Supporting Information for:

Enantioselective Hydrogenation of *N*-heteroaromatics Catalyzed by Chiral Diphosphines Modified Binaphthyl Palladium Nanoparticles

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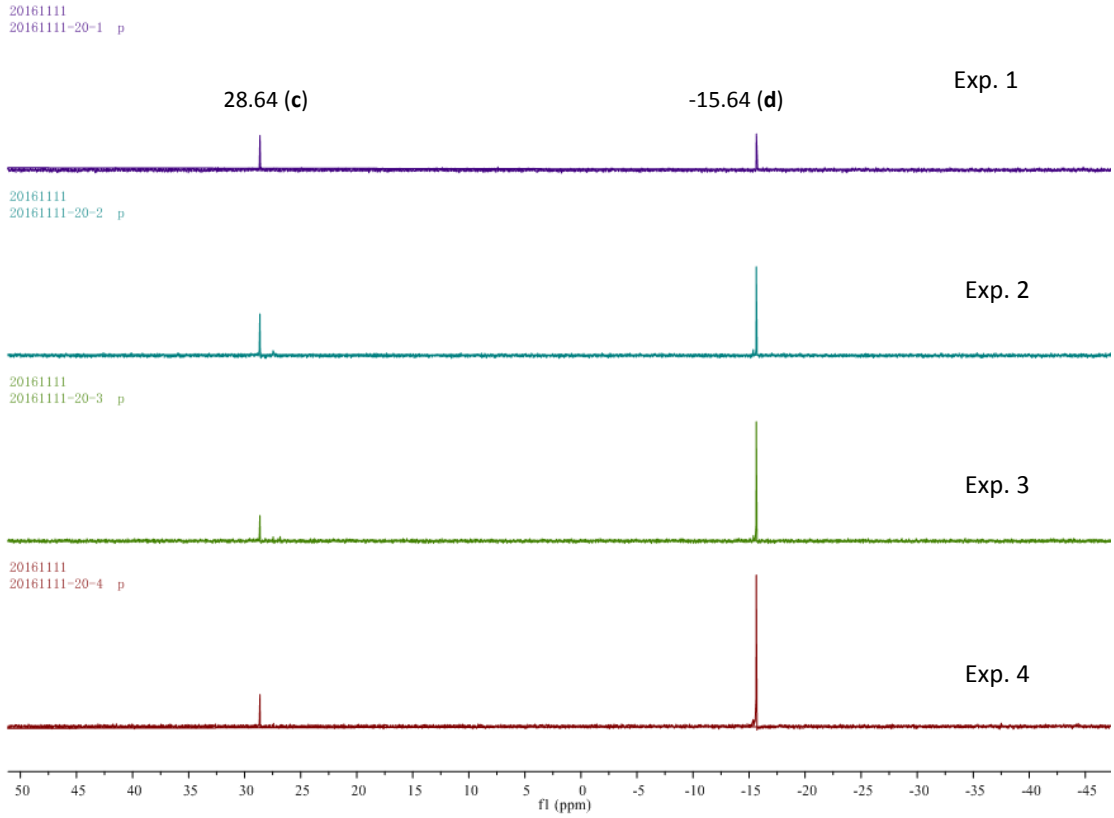
1. General Considerations

General Information: All reactions were carried out under nitrogen atmosphere unless otherwise noted. **^{1}H NMR** and **^{13}C NMR** spectra were measured on a Bruker Avance **NMR** spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). Enantiomeric excess was determined by HPLC analysis (ESSENTIA LC-16), using chiral column described below in detail. The configuration was determined by comparison of with the literature data.

Materials: Commercially available reagents were used directly without further purification other than those detailed below. Acetone was dried with anhydrous $CaSO_4$ and distilled over $KMnO_4$. Anhydrous dichloromethane was obtained by distillation over calcium hydroxide.

2. ^{31}P-NMR Experimental Details on the Coordination of (R)-BINAP with Bin-PdNPs

entry	(*R*)-BINAP (mg) (**a**)	Bin-PdNPs (mg) (**b**)	(*R*)-BINAP /Bin-PdNPs (molar ratios)	^{31}P-NMR integration ratio (**c**/**d**)	Percentage of coordinated (*R*)-BINAP/PdNPs* (***x***)
1	1.6	5.3	0.5:1	1:1	26%
2	2.3	5.3	0.75:1	0.6:1	28%
3	**3.7**	**5.3**	**1.2:1**	**0.4:1**	**34%**
4	4.7	5.3	1.5:1	0.2:1	25%



* Due to the existence of binaphthyl group, the phosphine ligand cannot entirely coordinate with the surface palladium atoms on PdNPs. The percentage of coordinated (R)-BINAP/PdNPs (***x***) is calculated based on the following formula, **which reflects the average value of coordinated surface over non-coordinated position on PdNPs surface**:

$$\boldsymbol{x}=[(\frac{\mathbf{c}}{\mathbf{c+d}}\times\frac{\mathbf{a}}{\mathbf{MW_{(BINAP)}}})\div\frac{\mathbf{b}\times 10.6\ wt\%}{\mathbf{MW_{(Pd)}}}]\times 100\%$$

a: the amount of (R)-BINAP used before coordination;

b: the amount of BIN-PdNPs;

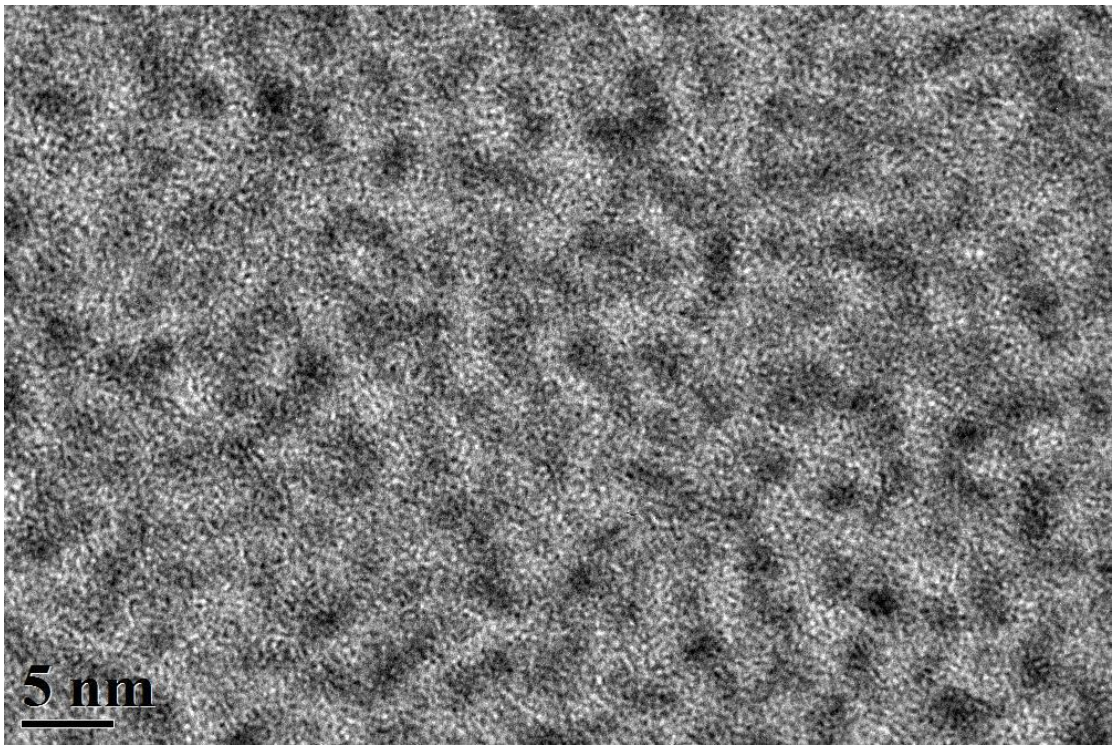
10.6 wt%: the palladium content of BIN-PdNPs based on ICP characterization;

c/**d**: ^{31}P-NMR integration ratios (**c**: coordinated ligand; **d**: free ligand);

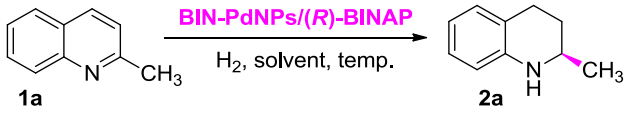
$\mathbf{MW_{(BINAP)}}$ = 622.67 g/mol;

$\mathbf{MW_{(Pd)}}$ = 106.42 g/mol.

3. TEM image of Bin-PdNPs/(R)-BINAP (1:1.2)

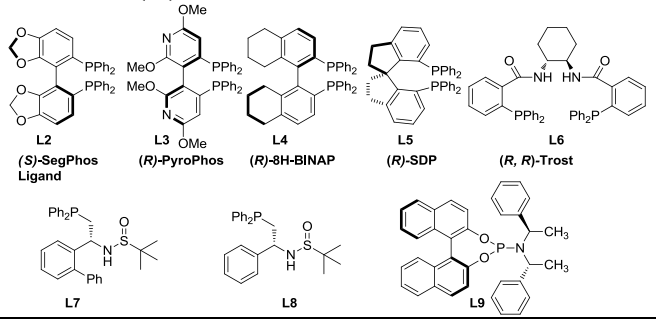


4. Condition Optimizations for Asymmetric Hydrogenation of Quinoline Derivatives



Entry	Catalyst/ Ligand (mol%)	Solvent/ Additive	H_2 pressure /temp (^oC)	Yield/*ee*(%)
1	2/0.5 (**L1**)	H_2O/-	balloon/25	>95/0
2	1/0.5 (**L1**)	H_2O/-	balloon/25	>95/0
3	1/1 (**L1**)	H_2O/-	balloon/25	>95/6
4	1/1 (**L1**)	toluene/-	balloon/25	>95/5
5	1/1 (**L1**)	ether/-	balloon/25	>95/8
6	1/1 (**L1**)	CH_2Cl_2/-	balloon/25	>95/12
7	1/2 (**L1**)	CH_2Cl_2/-	balloon/25	56/0
8	5/6 (**L1**)	CH_2Cl_2/-	30 atm/60	>95/8
9	5/6 (**L1**)	CH_2Cl_2/TFA(0.3)	30 atm/60	>95/32
10	**5/6 (L1)**	**CH_2Cl_2/TFA(0.6)**	**30 atm/60**	**>95/70**
11	5/6 (**L1**)	CH_2Cl_2/TFA(1)	30 atm/60	<10/40
12	5/6 (**L1**)	CH_2Cl_2/TFA(0.6)	10 atm/60	25/16
13	5/6 (**L1**)	CH_2Cl_2/TFA(0.6)	40 atm/60	50/36
14	5/6 (**L2**)	CH_2Cl_2/TFA(0.6)	30 atm/60	55/-21
15	5/6 (**L3**)	CH_2Cl_2/TFA(0.6)	30 atm/60	52/6
16	5/6 (**L4**)	CH_2Cl_2/TFA(0.6)	30 atm/60	56/21
17	5/6 (**L5**)	CH_2Cl_2/TFA(0.6)	30 atm/60	90/0
18	5/6 (**L6**)	CH_2Cl_2/TFA(0.6)	30 atm/60	88/0
19	5/6 (**L7**)	CH_2Cl_2/TFA(0.6)	30 atm/60	20/0
20	5/6 (**L8**)	CH_2Cl_2/TFA(0.6)	30 atm/60	0/0
21	5/6 (**L9**)	CH_2Cl_2/TFA(0.6)	30 atm/60	35/0
22[c]	5	CH_2Cl_2/TFA(0.6)	30 atm/60	85/8
23	**Bin-PdNPs**	CH_2Cl_2/TFA(0.6)	30 atm/60	>95/0
24	(R)-**Bin-PdNPs/L1**	CH_2Cl_2/TFA(0.6)	30 atm/60	>95/70
25	(S)-**Bin-PdNPs/L1**	CH_2Cl_2/TFA(0.6)	30 atm/60	>95/70
19[d]	**Bis-diazonium salts**/Pd(TFA)$_2$/**L1**	CH_2Cl_2/TFA	30 atm/60	trace

[a] Reaction conditions: 2-methylquinoline (**1a**, 0.1 mmol), 3 mL solvent, **Bin-PdNPs**/(R)-BINAP, 36 h; [b] Yields and *e.e.* values were determined by ^{1}HNMR and HPLC equipped with a chiral OJ-H column, respectively; [c] (R)-BINAP-PdNPs as catalyst; [d] Bis-diazonium salts (6.7 mg, 1.8 mol%), 5 mol% Pd(TFA)$_2$, 6 mol% (R)-BINAP.



5. Typical Procedures for Asymmetric Hydrogenation of Quinoline Derivatives

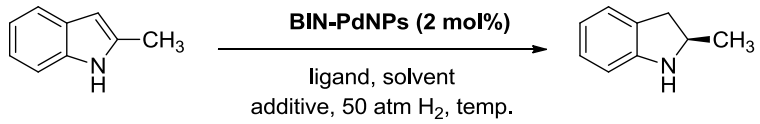
Bin-PdNPs (5.3 mg, 0.005 mmol), (*R*)-BINAP (3.7 mg, 0.006 mmol) and 1 mL anhydrous acetone were charged into an oven-dried tube under nitrogen atmosphere. After being stirred for 1.5 hours, the volatiles were evaporated under vacuum to give the catalyst. The solution of quinoline derivative (0.10 mmol) and TFA (6.8 mg, 0.06 mmol) in anhydrous dichloromethane (3.0 mL) was injected into the above tube and stirred for 5 min at room temperature. Then, the hydrogenation was performed at 60 ^{o}C under 30 atm H_2 in a stainless steel autoclave for 36 hours. After carefully releasing the hydrogen gas, saturated aqueous $NaHCO_3$ (5 mL) was added to quench the reaction and followed by extraction with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Further purification was performed by flash chromatography on silica gel (petroleum ether/EtOAc 10:1) to give the hydrogenated product. The enantiomeric excess of the products were determined by a HPLC equipped with a chiral column (OD-H, OJ-H or AD-H).

6. Hg Poisoning Experiment

A Hg poisoning experiment (refer to Angew. Chem. Int. Ed. 2010, 49, 1820) was performed to confirm the heterogeneous catalytic process.

After a standard reaction was initiated after 1 hour, 10 equivalents of Hg (to Pd content) were injected into the reaction tube and then the steel autoclave was recharged with hydogen gas, subjecting to react for 36 hours. Treatment with Hg in this way entirely inhibited the hydrogenation, deriving from full encapsulation of nanoparticle surfaces by a monolayer of Hg atoms.

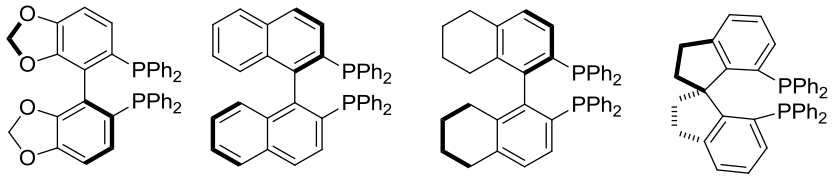
7. Condition Optimizations for Asymmetric Hydrogenation of Indole Derivatives



entry	ligands (mol%)	solvent	additive (1 eq.)	temp. (^{o}C)	yield (%)	*e.e.* (%)[a]
1	*R*-BINAP, 1	DCM/TFE (1:1)	L-CSA	25	-	-
2	*R*-BINAP, 1	DCM/TFE (1:1)	L-CSA	60	52	23
3	*R*-BINAP, 1.5	DCM/TFE (1:1)	L-CSA	60	56	32
4	*R*-BINAP, 2	DCM/TFE (1:1)	L-CSA	60	63	38
5	*R*-BINAP, 6	DCM/TFE (1:1)	L-CSA	60	90	37
6	*R*-BINAP, 2.4	DCM/TFE (1:1)	L-CSA	60	89	42
7	*R*-BINAP, 2.4	DCM/TFE (1:1)	TfOH	60	87	14
8	*R*-BINAP, 2.4	DCM/TFE (1:1)	TsOH-H_2O	60	56	41
9	*R*-BINAP, 2.4	DCM/TFE (1:1)	CF_3COOH	60	58	44.3
10	*R*-BINAP, 2.4	DCM/TFE (1:1)	*L*-proline	60	46	27
11	*S*-SegPhos, 2.4	DCM/TFE (1:1)	L-CSA	60	86	36
12	*R*-SDP, 2.4	DCM/TFE (1:1)	L-CSA	60	<10	17
13	*R*-8H-BINAP, 2.4	DCM/TFE (1:1)	L-CSA	60	85	64
14	*R*-8H-BINAP, 2.4	DCM	L-CSA	60	83	18
16	*R*-8H-BINAP, 2.4	DCM/TFE(1:5)	L-CSA	60	85	40
17	*R*-8H-BINAP, 2.4	$CHCl_3$	L-CSA	60	85	19
18[b]	*R*-BINAP-PdNPs, 2	DCM	L-CSA	60	0	-

[a]*e.e.* values were determined with a OD-H column on HPLC.

[b]The experiment was used to compare the catalytic effect of asymmetric hydrogenation of 2-methylindole with a well-coordinated R-BINAP-PdNPs. Interestingly, the reaction did not occur. This further confirms the advantages of covalent bond stabilization of nanoparticles.



S-SegPhos *R*-BINAP *R*-8H-BINAP *R*-SDP

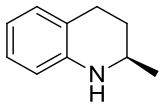
8. Typical Procedures for Asymmetric Hydrogenation of Indole Derivatives

Bin-PdNPS (5.3 mg, 0.005 mmol), (*R*)-8H-BINAP (3.8 mg, 0.006 mmol) and 1 mL anhydrous acetone were charged into an oven-dried tube under nitrogen atmosphere. After being stirred for 1.5 hours, the solvent was evaporated under vacuum to afford the catalyst.

L-CSA (0.25 mmol) and indole derivative (0.25 mmol) were stirred in 1 mL DCM/TFE (1:1, v/v) at room temperature for 5 min. Subsequently, the prepared catalyst together with the substrates and additives were combined and put into a stainless steel autoclave. The hydrogenation was performed at 60 ^{o}C under 50 atm H_2 for 24 hours. After carefully releasing the hydrogen gas, saturated aqueous $NaHCO_3$ (5 mL) was added to quench the reaction and followed by extraction with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Further Purification was performed by flash chromatography on silica gel (petroleum ether/EtOAc 10:1) to give the hydrogenated product. The enantiomeric excess of the products were determined by a HPLC equipped with a chiral column (OD-H, OJ-H or AD-H).

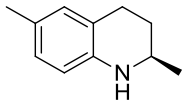
9. Characterization Data of Products

(R)-2-methyl-1, 2, 3, 4-tetrahydroquinoline (2a)[1]



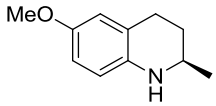
A colorless liquid, 83% yield, 70% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 6.7 Hz, 2H), 6.71 – 6.67 (m, 1H), 6.60 – 6.47 (m, 1H), 3.70 (s, 1H), 3.51 – 3.43 (m, 1H), 2.97 – 2.78 (m, 2H), 2.04 – 1.98 (m, 1H), 1.72 – 1.62 (m, 1H), 1.29 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 129.4, 126.8, 121.2, 117.1, 114.1, 47.2, 30.2, 26.7, 22.7. HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5 mL / min), (S) t1 = 17.8 min, **(R) t2 = 19.4 min**.

(R)-2, 6-dimethylquinoline (2b)[1]



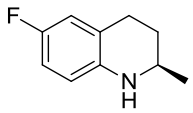
A colorless liquid, 95% yield, 62% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 7.6 Hz, 2H), 6.44 (d, *J* = 7.9 Hz, 1H), 3.60 (s, 1H), 3.43 – 3.35 (m, 1H), 2.89 – 2.81 (m, 1H), 2.76– 2.69 (m, 1H), 2.24 (s, 3H), 1.98 – 1.92 (m, 1H), 1.66 – 1.56 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 129.9, 127.2, 126.3, 121.5, 114.3, 47.3, 30.4, 26.6, 22.6, 20.4. HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5 mL / min), (S) t1 = 21.3 min, **(R) t2 = 25.9 min**.

(R)-6-Methoxyl-2-methyl-1, 2, 3, 4-tetrahydroquinoline (2c) [1]



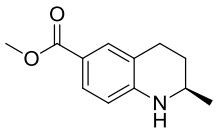
A colorless liquid, 95% yield, 46% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.63 – 6.60 (m, 2H), 6.48 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 3.39 – 3.22 (m, 1H), 2.91 – 2.70 (m, 2H), 1.97 – 1.91 (m, 1H), 1.65 – 1.22 (m, 1H), 1.23 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 138.9, 122.6, 115.4, 114.6, 112.9, 55.8, 47.5, 30.3, 26.9, 22.6. HPLC (OJ-H, elute: Hexanes / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), (S) t1 = 14.9 min, **(R) t2 = 18.2 min**.

(R)-6-fluorine-2-methyl-1, 2, 3, 4-tetrahydroquinoline (2d) [1]



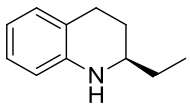
A colorless liquid, 71% yield, 54% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.70 (dd, *J* = 12.5, 5.6 Hz, 2H), 6.45 – 6.41 (m, 1H), 3.42 – 3.34 (m, 1H), 2.90 – 2.81 (m, 1H), 2.76 – 2.70 (m, 1H), 1.98– 1.92 (m, 1H), 1.64 – 1.54 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 155.5 (d, *J* = 234.6 Hz), 141.0, 122.5 (d, *J* = 6.8 Hz), 115.4 (d, *J* = 21.6 Hz), 114.7 (d, *J* = 7.6 Hz), 113.2 (d, *J* = 22.4 Hz), 47.3, 29.9, 26.7, 22.5. HPLC (OD-H, elute: Hexanes / *i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 0.8 mL / min), **(R) t1 = 6.8 min**, (S) t2 = 8.3 min.

(R)-methyl 2-methyl-1, 2, 3, 4-tetrahydroquinoline-6-carboxylate (2e) [1]



A colorless liquid, 63% yield, 59% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 6.41 (d, *J* = 8.8 Hz, 1H), 4.21 (s, 1H), 3.85 (s, 3H), 3.54 – 3.46 (m, 1H), 2.87 – 2.75 (m, 2H), 2.00 – 1.94(m, 1H), 1.63 – 1.53 (m, 1H), 1.25 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 148.8, 131.1, 129.1, 119.7, 117.6, 112.6, 51.5, 47.2, 29.5, 26.3, 22.5. HPLC (OJ-H, elute: Hexanes / *i*-PrOH = 15 / 85, detector: 254 nm, flow rate: 0.7 mL / min), **(R) t1 = 12.3 min**, (S) t2 = 15.2 min.

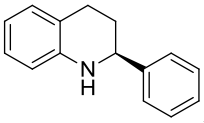
(R)-2-ethyl-1, 2, 3, 4-tetrahydroquinoline (2f)[1]



A colorless liquid, 86% yield, 66% *e.e.*, **^{1}HNMR** (400 MHz, $CDCl_3$) δ 6.99 (t, *J* = 7.3 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 1H), 3.32 – 3.19 (m, 1H), 2.85 – 2.77 (m, 2H), 2.01 – 1.98 (m, 1H), 1.67 – 1.62 (m, 1H), 1.55 (dd, *J* = 14.3, 7.2 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 129.2, 126.7, 121.4, 116.9, 114.0,

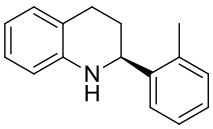
53.1, 29.4, 27.6, 26.4, 10.1. HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5 mL / min), (S) t1 = 15.5 min, **(R) t2 = 16.9 min**.

(S)-2-phenyl-1, 2, 3, 4-tetrahydroquinoline (2g) [2]



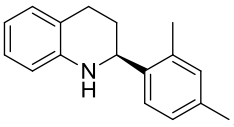
A pale yellow liquid, 91% yield, 56% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.71 (t, *J* = 7.1 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.49 (dd, *J* = 9.3, 3.2 Hz, 1H), 4.06 (s, 1H), 3.02 – 2.94(m, 1H), 2.82 – 2.76 (m, 1H), 2.22 – 2.14 (m, 1H), 2.09 – 2.00 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 144.7,129.3, 128.6, 127.5, 126.9, 126.6, 120.9, 117.2 114.0, 56.3, 31.0, 26.4. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.6 mL / min), **(S) t1 = 14.4 min,** (R) t2 = 17.9 min.

(S)-2-(o-tolyl)-1, 2, 3, 4-tetrahydroquinoline (2h) [2]



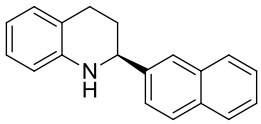
A yellow solid, 84% yield, 46% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.07 (t, *J* = 5.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 4.73 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.99 (s, 1H), 3.03 – 2.95 (m, 1H), 2.85 – 2.78 (m, 1H), 2.44 (s, 3H), 2.19 – 2.13 (m, 1H), 2.02 – 1.92 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 142.6, 134.8, 130.5, 129.4, 127.1,127.0, 126.5, 126.0, 120.9, 117.1, 114.0, 52.2, 29.2, 26.6, 19.1. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 8.7 min**, (R) t2 = 10.3 min.

(S)-2-(2, 4-dimethylphenyl)-1, 2, 3, 4-tetrahydroquinoline (2i) [2]



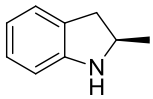
A colorless liquid, 82% yield, 52% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.08 – 7.04 (m, 4H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 4.67 (dd, *J* = 9.3, 2.4 Hz, 1H), 3.94 (s, 1H), 3.01 – 2.93 (m, 1H), 2.83 – 2.77 (m, 1H), 2.37 (d, *J* = 12.3 Hz, 6H) 2.14 – 2.10 (m, 1H), 1.99 – 1.89 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 139.6, 136.6, 134.7, 131.3, 129.3, 127.0,126.9, 126.0, 120.8, 117.0, 114.0, 52.0, 29.3, 26.7, 21.0, 19.0. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 7.7 min**, (R) t2 = 9.1 min.

(S)-2-(2-Naphthyl)-1, 2, 3, 4-tetrahydroquinoline (2j) [2]



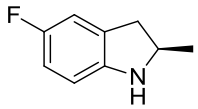
A white solid, 76% yield, 53% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 8.1 Hz, 4H), 7.57 – 7.51 (m, 3H), 7.15 – 6.01 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 4.65 (dd, *J* = 9.2, 3.1 Hz, 1H), 4.17 (s, 1H), 3.05 – 2.97 (m, 1H), 2.84– 2.78(m, 1H), 2.25 – 2.20 (m, 1H), 2.18 – 2.08(m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 142.2, 133.4, 133.0, 129.4, 128.4, 127.9, 127.8, 127.0, 126.2, 125.8, 125.1, 124.9, 121.0, 117.3, 114.1, 56.4, 31.0, 26.5. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 12.8 min**, (R) t2 = 21.3 min.

(R)-2-methylindoline (4a) [3]



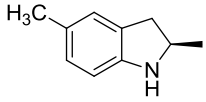
A colorless liquid, 85% yield, 64% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.04 (m, 2H), 6.81 – 6.77 (m, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 4.10 – 4.02 (m, 1H), 3.86 (s, 1H), 3.23 (dd, *J* = 15.4, 8.5 Hz, 1H), 2.72 (dd, *J* = 15.4, 7.8 Hz, 1H), 1.37 (dd, *J* = 6.2, 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 129.0, 127.3, 124.8, 118.6, 109.3, 55.3, 37.9, 22.4. HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 97 / 3, detector: 254 nm, flow rate: 0.8 mL / min), **(R) t1 = 9.2 min**, (S) t2 = 10.0 min.

(R)-5-fluoro-2-methylindoline (4b) [3]



A colorless liquid, 81% yield, 50% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.81 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.74 – 6.69 (m, 1H), 6.52 (dd, *J* = 8.4, 4.3 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.14 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.64 (dd, *J* = 15.6, 7.8 Hz, 1H), 1.30 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 234.7 Hz), 146.9, 130.7 (d, *J* = 8.0 Hz), 113.1 (d, *J* = 23.1 Hz), 112.1 (d, *J* = 23.7 Hz), 109.3 (d, *J* = 8.3 Hz), 55.9, 38.0, 22.2. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99 / 1, detector: 254 nm, flow rate: 1 mL / min), **(R) t1 = 8.6 min**, (S) t2 = 12.7 min.

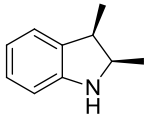
(R)-2,5-dimethylindoline (4c) [3]



A colorless liquid, 92% yield, 47% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.52 (s, 1H), 3.15 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.65 (dd, *J* = 15.4, 7.8 Hz, 1H), 2.30 (s, 3H), 1.33 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6, 129.3, 127.9, 127.5, 125.6, 109.2, 55.5, 37.9, 22.3, 20.9. HPLC

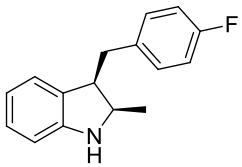
(OD-H, elute: Hexanes/*i*-PrOH = 99 / 1, detector: 254 nm, flow rate: 1 mL / min), **(R) t1 = 8.6 min**, (S) t2 = 10.5 min.

