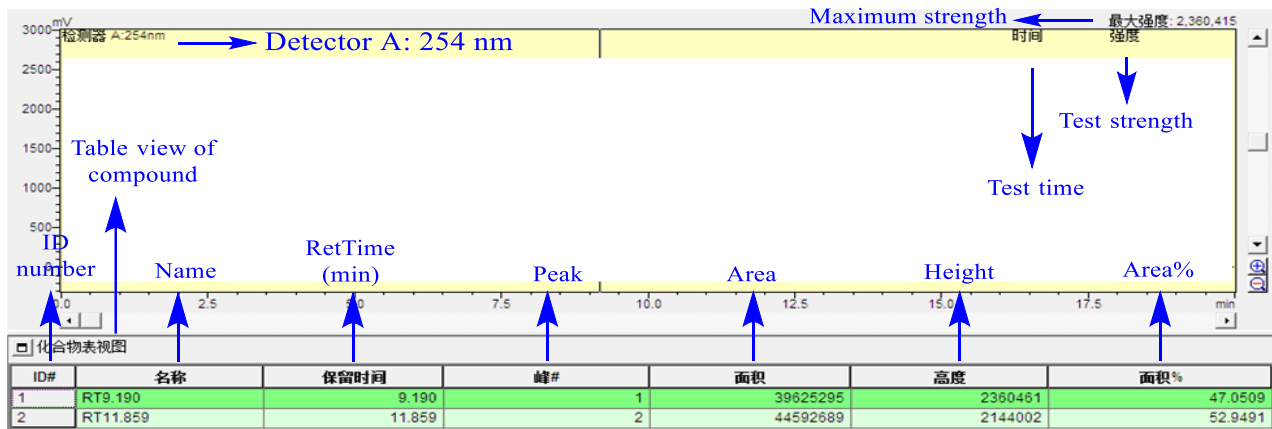
Translation of all characters (Chinese) in the above framework to English is as follows:



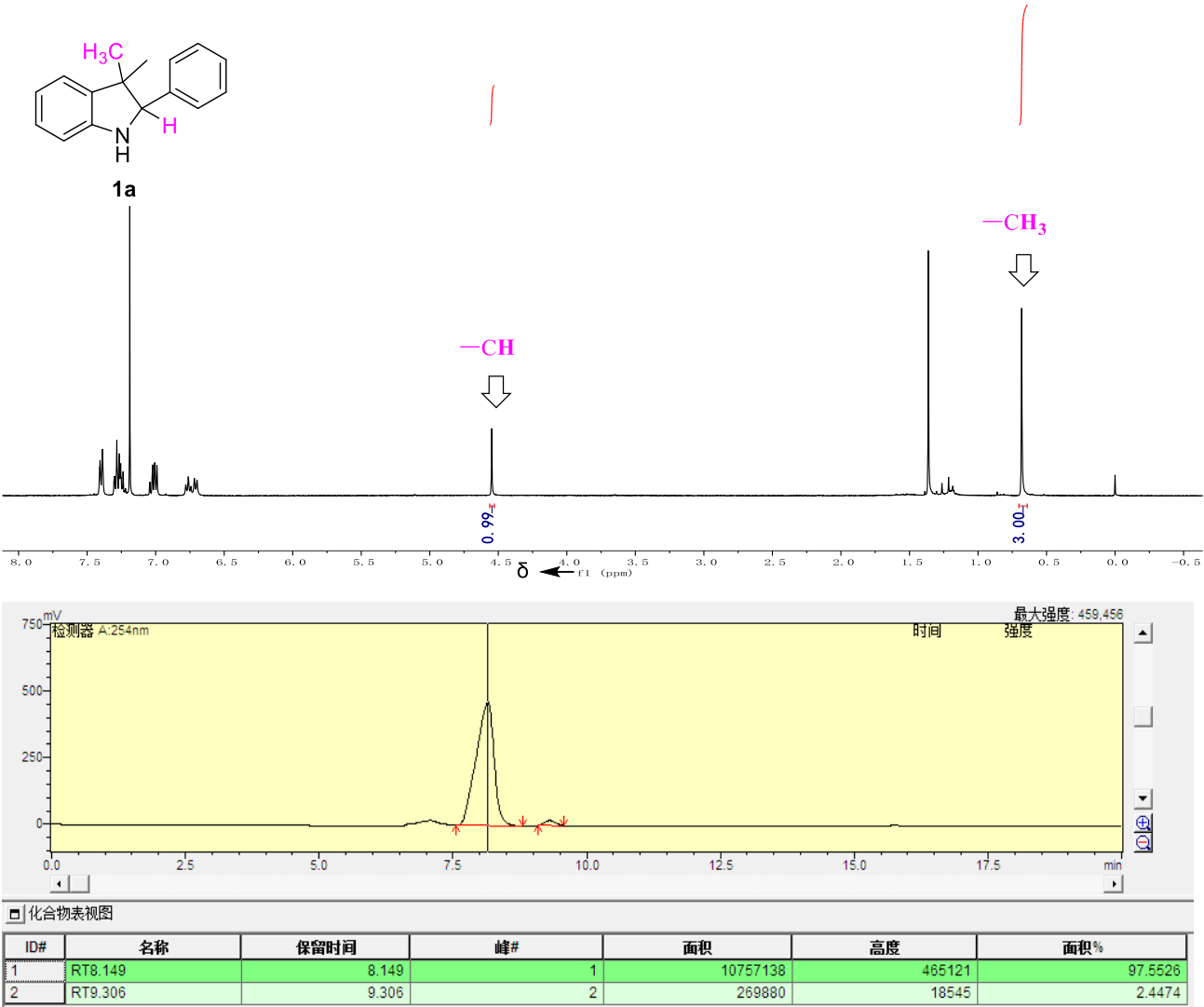
Entry 6 in Table 2 for **A** and **CPA-1** as catalysts and HTE-4 as a H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent.



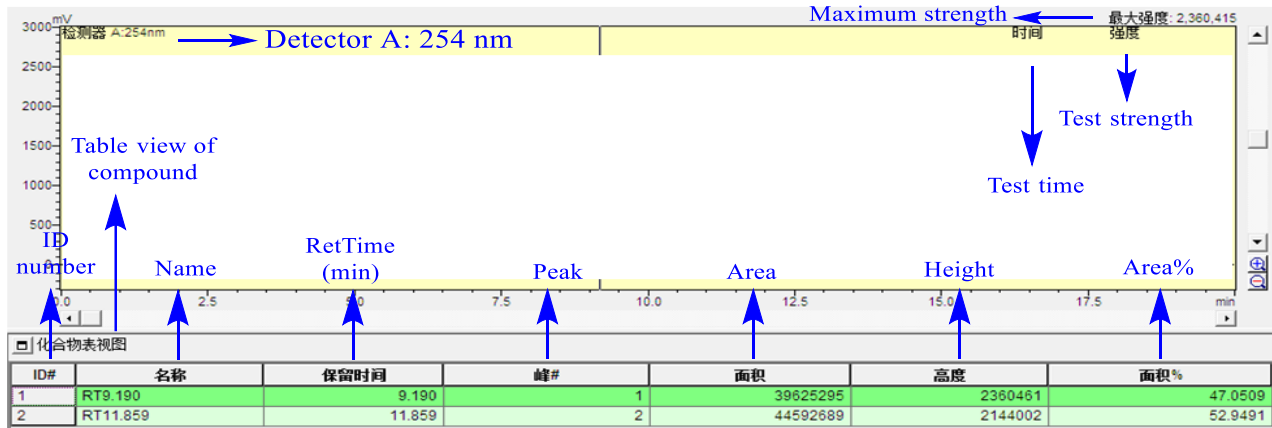
Translation of all characters (Chinese) in the above framework to English is as follows:



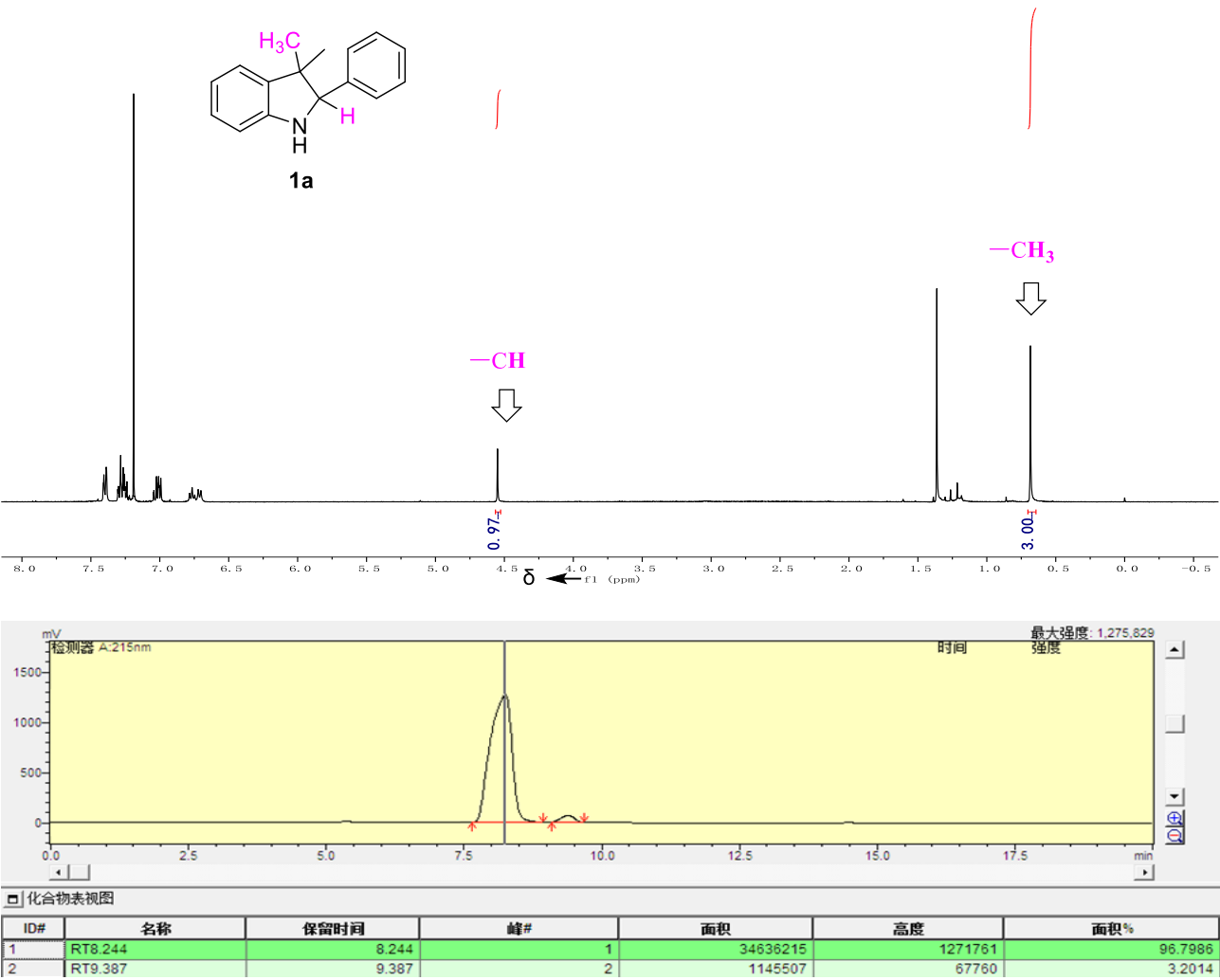
Entry 7 in Table 2 for **A** and **CPA-1** as catalysts and HTE-1 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 3/2) cosolvent.



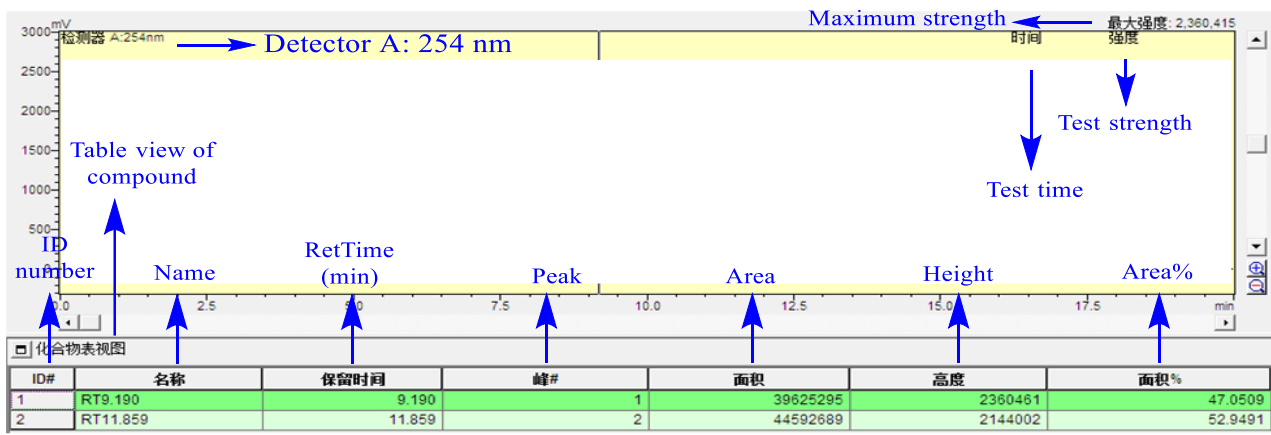
Translation of all characters (Chinese) in the above framework to English is as follows:



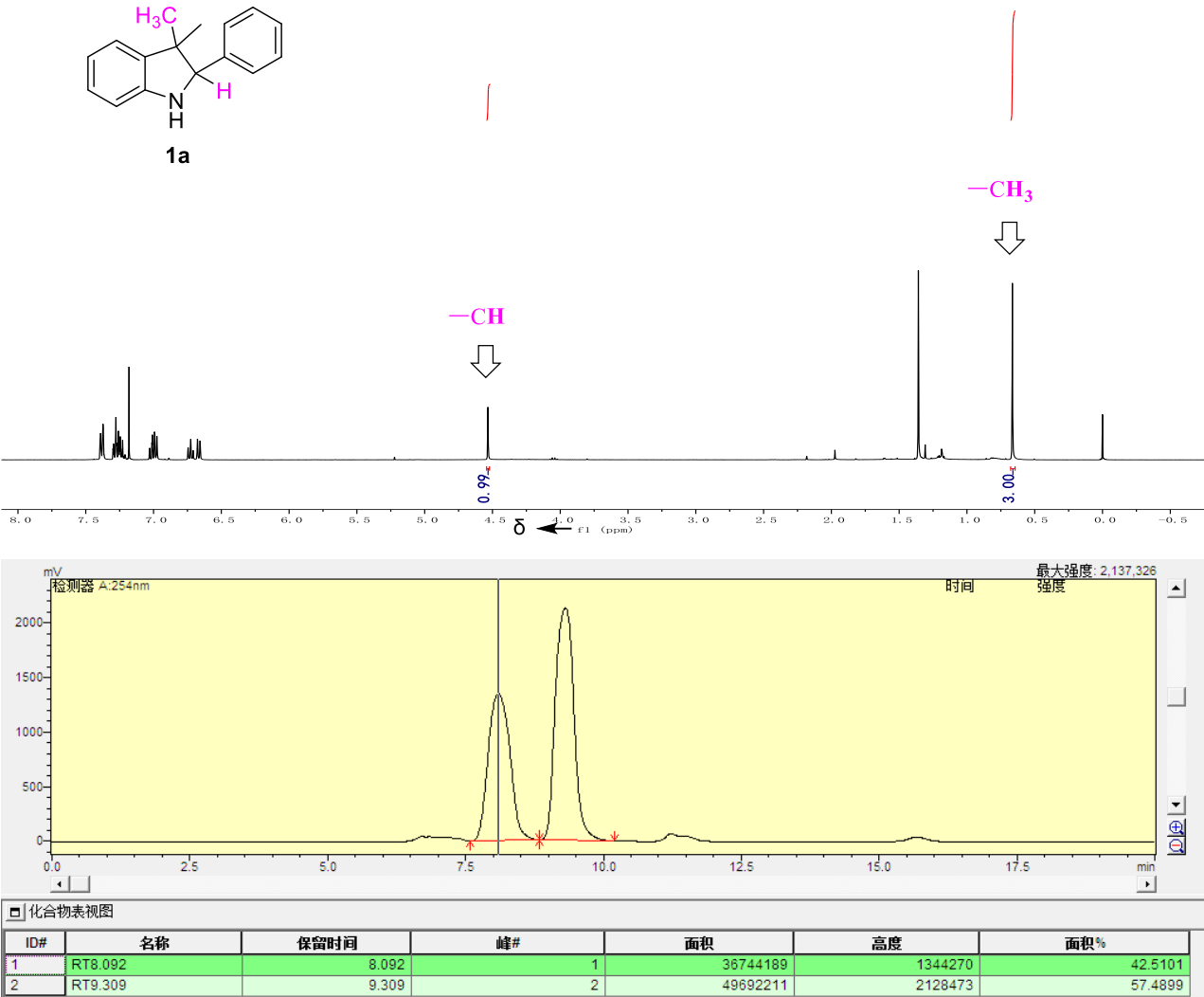
Entry 8 in Table 2 for **A** and **CPA-1** as catalysts and HTE-1 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 2/3) cosolvent.



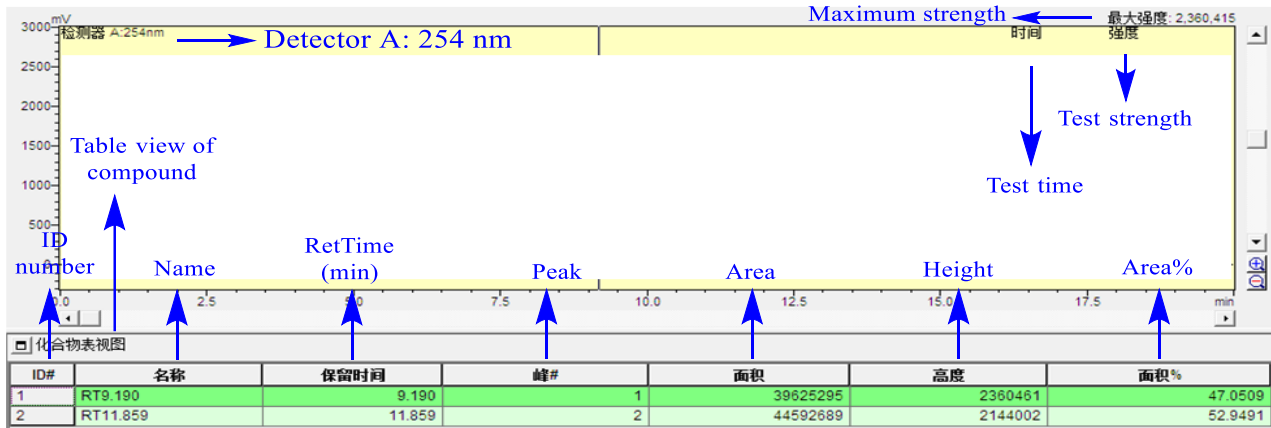
Translation of all characters (Chinese) in the above framework to English is as follows:



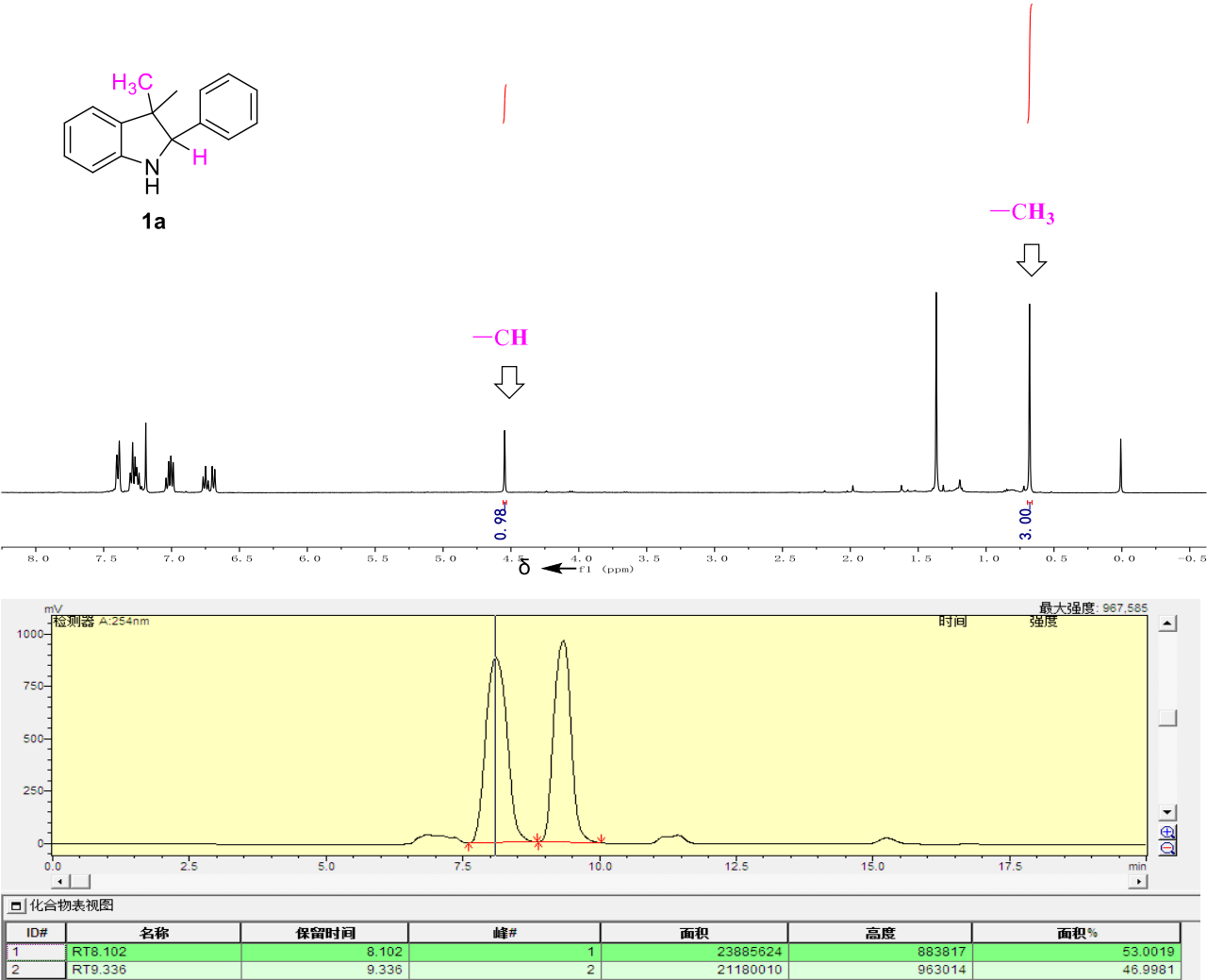
Entry 9 in Table 2 for **A** and **CPA-2** as catalysts and HTE-1 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent.



Translation of all characters (Chinese) in the above framework to English is as follows:



Entry 10 in Table 2 for **A** and **CPA-3** as catalysts and HTE-1 as an H-atom transfer reagent in the toluene/aqueous β -cyclodextrin emulsion (v/v = 1/1) cosolvent



Translation of all characters (Chinese) in the above framework to English is as follows:

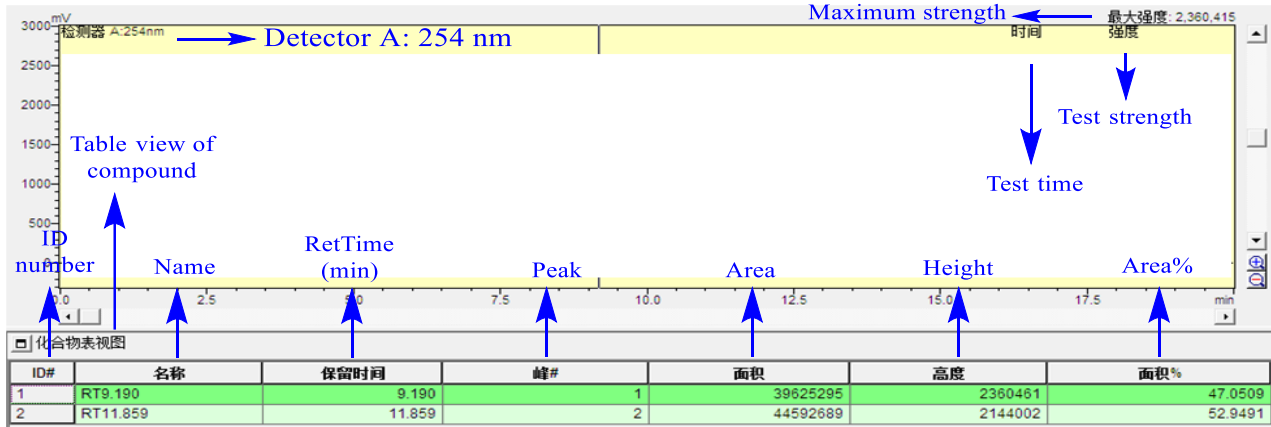


Figure S2. GC analysis of H₂ in the single-step oxidations of *rac*-**1a** in toluene.

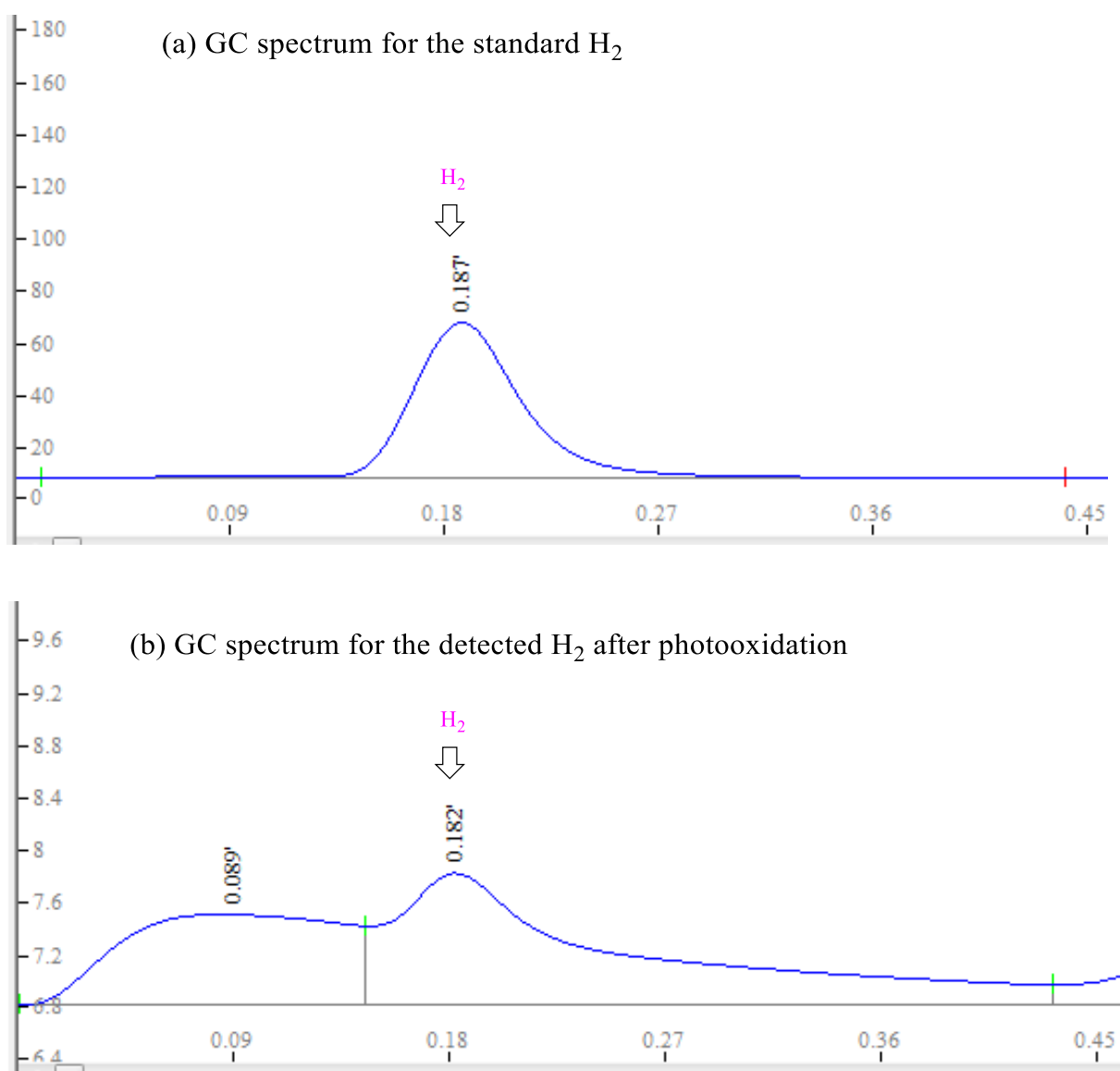


Figure S3. ^1H -NMR spectra of **2a**, CPA-1, and **2a**+CPA (mole ratio = 1:1) in CDCl_3 .

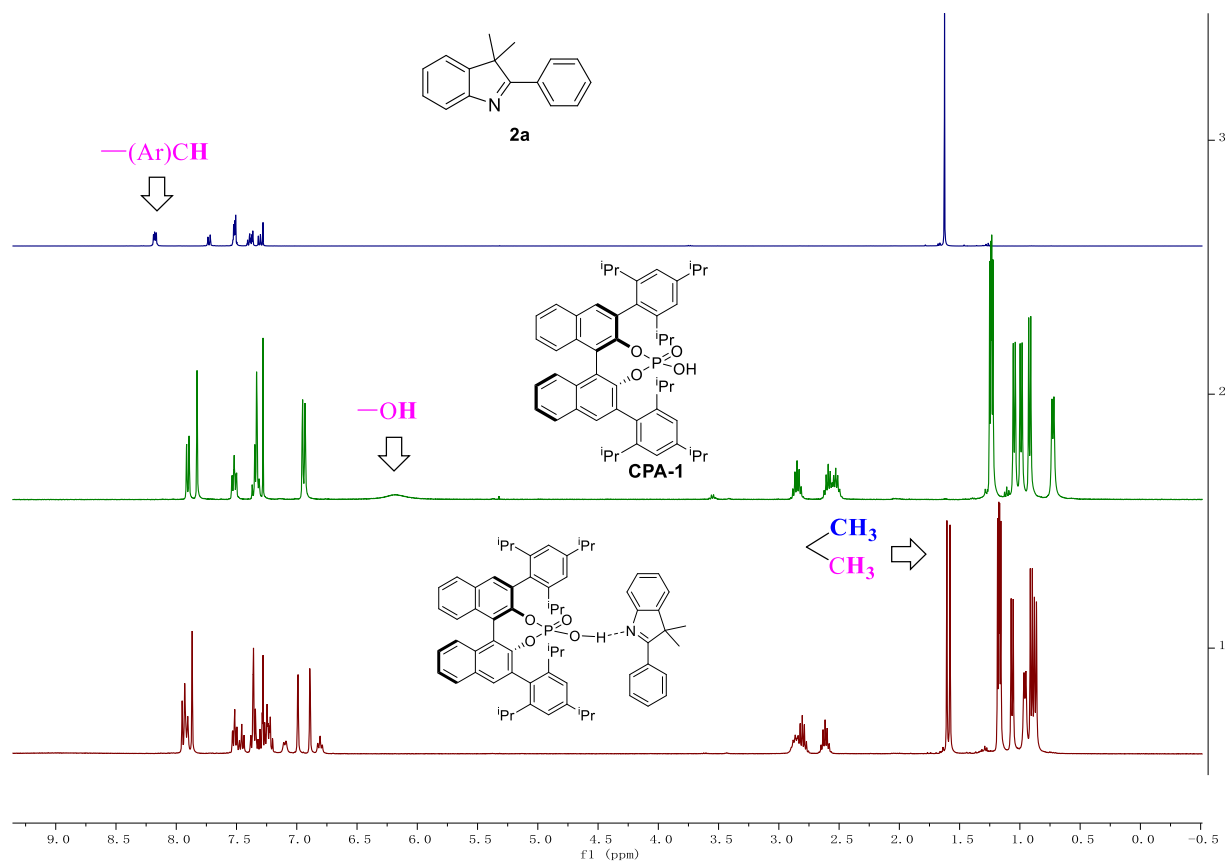
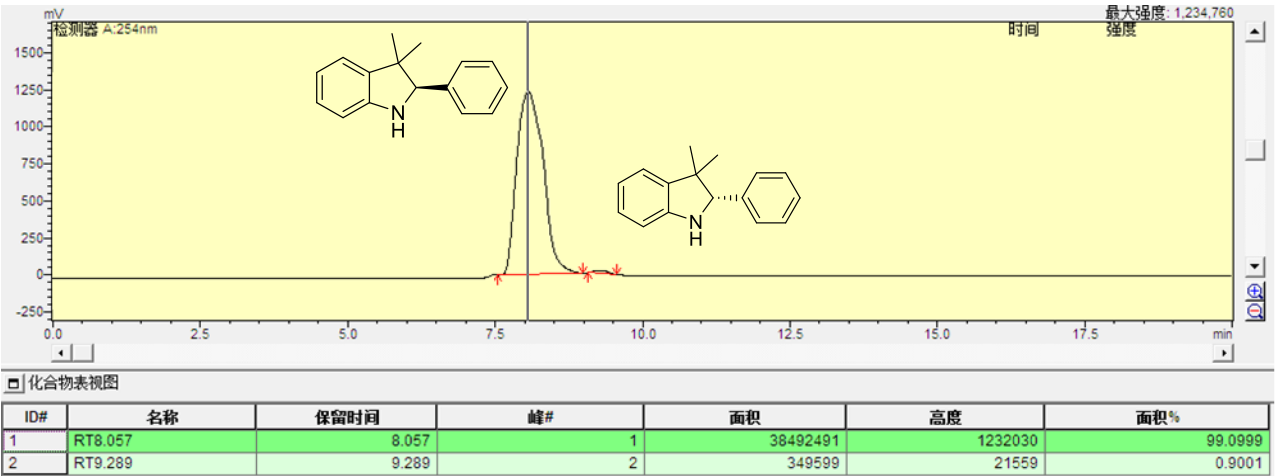
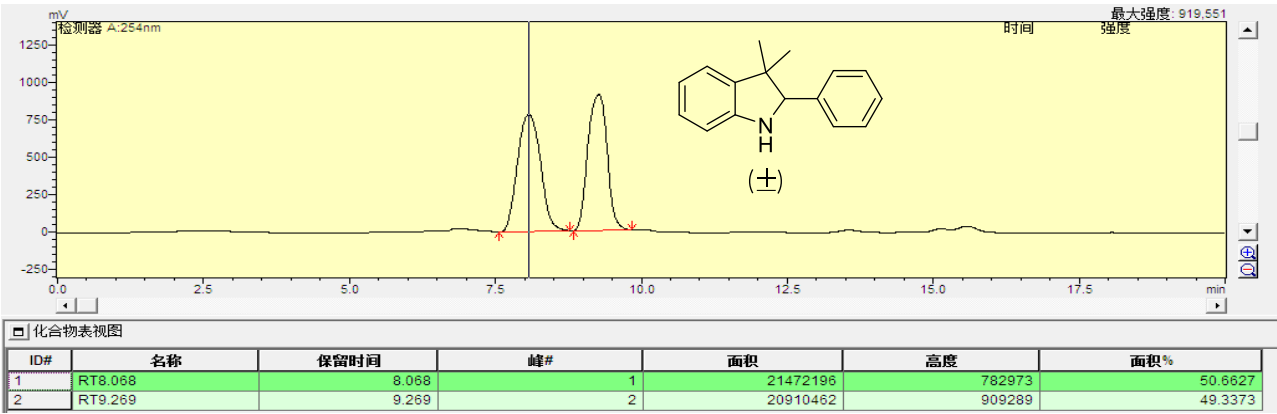
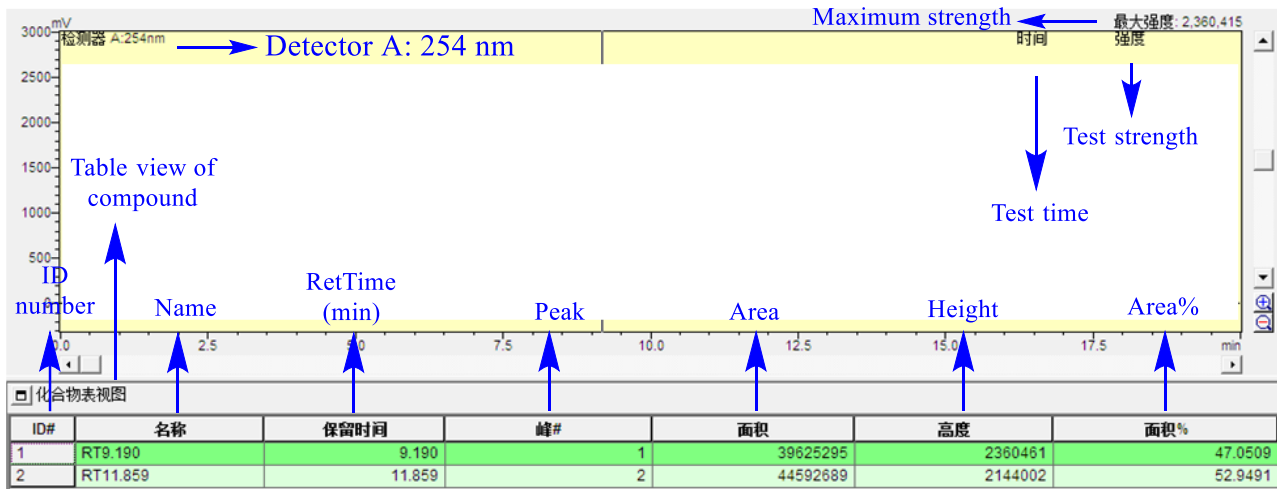


Figure S4. HPLC analyses for chiral products.

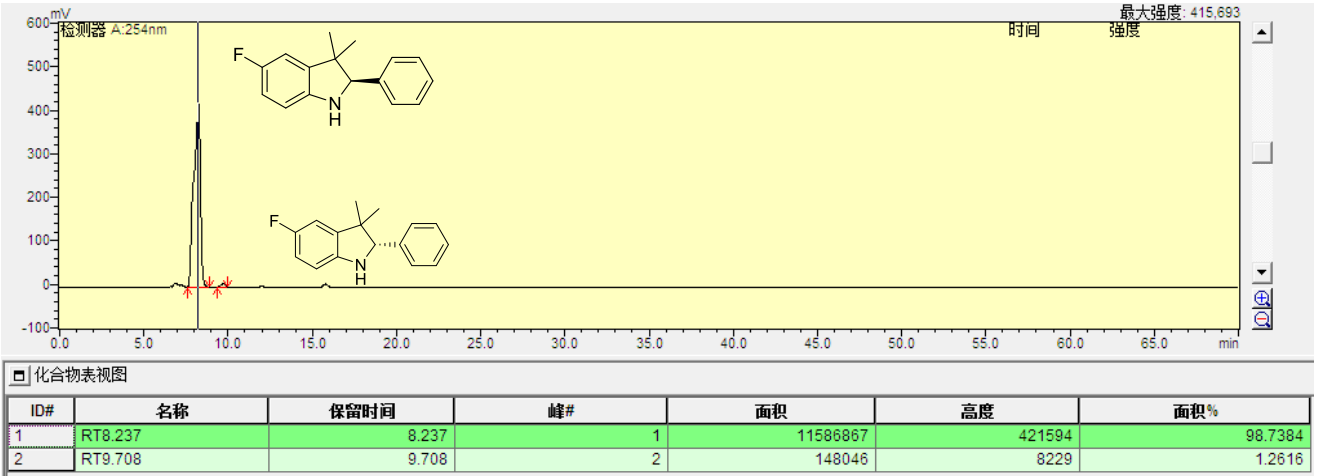
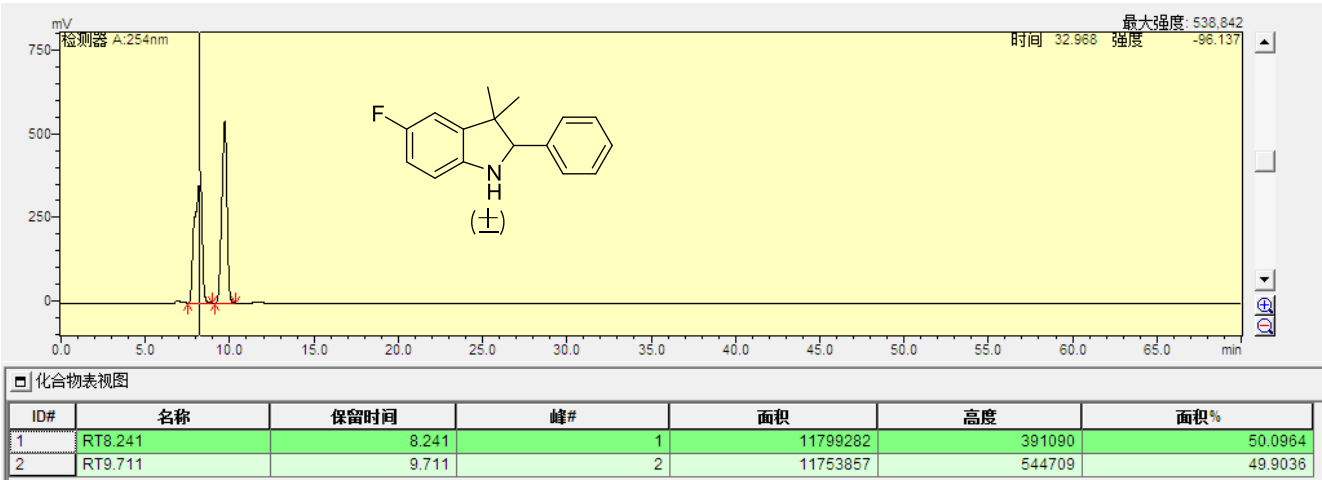
(R)-1a: (R)-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



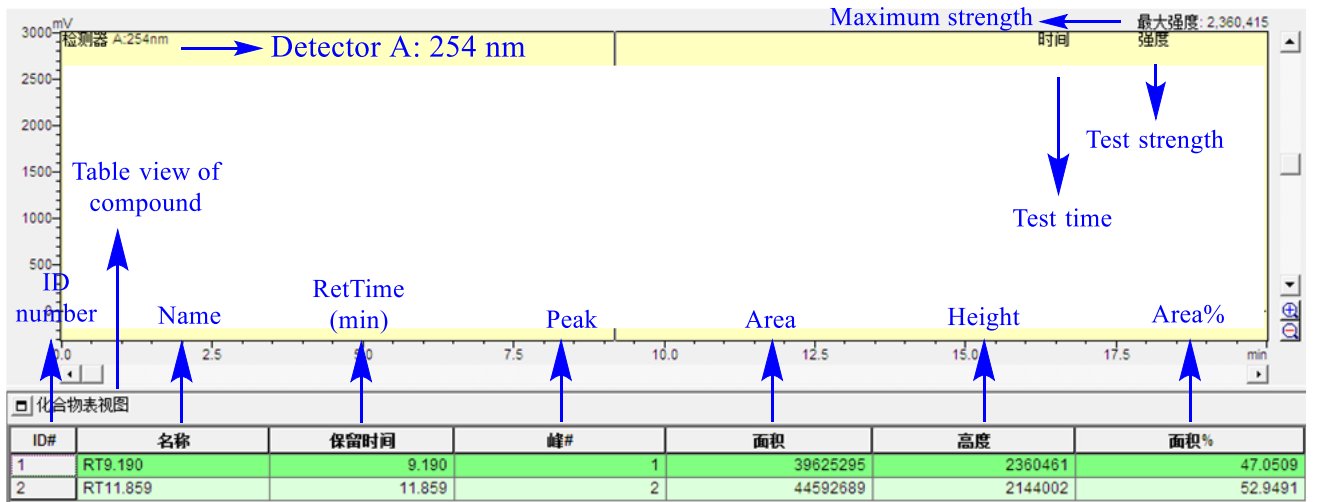
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



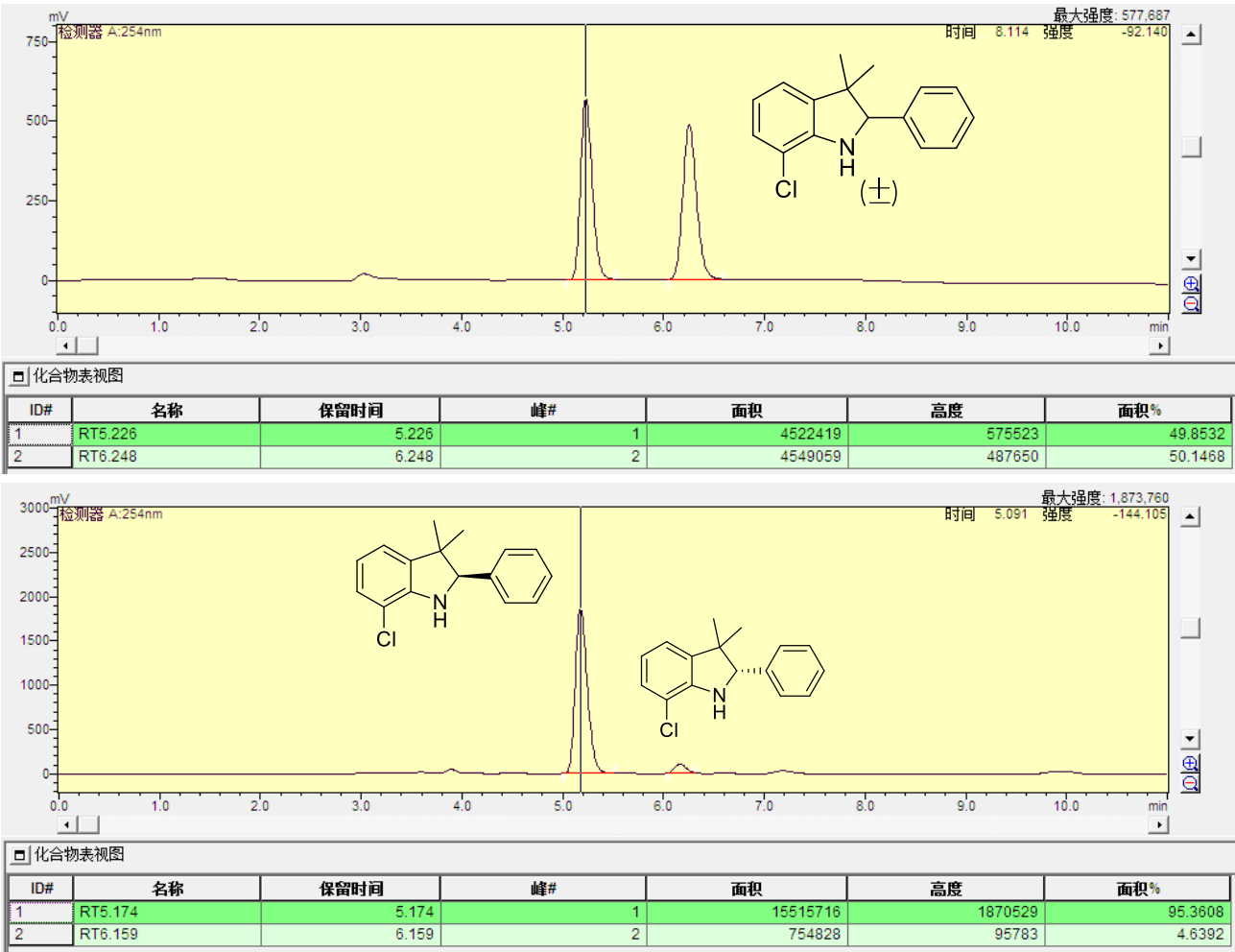
(R)-1b: (R)- 5-fluoro-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 1.0mL/min, 25 °C).



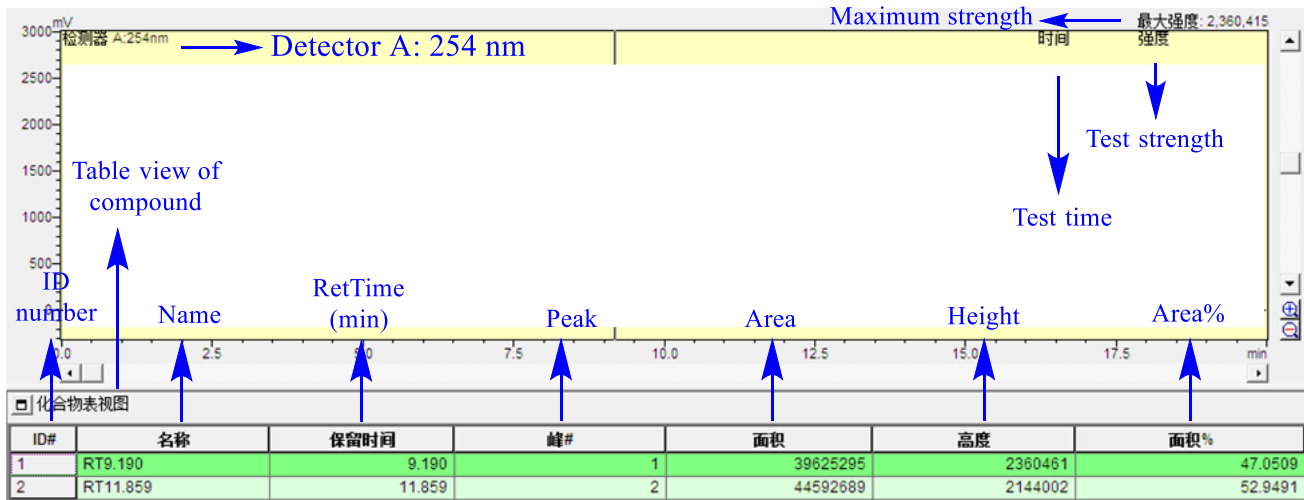
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



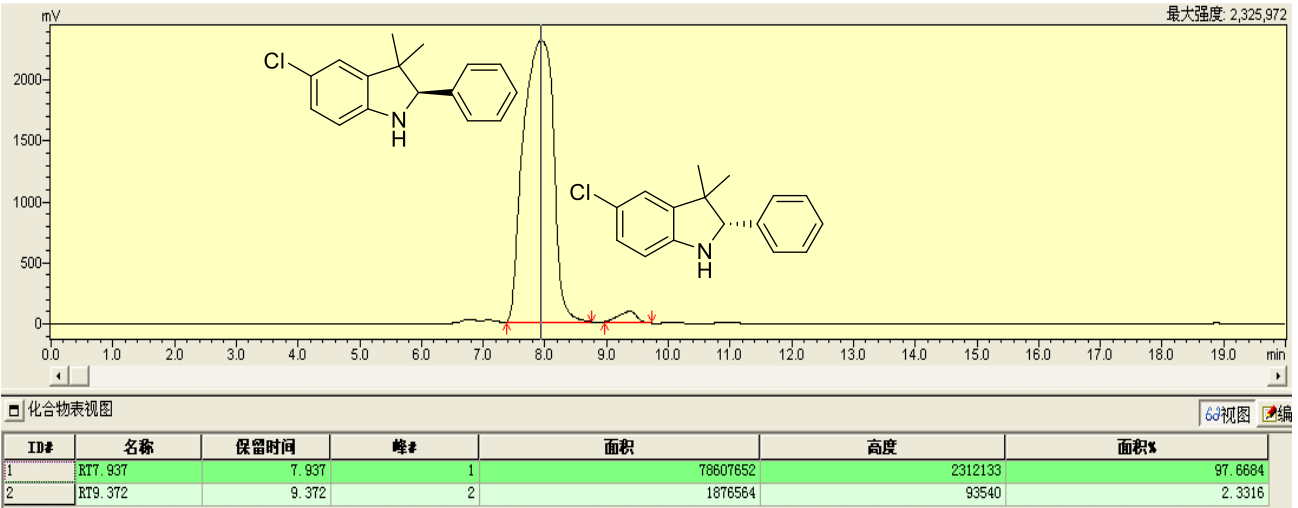
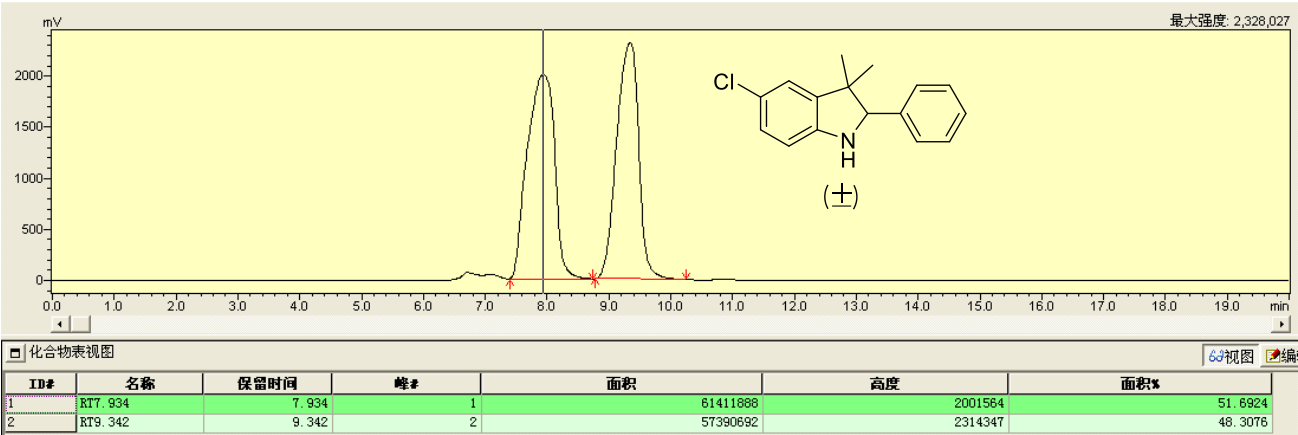
(R)-1c: (R)-4-chloro-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



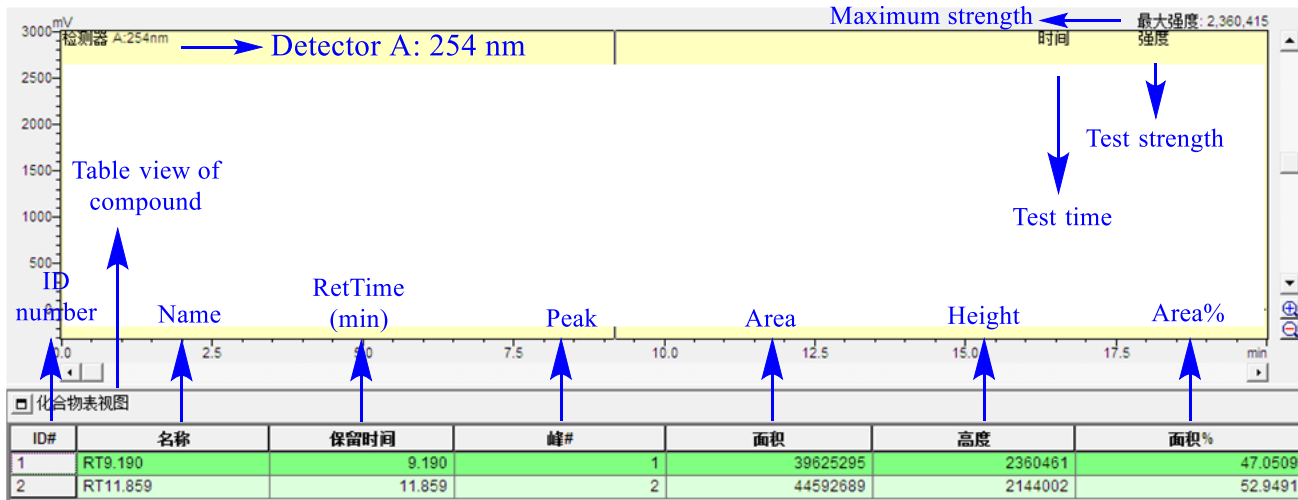
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



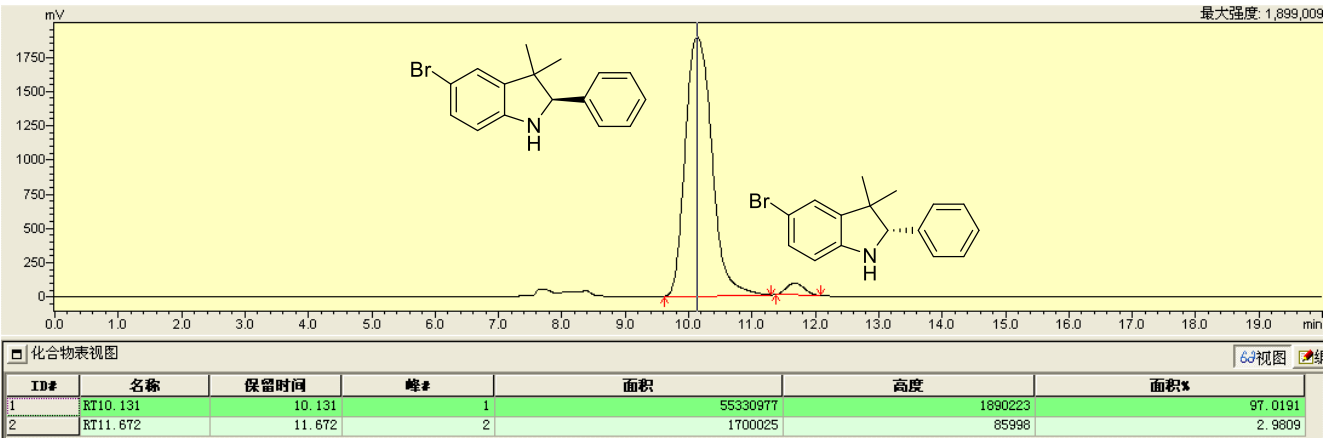
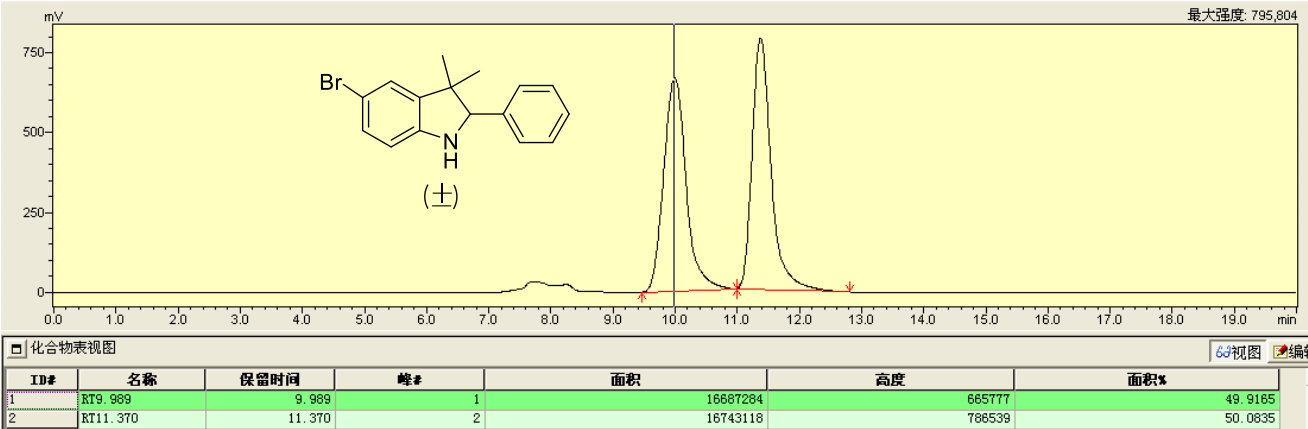
(R)-1d: (R)-5-chloro-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



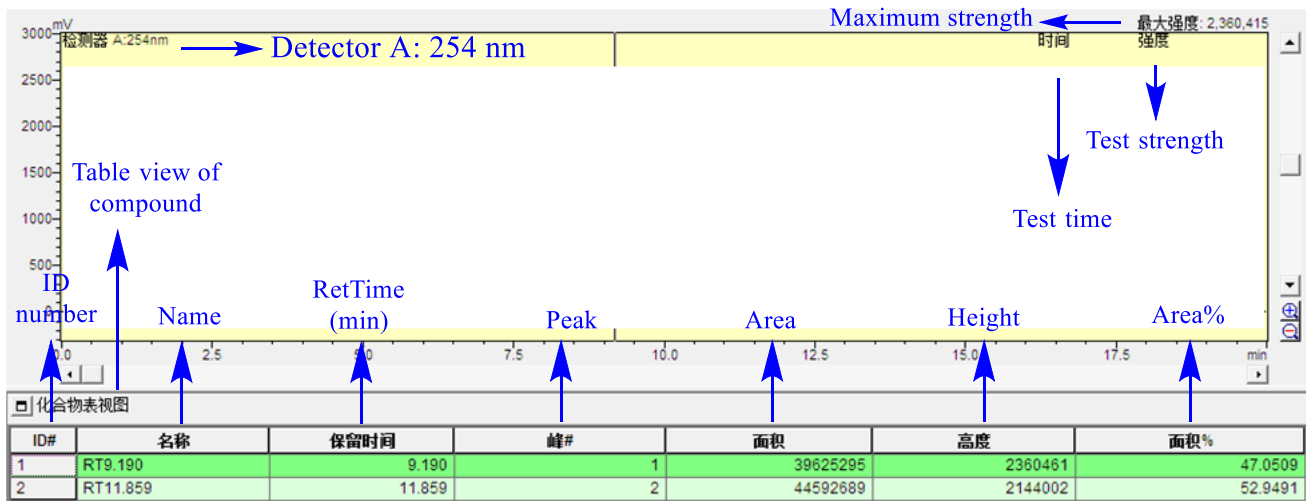
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



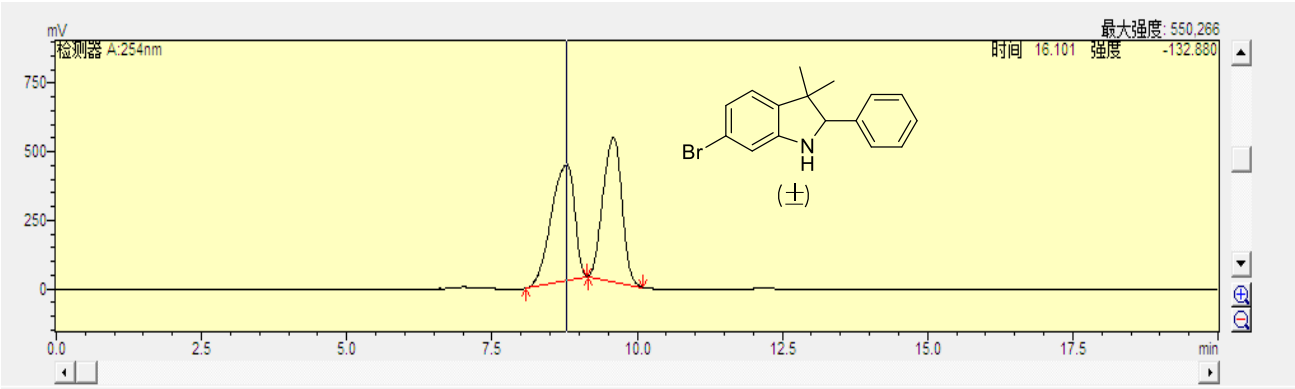
(R)-1e: (R)-5-bromo-3,3-dimethyl-2-phenylindoline : (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



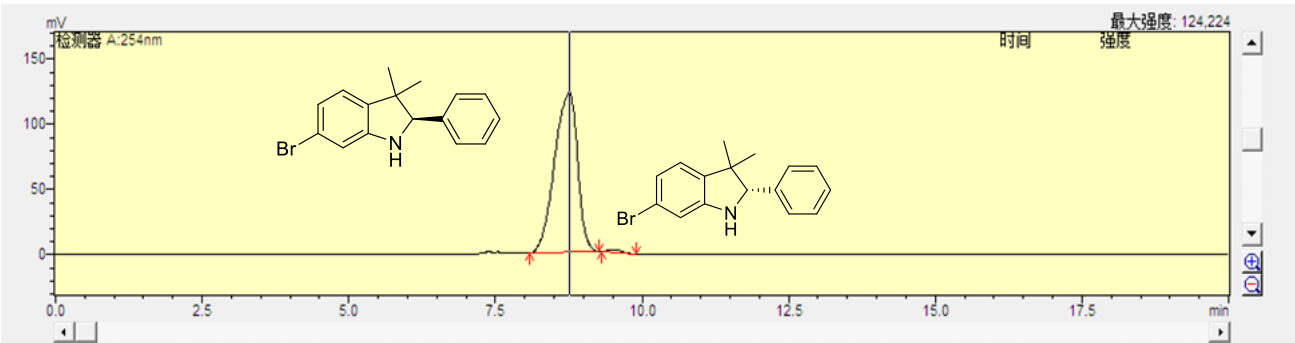
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(R)-1f: (R)-6-bromo-3,3-dimethyl-2-phenylindoline : (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).

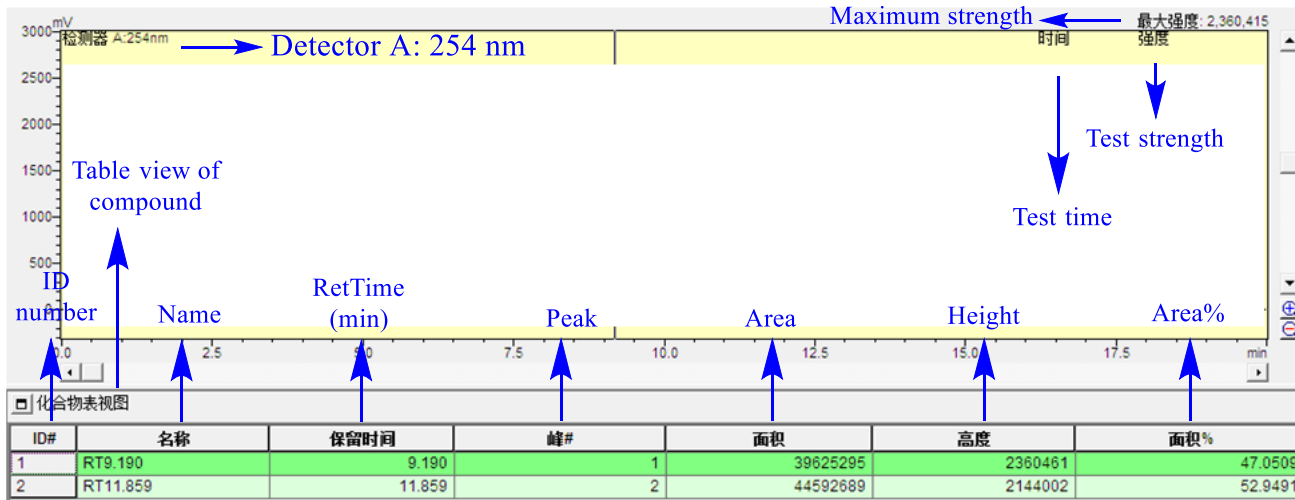


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.784	8.784	1	11798880	422225	49.8946
2	RT9.590	9.590	2	11848737	522376	50.1054



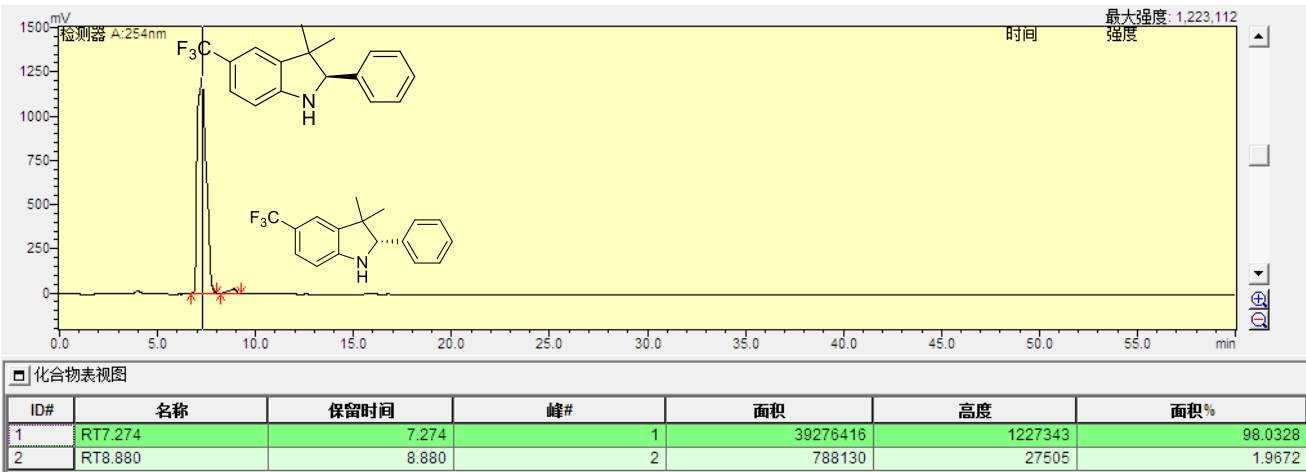
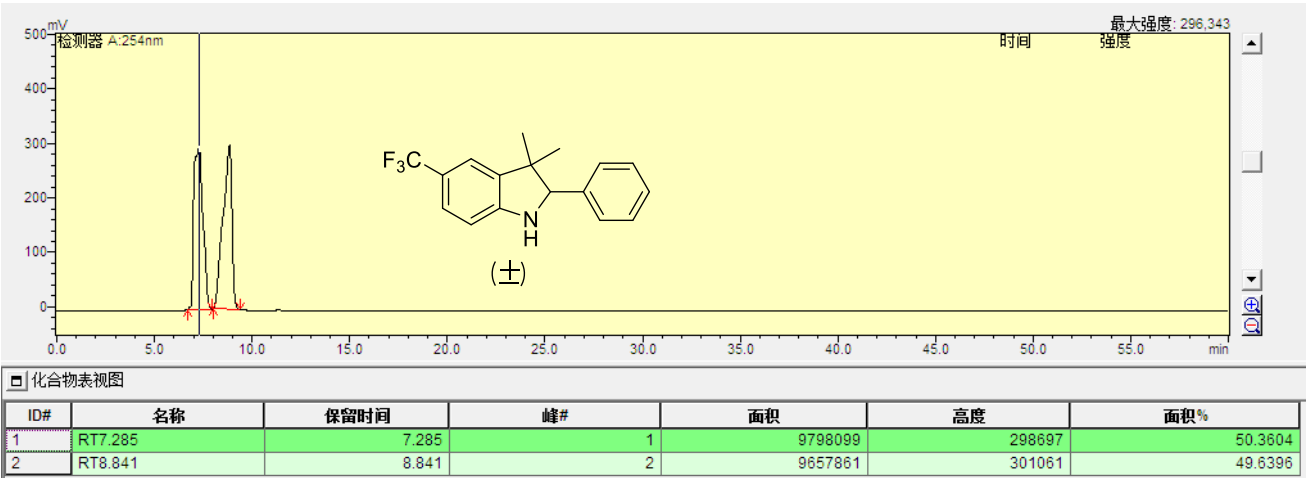
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.757	8.757	1	3348219	122292	98.9519
2	RT9.520	9.520	2	35466	2061	1.0481

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

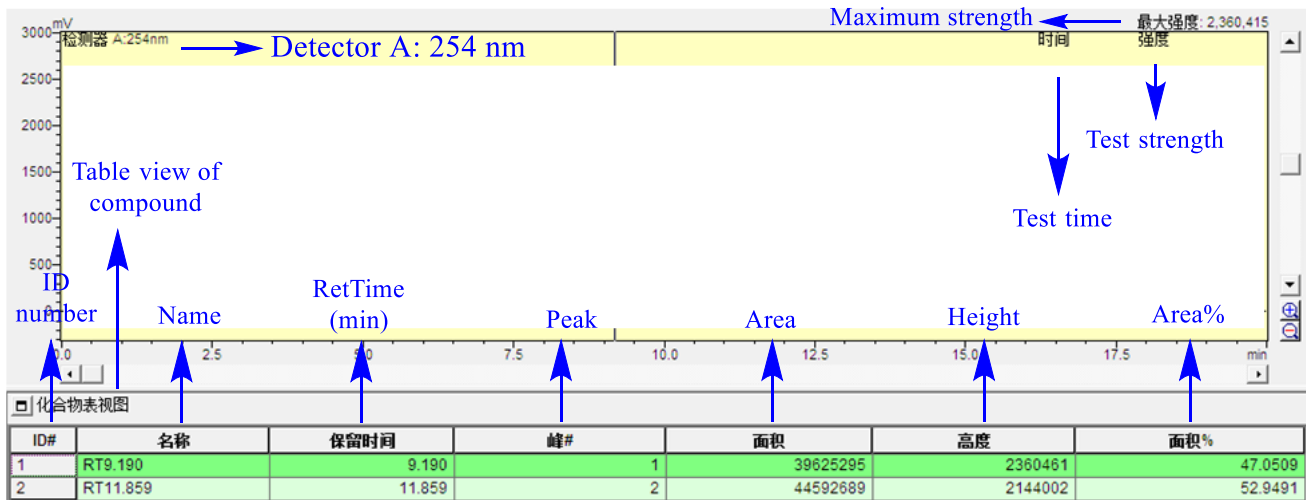


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.190	9.190	1	39625295	2360461	47.0509
2	RT11.859	11.859	2	44592689	2144002	52.9491

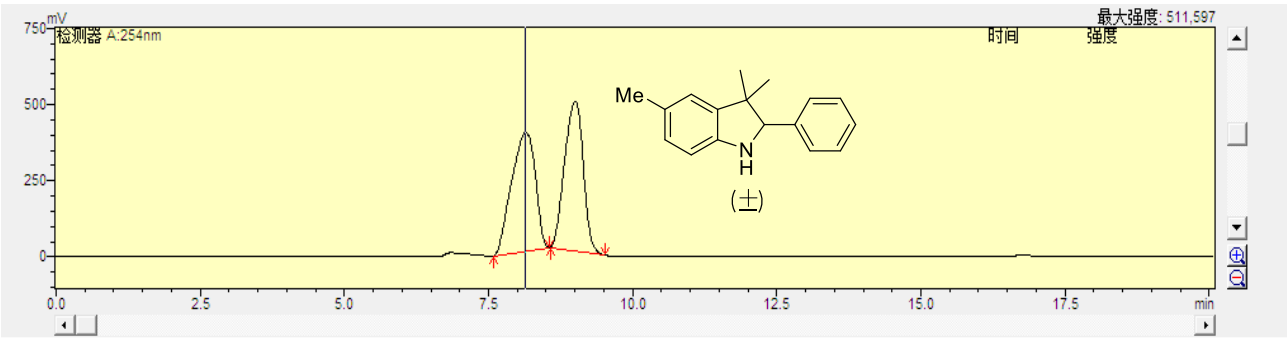
(R)-1g: (R)-3,3-dimethyl-2-phenyl-5-(trifluoromethyl)indoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



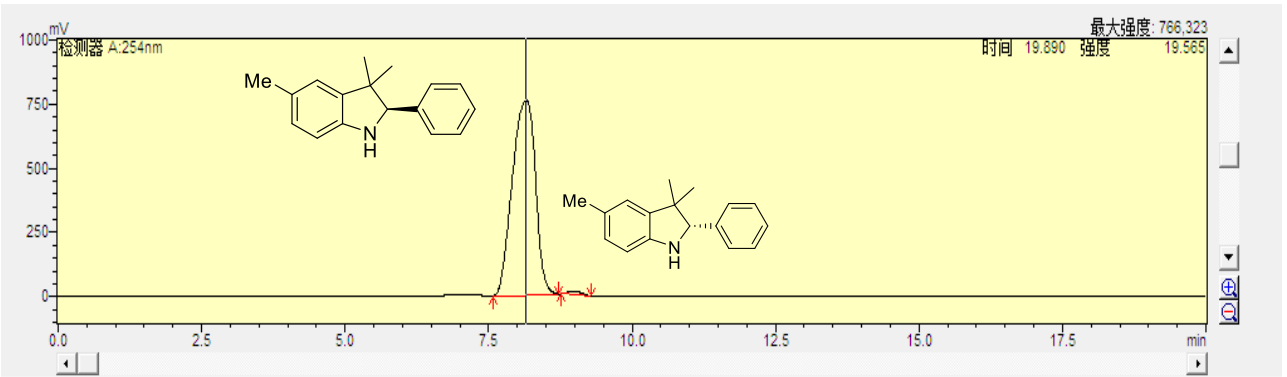
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(R)-1h: (R)-3,3,5-trimethyl-2-phenylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).

