# Supporting Information

## High Diastereo- and Enantioselective Michael Addition of 3-Acetoxy-2-oxindoles with Nitroalkenes Catalyzed by Nickel/PyBisulidine

Ruoran Wu, Peng Chen, Yu Chai, Junyu Zhou, Jianhua Ou, Yan Min, Haoting Wang, Guojuan Liang, Dong Zhang, Jing Zhou, Hui Zhou.

*Chongqing Research Center for Pharmaceutical Engineering, Chongqing Key Laboratory of Biochemistry and Molecular Pharmacology, School of pharmacy, Chongqing Medical University, Chongqing 400016, China*

## Table of Contents

## 1. General information

Various 3-acetoxy-2-oxindoles **1** were prepared according to literature method[1]. Nitroalkenes **2** were prepared according to literature method[2]. Other reagents were obtained from Adamas, Aladin, or Acros etc. without further purification unless otherwise noted. High resolution mass spectra were measured on commercial instruments. NMR spectra were recorded on commercial instruments and operating at 600 MHz for $^1$H NMR and 151 MHz for $^{13}$C NMR. Chemical shifts were reported in ppm from tetramethyl silane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26) in $^1$H NMR spectra and Chemical shifts were reported in ppm from the tetramethyl silane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0) in $^{13}$C NMR spectra. Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. The enantiomeric excess (*ee*) was determined by HPLC analysis. Analytical HPLC was performed on a Shimadzu liquid chromatography equipped, using a chiral DAICEL CHIRALCEL IC-H or DAICEL CHIRALCEL IB-H or DAICEL CHIRALCEL ID-H column at 254 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^T$(*c* = g/100 mL, solvent).

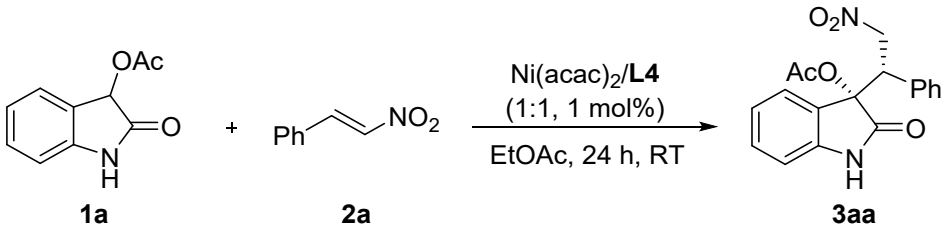
References

1. Y. Yang, C. Tang, G. Liang, P. Deng, J. Zhou, Z. Yang, P. Chen, H. Zhou, *J. Org. Chem.* **2021**, *86*, 7119-7130.

2. G. Chen, G. Liang, Y. Wang, P. Deng, H. Zhou, *Org. Biomol. Chem*. **2018**, *16*, 3841.

## 2. Other optimizations of the Michael addition reaction

**Table S1:** The effect of the molar ratio of **1a**/**2a**.[a]



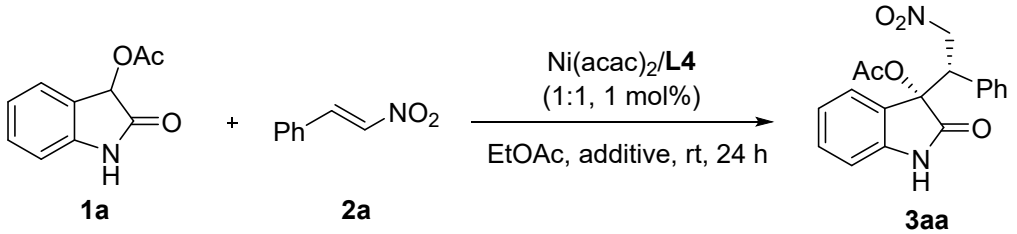

**1a** **2a** **3aa**

| Entry | Amount of **1a** | Amount of **2a** | Yield(%)[b] | dr[c] | *ee*(%)[d] |
|---|---|---|---|---|---|
| 1 | 0.10 | 0.12 | 57 | 51:1 | 99 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 0.10 | 0.15 | 62 | 55:1 | 99 |
| 3 | 0.10 | 0.20 | 58 | 50:1 | 99 |
| 4 | 0.12 | 0.10 | 50 | 52:1 | 99 |
| 5 | 0.15 | 0.10 | 53 | 53:1 | 99 |
| 6 | 0.20 | 0.10 | 42 | 55:1 | 99 |

[a] Unless otherwise noted, the reactions were performed with Ni(acac)$_2$/**L4** (1:1, 1 mol%), **1a**, **2a**, EtOAc (0.10 mL), at rt for 24 h. [b] Isolated yield. [c] Determined by HPLC. [d] Enantiomeric excess values of major diastereomers; Determined by chiral HPLC.

**Table S2:** The effects of additives.




**1a** **2a** **3aa**

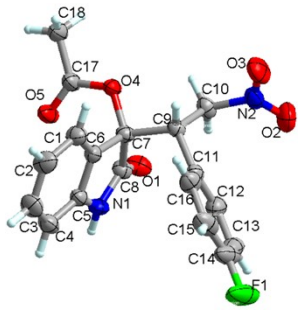
| Entry | Additive | Amount of Additive(mol%) | Yield(%)[b] | *dr*[c] | *ee*(%)[d] |
|---|---|---|---|---|---|
| 1 | none | -- | 62 | 55:1 | 99 |
| 2 | 3Å MS | 16.1 mg | 51 | 55:1 | 99 |
| 3 | 4Å MS | 16.1 mg | 63 | 54:1 | 99 |
| 4 | 5Å MS | 16.1 mg | 36 | 51:1 | 99 |
| 5 | $Et_3N$ | 20 mol% | 85 | 58:1 | 99 |
| 6 | DIPEA | 20 mol% | 71 | 40:1 | 99 |
| 7 | NMM | 20 mol% | 51 | 53:1 | 99 |
| 8 | *n*-$Bu_2NH$ | 20 mol% | 99 | 65:1 | 99 |
| 9 | *i*-$Bu_2NH$ | 20 mol% | 92 | 60:1 | 99 |
| 10 | $Cy_2NH$ | 20 mol% | 95 | 10:1 | 87 |
| 11 | Pyr | 20 mol% | 65 | 40:1 | 99 |
| 12 | PIP | 20 mol% | 61 | 11:1 | 92 |
| 13 | TMP | 20 mol% | 97 | 23:1 | 96 |
| 14 | *n*-$Bu_2NH$ | 10 mol% | 86 | 68:1 | 99 |
| 15 | *n*-$Bu_2NH$ | 5 mol% | 72 | 73:1 | 99 |
| 16 | *n*-$Bu_2NH$ | 30 mol% | 99 | 41:1 | 99 |
| 17 | *n*-$Bu_2NH$ | 40 mol% | 99 | 23:1 | 99 |

[a] Unless otherwise noted, the reactions were performed with Ni(acac)$_2$/**L4** (1:1, 1 mol%), **1a** (0.1 mmol), **2a** (0.15 mmol), EtOAc (0.10 mL), at rt for 24 h. [b] Isolated yield. [c] Determined by HPLC.

[d] Enantiomeric excess values of major diastereomers; Determined by chiral HPLC.

## 3. Crystal structure data of compound 3ae (CCDC 2219965)

**Preparation of the single crystals of enantiopure 3ae**: Compound **3ae** (15.0 mg, 70:1 dr, 99% *ee*) was dissolved in ethyl acetate (0.5 mL), then followed by the slowly addition of petroleum ether until a solid just appeared. Shaked the tube to make the solution clear. The tube was sealed, thus allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed at the bottom of the tube. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **3ae**. The data were collected by a Rigaku Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 293(2) K. CCDC 2219965 (**3ae**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk /data request/cif.



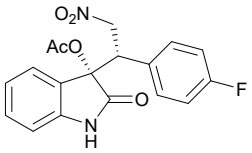




**Table S3.** Crystal data and structure refinement for **3ae**

Bond precision: C-C = 0.0063 A Wavelength=1.54184

Cell: a=8.98207(19) b=13.3543(3) c=29.0314(5)

alpha=90 beta=90 gamma=90

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 3482.30(12) | 3482.30(13) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C18 H15 F N2 O5 | C18 H15 F N2 O5 |
| Sum formula | C18 H15 F N2 O5 | C18 H15 F N2 O5 |

| | | |
|---|---|---|
| Mr | 358.32 | 358.32 |
| Dx,g cm-3 | 1.367 | 1.367 |
| Z | 8 | 8 |
| Mu (mm-1) | 0.917 | 0.917 |
| F000 | 1488.0 | 1488.0 |
| F000’ | 1493.42 | |
| h,k,lmax | 11,16,35 | 10,16,35 |
| Nref | 6707[ 3790] | 6579 |
| Tmin,Tmax | 0.886,0.912 | 0.899,1.000 |
| Tmin’ | 0.577 | |

Correction method= # Reported T Limits: Tmin=0.899 Tmax=1.000

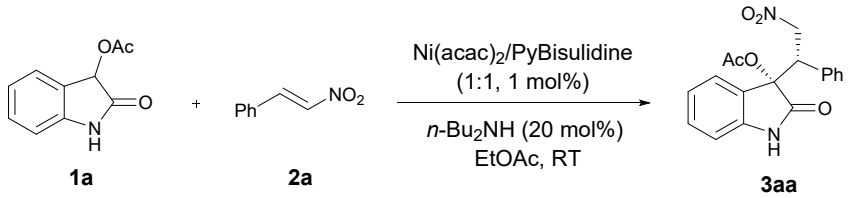
AbsCorr = MULTI-SCAN

Data completeness= 1.74/0.98 Theta(max)= 70.862

R(reflections)= 0.0473( 5430) wR2(reflections)=0.1287( 6579)

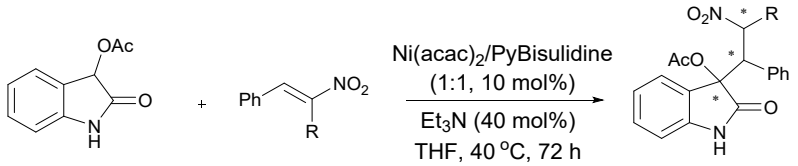
S = 1.042 Npar= 479

## 4. General procedure for the asymmetric synthesis 3aa




A mixture of $Ni(acac)_2$ (0.001 mmol) and PyBisulidine (0.001 mmol) was stirred in EtOAc (0.5 mL) at 35°C for 0.5 h. The mixture was cooled to rt, and then nitroalkene (0.15 mmol), 3-acyloxy-2-oxindole (0.1 mmol), *n*-$Bu_2NH$ (0.02 mmol) and EtOAc (0.5 mL) were added to the mixture. The stirring was continued for 24 h at rt. The residue was purified by column chromatography (petroleum ether/EtOAc = 5:1-4:1, v/v) on silica gel.

## 5. General procedure for the asymmetric synthesis 3aq/3ar



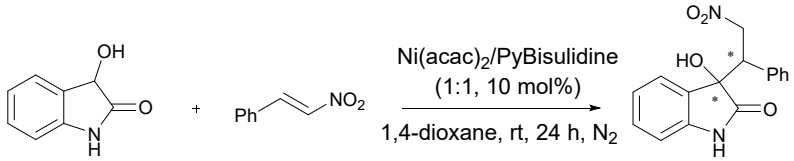

**1a**

**2q** : R = Me
**2r** : R = Et

**3aq** : R = Me
**3ar** : R = Et

A mixture of $Ni(acac)_2$ (0.01 mmol) and PyBisulidine (0.01 mmol) was stirred in THF (0.5 mL) at 35°C for 0.5 h. The mixture was cooled to rt, and then nitroalkene (0.15 mmol), 3-acyloxy-2-oxindole (0.1 mmol), $Et_3N$ (0.04 mmol) and THF (0.5 mL) were added to the mixture. The stirring was continued for 72 h at 40°C. The residue was purified by column chromatography (petroleum ether/EtOAc = 6:1, v/v) on silica gel.

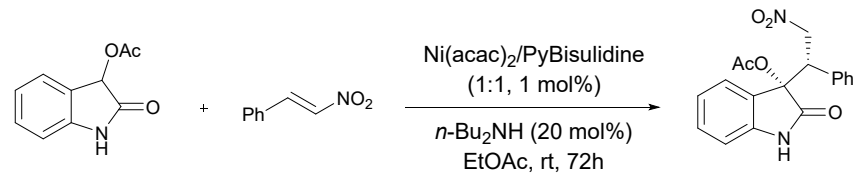
## 6. General procedure for the asymmetric synthesis 4aa




**4a** **2a** **4aa**

Under nitrogen, a mixture of $Ni(acac)_2$ (0.01 mmol) and PyBisulidine (0.01 mmol) was stirred in 1,4-dioxane (0.5 mL) at 35°C for 0.5 h. The mixture was cooled to rt, and then nitroalkene (0.15 mmol), 3-hydroxyindolin-2-one (0.1 mmol) and THF (0.5 mL) were added to the mixture. The stirring was continued for 24 h at rt. The residue was purified by column chromatography (petroleum ether/EtOAc = 3:1, v/v) on silica gel.

## 7. General procedure for the Large-Scale reaction




**1a**
4.0 mmol, 0.76 g

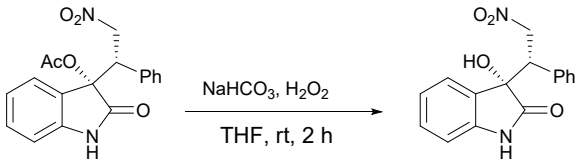
**2a**
6.0 mmol, 0.95 g

**3aa**
1.18g
87% yied, 47:1 dr, 99% *ee*

A mixture of $Ni(acac)_2$ (0.001 mmol) and PyBisulidine (0.001 mmol) was stirred in EtOAc (20 mL) at 35°C for 0.5 h. The mixture was cooled to rt, and then nitroalkene (6.0 mmol), 3-acyloxy-2-oxindole (4.0 mmol), *n*-$Bu_2NH$ (1.6 mmol) and EtOAc (20

mL) were added to the mixture. The stirring was continued for 72 h at rt. The residue was purified by column chromatography (petroleum ether/EtOAc = 5:1-4:1, v/v) on silica gel.

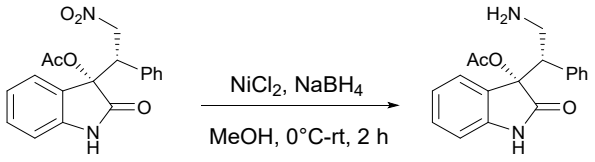
## 8. Transformation of 3aa to 3-substituted-3-hydroxy-2-oxindoles




**3aa** **4aa**

To the solution of **3aa** (0.3 mmol) in THF (5 mL) were added satd $NaHCO_3$ (5 mL) and $H_2O_2$ (0.3 mmol). The mixture was stirred at 25 °C for 2 h. It was poured over 10 mL of water and extracted with $CH_2Cl_2$. The combined organic extracts were washed with satd NaCl and dried with $Na_2SO_4$. The solvents were removed in vacuo and purified through column chromatography (petroleum ether/EtOAc = 3:1) on silica gel.

## 9. Nitro group is reduced to amino group in product 3aa

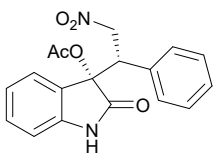



**3aa** **5aa**

To a solution of the compound **3aa** (0.2 mmol, 86.1mg) in methanol (2.0 mL) at 0 °C was added $NiCl_2$ (0.2 mmol, 25.8 mg) followed by $NaBH_4$ (2.4 mmol, 90.7 mg) under nitrogen. The mixture was stirred for 2 h. Then saturated aqueous $NH_4Cl$ (8 mL) was added, and the mixture was extracted with $CH_2Cl_2$, washed with brine, dried over $Na_2SO_4$, and concentrated under reduced press. The solvents were removed in vacuo and purified through column chromatography (petroleum ether/EtOAc = 2:1) on silica gel.

## 10. Characterization of products

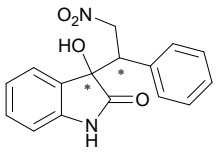
***(S)-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3aa).***




White solid; 33.5 mg, 99% yield, 65:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +5.1 (*c* 6.81, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.68 (s, 1H),

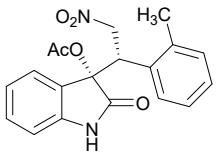
7.31 (d, $J$ = 7.2 Hz, 1H), 7.15-7.07 (m, 4H), 7.03 (td, $J$ = 8.4, 7.8, 1.2 Hz, 1H), 6.95 (d, $J$ = 7.2 Hz, 2H), 6.45 (d, $J$ = 7.8 Hz, 1H), 5.51 (dd, $J$ = 13.8, 6.0 Hz, 1H), 5.08 (dd, $J$ = 13.8, 8.4 Hz, 1H), 4.37 (dd, $J$ = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.1, 168.4, 140.6, 131.4, 130.3, 129.0, 128.3, 128.1, 126.0, 123.0, 122.8, 110.1, 80.4, 73.8, 49.6, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}N_2NaO_5$ 363.0957, found: 363.0957. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 25.9 min, 14.1 min; $t_r$ (major diastereomer) = 23.5 min

***3-hydroxy-3-(2-nitro-1-phenylethyl)indolin-2-one (4aa)***




White solid; 29.5mg, 99% yield, 2:1 dr, 88% *ee*; $[\alpha]^{20}_D$ = +6.3 (*c* 5.56, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.45-7.36 (m, 1H), 7.15-7.04 (m, 5H), 6.98-6.90 (m, 2H), 6.57 (d, $J$ = 7.8 Hz, 1H), 5.32 (dd, $J$ = 13.8, 4.8 Hz, 1H), 5.11 (dd, $J$ = 13.8, 12.0 Hz, 1H), 4.27-4.14 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 178.4, 139.8, 132.9, 130.3, 129.3, 128.6, 128.2, 128.0, 124.2, 123.3, 110.4, 77.8, 74.2, 51.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}N_2NaO_4$ 321.0851, found: 321.0853. HPLC: Chiralpak ID-H column, hexane/ethanol = 90/10, flow rate = 0.8 mL min$^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 13.8 min, 15.8 min; $t_r$ (major diastereomer) = 17.1 min (major enantiomer), 25.1 min (minor enantiomer).

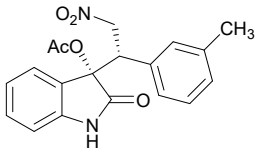
***(S)-3-((S)-2-nitro-1-(o-tolyl) ethyl)-2-oxoindolin-3-yl acetate (3ab).***




White solid; 33.6mg, 95% yield, 7.7:1 dr, 93% *ee*; $[\alpha]^{20}_D$ = +0.8 (*c* 4.26, $CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.31 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.27 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.12-7.02 (m, 3H), 6.98-6.94 (m, 1H), 6.93-6.89 (m, 1H), 6.52 (d, $J$ = 7.8 Hz, 1H), 5.41 (dd, $J$ = 13.8, 4.8 Hz, 1H), 4.98 (dd, $J$ = 13.8, 9.0 Hz, 1H), 4.81 (dd, $J$ = 9.0, 5.4 Hz, 1H), 2.22 (s, 3H), 2.10 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.7, 168.3, 140.7, 137.6, 130.8, 130.7, 130.5, 128.2, 126.8, 126.0, 125.8, 123.1, 122.3, 110.0, 80.8, 75.1, 43.9, 20.5, 19.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5^+$ 377.1113, found: 377.1110. HPLC: Chiralpak IB-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 14.1 min, 18.6 min; $t_r$ (major diastereomer) = 21.2

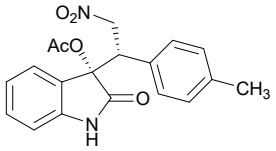
min (major enantiomer), 3.1 min (minor enantiomer).

***(S)-3-((S)-2-nitro-1-(m-tolyl) ethyl)-2-oxoindolin-3-yl acetate (3ac).***



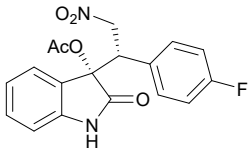
White solid; 35.1mg, 99% yield, 46:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +4.2 (*c* 5.55, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.41 (s, 1H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.11 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05-7.00 (m, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.50 (dd, *J* = 13.8, 6.0 Hz, 1H), 5.06 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.9, 168.4, 140.7, 137.8, 131.4, 130.2, 129.9, 129.0, 128.0, 126.2, 126.0, 123.1, 122.7, 110.0, 80.5, 73.9, 49.6, 21.1, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5$ 377.1113, found: 377.1112. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 28.9 min, 32.1 min; $t_r$ (major diastereomer) = 23.7 min (major enantiomer), 26.3 min (minor enantiomer).

***(S)-3-((S)-2-nitro-1-(p-tolyl) ethyl)-2-oxoindolin-3-yl acetate (3ad).***



White solid; 35.0mg, 99% yield, 46:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +10.4 (*c* 1.34, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.35 (s, 1H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.13 (td, *J* = 7.8, 1.2 Hz, 1H), 7.03 (td, *J* = 7.8, 1.2 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.48 (dd, *J* = 13.8, 5.8 Hz, 1H), 5.05 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.19 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.0, 168.3, 140.7, 138.0, 130.3, 128.9, 128.9, 128.4, 126.3, 123.0, 122.8, 110.0, 80.4, 74.0, 49.3, 21.0, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5$ 377.1113, found: 377.1114. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 34.3 min, 37.1 min; $t_r$ (major diastereomer) = 27.5 min (major enantiomer), 26.7 min (minor enantiomer).

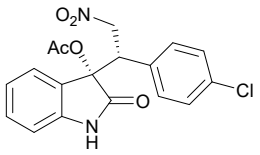
***(S)-3-((S)-1-(4-fluorophenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3ae).***



White solid; 35.4mg, 99% yield, 70:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +4.2 (*c* 8.01, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.80 (s, 1H), 7.29 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.10 (td, *J* = 7.8, 1.2 Hz, 1H),

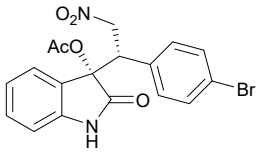
7.05 -7.00 (m, 1H), 6.95-6.90 (m, 2H), 6.78 (t, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 7.7 Hz, 1H), 5.47 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.08 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.34 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.0, 168.5, 163.2, 161.5, 140.6, 130.8, 130.7, 130.4, 127.2, 127.2, 125.8, 122.9, 122.8, 115.3, 115.1, 110.2, 80.3, 73.7, 48.9, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}FN_2NaO_5$ 381.0863, found: 381.0862. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/ min, 254 nm, $t_r$ (minor diastereomer) = 12.1 min, 14.1 min; $t_r$ (major diastereomer) = 18.7 min (major enantiomer), 20.5 min (minor enantiomer).

***(S)-3-((S)-1-(4-chlorophenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3af).***




White solid; 34.4mg, 92% yield, 60:1 dr, 86% *ee*; $[\alpha]^{20}_D$ = +5.7 (*c* 10.02, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.73 (s, 1H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.12 (td, *J* = 7.8, 1.2 Hz, 1H), 7.09-6.96 (m, 3H), 6.92-6.84 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.46 (dd, *J* = 13.8, 5.6 Hz, 1H), 5.07 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.8, 168.4, 140.6, 134.3, 130.5, 130.3, 130.0, 128.4, 125.7, 122.9, 122.8, 110.3, 80.1, 73.5, 49.0, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}ClN_2NaO_5$ 397.0567, found: 397.0569. HPLC: Chiralpak IB-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 21.6 min, 30.5 min; $t_r$ (major diastereomer) = 16.7 min (major enantiomer), 15.8 min (minor enantiomer).

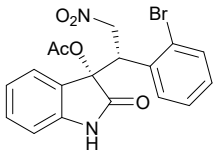
***(S)-3-((S)-1-(4-bromophenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3ag).***




White solid; 36.8mg, 88% yield, 5:1 dr, 75% *ee*; $[\alpha]^{20}_D$ = +4.4 (*c* 10.31, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 8.30 (s, 0.2H), 7.99 (s, 1H), 7.35 – 7.31 (m, 0.3H), 7.31 – 7.27 (m, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.16 – 7.07 (m, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.93 (dt, J = 14.6, 7.8 Hz, 0.2H), 6.82 (d, J = 8.4 Hz, 2H), 6.80 – 6.73 (m, 0.4H), 6.69 (dd, J = 14.8, 7.8 Hz, 0.2H), 6.53 (dd, J = 40.1, 7.8 Hz, 1H), 5.52 – 5.48 (m, 0.2H), 5.48 – 5.39 (m, 1H), 5.06 (dd, J = 13.8, 8.4 Hz, 1H), 4.93 (ddd, J = 13.2, 10.1, 2.8 Hz, 0.2H), 4.31 (dd, J = 8.7, 5.6 Hz, 1H), 3.99 (dt, J = 10.0, 4.9 Hz, 0.2H), 2.11 (d, J = 1.7 Hz, 0.7H), 2.09 (d, J = 3.1 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.4, 174.1, 168.5, 168.4, 140.7, 140.7,

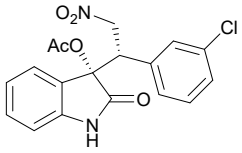
131.4, 131.4, 130.7, 130.7, 130.6, 130.6, 130.6, 130.5, 125.7, 125.7, 123.1, 123.0, 123.0, 122.9, 122.7, 122.6, 110.6, 110.5, 80.3, 80.2, 74.5, 73.5, 49.1, 48.3, 20.6, 20.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}BrN_2O_5$ 419.0243, found: 419.0243. HPLC: Chiralpak IB-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 23.3 min, 36.3 min; $t_r$ (major diastereomer) = 19.2 min (major enantiomer), 17.7 min (minor enantiomer).

***(S)-3-((S)-1-(2-bromophenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3ah).***



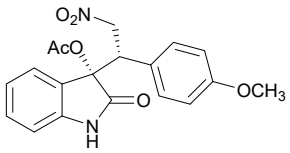

White solid; 41.4mg, 99% yield, 47:1 dr, 98% *ee*; $[\alpha]^{20}_D$ = -6.5 (*c* 5.64, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.82 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.22-7.16 (m, 1H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 7.02-6.94 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.45 (dd, *J* = 13.8, 4.8 Hz, 1H), 5.24 (dd, *J* = 9.0, 4.8 Hz, 1H), 5.02 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.12 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.4, 168.4, 140.4, 133.4, 132.0, 130.5, 129.8, 128.2, 127.5, 126.6, 124.7, 124.5, 122.4, 109.7, 80.5, 74.6, 46.6, 20.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}BrN_2O_5$ 419.0243, found: 419.0242. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 19.4 min, 28.7 min; $t_r$ (major diastereomer) = 22.8 min (major enantiomer), 24.7 min (minor enantiomer).

***(S)-3-((S)-1-(3-chlorophenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3ai).***



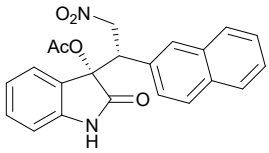

White solid; 34.4 mg, 92% yield, 29:1 dr, 97% *ee*; $[\alpha]^{20}_D$ = +4.6 (*c* 5.35, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.73 (s, 1H), 7.29 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.18-7.09 (m, 2H), 7.07-6.99 (m, 2H), 6.93 (t, *J* = 2.4 Hz, 1H), 6.87 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.47 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.06 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.8, 168.3, 140.6, 134.0, 133.7, 130.6, 129.4, 129.3, 128.6, 127.1, 125.7, 123.0, 110.3, 80.2, 73.5, 49.3, 20.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}ClN_2NaO_5$ 397.0567, found: 397.0566. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 19.3 min, 23.5 min; $t_r$ (major diastereomer) = 20.5 min (major enantiomer), 12.0 min (minor enantiomer).

***(S)-3-((S)-1-(4-methoxyphenyl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3aj).***



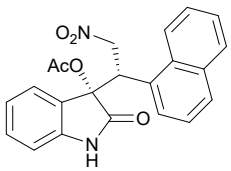
White solid; 36.6 mg, 99% yield, >99:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +7.6 (*c* 10.52, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 7.77 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.09 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.46 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.05 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.31 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.67 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (151 MHz, CDCl3) δ 174.2, 168.4, 159.3, 140.8, 130.2, 130.1, 126.2, 123.3, 122.9, 122.7, 113.6, 110.2, 80.5, 74.0, 55.0, 48.9, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_6$ 393.1063 found: 393.1056. HPLC: Chiralpak IB-H column, hexane/ ethanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 17.2 min,; $t_r$ (major diastereomer) = 15.5 min (major enantiomer), 16.6 min (minor enantiomer).

***(S)-3-((S)-1-(naphthalen-2-yl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3al).***



Yellow solid; 38.6mg, 99% yield, 32:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +7.8 (*c* 15.62, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.72-7.65 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 6.6, 3.6 Hz, 2H), 7.36 (dd, *J* = 5.4, 2.4 Hz, 1H), 7.05-7.00 (m, 3H), 6.30 (dd, *J* = 5.4, 2.4 Hz, 1H), 5.60 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.20 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.55 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.06 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.1, 168.4, 140.7, 132.7, 132.7, 130.3, 129.1, 128.3, 127.9, 127.7, 127.4, 126.6, 126.4, 126.2, 125.9, 122.9, 122.7, 110.2, 80.5, 73.9, 49.6, 20.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}N_2NaO_5^+$ 413.1113 found: 413.1115. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 43.6 min, 53.0 min; $t_r$ (major diastereomer) = 32.1 min (major enantiomer), 39.5 min (minor enantiomer).

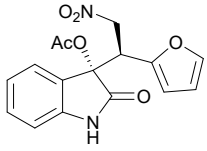
***(S)-3-((S)-1-(naphthalen-1-yl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3am).***



Yellow solid; 38.7 mg, 99% yield, >99:1 dr, 94% *ee*; $[\alpha]^{20}_D$ = -16.0 (*c* 8.14, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.67 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.51-7.45 (m, 2H), 7.39-7.33 (m, 2H), 7.24 (dd, *J* = 7.8, 1.2 Hz,

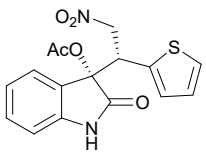
1H), 6.84 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.70 (td, *J* = 7.8, 1.2 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.60 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.52 (dd, *J* = 8.4, 5.4 Hz, 1H), 5.08 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.07 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.8, 168.4, 140.5, 133.5, 132.0, 130.2, 129.2, 128.6, 128.6, 126.0, 125.6, 125.1, 125.1, 124.6, 123.6, 123.1, 122.3, 109.9, 80.9, 75.0, 42.2, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}N_2NaO_5$ 413.1113 found: 413.1113. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 15.6 min, 17.3 min; $t_r$ (major diastereomer) = 36.1 min (major enantiomer), 41.4 min (minor enantiomer).

***(S)-3-((S)-1-(furan-2-yl)-2-nitroethyl)-2-oxoindolin-3-yl acetate (3an).***




Yellow solid; 32.8 mg, 99% yield, 61:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +0.3 (*c* 8.03, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.23 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.21-7.10 (m, 2H), 7.04 (td, *J* = 7.8, 1.2 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.11 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.91 (d, *J* = 3.6 Hz, 1H), 5.31 (dd, *J* = 13.8, 4.8 Hz, 1H), 5.05 (dd, *J* = 13.8, 9.0 Hz, 1H), 4.51 (dd, *J* = 9.0, 4.8 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.9, 168.3, 146.1, 142.9, 141.1, 130.5, 125.8, 123.1, 122.9, 110.4, 110.2, 109.9, 79.2, 72.4, 43.9, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}N_2NaO_6$ 353.0750 found: 353.0751. HPLC: Chiralpak IB-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 14.8 min, 19.7 min; $t_r$ (major diastereomer) = 33.7 min (major enantiomer), 24.4 min (minor enantiomer).

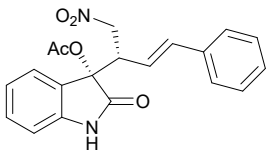
***(S)-3-((S)-2-nitro-1-(thiophen-2-yl)ethyl)-2-oxoindolin-3-yl acetate (3ao).***




Yellow solid; 34.2 mg, 99% yield, 34:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +2.7 (*c* 10.21, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.28 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.18 (td, *J* = 7.8, 1.2 Hz, 1H), 7.09-7.01 (m, 2H), 6.81-6.73 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.46 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.03 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.64 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.9, 168.2, 141.2, 133.4, 130.6, 127.2, 126.6, 126.0, 126.0, 123.1, 123.0, 110.3, 80.0, 74.5, 44.9, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}N_2NaO_5S$ 369.0521 found: 369.0520. HPLC: Chiralpak IC-H column, hexane/

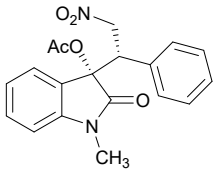
ethanol = 93/7, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 24.1 min, 28.4min; $t_r$ (major diastereomer) = 30.1 min (major enantiomer), 16.6 min (minor enantiomer).

***(S)-3-((S, E)-4-nitro-1-phenylbut-3-en-1-yl)-2-oxoindolin-3-yl acetate (3ap).***



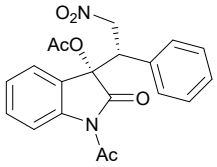

White solid; 35.1 mg, 96% yield, >99:1 dr, 78% *ee*; $[\alpha]^{20}_D$ = +4.6 (*c* 3.61, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.25-7.15 (m, 4H), 7.11 -7.04 (m, 3H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 5.71 (dd, *J* = 15.6, 9.0 Hz, 1H), 5.19 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.78 (dd, *J* = 13.2, 9.0 Hz, 1H), 3.90 (tdd, *J* = 9.0, 4.8, 0.6 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.0, 168.5, 141.0, 137.4, 135.8, 130.5, 128.5, 128.2, 126.5, 126.3, 123.2, 122.8, 119.2, 110.4, 79.7, 74.1, 47.5, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{18}N_2NaO_5$ 389.1113 found: 389.1119. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 38.4 min, 42.1min; $t_r$ (major diastereomer) = 26.6 min (major enantiomer), 23.4 min (minor enantiomer).

***(S)-1-methyl-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ba).***



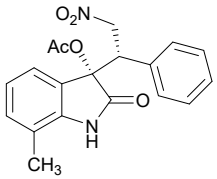

White solid; 35.0 mg, 99% yield, 1.3:1 dr, 39% *ee*; $[\alpha]^{20}_D$ = +0.6 (*c* 15.74, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 2H), 7.25 – 7.12 (m, 3H), 7.10 – 7.01 (m, 4H), 6.95 – 6.88 (m, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.66 (dd, *J* = 13.2, 7.8 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 5.4 Hz, 0.6H), 5.53 – 5.49 (m, 1H), 5.12 (dd, *J* = 13.8, 8.4 Hz, 0.6H), 4.98 (dd, *J* = 13.2, 9.6 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 4.04 – 3.95 (m, 0.6H), 2.94 (s, 2H), 2.91 (s, 3H), 2.11 (s, 2H), 2.08 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.4, 168.2, 168.1, 143.8, 143.3, 132.6, 131.5, 130.4, 130.2, 129.2, 128.8, 128.6, 128.2, 128.1, 127.8, 125.7, 125.6, 124.5, 124.4, 123.6, 122.8, 122.4, 122.3, 108.5, 108.1, 80.6, 80.4, 74.6, 73.8, 49.7, 48.9, 26.1, 25.9, 20.5, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5$ 377.1113 found: 377.1114. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 14.9 min, 30.6 min; $t_r$ (major diastereomer) = 21.1 min (major enantiomer), 12.6 min (minor enantiomer).

***(S)-1-acetyl-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ca).***



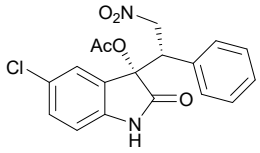
White solid; 39.4 mg, 99% yield, 1.2:1 dr, 9% *ee*; $[\alpha]^{20}_{D}$ = -0.3 (*c* 6.96, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.88-7.82 (m, 0.6H), 7.43 (dd, *J* = 7.2, 1.8 Hz, 0.7H), 7.40 (td, *J* = 8.4, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 6.6 Hz, 0.6H), 7.25-7.19 (m, 2H), 7.14 (ddd, *J* = 12.0, 7.2, 3.0 Hz, 2H), 7.08-7.01 (m, 2H), 6.81-6.69 (m, 3H), 5.54 (dd, *J* = 13.8, 6.6 Hz, 0.6H), 5.39 (dd, *J* = 13.2, 5.4 Hz, 1H), 5.06 (dd, *J* = 13.8, 7.8 Hz, 0.6H), 4.90 (dd, *J* = 13.2, 9.0 Hz, 1H), 4.40 (dd, *J* = 7.8, 6.6 Hz, 0.6H), 4.20 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.54 (s, 1.8H), 2.40 (s, 3H), 2.13 (s, 3H), 2.10 (s, 1.8H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.7, 173.5, 169.7, 169.5, 168.5, 168.3, 140.6, 140.1, 131.2, 131.0, 130.8, 130.7, 129.3, 129.0, 128.9, 128.5, 128.5, 128.4, 125.5, 125.1, 125.1, 123.5, 122.9, 122.1, 116.9, 116.5, 80.5, 80.2, 74.6, 73.5, 50.0, 49.5, 26.3, 26.0, 20.3, 20.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{18}N_2NaO_6$ 405.1063 found: 405.1061. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 19.5 min, 29.0 min; $t_r$ (major diastereomer) = 17.3 min (major enantiomer), 15.9 min (minor enantiomer).

***(S)-7-methyl-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3da).***



White solid;35.1mg, 99% yield, 35:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +0.4 (*c* 4.98 , $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-d) δ 8.22 (s, 1H), 7.16-7.10 (m, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.98-6.90 (m, 4H), 5.48 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.08 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.34 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.07 (s, 3H), 1.90 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.6, 168.3, 139.5, 131.6, 131.5, 128.9, 128.2, 128.0, 125.6, 122.6, 120.4, 119.4, 80.9, 73.9, 49.7, 20.4, 15.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5$ 377.1113 found: 377.1117. HPLC: Chiralpak IB-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 13.3 min, 15.5 min; $t_r$ (major diastereomer) = 17.2 min (major enantiomer), 11.0 min (minor enantiomer).

