Supporting Information

Enantioselective Pd&Cu-Catalyzed Coupling of Imine Esters with *gem*-Difluorinated Cyclopropanes

Deyue Ren,†[a] Jie Zhao,†[a] Jintao Xia,[b] He Zhang,[a] Yingchun Qiu,[a] Ziqi Yu,[a] Jinping Hu,[a] Tianhao Li[a] and Fang Xie*[a]

[a]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong 273165, China
[b]Hubei Provincial Institute for Food Supervision and Test, Wuhan, Hubei 430075, China
E-mail: hollyxfang@hotmail.com

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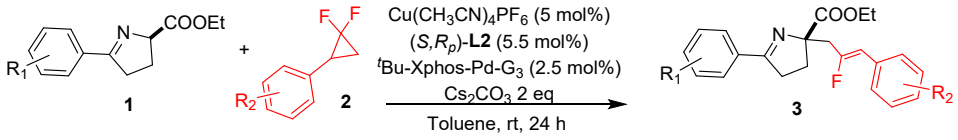
I. General Information

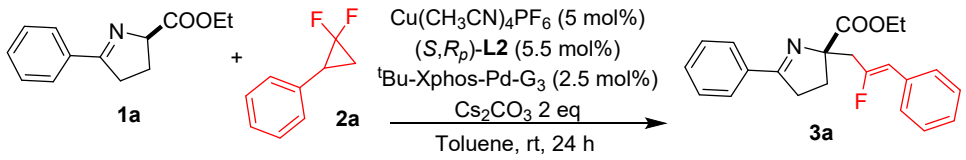
All chemicals were obtained from commercial sources and were used as received unless otherwise noted. NMR Spectra were recorded on a 500 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Data for the single crystal structure determination were collected with a Bruker D8 Quest diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu-Kα radiation (λ = 1.5418 Å). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate/petroleum ether. Imine esters[1] and *gem*-difluorinated cyclopropanes [2] were prepared according to literature procedures. The enantiomeric excesses (ee) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent HPLC 1260 Series using a Chiralpak® columns (25 cm) as noted for each. Optical rotations were measured on an Anton Parr Modular Circular Polarimeter 5100 and reported as follows: $[\alpha]_D^T$ = (C: g/100 mL in $CHCl_3$).

II. General Procedures for the Synthesis of Products 3

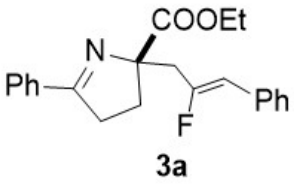


Typical Reaction Conditions for Synthesis of Chiral 3: A flame-dried 15 mL pressure tube equipped with a magnetic stir bar was evacuated and filled N_2 for three times before being transferred into a glovebox. $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol, 5 mol%), S,R_p-^{i}Pr-phosferrox (5.3 mg, 0.011 mmol, 5.5 mol%) and dry toluene (2mL) was added to the tube in succession. This mixture was stirred for 30 minutes. At this time, imine ester **1** (0.2 mmol, 1.0 equiv) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) were added in succession. After stirring for 5 mins, *gem*-DFCPs **2** (0.3 mmol, 1.5 equiv) and ^{t}Bu-Xphos-Pd-G_3 (4.0 mg, 0.005 mmol, 2.5 mol%) were added. The reaction tube was capped and taken out of the glovebox. The reaction mixture was stirred at room temperature in dark for 12 h. Upon complete consumption, the organic phase was concentrated in vacuo and the residue was purified by silica gel chromatography using EA/PE (ethyl acetate/petroleum ether = 1:30 to 1:4) to afford the product **3**. The ee of the product was determined by chiral HPLC analysis.

Preparation of Racemic Samples of **3**: To obtain racemic samples of **3**, the general procedure for synthesis of chiral 3 was followed except (±)-**L3** was used instead as the ligand. (±)-**L3** was prepared in a nitrogen filled glovebox by dissolving a mixture of (R,S_p)-**L3** (542.5 mg, 1.00 mmol) and (S,R_p)-**L3** (542.5 mg, 1.00 mmol) in THF (5 mL) followed by removal of the solvent in vacuo.



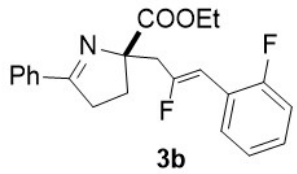
Scale-up synthesis of **3a**: A flame-dried pressure tube equipped with a magnetic stir bar was evacuated and filled N_2 for three times before being transferred into a glovebox. $Cu(CH_3CN)_4PF_6$ (74.6 mg, 0.2 mmol), *S,R*$_p$-iPr-phosferrox (105.9 mg, 0.22 mmol) and dry toluene (40 mL) was added to the tube in succession. This mixture was stirred at room temperature for 30 min. At this time, imino ester **1a** (868.9 mg, 4.0 mmol) and Cs_2CO_3 (2606.4 mg, 8 mmol) were added. After 5 min of stirring, freshly prepared *gem*-DFCP **2a** (925 mg, 6.0 mmol) and ^{t}Bu-Xphos-Pd-G$_3$ (79.5 mg, 0.1 mmol) were added. The reaction tube was capped and taken out of the glovebox. The reaction was stirred at room temperature and in dark for 12 h. After completion, the organic phase was concentrated in vacuo and the residue was purified by silica gel chromatography using EA/PE (EtOAc/PE) = 1:50 to 1:30 to afford the product **3a** (1.04 g, 74% yield). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.2 min, t_{major} = 10.2 min) indicated 98% ee.



3a

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

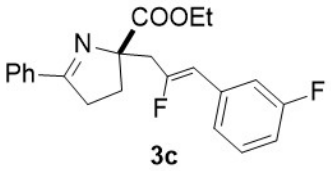
The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow solid (54.8 mg, 78% yield.), m.p. 59.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.37 (m, 5H), 7.29 – 7.26 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 5.59 (d, *J* = 39.0 Hz, 1H), 4.32 – 4.13 (m, 2H), 3.27 – 3.10 (m, 2H), 3.09 – 2.99 (m, 1H), 2.91 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.67 – 2.52 (m, 1H), 2.27 – 2.22 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.1, 157.2 (d, *J* = 265.0 Hz), 133.9, 133.4, 131.0, 128.48, 128.44, 128.42, 128.3 (d, *J* = 32.5 Hz), 127.0 (d, *J* = 2.1 Hz), 109.9 (d, *J* = 8.1 Hz), 82.4 (d, *J* = 2.6 Hz), 61.5, 41.6 (d, *J* = 23.8 Hz), 36.1, 30.5 (d, *J* = 1.5 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}FNO_2^+$ 352.1707, Found 352.1710. Specific rotation $[\alpha]_D^{25}$ = +103.6 (*c* = 0.77, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.2 min, t_{major} = 10.2 min) indicated 98% ee.



3b

Ethyl (*S,Z*)-2-(2-fluoro-3-(2-fluorophenyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure with the following modifications: the reaction was conducted in dioxane at 80 °C using $Cu(CH_3CN)_4PF_6$ (10 mol%), (S,R_p)-**L2** (11 mol%), ^{t}Bu-Xphos-Pd-G_3 (3.5 mol%). Purification by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (44.3 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (t, *J* = 9.6 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.20 – 7.13 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 5.87 (d, *J* = 38.8 Hz, 1H), 4.31 – 4.17 (m, 2H), 3.31 – 3.13 (m, 2H), 3.12 – 3.03 (m, 1H), 2.95 (dd, *J* = 21.1, 14.8 Hz, 1H), 2.65 - 2.59 (m, 1H), 2.26 – 2.20 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 172.9, 159.3 (d, *J* = 246.3 Hz), 158.5 (d, *J* = 267.5 Hz), 133.9, 131.1, 130.1 (dd, *J* = 12.8, 2.7 Hz), 128.51 (d, *J* = 2.5 Hz) 128.45, 128.2, 124.0 (d, *J* = 3.6 Hz), 121.1 (d, *J* = 2.4 Hz), 115.1 (d, *J* = 21.2 Hz), 101.28 (t, *J* = 7.1 Hz), 82.3, 61.6, 41.8 (d, *J* = 23.8 Hz), 36.1, 30.6, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1616. Specific rotation $[\alpha]_D^{25}$ = - 56.23 (*c* = 1.01, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 7.1 min, t_{major} = 8.9 min) indicated 96% ee.

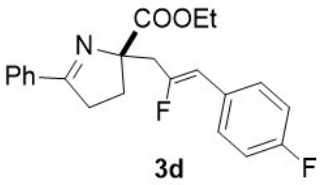


3c

Ethyl (*S,Z*)-2-(2-fluoro-3-(3-fluorophenyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure with the following modifications: the reaction was conducted in dioxane at 80 °C using $Cu(CH_3CN)_4PF_6$ (10 mol%), (S,R_p)-**L2** (11 mol%), ^{t}Bu-Xphos-Pd-G_3 (3.5 mol%). Purification by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (50.2 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.26 – 7.22 (m, 1H), 7.17 (d, *J* = 10.5 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.87 (m, 1H), 5.58 (d, *J* = 38.2 Hz, 1H), 4.30 – 4.16 (m, 2H), 3.27 – 3.11 (m, 2H), 3.10 – 3.02 (m, 1H), 2.93 (dd, *J* = 21.7, 14.8 Hz, 1H), 2.66 – 2.50 (m, 1H), 2.29 – 2.17 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 173.0, 162.8 (d, *J* = 242.5 Hz), 158.1 (d, *J* = 267.5Hz), 135.4 (dd, *J* = 8.4, 2.3 Hz), 133.8, 131.1, 129.7 (d, *J* = 8.4 Hz),

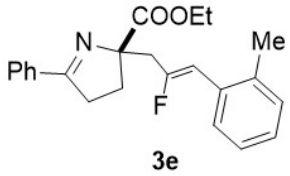
128.5, 128.1, 124.2 (dd, J = 6.6, 2.7 Hz), 115.1 (dd, J = 22.5, 8.8 Hz), 113.9 (dd, J = 21.4, 1.7 Hz), 109.0 (dd, J = 7.8, 2.6 Hz), 82.2 (d, J = 2.5 Hz), 61.6, 41.5 (d, J = 25 Hz), 36.1, 30.7, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1616. Specific rotation $[\alpha]_D^{25}$ = -75.1 (c = 0.70, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 7 min, t_{major} = 8.3 min) indicated 97% ee.



3d

Ethyl (*S,Z*)-2-(2-fluoro-3-(4-fluorophenyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow solid (54.6 mg, 74% yield), m.p. 85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.50 – 7.32 (m, 5H), 7.03 – 6.87 (m, 2H), 5.56 (d, J = 38.7 Hz, 1H), 4.30 – 4.14 (m, 2H), 3.24 – 3.11 (m, 2H), 3.08 – 3.02 (m, 1H), 2.91 (dd, J = 21.7, 14.8 Hz, 1H), 2.62 – 2.56 (m, 1H), 2.26 – 2.20 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 173.1, 161.6 (dd, J = 245.4, 3.5 Hz), 156.8 (dd, J = 264.5, 2.3 Hz), 133.8, 131.1, 130.1 (dd, J = 7.8, 7.8 Hz), 129.5 (dd, J = 2.6, 2.6 Hz), 128.5, 128.1, 115.3 (d, J = 21.4 Hz), 108.8 (d, J = 8.4 Hz), 82.3, 61.6, 41.5 (d, J = 24.8 Hz), 36.1, 30.6, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1616. Specific rotation $[\alpha]_D^{25}$ = -103.5 (c = 1.00, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.7 min, t_{major} = 7.8 min) indicated 97% *ee*.

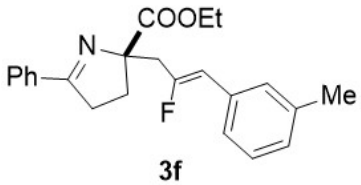


3e

Ethyl (*S,Z*)-2-(2-fluoro-3-(o-tolyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give colorless oil (51.9 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.23 – 7.04 (m, 3H), 5.72 (d, J = 38.2 Hz, 1H), 4.38 – 4.11 (m, 2H), 3.23 (dd, J = 19.1, 14.8 Hz, 1H), 3.19 – 3.03 (m, 2H), 2.98 (dd, J = 22.4, 14.8 Hz, 1H), 2.68 – 2.54 (m, 1H), 2.33 – 2.24 (m, 1H), 2.17 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.1, 156.7 (d, J = 263.9 Hz)), 135.6, 133.9, 131.9 (d, J = 1.4 Hz), 131.0, 129.9, 129.2 (d, J = 9.4 Hz), 128.4, 128.2, 127.1, 125.8, 107.5 (d, J = 9.3 Hz), 82.3 (d, J = 2.0 Hz), 61.6, 41.4 (d, J = 25.1 Hz), 36.1, 30.5 (d, J = 1.7 Hz), 20.0, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_2^+$ 366.1864, Found 366.1862. Specific

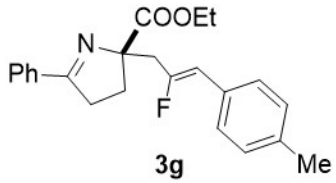
rotation $[\alpha]_D^{25}$ = -75.59 (*c* = 0.94, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.8 min, t_{major} = 8 min) indicated 97% ee.



3f

Ethyl (*S,Z*)-2-(2-fluoro-3-(m-tolyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give brown solid (50.4 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.36 (m, 3H), 7.23 – 7.14 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.55 (d, *J* = 39.1 Hz, 1H), 4.30 – 4.18 (m, 2H), 3.27 – 3.10 (m, 2H), 3.09 – 2.99 (m, 1H), 2.89 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.65 – 2.54 (m, 1H), 2.30 (s, 3H), 2.27 – 2.21 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.1, 157.0 (d, *J* = 265.0 Hz), 137.9, 134.0, 133.3 (d, *J* = 2.5 Hz), 131.0, 129.2 (d, *J* = 7.2 Hz), 128.4, 128.3, 128.1, 127.8 (d, *J* = 1.9 Hz), 125.6 (d, *J* = 7.3 Hz), 109.9 (d, *J* = 8.2 Hz), 82.4 (d, *J* = 2.6 Hz), 61.5, 41.6 (d, *J* = 24.8 Hz), 36.1, 30.5, 21.4, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_2^+$ 366.1864, Found 366.1862. Specific rotation $[\alpha]_D^{25}$ = -123.20 (*c* = 1.12, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 7.8 min, t_{major} = 9.7 min) indicated 98% ee.

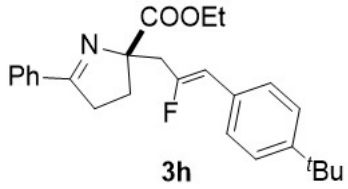


3g

Ethyl (*S,Z*)-2-(2-fluoro-3-(p-tolyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give brown solid (53.3 mg, 73% yield), m.p. 70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 39.2 Hz, 1H), 4.30 – 4.18 (m, 2H), 3.28 – 3.10 (m, 2H), 3.09 – 3.00 (m, 1H), 2.90 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.65 – 2.55 (m, 1H), 2.31 (s, 3H), 2.28 – 2.22 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 173.1, 156.6 (d, *J* = 265.0 Hz), 136.8 (d, *J* = 2.2 Hz), 134.0, 131.0, 130.6 (d, *J* = 2.4 Hz), 129.1, 128.4 (d, *J* = 6.3 Hz), 128.1, 109.74 (d, *J* = 8.3 Hz), 82.5 (d, *J* = 2.7 Hz), 61.5, 41.6 (d, *J* = 25.0 Hz), 36.1, 30.5 (d, *J* = 2.5 Hz), 21.2, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_2^+$ 366.1864, Found 366.1862. Specific rotation $[\alpha]_D^{25}$ = -105.78 (*c* = 1.01, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol,

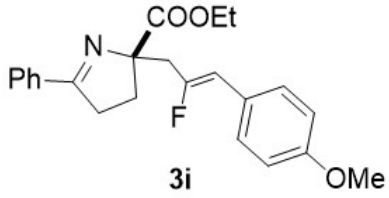
flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.7 min, t_{major} = 7.8 min) indicated 98% ee.



3h

Ethyl (*S,Z*)-2-(3-(4-(tert-butyl)phenyl)-2-fluoroallyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow oil (52.9 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.42-7.38 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.58 (d, *J* = 39.2 Hz, 1H), 4.29 – 4.19 (m, 2H), 3.28 – 3.11 (m, 2H), 3.10 – 3.02 (m, 1H), 2.91 (dd, *J* = 21.4, 14.8 Hz, 1H), 2.63 - 2.57 (m, 1H), 2.28 – 2.22 (m, 1H), 1.32 – 1.28 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 173.1, 156.7 (d, *J* = 265.0 Hz), 150.0, 134.0, 131.0, 130.6 (d, *J* = 2.3 Hz), 128.4, 128.2(d, *J* = 7.6 Hz), 128.1, 125.3, 109.6 (d, *J* = 8.4 Hz), 82.5 (d, *J* = 2.6 Hz), 61.5, 41.6 (d, *J* = 23.8 Hz), 36.1, 34.5, 31.3, 30.4, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{31}FNO_2^+$ 408.2333, Found 408.2336. Specific rotation $[\alpha]_D^{25}$ = -93.73 (*c* = 1.01, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.3 min, t_{major} = 7.5 min) indicated 98% ee.

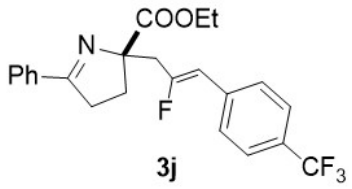


3i

Ethyl (*S,Z*)-2-(2-fluoro-3-(4-methoxyphenyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give brown solid (49.6 mg, 65% yield), m.p. 93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.45 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.52 (d, *J* = 39.3 Hz, 1H), 4.36 – 4.09 (m, 2H), 3.79 (s, 3H), 3.25 – 3.10 (m, 2H), 3.09 – 3.00 (m, 1H), 2.88 (dd, *J* = 21.7, 14.8 Hz, 1H), 2.64 – 2.52 (m, 1H), 2.28 - 2.21 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 173.1, 158.51 (d, *J* = 2.8 Hz), 155.8 (d, *J* = 262.5 Hz), 134.0, 131.0, 129.70 (d, *J* = 7.5 Hz), 128.4, 128.1, 126.16 (d, *J* = 2.4 Hz), 113.8, 109.3 (d, *J* = 8.6 Hz), 82.5 (d, *J* = 2.7 Hz), 61.5, 55.2, 41.6 (d, *J* = 25.0 Hz), 36.1, 30.5, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_3^+$ 382.1813, Found

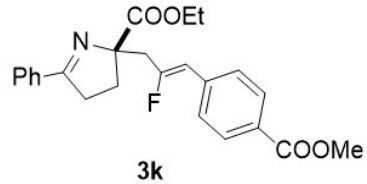
382.1815. Specific rotation $[\alpha]_D^{25}$ = -102.98 (*c* = 0.94, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 13.2 min, t_{major} =12 min) indicated 96% ee.



3j

Ethyl (*S,Z*)-2-(2-fluoro-3-(4-(trifluoromethyl)phenyl)allyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure with the following modifications: the reaction was conducted in dioxane at 80 °C using $Cu(CH_3CN)_4PF_6$ (10 mol%), (S,R_p)-**L2** (11 mol%), ^{t}Bu-Xphos-Pd-G_3 (3.5 mol%). Purification by column chromatography (EtOAc/PE = 1:30 to 1:10) to give orange solid (58.7 mg, 70% yield), m.p. 90 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.77 (m, 2H), 7.56 – 7.37 (m, 7H), 5.66 (d, *J* = 38.3 Hz, 1H), 4.30 – 4.18 (m, 2H), 3.26 – 3.11 (m, 2H), 3.10 – 3.02 (m, 1H), 2.97 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.65 – 2.55 (m, 1H), 2.25 – 2.20 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 172.9, 159.0 (d, *J* = 268.6 Hz), 136.9, 133.8, 131.1, 128.54 (d, *J* = 7.8 Hz), 128.48, 128.1, 125.3 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 269.0 Hz), 108.8 (d, *J* = 7.8 Hz), 82.2 (d, *J* = 2.4 Hz), 61.6, 41.6 (d, *J* = 24.4 Hz), 36.1, 30.8, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}F_4NO_2^+$ 420.1581, Found 420.1583. Specific rotation $[\alpha]_D^{25}$ = -68.3 (*c* = 0.83, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 5.8 min, t_{major} = 6.8min) indicated 97% ee.

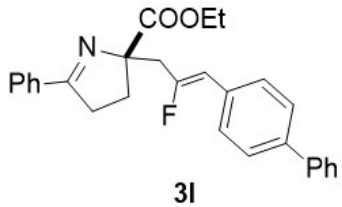


3k

Ethyl (*S,Z*)-2-(2-fluoro-3-(4-(methoxycarbonyl)phenyl)allyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give white solid (52.4 mg, 64% yield,), m.p. 70.7 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.77 (m, 2H), 7.50 – 7.35 (m, 5H), 5.65 (d, *J* = 38.5 Hz, 1H), 4.36 – 4.11 (m, 2H), 3.89 (s, 3H), 3.27 – 3.02 (m, 3H), 2.96 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.28 – 2.17 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 172.9, 166.8, 159.0 (d, *J* = 272.2 Hz), 138.0 (d, *J* = 2.5 Hz), 133.8, 131.1, 129.7, 128.5, 128.4 (d, *J* = 1.3 Hz), 128.3 (d, *J* = 7.6 Hz), 128.1, 109.3 (d, *J* = 7.7 Hz), 82.2, 61.6, 52.1, 41.7 (d, *J* = 23.9 Hz), 36.1, 30.8, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}FNO_4^+$ 410.1762,

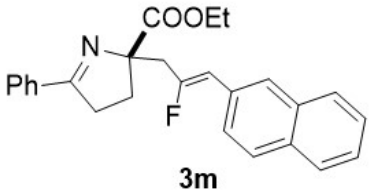
Found 410.1765. Specific rotation $[\alpha]_D^{25}$ = -111.5 (*c* = 0.4, $CHCl_3$). HPLC analysis (IC - 3 column, 85:15 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 17.1 min, t_{major} =21.7 min) indicated 98% ee.



3l

Ethyl (*S,Z*)-2-(3-([1,1'-biphenyl]-4-yl)-2-fluoroallyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give white solid (61.6 mg, 72% yield), m.p. 139 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.37 (m, 7H), 7.34 (t, *J* = 7.3 Hz, 1H), 5.65 (d, *J* = 39.0 Hz, 1H), 4.38 – 4.16 (m, 2H), 3.29 – 3.03 (m, 3H), 2.95 (dd, *J* = 21.6, 14.8 Hz, 1H), 2.72 – 2.50 (m, 1H), 2.30 – 2.24 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.1, 157.4 (d, *J* = 266.3 Hz), 140.7, 139.7 (d, *J* = 2.1 Hz), 134.0, 132.5 (d, *J* = 2.4 Hz), 131.0, 128.9 (d, *J* = 7.5 Hz), 128.8, 128.5, 128.2, 127.3, 127.1, 127.0, 109.56 (d, *J* = 8.2 Hz), 82.43 (d, *J* = 2.5 Hz), 61.6, 41.7 (d, *J* = 25.0 Hz), 36.1, 30.6, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}FNO_2^+$ 428.2020, Found 428.2022. Specific rotation $[\alpha]_D^{25}$ = -112.96 (*c* = 0.90, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 12.3 min, t_{major} = 11.4 min) indicated 95% ee.

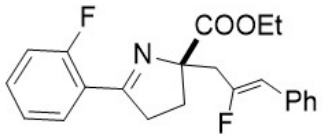


3m

Ethyl (*S,Z*)-2-(2-fluoro-3-(naphthalen-2-yl)allyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure with the following modifications: the reaction was conducted in dioxane at 80 °C. Purification by column chromatography (EtOAc/PE = 1:50 to 1:10) to give white solid (54.6 mg, 68% yield), m.p. 109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.82 (s, 1H), 7.79 – 7.72 (m, 3H), 7.57 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49 – 7.38 (m, 5H), 5.75 (d, *J* = 39.0 Hz, 1H), 4.38 – 4.14 (m, 2H), 3.27 (dd, *J* = 20.5, 14.8 Hz, 1H), 3.21 – 3.12 (m, 1H), 3.12 – 3.03 (m, 1H), 2.98 (dd, *J* = 21.7, 14.8 Hz, 1H), 2.69 – 2.55 (m, 1H), 2.34 – 2.26 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 173.1, 157.5 (d, J = 265.8 Hz), 134.0, 133.4, 132.4 (d, *J* = 1.4 Hz), 131.1, 130.9 (d, *J* = 2.6 Hz), 128.5,

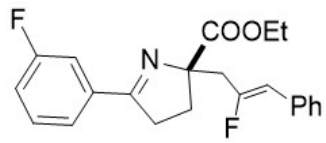
128.2, 128.0, 127.9, 127.5, 127.4 (d, J = 7.6 Hz), 126.5 (d, J = 7.5 Hz), 126.1, 125.9, 110.0 (d, J = 8.0 Hz), 82.4 (d, J = 1.6 Hz), 61.6, 41.7 (d, J = 24.8 Hz), 36.1, 30.6 (d, J = 1.1 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}FNO_2^+$ 402.1864, Found 402.1869. Specific rotation $[\alpha]_D^{25}$ = -94.05 (c = 1.08, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 11.8 min, t_{major} = 11.3 min) indicated 97% ee.



3n

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(2-fluorophenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (55.4 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (td, J = 7.7, 1.5 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.29 (t, J = 7.7 Hz, 2H), 7.23 – 7.15 (m, 2H), 7.08 (dd, J = 10.9, 8.6 Hz, 1H), 5.61 (d, J = 39.0 Hz, 1H), 4.36 – 4.13 (m, 2H), 3.32 – 3.03 (m, 3H), 2.95 (dd, J = 21.6, 14.8 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.32 – 2.17 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 172.8 (d, J = 2.5 Hz), 161.6 (d, J = 252.5 Hz), 157.1 (d, J = 266.3 Hz), 133.4 (d, J = 2.5 Hz), 132.5 (d, J = 8.7 Hz), 130.6 (d, J = 3.3 Hz), 128.5 (d, J = 7.3 Hz), 128.4, 127.0 (d, J = 2.2 Hz), 124.3 (d, J = 3.3 Hz), 122.1 (d, J = 11.9 Hz), 116.2 (d, J = 22.5 Hz), 110.0 (d, J = 8.1 Hz), 81.2 (d, J = 2.8 Hz), 61.6, 41.5 (d, J = 25.0 Hz), 38.8 (d, J = 7.3 Hz), 30.9, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1618. Specific rotation $[\alpha]_D^{25}$ = -85.70 (c = 0.93, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.7 min, t_{major} = 7.1 min) indicated 96% ee.

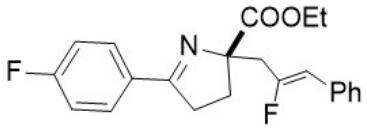


3o

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(3-fluorophenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (56.2 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 2H), 7.47 – 7.33 (m, 3H), 7.28 (t, J = 7.6 Hz, 2H), 7.24 – 7.17 (m, 1H), 7.16 - 7.12 (m, 1H), 5.59 (d, J = 39.0 Hz, 1H), 4.33 – 4.14 (m, 2H), 3.24 – 3.07 (m, 2H), 3.07 – 2.99 (m, 1H), 2.93 (dd, J = 21.5, 14.8 Hz, 1H), 2.67 – 2.53 (m, 1H), 2.29 – 2.24 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2 (d, J = 2.6 Hz), 172.9, 162.8 (d, J = 245.0 Hz),

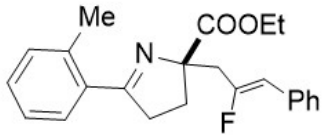
157.0 (d, J = 266.3 Hz), 136.1 (d, J = 7.5 Hz), 133.3 (d, J = 2.5 Hz), 130.0 (d, J = 8.0 Hz), 128.5 (d, J = 7.5 Hz), 128.4, 127.1 (d, J = 2.0 Hz), 123.9 (d, J = 2.9 Hz), 117.9 (d, J = 21.2 Hz), 114.9 (d, J = 22.5 Hz), 110.0 (d, J = 8.1 Hz), 82.5 (d, J = 2.7 Hz), 61.6, 41.5 (d, J = 25.0 Hz), 36.1, 30.6 (d, J = 1.4 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1618. Specific rotation $[\alpha]_D^{25}$ = -99.95 (c = 1.06, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 7.2 min, t_{major} = 8.4 min) indicated 96% ee.



3p

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(4-fluorophenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (57.6 mg, 78% yield) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 2H), 7.47 – 7.35 (m, 2H), 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 1H), 7.11 – 7.03 (m, 2H), 5.57 (d, J = 39.0 Hz, 1H), 4.32 – 4.14 (m, 2H), 3.27 – 2.96 (m, 2H), 2.90 (dd, J = 21.6, 14.7 Hz, 1H), 2.68 – 2.49 (m, 1H), 2.32 – 2.16 (m,1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.1, 164.6 (d, J = 250.1 Hz), 157.1 (d, J = 265.5 Hz), 133.4 (d, J = 2.5 Hz), 130.3 (d, J = 8.6 Hz), 130.2 (d, J = 3.3 Hz), 128.54, 128.48, 127.14 (d, J = 2.3 Hz), 115.6 (d, J = 21.6 Hz), 110.0 (d, J = 8.1 Hz), 82.4 (d, J = 2.8 Hz), 61.7, 41.7 (d, J = 24.7 Hz), 36.1, 30.70 (d, J = 1.7 Hz), 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}F_2NO_2^+$ 370.1613, Found 370.1618. Specific rotation $[\alpha]_D^{25}$ = -109.24 (c = 1.05, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.6 min, t_{major} = 7.8 min) indicated 98% ee.

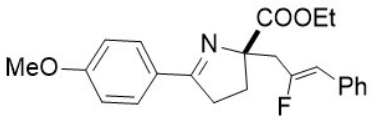


3q

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(o-tolyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (56.3 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.7 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 6.1 Hz, 1H), 7.15 – 7.08 (m, 3H), 5.55 (d, J = 39.2 Hz, 1H), 4.22 – 4.11 (m, 2H), 3.09 (dd, J = 19.8, 14.9 Hz, 1H), 3.04 – 2.87 (m, 3H), 2.51 – 2.42 (m, 1H), 2.40 (s, 3H), 2.21 – 2.13 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 173.2, 157.3 (d, J = 233.8 Hz), 137.2, 134.5,

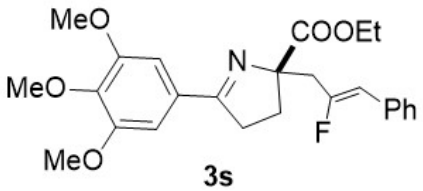
133.46 (d, *J* = 2.5 Hz), 131.2, 129.4,128.6 (d, *J* = 13.8 Hz), 128.44, 128.42, 127.03 (d, *J* = 2.2 Hz), 125.6, 109.9 (d, *J* = 8.0 Hz), 82.7 (d, *J* = 2.6 Hz), 61.5, 41.3 (d, *J* = 25.0 Hz), 39.5, 30.7 (d, *J* = 1.7 Hz), 21.2, 14.20. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_2^+$ 366.1864, Found 366.1867. Specific rotation $[\alpha]_D^{25}$ = -57.01 (*c* = 1.11, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.4 min, t_{major} = 7.4 min) indicated 95% ee.



3r

Ethyl (S,Z)-2-(2-fluoro-3-phenylallyl)-5-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow solid (49.6 mg, 65% yield), m.p. 65.4 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.56 (d, *J* = 39.1 Hz, 1H), 4.31 – 4.07 (m, 2H), 3.80 (s, 3H), 3.18 (dd, *J* = 20.6, 14.8 Hz, 1H), 3.12 – 2.94 (m, 2H), 2.86 (dd, *J* = 20.6, 14.8 Hz, 1H), 2.65 - 2.45 (m, 1H), 2.25 – 2.10 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 173.2, 162.0, 157.2 (d, *J* = 265.4 Hz), 133.5 (d, *J* = 2.5 Hz), 129.9, 128.5 (d, *J* = 7.3 Hz), 128.4, 127.0 (d, *J* = 1.9 Hz), 126.6, 113.8, 109.8 (d, *J* = 8.1 Hz), 82.1 (d, *J* = 2.2 Hz), 61.5, 55.4, 41.7 (d, *J* = 24.6 Hz), 35.9, 30.6, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}FNO_3^+$ 382.1813, Found 382.1816. Specific rotation $[\alpha]_D^{25}$ = -148.92 (*c* = 0.51, $CHCl_3$). HPLC analysis (IG - 3 column,85:15 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 15.0 min, t_{major} = 10.3 min) indicated 98% ee.

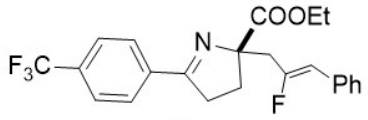


3s

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(3,4,5-trimethoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:6) to give brown oil (70.6 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (s, 2H), 5.58 (d, *J* = 39.0 Hz, 1H), 4.35 – 4.14 (m, 2H), 3.88 (m, 9H), 3.27 – 2.99 (m, 3H), 2.90 (dd, *J* = 21.8, 14.8 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.30 – 2.20 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 173.1, 157.1 (d, *J* = 265.0 Hz), 153.1, 140.8, 133.4 (d, *J* = 2.4 Hz), 129.5, 128.5,

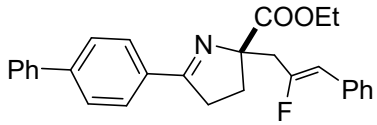
128.4, 127.0 (d, J = 1.9 Hz), 109.9 (d, J = 8.1 Hz), 105.5, 82.3 (d, J = 2.7 Hz), 61.5, 60.9, 56.3, 41.5 (d, J = 23.8 Hz), 36.2, 30.7, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}FNO_5^+$ 442.2024, Found 442.2027. Specific rotation $[\alpha]_D^{25}$ = -97.61 (c = 1.38, $CHCl_3$). HPLC analysis (IG - 3 column, 65:35 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 4.9 min, t_{major} = 5.4 min) indicated 92% ee.



3t

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow solid (53.7 mg, 64% yield), m.p. 85 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.06 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 5.82 (d, J = 40.6 Hz, 1H), 4.30 – 4.04 (m, 2H), 3.19 – 2.91 (m, 4H), 2.49 – 2.40 (m, 1H), 2.26 – 2.15 (m, 1H), 1.20 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 174.1, 172.8, 157.7 (d, J = 265.0 Hz), 137.7, 133.6, 131.3 (q, J = 31.3 Hz), 129.2, 129.0, 128.6 (d, J = 7.2 Hz), 127.6, 126.0 (q, J = 3.8 Hz), 124.5 (d, J = 270.0 Hz), 109.5 (d, J = 6.8 Hz), 82.4 (d, J = 2.1 Hz), 61.4, 41.4 (d, J = 24.4 Hz), 35.7, 31.2, 14.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}F_4NO_2^+$ 420.1581, Found 420.1579. Specific rotation $[\alpha]_D^{25}$ = -6.62 (c = 0.77, $CHCl_3$). HPLC analysis (IC- 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 5.5 min, t_{major} = 5.7 min) indicated 98% ee.

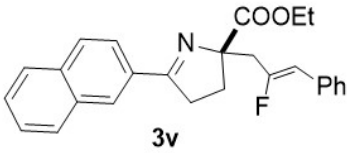


3u

Ethyl (*S,Z*)-5-([1,1'-biphenyl]-4-yl)-2-(2-fluoro-3-phenylallyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give white solid (62.4 mg, 73% yield), m.p. 115 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.68 – 7.58 (m, 4H), 7.50 – 7.35 (m, 5H), 7.29 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 5.61 (d, J = 39.0 Hz, 1H), 4.33 – 4.13 (m, 2H), 3.28 -3.05 (m, 3H), 2.94 (dd, J = 21.5, 14.8 Hz, 1H), 2.72 – 2.54 (m, 1H), 2.30 – 2.24 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 173.1, 157.2 (d, J = 266.3 Hz), 143.7, 140.3, 133.4 (d, J = 2.3 Hz), 132.8, 128.9, 128.6, 128.5 (d, J = 7.5 Hz), 128.4, 127.9, 127.2, 127.1, 127.0 (d, J = 2.5 Hz), 109.9 (d, J = 8.1 Hz), 82.4, 61.6, 41.7 (d, J = 25.0 Hz), 36.1, 30.6, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}FNO_2^+$ 428.2020, Found 428.2021. Specific rotation $[\alpha]_D^{25}$ = -76.66

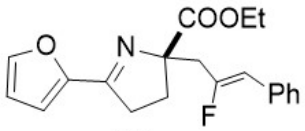
(c = 0.99, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 10.2 min, t_{major} = 13.1 min) indicated 98% ee.



3v

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

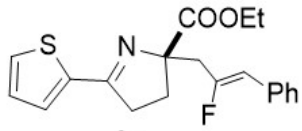
The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow solid (56.2 mg, 70% yield), m.p. 134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.92 – 7.79 (m, 3H), 7.58 – 7.47 (m, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.22 – 7.14 (m, 1H), 5.61 (d, J = 39.0 Hz, 1H), 4.44 – 4.12 (m, 2H), 3.40 – 3.10 (m, 3H), 2.95 (dd, J = 21.6, 14.8 Hz, 1H), 2.74 – 2.53 (m, 1H), 2.42 – 2.17 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 173.2, 157.2 (d, J = 265.6 Hz), 134.7, 133.5, 133.0, 131.5, 128.91, 128.88, 128.54 (d, J = 7.4 Hz), 128.48, 128.3, 127.9, 127.5, 127.1 (d, J = 2.3 Hz), 126.6, 124.9, 110.00 (d, J = 8.1 Hz), 82.58 (d, J = 2.8 Hz), 61.7, 41.8 (d, J = 24.8 Hz)), 36.2, 30.6, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}FNO_2^+$ 402.1864, Found 402.1864. Specific rotation $[\alpha]_D^{25}$ = -109.22 (c = 0.90, $CHCl_3$). HPLC analysis (IC - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 9.2 min, t_{major} = 15.4 min) indicated 97% ee.



3w

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(furan-2-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

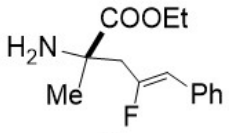
The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:6) to give yellow oil (43 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 1.1 Hz, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.4, 1.7 Hz, 1H), 5.58 (d, J = 39.0 Hz, 1H), 4.31 – 4.13 (m, 2H), 3.27 (dd, J = 20.5, 14.8 Hz, 1H), 3.12 – 2.93 (m, 2H), 2.86 (dd, J = 22.0, 14.8 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.25 – 2.15 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 165.5, 157.0 (d, J = 265.3 Hz), 149.2, 145.2, 133.4 (d, J = 2.5 Hz), 128.5 (d, J = 7.4 Hz), 128.4, 127.0 (d, J = 2.1 Hz), 114.6, 111.8, 109.9 (d, J = 8.0 Hz), 82.5 (d, J = 2.9 Hz), 61.6, 41.5 (d, J = 24.6 Hz), 35.9, 30.0 (d, J = 1.6 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FNO_3^+$ 342.1500, Found 342.1505. Specific rotation $[\alpha]_D^{25}$ = -87.63 (c =1.18, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 12.1 min, t_{major} = 11.3 min) indicated 94% ee.



3x

Ethyl (*S,Z*)-2-(2-fluoro-3-phenylallyl)-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:10) to give yellow oil (47.1 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.32 – 7.24 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.58 (d, *J* = 39.1 Hz, 1H), 4.32 – 4.13 (m, 2H), 3.23 (dd, *J* = 20.5, 14.8 Hz, 1H), 3.17 – 3.00 (m, 2H), 2.89 (dd, *J* = 22.0, 14.8 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.29 – 2.20 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 169.5, 157.1 (d, *J* = 265.0 Hz), 138.4, 133.4 (d, *J* = 2.5 Hz), 130.4, 130.1, 128.5 (d, *J* = 7.5 Hz), 128.4, 127.5, 127.0 (d, *J* = 2.1 Hz), 110.0 (d, *J* = 8.1 Hz), 82.2 (d, *J* = 2.8 Hz), 61.6, 41.4 (d, *J* = 25.0 Hz), 36.7, 30.8 (d, *J* = 1.5 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FNO_2S^+$ 358.1272, Found 358.1277. Specific rotation $[\alpha]_D^{25}$ = -126.22 (*c* = 0.84, $CHCl_3$). HPLC analysis (IG - 3 column, 75:25 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 12.2 min, t_{major} = 9.9 min) indicated 98% ee.

