

Electronic Supplementary Information

Visible light-induced aerobic oxidative cross-coupling of glycine esters with α -angelicalactone: a facile pathway to γ -lactams

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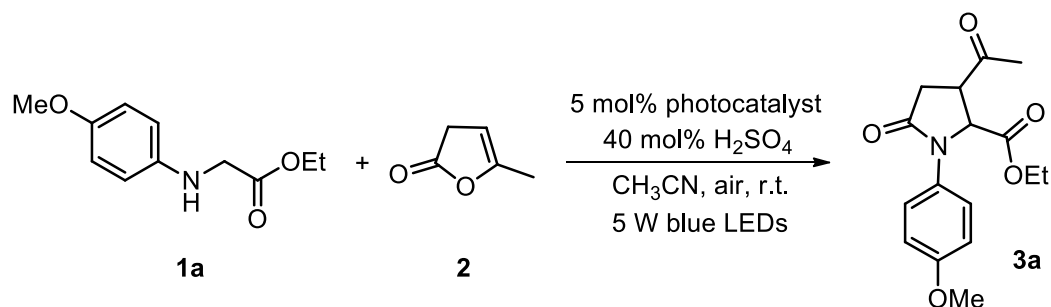
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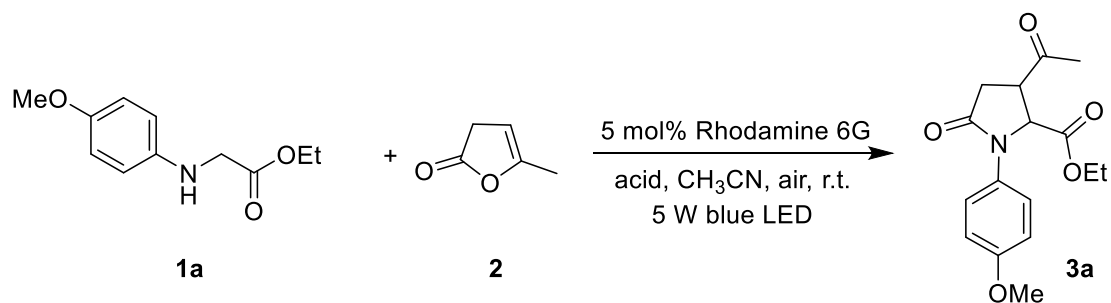
1. Optimization of Reaction Conditions

Table S1. Screening of Photocatalysts^a



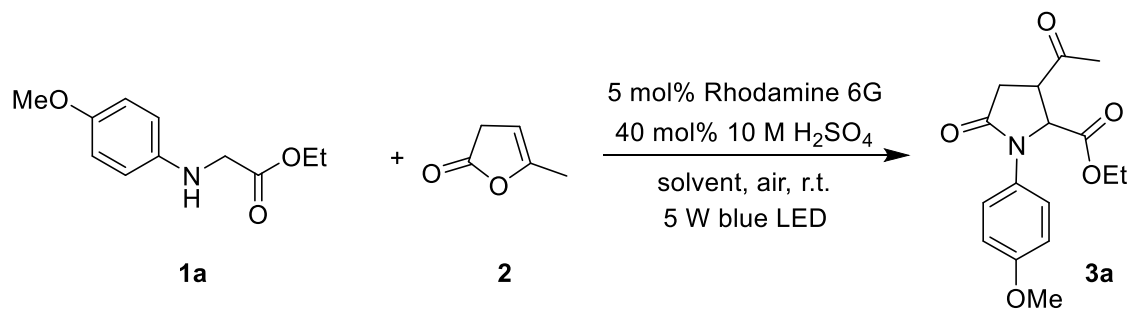
entry	photocatalyst	yield (%) ^e
1	Ru(bpy) ₃ Cl ₂ · 6H ₂ O	33
2	Eosin Y	29
3	Rose Bengal	41
4	Rhodamine 6G	54
5 ^b	Rhodamine 6G	48
6 ^c	Rhodamine 6G	42
7 ^d	Rhodamine 6G	32
8	Eosin B	37
9	Methylene Blue	48
10	9-Mesityl-10-methylacridinium perchlorate	32

^aReaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), CH₃CN (2 mL), H₂SO₄ (10 M, 40 mol%), photocatalyst (5 mol%), 5 W blue LED light irradiation in air at room temperature for 12 h. ^b2.5 mol% of Rhodamine 6G was used. ^c10 mol% of Rhodamine 6G was used. ^d20 mol% of Rhodamine 6G was used. ^eIsolated yields.

Table S2. Screening of Acids^a

entry	acid	time (h)	yield (%) ^j
1	HCl	15	23
2	AcOH	15	NR
3	H ₃ PO ₄	15	NR
4	TsOH H ₂ O	12	trace
5	TfOH	12	17
6	TFA	12	29
7 ^b	H ₂ SO ₄ (10 M)	12	27
8 ^c	H ₂ SO ₄ (10 M)	12	54
9 ^c	H ₂ SO ₄ (10 M)	6	46
10 ^d	H ₂ SO ₄ (10 M)	12	ND
11 ^{c,e}	H ₂ SO ₄ (10 M)	12	62
12 ^{c,f}	H ₂ SO ₄ (10 M)	12	59
13 ^{c,g}	H ₂ SO ₄ (10 M)	24	43
14 ^{c,e,h}	H ₂ SO ₄ (10 M)	12	34
15 ^{c,e}	conc. H ₂ SO ₄	12	38
16 ^c	citric acid	12	NR
17	HClO ₄	12	NR
18 ^c	HNO ₃	7	31
19 ⁱ	HBr	7	46
20 ^c	HI	12	56
21	CH ₃ SO ₃ H	15	41
22	C ₆ H ₅ SO ₃ H	15	36

^aReaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), CH₃CN (2 mL), acid (80 mol%), Rhodamine 6G (5 mol%), 5 W blue LED light irradiation in air at room temperature. ^b20 mol% of acid was used. ^c40 mol% of acid was used. ^d120 mol% of acid was used. ^e0.3 mmol **2** was used. ^f0.4 mmol **2** was used. ^g0.6 mmol **2** was used. ^hheated at 70 °C. ⁱ30 mol% of acid was used. ^jIsolated yields.

Table S3. Screening of the Solvent^a

entry	solvent	yield (%) ^b
1	ethanol	trace
2	methanol	trace
3	cyclohexane	NR
4	DCE	NR
5	1,4-dioxane	NR
6	methylene chloride	trace
7	chloroform	trace
8	THF	trace
9	acetic acid	43
10	DMSO	NR
11	DMF	NR
12	toluene	trace
13	CH ₃ CN	54
14	Cl ₃ CCN	trace
15	EtOAc	ND
16	1-Methylpyrrolidine	ND

^aReaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), solvent (2 mL), H₂SO₄ (10 M, 40 mol%), Rhodamine 6G (5 mol%), 5 W blue LED light irradiation in air at room temperature for 12 h.

^bIsolated yields.

2. Luminescence Quenching Experiments

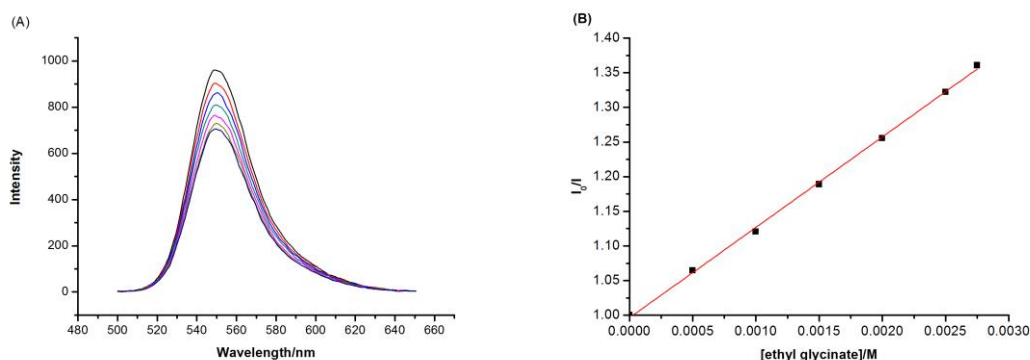


Figure S1. A) Changes in the fluorescence spectra of Rhodamine 6G (2.0×10^{-6} M) upon the progressive addition of **1a** (5.0×10^{-4} M) in CH₃CN; B) Stern–Volmer quenching plot of Rhodamine 6G in the presence of **1a**.

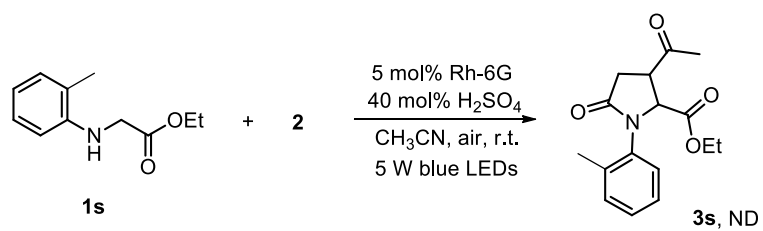
3. Experimental

General information

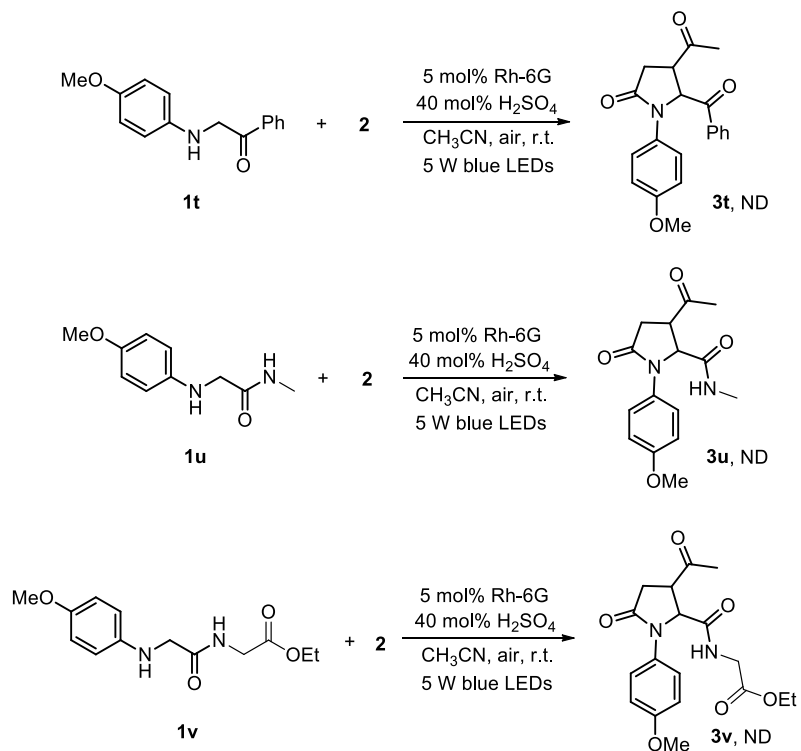
Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. N-arylglycine derivatives were prepared according to literature procedures¹. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using a 5 W blue LED bulb. The silica gel (200–300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QToF). Luminescence spectra were surveyed on a PerkinElmer LS 55 spectrophotometer.

General procedure for the visible-light-induced photocatalytic aerobic oxidative dehydrogenative formal [2 + 3] cyclization of glycine esters with α -angelicalactone

To a solution of N-arylglycine esters **1** (0.1 mmol, 1 equiv), Rh-6G (5 mol %) in dry CH₃CN (2.0 mL) was added H₂SO₄ (40 mol %). Under the irradiation of a 5 W blue LED bulb, α -angelicalactone **2** (0.3 mmol, 3 equiv) was added in three batches during 1 hour, then the mixture was stirred under the irradiation of blue LED at room temperature. After completion of the reaction as monitored by TLC, the solvent was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (with petroleum ether/acetone = 4:1 as eluent) to afford the products.



Scheme S1. Performance the reaction with ortho-substituted N-aryl glycine ester as substrate.

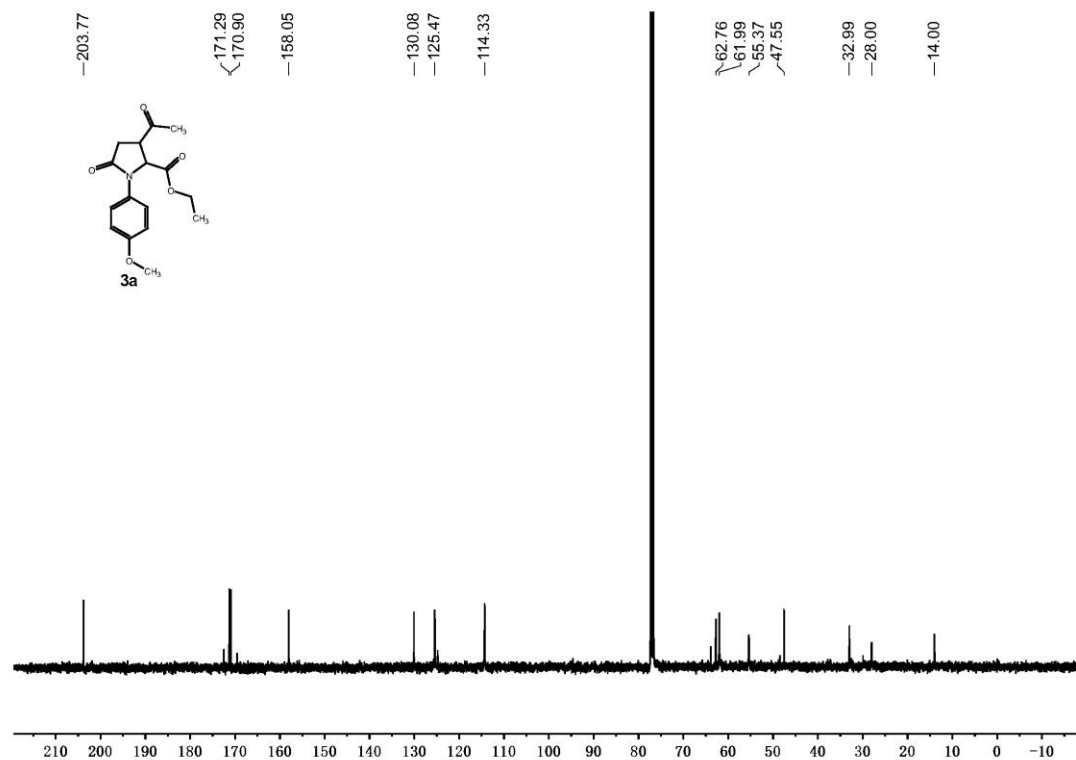
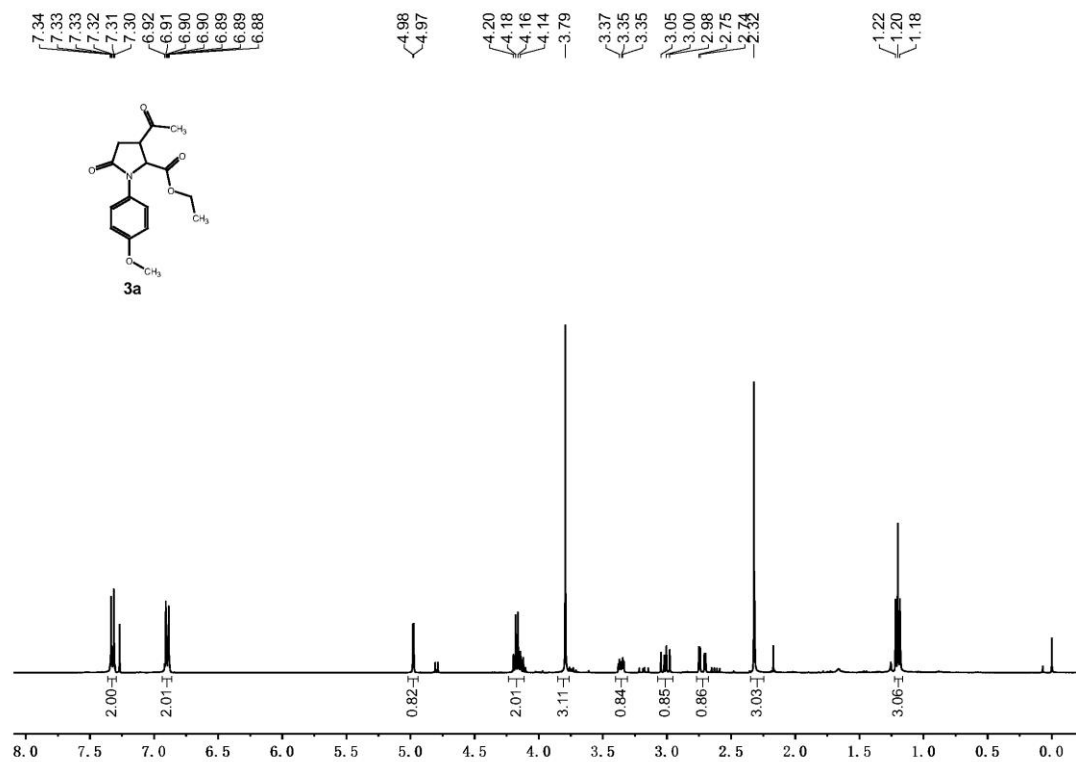