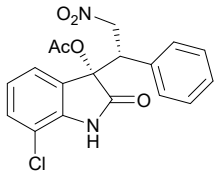
***(S)-5-chloro-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ea).***



White solid; 37.0mg, 99% yield, 14:1 dr, 96% *ee*; $[\alpha]^{20}_{D}$ = +21.6 (*c* 1.50 , $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.98 (s,

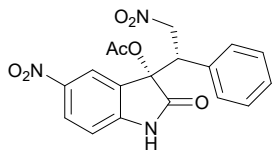
1H), 7.32-7.28 (m, 1H), 7.13 (dt, *J* = 14.4, 7.2 Hz, 3H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.36 (d, *J* = 8.4 Hz, 1H), 5.49 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.04 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.8, 168.5, 139.2, 131.1, 130.3, 129.0, 128.5, 128.4, 128.2, 127.8, 123.4, 111.2, 80.2, 73.7, 49.6, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}ClN_2NaO_5$ 397.0567 found: 397.0564. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL min$^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 14.7 min, 20.7 min; $t_r$ (major diastereomer) = 16.7 min (major enantiomer), 9.3 min (minor enantiomer).

***(S)-7-chloro-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3fa).***




White solid; 35.5 mg, 95% yield, 32:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +2.6 (*c* 6.68, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18-7.13 (m, 1H), 7.13-7.06 (m, 3H), 7.01-6.97 (m, 1H), 6.95-6.90 (m, 2H), 5.50 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.06 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.35 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.10 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.1, 168.3, 138.4, 131.1, 130.2, 128.9, 128.6, 128.3, 127.6, 123.6, 121.2, 115.3, 80.9, 73.7, 49.6, 20.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}ClN_2NaO_5$ 397.0567 found: 397.0577. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 23.7 min, 24.8 min; $t_r$ (major diastereomer) = 20.8 min (major enantiomer), 12.8 min (minor enantiomer).

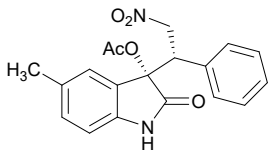
***(S)-5-nitro-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ga).***




White solid; 37.7mg, 98% yield, 7:1 dr, 97% *ee*; $[\alpha]^{20}_D$ = +6.74 (*c* 1.7 , $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18-7.14 (m, 1H), 7.13-7.07 (m, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 2H), 5.50 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.06 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.34 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.10 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.0, 168.3, 138.4, 131.1, 130.2, 128.9, 128.6, 128.3, 127.6, 123.7, 121.3, 115.3, 80.9, 73.7, 49.7, 20.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}N_3O_7$ 386.0988 found: 386.0971. HPLC: Chiralpak IC-H column,

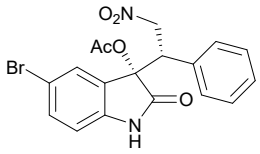
hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 23.1 min, 24.2 min; $t_r$ (major diastereomer) = 20.3 min (major enantiomer), 12.6 min (minor enantiomer).

***(S)-5-methyl-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ha).***



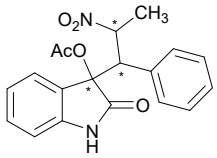

White solid; 35.1 mg, 99% yield, 4:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +7.7 (*c* 21.4, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.07 (s, 0.2H), 7.91 (s, 1H), 7.14-7.03 (m, 4H), 7.01-6.92 (m, 2H), 6.92-6.83 (m, 1H), 6.82-6.75 (m, 0.3H), 6.46 (d, *J* = 7.9 Hz, 0.2H), 6.34 (d, *J* = 7.9 Hz, 1H), 5.50 (dd, *J* = 13.7, 5.8 Hz, 1H), 5.47 – 5.41 (m, 0.2H), 5.06 (dd, *J* = 13.7, 8.3 Hz, 1H), 5.03 – 4.98 (m, 0.2H), 4.62 (dd, *J* = 8.6, 5.4 Hz, 0.2H), 4.34 (dd, *J* = 8.3, 5.7 Hz, 1H), 2.32 (s, 0.6H), 2.31 (s, 3H), 2.07 (s, 3H), 1.95 (s, 0.6H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.2, 174.0, 168.3, 168.2, 138.8, 138.3, 132.5, 132.2, 131.6, 130.9, 130.6, 130.6, 129.0, 128.1, 128.0, 127.0, 126.5, 125.9, 125.9, 123.6, 123.5, 110.0, 109.9, 80.6, 80.2, 74.5, 73.9, 49.6, 44.9, 21.0, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5$ 377.1113, found: 377.1114. HPLC: Chiralpak IB-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 27.0 min; $t_r$ (major diastereomer) = 21.0 min.

***(S)-5-bromo-3-((S)-2-nitro-1-phenylethyl)-2-oxoindolin-3-yl acetate (3ia).***



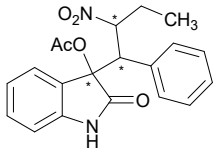

White solid; 41.4 mg, 99% yield, 49:1 dr, 99% *ee*; $[\alpha]^{20}_D$ = +14.0 (*c* 10.1, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.44 (s, 1H), 7.22 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.14 (dt, *J* = 14.4, 7.2 Hz, 3H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.34 (d, *J* = 8.4 Hz, 1H), 5.49 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.04 (dd, *J* = 13.8, 8.4 Hz, 1H), 4.33 (dd, *J* = 8.4, 6.0 Hz, 1H), 2.10 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.6, 168.5, 139.7, 133.1, 131.0, 129.0, 128.5, 128.4, 128.1, 126.1, 115.3, 111.6, 80.1, 73.6, 49.5, 20.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}BrN_2O_5$ 419.0243, found: 419.0248. HPLC: Chiralpak IC-H column, hexane/ethanol = 93/7, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 9.8 min, 15.3min; $t_r$ (major diastereomer) = 17.6 min (major enantiomer), 22.0min (minor enantiomer).

***3-(2-nitro-1-phenylpropyl)-2-oxoindolin-3-yl acetate (3aq).***



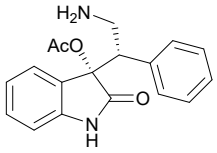
Purple solid; 33.6 mg, 93% yield, 3.6:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +1.2 (*c* 15.74 , $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.92 (s, 0.3H), 7.32 – 7.29 (m, 0.3H), 7.24 – 7.17 (m, 1H), 7.17 – 7.04 (m, 2H), 6.99 (tdd, *J* = 9.2, 7.2, 2.4 Hz, 6H), 6.94 (s, 0.3H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 0.2H), 6.09 (s, 0.2H), 5.87 – 5.73 (m, 1H), 4.23 (d, *J* = 10.2 Hz, 0.3 H), 4.04 (d, *J* = 10.8 Hz, 1H), 2.11 (s, 3H), 2.07 (d, *J* = 6.6 Hz, 3H), 1.99 (s, 1H), 1.29 (d, *J* = 6.6 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.4, 174.3, 168.4, 168.1, 140.5, 140.4, 132.3, 131.0, 130.0, 130.0, 128.0, 128.0, 128.0, 127.7, 126.8, 126.7, 122.8, 122.7, 122.6, 122.5, 110.0, 109.9, 85.2, 81.1, 80.2, 55.3, 54.6, 21.3, 20.9, 20.5, 20.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2NaO_5^+$ 377.1113, found: 377.1111. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_r$ (minor diastereomer) = 38.2 min; $t_r$ (major diastereomer) = 31.7 min.

***3-(2-nitro-1-phenylbutyl)-2-oxoindolin-3-yl acetate (3ar).***



Purple solid; 29.4mg, 90% yield, 4:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = +0.9 (*c* 5.66 , $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.58 (s, 0.2H), 7.30 (d, *J* = 7.2 Hz, 0.3H), 7.21 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.11-6.96 (m, 7H), 6.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.91 (d, *J* = 1.2 Hz, 0.2H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.93-5.83 (m, 0.3H), 5.62 (td, *J* = 10.8, 3.6 Hz, 1H), 4.21 (d, *J* = 10.2 Hz, 0.3H), 4.03 (d, *J* = 10.8 Hz, 1H), 2.74 (ddd, *J* = 14.4, 7.2, 3.6 Hz, 1H), 2.32-2.23 (m, 1H), 2.12 (s, 3H), 2.01 (s, 0.7H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 0.8H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 174.3, 174.1, 168.4, 168.0, 140.4, 140.2, 132.4, 131.3, 130.0, 130.0, 128.0, 128.0, 127.7, 127.0, 122.9, 122.8, 122.7, 122.6, 109.8, 109.8, 91.4, 86.3, 81.1, 80.6, 55.0, 53.9, 31.2, 29.7, 27.3, 26.9, 20.9, 20.2, 10.8, 9.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{20}N_2NaO_5$ 391.1270, found: 391.1274. HPLC: Chiralpak ID-H column, hexane/2-propanol = 90/10, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (minor diastereomer) = 34.9 min; $t_r$ (major diastereomer) = 25.8 min.

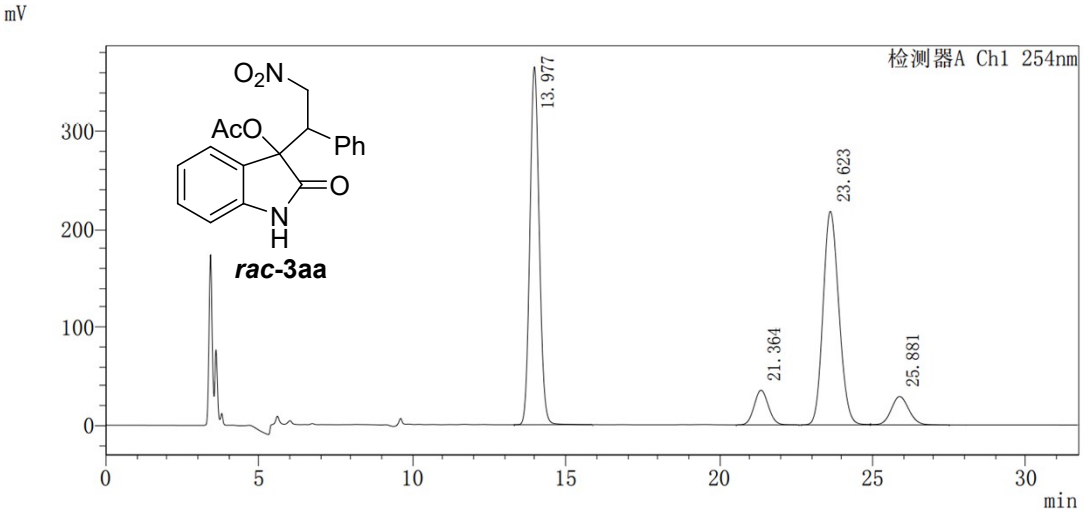
***(S)-3-((S)-2-amino-1-phenylethyl)-2-oxoindolin-3-yl acetate (5aa).***



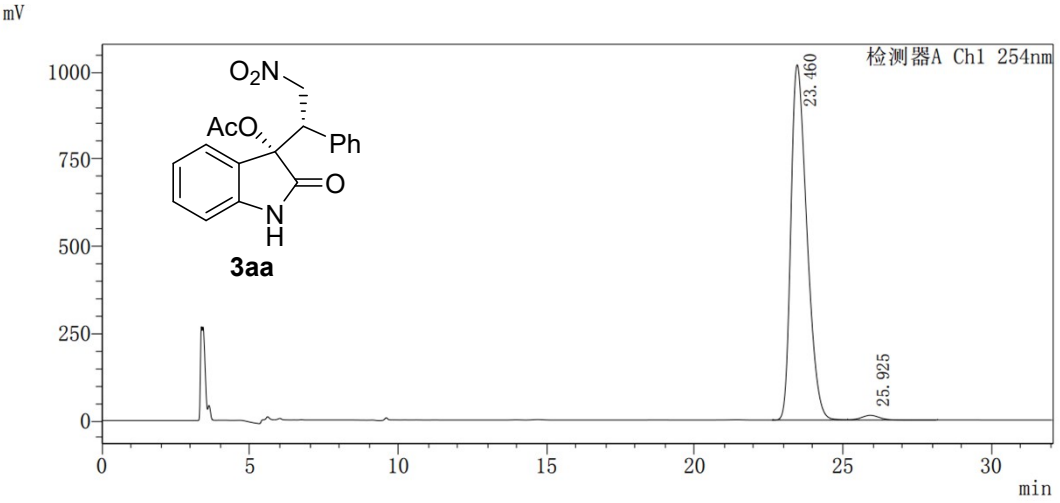
Yellow solid; 33.6 mg, 95% yield, 85:1 dr, 99% *ee*; $[\alpha]^{20}_{D}$ = -6.7 (*c* 11.26, $CHCl_3$); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.09 (s, 1H),

7.13-7.04 (m, 4H), 7.00-6.98 (m, 2H), 6.86 (t, $J$ = 7.8 Hz, 1H), 6.55 (d, $J$ = 7.8 Hz, 1H), 6.36 (t, $J$ = 5.4 Hz, 1H), 5.58 (s, 1H), 4.10-4.00 (m, 1H), 3.69-3.61 (m, 1H), 3.50-3.44 (m, 1H), 2.85 (s, 2H), 1.69 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 179.7, 170.8, 140.5, 135.9, 130.2, 129.4, 129.3, 127.9, 127.2, 124.5, 122.4, 110.3, 78.5, 52.1, 38.5, 23.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}N_2NaO_3$ 333.1215, found: 333.1216. HPLC: Chiralpak ID-H column, hexane/2-propanol = 85/15, flow rate = 1.0 mL $min^{-1}$, 254 nm, $t_r$ (major diastereomer) = 29.5 min.

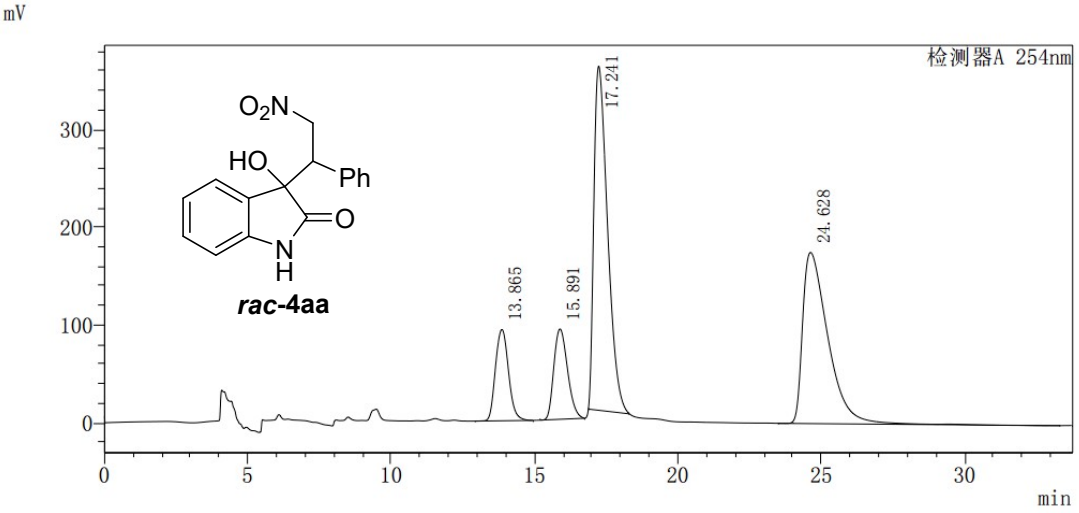
## 11.Copies of HPLC



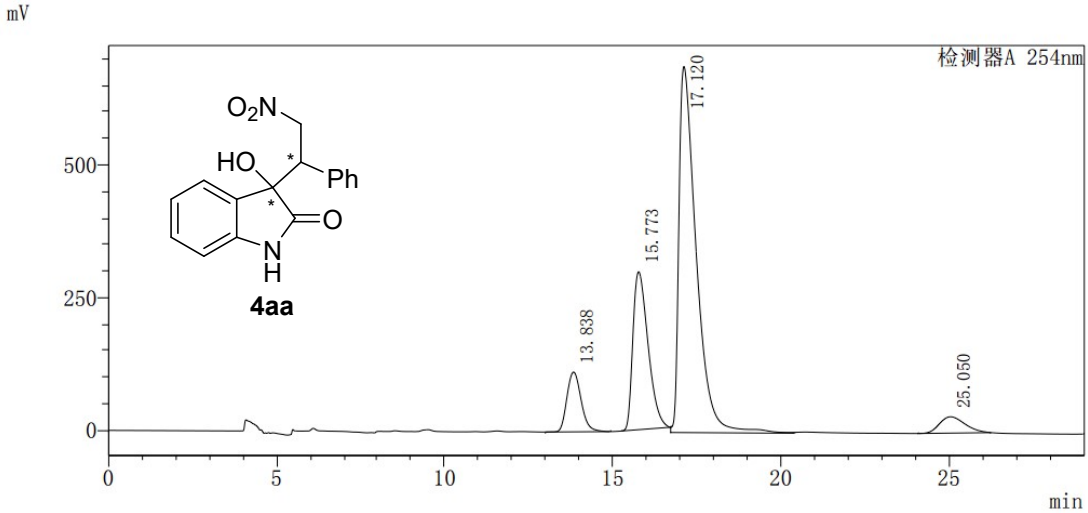

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 13.977 | 7737082 | 43.352 |
| 2 | 21.364 | 1137638 | 6.374 |
| 3 | 23.623 | 7814439 | 43.785 |
| 4 | 22.818 | 1157965 | 6.488 |



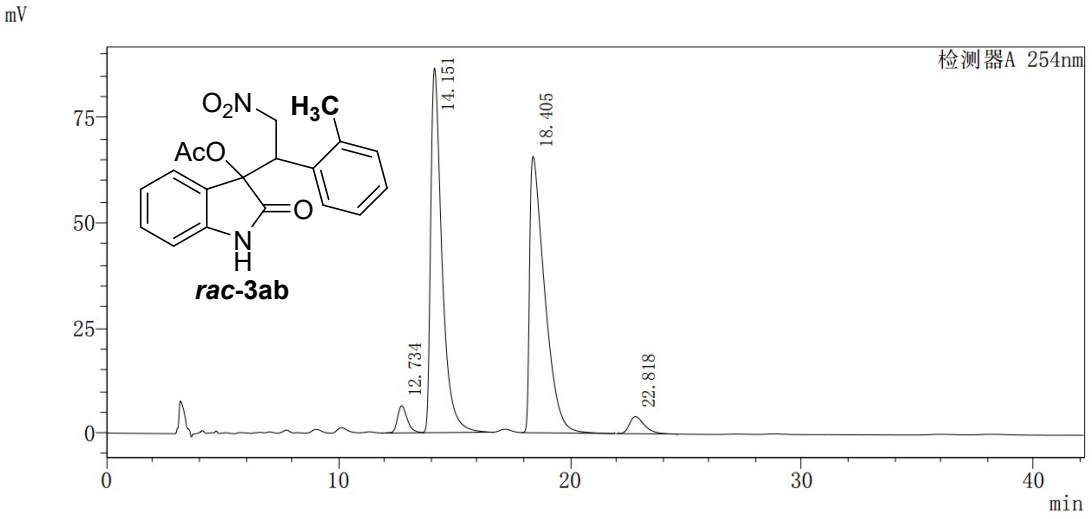

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 23.460 | 38185686 | 98.485 |
| 2 | 25.925 | 587329 | 1.515 |



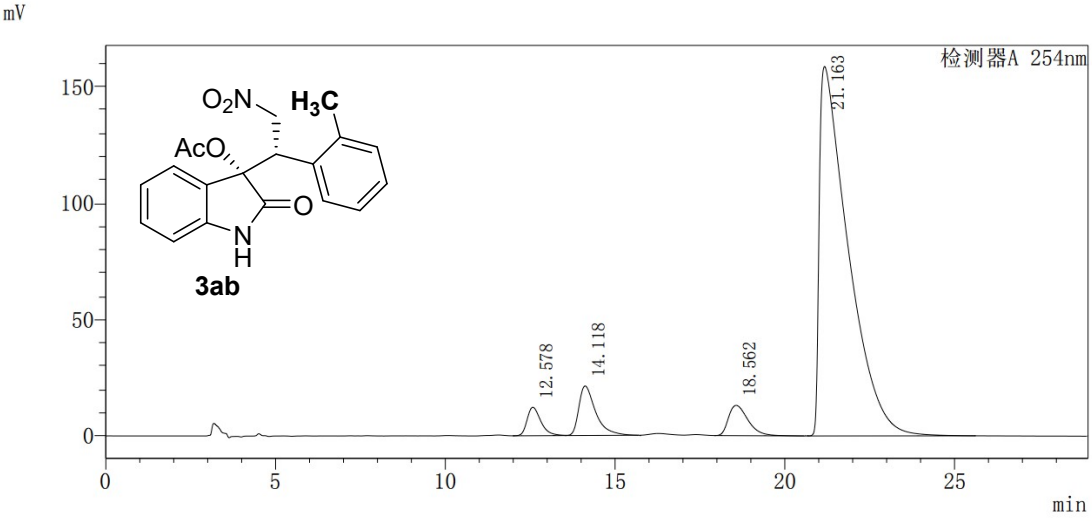

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 13.865 | 2946114 | 10.378 |
| 2 | 15.891 | 3062470 | 10.788 |
| 3 | 17.241 | 11660798 | 41.078 |
| 4 | 24.628 | 10717552 | 37.755 |



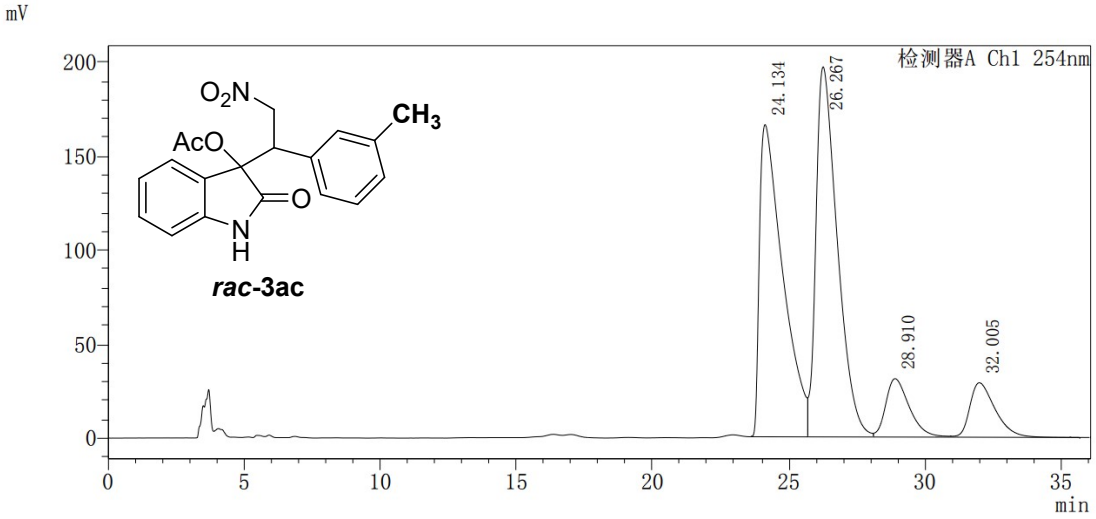

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 13.838 | 3304301 | 8.500 |
| 2 | 15.773 | 9314846 | 23.962 |
| 3 | 17.120 | 24636411 | 63.377 |
| 4 | 25.050 | 1617206 | 4.160 |



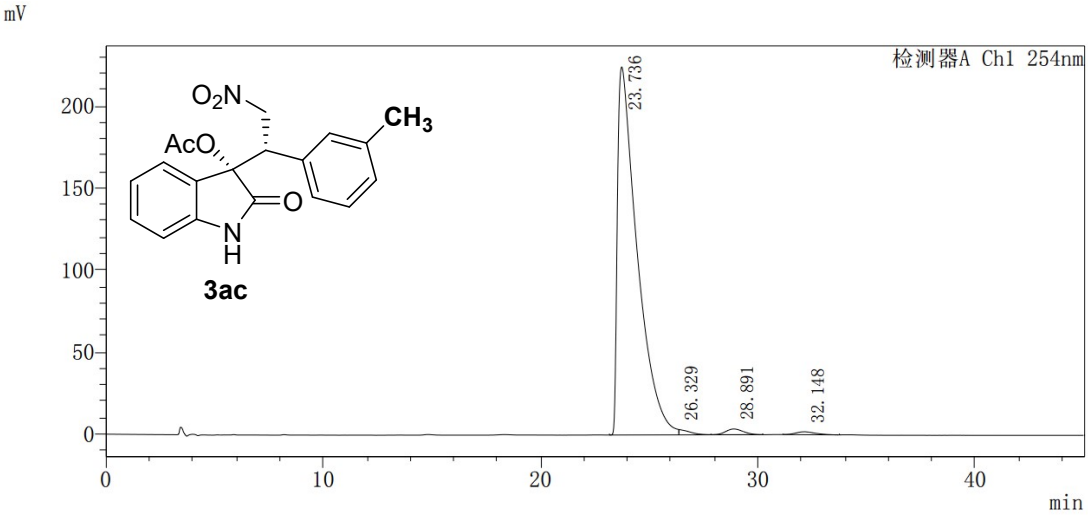

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.734 | 190334 | 3.029 |
| 2 | 14.151 | 2936640 | 46.740 |
| 3 | 18.405 | 2971784 | 47.300 |
| 4 | 22.818 | 184149 | 2.931 |



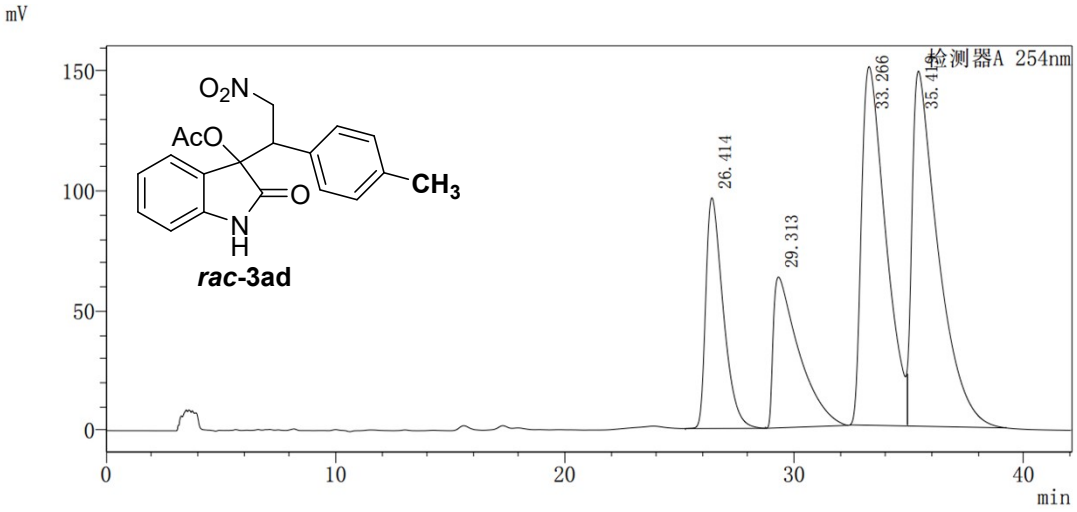

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.578 | 344538 | 3.135 |
| 2 | 14.118 | 730013 | 6.643 |
| 3 | 18.562 | 519939 | 4.731 |
| 4 | 21.163 | 9395240 | 85.491 |



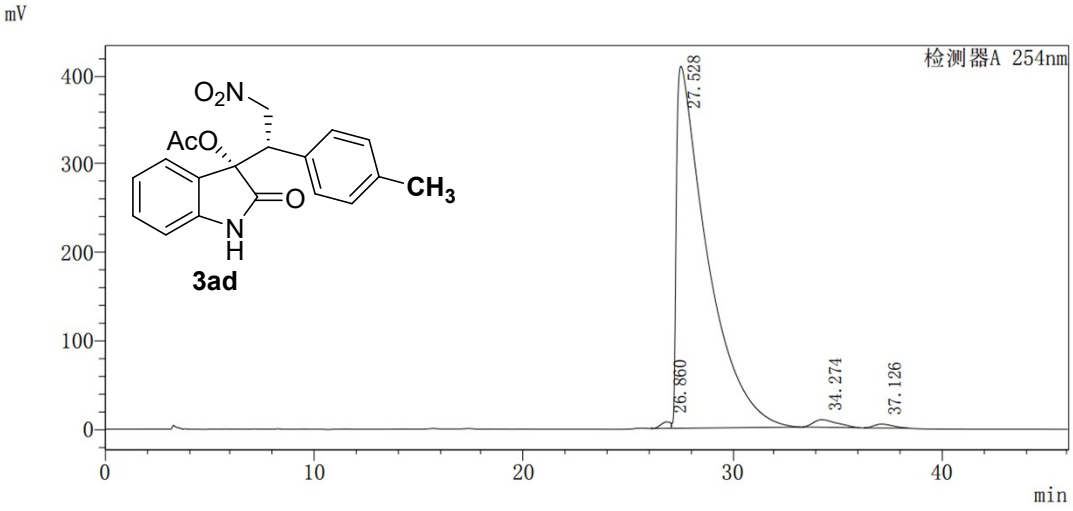

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 24.134 | 9919154 | 40.543 |
| 2 | 26.267 | 10789824 | 44.101 |
| 3 | 28.910 | 1878857 | 7.679 |
| 4 | 32.005 | 1878117 | 7.676 |



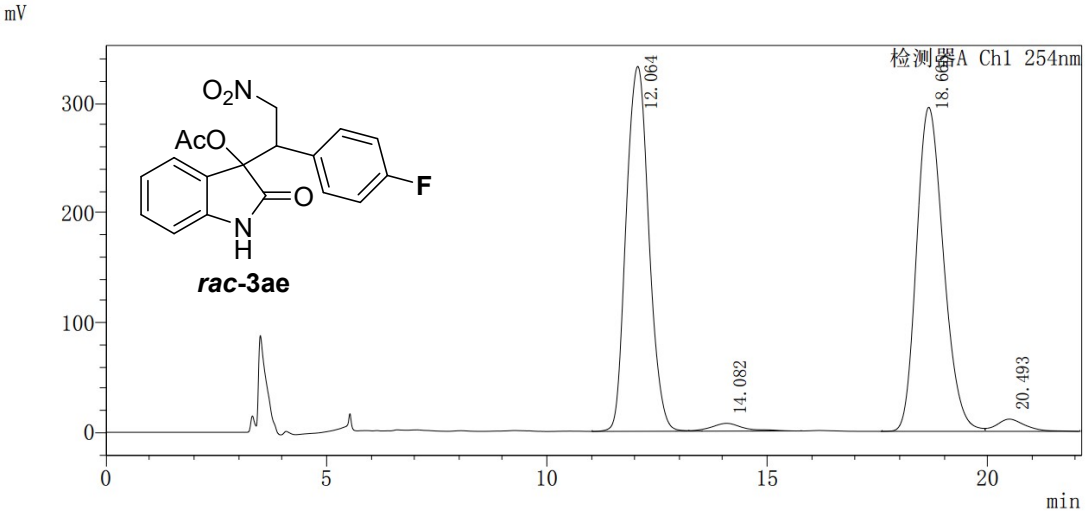

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 23.736 | 14144125 | 97.049 |
| 2 | 26.329 | 127883 | 0.877 |
| 3 | 28.891 | 193114 | 1.325 |
| 4 | 32.148 | 109089 | 0.749 |



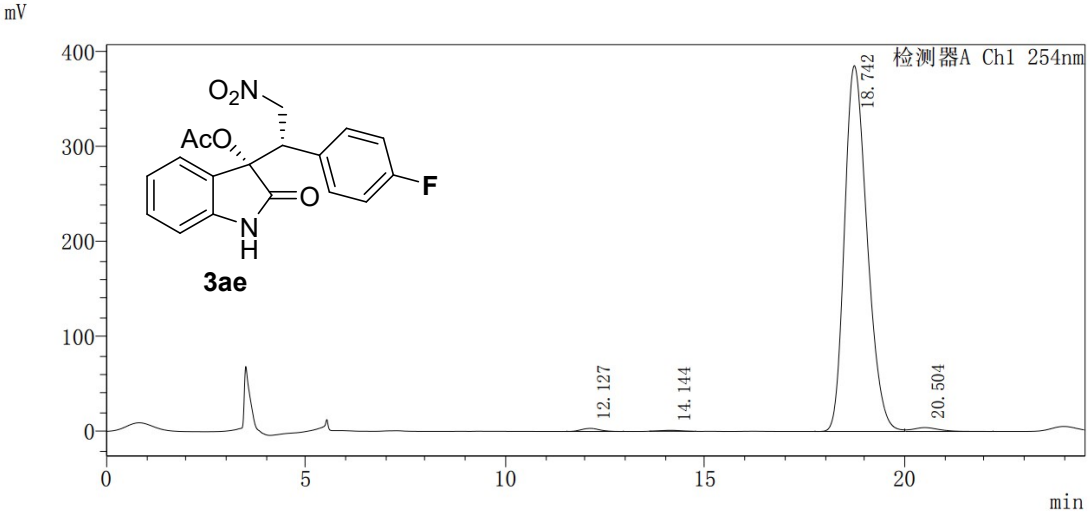

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 26.414 | 5080152 | 15.544 |
| 2 | 29.313 | 4898327 | 14.988 |
| 3 | 33.266 | 10918485 | 33.408 |
| 4 | 35.419 | 11785722 | 36.061 |



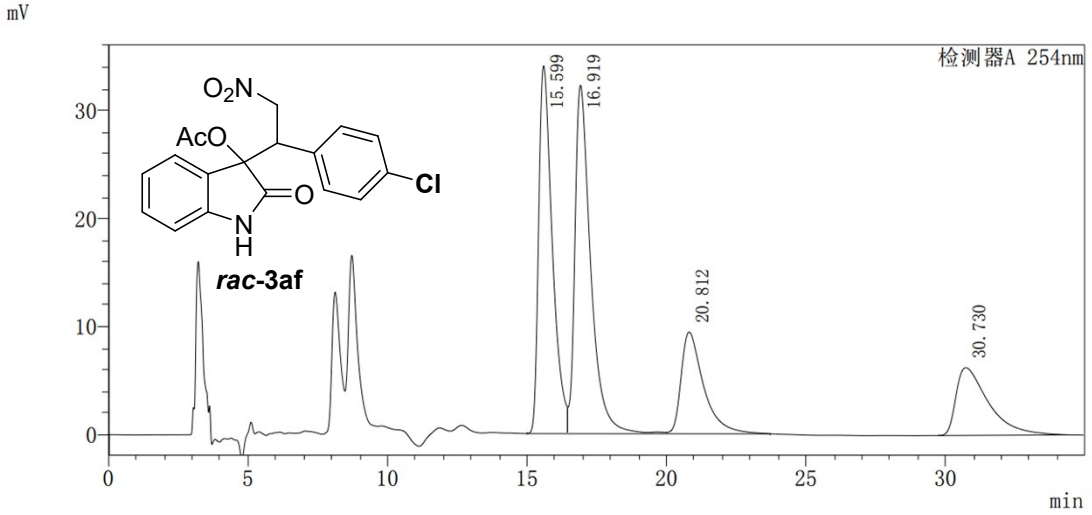

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 26.860 | 243809 | 0.566 |
| 2 | 27.528 | 41879963 | 97.229 |
| 3 | 34.274 | 682246 | 1.584 |
| 4 | 37.126 | 267532 | 0.621 |



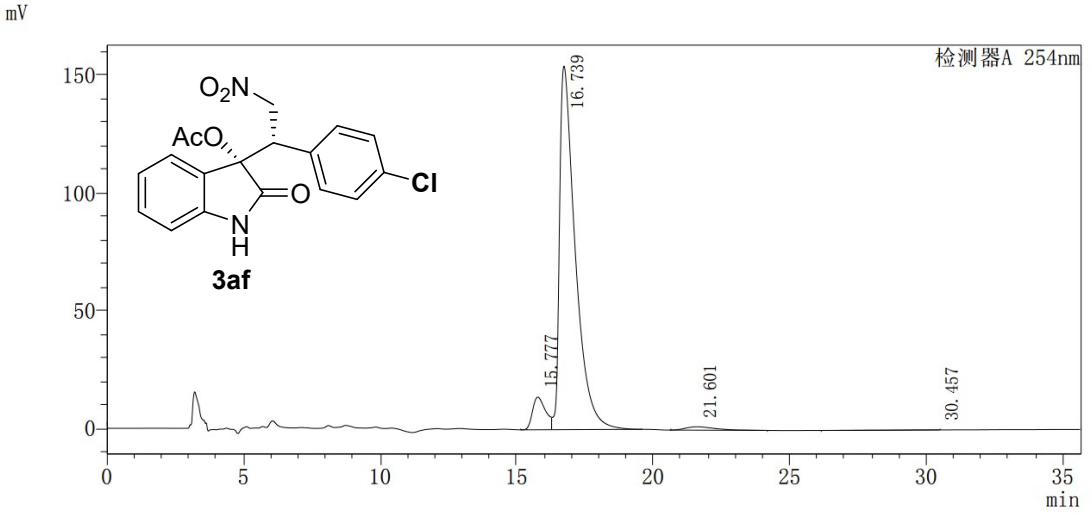

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.064 | 11925087 | 46.985 |
| 2 | 14.082 | 365562 | 1.440 |
| 3 | 18.665 | 12585122 | 49.586 |
| 4 | 20.493 | 504834 | 1.989 |



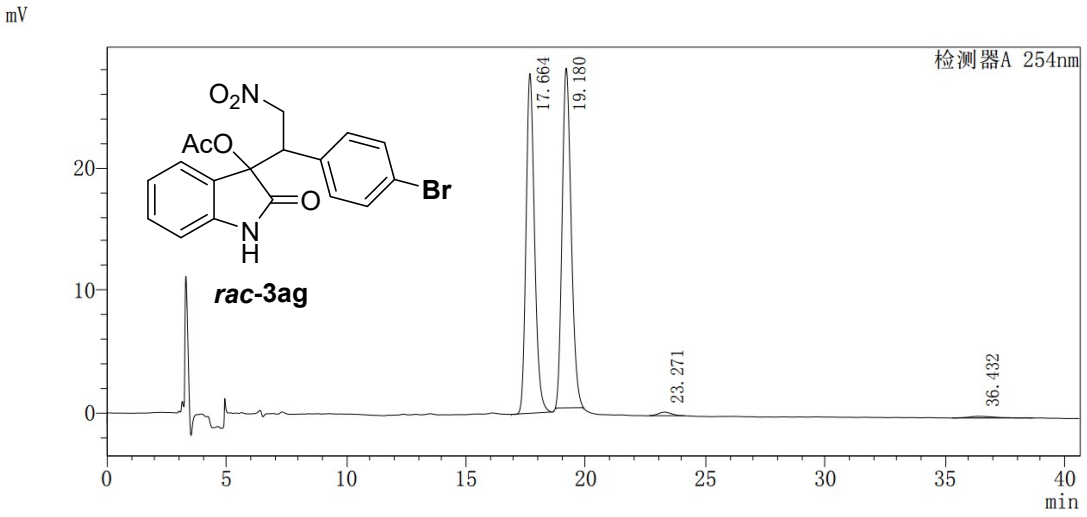

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.127 | 103656 | 0.667 |
| 2 | 14.144 | 35151 | 0.226 |
| 3 | 18.742 | 15207237 | 97.928 |
| 4 | 20.504 | 182978 | 1.178 |



