Electronic Supplementary Information

Nickel-catalyzed mild synthesis of functional γ-amino butyric acid esters via direct *α*-C(sp^3)–H allylation of N-alkyl anilines with allyl sulfones

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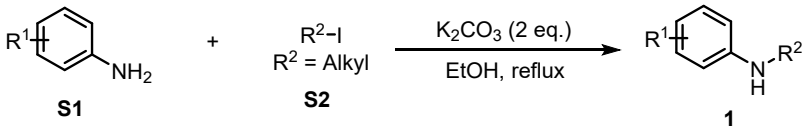
1. General information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-400. Mass spectra were recorded on Trace ISQ GC/MS. High-resolution mass spectra (HRMS) were recorded on a thermo scientific Q Exactive Ultimate 3000 UPLC spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m). Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254). All the reagents were purchased from *Bide Pharmatech Ltd.* and *Energy Chemical*, all the solvents were purchased from *Greagent* (Shanghai Titansci incorporated company) and used without further purification. All the reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

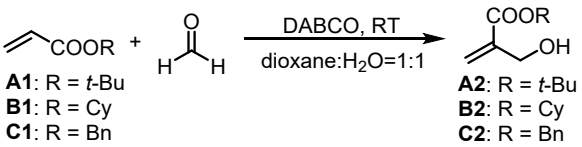
2. Substrate preparation

(1) Synthesis of aniline



To a solution of aniline **S1** (10 mmol) and Alkyl iodide **S2** (10 mmol) in 20 mL EtOH was added K_2CO_3 (2.7 g, 20 mmol). After 2.5 h of reflux, the mixture was cooled down and monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography (10% EtOAc/hexanes) to give **1**.

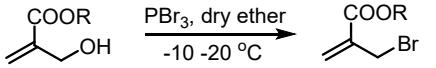
(2) Synthesis of Allyl Sulfones[1]



A1: R = *t*-Bu
B1: R = Cy
C1: R = Bn

A2: R = *t*-Bu
B2: R = Cy
C2: R = Bn

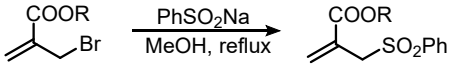
To a solution of paraformaldehyde (1.99 g, 66.6 mmol) and acrylic ester (**A1**, **B1**, **C1**) (50 mmol) in 40 mL dioxane-water (1:1, v/v) was added DABCO (7.48 g, 66.7 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (200 mL) and water (100 mL). The organic layer was separated and washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (50% EtOAc/hexanes) to afford (**A2**, **B2**, **C2**).



A2: R = *t*-Bu
B2: R = Cy
C2: R = Bn

A3: R = *t*-Bu
B3: R = Cy
C3: R = Bn

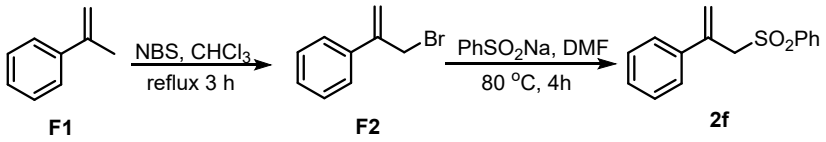
To a solution of **A2** or **B2** or **C2** (23.0 mmol) was added phosphorus (III) bromide (0.76 mL, 8.0 mmol) in dry ether (20 mL) at -10 °C. The temperature was allowed to rise to room temperature, and stirring was continued for 3 h. Water (10 mL) was then added and the mixture was extracted with petroleum ether (3 x 50 mL). The organic phase was washed with saturated sodium chloride solution (50 mL), dried with sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (10% hexanes/EtOAc) to give **A3** or **B3** or **C3**.



A3: R = *t*-Bu
B3: R = Cy
C3: R = Bn
D1: R = Et
E1: R = Me

2c: R = *t*-Bu
2d: R = Cy
2e: R = Bn
2a: R = Et
2b: R = Me

To a solution of **A3** or **B3** or **C3** or **D1** or **E1** (10.4 mmol) in dry methanol (25 mL) was added sodium phenylsulfinate (2.50 g, 15.2 mmol) and refluxed. After 2.5 h, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography (50% EtOAc/hexanes) to give **2a**-**2e**.

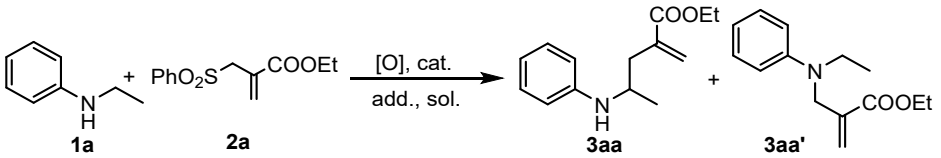


A solution of a-methyl styrene **F1** (8.3 mL, 64 mmol) and N-bromosuccinimide (NBS, 15.0 g, 84 mmol) in chloroform (15 mL) was heated to reflux for 3 h. The mixture was cooled down after reflux and the filtrated was evaporated and purified by chromatography (100% hexanes) to afford l-bromo-2-phenyl-2-propene **F2**.

Then to a solution of the l-bromo-2-phenyl-2-propene (2.61 g, 13.2 mmol) in dry DMF (40 mL) was added sodium benzenesulfinate. This mixture was heated to 80 °C for 4 h, cooled, and diluted with EtOAc (100 mL). The mixture was washed with water (3 x 50 mL), brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography (20% hexane/ EtOAc) afforded **2f** as a white solid.

3. Detailed Optimization Studies

Table S1 Optimization of reaction conditions[a]



Entry	Catalyst	[O]	Additive	Solvent	**3aa** (%)[b]	**3aa'** (%)
1	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	DMF	33	0
2	$NiCl_2{\cdot}6H_2O$	TBHP	-	DMF	20	0
3	$Ni(OTf)_2$	TBHP	-	DMF	25	0
4	NiI_2	TBHP	-	DMF	19	0
5	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	CH_3CN	trace	0
6	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	dioxane	0	0
7	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	DCE	23	0
8	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	EtOAc	39	0
9	$Ni(OAc)_2{\cdot}4H_2O$	TBHP	-	EtOH	42	0
10	$Ni(OAc)_2{\cdot}4H_2O$	$K_2S_2O_8$		EtOH	0	0
11	$Ni(OAc)_2{\cdot}4H_2O$	DDQ		EtOH	0	12
12	$Ni(OAc)_2{\cdot}4H_2O$	*m*-CPBA		EtOH	0	0
13	$Ni(OAc)_2{\cdot}4H_2O$	DCP		EtOH	trace	trace
14	$Ni(OAc)_2{\cdot}4H_2O$	O_2		EtOH	0	18

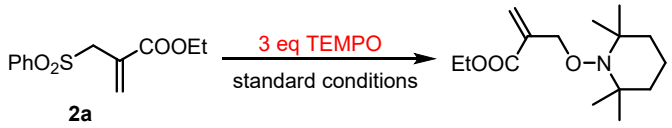
[a]Reaction conditions: unless otherwise stated, all the reactions were conducted with **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (30 mol %), oxidant (1.5 eq.) and solvent (1.5 mL) at 70 °C for 18 h under N_2 atmosphere. [b]Isolated yield.

4. Typical procedure for the synthesis of 3

The mixture of amine **1** (0.3 mmol), allyl sulfone **2** (3 eq., 0.9 mmol), TBHP (2.5 eq.,

0.75 mmol, 70 wt % in water), and $Ni(OAc)_2 \cdot 4H_2O$ (20 mmol %) in EtOH (1.5 mL) was introduced into a Schlenk tube (25 mL) was stirred at 70 °C for 18 h under N_2 atmosphere. After cooling down to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (20:1), which afforded **3** as a yellow oil.

5. Mechanistic Studies



2a

5, detected by HRMS
Calcd. for [M+H]+: 270.2064; Found: m/z 270.2064.

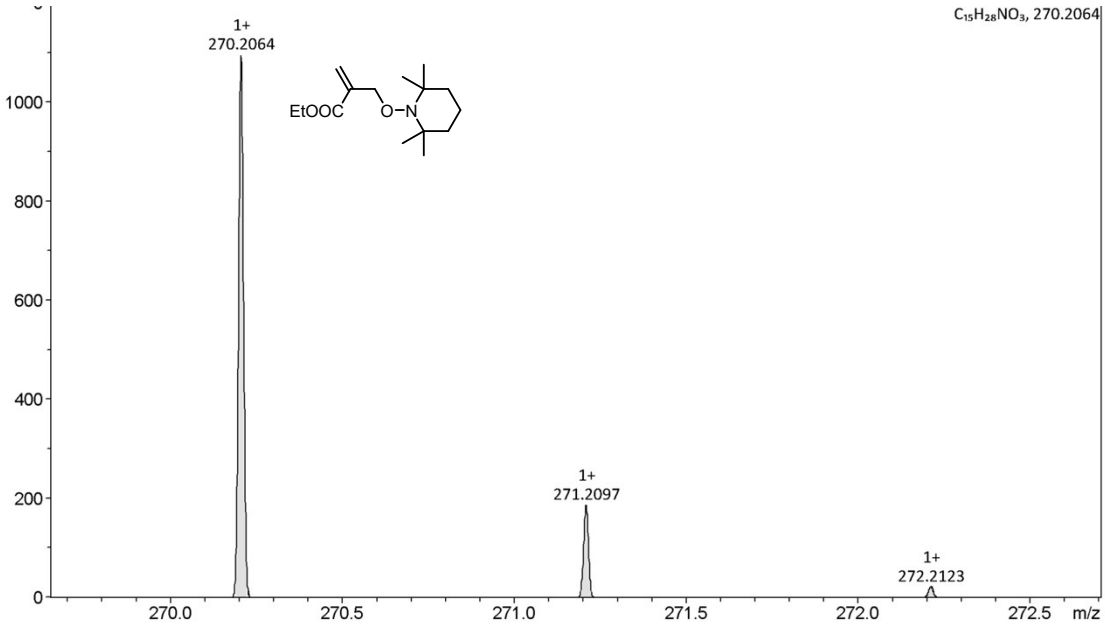
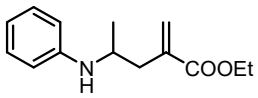


Figure S1 HRMS of compound 5

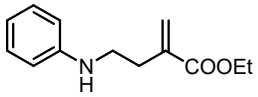
6. Analytic data of the obtained compound

(1) ethyl 2-methylene-4-(phenylamino)pentanoate (3aa)[2]



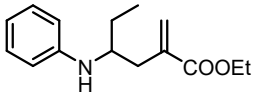
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.71 – 6.64 (m, 3H), 6.23 (s, 1H), 5.60 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.71 (q, *J* = 6.4 Hz, 1H), 2.75 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.33 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 147.5, 138.4, 129.4, 127.2, 117.3, 113.4, 61.0, 48.2, 39.4, 20.8, 14.3. MS (EI, m/z): 233.1 $[M]^+$.

(2) ethyl 2-methylene-4-(phenylamino)butanoate (3ba)



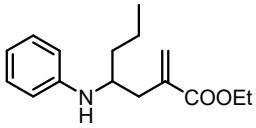
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 5.63 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 148.1, 138.4, 129.4, 126.7, 117.5, 113.0, 61.0, 43.0, 32.1, 14.3. MS (EI, m/z): 219.1 $[M]^+$.

(3) ethyl 2-methylene-4-(phenylamino)hexanoate (3ca)



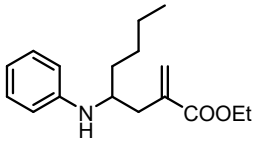
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.4 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 6.20 (s, 1H), 5.58 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.60 (s, 1H), 3.52 (q, *J* = 6.4 Hz, 1H), 2.61 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.44 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.62 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.47 (dt, *J* = 14.0, 7.0 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 147.9, 138.3, 129.4, 127.2, 116.9, 113.1, 61.0, 53.9, 37.1, 27.4, 14.3, 10.3. HRMS (ESI): Calcd. for $[M+H]^+$: 248.1641; Found: m/z 248.1645.

(4) ethyl 2-methylene-4-(phenylamino) heptanoate (3da)



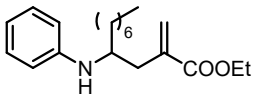
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.5 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 6.20 (s, 1H), 5.57 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.61 – 3.57 (m, 1H), 2.62 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.43 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.51 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.46 – 1.39 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 147.9, 138.3, 129.4, 127.2, 116.9, 113.0, 61.0, 52.3, 37.6, 37.1, 19.3, 14.3, 14.2. HRMS (ESI): Calcd. for $[M+H]^+$: 262.1798; Found: m/z 262.1802.

(5) ethyl 2-methylene-4-(phenylamino)octanoate (3ea)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.4 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 6.20 (s, 1H), 5.57 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.59 – 3.56 (m, 1H), 2.62 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.44 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.56 (d, *J* = 10.4 Hz, 1H), 1.42 (dd, *J* = 13.8, 6.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 147.9, 138.3, 129.4, 127.2, 116.8, 113.0, 61.0, 52.5, 37.6, 34.6, 28.2, 22.9, 14.3, 14.2. HRMS (ESI): Calcd. for $[M+H]^+$: 276.1955; Found: m/z 276.1958.

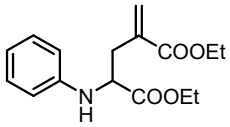
(6) ethyl 2-methylene-4-(phenylamino)hexanoate (3fa)



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.4 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 6.21 (d, *J* = 1.4 Hz, 1H), 5.6 – 5.56 (m, 1H), 4.21 (qd, *J* = 7.0, 2.6 Hz, 2H), 3.59 – 3.56 (m, 1H), 2.63 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.43 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.56 (dtd, *J* = 11.8, 6.6, 2.0 Hz, 1H), 1.43 (ddt, *J* = 12.8, 9.0, 3.4 Hz, 2H), 1.39 – 1.34 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 4H), 2.27 (s, 7H), 0.88 (t, *J* = 6.8 Hz,

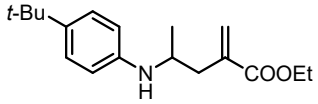
3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 147.9, 138.3, 129.4, 127.2, 116.8, 113.0, 60.9, 52.5, 37.6, 34.9, 31.9, 29.8, 29.4, 26.1, 22.8, 14.3, 14.2. HRMS (ESI): Calcd. for $[M+H]^+$: 318.2424; Found: m/z 318.2428.

(7) diethyl 2-methylene-4-(phenylamino) pentanedioate (3ga)



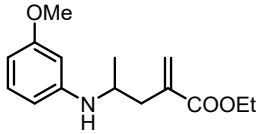
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.25 (s, 1H), 5.65 (s, 1H), 4.32 (d, *J* = 7.0 Hz, 1H), 4.23 (d, *J* = 7.0 Hz, 2H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.90 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.72 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.23 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 166.9, 146.6, 136.5, 129.4, 128.2, 118.4, 113.6, 61.3, 56.3, 35.7, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 292.1539; Found: m/z 292.1543.

(8) ethyl 4-((4-(tert-butyl)phenyl)amino)-2-methylenepentanoate (3ha)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.2 Hz, 2H), 6.24 (s, 1H), 5.62 (s, 1H), 4.24 (q, *J* = 6.4 Hz, 2H), 3.69 (q, *J* = 6.4 Hz, 1H), 3.54 (s, 1H), 2.76 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.32 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H), 1.19 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 145.0, 139.8, 138.3, 127.3, 126.1, 112.9, 60.9, 48.1, 39.4, 33.9, 31.7, 20.8, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 290.2111; Found: m/z 290.2115.

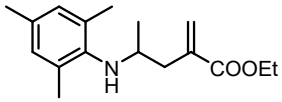
(9) ethyl 4-((3-methoxyphenyl) amino)-2-methylenepentanoate (3ia)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 6.22 (d, *J* = 5.8 Hz, 3H), 5.60 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 3.71 – 3.66 (m, 1H), 2.73 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.31 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.31 (t, *J* = 7.1

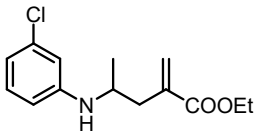
Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 161.0, 148.8, 138.2, 130.1, 127.3, 106.4, 102.3, 99.2, 61.0, 55.2, 48.1, 39.3, 20.7, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 264.1592; Found: m/z 264.1594.

(10) ethyl 4-(mesitylamino)-2-methylenepentanoate (3ja)



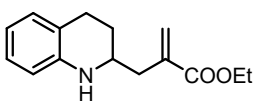
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 2H), 6.20 (s, 1H), 5.58 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.44 (q, *J* = 6.6 Hz, 1H), 2.61 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.32 (dd, *J* = 13.4, 7.8 Hz, 1H), 2.22 (s, 9H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 142.1, 138.9, 130.8, 129.6, 126.6, 60.8, 52.2, 40.8, 21.2, 20.7, 19.0, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 276.1955; Found: m/z 276.1958.

(11) ethyl 4-((3-chlorophenyl) amino)-2-methylenepentanoate (3ka)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (t, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 5.60 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.77 (s, 1H), 3.67 (q, *J* = 6.4 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.32 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 148.6, 138.0, 135.1, 130.3, 127.6, 116.8, 112.7, 111.5, 61.1, 48.1, 39.3, 20.6, 14.4. HRMS (ESI): Calcd. for $[M+H]^+$: 268. 1095; Found: m/z 268.1099.

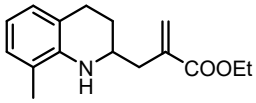
(12) ethyl 2-((1,2,3,4-tetrahydroquinolin-2-yl)methyl)acrylate (3la)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (t, *J* = 6.8 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 5.66 (s, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.45

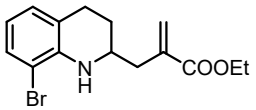
(d, J = 3.4 Hz, 1H), 2.79 (dt, J = 18.6, 5.2 Hz, 2H), 2.65 (dd, J = 13.4, 4.8 Hz, 1H), 2.41 (dd, J = 13.4, 8.0 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.67 (dd, J = 13.2, 4.0 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 144.3, 137.6, 129.4, 127.6, 126.9, 121.3, 117.3, 114.4, 61.1, 49.8, 39.4, 28.1, 26.2, 14.4. HRMS (ESI): Calcd. for $C_{15}H_{20}NO_2$ $[M+H]^+$: 246.1486; found: 246.1489.

(13) ethyl 2-((8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)methyl)acrylatem (3ma)



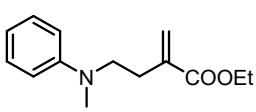
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (t, J = 6.8 Hz, 2H), 6.56 (t, J = 7.2 Hz, 1H), 6.30 (s, 1H), 5.66 (s, 1H), 4.24 (q, J = 6.8 Hz, 2H), 3.82 (s, 1H), 3.51 – 3.48 (m, 1H), 2.87 – 2.77 (m, 2H), 2.71 (dd, J = 13.6, 4.4 Hz, 1H), 2.42 (dd, J = 13.2, 7.8 Hz, 1H), 2.02 – 1.96 (m, 3H), 1.99 (d, J = 12.8, 1H), 1.73 – 1.63 (m, 1H), 1.32 (t, J = 12.0 Hz, 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 142.3, 137.9, 128.0, 127.3, 127.2, 121.2, 120.5, 116.6, 61.1, 50.2, 39.4, 28.0, 26.5, 17.2, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 260.1643; Found: m/z 260.1645.

(14) ethyl 2-((8-bromo-1,2,3,4-tetrahydroquinolin-2-yl)methyl)acrylate (3na)



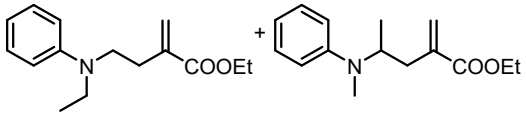
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 7.8 Hz, 1H), 6.89 (d, J = 7.4 Hz, 1H), 6.46 (t, J = 7.6 Hz, 1H), 6.33 (s, 1H), 5.69 (s, 1H), 4.24 (q, J = 7.0 Hz, 2H), 3.56 – 3.48 (m, 1H), 2.88 – 2.75 (m, 2H), 2.71 (dd, J = 13.6, 4.4 Hz, 1H), 2.40 (dd, J = 13.4, 8.2 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.70 – 1.61 (m, 1H), 1.32 (t, J = 16.0 Hz, 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1, 141.2, 137.3, 130.2, 128.3, 127.8, 122.9, 117.4, 109.1, 61.2, 50.2, 39.2, 27.7, 26.5, 14.4. HRMS (ESI): Calcd. for $[M+H]^+$: 324.0588; Found: m/z 324.0594.

(15) ethyl 4-(methyl(phenyl)amino)-2-methylenebutanoate (3oa)[2]



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.20 (s, 1H), 5.59 (s, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.53 – 3.47 (m, 2H), 2.96 (s, 3H), 2.63 – 2.56 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1, 149.1, 138.7, 129.3, 126.6, 116.4, 112.4, 60.9, 52.5, 38.4, 29.8, 14.4. MS (EI, m/z): 233.1 $[M]^+$.

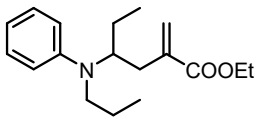
(16) the mixture of ethyl 4-(ethyl(phenyl)amino)-2-methylenebutanoate (3pa-1) and ethyl 4-(methyl(phenyl)amino)-2-methylenepentanoate (3pa-2)



3pa-1 **3pa-2**

Yellow oil. The molar ratio of **3pa-1** and **3pa-2** is 4:1. **3pa-1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, *J* = 8.2 Hz, 2H), 6.23 (s, 1H), 5.62 (s, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.46 – 3.41 (m, *2*H), 3.41 – 3.34 (m, 2H), 2.62 – 2.54 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1, 147.7, 138.6, 129.4, 126.8, 115.7, 111.9, 61.0, 50.2, 45.1, 30.6, 14.4, 12.6. **3pa-2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (t, *J* = 8.2 Hz, 0.5H), 6.15 (s, 0.25H), 5.56 (s, 0.25H), 4.19 (q, *J* = 7.0 Hz, 0.5H), 2.65 (dd, *J* = 13.8, 6.8 Hz, 0.25H), 2.46 (dd, *J* = 13.8, 6.8 Hz, 0.25H), 1.28 (t, *J* = 7.0 Hz, 0.77H), 1.14 (d, *J* = 8.0 Hz, 0.77H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 150.4, 138.5, 129.2, 126.8, 116.6, 113.3, 60.9, 52.7, 37.0, 30.0, 17.2, 14.3. ^{1}H NMR of mixture: 7.25 – 7.21 (m, 2.3H), 6.70 – 6.65 (m, 1.25H). HRMS (ESI): Calcd. for $[M+H]^+$: 248.1645; Found: m/z 248.1643.

