

Supplementary Information

N-Heterocyclic Carbene-Catalyzed Direct Enantioselective Synthesis of dihydroisoxazolo[5,4-*b*]pyridin-6-ones

Xiaoxia Huang, Yarui Li, Jieyin He, Shiyong Peng, Jian Wang* and Ming Lang*

School of Biotechnology and Health Sciences, Wuyi University, Jiangmen 529020, People's Republic of China.

E-mail: wangjian2012@tsinghua.edu.cn; langm2019@163.com.

Table of contents

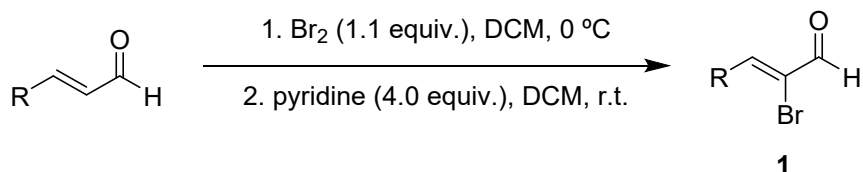
1. General Information-----	S2
2. Experiment Details-----	S3
2.1 General experimental procedure for the synthesis of α -bromoaldehydes (1)	
2.2 General experimental procedure for the synthesis of 5-aminoisoxazoles (2)	
2.3 General experimental procedure for the synthesis of products 3 and 4	
2.4 Procedure for the gram-scale synthesis of 3a	
2.5 Procedure for the synthesis of 5, 6 and 7	
3. Proposed Mechanism-----	S7
4. Analytical Data-----	S8
5. X-Ray Diffraction Data of 3a-----	
S36	
6. References-----	S38
7. Copies of NMR Spectra-----	S39
8. HPLC Chromatograms-----	S89

1. General Information

Unless otherwise noted, all the materials and solvents were purchased from commercial suppliers and used without further purification. Reactions were conducted in dry glassware using anhydrous solvent. Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Qingdao Weinaxipu New Material co., Ltd. and visualized using a combination of UV, iodine and Phosphomolybdic acid staining. Column chromatography was performed with silica gel (200-300 mesh). Melting points were determined with an SGW X-4B melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Ascend™ 500 spectrometer for ^1H at 500 MHz, ^{13}C NMR at 126 MHz, ^{19}F NMR at 471 MHz using TMS as internal standard. The peaks were internally referenced to residual undeuterated chloroform in CDCl_3 (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR) or DMSO in $\text{DMSO}-d_6$ (2.50 ppm for ^1H NMR, 39.52 ppm for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet or unresolved. Coupling constants were reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on a Thermo Scientific Q Exactive UHMR (Ultra-High Mass Range) Hybrid Quadrupole-Orbitrap™ mass spectrometer using ESI ionization. The *ee* values were determined on Waters 1525 HPLC using CHIRALPAK column with hexane and 2-propanol as eluent, Wavelength = 254 nm.

2. Experiment Details

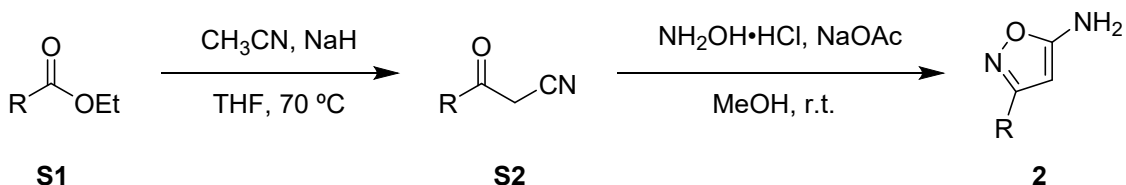
2.1 General experimental procedure for the synthesis of α -bromoenals (**1**)



All α -bromoenals were prepared from the corresponding enals according to procedures previously reported by our group.¹

To a solution of enals (20 mmol, 1.0 equiv.) in DCM (40 mL) at $0\text{ }^\circ\text{C}$ was added Br_2 (22 mmol, 1.1 equiv.) dropwise, the reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 30 min. Pyridine (80 mmol, 4.0 equiv.) was added dropwise and stirred at room temperature for another 2h. The reaction mixture was washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (aq.) solution (50 mL) and water (50 mL). The organic layer was dried with anhydrous Na_2SO_4 , concentrated and purified by column chromatography to give compound **1** as a white solid or colorless oil.

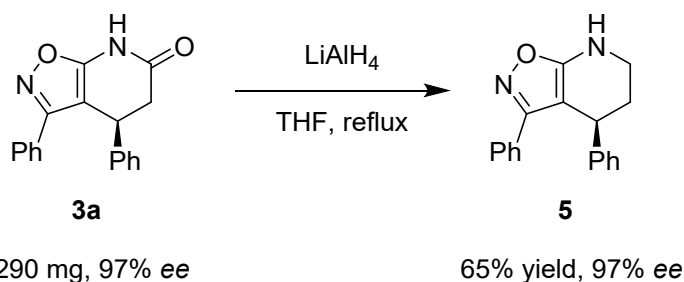
2.2 General experimental procedure for the synthesis of 5-aminoisoxazoles (**2**)



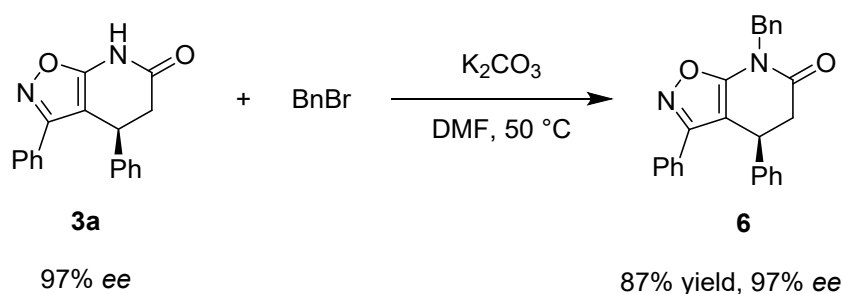
All 5-aminoisoxazoles were prepared from commercially available esters in two steps according to literature procedures.²

Step 1: To a suspension of NaH (20 mmol) in anhydrous THF (20 mL) at $0\text{ }^\circ\text{C}$ was added acetonitrile (30 mmol) and ester **S1** (10 mmol), the reaction mixture was stirred at $70\text{ }^\circ\text{C}$ for 3-5h. After completion of the reaction, the reaction mixture was cooled to $0\text{ }^\circ\text{C}$, pH of the solution was adjusted to neutral by 1M HCl . The mixture was extracted with ethyl acetate, dried with anhydrous Na_2SO_4 , and concentrated under reduced pressure. Purified by column chromatography on silica gel to afford compound **S2** as a white solid or colorless oil.

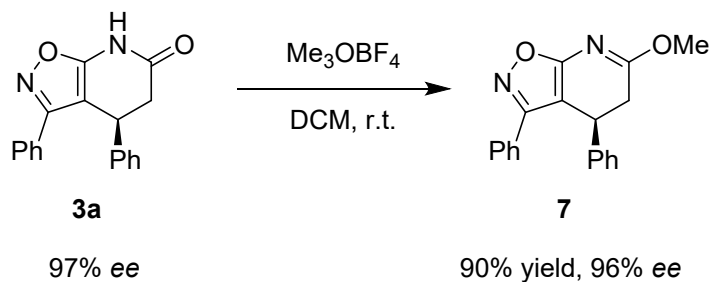
Step 2: A mixture of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (24 mmol) and NaOAc (24 mmol) in MeOH (20 mL) was stirred at room temperature for 1h. **S2** (8 mmol) was added to the reaction mixture, and stirred at room temperature until completion of the reaction. Water (30 mL) was added slowly to



To a suspension of LiAlH_4 (76 mg, 2 mmol) in anhydrous THF (20 mL) under argon atmosphere was added a solution of **3a** (290 mg, 1 mmol) in anhydrous THF (5 mL). The reaction mixture was stirred under reflux for 8h. After completion of the reaction, quenched by water and extracted by ethyl acetate (50 mL \times 2), The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , concentrated and purified by column chromatography to give the product **5** (65% yield, 97% ee) as a white solid.



To a solution of **3a** (0.2 mmol) in DMF (1.0 mL) was added K_2CO_3 (1.0 mmol) and BnBr (1.0 mmol), the reaction mixture was stirred at 50 °C for 4h. After completion of the reaction, cooled to room temperature, water (10 mL) was added and extracted ethyl acetate, the organic layer was dried with anhydrous Na_2SO_4 , concentrated and purified by column chromatography to afford product **6** (87% yield, 97% ee) as a colorless oil.

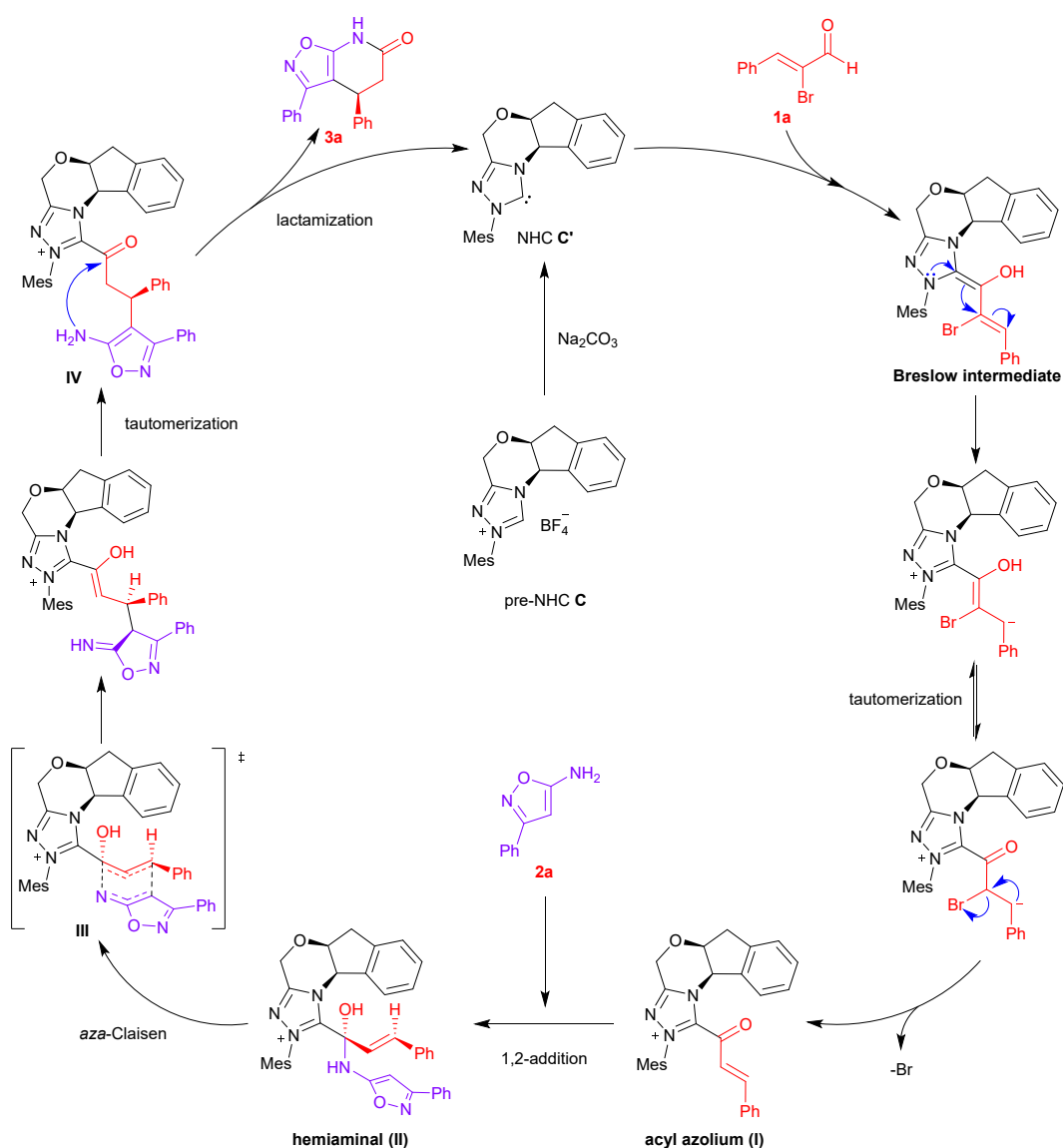


To a solution of **3a** (0.22 mmol) in anhydrous DCM (5 mL) under argon atmosphere was added trimethyloxonium tetrafluoroborate (0.2 mmol), the resulting reaction mixture was stirred at

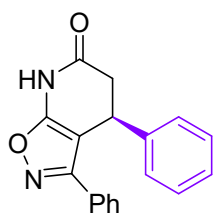
room temperature for 8h. After completion of the reaction, 10% NaHCO₃ (aq.) solution (10 mL) was added and the mixture was extracted with DCM. The organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by column chromatography to afford product **7** (90% yield, 96% *ee*) as a colorless oil.

3. Proposed Mechanism

The nucleophilic addition of chiral NHC **C'** generated from precatalyst **C** under basic conditions to the α -bromoaldehyde **1a** gives Breslow intermediate, which was tautomerized to bromoketone. The elimination of a bromide generates the crucial α,β -unsaturated acyl azolium intermediate **I**. 1,2-Addition of **2a** to intermediate **I** gives hemiaminal **II**, which undergoes aza-Claisen rearrangement and tautomerization to afford intermediate **IV**. Subsequent intramolecular lactamization leading to the formation of product **3a** with the release of NHC catalyst.



4. Analytical Data



3a

White solid, 99% yield, 99% *ee*.

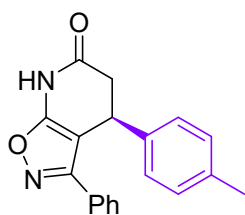
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.86 (s, 1H), 7.58 – 7.52 (m, 2H), 7.46 – 7.36 (m, 3H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 4.52 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.30 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.57 (dd, *J* = 16.2, 2.3 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.0, 164.1, 159.6, 142.4, 130.1, 129.1, 129.0, 128.5, 127.2, 127.0, 126.5, 92.7, 40.5, 33.0.

HRMS (ESI): exact mass calculated for C₁₈H₁₄N₂O₂Na [M + Na]⁺ 313.0956, found 313.0945.

m.p. = 178-180 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, *t*_R(major) = 18.110 min, *t*_R(minor) = 20.137 min.)



3b

White solid, 99% yield, 97% *ee*.

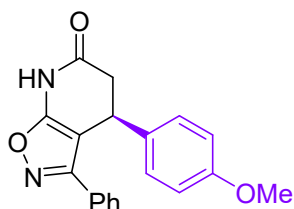
¹H NMR (500 MHz, CDCl₃) δ 9.01 (s, 1H), 7.53 – 7.47 (m, 2H), 7.41 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.31 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.17 (dd, *J* = 16.3, 8.1 Hz, 1H), 2.87 (dd, *J* = 16.3, 2.3 Hz, 1H), 2.31 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 169.5, 162.3, 160.9, 138.2, 137.5, 130.2, 130.1, 129.0, 128.6, 127.7, 126.7, 94.1, 41.0, 33.7, 21.2.

HRMS (ESI): exact mass calculated for C₁₉H₁₇N₂O₂ [M + H]⁺ 305.1287, found 305.1286.

m.p. = 165-167 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 15.610 min, t_R (minor) = 18.846 min.)



3c

White solid, 86% yield, 97% *ee*.

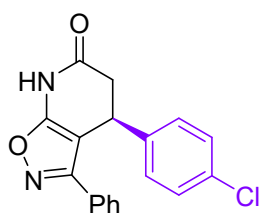
¹H NMR (500 MHz, CDCl₃) δ 8.98 (s, 1H), 7.52 – 7.47 (m, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.31 (m, 2H), 7.09 – 7.04 (m, 2H), 6.86 – 6.80 (m, 2H), 4.31 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.77 (s, 3H), 3.16 (dd, *J* = 16.3, 8.0 Hz, 1H), 2.86 (dd, *J* = 16.3, 2.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.4, 162.2, 160.9, 159.1, 133.3, 130.2, 129.0, 128.5, 127.9, 127.7, 114.8, 94.3, 55.4, 41.1, 33.4.

HRMS (ESI): exact mass calculated for C₁₉H₁₇N₂O₃ [M + H]⁺ 321.1236, found 321.1234.

m.p. = 143-145 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 11.300 min, t_R (minor) = 13.271 min.)



3d

White solid, 99% yield, 98% *ee*.

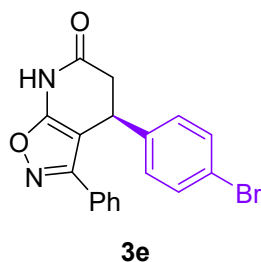
¹H NMR (500 MHz, CDCl₃) δ 9.40 (s, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.11 – 7.06 (m, 2H), 4.34 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.20 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.85 (dd, *J* = 16.4, 2.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.3, 162.4, 160.9, 139.8, 133.7, 130.3, 129.6, 129.0, 128.31, 128.25, 127.6, 93.5, 40.7, 33.6.

HRMS (ESI): exact mass calculated for C₁₈H₁₄ClN₂O₂ [M + H]⁺ 325.0747, found 325.0742.

m.p. = 195-197 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 8.145 min, t_R(minor) = 9.565 min.)



White solid, 99% yield, 98% *ee*.

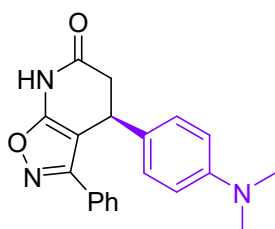
¹H NMR (500 MHz, CDCl₃) δ 9.07 (s, 1H), 7.50 – 7.38 (m, 5H), 7.37 – 7.31 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.33 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.19 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.85 (dd, *J* = 16.4, 2.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.0, 162.4, 160.9, 140.3, 132.6, 130.4, 129.1, 128.6, 128.3, 127.6, 121.8, 93.4, 40.7, 33.7.

HRMS (ESI): exact mass calculated for C₁₈H₁₄BrN₂O₂ [M + H]⁺ 369.0241, found 369.0234.

m.p. = 194-196 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 8.445 min, t_R(minor) = 10.020 min.)



3f

White solid, 52% yield, 96% *ee*.

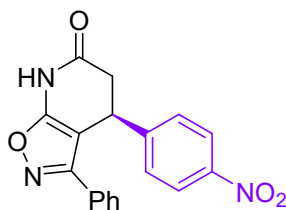
¹H NMR (500 MHz, CDCl₃) δ 8.70 (s, 1H), 7.54 (d, *J* = 6.9 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.26 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.13 (dd, *J* = 16.2, 7.9 Hz, 1H), 2.91 (s, 6H), 2.86 (dd, *J* = 16.2, 2.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.5, 162.1, 161.0, 150.0, 130.1, 128.9, 128.7, 127.7, 127.5, 113.3, 94.7, 41.2, 40.7, 33.2.

HRMS (ESI): exact mass calculated for C₂₀H₂₀N₃O₂ [M + H]⁺ 334.1553, found 334.1551.

m.p. = 182-184 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 12.019 min, t_R(minor) = 13.952 min.)



3g

White solid, 54% yield, 97% *ee*.

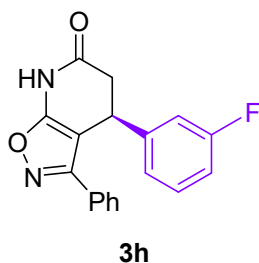
¹H NMR (500 MHz, CDCl₃) δ 8.99 (s, 1H), 8.20 – 8.14 (m, 2H), 7.47 – 7.37 (m, 3H), 7.34 (dd, *J* = 8.1, 6.0 Hz, 4H), 4.50 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.27 (dd, *J* = 16.5, 8.2 Hz, 1H), 2.88 (dd, *J* = 16.5, 3.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.3, 162.5, 160.9, 148.5, 147.6, 130.6, 129.1, 128.1, 127.9, 127.5, 124.8, 92.6, 40.3, 34.2.

HRMS (ESI): exact mass calculated for C₁₈H₁₄N₃O₄ [M + H]⁺ 336.0987, found 336.0980.

m.p. = 186-188 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 14.888 min, t_R (minor) = 21.451 min.)



White solid, 91% yield, 98% *ee*.

¹H NMR (500 MHz, CDCl₃) δ 8.95 (s, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.35 (m, 1H), 7.33 (dd, J = 8.4, 6.7 Hz, 2H), 7.26 (d, J = 7.3 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 7.00 – 6.94 (m, 1H), 4.69 (dd, J = 8.3, 2.5 Hz, 1H), 3.19 (dd, J = 16.6, 8.2 Hz, 1H), 2.91 (dd, J = 16.6, 2.6 Hz, 1H).

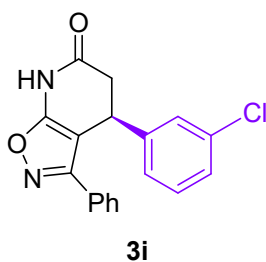
¹³C NMR (126 MHz, CDCl₃) δ 169.1, 162.7, 160.8, 160.3 (d, J = 247.0 Hz), 130.3, 129.7 (d, J = 8.3 Hz), 129.0, 128.33, 128.3 (d, J = 3.7 Hz), 127.9 (d, J = 13.9 Hz), 127.5, 124.9 (d, J = 3.6 Hz), 116.2 (d, J = 21.7 Hz), 92.4, 39.2, 27.8 (d, J = 3.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -118.2.

HRMS (ESI): exact mass calculated for C₁₈H₁₄FN₂O₂ [M + H]⁺ 309.1042, found 309.1035.

m.p. = 195-197 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IC column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 25.457 min, t_R (minor) = 28.930 min.)



White solid, 94% yield, 99% *ee*.

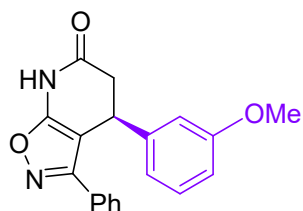
¹H NMR (500 MHz, CDCl₃) δ 9.03 (s, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H), 7.26 – 7.20 (m, 2H), 7.15 – 7.11 (m, 1H), 7.06 – 7.00 (m, 1H), 4.34 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.20 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.87 (dd, *J* = 16.5, 2.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.9, 162.4, 160.9, 143.3, 135.3, 130.8, 130.3, 129.0, 128.3, 128.2, 127.6, 127.1, 125.1, 93.2, 40.7, 33.9.

HRMS (ESI): exact mass calculated for C₁₈H₁₄ClN₂O₂ [M + H]⁺ 325.0747, found 325.0741.

m.p. = 201-203 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 9.321 min, t_R(minor) = 11.959 min.)



3j

White solid, 99% yield, 98% *ee*.

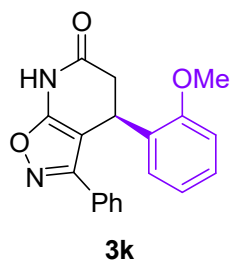
¹H NMR (500 MHz, CDCl₃) δ 8.73 (s, 1H), 7.53 – 7.46 (m, 2H), 7.42 – 7.35 (m, 1H), 7.34 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.74 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 2.2 Hz, 1H), 4.32 (dd, *J* = 8.1, 2.5 Hz, 1H), 3.73 (s, 3H), 3.18 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.89 (dd, *J* = 16.4, 2.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.1, 162.3, 161.0, 160.3, 142.9, 130.5, 130.2, 129.0, 128.5, 127.7, 119.1, 113.0, 112.7, 93.9, 55.3, 40.8, 34.1.

HRMS (ESI): exact mass calculated for C₁₉H₁₇N₂O₃ [M + H]⁺ 321.1234, found 321.1230.

m.p. = 161-163 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IC column (*n*-hexane/isopropanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 18.492 min, t_R(minor) = 22.455 min.)



White solid, 64% yield, 96% *ee*.

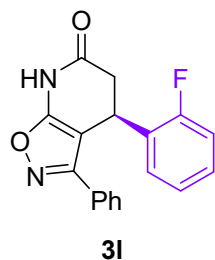
¹H NMR (500 MHz, CDCl₃) δ 8.75 (s, 1H), 7.49 – 7.42 (m, 2H), 7.40 – 7.34 (m, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 6.93 – 6.87 (m, 2H), 6.85 – 6.79 (m, 1H), 4.65 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.84 (s, 3H), 3.09 (dd, *J* = 16.6, 8.5 Hz, 1H), 2.90 (dd, *J* = 16.6, 2.1 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 170.0, 162.6, 161.0, 156.6, 130.0, 129.0, 128.9, 128.8, 128.7, 127.9, 127.7, 120.9, 110.9, 93.2, 55.3, 38.6, 28.8.

HRMS (ESI): exact mass calculated for C₁₉H₁₇N₂O₃ [M + H]⁺ 321.1236, found 321.1235.

m.p. = 90-92 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 19.343 min, t_R(minor) = 12.546 min.)



White solid, 92% yield, 93% *ee*.

¹H NMR (500 MHz, CDCl₃) δ 8.87 (s, 1H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.98 – 6.93 (m, 2H), 6.85 (dt, *J* = 9.6, 2.2 Hz, 1H), 4.36 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.20 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.88 (dd, *J* = 16.4, 2.6 Hz, 1H).

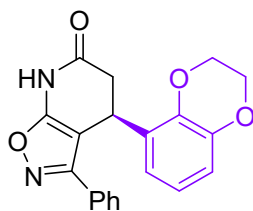
¹³C NMR (126 MHz, CDCl₃) δ 168.8, 164.4, 162.4, 160.9, 143.8 (d, *J* = 6.5 Hz), 131.1 (d, *J* = 8.4 Hz), 130.3, 129.0, 128.3, 127.6, 122.5 (d, *J* = 2.8 Hz), 115.0 (d, *J* = 21.1 Hz), 114.0 (d, *J* = 22.0 Hz), 93.3, 40.7, 34.0 (d, *J* = 1.7 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -111.5.

HRMS (ESI): exact mass calculated for $C_{18}H_{14}FN_2O_2$ $[M + H]^+$ 309.1042, found 309.1035.

m.p. = 176-178 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.841 min, t_R (minor) = 11.098 min.)



3m

White solid, 80% yield, 98% *ee*.

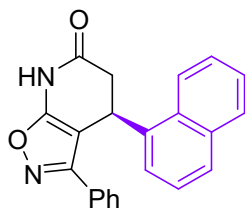
1H NMR (500 MHz, $DMSO-d_6$) δ 11.82 (s, 1H), 7.57 (dd, J = 7.6, 2.0 Hz, 2H), 7.48 – 7.39 (m, 3H), 6.80 – 6.74 (m, 1H), 6.60 – 6.54 (m, 2H), 4.40 (dd, J = 7.9, 2.1 Hz, 1H), 4.17 (s, 4H), 3.23 (dd, J = 16.1, 7.9 Hz, 1H), 2.53 (d, J = 2.1 Hz, 1H).

^{13}C NMR (126 MHz, $DMSO-d_6$) δ 169.1, 164.0, 159.4, 143.5, 142.5, 135.3, 130.1, 129.0, 128.5, 127.0, 119.1, 117.5, 115.0, 93.0, 64.1, 63.9, 40.6, 32.2.

HRMS (ESI): exact mass calculated for $C_{20}H_{17}N_2O_4$ $[M + H]^+$ 349.1185, found 349.1183.

m.p. = 209-211 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IC column (*n*-hexane/isopropanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 23.606 min, t_R (minor) = 27.257 min.)



3n

White solid, 98% yield, 99% *ee*.

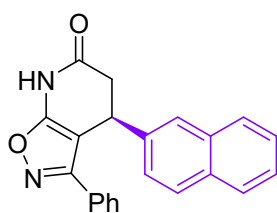
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.90 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 5.37 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.43 (dd, *J* = 16.2, 8.4 Hz, 1H), 2.56 (dd, *J* = 16.3, 1.8 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.0, 164.8, 159.6, 137.1, 134.0, 130.1, 129.9, 129.1, 129.0, 128.5, 128.0, 126.9, 126.7, 126.1, 125.6, 123.5, 123.0, 92.1, 28.8.

HRMS (ESI): exact mass calculated for C₂₂H₁₇N₂O₂ [M + H]⁺ 341.1288, found 341.1286.

m.p. = 231-233 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 19.262 min, t_R(minor) = 23.066 min.)



3o

White solid, 93% yield, 98% *ee*.

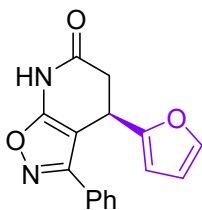
¹H NMR (500 MHz, CDCl₃) δ 8.97 (s, 1H), 7.81 (t, *J* = 7.5 Hz, 2H), 7.75 – 7.69 (m, 1H), 7.56 – 7.43 (m, 5H), 7.37 – 7.26 (m, 4H), 4.51 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.25 (dd, *J* = 16.4, 8.2 Hz, 1H), 2.99 (dd, *J* = 16.4, 2.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.3, 162.5, 161.1, 138.5, 133.6, 132.9, 130.2, 129.6, 129.0, 128.5, 128.0, 127.8, 127.7, 126.7, 126.3, 125.5, 125.0, 93.7, 40.8, 34.2.

HRMS (ESI): exact mass calculated for C₂₂H₁₇N₂O₂ [M + H]⁺ 341.1288, found 341.1285.

m.p. = 196-198 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 21.377 min, t_R(minor) = 27.950 min.)



3p

White solid, 69% yield, 99% *ee*.

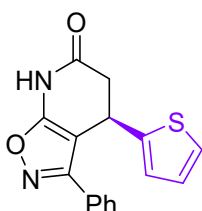
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.85 (s, 1H), 7.72 – 7.67 (m, 2H), 7.63 – 7.40 (m, 4H), 6.34 – 6.30 (m, 1H), 6.05 (s, 1H), 4.59 (d, *J* = 7.5 Hz, 1H), 3.21 (dd, *J* = 16.3, 7.7 Hz, 1H), 2.69 (d, *J* = 16.3 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.0, 164.0, 159.5, 154.6, 143.0, 130.3, 129.2, 128.5, 127.2, 110.6, 106.0, 91.2, 37.1, 27.4.

HRMS (ESI): exact mass calculated for C₁₆H₁₃N₂O₃ [M + H]⁺ 281.0928, found 281.0922.

m.p. = 152-154 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 17.491 min, t_R(minor) = 15.645 min.)



3q

White solid, 90% yield, >99% *ee*.

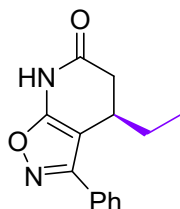
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.90 (s, 1H), 7.70 – 7.62 (m, 2H), 7.51 – 7.42 (m, 3H), 7.34 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 (dt, *J* = 3.5, 1.1 Hz, 1H), 4.86 – 4.81 (m, 1H), 3.32 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.68 (dd, *J* = 16.2, 2.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.7, 162.0, 160.6, 145.1, 130.4, 129.1, 128.4, 127.6, 127.5, 125.2, 124.8, 94.6, 41.4, 29.8.

HRMS (ESI): exact mass calculated for C₁₆H₁₃N₂O₂S [M + H]⁺ 297.0700, found 297.0697.

m.p. = 195-197 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 18.563 min, t_R (minor) = 16.349 min.)



3r

White solid, 48% yield, 99% *ee*.

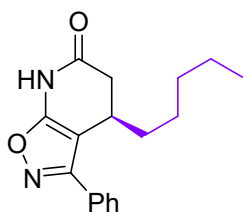
¹H NMR (500 MHz, CDCl₃) δ 8.52 (s, 1H), 7.76 – 7.68 (m, 2H), 7.51 – 7.43 (m, 3H), 3.21 – 3.13 (m, 1H), 2.92 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.71 (dd, *J* = 16.5, 2.1 Hz, 1H), 1.63 – 1.45 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.1, 161.3, 160.7, 130.2, 129.3, 129.1, 127.5, 95.3, 36.8, 30.0, 28.2, 10.8.

HRMS (ESI): exact mass calculated for C₁₄H₁₅N₂O₂ [M + H]⁺ 243.1134, found 243.1133.

m.p. = 90-92 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 15.793 min, t_R (minor) = 13.737 min.)



3s

White solid, 70% yield, >99% *ee*.

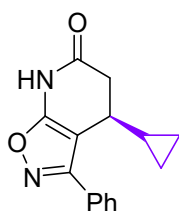
¹H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.75 – 7.66 (m, 2H), 7.52 – 7.43 (m, 3H), 3.20 (tdd, *J* = 7.6, 6.0, 2.1 Hz, 1H), 2.91 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.71 (dd, *J* = 16.5, 2.1 Hz, 1H), 1.58 – 1.41 (m, 2H), 1.23 – 1.08 (m, 6H), 0.81 – 0.75 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.1, 161.2, 160.7, 130.2, 129.3, 129.1, 127.6, 95.7, 37.1, 35.1, 31.6, 28.5, 25.9, 22.5, 14.0.

HRMS (ESI): exact mass calculated for C₁₇H₂₁N₂O₂ [M + H]⁺ 285.1605, found 285.1600.

m.p. = 97-99 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 10.942 min, t_R(minor) = 7.641 min.)



3t

White solid, 93% yield, 99% *ee*.

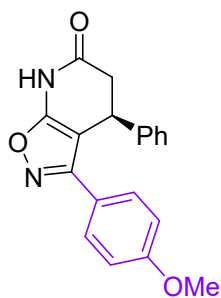
¹H NMR (500 MHz, CDCl₃) δ 8.96 (s, 1H), 7.77 – 7.70 (m, 2H), 7.50 – 7.43 (m, 3H), 3.01 – 2.92 (m, 2H), 2.85 – 2.77 (m, 1H), 0.95 – 0.85 (m, 1H), 0.47 – 0.38 (m, 1H), 0.37 – 0.28 (m, 1H), 0.08 – 0.02 (m, 1H), -0.02 – -0.08 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 170.5, 161.7, 161.0, 130.2, 129.1, 129.0, 127.8, 93.7, 38.3, 31.5, 15.9, 3.0, 2.7.

HRMS (ESI): exact mass calculated for C₁₅H₁₅N₂O₂ [M + H]⁺ 255.1134, found 255.1129.

m.p. = 140-142 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 15.911 min, t_R(minor) = 12.787 min.)



4a

White solid, 99% yield, 97% *ee*.

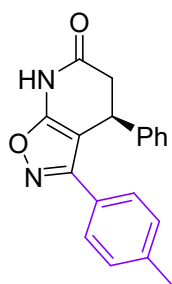
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.81 (s, 1H), 7.52 – 7.47 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.49 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.75 (d, *J* = 1.6 Hz, 3H), 3.30 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.56 (dt, *J* = 16.1, 1.8 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.0, 163.9, 160.5, 159.2, 142.4, 129.1, 128.4, 127.2, 126.6, 120.8, 114.4, 92.4, 55.3, 40.6, 33.0.

HRMS (ESI): exact mass calculated for C₁₉H₁₆N₂O₃Na [M + Na]⁺ 343.1055, found 343.1051.

m.p. = 182-184 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 23.634 min, t_R(minor) = 18.874 min.)



4b

White solid, 99% yield, 97% *ee*.

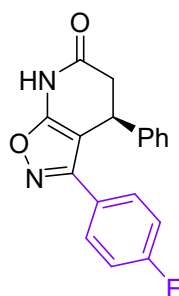
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.82 (s, 1H), 7.47 – 7.42 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.10 (m, 2H), 4.50 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.30 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.55 (dd, *J* = 16.3, 2.2 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 169.0, 163.9, 159.5, 142.4, 139.8, 129.5, 129.0, 127.2, 126.9, 126.5, 125.7, 92.6, 40.5, 33.0, 20.9.

HRMS (ESI): exact mass calculated for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 327.1106, found 327.1103.

m.p. = 191-193 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 11.735 min, t_{R} (minor) = 13.209 min.)



4c

White solid, 99% yield, 97% *ee*.

^1H NMR (500 MHz, DMSO- d_6) δ 11.88 (s, 1H), 7.63 – 7.55 (m, 2H), 7.34 – 7.19 (m, 5H), 7.16 – 7.11 (m, 2H), 4.52 (dd, J = 8.0, 2.6 Hz, 1H), 3.29 (dd, J = 16.2, 8.1 Hz, 1H), 2.59 (dd, J = 16.3, 2.5 Hz, 1H).

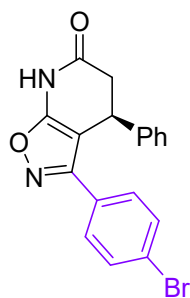
^{13}C NMR (126 MHz, DMSO- d_6) δ 169.0, 164.2, 163.0 (d, J = 247.7 Hz), 158.8, 142.2, 129.3 (d, J = 8.6 Hz), 129.1, 127.2, 126.6, 125.0 (d, J = 3.2 Hz), 116.1 (d, J = 21.9 Hz), 92.7, 40.5, 32.9.

^{19}F NMR (471 MHz, DMSO- d_6) δ -110.5.

HRMS (ESI): exact mass calculated for $\text{C}_{18}\text{H}_{14}\text{FN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 309.1042, found 309.1034.

m.p. = 154-156 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 8.249 min, t_{R} (minor) = 10.307 min.)



4d

White solid, 90% yield, 98% *ee*.

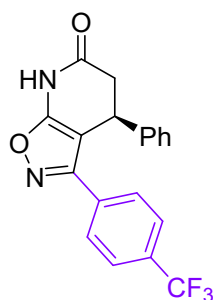
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.90 (s, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.47 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.15 – 7.10 (m, 2H), 4.53 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.29 (dd, *J* = 16.2, 8.0 Hz, 1H), 2.59 (dd, *J* = 16.2, 2.5 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.0, 164.3, 158.7, 142.2, 132.0, 129.1, 129.0, 127.7, 127.2, 126.6, 123.6, 92.8, 40.4, 32.9.

HRMS (ESI): exact mass calculated for C₁₈H₁₄BrN₂O₂ [M + H]⁺ 369.0241, found 369.0234.

m.p. = 189-191 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel ID column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, *t*_R(major) = 8.764 min, *t*_R(minor) = 11.827 min.)



4e

White solid, 89% yield, 97% *ee*.

¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 7.58 (s, 4H), 7.35 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.14 (dd, *J* = 7.2, 1.8 Hz, 2H), 4.35 (dd, *J* = 8.1, 2.9 Hz, 1H), 3.21 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.91 (dd, *J* = 16.4, 2.9 Hz, 1H).

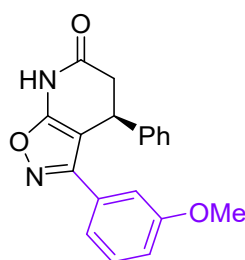
¹³C NMR (126 MHz, CDCl₃) δ 169.2, 162.8, 159.9, 141.0, 132.0 (t, *J* = 16.3 Hz), 129.6, 128.1, 128.0, 126.8, 125.9 (q, *J* = 3.7 Hz), 124.9, 122.8, 94.0, 40.8, 34.2.

^{19}F NMR (471 MHz, CDCl_3) δ -63.0.

HRMS (ESI): exact mass calculated for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 359.1004, found 359.1006.

m.p. = 169-171 $^\circ\text{C}$.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 7.647 min, t_{R} (minor) = 9.905 min.)



4f

White solid, 90% yield, 97% *ee*.

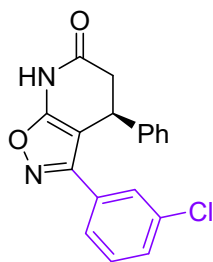
^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 11.88 (s, 1H), 7.36 – 7.29 (m, 3H), 7.27 – 7.20 (m, 1H), 7.18 – 7.13 (m, 3H), 7.02 – 6.94 (m, 2H), 4.51 (dd, J = 8.1, 2.1 Hz, 1H), 3.62 (s, 3H), 3.30 (dd, J = 16.2, 8.2 Hz, 1H), 2.55 (dd, J = 16.3, 2.1 Hz, 1H).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 169.0, 164.2, 159.5, 159.4, 142.4, 130.2, 129.7, 129.1, 127.3, 126.6, 119.2, 116.2, 112.0, 92.7, 55.0, 40.6, 33.0.

HRMS (ESI): exact mass calculated for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 343.1055, found 343.1052.

m.p. = 152-154 $^\circ\text{C}$.

The *ee* value was determined by HPLC analysis on a Chiralcel IC column (*n*-hexane/isopropanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 27.322 min, t_{R} (minor) = 21.884 min.)



4g

White solid, 99% yield, 95% *ee*.

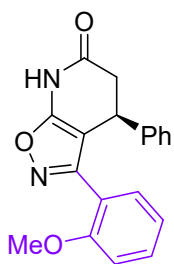
¹H NMR (500 MHz, CDCl₃) δ 8.56 (s, 1H), 7.49 (t, *J* = 1.9 Hz, 1H), 7.37 – 7.22 (m, 6H), 7.17 – 7.12 (m, 2H), 4.33 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.19 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.89 (dd, *J* = 16.4, 3.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.7, 162.5, 159.9, 141.1, 134.9, 130.24, 130.20, 130.15, 129.5, 128.0, 127.9, 126.8, 125.8, 94.0, 40.8, 34.3.

HRMS (ESI): exact mass calculated for C₁₈H₁₄ClN₂O₂ [M + H]⁺ 325.0738, found 325.0737.

m.p. = 202-204 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IC column (*n*-hexane/isopropanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 12.203 min, t_R(minor) = 16.334 min.)



4h

White solid, 99% yield, 96% *ee*.

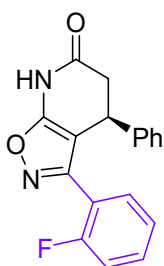
¹H NMR (500 MHz, CDCl₃) δ 8.87 (s, 1H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.17 – 7.05 (m, 3H), 7.02 – 6.97 (m, 2H), 6.90 (td, *J* = 7.5, 0.9 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 4.23 (t, *J* = 6.9 Hz, 1H), 3.47 (s, 3H), 3.07 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.80 (dd, *J* = 16.5, 6.6 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 161.2, 160.1, 157.0, 141.3, 131.5, 130.6, 128.6, 127.1, 126.9, 120.7, 117.6, 110.5, 96.2, 55.0, 41.2, 35.2.

HRMS (ESI): exact mass calculated for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 321.1234, found 321.1231.

m.p. = 198-200 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 16.723 min, t_{R} (minor) = 12.630 min.)



4i

White solid, 58% yield, 99% *ee*.

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 12.02 – 11.73 (m, 1H), 7.49 – 7.42 (m, 1H), 7.39 (td, J = 7.6, 1.8 Hz, 1H), 7.26 – 7.15 (m, 4H), 7.15 – 7.08 (m, 1H), 7.07 – 6.99 (m, 2H), 4.31 (dd, J = 7.6, 5.1 Hz, 1H), 3.14 (dd, J = 16.3, 7.7 Hz, 1H), 2.63 (dd, J = 16.3, 5.2 Hz, 1H).

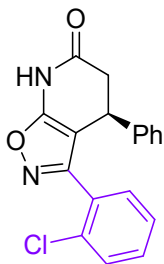
^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 169.3, 163.7, 159.1 (d, J = 249.7 Hz), 156.5, 141.9, 132.2 (d, J = 8.2 Hz), 130.3 (d, J = 2.9 Hz), 128.6, 126.9, 126.6, 124.7 (d, J = 3.4 Hz), 116.3 (d, J = 14.4 Hz), 116.1 (d, J = 21.3 Hz), 94.3, 40.4, 33.3 (d, J = 3.7 Hz).

^{19}F NMR (471 MHz, $\text{DMSO}-d_6$) δ -112.8.

HRMS (ESI): exact mass calculated for $\text{C}_{18}\text{H}_{14}\text{FN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 309.1042, found 309.1035.

m.p. = 164-166 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 11.549 min, t_{R} (minor) = 8.768 min.)



4j

White solid, 41% yield, 96% *ee*.

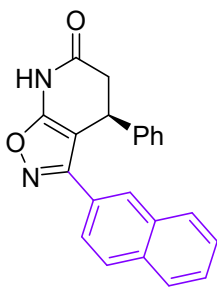
¹H NMR (500 MHz, CDCl₃) δ 8.66 (s, 1H), 7.29 – 7.22 (m, 2H), 7.21 – 7.13 (m, 2H), 7.13 – 7.05 (m, 3H), 7.00 – 6.94 (m, 2H), 4.29 (t, *J* = 7.3 Hz, 1H), 3.11 (dd, *J* = 16.6, 7.4 Hz, 1H), 2.87 (dd, *J* = 16.7, 7.3 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.3, 163.1, 159.4, 141.4, 132.1, 131.3, 131.1, 129.5, 128.4, 127.7, 127.1, 126.8, 126.8, 94.9, 40.2, 33.7.

HRMS (ESI): exact mass calculated for C₁₈H₁₄ClN₂O₂ [M + H]⁺ 325.0747, found 325.0739.

m.p. = 114-116 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel ID column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 11.106 min, t_R(minor) = 8.910 min.)



4k

White solid, 99% yield, 97% *ee*.

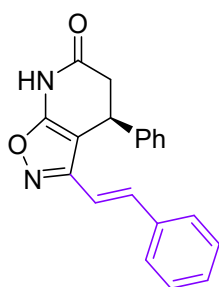
¹H NMR (500 MHz, CDCl₃) δ 8.11(s, 1H), 7.88 – 7.86 (m, 1H), 7.84 – 7.80 (m, 2H), 7.70 – 7.63 (m, 2H), 7.53 – 7.44 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 4.45 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.24 (dd, *J* = 16.4, 8.2 Hz, 1H), 2.92 (dd, *J* = 16.4, 2.5 Hz, 1H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 169.2, 164.3, 159.5, 142.7, 133.3, 132.6, 129.3, 128.7, 128.4, 127.8, 127.5, 127.3, 127.1, 127.0, 126.7, 126.0, 124.0, 93.1, 40.4, 33.2.

HRMS (ESI): exact mass calculated for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 341.1288, found 341.1284.

m.p. = 199-201 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 13.708 min, t_{R} (minor) = 17.532 min.)



4l

White solid, 99% yield, 98% *ee*.

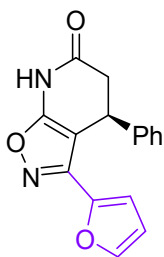
^1H NMR (500 MHz, CDCl_3) δ 8.57 (s, 1H), 7.36 (dd, J = 8.3, 6.8 Hz, 2H), 7.33 – 7.19 (m, 8H), 6.93 (d, J = 16.7 Hz, 1H), 6.71 (d, J = 16.7 Hz, 1H), 4.38 (dd, J = 8.1, 4.4 Hz, 1H), 3.20 (dd, J = 16.5, 8.1 Hz, 1H), 2.90 (dd, J = 16.5, 4.4 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 168.9, 161.7, 159.4, 141.2, 137.3, 135.7, 129.6, 129.2, 128.9, 128.0, 127.03, 127.01, 114.9, 93.6, 40.7, 34.6.

HRMS (ESI): exact mass calculated for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 317.1287, found 317.1287.

m.p. = 191-193 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 23.126 min, t_{R} (minor) = 17.188 min.)



4m

White solid, 82% yield, 97% *ee*.

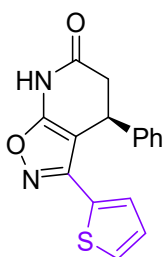
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.90 (s, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.74 (d, *J* = 3.6 Hz, 1H), 6.61 – 6.57 (m, 1H), 4.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.32 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.56 (dd, *J* = 16.3, 2.0 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.2, 163.7, 151.8, 145.0, 142.8, 142.5, 129.0, 127.2, 126.5, 111.9, 92.0, 40.1, 32.6.

HRMS (ESI): exact mass calculated for C₁₆H₁₃N₂O₃ [M + H]⁺ 281.0928, found 281.0920.

m.p. = 164-166 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 9.424 min, t_R(minor) = 12.132 min.)



4n

White solid, 82% yield, 95% *ee*.

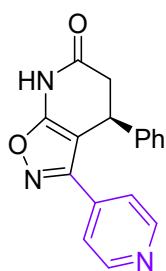
¹H NMR (500 MHz, DMSO-*d*₆) δ 11.89 (s, 1H), 7.71 – 7.66 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 4.53 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.32 (dd, *J* = 16.3, 8.3 Hz, 1H), 2.56 (dt, *J* = 16.4, 1.5 Hz, 1H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 169.0, 164.1, 154.9, 142.2, 129.1, 128.8, 128.4, 128.1, 127.3, 126.6, 92.2, 40.4, 32.7.

HRMS (ESI): exact mass calculated for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 297.0700, found 297.0694.

m.p. = 176-178 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 9.649 min, t_{R} (minor) = 12.160 min.)



4o

White solid, 56% yield, 99% *ee*.

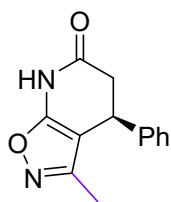
^1H NMR (500 MHz, CDCl_3) δ 9.78 (s, 1H), 8.64 – 8.59 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.24 (m, 3H), 7.14 (dd, J = 7.3, 1.7 Hz, 2H), 4.37 (dd, J = 8.1, 3.1 Hz, 1H), 3.21 (dd, J = 16.5, 8.1 Hz, 1H), 2.91 (dd, J = 16.5, 3.1 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 169.0, 163.4, 158.9, 150.3, 140.9, 136.4, 129.6, 128.2, 126.8, 121.9, 93.9, 40.8, 34.2.

HRMS (ESI): exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_2$ $[\text{M} + \text{H}]^+$ 292.1088, found 292.1079.

m.p. = 180-182 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 35.204 min, t_{R} (minor) = 29.772 min.)



4p

White solid, 99% yield, 97% *ee*.

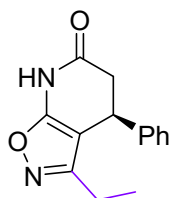
¹H NMR (500 MHz, CDCl₃) δ 8.91 (s, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.21 – 7.15 (m, 2H), 4.12 (t, *J* = 7.3 Hz, 1H), 3.08 (dd, *J* = 16.7, 7.7 Hz, 1H), 2.85 (dd, *J* = 16.7, 6.9 Hz, 1H), 1.89 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 169.7, 161.0, 159.1, 141.2, 129.3, 127.9, 127.1, 94.8, 40.5, 34.2, 10.6.

HRMS (ESI): exact mass calculated for C₁₃H₁₃N₂O₂ [M + H]⁺ 229.0976, found 229.0969.

m.p. = 154-156 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IH column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 16.872 min, t_R(minor) = 12.792 min.)



4q

White solid, 71% yield, 97% *ee*.

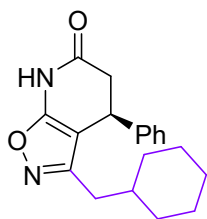
¹H NMR (500 MHz, CDCl₃) δ 8.76 (s, 1H), 7.37 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.19 – 7.14 (m, 2H), 4.13 (dd, *J* = 7.8, 6.2 Hz, 1H), 3.09 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.83 (dd, *J* = 16.7, 6.2 Hz, 1H), 2.41 – 2.18 (m, 2H), 1.03 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 169.5, 163.8, 161.1, 141.5, 129.3, 127.8, 127.1, 94.1, 40.7, 34.3, 19.2, 11.7.

HRMS (ESI): exact mass calculated for C₁₄H₁₅N₂O₂ [M + H]⁺ 243.1134, found 243.1129.

m.p. = 135-137 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 13.188 min, t_R (minor) = 16.045 min.)



4r

White solid, 91% yield, 94% *ee*.

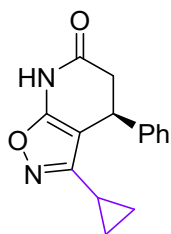
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.54 (s, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.18 – 7.13 (m, 2H), 4.10 (dd, J = 7.8, 6.1 Hz, 1H), 3.09 (dd, J = 16.6, 7.8 Hz, 1H), 2.82 (dd, J = 16.6, 6.1 Hz, 1H), 2.25 (dd, J = 14.2, 7.2 Hz, 1H), 2.04 (dd, J = 14.2, 7.1 Hz, 1H), 1.63 – 1.46 (m, 4H), 1.40 – 1.34 (m, 1H), 1.30 – 1.18 (m, 1H), 1.10 – 0.98 (m, 2H), 0.98 – 0.85 (m, 1H), 0.85 – 0.72 (m, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.3, 161.8, 161.0, 141.5, 129.3, 127.8, 127.1, 94.6, 40.8, 36.3, 34.5, 33.1, 32.9, 26.2, 26.1, 26.0.

HRMS (ESI): exact mass calculated for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 311.1756, found 311.1754.

m.p. = 170-172 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 15.838 min, t_R (minor) = 13.543 min.)



4s

White solid, 85% yield, 98% *ee*.

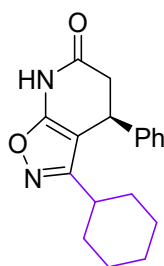
¹H NMR (500 MHz, CDCl₃) δ 8.61 (s, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 – 7.19 (m, 2H), 4.20 (dd, *J* = 7.8, 6.0 Hz, 1H), 3.12 (dd, *J* = 16.6, 7.8 Hz, 1H), 2.86 (dd, *J* = 16.6, 5.9 Hz, 1H), 1.37 (tt, *J* = 8.4, 5.1 Hz, 1H), 0.93 – 0.69 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 169.4, 164.3, 161.0, 141.5, 129.2, 127.8, 127.1, 94.8, 40.7, 34.1, 7.5, 7.5, 6.8.

HRMS (ESI): exact mass calculated for C₁₅H₁₅N₂O₂ [M + H]⁺ 255.1134, found 255.1128.

m.p. = 132-134 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 13.633 min, t_R(minor) = 16.834 min.)



4t

White solid, 77% yield, 97% *ee*.

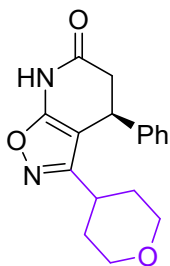
¹H NMR (500 MHz, CDCl₃) δ 8.67 (s, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.18 – 7.13 (m, 2H), 4.17 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.12 (dd, *J* = 16.5, 7.8 Hz, 1H), 2.84 (dd, *J* = 16.6, 5.0 Hz, 1H), 2.28 (tt, *J* = 12.0, 3.2 Hz, 1H), 1.83 – 1.55 (m, 5H), 1.50 – 1.39 (m, 1H), 1.34 – 1.04 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 169.4, 166.5, 161.0, 141.6, 129.2, 127.8, 127.0, 93.8, 40.8, 36.3, 34.4, 31.5, 30.4, 26.2, 26.1, 25.8.

HRMS (ESI): exact mass calculated for C₁₈H₂₁N₂O₂ [M + H]⁺ 297.1606, found 297.1599.

m.p. = 151-153 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 15.518 min, t_R(minor) = 13.371 min.)



4u

White solid, 72% yield, 95% *ee*.

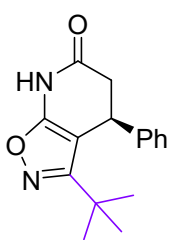
¹H NMR (500 MHz, CDCl₃) δ 8.84 (s, 1H), 7.37 – 7.27 (m, 3H), 7.16 – 7.11 (m, 2H), 4.16 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.94 – 3.86 (m, 2H), 3.30 – 3.19 (m, 2H), 3.11 (dd, *J* = 16.6, 7.9 Hz, 1H), 2.82 (dd, *J* = 16.6, 5.2 Hz, 1H), 2.57 – 2.47 (m, 1H), 1.84 – 1.72 (m, 1H), 1.68 – 1.59 (m, 2H), 1.59 – 1.52 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.2, 164.8, 161.5, 141.4, 129.4, 128.0, 127.0, 93.6, 67.6, 67.5, 40.8, 34.4, 33.6, 30.9, 30.1.

HRMS (ESI): exact mass calculated for C₁₇H₁₉N₂O₃ [M + H]⁺ 299.1398, found 299.1390.

m.p. = 159-161 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IB column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 21.863 min, t_R(minor) = 27.163 min.)



4v

White solid, 19% yield, 94% *ee*.

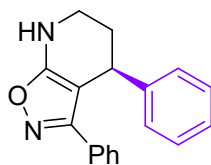
¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 1H), 7.26 – 7.19 (m, 2H), 7.19 – 7.11 (m, 1H), 7.01 – 6.96 (m, 2H), 4.21 – 4.16 (m, 1H), 3.09 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.70 (dd, *J* = 16.2, 1.6 Hz, 1H), 1.10 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 169.4, 168.4, 161.8, 141.8, 129.3, 127.7, 126.8, 93.4, 41.2, 35.0, 33.4, 28.9.

HRMS (ESI): exact mass calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 271.1448, found 271.1441.

m.p. = 165-167 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 12.757 min, t_{R} (minor) = 10.385 min.)



5

White solid, 65% yield, 97% *ee*.

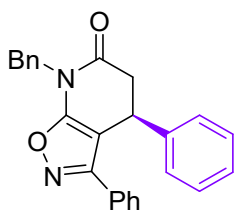
^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.43 (m, 2H), 7.32 – 7.16 (m, 8H), 4.82 (s, 1H), 4.20 (dd, J = 5.5, 2.9 Hz, 1H), 3.31 (dt, J = 12.0, 3.8 Hz, 1H), 3.18 (td, J = 11.8, 2.8 Hz, 1H), 2.13 (dddd, J = 13.6, 11.8, 5.5, 3.9 Hz, 1H), 1.93 (dq, J = 13.5, 3.1 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 167.5, 161.3, 145.1, 129.9, 129.3, 128.63, 128.55, 128.1, 127.6, 126.7, 88.4, 38.1, 36.3, 31.8.

HRMS (ESI): exact mass calculated for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$ 277.1335, found 277.1332.

m.p. = 167-169 °C.

The *ee* value was determined by HPLC analysis on a Chiralcel IG column (*n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_{R} (major) = 12.429 min, t_{R} (minor) = 19.025 min.)



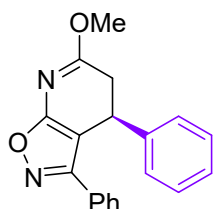
6

Colorless oil, 87% yield, 97% *ee*.

¹H NMR (500 MHz, CDCl₃) δ 7.44 (dt, *J* = 8.4, 2.2 Hz, 4H), 7.38 – 7.25 (m, 6H), 7.22 – 7.14 (m, 3H), 6.94 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.24 (d, *J* = 14.6 Hz, 1H), 4.98 (d, *J* = 14.6 Hz, 1H), 4.22 (dd, *J* = 7.9, 2.4 Hz, 1H), 3.19 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.92 (dd, *J* = 16.1, 2.4 Hz, 1H).
¹³C NMR (126 MHz, CDCl₃) δ 167.6, 164.0, 161.1, 141.0, 136.0, 130.1, 129.3, 128.9, 128.9, 128.8, 128.5, 128.2, 127.6, 127.5, 126.8, 94.8, 45.1, 41.6, 33.6.

HRMS (ESI): exact mass calculated for C₂₅H₂₁N₂O₂ [M + H]⁺ 381.1598, found 381.1593.

The *ee* value was determined by HPLC analysis on a Chiralcel IA column (*n*-hexane/isopropanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 6.004 min, t_R(minor) = 9.165 min.)



7

Colorless oil, 90% yield, 96% *ee*.

¹H NMR (500 MHz, CDCl₃) δ 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.06 (m, 5H), 7.03 – 6.98 (m, 2H), 4.10 (dd, *J* = 7.8, 4.2 Hz, 1H), 3.34 (s, 3H), 2.82 (dd, *J* = 15.5, 7.8 Hz, 1H), 2.60 (dd, *J* = 15.5, 4.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 180.5, 180.0, 160.3, 141.9, 131.6, 129.3, 129.0, 128.4, 127.4, 126.7, 125.5, 102.0, 40.8, 39.0, 35.0.

HRMS (ESI): exact mass calculated for C₁₉H₁₇N₂O₂ [M + H]⁺ 305.1285, found 305.1280.

The *ee* value was determined by HPLC analysis on a Chiralcel ID column (*n*-hexane/isopropanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, t_R(major) = 33.340 min, t_R(minor) = 46.483 min.)

5. X-Ray Diffraction Data

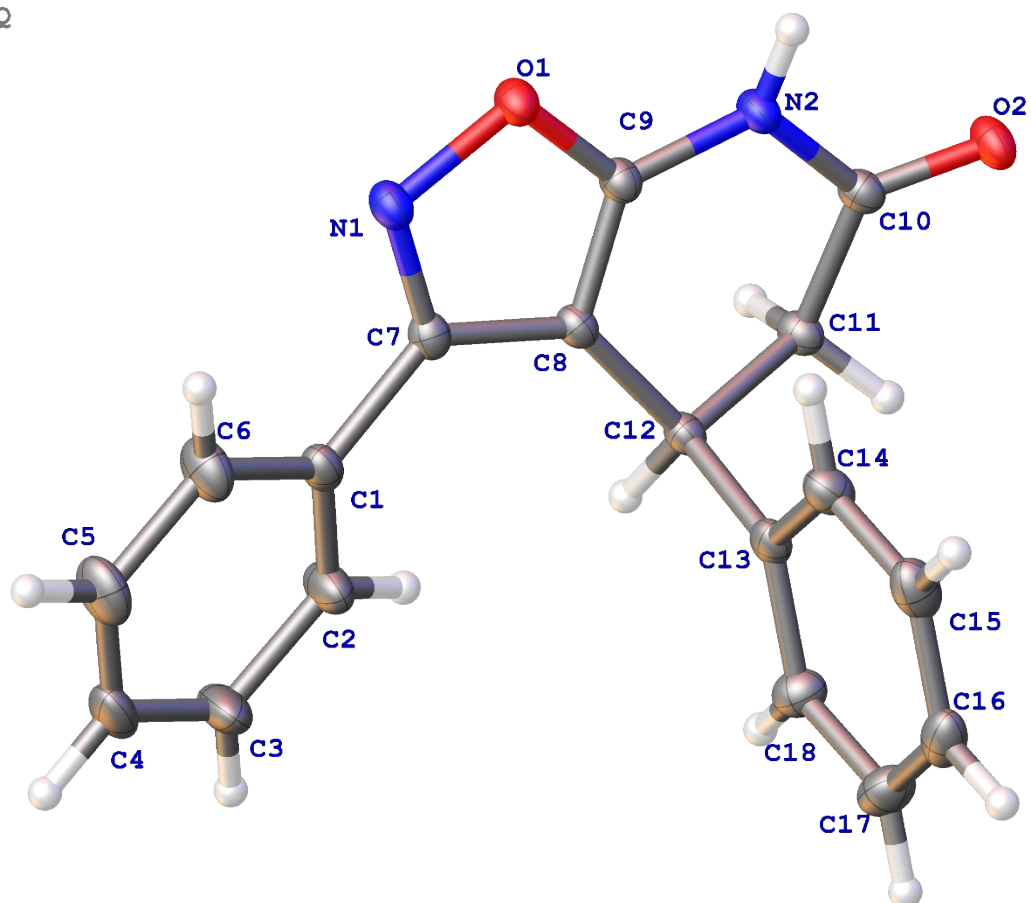
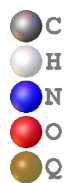


Table 1 Crystal data and structure refinement for 3a.