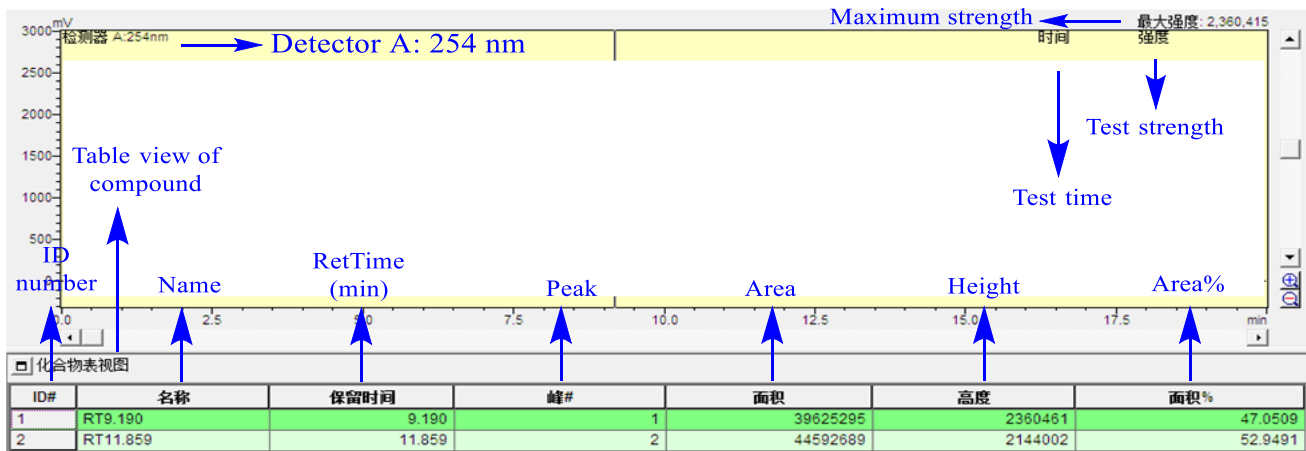


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.142	8.142	1	11169657	390352	50.1560
2	RT9.004	9.004	2	11100162	492300	49.8440



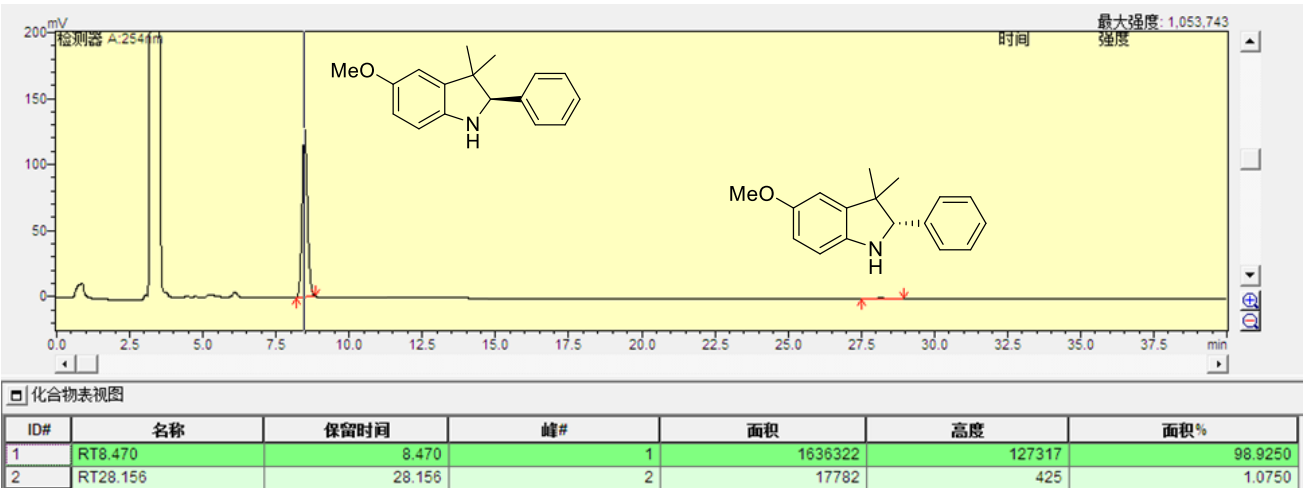
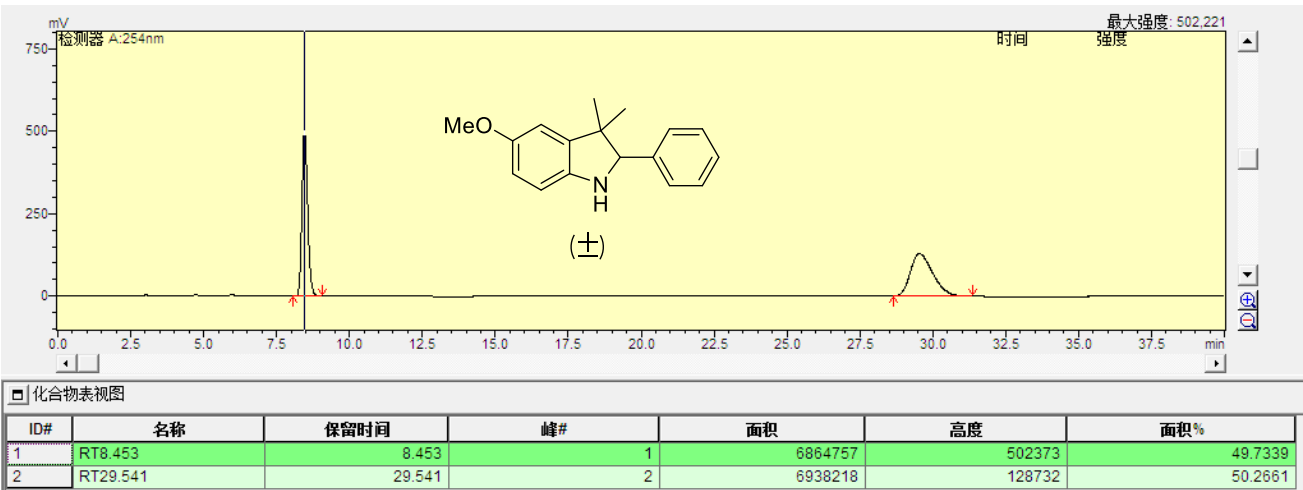
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.151	8.151	1	21319263	759381	98.8550
2	RT8.990	8.990	2	246935	15113	1.1450

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

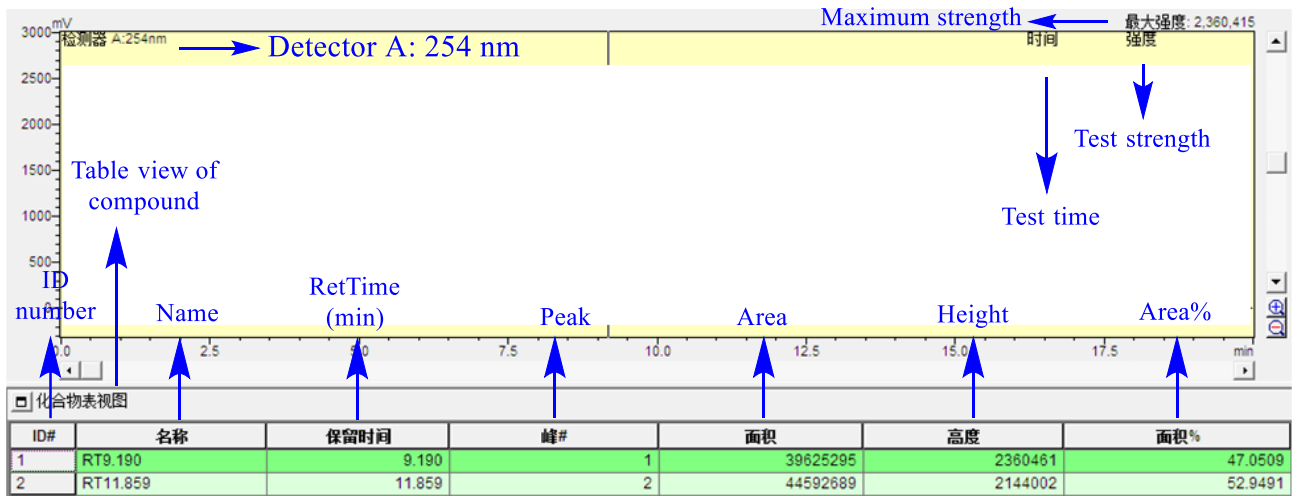


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.190	9.190	1	39625295	2360461	47.0509
2	RT11.859	11.859	2	44592689	2144002	52.9491

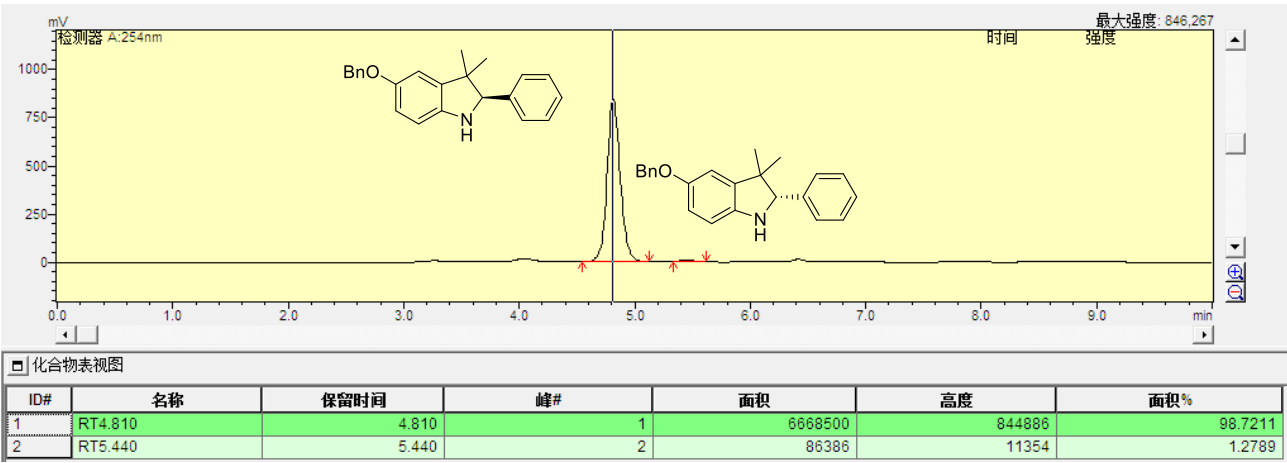
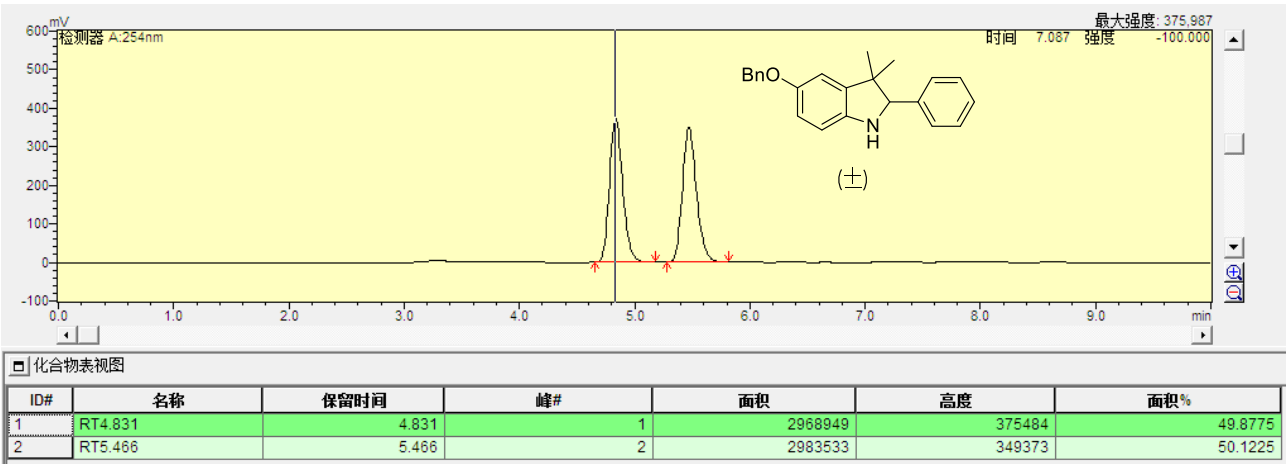
(R)-1i: (R)- 5-methoxy-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



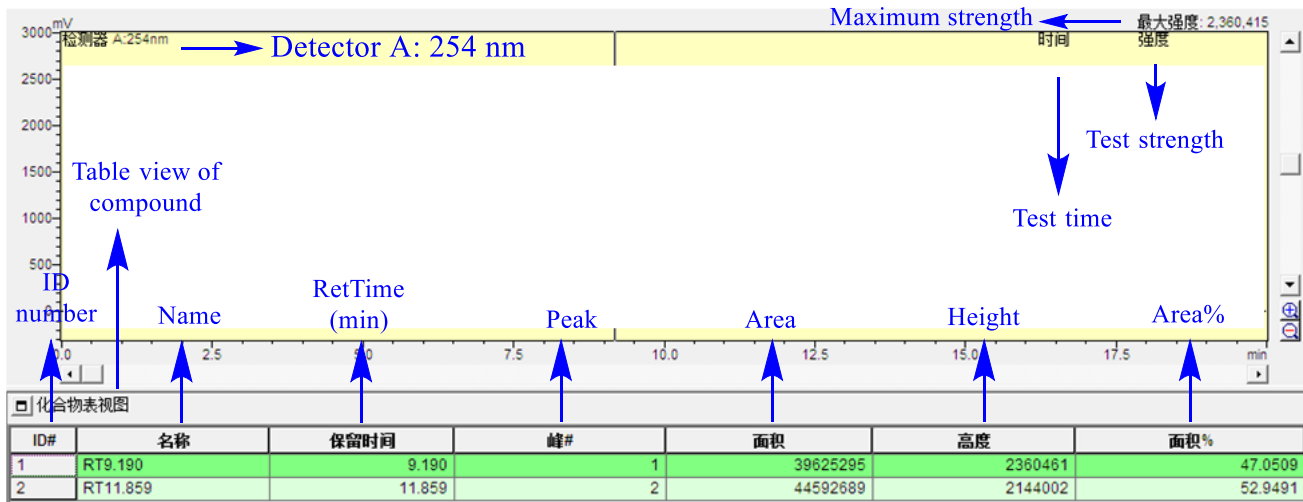
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



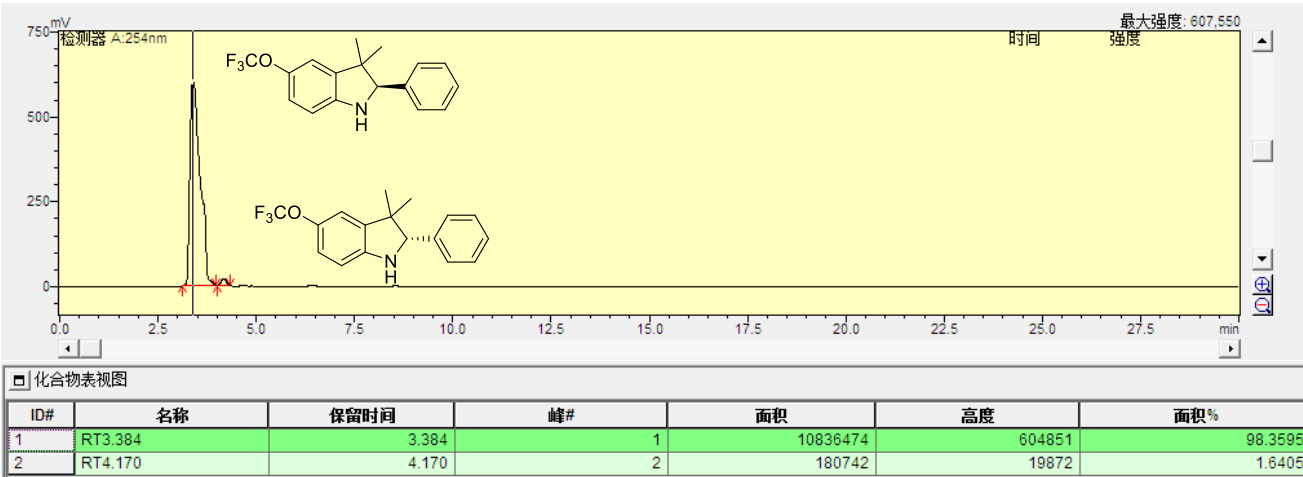
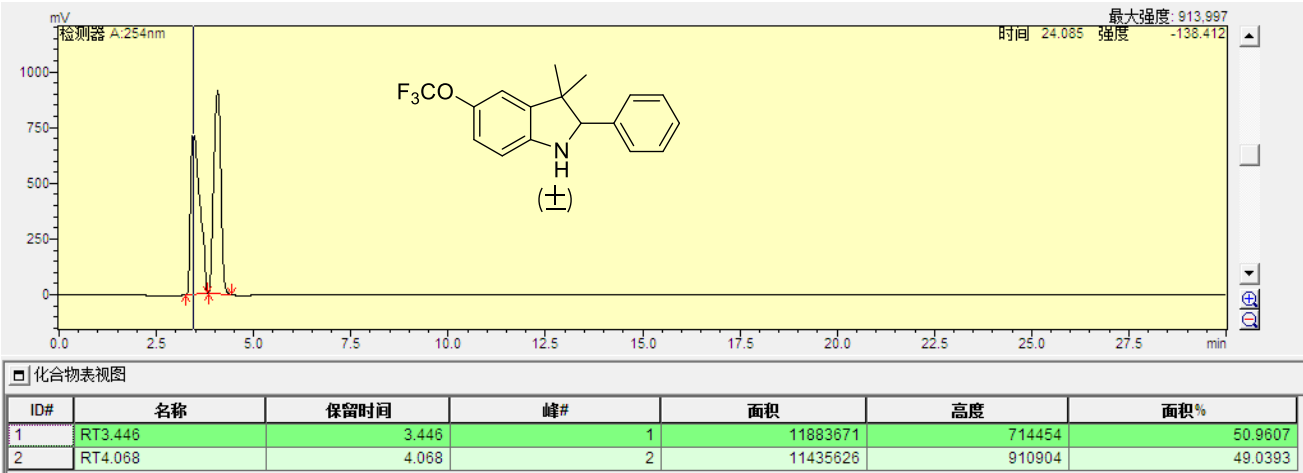
(R)-1j: (R)- 5-(benzyloxy)-3,3-dimethyl-2-phenylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



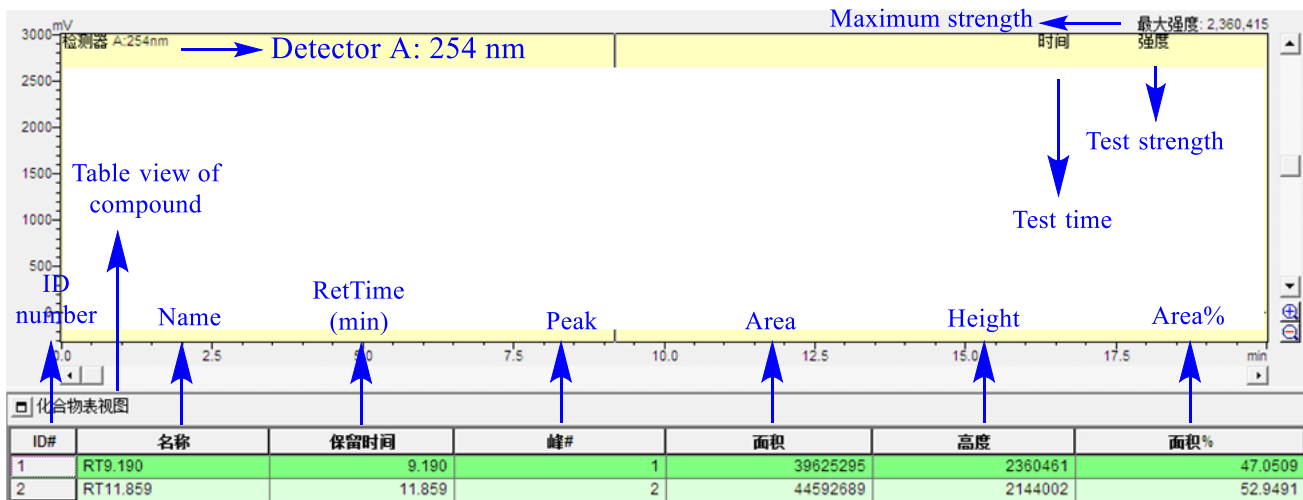
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



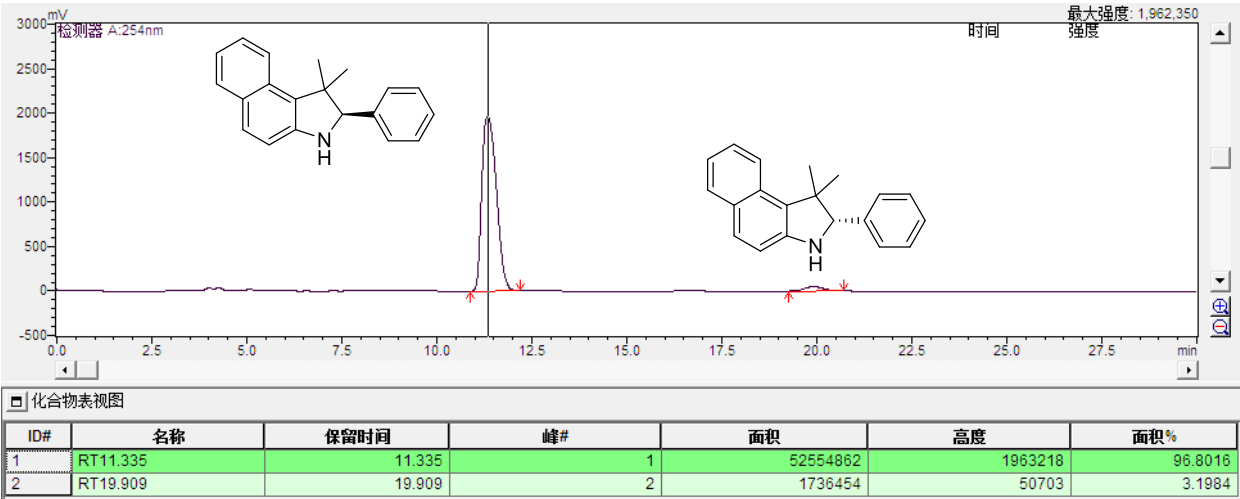
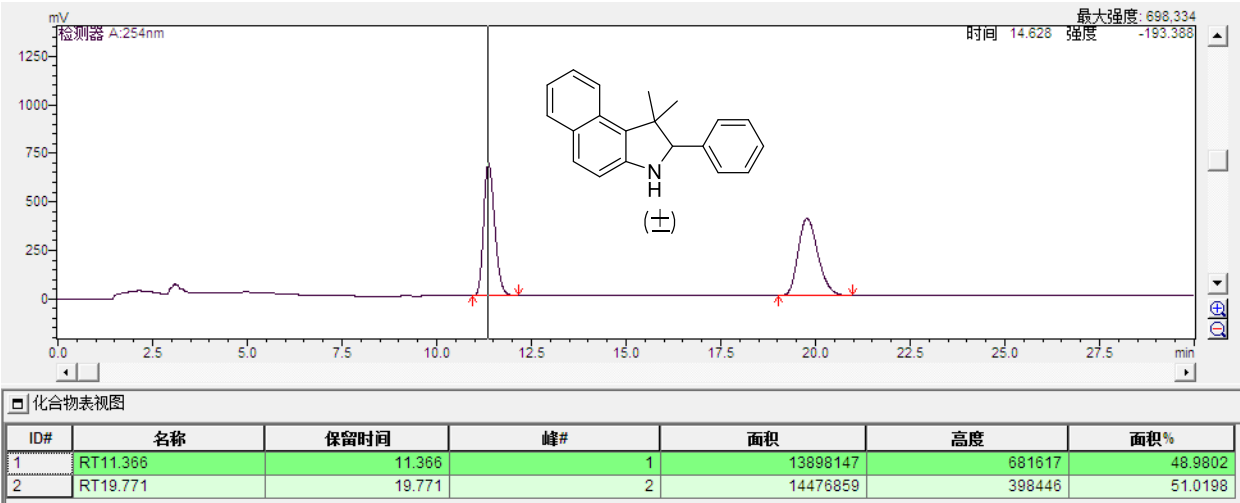
(R)-1k: (R)- 3,3-dimethyl-2-phenyl-5-(trifluoromethoxy)indoline : (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



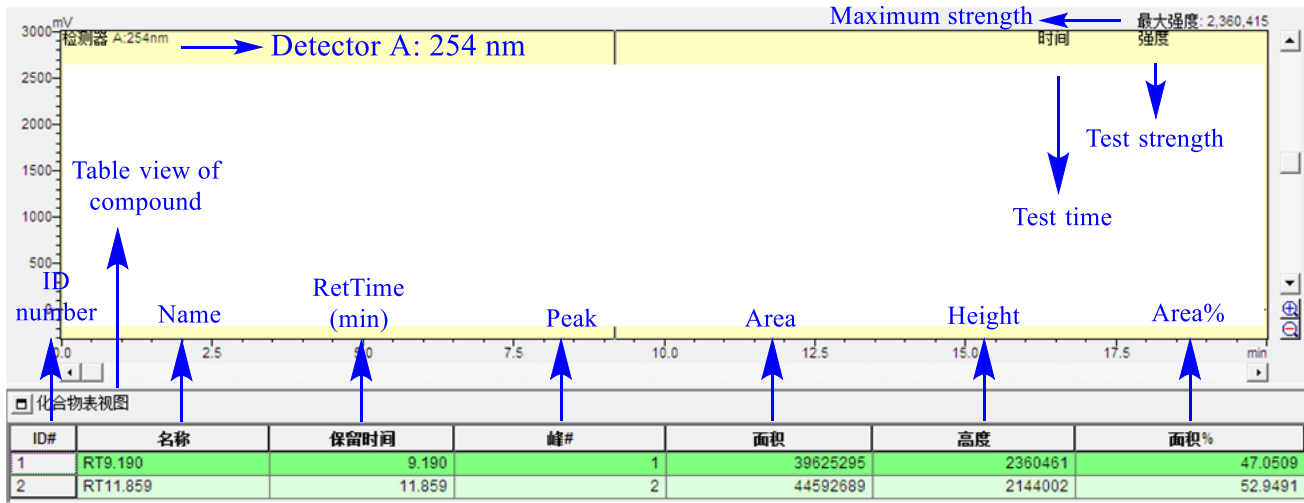
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



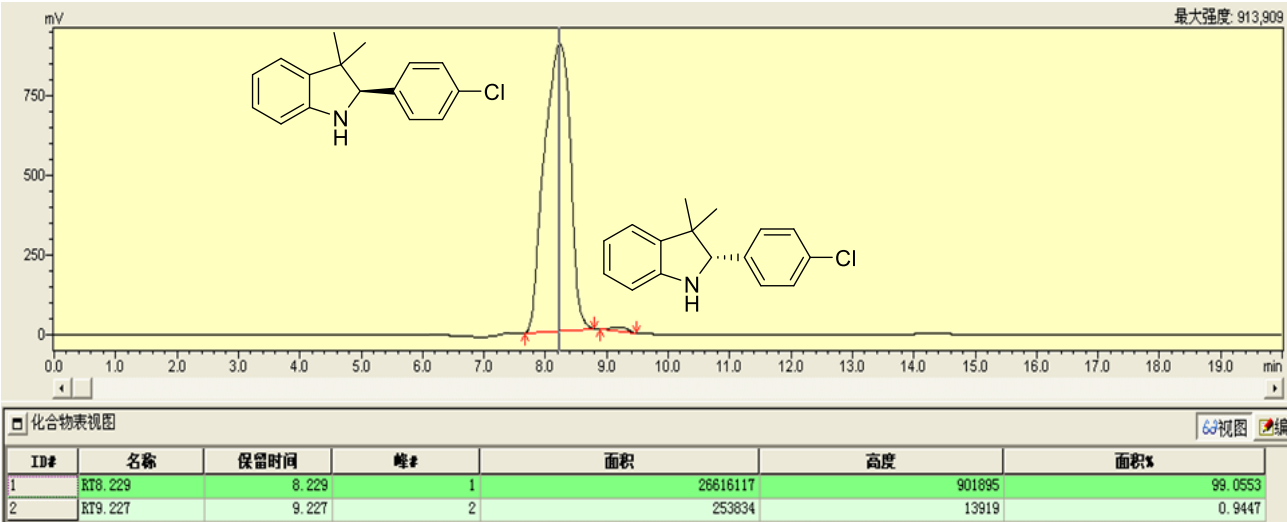
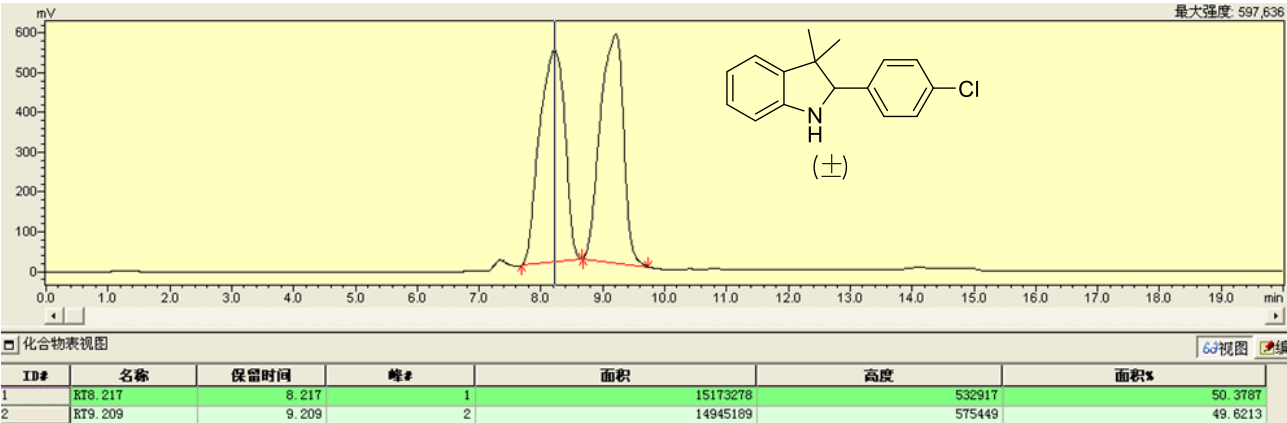
(R)-11: (R)-1,1-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[e]indole.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



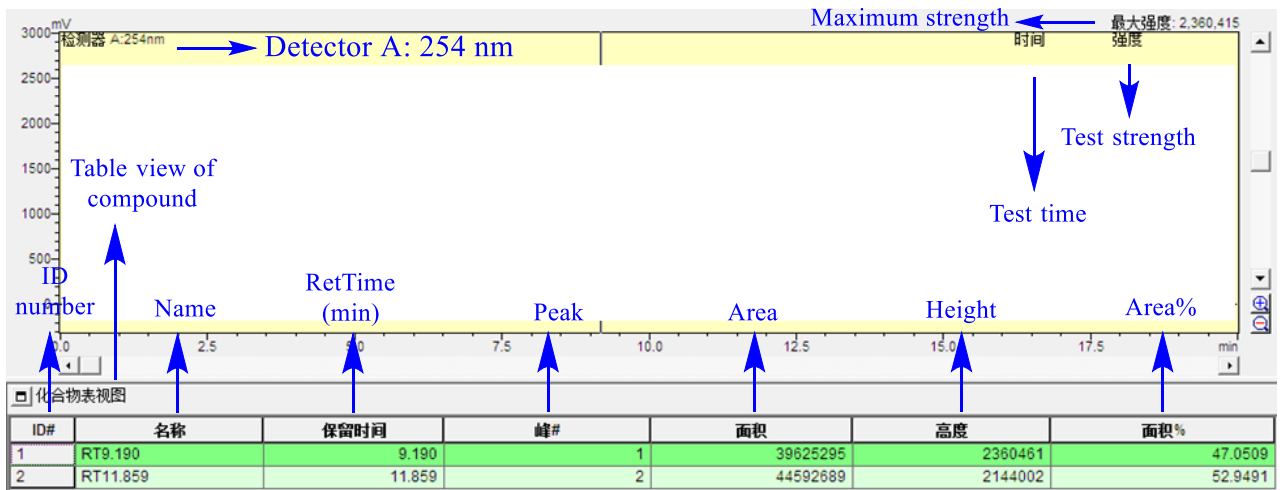
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



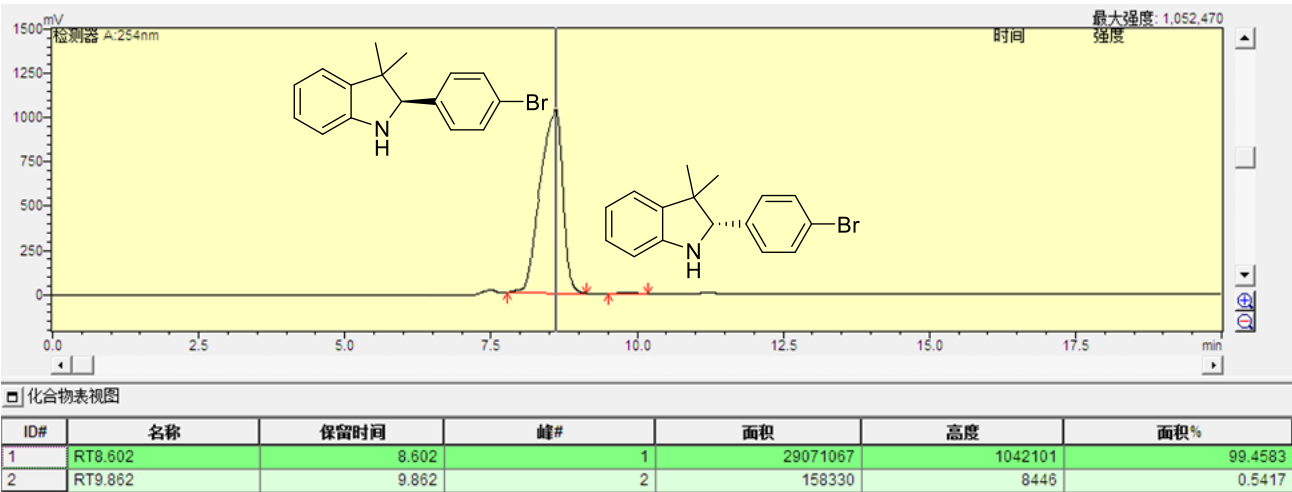
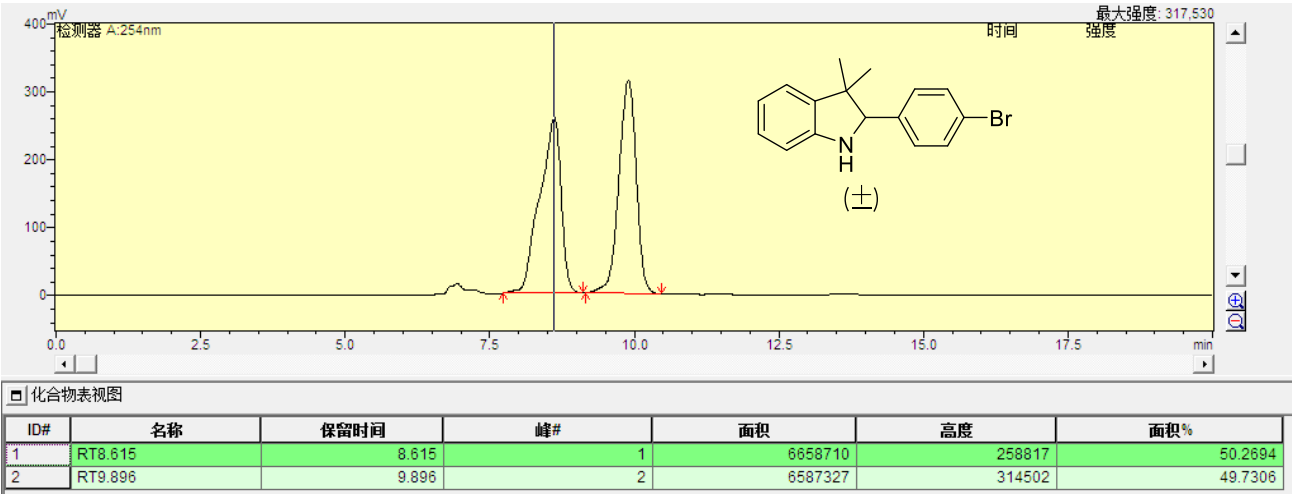
(R)-1m: (R)-2-(4-chlorophenyl)-3,3-dimethylindoline: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



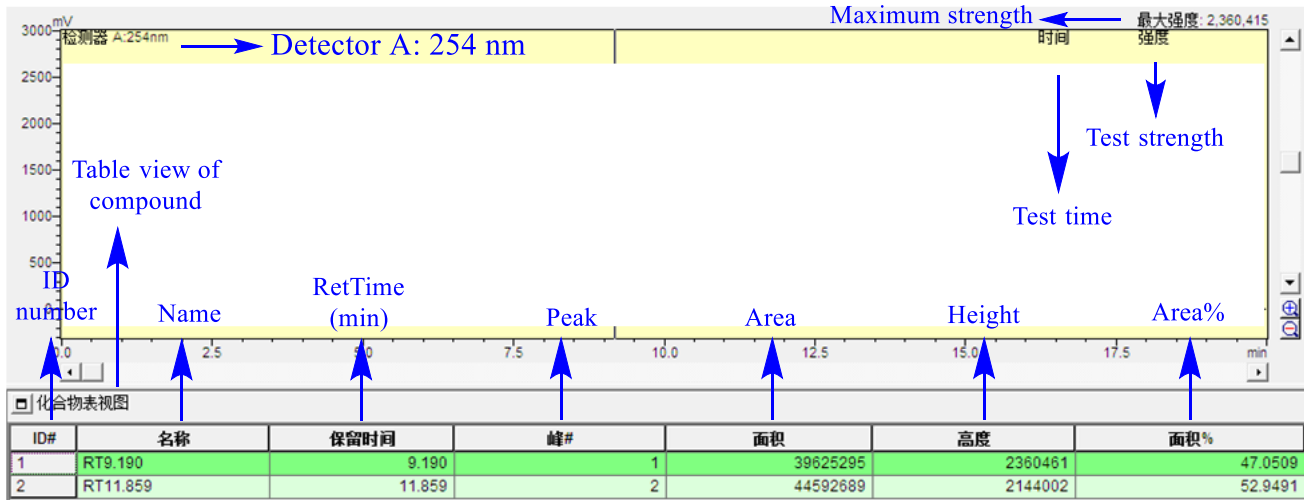
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



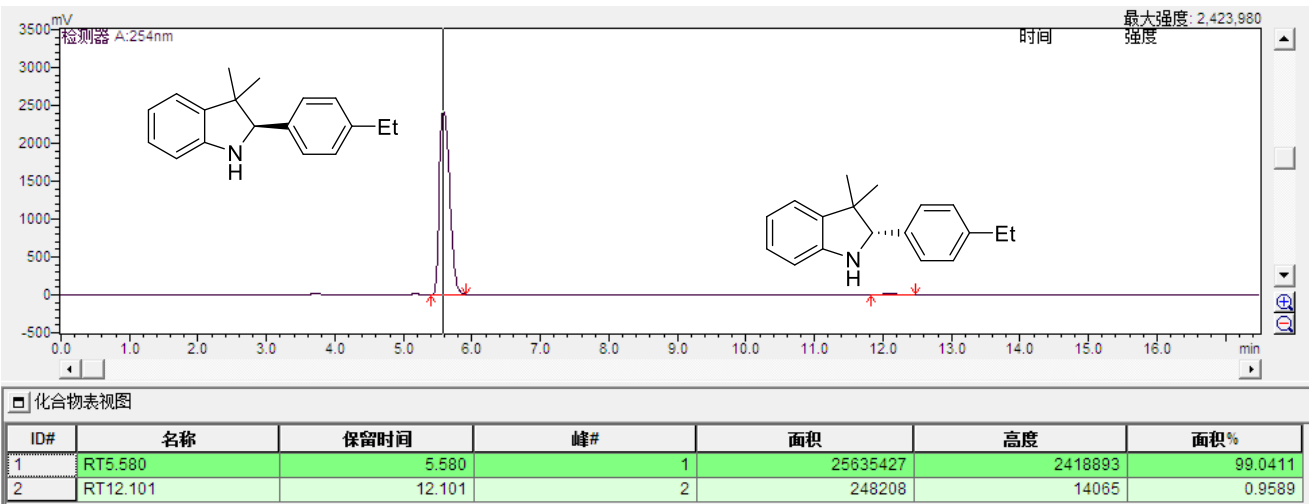
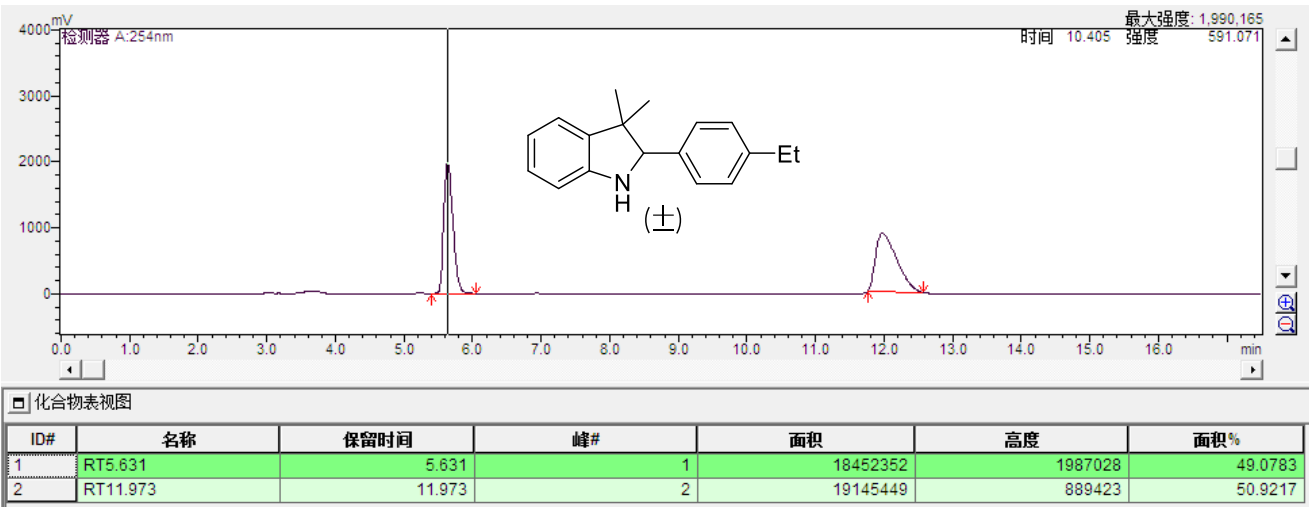
(R)-1n: (R)-2-(4-bromophenyl)-3,3-dimethylindoline.: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



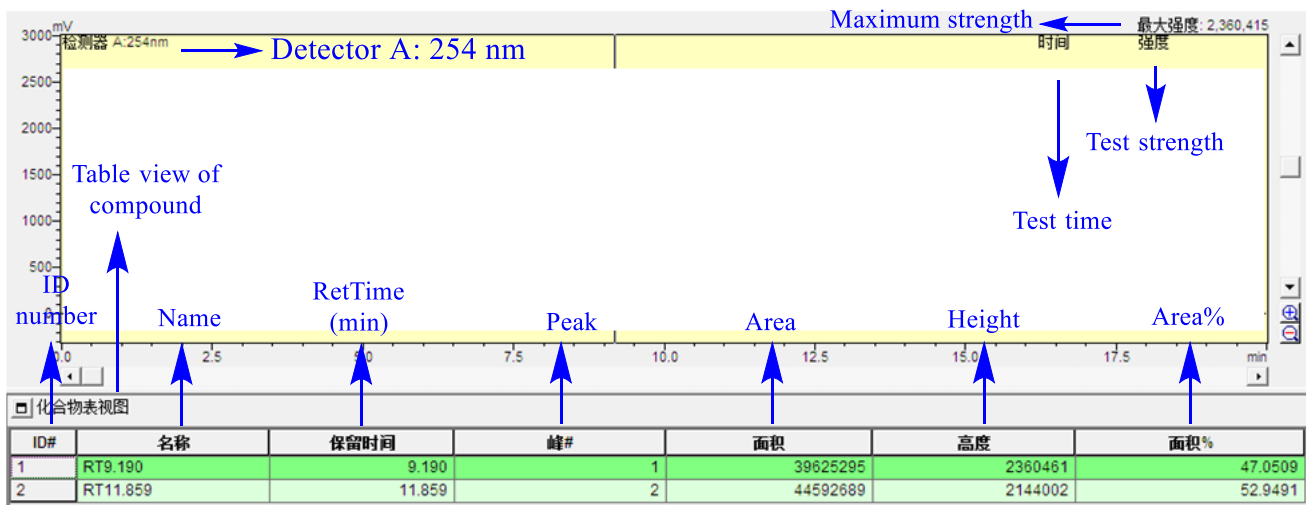
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



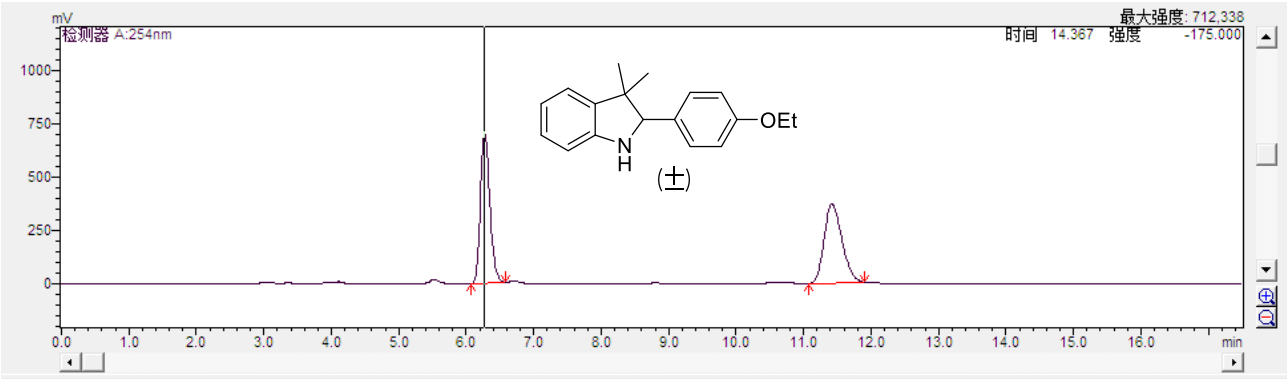
(R)-1o: (R)-2-(4-ethylphenyl)-3,3-dimethylindoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



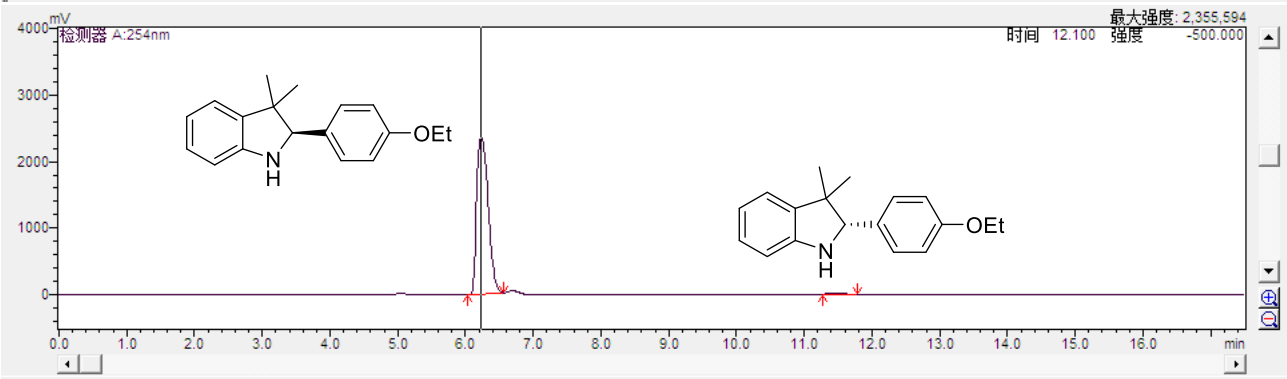
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(R)-1p: (R)-2-(4-methoxyphenyl)-3,3-dimethylindoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).

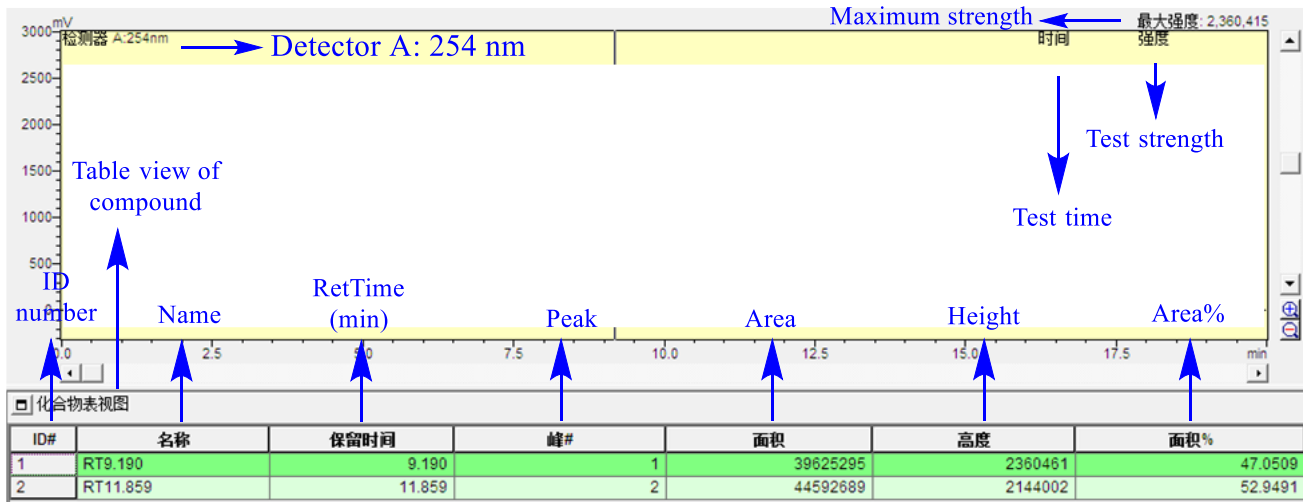


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT6.267	6.267	1	6838088	708872	50.0671
2	RT11.416	11.416	2	6819755	369708	49.9329



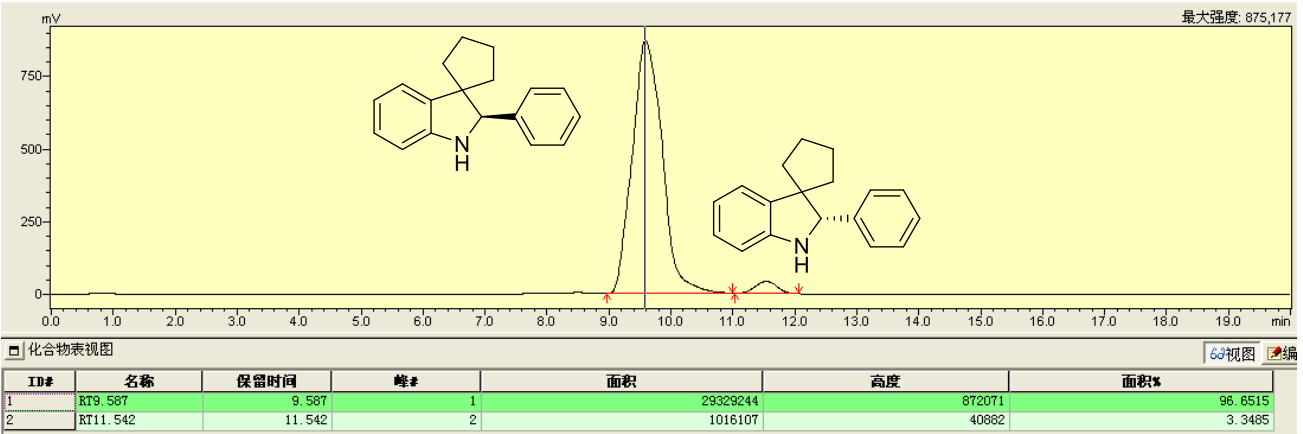
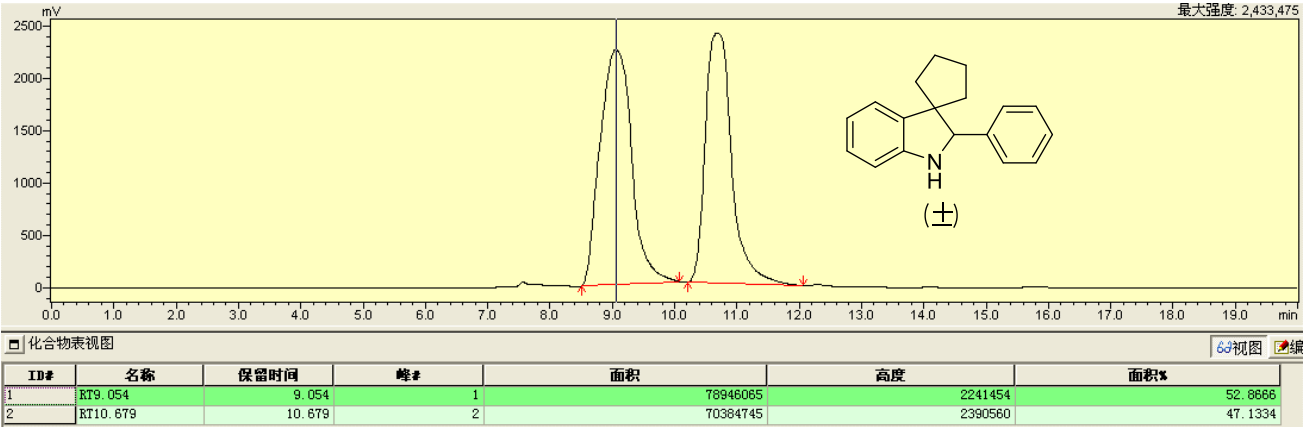
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT6.227	6.227	1	27793473	2344730	98.9796
2	RT11.472	11.472	2	286535	19104	1.0204

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

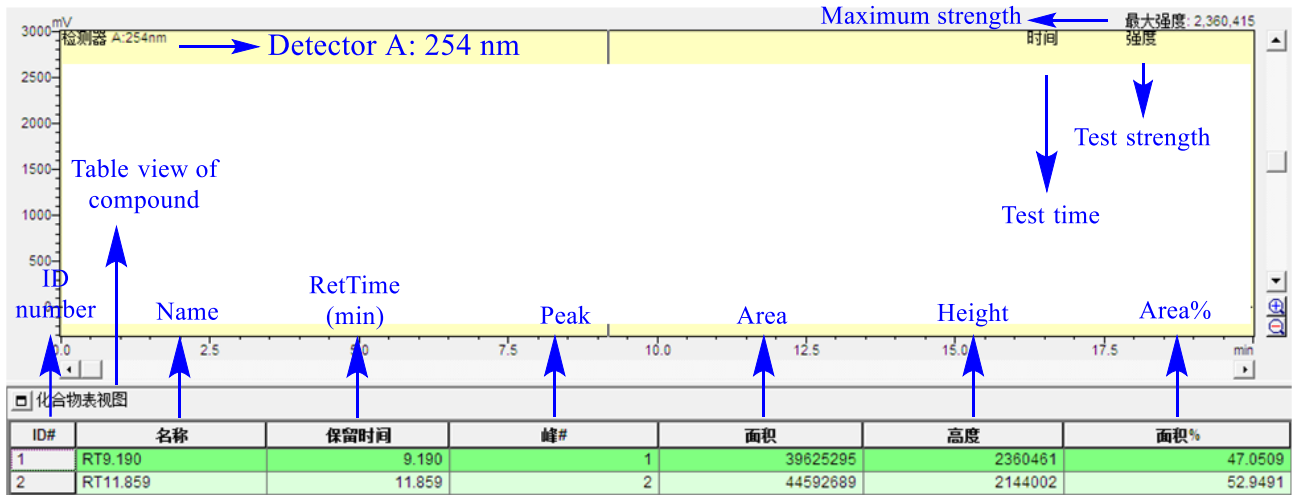


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.190	9.190	1	39625295	2360461	47.0509
2	RT11.859	11.859	2	44592689	2144002	52.9491

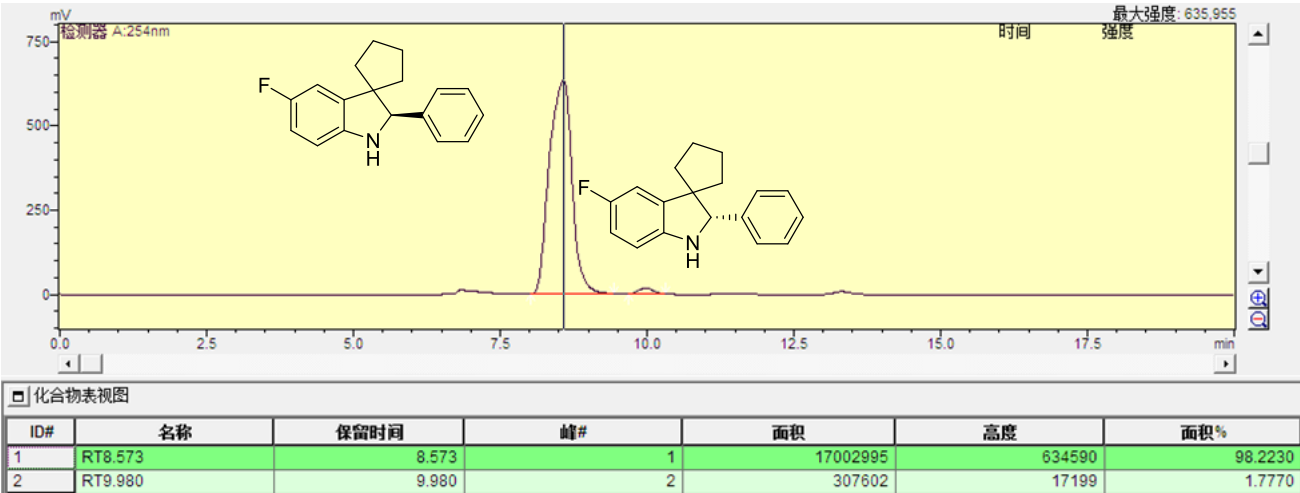
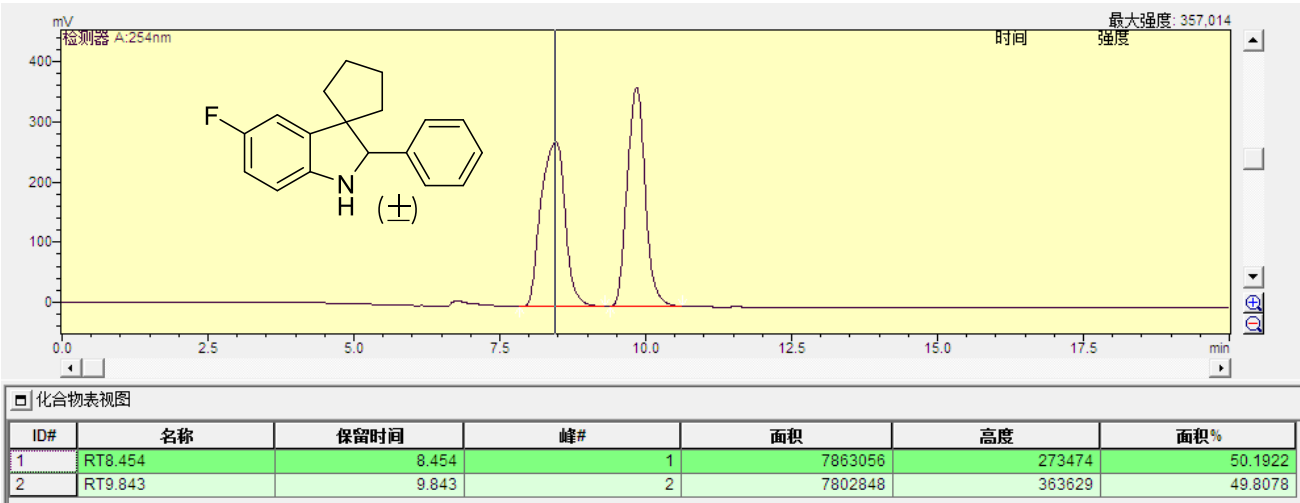
(R)-1q: (R)-2'-phenylspiro[cyclopentane-1,3'-indoline]: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



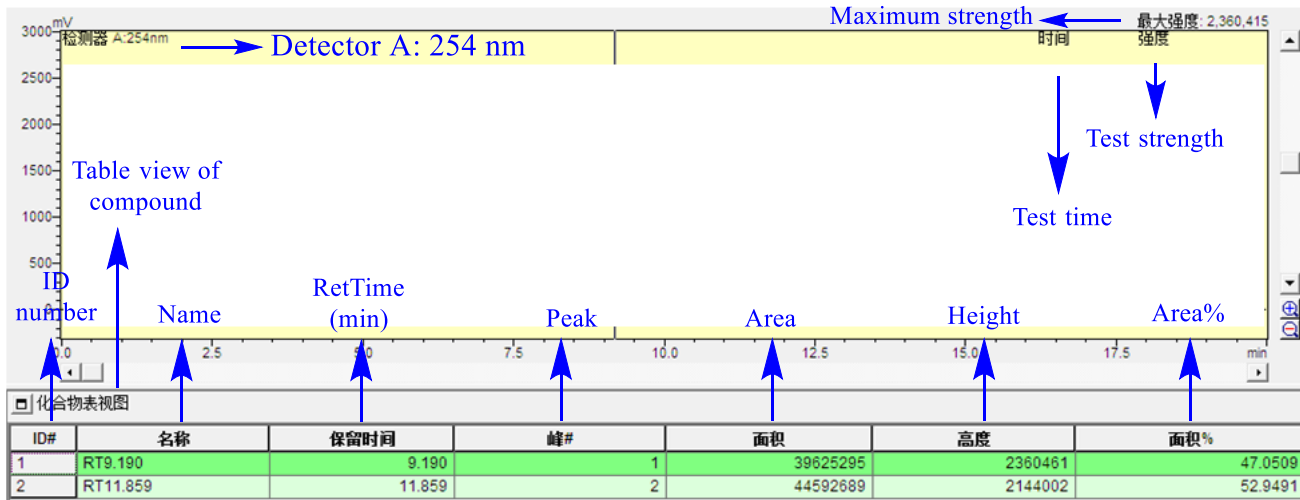
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



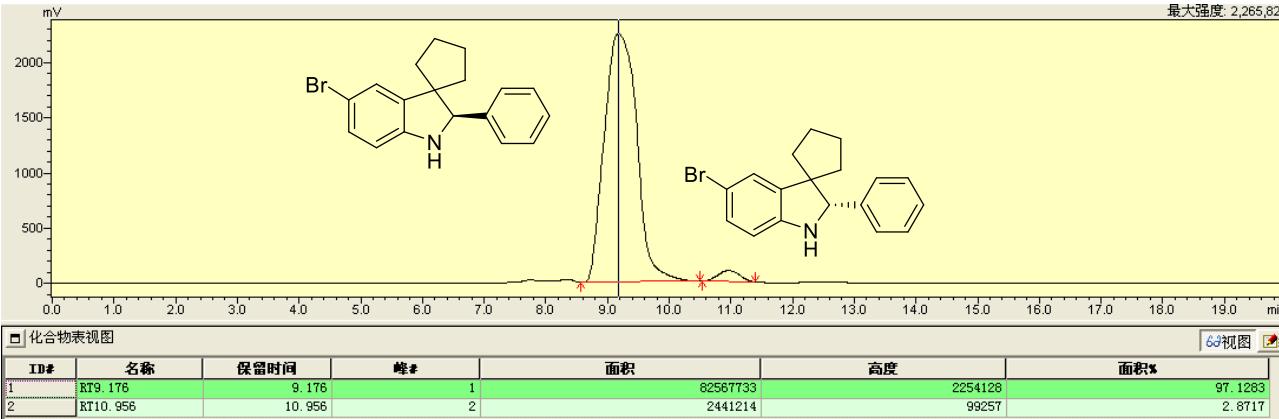
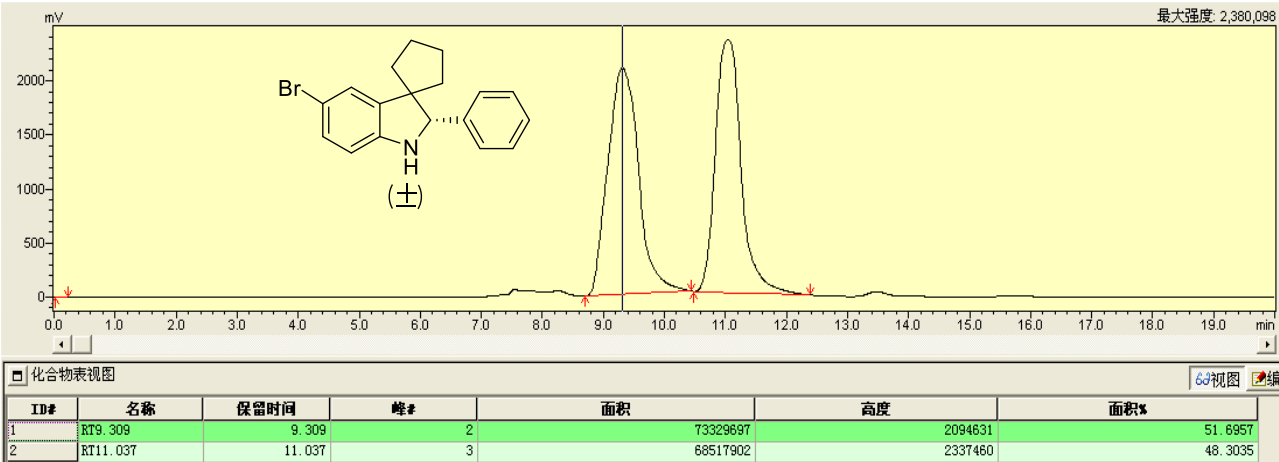
(R)-1r: (R)-5'-fluoro-2'-phenylspiro[cyclopentane-1,3'-indoline].: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



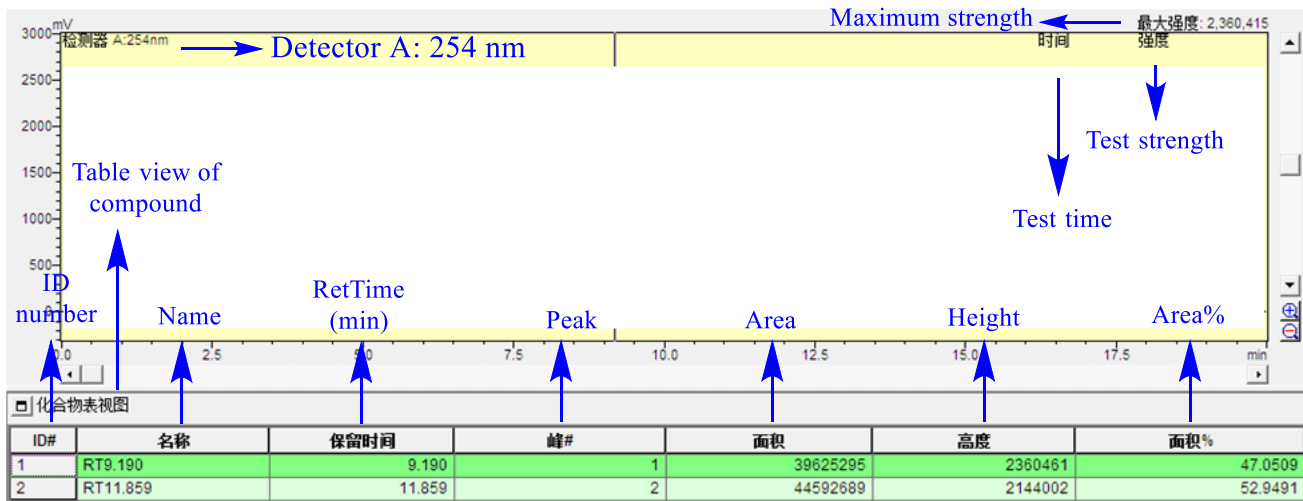
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



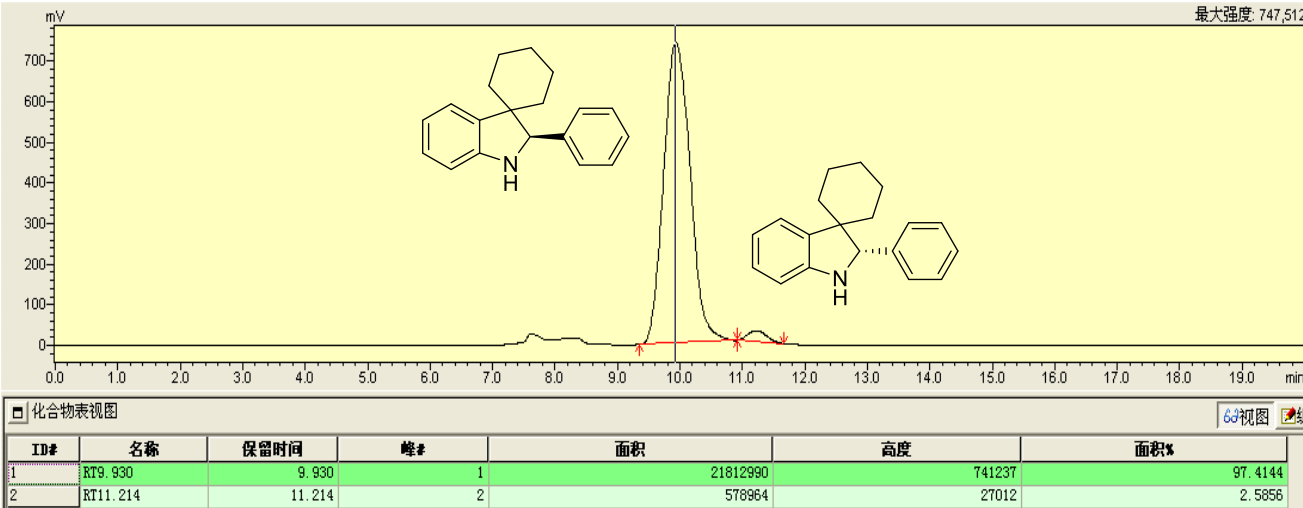
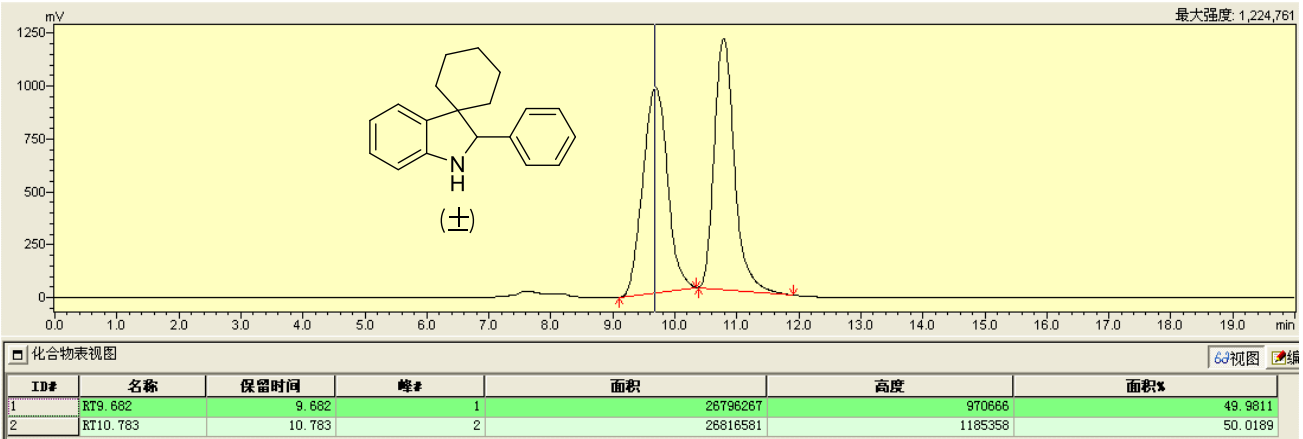
(R)-1s: (R)-5'-bromo-2'-phenylspiro[cyclopentane-1,3'-indoline] : (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



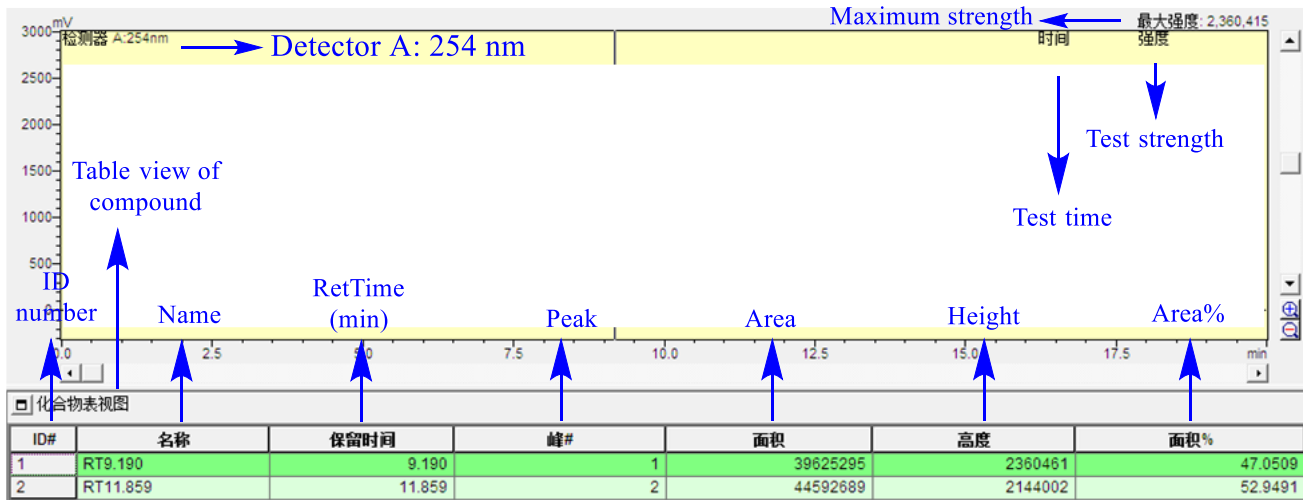
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



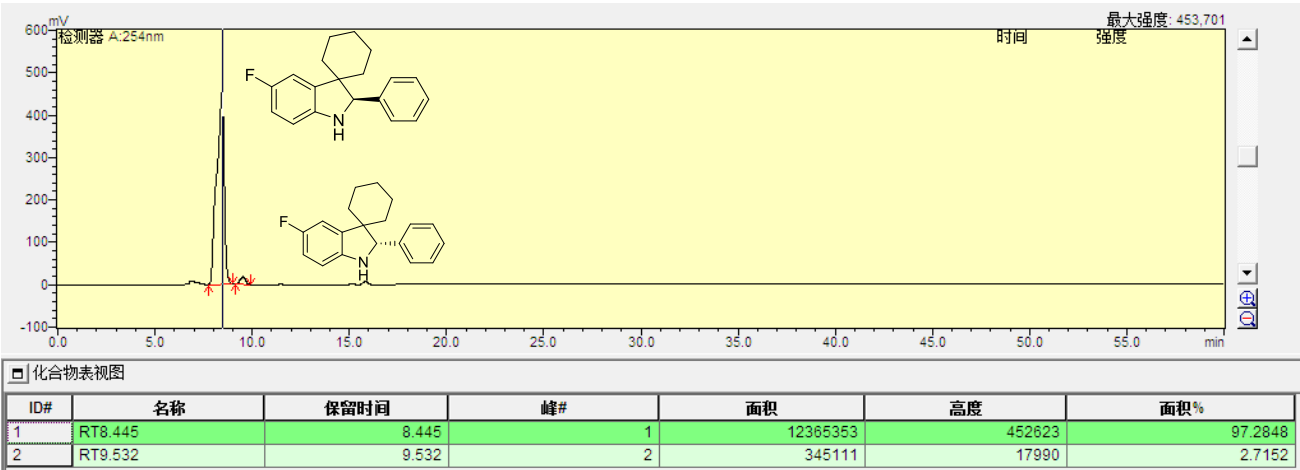
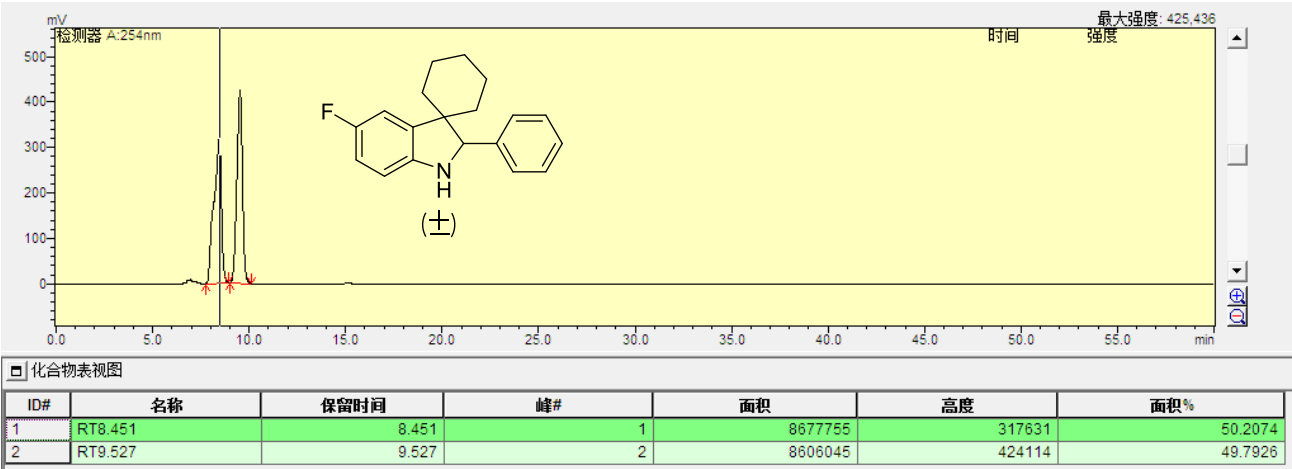
(R)-1t: (R)-2'-phenylspiro[cyclohexane-1,3'-indoline] : (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



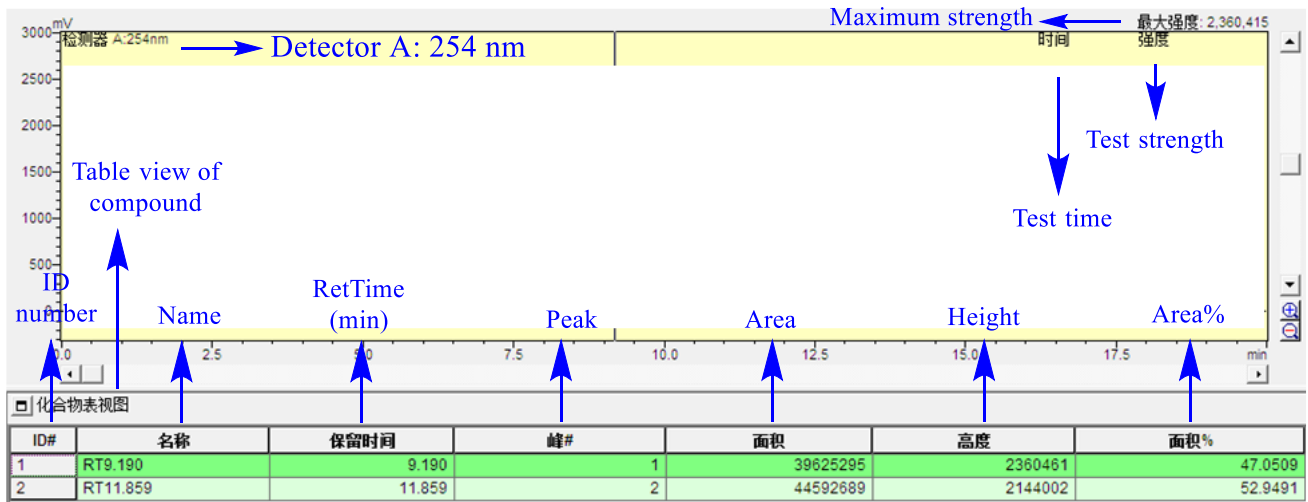
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