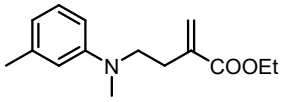
(17) ethyl 2-methylene-4-(phenyl(propyl)amino)hexanoate (3qa)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.65 (t, 7.0 Hz, 1H), 6.13 (s, 1H), 5.55 (s, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 4.00 (p, *J* = 7.2 Hz, 1H), 3.09 (t, *J* = 6.2 Hz, 2H), 5.27 (dq, *J* = 15.2, 7.6 Hz, 2H), 1.60 (dt, *J* = 14.2, 7.4 Hz, 4H), 1.28 (t, *J* = 7.0 Hz, 3H), 0.93 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 149.6, 138.6, 129.1, 126.9, 116.1, 113.8, 60.8, 59.8, 45.6,

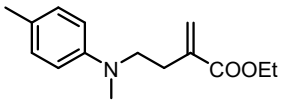
36.1, 26.0, 21.2, 14.3, 11.8, 11.7. HRMS (ESI): Calcd. for $[M+H]^+$: 290.2111; Found: m/z 290.2115.

(18) ethyl 4-(methyl(m-tolyl)amino)-2-methylenebutanoate (3ra)



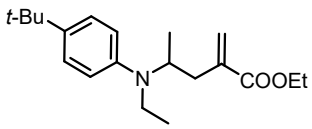
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.59 – 6.52 (m, 3H), 6.21 (s, 1H), 5.59 (s, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.50 – 3.46 (m, 2H), 2.94 (s, 3H), 2.59 – 2.55 (m, 2H), 2.32 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 149.1, 139.0, 138.7, 129.2, 126.7, 117.3, 113.0, 109.5, 60.9, 52.5, 38.5, 29.7, 22.1, 14.4. HRMS (ESI): calcd. for $[M+H]^+$: 248.1641; Found: m/z 248.1645.

(19) ethyl 4-(methyl(p-tolyl)amino)-2-methylenebutanoate (3sa)



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 6.20 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.48 – 3.44 (m, 2H), 2.92 (s, 3H), 2.58 – 2.54 (m, 2H), 2.26 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 150.0, 138.7, 129.9, 126.7, 125.5, 112.7, 60.9, 52.7, 38.6, 29.5, 20.3, 14.4. HRMS (ESI): Calcd. for $[M+H]^+$: 248.1641; Found: m/z 248.1645.

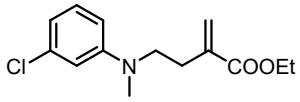
(20) (S)-ethyl 4-((4-(tert-butyl)phenyl)(ethyl)amino)-2-methylenepentanoate (3ta)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.21 (s, 1H), 5.61 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 4.22-4.15 (m, 1H), 3.33-3.22 (m, 2H), 2.71 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.42 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.35(s, 3H), 1.32 (s, 9H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 146.2, 138.8,

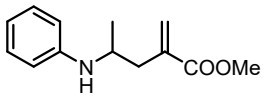
128.6, 126.9, 126.0, 113.1, 60.9, 52.5, 38.2, 37.0, 33.8, 31.7, 18.0, 14.9, 14.4. HRMS (ESI): Calcd. for $[M+H]^+$: 318.2428; Found: m/z 318.2425.

(21) ethyl 4-((3-chlorophenyl)(methyl)amino)-2-methylenebutanoate (3ua)



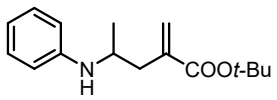
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.62 (dd, *J* = 16.0, 8.0 Hz, 2H), 6.21 (s, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.47 (t, *J* = 7.5Hz, 2H), 2.94 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0, 150.0, 138.2, 135.3, 130.2, 127.1, 116.0, 111.9, 110.2, 61.0, 52.3, 38.5, 29.8, 14.4. HRMS (ESI): Calcd. for $[M+H]^+$: 268.1095; Found: m/z 268.1099.

(22) methyl 2-methylene-4-(phenylamino)pentanoate (3vb)



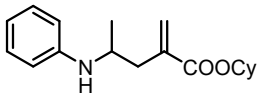
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.4 Hz, 2H), 6.67 (dd, *J* = 18.6, 7.6 Hz, 3H), 6.23 (s, 1H), 5.62 (s, 1H), 3.77 (s, 3H), 3.74 – 3.70 (m, 1H), 2.73 (dd, *J* = 13.8, 6.2, 1H), 2.34 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.19 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 147.2, 137.9, 129.4, 127.6, 117.3, 113.4, 52.1, 48.2, 39.4, 20.6. HRMS (ESI): Calcd. for $[M+H]^+$: 220.1329; Found: m/z 220.1329.

(23) tert-butyl 2-methylene-4-(phenylamino) pentanoate (3ac)



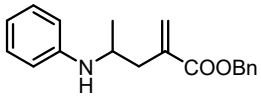
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 7.6 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 5.52 (s, 1H), 3.69 (q, *J* = 6.4 Hz, 1H), 2.67 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.33 (dd, *J* = 13.8, 6.4, 1H), 1.51 (s, 9H), 1.19 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 147.5, 139.7, 129.4, 126.3, 117.0, 113.2, 81.0, 48.4, 39.2, 28.2, 20.8. HRMS (ESI): Calcd. for $[M+H]^+$: 262.1799; Found: m/z 262.1802.

(24) cyclohexyl 2-methylene-4-(phenylamino) pentanoate (3ad)



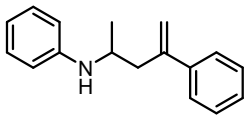
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 7.4 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 5.58 (s, 1H), 4.86 (tt, *J* = 8.6, 3.6 Hz, 1H), 3.72 (q, *J* = 6.4 Hz, 1H), 3.68 (s, 1H), 2.75 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.32 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.78 – 1.71 (m, 2H), 1.60 – 1.47 (m, 3H), 1.42 – 1.27 (m, 3H), 1.19 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 147.5, 138.7, 129.4, 127.1, 117.1, 113.3, 73.3, 48.1, 39.4, 31.8, 31.7, 25.6, 23.9, 20.7. HRMS (ESI): Calcd. for [M+H]+: 288.1953; Found: m/z 288.1958.

(25) benzyl 2-methylene-4-(phenylamino) pentanoate (3ae)



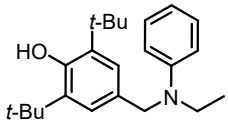
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.35 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.29 (s, 1H), 5.64 (s, 1H), 5.22 (d, *J* = 2.2 Hz, 2H), 3.73 (q, *J* = 6.4 Hz, 1H), 2.76 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.36 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 147.3, 138.0, 136.0, 129.4, 128.7, 128.4, 127.9, 117.1, 113.3, 66.8, 48.1, 39.4, 20.7. HRMS (ESI): Calcd. for [M+H]+: 296.1641; Found: m/z 296.1645.

(26) N-(4-phenylpent-4-en-2-yl) aniline (3af)



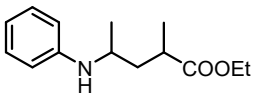
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 6.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 5.31 (s, 1H), 5.13 (s, 1H), 3.53 (q, *J* = 6.2 Hz, 1H), 2.93 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.51 (dd, *J* = 14.0, 7.6, 1H), 1.16 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 141.2, 129.4, 128.5, 127.7, 126.5, 117.5, 115.2, 113.7, 47.4, 43.2, 20.6. HRMS (ESI): Calcd. for $C_{17}H_{20}N$ $[M+H]^+$: 238.1586; found: 238.1590.

(27) 2,6-di-tert-butyl-4-((ethyl(phenyl)amino)methyl)phenol (4)



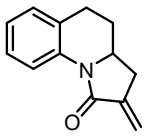
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.8 Hz, 2H), 7.06 (s, 2H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 5.11 (s, 1H), 4.45 (s, 2H), 3.45 (q, *J* = 7.0 Hz, 2H), 1.43 (s, 18H), 1.23-1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7, 149.1, 136.0, 129.6, 129.2, 123.5, 116.0, 112.7, 54.4, 44.8, 34.5, 30.5, 12.2. HRMS (ESI): Calcd. for $[M+H]^+$: 340.2635; Found: m/z 340.2631.

(28) ethyl 2-methyl-4-(phenylamino)pentanoate (3aa'')



Yellow oil. The ratio of diastereomers is 1:1. The mixture: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.11 (m, 4H), 6.67 (t, *J* = 7.2 Hz, 2H), 6.59 – 6.53 (m, 4H), 4.16 – 4.05 (m, 4H), 3.55 (dq, J = 14.2, 6.4 Hz, 2H), 3.36 (s, 1.5H), 2.71 – 2.62 (m, 1H),, 2.61 – 2.55 (m, 1H), 2.00 (ddd, *J* = 13.8, 8.4, 5.6 Hz, 1H), 1.90 (ddd, *J* = 14.0, 8.4, 5.6 Hz, 1H), 1.60 (ddd, *J* = 13.6, 7.6, 5.4 Hz, 1H), 1.49 (dt, *J* = 14.0, 5.8 Hz, 1H), 1.24 – 1.16 (m, 18H). One of the diastereomers : ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.1, 147.5, 129.4, 117.1, 113.2, 60.5, 47.1, 41.4, 37.4, 21.2, 18.0, 14.3. HRMS (ESI): Calcd. for $[M+H]^+$: 340.2635; Found: m/z 340.2631.

(29) 2-methylene-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinolin-1(2*H*)-one (6)[3]



White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 5.43 (s, 1H), 3.95 – 3.88 (m, 1H), 3.08 (dd, *J* = 16.8, 7.4 Hz, 1H), 3.00 (dd, 12.4, 5.6 Hz, 1H), 2.92 (dd, *J* = 16.8, 5.0 Hz, 1H), 2.56 – 2.49 (m, 1H), 2.25 – 1.19 (m, 1H), 1.78 (dq, *J* = 12.6, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 139.7, 136.8, 129.3, 126.9, 126.3, 124.2, 120.0, 116.6, 54.8, 31.4, 29.6, 27.7. MS (EI, m/z): 199.0 $[M]^+$.

7. References

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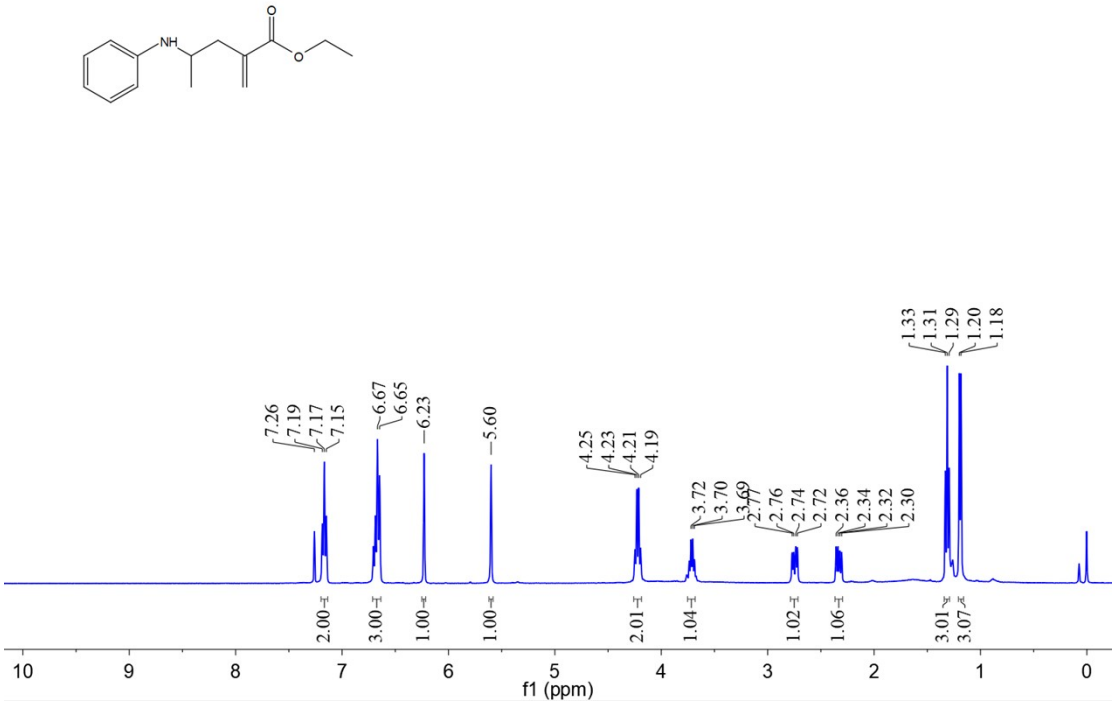
2. Y. Duan, M. Zhang, R Ruzi, Z. Wu and C. Zhu. The direct decarboxylative allylation of N-arylglycine derivatives by photoredox catalysis, *Org. Chem. Front.*, 2017, **4**, 525−528.

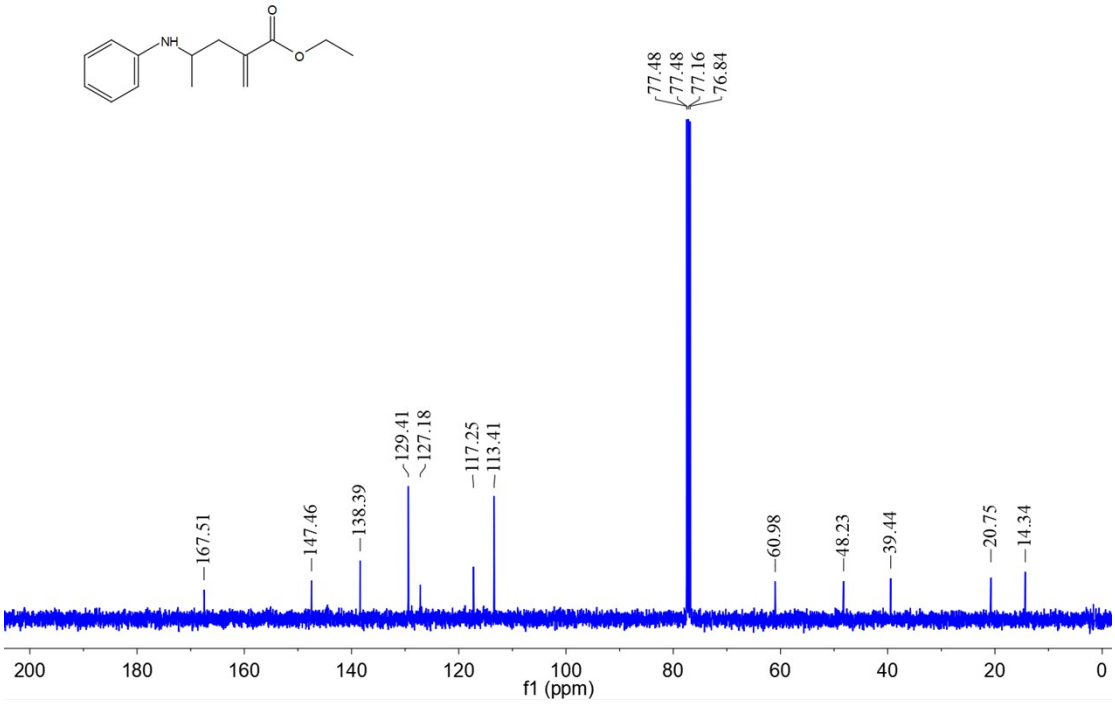
3. J. A. Sirvent, F. Foubelo, M. Yus, Stereoselective Synthesis of Indoline, Tetrahydroquinoline, and Tetrahydrobenzazepine Derivatives from o-Bromophenyl N-tert-Butylsulfinyl Aldimines, *J. Org. Chem.,* 2014, **79**, 1356−1367.

