Supporting Information for

Facile Synthesis of Chiral [2,3]-Fused Hydrobenzofuran *via* Asymmetric Cu(I)-Catalyzed Dearomative 1,3-Dipolar Cycloaddition

Lei Liang,[a] Hong-Ying Niu,[c] Dong-Chao Wang,*[,b] Xin-He Yang,[b] Gui-Rong Qu,[b] and Hai-Ming Guo*[,a,b]

[a]School of Environment and [b]Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan Province 453007, China

[c]School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan Province 453003, China

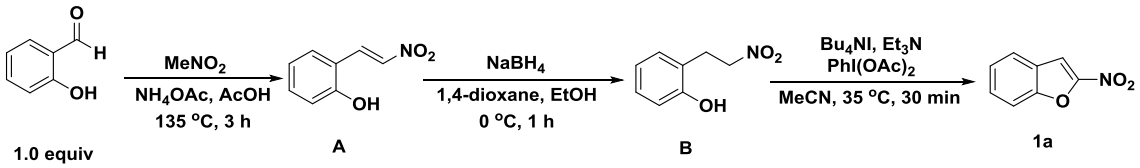
E-mail: ghm@htu.edu.cn

1. General information:

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quaternary, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/IE/ID/ODH in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). All regents and solvents were purchased from commercial sources and purified commonly before used.

2. Synthesis of starting materials

Synthesis of Variously Functionalized 2-Nitrobenzofurans (1a-1k):

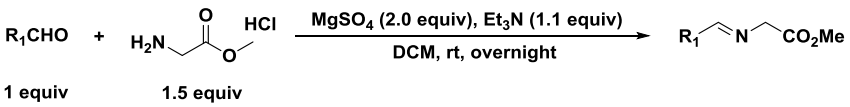


To a 25 mL flask were added nitromethane (5.0 mL), NH_4OAc (77 mg, 1.0 mmol), and acetic acid (2.0 mL). The mixture was stirred at 90 ℃ for 15 min before addition of salicylaldehyde (0.61 g, 5.0 mmol). The reaction mixture was heated at 135 ℃ for 3 h. After cooling to ambient temperature, the reaction was worked up with Et_2O (50 mL) and brine (50 mL). Purification by column chromatography on silica gel (n-pentane/EtOAc: 8/1) yielded product **A** (0.58 g, 70%) as a yellow solid.

$NaBH_4$ (45 mg, 1.2 mmol) was suspended in a mixture of 1,4-dioxane and EtOH (4.0 mL, 3:1). **A** (165 mg, 1 mmol) dissolved in 1,4-dioxane (3.0 mL) was added dropwise at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1 h, quenched with saturated aqueous NH_4Cl solution (10 mL), extracted with Et_2O (3 × 25 mL), washed with brine (50 mL), and dried over Na_2SO_4. The organic phase was removed under vacuum to afford the crude **B**.

To a 25 mL flask were added crude **B**, Bu_4NI (923 mg, 2.5 mmol), NEt_3 (202 mg, 2.0 mmol), $PhI(OAc)_2$ (966 mg, 3.0 equiv), and acetonitrile (10.0 mL). The mixture was stirred at 35 ℃ for 30 min, extracted with Et_2O (50 mL) and brine (3 × 25 mL), dried over Na_2SO_4. Purification by column chromatography on silica gel (n-pentane/Et_2O: 20/1) yielded 2-nitrobenzofuran **1a** (98 mg, 60%) as a light yellow solid. **1b**-**1k** were synthesized in the same reaction conditions

Synthesis of α-iminoesters (2a-2k):

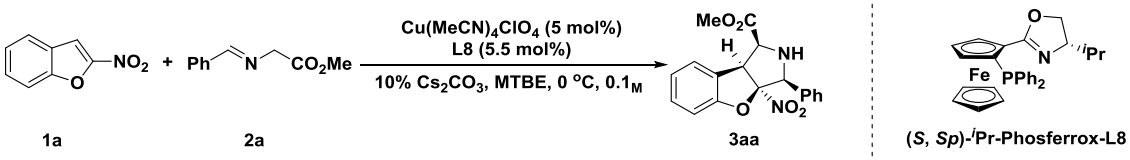


To a suspension of glycine methyl ester hydrochloride (1.5 equiv) and $MgSO_4$ (2.0 equiv) in CH_2Cl_2 was added Et_3N (1.1 equiv). Then, this solution was stirred at room temperature for 1 h. Subsequently, the aldehyde (1.0 equiv) was added and the reaction was stirred at room temperature overnight. Work up: $MgSO_4$ was removed by filtration and the filtrate was washed once with H_2O. The aqueous phase was extracted once with CH_2Cl_2 and the combined organic layers were washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated. Due to their instability, most of the α-iminoesters, once isolated, were immediately

used in the 1,3-dipolar cycloaddition reactions. But if necessary, further purification can be obtained via recrystallization from ethanol.

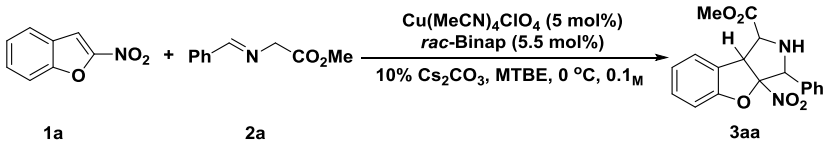
3. Typical producdure for the asymmertric dearomatization reaction

1) Procedure A: Synthesis of Chiral [2,3]-fused Hydrobenzofuranpyrrolidines (3aa-3ka)



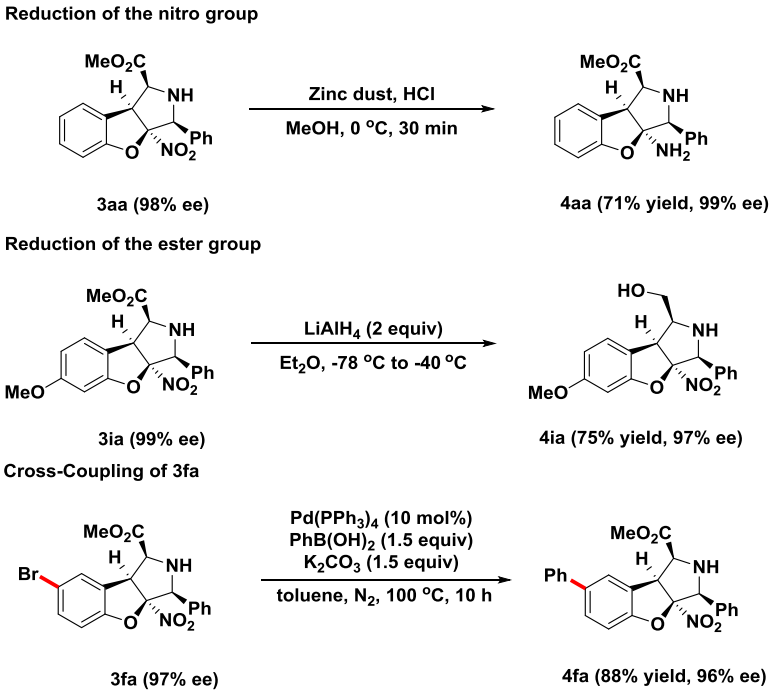
In a test tube, **L8** (5.3 mg, 0.011 mmol) and $Cu(MeCN)_4ClO_4$ (3.3 mg, 0.01 mmol) were dissolved in MTBE (2.0 mL) and stirred for 60 min at ambient temperature. Then, 2-nitrobenzofuran **1a** (32.6 mg, 0.2 mmol), N-benzylidene glycine methyl ester **2a** (53.1 mg, 0.3 mmol) and Cs_2CO_3 (6.5 mg, 0.02 mmol, 10 mol%) were added. The reaction mixture was stirred at 0 ^oC for 12 h. Upon consumption of 2-nitrobenzofuran **1a** (determined by TLC), The mixture was concentrated and the residue was purified by column chromatography (eluent: ethyl acetate/petroleum ether = 1:5) to afford the cycloadduct **3aa** in 83% yield (56.5 mg). Chiral **3ab**-**3ka** were synthesized in the same reaction conditions.

2) Procedure B: Synthesis of Racemic [2,3]-fused Hydrobenzofuranpyrrolidines (3aa-3ka)



In a test tube. *rac*-Binap (6.8 mg, 0.011 mmol), $Cu(CH_3CN)_4ClO_4$ (3.3 mg, 0.005 mmol), 2-nitrobenzofuran **1a** (32.6 mg, 0.02 mmol), N-benzylidene glycine methyl ester **2a** (53.1 mg, 0.3 mmol) and Cs_2CO_3 (6.5 mg, 0.02 mmol, 10 mol%) were added. The reaction tube was placed under vacuum and backfilled with argon three times. After that, MTBE (2.0 mL, 0.1 M) were added *via* syringe. The resulting mixture was stirred at rt for 6 h. The mixture was concentrated and the residue was purified by column chromatography. The mixture was concentrated and the residue was purified by column chromatography (eluent: ethyl acetate/petroleum ether = 1:5) to afford the corresponding racemic products. Racemic **3ab**-**3ka** were synthesized in the same reaction conditions.

4. Synthetic transformations of products.



Reduction of the nitro group (**3aa**-**4aa**)

A suspension of the cycloadduct **3aa** (51 mg, 0.15 mmol) in methanol (2.0 mL) and concentrated HCl (0.12 mL) was carefully treated with zinc dust (0.39 g, 6 mmol) at 0 ℃. The suspension was stirred at 0 ℃ for 30 min. A saturated aqueous $NaHCO_3$ solution was slowly added (until pH = 9). The mixture was filtered through celite, eluting with EtOAc. The filtrate was dried over Na_2SO_4, filtered, and evaporated. Purification by flash chromatography (CH_2Cl_2/methanol = 40:1) gave the product **4aa** (33 mg, 71%) as a yellow solid.

Reduction of ester group (**3ia**-**4ia**):

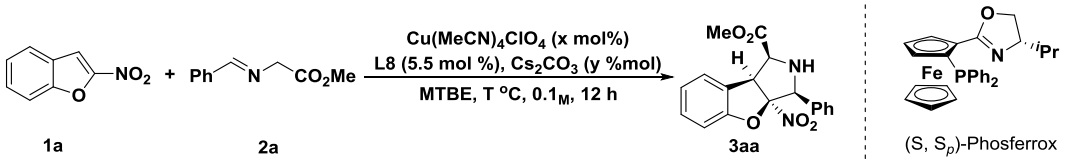
A solution of **3ia** (55.5 mg, 0.15 mmol) in dry Et_2O (1.5 mL) under nitrogen was cooled to -78 ^oC, then 0.3 mL $LiAlH_4$ (1 M in THF) was added *via* syringe slowly. The reaction mixture was stirred at -78 ℃ for 30 min and moved to -40 ℃ for another 10 min. Then water (0.2 mL) and 15% aqueous sodium hydroxide (0.2 mL) was added carefully. The mixture was filtered over anhydrous $MgSO_4$, and the filtrate was concentrated. The residue was subjected to the preparative thin layer chromatography (DCM/MeOH = 50:1) to afford **4ia** (38.5 mg, 75%) as light brown oil.

Suzuki-Myiyaura Cross-Coupling (**3fa**-**4fa**):

3fa (41.8 mg, 0.1 mmol), $PhB(OH)_2$ (18.5 mg, 0.15 mmol), $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 10 mol%), K_2CO_3 (21 mg, 0.15 mmol, 1.5 equiv) were stirred in Toluene (2 mL) under N_2 atmosphere at 105 ℃ for 12 h. The reaction mixture was partitioned between ethyl acetate and water. The combined organic phases were dried (Na_2SO_4), filtered and concentrated in vacuo to afford a crude oil. Purification by flash column chromatography (V_{PE}/V_{EA} = 8:1 as eluent) furnished desired product **4fa** (36.6 mg, 88%) as a colorless oil.

5. **Condition optimization**

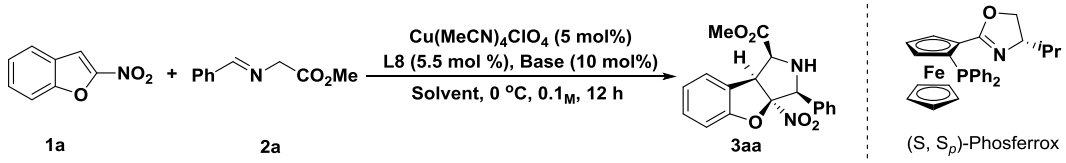
Table S1: Condition optimizations[a]



entry	x： y	T (^{o}C)	yield[b]	dr[c]	ee[d] (%)
1	5:5.5	0	83	9:1	98
2	3:3.3	0	62	8:1	95
[e]3	5:5.5	25	81	7:1	94
4	5:5.5	-20	79	9:1	98
5	5:5.5	-40	69	8:1	94

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Cu(MeCN)_4ClO_4$ (5 mol%), **L8** (5.5 mol%) and Cs_2CO_3 (10 mol%) in MTBE (2.0 mL), T ^{o}C, N_2, 2 h. [b]Yields of isolated product. [c]Determined by ^{1}H NMR analysis of the crude mixture. [d] Determined by chiral HPLC analysis. [e] 8 h.

Table S2: Solvents and Bases[a]

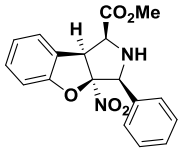


entry	solvent	base	yield[b] (%)	dr[c]	ee[d] (%)
1	MTBE	Cs_2CO_3	83	9:1	98
2	DCM	Cs_2CO_3	60	7:1	93
3	THF	Cs_2CO_3	45	5:1	91
4	toluene	Cs_2CO_3	35	2:1	89
5	MeCN	Cs_2CO_3	trace		
6	Et_2O	Cs_2CO_3	76	7:1	95
7	DCE	Cs_2CO_3	35	6:1	96
8	$CHCl_3$	Cs_2CO_3	66	6:1	94
9	MTBE	Na_2CO_3	55	8:1	93
10	MTBE	K_2CO_3	73	6:1	91
11	MTBE	Et_3N	trace		
12	MTBE	DIPEA	trace		
13	MTBE	DBU	39	5:1	82

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Cu(MeCN)_4ClO_4$ (5 mol%), **L** (5.5 mol%) and base (10 mol%) in solvent (2.0 mL), 0 ^oC, N_2, 12 h. [b]Yields of isolated product. [c]Determined by ^1H NMR analysis of the crude mixture. [d]Determined by chiral HPLC analysis.

6. Characterization of compounds

methyl (*1S,3S,3aS,8bS*)-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c]pyrrole -1-carboxylate (3aa)



3aa

Colorless oil. 56.5 mg, 83% yield, 9:1 dr, 96% ee.

$[\alpha]_D^{25}$ = 152.37 (c = 1.15, CH_2Cl_2).

m.p.: 143.2-146.5 ^oC

HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.880 min (major), 15.672 min (minor).

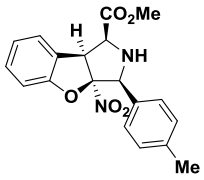
TLC: Rf = 0.30 (petroleum ether:ethyl acetate = 5:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.33-7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.00-6.97 (m, 2H), 5.13 (s, 1H), 4.74 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 2.69 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 , 132.2 , 130.5 , 129.1 , 128.7 , 127.7 , 124.9 , 123.3 , 123.0 , 122.7 , 110.6 , 69.9 , 64.2 , 58.4 , 52.3.

HRMS (ESI): m/z calcd. For $C_{18}H_{17}N_2O_5$ $[M+H]^+$ 341.1132, found m/z 341.1136.

methyl (*1S,3S,3aS,8bS*)-3a-nitro-3-(p-tolyl)-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c] pyrrole-1-carboxylate (3ab)



3ab

Light yellow oil. 57.3 mg, 81% yield, 8:1 dr, 99% ee.

$[\alpha]_D^{25}$ = 15.15 (c = 1.30, CH_2Cl_2).

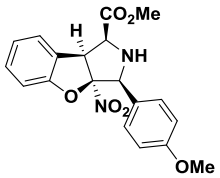
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.658 min (major), 20.653 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 (s, 4H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.02 – 6.95 (m, 2H), 5.06 (s, 1H), 4.73 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 158.9, 139.1, 130.5, 129.5, 129.3, 127.6, 125.0, 123.3, 123.2, 122.9, 110.7, 70.0, 64.4, 58.5, 52.4, 21.4.

HRMS (ESI): m/z calcd. For $C_{19}H_{18}N_2NaO_5$ $[M+Na]^+$ 377.1108, found m/z 377.1106.

methyl (*1S*,*3S*,*3aS*,*8bS*)-3-(4-methoxyphenyl)-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ac)



3ac

Light yellow oil. 62.9 mg, 85% yield, 10:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 15.15 (c = 1.30, CH_2Cl_2).

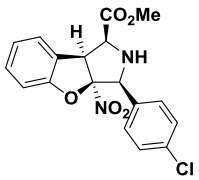
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 19.098 min (major), 23.383 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.09-7.06 (m, 1H), 7.03 – 6.98 (m, 2H), 6.94 – 6.90 (m, 2H), 5.06 (s, 1H), 4.74 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.74 (br s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 160.3, 158.9, 130.5, 129.1, 125.0, 124.4, 123.3, 123.2, 123.0, 114.2, 110.6, 77.4, 77.2, 77.0, 69.8, 64.3, 58.3, 55.4, 52.4.

HRMS (ESI): m/z calcd. For $C_{19}H_{18}N_2NaO_6$ $[M+Na]^+$ 393.1057, found m/z 393.1061.

methyl (*1S*,*3S*,*3aS*,*8bS*)-3-(4-chlorophenyl)-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ad)



3ad

Light yellow oil. 62.1 mg, 83% yield, 8:1 dr, 99% ee.

$[\alpha]_D^{25}$ = 51.46 (c = 1.30, CH_2Cl_2).

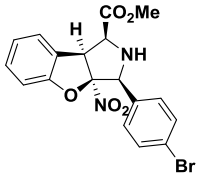
HPLC CHIRALCEL OJH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 25.693 min (major), 35.565 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.30 – 7.24 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03-6.96 (m, 2H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 4.65 (t, *J* = 8.8 Hz, 1H), 3.74 (s, 3H), 2.91 (t, *J* = 10.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 158.9, 135.2, 131.1, 130.6, 129.2, 129.0, 129.0, 127.6, 125.0, 123.4, 122.7, 122.7, 110.6, 69.3, 64.2, 58.2, 29.8.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}ClN_2NaO_5$ $[M+Na]^+$ 397.0562, found m/z 397.0556.

methyl (*1S,3S,3aS,8bS*)-3-(4-bromophenyl)-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ae)



3ae

Light brown oil. 66.8 mg, 80% yield, 7:1 dr, 96% ee.

$[\alpha]_D^{25}$ = 49.55 (c = 1.85, CH_2Cl_2).

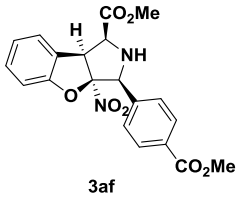
HPLC CHIRALCEL IE, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 18.290 min (minor), 19.733 min (major).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.02-6.96 (m, 2H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 4.64 (t, *J* = 9.0 Hz, 1H), 3.73 (s, 3H), 2.91 (t, *J* = 10.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 158.9, 132.0, 131.6, 130.6, 129.5, 125.0, 123.5, 123.4, 122.7, 122.6, 110.7, 69.4, 64.2, 58.2, 52.4.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}BrN_2NaO_5$ $[M+Na]^+$ 441.0057, found m/z 441.0062.

methyl (*1S,3S,3aS,8bS*)-3-(4-(methoxycarbonyl)phenyl)-3a-nitro-2,3,3a,8b-tetrahydro -1H-benzofuro[2,3-c]pyrrole-1-carboxylate (3af)



3af

Colorless oil. 59.7 mg, 75% yield, 9:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 51.46 (c = 1.30, CH_2Cl_2).

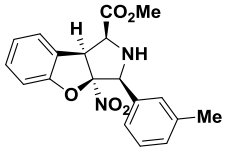
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 15.827 min (major), 23.255 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.01 (td, *J* = 7.2, 0.4 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.16 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 8.3 Hz, 1H), 4.71 – 4.64 (m, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 2.99 (t, *J* = 9.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 166.6, 158.8, 137.4, 130.8, 130.5, 129.9, 127.7, 124.9, 123.4, 122.6, 122.5, 110.6, 69.5, 64.2, 58.3, 52.3, 52.3.

HRMS (ESI): m/z calcd. For $C_{20}H_{18}N_2NaO_7$ $[M+Na]^+$ 421.1006, found m/z 421.1011.

methyl (*1S,3S,3aS,8bS*)-3a-nitro-3-(m-tolyl)-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ag)



3ag

Colorless oil. 51.7 mg, 73% yield, 5:1 dr, 97% ee.

$[\alpha]_D^{25}$ = 76.80 (c = 0.60, CH_2Cl_2).

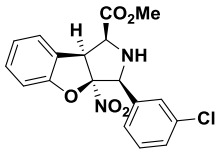
HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 15.355 min (major), 17.308 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (q, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.05 (m, 3H), 7.02 – 6.96 (m, 2H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 4.65 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.00 (t, *J* = 10.8 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 158.9, 138.5, 132.3, 130.5, 129.9, 128.6, 128.3, 124.9, 124.7, 123.3, 123.2, 122.9, 110.7, 70.0, 64.3, 58.6, 52.4, 29.8, 21.6.

HRMS (ESI): m/z calcd. For $C_{19}H_{18}N_2NaO_5$ $[M+Na]^+$ 377.1108, found m/z 377.1108.

methyl (*1S,3S,3aS,8bS*)-3-(3-chlorophenyl)-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ah)



3ah

White solid. 53.8 mg, 72% yield, 5:1 dr, 92% ee.

$[\alpha]_D^{25}$ = -99.24 (c = 0.35, CH_2Cl_2).

m.p.: 225.3-227.1 ^oC

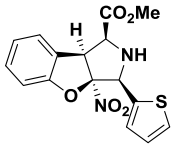
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.770 min (major), 11.933 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.97 (m, 2H), 5.08 (d, *J* = 11.3 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 4.65 (t, *J* = 9.0 Hz, 1H), 3.74 (s, 3H), 2.92 (t, *J* = 10.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 158.9, 134.8, 134.6, 130.6, 130.0, 129.4, 128.1, 126.1, 125.1, 123.5, 122.7, 122.6, 110.7, 69.3, 64.2, 58.3, 52.4.

HRMS (ESI): m/z calcd. For $C_{18}H_{16}ClN_2O_5$ $[M+H]^+$ 375.0742, found m/z 375.0738.

methyl (*1S,3R,3aS,8bS*)-3a-nitro-3-(thiophen-2-yl)-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ai)



3ai

Light brown oil. 49.1 mg, 71% yield, 10:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 88.95 (c = 0.65, CH_2Cl_2).

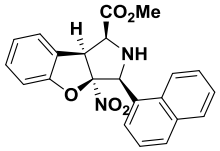
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 11.742 min (major), 19.582 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 7.10 – 6.98 (m, 4H), 5.34 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 8.0 Hz, 1H), 4.64 (d, *J* = 9.6 Hz, 1H), 3.71 (s, 3H), 2.99 (t, *J* = 11.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 158.9, 134.1, 130.6, 127.5, 127.0, 126.9, 125.0, 123.5, 122.7, 122.5, 110.8, 66.5, 64.4, 58.5, 52.4.

HRMS (ESI): m/z calcd. For $C_{16}H_{14}N_2NaO_5S$ $[M+Na]^+$ 369.0516, found m/z 369.0511.

methyl (*1S,3S,3aS,8bS*)-3-(naphthalen-1-yl)-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3aj)



3aj

Light brown oil. 63.2 mg, 81% yield, 8:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 39.57 (c = 1.3, CH_2Cl_2).

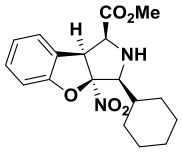
HPLC CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 11.742 min (major), 19.582 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.53 – 7.48 (m, 2H), 7.38 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.01 (td, *J* = 7.5, 0.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 8.4 Hz, 1H), 4.72 (t, *J* = 8.6 Hz, 1H), 3.12 (t, *J* = 10.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 158.9, 133.5, 133.1, 130.4, 129.8, 128.4, 128.2, 127.7, 127.2, 126.6, 126.5, 124.9, 124.8, 123.3, 123.1, 122.7, 110.6, 70.0, 64.3, 58.5, 52.3.

HRMS (ESI): m/z calcd. For $C_{22}H_{18}N_2NaO_5$ $[M+Na]^+$ 413.1108, found m/z 413.1105.

methyl (*1S,3S,3aS,8bS*)-3-cyclohexyl-3a-nitro-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c] pyrrole-1-carboxylate (3ak)



3ak

Light yellow oil. 56.1 mg, 81% yield, 7:1 dr, 96% ee.

$[\alpha]_D^{25}$ = 97.16 (c = 0.95, CH_2Cl_2).

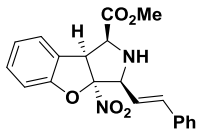
HPLC CHIRALCEL ID, n-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.266 min (minor), 10.217 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25,(m , 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.99 – 6.95 (m, 2H), 4.48 (s, 2H), 3.83 (d, *J* = 9.2 Hz, 1H), 3.67 (s, 3H), 2.30 (br s, 1H), 2.00 (d, J = 12.4 Hz, 1H), 1.83 – 1.63 (m, 5H), 1.35 – 1.11 (m, 5H), 1.07 – 0.90 (m, 1H).

^{13}C NMR (100MHz, $CDCl_3$) δ 168.9, 159.1 130.5, 124.9 123.3 123.0, 122.6, 110.6, 64.4, 60.5, 52.3, 37.7, 31.1, 29.8, 28.6, 26.1, 25.8, 25.6.

HRMS (ESI): m/z calcd. For $C_{18}H_{22}N_2NaO_5$ $[M+Na]^+$ 369.1421, found m/z 369.1425.

methyl (*1S,3S,3aS,8bS*)-3a-nitro-3-((*E*)-styryl)-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c] pyrrole-1-carboxylate (3al)



3al

Colorless oil. 51.2 mg, 70% yield, 6:1 dr, 96% ee.

$[\alpha]_D^{25}$ = 128.01 (c = 0.60, CH_2Cl_2).

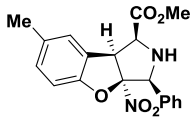
HPLC CHIRALCEL IA, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 14.337 min (minor), 16.935 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.8 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.09 – 7.05 (m, 2H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.28 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.73 (d, *J* = 8.4 Hz, 1H), 4.66 – 4.63 (m, 2H), 3.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 158.9, 136.7, 135.8, 130.6, 129.3, 128.8, 128.6, 127.0, 124.9, 123.8, 123.4, 122.9, 119.9, 110.8, 77.5, 77.2, 76.8, 69.4, 64.8, 58.4, 52.4.

HRMS (ESI): m/z calcd. For $C_{20}H_{18}N_2NaO_5$ $[M+Na]^+$ 389.1108, found m/z 389.1113.

methyl (*1S,3S,3aS,8bS*)-7-methyl-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ba)



3ba

Light yellow oil. 56.7 mg, 80% yield, 7:1 dr, 97% ee.

$[\alpha]_D^{25}$ = 99.01 (c = 1.0, CH_2Cl_2).

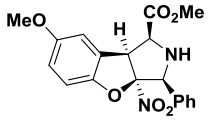
HPLC CHIRALCEL IA, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 14.882 min (minor), 16.022 min (major).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 3H), 7.31 – 7.29 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 2H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.65 (m, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.01 (t, *J* = 11.1 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 156.9, 132.9, 132.5, 130.9, 129.2, 128.8, 127.8, 125.4, 123.4, 122.8, 110.2, 70.0, 64.4, 58.8, 52.3, 21.0.

HRMS (ESI): m/z calcd. For $C_{19}H_{19}N_2O_5$ $[M+H]^+$ 355.1288, found m/z 355.1282.

methyl (*1S,3S,3aS,8bS*)-7-methoxy-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ca)



3ca

Colorless oil. 60.7 mg, 82% yield, 10:1 dr, 94% ee.

$[\alpha]_D^{25}$ = -113.20 (c = 1.0, CH_2Cl_2).

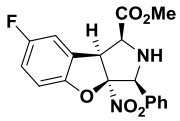
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 18.992 min (major), 35.137 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.38(m, 3H), 7.31 – 7.29 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 9.0 Hz, 1H), 4.65 (t, *J* = 9.3 Hz 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.06 – 2.99 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 156.1, 153.0, 132.5, 129.2, 128.8, 127.8, 123.8, 123.7, 115.4, 111.0, 110.8, 70.0, 64.3, 58.9, 56.1, 52.5, 29.9.

HRMS (ESI): m/z calcd. For $C_{19}H_{18}N_2NaO_6$ $[M+Na]^+$ 393.1057, found m/z 393.1061.

methyl (*1S,3S,3aS,8bS*)-7-fluoro-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3da)



3da

Light yellow oil. 53.7 mg, 75% yield, 9:1 dr, 95% ee.

$[\alpha]_D^{25}$ = -113.20 (c = 1.0, CH_2Cl_2).

HPLC CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 13.230 min (minor), 14.932 min (major).

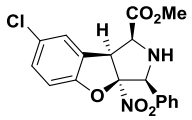
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 3H), 7.32 – 7.30 (m, 2H), 6.97 (td, *J* = 8.7, 2.6 Hz, 1H), 6.91 (dd, *J* = 8.9, 4.1 Hz, 1H), 6.79 (dd, *J* = 7.7, 2.6 Hz, 1H), 5.10 (s, 1H), 4.71 (d, *J* = 8.5 Hz, 1H), 4.67 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H), 2.29 (br s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 158.9 (d, $J_{C\text{-}F}$ = 238.5 Hz), 154.9, 132.2, 129.3, 128.9, 128.8, 127.8, 126.2, 124.3 (d, $J_{C\text{-}F}$ = 9.0 Hz), 123.6, 117.1 (d, $J_{C\text{-}F}$ = 25.5 Hz), 112.3 (d, $J_{C\text{-}F}$ = 25.5 Hz), 111.3, (d, $J_{C\text{-}F}$ = 9.0 Hz), 69.9, 64.1, 58.4, 52.6, 29.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -120.1 (s).

HRMS (ESI): m/z calcd. For $C_{18}H_{16}FN_2O_5$ $[M+H]^+$ 359.1038, found m/z 359.1038.

methyl (*1S,3S,3aS,8bS*)-7-chloro-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ea)



3ea

Light yellow oil. 59.1 mg, 79% yield, 8:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 80.67 (c = 0.65, CH_2Cl_2).

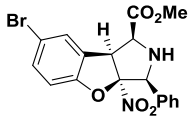
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 10.952 min (major), 16.840 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 3H), 7.32– 7.30 (m, 2H), 7.24 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.05 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.13 (s, 1H), 5.02 (s, 0H), 4.72 – 4.67 (m, 2H), 4.00 (s, 0H), 3.78 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 157.5, 131.9, 130.6, 129.4, 128.9, 128.5, 127.8, 125.3, 124.7, 123.2, 111.7, 58.1, 52.6, 29.9.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}ClN_2NaO_5$ $[M+Na]^+$ 397.0562, found m/z 397.0560.

methyl (*1S,3S,3aS,8bS*)-7-bromo-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3fa)



3fa

Light yellow oil. 65.2 mg, 78% yield, 6:1 dr, 97% ee.

$[\alpha]_D^{25}$ = 40.33 (c = 0.60, CH_2Cl_2).

m.p.: 160.3-162.8 °C

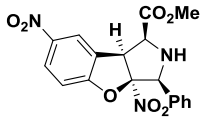
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 14.892 min (major), 25.466 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.32 – 7.27 (m, 2H), 7.20 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.70 (t, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H), 3.04 – 2.96 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 158.0, 133.4, 132.2, 129.3, 128.8, 128.2, 127.7, 125.3, 123.2, 115.4, 112.2, 69.9, 64.2, 58.1, 52.5.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}BrN_2NaO_5$ $[M+Na]^+$ 441.0057, found m/z 441.0059.

methyl (*1S,3S,3aS,8bS*)-3a,7-dinitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c] pyrrole-1-carboxylate (3ga)



3ga

Light yellow oil. 57.0 mg, 74% yield, 15:1 dr, 99% ee.

$[\alpha]_D^{25}$ = 103.03 (c = 0.43, CH_2Cl_2).

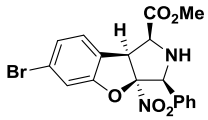
HPLC CHIRALCEL IA, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 254 nm, retention time: 14.002 min (major), 15.212 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.42-7.39 (m, 3H), 7.32-7.30 (m, 2H), 7.07 (d, *J* = 9.2 Hz, 1H), 5.16 (s, 1H), 4.78-4.72 (m, 2H), 3.83 (s, 3H), 2.65 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.3, 144.1, 131.7, 129.6, 128.9, 127.8, 127.5, 124.8, 123.3, 121.6, 110.9, 56.9, 52.8.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}N_3NaO_7$ $[M+Na]^+$ 408.0802, found m/z 408.0798.

methyl (*1S,3S,3aS,8bS*)-6-bromo-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ha)



3ha

Light yellow oil. 69.4 mg, 83% yield, 8:1 dr, 95% ee.

$[\alpha]_D^{25}$ = 86.14 (c = 0.45, CH_2Cl_2).

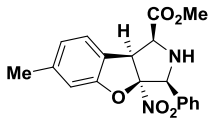
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 11.603 min (major), 17.175 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 3H), 7.30 – 7.29 (m, 2H), 7.15 – 7.13 (m, 2H), 6.94 (d, *J* = 8.4Hz, 1H), 5.10 (d, *J* = 11.3 Hz, 1H), 4.66 – 4.64 (m, 2H), 3.74 (s, 3H), 2.99-2.93 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 159.6, 132.2, 129.3, 128.8, 127.8, 126.6, 126.1, 123.8, 123.3, 122.2, 114.4, 69.9, 64.1, 57.9, 52.5.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}BrN_2NaO_5$ $[M+Na]^+$ 441.0057, found m/z 441.0058.

methyl (*1S,3S,3aS,8bS*)-6-methyl-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ia)



3ia

Light yellow oil. 60.9 mg, 86% yield, 11:1 dr, 99% ee.

$[\alpha]_D^{25}$ = 86.14 (c = 0.45, CH_2Cl_2).

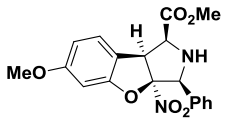
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.420 min (major), 15.513 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 3H), 7.32 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.13 (s, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H), 2.78 (br s, 1H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 159.2, 141.2, 132.3, 129.2, 128.8, 127.8, 124.5, 124.2, 123.3, 119.7, 111.3, 69.8, 64.2, 58.3, 52.4, 29.8, 21.7.

HRMS (ESI): m/z calcd. For $C_{19}H_{19}N_2O_5$ $[M+H]^+$ 355.1288, found m/z 355.1283.

methyl (*1S,3S,3aS,8bS*)-6-methoxy-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ja)



3ja

Colorless oil. 61.4 mg, 83% yield, 10:1 dr, 99% ee.

$[\alpha]_D^{25}$ = 34.30 (c = 0.85, CH_2Cl_2).

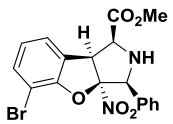
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.420 min (major), 15.513 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 3H), 7.27 – 7.22 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.47 (m, 2H), 5.06 (s, 1H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.57 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 2.91 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 162.1, 160.2, 132.2, 129.3, 128.8, 127.8, 125.2, 123.7, 114.2, 109.8, 96.8, 69.7, 64.2, 58.0, 55.7, 52.5.

HRMS (ESI): m/z calcd. For $C_{19}H_{18}N_2NaO_6$ $[M+Na]^+$ 393.1057, found m/z 393.1053.

methyl (*1S,3S,3aS,8bS*)-5-bromo-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3ka)



3ka

Light yellow oil. 66.0 mg, 79% yield, 9:1 dr, 98% ee.

$[\alpha]_D^{25}$ = 95.14 (c = 0.50, CH_2Cl_2).

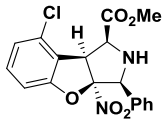
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 11.717 min (major), 14.002 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.39 (m, 3H), 7.38 – 7.36 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 5.11 (s, 1H), 4.80 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 3.73 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 156.4, 133.7, 131.9, 129.4, 128.8, 128.3, 124.5, 124.2, 123.9, 122.1, 103.3, 70.1, 64.3, 59.0, 52.5.

HRMS (ESI): m/z calcd. For $C_{18}H_{15}BrN_2NaO_5$ $[M+Na]^+$ 441.0057, found m/z 441.0060.

methyl (*1S,3S,3aS,8bS*)-8-chloro-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro [2,3-c]pyrrole-1-carboxylate (3la)



3la

Light yellow oil. 61.3 mg, 82% yield, 10:1 dr, 92% ee.

$[\alpha]_D^{25}$ = 100.33 (c = 0.70, CH_2Cl_2).

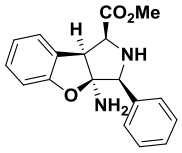
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 254 nm, retention time: 9.168 min (major), 11.119 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 3H), 7.33 –7.31 (m, 2H), 7.22 (t, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 1H), 4.82 (d, *J* = 8.4 Hz, 1H), 4.62 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 0H), 3.71 (s, 3H), 2.96 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 159.3, 131.8, 131.7, 130.7, 129.3, 128.9, 128.9, 127.6, 126.0, 123.9, 123.5, 122.3, 109.4, 69.4, 63.5, 58.9, 52.8.

HRMS (ESI): m/z calcd. For $C_{18}H_{16}ClN_2O_5$ $[M+H]^+$ 375.0742, found m/z 375.0741.

methyl (*1S,3S,3aS,8bS*)-3a-amino-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c] pyrrole-1-carboxylate (4aa)



4aa

White solid. 33 mg, 71% yield, 99% ee.

$[\alpha]_D^{25}$ = -30.05 (c = 0.92, CH_2Cl_2).

m.p.: 121.7-124.5 ^oC

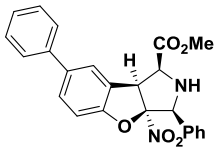
HPLC CHIRALCEL ID, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 18.477 min (major), 24.298 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.14 (m, 4H), 7.01 (t, *J* = 6.6 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.67 (t, *J* = 6.9 Hz, 1H), 4.65 (s, 1H), 4.41 (d, *J* = 6.6 Hz, 1H), 4.14 (d, *J* = 6.6 Hz, 1H), 3.33 (s, 3H).

^{13}C NMR (150 MHz, MeOD) δ 171.6, 163.2, 155.9, 139.1, 133.7, 132.7, 129.9, 129.8, 129.7, 129.3, 129.2, 129.0, 128.9, 128.4, 124.8, 120.1, 116.9, 65.1, 64.4, 52.1.

HRMS (ESI): m/z calcd. For $C_{18}H_{19}N_2O_3$ $[M+H]^+$ 311.1390, found m/z 311.1384.

methyl(*1S,3S,3aS,8bS*)-3a-nitro-3,7-diphenyl-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c] pyrrole-1-carboxylate (4fa)



4fa

Colorless oil. 36.6 mg, 88% yield, 96% ee.

$[\alpha]_D^{25}$ = 167.11 (c = 0.40, CH_2Cl_2).

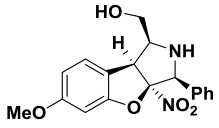
HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 11.760 min (major), 19.002 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 3H), 7.44 – 7.41 (m, 5H), 7.36 – 7.33 (m, 3H), 7.30 (s, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 5.17 (s, 1H), 4.79 (d, *J* = 9.0 Hz, 1H), 4.74 (d, *J* = 9.0 Hz, 1H), 3.72 (s, 3H), 2.22 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 158.4, 140.4, 137.2, 131.9, 129.8, 129.4, 129.0, 128.9, 127.9, 127.5, 126.9, 123.9, 123.4, 123.1, 110.9, 69.8, 64.2, 58.2, 52.6.