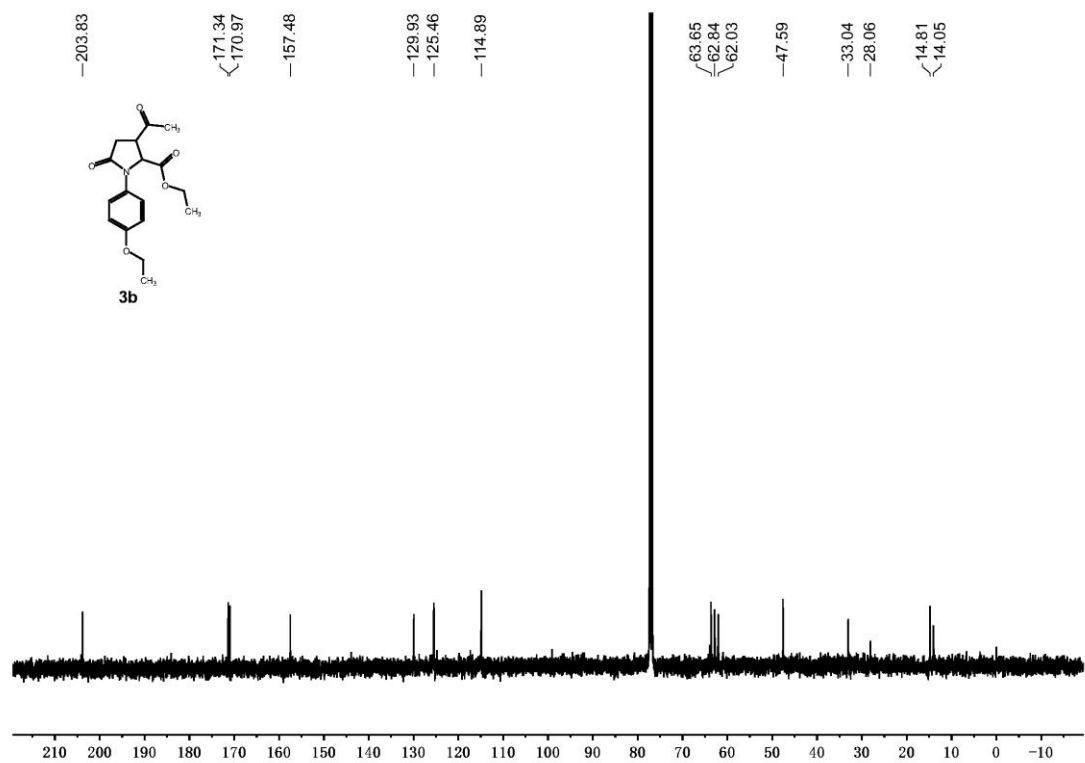
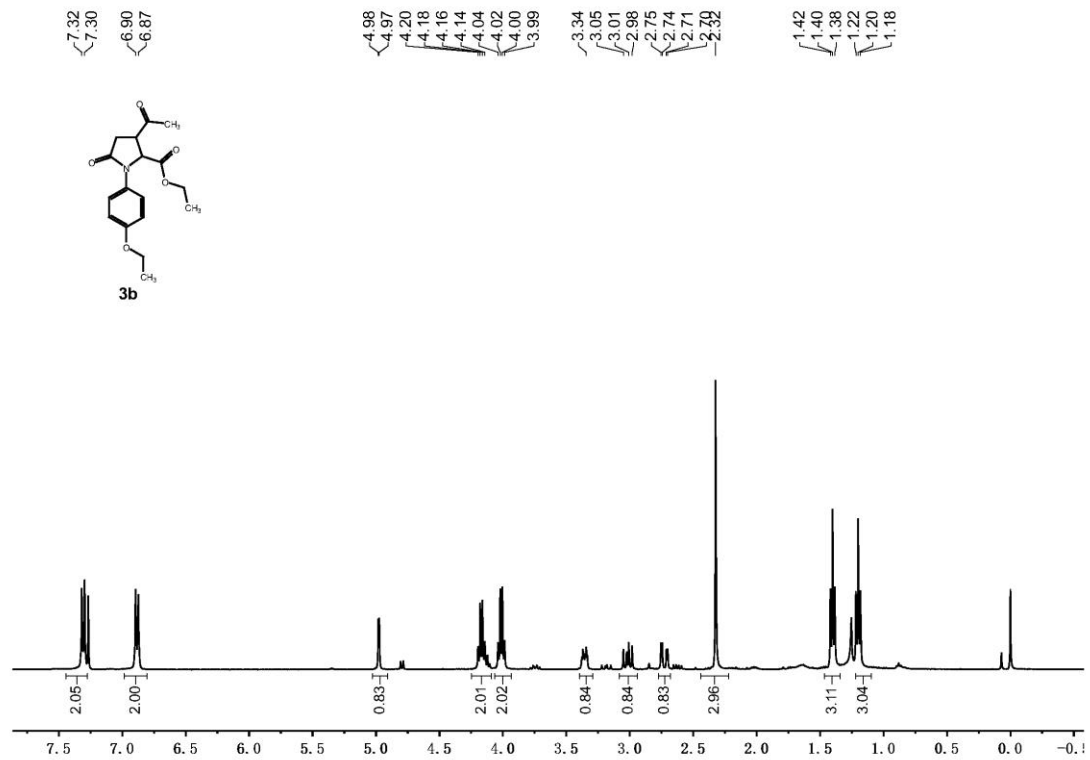
Scheme S2. Performance the reaction with other α -amino carbonyls as substrate.

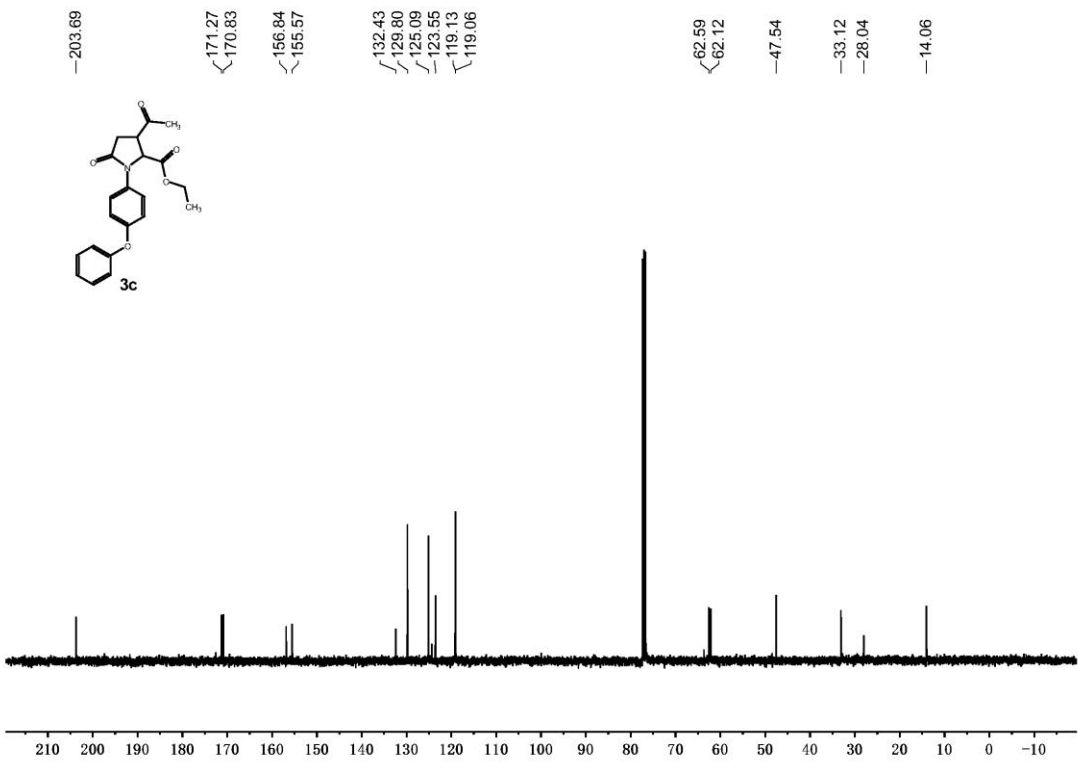
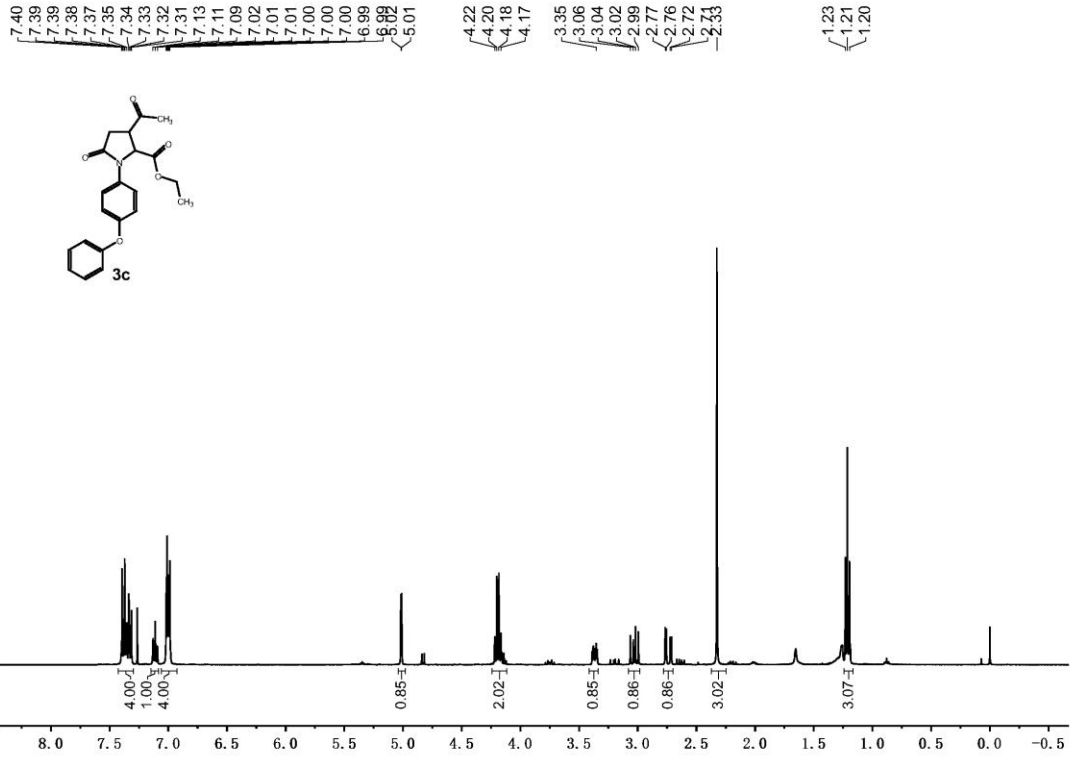
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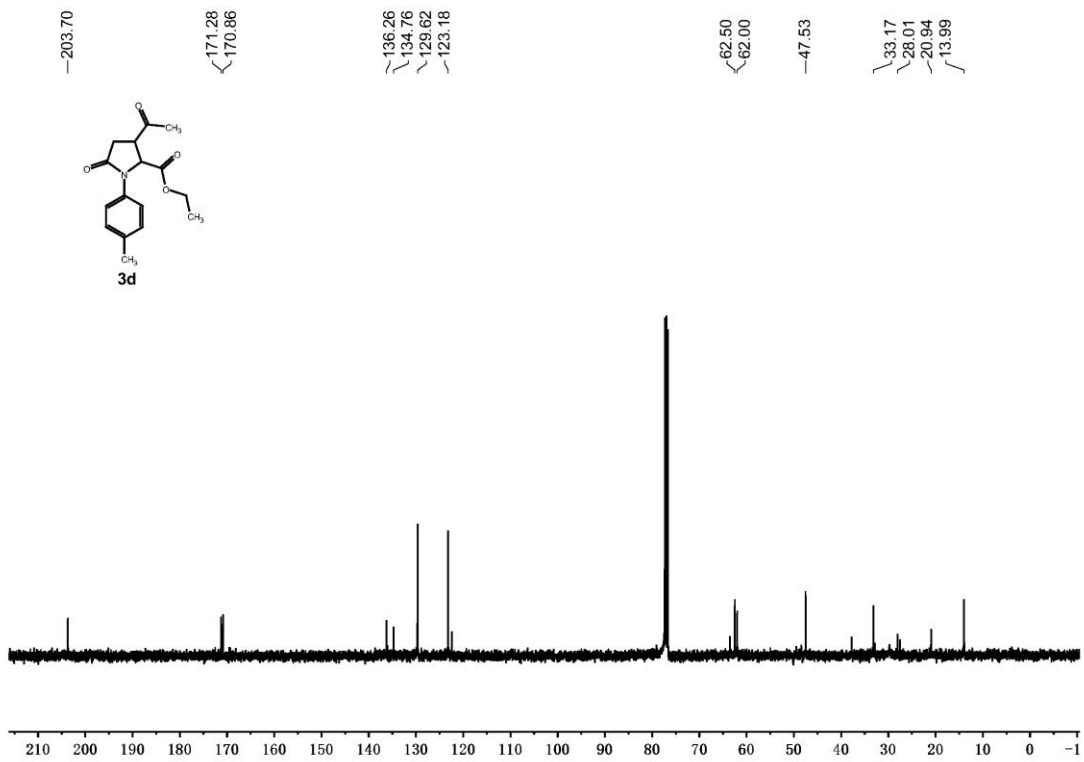
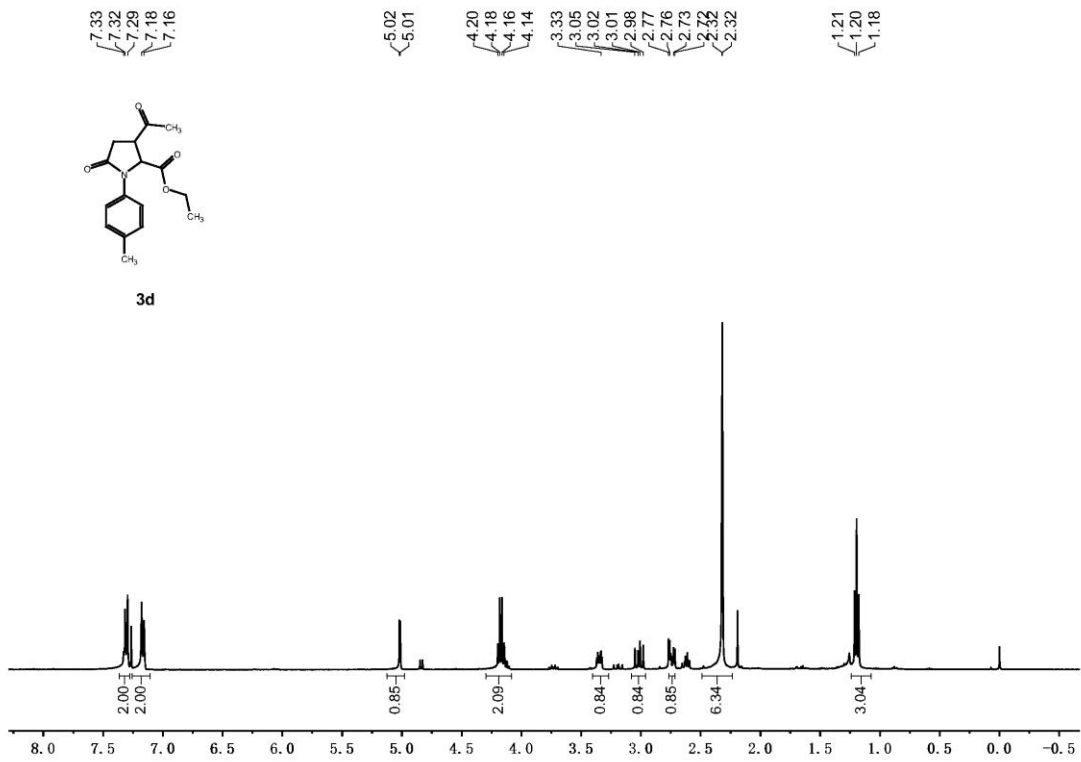
- [1] J. Xie and Z. Z. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 10181-10185.