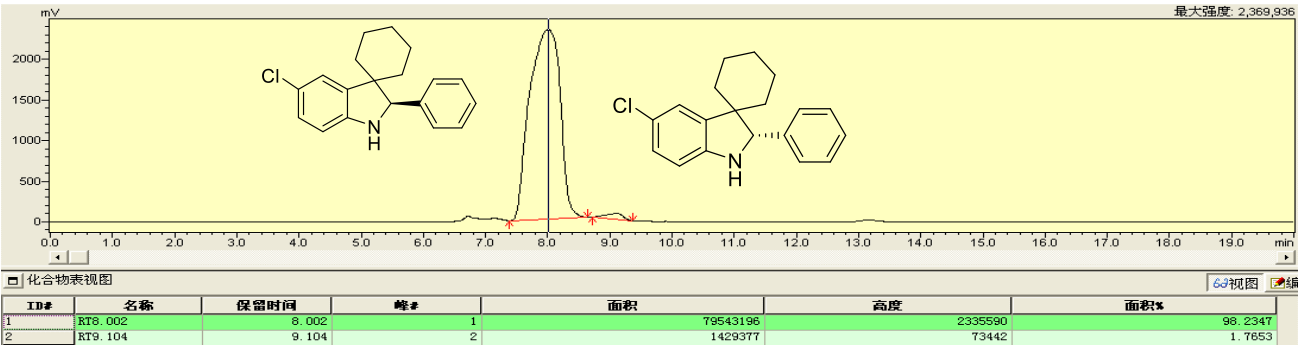
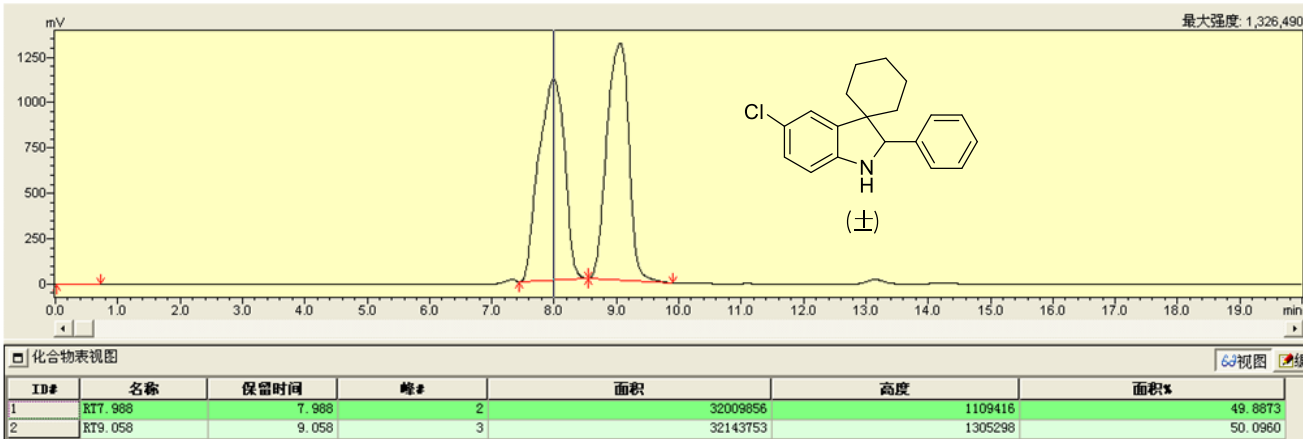
(R)-1u: (R)-5'-fluoro-2'-phenylspiro[cyclohexane-1,3'-indoline]: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



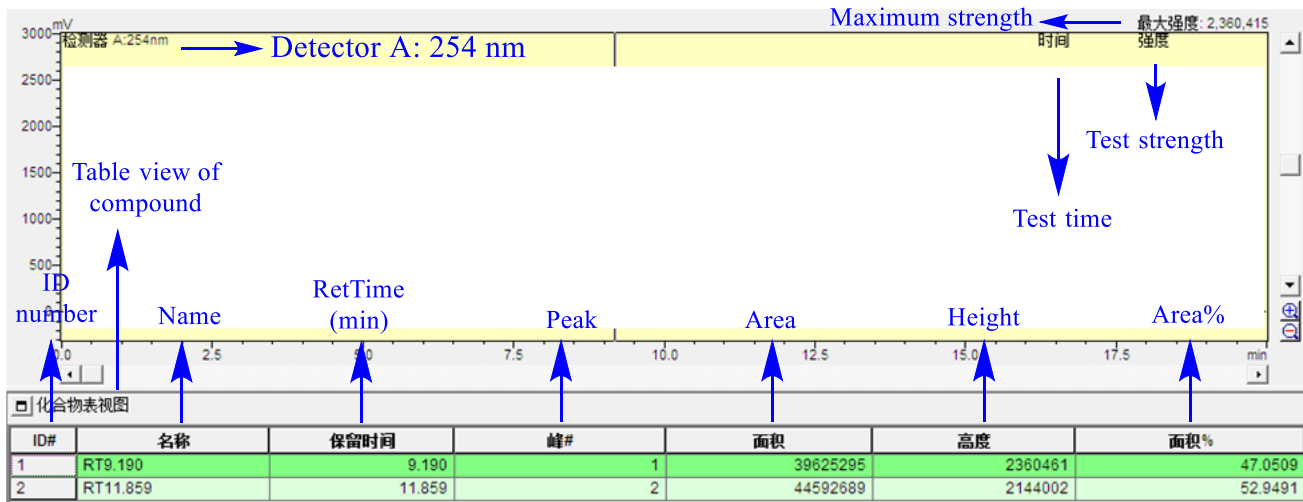
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



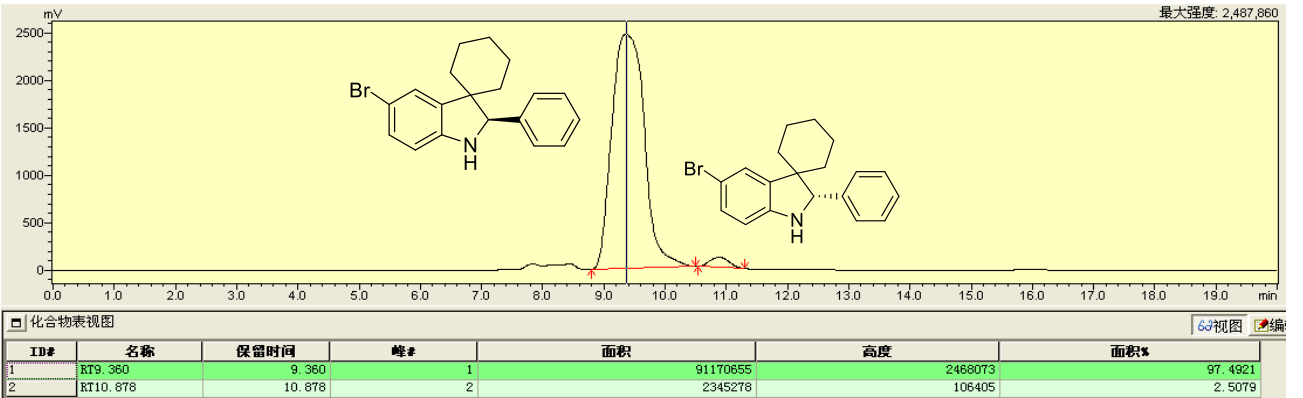
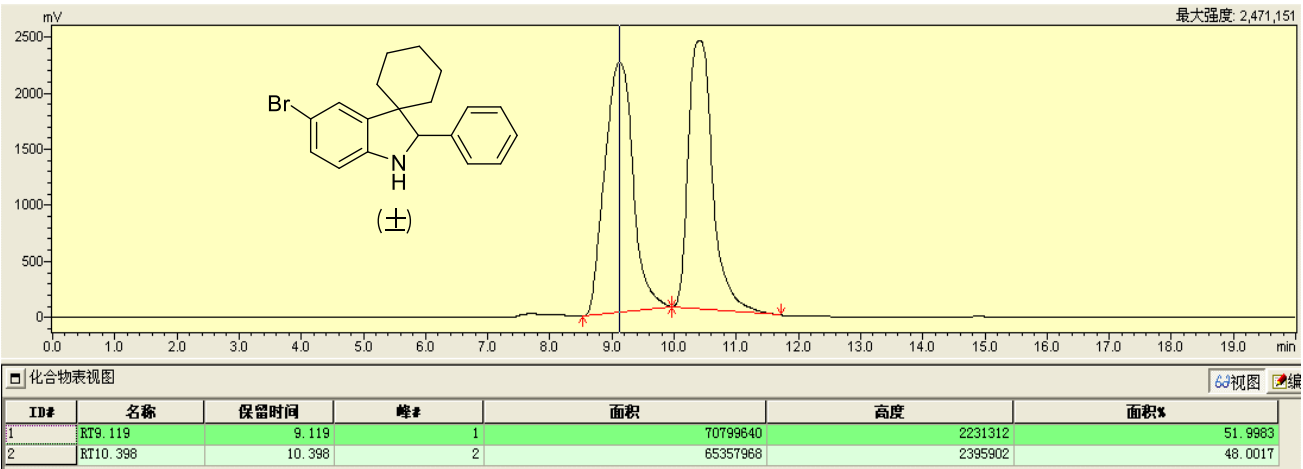
(R)-1v: (R)-5'-chloro-2'-phenylspiro[cyclohexane-1,3'-indoline]: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



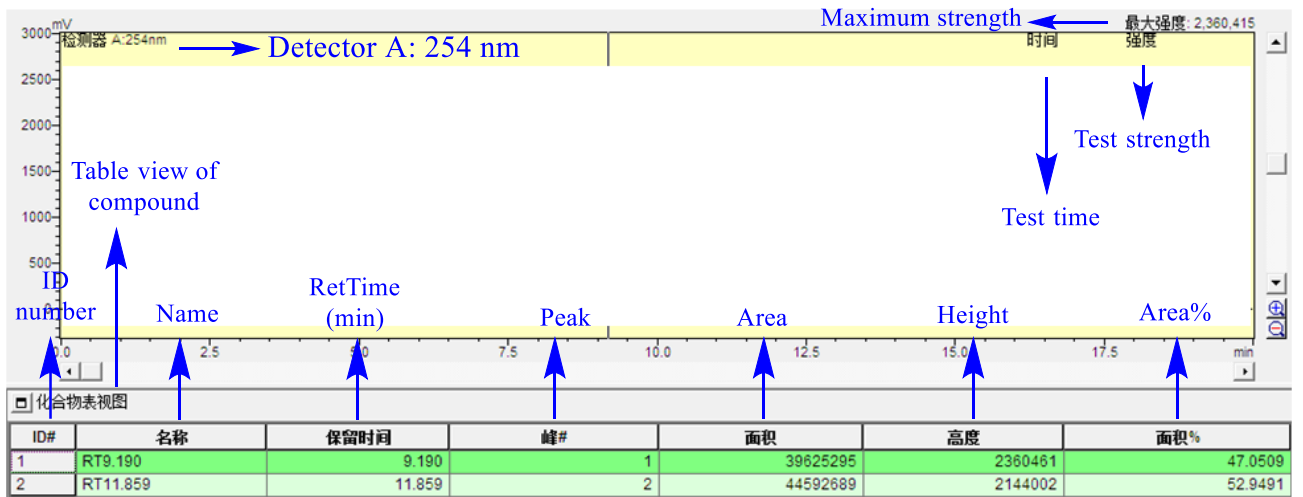
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



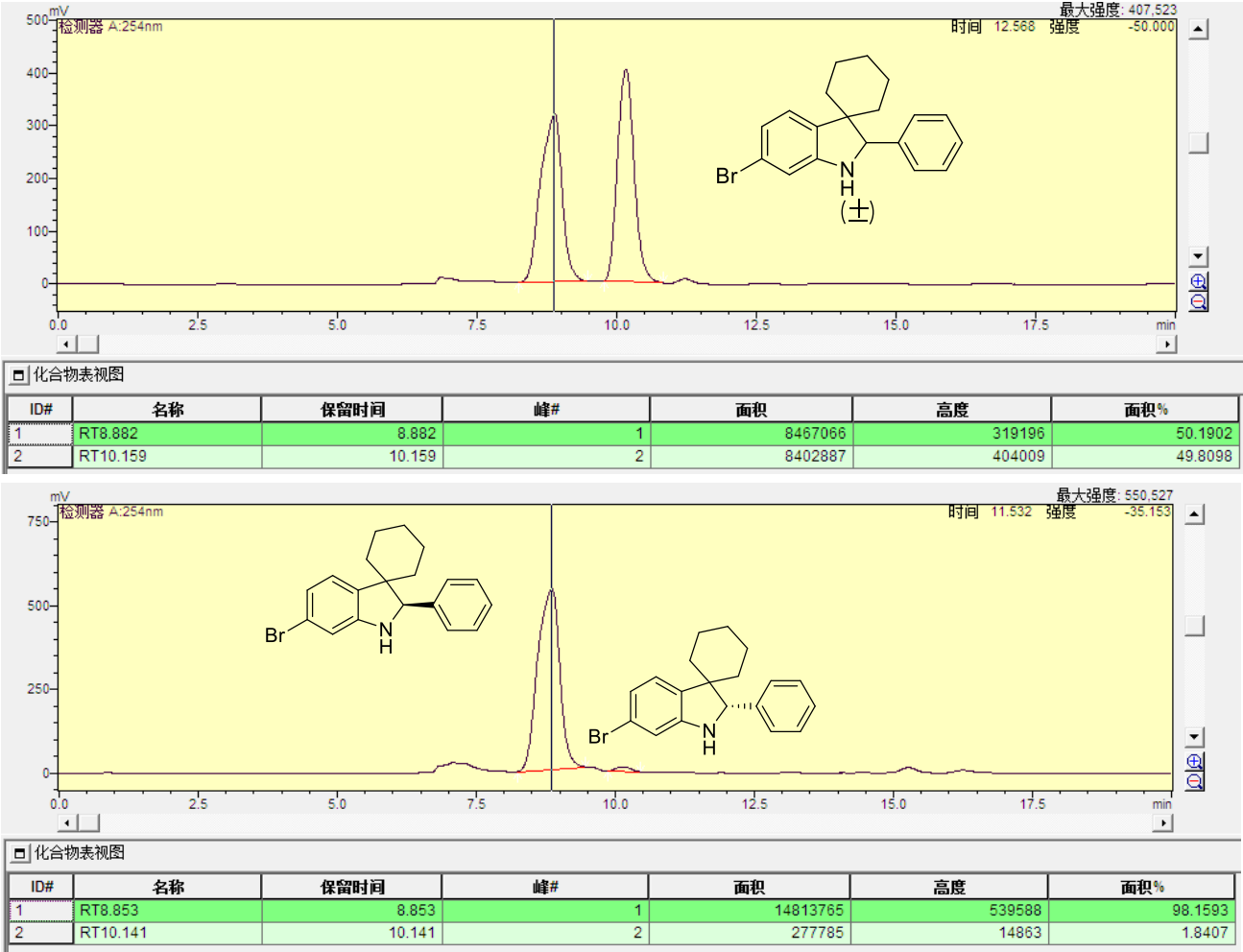
(R)-1w: (R)-5'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline]: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



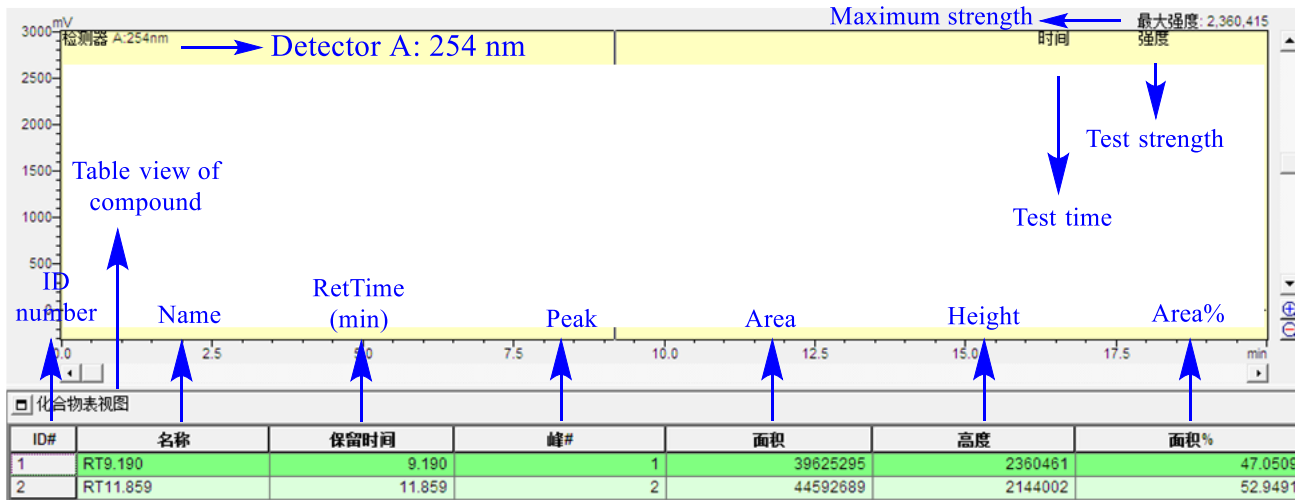
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



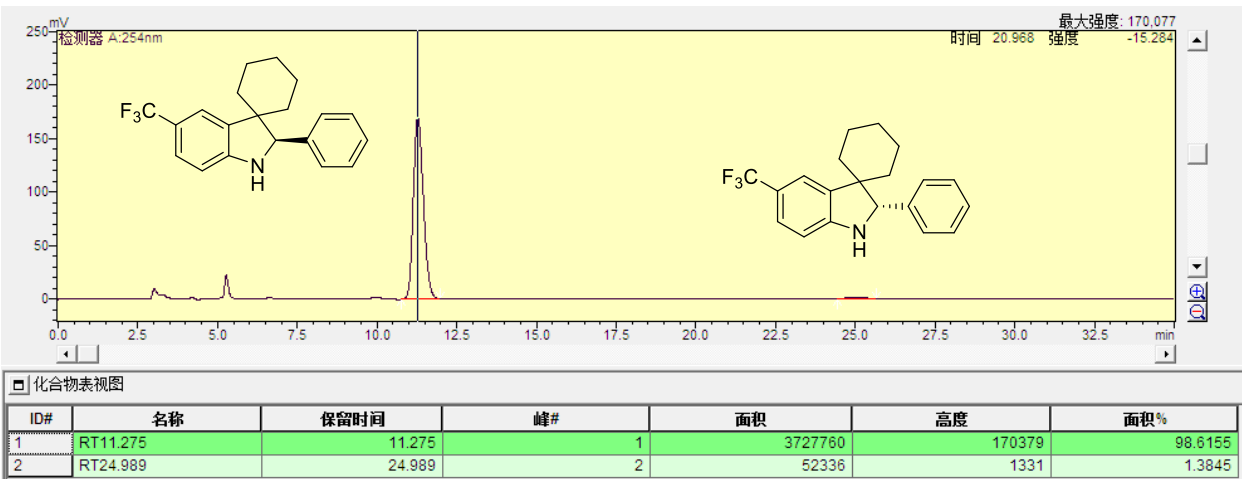
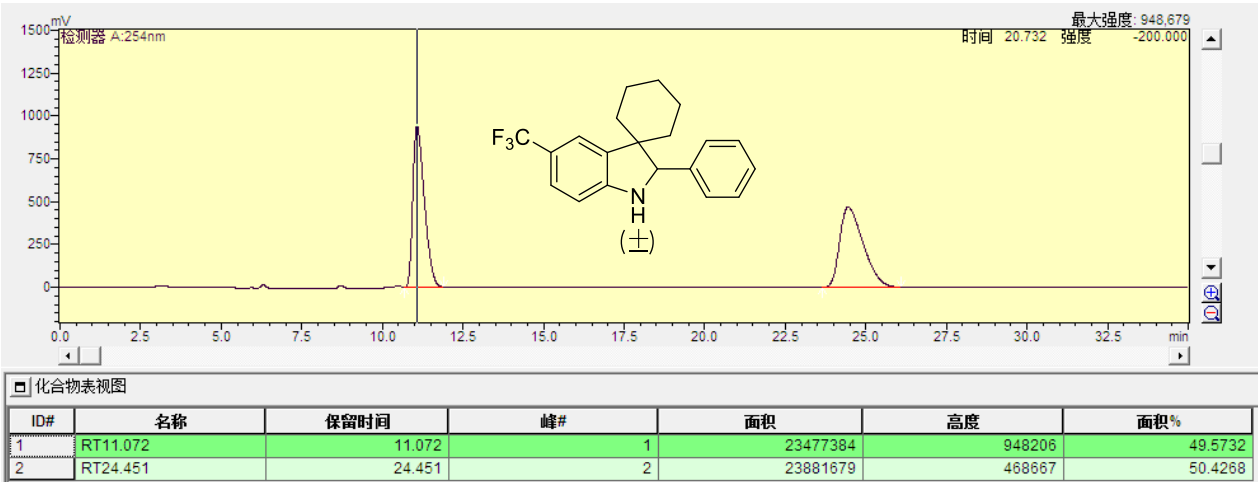
(R)-1x: (R)-6'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline].: (HPLC: Chiracel IC-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/03, flow rate = 0.5mL/min, 25 °C).



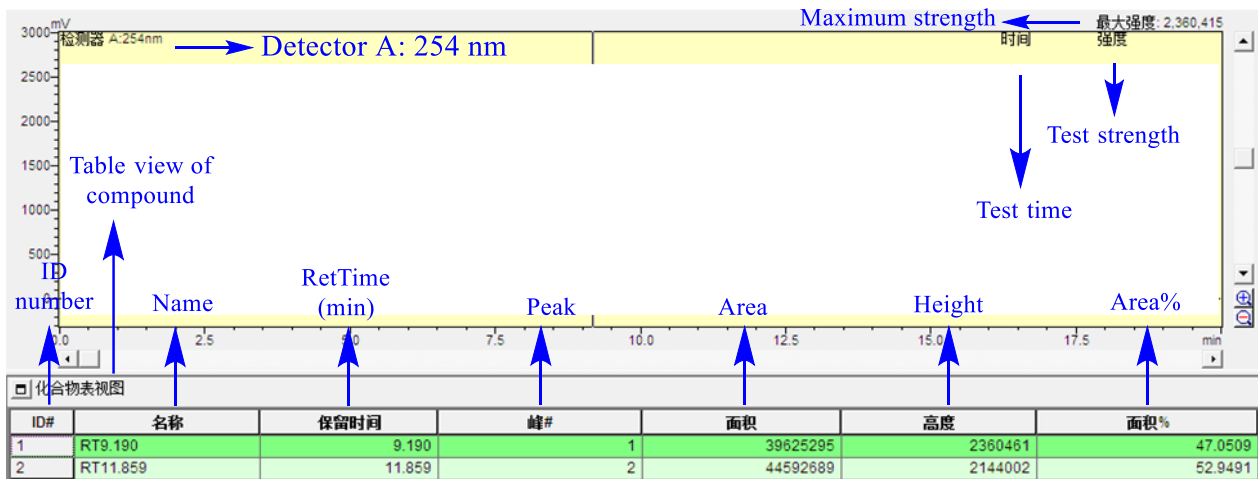
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



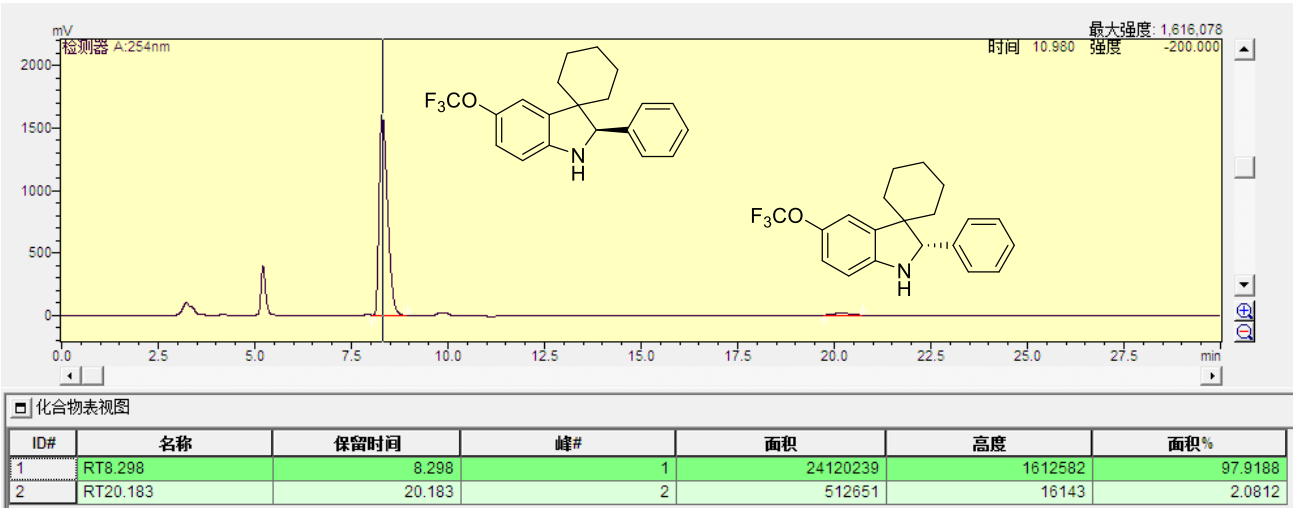
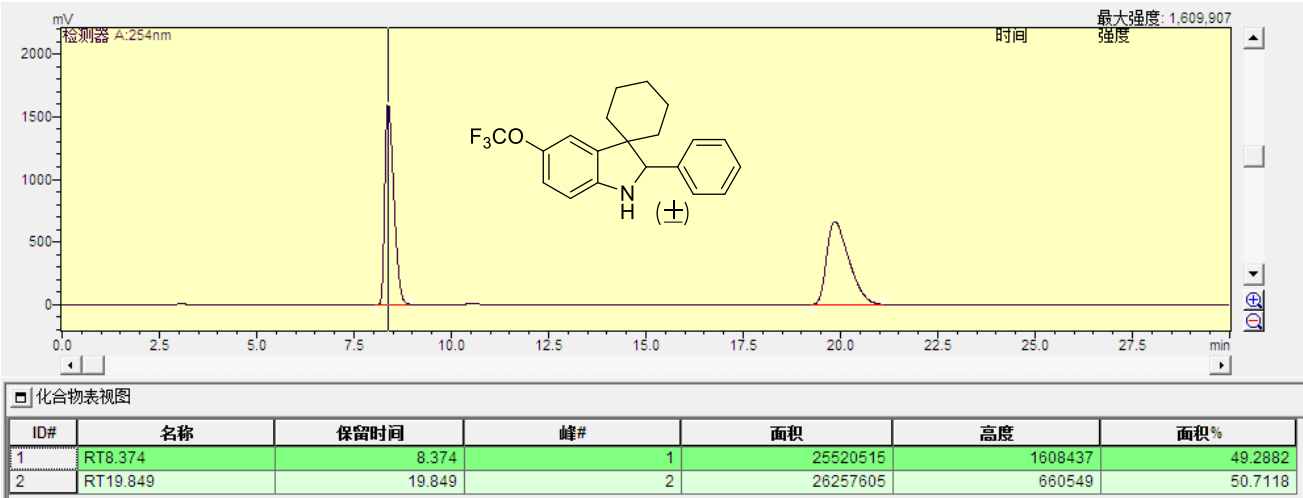
(R)-1y: (R)-2'-phenyl-5'-(trifluoromethyl)spiro[cyclohexane-1,3'-indoline].: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



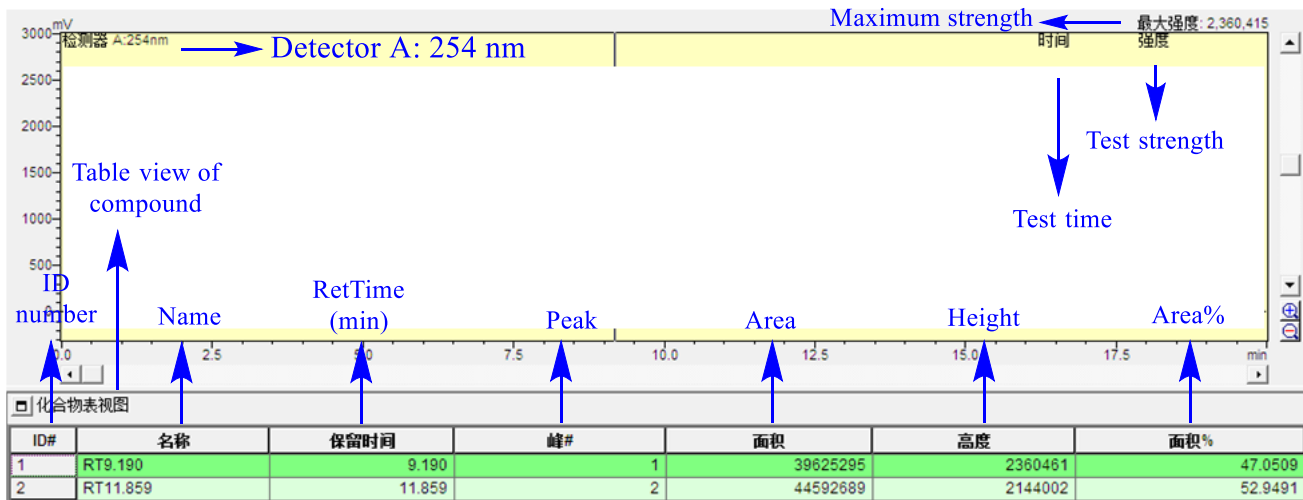
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



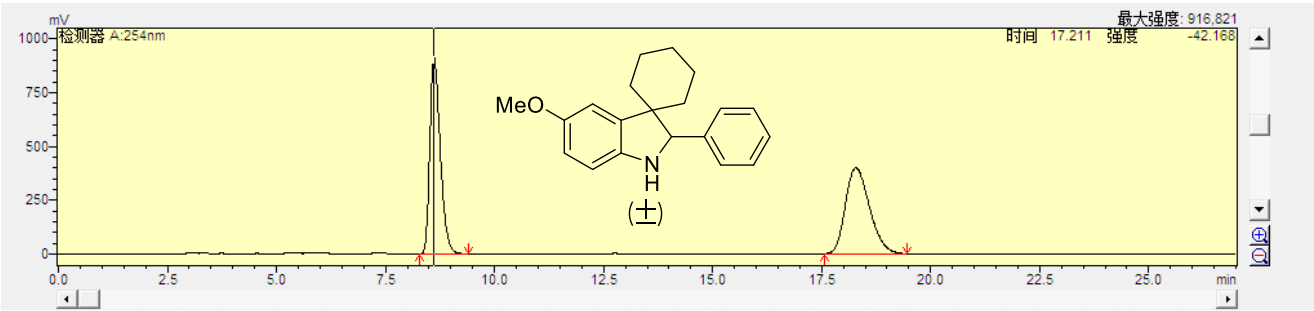
(R)-1z: (R)-2'-phenyl-5'-(trifluoromethoxy)spiro[cyclohexane-1,3'-indoline].: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



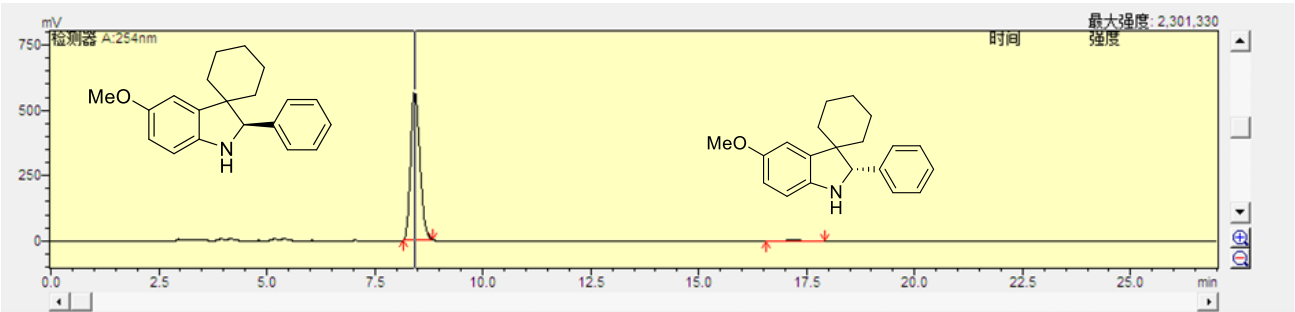
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(R)-1z': (R)- 5'-methoxy-2'-phenylspiro[cyclohexane-1,3'-indoline]: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).

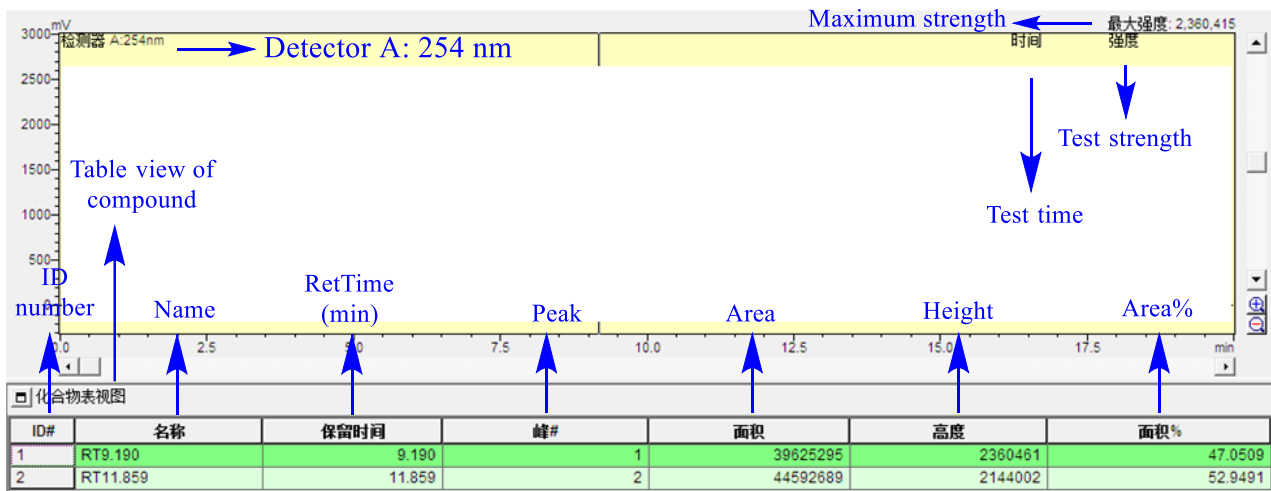


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.612	8.612	1	15228187	915696	49.7585
2	RT18.283	18.283	2	15375993	400170	50.2415

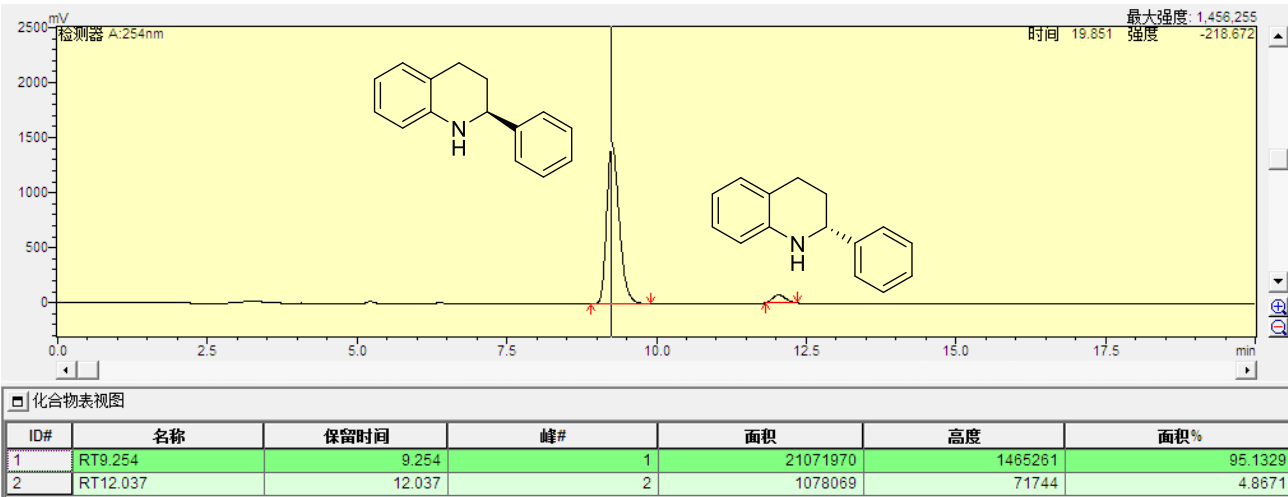
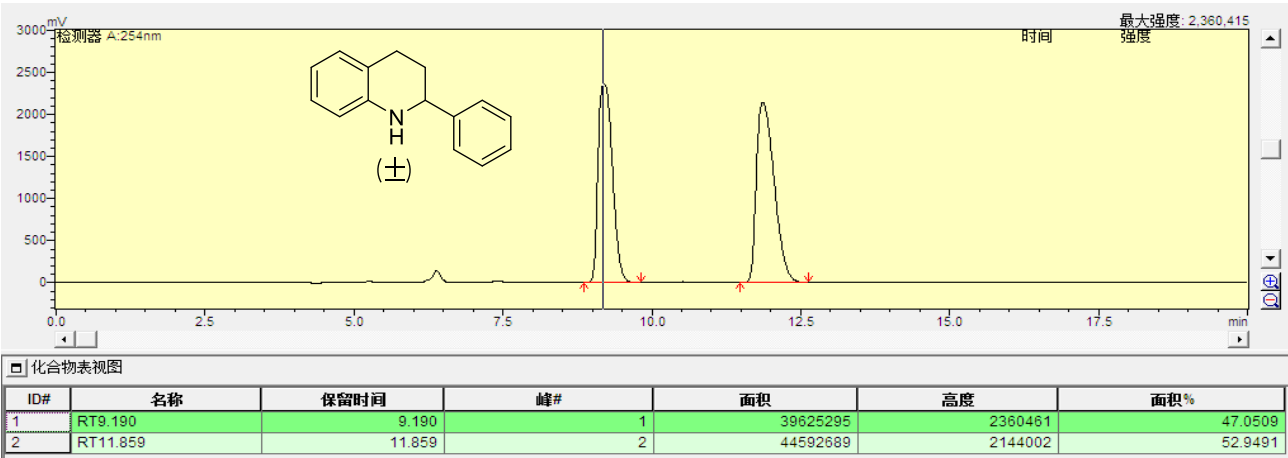


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT8.423	8.423	1	8534571	572818	98.3296
2	RT17.193	17.193	2	144986	4523	1.6704

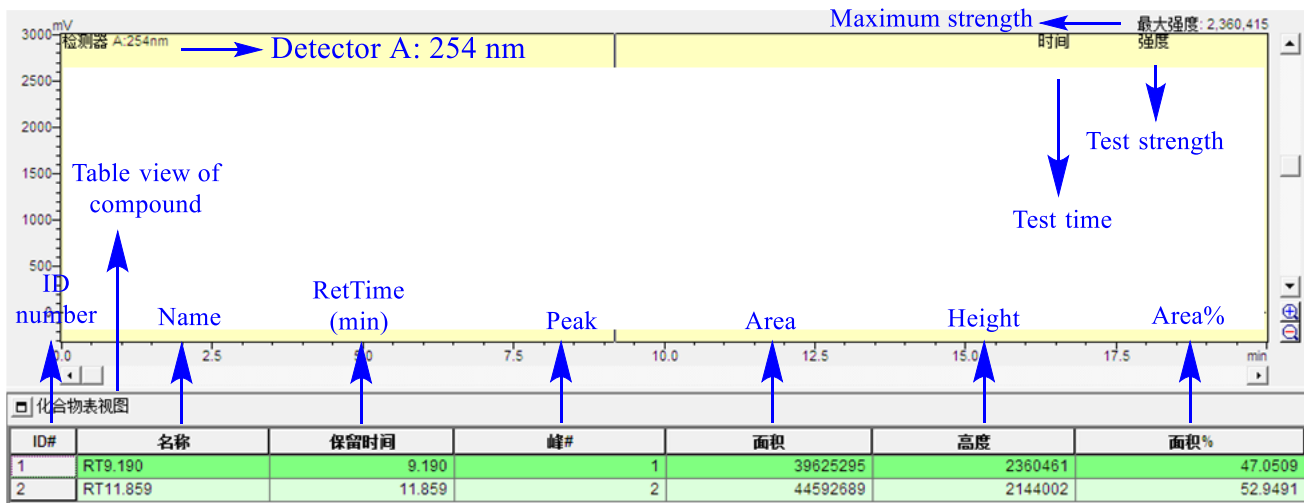
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



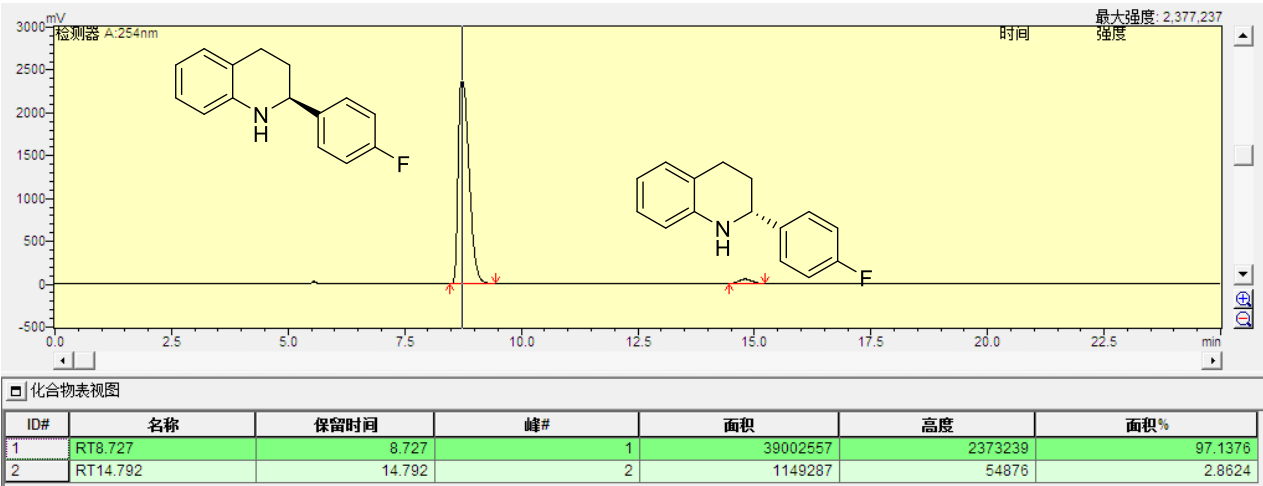
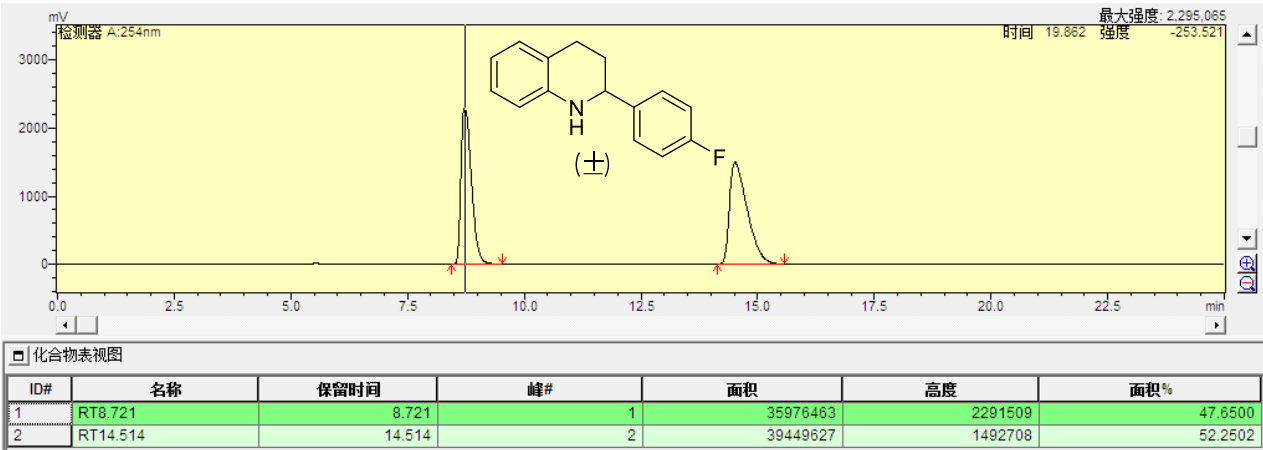
(S)-3a: (S)-2-phenyl-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



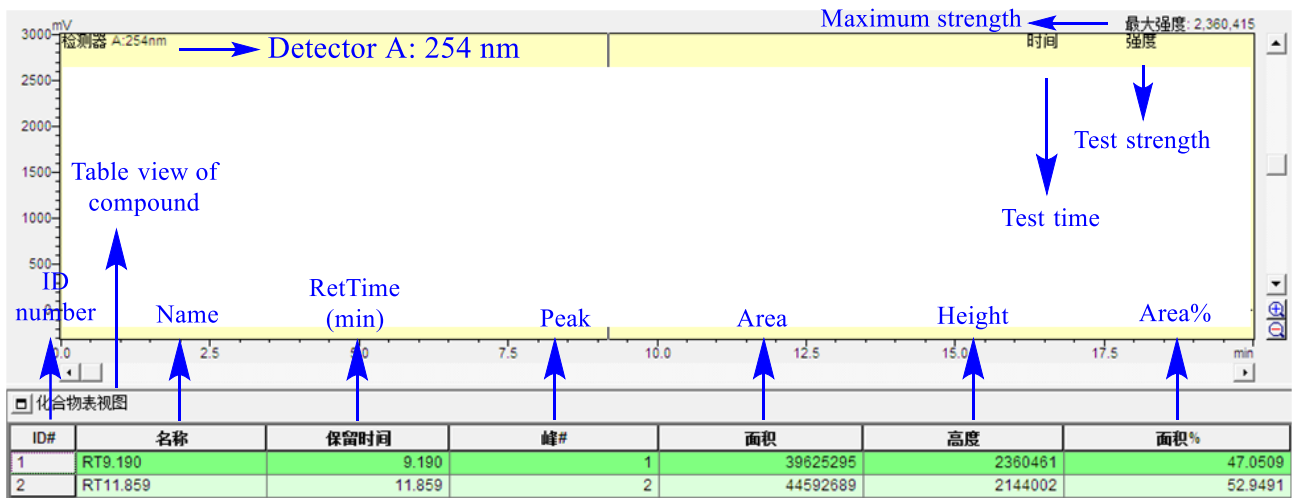
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



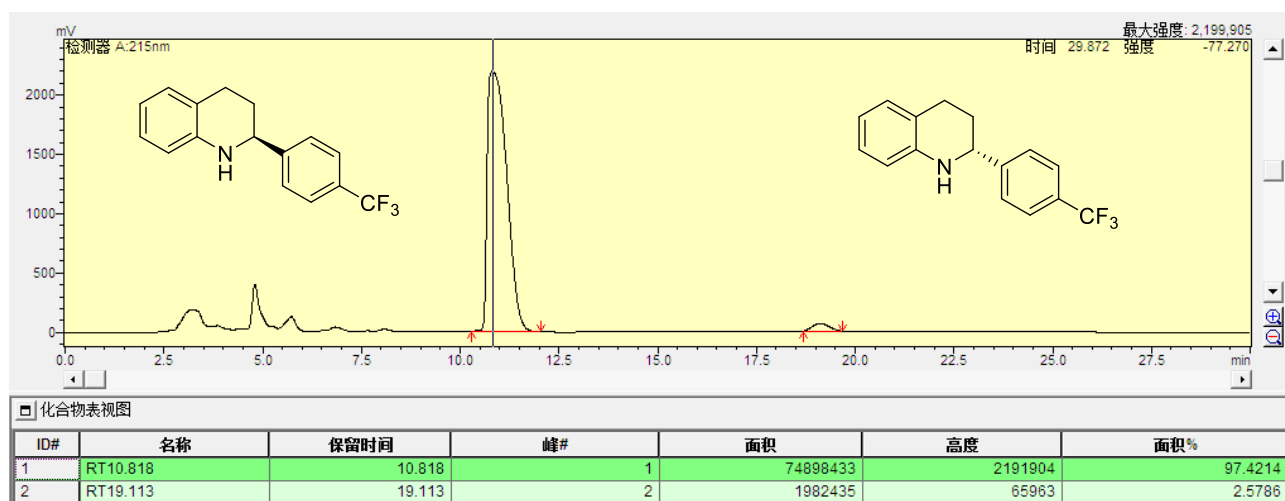
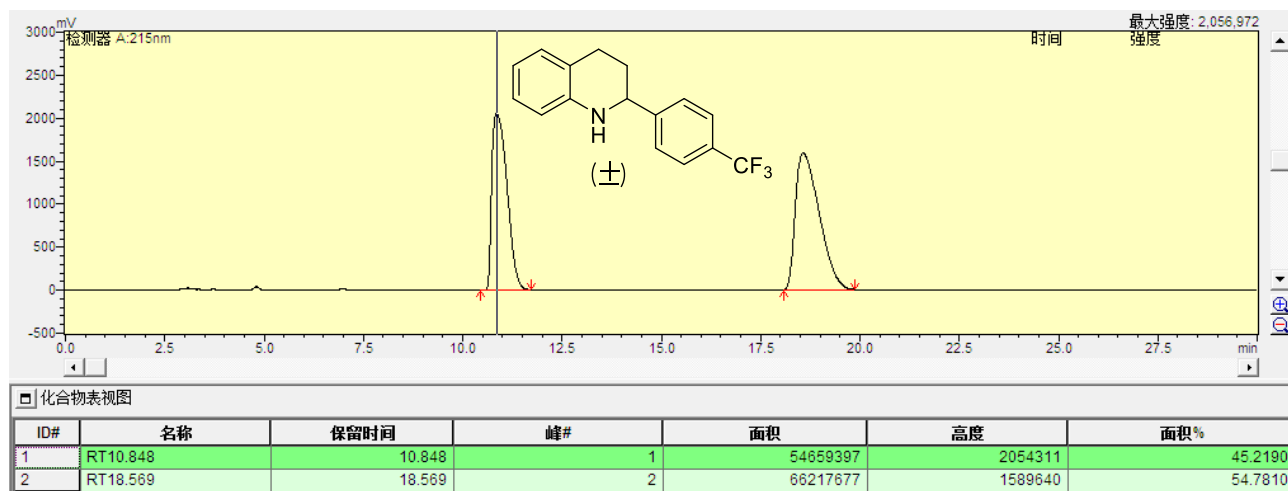
(S)-3b: (S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



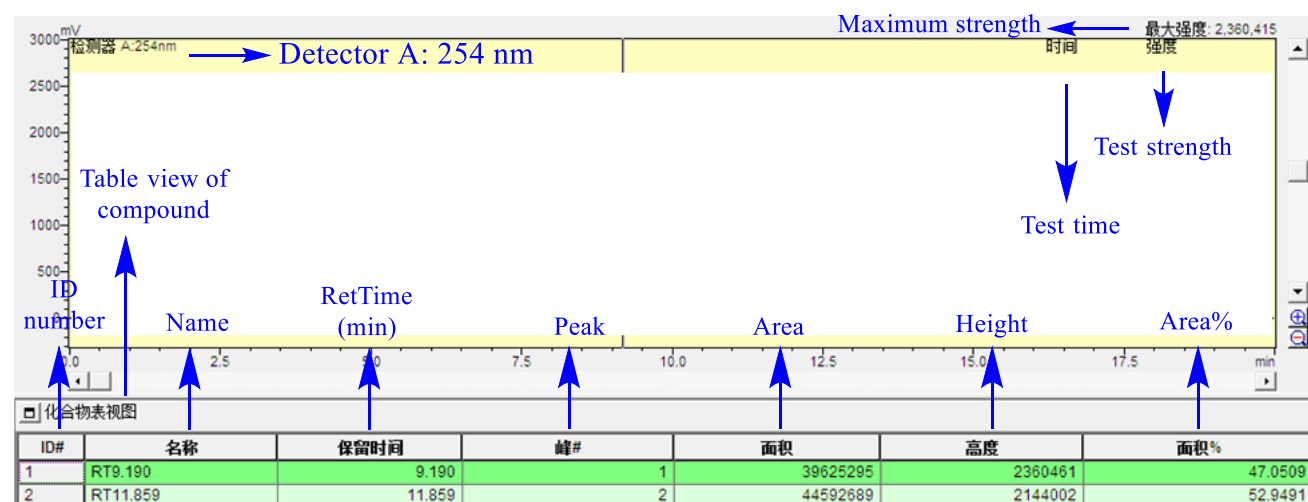
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



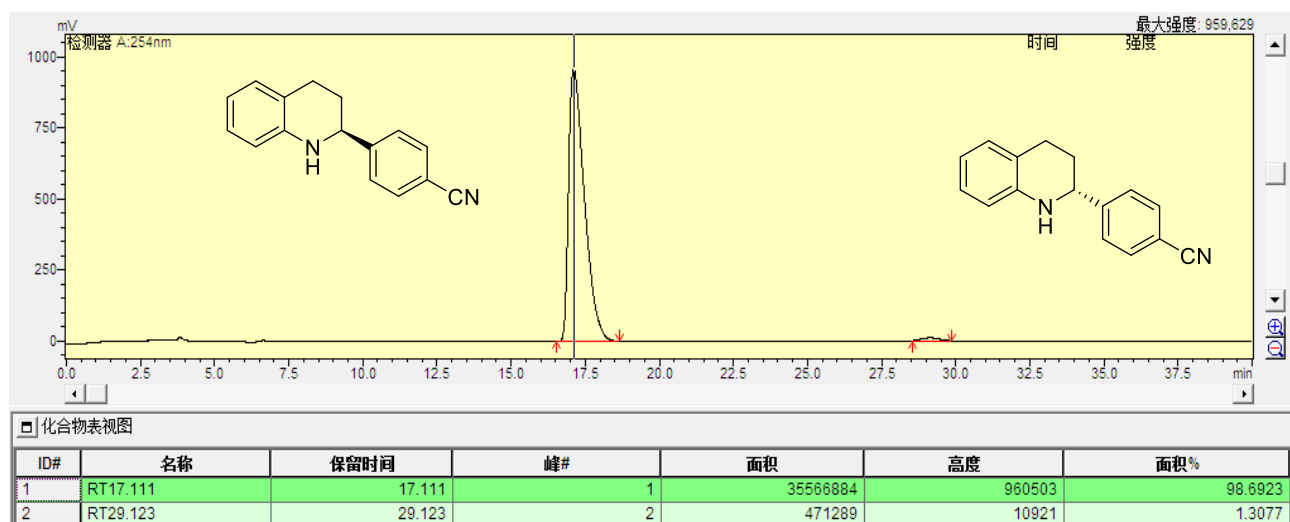
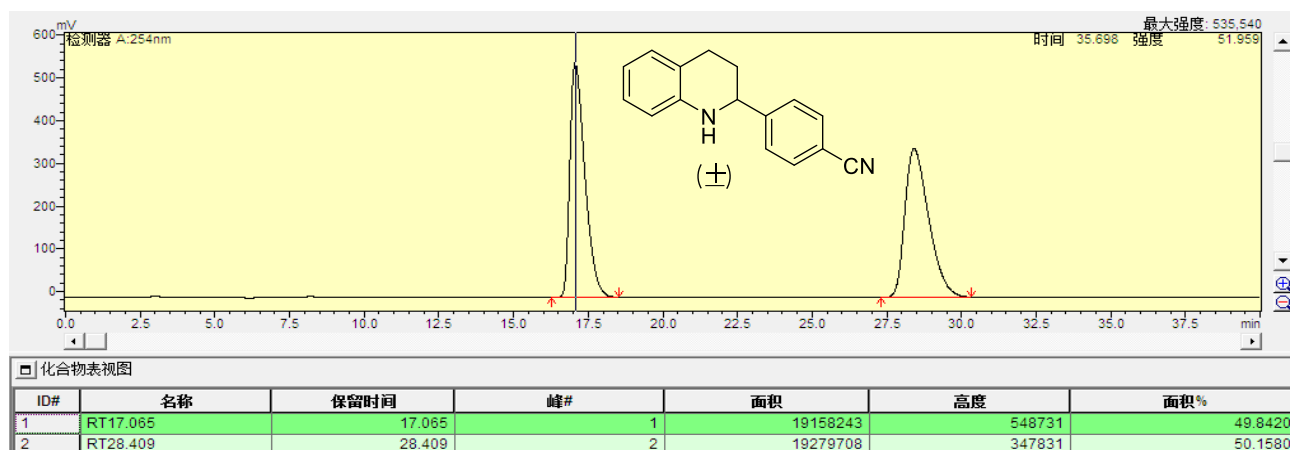
(S)-3c: (S)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



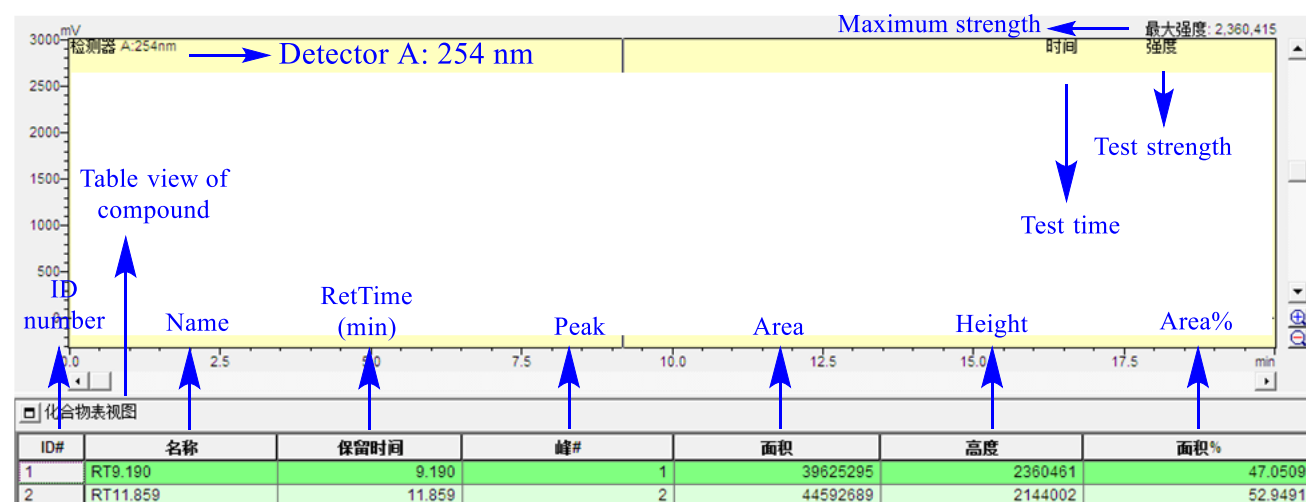
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



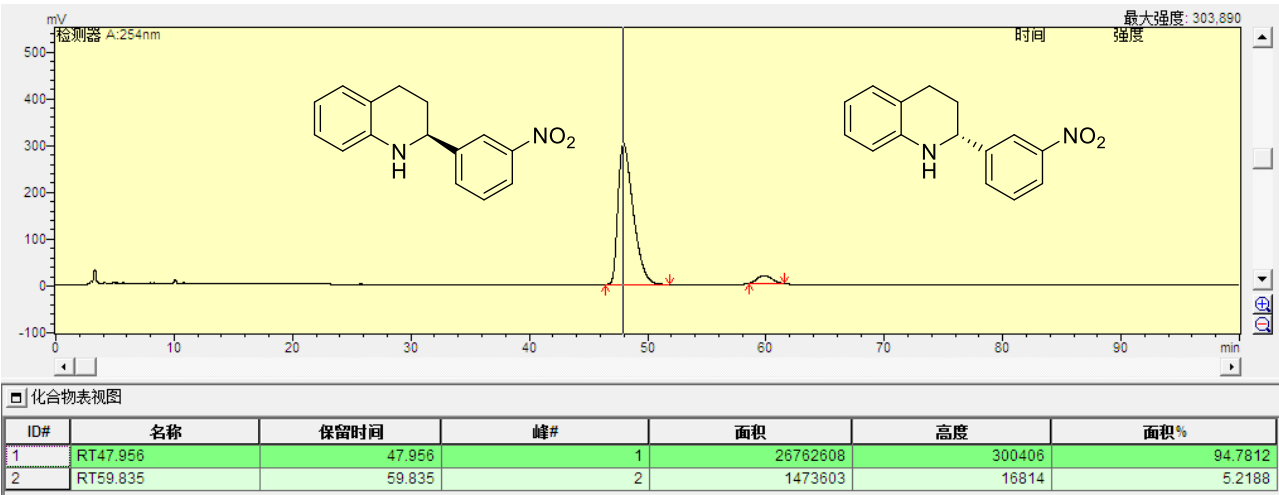
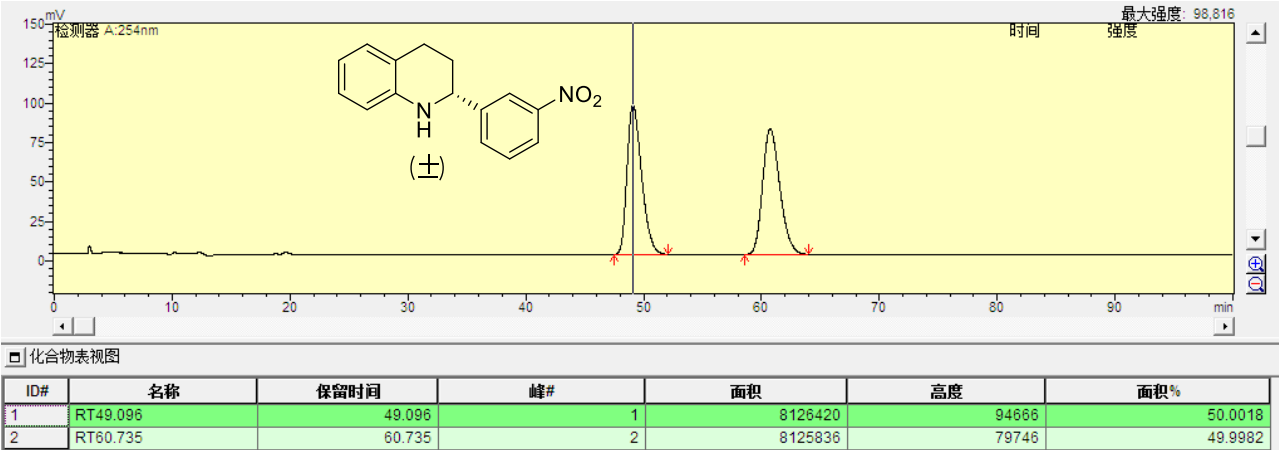
(S)-3d: (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzonitrile: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 80/20, flow rate = 1mL/min, 25 °C).



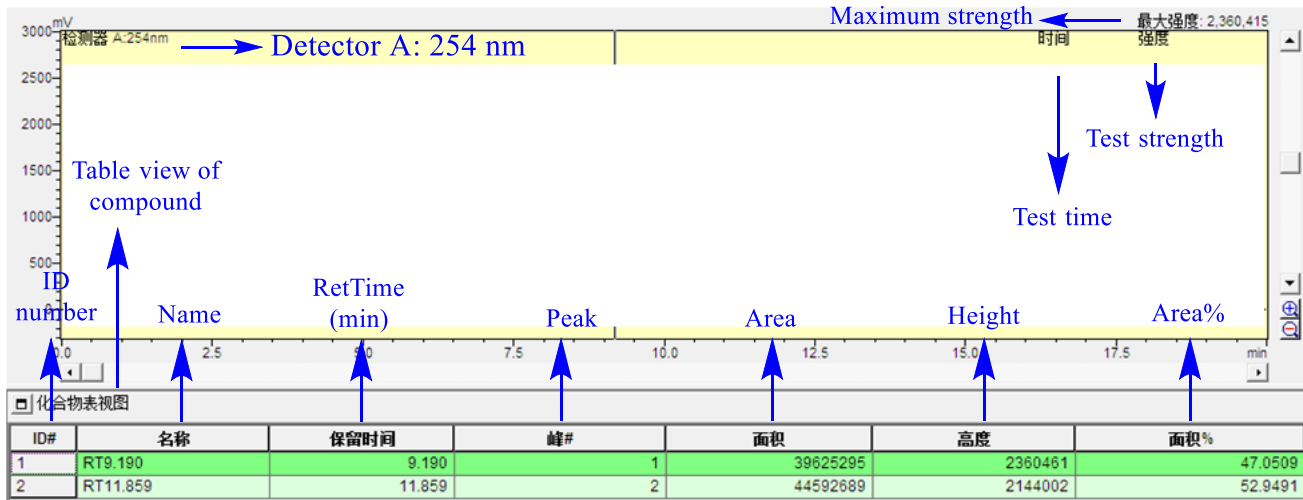
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



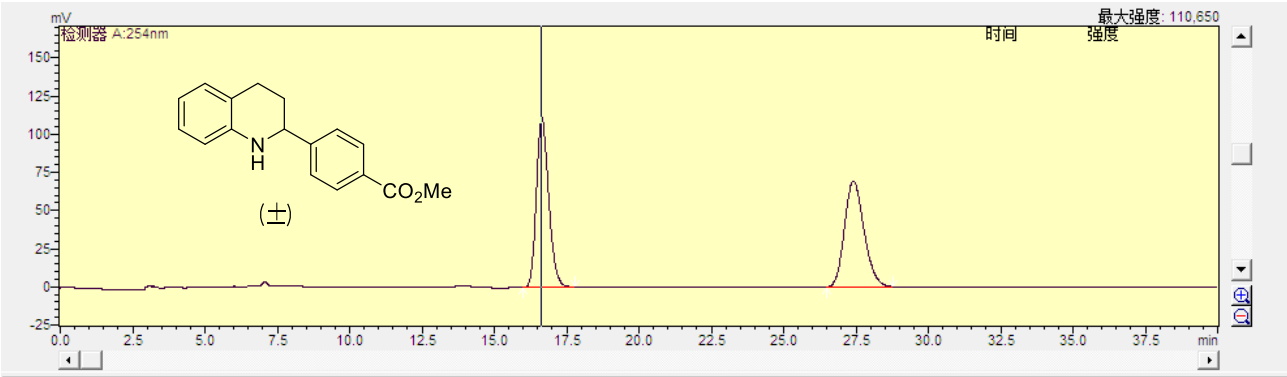
(S)-3e: (S)-2-(3-nitrophenyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



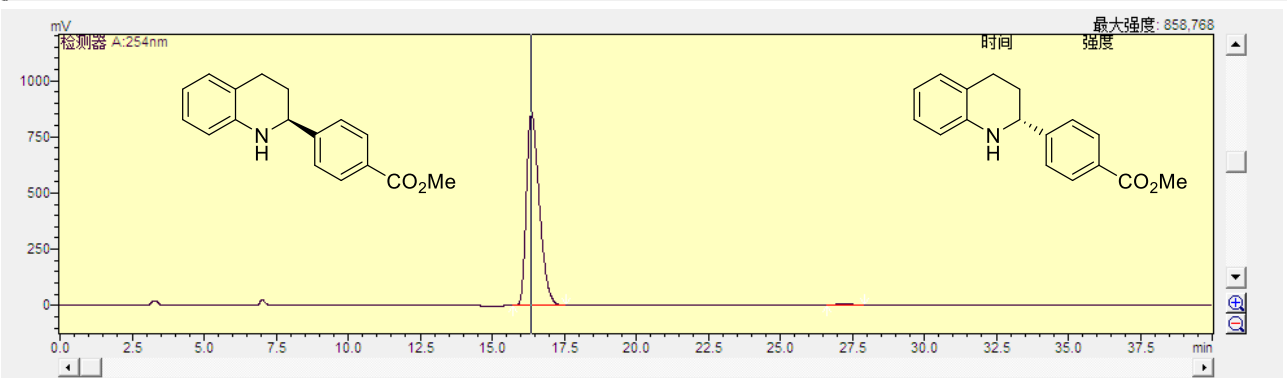
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



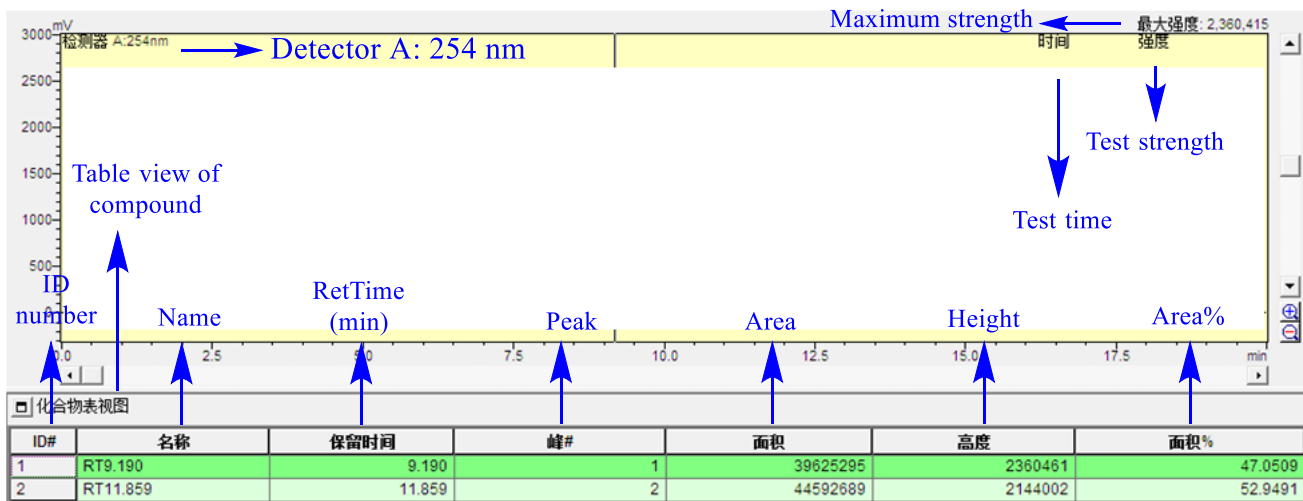
(S)-3f: methyl (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzoate.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT16.641	16.641	1	3271803	110804	50.1150
2	RT27.405	27.405	2	3256788	69497	49.8850

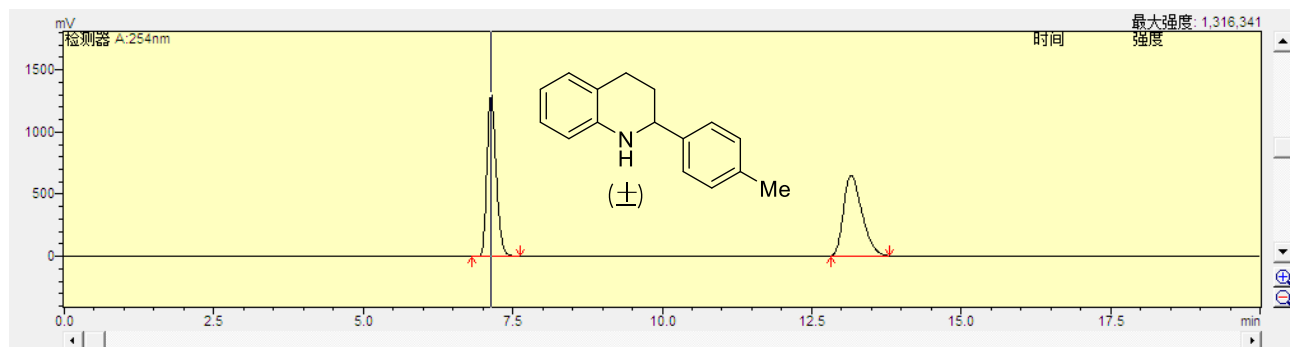


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT16.366	16.366	1	26766476	858838	99.0611
2	RT27.195	27.195	2	253705	6361	0.9389

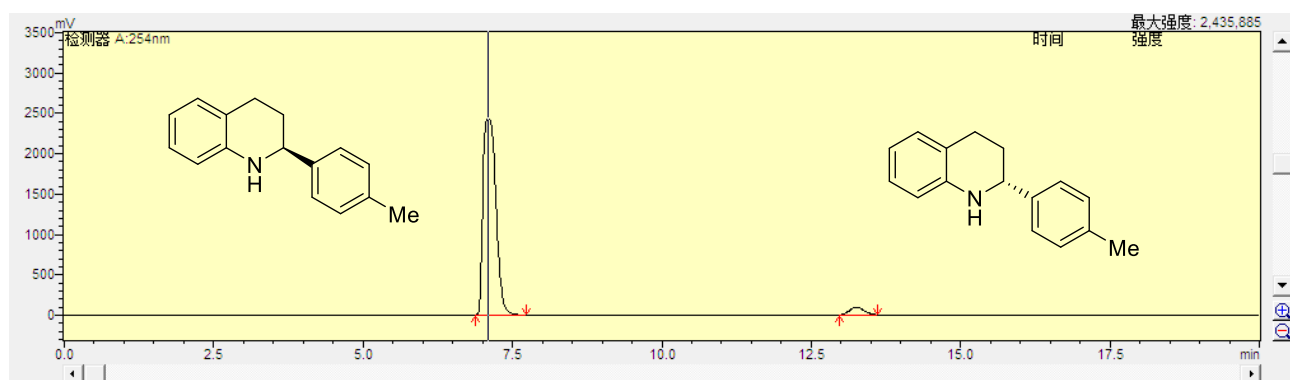


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.190	9.190	1	39625295	2360461	47.0509
2	RT11.859	11.859	2	44592689	2144002	52.9491

(S)-3g: (S)-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).