HRMS (ESI): m/z calcd. For $C_{24}H_{21}N_2O_5$ $[M+H]^+$ 417.1445, found m/z 417.1442.

((*1S,3S,3aS,8bS*)-6-methoxy-3a-nitro-3-phenyl-2,3,3a,8b-tetrahydro-1H-benzofuro[2,3-c]pyrrol-1-yl)methanol (4ia)



4ia

Light yellow oil. 38.5 mg, 75% yield, 96% ee.

$[\alpha]_D^{25}$ = 50.43 (c = 0.60, CH_2Cl_2).

HPLC CHIRALCEL ODH, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 11.760 min (major), 19.002 min (minor).

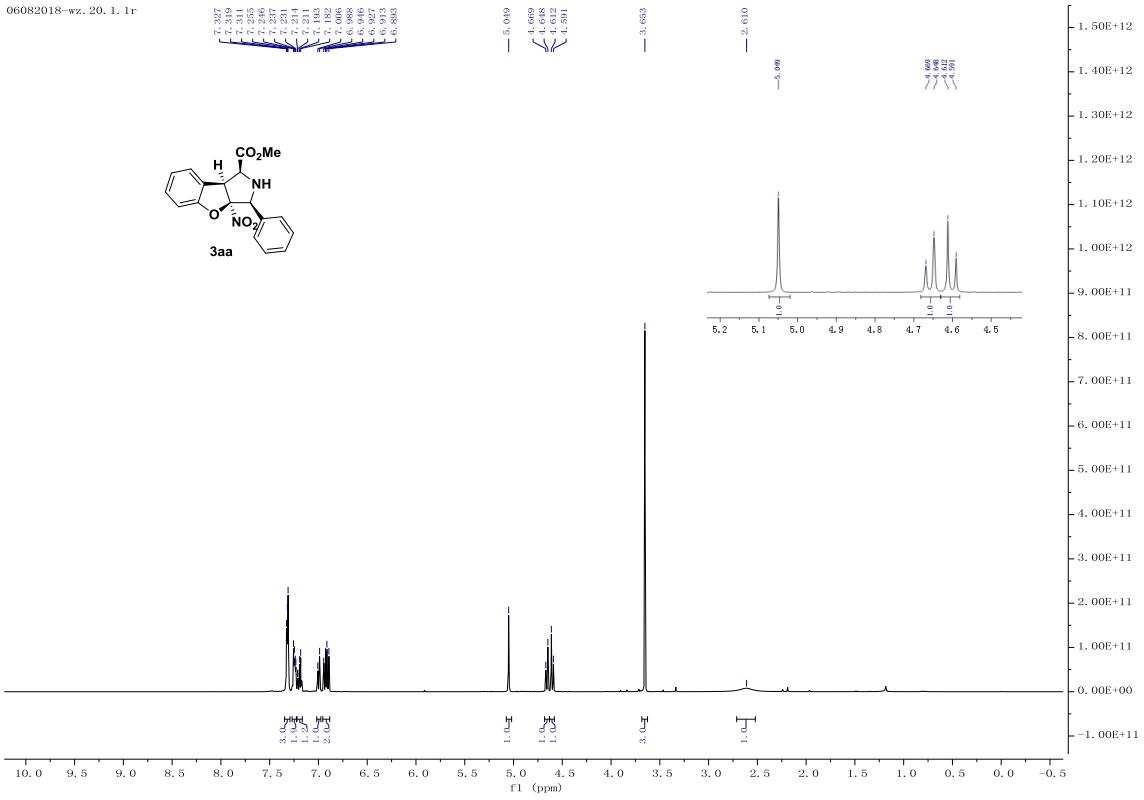
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 3H), 7.33 (s, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 9.0 Hz, 2H), 5.11 (s, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.96 (q, *J* = 6.0 Hz, 1H), 3.80 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.77 (s, 3H), 3.69 (dd, *J* = 10.2, 6.0 Hz, 1H), 2.51 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 160.3, 133.3, 129.8, 129.2, 128.6, 128.2, 125.6, 123.8, 115.4, 114.4, 109.4, 96.8, 69.9, 62.1, 61.9, 56.4, 55.7, 29.8.

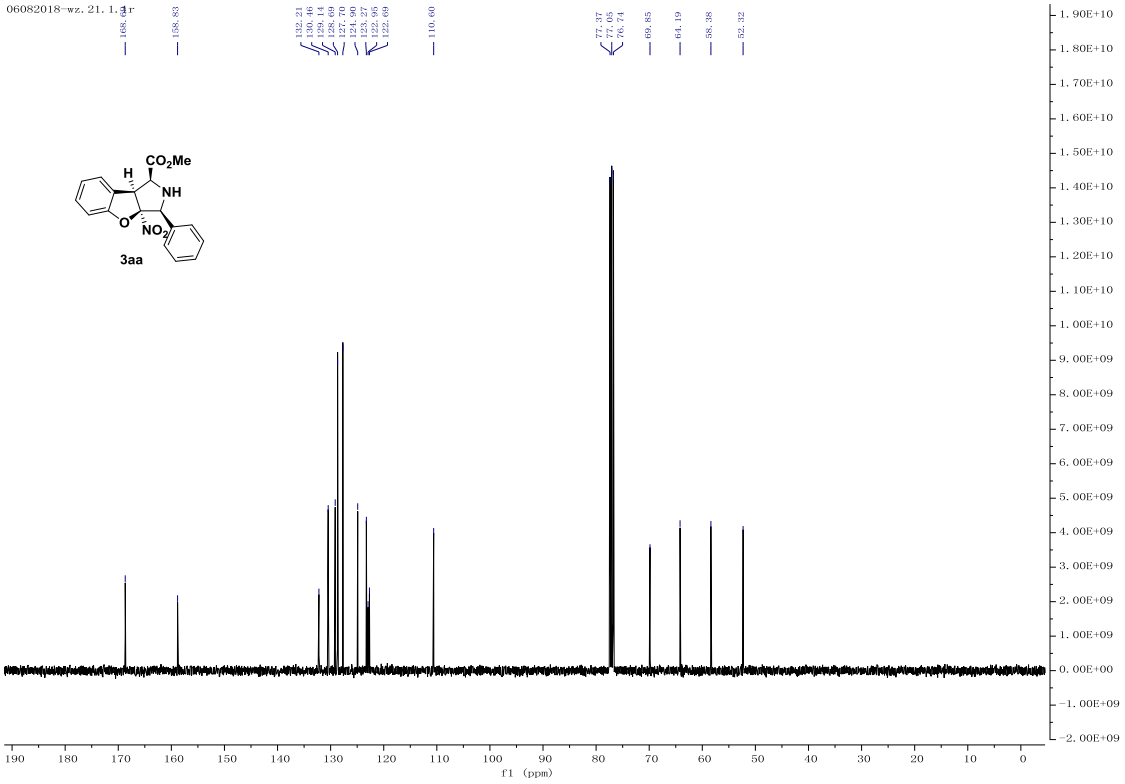
HRMS (ESI): m/z calcd. For $C_{18}H_{18}N_2NaO_5$ $[M+Na]^+$ 365.1108, found m/z 365.1115.

