Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

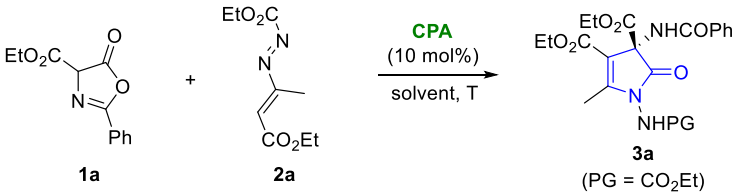
Contents

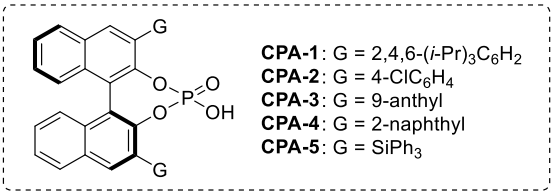
1. General Methods

Unless otherwise specified, all reactions were conducted under an inert atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$ on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm). The data are reported as follows: for ^{1}H NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for ^{13}C NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator ($CDCl_3$ δ 77.1 ppm), multiplicity with respect to protons. All high-resolution mass spectra were obtained on a Q-TOF Micro LC/MS System ESI spectrometer to be given in m/z. Enantiomeric excesses values were determined with HPLC (chiral column; mobile phase hexane/i-PrOH). Ethyl 5-oxo-2-phenyl-4,5-dihydrooxazole-4-carboxylate **1** were synthesized according to modified literature-reported procedures[1-3]; azoalkenes **2** were either employed directly from commercial sources or prepared according to the literature[4].

2. Representative Procedures

2.1 Optimization of the reaction conditions[a]



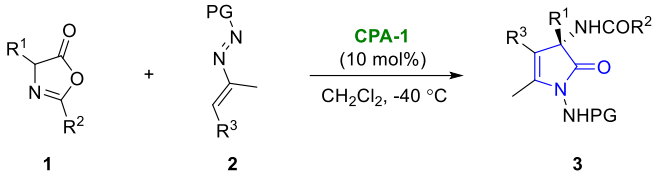


Entry	**CPA**	solvent	T (℃)	Additive	Yield (%)[b]	*ee* (%)[c]
1	**CPA-1**	toluene	r.t.	None	82	74
2	**CPA-2**	toluene	r.t.	None	80	14
3	**CPA-3**	toluene	r.t.	None	81	74
4	**CPA-4**	toluene	r.t.	None	78	8
5	**CPA-5**	toluene	r.t.	None	79	20
6	**CPA-1**	THF	r.t.	None	76	4
7	**CPA-1**	CH_3CN	r.t.	None	73	51
8	**CPA-1**	CH_2Cl_2	r.t.	None	84	89
9	**CPA-1**	DCE	r.t.	None	85	86
10	**CPA-1**	CCl_4	r.t.	None	83	93
11	**CPA-3**	CCl_4	r.t.	None	82	87
12	**CPA-3**	CH_2Cl_2	r.t.	None	85	85
13	**CPA-3**	$CHCl_3$	r.t.	None	73	16
14	**CPA-3**	DCE	r.t.	None	83	81
15	**CPA-1**	CH_2Cl_2	r.t	3Å MS	62	2
16	**CPA-1**	CH_2Cl_2	r.t	4Å MS	65	6
17	**CPA-1**	CH_2Cl_2	r.t	5Å MS	63	4
18	**CPA-3**	CH_2Cl_2	r.t	3Å MS	65	-4
19	**CPA-3**	CH_2Cl_2	r.t	4Å MS	63	10
20	**CPA-3**	CH_2Cl_2	r.t	5Å MS	61	8
21	**CPA-1**	CH_2Cl_2	0 ℃	None	85	90
22	**CPA-1**	CH_2Cl_2	-40 ℃	None	89	94

[a]Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), and **Cat.** (10 mol%) in the solvent specified (1 mL) for 3d.

[b]Isolated yields. [c]Determined by chiral HPLC analysis.

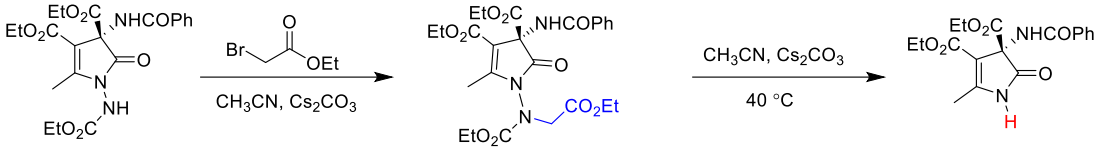
2.2 General procedure for the synthesis of products



1 2 3

Azlactone **1** (0.15 mmol) was dissolved in CH_2Cl_2 (1.5 ml), **CPA-1** was added and stirred at -40 ºC for 20 min. Azoalkene **2** (0.3 mmol) was dissolved in CH_2Cl_2 (1.5 ml) and added to the above system and reacted at -40 ºC for 3d. After the completion of the reaction which was indicated by TLC, the reaction mixture was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford pure product **3**.

2.3 Derivatization of 3a into compounds 4-5



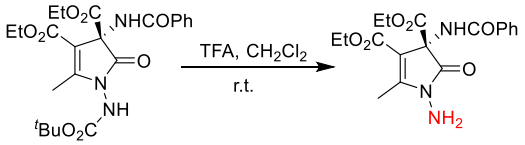
3a 93% ee

4 98% yield, dr 1.5:1, 92% ee, 93% ee

5 82% yield, 92% ee

To the solution of compound **3a** (89.5 mg, 0.2 mmol) in CH_3CN (1 mL) was added ethyl 2-bromoacetate (66.8 mg, 0.4 mmol). Then, Cs_2CO_3 (78.2 mg, 0.24 mmol) was added to the reaction mixture, which was stirred at room temperature for 5 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **4**.

Add Cs_2CO_3 (39.1 mg, 0.12 mmol) to the CH_3CN (1 ml) solution of compound **4** (53.4 mg, 0.1 mmol) and then, stir the resulting mixture at 40 °C for 4d. After the reaction indicated by TLC is completed, the reaction mixture is purified by preparation of thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to obtain pure product **5**.

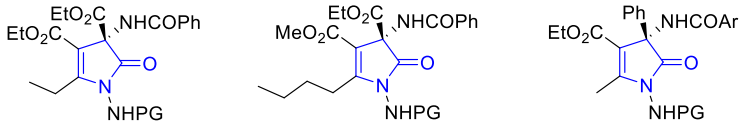


3e 87% ee

6 97% yield, 87% ee

To the solution of compound **3e** (47.5 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) was added TFA (0.3 ml), the reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was extracted with NaCl and CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to afford pure product **6**.

2.4 Failed examples (PG = CO_2Et)

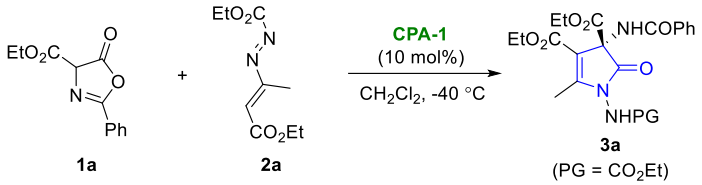


S1 35% yield, 17% *ee*

S2 33% yield, <5% *ee*

S3 (Ar = PMP) *No Reaction*

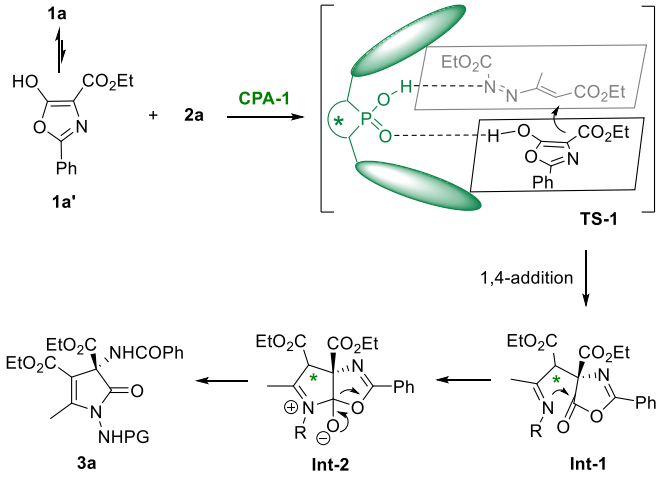
2.5 Large-scale synthesis



Azlactone **1** (1.5 mmol) was dissolved in CH_2Cl_2 (10 ml), **CPA-1** (10 mol%) was added and stirred at -40 ºC for 20 min. Azoalkene **2** (3.0 mmol) was dissolved in CH_2Cl_2 (10 ml) and added to the above system and reacted at -40 ºC for 3d. After the completion of the reaction which was indicated by TLC, the reaction was quenched by adding water. The reaction mixture was then extracted twice with CH_2Cl_2. The combined organic phase was dried by Na_2SO_4, and concentrated in vacuum. The resulting mixture was purified through column on silica gel (petroleum ether/ethyl acetate = 3:1) to afford pure product **3a** in 86% yield (576 mg) with the retinted enantioselectivity (93% *ee*).

2.6 Mechanism considerations

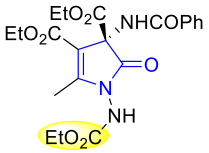
Based on the previous reports (*iScience*, 2020, **23**, 100873; *Angew. Chem. Int. Ed.*, 2022, **61**, e202207517; *Chem Catal.*, 2022, **2**, 386-399), a plausible reaction pathway was suggested in Scheme 4. In transition state (**TS-1**), the **CPA-1** catalyst simultaneously activated both azoalkene **2a** and enolized azlactone **1a′** via dual hydrogen-bonding interactions. Asymmetric 1,4-addition reaction took place to afford the hydrazone intermediate (**Int-1**). The intramolecular cyclization followed by ring-opening and iminium–enamine tautomerization completed the whole (3 + 2) process, allowing the formation of 4-pyrrolin-2-one **3a**.



Scheme S1. Plausible reaction pathway (PG = CO_2Et).

3. Characterization of Products

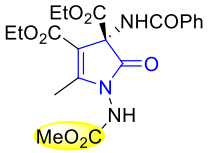
Diethyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3a**:



3a

A yellow oil; 59.7 mg; isolated yield = 89%; $[\alpha]^{27.5}_{D}$ = +63.68 (*c* 0.38, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.91 min (major), t_2 = 9.92 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.34 (m, 7H), 4.27 – 4.07 (m, 6H), 2.42 – 4.10 (m, 3H), 1.22 – 1.16 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 165.9, 165.7, 162.5, 158.7, 155.3, 132.5, 132.2, 128.6, 128.6, 127.3, 104.0, 64.7, 63.7, 62.7, 60.2, 14.3, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{21}H_{25}N_3O_8Na$ $[M + Na]^+$ = 470.1534, found = 470.1529.

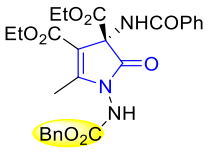
Diethyl (*S*)-3-benzamido-1-((methoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3b**:



3b

A yellow oil; 54.6 mg; isolated yield = 84%; $[\alpha]^{27.5}_{D}$ = +160.59 (*c* 0.51, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.51 min (major), t_2 = 10.30 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 4H), 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 2H), 4.43 – 4.13 (m, 4H), 3.77 (s, 3H), 2.49 – 2.25 (m, 3H), 1.30 – 1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 165.9, 165.7, 162.5, 158.6, 155.8, 132.5, 132.3, 128.8, 128.6, 127.4, 104.0, 64.7, 63.7, 60.2, 53.4, 14.3, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3O_8Na$ $[M + Na]^+$ = 456.1377, found = 456.1382.

Diethyl (*S*)-3-benzamido-1-(((benzyloxy)carbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3c**:

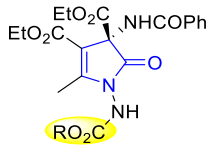


3c

A yellow oil; 67.2 mg; isolated yield = 88%; $[\alpha]^{27.6}_{D}$ = +71.43 (*c* 0.63, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.04 min (major), t_2 = 9.80 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.69 (m, 4H), 7.52 – 7.47 (m, 1H), 7.42 – 7.28 (m, 7H), 5.20 (s, 2H), 4.43 – 4.06 (m, 4H), 2.44 – 2.33 (m, 3H), 1.28 – 1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

167.7, 166.0, 165.7, 162.5, 158.6, 155.3, 135.3, 132.4, 132.2, 128.8, 128.6, 128.6, 128.5, 128.4, 128.0, 127.5, 127.5, 127.4, 104.1, 68.1, 64.7, 63.7, 60.2, 14.3, 13.8, 11.8; HRMS (ESI) m/z calcd for $C_{26}H_{27}N_3O_8Na$ $[M + Na]^+$ = 532.1690, found = 532.1697.

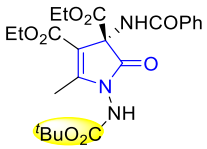
Diethyl (*S*)-1-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-benzamido-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3d**:



3d (R = fluorenylmethyl)

A yellow oil; 74.4 mg; isolated yield = 83%; $[\alpha]^{27.6}_D$ = +83.24 (*c* 0.68, CH_2Cl_2); HPLC (ID column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 12.89 min (major), t_2 = 44.84 min (minor), *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 7.06 (m, 15H), 4.50 – 4.03 (m, 7H), 2.39 – 2.26 (m, 3H), 1.25 – 1.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 166.1, 165.7, 162.6, 158.7, 155.2, 143.5, 141.3, 141.3, 132.5, 132.3, 131.0, 128.7, 127.9, 127.4, 127.2, 125.2, 120.0, 104.2, 68.4, 64.8, 63.8, 60.3, 46.8, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{33}H_{31}N_3O_8Na$ $[M + Na]^+$ = 620.2003, found = 620.2020.

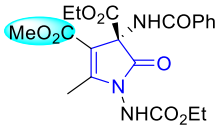
Diethyl (*S*)-3-benzamido-1-((tert-butoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3e**:



3e

A yellow oil; 52.1 mg; isolated yield = 73%; $[\alpha]^{27.6}_D$ = +60.00 (*c* 0.50, CH_2Cl_2); HPLC (ID column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 10.24 min (major), t_2 = 36.52 min (minor), *ee* = 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.32 (m, 7H), 4.41 – 4.10 (m, 4H), 2.49 – 2.13 (m, 3H), 1.49 – 1.46 (m, 9H), 1.29 – 1.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.8, 165.8, 162.6, 159.0, 154.1, 132.5, 132.2, 128.7, 128.6, 127.4, 127.3, 103.9, 82.5, 64.7, 63.6, 60.1, 28.1, 28.0, 27.8, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3O_8Na$ $[M + Na]^+$ = 498.1847, found = 498.1860.

3-ethyl-4-methyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3f**:

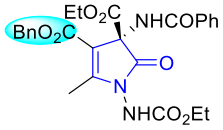


3f

A colorless solid; 53.3 mg; isolated yield = 82%; m.p. 137.1-137.7°C; $[\alpha]^{27.6}_D$ = +158.00 (*c* 0.20, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,

λ = 254 nm), product: t_1 = 7.37 min (major), t_2 = 8.60 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.70 (m, 4H), 7.57 – 7.49 (m, 1H), 7.44 – 7.41 (m, 2H), 4.37 – 4.17 (m, 4H), 3.71 (s, 3H), 2.49 – 2.46 (m, 3H), 1.29 – 1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 166.0, 165.7, 163.0, 159.0, 155.3, 132.4, 132.3, 128.6, 127.4, 103.8, 64.7, 63.7, 62.7, 51.3, 14.3, 13.8, 11.8; HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3O_8Na$ $[M + Na]^+$ = 456.1377, found = 456.1386.

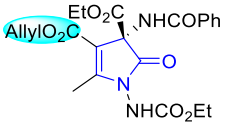
4-benzyl-3-ethyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3g**:



3g

A yellow oil; 62.7 mg; isolated yield = 82%; $[\alpha]^{27.6}_D$ = +67.83 (*c* 0.60, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 6.94 min (major), t_2 = 8.81 min (minor), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.11 (m, 12H), 5.19 – 4.95 (m, 2H), 4.25 – 4.03 (m, 4H), 2.42 – 2.06 (m, 3H), 1.23 – 1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.9, 165.7, 162.2, 159.7, 155.3, 135.8, 132.4, 132.2, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.3, 103.6, 65.9, 64.6, 63.7, 62.7, 14.3, 13.8, 11.8; HRMS (ESI) m/z calcd for $C_{26}H_{27}N_3O_8Na$ $[M +]^+$ = 532.1690, found = 532.1704.

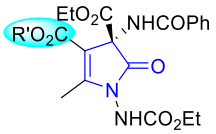
4-allyl-3-ethyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3h**:



3h

A yellow oil; 58.6 mg; isolated yield = 85%; $[\alpha]^{27.6}_D$ = +76.20 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 6.45 min (major), t_2 = 7.64 min (minor), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 4H), 7.46 – 7.43 (m, 1H), 7.37 – 7.33 (m, 2H), 5.86 – 5.76 (m, 1H), 5.28 – 5.06 (m, 2H), 4.56 – 4.54 (m, 2H), 4.25 – 4.14 (m, 4H), 2.43 – 4.25 (m, 3H), 1.22 – 1.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 166.0, 165.7, 162.2, 159.3, 155.3, 132.4, 132.3, 132.0, 128.6, 127.4, 118.1, 103.7, 64.8, 64.6, 63.8, 62.7, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{22}H_{25}N_3O_8Na$ $[M + Na]^+$ = 482.1534, found = 482.1536.

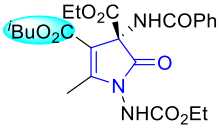
3-ethyl-4-(2-methoxyethyl) (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3i**:



3i (R' = 2-methoxyethyl)

A yellow oil; 60.2 mg; isolated yield = 84%; $[\alpha]^{27.3}_D$ = +82.59 (*c* 0.58, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 11.39 min (major), t_2 = 15.45 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.53 – 7.49 (m, 1H), 7.44 – 7.40 (m, 2H), 4.37 – 4.16 (m, 6H), 3.57 – 3.54 (m, 2H), 3.30 (s, 3H), 2.50 – 2.43 (m, 3H), 1.30 – 1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.9, 165.7, 162.4, 159.3, 155.3, 132.6, 132.2, 128.6, 127.4, 103.7, 70.3, 64.6, 63.6, 63.0, 62.7, 58.7, 14.3, 13.8, 11.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_9Na$ $[M + Na]^+$ = 500.1640, found = 500.1644.

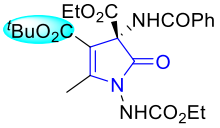
3-ethyl-4-isobutyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3j**:



3j

A colorless solid; 60.6 mg; isolated yield = 85%; m.p. 142.4-143.2°C; $[\alpha]^{27.1}_D$ = +74.55 (*c* 0.55, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.71 min (major), t_2 = 10.70 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 4H), 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 2H), 4.34 – 4.20 (m, 4H), 3.95 – 3.87 (m, 2H), 2.51 – 2.25 (m, 3H), 1.96 – 1.86 (m, 1H), 1.30 – 1.25 (m, 6H), 0.92 – 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 165.8, 162.7, 158.9, 155.3, 132.4, 132.3, 128.6, 127.3, 104.0, 70.5, 64.6, 63.7, 62.7, 27.8, 19.2, 19.1, 14.3, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3O_{58}Na$ $[M + Na]^+$ = 498.1847, found = 498.1858.

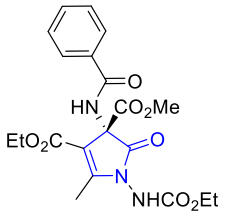
4-(tert-butyl)-3-ethyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3k**:



3k

A yellow oil; 51.4 mg; isolated yield = 72%; $[\alpha]^{27.6}_D$ = +62.17 (*c* 0.46, CH_2Cl_2); HPLC (ID column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 9.95 min (major), t_2 = 44.11 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.67 (m, 4H), 7.56 – 7.50 (m, 1H), 7.47 – 7.40 (m, 2H), 4.40 – 4.19 (m, 4H), 2.46 – 2.14 (m, 3H), 1.44 (s, 9H), 1.33 – 1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 165.9, 165.7, 161.7, 157.9, 155.3, 132.6, 132.2, 128.7, 127.5, 127.4, 127.2, 105.3, 81.2, 64.7, 63.6, 62.7, 28.3, 14.3, 14.0, 11.5; HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3O_8Na$ $[M + Na]^+$ = 498.1847, found = 498.1853.

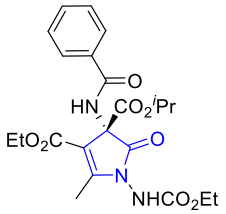
4-ethyl-3-methyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3l**:



3l

A yellow oil; 61.1 mg; isolated yield = 94%; $[\alpha]^{20.0}_{D}$ = +79.01 (*c* 0.54, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 12.30 min (major), t_2 = 14.44 min (minor), *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.66 (m, 4H), 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 2H), 4.24 – 4.15 (m, 4H), 3.85 (s, 3H), 2.47 – 2.38 (m, 3H), 1.26 – 1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.4, 165.9, 162.5, 158.7, 155.4, 132.5, 132.3, 128.8, 128.6, 127.5, 127.4, 127.3, 103.9, 64.6, 62.8, 60.2, 54.3, 14.3, 11.8; HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3O_8Na$ $[M + Na]^+$ = 456.1377, found = 456.1384.

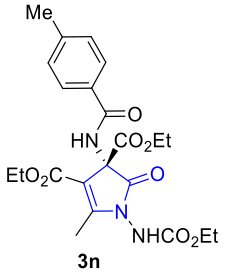
4-ethyl-3-isopropyl (*S*)-3-benzamido-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3m**:



3m

A yellow oil; 58.1 mg; isolated yield = 84%; $[\alpha]^{27.3}_{D}$ = +93.27 (*c* 0.55, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 6.20 min (major), t_2 = 8.06 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 7.33 (m, 7H), 5.30 – 4.90 (m, 1H), 4.23 – 4.17 (m, 4H), 2.49 – 2.25 (m, 3H), 1.37 – 1.15 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 166.2, 165.1, 162.5, 158.6, 154.8, 132.5, 132.3, 128.7, 127.3, 104.1, 72.0, 64.7, 62.7, 60.2, 21.3, 21.3, 14.3, 11.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_8Na$ $[M + Na]^+$ = 484.1690, found = 484.1695.

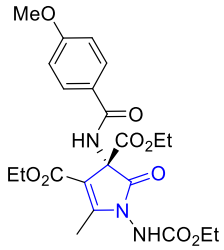
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-5-methyl-3-(4-methylbenzamido)-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3n**:



3n

A yellow oil; 59.5 mg; isolated yield = 86%; $[\alpha]^{27.5}_D$ = +115.10 (*c* 0.49, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 10.64 min (major), t_2 = 14.51 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.64 (m, 4H), 7.23 – 7.21 (m, 2H), 4.38 – 4.09 (m, 6H), 2.49 – 2.29 (m, 6H), 1.31 – 1.21 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 165.8, 162.6, 158.6, 155.3, 142.8, 129.6, 129.3, 127.5, 127.3, 104.1, 64.6, 63.6, 62.7, 60.2, 21.5, 14.3, 14.3, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_8Na$ $[M + Na]^+$ = 484.1690, found = 484.1698.

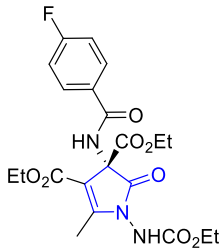
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-3-(4-methoxybenzamido)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3o**:



3o

A yellow oil; 68.0 mg; isolated yield = 95%; $[\alpha]^{27.5}_D$ = +154.44 (*c* 0.45, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 11.23 min (major), t_2 = 14.57 min (minor), ee = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 4H), 7.00 – 6.84 (m, 2H), 4.40 – 4.10 (m, 6H), 3.84 (s, 3H), 2.49 – 2.41 (m, 3H), 1.30 – 1.23 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.9, 165.4, 162.7, 162.6, 158.5, 155.3, 129.3, 124.8, 113.8, 104.2, 64.7, 63.6, 62.7, 60.1, 55.4, 14.3, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_9Na$ $[M + Na]^+$ = 500.1640, found = 500.1646.

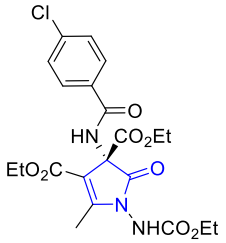
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-3-(4-fluorobenzamido)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3p**:



3p

A yellow oil; 60.7 mg; isolated yield = 87%; $[\alpha]^{27.5}_D$ = +102.64 (*c* 0.53, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.73 min (minor), t_2 = 10.55 min (major), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.69 (m, 4H), 7.12 – 7.08 (m, 2H), 4.39 – 4.08 (m, 6H), 2.49 – 2.33 (m, 3H), 1.30 – 1.23 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.7, 165.1 (*J* = 252 Hz), 164.9, 162.5, 158.6, 155.3, 129.9, 129.8, 128.7, 115.7, (*J* = 22 Hz), 104.0, 64.7, 63.7, 62.7, 60.2, 14.3, 14.1, 13.9, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -106.86; HRMS (ESI) m/z calcd for $C_{21}H_{24}FN_3O_8Na$ $[M + Na]^+$ = 488.1440, found = 488.1451.

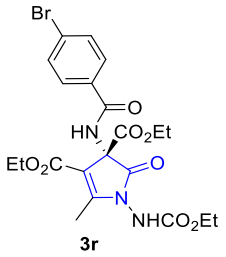
Diethyl (*S*)-3-(4-chlorobenzamido)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3q**:



3q

A yellow oil; 63.6 mg; isolated yield = 88%; $[\alpha]^{27.6}_{D}$ = +109.6 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.28 min (minor), t_2 = 11.34 min (major), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 4H), 7.45 – 7.36 (m, 2H), 4.40 – 4.12 (m, 6H), 2.49 – 2.27 (m, 3H), 1.43 – 1.18 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.7, 164.9, 162.5, 158.7, 155.3, 138.6, 130.9, 128.9, 128.8, 103.9, 64.7, 63.8, 62.8, 60.3, 14.3, 14.1, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{21}H_{24}ClN_3O_8Na$ $[M + Na]^+$ = 504.1144, found = 504.1145.

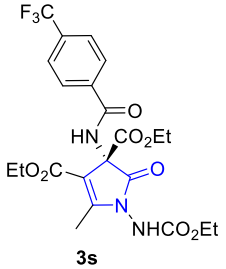
Diethyl (*S*)-3-(4-bromobenzamido)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3r**:



3r

A yellow oil; 67.9 mg; isolated yield = 86%; $[\alpha]^{27.5}_{D}$ = +228.75 (*c* 0.56, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.77 min (minor), t_2 = 13.06 min (major), *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.51 (m, 6H), 4.49 – 4.09 (m, 6H), 2.46 – 2.31 (m, 3H), 1.30 – 1.22 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.7, 165.0, 162.5, 158.7, 155.3, 131.9, 131.4, 129.1, 129.0, 127.0, 103.9, 64.7, 63.8, 62.7, 60.3, 14.3, 14.1, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{21}H_{24}BrN_3O_8Na$ $[M + Na]^+$ = 548.0639, found = 548.0645.

Diethyl (*S*)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-3-(4-(trifluoromethyl)benzamido)-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3s**:

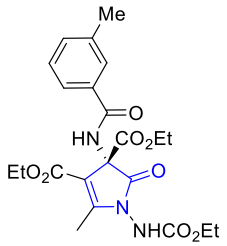


3s

A yellow oil; 65.7 mg; isolated yield = 85%; $[\alpha]^{27.5}_{D}$ = +99.51 (*c* 0.61, CH_2Cl_2); HPLC

(IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 5.14 min (minor), t_2 = 7.43 min (major), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.52 (m, 6H), 4.47 – 4.09 (m, 6H), 2.50 – 2.08 (m, 3H), 1.31 – 1.23 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.6, 164.6, 162.5, 158.7, 155.2, 135.8, 133.8 (*J* = 33.4 Hz), 127.9, 125.7 (*J* = 3.5 Hz), 123.5 (*J* = 272.6 Hz), 103.8, 64.7, 63.8, 62.8, 60.3, 14.3, 14.1, 13.9, 11.8.; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.09; HRMS (ESI) m/z calcd for $C_{22}H_{24}F_3N_3O_8Na$ $[M + Na]^+$ = 538.1408, found = 538.1415.

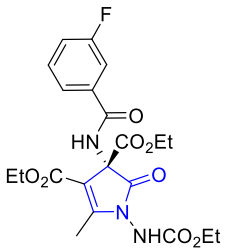
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-5-methyl-3-(3-methylbenzamido)-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3t**:



3t

A yellow oil; 60.9 mg; isolated yield = 88%; $[\alpha]^{27.5}_D$ = +95.47 (*c* 0.53, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 9.05 min (major), t_2 = 12.04 min (minor), *ee* = 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.50 (m, 4H), 7.32 – 7.30 (m, 2H), 4.42 – 4.06 (m, 6H), 2.49 – 2.47 (m, 3H), 2.37 (s, 3H), 1.30 – 1.23 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 166.1, 165.8, 162.6, 158.7, 155.3, 138.5, 132.9, 132.4, 128.5, 128.0, 124.4, 104.0, 64.7, 63.6, 62.7, 60.2, 21.3, 14.3, 14.1, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_8Na$ $[M + Na]^+$ = 484.1690, found = 484.1697.

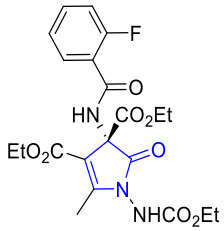
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-3-(3-fluorobenzamido)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3u**:



3u

A yellow oil; 58.6 mg; isolated yield = 84%; $[\alpha]^{27.5}_D$ = +65.20 (*c* 0.25, CH_2Cl_2); HPLC (IE column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 9.26 min (major), t_2 = 18.91 min (minor), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.37 (m, 5H), 7.25 – 7.20 (m, 1H), 4.39 – 4.08 (m, 6H), 2.50 – 2.03 (m, 3H), 1.39 – 1.18 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.6, 164.5, 162.7 (*J* = 246 Hz), 162.5, 158.8, 155.2, 134.7, 130.4, 130.3, 122.8, 122.7, 119.4, 119.2, 114.7 (*J* = 23 Hz), 103.9, 64.7, 63.8, 62.82, 60.3, 14.3, 14.2, 13.9, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -111.48; HRMS (ESI) m/z calcd for $C_{21}H_{24}FN_3O_8Na$ $[M + Na]^+$ = 488.1440, found = 488.1449.

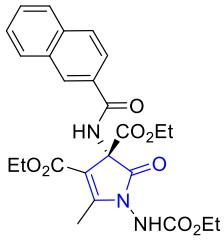
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-3-(2-fluorobenzamido)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3v**:



3v

A yellow oil; 57.9 mg; isolated yield = 83%; $[\alpha]^{27.6}_{D}$ = +100.27 (*c* 0.37, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.34 min (major), t_2 = 8.46 min (minor), *ee* = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.42 (m, 1H), 7.95 – 7.91 (m, 1H), 7.75 – 7.66 (m, 1H), 7.54 – 7.45 (m, 1H), 7.26 – 7.09 (m, 2H), 4.39 – 4.08 (m, 6H), 2.50 – 2.27 (m, 3H), 1.30 – 1.22 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.4, 162.4, 161.7, 160.9 (*J* = 248 Hz), 158.8, 155.3, 134.2, 134.1, 131.9, 124.8, 124.7, 119.5, 119.4, 116.2 (*J* = 24 Hz), 104.0, 64.9, 63.6, 62.7, 60.2, 14.3, 14.1, 13.9, 11.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -111.98; HRMS (ESI) m/z calcd for $C_{21}H_{24}FN_3O_8Na$ $[M + Na]^+$ = 488.1440, found = 488.1441.

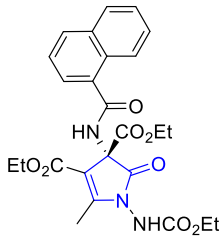
Diethyl (*S*)-3-(2-naphthamido)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3w**:



3w

A yellow oil; 65.7 mg; isolated yield = 88%; $[\alpha]^{27.5}_{D}$ = +147.59 (*c* 0.54, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.55 min (minor), t_2 = 8.76 min (major), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 8.00 – 7.75 (m, 6H), 7.62 – 7.45 (m, 2H), 4.40 – 4.13 (m, 6H), 2.56 – 2.36 (m, 3H), 1.32 – 1.20 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 166.0, 165.9, 162.6, 158.7, 155.4, 135.0, 132.5, 129.7, 129.1, 128.5, 128.3, 128.0, 127.7, 126.8, 123.5, 104.1, 64.8, 63.7, 62.7, 60.2, 14.3, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{25}H_{27}N_3O_8Na$ $[M + Na]^+$ = 520.1690, found = 520.1698.

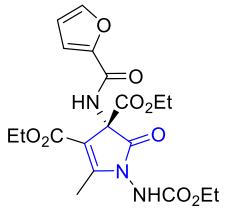
Diethyl (*S*)-3-(1-naphthamido)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3x**:



3x

A colorless solid; 64.2 mg; isolated yield = 86%; m.p. 127.5-128.1℃; $[\alpha]^{27.5}_D$ = +10.85 (*c* 0.47, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.25 min (minor), t_2 = 8.32 min (major), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 7.43 (m, 9H), 4.38 – 4.19 (m, 6H), 2.53 – 2.24 (m, 3H), 1.34 – 1.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.2, 165.5, 162.6, 158.9, 155.2, 133.6, 132.0, 131.4, 130.2, 128.3, 127.4, 126.5, 126.0, 125.2, 124.6, 104.0, 64.9, 63.6, 62.8, 60.3, 14.4, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{25}H_{27}N_3O_8Na$ $[M + Na]^+$ = 520.1690, found = 520.1696.

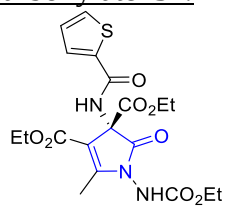
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-3-(furan-2-carboxamido)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3y**:



3y

A yellow oil; 53.8 mg; isolated yield = 82%; $[\alpha]^{27.4}_D$ = +111.43 (*c* 0.35, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.91 min (major), t_2 = 11.56 min (minor), *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.62 – 7.47 (m, 2H), 7.10 – 7.09 (m, 1H), 6.49 – 6.48 (m, 1H), 4.42 – 4.11 (m, 6H), 2.48 – 2.10 (m, 3H), 1.30 – 1.22 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.3, 162.4, 158.5, 156.8, 155.2, 146.6, 144.8, 115.6, 112.2, 104.2, 64.2, 63.6, 62.8, 60.2, 14.3, 14.2, 13.9, 11.7; HRMS (ESI) m/z calcd for $C_{19}H_{23}N_3O_9Na$ $[M + Na]^+$ = 460.1327, found = 460.1338.

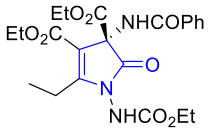
Diethyl (*S*)-1-((ethoxycarbonyl)amino)-5-methyl-2-oxo-3-(thiophene-2-carboxamido)-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **3z**:



3z

A yellow oil; 55.8 mg; isolated yield = 82%; $[\alpha]^{27.3}_D$ = +119.36 (*c* 0.47, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.94 min (major), t_2 = 10.82 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.43 (m, 4H), 7.09 – 7.07 (m, 1H), 4.40 – 4.08 (m, 6H), 2.49 – 2.23 (m, 3H), 1.34 – 1.19 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.6, 162.5, 160.4, 158.6, 155.2, 136.9, 131.2, 129.3, 127.9, 104.1, 64.6, 63.7, 62.8, 60.2, 14.3, 14.3, 13.9, 11.8; HRMS (ESI) m/z calcd for $C_{19}H_{23}N_3O_8SNa$ $[M + Na]^+$ = 476.1098, found = 476.1103.

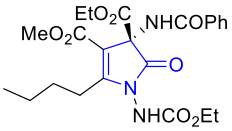
Diethyl-3-benzamido-1-((ethoxycarbonyl)amino)-5-ethyl-2-oxo-2,3-dihydro-1H-pyrrole-3,4-dicarboxylate **S1**:



S1

A yellow oil; 24.2 mg; isolated yield = 35%; HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 6.11 min (major), t_2 = 6.86 min (minor), *ee* = 17%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.55 (m, 4H), 7.54 – 7.47 (m, 1H), 7.44 – 7.40 (m, 2H), 4.49 – 3.94 (m, 6H), 2.94 – 2.37 (m, 2H), 1.32 – 1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.9, 165.7, 163.7, 162.3, 155.4, 132.5, 132.2, 128.6, 128.5, 127.3, 127.2, 103.1, 64.6, 63.6, 62.7, 60.1, 18.9, 14.3, 14.2, 13.8, 11.9; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_8Na$ $[M + Na]^+$ = 484.1690, found = 484.1697.

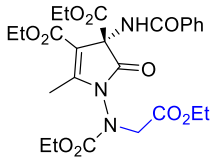
3-ethyl-4-methyl-3-benzamido-1-((ethoxycarbonyl)amino)-2-oxo-5-pentyl-2,3-dihydro-1H-pyrrole-3,4-dicarboxylate **S2**:



S2

A yellow oil; 23.5 mg; isolated yield = 33%; HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 7.91 min (major), t_2 = 9.01 min (minor), *ee* = <5%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.63 (m, 4H), 7.54 – 7.48 (m, 1H), 7.44 – 7.40 (m, 2H), 4.43 – 4.13 (m, 4H), 3.80 – 3.71 (m, 3H), 3.02 – 2.29 (m, 2H), 1.65 – 1.16 (m, 10H), 0.95 – 0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 165.9, 165.7, 162.9, 162.7, 155.3, 132.5, 132.2, 128.6, 128.5, 127.4, 103.6, 64.6, 63.6, 62.7, 51.3, 29.4, 25.1, 22.3, 14.3, 13.8, 13.7; HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3O_8Na$ $[M + Na]^+$ = 498.1847, found = 498.1858.

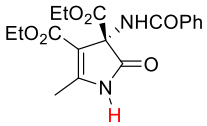
Diethyl (*S*)-3-benzamido-1-((2-ethoxy-2-oxoethyl)(ethoxycarbonyl)amino)-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **4**:



4

A yellow oil; 104.6 mg; isolated yield = 98%; dr = 1.5:1; $[\alpha]^{20.2}_D$ = +52.11 (*c* 0.19, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 16.46 min (minor), t_2 = 21.44 min (major), *ee* = 92%; minor product: t_1 = 18.14 min (major), t_2 = 50.29 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.37 (m, 6H), 5.11 – 3.90 (m, 10H), 2.73 – 2.31 (m, 3H), 1.43 – 1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.2, 165.7, 165.0, 162.5, 158.6, 155.3, 132.6, 132.1, 132.0, 128.6, 127.3, 104.4, 64.6, 63.5, 63.4, 61.4, 60.1, 50.8, 14.2, 14.1, 13.8, 12.2; HRMS (ESI) m/z calcd for $C_{25}H_{31}N_3O_{10}Na$ $[M + Na]^+$ = 556.1902, found = 556.1906.

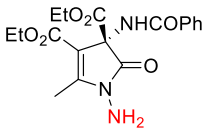
Diethyl (*S*)-3-benzamido-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **5**:



5

A yellow solid; 29.6 mg; isolated yield = 82%; m.p. 203.2-203.8℃; $[\alpha]^{20.0}_{D}$ = +28.86 (*c* 0.35, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 9.04 min (major), t_2 = 20.57 min (minor), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 – 9.22 (m, 1H), 8.07 – 7.66 (m, 3H), 7.62 – 7.51 (m, 1H), 7.50 – 7.40 (m, 2H), 4.34 – 4.28 (m, 2H), 4.18 – 4.10 (m, 2H), 2.42 (s, 3H), 1.29 – 1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 166.4, 165.6, 162.9, 158.0, 132.7, 132.2, 128.9, 128.7, 127.6, 127.3, 105.5, 67.0, 63.4, 59.8, 14.3, 14.0, 13.9; HRMS (ESI) m/z calcd for $C_{18}H_{20}N_2O_6Na$ $[M + Na]^+$ = 383.1214, found = 383.1217.

