Ruthenium(II)-Catalyzed Regioselective Reductive Coupling of α-Imino Esters with Dienes

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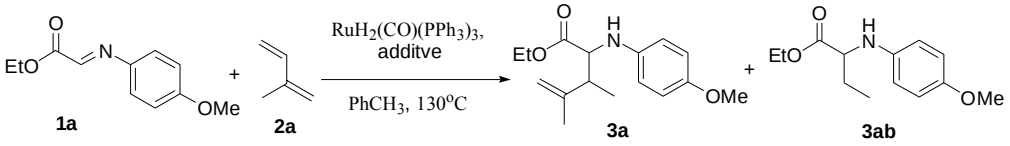
1. 1 General methods

Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using silica gel (40- 63 mm) from Qingdao Haiyang Chemical Co. Ltd. Melting point was mearsured on BÜCHI Melting point B-545. Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were recorded using an Waters HPLC/ZQ4000 Mass Spectrometer. High resolution exact mass measurements (HRMS) were performed on a Finnigan Mat 95 mass spectrometer. Crystal data were collected on a Bruker SMART 1000 CCD detector employing graphite monochromated Mo-Kα radiation (λ=0.71073 Å) at 173(2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

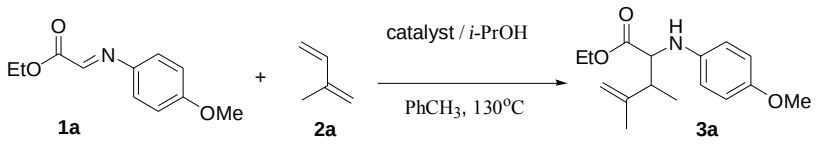
1. 2 The effect of the additives on reductive coupling of α-imino ester 1a with isoprene [a]



entry	Additive	**3a** yield(%)[b]	**3ab** yield(%)[b]
1	-	12	0
2	HCO_2H/Et_3N[c]	16	0
3	Et_2Zn	<5	42
4	Et_3B	36	8
5	CH_3OH	21	0
6	*i*-PrOH	70	0

[a]Reactions were run with **1a** (0.2 mmol), **2a** (0.8 mmol), $RuH_2(CO)(PPh_3)_3$ (10 mol %), additive (200 mol %), toluene (3.0 mL) under Ar in a sealed pressure tube at 130 ˚C for 24 h, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]HCO_2H/Et_3N (200 mol % / 100 mol %).

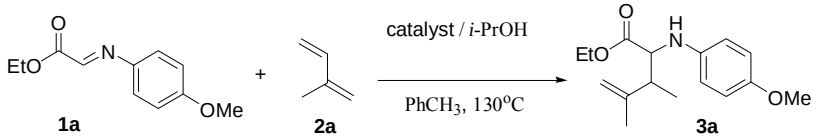
1. 3 Catalyst screening for reductive coupling of α-imino ester 1a with isoprene [a]



entry	catalyst	yield(%)[b]
1	$RuCl_3$	trace
2	$RuH_2(PPh_3)_4$	8
3	RuCl[(S)-BINAP](p-cymene)	trace
5	RuCl[(R, R)-Tsdpen](p-cymene)	trace
6	$Ru_3(CO)_{12}$	trace
7	$RuHCl(PPh_3)_3PhCH_3$	47
8	$RuH_2(CO)(PPh_3)_3$	70
9	$RuHCl(CO)(PPh_3)_3$	90

[a]All reactions were run with **1a** (0.2 mmol), **2a** (0.8 mmol), catalyst (10 mol %), *i*-PrOH (200 mol %), toluene (3.0 mL) under Ar in a sealed pressure tube at 130 ˚C for 24 h, followed by flash chromatography on SiO_2. [b]Isolated yield.

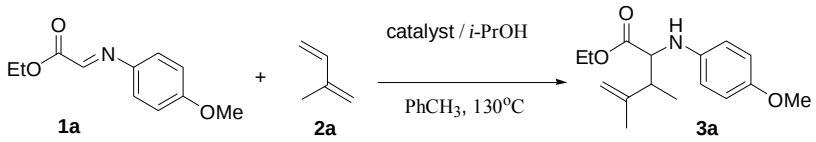
1. 4 The effect of the reaction time and temperature on reductive coupling of α-imino ester 1a with isoprene [a]



entry	temp(℃)	time (h)	yield(%)[b]
1	110	24	83
2	120℃	24	88
3	130℃	24	90
4	130℃	12	80
5	130℃	36	89

[a]All reactions were run with **1a** (0.2 mmol), **2a** (0.8 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol %), *i*-PrOH (200 mol %), toluene (3.0 mL) under Ar in a sealed pressure tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

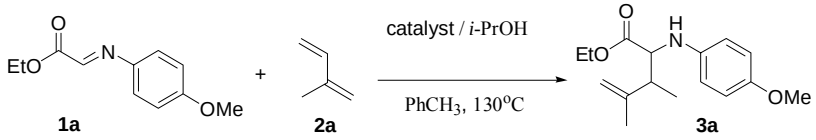
1. 5 The Effect of the catalyst loading, the equiv of additives and the ratio of 1a/2a on the reductive coupling of α-imino ester 1a with isoprene [a]



entry	catalyst	Additive	isoprene	yield(%)[b]
1	10 mol % cat.	200 mol % CH_3OH	4 equiv.	73
2	10 mol % cat.	-	4 equiv.	35
3	10 mol % cat.	100 mol % *i*-PrOH	4 equiv.	87
4	5 mol % cat.	200 mol % *i*-PrOH	4 equiv.	76
5	10 mol % cat.	200 mol % *i*-PrOH	4 equiv.	90
6	10 mol % cat.	200 mol % *i*-PrOH	2 equiv.	81

[a]All reactions were run with **1a** (0.2 mmol), isoprene (2.0 or 4.0 equiv), $RuHCl(CO)(PPh_3)_3$, additive, toluene (3.0 mL) under Ar in a sealed pressure tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

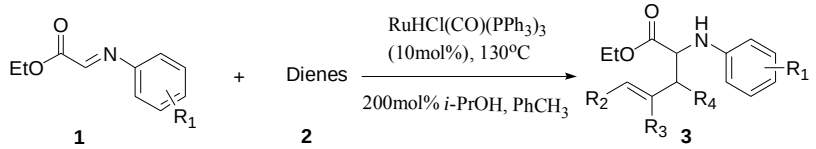
1. 6 The Effect of the solvent on the reductive coupling reaction of α-imino ester 1a with isoprene [a]



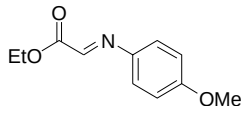
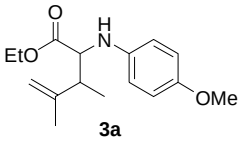
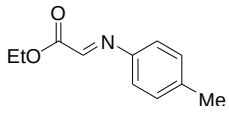
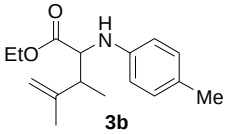
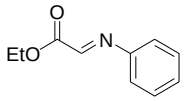
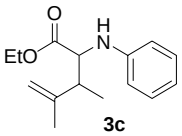
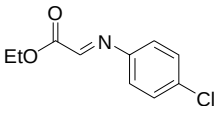
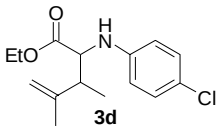
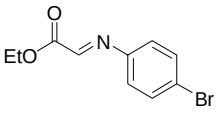
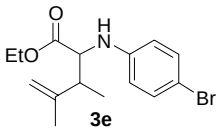
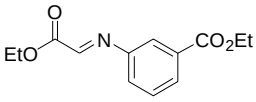
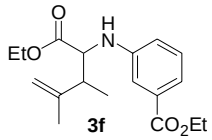
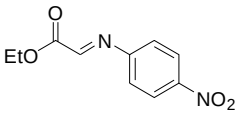
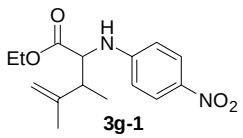
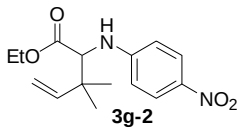
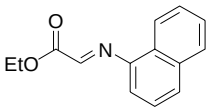
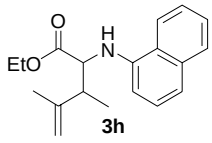
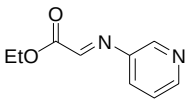
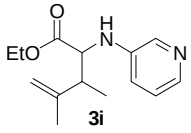
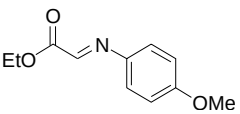
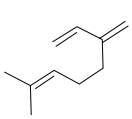
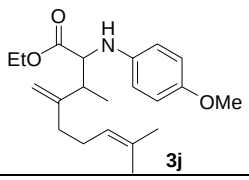
entry	Solvent	yield(%)[b]
1	Toluene	90
2	1,4-dioxane	50
3	THF	55
4	$PhCF_3$	59
5	DMF	31
6	acetonitrile	36

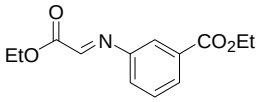
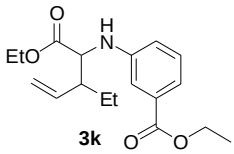
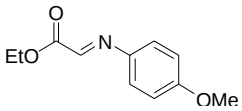
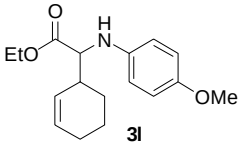
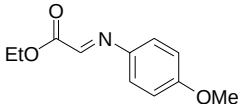
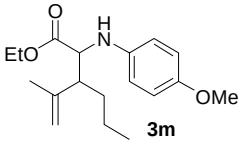
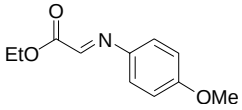
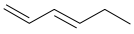
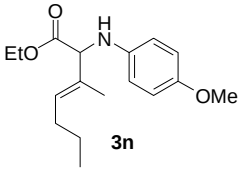
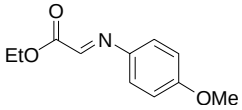
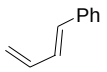
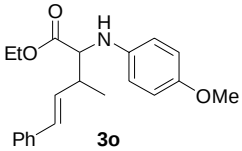
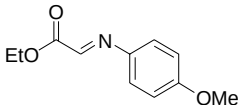
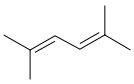
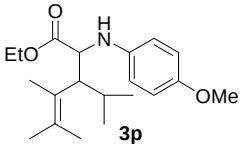
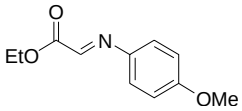
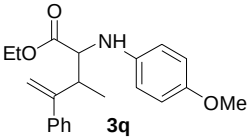
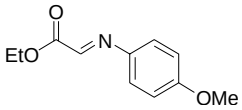
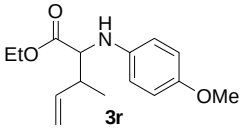
[a]All reactions were carried out with **1a** (0.2 mmol), **2a** (0.8 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol %), *i*-PrOH(200 mol %), solvent (3.0 mL) under Ar in a sealed pressure tube at 130 ˚C for 24 h, followed by flash chromatography on SiO_2. [b]Isolated yield

1. 7 Ru(II)-catalyzed reductive coupling reaction of α-imino esters with various dienes[a]



entry	α-imino ester	diene	product	yield(%)[b]	*syn*: *anti*

1			 **3a**	90	2.5: 1
2			 **3b**	87	2.3: 1
3			 **3c**	74	2.0: 1
4			 **3d**	73	2.4: 1
5			 **3e**	83	1.4: 1
6			 **3f**	89	1.5: 1
7			 **3g-1**	54	2.1: 1
			 **3g-2**	17	-
8			 **3h**	50	1.7: 1
9			 **3i**	56	1.5: 1
10			 **3j**	77	1.7: 1

11			 **3k**	62[c]	1.1: 1
12			 **3l**	33[d]	1.0: 1
13			 **3m**	59[d]	1.4: 1
14			 **3n**	65	1.4: 1
15			 **3o**	48	1.5: 1
16			 **3p**	0	-
17			 **3q**	83	3.0: 1
18			 **3r**	95	1.3: 1

[a] Unless otherwise noted, all reactions were run with **1** (0.2 mmol), **2** (0.8 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol %), *i*-PrOH (200 mol %), toluene (3.0 mL) under Ar in a sealed pressure tube at 130 ˚C for 24 h, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]Carried out at 110 ˚C. [d] The reaction was carried out using 20 mol % $RuHCl(CO)(PPh_3)_3$ for 48 h.

2. 1 General procedure for the preparation of α-imino esters

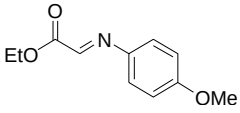
a) General procedure for the synthesis of **1a**, **1b** and **1c**:

To a solution of amine (0.2 mmol) in dry toluene (2 mL) in a vial was added anhydrous sodium sulfate (1 mmol) and ethyl glyoxylate (50% in toluene, 0.2 mmol). After stirring at room temperature for 0.5 hour, sodium sulfate was removed by filtration through a pad of celite and the solvent was removed in vacuum to afford α-imino esters **1a**, **1b** and **1c** which could be used directly for the next step without further purification.

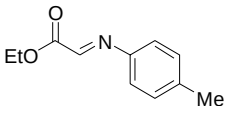
b) General procedure for the synthesis of **1d**, **1e, 1f**, **1g, 1h** and **1i**:

To a solution of amine (0.2 mmol) in dry toluene (2 mL) in a vial was added anhydrous sodium sulfate (1 mmol) and ethyl glyoxylate (50% in toluene, 0.2 mmol). The corresponding reaction mixture was then refluxed at 110 ^{o}C for 1 h, and cooled to room temperature. After sodium sulfate was removed by filtration through a pad of celite, the corresponding filtrate was concertrated in vacuum to afford α-imino esters **1d-1g** which could be used directly for the next step without further purification.

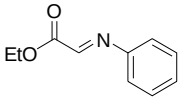
It should be noted that for the starting substrates **1h** and **1i**, we did not get their clean ^{1}H NMR and ^{13}C NMR spectra, and their corresponding crude product still could be used directly for the next step.



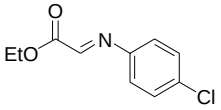
Ethyl 2-(4-methoxyphenylimino)acetate (**1a**) [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.42 – 7.32 (m, 2H), 6.99 – 6.87 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). MS (ESI): m/z= 208.7 $[M]^{+}$.



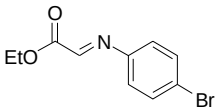
Ethyl 2-(*p*-tolylimino)acetate (**1b**) [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.25 – 7.18 (m, 4H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). MS (ESI): m/z= 192.7 $[M]^{+}$.



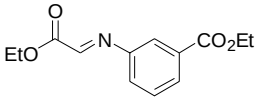
Ethyl 2-(phenylimino)acetate (**1c**) [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.45 – 7.25 (m, 5H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). MS (ESI): m/z= 178.6 $[M]^{+}$.



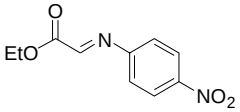
Ethyl 2-(4-chlorophenylimino)acetate (**1d**) [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.43 – 7.34 (m, 2H), 7.27 – 7.21 (m, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). MS(ESI): m/z= 212.6 $[M]^{+}$.



Ethyl 2-(4-bromophenylimino)acetate (**1e**) [2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.52 (t, *J* = 10.0 Hz, 2H), 7.18 (t, *J* = 15.3 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). MS (ESI): m/z= 258.6 $[M]^{+}$.

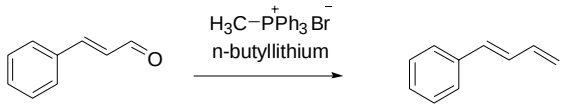


Ethyl 3-(2-ethoxy-2-oxoethylideneamino)benzoate (**1f**) [3]: ^{1}H NMR (400 MHz, CDCl3) δ 8.04 – 7.99 (m, 1H), 7.96 (s, 1H), 7.94 (s, 1H), 7.51 – 7.47 (m, 2H), 4.46 – 4.36 (m, 4H), 1.44 – 1.38 (m, 6H); MS(ESI): m/z= 250.7 $[M]^+$.

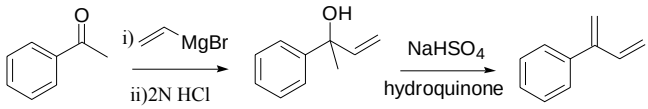


Ethyl 2-(4-nitrophenylimino)acetate (**1g**) [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H) 8.14 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H) 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). MS (ESI): m/z= 223.9 $[M]^-$.

2. 2 General procedures for synthesis of dienes 2h and 2j



Preparation of (*E*)-1-phenyl-1,3-butadiene(2h) [4]: To a suspension of methyltriphenylphosphonium bromide (3.57 g, 10 mmol) in THF (50 ml) at 0 °C was added dropwise n-butyllithium (2 M in n-hexane, 5 mL, 10 mmol). The reaction mixture was stirred for 15 min and the cinnamaldehyde (1.0 ml, 8 mmol) was added as a solution in THF (10 mL). After 1 h the solution was warmed to room temperature and stirred for additional 1 h. A saturated solution of NH_4Cl (50 mL) was added and the mixture was extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (100 ml), dried over $MgSO_4$, and the solvents were removed under reduced pressure (300 mbar, 40 ºC). The residue was was purified by flash column chromatography on silica gel using 1 % ethyl acetate in petroleum ether as eluent to give the title compound (0.94 g, 90%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 5H), 6.78 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.51 (ddd, *J* = 20.5, 16.3, 10.5 Hz, 2H), 5.32 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 10.0 Hz, 1H); MS(ESI): m/z= 130 $[M]^+$.



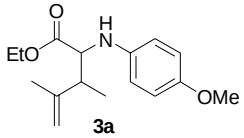
Preparation of 2-phenyl-1,3-butadiene (2j) [5]: 1) Acetophenone (5 mL, 40 mmol) dissolved in THF (15 mL) was added dropwise over 0.5 h at 0 °C to a solution of vinylmagnesium bromide (50 mL, 50 mmol, 1 M THF solution). The mixture was allowed to warm to room temperature and stirred for 0.5 h at the same temperature. The mixture was filtered through a glass filter. The filtrate was partitioned into 2 N HCl and Et_2O. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The oily residue was purified by flash column chromatography on silica gel using 20 % ethyl acetate in petroleum ether as eluent to give 2-phenylbut-3-en-2-ol in 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.6 Hz, 1H), 2.14 (s, 1H), 1.69 (s, 3H); m/z= 148 $[M]^+$.

2) 2-Phenyl-3-buten-2-ol (2.4 g, 16 mmol), $NaHSO_4$ (0.01 g, 5 mol%), and hydroquinone (18 mg, 1 mol%) were heated at 120 °C under reduced pressure (30 mm Hg) in a Kugelrohr oven. Once dehydration started, the pressure was reduced (10 mm Hg) in order to remove the product as quickly as possible (0.9 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 6.60 (dd, *J* = 17.2, 11.2 Hz,

1H), 5.24 (dd, *J* = 34.8, 0.8 Hz, 2H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.19 (dd, *J* = 24.4, 0.8 Hz, 1H); MS(ESI): m/z= 130 $[M]^+$.

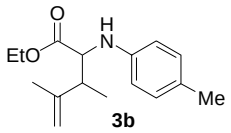
2. 3 General procedures for synthesis of 3a-3r

To a solution of α-imino ester **1** (0.2 mmol) in dry toluene (3.0 mL) were added $RuHCl(CO)(PPh_3)_3$ (10 mol %), diene (0.8 mmol) and *i*-PrOH (200 mol %) in a sealed tube under an Ar atmosphere. Then the corressponding reaction mixture was stirred at 130℃ for given time. Upon completion as monitored by TLC, the crude material was concentrated under vacuum, and purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:30 to 1:10) to furnish the corresponding target product.



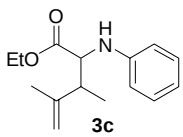
3a

Ethyl 2-((4-methoxyphenyl)amino)-3,4-dimethylpent-4-enoate(**3a**)[6]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 9.0, 2.6 Hz, 2.00H), 6.59 (dd, *J* = 10.2, 6.6 Hz, 2.00H), 4.88 (s, 1.44H), 4.82 (s, 0.57H), 4.17 – 4.06 (m, 2.05H), 3.92 (d, *J* = 7.5 Hz, 0.38H), 3.77 (d, *J* = 8.4 Hz, 1.62H), 3.72 (s, 3.00H), 2.62 (dd, *J* = 15.8, 8.2 Hz, 1.03H), 1.78 (s, 0.90H), 1.68 (s, 2.36H), 1.24 (t, *J* = 7.2 Hz, 2.52H), 1.20 – 1.18 (m, 1.48H), 1.12 (d, *J* = 6.9 Hz, 2.08H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.14, 173.75, 152.78, 152.64, 146.00, 145.96, 141.42, 141.19, 115.29, 114.83, 114.76, 113.40, 112.88, 61.69, 61.00, 60.88, 60.70, 55.70, 44.72, 44.40, 29.70, 19.54, 18.31, 16.41, 15.46, 14.27, 14.21; HRMS (EI) calcd for $[M+1]^+$: $C_{16}H_{23}NO_3$ 278.1751, found 278.1749; IR (KBr): 3397, 2972, 2361, 1733, 1646, 1513, 1462, 1372, 1240, 1181, 1035, 895, 821, 759, 541 cm^{-1}.



3b

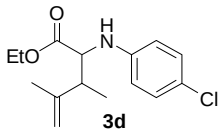
Ethyl 3, 4-dimethyl-2-(p-tolylamino)pent-4-enoate (**3b**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.2 Hz, 2.00H), 6.58 – 5.55 (m, 2.01H), 4.91 (s, 1.35H), 4.84 (s, 0.60H), 4.22 – 4.18 (m, 1.44H), 4.15 – 4.12 (m, 0.54H), 2.75 – 2.58 (m, 0.99H), 2.24 (s, 3.03H), 1.80 (s, 0.92H), 1.69 (s, 2.08H), 1.27 (t, *J* = 7.1 Hz, 2.44H), 1.23 (t, *J* = 7.1 Hz, 0.77H), 1.20 (d, *J* = 6.9 Hz, 1.12H), 1.15 (d, *J* = 6.9 Hz, 2.05H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.07, 173.63, 145.99, 145.93, 145.02, 144.73, 129.77, 127.60, 127.39, 113.86, 113.49, 113.38, 112.93, 60.93, 60.82, 60.73, 60.20, 44.73, 44.37, 20.41, 19.57, 18.26, 16.40, 15.48, 14.30, 14.24; HRMS (EI) calcd for $[M+1]^+$: $C_{16}H_{23}NO_2$ 262.1802, found 262.1812; IR (KBr): 3380, 2932, 1733, 1645, 1619, 1514, 1462, 1372, 1240, 1182, 1104, 1036, 896, 821, 760, 537 cm^{-1}.



3c

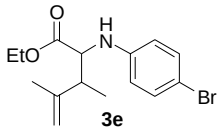
Ethyl 3,4-dimethyl-2-(phenylamino)pent-4-enoate (**3c**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.17 (dd, *J* = 10.7, 4.7 Hz, 2.00H), 6.74 (dt, *J* = 12.2, 5.9 Hz, 1.09H), 6.64 (t, *J* = 7.6 Hz, 2.00H), 4.92 (s, 1.39H), 4.85 (s, 0.61H), 4.21 (dd, *J* = 6.9 Hz, 1.47H), 4.16 – 4.11 (m, 0.68H), 4.05 (s, 1.27H), 3.92 – 3.83 (m, 0.70H), 2.77 – 2.57 (m, 0.99H), 1.80 (s, 1.07H), 1.70 (s, 2.14H), 1.27 (t, *J* = 7.2 Hz, 2.58H), 1.22 (t, J = 7.2 Hz, 0.63H), 1.21 (d, *J* = 6.9 Hz, 1.09H), 1.16 (d, *J* = 6.9 Hz, 1.91H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.89, 173.45, 147.31, 147.00, 145.91, 145.83, 129.28, 118.38, 118.20, 113.67, 113.54, 113.23, 113.00, 60.98, 60.80, 60.44, 59.85, 44.69, 44.38, 19.58, 18.29, 16.38, 15.47, 14.28, 14.22; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{21}NO_2$ 248.1645, found 248.1641; IR (KBr): 3401, 2969, 1734, 1646, 1625, 1515, 1460, 1371, 1239, 1180, 1022, 896, 762, 531 cm^{-1}.