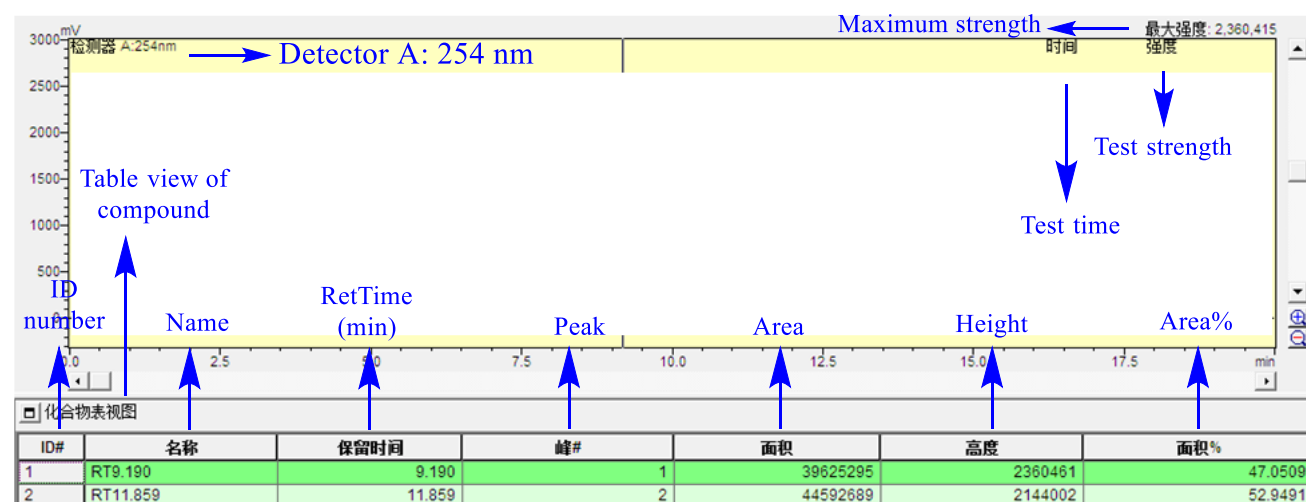


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT7.132	7.132	1	14089864	1317752	50.0993
2	RT13.154	13.154	2	14034007	647553	49.9007

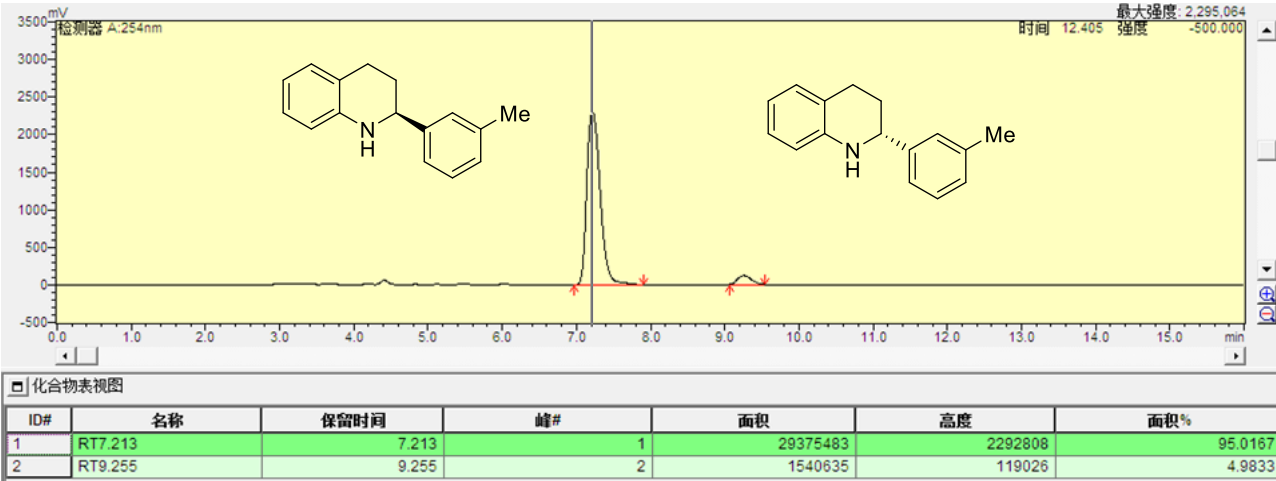
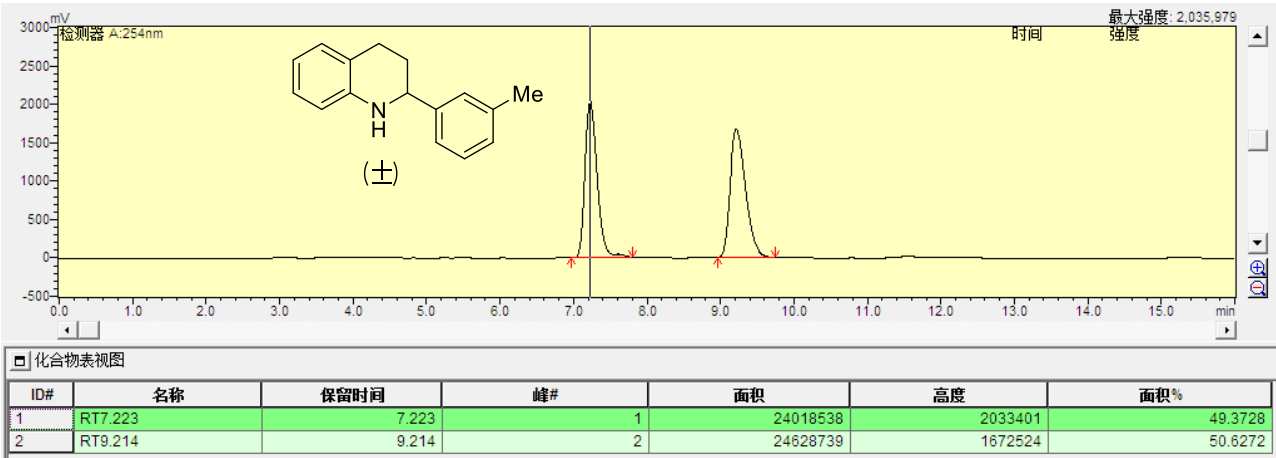


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT7.087	7.087	1	36645117	2435607	95.6481
2	RT13.251	13.251	2	1667328	96781	4.3519

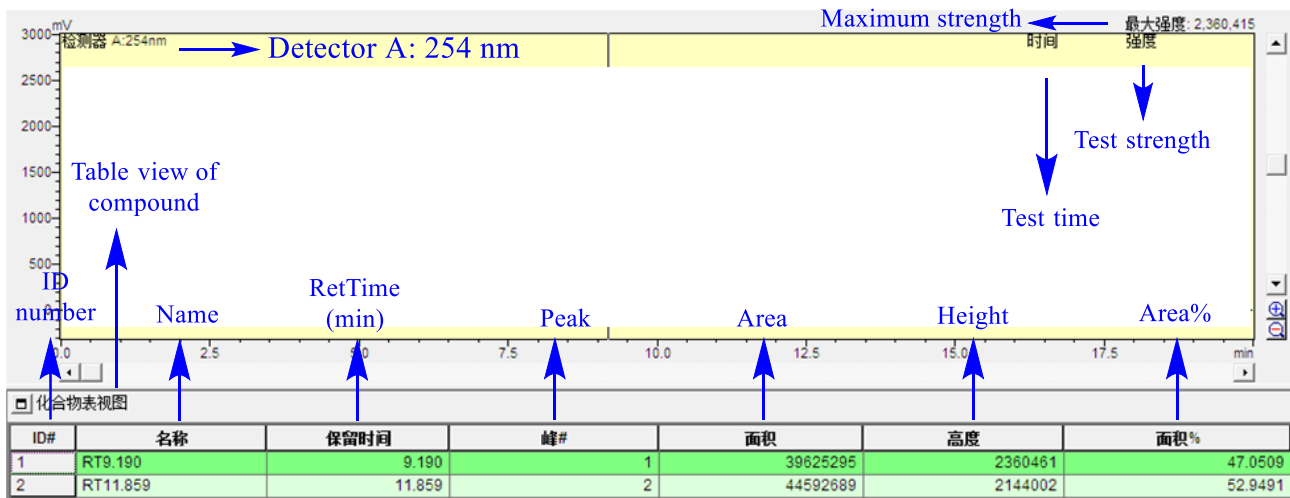
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



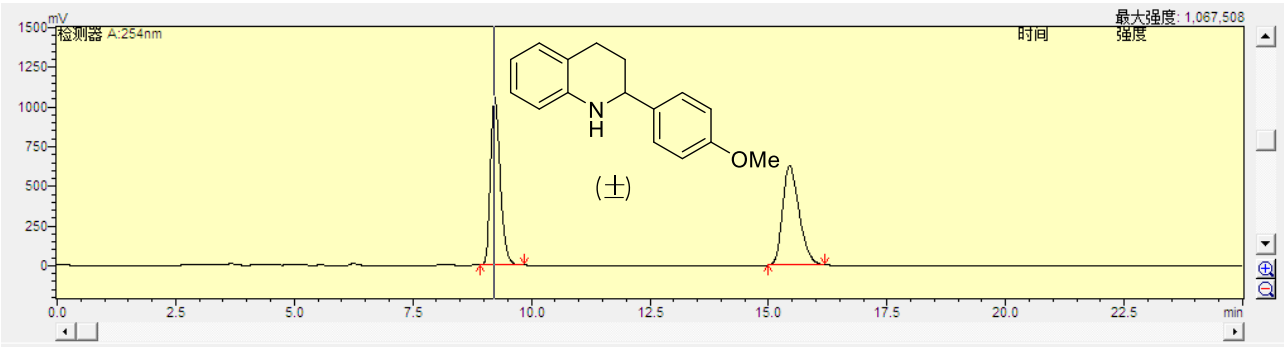
(S)-3h: (S)-2-(m-tolyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



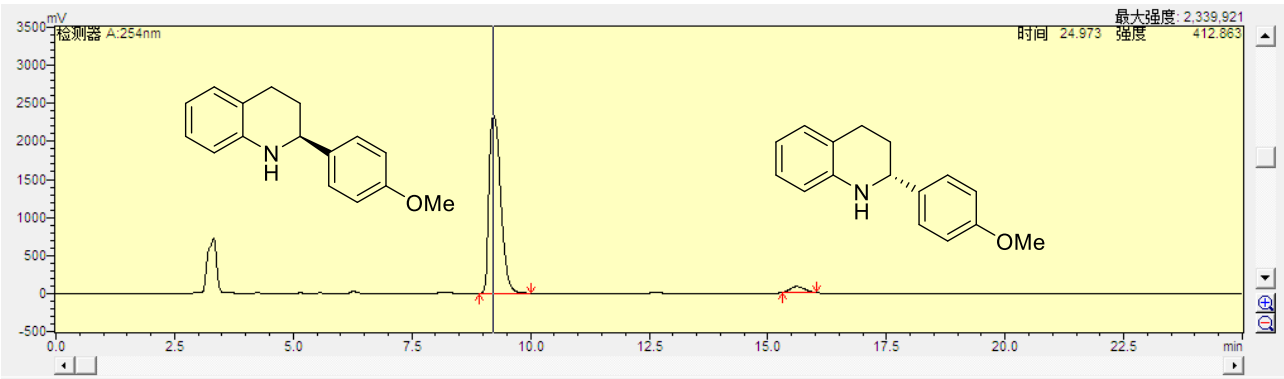
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(S)-3i: (S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).

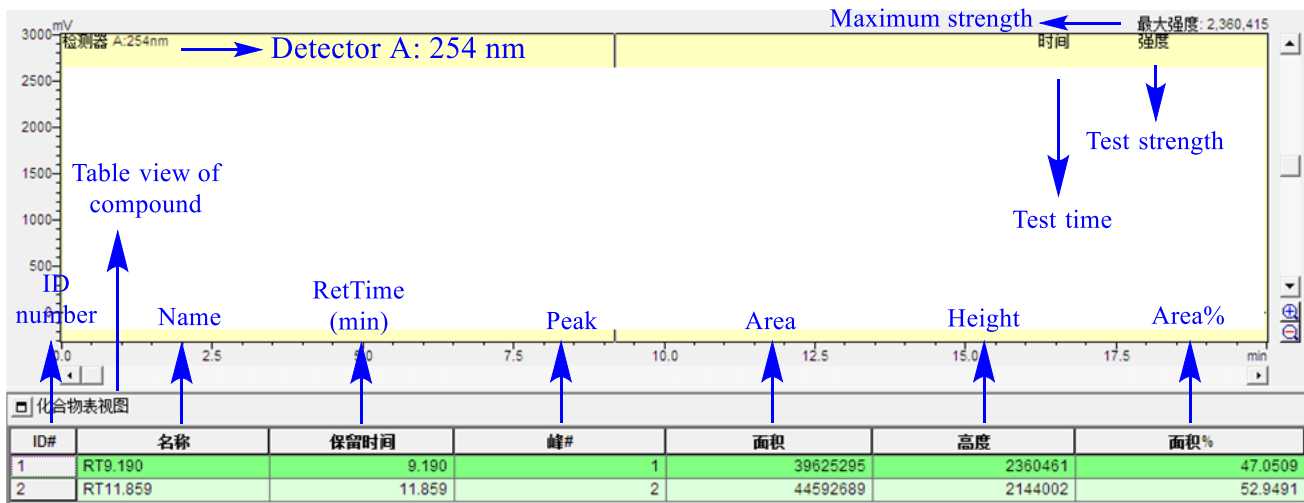


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.222	9.222	1	15186047	1063229	49.9242
2	RT15.442	15.442	2	15232185	624860	50.0758

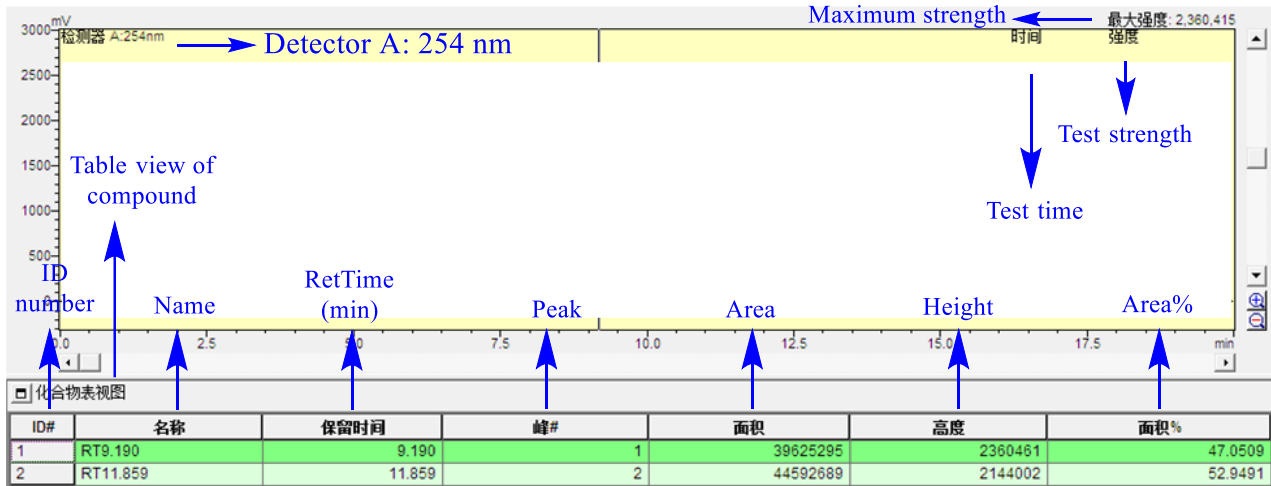
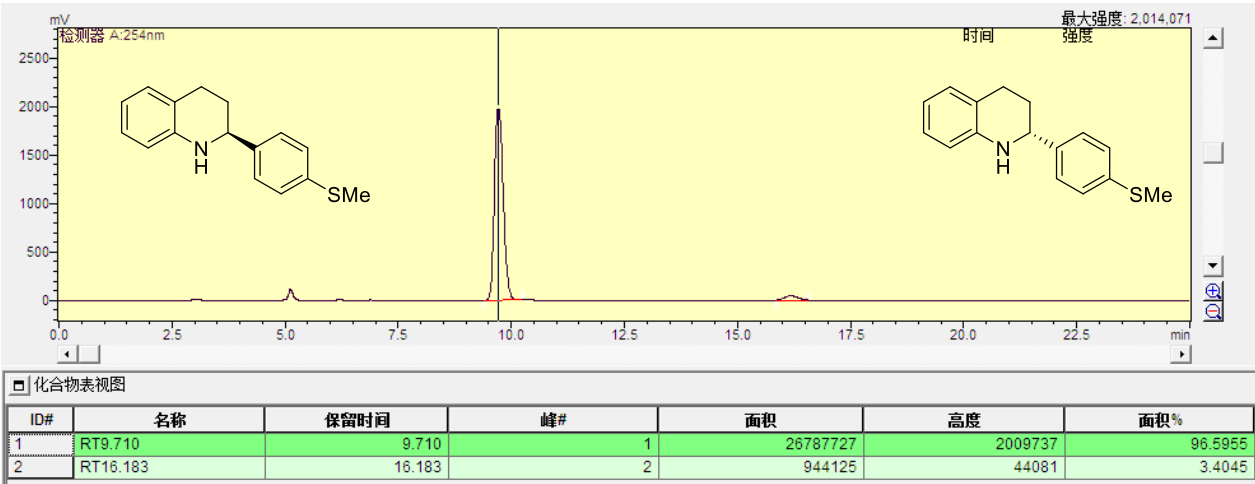
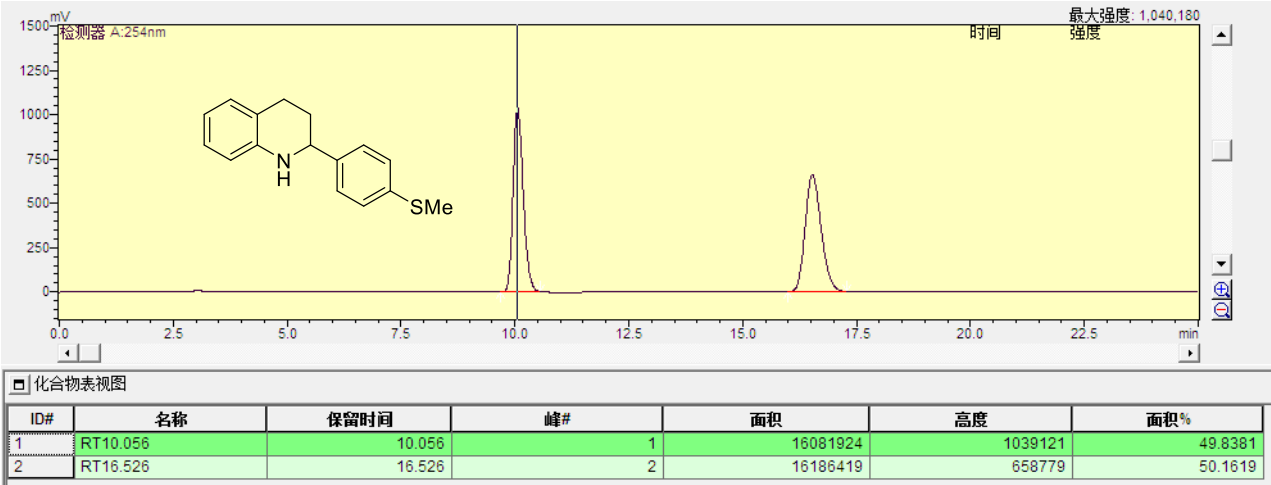


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.218	9.218	1	40114723	2336032	95.9625
2	RT15.607	15.607	2	1687786	79513	4.0375

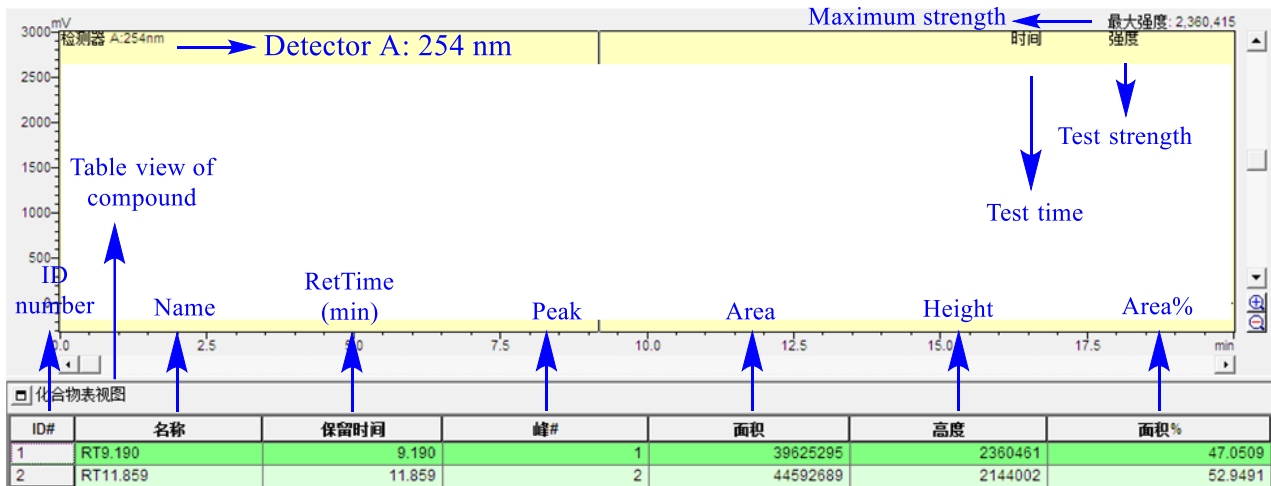
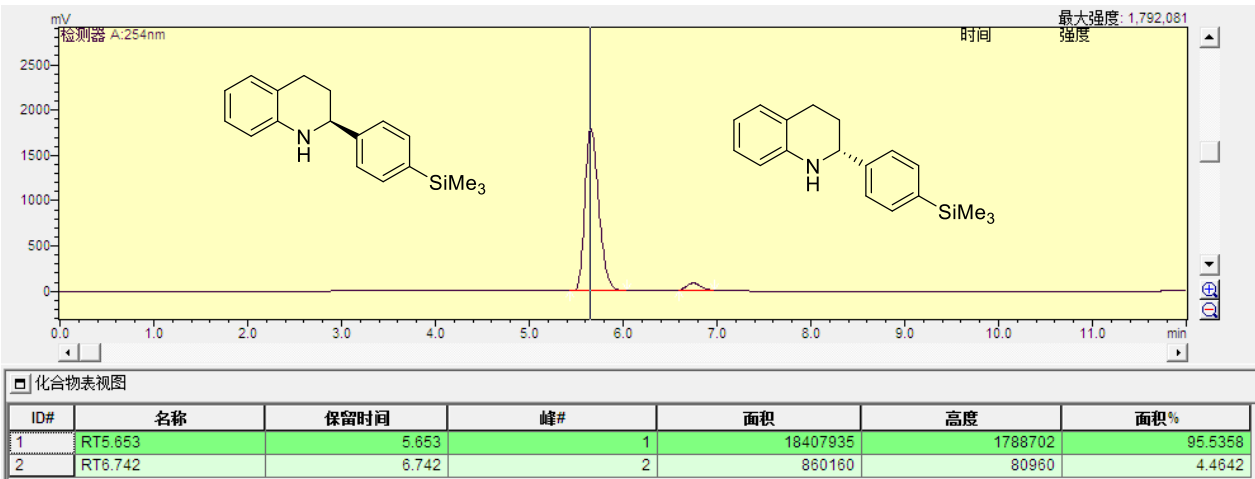
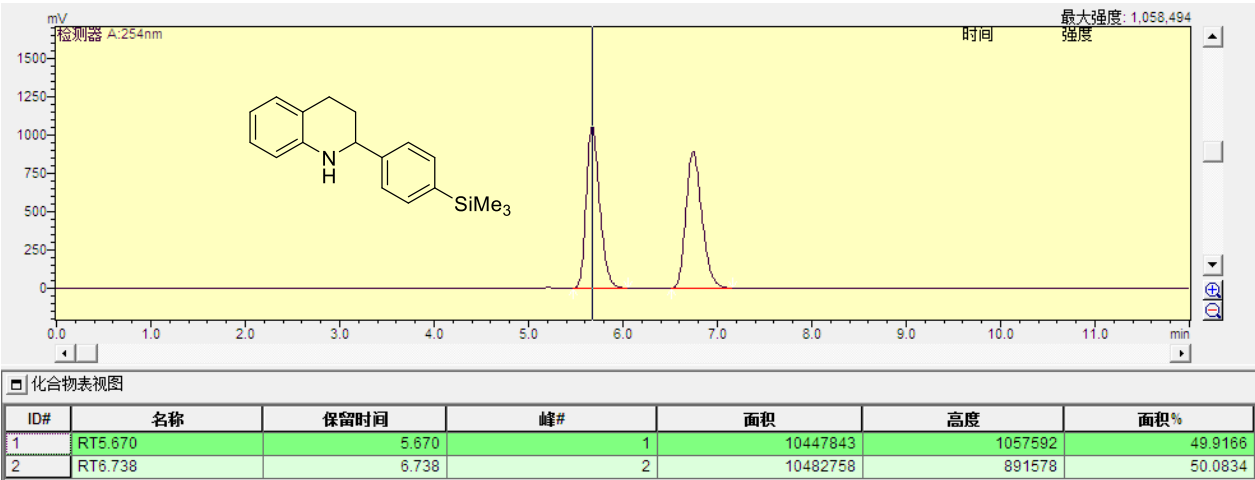
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



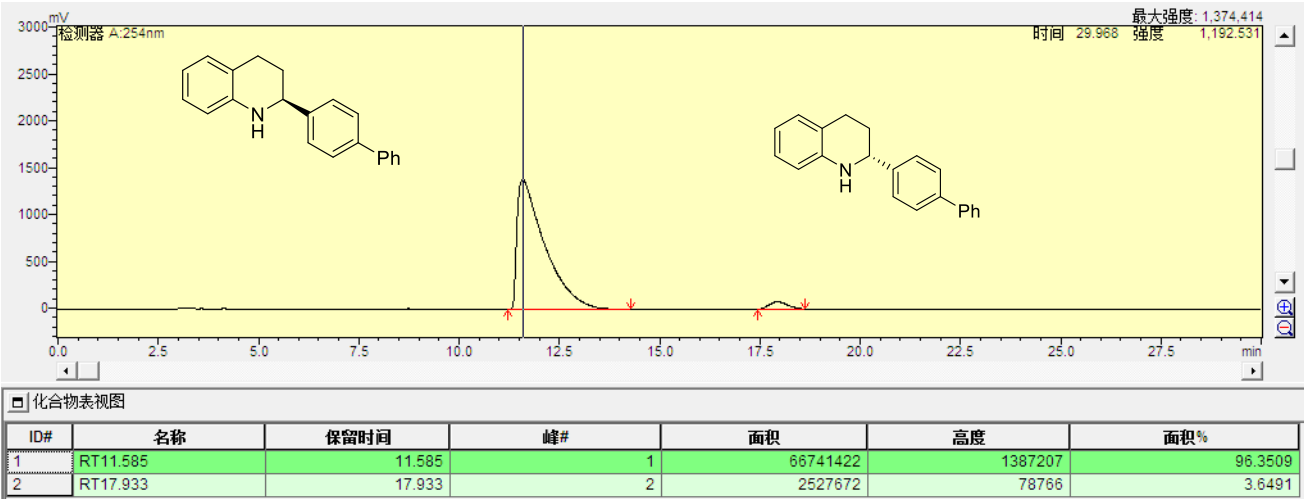
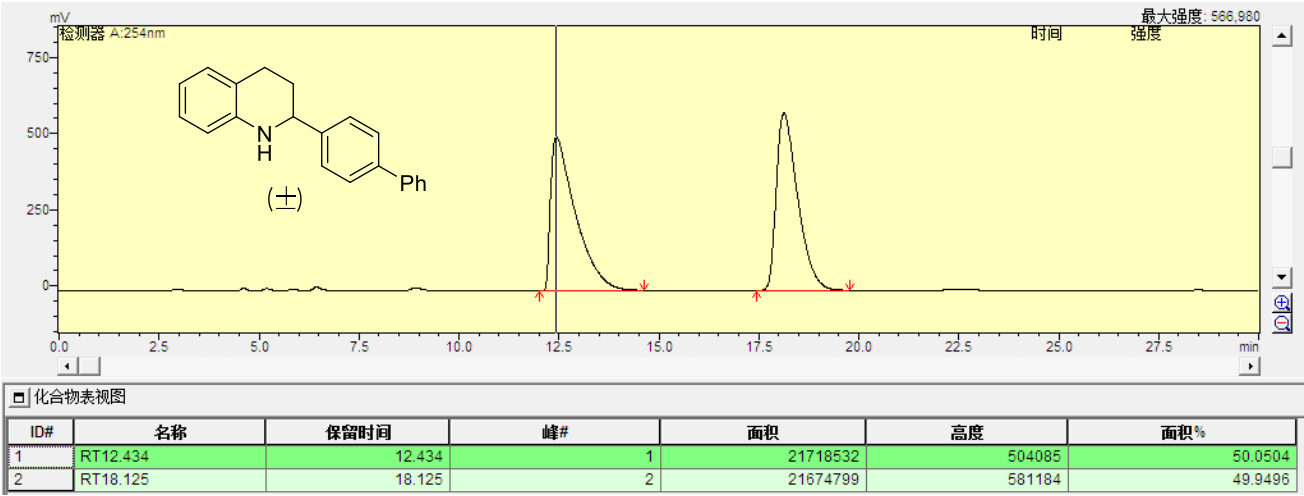
(S)-3j: (S)-2-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



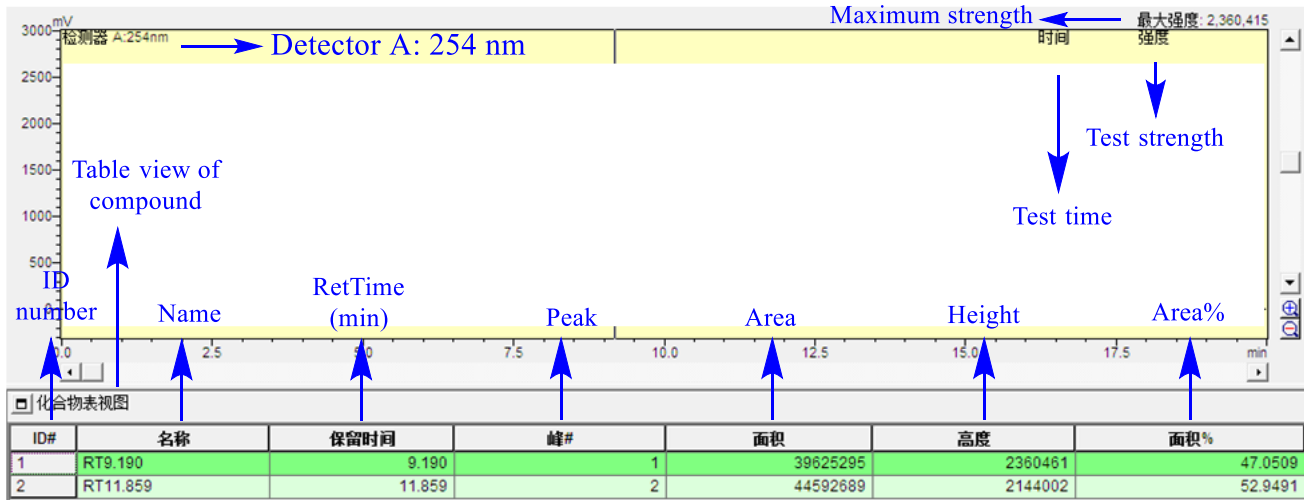
(S)-3k: (S)-2-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



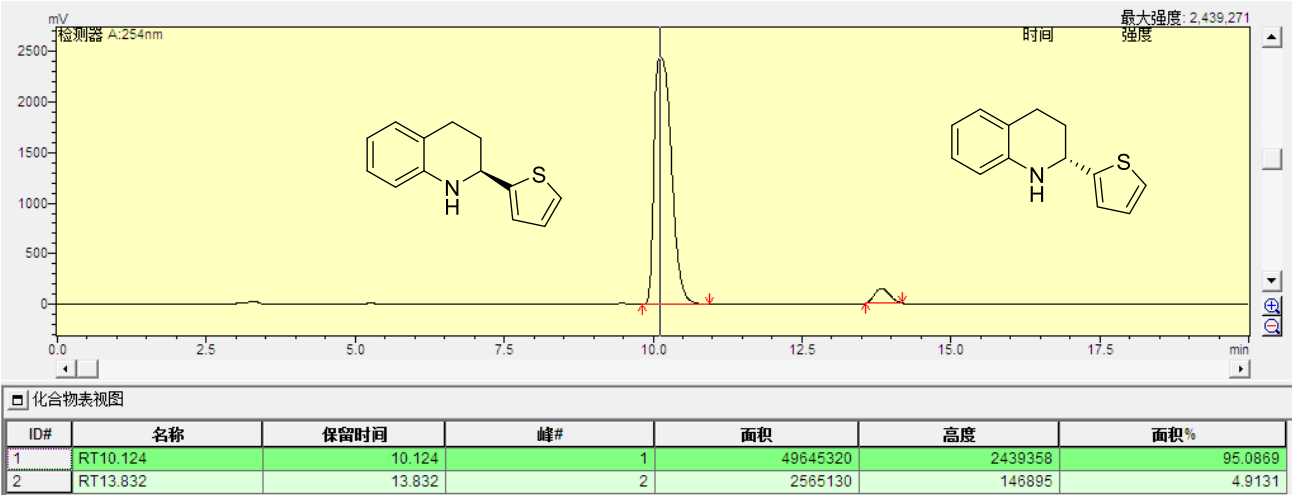
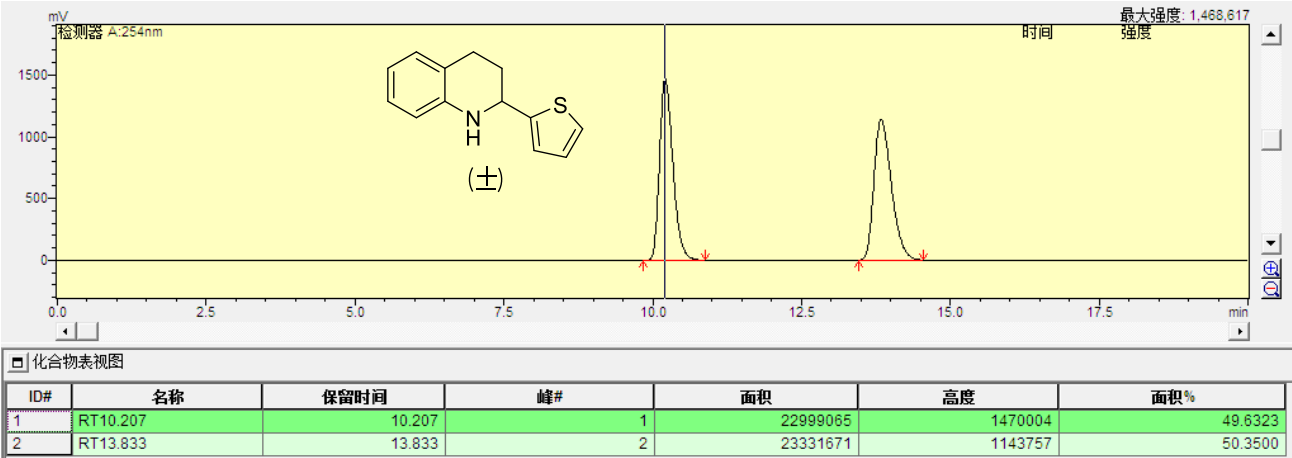
(S)-3l: (S)-2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



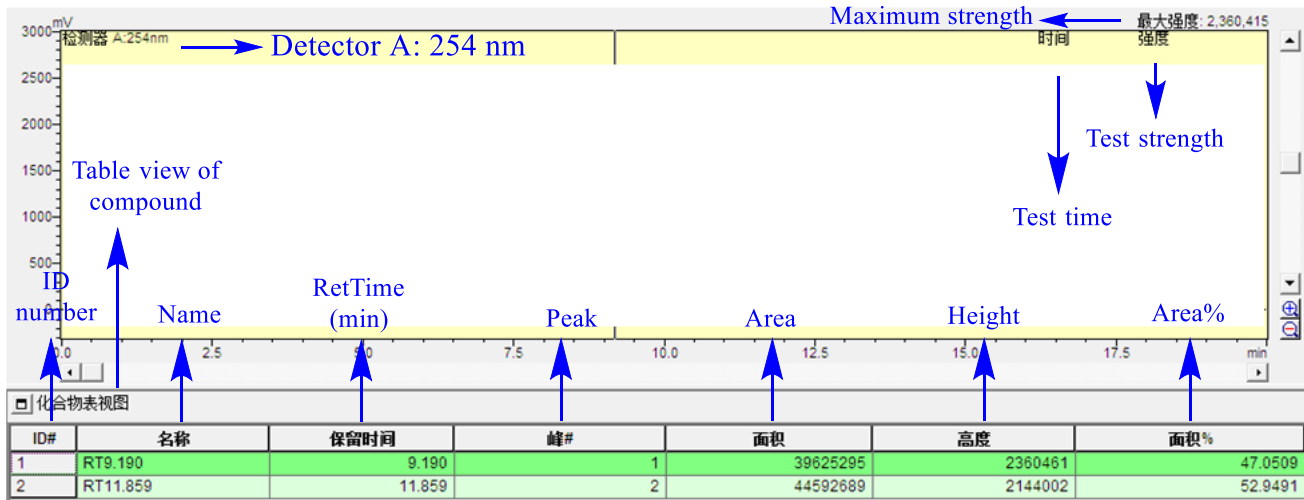
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



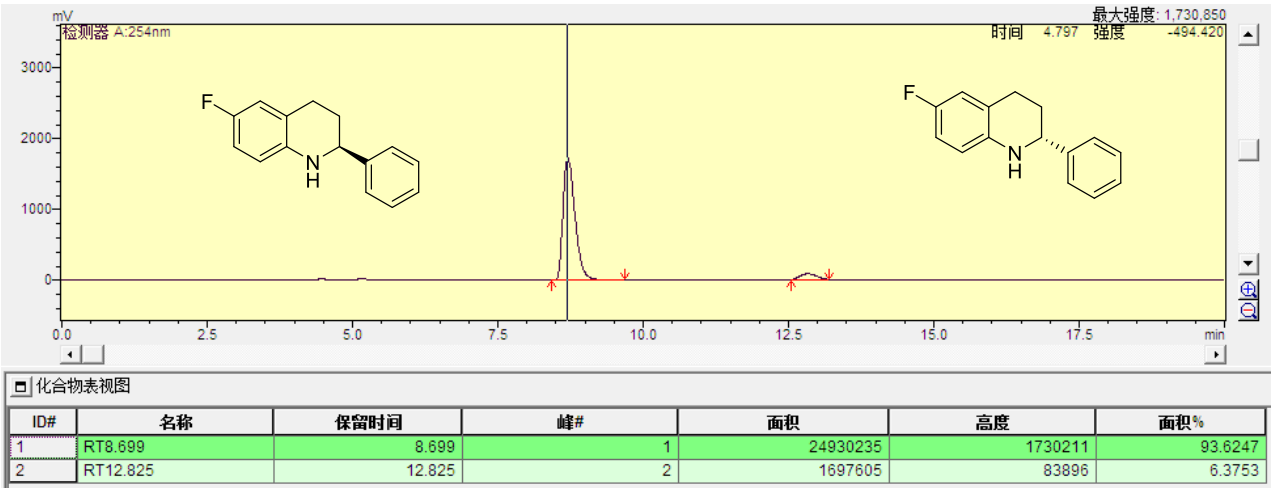
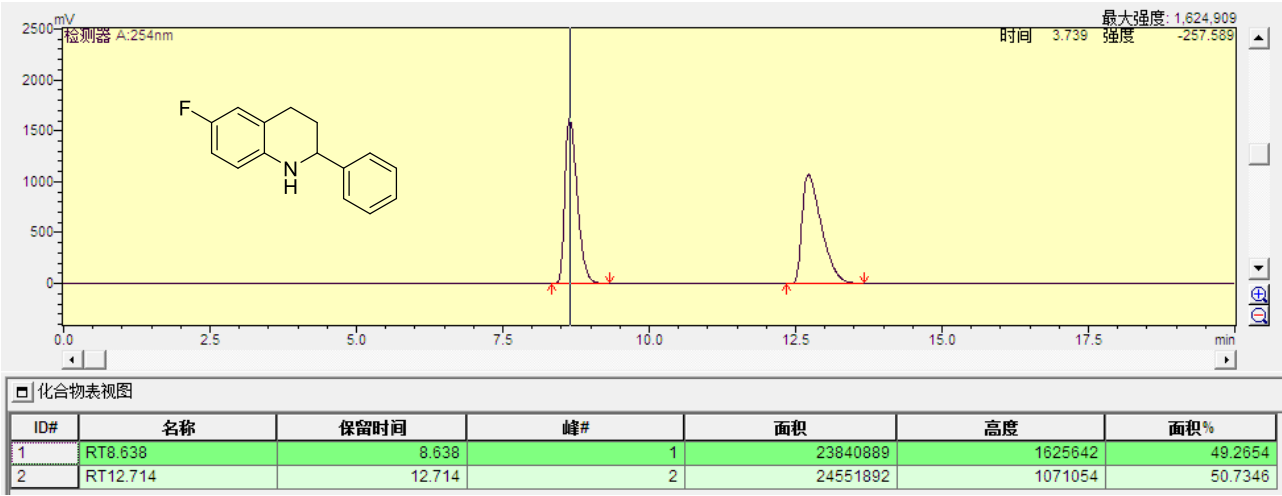
(S)-3m: (S)-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1mL/min, 25 °C).



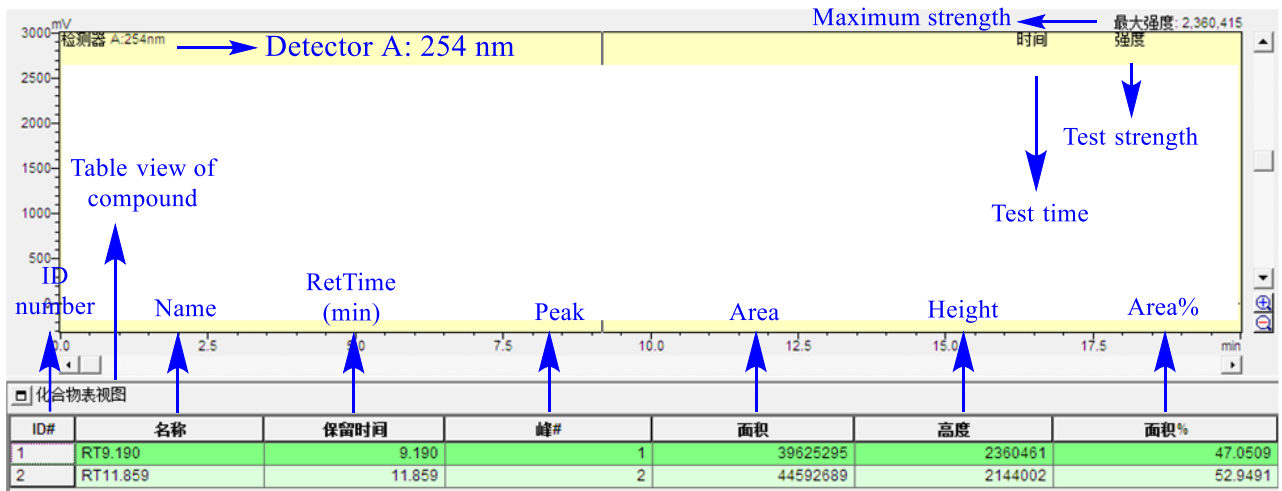
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



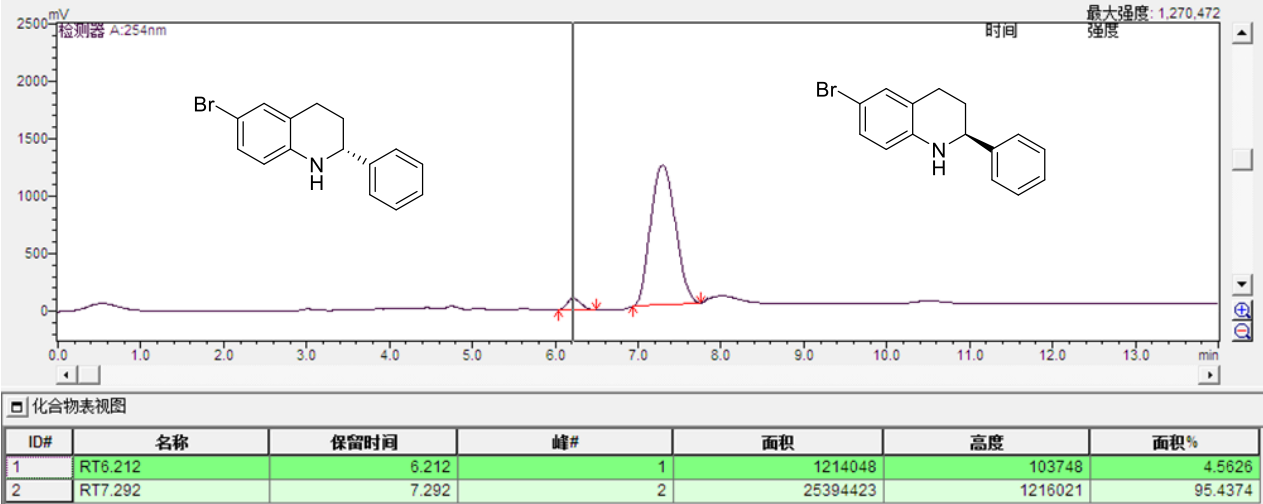
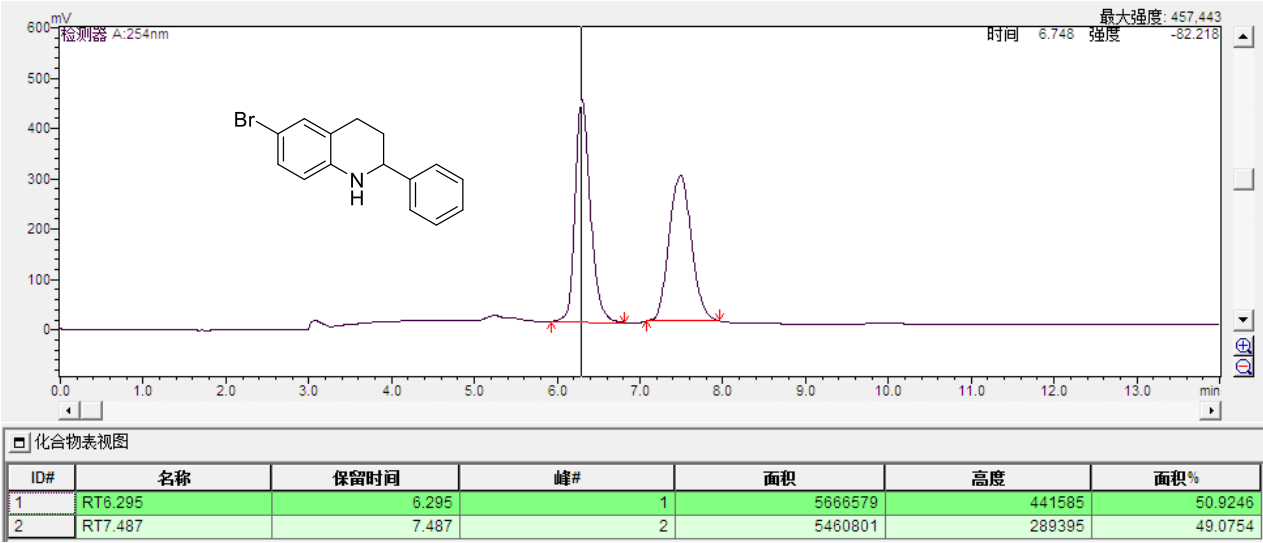
(S)-3n: (S)-6-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



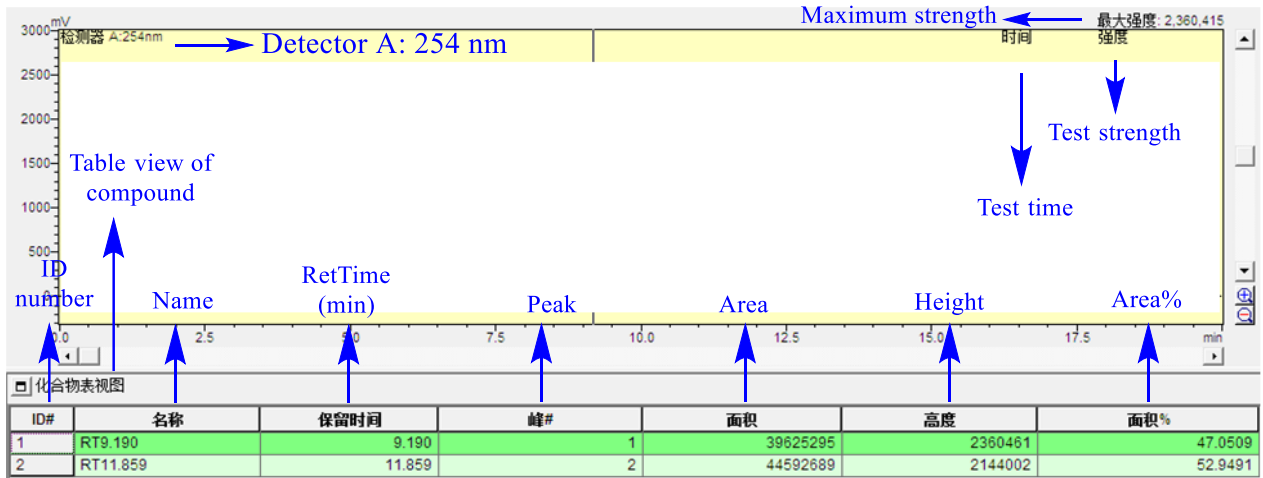
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



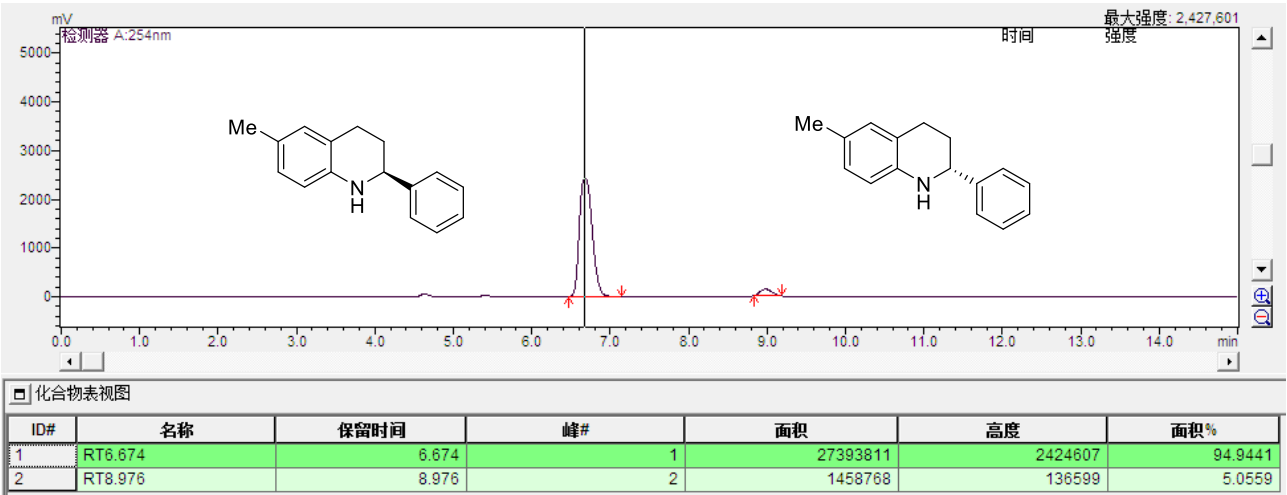
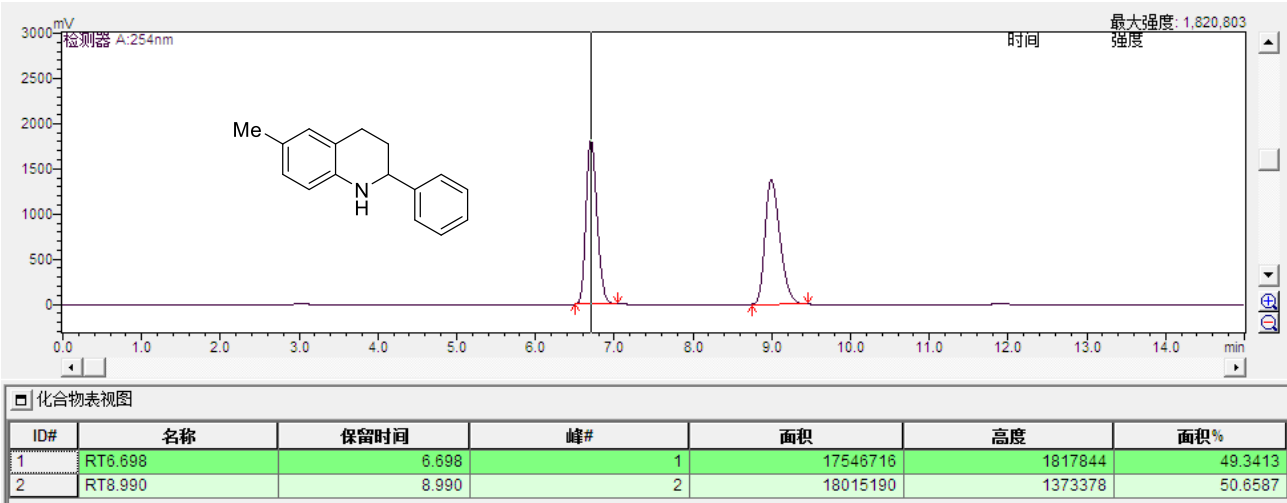
(S)-3o: (S)-6-bromo-2-phenyl-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



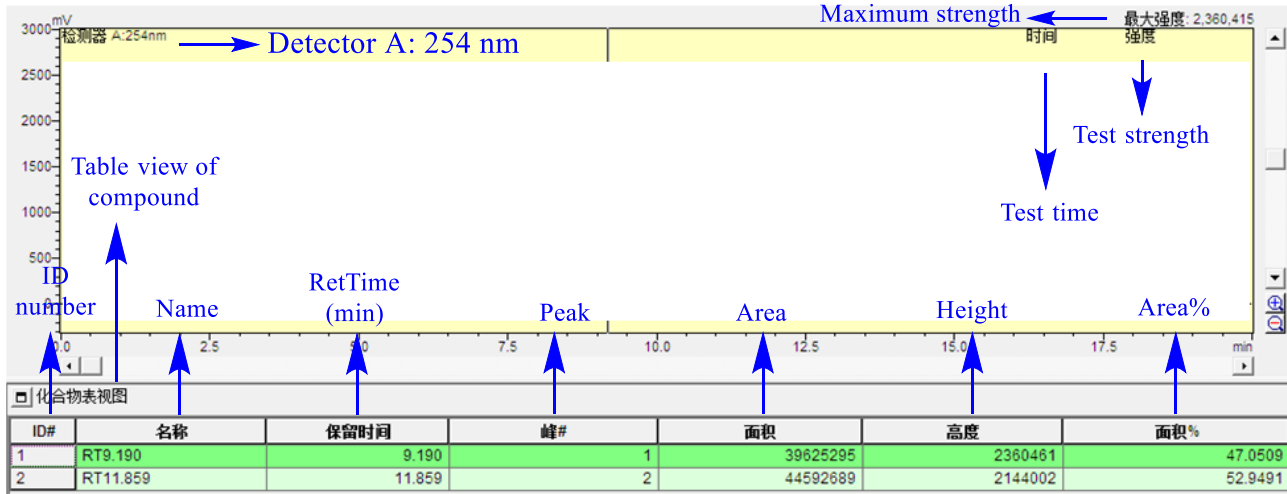
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



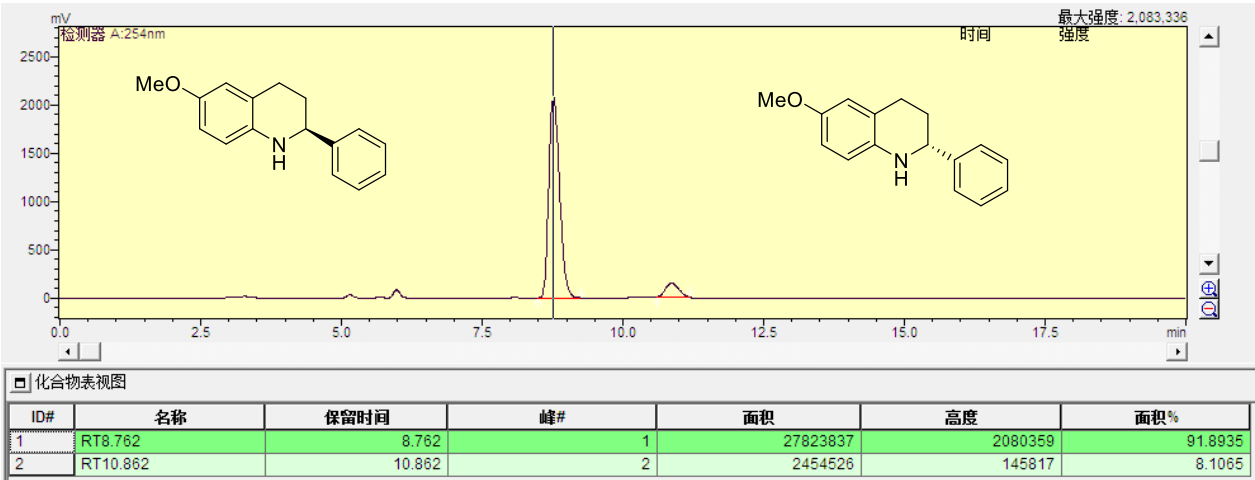
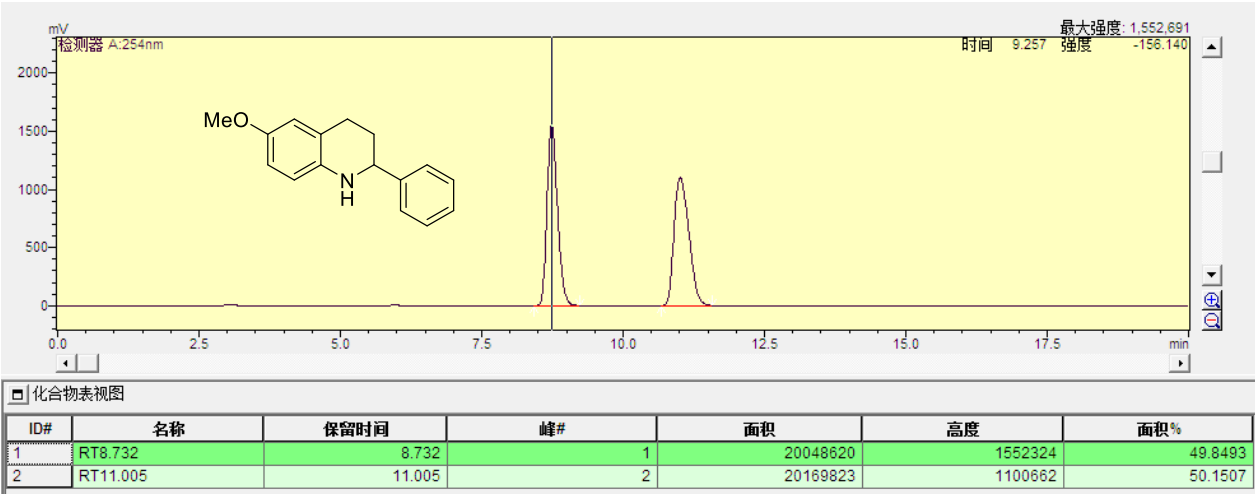
(S)-3p: (S)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



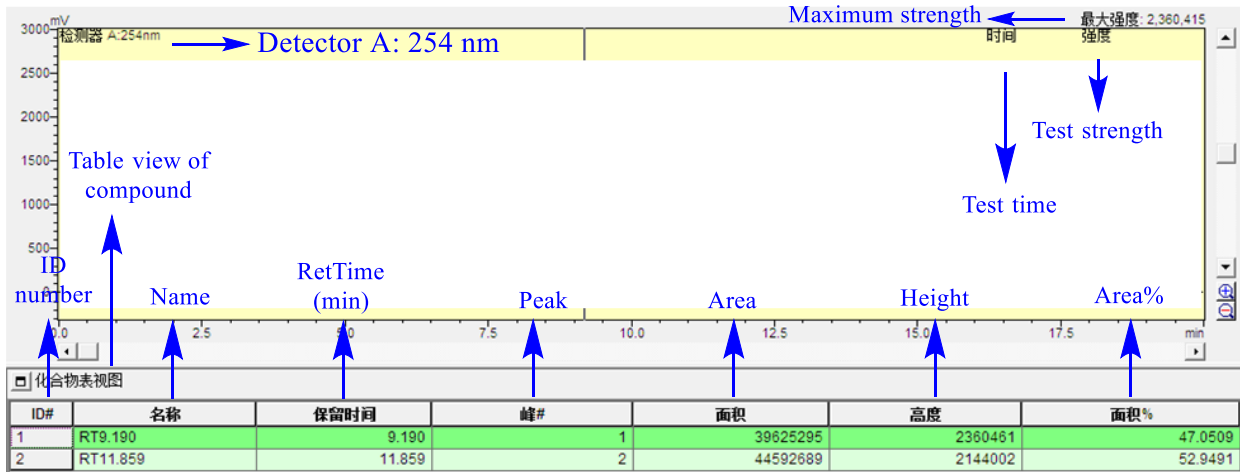
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



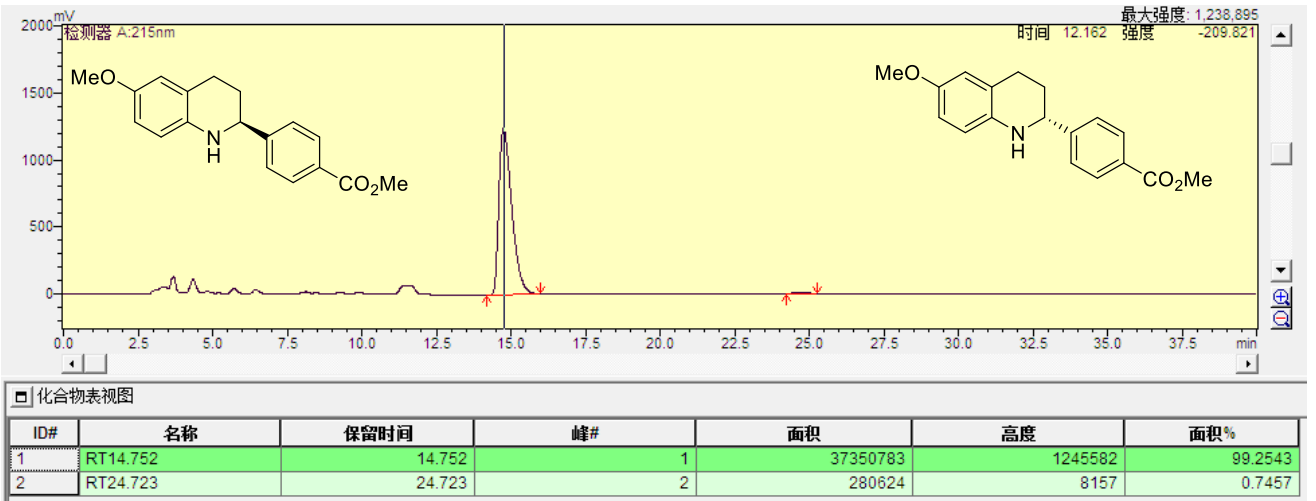
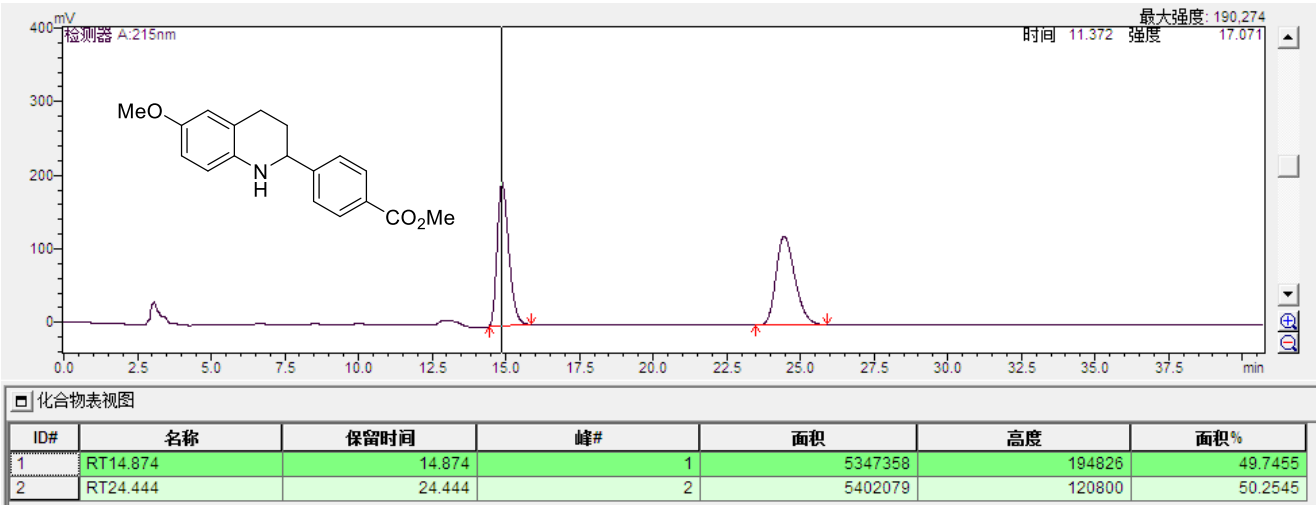
(S)-3q: (S)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



Translation of all characters (Chinese) in the above two frameworks to English is as follows:



(S)-3r: methyl (S)-4-(6-methoxy-1,2,3,4-tetrahydroquinolin-2-yl)benzoate.: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25 °C).



Translation of all characters (Chinese) in the above two frameworks to English is as follows:

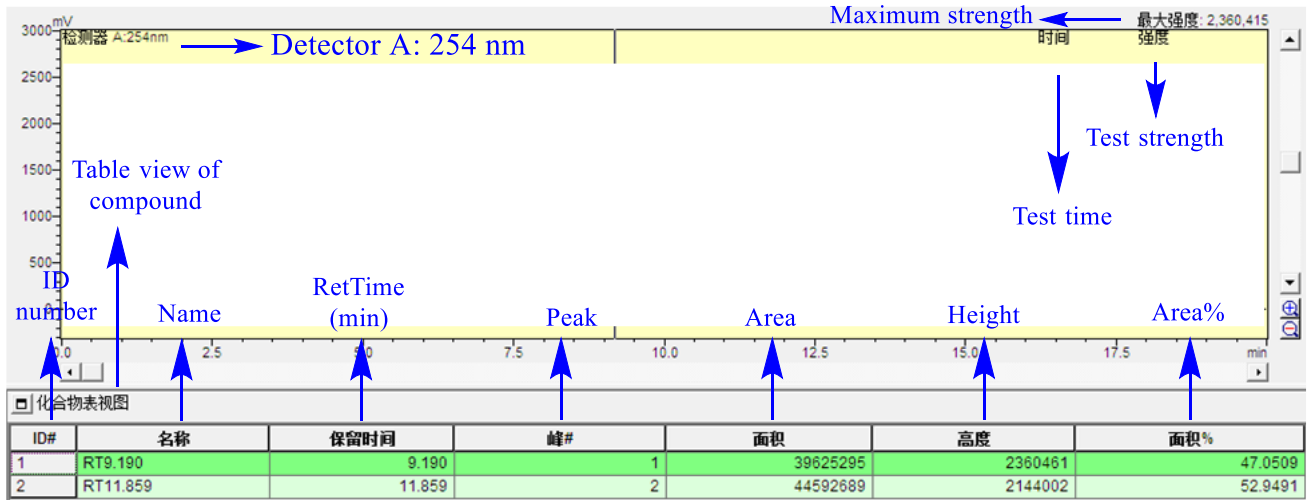
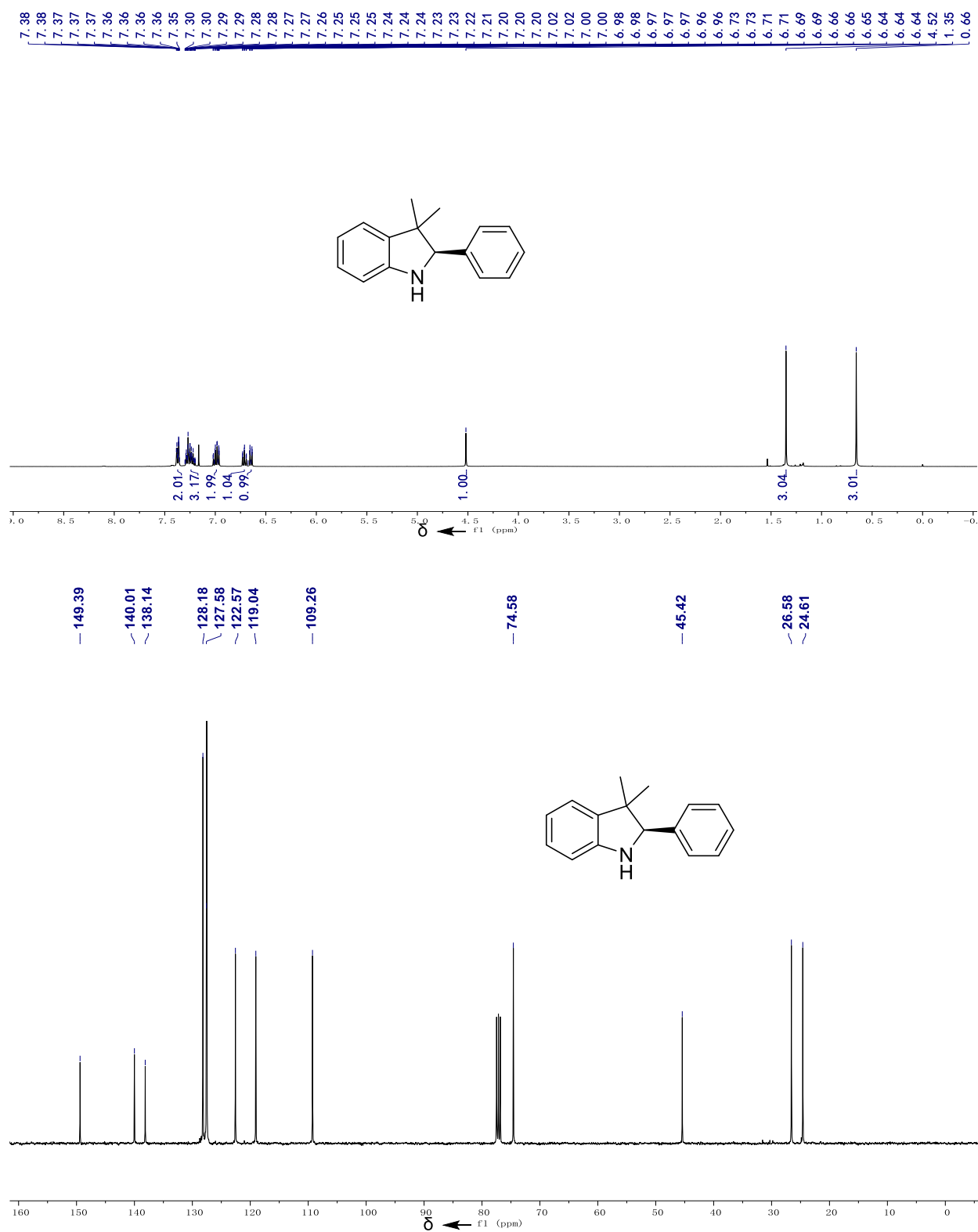
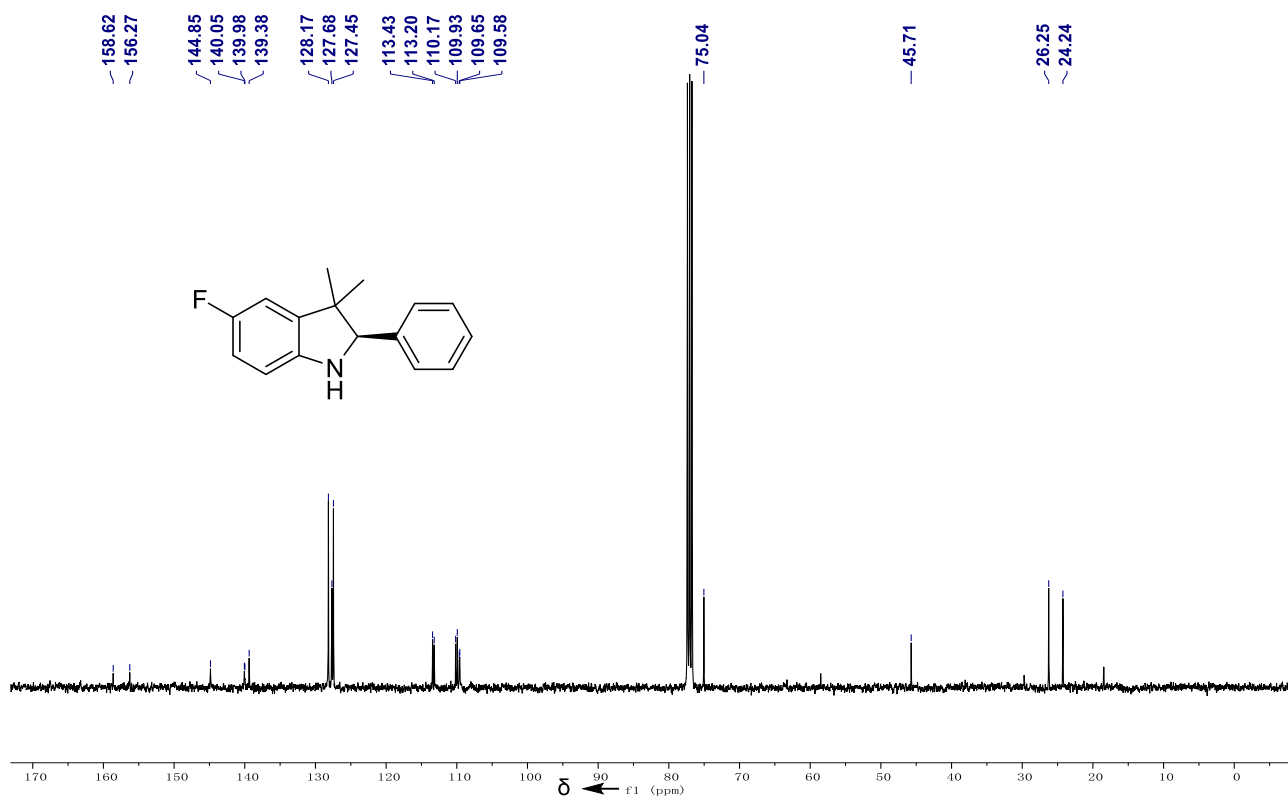
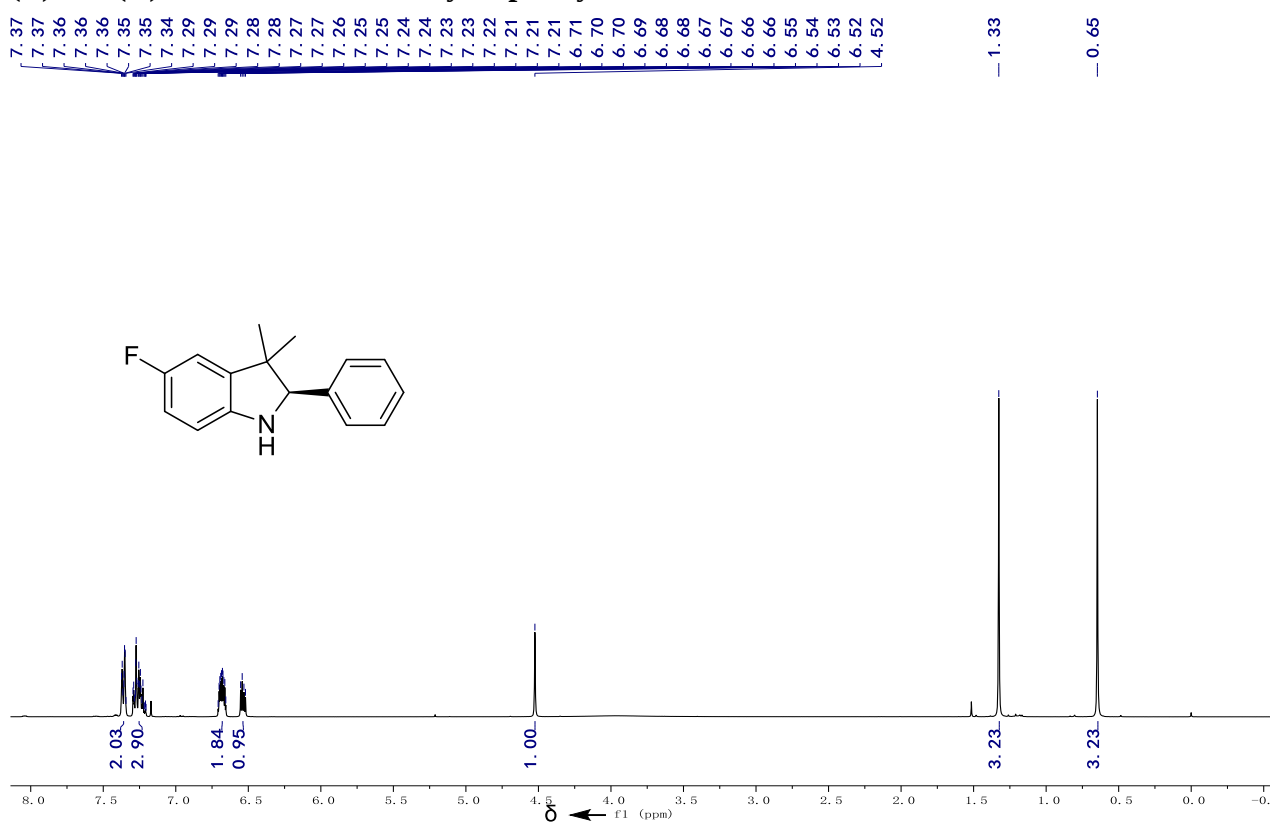


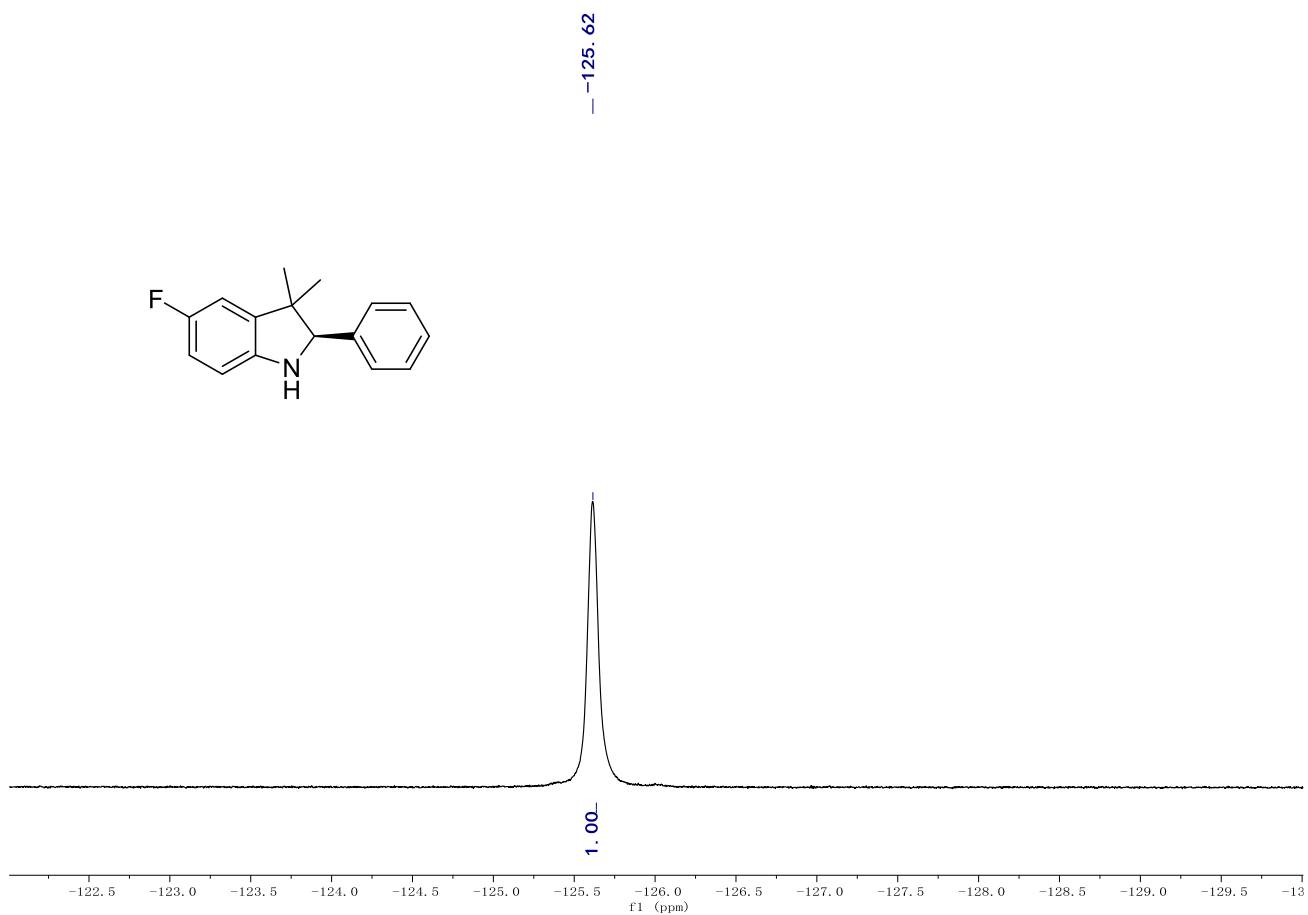
Figure S5. Characterization of chiral products (The ^1H NMR and ^{13}C NMR spectra of all chiral products).