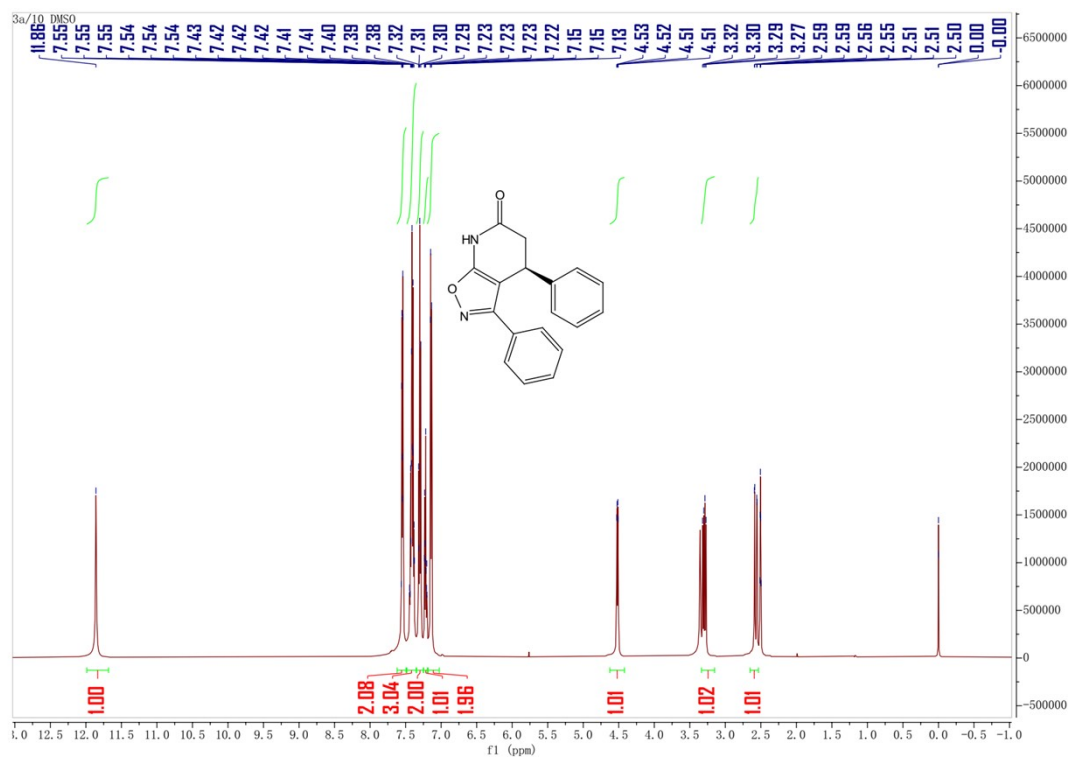
Identification code	3a
Empirical formula	C ₁₈ H ₁₄ N ₂ O ₂
Formula weight	290.31
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	I2
a/Å	8.5336(3)
b/Å	6.6348(2)
c/Å	25.9444(9)
α/°	90
β/°	97.641(3)
γ/°	90
Volume/Å ³	1455.89(8)

Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.324
μ/mm^{-1}	0.709
F(000)	608.0
Crystal size/ mm^3	$0.14 \times 0.1 \times 0.08$
Radiation	Cu K α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	6.876 to 142.694
Index ranges	$-10 \leq h \leq 10, -7 \leq k \leq 5, -31 \leq l \leq 21$
Reflections collected	3176
Independent reflections	1806 [$R_{\text{int}} = 0.0171, R_{\text{sigma}} = 0.0226$]
Data/restraints/parameters	1806/1/203
Goodness-of-fit on F^2	1.052
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0328, wR_2 = 0.0865$
Final R indexes [all data]	$R_1 = 0.0335, wR_2 = 0.0876$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.19/-0.18
Flack parameter	-0.1(2)

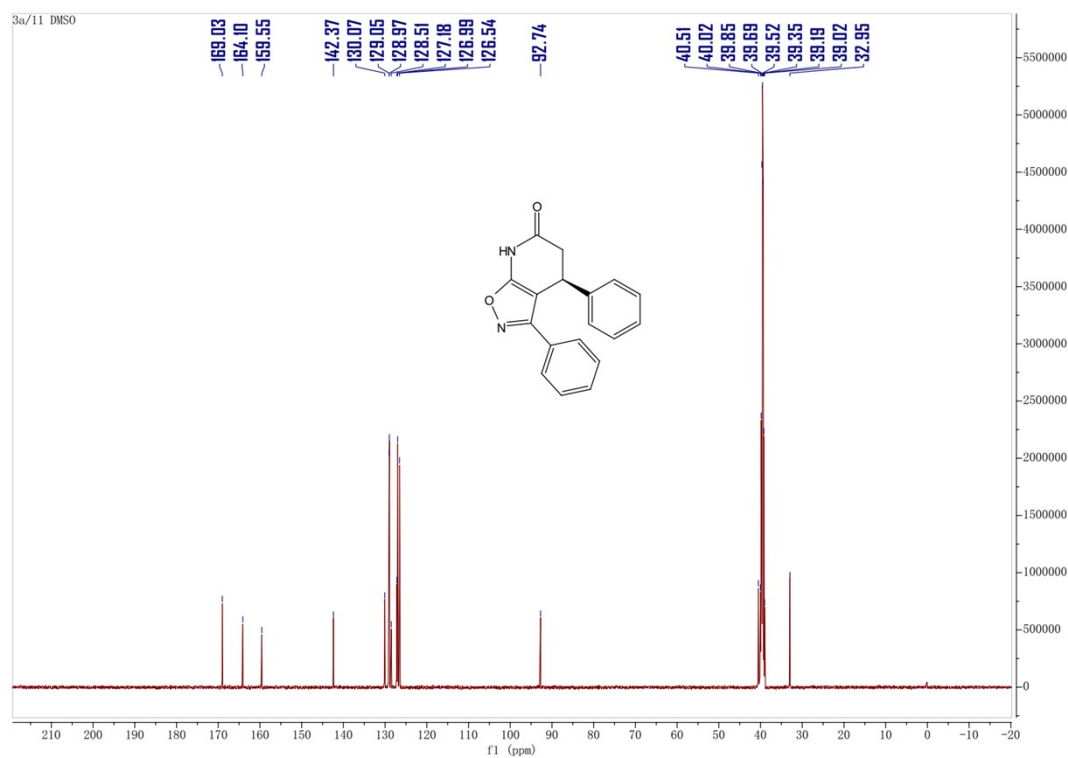
6. References

1. M. Lang and J. Wang, N-Heterocyclic Carbene-Catalyzed Enantioselective β -Amination of α -Bromoaldehydes Enabled by a Proton-Shuttling Strategy, *Eur. J. Org. Chem.*, 2018, **2018**, 2958.
2. Y. Ge, W. Sun, Y. Chen, Y. Huang, Z. Liu, Y. Jiang and T.-P. Loh, Reactions of 5-Aminoisoxazoles with α -Diazocarbonyl Compounds: Wolff Rearrangement vs N-H Insertion, *J. Org. Chem.* 2019, **84**, 2676.