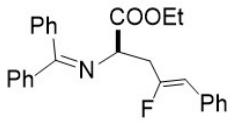


3y

Ethyl (S,Z)-2-amino-4-fluoro-2-methyl-5-phenylpent-4-enoate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:50 to 1:4) to give yellow oil (37.7 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.58 (d, *J* = 39.1 Hz, 1H), 4.30 – 4.10 (m, 1H), 2.87 (dd, *J* = 18.0, 14.4 Hz, 1H), 2.55 (dd, *J* = 26.2, 14.4 Hz, 1H), 1.87 (s, 2H), 1.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 157.0 (d, *J* = 264.9 Hz), 133.2 (d, *J* = 2.9 Hz), 128.6 (d, *J* = 7.5 Hz), 128.5, 127.3 (d, *J* = 2.7 Hz), 110.0 (d, *J* = 8.2 Hz), 61.5, 57.1 (d, *J* = 3.5 Hz), 44.7 (d, *J* = 24.7 Hz), 26.7, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}FNO_2^+$ 252.1394, Found 252.1397. Specific rotation $[\alpha]_D^{25}$ = +21.52 (*c* = 0.79, $CHCl_3$). HPLC analysis (IG - 3 column, 70:30 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 11.9 min, t_{major} = 5.3 min) indicated 91% ee.

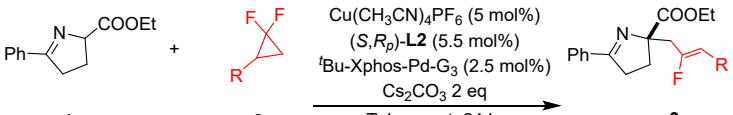


3z

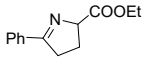
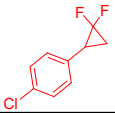
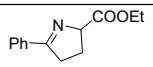
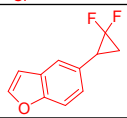
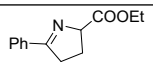
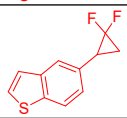
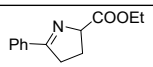
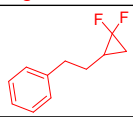
Ethyl (*R,Z*)-2-((diphenylmethylene)amino)-4-fluoro-5-phenylpent-4-enoate

The title compound was prepared according to General Procedure and purified by column chromatography (EtOAc/PE = 1:30 to 1:10) to give yellow oil (54.1 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.35 (m, 6H), 7.34 – 7.27 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.11 (m, 2H), 5.56 (d, *J* = 39.0 Hz, 1H), 4.44 (dd, *J* = 9.0, 4.2 Hz, 1H), 4.31 – 4.10 (m, 2H), 3.10 – 3.00 (m, 1H), 2.98 – 2.86 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 171.2, 157.0 (d, *J* = 264.9 Hz), 139.5, 136.0, 133.5 (d, *J* = 2.6 Hz), 132.4, 130.5, 130.1, 128.9, 128.8, 128.5, 128.4, 128.0 (d, *J* = 8.9 Hz), 126.9 (d, *J* = 2.0 Hz), 108.74 (d, *J* = 7.9 Hz), 62.8, 61.3, 37.5 (d, *J* = 25.9 Hz), 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}FNO_2^+$ 402.1864, Found 402.1870. Specific rotation $[\alpha]_D^{25}$ = +62.19(*c* = 0.41, $CHCl_3$). HPLC analysis (OX - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.8 min, t_{major} = 5.4 min) indicated 56% ee.

Table S1. Unsuccessful examples of preparation of **3**[a]

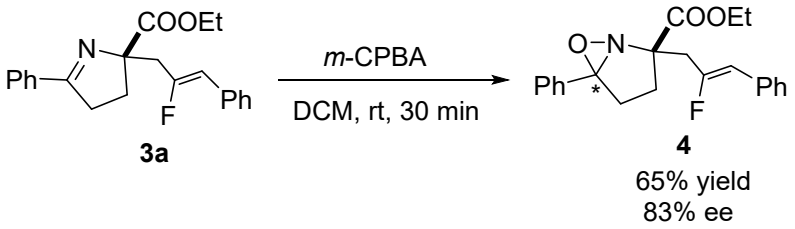


1a **2** **3**

Entry	1	2	3
1			10%
2			nd
3			nd
4			nd

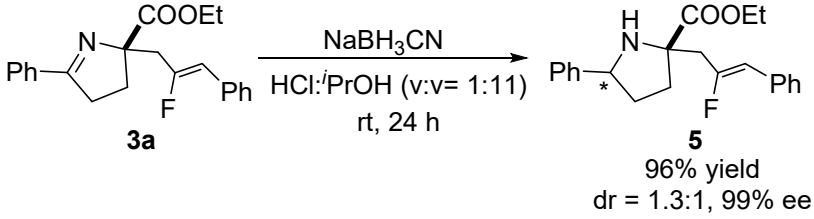
[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol%), (S,R_p)-**L2** (5.5 mol%), ^{t}Bu-Xphos-Pd-G_3 (2.5 mol%) and Cs_2CO_3 (0.4 mmol) were stirred in toluene (2.0 mL) under N_2 at room temperature for 24 h.

III. General Procedures for the Synthetic Transformations



Ethyl (2*S*)-2-((*Z*)-2-fluoro-3-phenylallyl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (**4**)

To a solution of 3a (70.3 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added *m*-CPBA (85% purity) (101.6 mg, 0.25 mmol, 2.5 equiv) at 25 ℃. The solution was stirred for about 30 min until complete consumption of the substrate 3a (monitored by TLC). The reaction mixture was concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to afford **4** as a white solid (47.8 mg, 65% yield). m.p. 57.8 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.49 – 7.45 (m, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 5.71 (d, *J* = 38.9 Hz, 1H), 4.26 – 4.19 (m, 2H), 3.20 (dd, *J* = 19.4, 14.8 Hz, 1H), 2.95 (dd, *J* = 20.6, 14.8 Hz, 1H), 2.72 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.25 (dd, *J* = 13.2, 8.2 Hz, 1H), 1.90 – 1.82 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 156.5 (d, *J* = 265.0 Hz), 134.5, 133.4 (d, *J* = 2.7 Hz), 129.5, 128.6 (d, *J* = 7.3 Hz), 128.40, 128.38, 127.1, 127.0 (d, *J* = 2.1 Hz), 109.5 (d, *J* = 8.0 Hz), 88.8, 76.1 (d, *J* = 2.2 Hz), 61.9, 38.9 (d, *J* = 25.9 Hz), 29.3, 14.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}FNO_3^+$ 368.1656, Found 368.1659. Specific rotation $[\alpha]_D^{25}$ = -13.78 (*c* = 0.37, $CHCl_3$). HPLC analysis (IG - 3 column, 95:5 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 ºC, λ = 254 nm, t_{minor} = 8.2min, t_{major} = 8.8 min) indicated 83% ee.

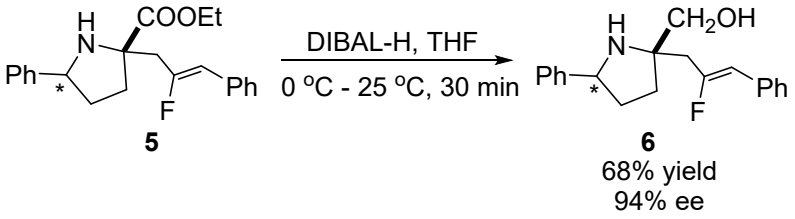


Ethyl (2*S*)-2-((*Z*)-2-fluoro-3-phenylallyl)-5-phenylpyrrolidine-2-carboxylate (**5**&**5'**)

To a flame-dried pressure tube equipped with a magnetic stir bar was added the substrate of **3a** (24.1 mg, 0.3 mmol, 1 equiv), 3.6 mL of conc. HCl/^{i}PrOH (v/v = 1:11, pH = 1-3) and $NaBH_3CN$ (94.3 mg, 1.5 mmol, 5 equiv) successively. The pressure tube was then sealed and stirred at room temperature for 24 h. After completion, the reaction mixtures was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was finally purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the both diastereomers 5 and 5'. Isomer 5: Colorless oil (57.2 mg, 54% yield). ^{1}H NMR (500

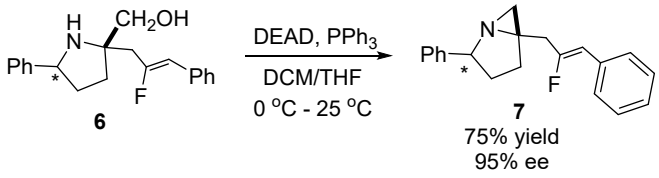
MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.37 – 7.28 (m, 4H), 7.27 – 7.19 (m, 2H), 5.59 (d, *J* = 39.2 Hz, 1H), 4.35 (dd, *J* = 9.5, 6.1 Hz, 1H), 4.30 – 4.20 (m, 2H), 2.93 (dd, *J* = 18.5, 14.6 Hz, 1H), 2.82 – 2.60 (m, 2H), 2.58 – 2.49 (m, 1H), 2.25 – 2.16 (m, 1H), 2.07 – 2.01 (m, 1H), 1.81 – 1.71 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 157.6 (d, *J* = 264.9 Hz), 143.7, 133.4 (d, *J* = 1.9 Hz), 128.6, 128.5, 128.4, 127.2, 127.04 (d, *J* = 1.4 Hz), 126.8, 109.3 (d, *J* = 8.1 Hz), 68.7 (d, *J* = 2.3 Hz), 63.1, 61.5, 43.5 (d, *J* = 24.4 Hz), 36.7, 35.1, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}FNO_2^+$ 354.1864, Found 354.1866. Specific rotation $[\alpha]_D^{25}$ = +35.06 (*c* = 0.45, $CHCl_3$). HPLC analysis (IG - 3 column, 90:10 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 5.5min, t_{major} = 5.8 min) indicated 99% ee.

Isomer 5': Colorless oil (44.5 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.15 – 7.07 (m, 2H), 5.52 (d, *J* = 39.0 Hz, 1H), 4.23 (t, *J* = 7.7 Hz, 1H), 4.18 – 4.08 (m, 2H), 2.88 (dd, *J* = 18.4, 14.3 Hz, 1H), 2.62 (dd, *J* = 24.8, 14.3 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.11 – 2.02 (m, 1H), 2.00 – 1.90 (m, 1H), 1.69 – 1.59 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 157.8 (d, *J* = 265.0 Hz), 144.9, 133.5 (d, *J* = 2.4 Hz), 128.5 (d, *J* = 7.4 Hz), 128.4, 128.3, 127.0 (d, *J* = 2.0 Hz), 126.9, 126.6, 109.2 (d, *J* = 8.1 Hz), 68.1 (d, *J* = 2.8 Hz), 61.6, 61.5, 44.4 (d, *J* = 24.5 Hz), 35.1, 34.2, 14.3.



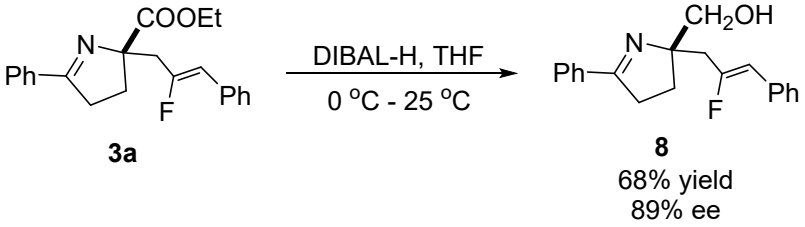
((2*S*)-2-((*Z*)-2-fluoro-3-phenylallyl)-5-phenylpyrrolidin-2-yl)methanol (**6**)

5 (70.7 mg, 0.2 mmol, 1.0 equiv) was dissolved in THF (2mL) and cooled to 0 ℃, then 0.4 mL of DABAL-H in toluene (1.5 M, 0.6mmol, 3.0 equiv) was added. The solution was stirred for about 30min at 25 ℃ until complete consumption of the substrate **5** (monitored by TLC). The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **6** as a white solid (42.3 mg, 68%). m.p.77.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.29 (q, *J* = 7.4 Hz, 4H), 7.26 – 7.22 (m, 2H), 5.59 (d, *J* = 39.2 Hz, 1H), 4.42 (dd, *J* = 10.0, 6.2 Hz, 1H), 3.49 (dd, *J* = 34.6, 10.5 Hz, 2H), 2.61 (d, *J* = 23.7 Hz, 2H), 2.41 – 2.19 (m, 3H), 2.04 – 1.94 (m, 2H), 1.84 – 1.74 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1 (d, *J* = 264.6 Hz), 144.2, 133.2 (d, *J* = 2.4 Hz), 128.54, 128.49 (d, *J* = 7.5 Hz), 128.42, 127.2 (d, *J* = 2.2 Hz), 127.1, 126.4, 109.8 (d, *J* = 8.7 Hz), 67.9 (d, *J* = 1.7 Hz), 64.3 (d, *J* = 3.6 Hz), 61.8, 41.2 (d, *J* = 23.9 Hz), 35.4 33.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}FNO^+$ 312.1758, Found 312.1759. Specific rotation $[\alpha]_D^{25}$ = +49.44 (*c* = 0.36, $CHCl_3$). HPLC analysis (IG - 3 column, 70:30 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 5.5min, t_{major} = 5.8 min) indicated 94% ee.



(5*S*)-5-((*Z*)-2-fluoro-3-phenylallyl)-2-phenyl-1-azabicyclo[3.1.0]hexane (**7**)

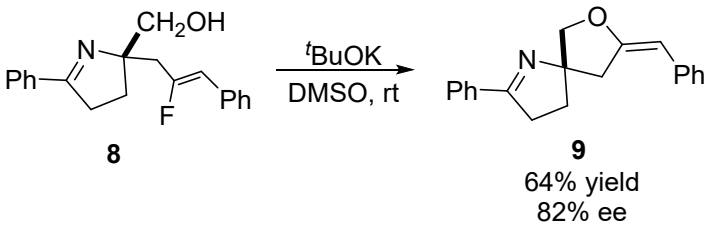
Under argon atmosphere, PPh_3 (52.5 mg, 0.2 mmol, 2.0 equiv) was dissolved in dry DCM (2 mL) and cooled to 0 ℃, then DEAD (35 μL, 0.22 mmol, 2.2 equiv) in THF (0.75 mL) was added. The solution was stirred for 30 minutes at 0 ℃, followed by addition of **6** (25.9 mg, 0.1 mmol, 1.0 equiv) in THF (0.75 mL). The final solution was stirred at 25 ℃ for about 12 hours until complete consumption of the substrate **6** (monitored by TLC). The reaction mixture was concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **7** as a white solid (22 mg, 75%). m.p.73.9 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.20 – 7.12 (m, 2H), 5.54 (d, *J* = 39.1 Hz, 1H), 4.43 (dd, *J* = 11.0, 6.9 Hz, 1H), 2.73 (dd, *J* = 19.5, 15.2 Hz, 1H), 2.49 (dd, *J* = 20.6, 15.1 Hz, 1H), 2.28 (dd, *J* = 12.9, 7.9 Hz, 1H), 2.13 – 1.94 (m, 2H), 1.59 – 1.49 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4 (d, *J* = 266.0 Hz), 141.5, 133.6 (d, *J* = 2.5 Hz), 128.5, 128.4, 128.3, 127.0 (d, *J* = 2.25 Hz), 126.83, 126.76, 107.8 (d, *J* = 7.9 Hz), 65.8, 47.8, 39.9 (d, *J* = 25.4 Hz), 30.4, 29.2, 27.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FN^+$ 294.1653, Found 294.1651. Specific rotation $[\alpha]_D^{25}$ = -24.11 (*c* = 0.51, $CHCl_3$). HPLC analysis (IG - 3 column, 85:15 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 5.4 min, t_{major} = 5.9 min) indicated 95% ee.



(*S*,*Z*)-(2-(2-fluoro-3-phenylallyl)-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methanol (**8**)

3a (70.3 mg, 0.2 mmol, 1.0 equiv) was dissolved in THF (2mL) and cooled to 0 ℃, then 0.4 mL of DABAL-H in toluene (1.5 M, 0.6mmol, 3.0 equiv) was added. The solution was stirred for about 10 min at 25 ℃ until complete consumption of the substrate **3a** (monitored by TLC). The reaction mixture was concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **8** as a yellow oil (42.1 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.21 – 7.17 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 5.47 (d, *J* = 39.0 Hz, 1H), 3.90 (d, *J* = 11.5 Hz, 1H), 3.55 (d, *J* = 11.5 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.71 – 2.52 (m, 2H), 2.10 – 1.94 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 159.0 (d, *J* = 265.0 Hz), 133.7, 133.6 (d, *J* = 2.4 Hz), 130.8, 128.383 (d, *J* = 7.3 Hz), 128.380, 128.3, 128.0, 126.9 (d, *J* = 2.0 Hz), 109.5 (d, *J* = 8.5 Hz), 80.2 (d, *J* =

3.6 Hz), 68.8, 40.3 (d, J = 24.5 Hz), 36.2, 27.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FNO^+$ 310.1602, Found 310.1603. Specific rotation $[\alpha]_D^{25}$ = +115.02 (c = 0.36, $CHCl_3$). HPLC analysis (IG - 3 column, 80:20 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 6.3min, t_{major} = 7.3 min) indicated 89% ee.



(*S*,*E*)-8-benzylidene-2-phenyl-7-oxa-1-azaspiro[4.4]non-1-ene (**9**)

To a solution of **8** (31.0 mg, 0.1 mmol, 1.0 equiv) in DMSO (2 mL) was added ^{t}BuOK (16.8 mg, 0.15 mmol, 1.5 equiv) at 25 ℃. The solution was stirred for about 30 min until complete consumption of the substrate **8** (monitored by TLC). The final solution was directly purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to afford **9** as a white solid (18.5 mg, 64%). m.p.114.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.29 (t, J = 7.4 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.29 (s, 1H), 4.48 (d, J = 8.5 Hz, 1H), 4.20 (d, J = 8.5 Hz, 1H), 3.17 (dd, J = 15.6, 1.3 Hz, 1H), 3.13 – 3.06 (m, 2H), 2.75 (d, J = 15.5 Hz, 1H), 2.23 – 2.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 157.0, 136.8, 134.1, 130.9, 128.5, 128.2, 127.9, 127.3, 124.8, 98.2, 80.5, 80.2, 44.5, 35.1, 32.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO^+$ 290.1539, Found 290.1541. Specific rotation $[\alpha]_D^{25}$ = -38.18 (c = 0.33, $CHCl_3$). HPLC analysis (IG - 3 column, 95:5 hexanes/2-propanol, flow rate 1.0 mL/min, T = 25 °C, λ = 254 nm, t_{minor} = 8.6min, t_{major} = 9.3 min) indicated 82% ee.

IV. X-ray Crystallographic Data of 3v

Single crystals of compound **3v** was grown from slow evaporation of a mixed solvent of dichloromethane and hexane at rt. The structure is shown in Figure S1 and X-ray diffraction data are shown in Table S2. CIF file can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 2346401.

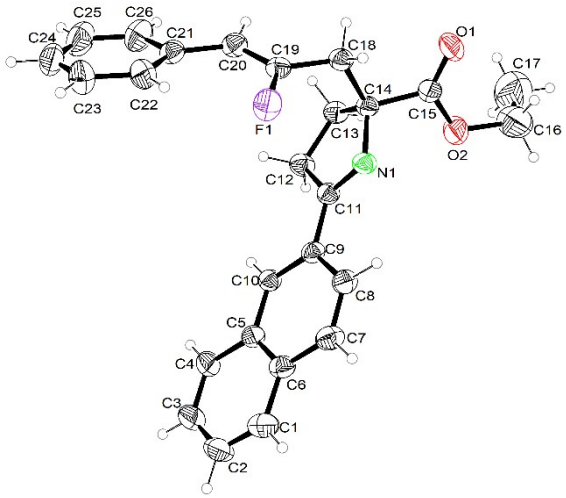


Figure S1. An ORTEP diagram of **3v** showing 30% probability thermal ellipsoids.

Table S2 Crystal data and structure refinement for **3v**

Identification code	CCDC#2346401
Empirical formula	C26H24FNO2
Formula weight	401.46
Temperature/K	273.15
Crystal system	orthorhombic
Space group	P212121
a/Å	5.8725(2)
b/Å	17.5018(6)
c/Å	20.6518(7)
α/°	90
β/°	90
γ/°	90
Volume/Å3	2122.58(13)
Z	4
ρcalcg/cm3	1.256
μ/mm-1	0.684
F(000)	848.0
Crystal size/mm3	0.22 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.62 to 133.152
Index ranges	-6 ≤ h ≤ 6, -18 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	20585

Independent reflections	3719 [Rint = 0.0442, Rsigma = 0.0340]
Data/restraints/parameters	3719/1/272
Goodness-of-fit on F2	1.069
Final R indexes [I>=2σ (I)]	R1 = 0.0639, wR2 = 0.1819
Final R indexes [all data]	R1 = 0.0663, wR2 = 0.1857
Largest diff. peak/hole / e Å-3	0.81/-0.39
Flack parameter	0.08(6)

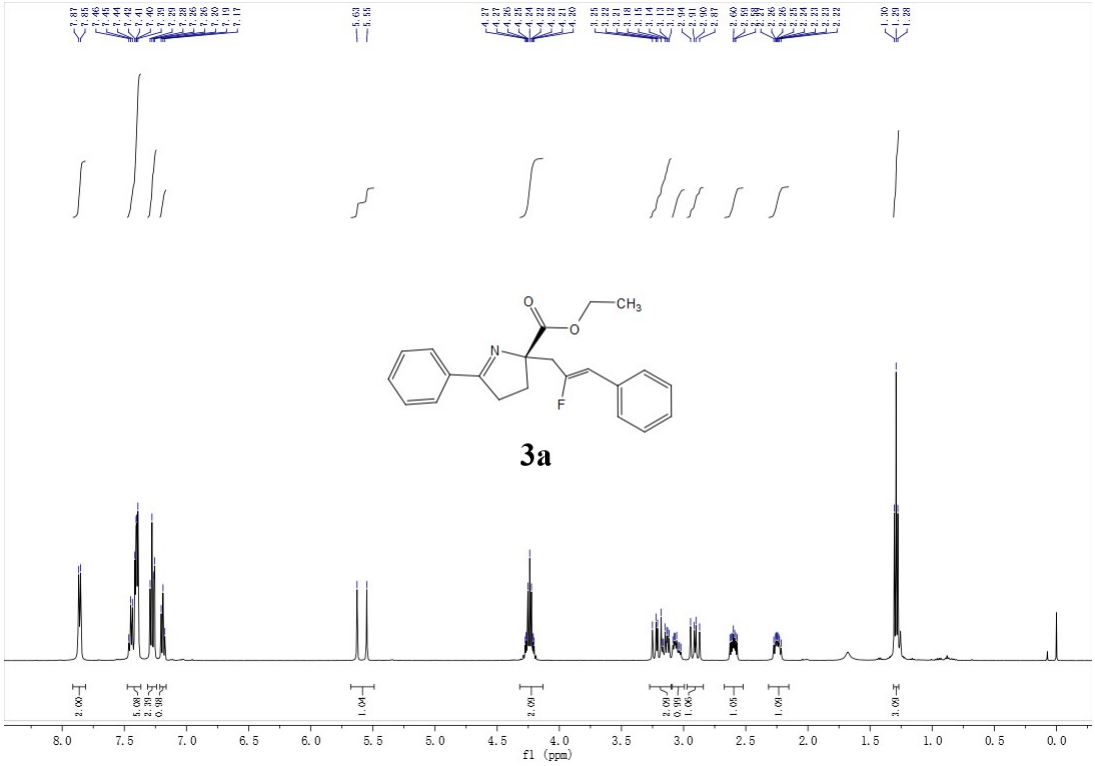
V. References

[1] (a) Y. Peng, X. Huo, Y. Luo, L. Wu and W. Zhang, *Angew. Chem. Int. Ed.* **2021**, *60*, 24941-24949. (b) L. Zhao, G. Li, R. He, P. Liu, F. Wang, X. Huo, M. Zhao and W. Zhang, *Org. Biomol. Chem.* **2021**, *19*, 1955-1959. (c) Z. Chen, H. Lin, J. Han, D. Fang, M. Wang and J. Liao, *Org. Lett.* **2021**, *23*, 9146-9150.

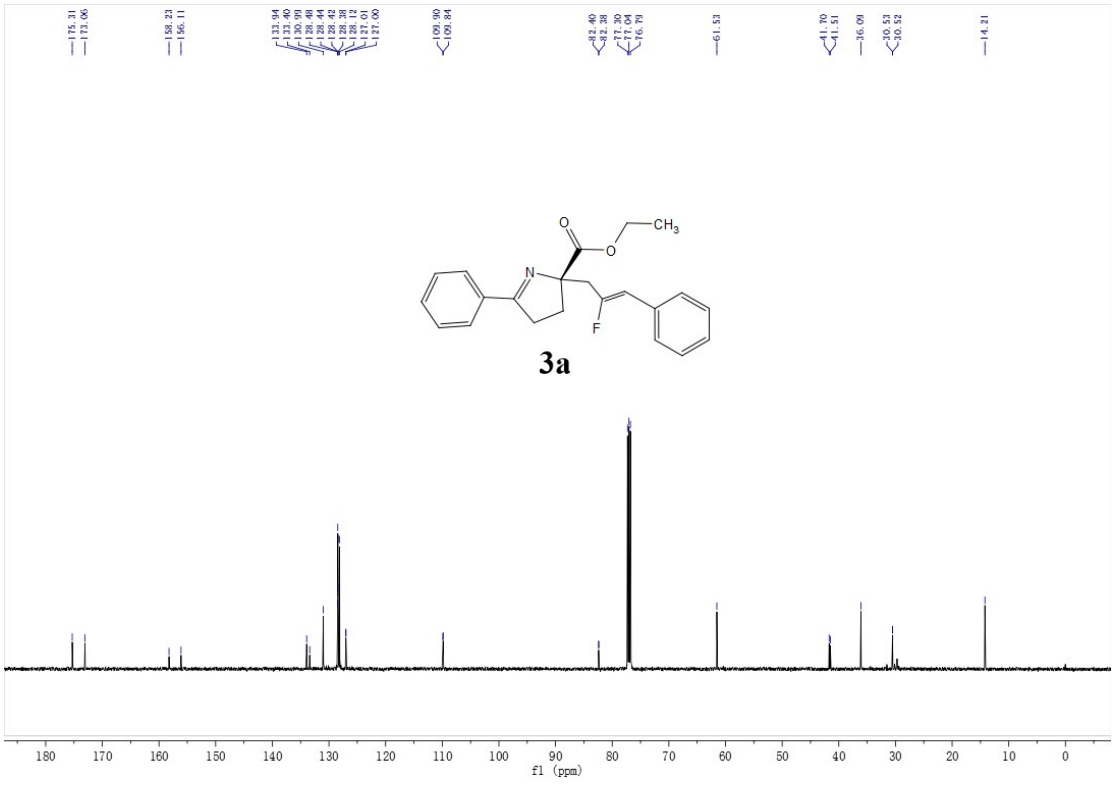
[2] (a) F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash and G. A. Olah, *Angew. Chem. Int. Ed.* **2011**, 50, 7153-7157. (b)) J. Xu, E.-A. Ahmed, B. Xiao, Q.-Q. Lu, Y.-L. Wang, C.-G. Yu and Y. Fu, *Angew. Chem. Int. Ed.* **2015**, *54*, 8231-8235. (c) L. Lv and C.-J. Li, *Angew. Chem. Int. Ed.* 2021, 60, 13098-13104. (d) L. Lv, H. Qian, Y. Ma, S. Huang, X. Yan and Z. Li, *Chem. Sci.* **2021**, *12*, 15511-15518.

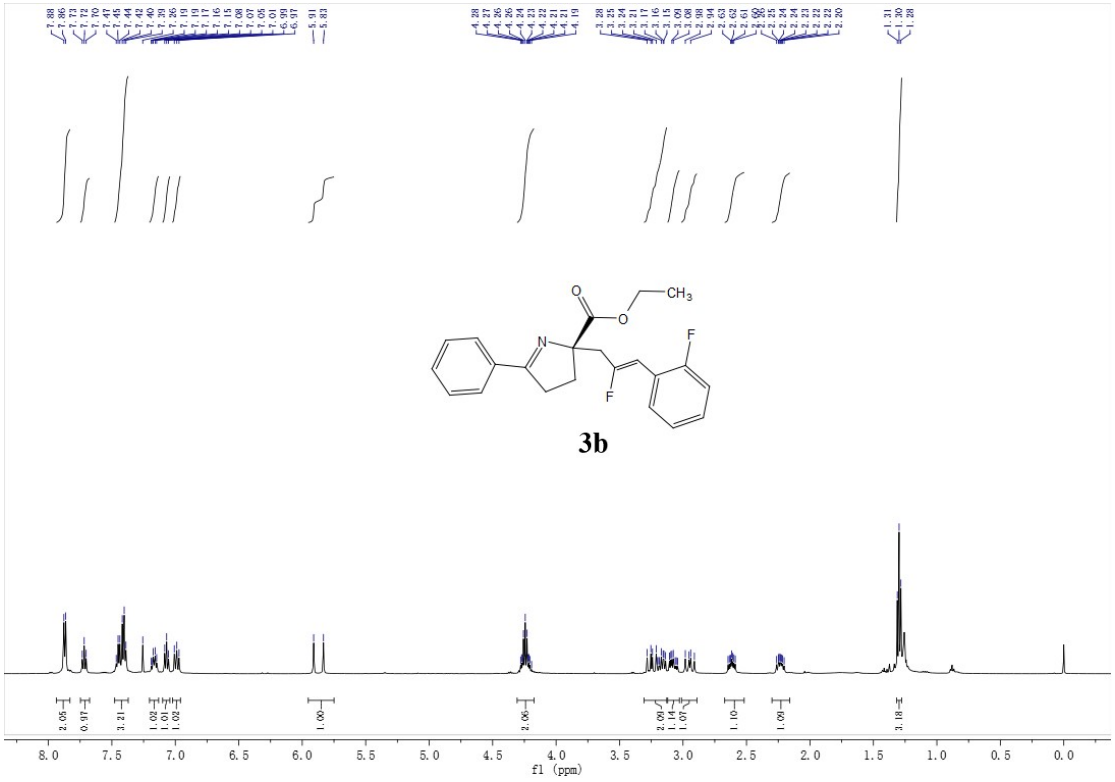
VI. NMR Spectra of Products

500 MHz, Chloroform-*d*



126 MHz, Chloroform-*d*

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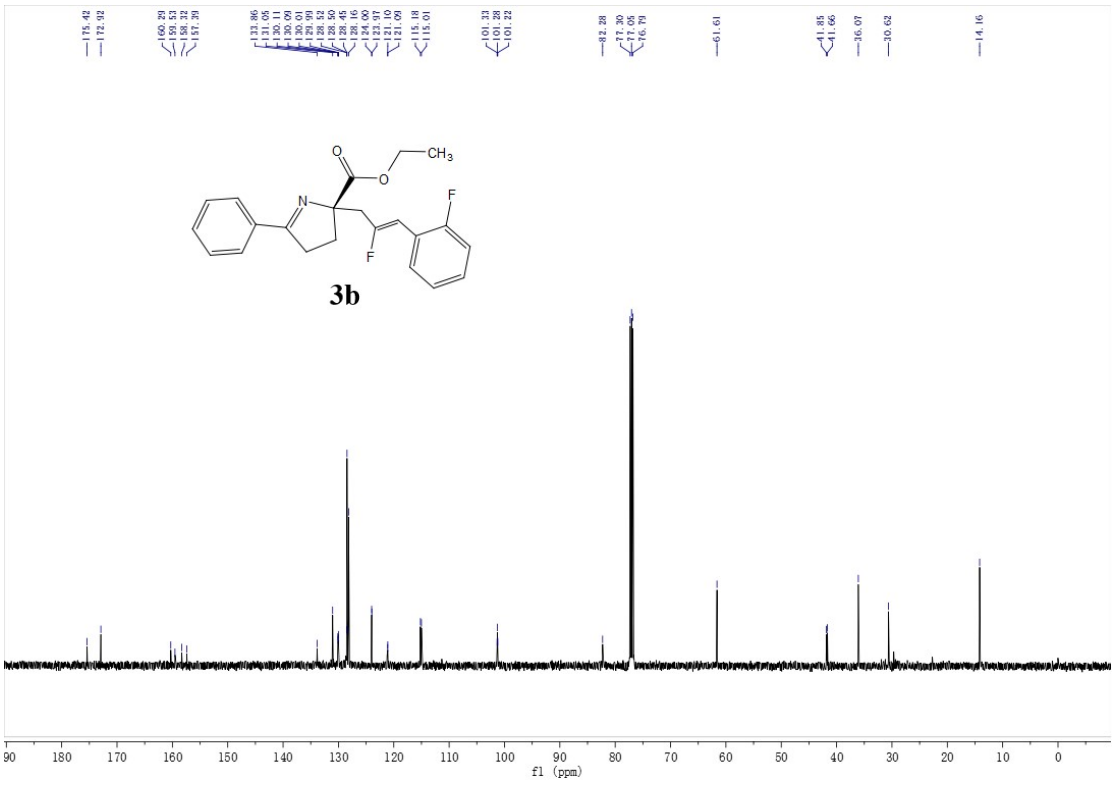
N
F
F
3b
f1 (ppm)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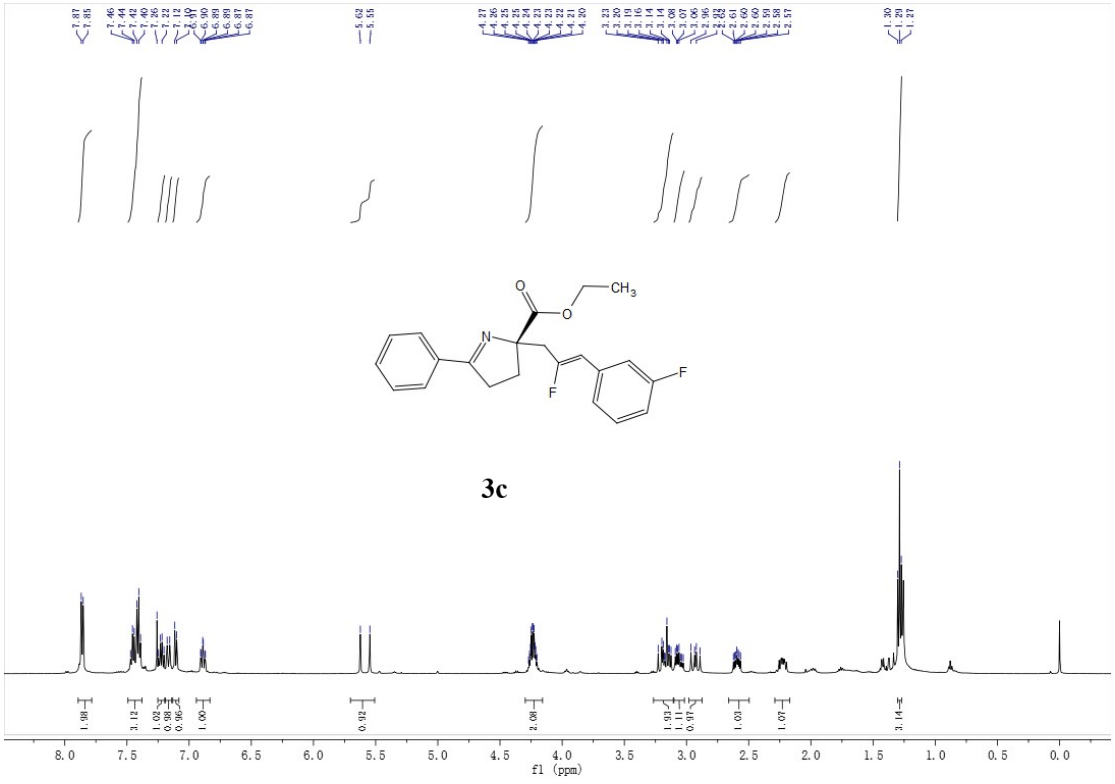
O
CH3
N
F
F
3b
f1 (ppm)



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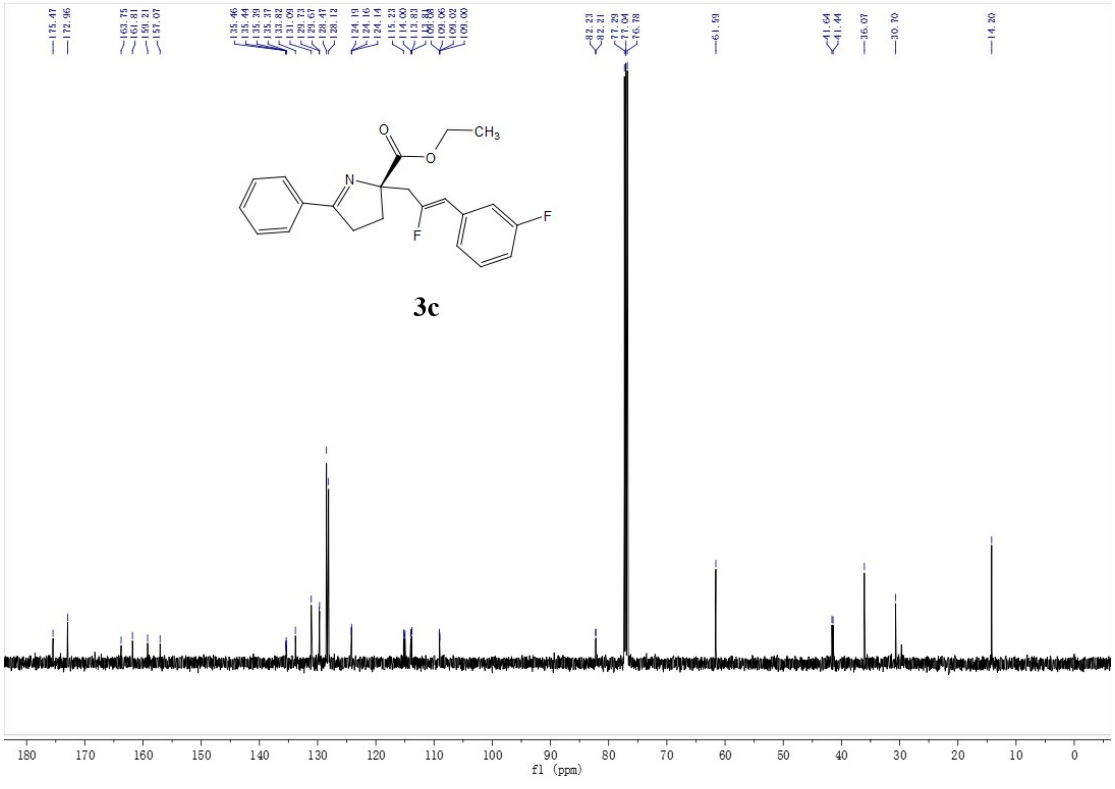

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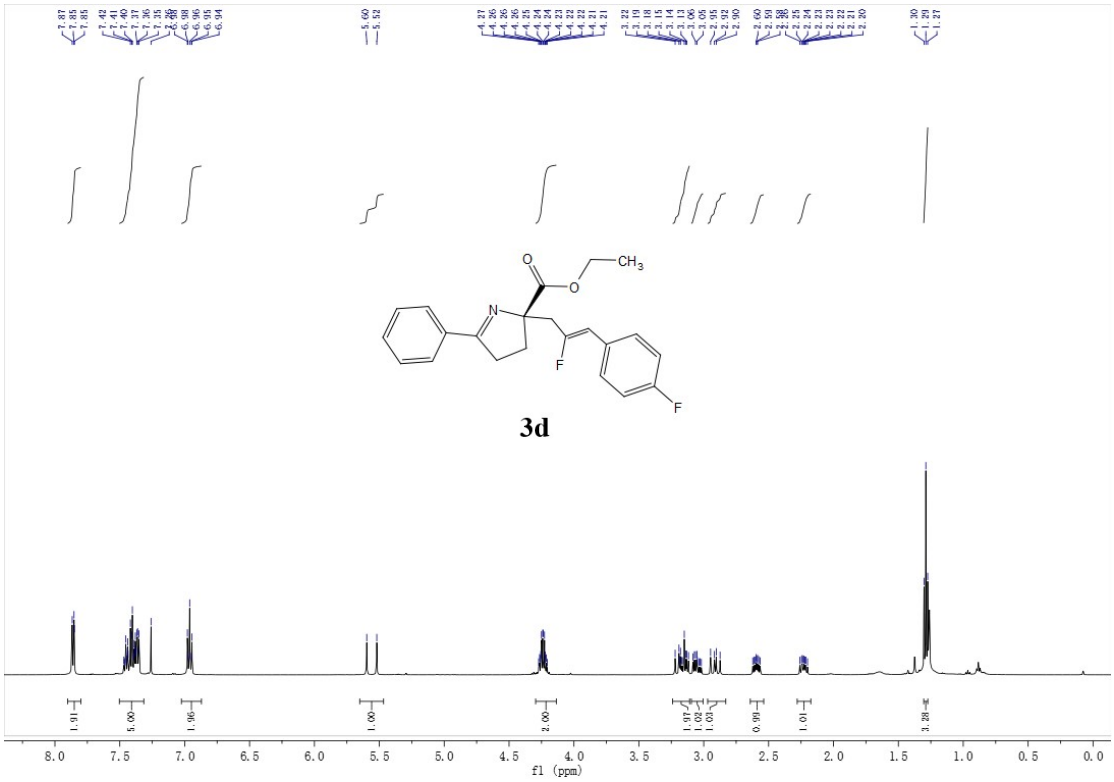