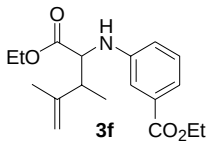
3d

Ethyl 2-((4-chlorophenyl)amino)-3,4-dimethylpent-4-enoate (**3d**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.07 (m, 2.00H), 6.57 – 6.51 (m, 2.01H), 4.89 (s, 1.28H), 4.84 (dd, *J* = 5.2, 3.7 Hz, 0.57H), 4.19 (q, *J* = 8.5 Hz, 1H), 4.15 – 4.09 (m, 0.63H), 4.04 (t, *J* = 7.9 Hz, 0.73H), 3.99 – 3.93 (m, 0.30H), 3.82 – 3.76 (m, 0.67H), 2.70 – 2.60 (m, 0.97H), 1.77 (s, 0.87H), 1.66 (s, 2.13H), 1.25 (t, *J* = 7.1 Hz, 2.66H), 1.22 (t, *J* = 7.1 Hz, 0.85H), 1.17 (d, *J* = 7.0 Hz, 1.11H), 1.13 (d, *J* = 6.9 Hz, 1.90H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58, 173.12, 145.89, 145.68, 145.59, 145.56, 129.10, 122.97, 122.81, 114.75, 114.31, 113.72, 113.16, 61.11, 60.94, 60.47, 59.90, 44.50, 44.33, 19.59, 18.21, 16.40, 15.34, 14.27, 14.21; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{20}ClNO_2$ 282.1855, found 282.1858; IR (KBr): 3406, 2976, 1733, 1647, 1600, 1501, 1382, 1262, 1181, 1093, 1023, 897, 749, 502 cm^{-1}.



3e

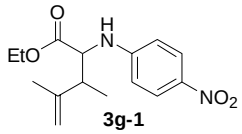
Ethyl 2-((4-bromophenyl)amino)-3,4-dimethylpent-4-enoate (**3e**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2.00H), 6.52 – 6.46 (m, 2.00H), 4.89 (s, 1.13H), 4.83 (d, *J* = 9.0 Hz, 0.83H), 4.22 – 4.17 (m, 1.19H), 4.16 – 4.09 (m, 0.83H), 4.05 –4.02 (m, 0.90H), 3.99 – 3.92 (m, 0.48H), 3.81 – 3.70 (m, 0.62H), 2.69 – 2.60 (m, 1.01H), 1.76 (s, 1.31H), 1.66 (s, 1.81H),1.25 (t, *J* = 7.1 Hz, 2.23H), 1.22 (t, *J* = 7.0 Hz, 1.54H), 1.17 (d, *J* = 7.0 Hz, 1.35H), 1.12 (d, *J* = 6.9 Hz, 1.61H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54, 173.06, 146.31, 145.97, 145.65, 145.55, 131.99, 115.21, 114.77, 113.77, 113.18, 110.04, 109.88, 61.14, 60.97, 60.32, 59.77, 44.46, 44.32, 19.61, 18.19, 16.40, 15.32, 14.28, 14.22; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{20}BrNO_2$ 326.0750, found 326.0754; IR (KBr): 3388, 2975, 1733, 1645, 1596, 1500, 1372, 1263, 1182, 1098, 1024, 898, 814, 499 cm^{-1}.



3f

Ethyl 3-((1-ethoxy-3,4-dimethyl-1-oxopent-4-en-2-yl)amino)benzoate (**3f**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 1.00H), 7.21 (s, 1.03H), 7.12 (t, *J* = 7.8 Hz, 1.00H), 6.78 – 6.67 (m, 1.00H), 4.82 (s, 1.30H), 4.76 (d, *J* = 4.8 Hz, 0.70H), 4.26 (q, *J* = 7.1 Hz, 2.11H), 4.16 –4.07

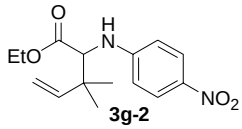
(m, 2.59H), 4.04 – 3.92 (m, 0.68H), 3.87 – 3.78 (m, 0.68H), 2.64 – 2.57 (m, 1.01H), 1.70 (s, 1.27H), 1.60 (s, 1.93H), 1.29 (t, *J* = 7.1 Hz, 3.13H), 1.18 (t, *J* = 7.2 Hz, 2.40H), 1.13 (t, *J* = 7.2 Hz, 1.03H), 1.09 (d, *J* = 6.9 Hz, 0.99H), 1.06 (d, *J* = 6.9 Hz, 2.06H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58, 173.11, 166.80, 147.30, 146.92, 145.68, 145.61, 131.46, 129.18, 119.45, 119.30, 117.83, 117.42, 114.32, 113.84, 113.70, 113.11, 61.07, 60.91, 60.81, 60.15, 59.60, 44.45, 44.30, 19.69, 18.32, 16.35, 15.26, 14.31, 14.24, 14.19; HRMS (EI) calcd for $[M+1]^+$: $C_{18}H_{26}NO_4$ 320.1856, found 320.1858; IR (KBr): 3381, 3074, 2978, 1718, 1646, 1607, 1514, 1442, 1369, 1247, 1183, 1024, 896, 806, 754, 685, 543 cm^{-1}.



3g-1

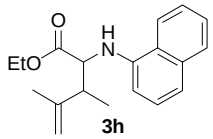
Ethyl 3,4-dimethyl-2-((4-nitrophenyl)amino) pent-4-enoate(1, 2- *syn*- **3g-1**): Light yellow solid, m.p:92-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 4.91 (s, 2H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.92 (t, *J* = 8.0 Hz, 1H), 2.76 – 2.63 (m, 1H), 1.66 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H)；^{13}C NMR (101 MHz, $CDCl_3$) δ 172.36, 152.00, 145.01, 138.88, 126.31, 114.33, 111.62, 61.57, 58.91, 44.23, 18.33, 16.28, 14.23; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{21}N_2O_4$ 293.1496, found 293.1504; IR (KBr): 3449, 3365, 2923, 2852, 2360, 1732, 1600, 1505, 1374, 1325, 1186, 1111, 836, 752, 693, 545 cm^{-1}.

Ethyl 3,4-dimethyl-2-((4-nitrophenyl)amino) pent-4-enoate(1, 2-*anti*- **3g-1**): Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.85 (d, *J* = 16.5 Hz, 1H), 4.81 (m, 1H), 4.20 – 4.11 (m, 3H), 2.77 – 2.63 (m, 1H), 1.77 (s, 3H), 1.25 (t, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.88, 152.35, 144.85, 138.98, 126.30, 113.74, 111.88, 29.70, 19.82, 15.09, 14.19; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{21}N_2O_4$ 293.1496, found 293.1504; IR (KBr): 3449, 3364, 2925, 2848, 2364, 1734, 1600, 1502, 1401, 1321, 1153, 1110, 748, 546cm^{-1}.



3g-2

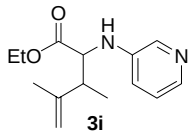
Ethyl 3,3-dimethyl-2-((4-nitrophenyl)amino)pent-4-enoate (**3g-2**): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 9.1 Hz, 2H), 5.92 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.19 (dd, *J* = 25.6, 14.1 Hz, 2H), 4.83 (d, *J* = 9.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.91 (d, *J* = 9.4 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.34, 152.41, 142.36, 138.91, 126.30, 115.20, 111.94, 63.65, 61.33, 40.46, 24.77, 23.78, 14.28; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{21}N_2O_4$ 293.1496, found 293.1504; IR (KBr): 3402, 2926, 2363, 1733, 1599, 1506, 1478, 1320, 1186, 1110, 836, 751 cm^{-1}.



3h

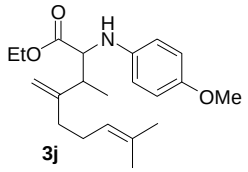
Ethyl 3,4-dimethyl-2-(naphthalen-1-ylamino)pent-4-enoate (**3h**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 0.47H), 7.89 – 7.77 (m, 1.62H), 7.59 – 7.42 (m, 2.03H), 7.41 – 7.25 (m, 2.24H), 6.62 (t, *J* = 6.5 Hz, 1.00H), 5.07 (d, *J* = 33.6 Hz, 1.36H), 4.95 (d, *J* = 9.4 Hz, 0.92H), 4.88 (s,

0.89H), 4.36 – 4.15 (m, 2.56H), 4.04 (d, *J* = 8.9 Hz, 0.61H), 3.01 – 2.80 (m, 1.05H), 1.86 (s, 1.12H), 1.74 (s, 1.89H), 1.35 (d, *J* = 7.0 Hz, 1.38H), 1.33 – 1.23 (m, 5.27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94, 173.46, 146.37, 145.93, 142.47, 142.24, 134.40, 128.65, 128.61, 126.47, 126.40, 125.82, 124.92, 124.85, 123.97, 123.57, 120.12, 120.06, 118.44, 118.05, 113.83, 113.22, 105.49, 104.62, 61.10, 60.91, 60.35, 59.75, 44.79, 44.62, 19.66, 18.24, 16.43, 15.70, 14.29, 14.24; HRMS (EI) calcd for $[M+1]^+$: $C_{19}H_{23}NO_2$ 298.1801, found 298.1809; IR (KBr): 3423, 3070, 2974, 2390, 1732, 1646, 1581, 1528, 1482, 1371, 1343, 1255, 1179, 1147, 1095, 1024, 896, 767, 569 cm^{-1}.



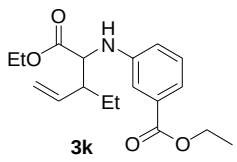
3i

Ethyl 3,4-dimethyl-2-(pyridin-3-ylamino)pent-4-enoate (**3i**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.94 (m, 2.00H), 7.06 – 7.04 (m, 1.00H), 6.92 – 6.83 (m, 0.99H), 4.90 (s, 1.22H), 4.84 (d, *J* = 9.6 Hz, 0.75H), 4.25 – 4.12 (m, 1.99H), 4.10 – 3.97 (m, 1.57H), 3.82 (t, *J* = 8.2 Hz, 0.68H), 2.71 – 2.64 (m, 1.04H), 1.77 (s, 1.28H), 1.67 (s, 1.92H), 1.25 (t, *J* = 7.1 Hz, 2.59H), 1.22 (t, *J* = 7.2 Hz, 1.13H), 1.18 (d, *J* = 7.0 Hz, 1.21H), 1.14 (d, *J* = 6.9 Hz, 1.95H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.27, 172.83, 145.45, 145.41, 143.31, 142.97, 139.78, 139.63, 136.71, 136.29, 123.70, 113.92, 113.29, 61.25, 61.11, 59.92, 59.37, 44.34, 29.69, 19.71, 18.32, 16.38, 15.18, 14.23, 14.18; HRMS (EI) calcd for $[M+1]^+$: $C_{14}H_{21}N_2O_2$ 249.1598, found 249.1601; IR (KBr): 3391, 2974, 2923, 2362, 1734, 1645, 1618, 1520, 1451, 1372, 1299, 1262, 1182, 1153, 1105, 1025, 895, 808, 701, 543 cm^{-1}.



3j

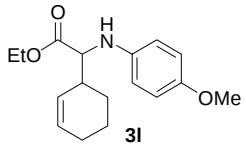
Ethyl 2-((4-methoxyphenyl)amino)-3,8-dimethyl-4-methylenenon-7-enoate (**3j**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.8 Hz, 2.00H), 6.63 – 6.53 (m, 1.96H), 5.17 – 5.04 (m, 1.15H), 4.92 (t, *J* = 12.7 Hz, 1.99H), 4.17 (q, *J* = 7.1 Hz, 1.39H), 4.13 – 4.08 (m, 0.66H), 3.95 (d, *J* = 6.9 Hz, 0.35H), 3.84 (d, *J* = 8.4 Hz, 0.73H), 3.79 (s, 0.84H), 3.72 (s, 2.92H), 2.71 – 2.59 (m, 1.00H), 2.17 – 2.09 (m, 2.26H), 2.08 – 1.89 (m, 2.13H), 1.69 (s, 1.10H), 1.66 (s, 1.90H), 1.62 (s, 1.10H), 1.57 (s, 1.90H), 1.24 (t, *J* = 7.1 Hz, 2.56H), 1.21 – 1.16 (m, 1.85H), 1.14 (d, *J* = 7.0 Hz, 2.00H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.04, 173.76, 152.77, 152.64, 149.93, 149.85, 141.50, 141.22, 131.84, 131.76, 124.02, 123.92, 115.31, 114.88, 114.83, 114.80, 111.60, 111.16, 61.70, 61.25, 60.82, 60.73, 55.68, 43.76, 43.49, 33.75, 32.48, 26.46, 26.37, 25.67, 25.64, 17.68, 16.80, 15.58, 14.25; HRMS (EI) calcd for $[M+1]^+$: $C_{21}H_{32}NO_3$ 346.2377, found 346.2373; IR (KBr): 3447, 2929, 2870, 1733, 1642, 1513, 1458, 1372, 1240, 1181, 1036, 897, 821 cm^{-1}.



3k

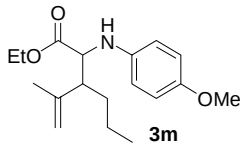
Ethyl 3-((1-ethoxy-3-ethyl-1-oxopent-4-en-2-yl)amino)benzoate (**3k**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1.03H), 7.30 (s, 1.02H), 7.21 (t, *J* = 7.8 Hz, 1.06H), 6.79 (d, *J* =

7.8 Hz, 1.00H), 5.77 – 5.53 (m, 1.06H), 5.29 – 5.05 (m, 1.88H), 4.34 (dd, *J* = 14.1, 7.1 Hz, 2.52H), 4.27 – 4.14 (m, 2.43H), 4.14 – 4.03 (m, 1.15H), 2.60 – 2.42 (m, 0.46H), 2.37 – 2.34 (m, 0.52H), 1.77 – 1.54 (m, 1.89H), 1.37 (t, *J* = 7.1 Hz, 3.20H), 1.26 – 1.20 (m, 3.50H), 0.92 (dt, *J* = 16.3, 8.1 Hz, 3.01H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.06, 172.55, 166.81, 147.22, 146.88, 137.22, 137.19, 131.49, 129.21, 129.18, 119.46, 119.37, 118.64, 118.32, 117.93, 117.81, 114.38, 114.14, 61.14, 60.90, 60.82, 59.96, 59.67, 49.46, 48.51, 29.69, 24.00, 23.68, 14.32, 14.29, 11.81, 11.76; HRMS (EI) calcd for $[M+1]^+$: $C_{18}H_{26}NO_4$ 320.1856, found 320.1858; IR (KBr): 3419, 3071, 2993, 1768, 1611, 1513, 1457, 1379, 1243, 1173, 1055, 915, 806, 746, 623 cm^{-1}.



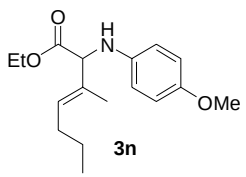
3l

Ethyl 2-(cyclohex-2-en-1-yl)-2-((4-methoxyphenyl)amino)acetate (**3l**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.72 (m, 2.01H), 6.65 – 6.56 (m, 2.00H), 5.94 – 5.80 (m, 0.45H), 5.73 – 5.50 (m, 1.56H), 4.26 – 4.10 (m, 1.99H), 3.90 – 3.79 (m, 1.89H), 3.73 (s, 3.03H), 2.23 – 2.01 (m, 3.24H), 1.96 – 1.37 (m, 4.00H), 1.29 – 1.19 (m, 3.35H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.91, 173.74, 152.75, 141.57, 141.45, 130.73, 126.99, 126.86, 126.28, 125.70, 115.33, 115.28, 115.05, 114.87, 62.54, 61.90, 60.82, 55.73, 38.85, 37.38, 37.23, 29.70, 28.28, 27.78, 26.33, 25.52, 25.17, 25.01, 24.86, 21.67, 14.30; HRMS (EI) calcd for $[M+1]^+$: $C_{17}H_{23}N_2O_4$ 290.1751, found 290.1753; IR (KBr): 3444, 2925, 2854, 2390, 2285, 1732, 1649, 1513, 1458, 1371, 1239, 1179, 1036, 820, 742 cm^{-1}.



3m

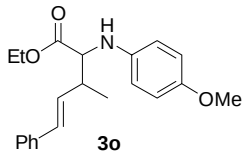
Ethyl 2-((4-methoxyphenyl)amino)-3-(prop-1-en-2-yl)hexanoate (**3m**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.73 (m, 2.00H), 6.62 –6.57 (m, 2.03H), 4.88 (dd, *J* = 39.6, 26.1 Hz, 2.05H), 4.23 – 4.13 (m, 1.22H), 4.10 – 4.04 (m, 0.72H), 3.88 (d, *J* = 8.3 Hz, 0.45H), 3.80 (d, *J* = 8.3 Hz, 0.40H), 3.75 (d, *J* = 7.6 Hz, 1.08H), 3.72 (s, 3.04H), 2.56 – 2.37 (m, 1.06H), 1.73 (s, 1.29H), 1.60 (s, 1.77H), 1.52 – 1.42 (m, 1.06H), 1.39 – 1.30 (m, 1.99H), 1.24 (t, *J* = 7.2 Hz, 2.36H), 1.19 – 1.17 (m, 2.02H), 0.92 – 0.87 (m, 3.25H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.39, 173.75, 152.79, 152.62, 143.83, 143.53, 141.38, 141.31, 115.40, 115.35, 114.89, 114.85, 114.81, 114.73, 61.66, 60.87, 60.55, 60.50, 55.70, 51.20, 50.07, 31.42, 31.14, 20.41, 20.38, 18.57, 17.82, 14.27, 14.17, 14.01, 13.87; HRMS (EI) calcd for $[M+1]^+$: $C_{18}H_{27}NO_3$ 306.2064, found 306.2070; IR (KBr): 3385, 2958, 2362, 1734, 1643, 1514, 1462, 1381, 1241, 1179, 1101, 896, 821, 758, 520 cm^{-1}.



3n

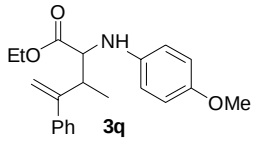
Ethyl 2-((4-methoxyphenyl)amino)-3-methylhept-3-enoate (**3n**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.8 Hz, 2.00H), 6.69 – 6.53 (m, 2.00H), 5.80 – 5.60 (m, 0.82H), 4.36 (s, 0.75H), 4.28 – 4.10 (m, 2.09H), 3.99 – 3.86 (m, 0.56H), 3.73 (s, 3.03H), 2.21 – 2.02 (m, 1.81H), 1.67 (d, *J* =

6.8 Hz, 3.05H), 1.45 – 1.37 (m, 2.03H), 1.27 – 1.22 (m, 3.08H), 0.90 (t, J = 7.3 Hz, 3.00H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.91, 152.35, 141.02, 136.88, 124.45, 114.81, 114.78, 63.16, 61.21, 55.73, 30.31, 21.77, 14.30, 14.20, 14.13, 13.54; HRMS (EI) calcd for $[M+1]^+$: $C_{17}H_{25}NO_{43}$ 292.1907, found 292.1913; IR (KBr): 3448, 2993, 2360, 1769, 1510, 1470, 1457, 1375, 1243, 1055, 914, 746, 531 cm^{-1}.



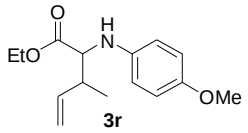
3o

Ethyl 2-((4-methoxyphenyl)amino)-3-methyl-5-phenylpent-4-enoate (**3o**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2.05H), 7.27 – 7.21 (m, 3.02H), 6.77 – 6.69 (m, 2.00H), 6.55 (d, J = 8.9 Hz, 2.00H), 5.85 – 5.73 (m, 1.00H), 5.66 – 5.59 (m, 1.00H), 4.20 (d, J = 6.5 Hz, 0.94H), 4.09 (q, J = 7.1 Hz, 1.78H), 3.98 – 3.88 (m, 0.56H), 3.72 (s, 0.92H), 3.71 (s, 2.36H), 1.70 (s, 1.75H), 1.68 (s, 1.19H), 1.16 (t, J = 7.1 Hz, 2.57H), 0.99 (t, J = 7.1 Hz, 0.72H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.17, 152.84, 140.95, 140.38, 129.62, 128.65, 128.54, 128.25, 127.90, 127.01, 115.40, 114.77, 62.91, 60.74, 55.69, 52.32, 29.70, 17.97, 14.18; HRMS (EI) calcd for $[M+1]^+$: $C_{21}H_{25}NO_3$ 340.1907, found 340.1915; IR (KBr): 3436, 2923, 2370, 1733, 1647, 1513, 1445, 1372, 1254, 1180, 1032, 897, 815 cm^{-1}.



3q

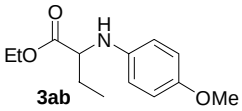
Ethyl 2-((4-methoxyphenyl)amino)-3-methyl-4-phenylpent-4-enoate (**3q**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5.05H), 6.73 (d, J = 8.8 Hz, 1.49H), 6.68 (d, J = 8.8 Hz, 0.46H), 6.52 (d, J = 8.7 Hz, 1.53H), 6.43 (d, J = 8.8 Hz, 0.46H), 5.35 (s, 0.28H), 5.28 (s, 0.73H), 5.20 (s, 0.26H), 5.18 (s, 0.73H), 4.17 – 4.04 (m, 0.64H), 3.99 – 3.87 (m, 3.08H), 3.73 (s, 2.21H), 3.71 (s, 0.71H), 3.35 – 3.24 (m, 1.00H), 1.27 (d, J = 7.0 Hz, 3.19H), 1.21 (t, J = 7.1 Hz, 0.89H), 1.15 (t, J = 7.1 Hz, 2.66H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.55, 172.99, 152.79, 152.67, 150.39, 142.04, 141.75, 141.43, 140.95, 128.40, 128.21, 127.58, 127.54, 127.24, 126.91, 115.68, 115.26, 114.83, 114.70, 114.65, 114.41, 61.72, 61.08, 60.95, 60.74, 55.72, 55.68, 41.31, 40.64, 29.71, 16.38, 15.05, 14.23, 14.13; HRMS (EI) calcd for $[M+1]^+$: $C_{21}H_{25}NO_3$ 340.1907, found 340.1915; IR (KBr): 3411, 2965, 2370, 1734, 1646, 1620, 1510, 1464, 1372, 1240, 1181, 896, 761 cm^{-1}.



3r

Ethyl 2-((4-methoxyphenyl)amino)-3-methylpent-4-enoate (**3r**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, J = 8.8 Hz, 2.07H), 6.61 – 6.58 (m, 2.00H), 5.81 – 5.76 (m, 1.08H), 5.16 – 5.11 (m, 2.11H), 4.17 – 4.13 (m, 2.05H), 3.90 – 3.84 (m, 2.05H), 3.73 (s, 3.01H), 2.73 – 2.68 (m, 0.61H), 2.66 – 2.63 (m, 0.48H),1.23 (m, 3.16H), 1.15 (d, J = 5.2 Hz, 3.00H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.45, 173.14, 152.79, 152.72, 141.33, 141.12, 139.33, 139.12, 116.30, 116.26, 115.39, 115.15, 114.85, 62.57, 62.35, 60.92, 60.77, 55.70, 41.42, 40.65, 16.51, 14.31; HRMS (EI) calcd for $[M+1]^+$: $C_{15}H_{22}NO_3$ 264.1594, found 264.1590; IR (KBr): 3381, 2931, 2361, 1734, 1640, 1513, 1462, 1371, 1241, 1185,

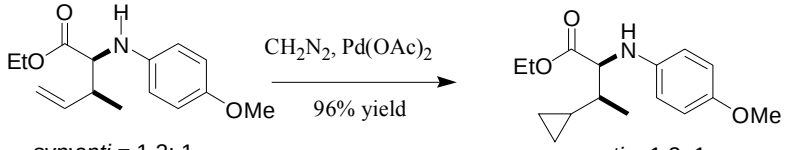
919, 821, 759, 522 cm^{-1}.



3ab

Ethyl 2-((4-methoxyphenyl)amino)butanoate (**3ab**) [7]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.68 (m, 2.00H), 6.67 – 6.50 (m, 2.00H), 4.17 (q, *J* = 7.2 Hz, 2.03H), 3.92 (t, *J* = 6.3 Hz, 1.07H), 3.73 (s, 3.03H), 1.94 – 1.65 (m, 2.16H), 1.24 (t, *J* = 7.1 Hz, 3.34H), 1.00 (t, *J* = 7.5 Hz, 3.06H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.31, 152.70, 141.10, 115.12, 114.90, 60.87, 59.04, 55.73, 26.25, 14.26, 9.98; GC-MS(ESI): m/z= 237.03 $[M]^+$; IR (KBr): 3396, 2922, 2361, 1734, 1640, 1513, 1461, 1240, 1025, 896, 751 cm^{-1}.