8. NMR spectra of products

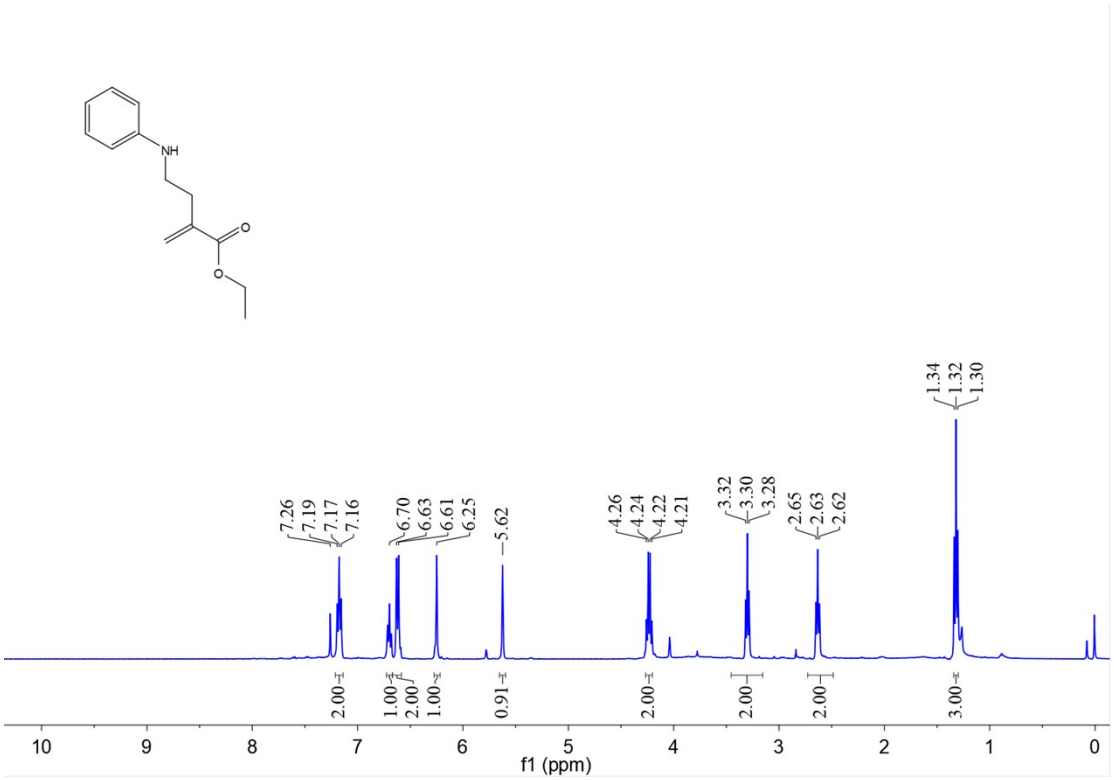
^{1}H-NMR spectrum of 3aa



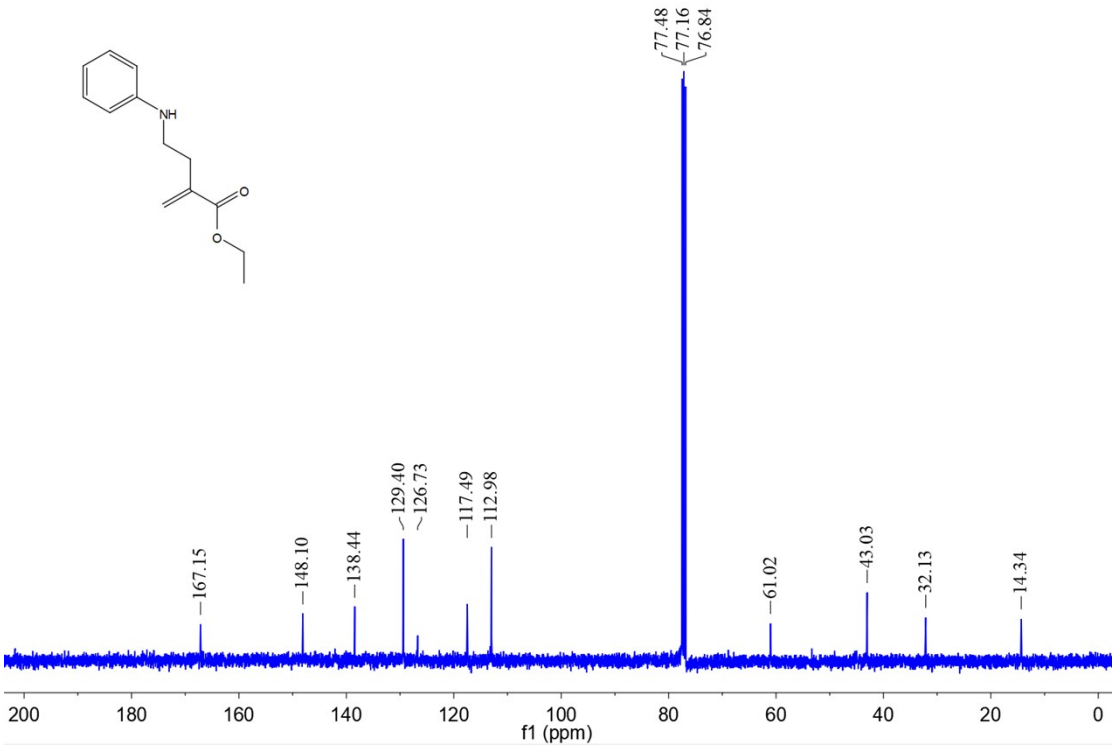
^{13}C-NMR spectrum of 3aa



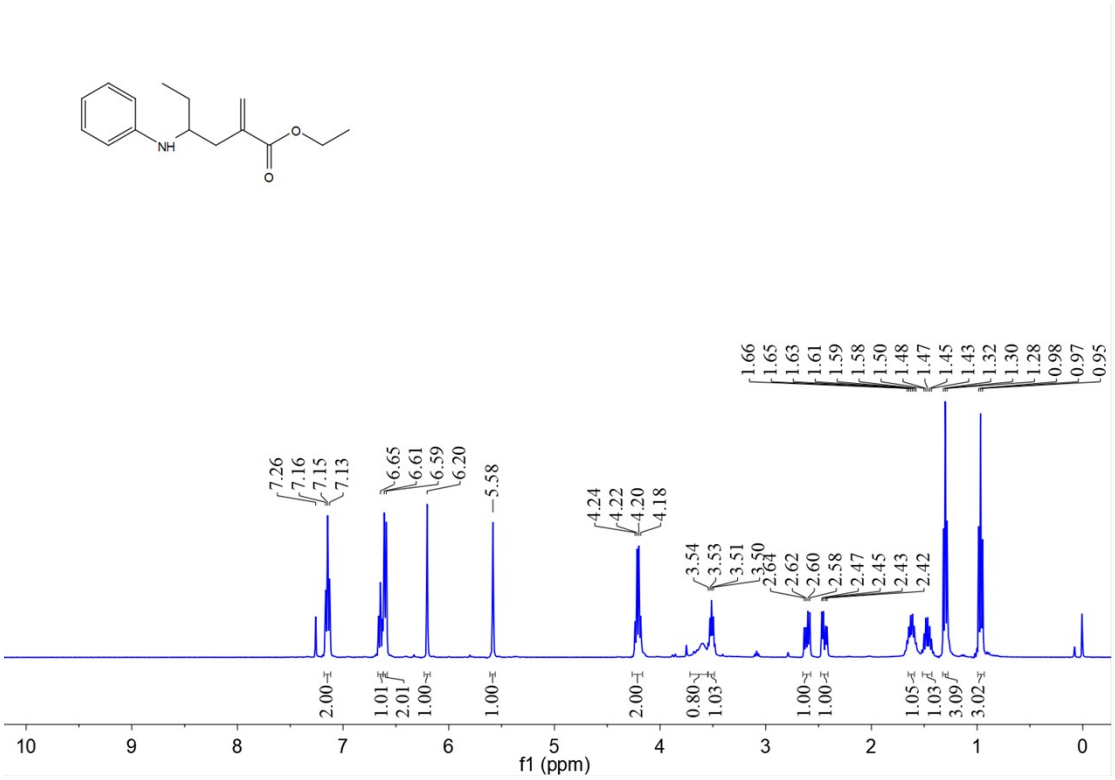
^{1}H-NMR spectrum of 3ba



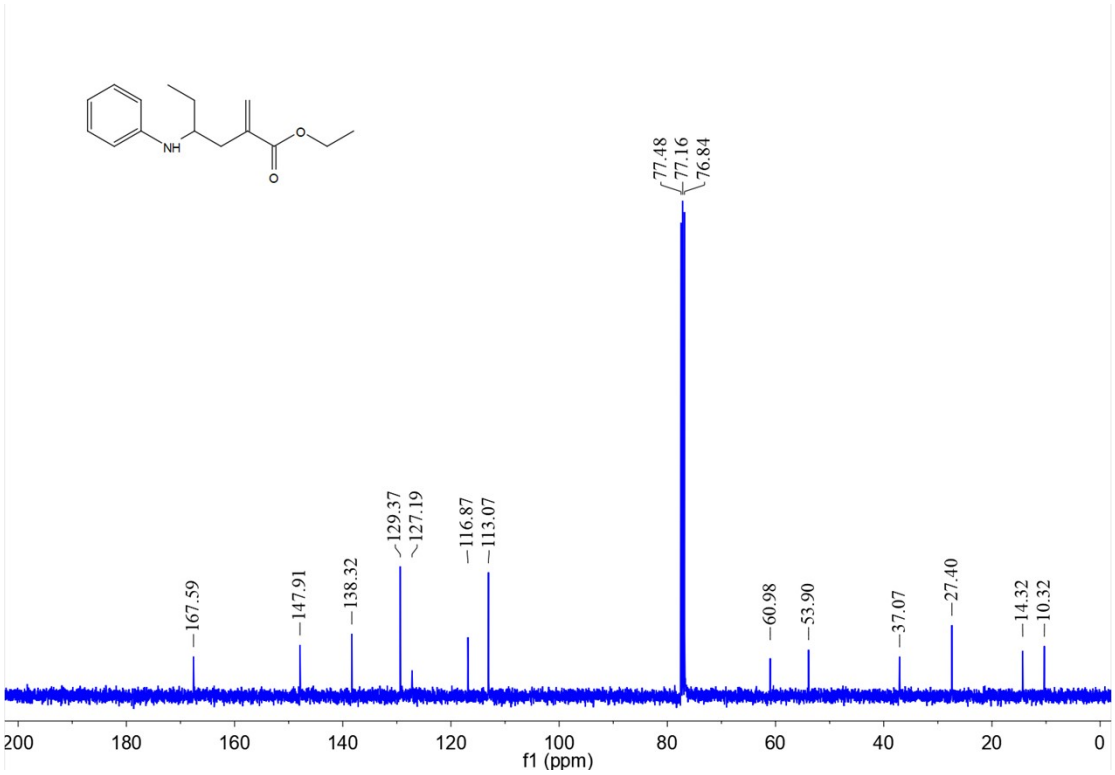
^{13}C-NMR spectrum of 3ba



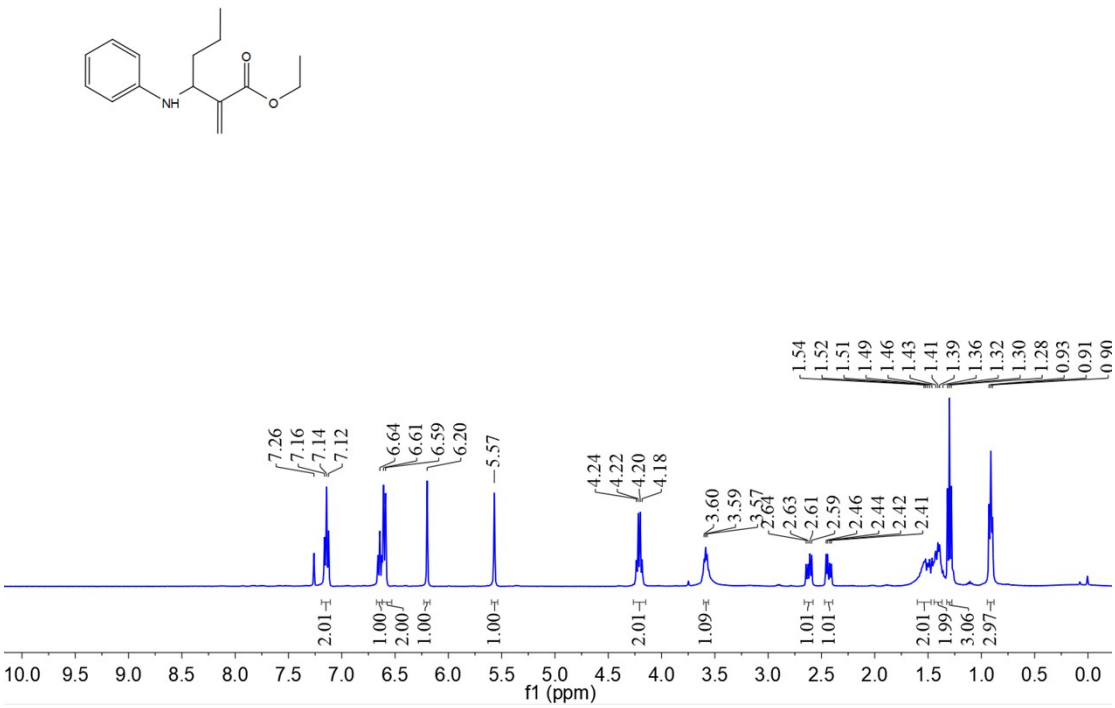
^{1}H-NMR spectrum of 3ca



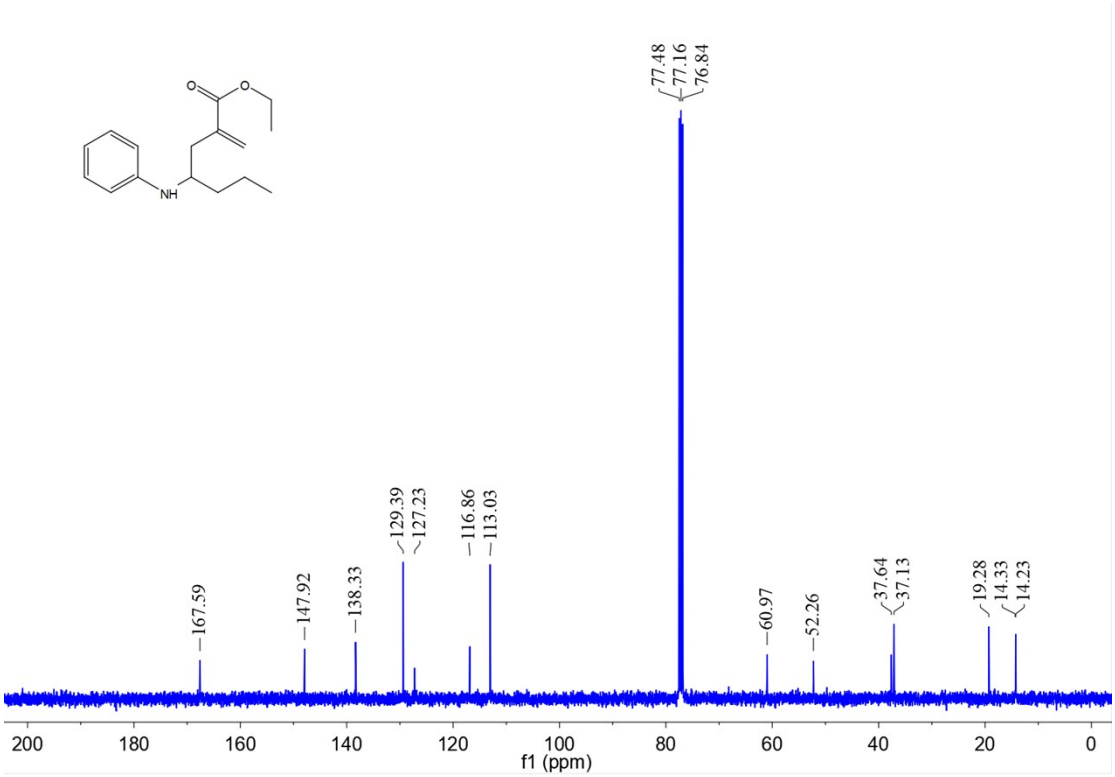
^{13}C-NMR spectrum of 3ca



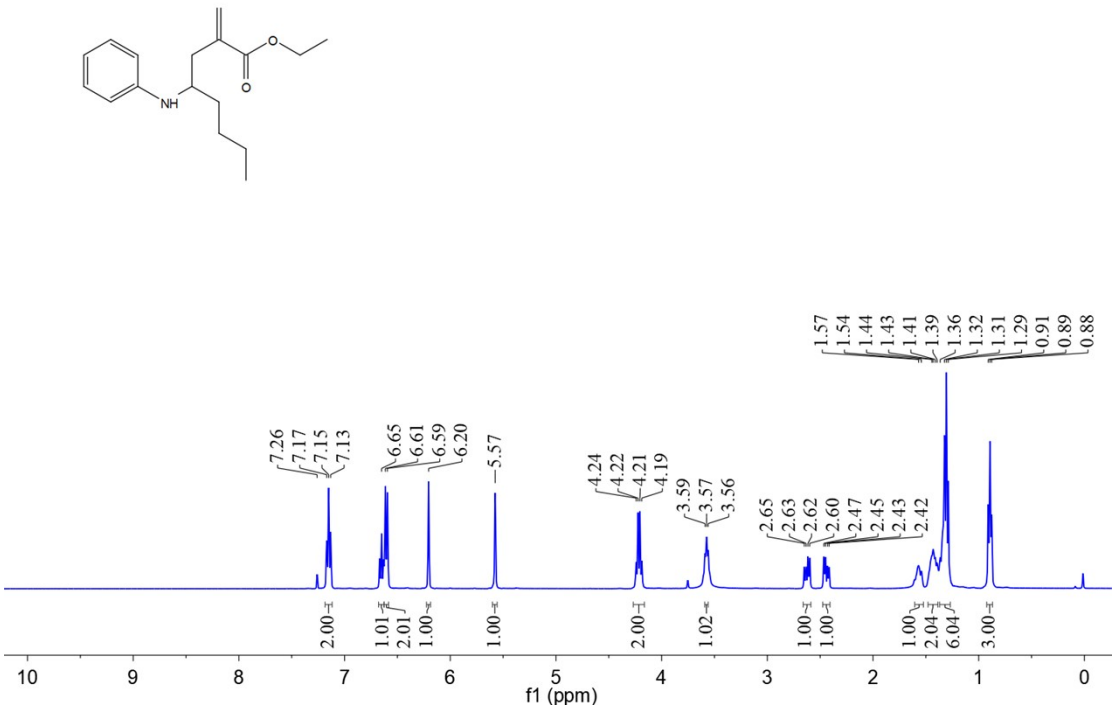
^{1}H-NMR spectrum of 3da



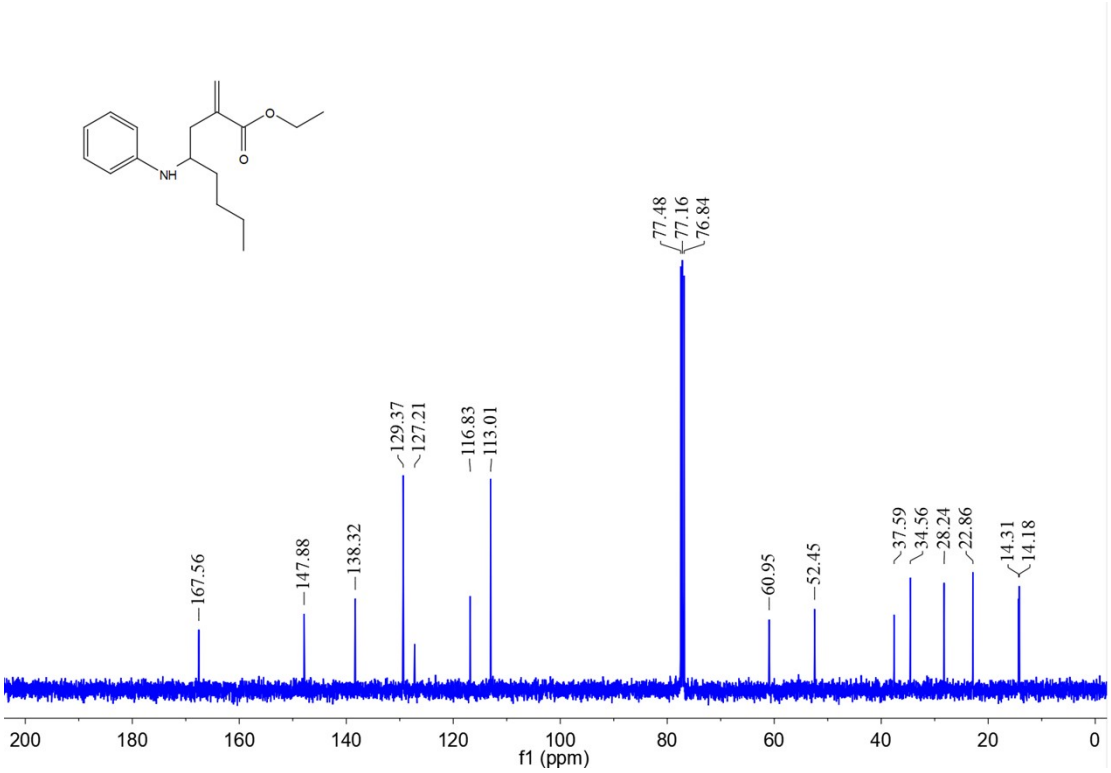
^{13}C-NMR spectrum of 3da



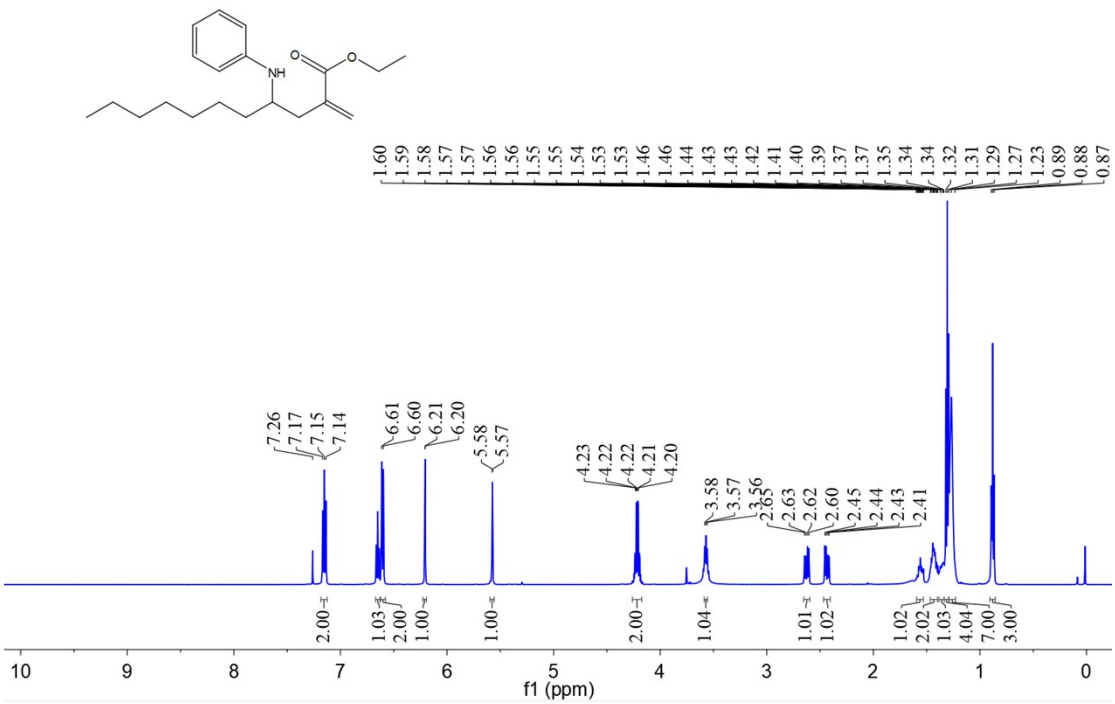
^{1}H-NMR spectrum of 3ea



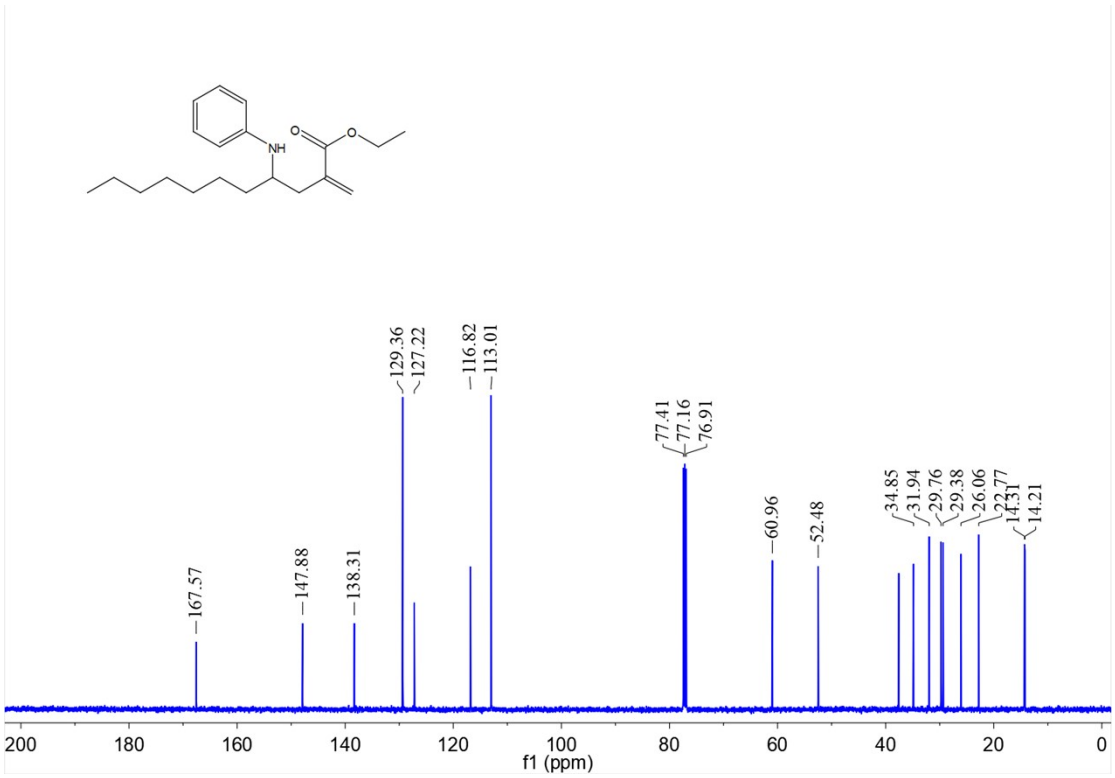
^{13}C-NMR spectrum of 3ea



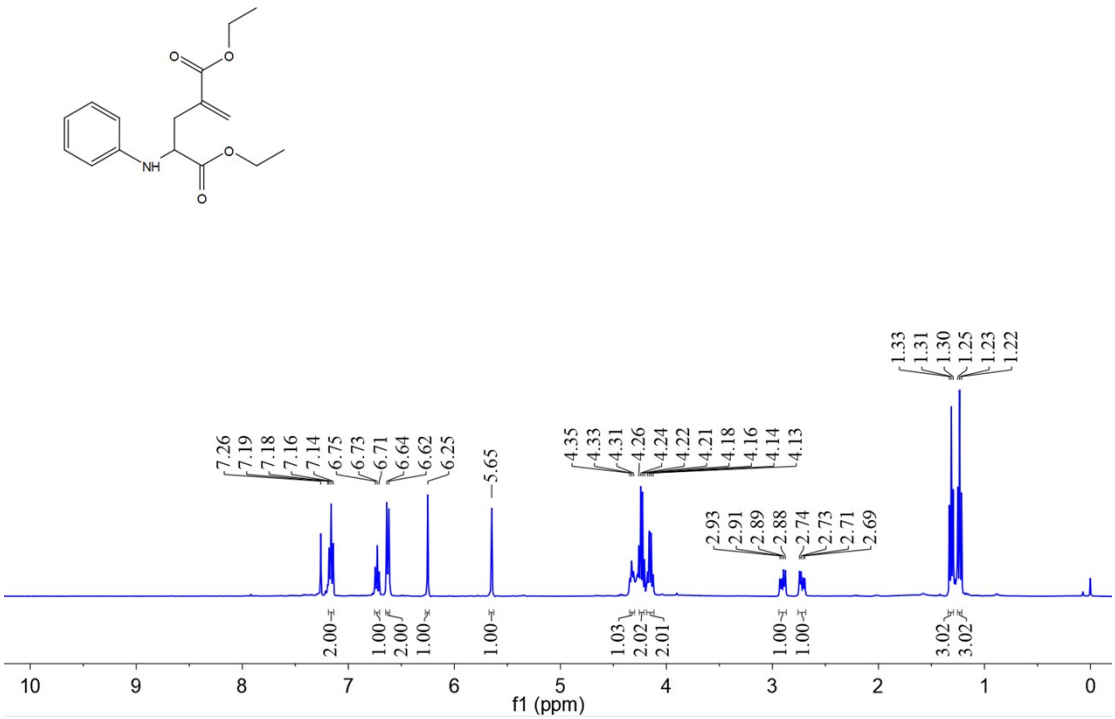
^{1}H-NMR spectrum of 3fa