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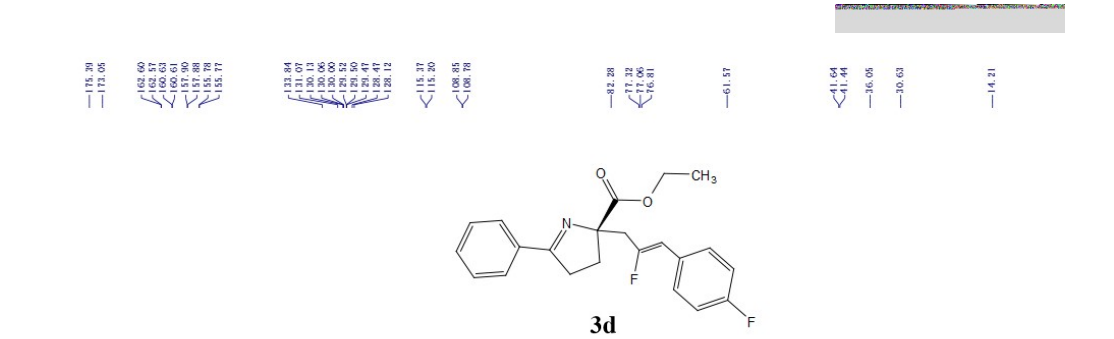

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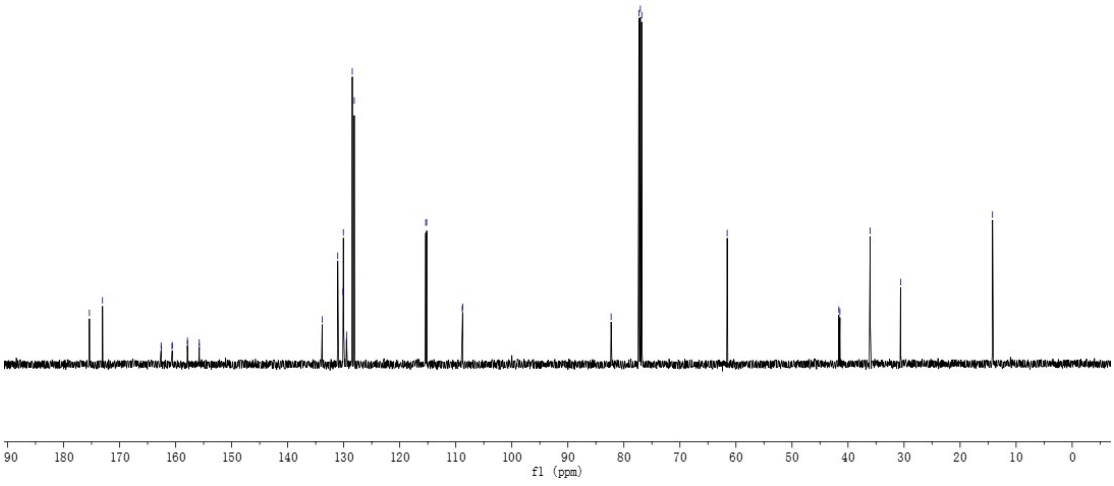

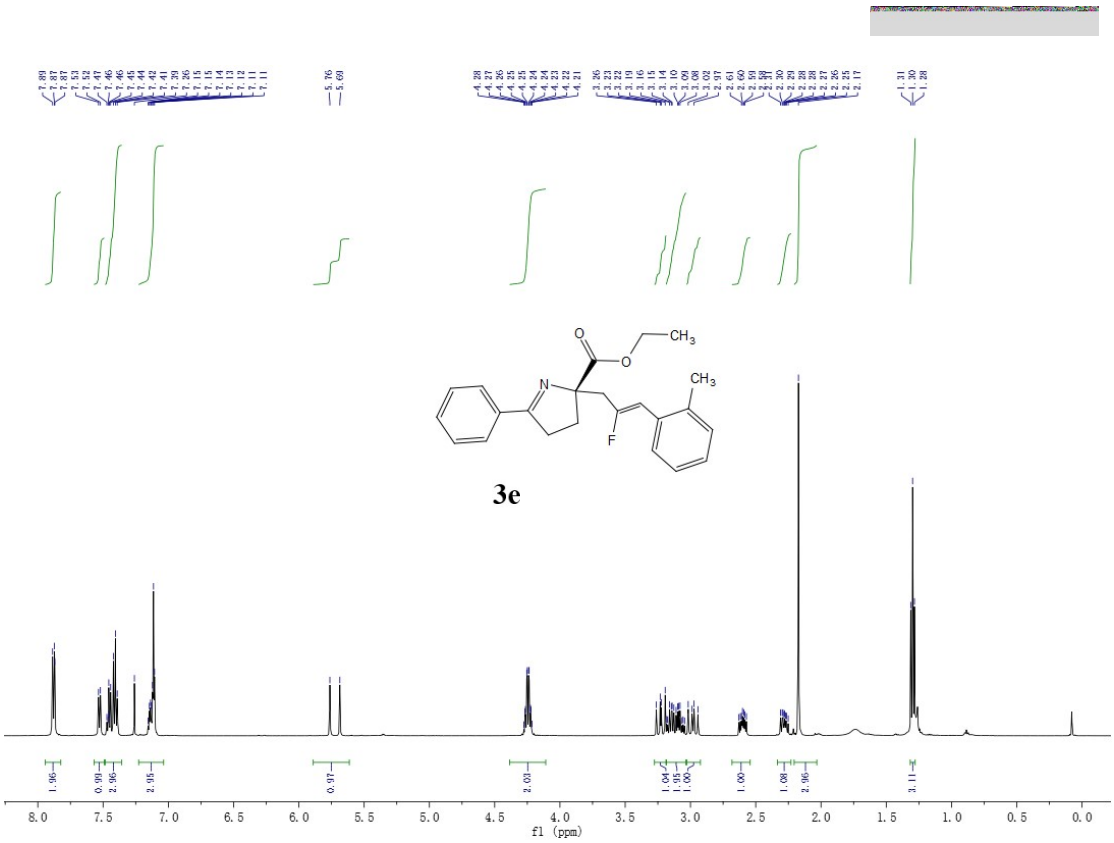
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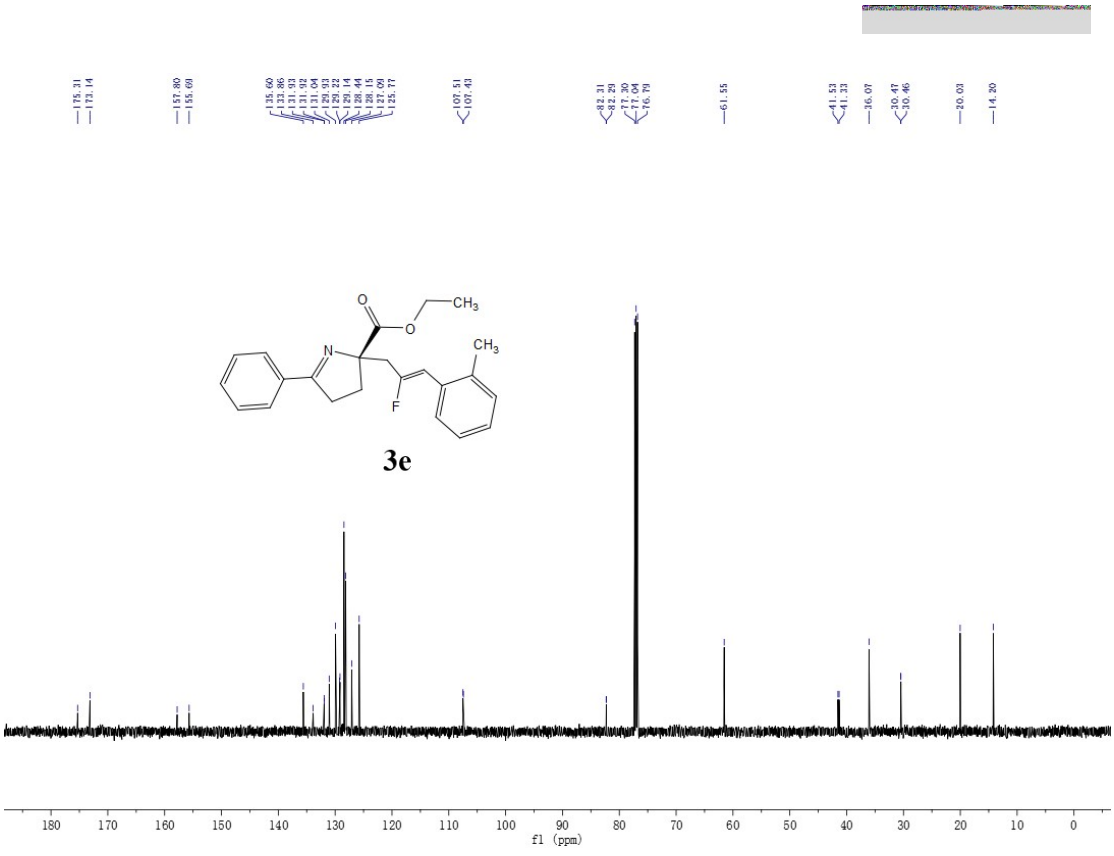
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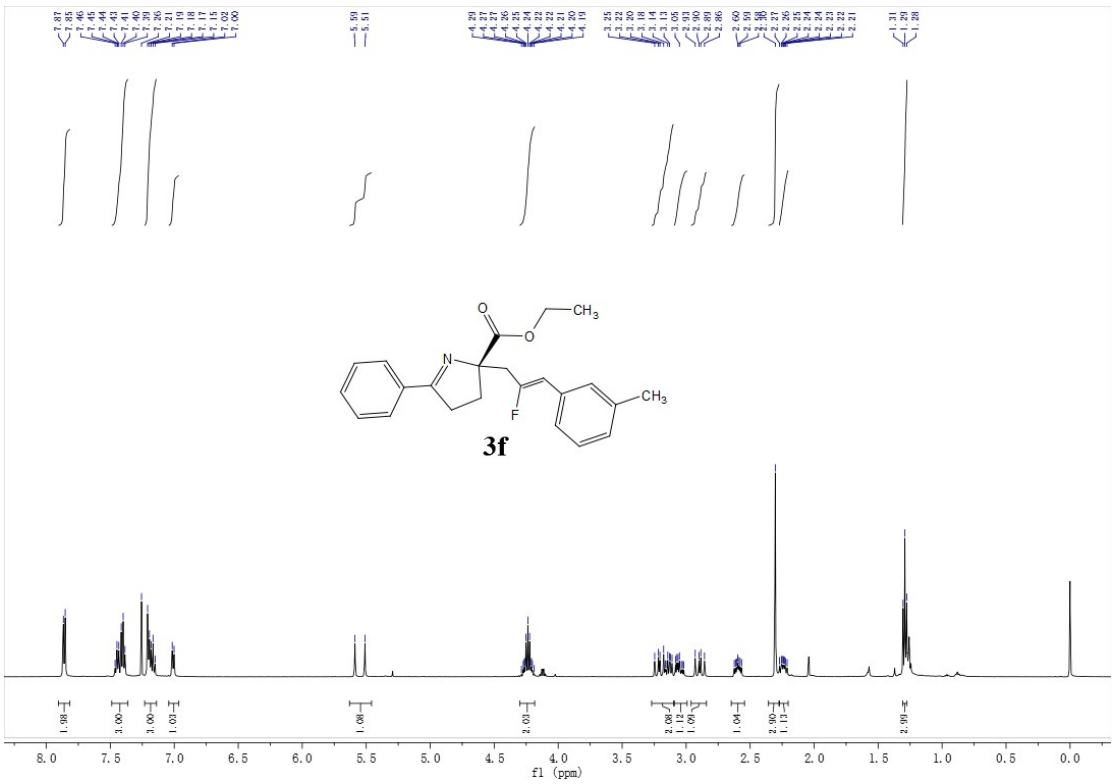
f1 (ppm)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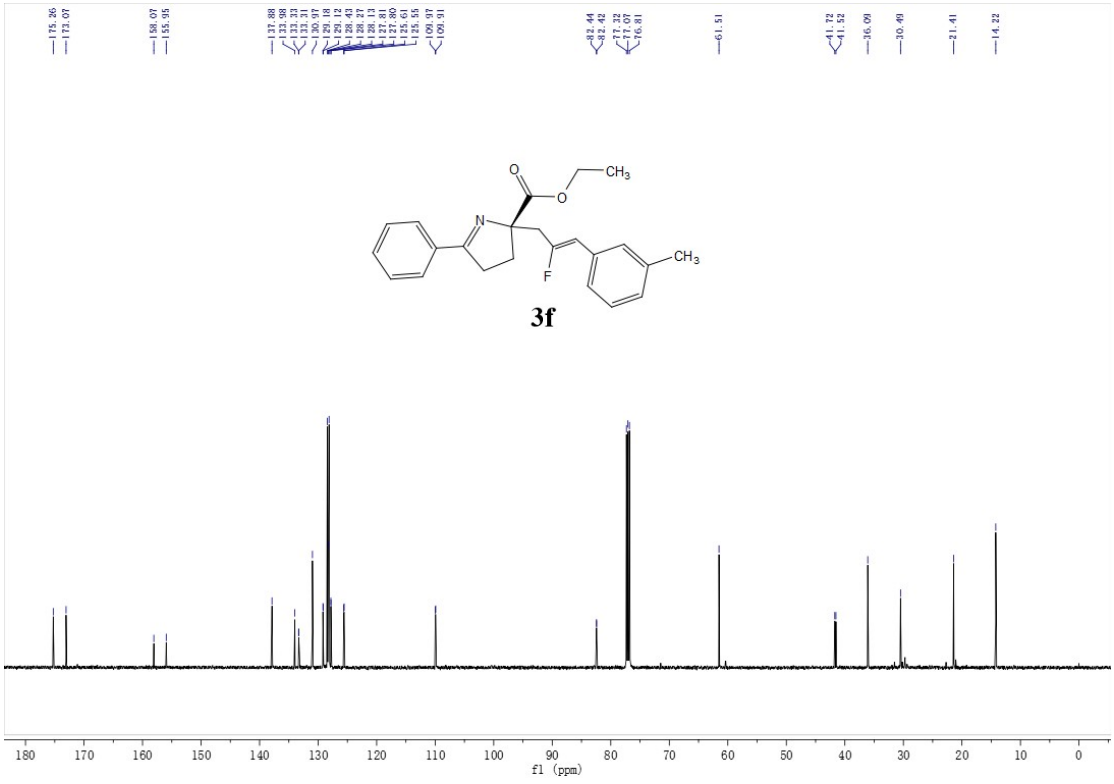
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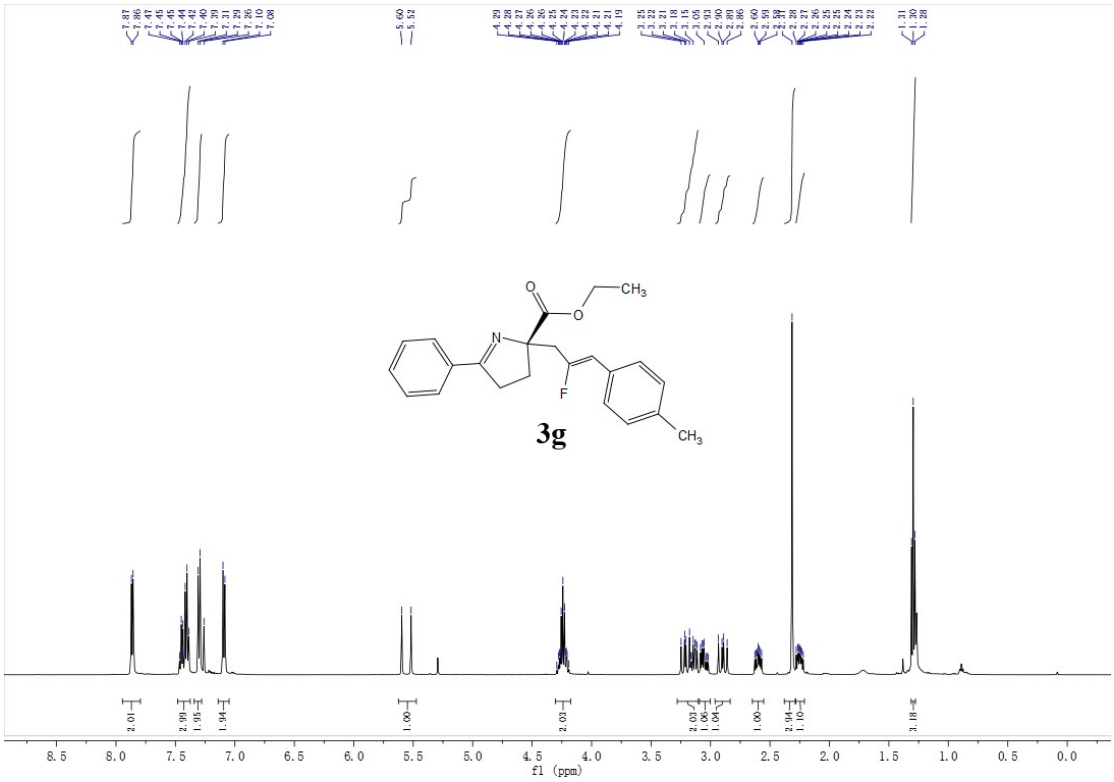
f1 (ppm)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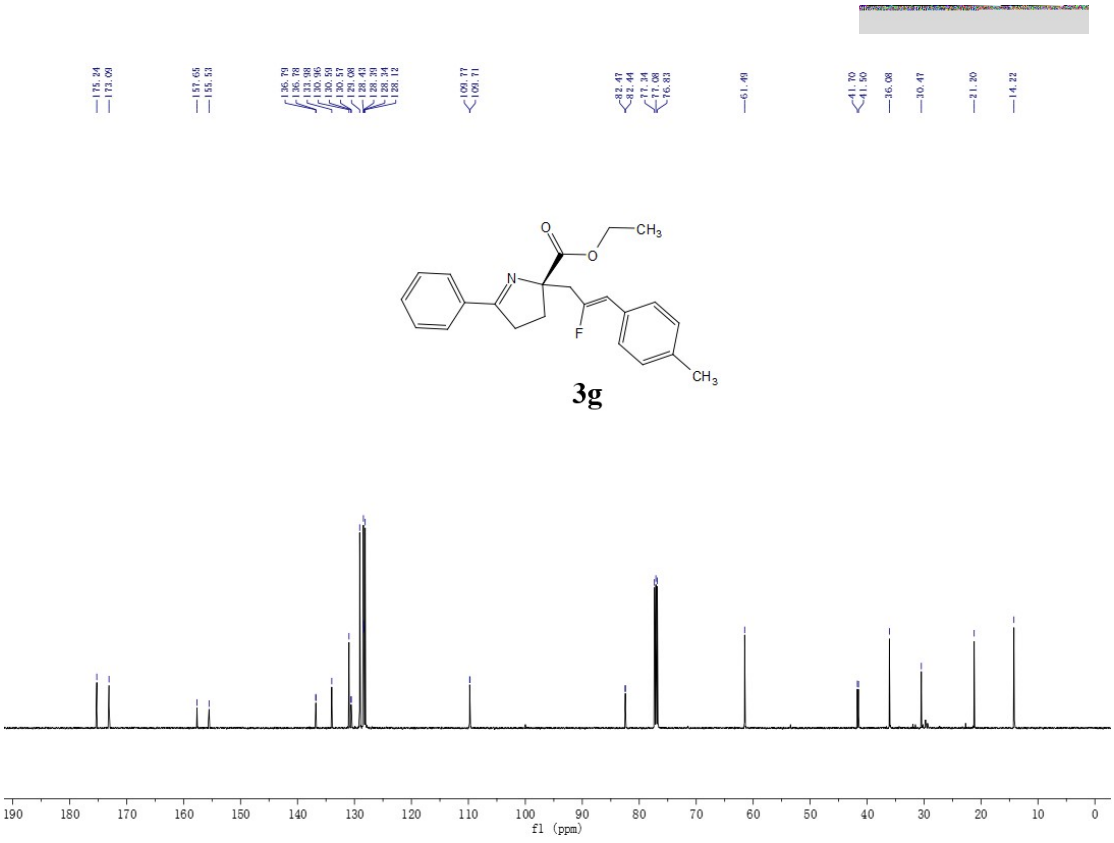
O
CH3
N
F
CH3
3g
f1 (ppm)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CH3
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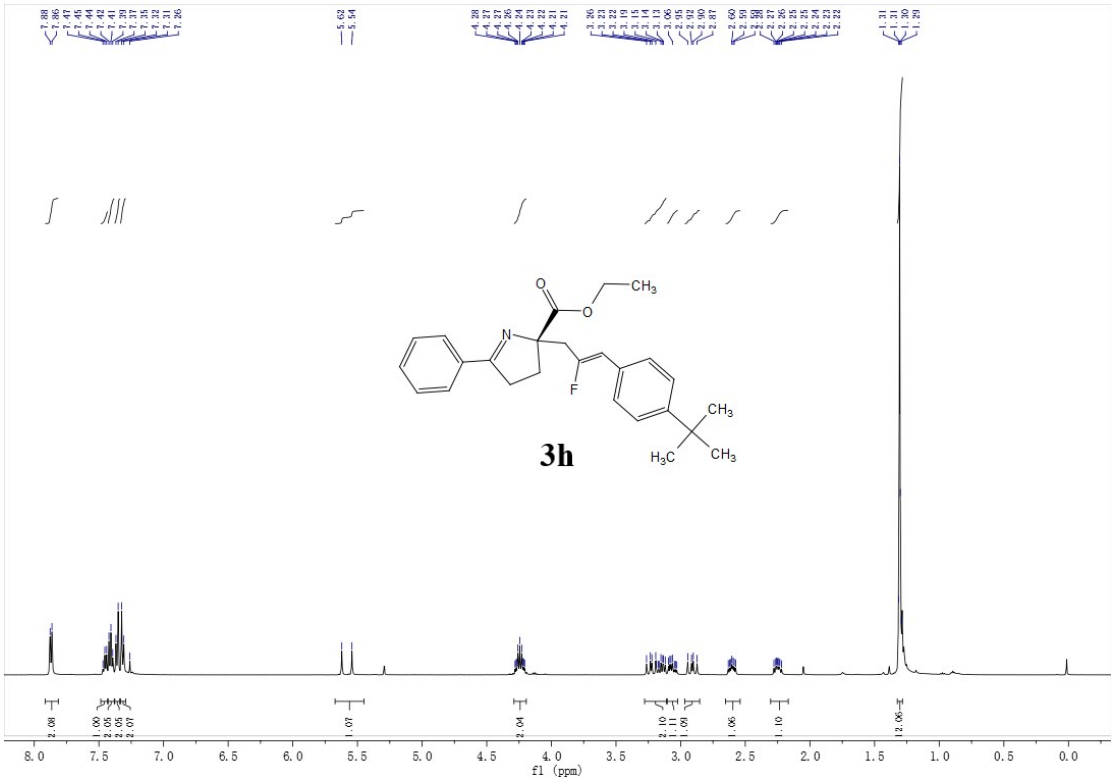
f1 (ppm)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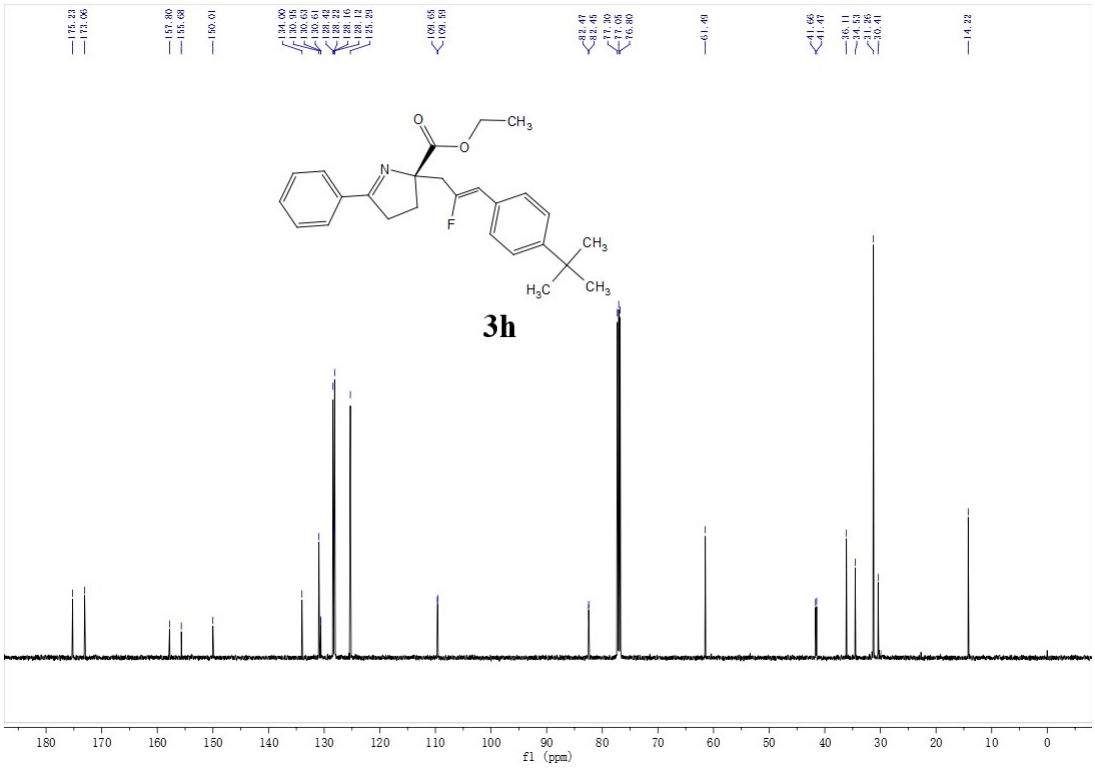
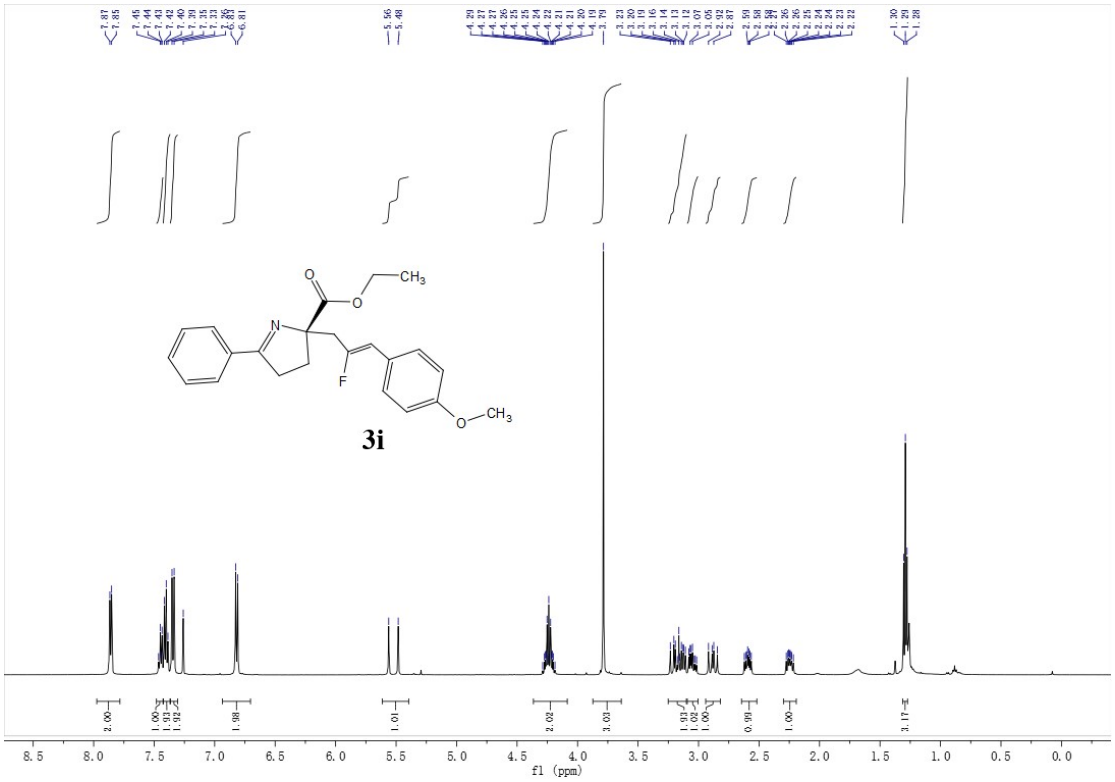
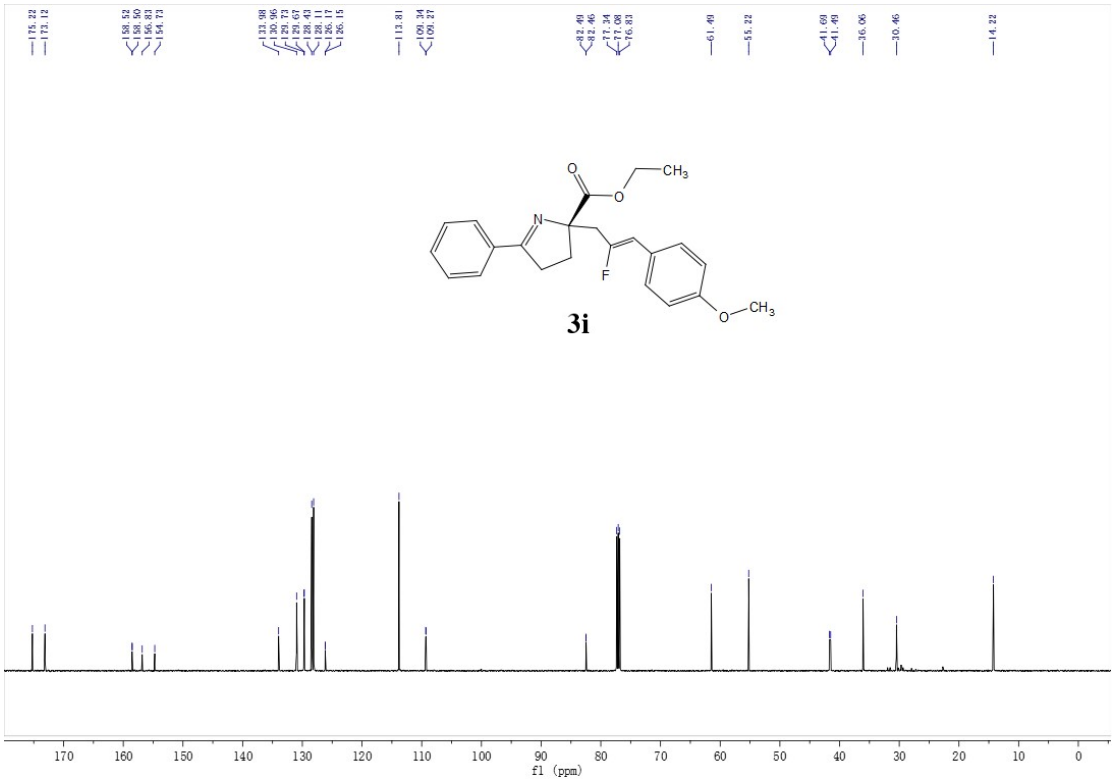
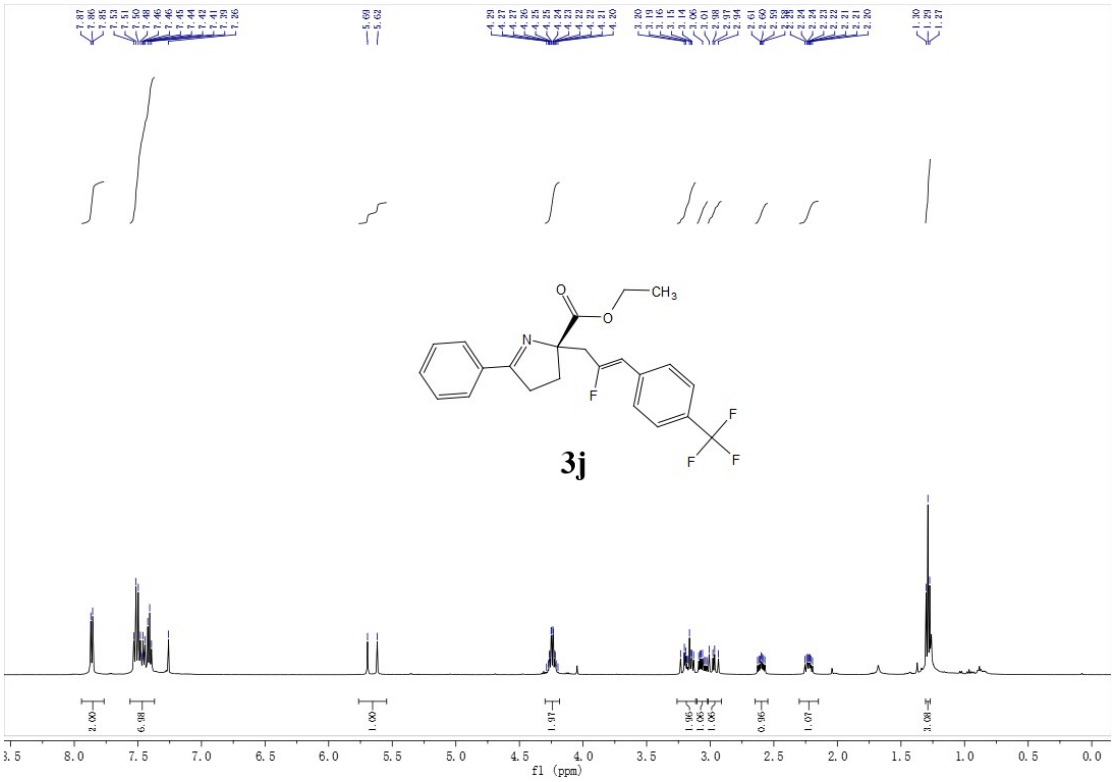
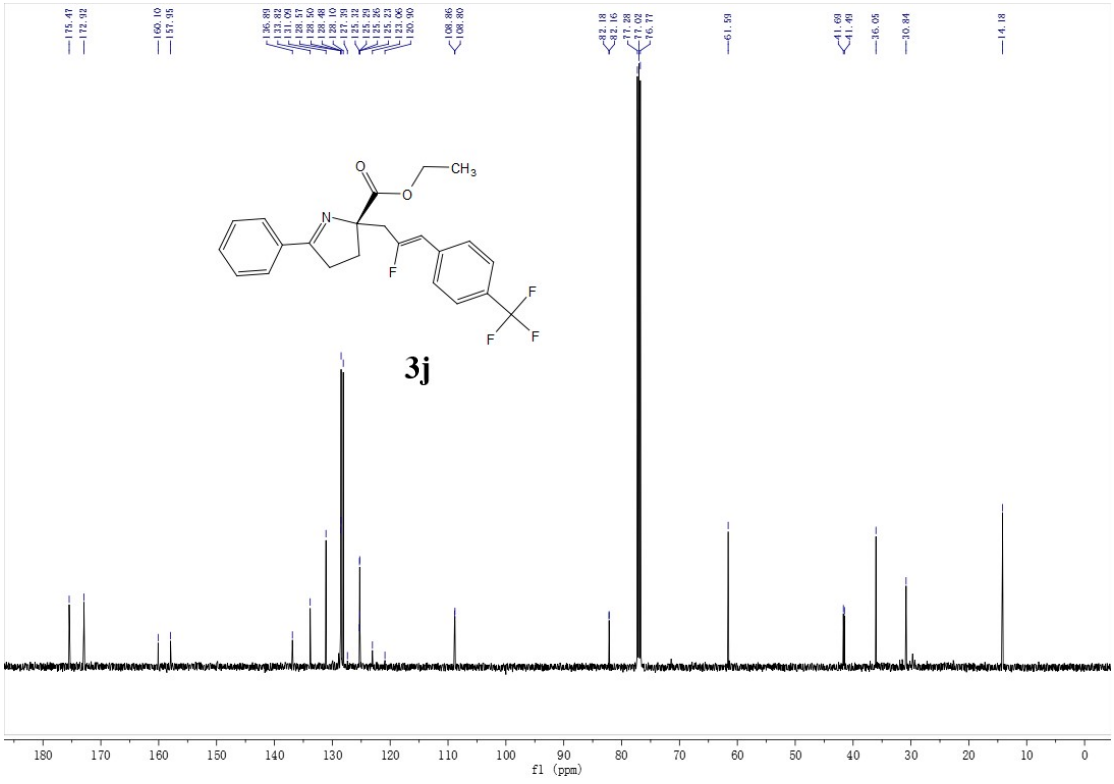
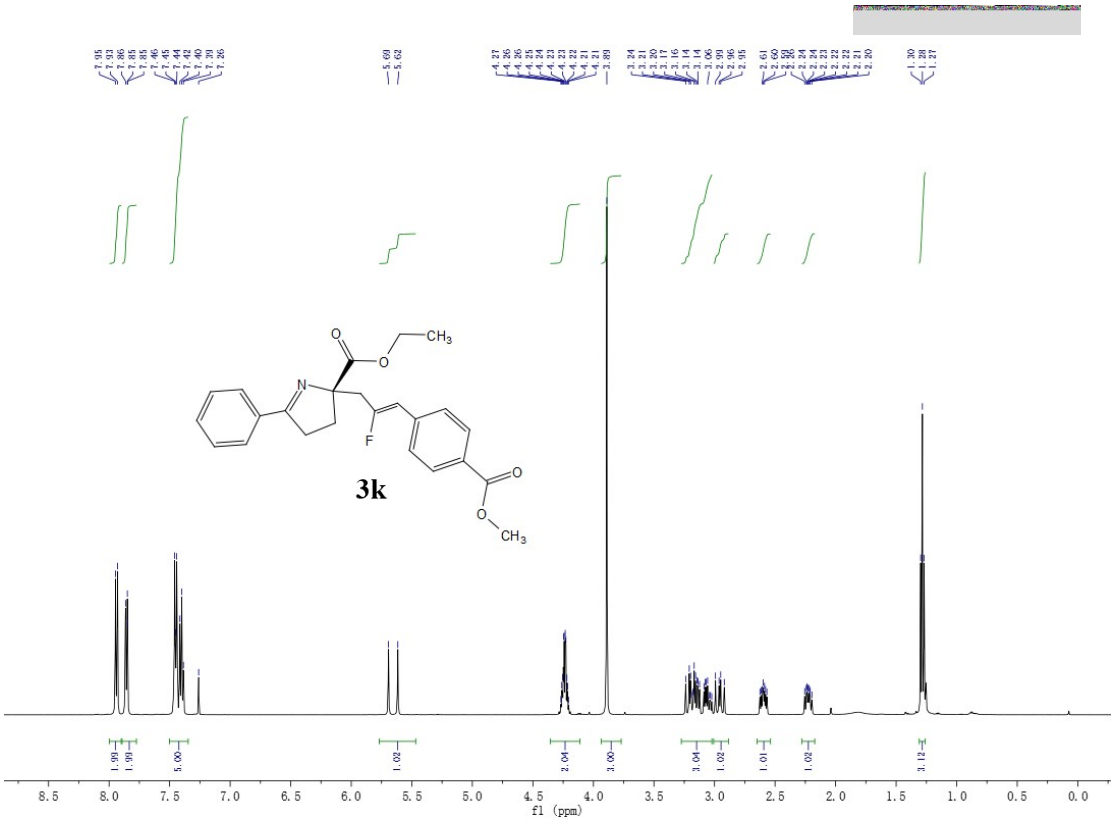

3h
f1 (ppm)