(2R, 3R)-2, 3-dimethylindoline (4d) [4]



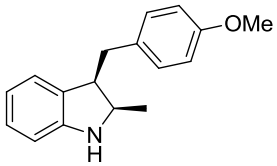
A colorless liquid, 95% yield, 51% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.68 (s, 1H), 3.34 – 3.27(m, 1H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 134.3, 127.3, 123.8, 118.7, 109.4, 58.4, 39.5, 16.3, 13.7. HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 99/ 1, detector: 254 nm, flow rate: 1 mL / min), (S) t1 = 18.1 min, **(R) t2 = 23.1 min**.

(2R, 3R)-3-(4-fluorobenzyl)-2-methylindoline (4e) [4]



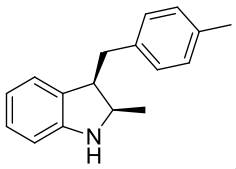
A colorless liquid, 83% yield, 48% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.07 – 7.00 (m, 3H), 6.67 (t, *J* = 8.3 Hz, 1H), 6.63 – 6.59 (m, 1H), 6.53 (d, *J* = 7.3 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.66 (s, 1H), 3.47 (dd, *J* = 16.3, 7.5 Hz, 1H), 2.97 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.83 (dd, *J* = 13.8, 9.4 Hz, 1H), 1.27 (t, *J* = 8.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$)δ 161.4 (d, *J* = 243.6 Hz), 150.4, 135.9 (d, *J* = 3.2 Hz), 131.8, 130.6 (d, *J* = 7.7 Hz), 127.6, 125.0, 118.3, 115.0 (d, *J* = 21.0 Hz), 109.5, 58.5, 46.2, 33.5, 16.4. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1mL / min), (S) t1 = 8.3 min, **(R) t2 = 12.2 min**.

(2R, 3R)-3-(4-methoxybenzyl)-2-methylindoline (4f) [4]



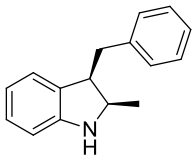
A pale yellow liquid, 86% yield, 54% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 7.08 – 7.04 (m, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.69 – 6.61 (m, 3H), 4.06 – 3.99 (m, 1H), 3.86 (s, 3H), 3.52 (dd, *J* = 16.1, 7.8 Hz, 1H), 2.96 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.85 (dd, *J* = 13.9, 9.1 Hz, 1H), 1.27 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 150.4, 132.3, 132.1, 130.1, 127.4, 125.0, 118.3, 113.7, 109.4, 58.5, 55.3, 46.2, 33.4, 16.5. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (S) t1 = 7.0 min, **(R) t2 = 9.0 min**.

(2R, 3R)-2-methyl-3-(4-methylbenzyl)indoline (4g) [4]



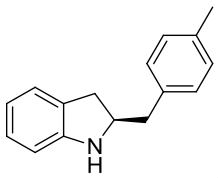
A colorless liquid, 92% yield, 55% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (q, *J* = 8.1 Hz, 4H), 7.09 – 7.05 (m, 1H), 6.70 – 6.63 (m, 3H), 4.07 – 4.00 (m, 1H), 3.69 (d, *J* = 6.2 Hz, 1H), 3.57 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.40 (s, 3H), 1.26 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 137.2, 135.5, 132.1, 129.1, 129.0, 127.5, 124.9, 118.3, 109.5, 58.5, 46.0, 33.8, 21.1, 16.6. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), (S) t1 = 8.4 min, **(R) t2 = 10.8 min**.

(2R, 3R)-3-benzyl-2-methylindoline (4h) [4]



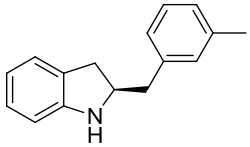
A colorless liquid, 90% yield, 53% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.20 (m, 3H), 7.12 – 6.97 (m, 1H), 6.70 – 6.60 (m, 3H), 4.08 – 4.01 (m, 1H), 3.71 (s, 1H), 3.58 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.02 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.93 (dd, *J* = 13.9, 8.9 Hz, 1H), 1.28 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 140.4, 132.0, 129.2, 128.3, 127.5, 126.0, 124.9, 118.3, 109.5, 58.5, 46.0, 34.3, 16.5. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), (S) t1 = 9.9 min, **(R) t2 = 13.5 min**.

(R)-2-(4-methylbenzyl)indoline (4i) [3]



A pale yellow liquid, 81% yield, 55% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.14 - 7.05 (m, 5H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.16 –4.08 (m, 1H), 3.19 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.96 – 2.75 (m, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 136.0, 129.4, 129.0, 128.5, 127.4, 124.9,118.6, 109.2, 61.1, 42.2, 35.9, 21.1. HPLC (OD-H, elute: Hexanes/i-PrOH = 99 / 1, detector: 254 nm, flow rate: 1 mL / min), **(R) t_1 = 11.1 min**, (S) t_2 = 12.4 min.

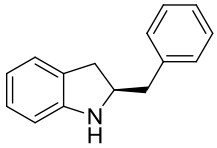
(R)-2-(3-methylbenzyl)indoline (4j) [3]



A pale yellow liquid, 86% yield, 53% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.14 – 7.04 (m, 5H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.16 –

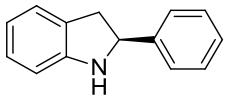
4.08 (m, 1H), 3.19 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.94 – 2.81 (m, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 139.0, 138.3, 130.0, 128.5, 127.3, 126.1, 124.8, 118.5, 109.1, 61.0, 42.6, 36.0, 21.5. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99 / 1, detector: 254 nm, flow rate: 1 mL / min), **(R) t1 = 10.9 min**, (S) t2 = 12.1 min.

(R)-2-benzylindoline (4k) [3]



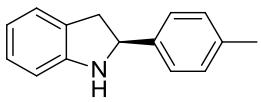
A yellow liquid, 93% yield, 54% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.24 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 4.17 – 4.09(m, 1H), 3.86 (s, 1H), 3.19 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.04 – 2.76 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 139.1, 129.2, 128.7, 128.4, 127.4, 126.5, 124.9, 118.6, 109.2, 61.1, 42.7, 36.0. HPLC (OD-H, elute: Hexanes / *i*-PrOH = 99 / 1, detector: 254 nm, flow rate: 1 mL / min), **(R) t1 = 13.1 min**, (S) t2 = 14.8 min.

(S)-2-phenylindoline (4l) [4]



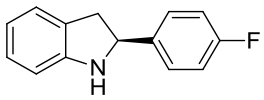
A colorless solid, 76% yield, 31% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.15 – 7.11 (m, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.00 (t, *J* = 9.0 Hz, 1H), 4.15 (s, 1H), 3.49 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.04 (dd, *J* = 15.6, 8.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 144.6, 128.6, 128.1, 127.6, 127.4, 126.3, 124.6, 118.8, 108.9, 63.6, 39.6. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 5 /1, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 9.8 min,** (R) t2 = 15.1 min.

(S)-2-(p-tolyl)indoline (4m) [4]



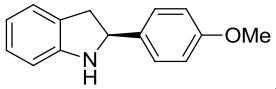
A colorless liquid, 93% yield, 32% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.11 (dd, *J* = 13.0, 7.2 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 4.95 (t, *J* = 9.0 Hz, 1H), 4.13 (s, 1H), 3.46 (dd, *J* = 15.6, 9.1 Hz, 1H), 3.01 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 141.6, 137.1, 129.3, 128.2, 127.6, 126.3, 124.6, 118.8, 108.8, 63.4, 39.6, 21.1. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 8.0 min**, (R) t2 = 13.6 min.

(S)-2-(4-fluorophenyl)indoline (4n) [4]



A pale yellow liquid, 51% yield, 35% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.14–7.04(m, 4H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 4.97 (t, *J* = 9.1 Hz, 1H), 4.15 (s, 1H), 3.46 (dd, *J* = 15.6, 9.2 Hz, 1H), 2.97 (dd, *J* = 15.6, 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.1Hz), 160.9, 150.8, 140.4, 128.2, 124.6, 119.0, 115.5, 115.3, 108.9, 62.9, 39.8. HPLC (OD-H, elute: Hexanes / *i*-PrOH = 5 / 1, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 8.5 min**, (R) t2 = 17.9 min.

(S)-2-(4-methoxyphenyl)indoline (4o) [4]



A pale yellow liquid, 86% yield, 22% *e.e.*, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.10 (dd, *J* = 14.4, 7.3 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 4.93 (t, *J* = 9.0 Hz, 1H), 3.83 (s, 3H), 3.43 (dd, *J* = 15.6, 9.1 Hz, 1H), 2.99 (dd, *J* = 15.6, 8.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 151.0, 136.7, 128.2, 127.5,127.4, 124.6, 118.8, 113.9, 108.8, 63.1, 55.3, 39.6. HPLC (OD-H, elute: Hexanes/*i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), **(S) t1 = 9.1 min**, (R) t2 = 15.6 min.

[**References for Known Compounds**]:

[1] W.-B. Wang, S.-M. Lu, P.-Y. Yang, X.-W. Han, Y.-G. Zhou, *J. Am. Chem.Soc.* **2003**, *125*, 10536-10537.

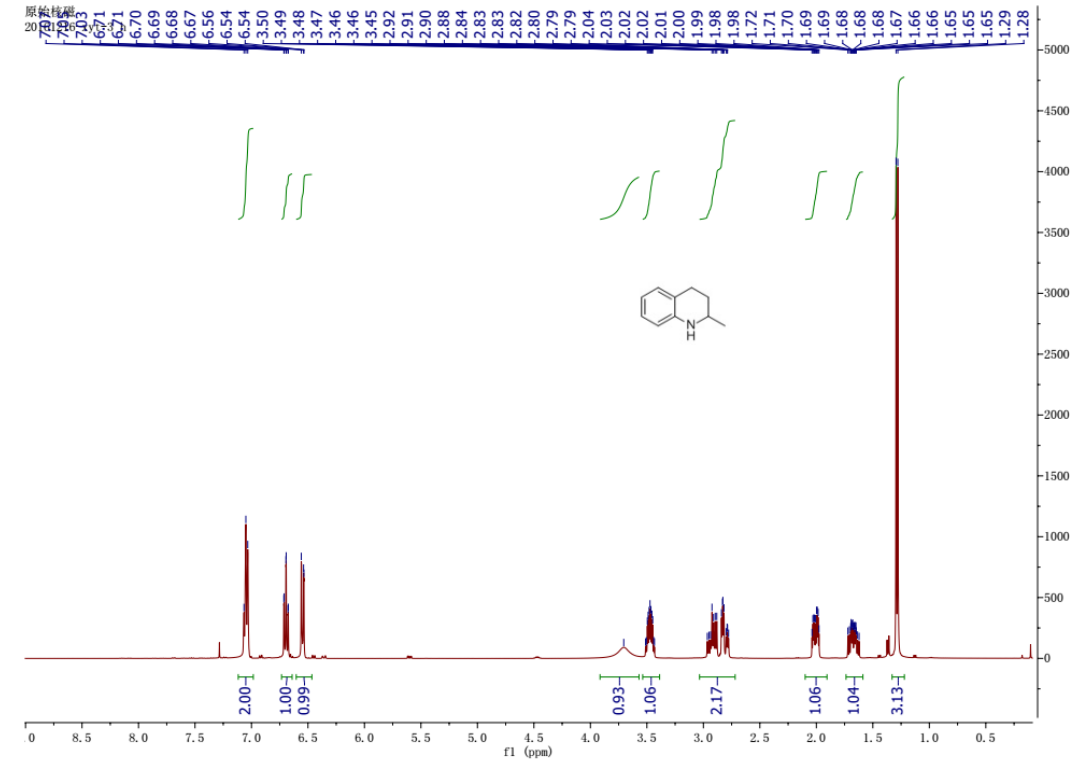
[2] T. Wang, L.-G. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 9878-9891.

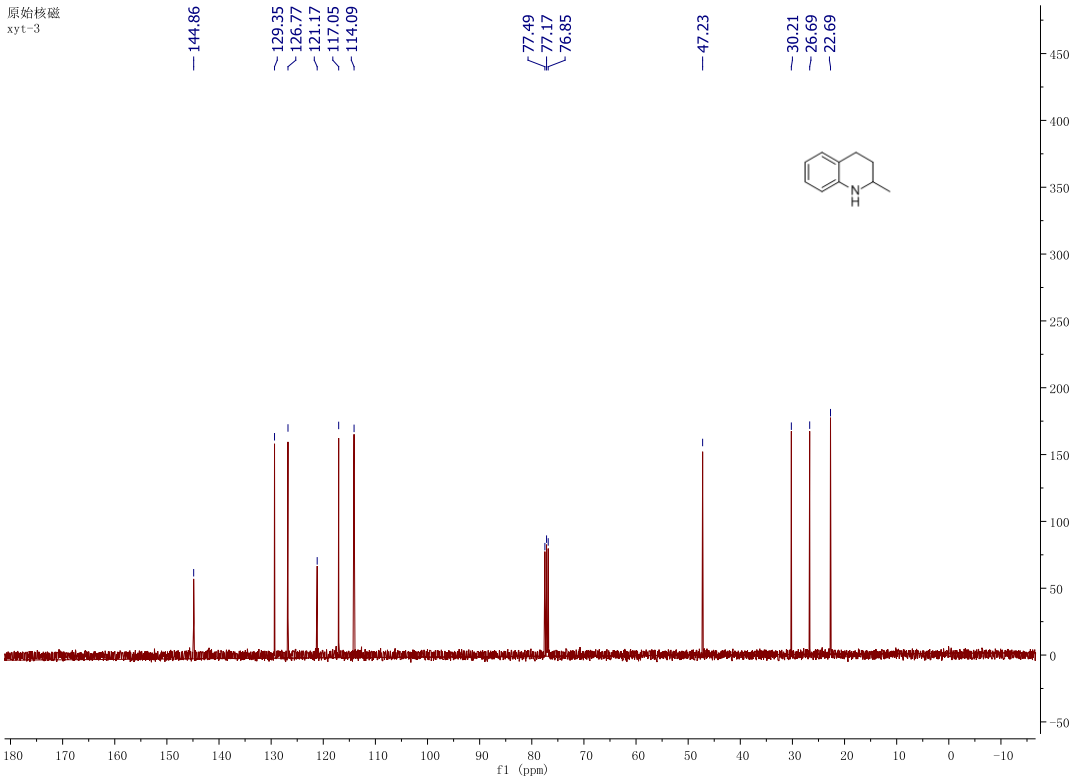
[3] D.-S. Wang, Q.-A. Chen, W. Li, C.-B.Yu, Y.-G. Zhou, and X. Zhang, *J. Am. Chem. Soc*. **2010**, *132*, 8909-8911.

[4] a) Y. Duan, L. Li, M.-W. Chen, C.-B. Yu, H.-J. Fan, Y.-G. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 7688-7700; b) T. Touge, T. Arai, *J. Am. Chem. Soc.* **2016**, *138*, 11299-11305; c) K. Saito, Y. Shibata, M. Yamanaka, T. Akiyama, *J. Am. Chem. Soc*. **2013**, 135, 11740-11743.

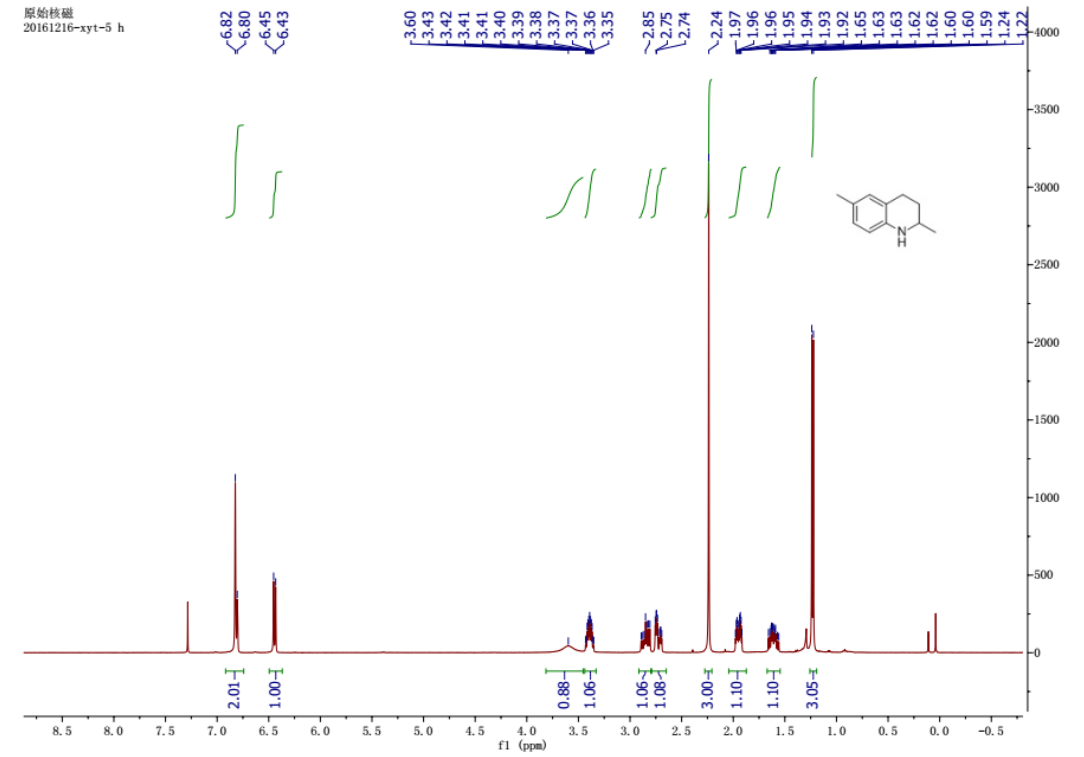
10. ^{1}H and ^{13}C NMR Spectra of the Products

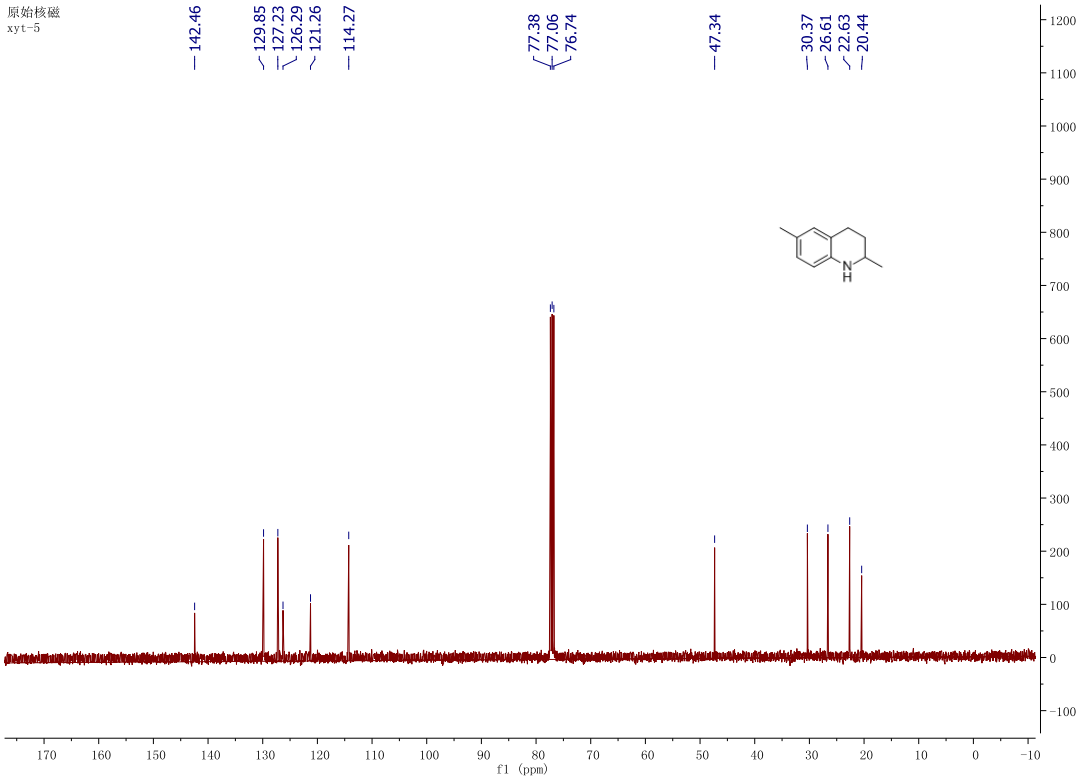
2a



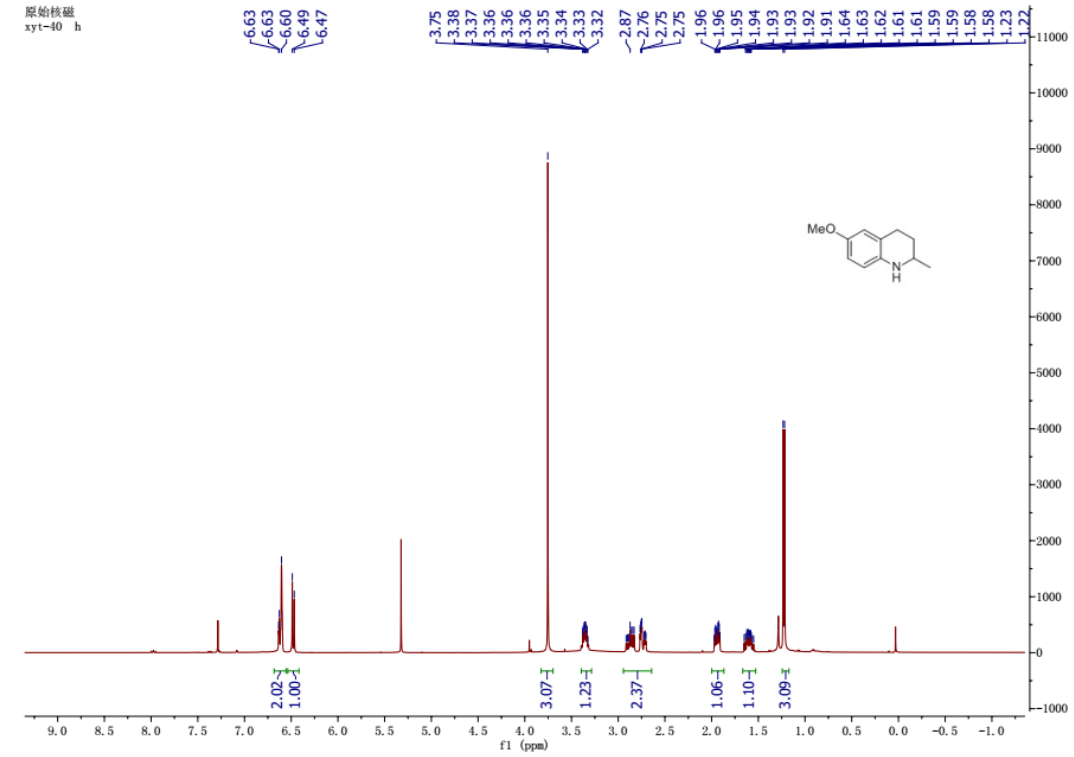


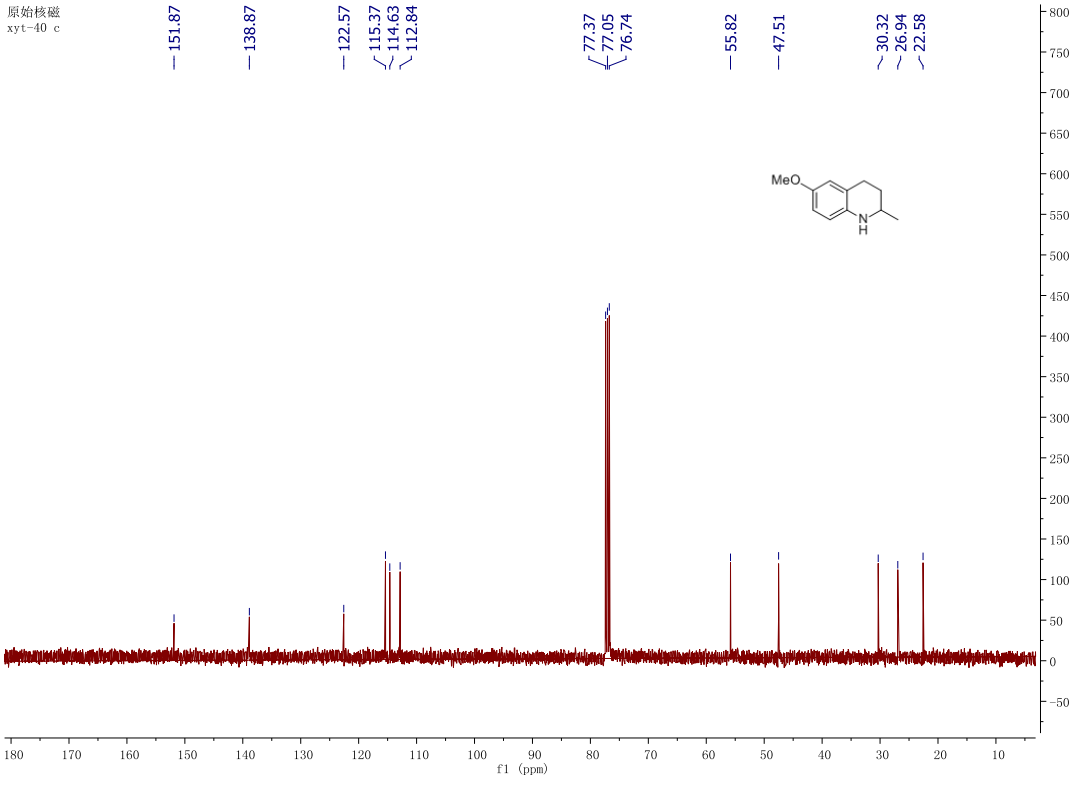
2b



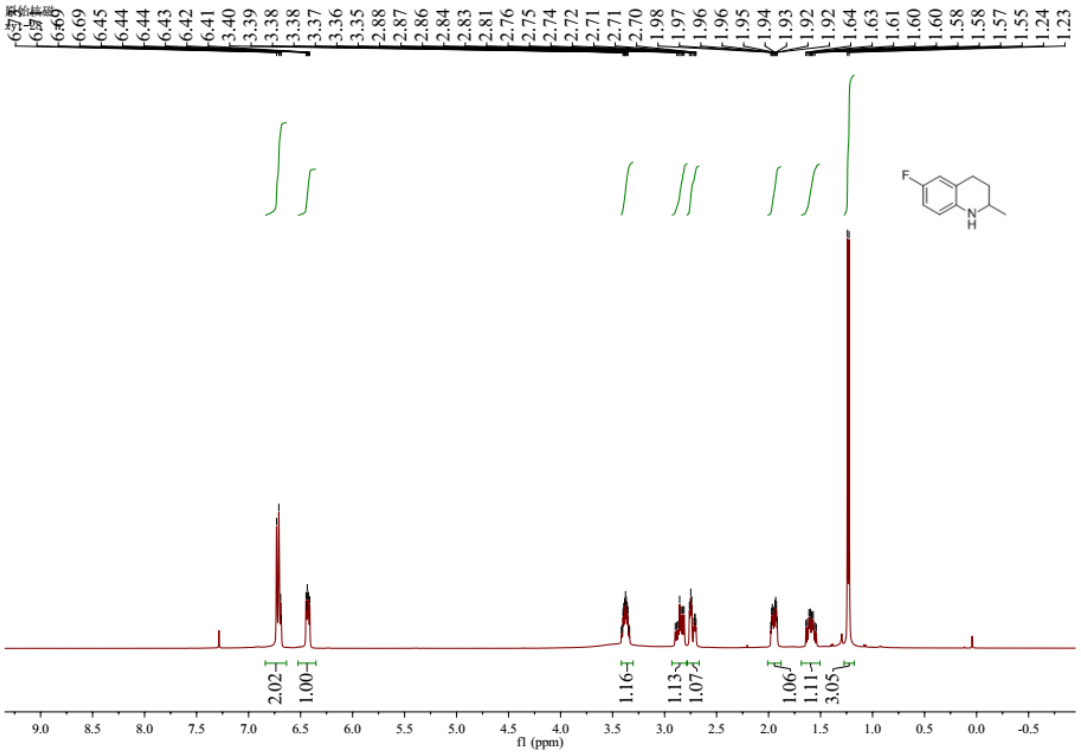


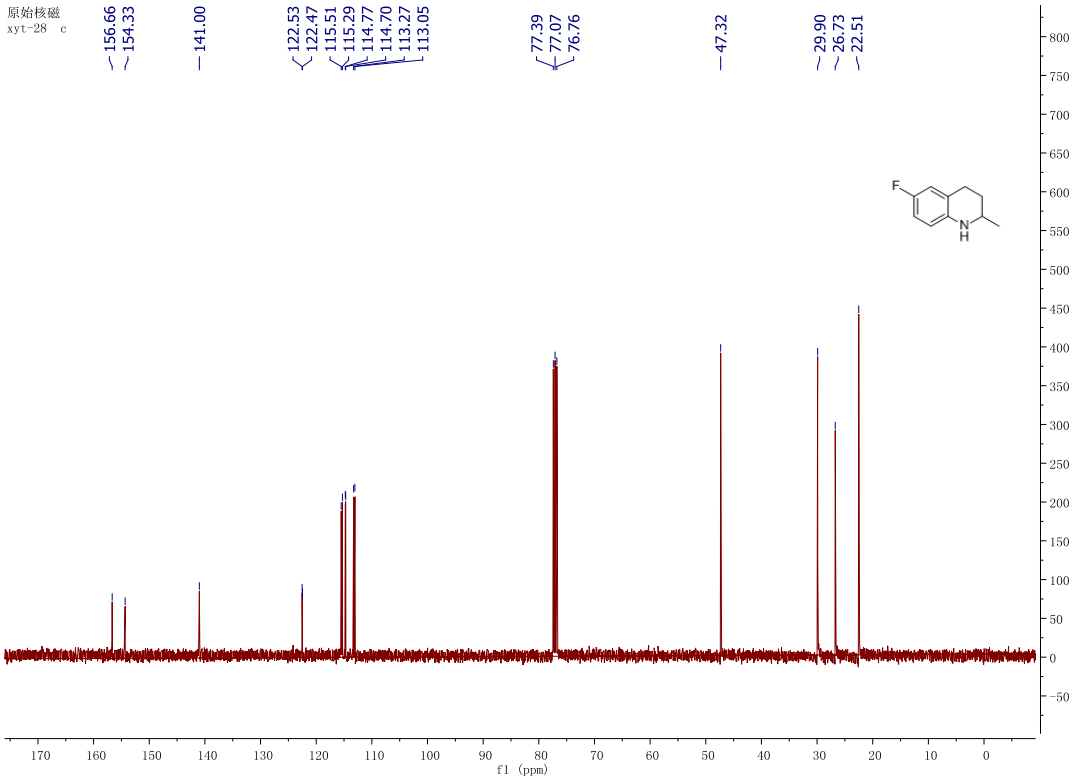
2c


原始核磁
xyt-40 h
6.63
6.63
6.60
6.49
6.47
3.75
3.38
3.37
3.36
3.36
3.36
3.35
3.34
3.33
3.32
2.87
2.76
2.75
2.75
1.96
1.96
1.95
1.94
1.93
1.93
1.92
1.91
1.64
1.63
1.62
1.61
1.61
1.59
1.59
1.58
1.58
1.23
1.22
MeO
N
H
2.02
1.00
3.07
1.23
2.37
1.06
1.10
3.09
f1 (ppm)