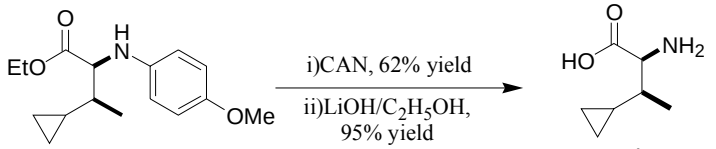
3 General procedures for synthesis of 2-amino-3-cyclopropylbutanoic acid 3r-2



syn:*anti* = 1.3: 1 **3r**

syn:*anti* = 1.3: 1 **3r-1**

The procedures for cyclopropanation of the terminal double bond was same as the reference [8]: A solution of a mixture of diastereomers **3r** (the ration of cis/trans = 1.3:1) (263 mg, 1 mmol) and diazomethane (prepared from 4 g of *N*-methyl-*N*-nitrosourea) [9] in ether (10 mL) is cooled in an ice-water bath, and palladium(II) acetate (10 mg) is added. After 0.5 h the ether is removed in vacuo and the residual product was purified by flash chromatography on silica gel using 10 % ethyl acetate in petroleum ether as eluent to offer desired compound **3r-1** (the ration of cis/trans = 1.3:1), yield: 96%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.8 Hz, 2.05H), 6.64 (dd, *J* = 17.2, 8.9 Hz, 2.00H), 4.16 (dq, *J* = 10.3, 7.1 Hz, 2.08H), 4.06 (s, 0.90H), 3.97 (s, 1.05H), 3.73 (s, 3.02H), 1.34 – 1.31 (m, 0.90H), 1.24 (dd, *J* = 15.0, 7.3 Hz, 3.32H), 1.12 – 1.06 (m, 3.06H), 0.83 – 0.71 (m, 1.06H), 0.57 – 0.43 (m, 2.01H), 0.27 – 0.25 (m, 0.44H), 0.22 – 0.19 (m, 0.56H), 0.08 (dt, *J* = 9.9, 4.6 Hz, 1.02H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.08, 173.69, 152.69, 152.64, 141.83, 141.68, 115.40, 115.25, 114.87, 114.84, 63.29, 63.05, 60.80, 55.72, 42.56, 41.57, 16.57, 16.32, 15.11, 14.27, 13.90, 5.06, 4.68, 3.73, 3.08; HRMS (EI) calcd for $[M+1]^+$: $C_{16}H_{23}NO_3$ 278.1751, found 278.1749; IR (KBr): 3420, 2923, 2363, 1730, 1620, 1510, 1430, 1360, 1208, 1011, 871, 613 cm^{-1}.



syn:*anti* = 1.3:1 **3r-1**

syn:*anti* = 1.3:1 **3r-2**

The procedures for removing the PMP protecting group was same as the literature [10, 11]: To a CH_3CN(2.0 mL) solution of a mixture of diastereomers **3r-1** (the ration of cis/trans = 1.3:1) (0.2 mmol) at 0 °C was added a H_2O (1.5 mL) solution of cerium ammonium nitrate (CAN, 383 mg, 0.7 mmol, 3.5 eqiv). The resulting solution was stirred under ambient temperature for 2 h, then treated with 2N HCl to achieve an approximate pH = 1. The aqueous phase was washed with EtOAc (6 mL × 3) and brought to basic by the addition of saturated $NaHCO_3$. The resulting aqueous layer was then extracted with CH_2Cl_2 (15 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of

the solvent in vacuum, ethyl 2-amino-3-cyclopropylbutanoate **3r-1a** (21 mg, 62% yield) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 – 4.15 (m, 1.95H), 3.48 (d, *J* = 3.9 Hz, 0.41H), 3.43 (d, *J* = 3.9 Hz, 0.54H), 1.29 – 1.26 (m, 2.98H), 1.04 (d, *J* = 6.9 Hz, 1.73H), 0.96 (d, *J* = 6.5 Hz, 1.32H), 0.87 – 0.82 (m, 1.04H), 0.77 – 0.70 (m, 0.50H), 0.67 – 0.58 (m, 0.64H), 0.52 – 0.36 (m, 2.00H), 0.20 – 0.00 (m, 2.05H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.61, 175.42, 60.68, 60.63, 59.45, 59.16, 42.94, 42.77, 29.68, 16.95, 15.05, 14.68, 14.23, 12.95, 4.47, 4.38, 4.02, 2.71; HRMS (EI) calcd for $[M+1]^+$: $C_9H_{18}NO_2$ 172.1332, found 172.1330; IR (KBr): 3390, 2920, 2364, 1623, 1587, 1501, 1423, 1208, 870, 613 cm^{-1}.

The procedure for the hydrolysis of ethyl 2-amino-3-cyclopropylbutanoate (**3r-2**) [12]: To a stirred solution of ethyl 2-amino-3-cyclopropylbutanoate (34 mg, 0.2 mmol) in ethanol (2 mL) was added 1.0 M lithium hydroxide (2.5 mL, 2.5 mmol). After the reaction mixture was stirred at room temperature for 2 h, then adjusted its pH value to 2 using 1 N HCl, and diluted it with 10 mL of EtOH. The mixture was purified by an ion-exchange cartridge (5 g SCX resin) using methanol and ammonium hydroxide as eluent to afford 95% yield of 2-amino-3-cyclopropylbutanoic acid (**3r-2**) (the ration of cis/trans = 1.3:1). [13, 14, 15] ^{1}H NMR (400 MHz, D_2O) δ 3.19 (d, *J* = 4.5 Hz, 0.60H), 3.08 (d, *J* = 4.6 Hz, 0.45H), 2.64 (s, 0.72H), 0.91 (d, *J* = 6.8 Hz, 1.73H), 0.83 (d, *J* = 6.7 Hz, 1.38H), 0.59 (dd, *J* = 8.5, 4.4 Hz, 0.60H), 0.53 (dd, *J* = 10.4, 5.9 Hz, 0.45H), 0.36 (ddd, *J* = 15.9, 8.0, 3.7 Hz, 2.02H), 0.15 – -0.09 (m, 2.05H); ^{13}C NMR (101 MHz, D_2O) δ 181.33, 181.28, 59.63, 58.97, 40.66, 40.53, 15.07, 13.03, 12.28, 11.05, 2.26, 1.85, 1.70; MS (ESI): m/z= 166.4 $[M+Na]^+$; IR (KBr): 3450, 2536, 2364, 1581, 1428, 1207, 1018, 866, 615, 439 cm^{-1}.

4. Deuterium Labeling experiment[16, 17]

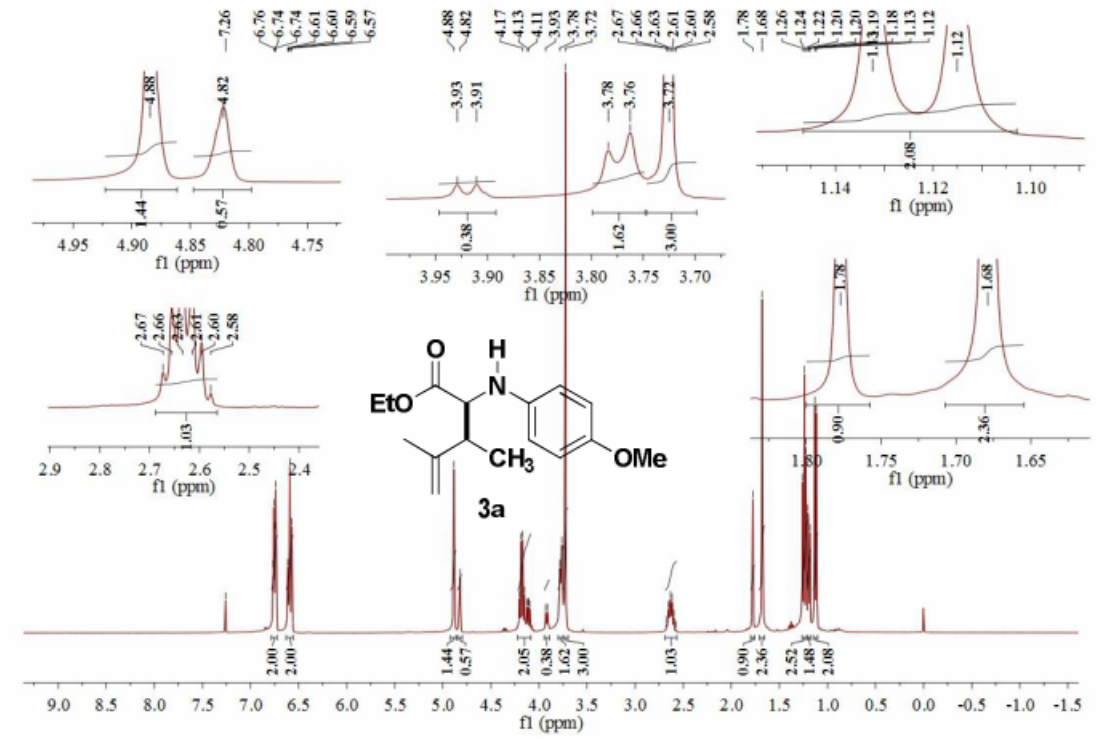
Procedure for the preparation $RuHCl(CO)(PPh_3)_3$, $RuDCl(CO)(PPh_3)_3$, **3a-1**, **3a-2**

Preparation of $RuHCl(CO)(PPh_3)_3$[16]: a solution of hydrated ruthenium trichloride (0.26 g, 1 mmol) in 2-methoxyethanol (20 mL) and aqueous formaldehyde (20 mL, 40% w/v solution) were added rapidly to a vigorously stirred boiling solution of triphenylphosphine (1.58 g, 6.05 mmol) in 2-methoxyethanol (60 mL). Then the corresponding solution was refluxed for 30 min and allowed to cool. The resultant cream-white microcrystalline precipitate was separated, washed successively with ethanol, water, ethanol and n-hexane, and then dried in vacuo to give 95% yield of $RuHCl(CO)(PPh_3)_3$ (3.45 g).

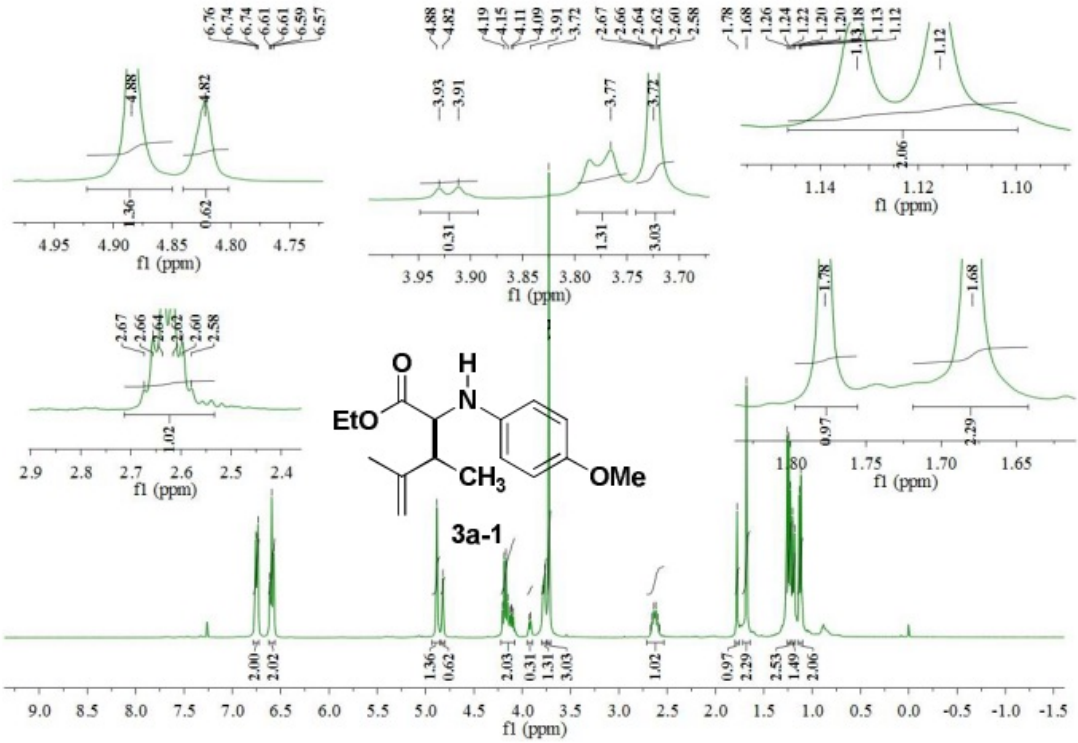
Preparation of $RuDCl(CO)(PPh_3)_3$ [17]: A THF solution (2 mL) containing $RuHCl(CO)(PPh_3)_3$ (0.10 mmol) and D_2O (100 mL, 5.6 mmol) in a stoppered Schlenck tube was stirred and heated by an oil bath at 100 ^oC for 1 h. Then solvents were removed under vacuum, and the corresponding residue was washed with hexane (3 mL) and diethylether (2 mL×3), respectively. The resulting solid was dried under vacuum to give 63% yield of $RuDCl(CO)(PPh_3)_3$ (60 mg).

3a-1, **3a-2** was prepared under standard condition: To a solution of α-imino ester **1** (0.2 mmol) in dry toluene (3.0 mL) were added catalyst (10 mol %), diene (0.8 mmol) and additive (200 mol %) in a sealed tube under an Ar atmosphere. After the corressponding reaction mixture was stirred at 130℃ for 24 h, the mixture was cooled to room temperature and concentrated under vacuum. The resulting crude product was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:15) to furnish the target product **3a-1** and **3a-2**.

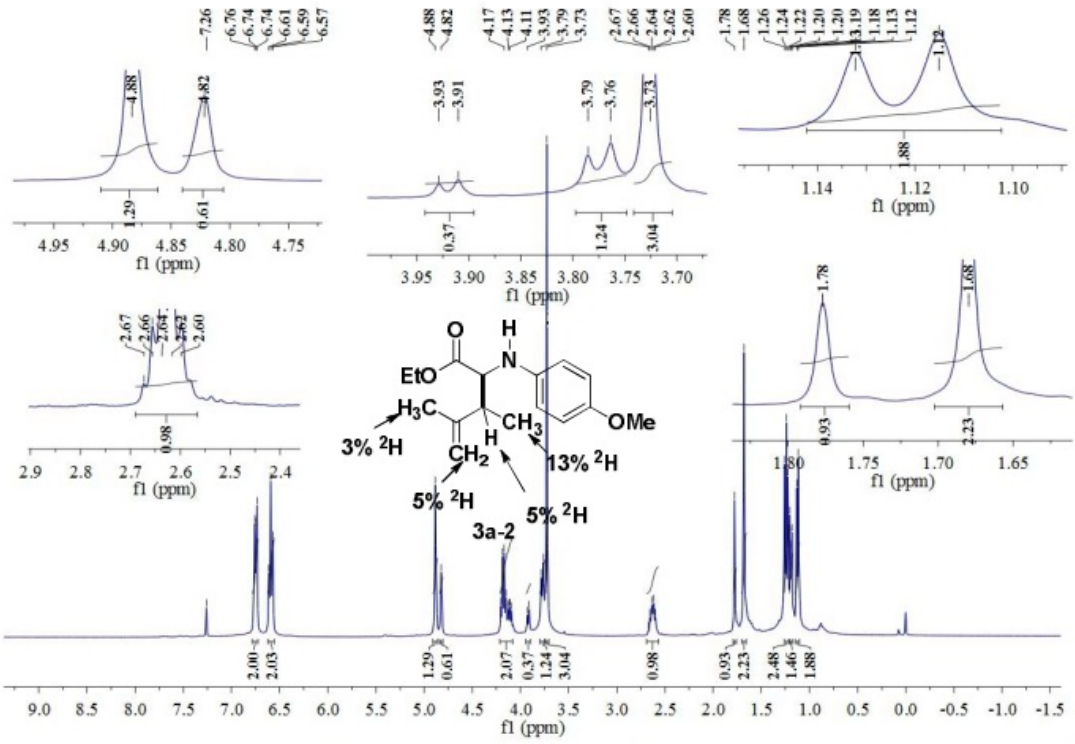
^1H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



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



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a-2**



5. Single crystal structure and crystallographic data for 1, 2-*syn*- 3g-1

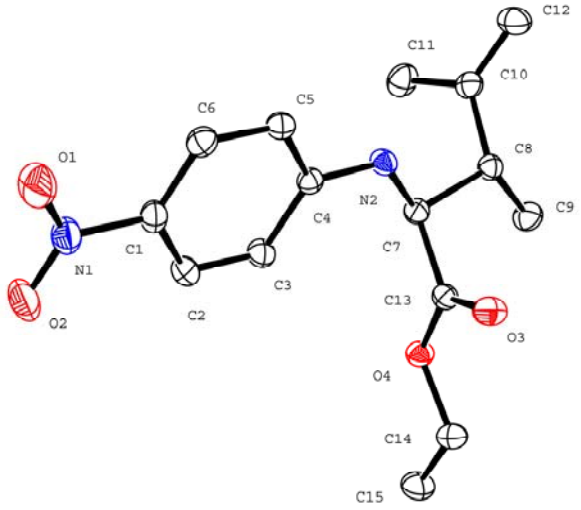


Figure 1. The Single crystal structure of compound 1, 2-*syn*-3g-1

Crystals 1, 2-*syn*- **3g-1** were obtained by slow volatilizating of hexane.

Table 1. Crystal data and structure refinement for 1, 2-*syn*- 3g-1.

Identification code	1, 2- *syn* - 3g-1
Empirical formula	$C_{15}H_{20}N_2O_4$
Formula weight	292.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic
Unit cell dimensions	a = 11.861(2) A alpha = 90 deg.
b = 11.981(2) A	beta = 118.89(2) deg.
c = 12.370(6) A	gamma = 90 deg.
Volume	1539.1(8) A^3
Z, Calculated density	4, 1.262 Mg/m^3
Absorption coefficient	0.092 mm^-1
F(000)	624
Crystal size	0.10 x 0.10 x 0.10 mm^3
Theta range for data collection	3.30 to 27.45 deg.
Limiting indices	-15<=h<=15, -15<=k<=15, -15<=l<=16
Reflections collected / unique	14617 / 3487 [R(int) = 0.0236]
Completeness to theta = 27.45	99.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3487 / 0 / 191
Goodness-of-fit on F^2	1.142
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1383

R indices (all data)	R1 = 0.0711, wR2 = 0.1574
Extinction coefficient	0.010(3)
Largest diff. peak and hole	0.452 and -0.312 e.A^-3

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1, 2-*syn*- 3g-1.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor**.**

	x	y	z	U(eq)
O(4)	2760(1)	4991(1)	8450(1)	48(1)
O(3)	974(1)	4285(1)	6885(1)	60(1)
N(2)	1652(1)	5673(1)	5359(1)	45(1)
C(7)	1857(1)	5993(1)	6565(1)	41(1)
C(5)	2157(2)	4753(2)	3930(1)	46(1)
C(8)	782(2)	6805(1)	6416(1)	44(1)
C(13)	1806(1)	4985(1)	7291(1)	42(1)
C(10)	739(2)	7840(1)	5703(1)	49(1)
C(3)	3624(2)	4594(2)	6107(1)	51(1)
C(4)	2474(1)	5020(1)	5149(1)	41(1)
N(1)	4938(2)	3022(1)	4375(2)	63(1)
C(1)	4086(2)	3703(1)	4645(2)	49(1)
C(2)	4413(2)	3942(2)	5848(2)	54(1)
O(2)	5954(1)	2707(2)	5237(2)	88(1)
C(6)	2954(2)	4112(2)	3678(2)	51(1)
O(1)	4597(2)	2783(2)	3300(2)	97(1)
C(9)	882(2)	7115(2)	7658(2)	60(1)
C(14)	2706(2)	4139(2)	9263(2)	58(1)
C(12)	-375(2)	8166(2)	4755(2)	70(1)
C(15)	3843(2)	4291(2)	10508(2)	72(1)
C(11)	1951(2)	8488(2)	6137(2)	71(1)

Table 3. Bond lengths [A] and angles [deg] for 1, 2- *syn*- 3g-1.

O(4)-C(13)	1.3300(19)
O(4)-C(14)	1.456(2)
O(3)-C(13)	1.2044(19)
N(2)-C(4)	1.368(2)
N(2)-C(7)	1.4423(19)
N(2)-H(2A)	0.8600
C(7)-C(13)	1.523(2)

C(7)-C(8)	1.542(2)
C(7)-H(7A)	0.9800
C(5)-C(6)	1.366(2)
C(5)-C(4)	1.404(2)
C(5)-H(5A)	0.9300
C(8)-C(10)	1.508(2)
C(8)-C(9)	1.529(2)
C(8)-H(8A)	0.9800
C(10)-C(12)	1.333(3)
C(10)-C(11)	1.487(3)
C(3)-C(2)	1.370(2)
C(3)-C(4)	1.402(2)
C(3)-H(3A)	0.9300
N(1)-O(2)	1.221(2)
N(1)-O(1)	1.222(2)
N(1)-C(1)	1.457(2)
C(1)-C(2)	1.374(2)
C(1)-C(6)	1.386(2)
C(2)-H(2B)	0.9300
C(6)-H(6A)	0.9300
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(14)-C(15)	1.490(3)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600

C(13)-O(4)-C(14)	116.22(13)
C(4)-N(2)-C(7)	124.64(13)
C(4)-N(2)-H(2A)	117.7
C(7)-N(2)-H(2A)	117.7
N(2)-C(7)-C(13)	111.35(13)
N(2)-C(7)-C(8)	109.11(12)
C(13)-C(7)-C(8)	107.72(12)
N(2)-C(7)-H(7A)	109.5
C(13)-C(7)-H(7A)	109.5

C(8)-C(7)-H(7A)	109.5
C(6)-C(5)-C(4)	121.22(15)
C(6)-C(5)-H(5A)	119.4
C(4)-C(5)-H(5A)	119.4
C(10)-C(8)-C(9)	110.61(14)
C(10)-C(8)-C(7)	112.42(12)
C(9)-C(8)-C(7)	112.01(13)
C(10)-C(8)-H(8A)	107.2
C(9)-C(8)-H(8A)	107.2
C(7)-C(8)-H(8A)	107.2
O(3)-C(13)-O(4)	123.54(14)
O(3)-C(13)-C(7)	124.36(14)
O(4)-C(13)-C(7)	112.04(13)
C(12)-C(10)-C(11)	122.61(18)
C(12)-C(10)-C(8)	119.65(17)
C(11)-C(10)-C(8)	117.68(15)
C(2)-C(3)-C(4)	120.46(15)
C(2)-C(3)-H(3A)	119.8
C(4)-C(3)-H(3A)	119.8
N(2)-C(4)-C(3)	122.69(14)
N(2)-C(4)-C(5)	119.27(14)
C(3)-C(4)-C(5)	118.03(14)
O(2)-N(1)-O(1)	123.09(16)
O(2)-N(1)-C(1)	118.32(17)
O(1)-N(1)-C(1)	118.59(16)
C(2)-C(1)-C(6)	120.67(15)
C(2)-C(1)-N(1)	120.00(16)
C(6)-C(1)-N(1)	119.32(15)
C(3)-C(2)-C(1)	120.26(16)
C(3)-C(2)-H(2B)	119.9
C(1)-C(2)-H(2B)	119.9
C(5)-C(6)-C(1)	119.35(15)
C(5)-C(6)-H(6A)	120.3
C(1)-C(6)-H(6A)	120.3
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(4)-C(14)-C(15)	107.96(16)
O(4)-C(14)-H(14A)	110.1
C(15)-C(14)-H(14A)	110.1
O(4)-C(14)-H(14B)	110.1

C(15)-C(14)-H(14B)	110.1
H(14A)-C(14)-H(14B)	108.4
C(10)-C(12)-H(12A)	108.5
C(10)-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	109.5
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1, 2-*syn*- 3g-1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\,hka^*b^*U^{12}]$

	U11	U22	U33	U23	U13	U12
O(4)	45(1)	53(1)	37(1)	4(1)	14(1)	-2(1)
O(3)	53(1)	55(1)	54(1)	3(1)	11(1)	-14(1)
N(2)	43(1)	53(1)	35(1)	0(1)	15(1)	7(1)
C(7)	40(1)	44(1)	37(1)	-2(1)	17(1)	-2(1)
C(5)	46(1)	51(1)	40(1)	2(1)	19(1)	2(1)
C(8)	44(1)	46(1)	45(1)	-1(1)	22(1)	1(1)
C(13)	39(1)	44(1)	39(1)	-1(1)	16(1)	1(1)
C(10)	60(1)	47(1)	47(1)	1(1)	32(1)	7(1)
C(3)	43(1)	65(1)	39(1)	-1(1)	16(1)	3(1)
C(4)	41(1)	40(1)	41(1)	0(1)	20(1)	-3(1)
N(1)	60(1)	60(1)	79(1)	1(1)	42(1)	7(1)
C(1)	48(1)	46(1)	61(1)	-1(1)	32(1)	1(1)
C(2)	41(1)	62(1)	53(1)	4(1)	18(1)	5(1)
O(2)	62(1)	100(1)	103(1)	5(1)	42(1)	27(1)
C(6)	58(1)	54(1)	46(1)	-3(1)	28(1)	-1(1)
O(1)	108(1)	114(2)	84(1)	-8(1)	58(1)	35(1)
C(9)	75(1)	64(1)	54(1)	3(1)	41(1)	11(1)
C(14)	61(1)	59(1)	51(1)	14(1)	24(1)	5(1)
C(12)	84(1)	75(1)	55(1)	11(1)	37(1)	27(1)

C(15)	71(1)	88(2)	46(1)	16(1)	20(1)	14(1)
C(11)	81(1)	54(1)	90(1)	3(1)	51(1)	-8(1)