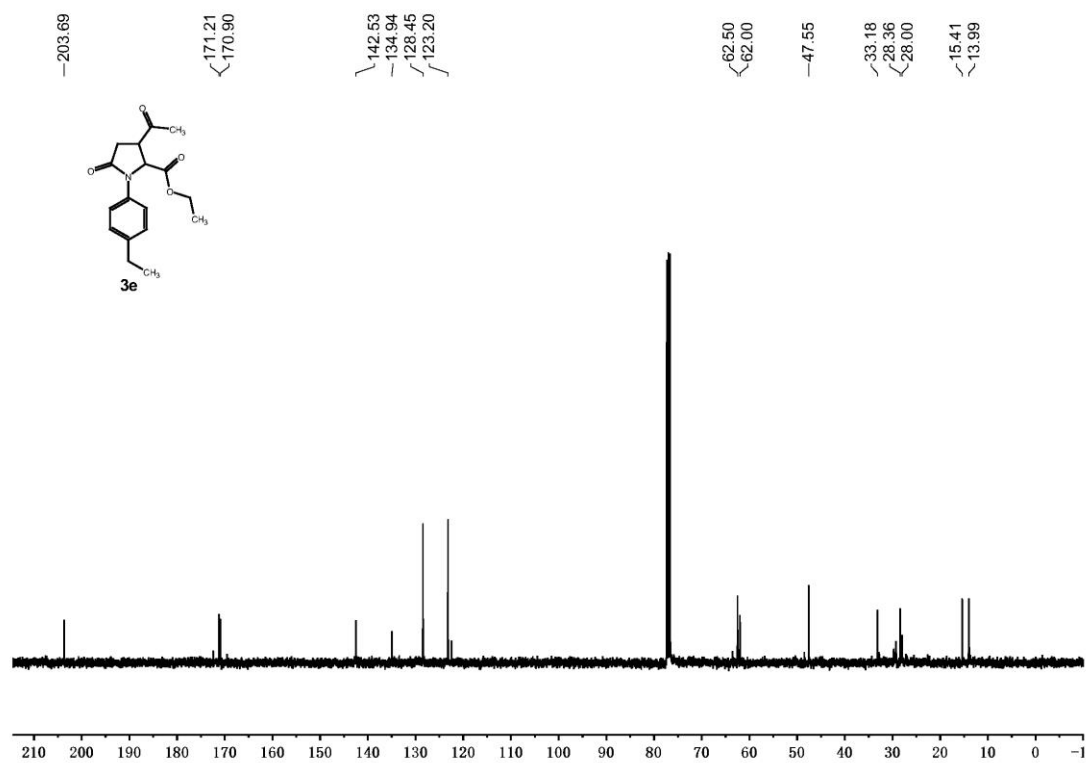
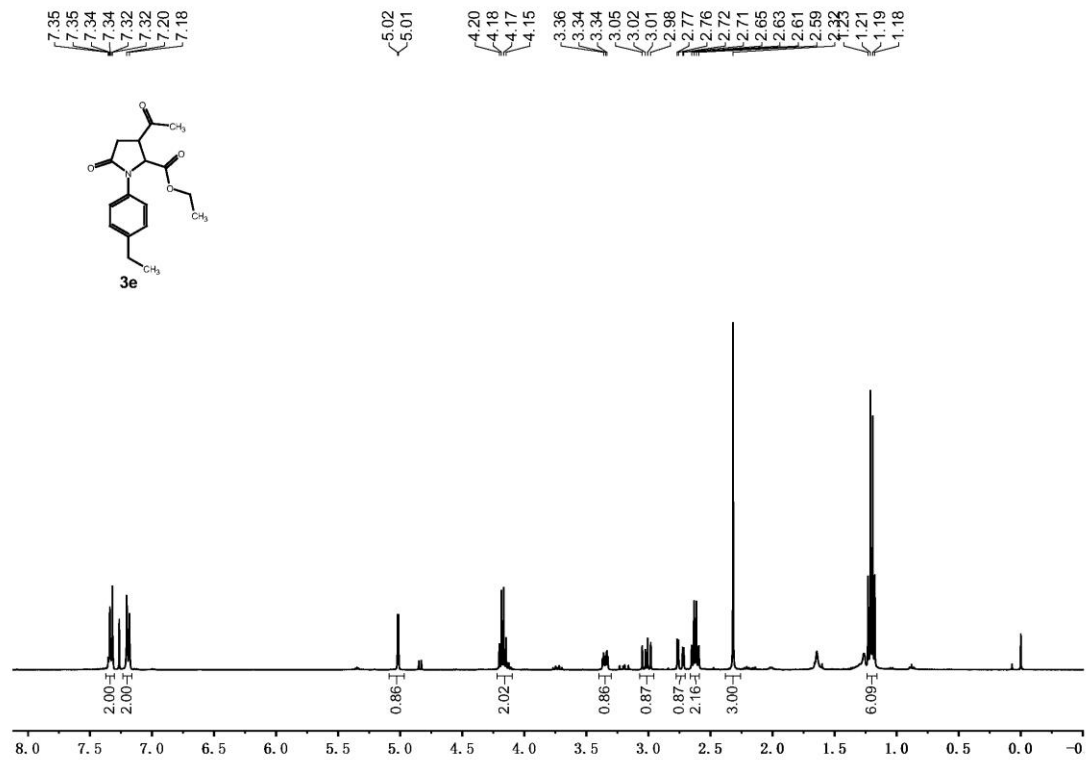
4. Copies of ^1H and ^{13}C Spectra

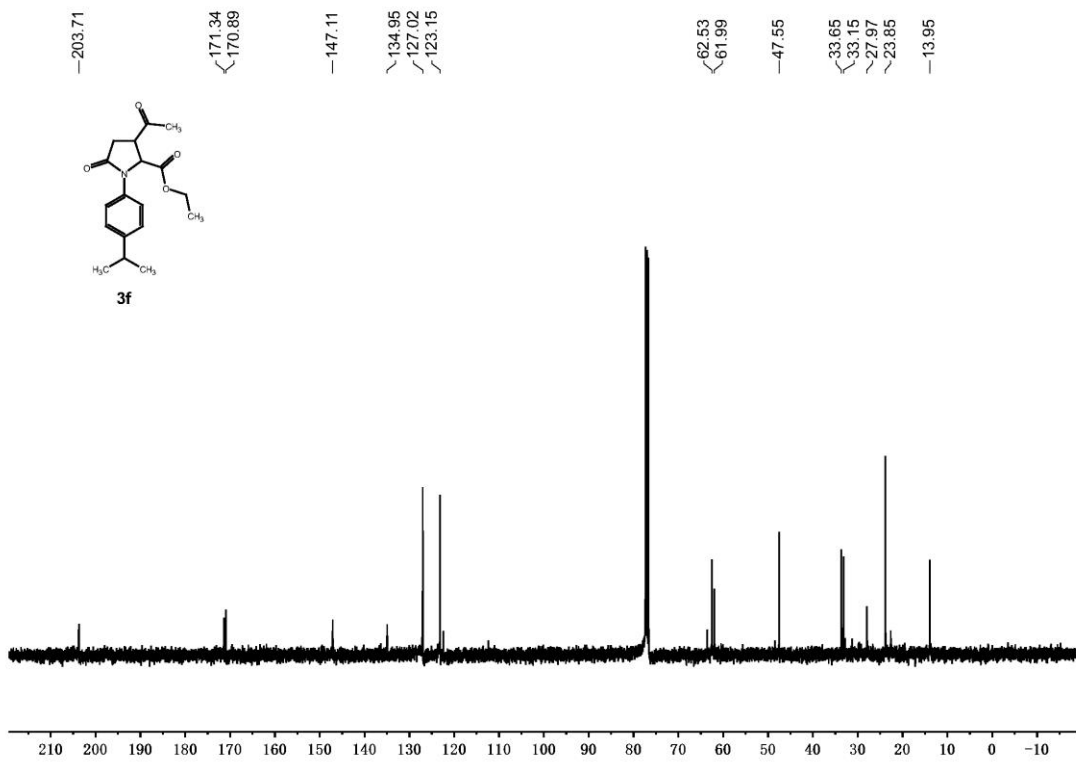
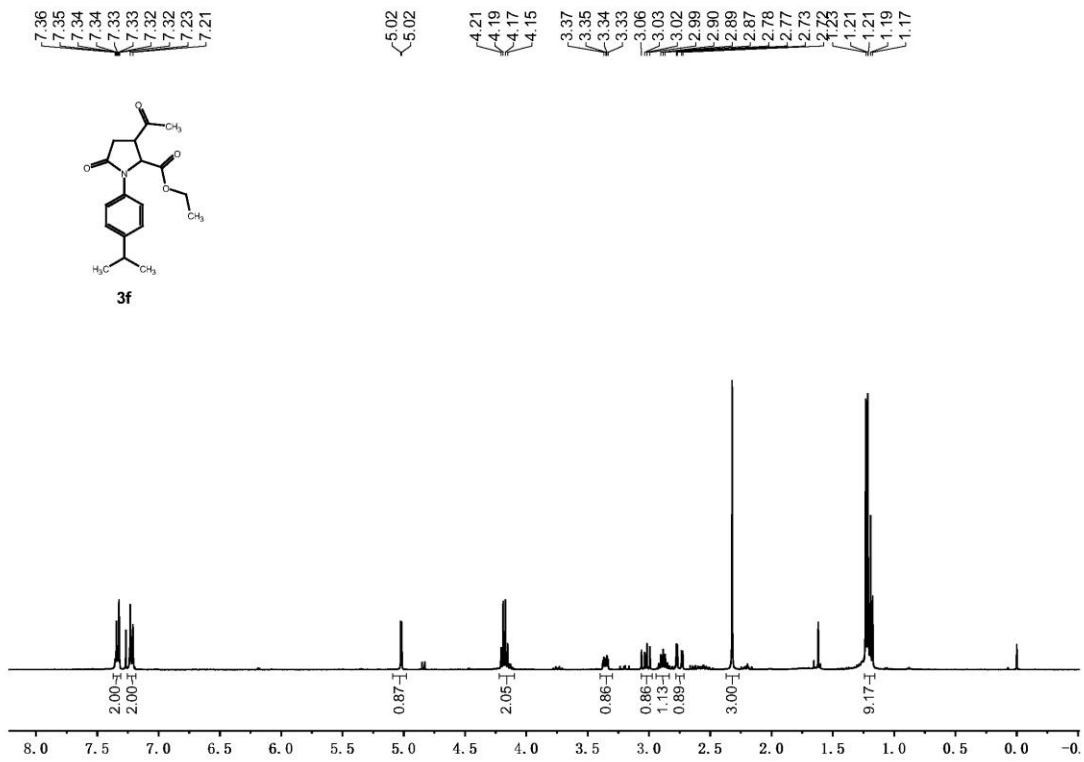