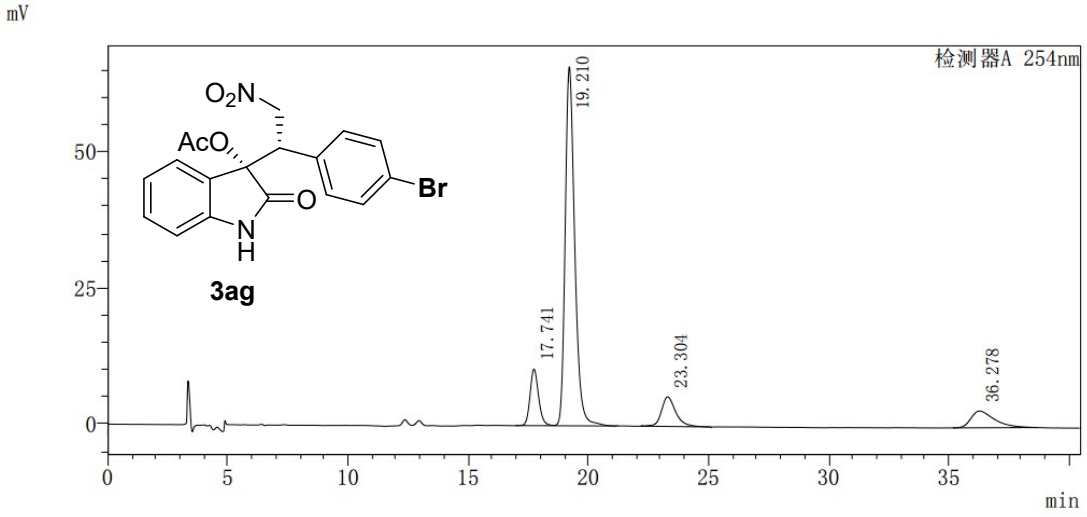

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.599 | 1162264 | 33.558 |
| 2 | 16.919 | 1267305 | 36.591 |
| 3 | 20.812 | 527530 | 15.232 |
| 4 | 30.730 | 506310 | 14.619 |




| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.777 | 471344 | 6.957 |
| 2 | 16.739 | 6191973 | 91.398 |
| 3 | 21.601 | 111034 | 1.639 |
| 4 | 30.457 | 420 | 0.006 |

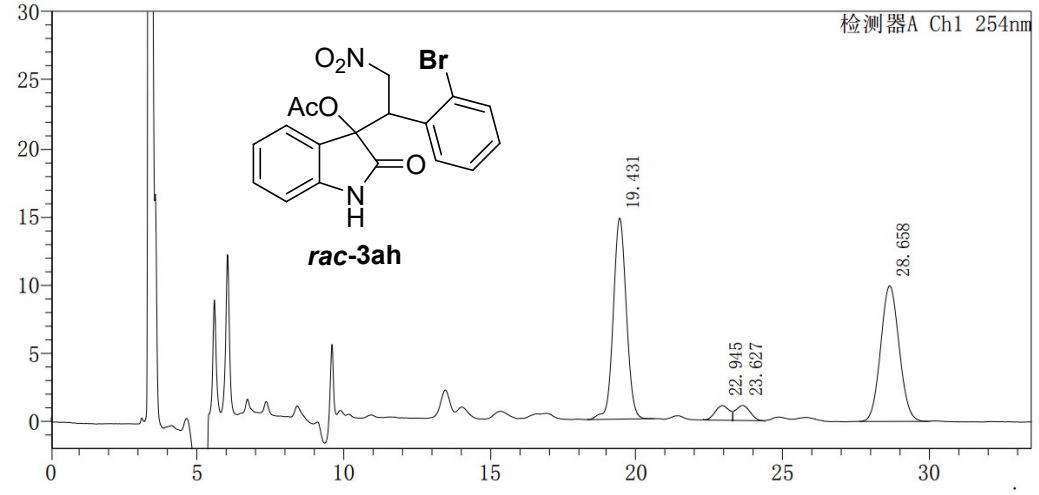



| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 17.664 | 27723 | 47.655 |
| 2 | 19.180 | 27723 | 50.837 |
| 3 | 23.271 | 288 | 0.757 |
| 4 | 36.432 | 143 | 0.751 |



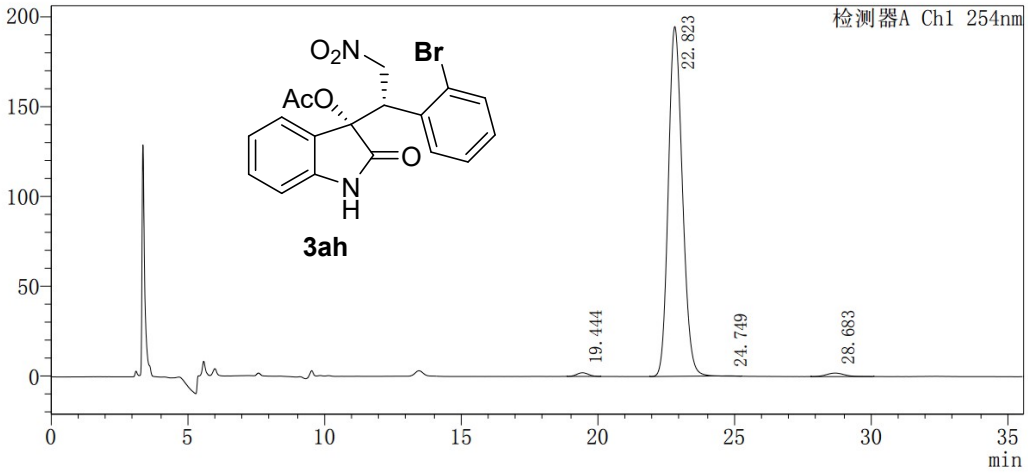

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 17.741 | 257725 | 10.262 |
| 2 | 19.210 | 1817490 | 72.370 |
| 3 | 23.304 | 224782 | 8.950 |
| 4 | 36.278 | 211395 | 8.417 |

mV

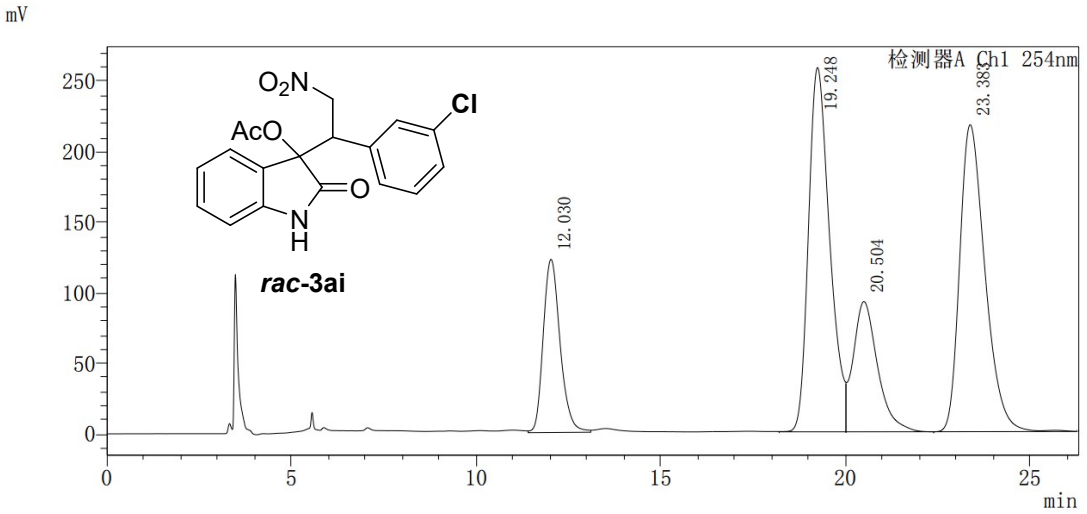



| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 19.431 | 456826 | 47.282 |
| 2 | 22.945 | 36220 | 3.749 |
| 3 | 23.627 | 37184 | 3.849 |
| 4 | 28.658 | 435939 | 45.120 |

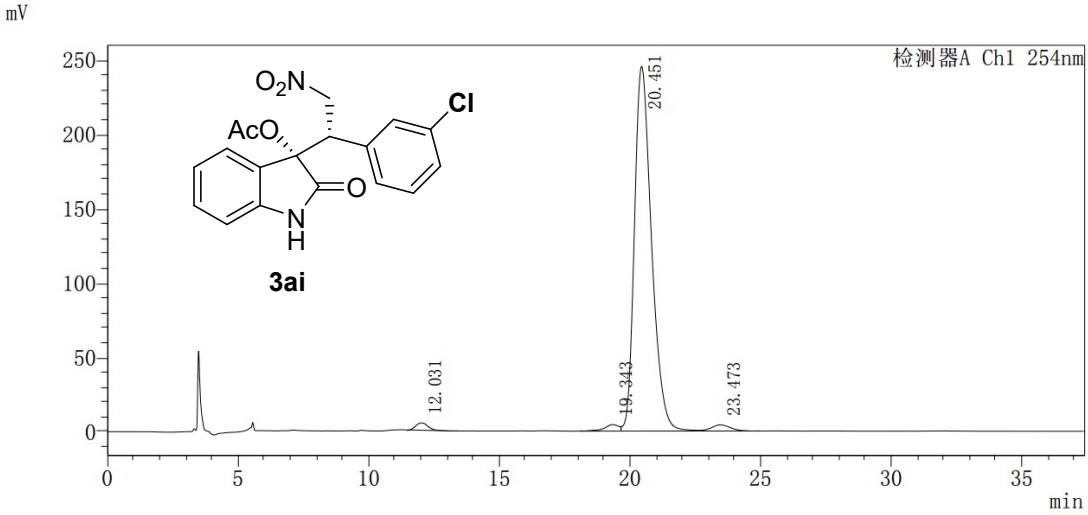
mV



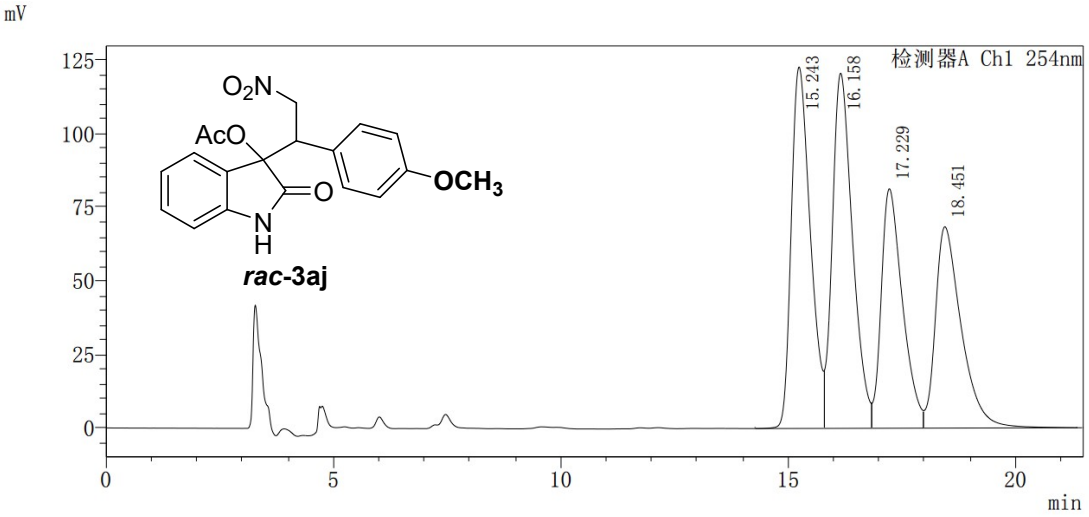

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 19.444 | 60314 | 0.852 |
| 2 | 22.823 | 6924423 | 97.851 |
| 3 | 24.749 | 4563 | 0.064 |
| 4 | 28.683 | 87208 | 1.232 |



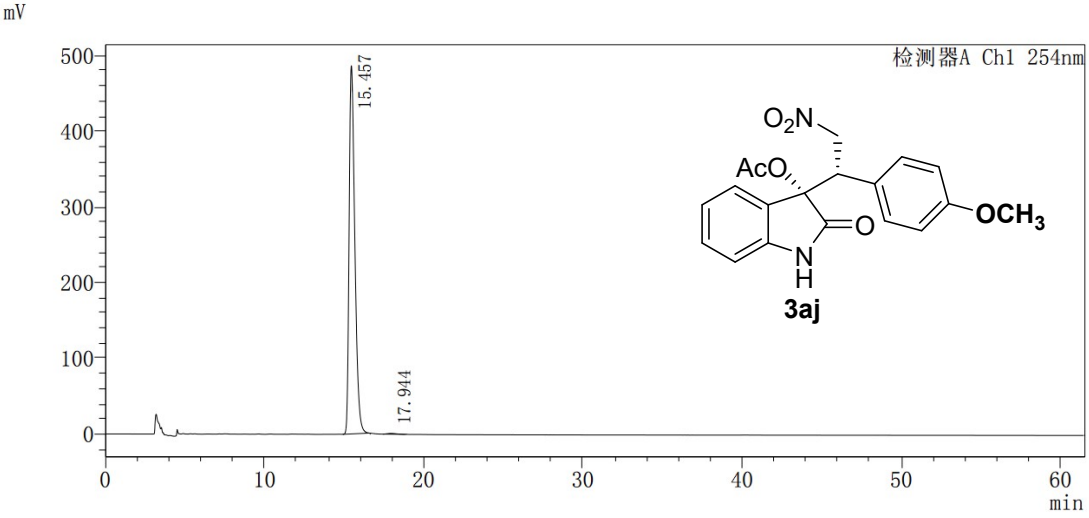

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.030 | 122780 | 13.526 |
| 2 | 19.248 | 258250 | 35.867 |
| 3 | 20.504 | 92347 | 14.619 |
| 4 | 23.383 | 217678 | 35.987 |



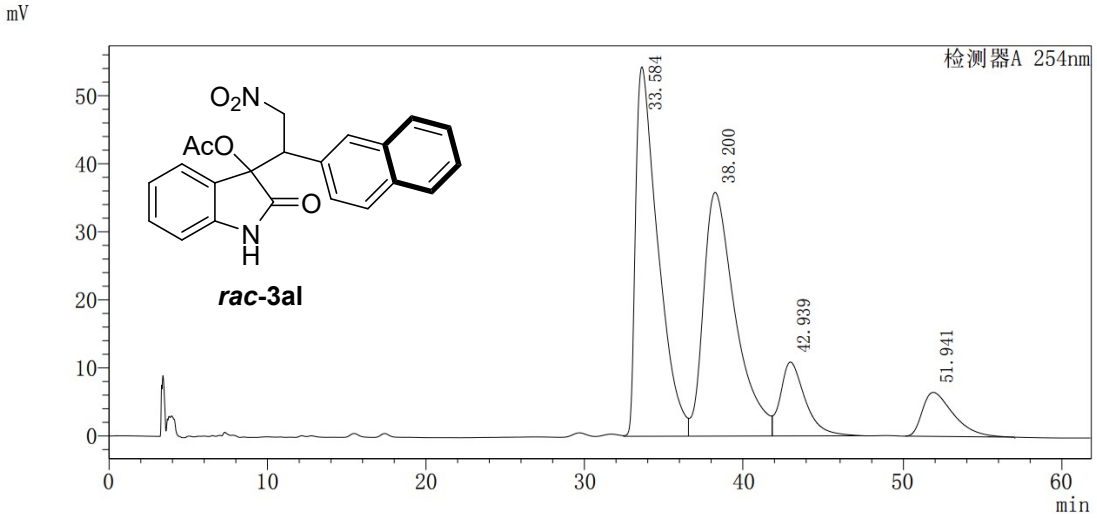

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.031 | 160047 | 1.368 |
| 2 | 19.343 | 168666 | 1.442 |
| 3 | 20.451 | 11155513 | 95.346 |
| 4 | 23.473 | 215808 | 1.845 |



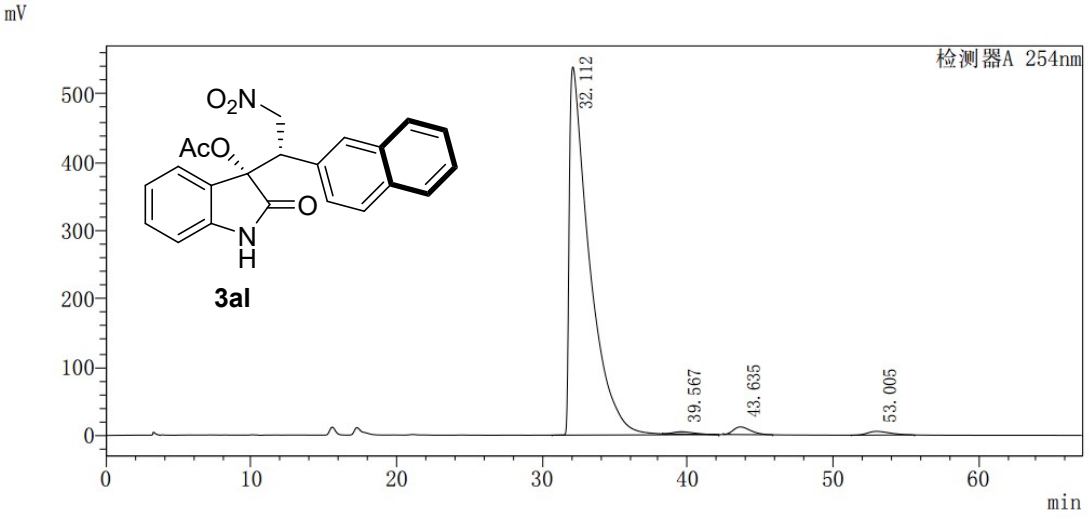

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.243 | 3580015 | 28.174 |
| 2 | 16.158 | 3755870 | 29.558 |
| 3 | 17.229 | 2653128 | 20.879 |
| 4 | 18.451 | 2717854 | 21.389 |



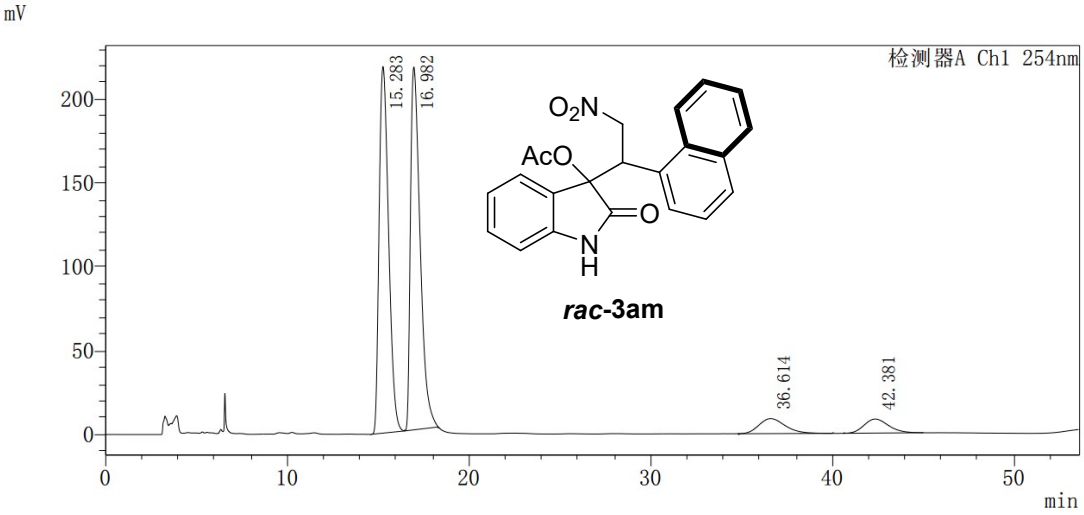

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.457 | 12125125 | 99.675 |
| 2 | 17.944 | 39477 | 0.325 |



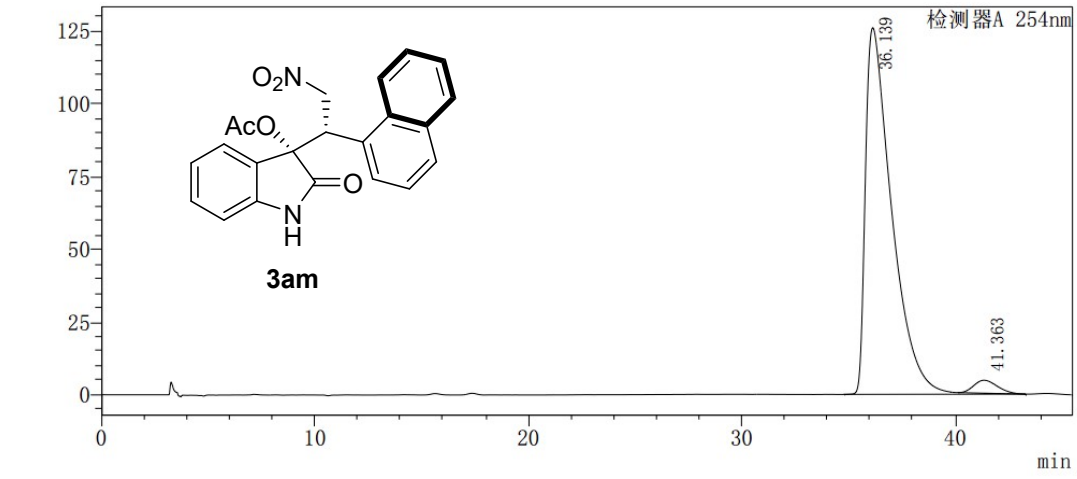

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 33.584 | 5310223 | 42.913 |
| 2 | 38.200 | 4998420 | 40.393 |
| 3 | 42.939 | 1188785 | 9.607 |
| 4 | 51.941 | 877071 | 7.088 |



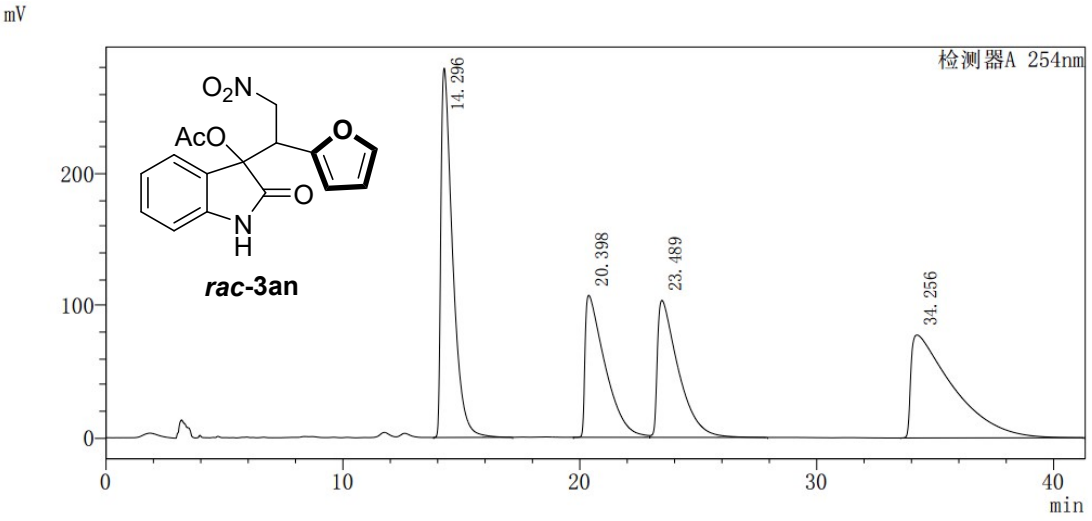

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 32.112 | 51860614 | 96.589 |
| 2 | 39.567 | 329588 | 0.614 |
| 3 | 43.635 | 926720 | 1.726 |
| 4 | 53.005 | 575078 | 1.071 |



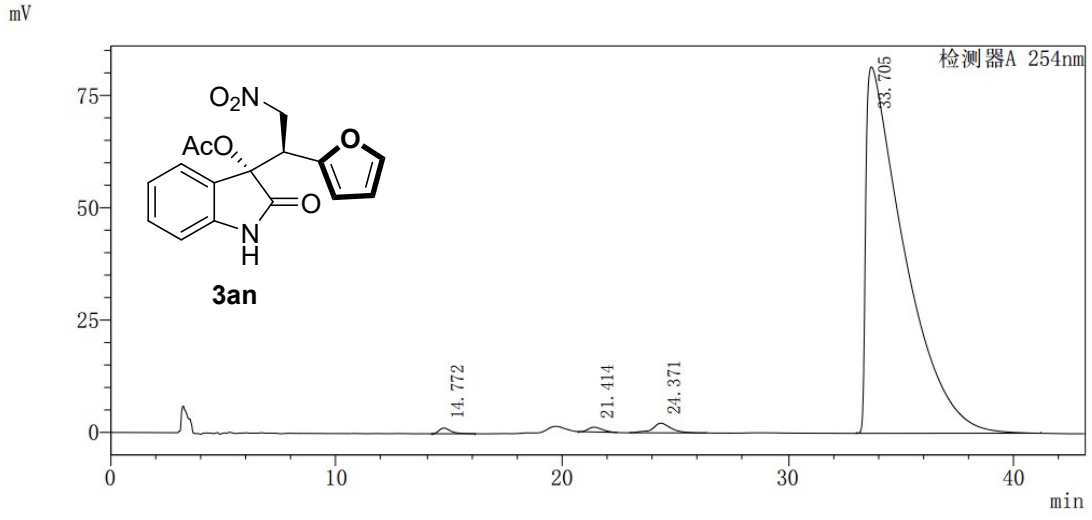

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.283 | 7917637 | 44.914 |
| 2 | 16.982 | 8014701 | 45.465 |
| 3 | 36.614 | 906554 | 5.143 |
| 4 | 42.381 | 789535 | 4.479 |



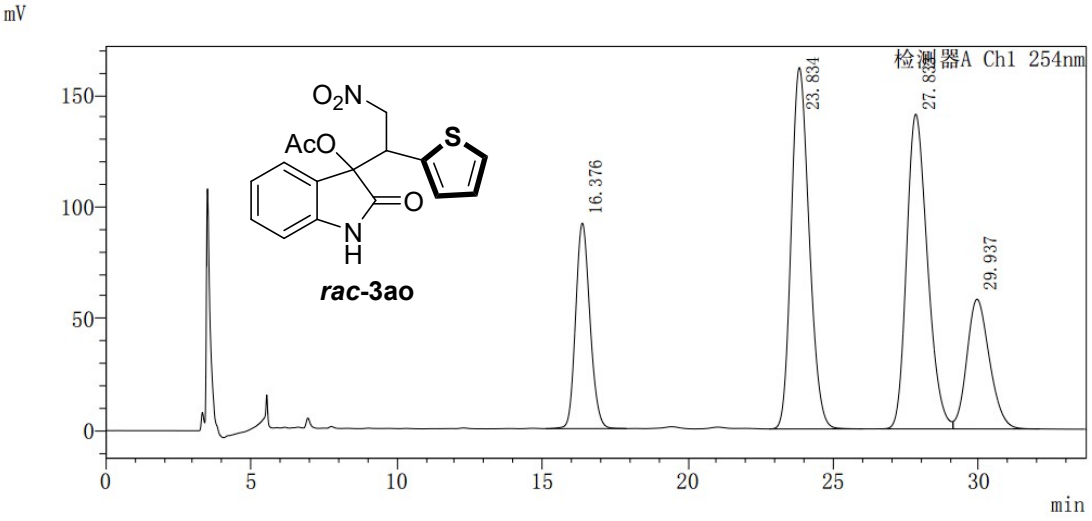

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 36.139 | 10791252 | 96.933 |
| 2 | 41.363 | 341471 | 3.067 |



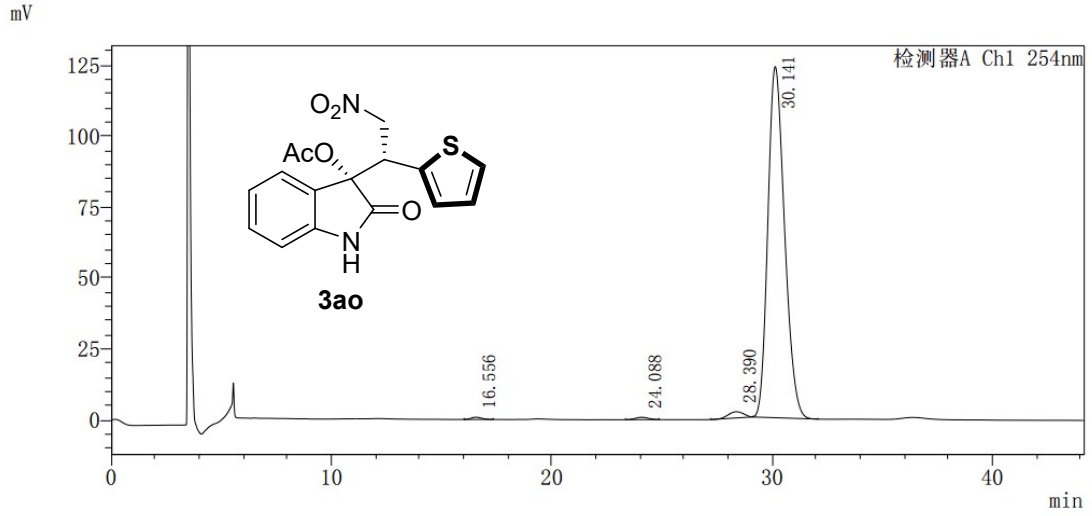

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 14.296 | 9629139 | 30.158 |
| 2 | 20.398 | 6317895 | 19.787 |
| 3 | 23.489 | 6384456 | 19.996 |
| 4 | 34.256 | 9597408 | 30.059 |



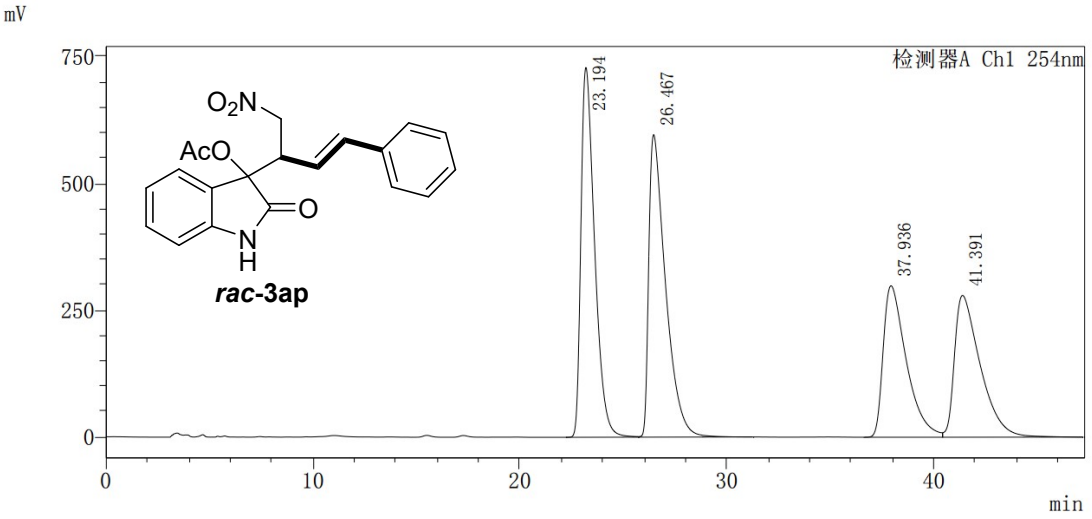

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 14.772 | 45642 | 0.462 |
| 2 | 21.414 | 45616 | 0.462 |
| 3 | 24.371 | 122151 | 1.236 |
| 4 | 33.705 | 9667330 | 97.840 |



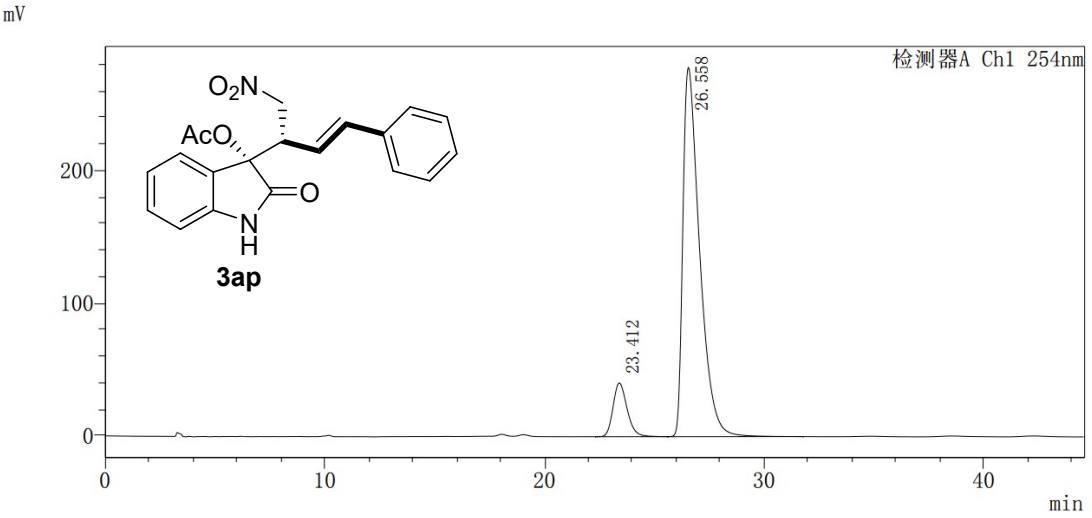

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 16.376 | 3136696 | 15.510 |
| 2 | 23.834 | 6923677 | 34.235 |
| 3 | 27.833 | 7015161 | 34.688 |
| 4 | 29.937 | 3148310 | 15.567 |



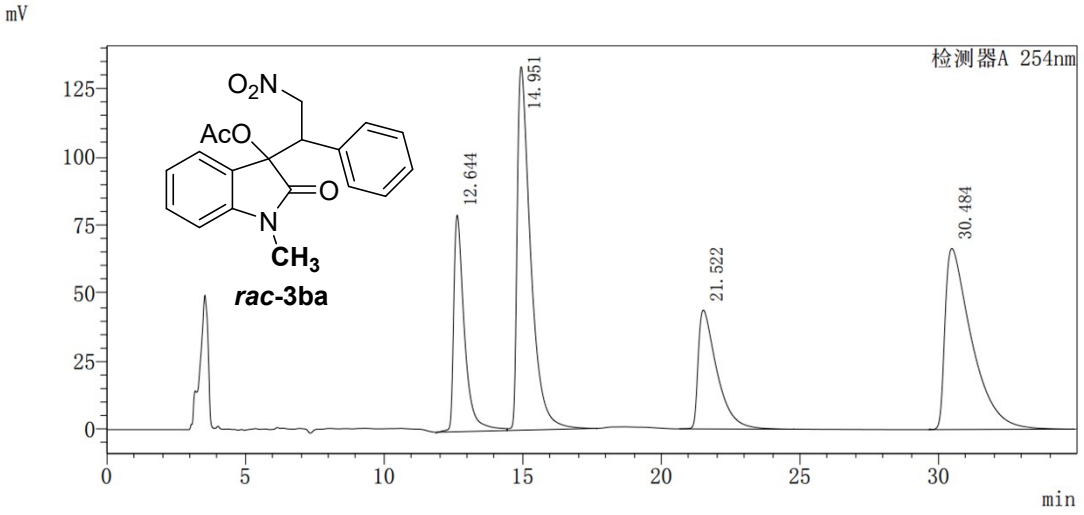

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 16.556 | 26341 | 0.394 |
| 2 | 24.088 | 33953 | 0.508 |
| 3 | 28.390 | 104305 | 1.561 |
| 4 | 30.141 | 6515397 | 97.536 |



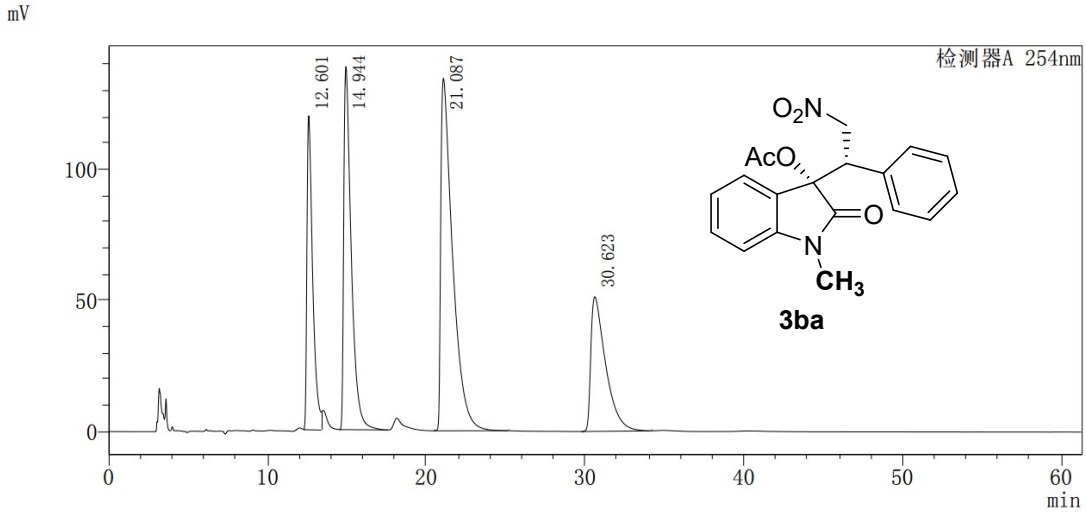

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 23.194 | 33449107 | 29.213 |
| 2 | 26.467 | 33548438 | 29.300 |
| 3 | 37.936 | 23232176 | 20.290 |
| 4 | 41.391 | 24270092 | 21.197 |