(R)-1a: (R)-3,3-dimethyl-2-phenylindoline.

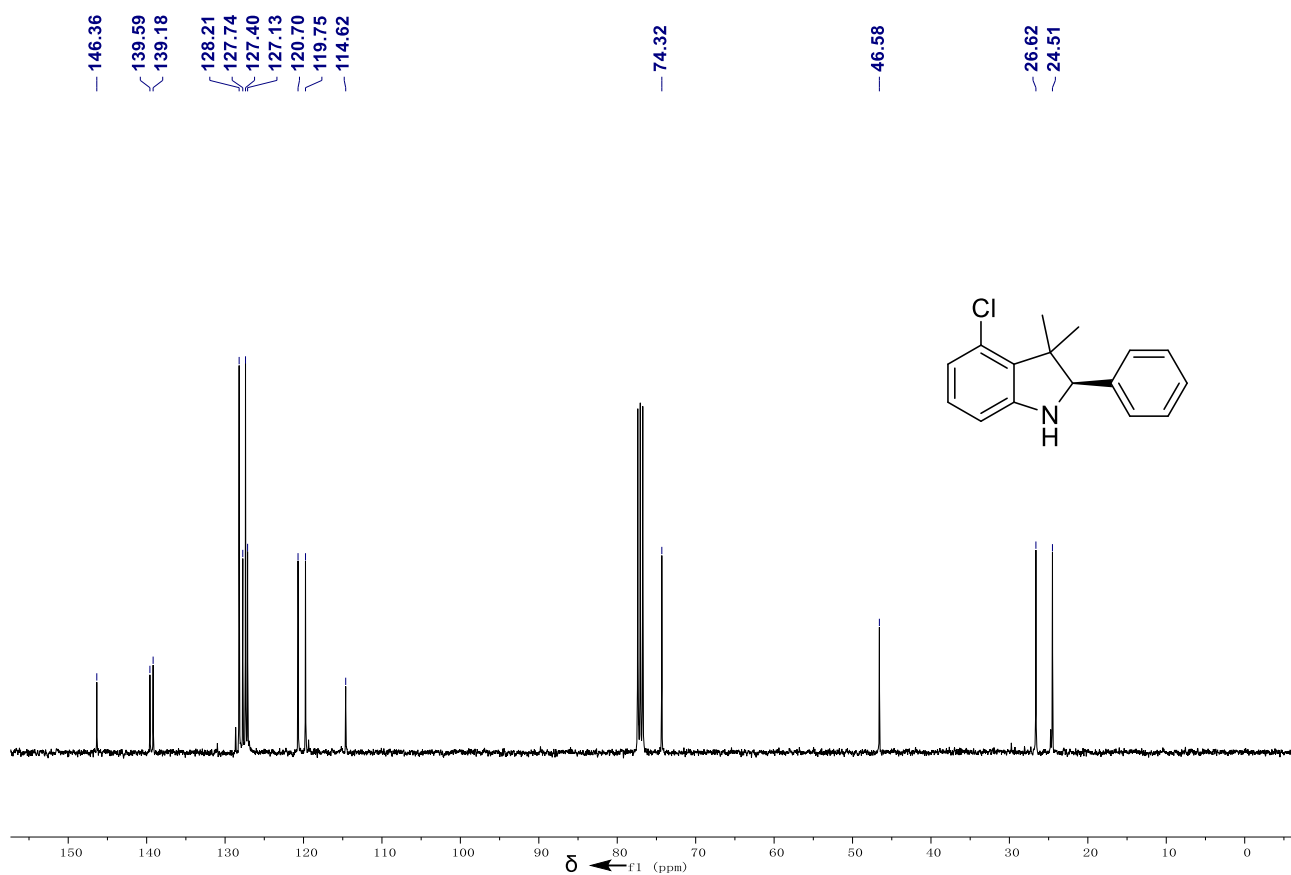
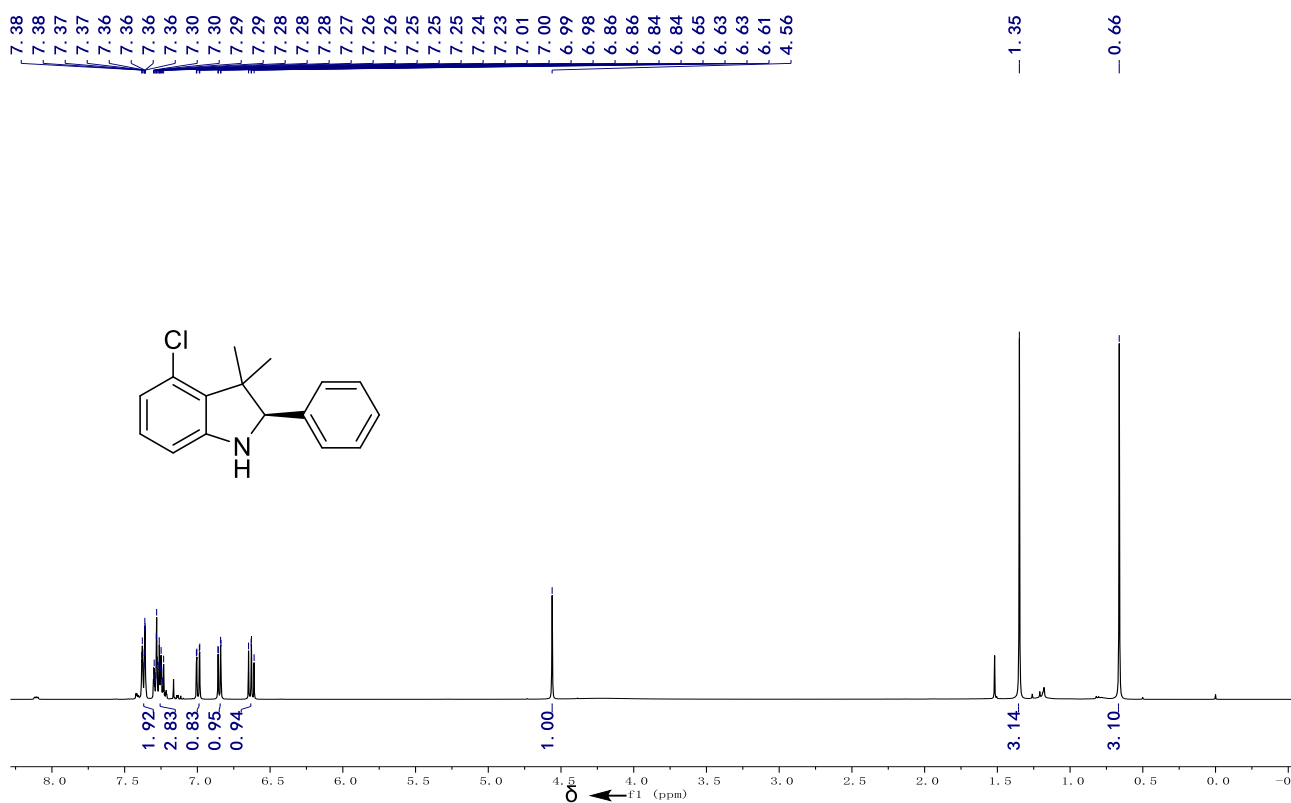


(R)-1b: (R)- 5-fluoro-3,3-dimethyl-2-phenylindoline.

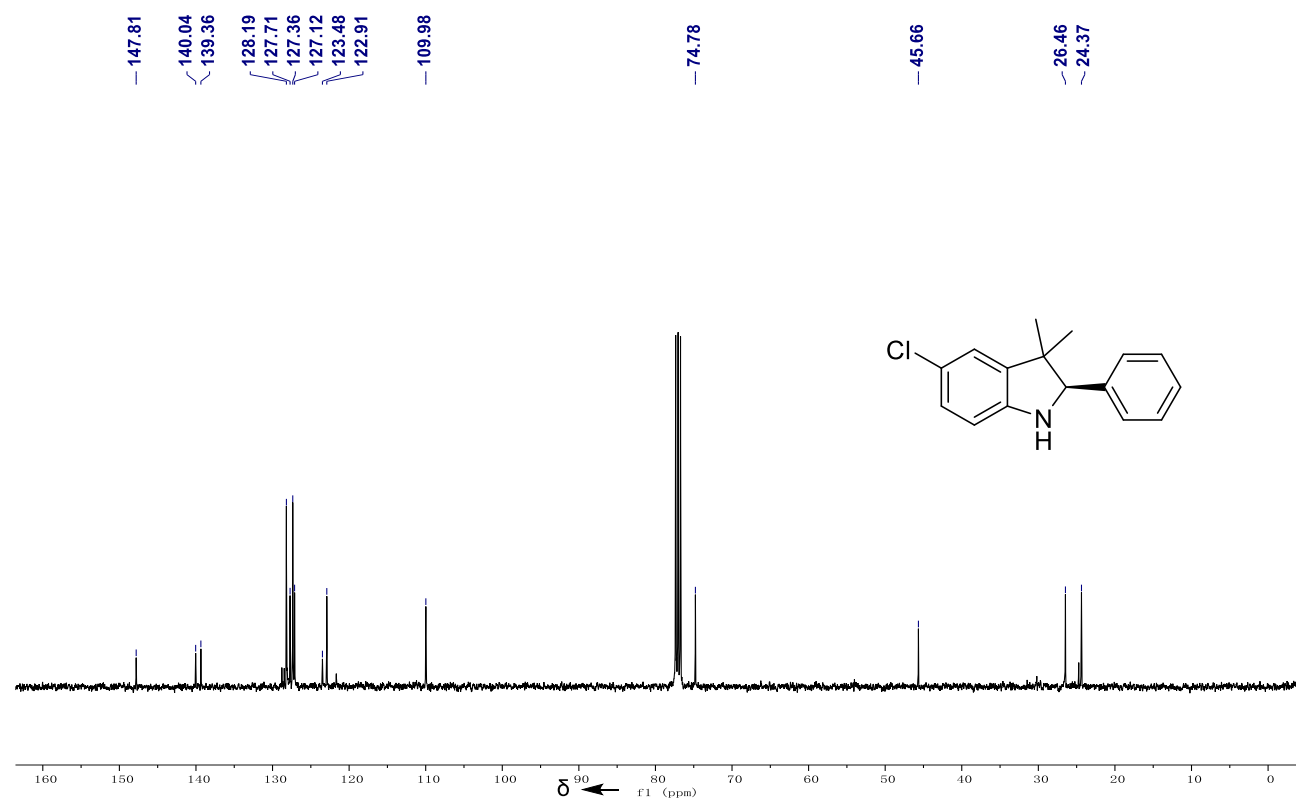
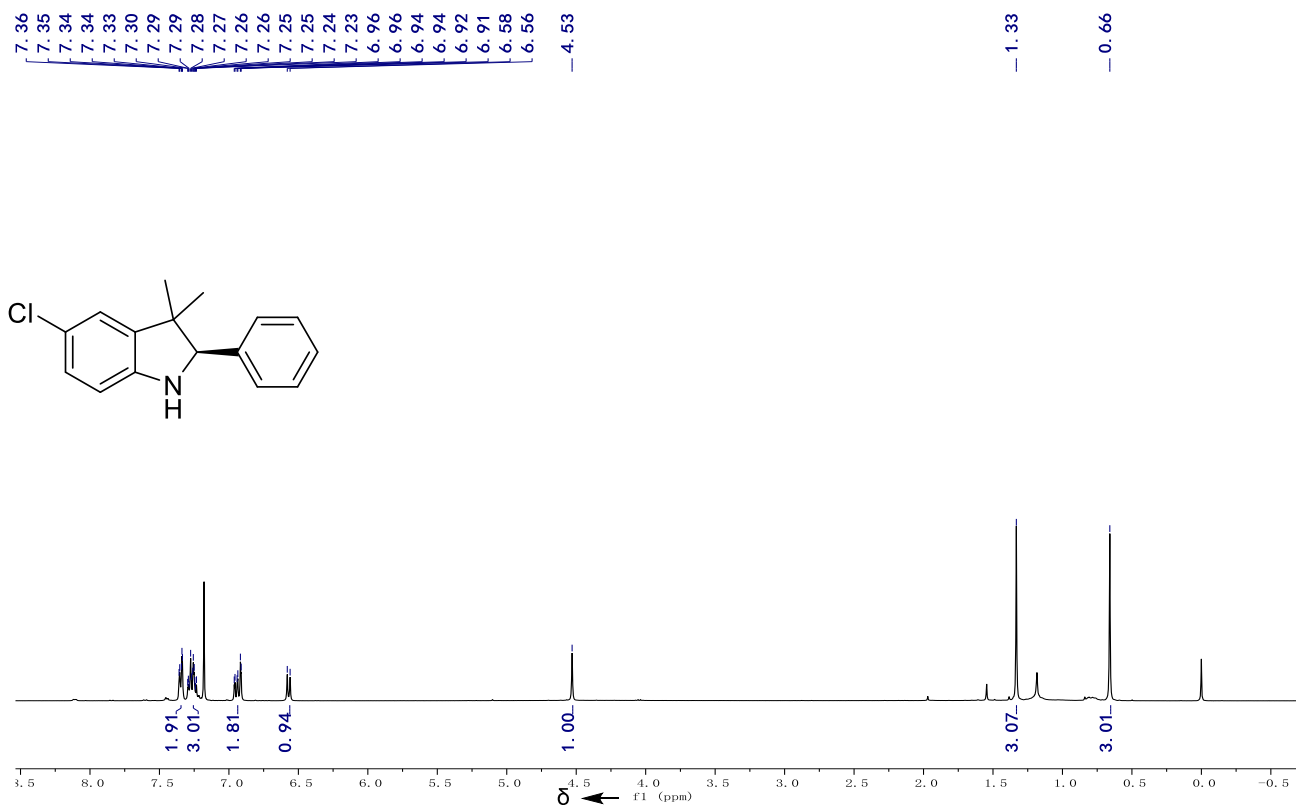




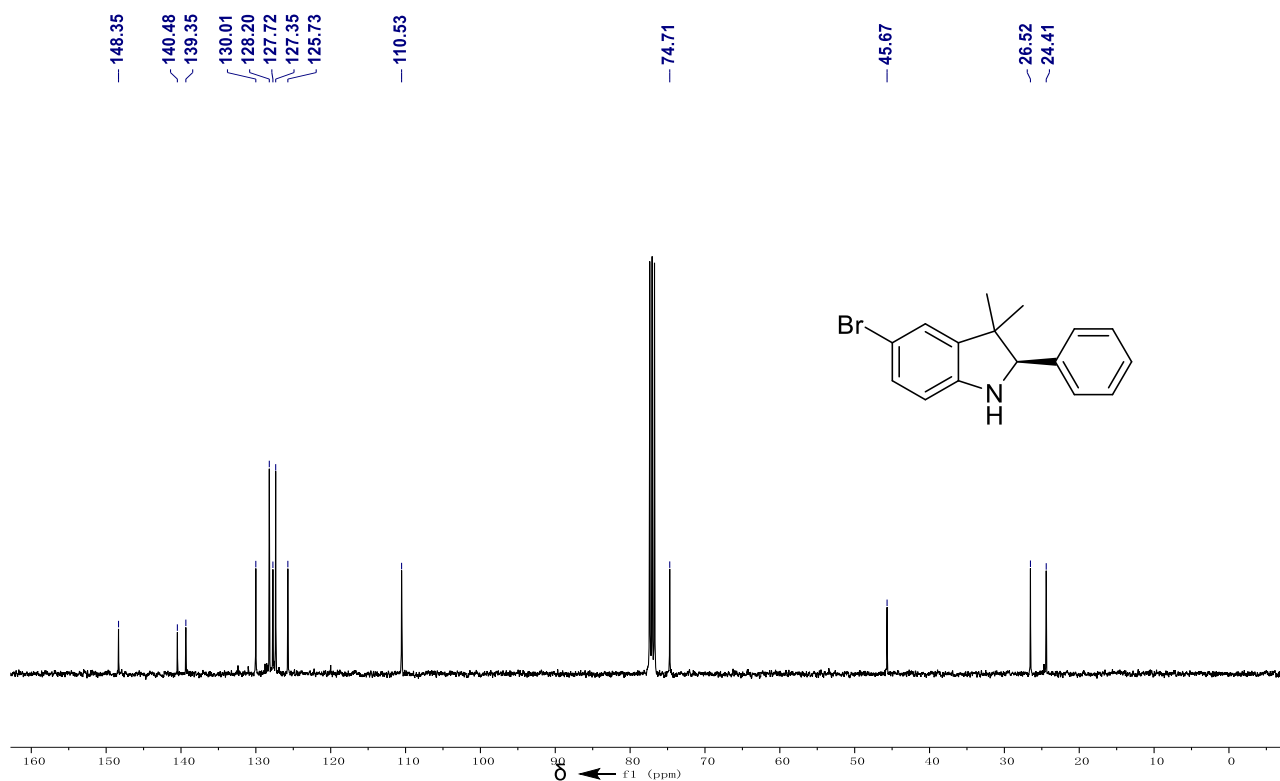
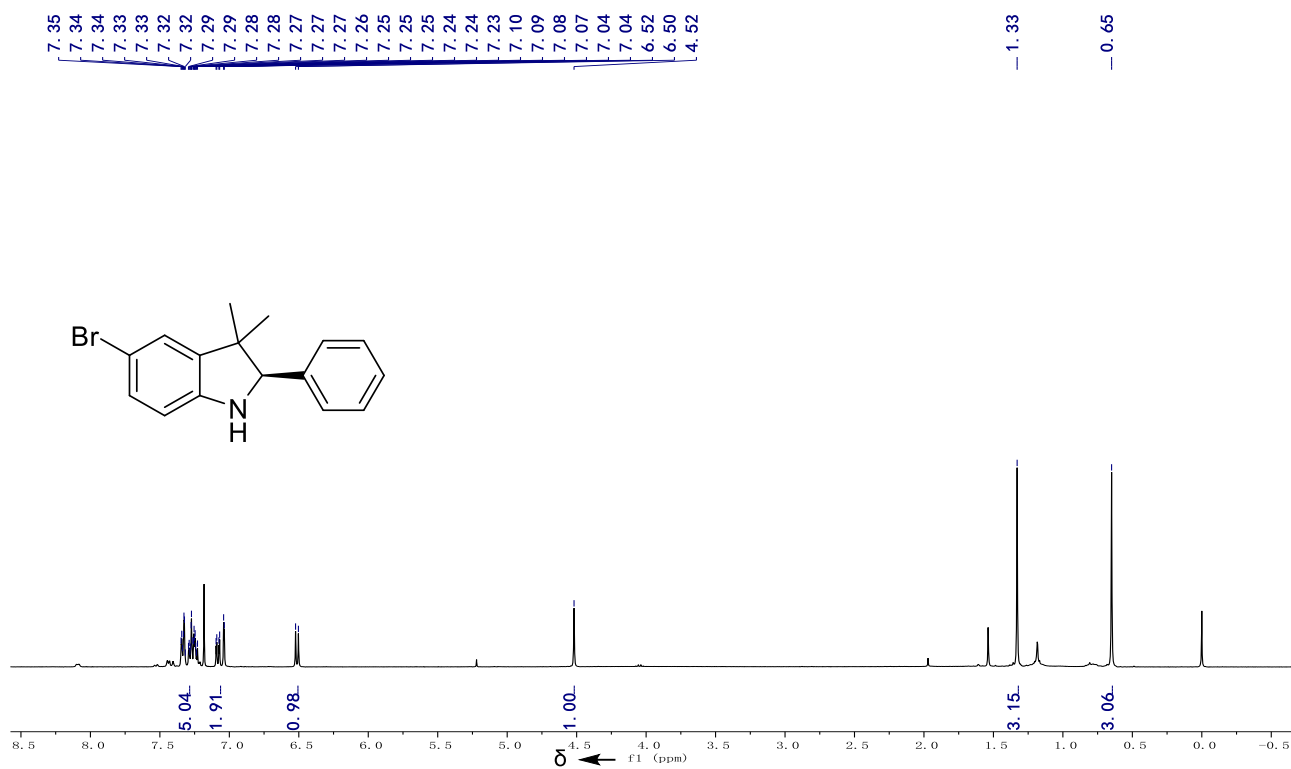
(R)-1c: (R)-4-chloro-3,3-dimethyl-2-phenylindoline



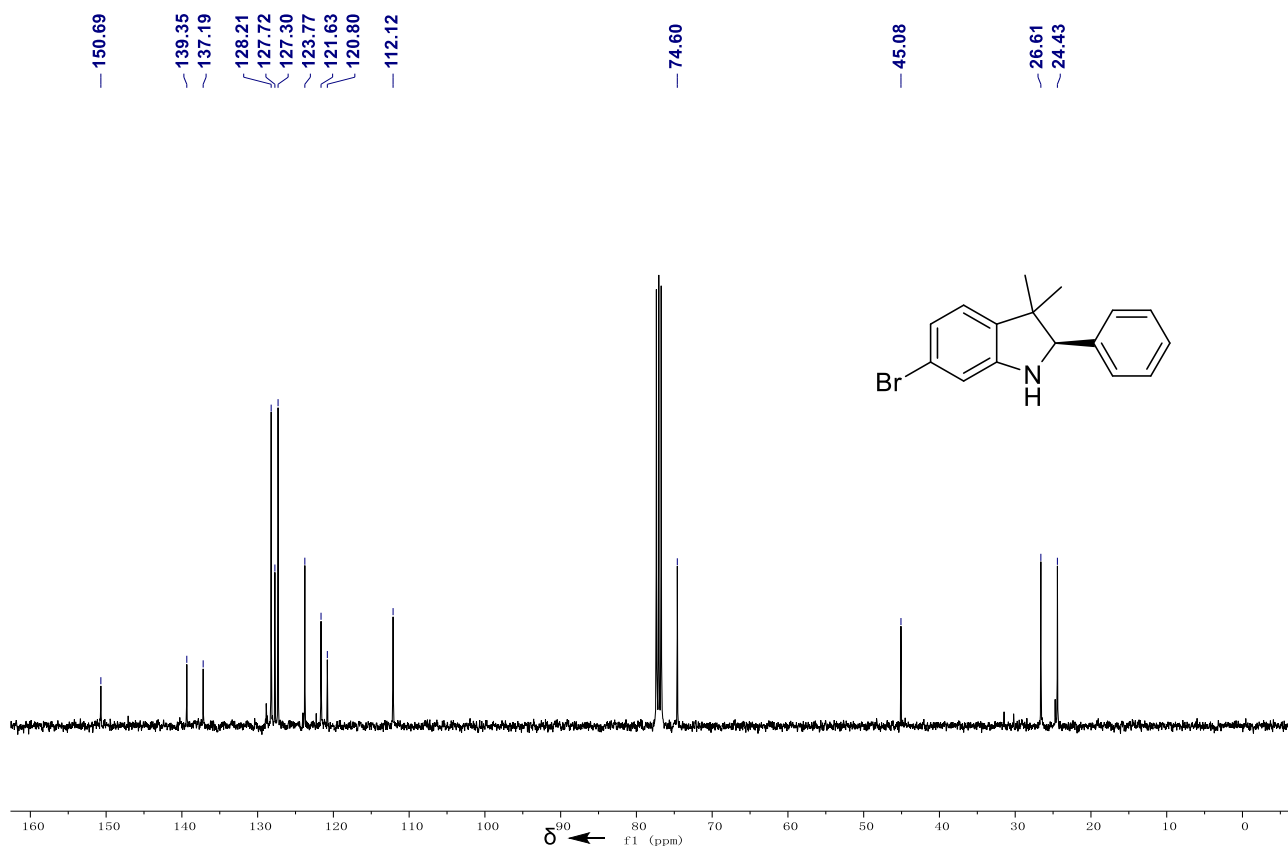
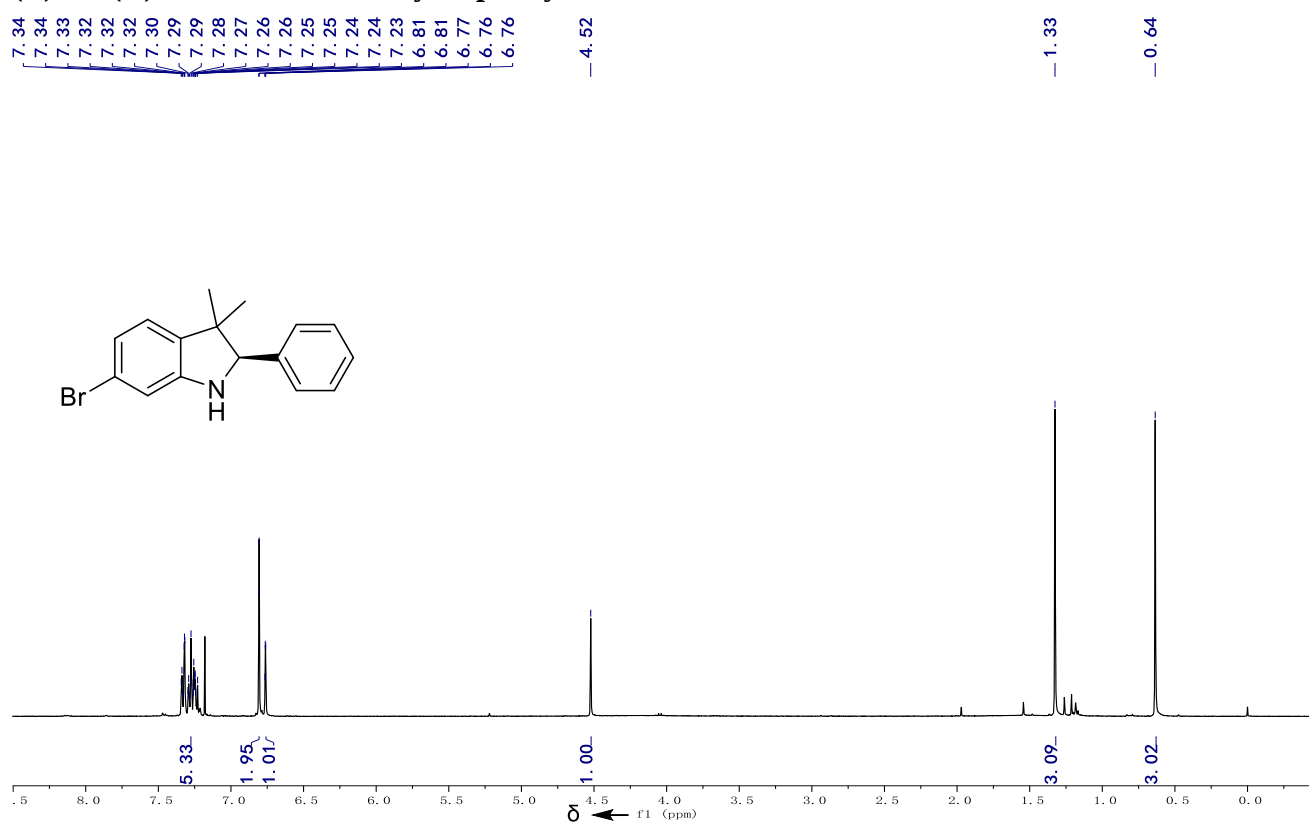
(R)-1d: (R)-5-chloro-3,3-dimethyl-2-phenylindoline.



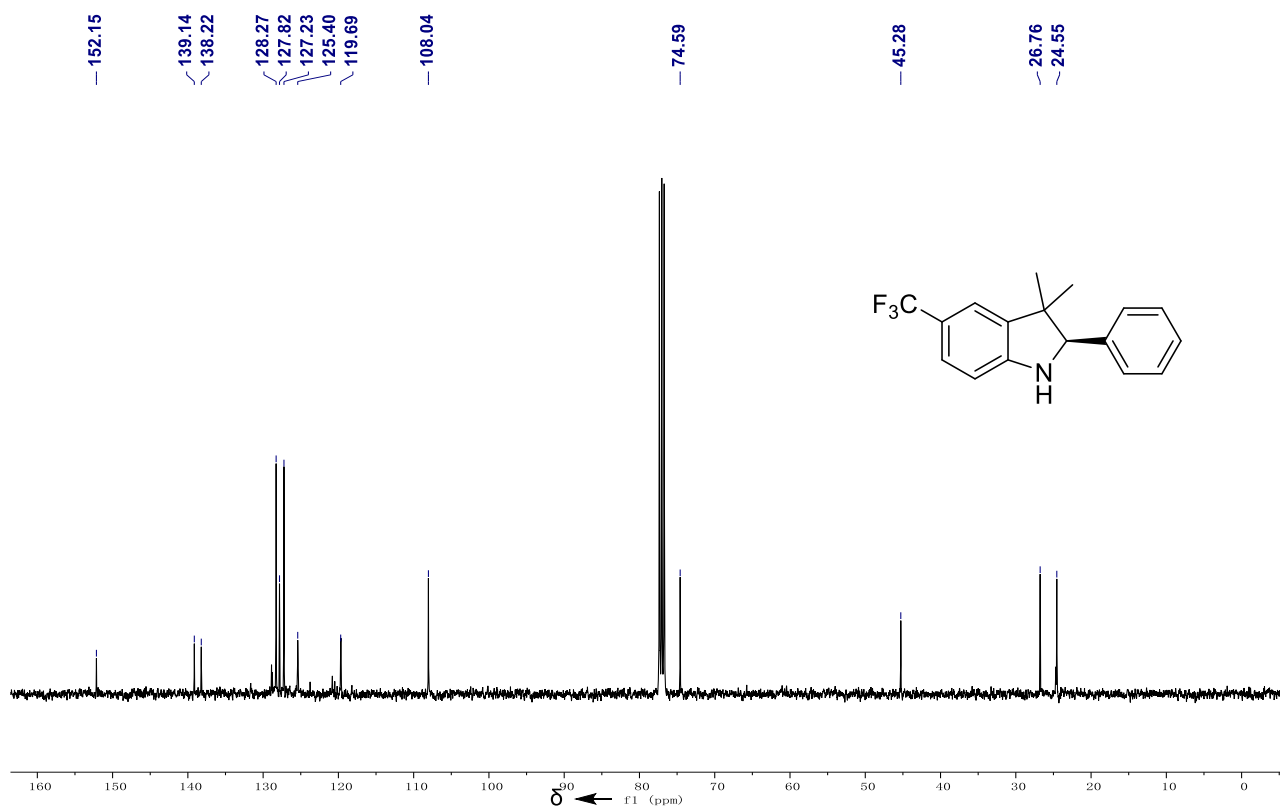
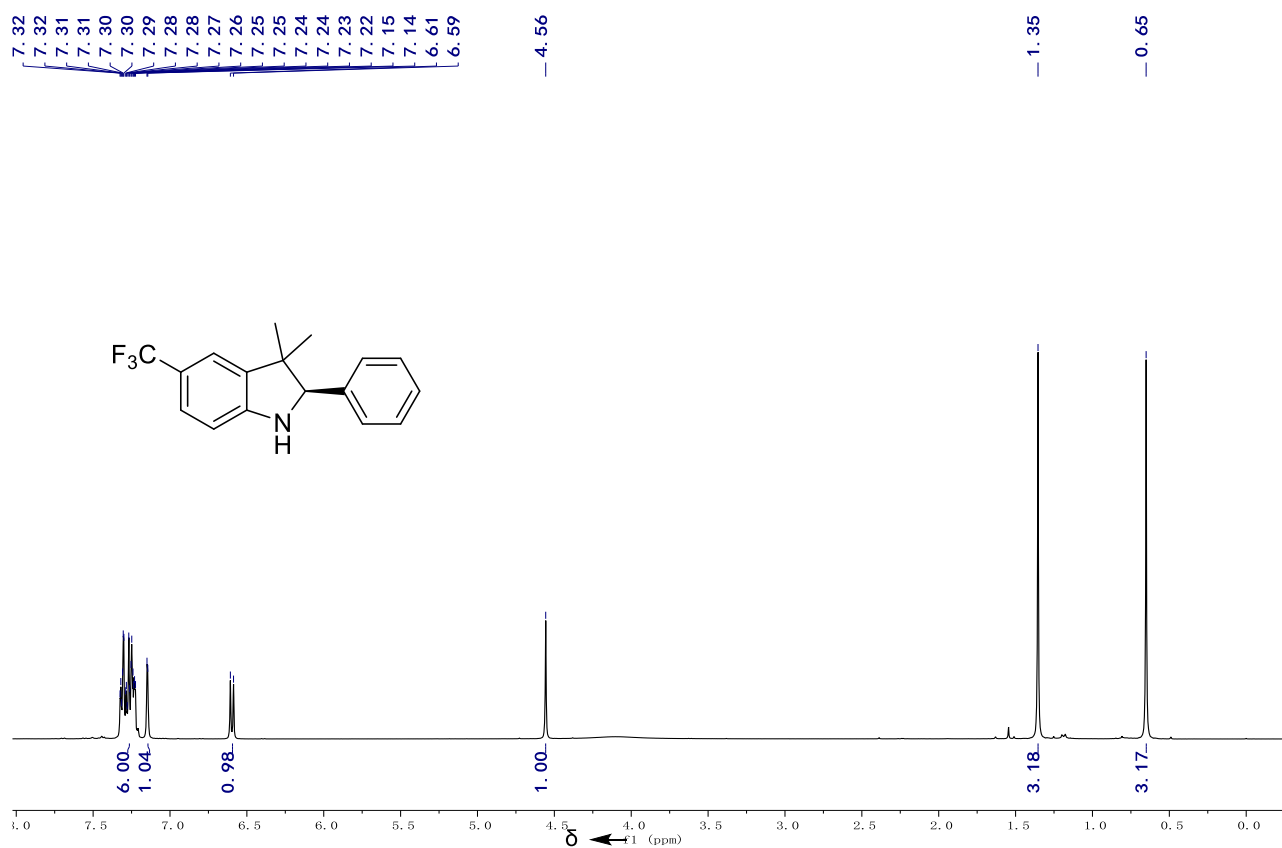
(R)-1e: (R)-5-bromo-3,3-dimethyl-2-phenylindolin.

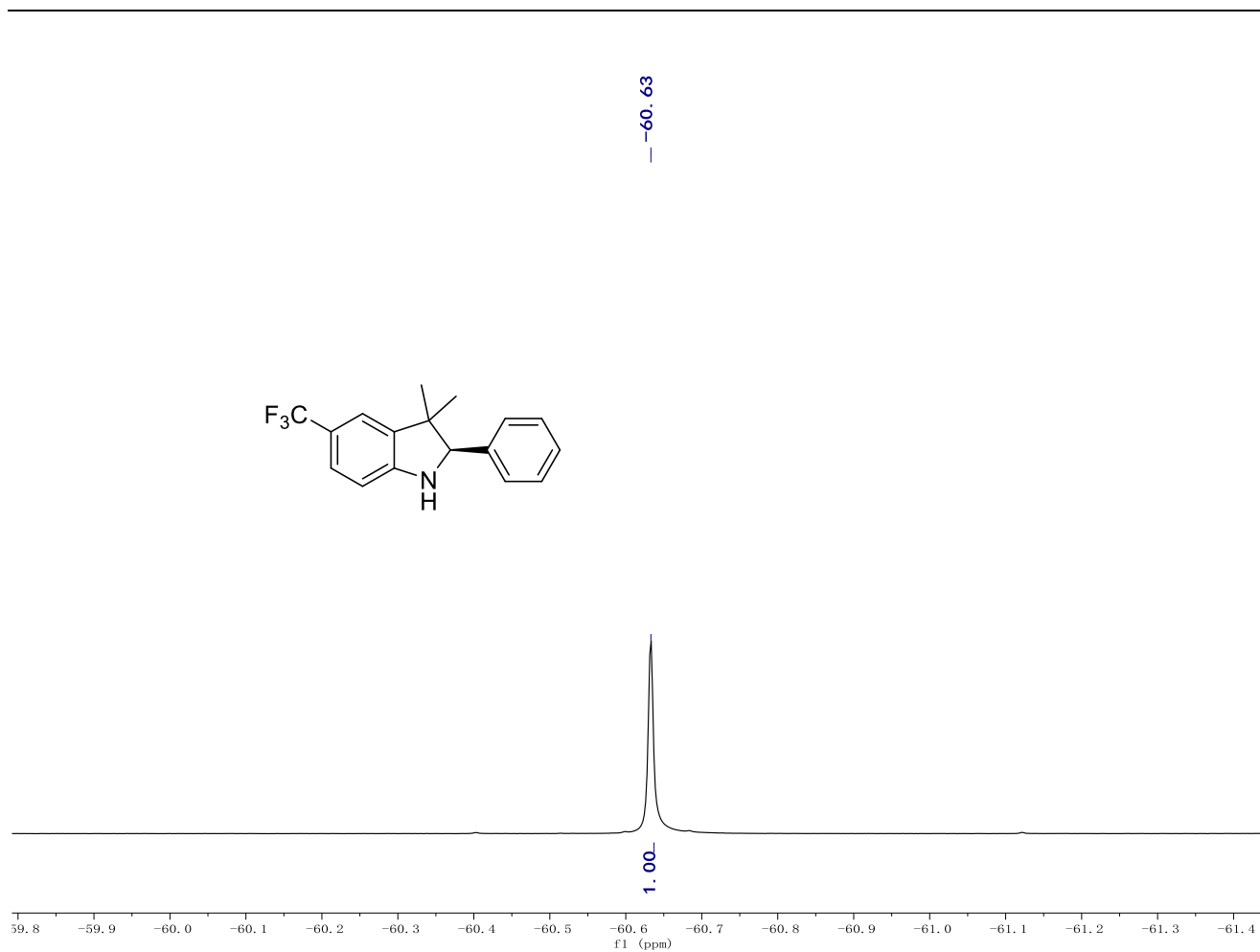


(R)-1f: (R)-6-bromo-3,3-dimethyl-2-phenylindoline.

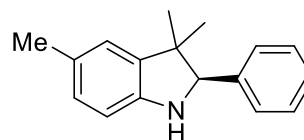
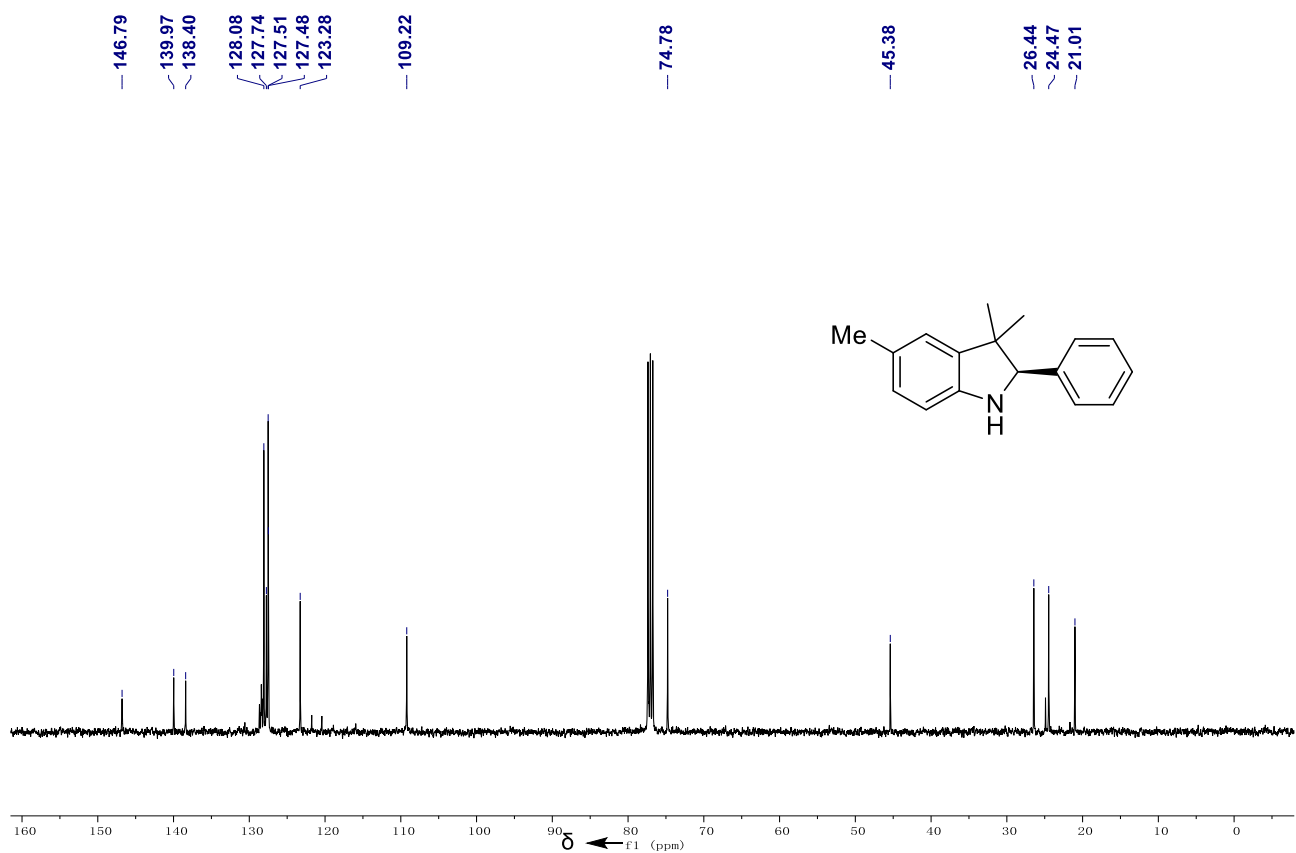
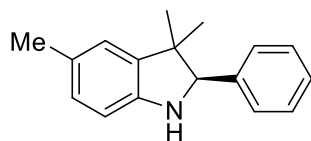
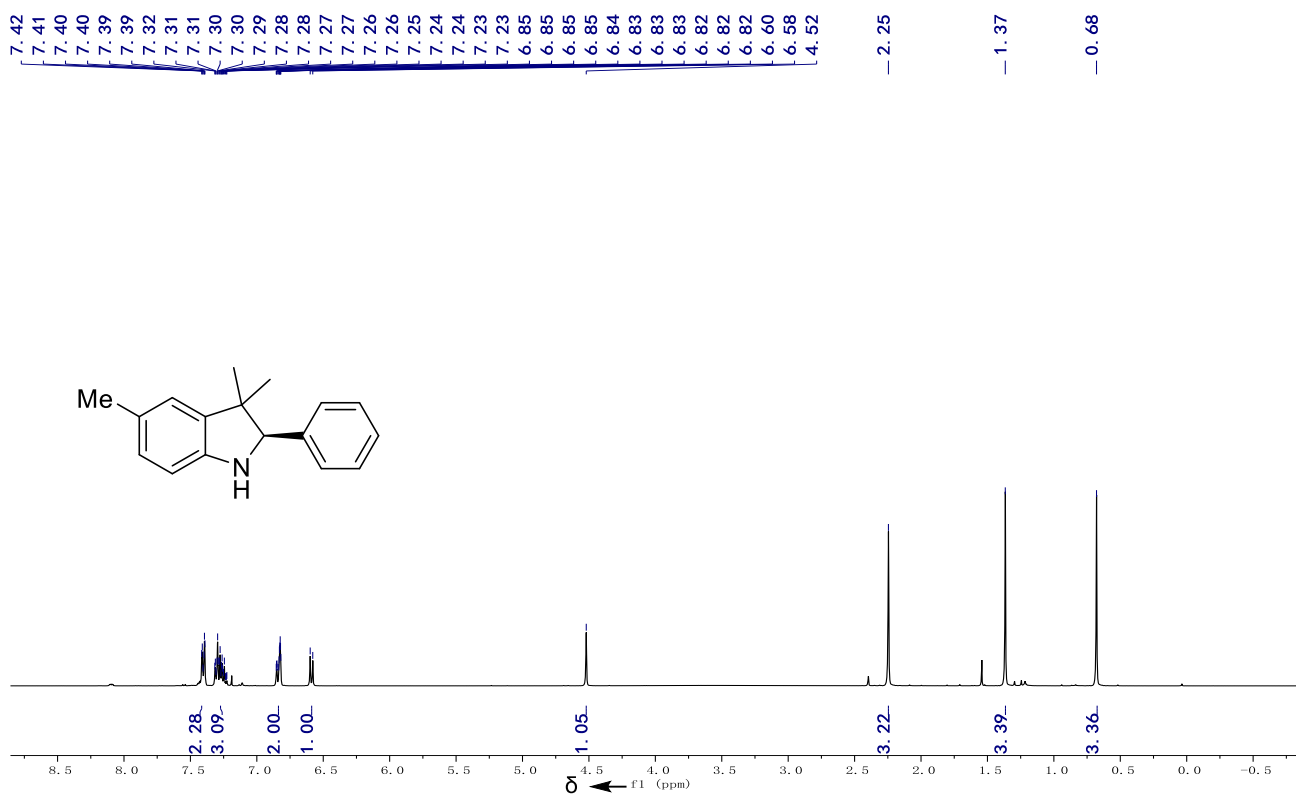


(R)-1g: (R)- 3,3-dimethyl-2-phenyl-5-(trifluoromethyl)indoline.

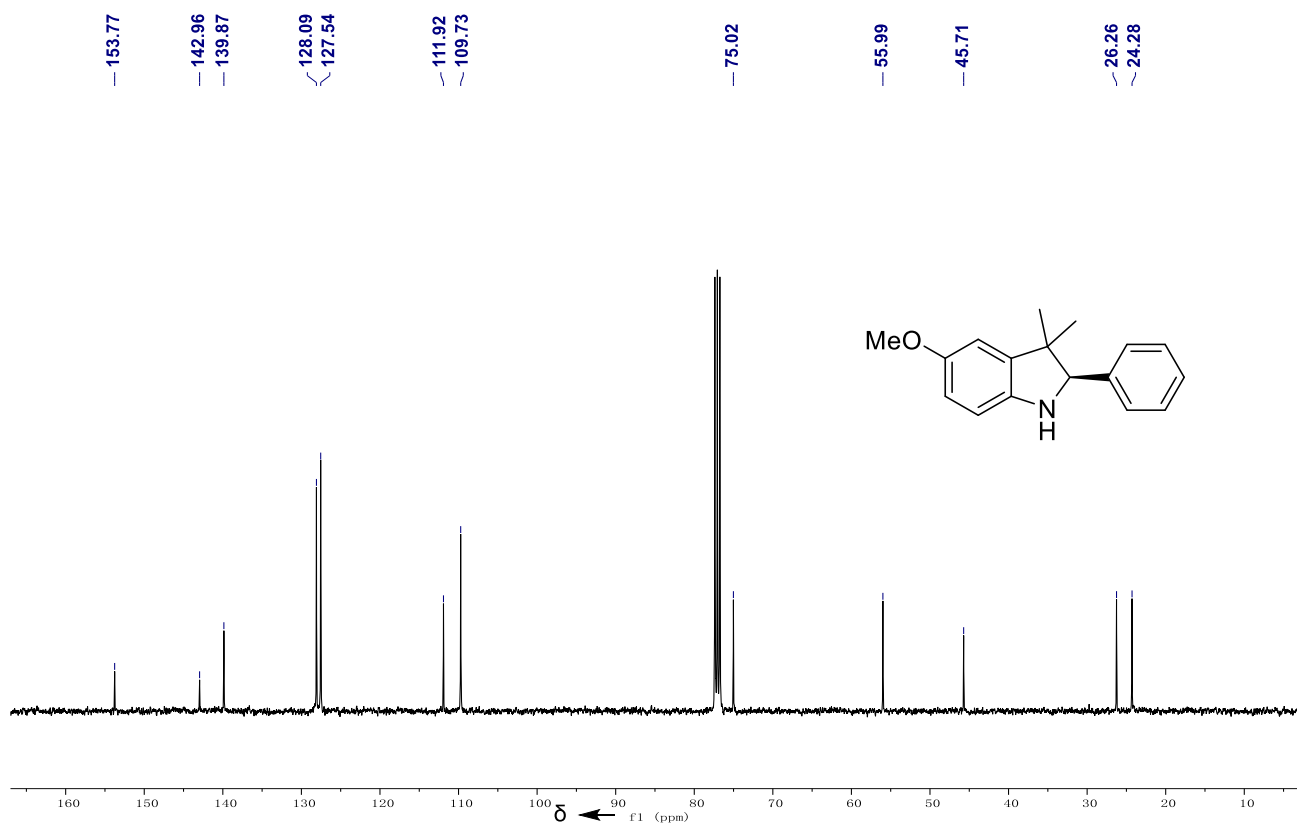
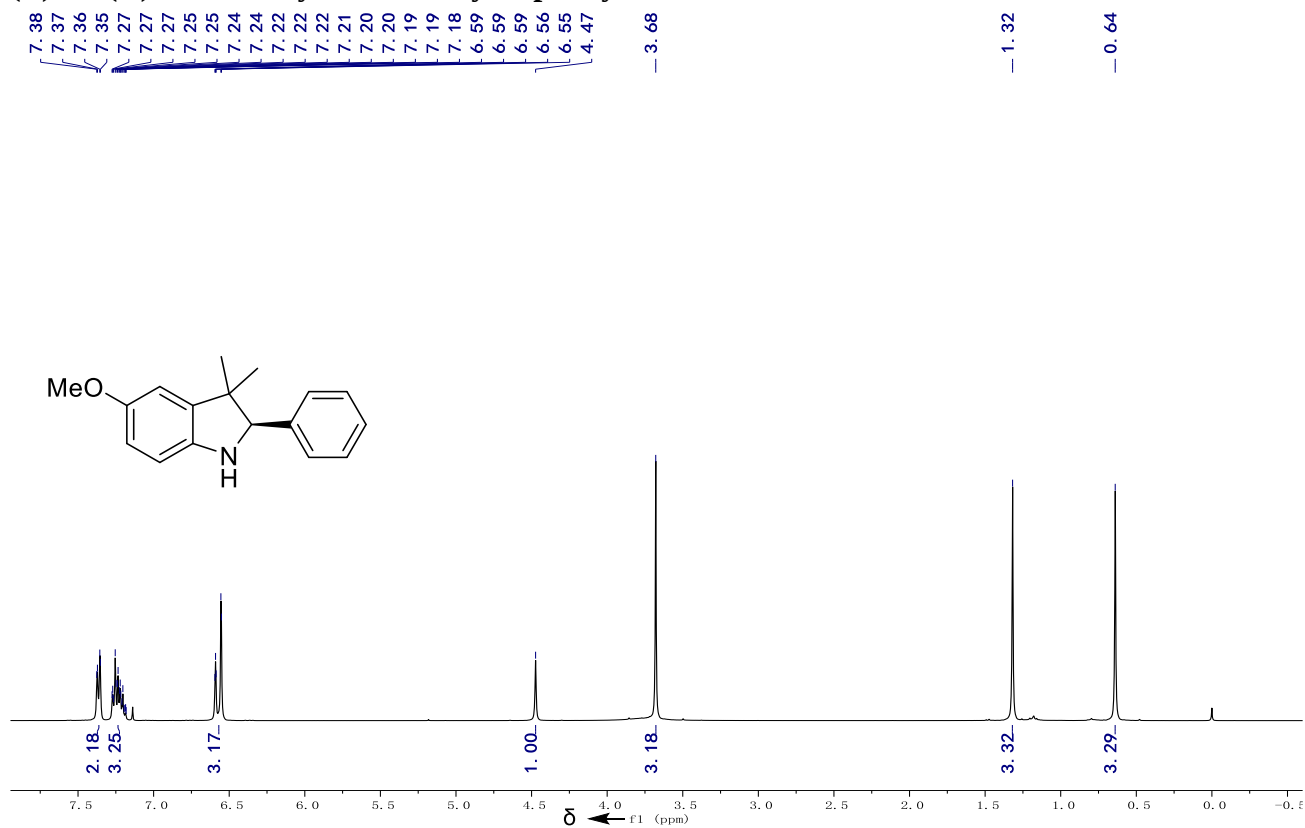




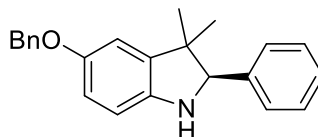
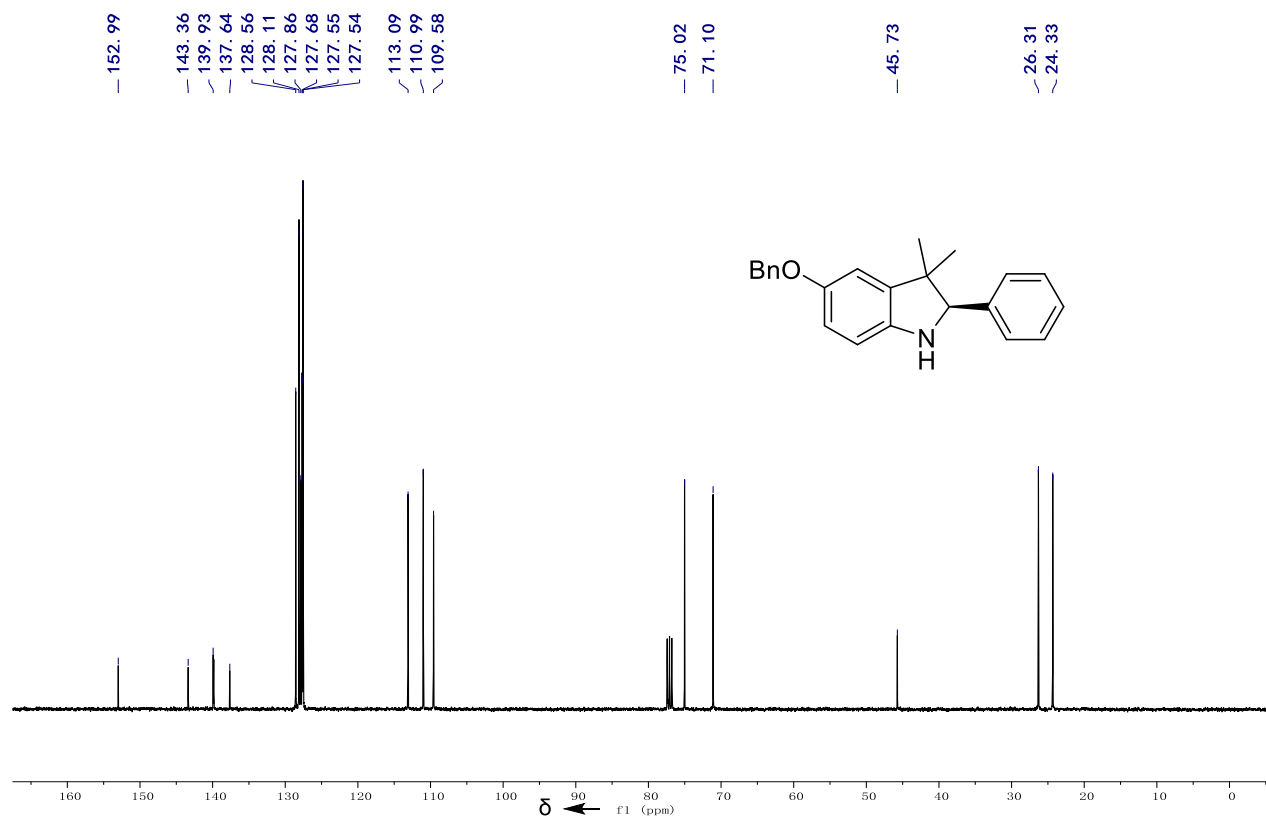
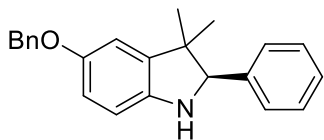
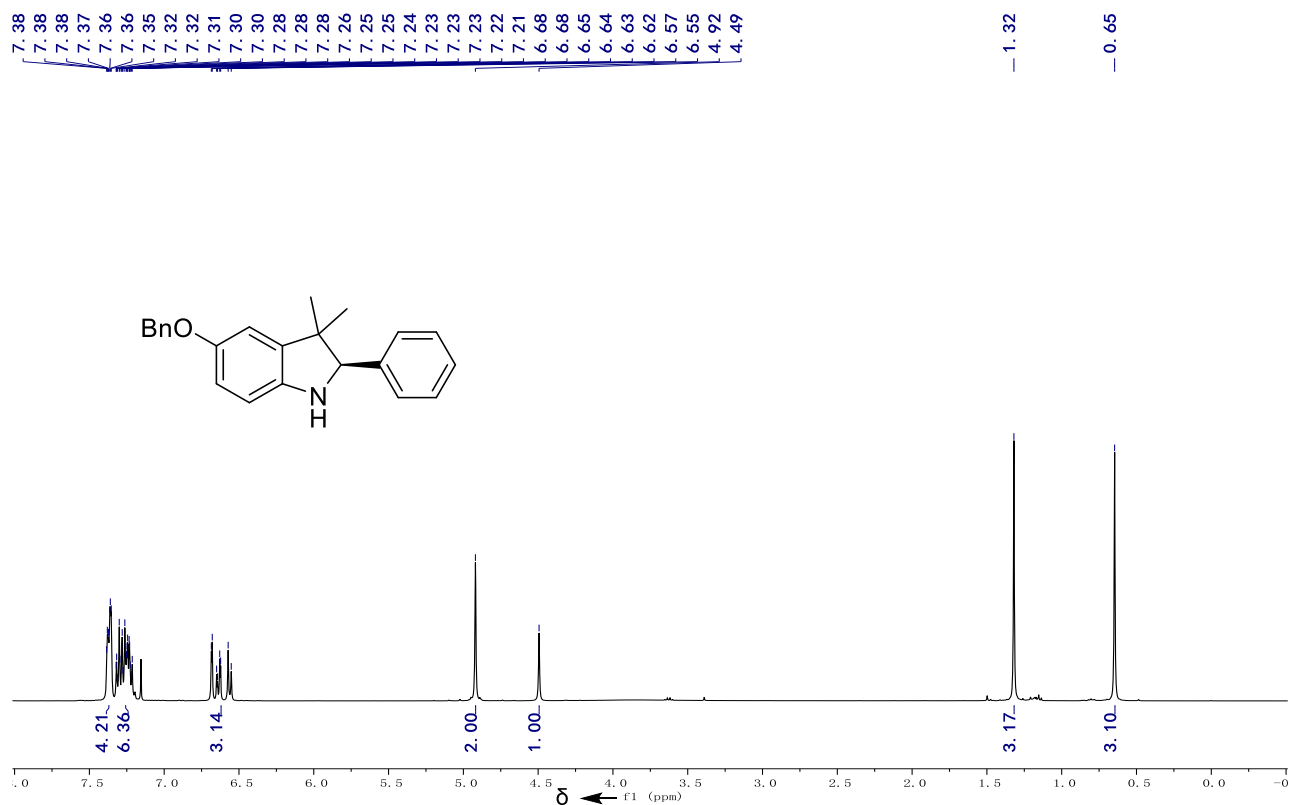
(R)-1h: (R)-3,3,5-trimethyl-2-phenylindoline.



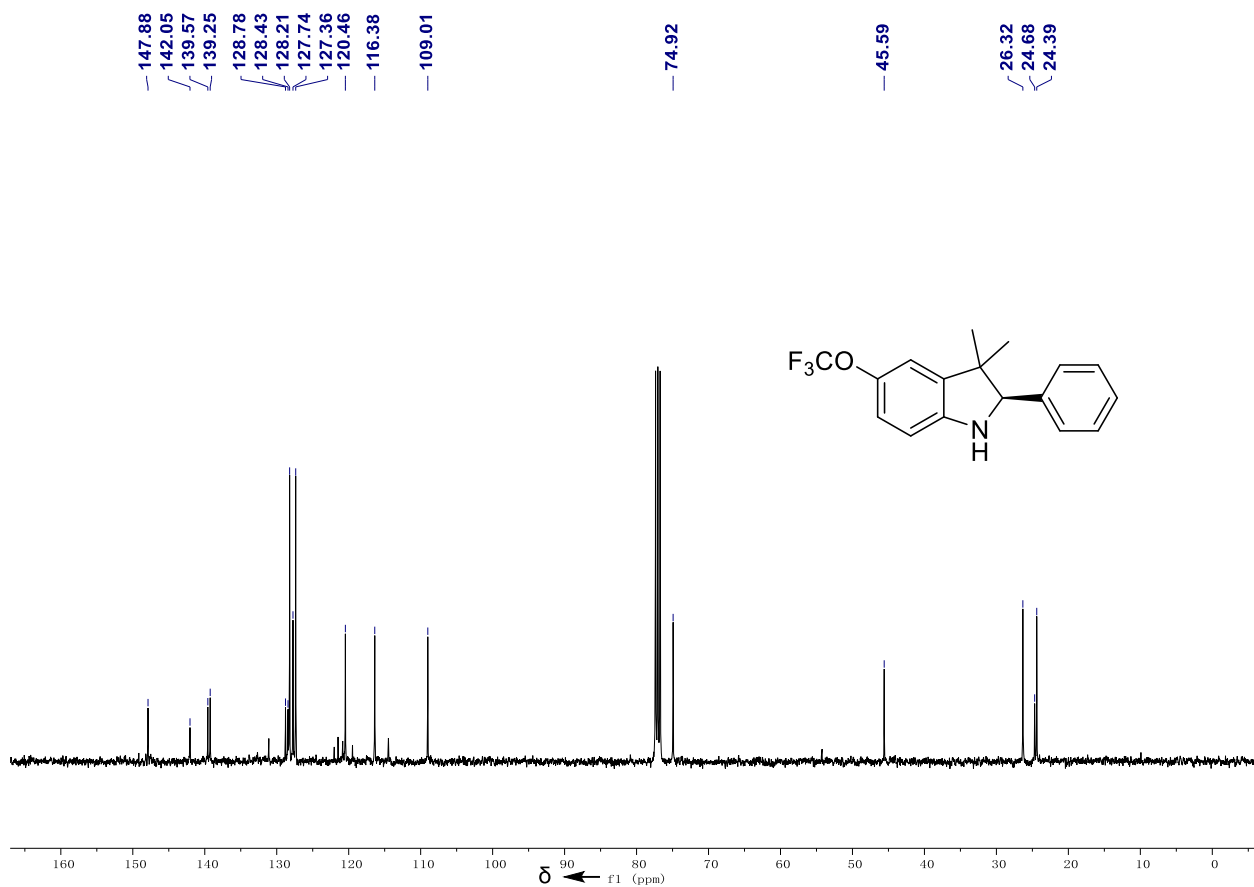
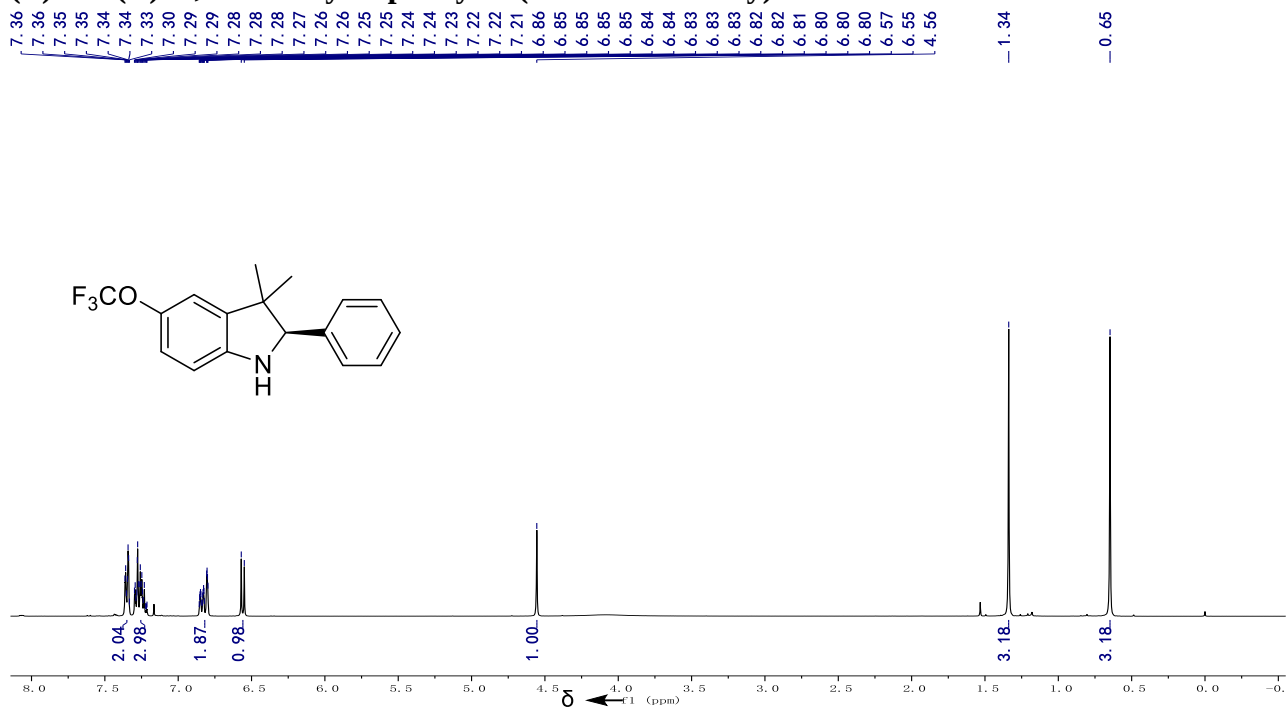
(R)-1i: (R)- 5-methoxy-3,3-dimethyl-2-phenylindoline.

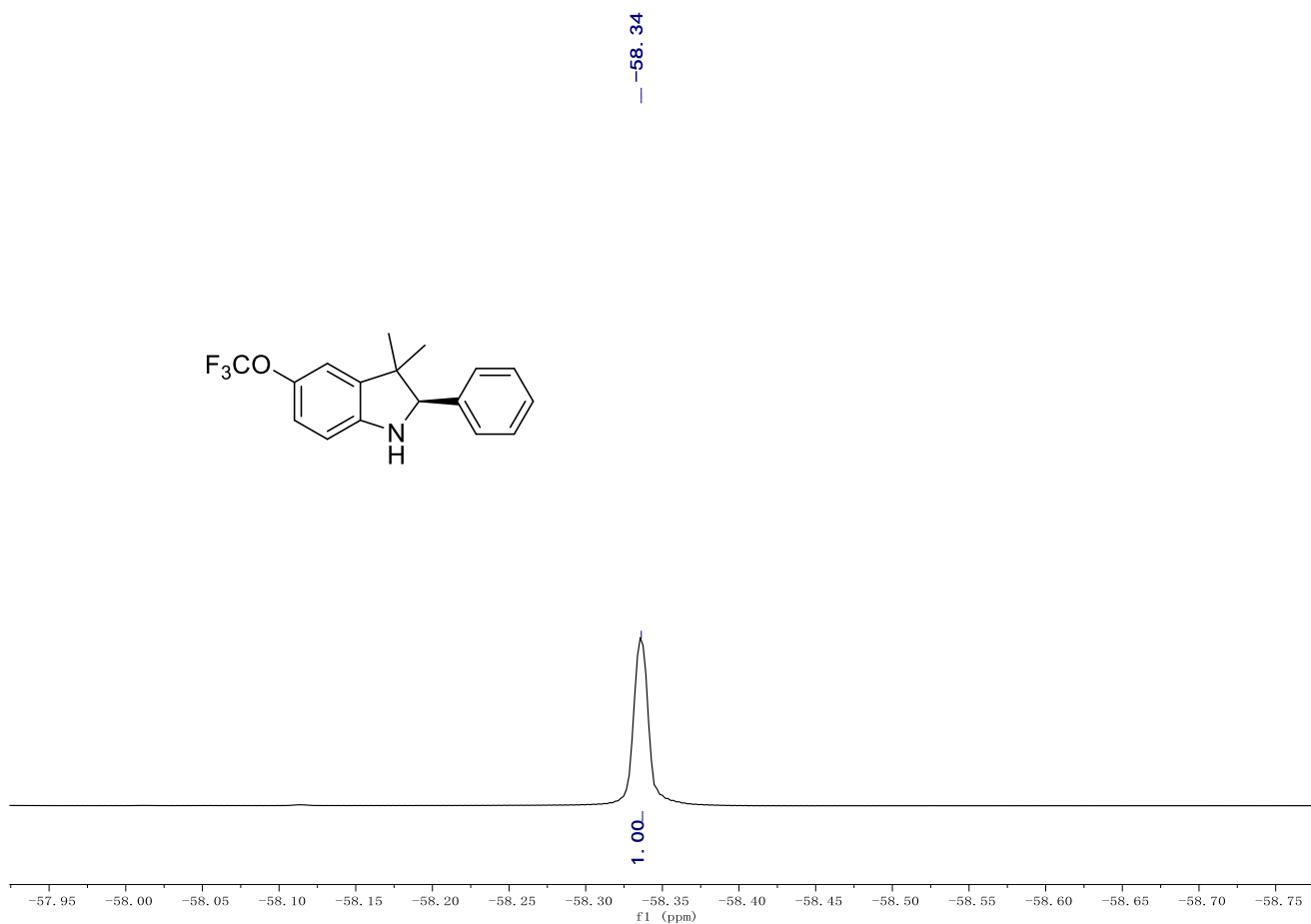


(R)-1j: (R)- 5-(benzyloxy)-3,3-dimethyl-2-phenylindoline.

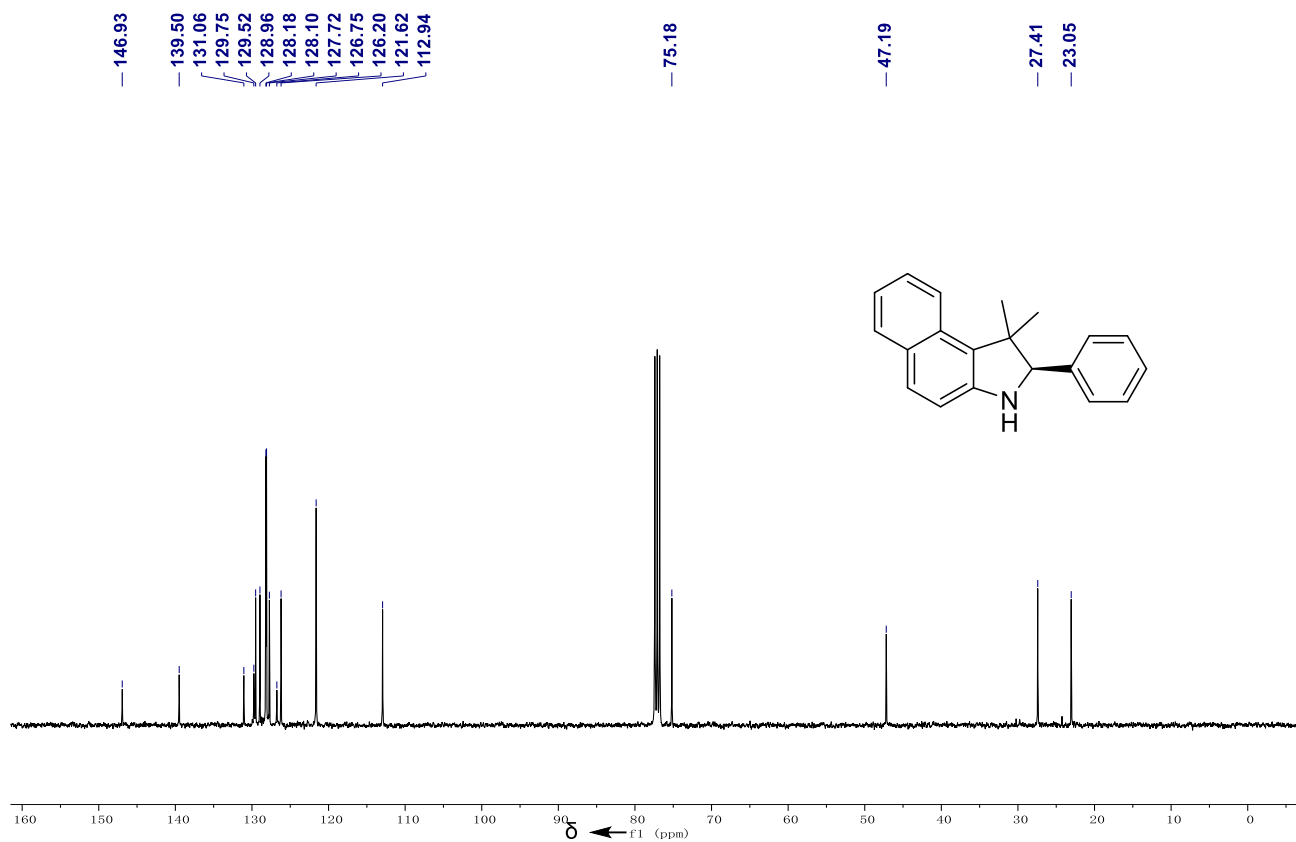
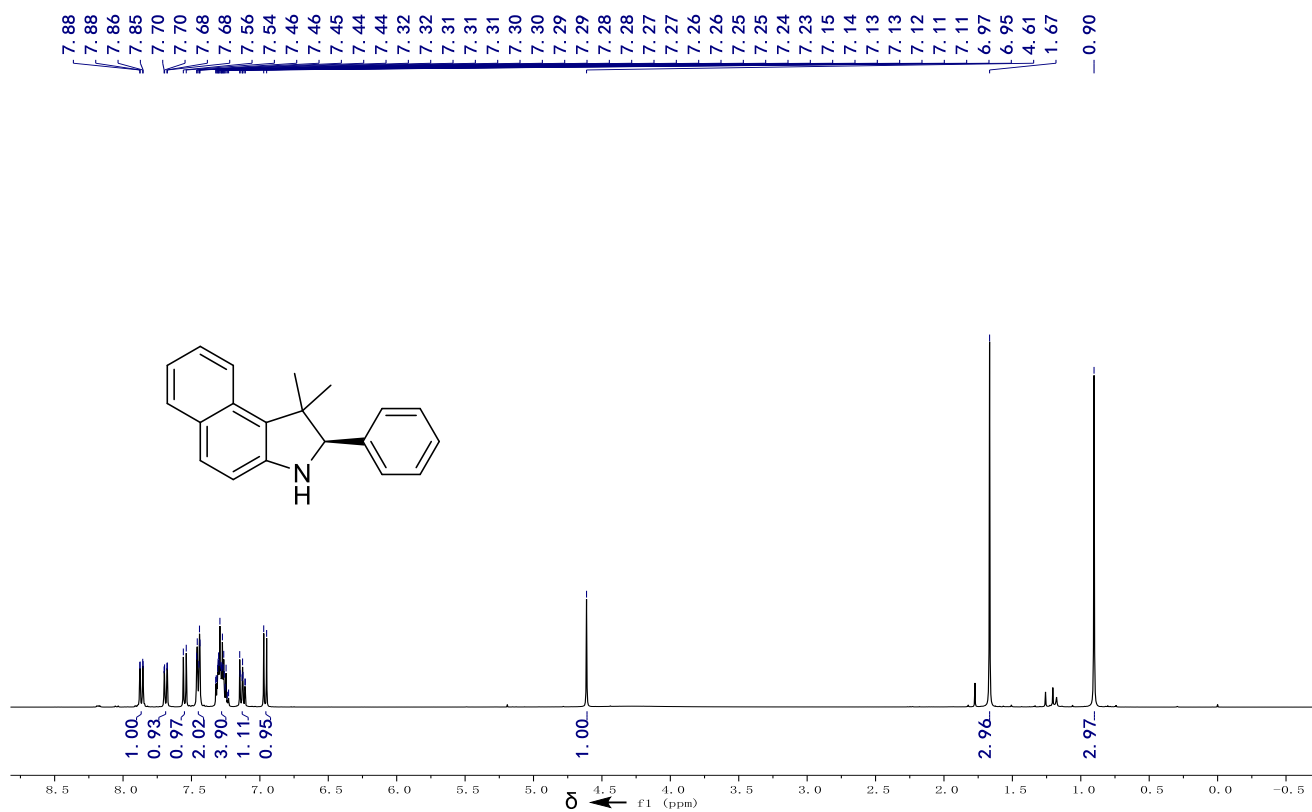


(R)-1k: (R)- 3,3-dimethyl-2-phenyl-5-(trifluoromethoxy)indoline.