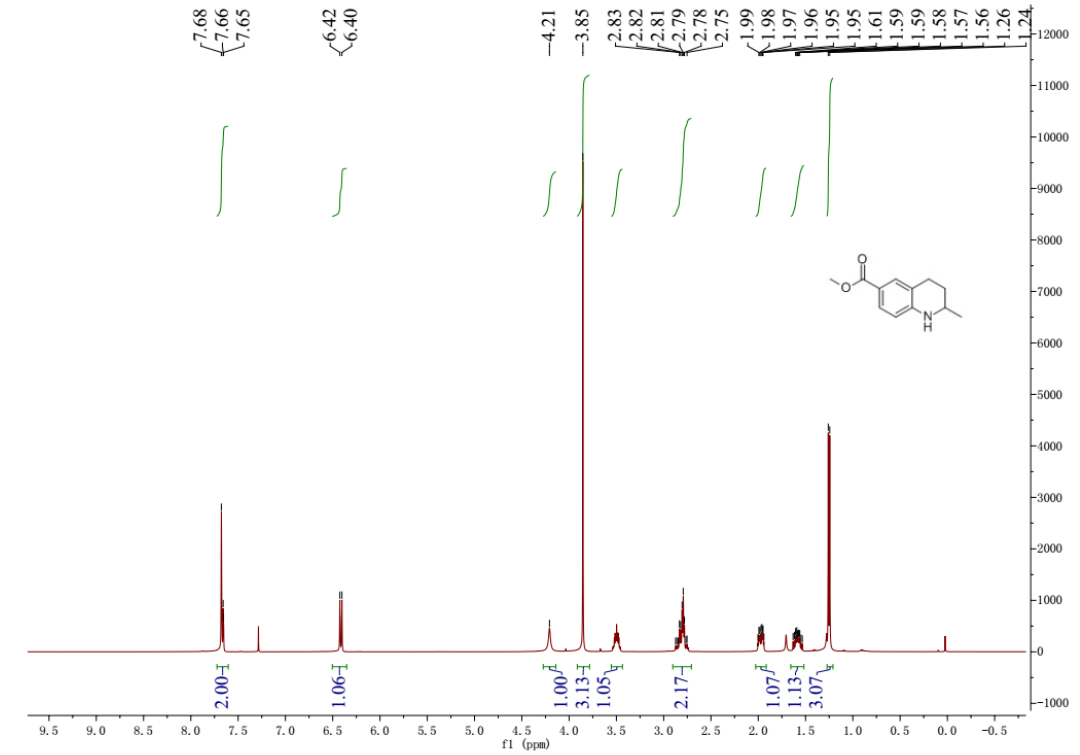

原始核磁
xyt-40 c
151.87
138.87
122.57
115.37
114.63
112.84
77.37
77.05
76.74
55.82
47.51
30.32
26.94
22.58
MeO
N
H
f1 (ppm)

2d


6.69
6.45
6.44
6.44
6.43
6.42
6.41
3.40
3.39
3.38
3.38
3.37
3.36
3.35
2.88
2.87
2.86
2.84
2.83
2.81
2.76
2.75
2.74
2.72
2.71
2.71
2.70
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.92
1.92
1.64
1.63
1.61
1.60
1.60
1.58
1.58
1.57
1.55
1.24
1.23
F
N
H
2.02
1.00
1.16
1.13
1.07
1.06
1.11
3.05
f1 (ppm)


原始核磁
xyt-28 c
156.66
154.33
141.00
122.53
122.47
115.51
115.29
114.77
114.70
113.27
113.05
77.39
77.07
76.76
47.32
29.90
26.73
22.51
F
N
H
f1 (ppm)

2e


7.68
7.66
7.65
6.42
6.40
4.21
3.85
2.83
2.82
2.81
2.79
2.78
2.75
1.99
1.98
1.97
1.96
1.95
1.95
1.61
1.59
1.59
1.58
1.57
1.56
1.26
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1.06
1.00
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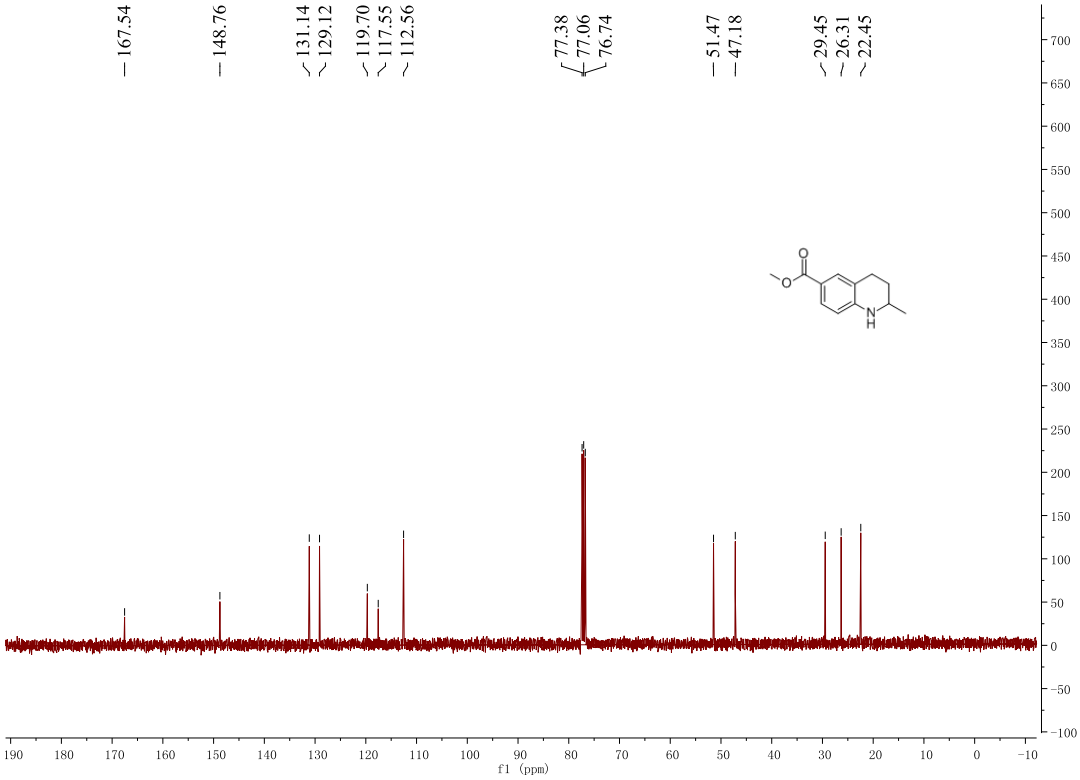
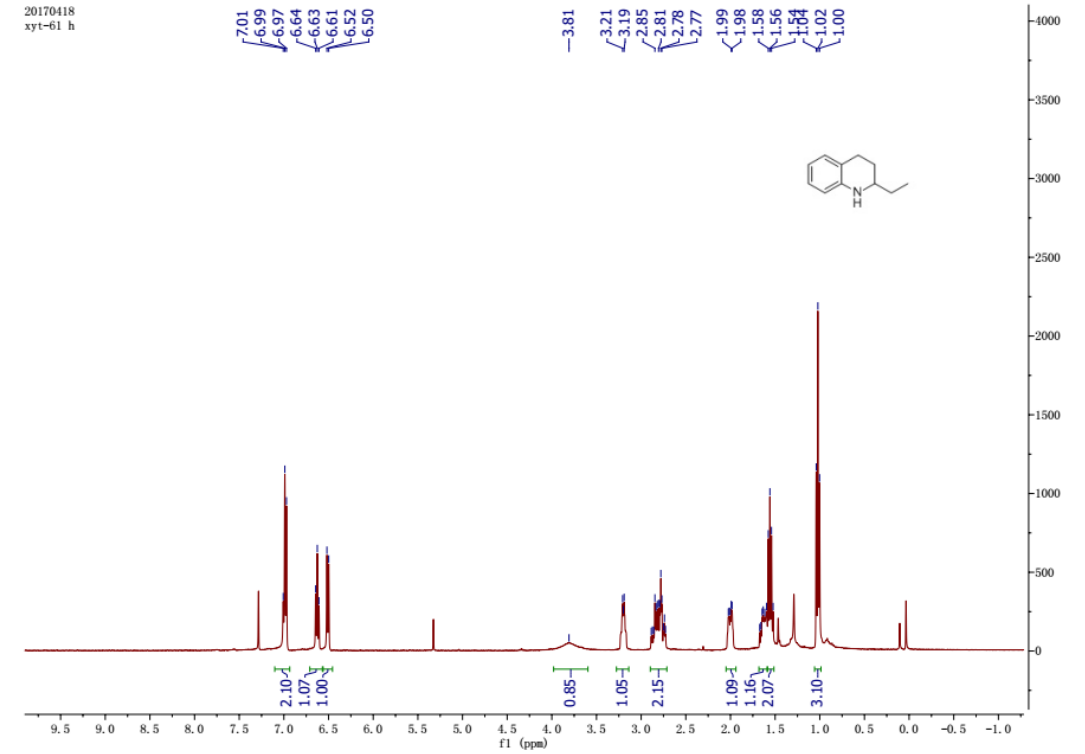
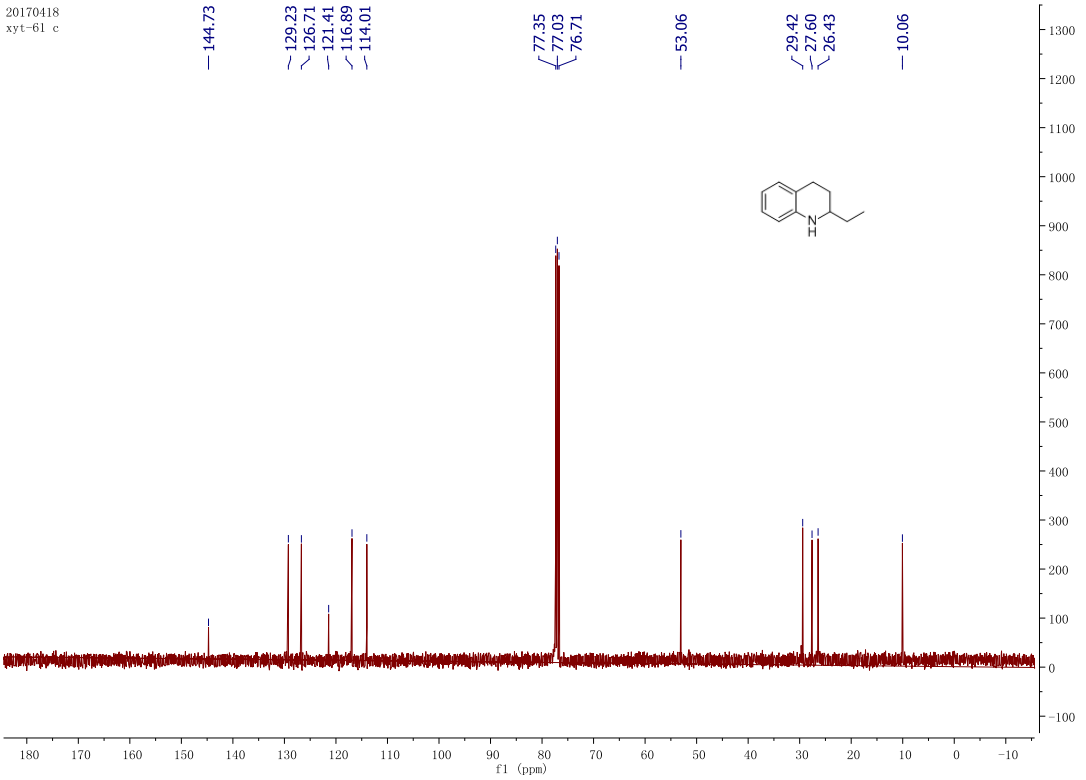
1.05
2.17
1.07
1.13
3.07
f1 (ppm)

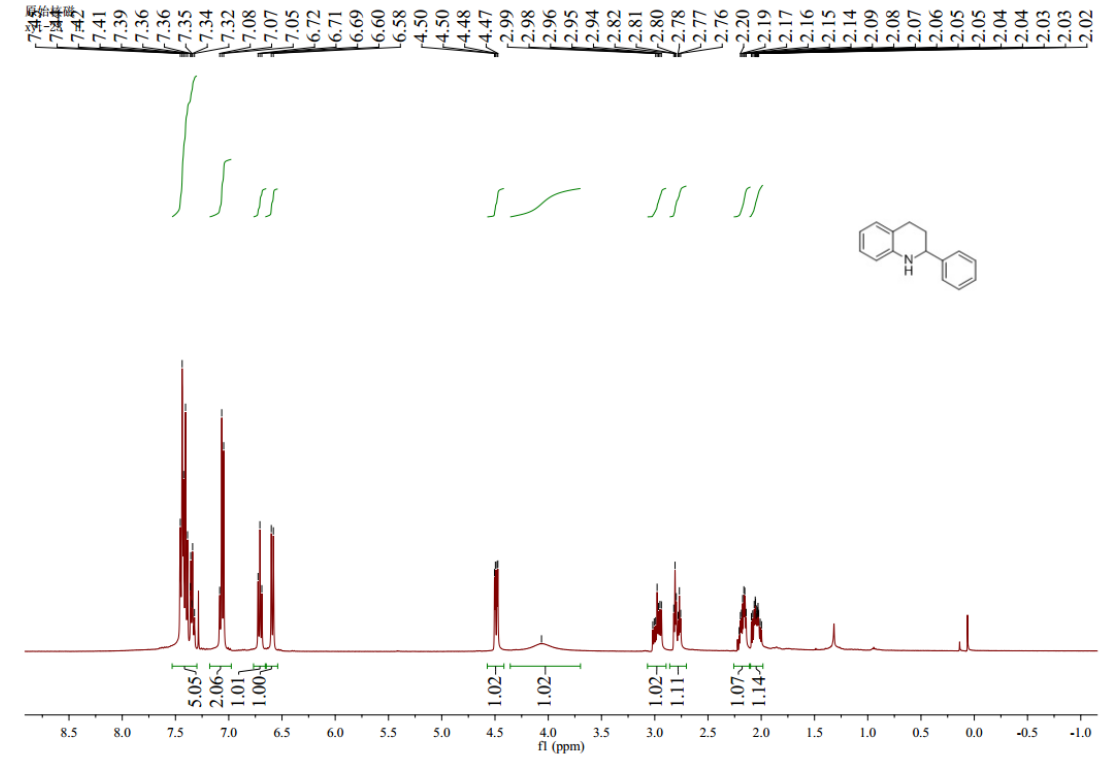

167.54
148.76
131.14
129.12
119.70
117.55
112.56
77.38
77.06
76.74
51.47
47.18
29.45
26.31
22.45
f1 (ppm)

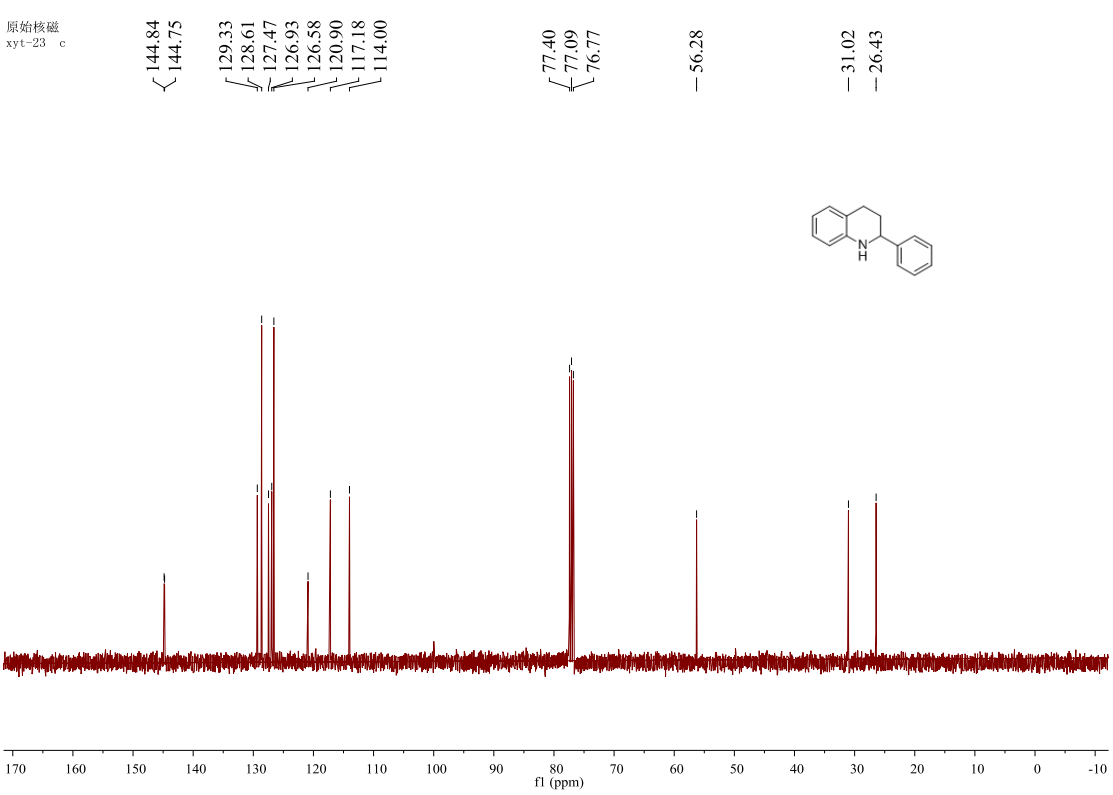
2f


20170418
xyt-61 h
7.01
6.99
6.97
6.64
6.63
6.61
6.52
6.50
3.81
3.21
3.19
2.85
2.81
2.78
2.77
1.99
1.98
1.58
1.56
1.54
1.04
1.02
1.00
2.10
1.07
1.00
0.85
1.05
2.15
1.09
1.16
2.07
3.10
f1 (ppm)

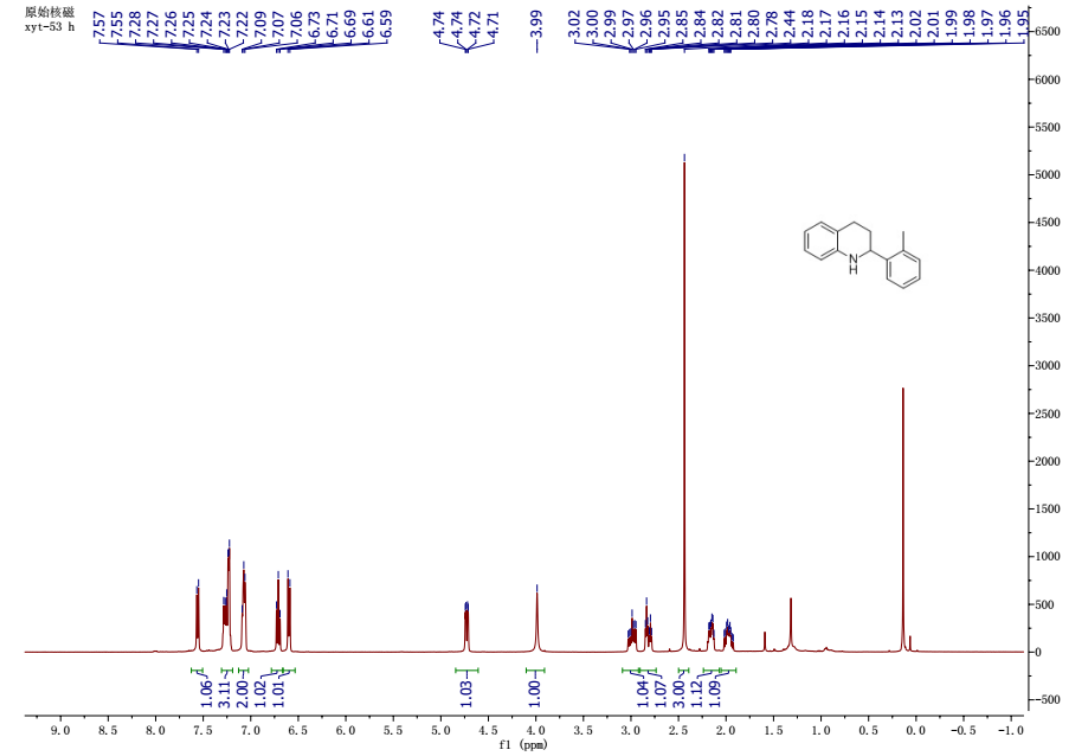

20170418
xyt-61 c
144.73
129.23
126.71
121.41
116.89
114.01
77.35
77.03
76.71
53.06
29.42
27.60
26.43
10.06
f1 (ppm)

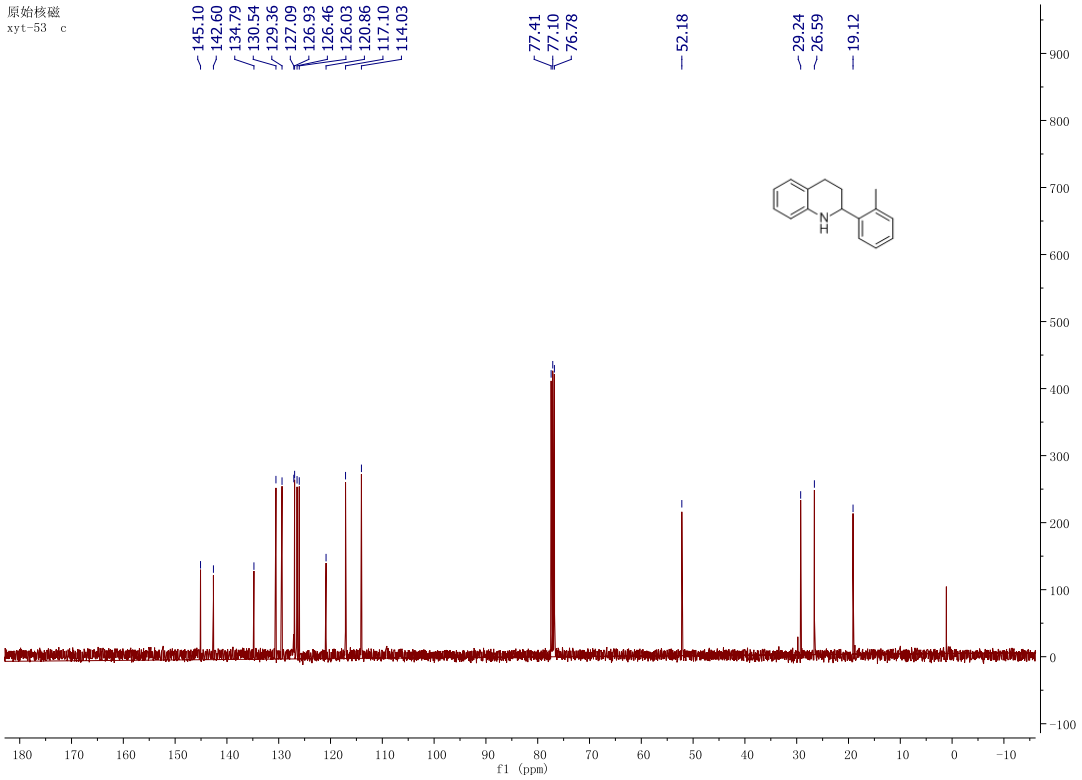
2g


7.41 7.39 7.36 7.36 7.35 7.34 7.32 7.08 7.07 7.05 6.72 6.71 6.69 6.60 6.58
4.50 4.50 4.48 4.47
2.99 2.98 2.96 2.95 2.94 2.82 2.81 2.80 2.78 2.77 2.76
2.20 2.19 2.17 2.16 2.15 2.14 2.09 2.08 2.07 2.06 2.05 2.05 2.04 2.04 2.03 2.03 2.02
5.05 2.06 1.01 1.00 1.02 1.02 1.02 1.11 1.07 1.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

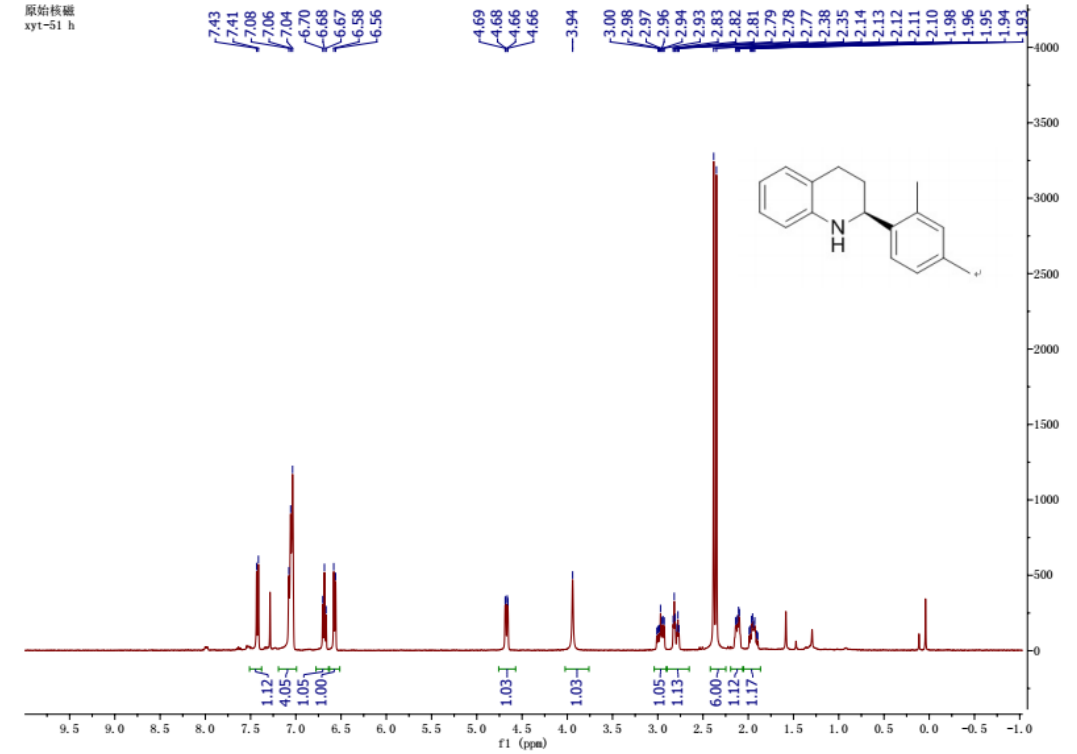

原始核磁
xyt-23 c
144.84 144.75 129.33 128.61 127.47 126.93 126.58 120.90 117.18 114.00
77.40 77.09 76.77
56.28
31.02 26.43
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