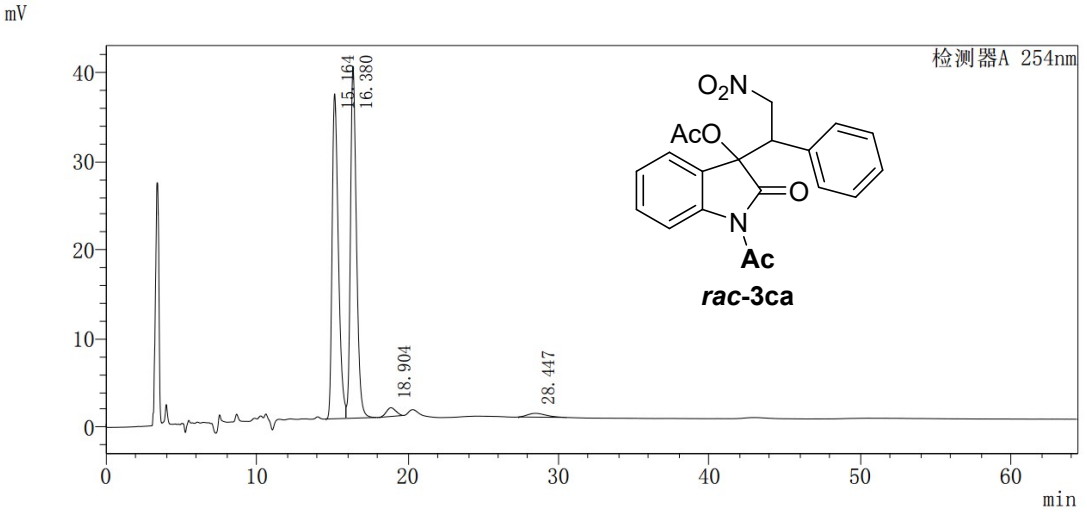

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 23.412 | 1804309 | 10.909 |
| 2 | 26.558 | 14735161 | 89.091 |



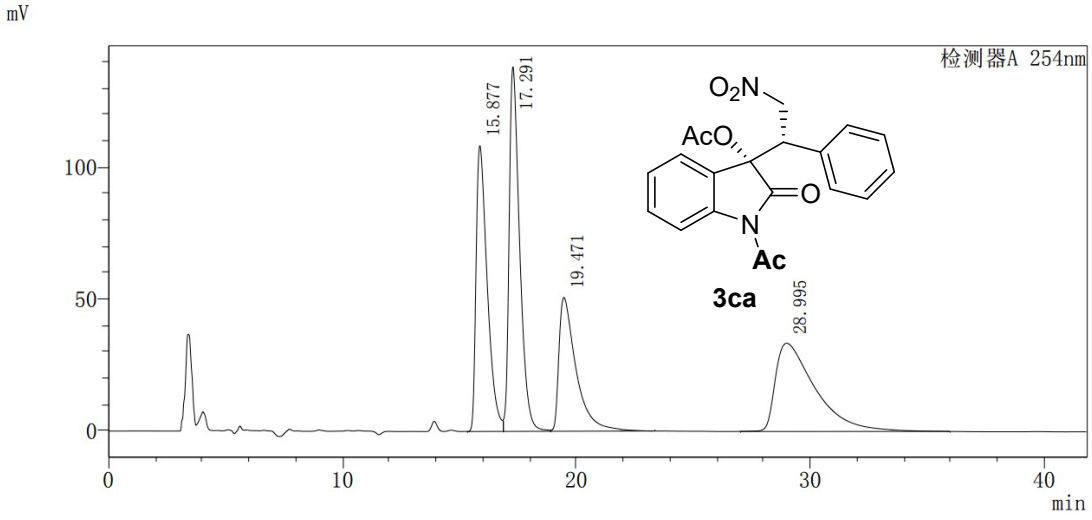

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.644 | 2143978 | 16.332 |
| 2 | 14.951 | 4489731 | 34.200 |
| 3 | 21.522 | 2049045 | 15.608 |
| 4 | 30.484 | 4445071 | 33.860 |



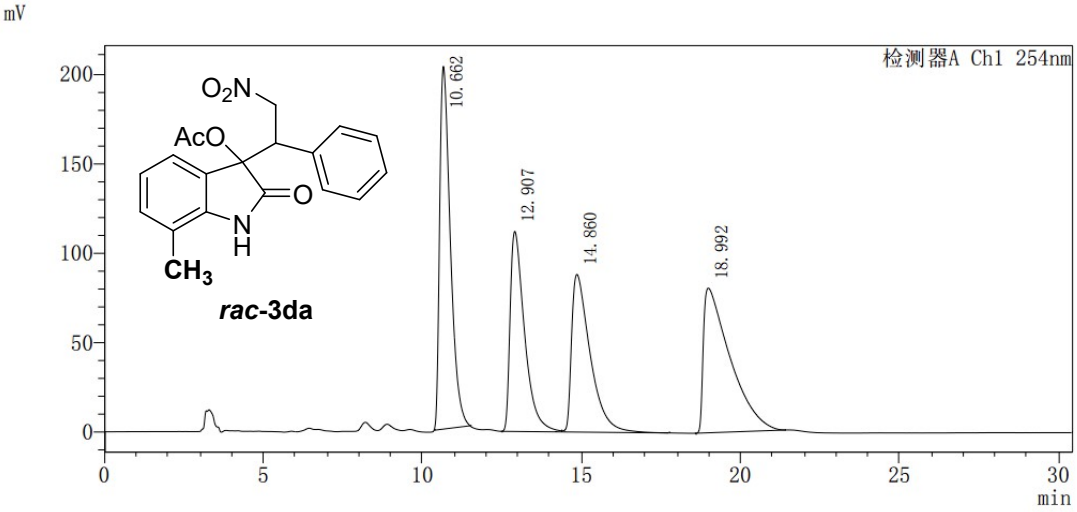

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.601 | 3025141 | 16.898 |
| 2 | 14.944 | 4566490 | 25.508 |
| 3 | 21.087 | 6976516 | 38.970 |
| 4 | 30.623 | 3334004 | 18.623 |



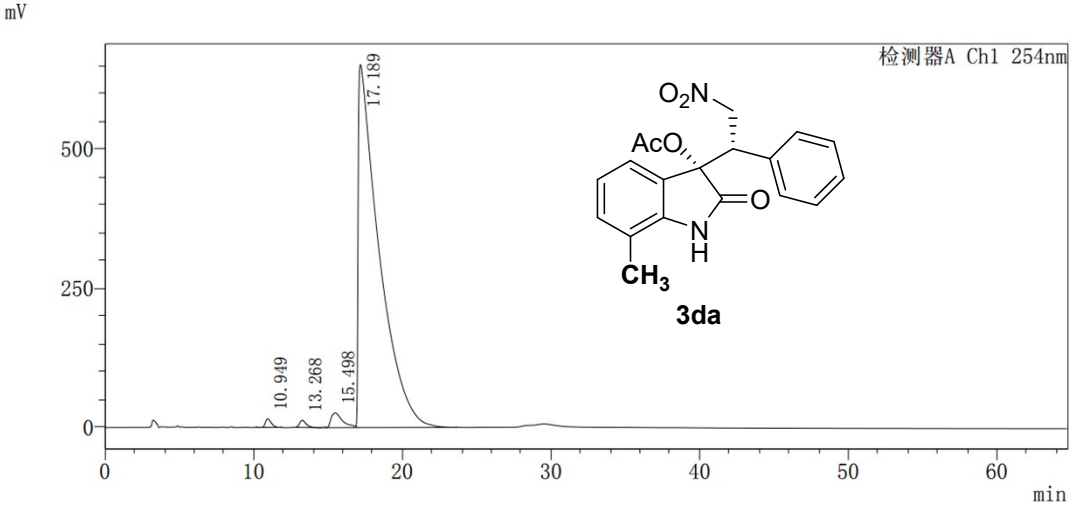

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.164 | 1058440 | 47.405 |
| 2 | 16.380 | 1094912 | 49.038 |
| 3 | 18.904 | 43433 | 1.945 |
| 4 | 28.447 | 35992 | 1.612 |



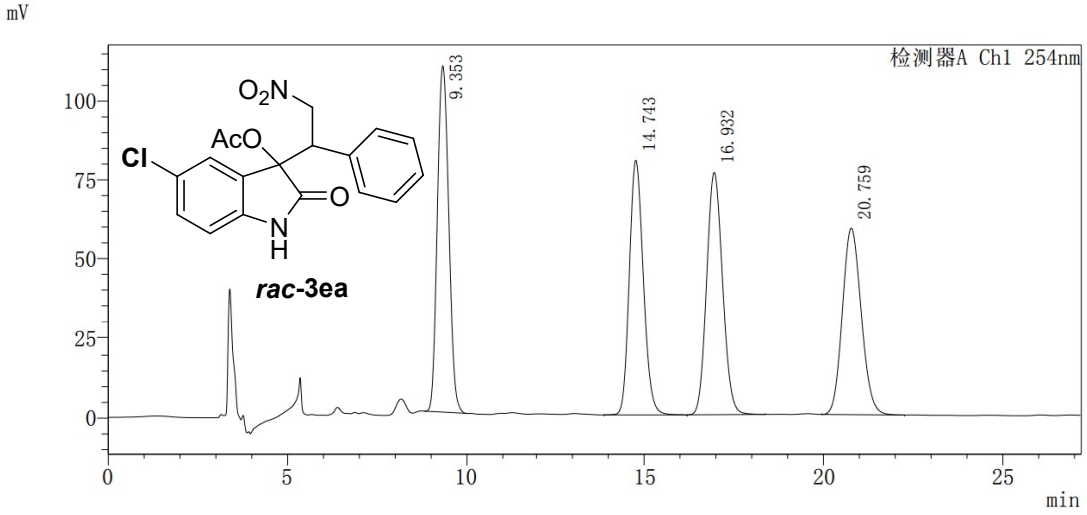

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 15.877 | 3588668 | 24.806 |
| 2 | 17.291 | 4326851 | 29.908 |
| 3 | 19.471 | 2589249 | 17.898 |
| 4 | 28.995 | 3962301 | 27.388 |



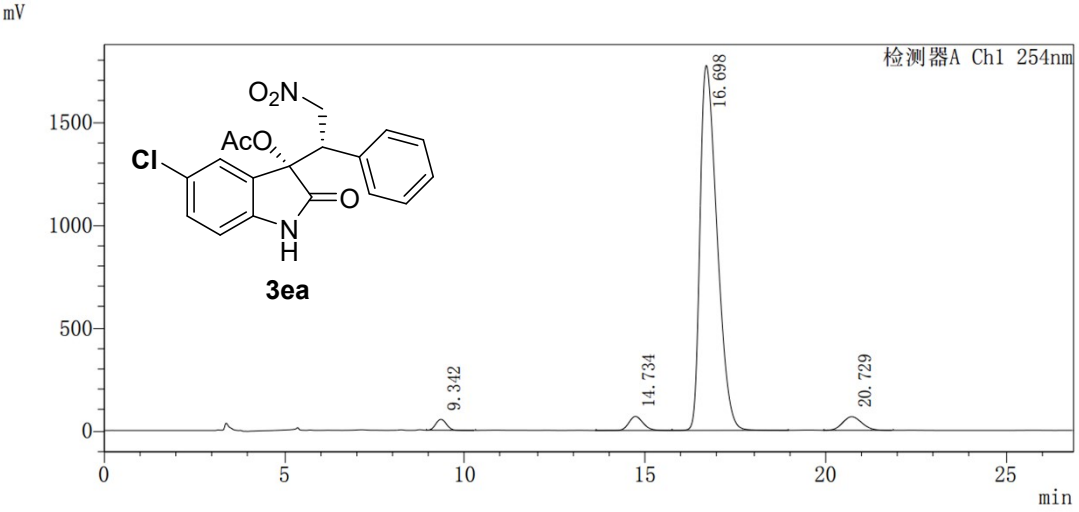

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 10.662 | 4734250 | 28.606 |
| 2 | 12.907 | 3524749 | 21.297 |
| 3 | 14.860 | 3574600 | 21.599 |
| 4 | 18.992 | 4716471 | 28.498 |



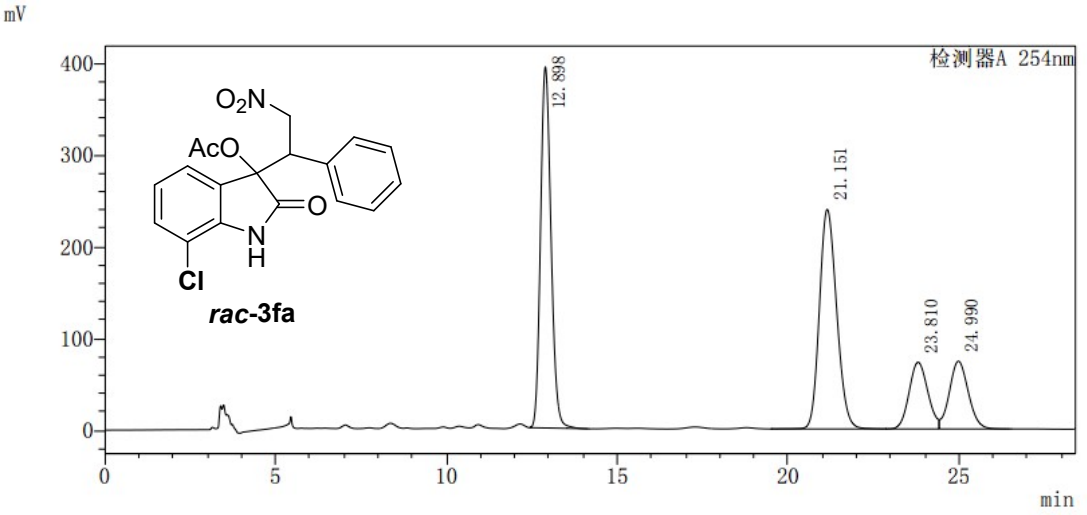

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 10.949 | 422466 | 0.647 |
| 2 | 13.268 | 401365 | 0.615 |
| 3 | 15.498 | 1417558 | 2.172 |
| 4 | 17.189 | 63018181 | 96.565 |



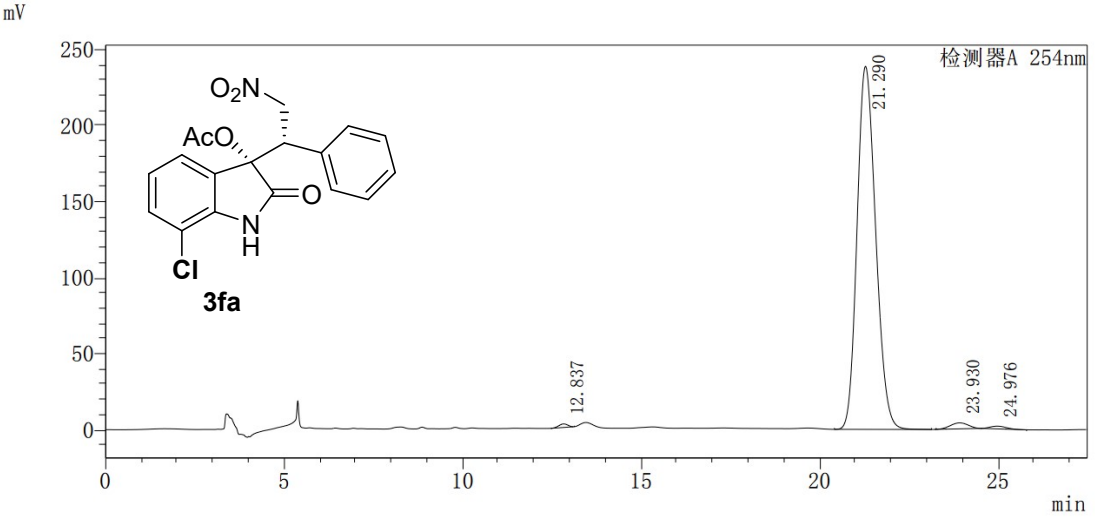

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 9.353 | 2426161 | 26.505 |
| 2 | 14.743 | 2191644 | 23.943 |
| 3 | 16.932 | 2373961 | 25.935 |
| 4 | 20.759 | 2161753 | 23.617 |



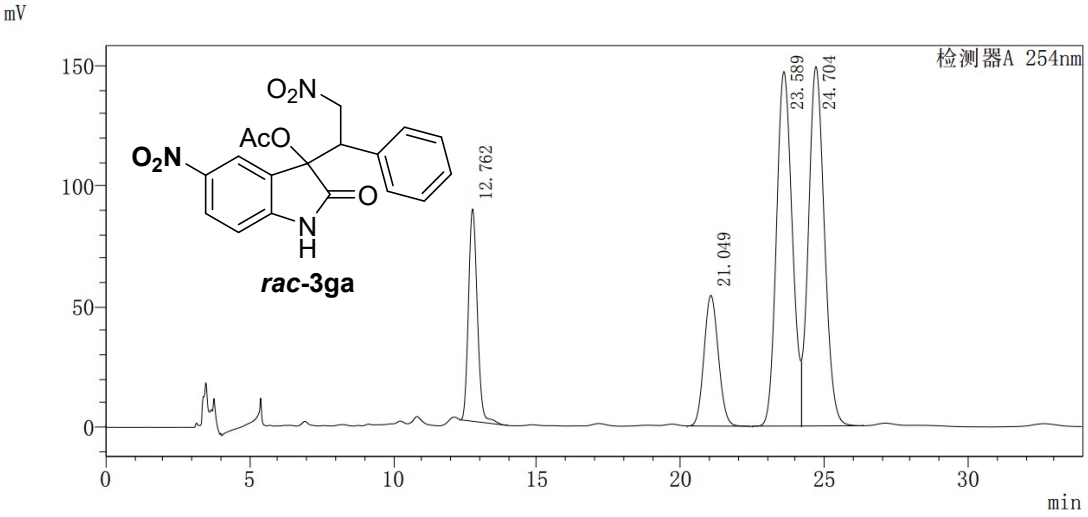

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 9.342 | 1082964 | 1.708 |
| 2 | 14.734 | 1863798 | 2.940 |
| 3 | 16.698 | 58009773 | 91.493 |
| 4 | 20.729 | 2447039 | 3.859 |



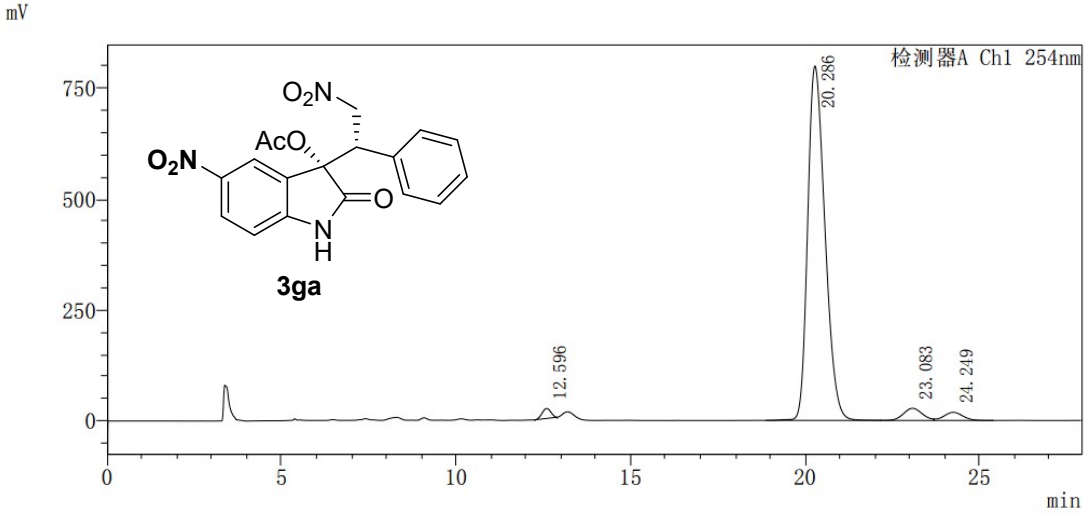

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.898 | 8357619 | 37.353 |
| 2 | 21.151 | 8398125 | 37.534 |
| 3 | 23.810 | 2772953 | 12.393 |
| 4 | 24.990 | 2846003 | 12.720 |



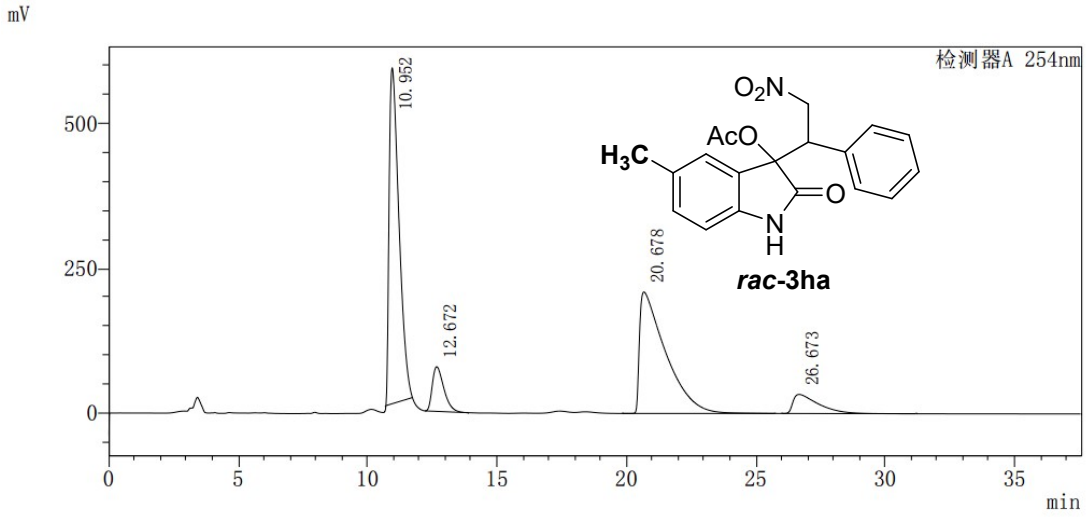

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.837 | 40771 | 0.459 |
| 2 | 21.290 | 8648582 | 97.346 |
| 3 | 23.930 | 138695 | 1.561 |
| 4 | 24.976 | 56325 | 0.634 |



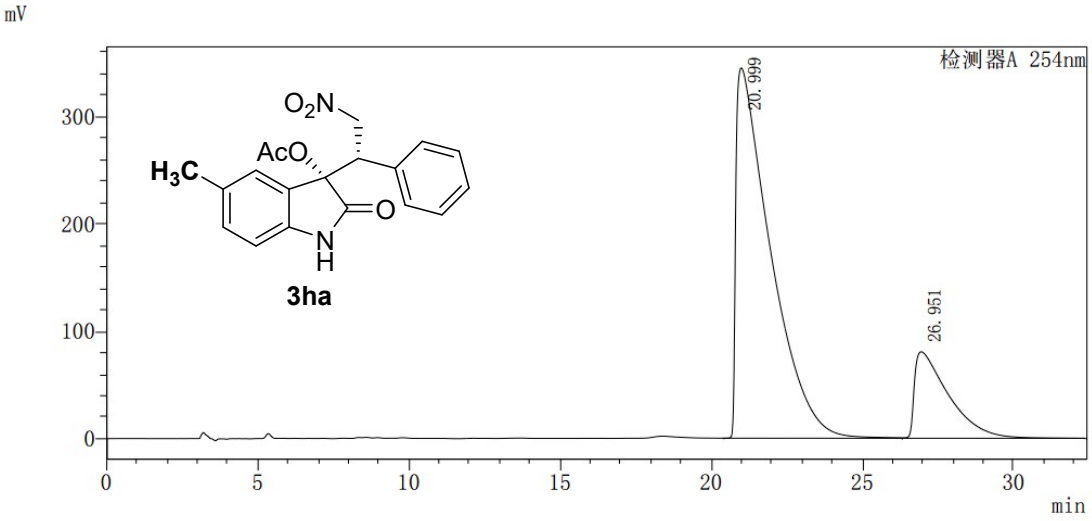

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.762 | 1887528 | 12.479 |
| 2 | 21.049 | 1881327 | 12.438 |
| 3 | 23.589 | 5588881 | 36.949 |
| 4 | 24.704 | 5768184 | 38.134 |



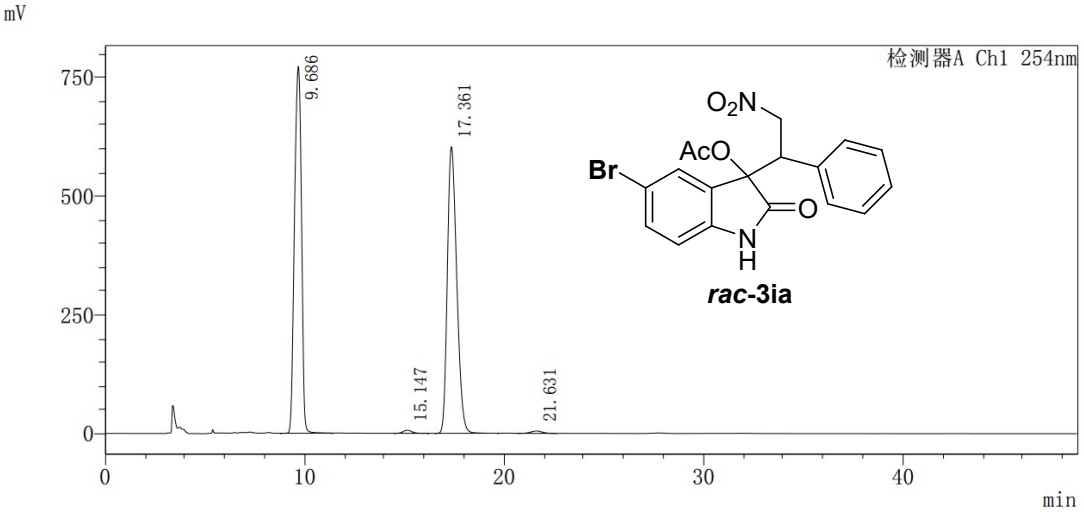

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 12.596 | 393854 | 1.331 |
| 2 | 20.286 | 27478574 | 92.868 |
| 3 | 23.083 | 1029512 | 3.479 |
| 4 | 24.249 | 686854 | 2.321 |



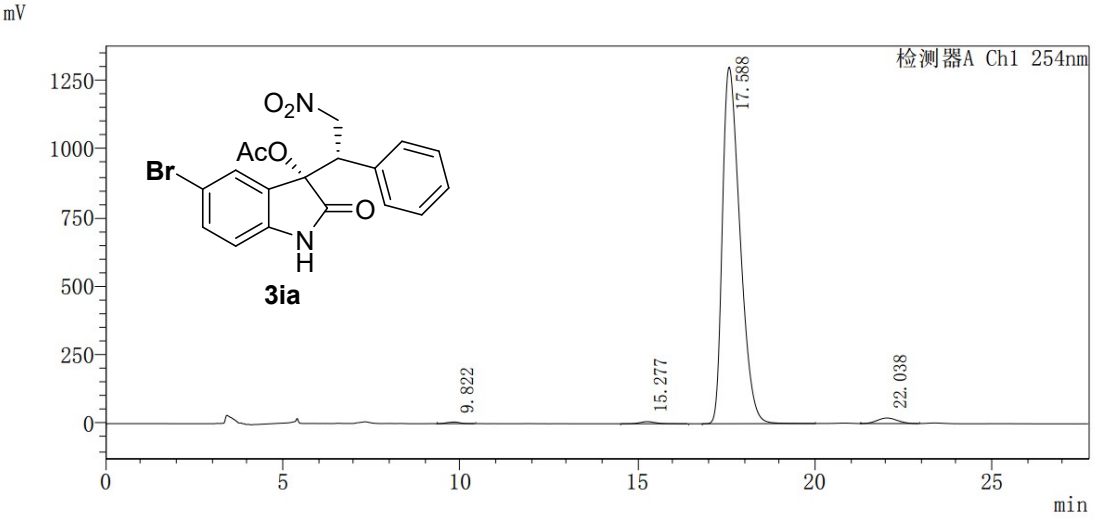

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 10.952 | 15311914 | 44.181 |
| 2 | 12.672 | 2387545 | 6.889 |
| 3 | 20.678 | 14706531 | 42.434 |
| 4 | 26.673 | 2251080 | 6.495 |



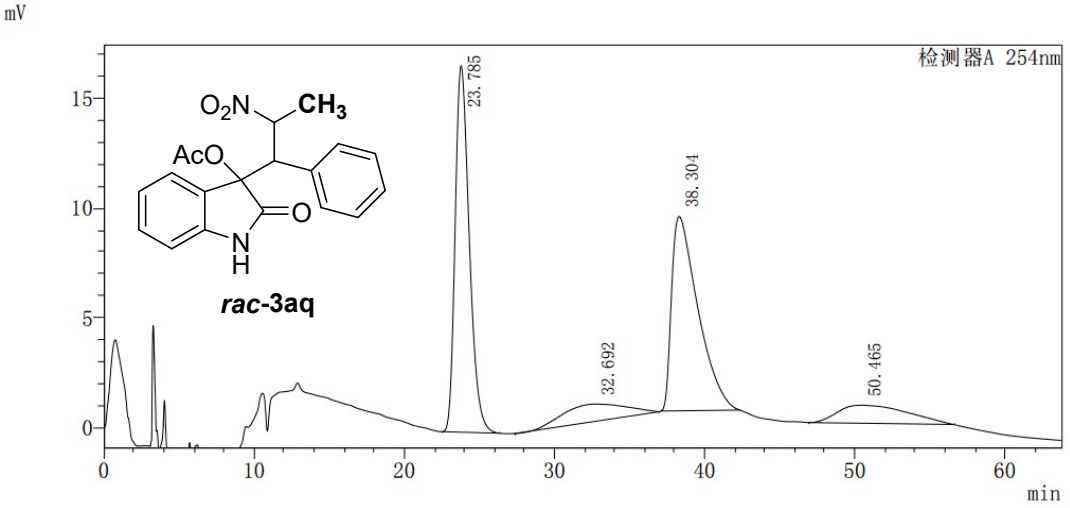

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 20.999 | 27395912 | 81.270 |
| 2 | 26.951 | 6313850 | 18.730 |



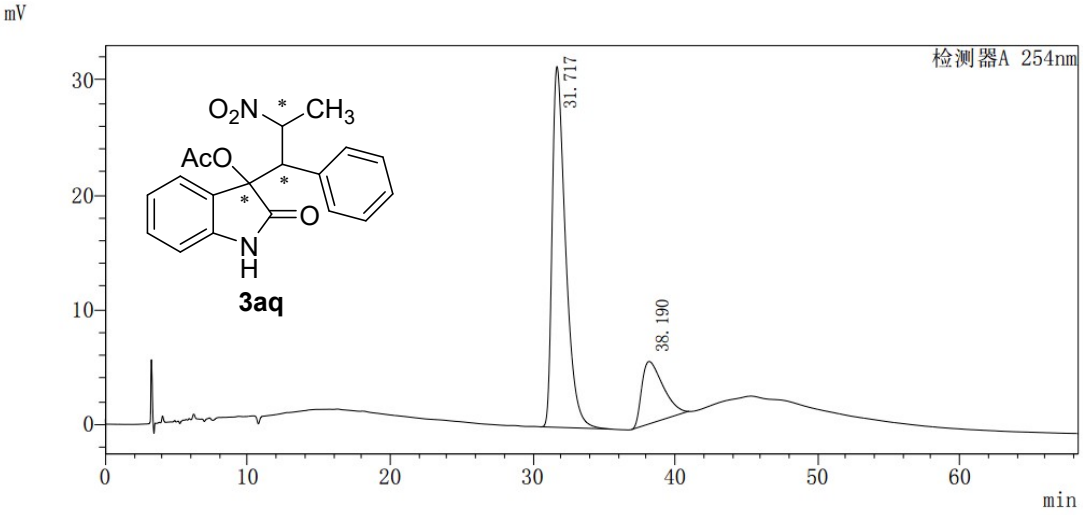

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 9.686 | 18821281 | 48.306 |
| 2 | 15.147 | 197888 | 0.508 |
| 3 | 17.361 | 19744294 | 50.675 |
| 4 | 21.631 | 198822 | 0.510 |



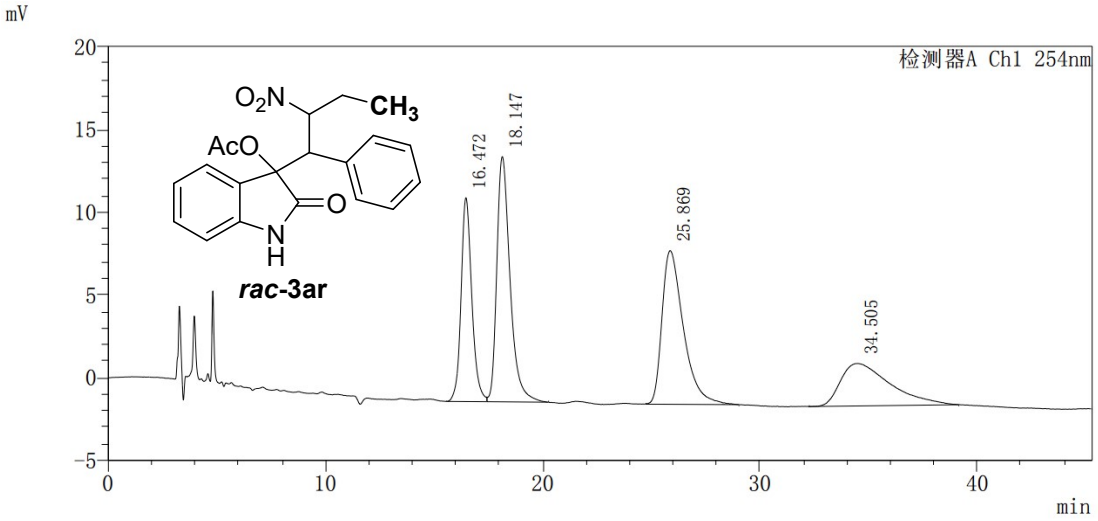

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 9.822 | 145523 | 0.317 |
| 2 | 15.277 | 236541 | 0.516 |
| 3 | 17.588 | 44679881 | 97.443 |
| 4 | 22.038 | 790361 | 1.724 |



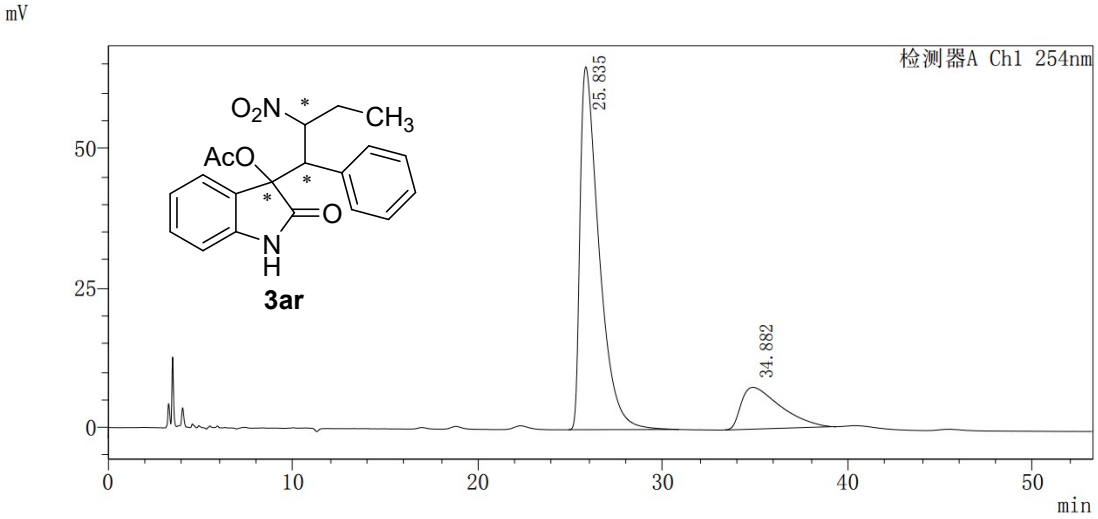

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 23.785 | 1091385 | 40.887 |
| 2 | 32.692 | 231644 | 8.678 |
| 3 | 38.304 | 1079743 | 40.451 |
| 4 | 50.465 | 266483 | 9.983 |



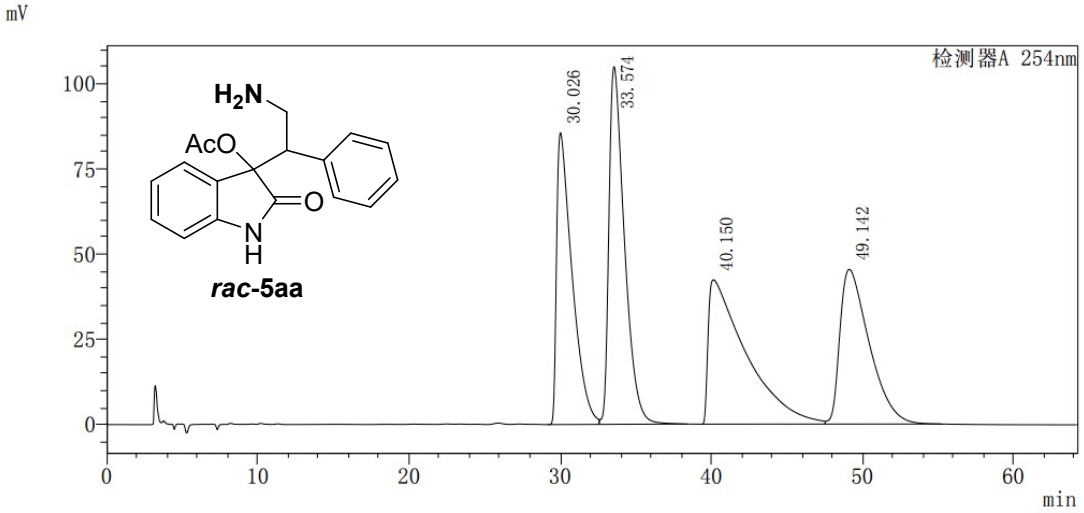

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 31.717 | 2057424 | 78.469 |
| 2 | 38.190 | 564519 | 21.531 |