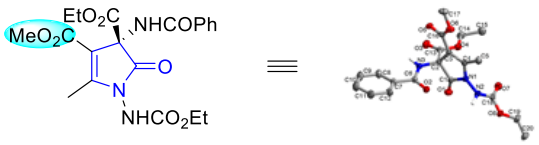
Diethyl (*S*)-1-amino-3-benzamido-5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate **6**:



6

A yellow oil; 54.6 mg; isolated yield = 97%; $[\alpha]^{27.3}_{D}$ = +90.87 (*c* 0.46, CH_2Cl_2); HPLC (IE column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 6.96 min (minor), t_2 = 9.03 min (major), *ee* = 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.74 (m, 3H), 7.59 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 4.45 – 4.10 (m, 4H), 2.45 – 2.31 (m, 3H), 1.31 – 1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.8, 165.2, 162.2, 156.7, 132.5, 132.2, 128.8, 127.3, 105.1, 64.9, 64.0, 60.5, 14.2, 13.7, 11.3; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3O_6Na$ $[M + Na]^+$ = 398.1323, found = 398.1332.

4. X-ray Single Crystal Data for (*S*)-3f



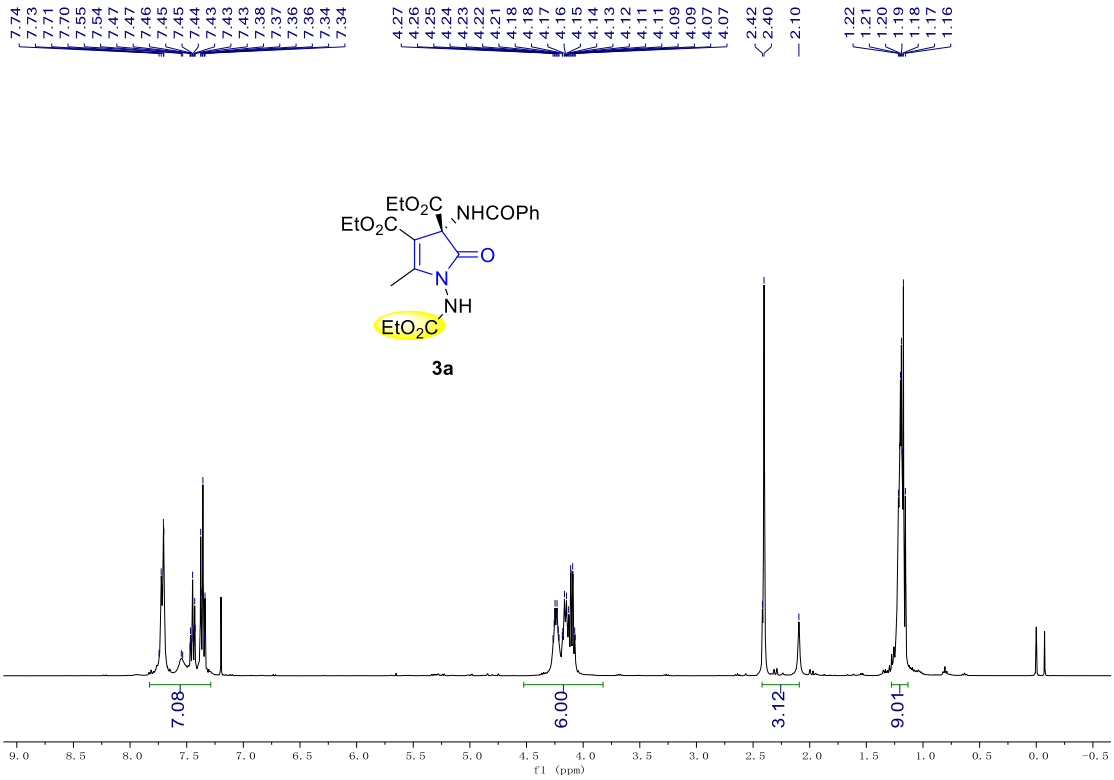
CCDC: 2246700 for (+)-3f

Table S1 Crystal data and structure refinement for 20230221A.

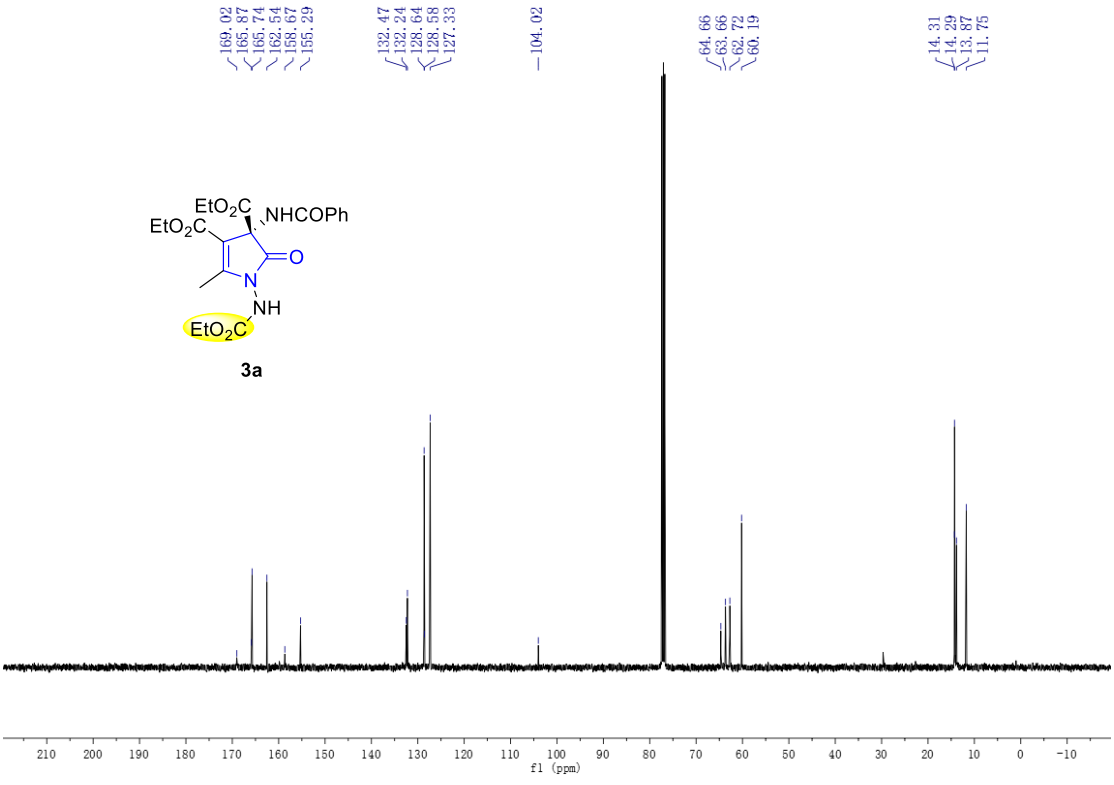
Identification code	20230221A
Empirical formula	$C_{20}H_{23}N_3O_8$
Formula weight	433.41
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2
a/Å	21.0745(7)
b/Å	12.0391(4)
c/Å	9.3014(3)
α/°	90
β/°	107.027(3)
γ/°	90
Volume/Å^3	2256.50(14)
Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.845
F(000)	912.0
Crystal size/mm^3	0.17 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.556 to 141.706
Index ranges	-25 ≤ h ≤ 24, -14 ≤ k ≤ 12, -11 ≤ l ≤ 11
Reflections collected	11094
Independent reflections	3802 [R_{int} = 0.0254, R_{sigma} = 0.0241]
Data/restraints/parameters	3802/5/288
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.1102
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.1161
Largest diff. peak/hole / e Å^{-3}	0.20/-0.15
Flack parameter	0.14(11)

5. NMR Spectra

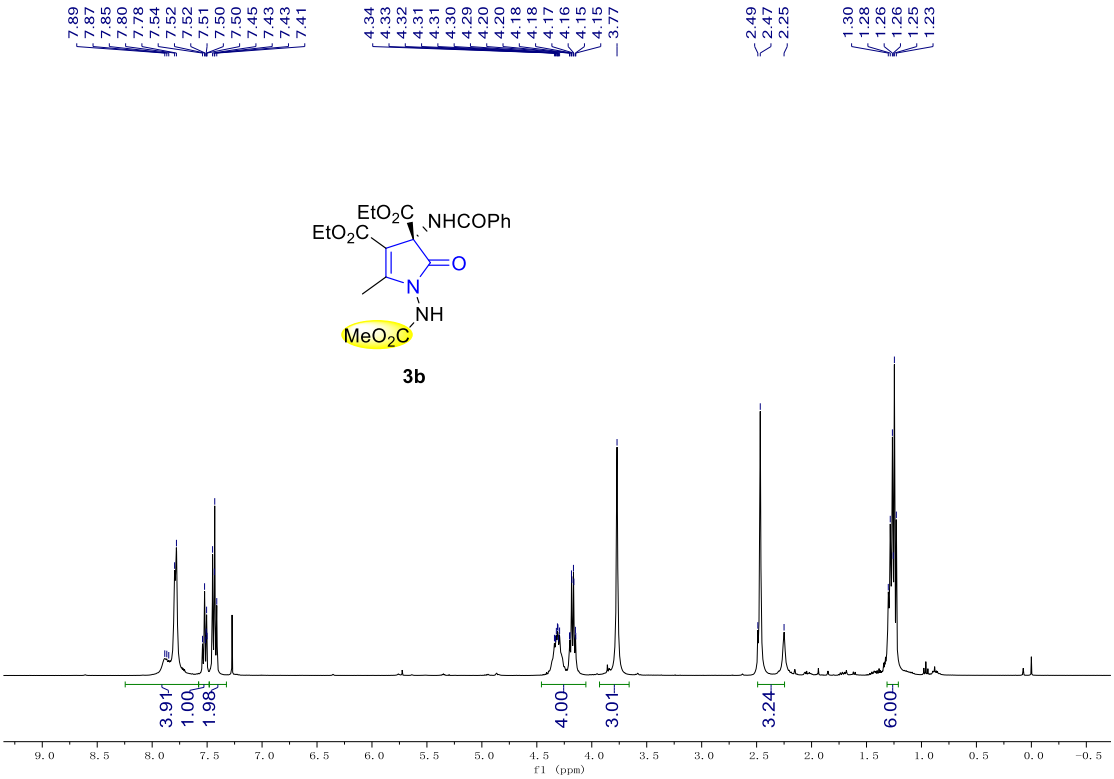
^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz)



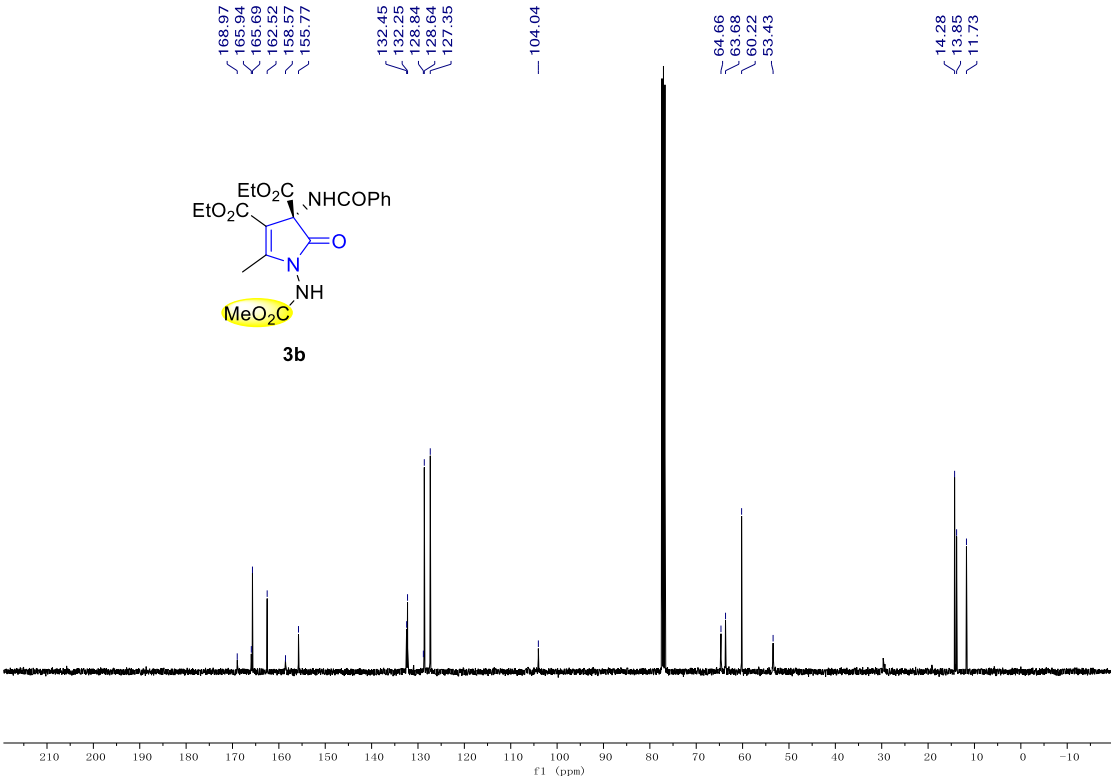
^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz)



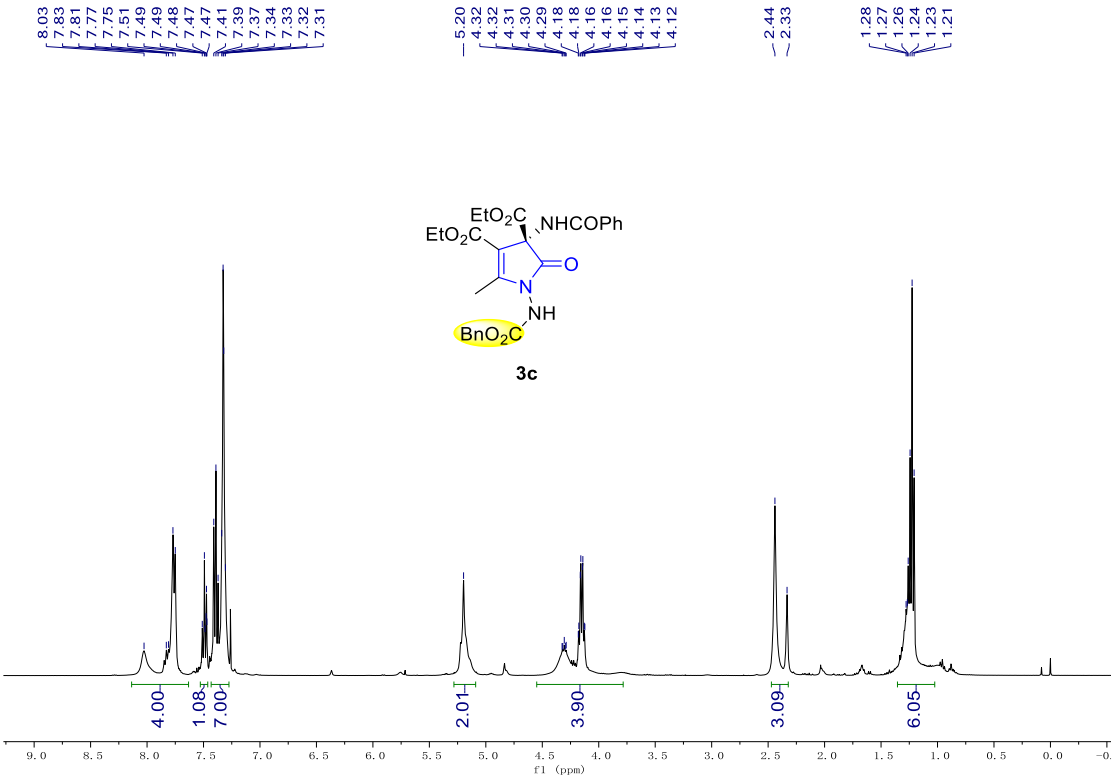
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)



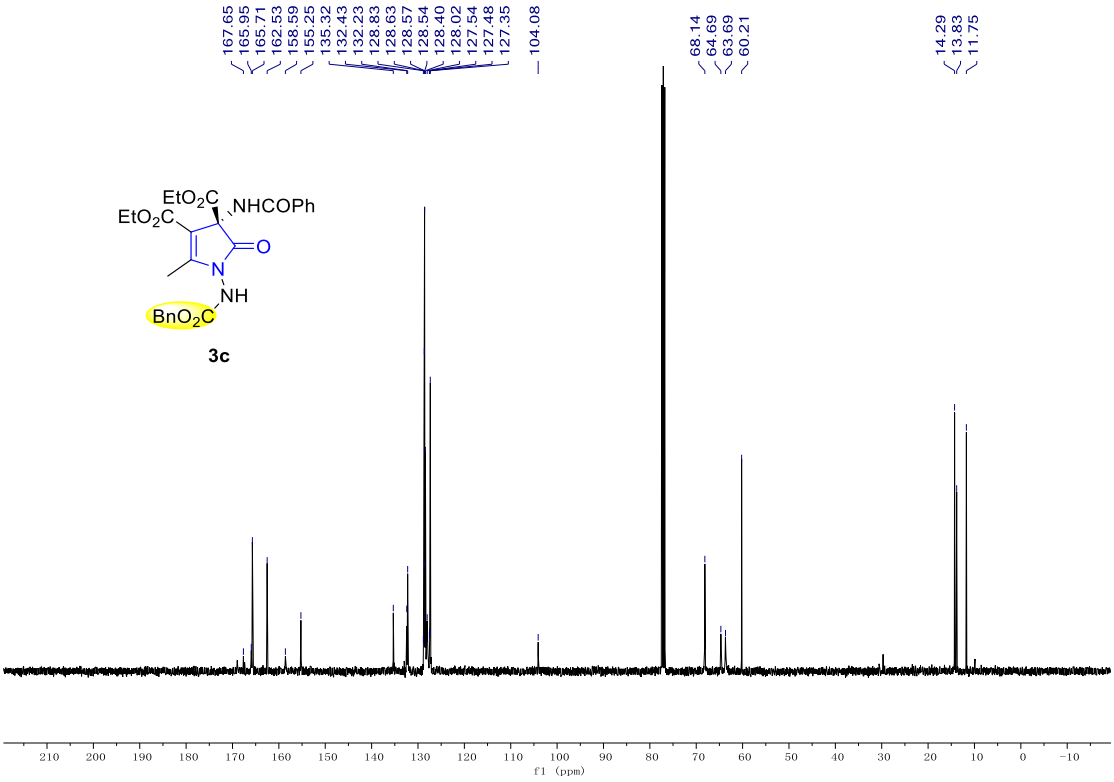
^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz)



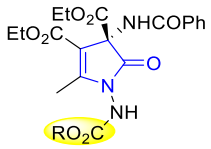
^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz)



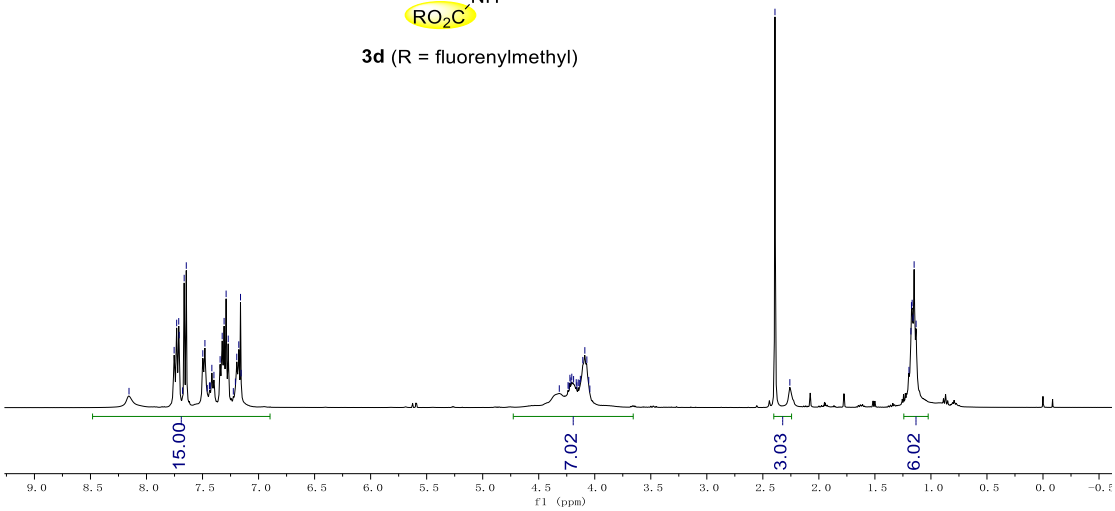
^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz)



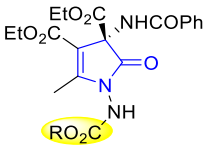
^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)



3d (R = fluorenylmethyl)

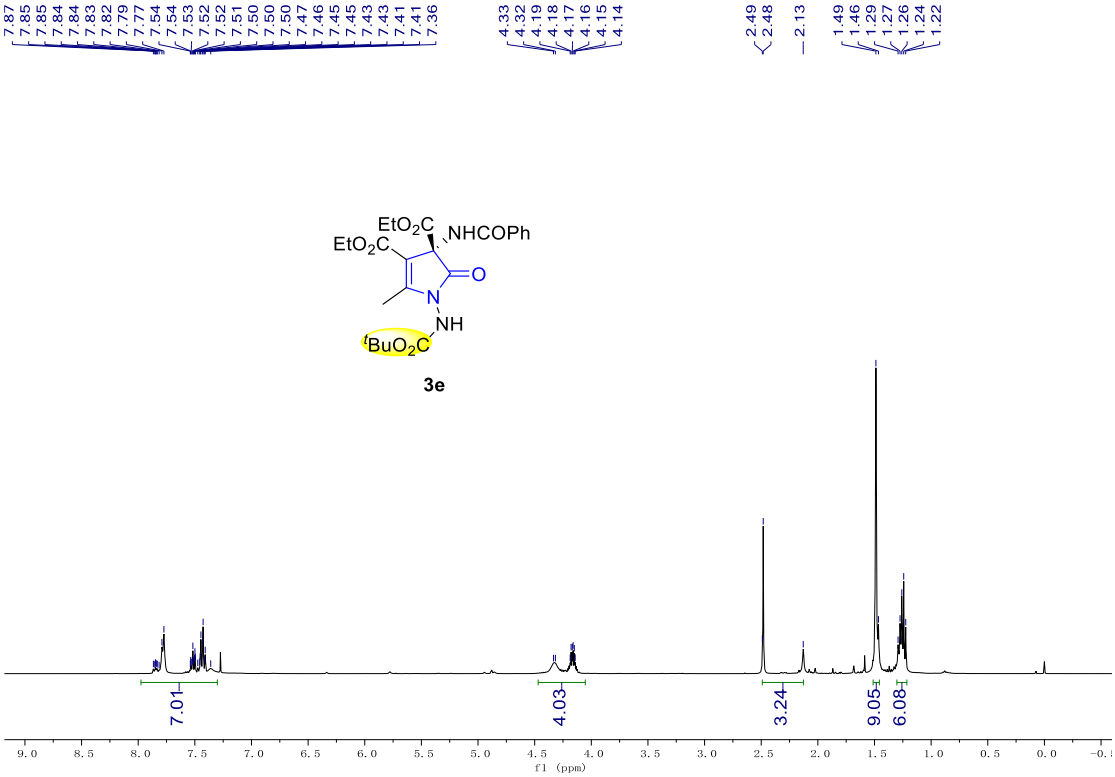


^{13}C NMR spectrum of compound **3d** ($CDCl_3$, 100 MHz)

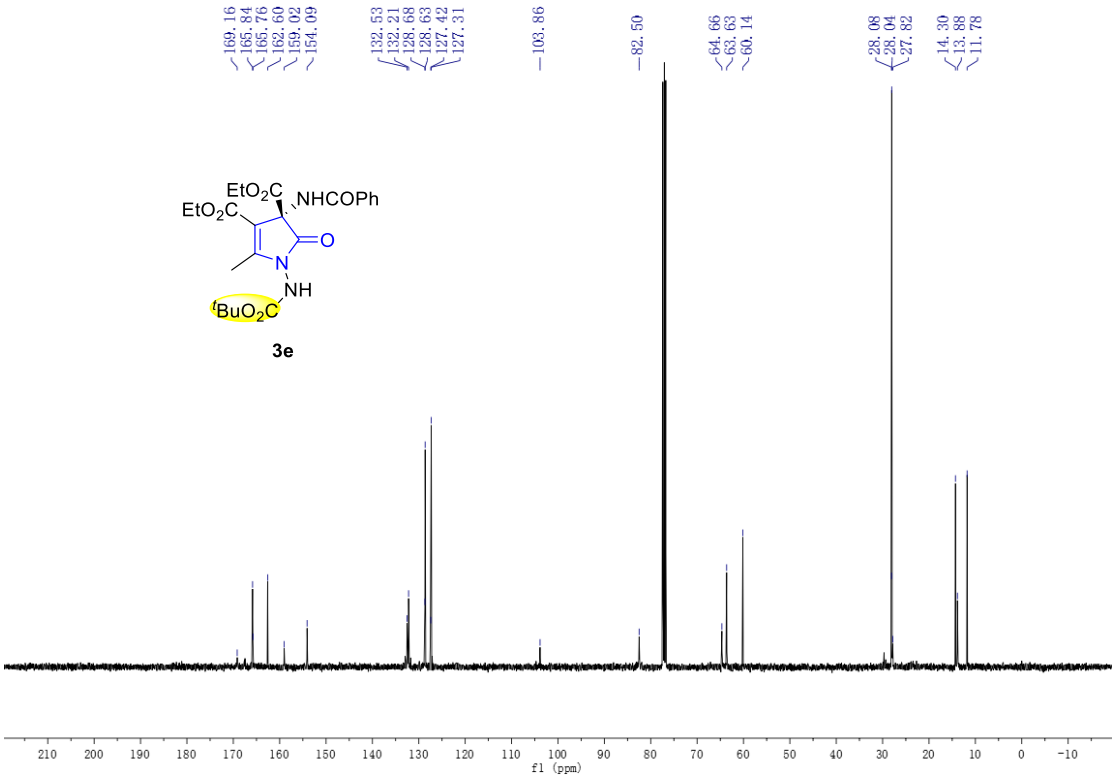


3d (R = fluorenylmethyl)

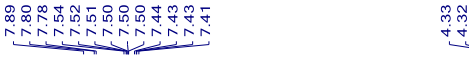
^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 400 MHz)

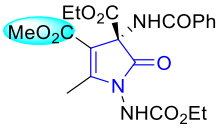


^{13}C NMR spectrum of compound **3e** ($CDCl_3$, 100 MHz)

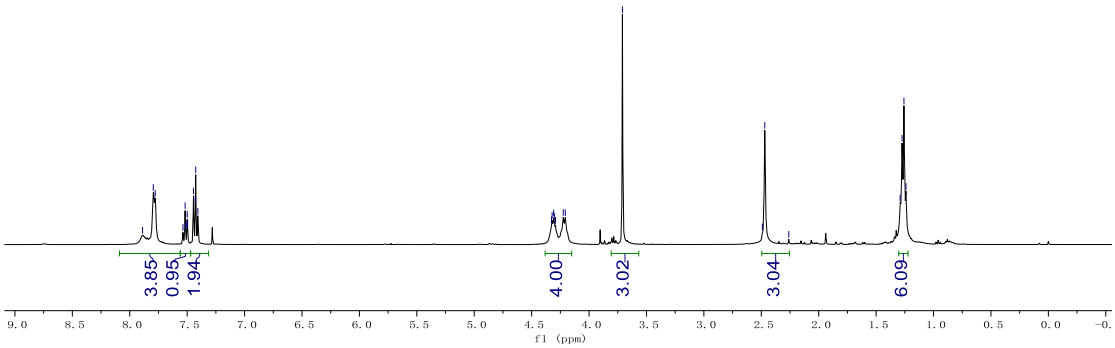


^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 400 MHz)

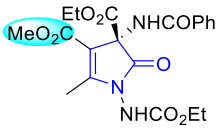




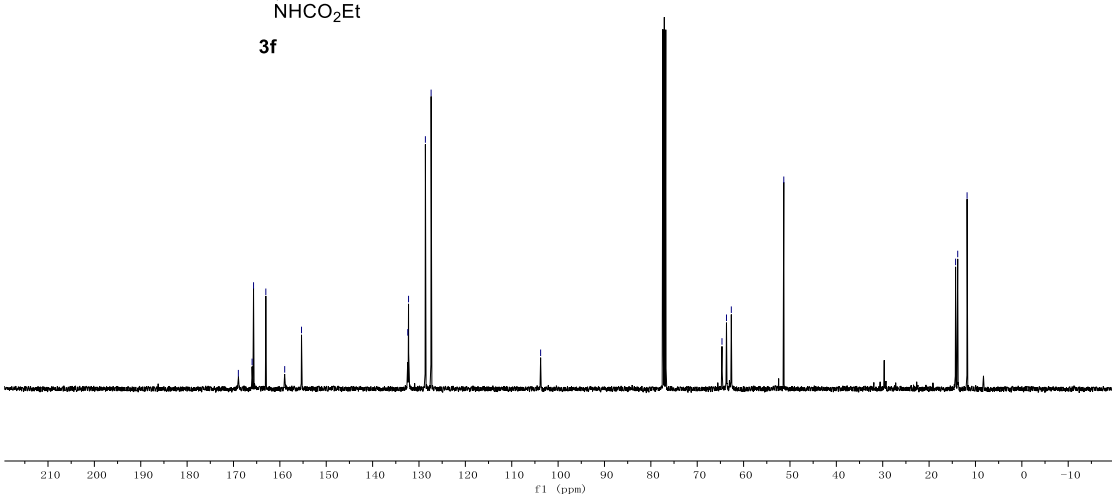
3f



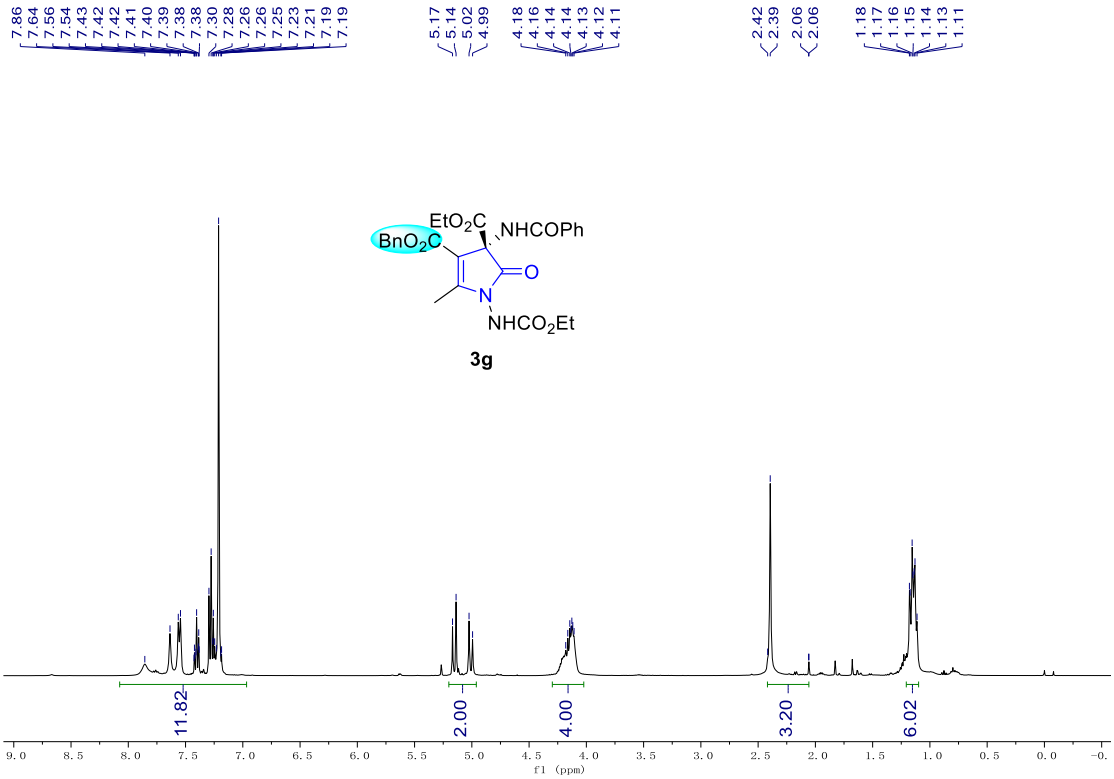
^{13}C NMR spectrum of compound **3f** ($CDCl_3$, 100 MHz)



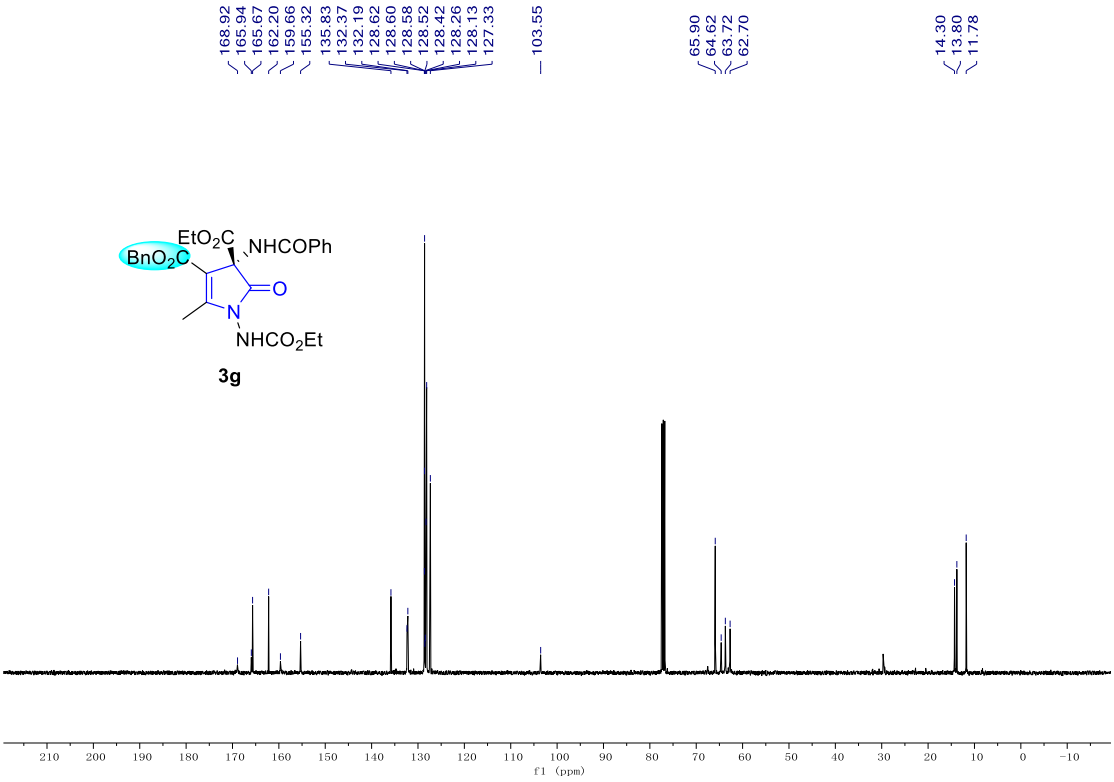
3f



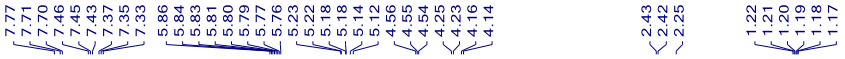
^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 400 MHz)

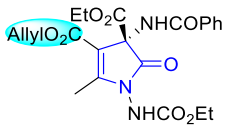


^{13}C NMR spectrum of compound **3g** ($CDCl_3$, 100 MHz)

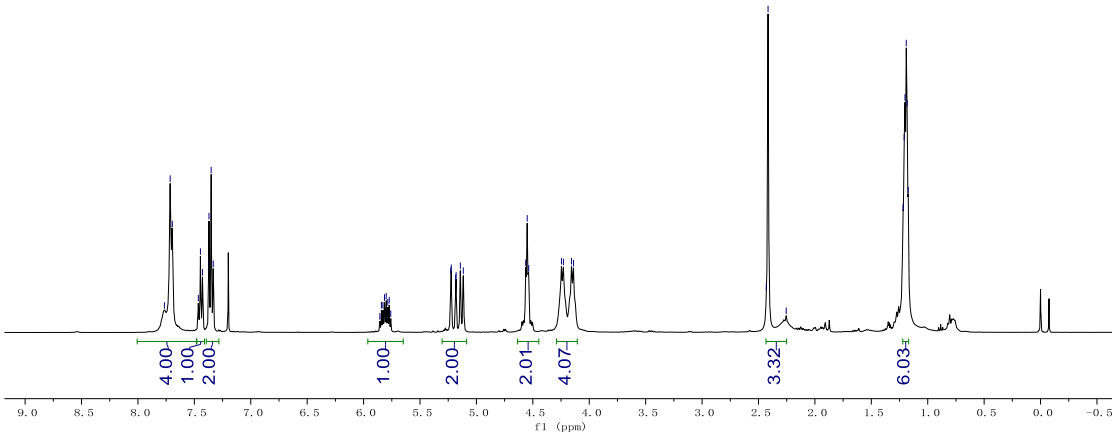


^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 400 MHz)

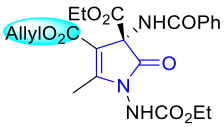




3h

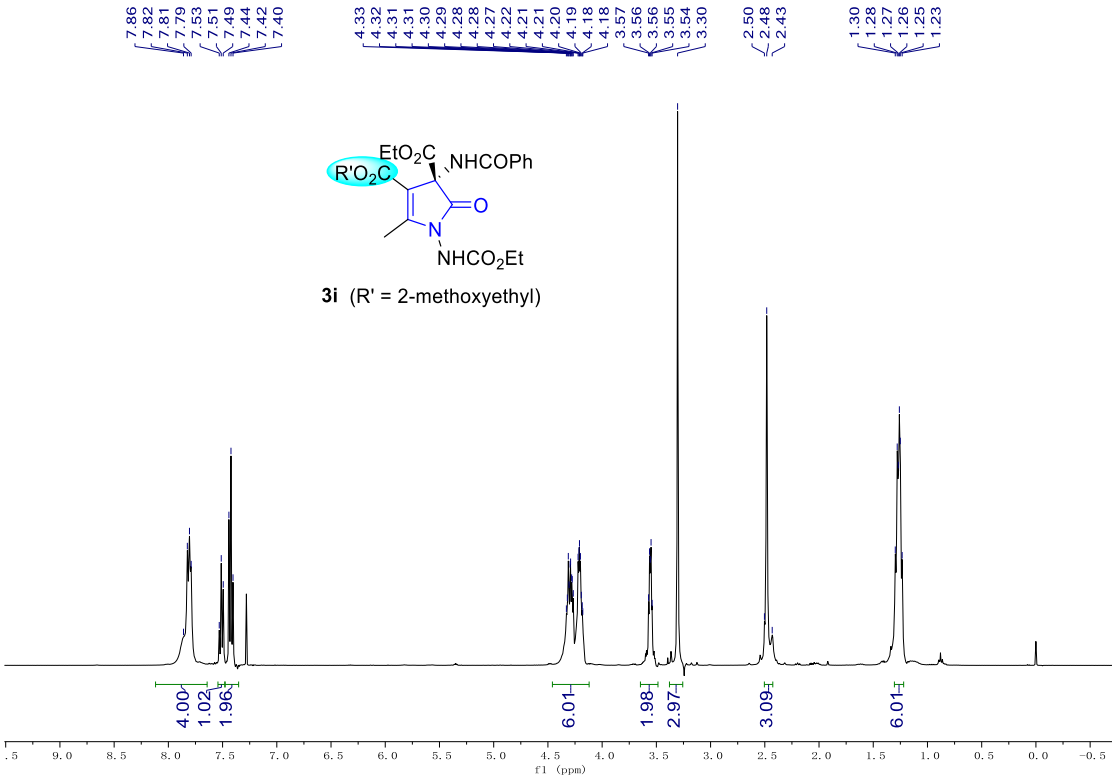


^{13}C NMR spectrum of compound **3h** ($CDCl_3$, 100 MHz)

