Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible Light Mediated Regioselective 1,3-Oxylallylation of Aryl Cyclopropanes Under Redox-Neutral Conditions

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General Information

The reactions were conducted in oven-dried reaction tube. And the photoinduced reactions were carried out in oven-dried Schlenk-tube with blue LEDs Irradiation Parallel Reactor. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. All solvents were dried by passing through a column of neutral alumina under nitrogen prior to use. Organic solvents were concentrated under reduced pressure on an IKA RV 10 rotary evaporator. Chromatography was performed using silica gel with distilled solvents. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates visualized under UV light (254 nm) and dyed with cerous molybdate solution by heating.

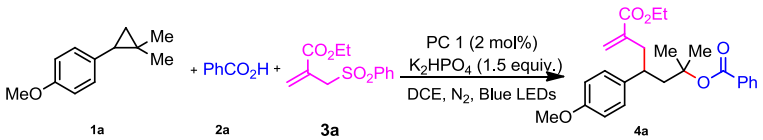
^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (100 MHz for ^{13}C NMR) spectrometer at ambient temperature. Chemical shifts are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.0$). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). Active hydrogen of products didn't show due to hydrogen deuterium exchange in $CDCl_3$. High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

The photocatalyst Acr-Mes-$Ph^{+}BF_4^{-}$(PC 1)[1], [Ir(dF(CF_3)ppy)$_2$(4,4'-dtbbpy)]PF_6(PC 4), [Ir(dF(CF_3)ppy)$_2$(4,4'-dCF_3bpy)]PF_6(PC 5) and [Ir(dF(CF_3)ppy)$_2$(5,5'-dCF_3bpy)]PF_6(PC 6),[2]were prepared following literature procedures. Acr-Mes-$Me^{+}ClO_4^{-}$ (PC 3) and Acr-Mes-$Me^{+}BF_4^{-}$ (PC 2) were purchased from Energy.

Starting materials like aryl cyclopropanes **1** and allyl sulfone **3** were prepared according to the literature.[3,4] The NMR spectra of the known compounds were in full accordance with the data in the literatures.

Reaction Condition Optimization

The screen of Photocatalyst[a]

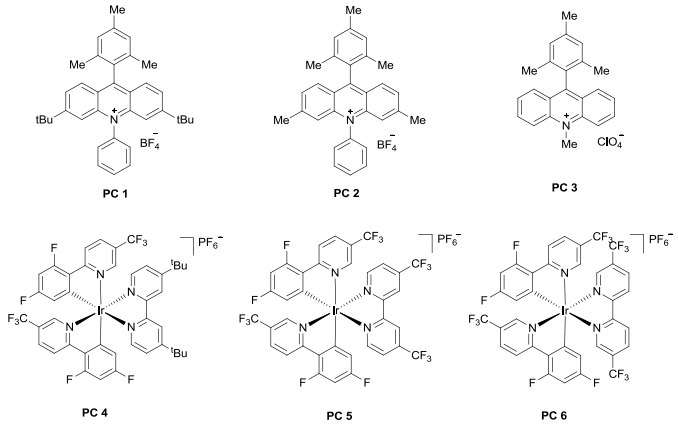


1a 2a 3a 4a

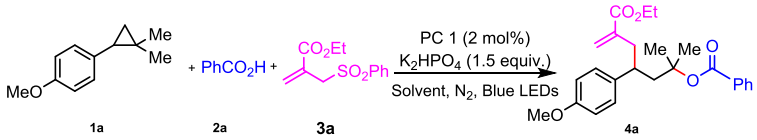
Entry	Photocatalyst	Yield(%)
1	*PC 1*	*47(43)*[b]
2	PC 2	*43*
3	PC 3	*20*
4	PC 4	*31*
5	PC 5	*30*
6	PC 6	*31*

[a] Unless otherwise noted, reaction conditions: **1a** (0.1 mmol), **2a** (0.2mmol, 2.0 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (2 mol%), K_2HPO_4 (1.5 equiv.), DCE (1.0

mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere. [b] Isolated yield



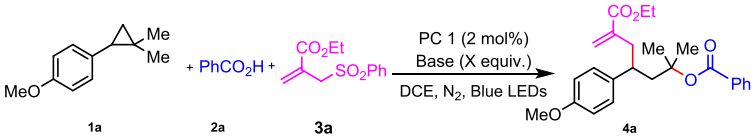
The screen of the solvent[a]



Entry	Solvent	Yield (%)
1	DCE	47(43)[b]
2	DCM	36
3	$CHCl_3$	16
4	DMSO	trace
5	DMF	trace
6	DMA	0
7	MeCN	35
8	THF	14
9	Actone	17
10	MTBE	10
11	DME	trace
12	Dioxane	7
13	Et_2O	0
14	Toluene	0
15	Beneze	0
16[c]	DCE(0.25mL)	59
17[c]	DCE(0.5mL)	72(65)[b]
18[c]	DCE(0.75mL)	63
19[c]	DCE(1.0mL)	54

[a] Unless otherwise noted, the reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2mmol, 2.0 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (2 mol%), K_2HPO_4 (1.5 equiv.), solvent (1.0 mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere with NMR yields were determined by crude ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yield. [c] The reactions were carried out by using **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), **3a** (0.6 mmol, 3.0 equiv.), PC (2 mol%), K_2HPO_4 (0.2 equiv.), DCE, irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere.