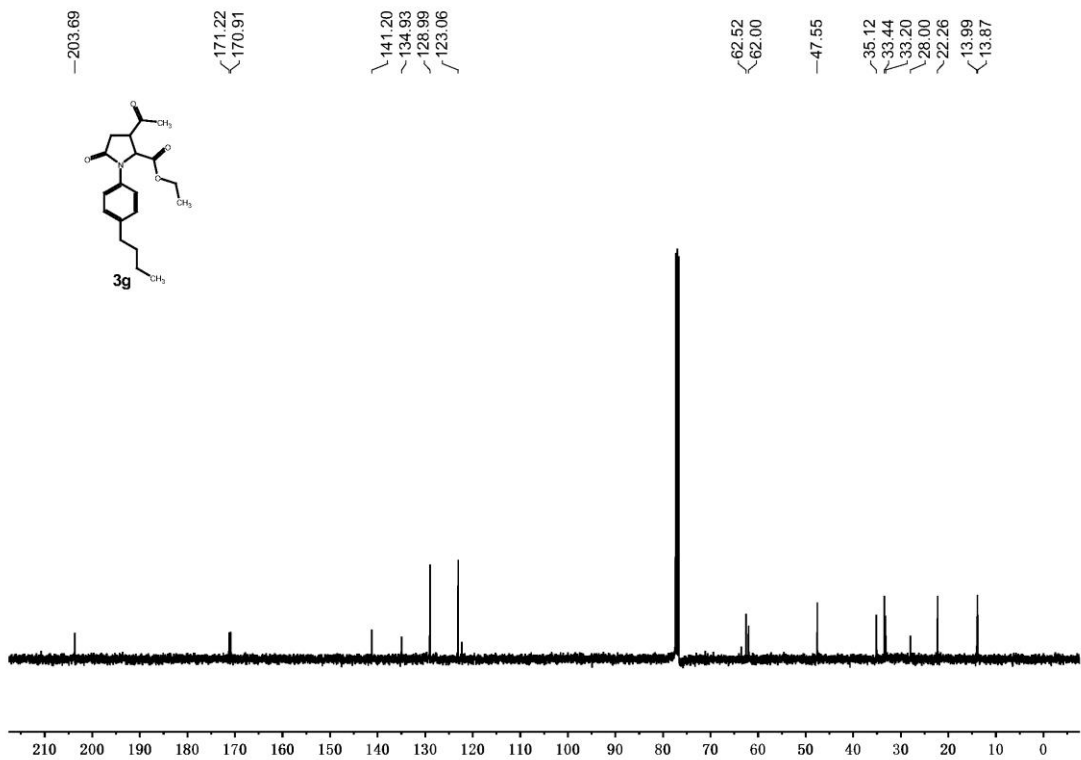
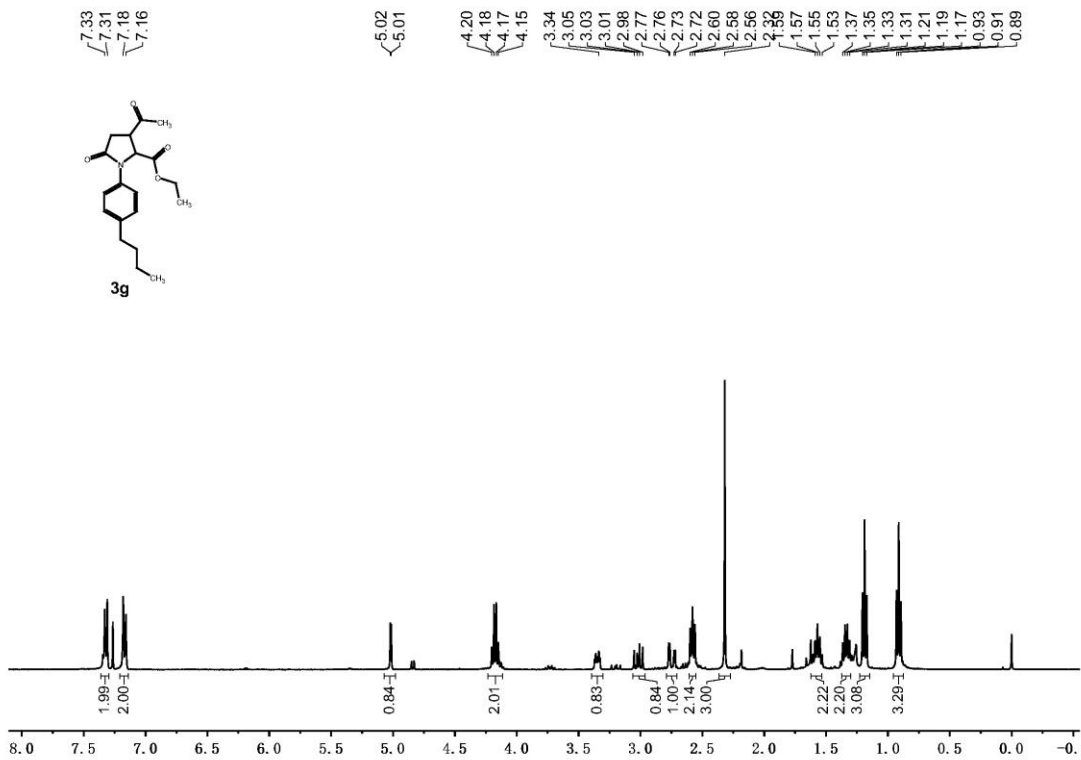


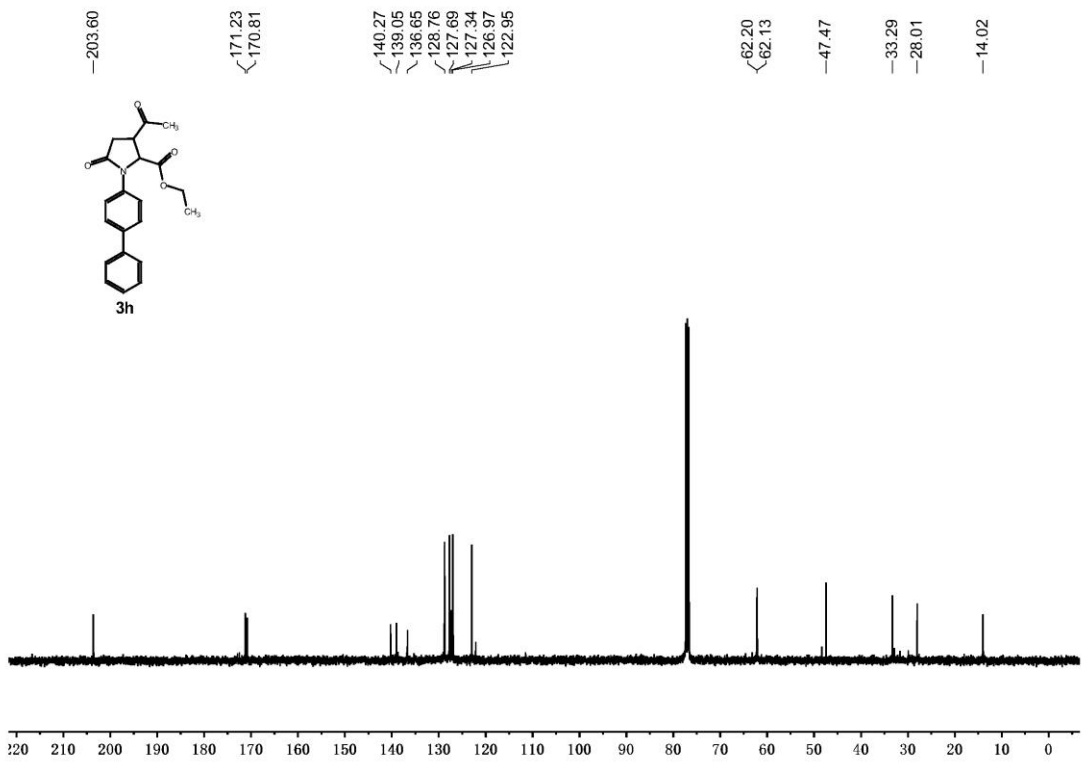
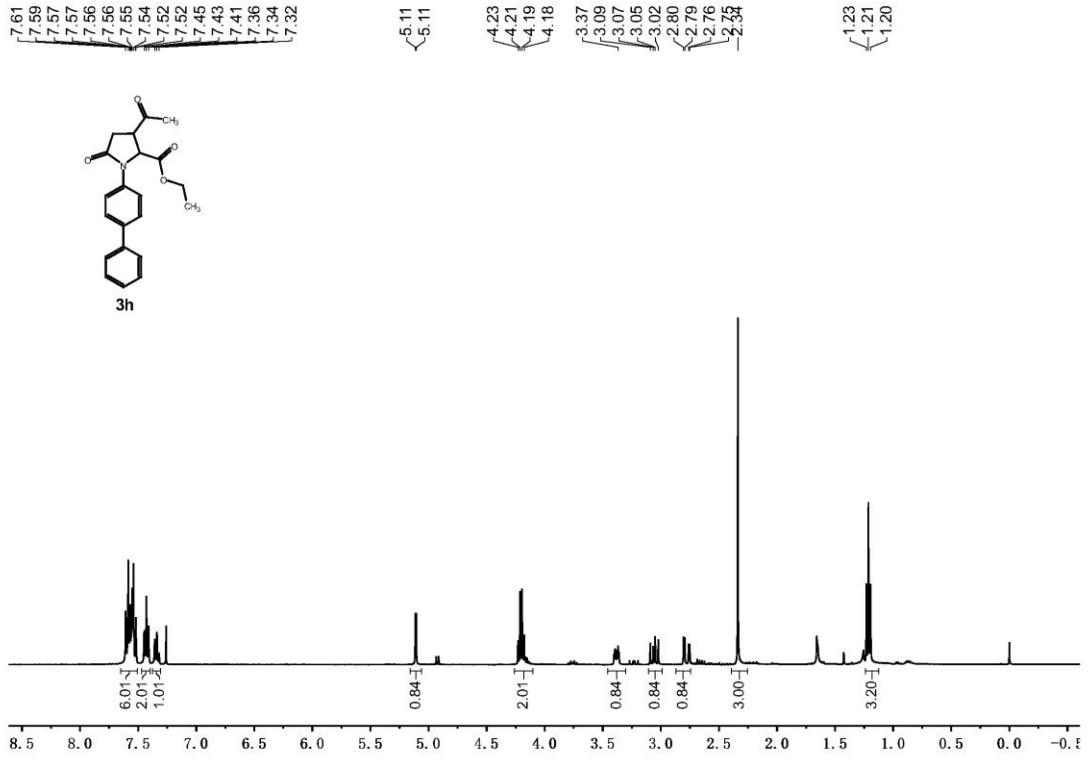


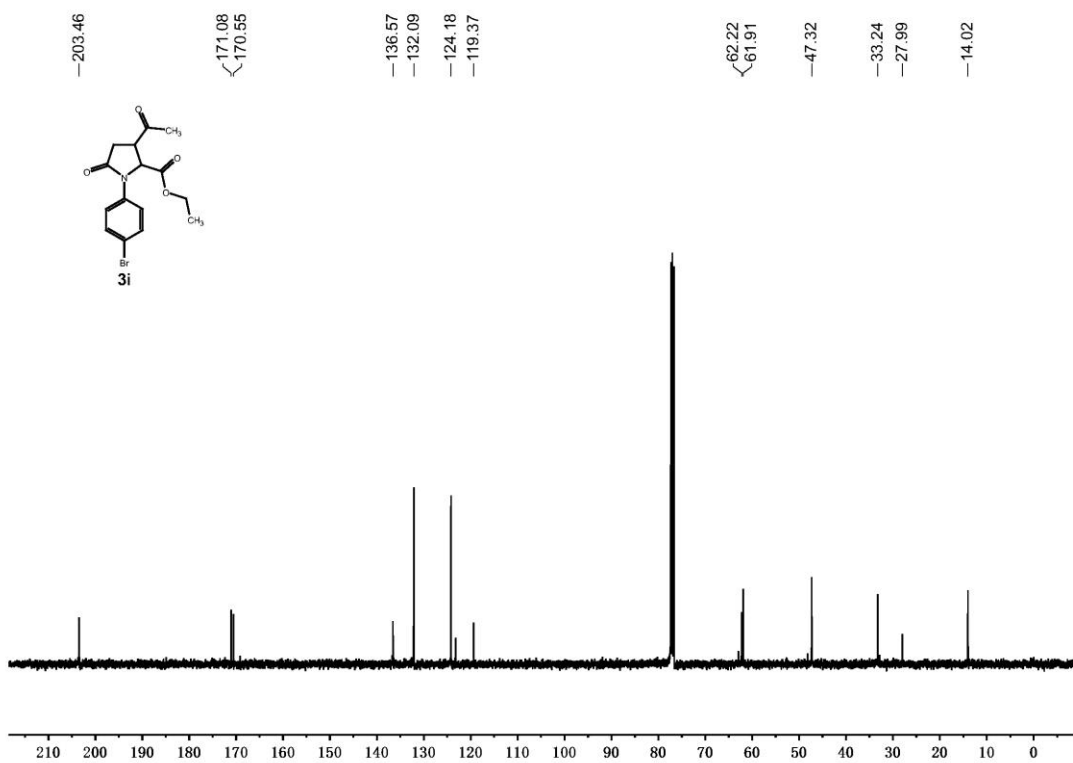
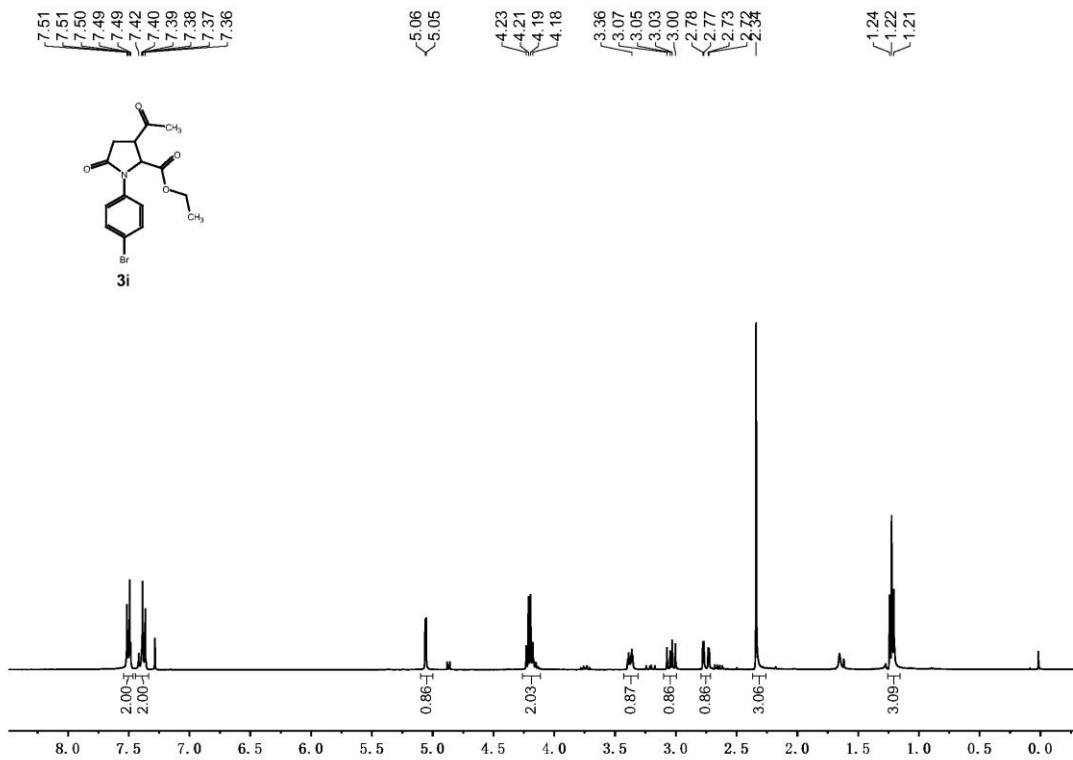