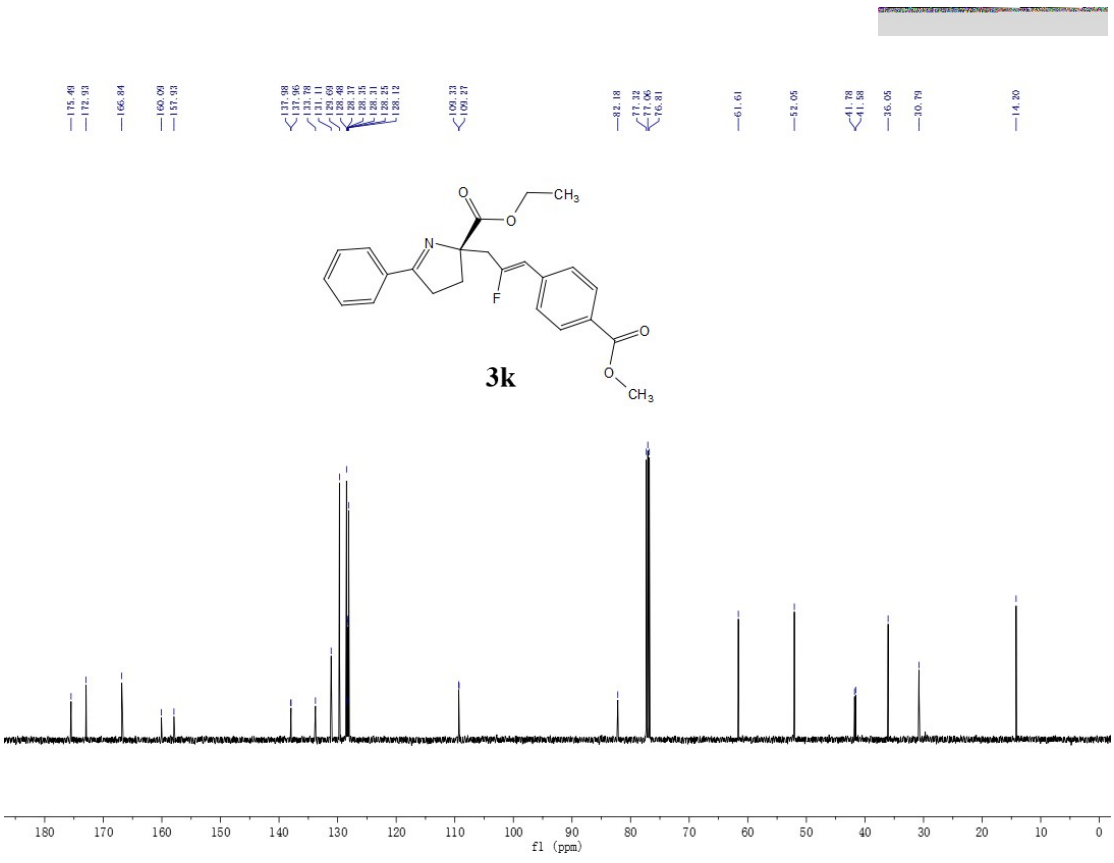

3i
f1 (ppm)

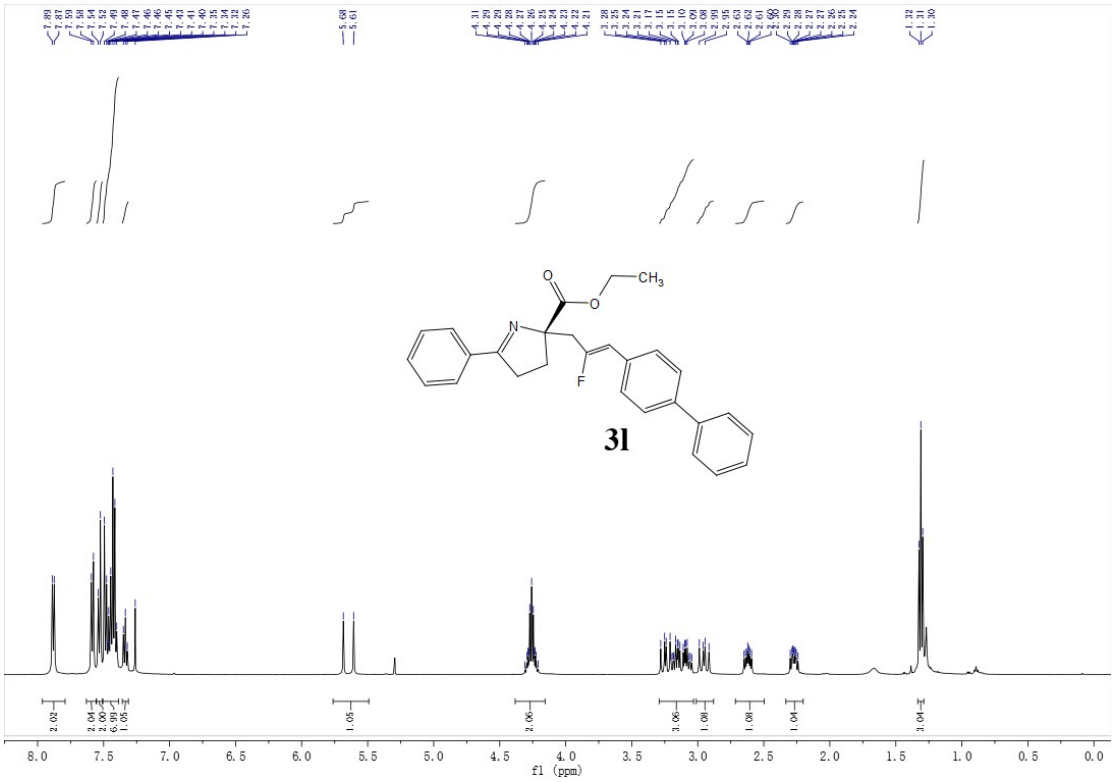

3i
f1 (ppm)

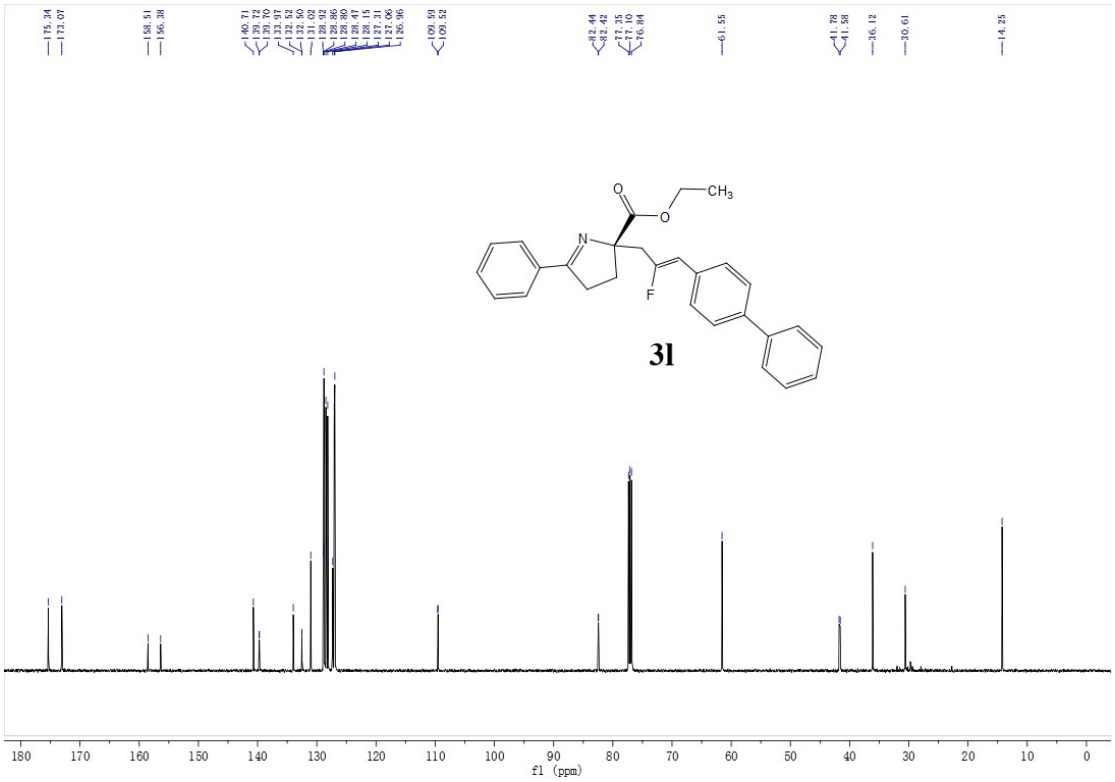

O
O
CH3
N
F
F
F
F
3j
f1 (ppm)

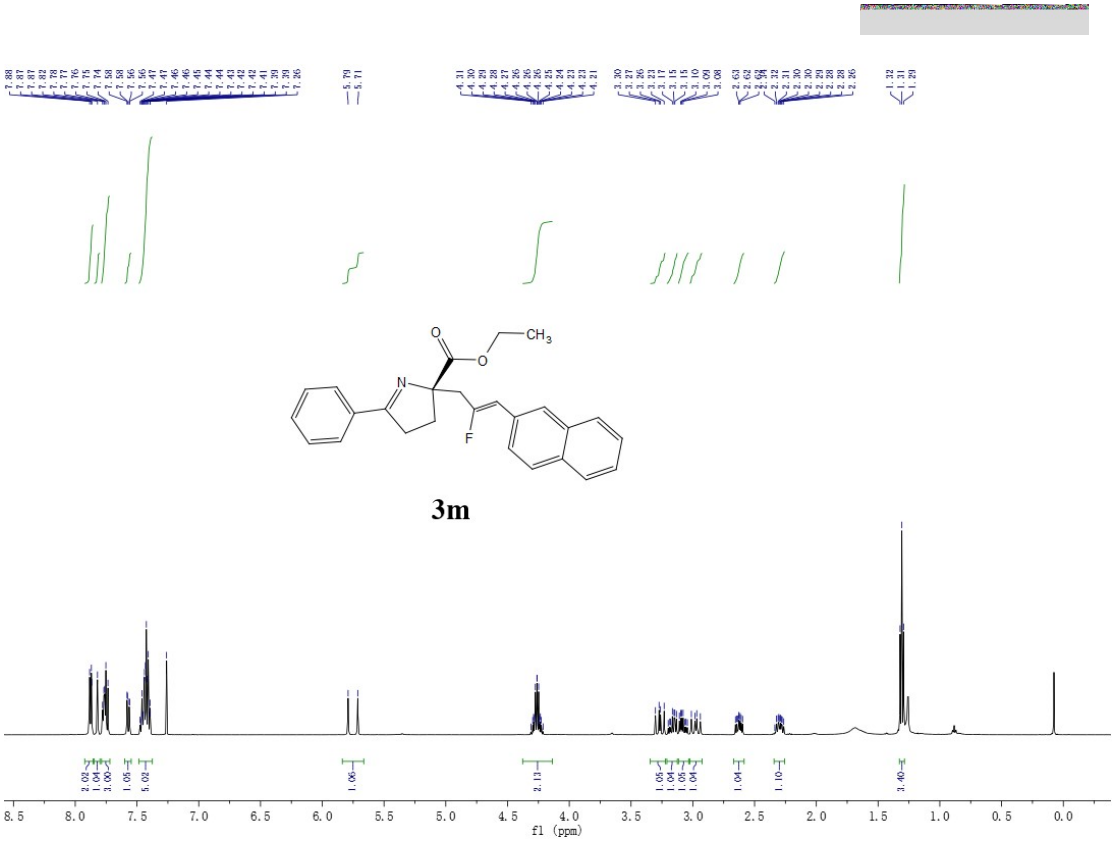

O
O
CH3
N
F
F
F
F
3j
f1 (ppm)


3k
f1 (ppm)

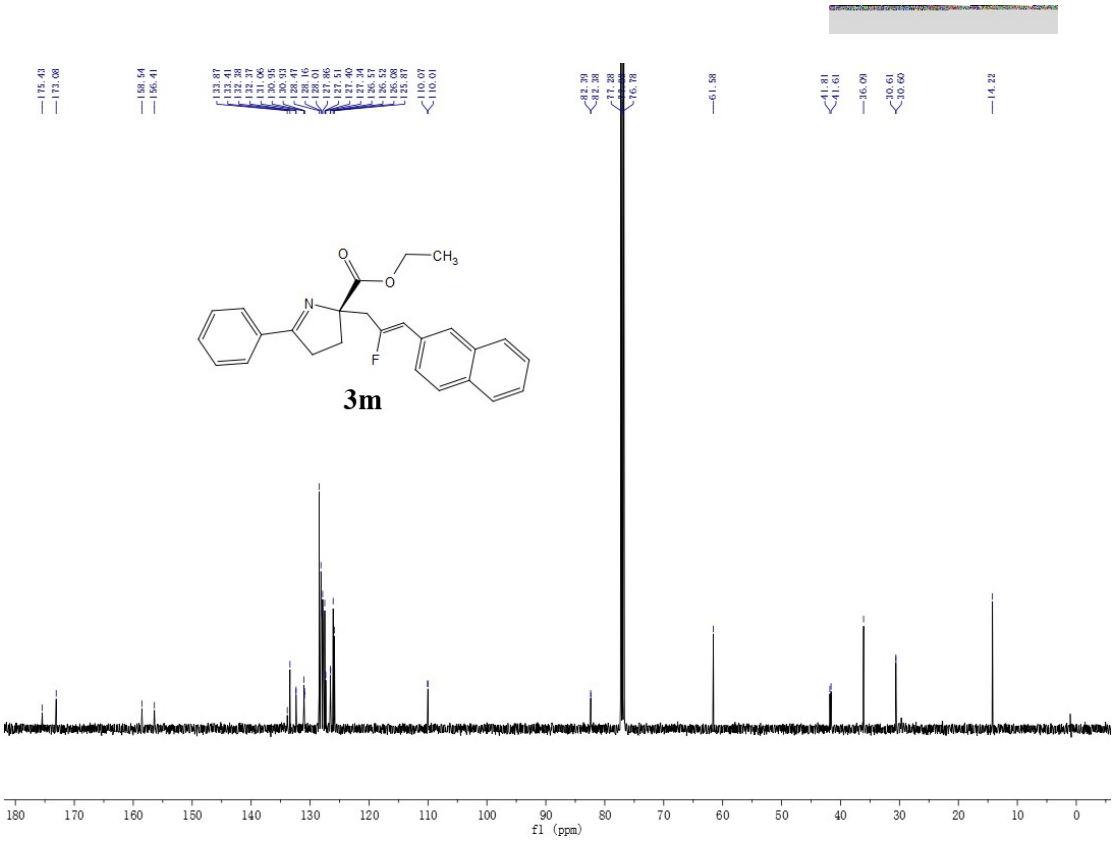

3k
f1 (ppm)


3l
f1 (ppm)

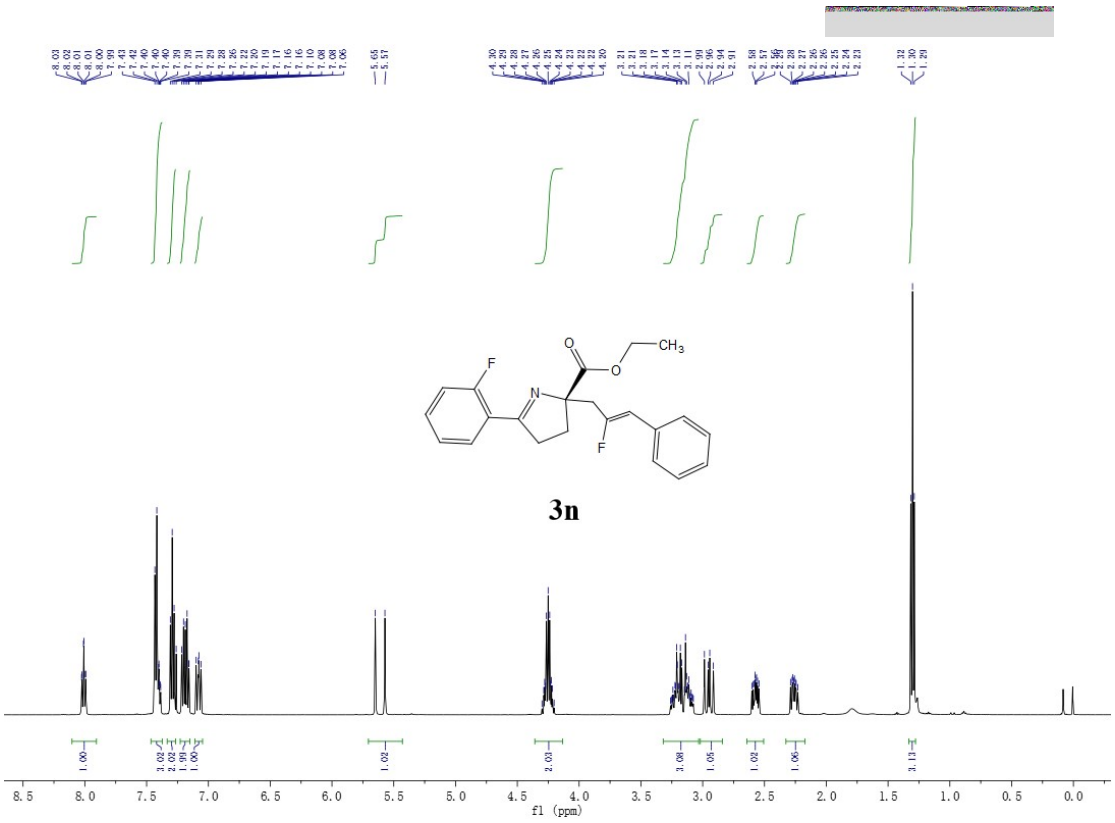

3l
f1 (ppm)

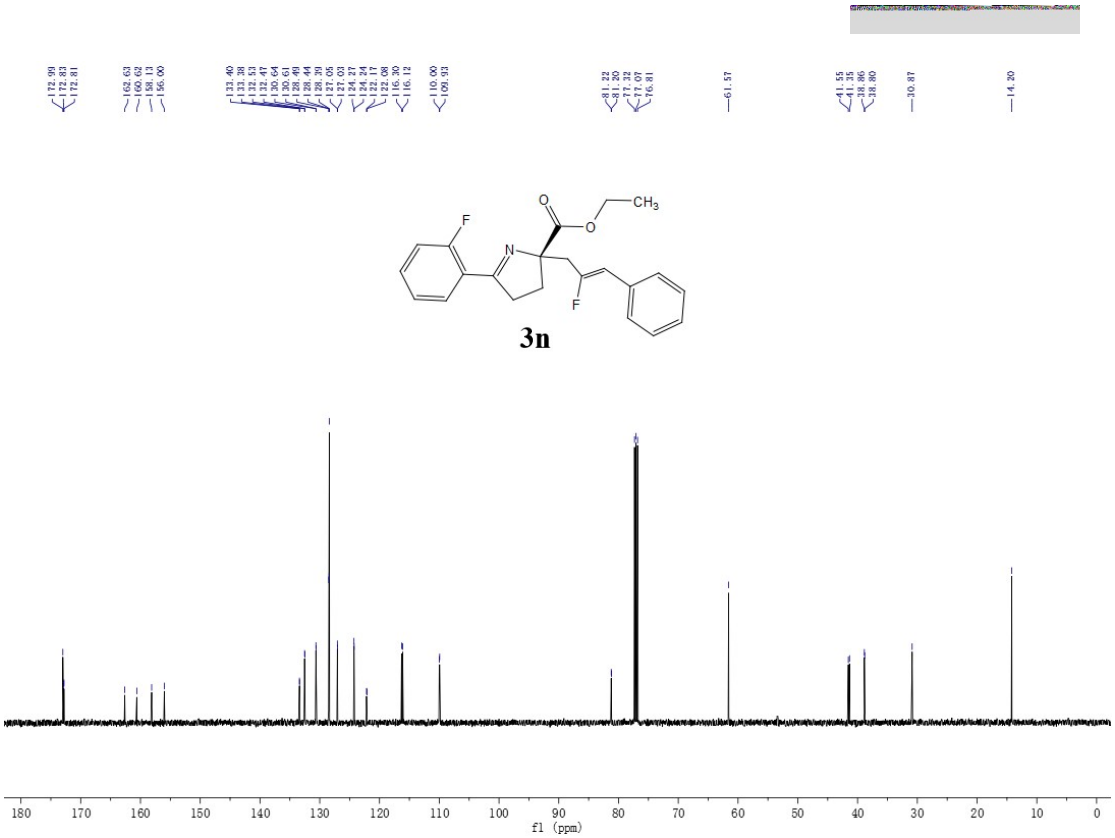


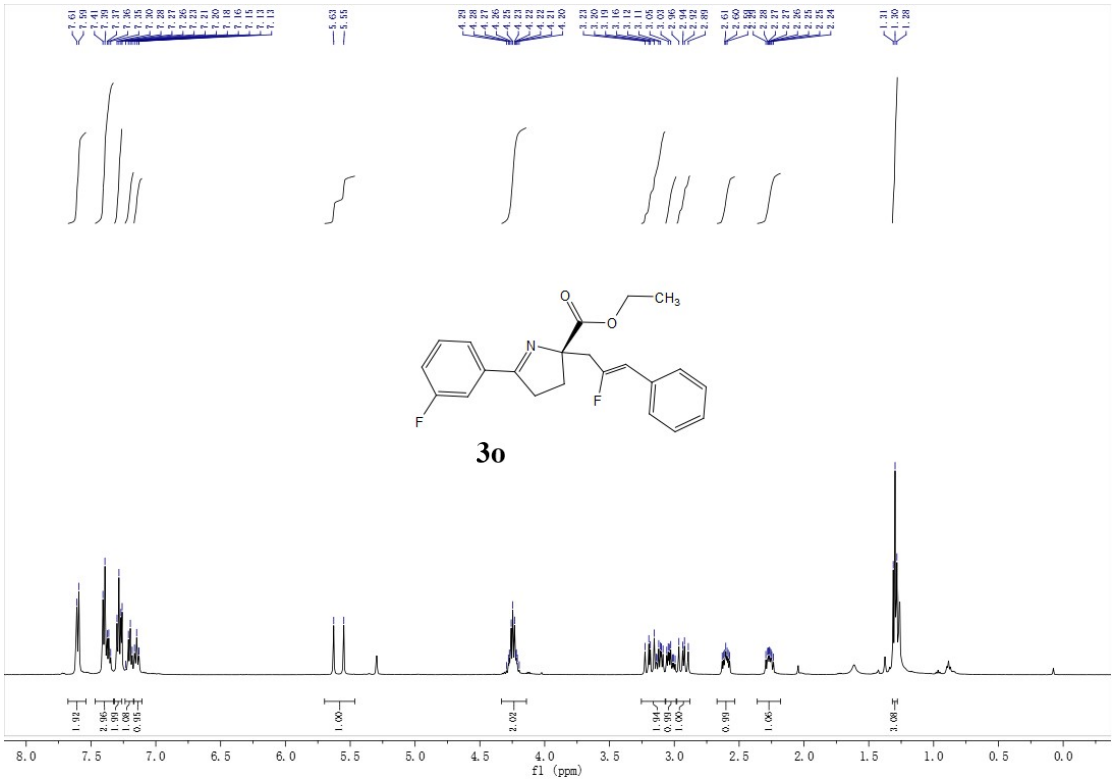
3m



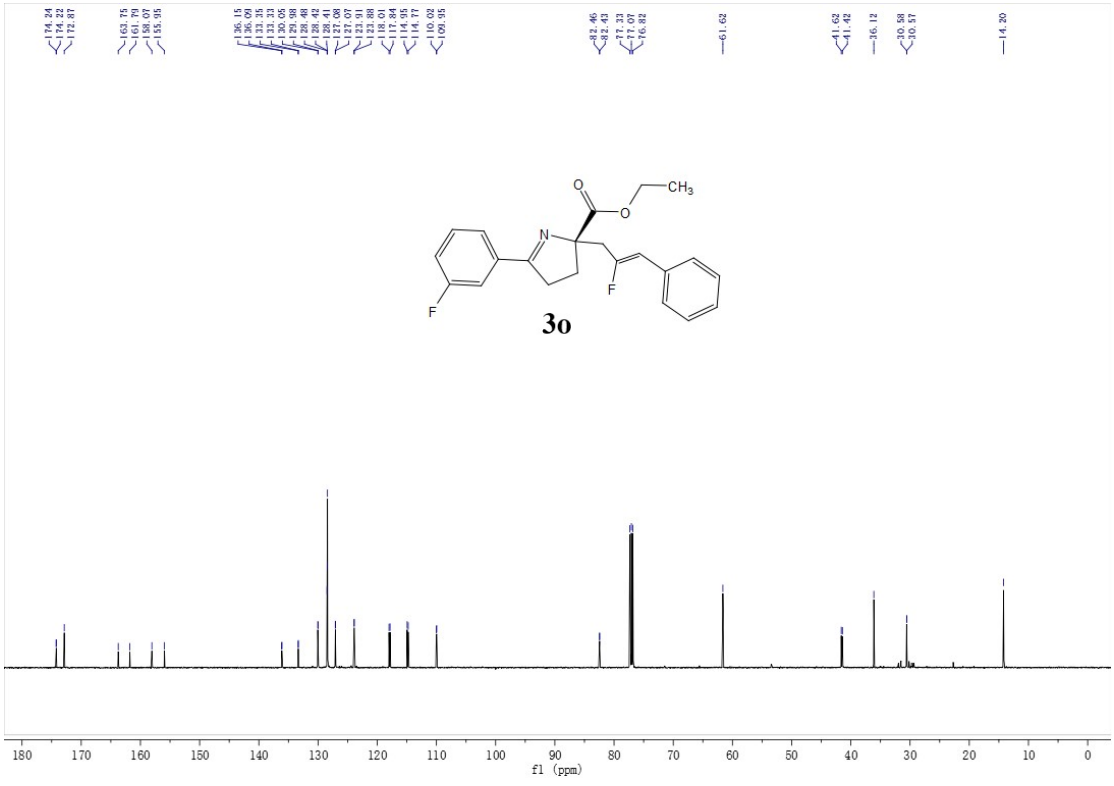
3m


F
O
O
CH3
N
F
3n
1.00
3.02
2.02
1.00
1.00
1.02
2.03
3.08
1.05
1.02
1.06
3.13
f1 (ppm)


F
O
O
CH3
N
F
3n
f1 (ppm)

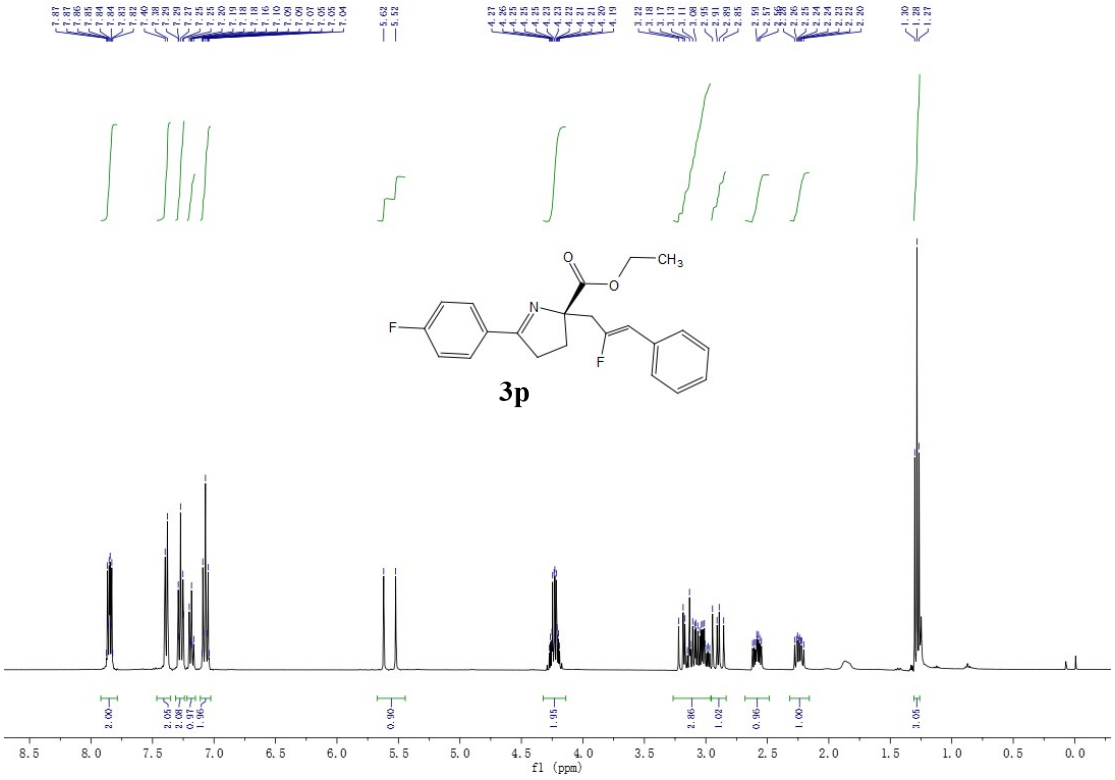

O
O
CH3
N
F
F
1.92
2.96
1.08
0.95
1.00
2.02
1.94
0.99
1.00
0.99
1.06
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3o