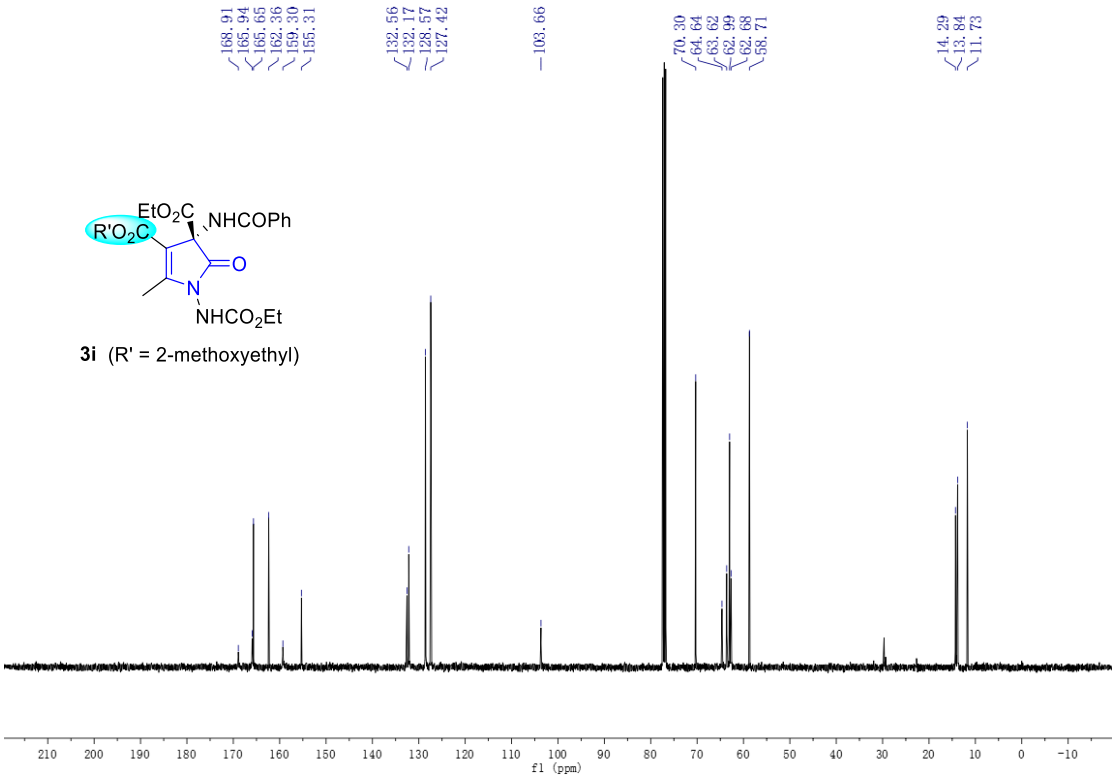


3h

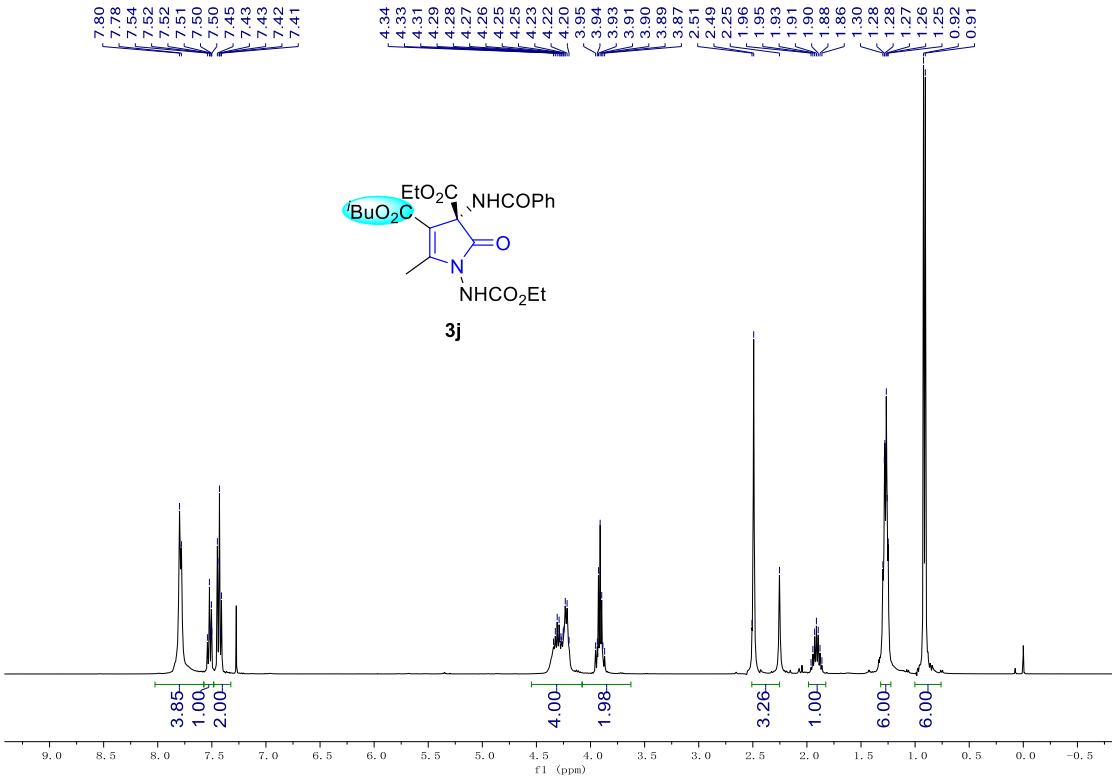
^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 400 MHz)



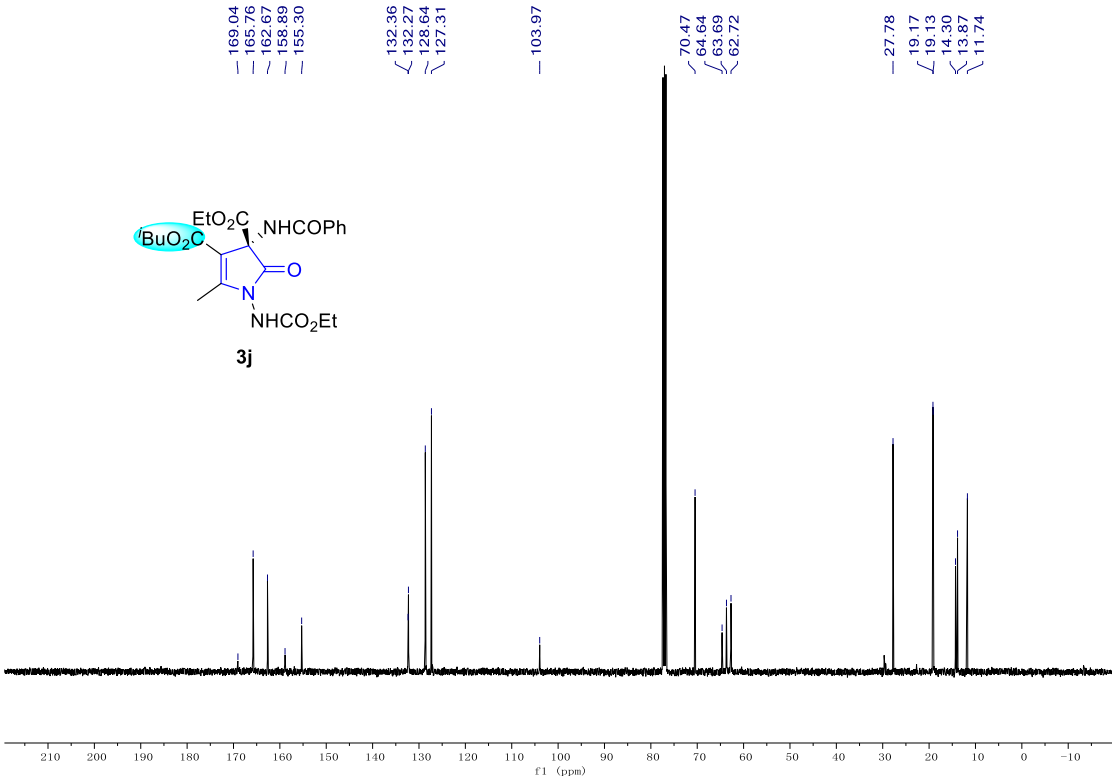
^{13}C NMR spectrum of compound **3i** ($CDCl_3$, 100 MHz)



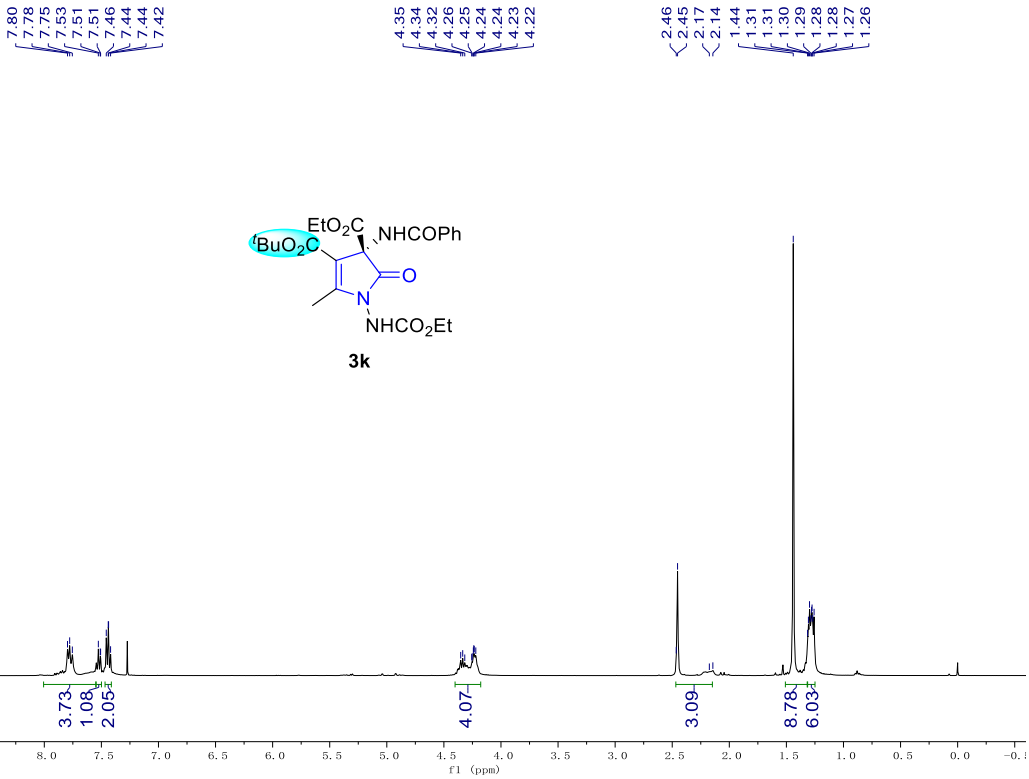
^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 400 MHz)



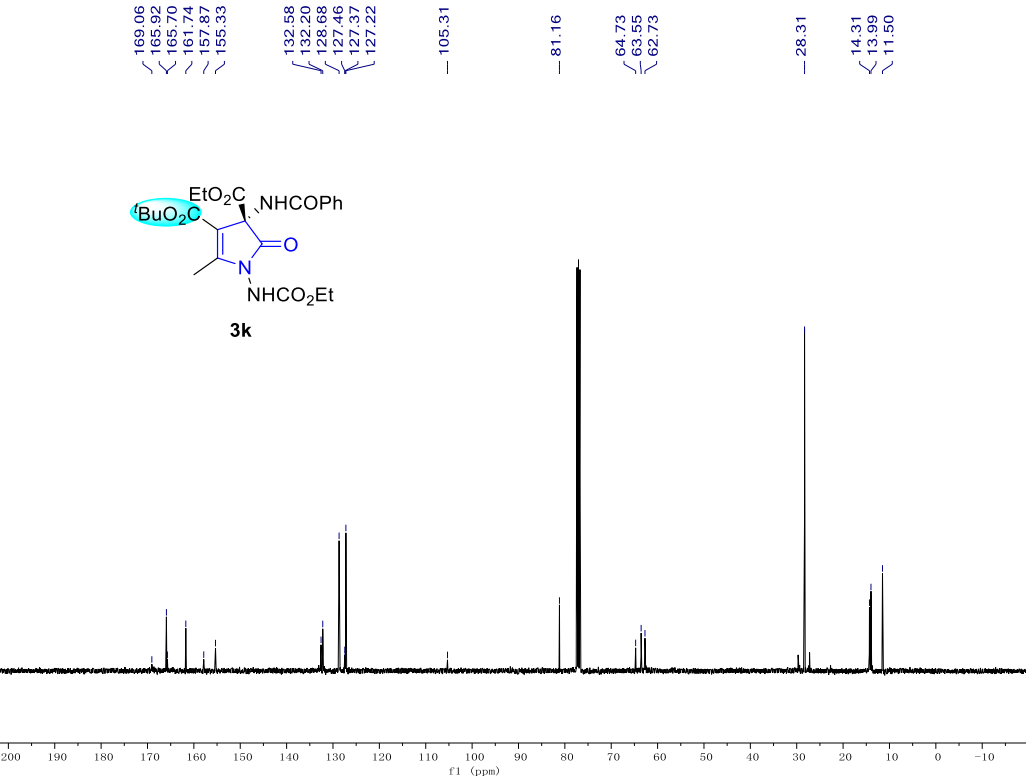
^{13}C NMR spectrum of compound **3j** ($CDCl_3$, 100 MHz)



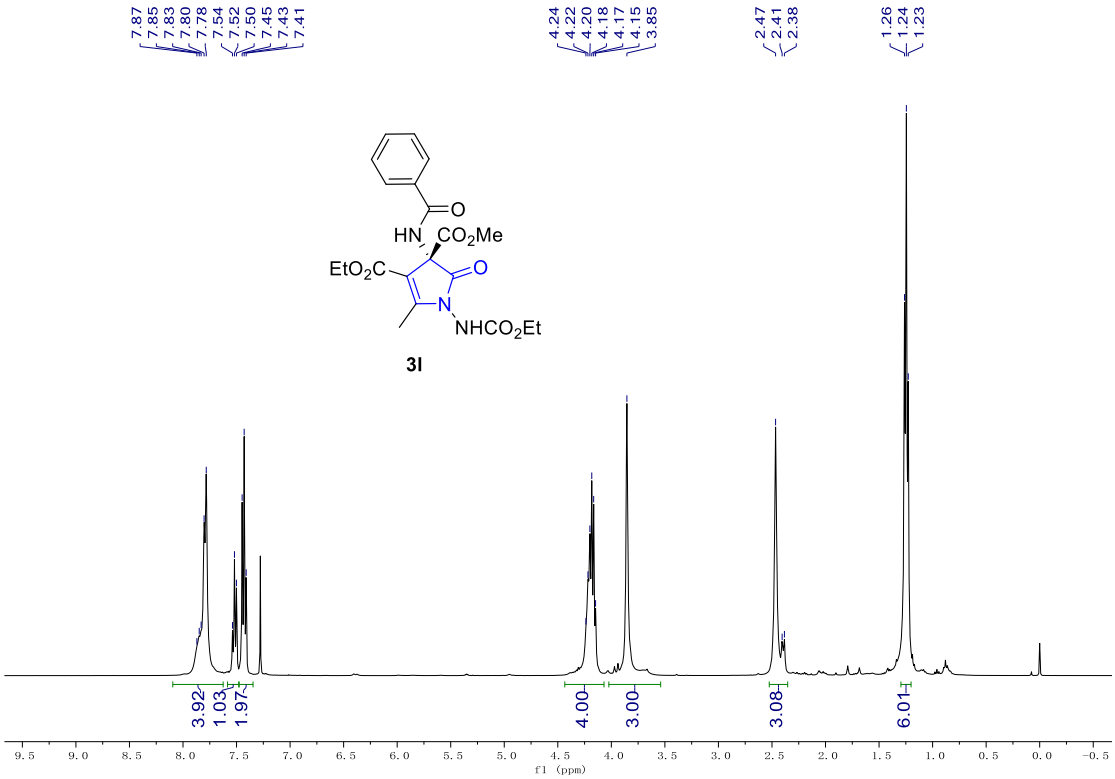
^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 400 MHz)



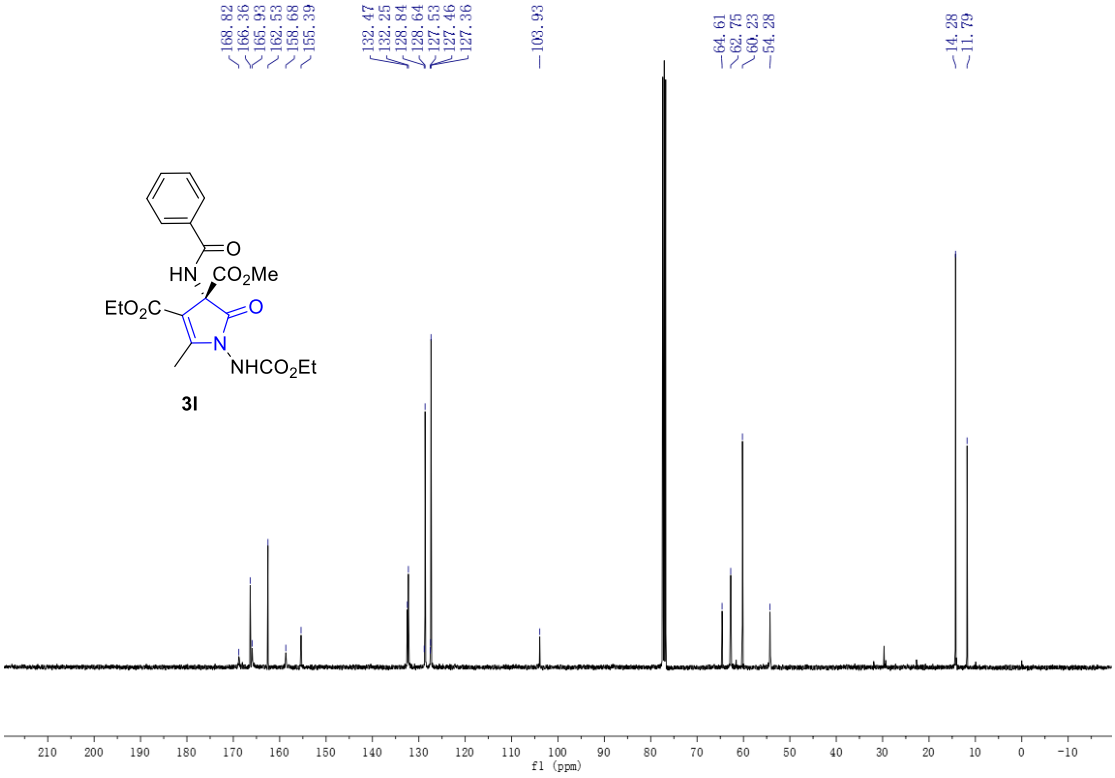
^{13}C NMR spectrum of compound **3k** ($CDCl_3$, 100 MHz)



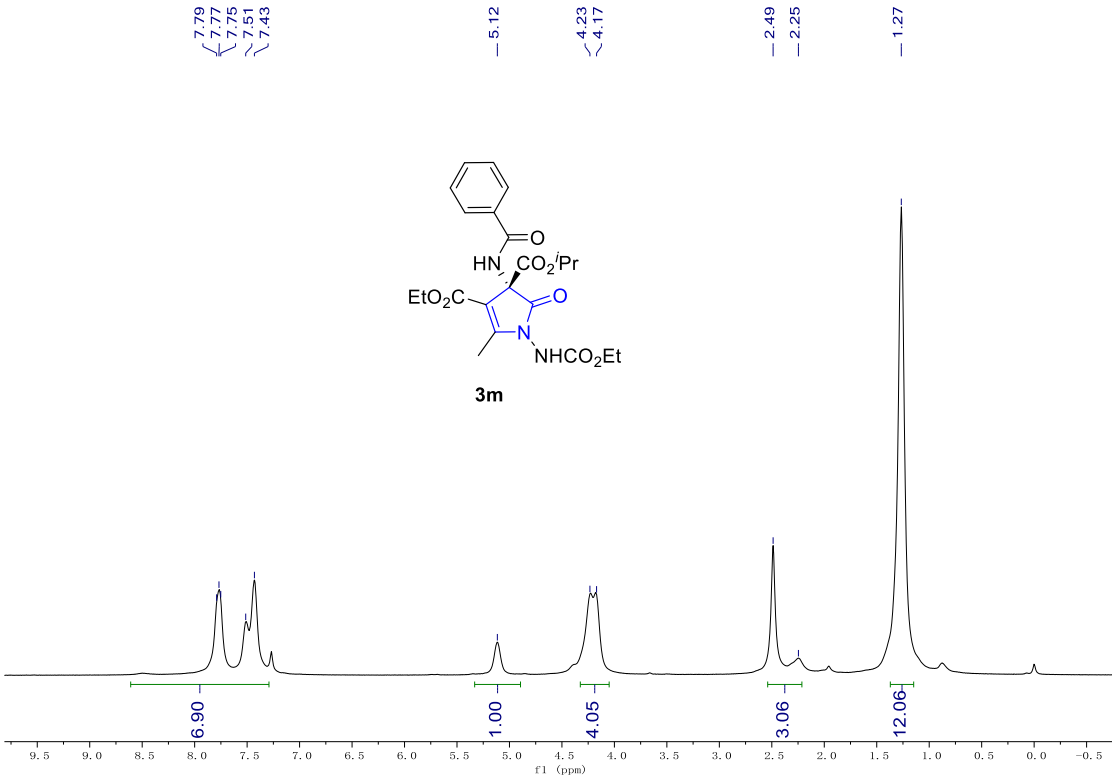
^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 400 MHz)



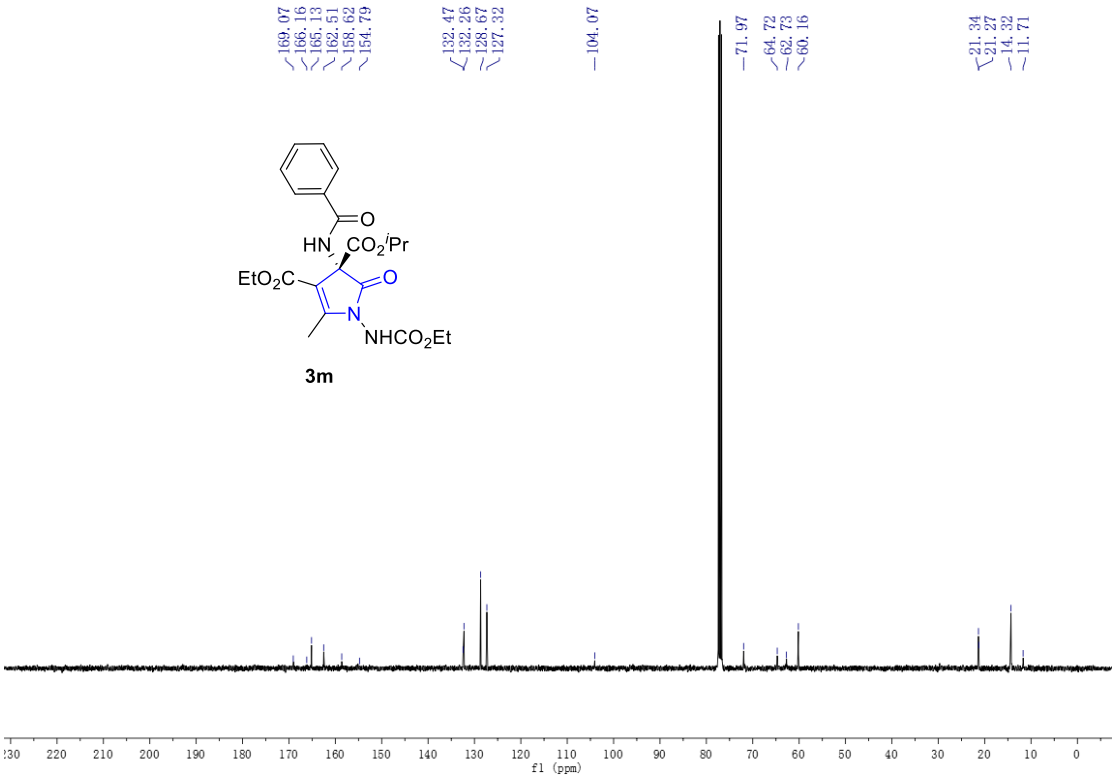
^{13}C NMR spectrum of compound **3l** ($CDCl_3$, 100 MHz)



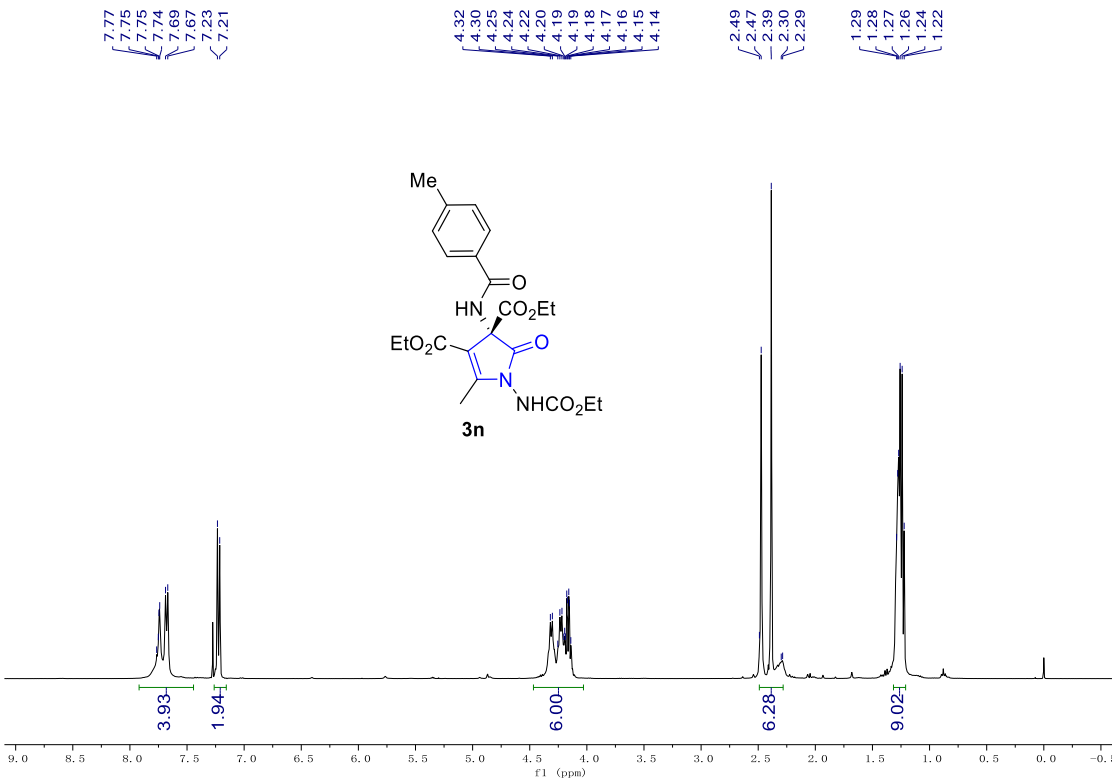
^{1}H NMR spectrum of compound **3m** ($CDCl_3$, 400 MHz)



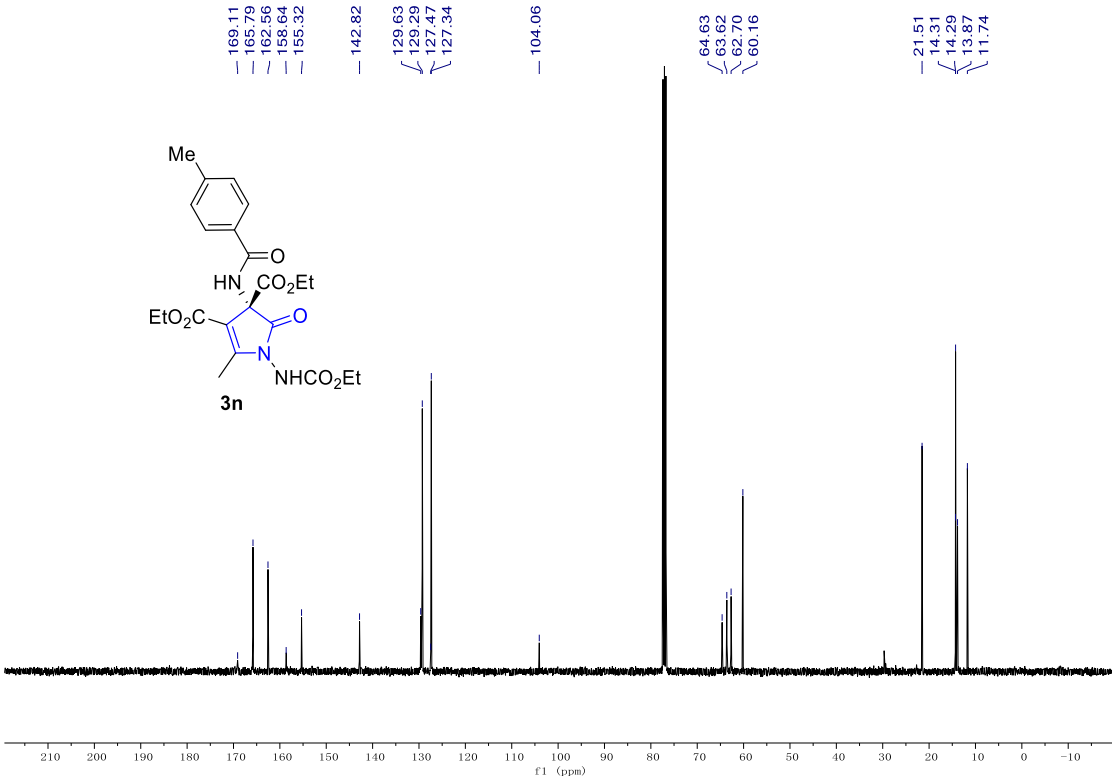
^{13}C NMR spectrum of compound **3m** ($CDCl_3$, 100 MHz)



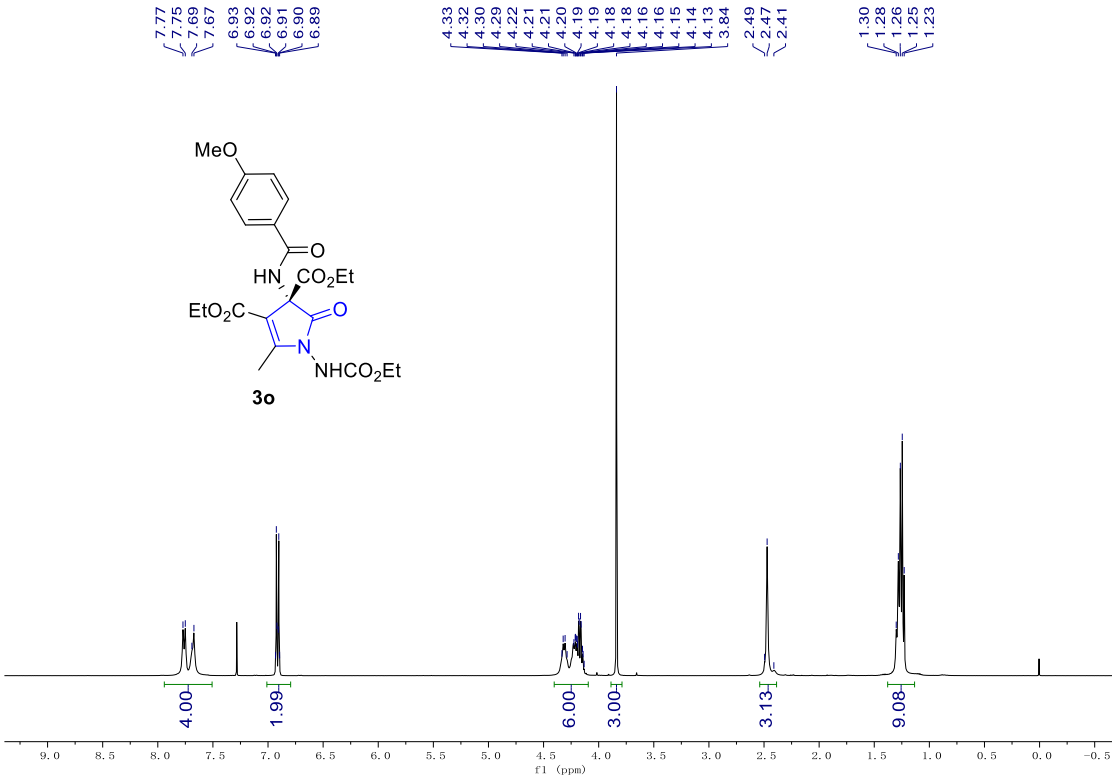
^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 400 MHz)



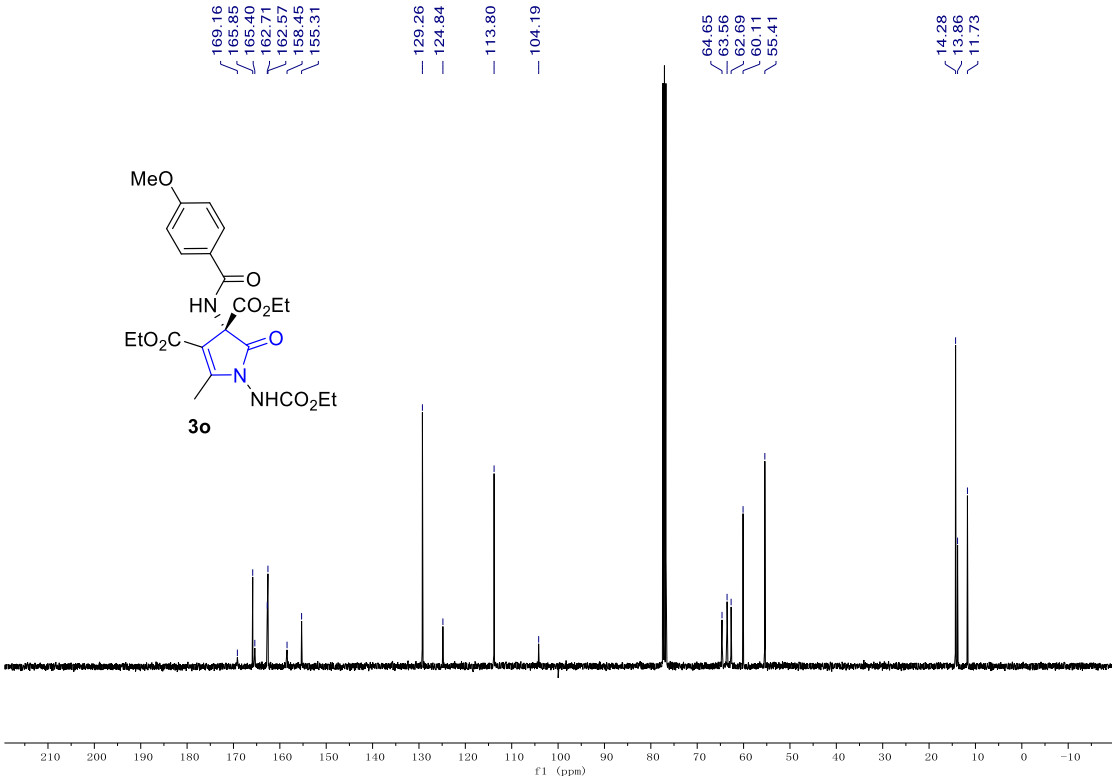
^{13}C NMR spectrum of compound **3n** ($CDCl_3$, 100 MHz)



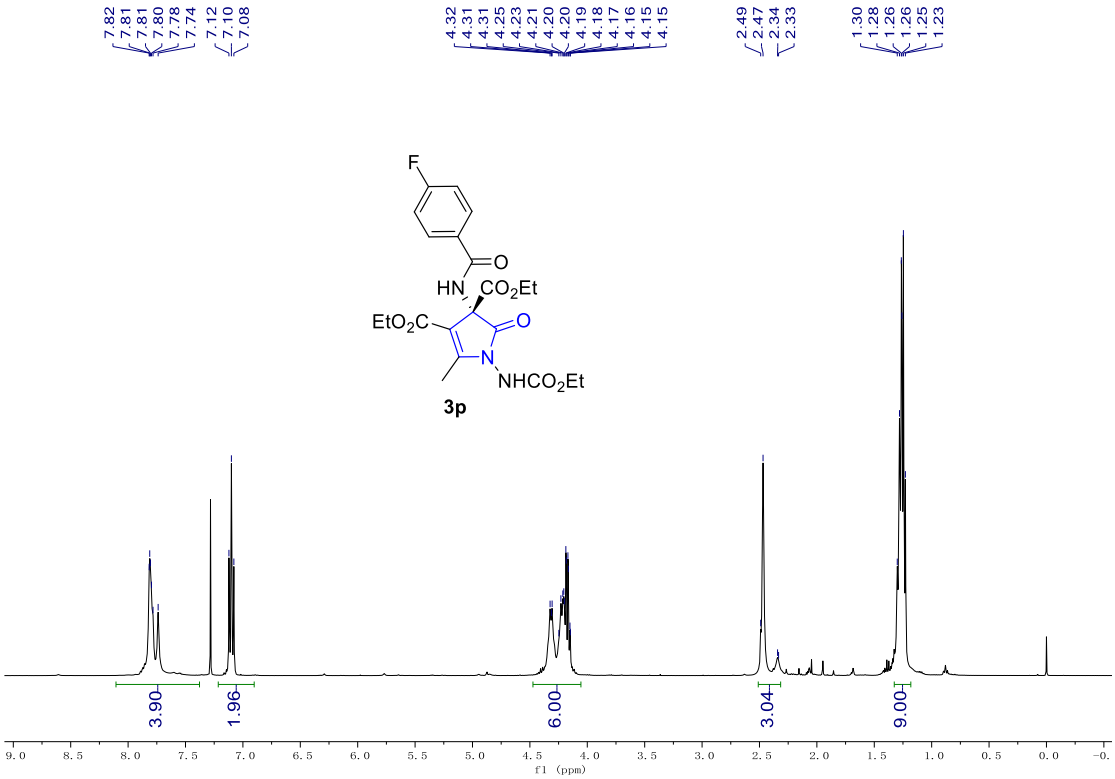
^{1}H NMR spectrum of compound **3o** ($CDCl_3$, 400 MHz)



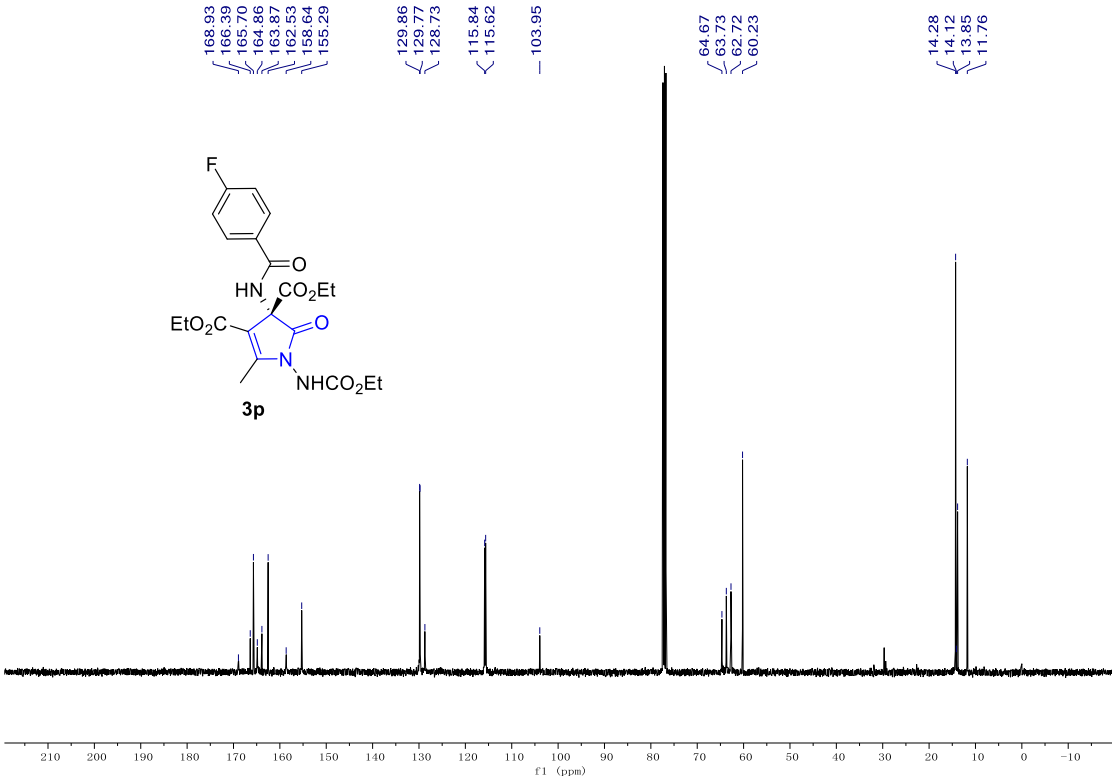
^{13}C NMR spectrum of compound **3o** ($CDCl_3$, 100 MHz)