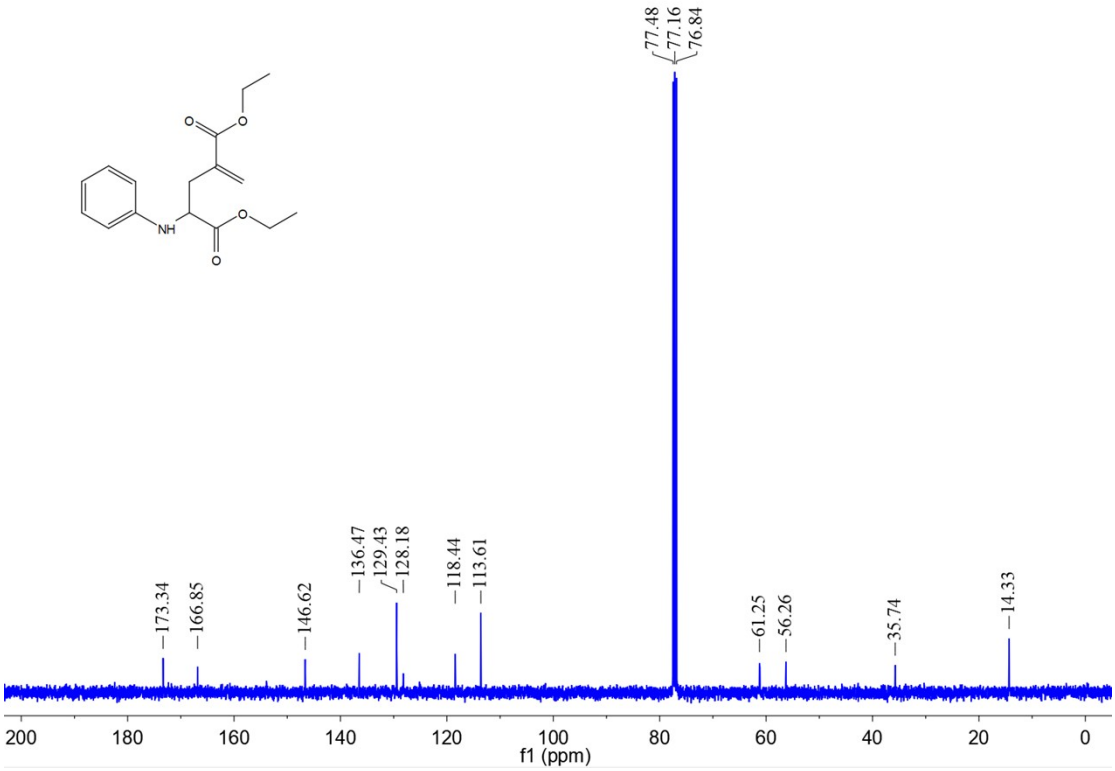
^{13}C-NMR spectrum of 3fa



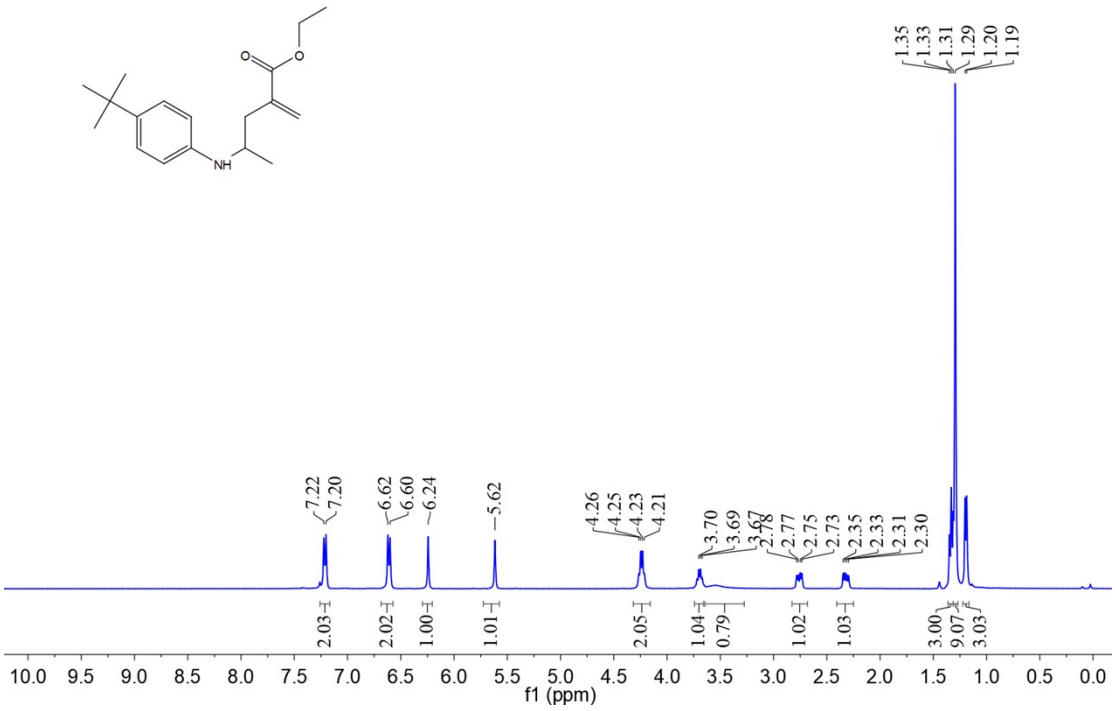
^{1}H-NMR spectrum of 3ga



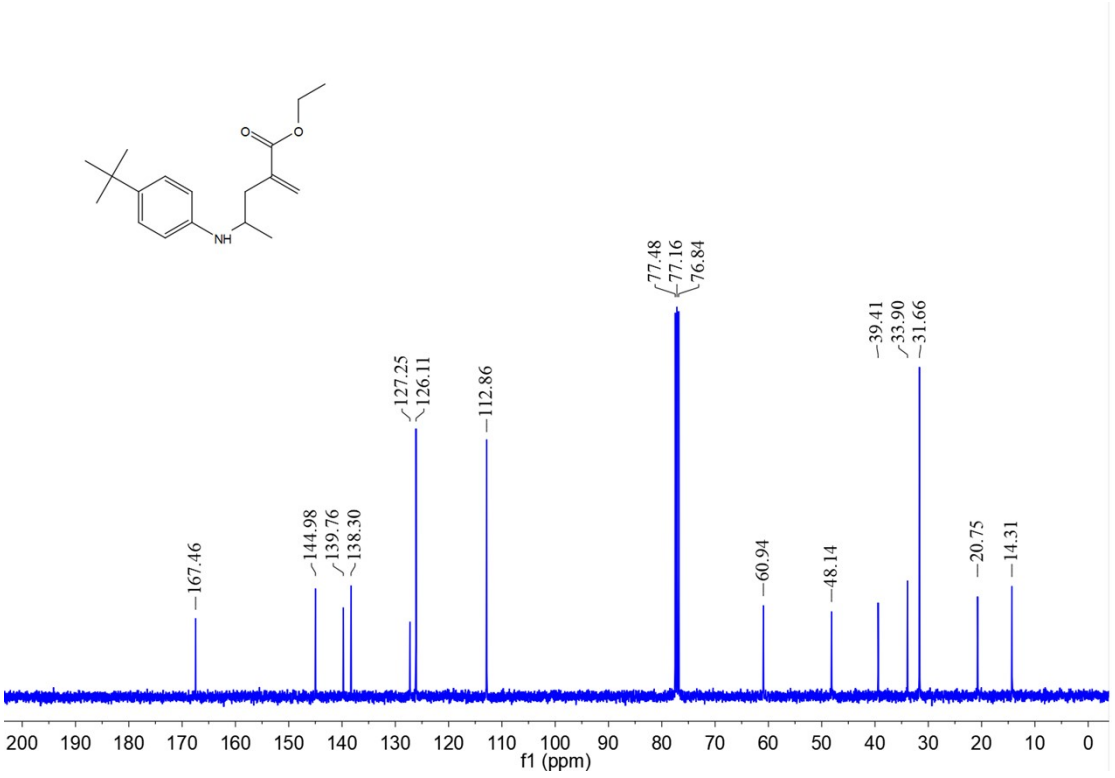
^{13}C-NMR spectrum of 3ga



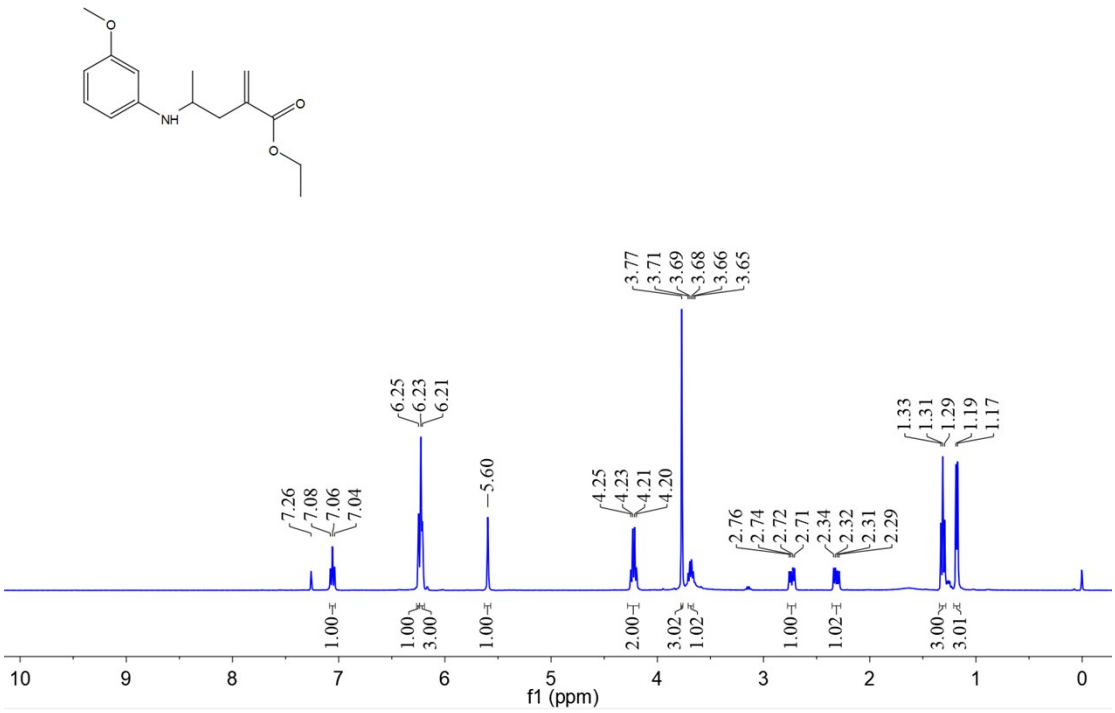
^{1}H-NMR spectrum of 3ha



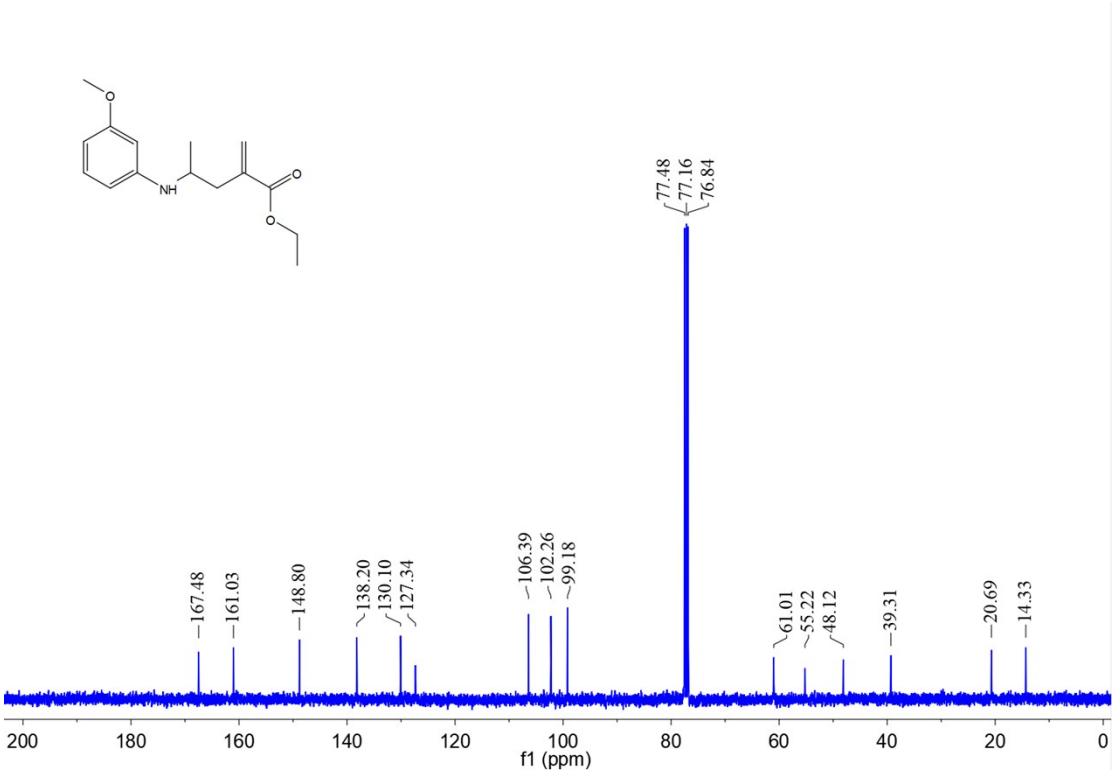
^{13}C-NMR spectrum of 3ha



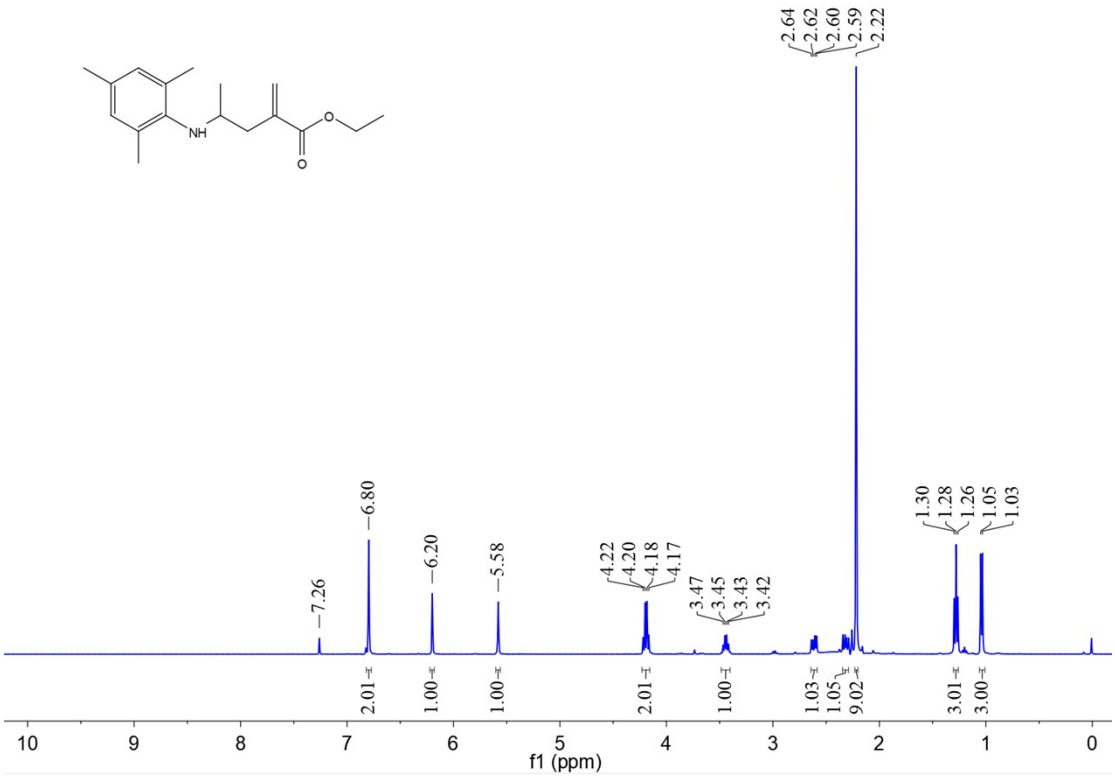
^{1}H-NMR spectrum of 3ia



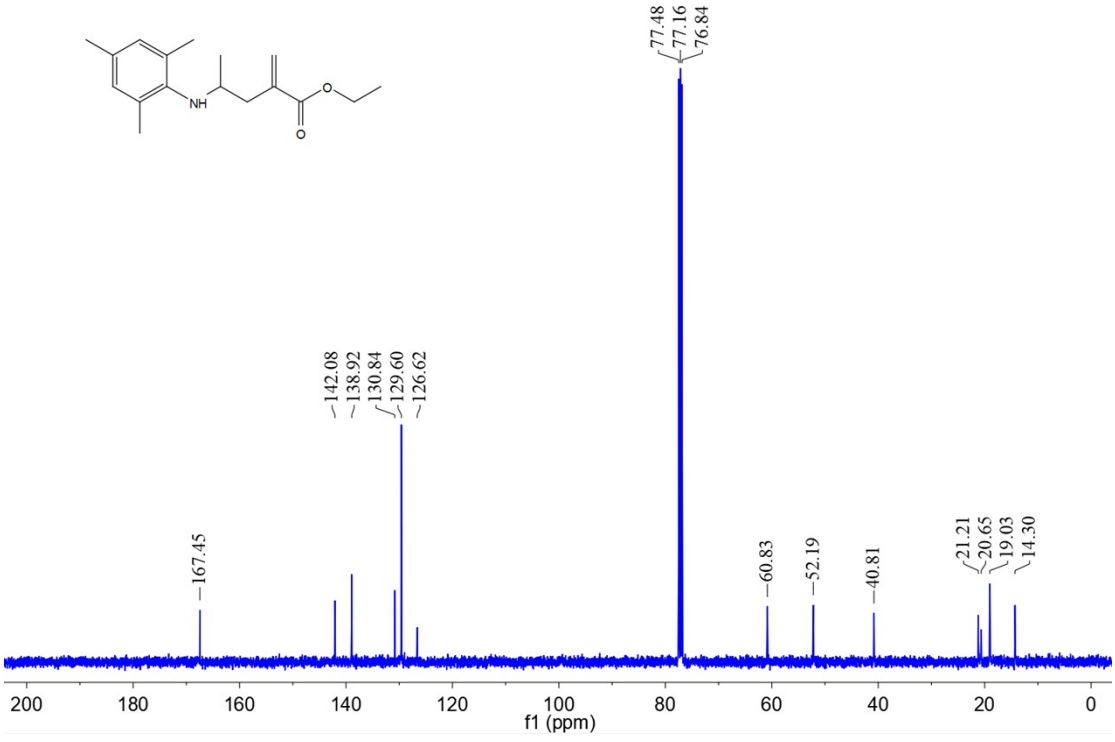
^{13}C-NMR spectrum of 3ia



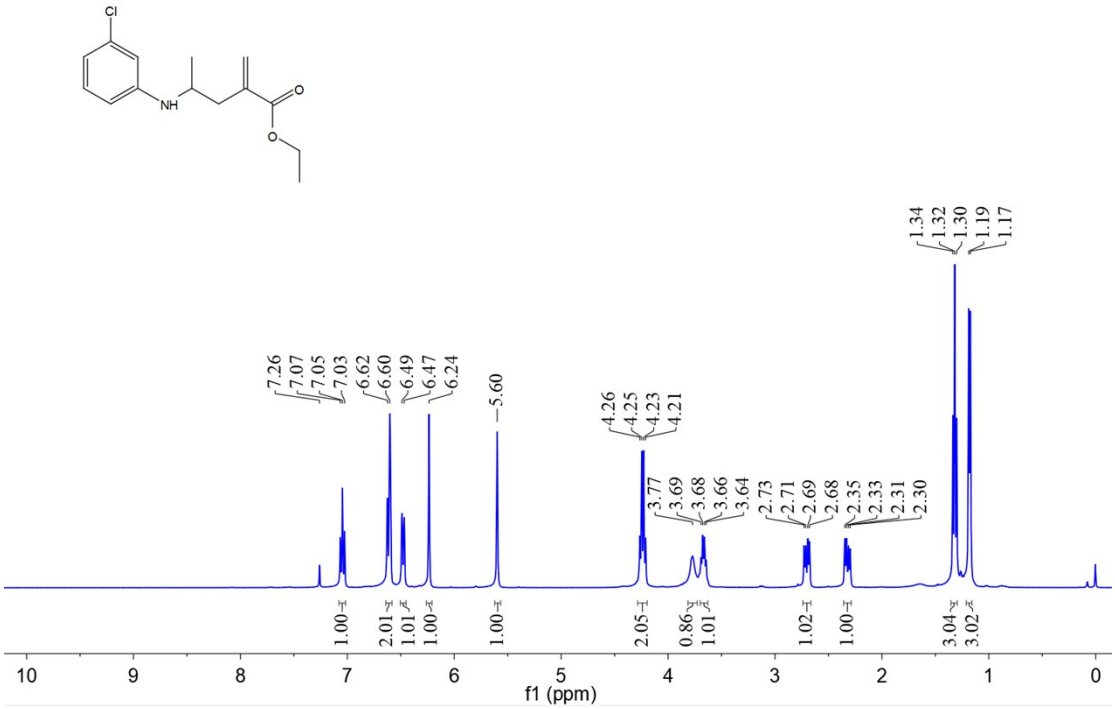
^{1}H-NMR spectrum of 3ja



^{13}C-NMR spectrum of 3ja



^{1}H-NMR spectrum of 3ka



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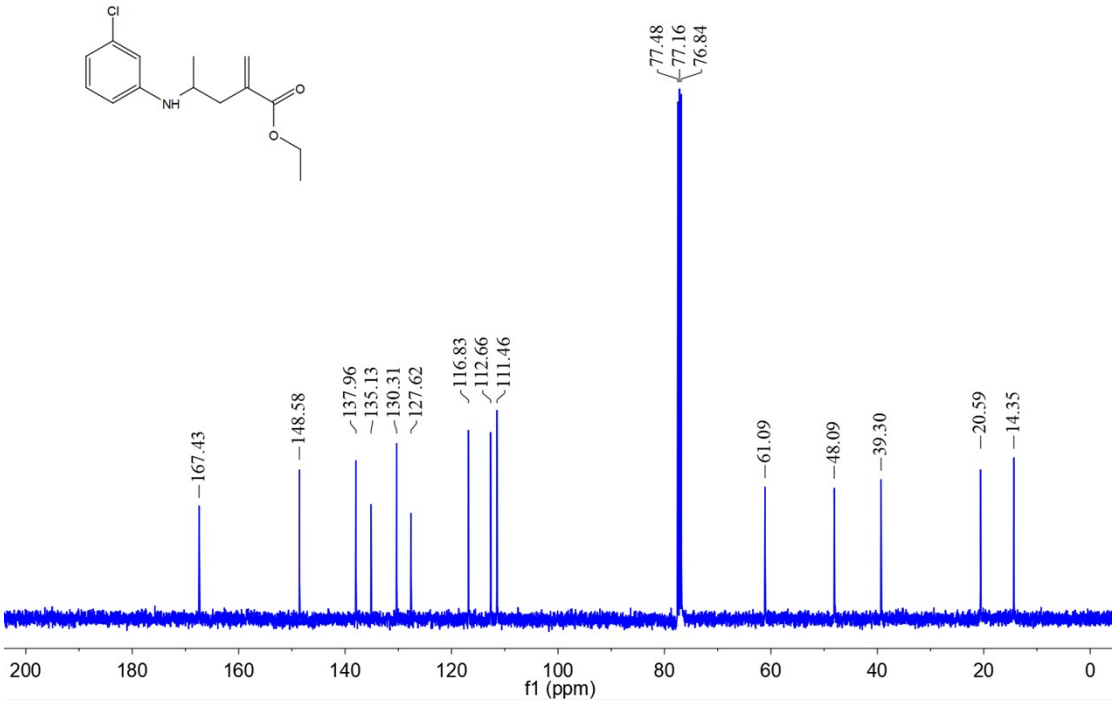
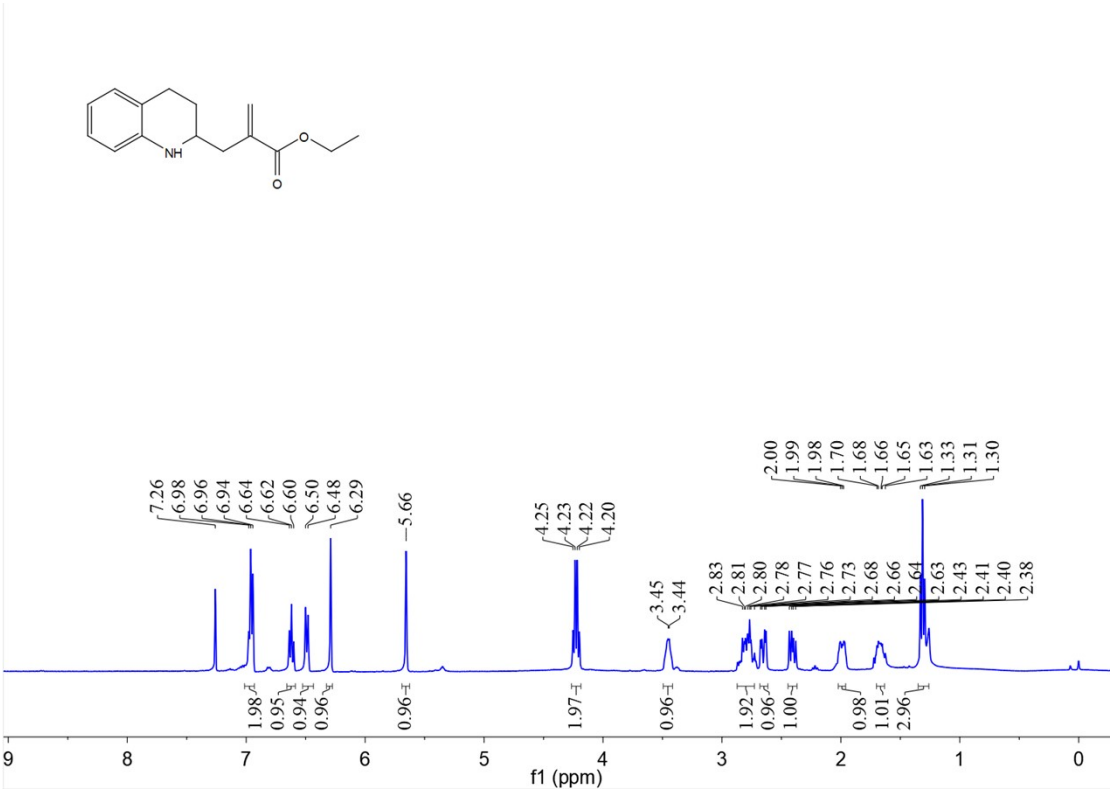
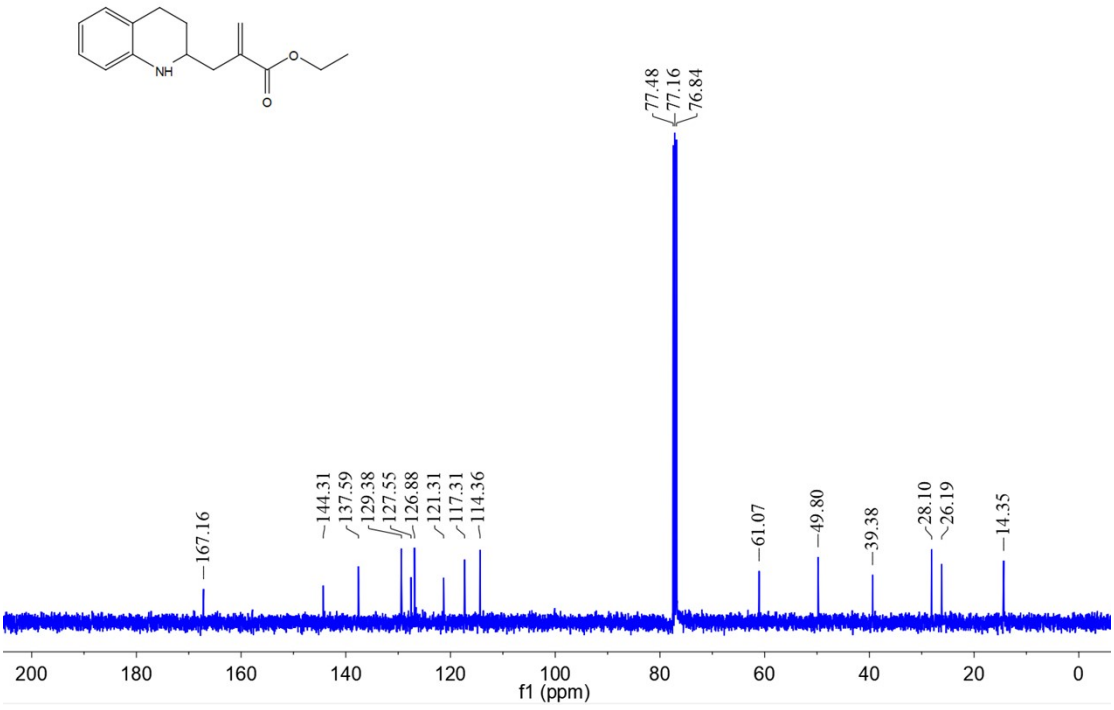