The screen of base[a]

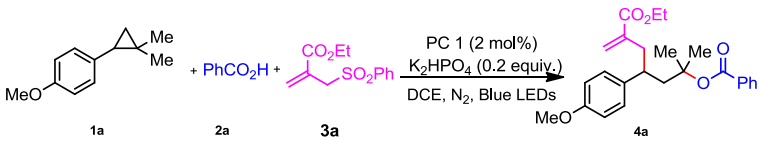


1a 2a 3a 4a

Entry	Base	Yield (%)
1	None	24
2	K_2HPO_4(2 equiv.)	63
3	K_2CO_3 (2 equiv.)	50
4	$KHCO_3$ (2 equiv.)	58
5	K_3PO_4 (2 equiv.)	56
6	Na_2CO_3 (2 equiv.)	47
7	Li_2CO_3 (2 equiv.)	64
8	Cs_2CO_3 (3 equiv.)	42
9	pyridine(2 equiv.)	32
10	DABCO (2 equiv.)	24
11	2,6-lutidine (2 equiv.)	56
12	2,4,6-collidine(2 equiv.)	49
13	KO^{t}Bu(2 equiv.)	31
14	DBU(2 equiv.)	58
15	K_2HPO_4 (1 equiv.)	61
16	KH_2PO_4(0.5 equiv.)	65
17	KH_2PO_4(0.2 equiv.)	69(65)[b]
18	KH_2PO_4(0.1 equiv.)	69
19	KH_2PO_4(0.05 equiv.)	68

[a] Unless otherwise noted, the reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (2 mol%), Base (X equiv.), DCE (0.5 mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere with NMR yields were determined by crude ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yield.

Ratio of 1a:2a:3a[a]



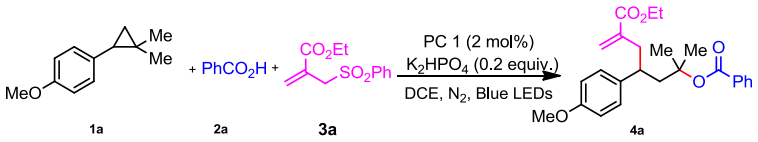
1a 2a 3a 4a

Entry	1a: 2a: 3a	Yield(%)
1	1: 1: 3	65
2	1: 1.5: 3	78(74)[b]
3	1: 2: 3	69
4	1: 1.5: 2	40
5	1: 1.5: 4	62
6	1: 1.5: 5	72

[a] Unless otherwise noted, the reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (2 mol%), K_2HPO_4 (0.2

equiv.), DCE (0.5 mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere with NMR yields were determined by crude ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Screening photocatalyst loading[a]

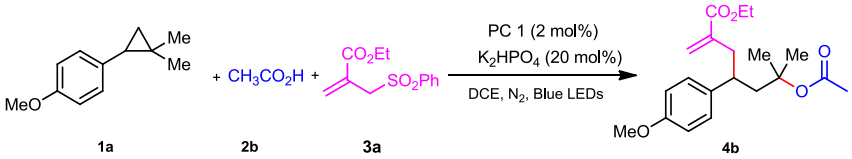


1a 2a 3a 4a

Entry	PC 1(X mol%)	Yield(%)
1	0.5	68
2	1.0	70
3	2.0	75
4	5.0	78

[a] Unless otherwise noted, the reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (X mol%), K_2HPO_4 (0.2 equiv.), DCE (0.5 mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere with NMR yields were determined by crude ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Controlled experiments

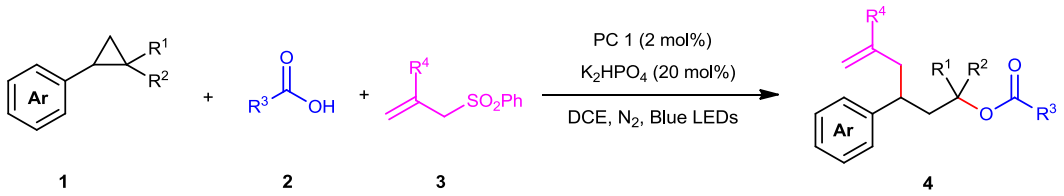


1a 2b 3a 4b

Entry	Conditions	Yield(%)
1	-	*77*
2	Without PC 1	*n.r.*
3	In the dark	*n.r.*
4	Air	*n.d.p.*
5	Purple LEDs instead of blue LEDs	*72*
6	AcOK(2.0 equiv.) instead of 2b and base	*47*

[a] Unless otherwise noted, the reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), **3a** (0.3 mmol, 3.0 equiv.), PC (2 mol%), K_2HPO_4 (0.2 equiv.), DCE (0.5 mL), irradiation with 5 W blue LEDs at room temperature for 16 h under N_2 atmosphere

General procedure for 1,3-Oxylallylation of Aryl Cyclopropanes



1 2 3 4

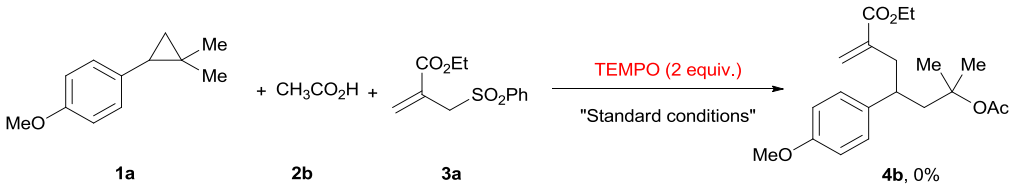
In an over dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane **1** (0.2 mmol, 1.0 equiv.), carboxylic acid **2** (0.3 mmol, 1.5 equiv.), allyl sulfone **3** (0.6 mmol, 3.0 equiv.), K_2HPO_4 (0.04 mmol, 6.9 mg) and photocatalyst (0.004 mmol, 2.2 mg) with DCE (0.5 mL) were added under N_2 and then the reaction tube was capped, and the resulting mixture was irradiated under 5 W blue LEDs. When the reaction was determined to be completed by TLC, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel (PE : EtOAc = 100:0 to 20:1) to afford the desired product **4**.

Reaction apparatus

Irradiation of visible light was performed with a 5 W Blue LED lamp. With the help of fan, the heating effect from LED irradiation conditions above was minimal. With 3 hours irradiation, the increase of temperature was less than 5 ℃. The distance between vial and lamp was approximately 2 cm.