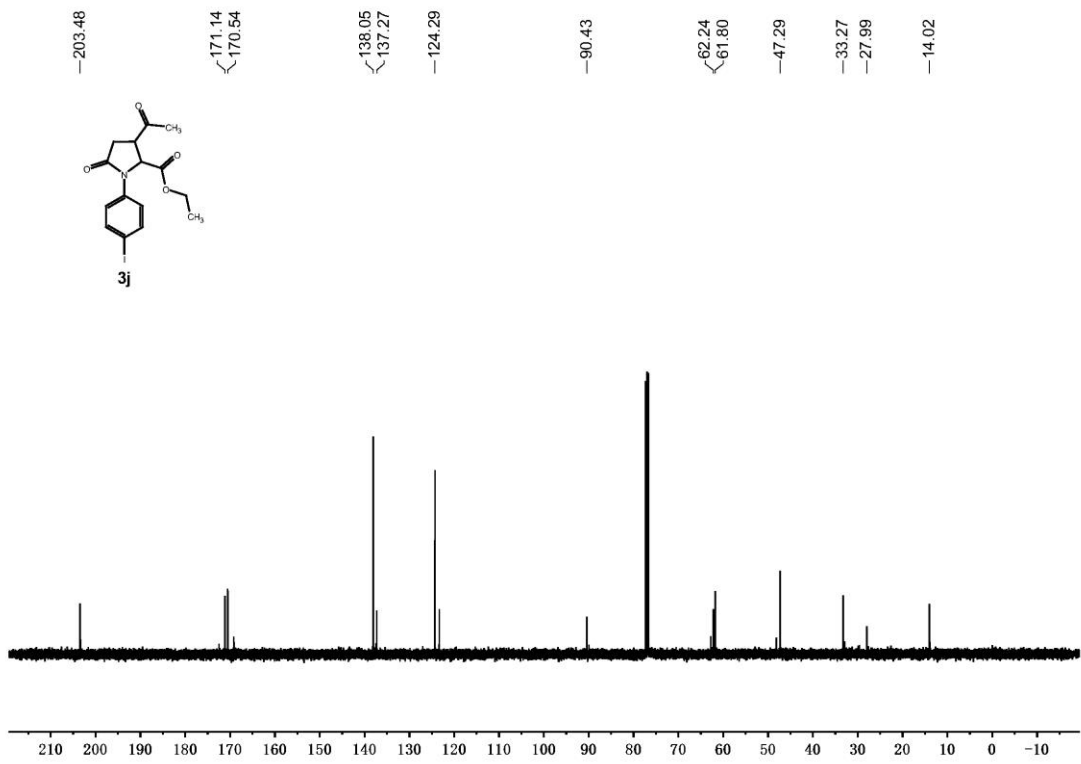
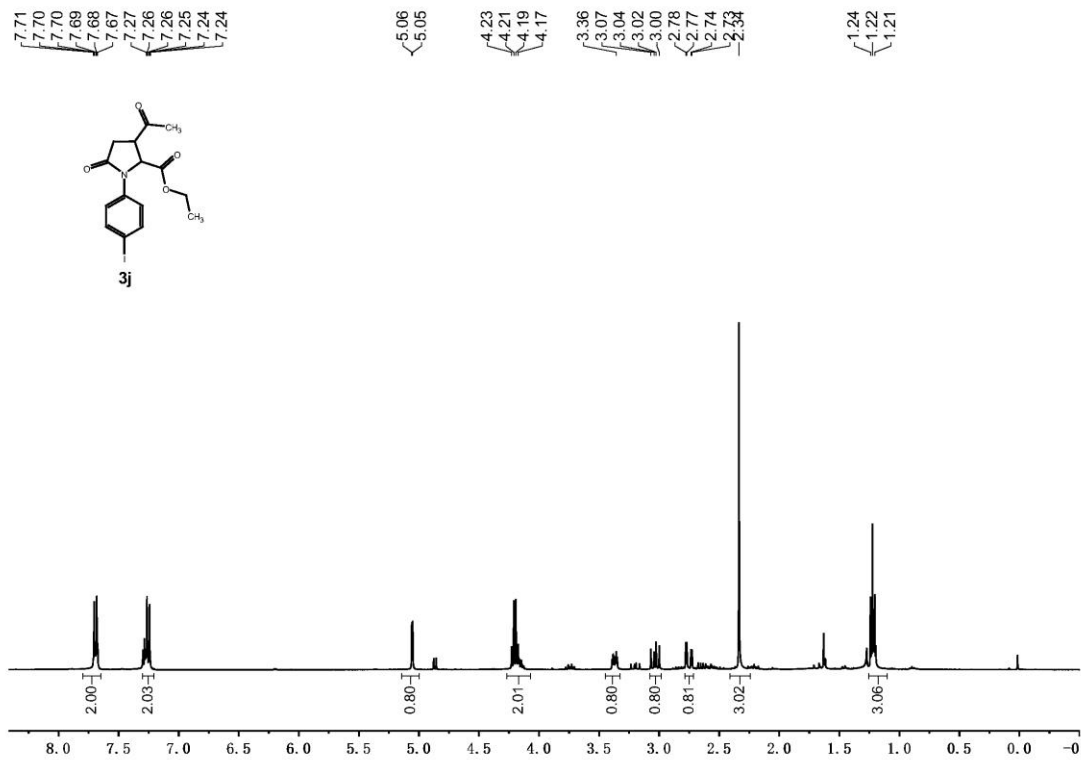


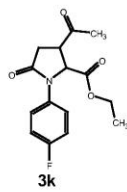
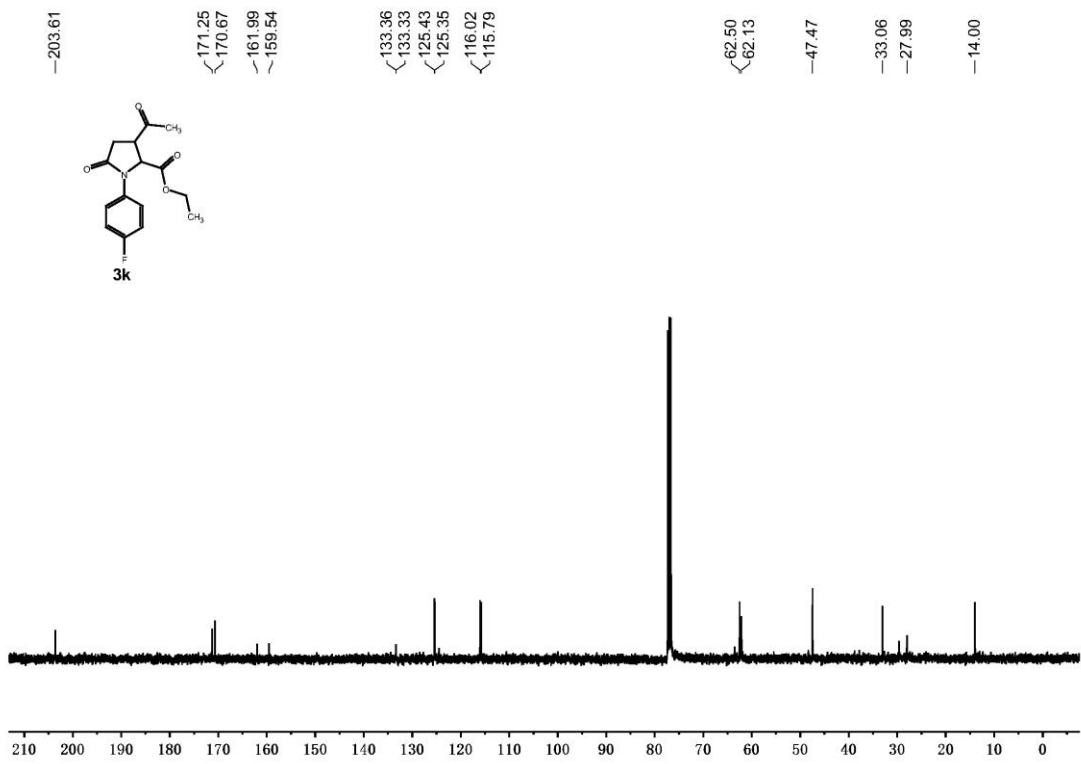
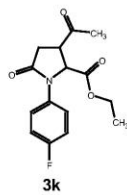
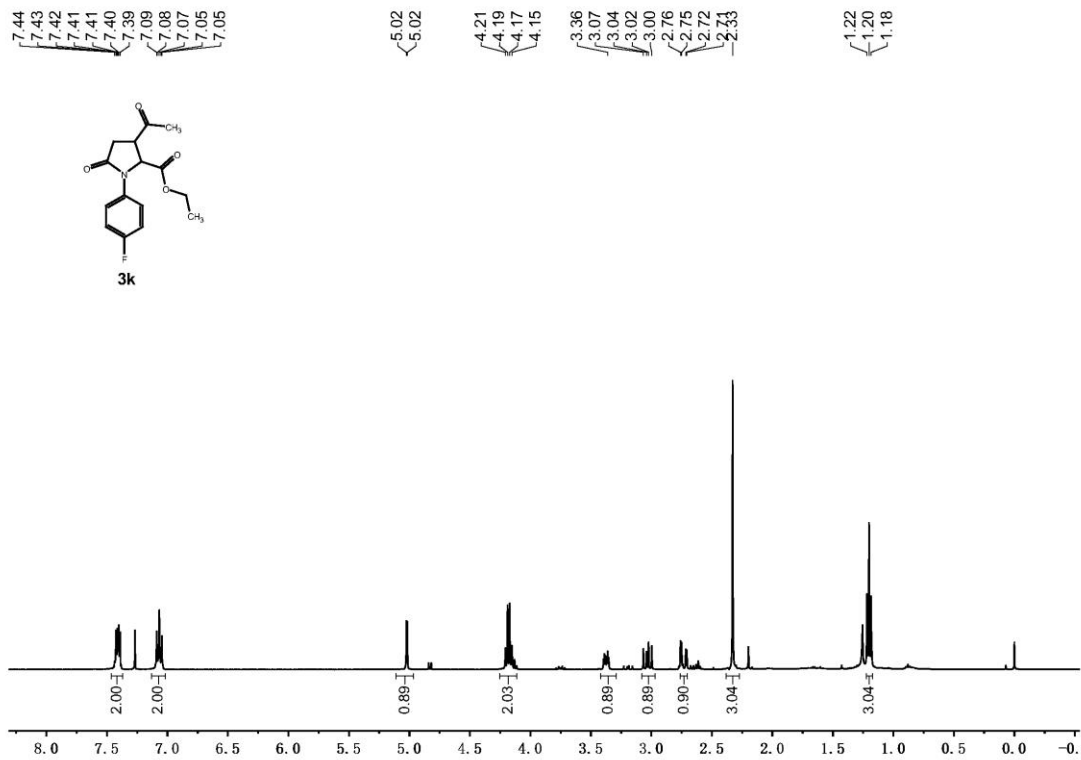


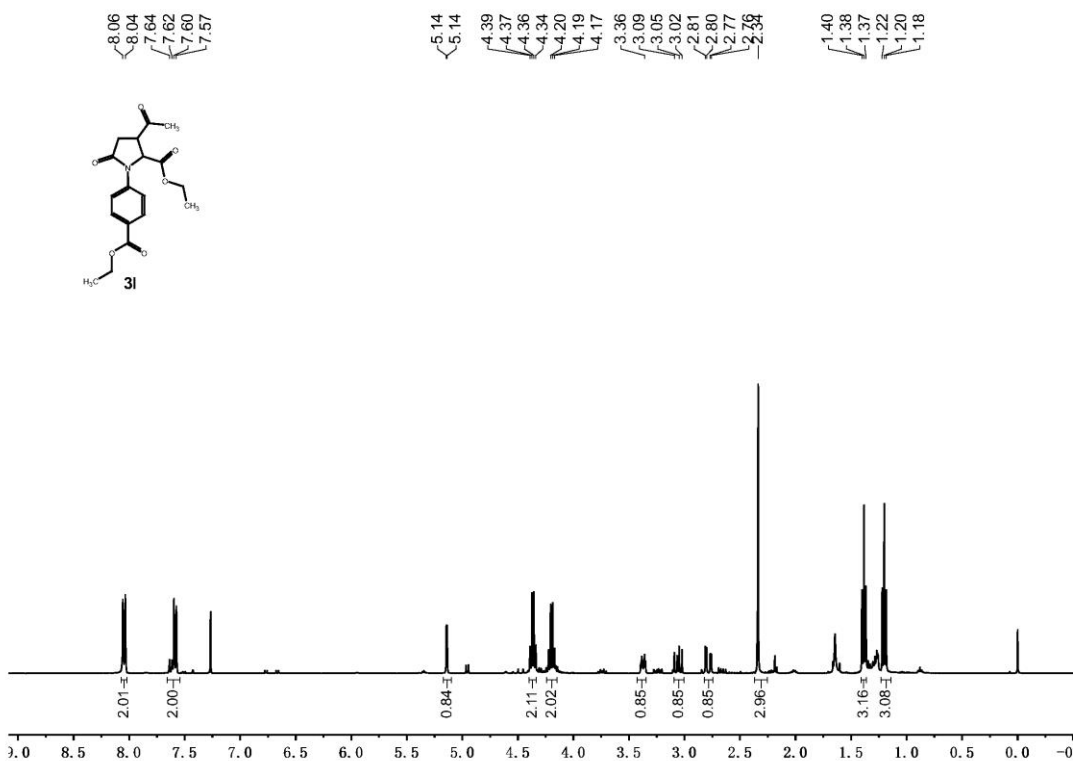
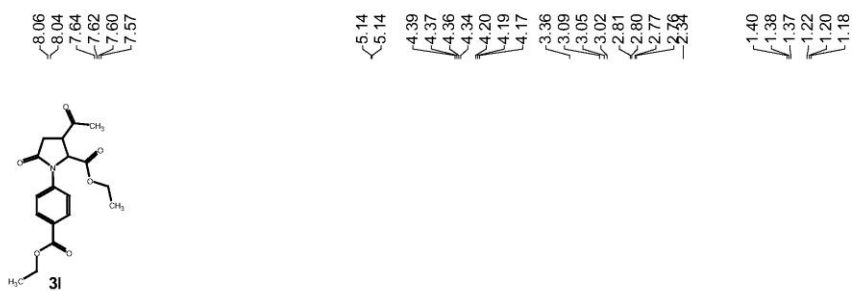
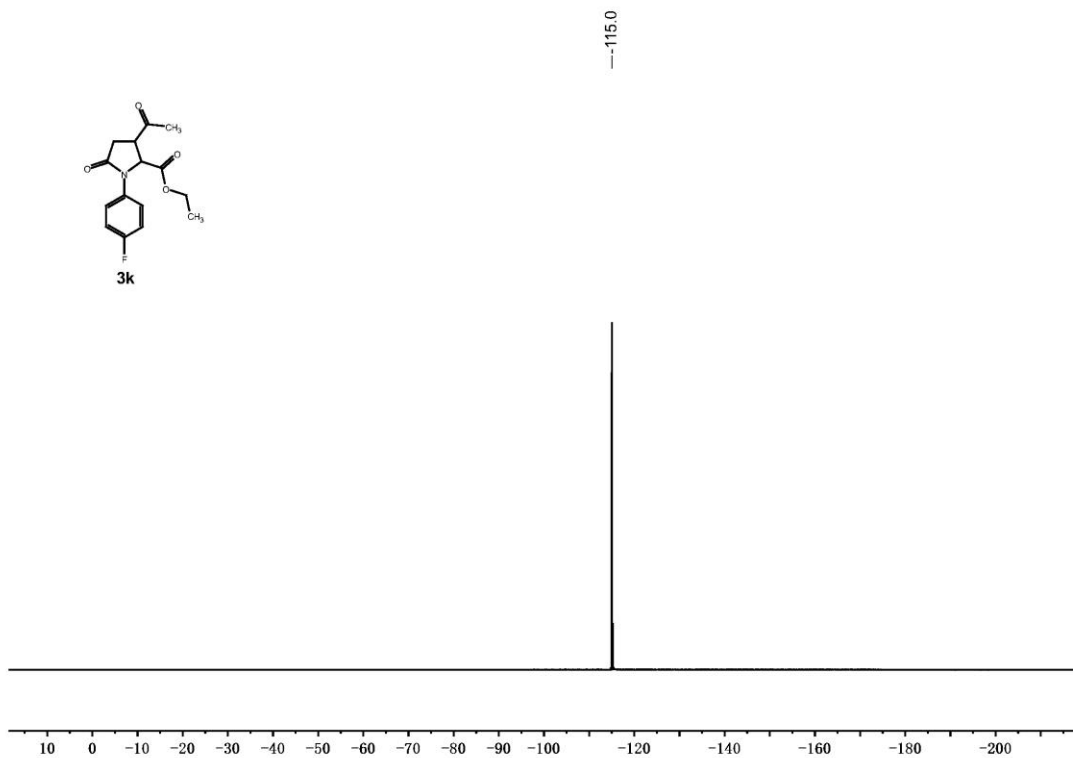
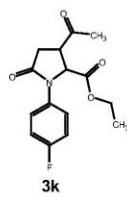