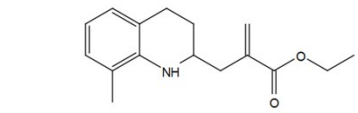
^{1}H-NMR spectrum of 3la

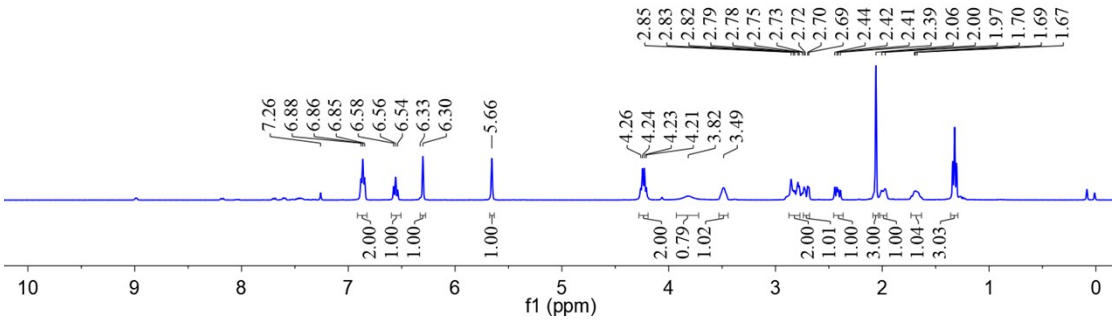


^{13}C-NMR spectrum of 3la

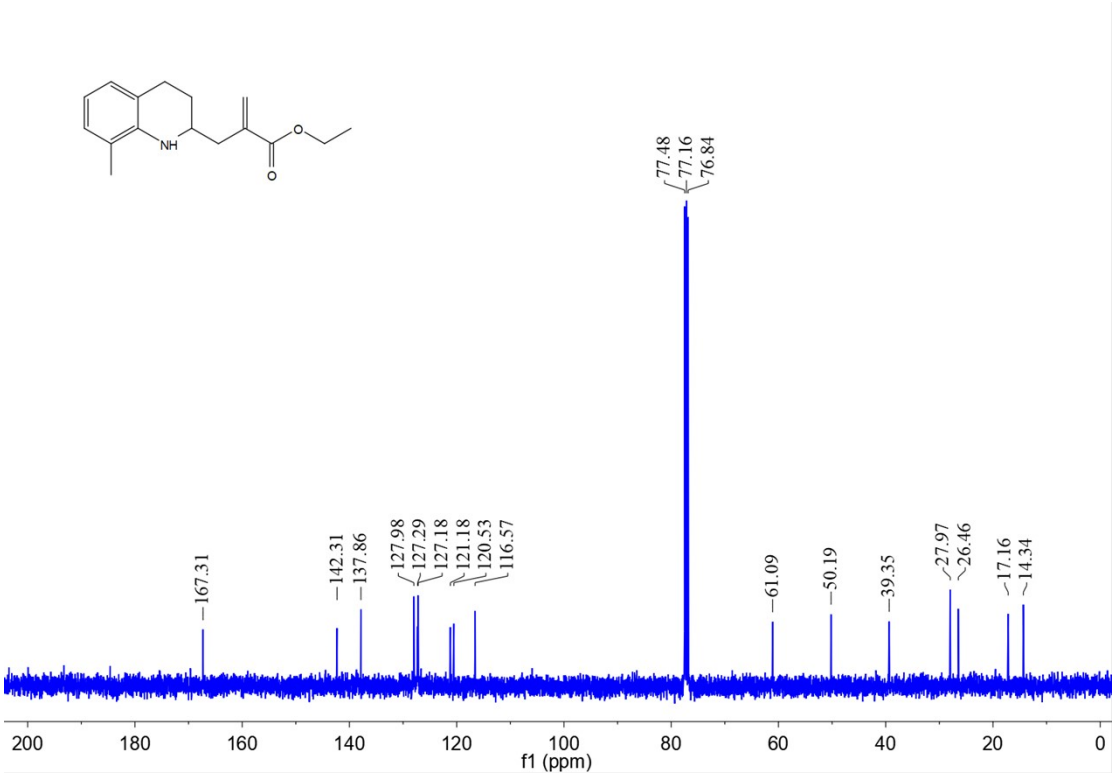


^{1}H-NMR spectrum of 3ma

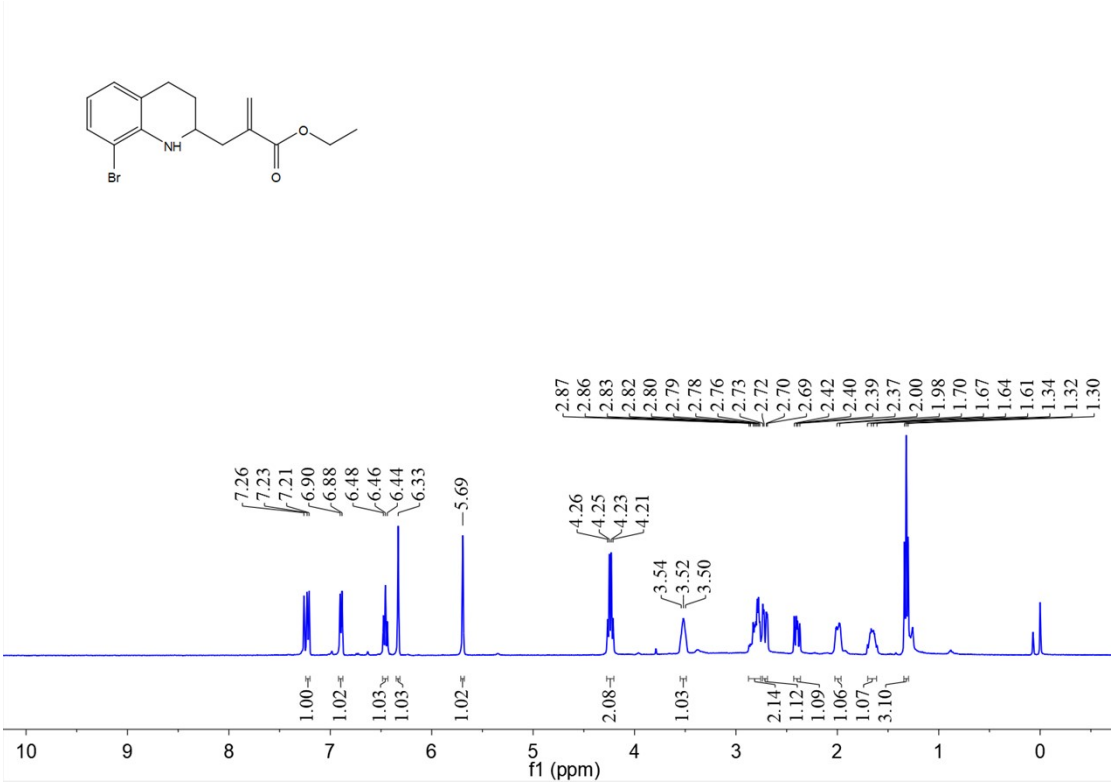




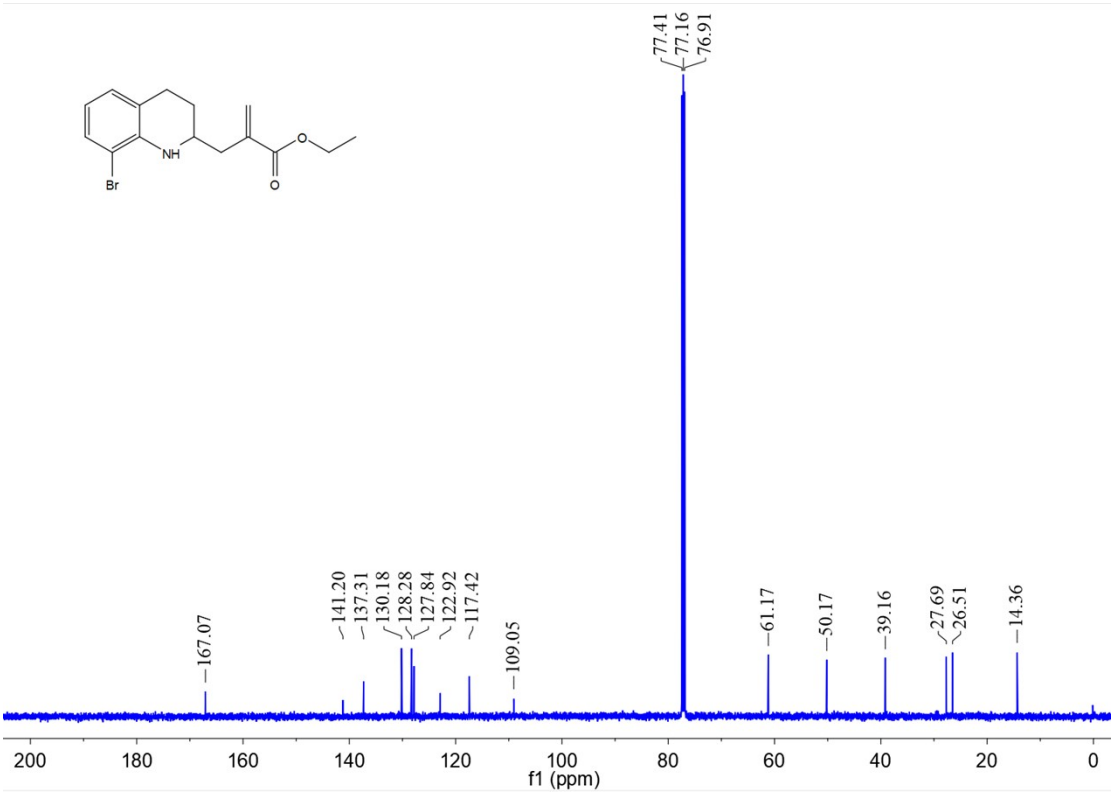
^{13}C-NMR spectrum of 3ma



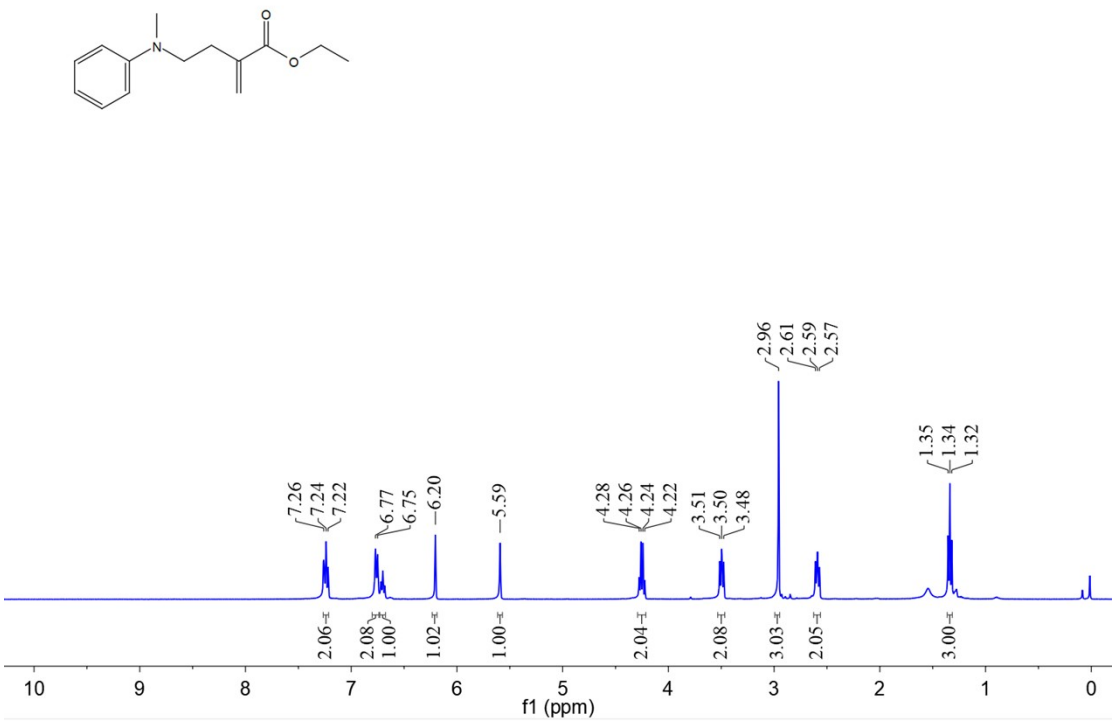
^{1}H-NMR spectrum of 3na



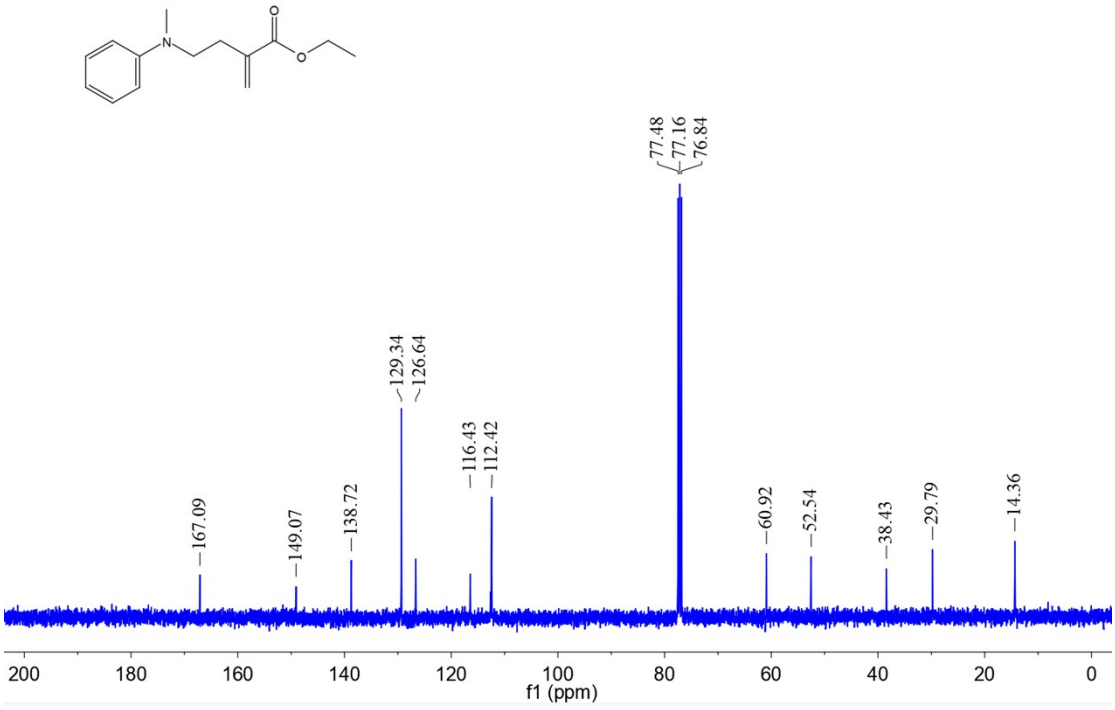
^{13}C-NMR spectrum of 3na



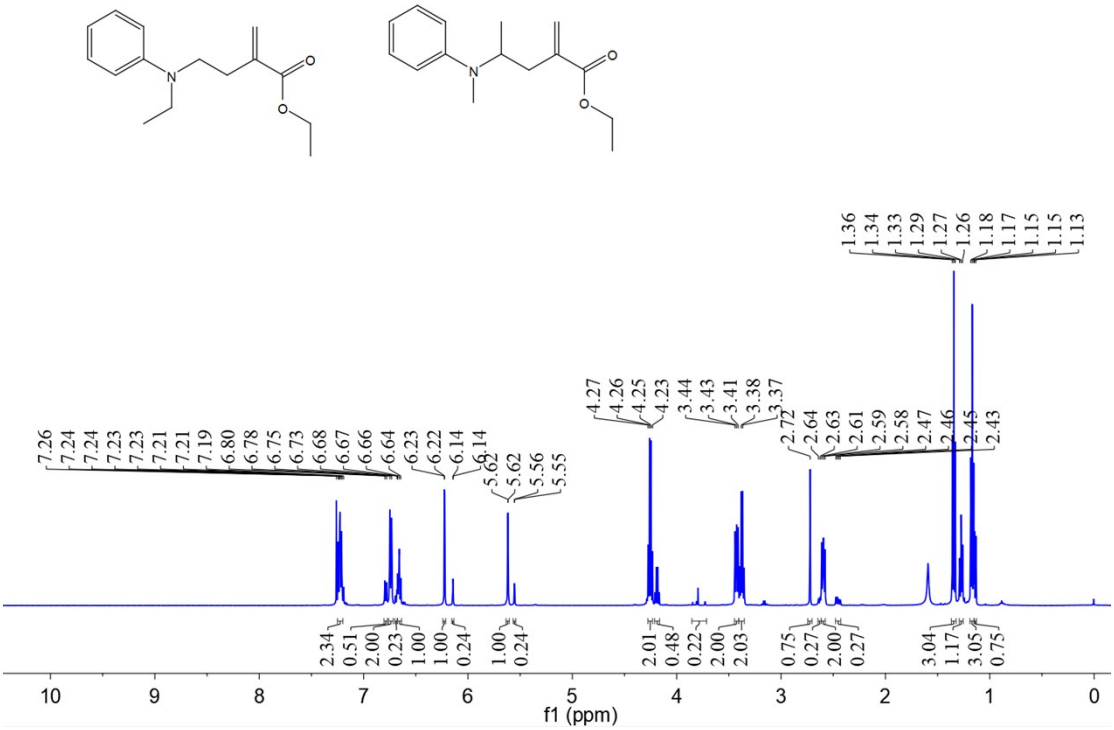
^{1}H-NMR spectrum of 3oa



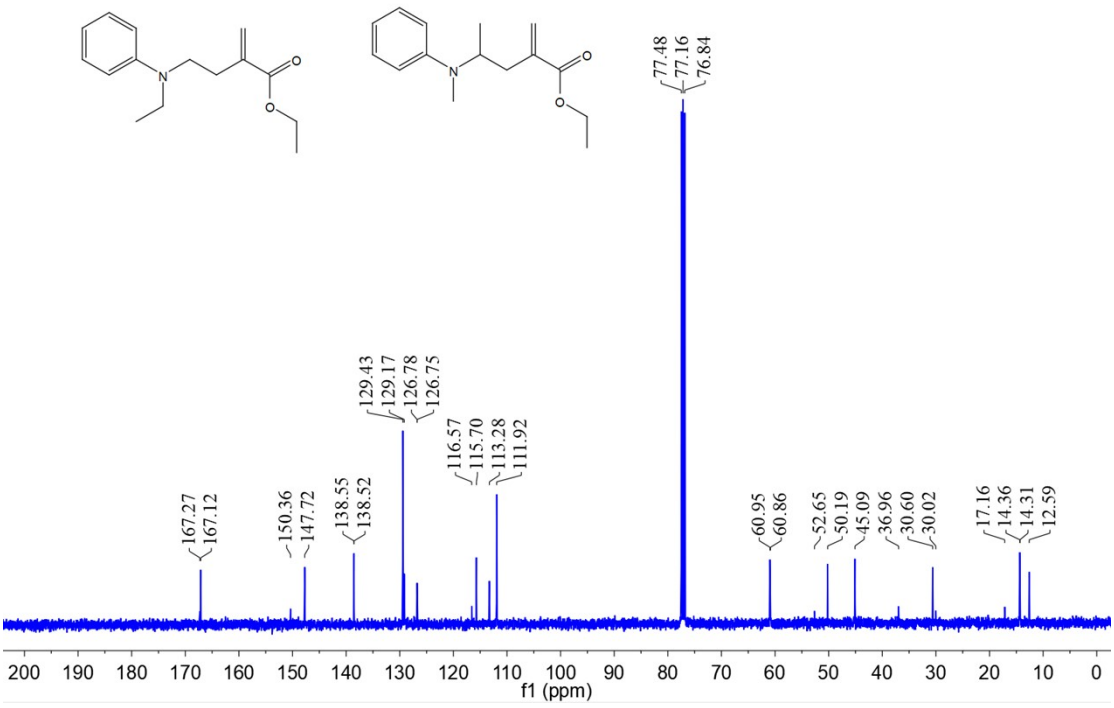
^{13}C-NMR spectrum of 3oa



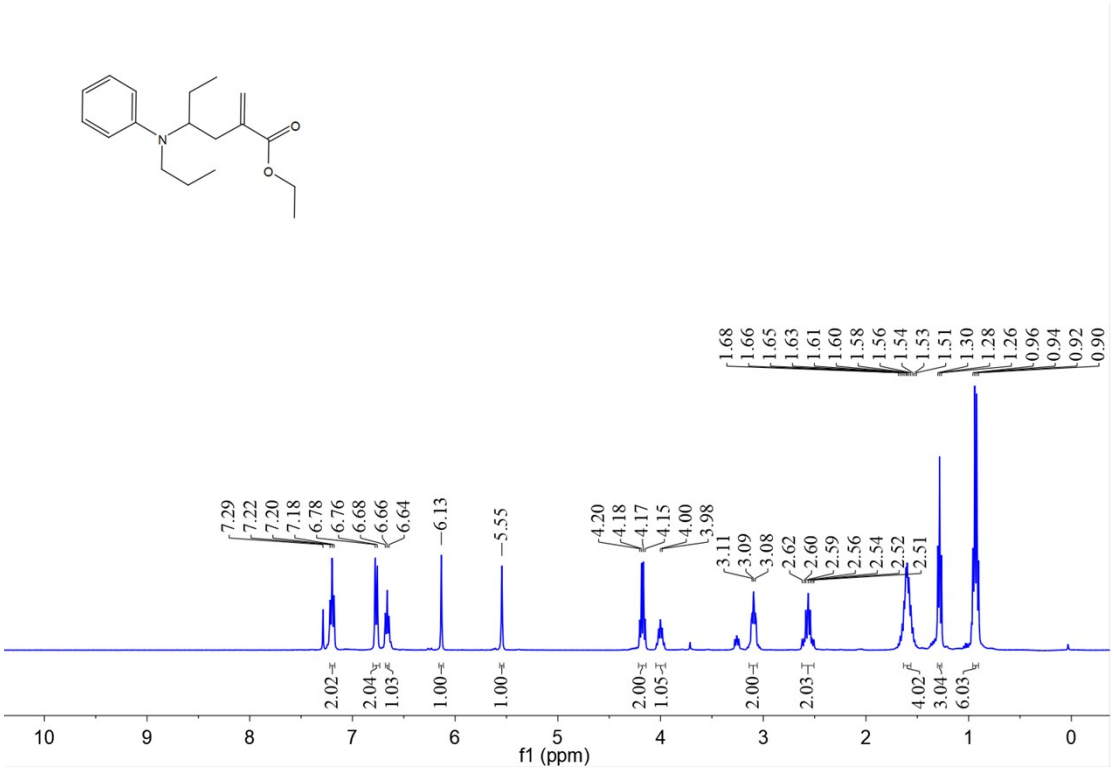
^{1}H-NMR spectrum of 3pa-1 and 3pa-2