Mechanistic study

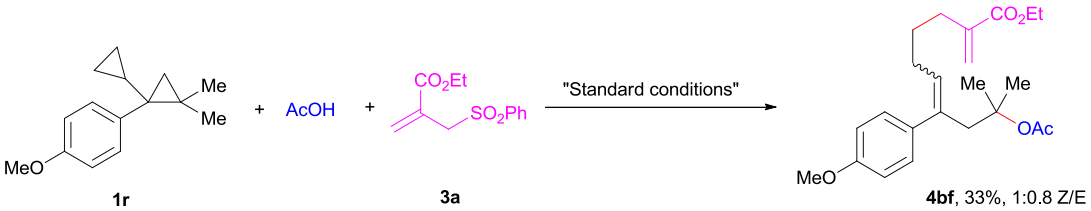
TEMPO quenching experiments



1a **2b** **3a** **4b**, 0%

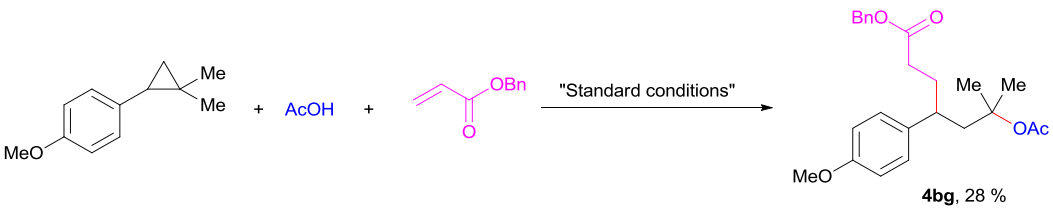
In an over dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane **1a** (0.2 mmol, 1.0 equiv.), acetic acid **2b** (0.3 mmol, 1.5 equiv.), allyl sulfone **3a** (0.6 mmol, 3.0 equiv.), K_2HPO_4 (0.04 mmol, 6.9 mg) and PC 1 (0.004 mmol, 2.2 mg) with DCE (0.5 mL) and TEMPO (0.4 mmol) were added under N_2 and then the reaction tube was capped, and the resulting mixture was irradiated under 5 W blue LEDs for 36 h, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was directly identified by ^1H and GC-MS. Neither **4b** nor TEMPO adduct was detected.

Radical clock reaction



1r **3a** **4bf**, 33%, 1:0.8 Z/E

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, K_2HPO_4 (0.04 mmol, 6.9 mg), photocatalyst (PC-VIII) (2.3 mg, 0.004 mmol, 2 mol%) were added. The Schlenk tube was purged with nitrogen three times, then acetic acid **2b** (0.3 mmol, 1.5 equiv.), allyl sulfone **3a** (0.6 mmol, 3.0 equiv.), **1r** (43.2 mg, 0.2 mmol, 1.0 equiv.) and DCE (0.5 mL) were added. The Schlenk tube was sealed and irradiated with a 5 W blue LED lamp (l = 459 nm) at room temperature for 48 h. When the reaction was determined to be completed by TLC analysis, the mixture was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel (PE : EtOAc = 20 : 1 to 10 : 1) to afford the desired product **4bf (**1:0.8 alkene isomeric mixture**)**.

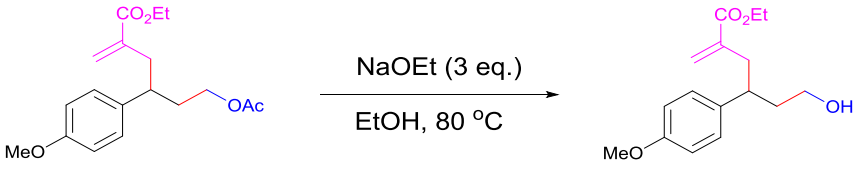


4bg, 28 %

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, K_2HPO_4 (0.04 mmol, 6.9 mg), photocatalyst (PC-VIII) (2.3 mg, 0.004 mmol, 2 mol%) were added. The Schlenk tube was purged with nitrogen three times, then acetic acid **2b** (0.3 mmol, 1.5 equiv.), benzyl acrylate (0.6 mmol, 3.0 equiv.), **1a** (0.2 mmol, 1.0 equiv.) and dichloroethane (0.5 mL) were added. The Schlenk tube was sealed and irradiated with a 5 W blue LED lamp (l = 459 nm) at room temperature for 48 h. When the reaction was determined to be completed by TLC analysis, the mixture was evaporated to dryness under reduced pressure and

the crude residue was purified by column chromatography on silica gel (PE : EtOAc = 20 : 1 to 10 : 1) to afford the desired product **4bg**.

Hydrolysis of 4k



4k **4bh**

54% (84% brsm)

Ethyl 6-hydroxy-4-(4-methoxyphenyl)-2-methylenehexanoate (4bh)

A solution of **4k** (26 mg, 0.08 mmol) in EtOH (1.0 mL) was added NaOEt (3.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. After completion, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic layer was dried by Na_2SO_4 and evaporated under reduced pressure. Then the residue was purified by purified by column chromatography on silica gel (hexane/ethyl acetate = 5:1) to afford the desired product **4bh** as a colorless oil (12 mg, 53% yield) together with recovery of 9.6 mg of **4k**.

Emission quenching experiments (Stern-Volmer studies)

Emission intensities were recorded using PerkinElemer LS 55 Fluorescence Spectrometer for all experiments. All solutions Acr-Mes-$Ph^+BF_4^-$(PC1) (10^{-4} mM) were excited at 375 nm and the emission intensity at 575 nm was collected at room temperature under an air atmosphere. Samples were prepared by adding solutions of photocatalyst, quencher, and DCE to obtain a total volume of 3.0 mL under air. The sample was shaken for 1 min and then the emission of the sample was collected. The data show that 1-(2,2-dimethylcyclopropyl)-4-methoxybenzene **1a** was competent at quenching the excited state of the photocatalyst. while acetic acid **2b** and ethyl 2-((phenylsulfonyl)methyl)acrylate **3a** was shown unable to quench the excited state of photocatalyst.