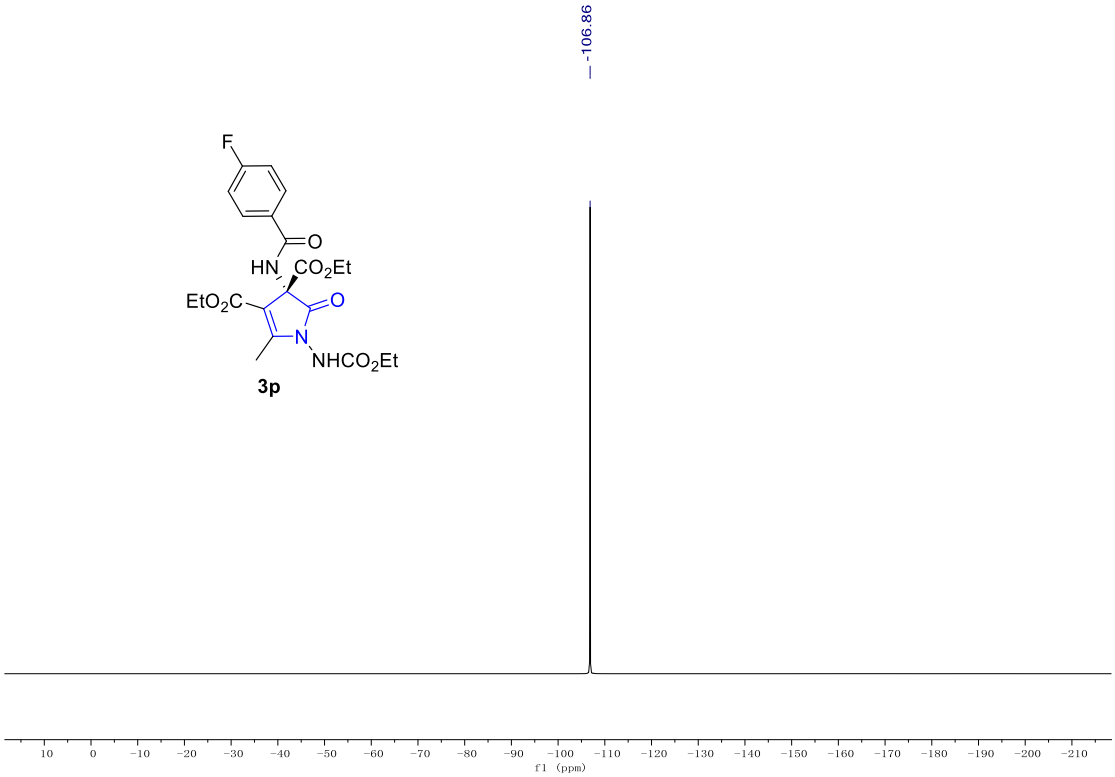
^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 400 MHz)



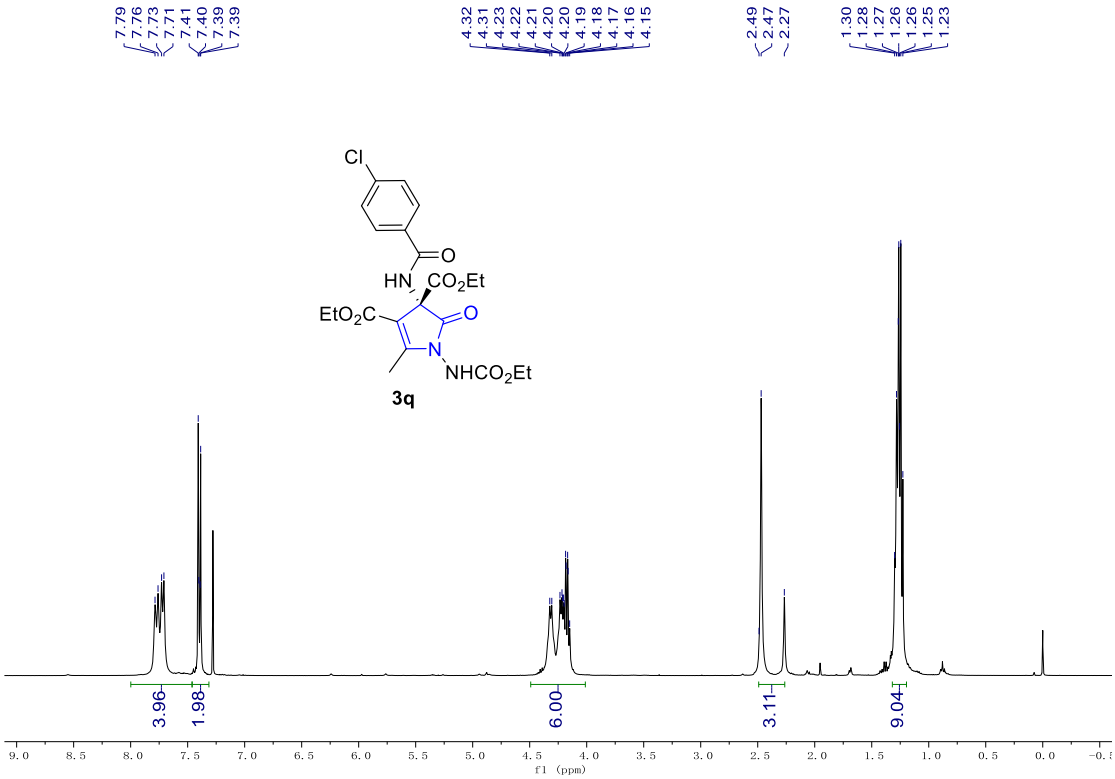
^{13}C NMR spectrum of compound **3p** ($CDCl_3$, 100 MHz)



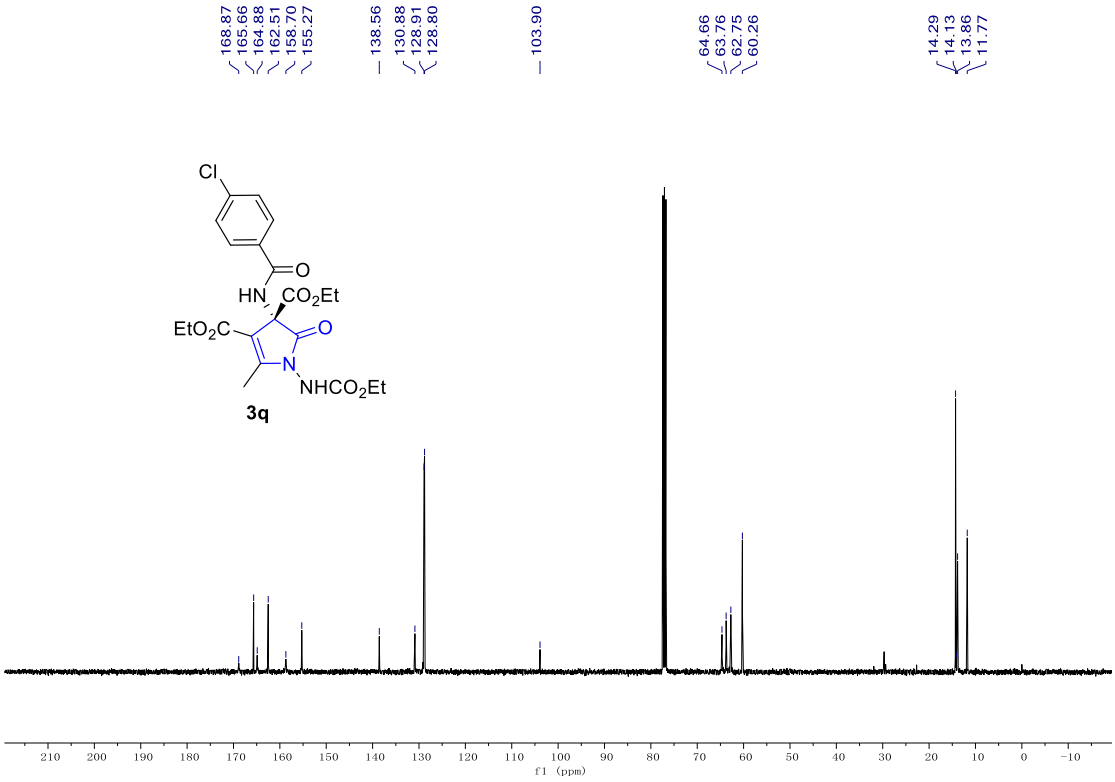
^{19}F NMR spectrum of compound **3p** ($CDCl_3$, 376 MHz)



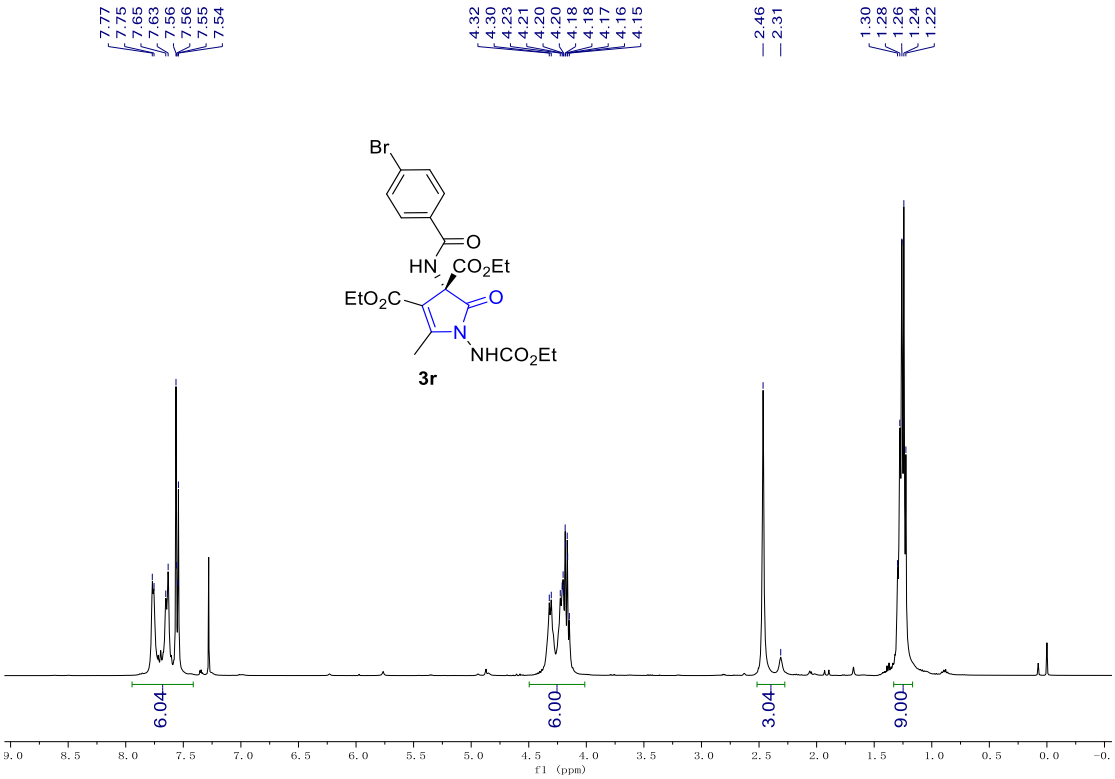
^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 400 MHz)



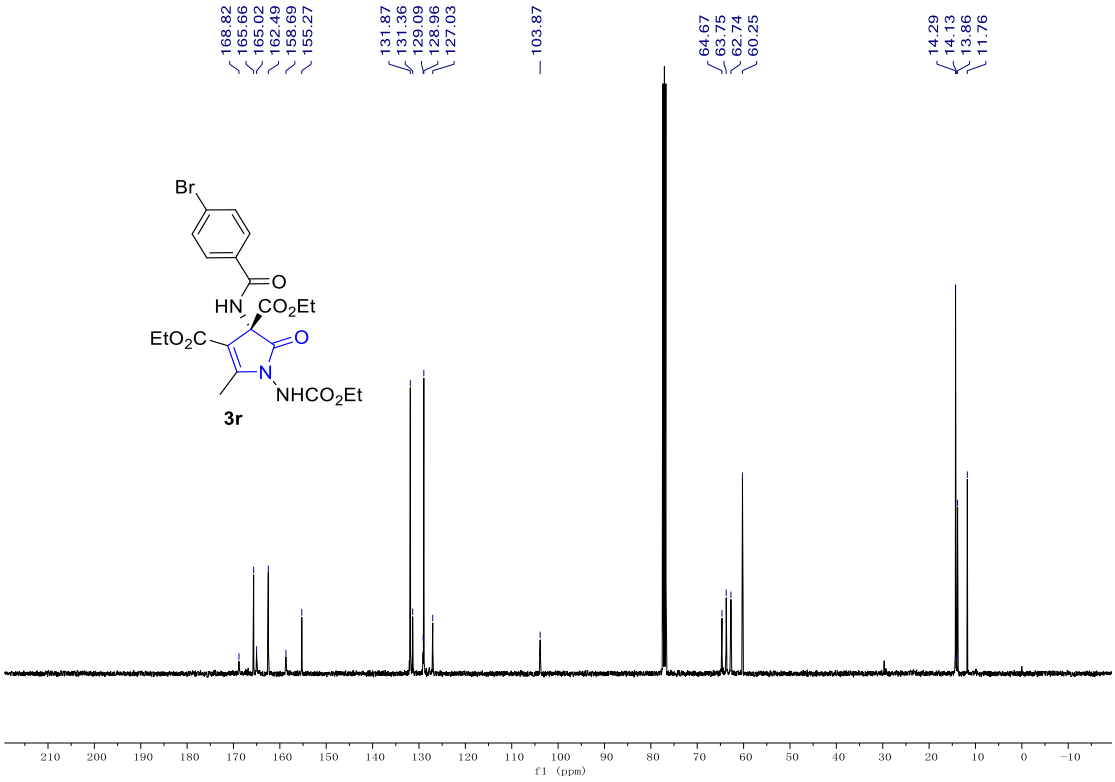
^{13}C NMR spectrum of compound **3q** ($CDCl_3$, 100 MHz)



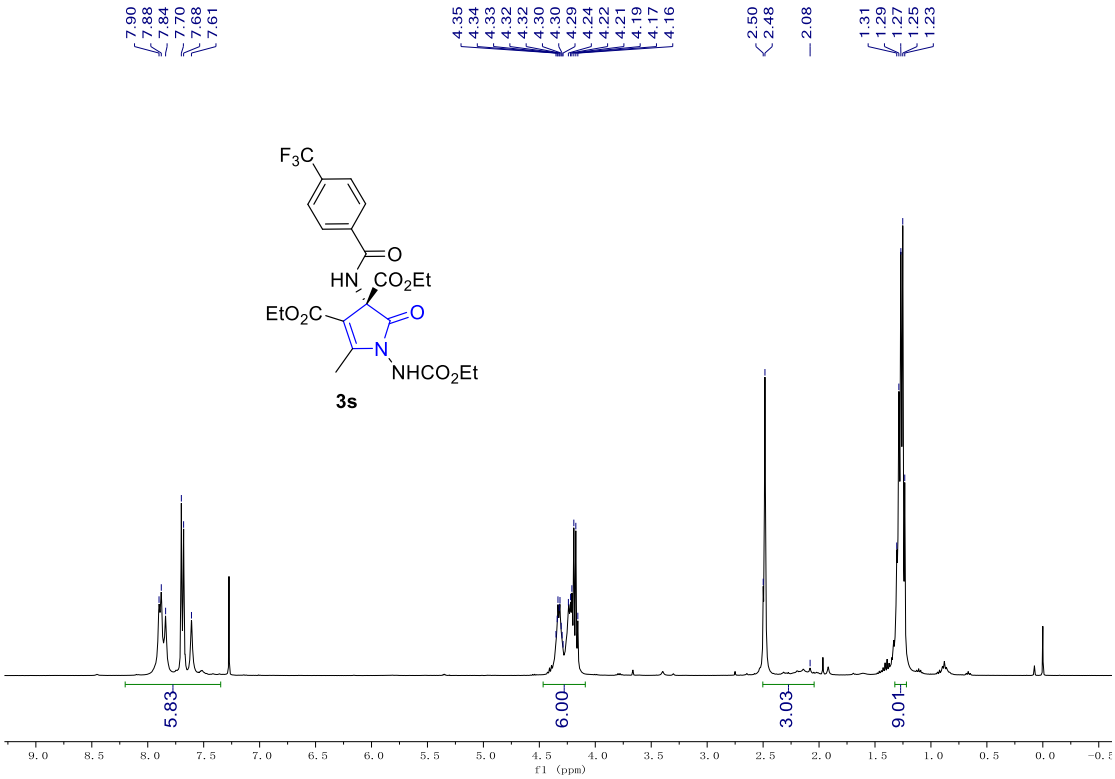
^{1}H NMR spectrum of compound **3r** ($CDCl_3$, 400 MHz)



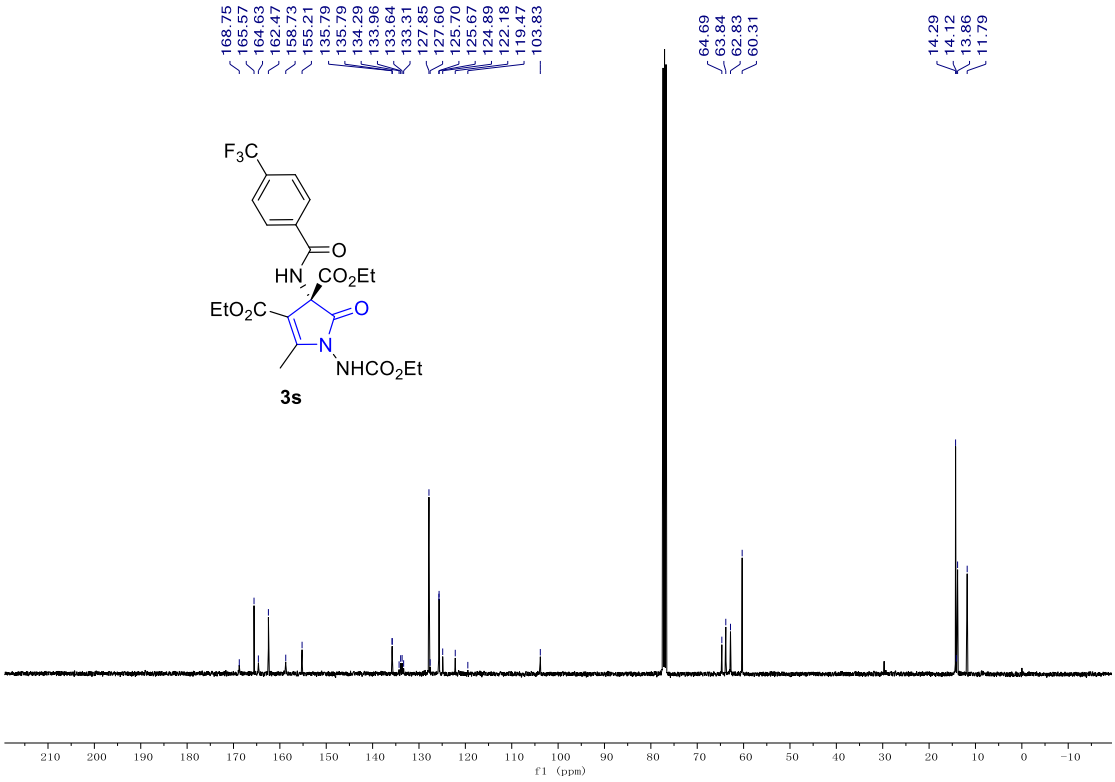
^{13}C NMR spectrum of compound **3r** ($CDCl_3$, 100 MHz)



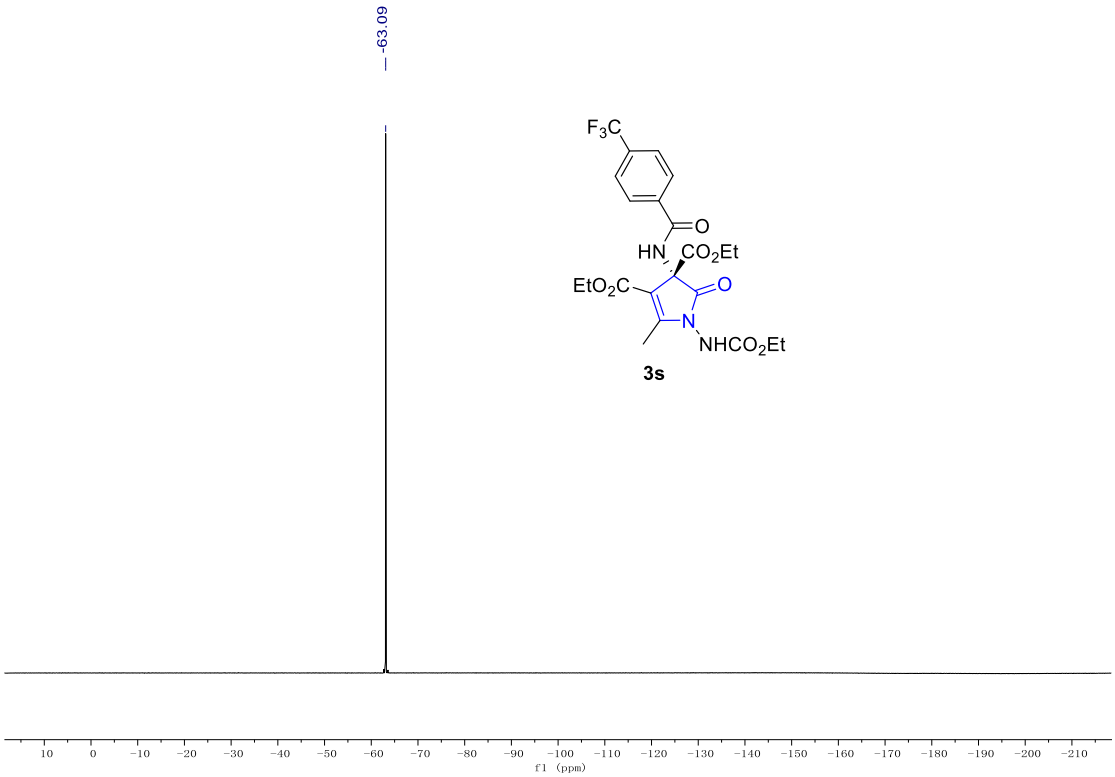
^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 400 MHz)



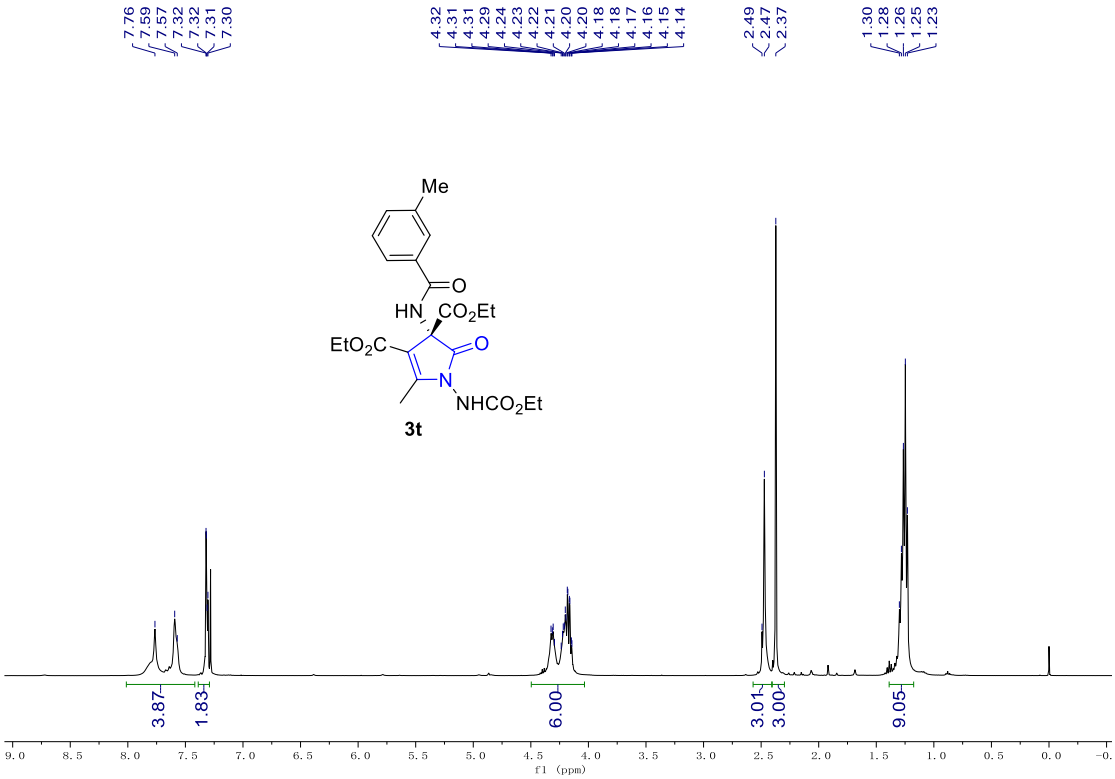
^{13}C NMR spectrum of compound **3s** ($CDCl_3$, 100 MHz)



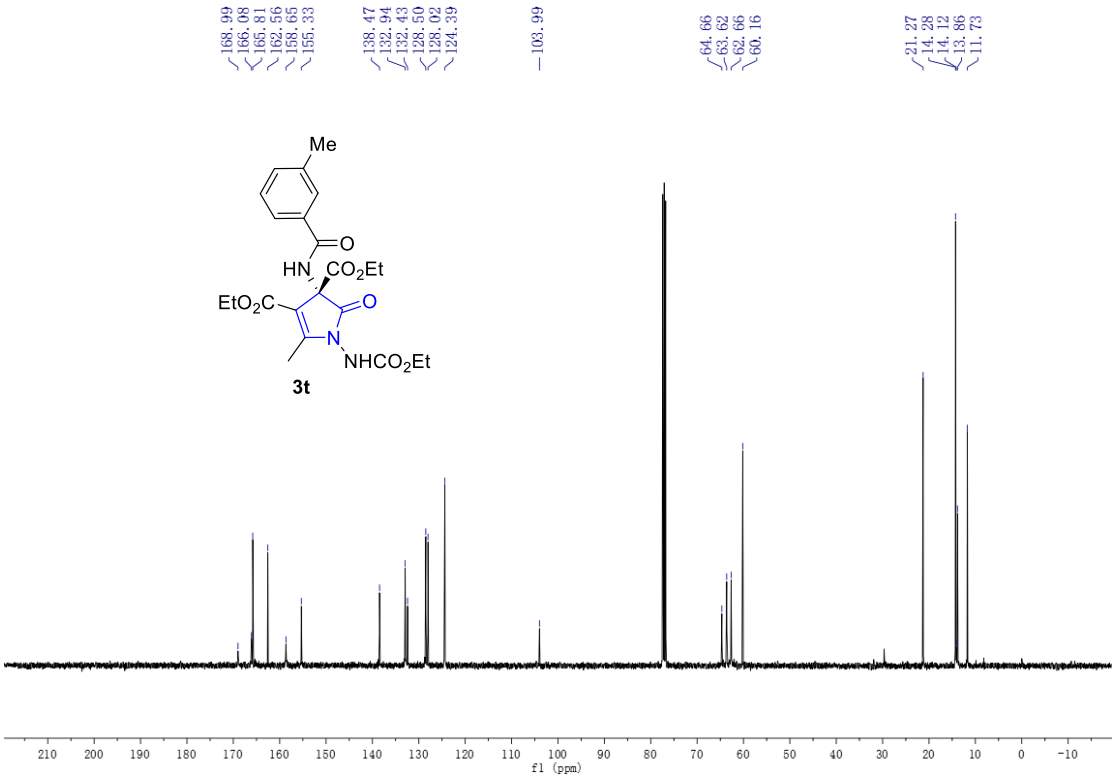
^{19}F NMR spectrum of compound **3s** ($CDCl_3$, 376 MHz)



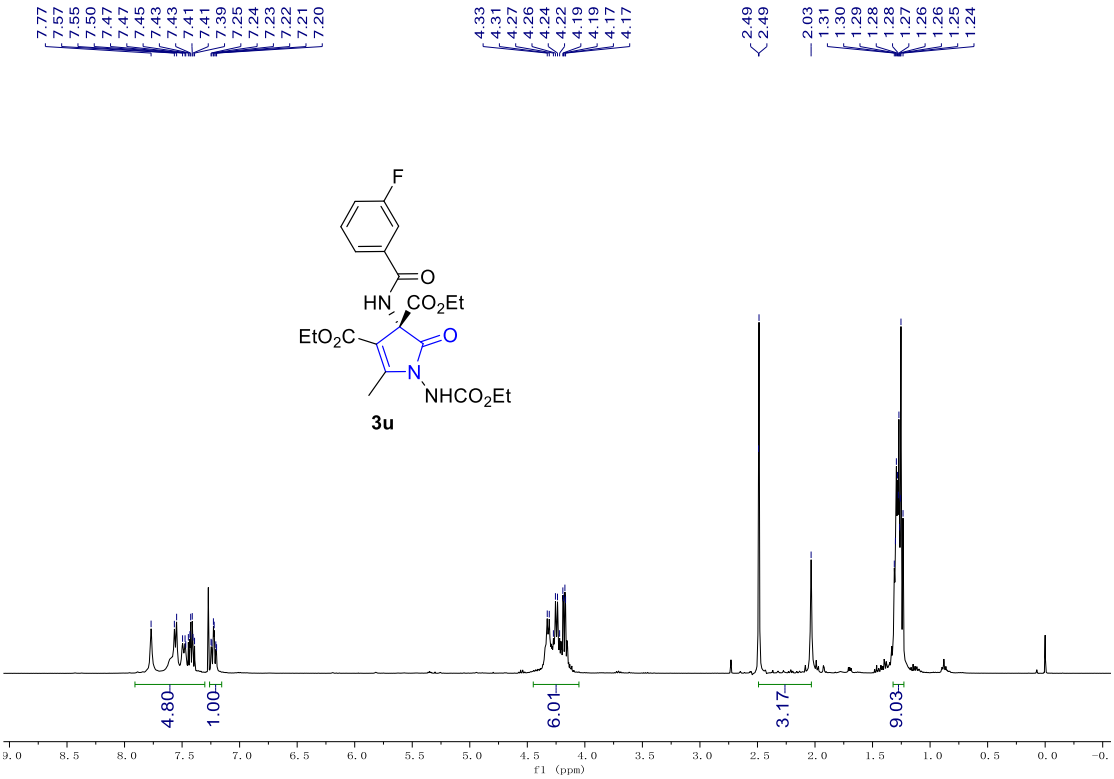
^{1}H NMR spectrum of compound **3t** ($CDCl_3$, 400 MHz)



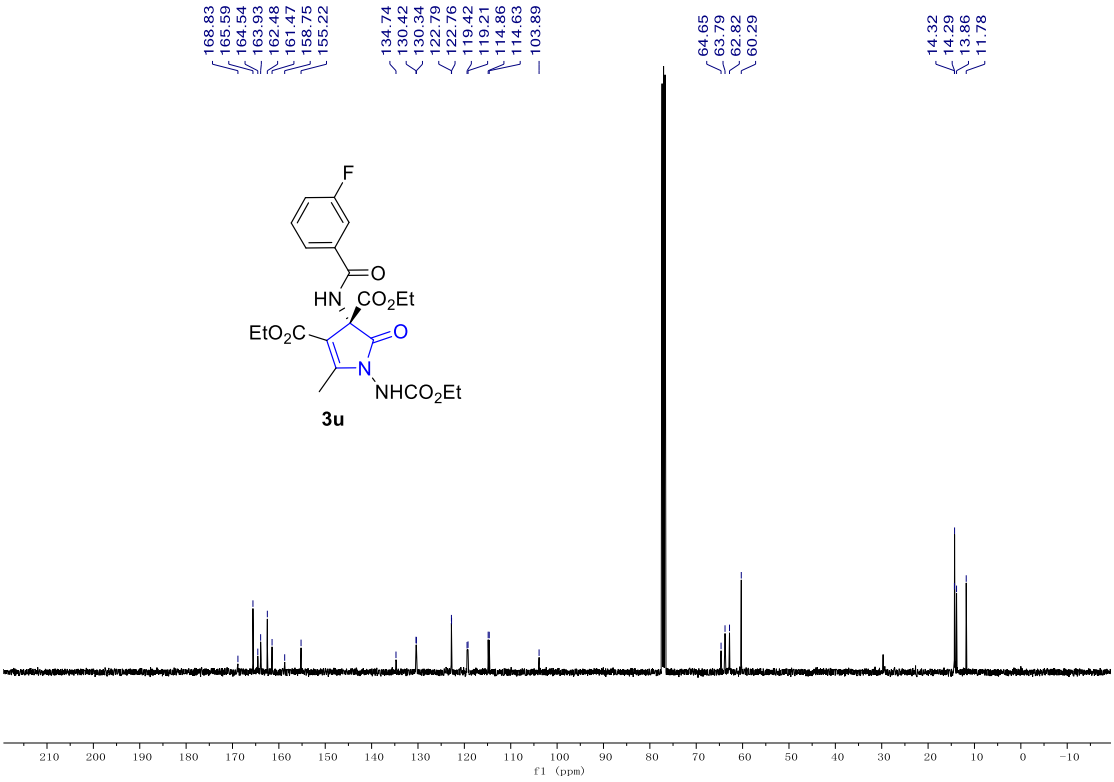
^{13}C NMR spectrum of compound **3t** ($CDCl_3$, 100 MHz)



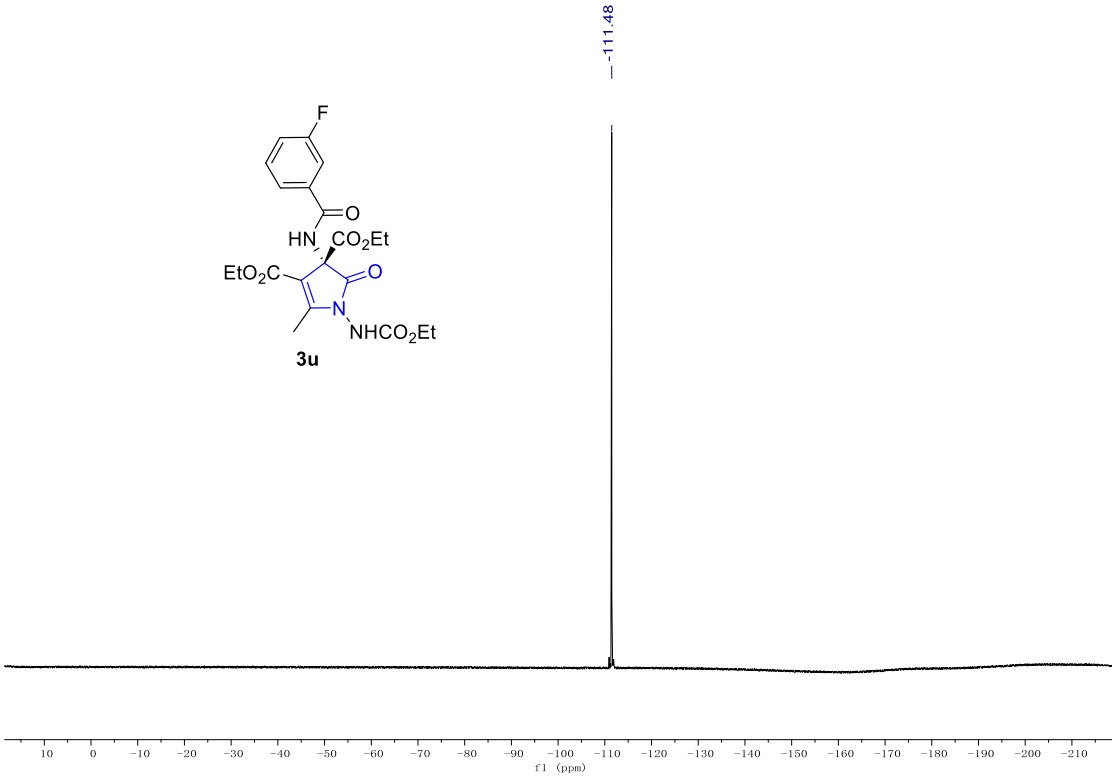
^{1}H NMR spectrum of compound **3u** ($CDCl_3$, 400 MHz)



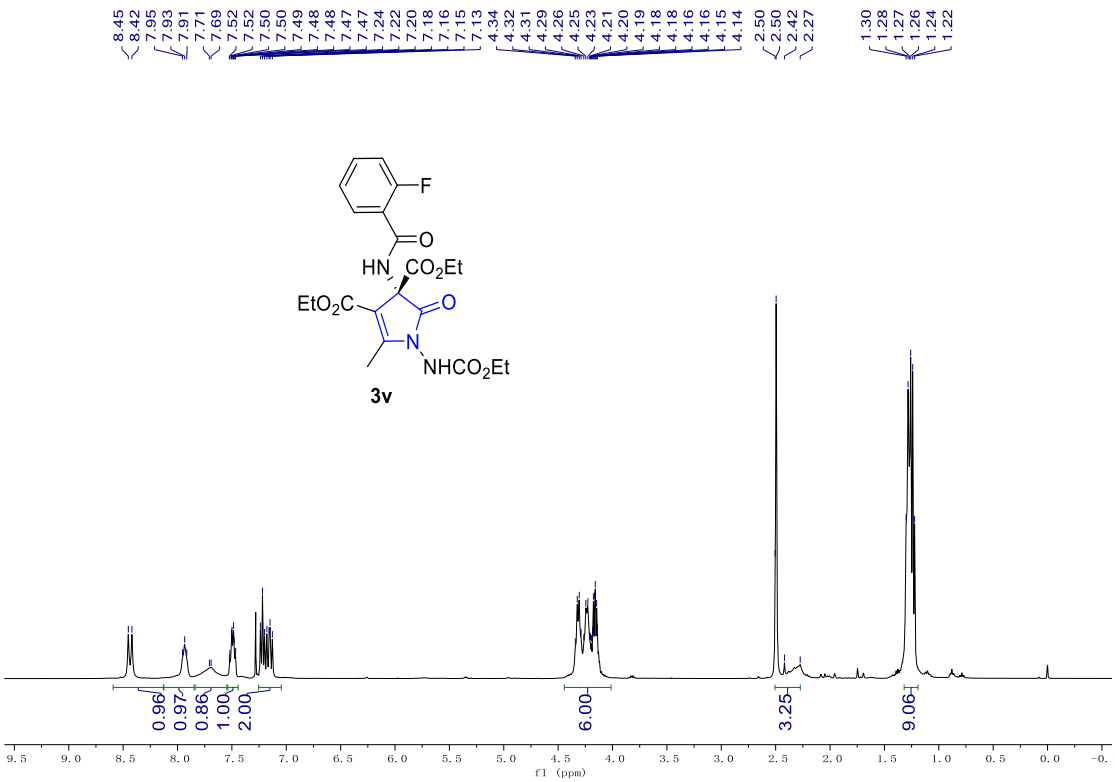
^{13}C NMR spectrum of compound **3u** ($CDCl_3$, 100 MHz)