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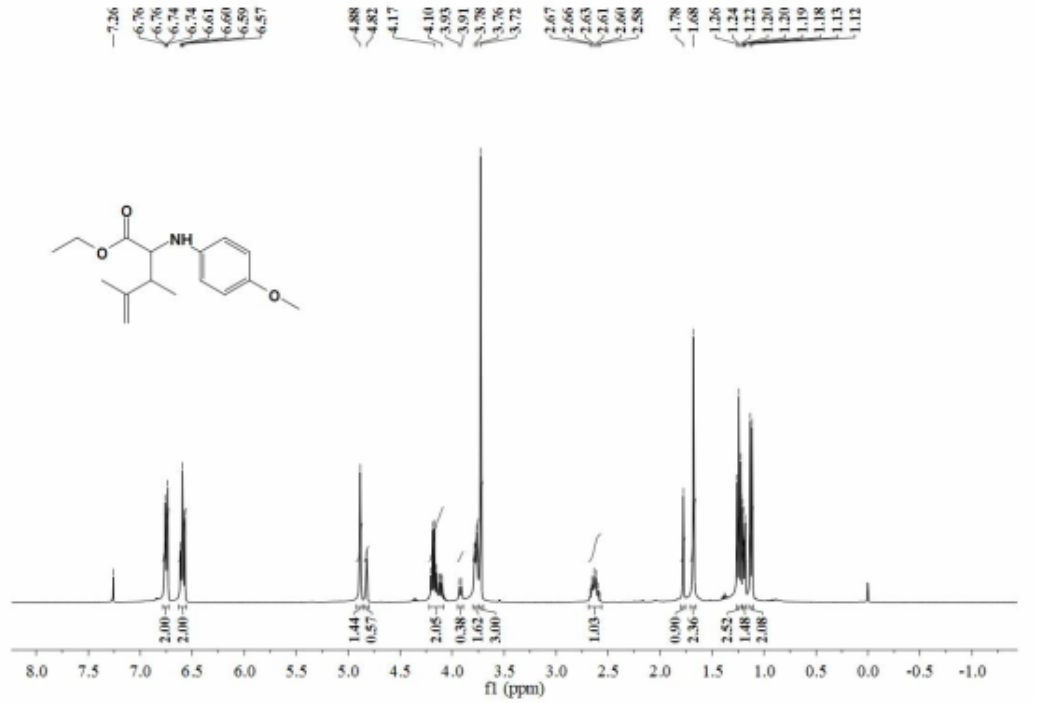
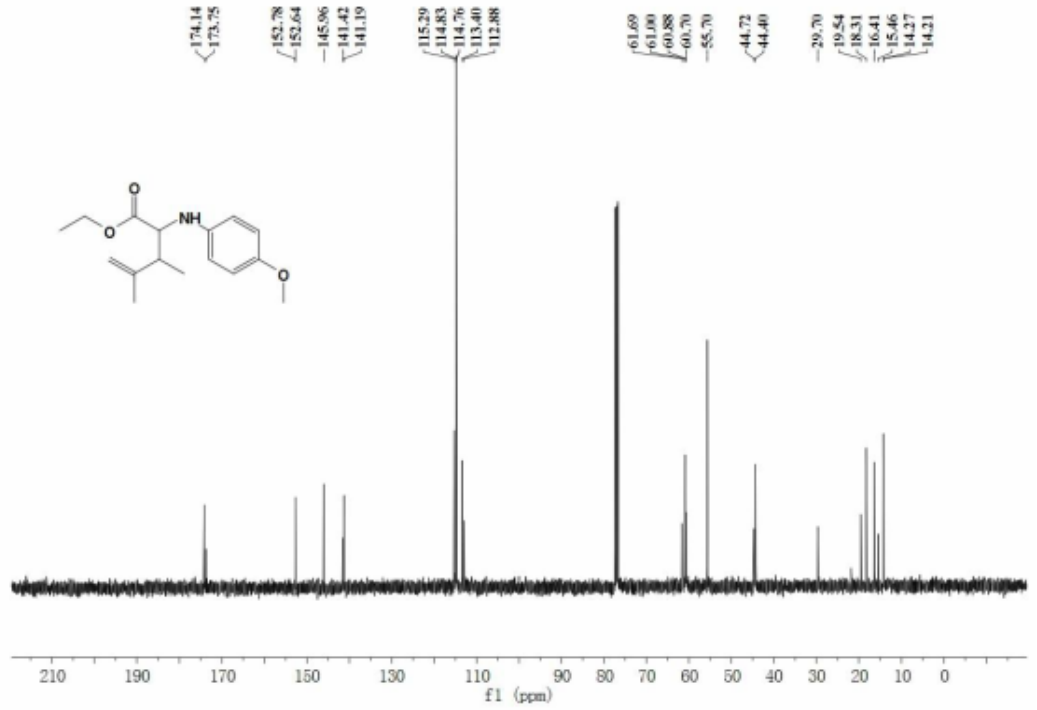
7. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3r, 3r-1, 3r-1a, 3r-2, 3ab

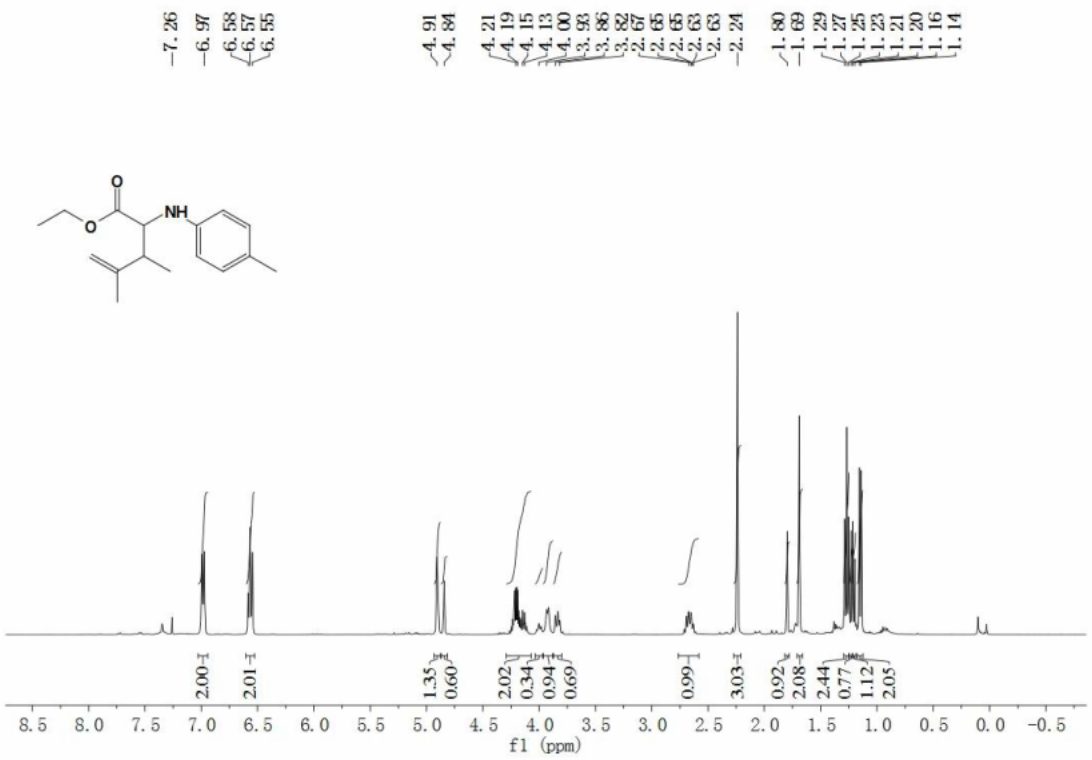
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



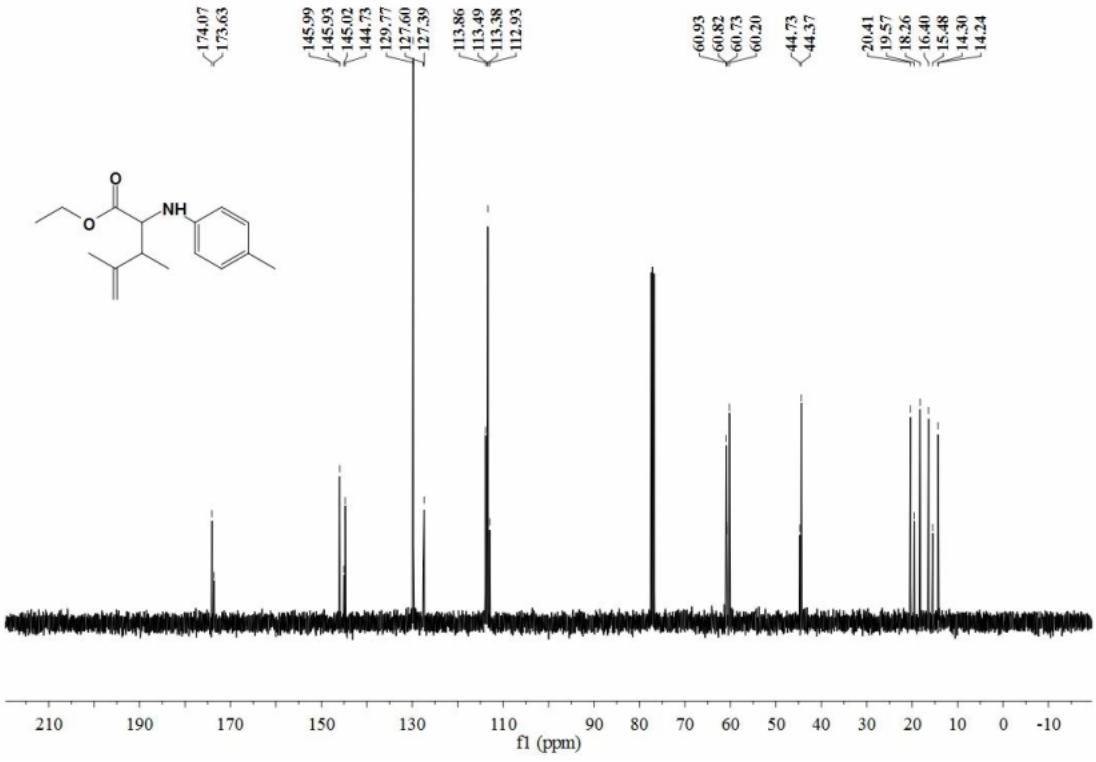
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3a**



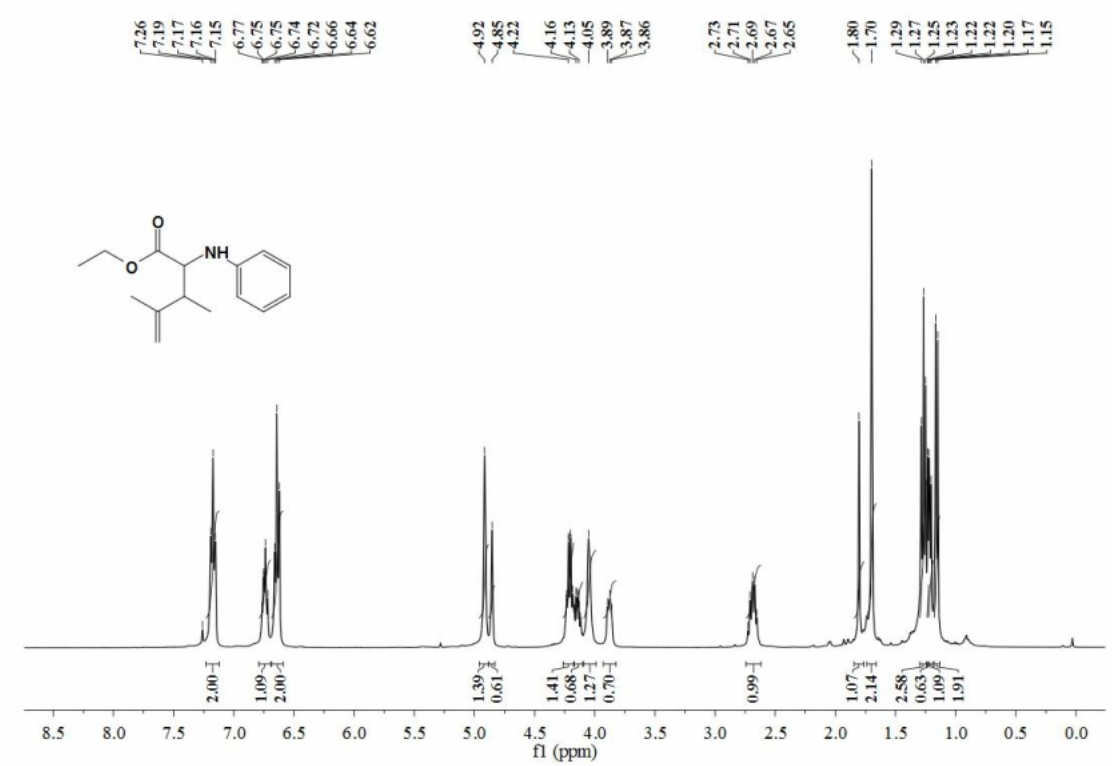
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



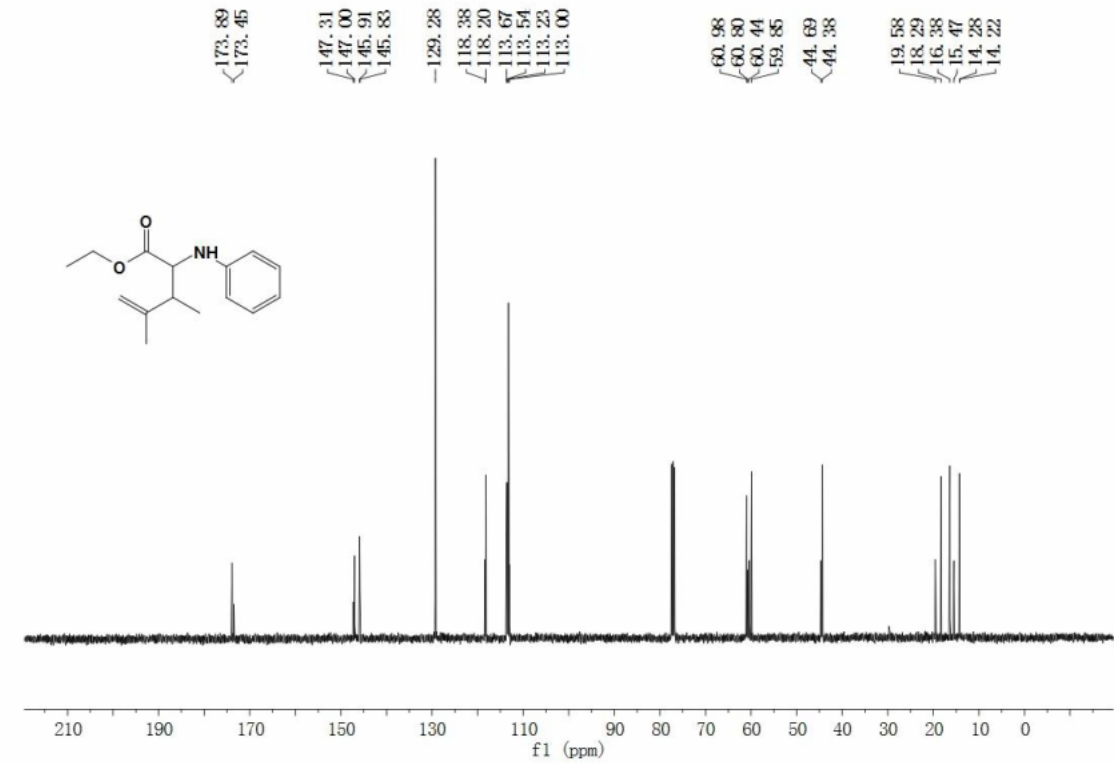
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3b**



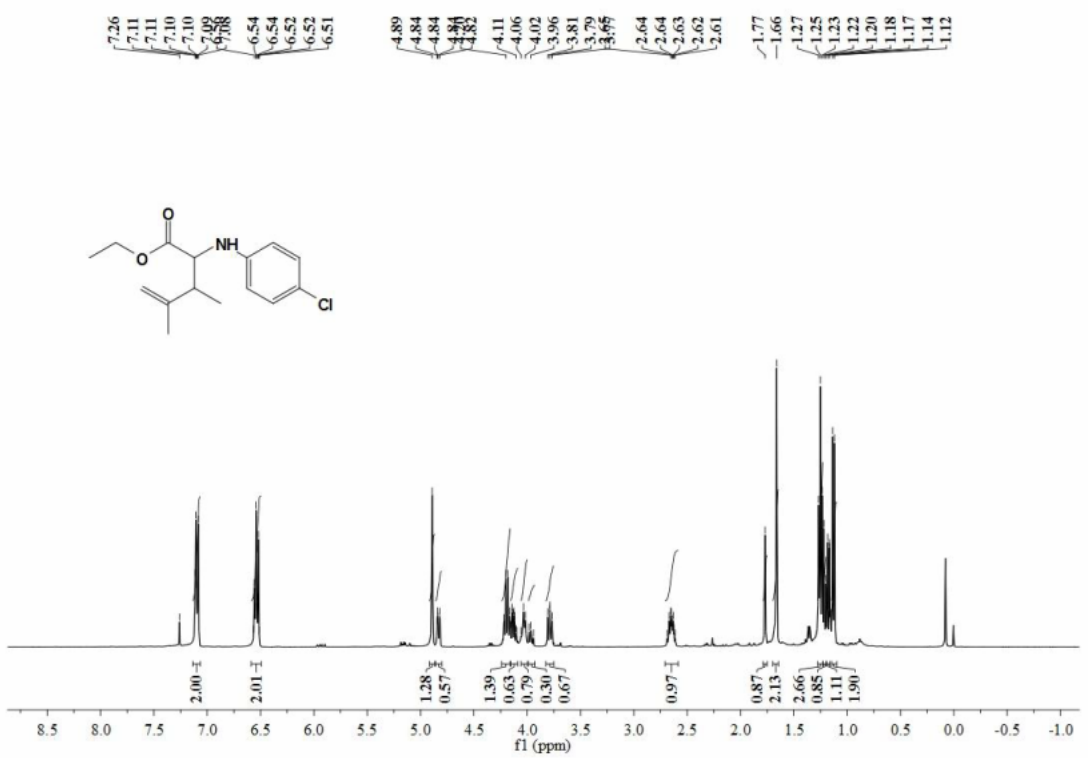
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**



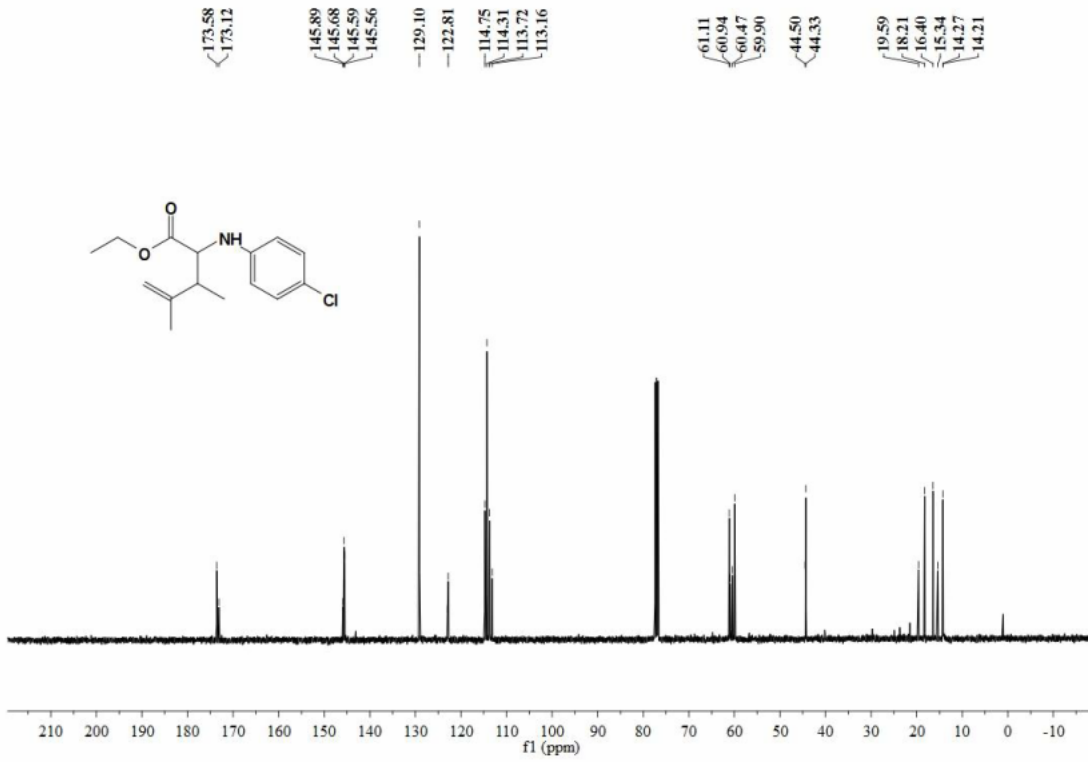
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3c**



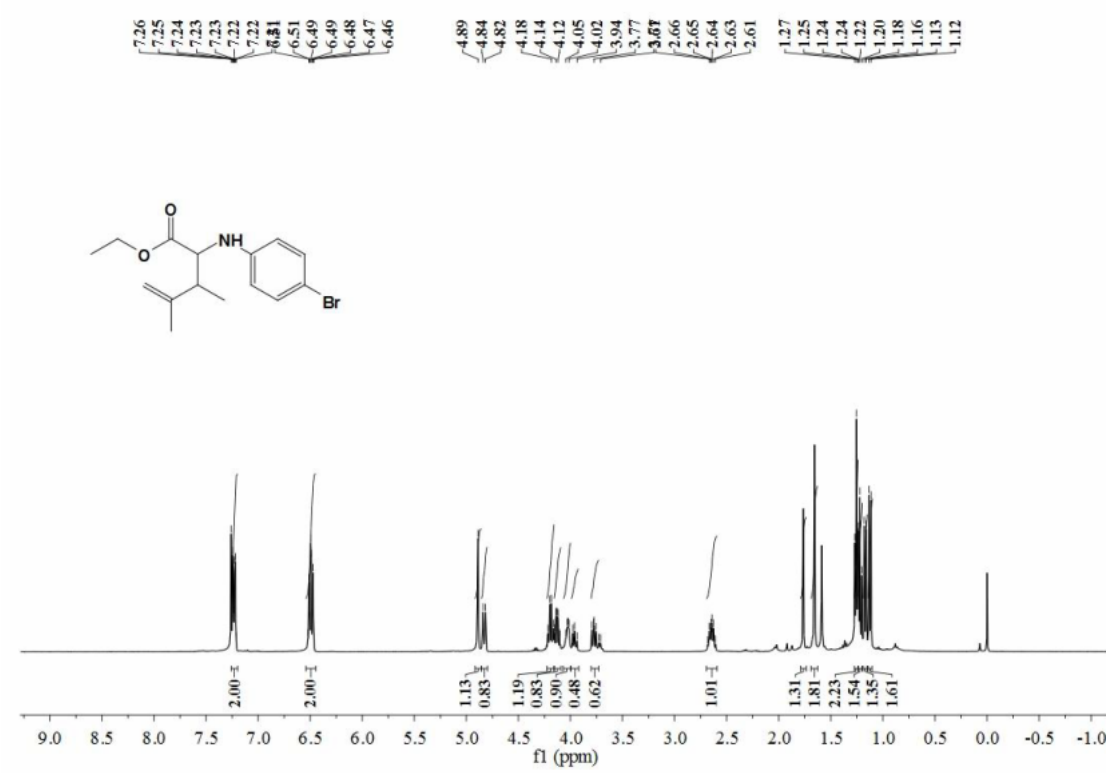
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**



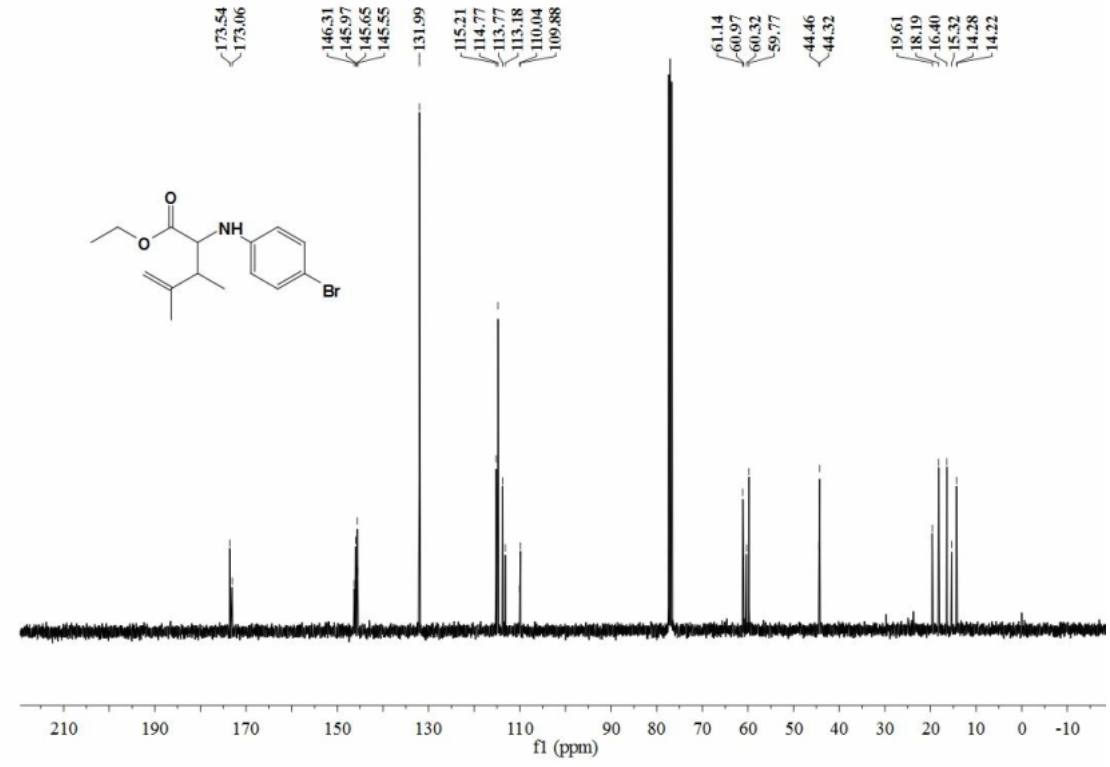
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3d**