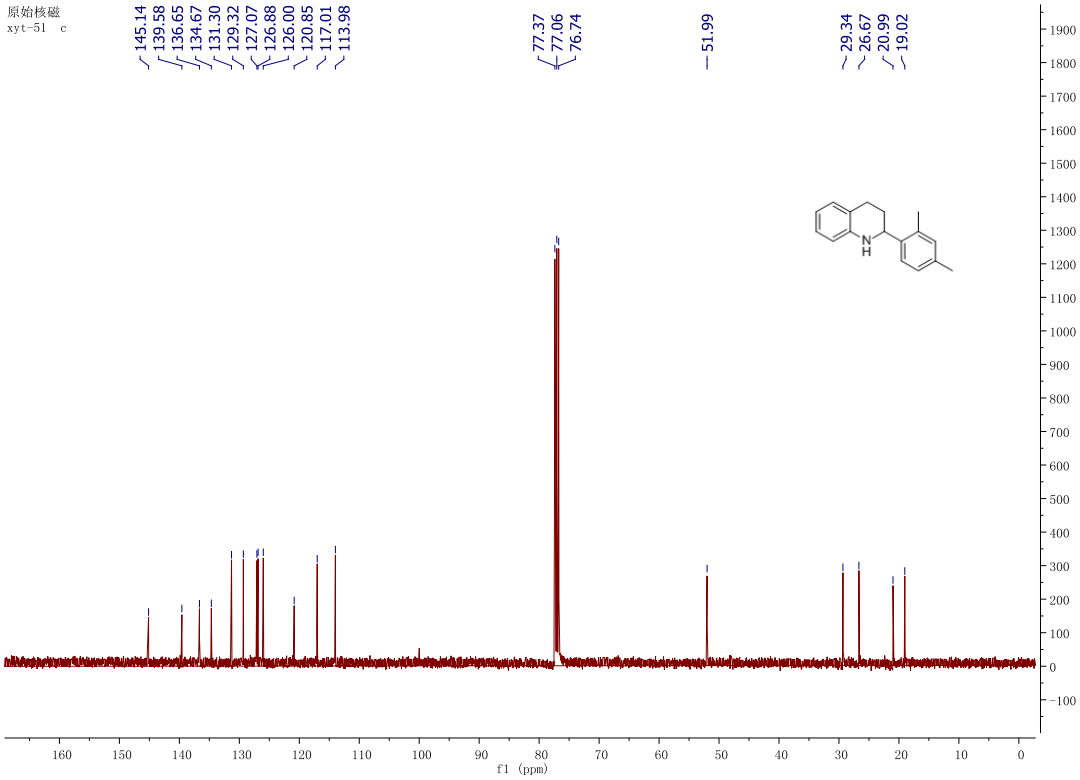
2h


原始核磁
xyt-53 h
7.57
7.55
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.09
7.07
7.06
6.73
6.71
6.69
6.61
6.59
4.74
4.74
4.72
4.71
3.99
3.02
3.00
2.99
2.97
2.96
2.95
2.85
2.84
2.82
2.81
2.80
2.78
2.44
2.18
2.17
2.16
2.15
2.14
2.13
2.02
2.01
1.99
1.98
1.97
1.96
1.95
1.06
3.11
2.00
1.02
1.01
1.03
1.00
1.04
1.07
3.00
1.12
1.09
f1 (ppm)


原始核磁
xyt-53 c
145.10
142.60
134.79
130.54
129.36
127.09
126.93
126.46
126.03
120.86
117.10
114.03
77.41
77.10
76.78
52.18
29.24
26.59
19.12
f1 (ppm)

2i


原始核磁
xyt-51 h
7.43
7.41
7.08
7.06
7.04
6.70
6.68
6.67
6.58
6.56
4.69
4.68
4.66
4.66
3.94
3.00
2.98
2.97
2.96
2.94
2.93
2.83
2.82
2.81
2.79
2.78
2.77
2.38
2.35
2.14
2.13
2.12
2.11
2.10
1.98
1.96
1.95
1.94
1.93
1.12
4.05
1.05
1.00
1.03
1.03
1.05
1.13
6.00
1.12
1.17
f1 (ppm)


原始核磁
xyt-51 c
145.14
139.58
136.65
134.67
131.30
129.32
127.07
126.88
126.00
120.85
117.01
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77.06
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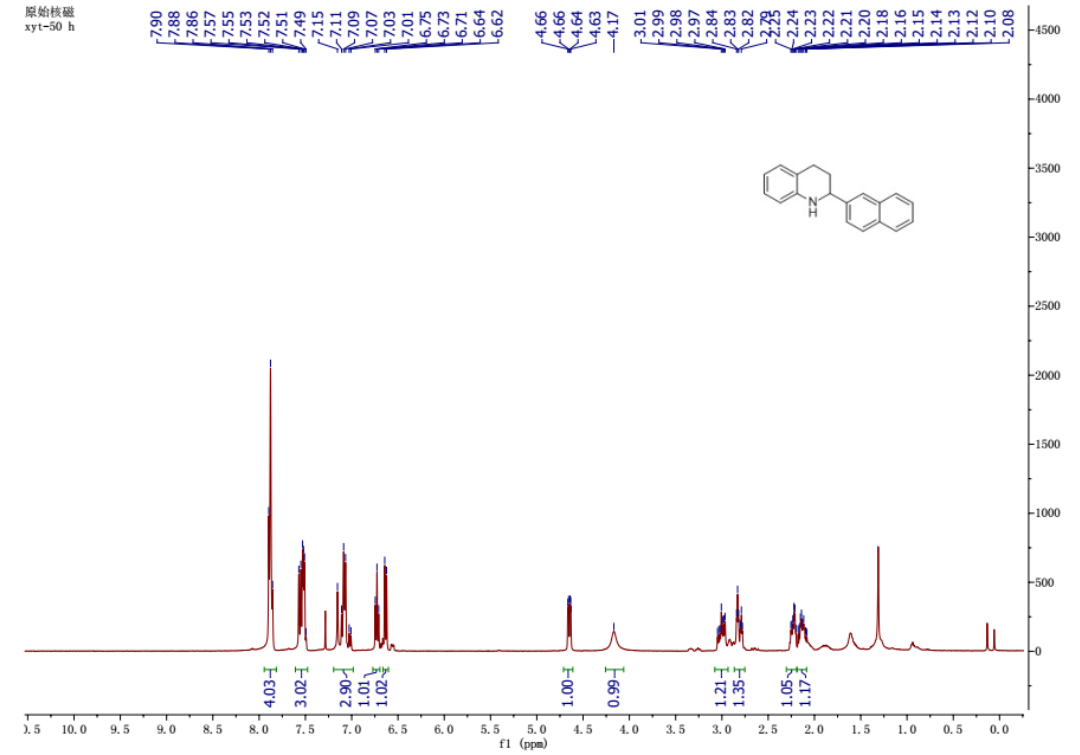
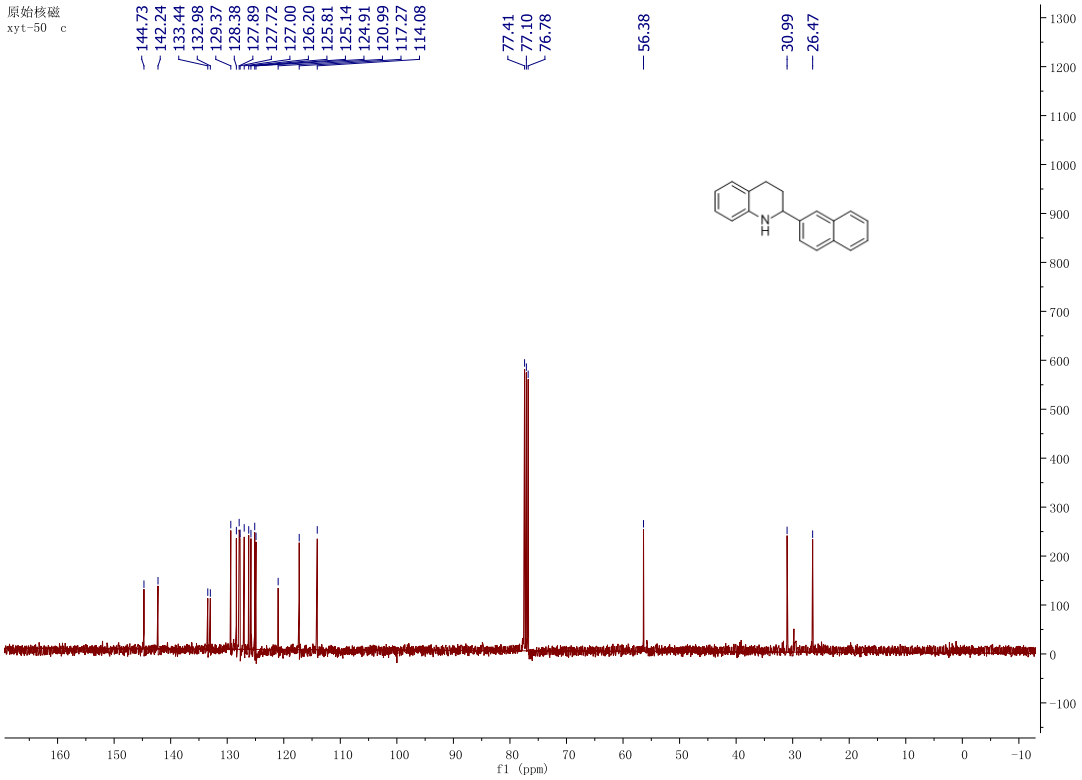
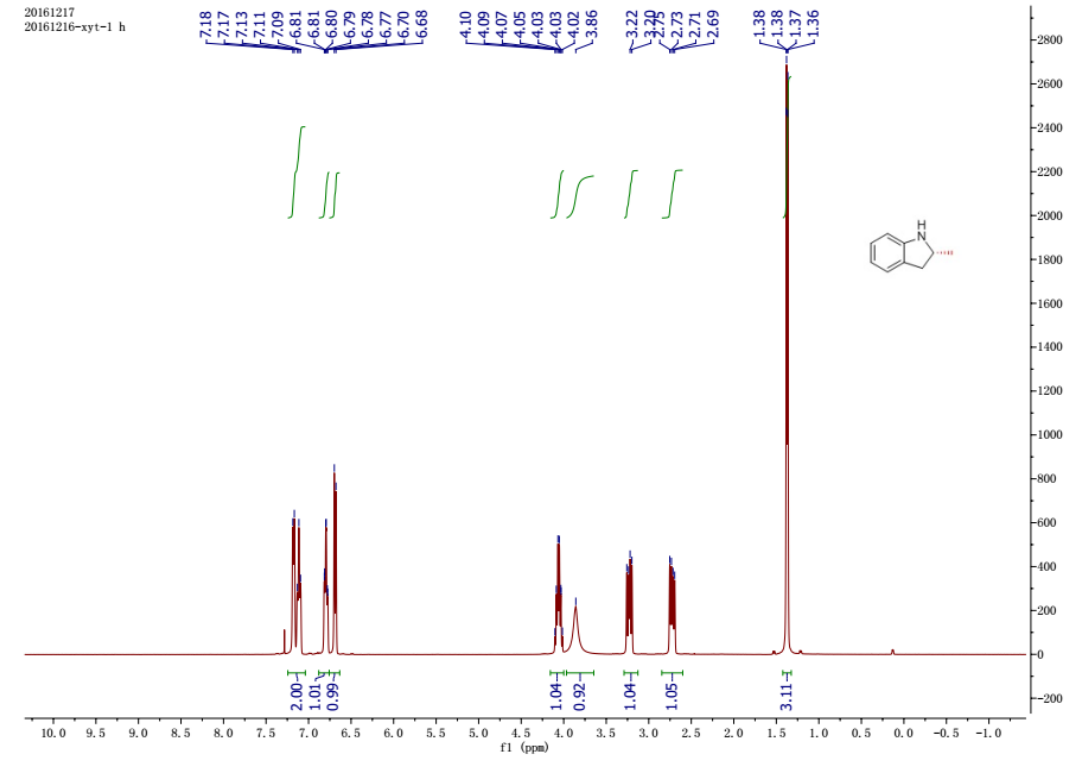
51.99
29.34
26.67
20.99
19.02
f1 (ppm)

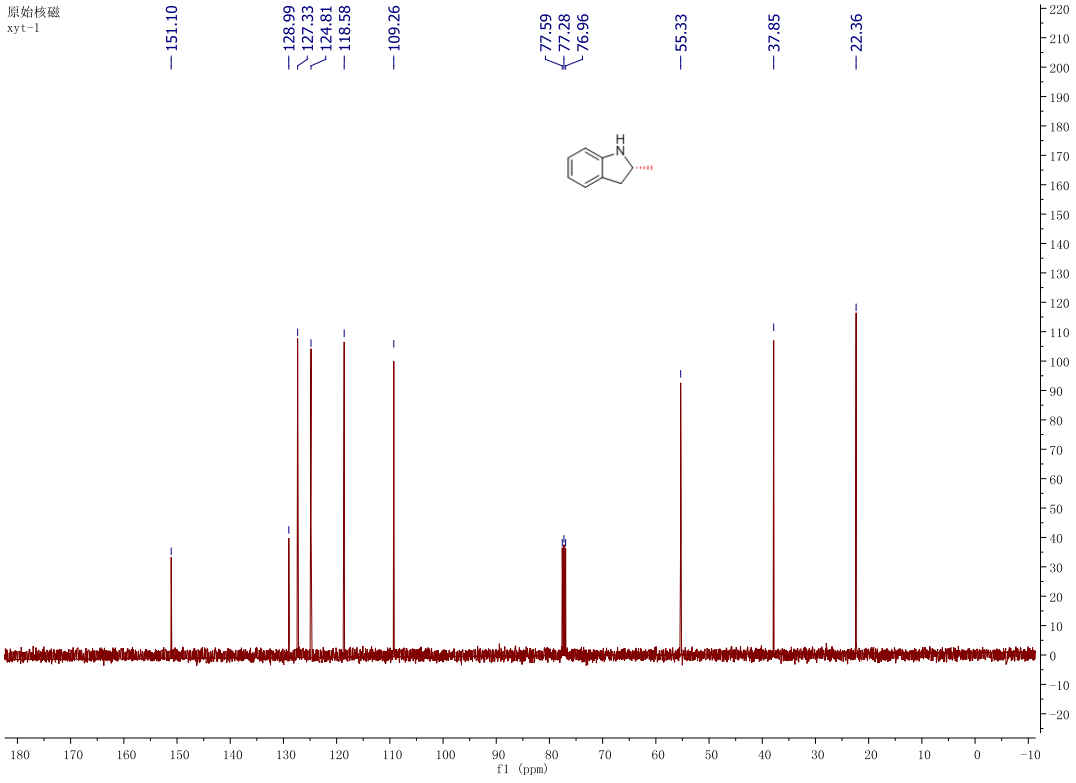
2j


原始核磁
xyt-50 h
7.90
7.88
7.86
7.57
7.55
7.53
7.52
7.51
7.49
7.15
7.11
7.09
7.07
7.03
7.01
6.75
6.73
6.71
6.64
6.62
4.66
4.66
4.64
4.63
4.17
3.01
2.99
2.98
2.97
2.84
2.83
2.82
2.24
2.23
2.22
2.21
2.20
2.18
2.16
2.15
2.14
2.13
2.12
2.10
2.08
4.03
3.02
2.90
1.01
1.02
1.00
0.99
1.21
1.35
1.05
1.17
f1 (ppm)

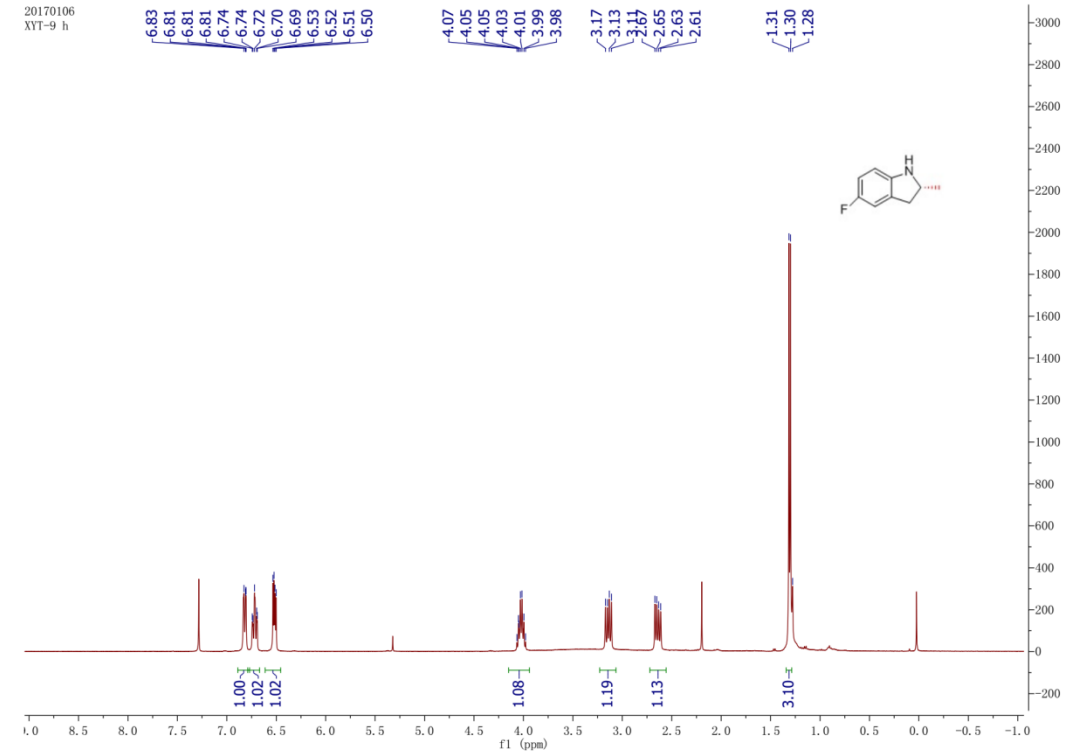

原始核磁
xyt-50 c
144.73
142.24
133.44
132.98
129.37
128.38
127.89
127.72
127.00
126.20
125.81
125.14
124.91
120.99
117.27
114.08
77.41
77.10
76.78
56.38
30.99
26.47
f1 (ppm)

4a


20161217
20161216-xyt-1 h
7.18
7.17
7.13
7.11
7.09
6.81
6.81
6.80
6.79
6.78
6.77
6.70
6.68
4.10
4.09
4.07
4.05
4.03
4.03
4.02
3.86
3.22
2.73
2.71
2.69
1.38
1.38
1.37
1.36
2.00
1.01
0.99
1.04
0.92
1.04
1.05
3.11
f1 (ppm)


原始核磁
xyt-1
151.10
128.99
127.33
124.81
118.58
109.26
77.59
77.28
76.96
55.33
37.85
22.36
f1 (ppm)

4b


20170106
XYT-9 h
6.83
6.81
6.81
6.81
6.74
6.72
6.70
6.69
6.53
6.52
6.51
6.50
4.07
4.05
4.05
4.03
4.01
3.99
3.98
3.17
3.13
2.65
2.63
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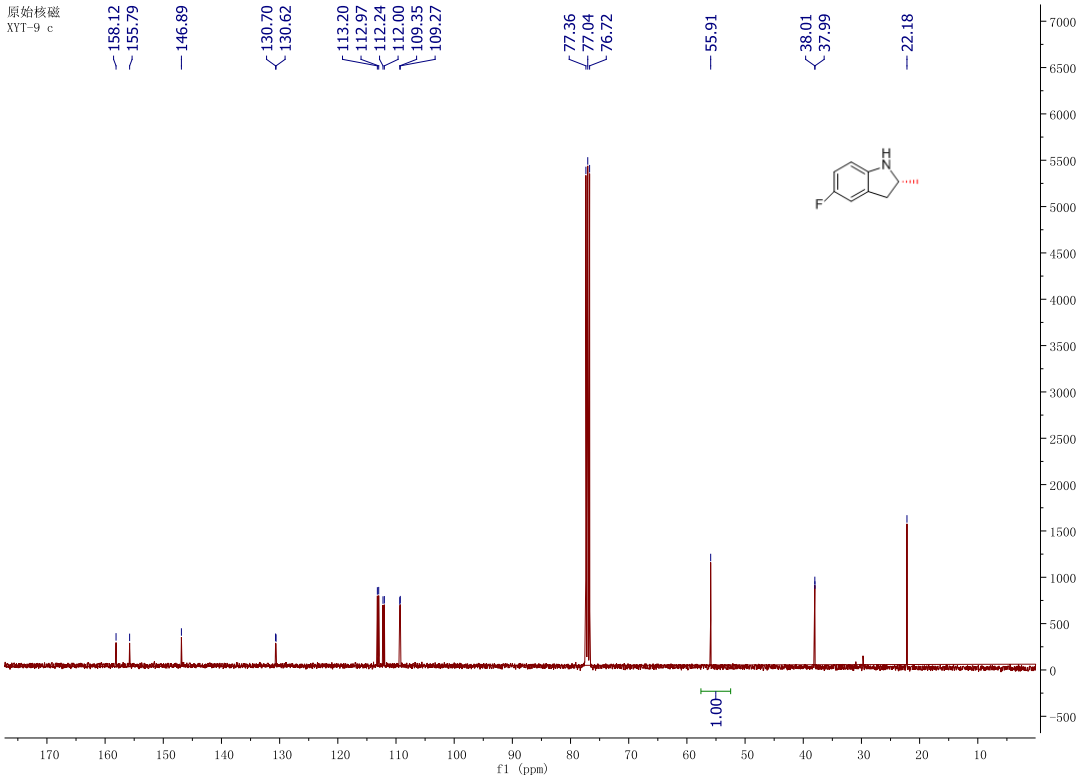
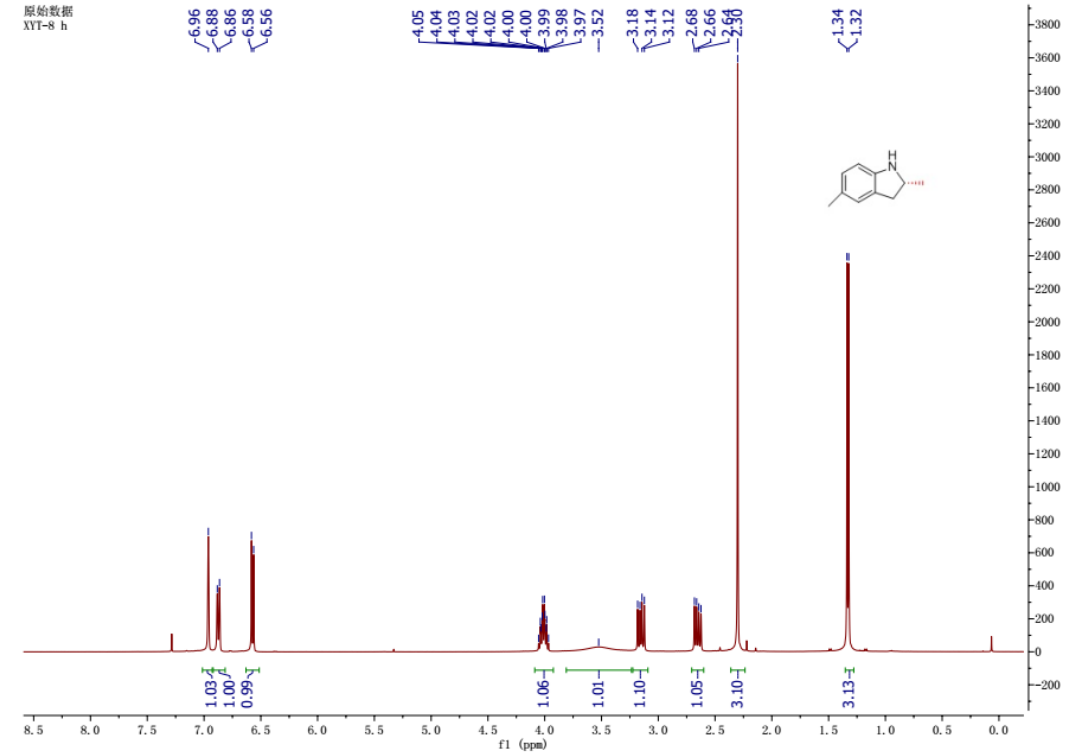
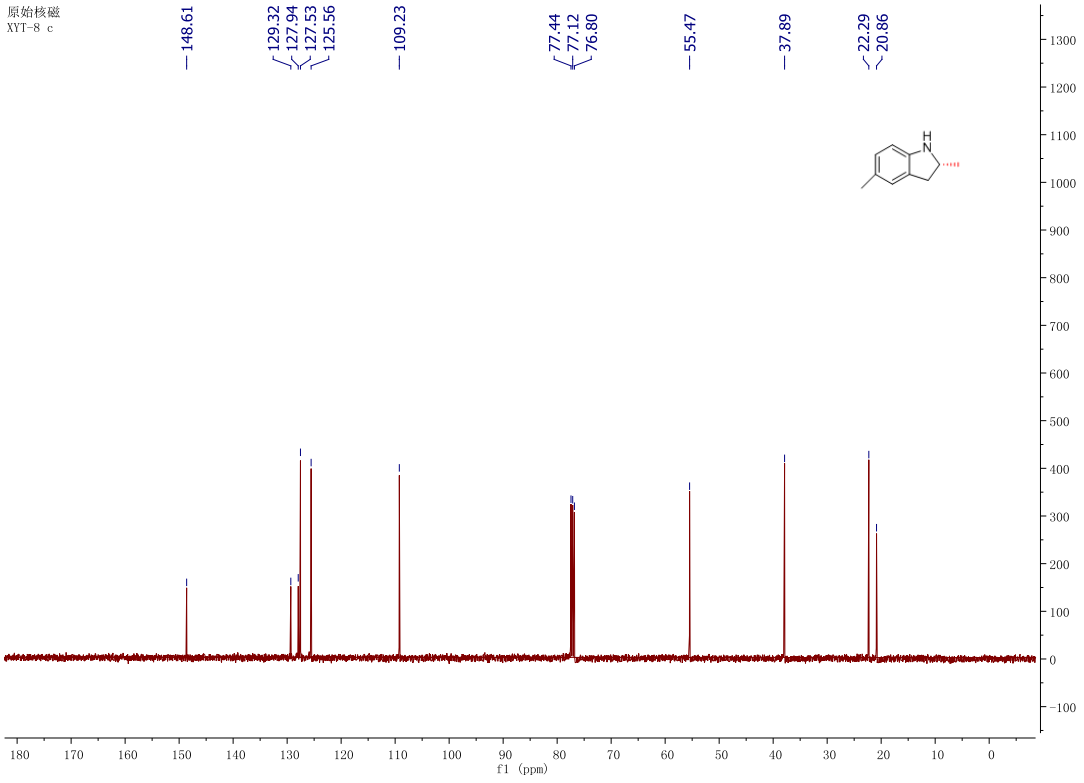
1.02
1.08
1.19
1.13
3.10
f1 (ppm)

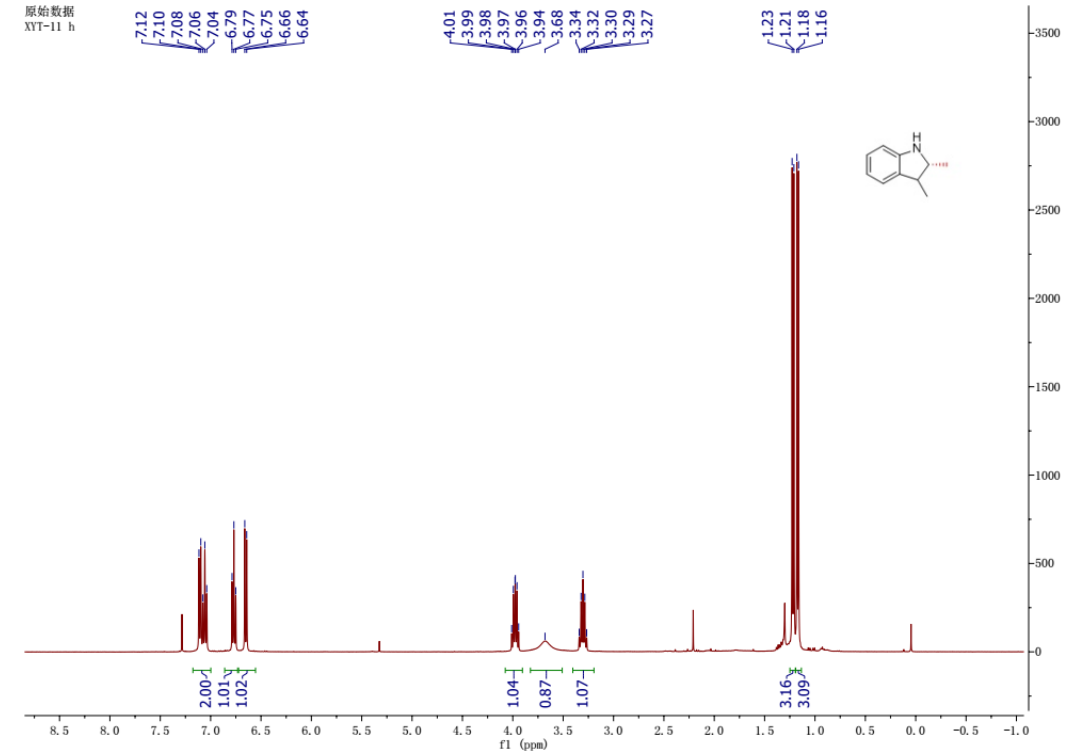

原始核磁
XYT-9 c
158.12
155.79
146.89
130.70
130.62
113.20
112.97
112.24
112.00
109.35
109.27
77.36
77.04
76.72
55.91
38.01
37.99
22.18
1.00
f1 (ppm)