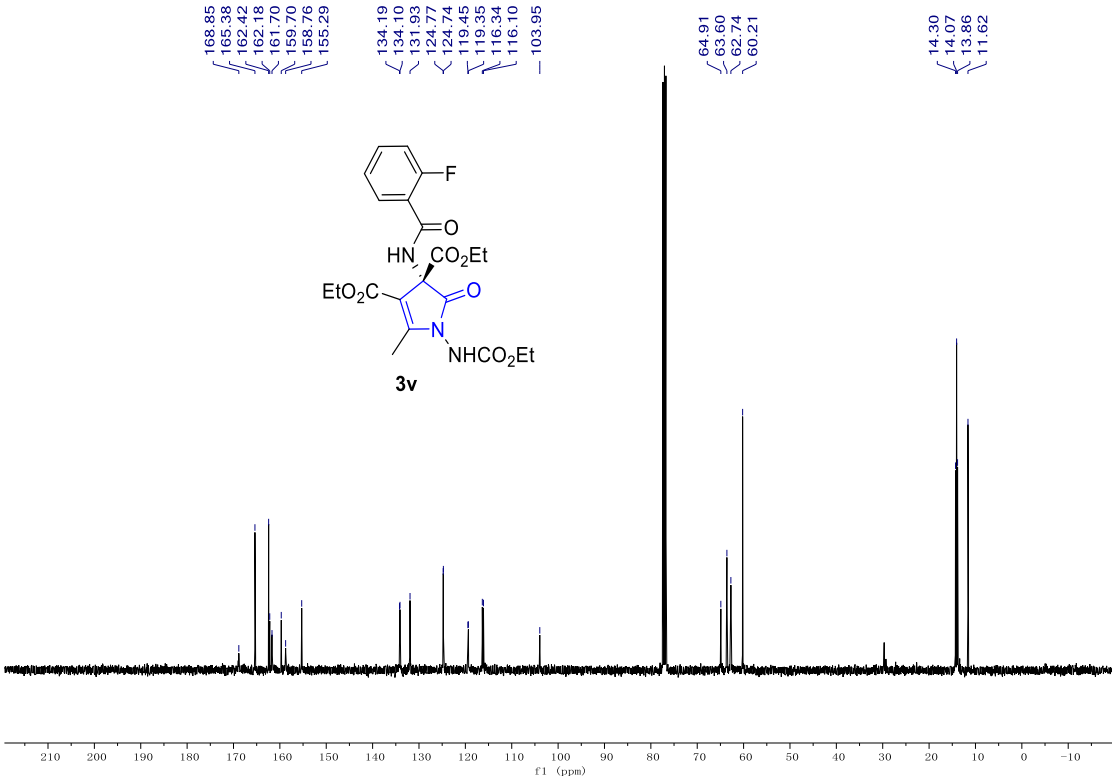
^{19}F NMR spectrum of compound **3u** ($CDCl_3$, 376 MHz)



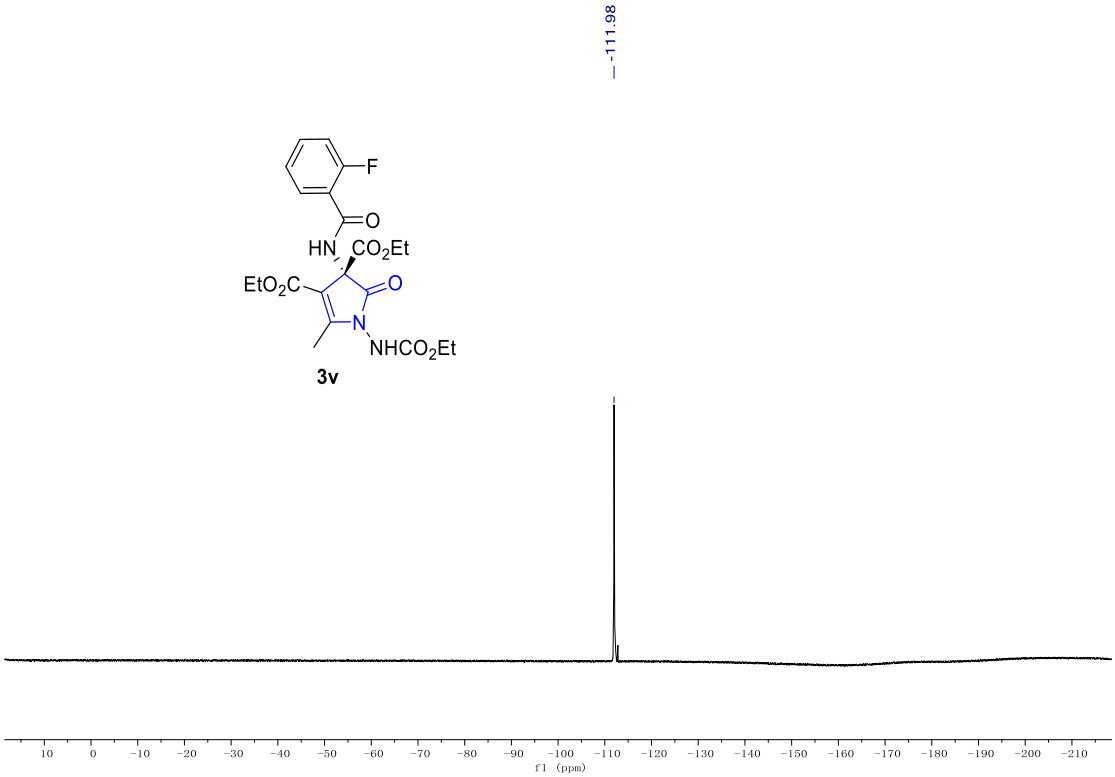
^{1}H NMR spectrum of compound **3v** ($CDCl_3$, 400 MHz)



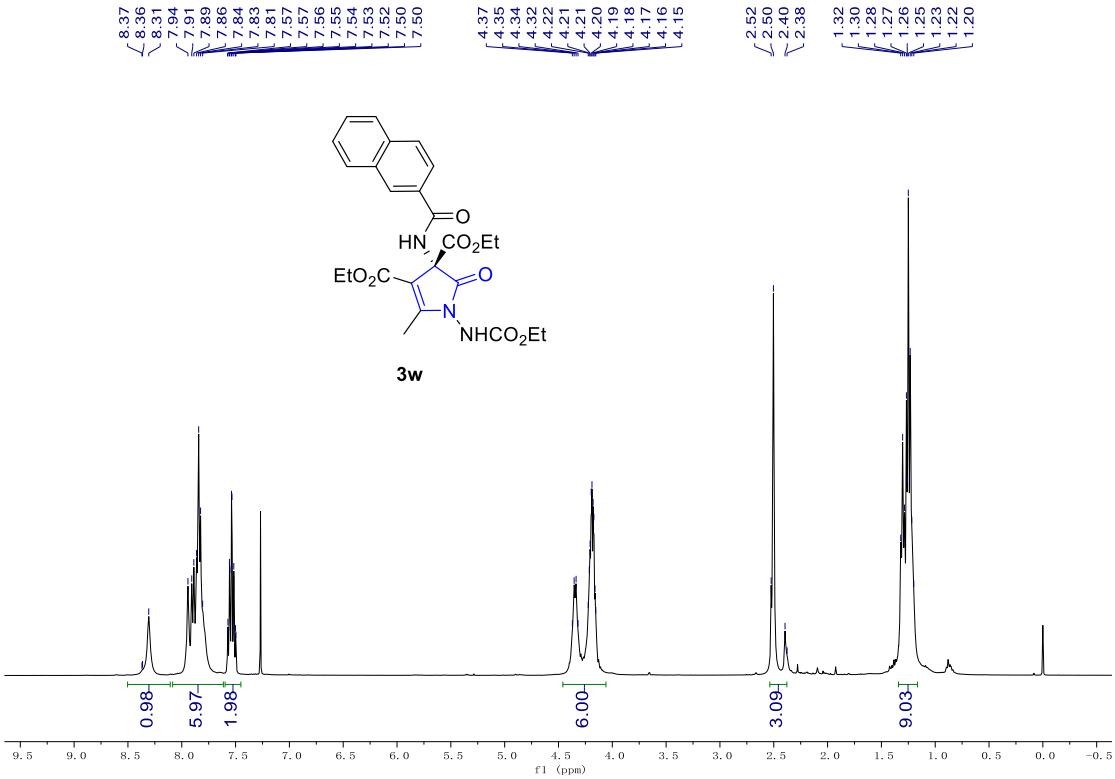
^{13}C NMR spectrum of compound **3v** ($CDCl_3$, 100 MHz)



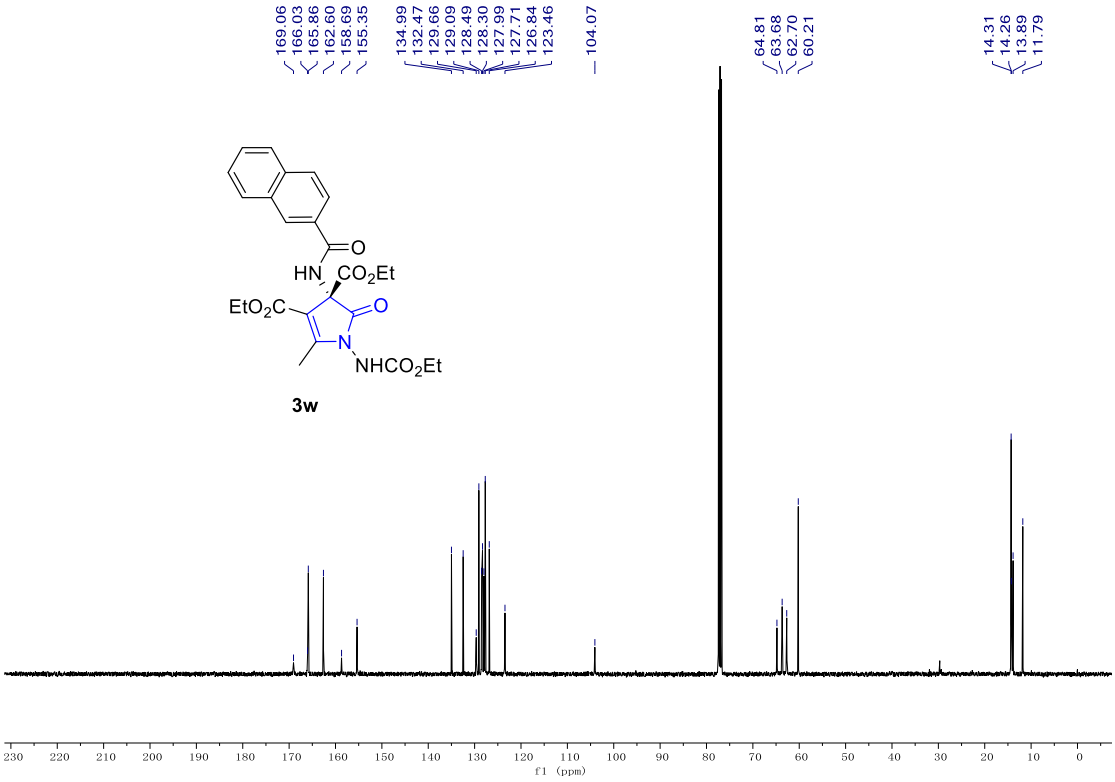
^{19}F NMR spectrum of compound **3v** ($CDCl_3$, 376 MHz)



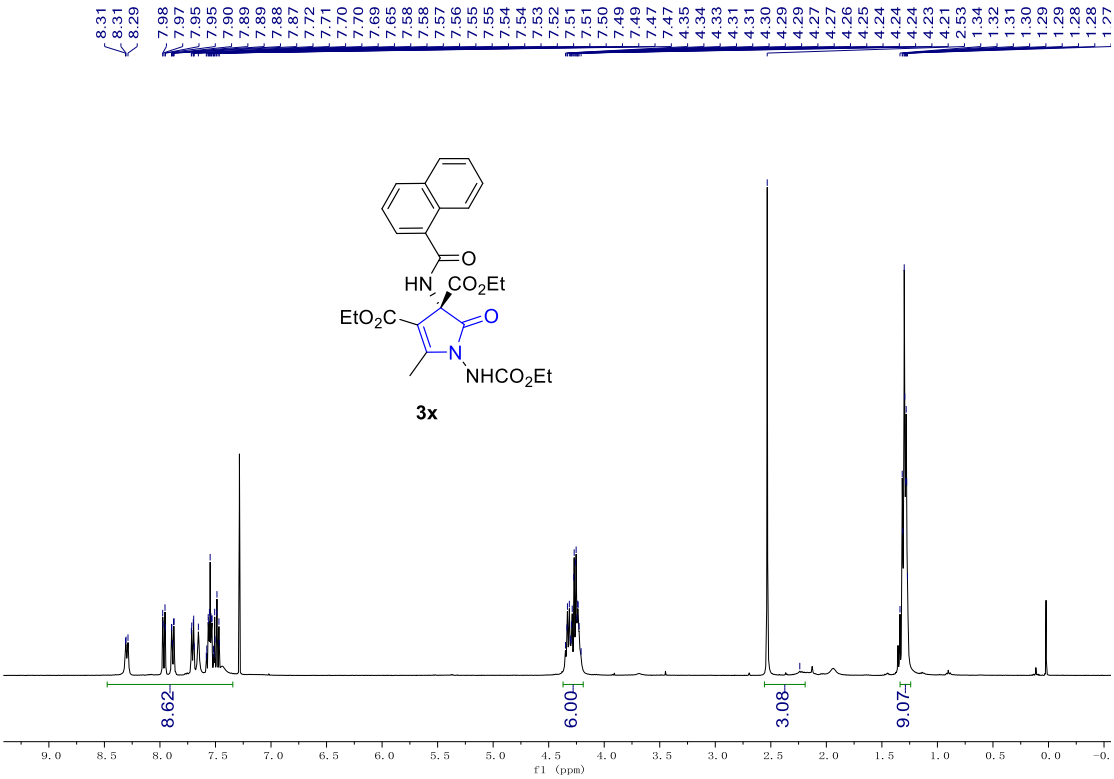
^{1}H NMR spectrum of compound **3w** ($CDCl_3$, 400 MHz)



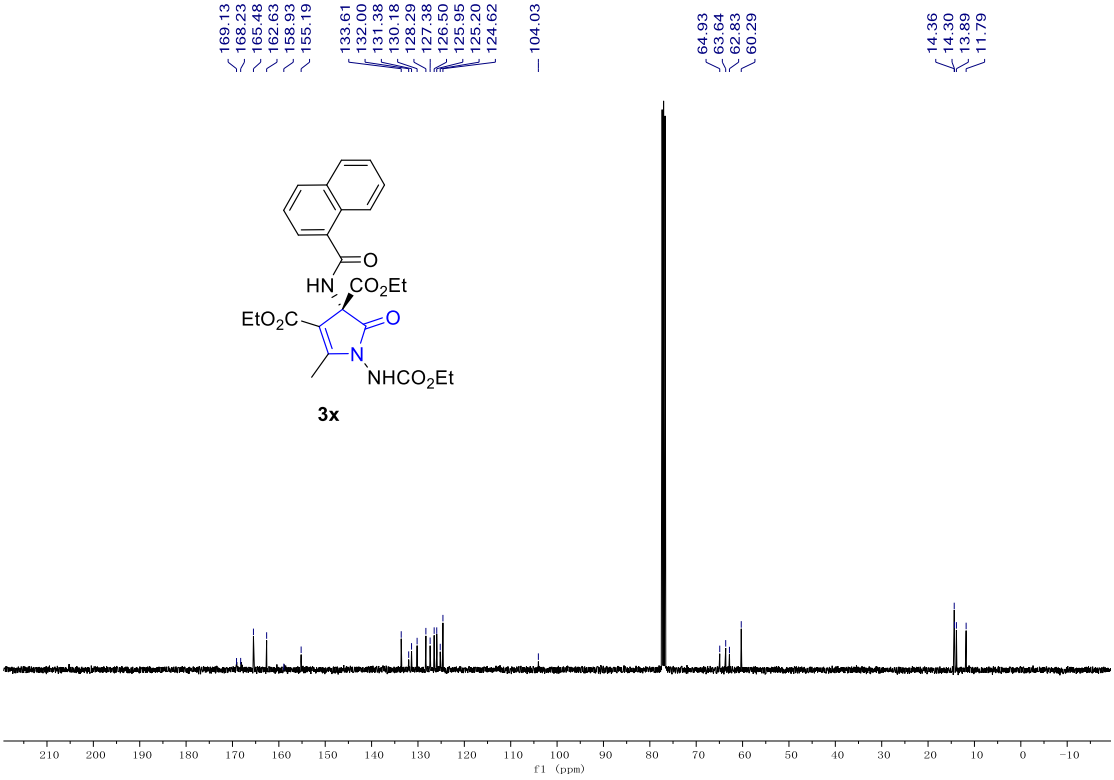
^{13}C NMR spectrum of compound **3w** ($CDCl_3$, 100 MHz)



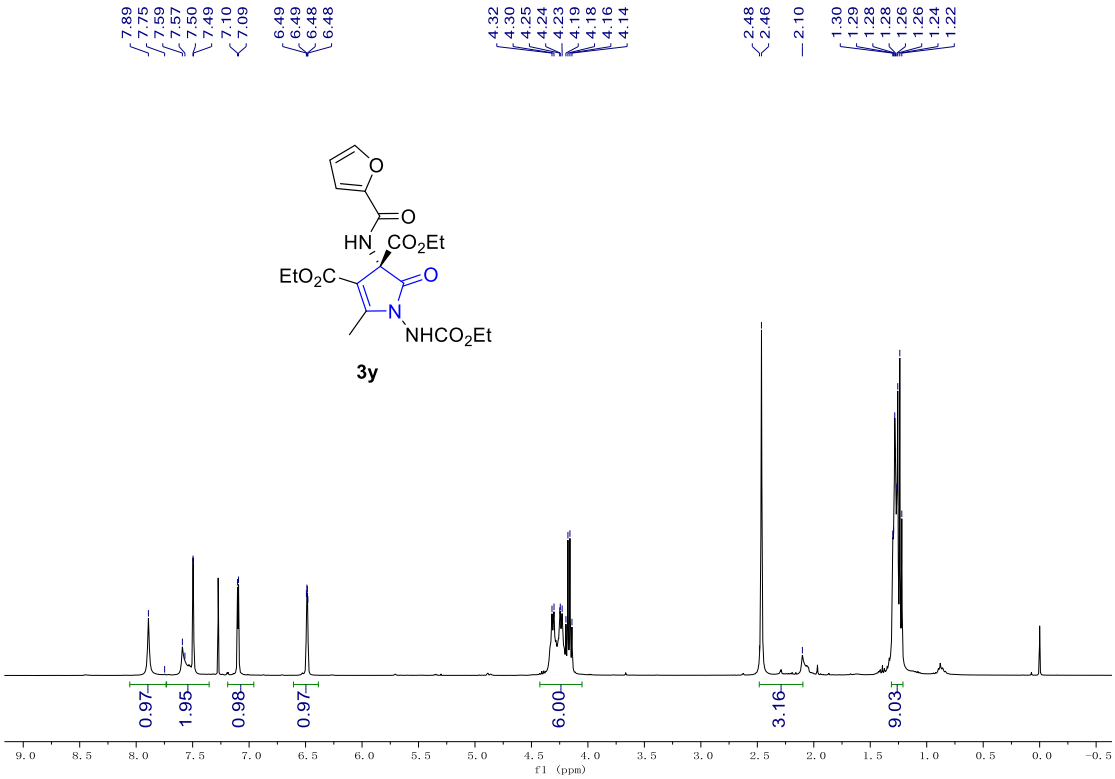
^{1}H NMR spectrum of compound **3x** ($CDCl_3$, 400 MHz)



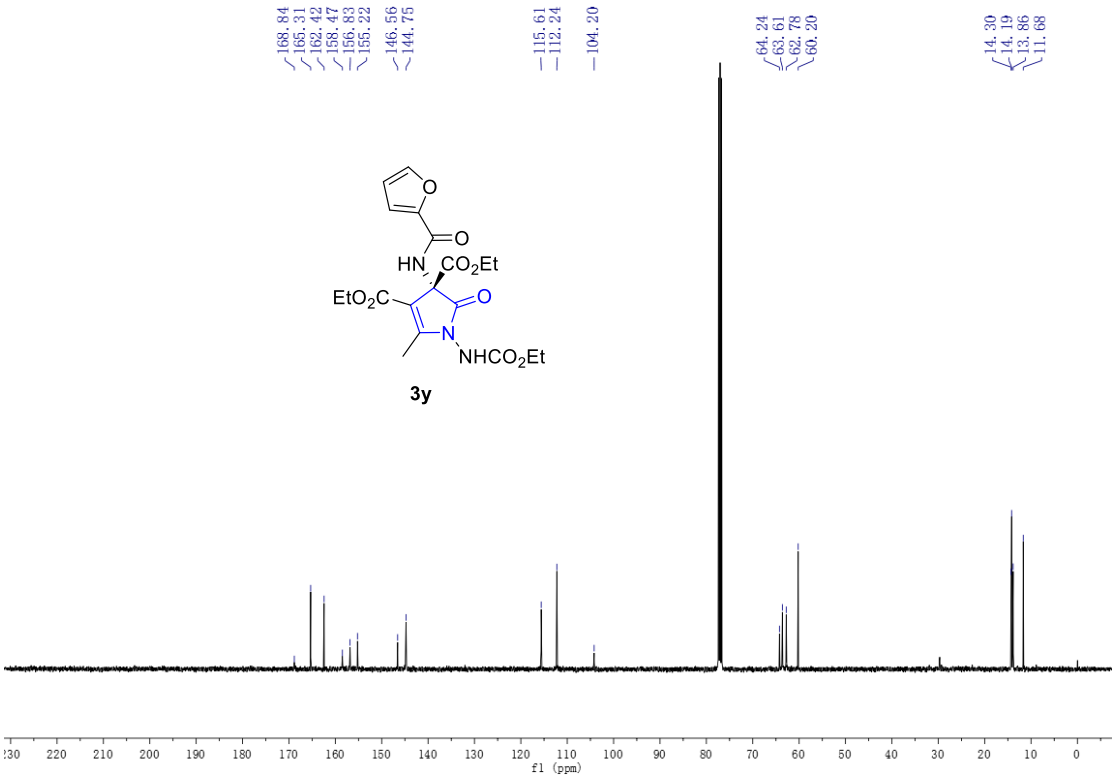
^{13}C NMR spectrum of compound **3x** ($CDCl_3$, 100 MHz)



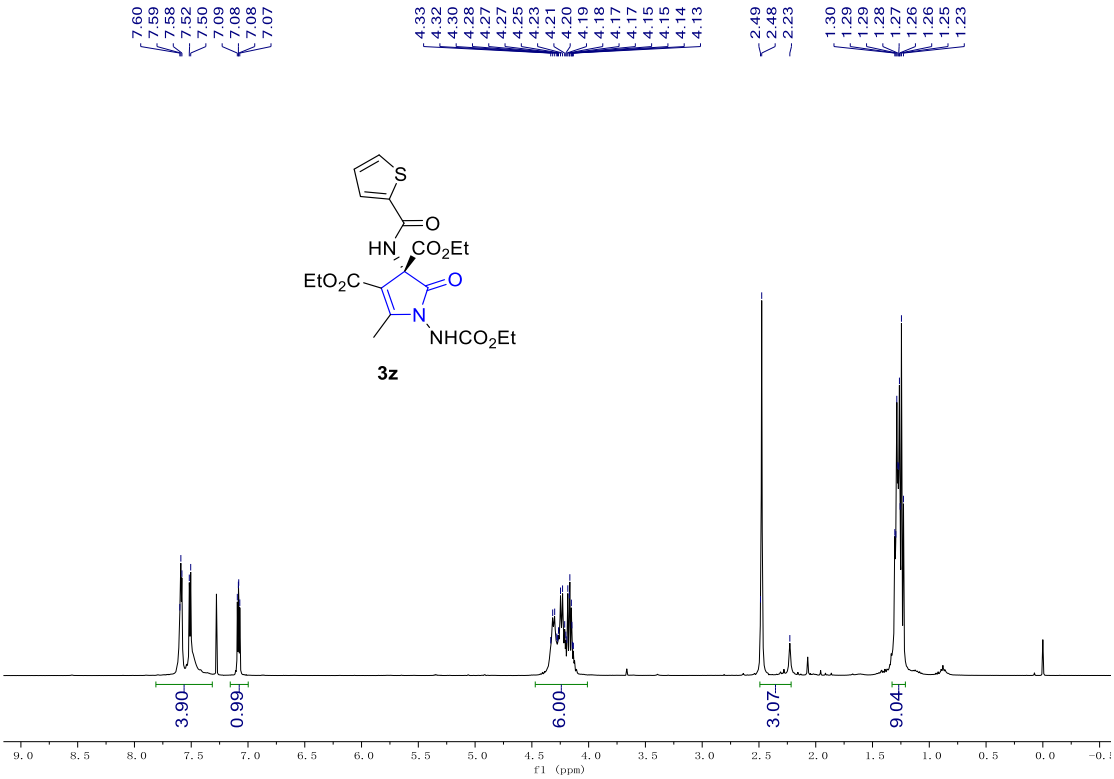
^{1}H NMR spectrum of compound **3y** ($CDCl_3$, 400 MHz)



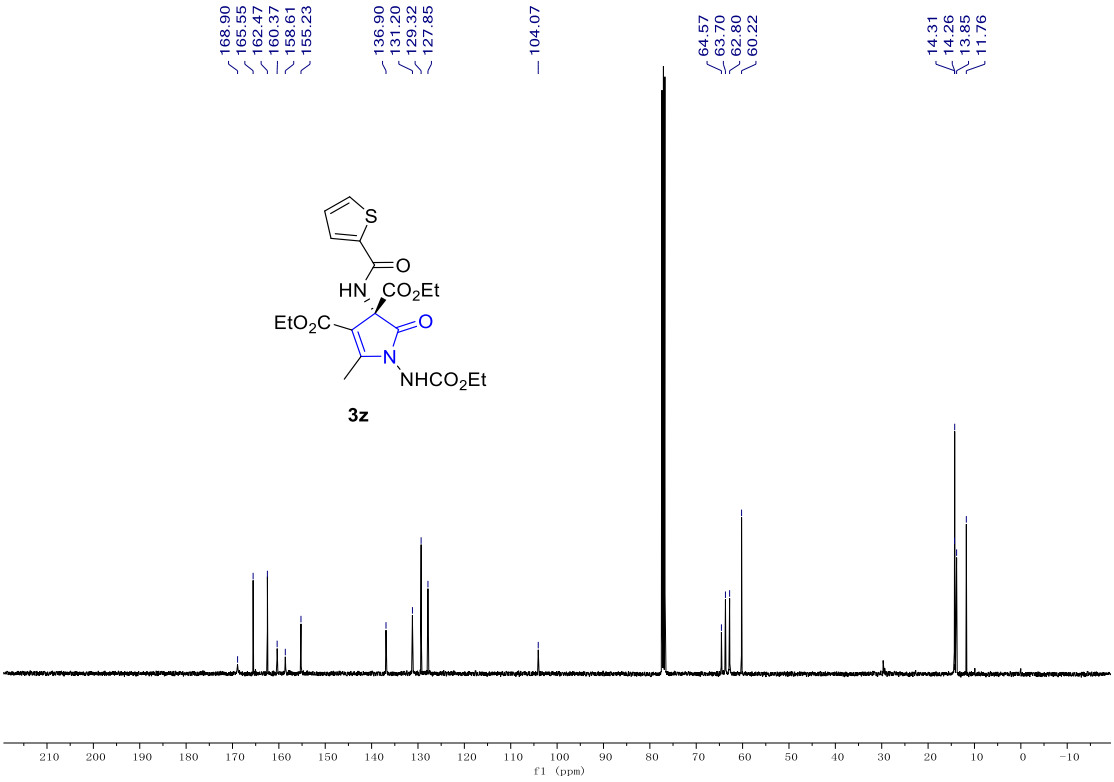
^{13}C NMR spectrum of compound **3y** ($CDCl_3$, 100 MHz)



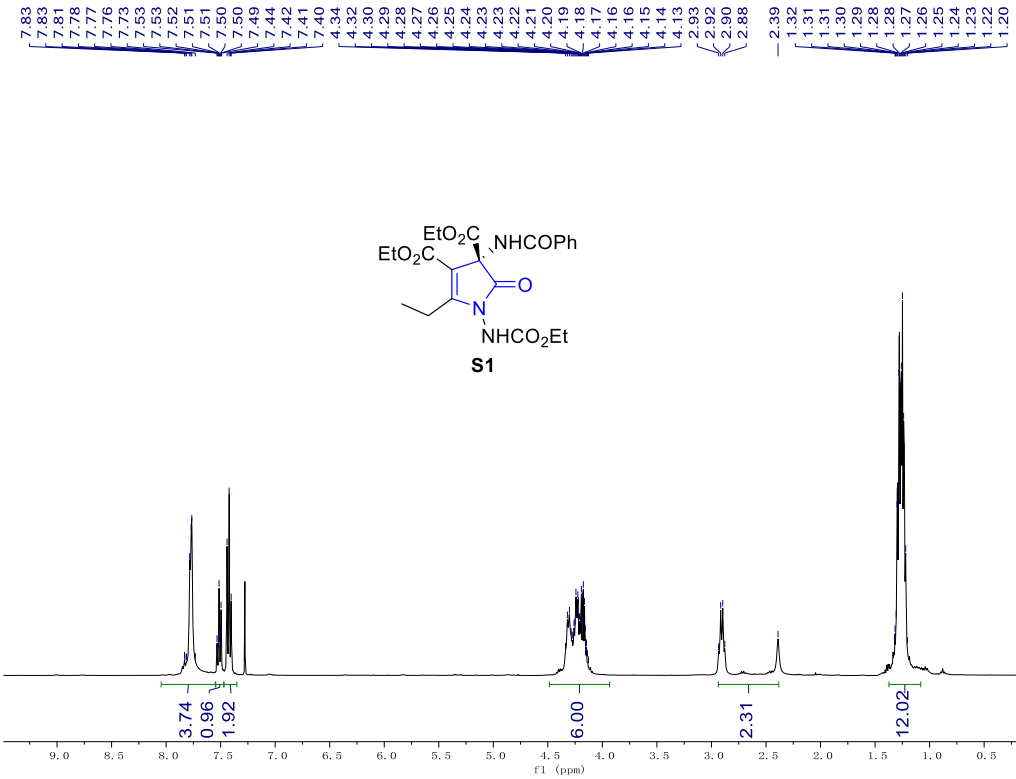
^{1}H NMR spectrum of compound **3z** ($CDCl_3$, 400 MHz)



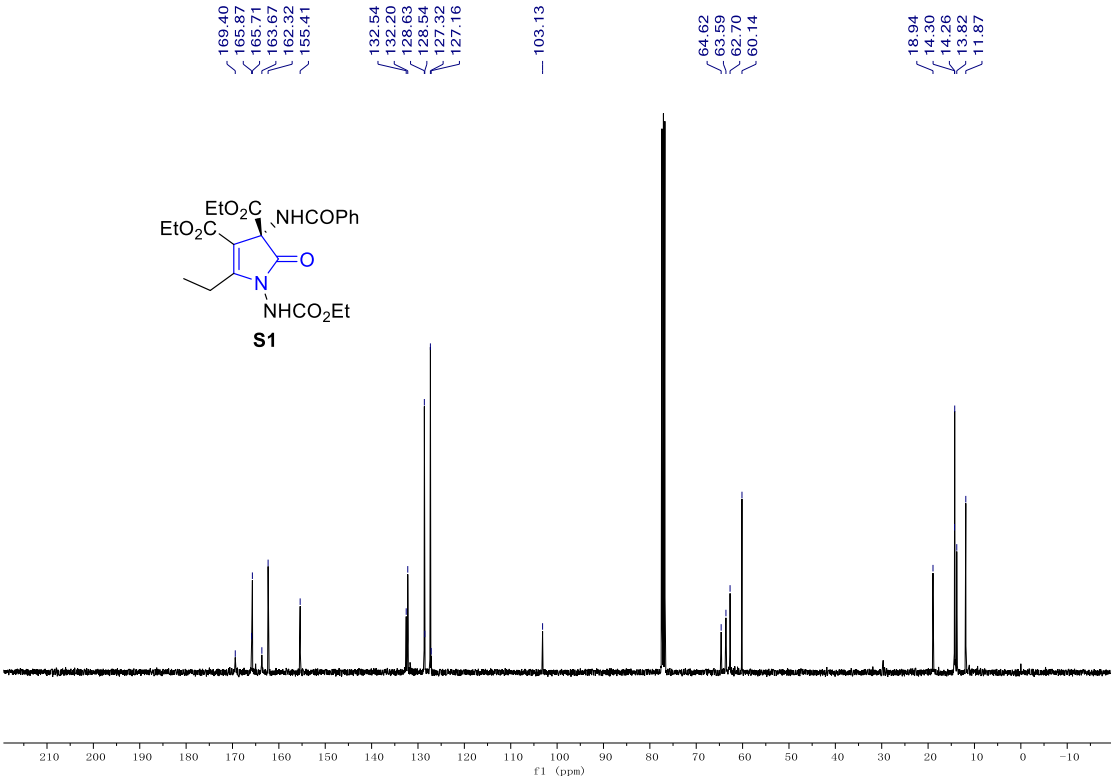
^{13}C NMR spectrum of compound **3z** ($CDCl_3$, 100 MHz)



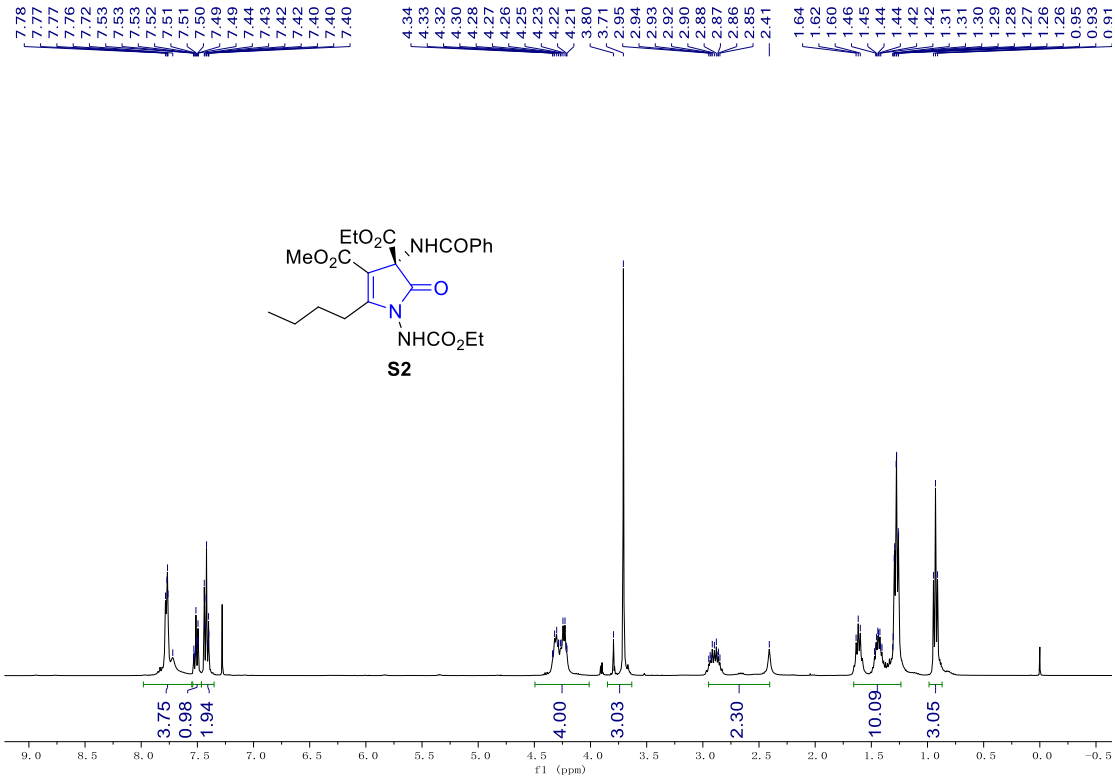
^{1}H NMR spectrum of compound **S1** ($CDCl_3$, 400 MHz)



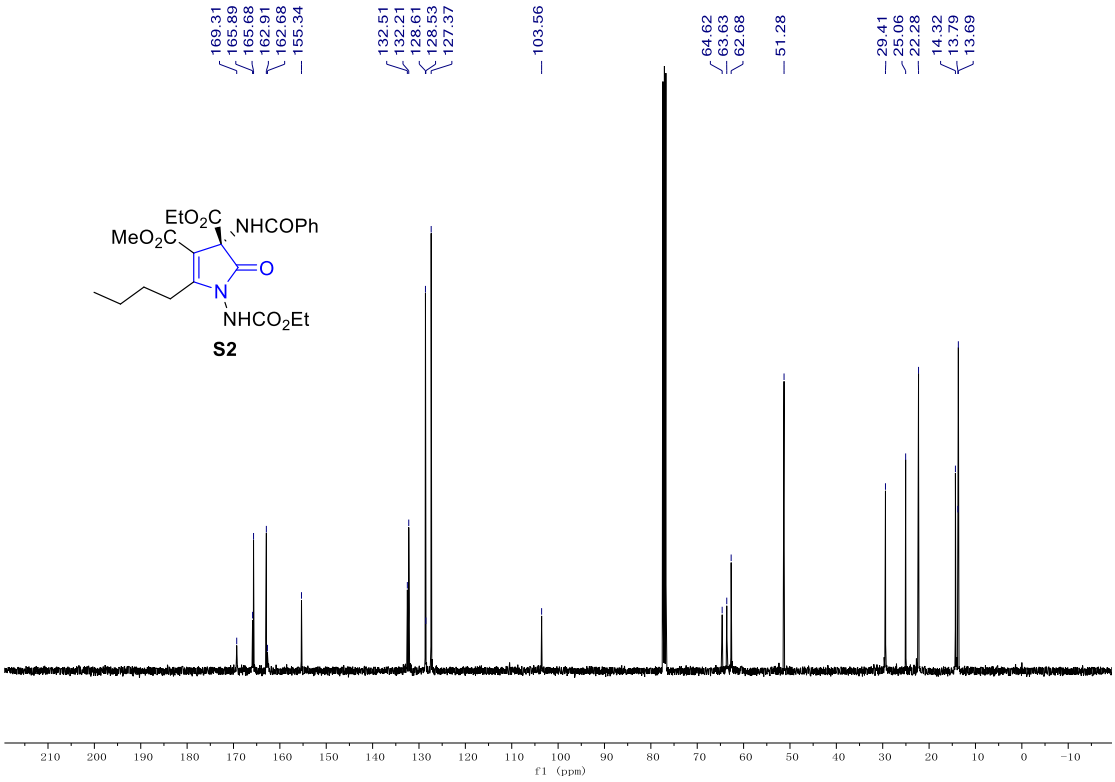
^{13}C NMR spectrum of compound **S1** ($CDCl_3$, 100 MHz)



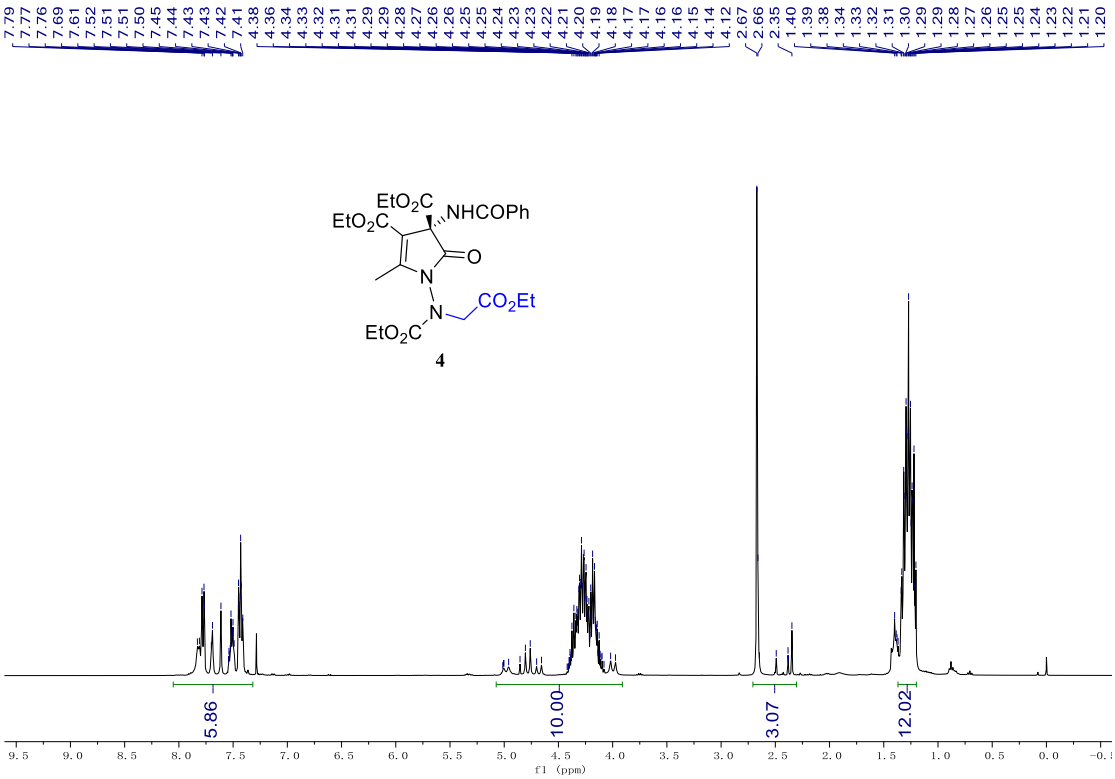
^{1}H NMR spectrum of compound **S2** ($CDCl_3$, 400 MHz)