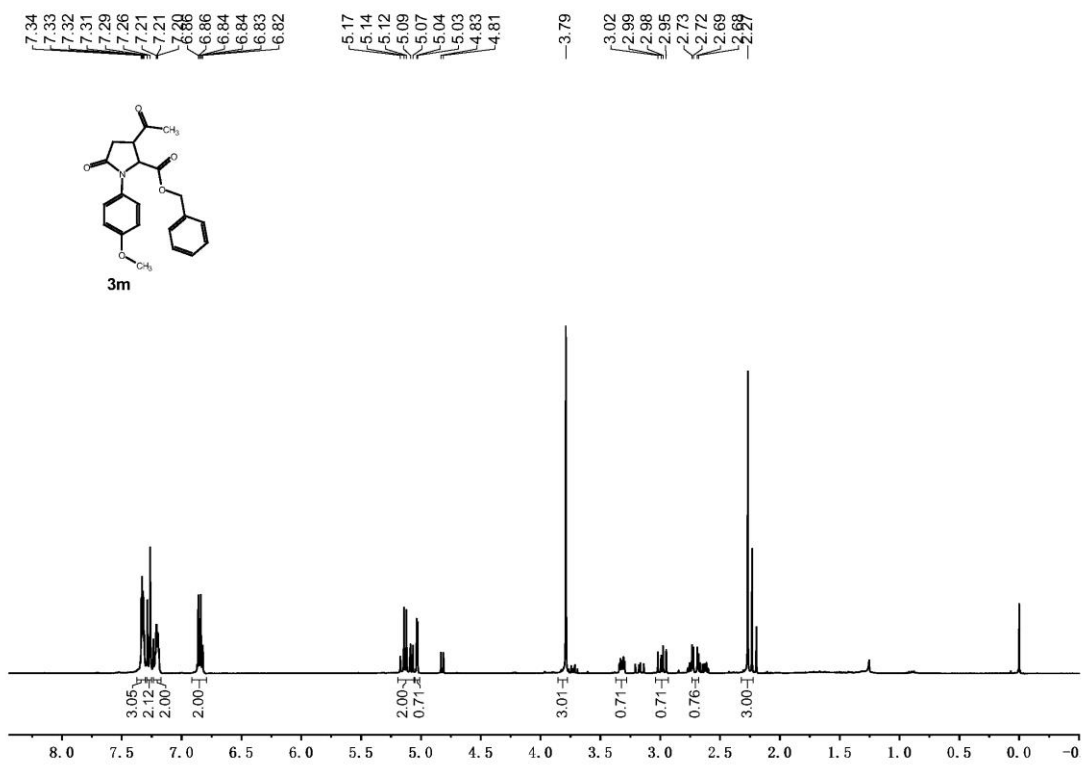
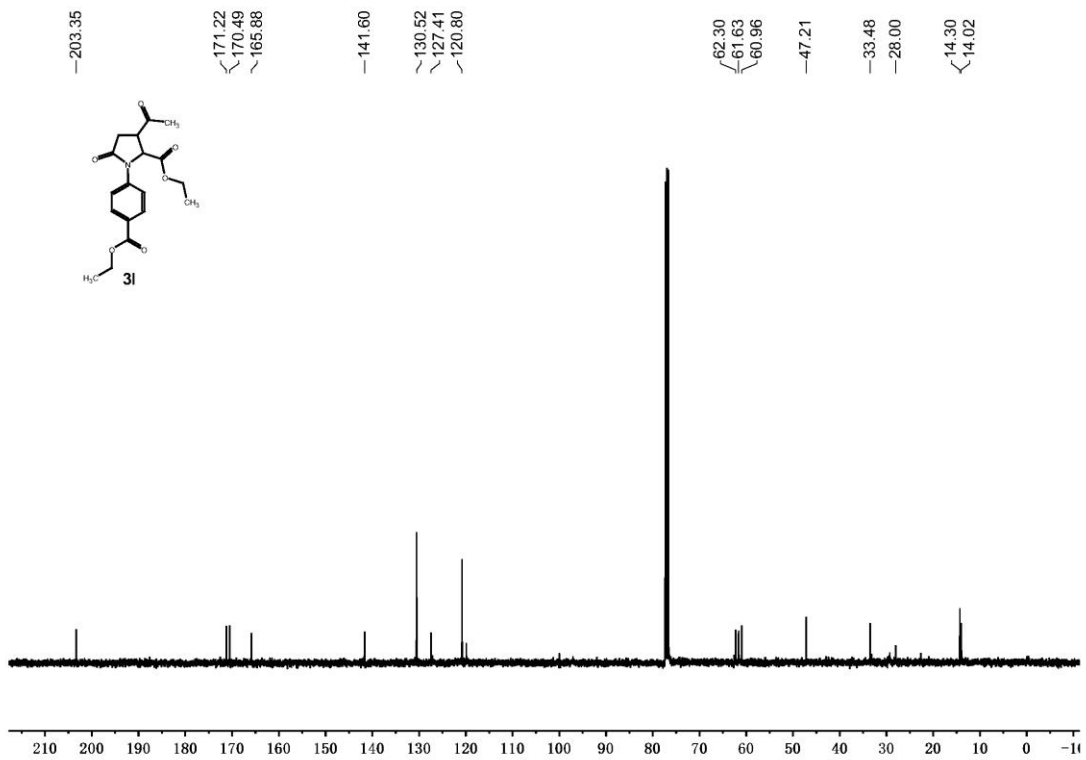


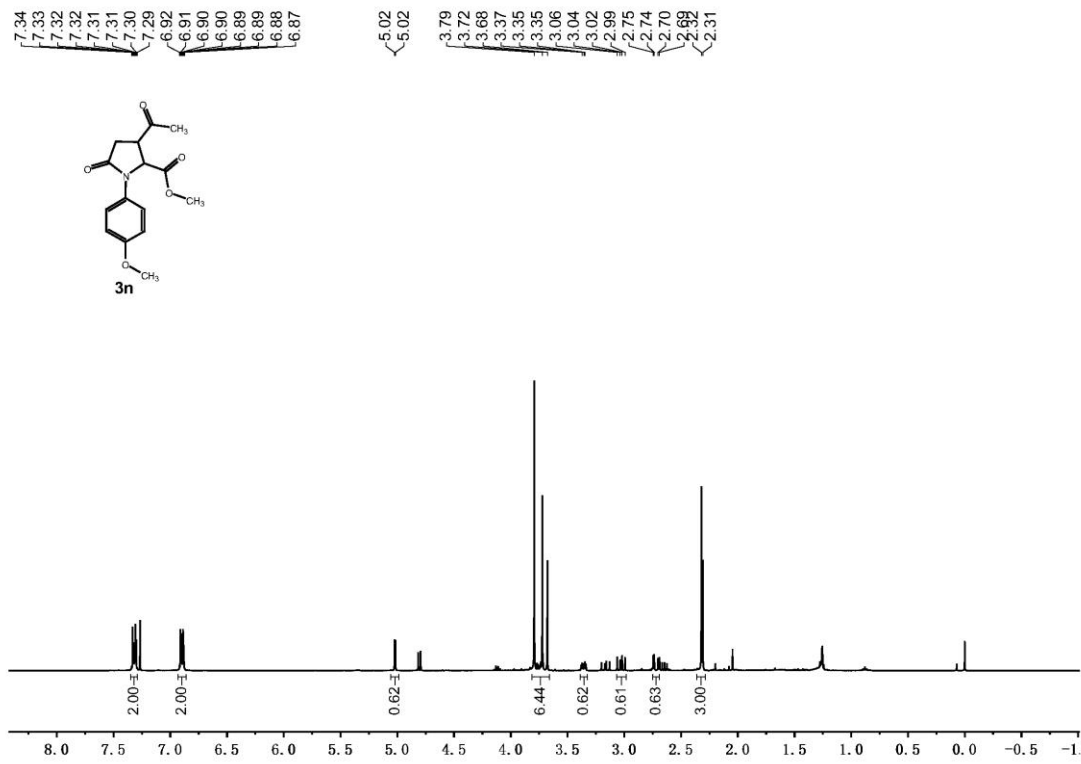
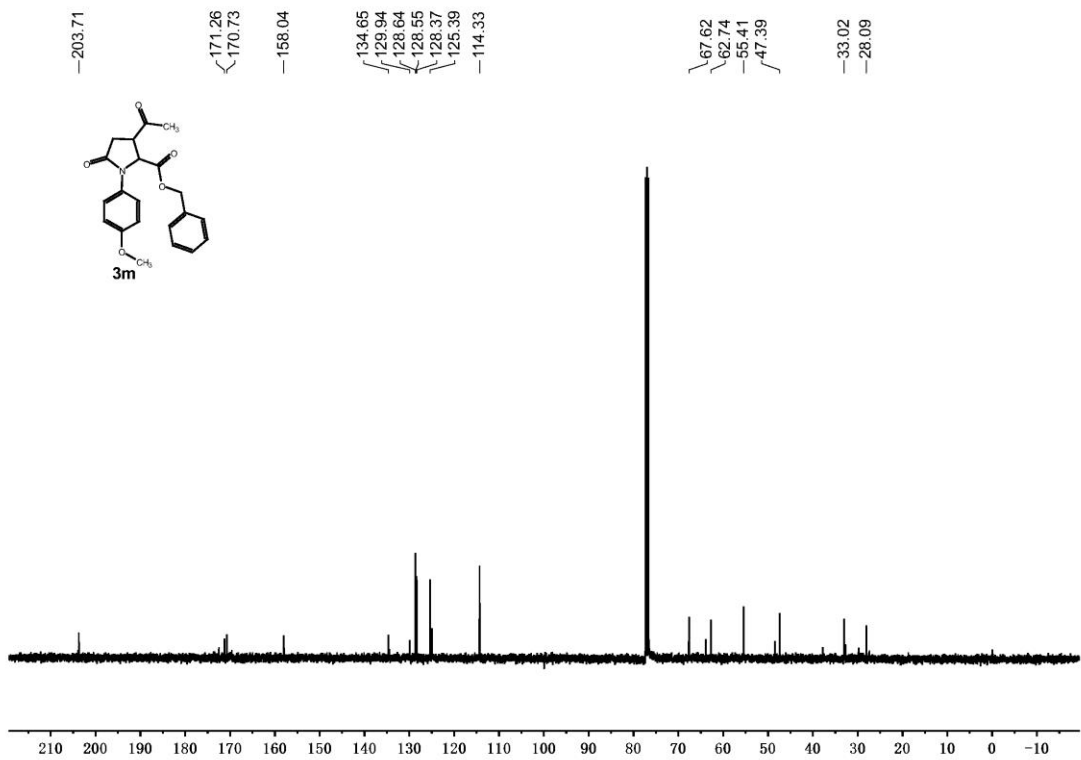