O
O
CH3
N
F
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

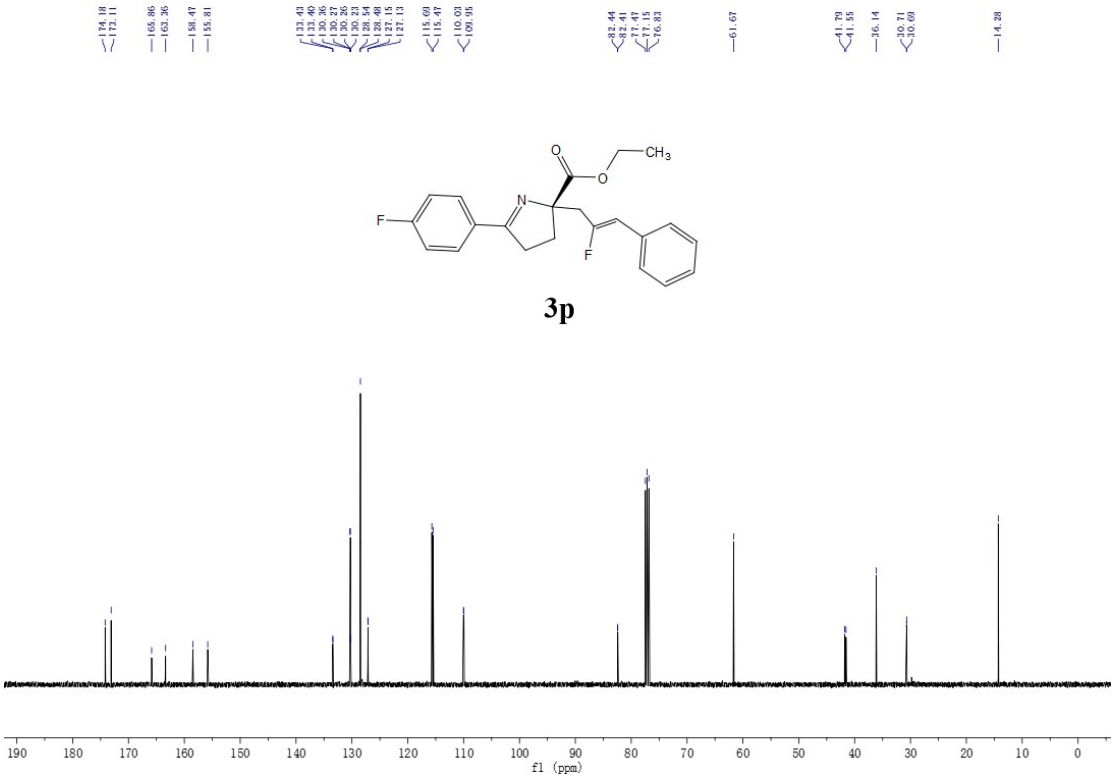
3o

400 MHz, Chloroform-*d*

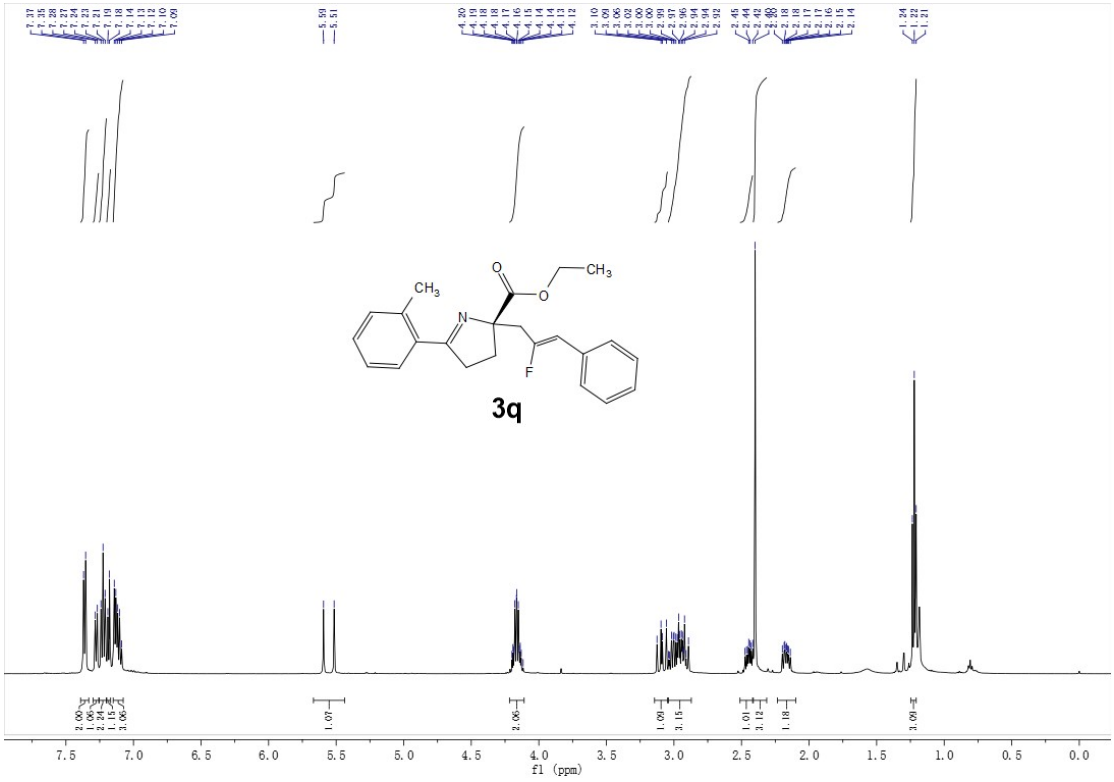


3p

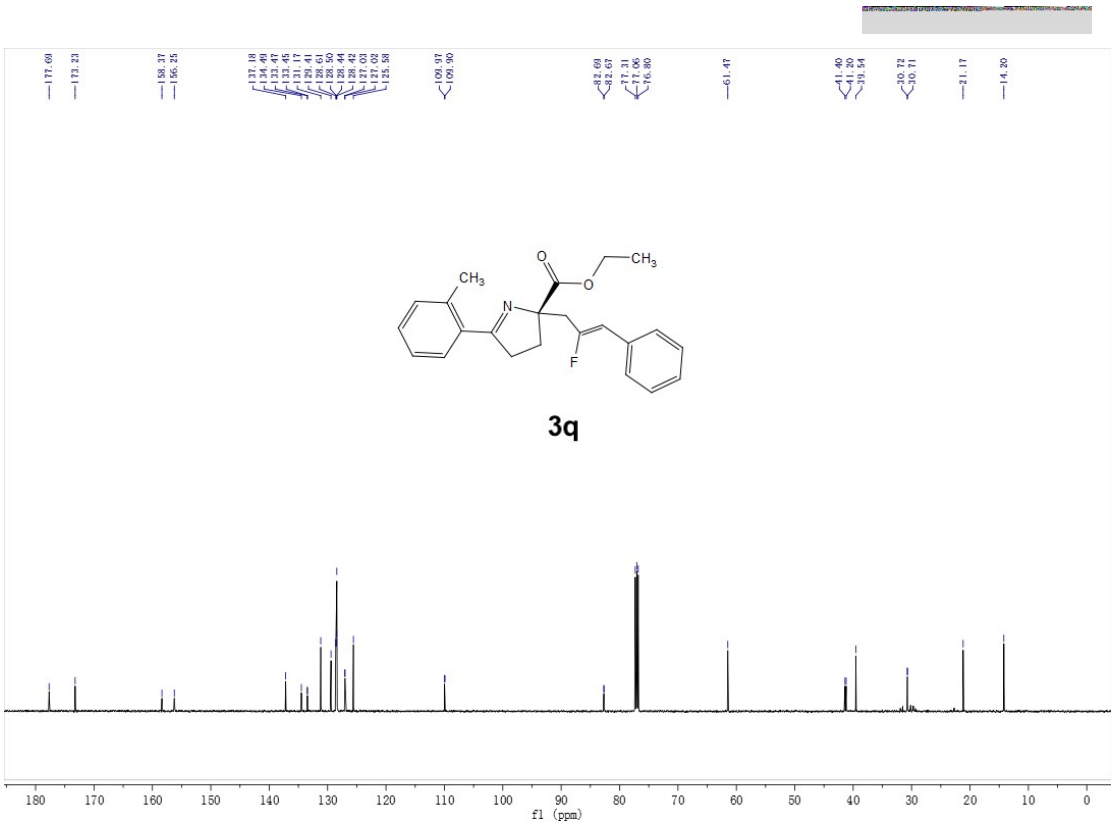
101 MHz, Chloroform-*d*



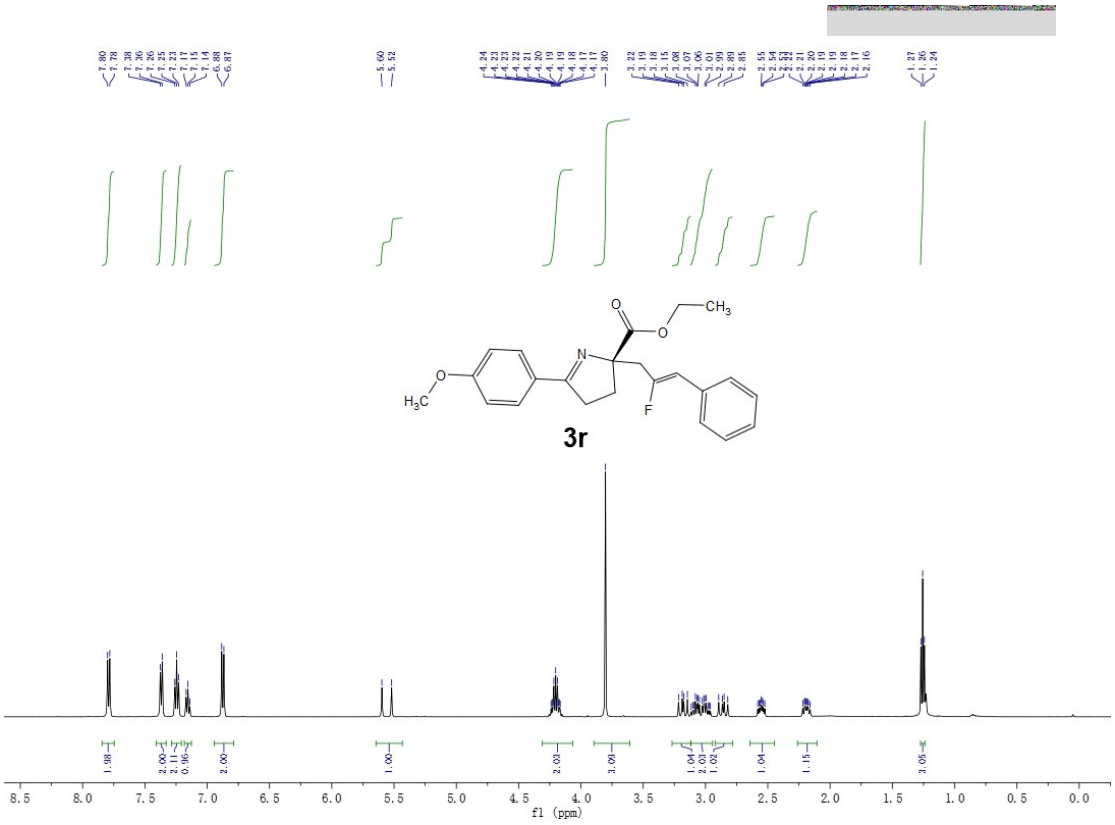
3p

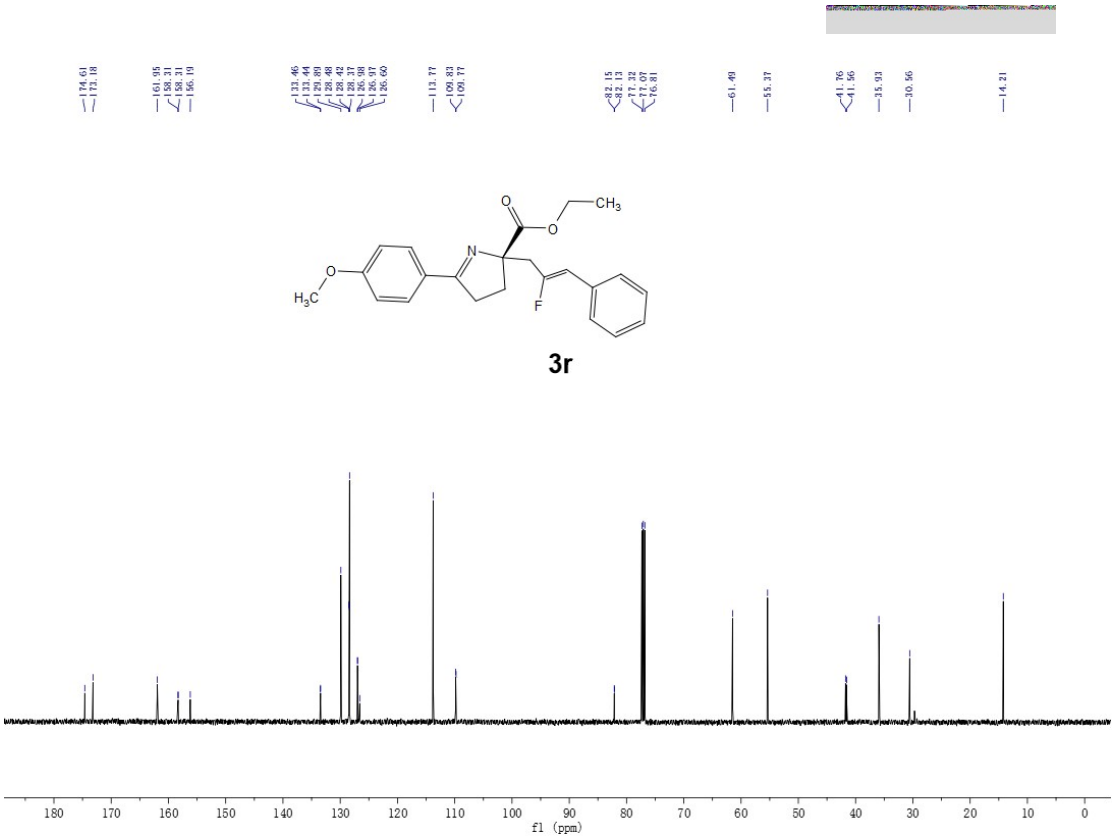


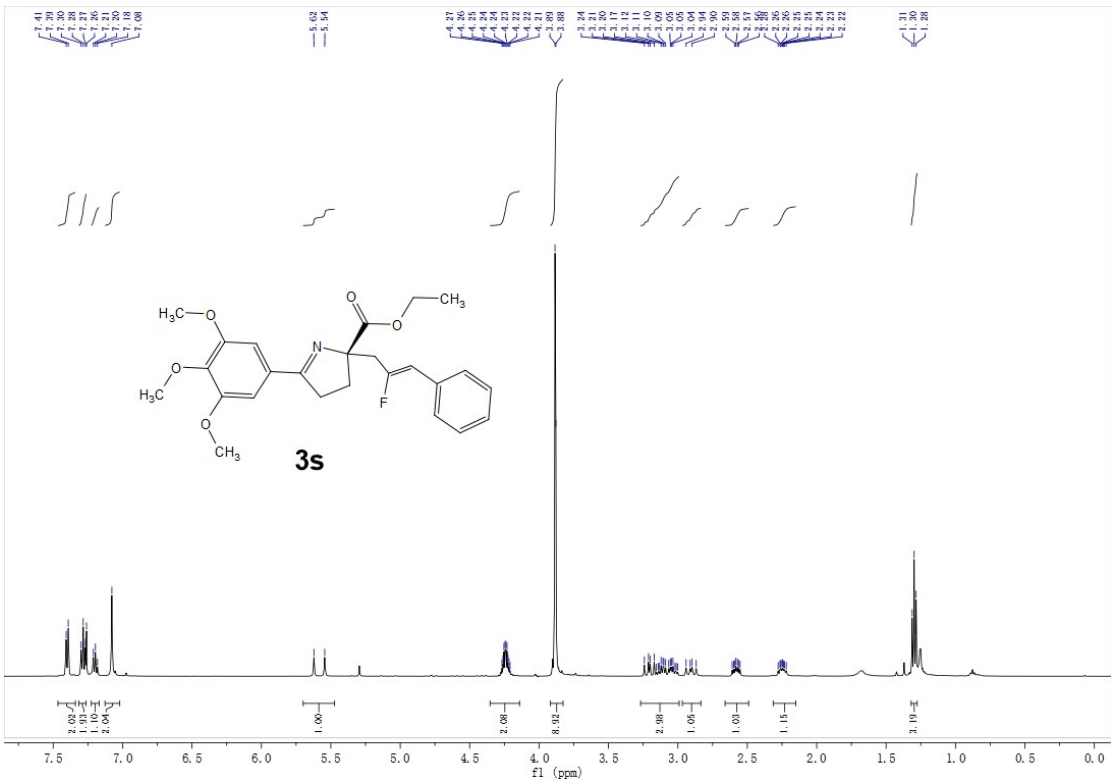
3q

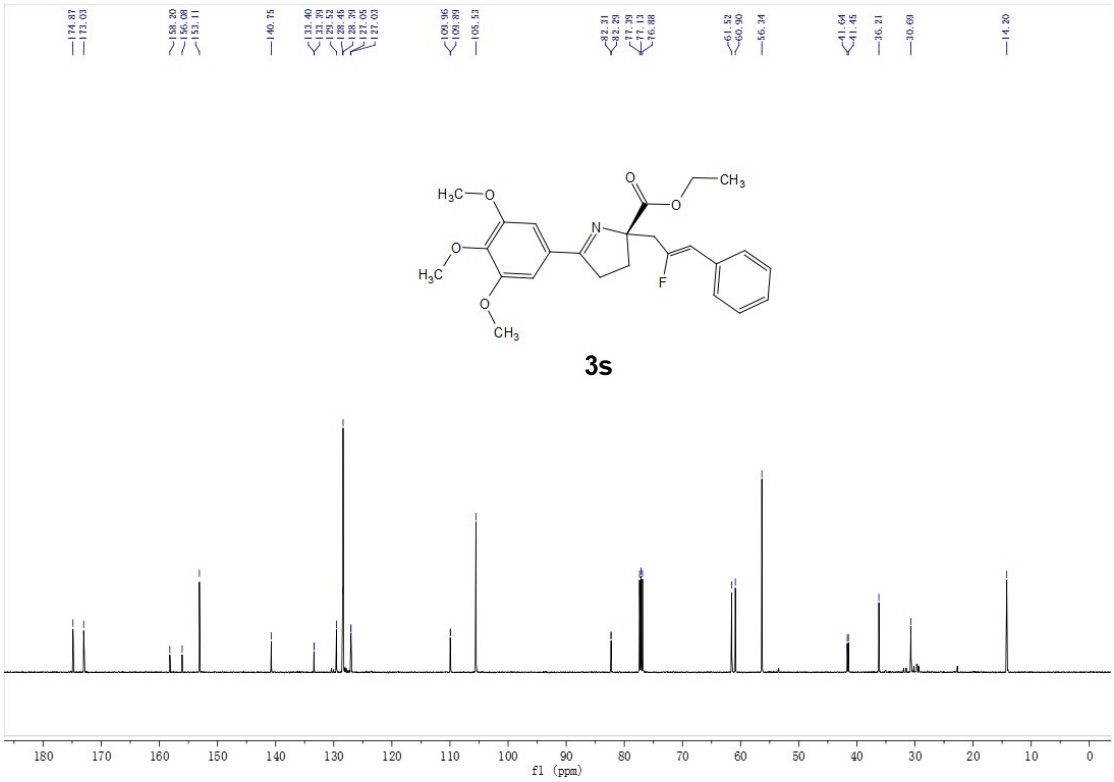


3q

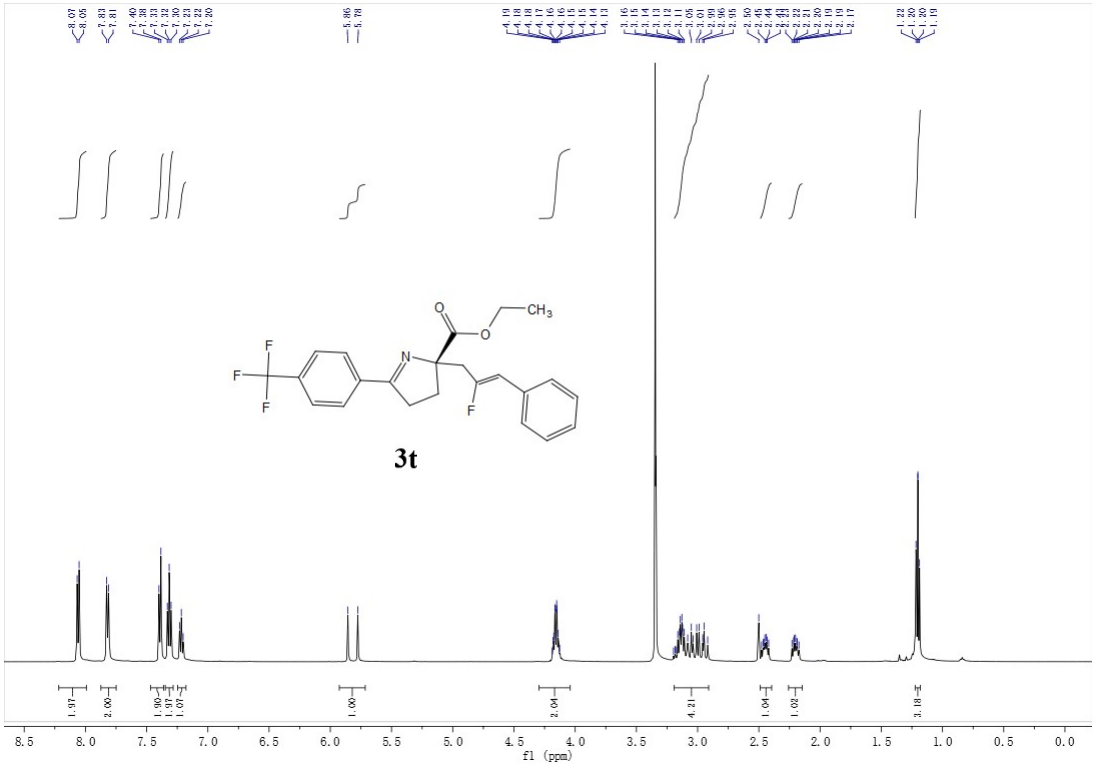

7.80
7.78
7.38
7.36
7.26
7.25
7.23
7.17
7.15
7.14
6.88
6.87
5.60
5.52
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.17
3.80
3.22
3.19
3.18
3.15
3.08
3.07
3.06
3.01
2.99
2.89
2.86
2.55
2.54
2.22
2.21
2.20
2.19
2.19
2.18
2.17
2.16
1.27
1.24
O
CH3
O
N
O
H3C
F
3r
1.98
2.00
2.11
0.96
2.00
1.00
2.03
3.09
1.04
2.02
1.02
1.04
1.15
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.61
173.18
161.95
158.31
158.31
156.19
133.46
133.44
129.89
128.48
128.42
128.37
126.98
126.97
126.60
113.77
109.83
109.77
82.15
82.13
77.32
77.07
76.81
61.49
55.37
41.76
41.56
35.93
30.56
14.21
O
CH3
O
N
O
H3C
F
3r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

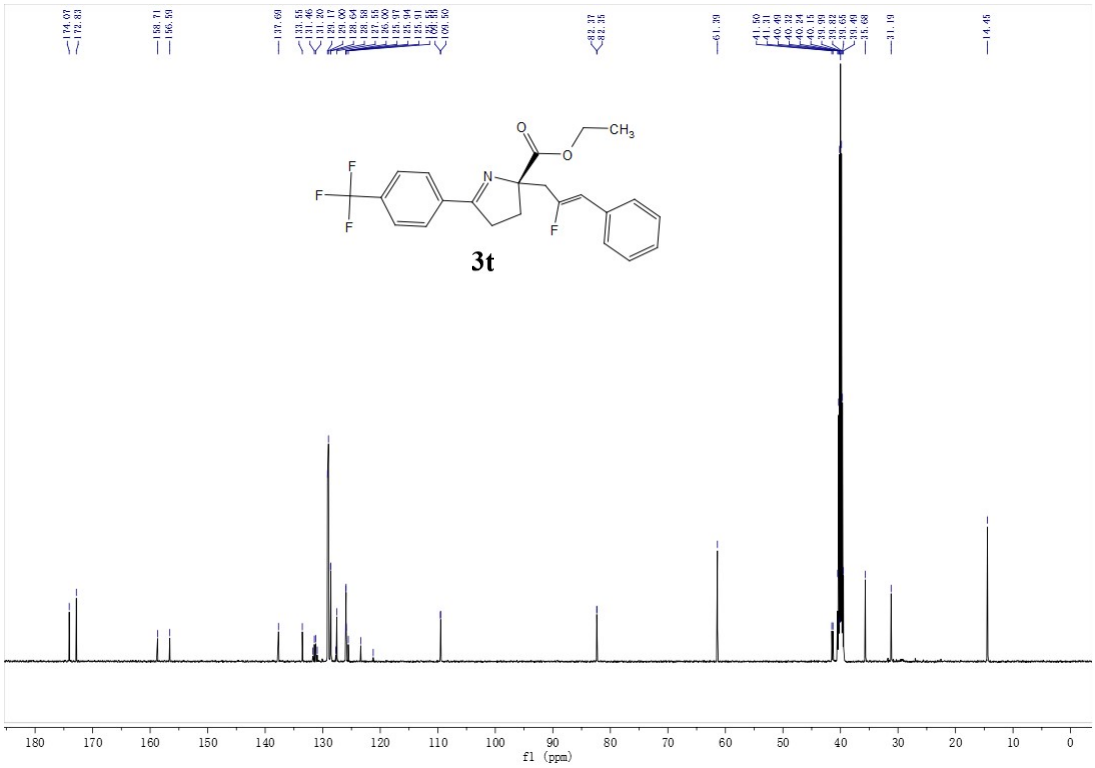

3s
f1 (ppm)

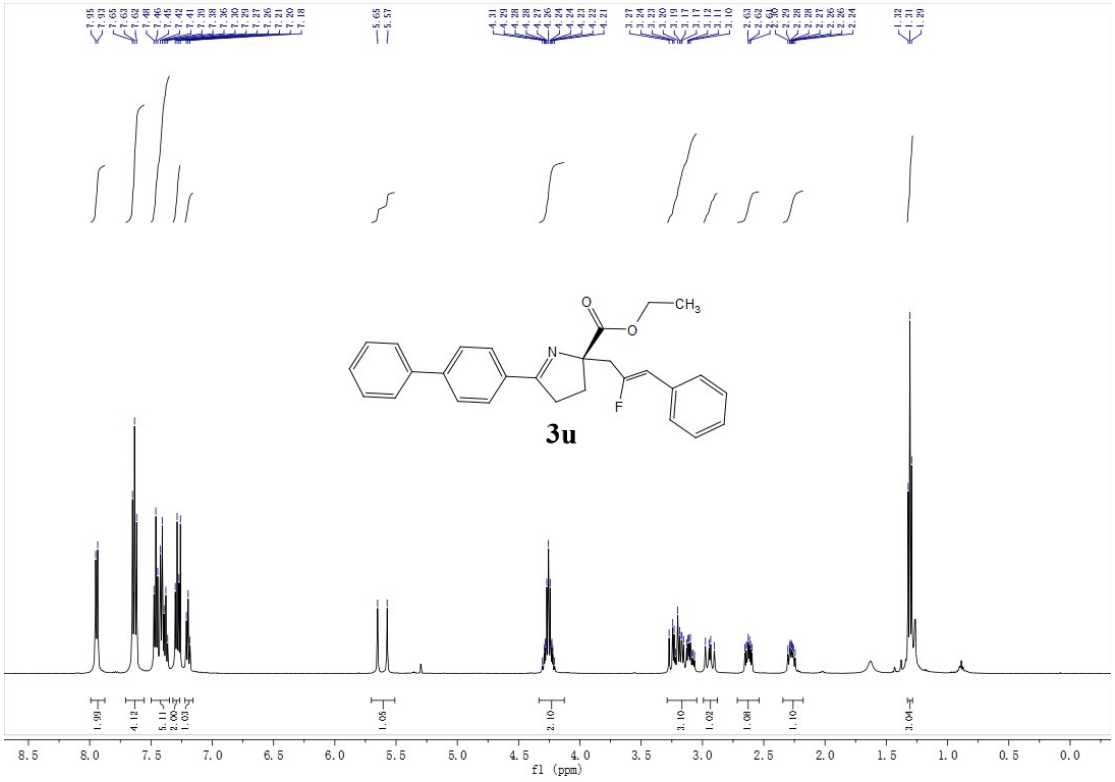

3s
f1 (ppm)

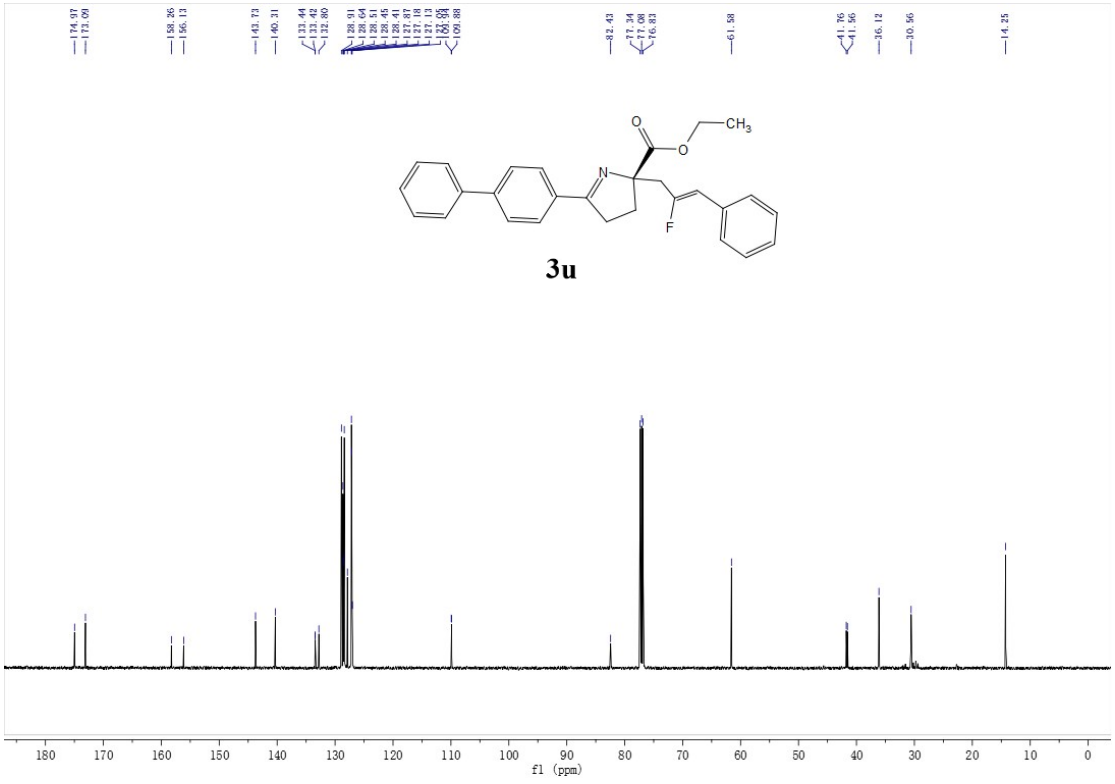
500 MHz, DMSO-d_6

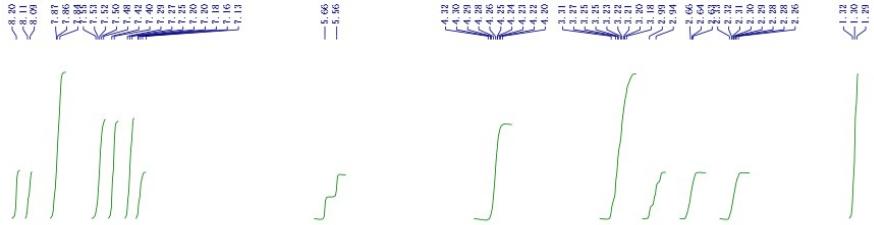


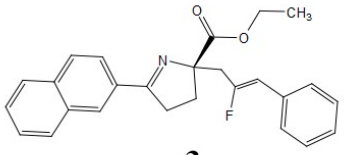
126 MHz, DMSO-d_6



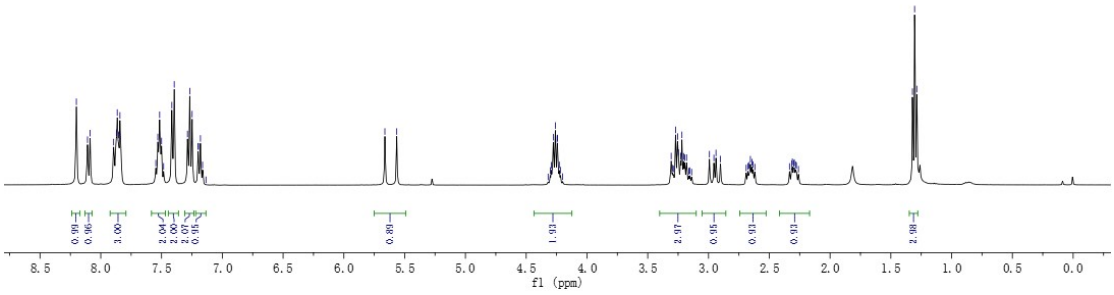

3u
f1 (ppm)

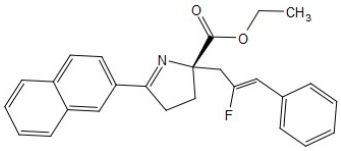

3u
f1 (ppm)