7. Copies of NMR spectra

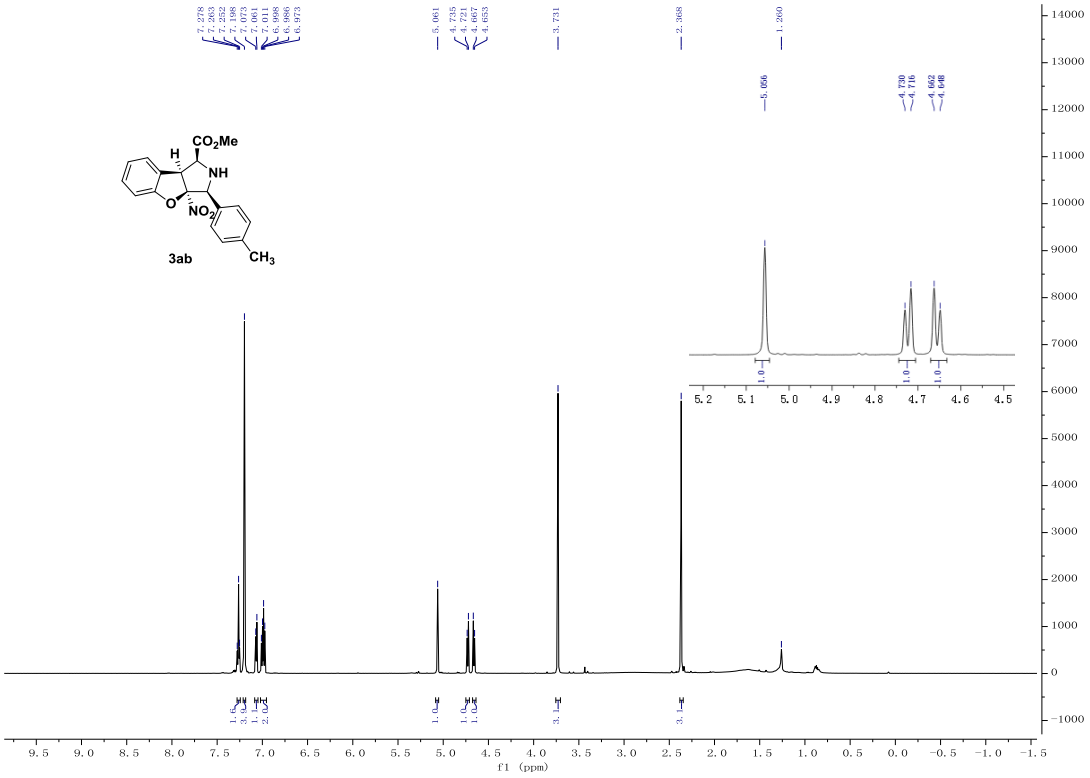
^{1}H NMR of 3aa



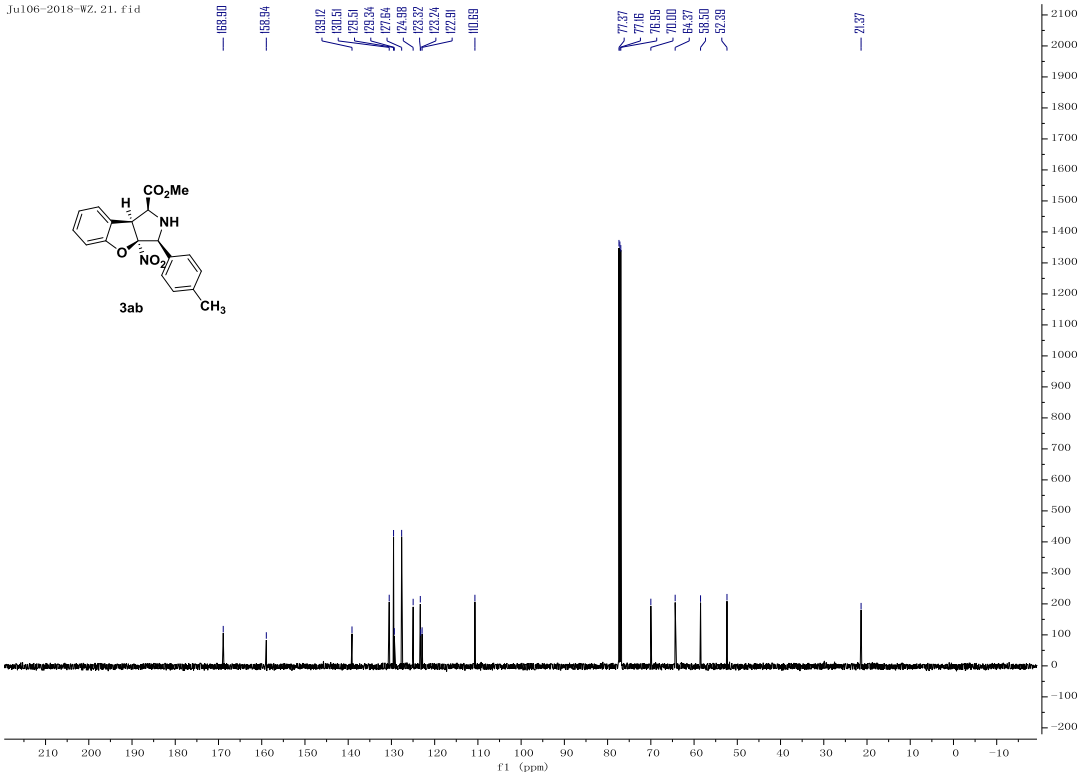
^{13}C NMR of 3aa



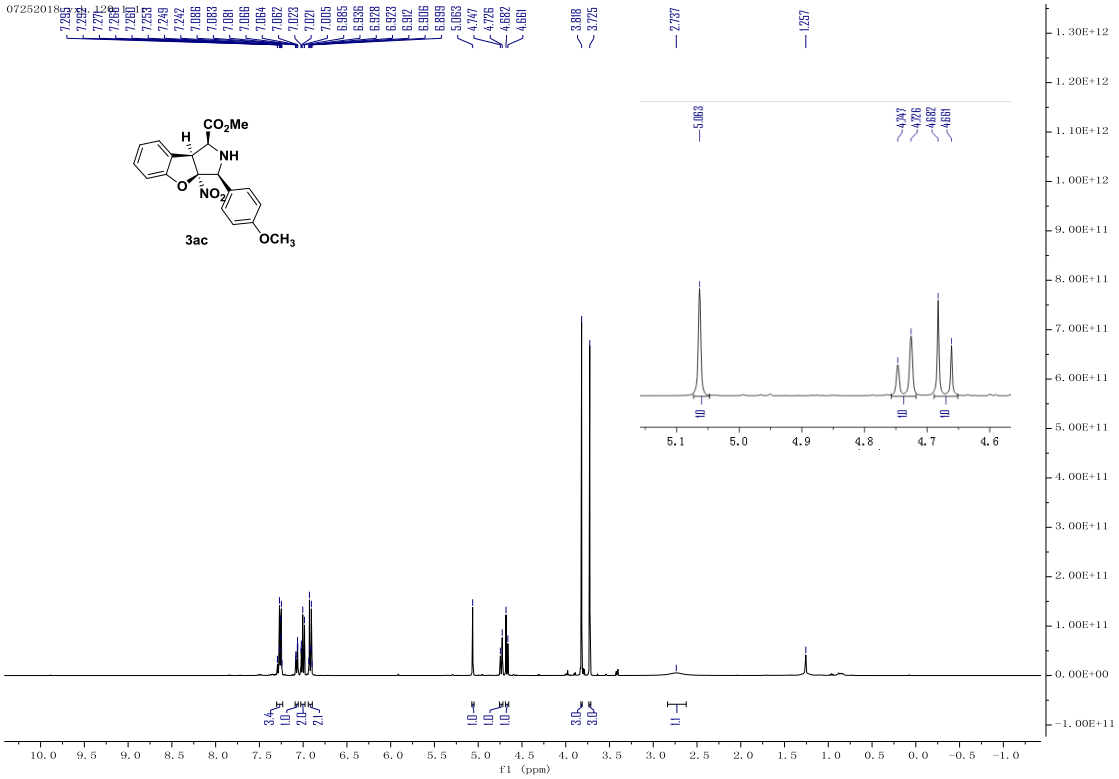
^{1}H NMR of 3ab



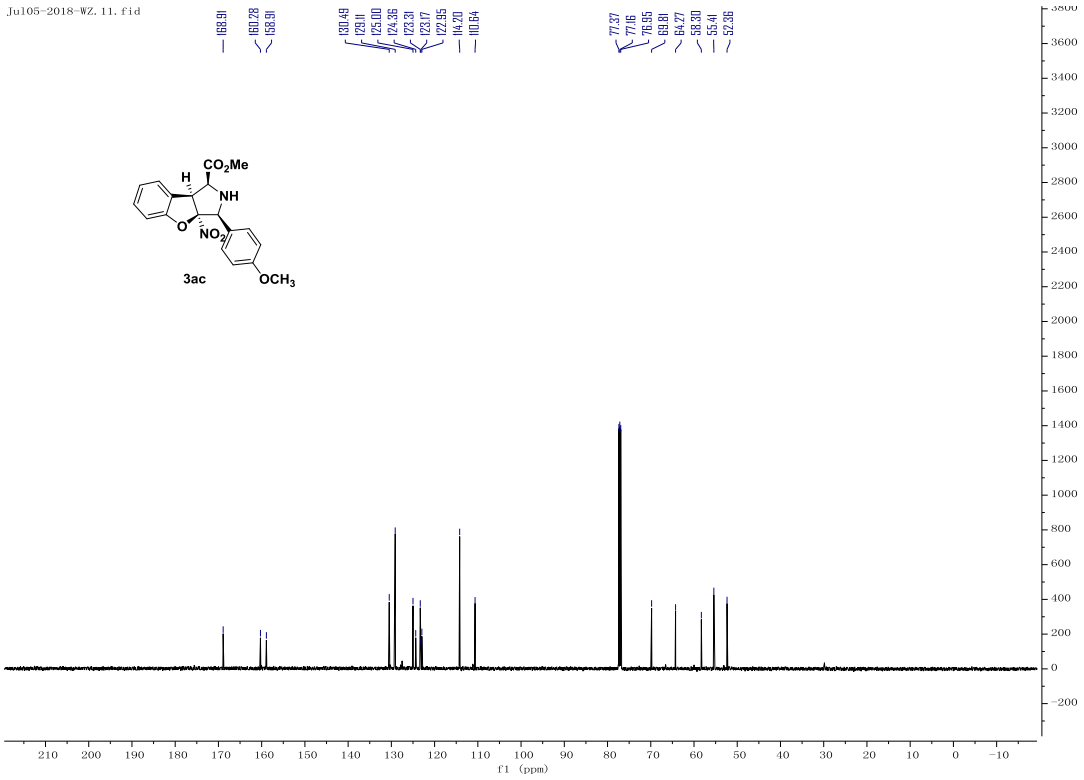
^{13}C NMR of 3ab



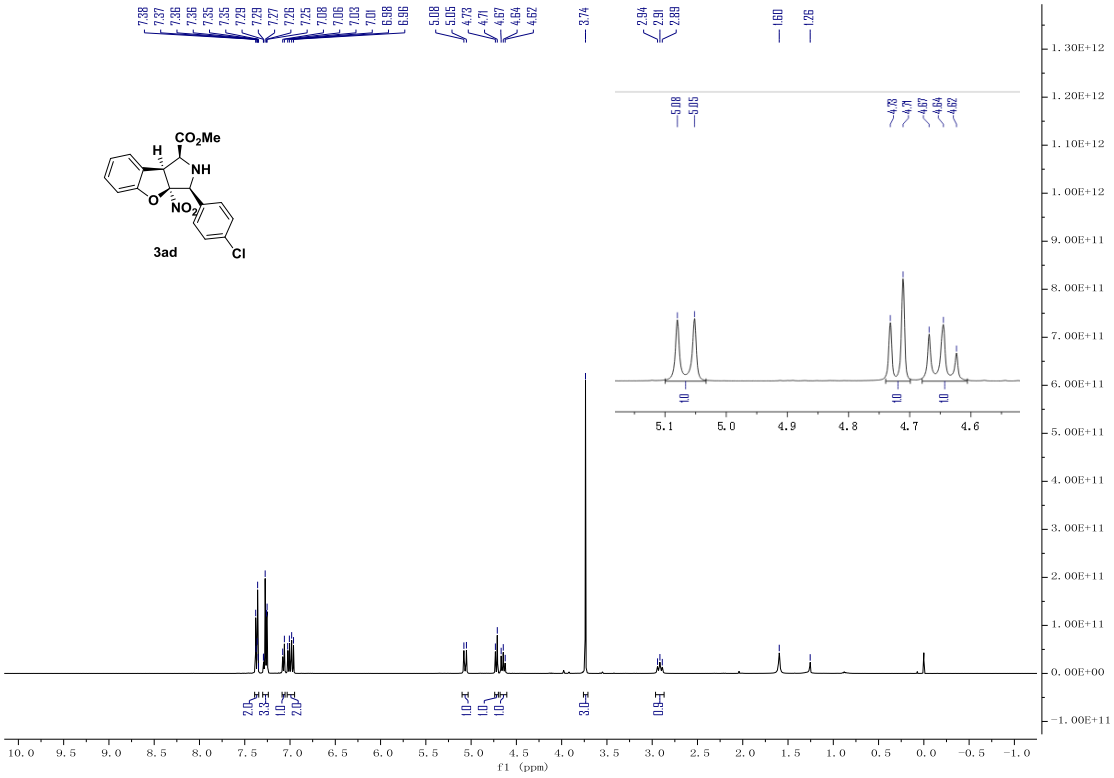
^{1}H NMR of 3ac



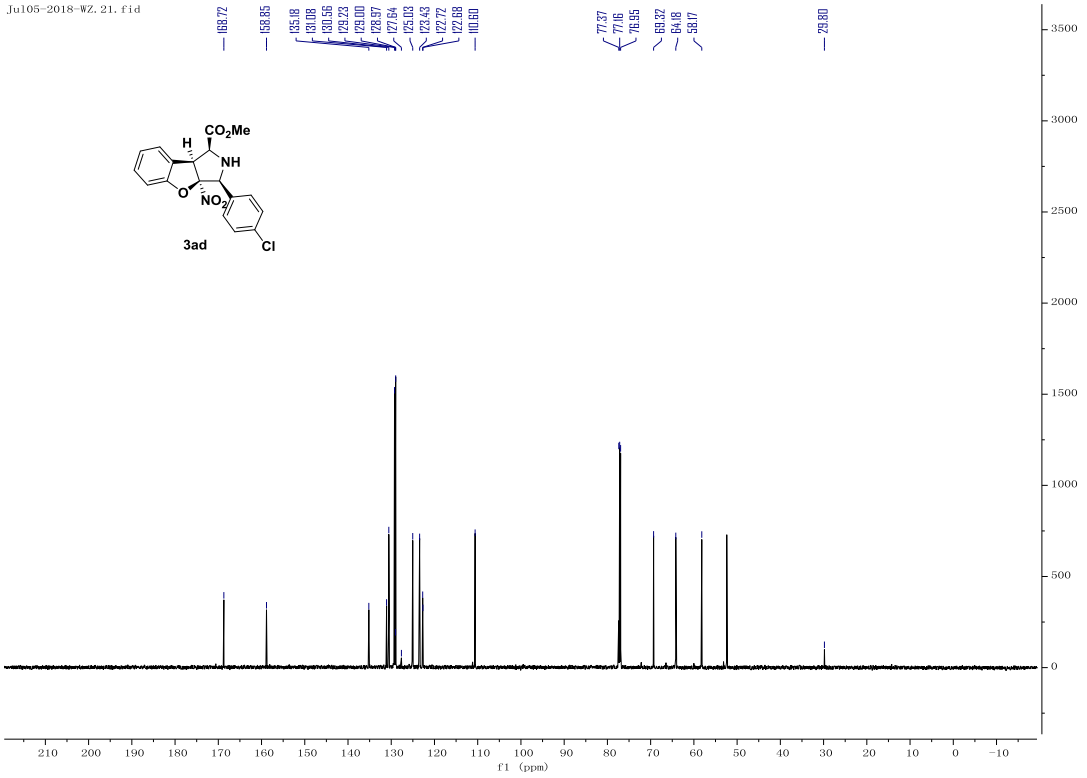
^{13}C NMR of 3ac



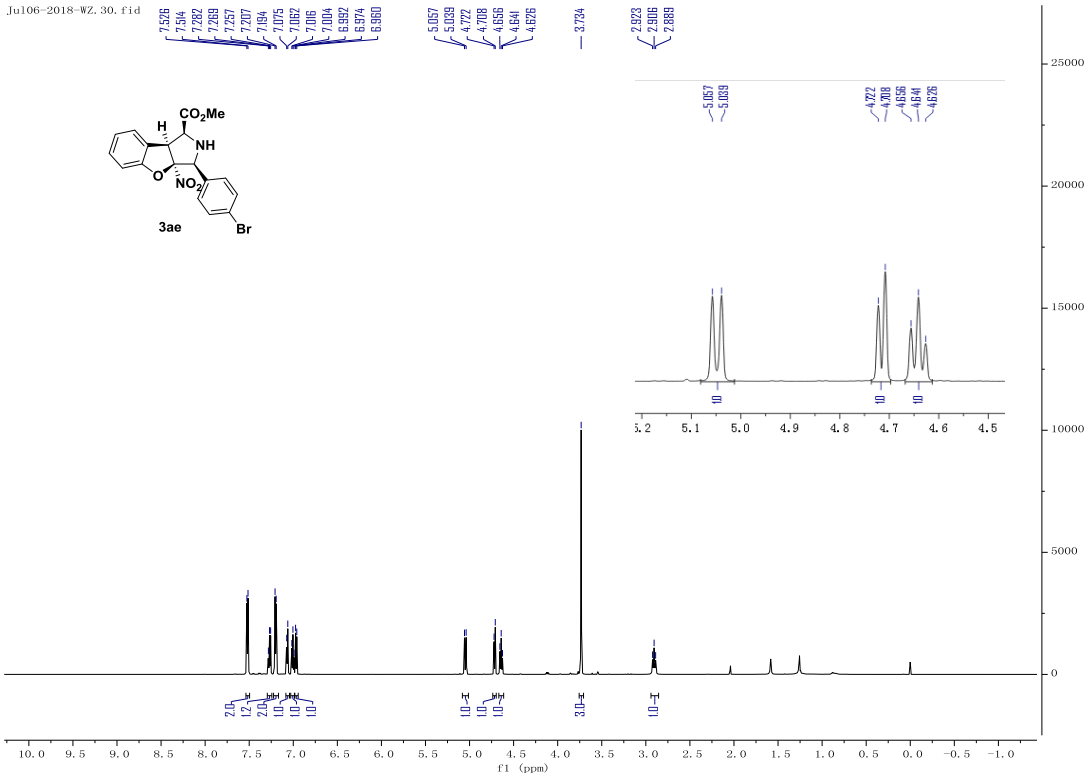
^{1}H NMR of 3ad



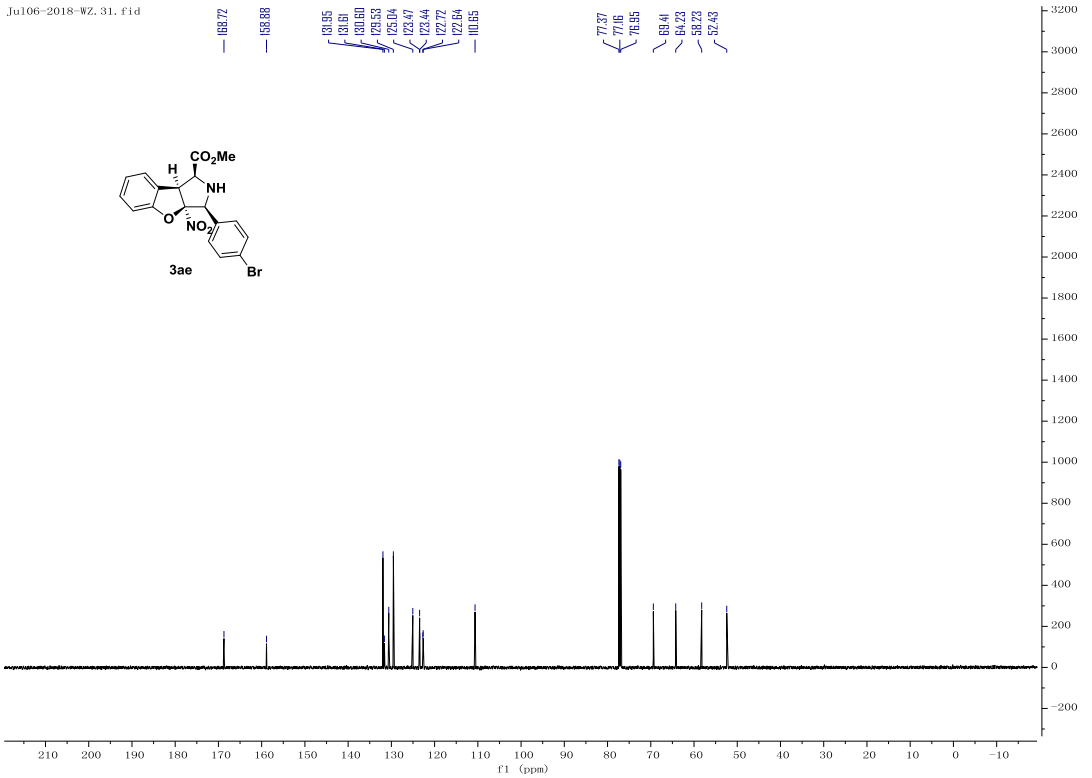
^{13}C NMR of 3ad



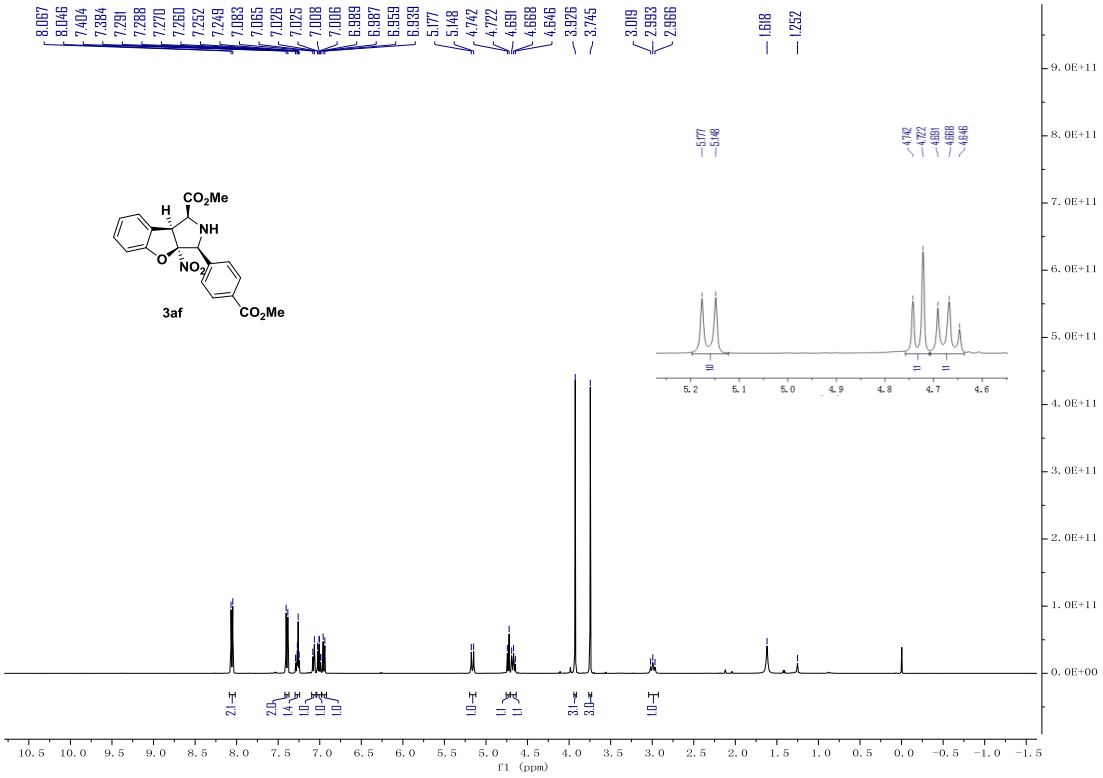
^{1}H NMR of 3ae



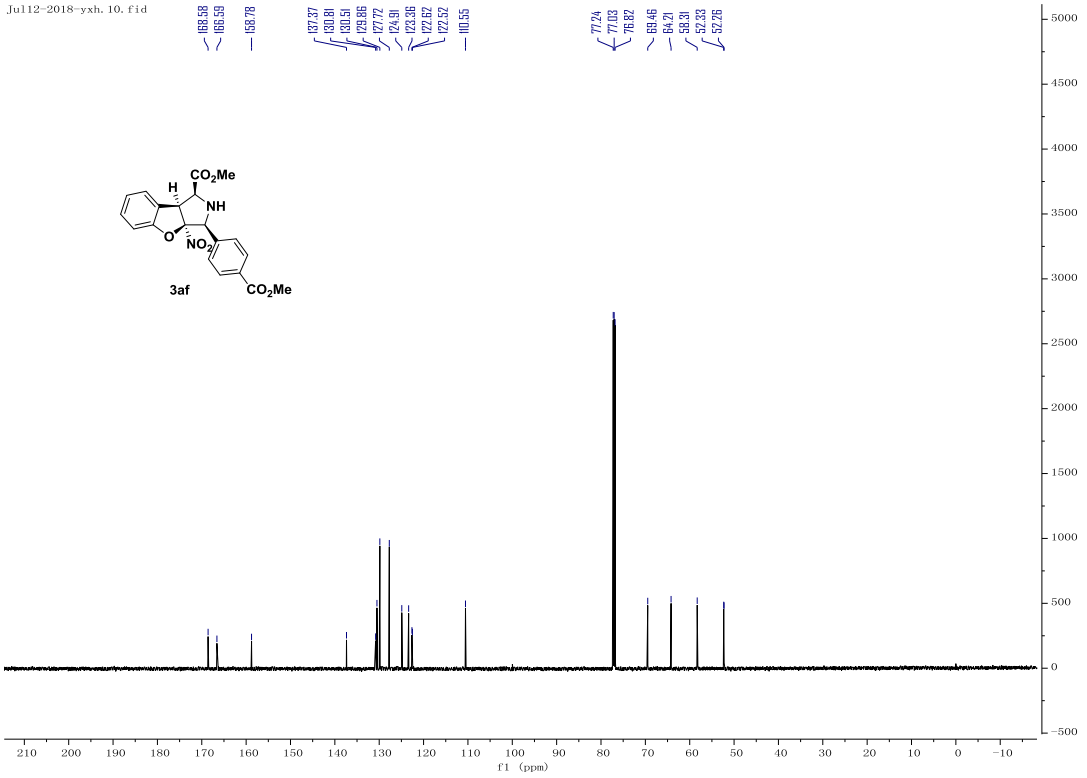
^{13}C NMR of 3ae



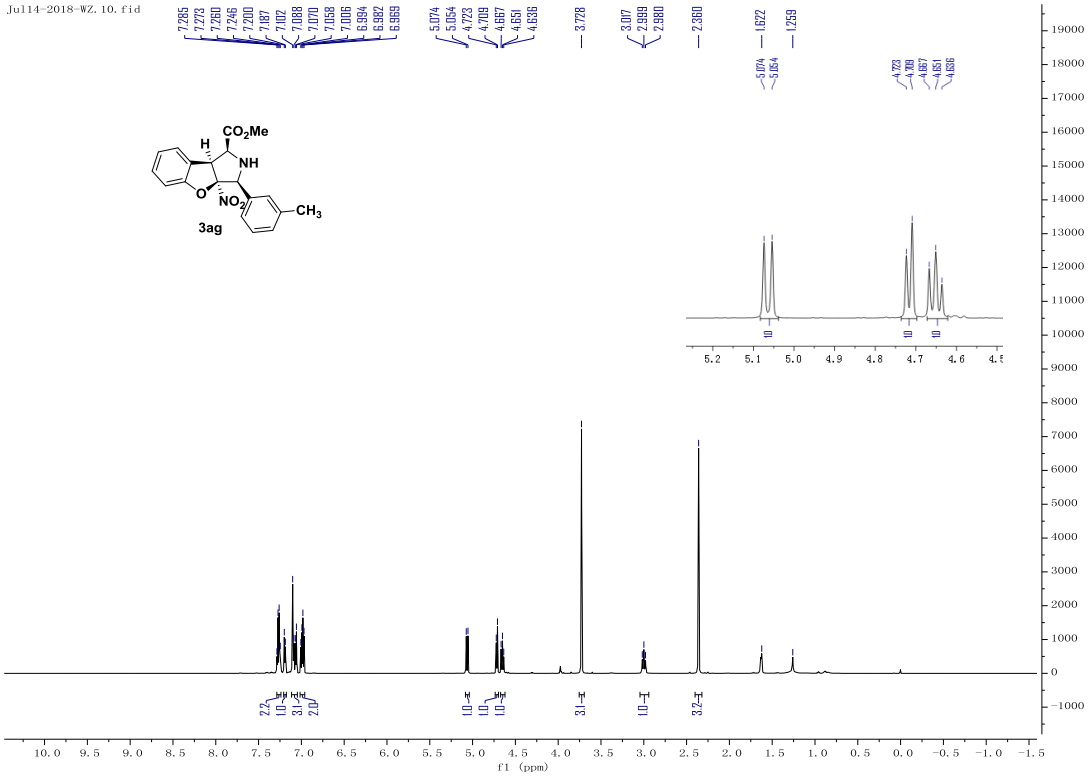
^{1}H NMR of 3af



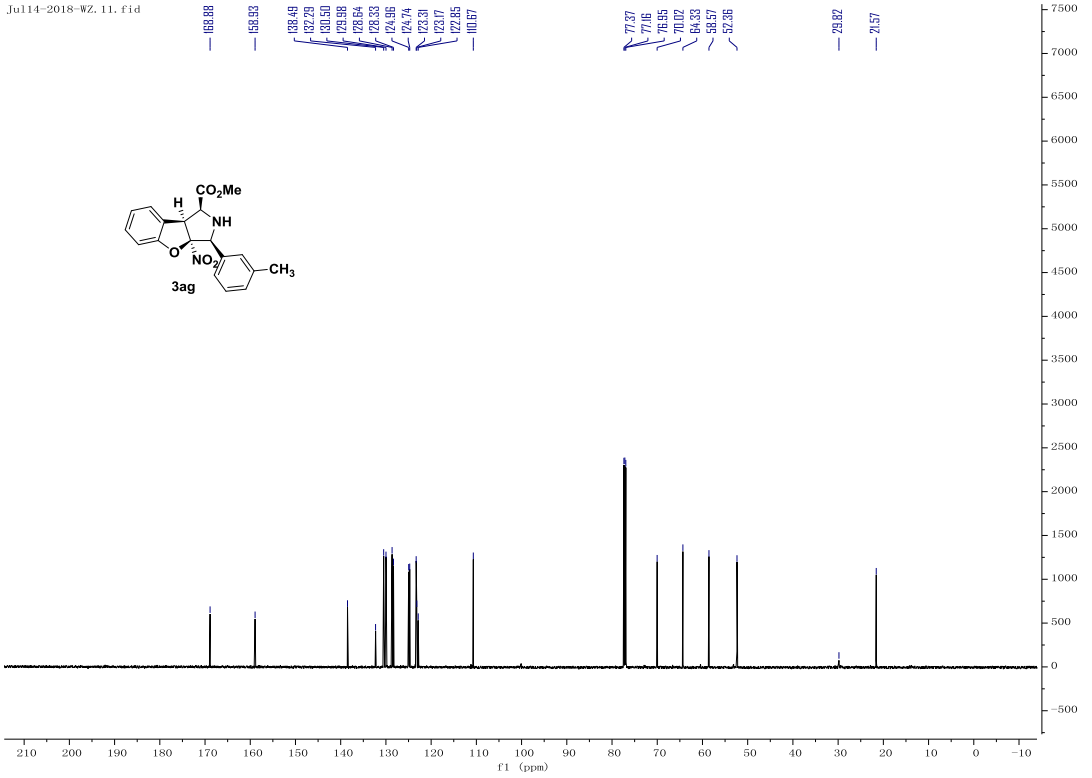
^{13}C NMR of 3af



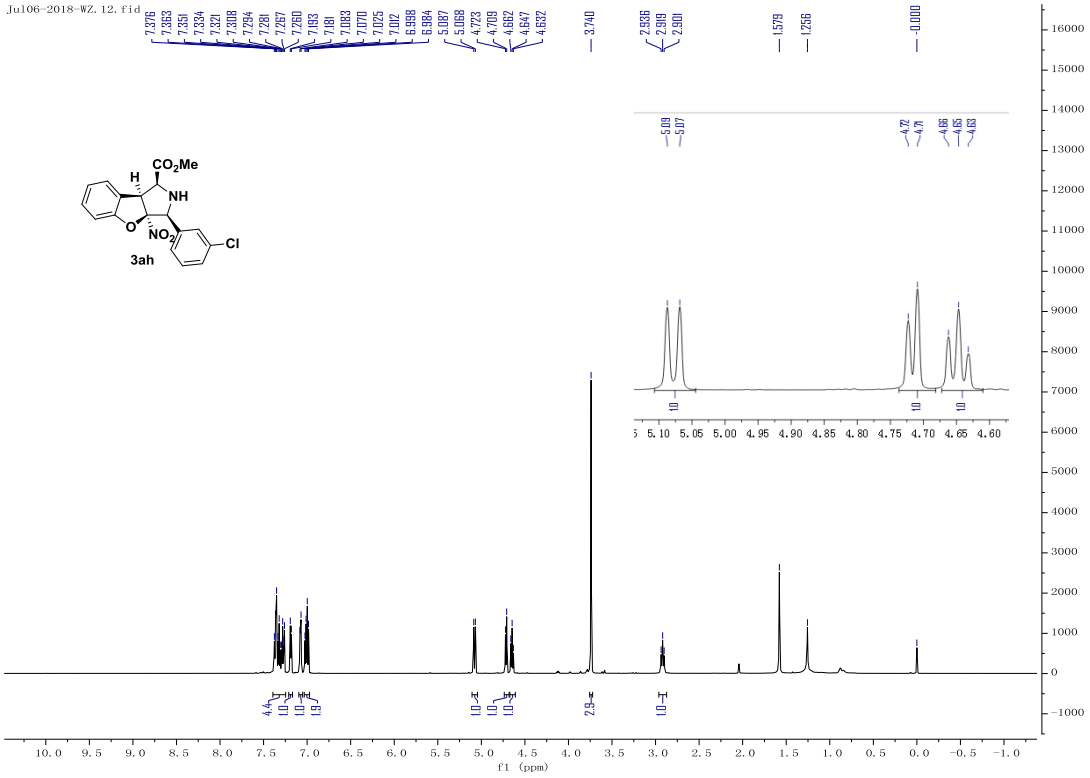
^{1}H NMR of 3ag



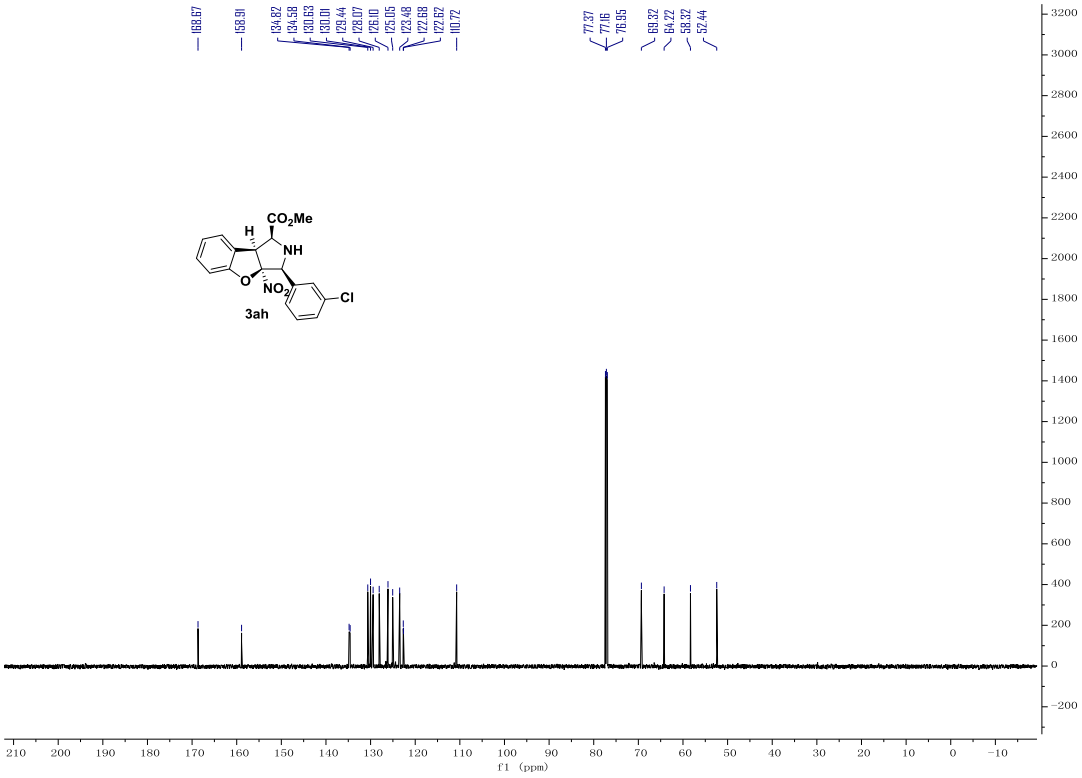
^{13}C NMR of 3ag



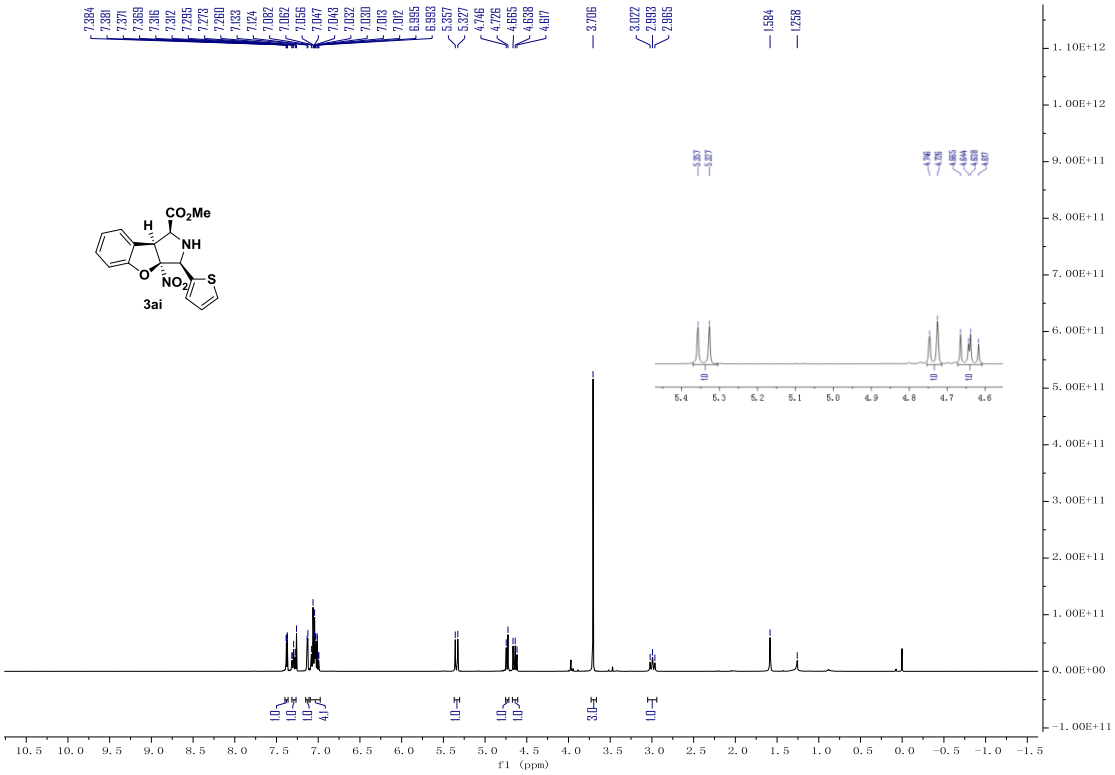
^{1}H NMR of 3ah



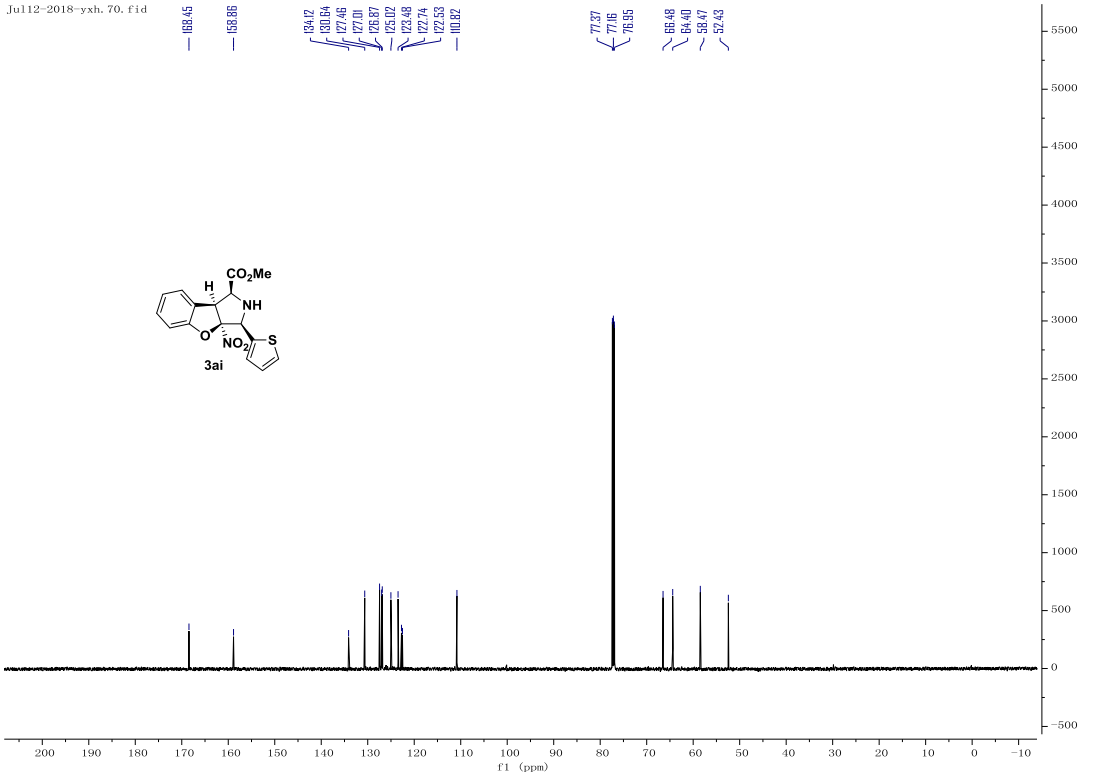
^{13}C NMR of 3ah



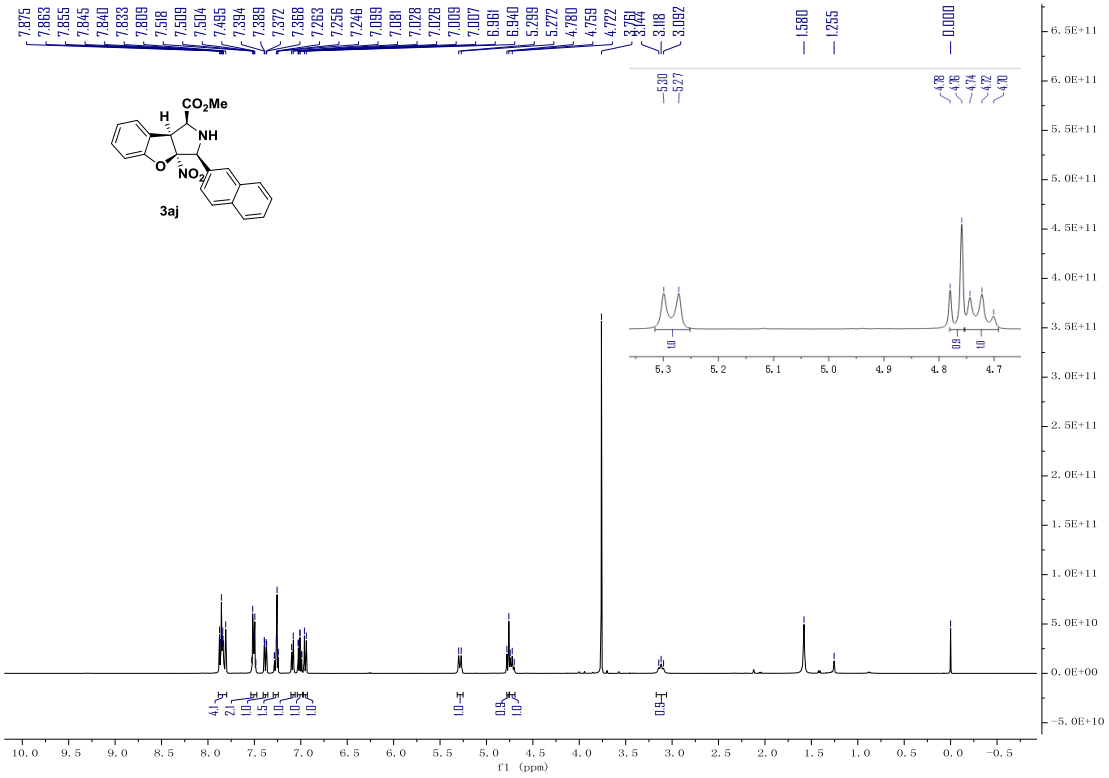
^{1}H NMR of 3ai



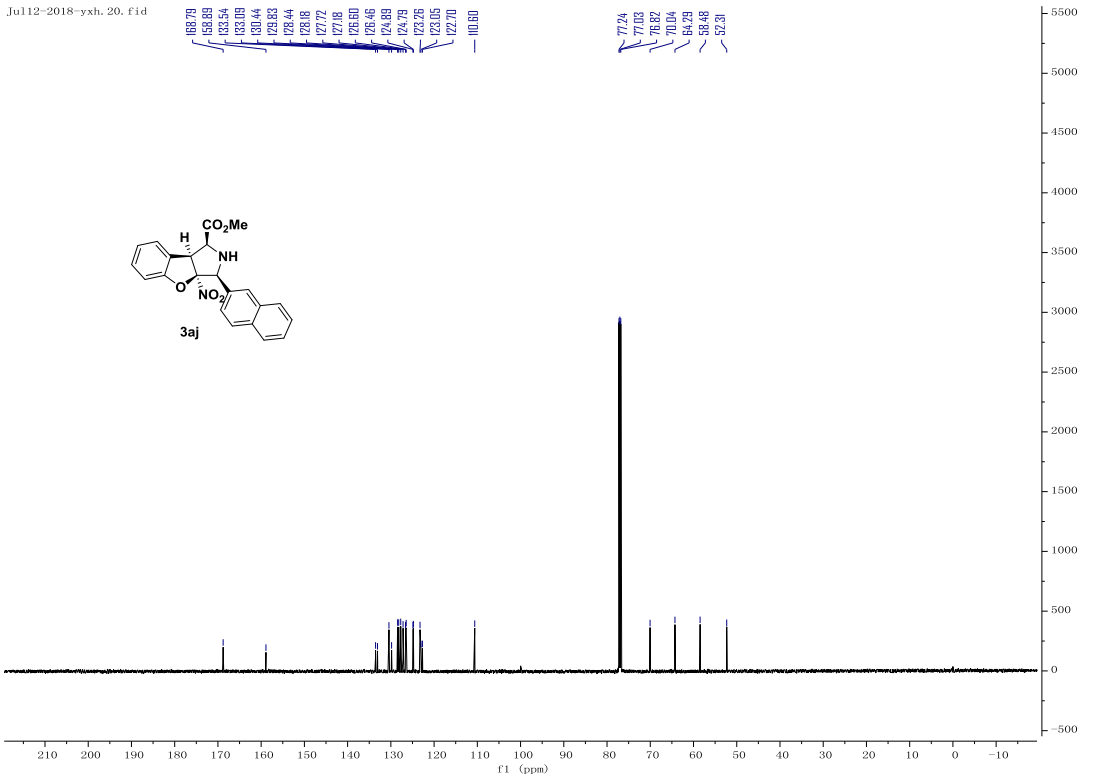
^{13}C NMR of 3ai



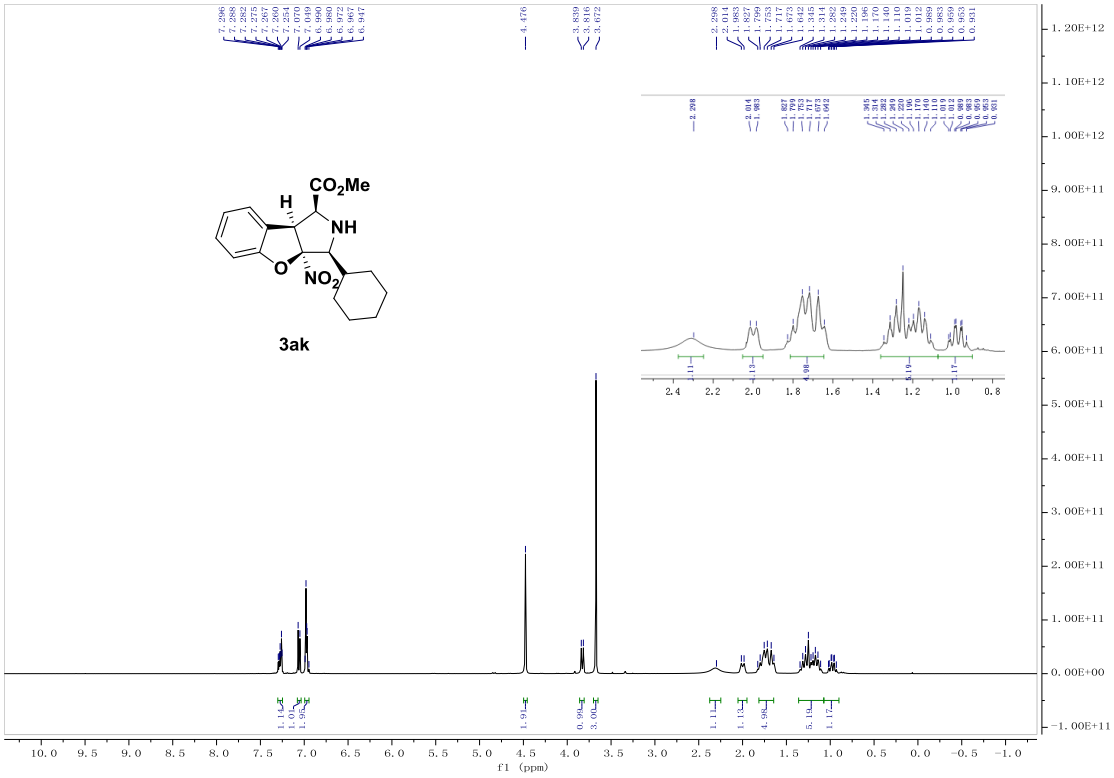
^{1}H NMR of 3aj



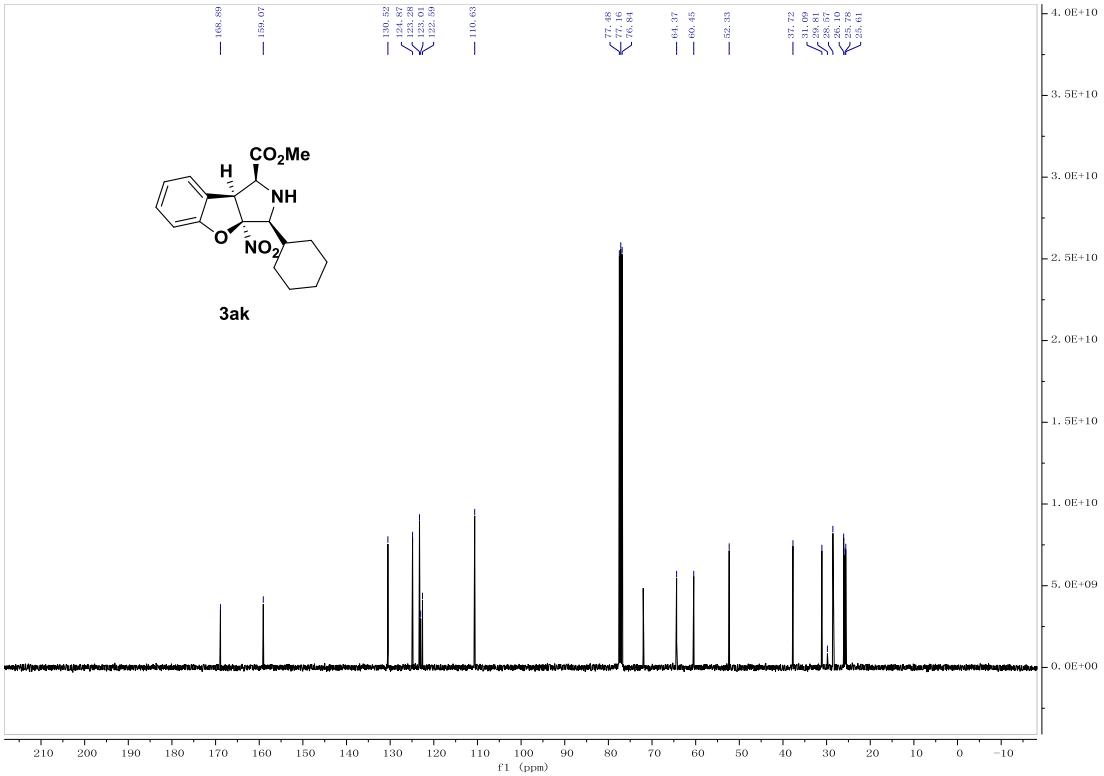
^{13}C NMR of 3aj



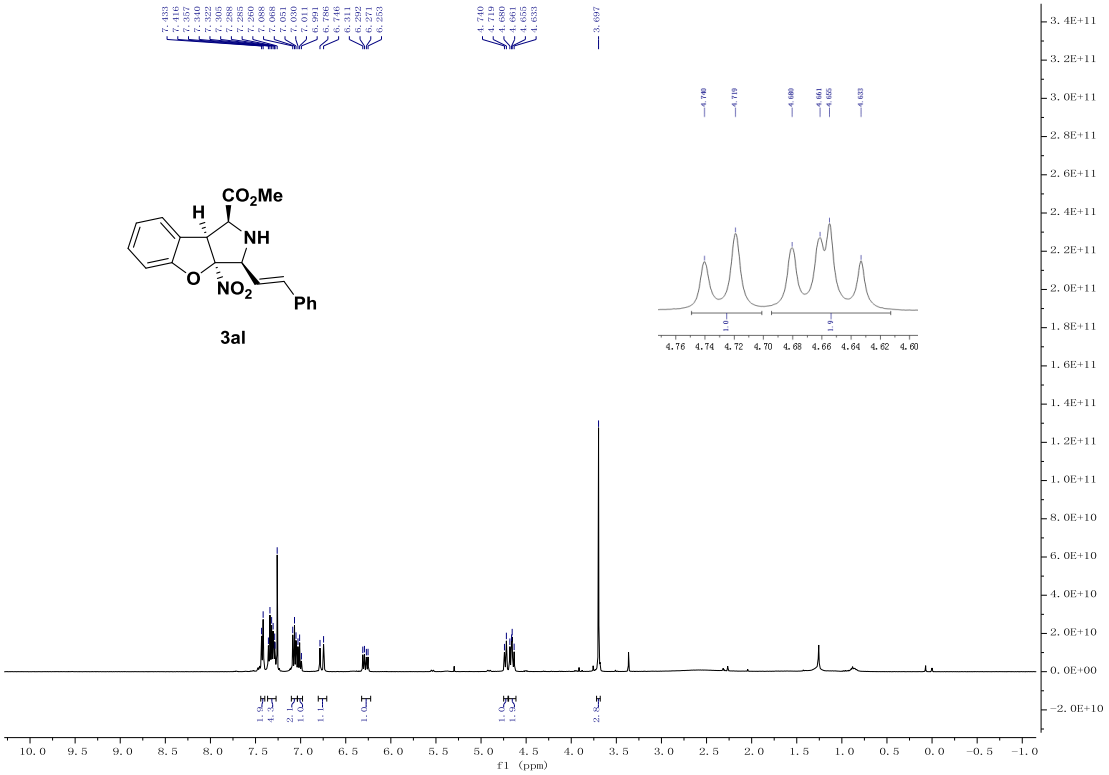
^{1}H NMR of 3ak



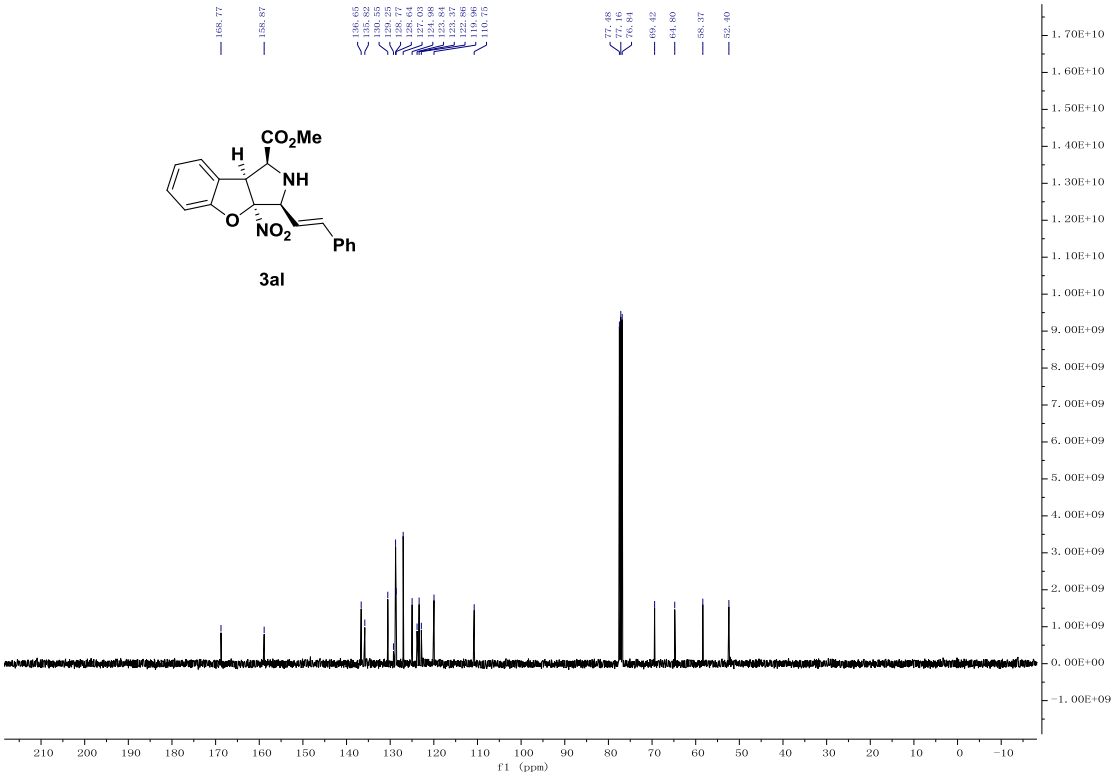
^{13}C NMR of 3ak



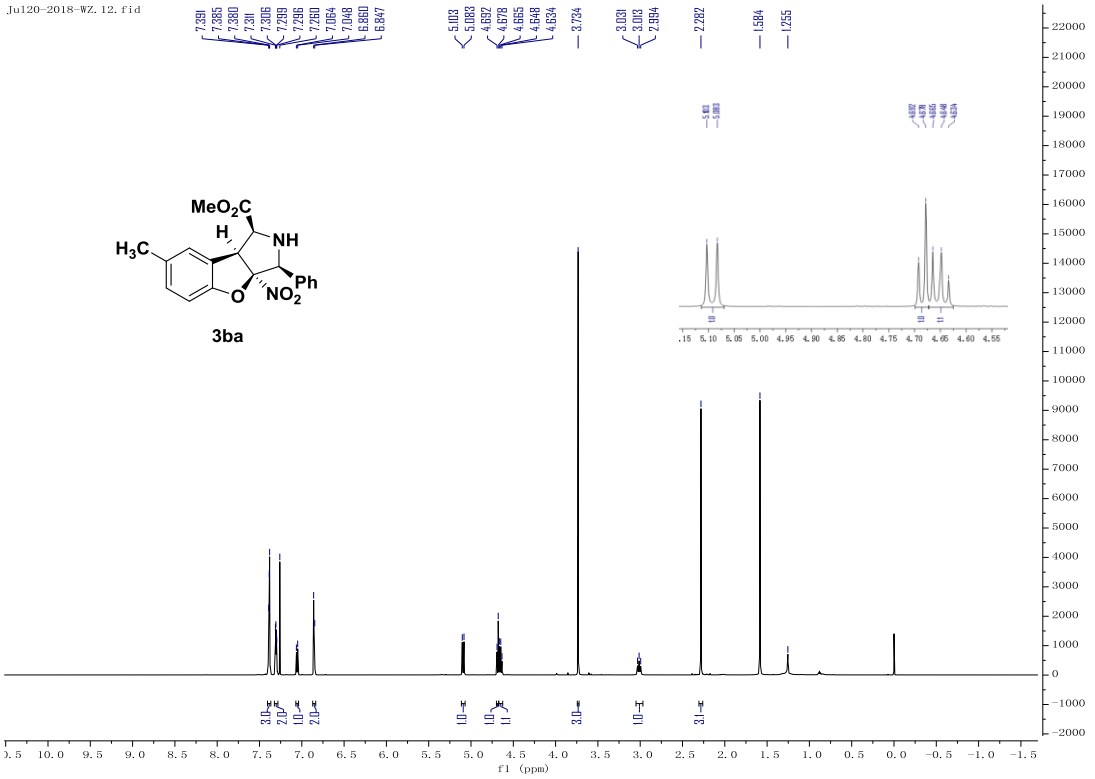
^{1}H NMR of 3al



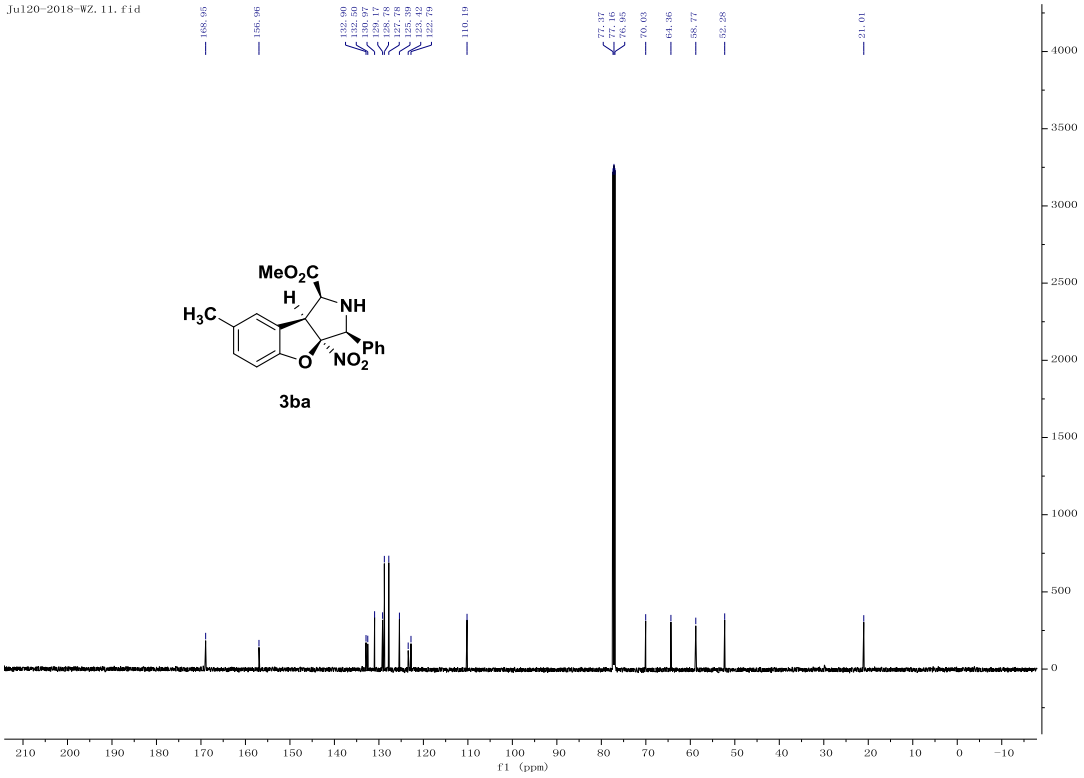
^{13}C NMR of 3al