Species	Concentration (mM)
Acr-Mes-$Ph^+BF_4^-$ (PC1)	1×10^{-4}
quencher	varied

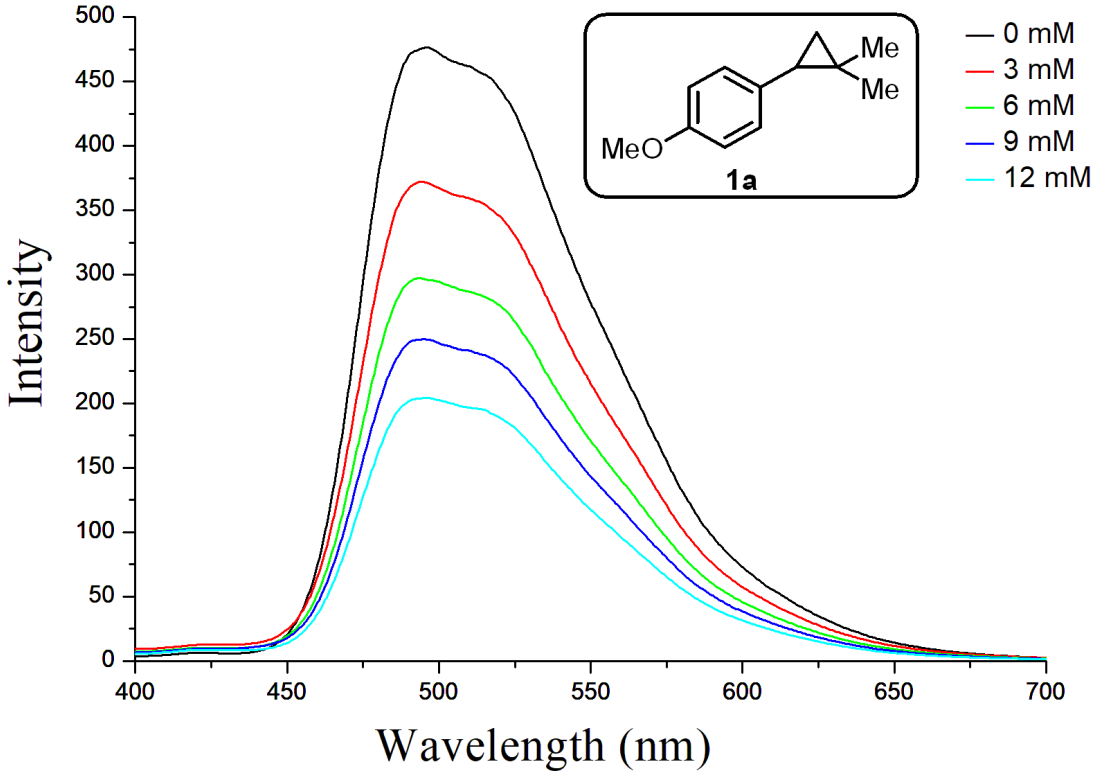


Figure S1. Fluorescence spectra of photocatalyst with different concentration of 1a.

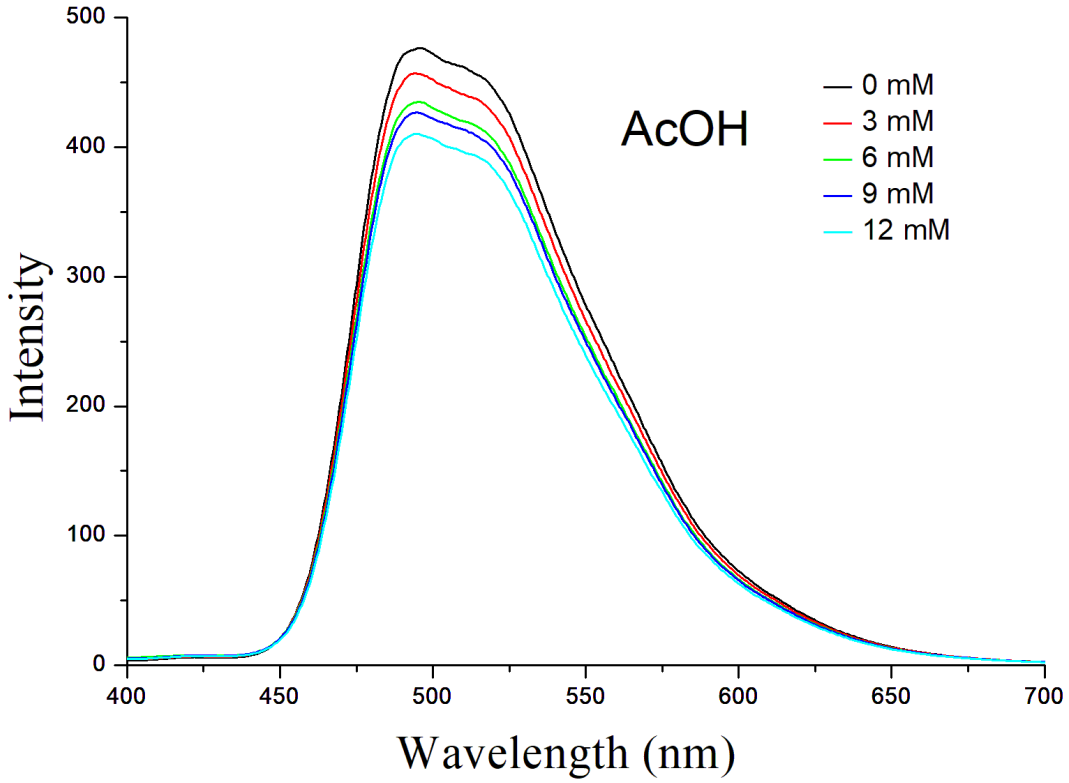


Figure S2. Fluorescence spectra of photocatalyst with different concentration of acetic acid.