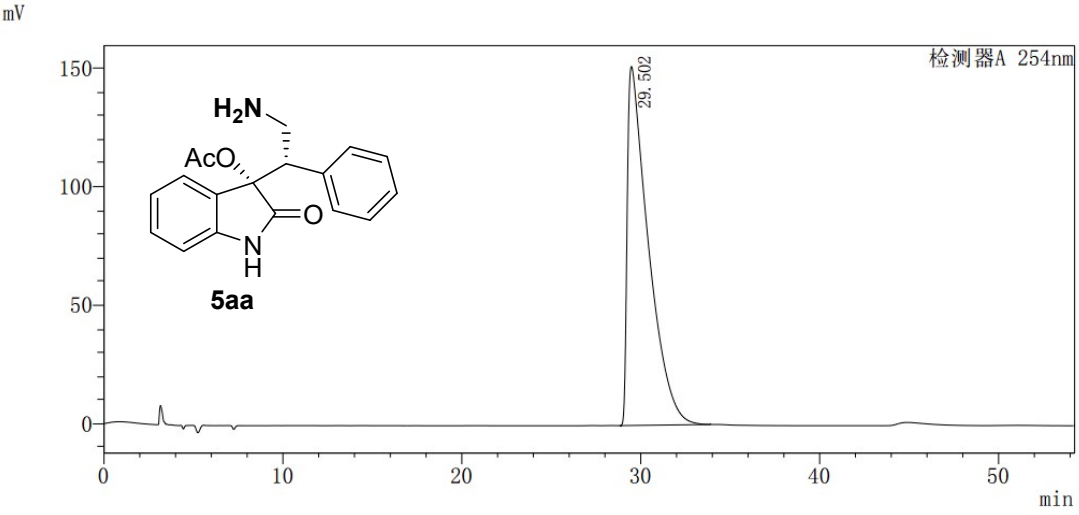

| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 16.472 | 423445 | 20.210 |
| 2 | 18.147 | 628496 | 29.996 |
| 3 | 25.869 | 635865 | 30.348 |
| 4 | 34.505 | 407443 | 19.446 |




| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 25.835 | 4653963 | 80.798 |
| 2 | 34.882 | 1106035 | 19.202 |

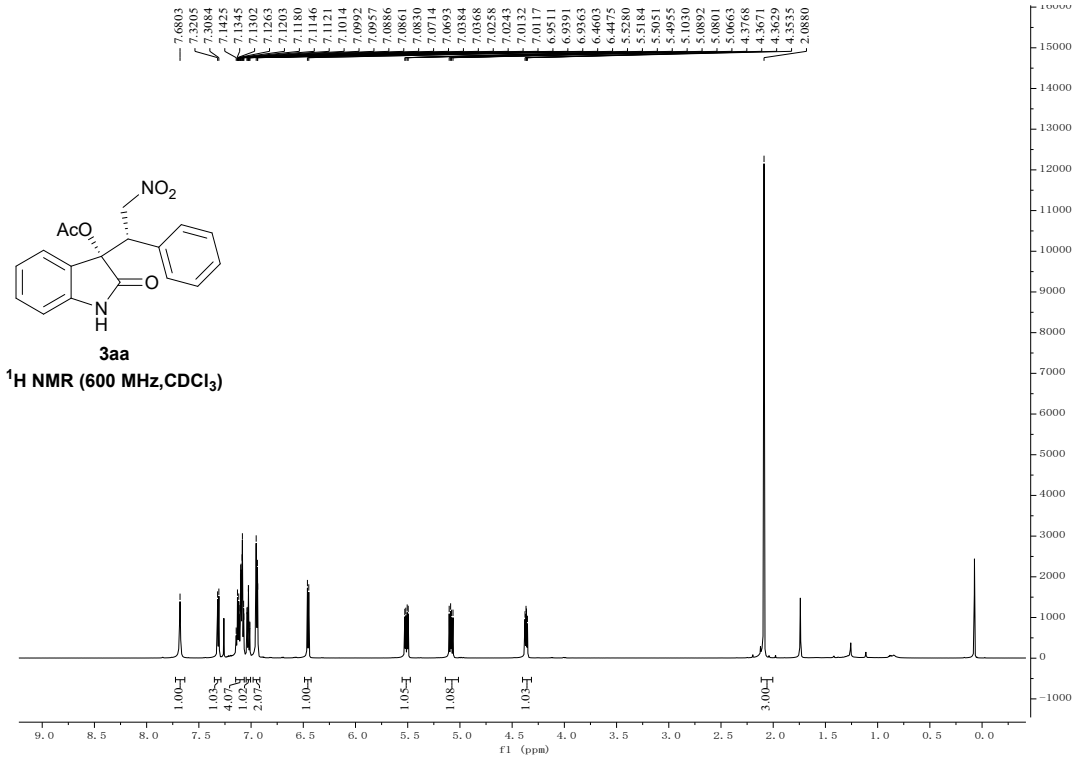



| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 30.026 | 6114691 | 22.558 |
| 2 | 33.574 | 7484515 | 27.611 |
| 3 | 40.150 | 7379103 | 27.222 |
| 4 | 49.142 | 6128569 | 22.609 |

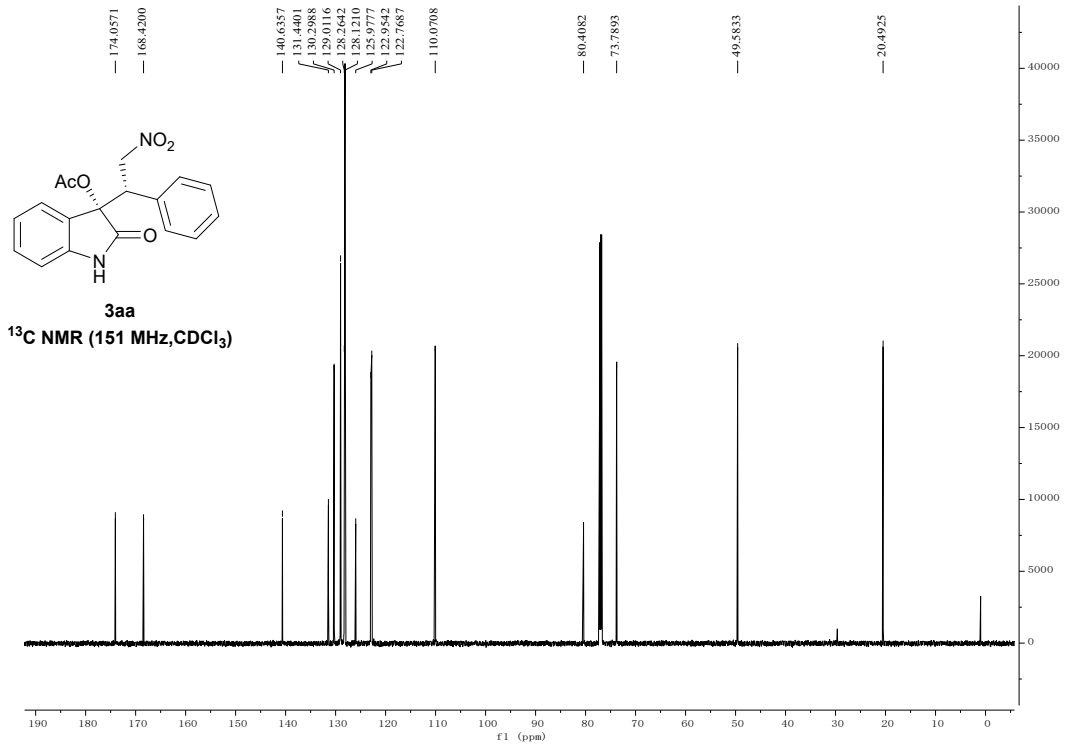



| Peak# | Retention Time | Area | Area% |
|---|---|---|---|
| 1 | 29.502 | 12374432 | 100.000 |