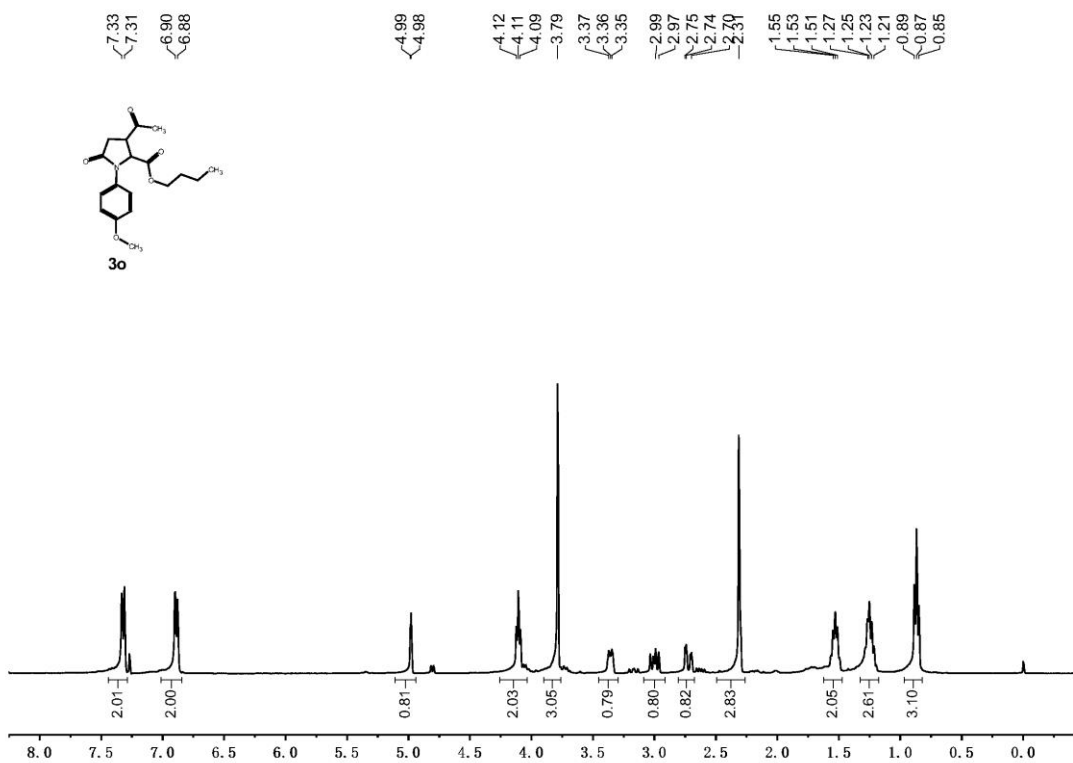
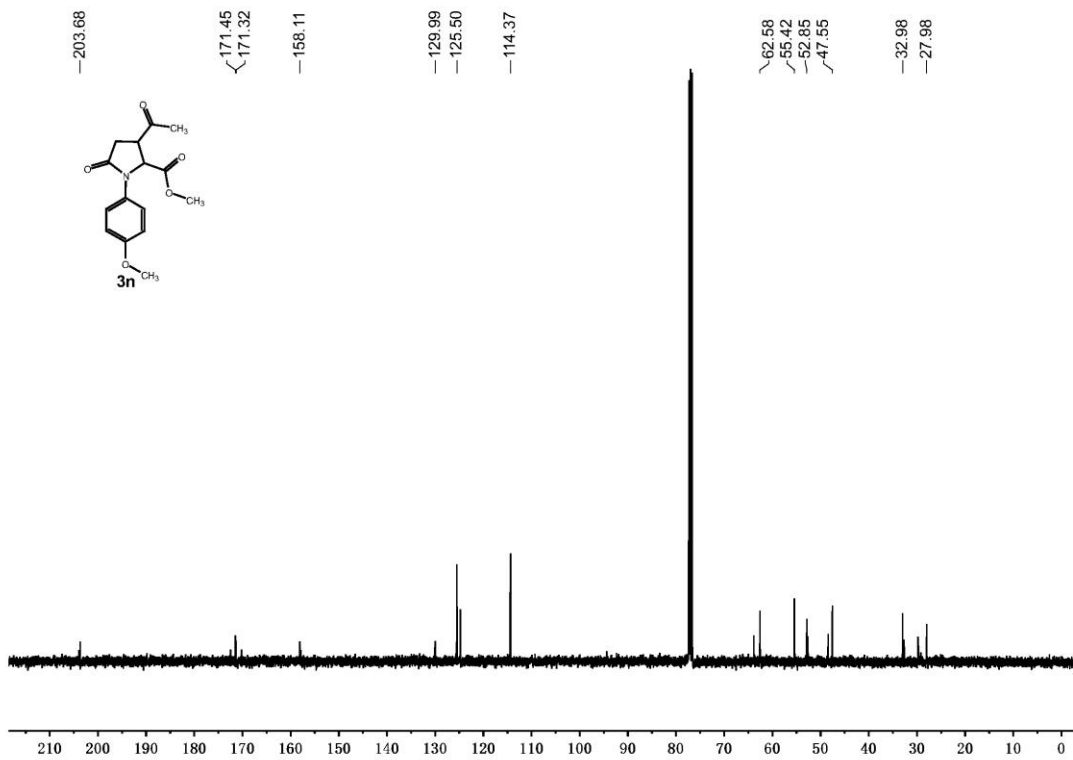


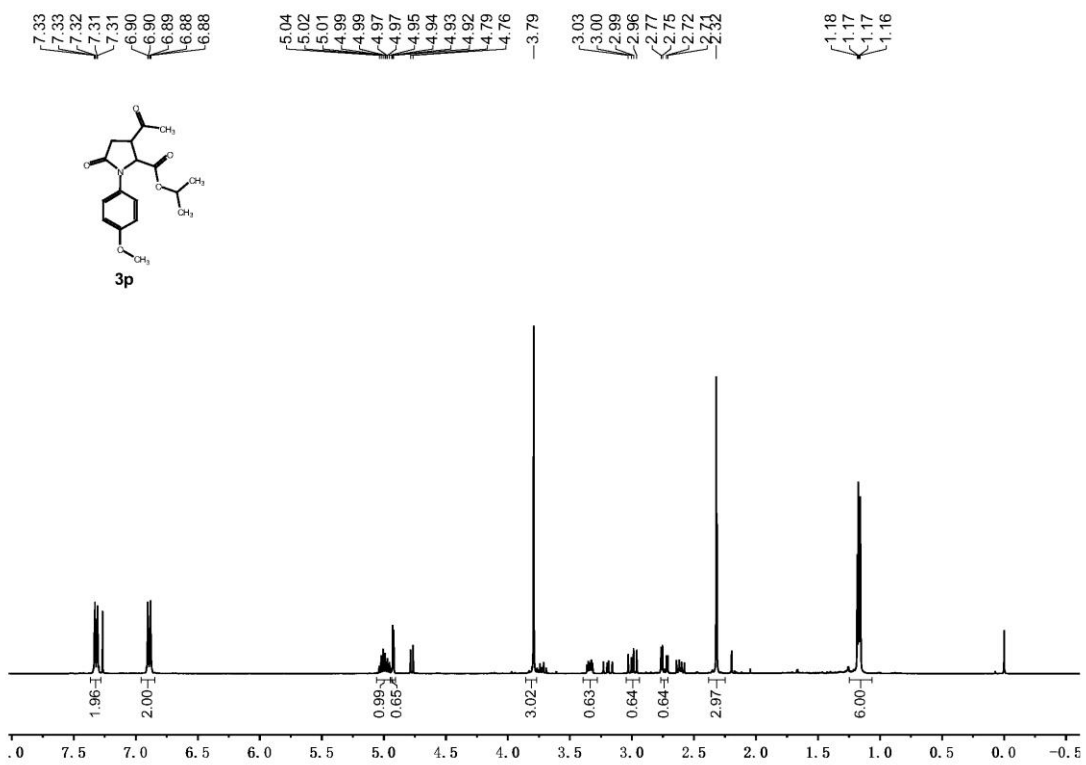
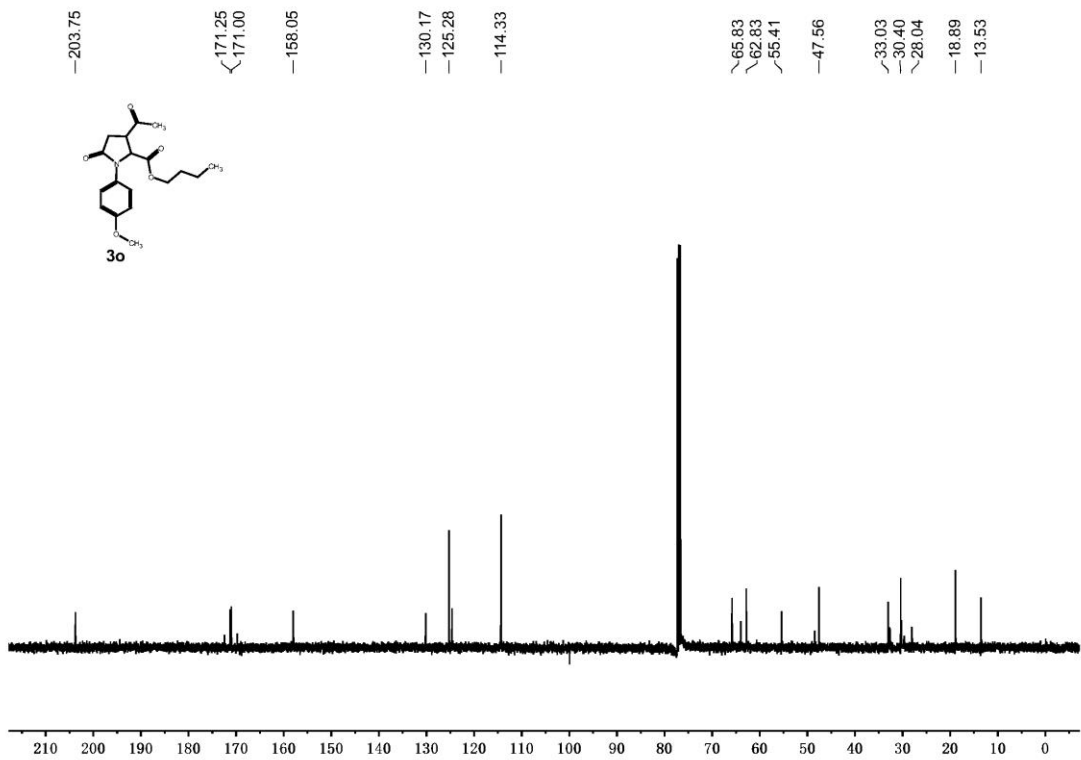


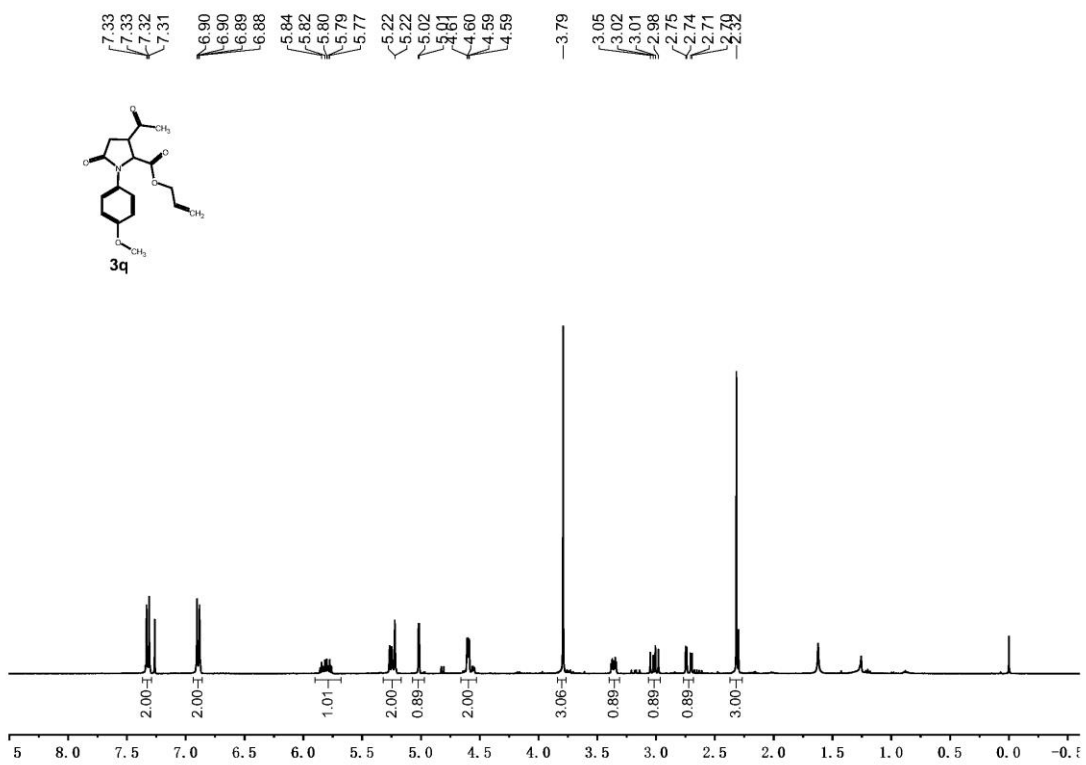
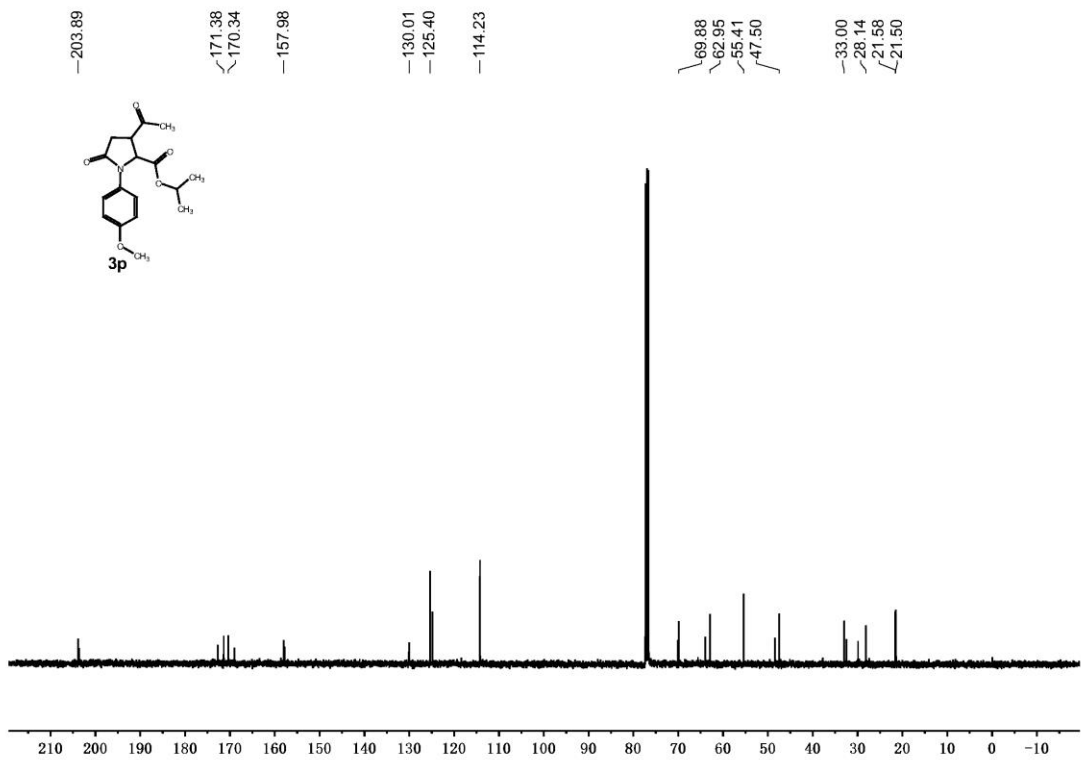