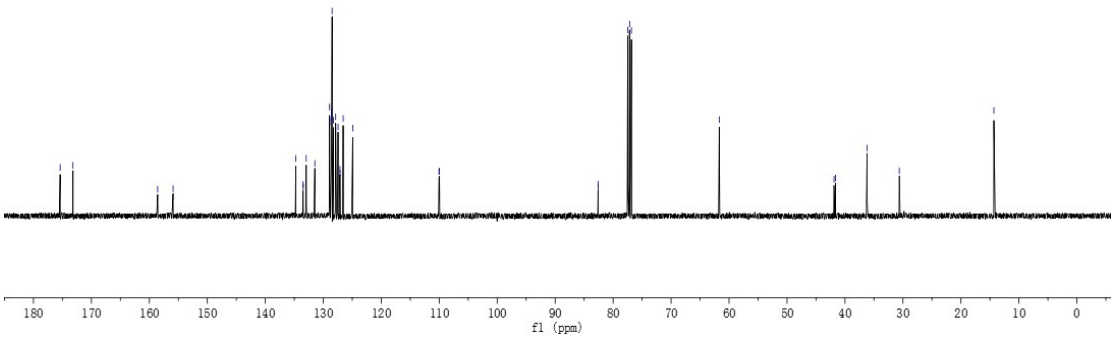


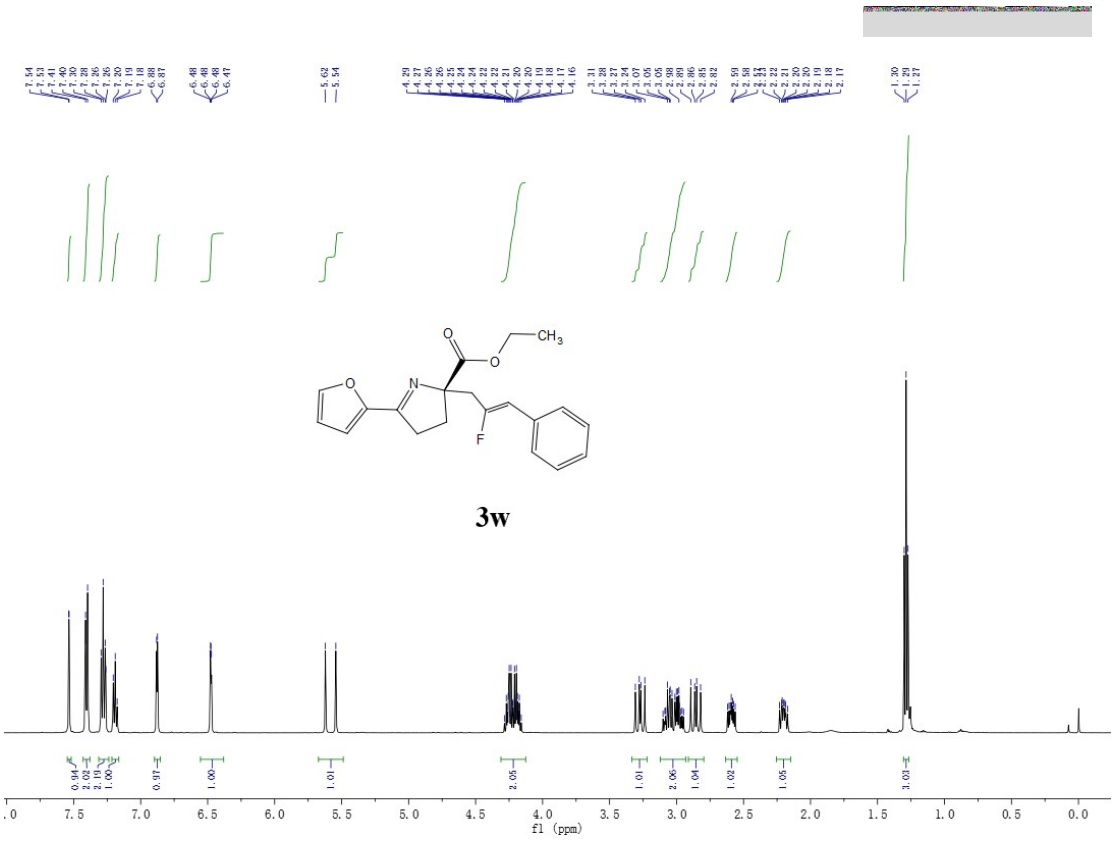
3v



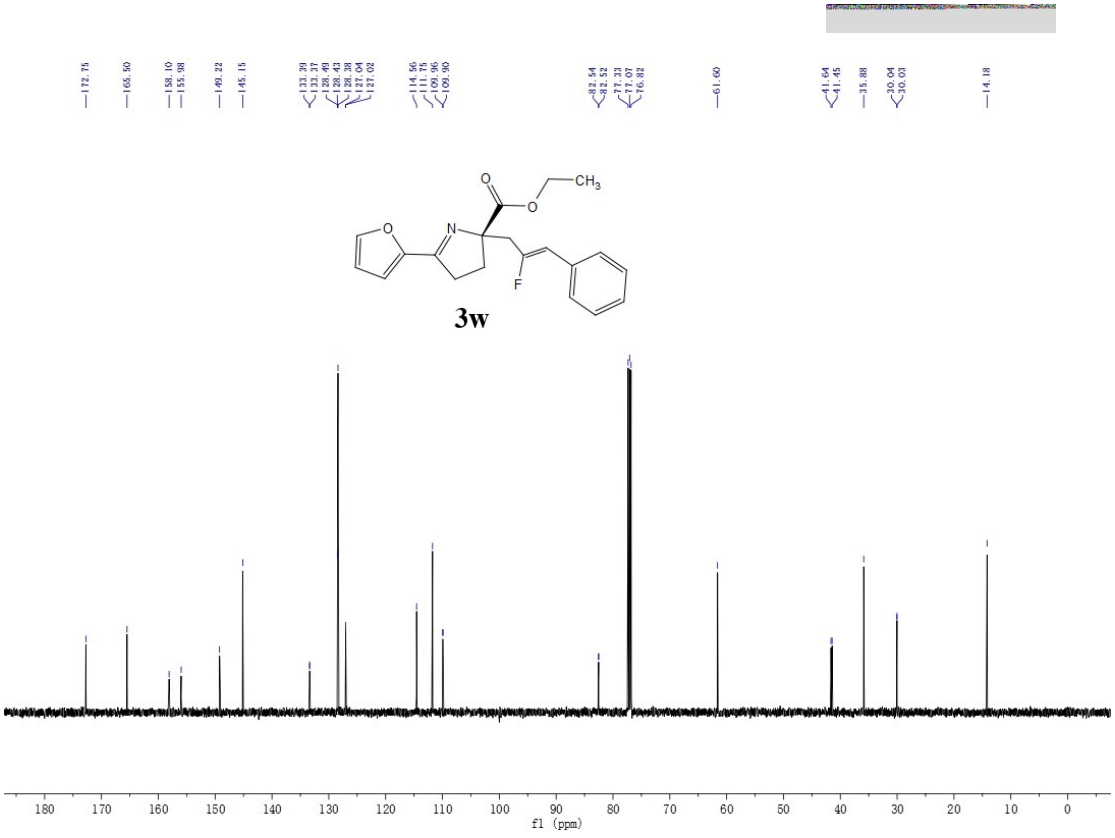


3v

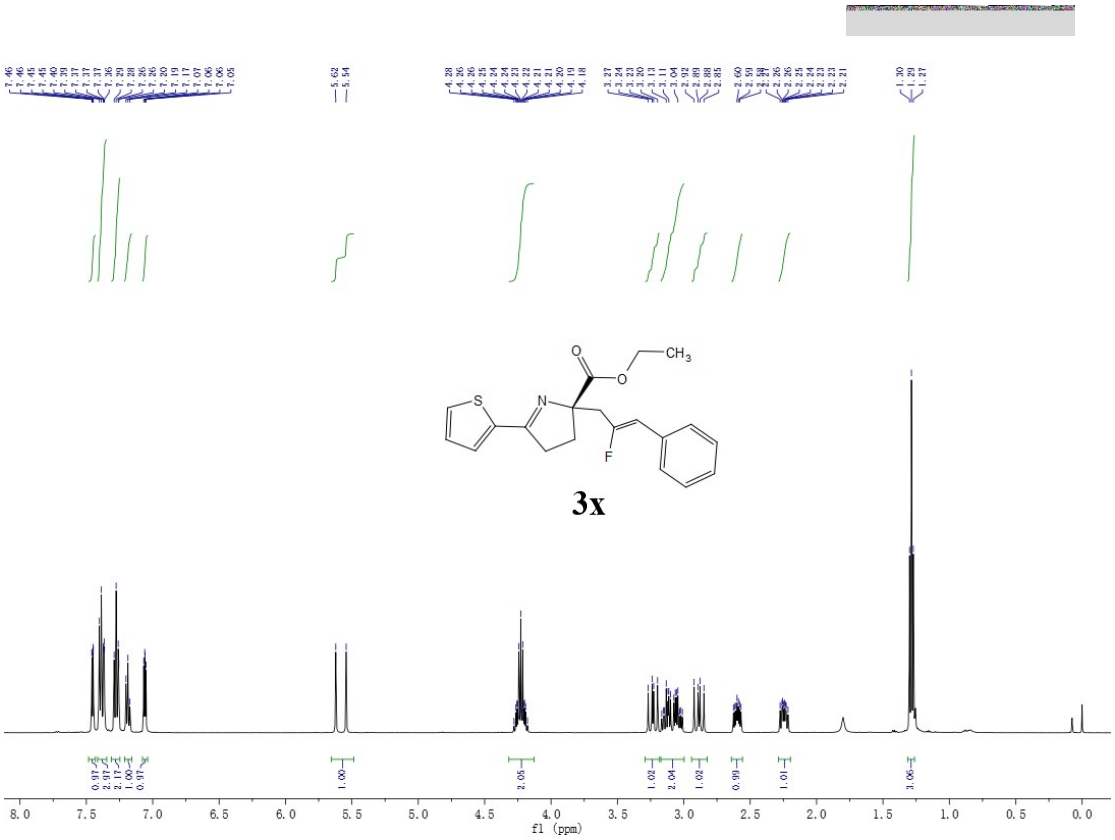




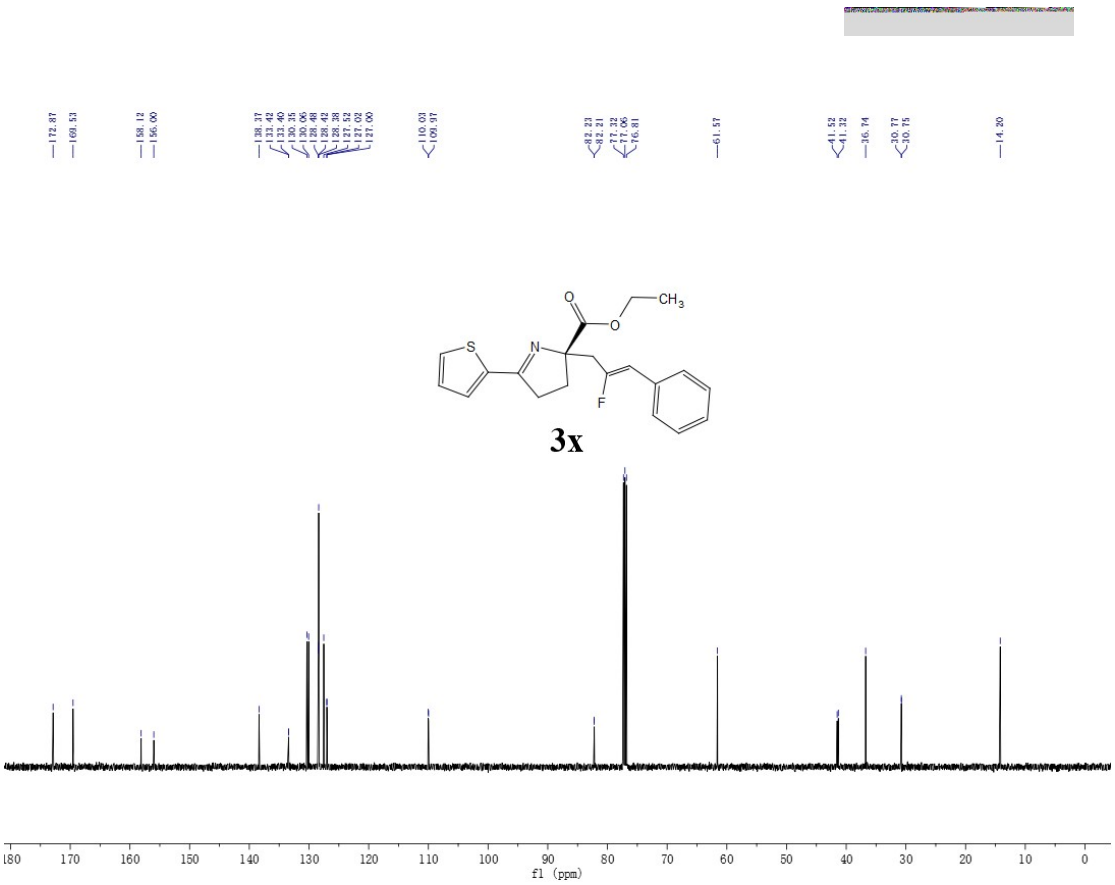
3w



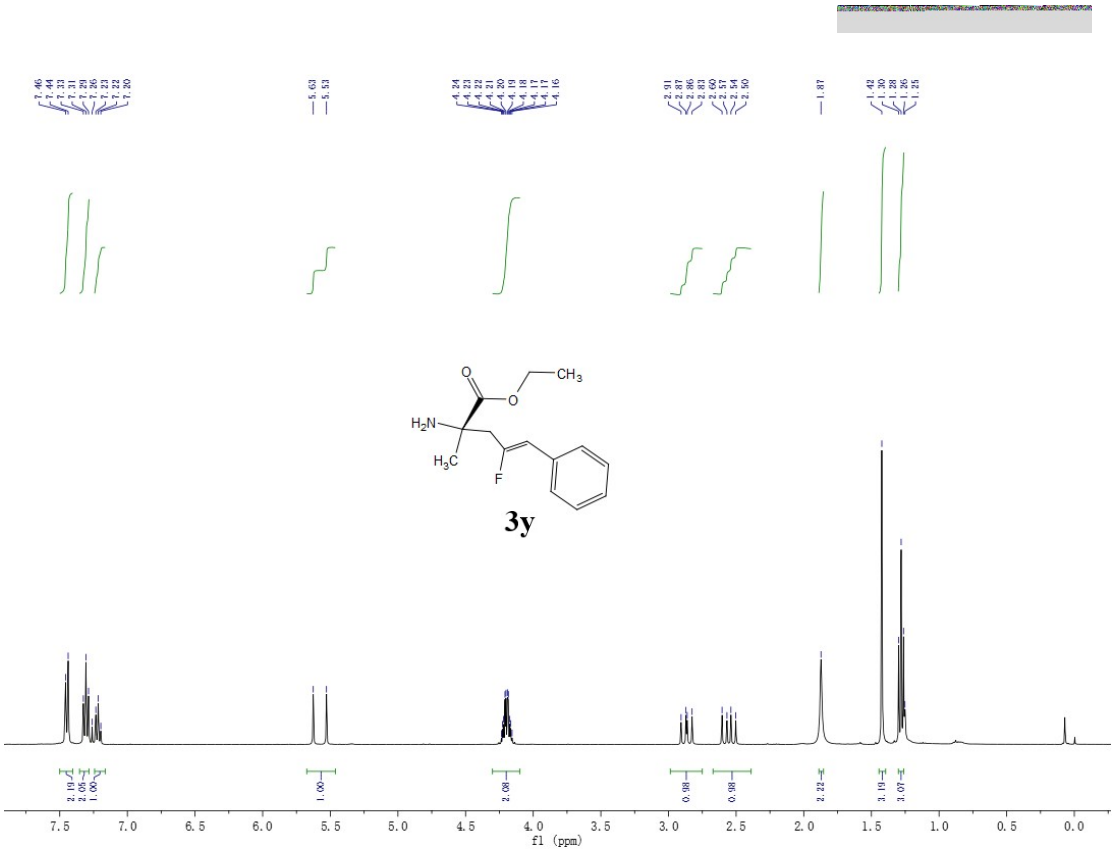
3w

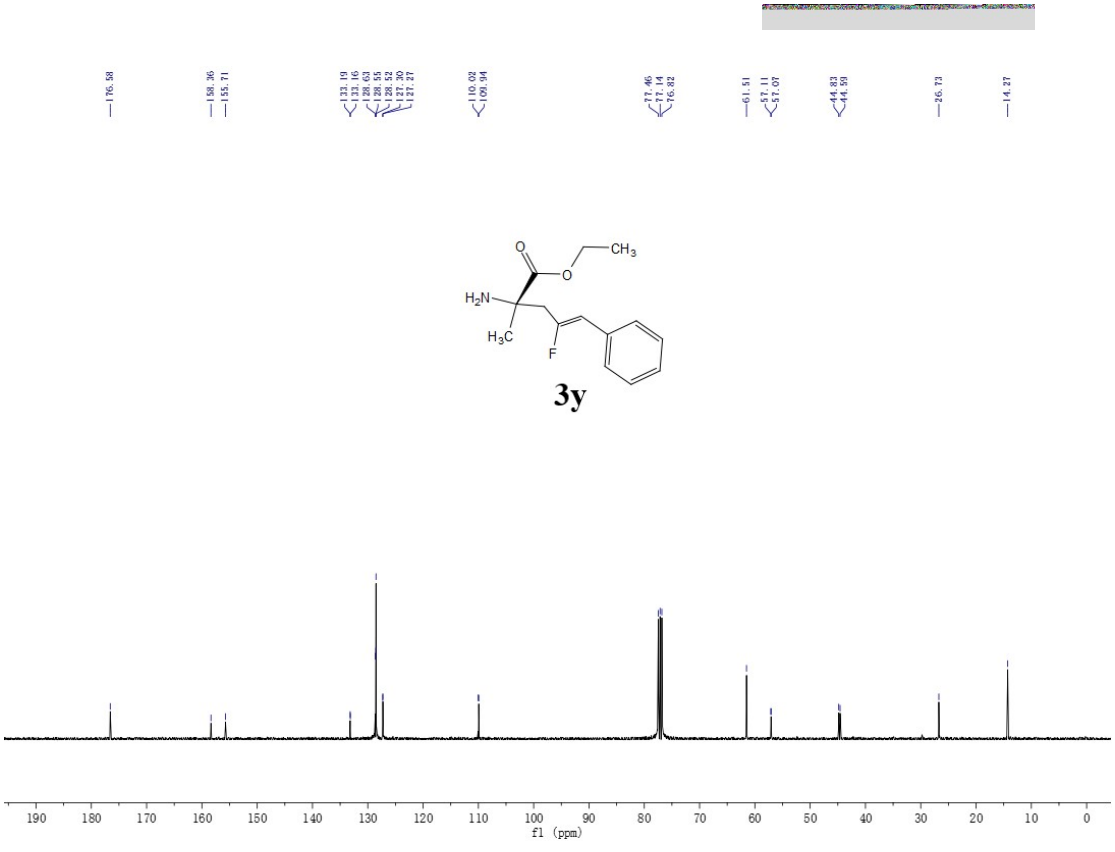


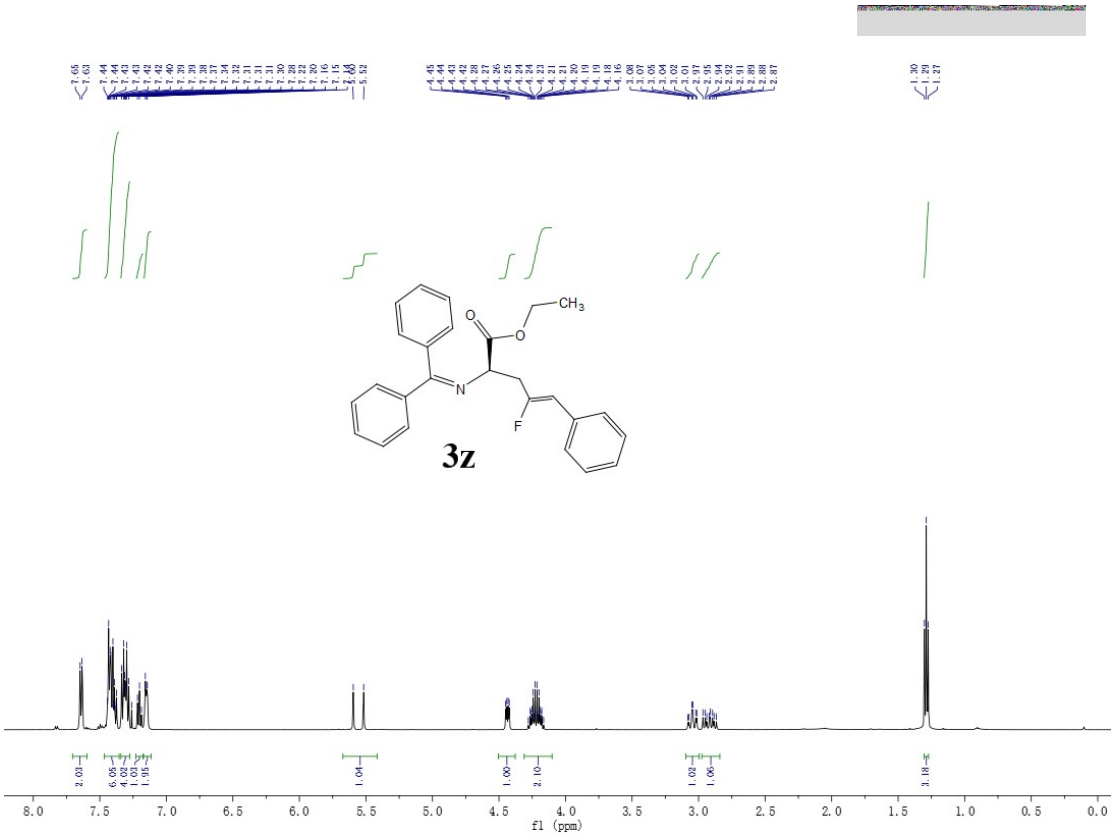
3x

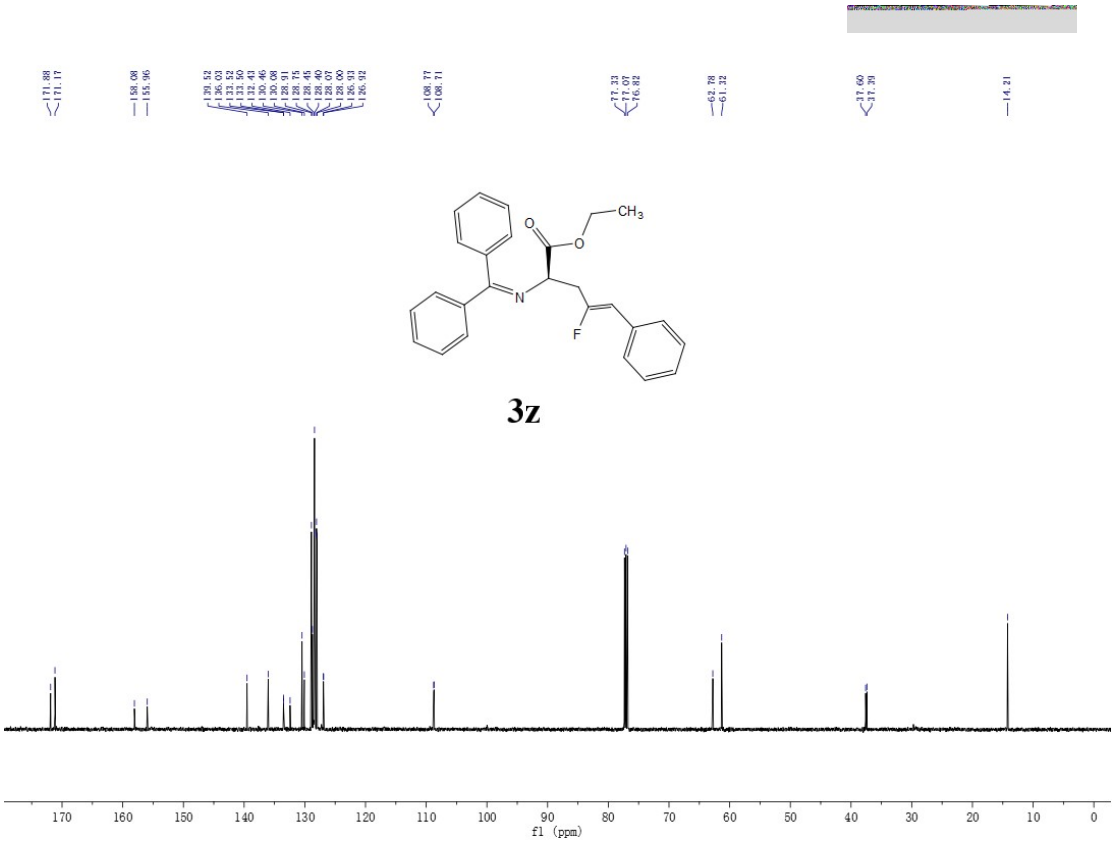


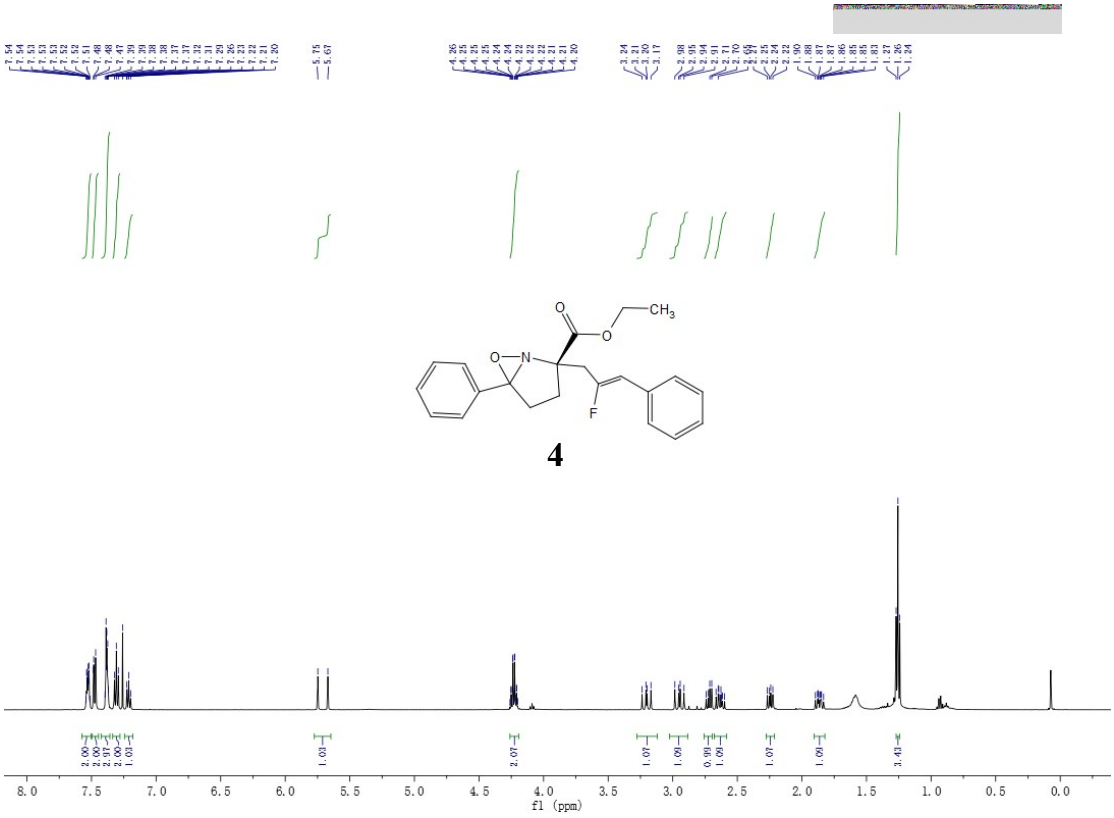
3x


3y
fl (ppm)

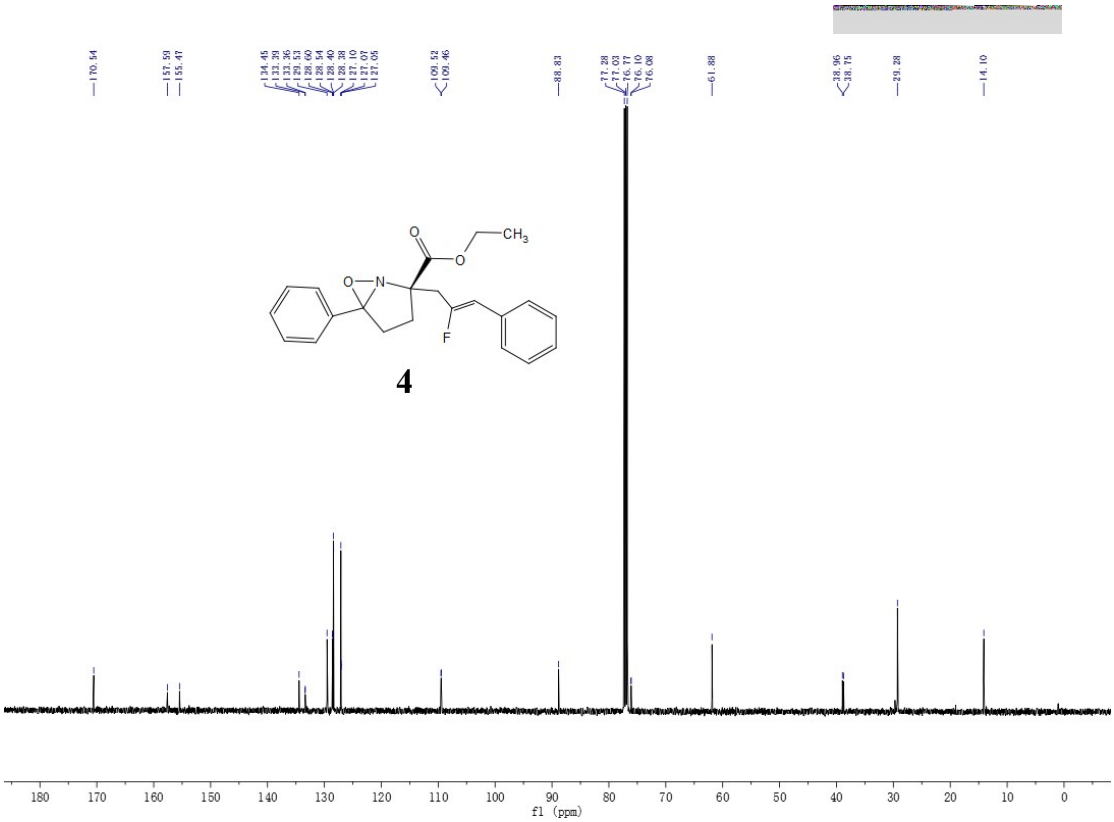

3y
fl (ppm)


CH3
O
O
N
F
3z
f1 (ppm)

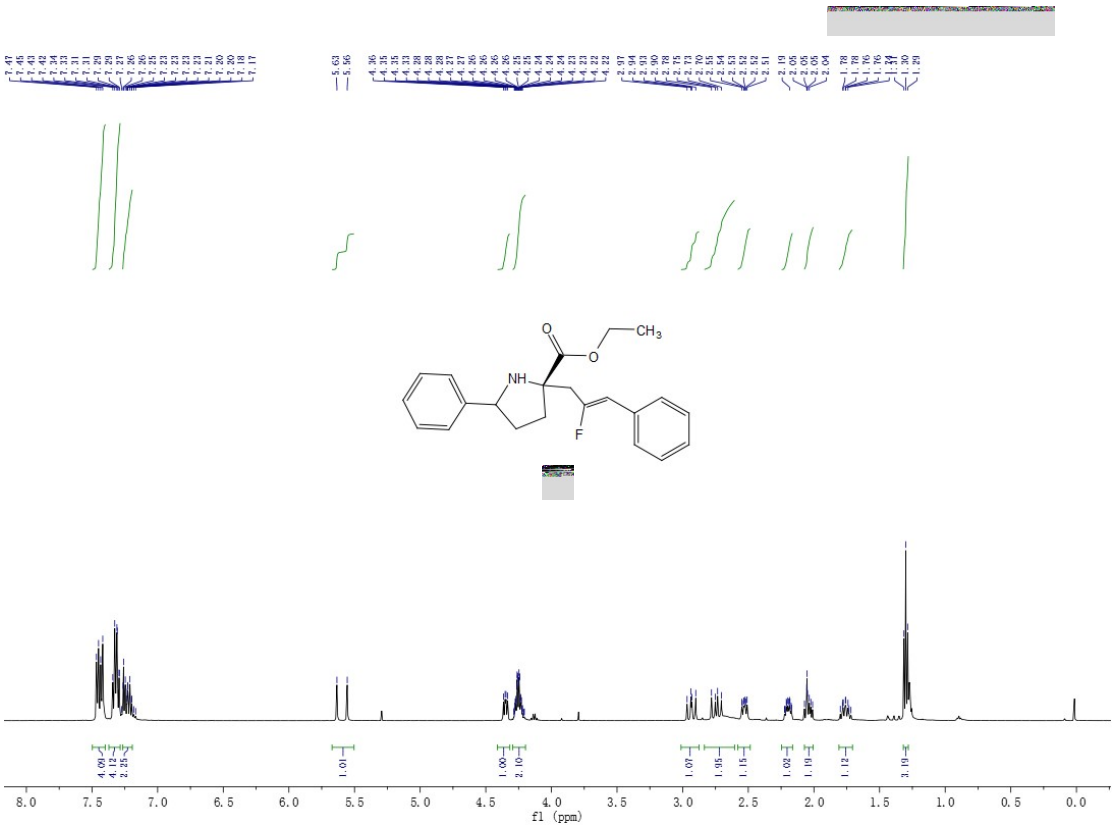

CH3
O
O
N
F
3z
f1 (ppm)

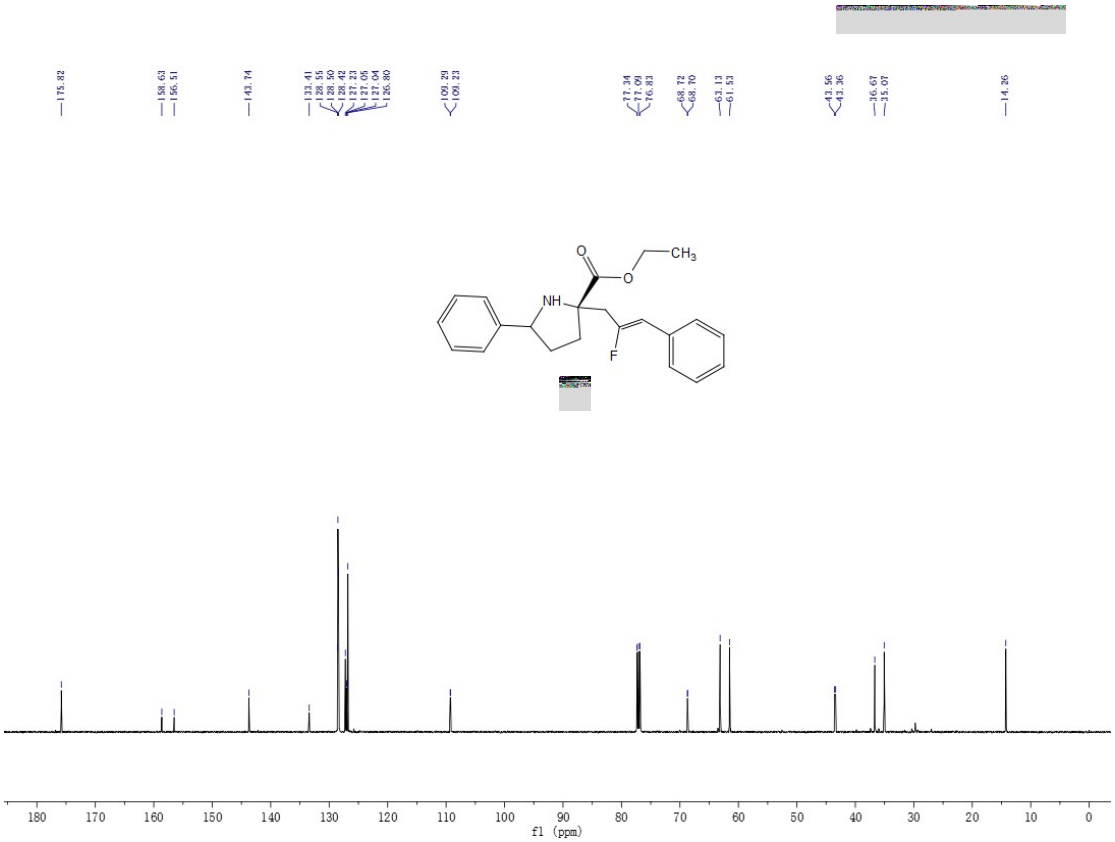


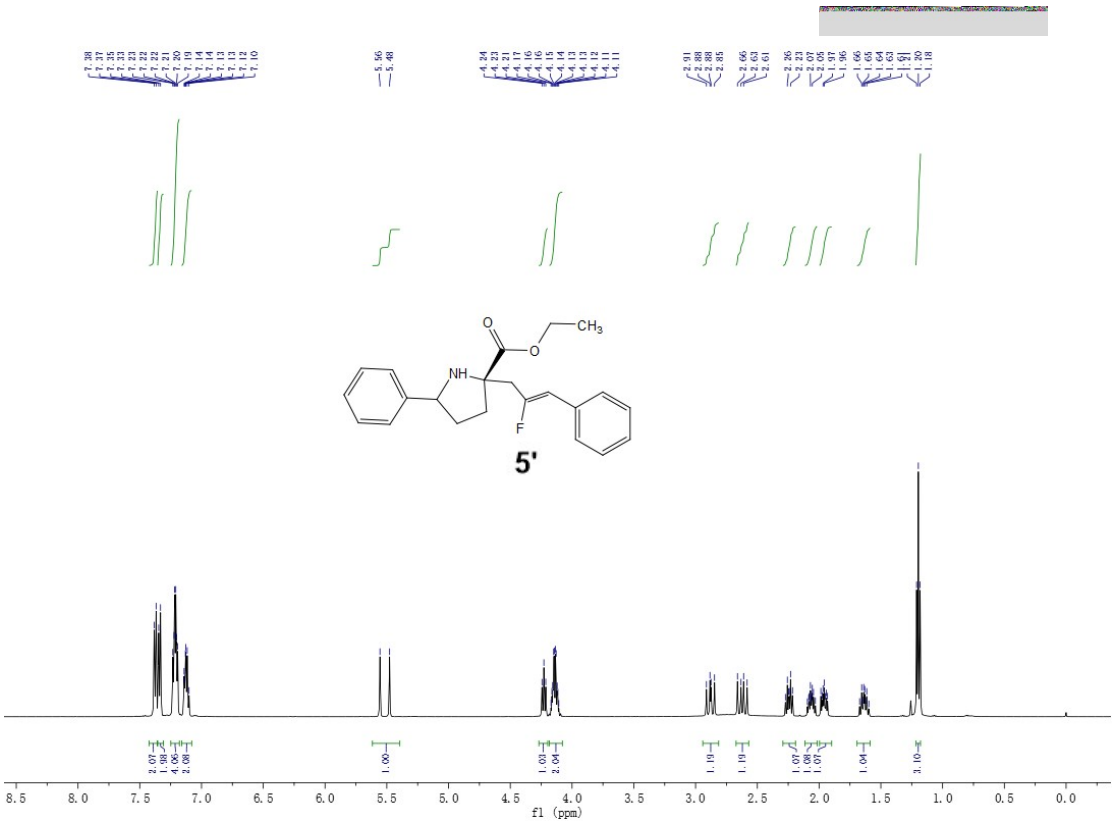
4

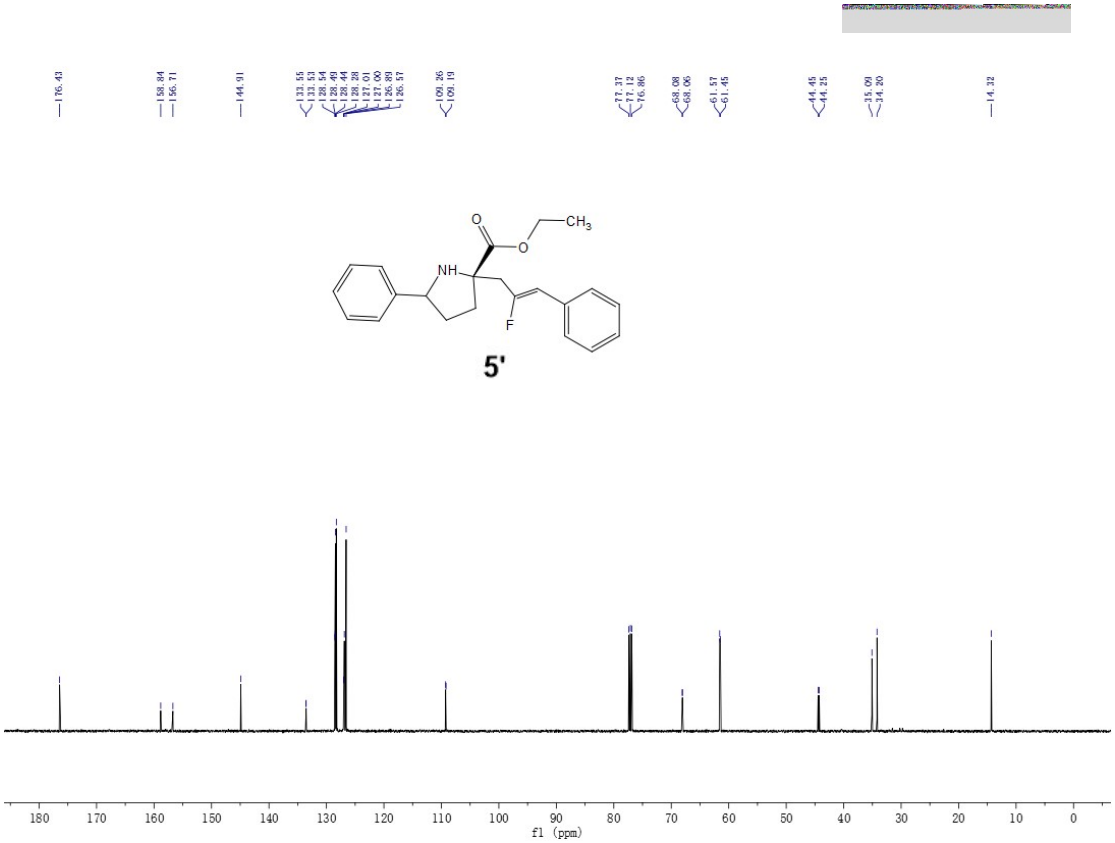


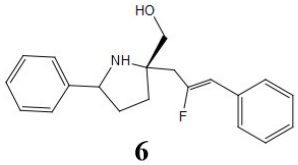
4


O
CH3
O
NH
F
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

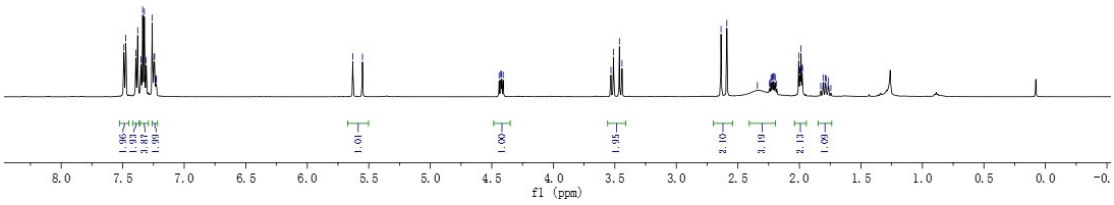

O
CH3
O
NH
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

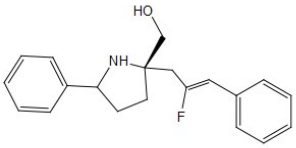

O
CH3
O
NH
F
5'
f1 (ppm)


O
CH3
O
NH
F
5'
f1 (ppm)

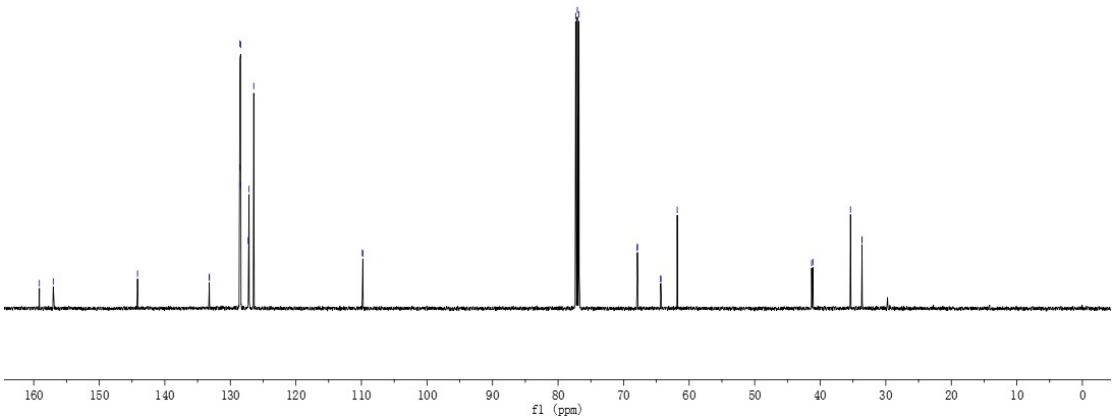

HO
NH
F

6


1.96
1.93
3.87
1.99
1.01
1.00
1.95
2.10
3.19
2.13
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
NH
F

6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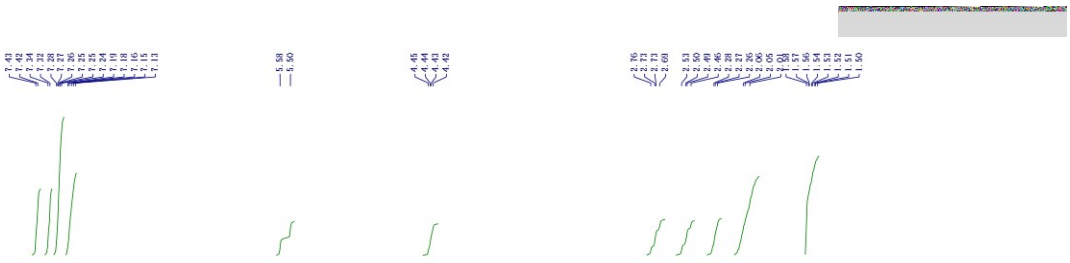

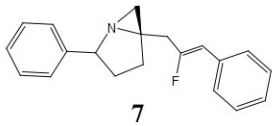

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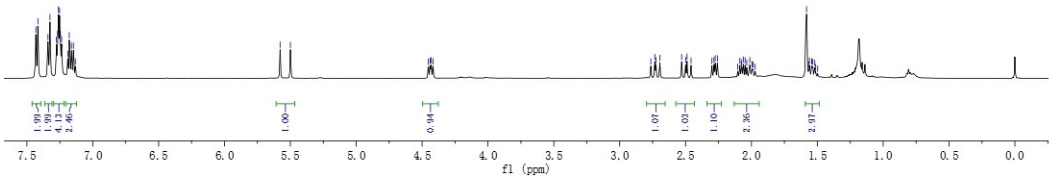

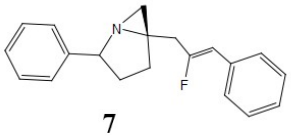

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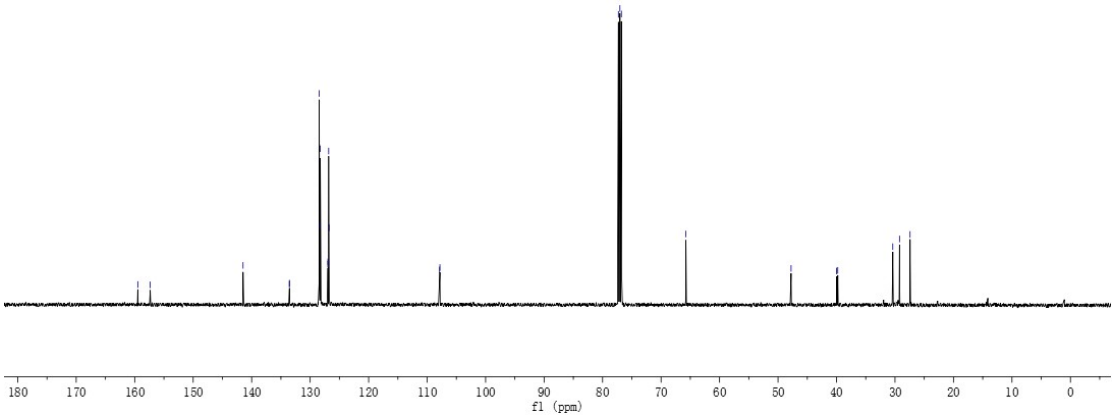
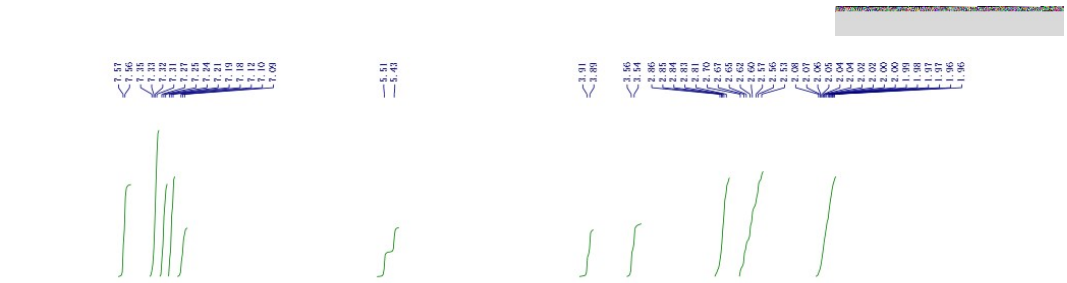
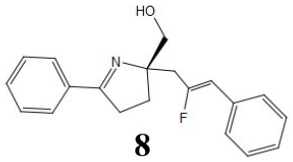
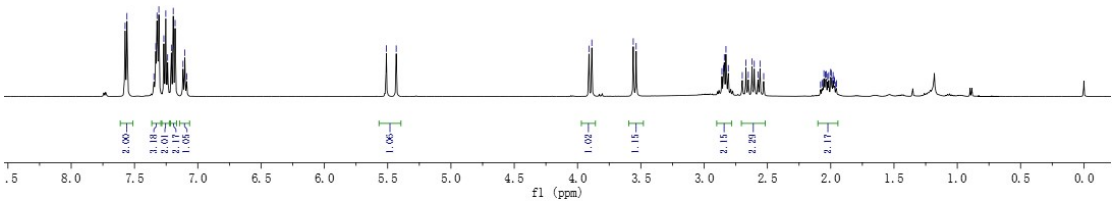





HO
N
F

8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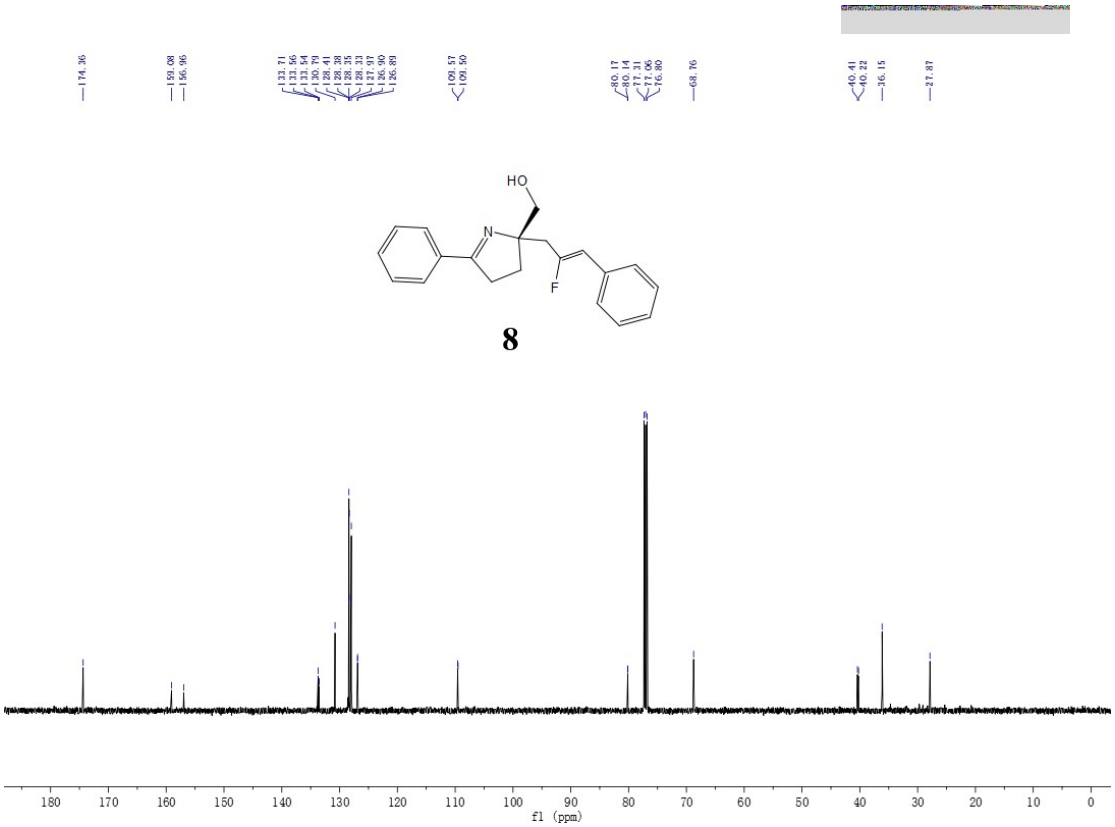
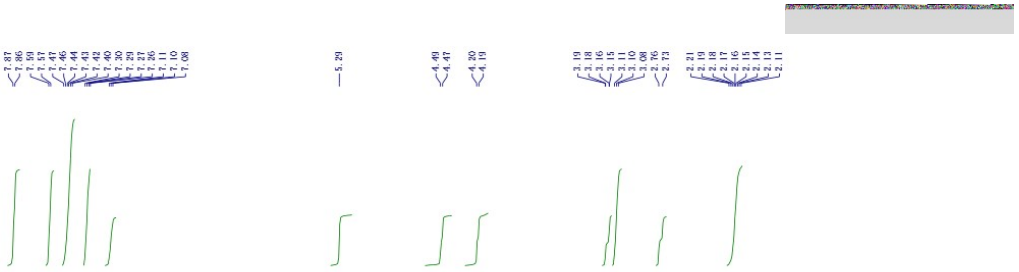
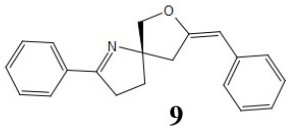


HO
N
F

8

f1 (ppm)





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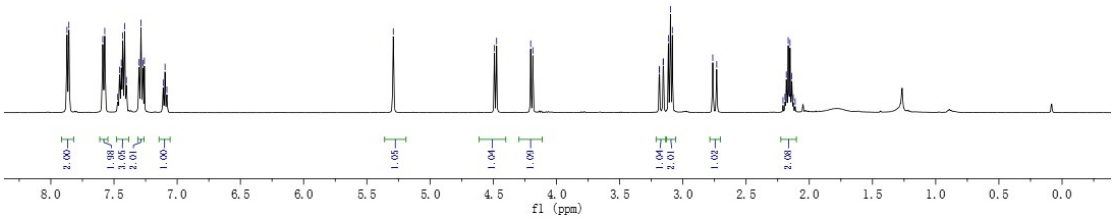

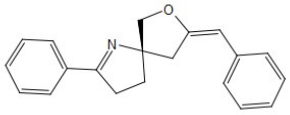

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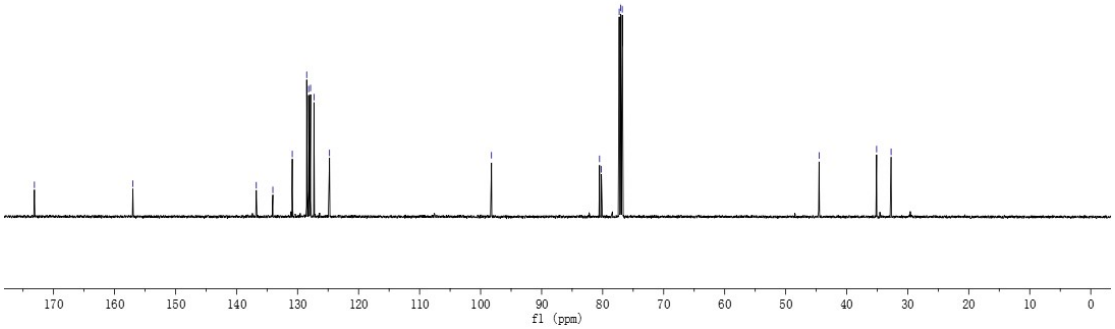
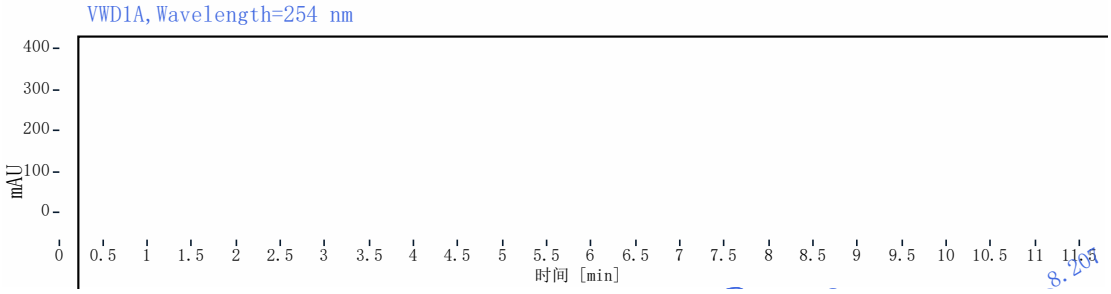
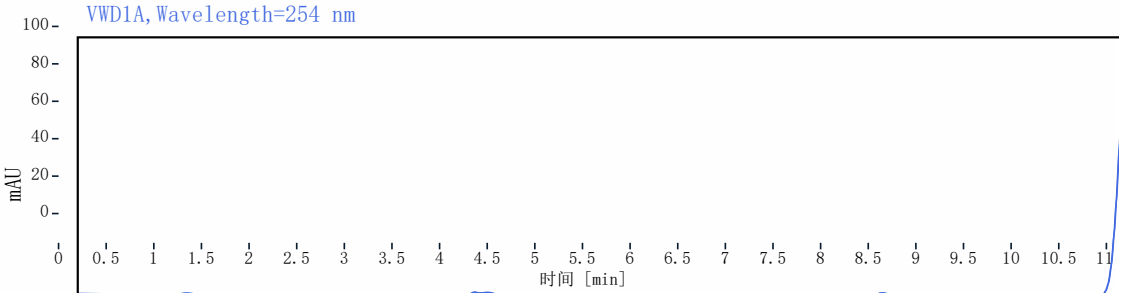