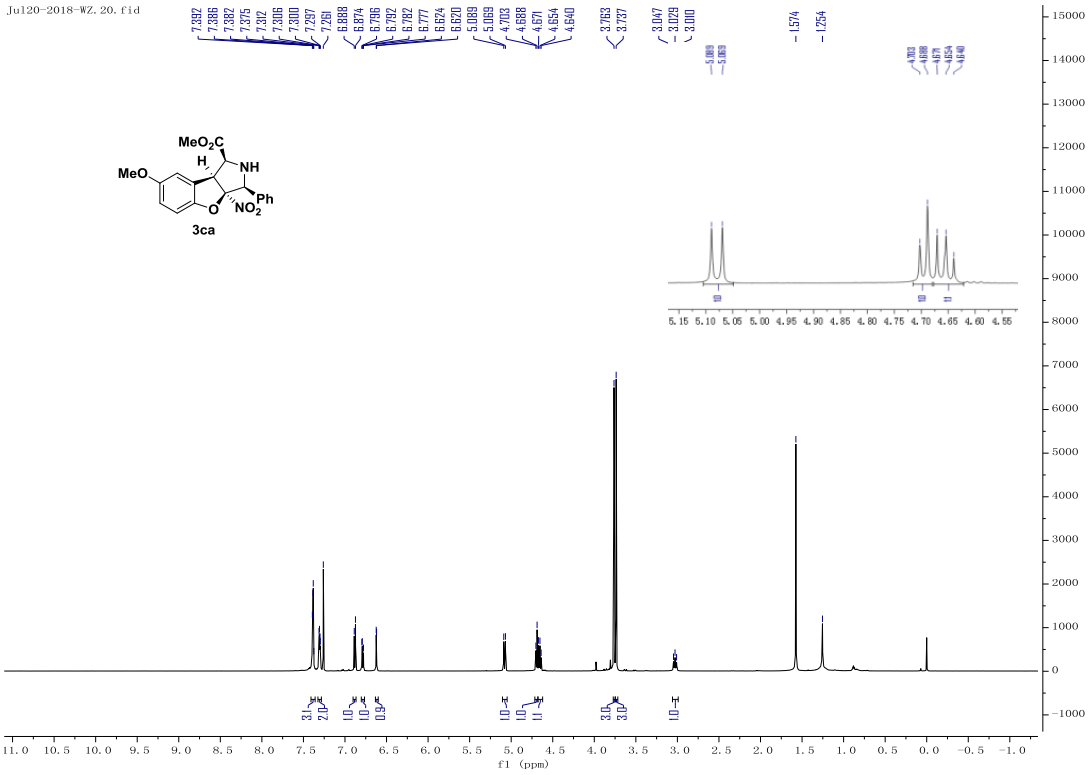
^{1}H NMR of 3ba



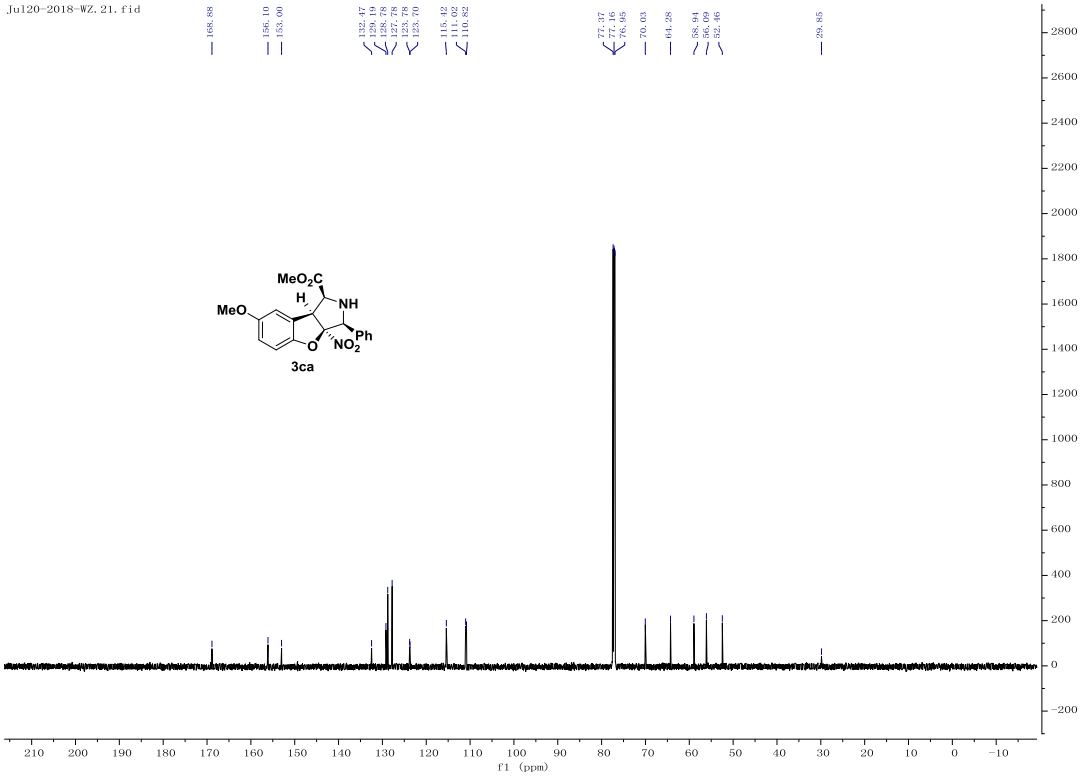
^{13}C NMR of 3ba



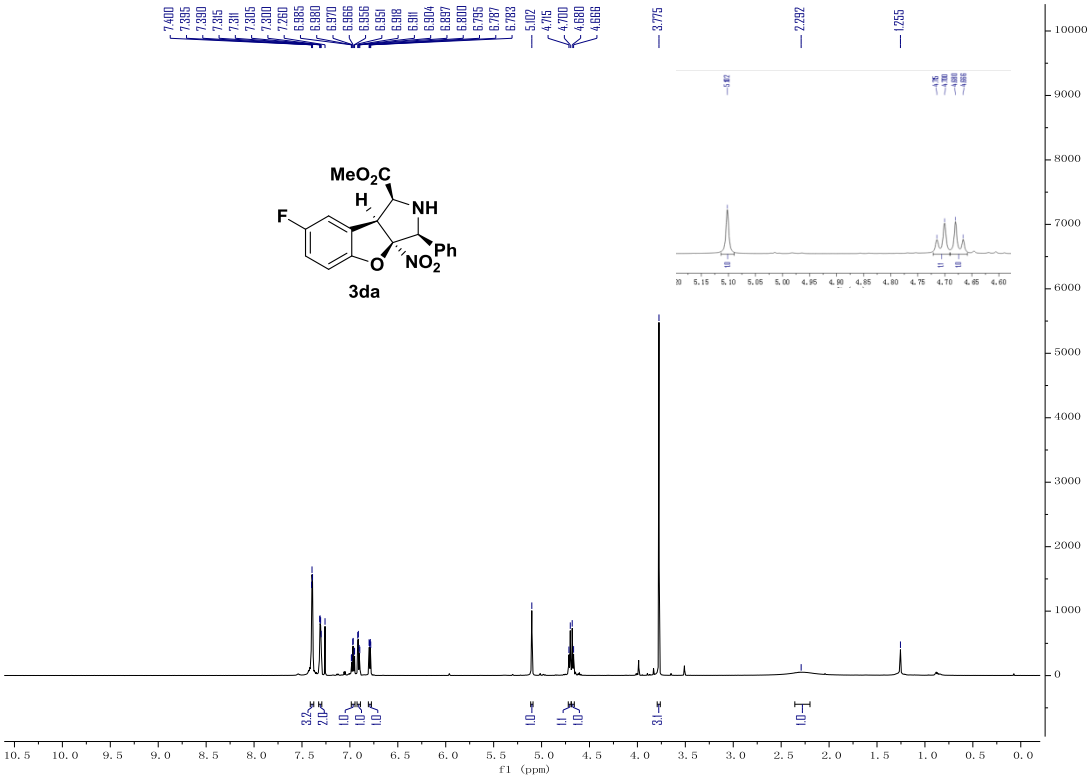
^{1}H NMR of 3ca



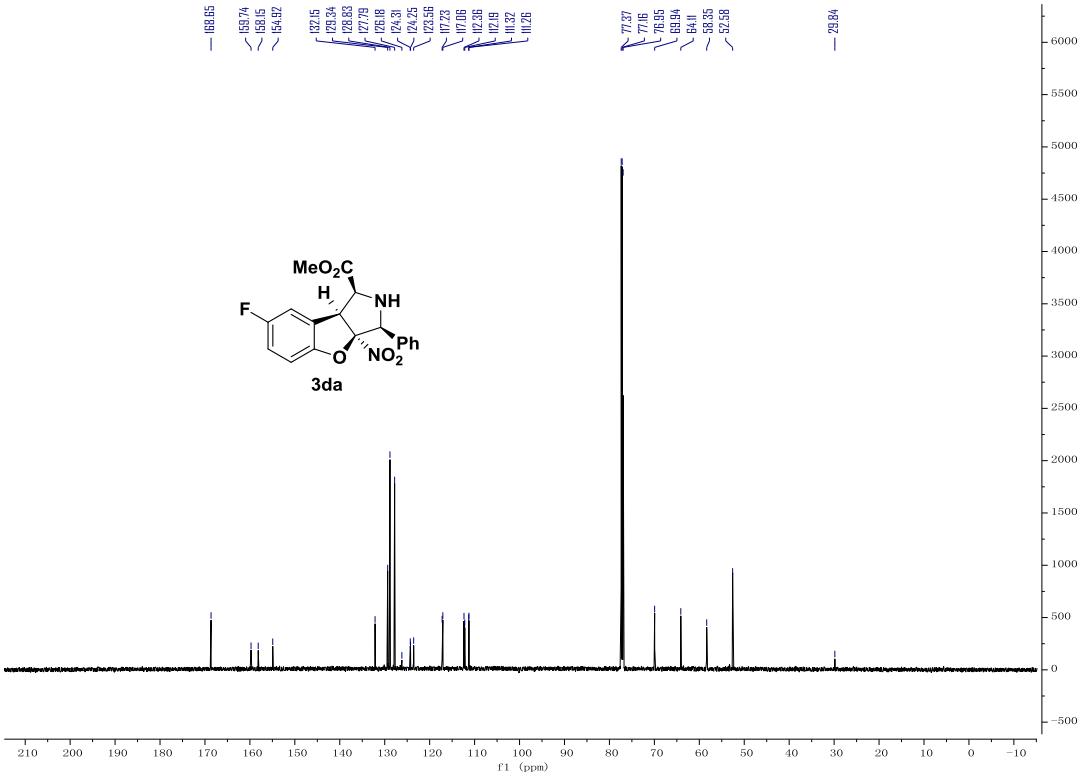
^{13}C NMR of 3ca



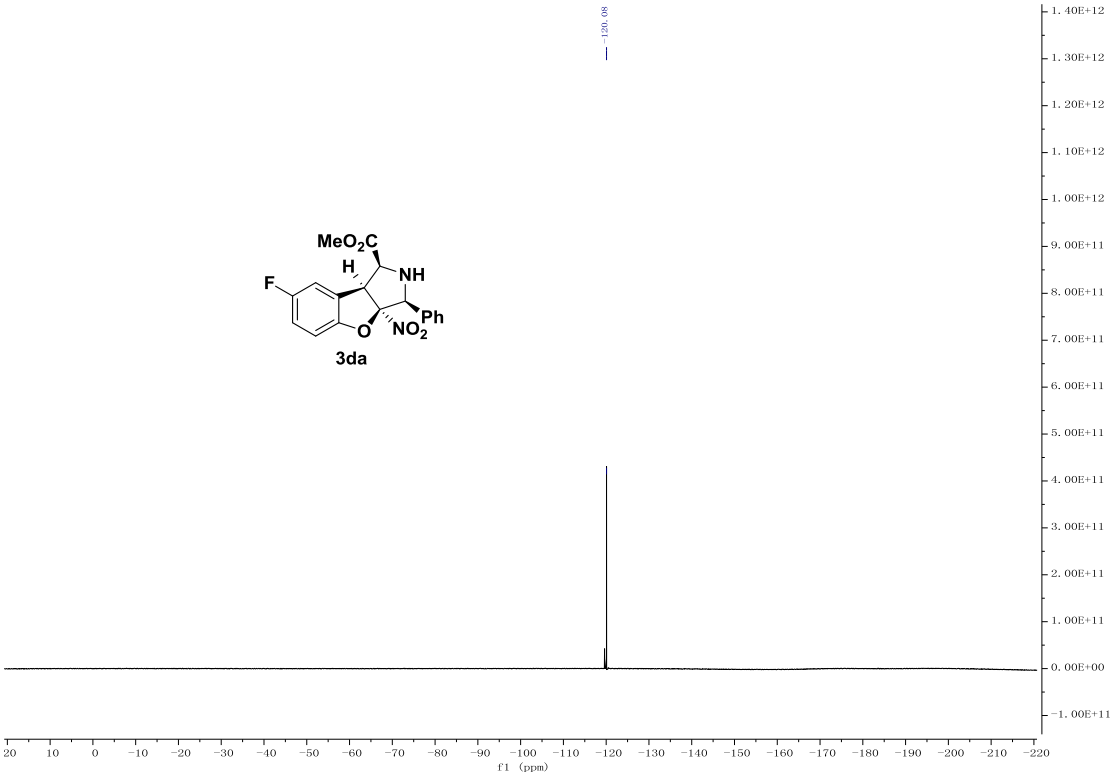
^{1}H NMR of 3da



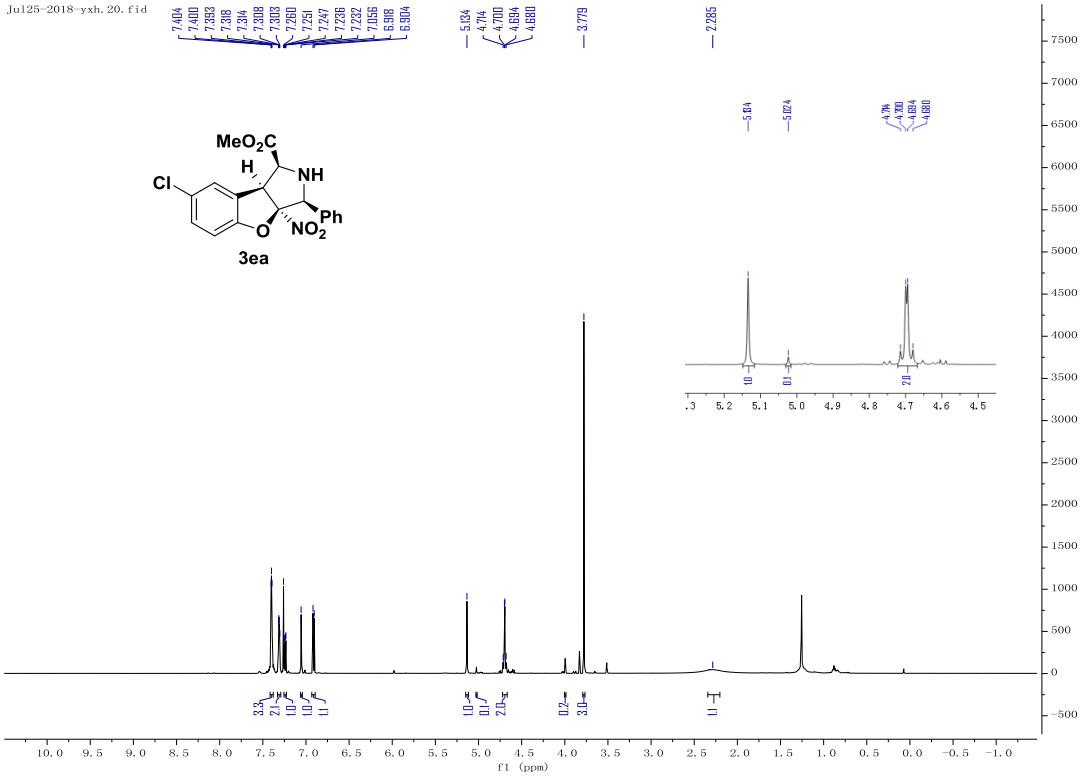
^{13}C NMR of 3da



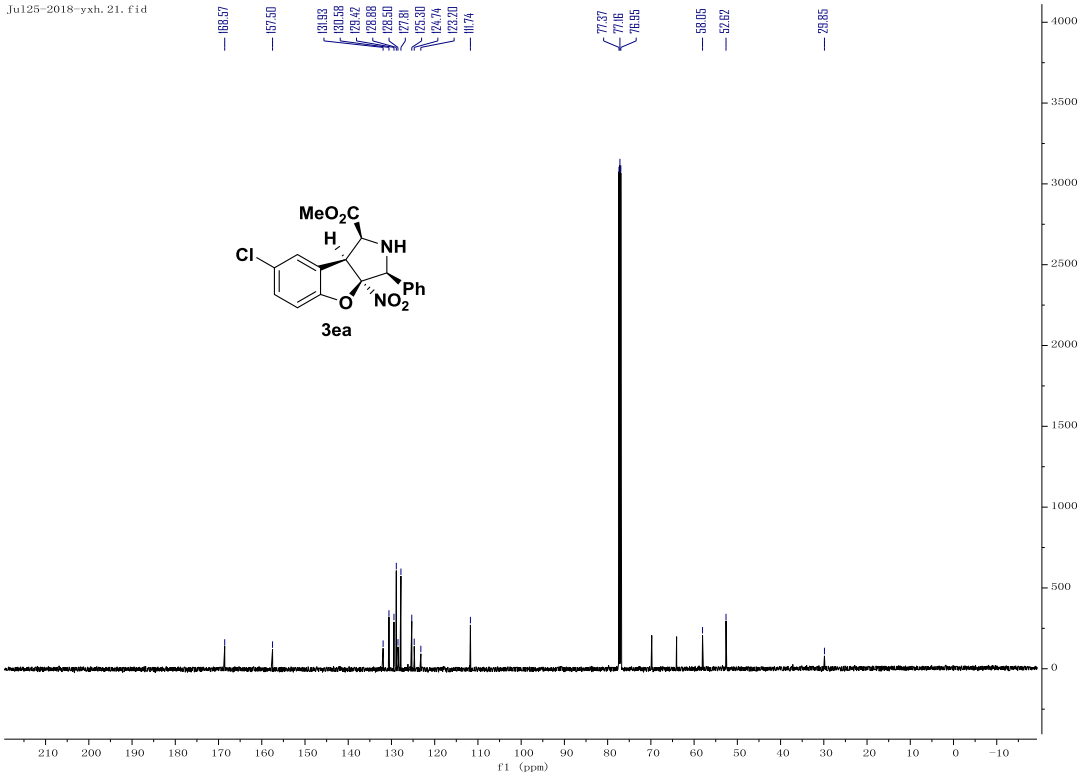
^{19}F NMR of 3da



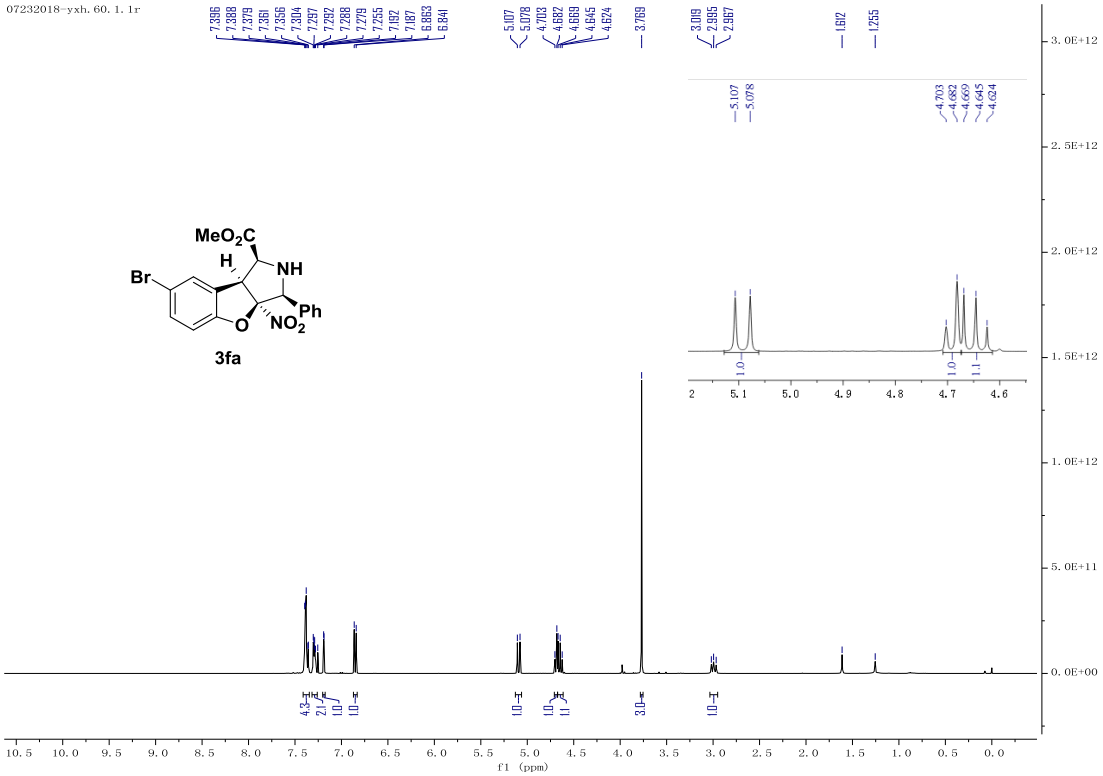
^{1}H NMR of 3ea



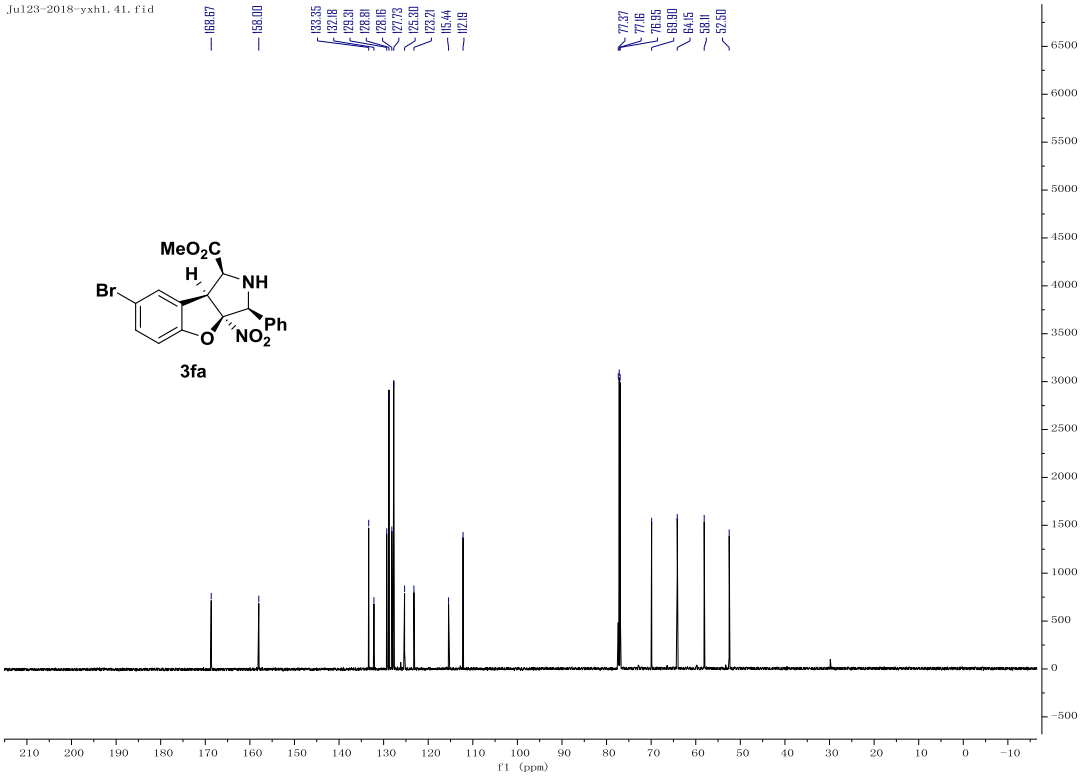
^{13}C NMR of 3ea



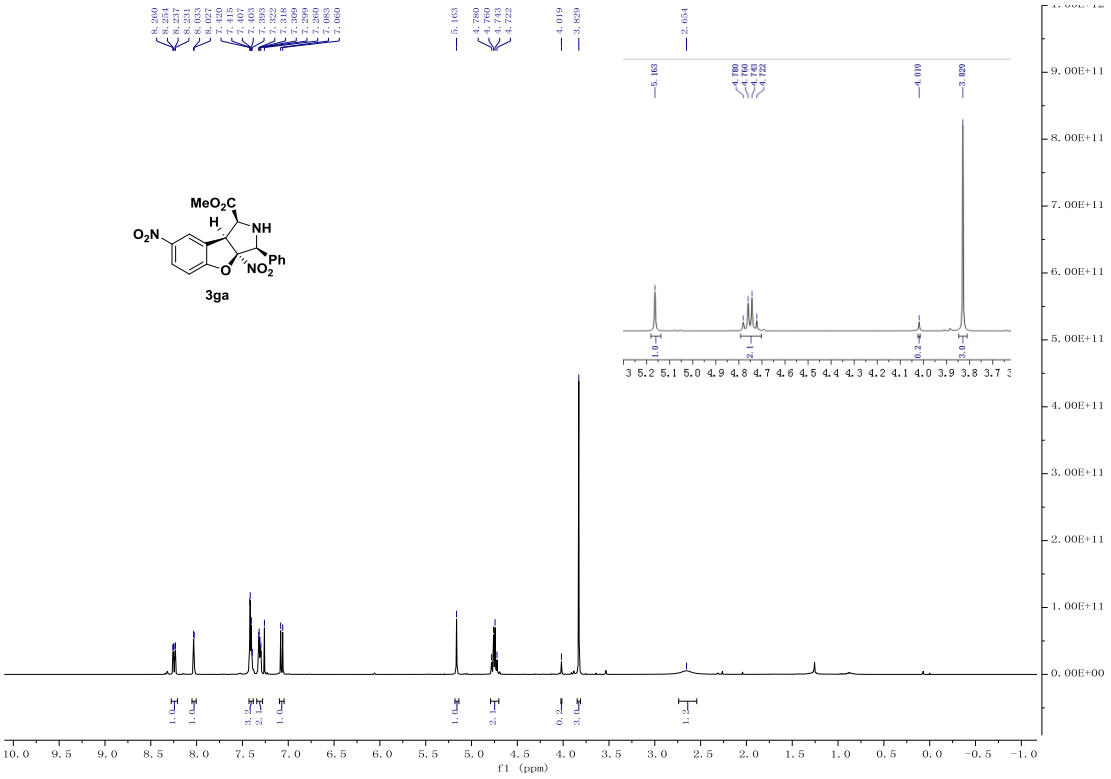
^{1}H NMR of 3fa



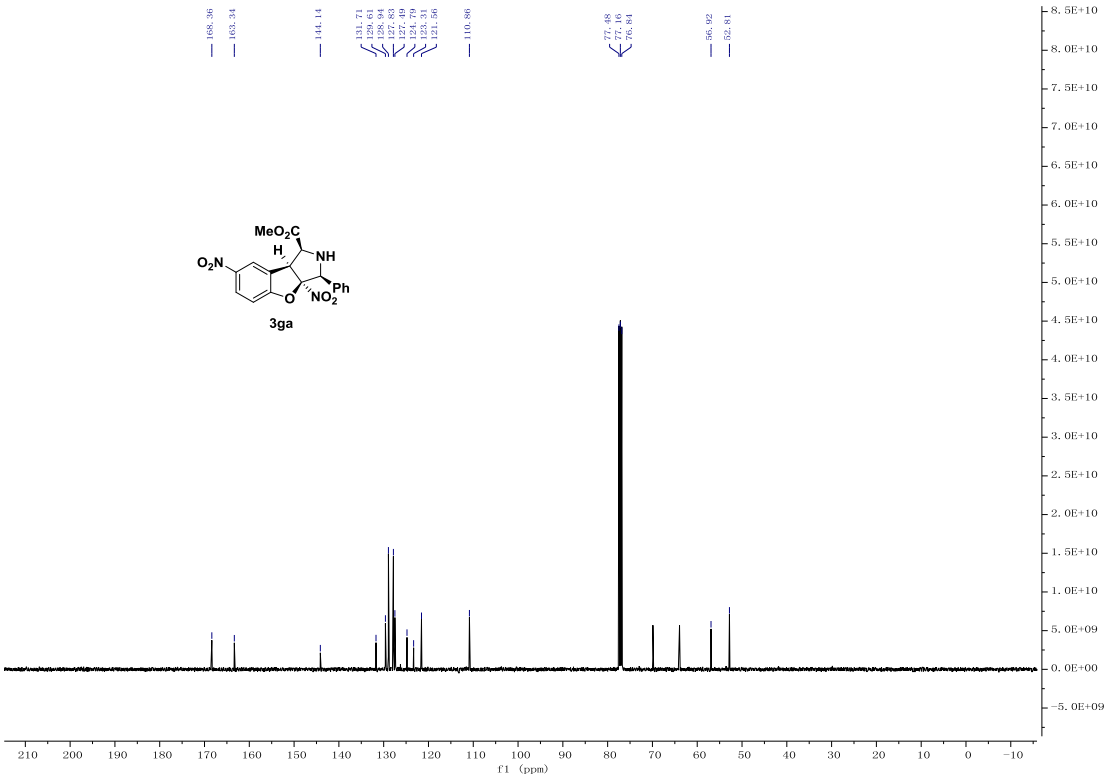
^{13}C NMR of 3fa



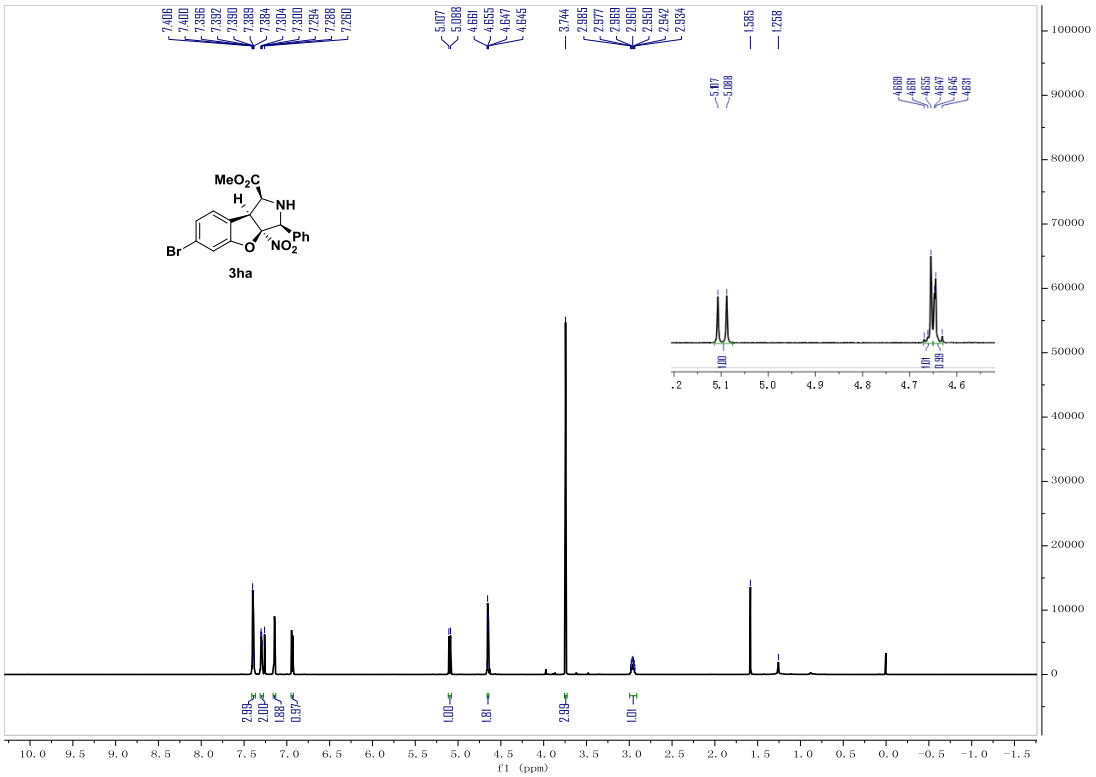
^{1}H NMR of 3ga



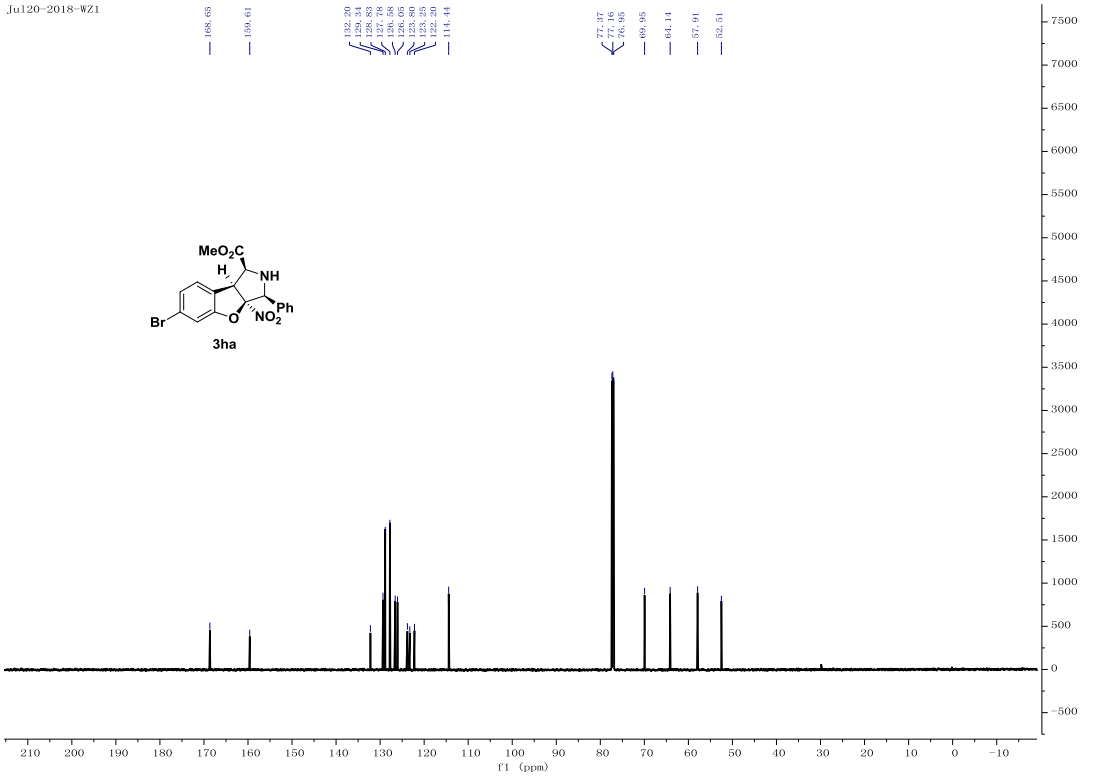
^{13}C NMR of 3ga



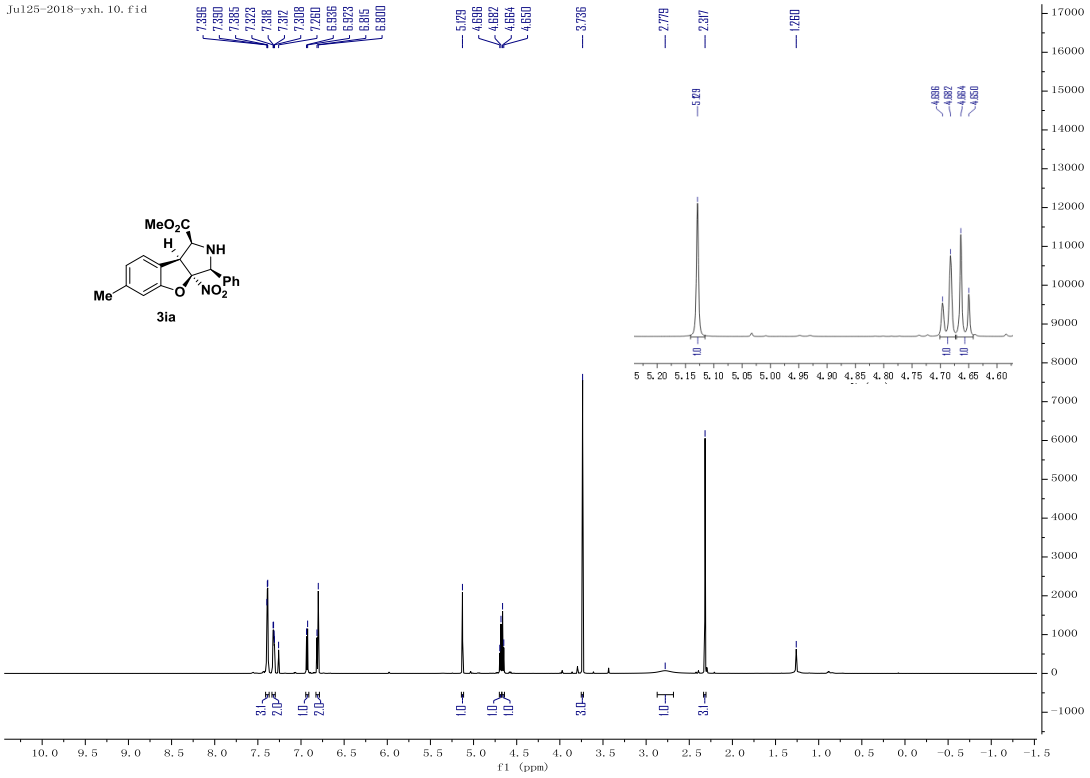
^{1}H NMR of 3ha



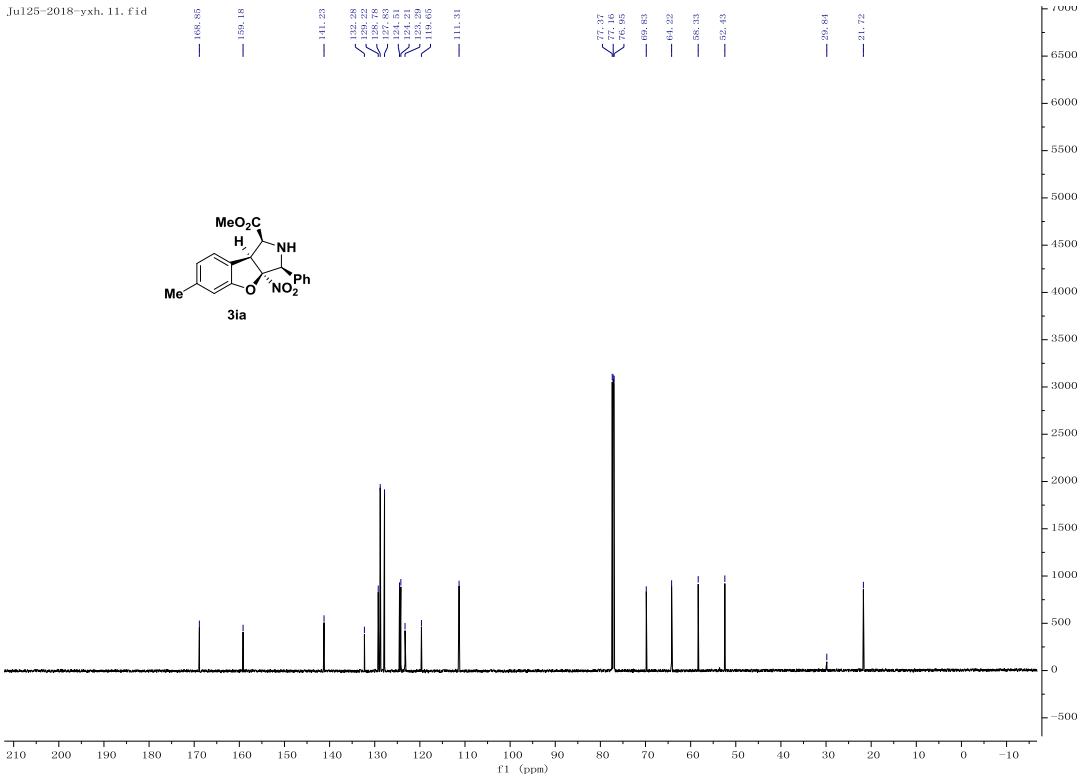
^{13}C NMR of 3ha



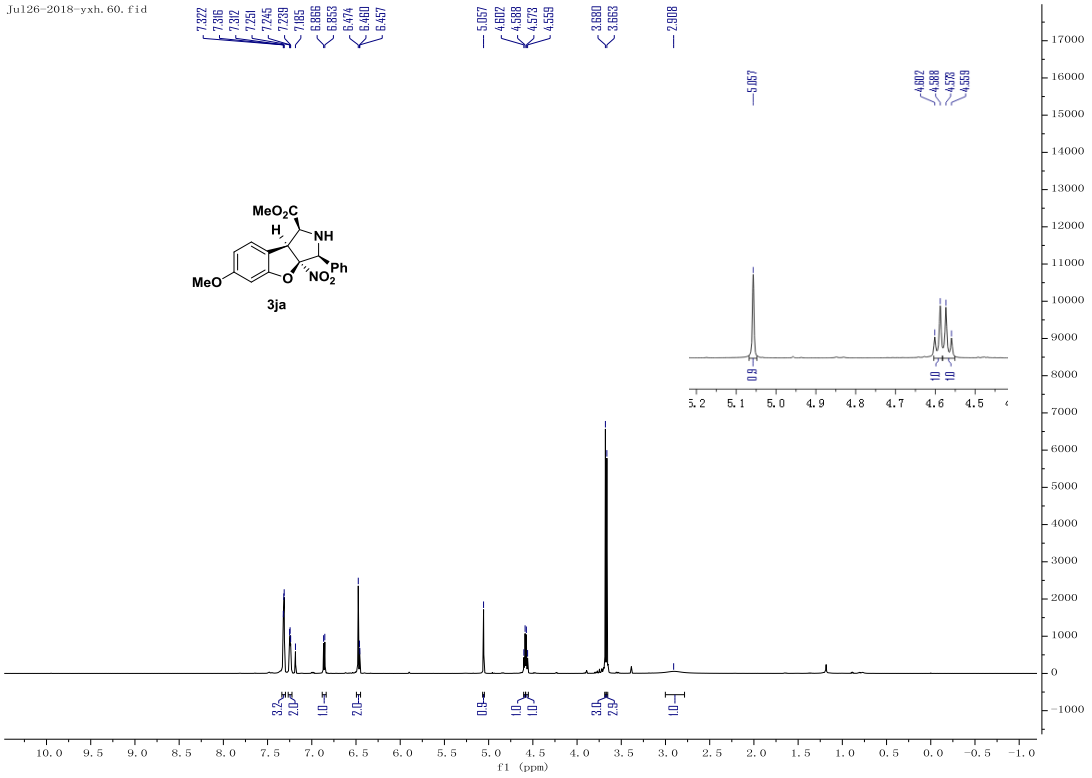
^{1}H NMR of 3ia



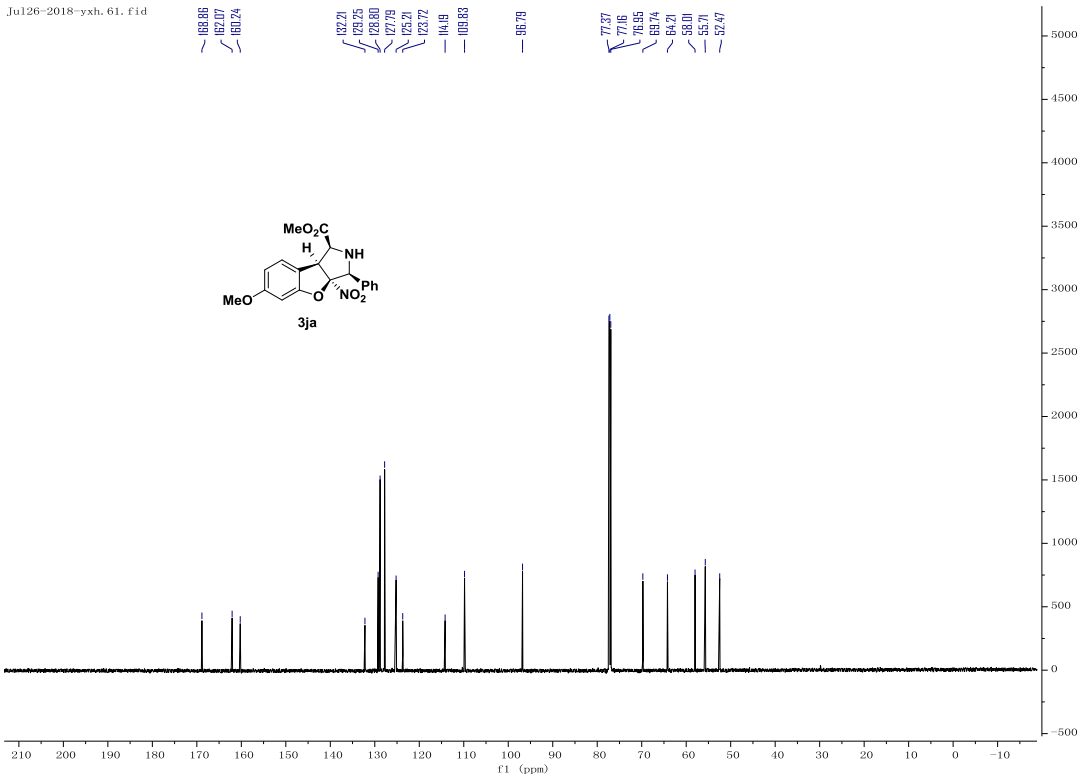
^{13}C NMR of 3ia



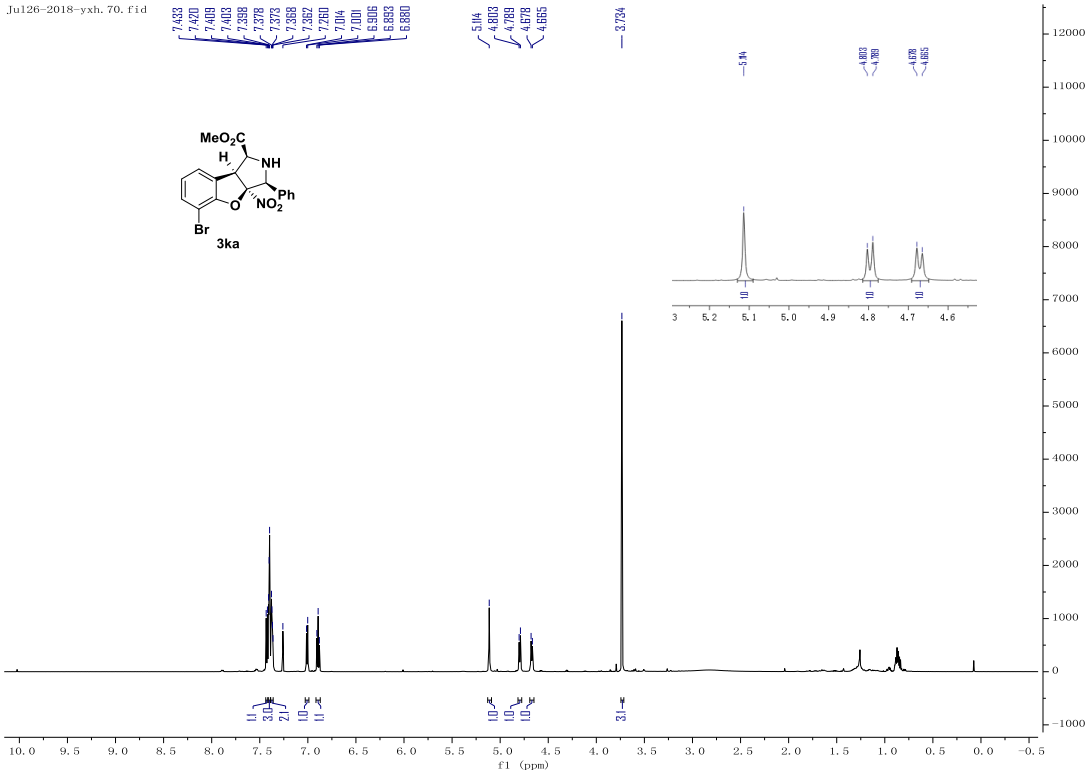
^{1}H NMR of 3ja



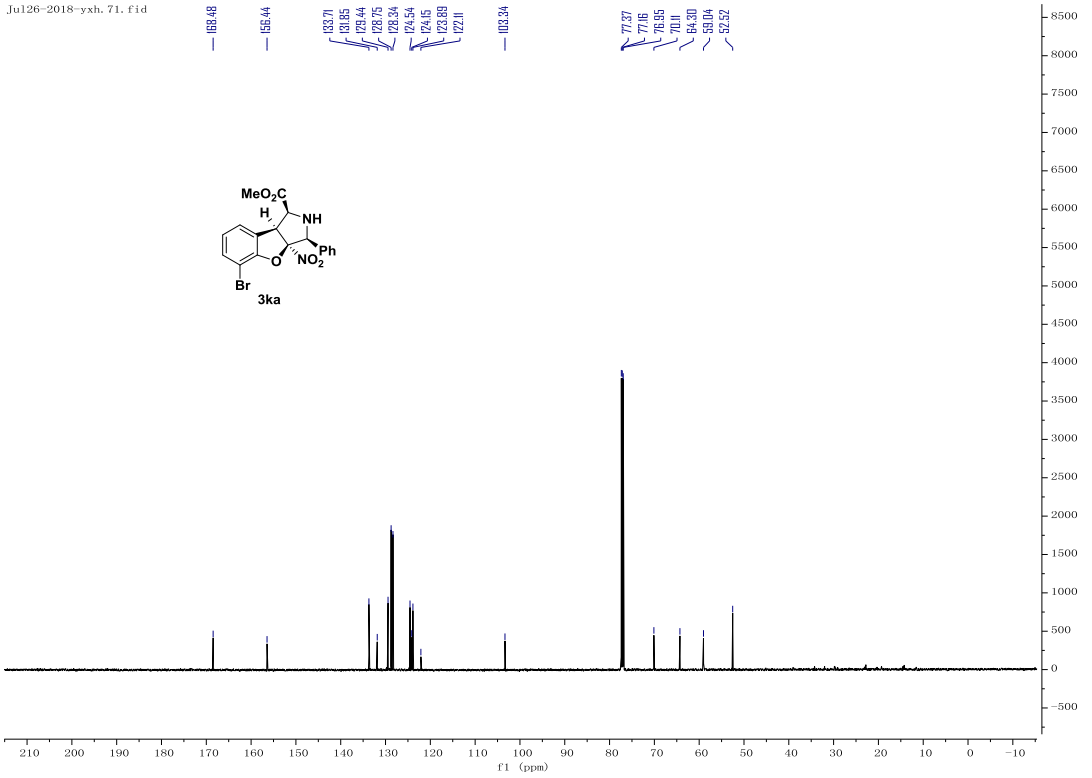
^{13}C NMR of 3ja



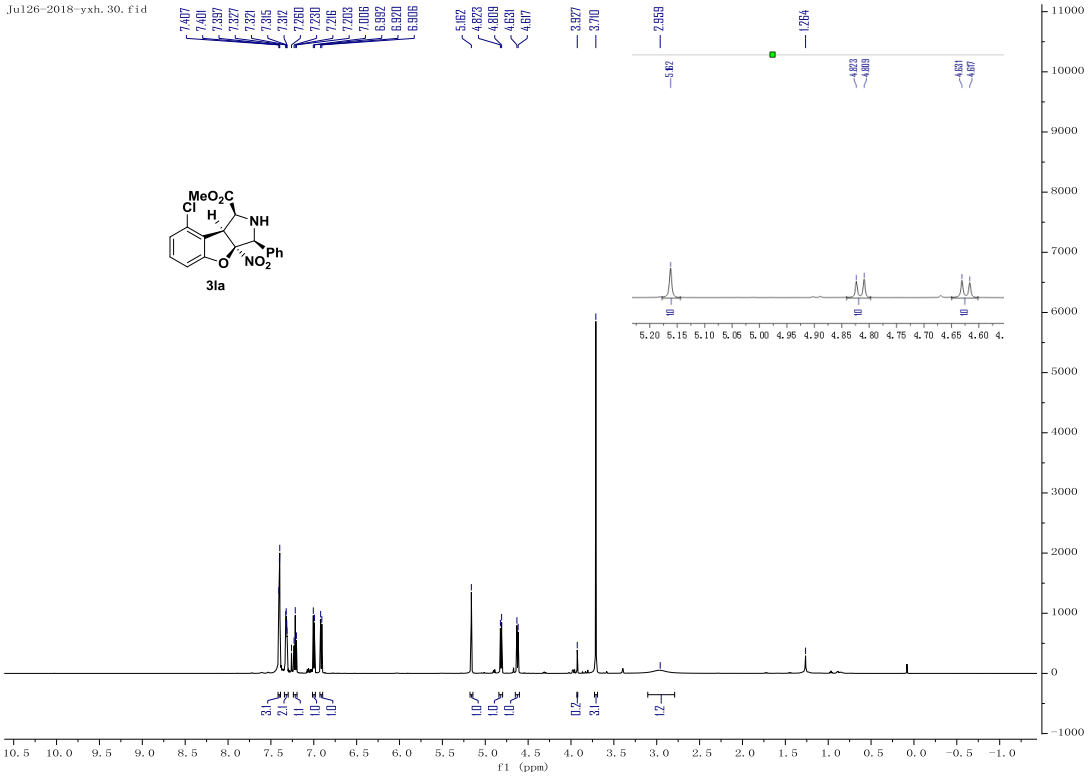
^{1}H NMR of 3ka



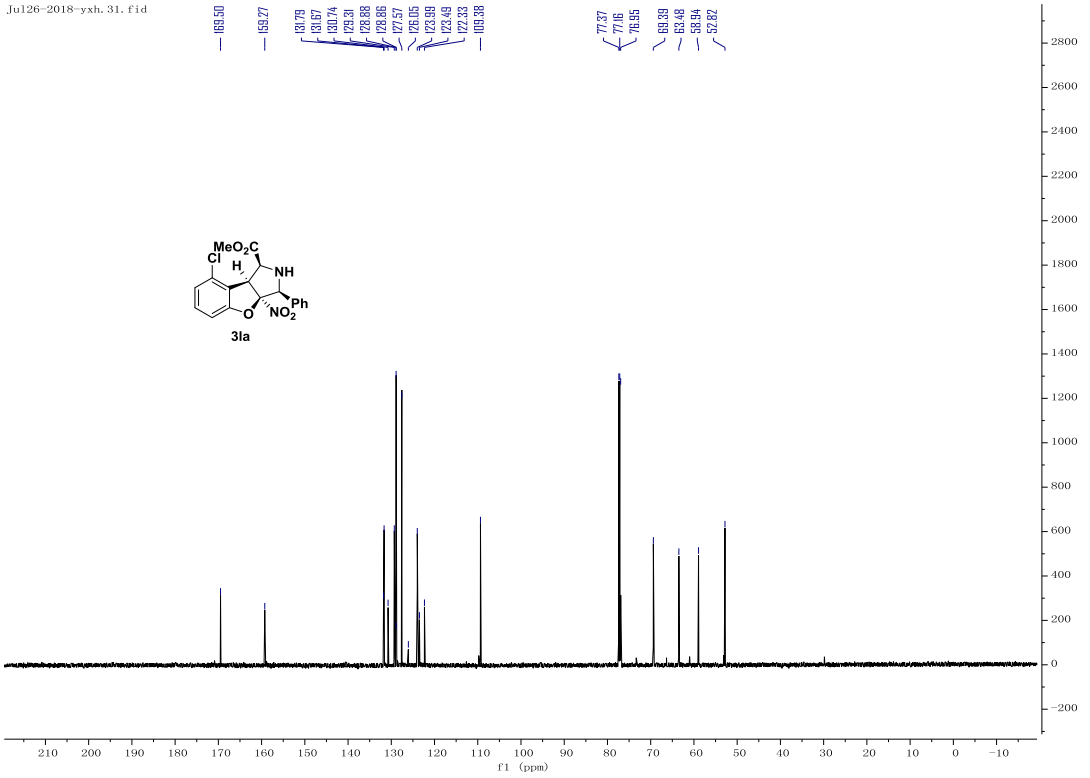
^{13}C NMR of 3ka



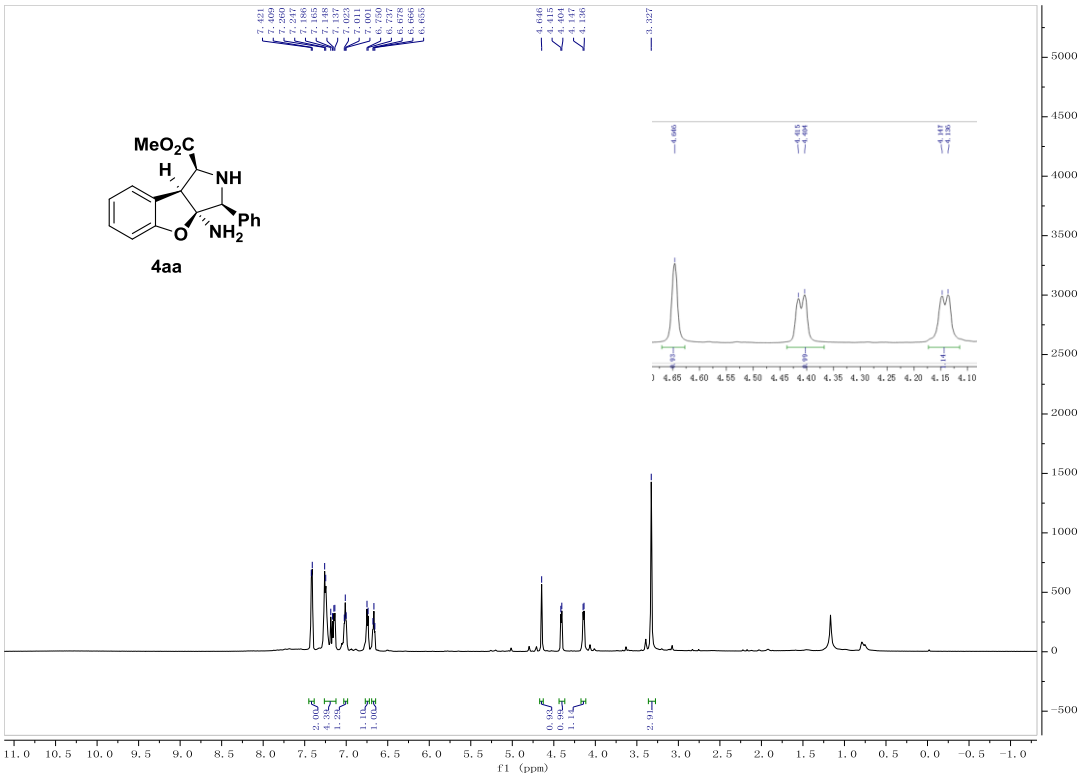
^{1}H NMR of 3la



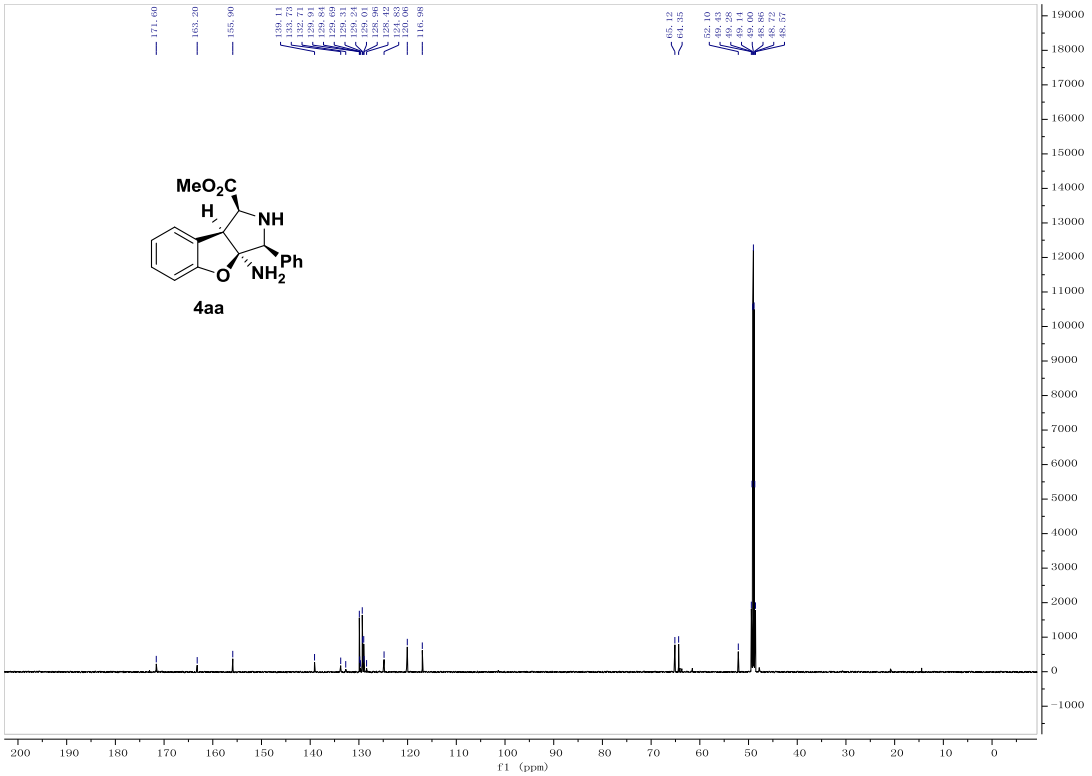
^{13}C NMR of 3la



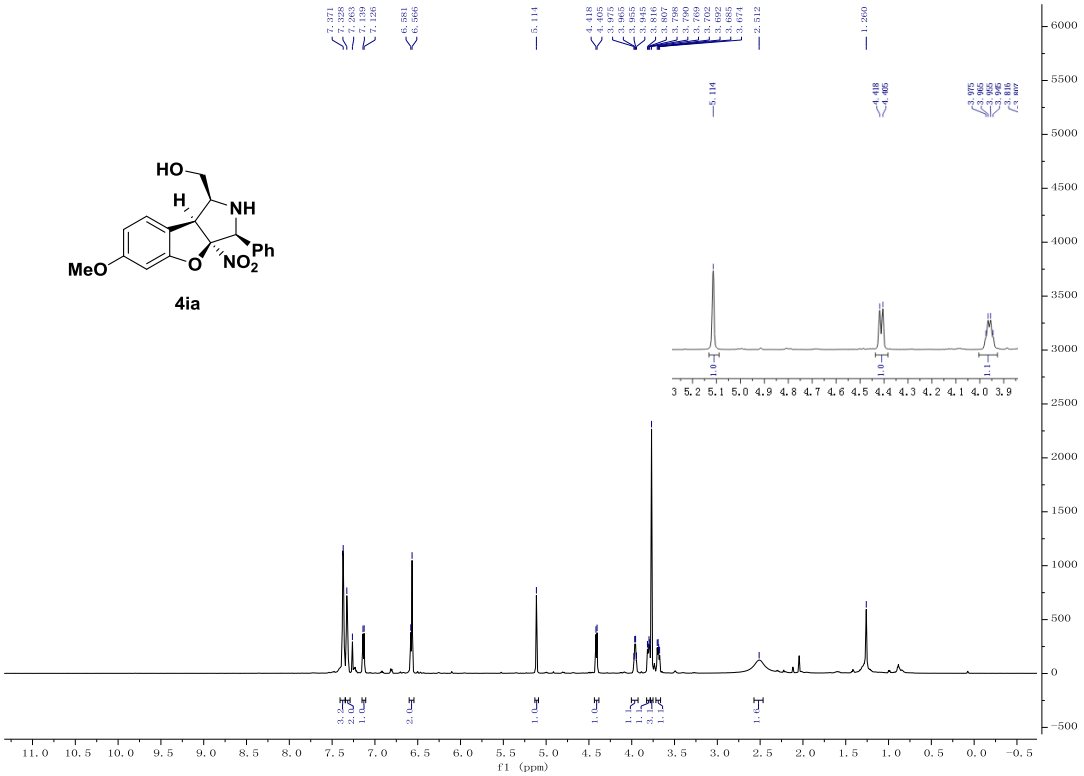
^{1}H NMR of 4aa



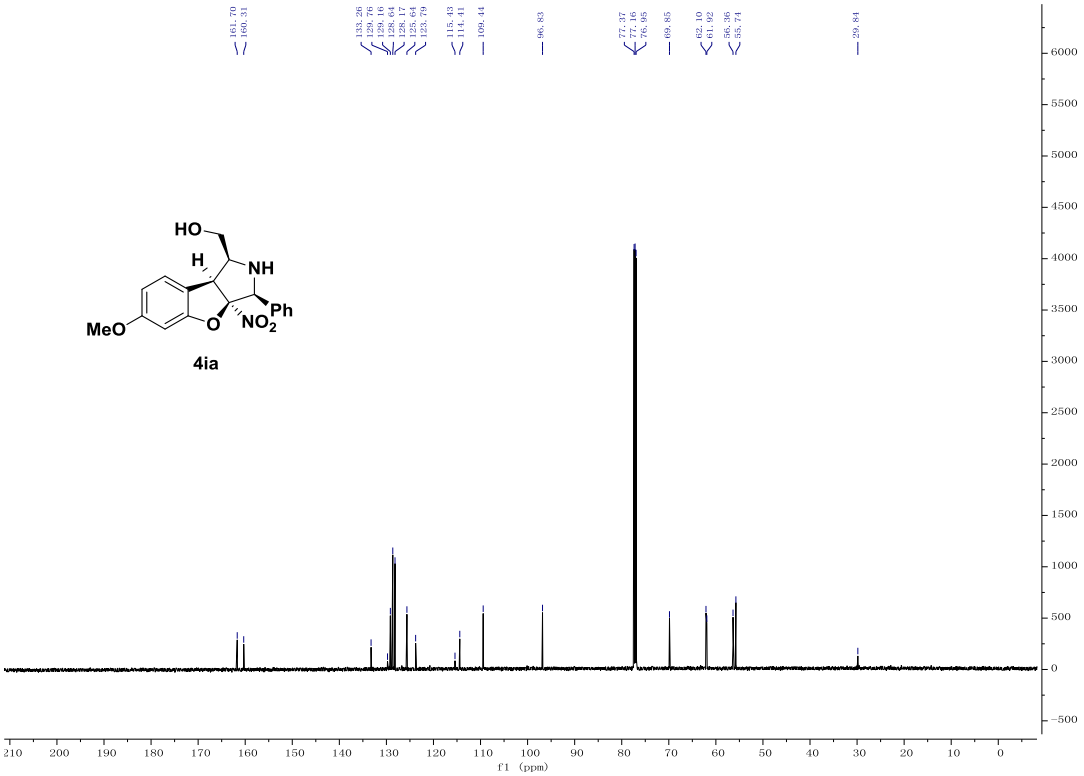