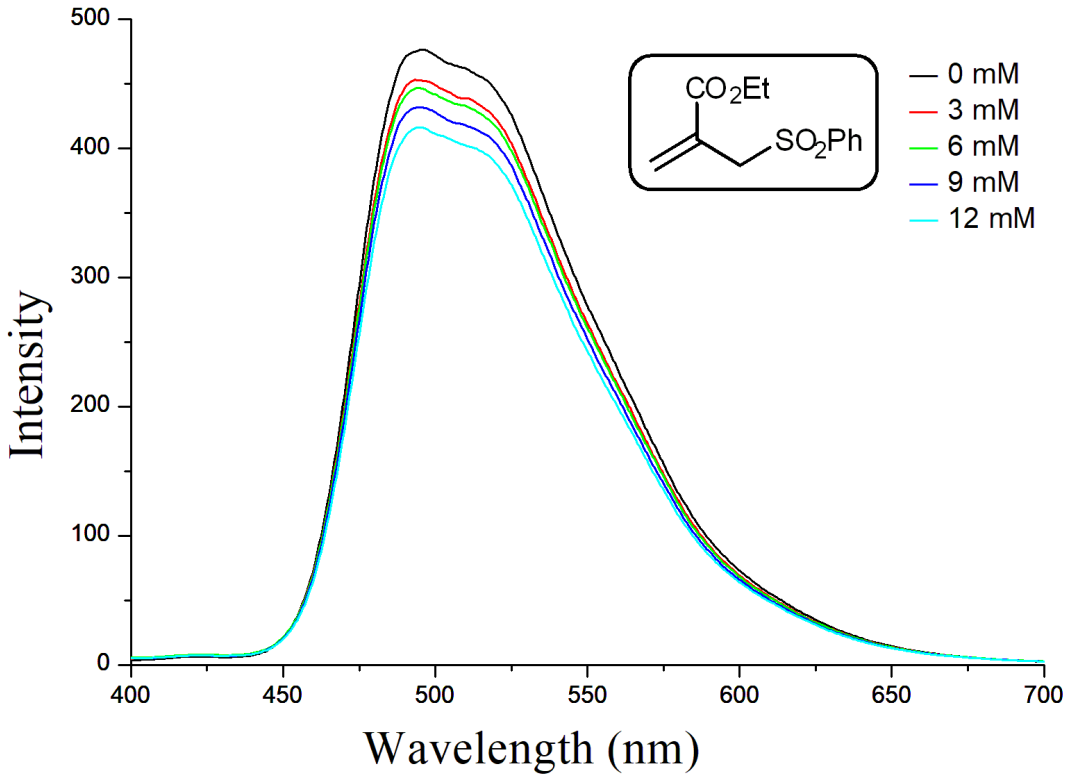


Figure S3. Fluorescence spectra of photocatalyst with different concentration of allyl sulfone.

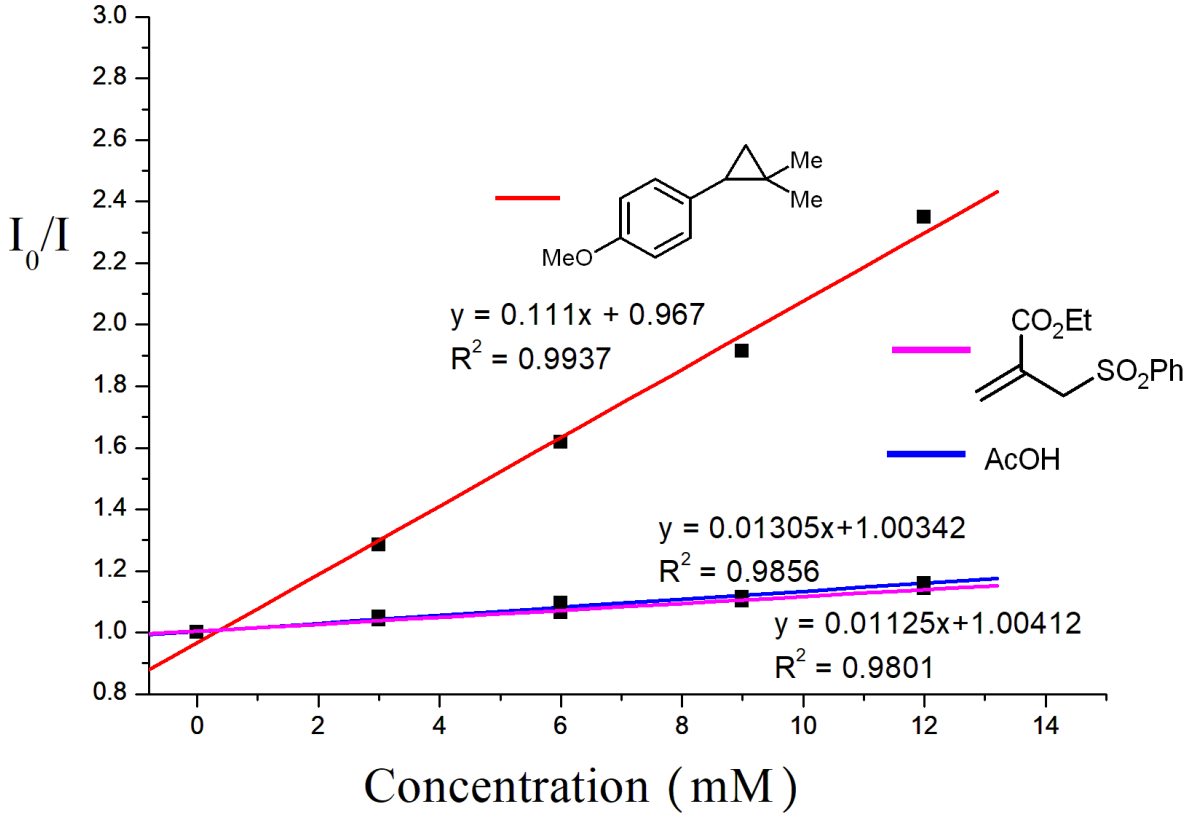
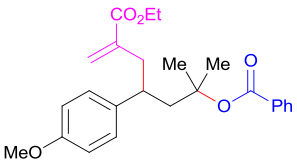


Figure S4. linear fittings of photocatalyst with different concentration of three reactants.