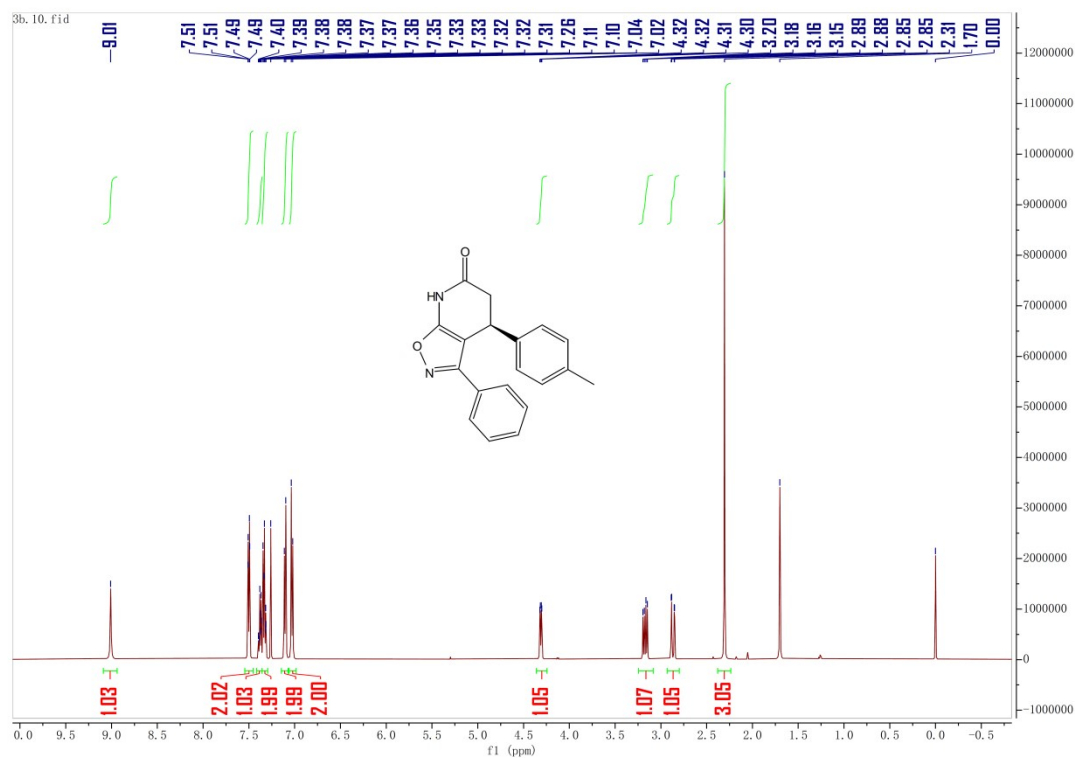
7. Copies of NMR Spectra



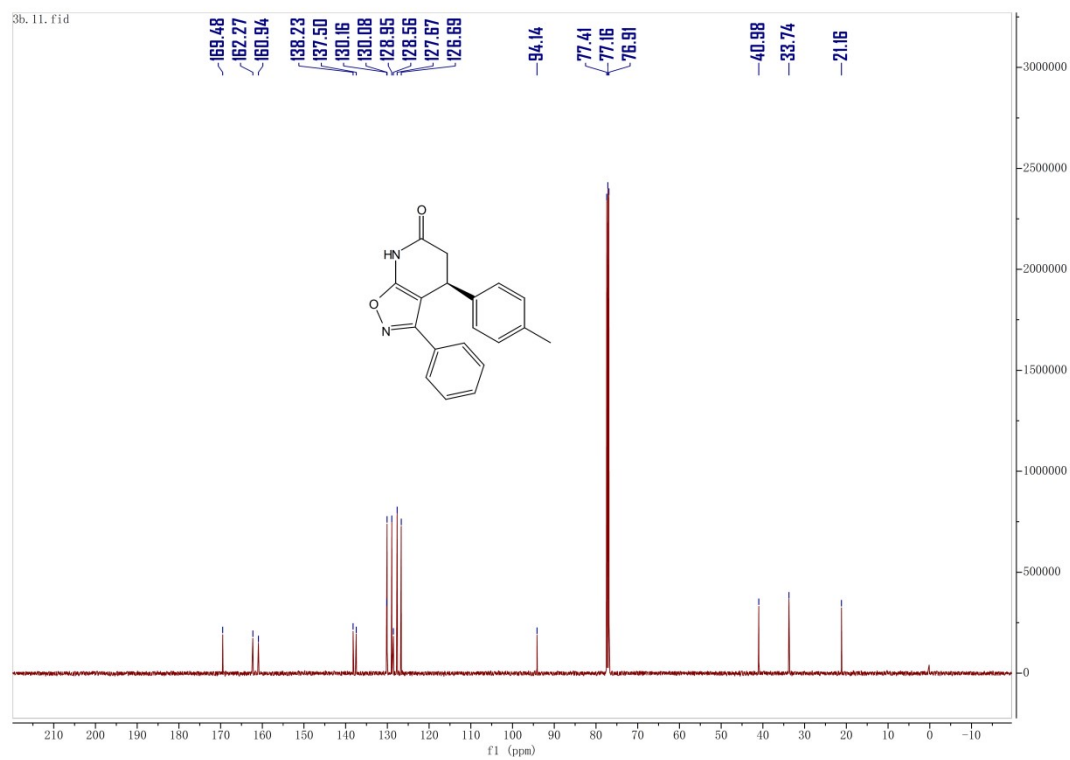
^1H NMR spectrum of **3a**



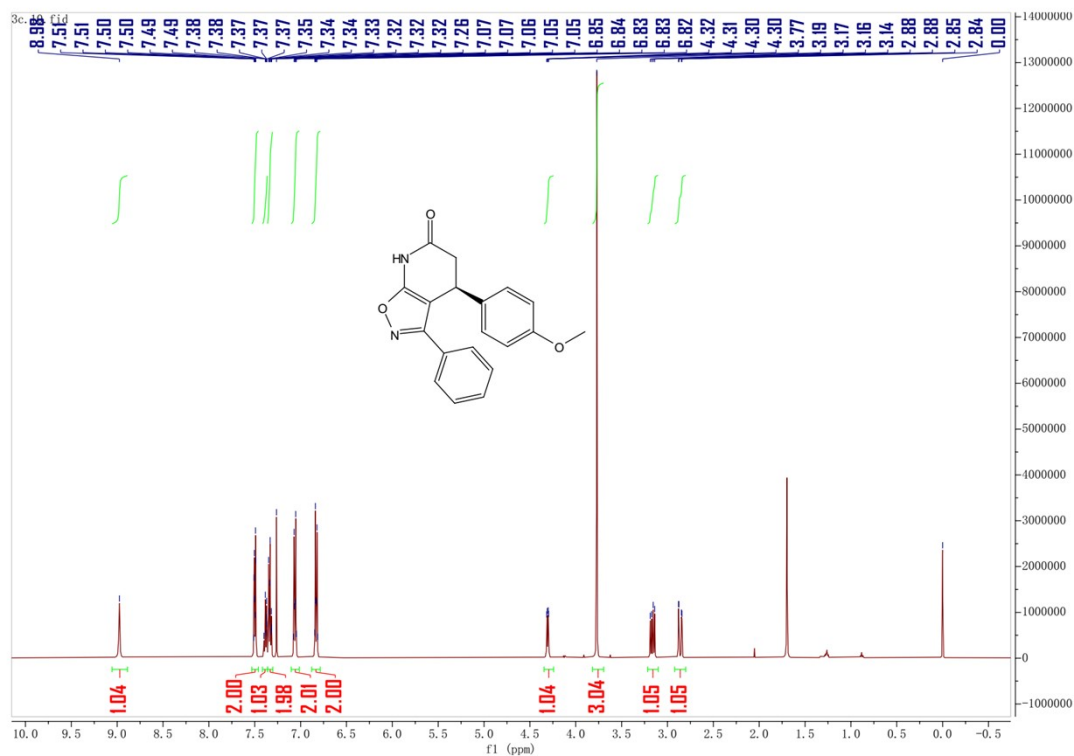
^{13}C NMR spectrum of **3a**



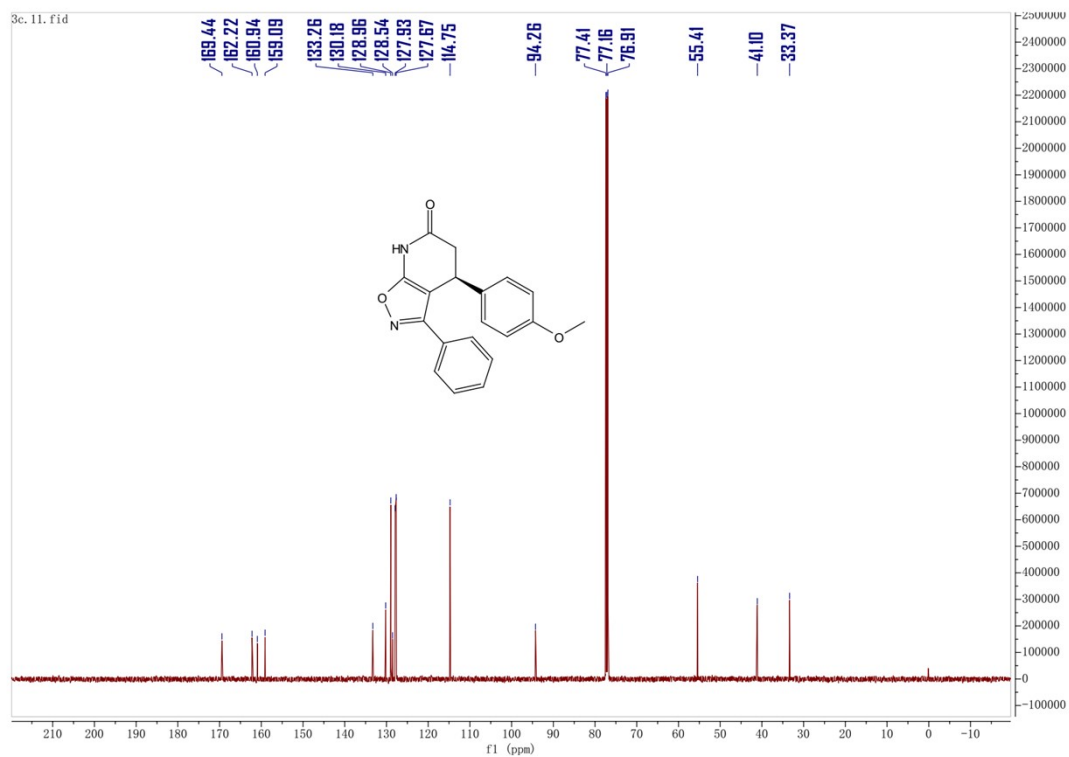
$^1\text{H NMR}$ spectrum of **3b**



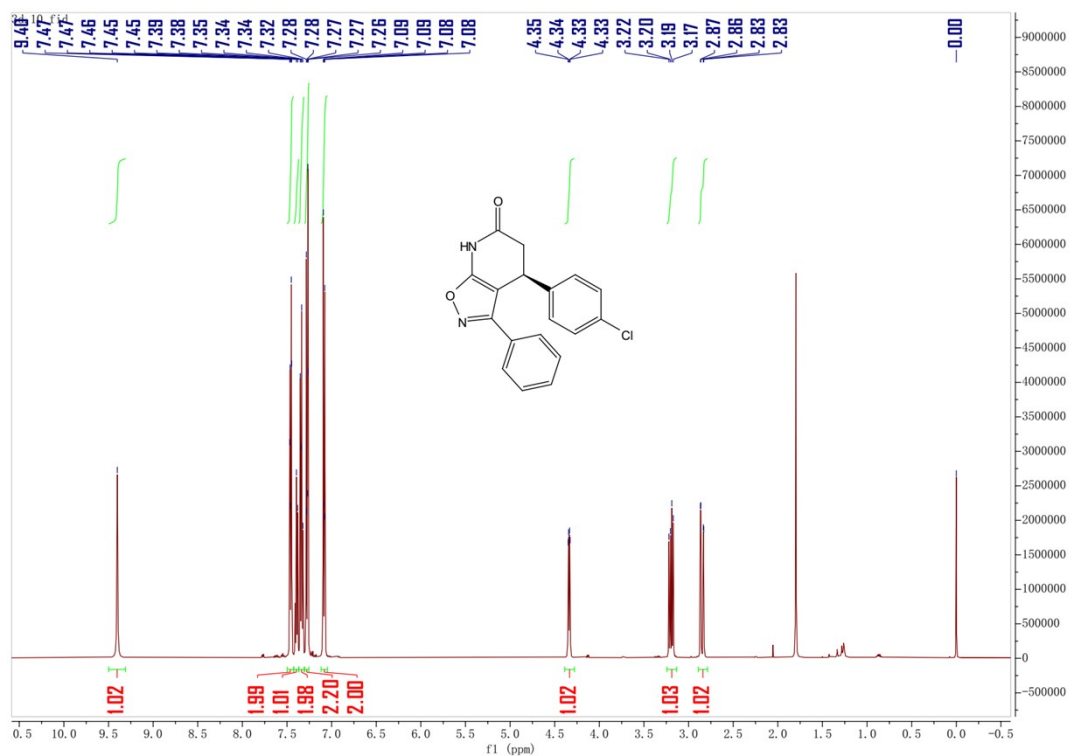
$^{13}\text{C NMR}$ spectrum of **3b**



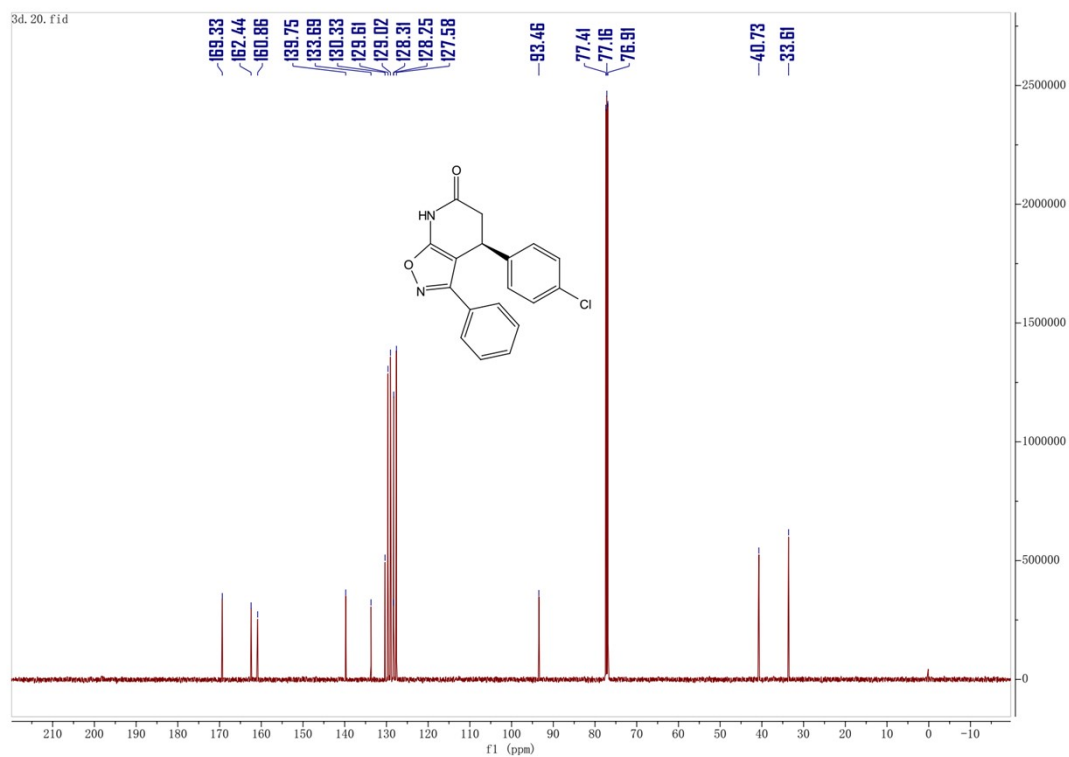
^1H NMR spectrum of **3c**



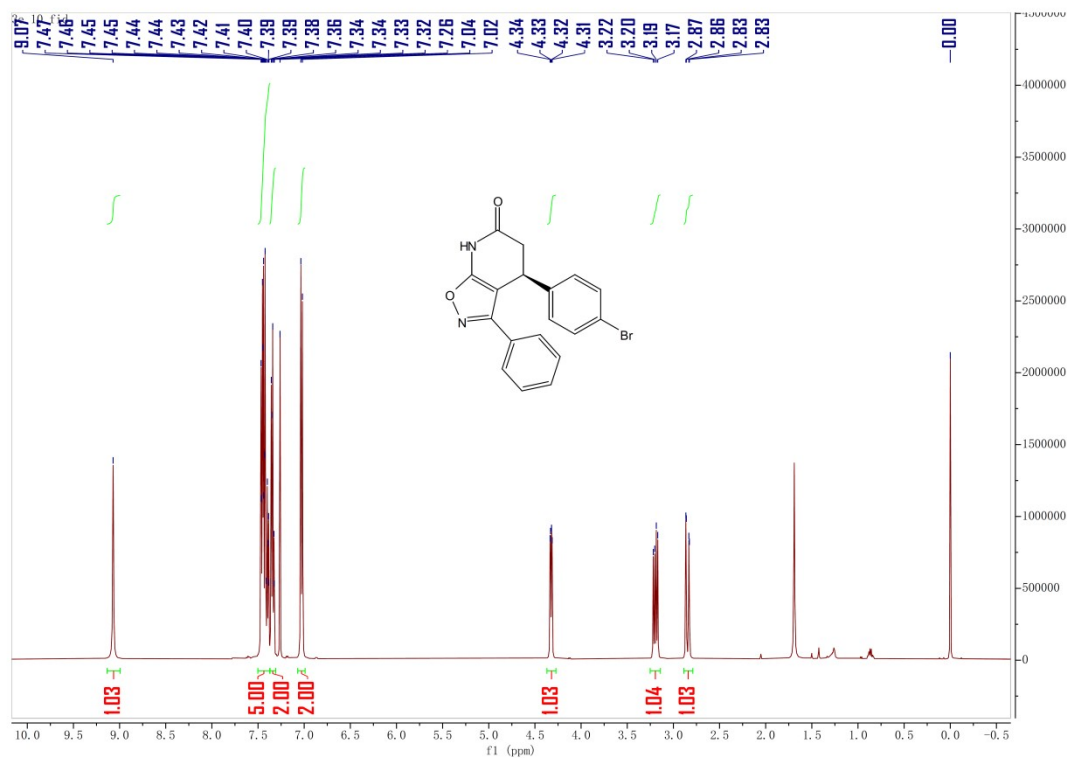
^{13}C NMR spectrum of **3c**



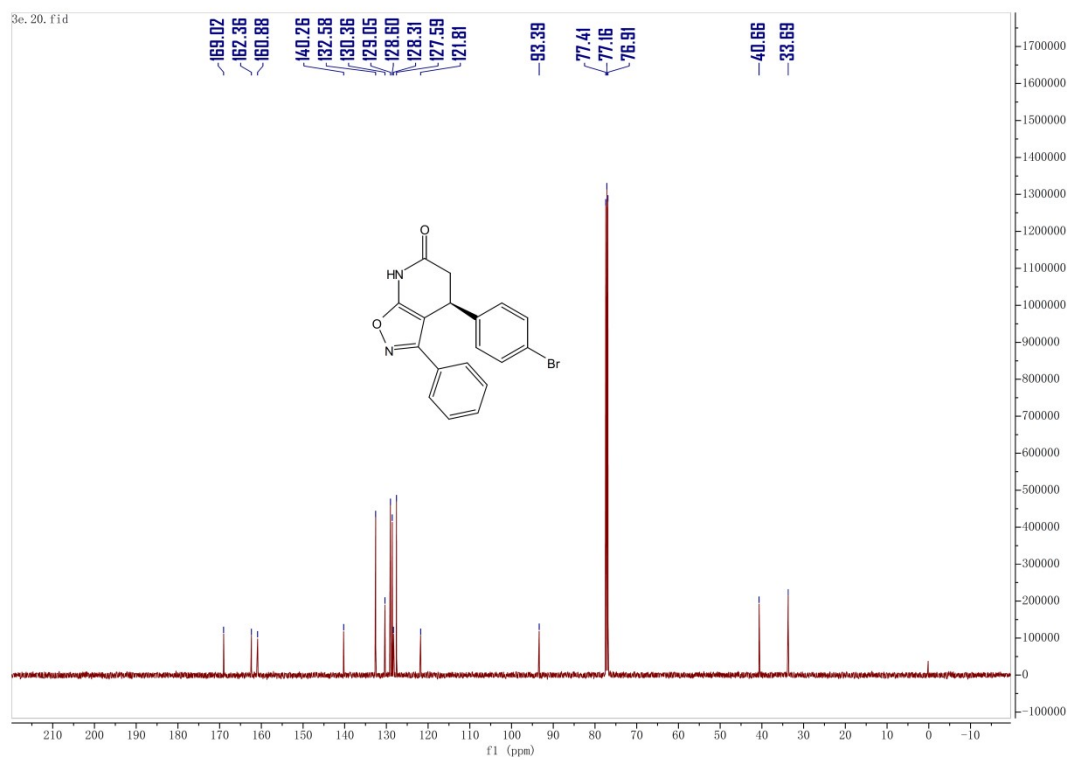
¹H NMR spectrum of 3d



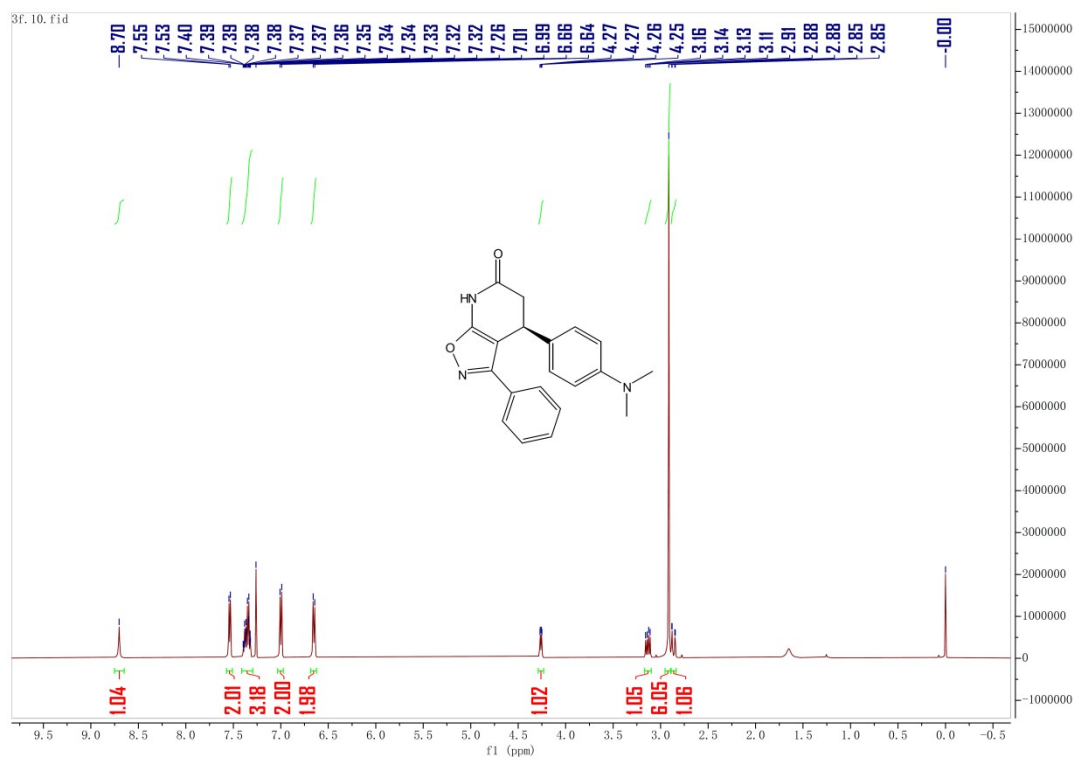
¹³C NMR spectrum of 3d



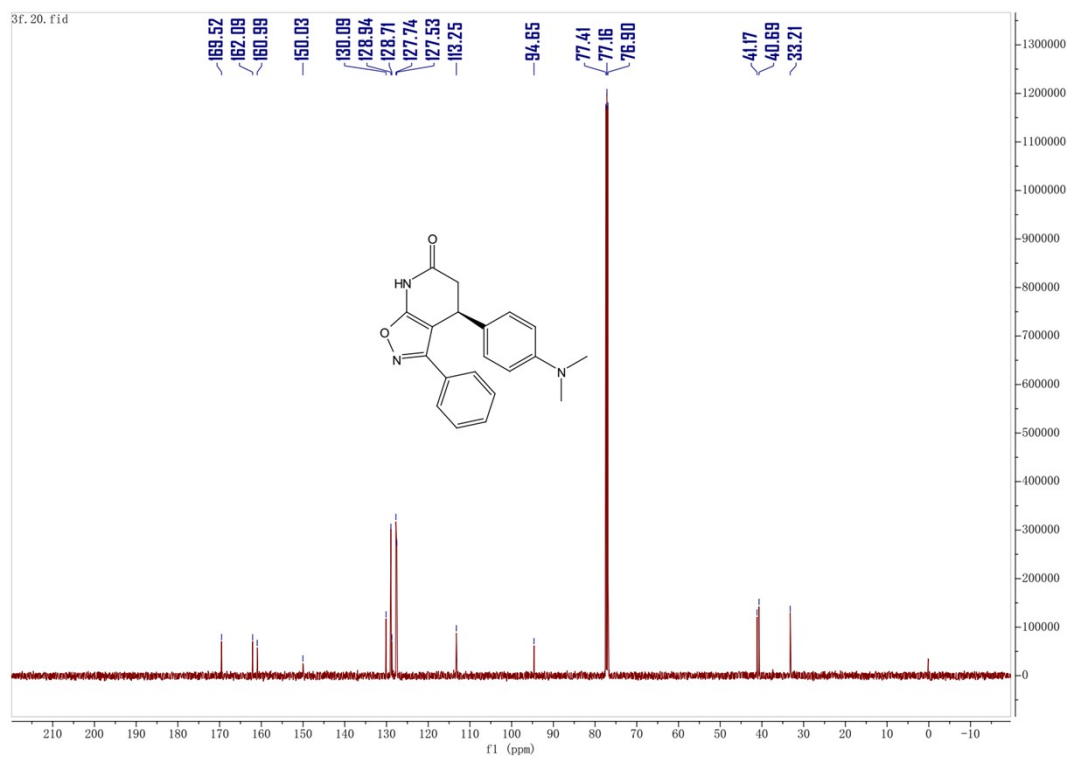
¹H NMR spectrum of 3e



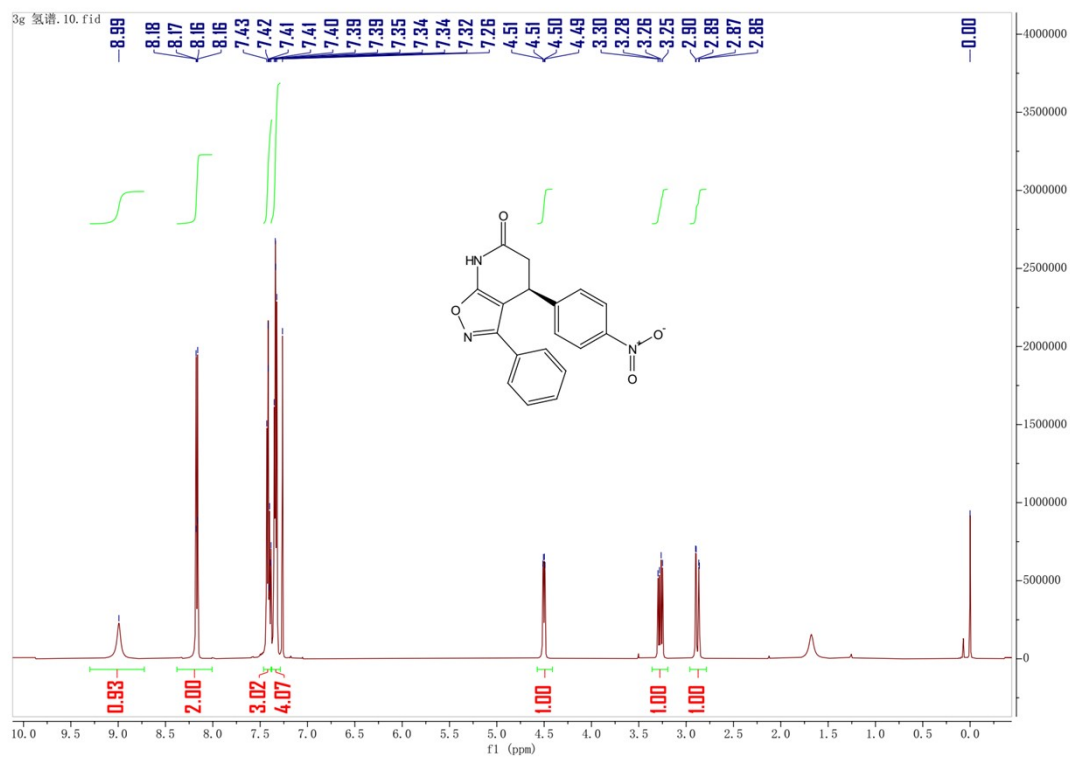
¹³C NMR spectrum of 3e



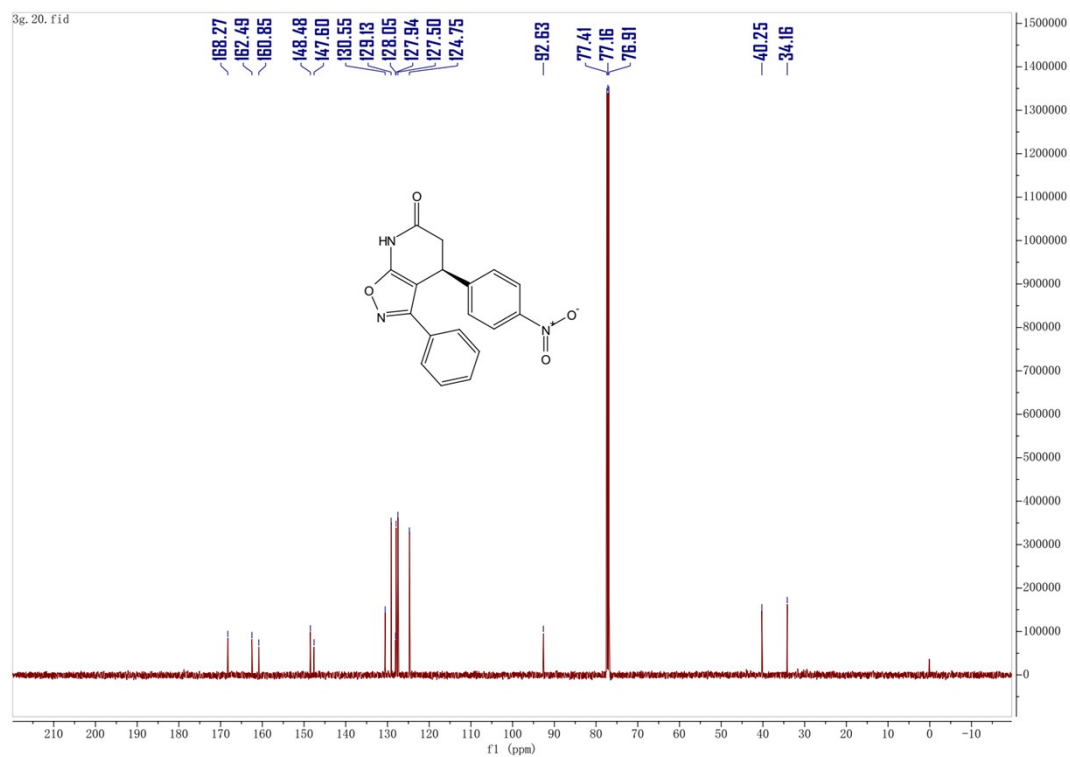
^1H NMR spectrum of **3f**



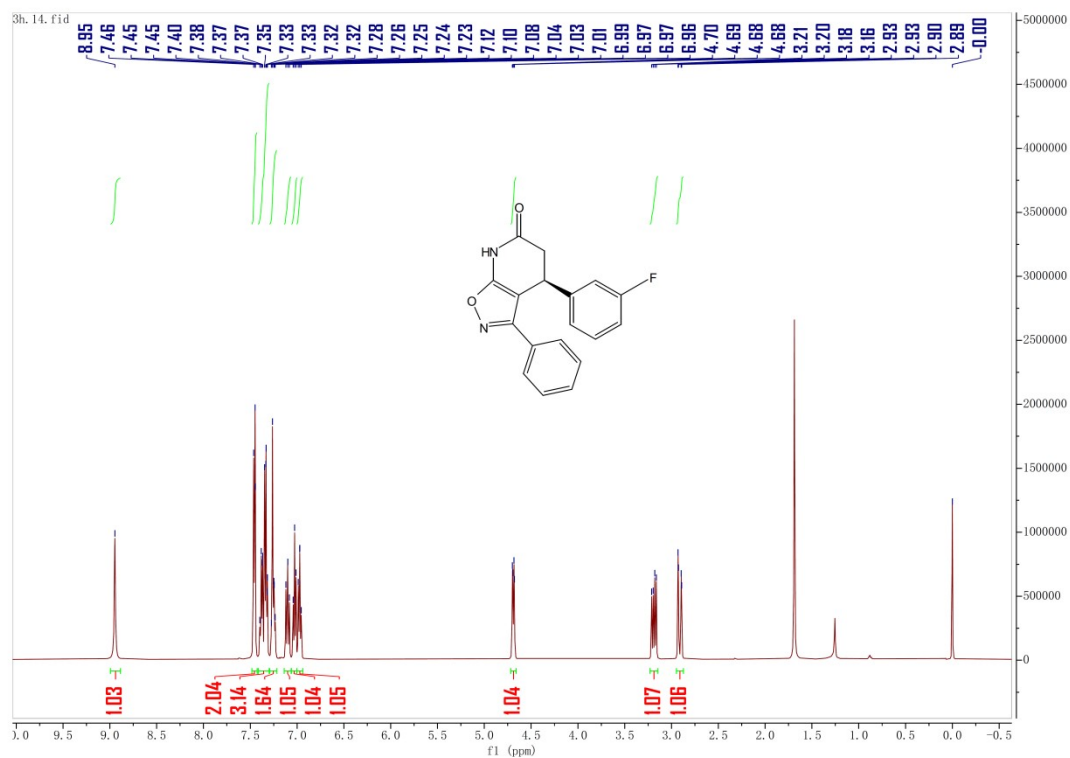
^{13}C NMR spectrum of **3f**



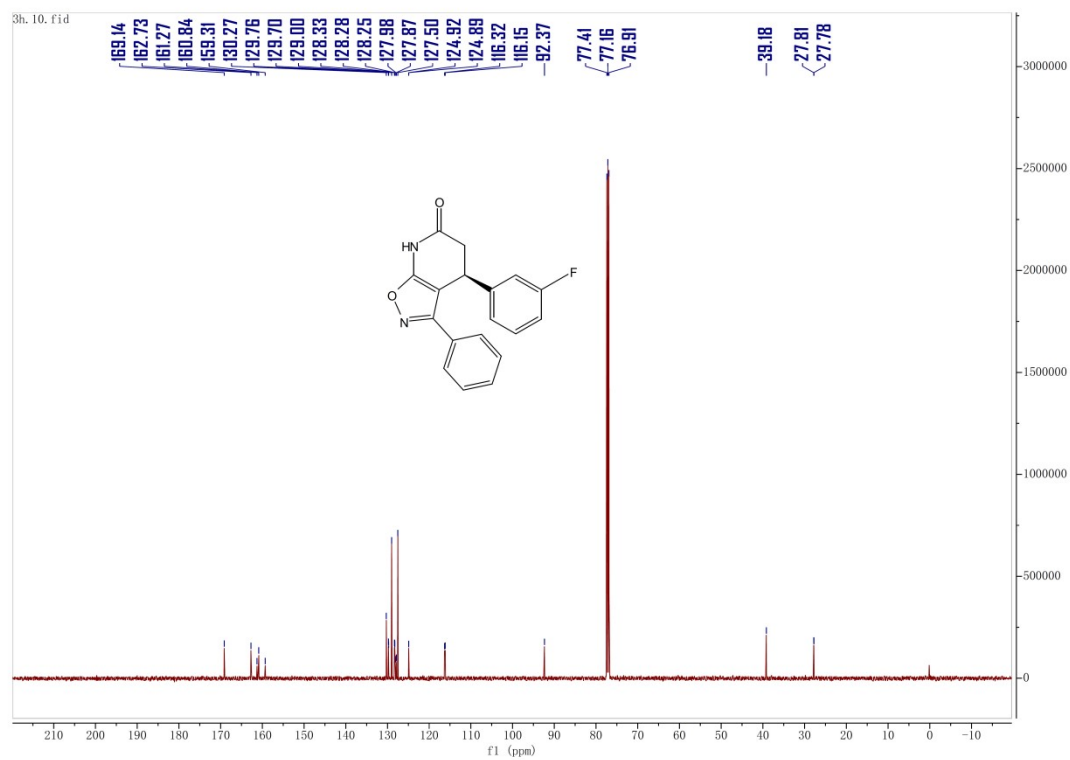
^1H NMR spectrum of **3g**



^{13}C NMR spectrum of **3g**



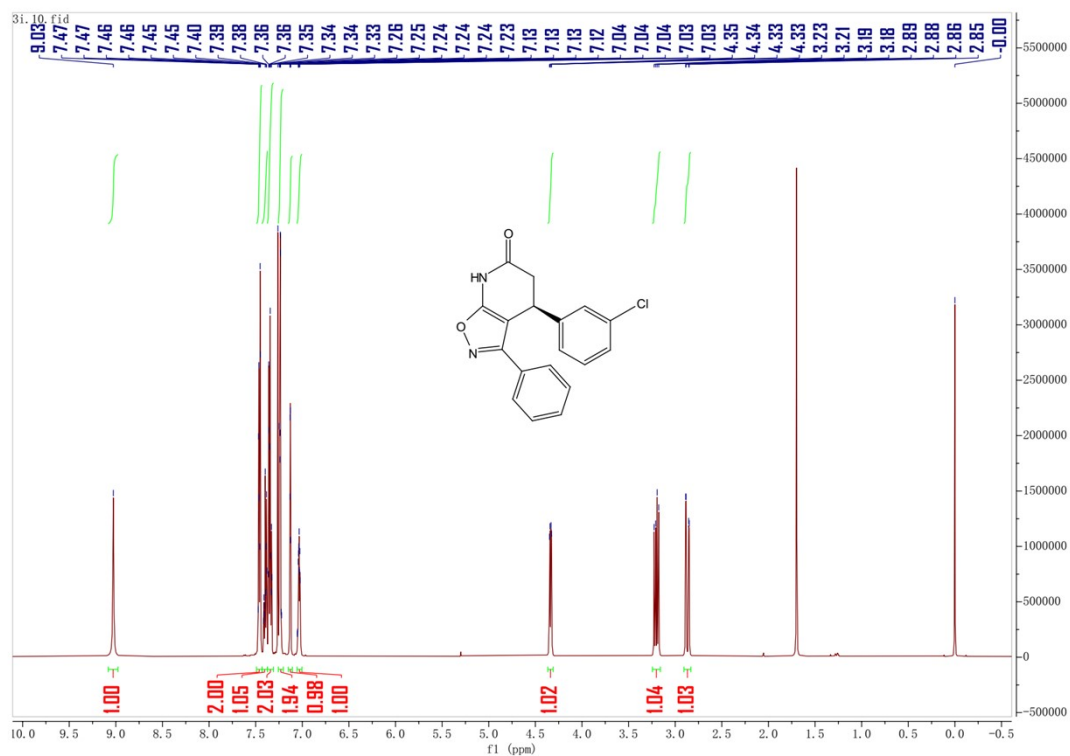
^1H NMR spectrum of **3h**



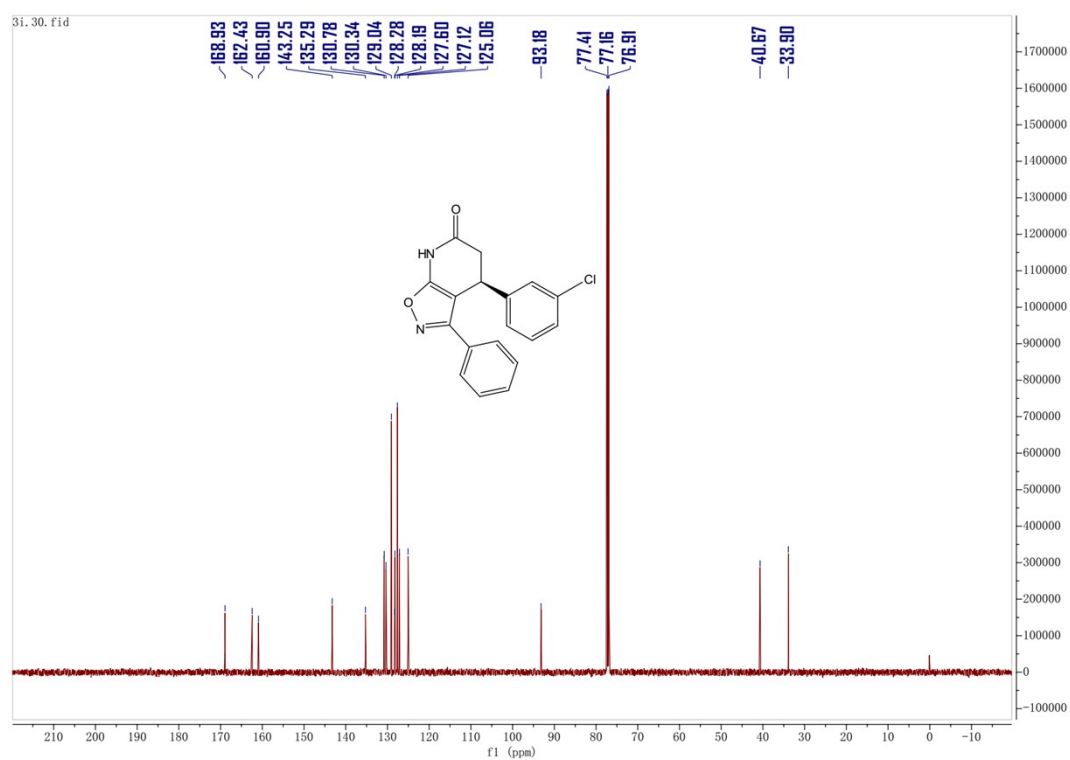
^{13}C NMR spectrum of **3h**



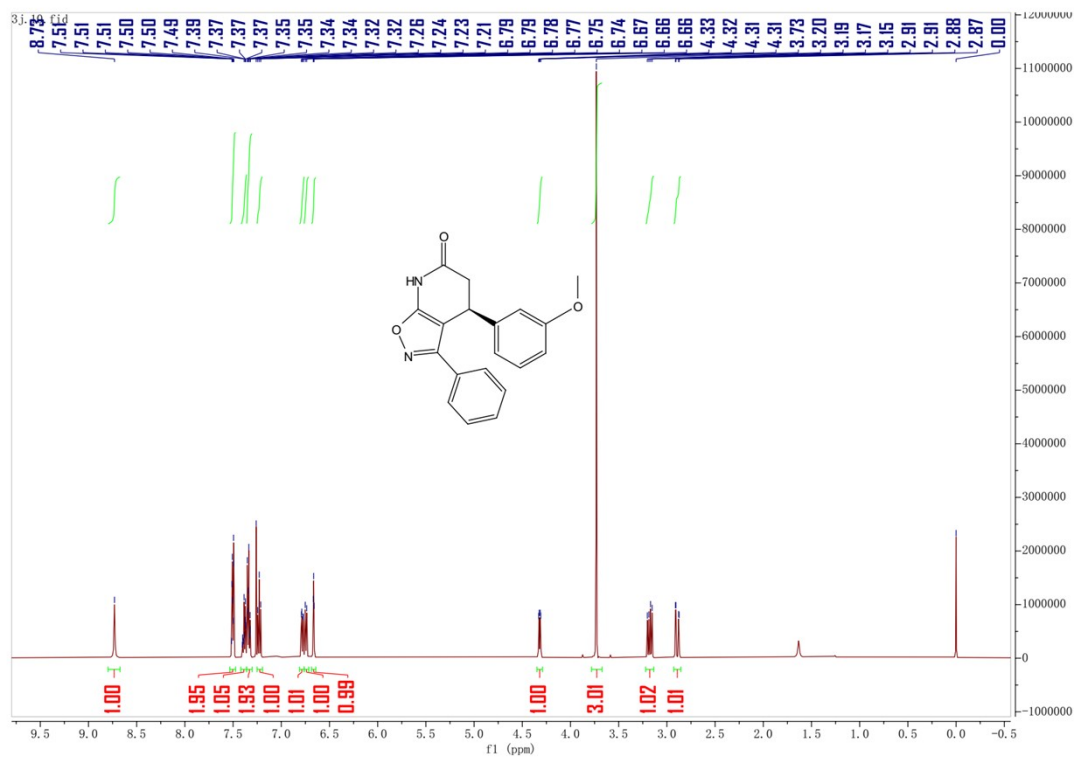
^{19}F NMR spectrum of **3h**



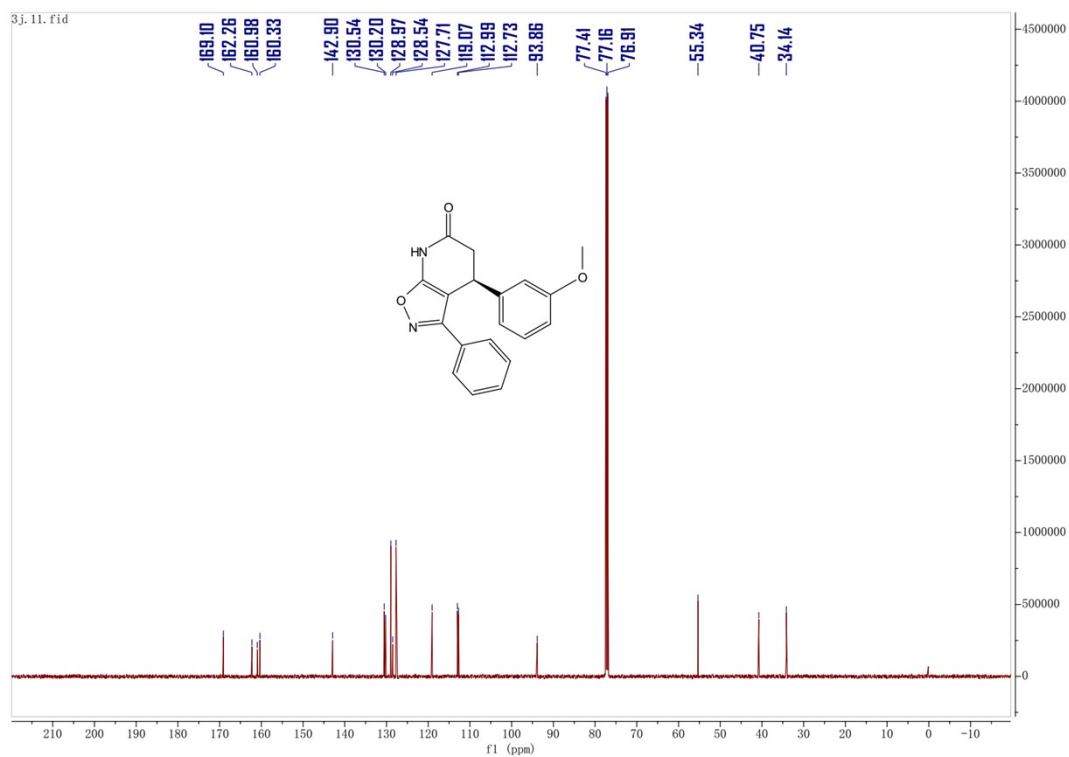
¹H NMR spectrum of **3i**



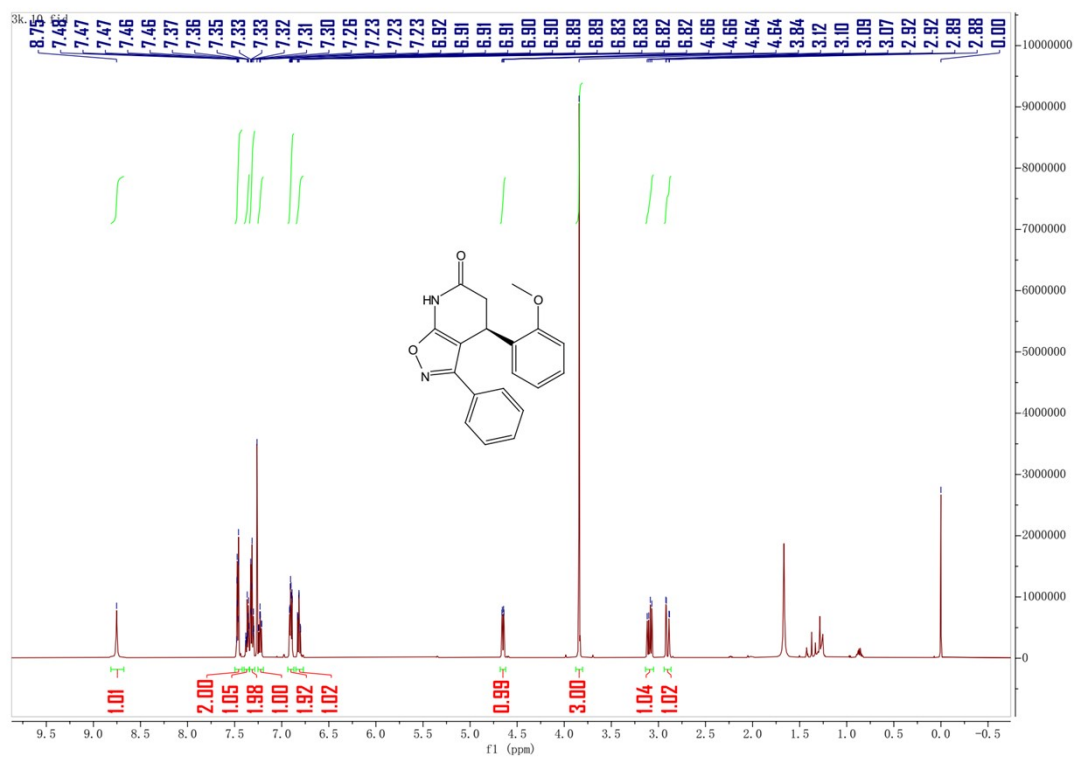
¹³C NMR spectrum of **3i**



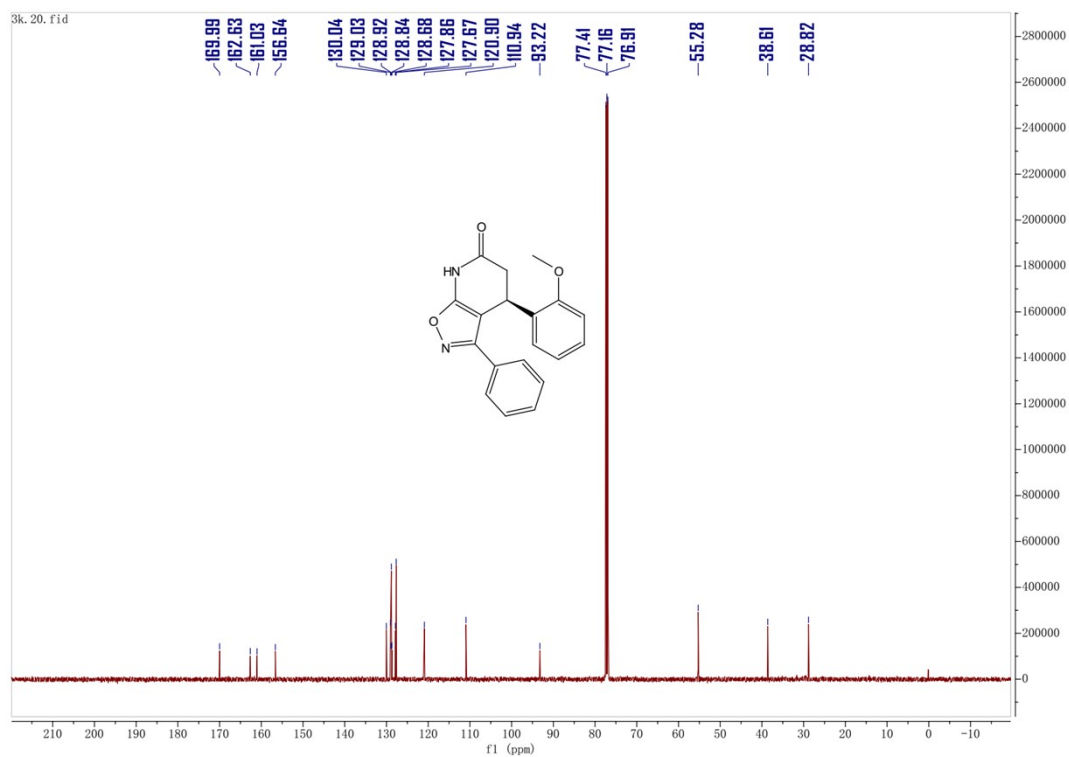
^1H NMR spectrum of **3j**



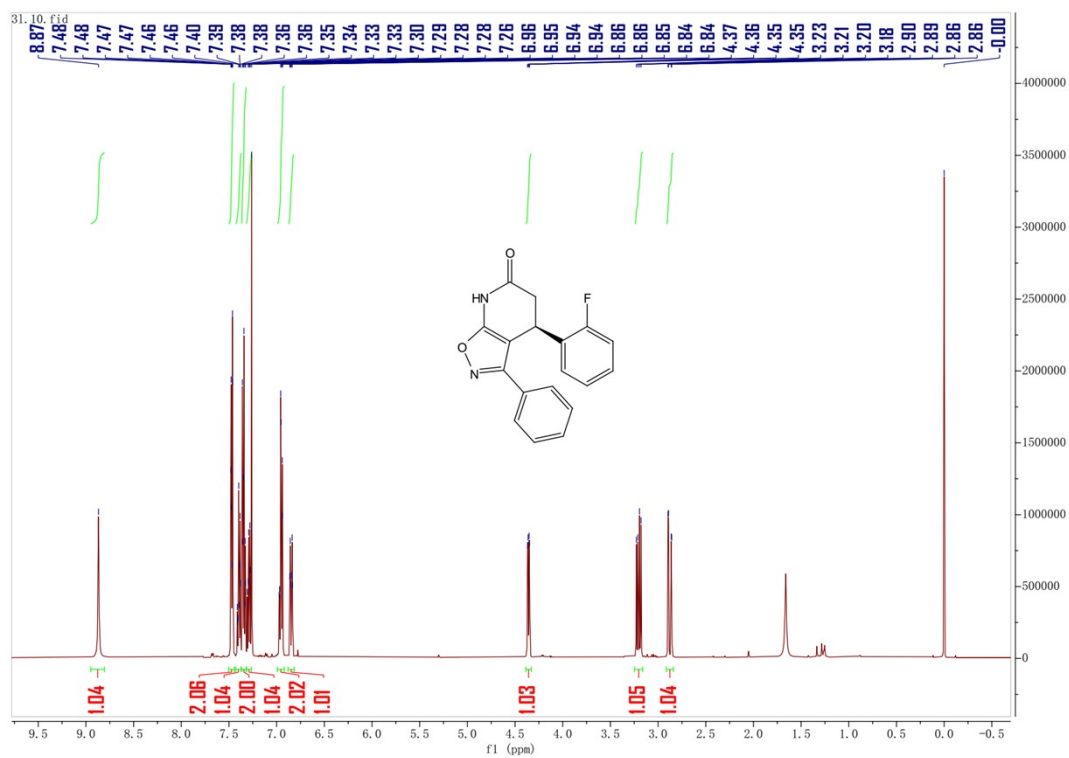
^{13}C NMR spectrum of **3j**



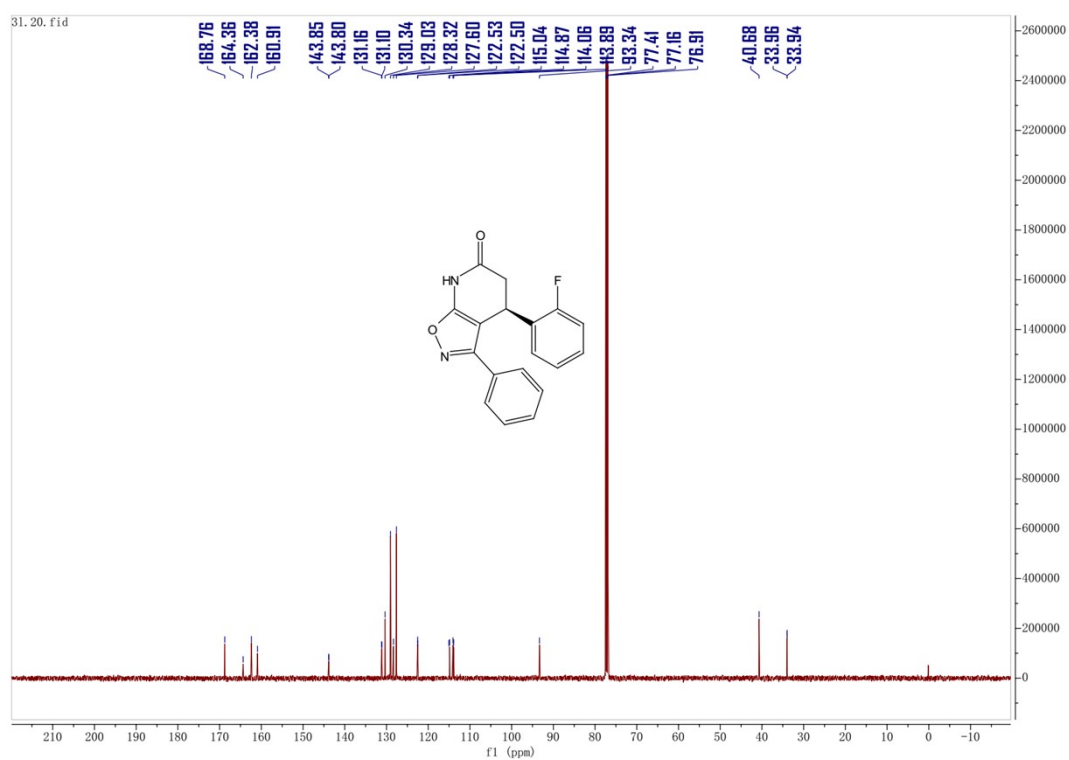
^1H NMR spectrum of **3k**



^{13}C NMR spectrum of **3k**



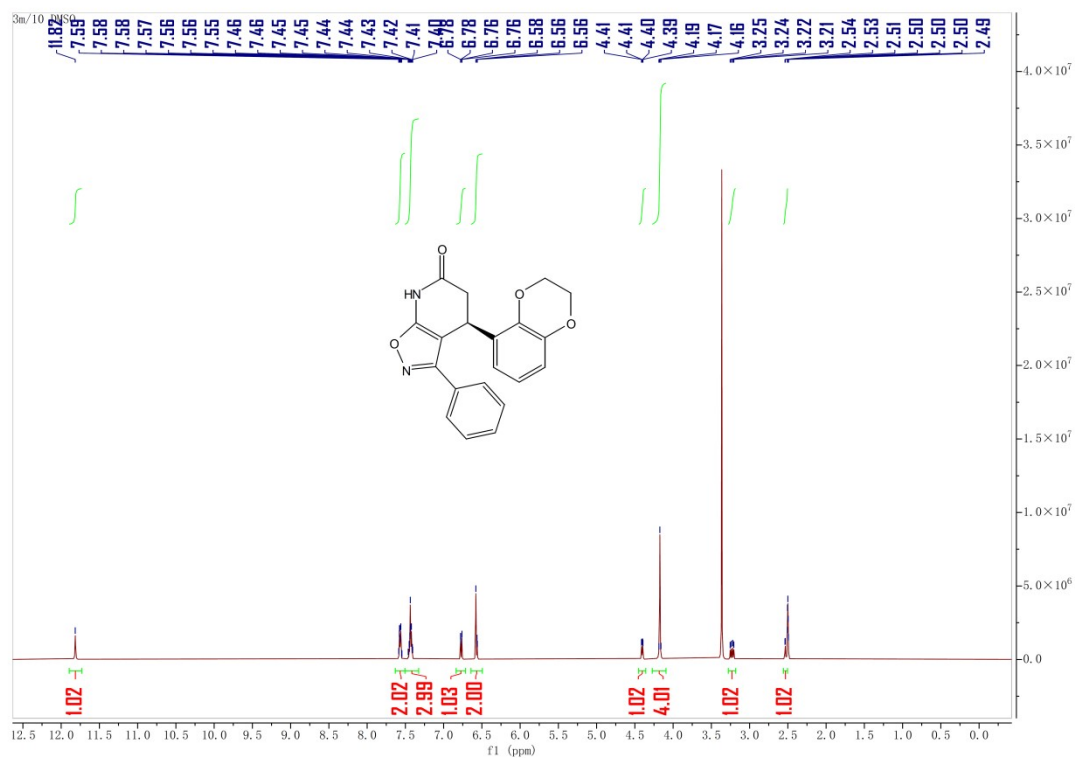
¹H NMR spectrum of **31**



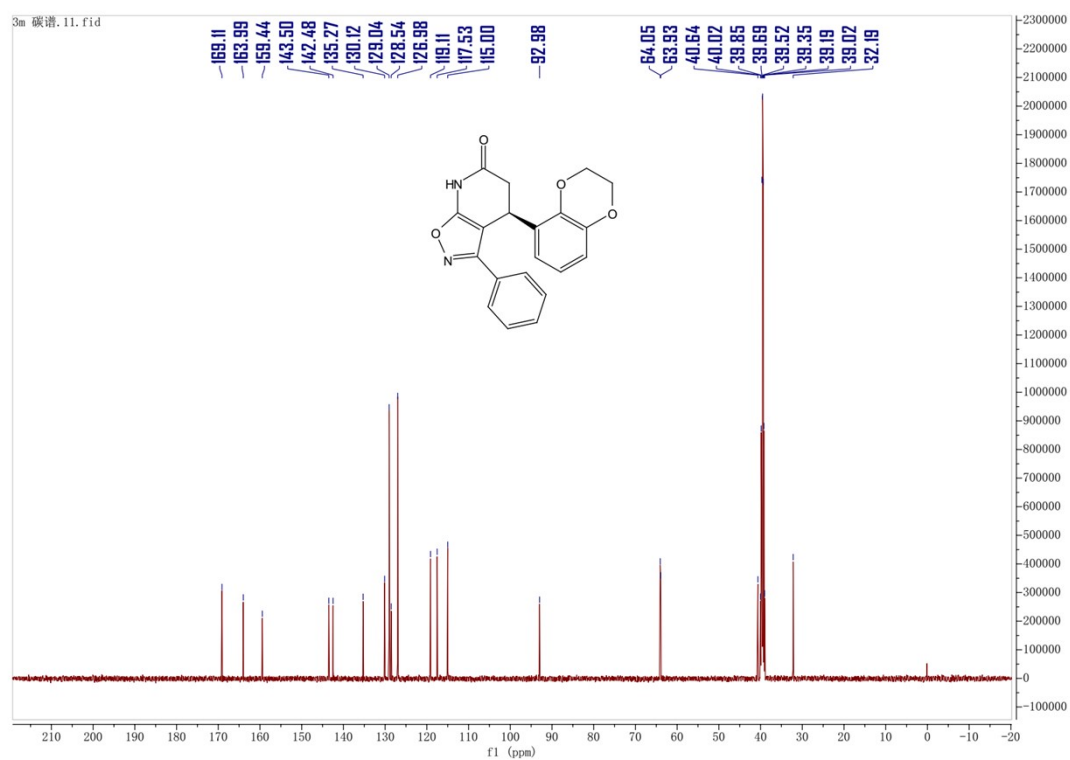
¹³C NMR spectrum of **31**



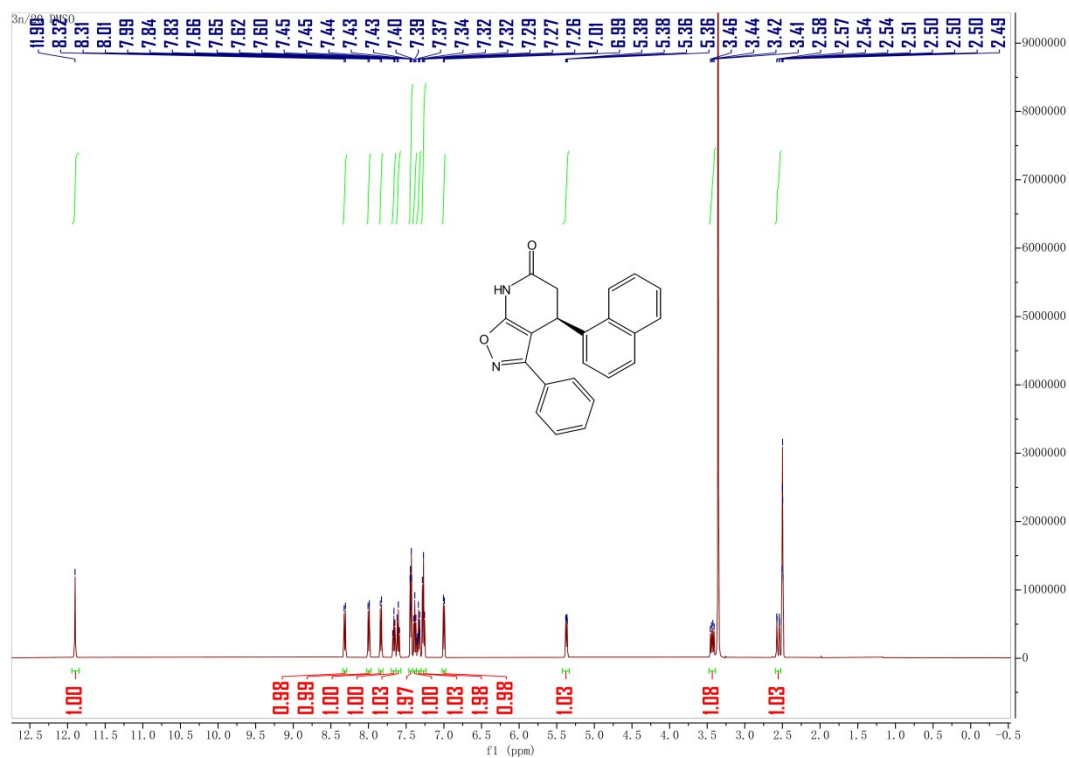
^{19}F NMR spectrum of **31**



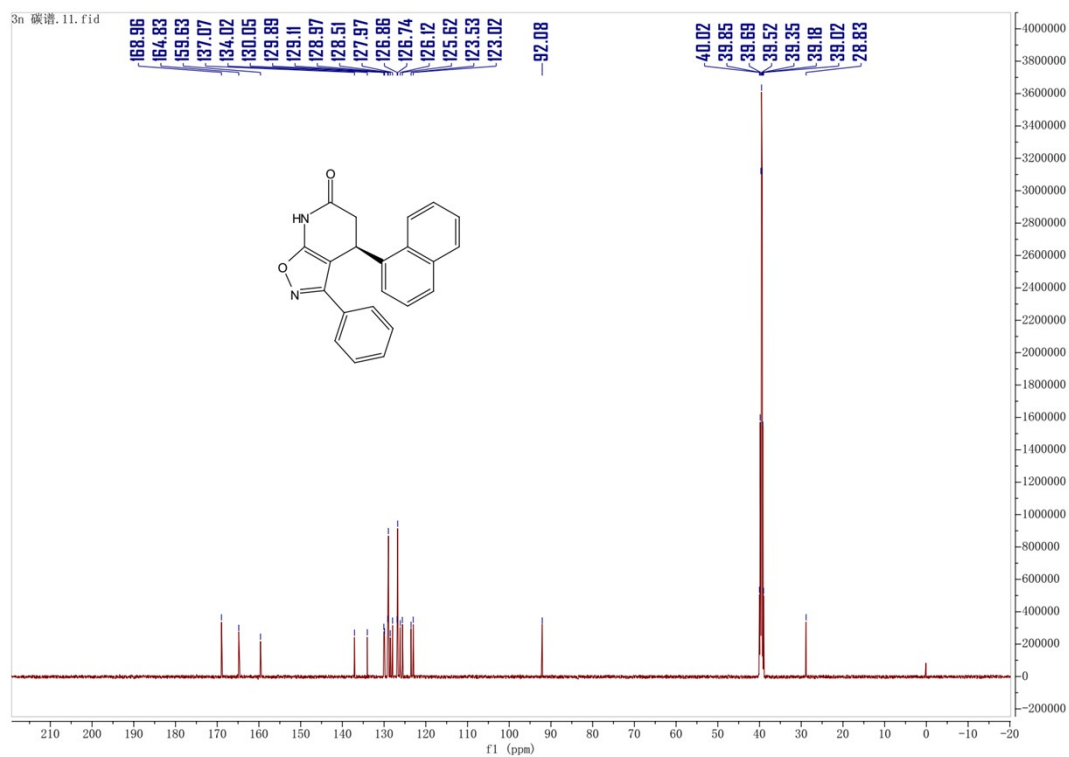
^1H NMR spectrum of **3m**



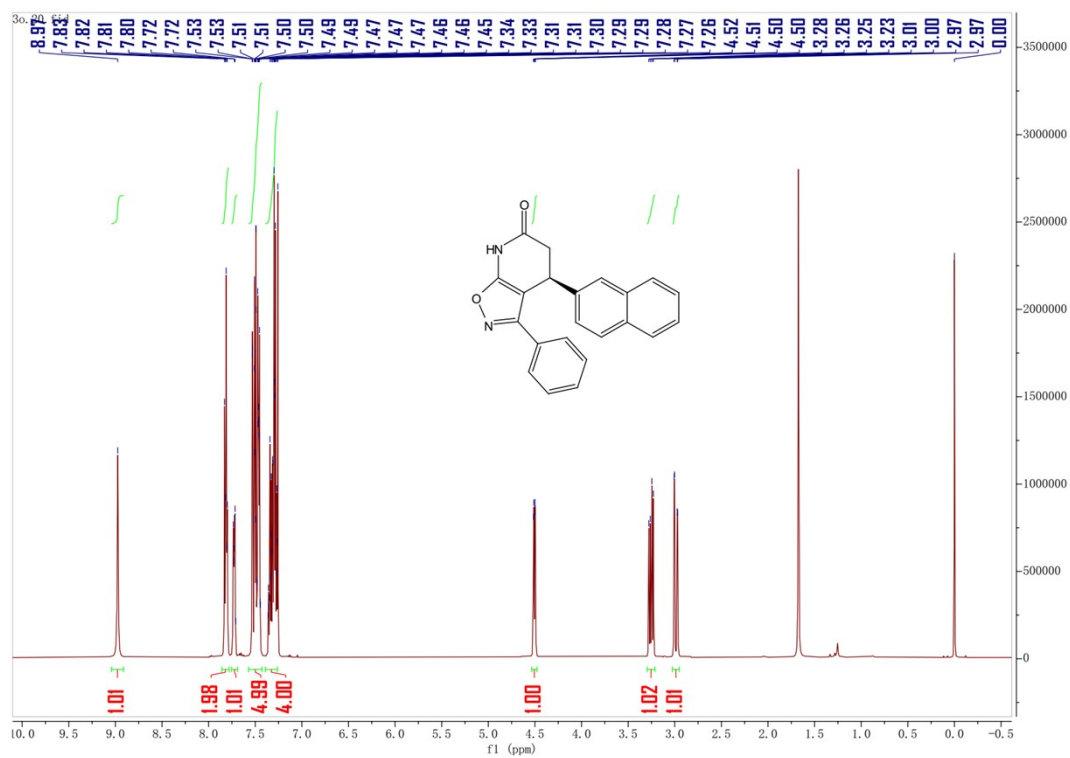
^{13}C NMR spectrum of **3m**



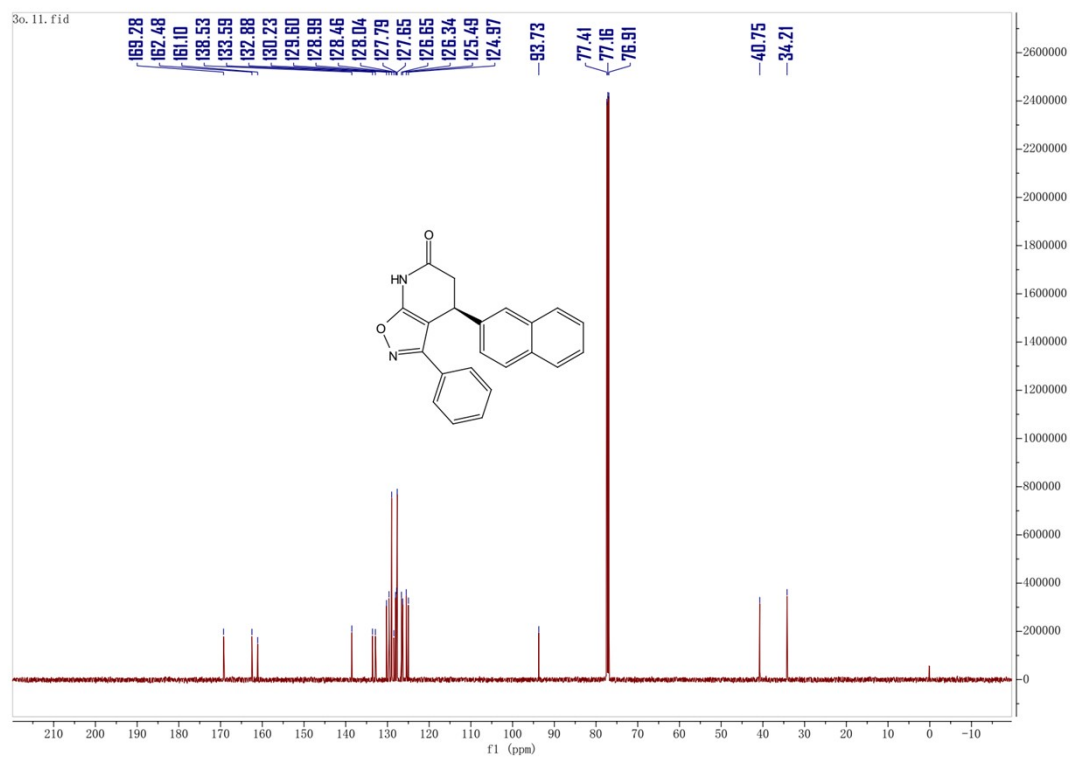
^1H NMR spectrum of **3n**



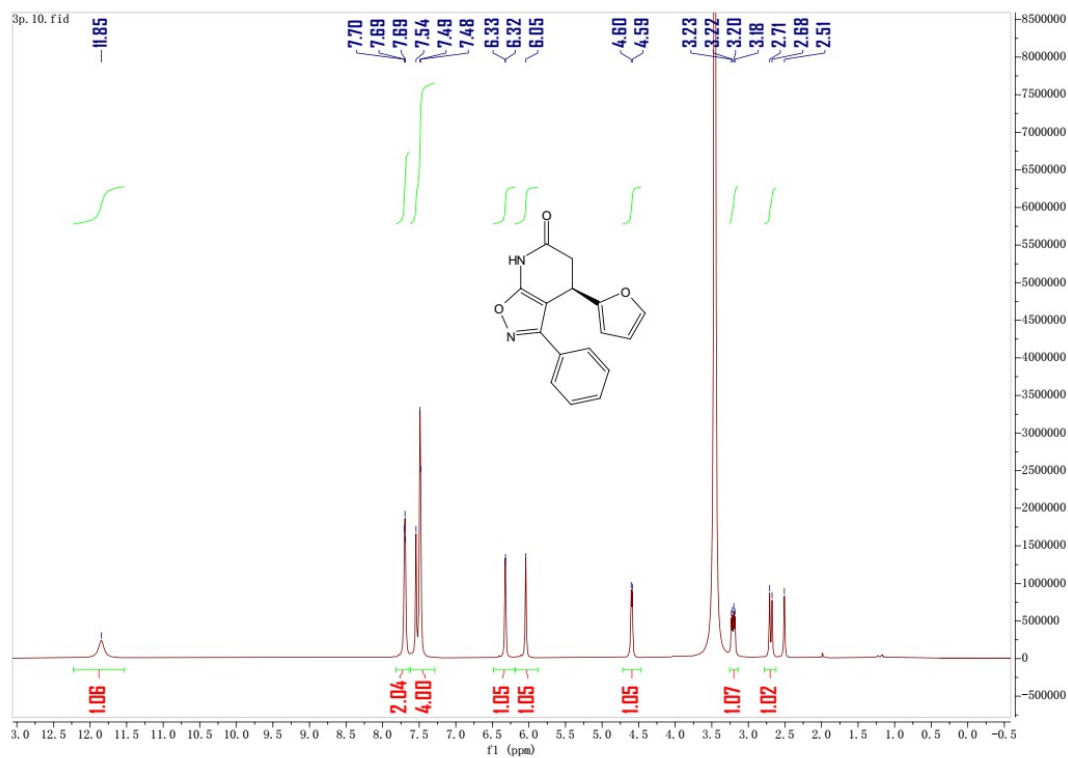
^{13}C NMR spectrum of **3n**



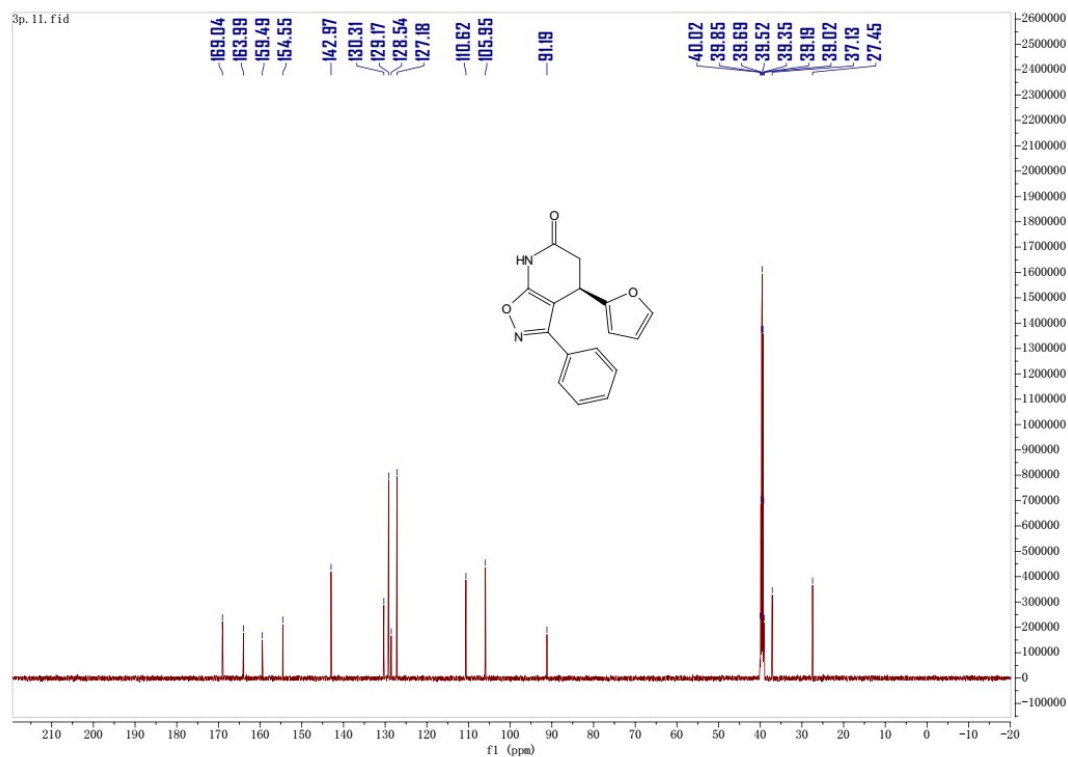
^1H NMR spectrum of **3o**



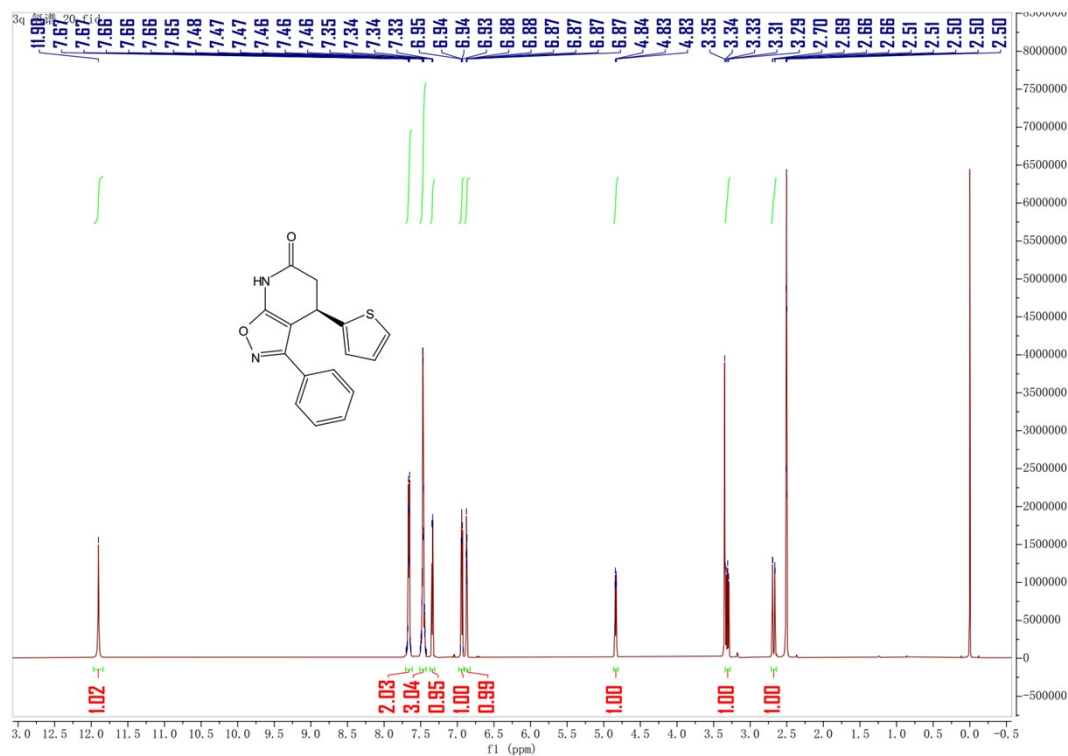
^{13}C NMR spectrum of **3o**



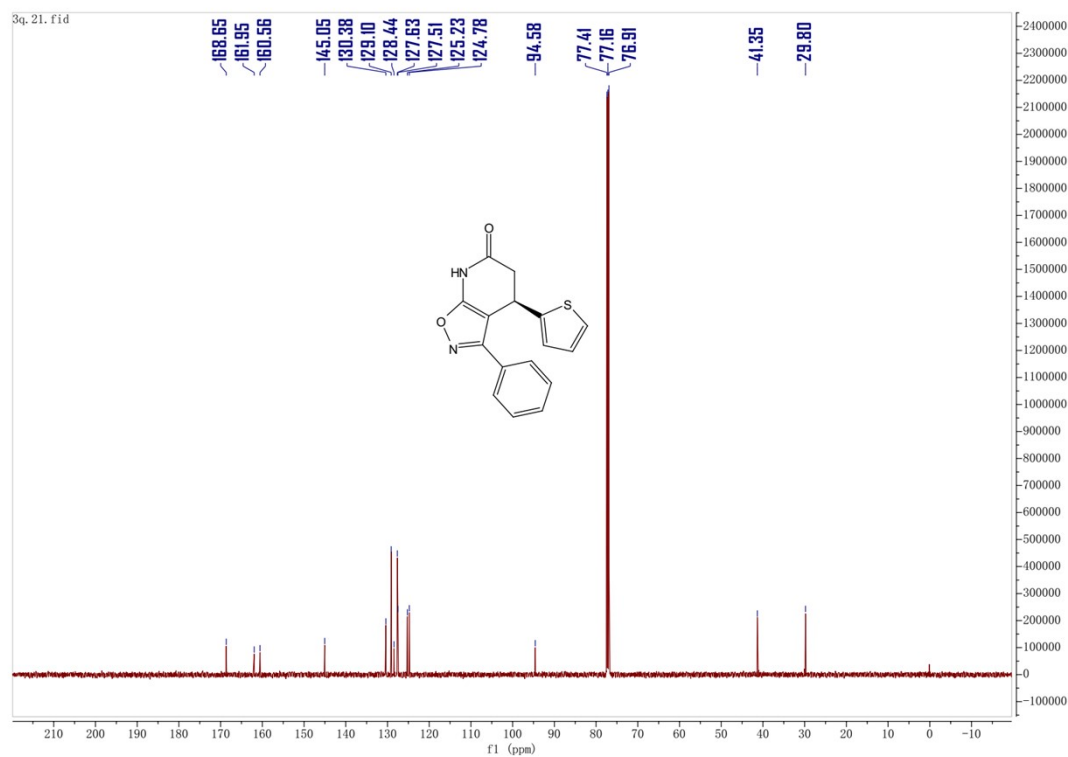
^1H NMR spectrum of **3p**



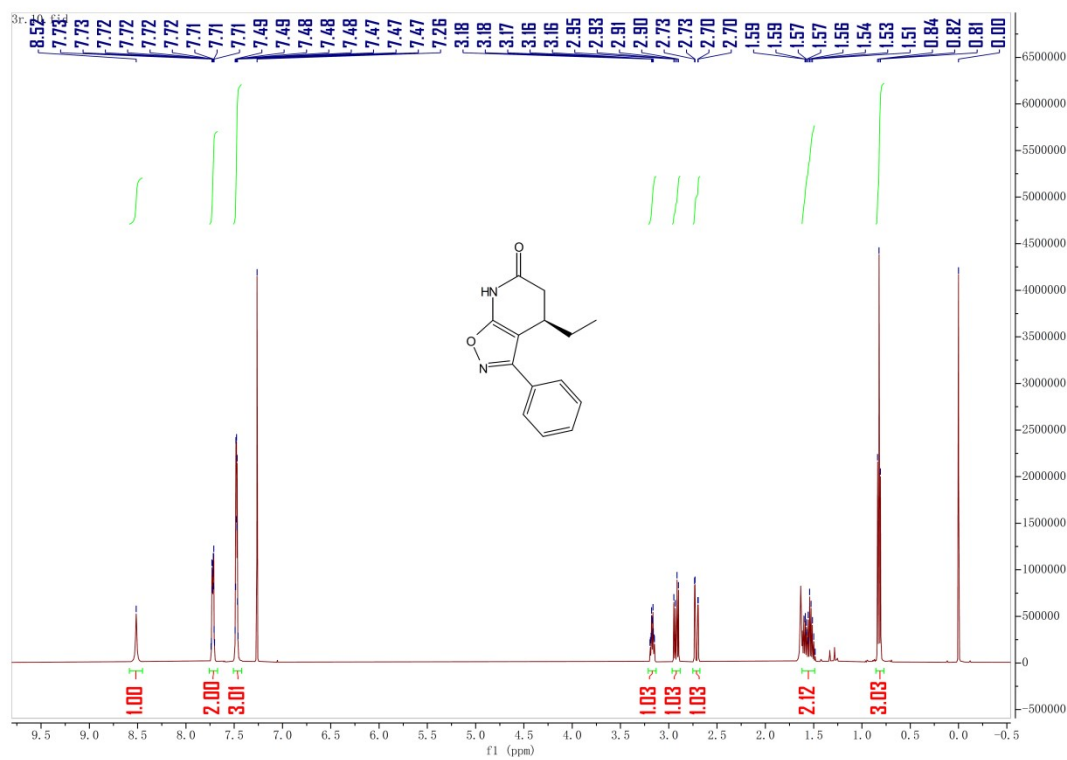
^{13}C NMR spectrum of **3p**



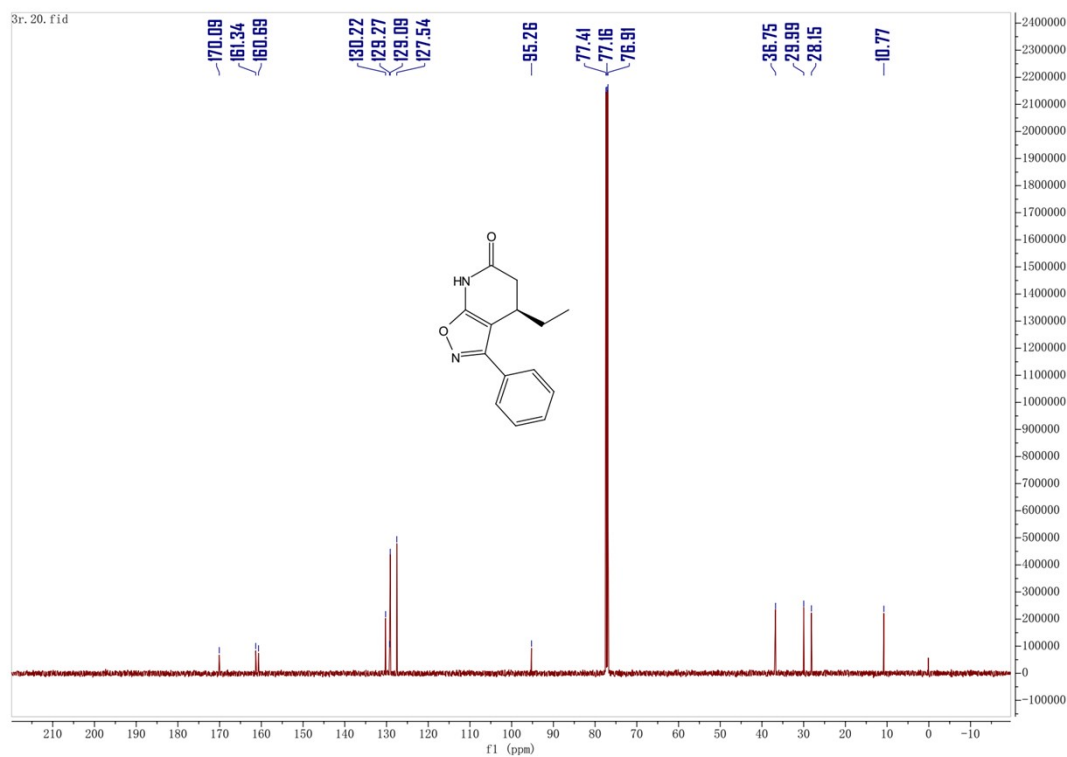
^1H NMR spectrum of **3q**



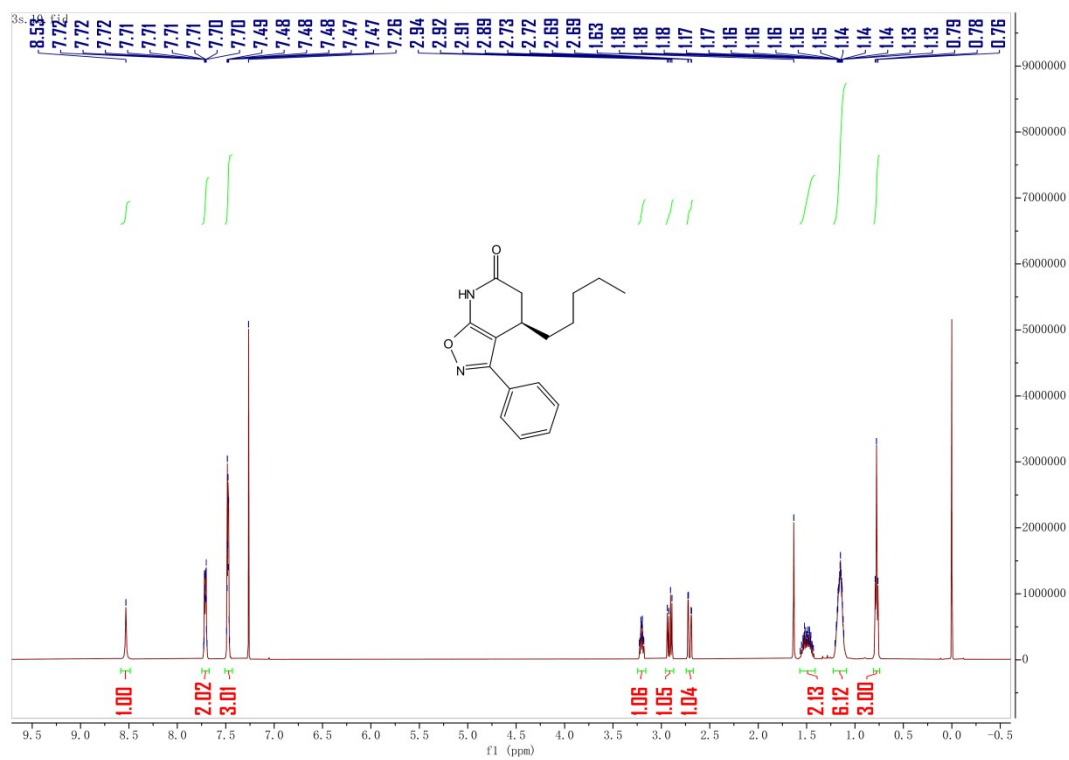
^{13}C NMR spectrum of **3q**



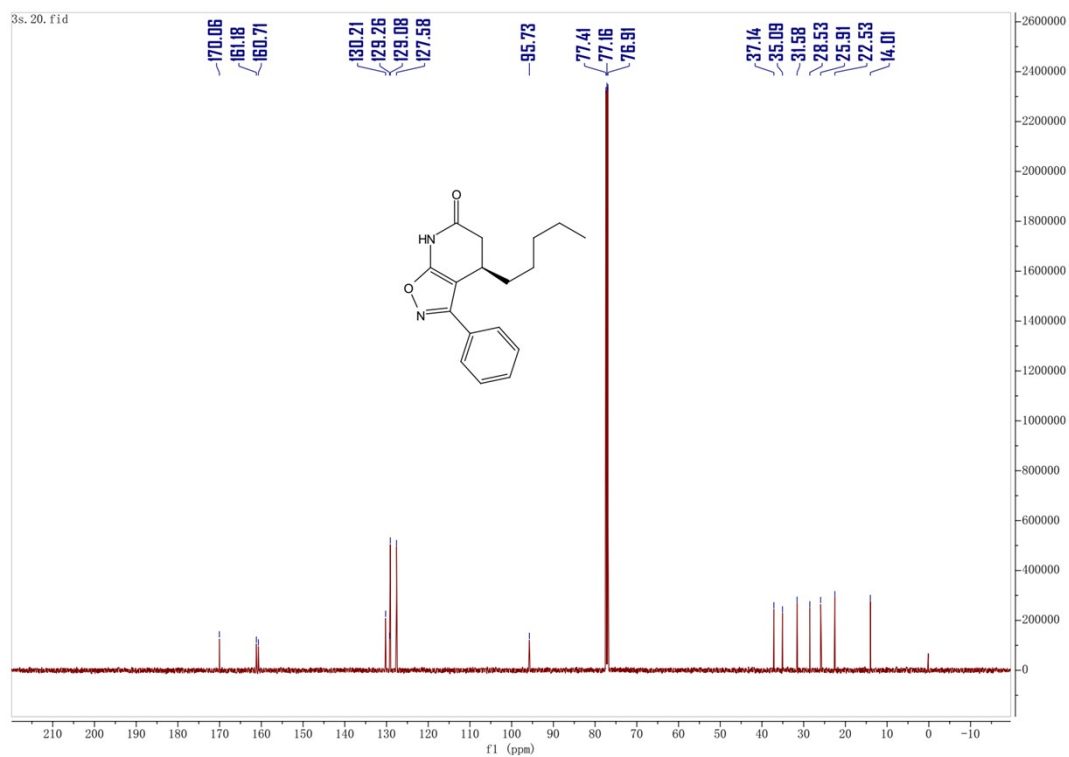
¹H NMR spectrum of 3r



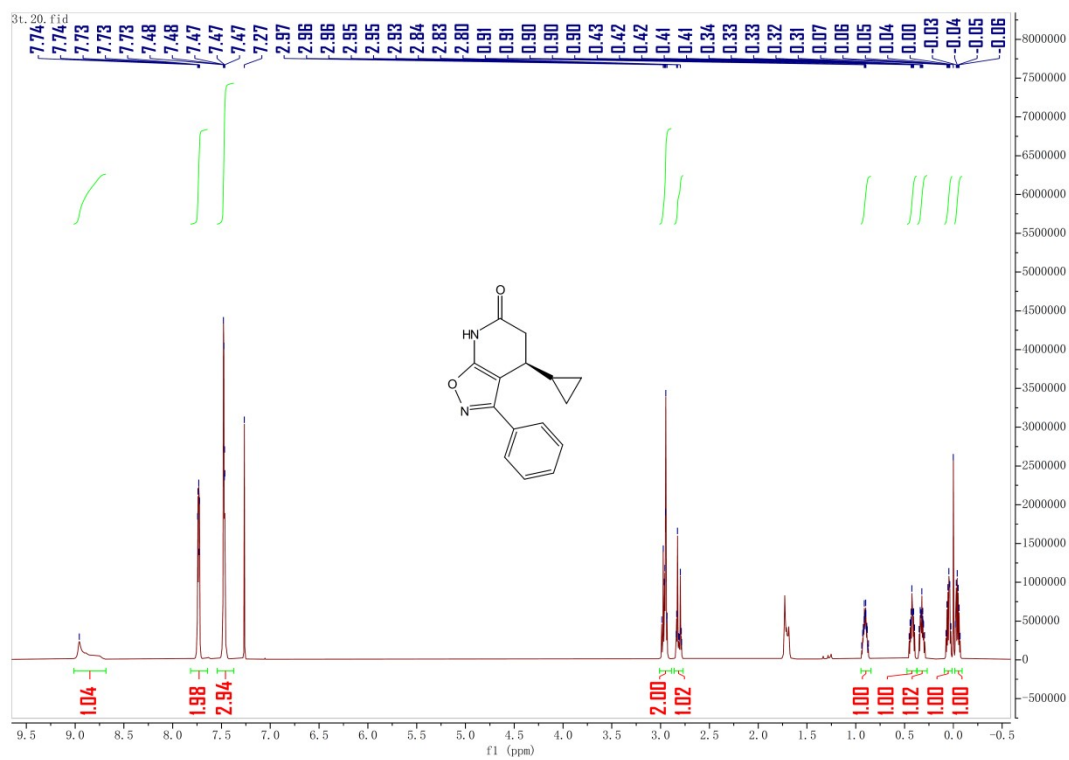
¹³C NMR spectrum of 3r



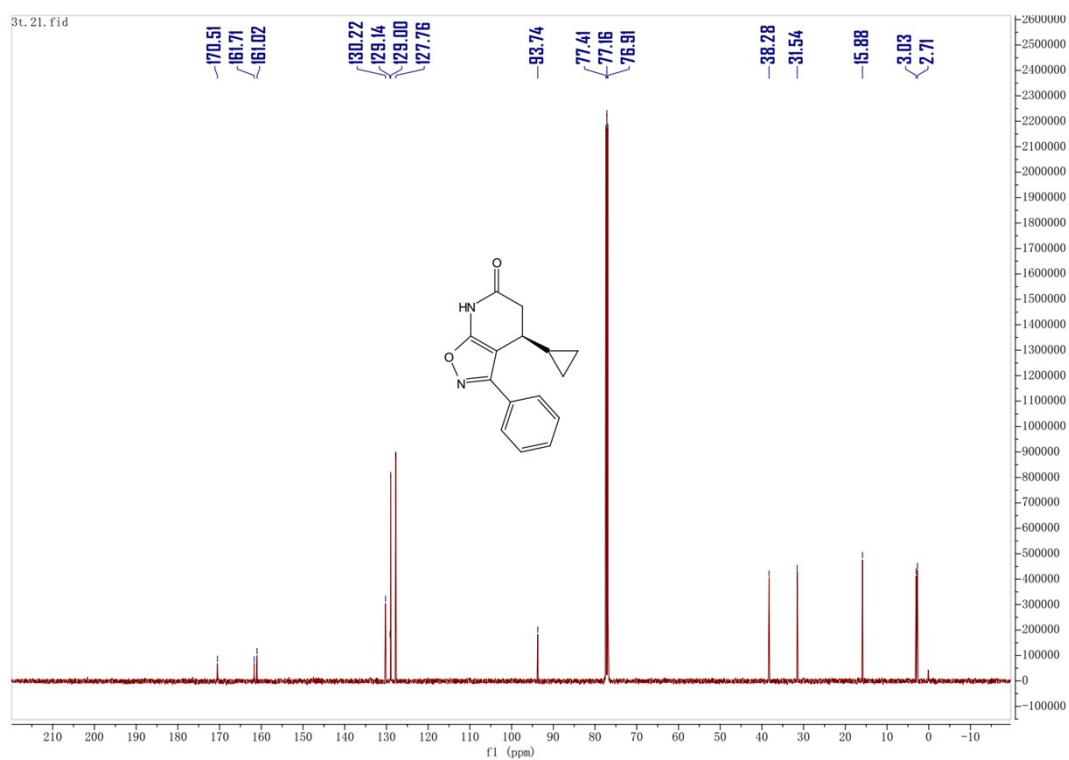
¹H NMR spectrum of 3s



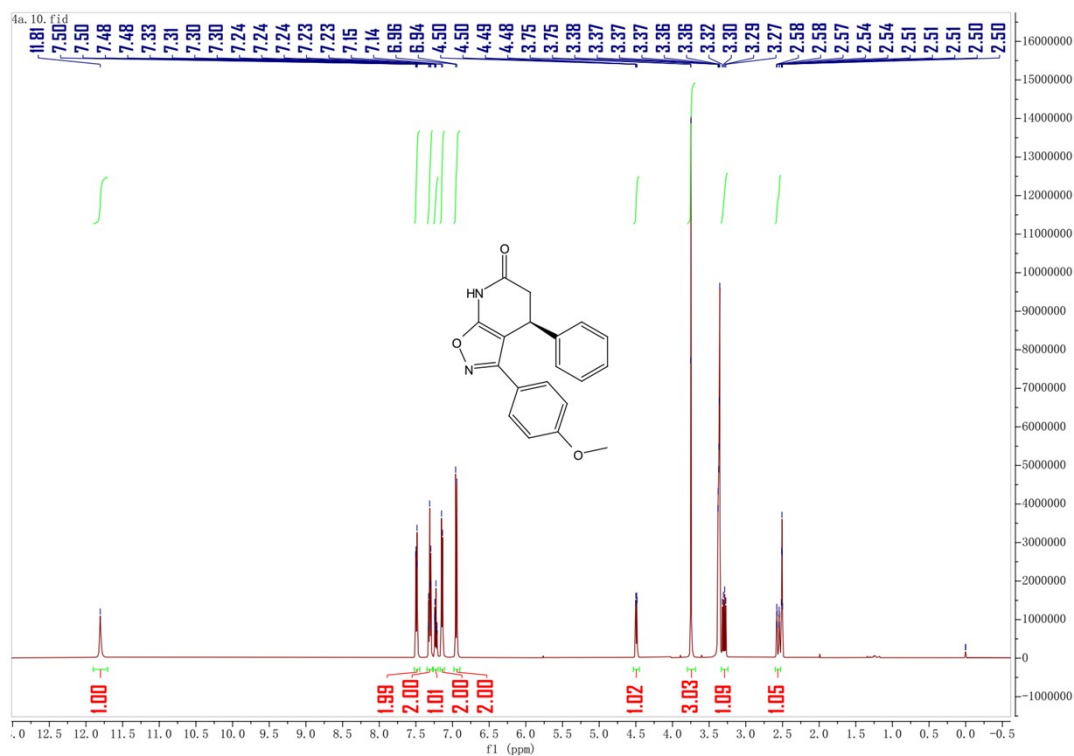
¹³C NMR spectrum of 3s



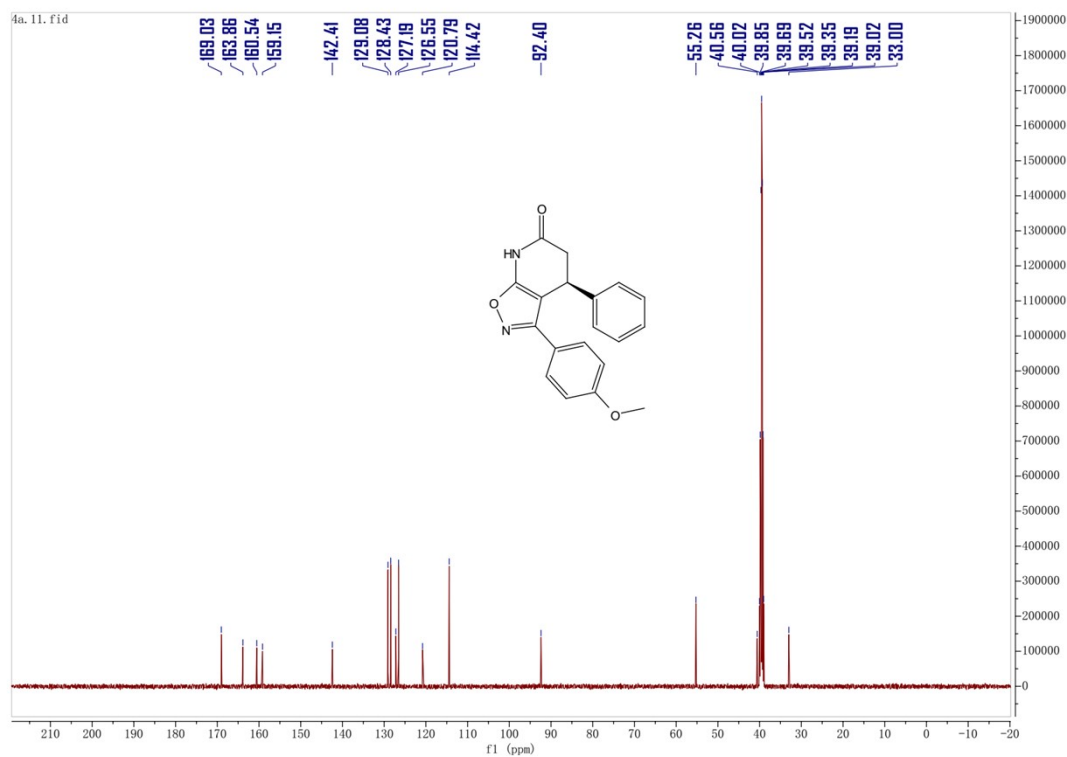
^1H NMR spectrum of 3t