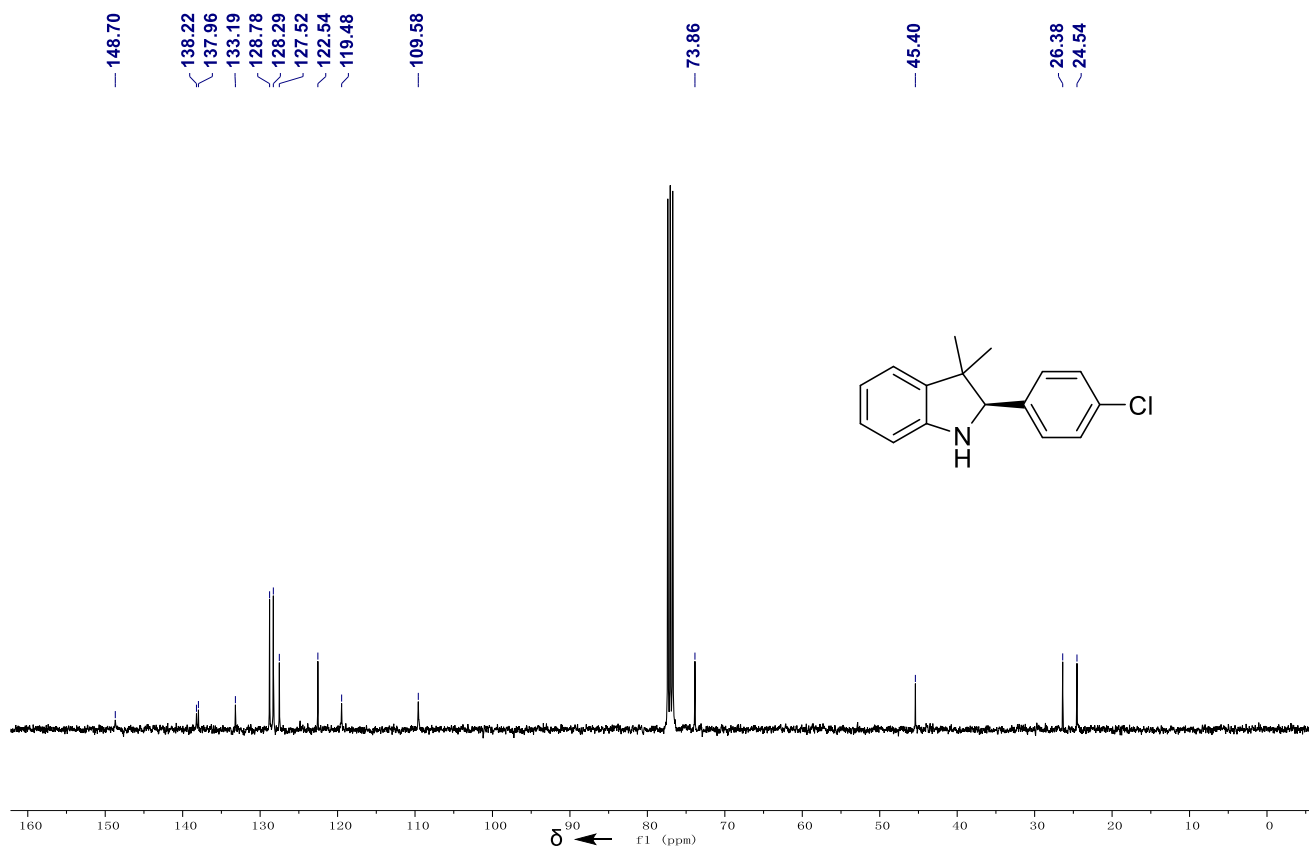
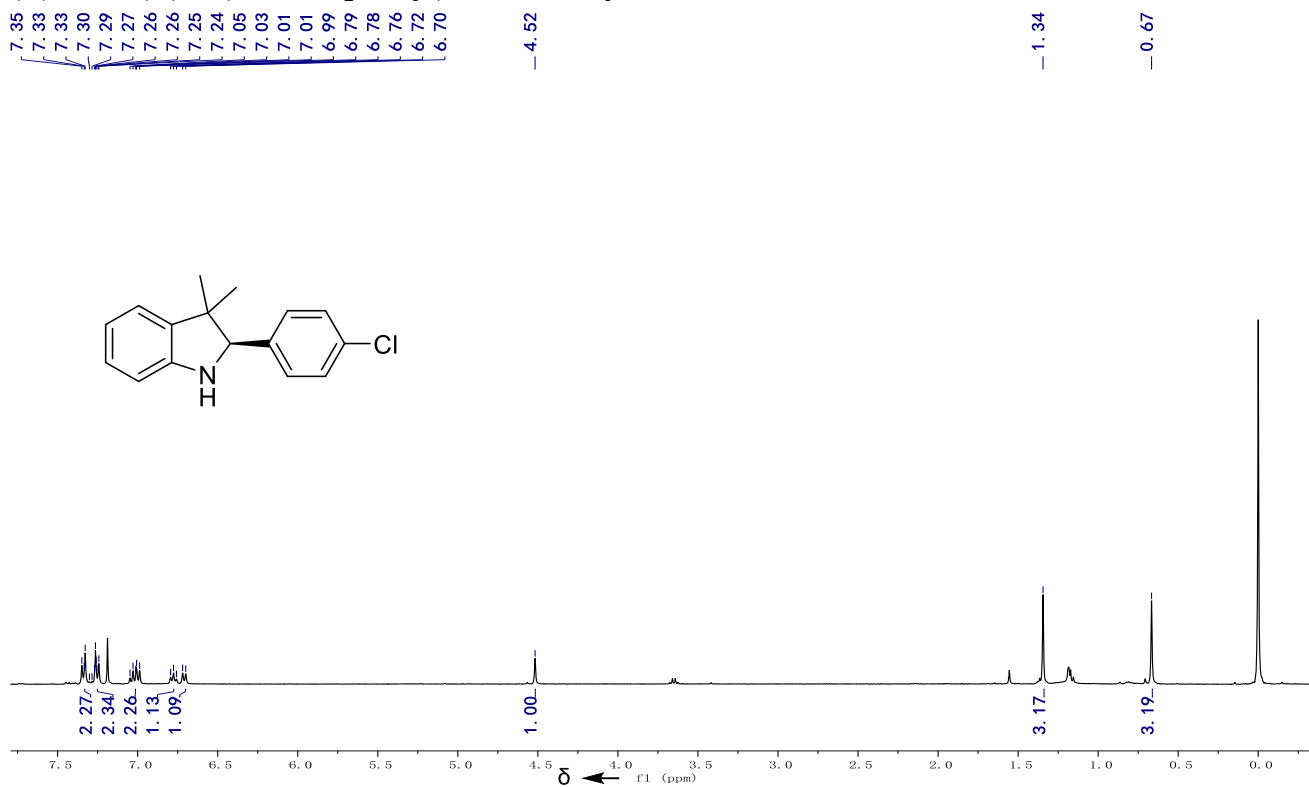




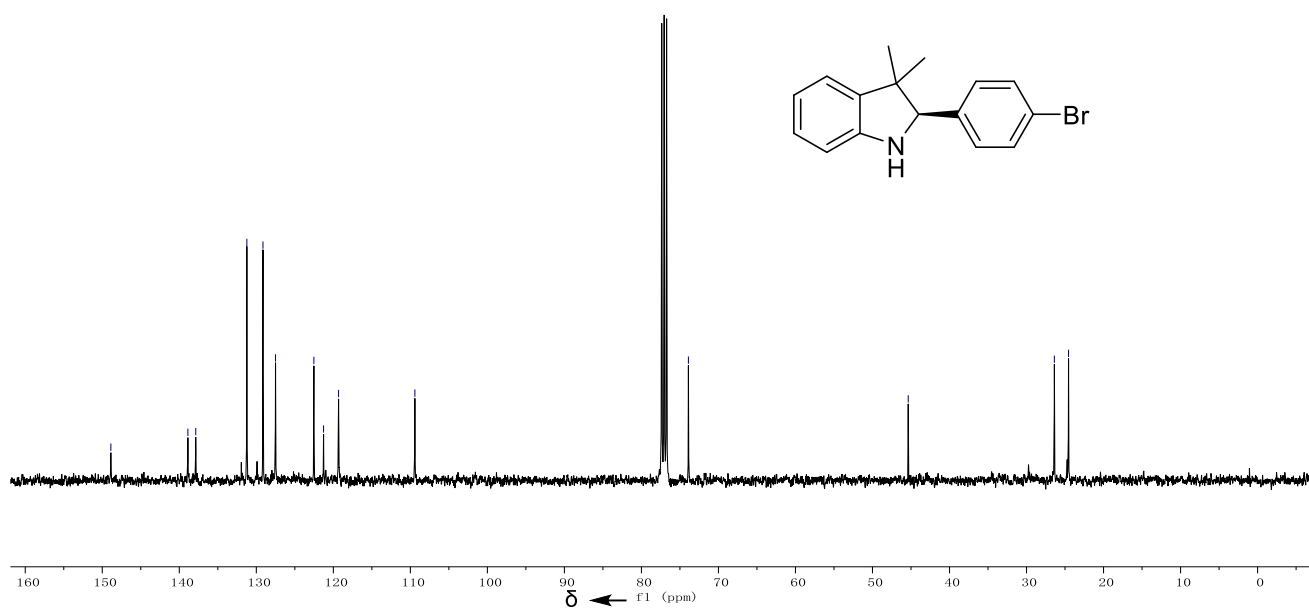
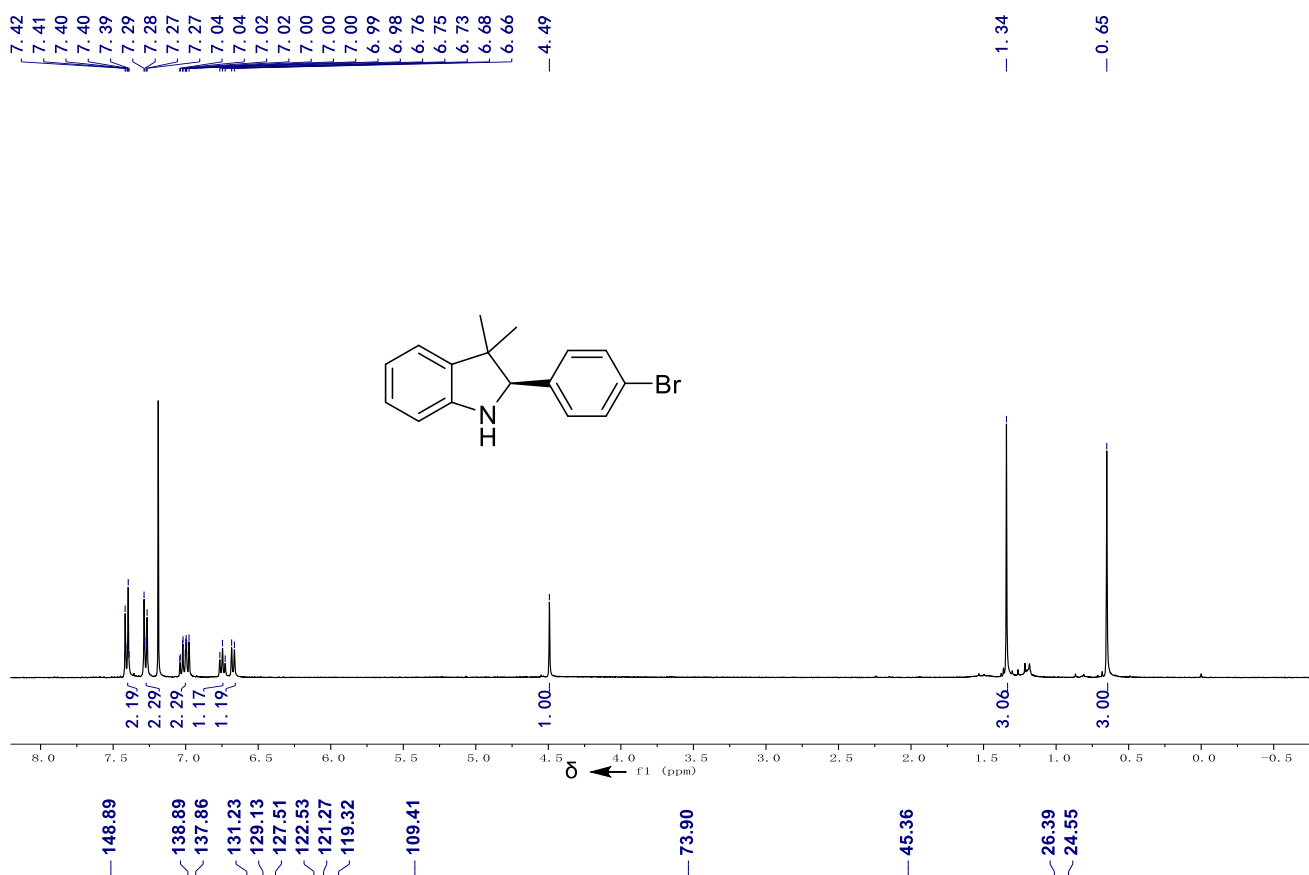
(R)-1l: (R)-1,1-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[e]indole



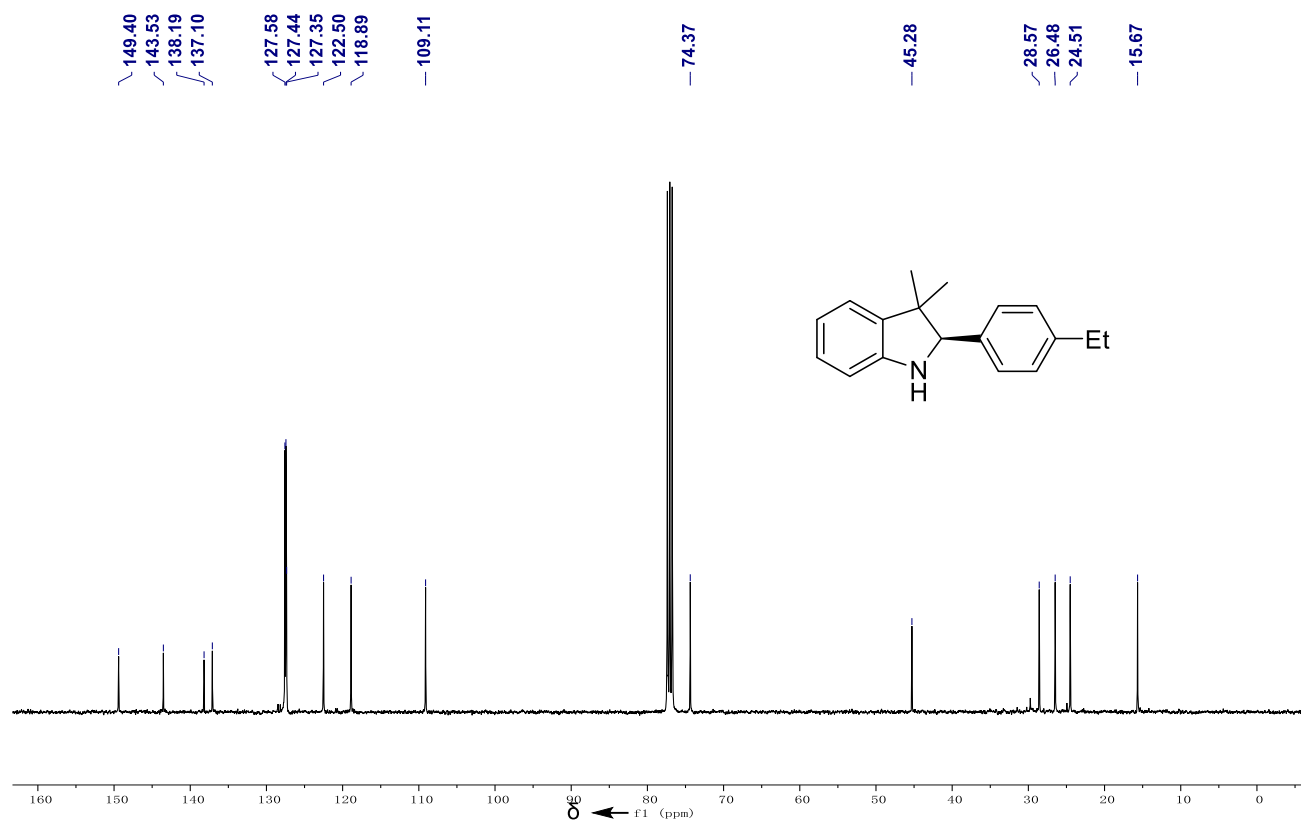
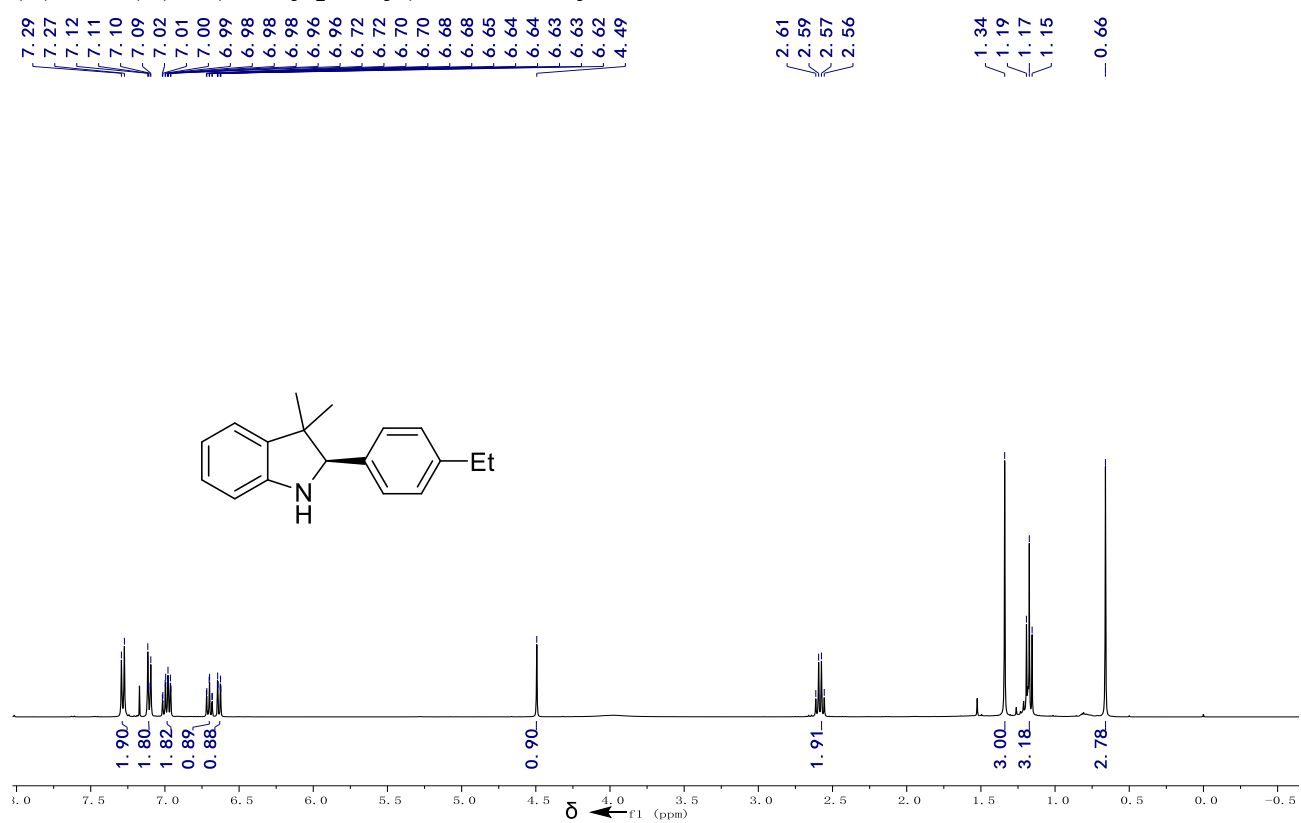
(R)-1m: (R)-2-(4-chlorophenyl)-3,3-dimethylindoline.



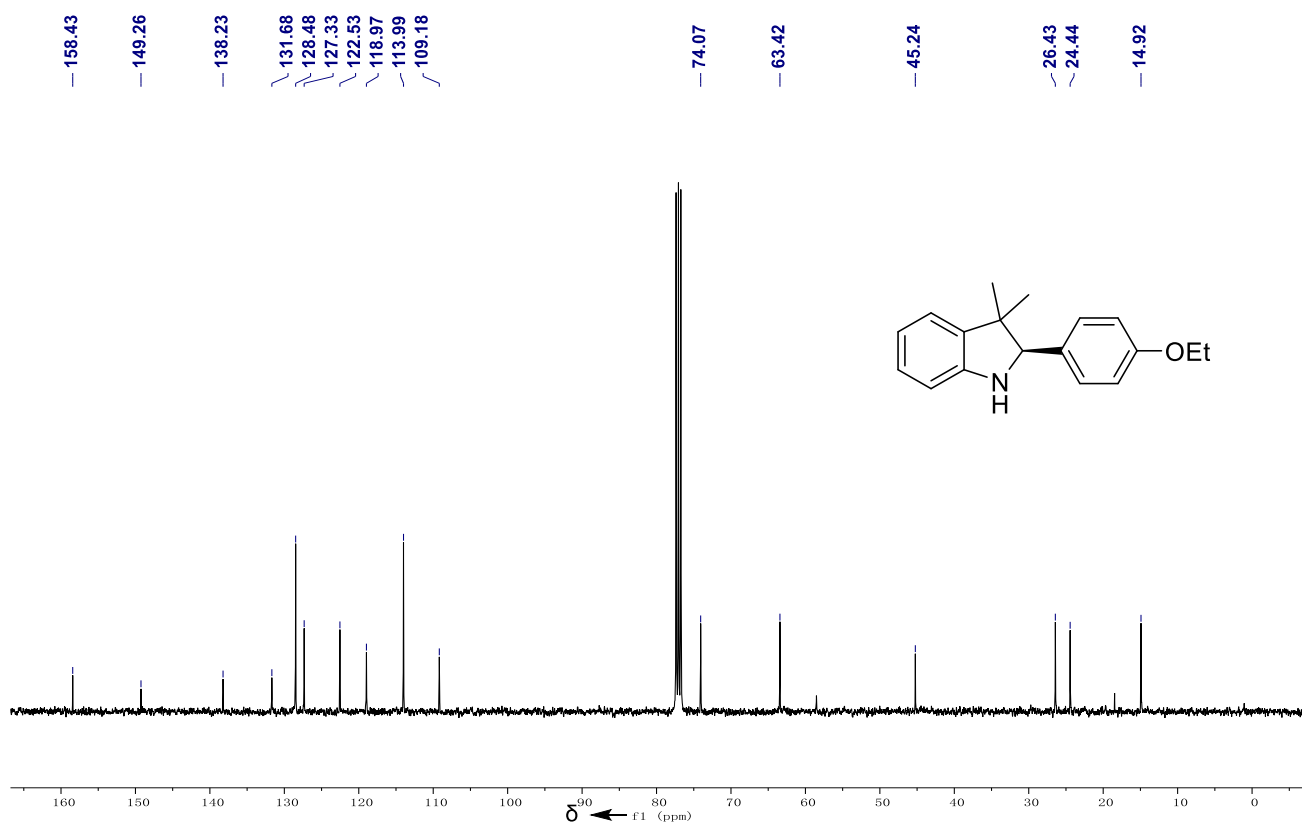
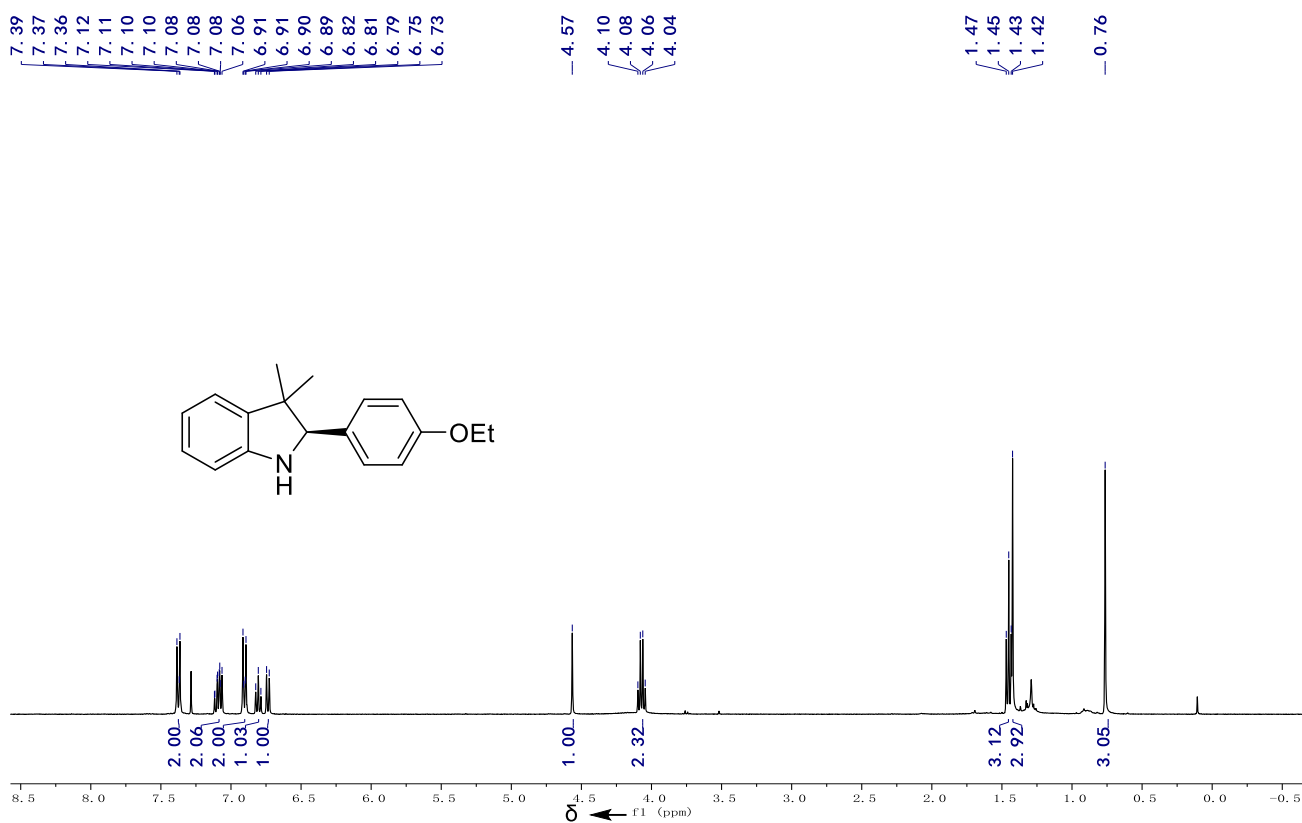
(R)-1n: (R)-2-(4-bromophenyl)-3,3-dimethylindoline.



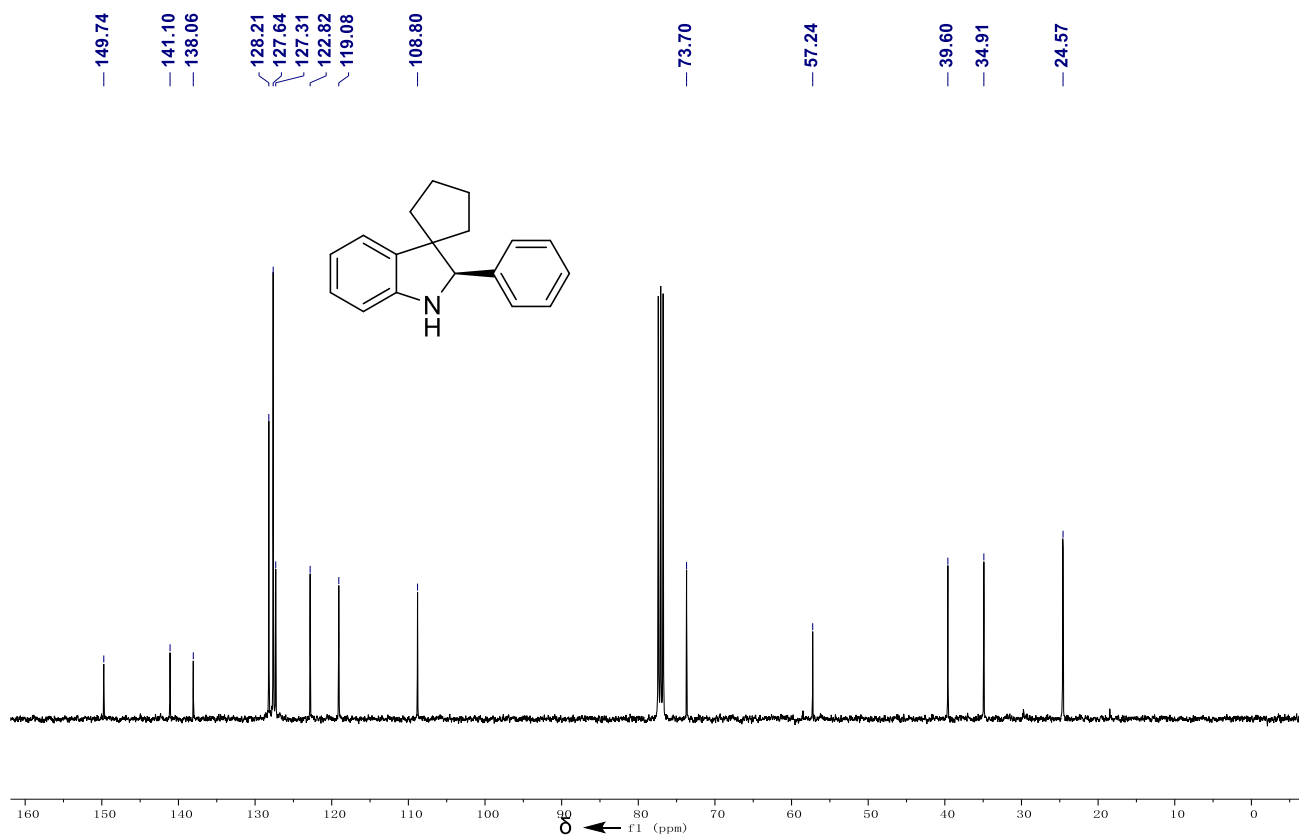
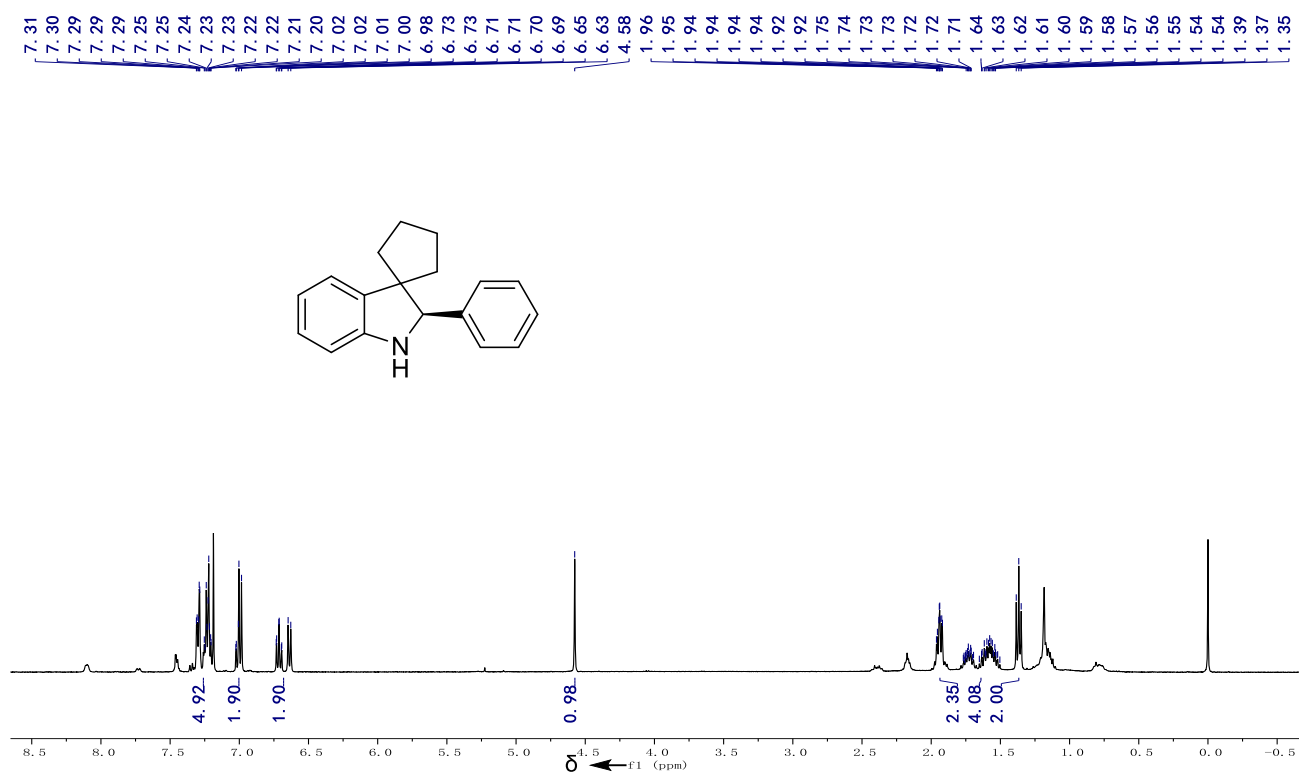
(R)-1o: (R)-2-(4-ethylphenyl)-3,3-dimethylindoline



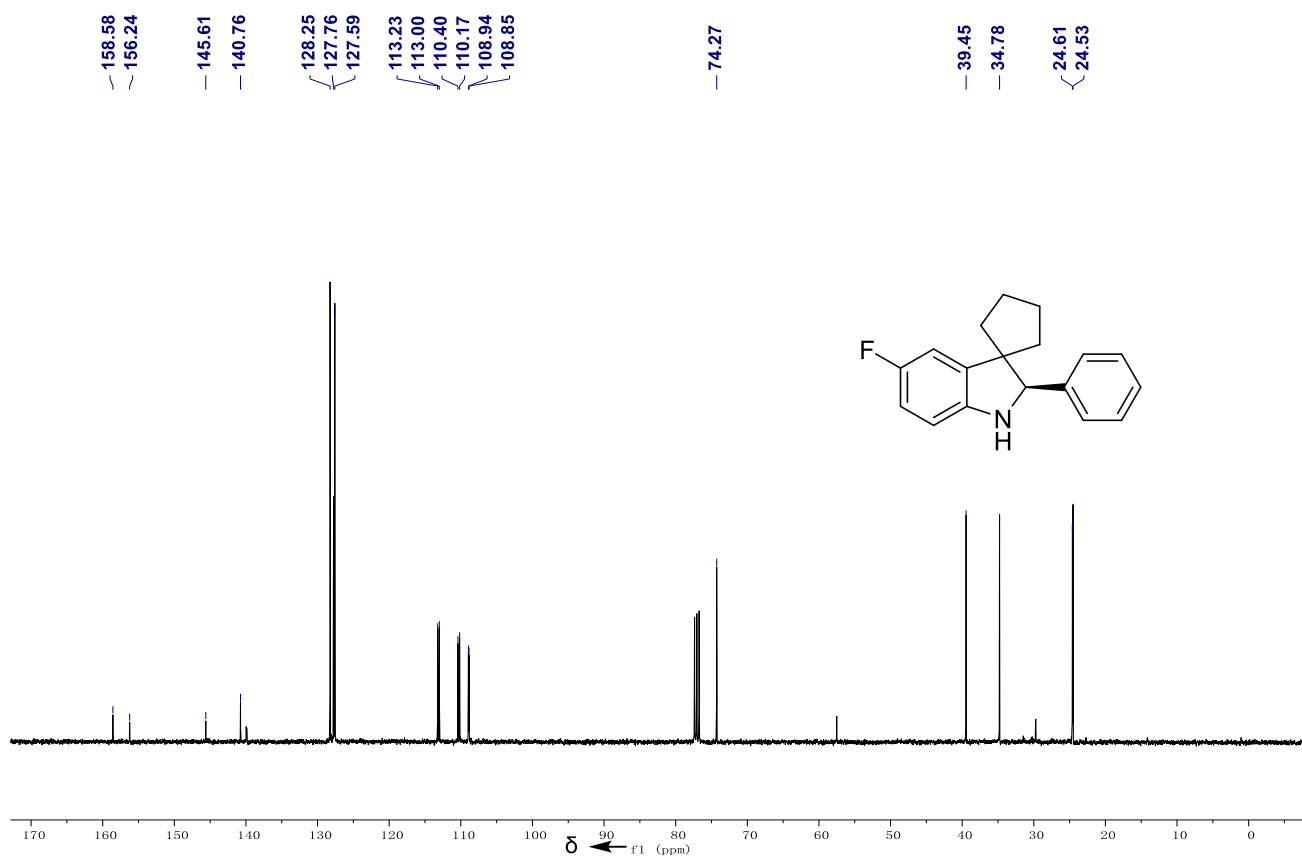
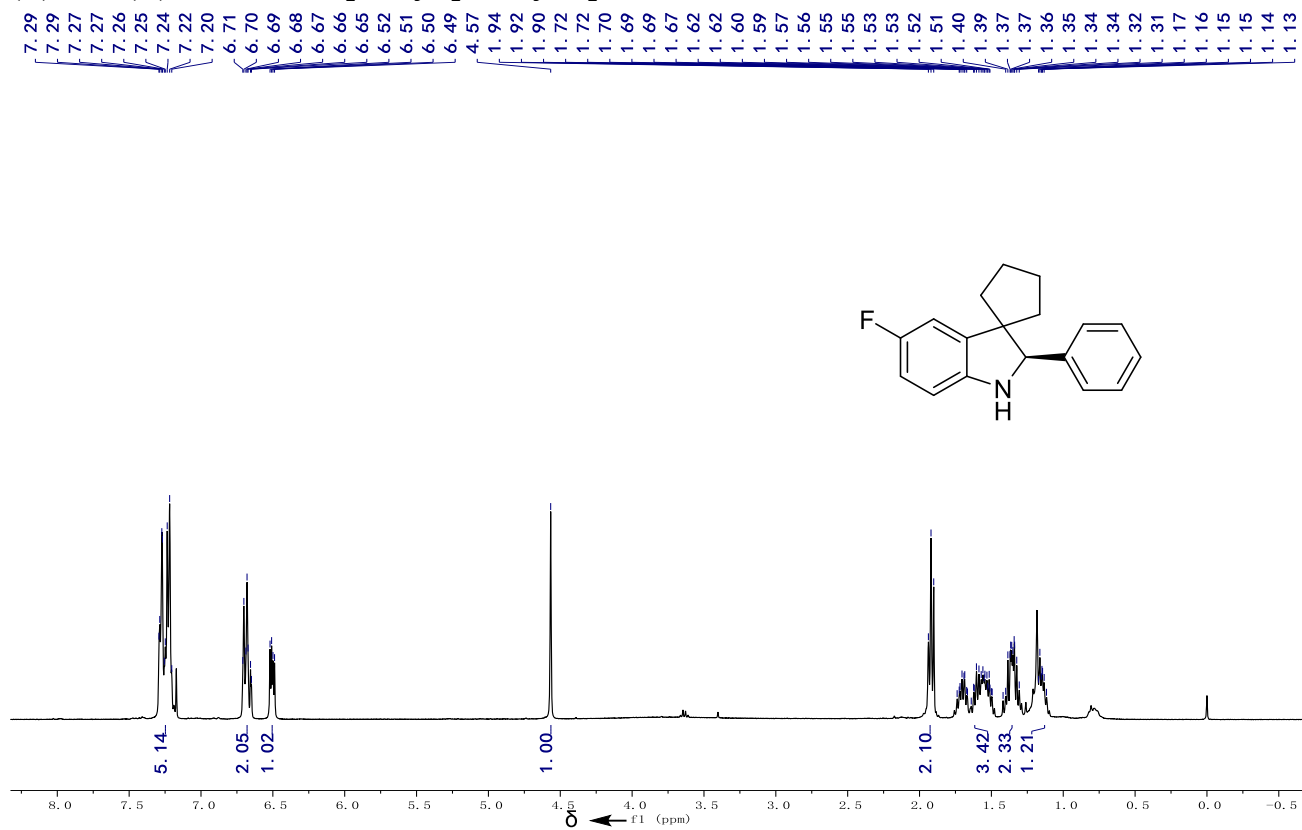
(R)-1p: (R)-3,3-dimethyl-2-(4-propoxyphenyl)indoline

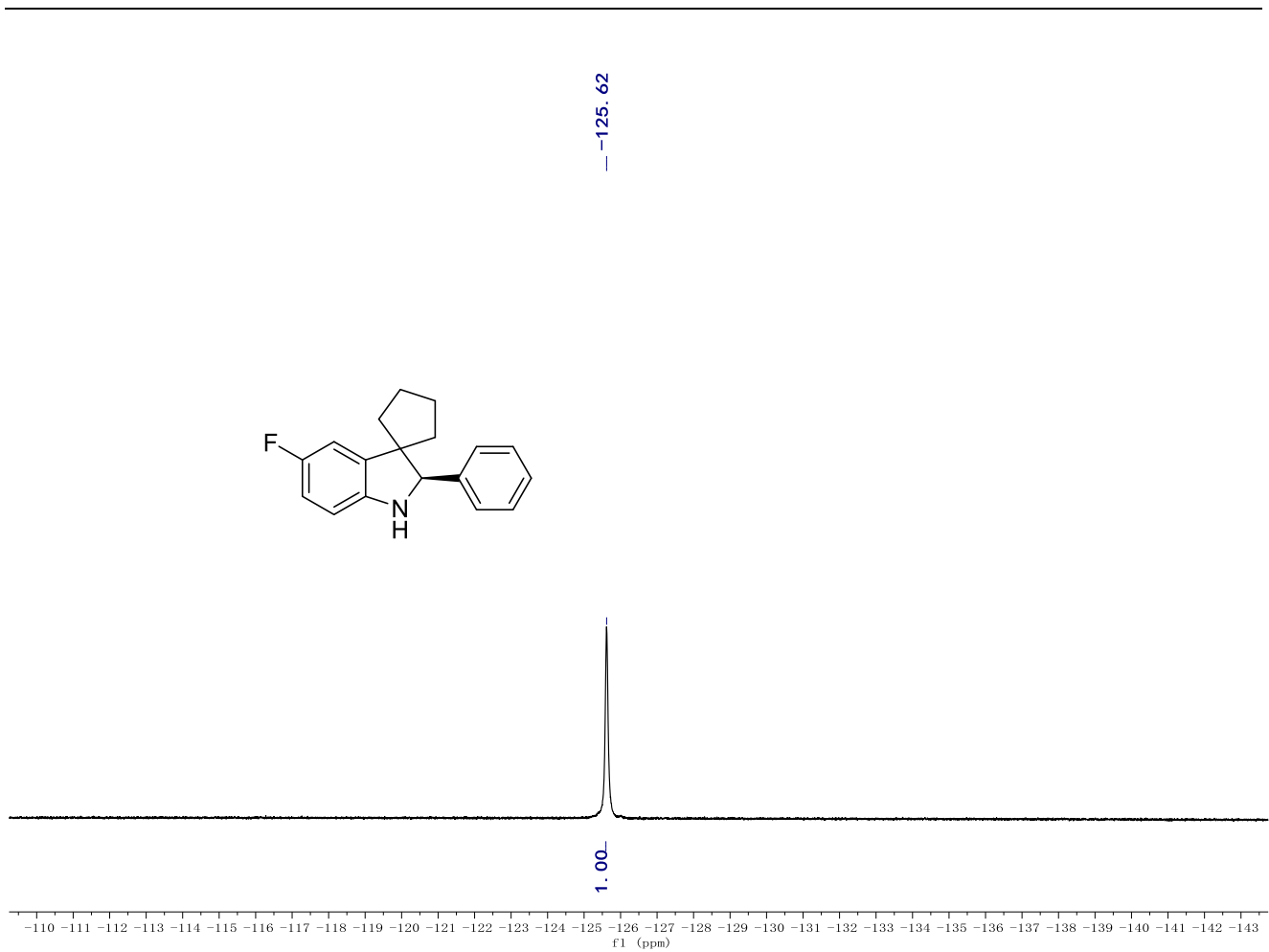


(R)-1q: (R)-2'-phenylspiro[cyclopentane-1,3'-indoline].

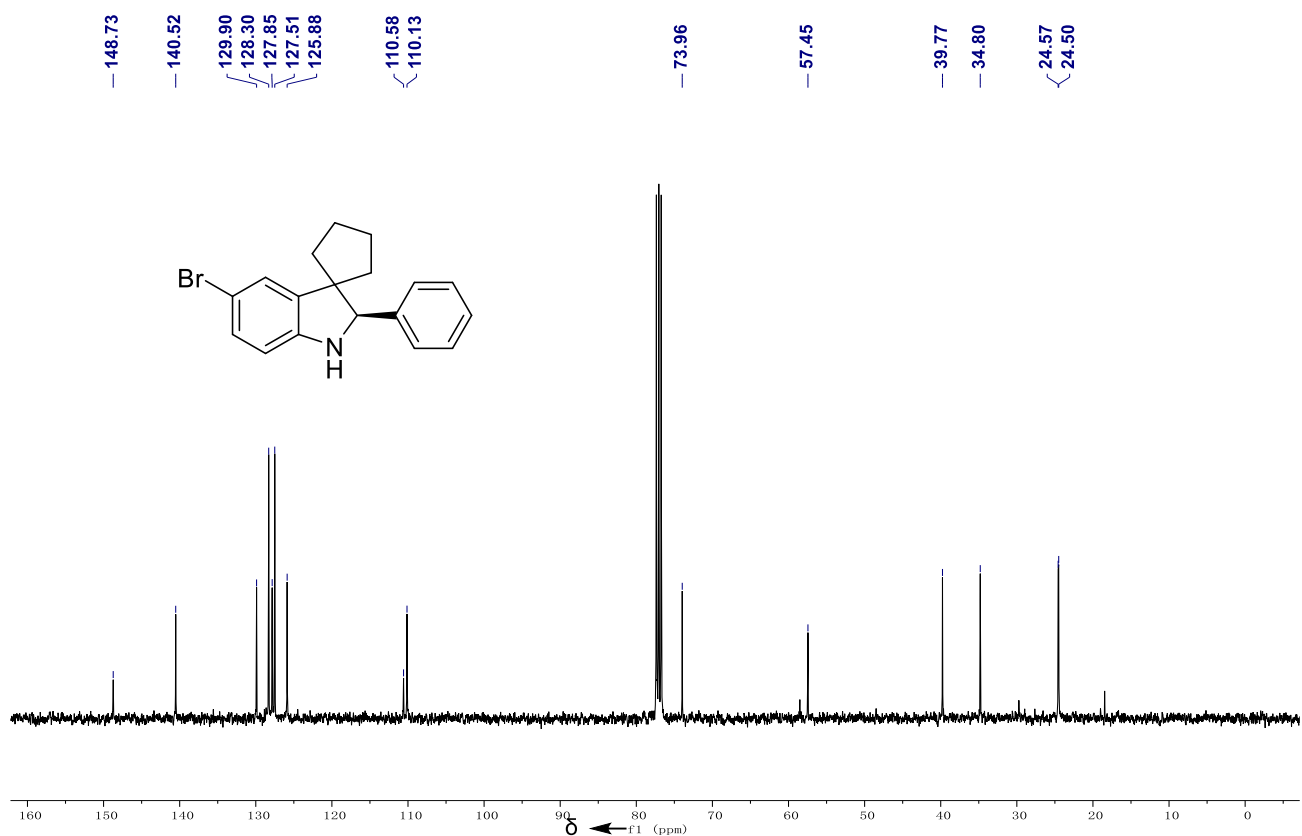
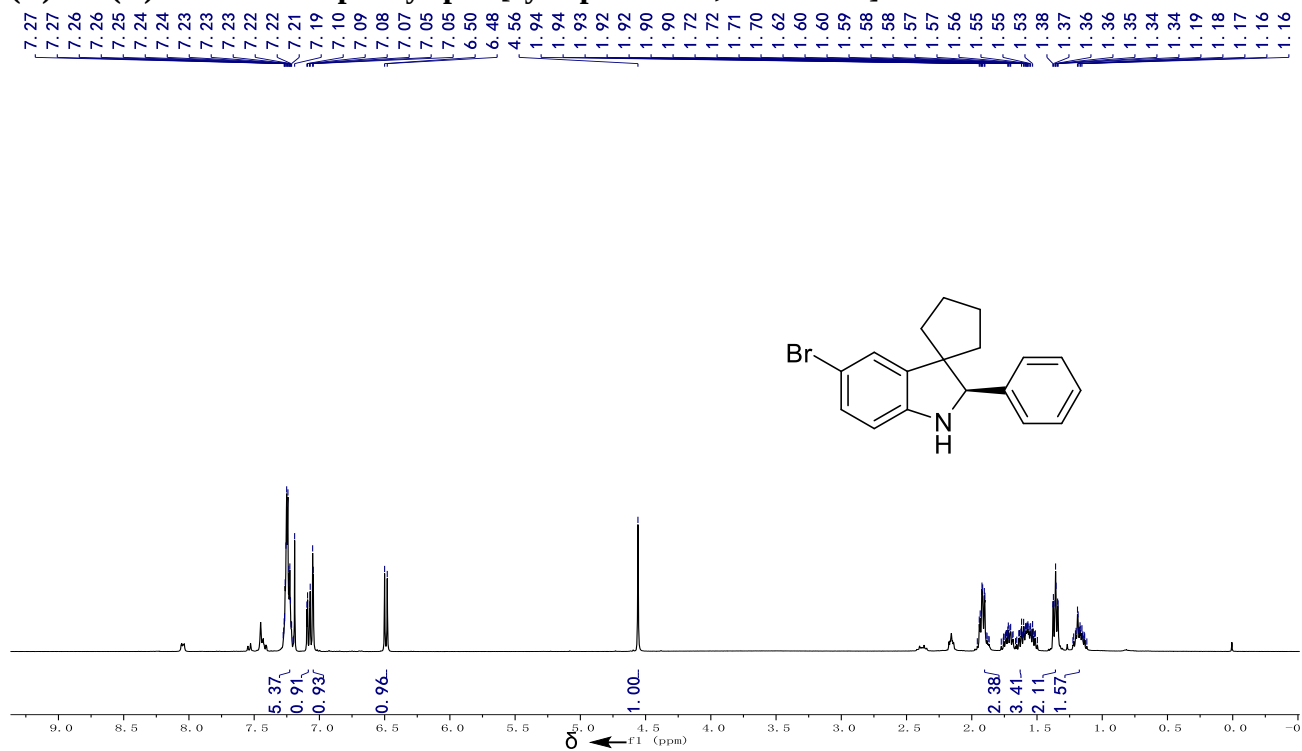


(R)-1r: (R)-5'-fluoro-2'-phenylspiro[cyclopentane-1,3'-indoline]

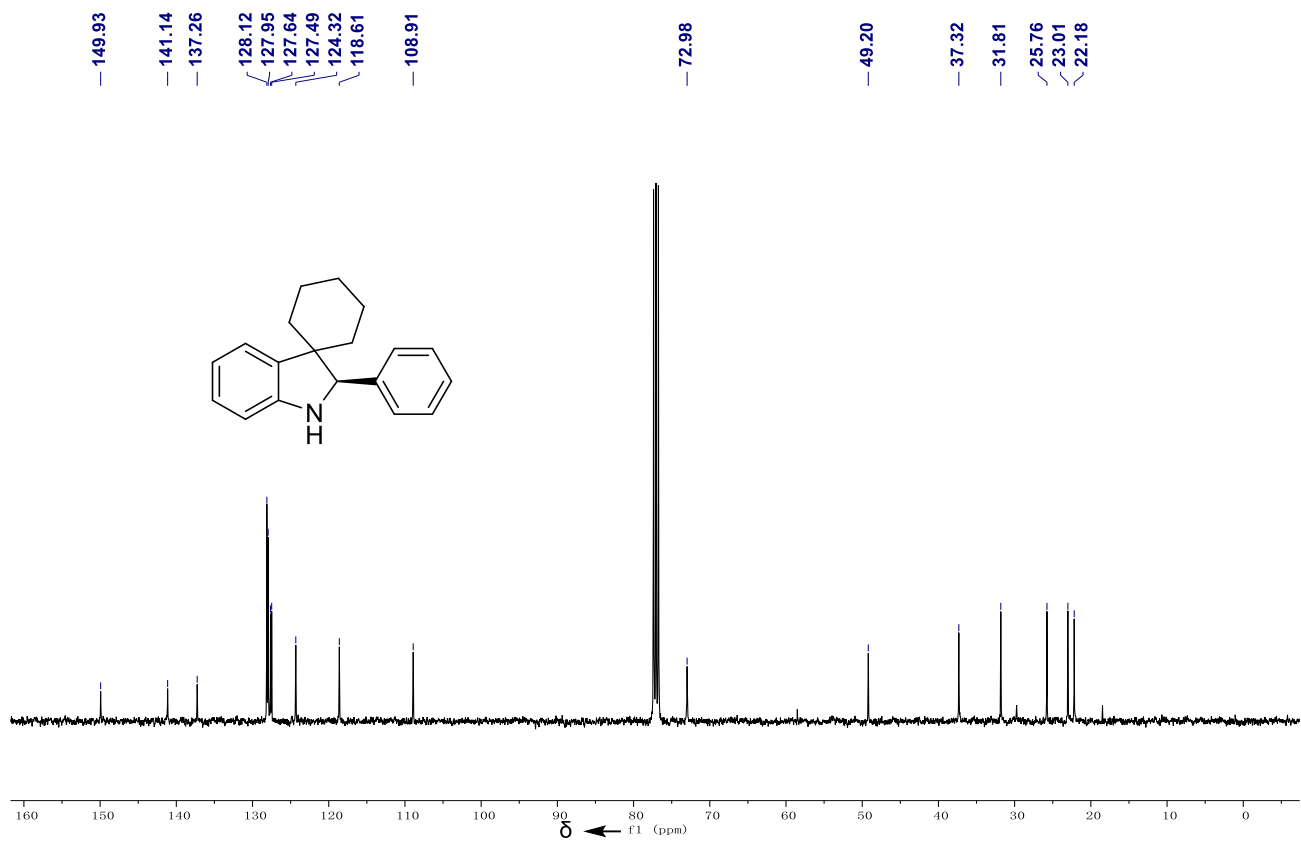
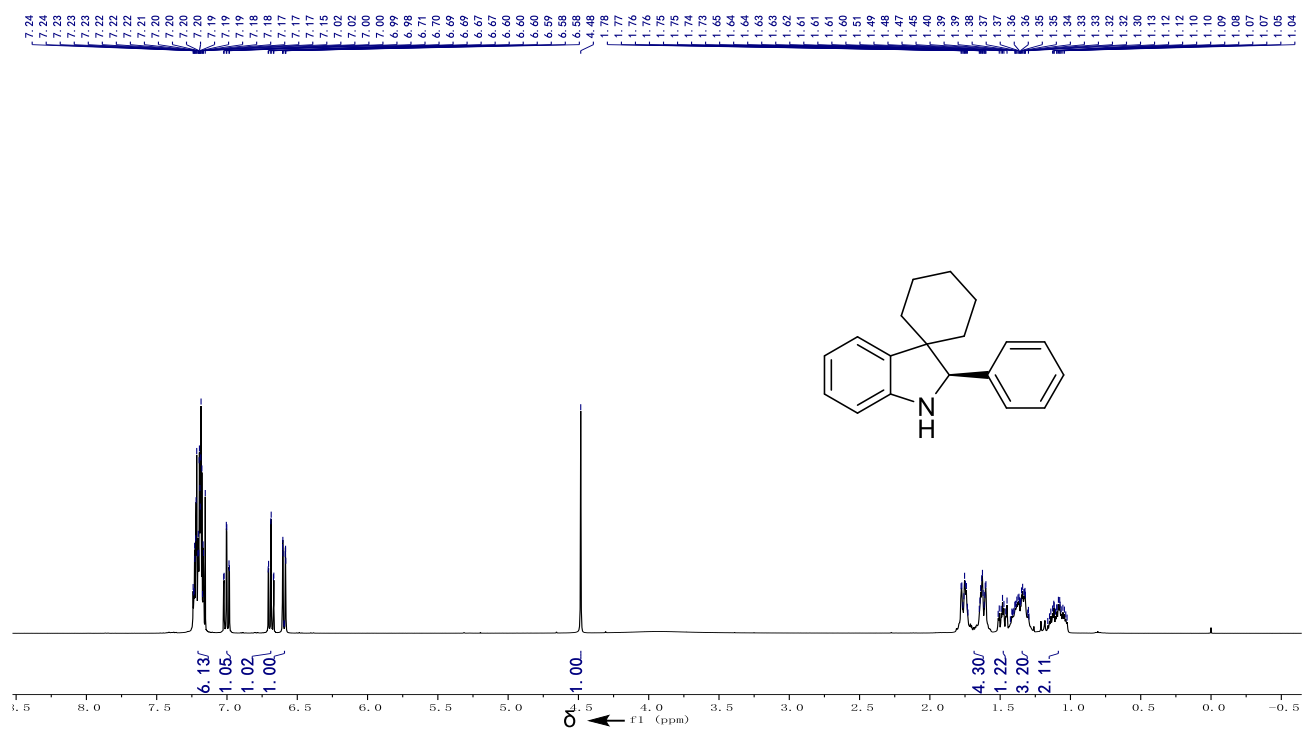




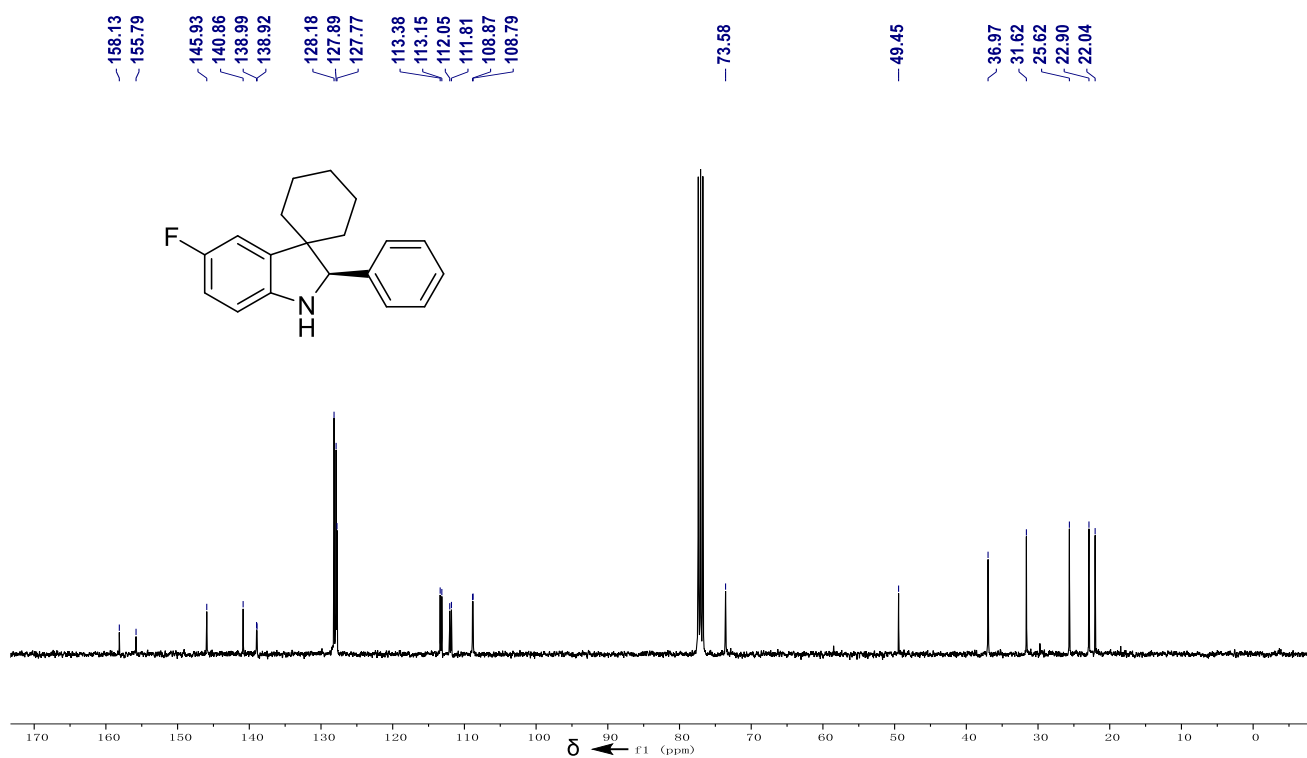
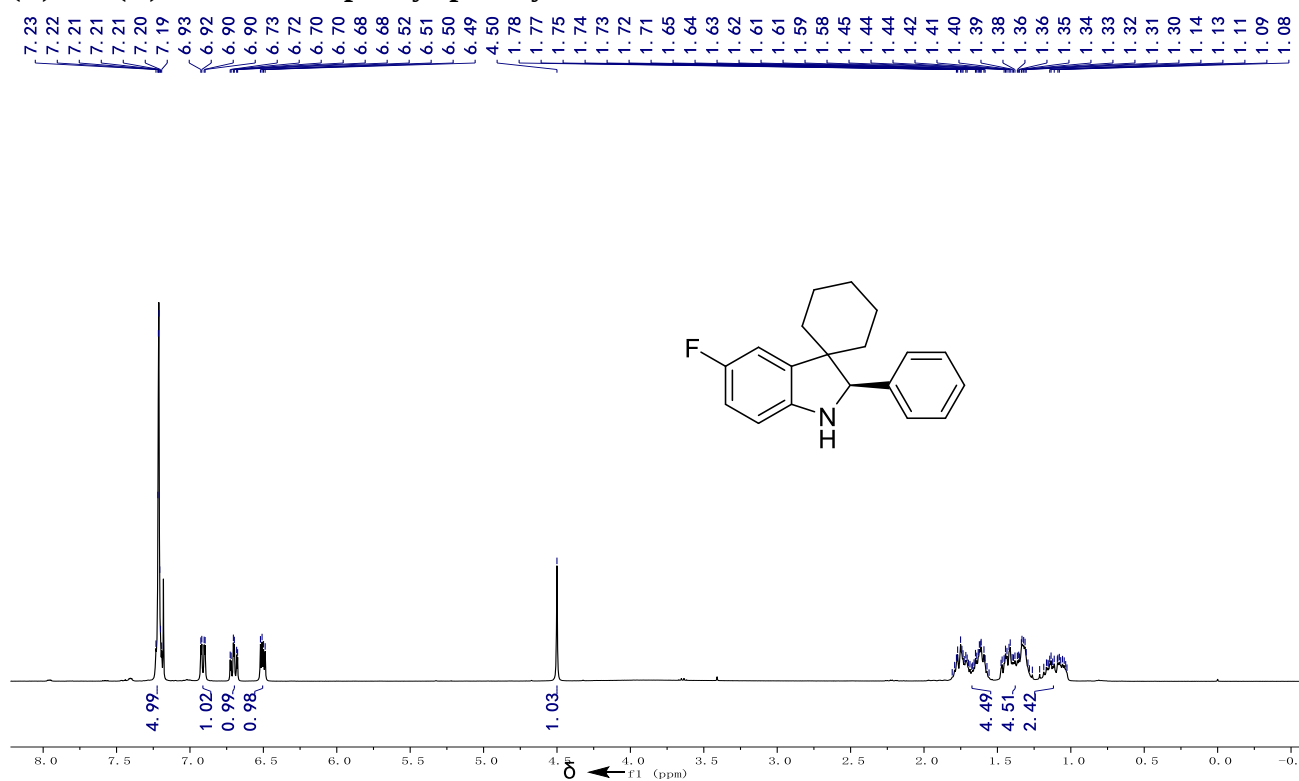
(R)-1s: (R)-5'-bromo-2'-phenylspiro[cyclopentane-1,3'-indoline].

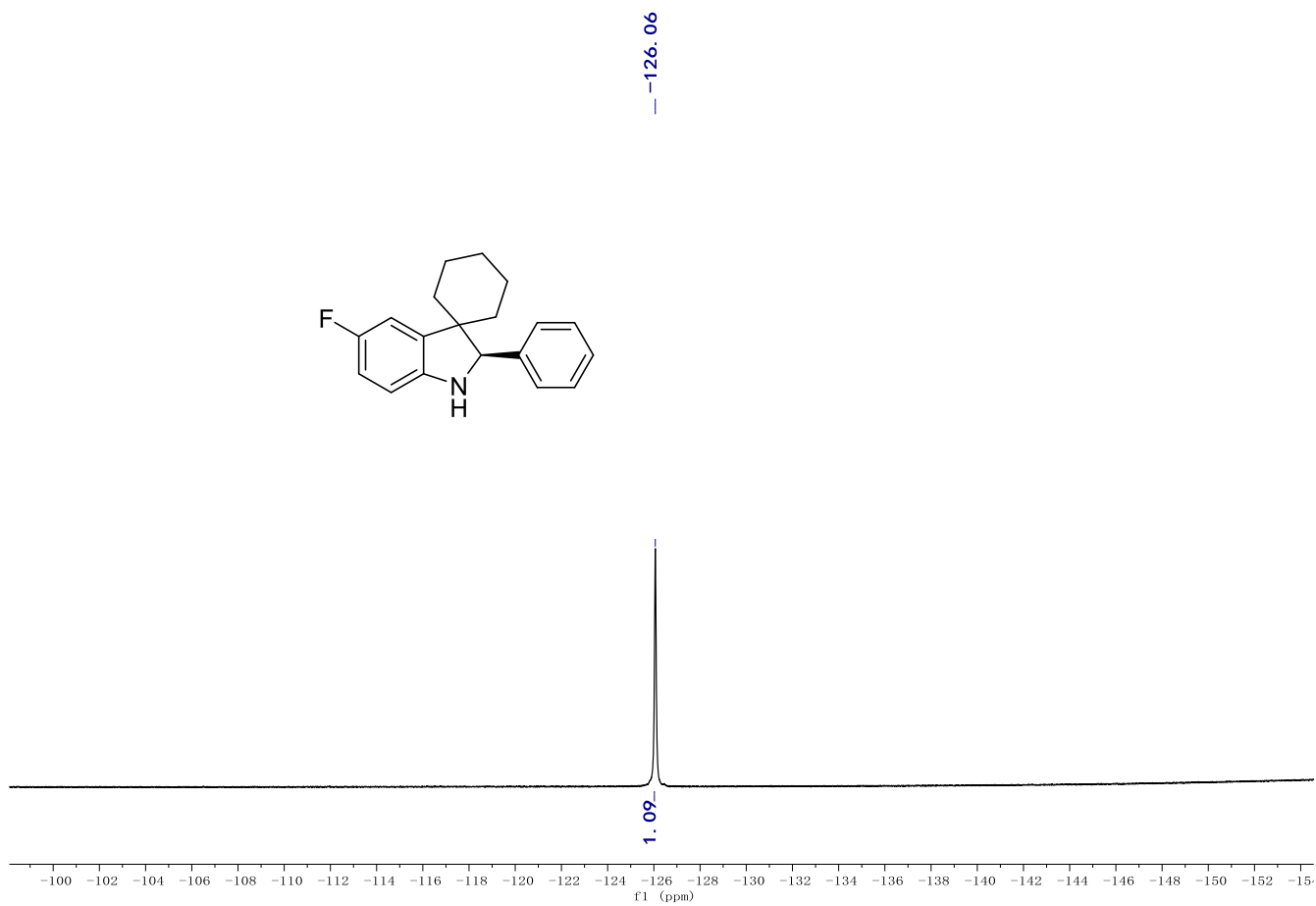


(R)-1t: (R)-2'-phenylspiro[cyclohexane-1,3'-indoline].

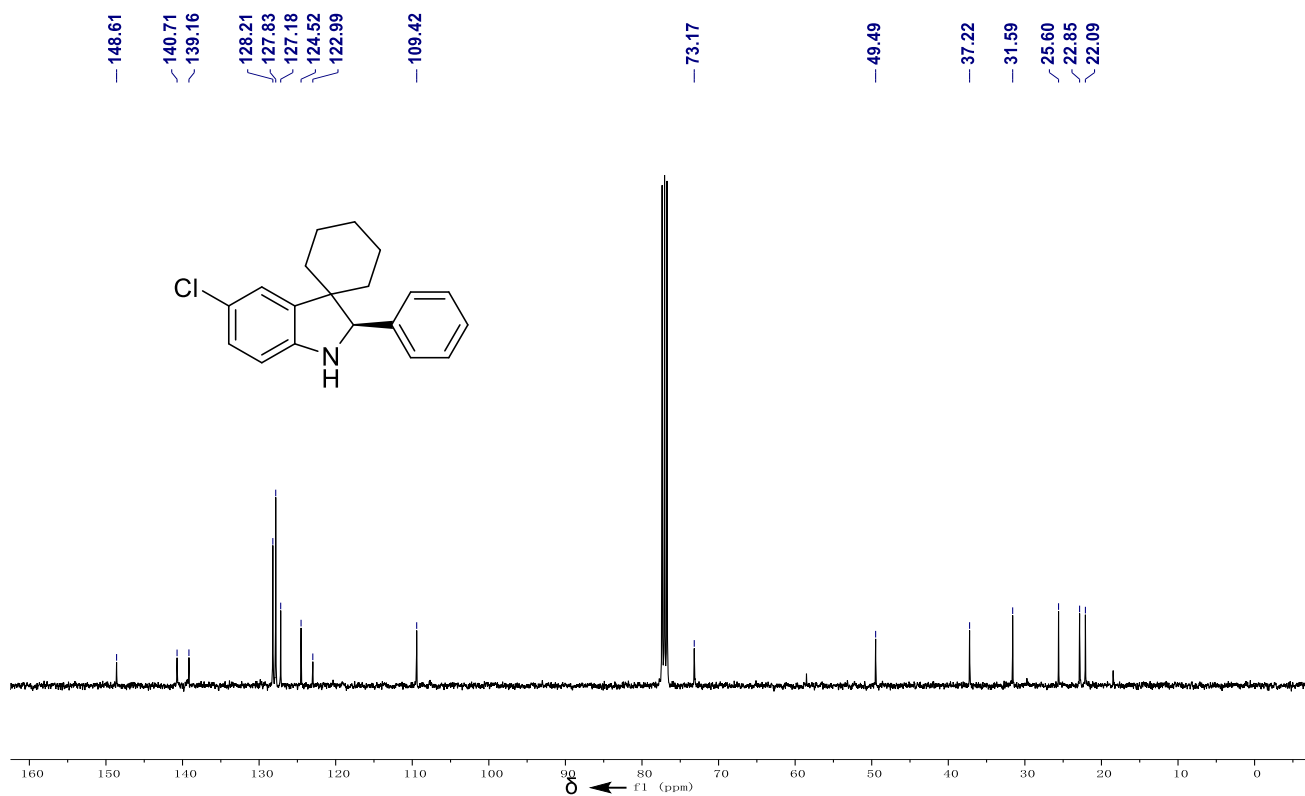
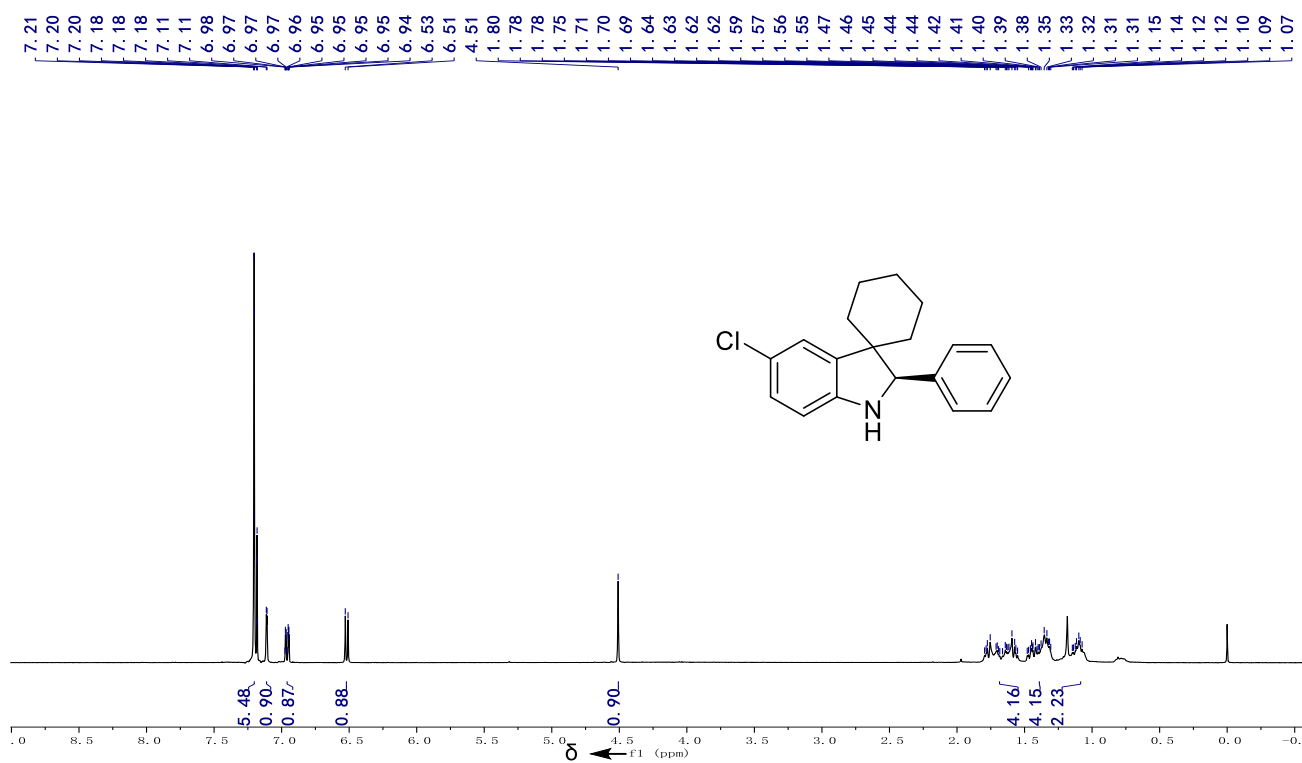


(R)-1u: (R)- 5'-fluoro-2'-phenylspiro[cyclohexane-1,3'-indoline].