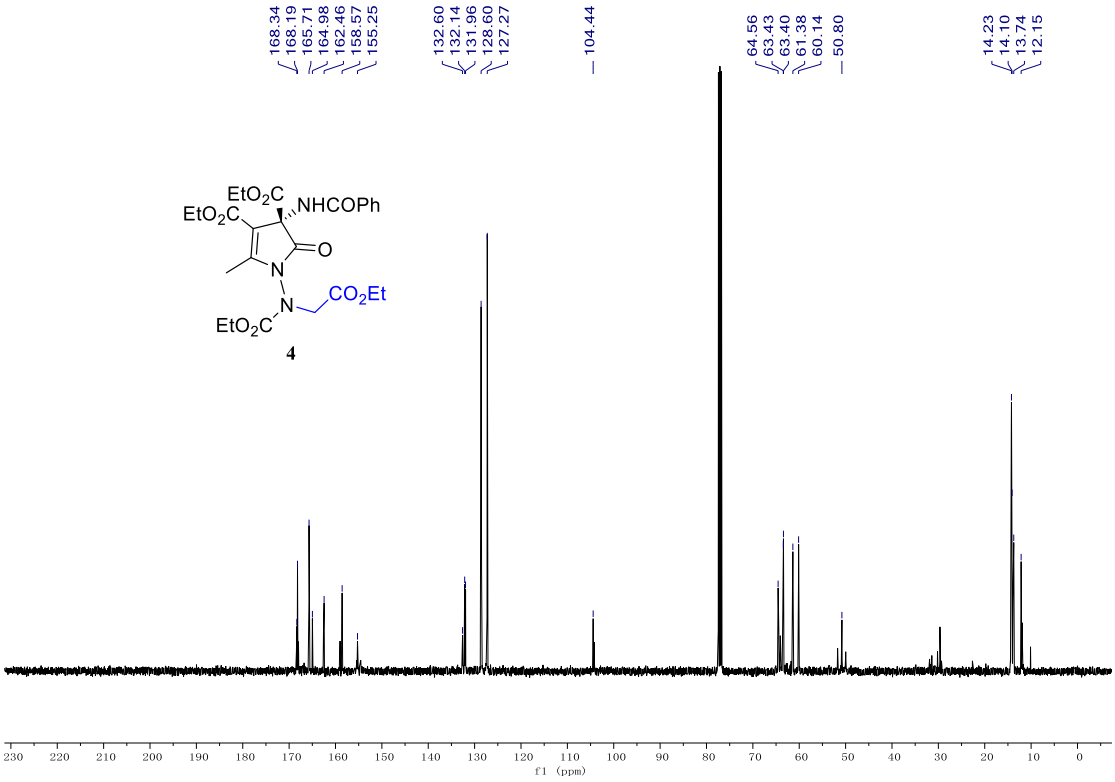
^{13}C NMR spectrum of compound **S2** ($CDCl_3$, 100 MHz)



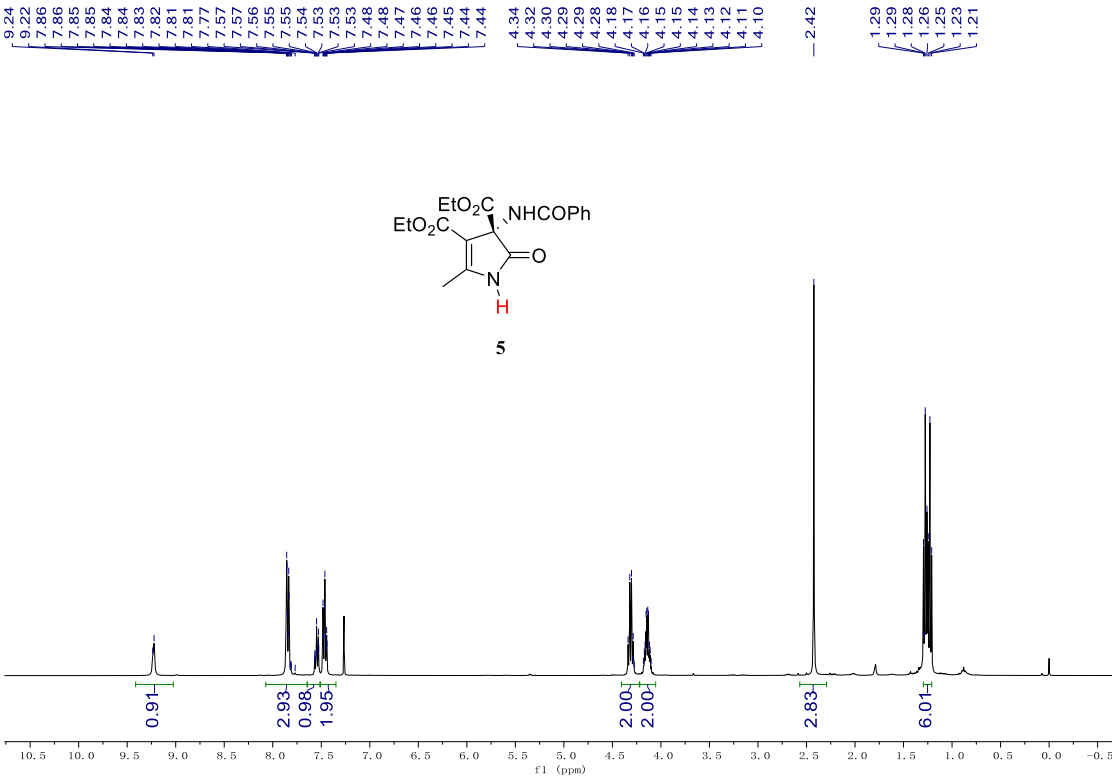
^{1}H NMR spectrum of compound **4** (dr = 1.5:1) ($CDCl_3$, 400 MHz)



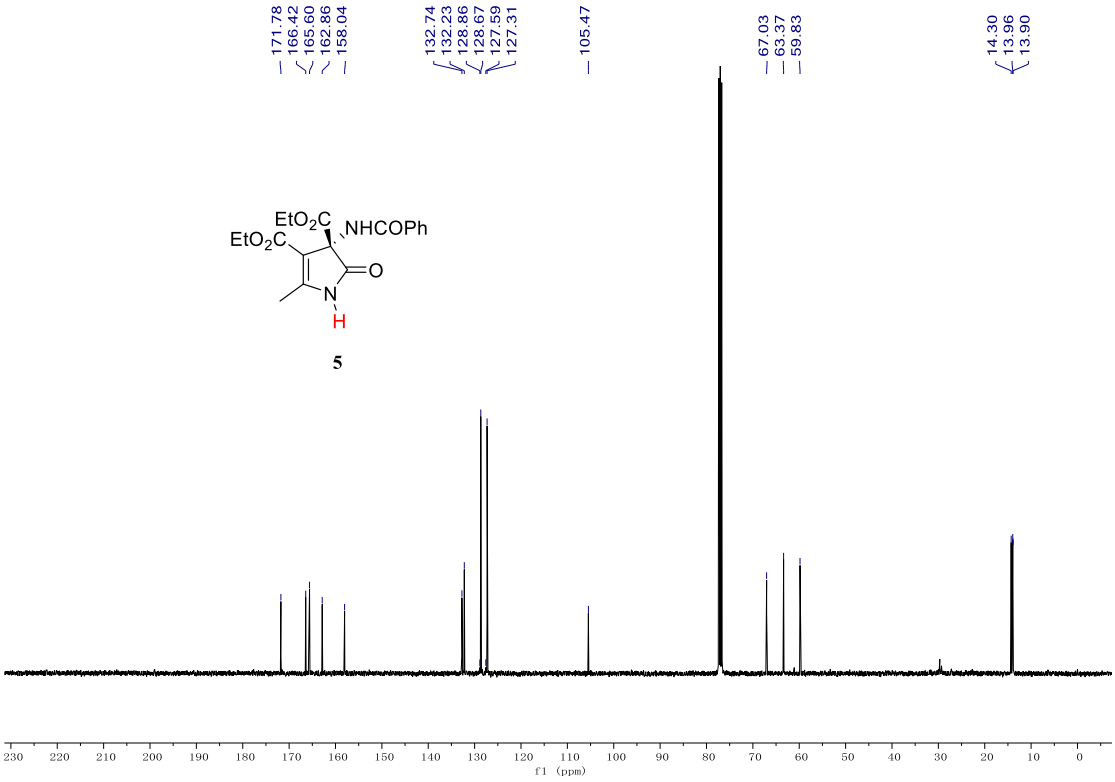
^{13}C NMR spectrum of compound **4** ($CDCl_3$, 100 MHz)



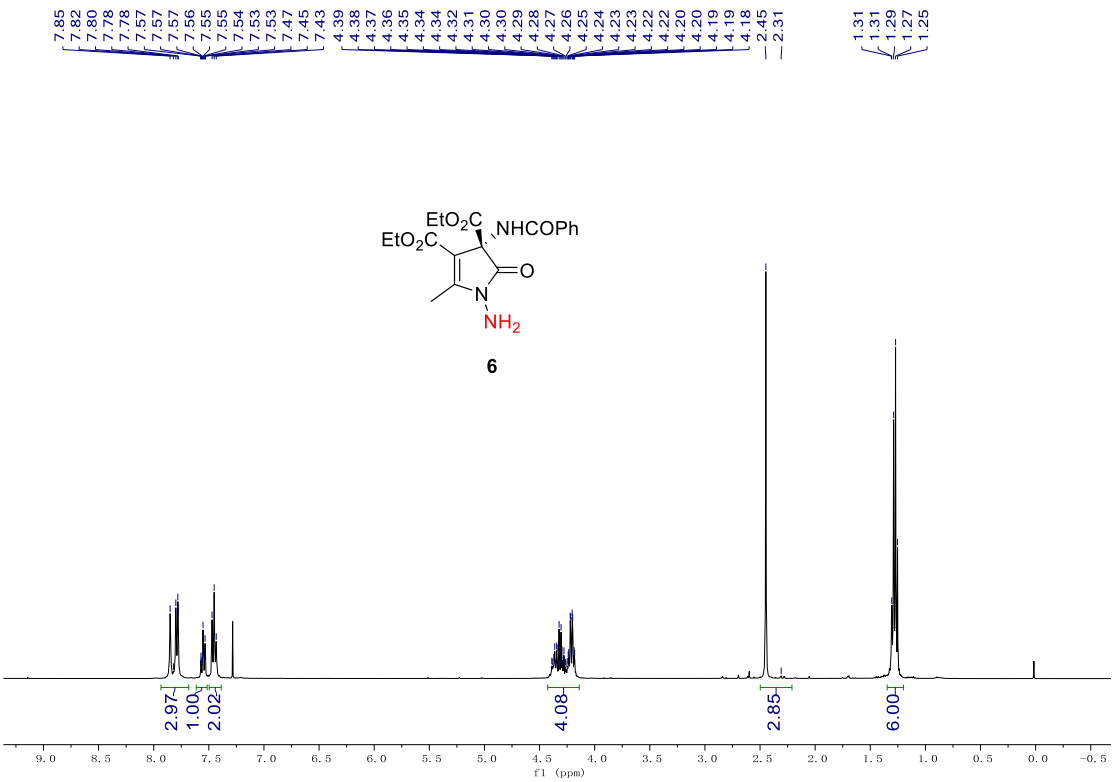
^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)



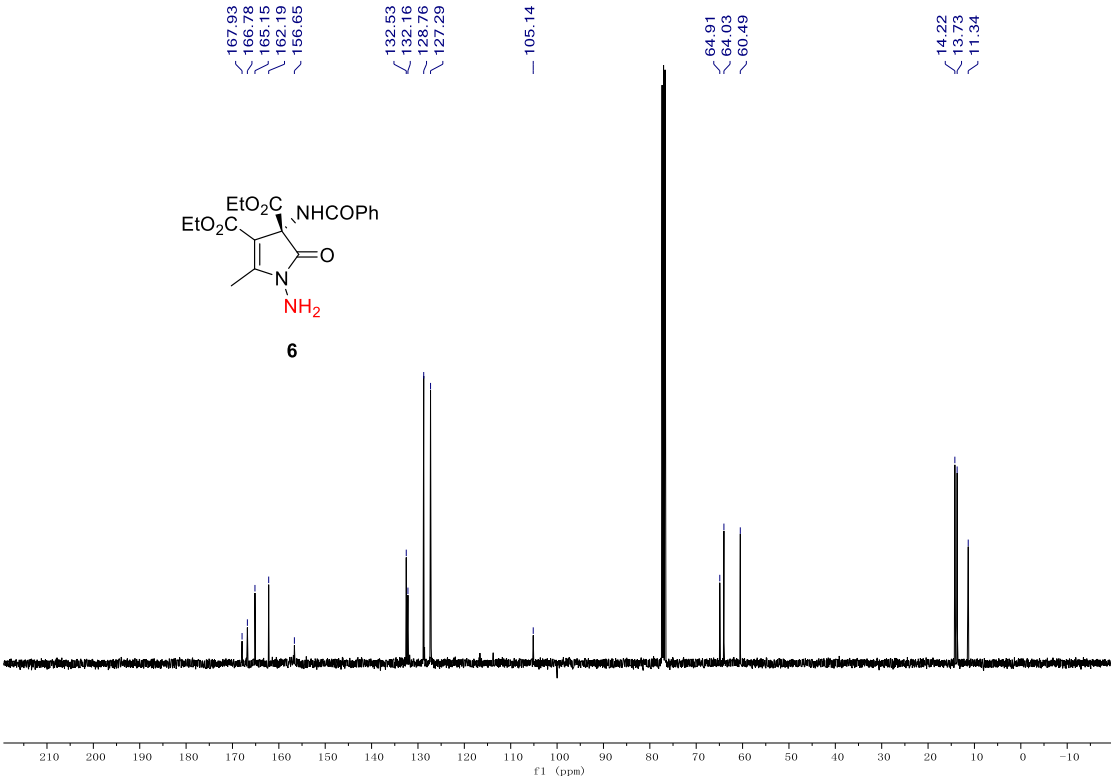
^{13}C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)



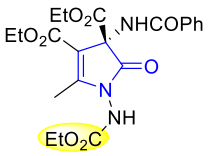
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz)



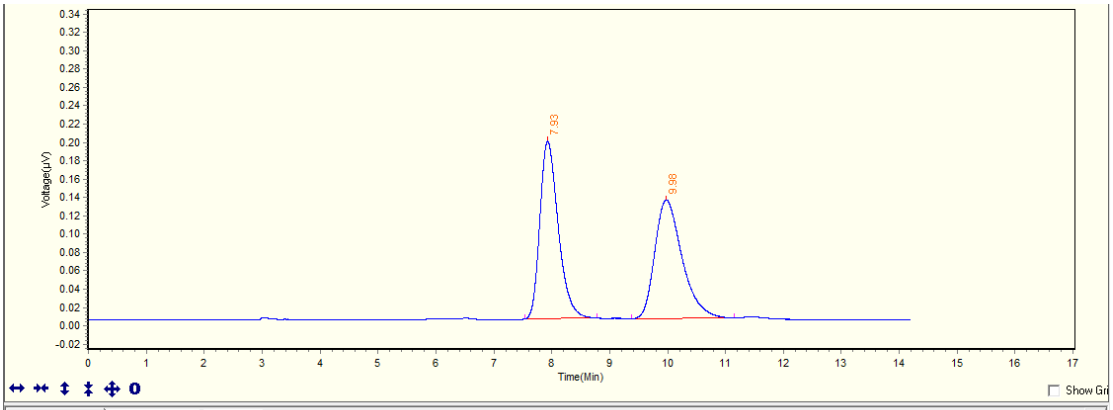
^{13}C NMR spectrum of compound **6** ($CDCl_3$, 100 MHz)



6. HPLC Spectra

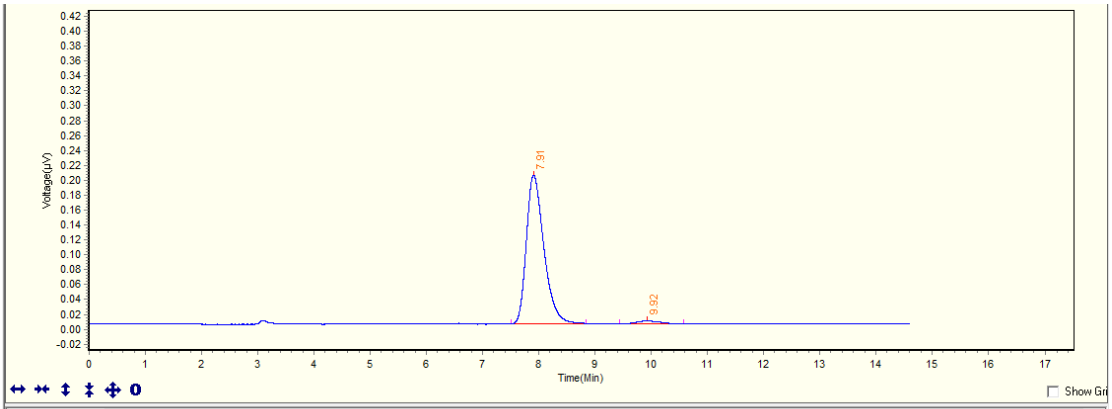


3a



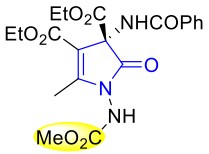
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.93	2127735	96733	50.12%	1.24	BB
2	9.98	2117609	64624	49.88%	1.783	BB
Total		4,245,344	161,357	100.00%		

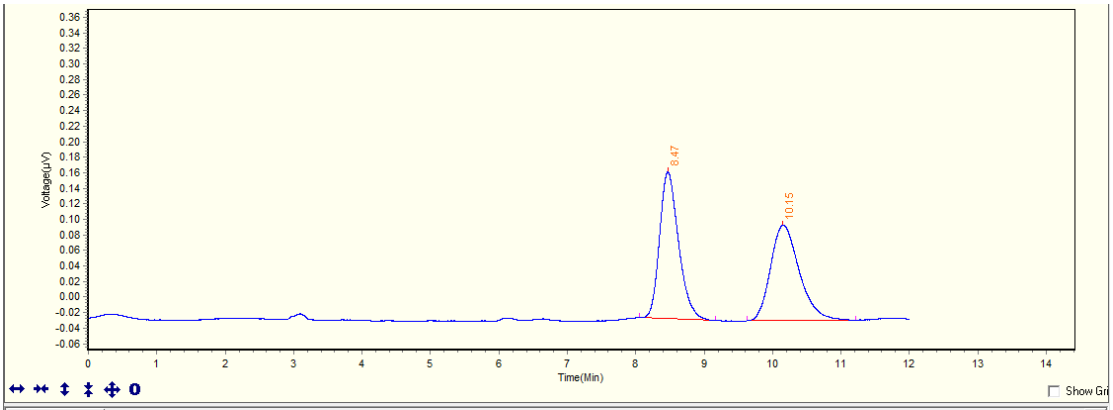


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.91	2157275	99645	97.35%	1.333	BB
2	9.92	58638	2026	2.65%	1.135	BB
Total		2,215,913	101,671	100.00%		

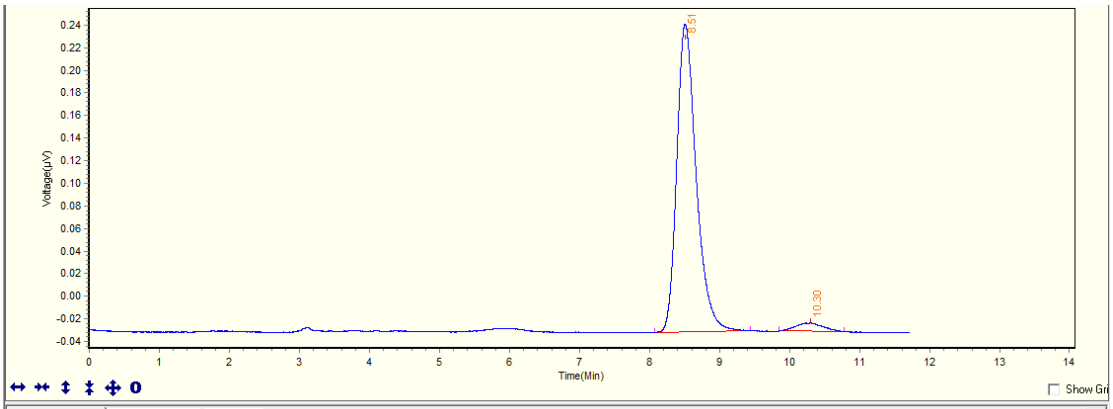


3b



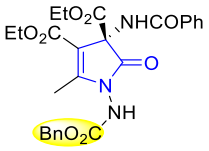
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.47	1822290	94368	50.45%	1.111	BB
2	10.15	1790116	61457	49.55%	1.588	BB
Total		3,612,406	155,825	100.00%		

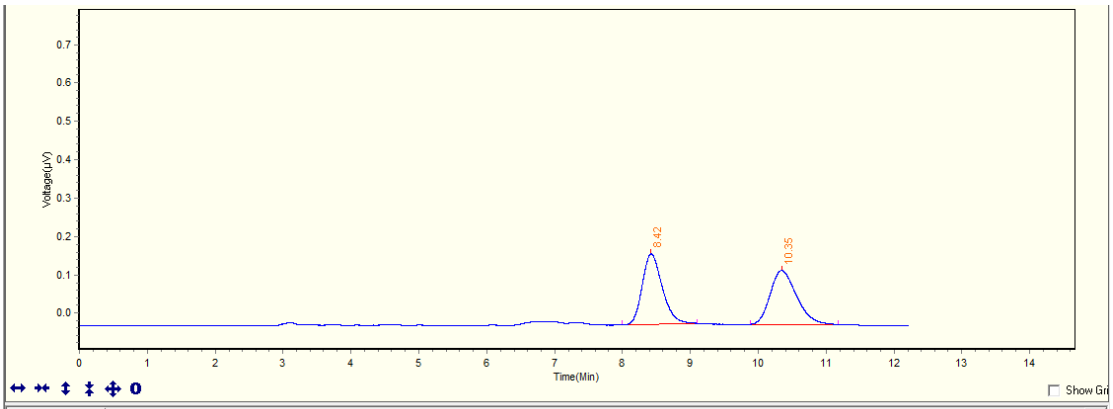


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.51	2622567	136178	96.48%	1.367	BB
2	10.30	95618	3628	3.52%	0.931	BB
Total		2,718,185	139,806	100.00%		

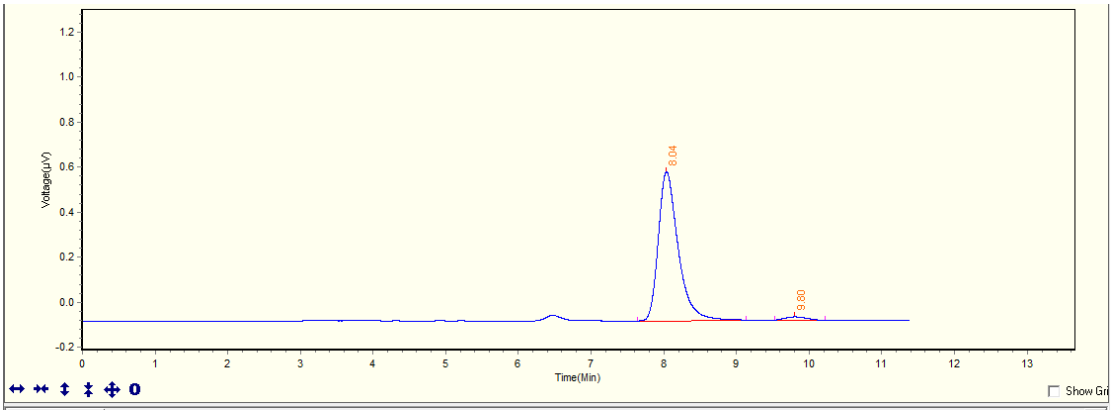


3c



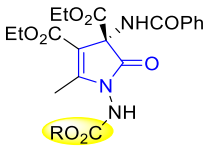
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.42	1872517	91728	49.73%	1.105	BB
2	10.35	1892694	70218	50.27%	1.293	BB
Total		3,765,211	161,946	100.00%		

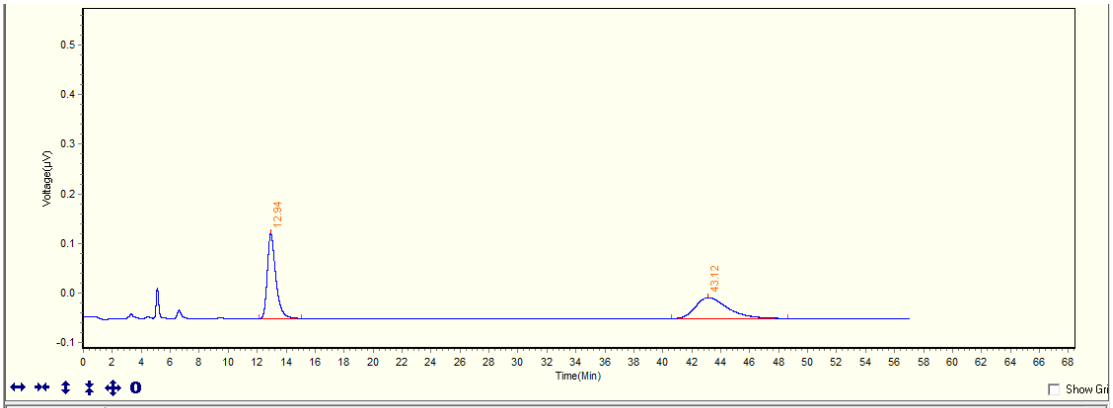


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.04	6260857	330487	97.56%	1.495	BB
2	9.80	156307	7461	2.44%	0.693	BB
Total		6,417,164	337,948	100.00%		

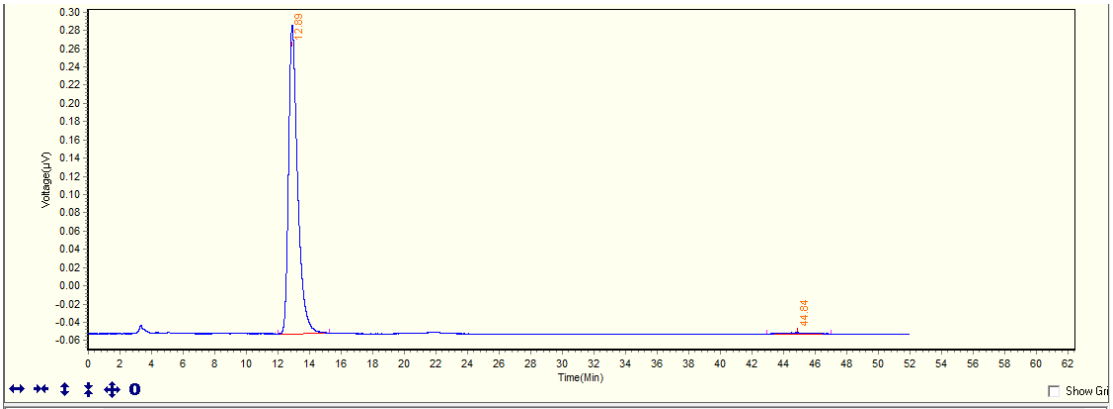


3d (R = fluorenylmethyl)



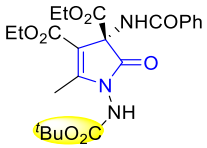
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.94	3491962	85906	51.62%	2.928	BB
2	43.12	3272725	21182	48.38%	8.037	BB
Total		6,764,687	107,088	100.00%		

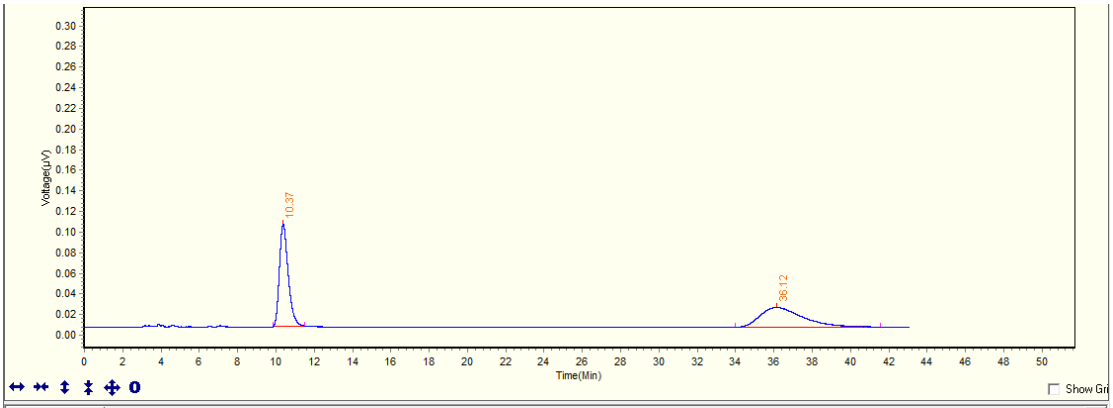


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.89	6746905	169154	98.85%	3.249	BB
2	44.84	78469	666	1.15%	4.062	BB
Total		6,825,374	169,820	100.00%		

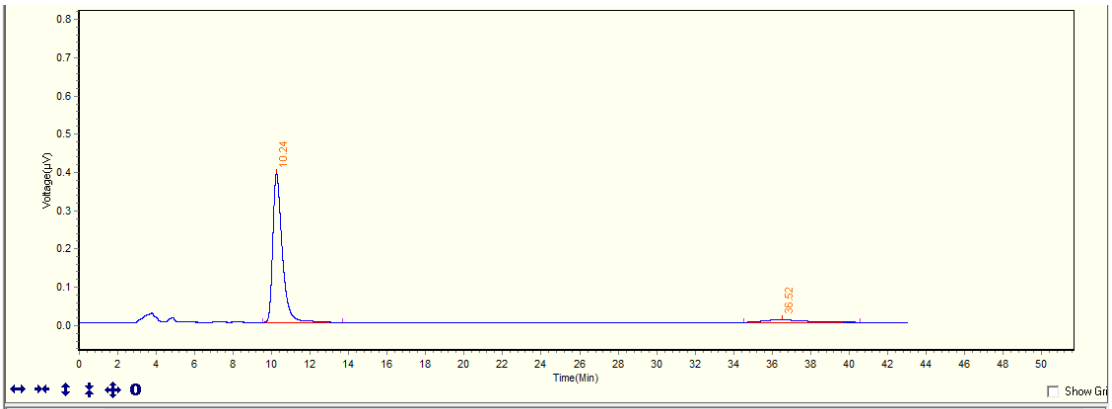


3e



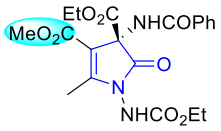
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.37	1577692	49647	51.59%	1.65	BB
2	36.12	1480272	9655	48.41%	7.579	BB
Total		3,057,964	59,302	100.00%		

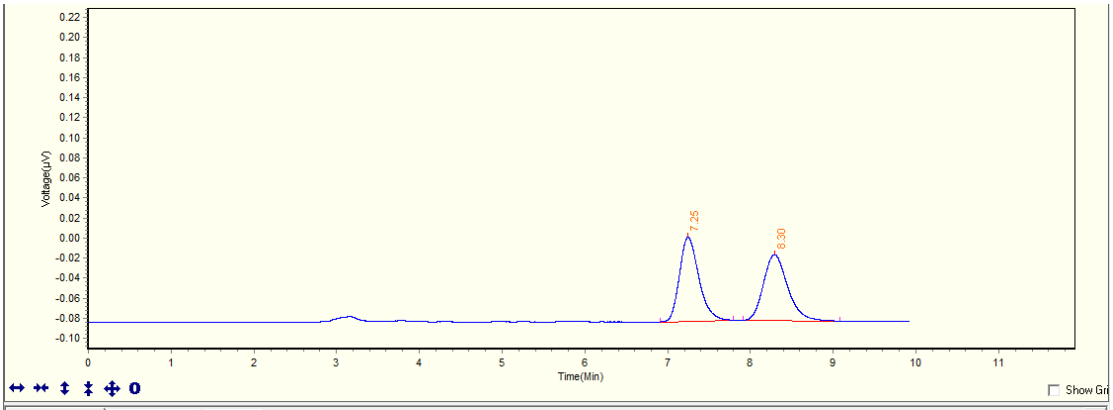


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.24	6616005	194637	93.30%	4.149	BB
2	36.52	475106	3285	6.70%	6.045	BB
Total		7,091,111	197,922	100.00%		

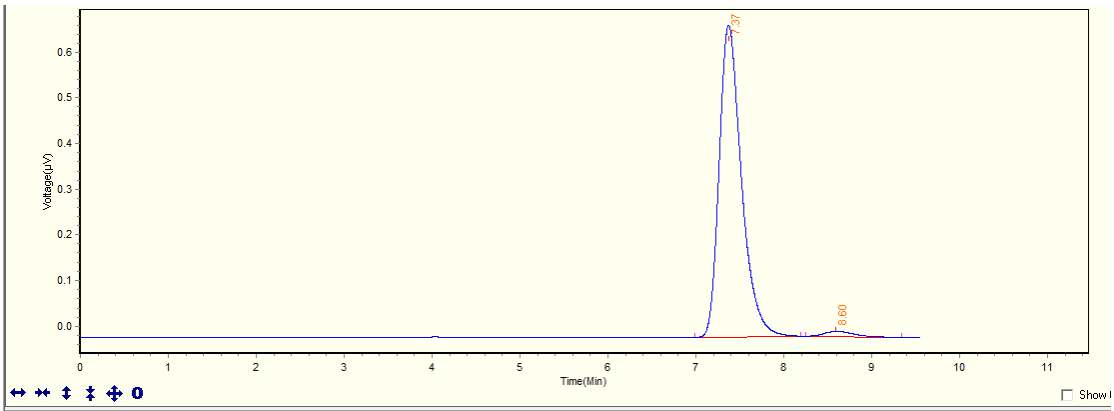


3f



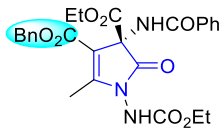
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.25	681534	41947	50.58%	0.883	BB
2	8.30	665960	32910	49.42%	1.17	BB
Total		1,347,494	74,857	100.00%		

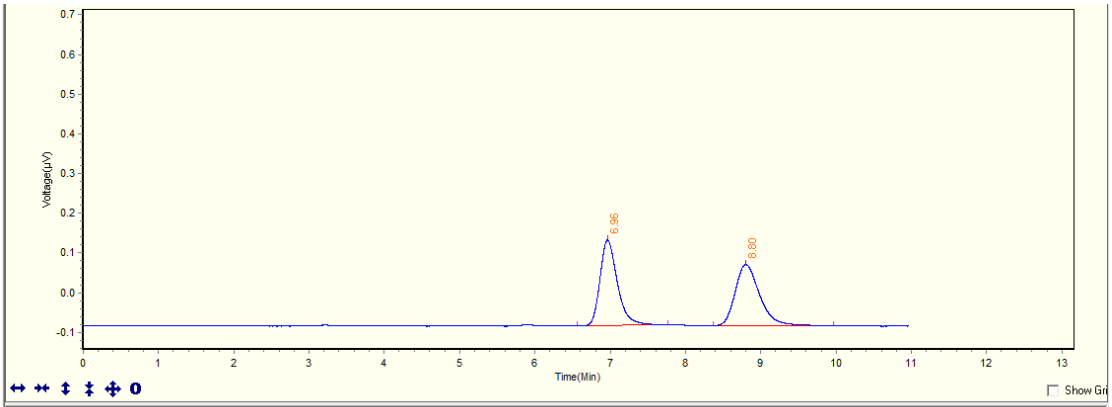


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.37	6007143	341204	97.92%	1.205	BB
2	8.60	127788	5618	2.08%	1.091	BB
Total		6,134,931	346,822	100.00%		

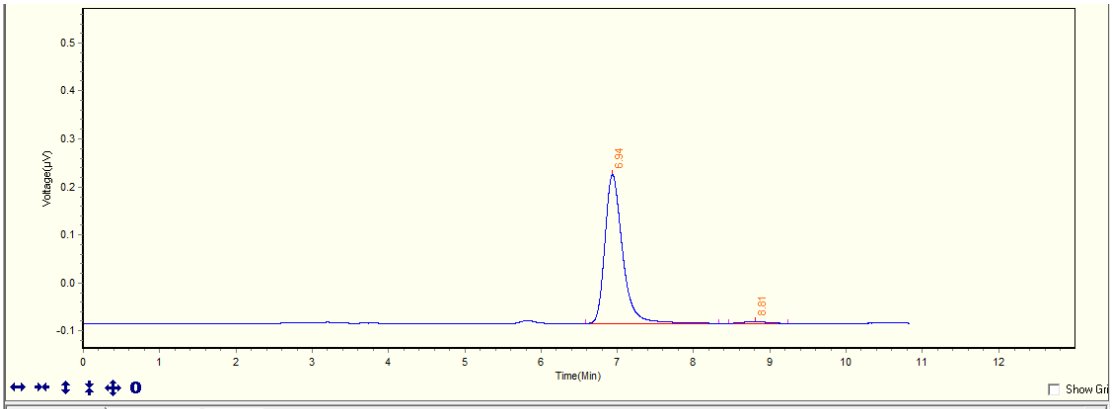


3g



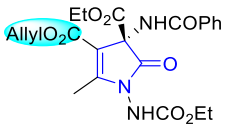
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.96	1728003	107757	49.79%	1.205	BB
2	8.80	1742430	77352	50.21%	1.594	BB
Total		3,470,433	185,109	100.00%		

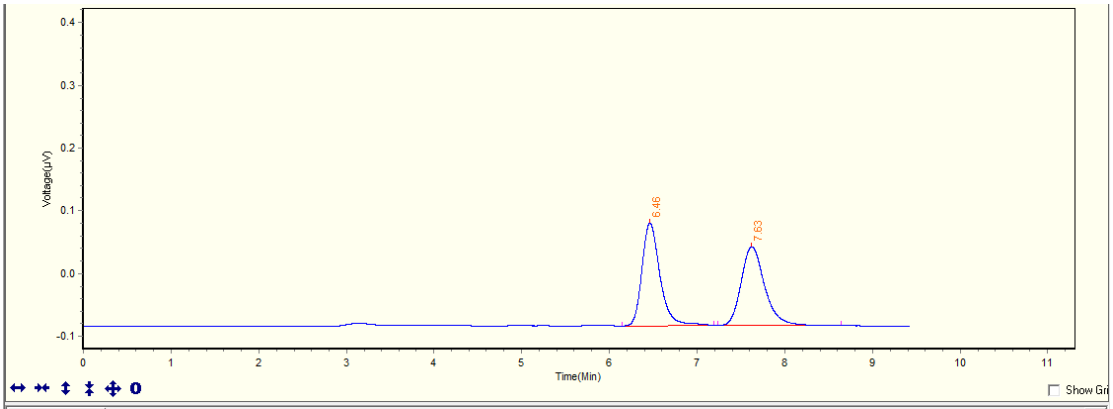


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.94	2485896	155218	98.45%	1.743	BB
2	8.81	39233	1905	1.55%	0.781	BB
Total		2,525,129	157,123	100.00%		