VII. Copies of HPLC data for Products

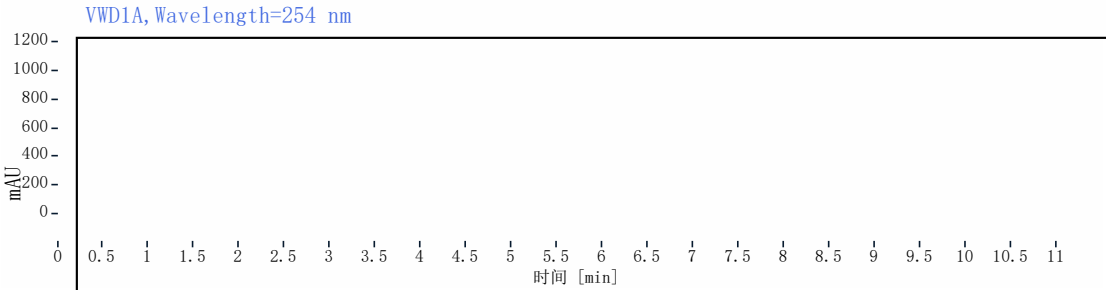


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.207	VWD1A, Wavelength=254 nm	0.159	56.4	5.5	1.03
10.203	VWD1A, Wavelength=254 nm	1.630	5403.0	418.6	98.97

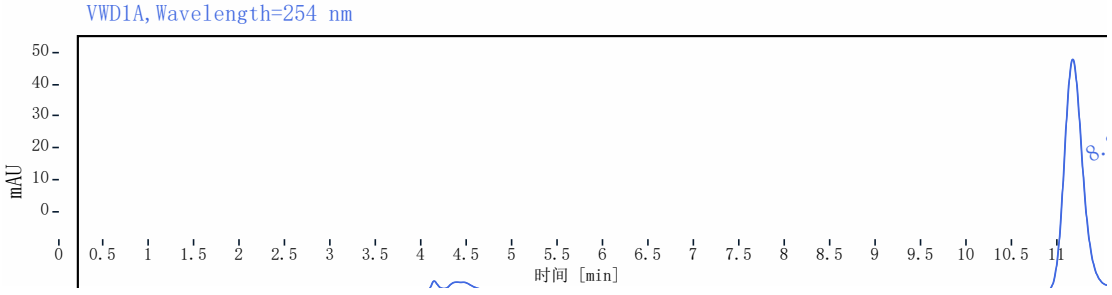


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.250	VWD1A, Wavelength=254 nm	1.148	967.8	93.7	50.74
10.201	VWD1A, Wavelength=254 nm	1.167	939.6	72.3	49.26

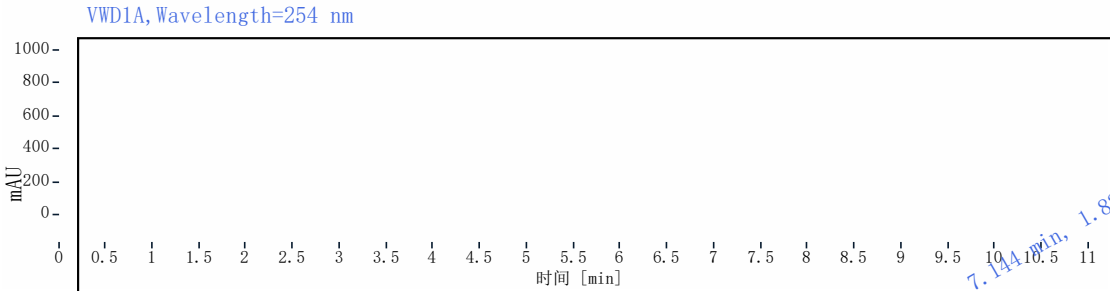
Scale-up synthesis of 3a



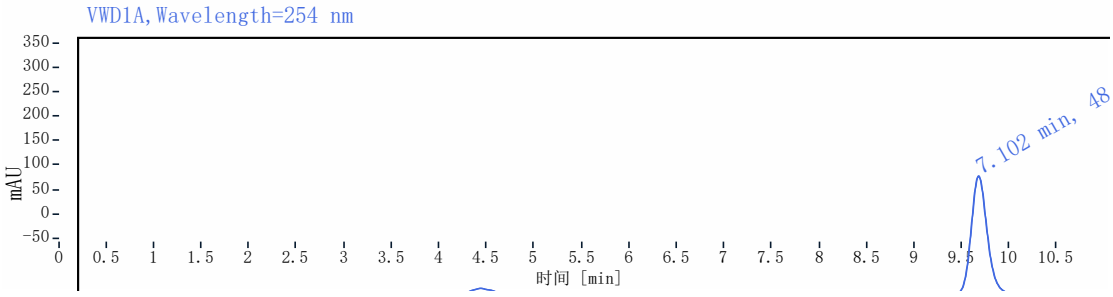
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
10.200	VWD1A,Wavelength=254 nm	1.400	16033.8	1197.3	99.16



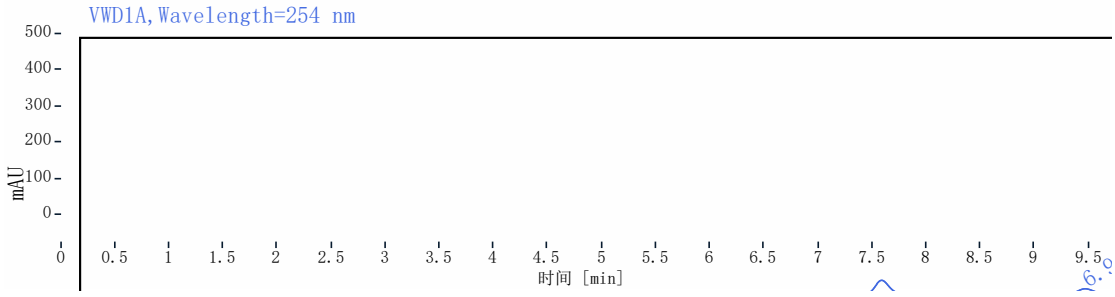
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.211	VWD1A,Wavelength=254 nm	0.536	577.8	53.7	50.05
10.189	VWD1A,Wavelength=254 nm	1.277	576.7	43.4	49.95



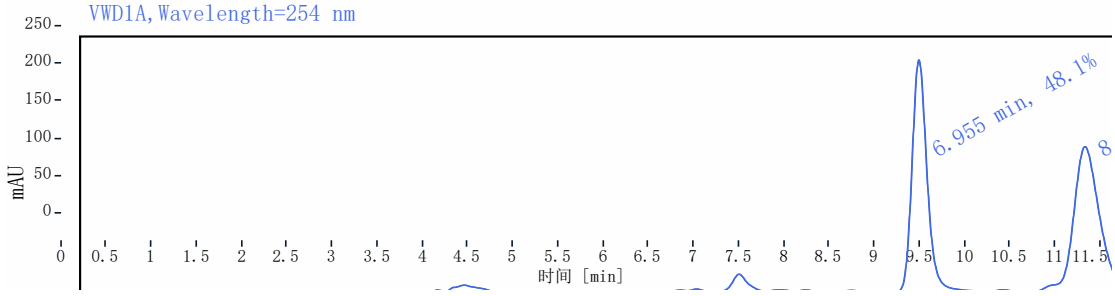
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.144	VWD1A, Wavelength=254 nm	0.357	93.4	10.2	1.82
8.925	VWD1A, Wavelength=254 nm	1.133	5048.6	1044.5	98.18



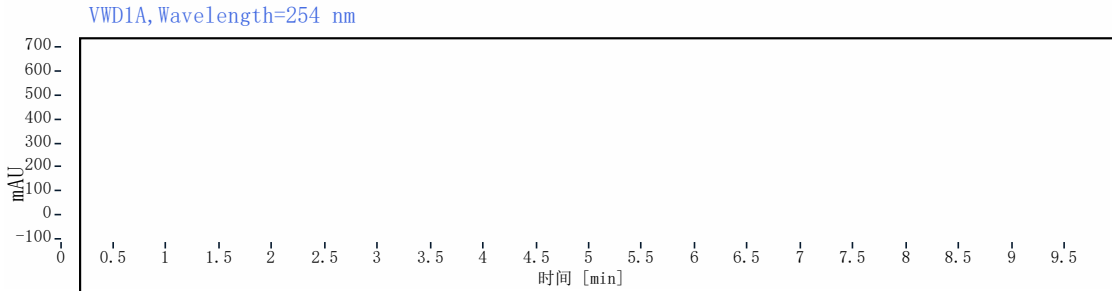
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.102	VWD1A, Wavelength=254 nm	0.586	1566.6	179.1	48.50
8.878	VWD1A, Wavelength=254 nm	0.760	1663.7	353.9	51.50



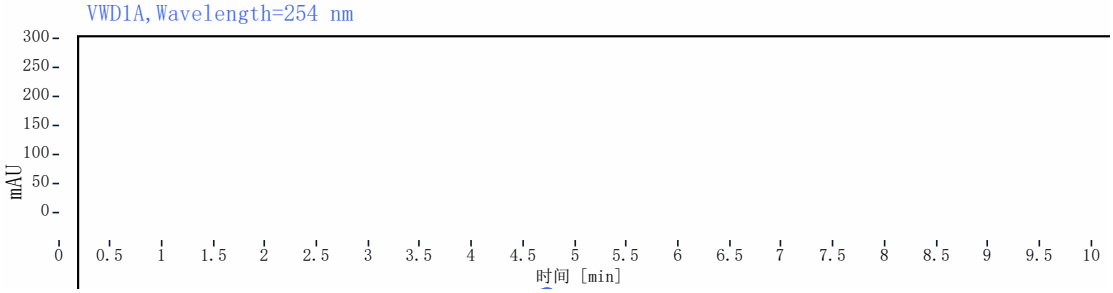
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.966	VWD1A, Wavelength=254 nm	0.353	97.5	11.5	1.44
8.340	VWD1A, Wavelength=254 nm	0.912	6670.9	474.3	98.56



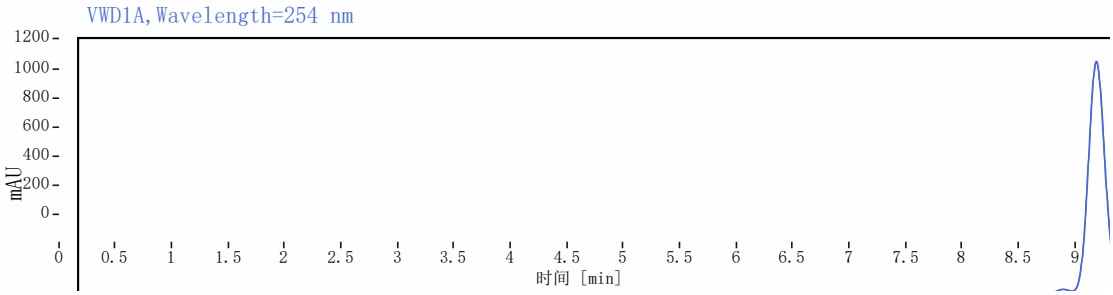
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.955	VWD1A, Wavelength=254 nm	0.794	1994.6	228.6	48.10
8.333	VWD1A, Wavelength=254 nm	0.971	2152.5	143.0	51.90



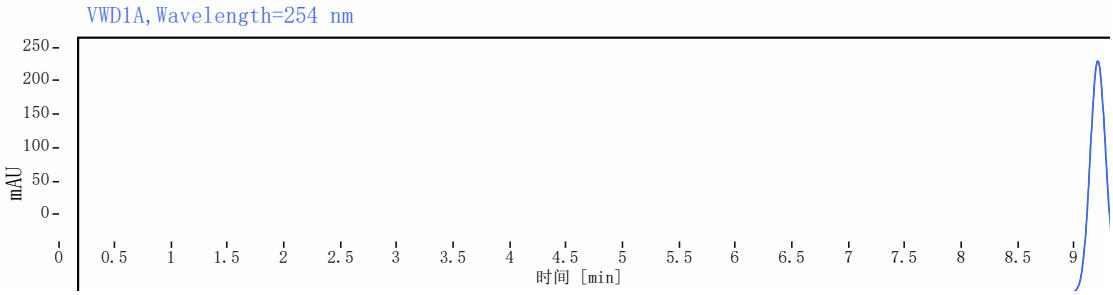
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.854	VWD1A,Wavelength=254 nm	1.163	6902.3	717.6	98.61
8.739	VWD1A,Wavelength=254 nm	0.520	96.9	9.1	1.39



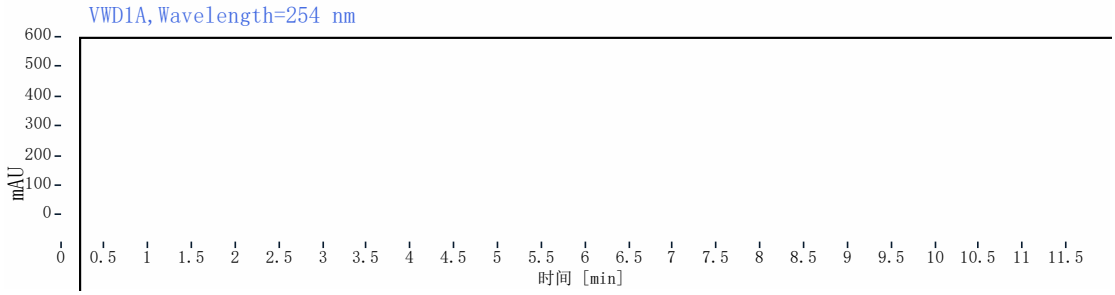
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.985	VWD1A,Wavelength=254 nm	0.670	2880.6	298.3	50.75
8.913	VWD1A,Wavelength=254 nm	1.233	2795.6	258.2	49.25



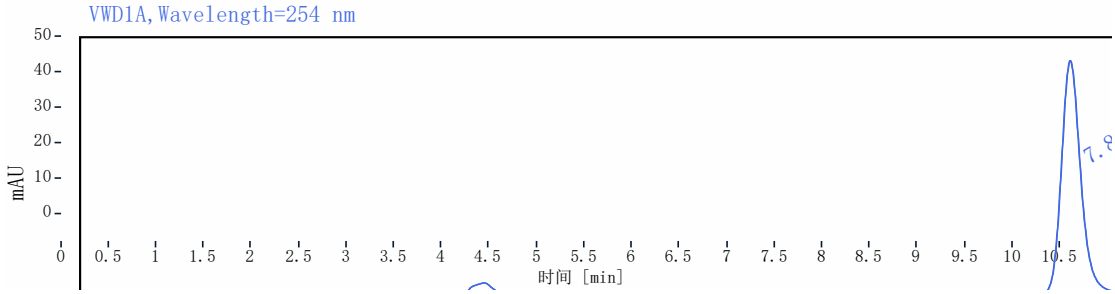
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.758	VWD1A,Wavelength=254 nm	0.605	9366.0	1180.6	98.53
8.012	VWD1A,Wavelength=254 nm	0.555	139.5	11.7	1.47



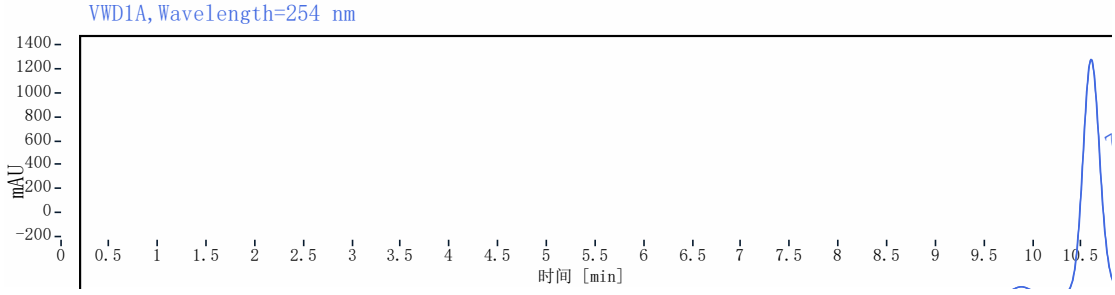
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.775	VWD1A,Wavelength=254 nm	0.712	2031.1	258.3	50.15
8.064	VWD1A,Wavelength=254 nm	0.706	2018.7	198.2	49.85



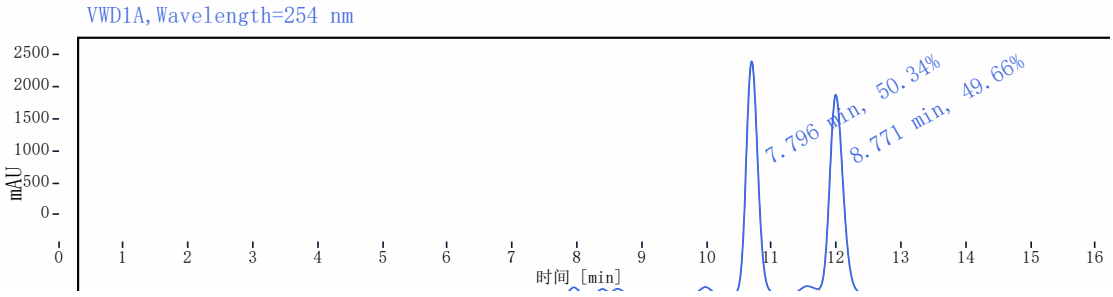
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
9.710	VWD1A,Wavelength=254 nm	1.148	7480.4	581.2	99.04



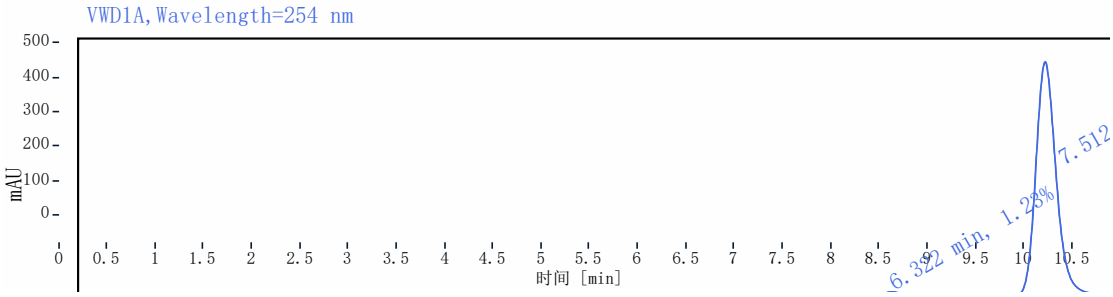
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.801	VWD1A,Wavelength=254 nm	0.664	507.1	48.7	50.15
9.714	VWD1A,Wavelength=254 nm	0.652	504.0	40.1	49.85



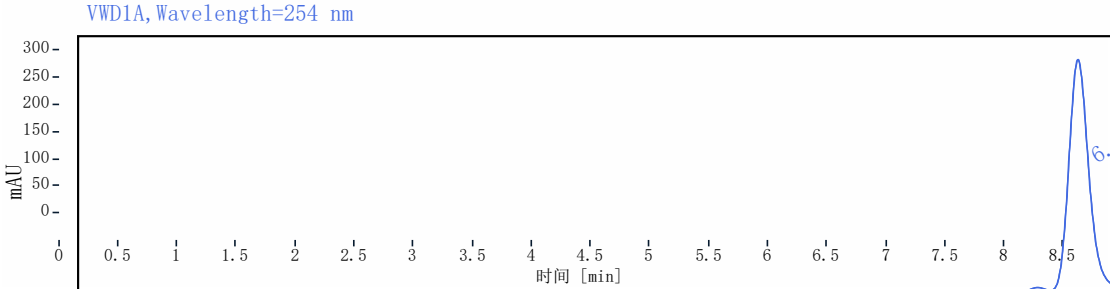
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.800	VWD1A,Wavelength=254 nm	0.198	13638.9	1348.8	99.17



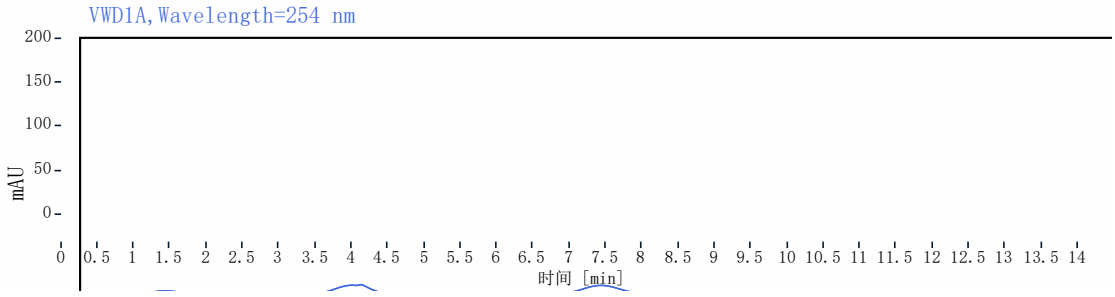
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.796	VWD1A,Wavelength=254 nm	0.184	25662.5	2487.1	50.34
8.771	VWD1A,Wavelength=254 nm	0.189	25319.5	2234.8	49.66



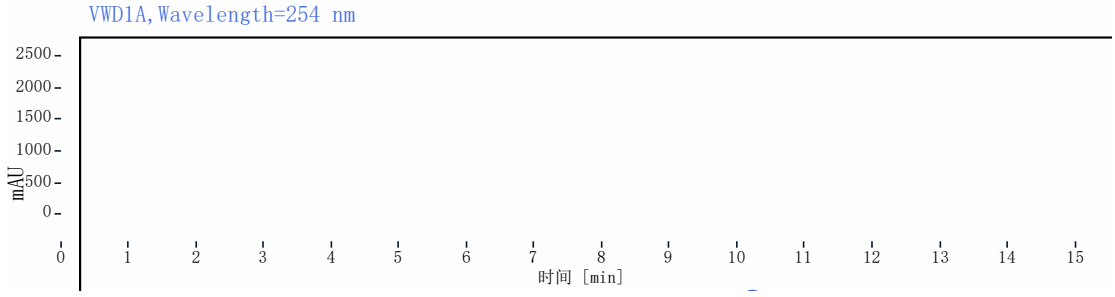
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.322	VWD1A,Wavelength=254 nm	0.518	68.5	7.8	1.23
7.512	VWD1A,Wavelength=254 nm	1.309	5496.3	500.9	98.77



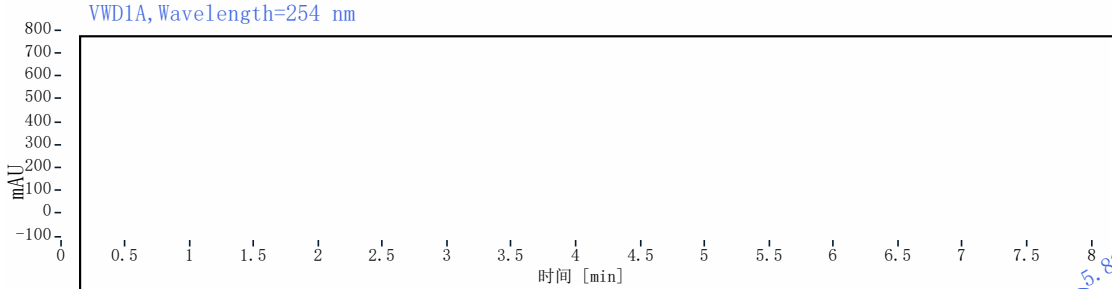
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.343	VWD1A,Wavelength=254 nm	0.970	2885.7	317.9	48.84
7.544	VWD1A,Wavelength=254 nm	0.865	3022.3	271.5	51.16



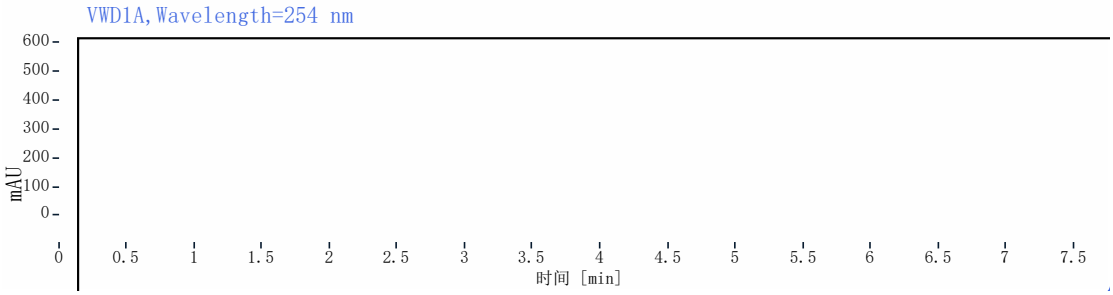
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
12.006	VWD1A,Wavelength=254 nm	0.232	2939.1	195.7	97.98
13.249	VWD1A,Wavelength=254 nm	0.912	60.7	3.7	2.02



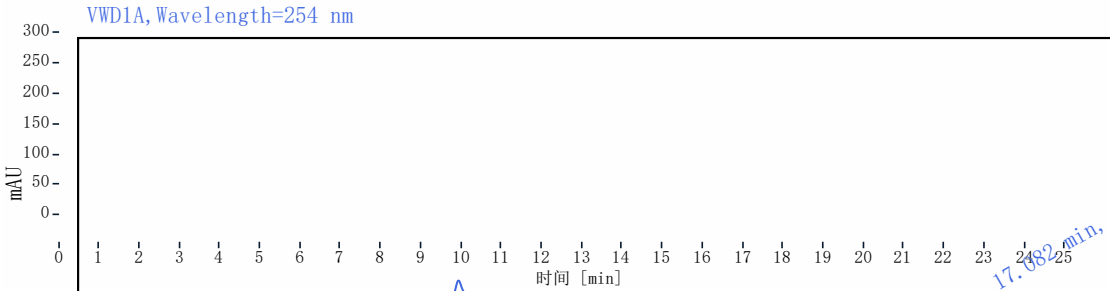
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
12.144	VWD1A,Wavelength=254 nm	1.239	41900.3	2717.6	50.78
13.385	VWD1A,Wavelength=254 nm	1.474	40610.1	2312.7	49.22



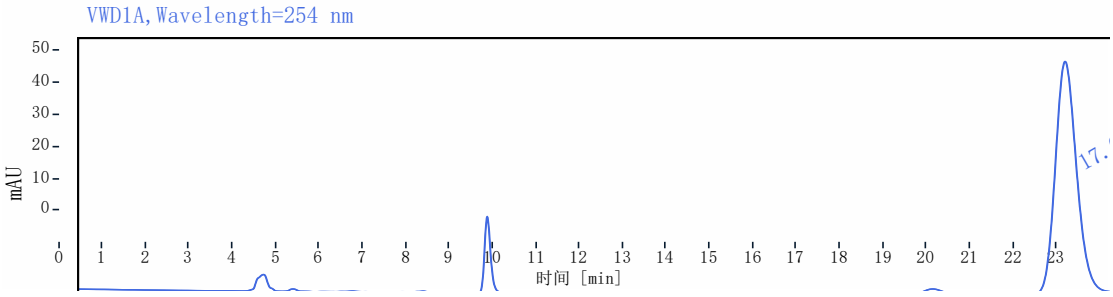
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.836	VWD1A,Wavelength=254 nm	0.828	115.6	14.2	1.62
6.835	VWD1A,Wavelength=254 nm	1.177	7035.3	754.5	98.38



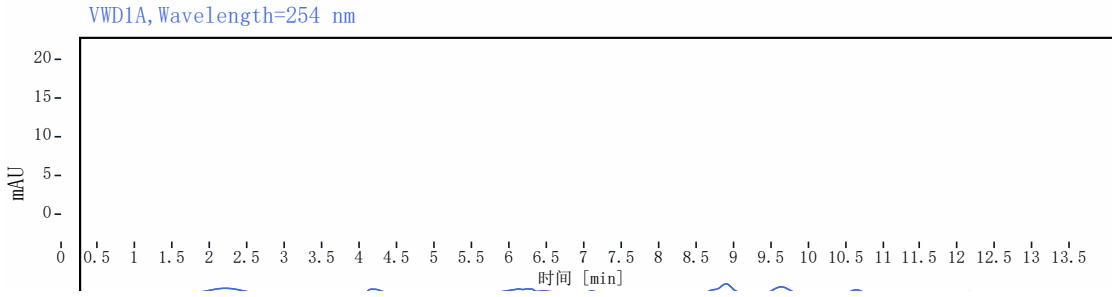
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.834	VWD1A,Wavelength=254 nm	0.933	4594.9	601.4	50.61
6.836	VWD1A,Wavelength=254 nm	0.540	4483.5	491.2	49.39



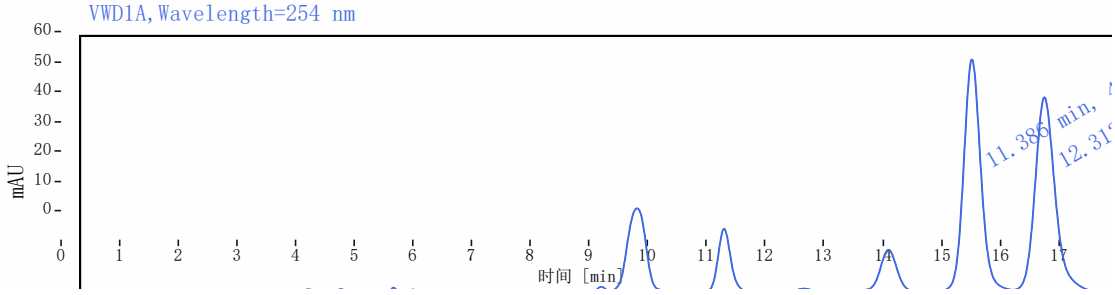
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
17.082	VWD1A,Wavelength=254 nm	1.503	102.6	3.7	1.09
21.734	VWD1A,Wavelength=254 nm	4.252	9302.1	283.9	98.91



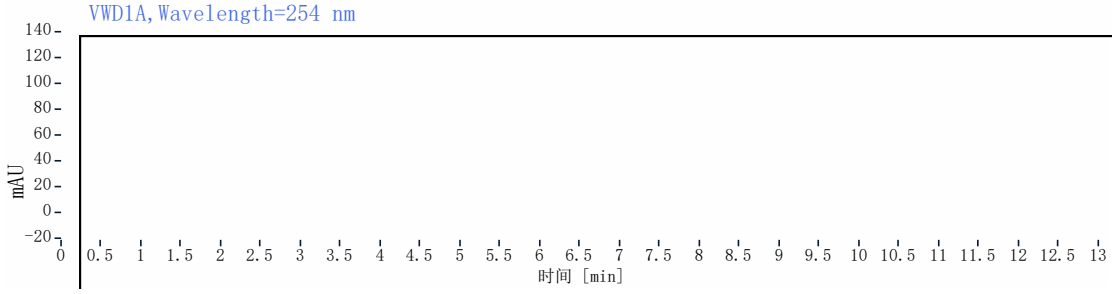
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
17.059	VWD1A,Wavelength=254 nm	1.608	1390.5	53.9	49.93
21.820	VWD1A,Wavelength=254 nm	2.645	1394.1	42.3	50.07



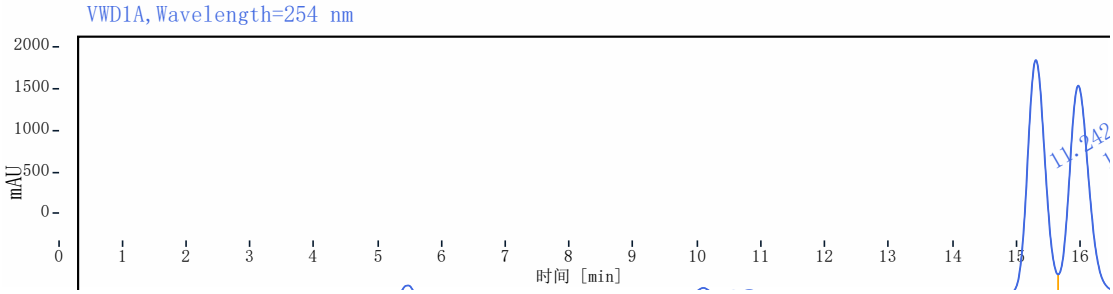
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.371	VWD1A,Wavelength=254 nm	0.256	325.3	21.6	97.32
12.287	VWD1A,Wavelength=254 nm	0.239	9.0	0.6	2.68



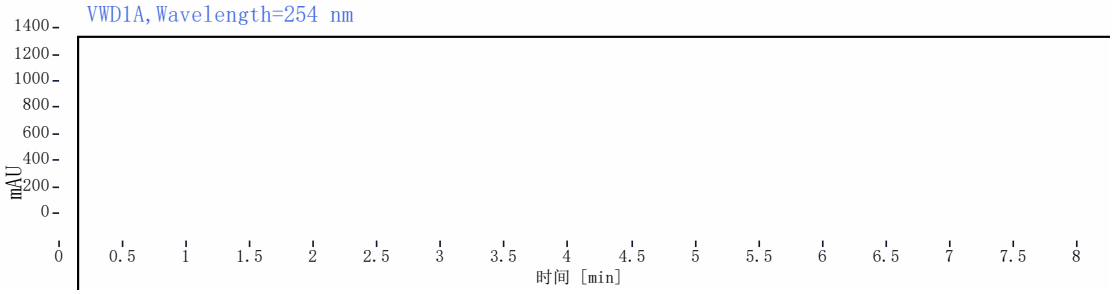
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.386	VWD1A,Wavelength=254 nm	0.999	885.5	56.9	49.99
12.312	VWD1A,Wavelength=254 nm	1.803	885.7	47.8	50.01



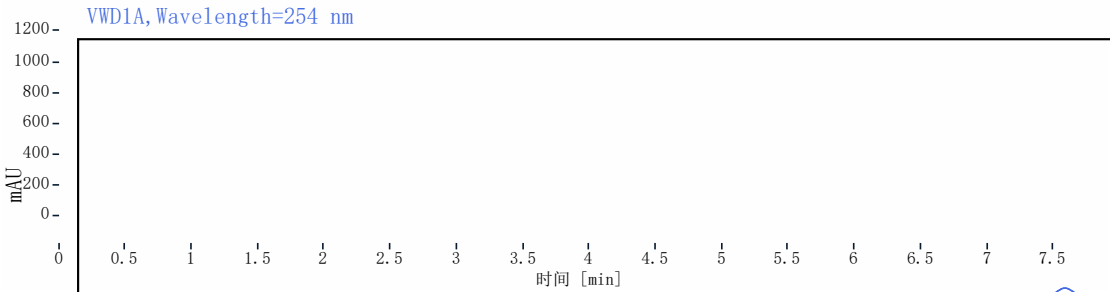
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.260	VWD1A,Wavelength=254 nm	0.730	1867.7	132.9	98.34
11.766	VWD1A,Wavelength=254 nm	0.389	31.6	2.2	1.66



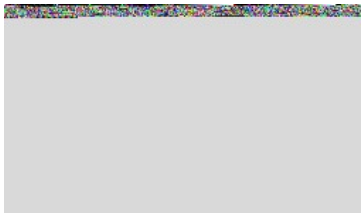
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.242	VWD1A,Wavelength=254 nm	0.661	29852.7	2081.5	50.08
11.739	VWD1A,Wavelength=254 nm	1.358	29762.0	1854.0	49.92

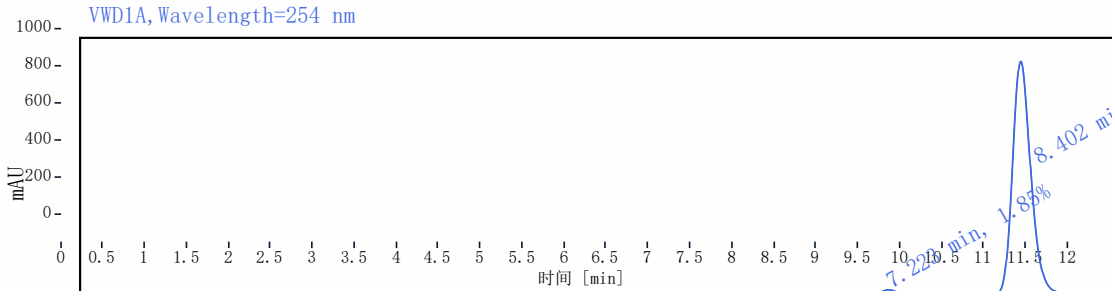


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.686	VWD1A,Wavelength=254 nm	0.395	259.3	34.1	2.07
7.095	VWD1A,Wavelength=254 nm	0.973	12263.0	1304.1	97.93

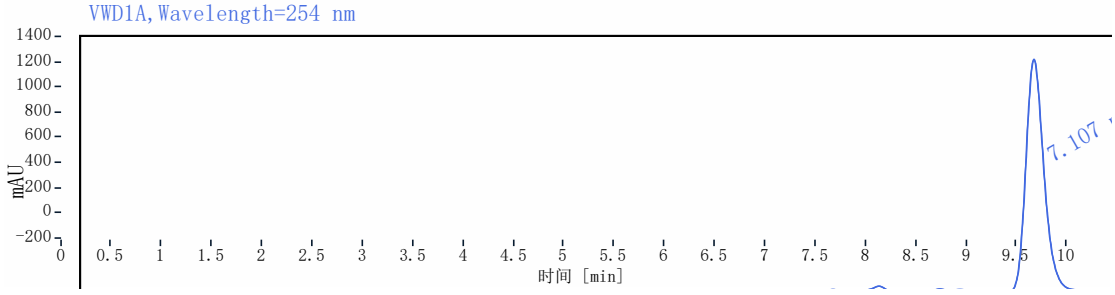


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.681	VWD1A,Wavelength=254 nm	0.430	8600.1	1116.6	49.17
7.098	VWD1A,Wavelength=254 nm	0.515	8888.9	939.3	50.83

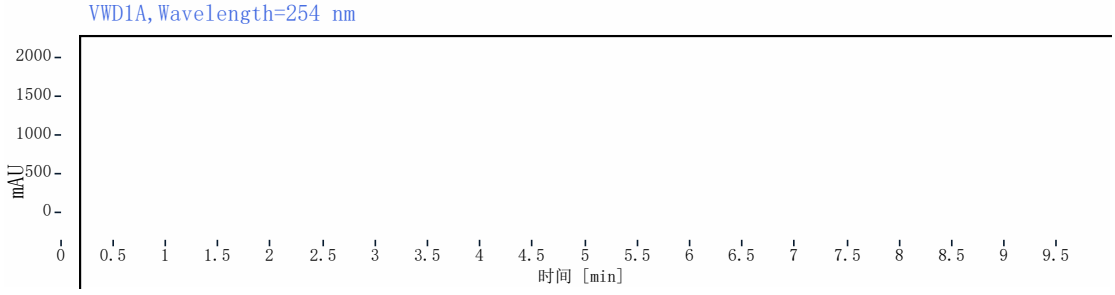




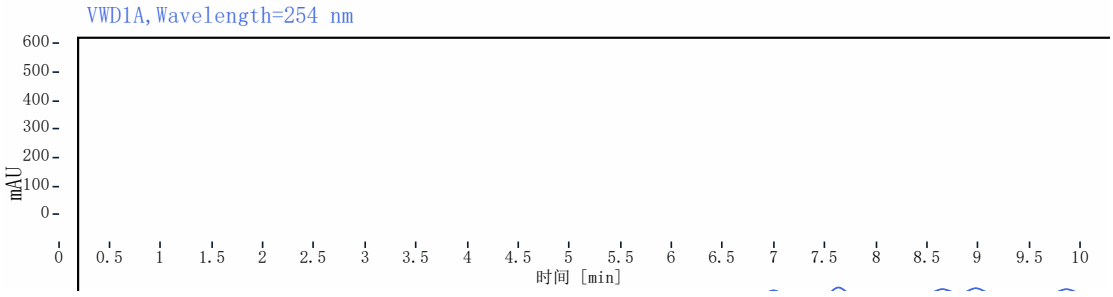
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.223	VWD1A,Wavelength=254 nm	0.808	200.4	19.6	1.85
8.402	VWD1A,Wavelength=254 nm	1.665	10640.7	927.9	98.15



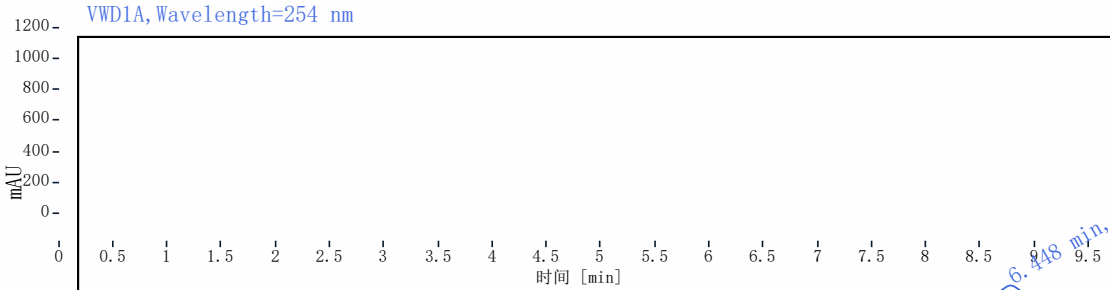
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.107	VWD1A,Wavelength=254 nm	0.791	12950.5	1368.9	49.69
8.242	VWD1A,Wavelength=254 nm	1.067	13110.1	1179.9	50.31