^{13}C NMR of 4aa



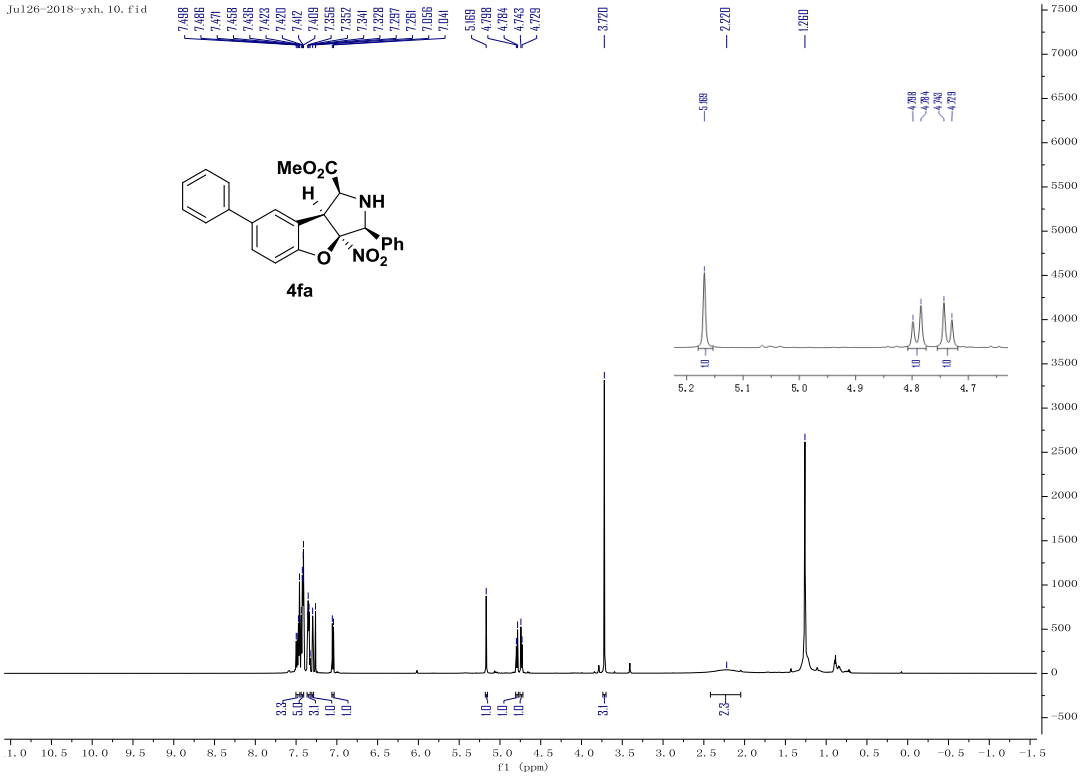
^{1}H NMR of 4ia



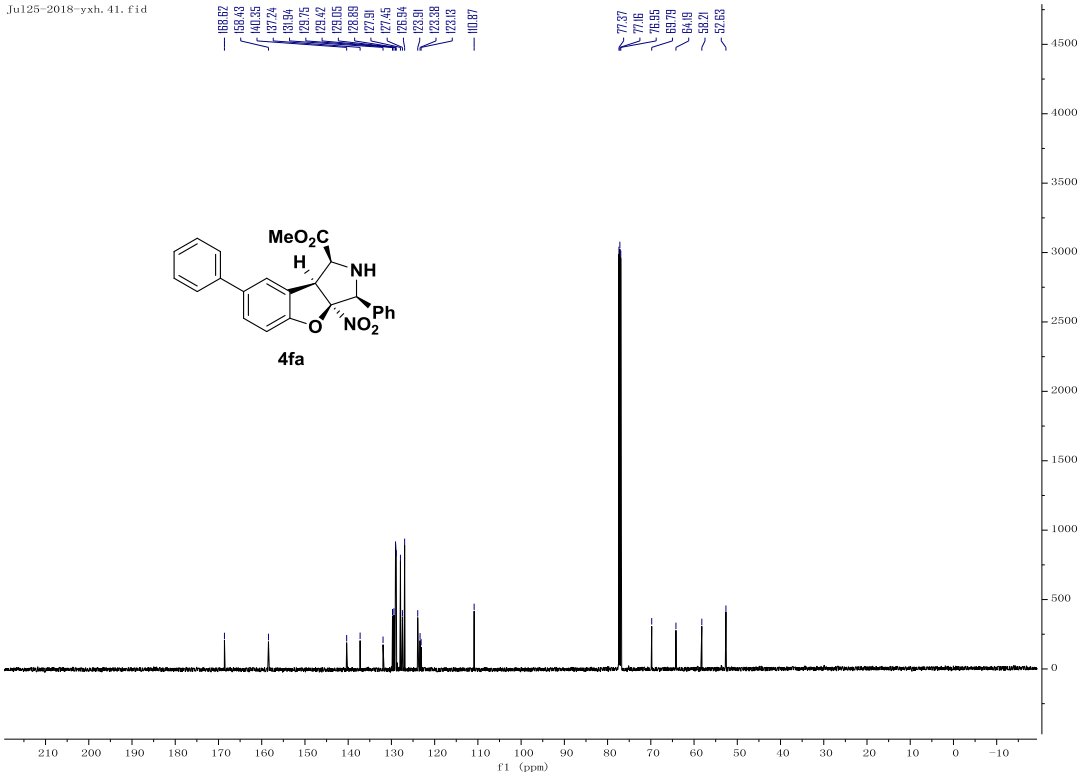
^{13}C NMR of 4ia



^{1}H NMR of 4fa

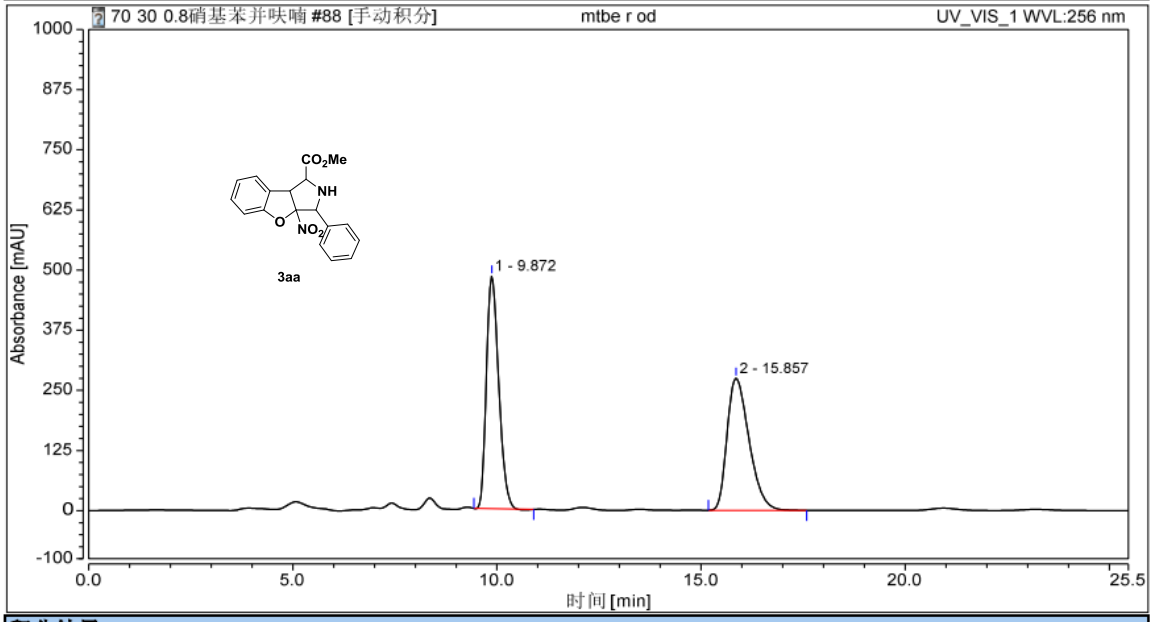


^{13}C NMR of 4fa



8. Copies of HPLC spectra for racemic and chiral compounds

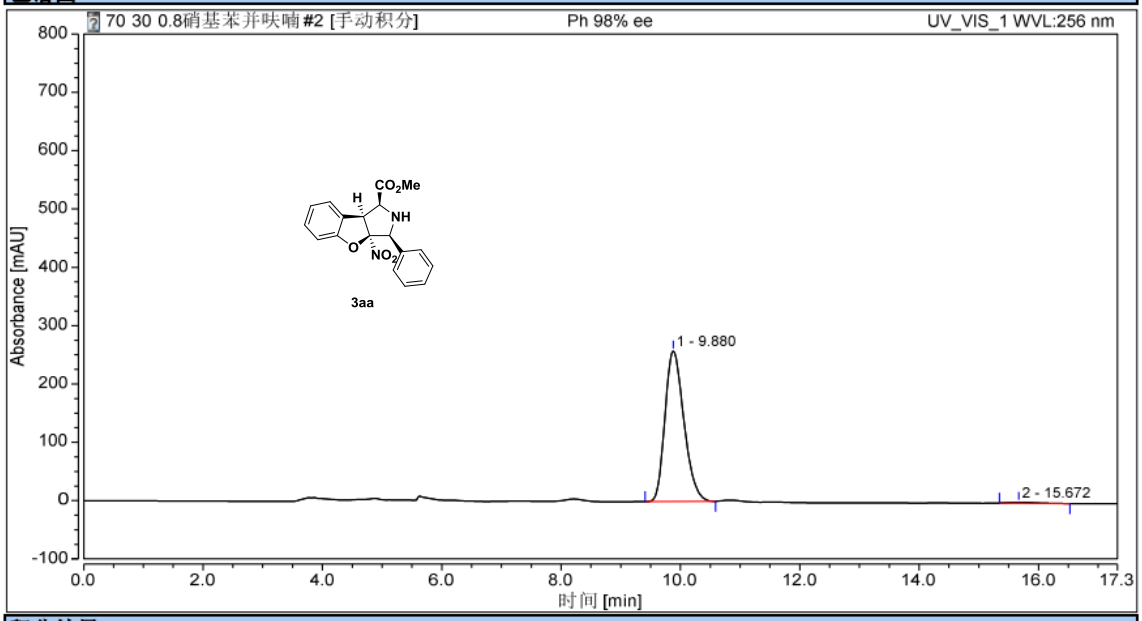
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.872	168.341	483.730	49.47	63.79	n.a.
2		15.857	171.952	274.573	50.53	36.21	n.a.
总和:			**340.293**	**758.303**	**100.00**	**100.00**	

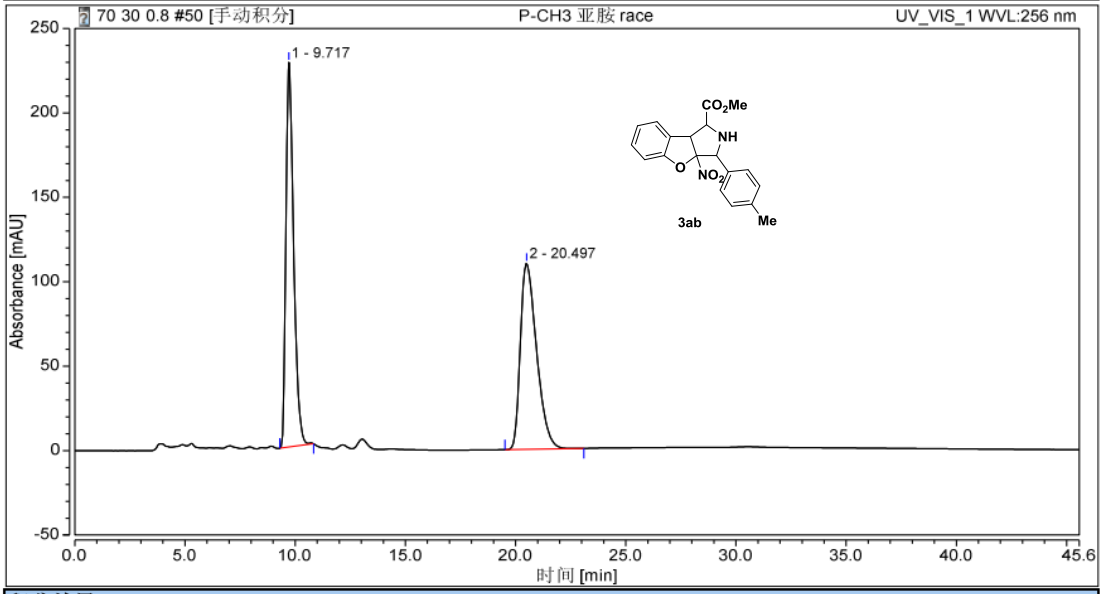
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.880	94.916	257.961	99.19	99.40	n.a.
2		15.672	0.780	1.555	0.81	0.60	n.a.
总和:			**95.696**	**259.515**	**100.00**	**100.00**	

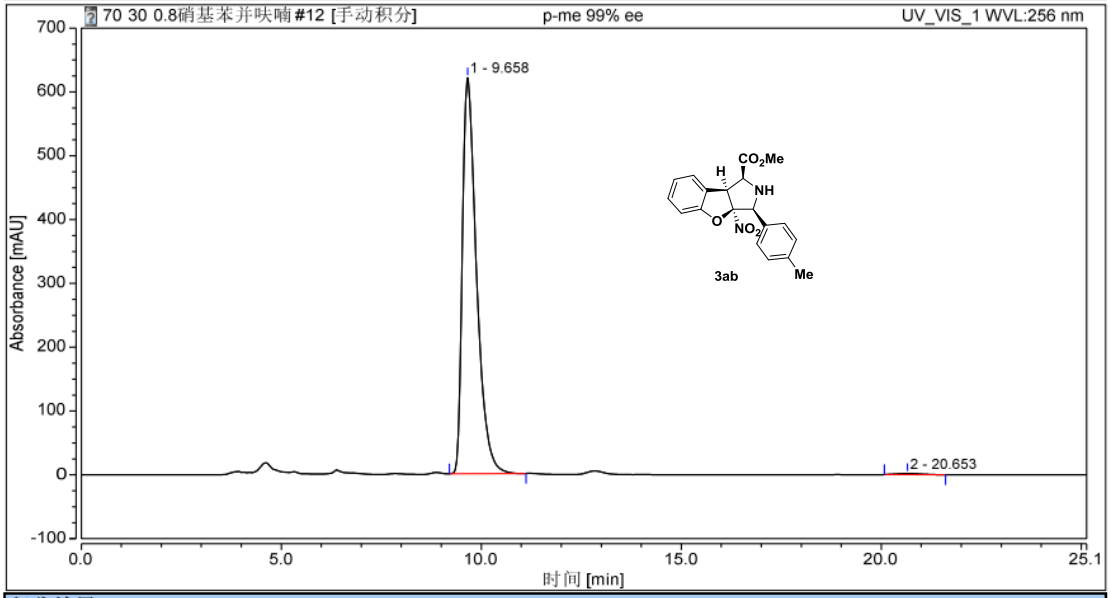
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.717	92.031	227.807	49.49	67.39	n.a.
2		20.497	93.924	110.234	50.51	32.61	n.a.
总和:			**185.955**	**338.041**	**100.00**	**100.00**	

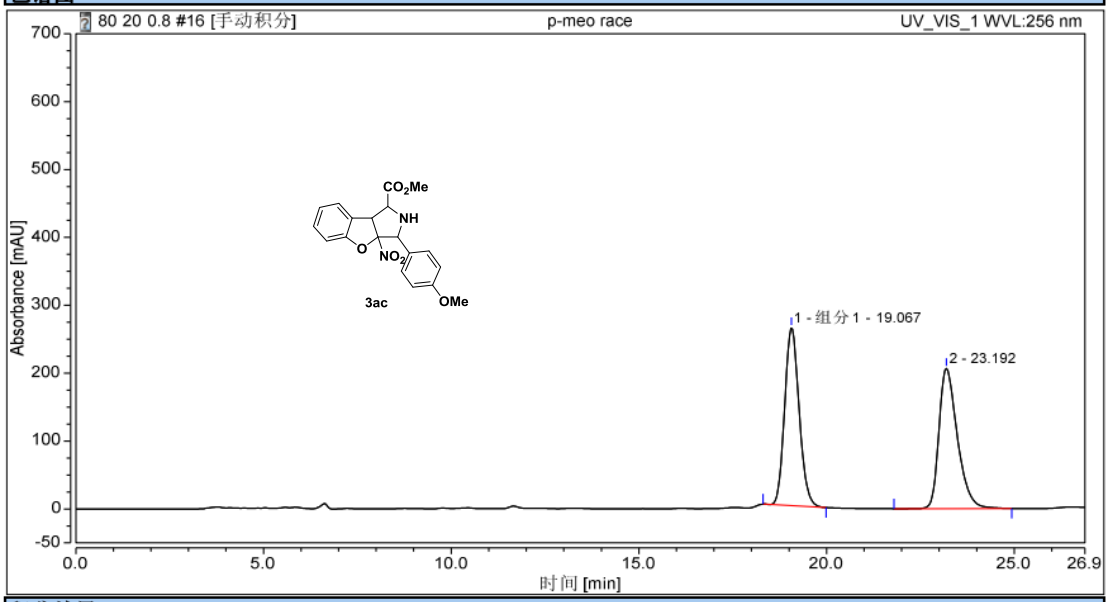
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.658	254.821	620.430	99.47	99.70	n.a.
2		20.653	1.359	1.874	0.53	0.30	n.a.
总和:			**256.180**	**622.304**	**100.00**	**100.00**	

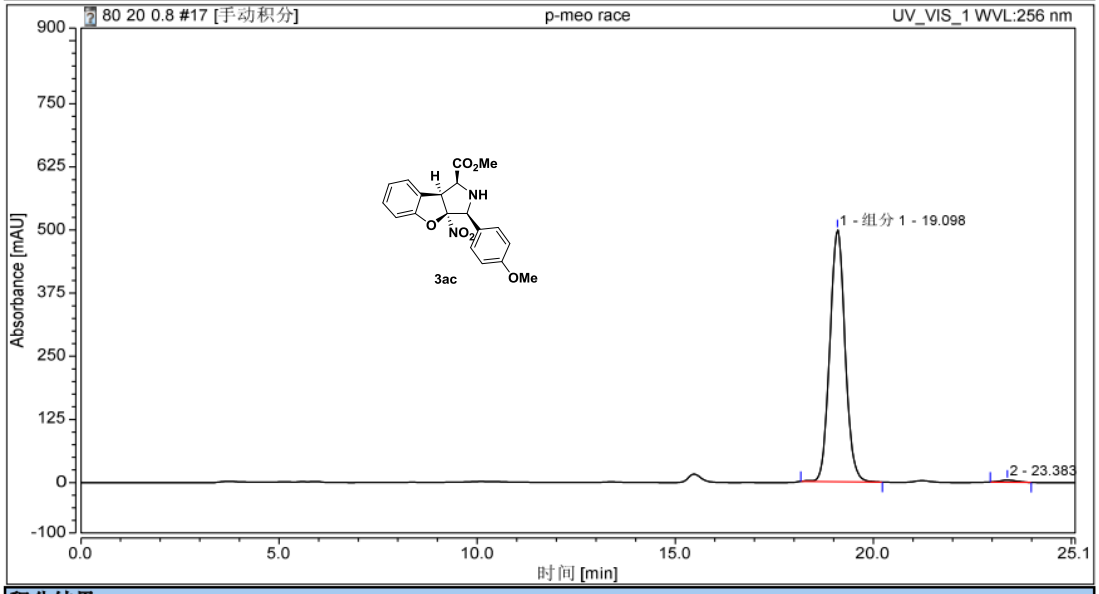
色谱图



积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
1	组分 1	19.067	117.158	262.485	49.96	55.95	n.a.
n.a.	组分 2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2		23.192	117.366	206.629	50.04	44.05	n.a.
总和:			**234.523**	**469.114**	**100.00**	**100.00**	