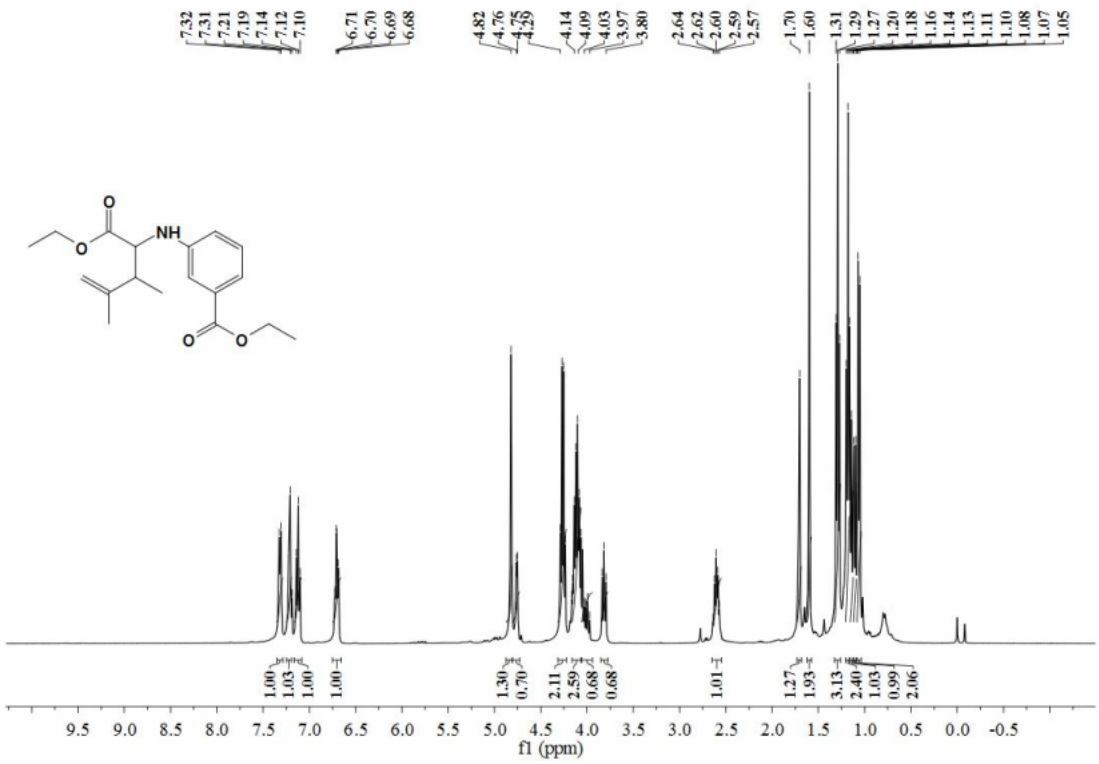
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**



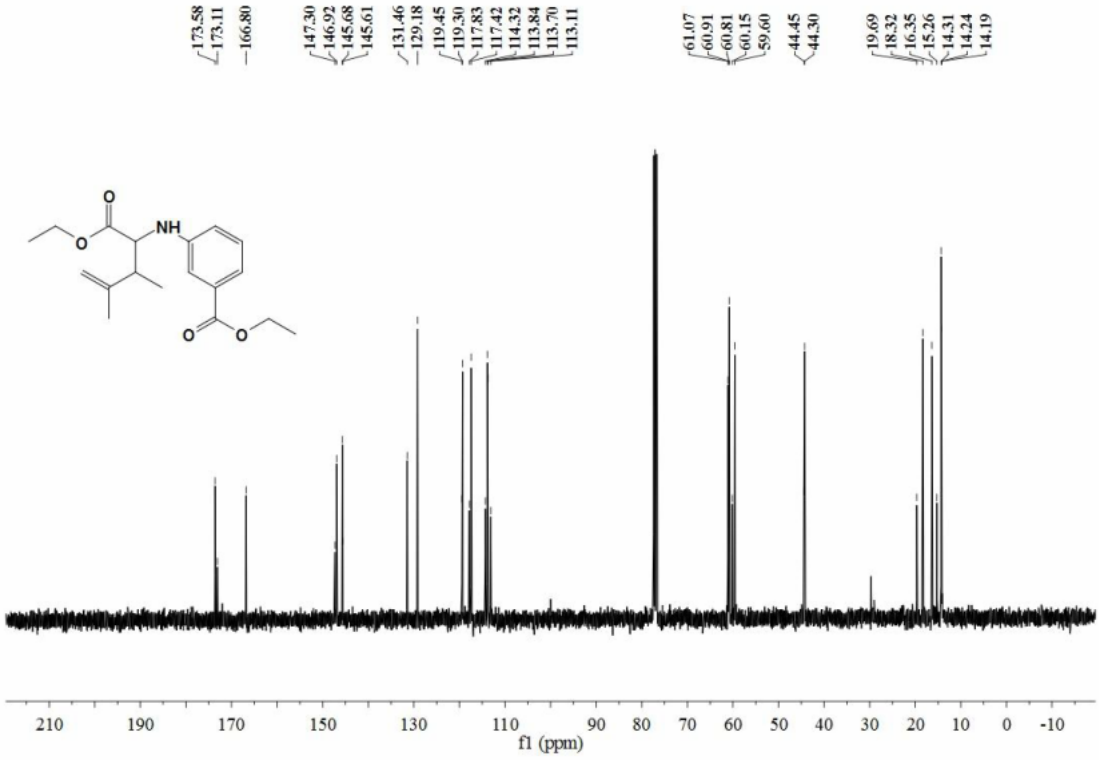
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3e**



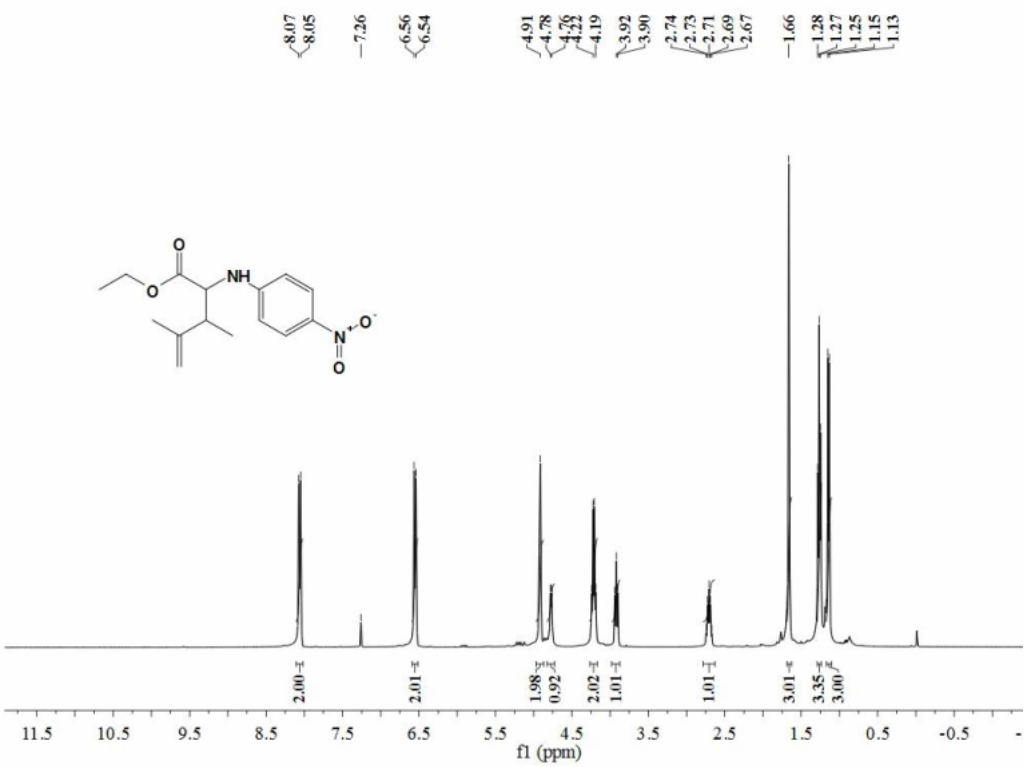
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3f**



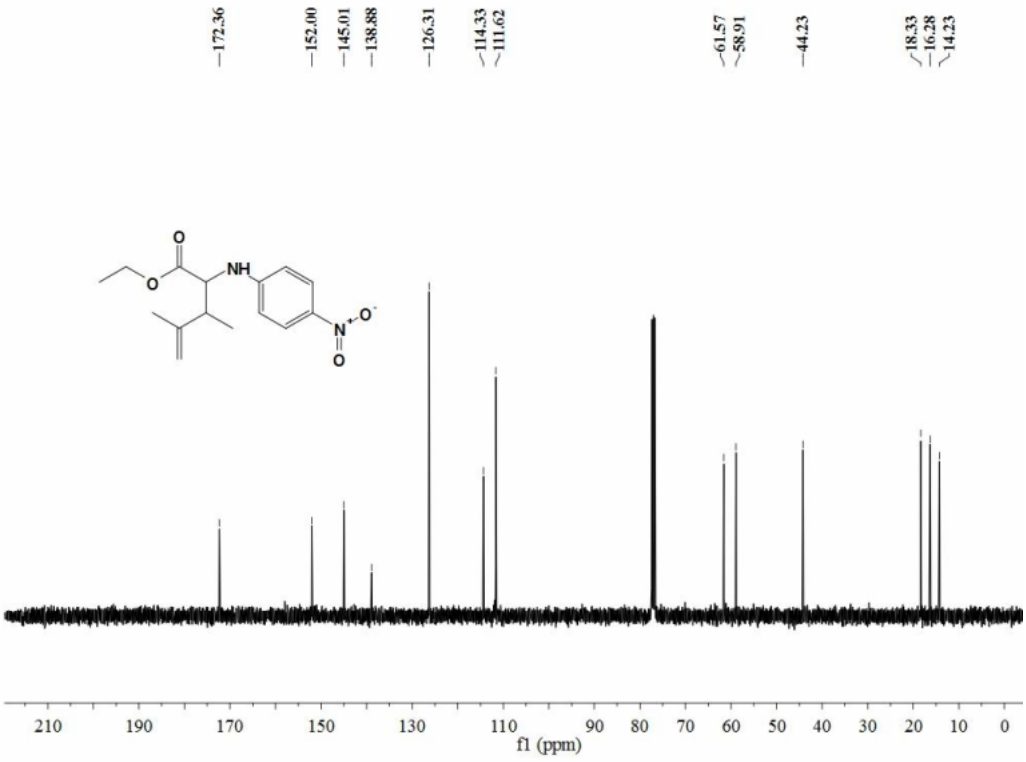
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3f**



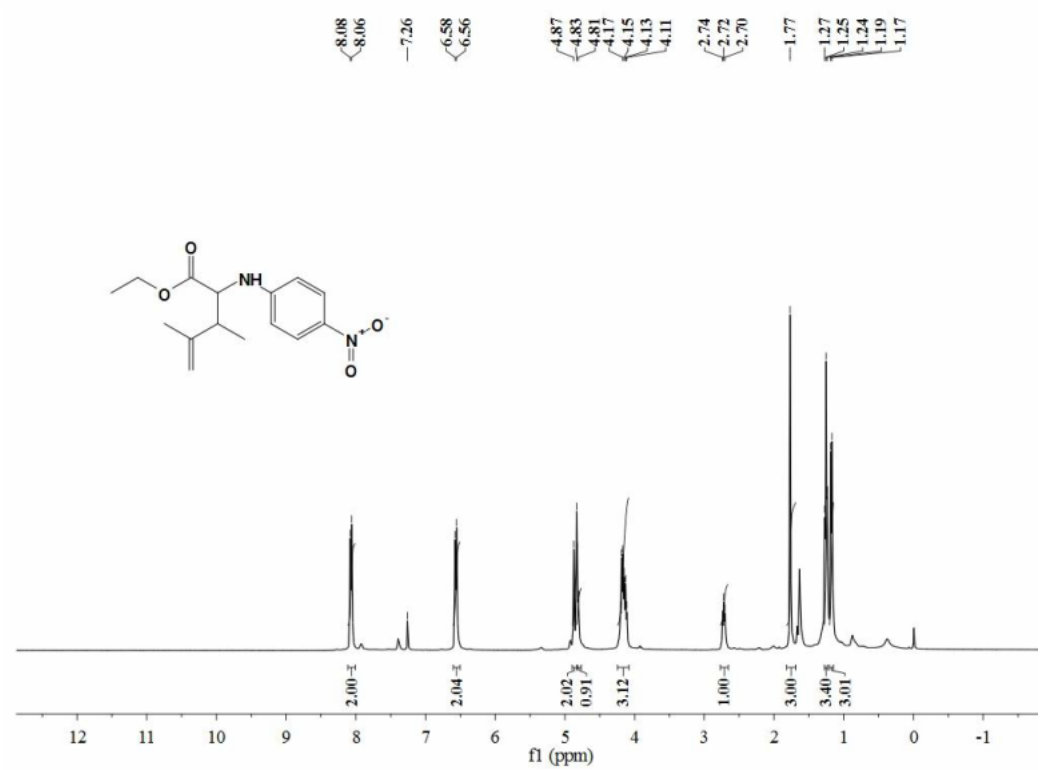
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1, 2- *syn*- 3g-1**



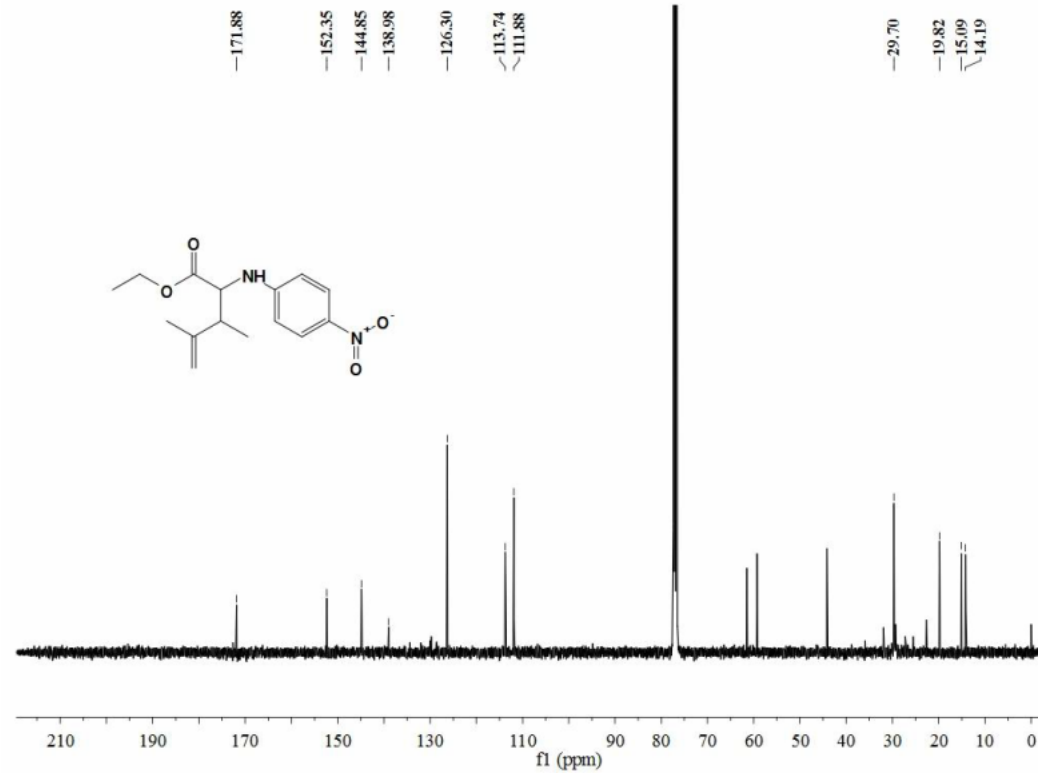
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1, 2- *syn*- 3g-1**



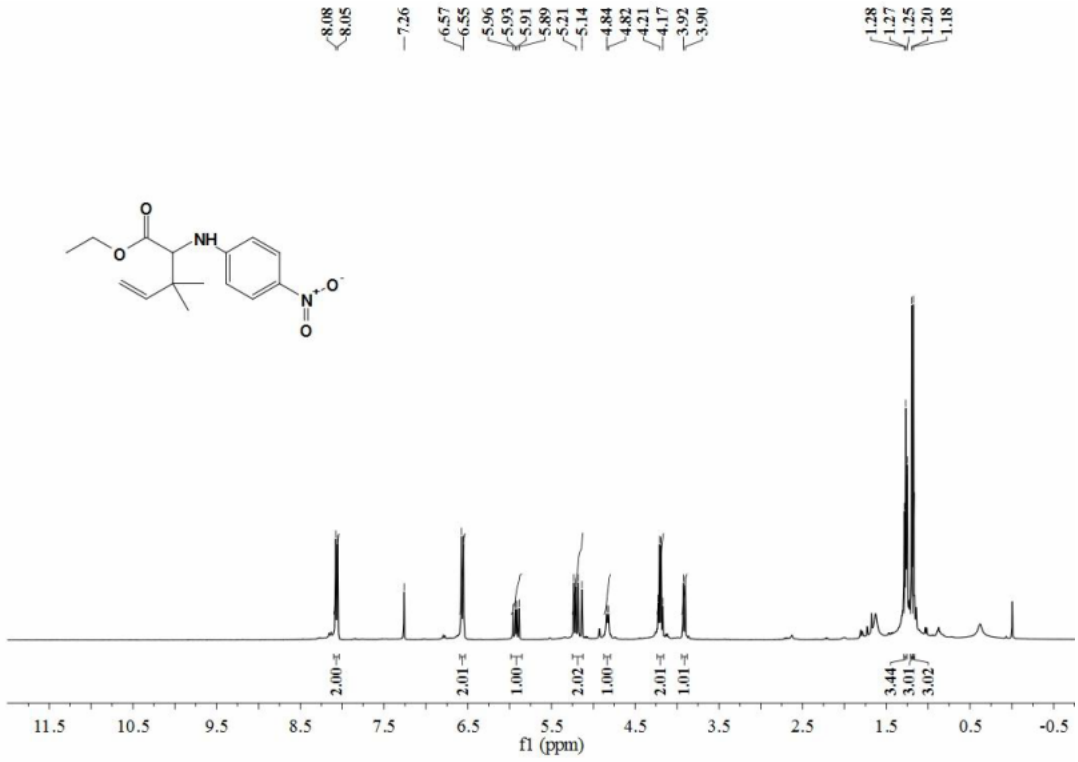
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1, 2- *anti*- 3g-1**



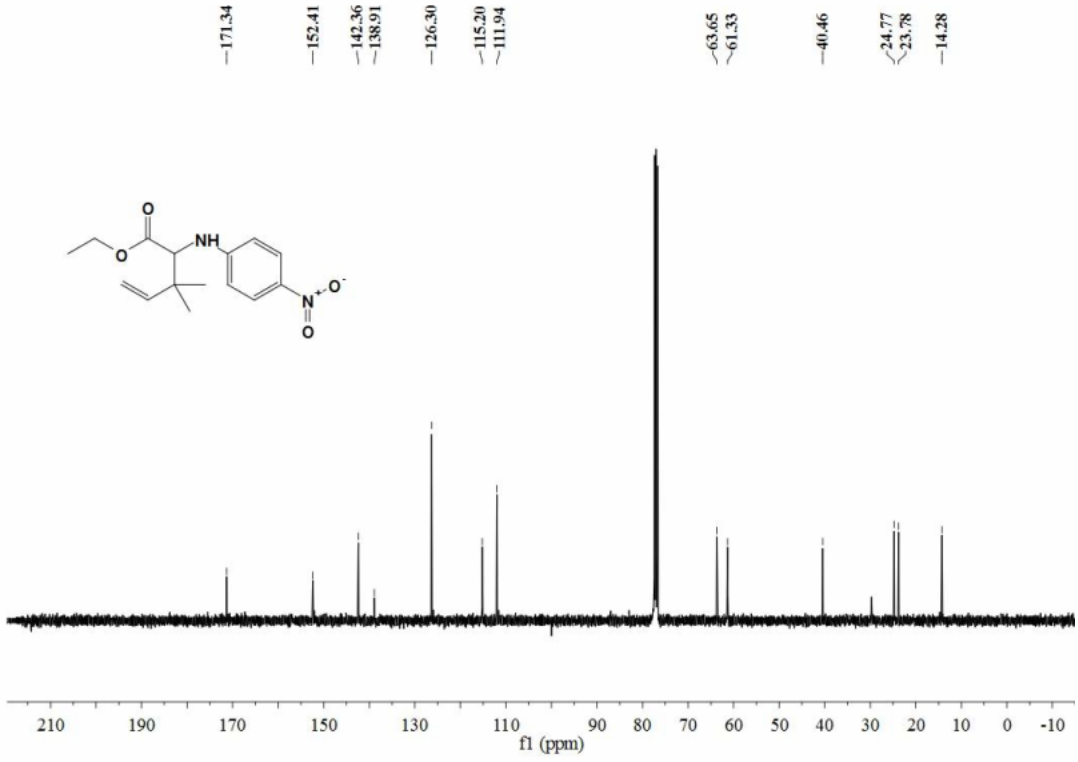
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1, 2- *anti*- 3g-1**



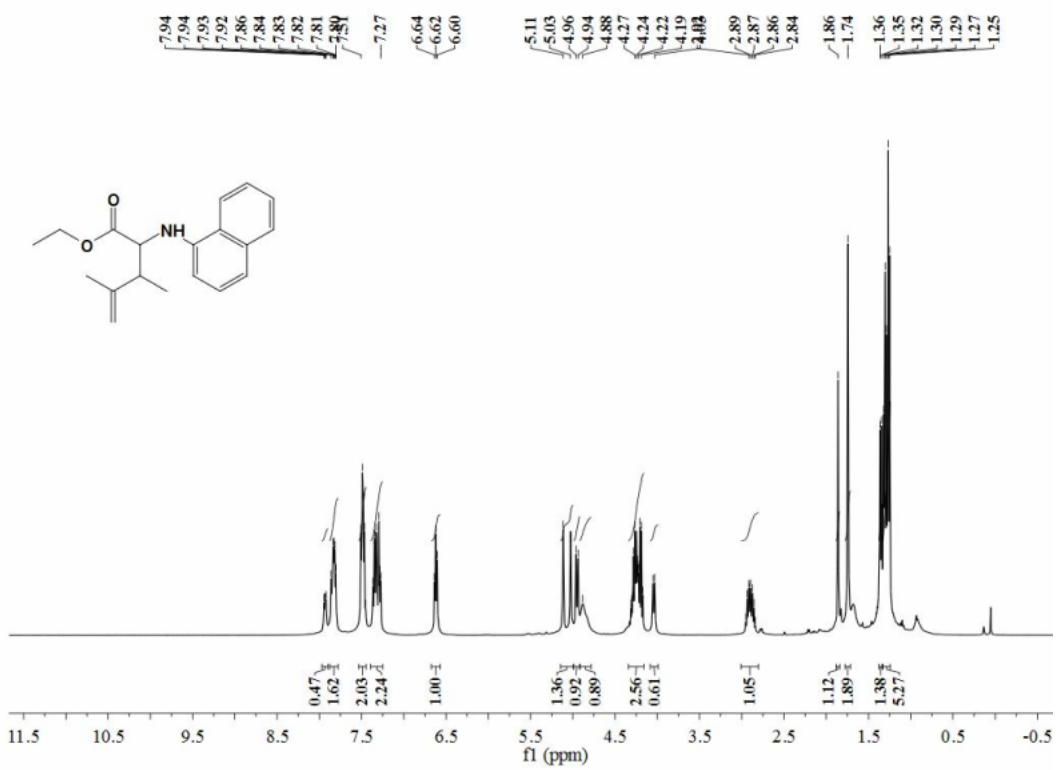
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g-2**