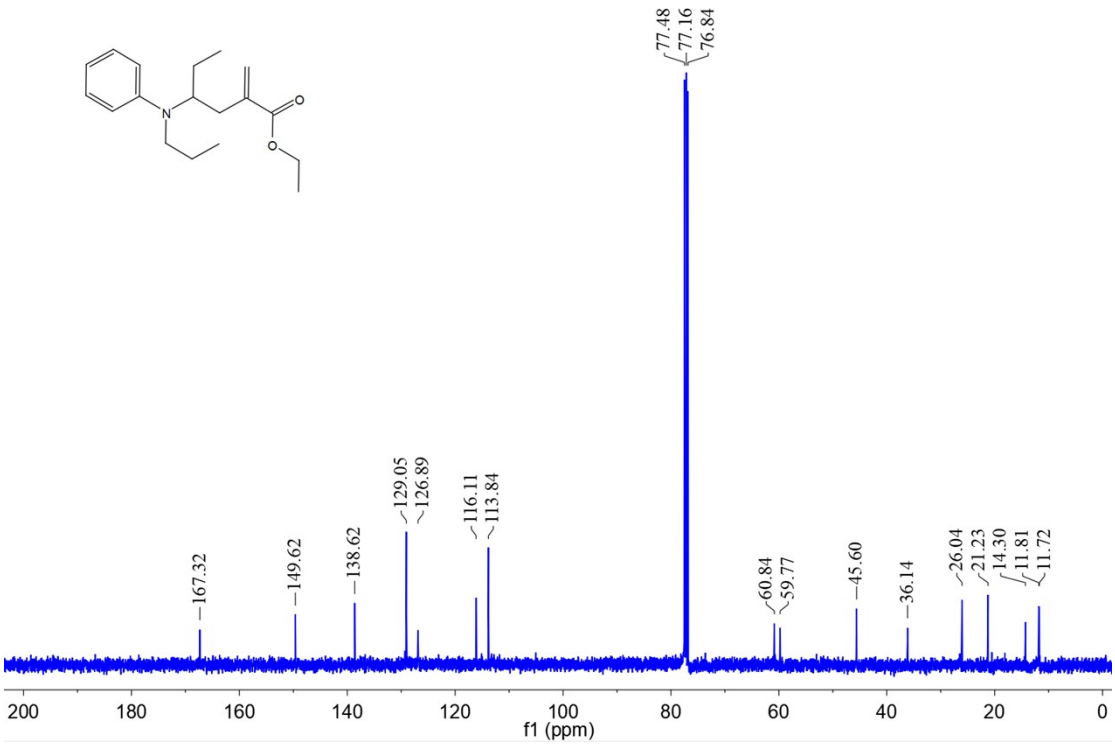
^{13}C-NMR spectrum of 3pa-1 and 3pa-2



^{1}H-NMR spectrum of 3qa



^{13}C-NMR spectrum of 3qa



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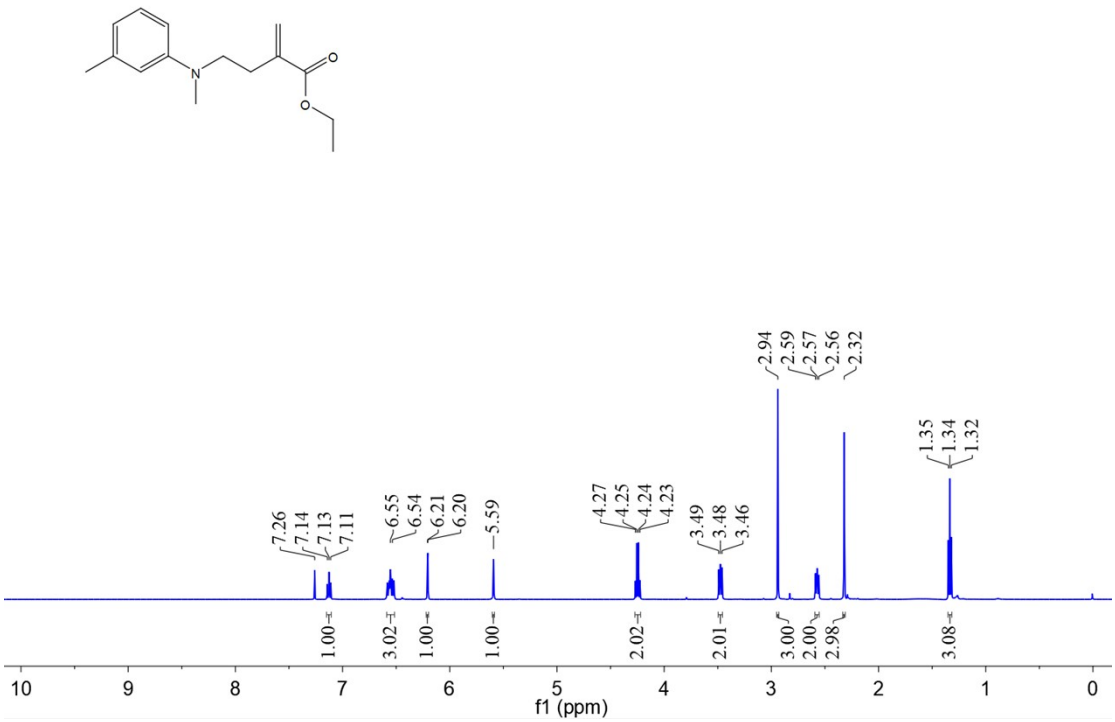

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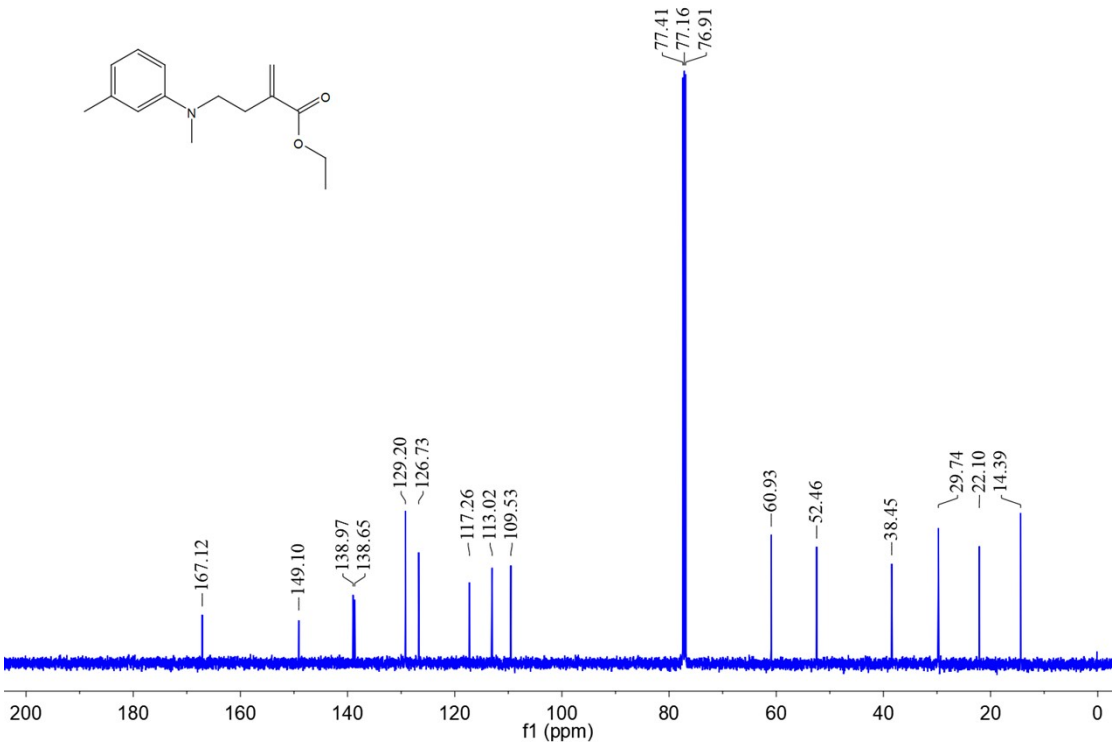

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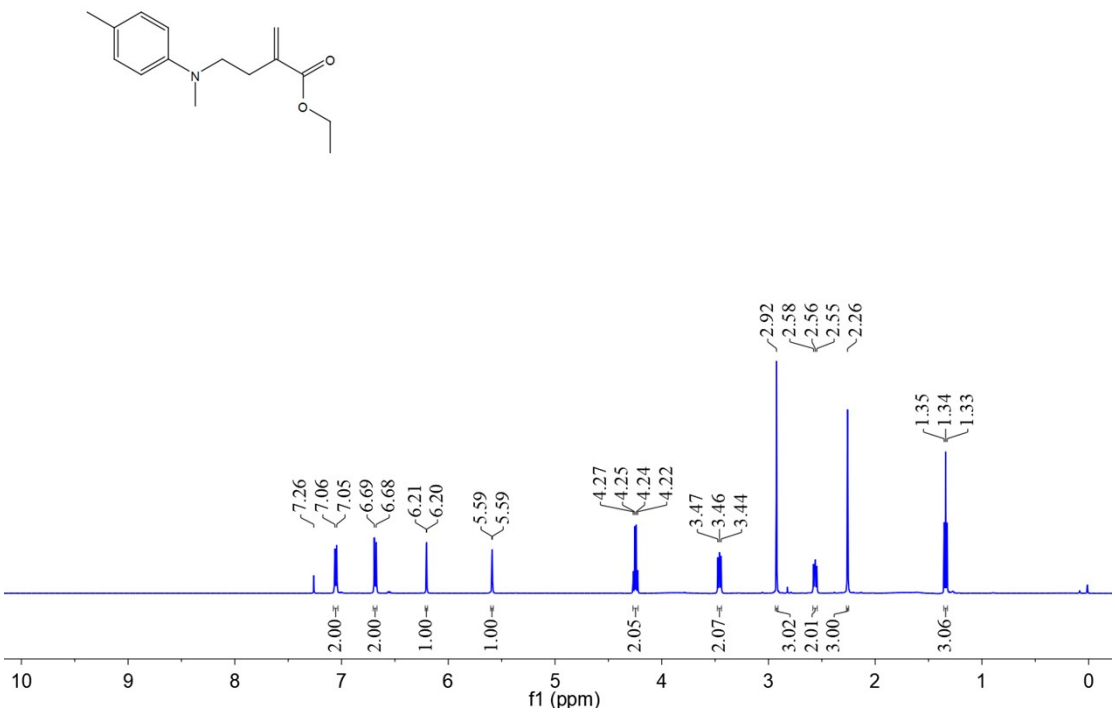
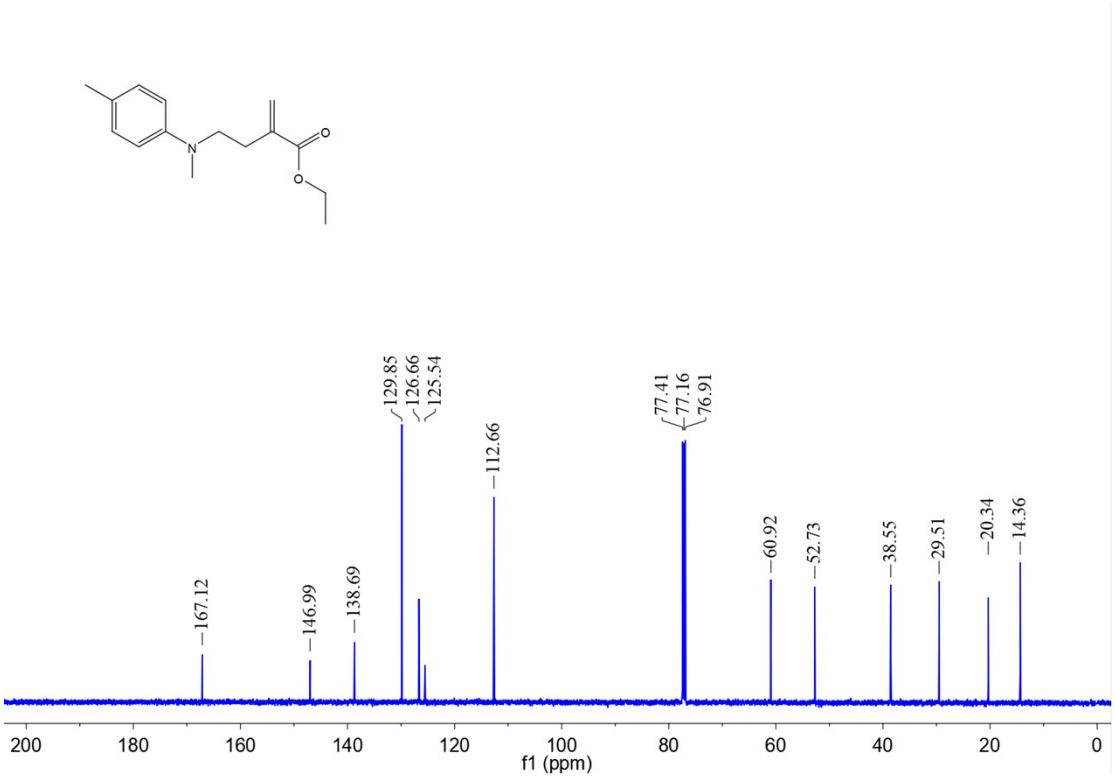


^{13}C-NMR spectrum of 3sa



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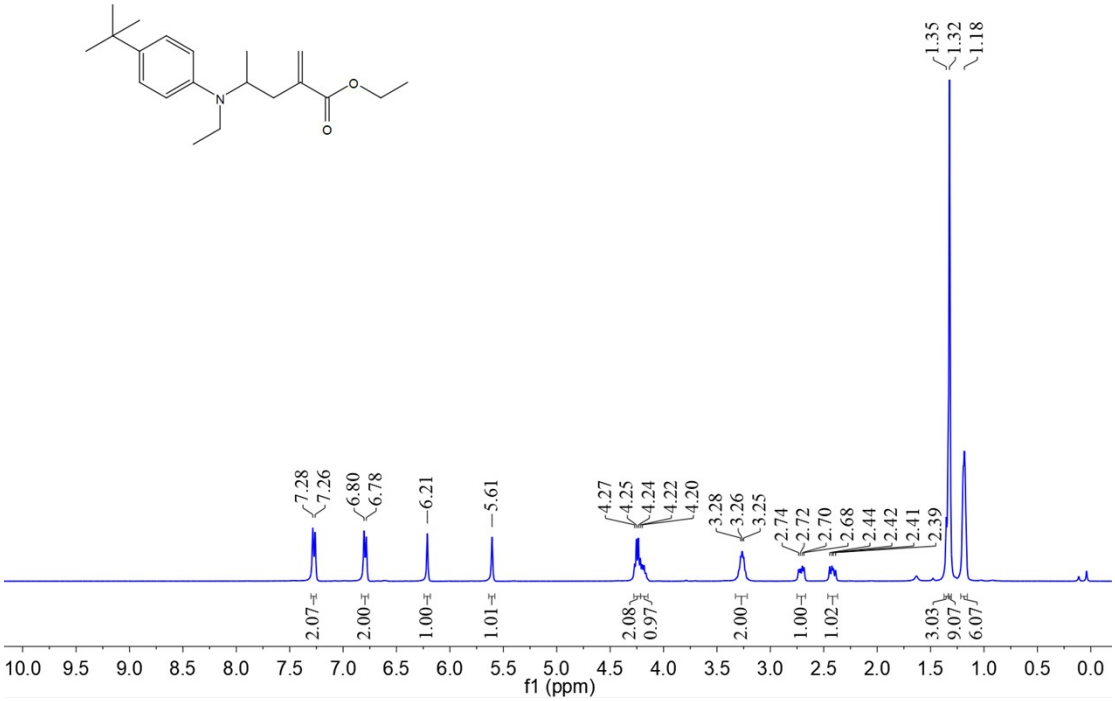
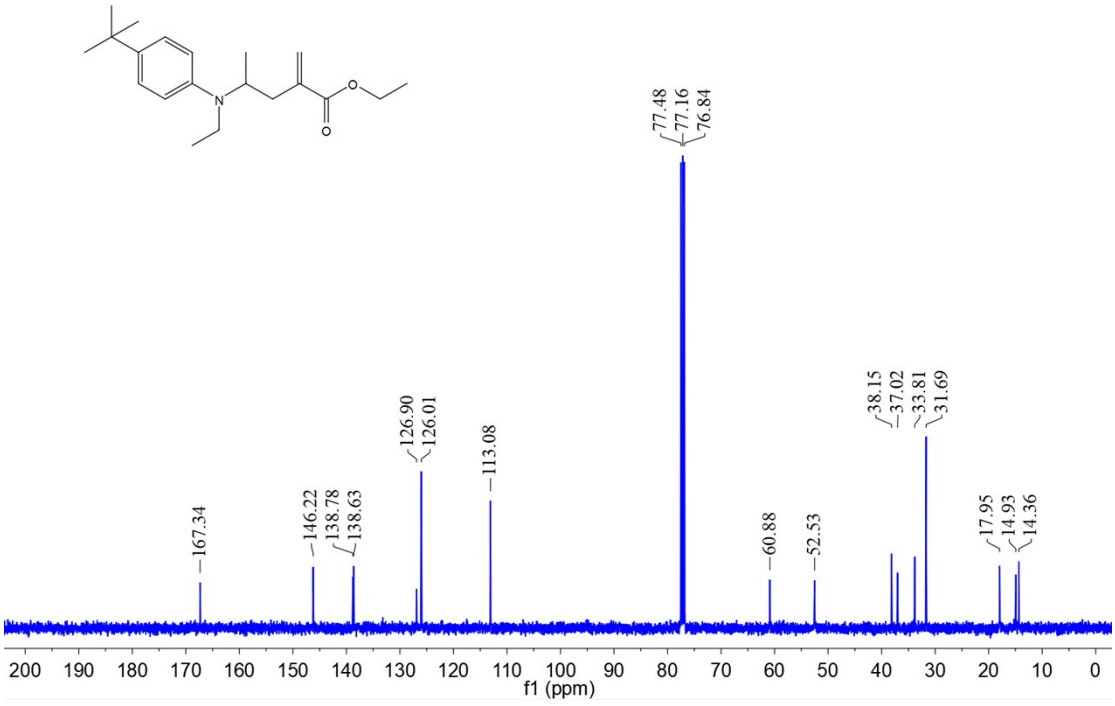
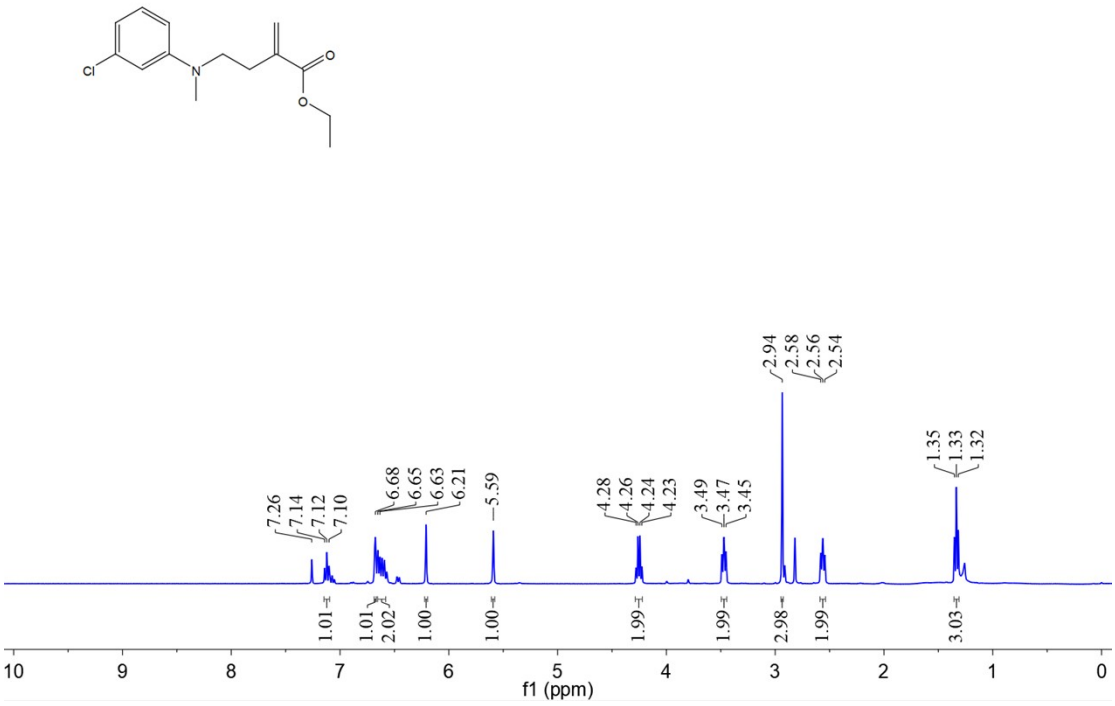