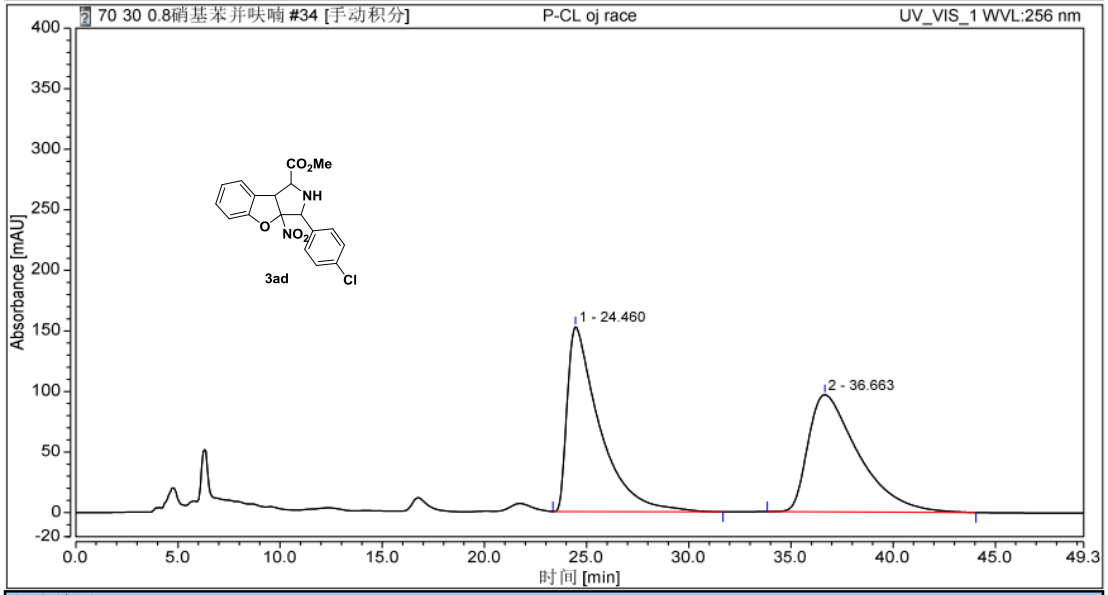
色谱图



积分结果

序号	Name	Rettime min	Area mAU*min	Height mAU	Area %	Height %	样品量
1	组分 1	19.098	223.214	498.987	99.09	99.17	n.a.
n.a.	组分 2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2		23.383	2.054	4.195	0.91	0.83	n.a.
总和:			**225.268**	**503.182**	**100.00**	**100.00**	

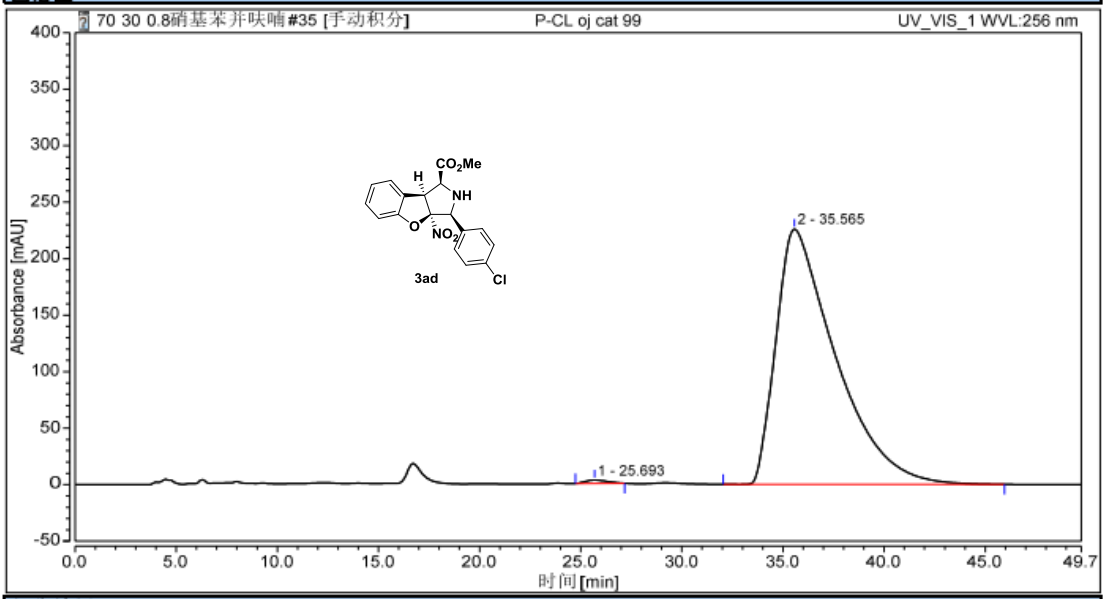
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		24.460	280.343	152.569	50.45	61.22	n.a.
2		36.663	275.349	96.655	49.55	38.78	n.a.
总和:			**555.692**	**249.223**	**100.00**	**100.00**	

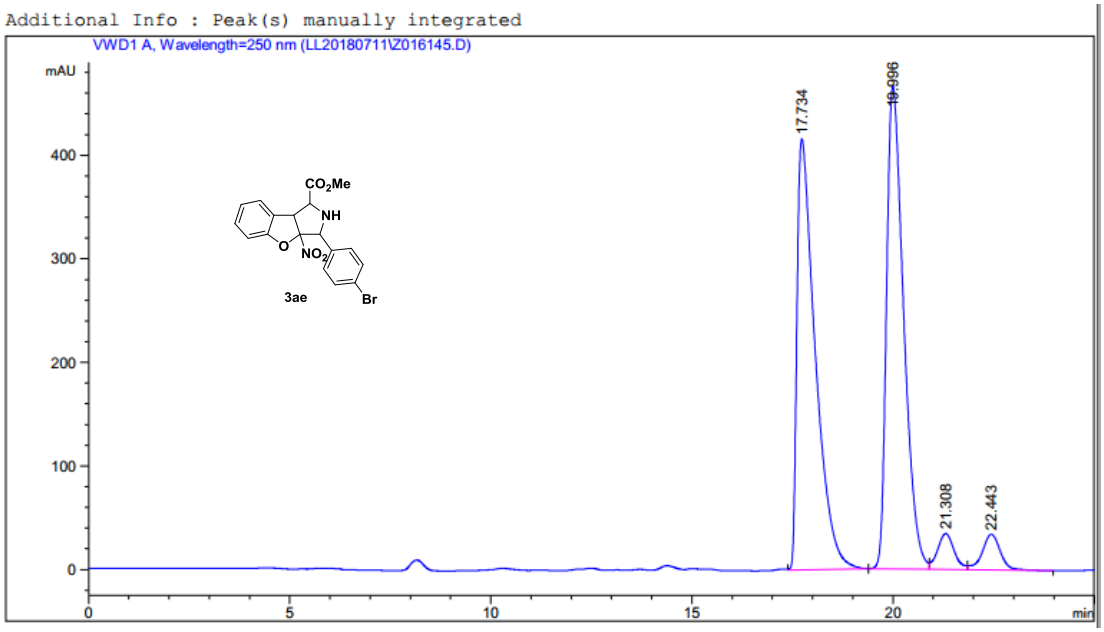
色谱图



积分结果

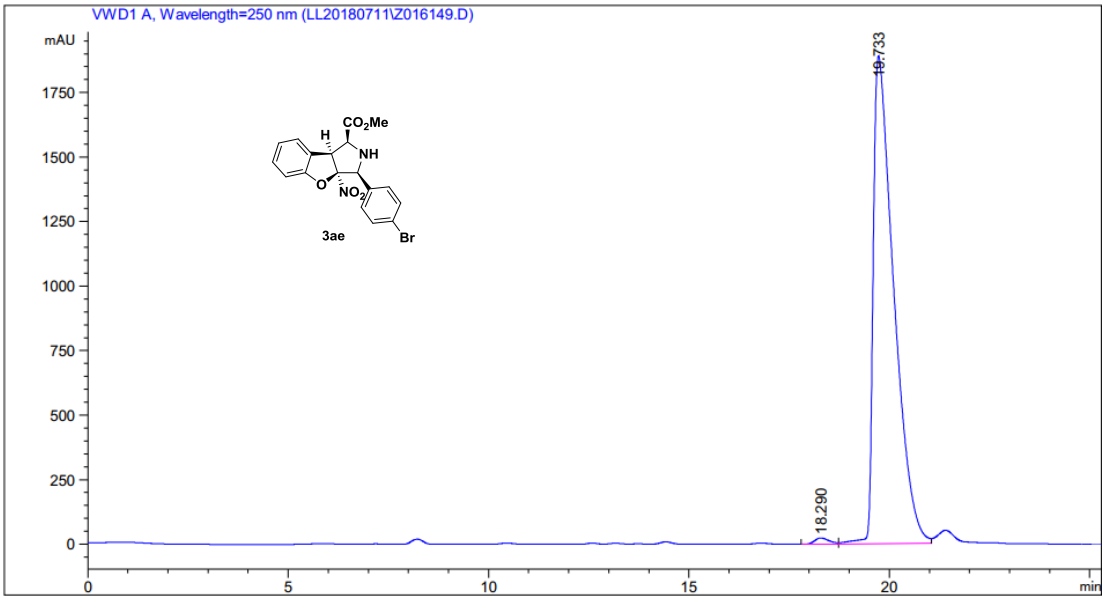
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		25.693	3.645	2.932	0.47	1.28	n.a.
2		35.565	770.266	225.911	99.53	98.72	n.a.
总和:			**773.911**	**228.843**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



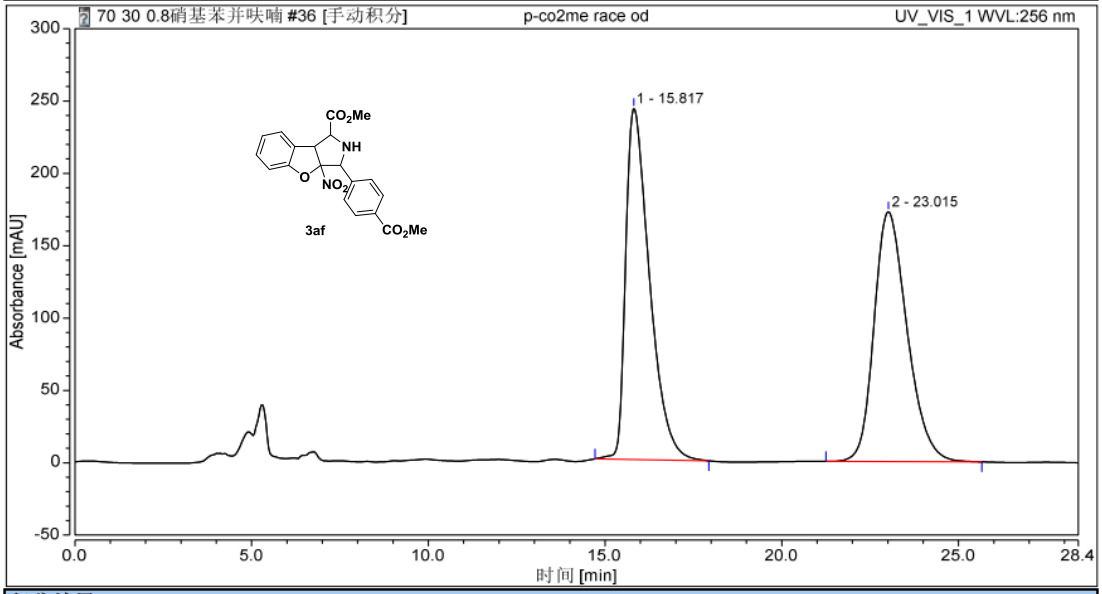
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.734	VB	0.4596	1.31287e4	416.35712	45.3998
2	19.996	BV	0.4530	1.37316e4	466.00653	47.4844
3	21.308	VV	0.4380	988.45911	34.60992	3.4181

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.290	BV	0.3825	594.98419	23.87268	0.8770
2	19.733	VV	0.5244	6.72474e4	1889.38611	99.1230

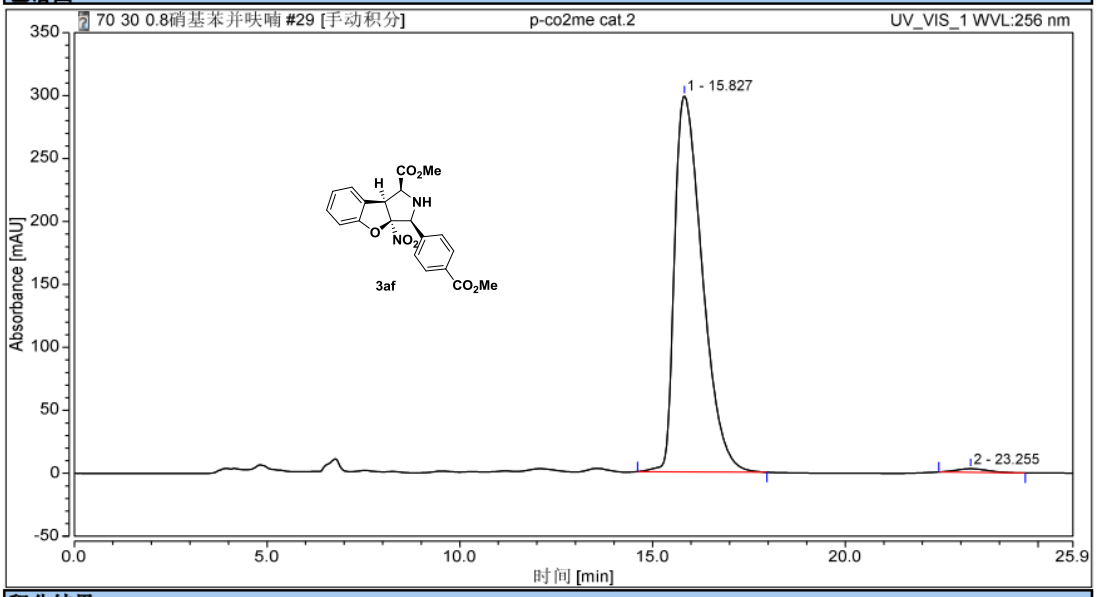
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		15.817	189.707	242.708	50.31	58.43	n.a.
2		23.015	187.371	172.687	49.69	41.57	n.a.
总和:			**377.078**	**415.394**	**100.00**	**100.00**	

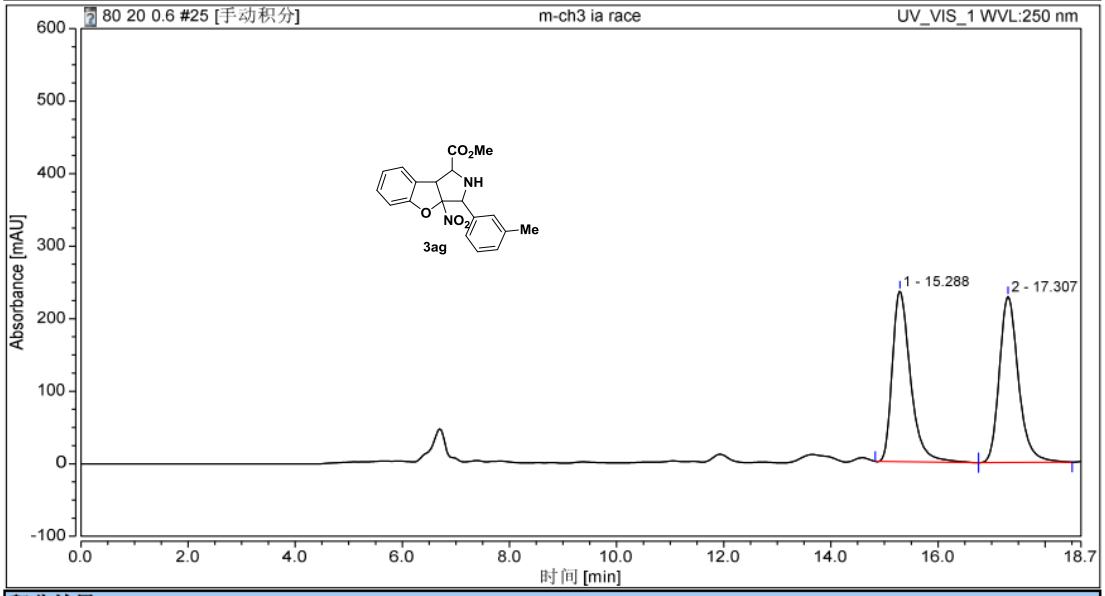
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		15.827	249.523	298.662	98.96	99.06	n.a.
2		23.255	2.634	2.831	1.04	0.94	n.a.
总和:			**252.157**	**301.494**	**100.00**	**100.00**	

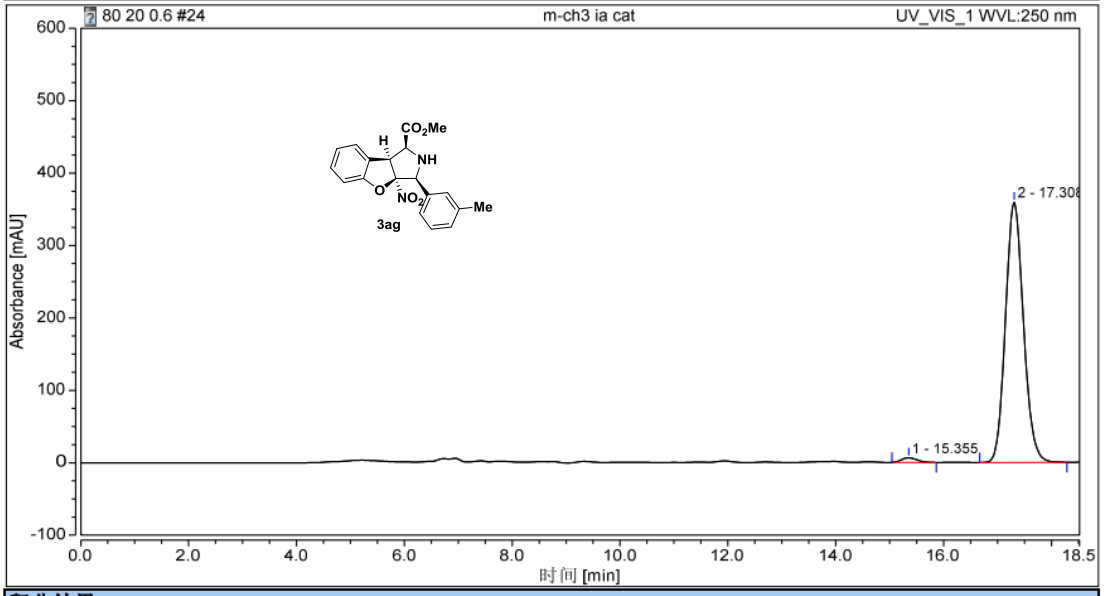
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.288	92.856	235.275	49.55	50.68	n.a.
2		17.307	94.548	228.936	50.45	49.32	n.a.
总和:			**187.404**	**464.210**	**100.00**	**100.00**	

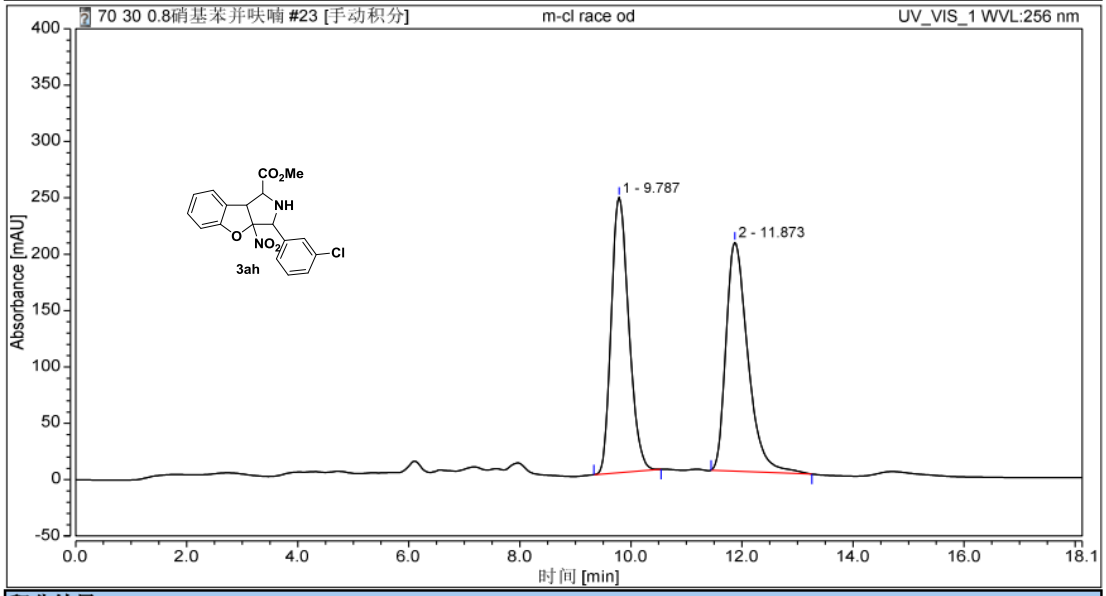
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.355	2.155	6.391	1.53	1.75	n.a.
2		17.308	139.040	359.338	98.47	98.25	n.a.
总和:			**141.195**	**365.729**	**100.00**	**100.00**	

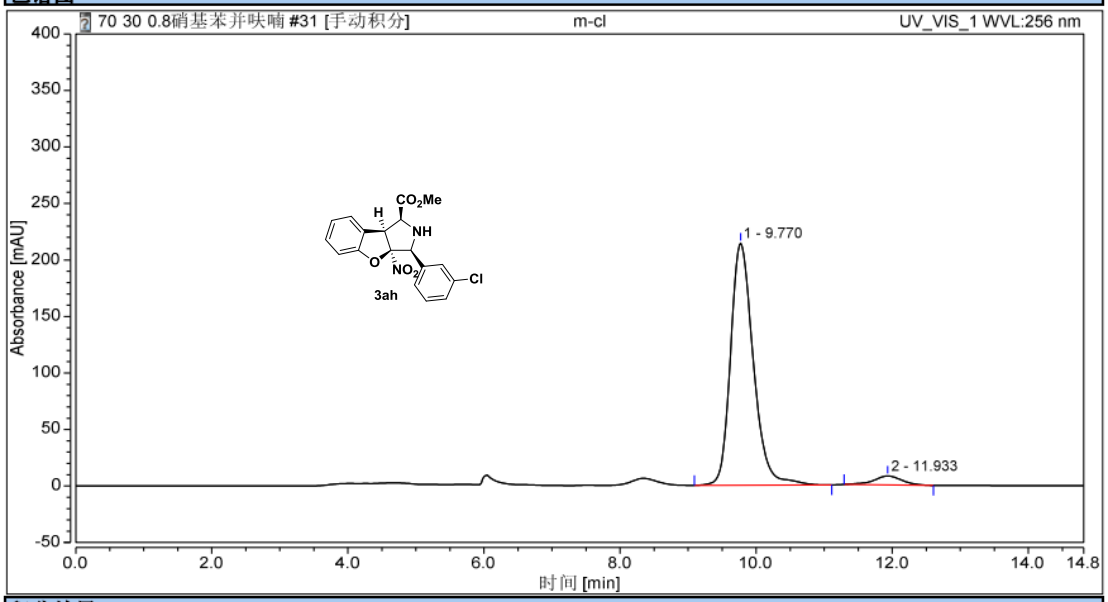
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.787	89.618	244.353	49.10	54.62	n.a.
2		11.873	92.888	203.018	50.90	45.38	n.a.
总和:			**182.506**	**447.371**	**100.00**	**100.00**	

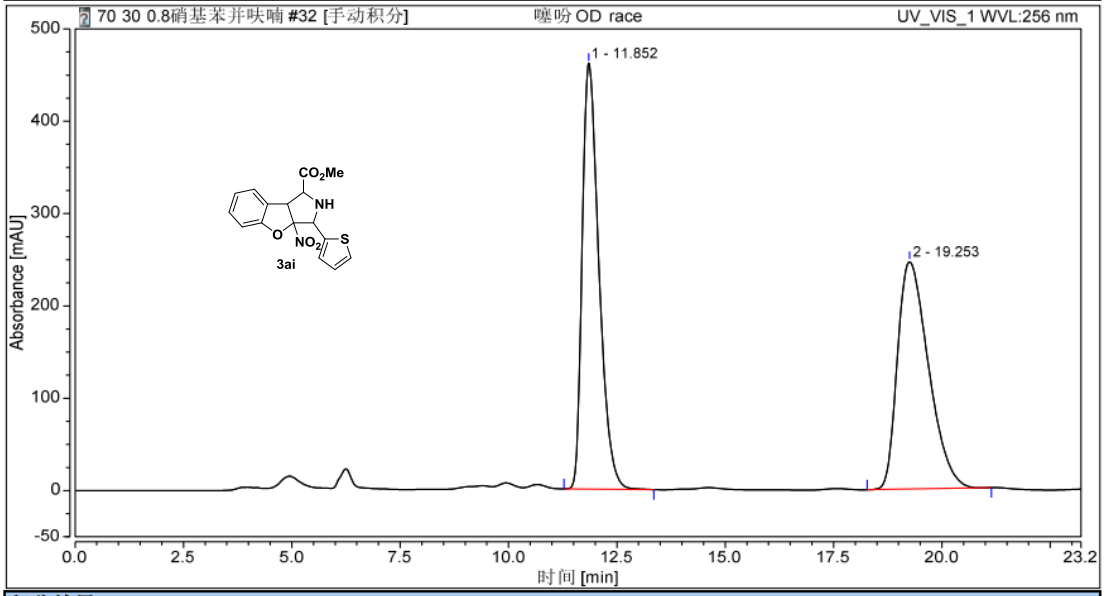
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.770	83.046	214.194	95.72	96.46	n.a.
2		11.933	3.714	7.849	4.28	3.54	n.a.
总和:			**86.760**	**222.044**	**100.00**	**100.00**	

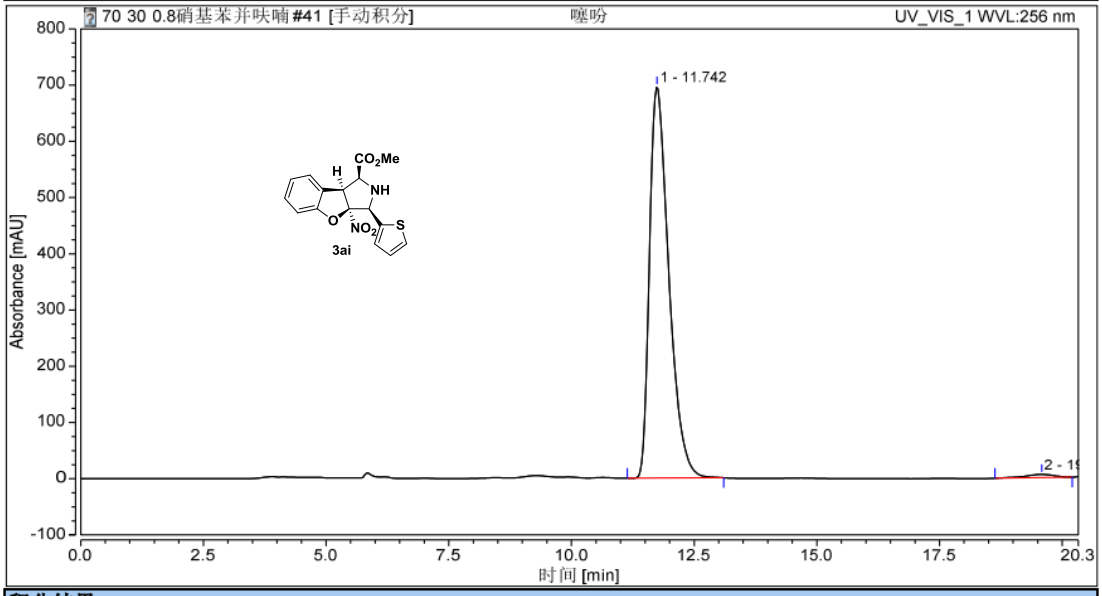
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.852	206.394	461.125	50.27	65.19	n.a.
2		19.253	204.146	246.261	49.73	34.81	n.a.
总和:			**410.540**	**707.387**	**100.00**	**100.00**	

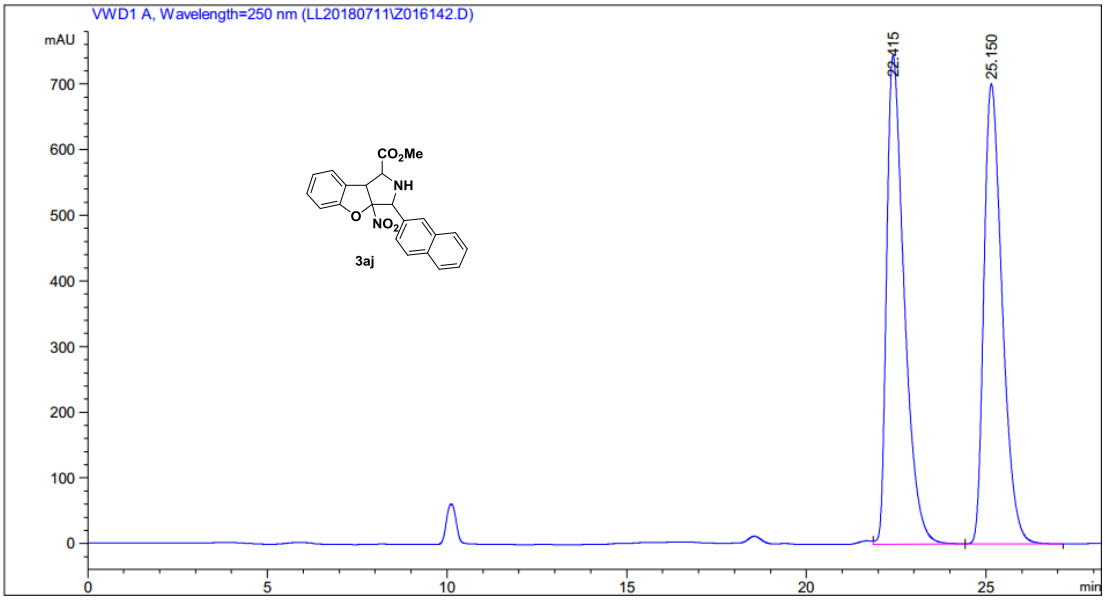
色谱图



积分结果

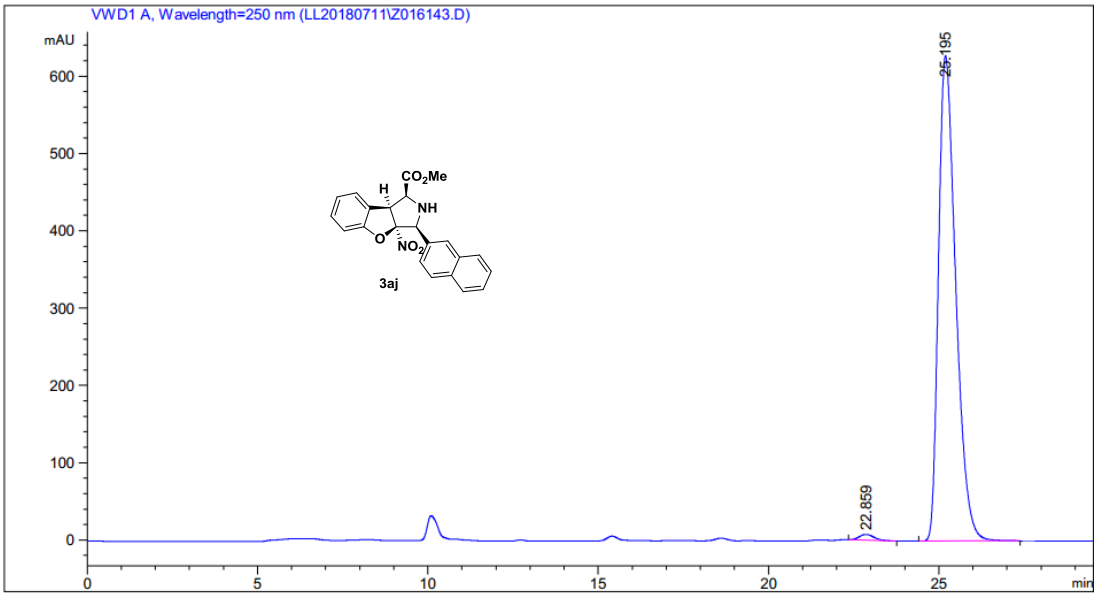
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.742	317.742	696.016	98.81	99.19	n.a.
2		19.582	3.838	5.650	1.19	0.81	n.a.
总和:			**321.580**	**701.666**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



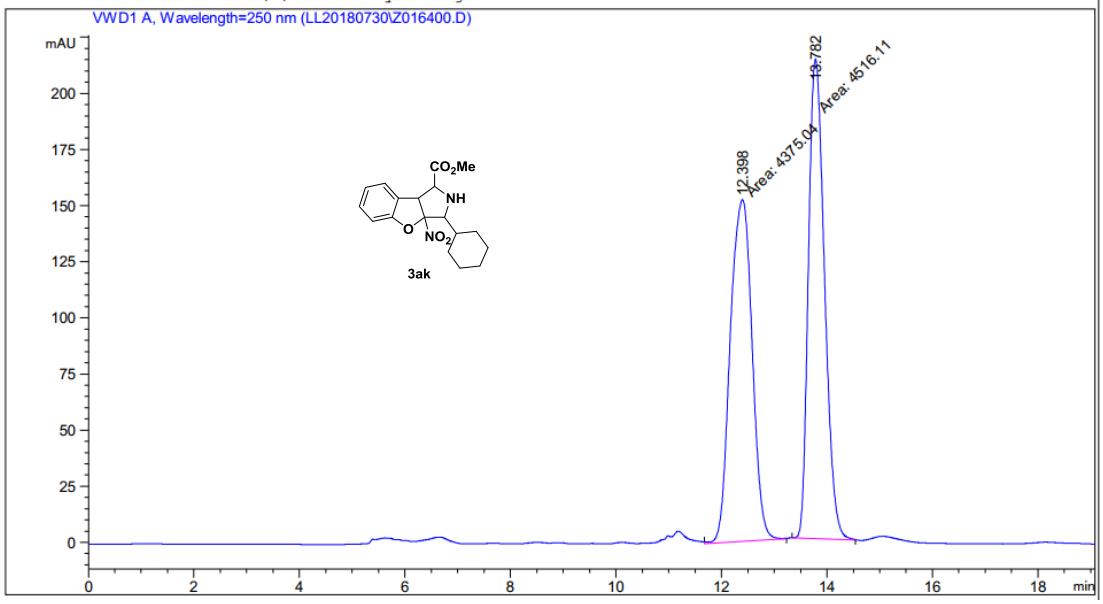
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.415	VB	0.5101	2.52935e4	744.15082	50.5064
2	25.150	BB	0.5438	2.47864e4	700.53308	49.4936

Additional Info : Peak(s) manually integrated



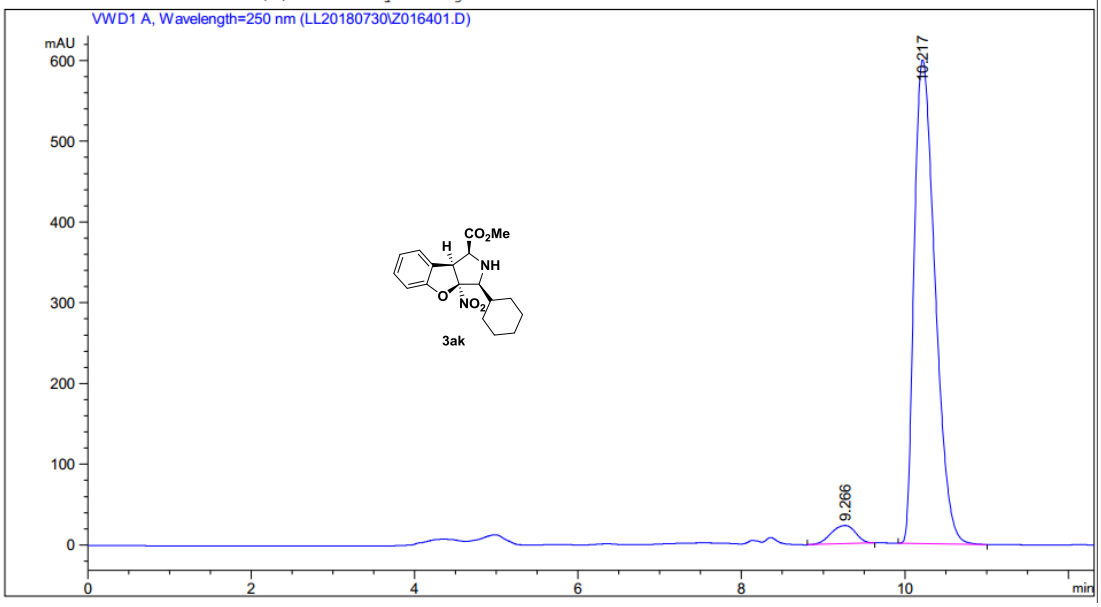
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.859	BB	0.4607	221.57669	7.44716	0.9925
2	25.195	BB	0.5375	2.21044e4	627.75745	99.0075

Additional Info : Peak(s) manually integrated



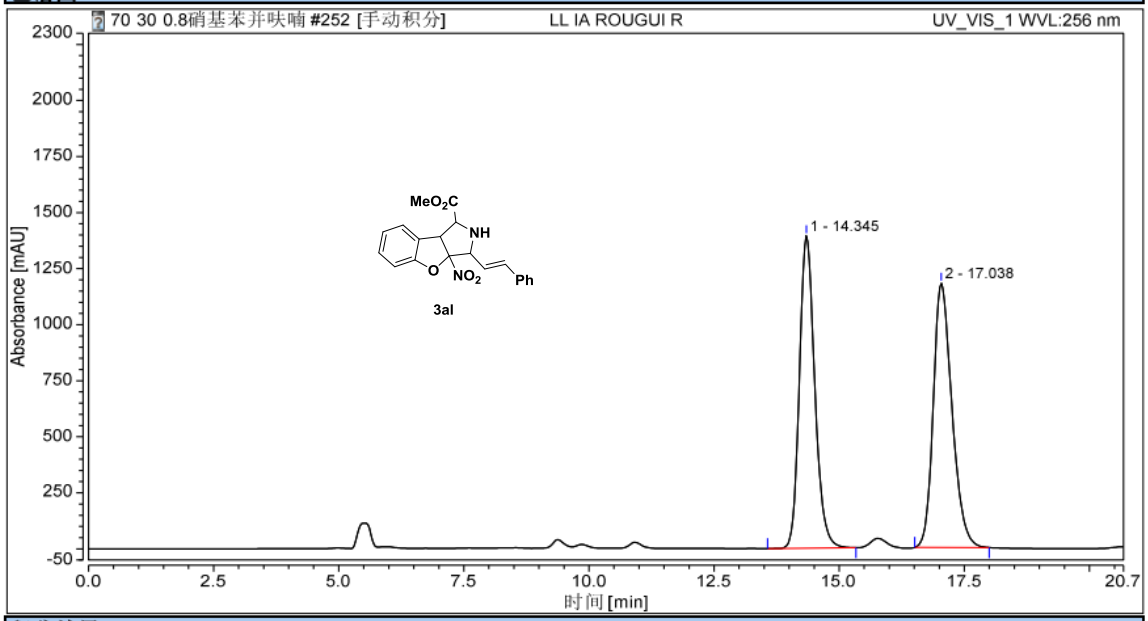
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.398	MM	0.4792	4375.03516	152.17900	49.2066
2	13.782	MM	0.3526	4516.11230	213.46397	50.7934

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.266	BB	0.3402	470.38248	22.61916	4.2473
2	10.217	BB	0.2807	1.06046e4	599.28125	95.7527