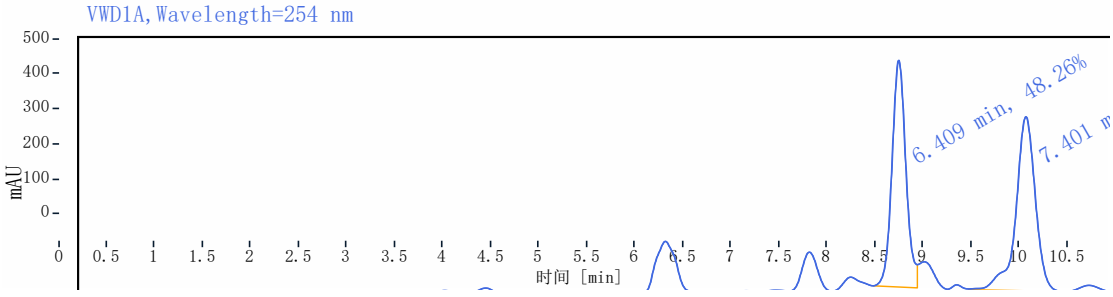
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.781	VWD1A,Wavelength=254 nm	1.094	21353.3	2220.2	99.19



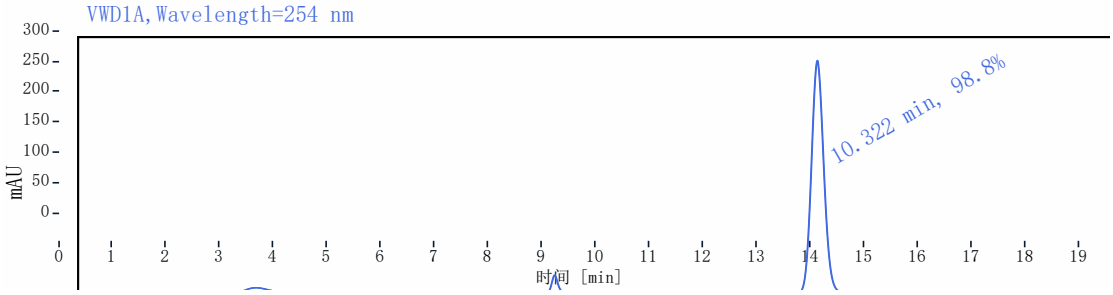
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
7.784	VWD1A,Wavelength=254 nm	0.876	5792.2	606.3	50.50
8.652	VWD1A,Wavelength=254 nm	0.678	5678.5	513.5	49.50



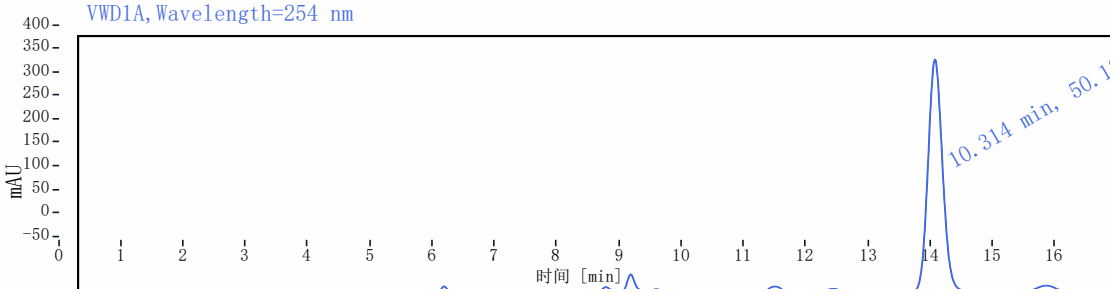
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.448	VWD1A,Wavelength=254 nm	0.378	287.3	39.4	2.57
7.428	VWD1A,Wavelength=254 nm	1.149	10878.7	1111.8	97.43



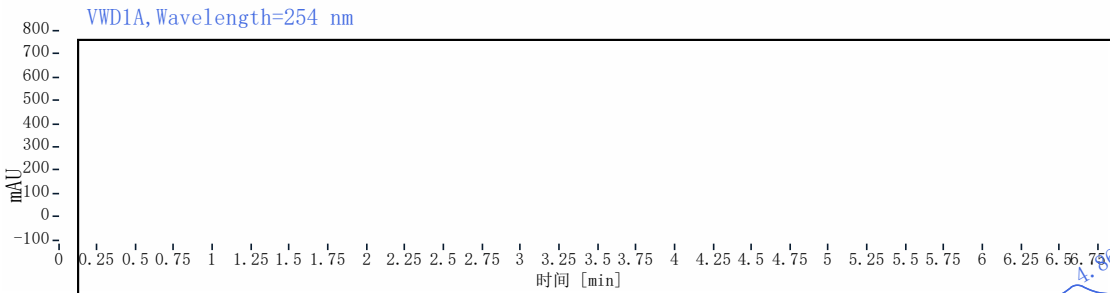
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.409	VWD1A,Wavelength=254 nm	0.346	3632.8	478.4	48.26
7.401	VWD1A,Wavelength=254 nm	0.745	3894.6	367.4	51.74



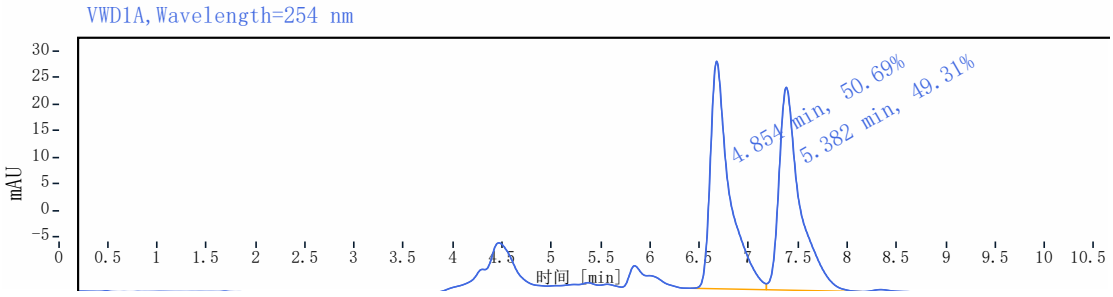
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
10.322	VWD1A,Wavelength=254 nm	2.553	3483.6	283.0	98.80
15.016	VWD1A,Wavelength=254 nm	1.135	42.5	1.7	1.20



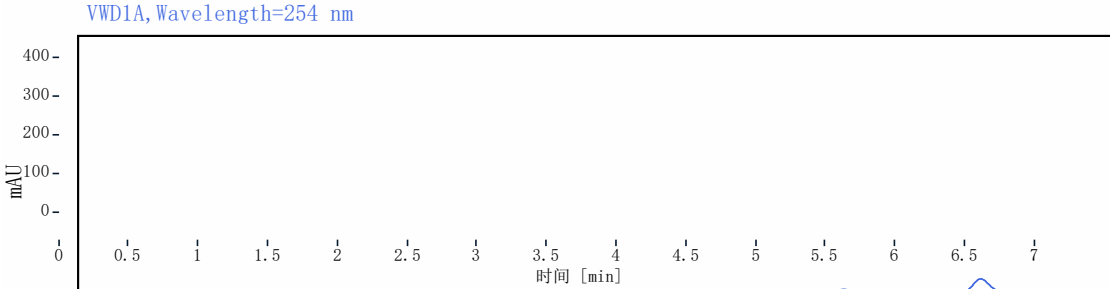
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
10.314	VWD1A,Wavelength=254 nm	0.939	4504.0	368.1	50.18
14.723	VWD1A,Wavelength=254 nm	2.048	4471.8	168.1	49.82



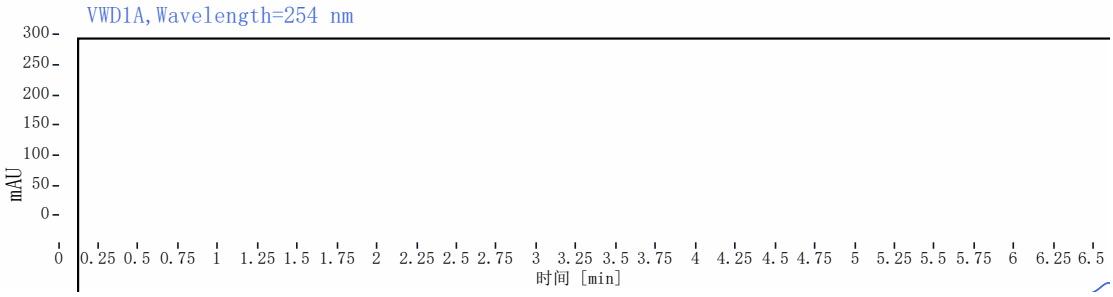
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
4.863	VWD1A,Wavelength=254 nm	0.510	358.6	36.5	4.24
5.389	VWD1A,Wavelength=254 nm	1.417	8103.2	741.3	95.76



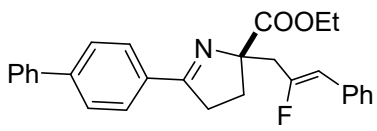
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
4.854	VWD1A,Wavelength=254 nm	0.575	323.7	31.8	50.69
5.382	VWD1A,Wavelength=254 nm	0.725	314.8	28.3	49.31



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.749	VWD1A,Wavelength=254 nm	0.993	3243.8	443.8	99.08



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.476	VWD1A,Wavelength=254 nm	0.345	2020.3	286.0	50.75
5.748	VWD1A,Wavelength=254 nm	0.525	1960.3	268.4	49.25



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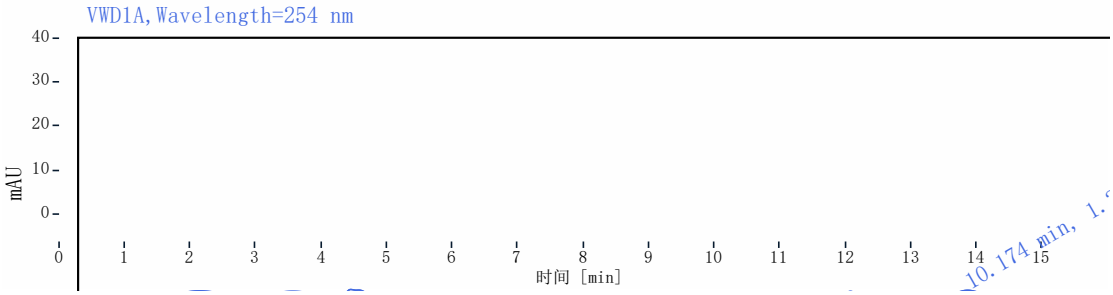
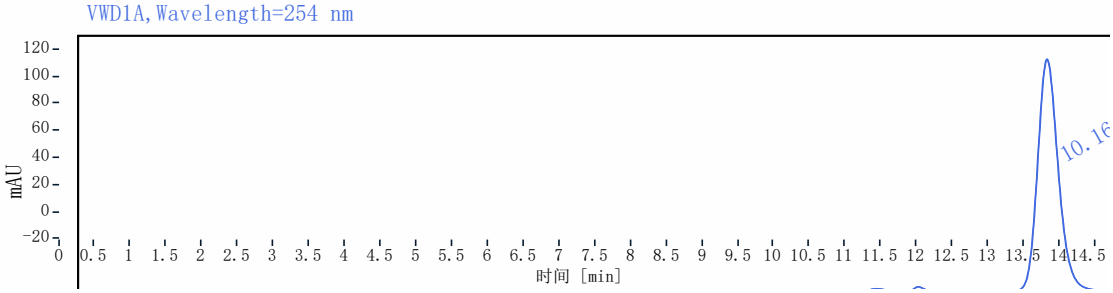
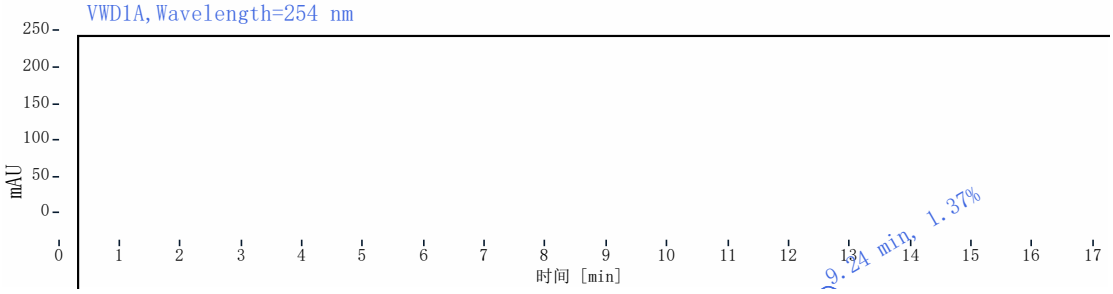


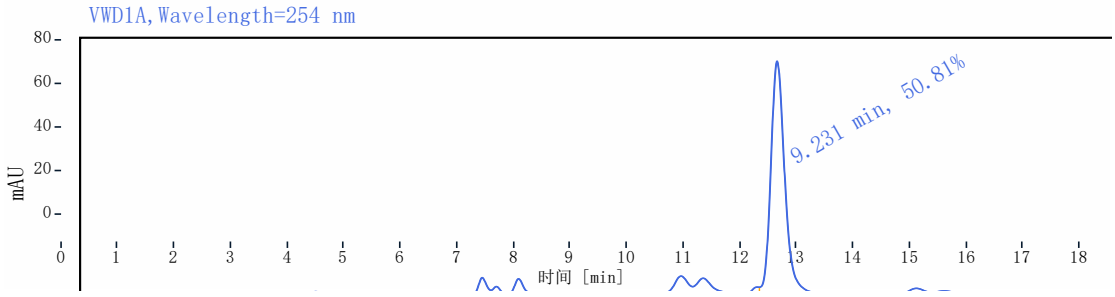
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
10.174	VWD1A,Wavelength=254 nm	0.930	9.7	0.6	1.25
13.118	VWD1A,Wavelength=254 nm	0.302	770.5	39.2	98.75



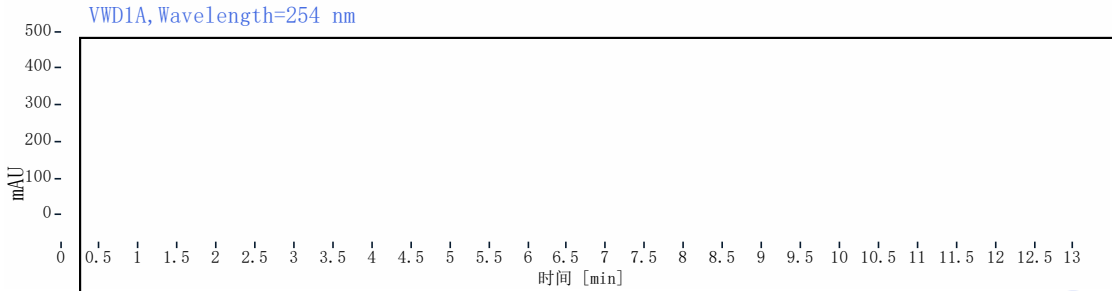
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
10.162	VWD1A,Wavelength=254 nm	1.234	1938.1	127.2	50.40
13.137	VWD1A,Wavelength=254 nm	0.301	1907.6	97.5	49.60



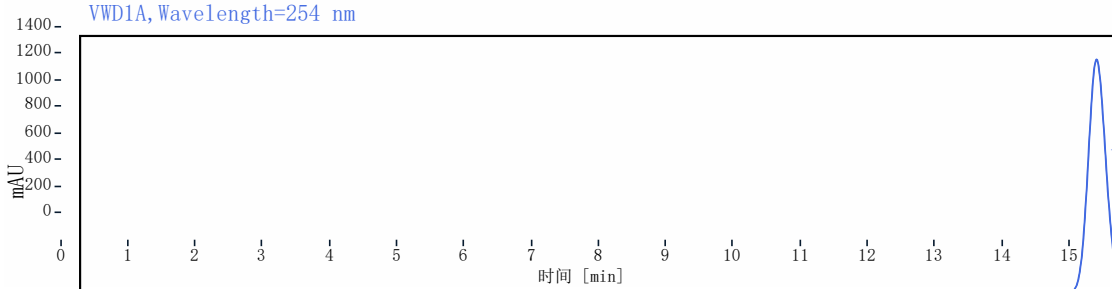
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
9.240	VWD1A,Wavelength=254 nm	0.596	74.2	6.1	1.37
15.394	VWD1A,Wavelength=254 nm	2.000	5334.1	237.4	98.63



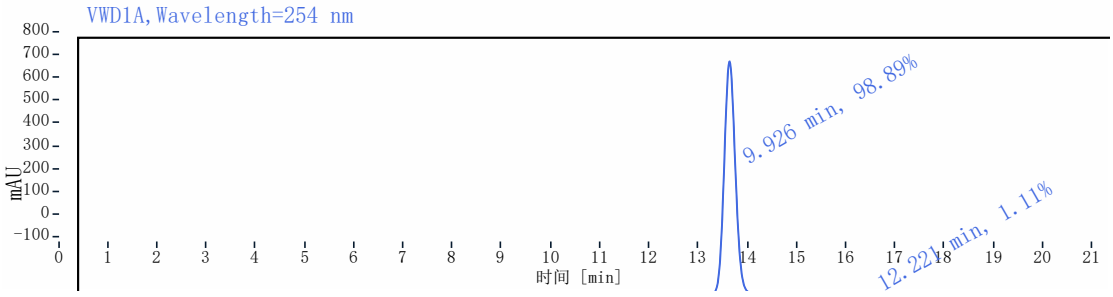
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
9.231	VWD1A,Wavelength=254 nm	1.149	1007.6	78.8	50.81
15.386	VWD1A,Wavelength=254 nm	1.248	975.5	43.9	49.19



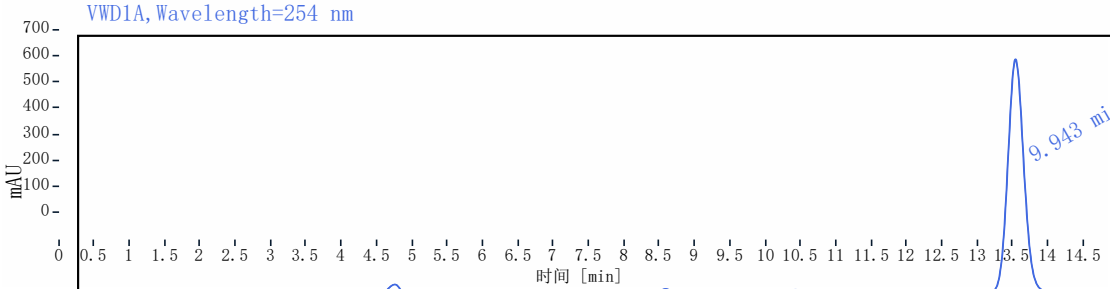
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.276	VWD1A,Wavelength=254 nm	0.246	6612.5	463.6	97.13
12.075	VWD1A,Wavelength=254 nm	0.271	195.3	11.9	2.87



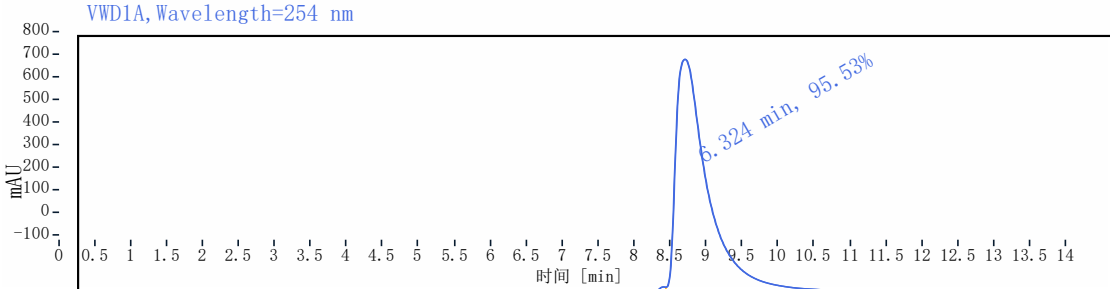
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
11.340	VWD1A,Wavelength=254 nm	0.824	18160.8	1279.1	49.77
12.130	VWD1A,Wavelength=254 nm	1.292	18325.1	1141.8	50.23



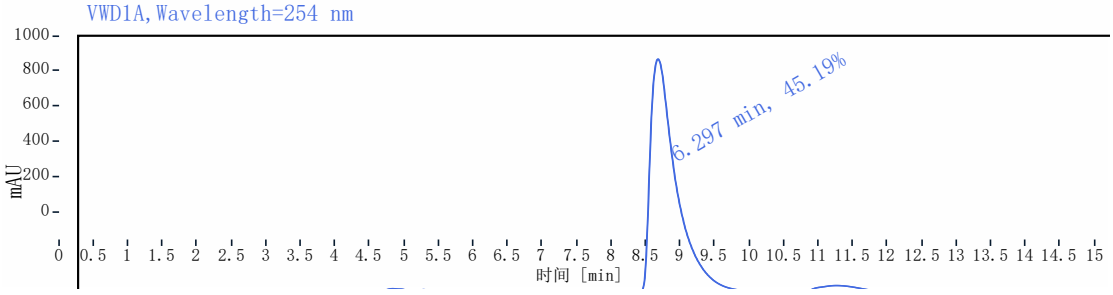
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
9.926	VWD1A,Wavelength=254 nm	1.720	9022.0	759.2	98.89
12.221	VWD1A,Wavelength=254 nm	0.752	101.5	6.6	1.11



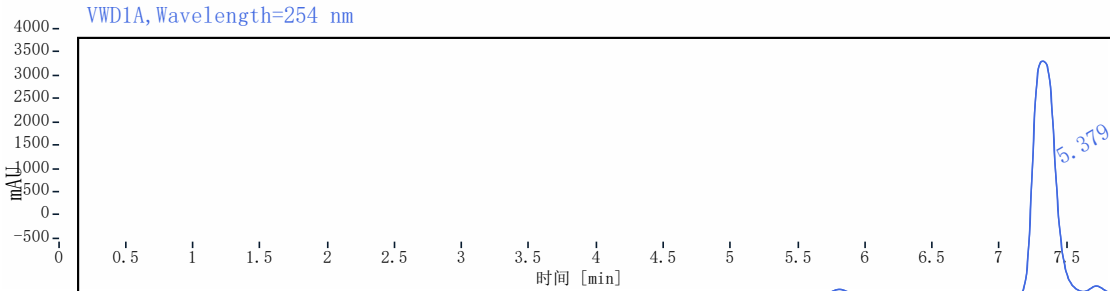
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
9.943	VWD1A,Wavelength=254 nm	1.522	7857.8	660.2	50.05
12.215	VWD1A,Wavelength=254 nm	0.855	7842.6	516.1	49.95



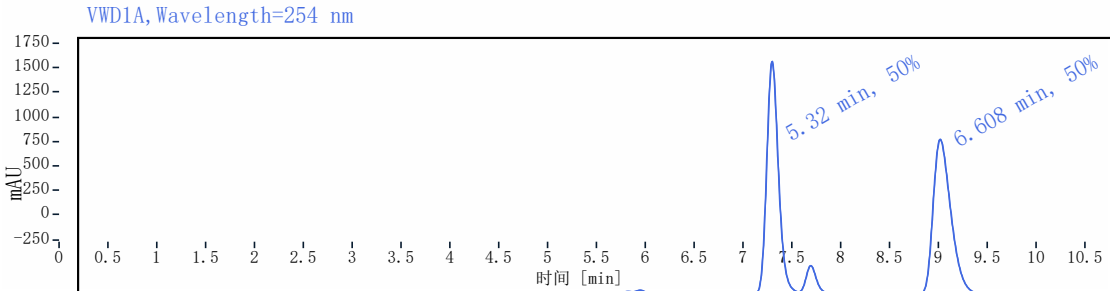
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.324	VWD1A,Wavelength=254 nm	3.441	18332.6	766.7	95.53
11.938	VWD1A,Wavelength=254 nm	1.570	858.6	28.7	4.47



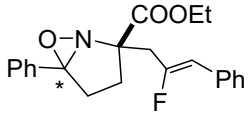
Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.297	VWD1A, Wavelength=254 nm	1.777	19302.6	974.8	45.19
11.516	VWD1A, Wavelength=254 nm	3.666	23407.1	810.7	54.81



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.379	VWD1A, Wavelength=254 nm	0.419	31790.6	3710.5	78.12
6.771	VWD1A, Wavelength=254 nm	1.120	8903.2	861.9	21.88



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.320	VWD1A, Wavelength=254 nm	0.364	11155.5	1760.3	50.00
6.608	VWD1A, Wavelength=254 nm	0.717	11156.9	1173.5	50.00



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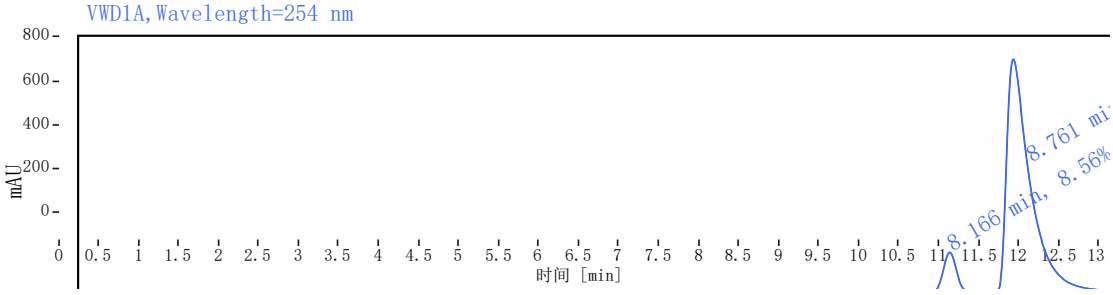
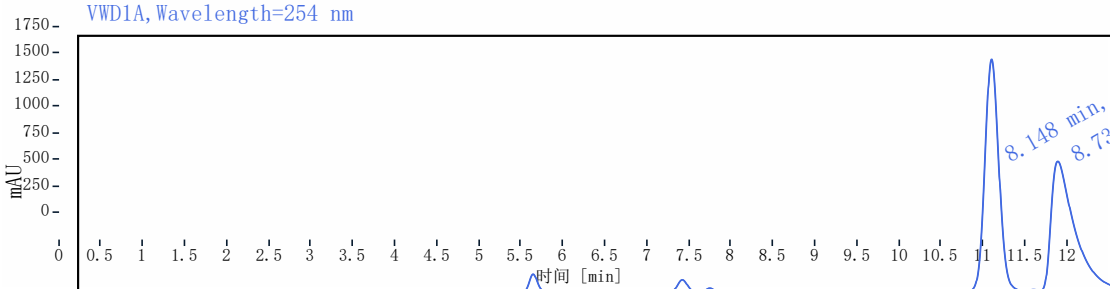
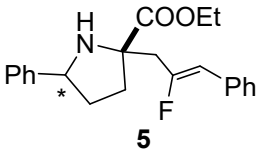


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.166	VWD1A,Wavelength=254 nm	0.457	1148.9	135.2	8.56
8.761	VWD1A,Wavelength=254 nm	1.982	12277.1	787.3	91.44



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.148	VWD1A,Wavelength=254 nm	0.506	13950.2	1611.9	50.59
8.739	VWD1A,Wavelength=254 nm	1.268	13623.0	902.2	49.41



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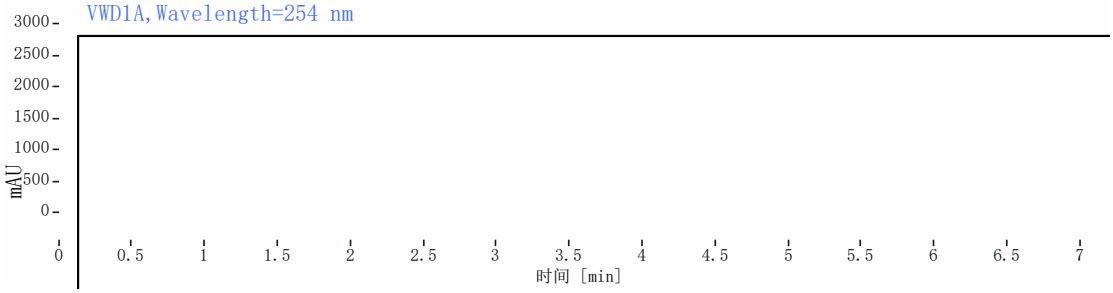
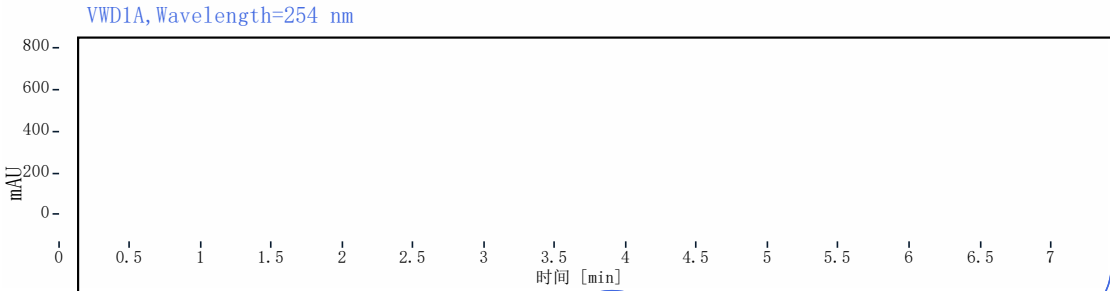
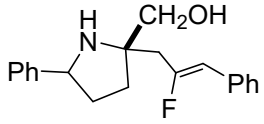


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.800	VWD1A,Wavelength=254 nm	0.492	19872.0	2746.0	99.52



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.544	VWD1A,Wavelength=254 nm	0.315	5439.3	830.0	49.03
5.803	VWD1A,Wavelength=254 nm	0.507	5653.8	797.1	50.97



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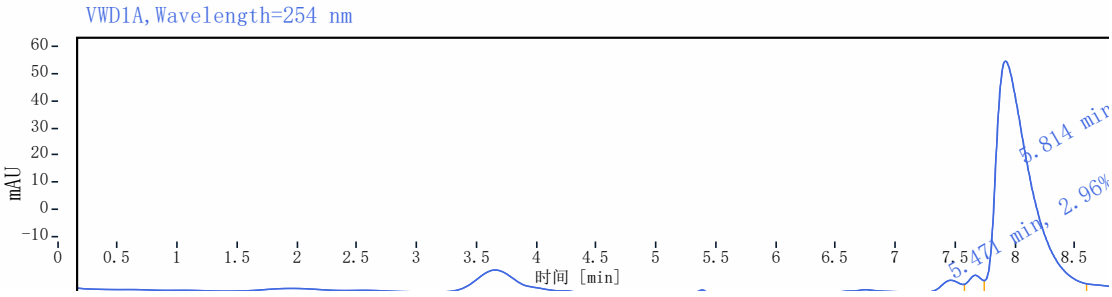
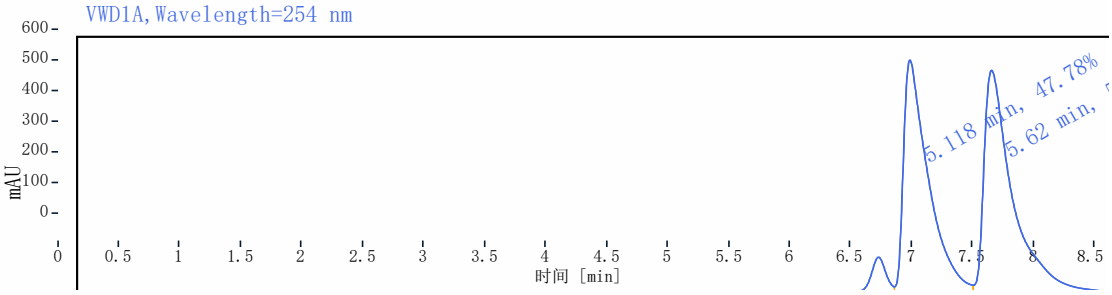
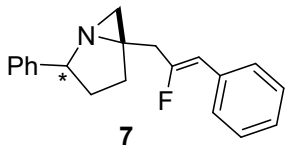


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.471	VWD1A,Wavelength=254 nm	0.126	28.4	3.4	2.96
5.814	VWD1A,Wavelength=254 nm	0.220	931.4	62.8	97.04



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.118	VWD1A,Wavelength=254 nm	0.485	5993.2	560.3	47.78
5.620	VWD1A,Wavelength=254 nm	1.204	6549.1	535.1	52.22



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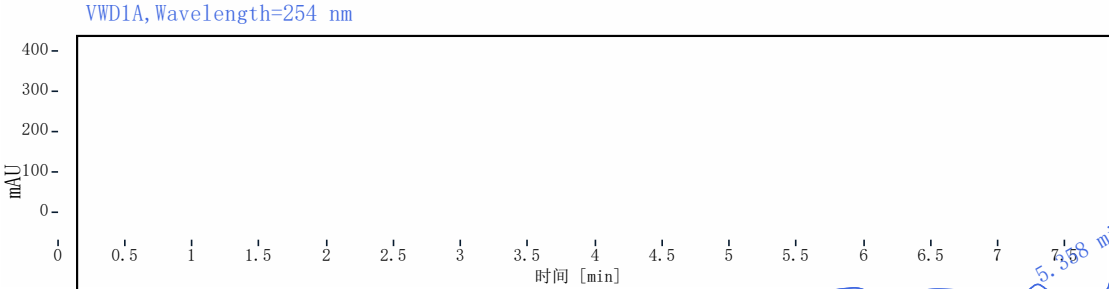
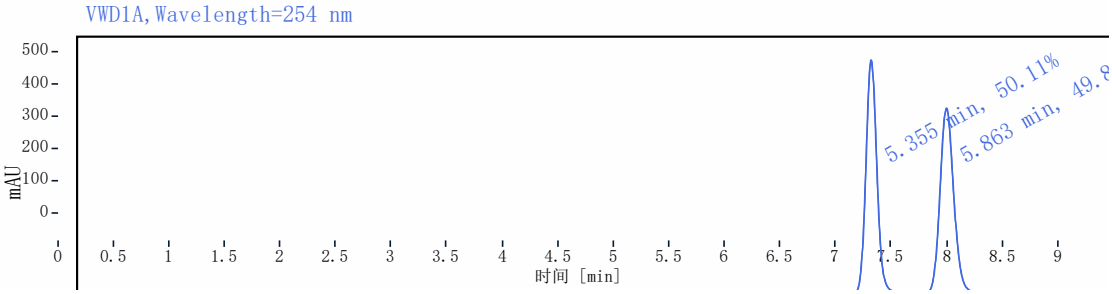
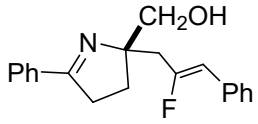


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.358	VWD1A,Wavelength=254 nm	0.263	73.7	14.5	2.59
5.858	VWD1A,Wavelength=254 nm	0.830	2767.0	428.5	97.41



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
5.355	VWD1A,Wavelength=254 nm	0.483	2757.7	535.4	50.11
5.863	VWD1A,Wavelength=254 nm	0.821	2745.4	424.5	49.89



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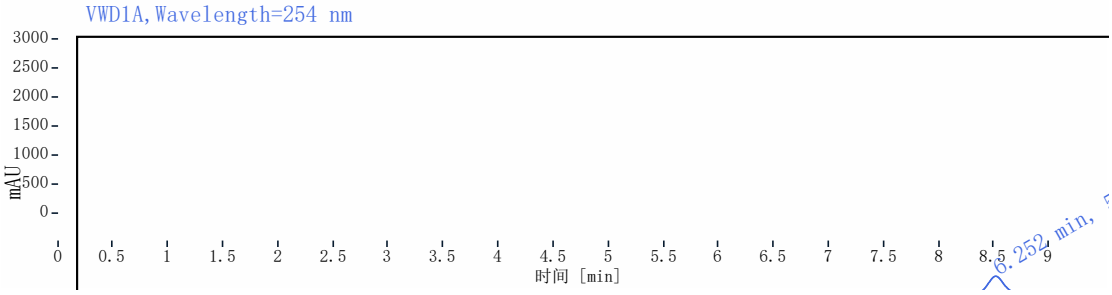
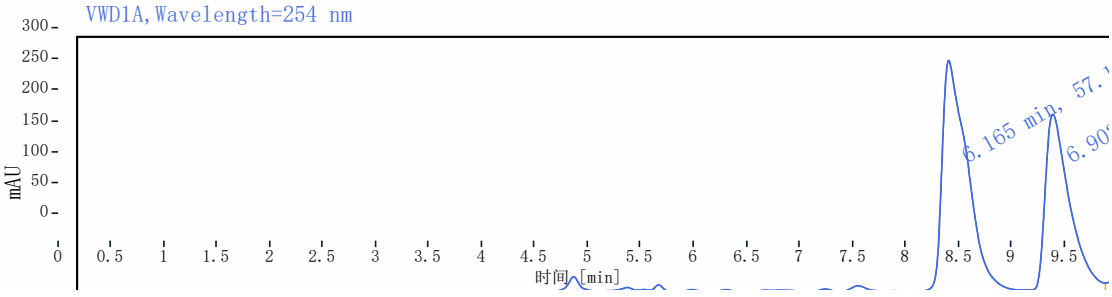
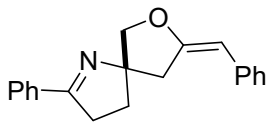


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.252	VWD1A,Wavelength=254 nm	0.829	1729.4	221.5	5.45
7.360	VWD1A,Wavelength=254 nm	1.601	29990.8	2969.8	94.55



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
6.165	VWD1A,Wavelength=254 nm	0.761	3441.9	276.6	57.17
6.902	VWD1A,Wavelength=254 nm	0.529	2578.5	212.0	42.83



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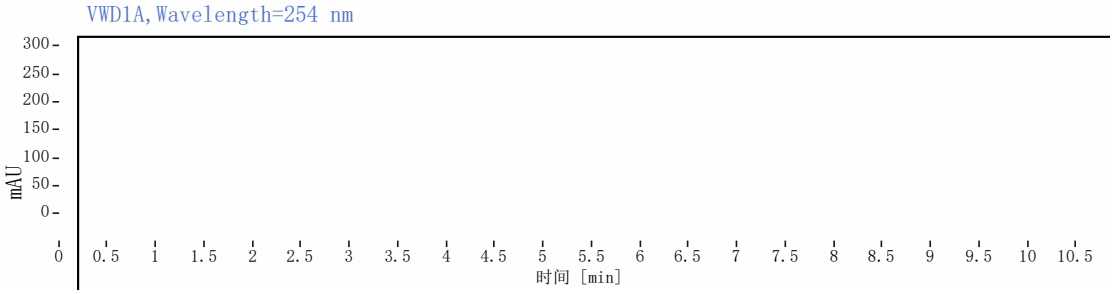
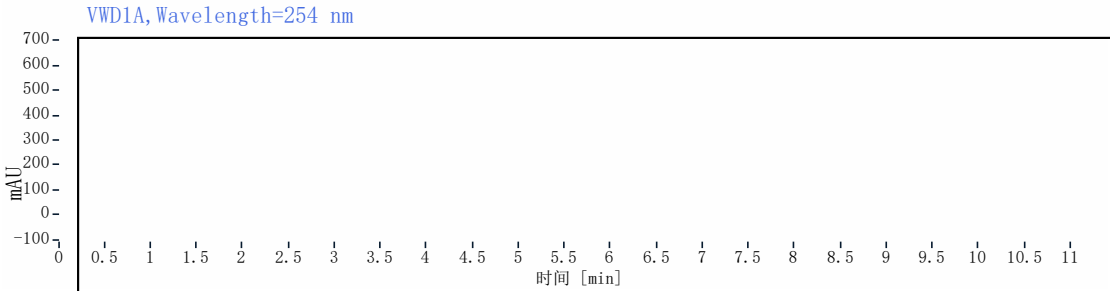


Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.649	VWD1A,Wavelength=254 nm	0.697	305.3	31.2	9.24
9.290	VWD1A,Wavelength=254 nm	1.493	2996.9	309.6	90.76



Retention time (min)	Absorption wavelength	Peak wideth (min)	Peak area	Peak hight	Peak area %
8.613	VWD1A,Wavelength=254 nm	0.680	6042.4	692.6	50.13
9.247	VWD1A,Wavelength=254 nm	1.361	6009.9	620.1	49.87