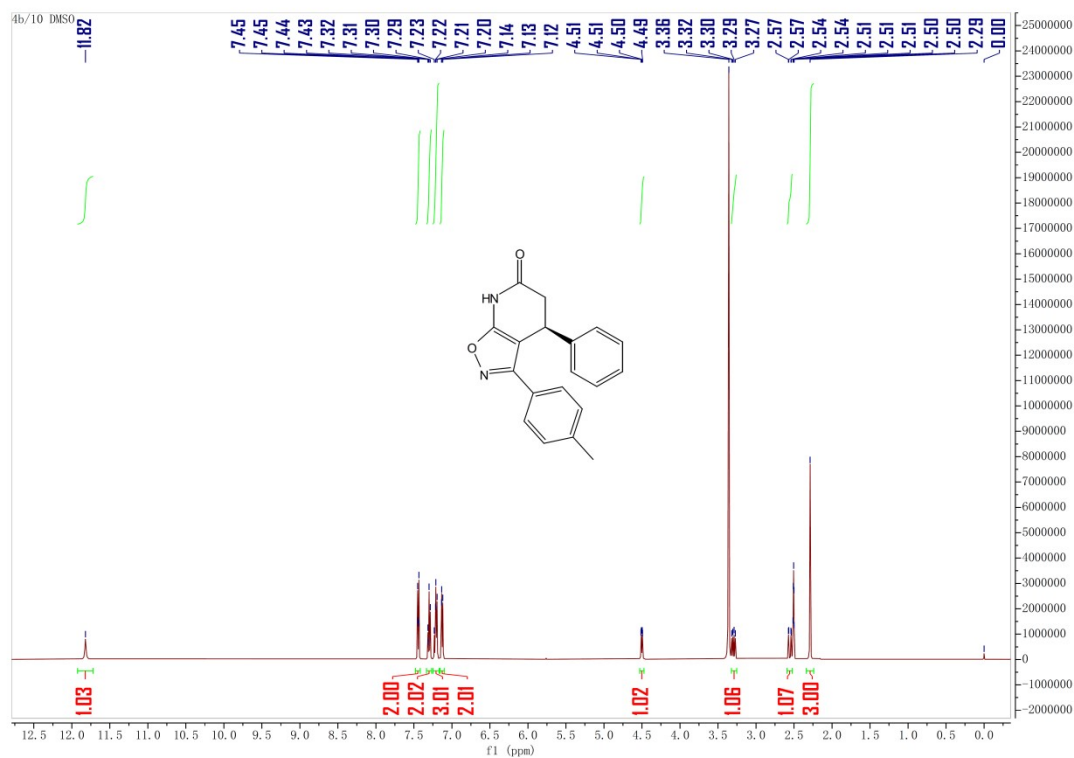
^{13}C NMR spectrum of 3t



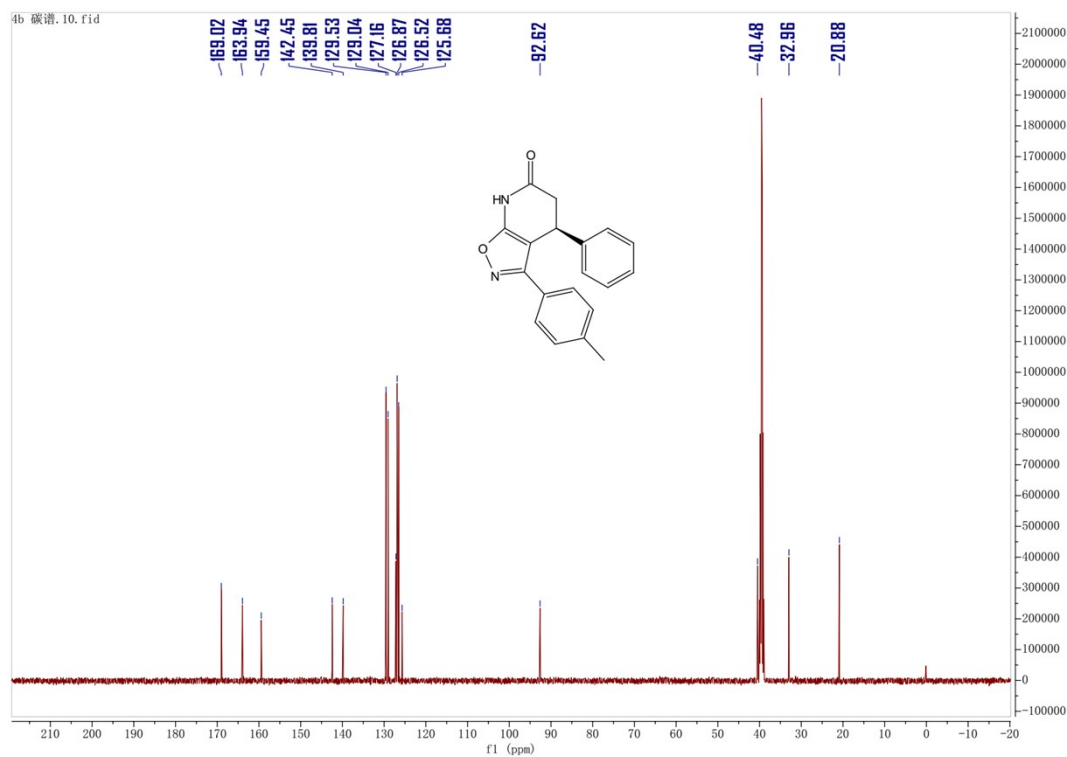
^1H NMR spectrum of 4a



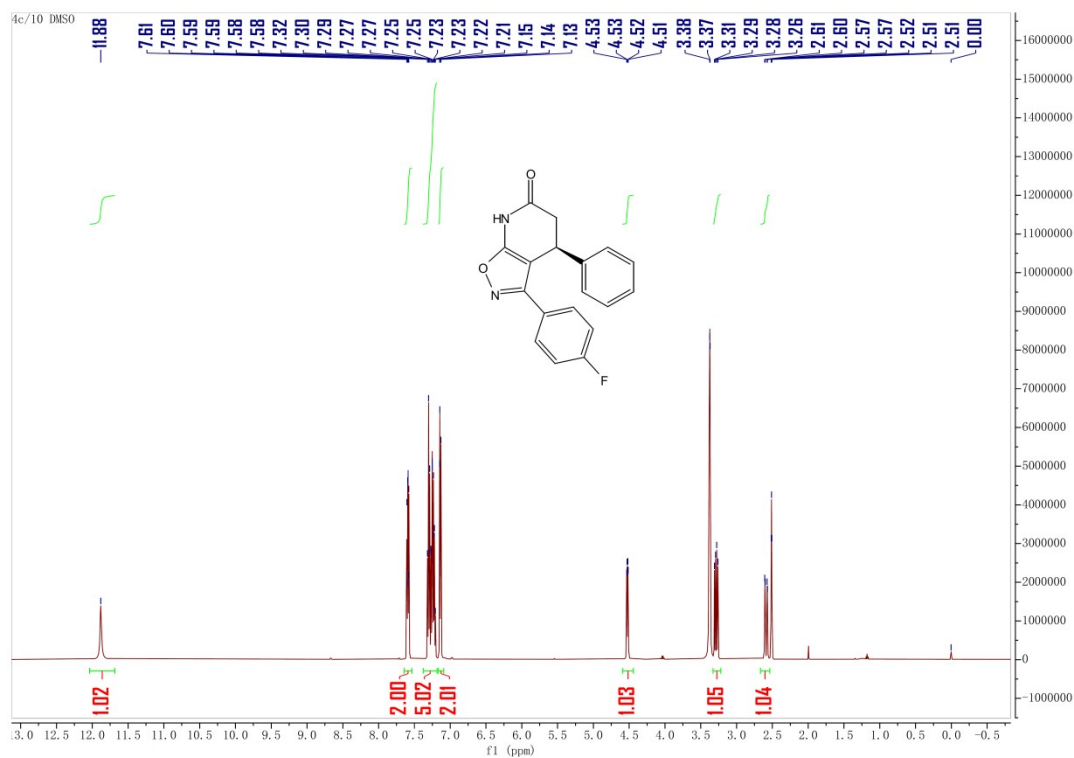
^{13}C NMR spectrum of 4a



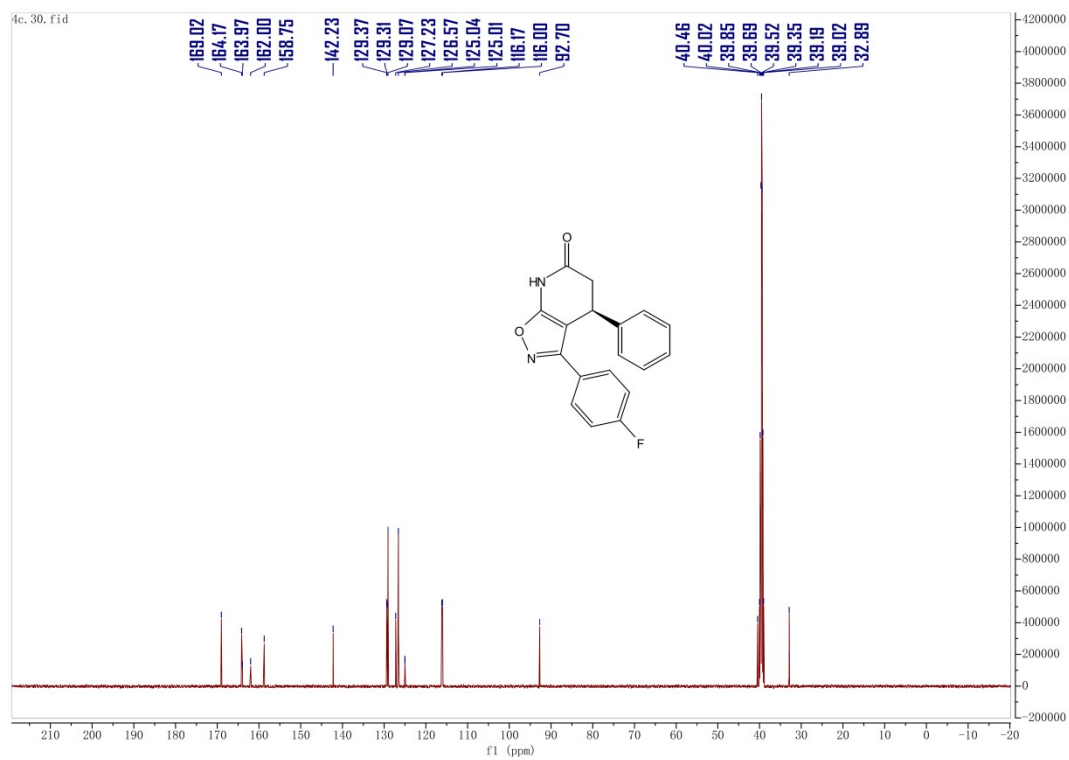
^1H NMR spectrum of **4b**



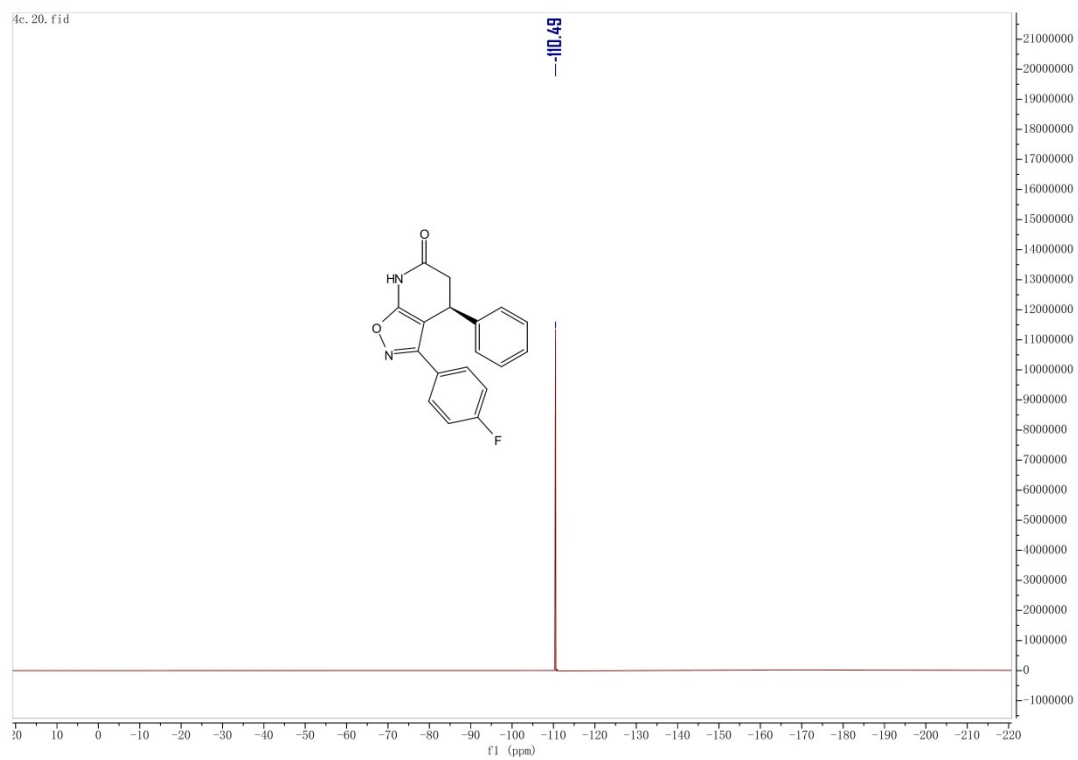
^{13}C NMR spectrum of **4b**



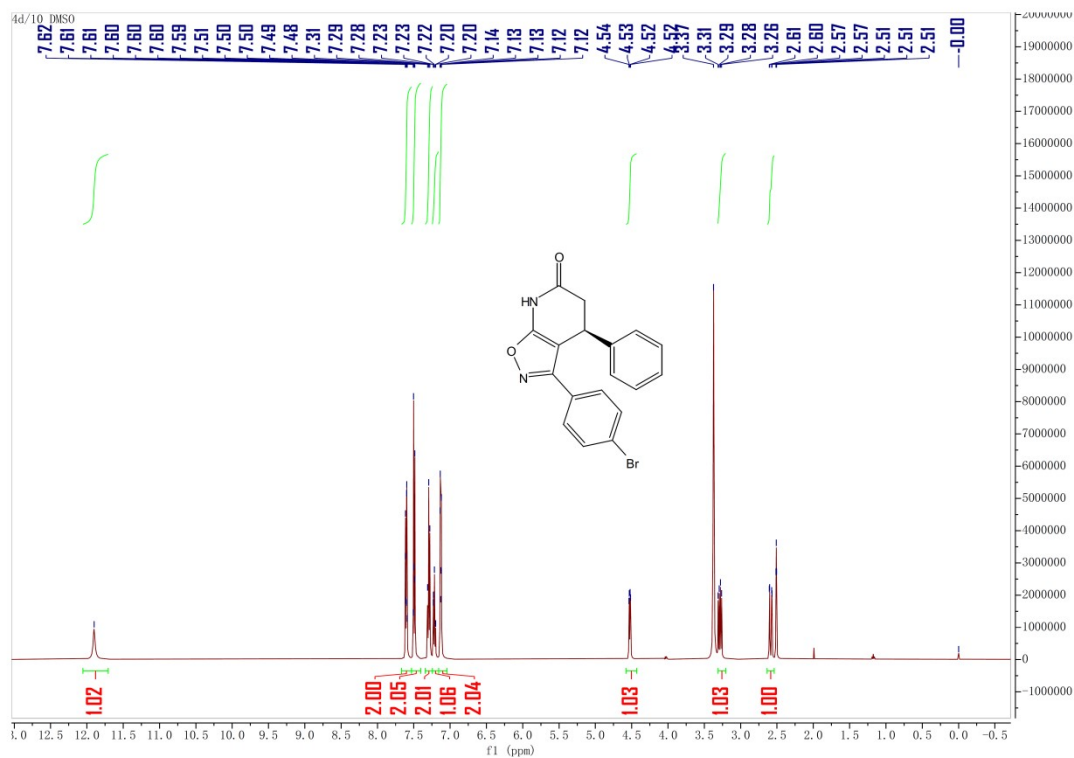
^1H NMR spectrum of 4c



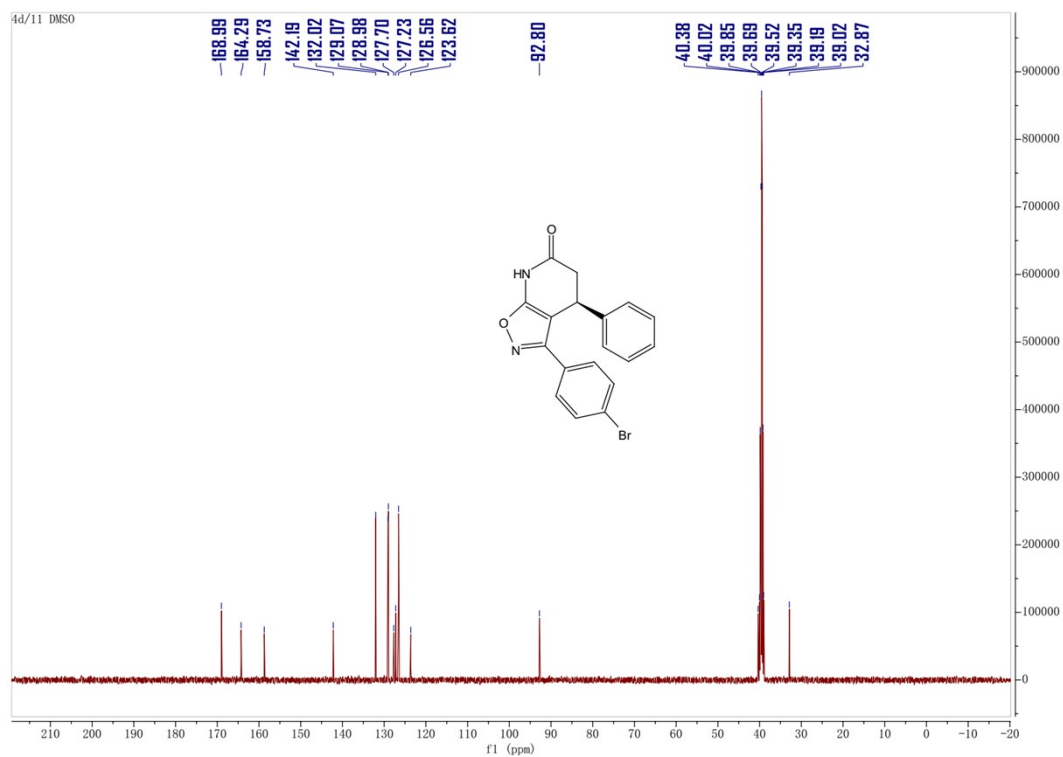
^{13}C NMR spectrum of 4c



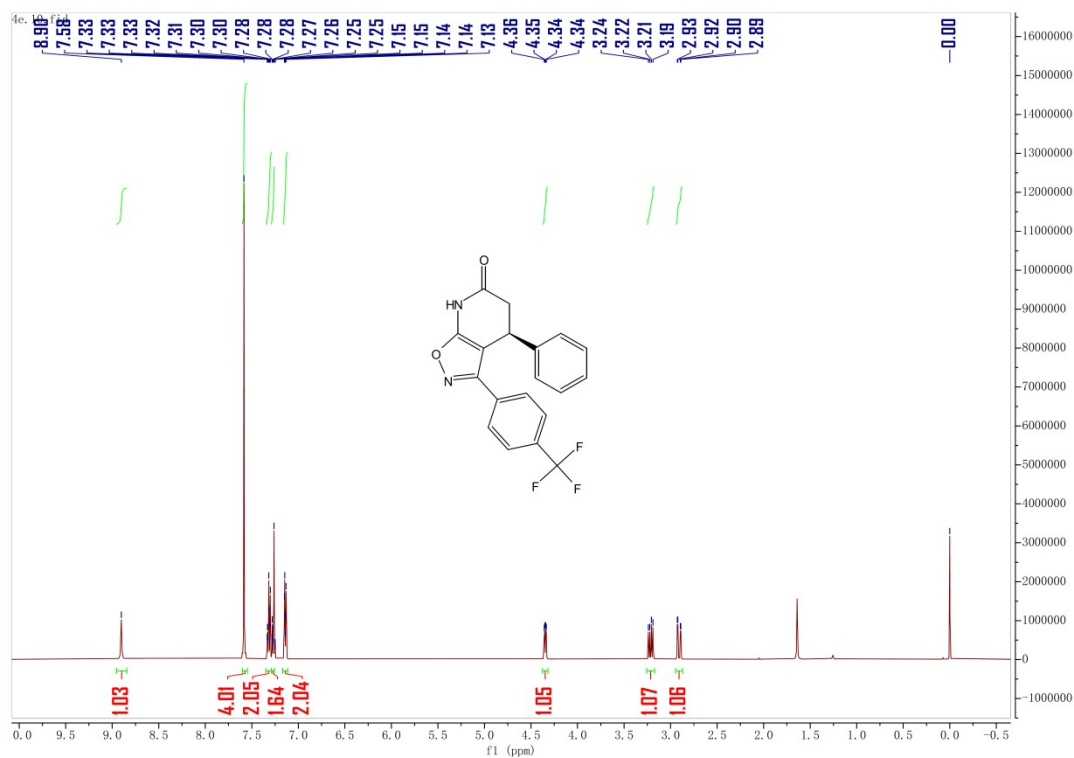
^{19}F NMR spectrum of **4c**



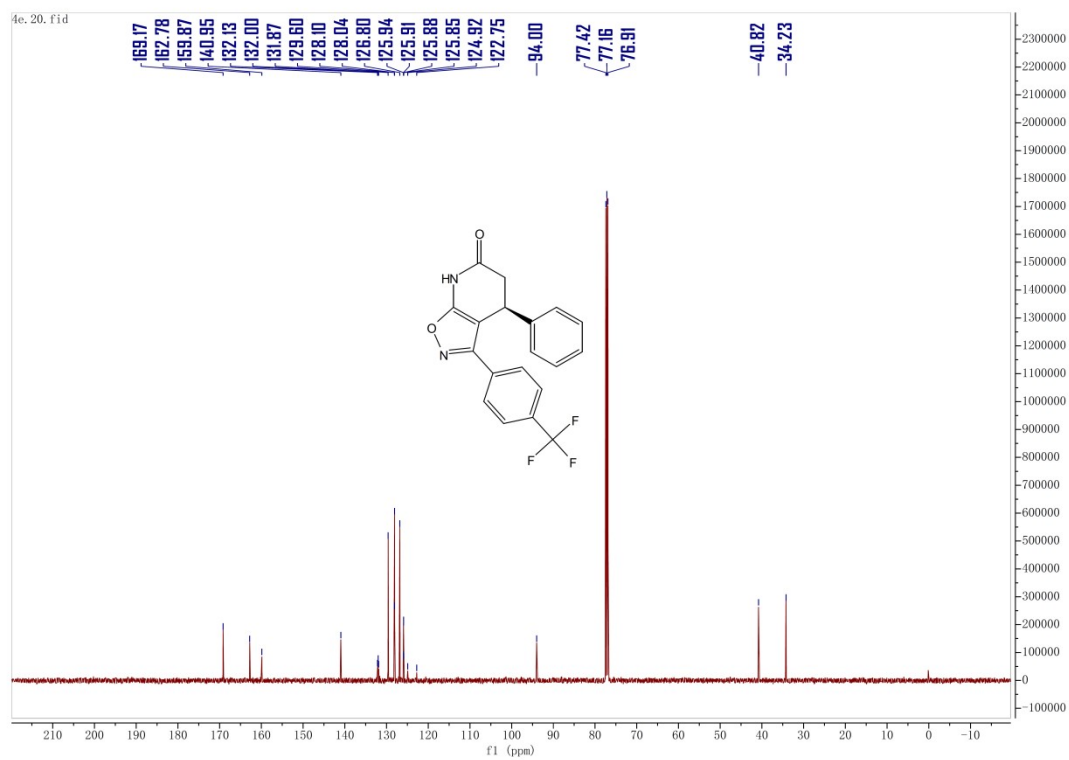
^1H NMR spectrum of 4d



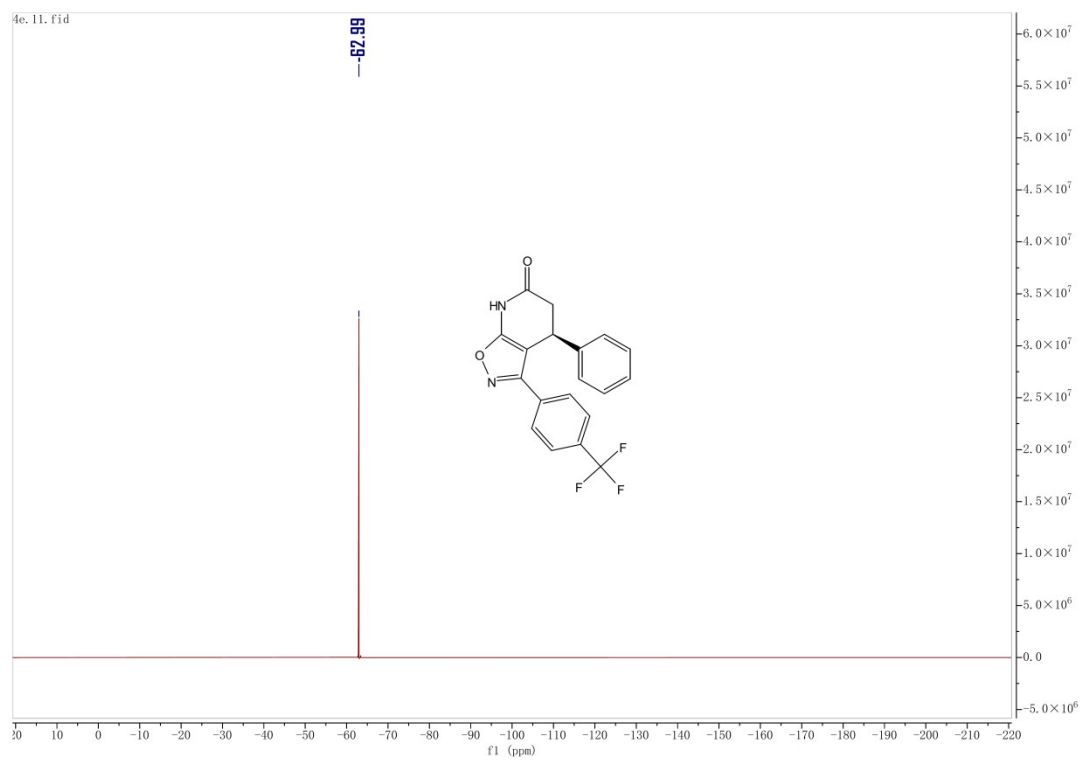
^{13}C NMR spectrum of 4d



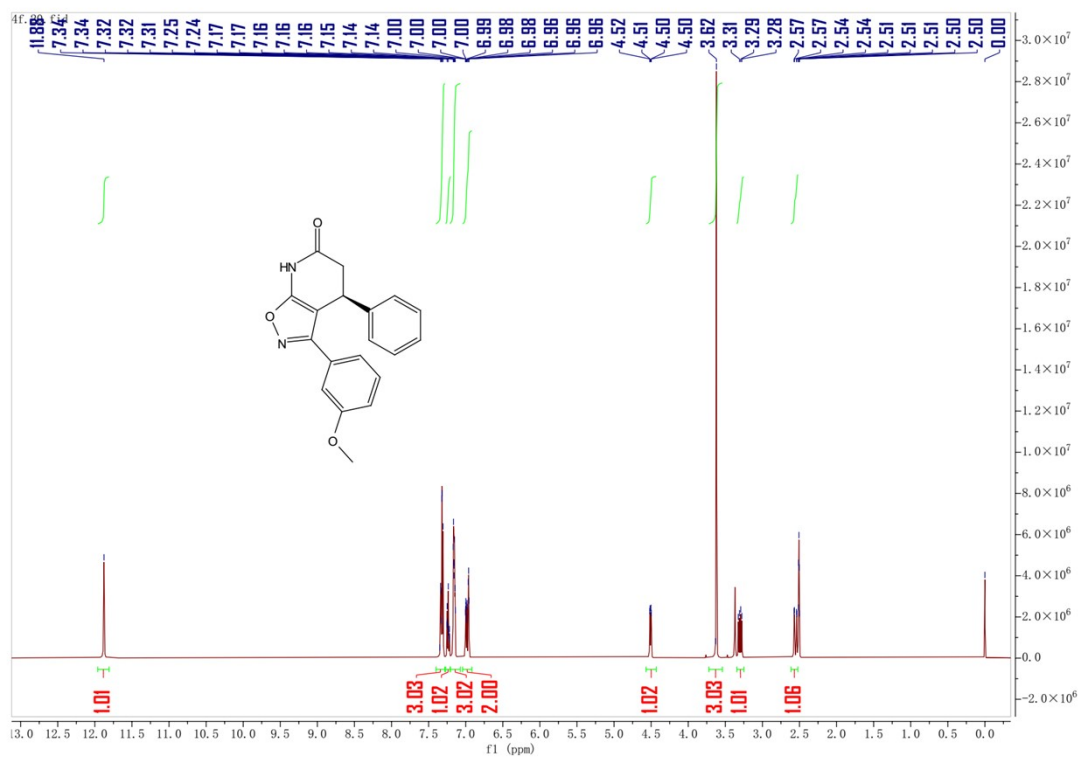
¹H NMR spectrum of 4e



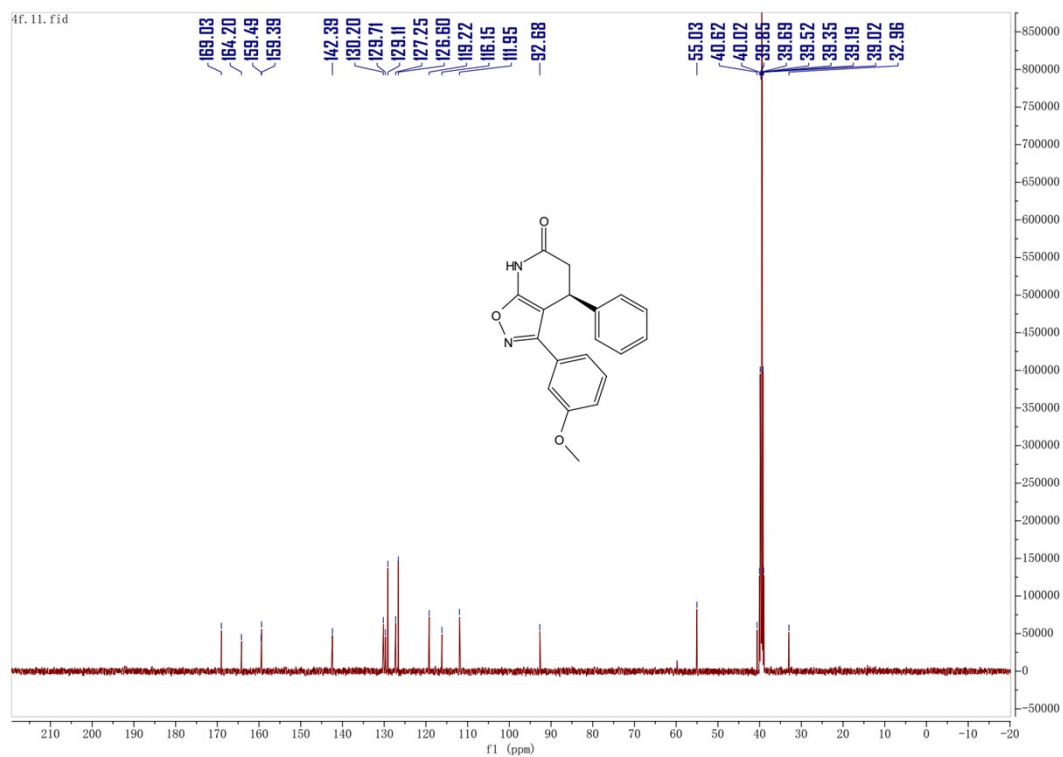
¹³C NMR spectrum of 4e



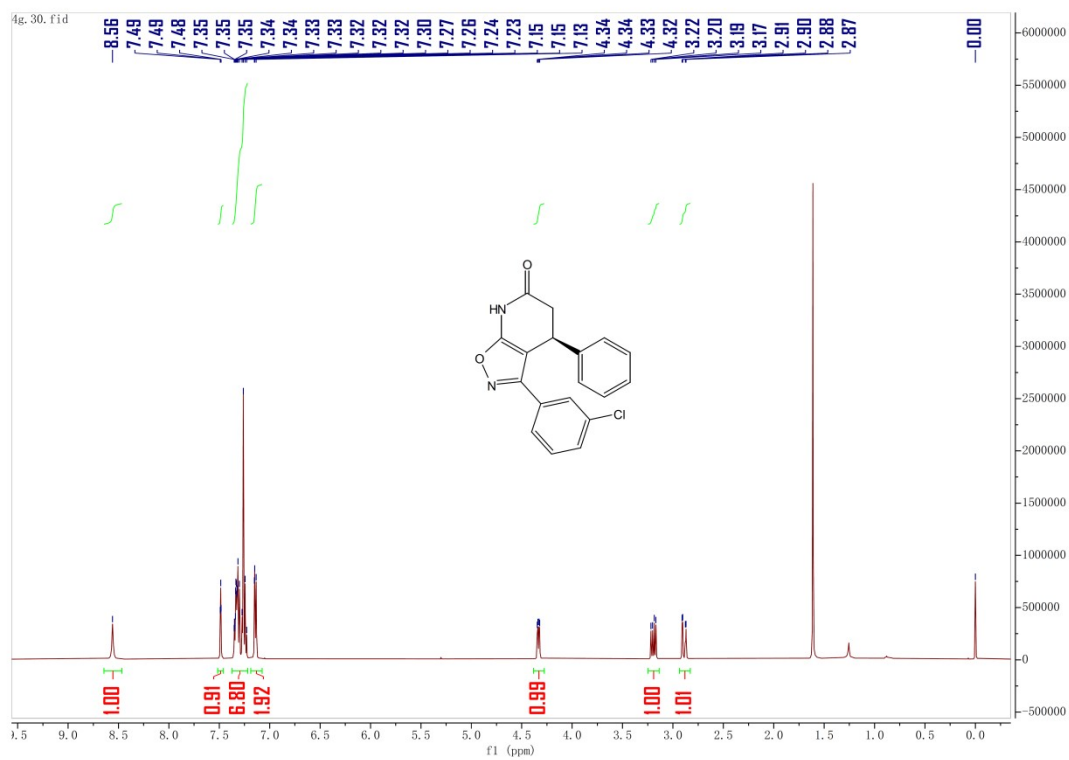
¹⁹F NMR spectrum of **4e**



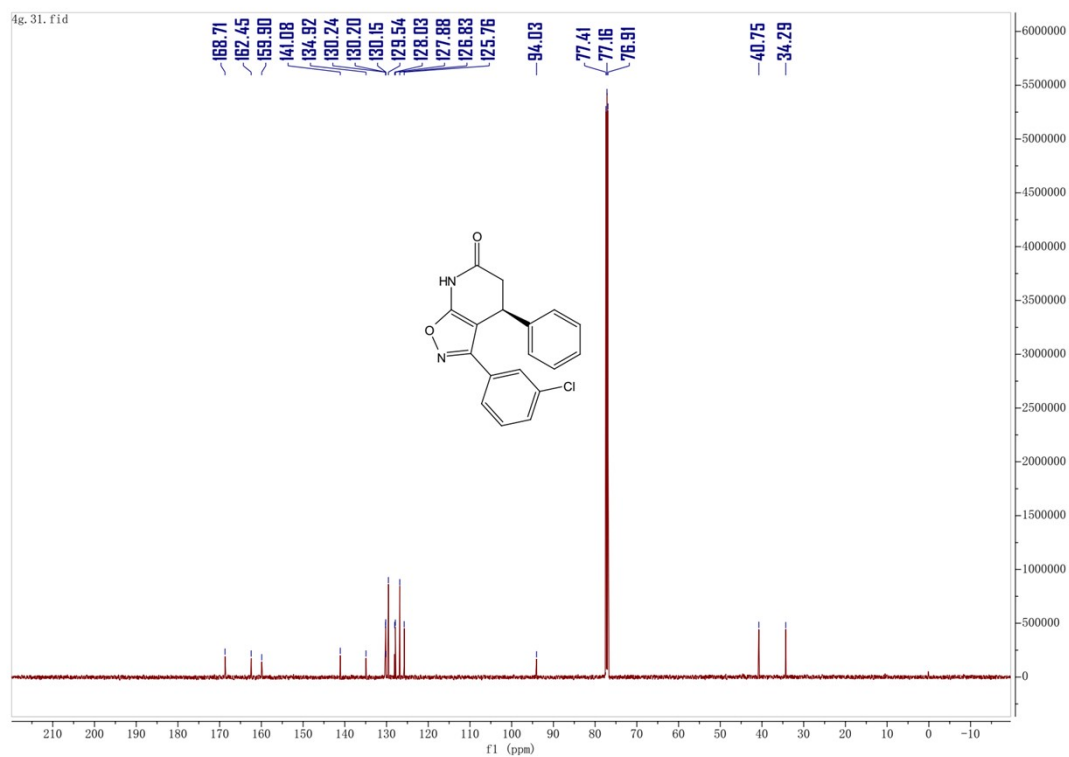
¹H NMR spectrum of **4f**



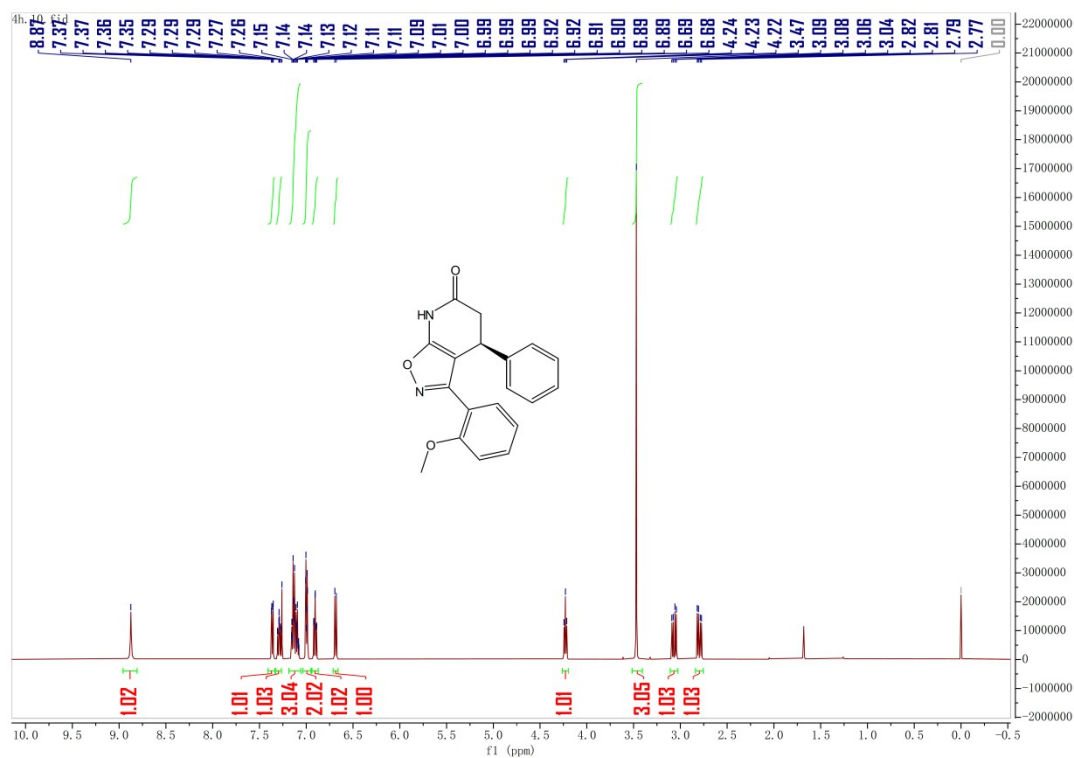
¹³C NMR spectrum of **4f**



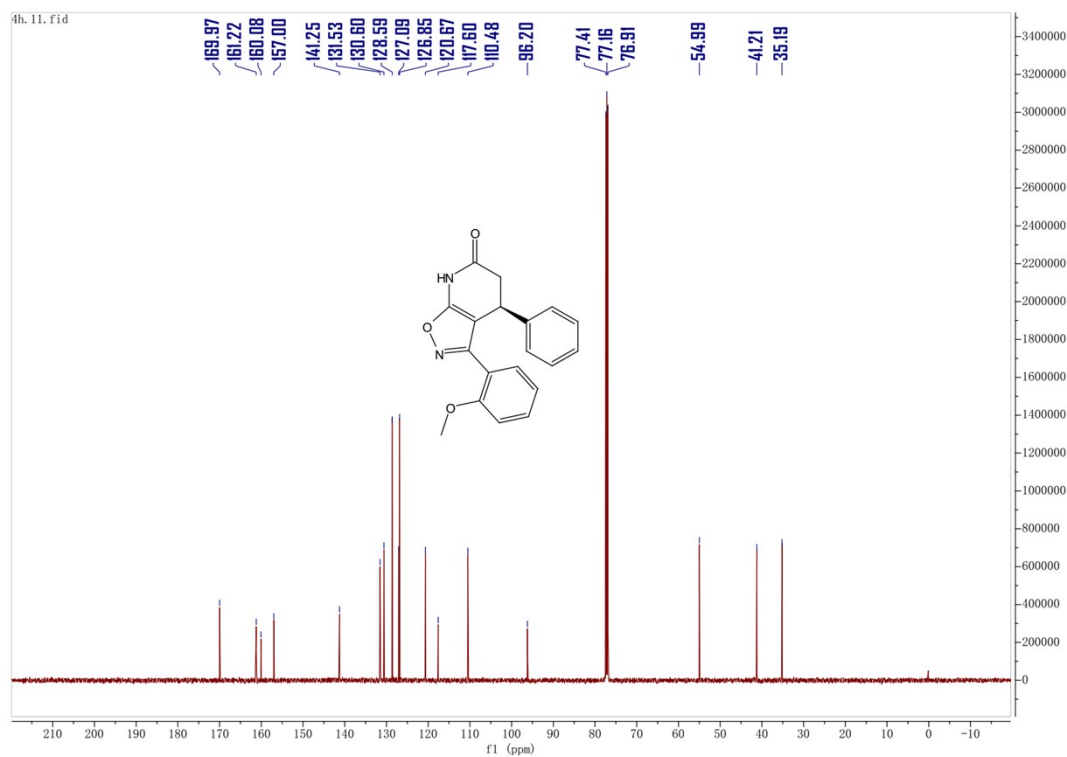
¹H NMR spectrum of 4g



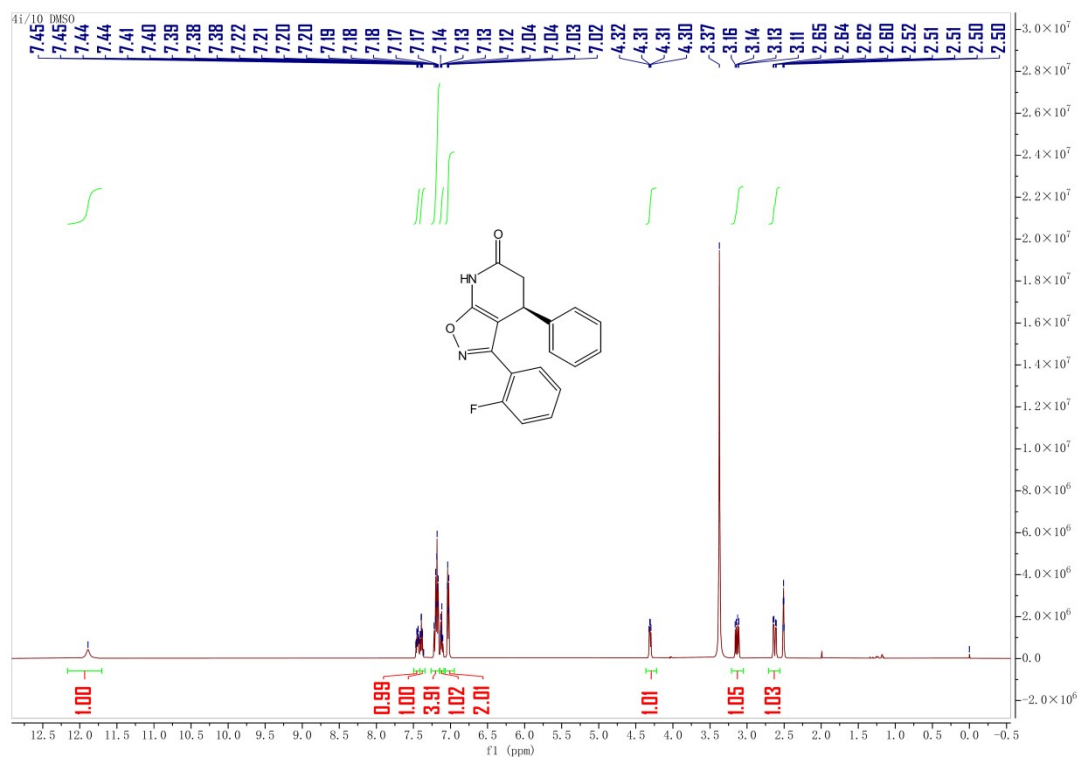
¹³C NMR spectrum of 4g



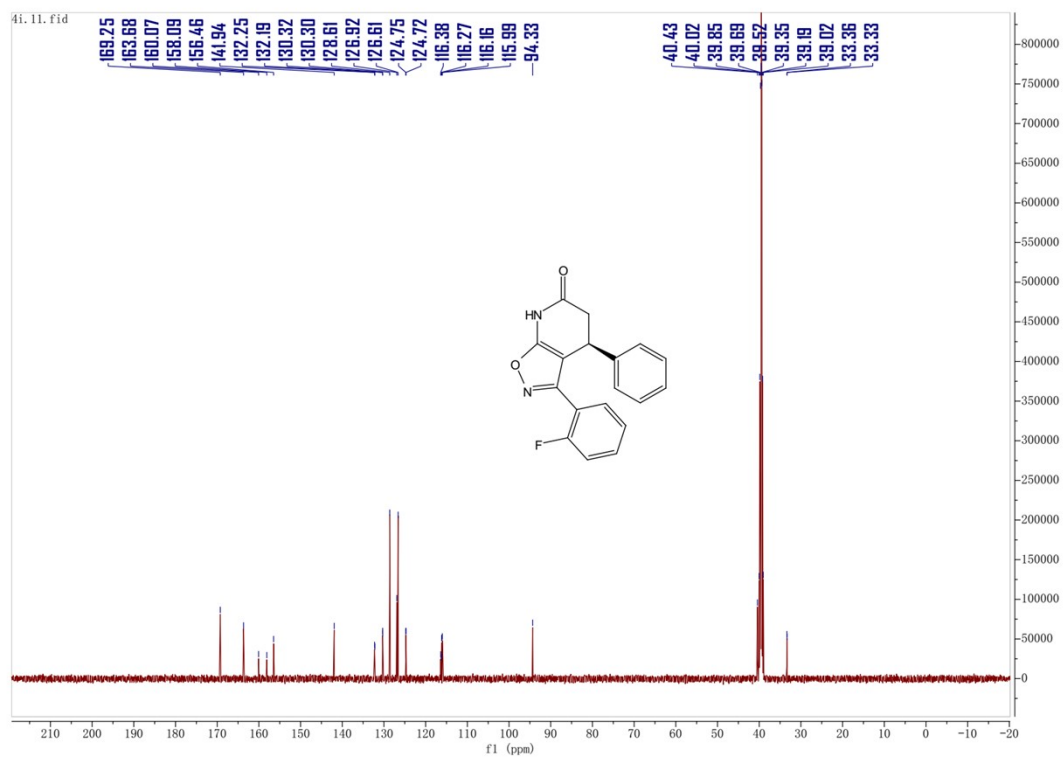
¹H NMR spectrum of 4h



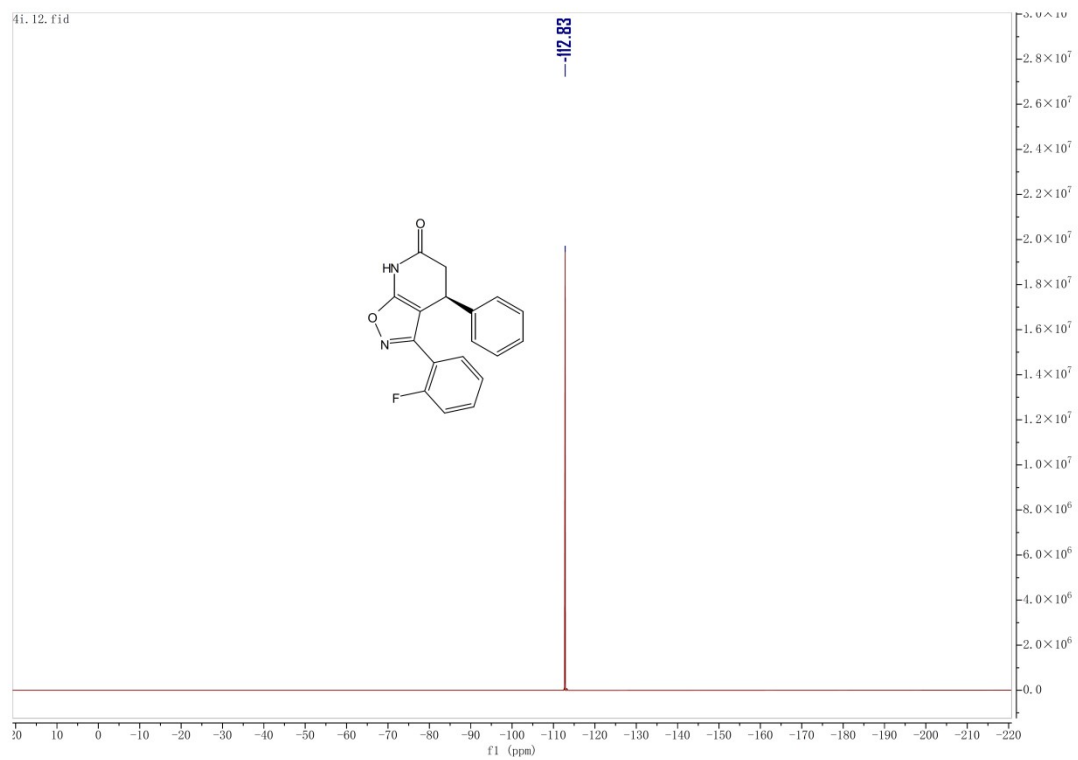
¹³C NMR spectrum of 4h



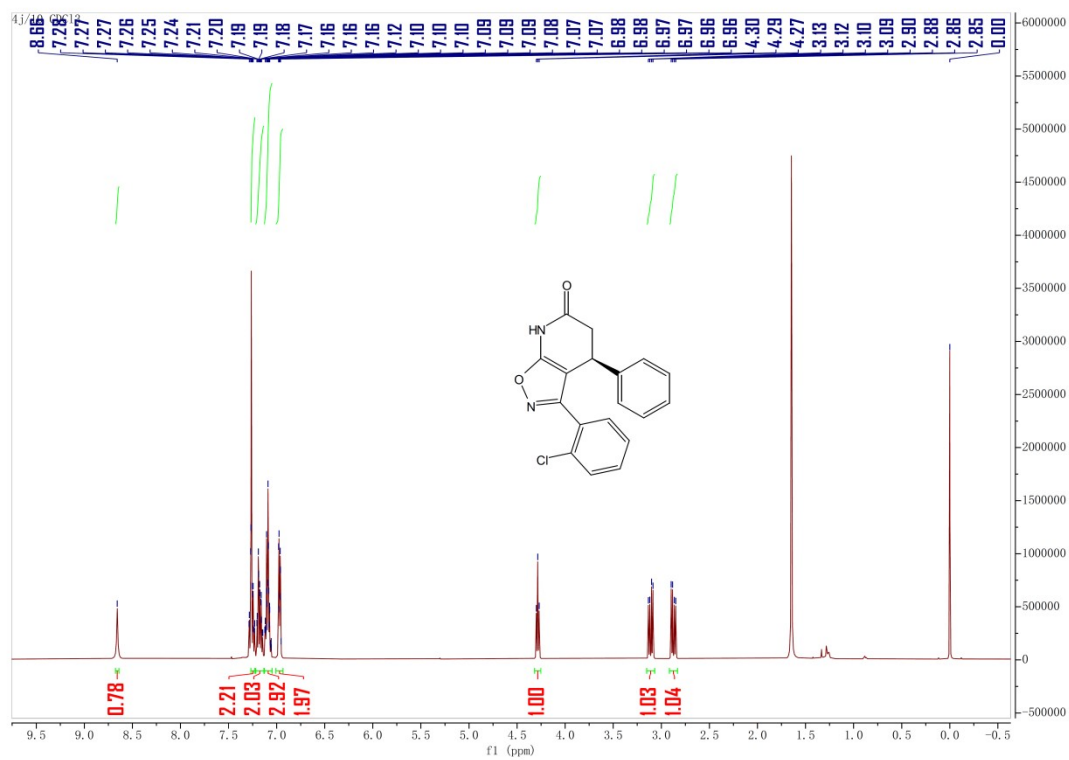
^1H NMR spectrum of **4i**



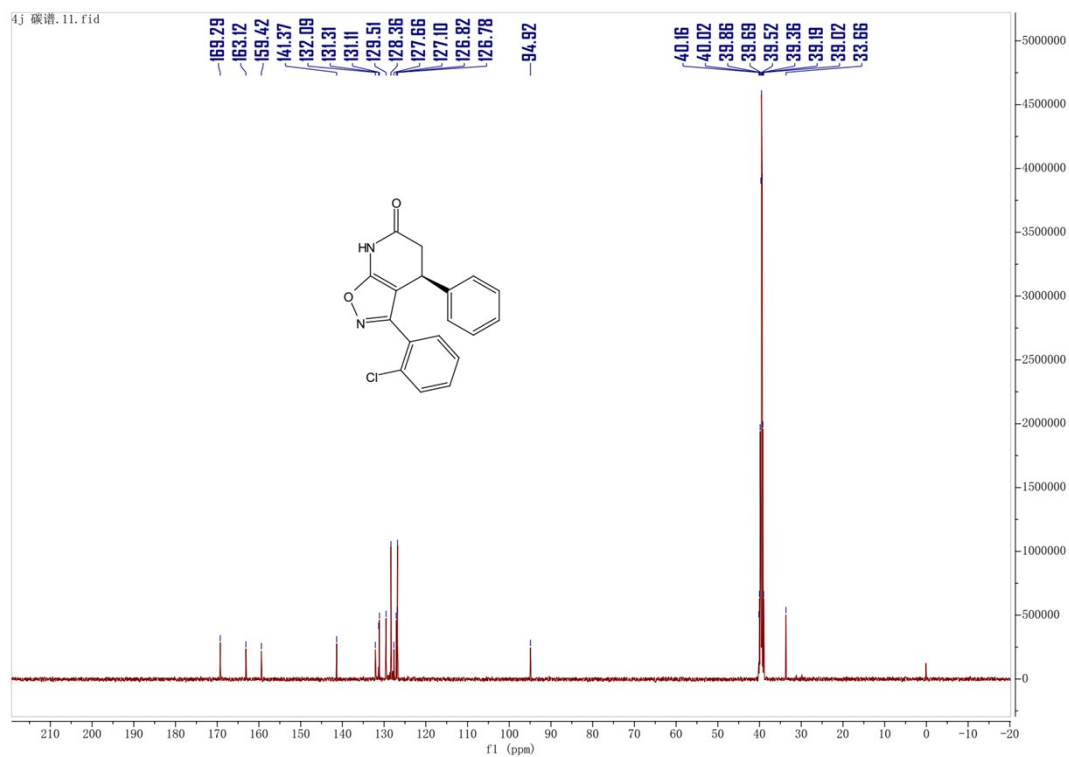
^{13}C NMR spectrum of **4i**



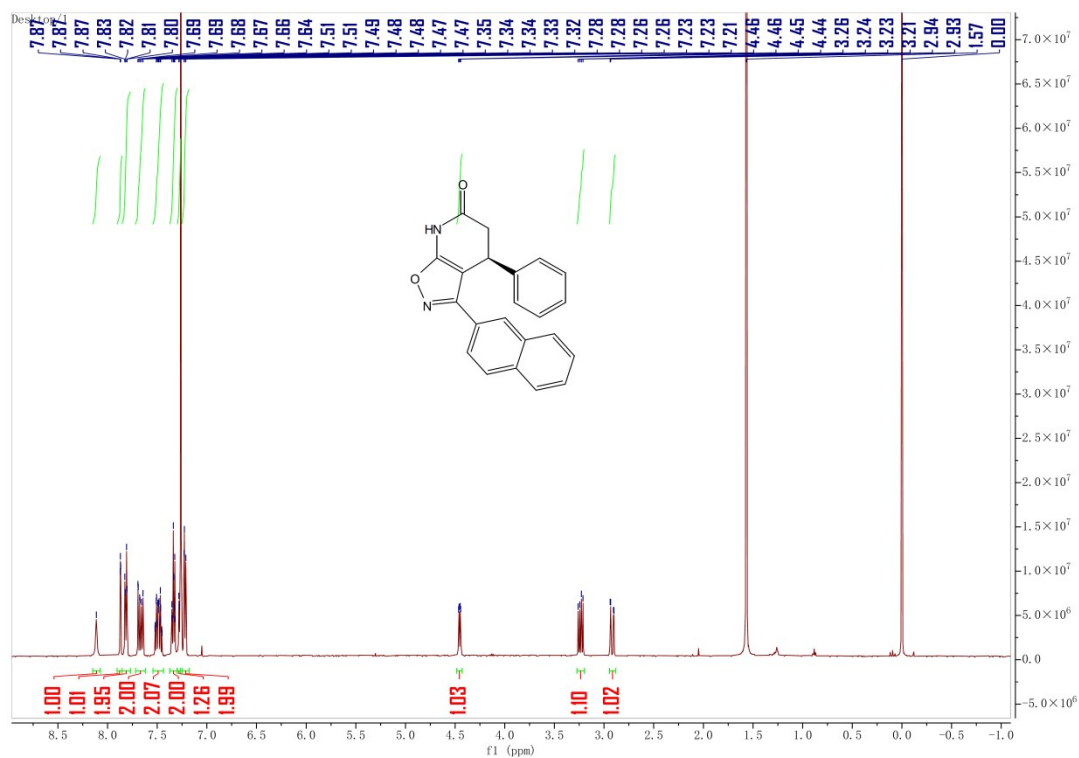
^{19}F NMR spectrum of **4i**



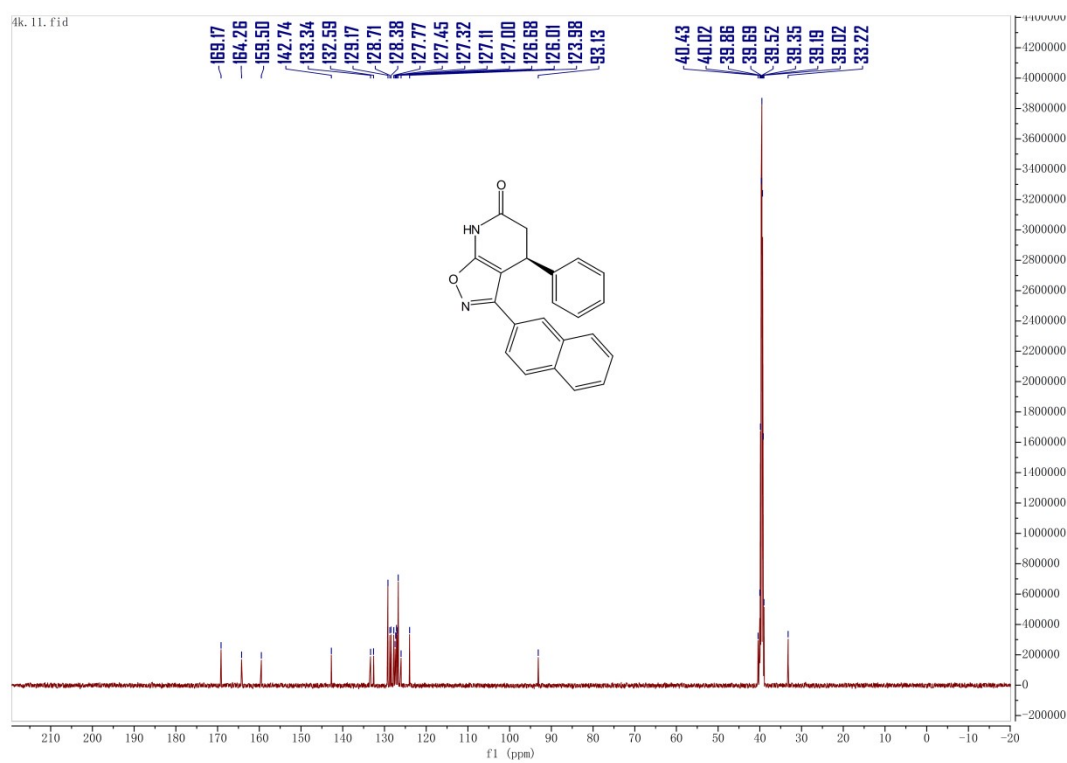
^1H NMR spectrum of **4j**



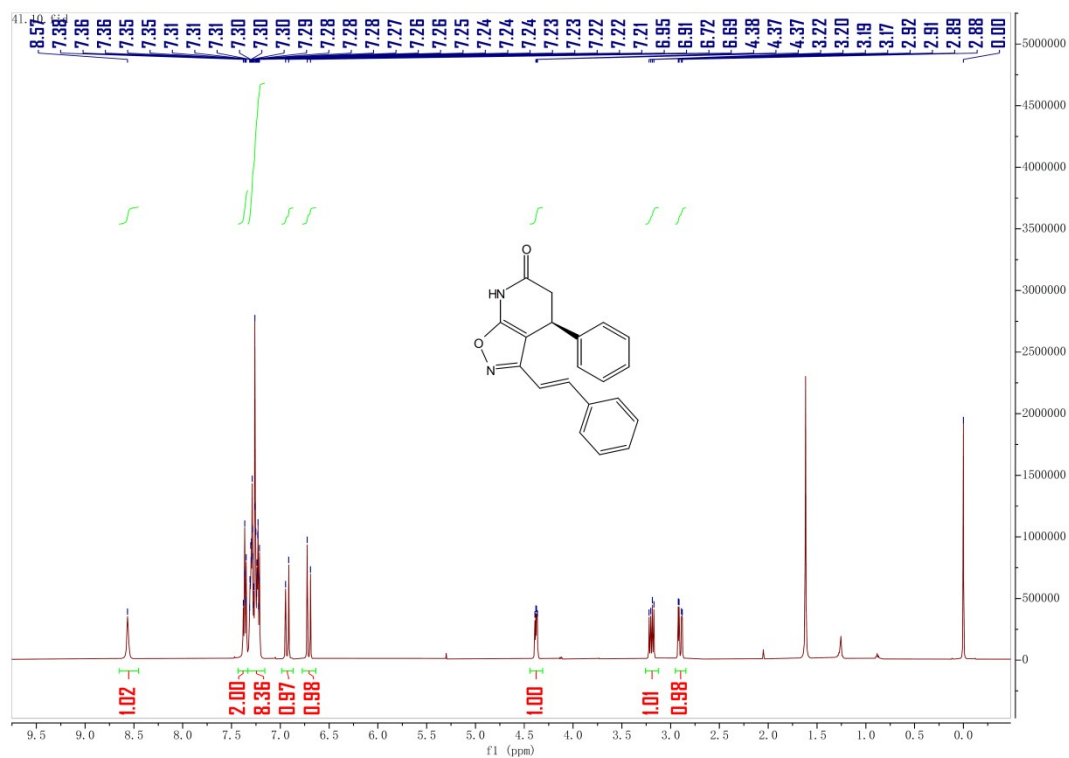
^{13}C NMR spectrum of **4j**



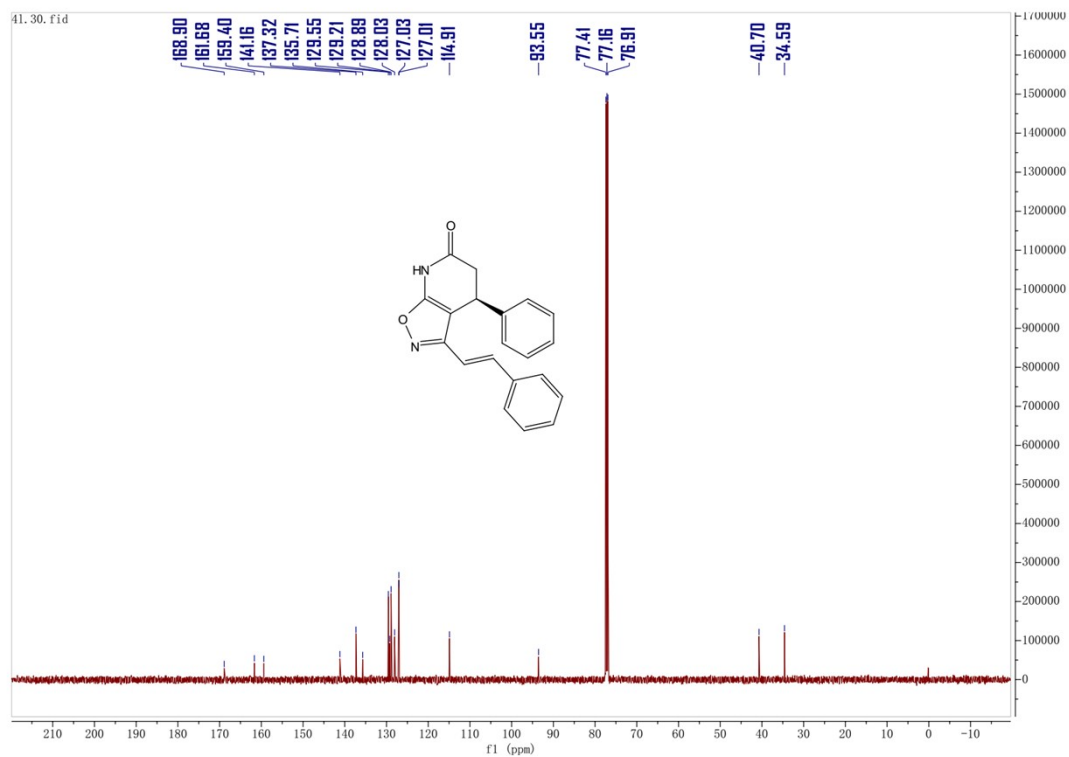
¹H NMR spectrum of **4k**



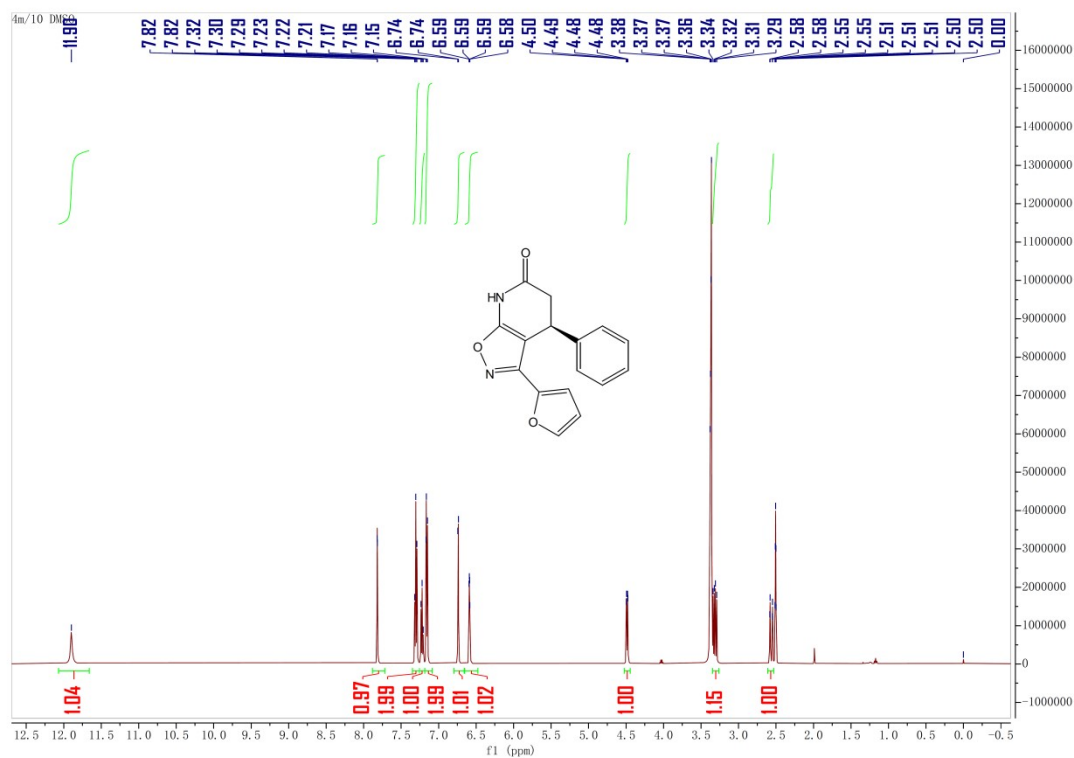
¹³C NMR spectrum of **4k**



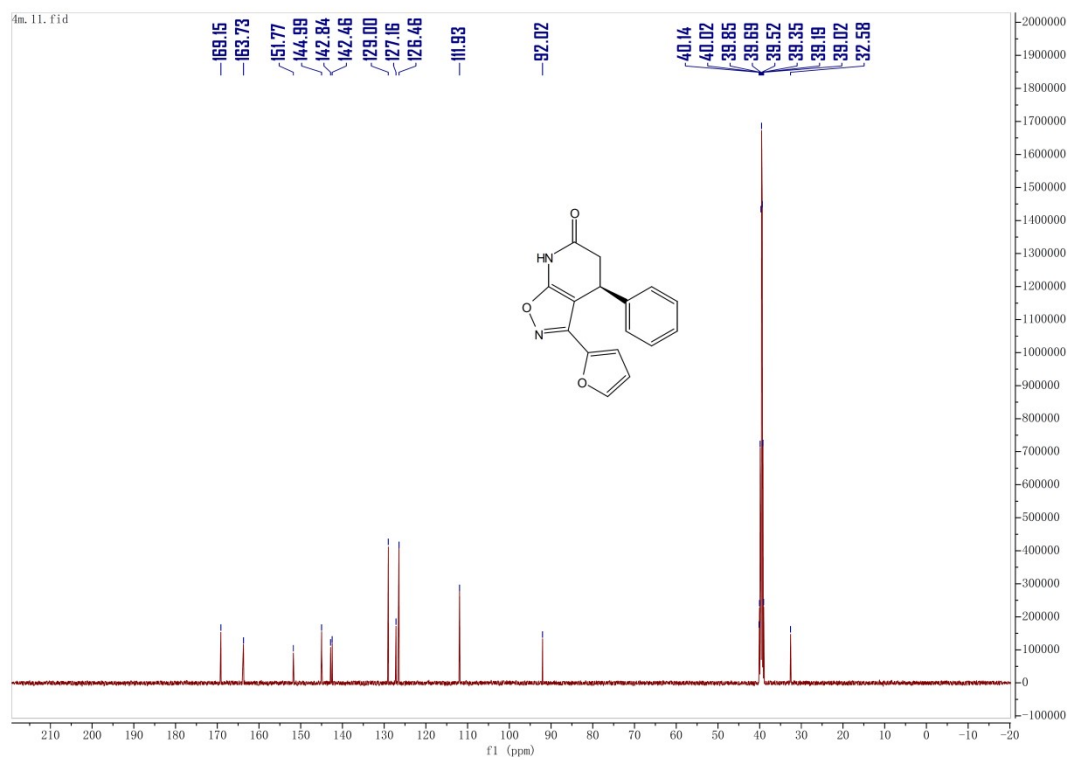
¹H NMR spectrum of 41



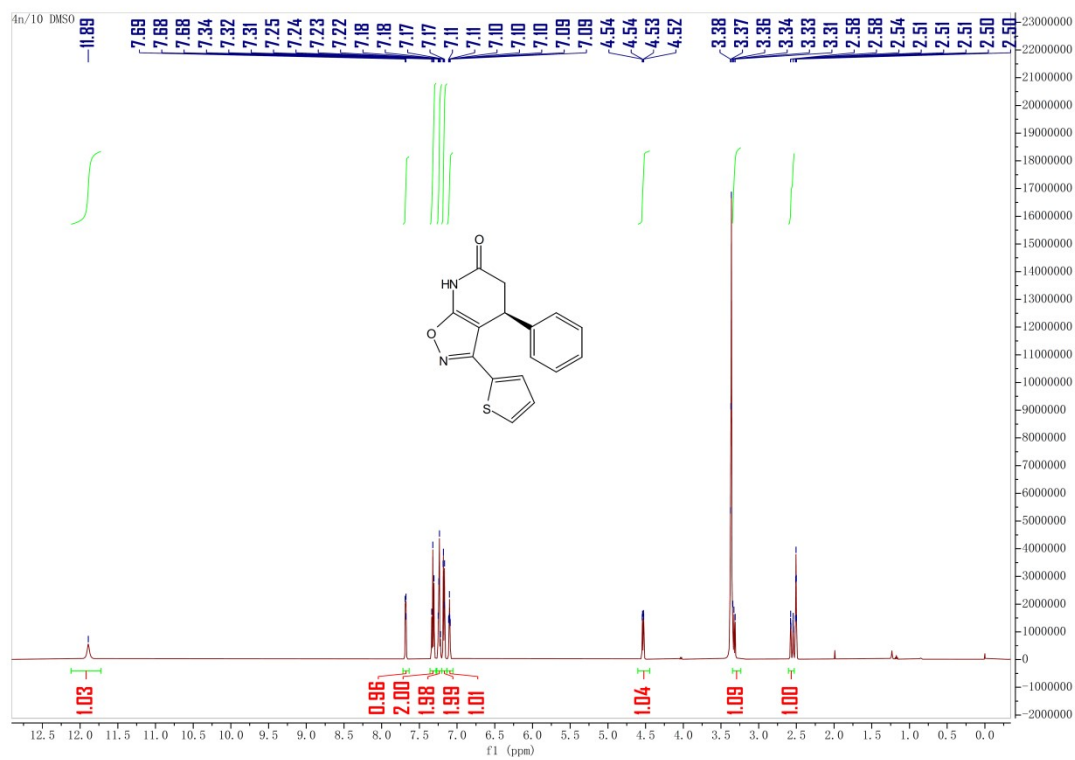
¹³C NMR spectrum of 41



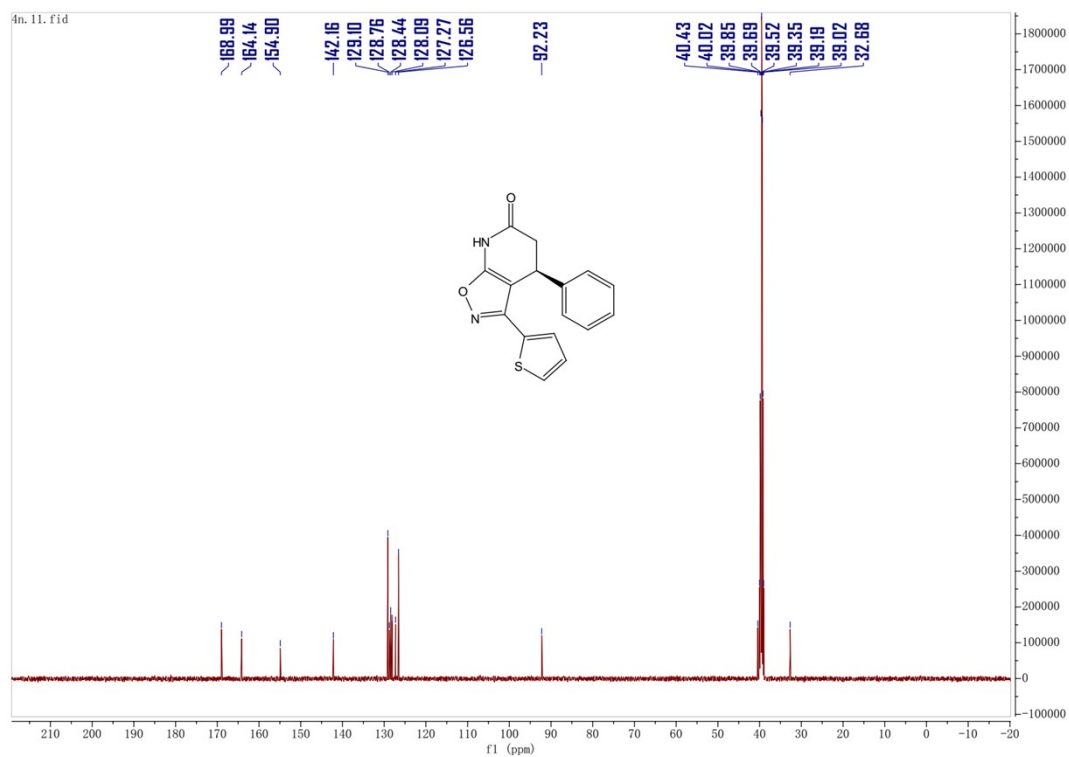
^1H NMR spectrum of **4m**



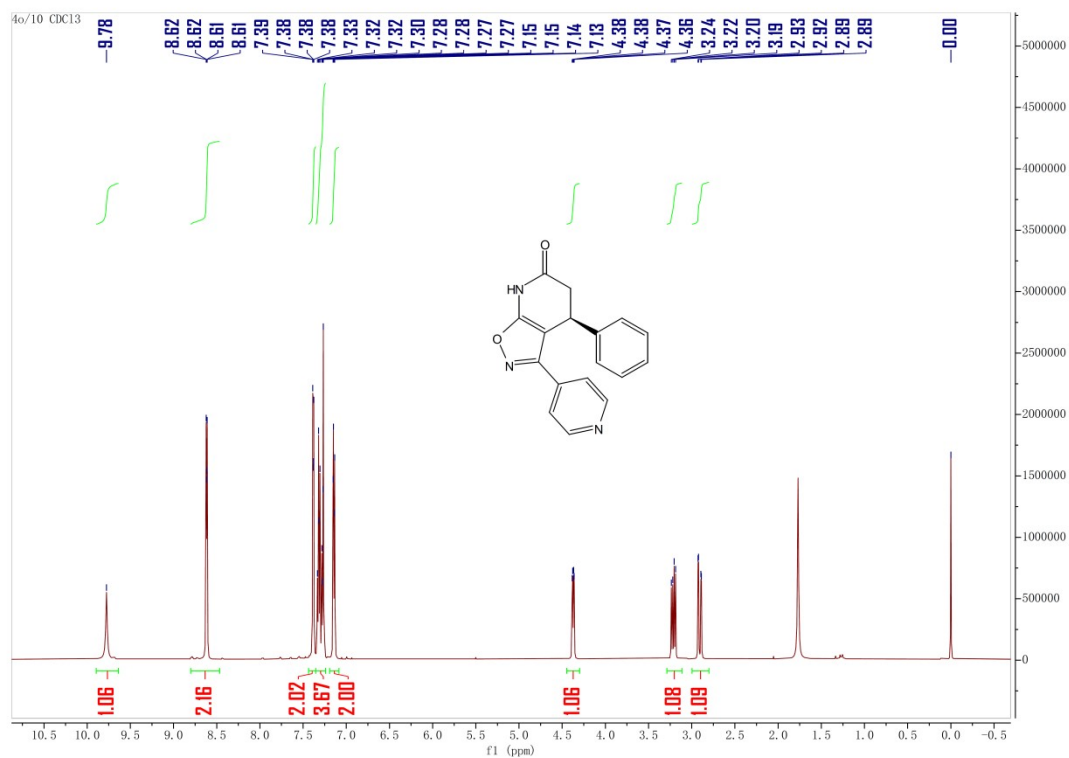
^{13}C NMR spectrum of **4m**



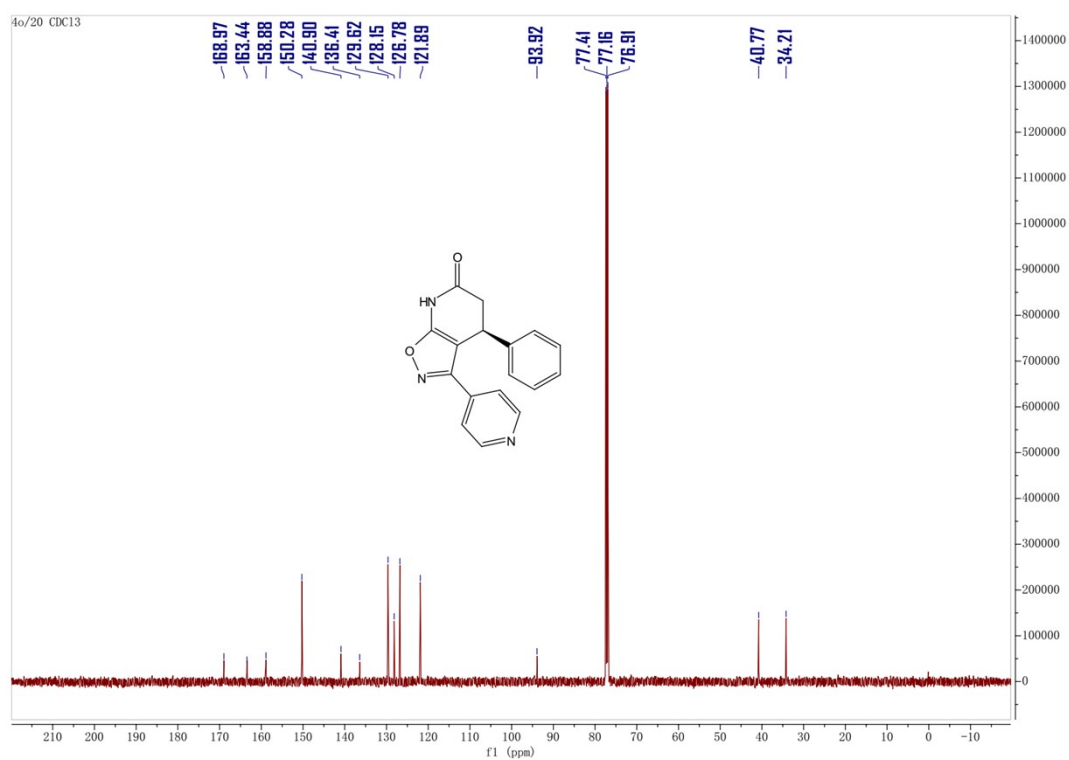
^1H NMR spectrum of 4n



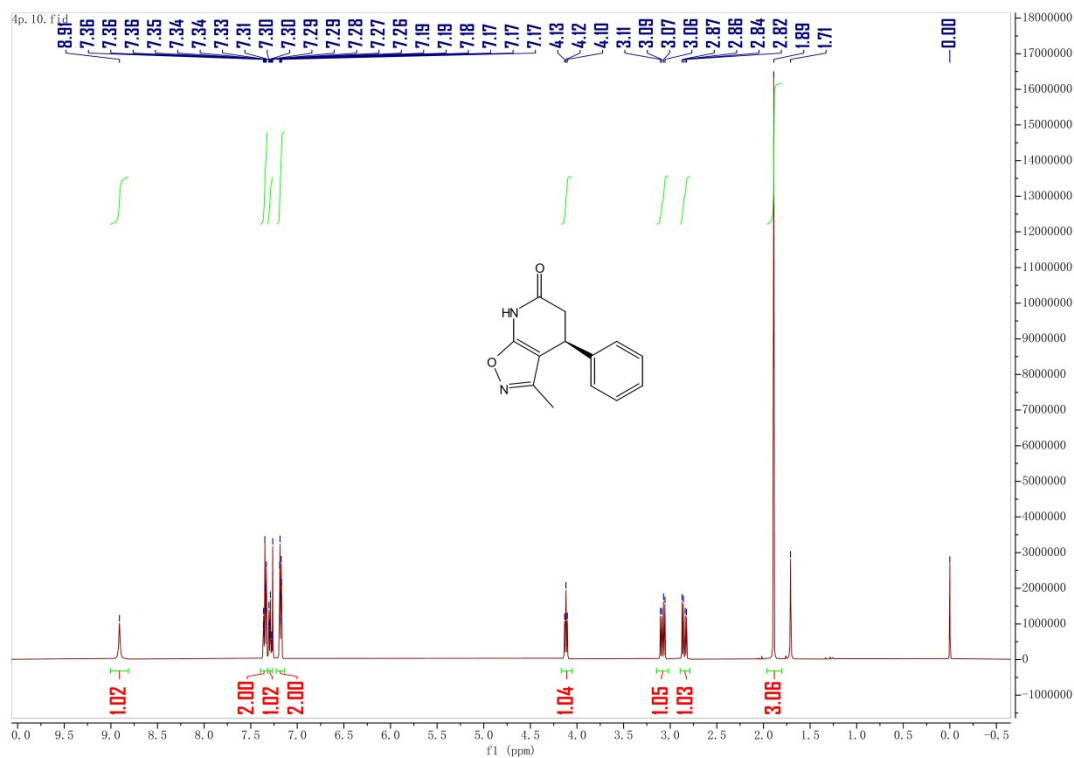
^{13}C NMR spectrum of 4n



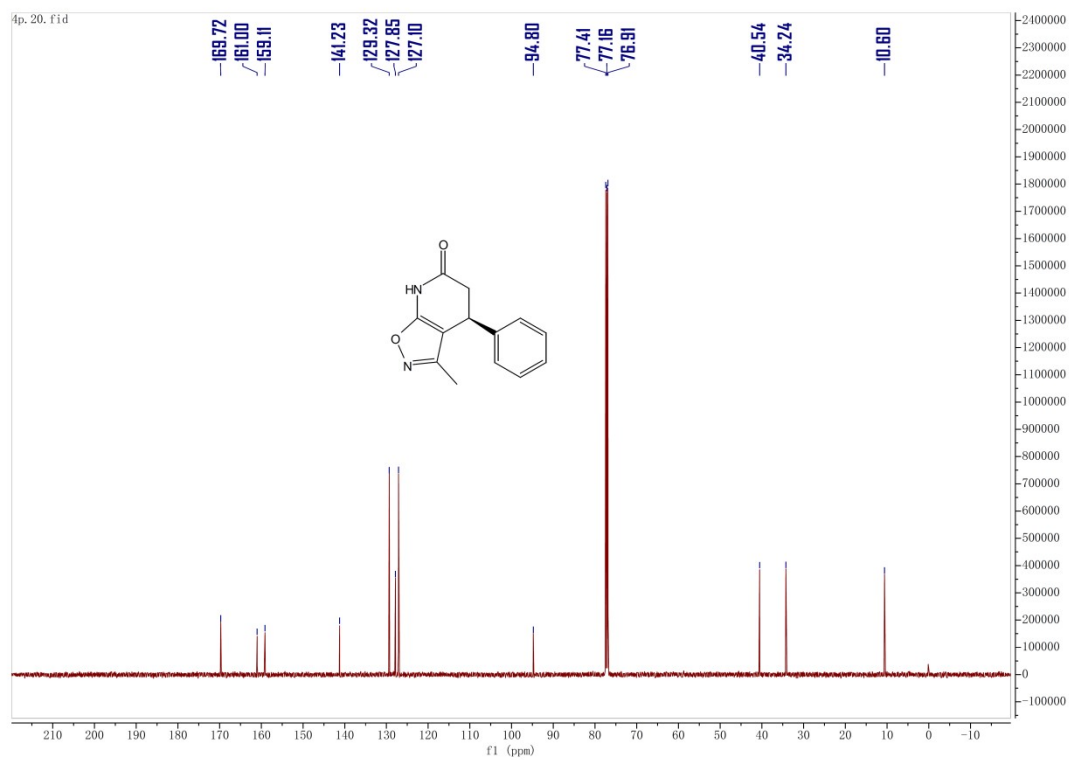
^1H NMR spectrum of **4o**



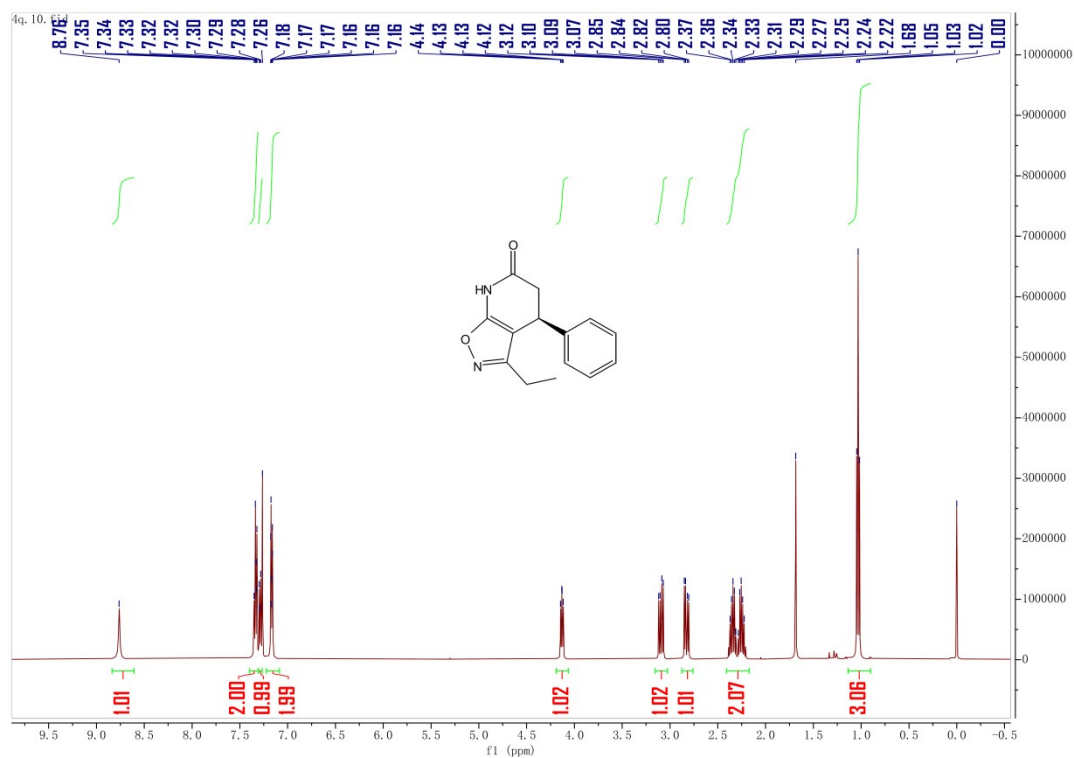
^{13}C NMR spectrum of **4o**



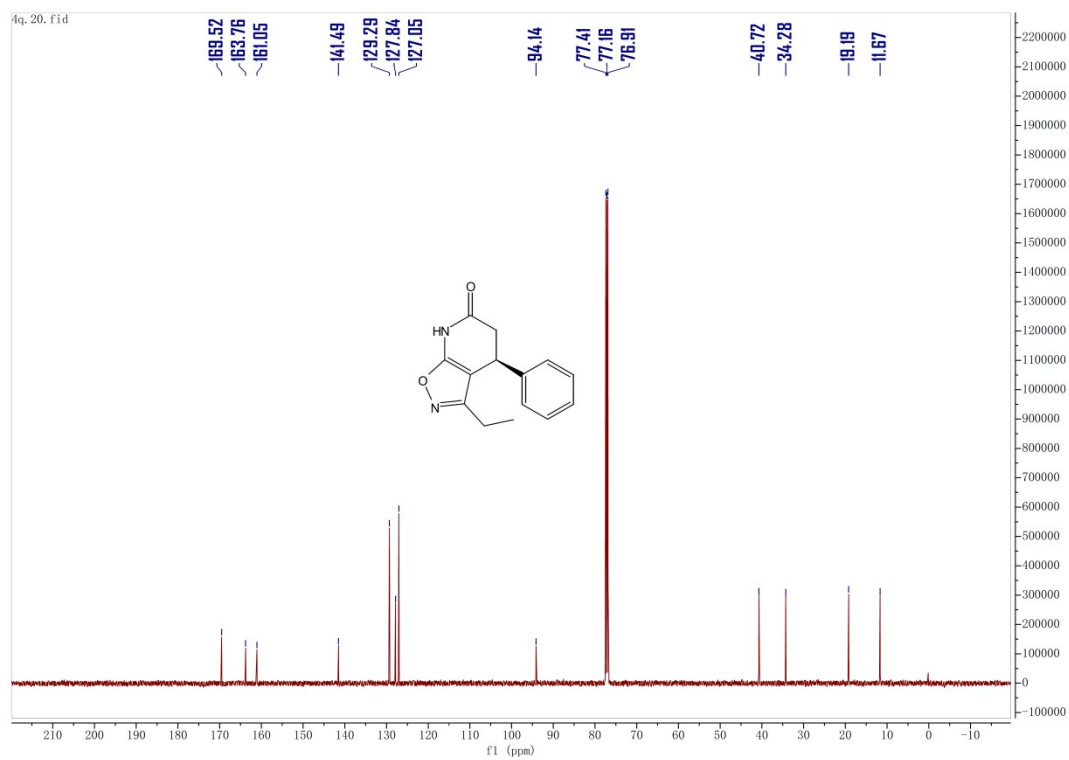
^1H NMR spectrum of 4p



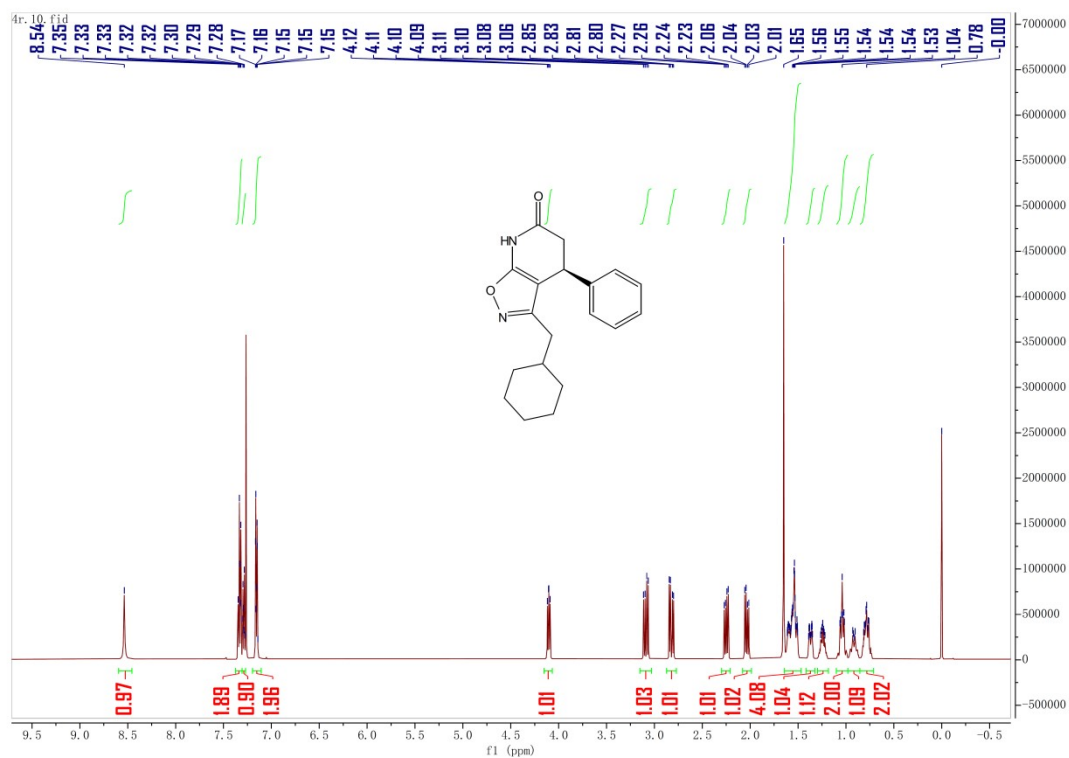
^{13}C NMR spectrum of 4p



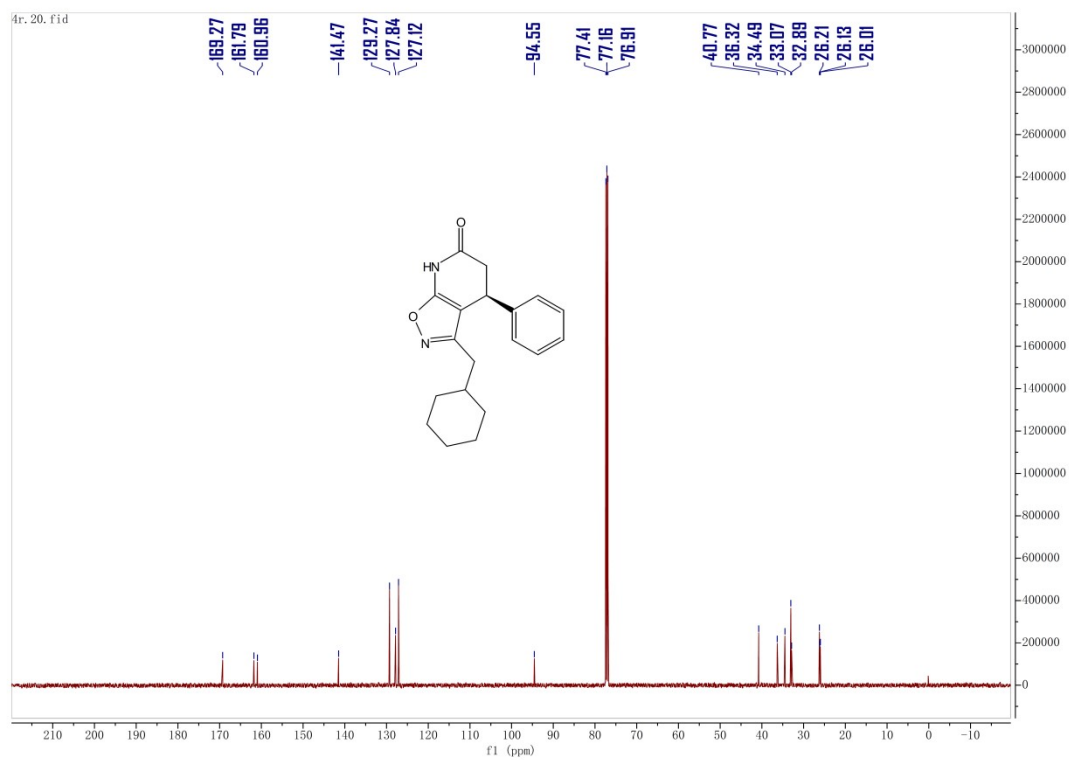
^1H NMR spectrum of **4q**



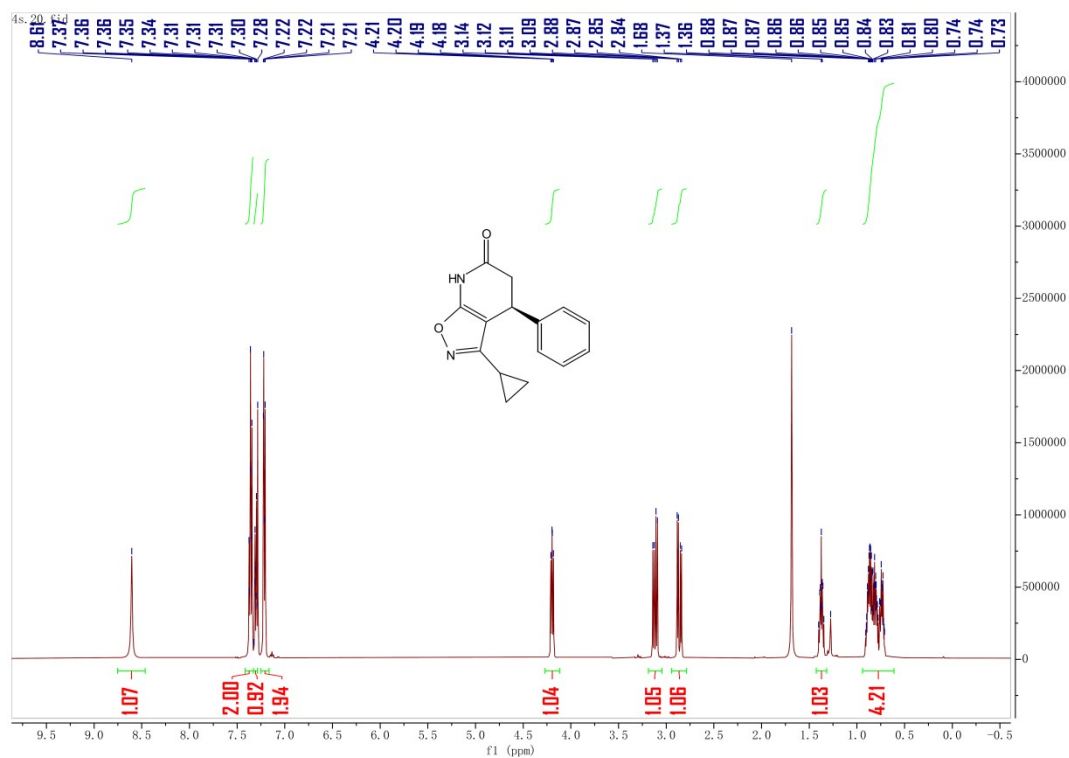
^{13}C NMR spectrum of **4q**



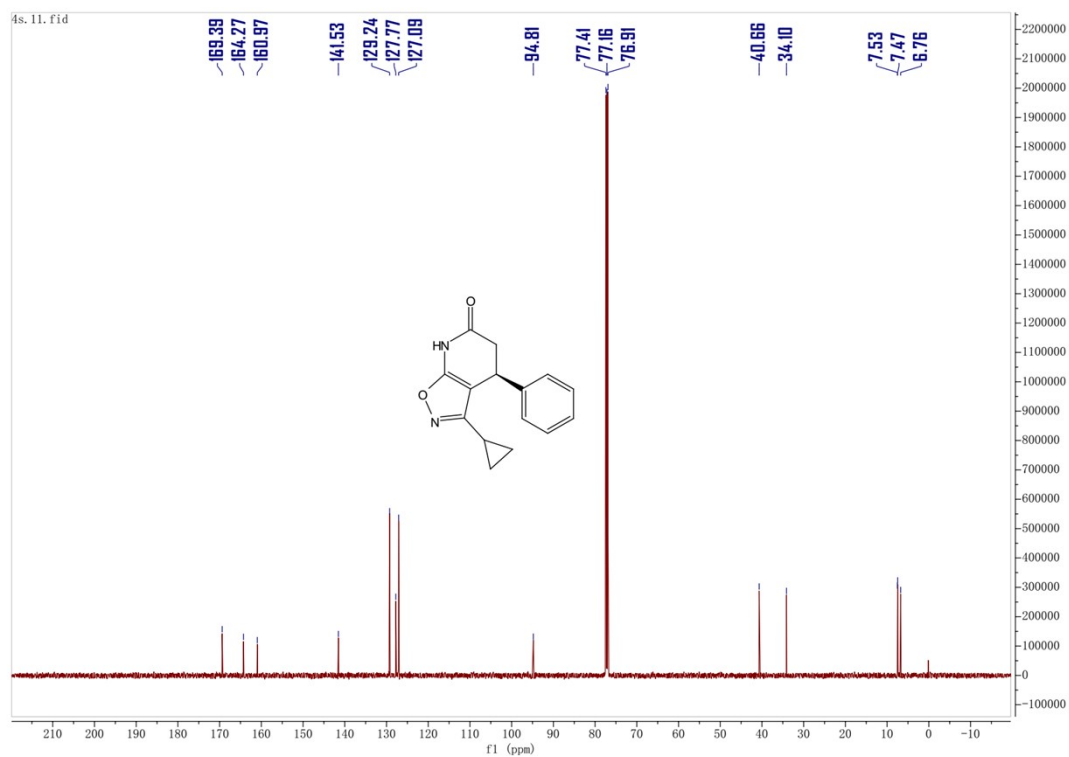
^1H NMR spectrum of 4r



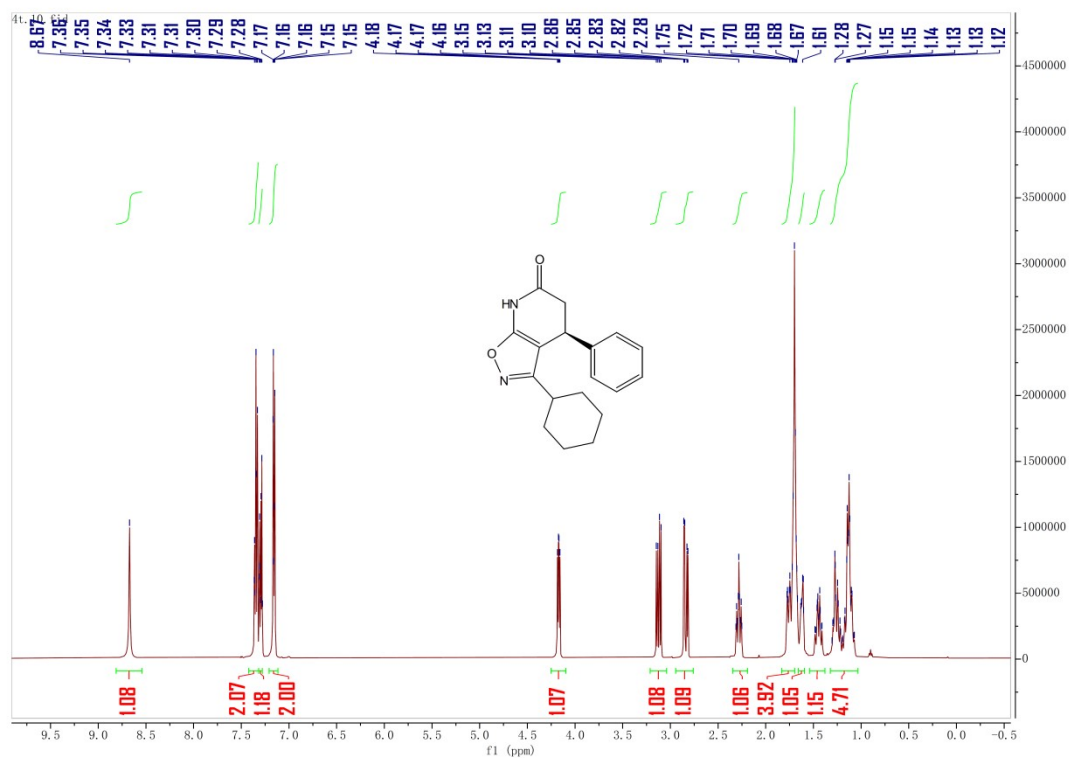
^{13}C NMR spectrum of 4r



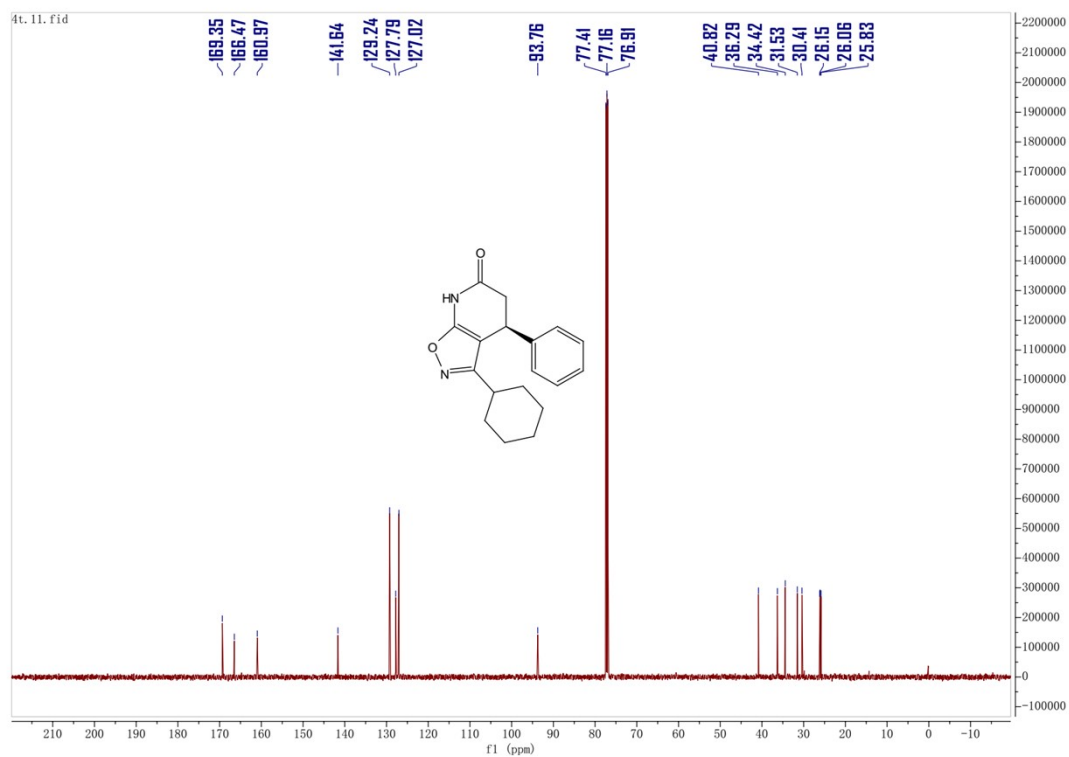
^1H NMR spectrum of 4s



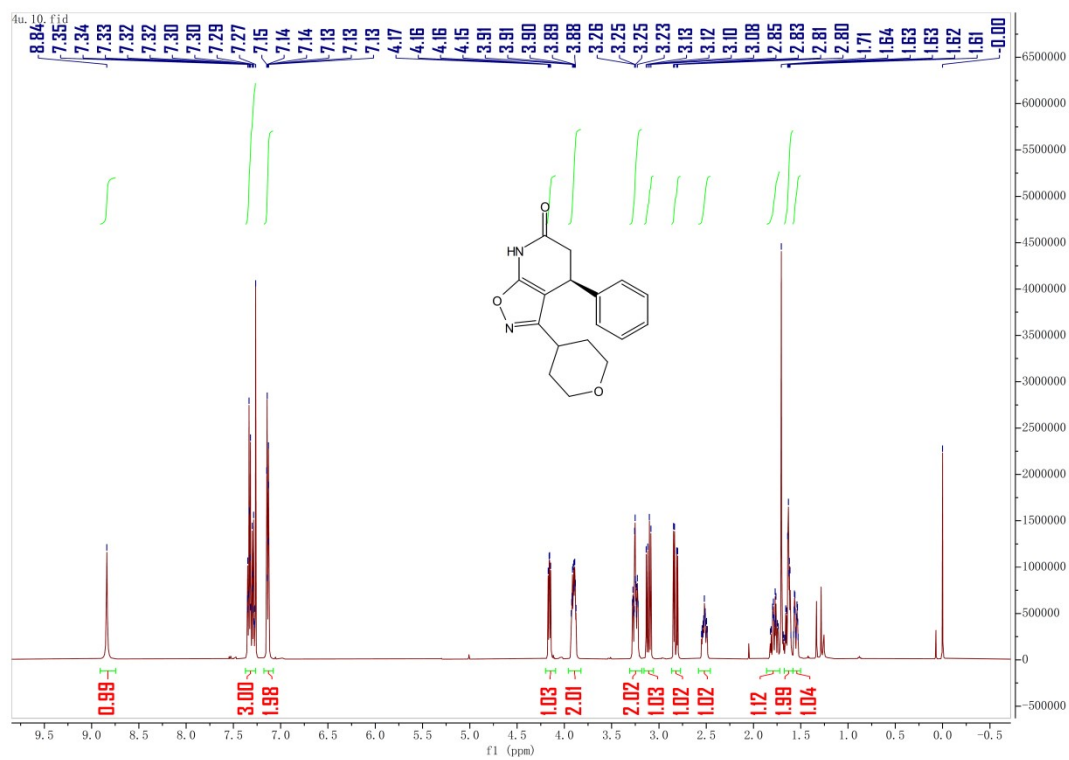
^{13}C NMR spectrum of 4s