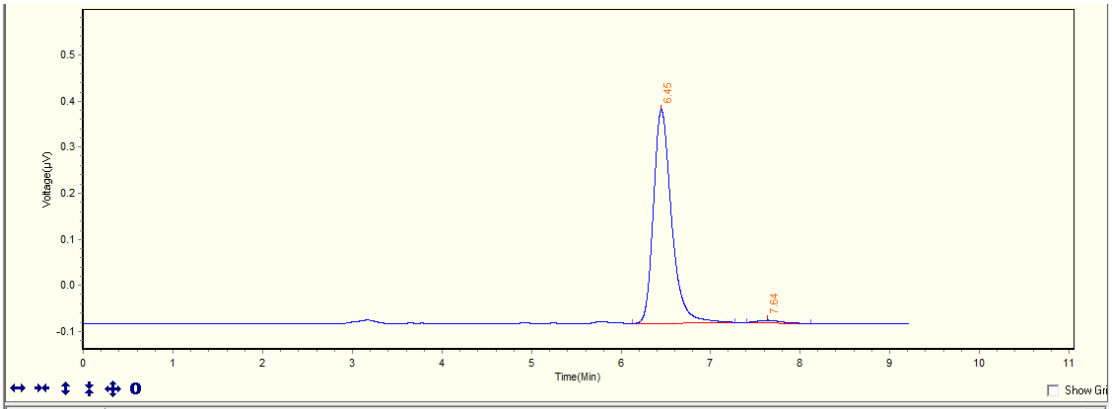


3h



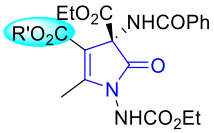
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.46	1163992	81856	50.04%	1.042	BB
2	7.63	1162010	62647	49.96%	1.404	BB
Total		2,326,002	144,503	100.00%		

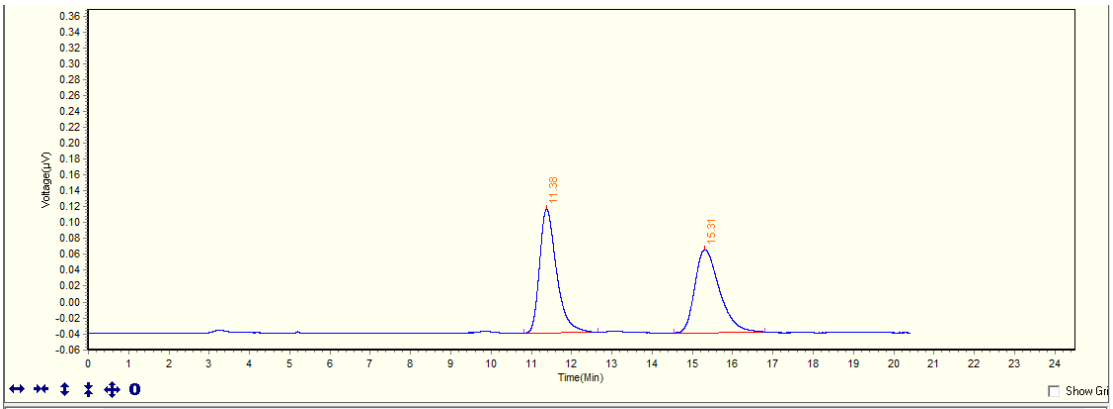


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.45	3248019	232066	98.61%	1.143	BB
2	7.64	45668	2745	1.39%	0.715	BB
Total		3,293,687	234,811	100.00%		

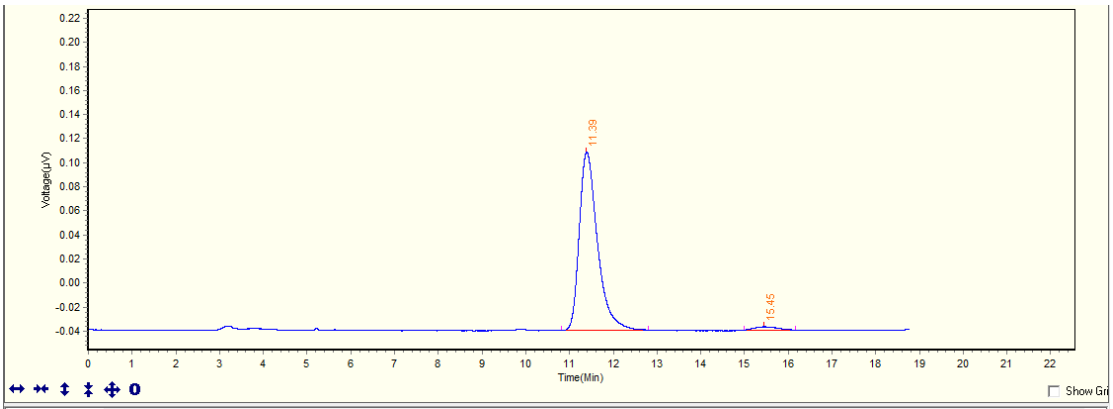


3i (R' = 2-methoxyethyl)



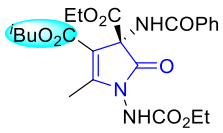
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	11.38	2275616	77790	50.84%	1.839	BB
2	15.31	2199996	52167	49.16%	2.256	BB
Total		4,475,612	129,957	100.00%		

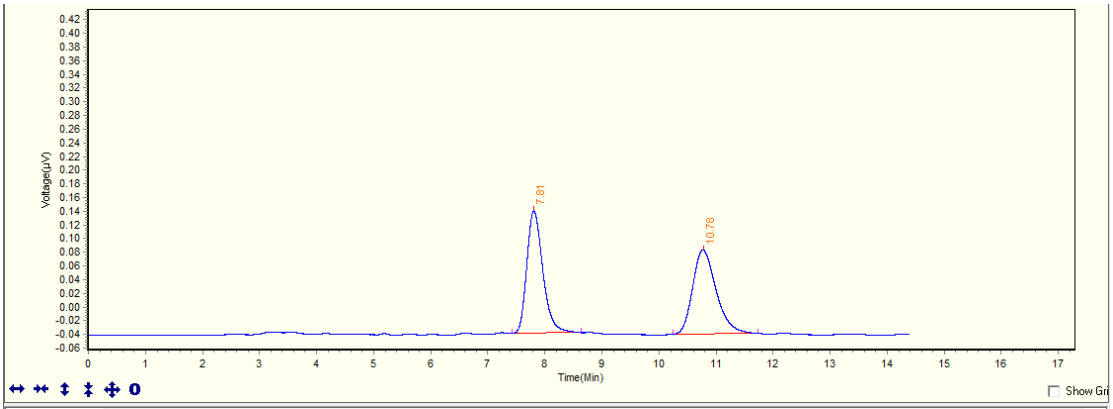


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	11.39	2138369	74197	97.75%	1.987	BB
2	15.45	49122	1378	2.25%	1.174	BB
Total		2,187,491	75,575	100.00%		

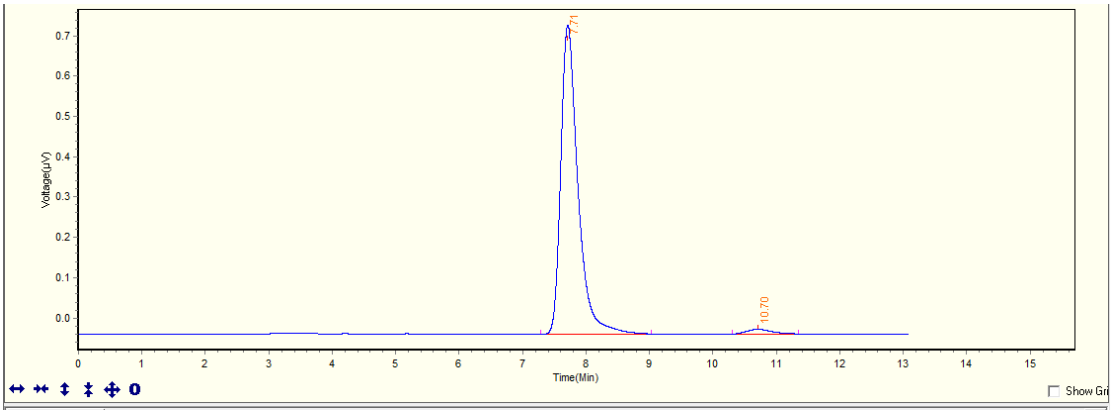


3j



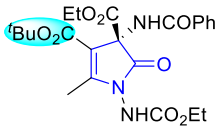
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.81	1751293	89439	49.94%	1.212	BB
2	10.78	1755473	61375	50.06%	1.488	BB
Total		3,506,766	150,814	100.00%		

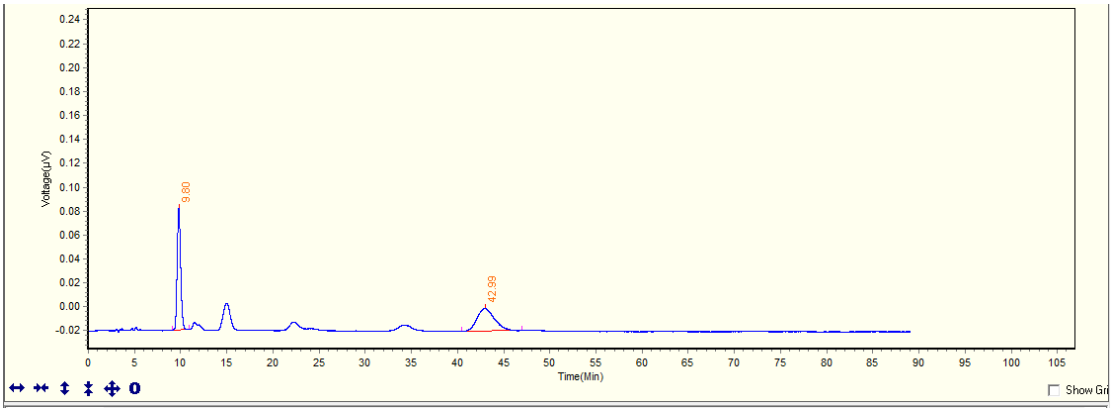


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.71	7174554	383339	97.91%	1.743	BB
2	10.70	153040	5712	2.09%	1.043	BB
Total		7,327,594	389,051	100.00%		

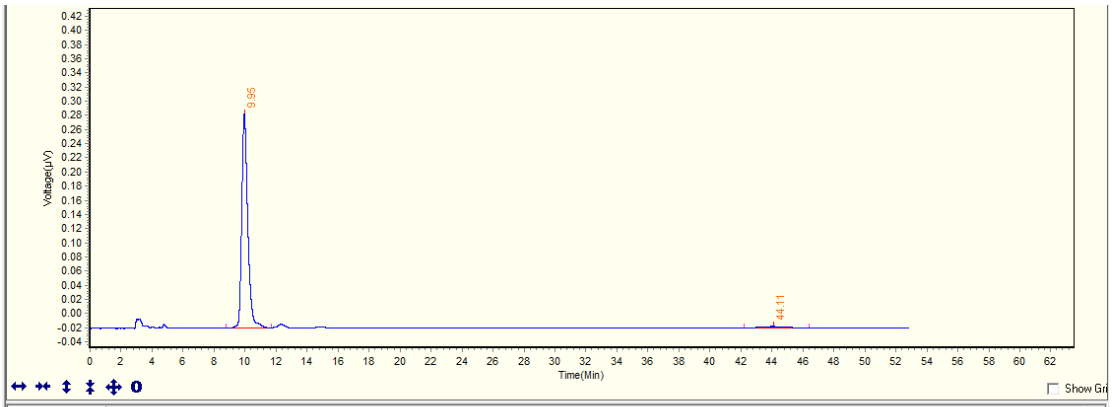


3k



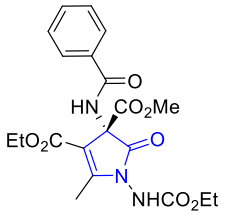
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.80	1337602	50905	52.31%	1.858	BB
2	42.99	1219258	9347	47.69%	6.527	BB
Total		2,556,860	60,252	100.00%		

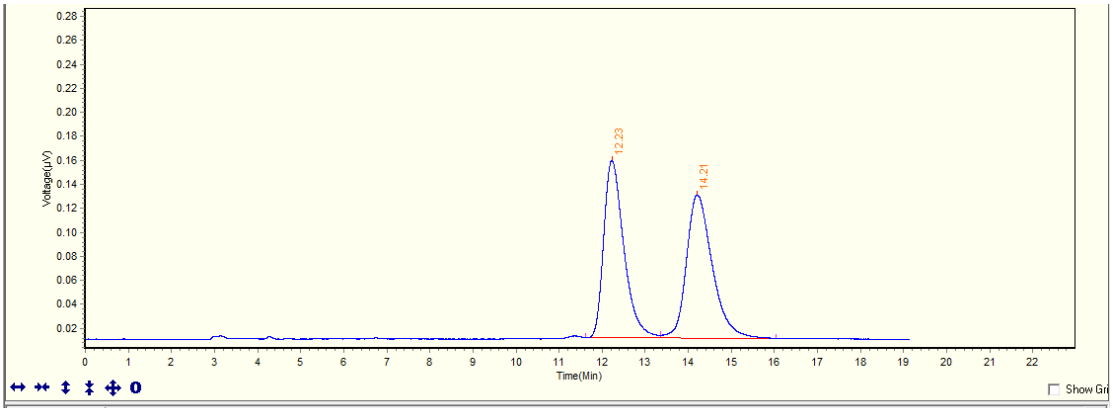


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.95	4072984	150957	96.77%	2.923	BB
2	44.11	135755	1146	3.23%	4.195	BB
Total		4,208,739	152,103	100.00%		

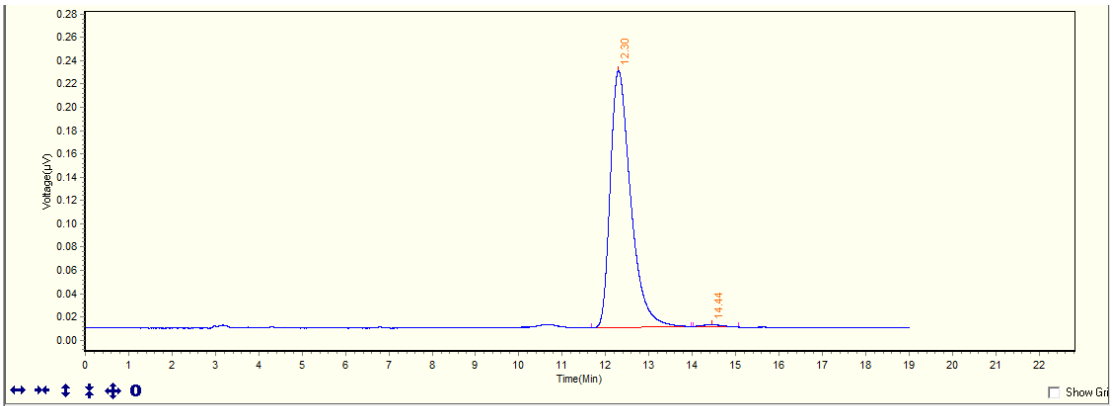


3l



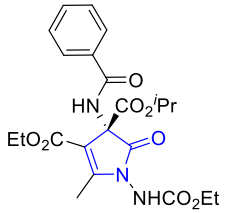
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.23	2400142	73810	49.15%	1.742	BV
2	14.21	2483612	59665	50.85%	2.679	VB
Total		4,883,754	133,475	100.00%		

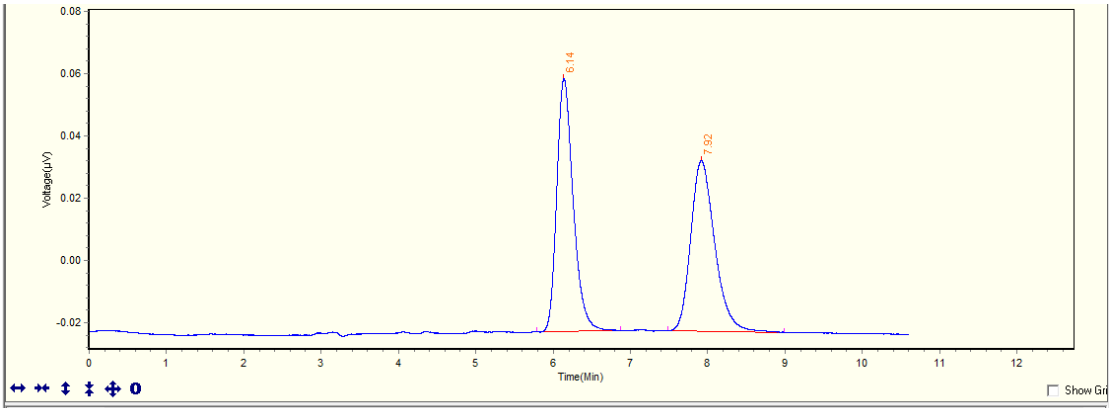


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.30	3600625	110172	99.32%	2.298	BB
2	14.44	24702	816	0.68%	1.047	BB
Total		3,625,327	110,988	100.00%		

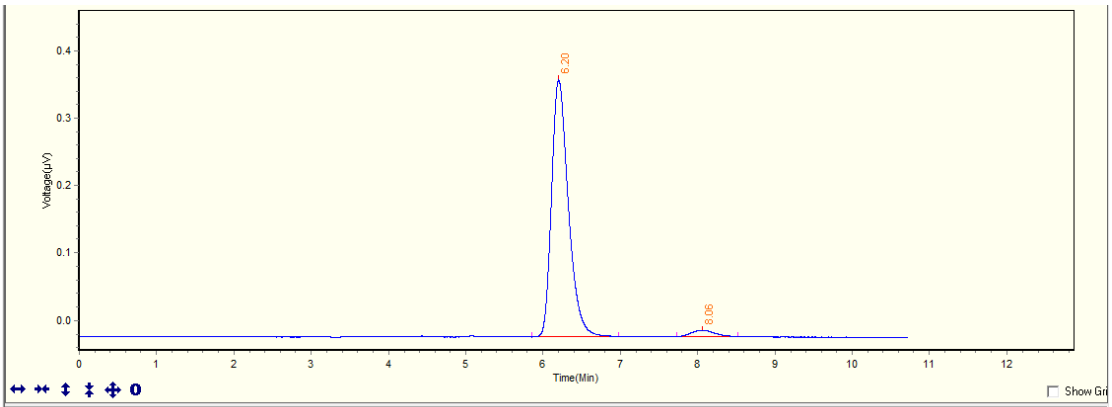


3m



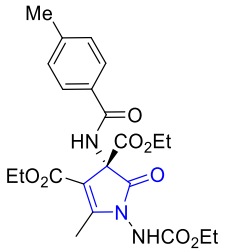
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.14	600395	40632	50.37%	1.083	BB
2	7.92	591490	27482	49.63%	1.504	BB
Total		1,191,885	68,114	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.20	2871928	190593	96.62%	1.133	BB
2	8.06	100432	4811	3.38%	0.791	BB
Total		2,972,360	195,404	100.00%		



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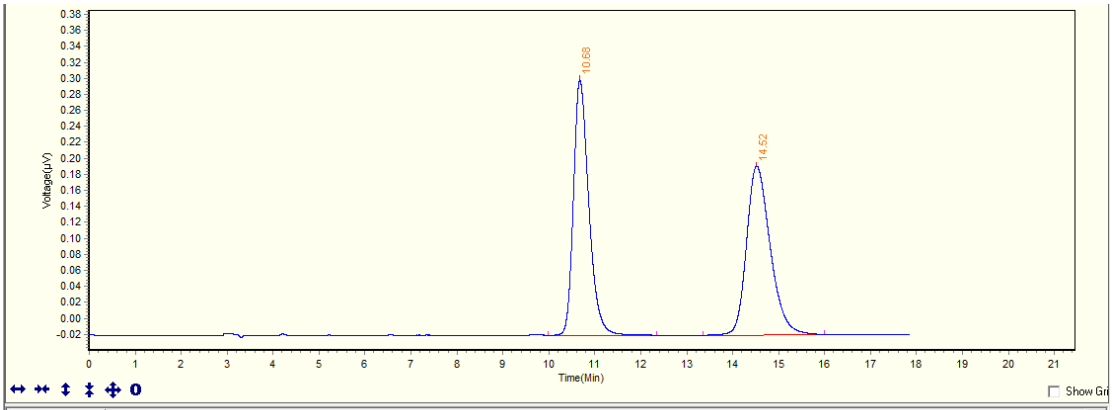
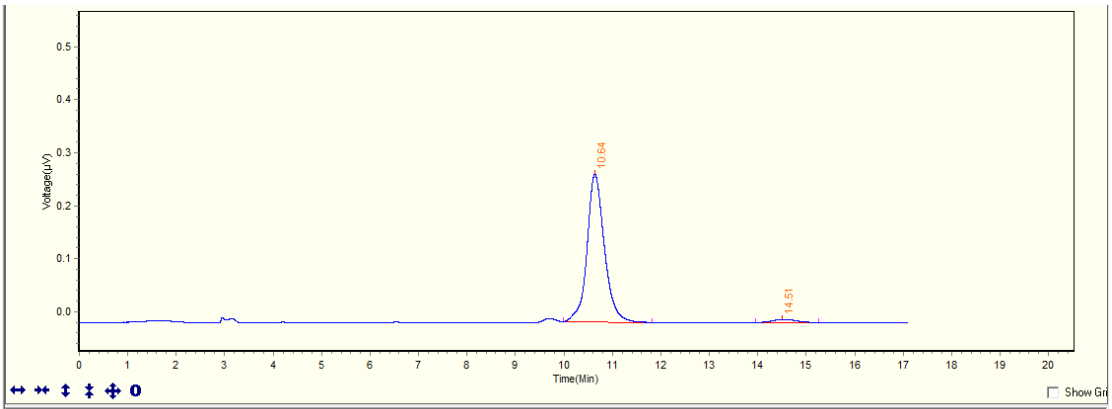


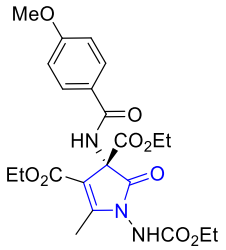
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.68	3705555	159526	49.49%	2.362	BB
2	14.52	3781726	105477	50.51%	2.641	BB
Total		7,487,281	265,003	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.64	3459427	139425	97.06%	1.831	BB
2	14.51	104758	3109	2.94%	1.315	BB
Total		3,564,185	142,534	100.00%		



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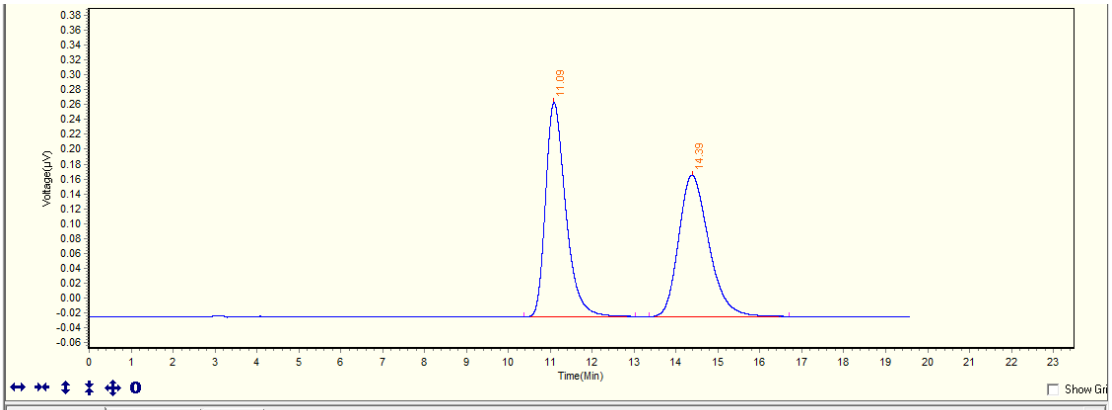
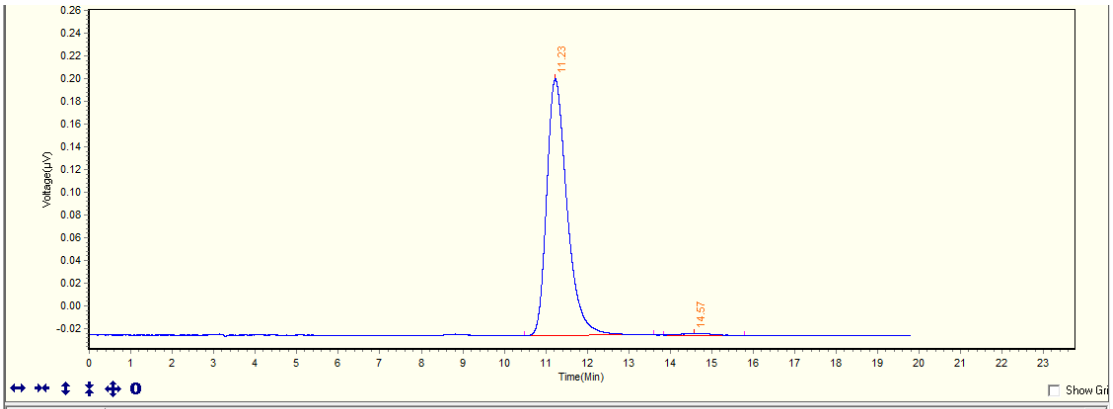


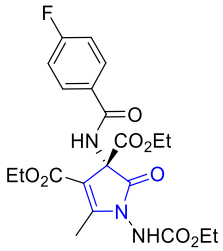
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	11.09	4814897	144015	50.47%	2.657	BB
2	14.39	4724873	95057	49.53%	3.339	BB
Total		9,539,770	239,072	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	11.23	3861602	113043	98.92%	3.114	BB
2	14.57	42332	884	1.08%	1.949	BB
Total		3,903,934	113,927	100.00%		



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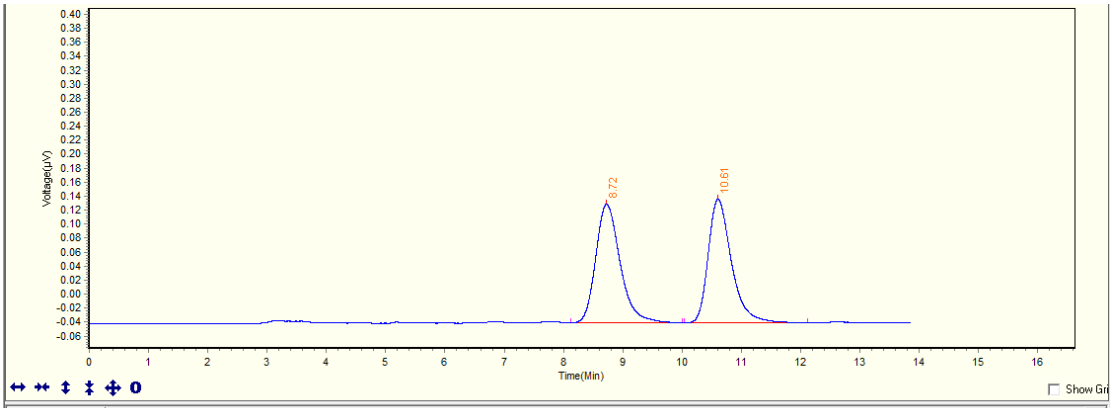
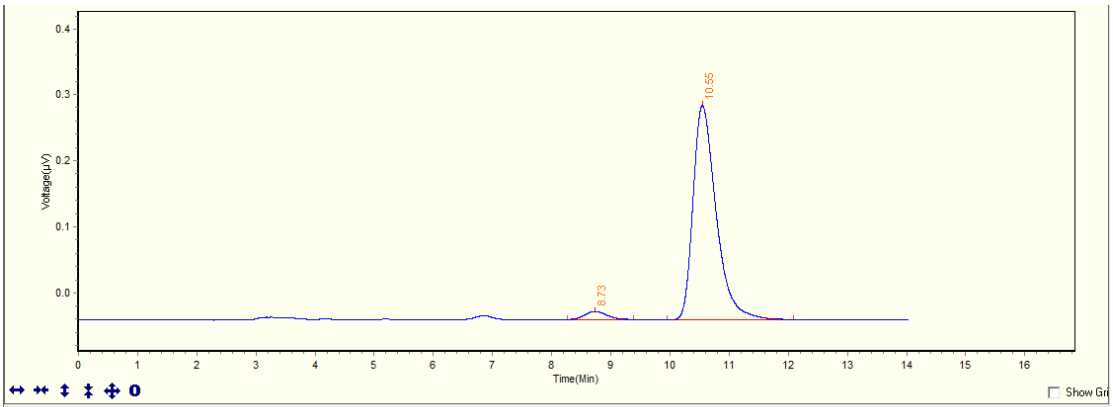


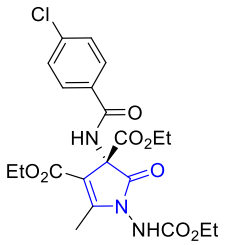
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.72	2420088	84666	50.33%	1.881	BB
2	10.61	2388298	88181	49.67%	2.081	BB
Total		4,808,386	172,847	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.73	161392	6156	3.54%	1.119	BB
2	10.55	4397784	162176	96.46%	2.142	BB
Total		4,559,176	168,332	100.00%		



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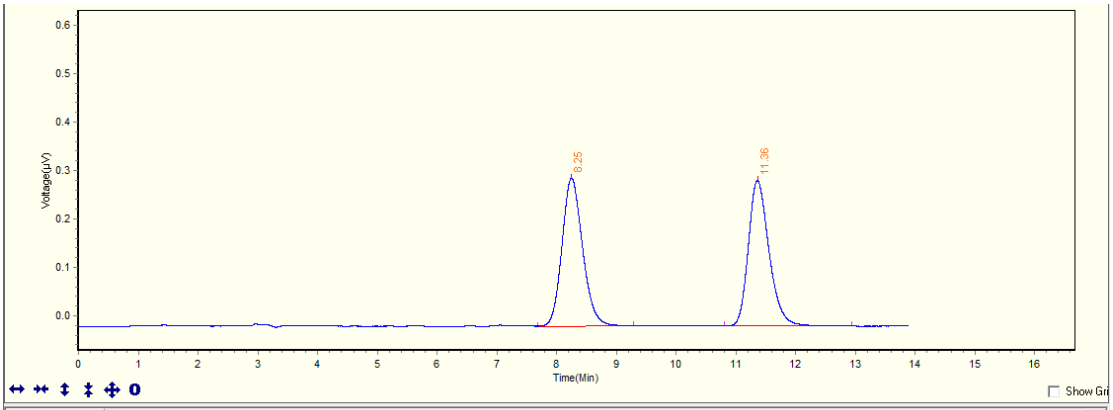
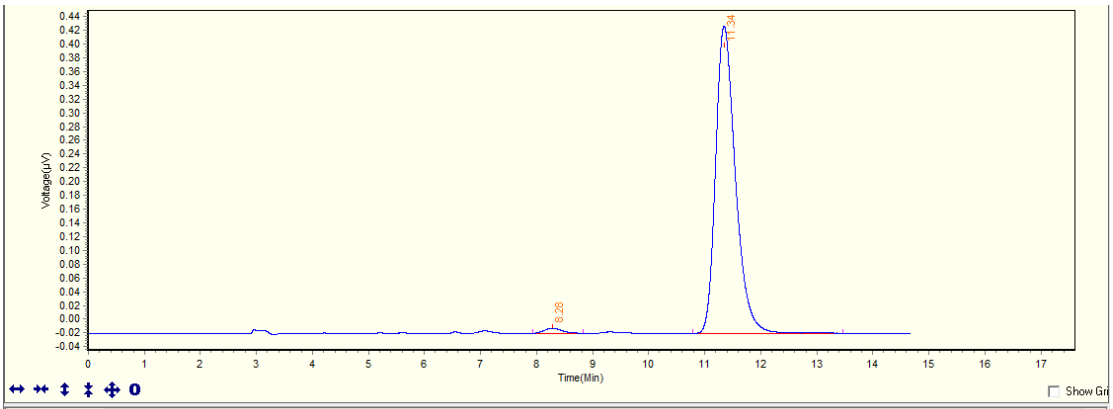


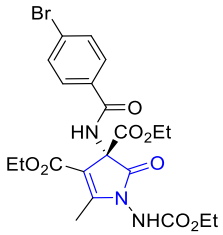
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.25	3635929	152209	50.12%	1.603	BB
2	11.36	3618957	150232	49.88%	2.12	BB
Total		7,254,886	302,441	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.28	85221	3734	1.53%	0.898	BB
2	11.34	5494272	223655	98.47%	2.678	BB
Total		5,579,493	227,389	100.00%		



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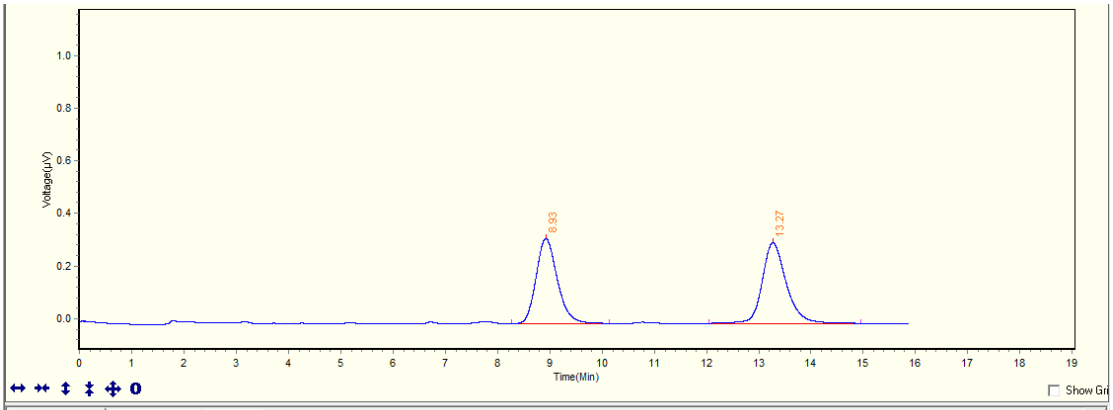
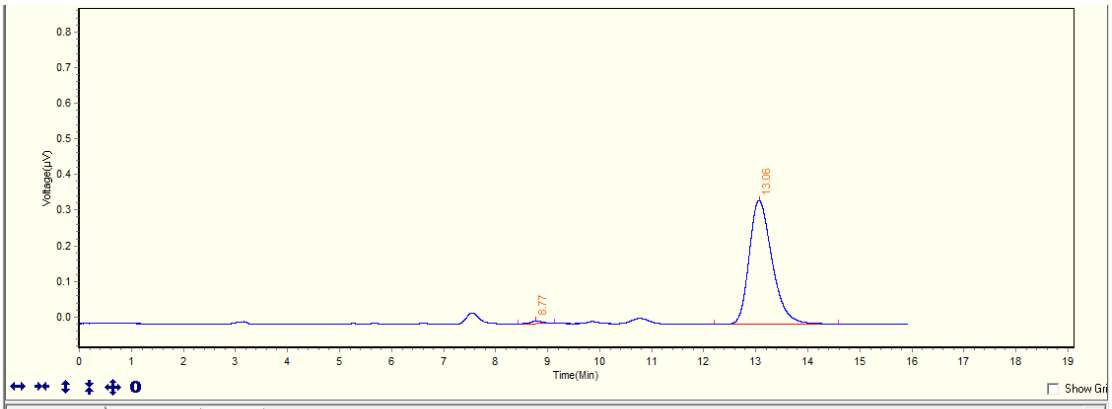


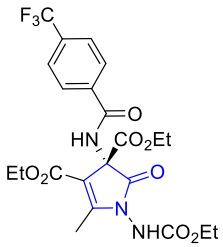
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.93	4565267	162017	48.26%	1.869	BB
2	13.27	4893634	153139	51.74%	2.908	BB
Total		9,458,901	315,156	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.77	58127	3397	1.09%	0.701	BB
2	13.06	5279798	173517	98.91%	2.388	BB
Total		5,337,925	176,914	100.00%		



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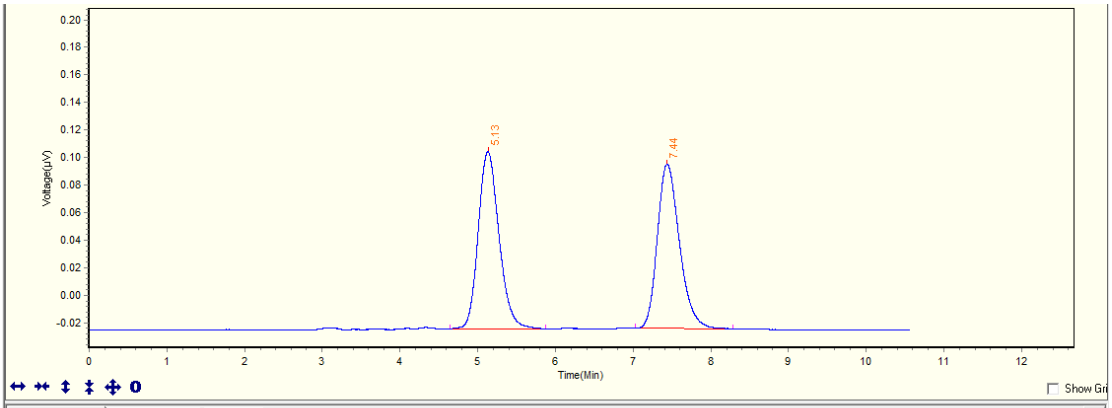
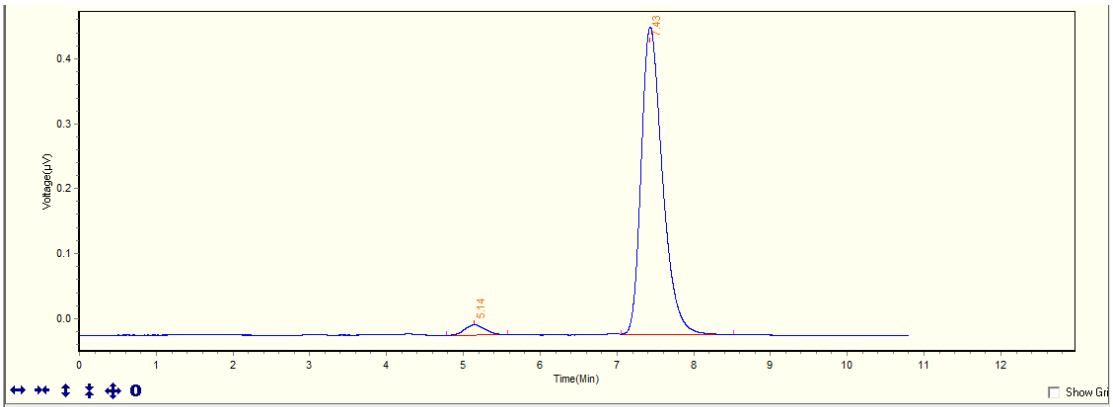


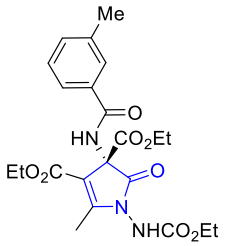
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	5.13	1194472	64235	50.35%	1.231	BB
2	7.44	1177688	59541	49.65%	1.256	BB
Total		2,372,160	123,776	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	5.14	144695	7788	3.10%	0.796	BB
2	7.43	4526049	236186	96.90%	1.464	BB
Total		4,670,744	243,974	100.00%		