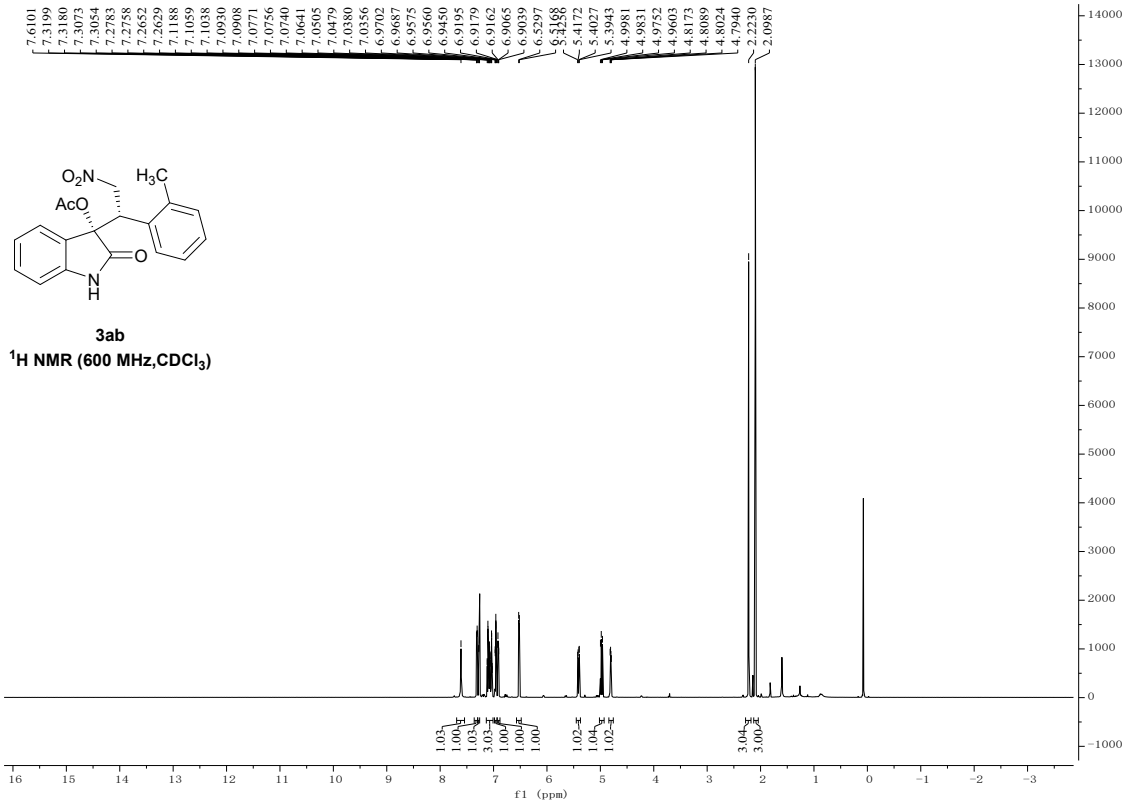
# 12.Copies of NMR Spectra



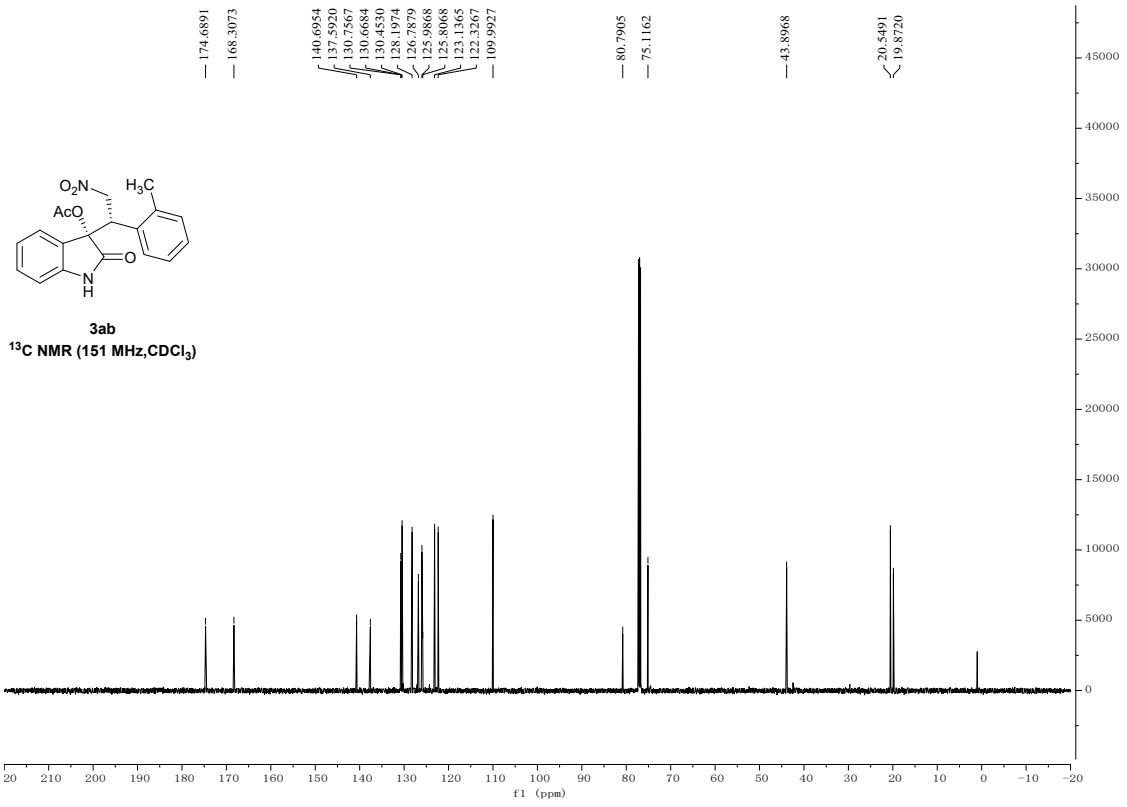

**The $^{1}$H-NMR of 3aa**



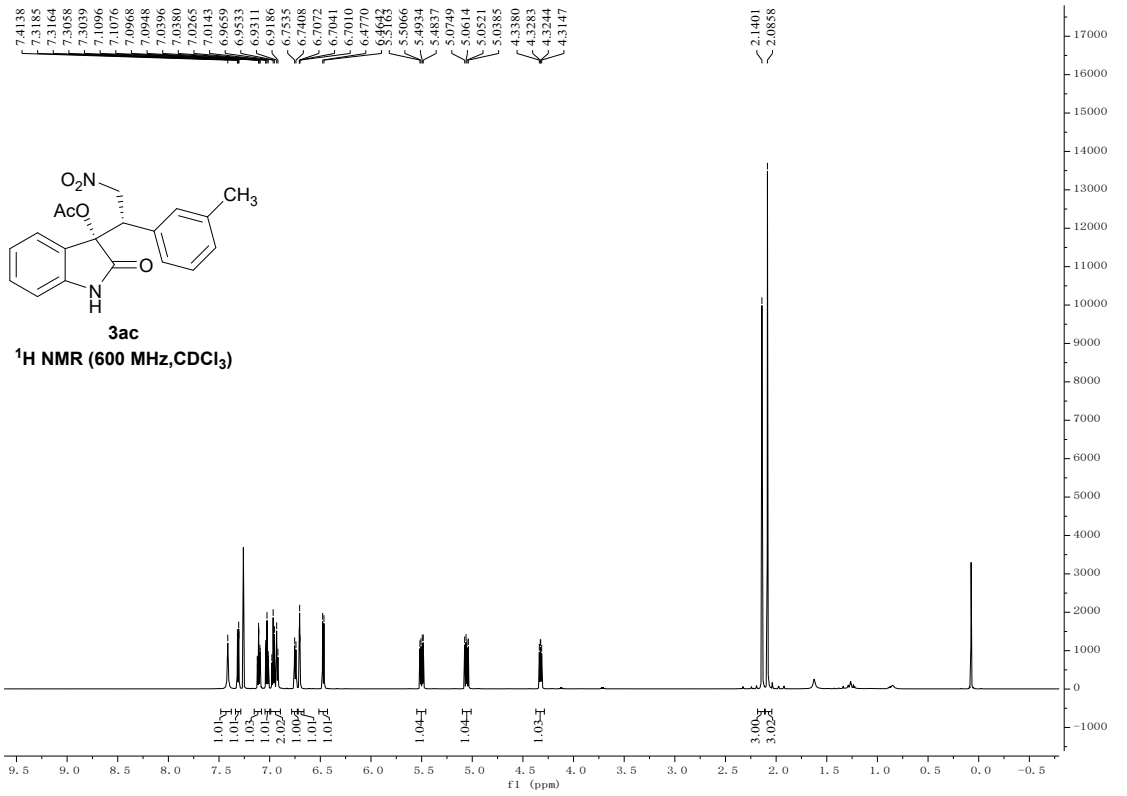

**The $^{13}$C-NMR of 3aa**



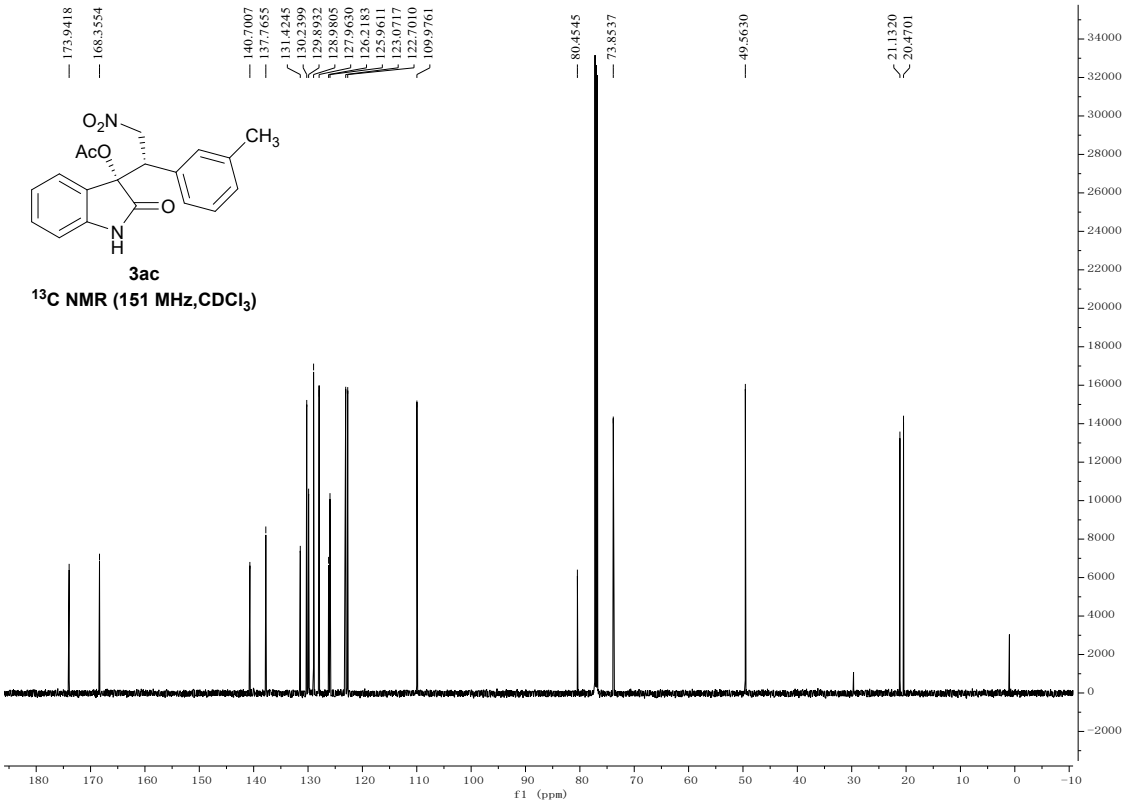

**The $^{1}$H-NMR of 3ab**



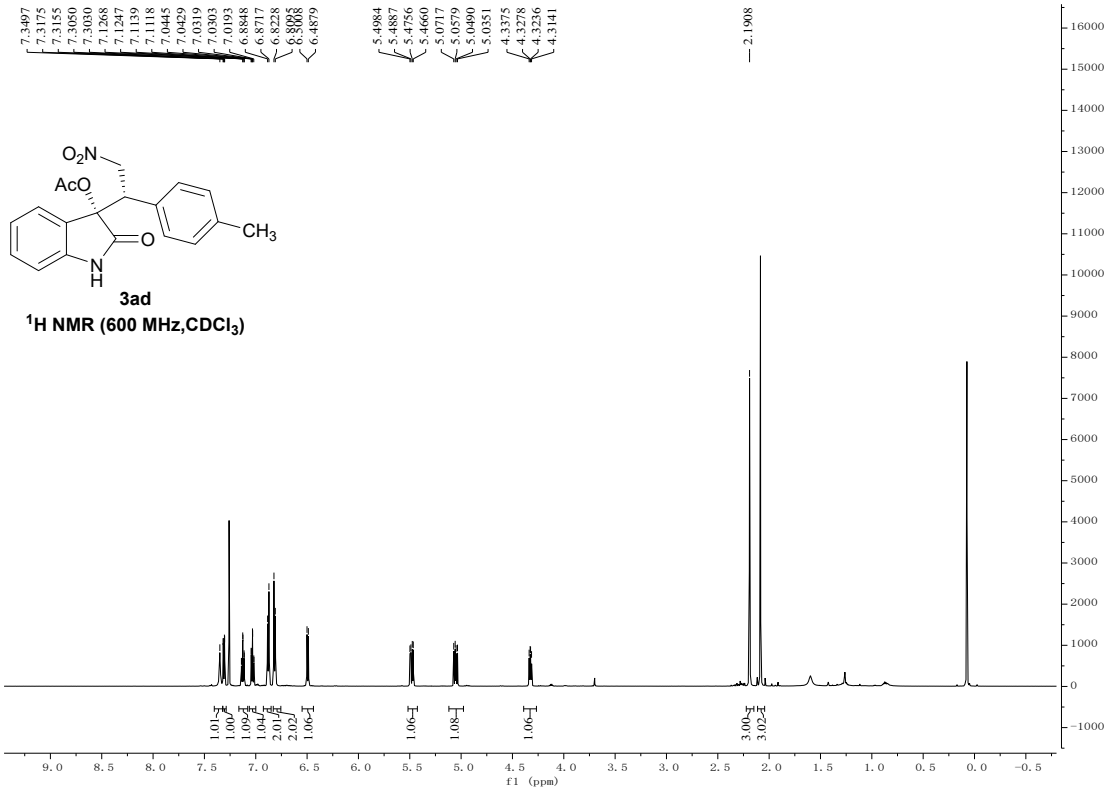

**The $^{13}$C-NMR of 3ab**



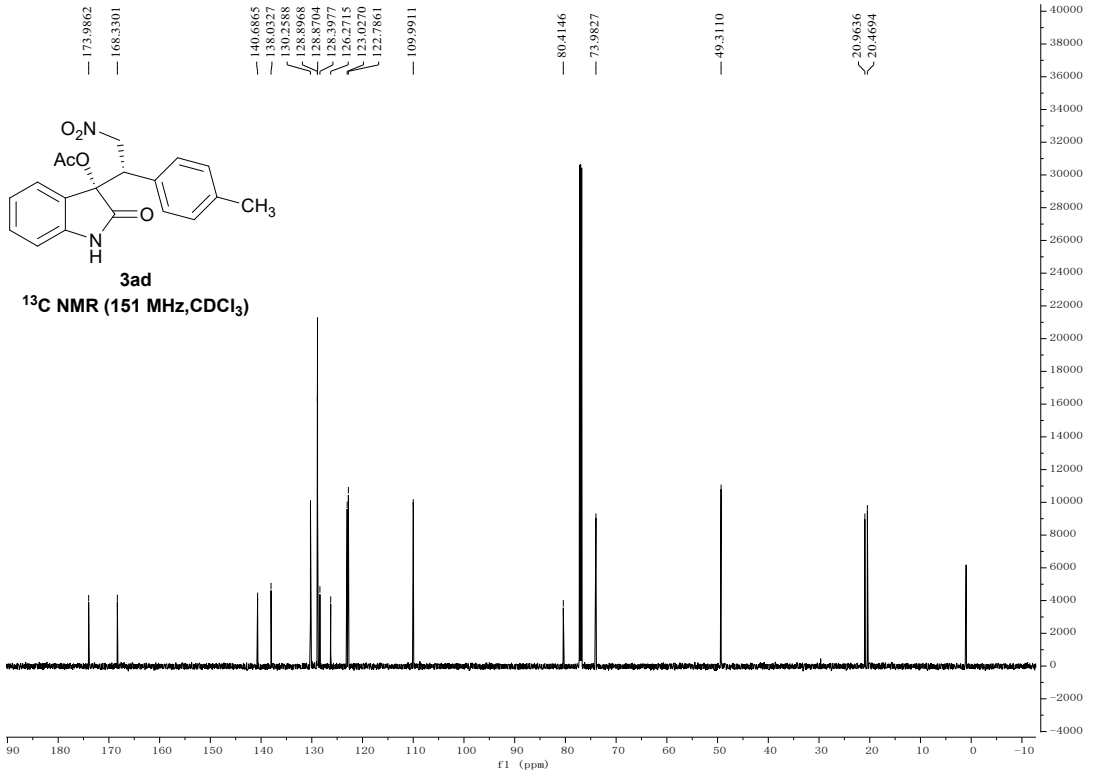

**The $^{1}$H-NMR of 3ac**



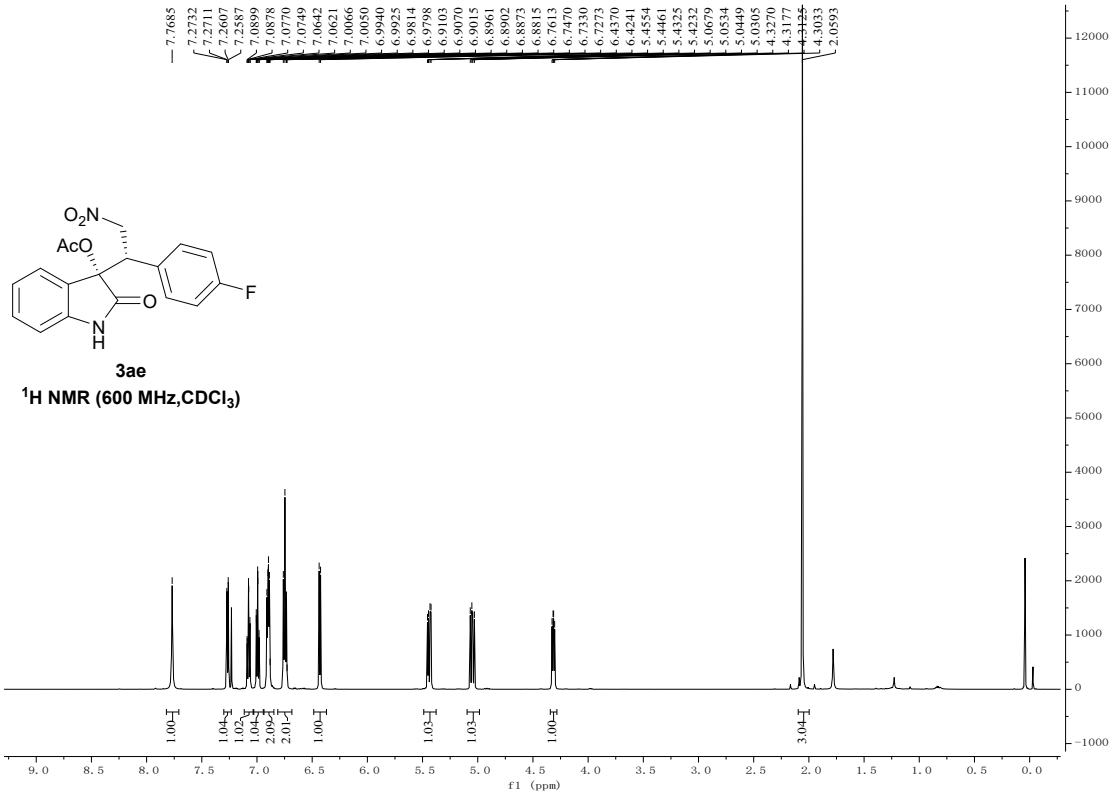

**The $^{13}$C-NMR of 3ac**



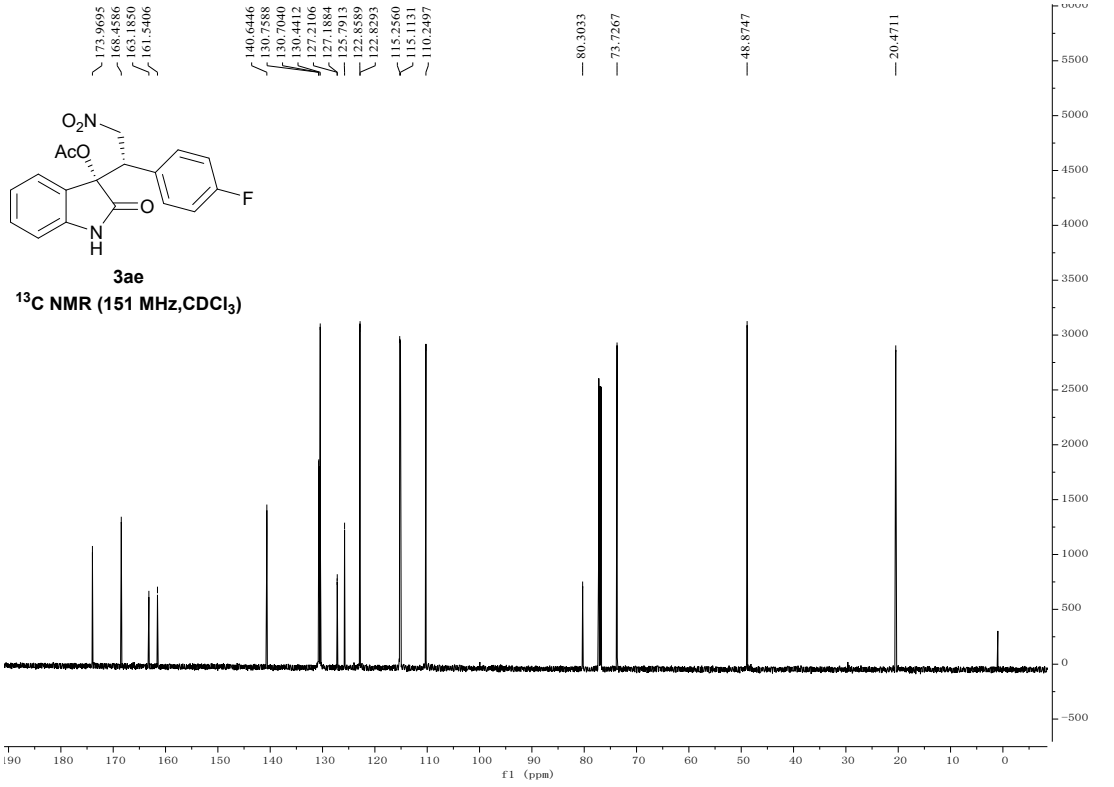

**The $^{1}$H-NMR of 3ad**



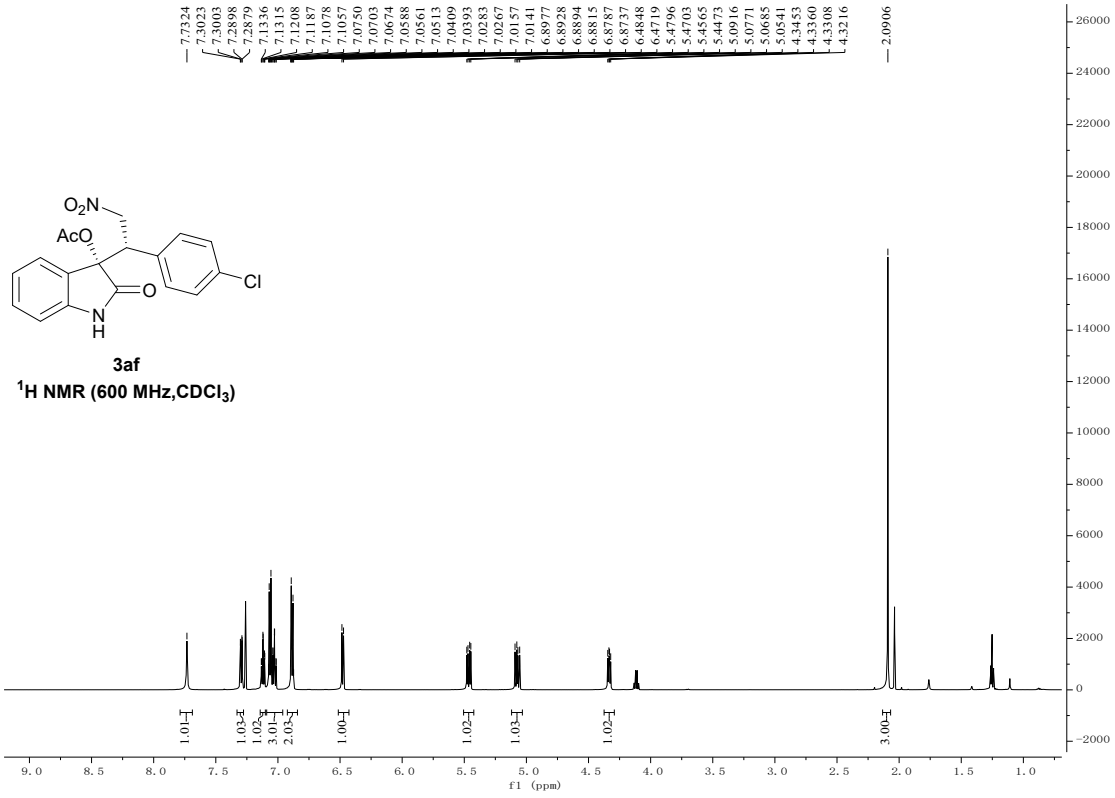

**The $^{13}$C-NMR of 3ad**



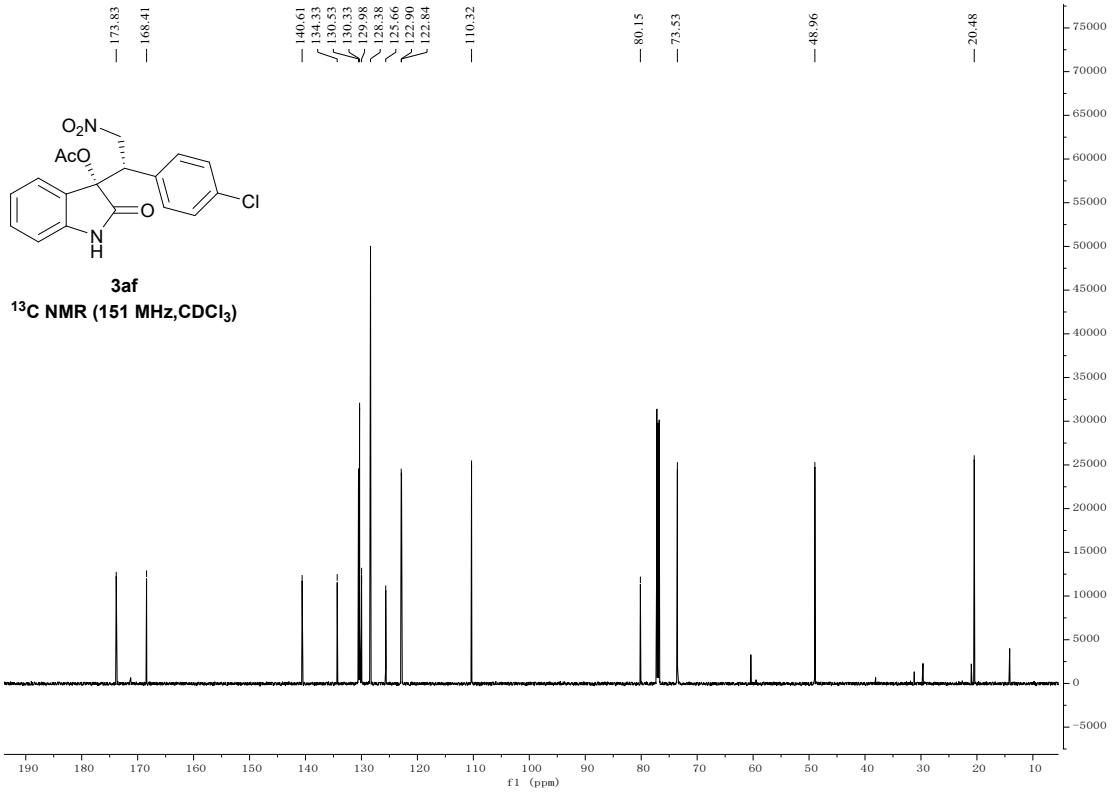

**The $^{1}$H-NMR of 3ae**



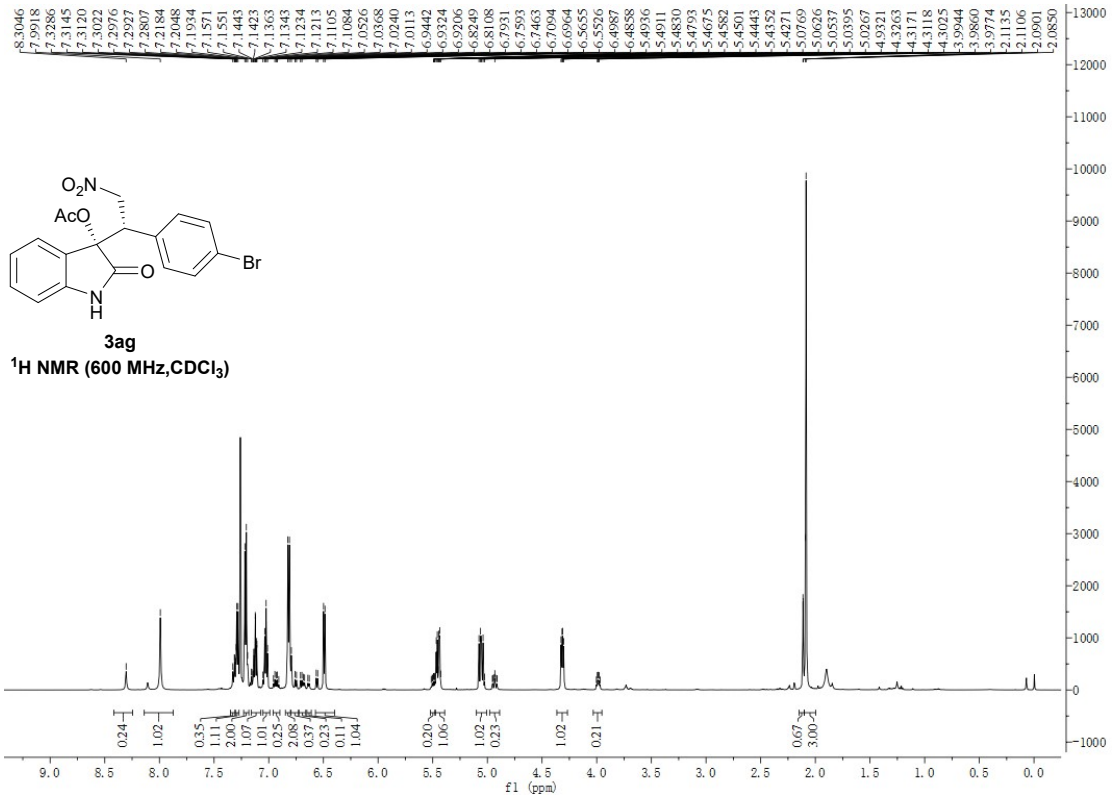

**The $^{13}$C-NMR of 3ae**



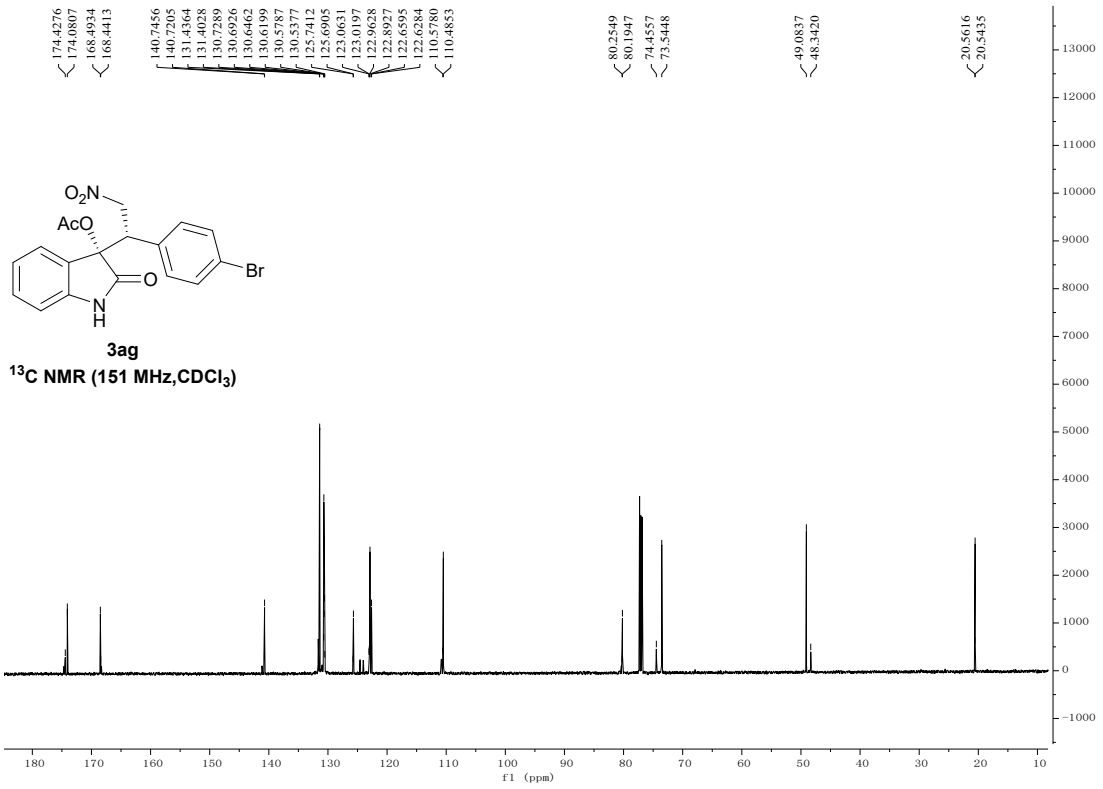

**The $^{1}$H-NMR of 3af**



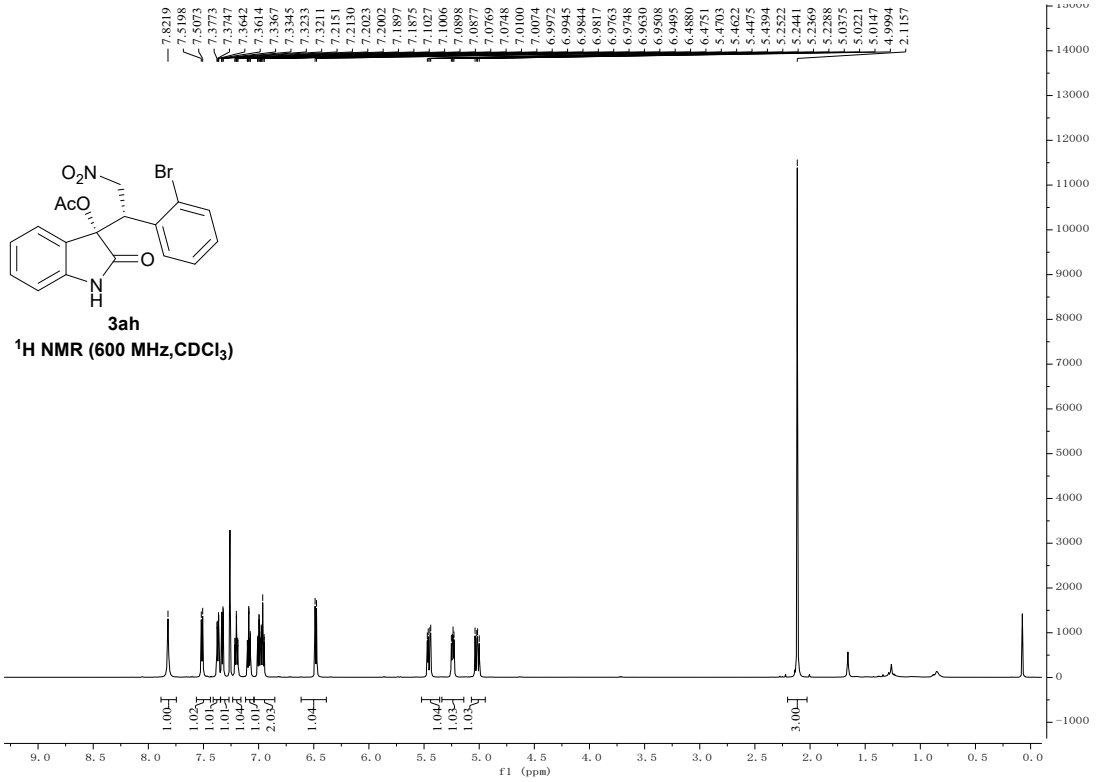

**The $^{13}$C-NMR of 3af**



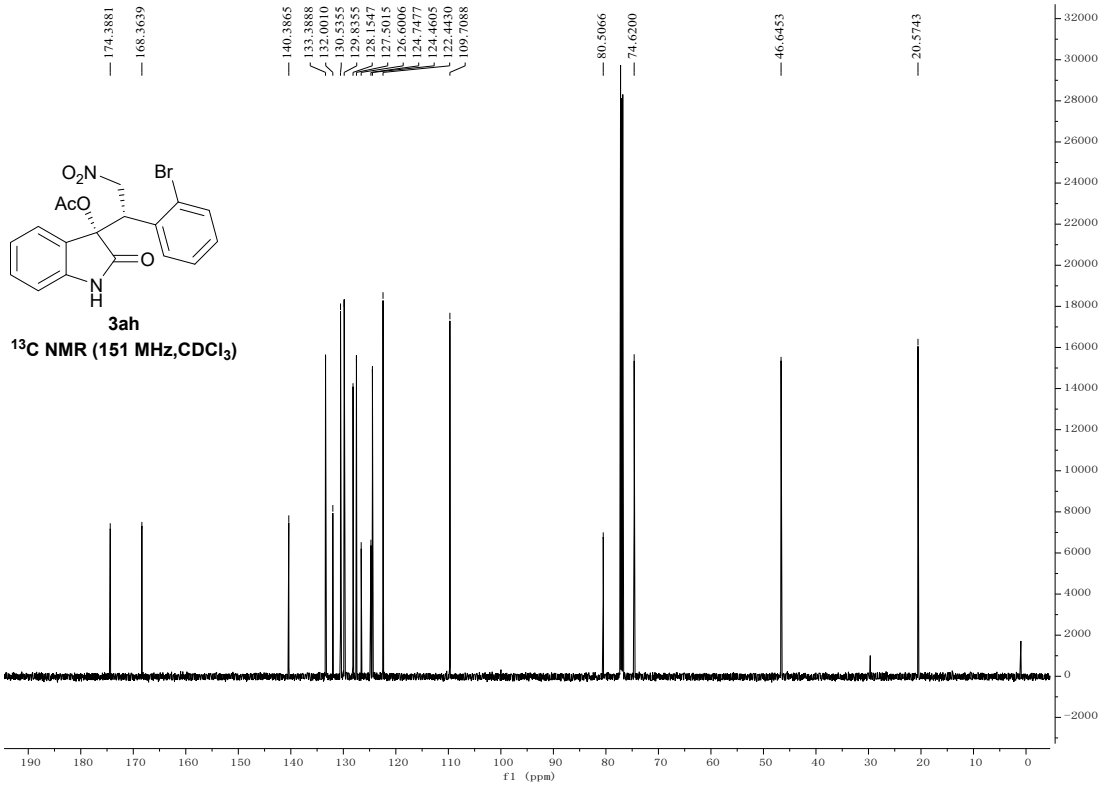

**The $^{1}$H-NMR of 3ag**



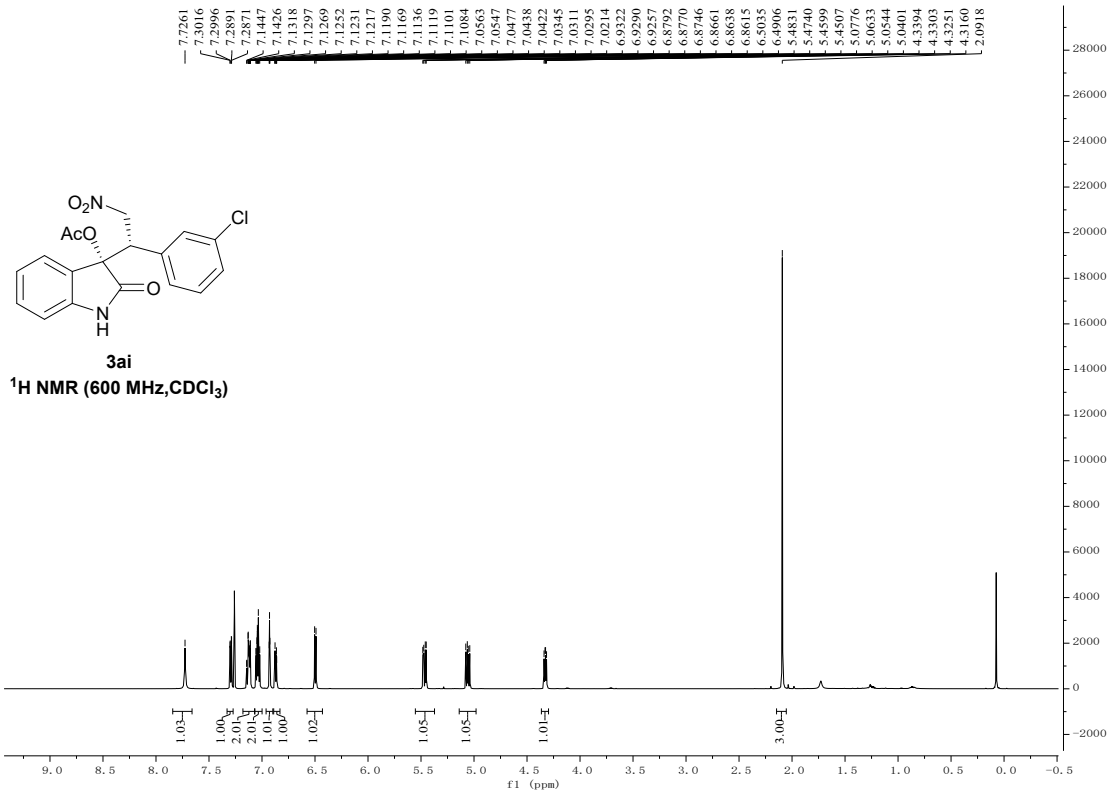

**The $^{13}$C-NMR of 3ag**



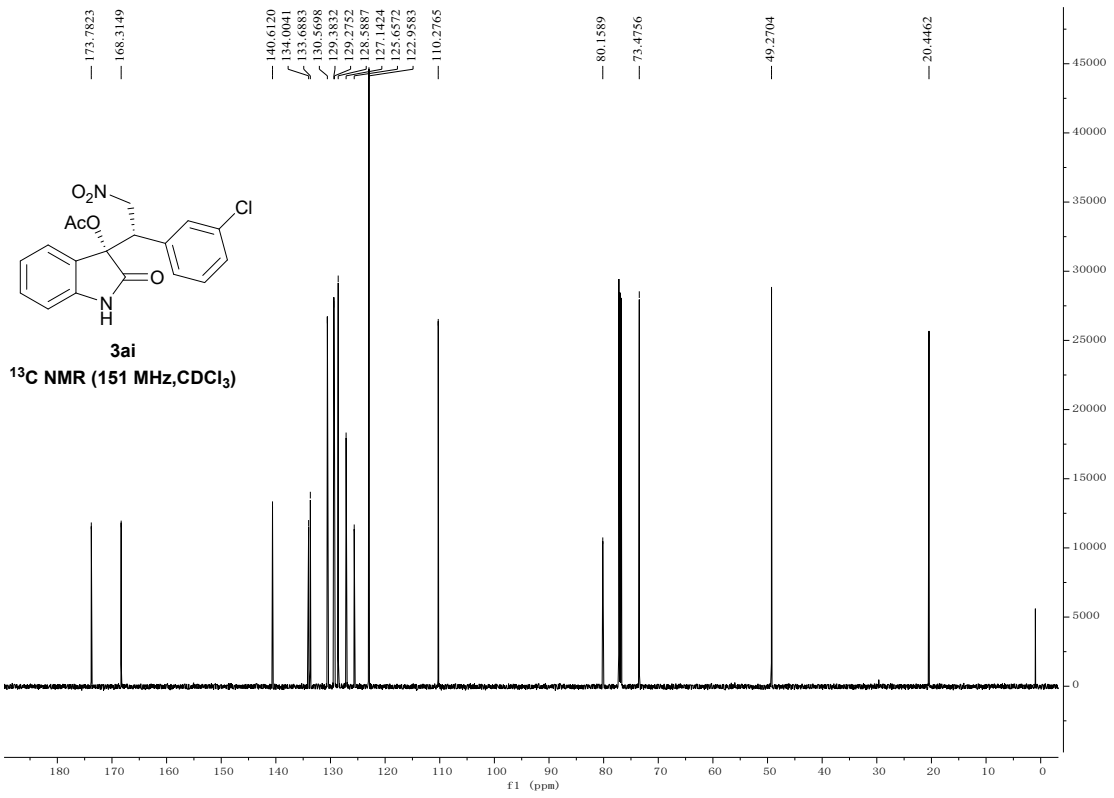

**The $^{1}$H-NMR of 3ah**



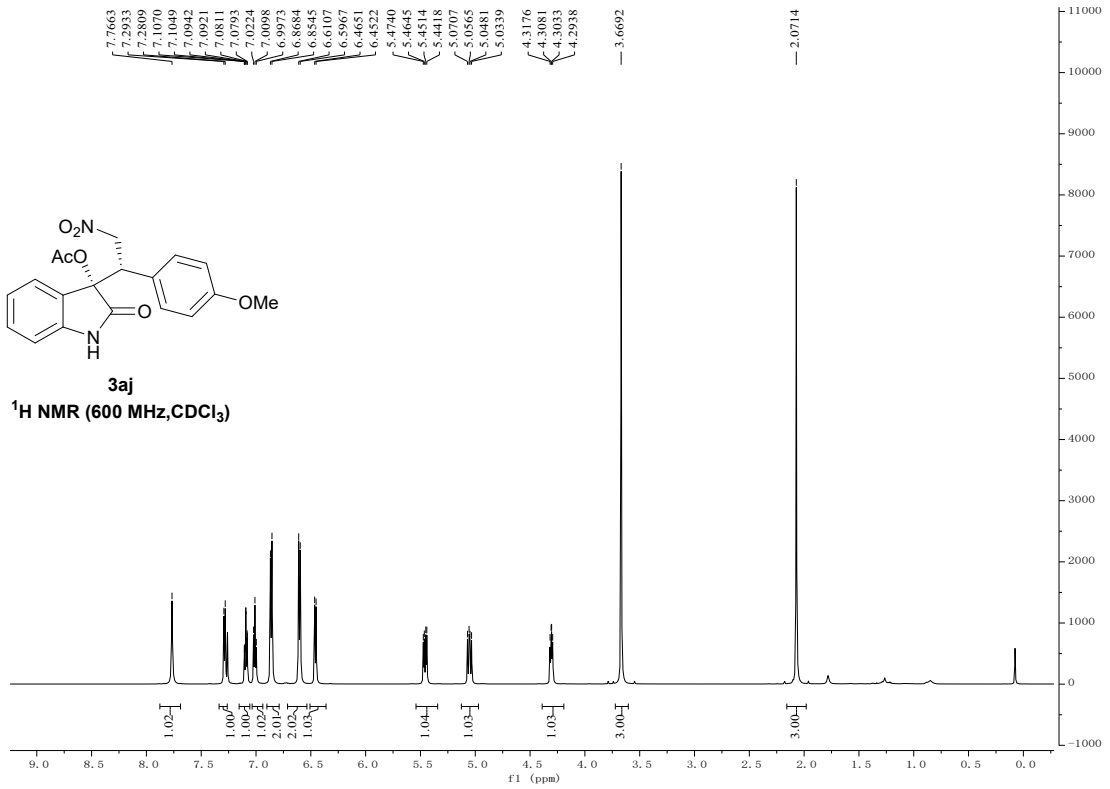

**The $^{13}$C-NMR of 3ah**



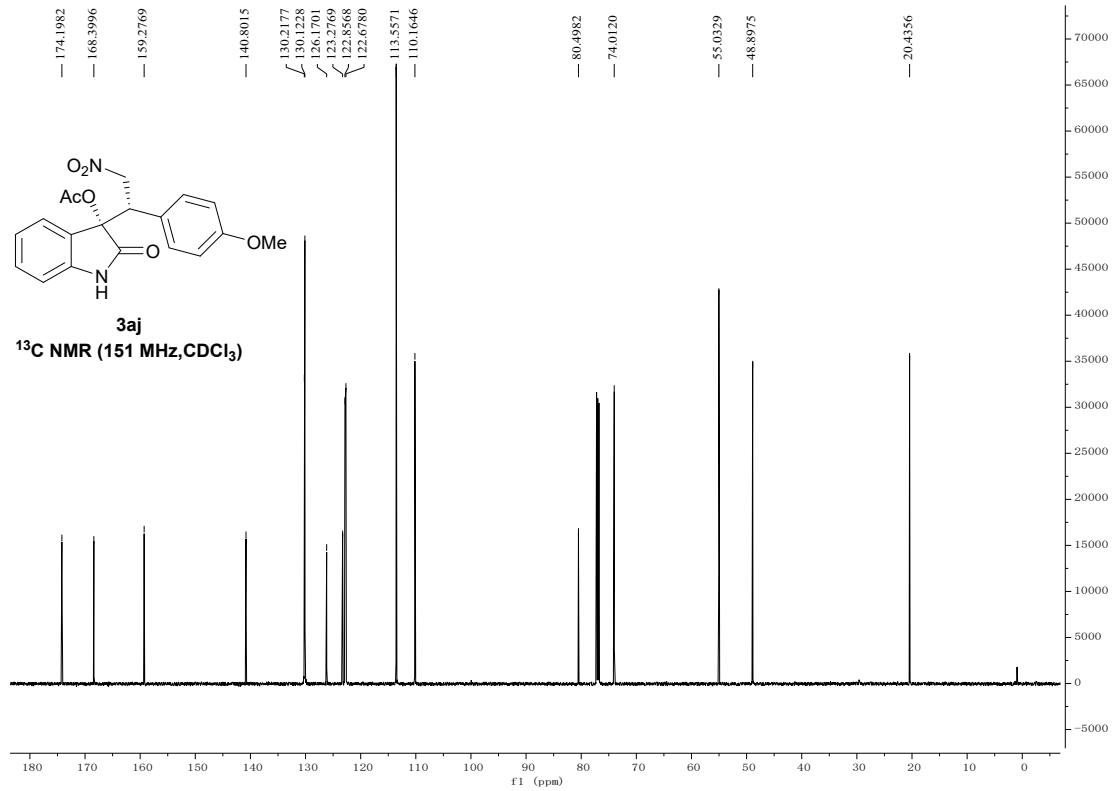

**The $^{1}$H-NMR of 3ai**



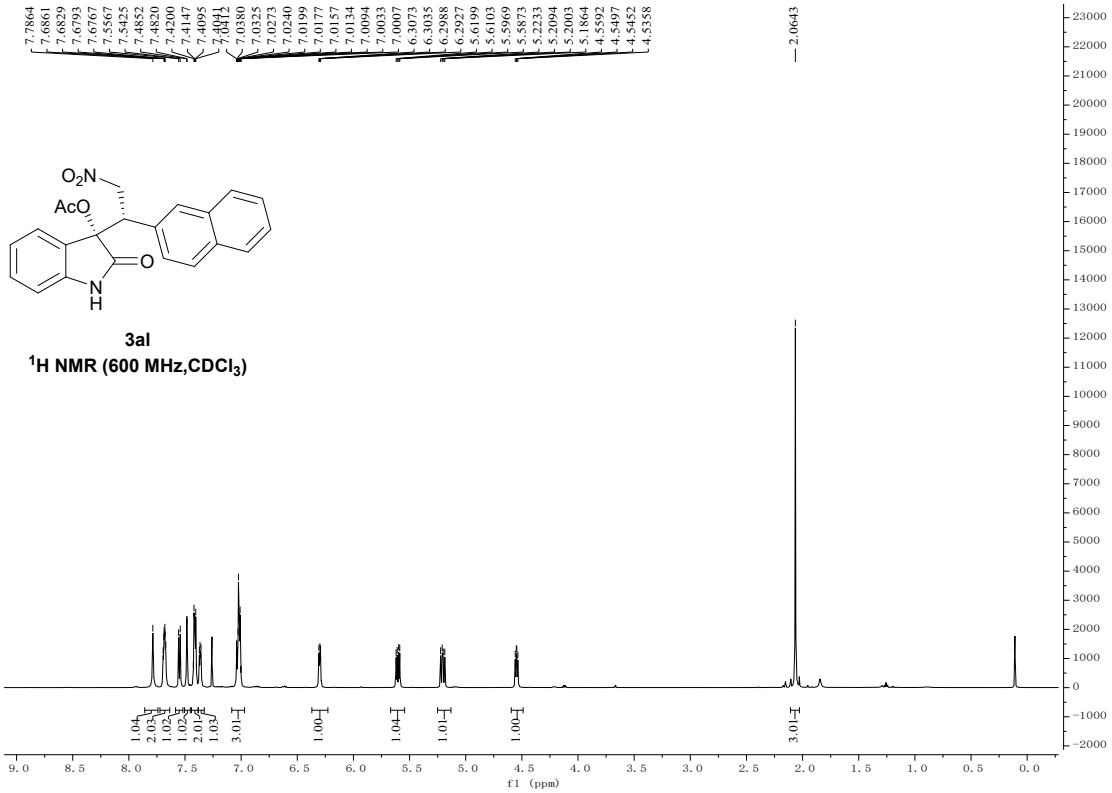