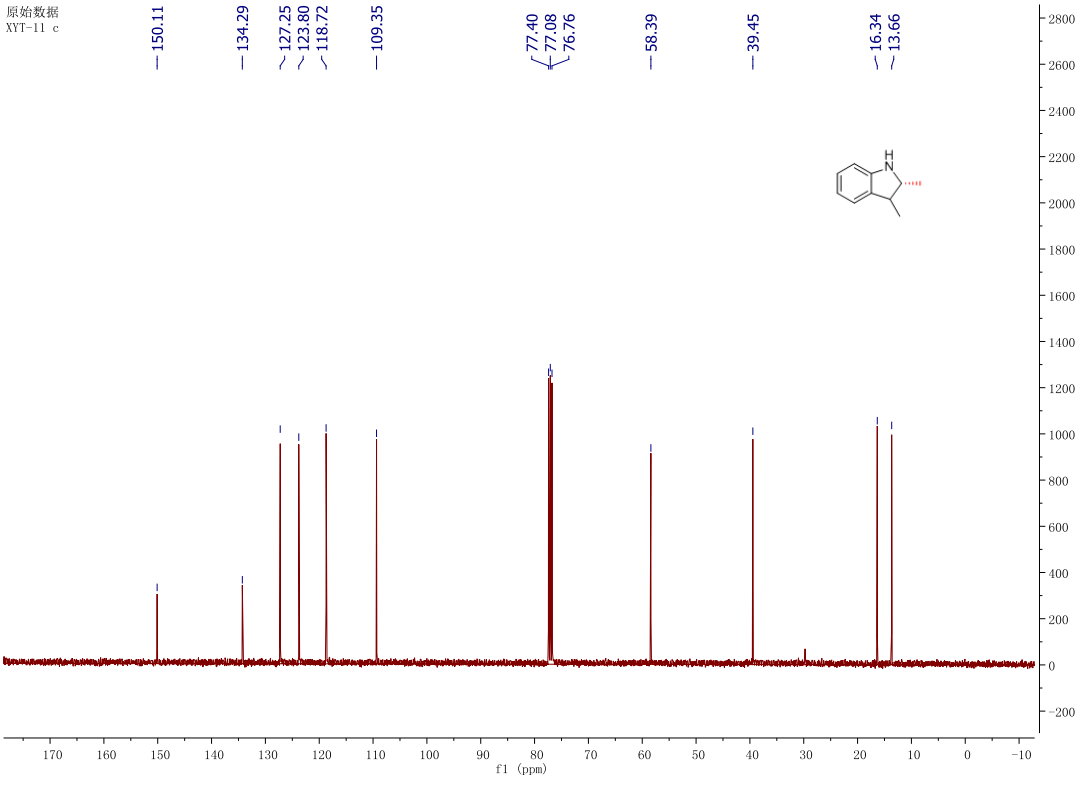
4c


原始数据
XYT-8 h
6.96
6.88
6.86
6.58
6.56
4.05
4.04
4.03
4.02
4.02
4.00
4.00
3.99
3.98
3.97
3.52
3.18
3.14
3.12
2.68
2.66
2.64
2.50
1.34
1.32
1.03
1.00
0.99
1.06
1.01
1.10
1.05
3.10
3.13
f1 (ppm)

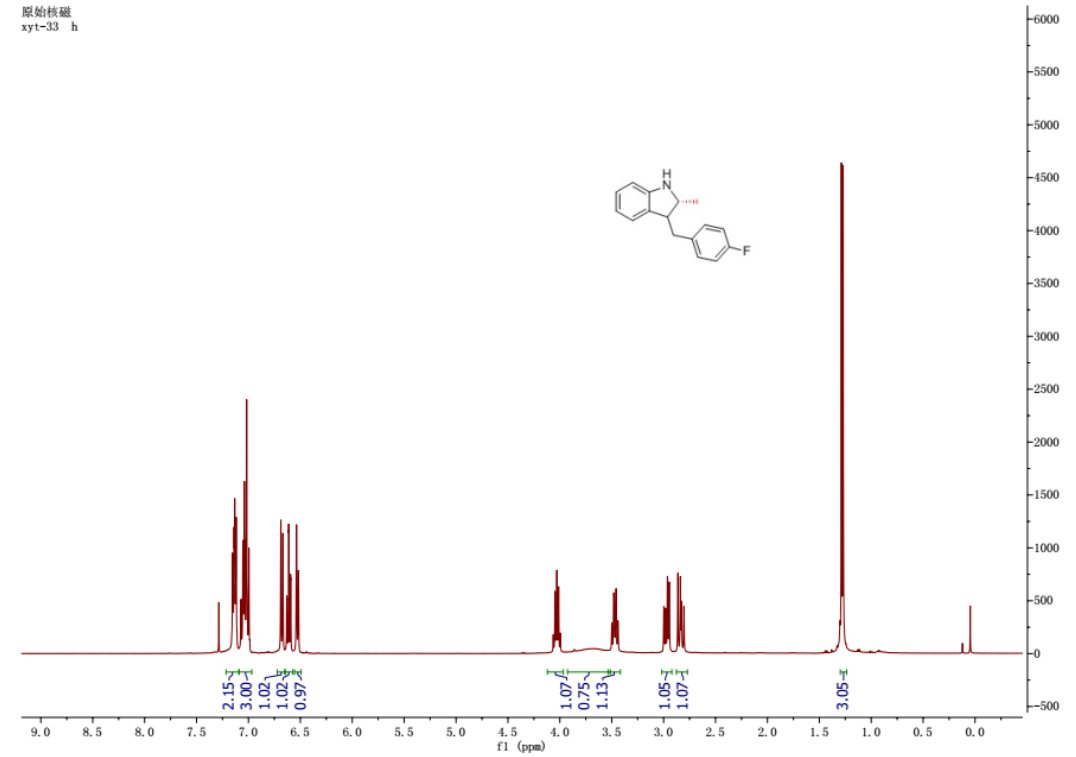

原始核磁
XYT-8 c
148.61
129.32
127.94
127.53
125.56
109.23
77.44
77.12
76.80
55.47
37.89
22.29
20.86
f1 (ppm)

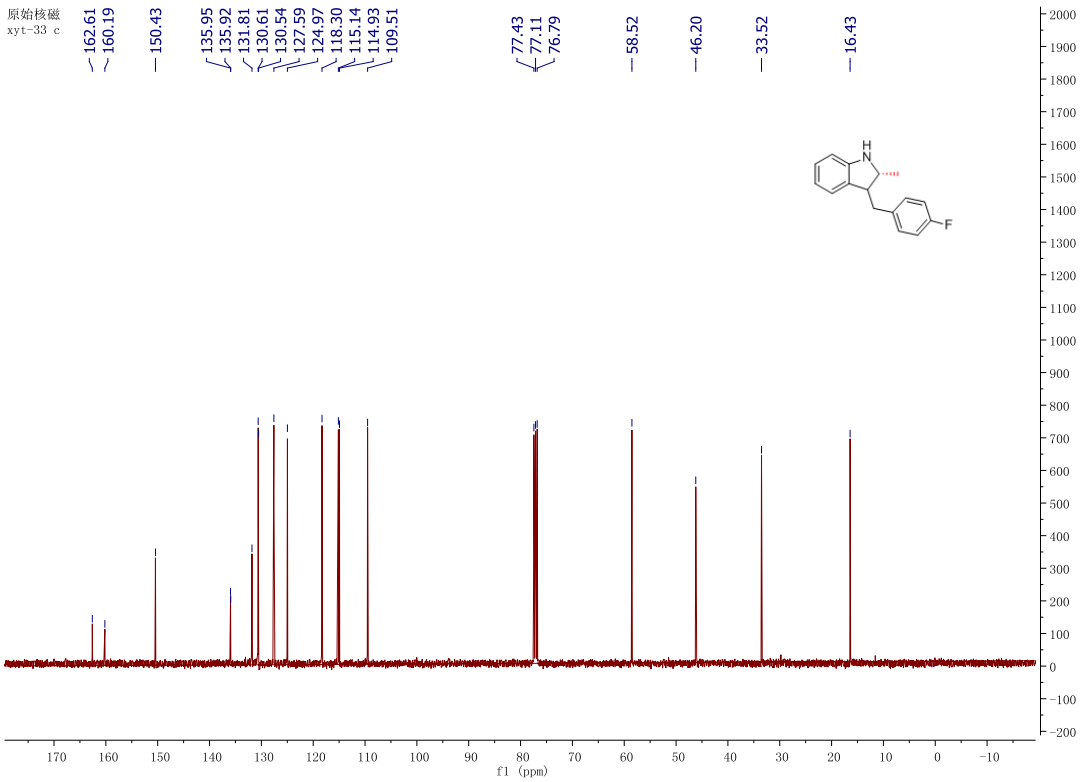
4d


原始数据
XYT-11 h
7.12
7.10
7.08
7.06
7.04
6.79
6.77
6.75
6.66
6.64
4.01
3.99
3.98
3.97
3.96
3.94
3.68
3.34
3.32
3.30
3.29
3.27
1.23
1.21
1.18
1.16
2.00
1.01
1.02
1.04
0.87
1.07
3.16
3.09
f1 (ppm)

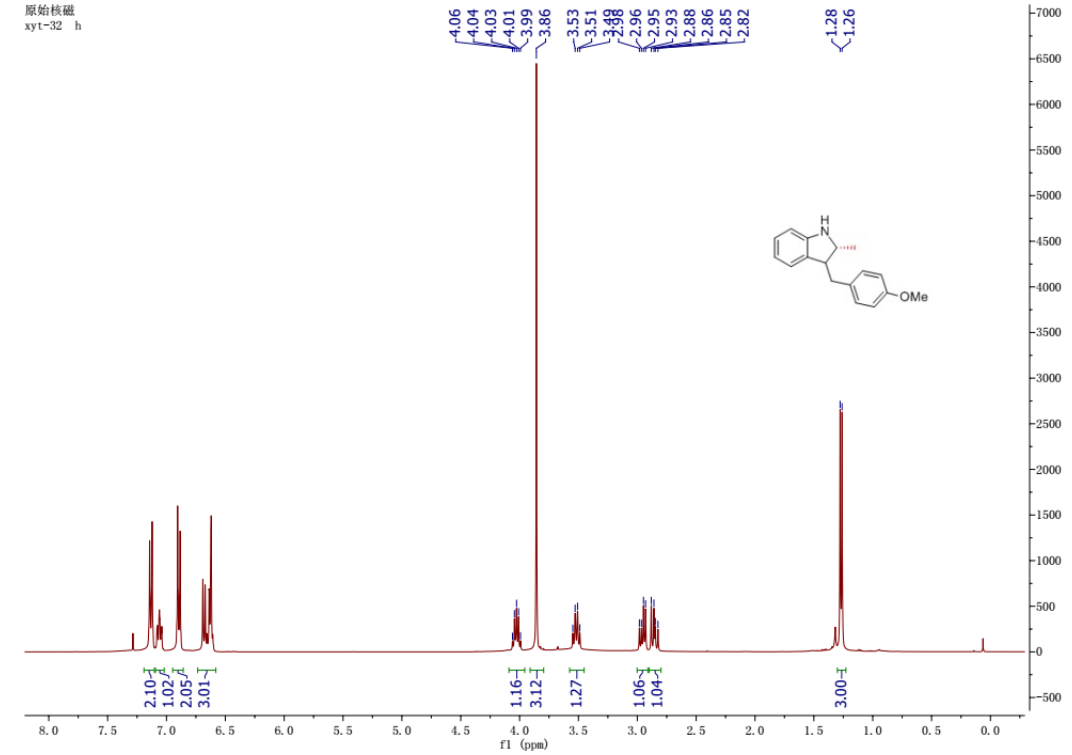

原始数据
XYT-11 c
150.11
134.29
127.25
123.80
118.72
109.35
77.40
77.08
76.76
58.39
39.45
16.34
13.66
f1 (ppm)

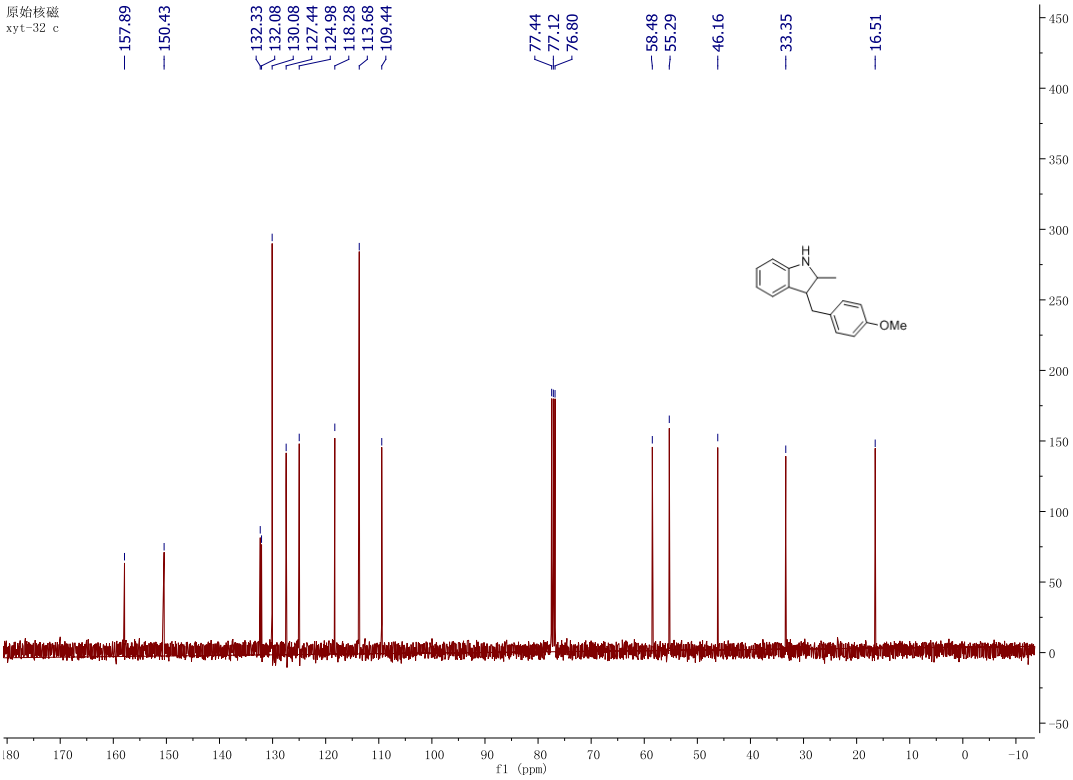
4e


原始核磁
xyt-33 h
2.15
3.00
1.02
1.02
0.97
1.07
0.75
1.13
1.05
1.07
3.05
f1 (ppm)

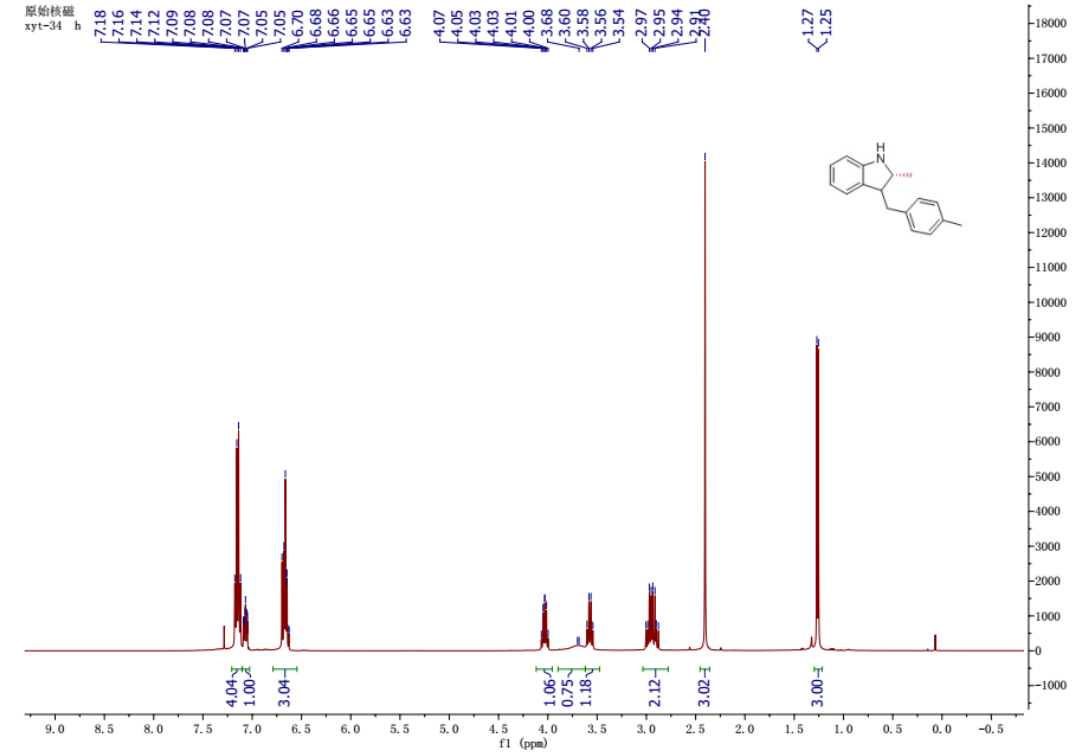

原始核磁
xyt-33 c
162.61
160.19
150.43
135.95
135.92
131.81
130.61
130.54
127.59
124.97
118.30
115.14
114.93
109.51
77.43
77.11
76.79
58.52
46.20
33.52
16.43
f1 (ppm)

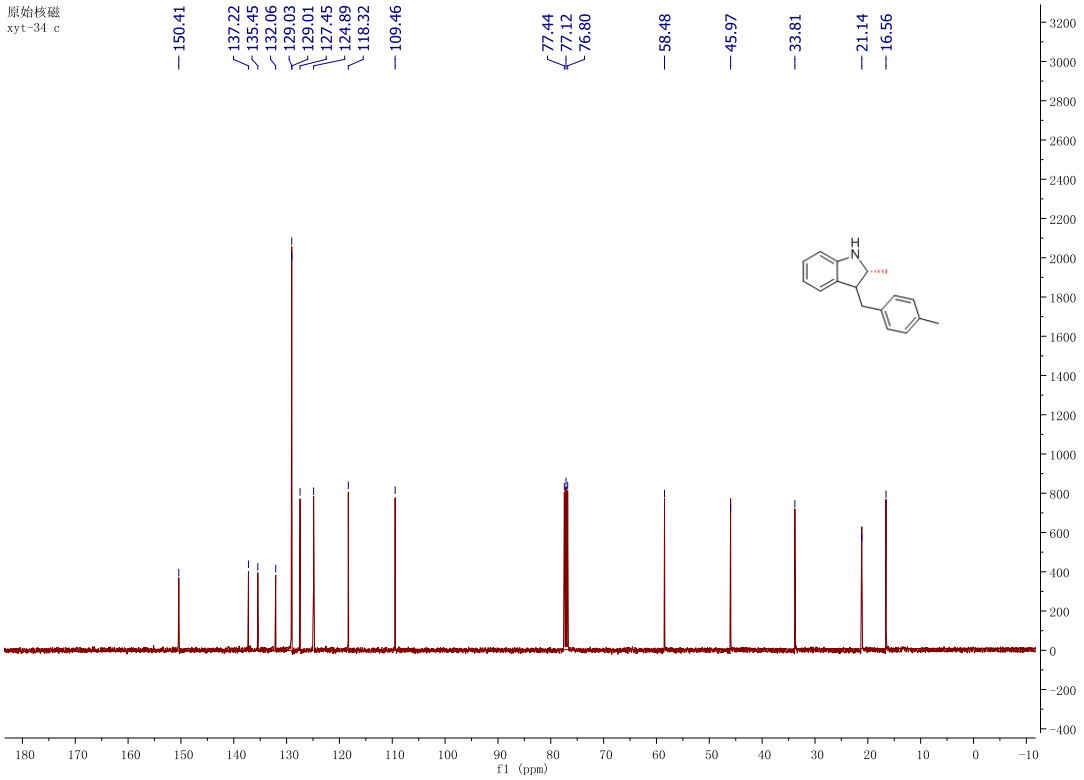
4f


原始核磁
xyt-32 h
4.06
4.04
4.03
4.01
3.99
3.86
3.53
3.51
2.96
2.95
2.93
2.88
2.86
2.85
2.82
1.28
1.26
OMe
2.10
1.02
2.05
3.01
1.16
3.12
1.27
1.06
1.04
3.00
f1 (ppm)

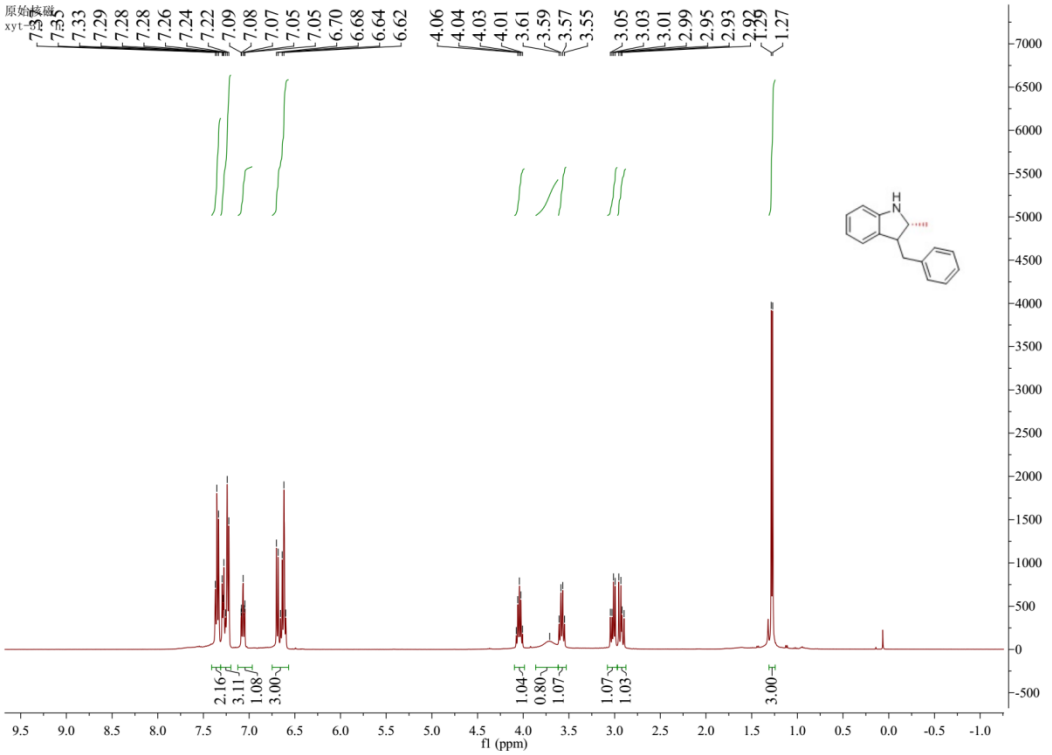

原始核磁
xyt-32 c
157.89
150.43
132.33
132.08
130.08
127.44
124.98
118.28
113.68
109.44
77.44
77.12
76.80
58.48
55.29
46.16
33.35
16.51
OMe
f1 (ppm)

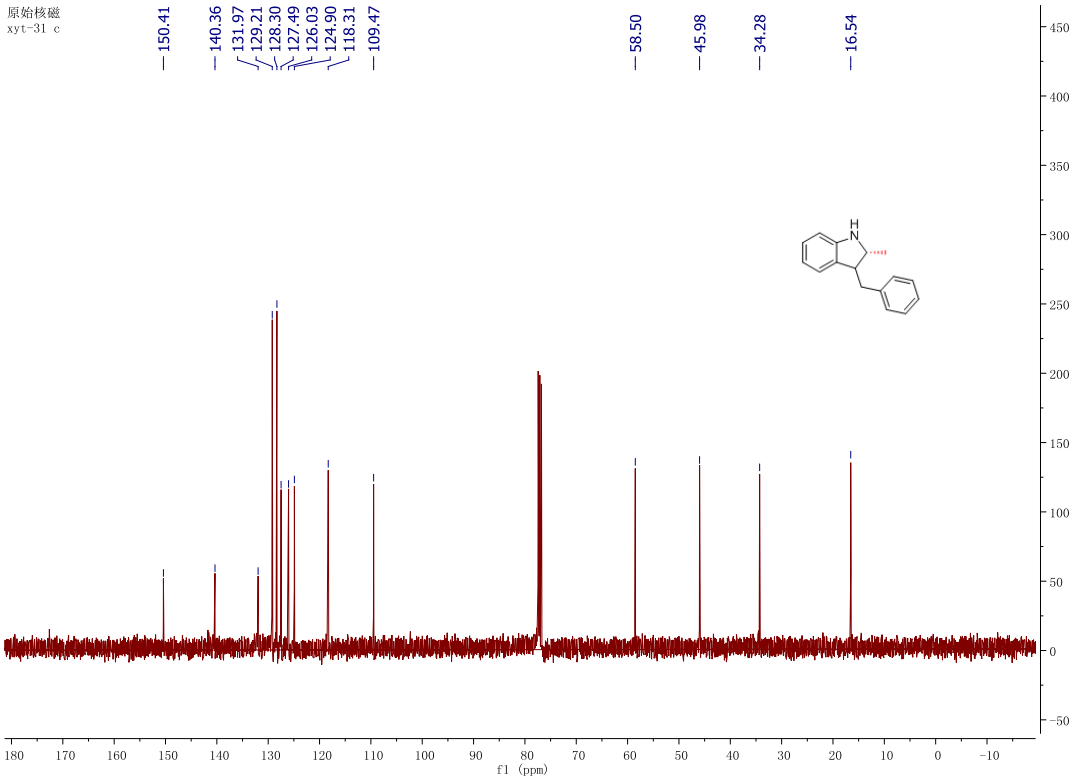
4g


原始核磁
xyt-34 h
7.18
7.16
7.14
7.12
7.09
7.08
7.08
7.07
7.07
7.05
7.05
6.70
6.68
6.66
6.65
6.65
6.63
6.63
4.07
4.05
4.03
4.03
4.01
4.00
3.68
3.60
3.58
3.56
3.54
2.97
2.95
2.94
2.91
2.40
1.27
1.25
4.04
1.00
3.04
1.06
0.75
1.18
2.12
3.02
3.00
f1 (ppm)

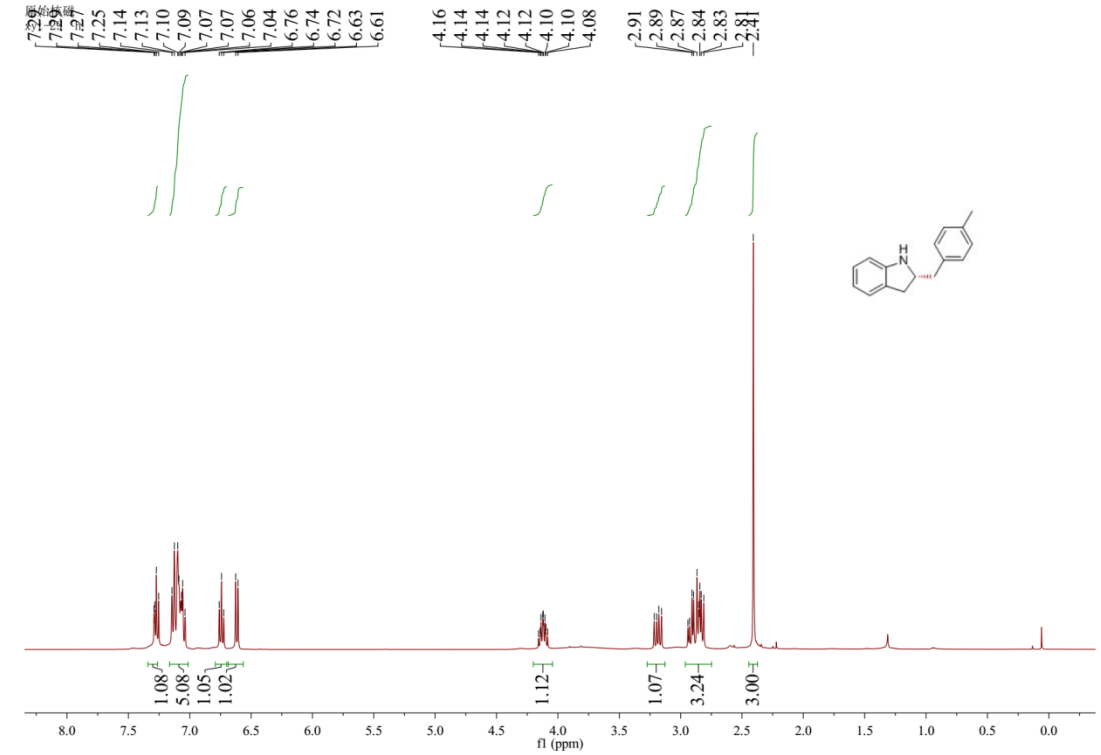

原始核磁
xyt-34 c
150.41
137.22
135.45
132.06
129.03
129.01
127.45
124.89
118.32
109.46
77.44
77.12
76.80
58.48
45.97
33.81
21.14
16.56
f1 (ppm)