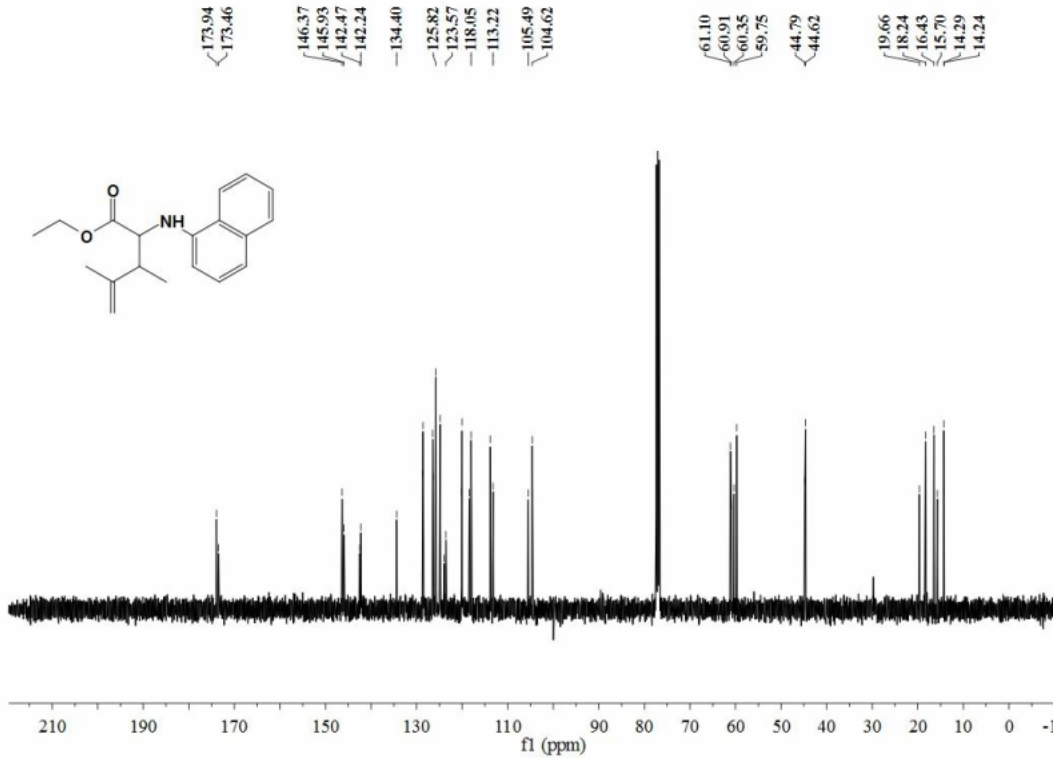
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3g-2**



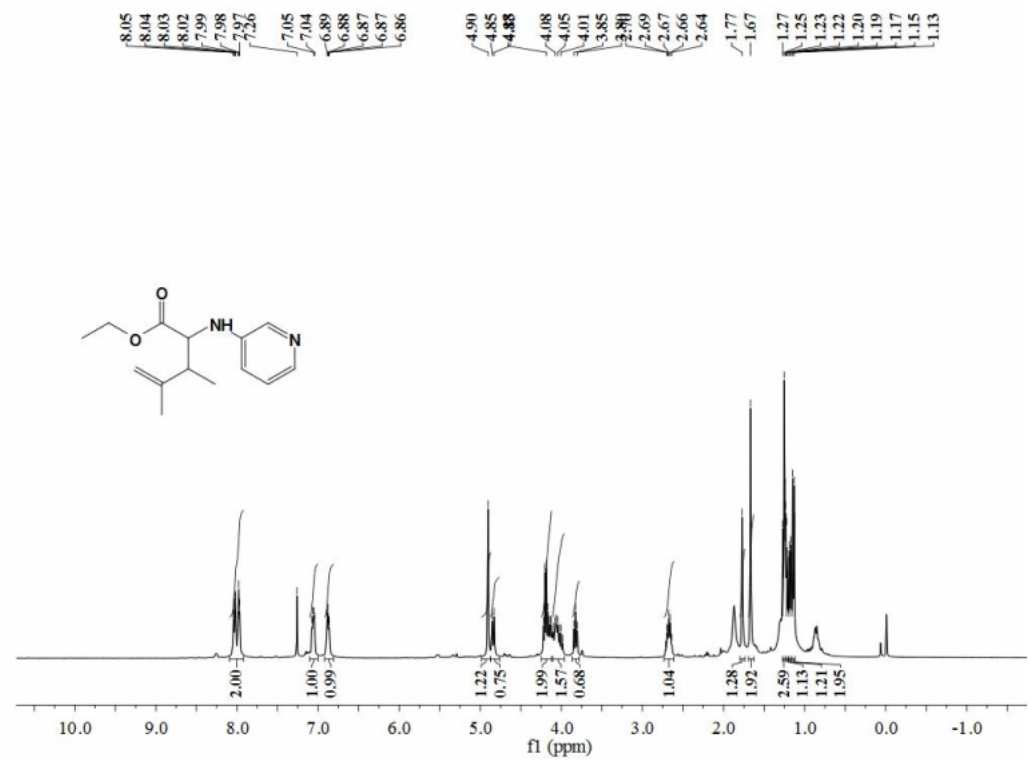
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



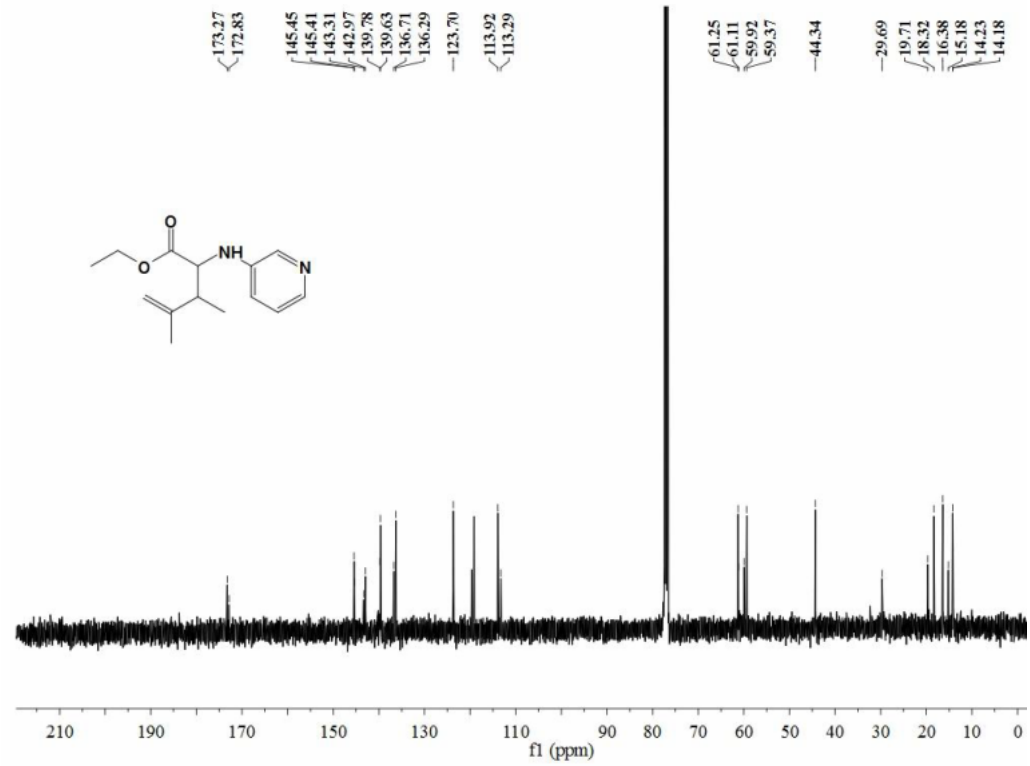
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3h**



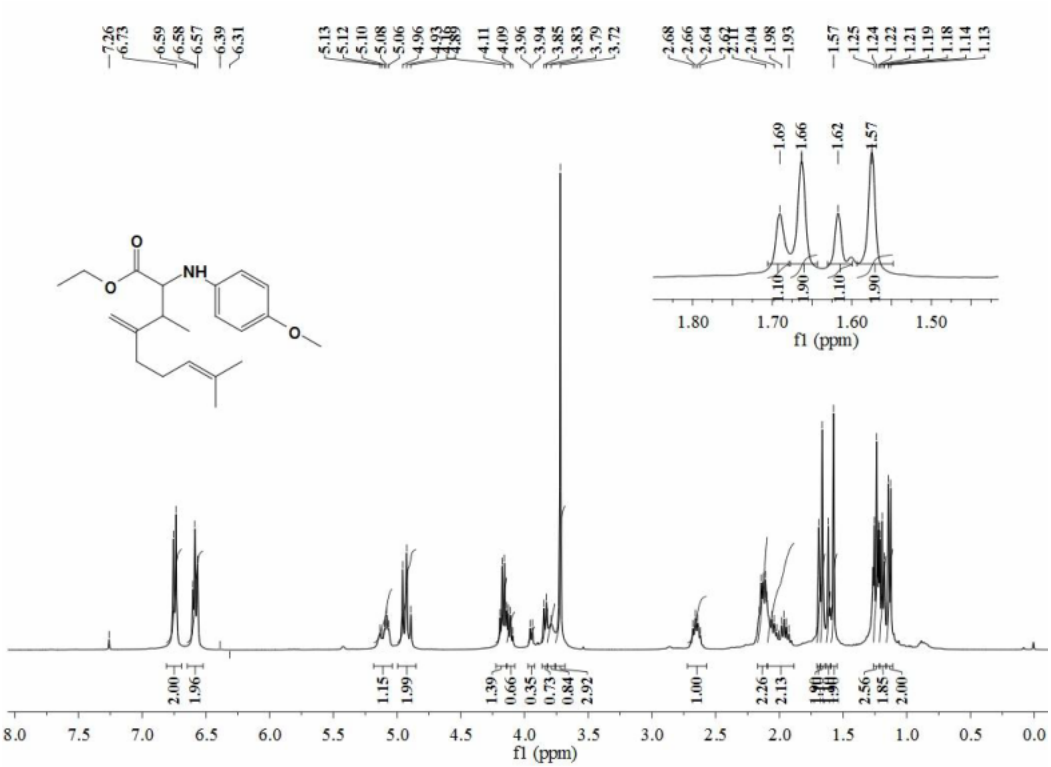
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3i**



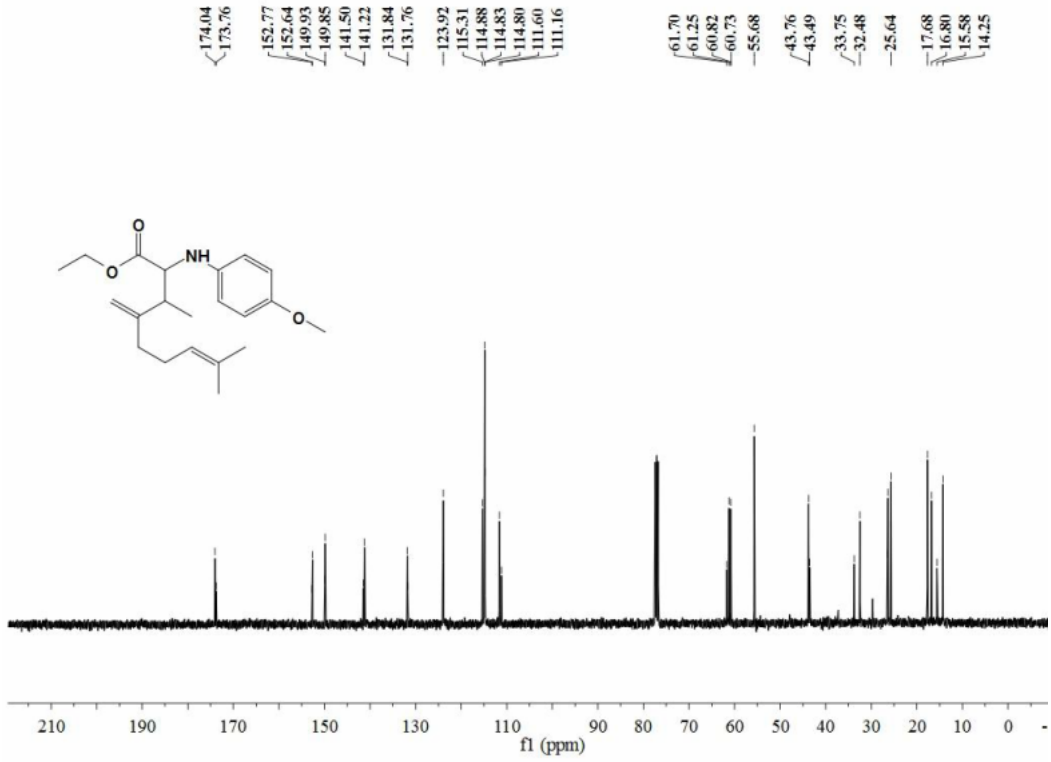
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3i**



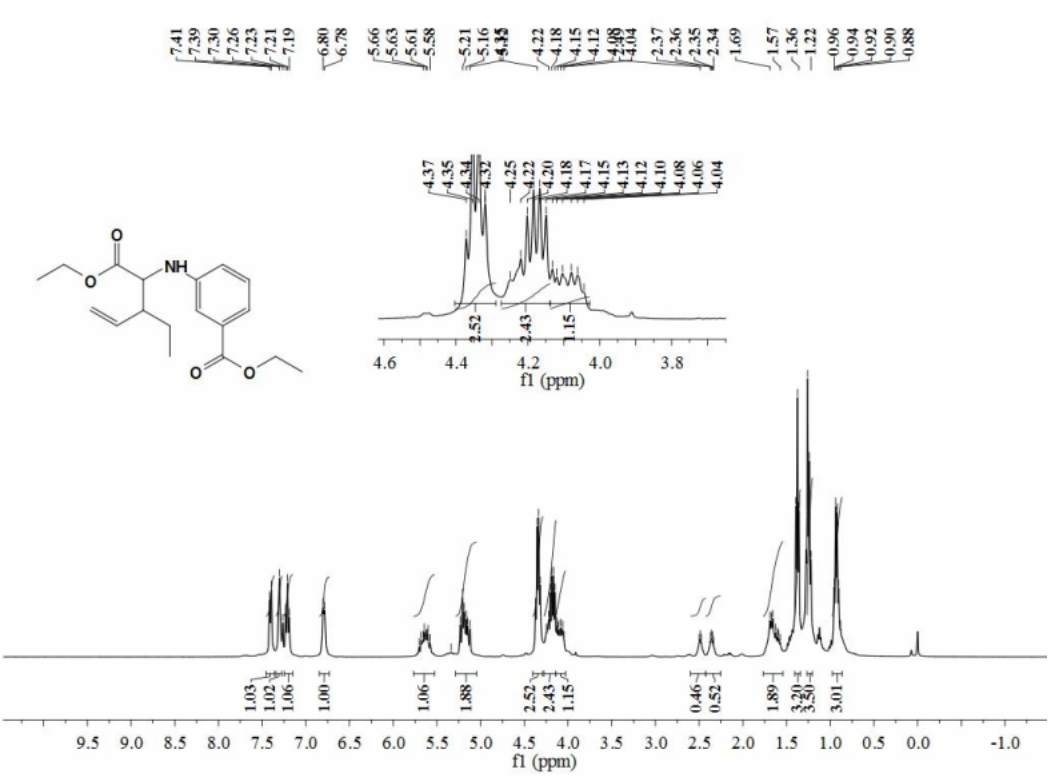
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3j**



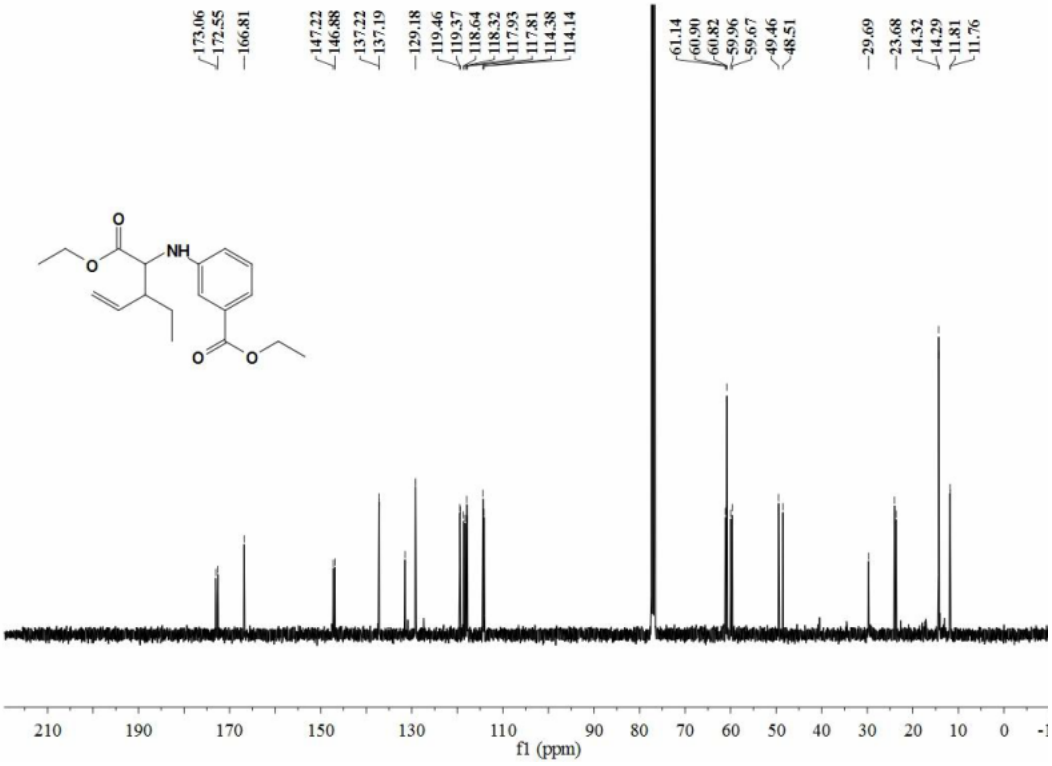
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3j**



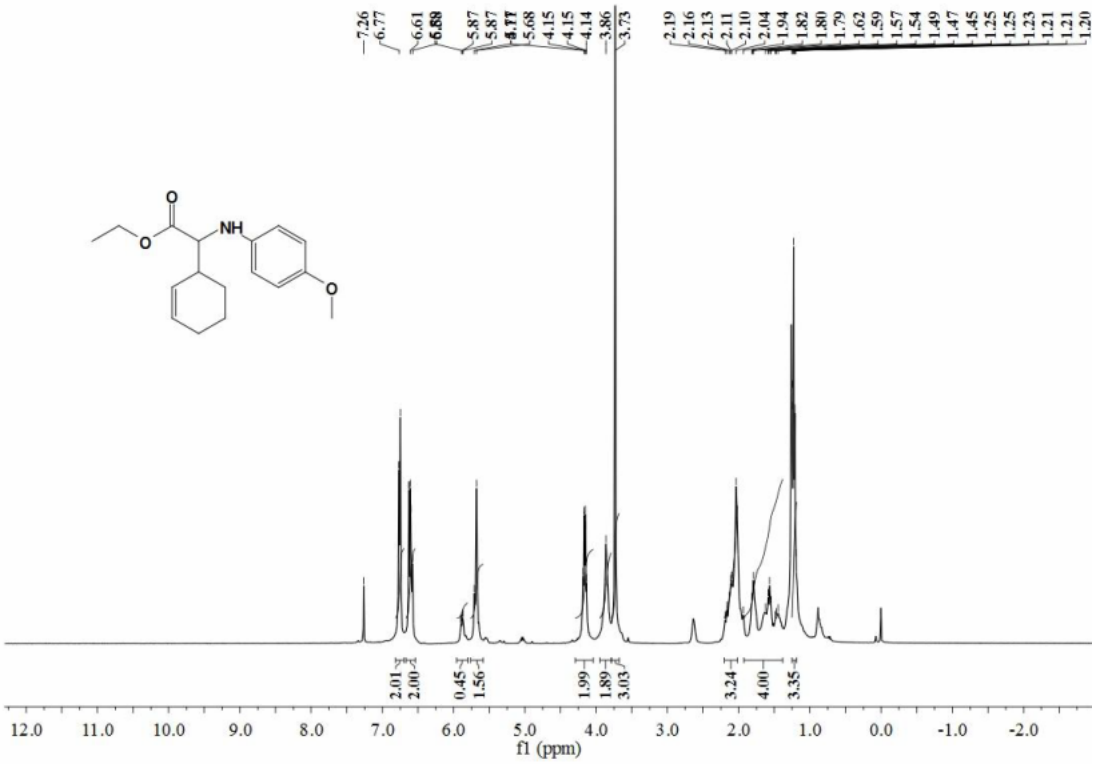
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3k**



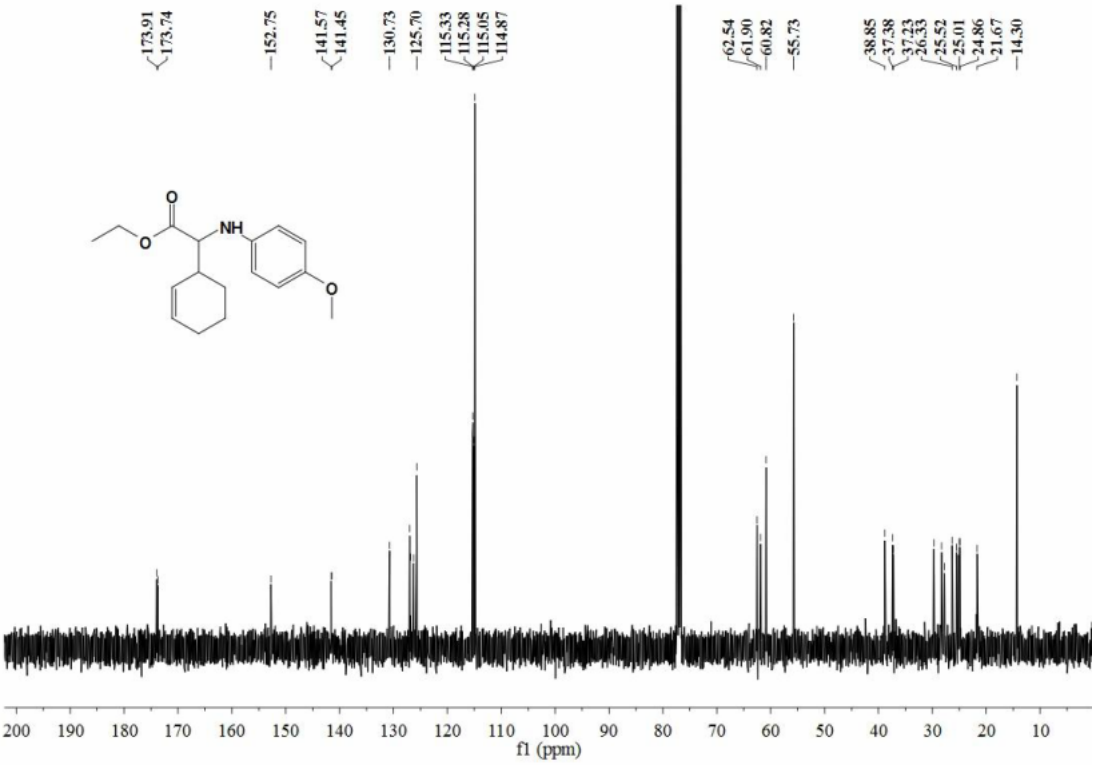
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3k**



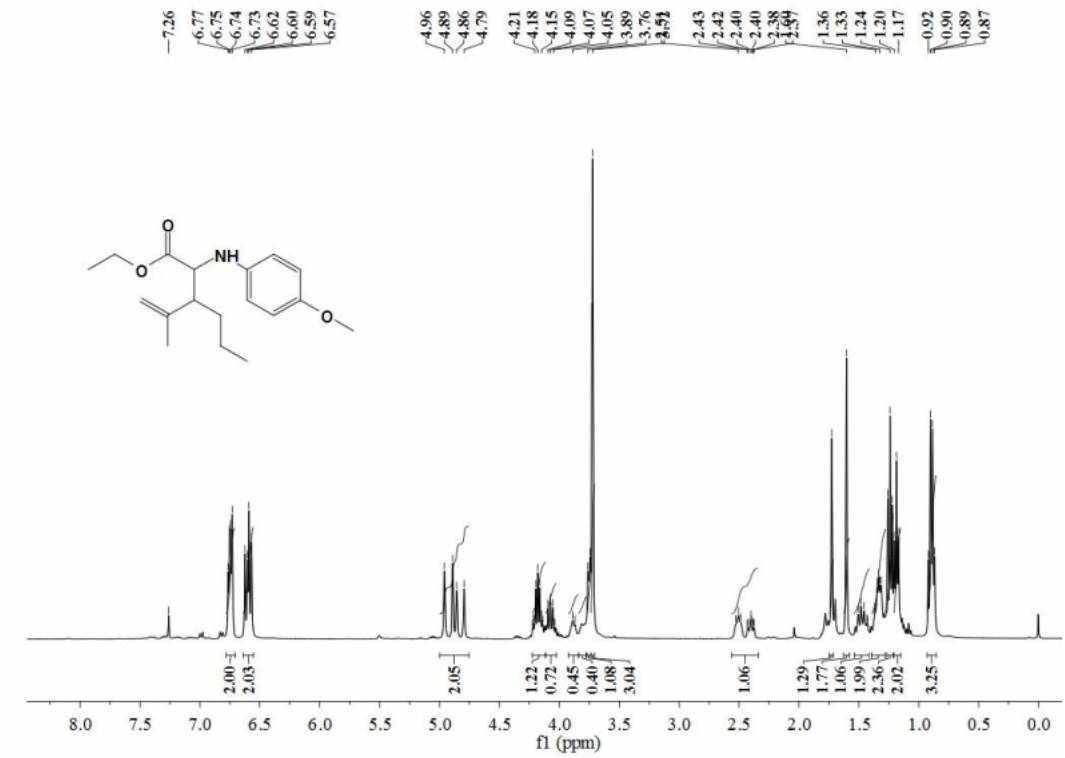
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3l**