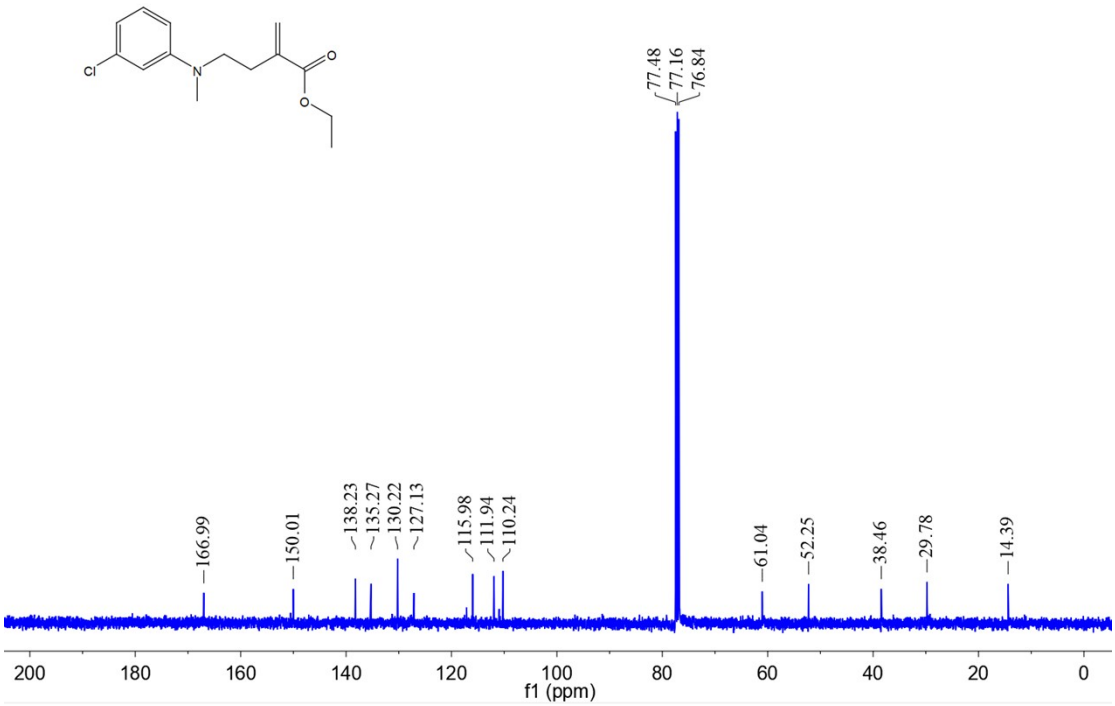
^{13}C-NMR spectrum of 3ta



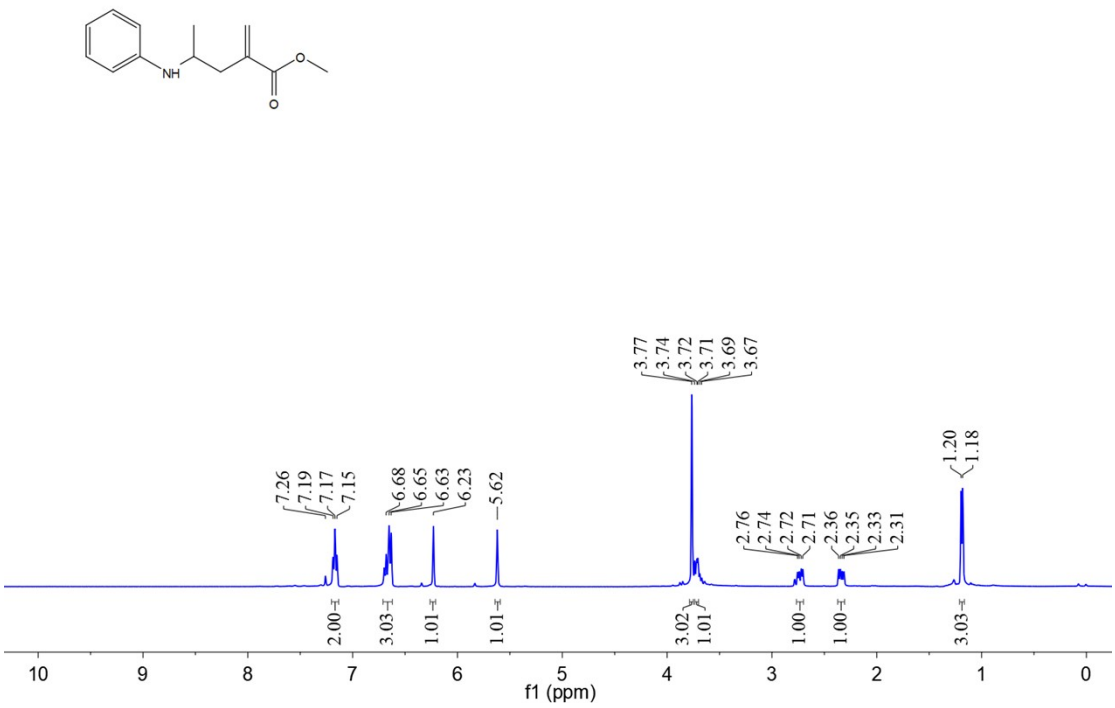
^{1}H-NMR spectrum of 3ua



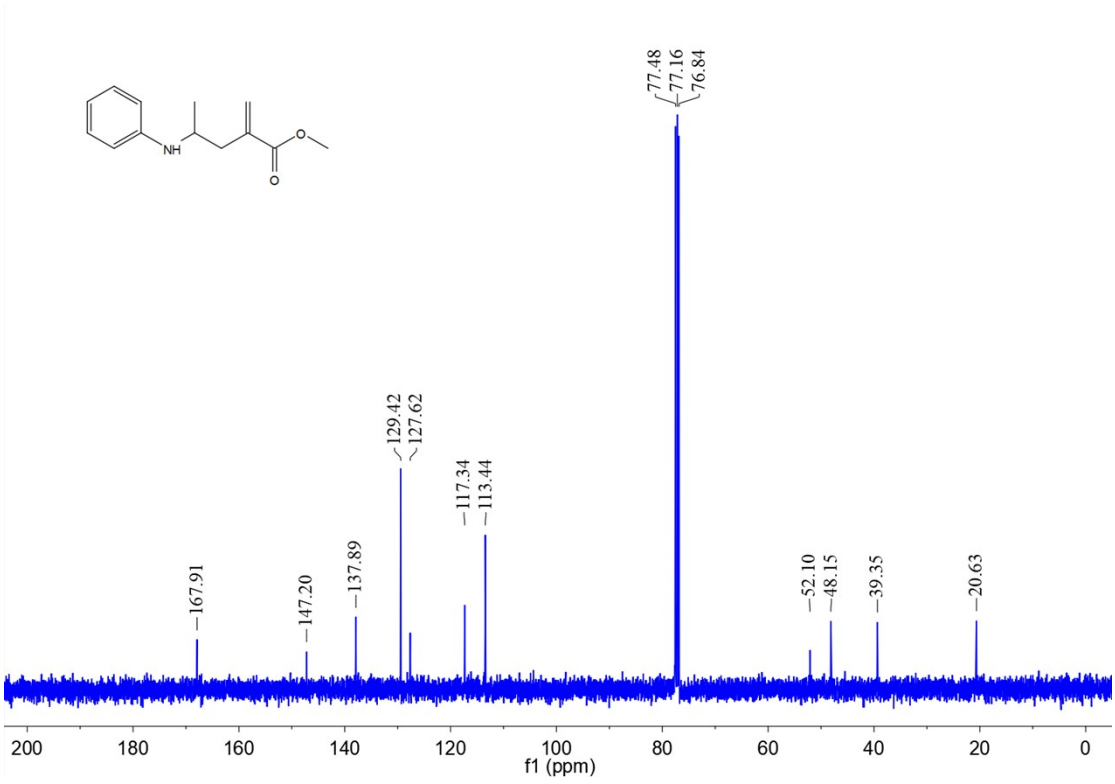
^{13}C-NMR spectrum of 3ua



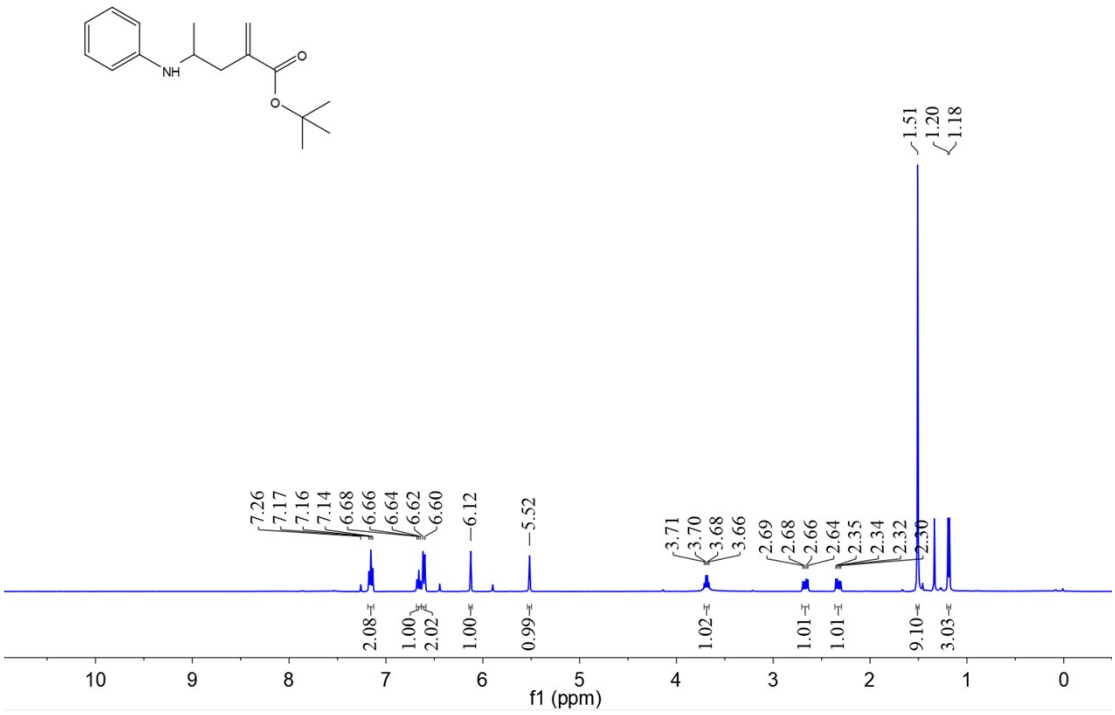
^{1}H-NMR spectrum of 3ab



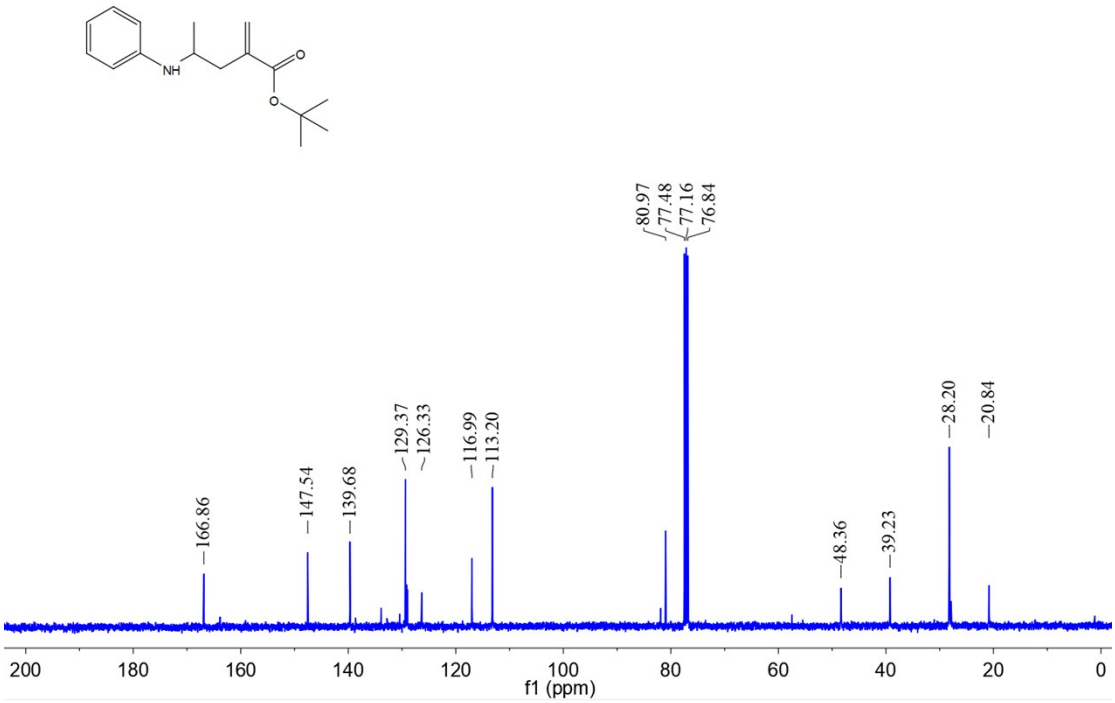
^{13}C-NMR spectrum of 3ab



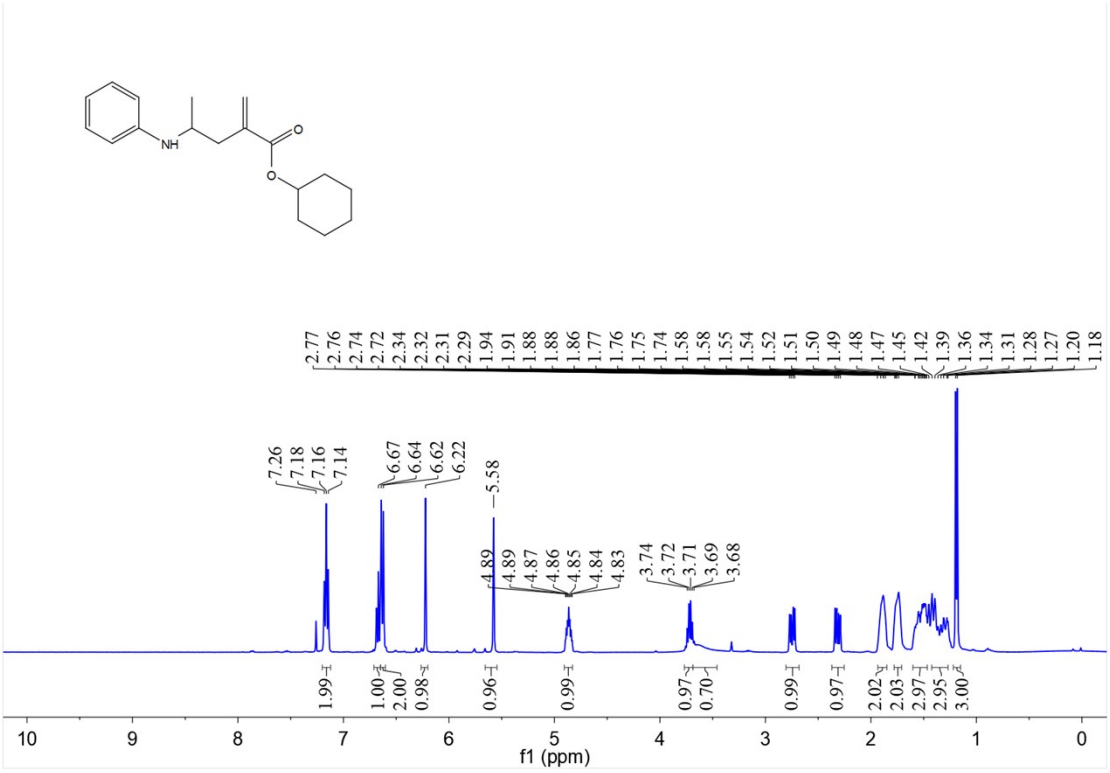
^{1}H-NMR spectrum of 3ac



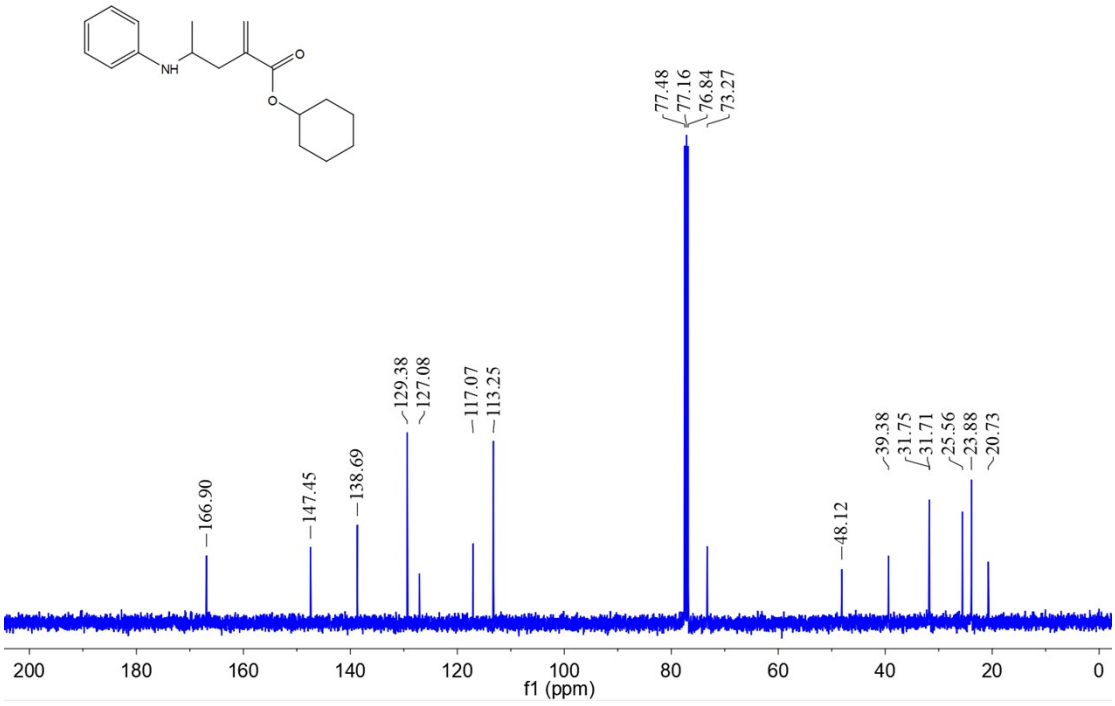
^{13}C-NMR spectrum of 3ac



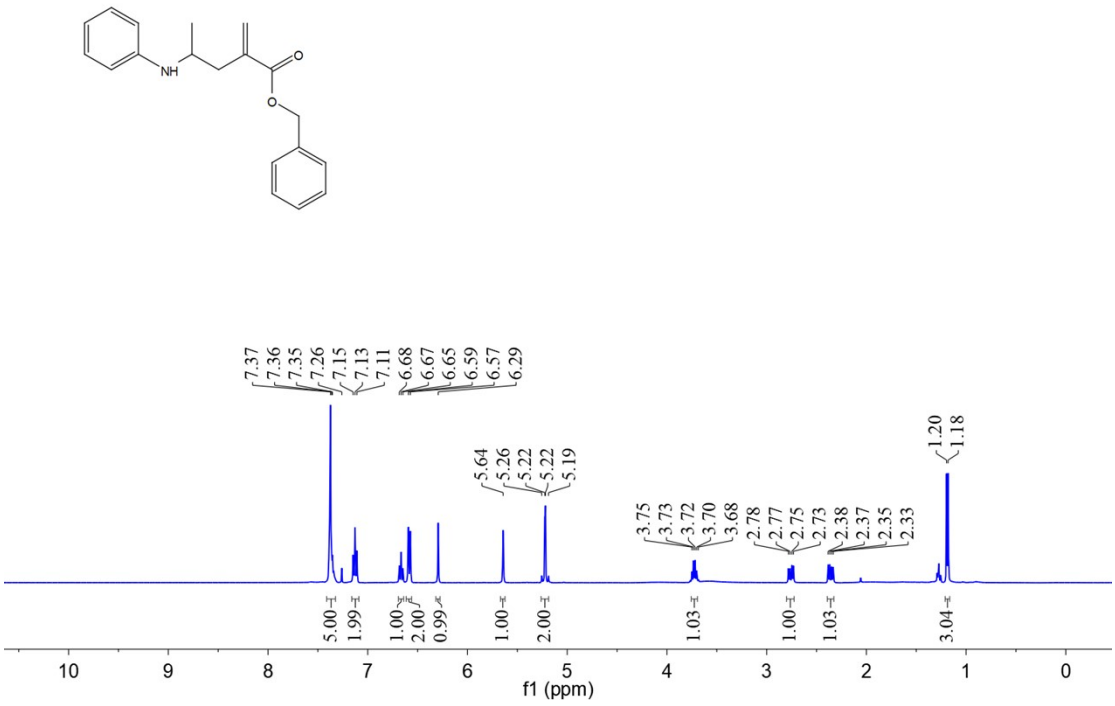
^{1}H-NMR spectrum of 3ad



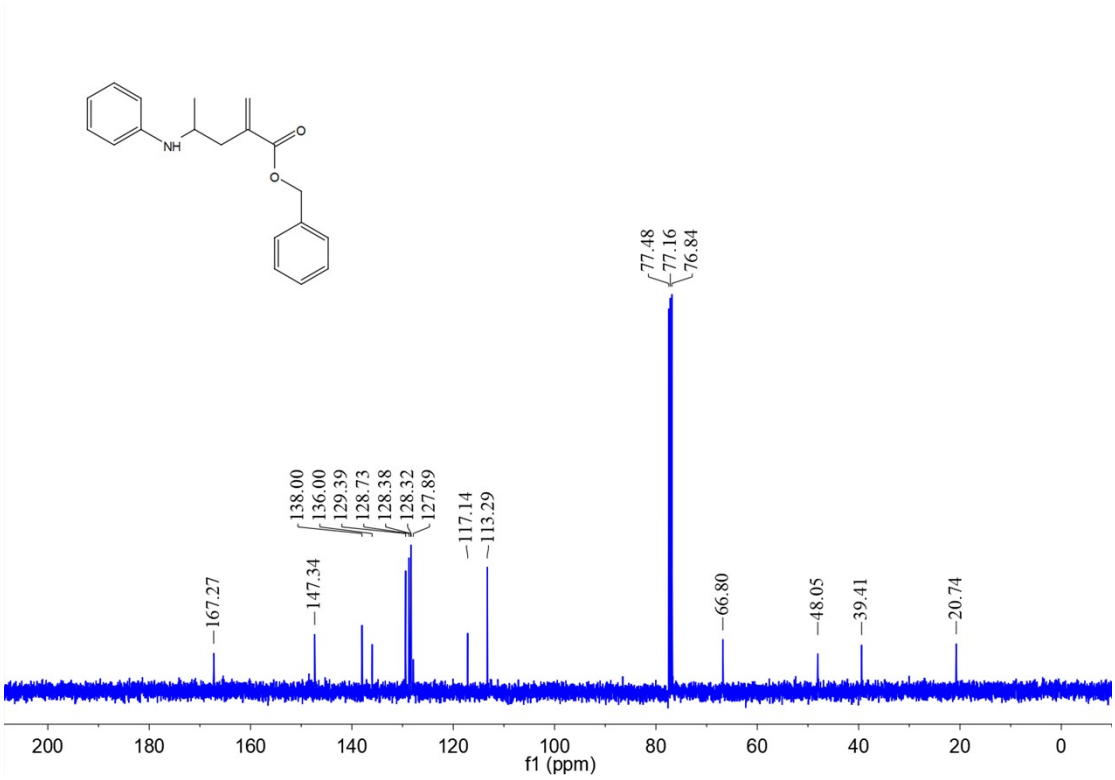