**The $^{13}$C-NMR of 3ai**



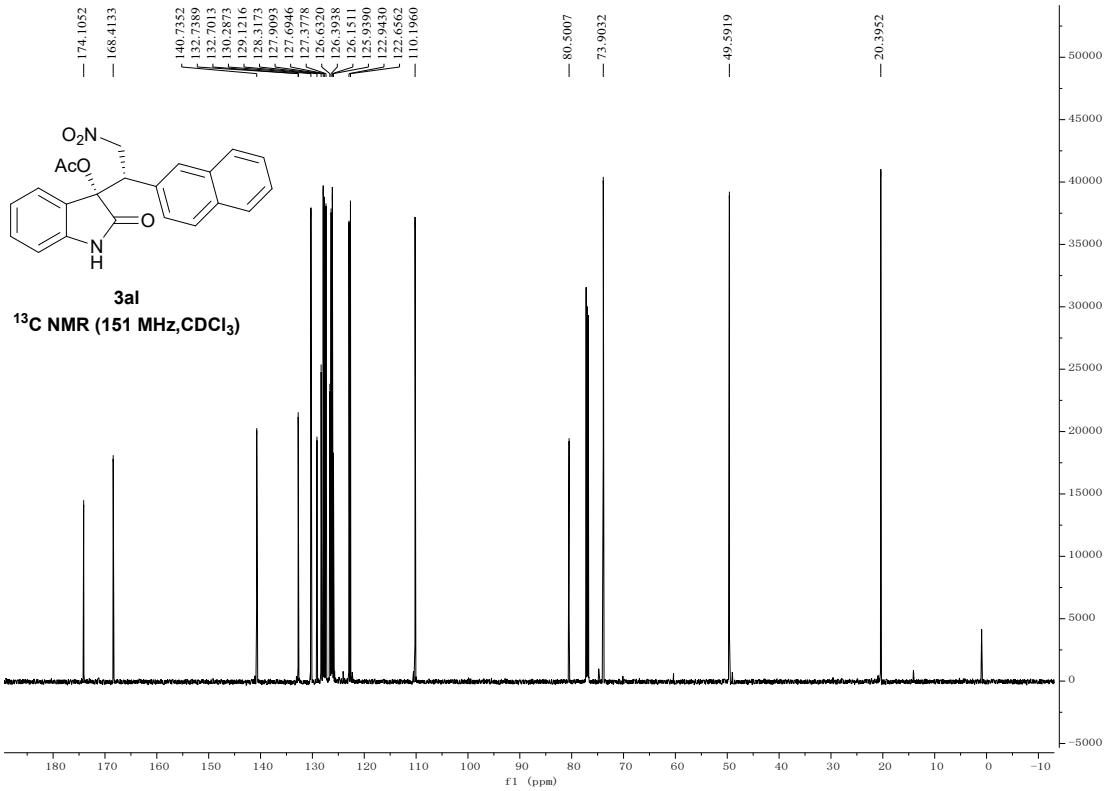

**The $^{1}$H-NMR of 3aj**



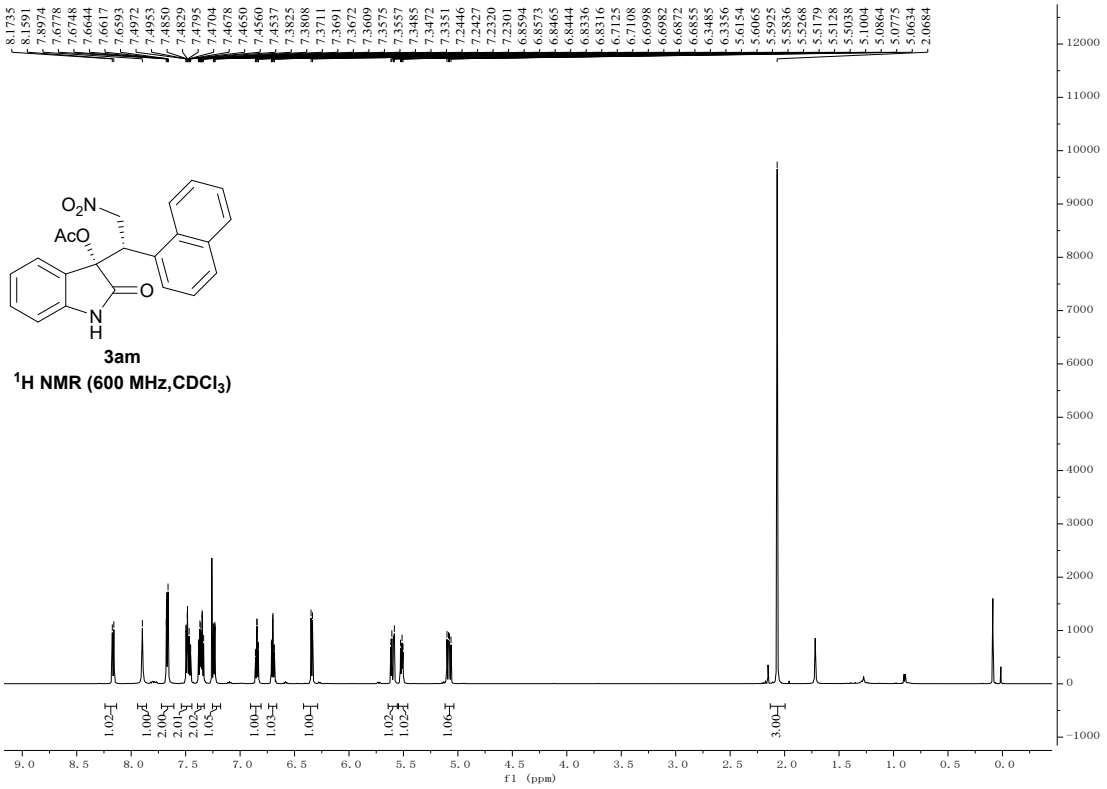

**The $^{13}$C-NMR of 3aj**



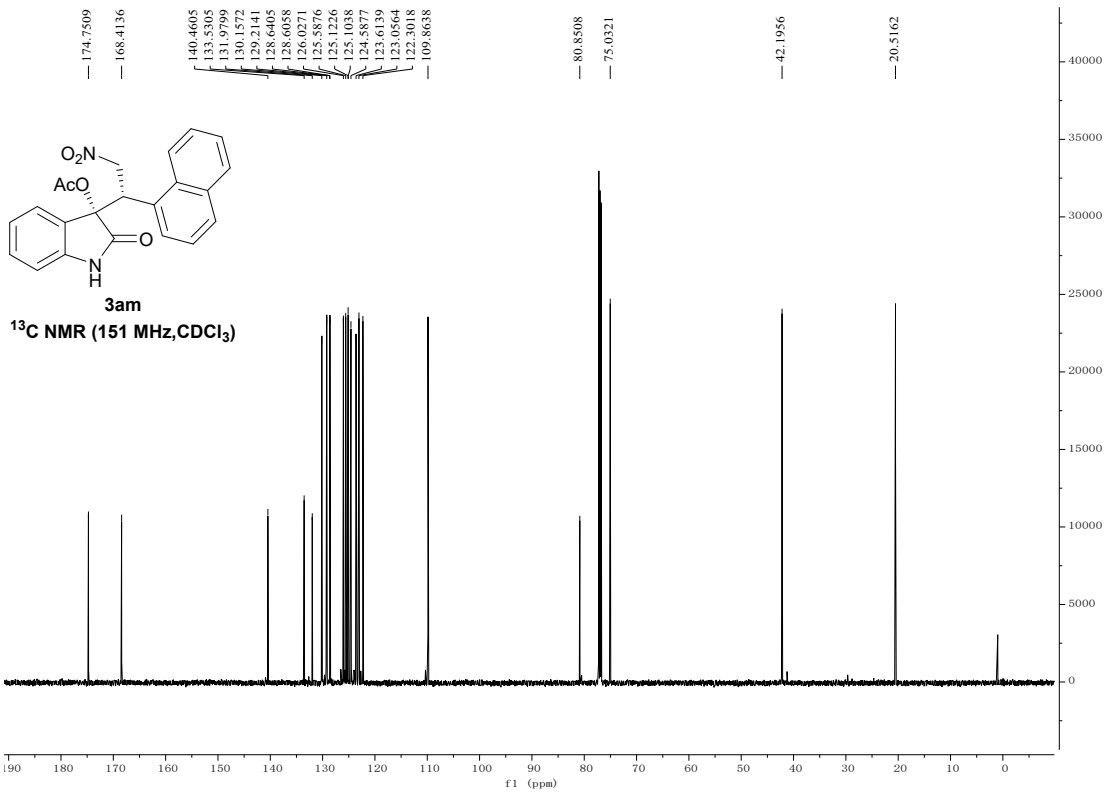

**The $^{1}$H-NMR of product 3al**



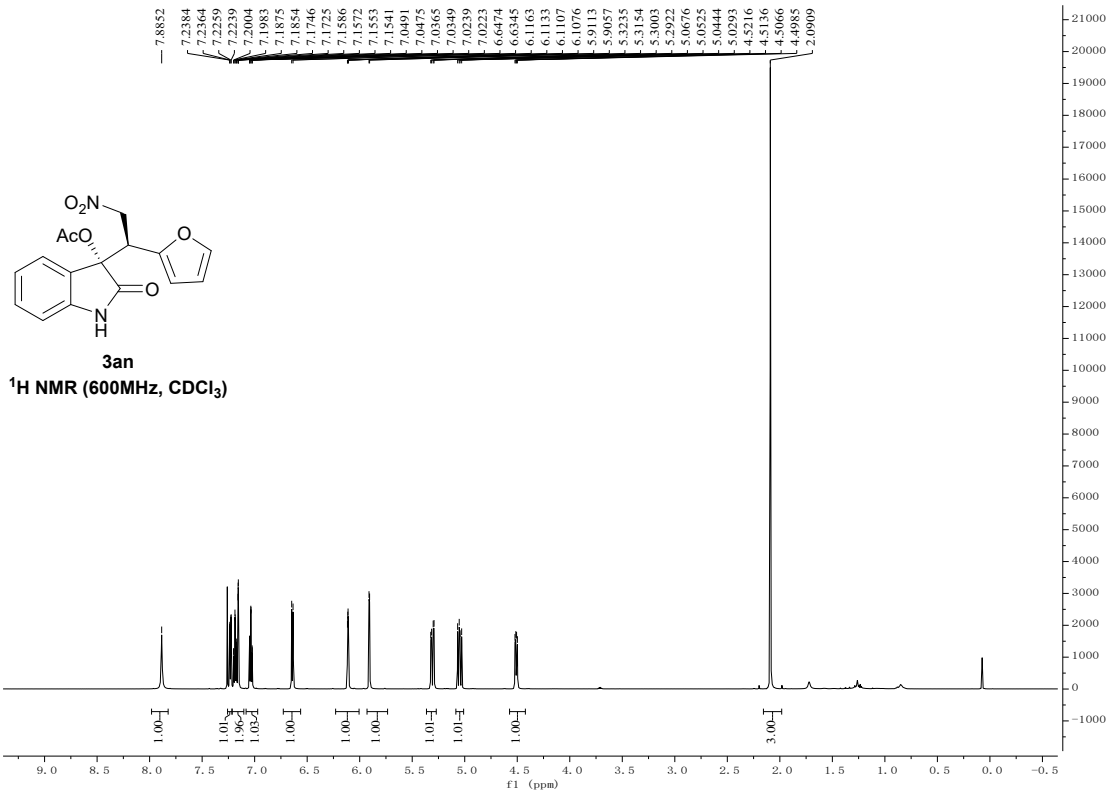

**The $^{13}$C-NMR of product 3al**



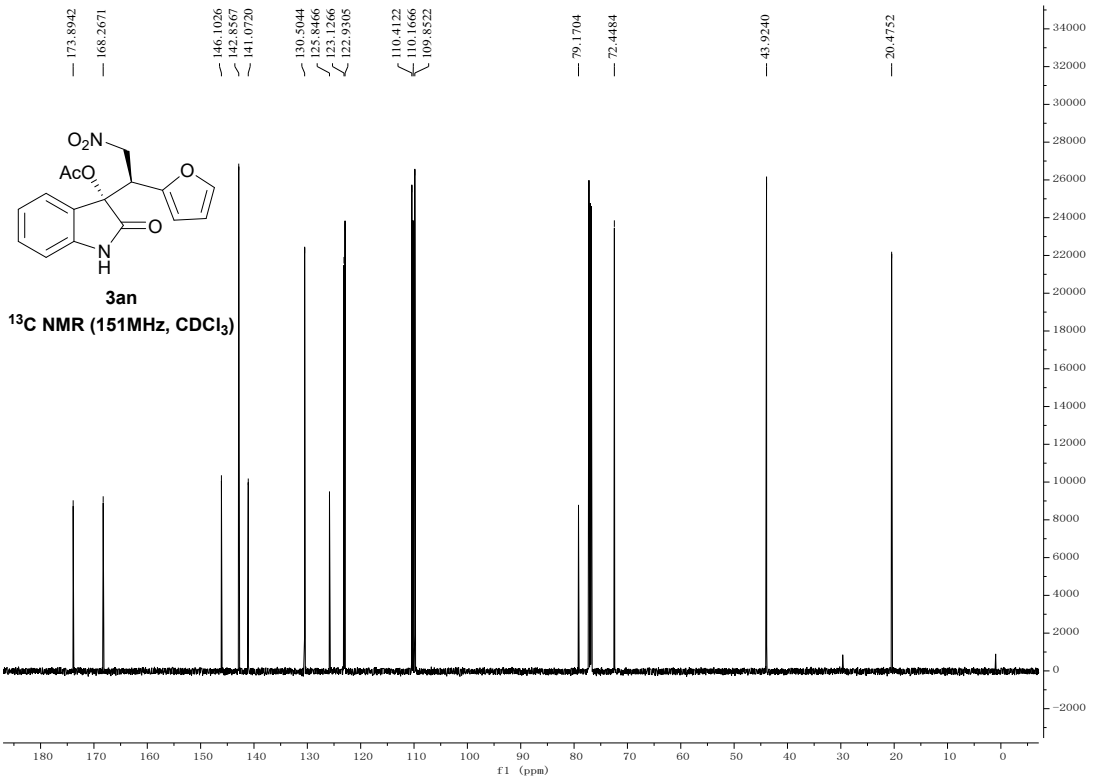

**The $^{1}$H-NMR of product 3am**



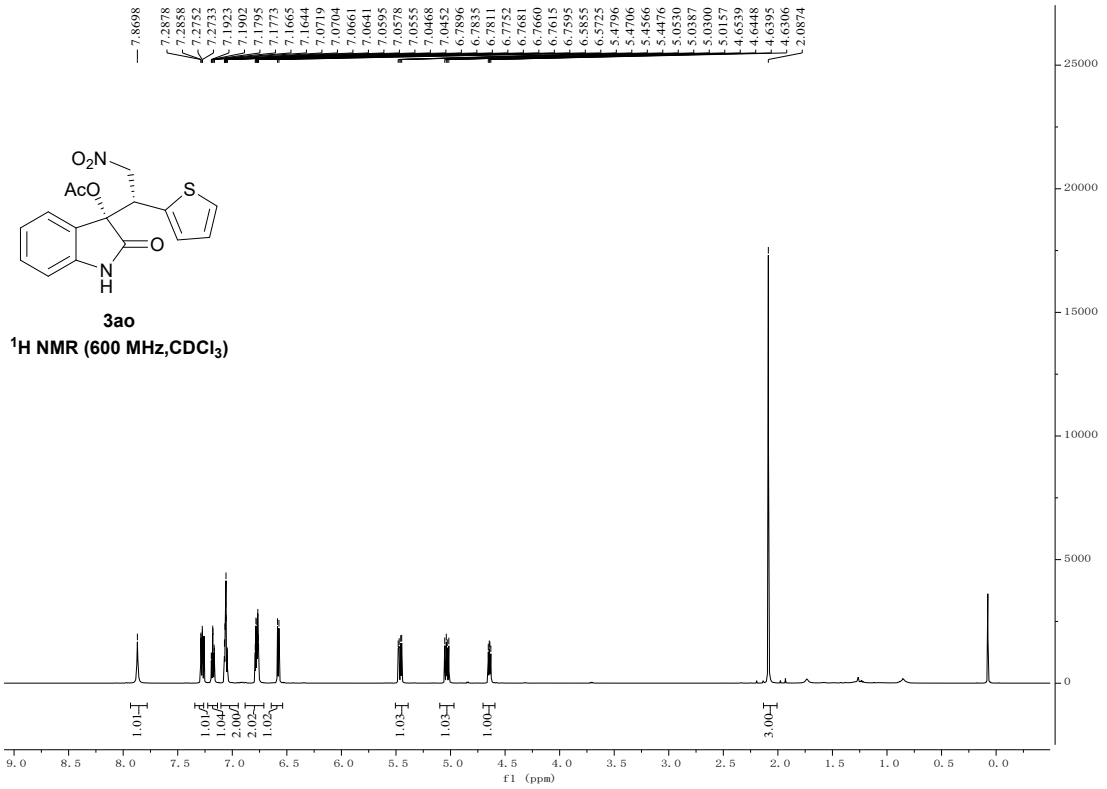

**The $^{13}$C-NMR of product 3am**



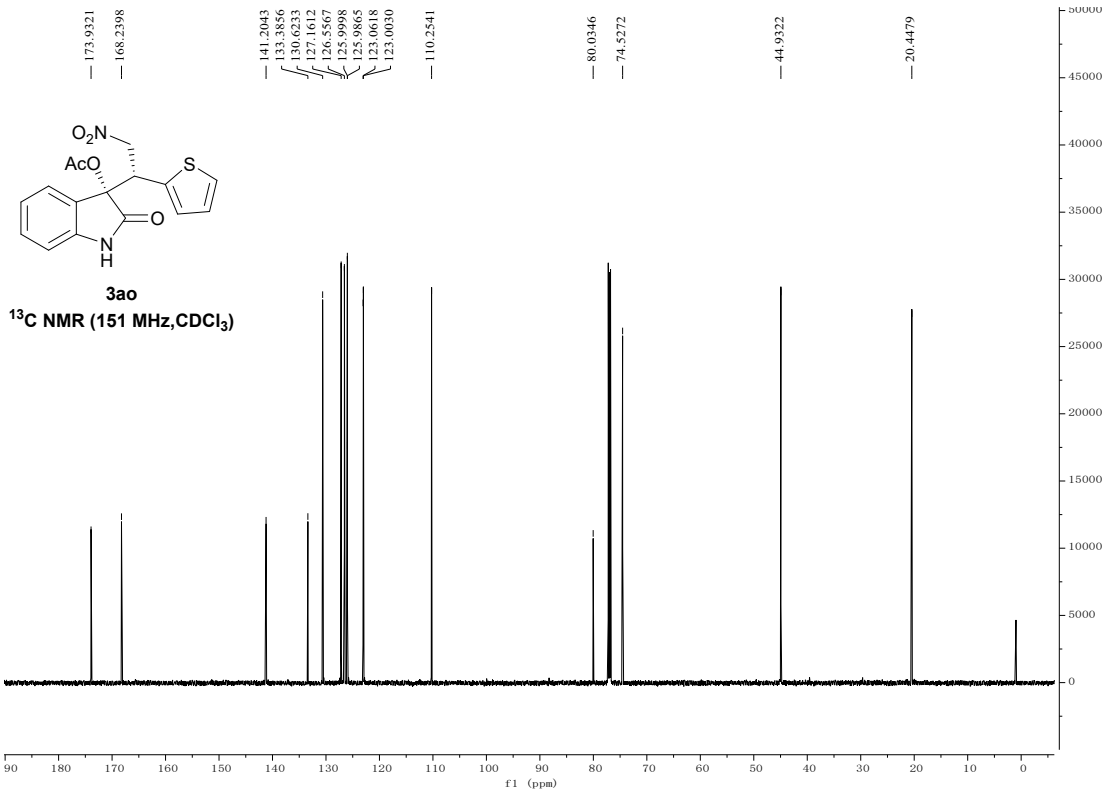

**The $^{1}$H-NMR of product 3an**



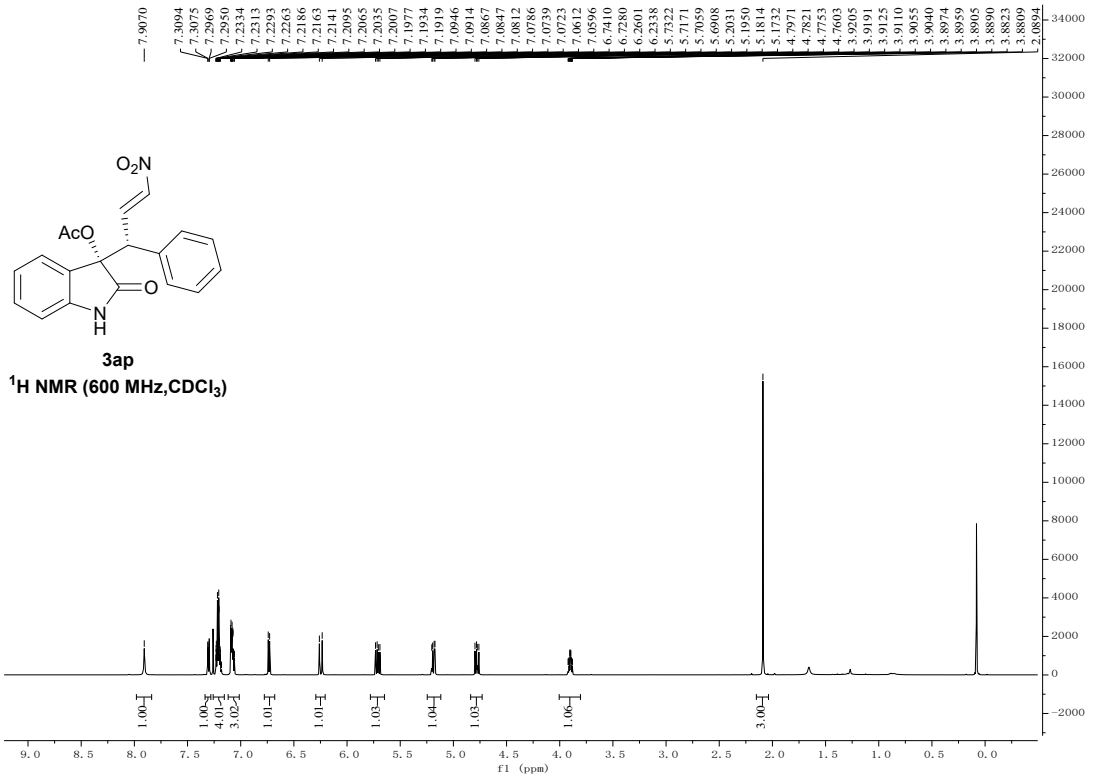

**The $^{13}$C-NMR of product 3an**



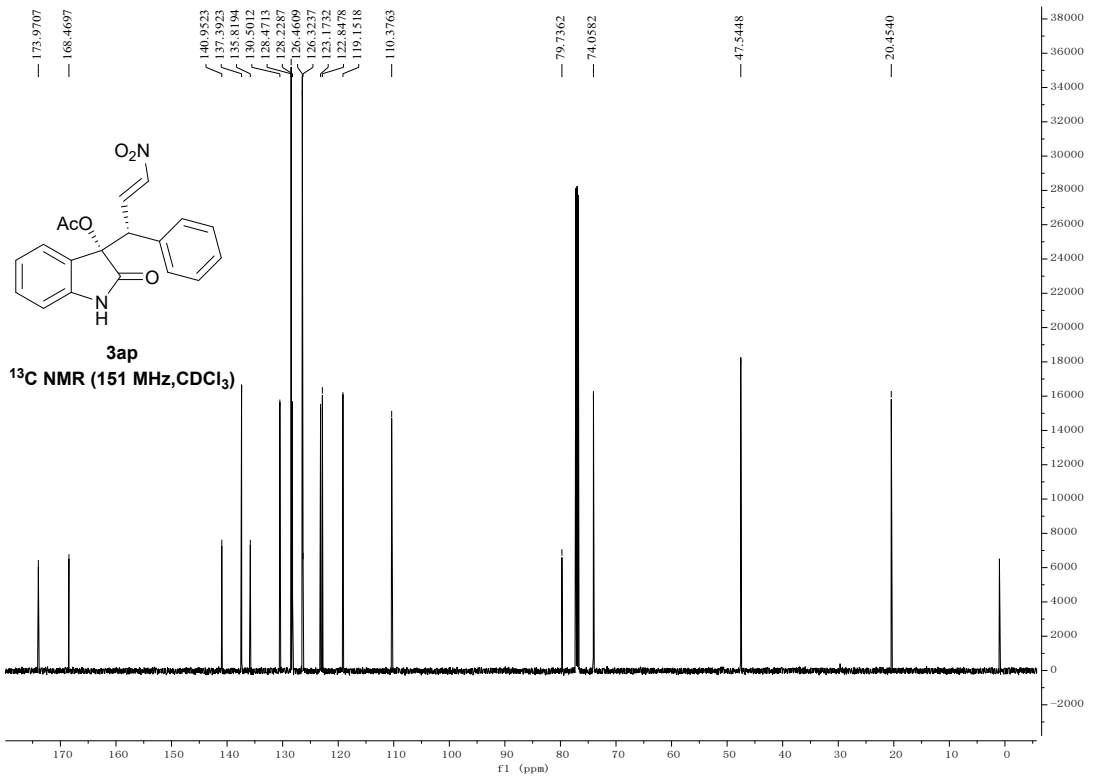

**The $^{1}$H-NMR of product 3ao**



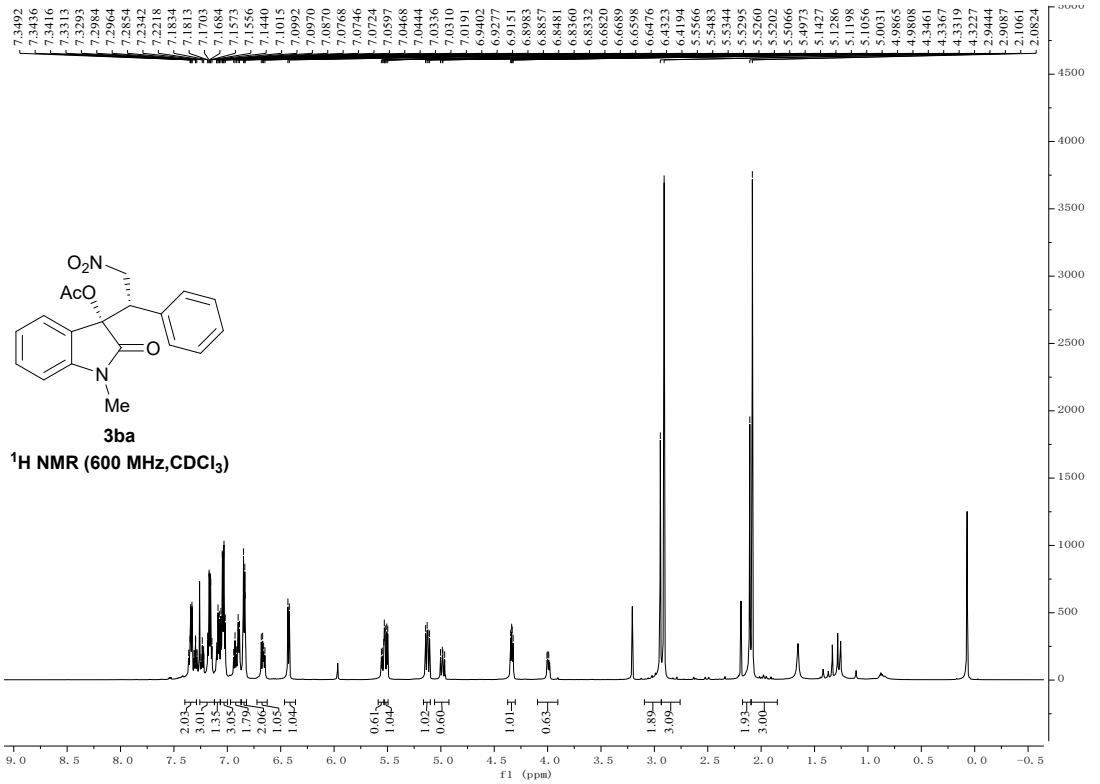

**The $^{13}$C-NMR of product 3ao**



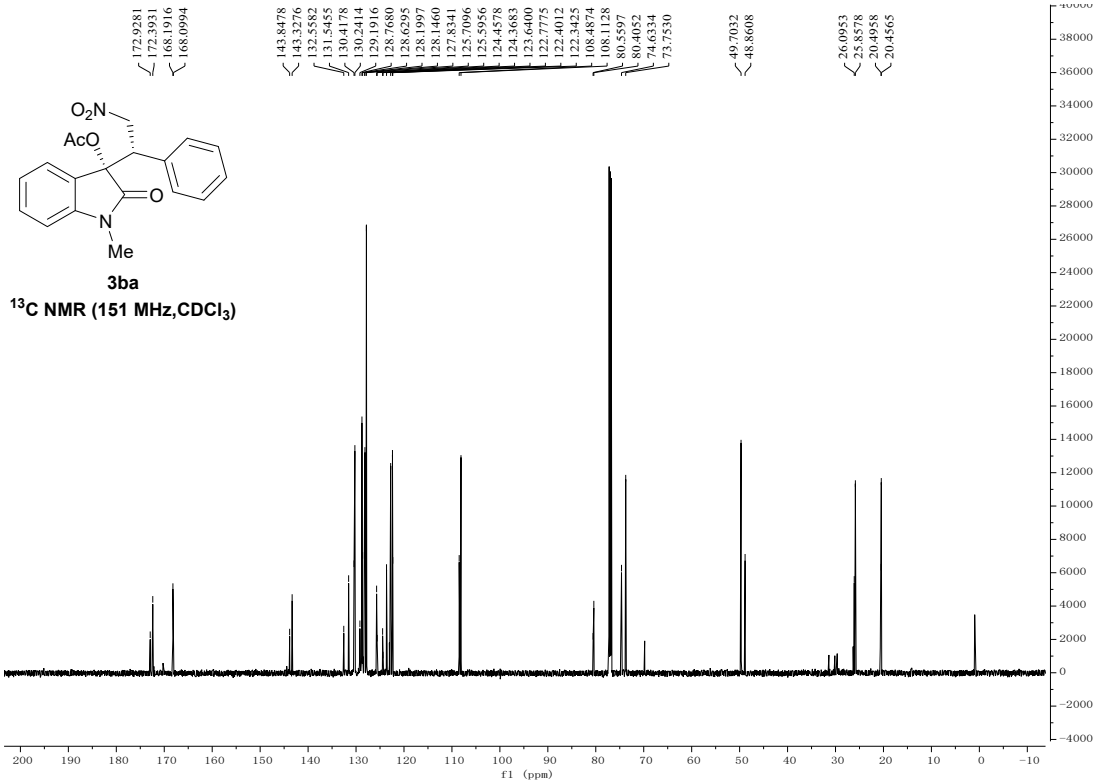

**The $^{1}$H-NMR of product 3ap**



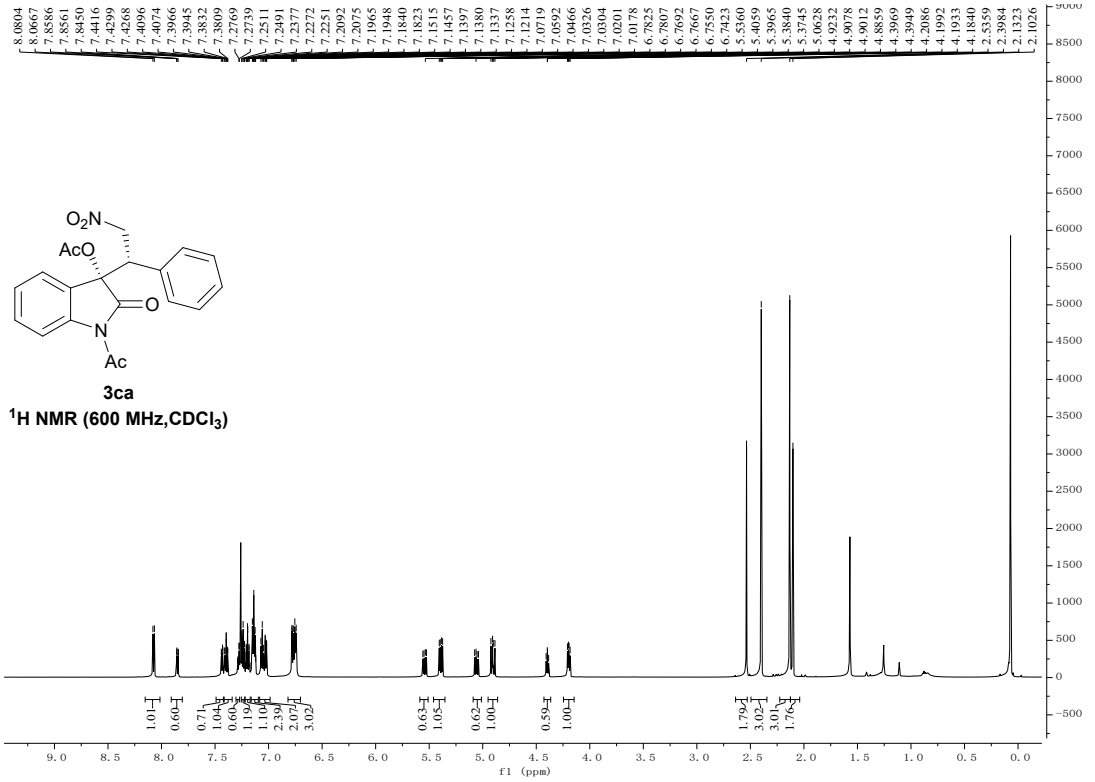

**The $^{13}$C-NMR of product 3ap**



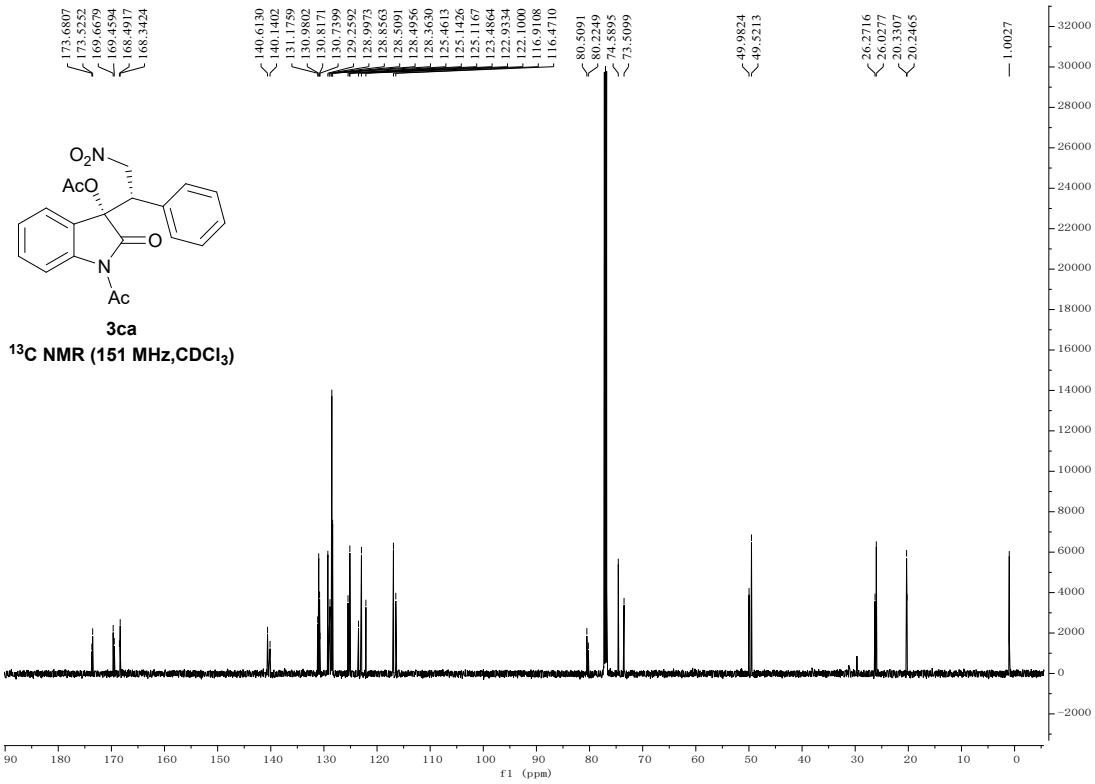

**The $^{1}$H-NMR of product 3ba**



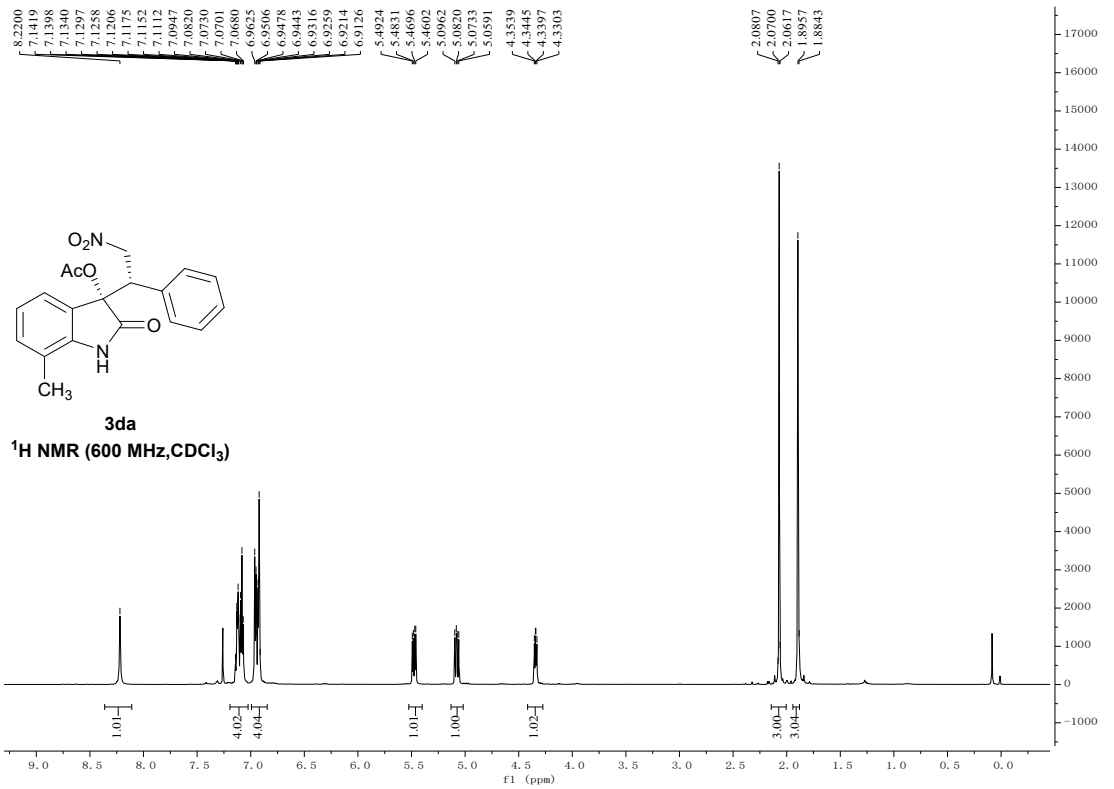

**The $^{13}$C-NMR of product 3ba**



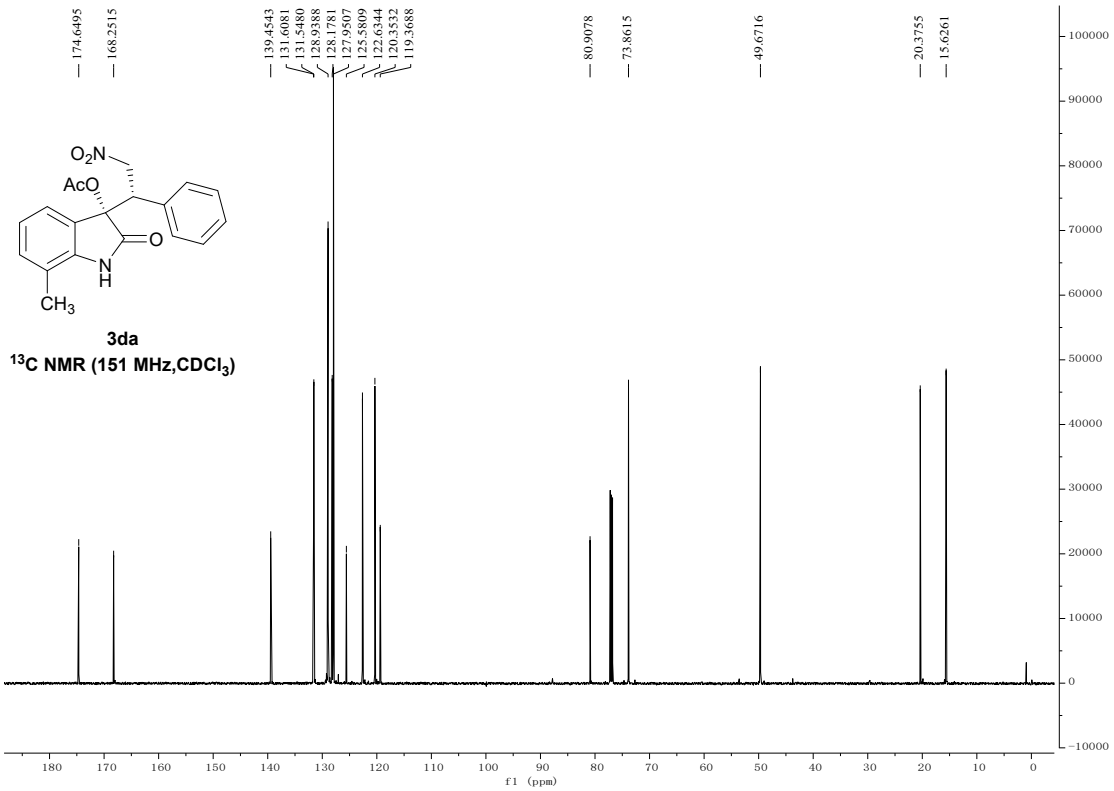

**The $^{1}$H-NMR of product 3ca**



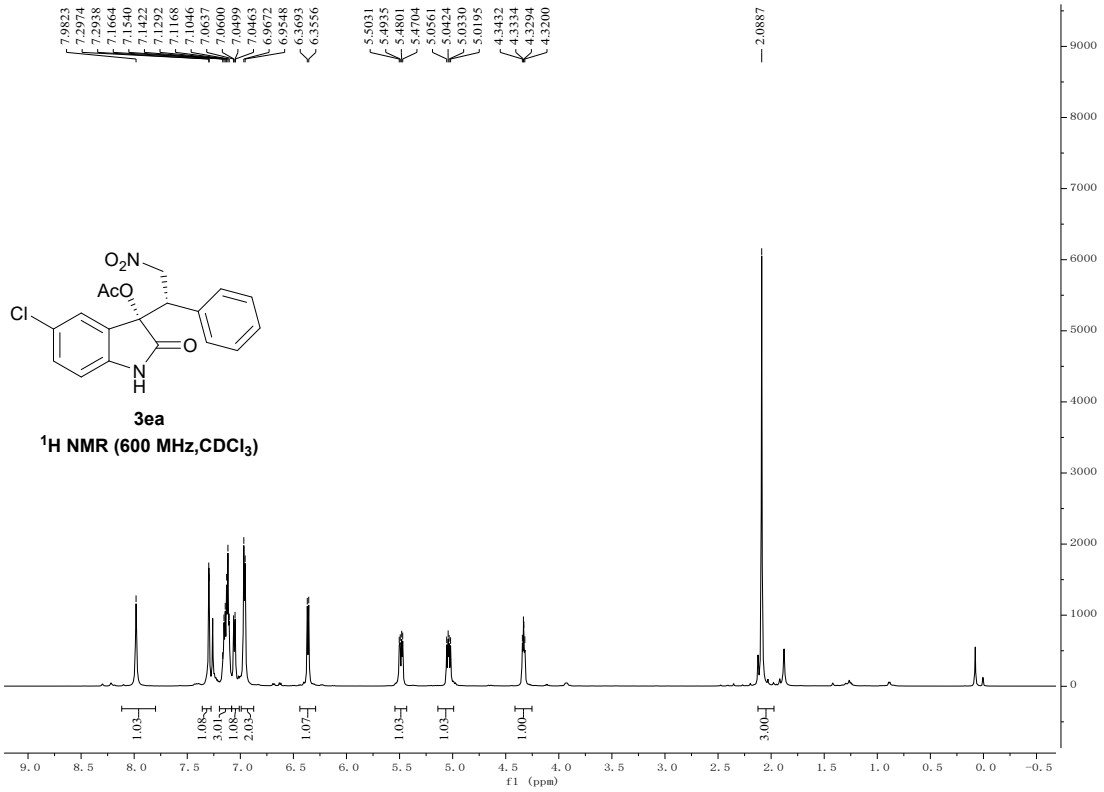

**The $^{13}$C-NMR of product 3ca**



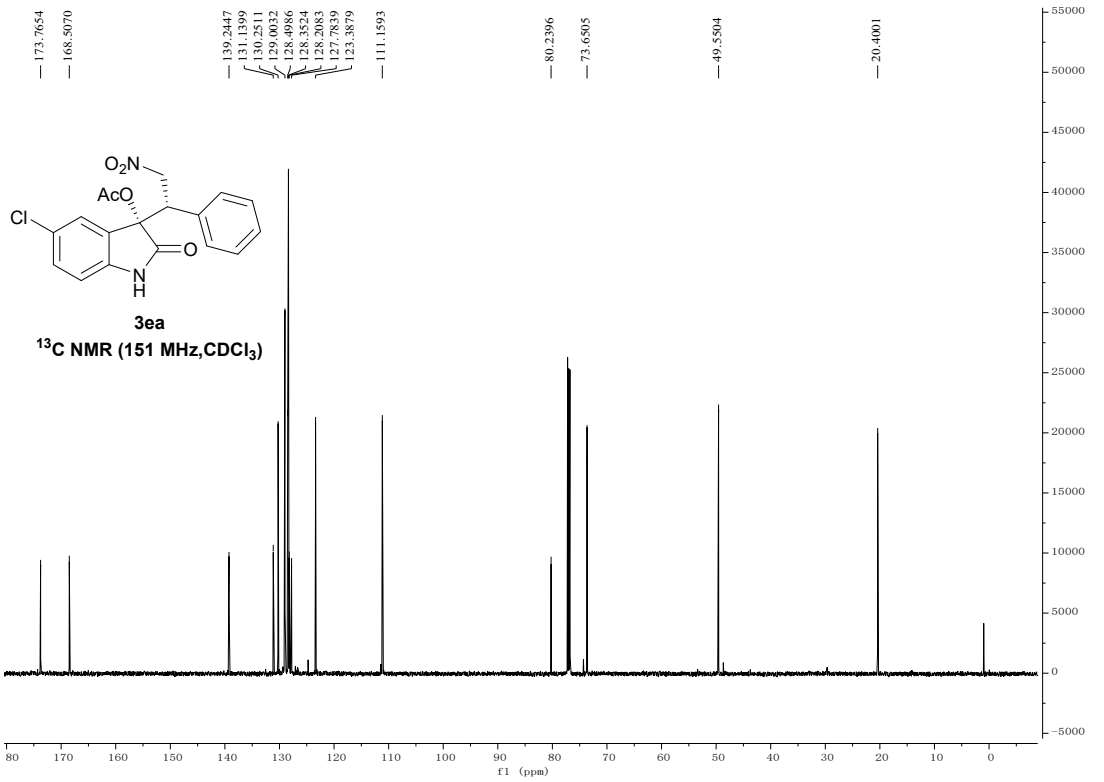

**The $^{1}$H-NMR of product 3da**



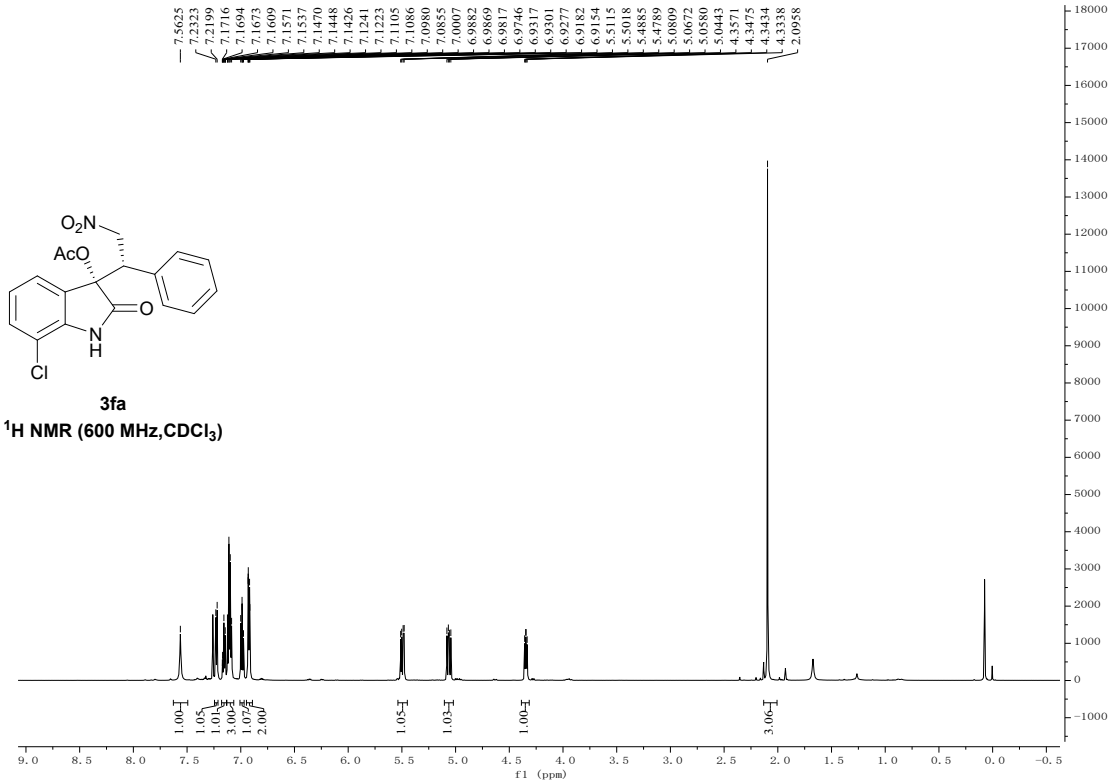