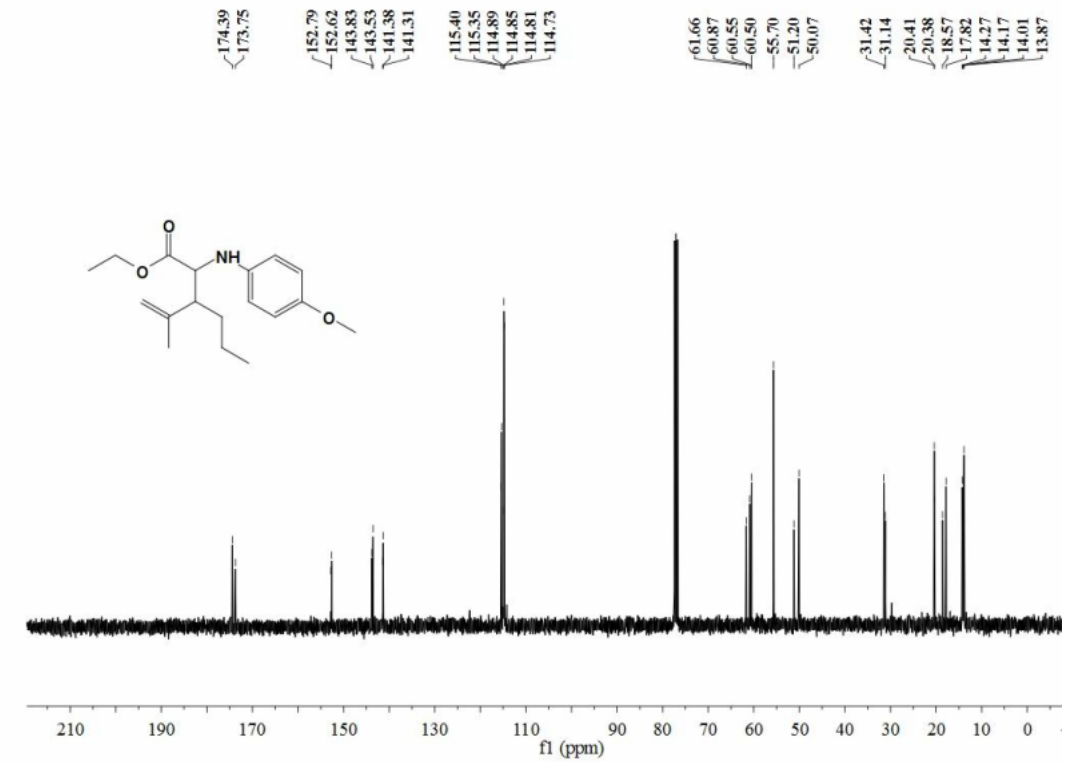
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3l**



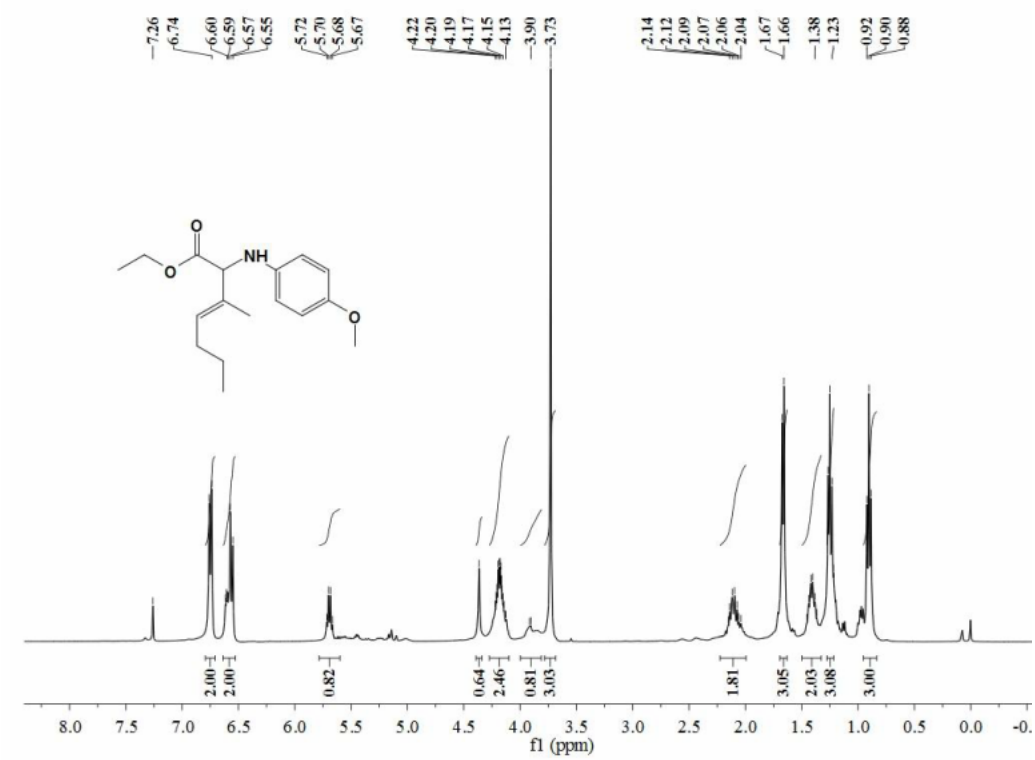
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3m**



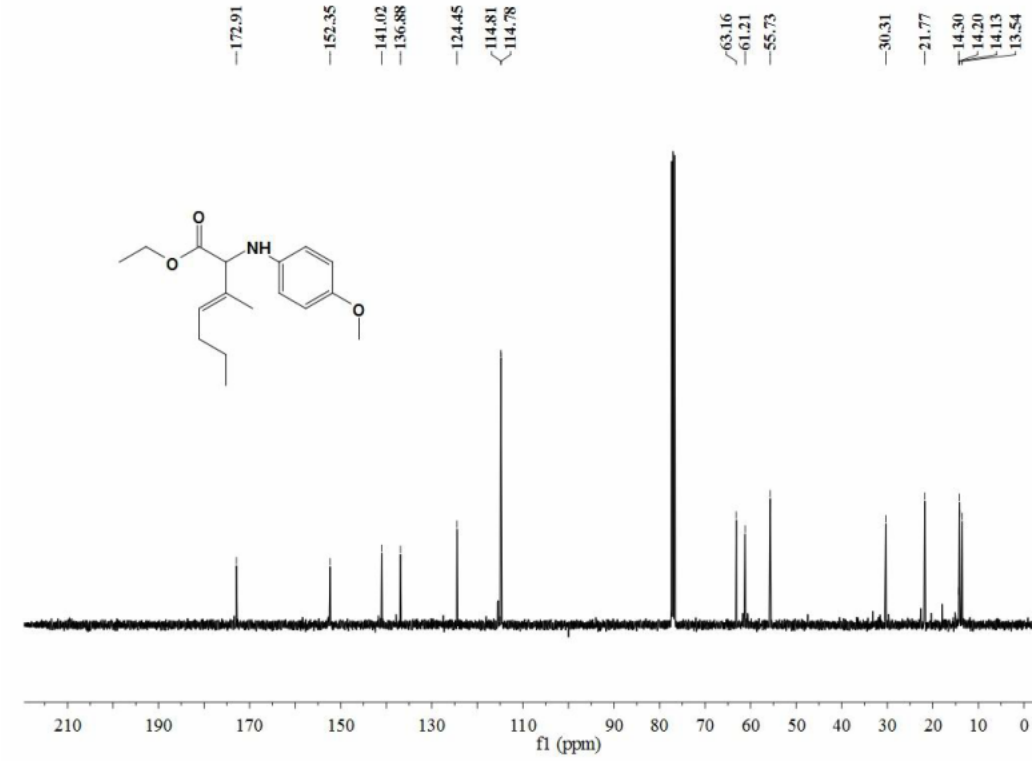
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3m**



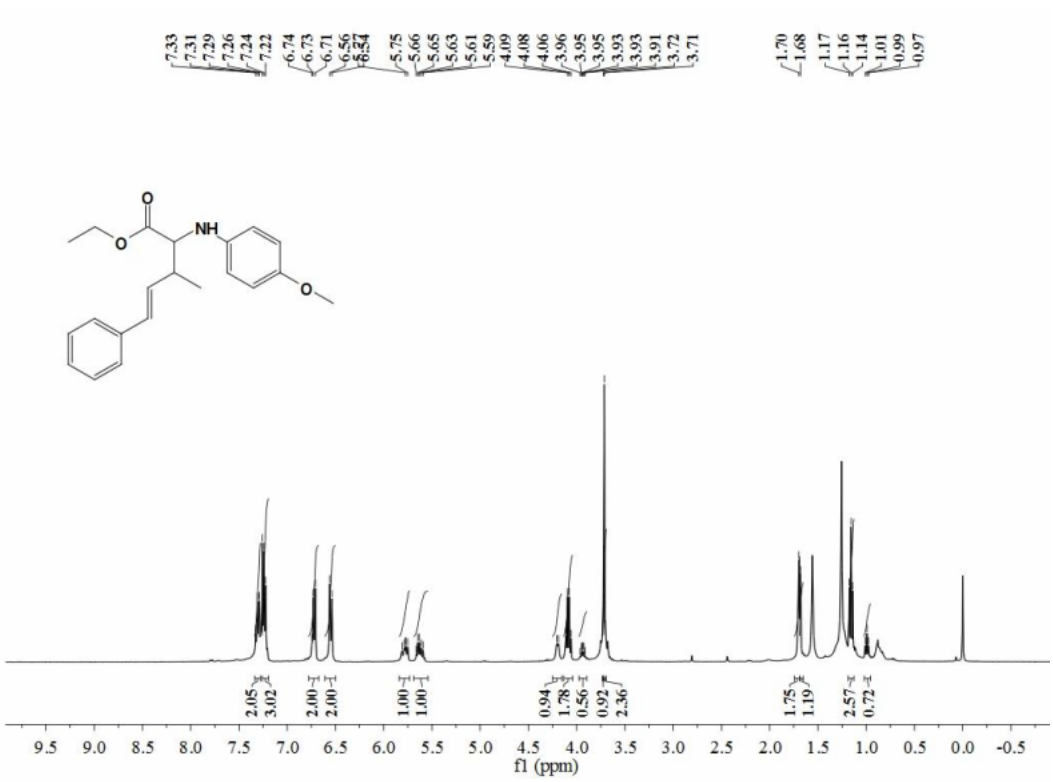
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3n**



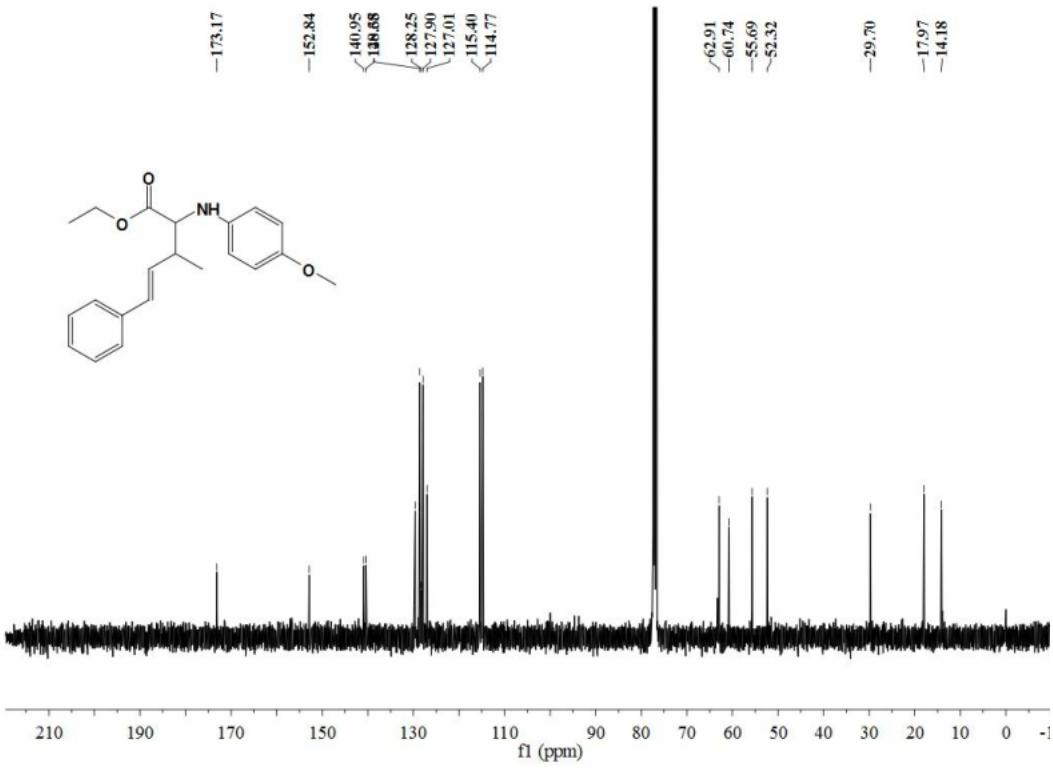
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3n**



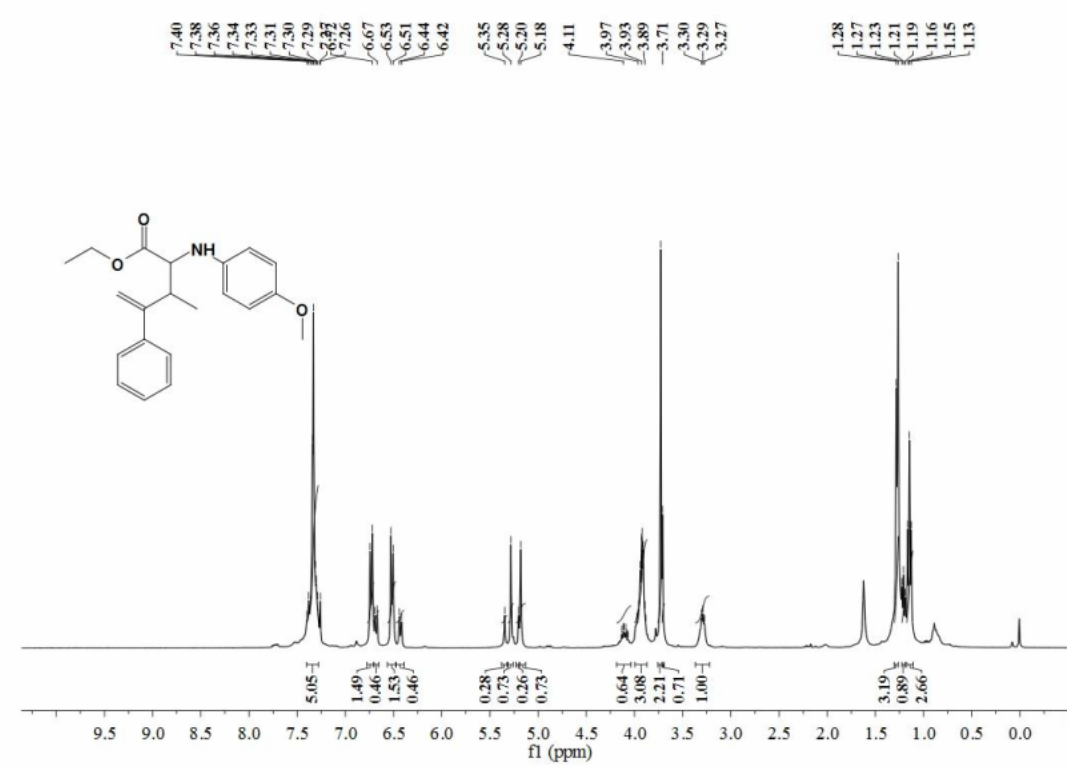
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3o**



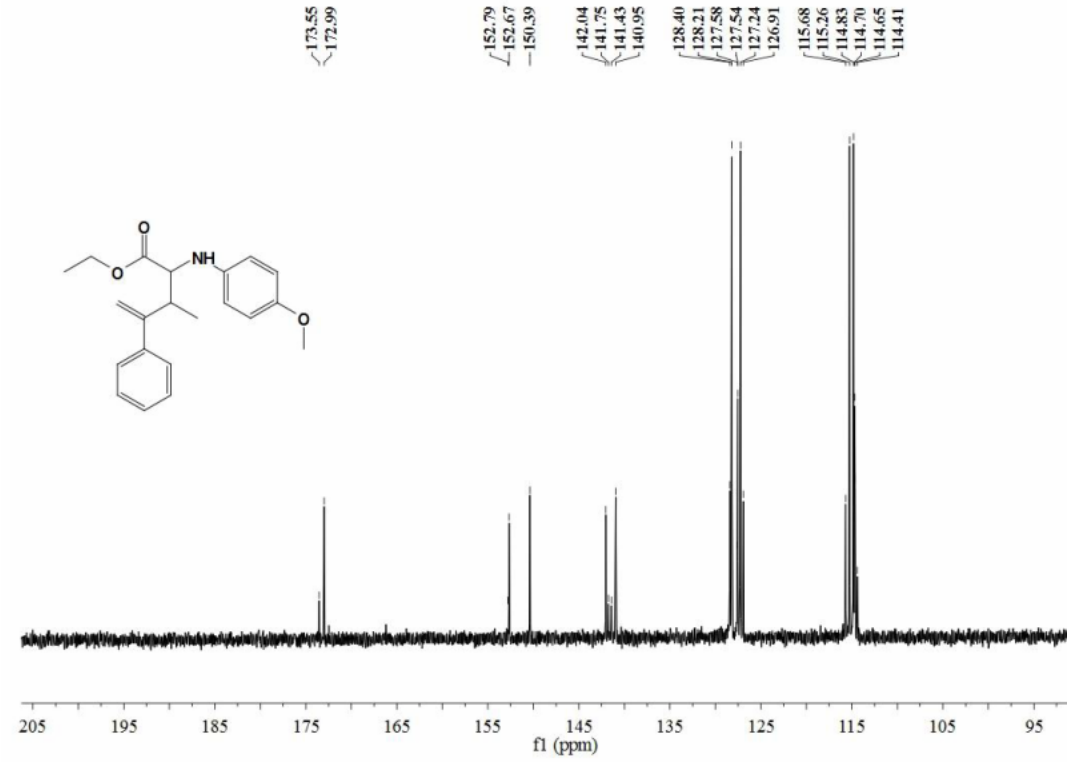
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3o**



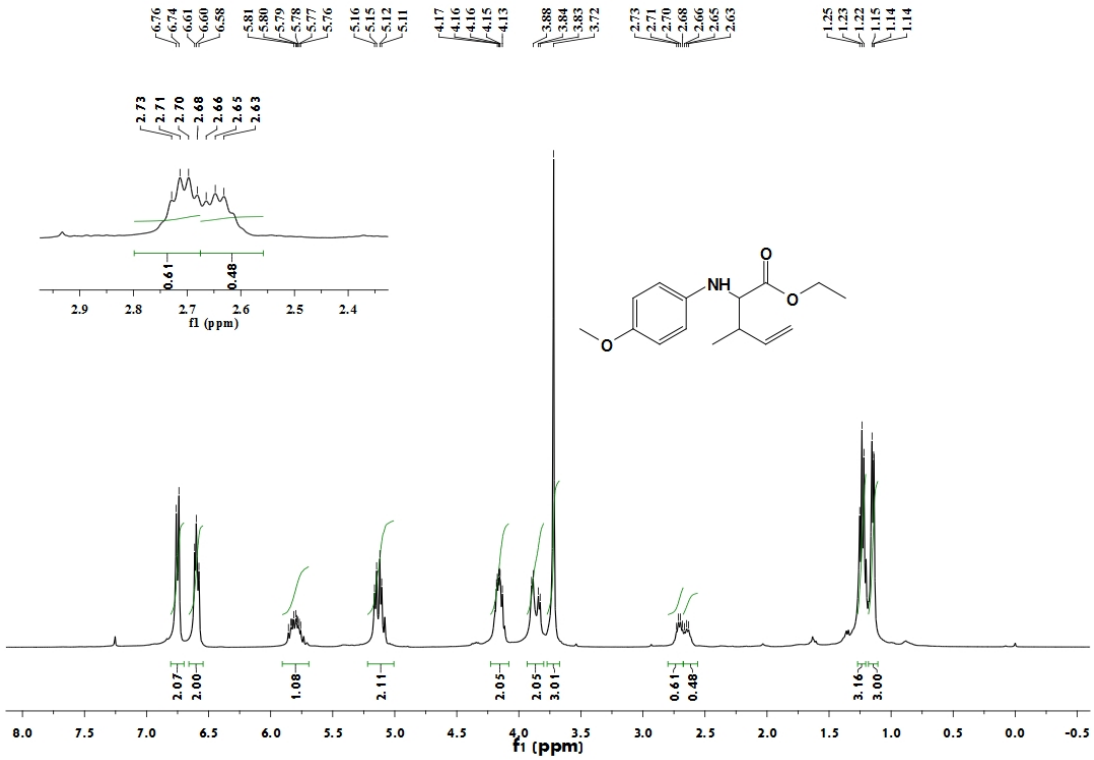
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3q**



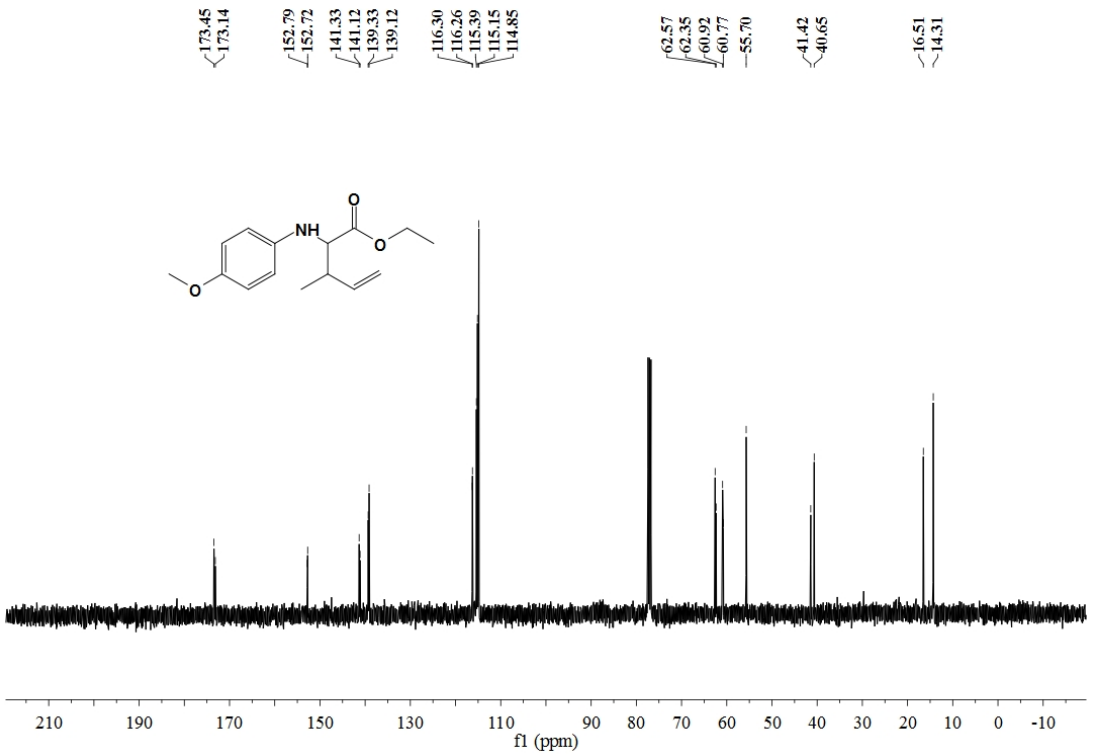
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3q**