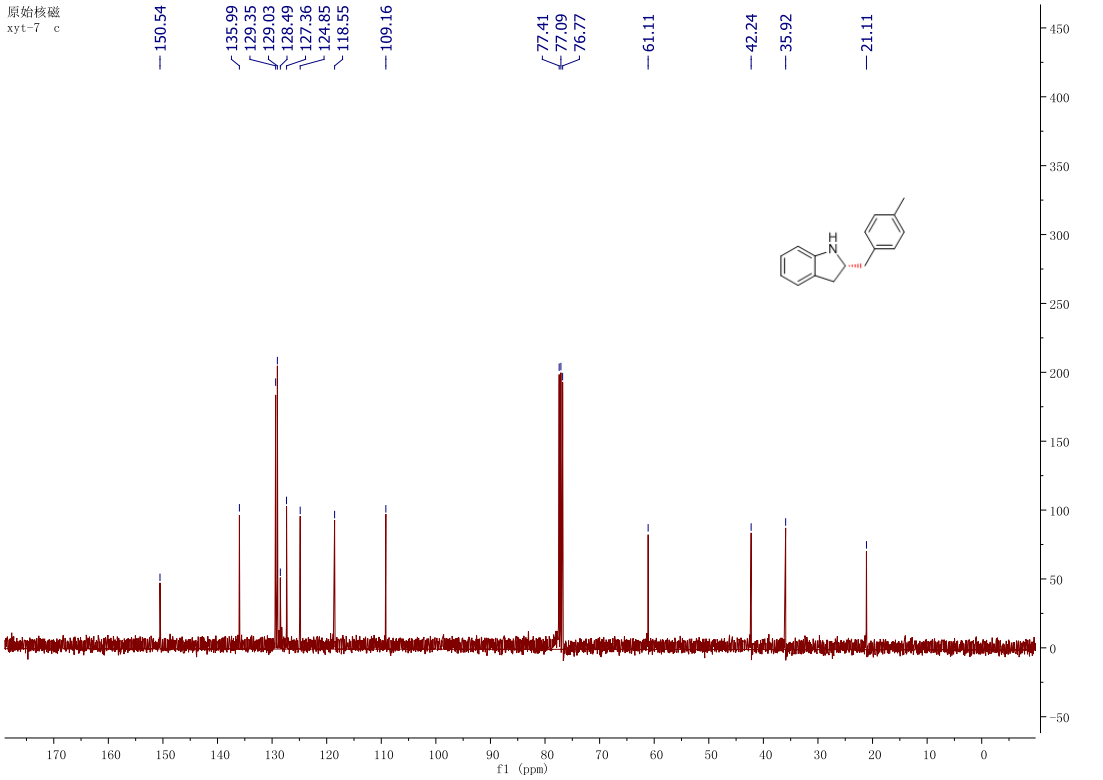
4h


7.35
7.33
7.29
7.28
7.28
7.26
7.24
7.22
7.09
7.08
7.07
7.05
7.05
6.70
6.68
6.64
6.62
4.06
4.04
4.03
4.01
3.61
3.59
3.57
3.55
3.05
3.03
3.01
2.99
2.95
2.93
2.92
1.29
1.27
2.16
3.11
1.08
3.00
1.04
0.80
1.07
1.07
1.03
3.00
f1 (ppm)

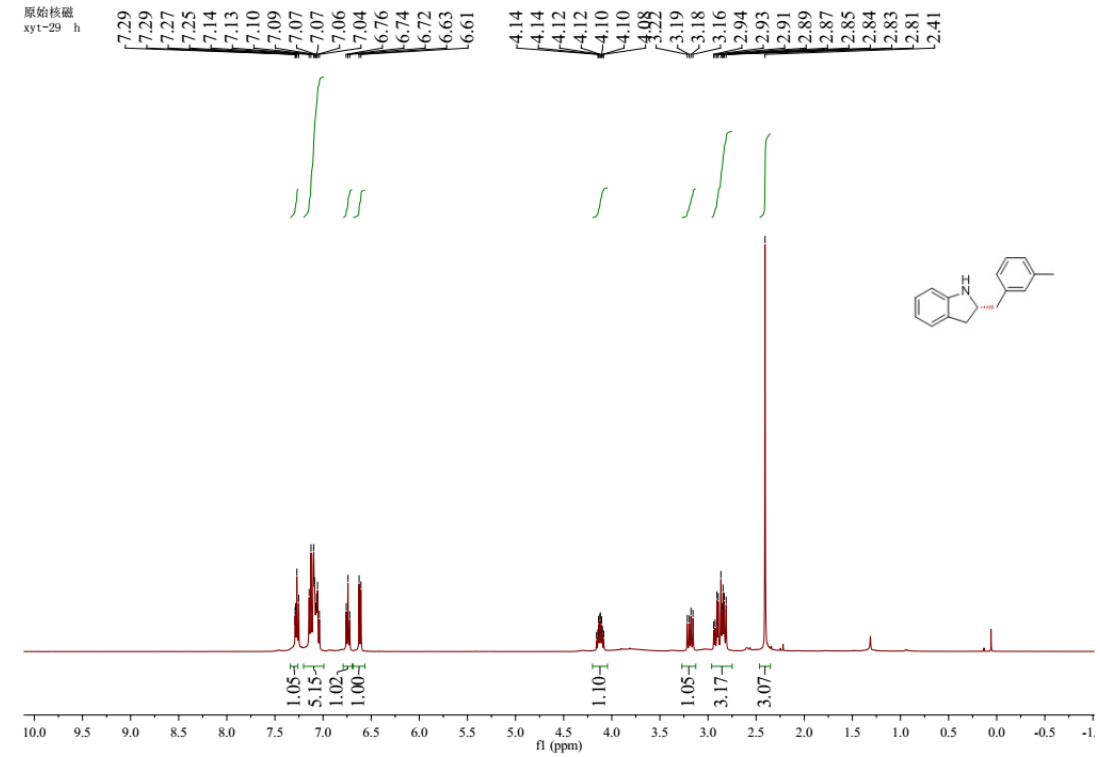

原始核磁
xyt-31 c
150.41
140.36
131.97
129.21
128.30
127.49
126.03
124.90
118.31
109.47
58.50
45.98
34.28
16.54
f1 (ppm)

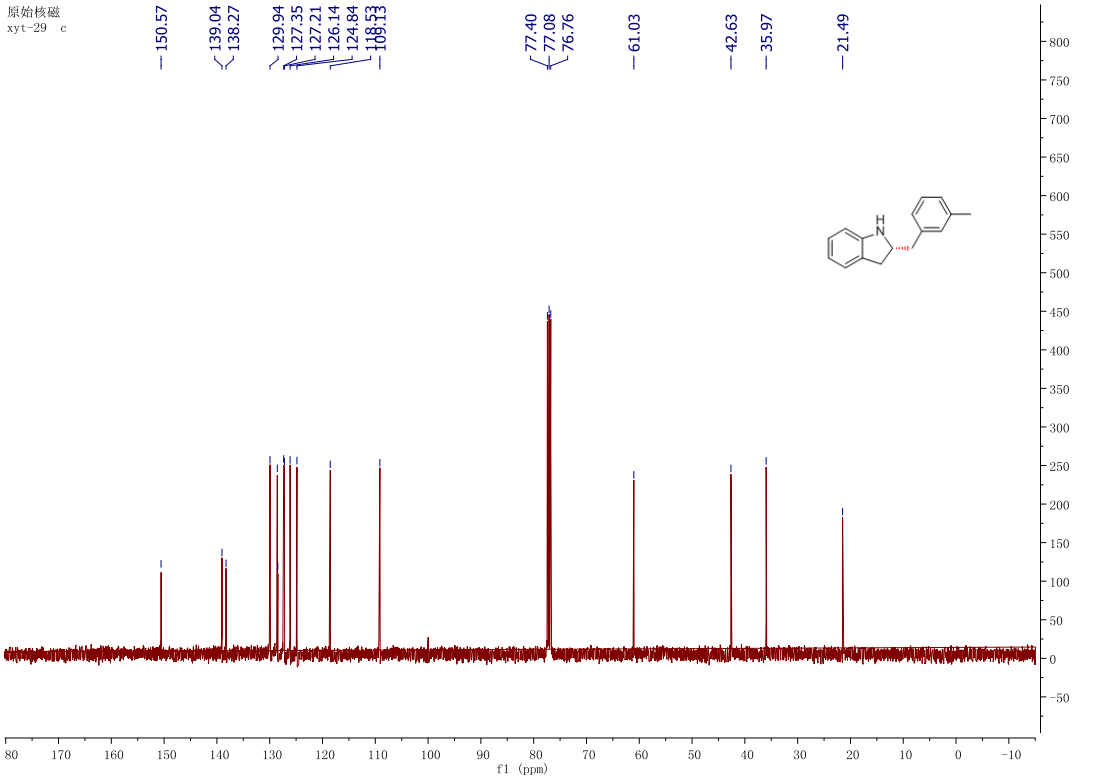
4i


7.25
7.14
7.13
7.10
7.09
7.07
7.07
7.06
7.04
6.76
6.74
6.72
6.63
6.61
4.16
4.14
4.14
4.12
4.12
4.10
4.10
4.08
2.91
2.89
2.87
2.84
2.83
2.81
2.41
1.08
5.08
1.05
1.02
1.12
1.07
3.24
3.00
f1 (ppm)

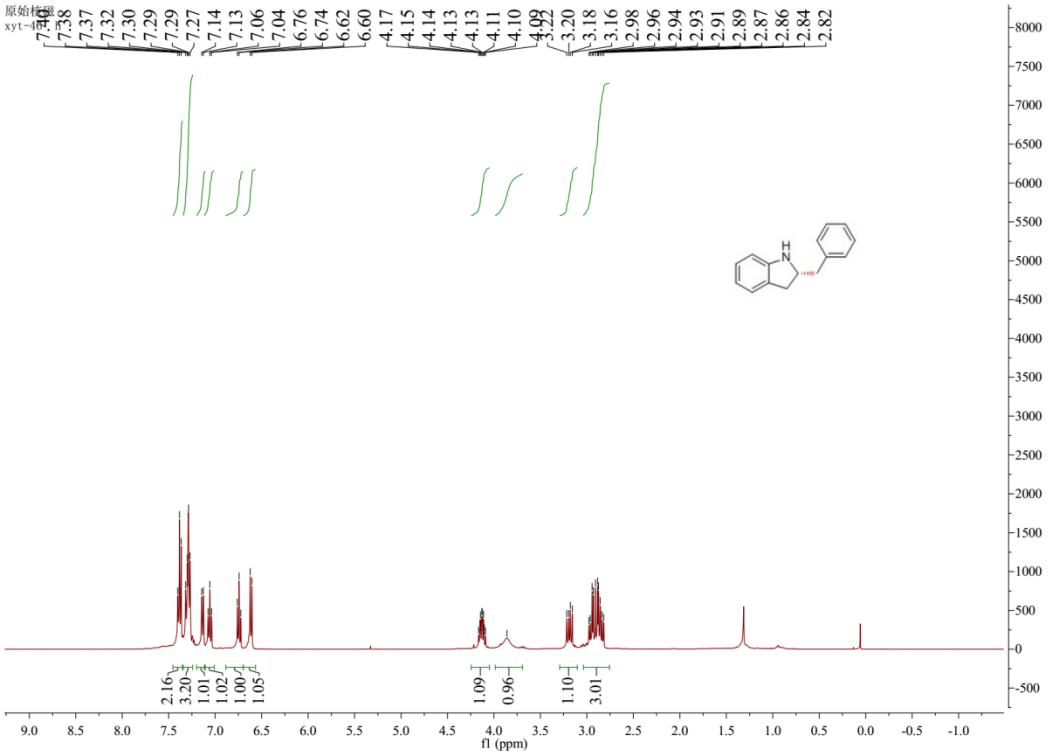

原始核磁
xyt-7 c
150.54
135.99
129.35
129.03
128.49
127.36
124.85
118.55
109.16
77.41
77.09
76.77
61.11
42.24
35.92
21.11
f1 (ppm)

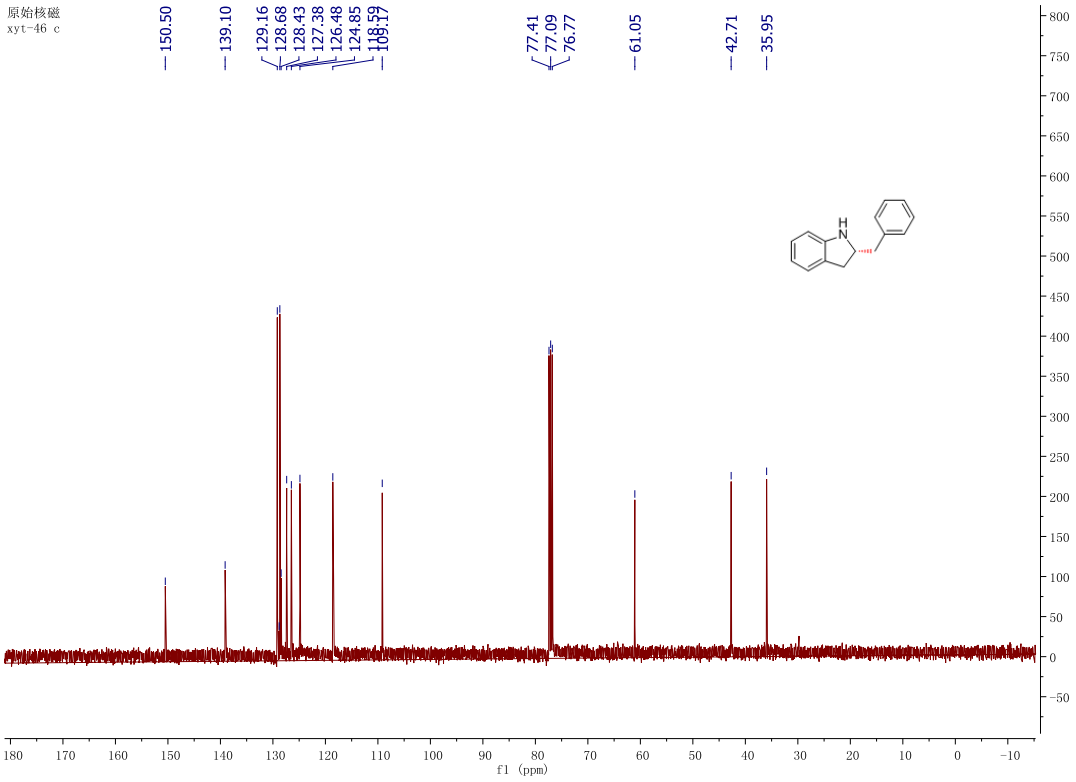
4j


原始核磁
xyt-29 h
7.29
7.29
7.27
7.25
7.14
7.13
7.10
7.09
7.07
7.07
7.06
7.04
6.76
6.74
6.72
6.63
6.61
4.14
4.14
4.12
4.12
4.10
4.10
4.08
3.22
3.19
3.18
3.16
2.94
2.93
2.91
2.89
2.87
2.85
2.84
2.83
2.81
2.41
1.05
5.15
1.02
1.00
1.10
1.05
3.17
3.07
f1 (ppm)

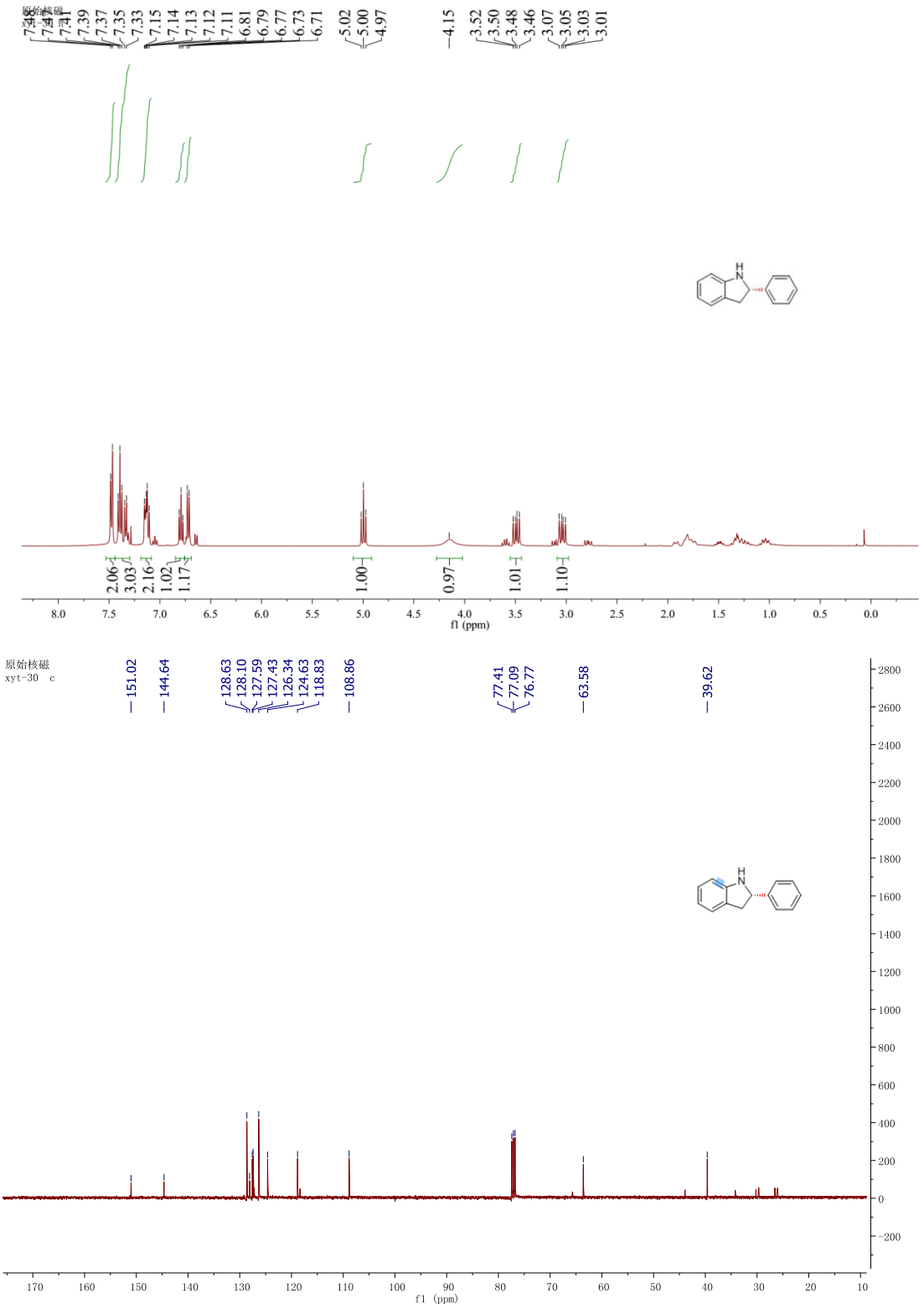

原始核磁
xyt-29 c
150.57
139.04
138.27
129.94
127.35
127.21
126.14
124.84
118.53
109.13
77.40
77.08
76.76
61.03
42.63
35.97
21.49
f1 (ppm)

4k

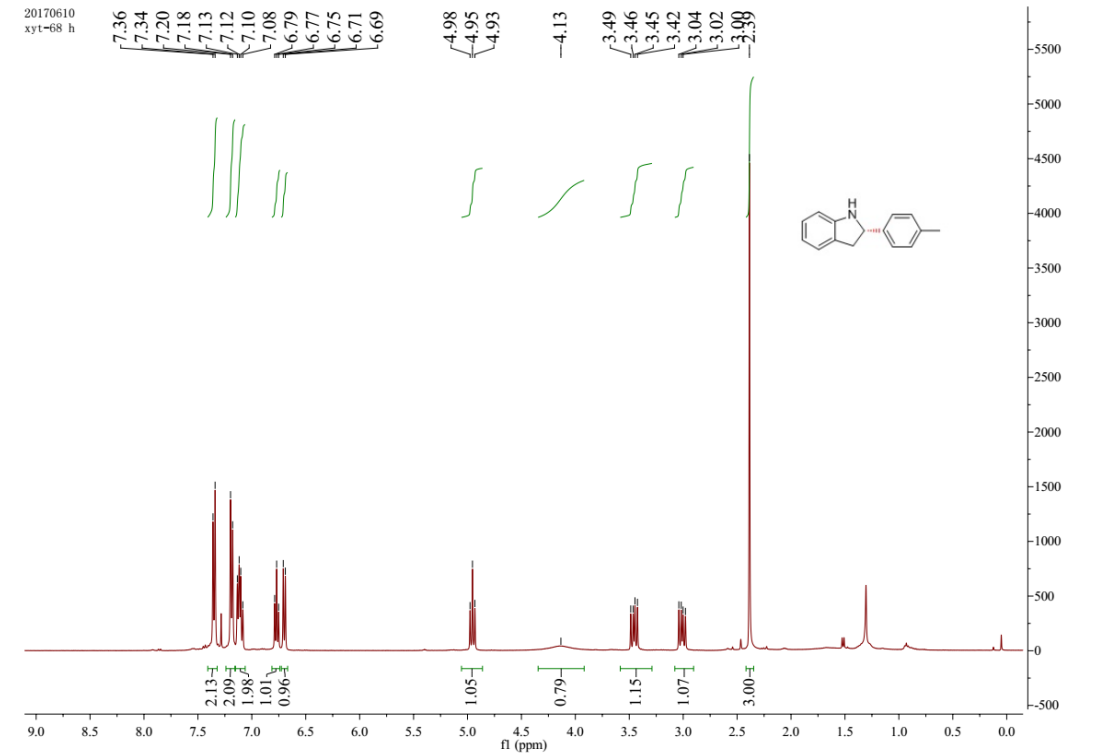

原始核磁
xyt-46
7.40
7.38
7.37
7.32
7.30
7.29
7.29
7.27
7.14
7.13
7.06
7.04
6.76
6.74
6.62
6.60
4.17
4.15
4.14
4.13
4.13
4.11
4.10
4.09
3.22
3.20
3.18
3.16
2.98
2.96
2.94
2.93
2.91
2.89
2.87
2.86
2.84
2.82
2.16
3.20
1.01
1.02
1.00
1.05
1.09
0.96
1.10
3.01
f1 (ppm)

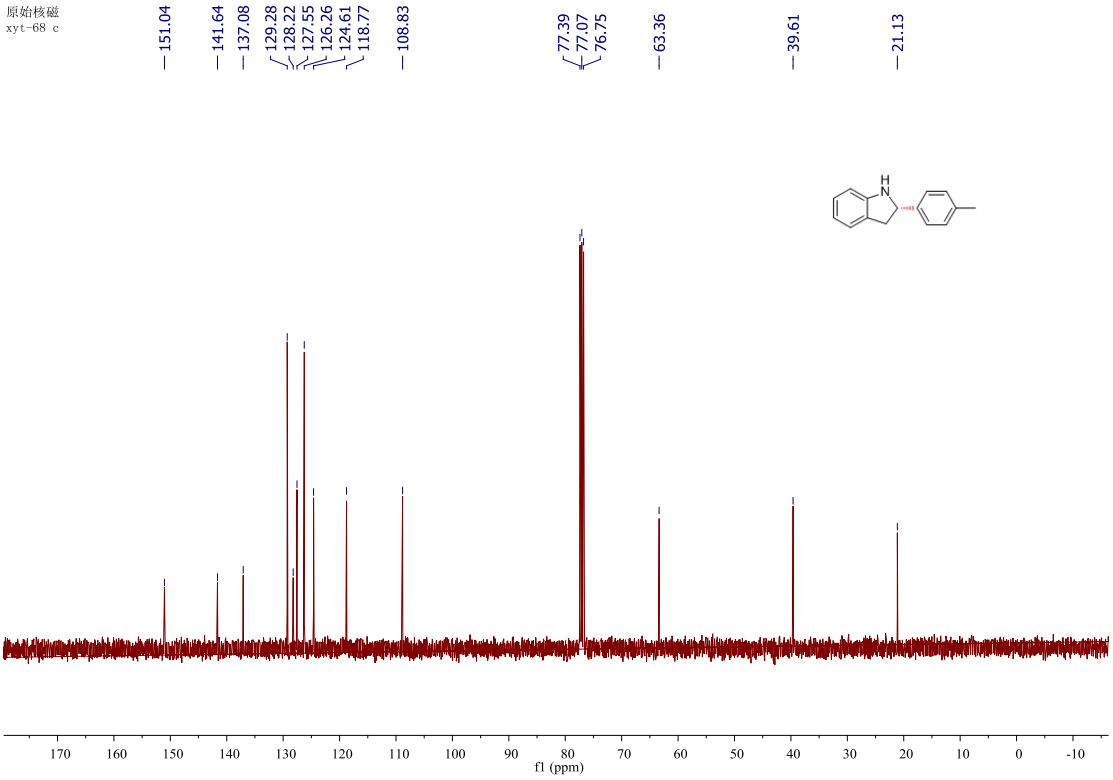

原始核磁
xyt-46 c
150.50
139.10
129.16
128.68
128.43
127.38
126.48
124.85
118.59
109.17
77.41
77.09
76.77
61.05
42.71
35.95
f1 (ppm)

4l

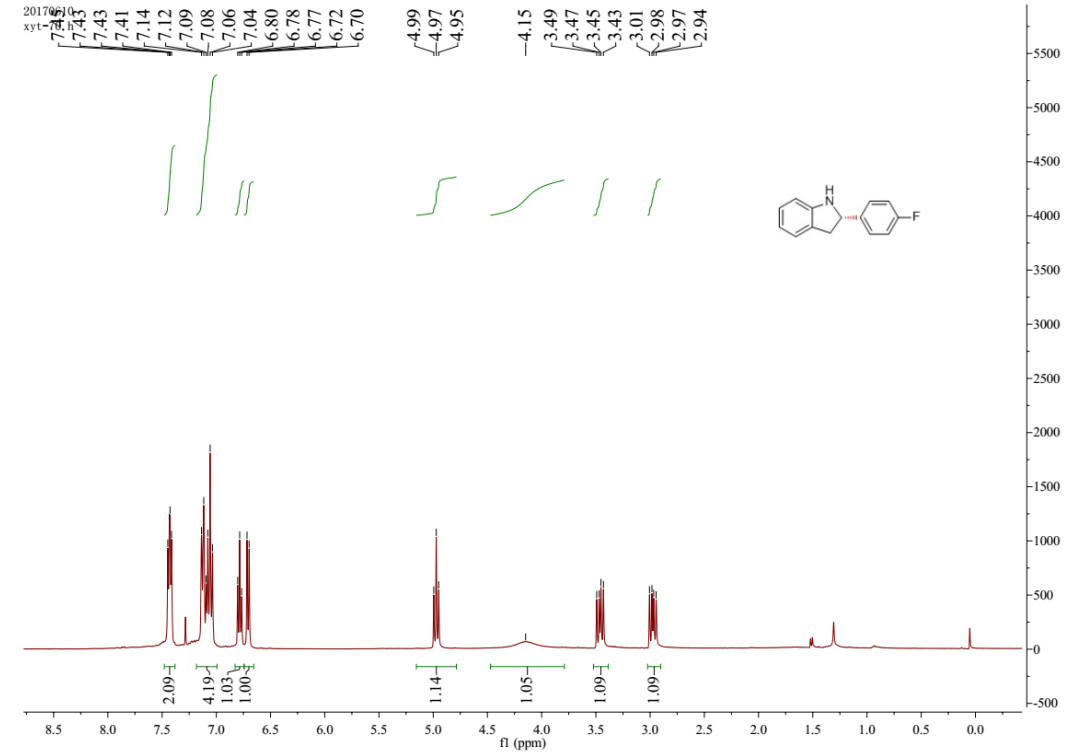

7.39
7.37
7.35
7.33
7.15
7.14
7.13
7.12
7.11
6.81
6.79
6.77
6.73
6.71
5.02
5.00
4.97
4.15
3.52
3.50
3.48
3.46
3.07
3.05
3.03
3.01
2.06
3.03
2.16
1.02
1.17
1.00
0.97
1.01
1.10
f1 (ppm)
原始核磁
xyt-30 c
151.02
144.64
128.63
128.10
127.59
127.43
126.34
124.63
118.83
108.86
77.41
77.09
76.77
63.58
39.62
f1 (ppm)