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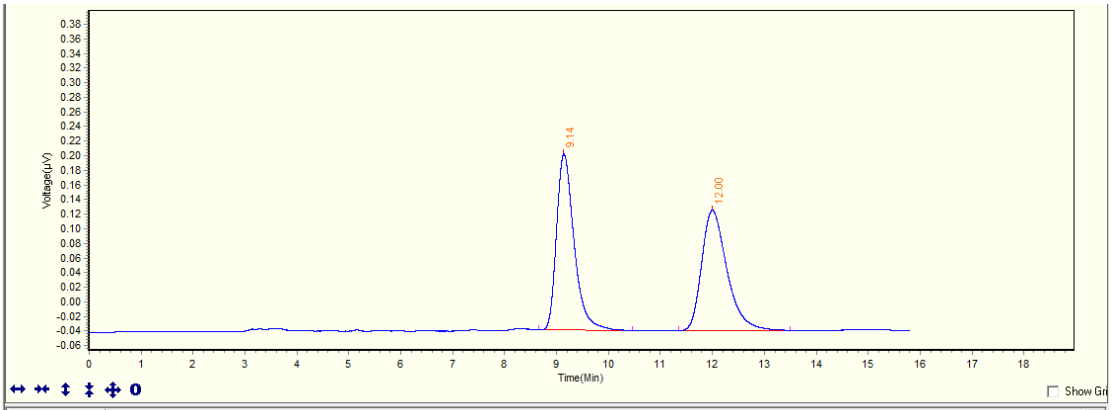
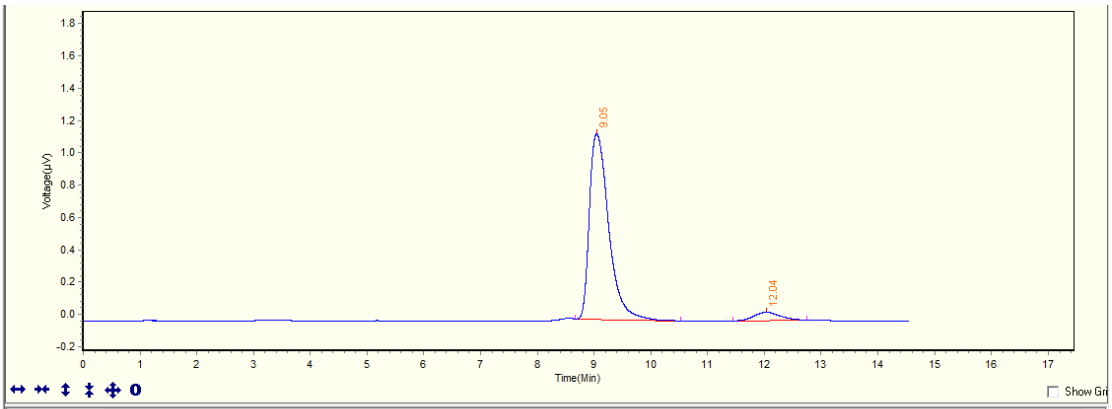


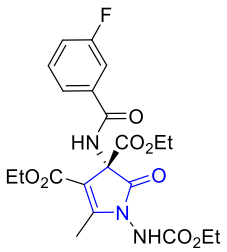
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.14	2831417	120408	50.34%	1.803	BB
2	12.00	2793146	82439	49.66%	2.145	BB
Total		5,624,563	202,847	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.05	13511122	572726	94.33%	1.858	BB
2	12.04	811912	25411	5.67%	1.303	BB
Total		14,323,034	598,137	100.00%		



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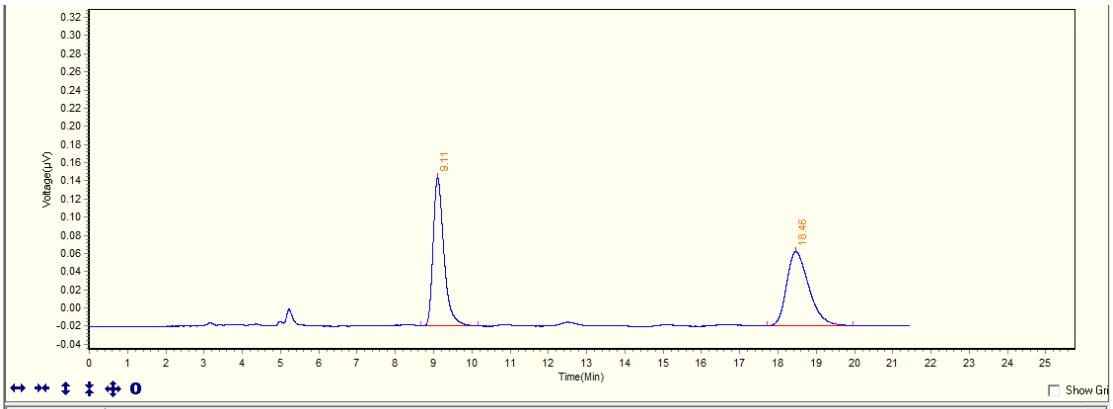
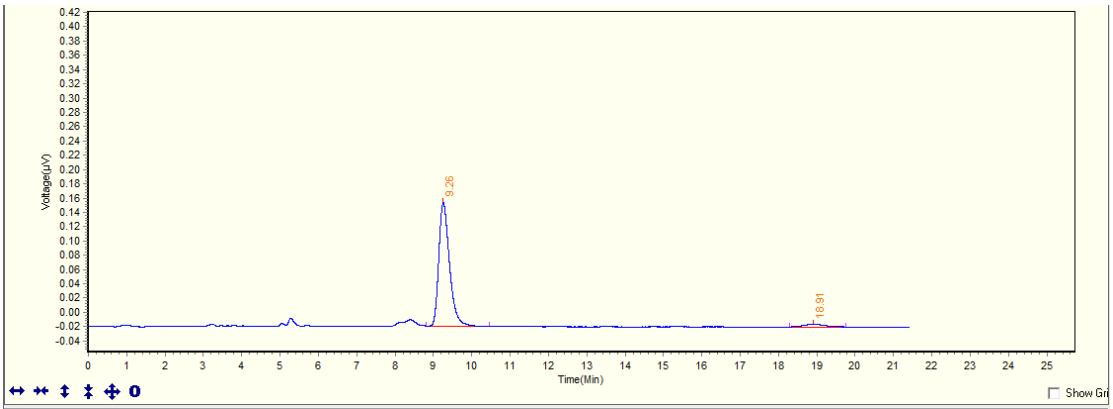


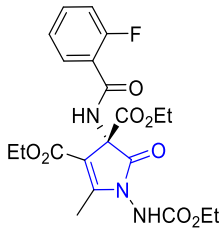
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.11	1602025	81627	49.44%	1.496	BB
2	18.46	1638108	40722	50.56%	2.243	BB
Total		3,240,133	122,349	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.26	1672424	86403	95.99%	1.648	BB
2	18.91	69785	1764	4.01%	1.467	BB
Total		1,742,209	88,167	100.00%		



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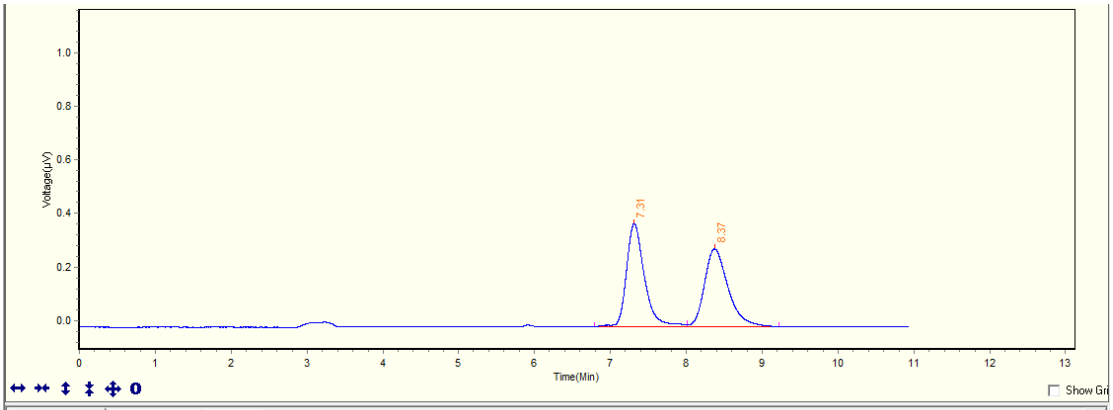
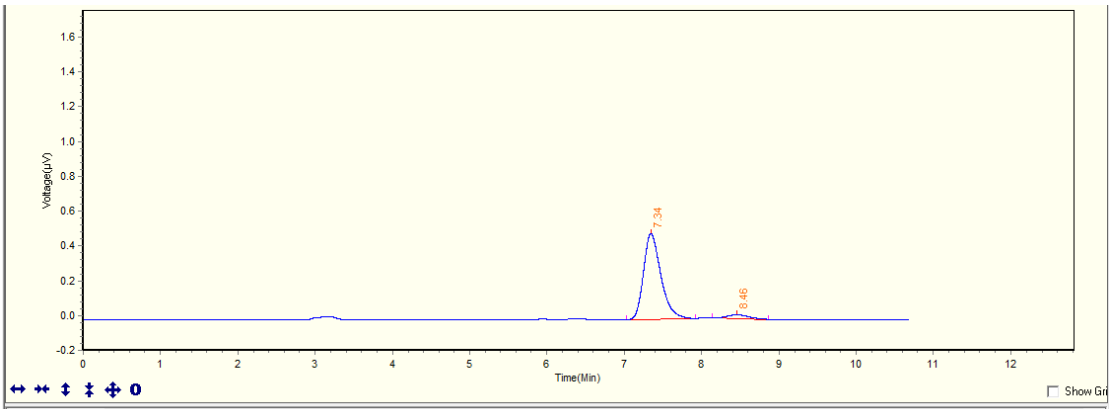


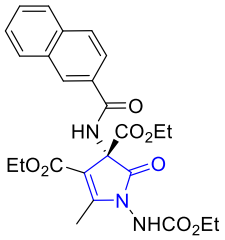
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.31	3178406	192250	50.45%	1.223	BV
2	8.37	3121364	145067	49.55%	1.209	VB
Total		6,299,770	337,317	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.34	3836192	245784	95.05%	0.892	BB
2	8.46	199592	10356	4.95%	0.727	BB
Total		4,035,784	256,140	100.00%		



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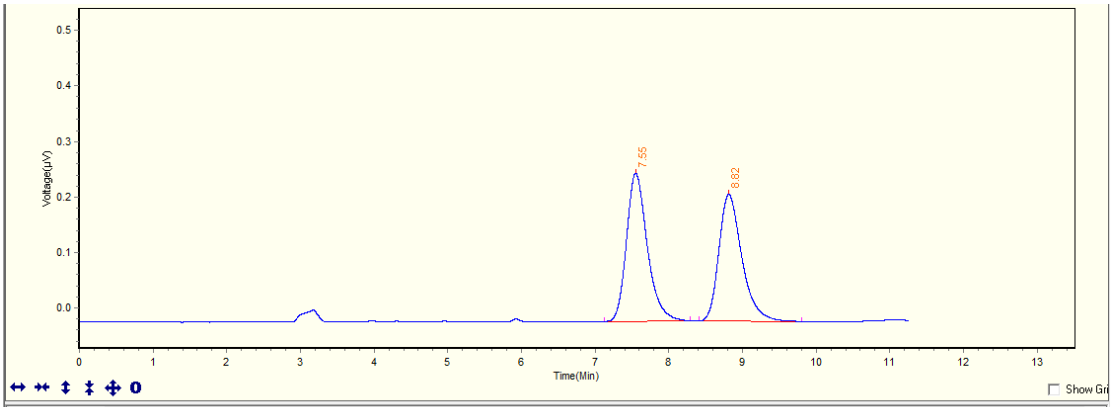
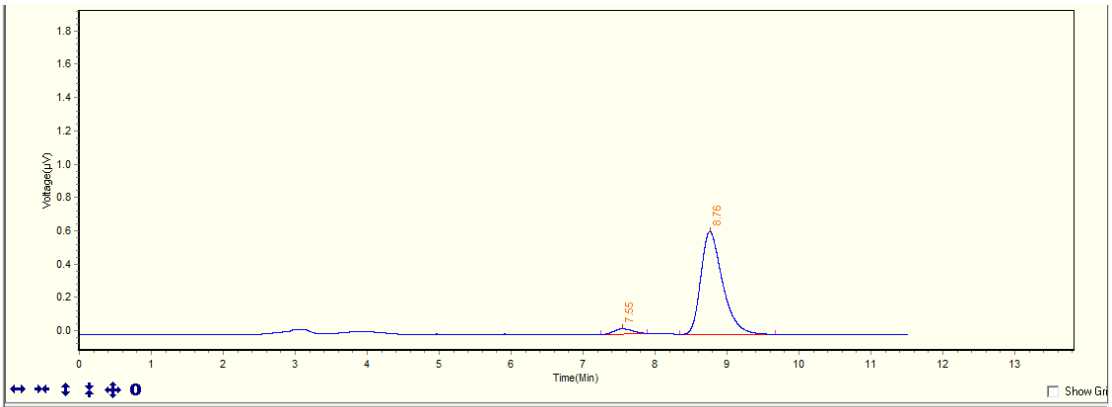


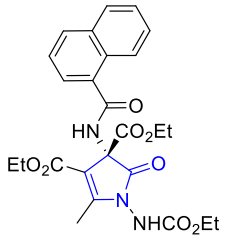
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.55	2618331	133239	51.44%	1.165	BB
2	8.82	2471713	114014	48.56%	1.393	BB
Total		5,090,044	247,253	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.55	281681	15617	4.18%	0.644	BB
2	8.76	6457521	308766	95.82%	1.329	BB
Total		6,739,202	324,383	100.00%		



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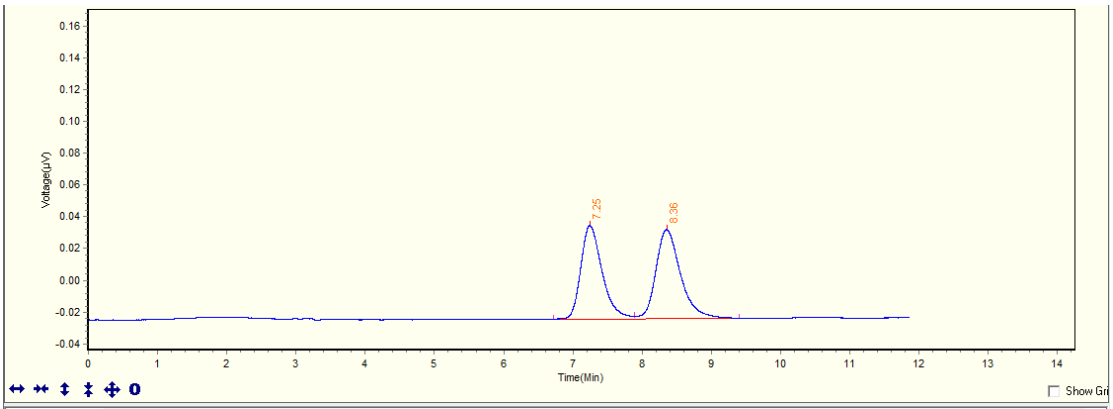
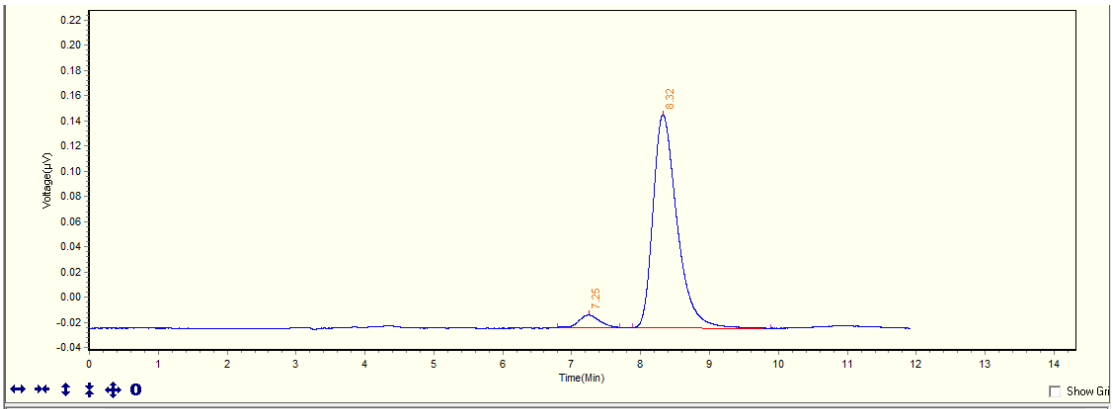


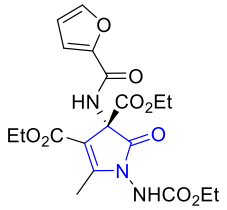
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.25	627874	29380	47.53%	1.17	BV
2	8.36	693209	27995	52.47%	1.512	VB
Total		1,321,083	57,375	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.25	98155	4919	4.59%	0.903	BB
2	8.32	2041473	84582	95.41%	2.007	BB
Total		2,139,628	89,501	100.00%		



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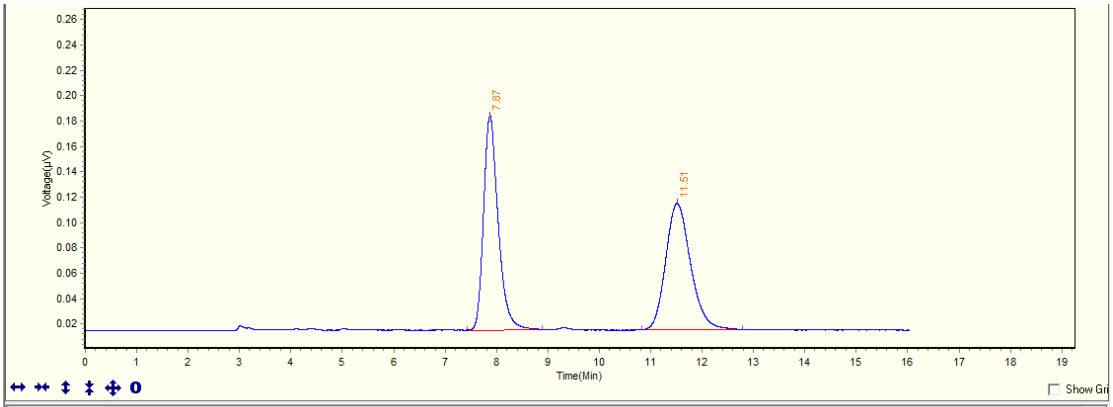
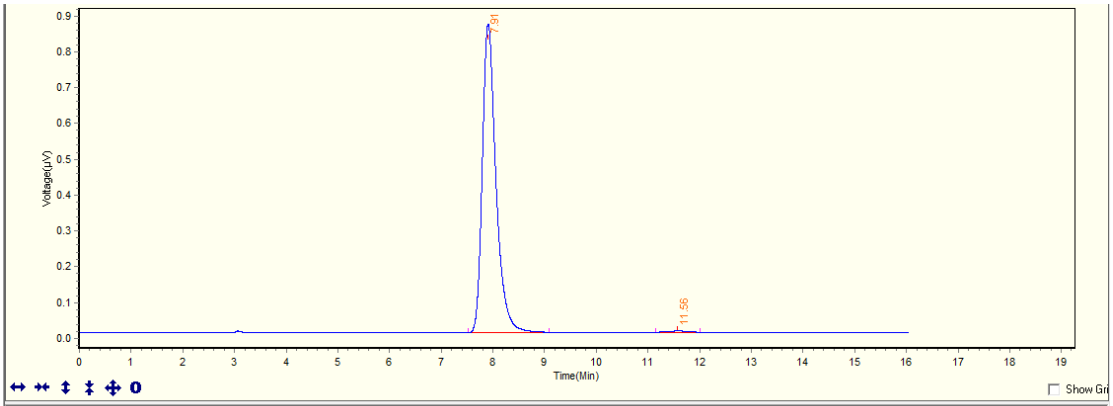


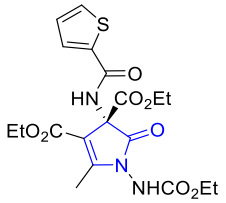
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.87	1664874	84324	49.97%	1.459	BB
2	11.51	1666814	49715	50.03%	1.958	BB
Total		3,331,688	134,039	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.91	7894472	430923	99.41%	1.565	BB
2	11.56	47050	1777	0.59%	0.859	BB
Total		7,941,522	432,700	100.00%		



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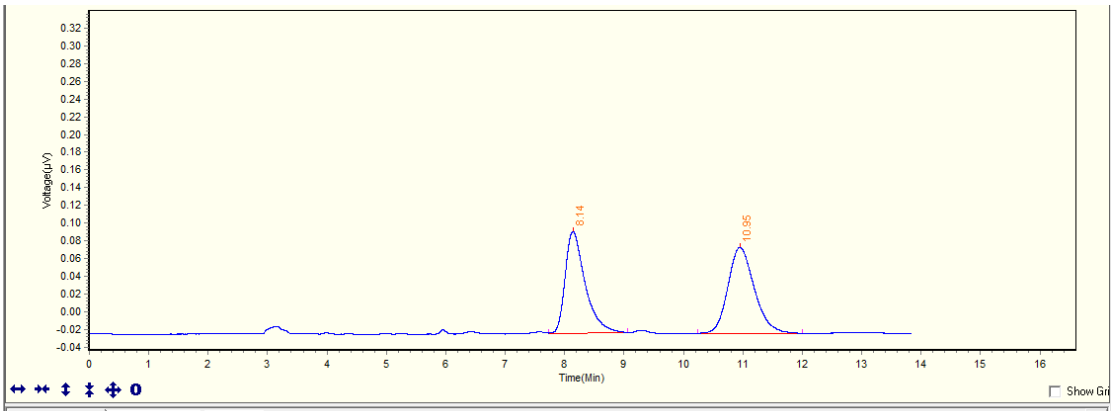
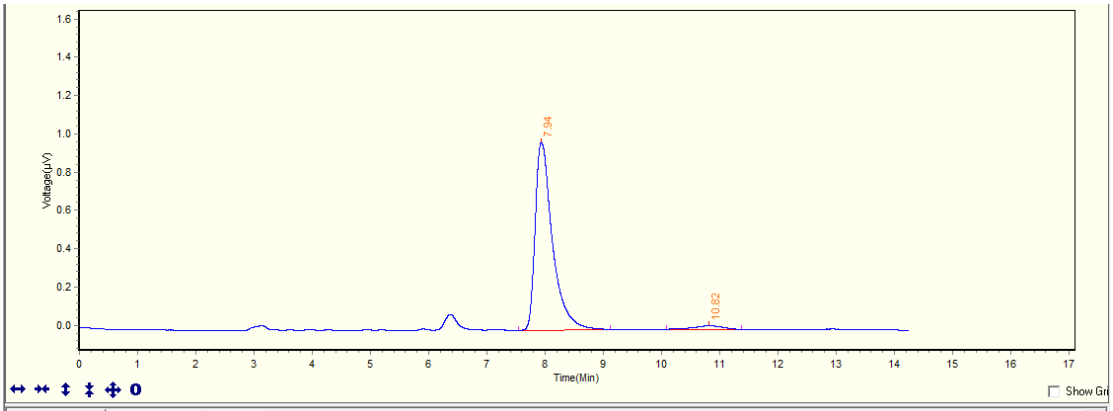


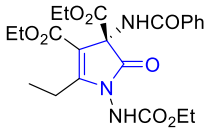
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	8.14	1326061	57185	47.16%	1.33	BB
2	10.95	1485799	48382	52.84%	1.762	BB
Total		2,811,860	105,567	100.00%		

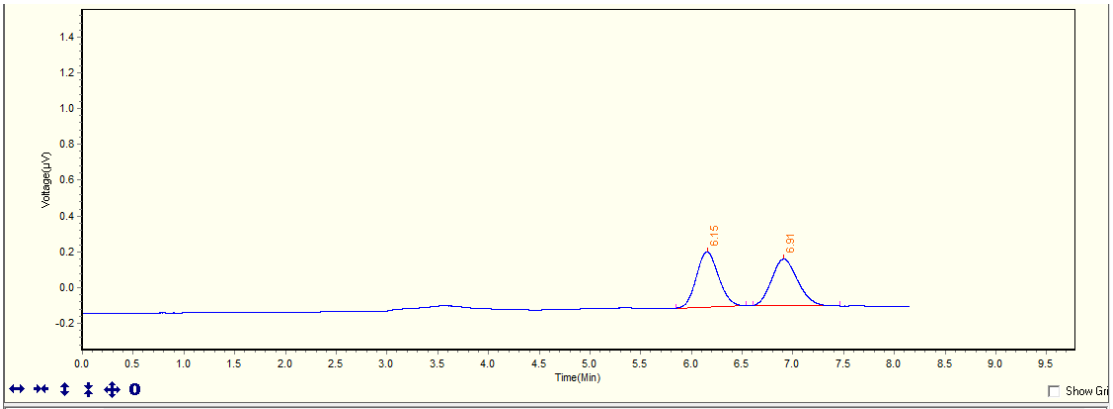


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.94	10071768	489715	96.91%	1.576	BB
2	10.82	321532	9371	3.09%	1.288	BB
Total		10,393,300	499,086	100.00%		

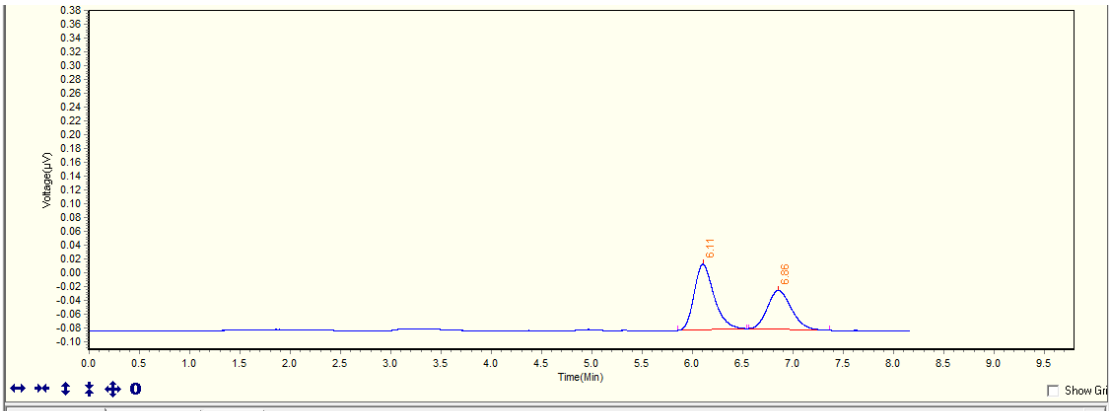


S1



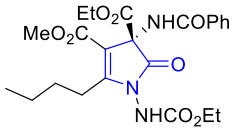
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.15	2333260	154381	50.27%	0.691	BB
2	6.91	2308230	129814	49.73%	0.857	BB
Total		4,641,490	284,195	100.00%		

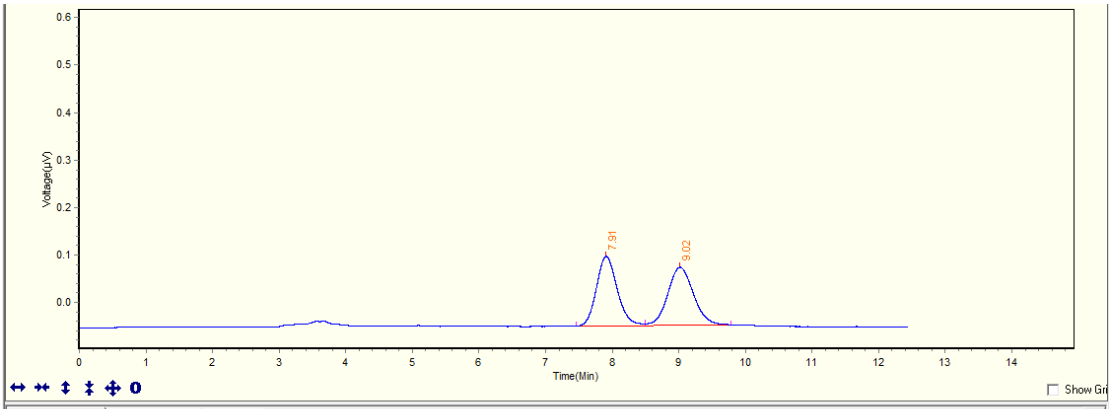


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.11	650542	47568	58.39%	0.686	BB
2	6.86	463575	28101	41.61%	0.804	BB
Total		1,114,117	75,669	100.00%		

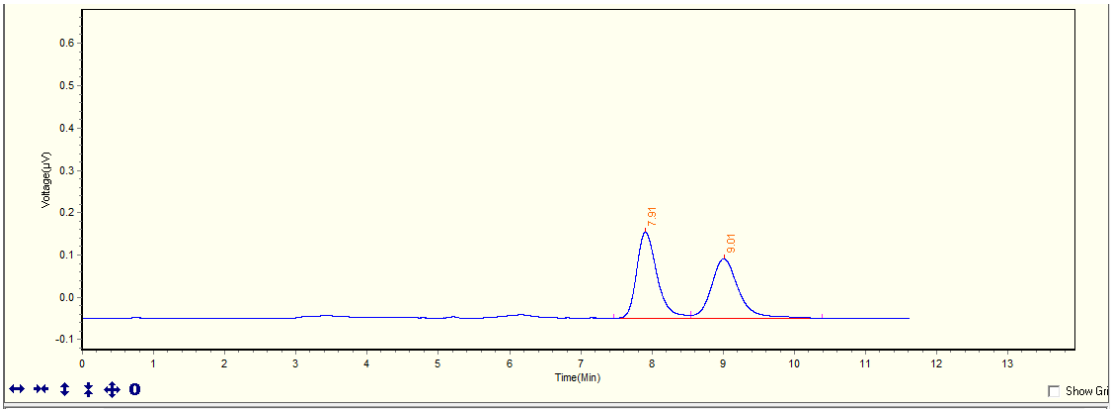


S2



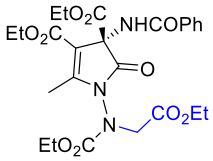
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.91	1582416	73012	49.33%	1.036	BV
2	9.02	1625198	60826	50.67%	1.287	VB
Total		3,207,614	133,838	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.91	2009396	101656	52.00%	1.074	BV
2	9.01	1854772	70221	48.00%	1.856	VB
Total		3,864,168	171,877	100.00%		



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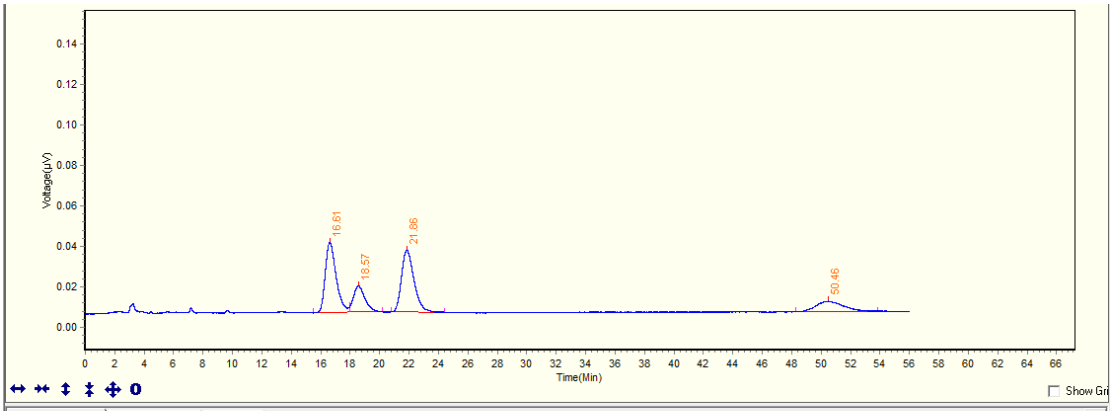
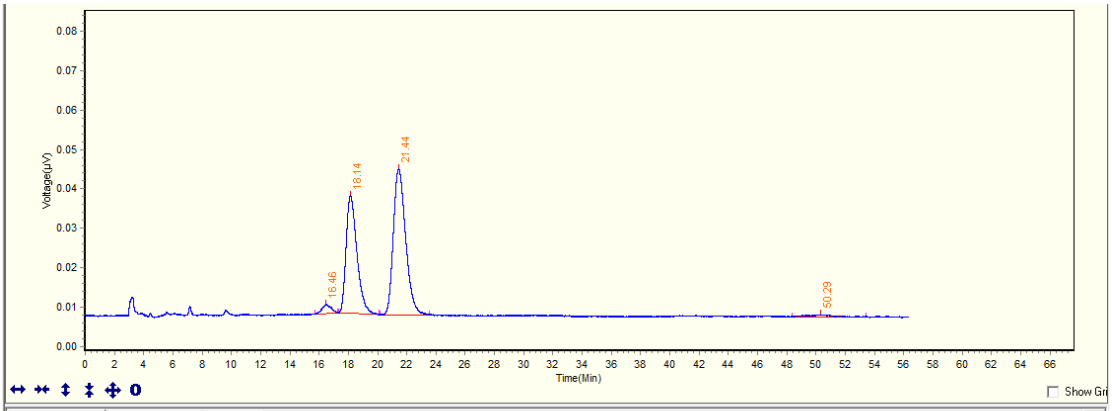


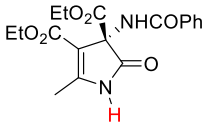
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.61	893207	17314	36.35%	2.483	BV
2	18.57	349041	6464	14.21%	2.211	VB
3	21.86	893884	15255	36.38%	3.62	BB
4	50.46	320986	2577	13.06%	5.565	BB
Total		2,457,118	41,610	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.46	47625	1151	2.49%	1.552	BB
2	18.14	760514	14878	39.79%	2.765	BB
3	21.44	1076547	18502	56.33%	3.373	BB
4	50.29	26620	286	1.39%	5.021	BB
Total		1,911,306	34,817	100.00%		



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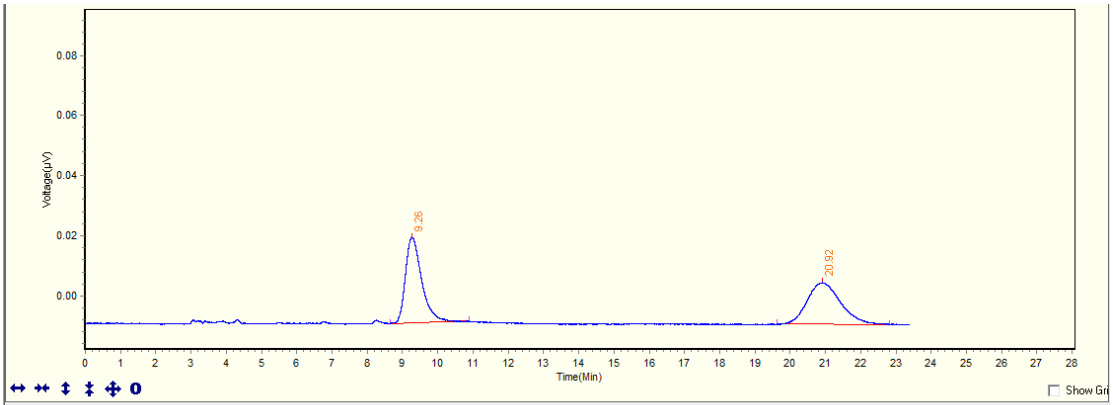
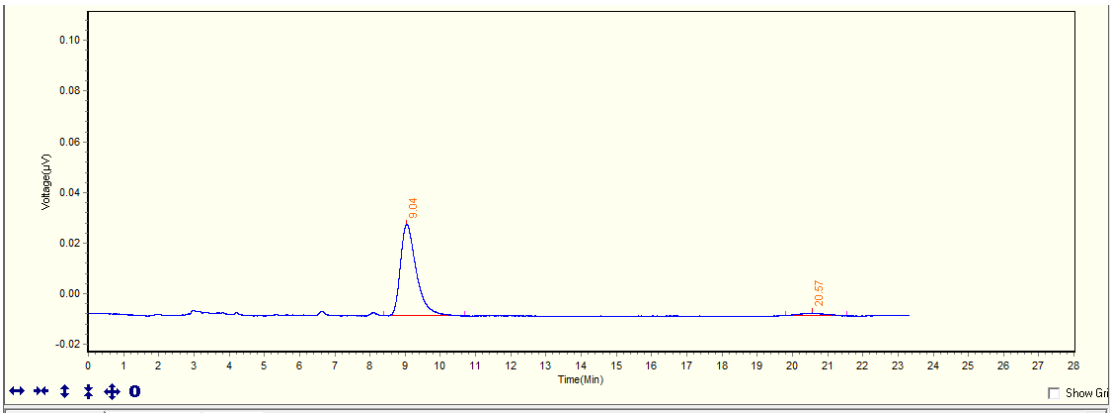


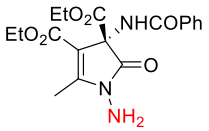
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.26	452338	14186	49.81%	2.22	BB
2	20.92	455755	6908	50.19%	3.205	BB
Total		908,093	21,094	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.04	565870	17999	96.06%	2.301	BB
2	20.57	23224	509	3.94%	1.739	BB
Total		589,094	18,508	100.00%		



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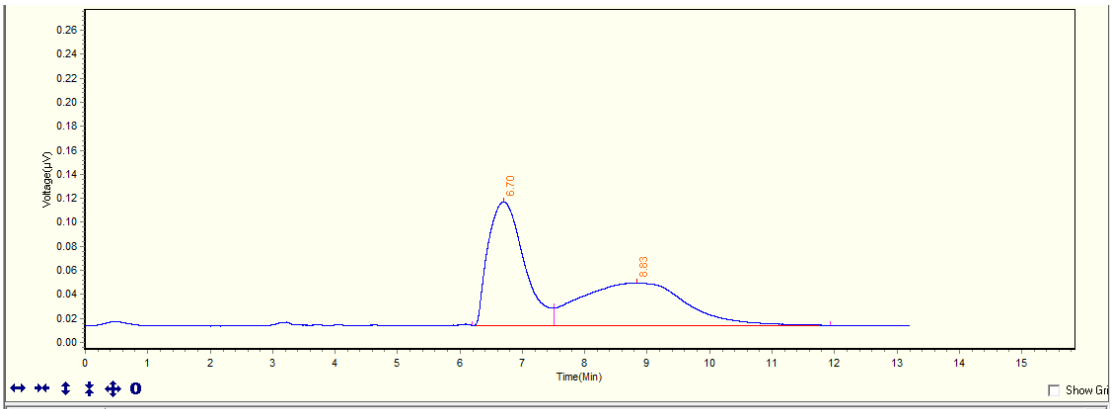
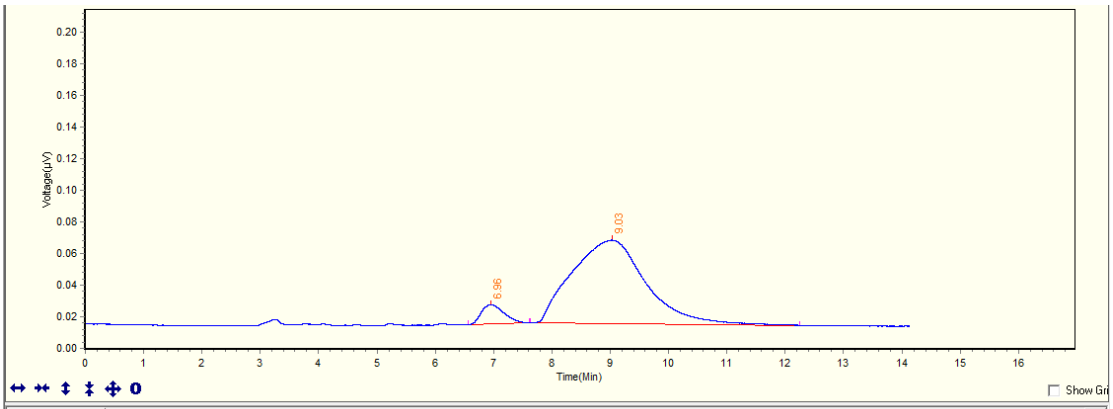


Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.70	2040852	51345	49.83%	1.312	BV
2	8.83	2054980	17623	50.17%	4.424	VB
Total		4,095,832	68,968	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.96	164936	6141	6.63%	1.049	BB
2	9.03	2324298	26414	93.37%	4.619	BB
Total		2,489,234	32,555	100.00%		

7. References

[1] X.-P. Chen, J.-X. Liu, H.-Y. Li, Y.-C. Xiao, F.-E. Chen. *Adv. Synth. Catal*. **2022**, *364*, 2067–2071.
[2] Robert A. Mosey, Jason S. Fisk, Timothy L. Friebe, Jetze J. Tepe. *Org. Lett*. **2008**, *10*, 825-828.
[3] Ansgar Oberheide, Hans-Dieter Arndt. *Adv. Synth. Catal*. 2021, 363, 1132 – 1136.
[4] Nelson A. M. Pereira, Américo Lemos, Arménio C. Serraa, Teresa M. V. D. Pinho e Melo. *Tetrahedron. Lett.* **2013**, *54*, 1553-1557.