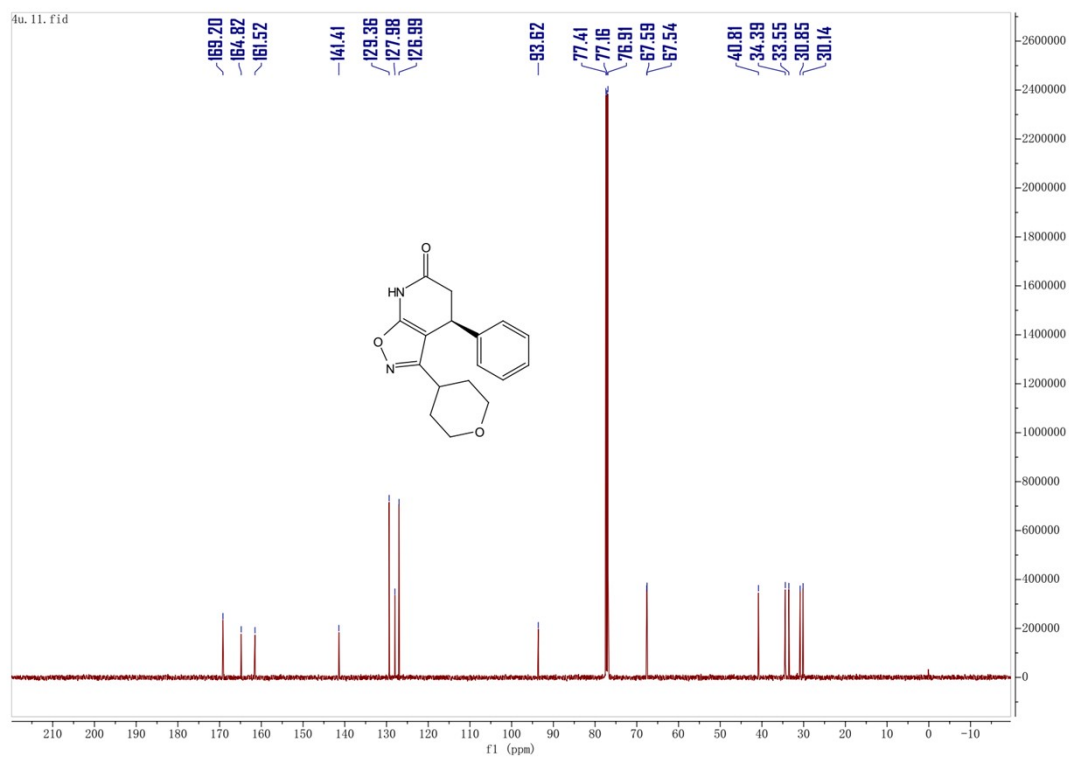
¹H NMR spectrum of 4t



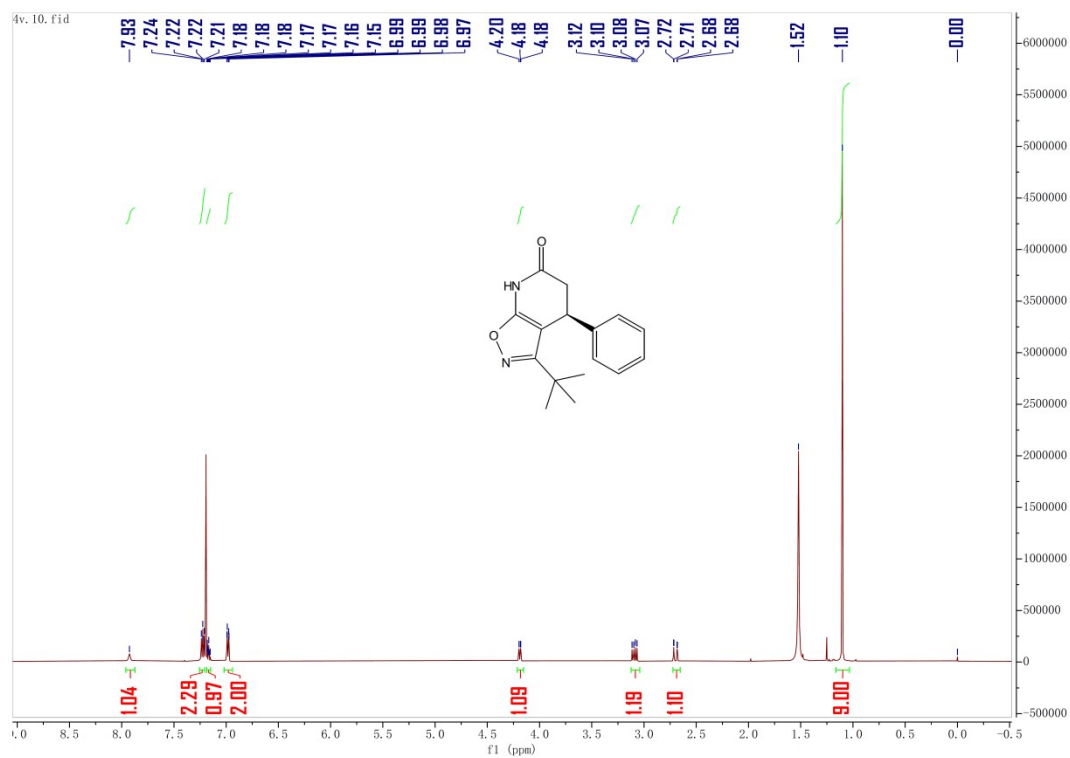
¹³C NMR spectrum of 4t



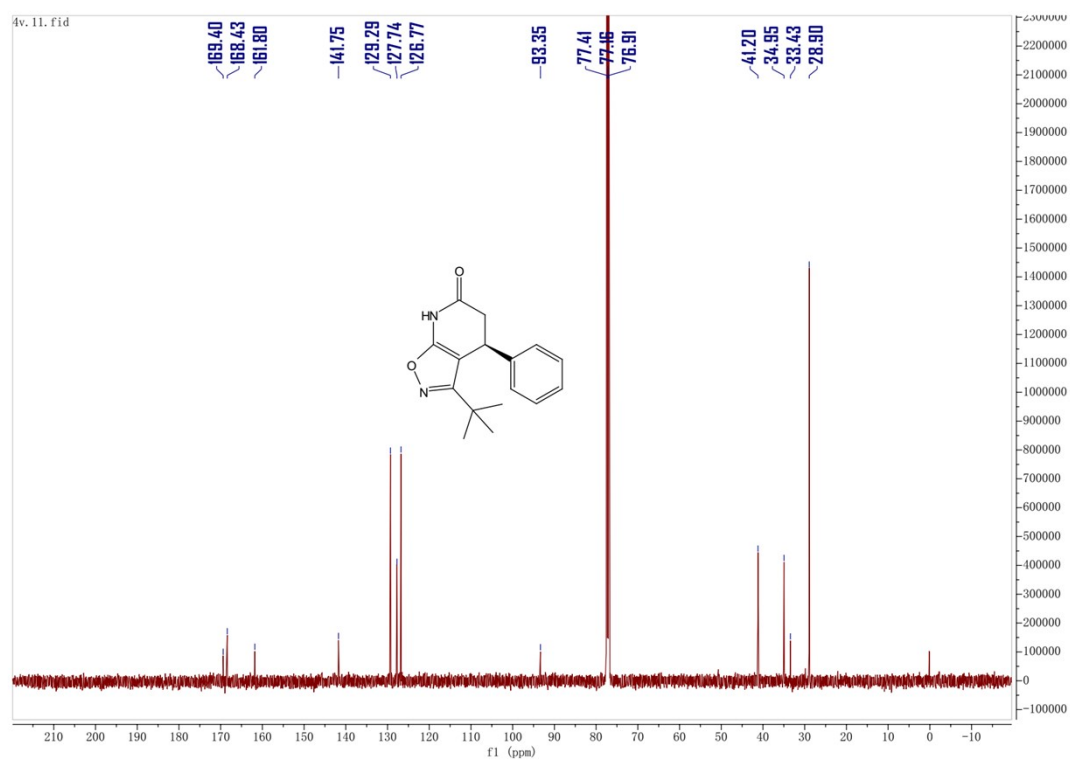
^1H NMR spectrum of **4u**



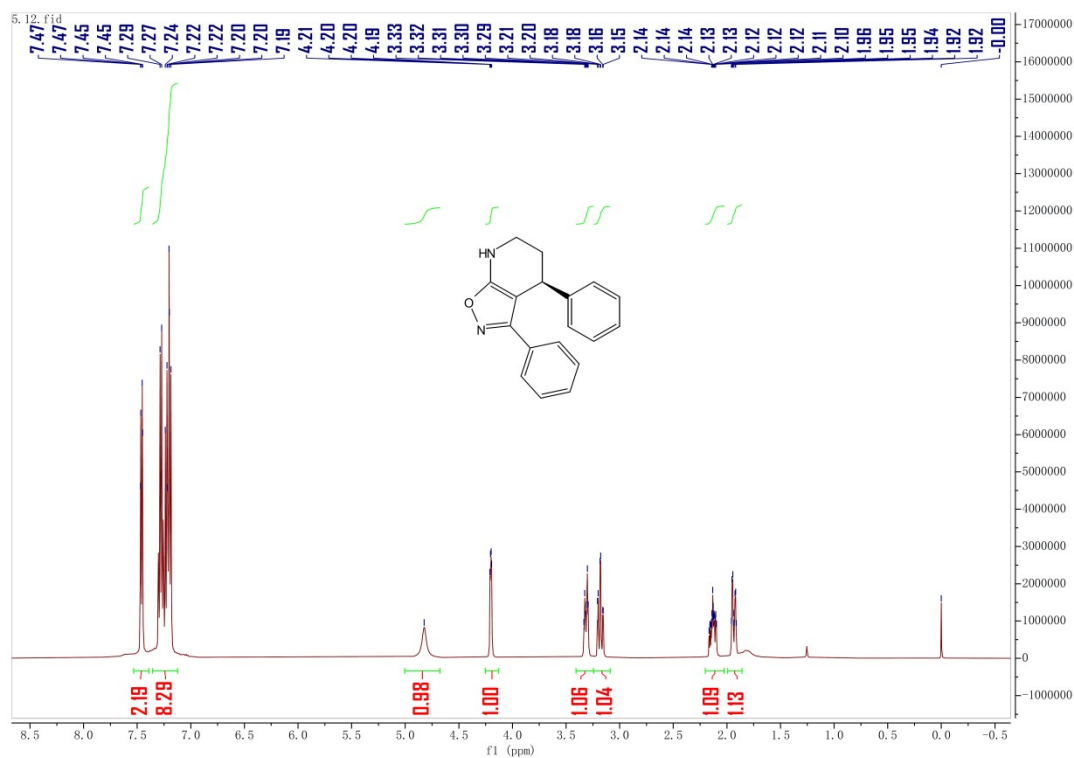
^{13}C NMR spectrum of **4u**



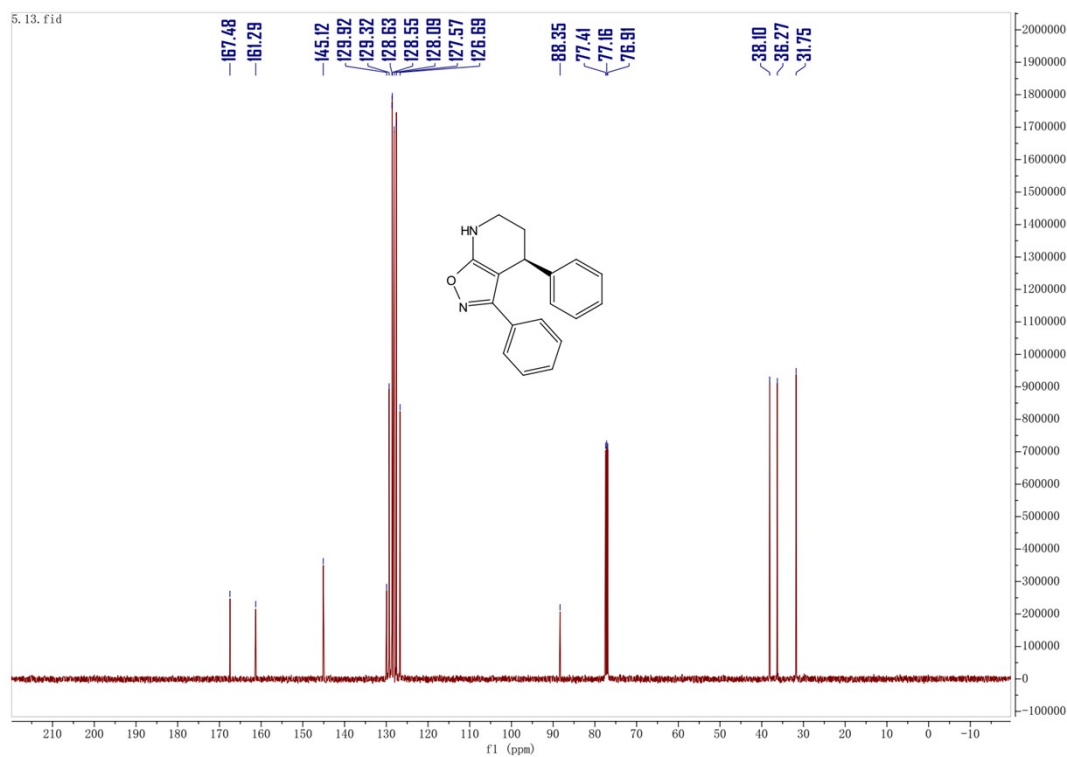
^1H NMR spectrum of 4v



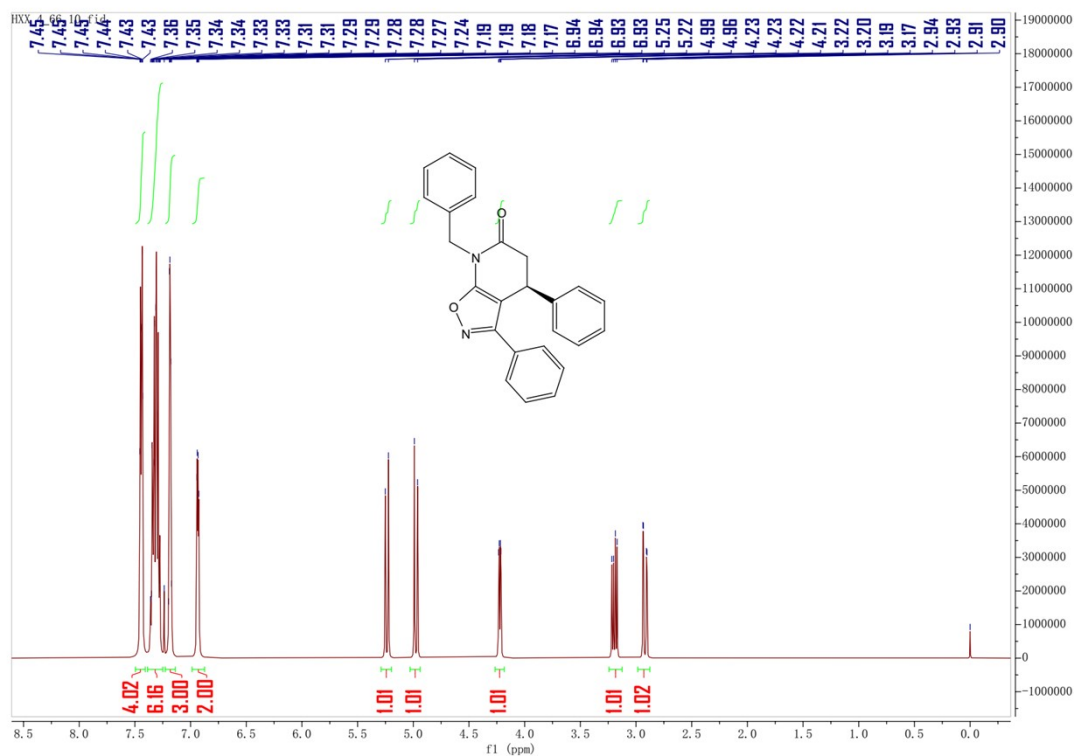
^{13}C NMR spectrum of 4v



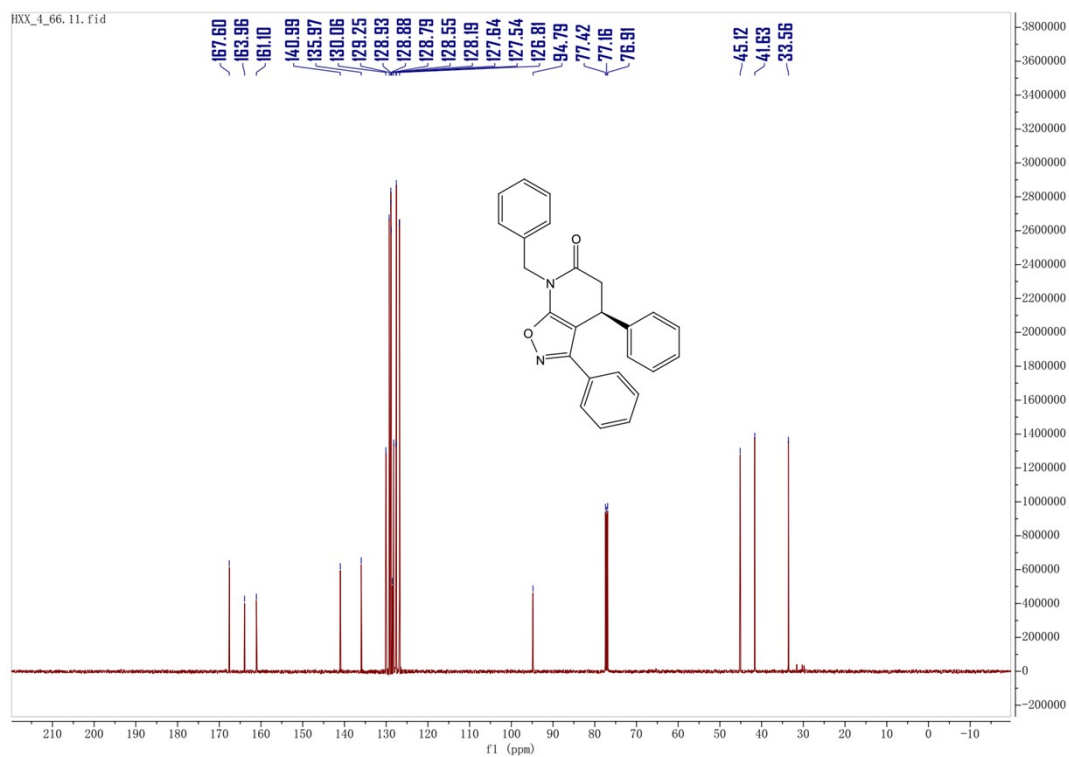
^1H NMR spectrum of **5**



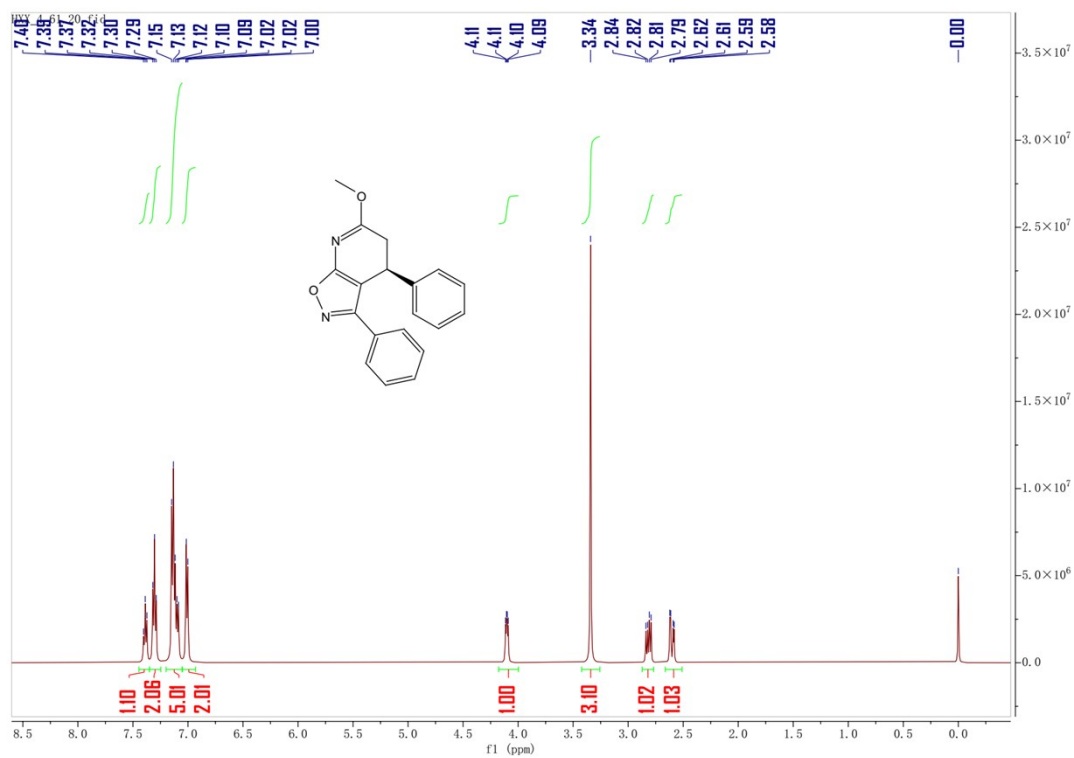
^{13}C NMR spectrum of **5**



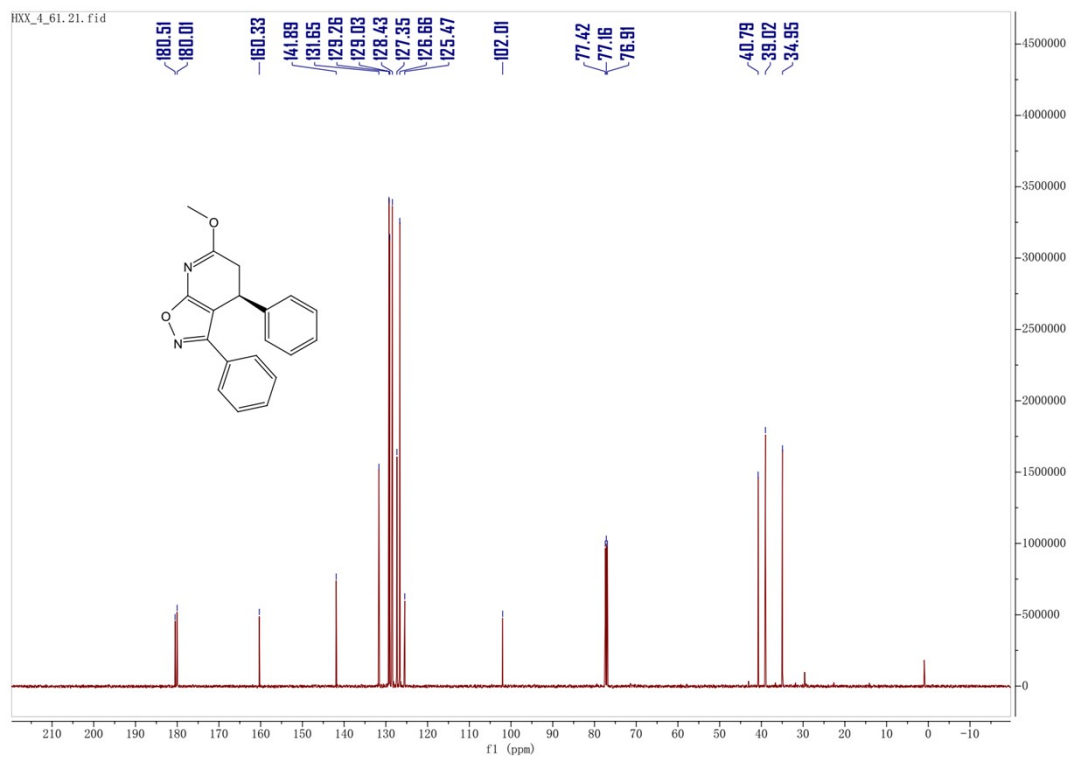
^1H NMR spectrum of **6**



^{13}C NMR spectrum of **6**

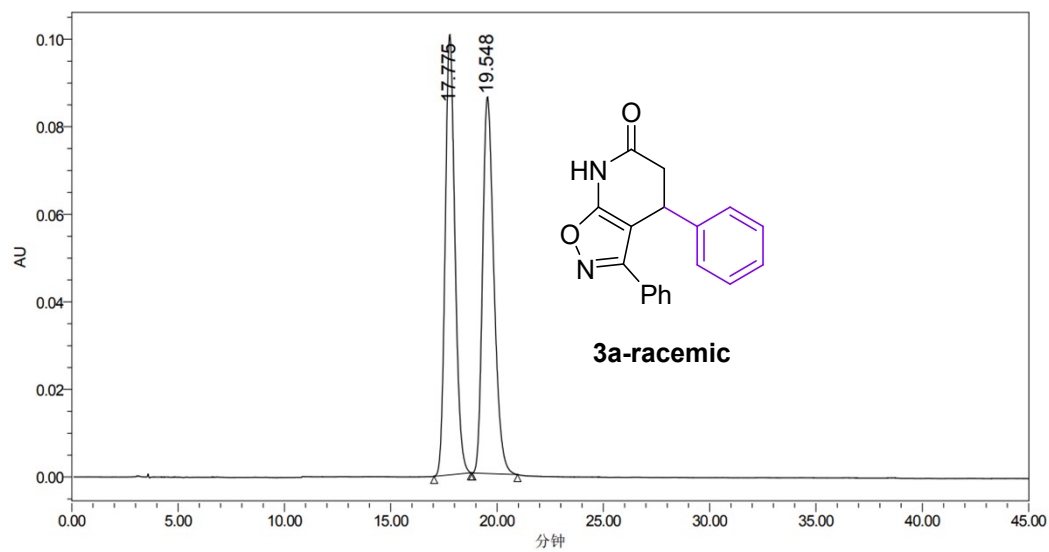


¹H NMR spectrum of 7

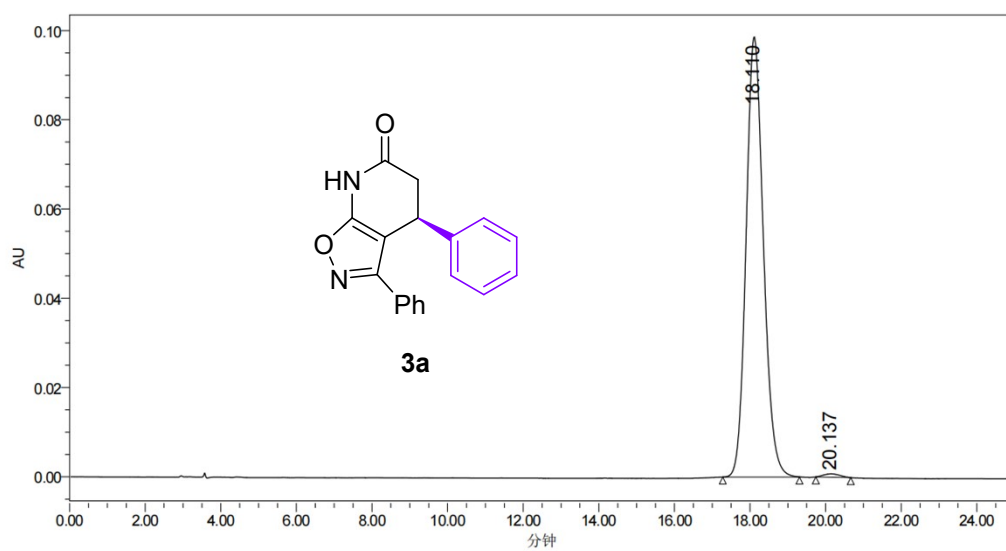


¹³C NMR spectrum of 7

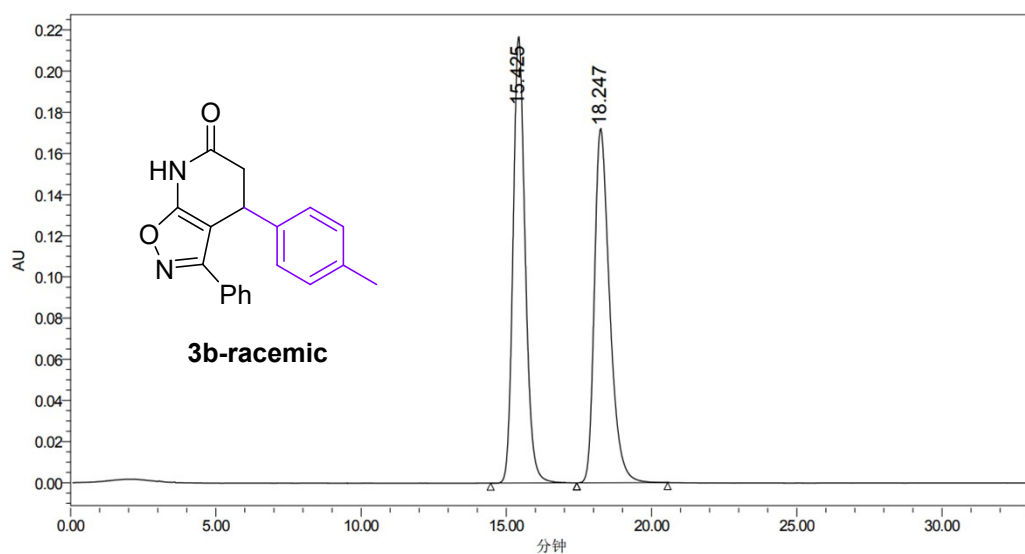
8. HPLC Chromatograms



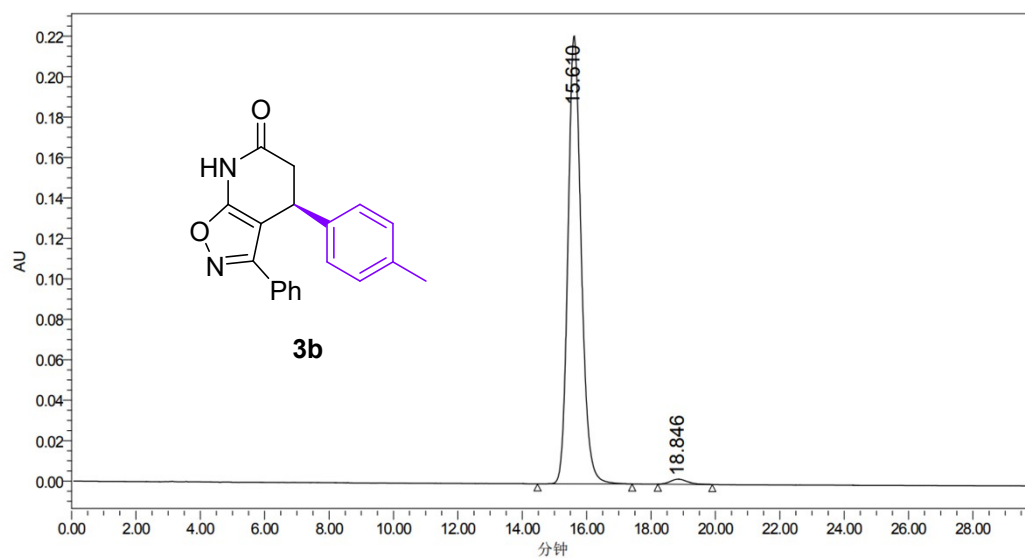
Peak	Ret.Time	Area	Height	Area%	Height%
1	17.775	3191204	100549	50.03	53.90
2	19.548	3187240	86002	49.97	46.10
Total		6378444	186551	100.00	100.00



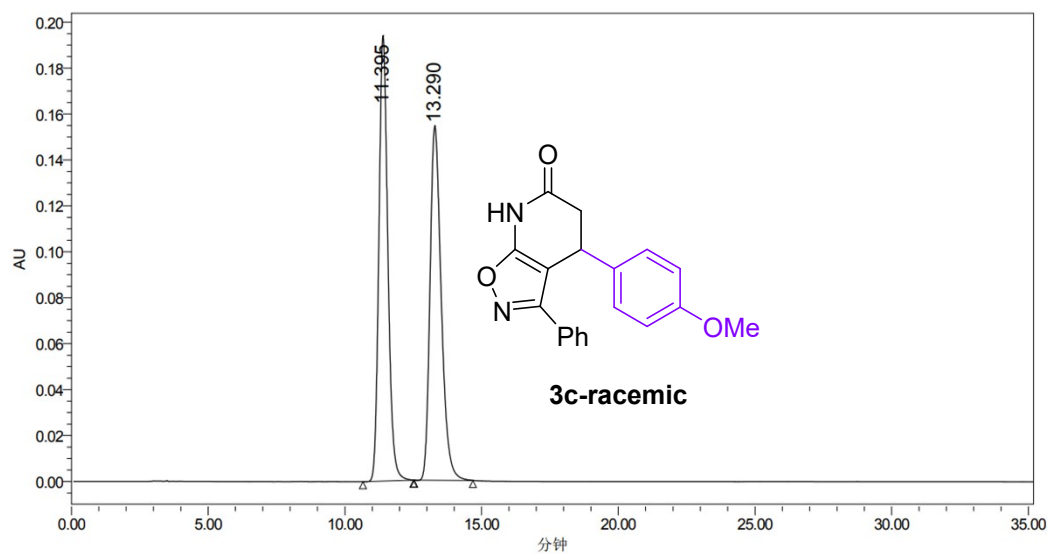
Peak	Ret.Time	Area	Height	Area%	Height%
1	18.110	3140860	98578	99.30	99.24
2	20.137	22284	753	0.70	0.76
Total		3163144	99331	100.00	100.00



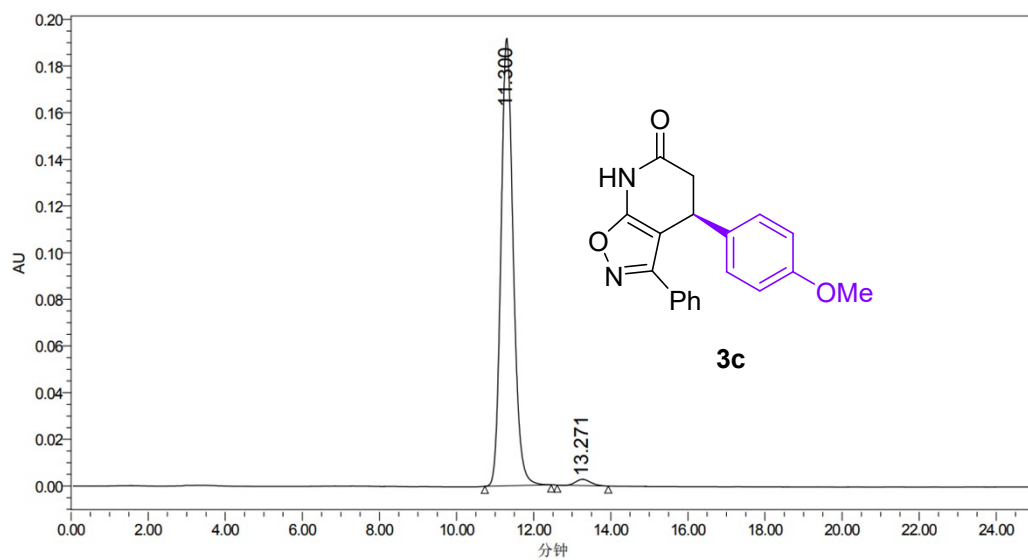
Peak	Ret.Time	Area	Height	Area%	Height%
1	15.425	6299042	216776	50.08	55.75
2	18.247	6278738	172049	49.92	44.25
Total		12577780	388825	100.00	100.00



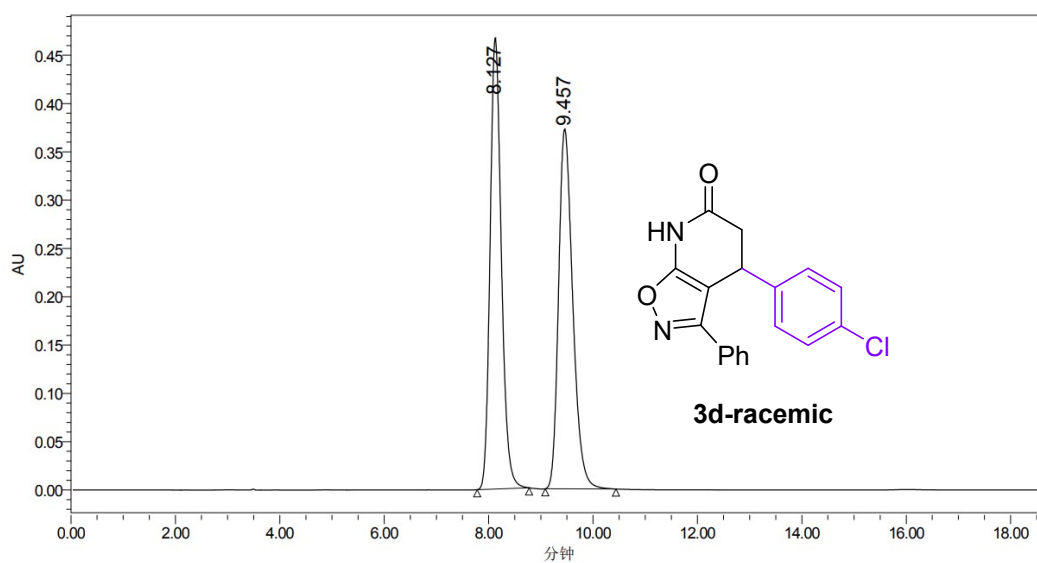
Peak	Ret.Time	Area	Height	Area%	Height%
1	15.610	6331856	221380	98.56	98.88
2	18.846	92683	2515	1.44	1.12
Total		6424539	223895	100.00	100.00



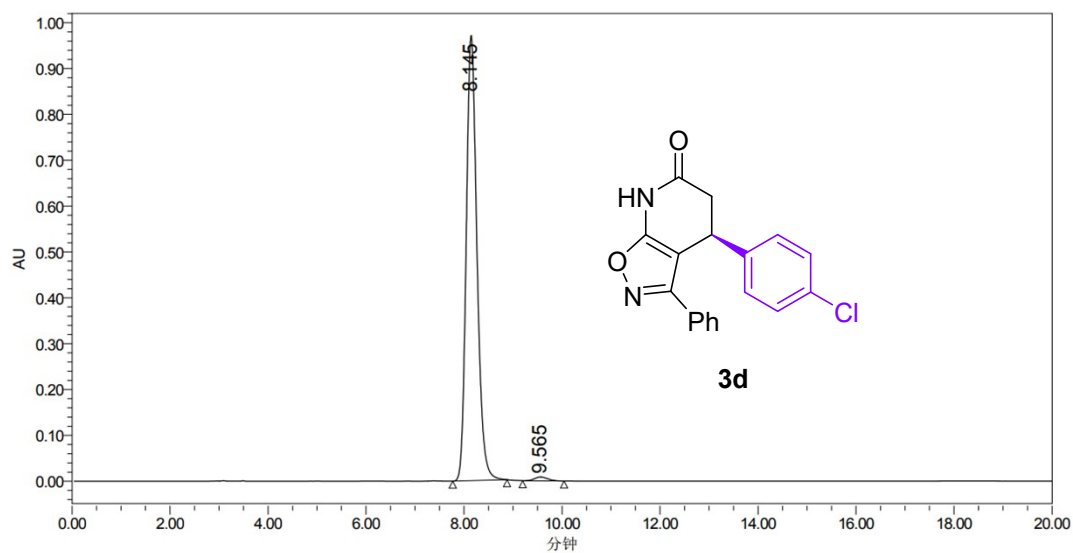
Peak	Ret.Time	Area	Height	Area%	Height%
1	11.395	4417859	193976	50.14	55.68
2	13.290	4393973	154386	49.86	44.32
Total		8811832	348362	100.00	100.00



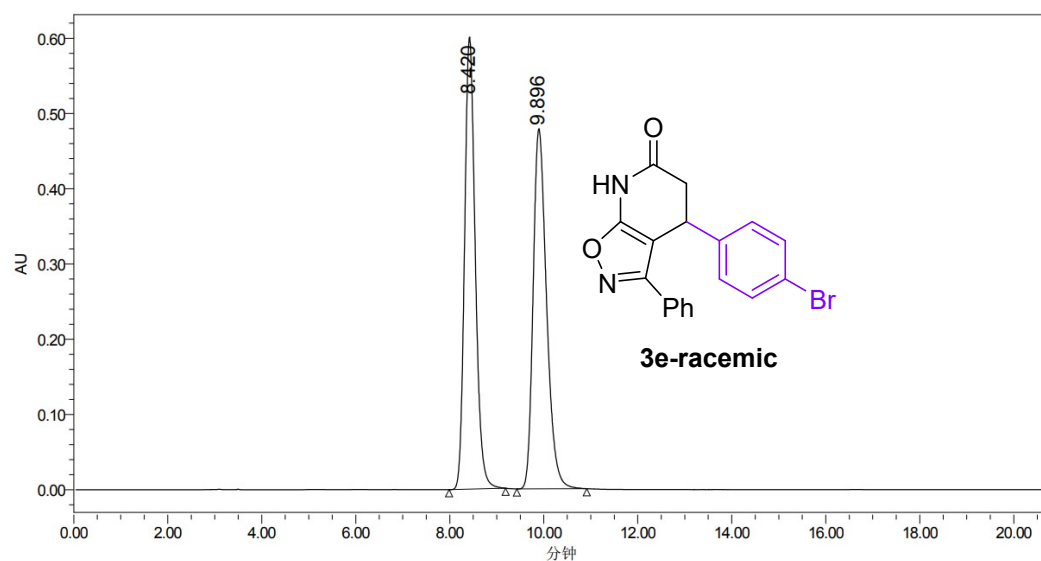
Peak	Ret.Time	Area	Height	Area%	Height%
1	11.300	4237595	191740	98.31	98.61
2	13.271	72868	2696	1.69	1.39
Total		4310463	194436	100.00	100.00



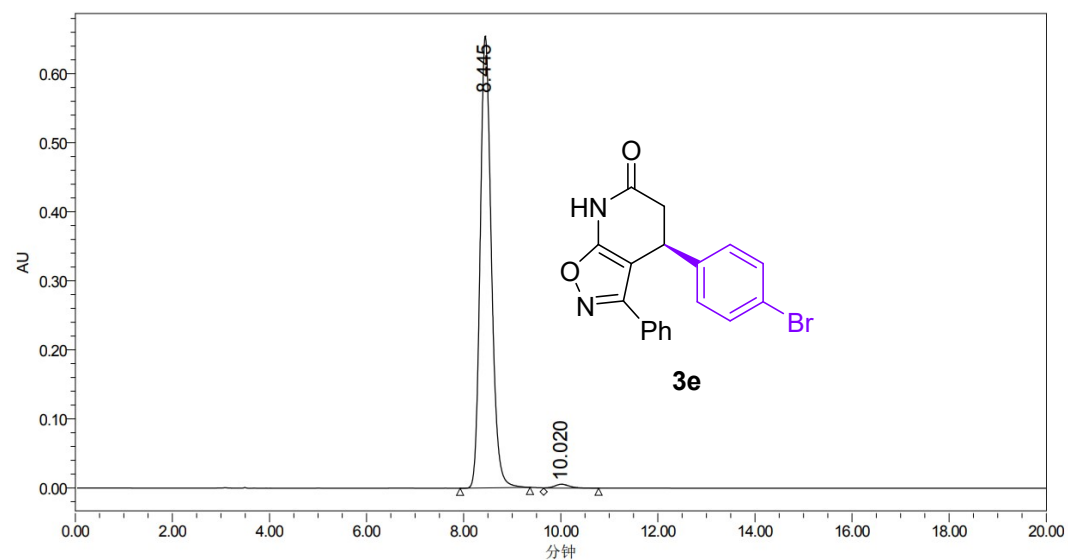
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.127	6995249	466998	49.91	55.65
2	9.457	7019254	372242	50.09	44.35
Total		14014503	839240	100.00	100.00



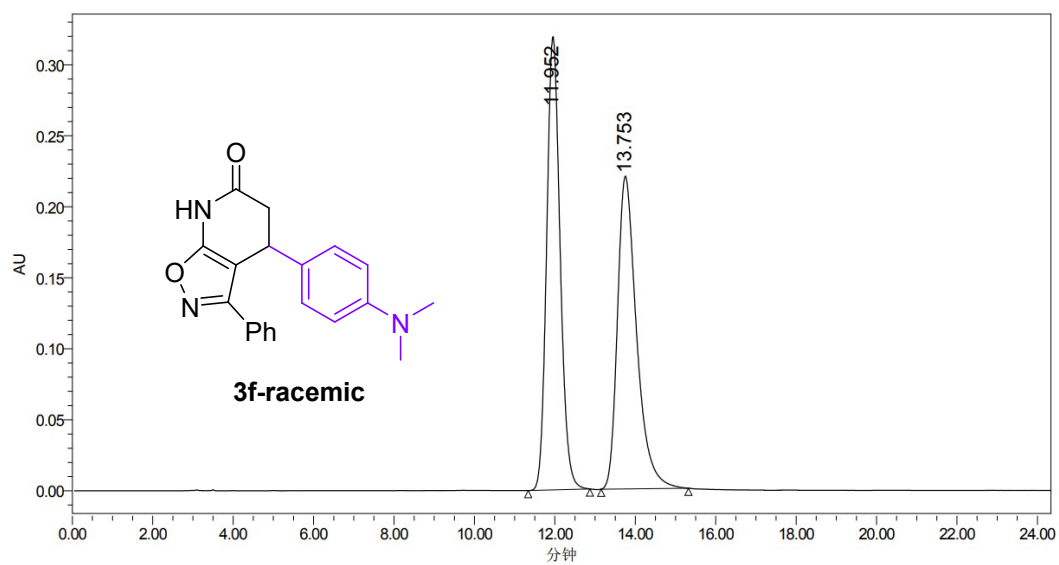
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.145	14690057	970288	98.99	99.16
2	9.565	150504	8207	1.01	0.84
Total		14840561	978495	100.00	100.00



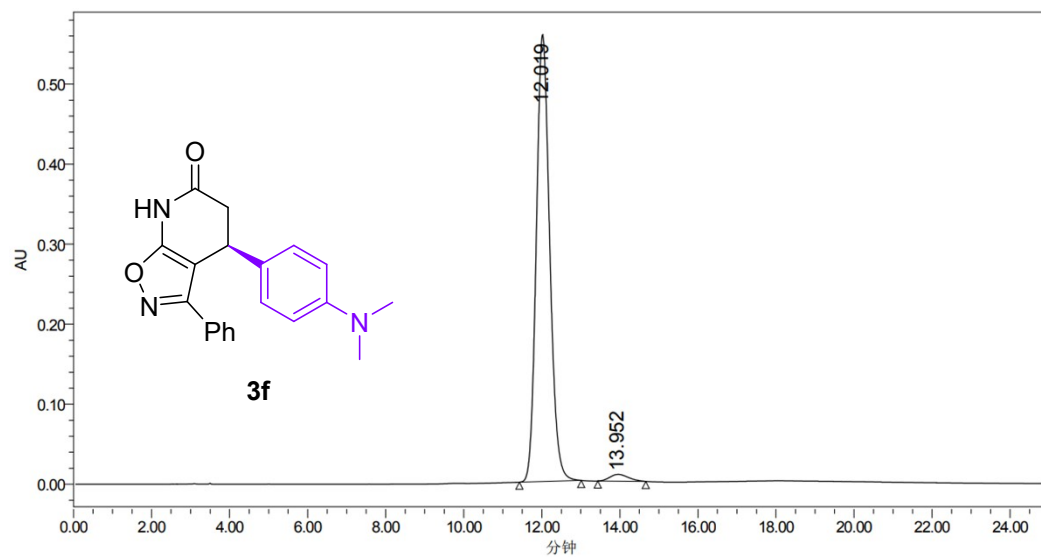
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.420	9478336	600493	49.98	55.66
2	9.896	9484897	478348	50.02	44.34
Total		18963233	1078841	100.00	100.00



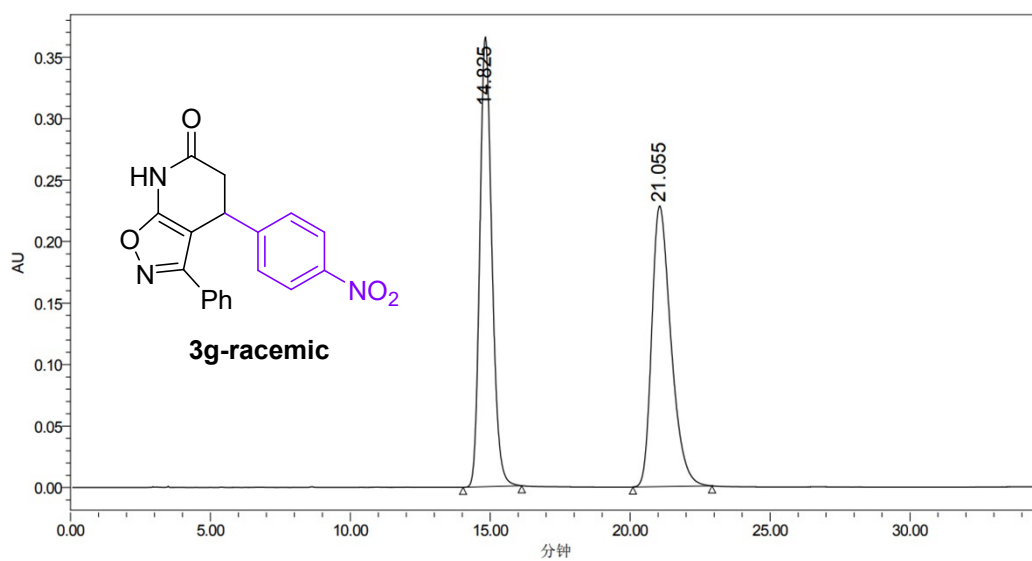
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.445	10441871	654455	98.84	99.14
2	10.020	122695	5647	1.16	0.86
Total		10564566	660102	100.00	100.00



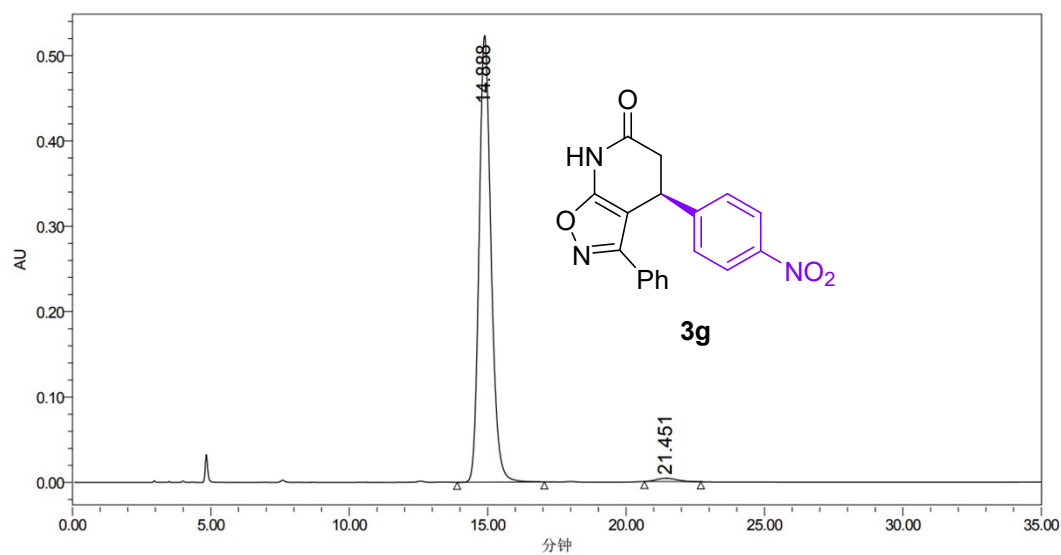
Peak	Ret.Time	Area	Height	Area%	Height%
1	11.952	7418534	319044	50.49	59.18
2	13.753	7275266	220088	49.51	40.82