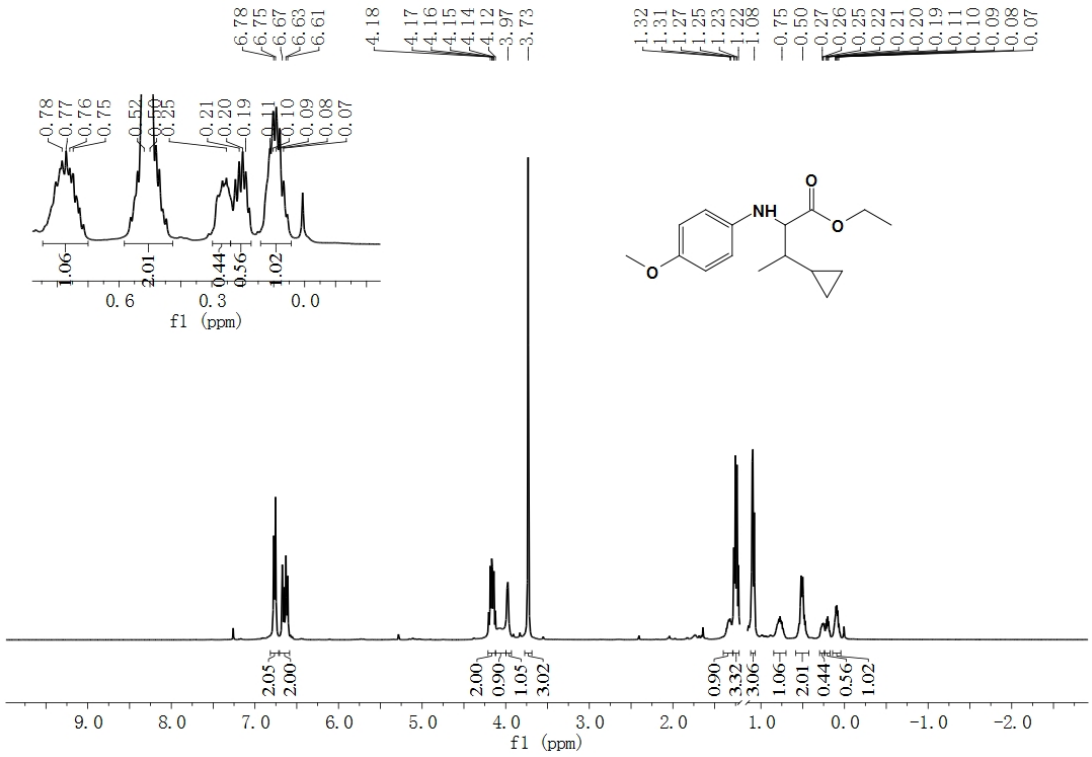
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r**



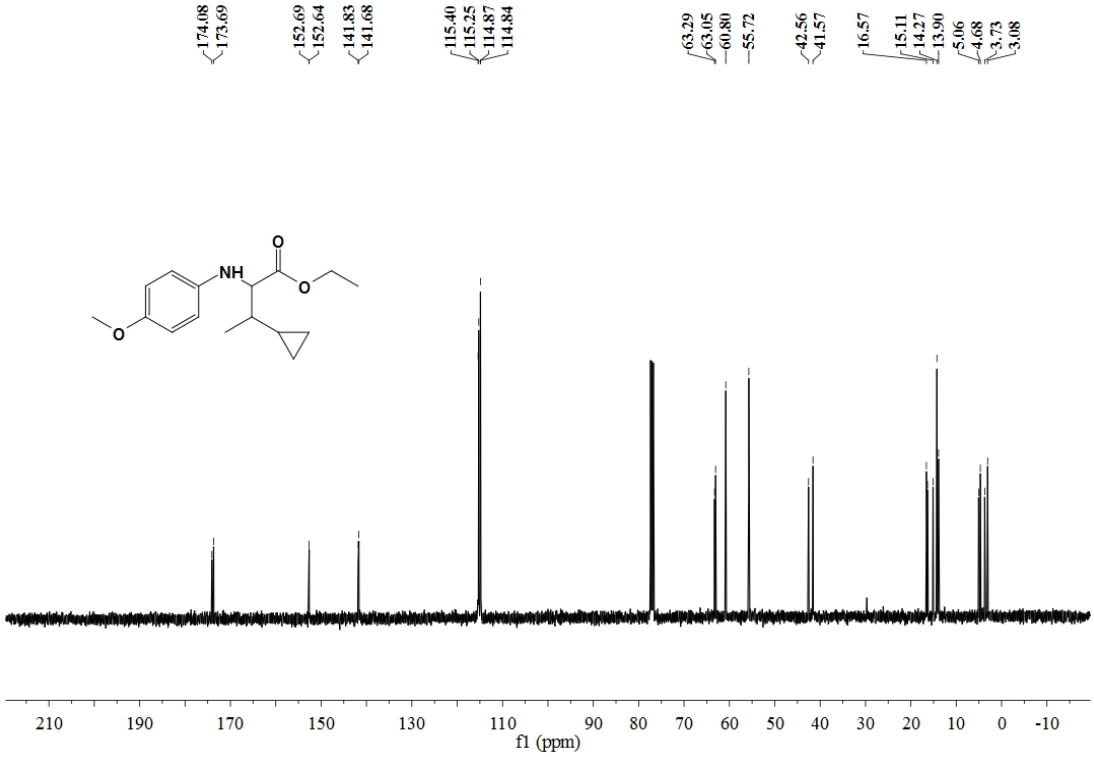
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3r**



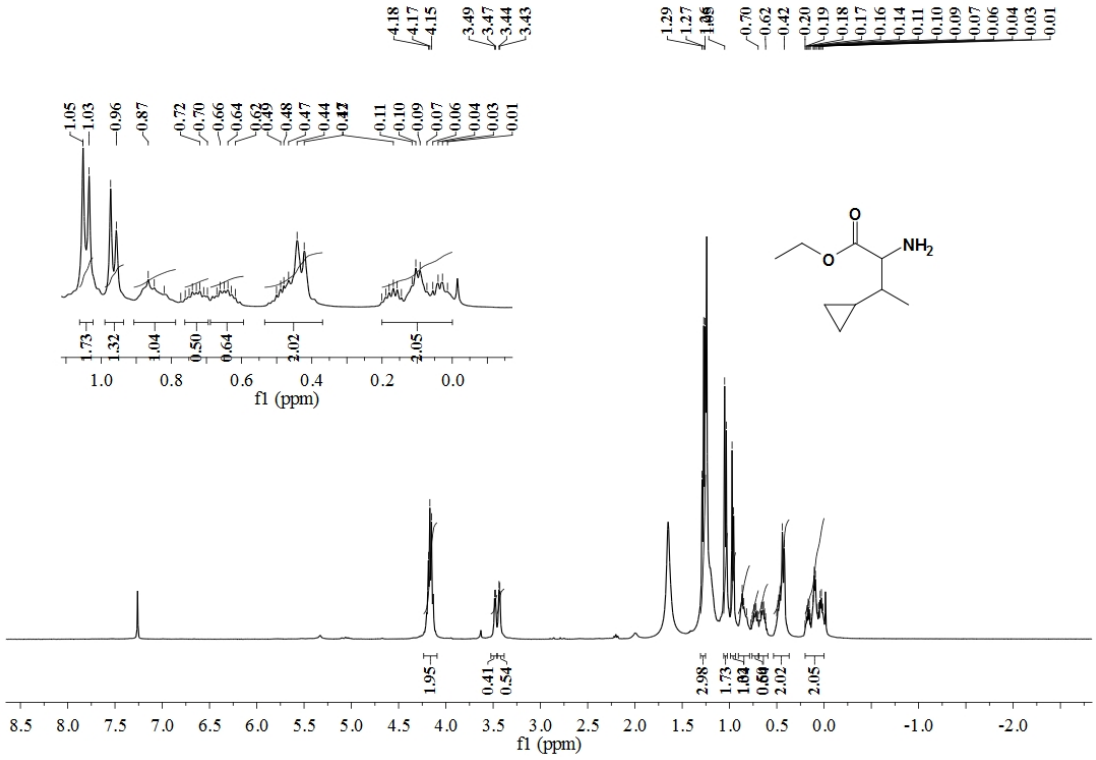
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r-1**



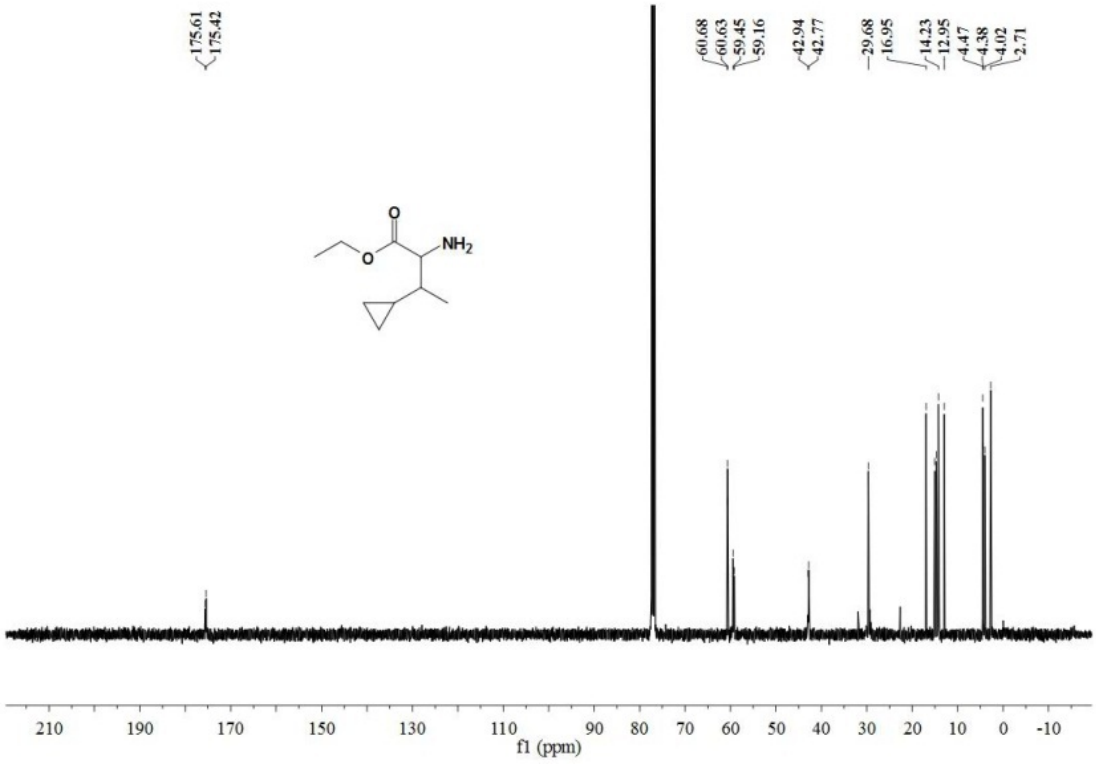
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3r-1**



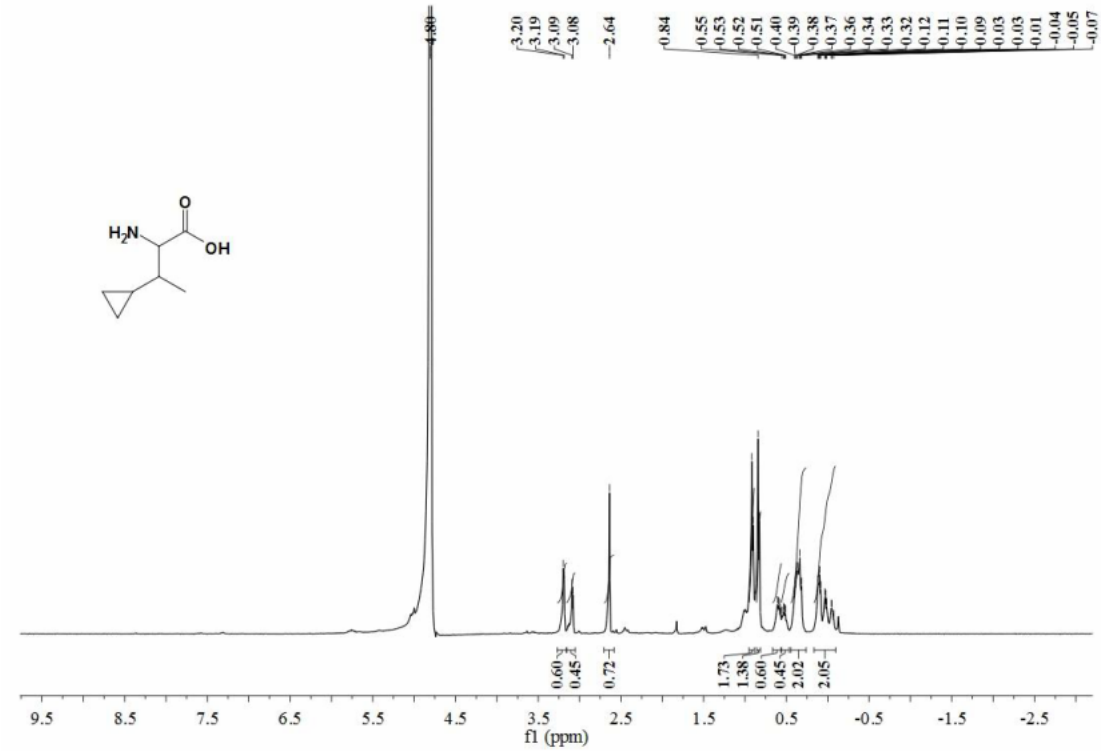
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r-1a**



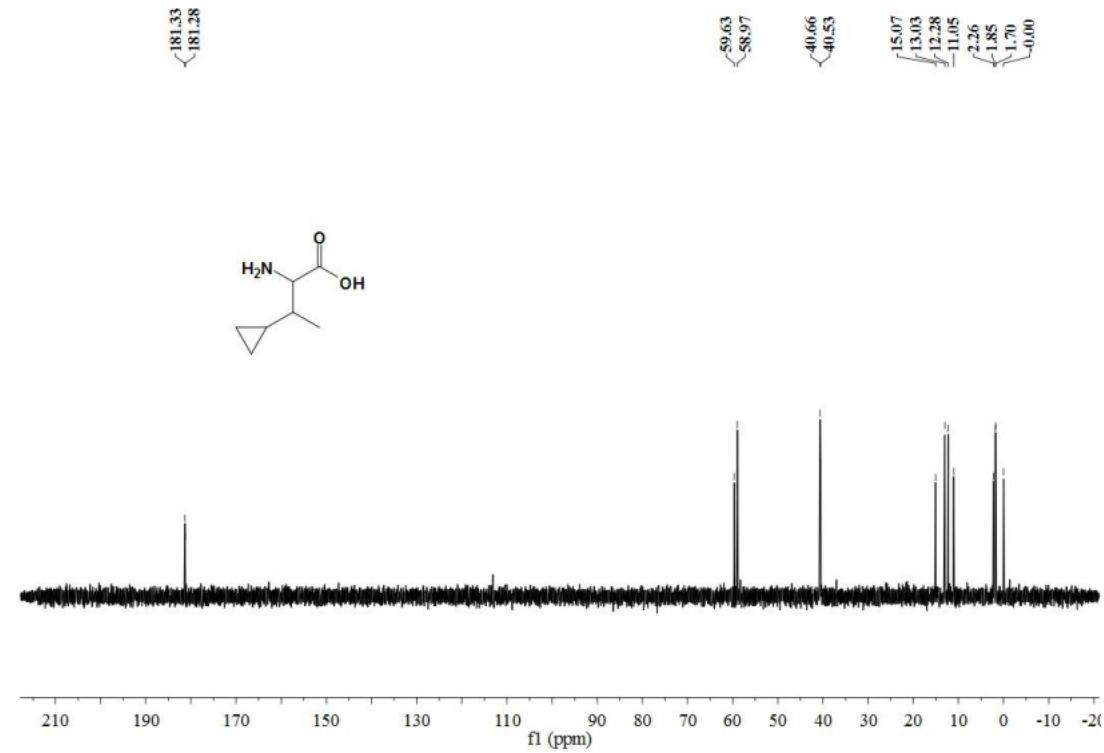
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3r-1a**



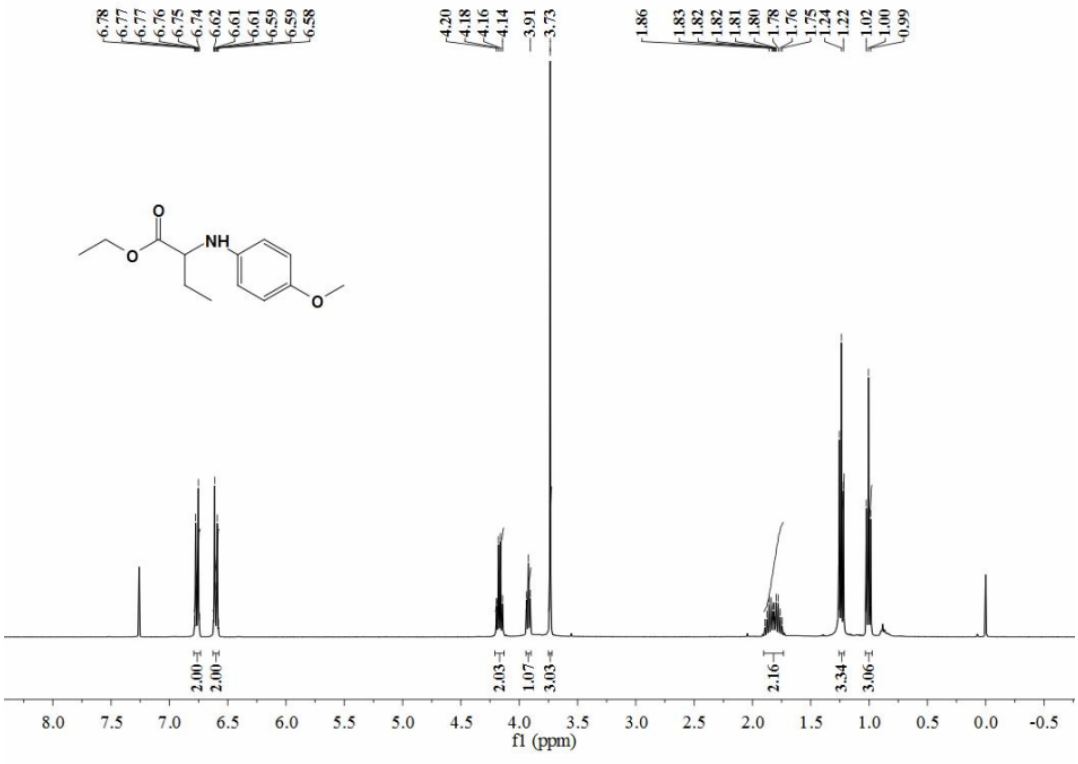
^{1}H NMR spectrum (400 MHz, D_2O) of **3r-2**



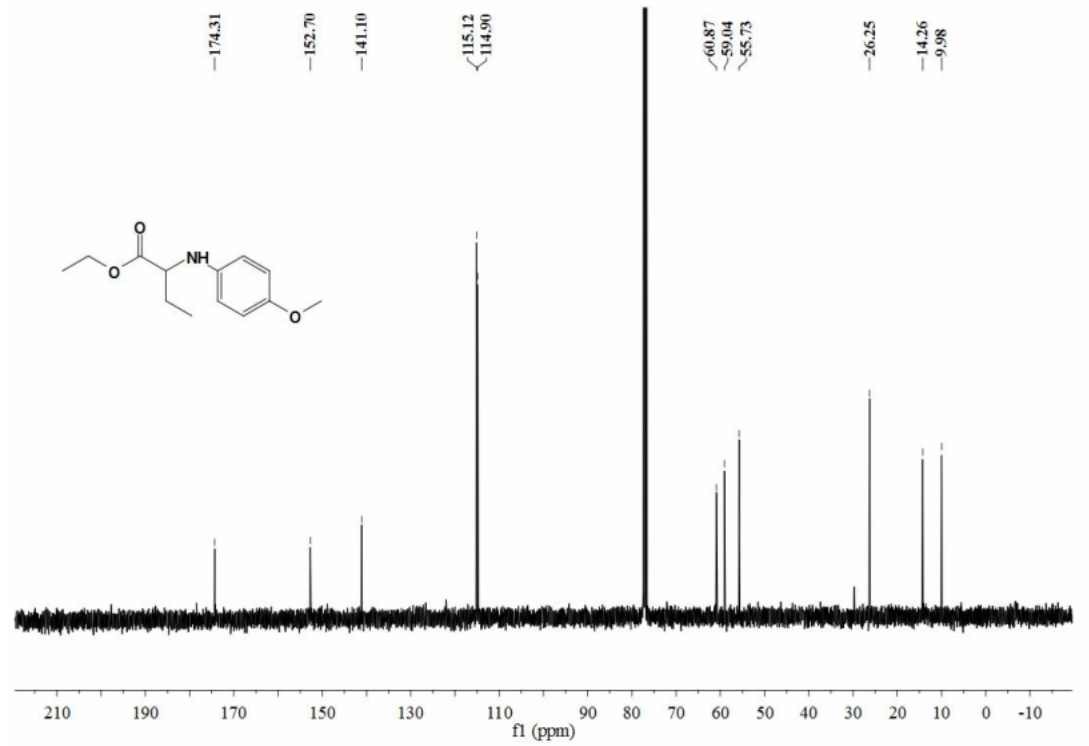
^{13}C NMR spectrum (101 MHz, D_2O) of **3r-2**



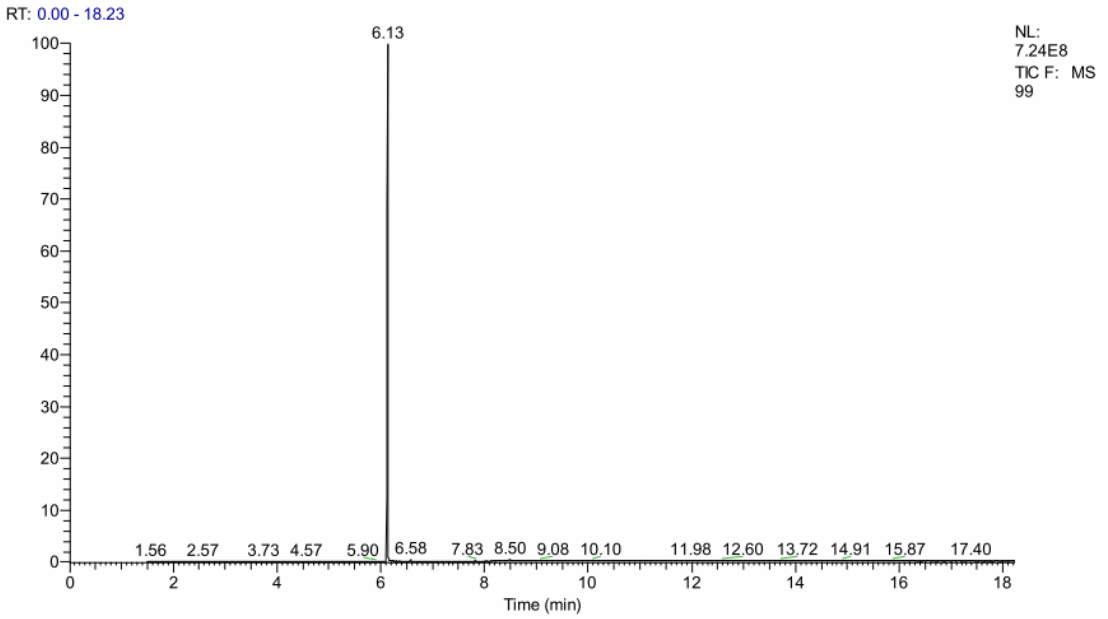
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ab**



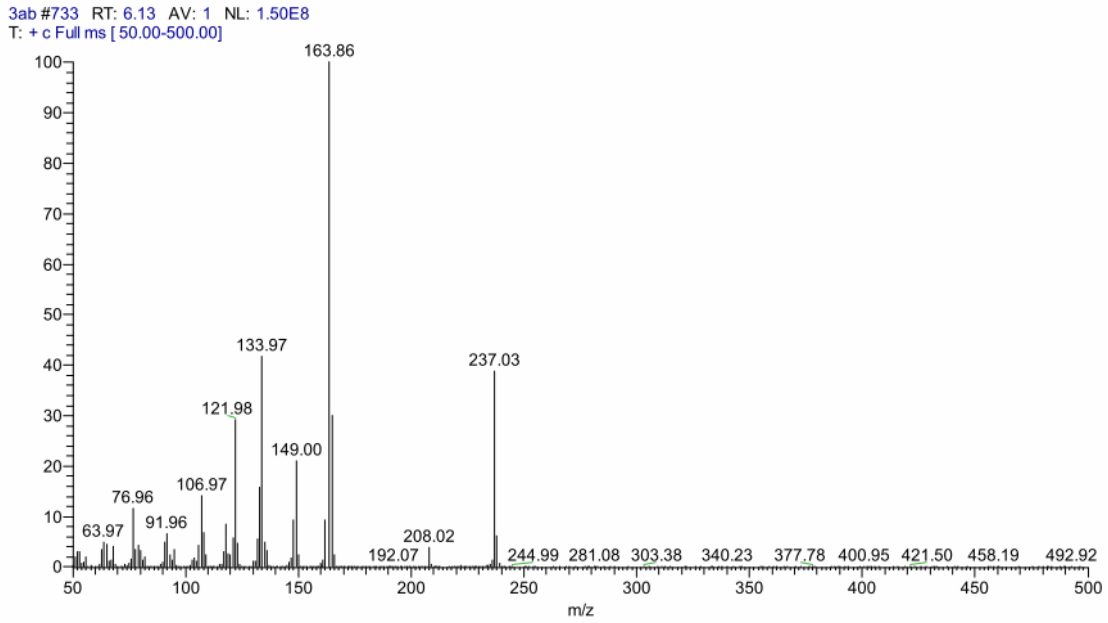
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ab**



8. Copies of GC-MS spectra of 3ab



The GC spectra for the compound **3ab**



The GC-MS spectra for the compound **3ab**