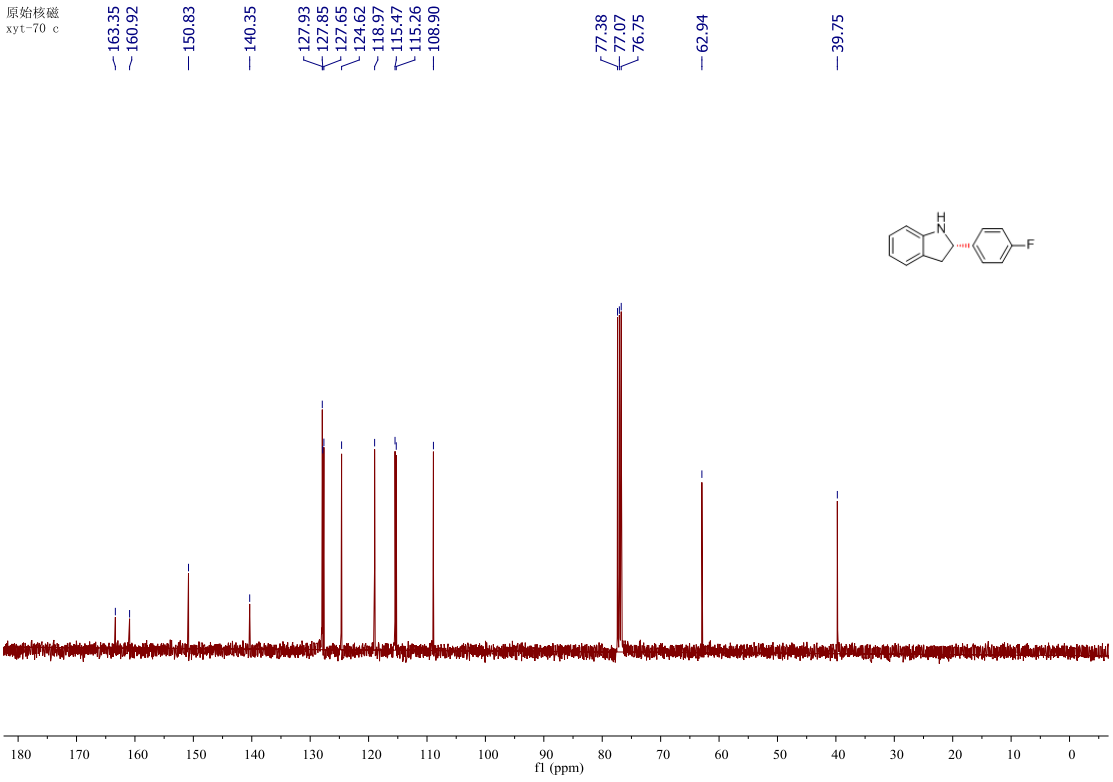
4m


20170610
xyt-68 h
7.36
7.34
7.20
7.18
7.13
7.12
7.10
7.08
6.79
6.77
6.75
6.71
6.69
4.98
4.95
4.93
4.13
3.49
3.46
3.45
3.42
3.04
3.02
3.00
2.39
2.13
2.09
1.98
1.01
0.96
1.05
0.79
1.15
1.07
3.00
f1 (ppm)

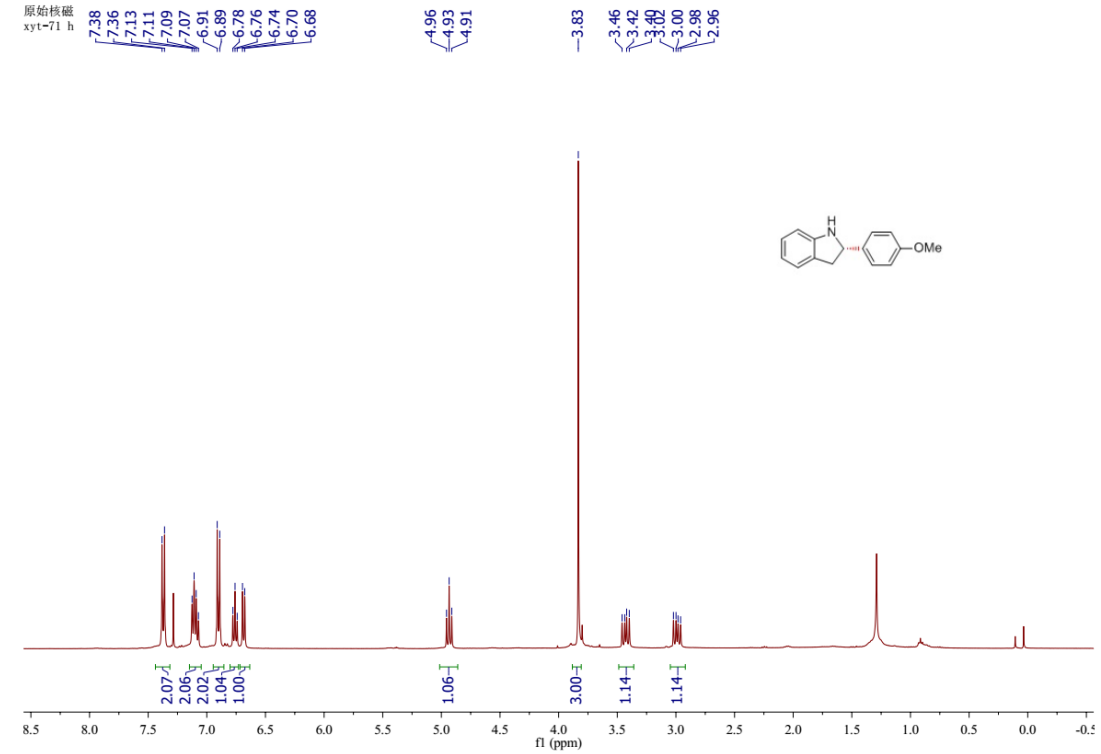

原始核磁
xyt-68 c
151.04
141.64
137.08
129.28
128.22
127.55
126.26
124.61
118.77
108.83
77.39
77.07
76.75
63.36
39.61
21.13
f1 (ppm)

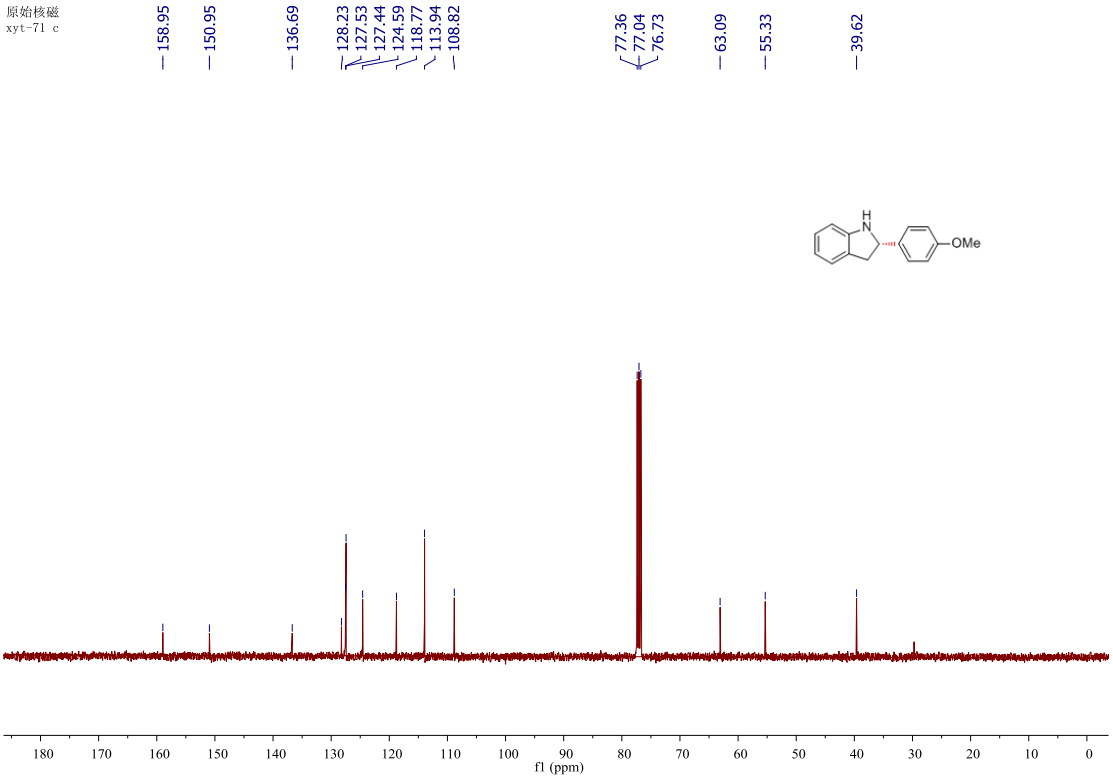
4n


7.45
7.43
7.41
7.14
7.12
7.09
7.08
7.06
7.04
6.80
6.78
6.77
6.72
6.70
4.99
4.97
4.95
4.15
3.49
3.47
3.45
3.43
3.01
2.98
2.97
2.94
2.09
4.19
1.03
1.00
1.14
1.05
1.09
1.09
f1 (ppm)

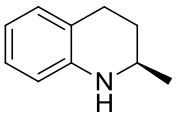

原始核磁
xyt-70 c
163.35
160.92
150.83
140.35
127.93
127.85
127.65
124.62
118.97
115.47
115.26
108.90
77.38
77.07
76.75
62.94
39.75
f1 (ppm)

4o


原始核磁
xyt-71 h
7.38
7.36
7.13
7.11
7.09
7.07
6.91
6.89
6.78
6.76
6.74
6.70
6.68
4.96
4.93
4.91
3.83
3.46
3.42
3.00
2.98
2.96
OMe
2.07
2.06
2.02
1.04
1.00
1.06
3.00
1.14
1.14
f1 (ppm)


原始核磁
xyt-71 c
158.95
150.95
136.69
128.23
127.53
127.44
124.59
118.77
113.94
108.82
77.36
77.04
76.73
63.09
55.33
39.62
OMe
f1 (ppm)

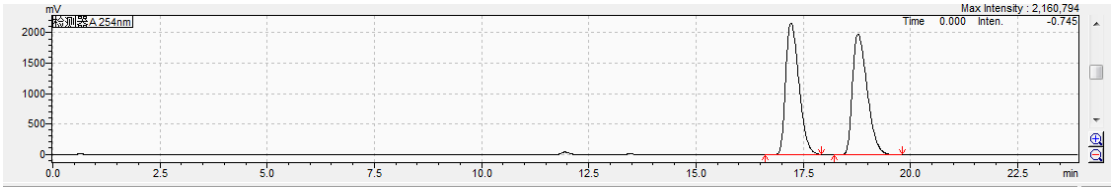
11. Chiral HPLC Chromatographic Analysis



2a

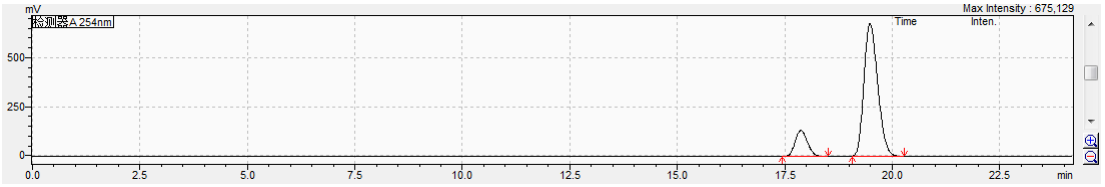
＊Chiralpak OJ-H, 10% *i*-PrOH/Hexane at 0.5 mL/min, enantiomeric excess determined at 254 nm; 17.8 min (*S*), **19.4 min (*R*)**.

(Ⅰ) Racemic standard:

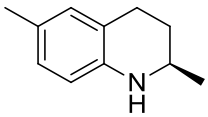


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	17.217	46847864	2169444	M	49.611				49.611
2	18.781	47582281	1989630	M	50.389				50.389
总计		94430144	4159073		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **70% *e.e***



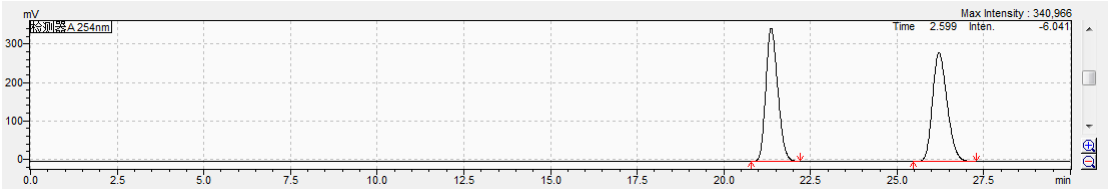
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	17.874	2689571	133751	M	15.111				15.111
2	19.483	15108963	678203	M	84.889				84.889
总计		17798534	811953		100.000				100.000



2b

＊Chiralpak OJ-H, 10% *i*-PrOH/Hexane at 0.5 mL/min, enantiomeric excess determined at 254 nm; 21.3 min (*S*), **25.9 min (*R*)**.

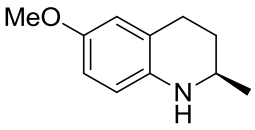
(Ⅰ) Racemic standard:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	21.366	8355859	346747	M	50.049				50.049
2	26.207	8339393	282927	M	49.951				49.951
总计		16695252	629673		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **62% *e.e.***

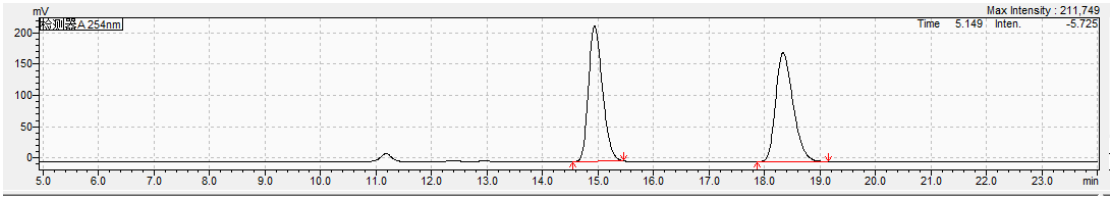
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	21.304	8226101	343804	M	19.114				19.114
2	25.969	34812027	1118867	M	80.886				80.886
总计		43038127	1462671		100.000				100.000



2c

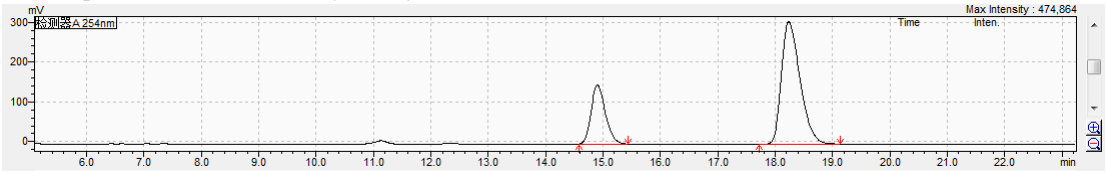
* Chiralpak OJ-H, 10% *i*-PrOH/Hexane at 1 mL/min, enantiomeric excess determined at 254 nm; 14.9 min **(*S*), 18.2 min (*R*)**.

(Ⅰ) Racemic standard:

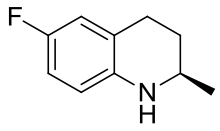


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.939	3792117	217166	M	49.838				49.838
2	18.335	3816700	174274	M	50.162				50.162
总计		7608817	391440		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **46% *e.e.***



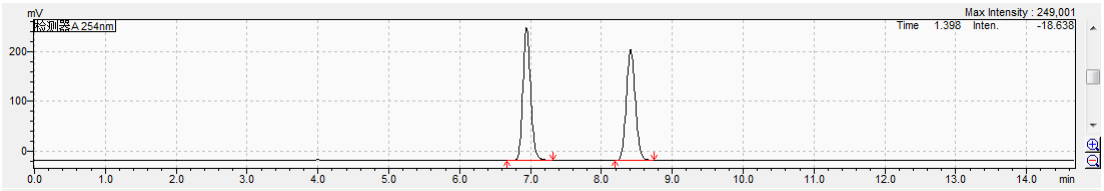
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.901	2557433	147586	M	26.987				26.987
2	18.237	6919277	307153	M	73.013				73.013
总计		9476709	454739		100.000				100.000



2d

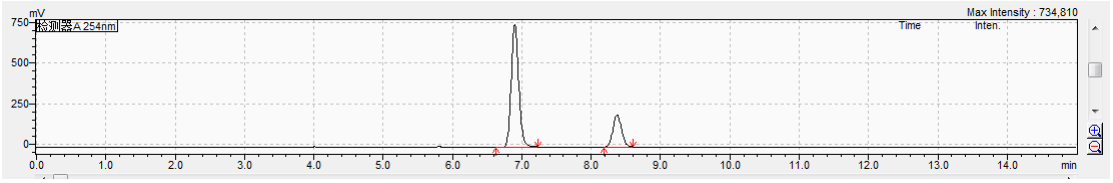
＊Chiralpak OD-H, 5% *i*-PrOH/Hexane at 0.8 mL/min, enantiomeric excess determined at 254 nm; **6.8 min (*R*)**, 8.3 min (*S*).

(Ⅰ) Racemic standard:

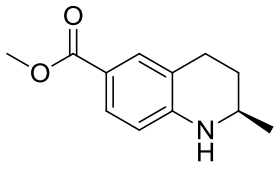


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.943	2038423	267434	M	50.772				50.772
2	8.413	1976402	222245	M	49.228				49.228
总计		4014825	489679		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **54% *e.e.***



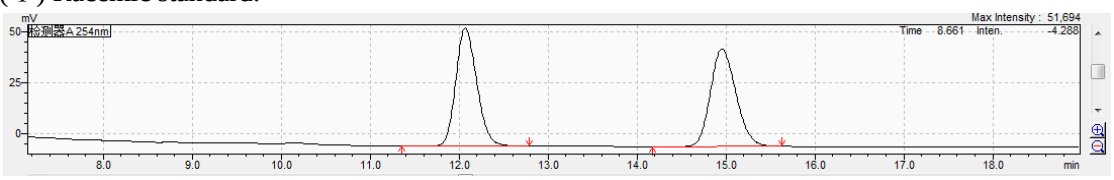
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.897	5675260	751930	M	76.929				76.929
2	8.374	1701984	196746	M	23.071				23.071
总计		7377244	948676		100.000				100.000



2e

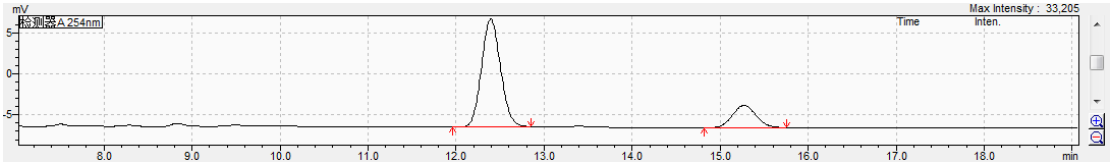
＊Chiralpak OD-H, 15% *i*-PrOH/Hexane at 0.7 mL/min, enantiomeric excess determined at 254 nm; **12.3 min (*R*)**, 15.2 min (*S*).

(Ⅰ) Racemic standard:

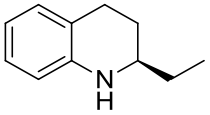


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.070	944443	57754	M	49.869				49.869
2	14.955	949391	47658	M	50.131				50.131
总计		1893834	105411		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **59% *e.e.***



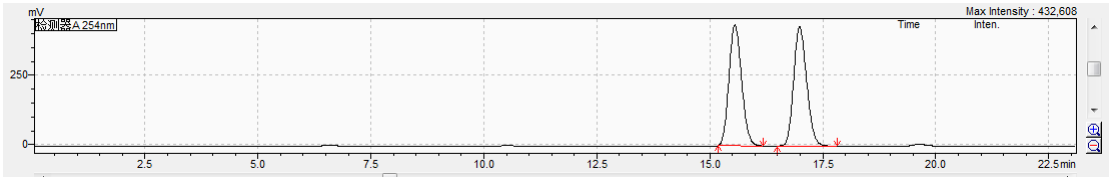
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.393	197288	13144	M	79.575				79.575
2	15.270	50638	2711	M	20.425				20.425
总计		247926	15856		100.000				100.000



2f

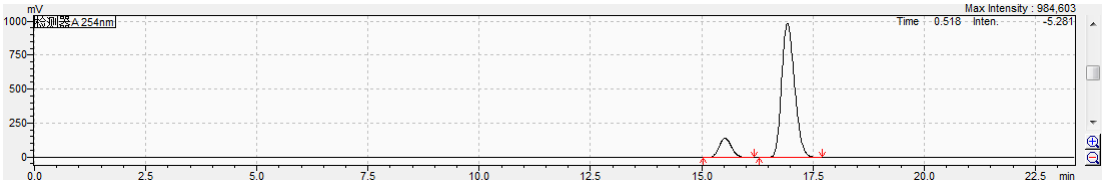
∗Chiralpak OJ-H, 10% *i*-PrOH/Hexane at 0.5 mL/min, enantiomeric excess determined at 254 nm; 15.5 min (*S*)**, 16.9 min (*R*)**.

(Ⅰ) Racemic standard:

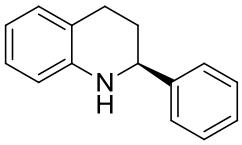


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.554	8546417	436759	M	49.869				49.869
2	16.988	8591404	429034	M	50.131				50.131
总计		17137821	865792		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **66% *e.e.***



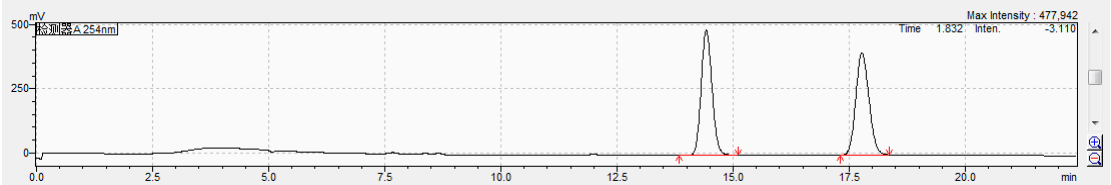
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.526	2796360	143239	M	12.215				12.215
2	16.929	20095996	989526	M	87.785				87.785
总计		22892356	1132766		100.000				100.000



2g

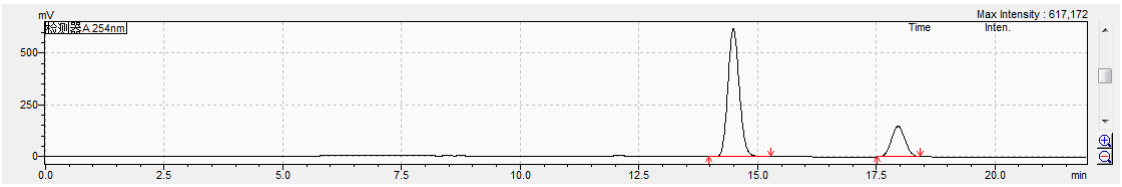
＊ Chiralpak OD-H, 10% *i*-PrOH/Hexane at 0.6 mL/min, enantiomeric excess determined at 254 nm; **14.4 min (*S*)**, 17.9 min (*R*).

(Ⅰ) Racemic standard:

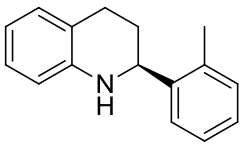


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.422	7888566	486341	M	50.160				50.160
2	17.774	7838288	397758	M	49.840				49.840
总计		15726853	884099		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **56% *e.e.***



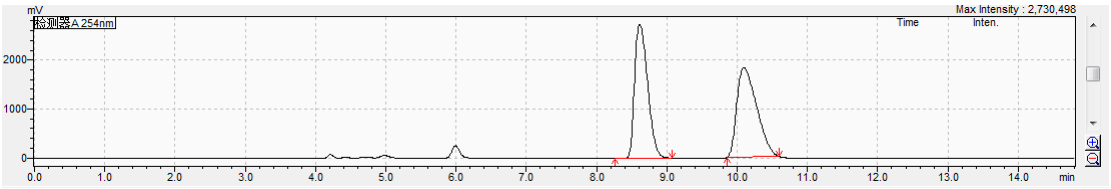
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.487	10238495	616511	M	77.877				77.877
2	17.956	2908585	147070	M	22.123				22.123
总计		13147080	763581		100.000				100.000



2h

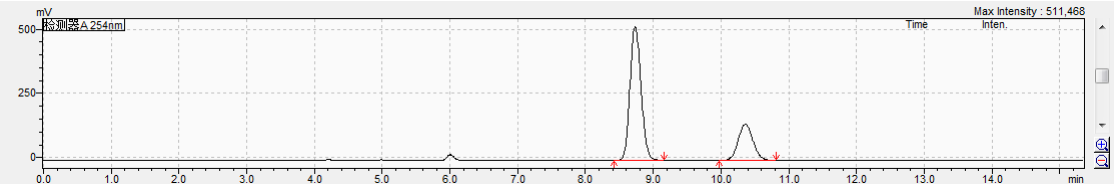
＊Chiralpak OD-H, 10% *i*-PrOH/Hexane at 1 mL/min, enantiomeric excess determined at 254 nm; **8.7 min (*S*)**, 10.3 min (*R*).

(Ⅰ) Racemic standard:

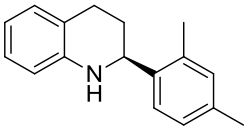


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.612	35262926	2736705	M	49.601				49.601
2	10.096	35830752	1821644	M	50.399				50.399
总计		71093678	4558349		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **46% *e.e.***



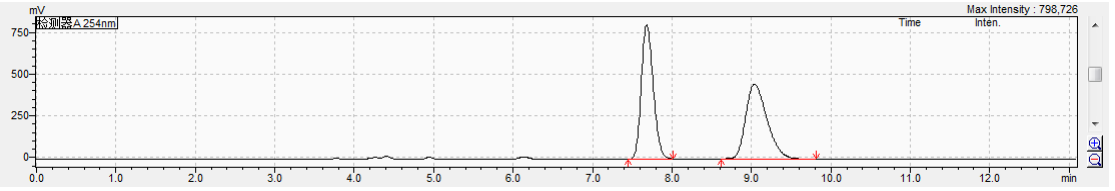
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.733	5874205	521601	M	73.391				73.391
2	10.360	2129827	140939	M	26.609				26.609
总计		8004031	662540		100.000				100.000



2i

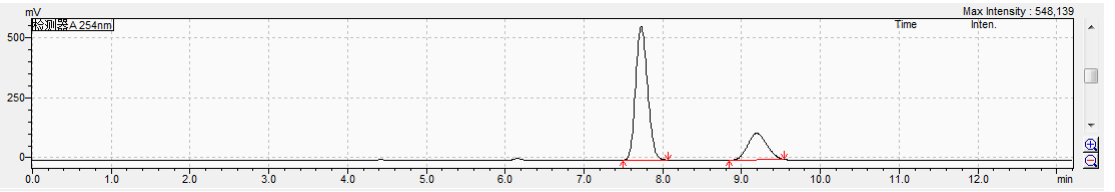
* Chiralpak OD-H, 10% *i*-PrOH/Hexane at 1 mL/min, enantiomeric excess determined at 254 nm; **7.7 min (*S*)**, 9.1 min (*R*).

(Ⅰ) Racemic standard:

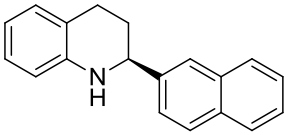


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.683	8494317	808319	M	50.140				50.140
2	9.039	8446953	449808	M	49.860				49.860
总计		16941270	1258127		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **52% *e.e.***



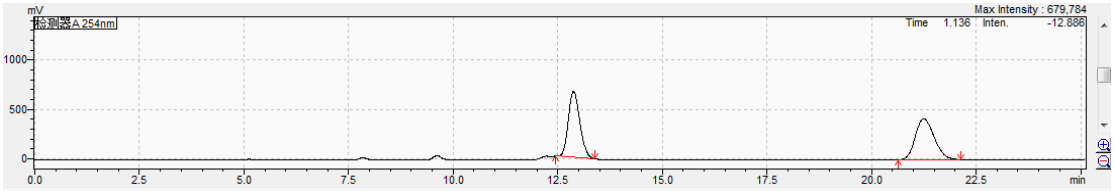
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.727	5833838	558156	M	75.848				75.848
2	9.194	1857608	110353	M	24.152				24.152
总计		7691446	668510		100.000				100.000



2j

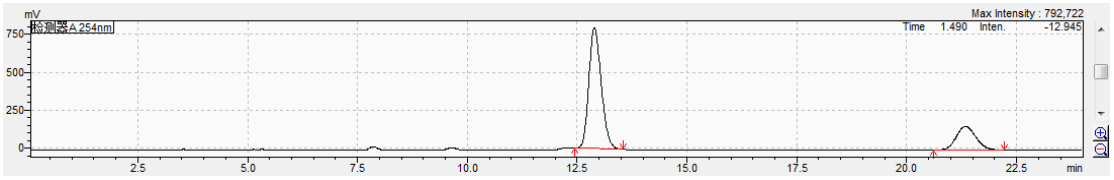
＊Chiralpak OD-H, 10% *i*-PrOH/Hexane at 1 mL/min, enantiomeric excess determined at 254 nm; **12.8 min (*S*),** 21.3 min (*R*).

(Ⅰ) Racemic standard:

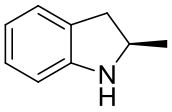


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.877	12923755	668413	M	49.620				49.620
2	21.247	13121543	418180	M	50.380				50.380
总计		26045299	1086593		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **53% *e.e.***



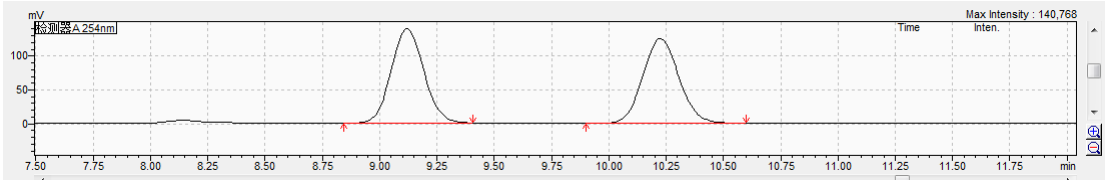
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.892	15661319	796048	M	76.491				76.491
2	21.338	4813465	155503	M	23.509				23.509
总计		20474784	951552		100.000				100.000



4a

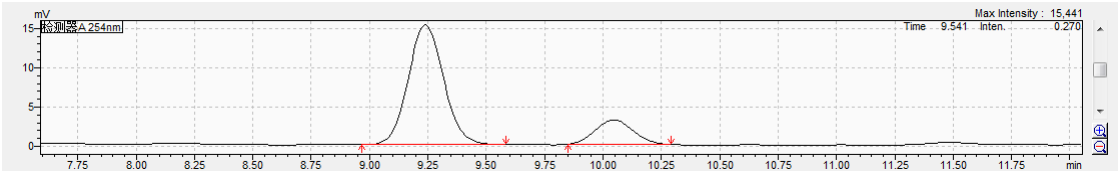
＊Chiralpak OJ-H, 3% *i*-PrOH/Hexane at 0.8 mL/min, enantiomeric excess determined at 254 nm; **9.2 min (*R*)**, 10.0 min (*S*).