^{13}C-NMR spectrum of 3ad



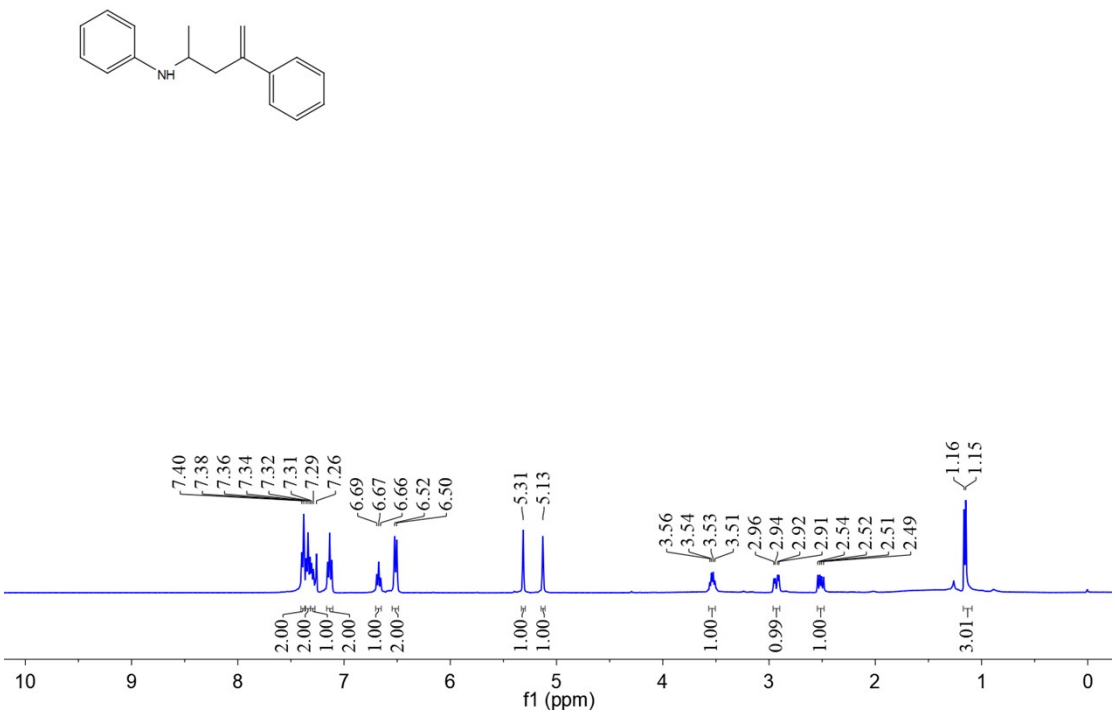
^{1}H-NMR spectrum of 3ae



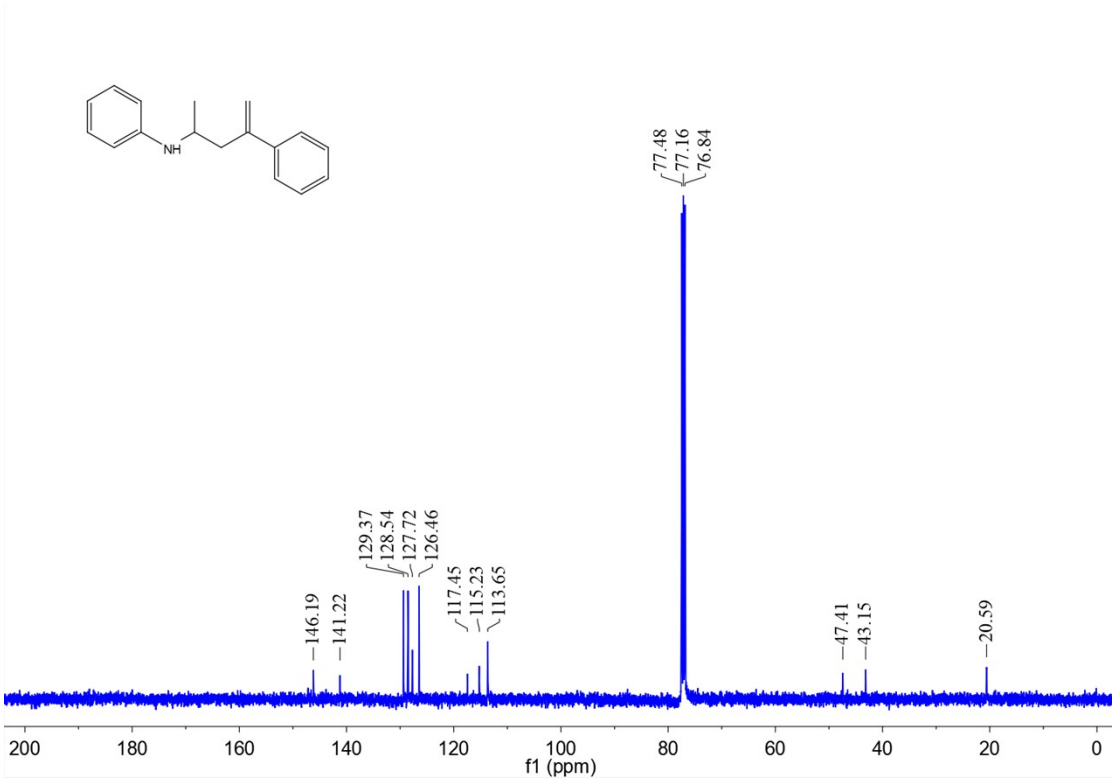
^{13}C-NMR spectrum of 3ae



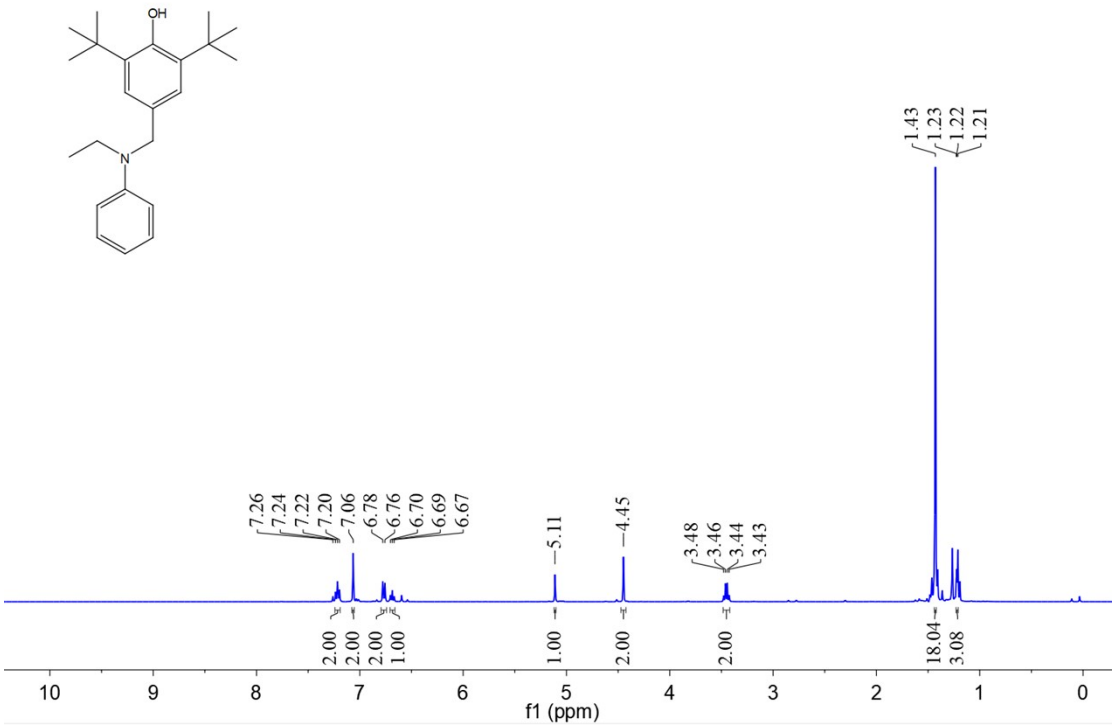
^{1}H-NMR spectrum of 3af



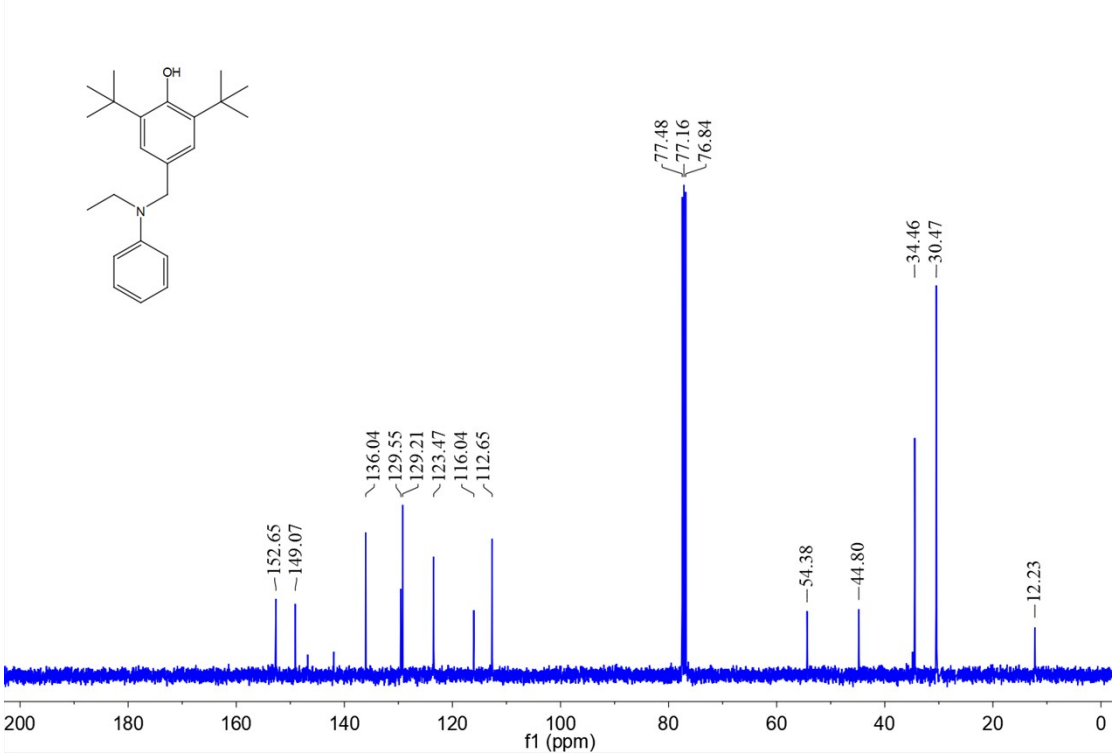
^{13}C-NMR spectrum of 3af



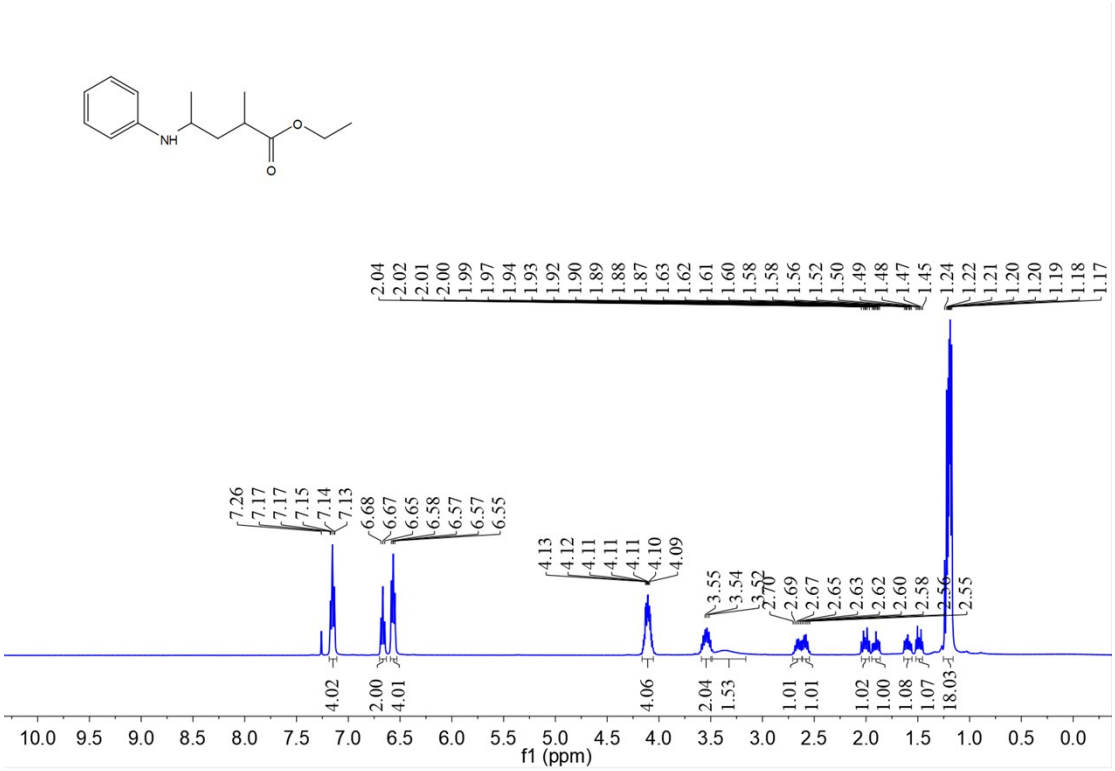
^{1}H-NMR spectrum of 4



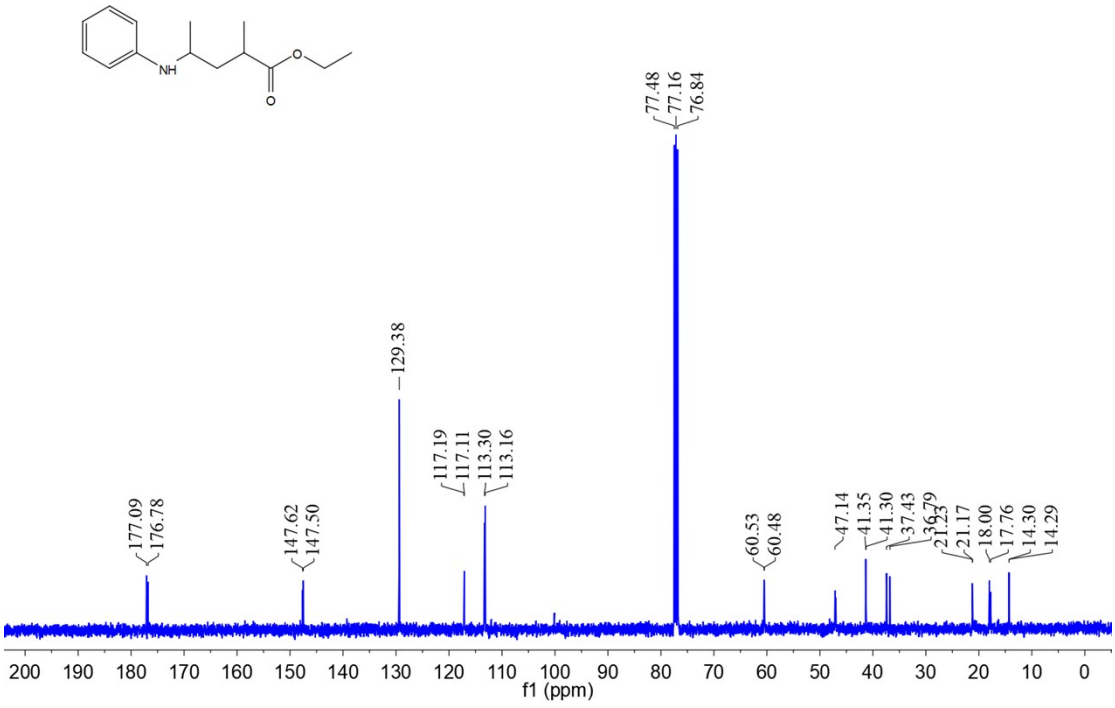
^{13}C-NMR spectrum of 4



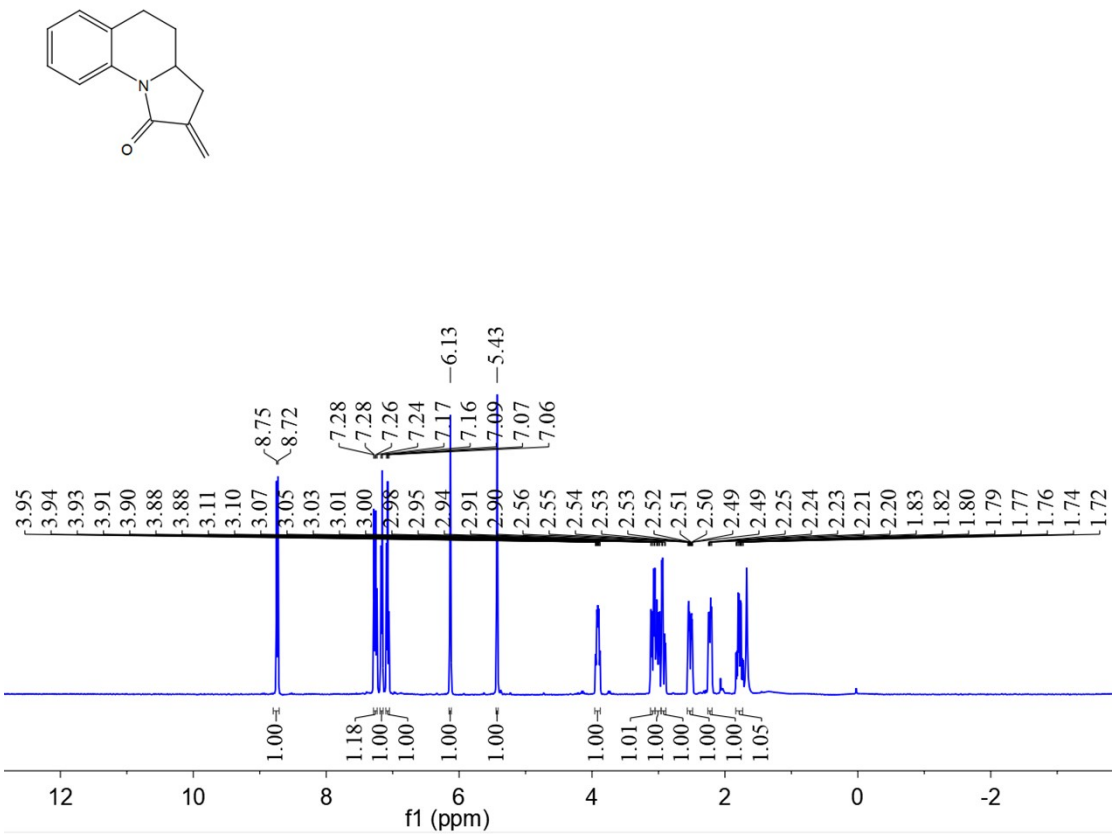
^{13}C-NMR spectrum of 3aa''



^{13}C-NMR spectrum of 3aa''



^{1}H-NMR spectrum of 6



^{13}C-NMR spectrum of 6