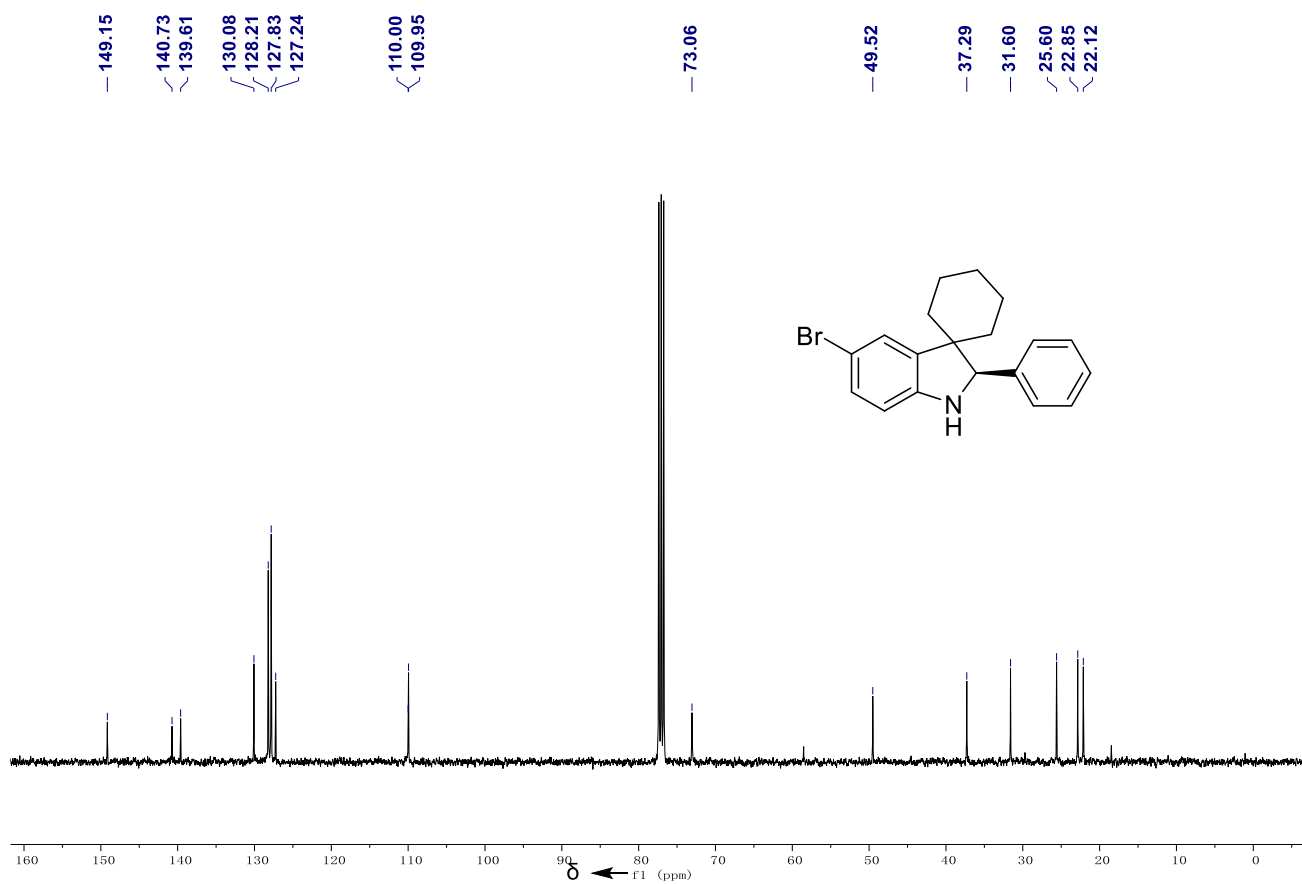
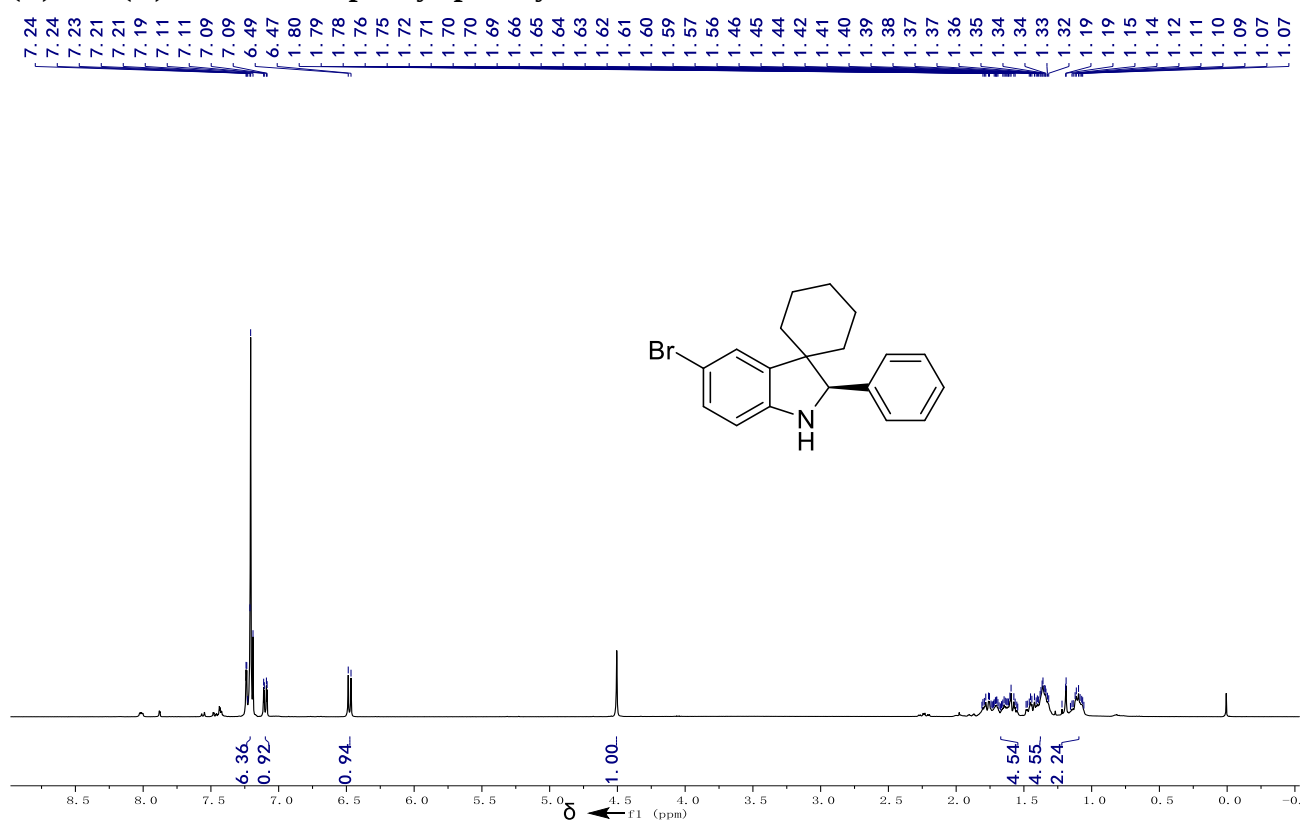




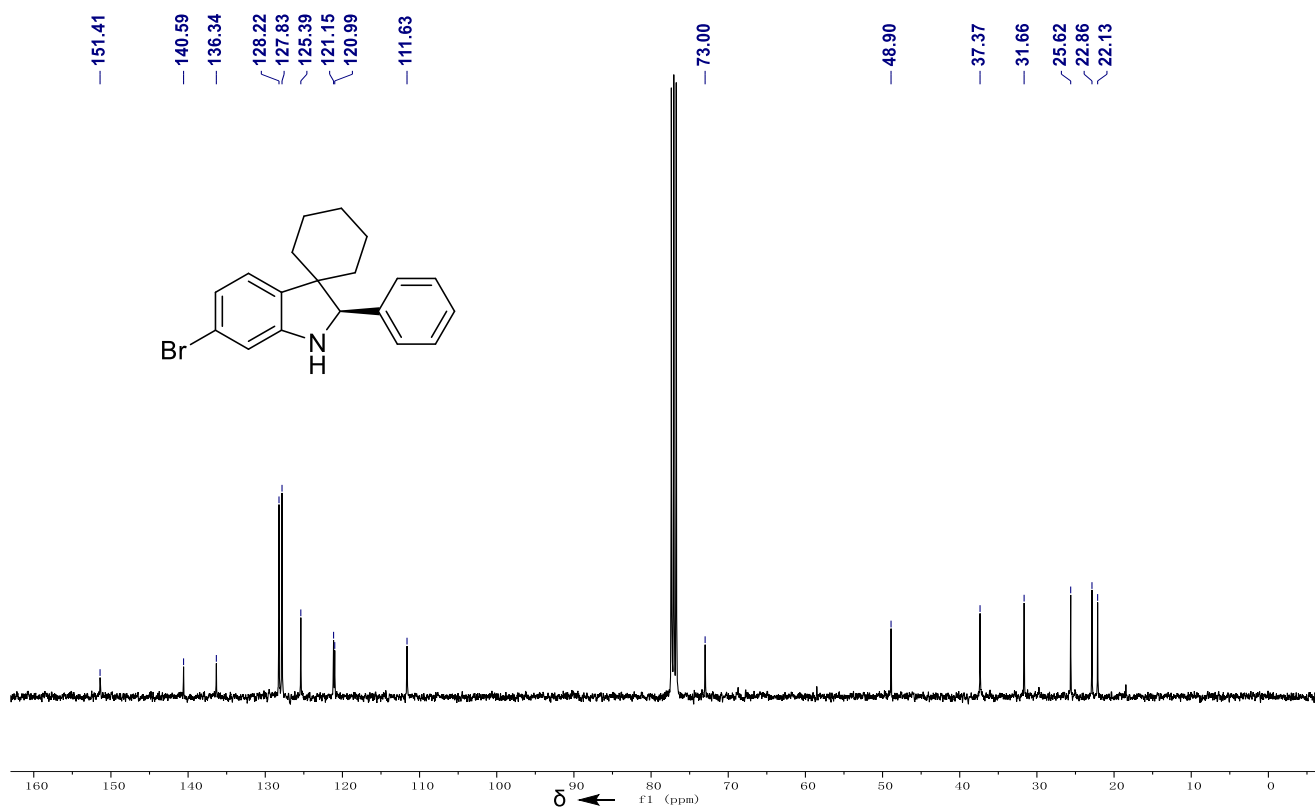
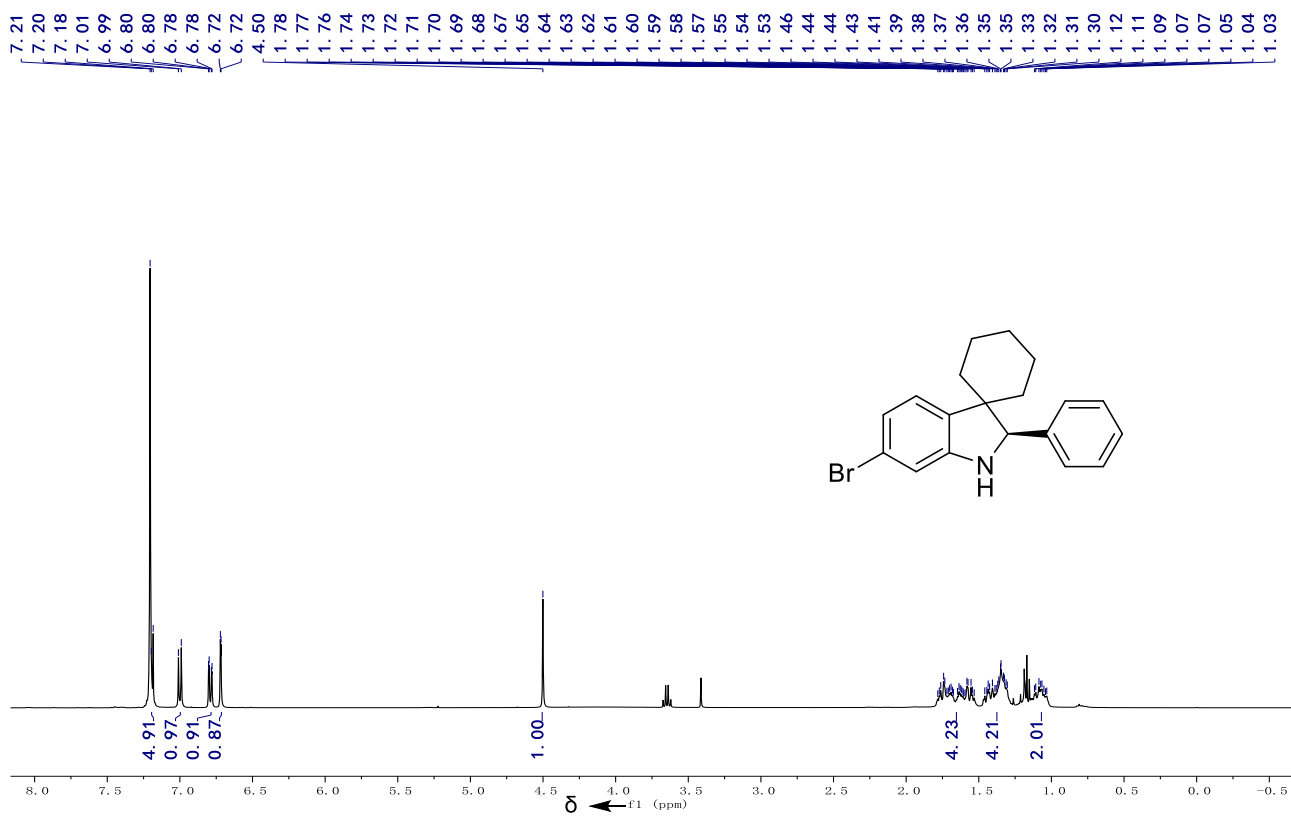
(R)-1v: (R)-5'-chloro-2'-phenylspiro[cyclohexane-1,3'-indoline].



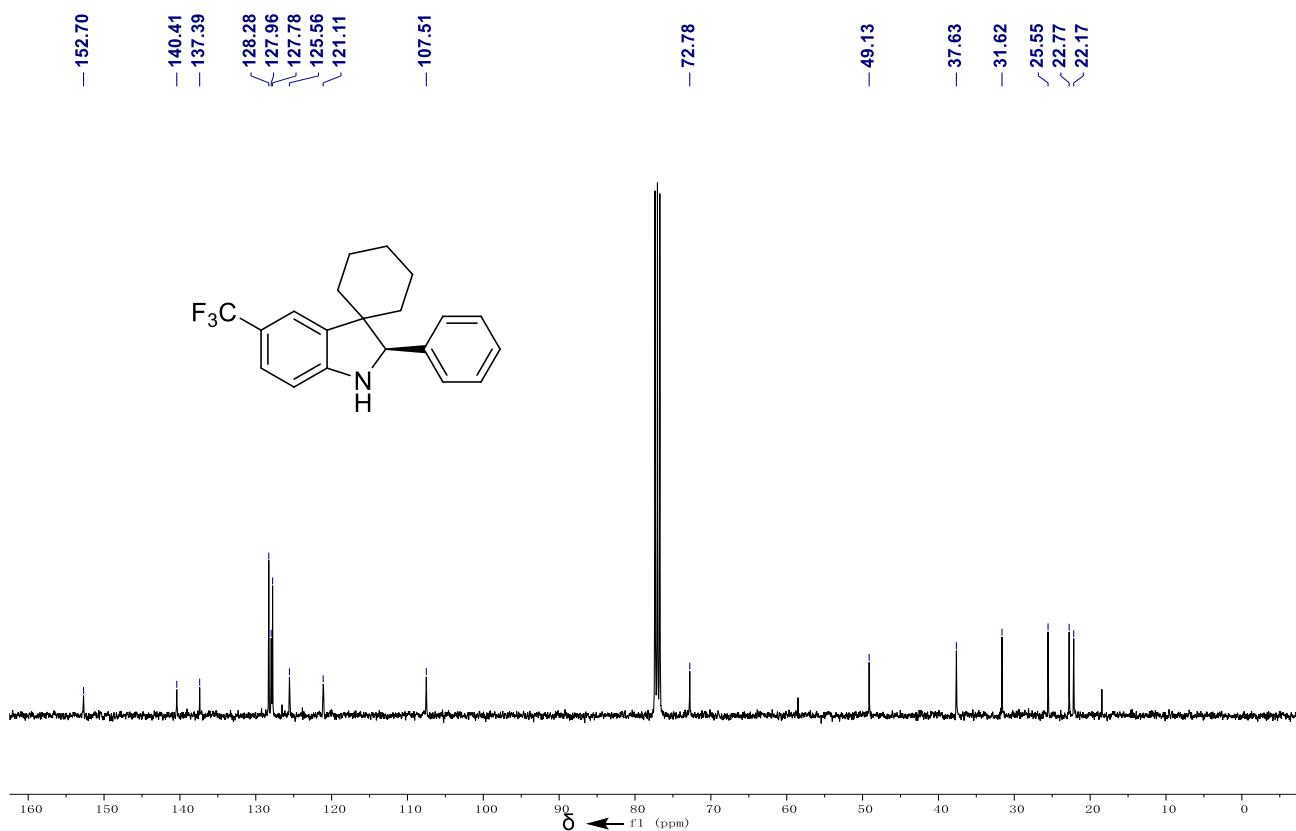
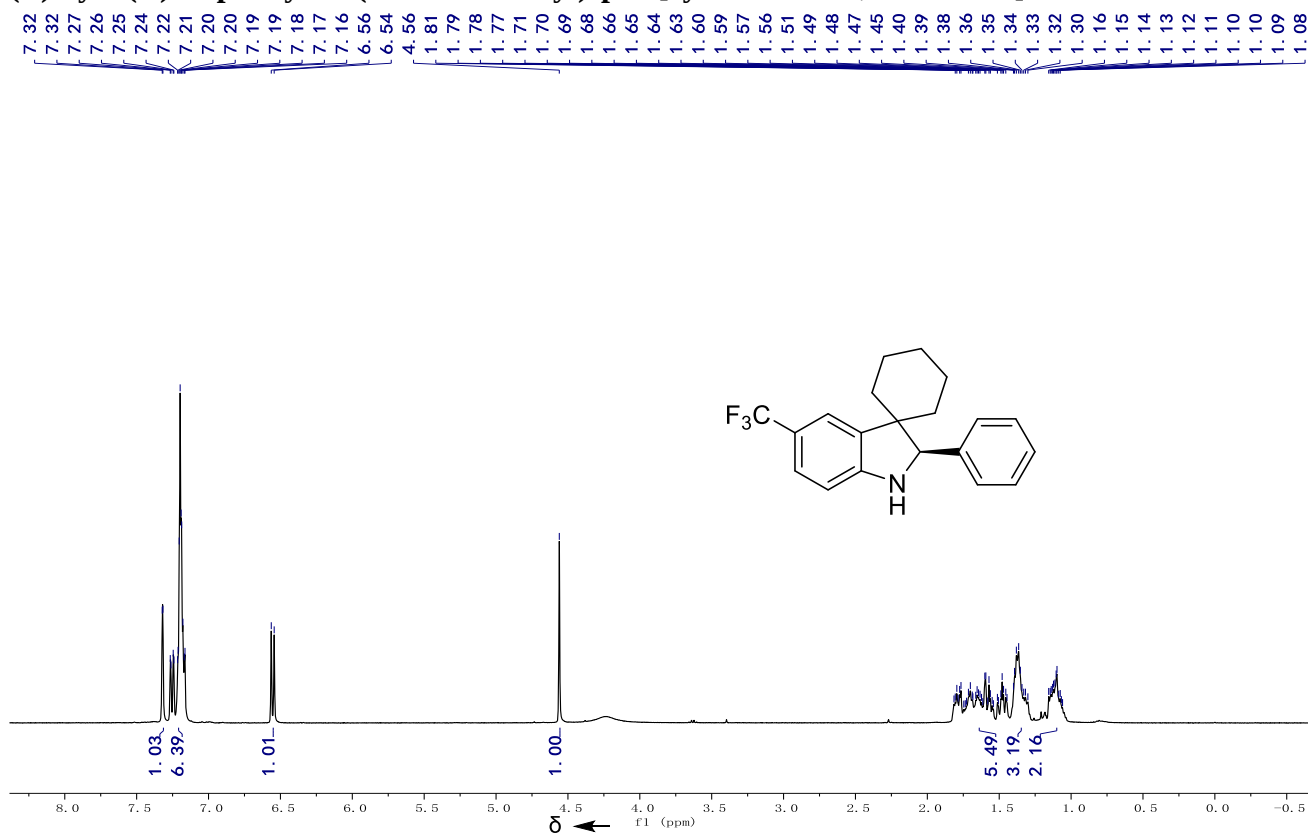
(R)-1w: (R)-5'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline].

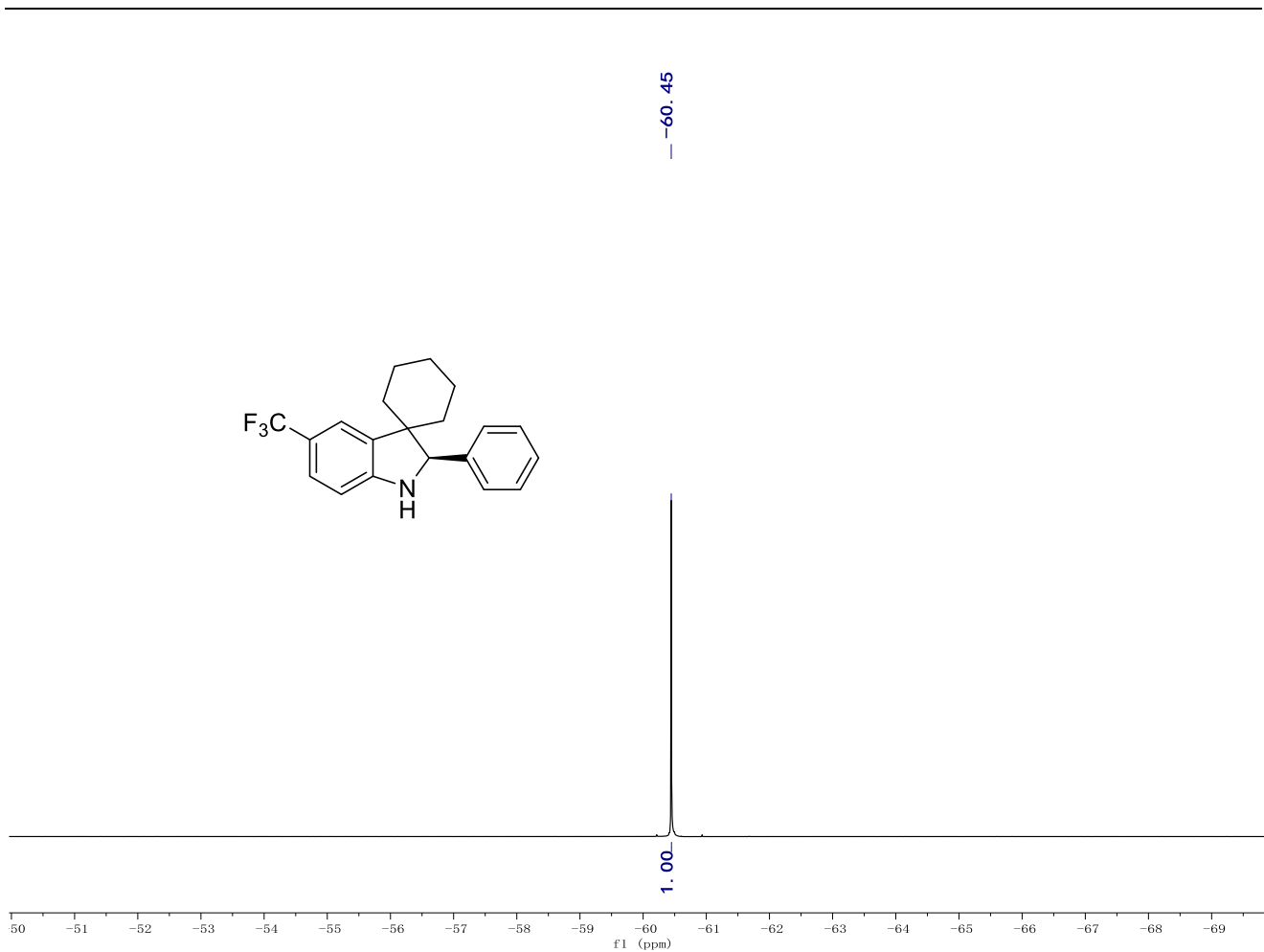


(R)-1x: (R)-6'-bromo-2'-phenylspiro[cyclohexane-1,3'-indoline]

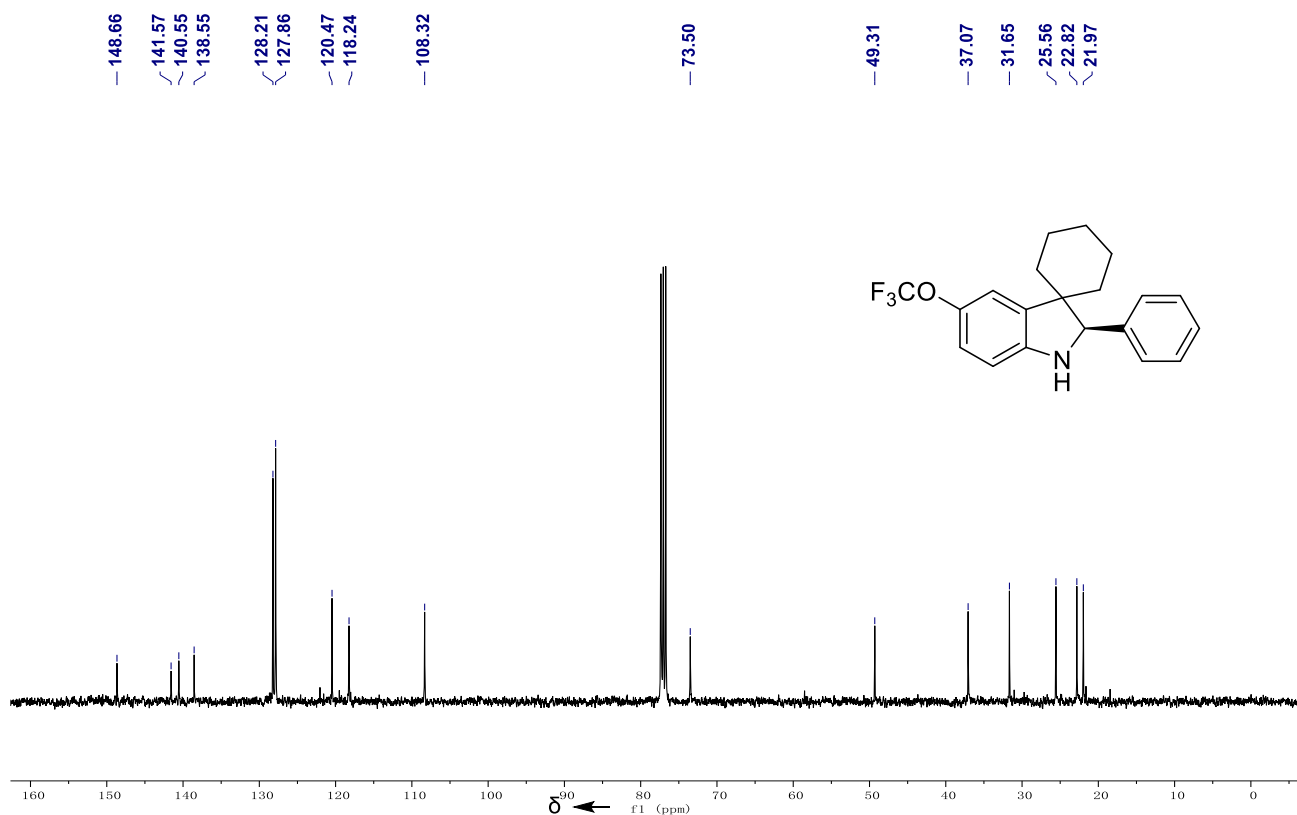
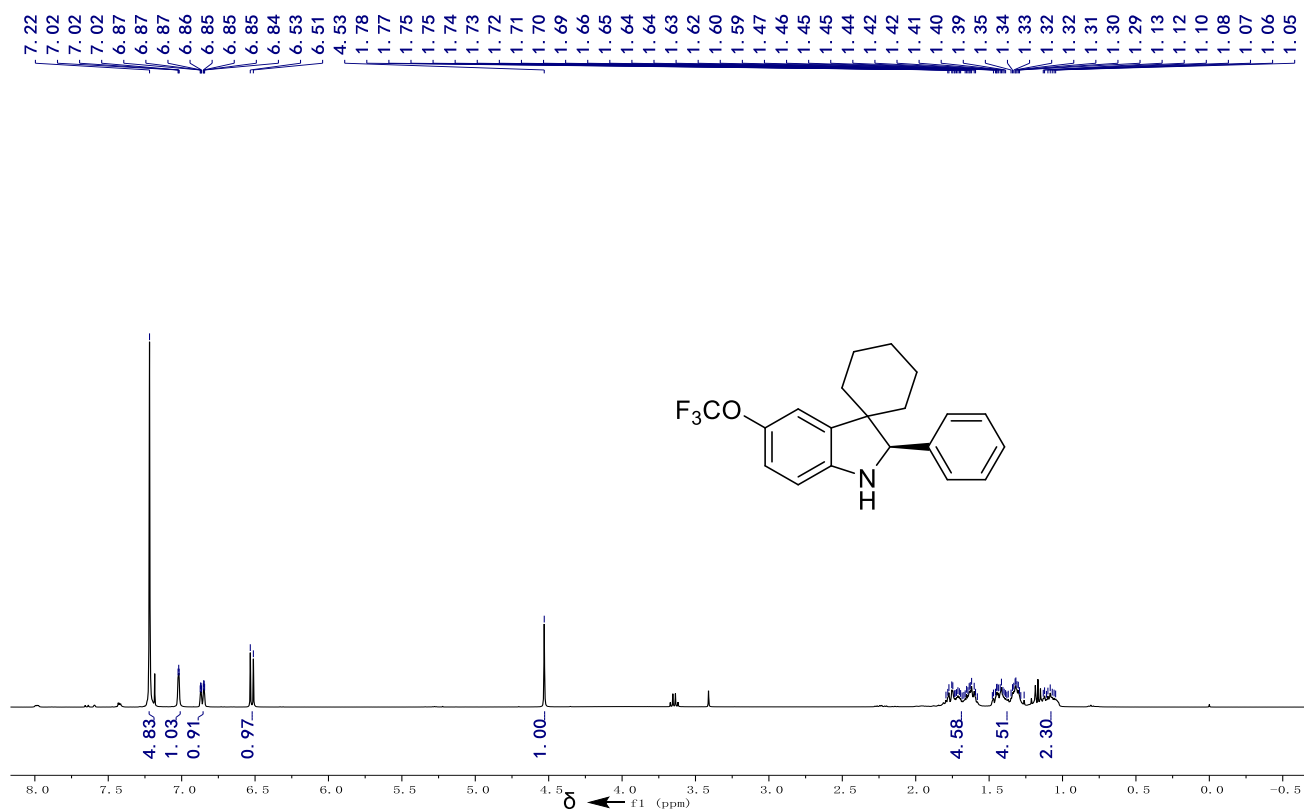


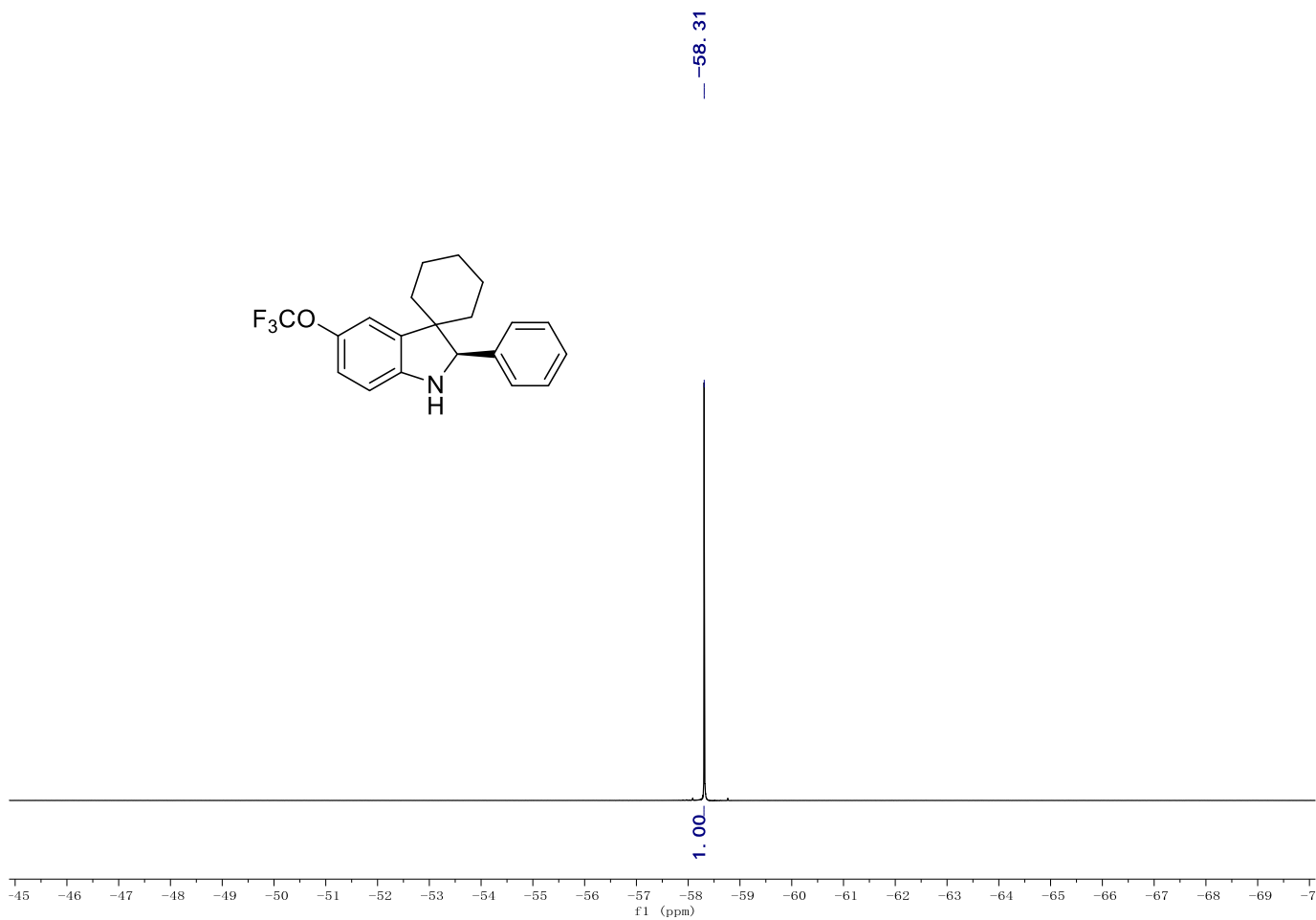
(R)-1y: (R)-2'-phenyl-5'-(trifluoromethyl)spiro[cyclohexane-1,3'-indoline]



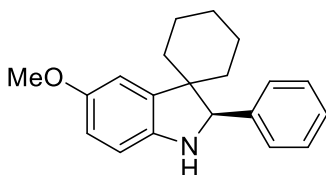
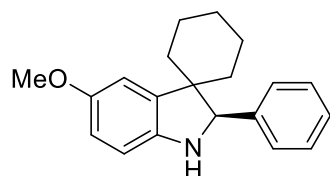


(R)-1z: (R)-2'-phenyl-5'-(trifluoromethoxy)spiro[cyclohexane-1,3'-indoline]

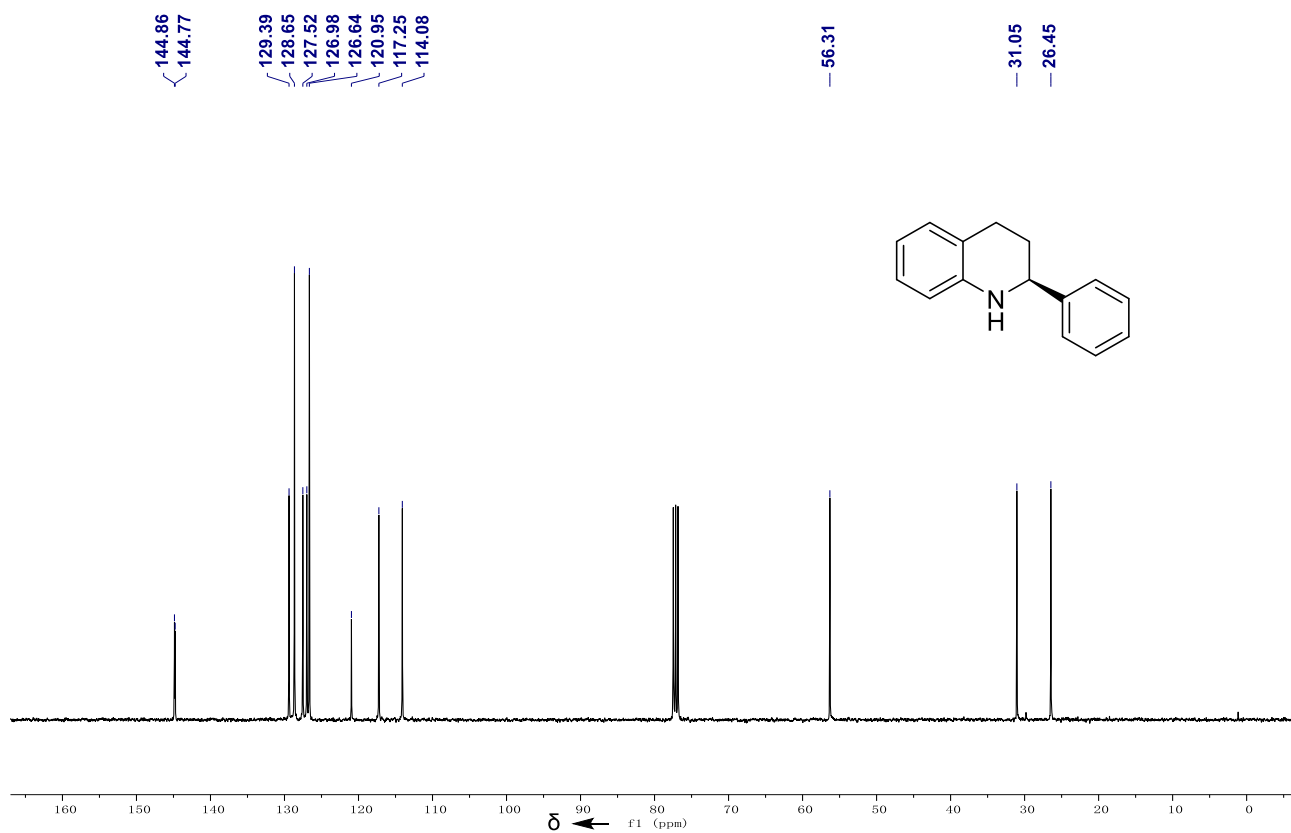
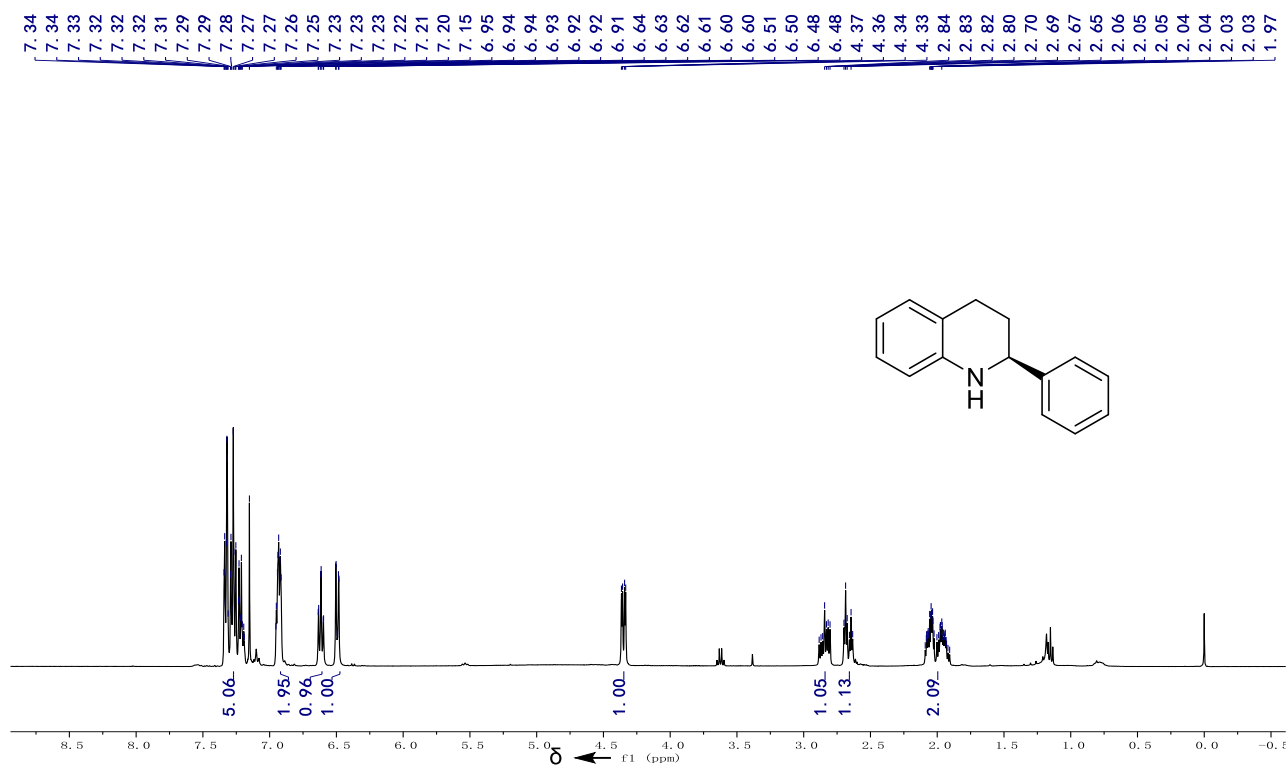




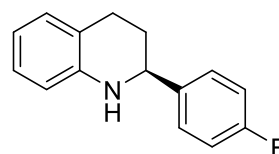
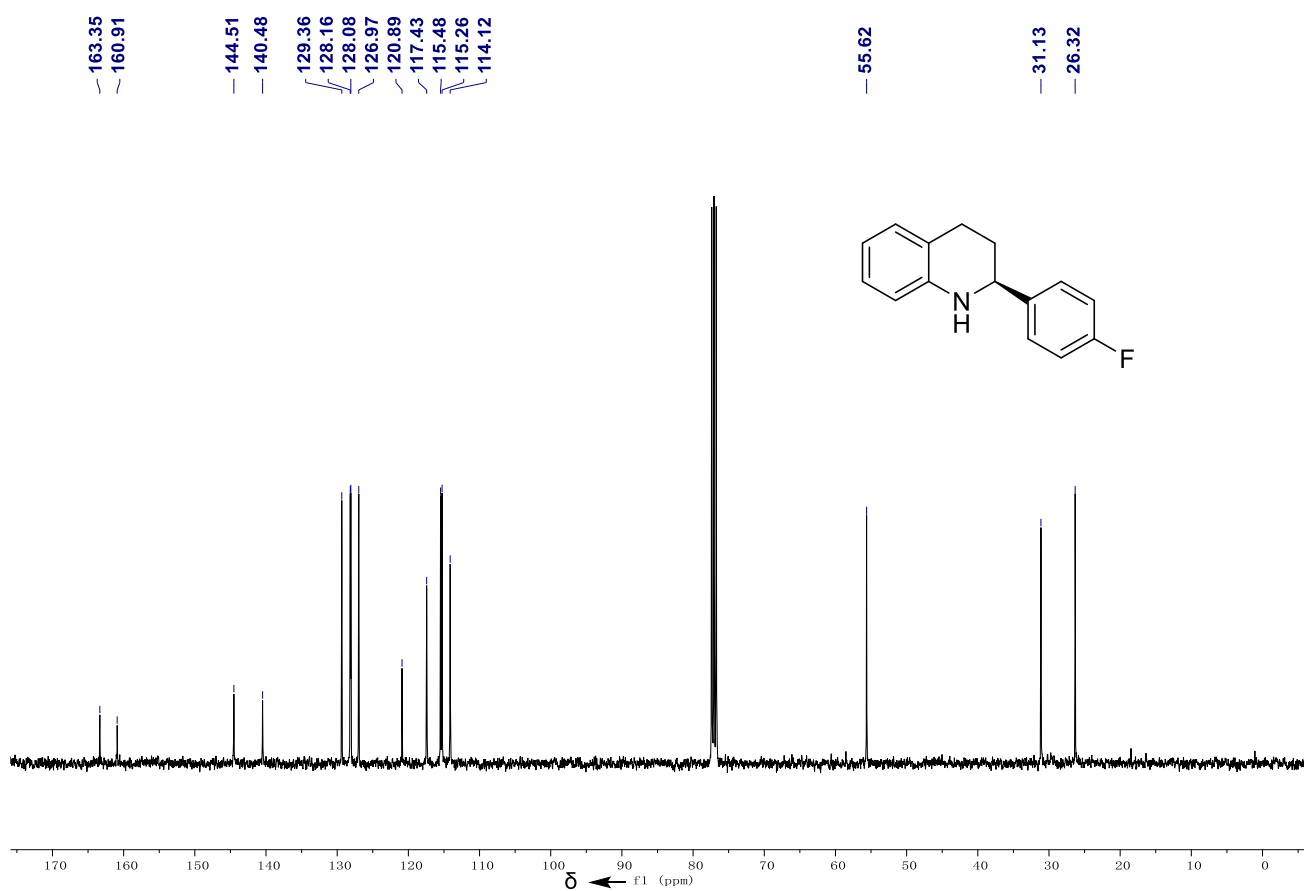
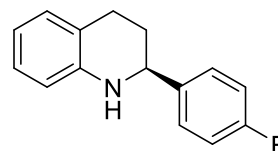
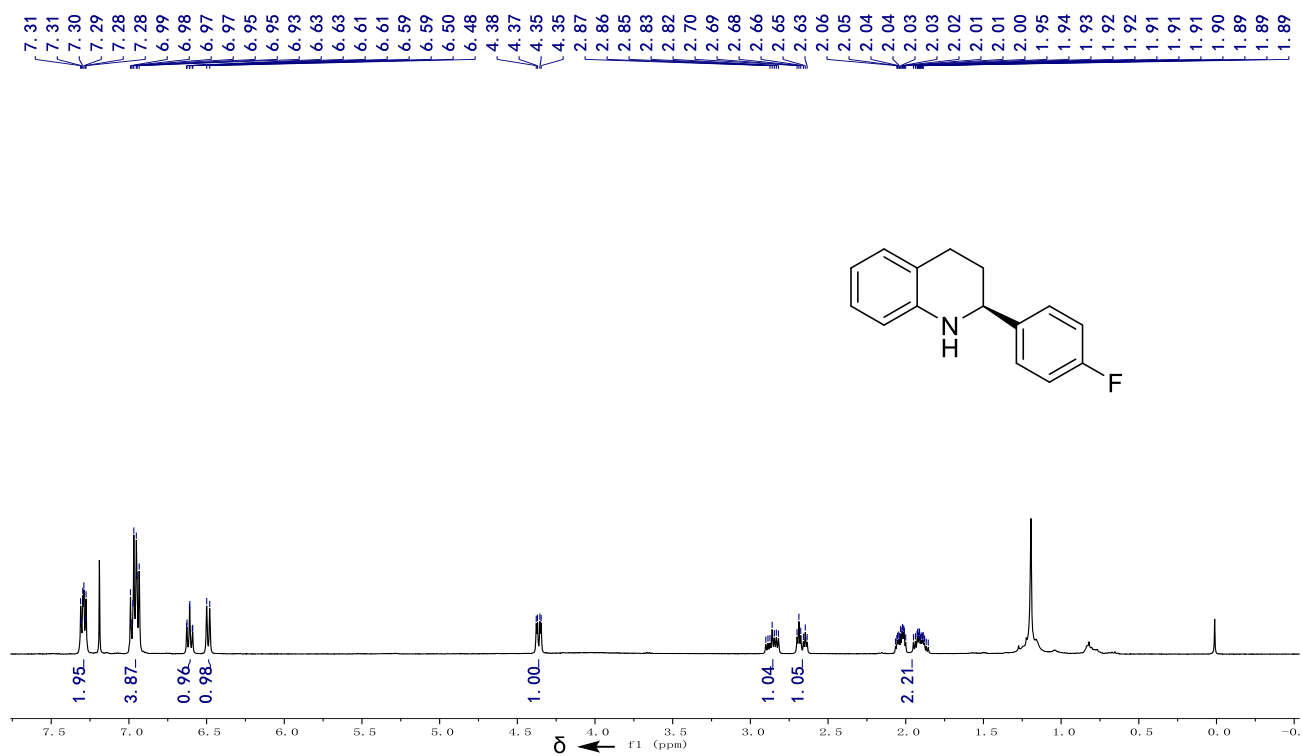
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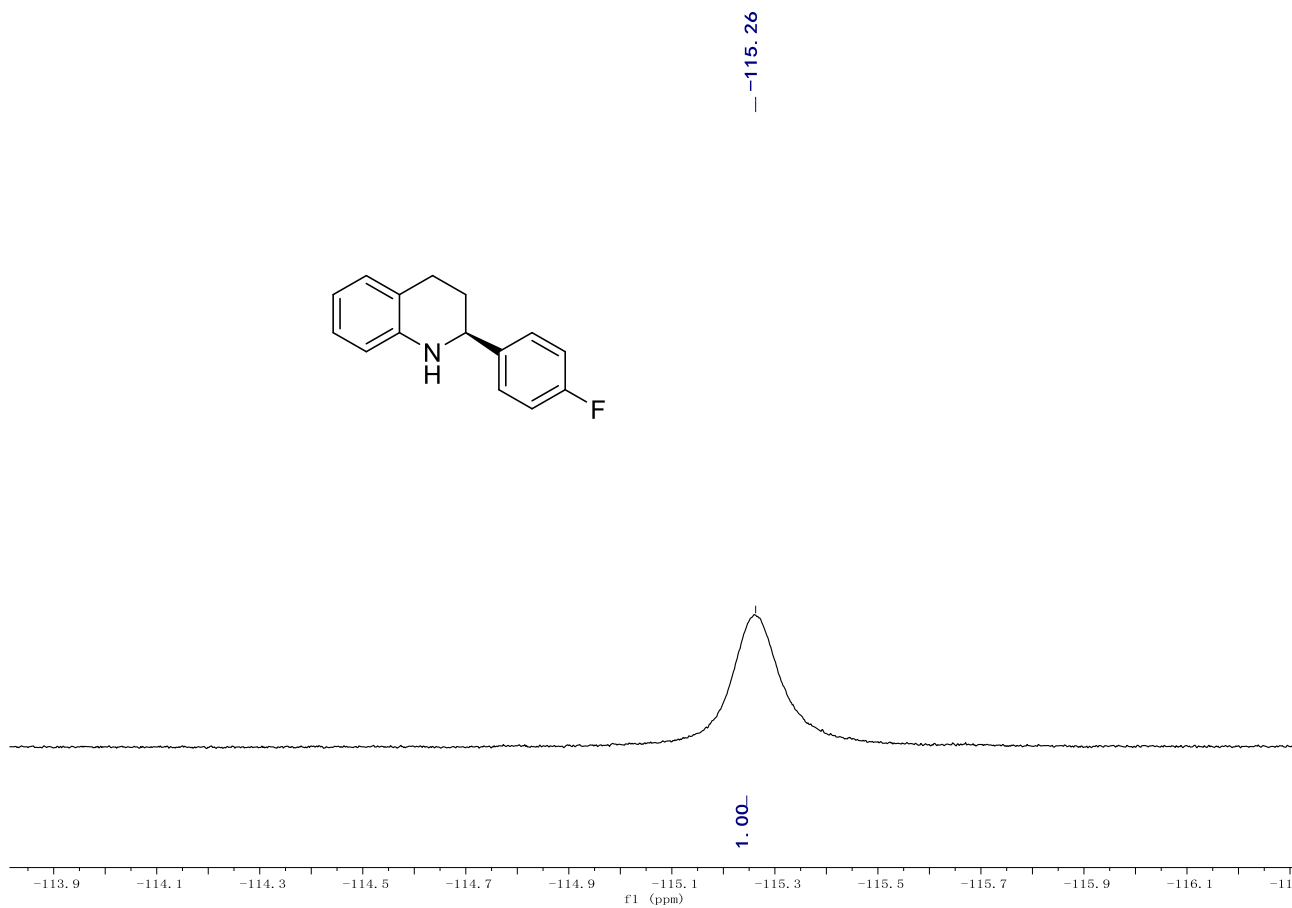


(S)-3a: (S)-2-phenyl-1,2,3,4-tetrahydroquinoline.

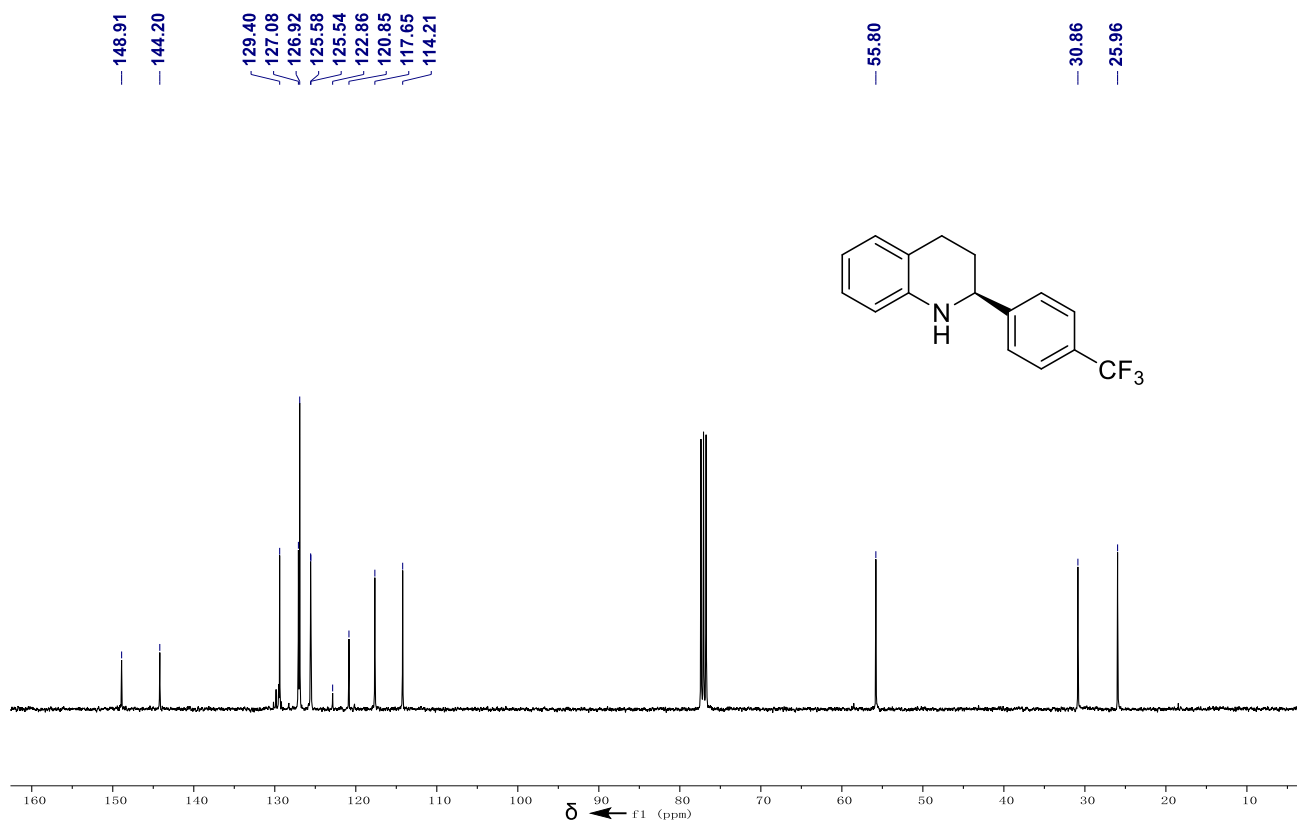
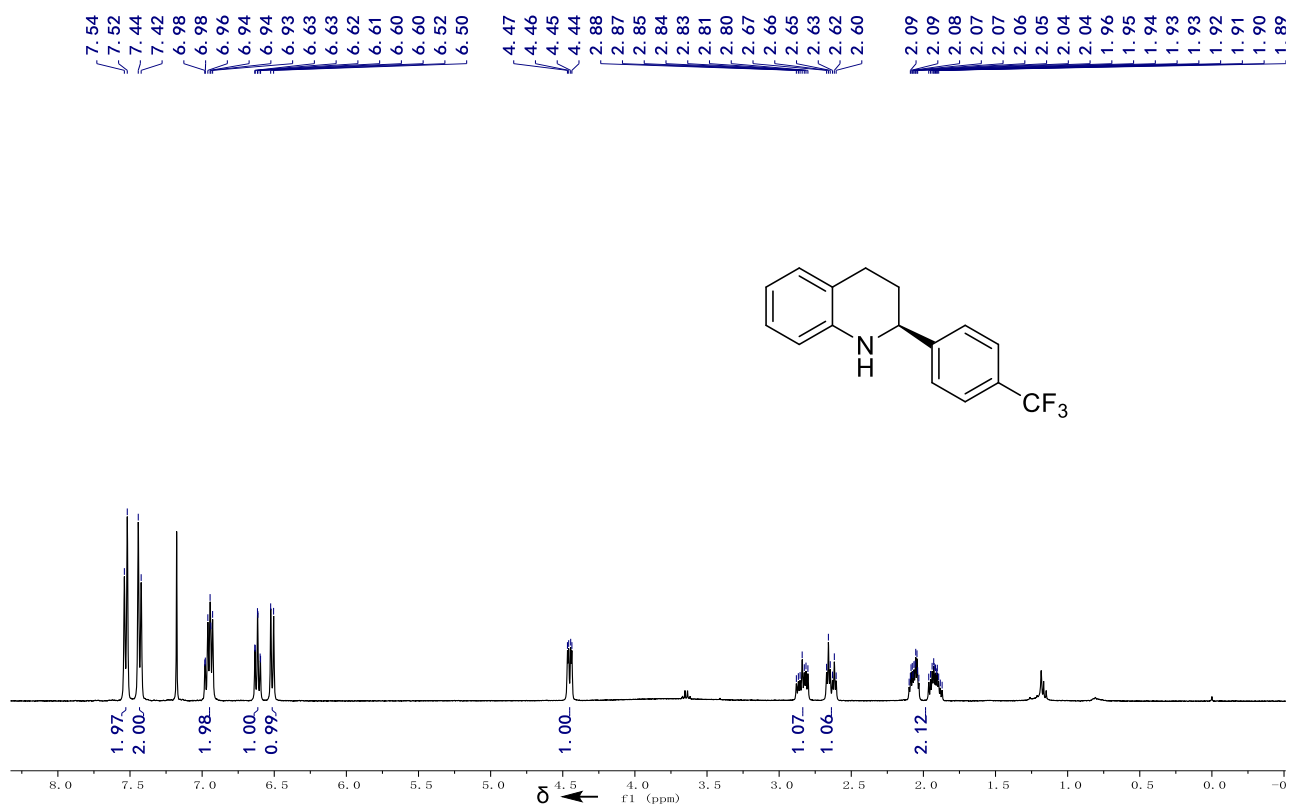


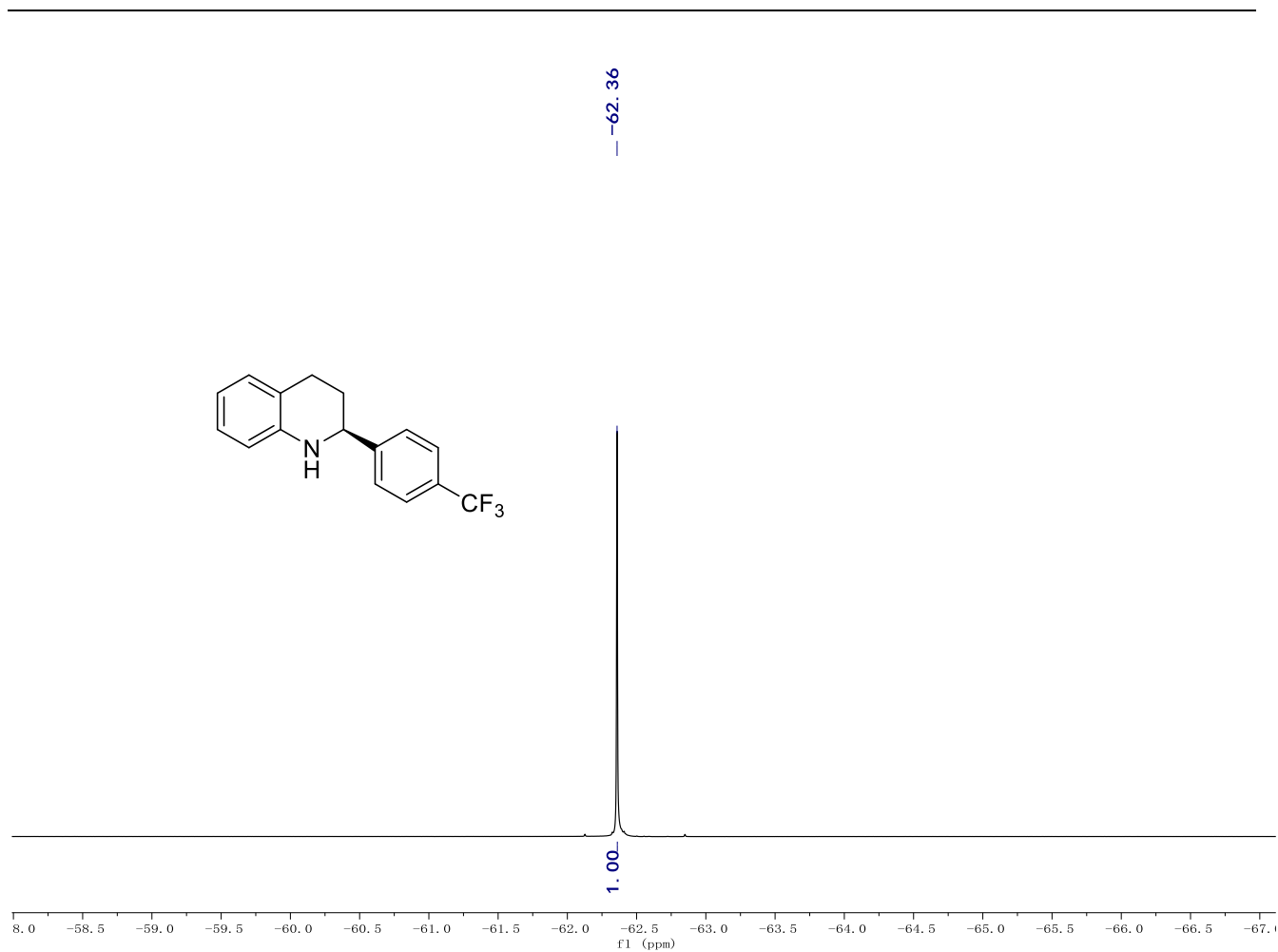
(S)-3b: (S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline.



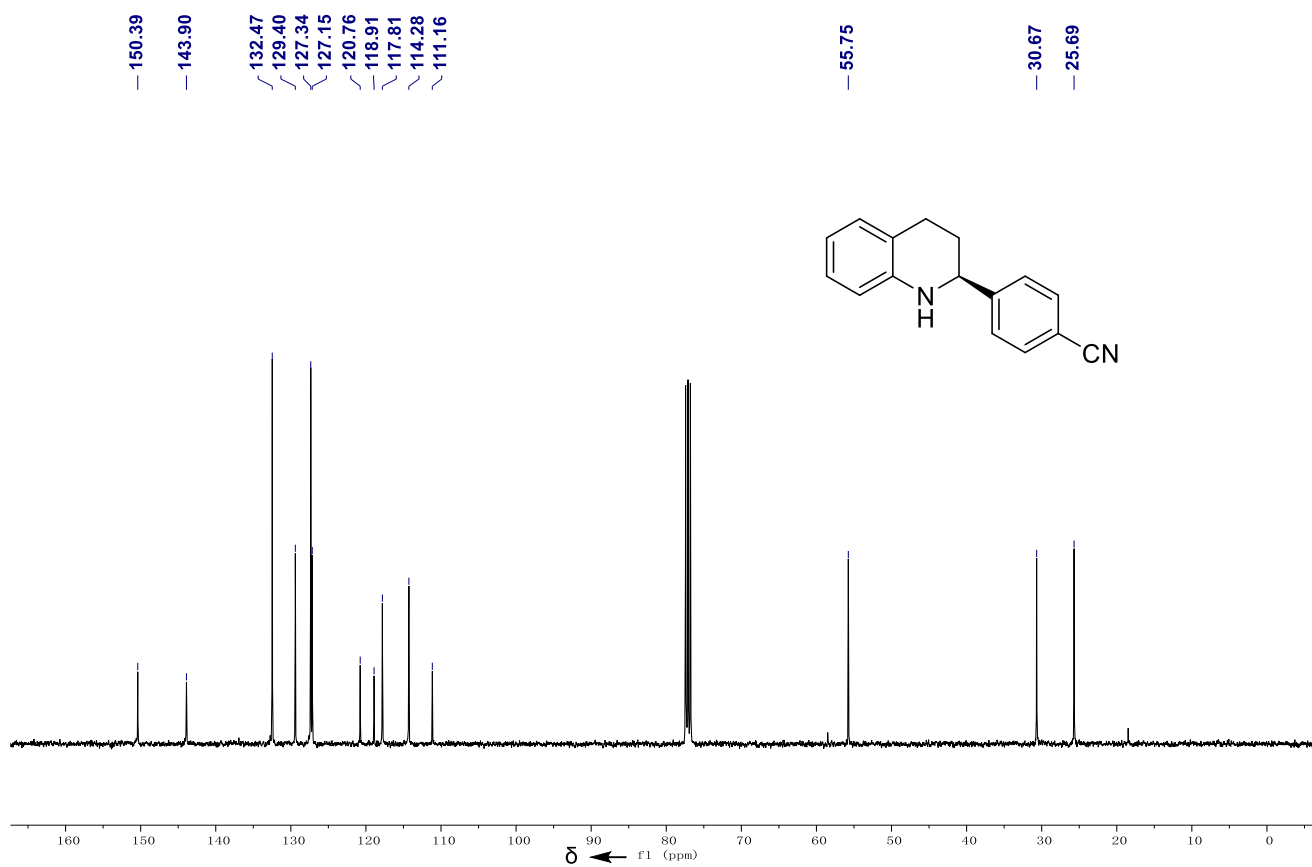
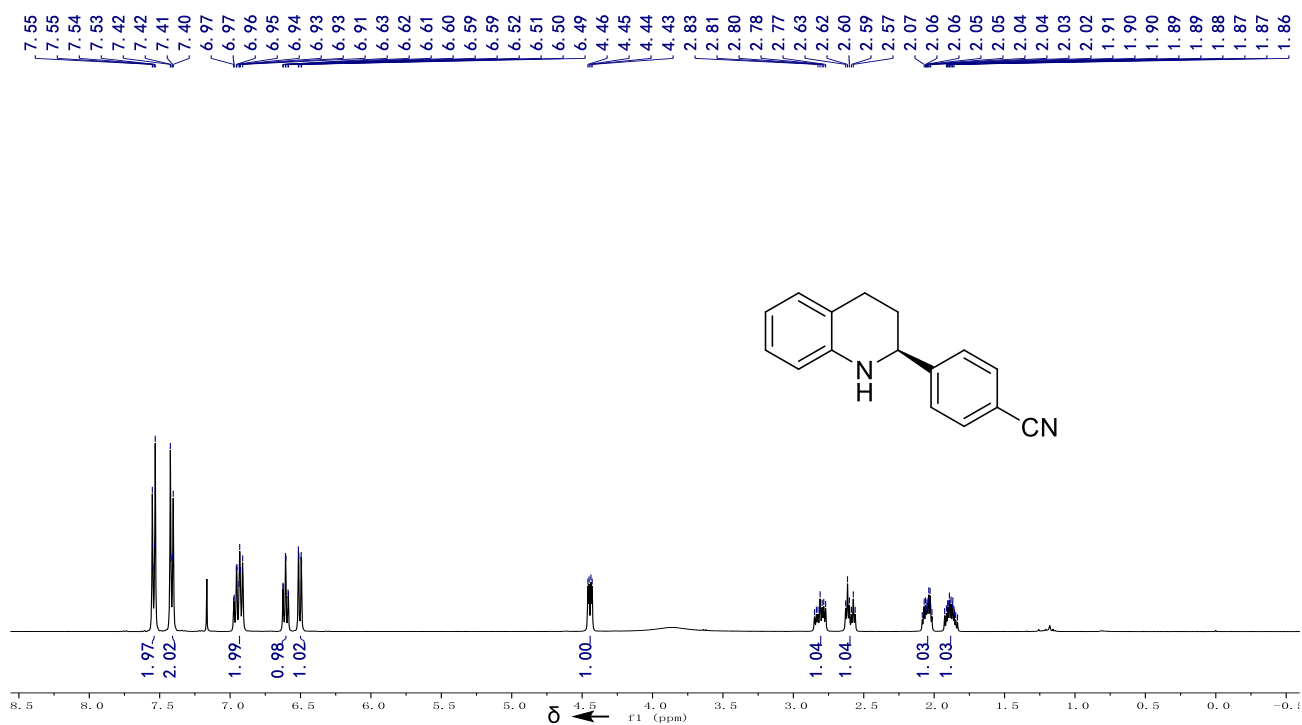


(S)-3c: (S)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline.

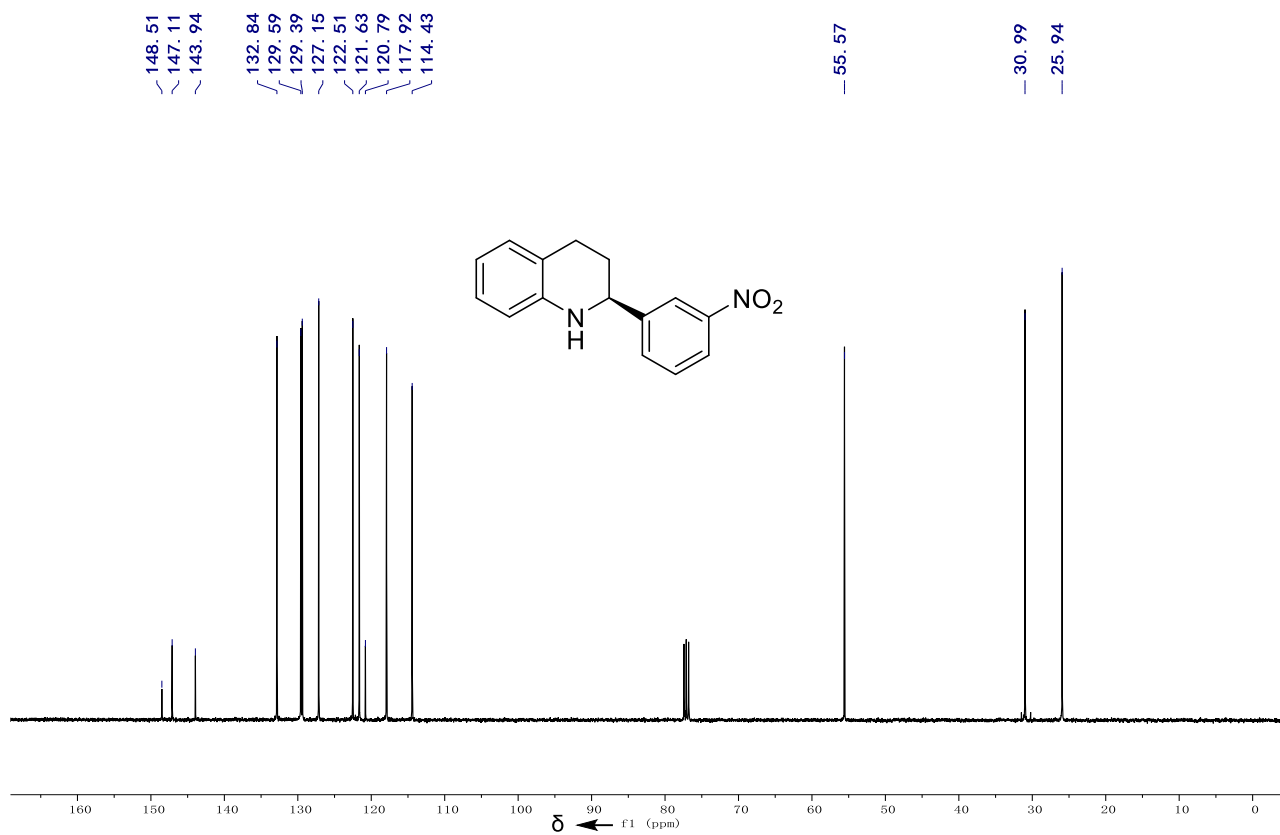
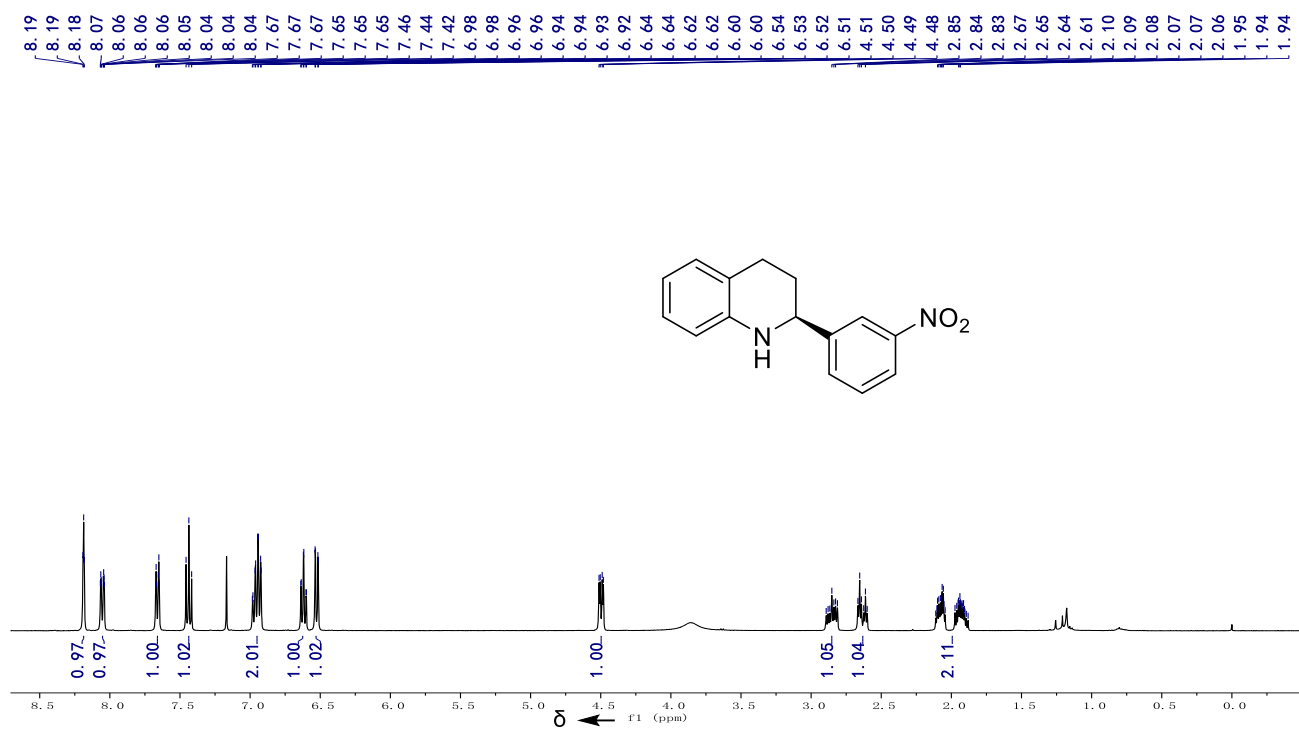




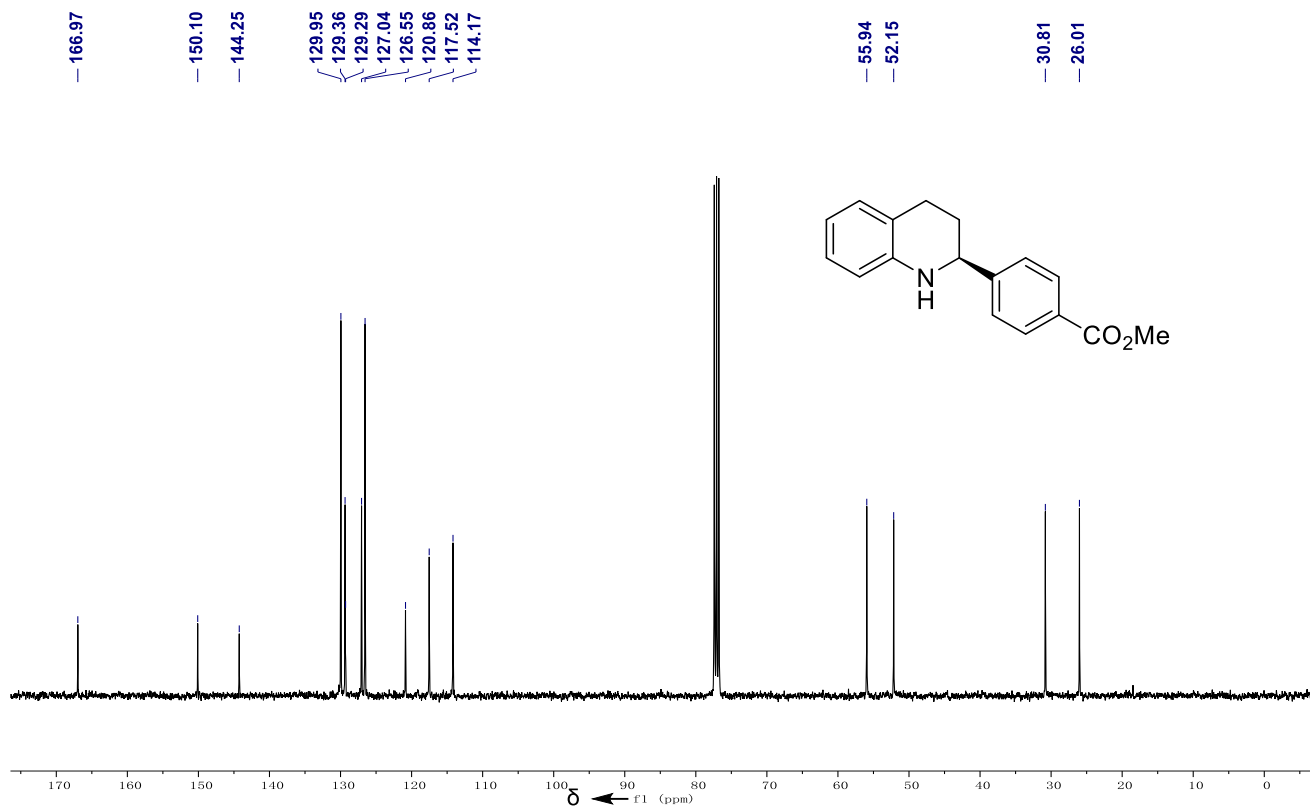
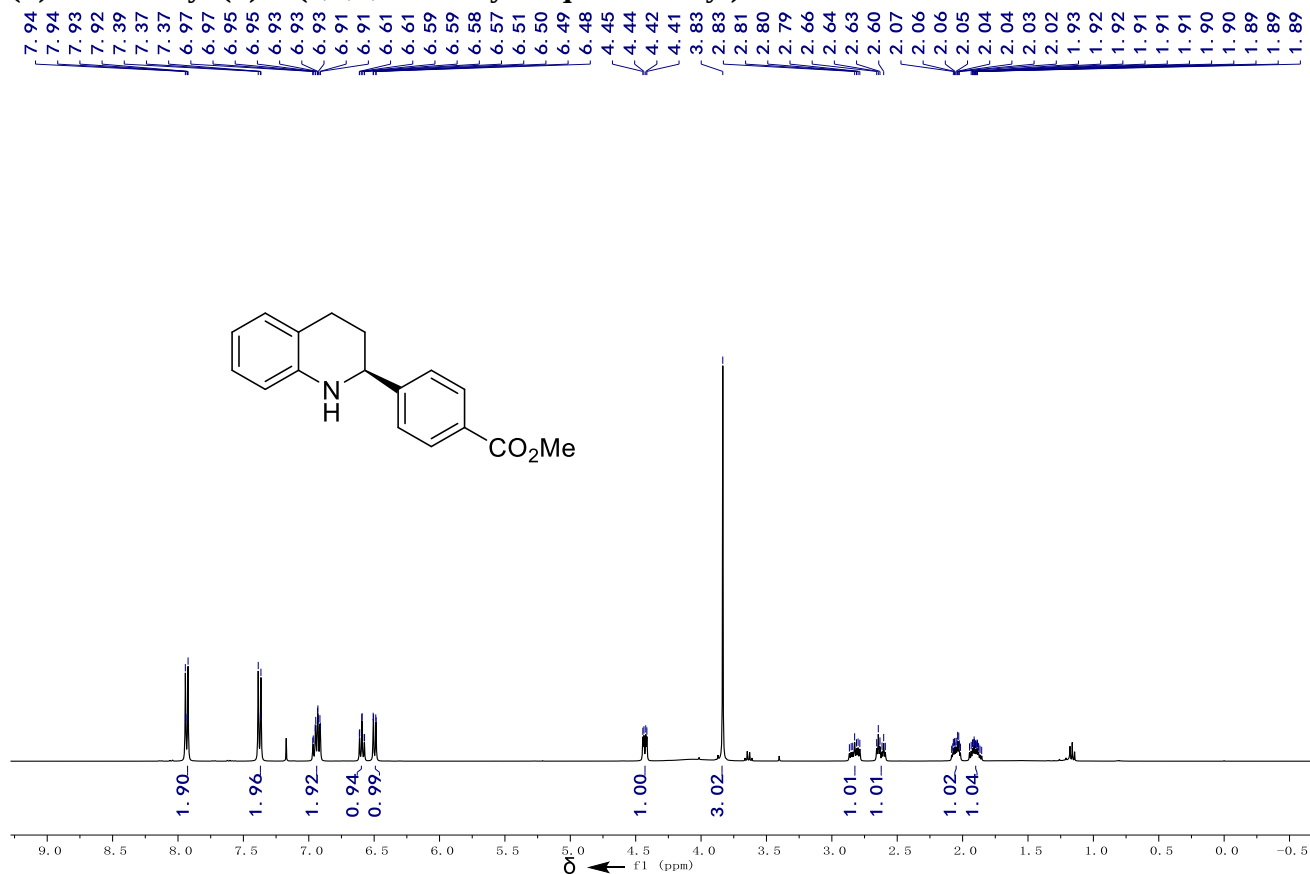
(S)-3d: (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzonitrile.