**The $^{13}$C-NMR of product 3da**



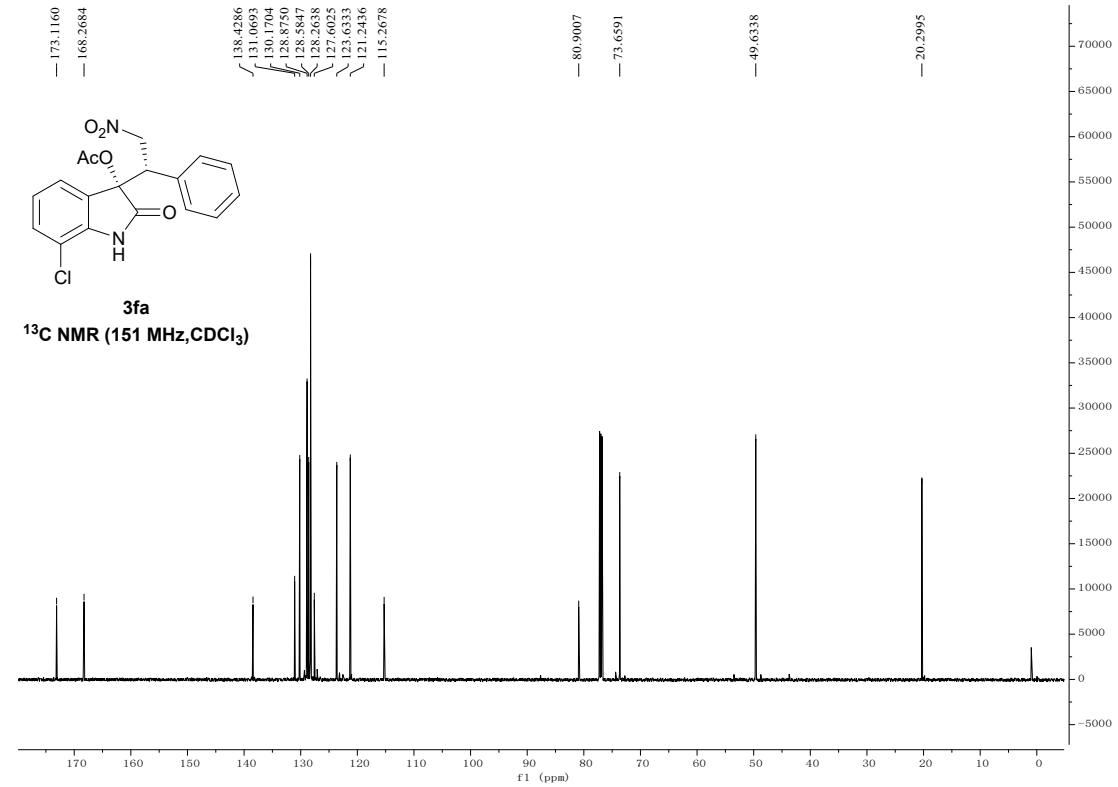

**The $^{1}$H-NMR of product 3ea**



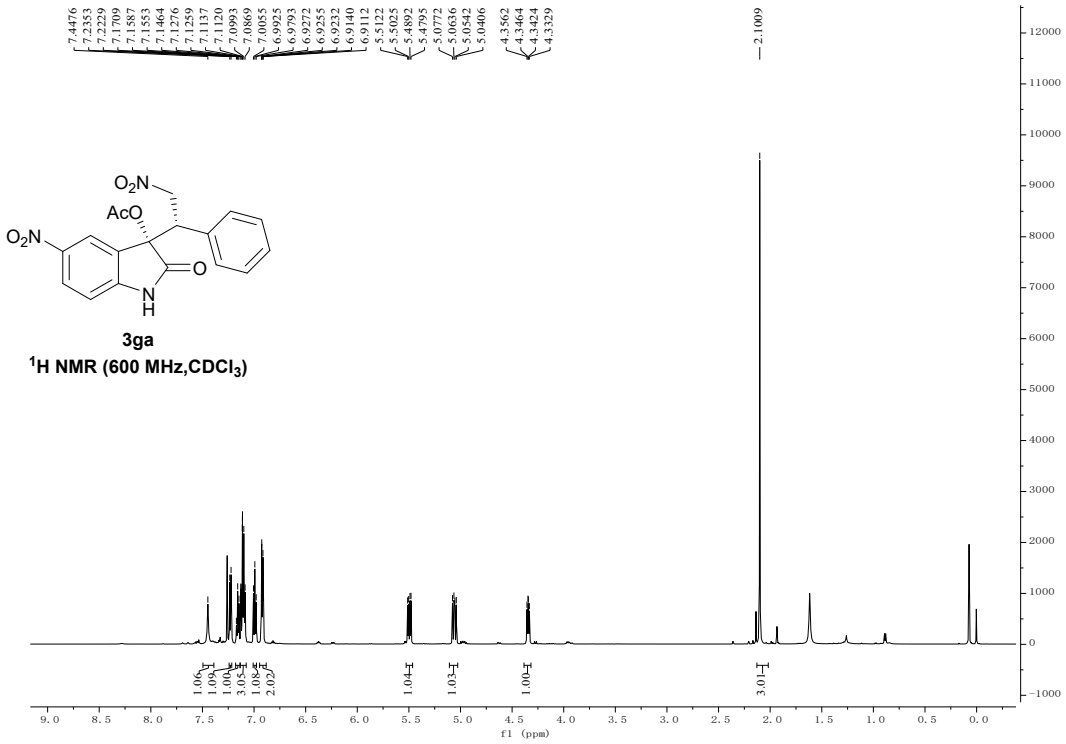

**The $^{13}$C-NMR of product 3ea**



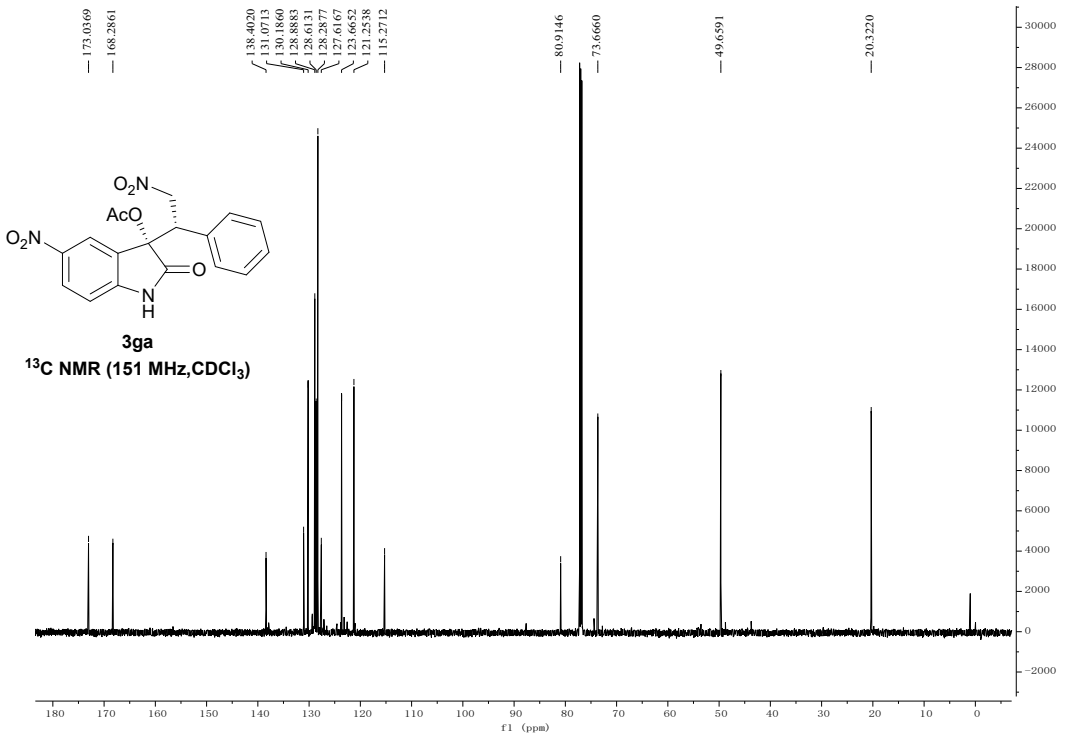

**The $^{1}$H-NMR of product 3fa**



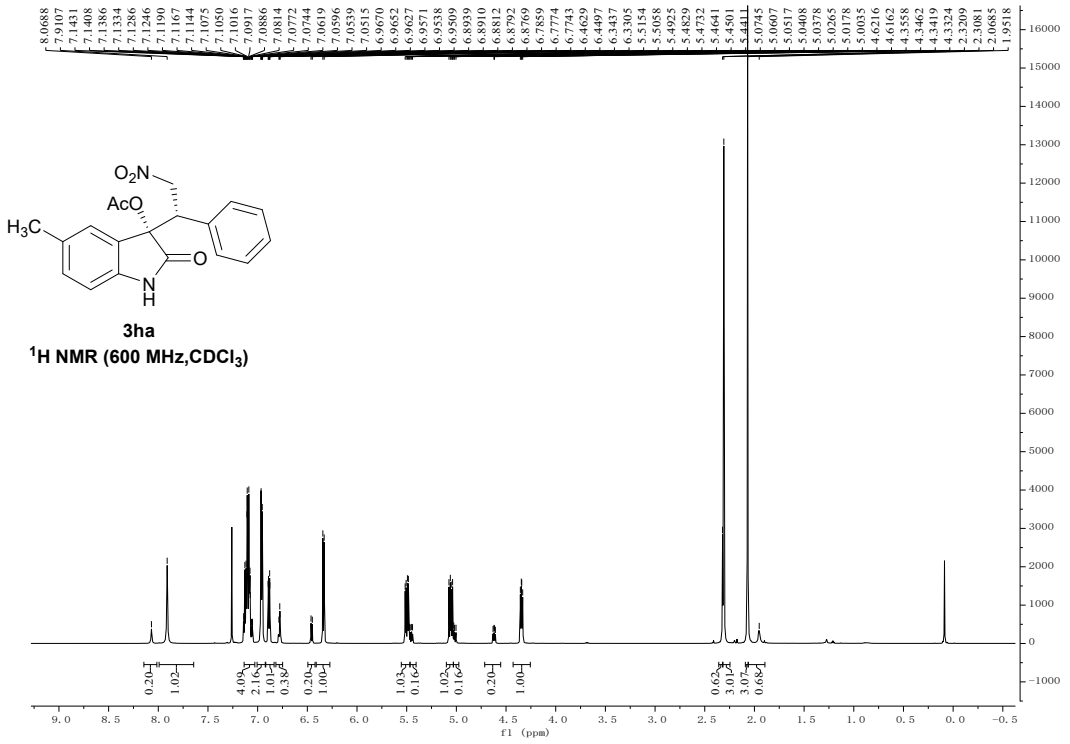

**The $^{13}$C-NMR of product 3fa**



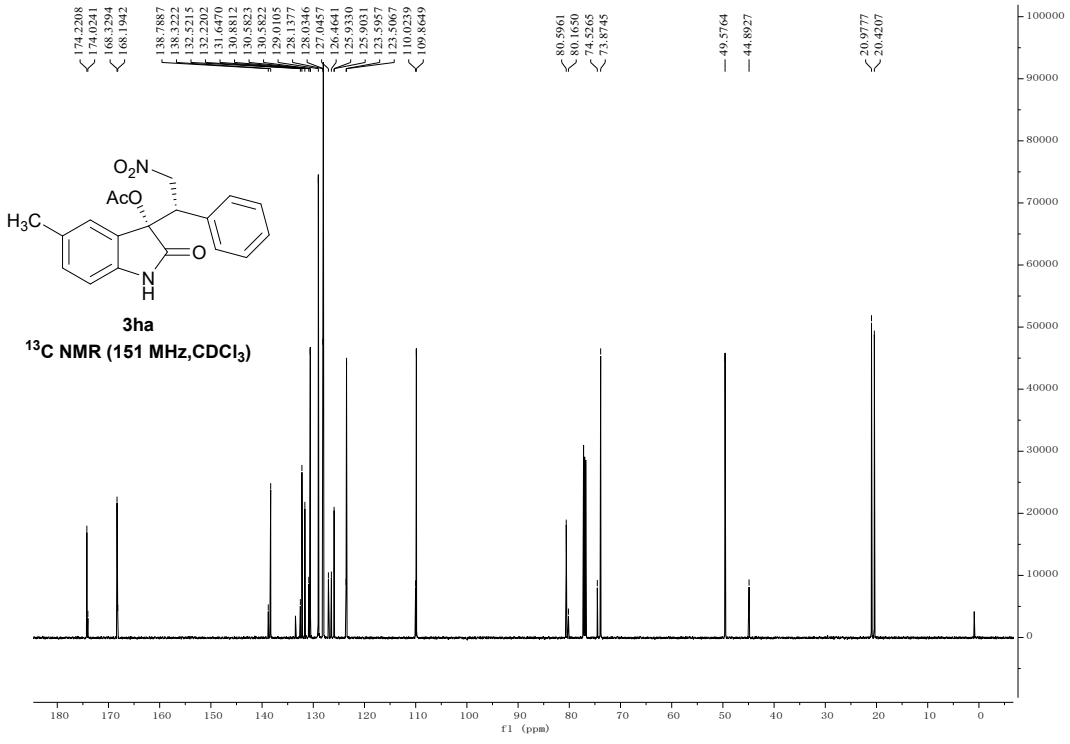

**The $^{1}$H-NMR of product 3ga**



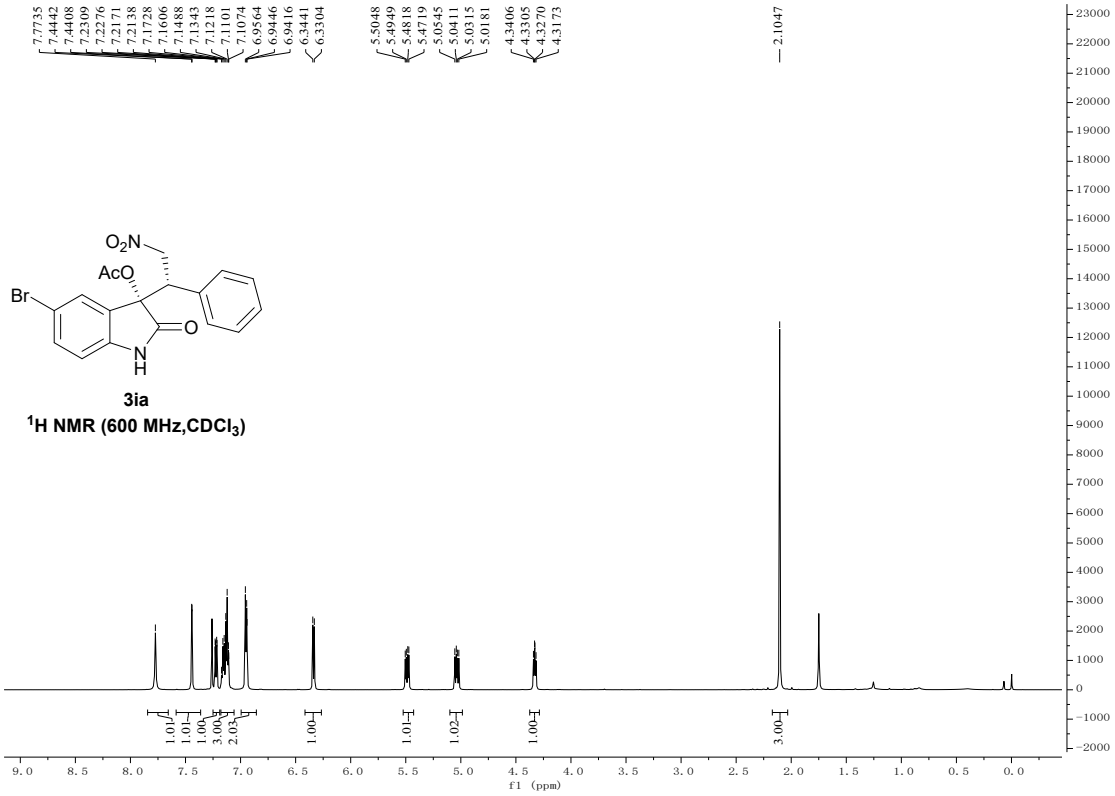

**The $^{13}$C-NMR of product 3ga**



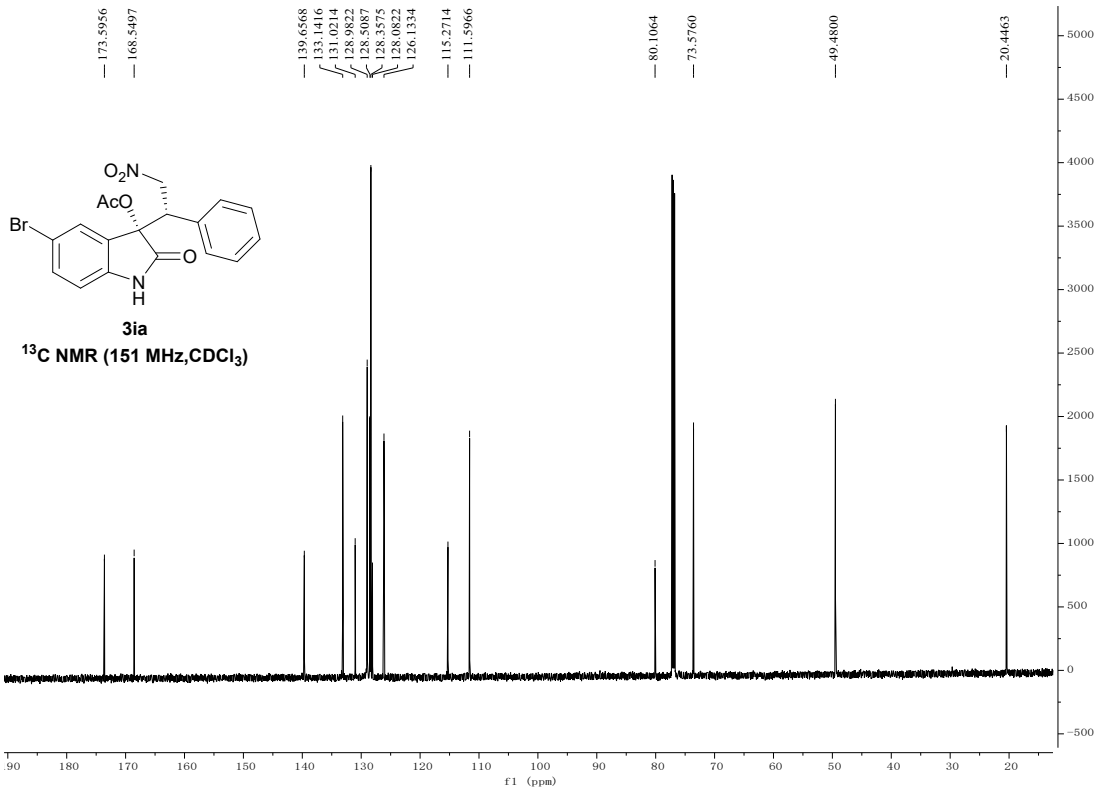

**The $^{1}$H-NMR of product 3ha**



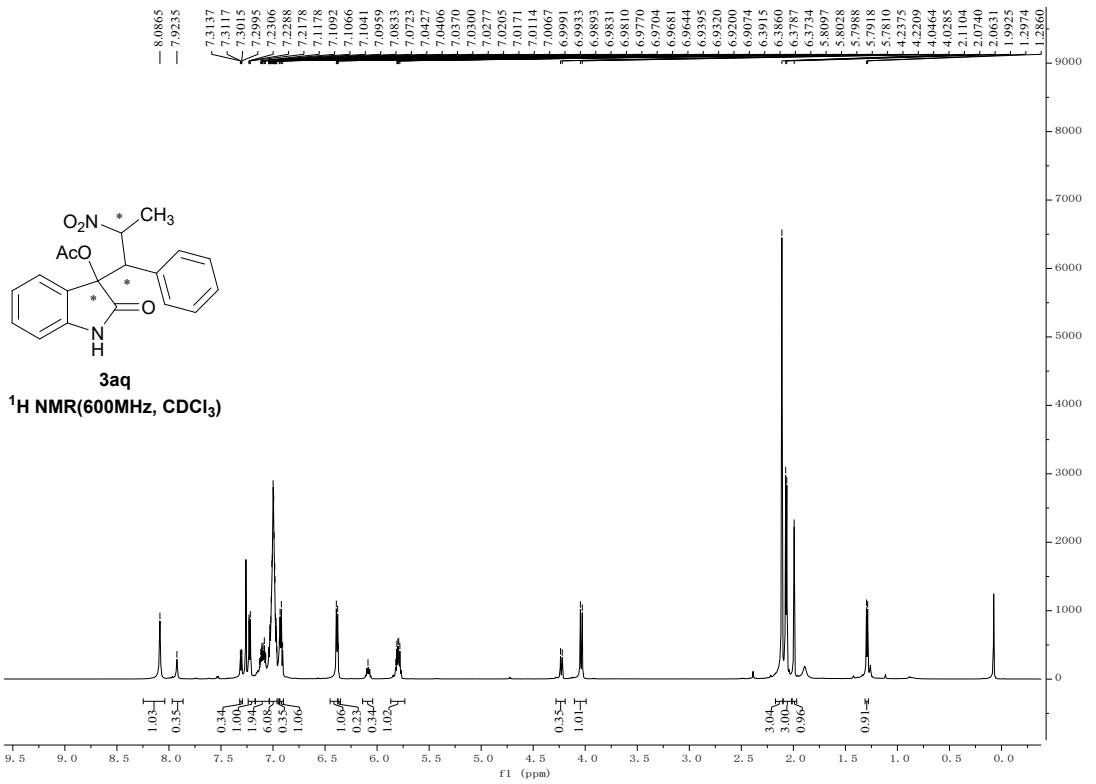

**The $^{13}$C-NMR of product 3ha**



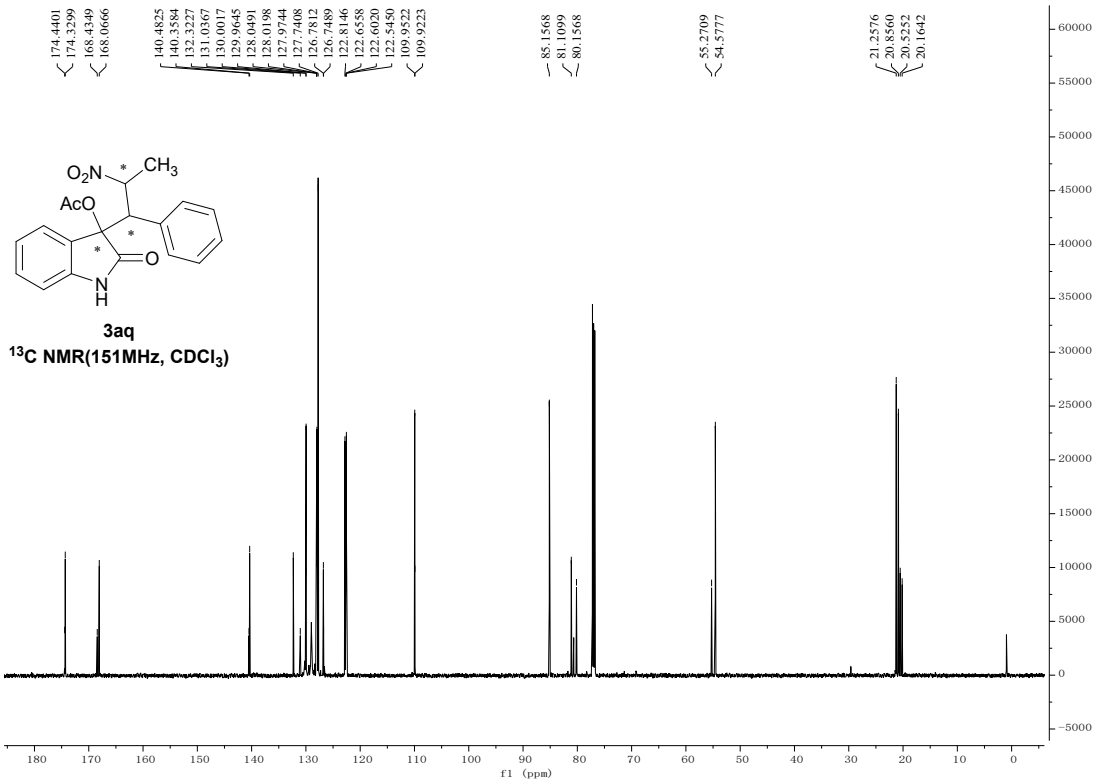

**The $^{1}$H -NMR of product 3ia**



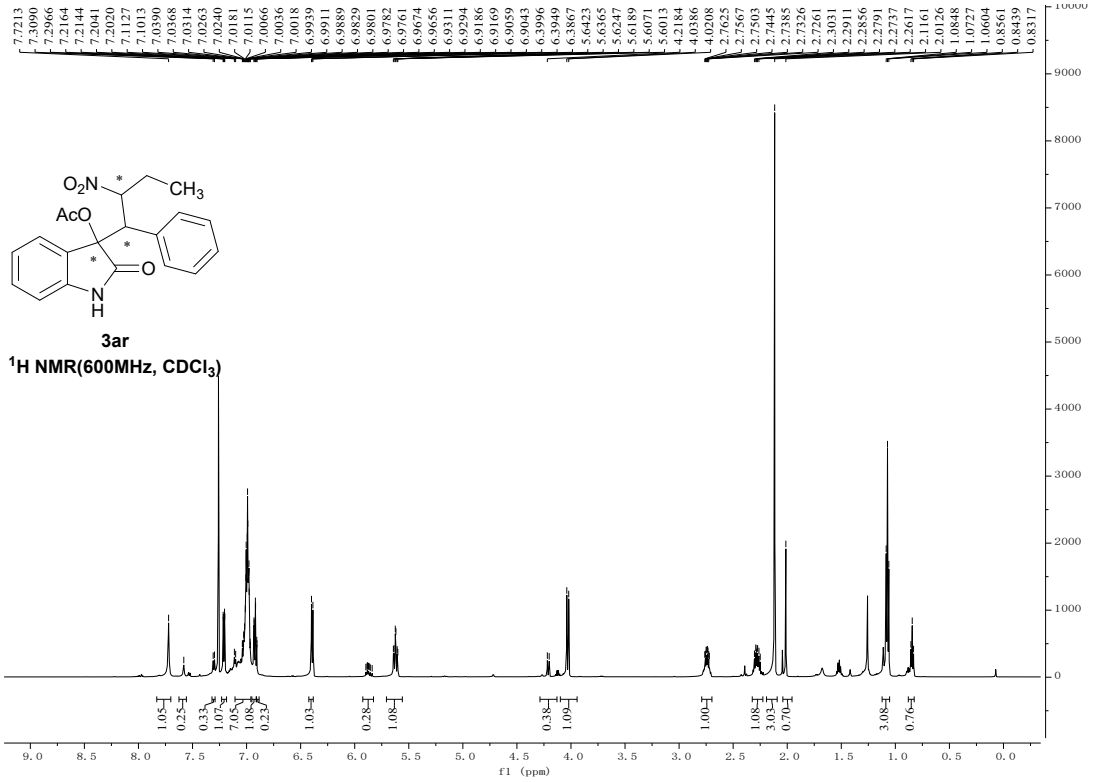

**The $^{13}$C -NMR of product 3ia**



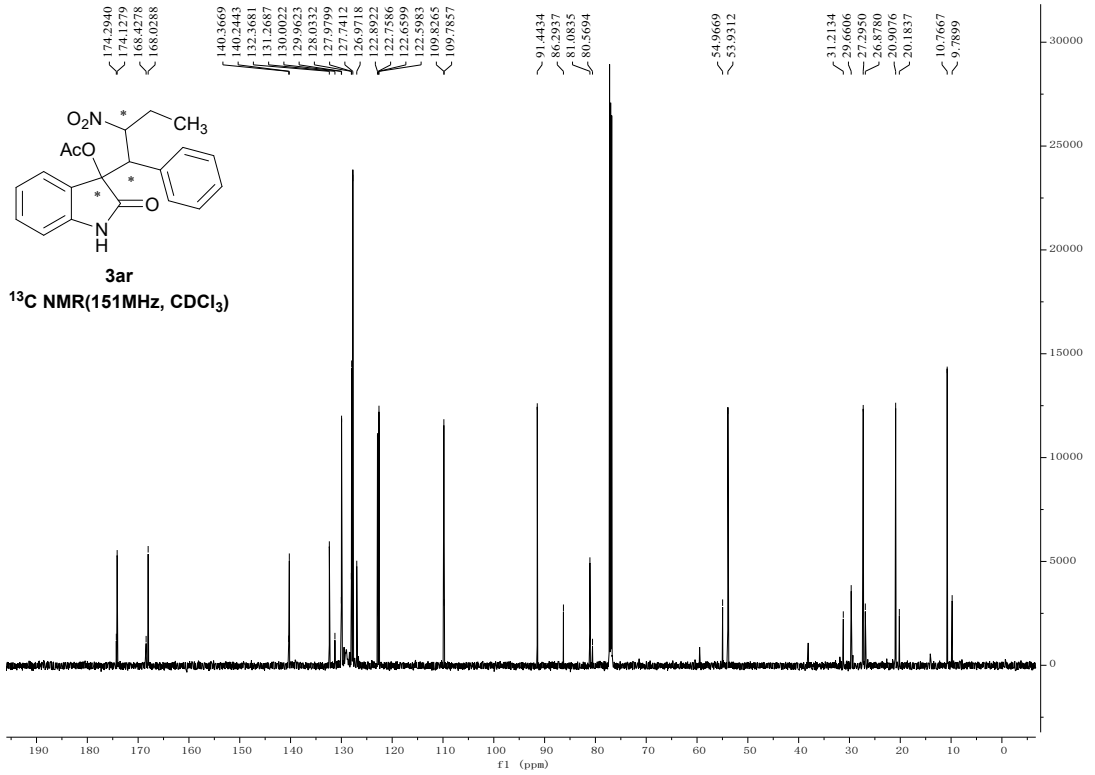

**The $^{1}$H-NMR of product 3aq**



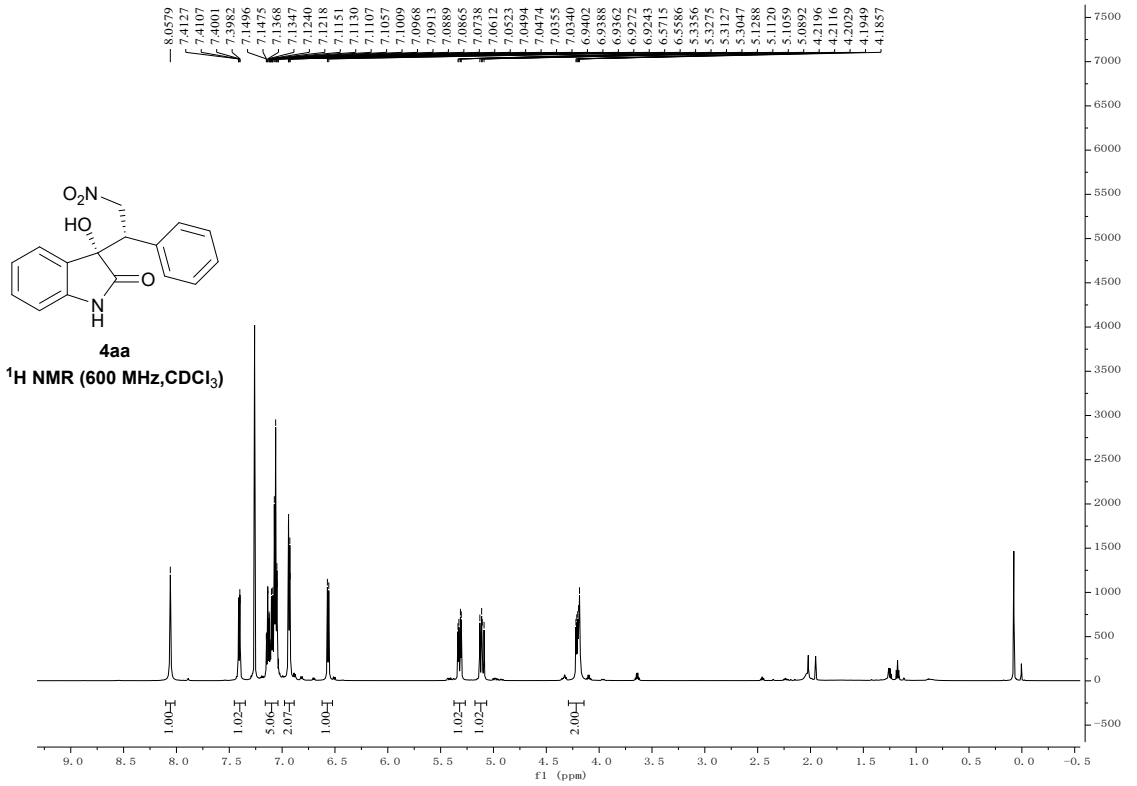

**The $^{13}$C-NMR of product 3aq**



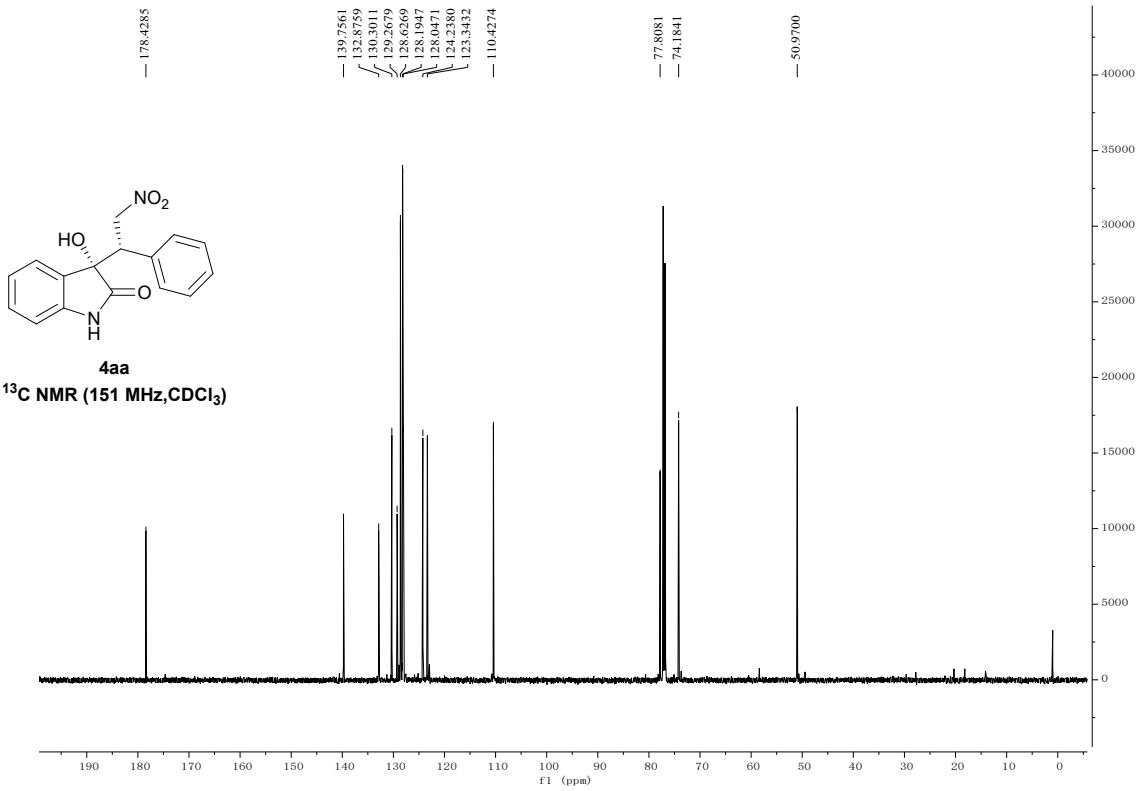

**The $^{1}$H-NMR of product 3ar**



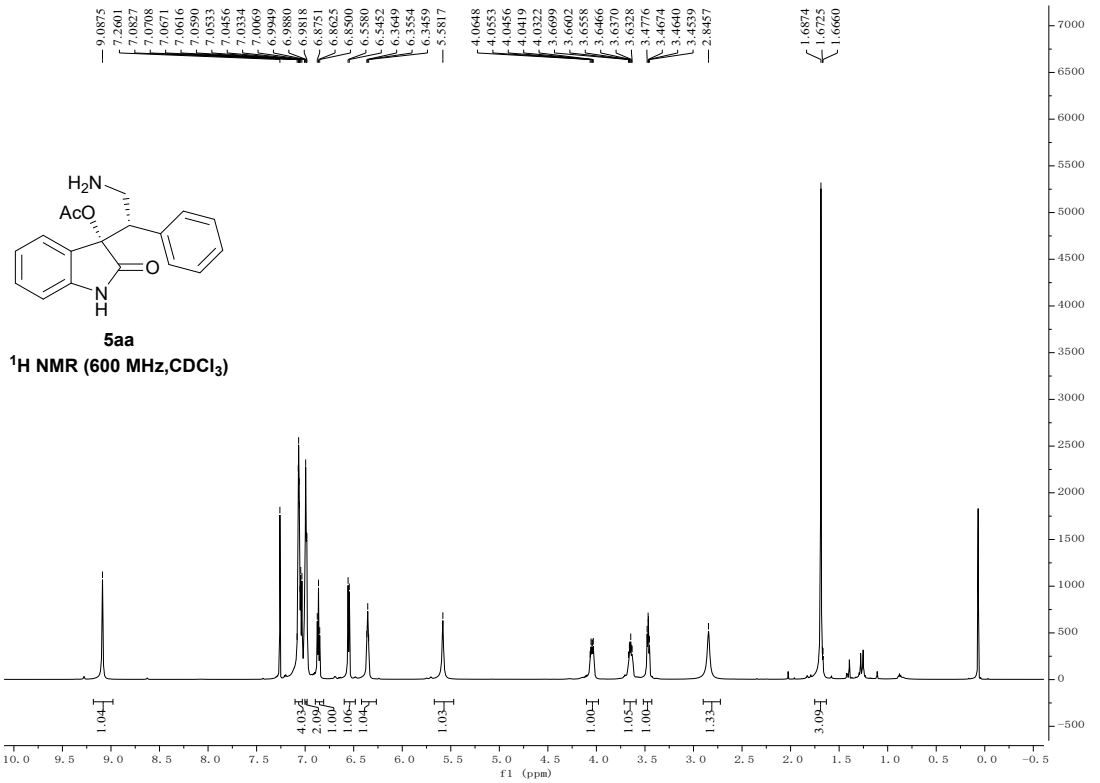

**The $^{13}$C-NMR of product 3ar**



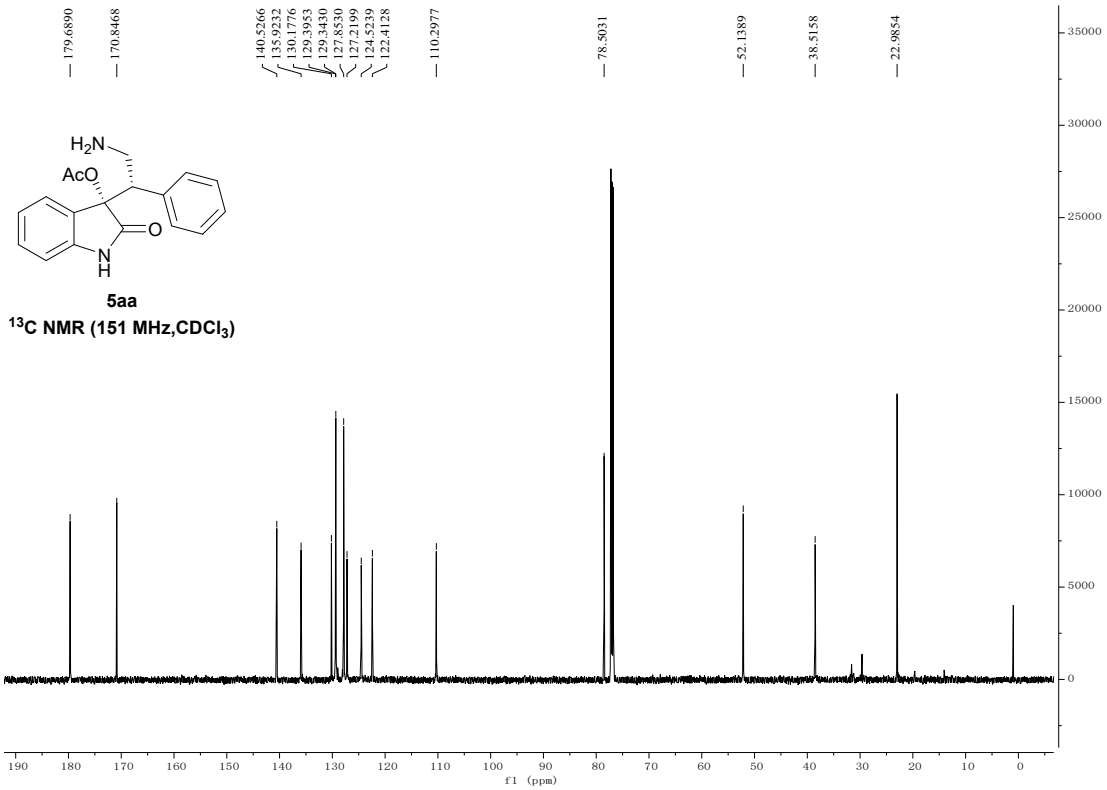

**The $^{1}$H-NMR of product 4aa**




**The $^{13}$C-NMR of product 4aa**




**The $^{1}$H-NMR of product 5aa**




**The $^{13}$C-NMR of product 5aa**