Characterization data for all new compounds

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl benzoate (4a)



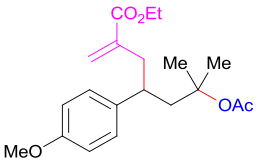
4a was obtained as a yellow oil (60.8 mg, 16 h, yield: 74%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.40

^{1}H NMR (400 MHz, $CDCl_3$): 7.66 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.51 – 7.37 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.64 (s, 3H), 3.10 (ddt, *J* = 9.8, 6.8, 3.2 Hz, 1H), 2.63 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.53 – 2.38 (m, 2H), 2.12 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.48 (d, *J* = 1.7 Hz, 6H), 1.23 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.16, 165.68, 157.79, 138.66, 137.17, 132.28, 131.78, 129.41, 128.76, 127.93, 127.04, 113.74, 83.08, 60.63, 55.10, 45.72, 41.88, 40.09, 27.18, 26.87, 14.30.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 433.1985, found: 433.1994.

Ethyl 6-acetoxy-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4b):



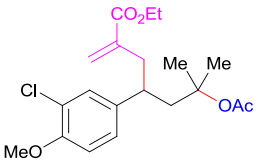
4b was obtained as a yellow oil (53.6 mg, 16 h, yield: 77%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.1 Hz, 1H), 4.19 – 4.13 (m, 2H), 3.75 (s, 3H), 3.04 – 2.97 (m, 1H), 2.60 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.41 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.33 (dd, *J* = 14.4, 9.7 Hz, 1H), 1.97 (dd, *J* = 14.5, 3.5 Hz, 1H), 1.63 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.2, 157.8, 138.7, 137.3, 128.8, 126.9, 113.7, 82.2, 60.6, 55.3, 45.2, 41.7, 40.0, 27.0, 26.9, 22.3, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 371.1829, found: 371.1837.

Ethyl 6-acetoxy-4-(3-chloro-4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4c):



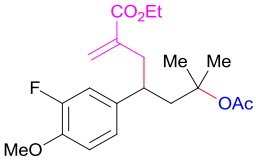
4c was obtained as a yellow oil (42.2 mg, 16 h, yield: 55%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 2.1 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.24 (s, 1H), 4.20 – 4.13 (m, 2H), 3.84 (s, 3H), 3.03 – 2.96 (m, 1H), 2.59 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.39 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.29 (dd, *J* = 14.6, 9.7 Hz, 1H), 1.95 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.64 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 167.0, 153.2, 138.6, 138.4, 129.6, 127.2, 122.0, 111.9, 82.0, 60.7, 56.2, 45.2, 41.6, 39.9, 27.0, 26.8, 22.2, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 405.1439, found:405.1437.

Ethyl 6-acetoxy-4-(3-fluoro-4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4d):



4d was obtained as a yellow oil (43.8 mg, 16 h, yield: 60%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.45.

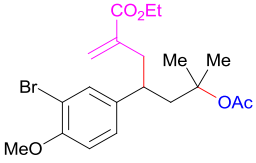
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.78 (m, 3H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.24 – 5.23 (m, 1H), 4.17 (qd, *J* = 7.1, 1.8 Hz, 2H), 3.83 (s, 3H), 3.00 (dtt, *J* = 9.4, 7.2, 3.5 Hz, 1H), 2.59 (dd, *J* = 13.4, 6.2 Hz, 1H), 2.38 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.27 (dd, *J* = 14.6, 9.6 Hz, 1H), 1.97 (dd, *J* = 14.6, 3.5 Hz, 1H), 1.67 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H)

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.47 (s, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 167.0, 152.3 (d, *J* = 245.1 Hz), 145.7 (d, *J* = 10.8 Hz), 138.5 (d, *J* = 5.6 Hz), 138.4, 127.1, 123.6 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 18.0 Hz), 113.2 (d, *J* = 2.2 Hz), 82.1, 60.7, 56.3, 45.3, 41.6, 40.0, 26.9, 26.8, 22.2, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 389.1735, found: 389.1743.

Ethyl 6-acetoxy-4-(3-bromo-4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4e):



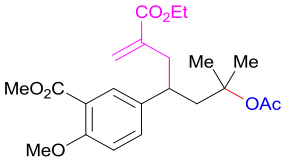
4e was obtained as a yellow oil (53.6 mg, 16 h, yield: 63%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.04 – 6.97 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 5.25 (s, 1H), 4.16 (q, *J* = 7.2, 6.7 Hz, 2H), 3.84 (s, 3H), 2.99 (qd, *J* = 9.6, 3.4 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.39 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.29 (dd, *J* = 14.6, 9.7 Hz, 1H), 1.95 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.64 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 167.0, 154.1, 139.0, 138.4, 132.6, 127.9, 127.2, 111.8, 111.3, 82.0, 60.7, 56.3, 45.2, 41.6, 39.8, 27.0, 26.8, 22.2, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 499.0934, found: 499.0932.