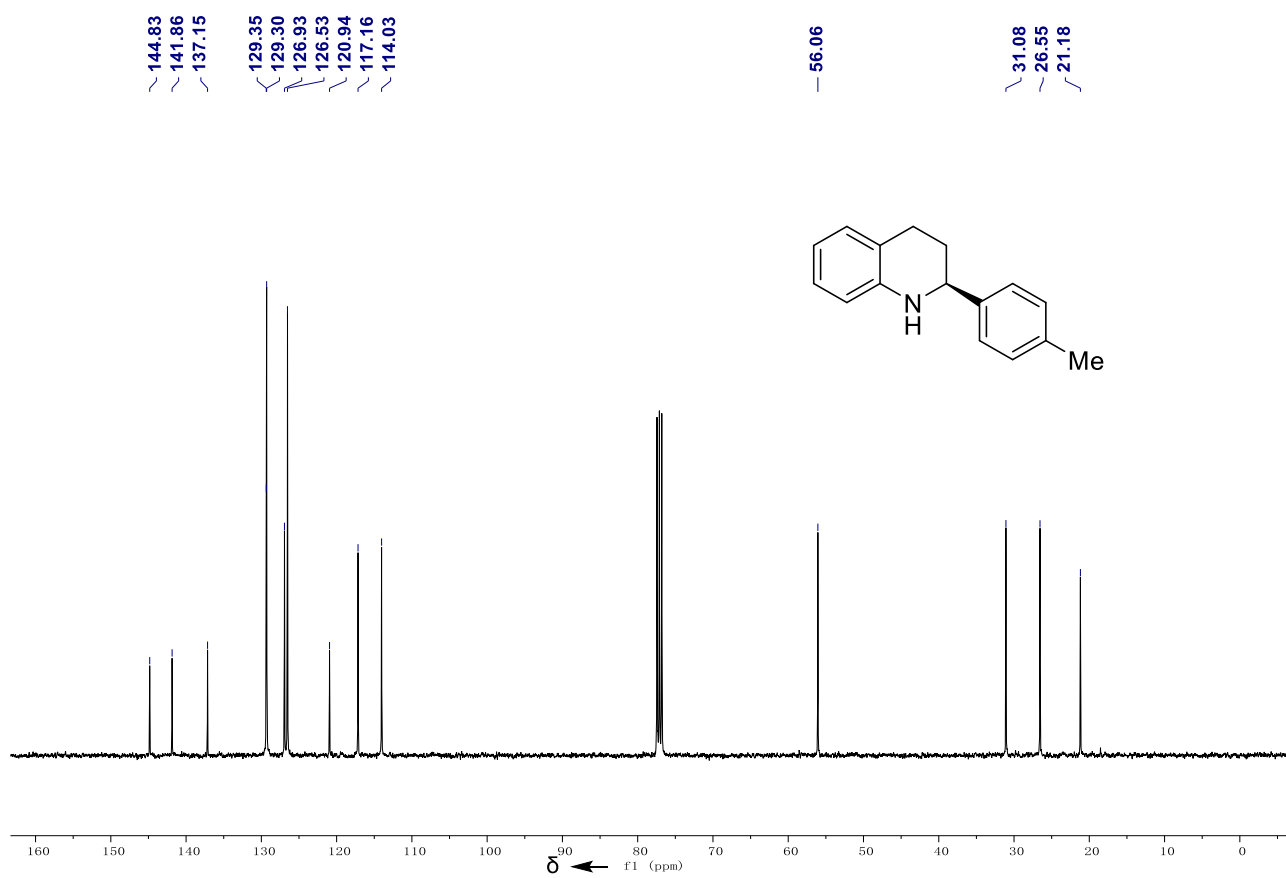
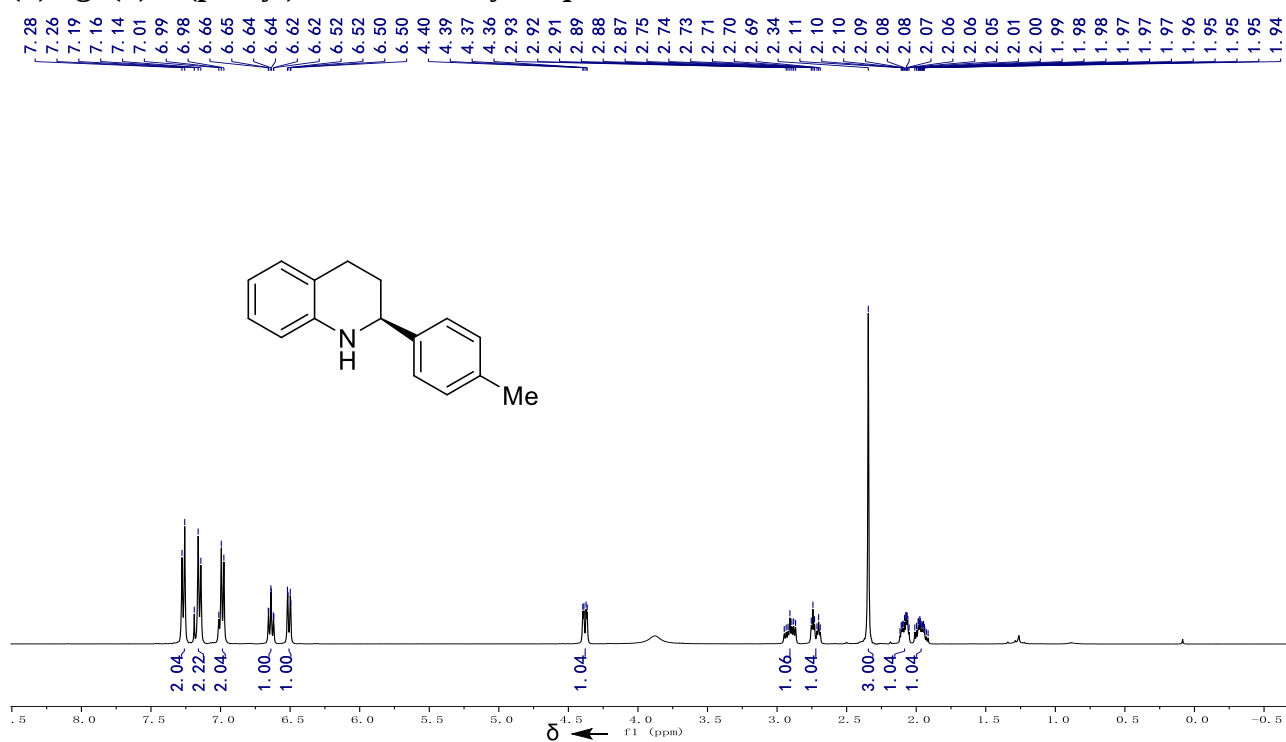
(S)-3e: (S)-2-(3-nitrophenyl)-1,2,3,4-tetrahydroquinoline.



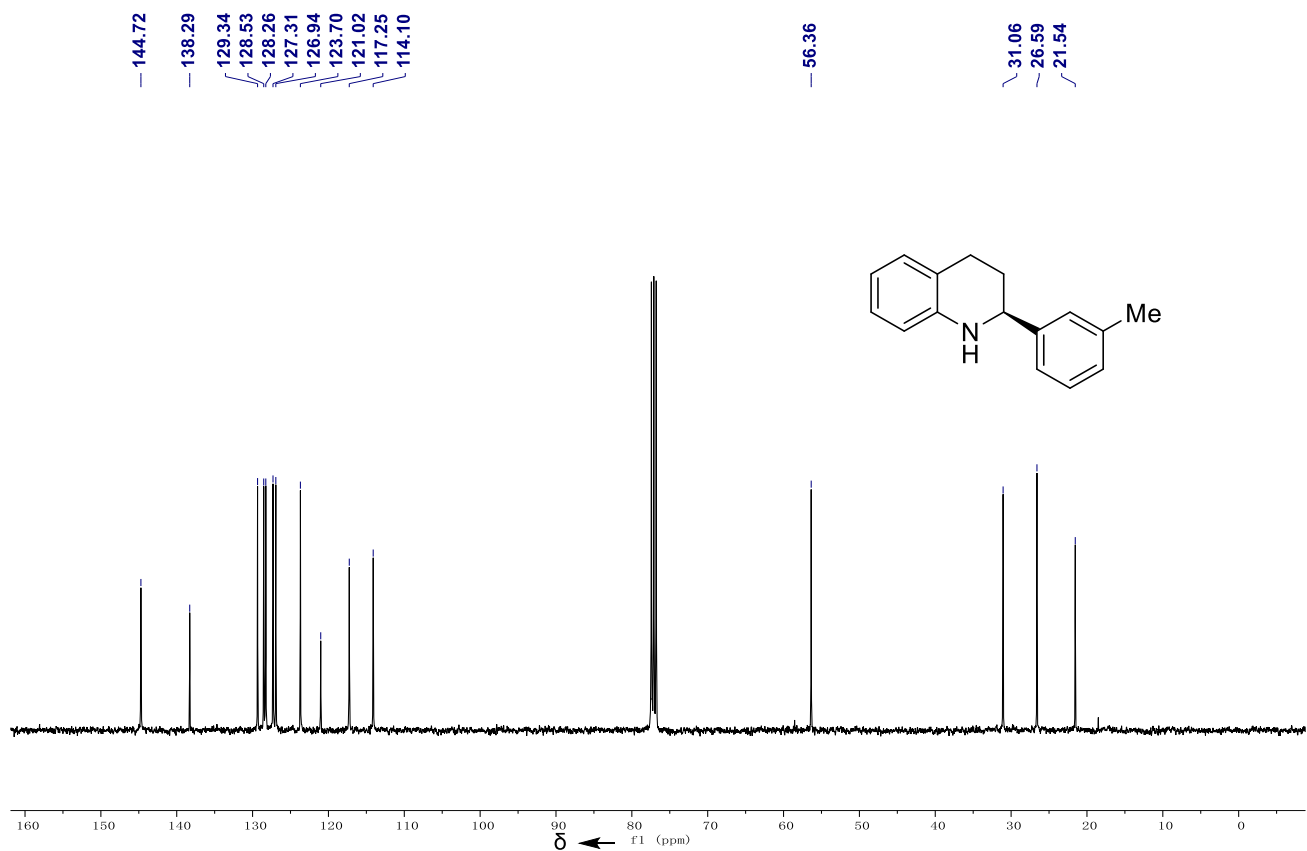
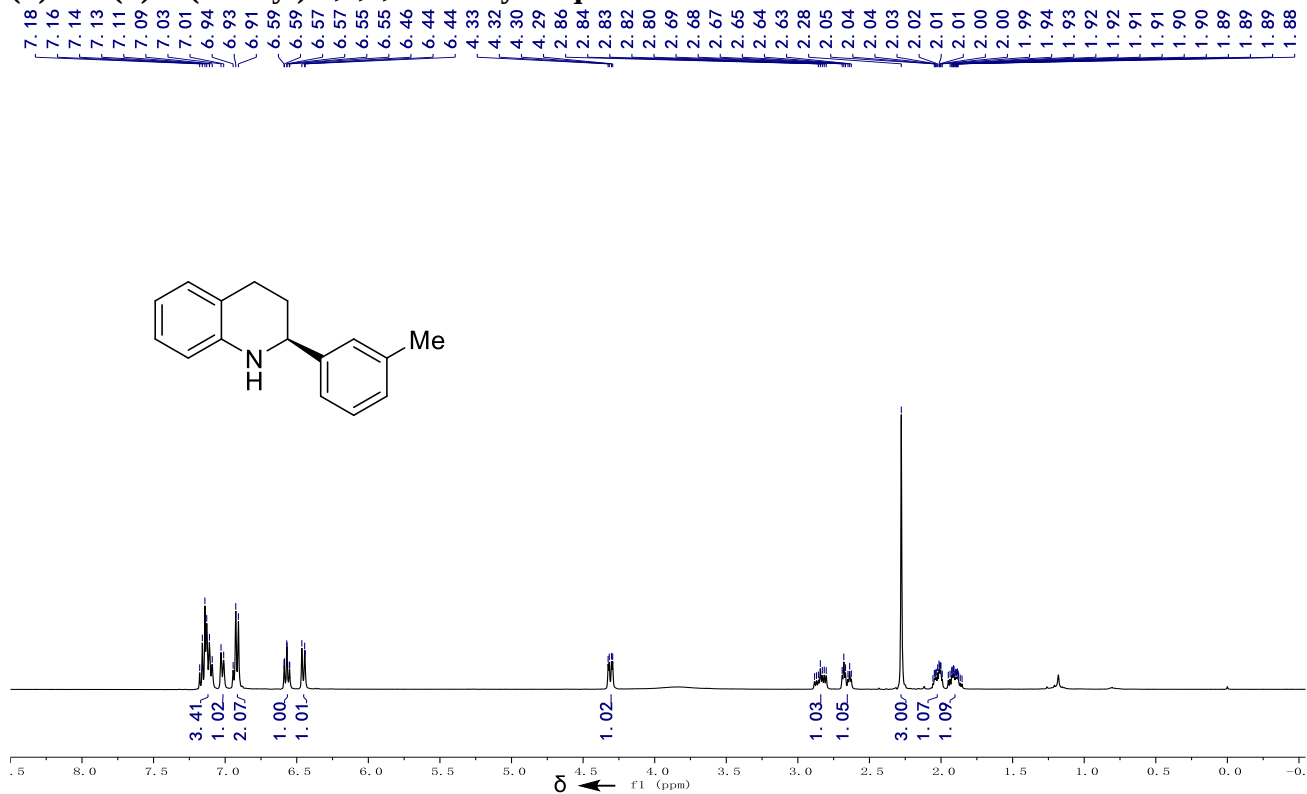
(S)-3f: methyl (S)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzoate.



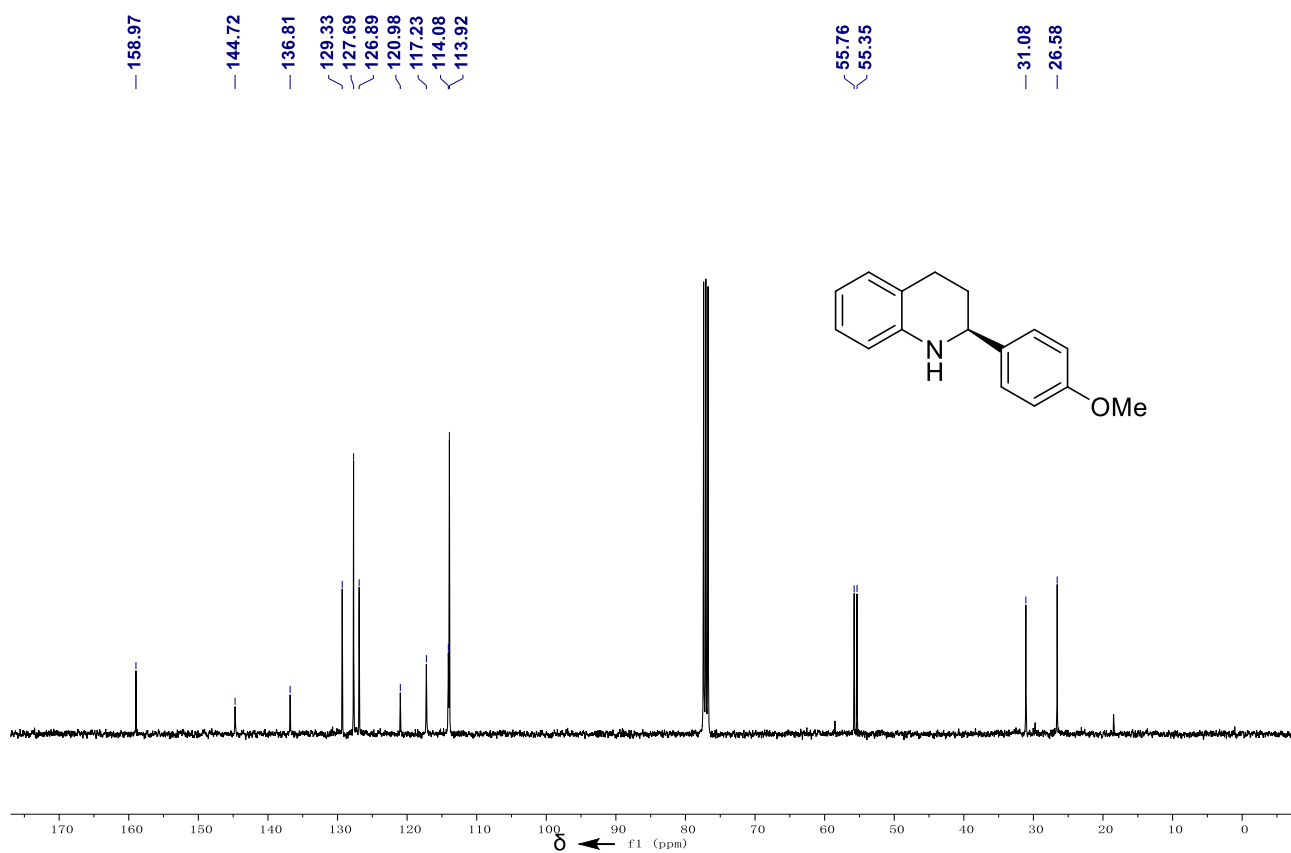
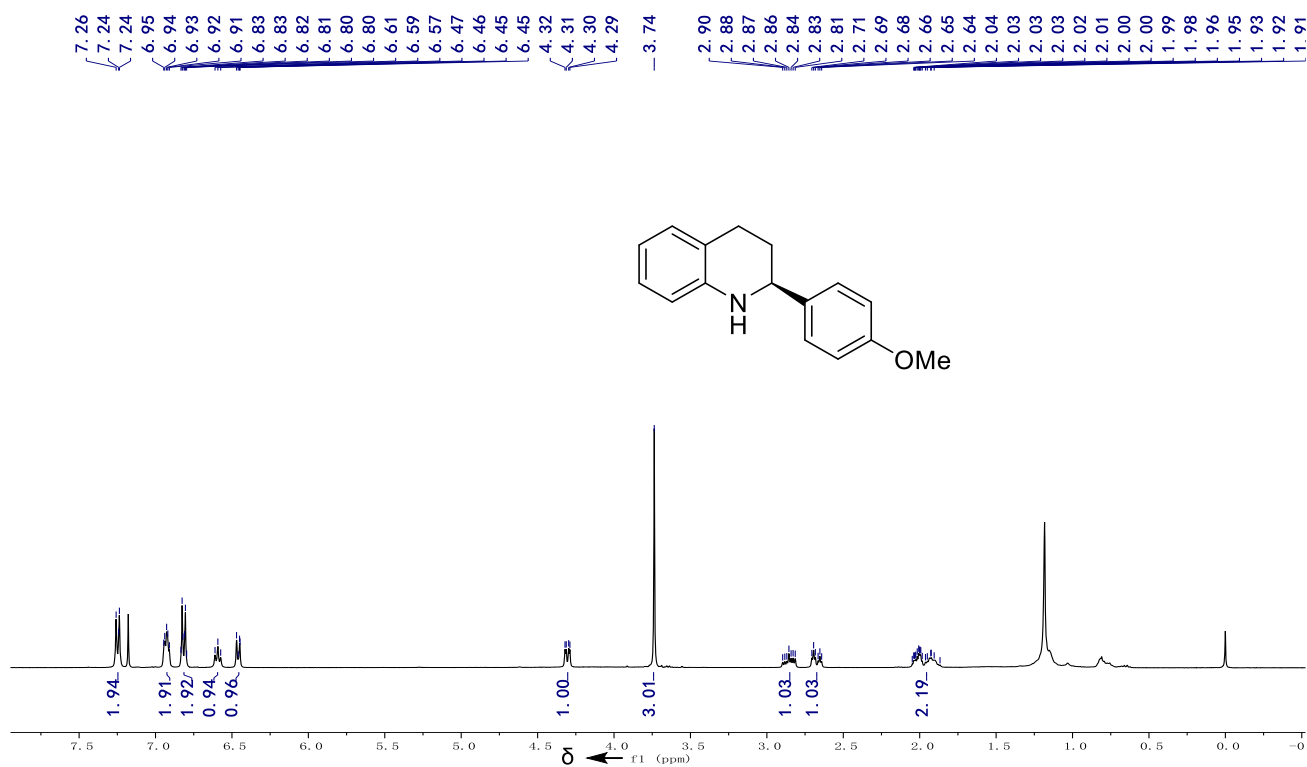
(S)-3g: (S)-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline.



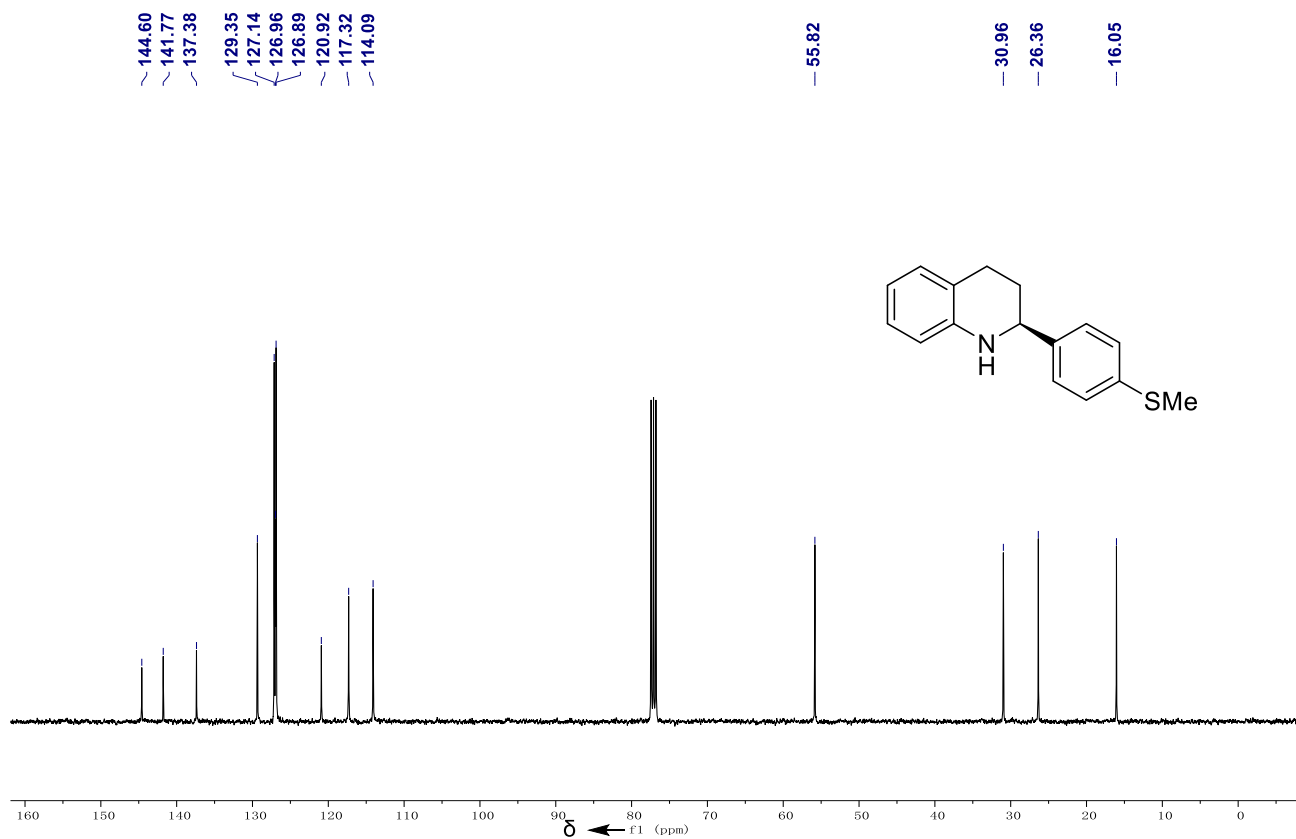
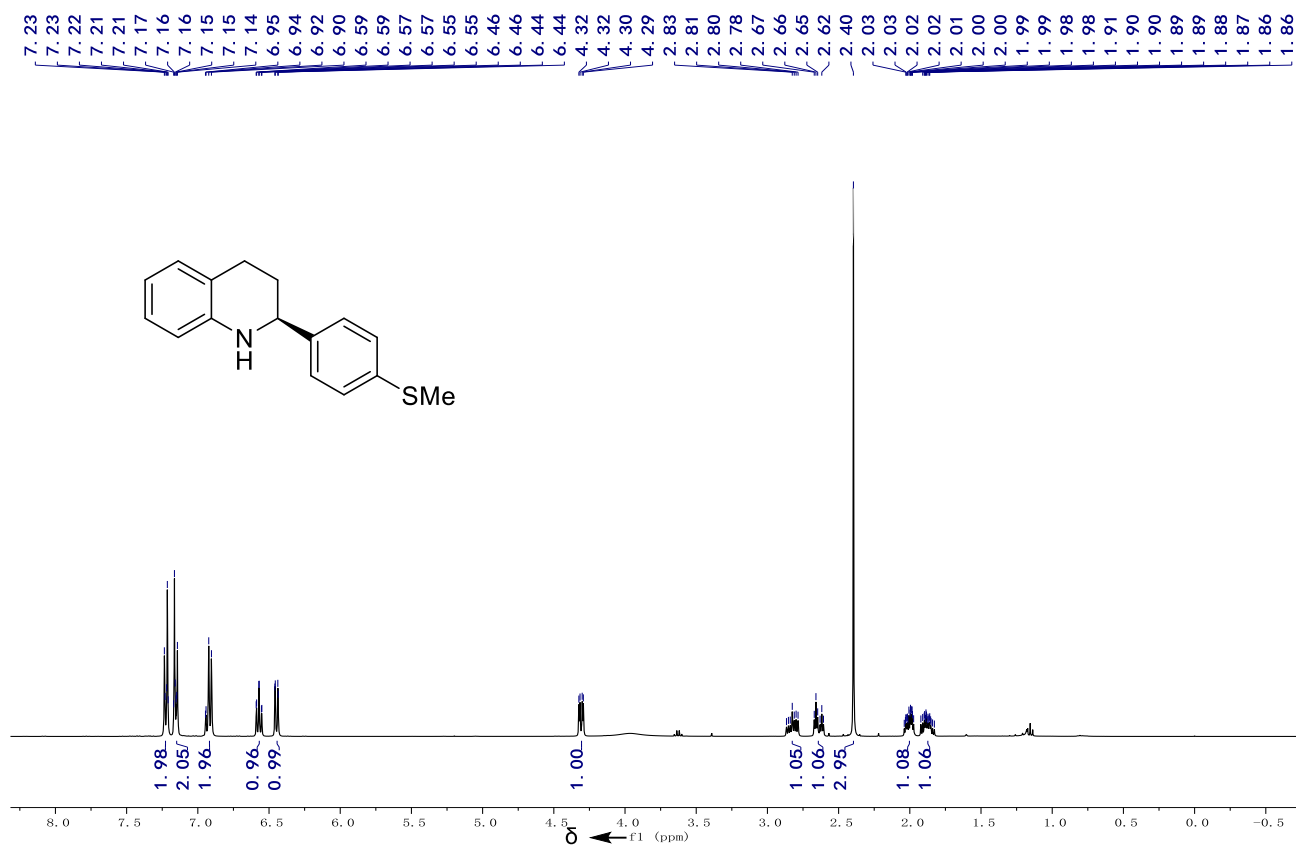
(S)-3h: (S)-2-(m-tolyl)-1,2,3,4-tetrahydroquinoline.



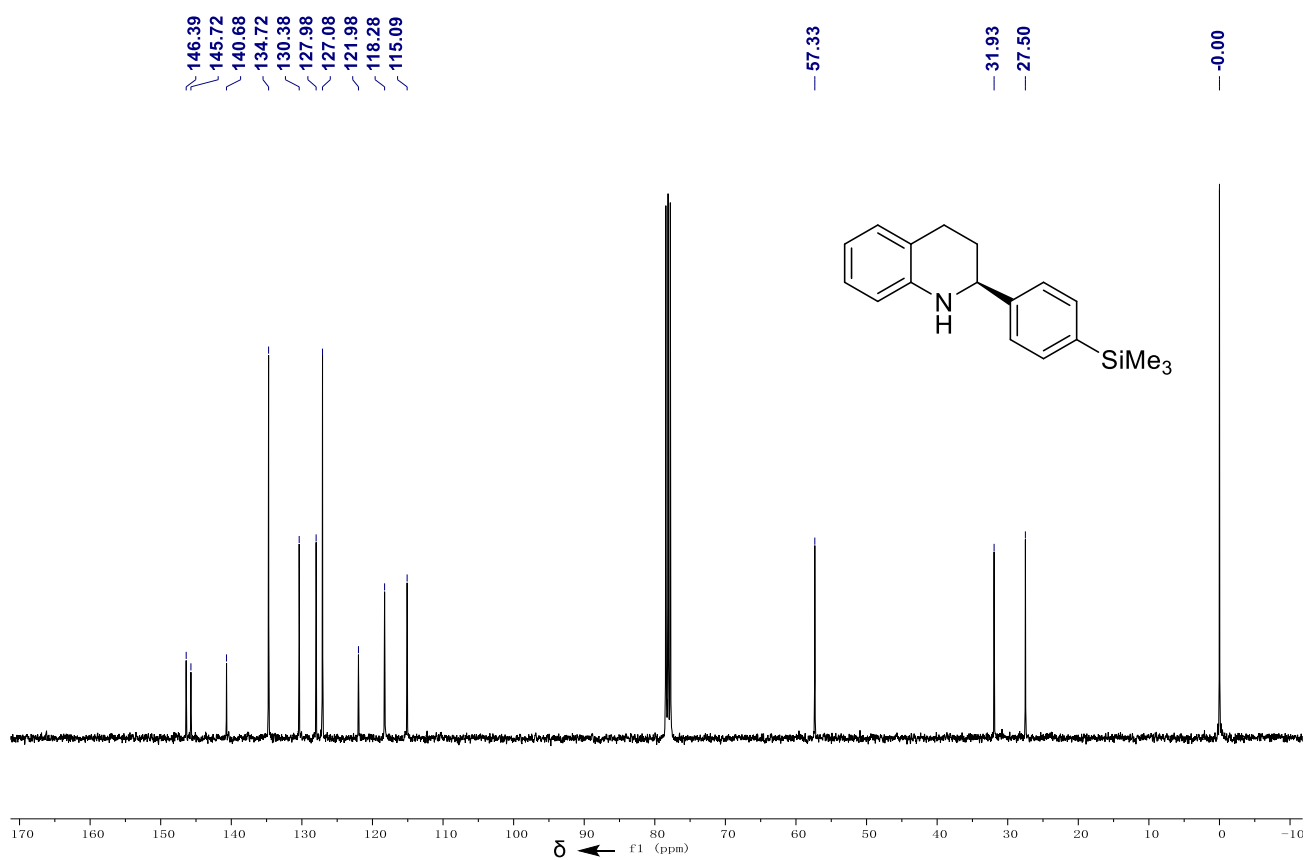
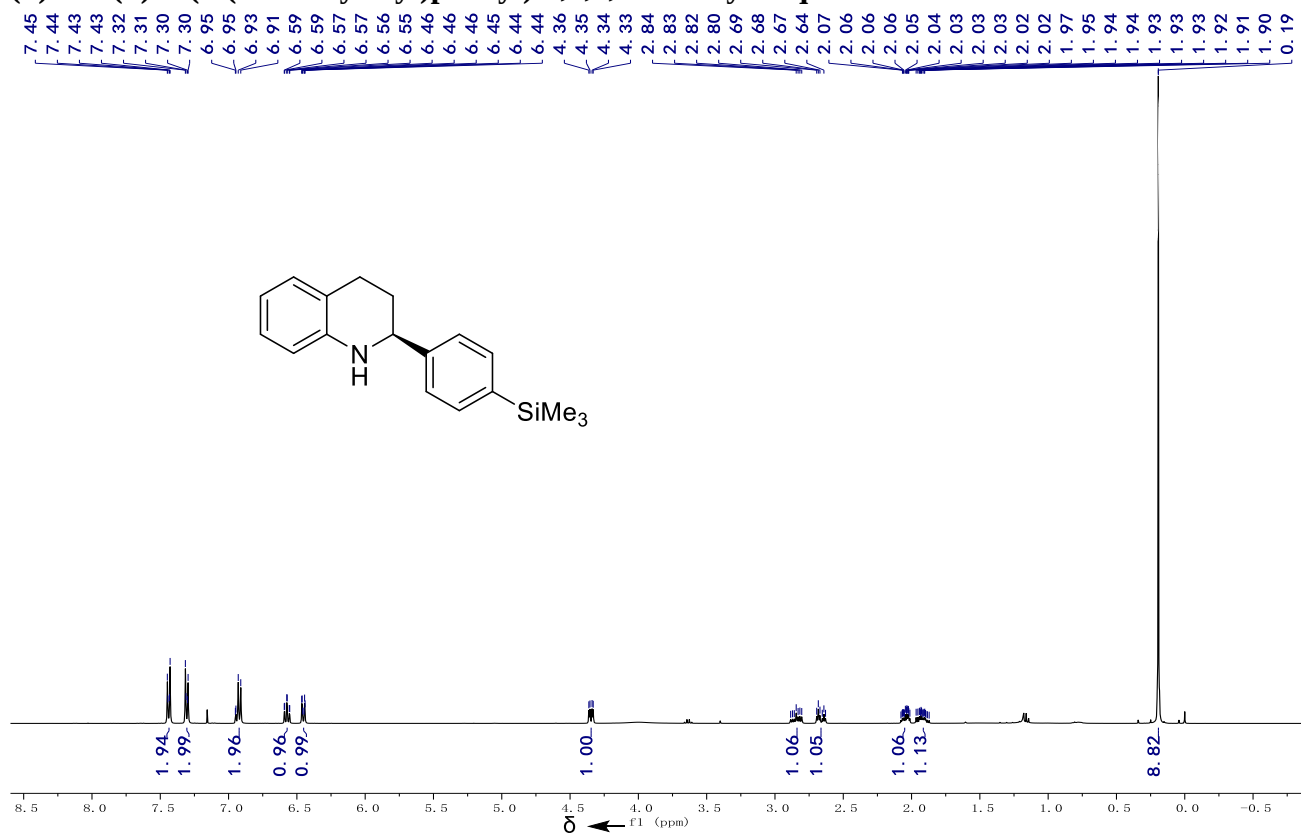
(S)-3i: (S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline.



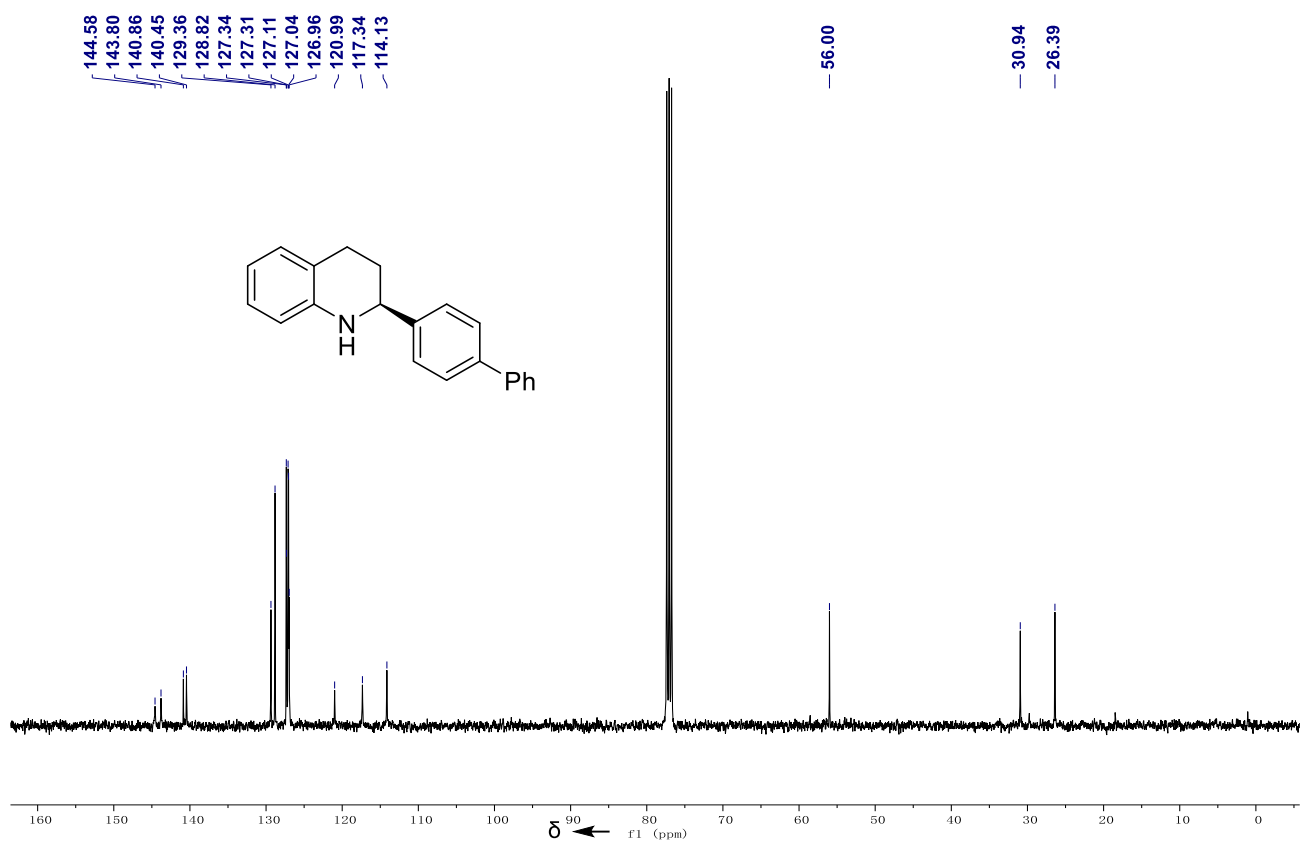
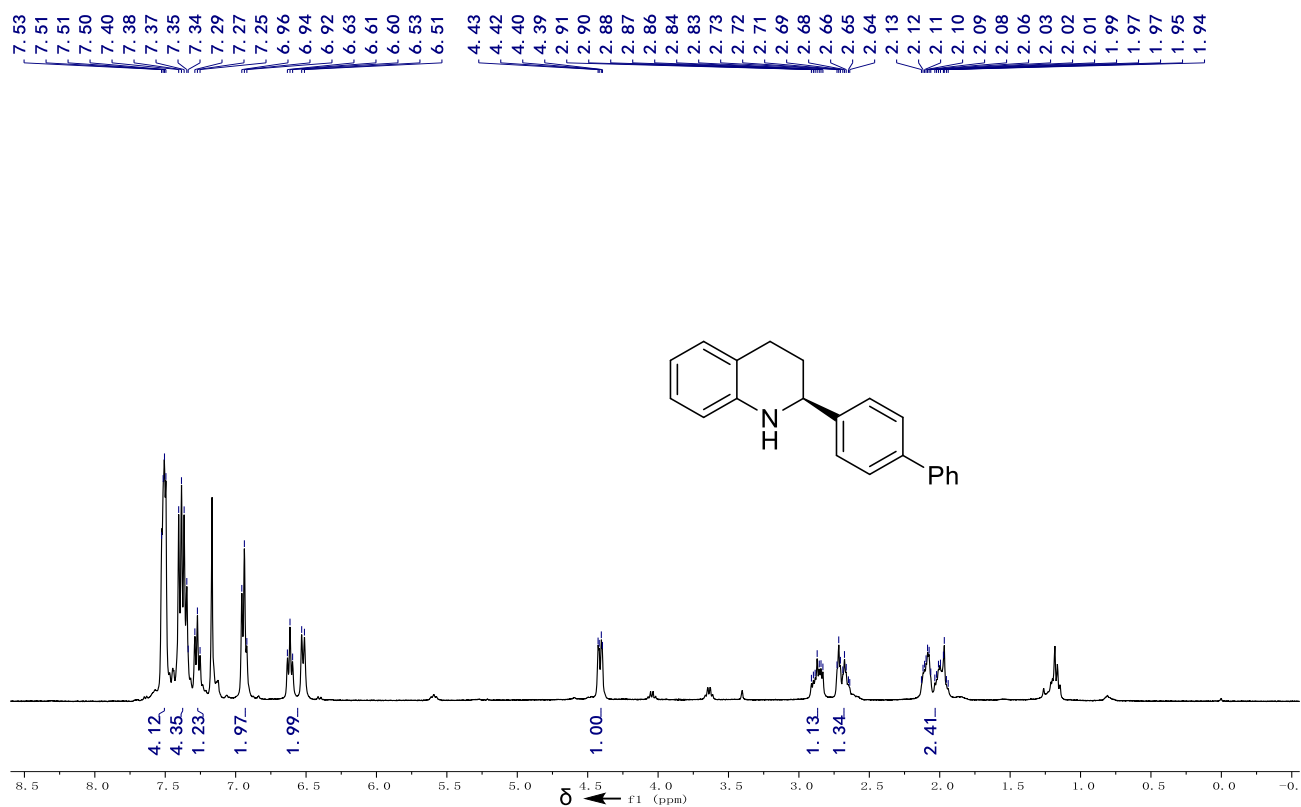
(S)-3j: (S)-2-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline.



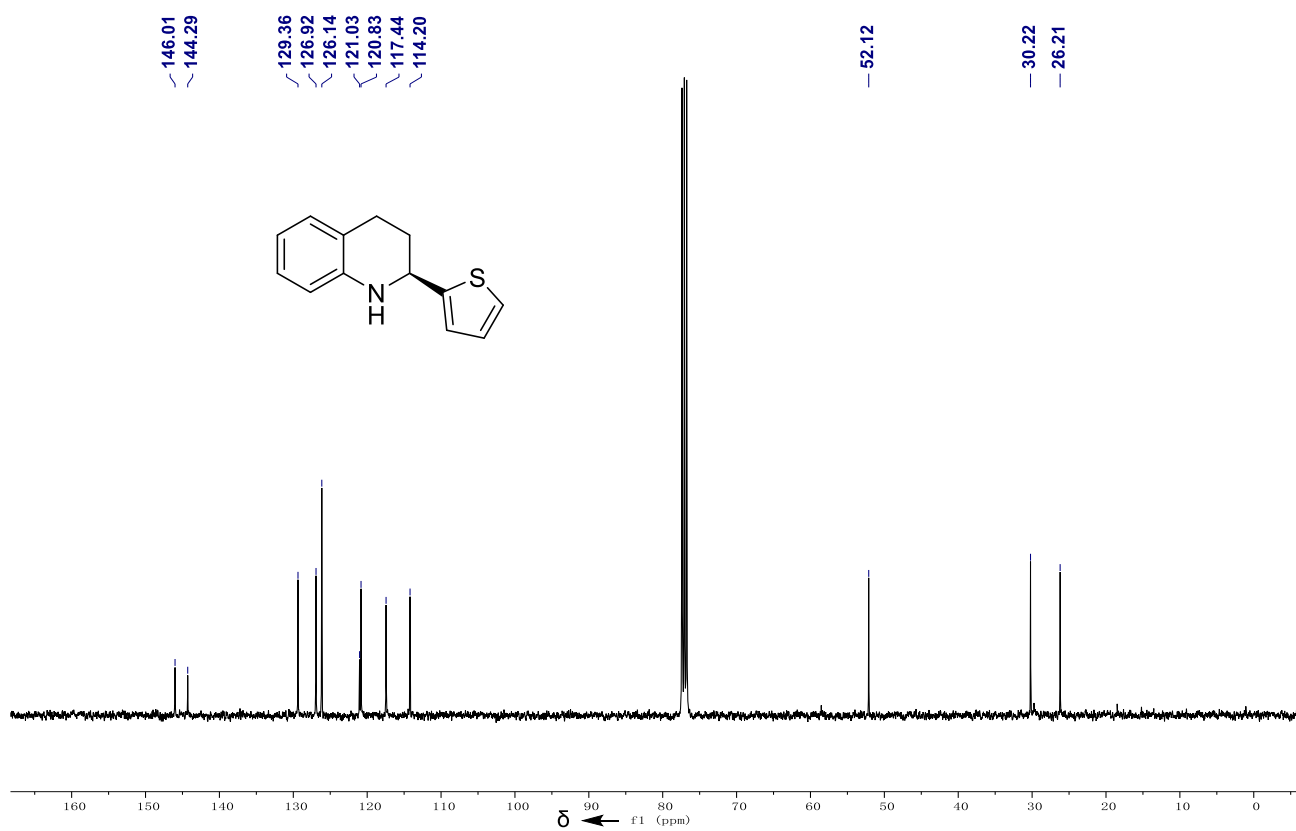
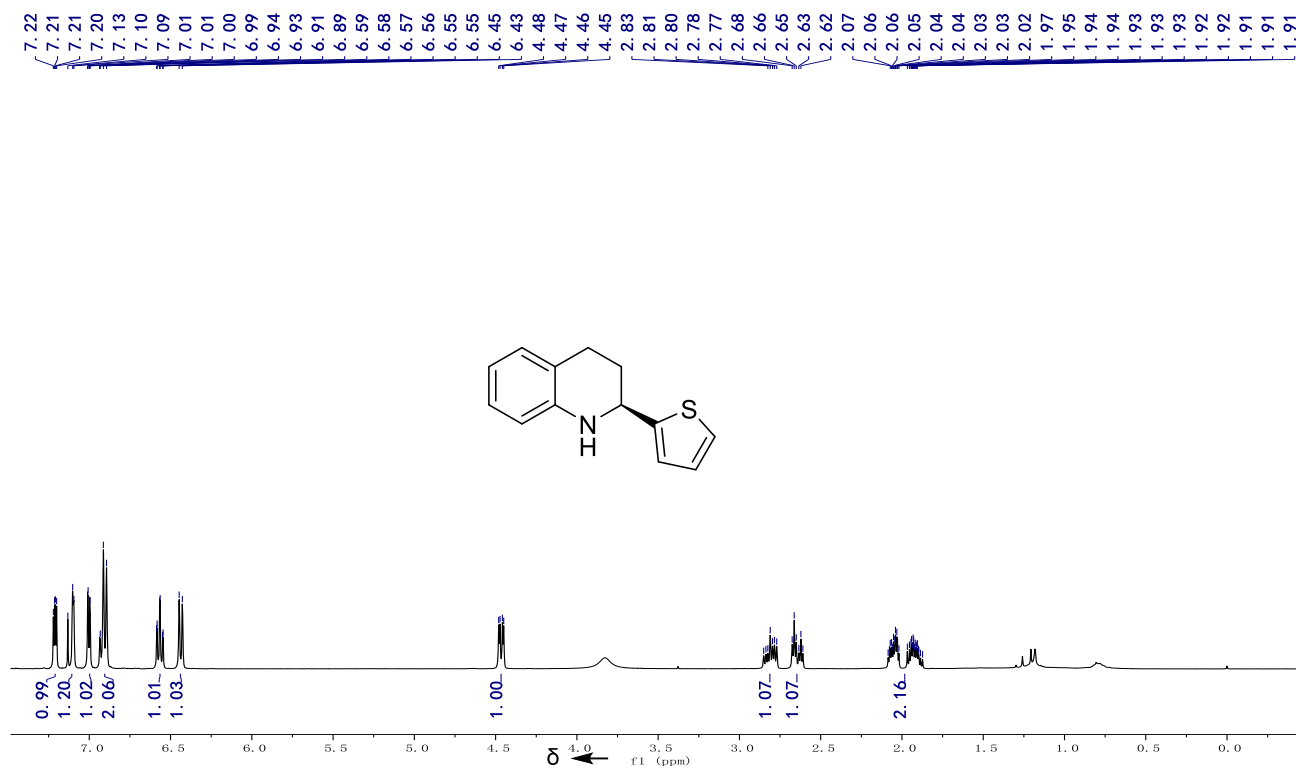
(S)-3k: (S)-2-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline.



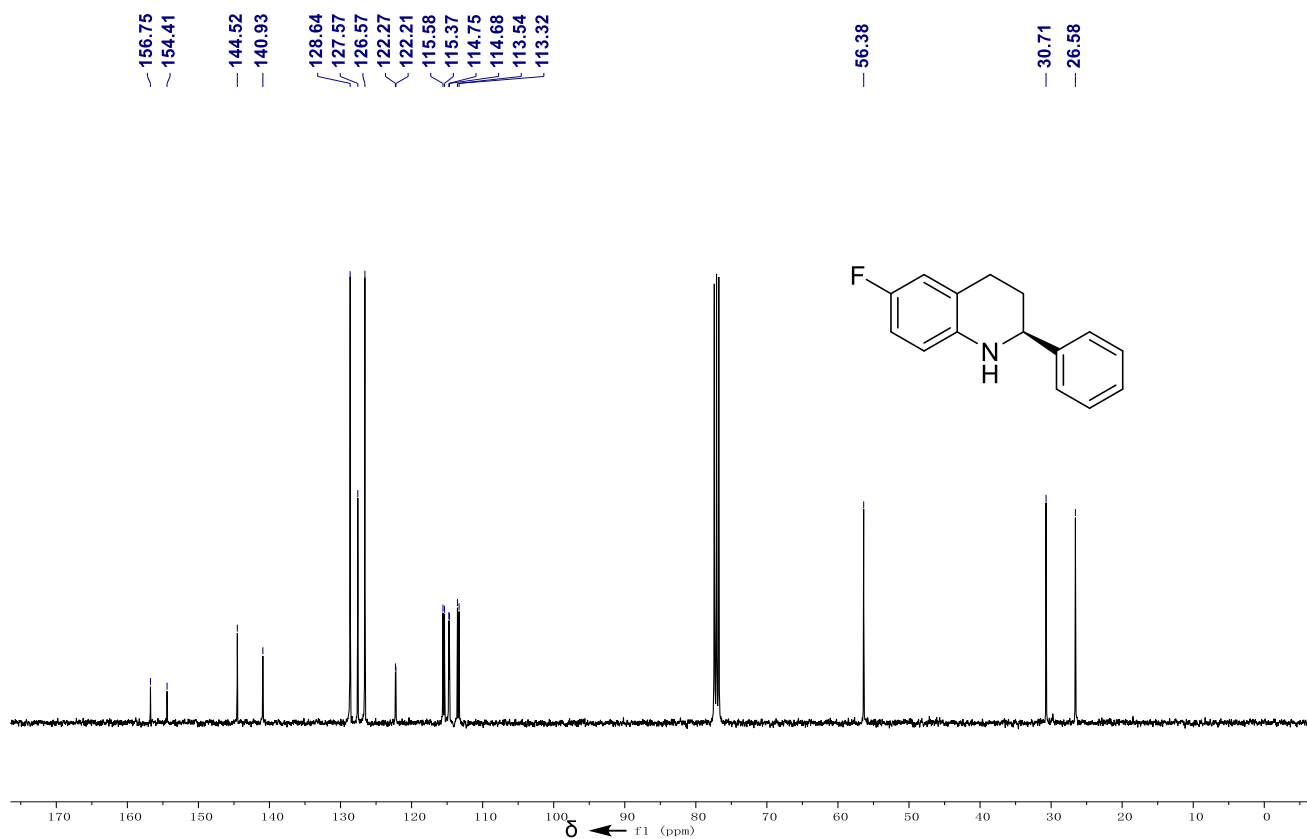
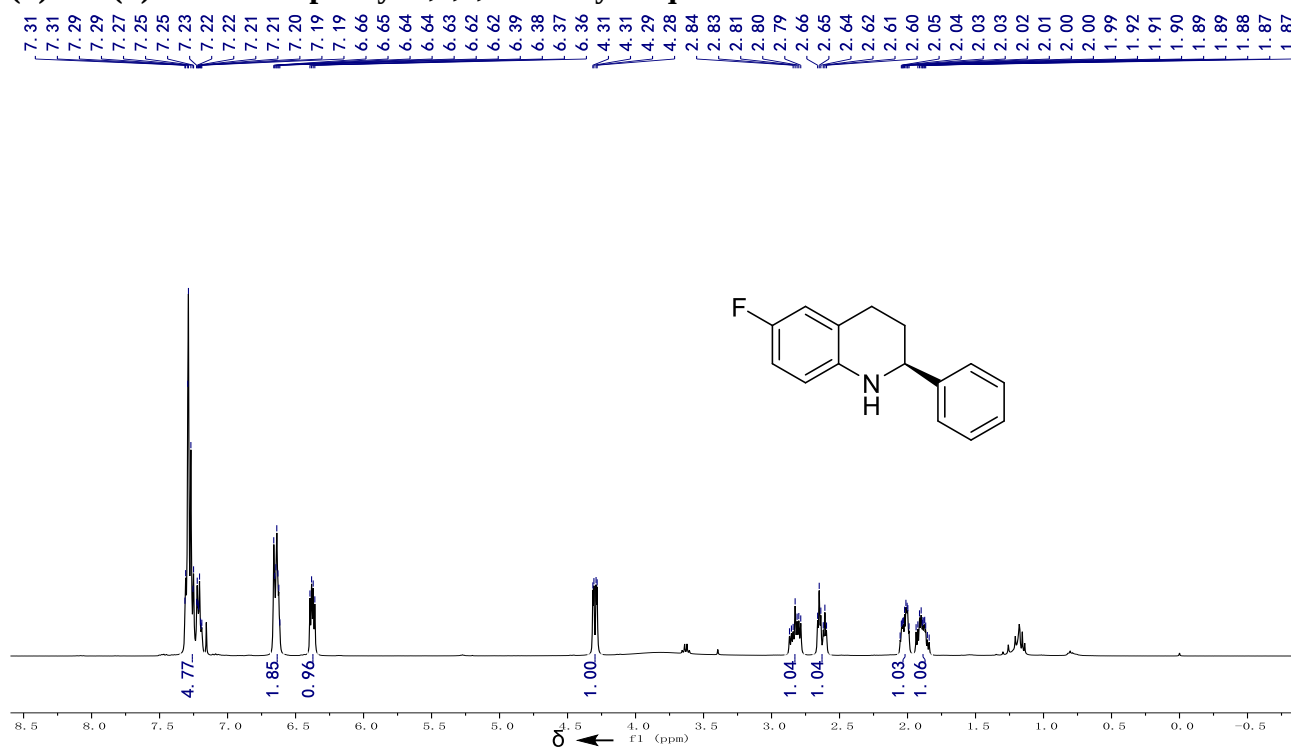
(S)-3l: (S)-2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline.

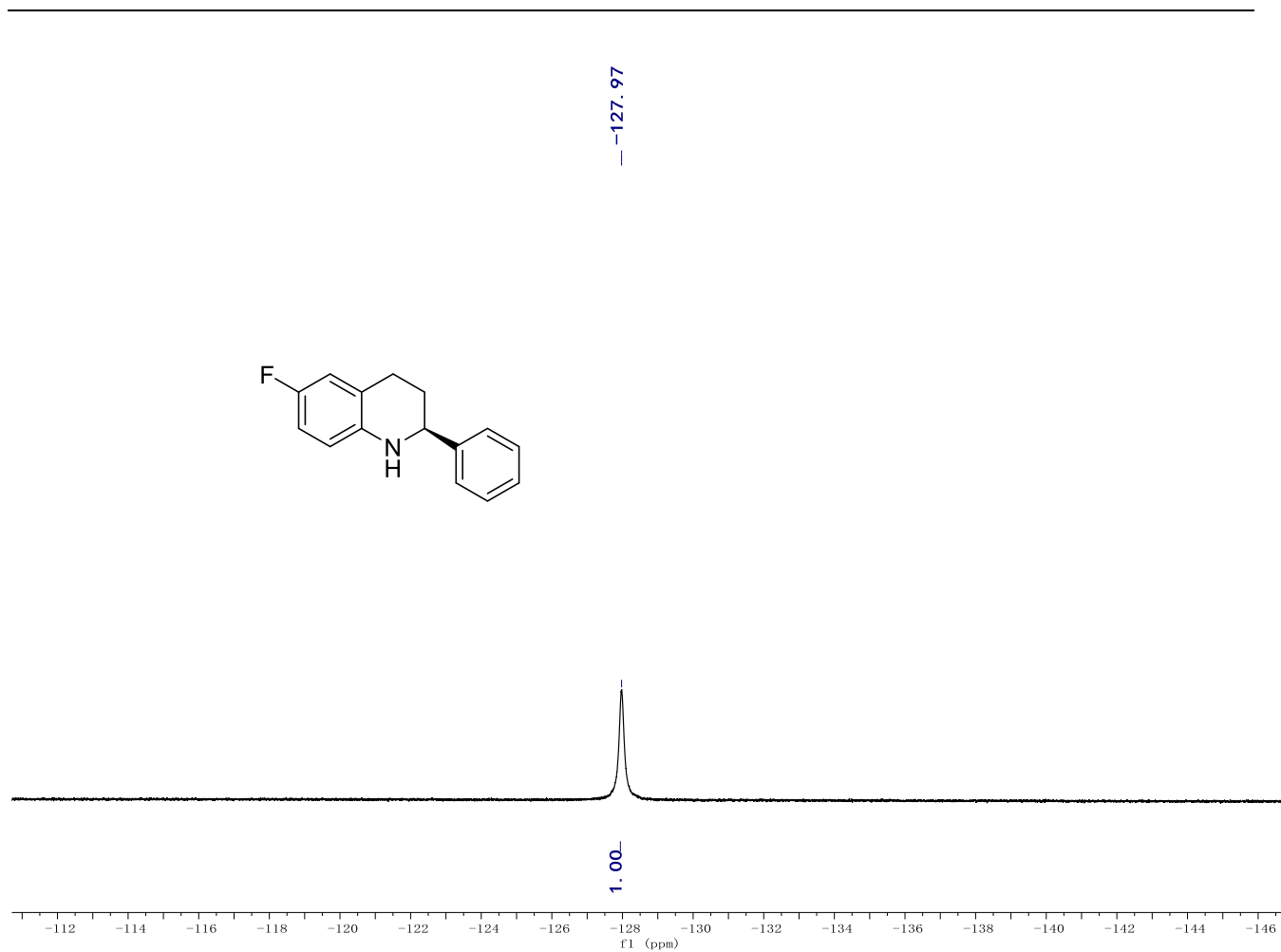


(S)-3m: (S)-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline.

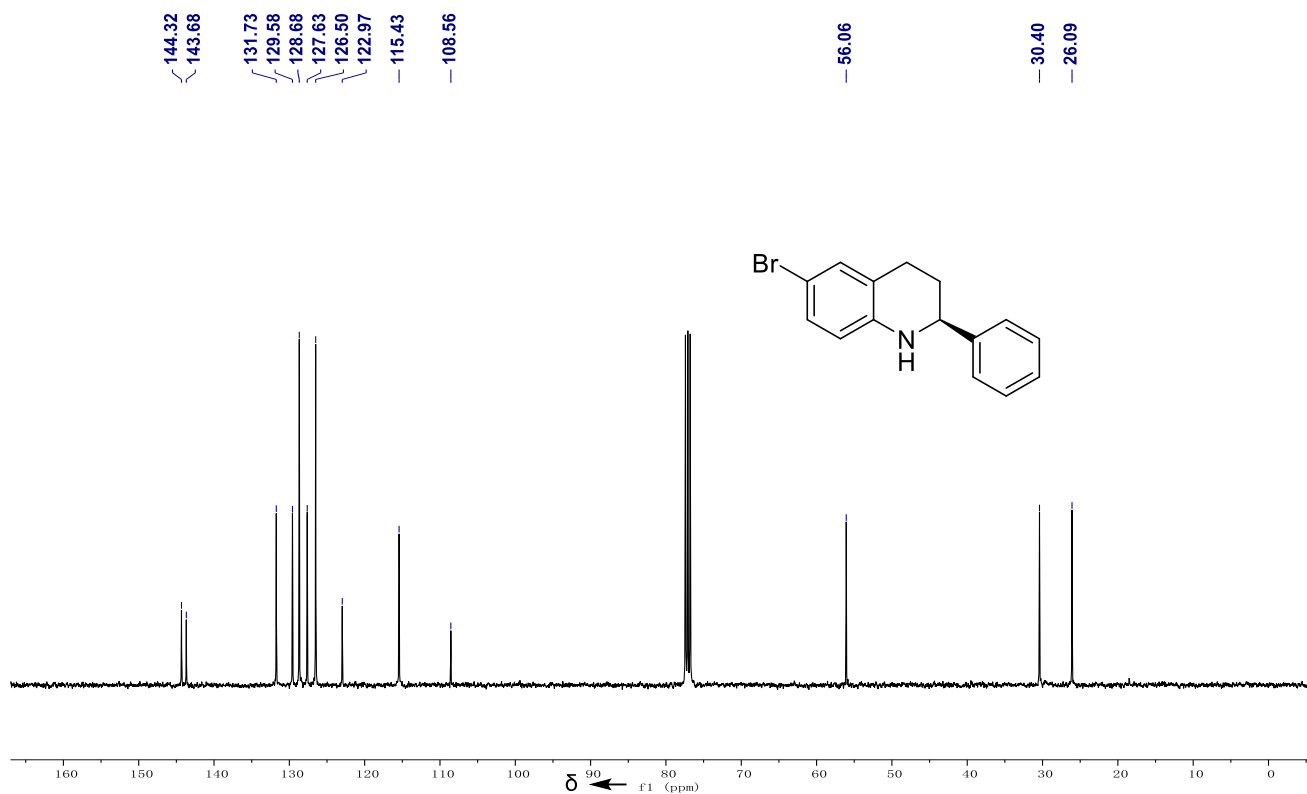
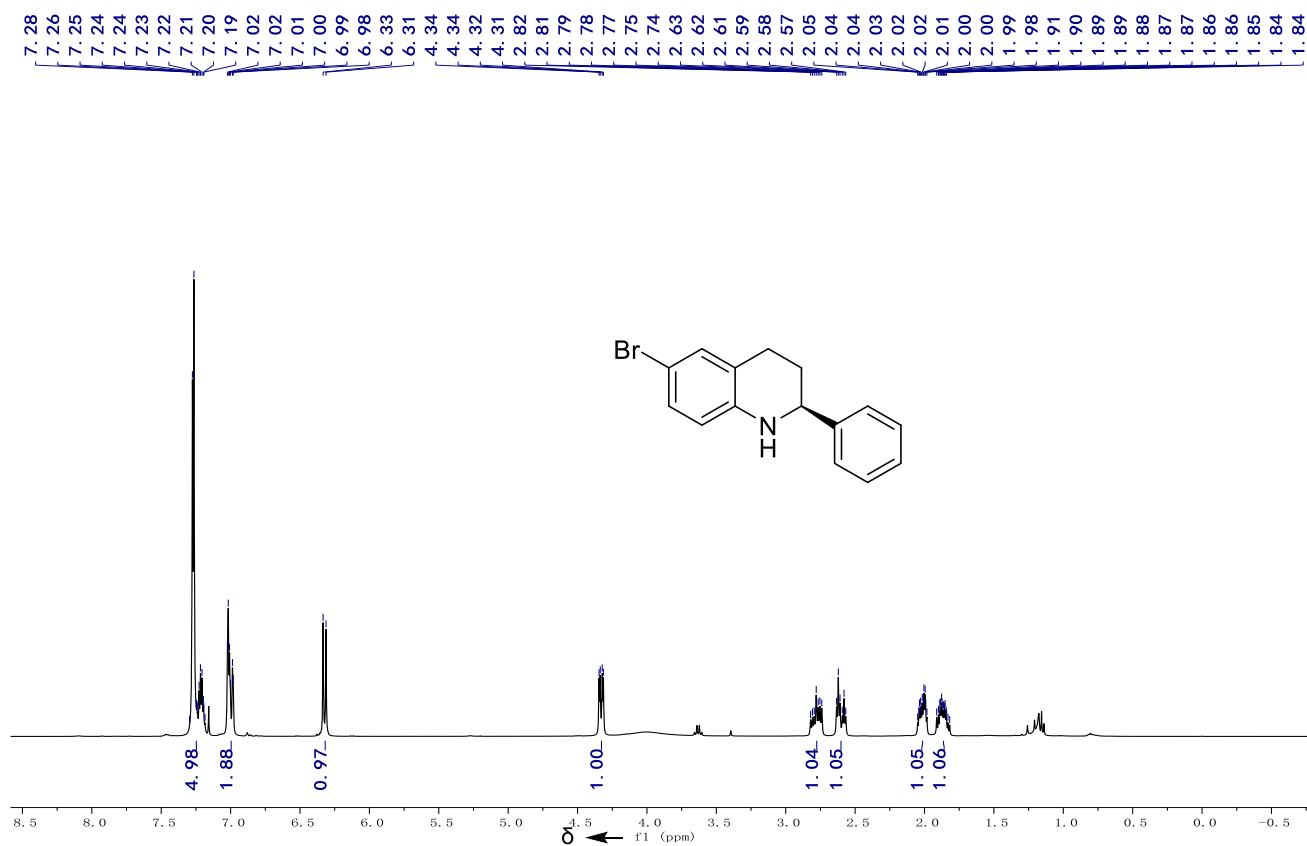


(S)-3n: (S)-6-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.

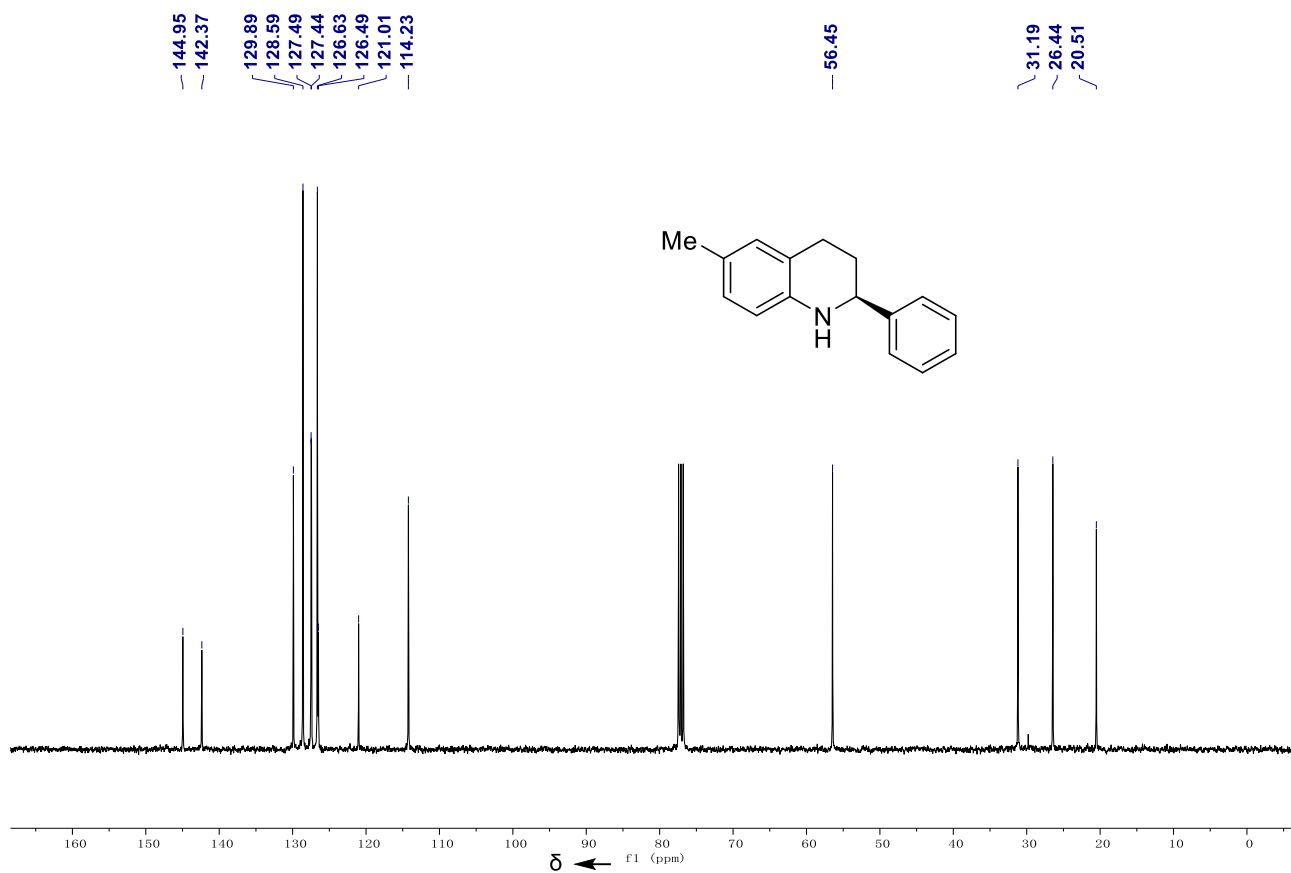
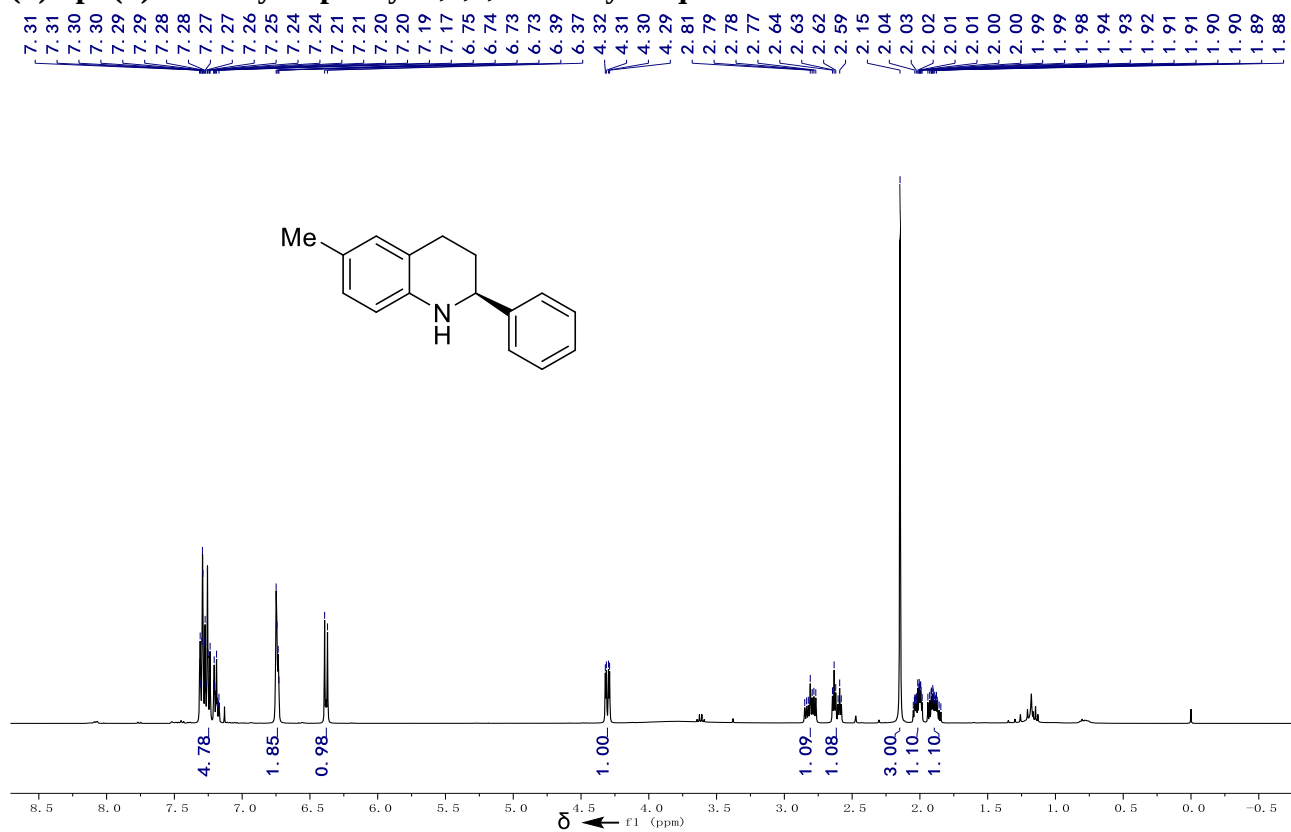




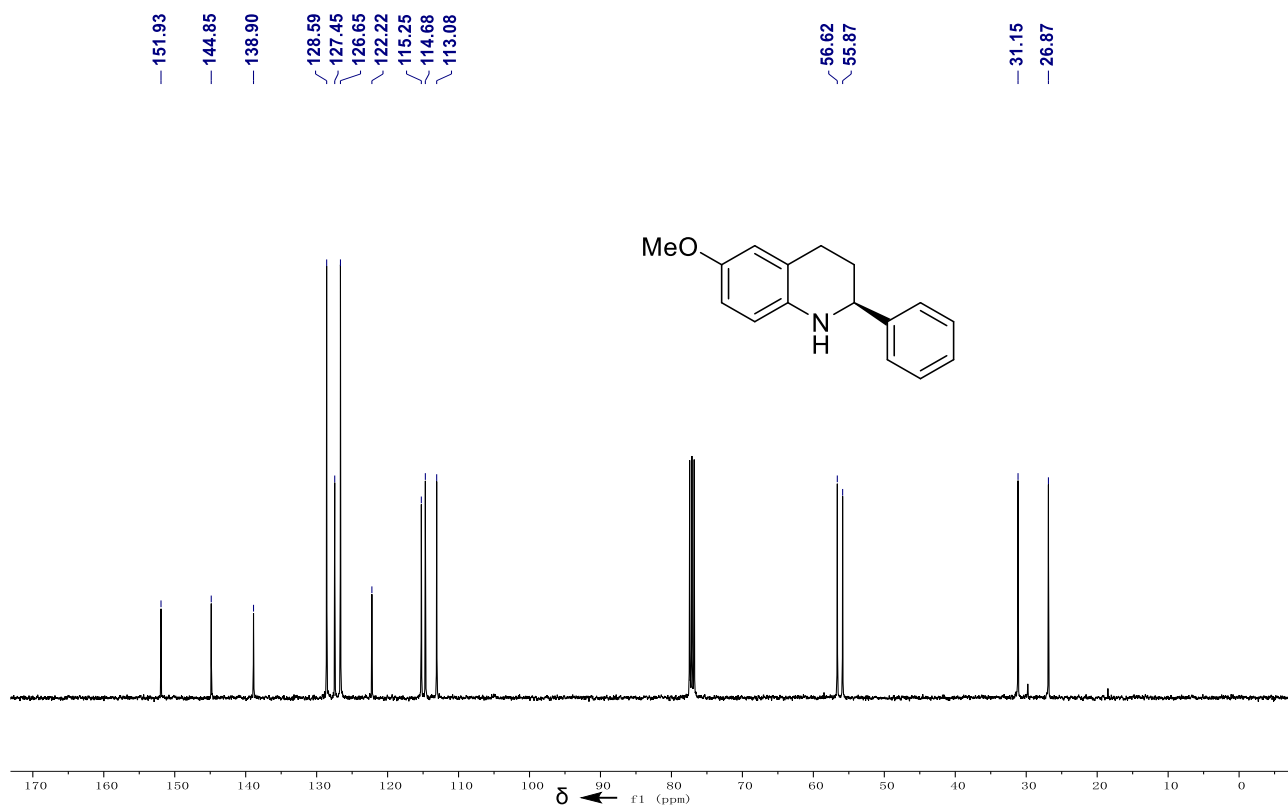
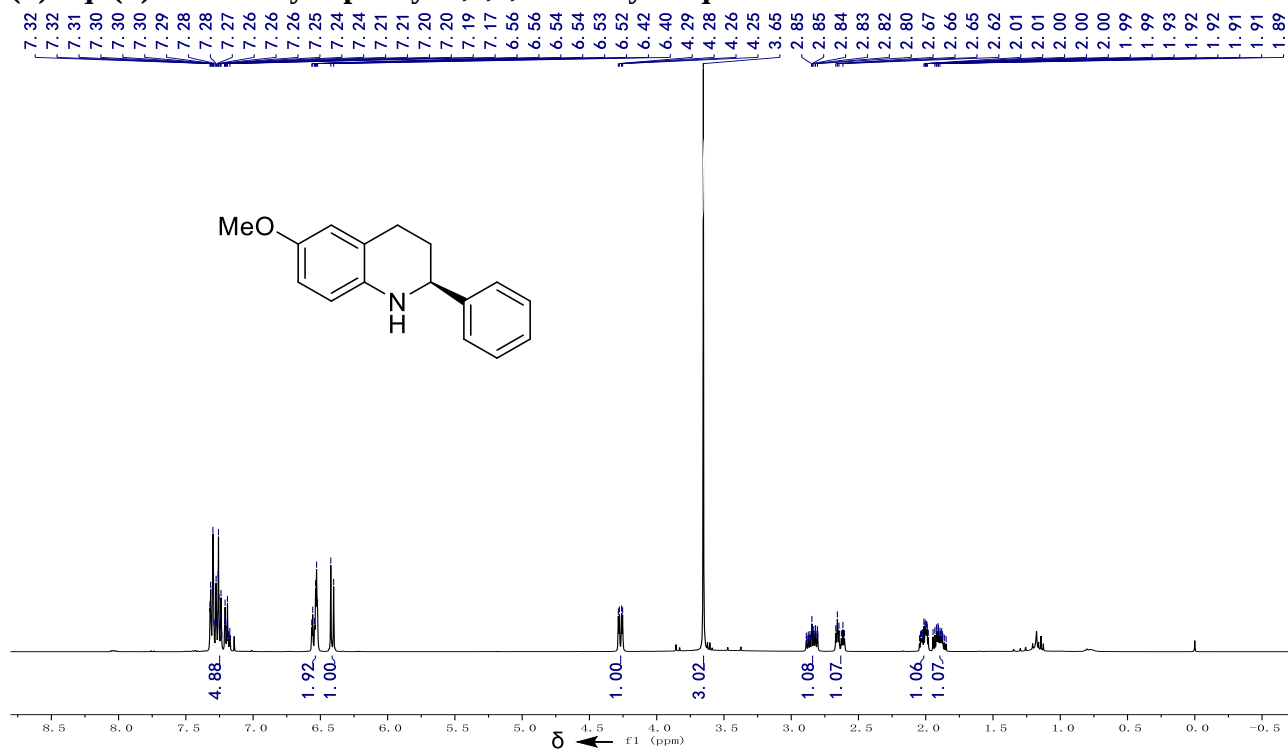
(S)-3o: (S)-6-bromo-2-phenyl-1,2,3,4-tetrahydroquinoline.



(S)-3p: (S)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline.



(S)-3q: (S)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline.



(S)-3r: methyl (S)-4-(6-methoxy-1,2,3,4-tetrahydroquinolin-2-yl)benzoate.