Total		14693800	539132	100.00	100.00



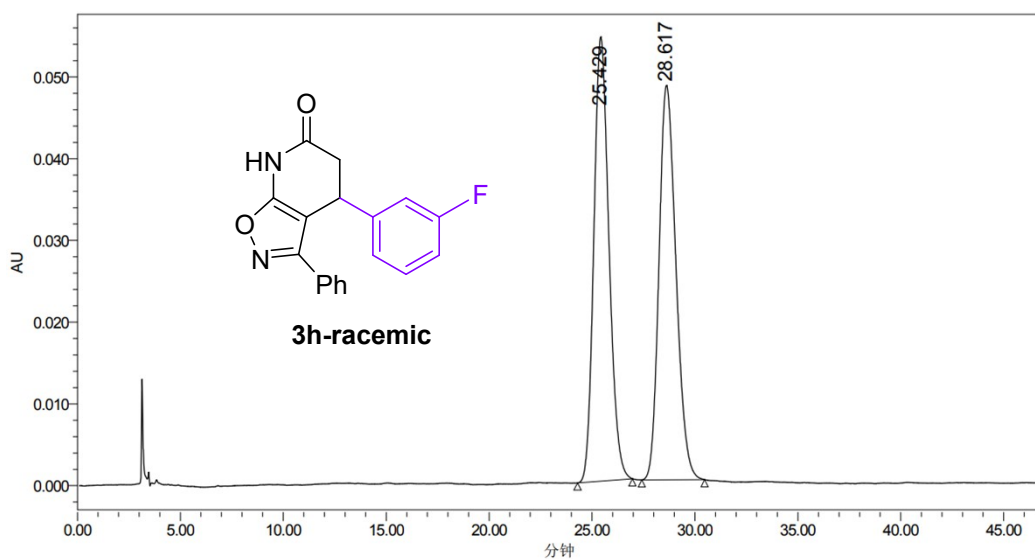
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.019	13278580	558258	97.91	98.50
2	13.952	283379	8525	2.09	1.50
Total		13561959	566783	100.00	100.00



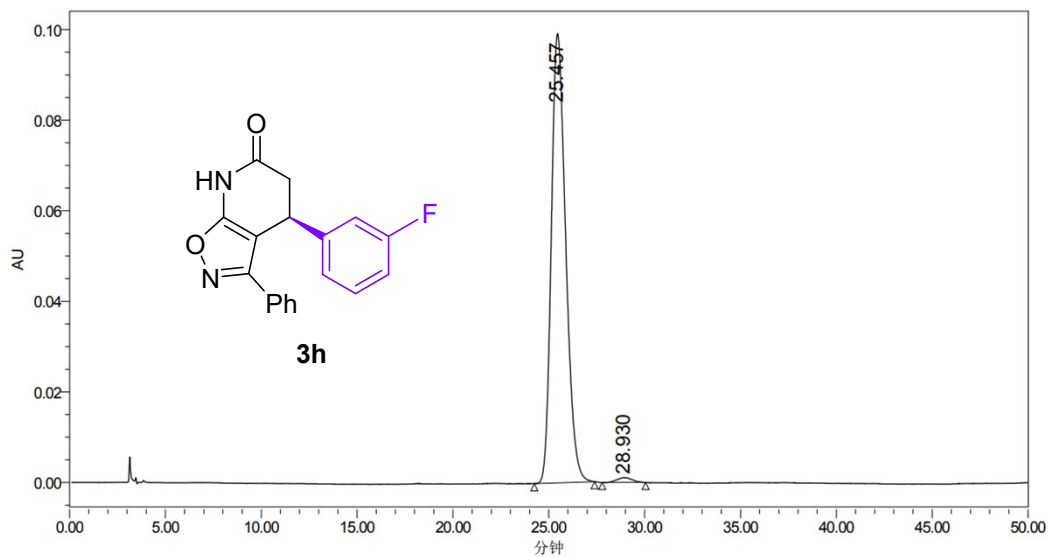
Peak	Ret.Time	Area	Height	Area%	Height%
1	14.825	10953482	365531	50.05	61.56
2	21.055	10930748	228235	49.95	38.44
Total		21884230	593766	100.00	100.00



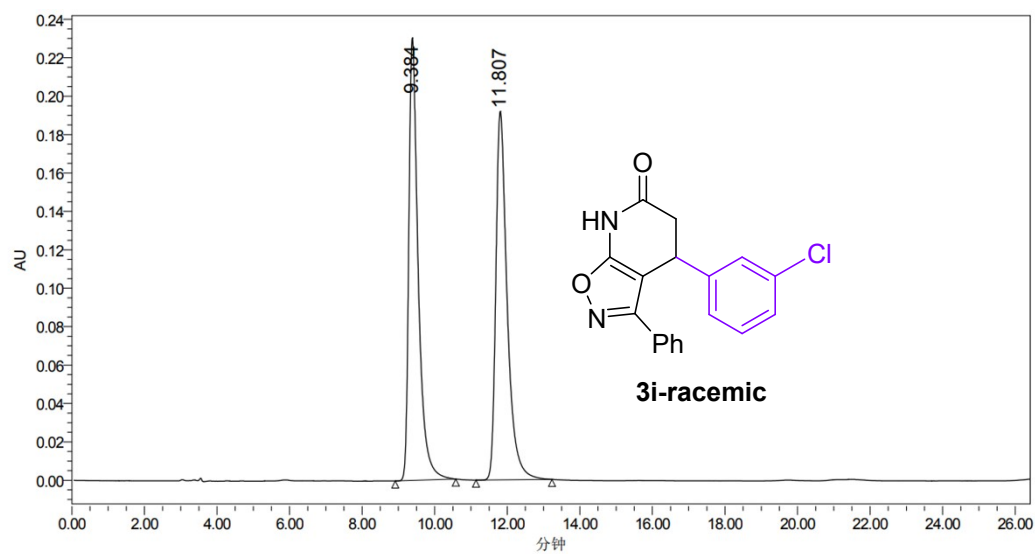
Peak	Ret.Time	Area	Height	Area%	Height%
1	14.888	15719193	522900	98.70	99.25
2	21.451	206611	3953	1.30	0.75
Total		15925804	526853	100.00	100.00



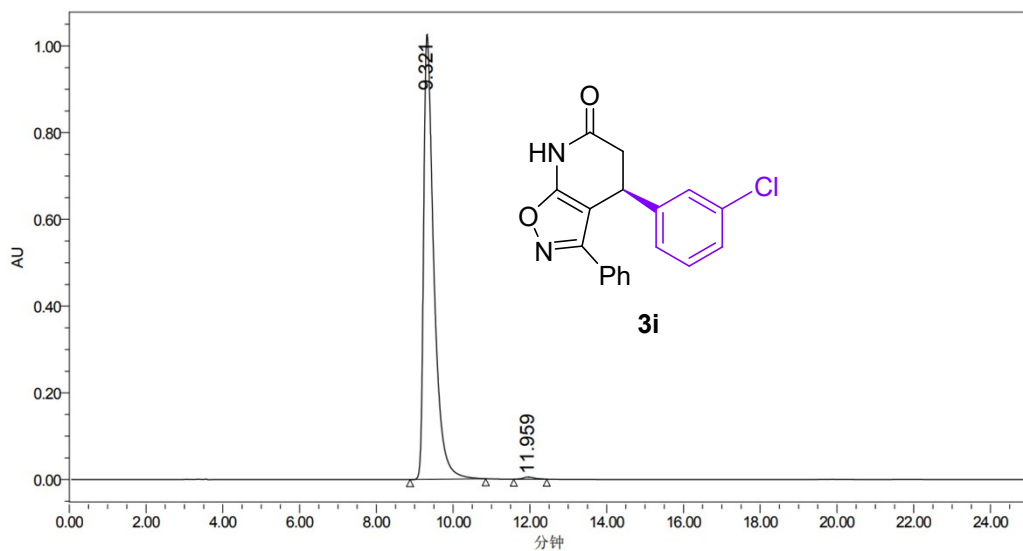
Peak	Ret.Time	Area	Height	Area%	Height%
1	25.429	2770319	54350	50.05	52.96
2	28.617	2765121	48268	49.95	47.04
Total		5535440	102618	100.00	100.00



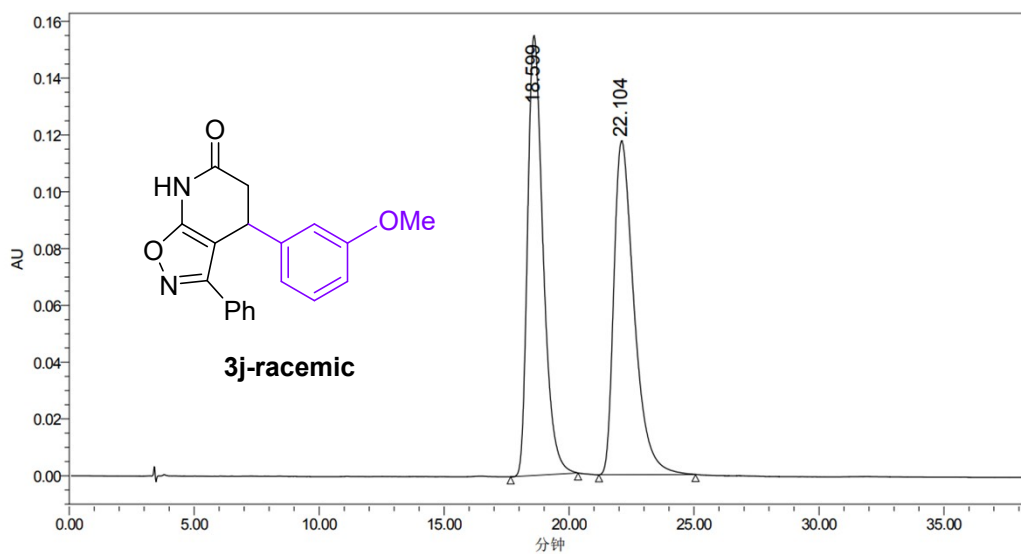
Peak	Ret.Time	Area	Height	Area%	Height%
1	25.457	5168533	99156	98.88	98.94
2	28.930	58756	1061	1.12	1.06
Total		5227289	100217	100.00	100.00



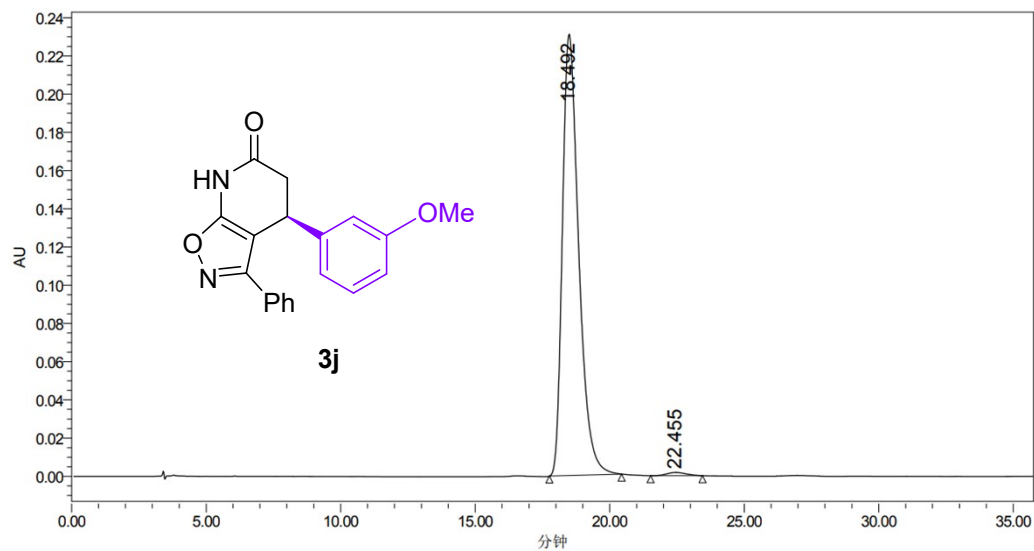
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.384	4143918	230412	49.86	54.57
2	11.807	4167929	191794	50.14	45.43
Total		8311847	422206	100.00	100.00



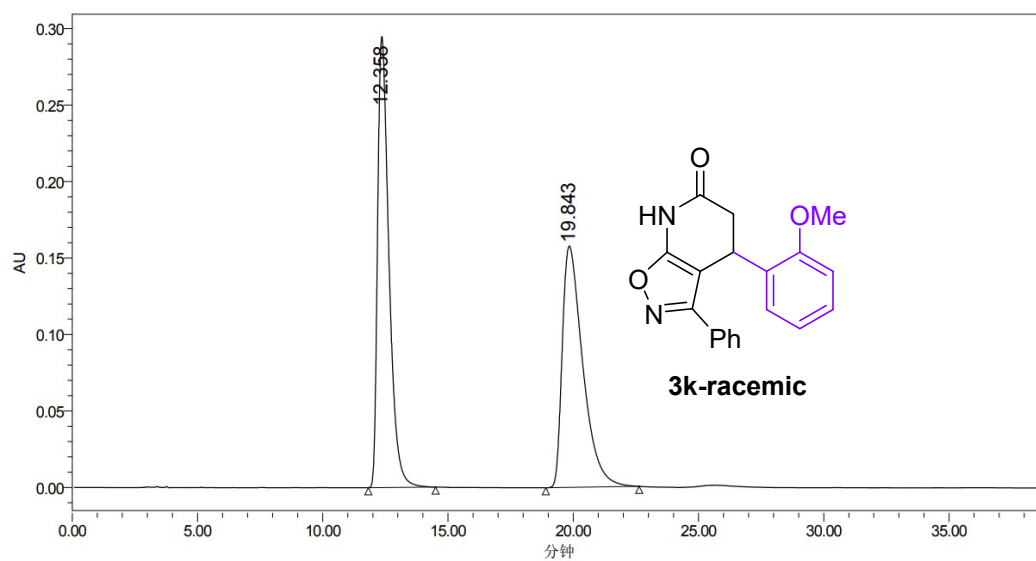
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.321	19023313	1026097	99.47	99.53
2	11.959	101056	4864	0.53	0.47
Total		19124369	1030961	100.00	100.00



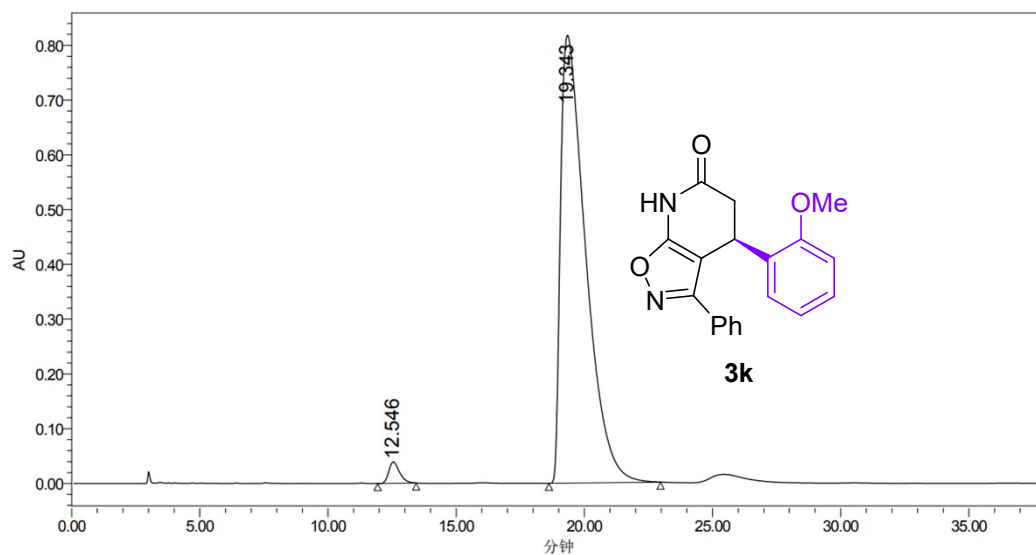
Peak	Ret. Time	Area	Height	Area%	Height%
1	18.599	6665658	154845	50.16	56.83
2	22.104	6622751	117605	49.84	43.17
Total		13288409	272450	100.00	100.00



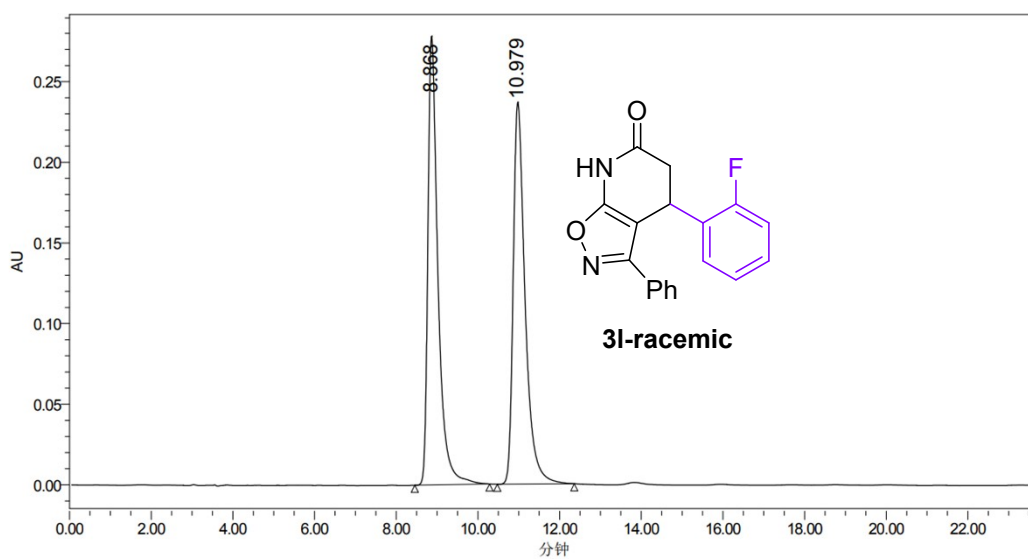
Peak	Ret. Time	Area	Height	Area%	Height%
1	18.492	9720964	230867	99.12	99.26
2	22.455	86194	1732	0.88	0.74
Total		9807158	232599	100.00	100.00



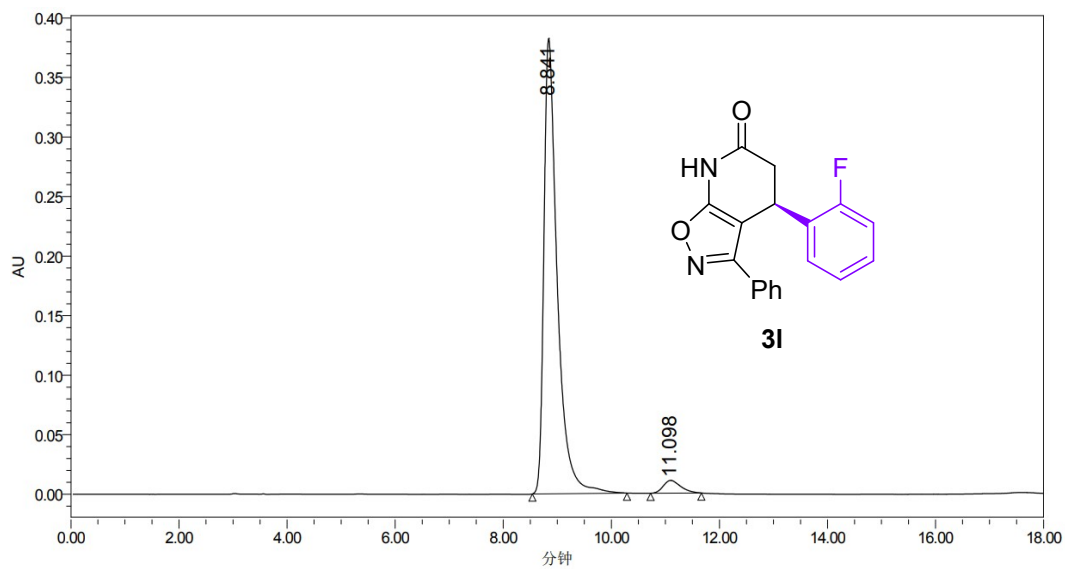
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.358	9289340	294718	50.81	65.13
2	19.843	8991588	157772	49.19	34.87
Total		18280928	452490	100.00	100.00



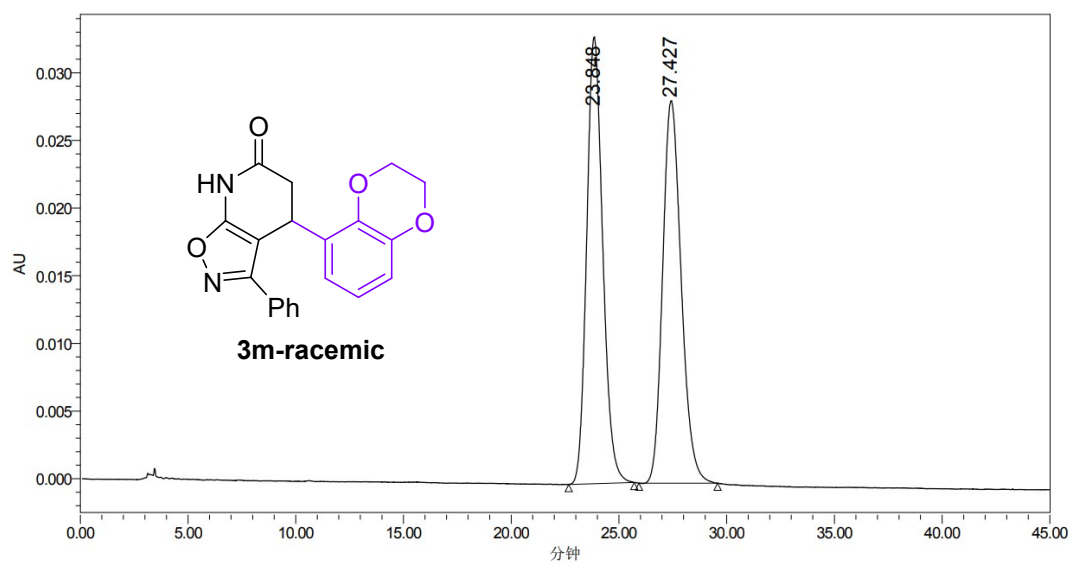
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.546	1139695	38948	2.01	4.55
2	19.343	55490471	817237	97.99	95.45
Total		56630166	856185	100.00	100.00



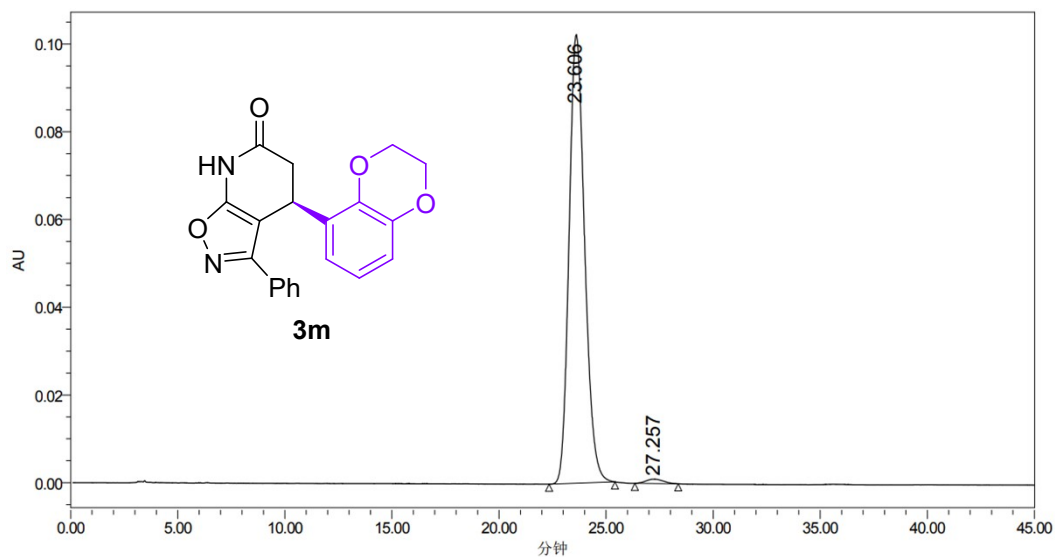
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.868	4773979	278298	49.96	54.03
2	10.979	4782576	236753	50.04	45.97
Total		9556555	515051	100.00	100.00



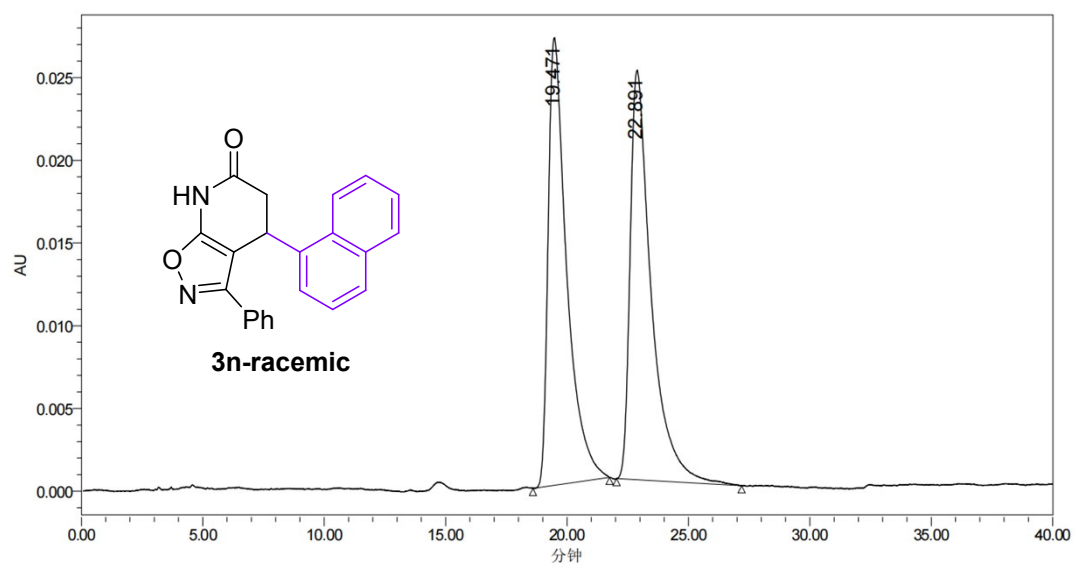
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.841	6565632	382368	96.49	97.29
2	11.098	238955	10648	3.51	2.71
Total		6804587	393016	100.00	100.00



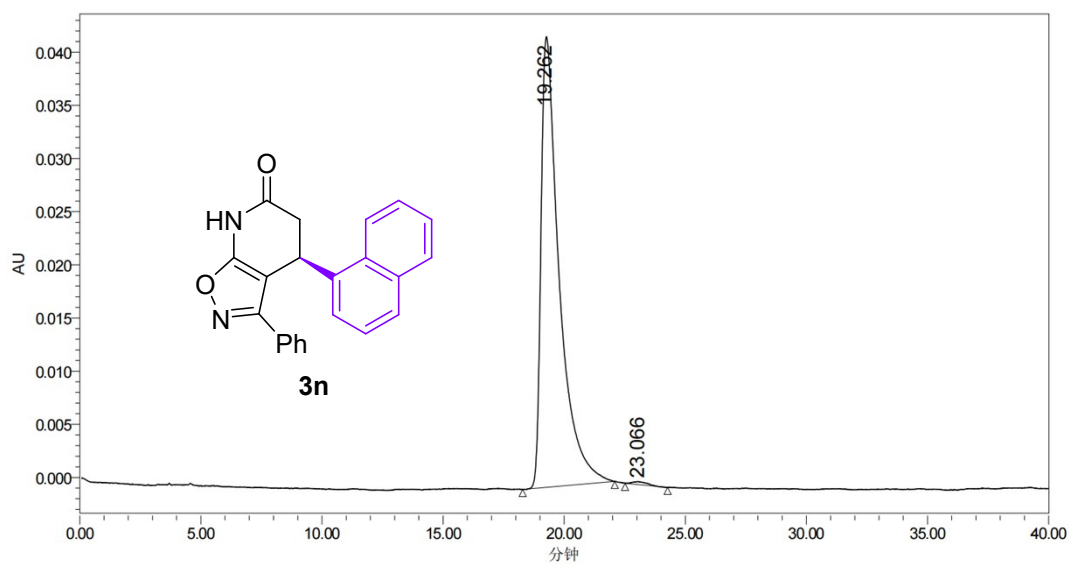
Peak	Ret. Time	Area	Height	Area%	Height%
1	23.848	1706838	33002	50.18	53.88
2	27.427	1694806	28251	49.82	46.12
Total		3401644	61253	100.00	100.00



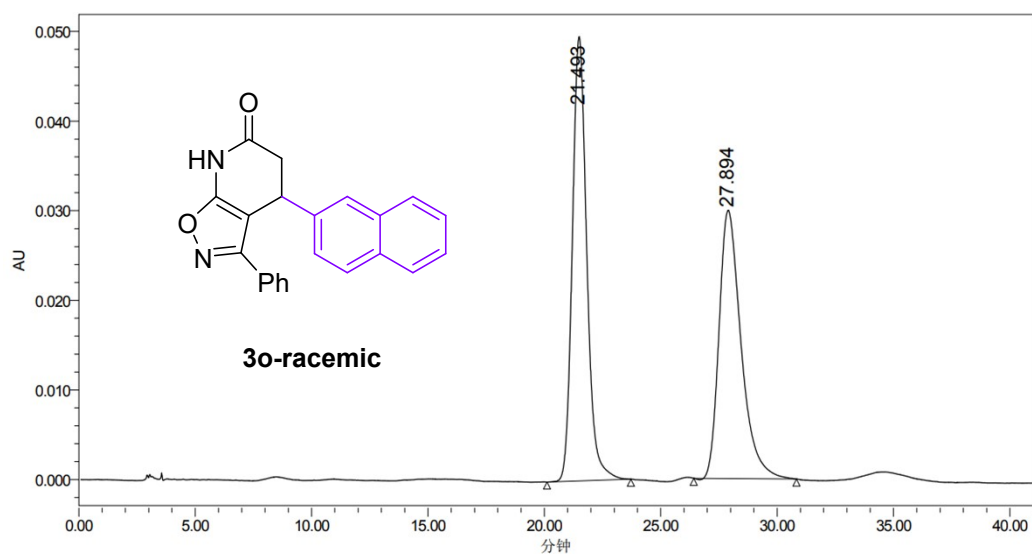
Peak	Ret. Time	Area	Height	Area%	Height%
1	23.606	5158448	102222	98.95	99.03
2	27.257	54805	996	1.05	0.97
Total		5213253	103218	100.00	100.00