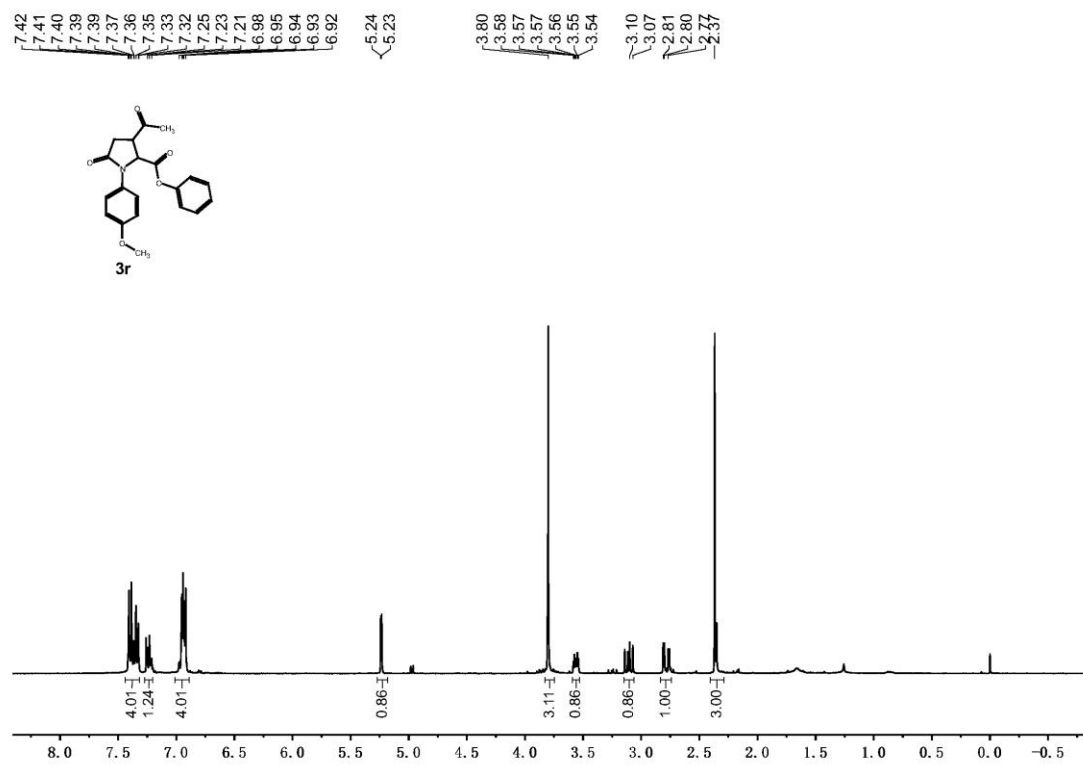
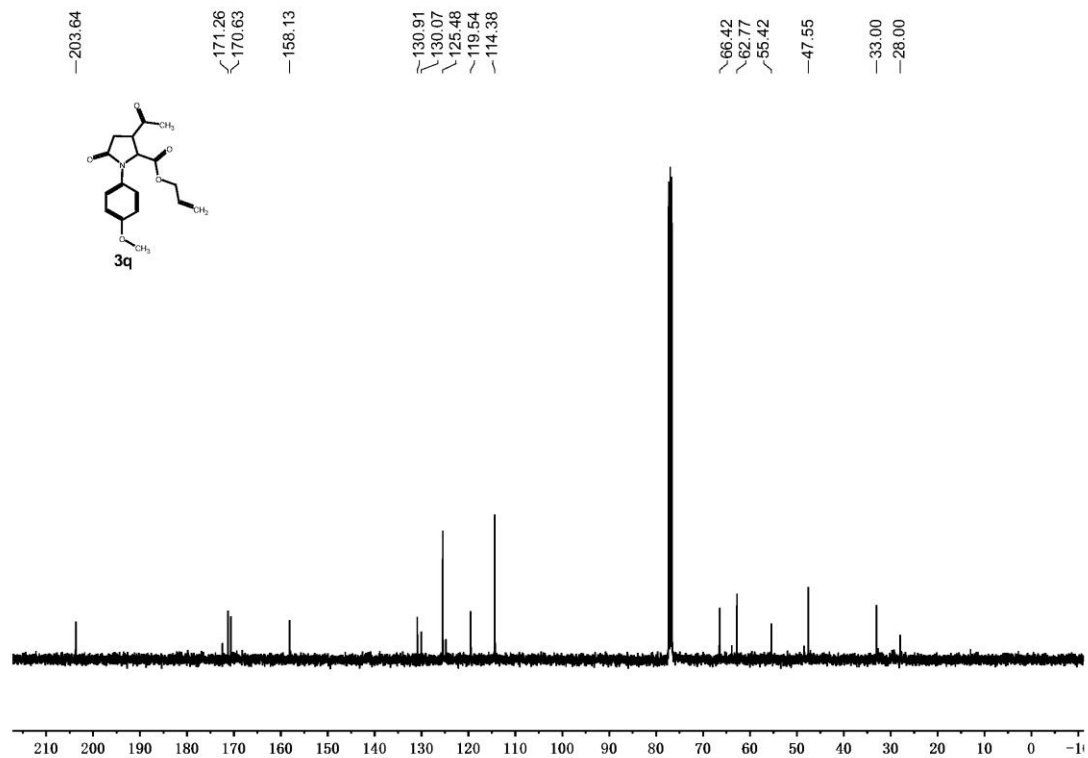


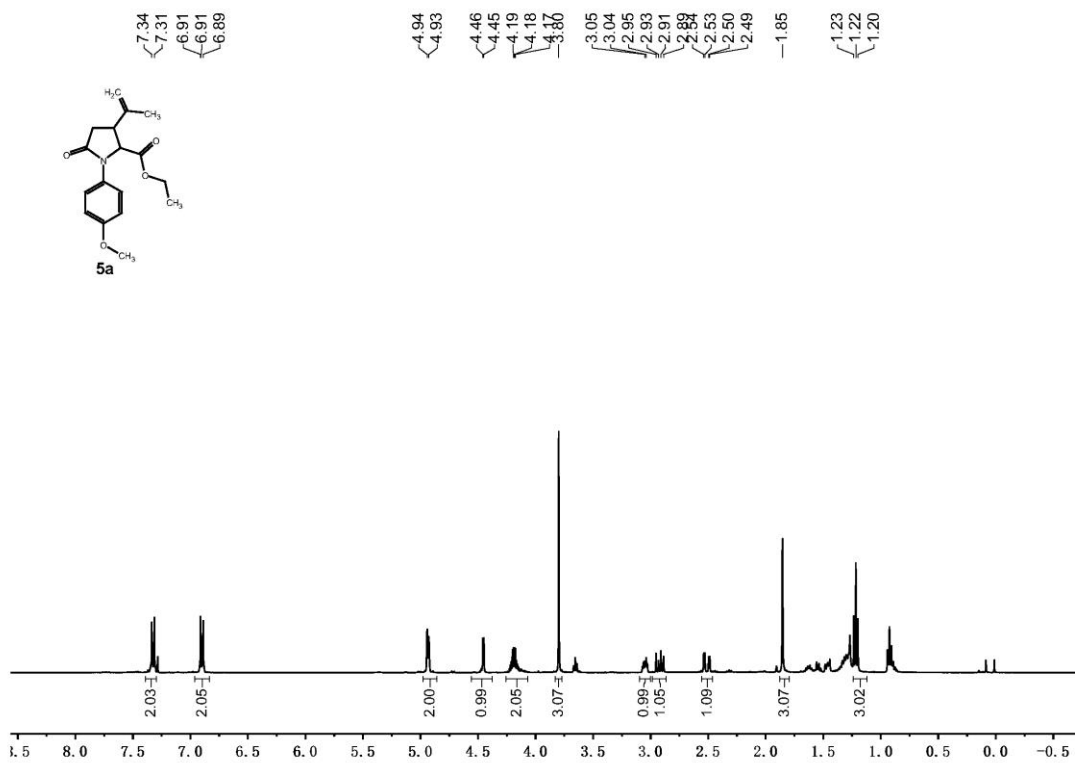
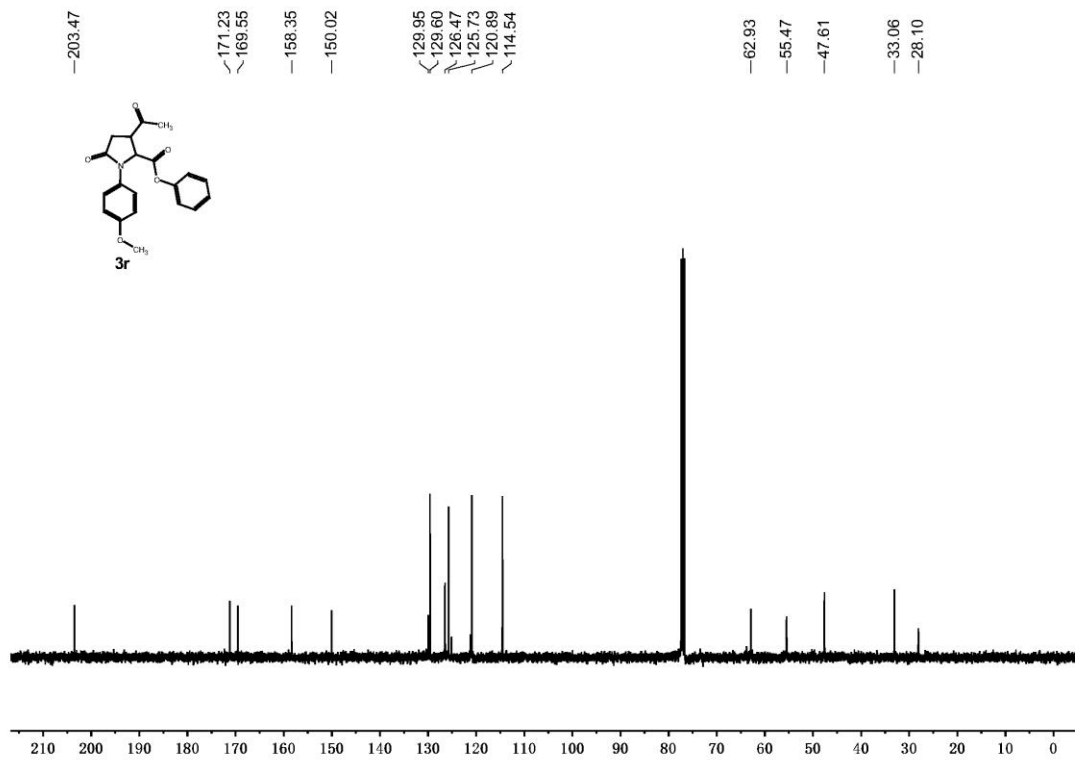


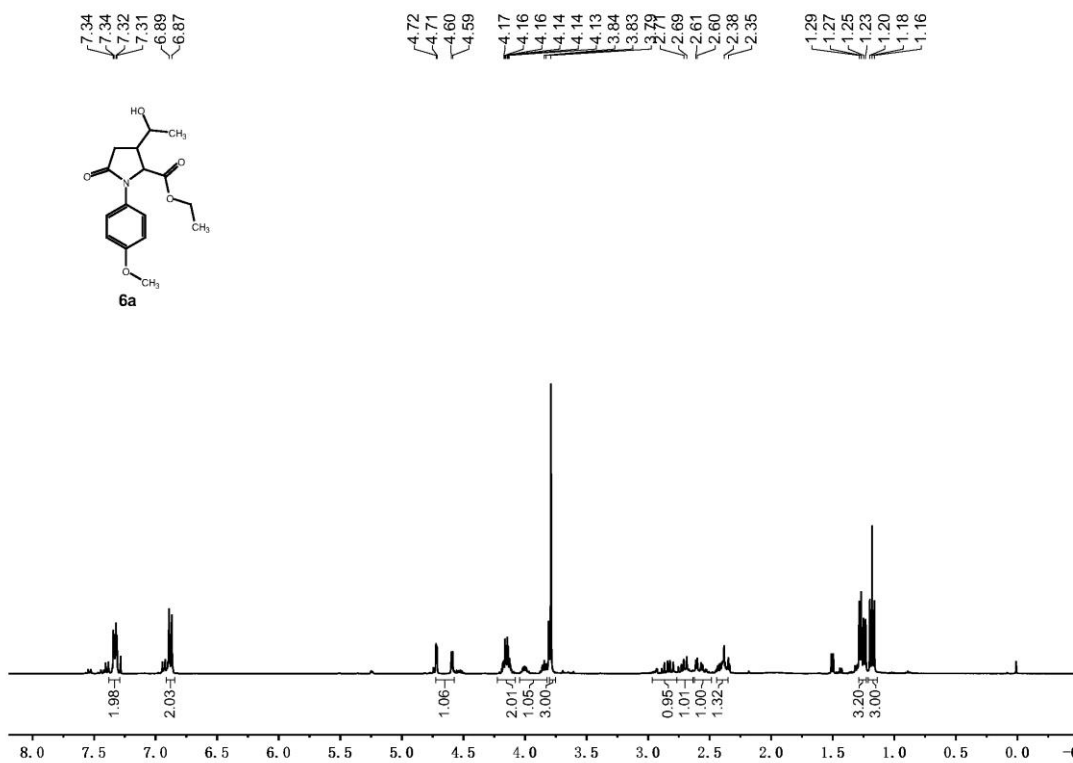
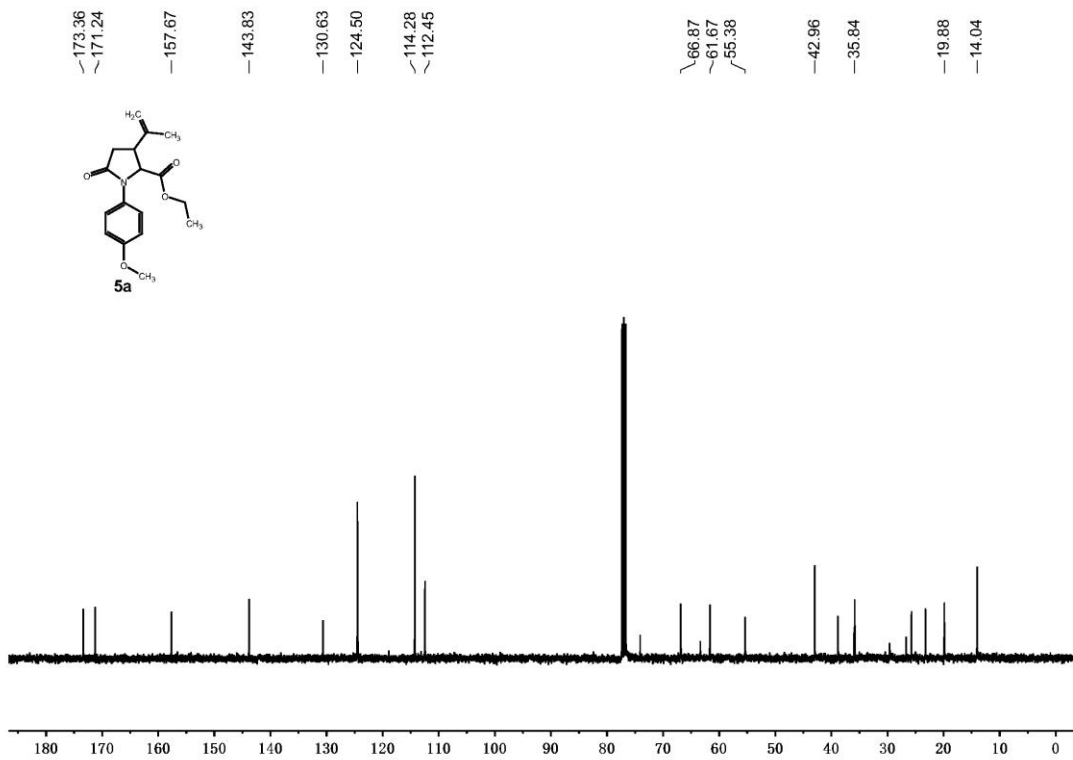












~173.6
~171.9

—157.7

—130.6

—124.9

—114.2

~69.1

~64.3

~61.6

~55.4

—43.2

—34.3

—21.1

—14.0