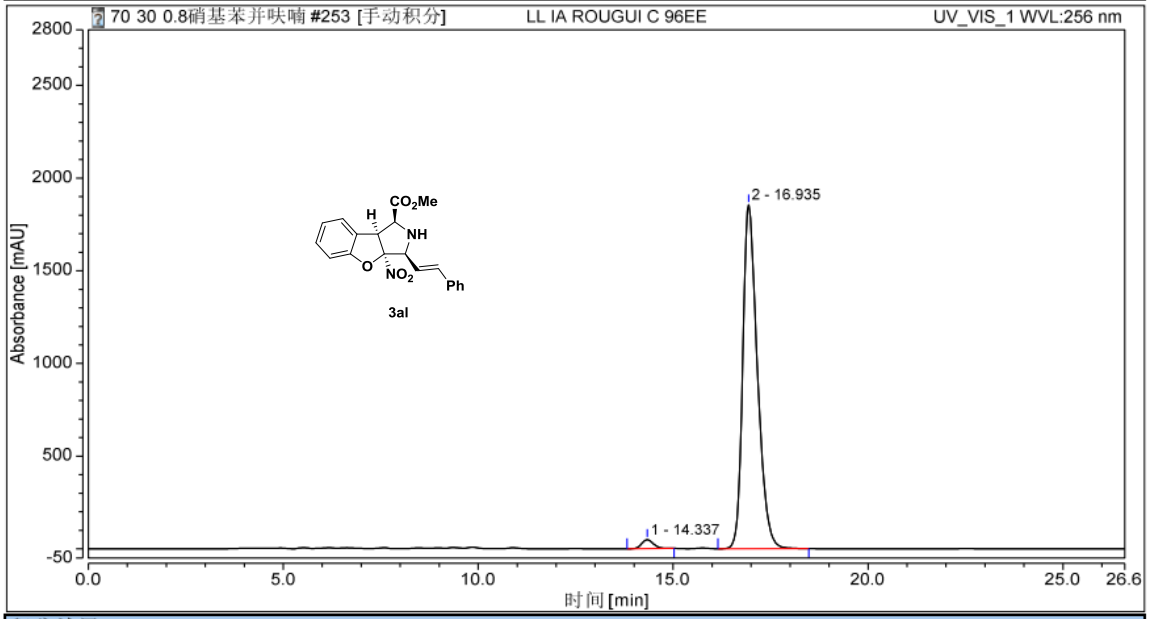
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		14.345	495.599	1394.324	49.27	54.18	n.a.
2		17.038	510.219	1179.002	50.73	45.82	n.a.
总和:			**1005.818**	**2573.325**	**100.00**	**100.00**	

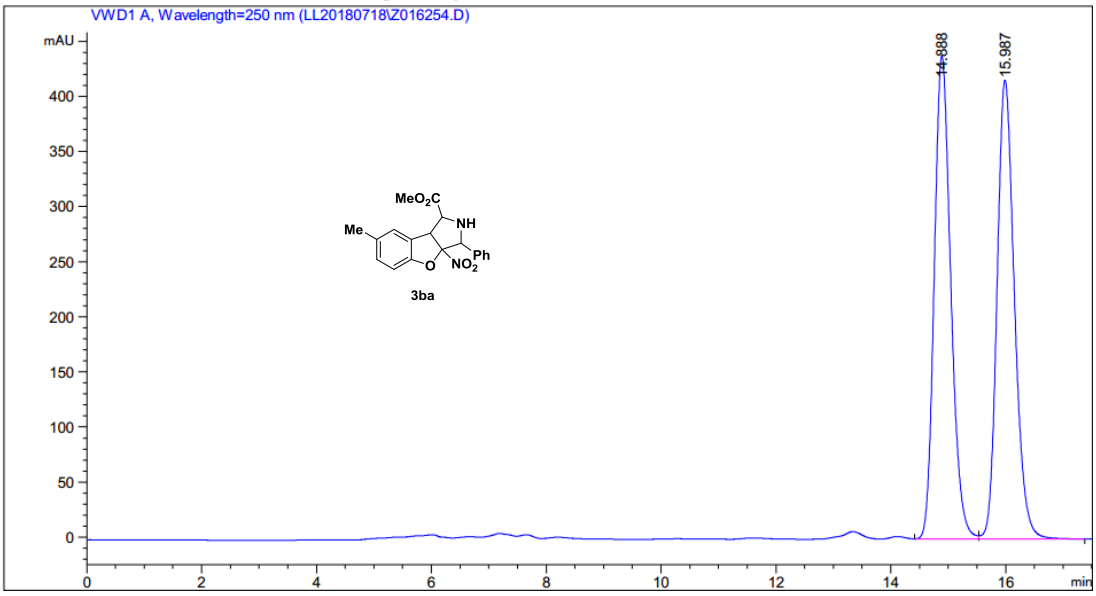
色谱图



积分结果

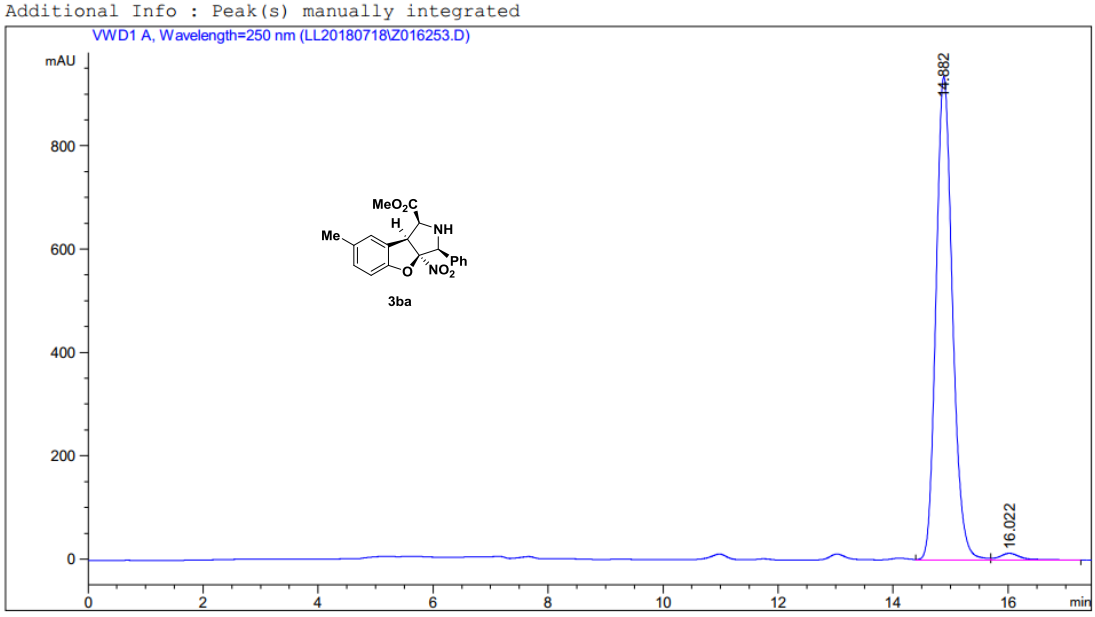
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		14.337	16.488	48.125	2.00	2.53	n.a.
2		16.935	808.894	1854.654	98.00	97.47	n.a.
总和:			**825.382**	**1902.779**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



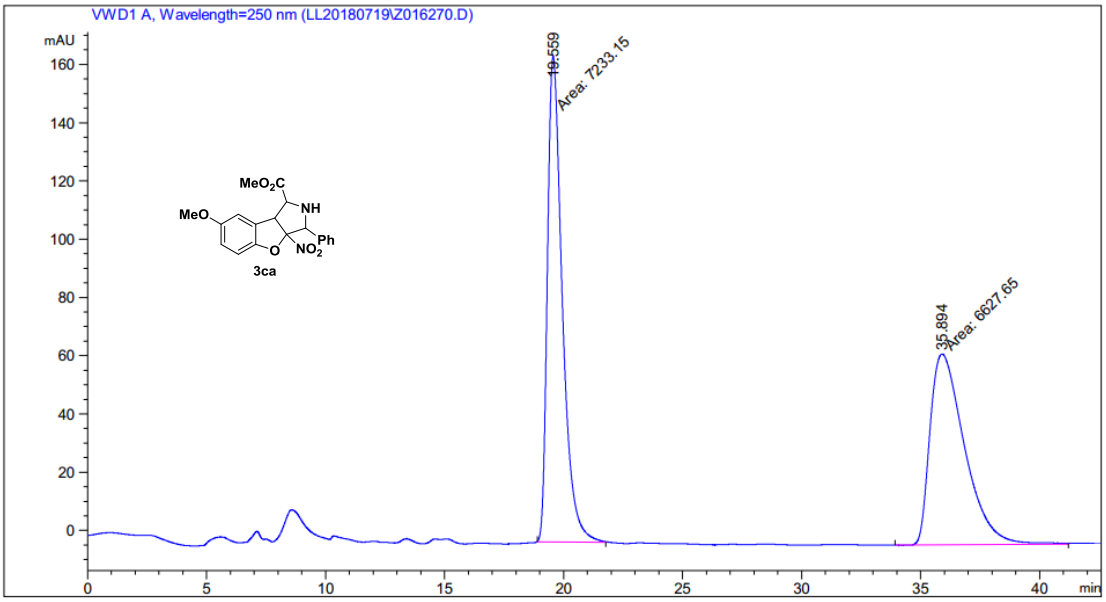
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.373	BV	0.2092	7241.98730	533.86945	49.3536
2	10.066	VV	0.2232	7431.68945	507.80945	50.6464

Additional Info : Peak(s) manually integrated



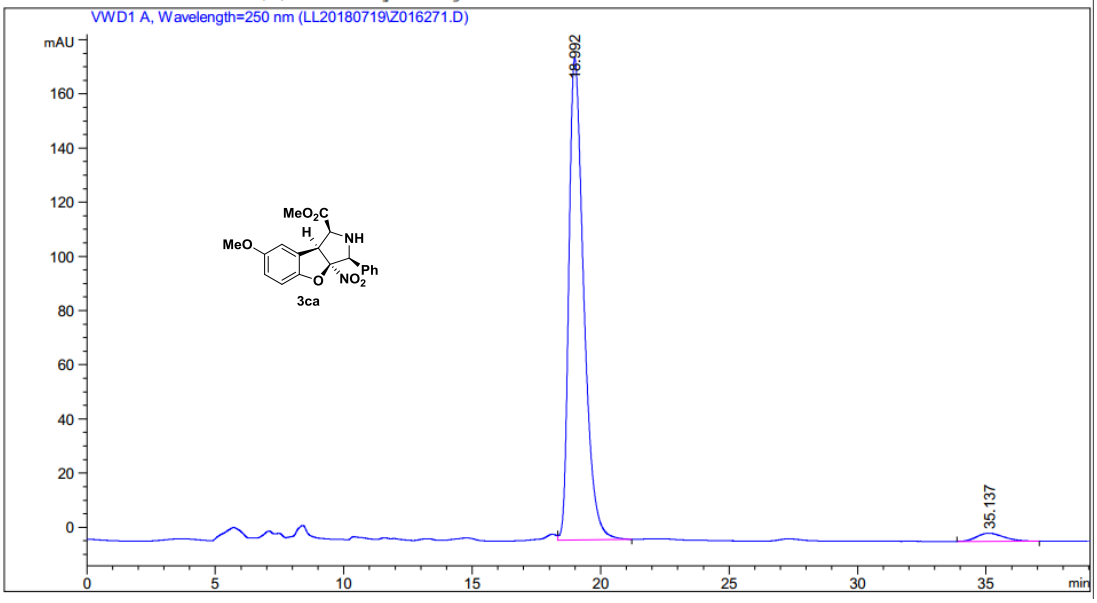
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.882	VV	0.3066	1.86307e4	935.45349	98.2730
2	16.022	VB	0.3732	327.40701	12.90335	1.7270

Additional Info : Peak(s) manually integrated



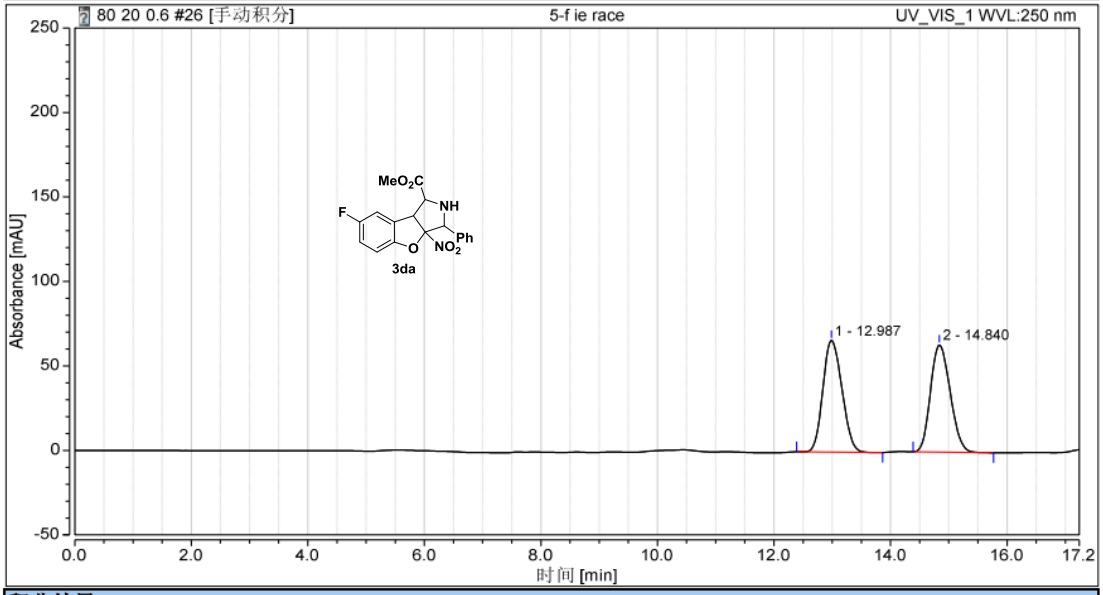
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.559	MM	0.7170	7155.06250	166.32347	50.0973
2	35.894	MM	1.7884	7127.25781	66.42270	49.9027

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.992	VB	0.6123	7160.63574	177.88194	97.0050
2	35.137	BB	0.8725	221.08228	2.99099	2.9950

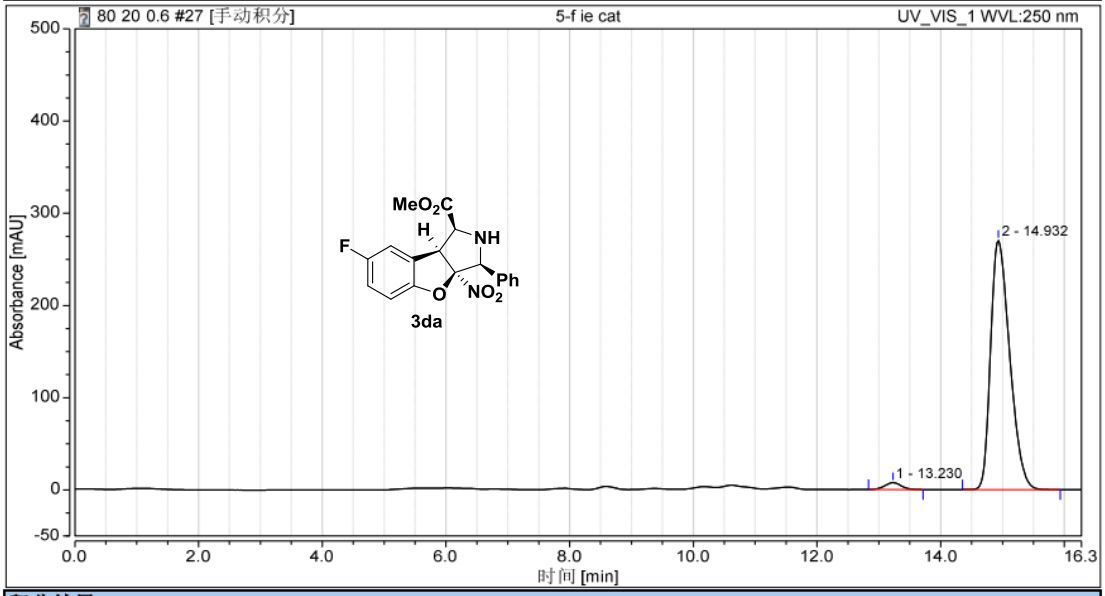
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.987	25.037	66.140	50.22	51.06	n.a.
2		14.840	24.820	63.394	49.78	48.94	n.a.
总和:			**49.857**	**129.534**	**100.00**	**100.00**	

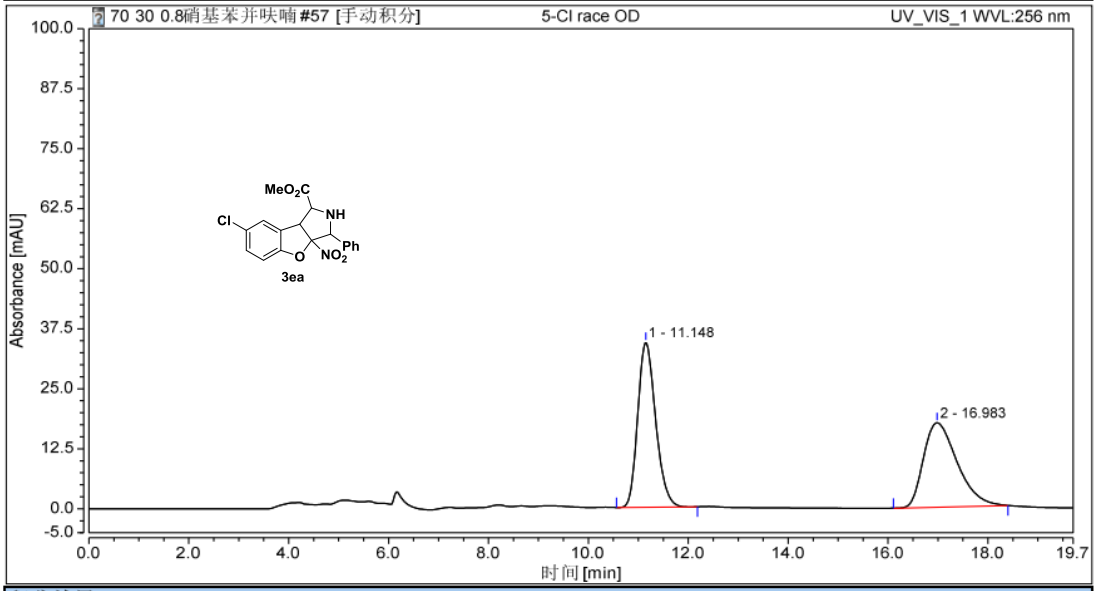
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.230	2.299	7.476	2.32	2.69	n.a.
2		14.932	96.706	270.382	97.68	97.31	n.a.
总和:			**99.005**	**277.859**	**100.00**	**100.00**	

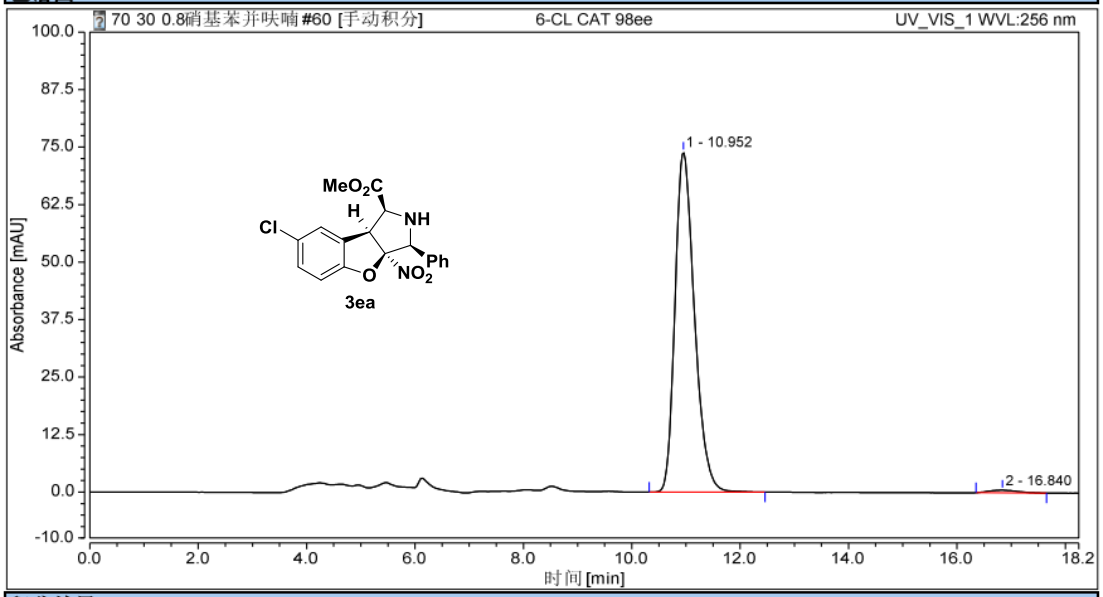
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.148	14.250	34.345	50.89	66.15	n.a.
2		16.983	13.751	17.574	49.11	33.85	n.a.
总和:			**28.002**	**51.919**	**100.00**	**100.00**	

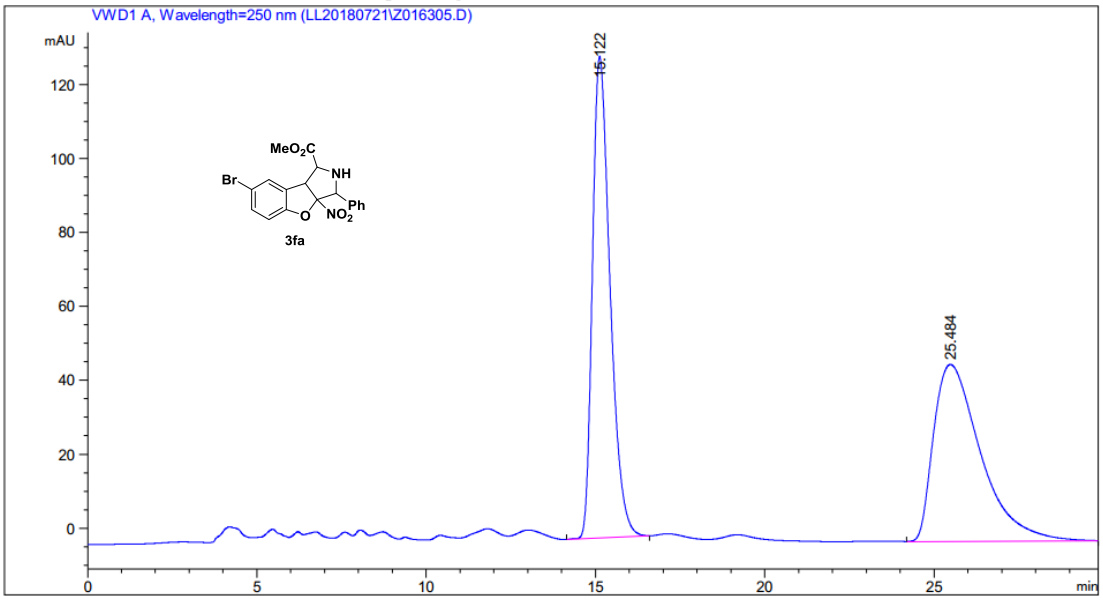
色谱图



积分结果

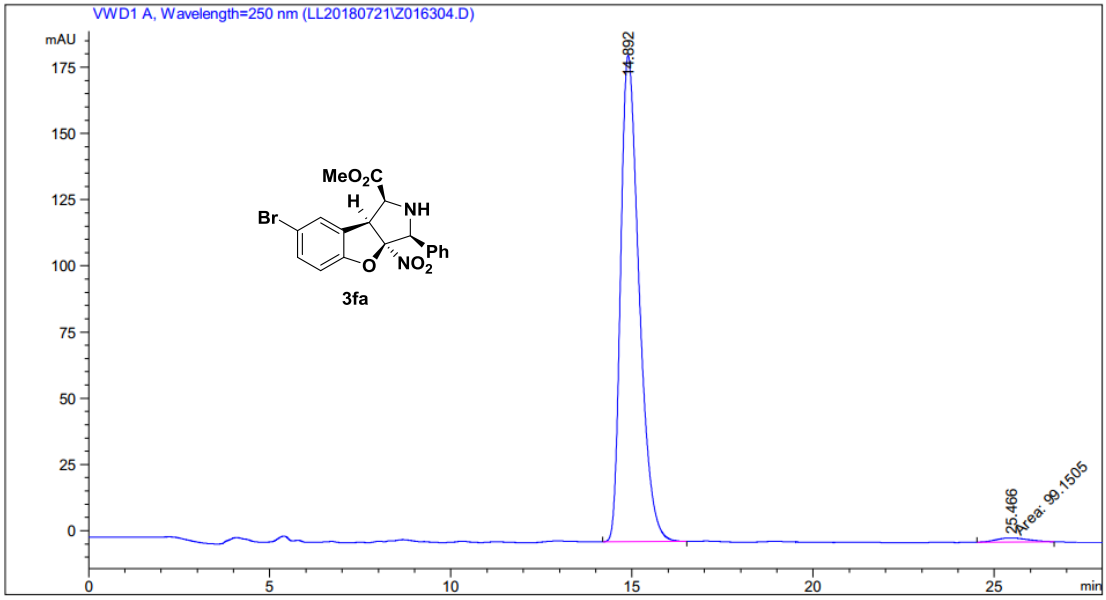
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		10.952	30.811	73.938	98.90	99.23	n.a.
2		16.840	0.343	0.577	1.10	0.77	n.a.
总和:			**31.154**	**74.515**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



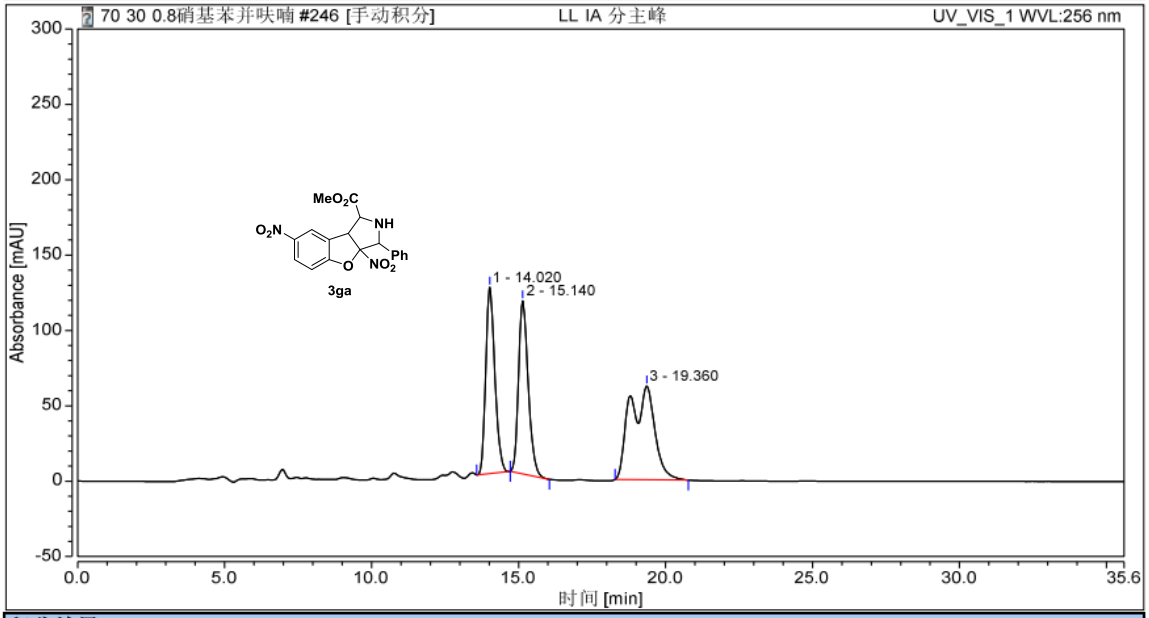
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.122	BB	0.5571	4710.84521	130.31750	50.4912
2	25.484	BBA	1.4389	4619.19141	47.86678	49.5088

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.892	BB	0.5425	6499.38818	183.62541	98.4974
2	25.466	MM	1.0272	99.15053	1.60879	1.5026

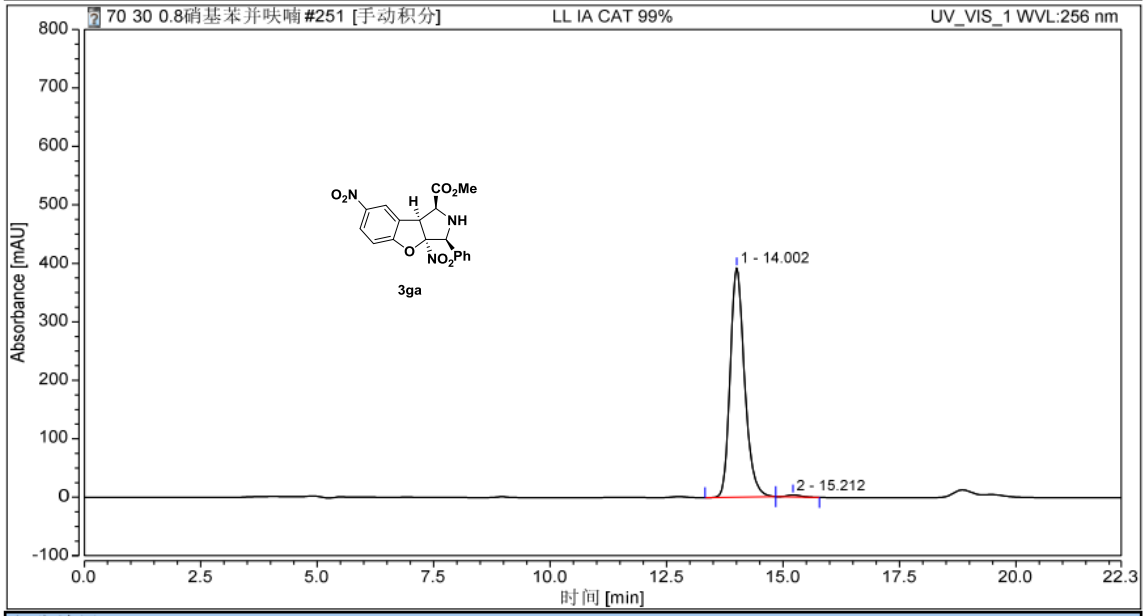
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		14.020	44.369	123.568	29.79	41.10	n.a.
2		15.140	43.981	114.726	29.53	38.16	n.a.
3		19.360	60.600	62.326	40.68	20.73	n.a.
总和:			**148.950**	**300.620**	**100.00**	**100.00**	

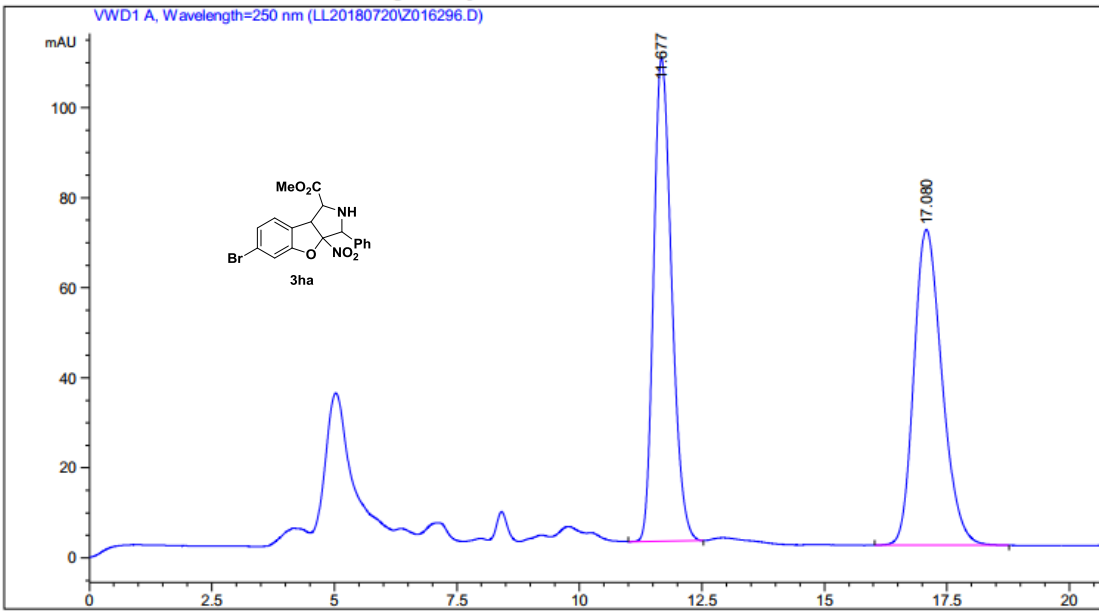
色谱图



积分结果

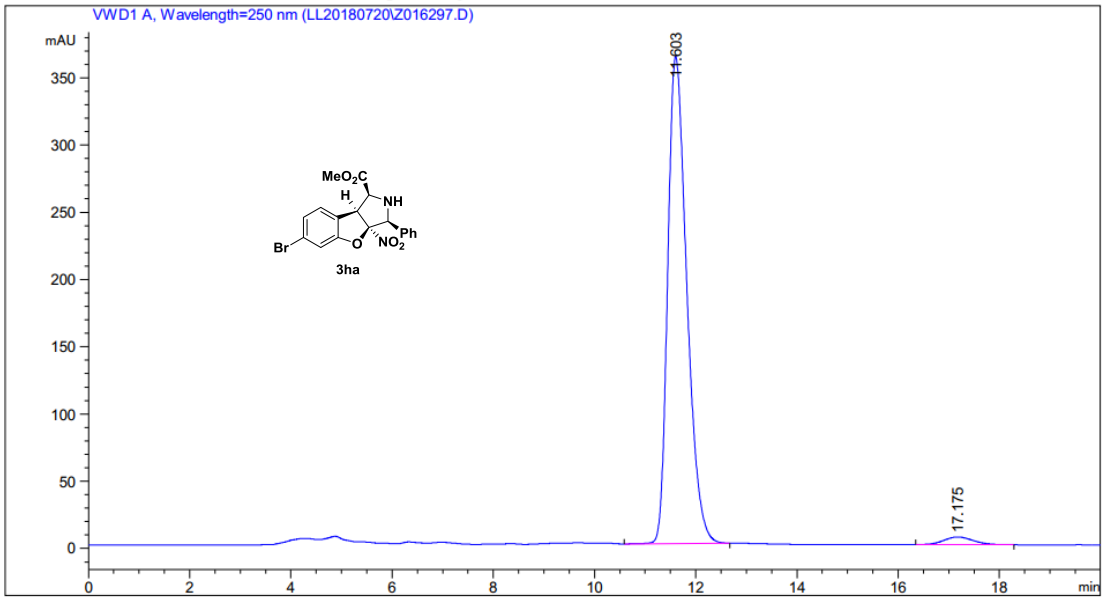
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		14.002	140.578	392.139	99.24	99.17	n.a.
2		15.212	1.074	3.269	0.76	0.83	n.a.
总和:			**141.652**	**395.408**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



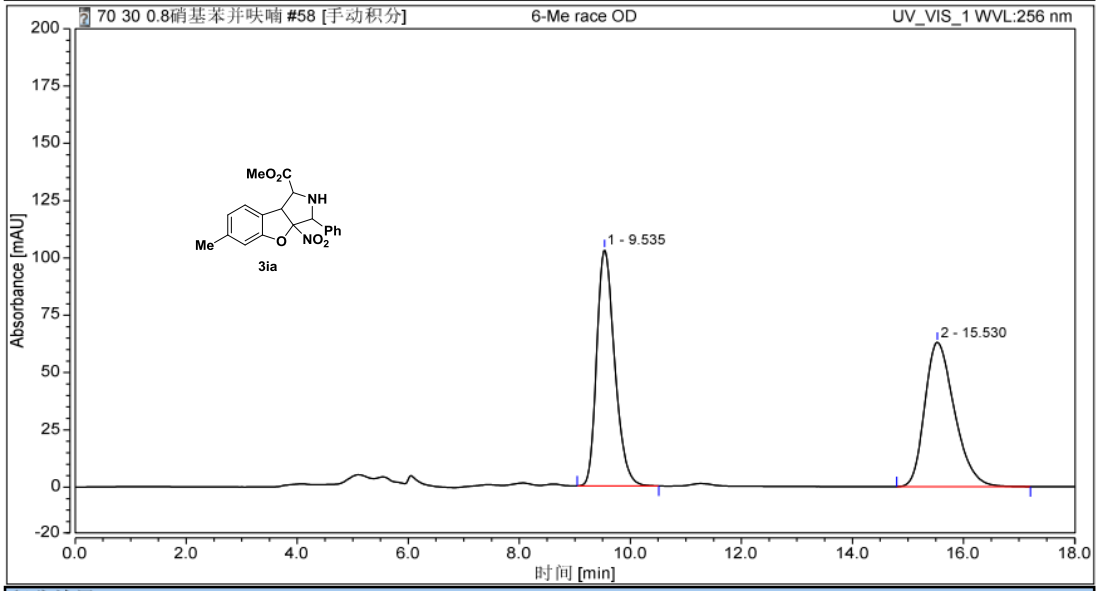
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.677	BB	0.3938	2737.75195	107.29388	49.4639
2	17.080	BB	0.6179	2797.10083	70.17310	50.5361

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.603	BB	0.4036	9459.96191	362.35269	97.5978
2	17.175	BB	0.5756	232.84355	5.77000	2.4022

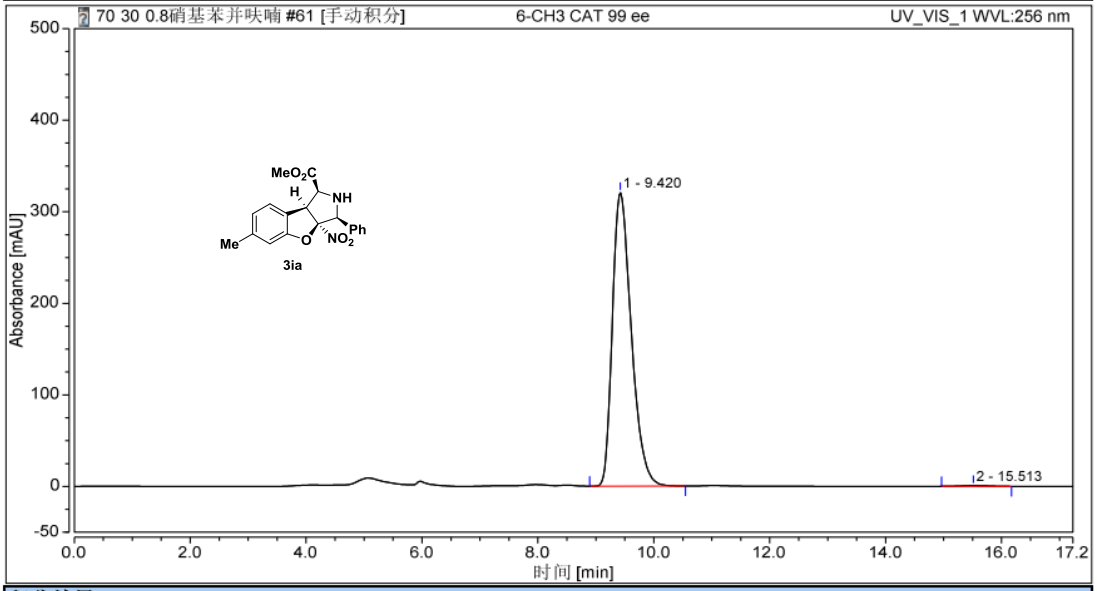
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.535	38.628	103.095	49.75	62.09	n.a.
2		15.530	39.009	62.945	50.25	37.91	n.a.
总和:			**77.638**	**166.041**	**100.00**	**100.00**	