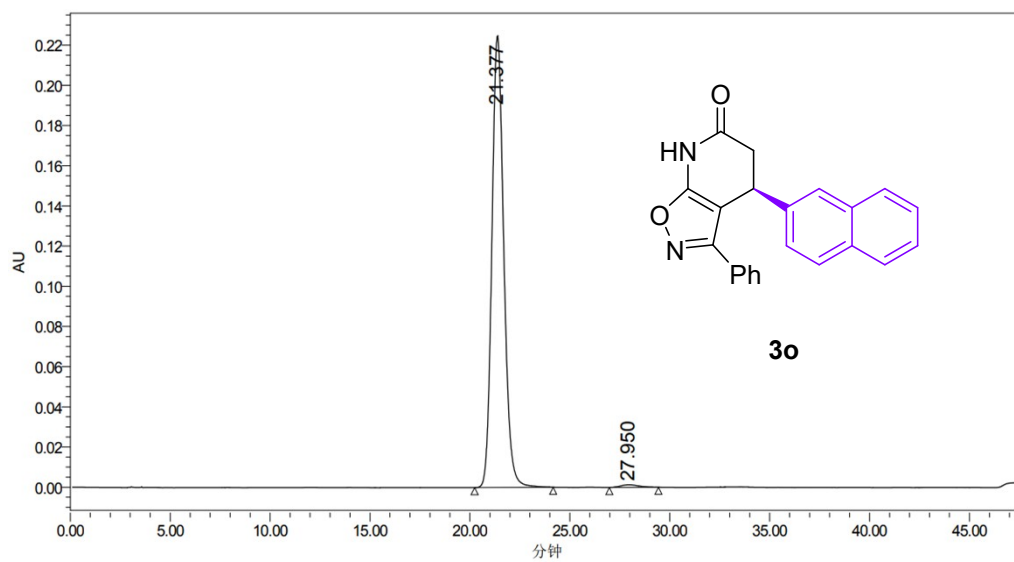
Peak	Ret.Time	Area	Height	Area%	Height%
1	19.471	1439043	27056	49.13	52.22
2	22.891	1489865	24753	50.87	47.78
Total		2928908	51809	100.00	100.00



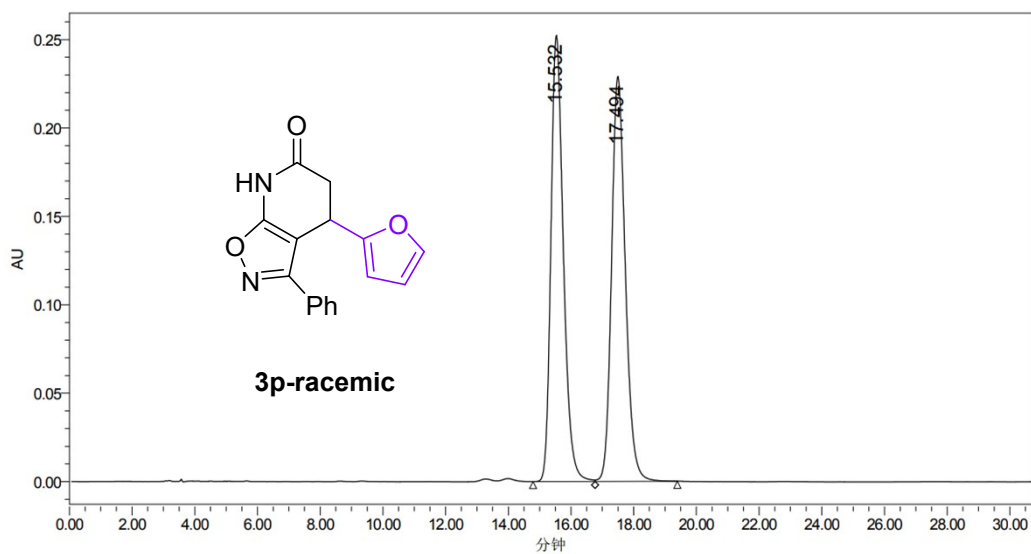
Peak	Ret.Time	Area	Height	Area%	Height%
1	19.262	2214857	42383	99.45	99.33
2	23.066	12235	284	0.55	0.67
Total		2227092	42667	100.00	100.00



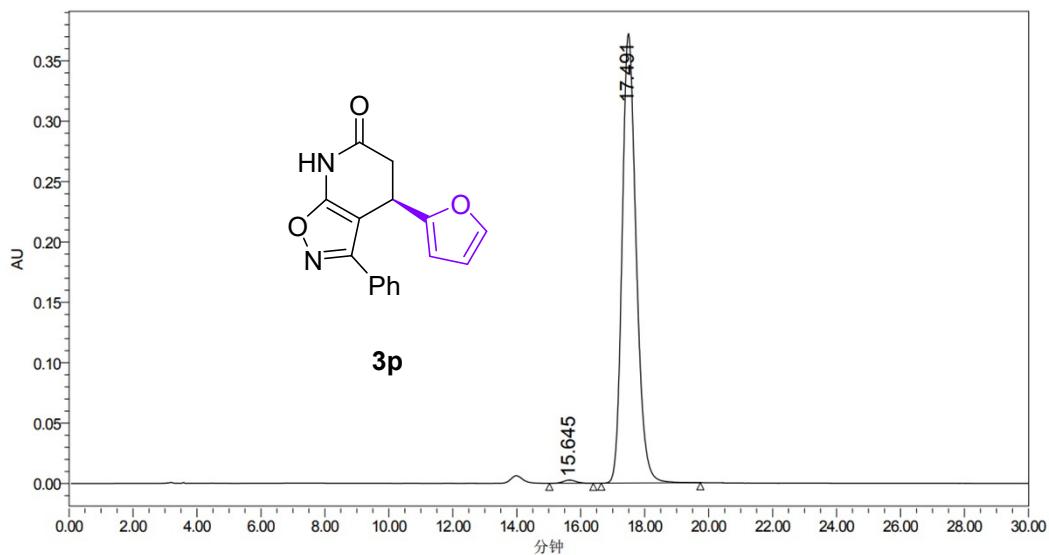
Peak	Ret.Time	Area	Height	Area%	Height%
1	21.493	2133441	49560	51.98	62.34
2	27.894	1971121	29938	48.02	37.66
Total		4104562	79498	100.00	100.00



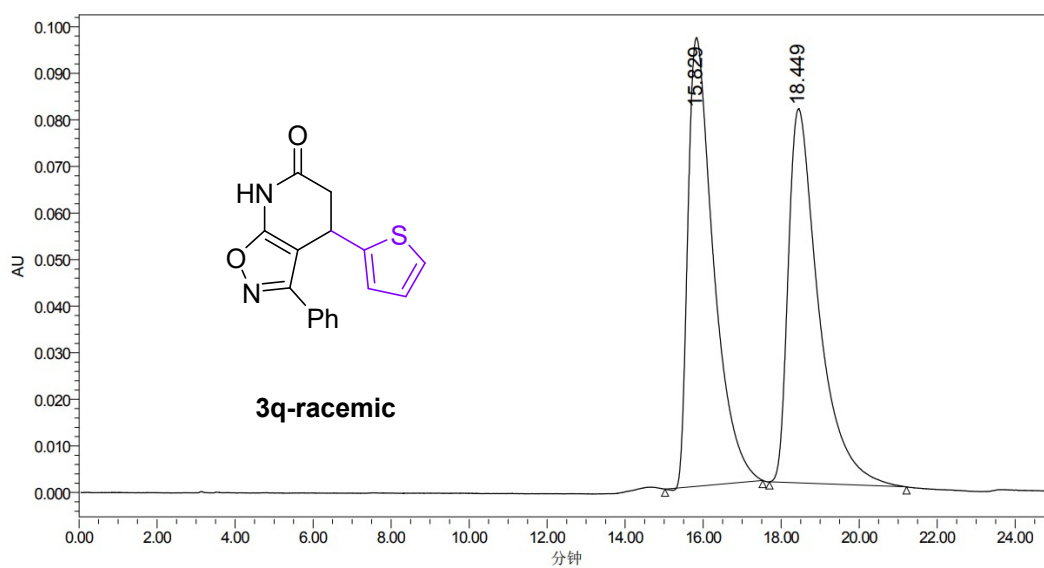
Peak	Ret.Time	Area	Height	Area%	Height%
1	21.377	9307201	224778	99.15	99.43
2	27.950	79864	1285	0.85	0.57
Total		9387065	226063	100.00	100.00



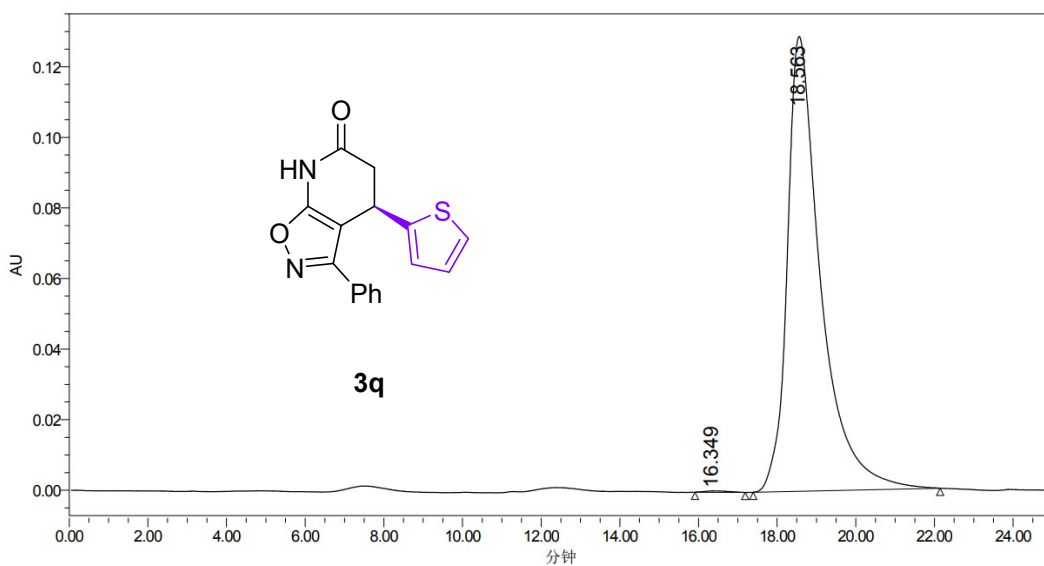
Peak	Ret.Time	Area	Height	Area%	Height%
1	15.532	6941175	252270	49.90	52.42
2	17.494	6969218	228956	50.10	47.58
Total		13910393	481226	100.00	100.00



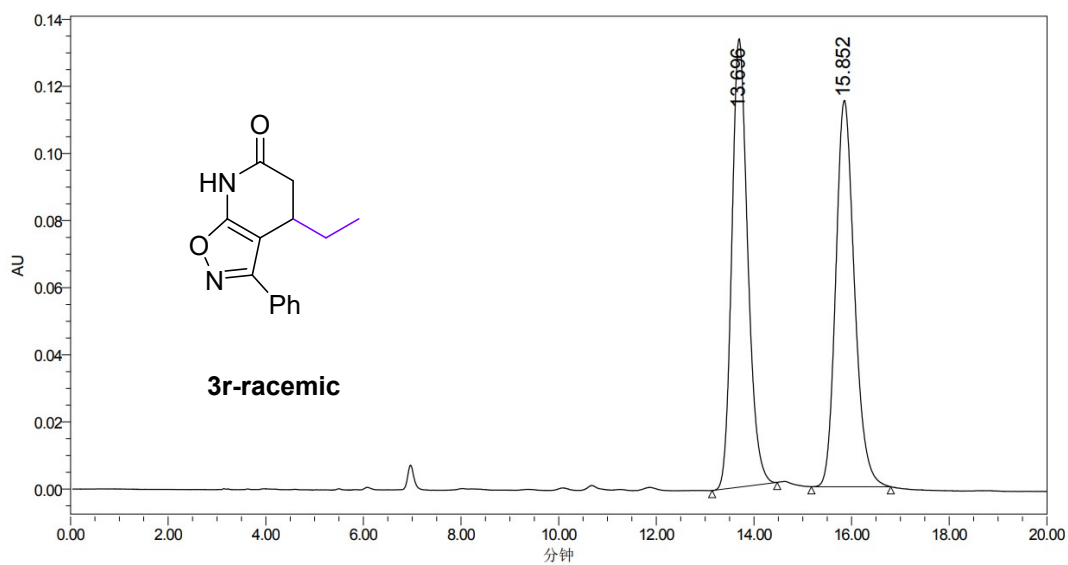
Peak	Ret.Time	Area	Height	Area%	Height%
1	15.645	71876	2613	0.63	0.70
2	17.491	11352993	371954	99.37	99.30
Total		11424869	374567	100.00	100.00



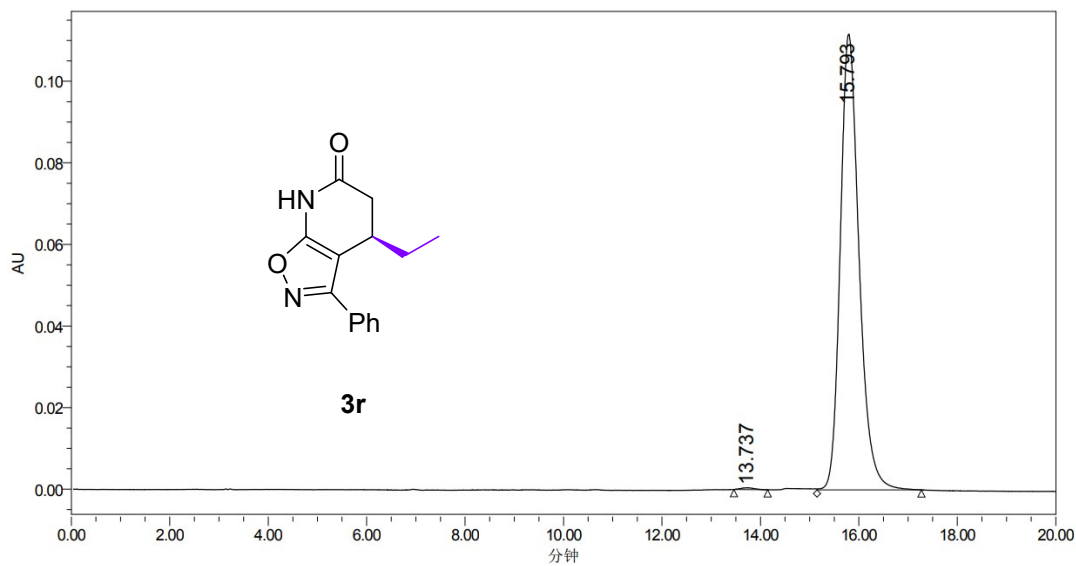
Peak	Ret.Time	Area	Height	Area%	Height%
1	15.829	4400497	96335	50.33	54.53
2	18.449	4342809	80331	49.67	45.47
Total		8743306	176666	100.00	100.00



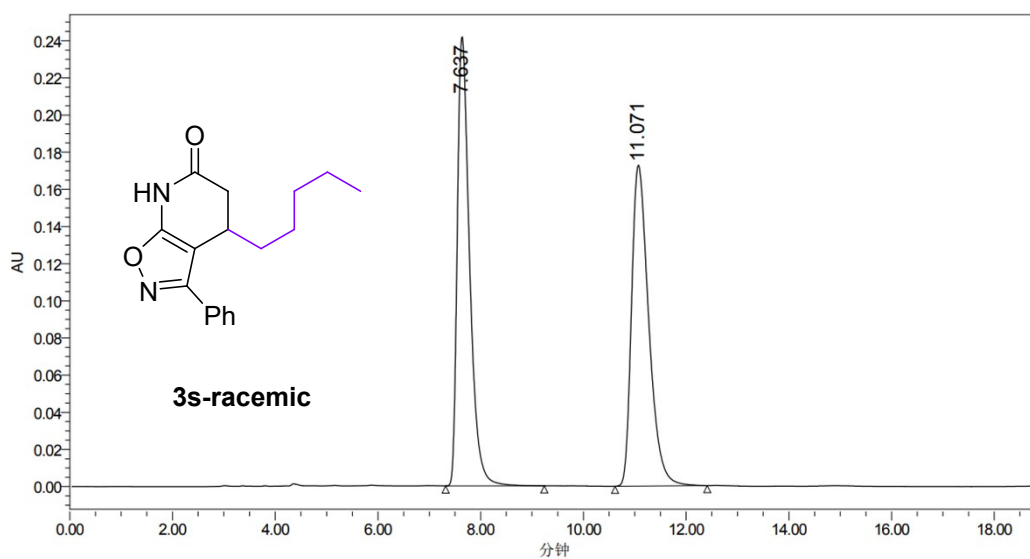
Peak	Ret.Time	Area	Height	Area%	Height%
1	16.349	16155	417	0.21	0.32
2	18.563	7604142	128815	99.79	99.68
Total		7620297	129232	100.00	100.00



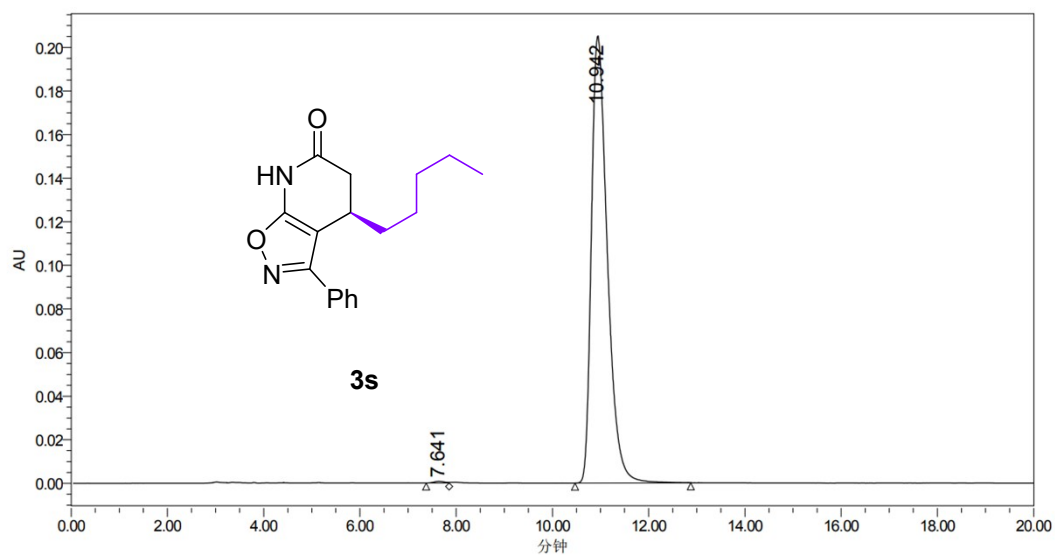
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.696	3028455	133597	49.74	53.72
2	15.852	3059967	115107	50.26	46.28
Total		6088422	248704	100.00	100.00



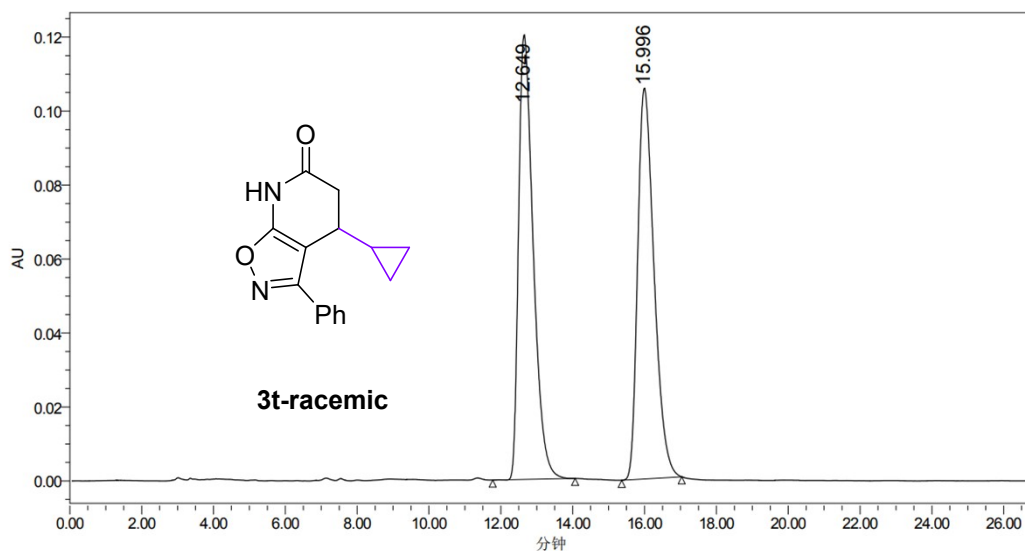
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.737	8985	474	0.30	0.42
2	15.793	2958826	111702	99.70	99.58
Total		2967811	112176	100.00	100.00



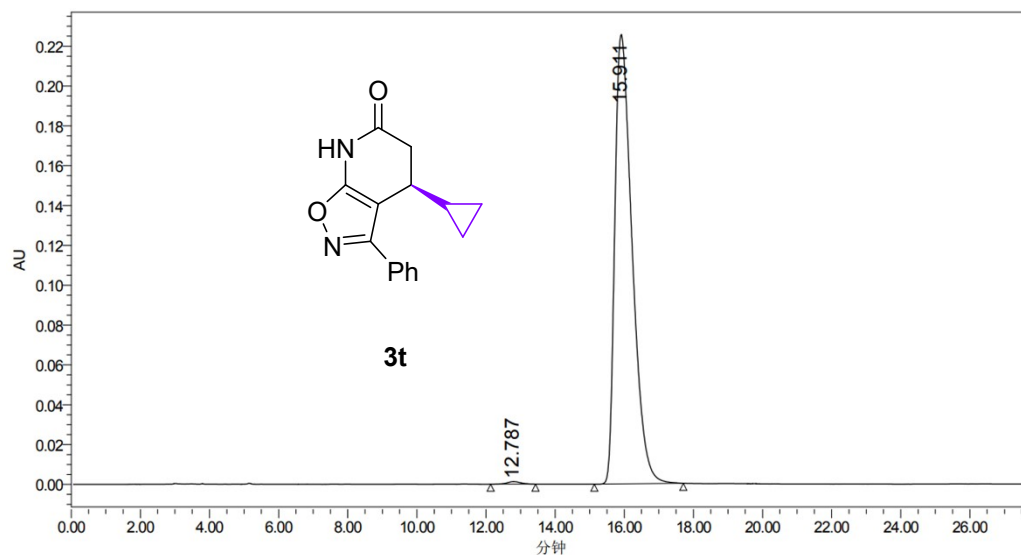
Peak	Ret.Time	Area	Height	Area%	Height%
1	7.637	4022946	241577	50.08	58.32
2	11.071	4009653	172665	49.92	41.68
Total		8032599	414242	100.00	100.00



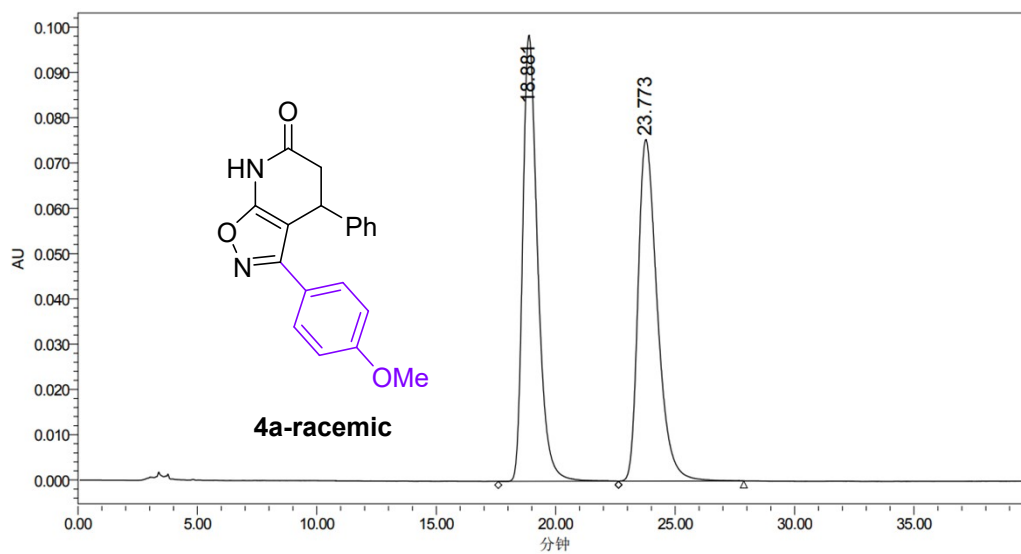
Peak	Ret.Time	Area	Height	Area%	Height%
1	7.641	11652	772	0.25	0.38
2	10.942	4706881	204970	99.75	99.62
Total		4718533	205742	100.00	100.00



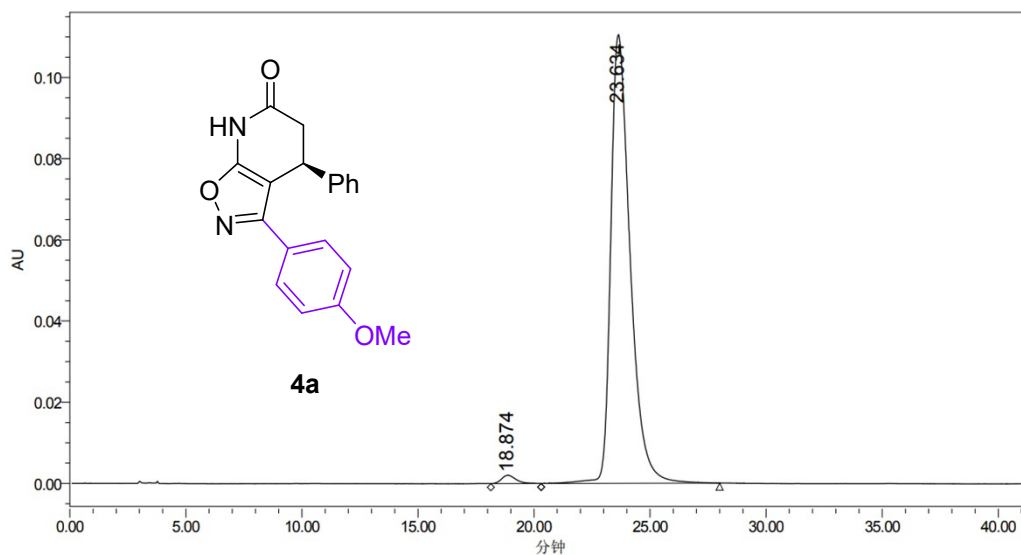
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.649	3388860	120162	50.22	53.21
2	15.996	3359115	105645	49.78	46.79
Total		6747975	225807	100.00	100.00



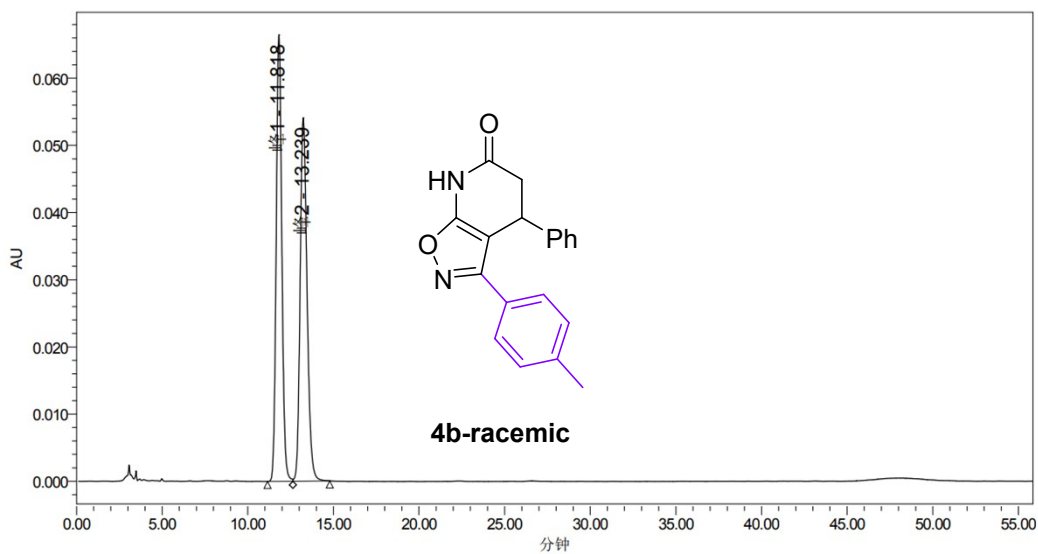
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.787	34793	1271	0.44	0.56
2	15.911	7851590	225496	99.56	99.44
Total		7886383	226767	100.00	100.00



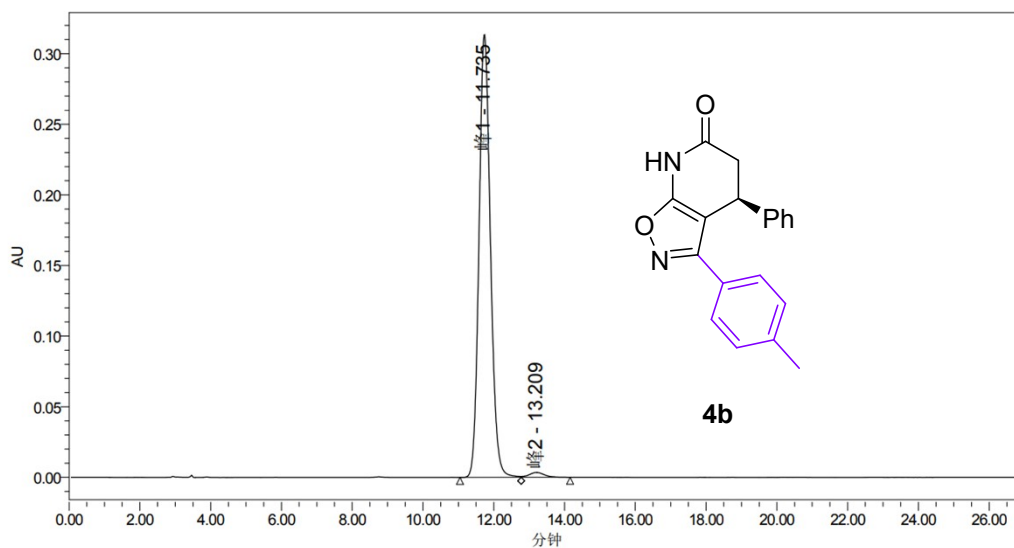
Peak	Ret.Time	Area	Height	Area%	Height%
1	18.881	4253496	98491	50.19	56.63
2	23.773	4221362	75423	49.81	43.37
Total		8474858	173914	100.00	100.00



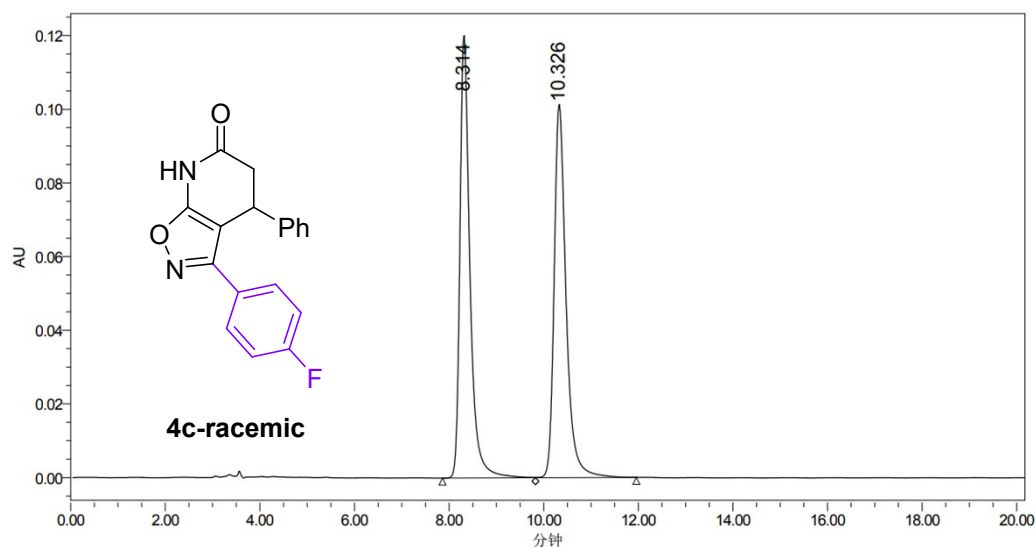
Peak	Ret.Time	Area	Height	Area%	Height%
1	18.874	91022	2081	1.40	1.85
2	23.634	6418336	110515	98.60	98.15
Total		6509358	112596	100.00	100.00



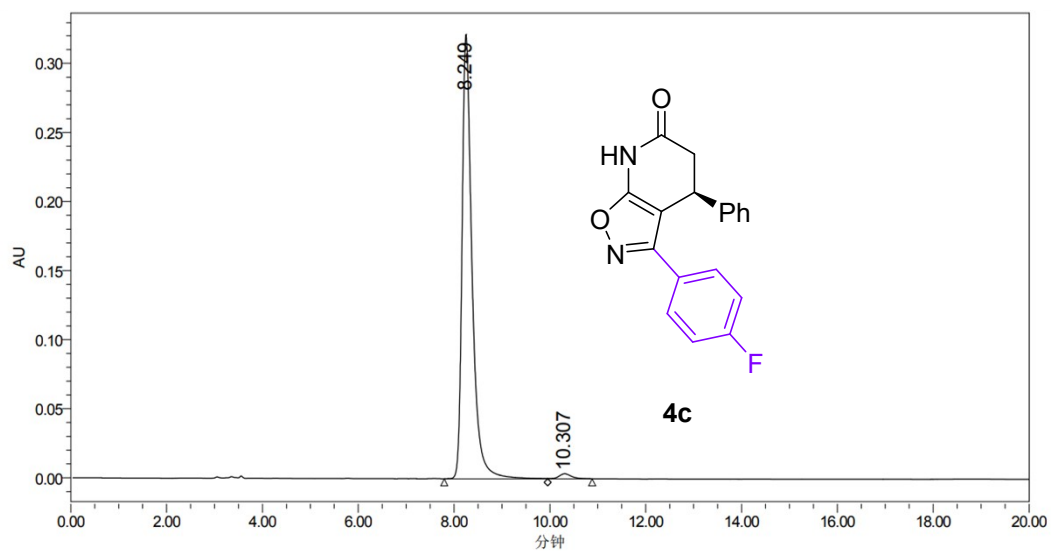
Peak	Ret.Time	Area	Height	Area%	Height%
1	11.818	1512799	66496	49.95	55.15
2	13.239	1515686	54084	50.05	44.85
Total		3028485	120580	100.00	100.00



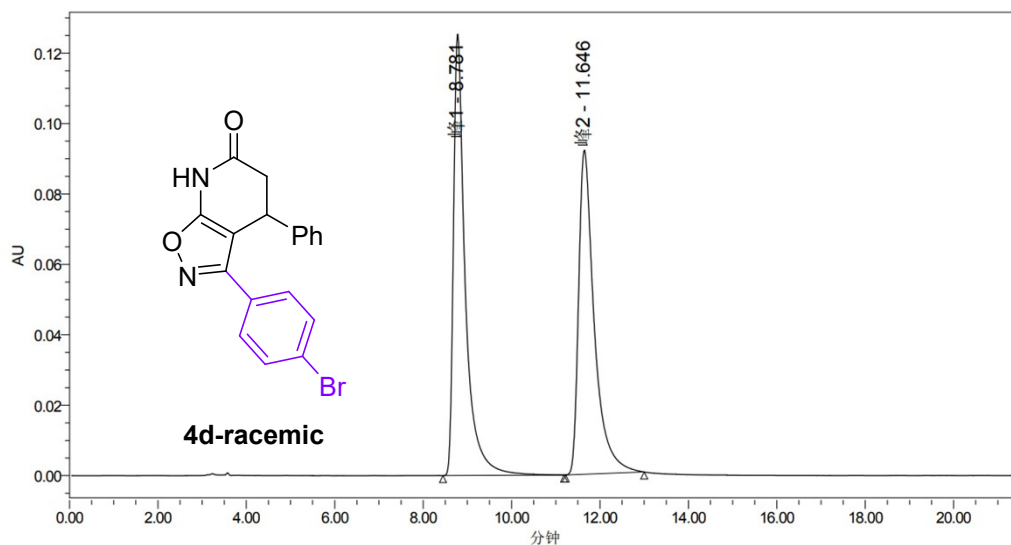
Peak	Ret.Time	Area	Height	Area%	Height%
1	11.735	7014202	313389	98.55	98.91
2	13.209	102878	3442	1.45	1.09
Total		7117080	316831	100.00	100.00



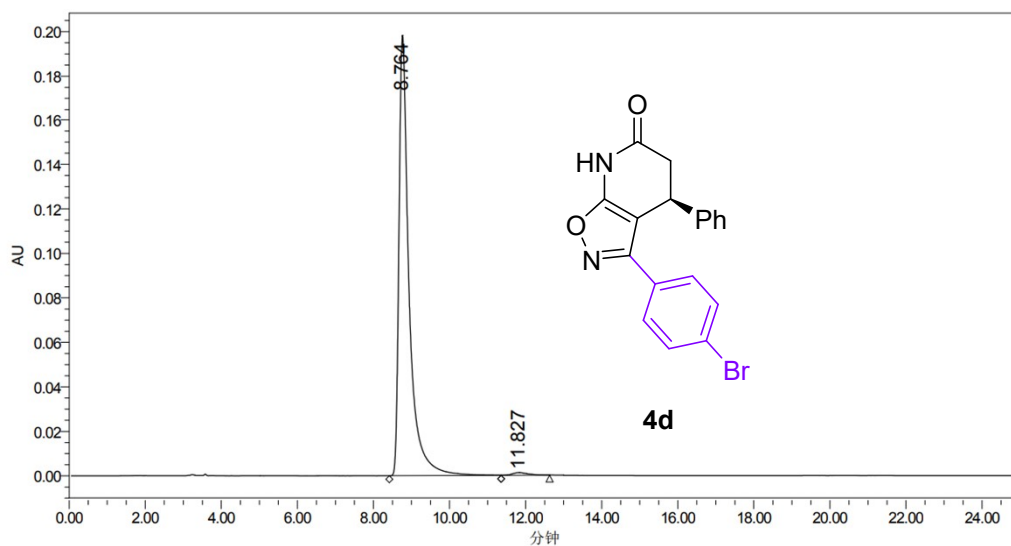
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.314	1769943	120075	49.99	54.24
2	10.326	1770462	101301	50.01	45.76
Total		3540405	221376	100.00	100.00



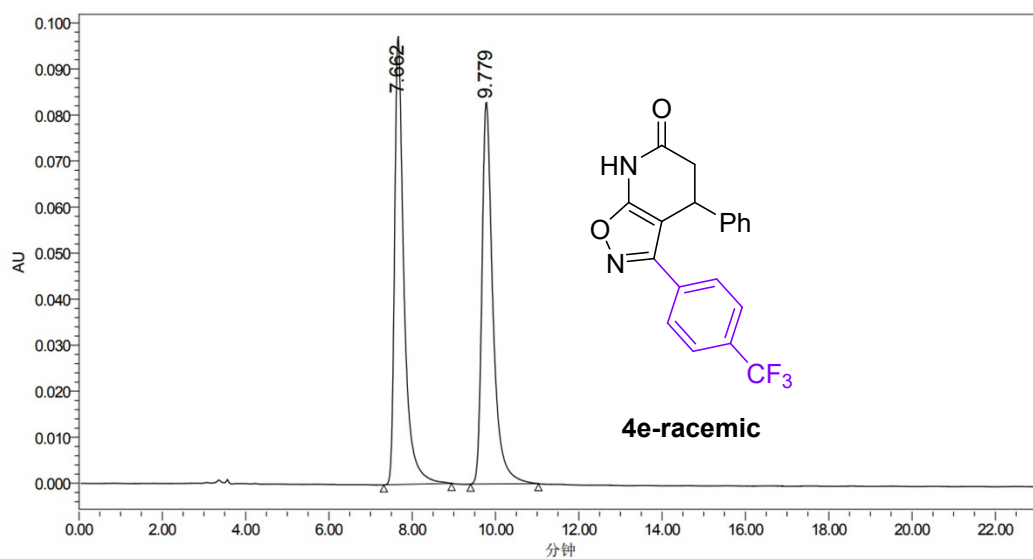
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.249	4657025	321611	98.61	98.88
2	10.307	65429	3655	1.39	1.12
Total		4722454	325266	100.00	100.00



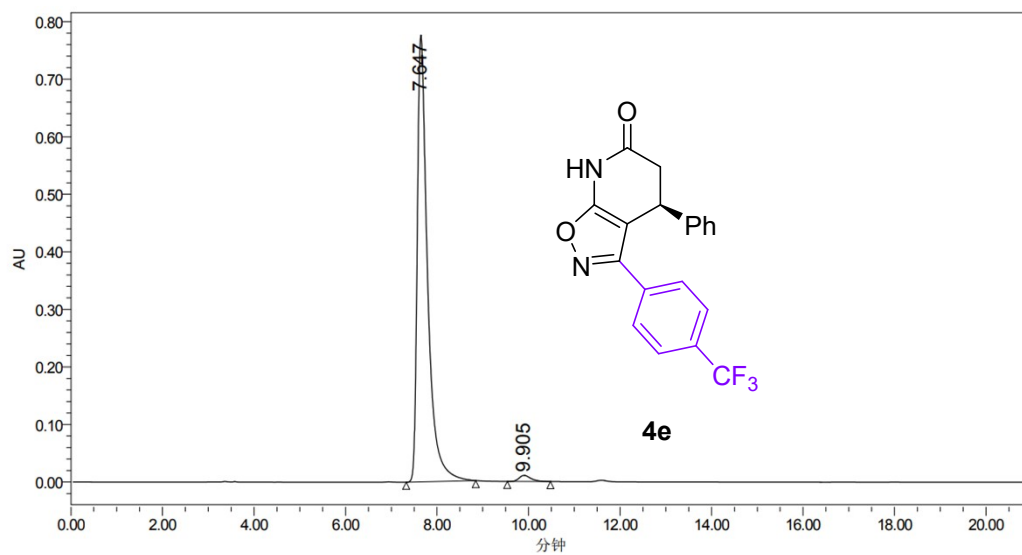
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.781	2333666	125274	50.80	57.66
2	11.646	2260351	91999	49.20	42.34
Total		4594017	217273	100.00	100.00



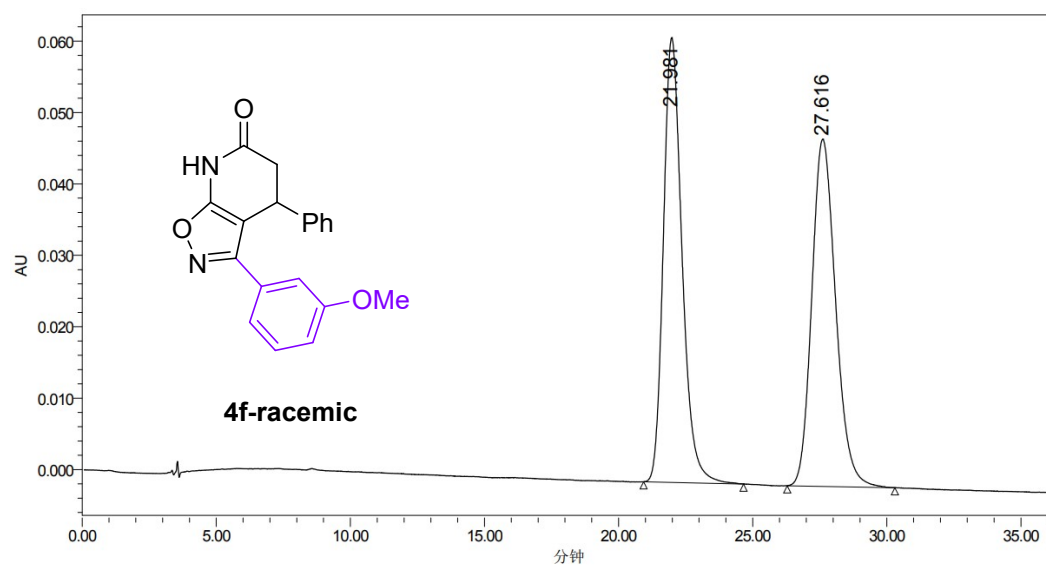
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.764	3666798	198325	99.11	99.41
2	11.827	32979	1167	0.89	0.59
Total		3699777	199492	100.00	100.00



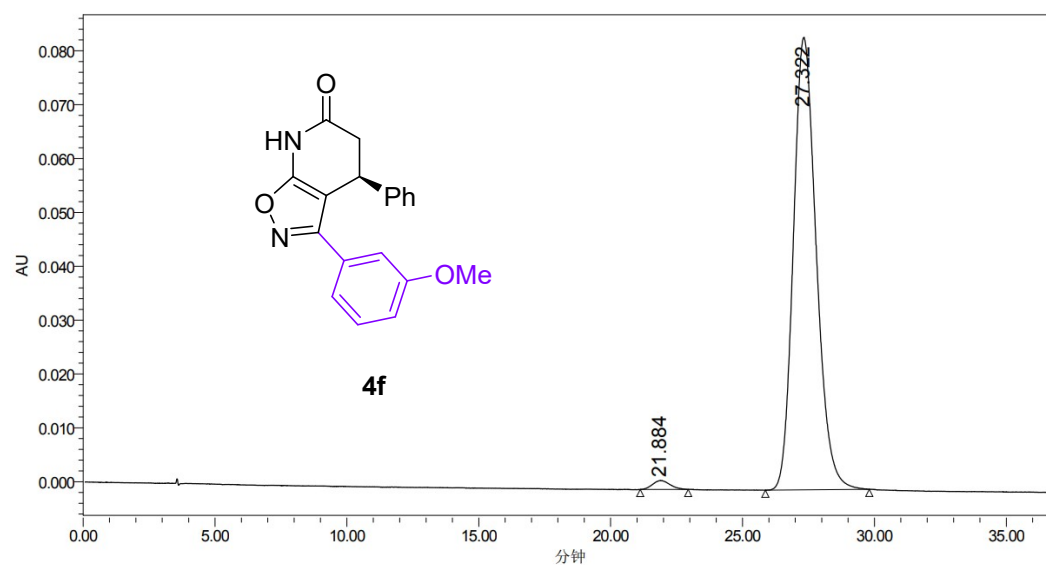
Peak	Ret.Time	Area	Height	Area%	Height%
1	7.662	1526820	97257	50.07	53.98
2	9.779	1522379	82921	49.93	46.02
Total		3049199	180178	100.00	100.00



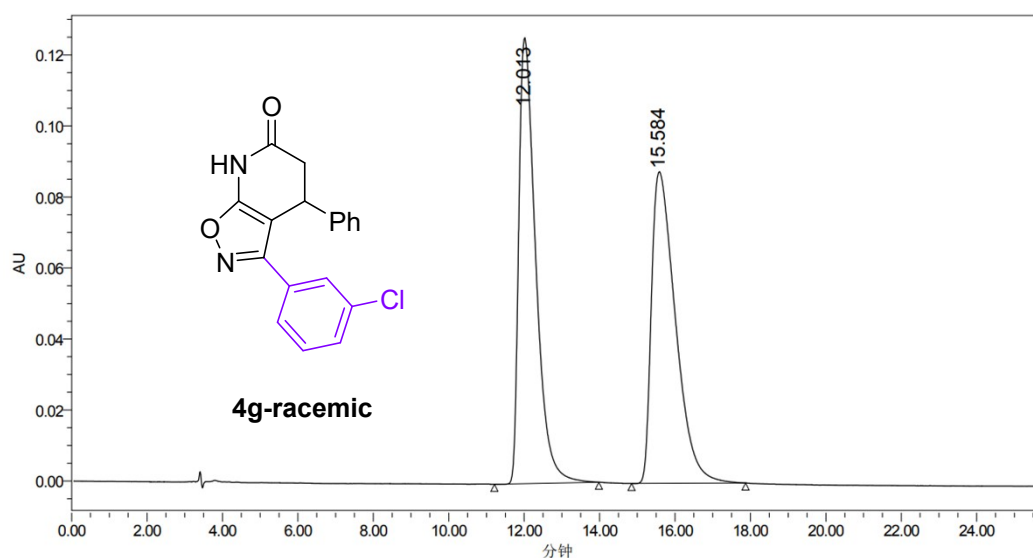
Peak	Ret.Time	Area	Height	Area%	Height%
1	7.647	12101385	776260	98.44	98.64
2	9.905	191690	10684	1.56	1.36
Total		12293075	786944	100.00	100.00



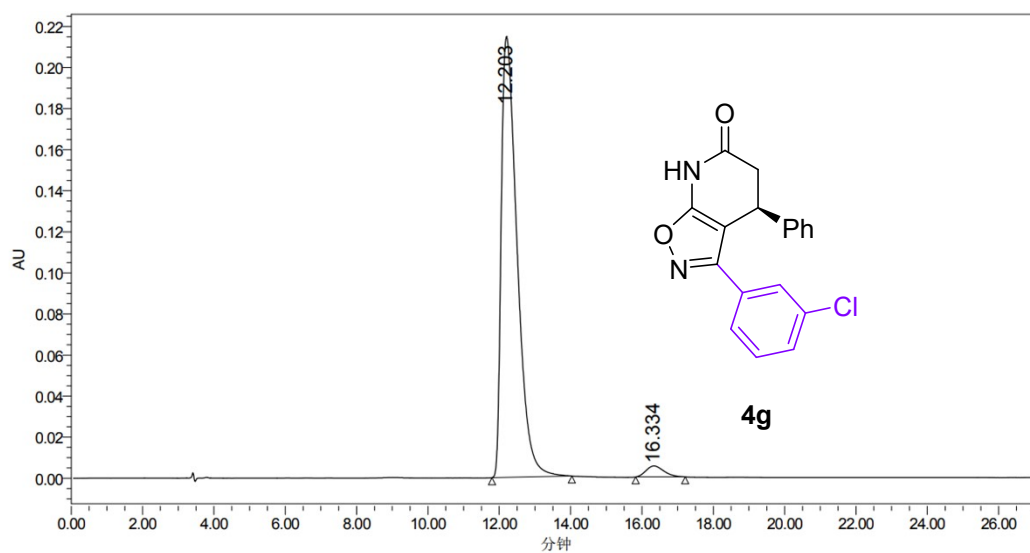
Peak	Ret.Time	Area	Height	Area%	Height%
1	21.981	3004020	62262	50.00	56.15
2	27.616	3004376	48616	50.00	43.85
Total		6008396	110878	100.00	100.00



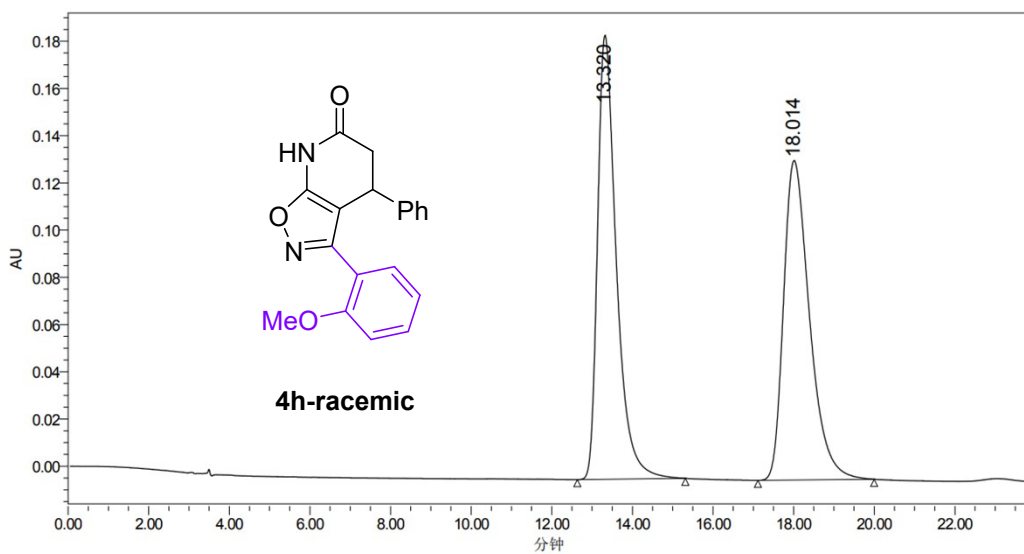
Peak	Ret.Time	Area	Height	Area%	Height%
1	21.884	76505	1655	1.49	1.93
2	27.322	5057551	83972	98.51	98.07
Total		5134056	85627	100.00	100.00



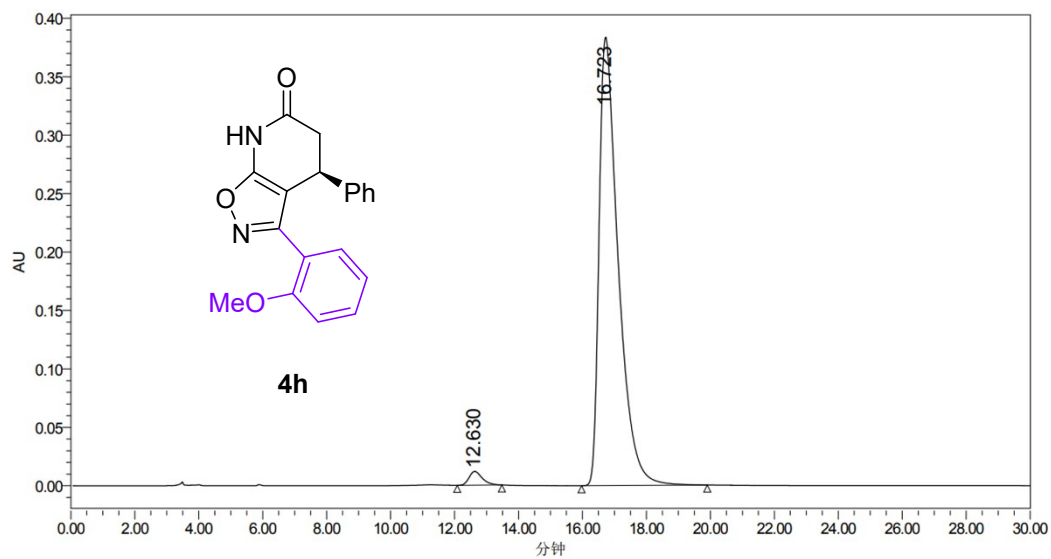
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.013	3906507	125520	50.15	58.86
2	15.584	3882849	87749	49.85	41.14
Total		7789356	213269	100.00	100.00



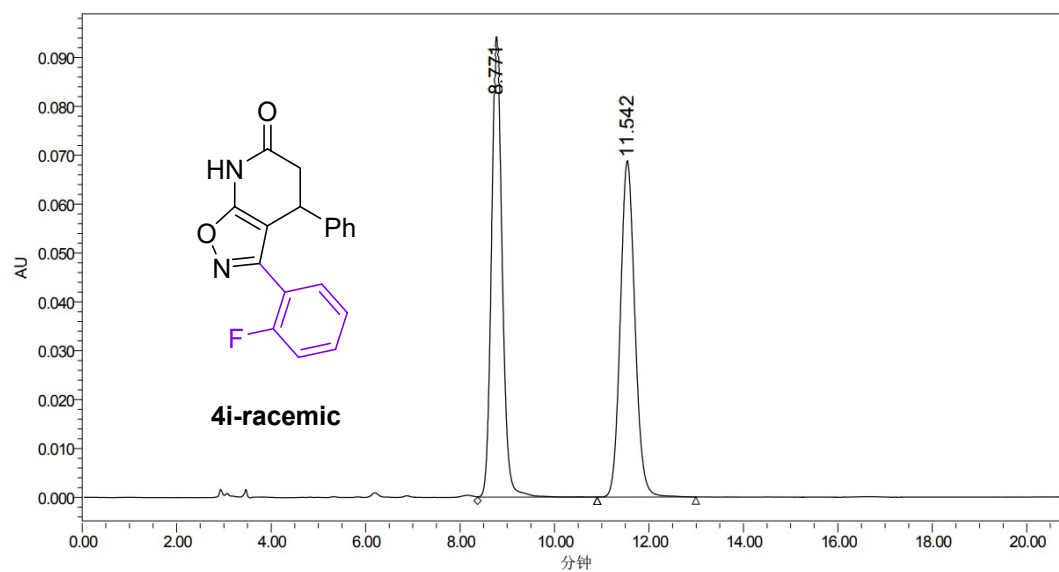
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.203	6599585	214685	97.27	97.56
2	16.334	185037	5360	2.73	2.44
Total		6784622	220045	100.00	100.00



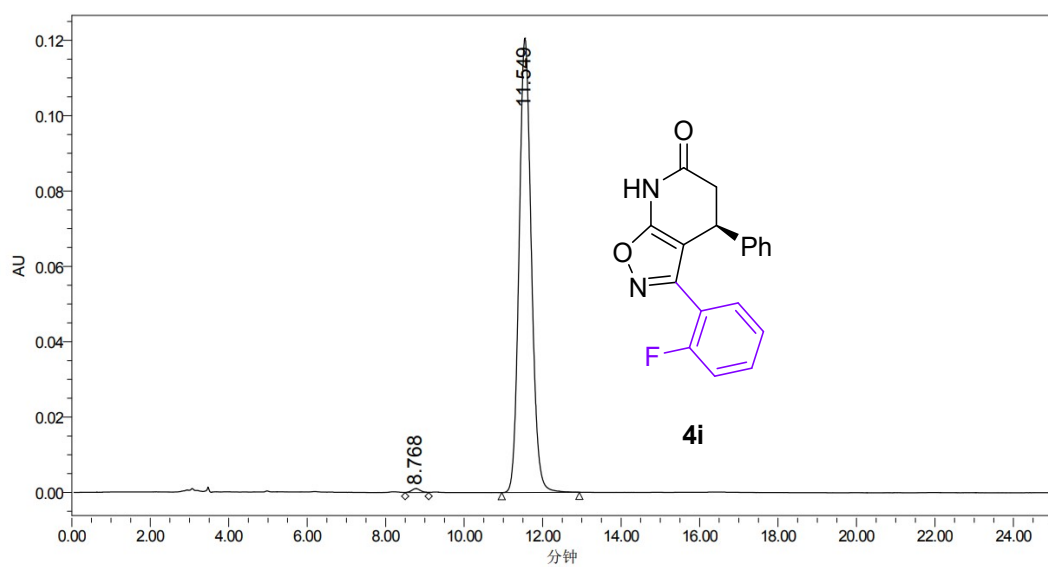
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.320	6090070	188009	50.17	58.15
2	18.014	6047635	135289	49.83	41.85
Total		12137705	323298	100.00	100.00



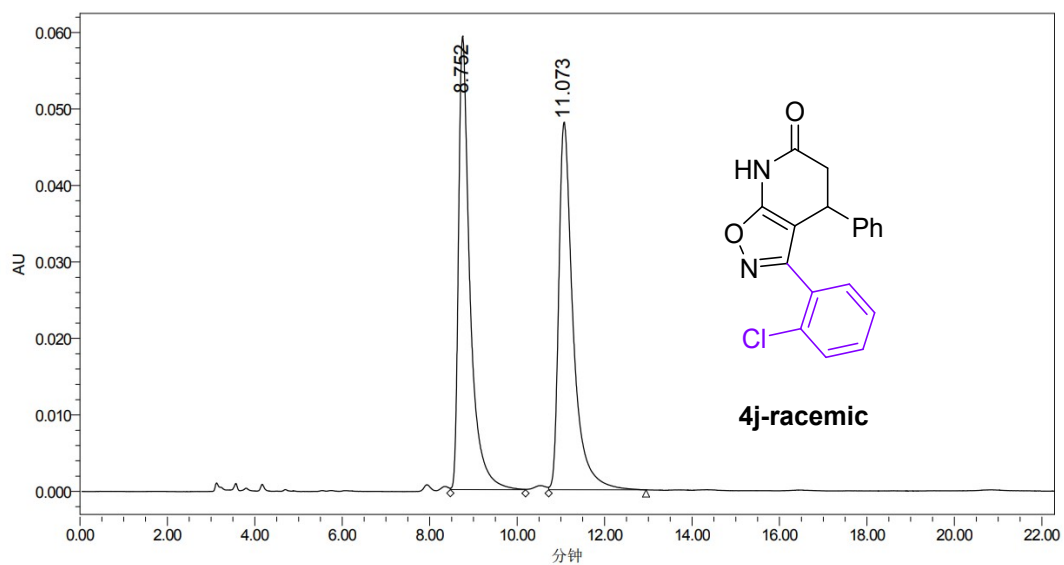
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.630	338317	11776	2.08	2.98
2	16.723	15942477	383473	97.92	97.02
Total		16280794	395249	100.00	100.00



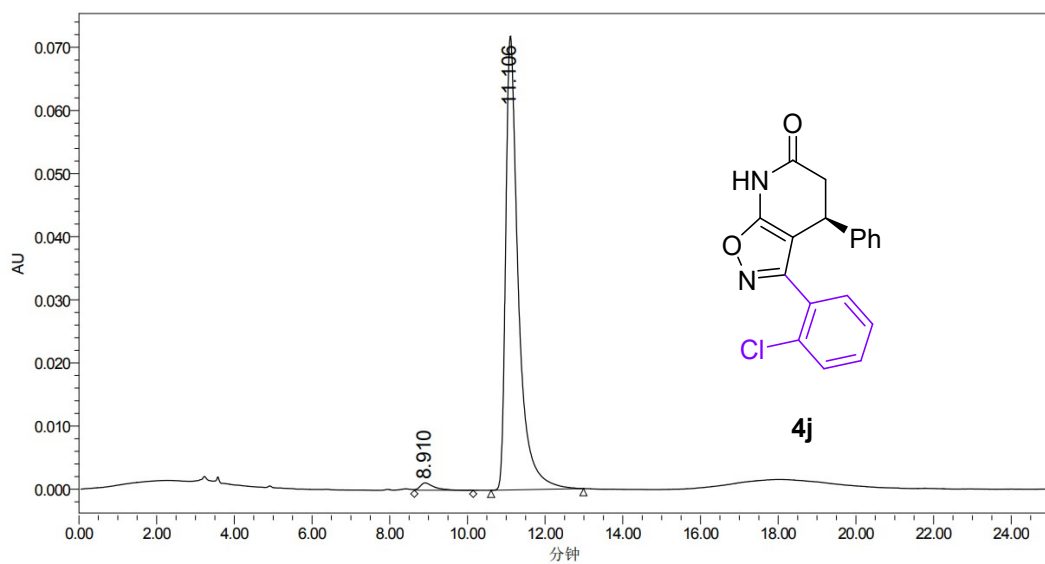
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.771	1483320	94173	50.16	57.79
2	11.542	1473843	68770	49.84	42.21
Total		2957163	162943	100.00	100.00