(Ⅰ) Racemic standard:



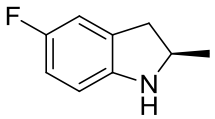
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.120	1377857	139466	M	50.138				50.138
2	10.225	1370260	125066	M	49.862				49.862
总计		2748118	264532		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **64% *e.e.***



峰表 | 化合物 | 组 | 校准曲线

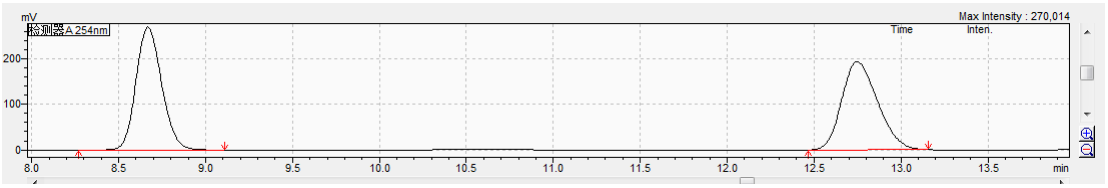
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.239	160118	15185	M	82.078				82.078
2	10.046	34963	3106	M	17.922				17.922
总计		195081	18291		100.000				100.000



4b

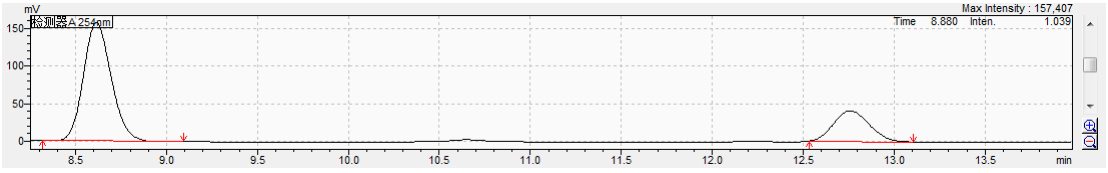
＊Chiralpak OD-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; **8.6 min (*R*)**, 12.7 min (*S*).

(Ⅰ) Racemic standard:

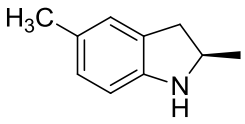


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.668	2785615	270347	M	49.997				49.997
2	12.748	2785965	193452	M	50.003				50.003
总计		5571579	463799		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **50% *e.e.***



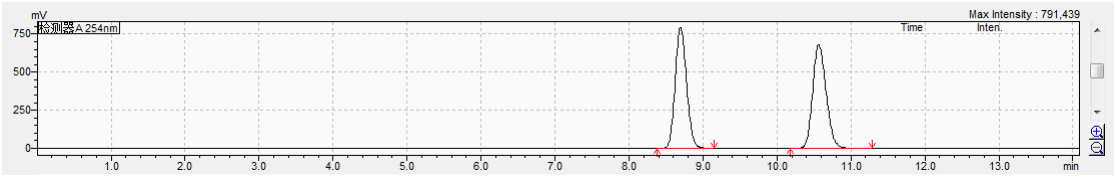
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.613	1657465	156858	M	75.075				75.075
2	12.759	550267	40687	M	24.925				24.925
总计		2207732	197345		100.000				100.000



4c

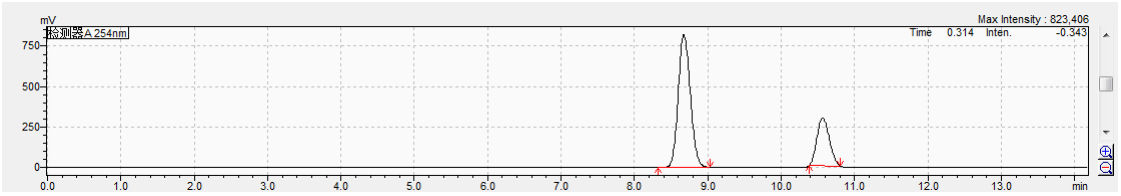
＊Chiralpak OD-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; **8.6 min (*R*)**, 10.5 min (*S*).

(Ⅰ) Racemic standard:

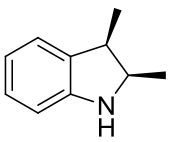


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.696	8495226	791164	M	49.746				49.746
2	10.564	8582005	678941	M	50.254				50.254
总计		17077230	1470105		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: ***47% e.e.***



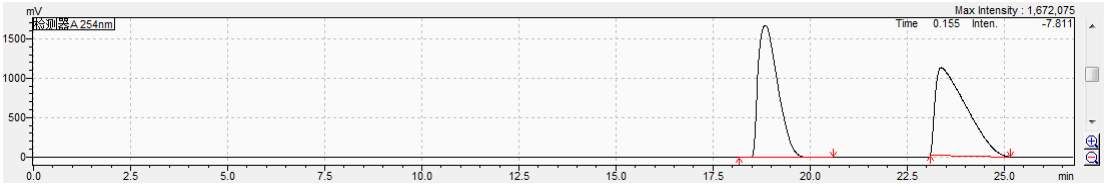
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.674	9441007	822327	M	73.295				73.295
2	10.567	3439777	293886	M	26.705				26.705
总计		12880783	1116213		100.000				100.000



4d

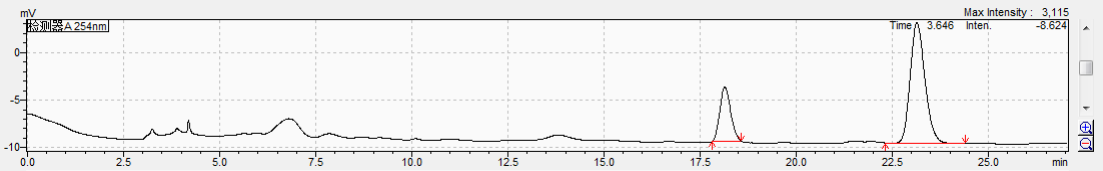
＊Chiralpak OJ-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; 18.1 min (*S*), **23.1 min (*R*)**.

(Ⅰ) Racemic standard:

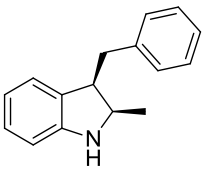


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	18.846	59045711	1680652	M	48.882				48.882
2	23.379	61747388	1115548	M	51.118				51.118
总计		120793100	2796200		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **51% *e.e.***



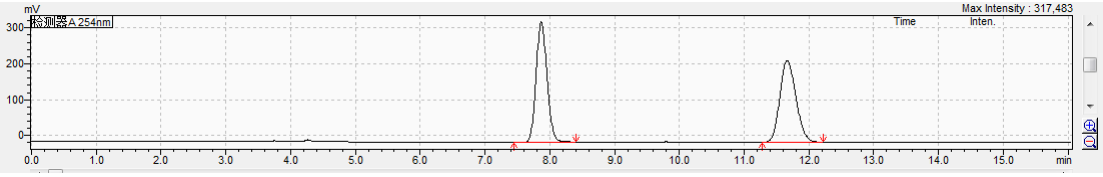
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	18.142	110705	5670	M	24.773				24.773
2	23.139	336164	12628	M	75.227				75.227
总计		446869	18298		100.000				100.000



4e

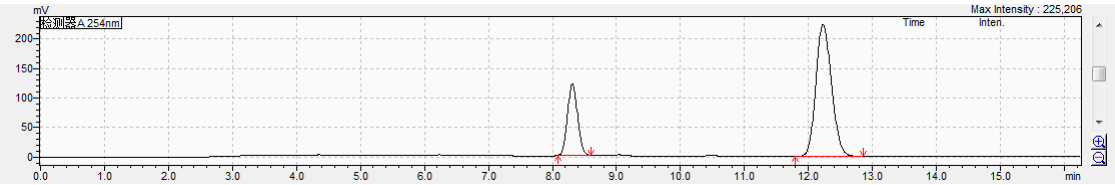
* Chiralpak OD-H, 10% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; 8.3 min (*S*), **12.2 min (*R*)**.

(Ⅰ) Racemic standard:

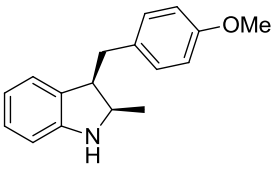


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.867	3936397	335818	M	50.005				50.005
2	11.664	3935554	228057	M	49.995				49.995
总计		7871951	563875		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **48% *e.e.***



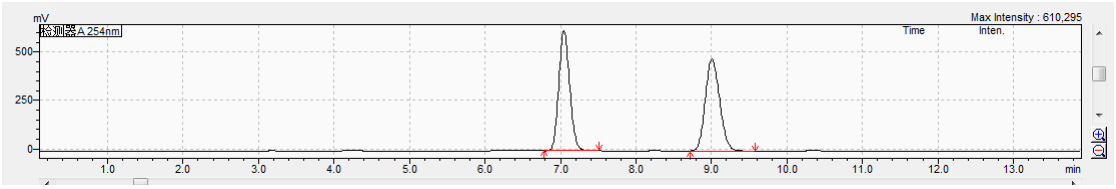
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.311	1335245	121904	M	25.982				25.982
2	12.227	3803937	223921	M	74.018				74.018
总计		5139182	345825		100.000				100.000



4f

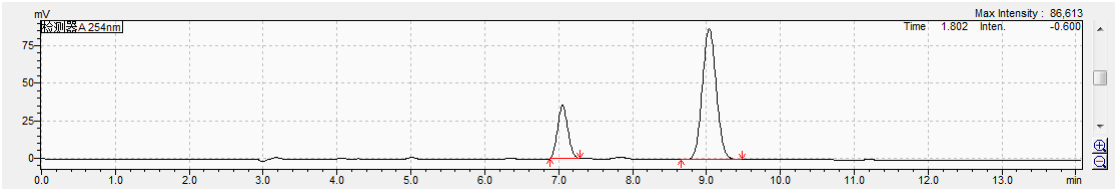
＊Chiralpak OD-H, 20% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; 7.0 min (*S*), **9.0 min (*R*)**.

(Ⅰ) Racemic standard:

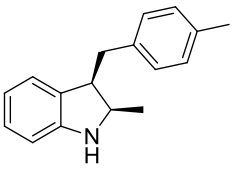


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.045	6247731	620222	M	49.922				49.922
2	9.007	6267155	473807	M	50.078				50.078
总计		12514886	1094029		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **<u>54% *e.e.*</u>**



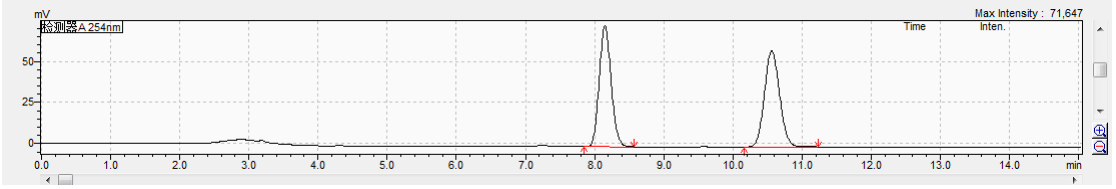
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.052	343258	35399	M	23.027				23.027
2	9.036	1147413	87530	M	76.973				76.973
总计		1490671	122929		100.000				100.000



4g

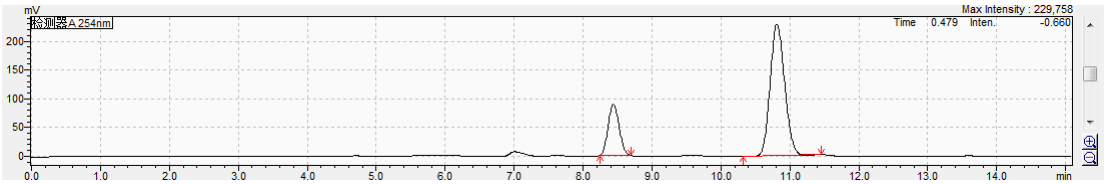
＊Chiralpak OD-H, 5% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; 8.4 min (*S*), **10.8 min (*R*)**.

(Ⅰ) Racemic standard:

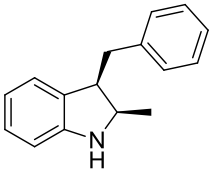


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.148	880157	73565	M	49.785				49.785
2	10.562	887768	58411	M	50.215				50.215
总计		1767925	131976		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **55% *e.e.***



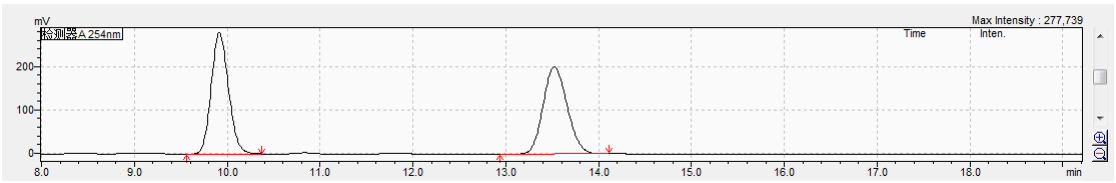
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.440	977141	89170	M	22.752				22.752
2	10.811	3317636	228636	M	77.248				77.248
总计		4294777	317806		100.000				100.000



4h

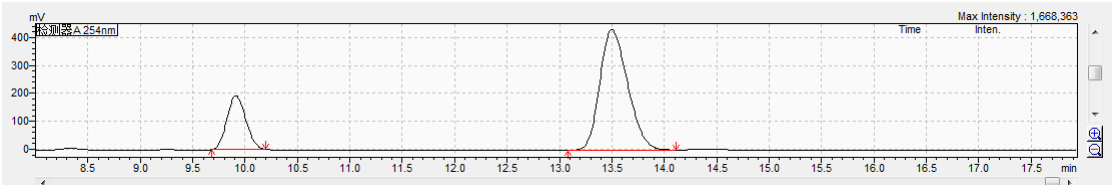
* Chiralpak OD-H, 5% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; 9.9 min (*S*), **13.5 min (*R*)**.

(Ⅰ) Racemic standard:

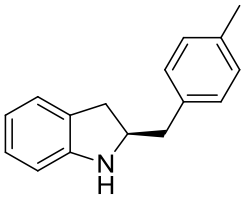


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.914	3625271	279632	M	50.076				50.076
2	13.522	3614257	201075	M	49.924				49.924
总计		7239529	480707		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **53% *e.e.***



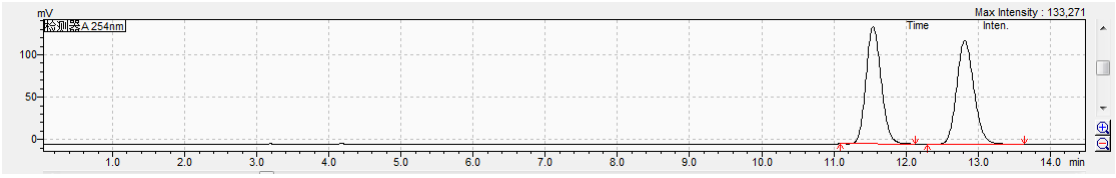
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.912	2421862	192888	M	23.342				23.342
2	13.500	7953502	430475	M	76.658				76.658
总计		10375364	623363		100.000				100.000



4i

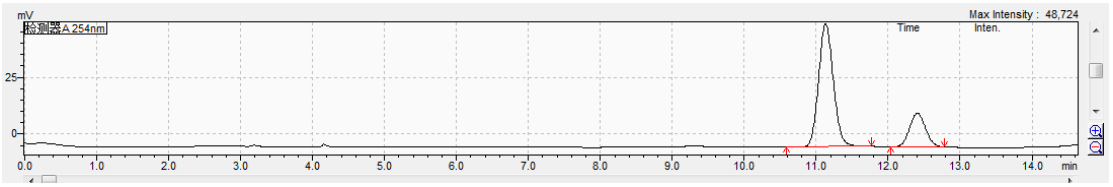
＊Chiralpak OD-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; **11.1 min (*R*)**, 12.4 min (*S*).

(Ⅰ) Racemic standard:

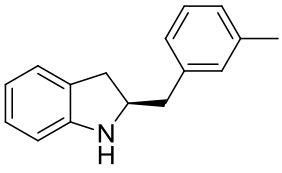


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.545	2020771	138261	M	49.934				49.934
2	12.816	2026120	121924	M	50.066				50.066
总计		4046890	260185		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **55% *e.e.***



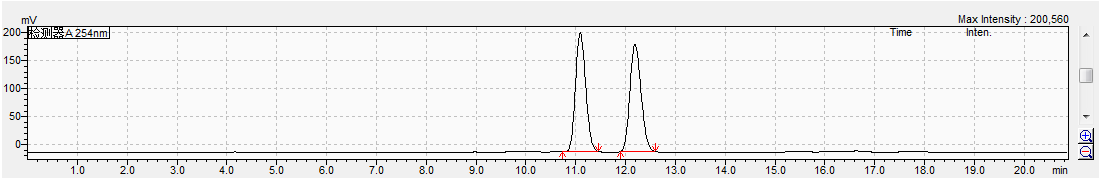
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.131	770619	54245	M	77.282				77.282
2	12.407	226535	14765	M	22.718				22.718
总计		997154	69011		100.000				100.000



4j

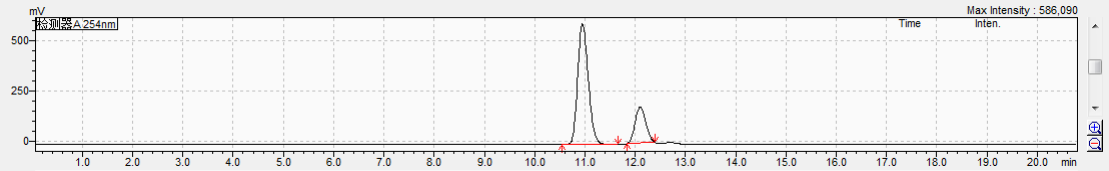
＊Chiralpak OD-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; **10.9 min (*R*)**, 12.0 min (*S*).

(Ⅰ) Racemic standard:

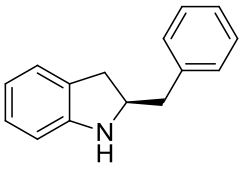


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.091	3037563	213098	M	50.309				50.309
2	12.191	3000231	192069	M	49.691				49.691
总计		6037794	405167		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **53% *e.e.***



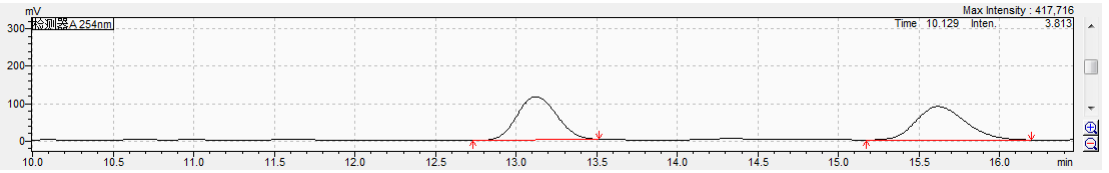
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.949	8741522	599234	M	76.472				76.472
2	12.098	2689513	180905	M	23.528				23.528
总计		11431035	780139		100.000				100.000



4k

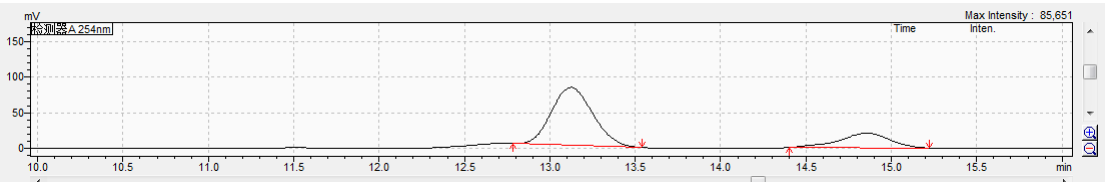
* Chiralpak OD-H, 1% *i*-PrOH/Hexane at 1.0 mL/min, enantiomeric excess determined at 254 nm; **13.1 min (*R*)**, 14.8 min (*S*).

(Ⅰ) Racemic standard:

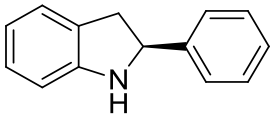


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.121	1957555	115214	M	50.778				50.778
2	15.619	1897544	89509	M	49.222				49.222
总计		3855099	204722		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **54% *e.e.***



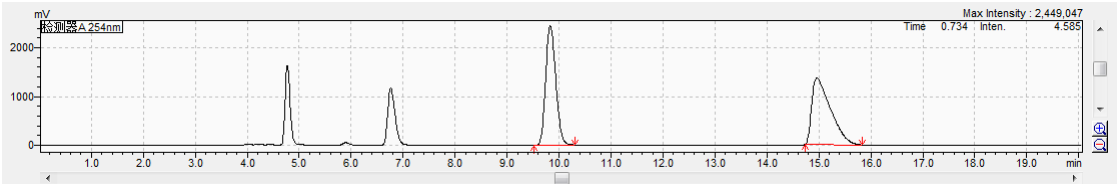
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.122	1390098	82116	M	76.736				76.736
2	14.852	421426	20744	M	23.264				23.264
总计		1811524	102859		100.000				100.000



4l

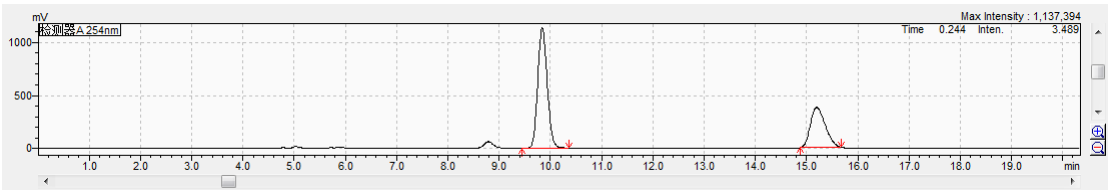
＊Chiralpak OD-H, 16.7% *i*-PrOH/Hexane(1/5) at 1.0 mL/min, enantiomeric excess determined at 254 nm; **9.8 min (*R*)**, 15.1 min (*S*).

(Ⅰ) Racemic standard:

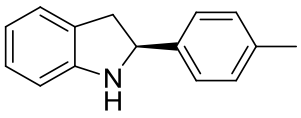


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.831	32965895	2440876	M	49.295				49.295
2	14.961	33908626	1357572	M	50.705				50.705
总计		66874521	3798447		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **31% *e.e.***



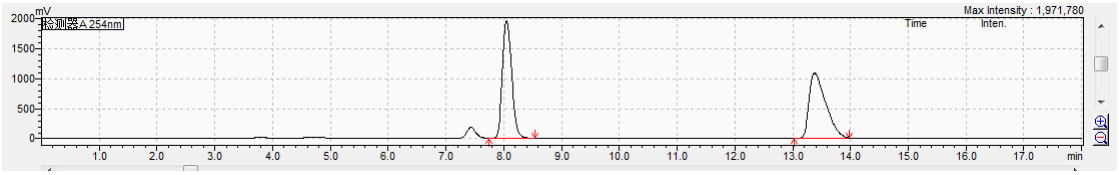
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.841	14482486	1132681	M	65.529				65.529
2	15.198	7618243	377770	M	34.471				34.471
总计		22100729	1510451		100.000				100.000



4m

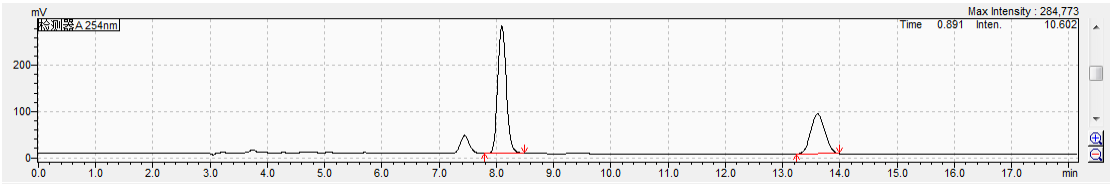
＊Chiralpak OD-H, 20% *i*-PrOH/Hexane(20/80) at 1.0 mL/min, enantiomeric excess determined at 254 nm; **8.0 min (*R*)**, 13.6 min (*S*).

(Ⅰ) Racemic standard:

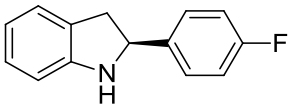


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.048	21918999	1961416	M	50.355				50.355
2	13.377	21610002	1083741	M	49.645				49.645
总计		43529002	3045156		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **32% *e.e.***



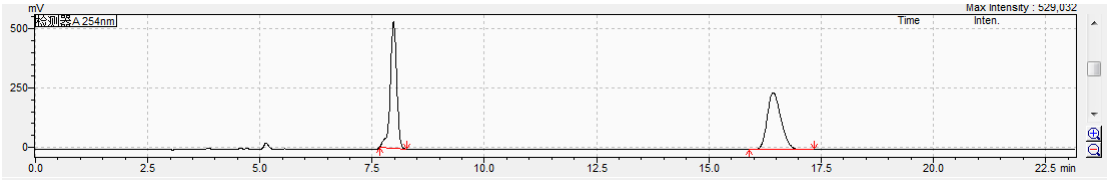
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.094	2844881	275177	M	65.732				65.732
2	13.610	1483098	86411	M	34.268				34.268
总计		4327979	361588		100.000				100.000



4n

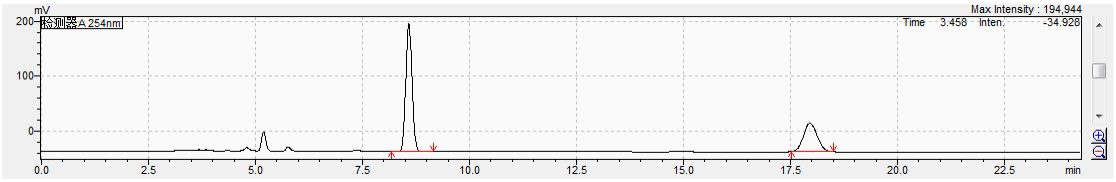
∗Chiralpak OD-H, 16.7% *i*-PrOH/Hexane(1/5) at 1.0 mL/min, enantiomeric excess determined at 254 nm; **8.5 min (*R*)**, 15.1 min (*S*).

(Ⅰ) Racemic standard:

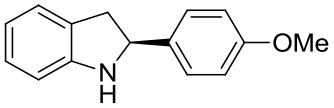


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.976	5300718	532801	M	50.918				50.918
2	16.431	5109499	240453	M	49.082				49.082
总计		10410217	773254		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **35% *e.e.***



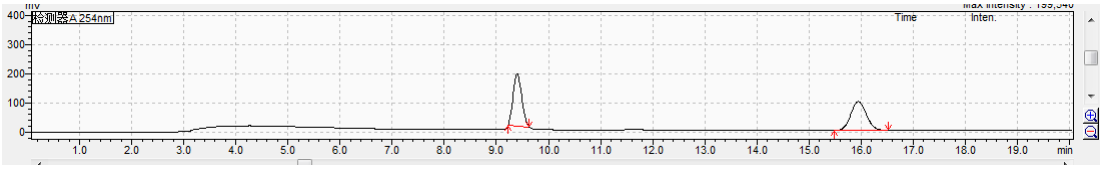
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.583	2388432	232146	M	67.323				67.323
2	17.956	1159314	51675	M	32.677				32.677
总计		3547746	283821		100.000				100.000



4o

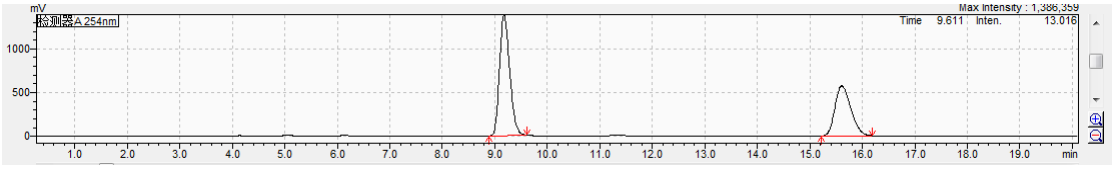
∗Chiralpak OD-H, 16.7% *i*-PrOH/Hexane(1/5) at 1.0 ml/min, enantiomeric excess determined at 254 nm; **9.8 min (*R*)**, 15.1 min (*S*).

(Ⅰ) Racemic standard:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.398	2068447	178554	M	50.551				50.551
2	15.945	2023379	98527	M	49.449				49.449
总计		4091826	277080		100.000				100.000

(Ⅱ) Experimental result catalyzed by Pd-NPS: **22% *e.e.***



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.175	18824093	1380910	M	61.120				61.120
2	15.606	11974505	571580	M	38.880				38.880
总计		30798598	1952489		100.000				100.000