Methyl 5-(6-acetoxy-2-(ethoxycarbonyl)-6-methylhept-1-en-4-yl)-2-methoxybenzoate (4f):



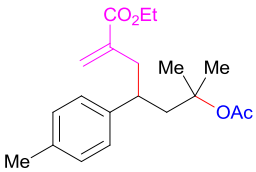
4f was obtained as a yellow oil (49.4 mg, 18 h, yield: 61%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.3 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.03 – 5.98 (m, 1H), 5.23 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.09 – 3.02 (m, 1H), 2.61 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.41 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.31 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.63 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52, 166.80, 157.53, 138.33, 137.02, 132.99, 131.13, 129.13, 128.88, 127.30, 119.57, 111.98, 82.07, 60.73, 56.14, 52.13, 45.23, 41.53, 39.80, 27.00, 26.78, 22.27, 14.31.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 429.1884, found: 429.1892.

Ethyl 6-acetoxy-6-methyl-2-methylene-4-(p-tolyl) heptanoate (4g):



4g was obtained as a yellow oil (36.6 mg, 16 h, yield: 55%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.54

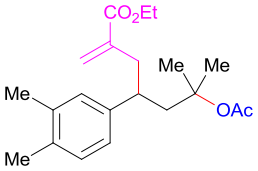
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.02 (s, 1H), 5.25 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.03 (dtt, *J* = 9.7, 7.0, 3.5 Hz, 1H), 2.62 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.45 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.36 (dd, *J* =

14.5, 9.7 Hz, 1H), 2.29 (s, 3H), 1.98 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.62 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.2 142.2, 138.7, 135.4, 129.0, 127.8, 126.9, 82.2, 60.64, 45.1, 41.5, 40.3, 27.0, 26.9, 22.2, 21.1, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 355.1880, found: 355.1883.

Ethyl 6-acetoxy-4-(3,4-dimethylphenyl)-6-methyl-2-methyleneheptanoate (4h):



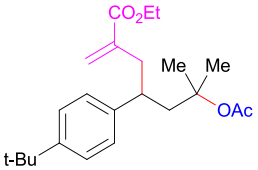
4h was obtained as a yellow oil (38 mg, 16 h, yield: 55%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.82 (m, 2H), 6.03 (d, *J* = 1.4 Hz, 1H), 5.28 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.04 – 2.93 (m, 1H), 2.59 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.45 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.30 (dd, *J* = 14.5, 9.4 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H), 1.98 (dd, *J* = 14.5, 3.6 Hz, 1H), 1.36 (s, 3H), 1.33 (s, 3H), 1.29 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 167.2, 142.8, 138.8, 136.2, 134.0, 129.6, 129.2, 126.8, 125.3, 82.3, 60.6, 45.1, 41.5, 40.2, 29.8, 26.9, 22.2, 19.9, 19.4, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:369.2036, found: 369.2040.

Ethyl 6-acetoxy-4-(4-(tert-butyl)phenyl)-6-methyl-2-methyleneheptanoate (4i):



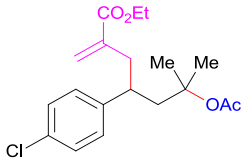
4i was obtained as a yellow oil (41.8 mg, 16 h, yield: 56%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.03 (d, *J* = 1.6 Hz, 1H), 5.28 (d, *J* = 1.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.05 – 2.98 (m, 1H), 2.57 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.48 (dd, *J* = 13.4, 7.5 Hz, 1H), 2.42 (dd, *J* = 14.6, 10.1 Hz, 1H), 1.89 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.48 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.2, 148.6, 142.0, 138.8, 127.6, 126.9, 125.1, 82.0, 60.7, 44.5, 41.4, 40.3, 34.4, 31.5, 27.2, 26.8, 22.1, 14.4.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:397.2349, found: 397.2357.

Ethyl 6-acetoxy-4-(4-chlorophenyl)-6-methyl-2-methyleneheptanoate (4j):



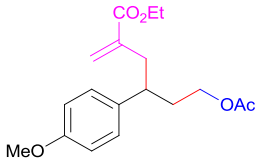
4j was obtained as a yellow oil (41.6 mg, 22 h, yield: 59%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.23 (d, *J* = 1.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.06 (ddt, *J* = 12.3, 6.5, 3.4 Hz, 1H), 2.61 (ddd, *J* = 13.6, 6.5, 1.1 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.39 – 2.33 (m, 1H), 1.97 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.60(s, 3H), 1.34 (d, *J* = 7.3 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 167.0, 143.8, 138.3, 131.6, 129.4, 128.4, 127.2, 82.0, 60.7, 45.1, 41.5, 40.3, 27.1, 26.8, 22.1, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:375.1334, found: 375.1341.

Ethyl 6-acetoxy-4-(4-methoxyphenyl)-2-methylenehexanoate (4k):



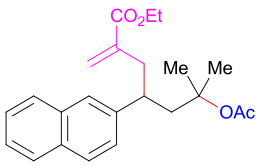
4k was obtained as a yellow oil (30.7 mg, 22 h, yield: 48%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.05 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 1.3 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.95 (ddd, *J* = 11.0, 7.4, 5.3 Hz, 1H), 3.84 (dt, *J* = 11.0, 7.3 Hz, 1H), 3.76 (s, 3H), 2.96 – 2.82 (m, 1H), 2.05 – 1.98 (m, 1H), 1.97 (s, 3H), 1.84 (dddd, *J* = 13.7, 10.4, 7.1, 5.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 167.16, 158.19, 138.59, 135.37, 128.59, 126.76, 113.92, 62.95, 60.70, 55.27, 40.82, 39.75, 34.71, 21.01, 14.28.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:343.1516, found: 343.1516.