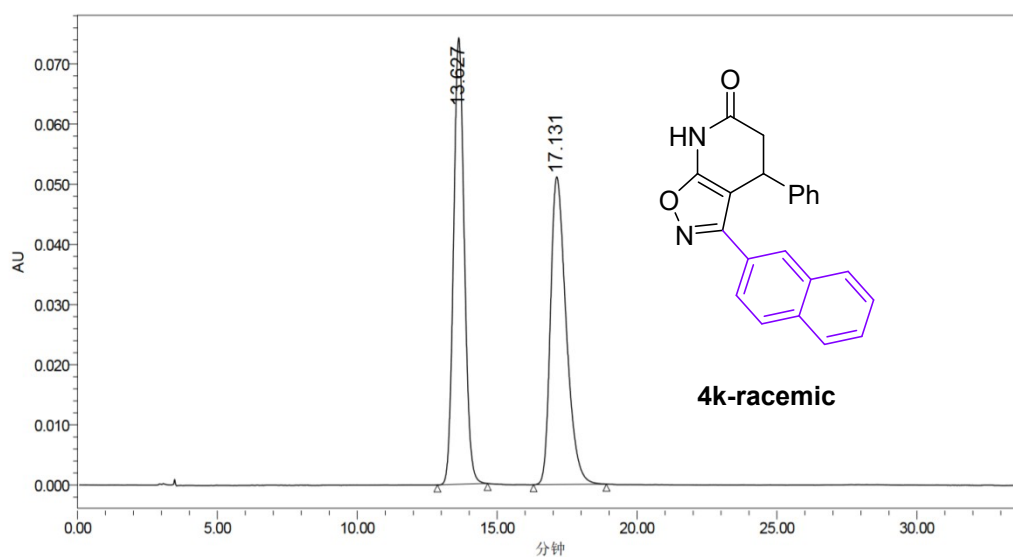
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.768	16167	1028	0.62	0.85
2	11.549	2607796	120587	99.38	99.15
Total		2623963	121615	100.00	100.00



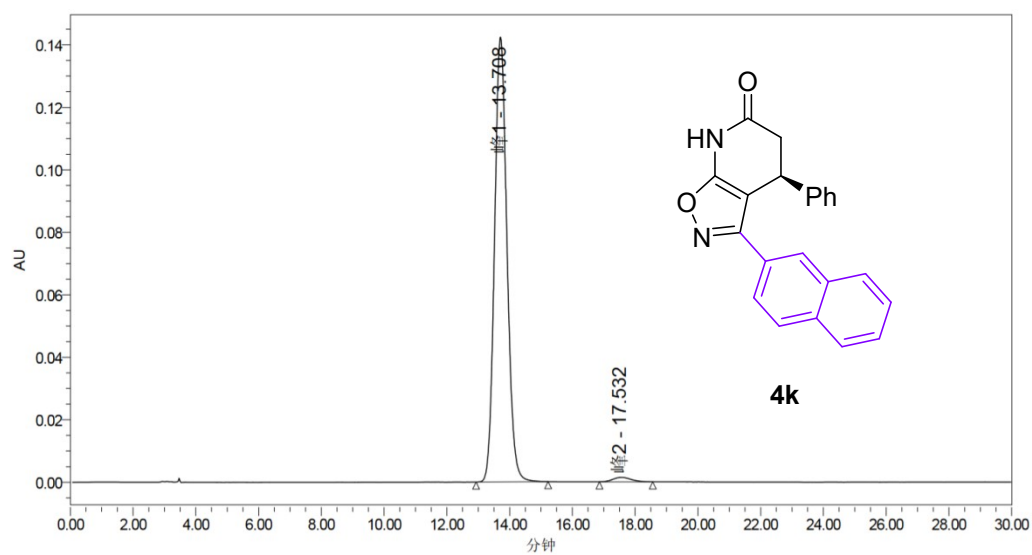
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.752	1077839	59283	49.67	55.23
2	11.073	1092207	48057	50.33	44.77
Total		2170046	107340	100.00	100.00



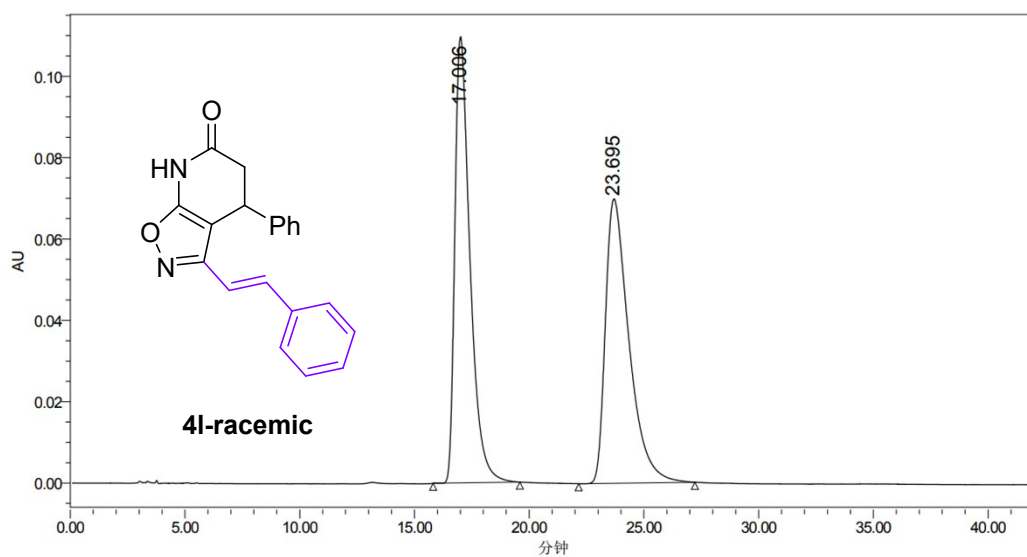
Peak	Ret.Time	Area	Height	Area%	Height%
1	8.910	29198	1159	1.77	1.59
2	11.106	1623560	71885	98.23	98.41
Total		1652758	73044	100.00	100.00



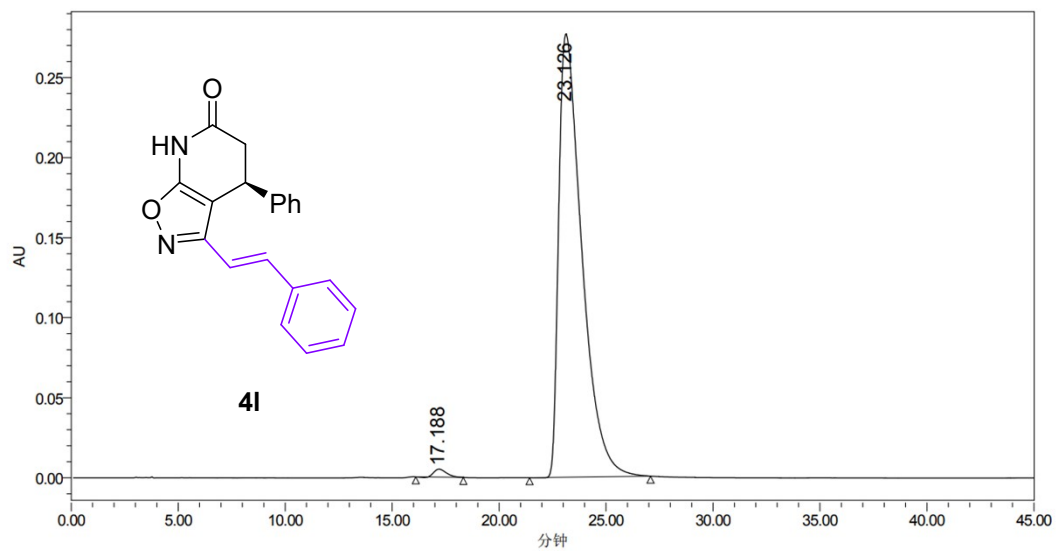
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.627	1983515	74238	49.85	59.21
2	17.131	1995152	51136	50.15	40.79
Total		3978667	125374	100.00	100.00



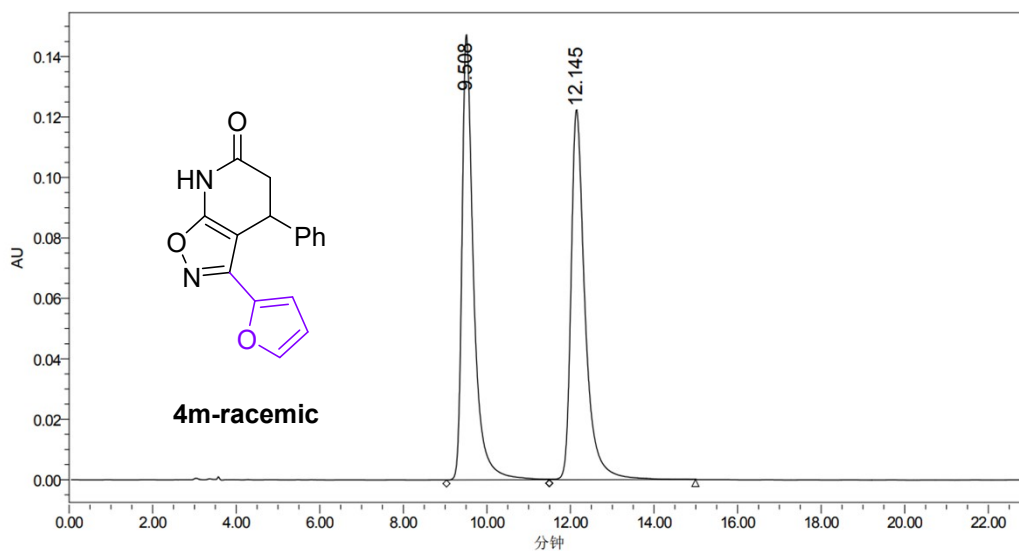
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.708	3911627	142384	98.49	98.99
2	17.532	59866	1456	1.51	1.01
Total		3971493	143840	100.00	100.00



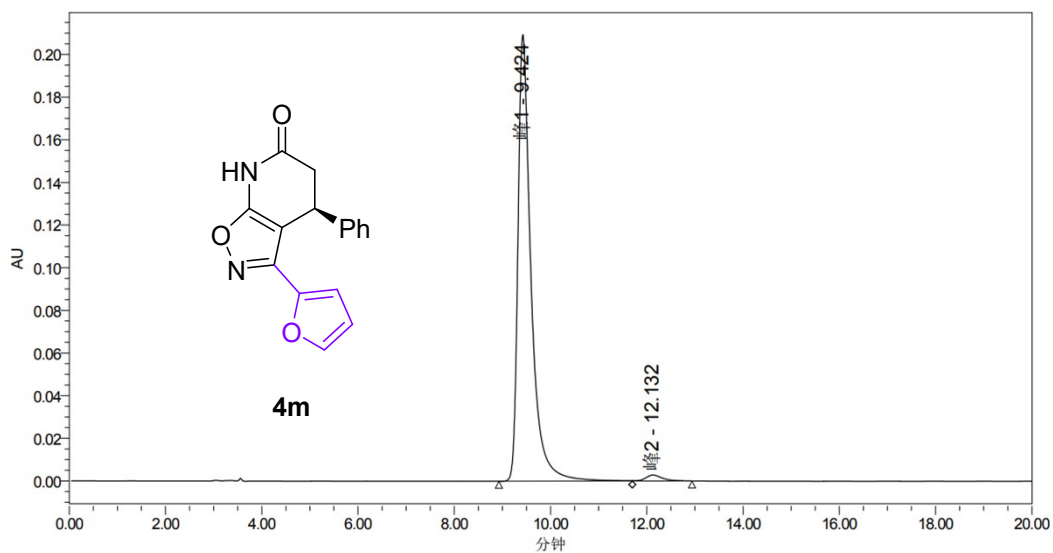
Peak	Ret.Time	Area	Height	Area%	Height%
1	17.006	5030399	109634	50.26	61.07
2	23.695	4978584	69877	49.74	38.93
Total		10008983	179511	100.00	100.00



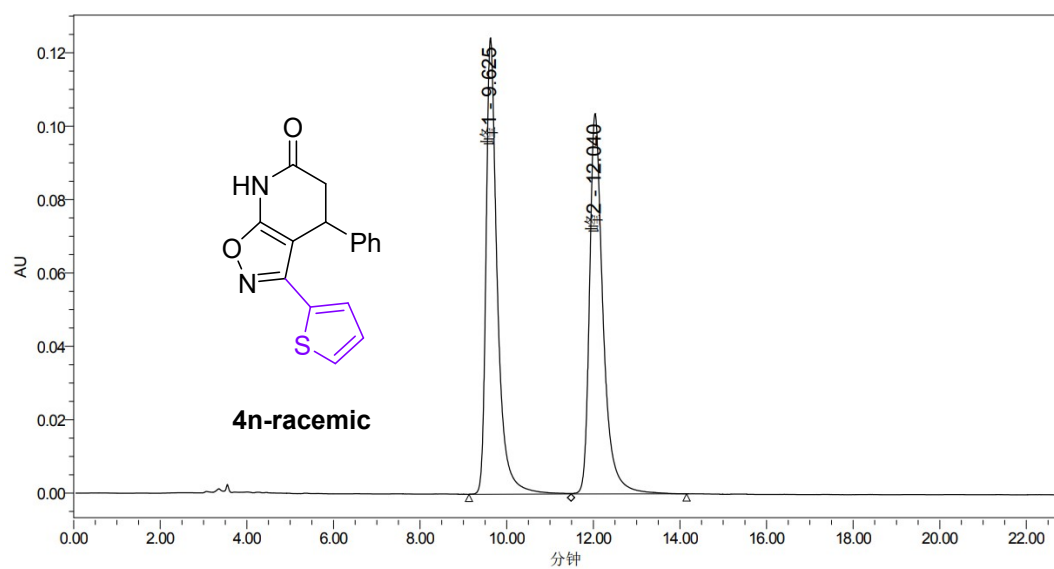
Peak	Ret.Time	Area	Height	Area%	Height%
1	17.188	214038	5012	1.02	1.78
2	23.126	20764558	276932	98.98	98.22
Total		20978596	281944	100.00	100.00



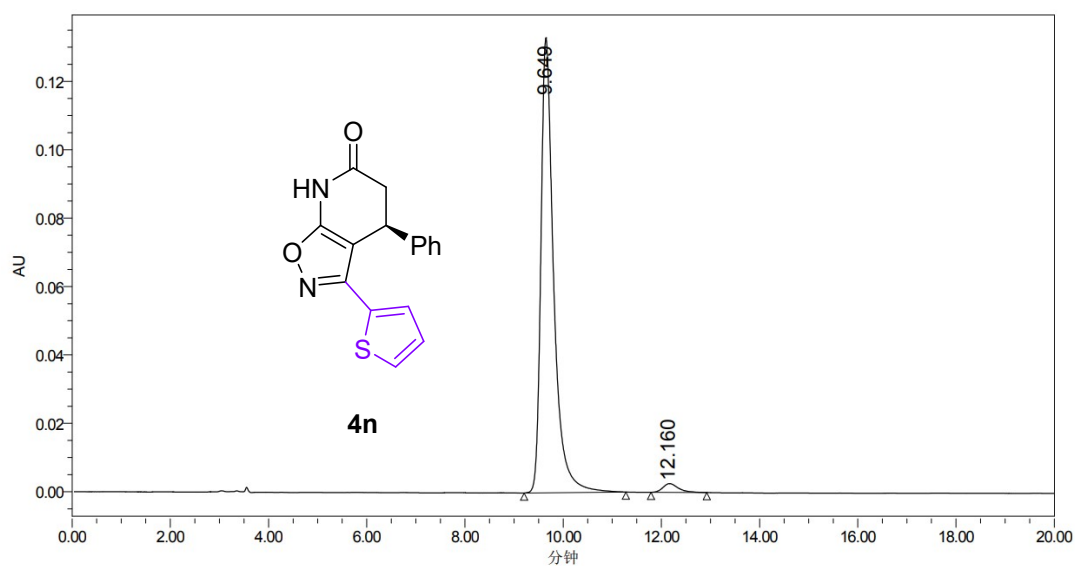
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.508	2842676	147259	49.89	54.61
2	12.145	2855325	122417	50.11	45.39
Total		5698001	269676	100.00	100.00



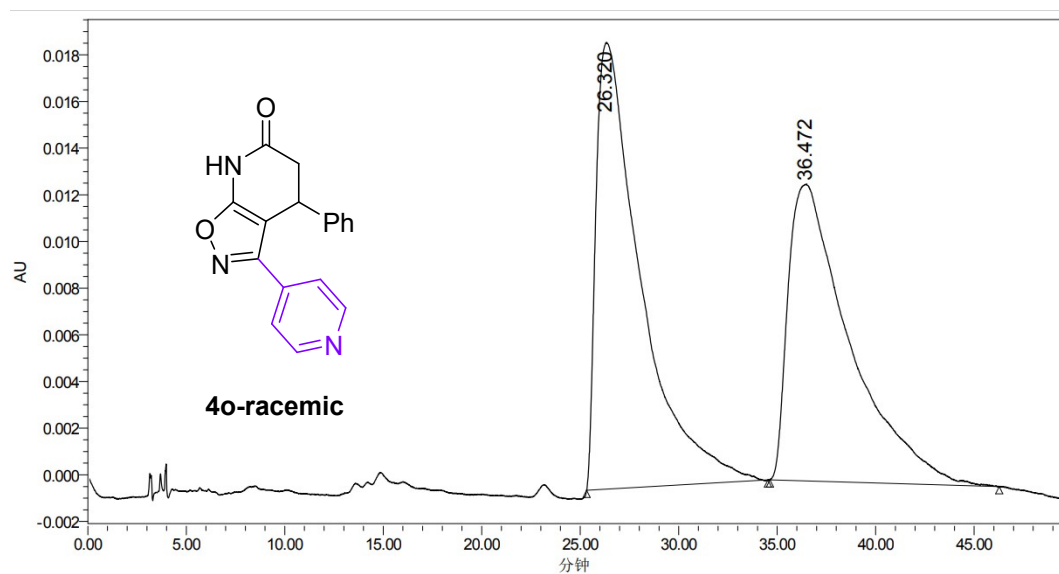
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.424	3950071	209292	98.34	98.68
2	12.132	66573	2792	1.66	1.32
Total		4016644	212084	100.00	100.00



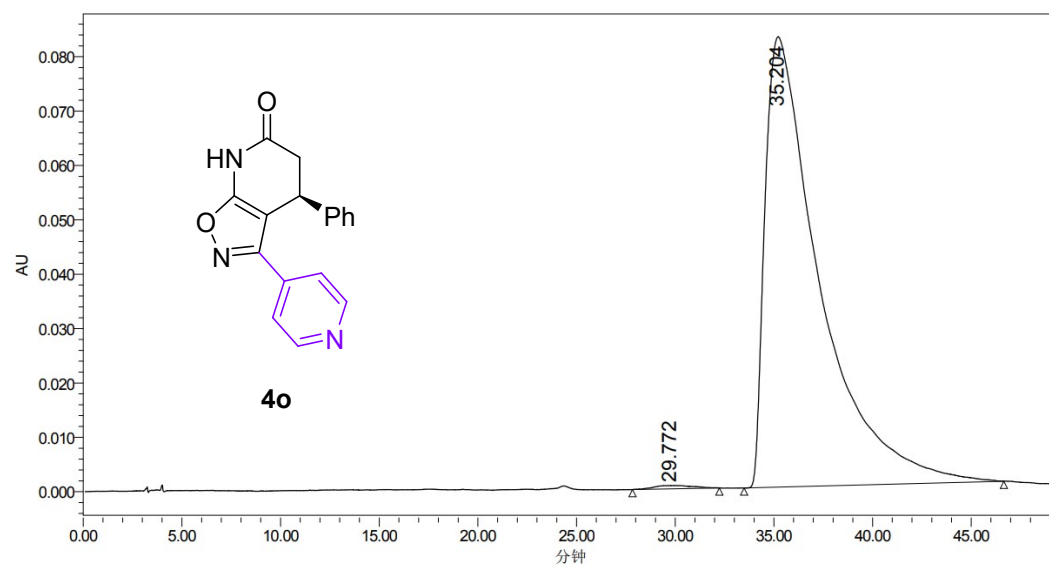
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.625	2253595	124304	50.09	54.54
2	12.040	2245412	103620	49.91	45.46
Total		4499007	227924	100.00	100.00



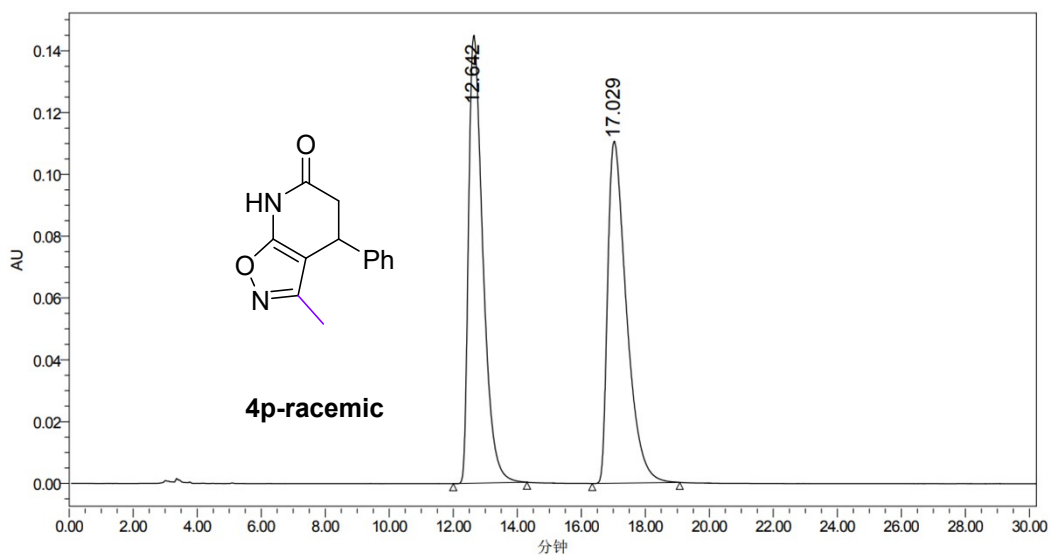
Peak	Ret.Time	Area	Height	Area%	Height%
1	9.649	2404937	133047	97.70	98.11
2	12.160	56497	2565	2.30	1.89
Total		2461434	135612	100.00	100.00



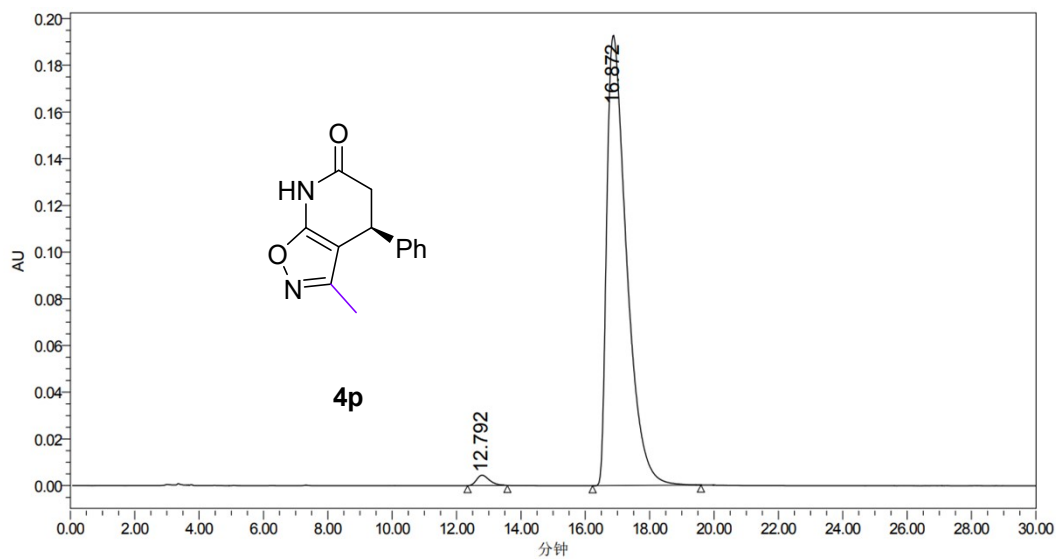
Peak	Ret.Time	Area	Height	Area%	Height%
1	26.320	3013356	19145	52.23	60.07
2	36.472	2755728	12725	47.77	39.93
Total		5769084	31870	100.00	100.00



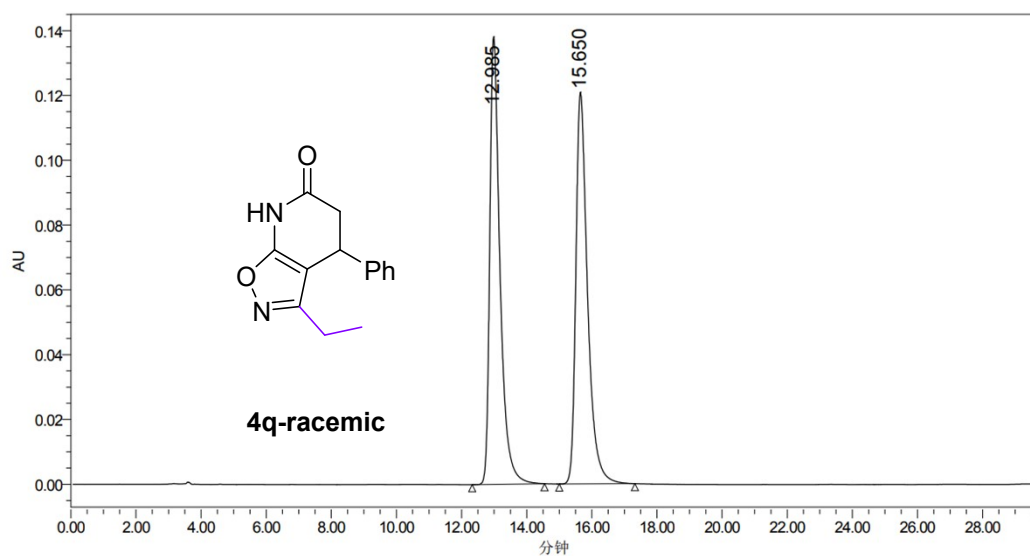
Peak	Ret.Time	Area	Height	Area%	Height%
1	29.772	83740	624	0.52	0.75
2	35.204	15909060	82821	99.48	99.25
Total		15992800	83445	100.00	100.00



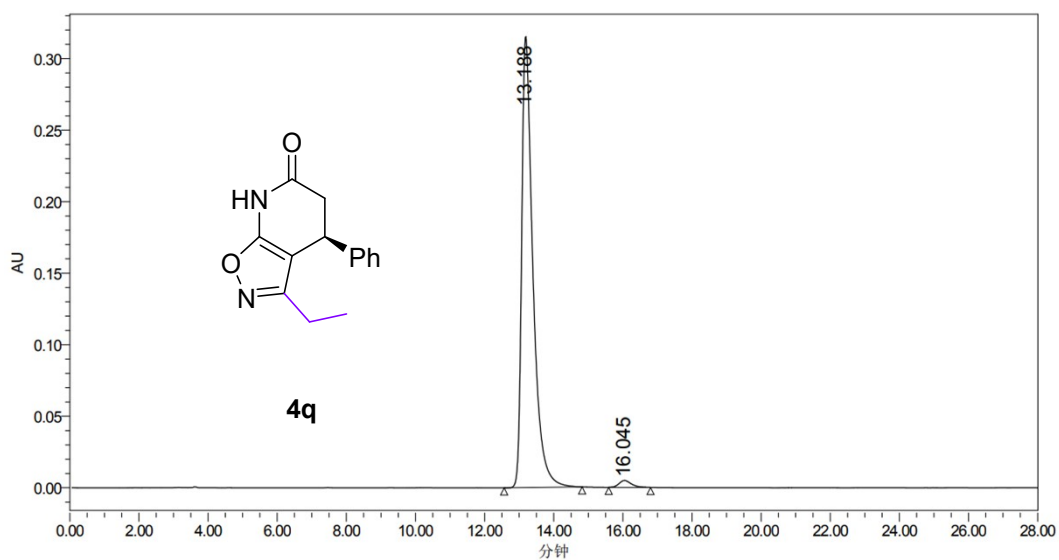
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.642	4514366	144887	50.08	56.71
2	17.029	4499549	110615	49.92	43.29
Total		9013915	255502	100.00	100.00



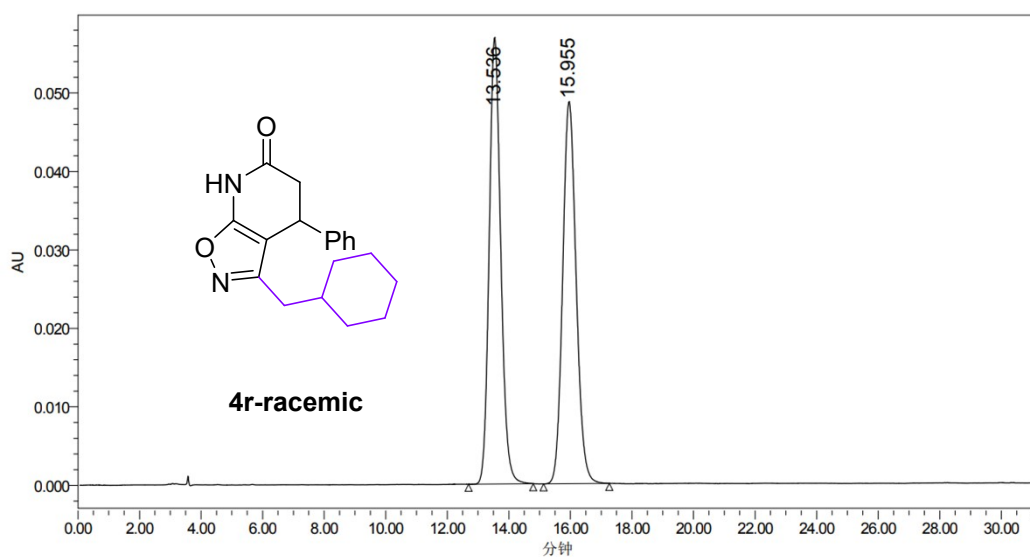
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.792	122591	4428	1.47	2.25
2	16.872	8237442	192733	98.53	97.75
Total		8360033	197161	100.00	100.00



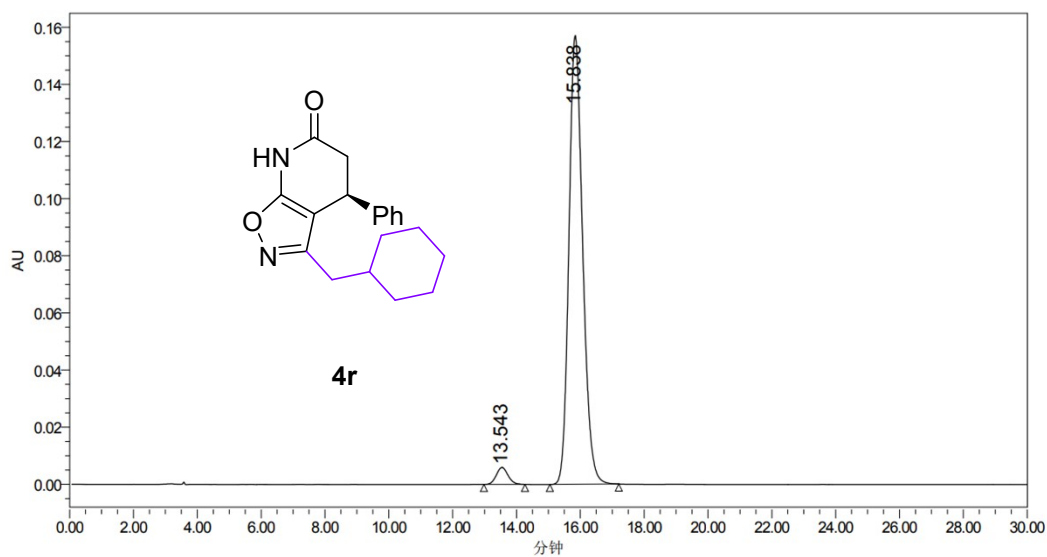
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.985	3007075	138145	49.97	53.32
2	15.650	3010885	120917	50.03	46.68
Total		6017960	259062	100.00	100.00



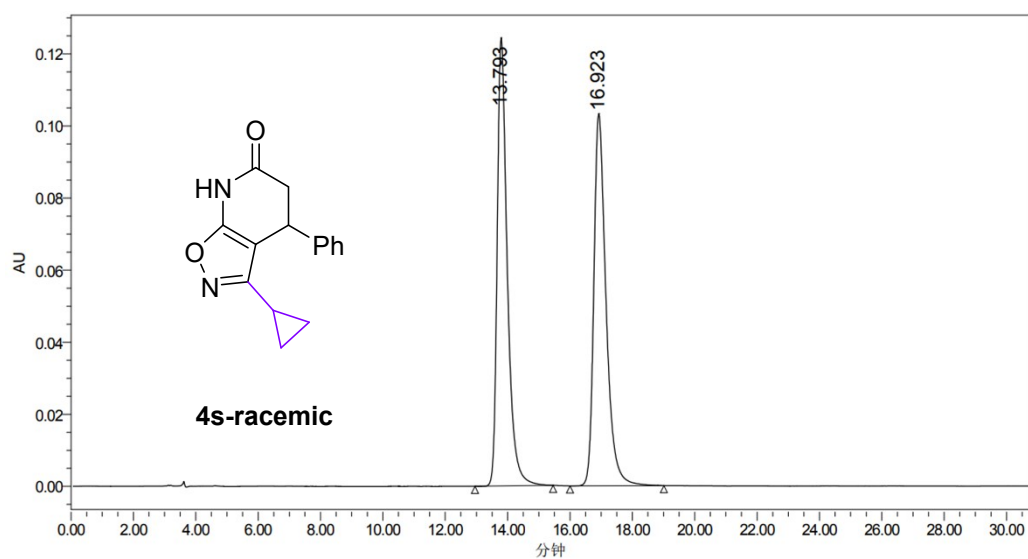
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.188	7099793	315112	98.37	98.50
2	16.045	118004	4796	1.63	1.50
Total		7217797	319908	100.00	100.00



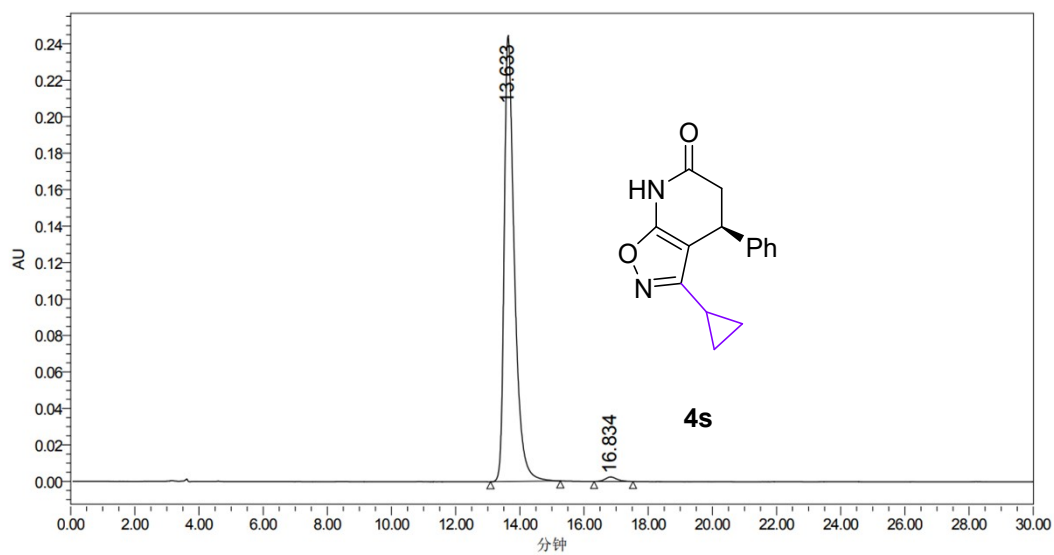
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.536	1483395	56884	50.02	53.89
2	15.955	1482012	48671	49.98	46.11
Total		2965407	105555	100.00	100.00



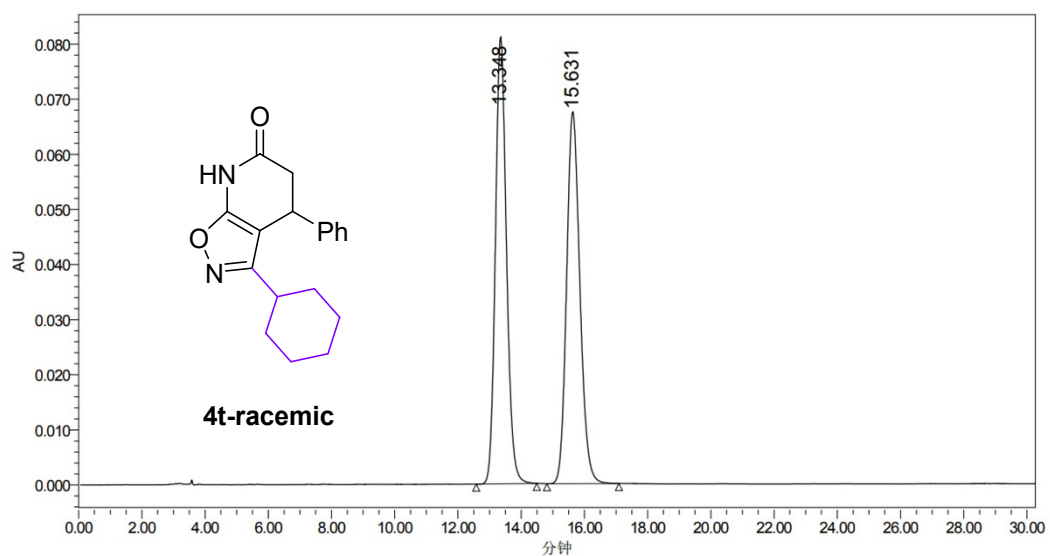
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.543	151131	5937	3.12	3.64
2	15.838	4689822	157027	96.88	96.36
Total		4840953	162964	100.00	100.00



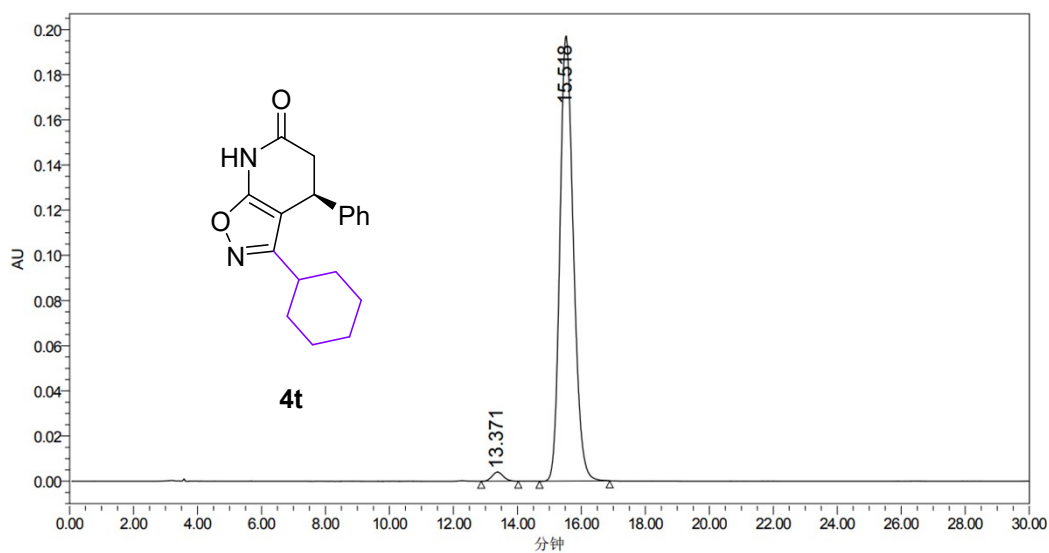
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.793	2792839	124394	49.92	54.64
2	16.923	2801245	103270	50.08	45.36
Total		5594084	227664	100.00	100.00



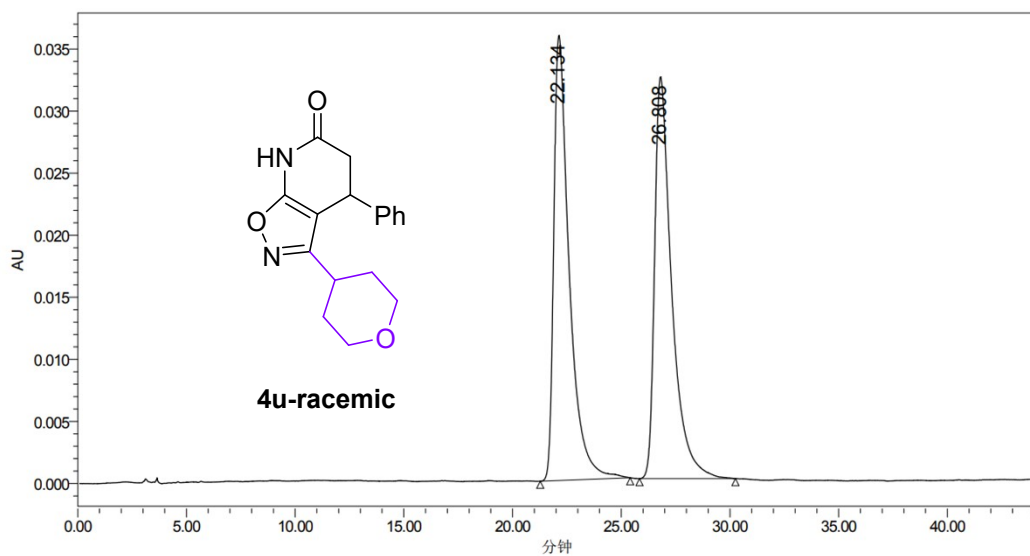
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.633	5397478	244591	98.88	99.02
2	16.834	61025	2421	1.12	0.98
Total		5458503	247012	100.00	100.00



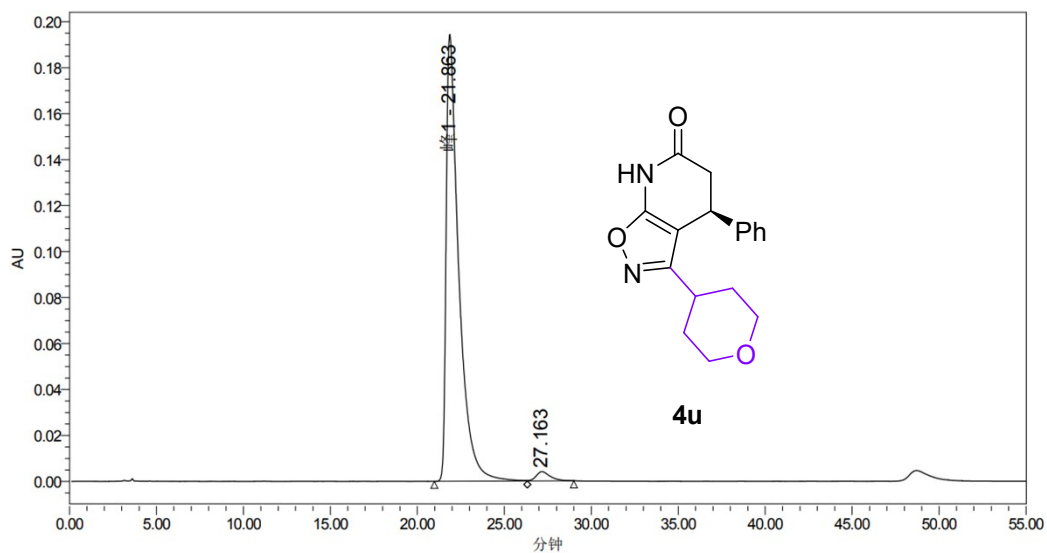
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.348	1970493	81064	49.93	54.58
2	15.631	1975825	67449	50.07	45.42
Total		3946318	148513	100.00	100.00



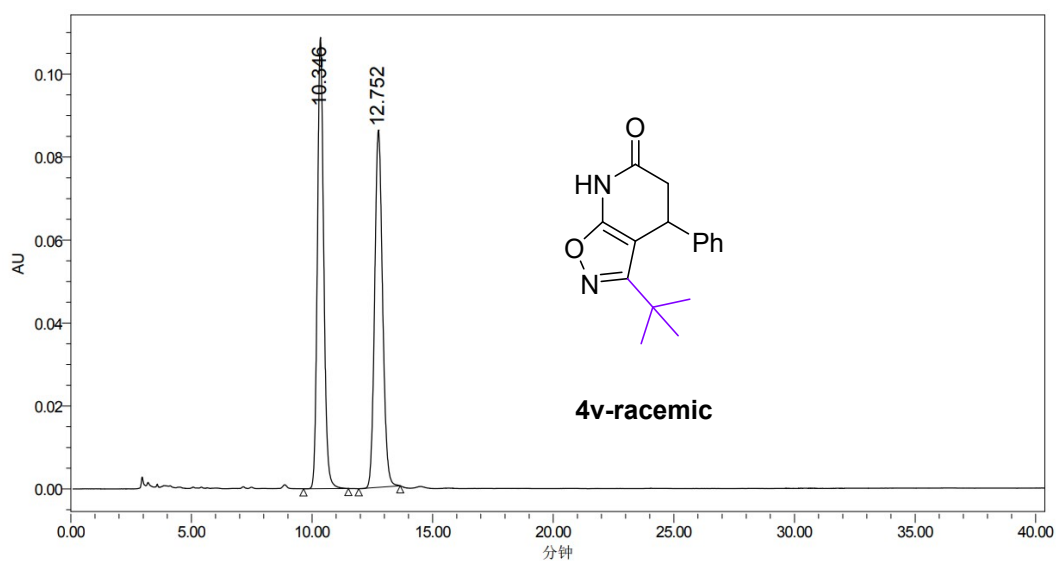
Peak	Ret.Time	Area	Height	Area%	Height%
1	13.371	97035	4020	1.65	2.00
2	15.518	5783237	197025	98.35	98.00
Total		5880272	201045	100.00	100.00



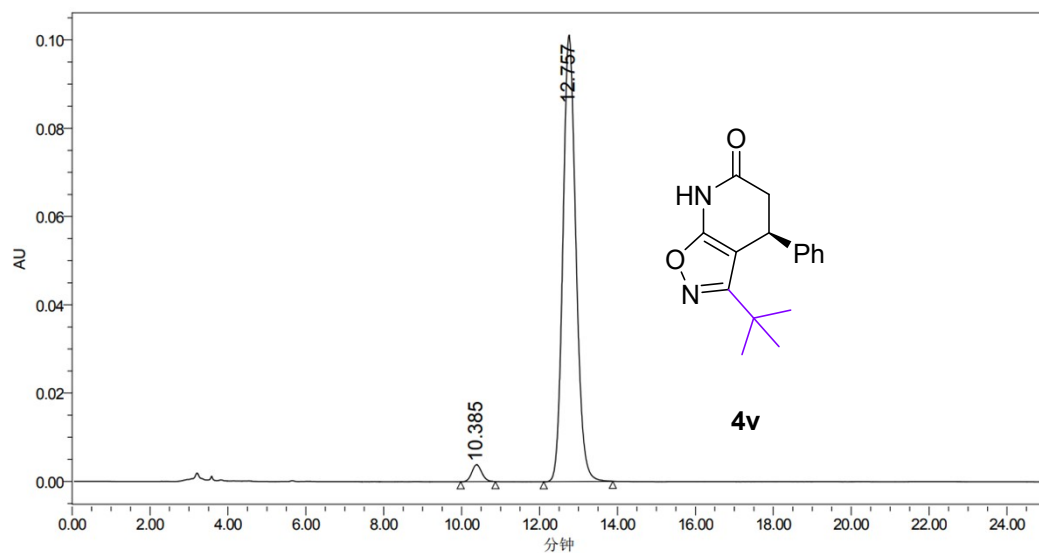
Peak	Ret.Time	Area	Height	Area%	Height%
1	22.134	1769046	35852	50.07	52.56
2	26.808	1764336	32361	49.93	47.44
Total		3533382	68213	100.00	100.00



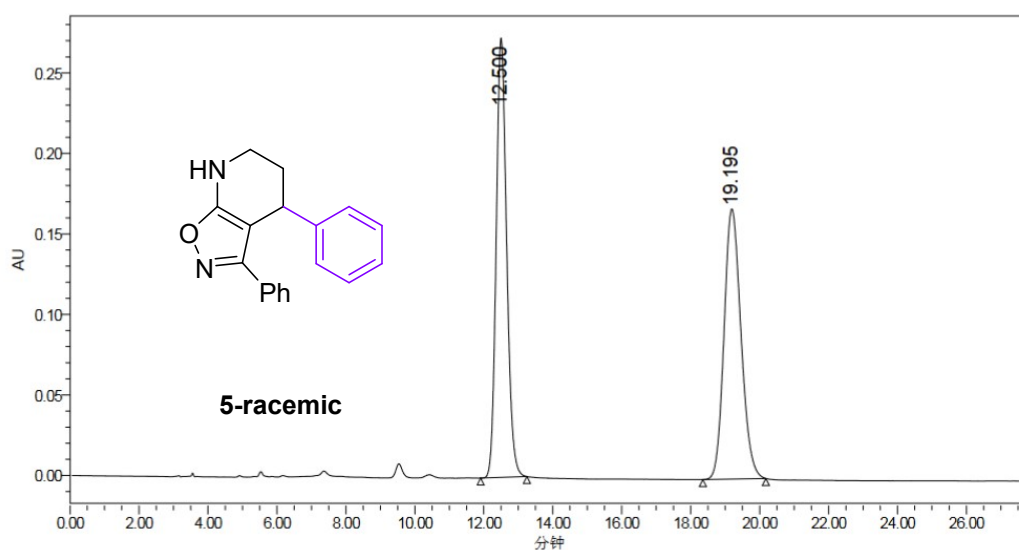
Peak	Ret.Time	Area	Height	Area%	Height%
1	21.863	9791219	194288	97.75	97.96
2	27.163	225755	4043	2.25	2.04
Total		10016974	198331	100.00	100.00



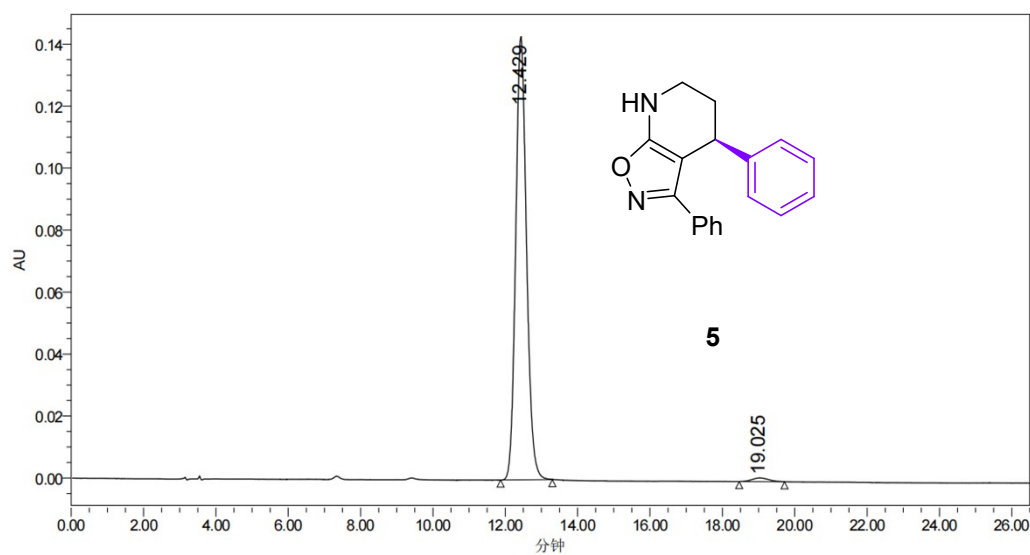
Peak	Ret.Time	Area	Height	Area%	Height%
1	10.346	1980299	108740	50.23	55.80
2	12.752	1961889	86121	49.77	44.20
Total		3942188	194861	100.00	100.00



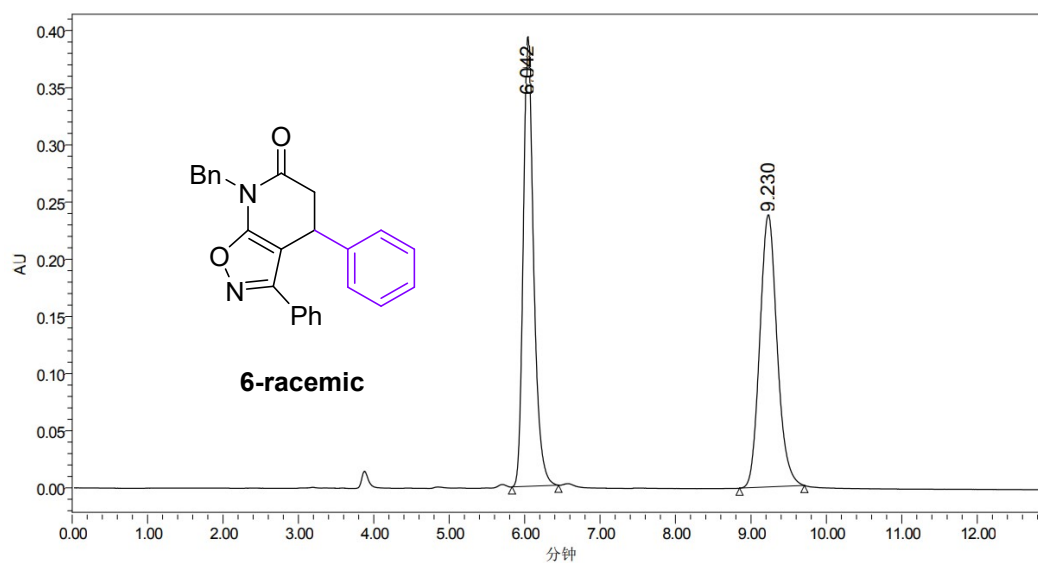
Peak	Ret.Time	Area	Height	Area%	Height%
1	10.385	68534	3841	2.84	3.66
2	12.757	2341194	101118	97.16	96.34
Total		2409728	104959	100.00	100.00



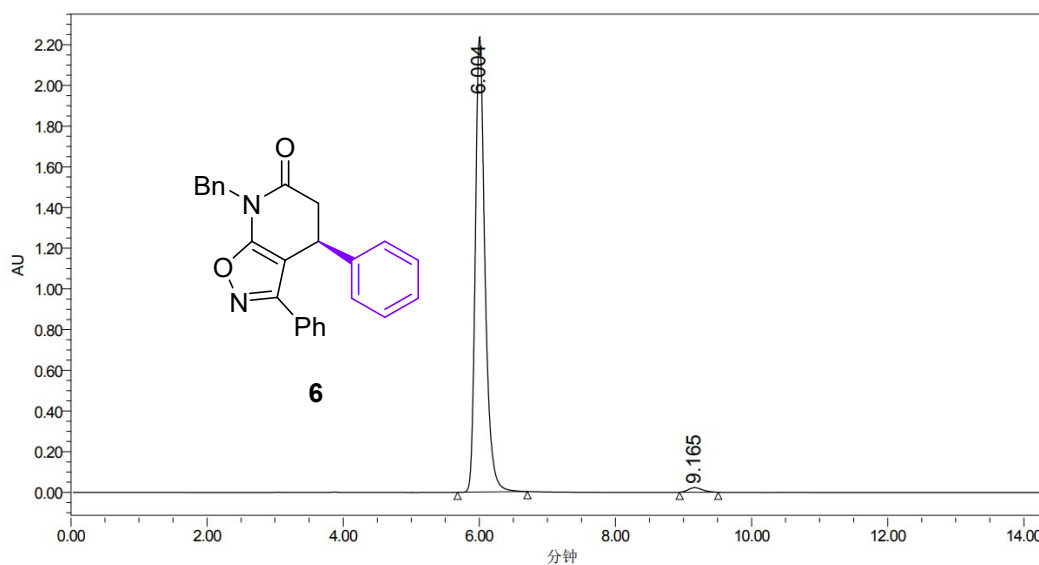
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.500	5733646	272832	50.10	61.92
2	19.195	5710779	167765	49.90	38.08
Total		11444425	440597	100.00	100.00



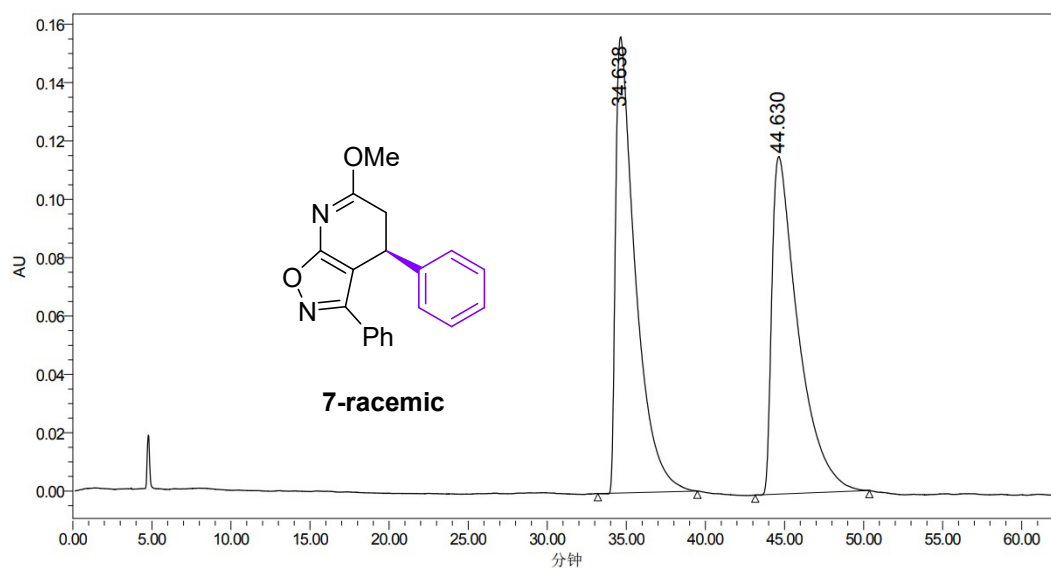
Peak	Ret.Time	Area	Height	Area%	Height%
1	12.429	2962808	142967	98.74	99.17
2	19.025	37682	1195	1.26	0.83
Total		3000490	144162	100.00	100.00



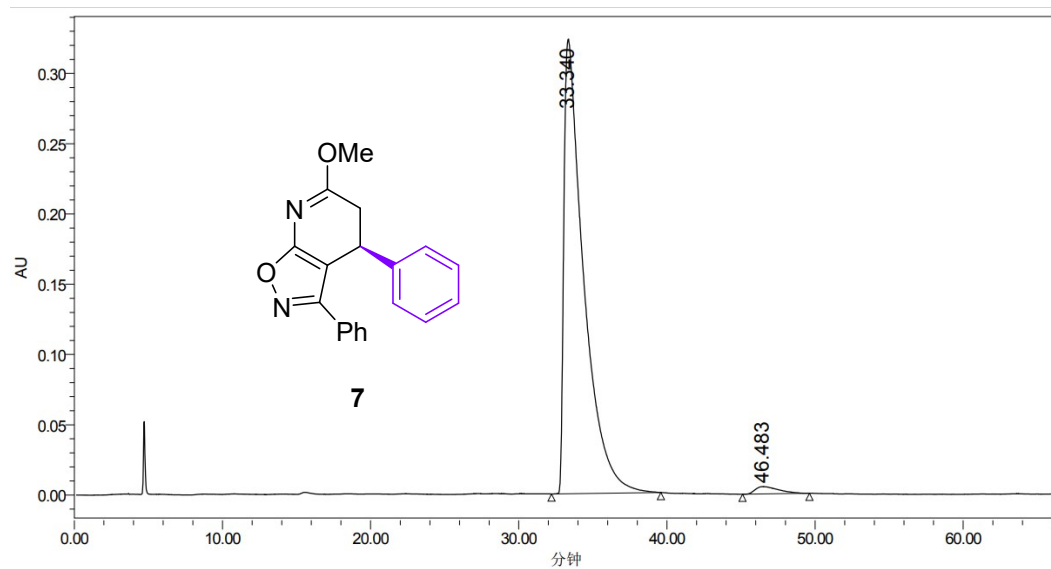
Peak	Ret.Time	Area	Height	Area%	Height%
1	6.042	3790163	393061	49.98	62.29
2	9.230	3793407	237914	50.02	37.71
Total		7583570	630975	100.00	100.00



Peak	Ret.Time	Area	Height	Area%	Height%
1	6.004	22141755	2236748	98.55	99.01
2	9.165	324864	22305	1.45	0.99
Total		22466619	2259053	100.00	100.00



Peak	Ret.Time	Area	Height	Area%	Height%
1	34.638	13598748	156299	50.39	57.46
2	44.630	13386996	115720	49.61	42.54
Total		26985744	272019	100.00	100.00



Peak	Ret.Time	Area	Height	Area%	Height%
1	33.340	29832632	323352	98.15	98.41
2	46.483	561990	5224	1.85	1.59
Total		30394622	328576	100.00	100.00