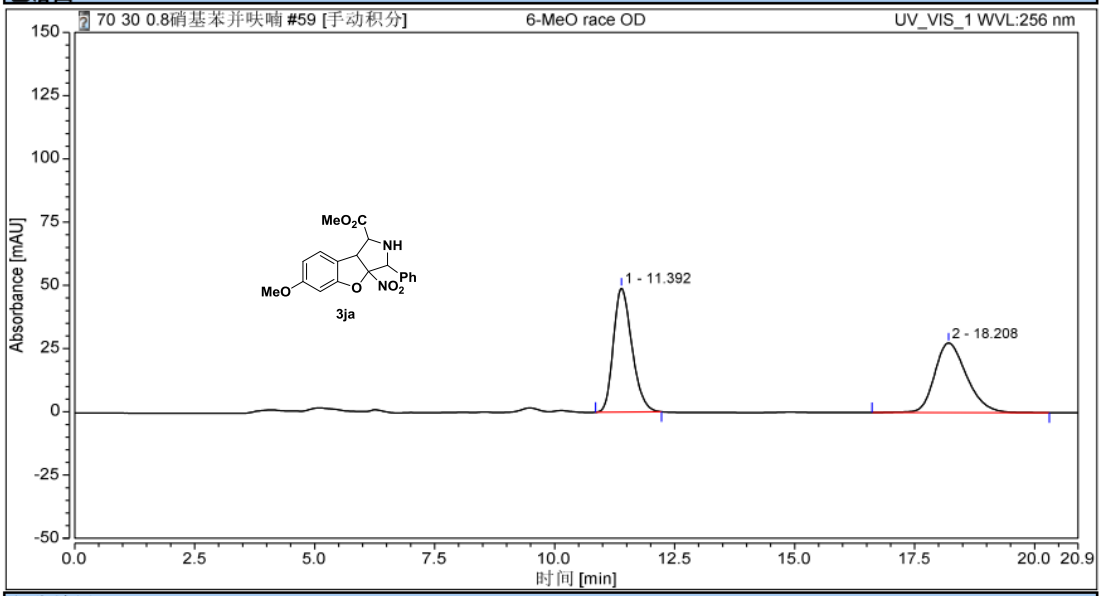
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		9.420	121.141	320.751	99.59	99.73	n.a.
2		15.513	0.499	0.875	0.41	0.27	n.a.
总和:			**121.641**	**321.627**	**100.00**	**100.00**	

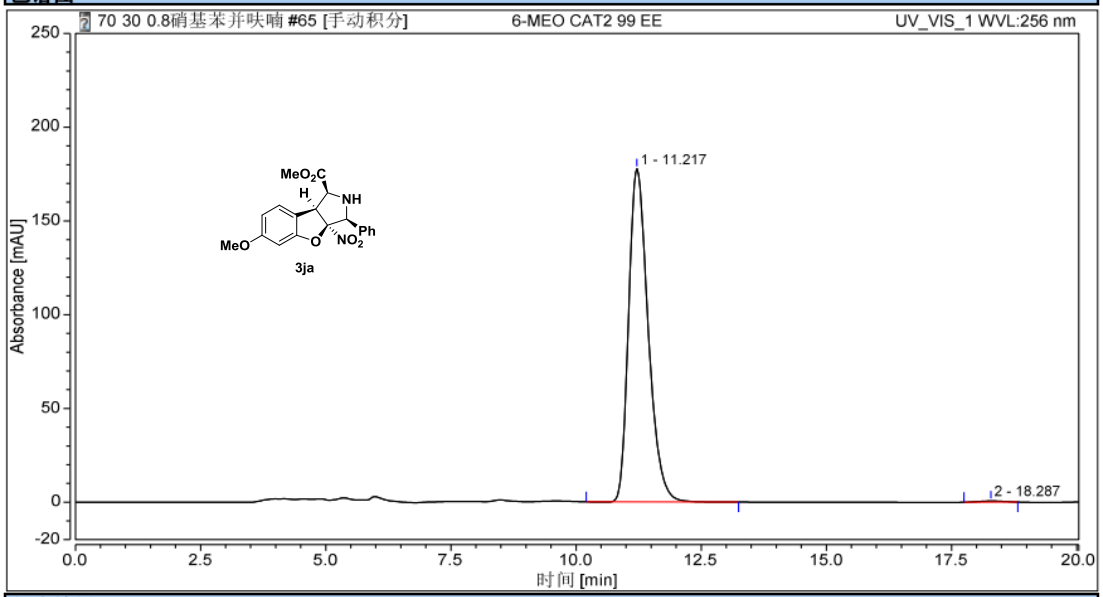
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.392	21.927	48.967	50.71	64.01	n.a.
2		18.208	21.314	27.532	49.29	35.99	n.a.
总和:			**43.241**	**76.499**	**100.00**	**100.00**	

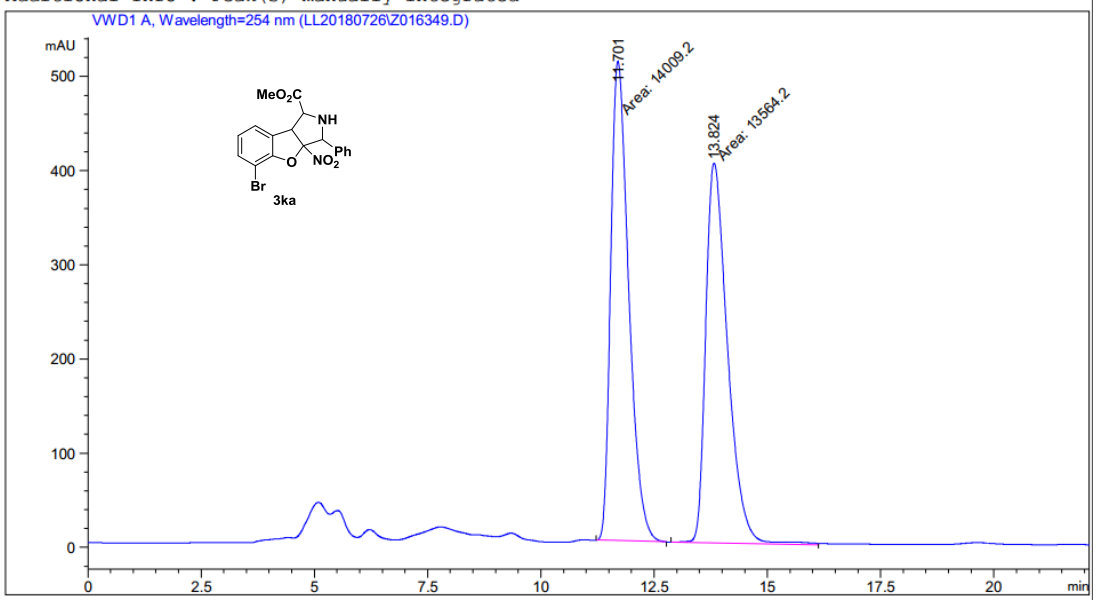
色谱图



积分结果

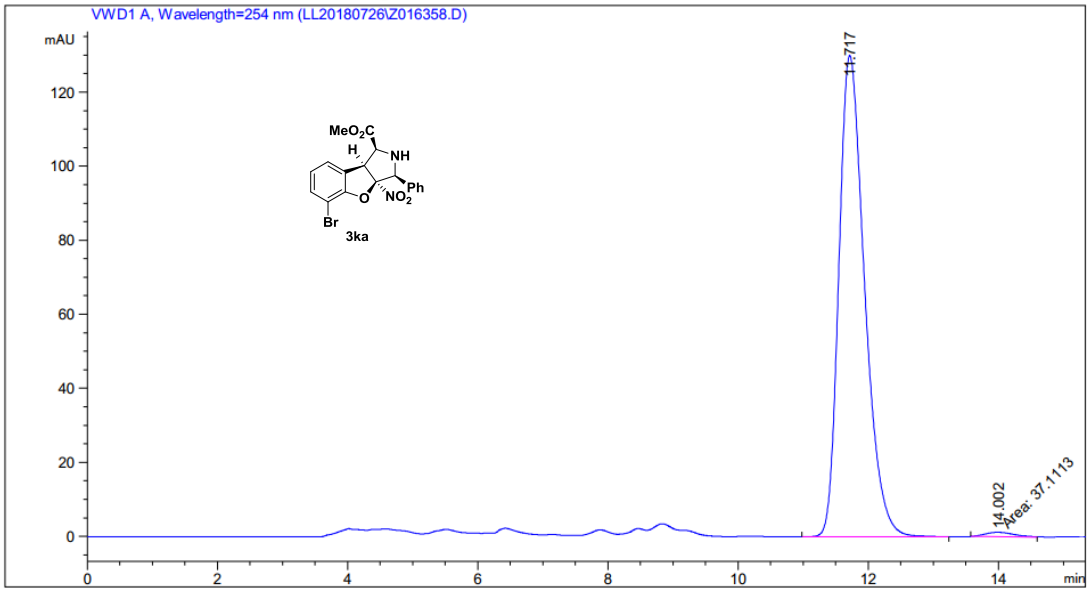
序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.217	80.440	177.692	99.54	99.65	n.a.
2		18.287	0.371	0.625	0.46	0.35	n.a.
总和:			**80.810**	**178.317**	**100.00**	**100.00**	

Additional Info : Peak(s) manually integrated



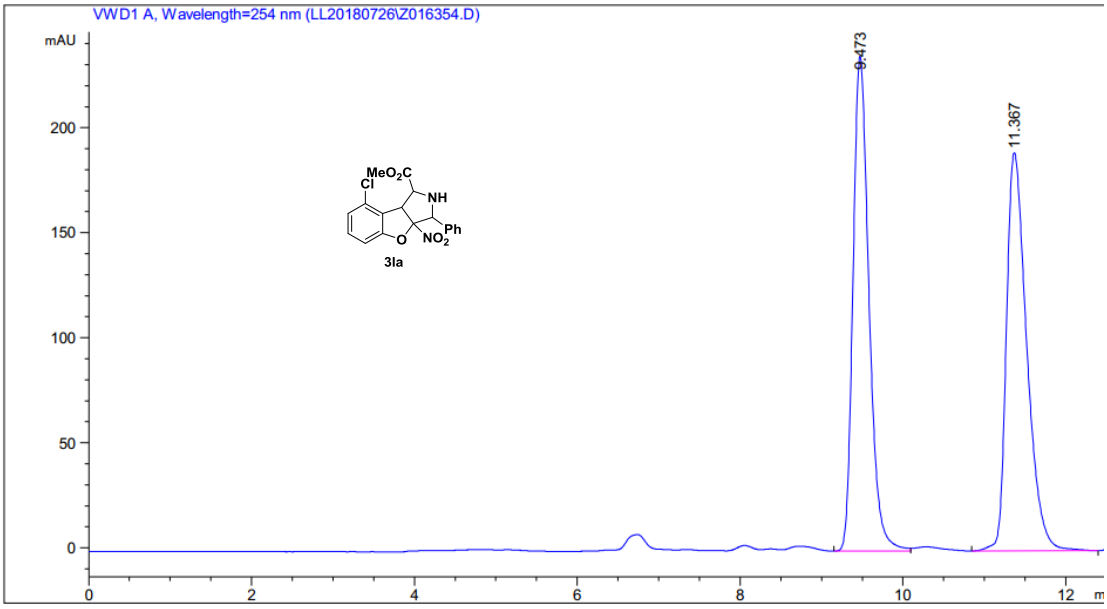
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.701	MM	0.4588	1.40092e4	508.85767	50.8069
2	13.824	MM	0.5604	1.35642e4	403.37881	49.1931

Additional Info : Peak(s) manually integrated



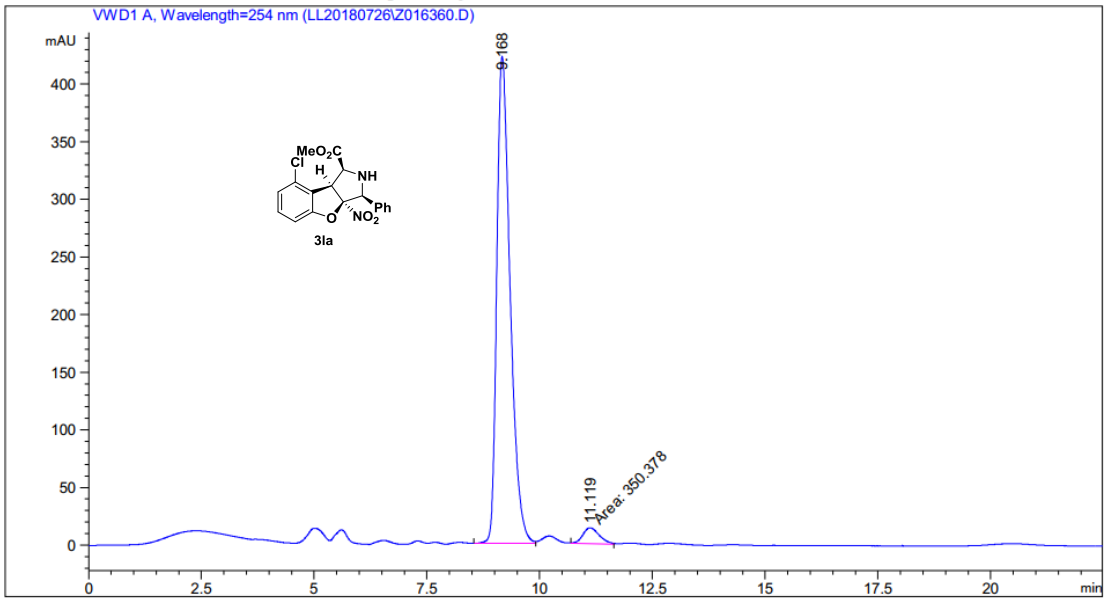
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.717	BB	0.4217	3565.19727	130.06592	98.9698
2	14.002	MM	0.5122	37.11134	1.20751	1.0302

Additional Info : Peak(s) manually integrated



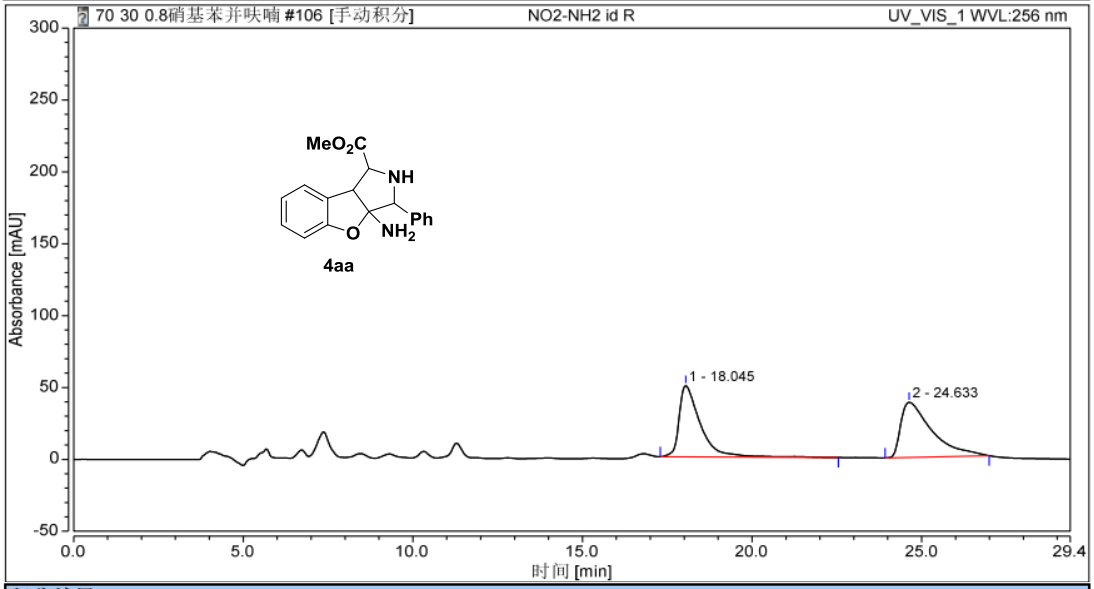
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.473	BV	0.2083	3205.51685	235.50203	49.3693
2	11.367	BB	0.2649	3287.41260	189.56013	50.6307

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.168	BV	0.3144	8690.19531	422.22791	96.1244
2	11.119	MM	0.4210	350.37836	13.86924	3.8756

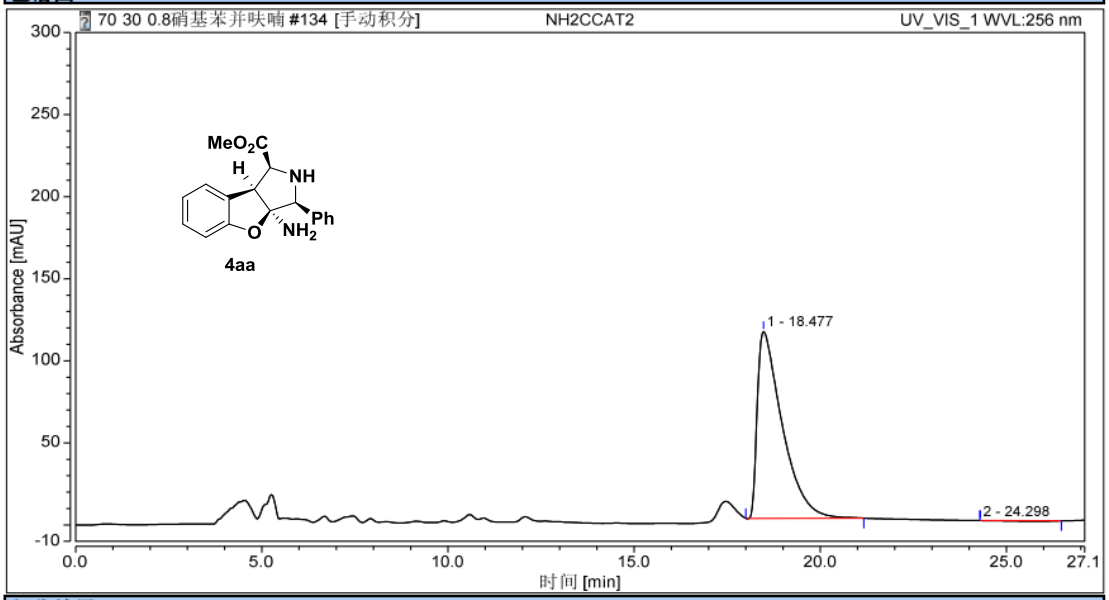
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.045	36.249	49.631	48.54	56.94	n.a.
2		24.633	38.425	37.532	51.46	43.06	n.a.
总和:			**74.674**	**87.163**	**100.00**	**100.00**	

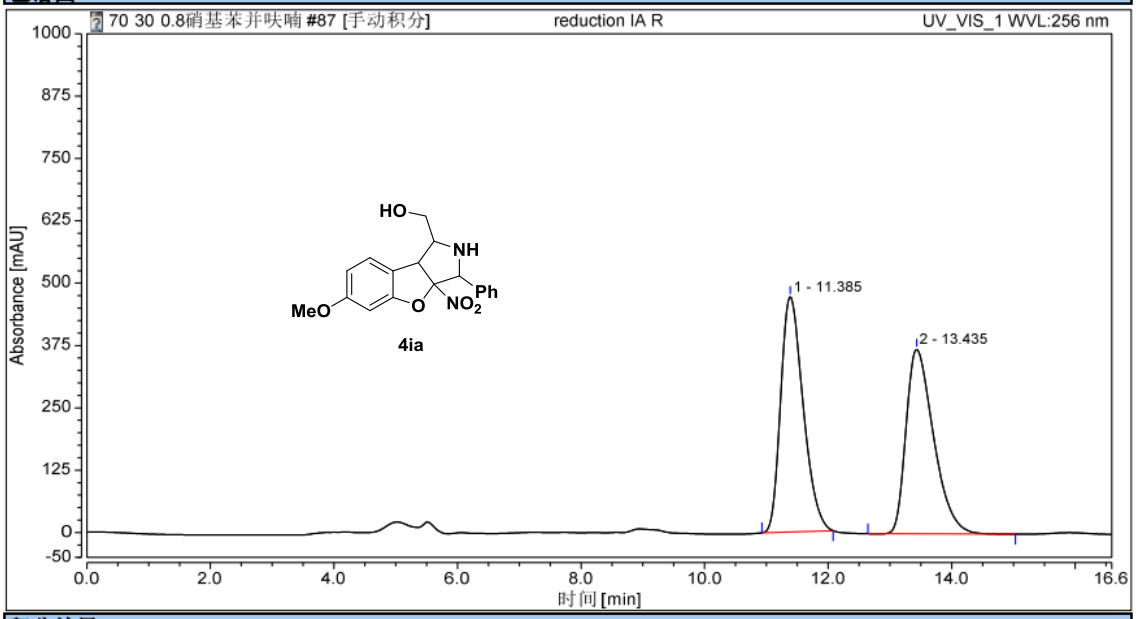
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		18.477	88.170	113.873	99.54	100.00	n.a.
2		24.298	0.404	0.002	0.46	0.00	n.a.
总和:			**88.574**	**113.874**	**100.00**	**100.00**	

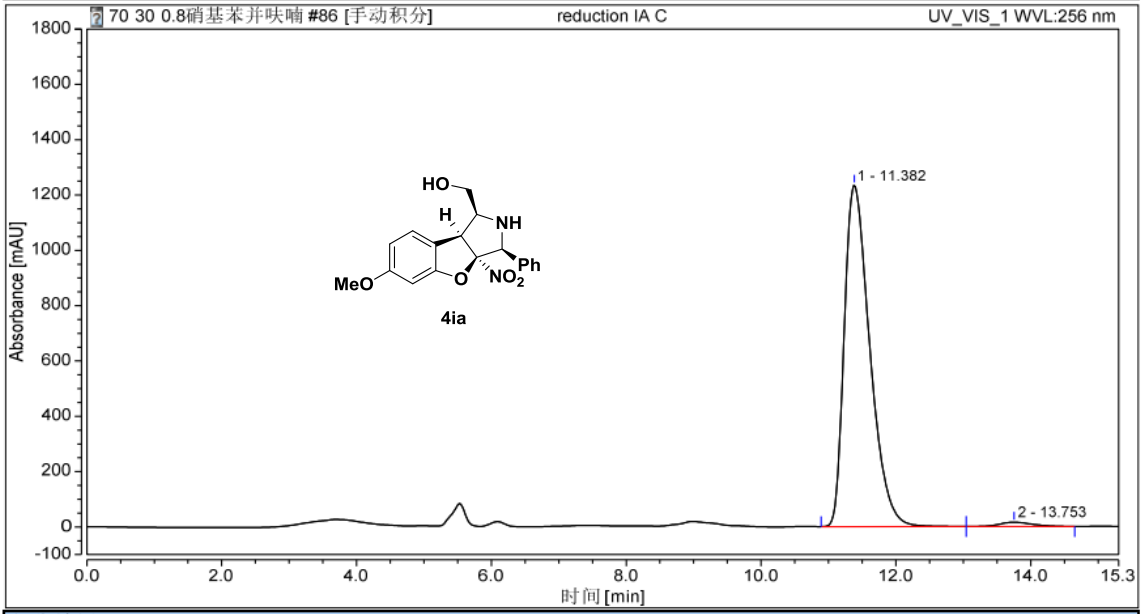
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.385	198.520	472.104	50.91	56.06	n.a.
2		13.435	191.432	370.046	49.09	43.94	n.a.
总和:			**389.951**	**842.151**	**100.00**	**100.00**	

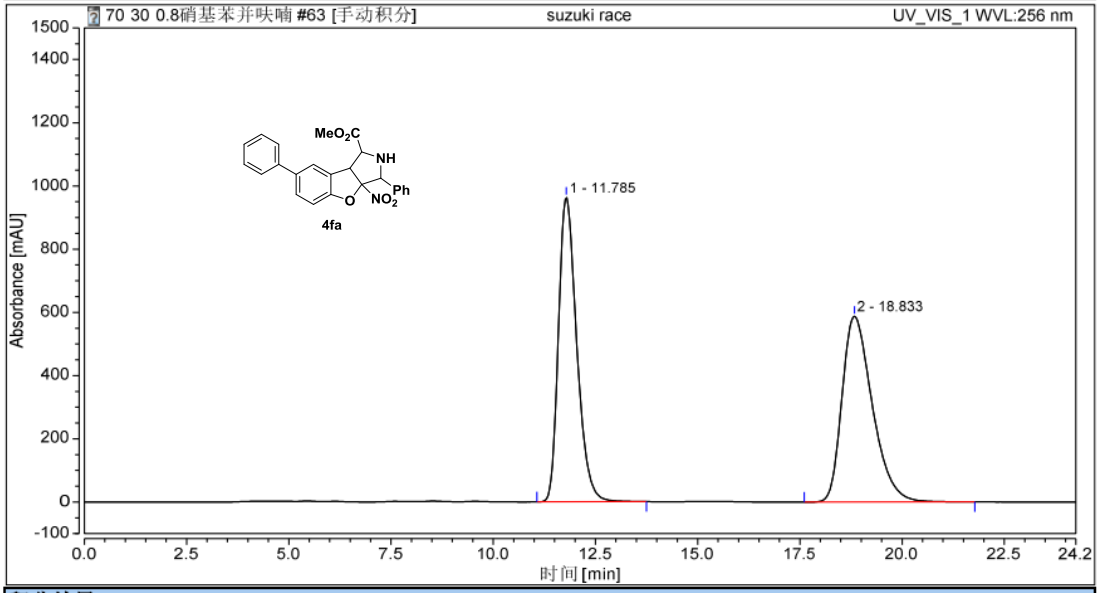
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.382	541.875	1234.466	98.36	98.75	n.a.
2		13.753	9.043	15.657	1.64	1.25	n.a.
总和:			**550.918**	**1250.124**	**100.00**	**100.00**	

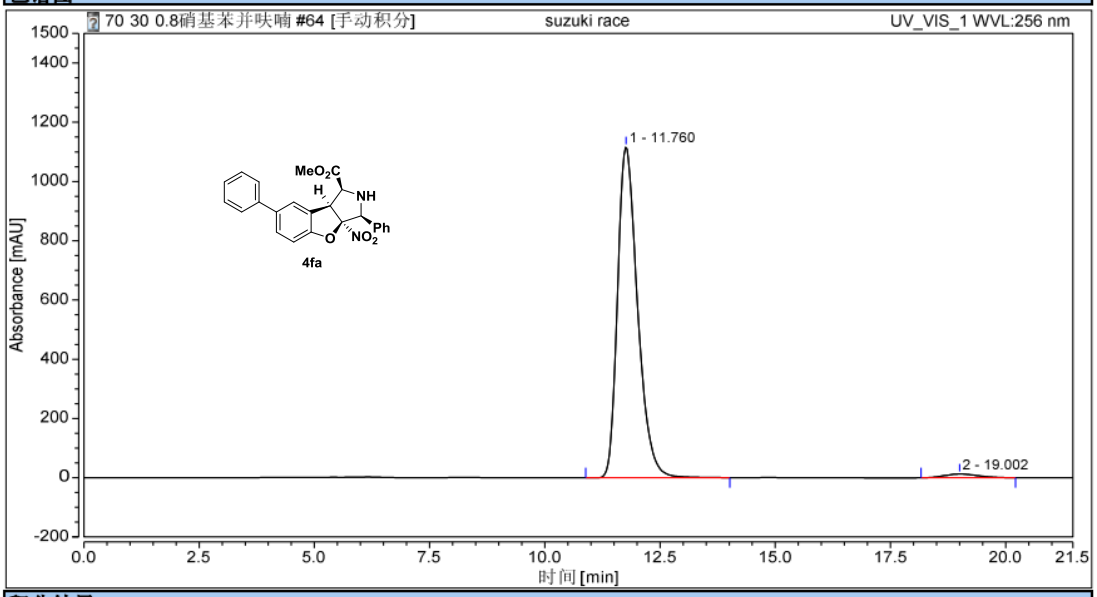
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.785	498.393	964.257	49.71	62.15	n.a.
2		18.833	504.300	587.313	50.29	37.85	n.a.
总和:			**1002.693**	**1551.570**	**100.00**	**100.00**	

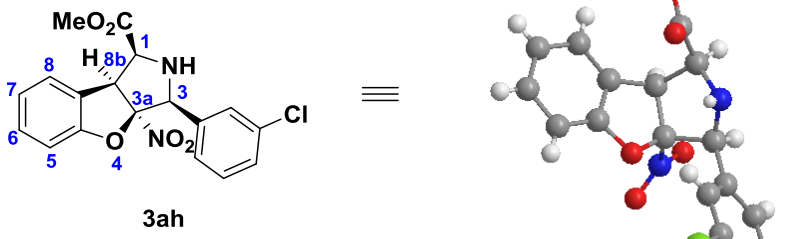
色谱图



积分结果

序号	Name	RetTime min	Area mAU*min	Height mAU	Area %	Height %	样品量 n.a.
1		11.760	562.257	1117.084	98.14	98.87	n.a.
2		19.002	10.632	12.743	1.86	1.13	n.a.
总和:			**572.890**	**1129.827**	**100.00**	**100.00**	

9. Crystal data and structure refinement for 3ah



3ah

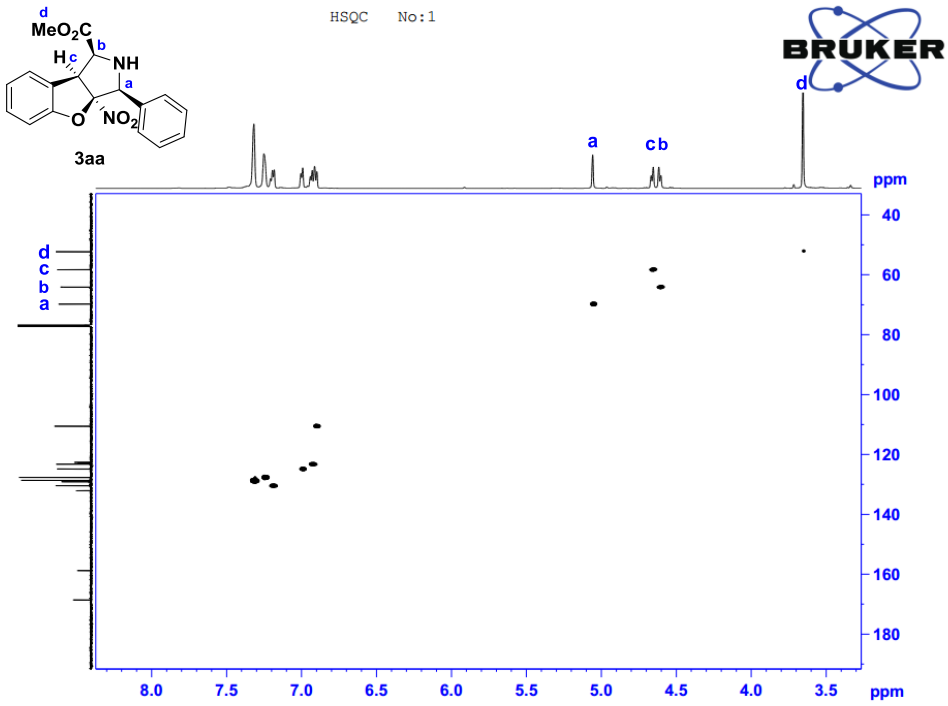
Table 1 Crystal data and structure refinement for LL_1.

Identification code	LL_1
Empirical formula	$C_{18}H_{15}ClN_2O_5$
Formula weight	374.77
Temperature/K	120.00(10)
Crystal system	trigonal
Space group	$P3_2$
a/Å	11.0671(2)
b/Å	11.0671(2)
c/Å	11.8214(2)
α/°	90
β/ °	90
γ/°	120
Volume/Å^3	1253.91(5)
Z	3
ρ_{calc}g/cm^3	1.489
μ/mm^{-1}	2.329
F(000)	582.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.228 to 146.992
Index ranges	$-8 \le h \le 13$, $-13 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	8112
Independent reflections	3098 [R_{int} = 0.0270, R_{sigma} = 0.0245]
Data/restraints/parameters	3098/1/240
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0775
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0775

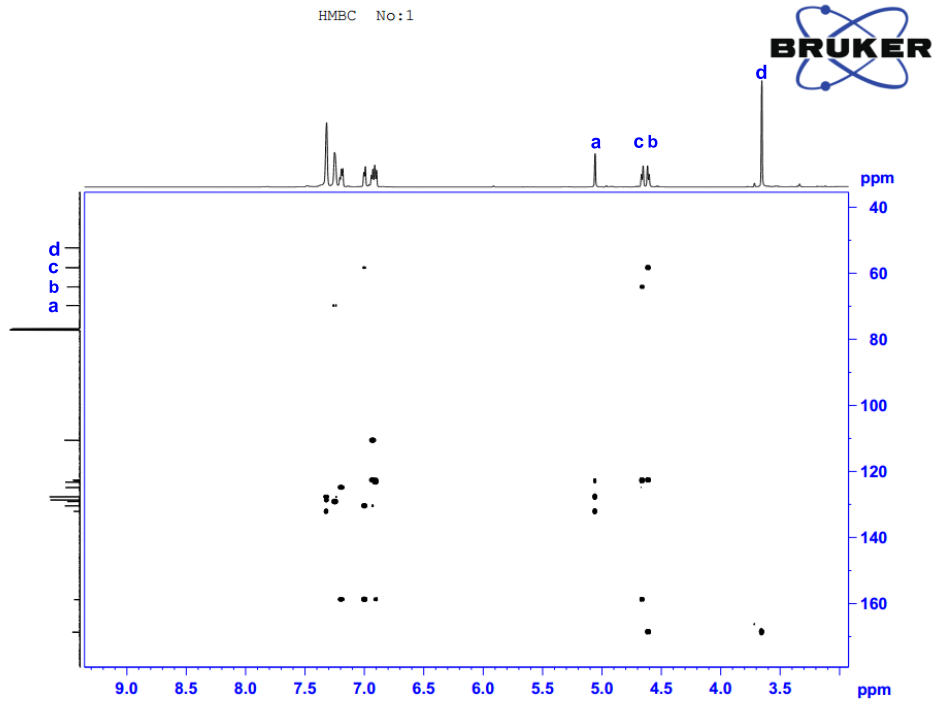
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.30
Flack parameter	0.007(7)/0.007(5)

10. Copies of HSQC, HMBC and Noesy

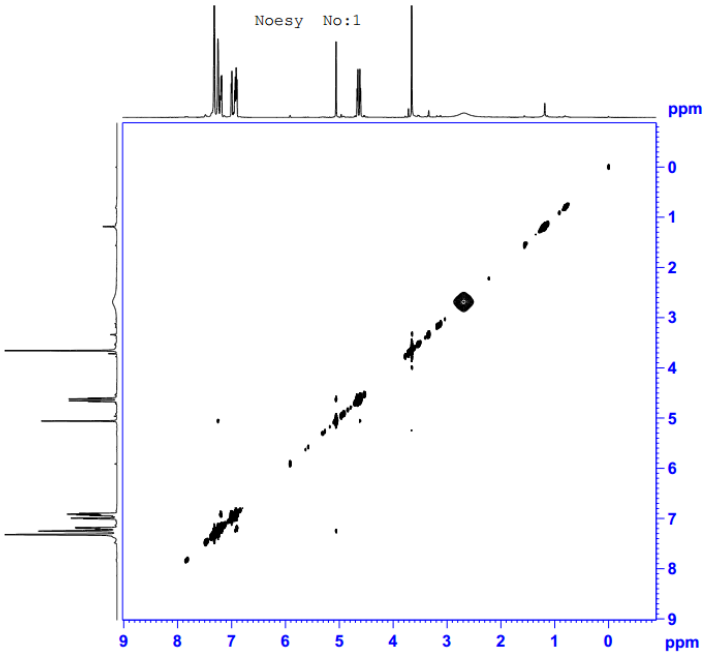
HSQC of 3aa



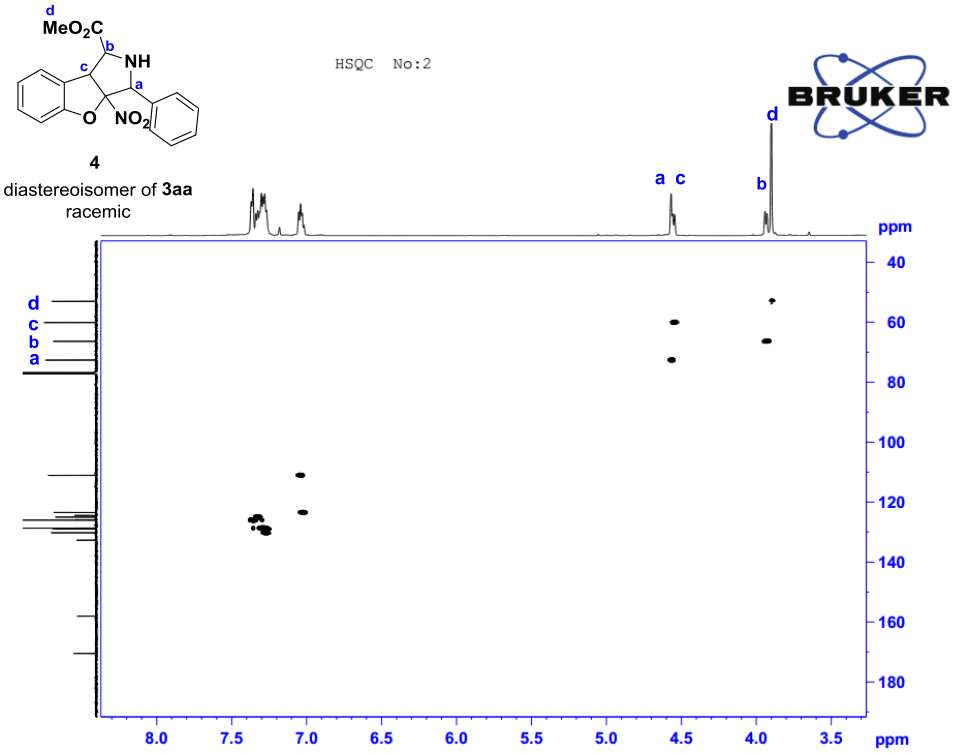
HMBC of 3aa



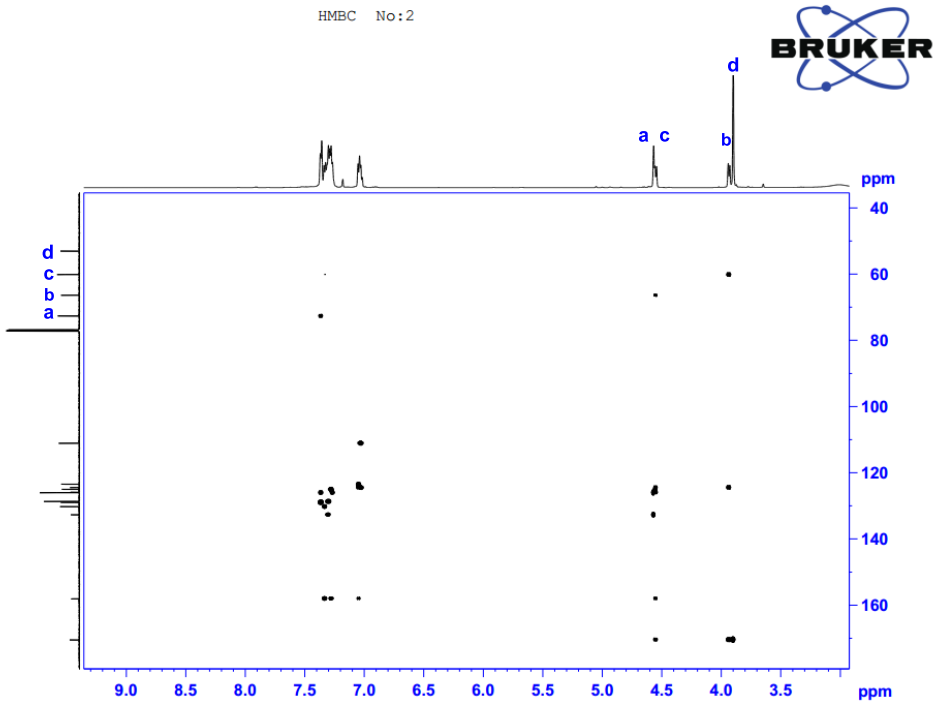
Noesy of 3aa



HSQC of 4



HMBC of 4



Noesy of 4