Ethyl 6-acetoxy-6-methyl-2-methylene-4-(naphthalen-2-yl)heptanoate (4l):



4l was obtained as a colorless solid (21.4 mg, 36 h, yield: 29%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.35

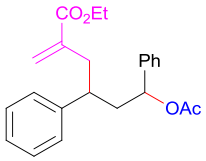
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dq, *J* = 7.0, 3.4, 2.6 Hz, 3H), 7.54 (d, *J* = 1.3 Hz, 1H), 7.42 (dtd, *J* = 14.0, 6.8, 1.5 Hz, 2H), 7.32 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.97 (d, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 1.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.26 (dtd, *J*

= 12.2, 6.6, 3.4 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.59 – 2.54 (m, 1H), 2.53 – 2.47 (m, 2H), 2.07 (dd, *J* = 14.5, 3.5 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.1, 142.7, 138.4, 133.5, 132.2, 128.0, 127.6, 127.6, 127.2, 126.7, 126.2, 125.9, 125.3, 82.2, 60.7, 45.1, 41.5, 41.0, 27.1, 26.9, 22.2, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:391.1880, found: 391.1890.

Ethyl 6-acetoxy-2-methylene-4,6-diphenylhexanoate (4m):



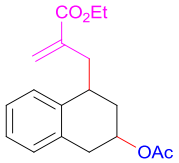
4m was obtained as a colorless oil (54.9 mg, d.r. = 2:3, 36 h, yield: 75%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$, for both diastereomers, d.r. = 2:3**)** δ 7.34 – 7.27 (m, 5H), 7.25 – 7.20 (m, 3H), 7.12 – 7.09 (m, 2H),), 6.07 (d, *J* = 1.4 Hz, 0.4H), 6.03 (d, *J* = 1.6 Hz, 0.6H), 5.55 (dd, *J* = 8.0, 6.8 Hz, 0.6H), 5.45 (dd, *J* = 10.0, 3.5 Hz, 0.4H), 5.31 (d, *J* = 1.3 Hz, 0.4H), 5.23 (d, *J* = 1.4 Hz, 0.6H), 4.17 (q, *J* = 7.1 Hz, 1H), 4.08 (qd, *J* = 7.1, 1.8 Hz, 1H), 3.1 – 3.0 (m, 0.4H), 2.74 – 2.60 (m, 0.6H), 2.60 – 2.45 (m, 2H), 2.40 – 2.25 (m, 1H), 2.16 (ddd, *J* = 13.8, 8.0, 4.5 Hz, 1H), 2.03 (s, 1.2H), 1.88 (s, 1.8H), 1.28 (t, *J* = 7.1 Hz, 1.3H), 1.18 (t, *J* = 7.1 Hz, 1.7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.2, 167.1, 167.0, 143.5, 143.4, 141.3, 140.1, 138.6, 138.4, 128.7, 128.6, 128.5, 128.5, 128.2, 127.9, 127.8, 127.1, 126.9, 126.8, 126.7, 126.6, 126.12, 75.0, 74.2, 60.7, 60.7 43.0, 41.5, 41.4, 41.2, 40.3, 39.6, 21.2, 14.3, 14.2.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:389.1723, found: 389.1730.

Ethyl 2-((3-acetoxy-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)acrylate (4n):



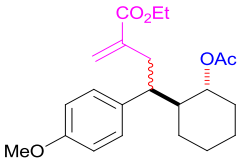
4n was obtained as a colorless oil (47.8 mg, 24 h, yield: 79%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 4H), 6.25 (s, 1H), 5.57 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.01 (dd, *J* = 7.2, 2.0 Hz, 2H), 3.25 – 3.10 (m, 2H), 2.75 – 2.66 (m, 2H), 2.50 – 2.44 (m, 2H), 2.03 (s, 3H), 1.39 – 1.28 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 167.2, 145.4, 141.7, 139.1, 127.0, 126.7, 126.6, 124.9, 124.7, 67.2, 60.9, 46.2, 43.0, 38.2, 34.6, 21.0, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:325.1410, found:325.1418.

Ethyl 4-((1S,2R)-2-acetoxycyclohexyl)-4-(4-methoxyphenyl)-2-methylenebutanoate (4o):



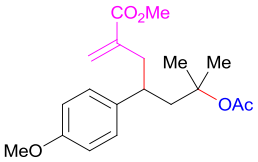
4o was obtained as a colorless oil (36.7 mg, 24 h, yield: 49%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, for both diastereomers, d.r. = 3:1) δ 7.00 (d, *J* = 8.7 Hz, 1.5H), 6.89 (d, *J* = 8.7 Hz, 0.5H), 6.82 – 6.74 (m, 2H), 6.06 (s, 0.25H), 5.94 (s, 0.75H), 5.35 (q, *J* = 1.4 Hz, 0.25H), 5.22 – 5.19 (m, 0.75H), 4.65 (td, *J* = 9.3, 4.0 Hz, 0.75H), 4.26 (td, *J* = 10.0, 4.2 Hz, 0.25H), 4.14 (dq, *J* = 21.3, 7.1 Hz, 2H), 3.75 (s, 3H), 3.19 (td, *J* = 7.7, 3.5 Hz, 0.25H), 3.08 (dt, *J* = 11.6, 3.9 Hz, 0.75H), 2.76 – 2.65 (m, 1.5H), 2.58 – 2.47 (m, 0.5H), 2.10 (s, 0.75H), 2.03 (s, 2.25H), 2.00 – 1.53 (m, 6H), 1.37 – 1.02 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 167.2, 157.9, 139.1, 134.5, 129.6, 126.2, 113.5, 74.3, 60.6, 55.2, 47.5, 43.6, 32.0, 31.5, 25.8, 24.9, 24.1, 21.5, 14.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:397.1985, found: 397.1990.

Methyl 6-acetoxy-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4p):



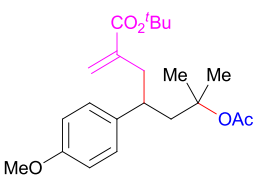
4p was obtained as a colorless oil (42.8 mg, 16 h, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.99 (d, *J* = 1.4 Hz, 1H), 5.25 – 5.20 (m, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 2.99 (tdd, *J* = 9.6, 6.5, 3.5 Hz, 1H), 2.60 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.40 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.32 (dd, *J* = 14.5, 9.7 Hz, 1H), 1.98 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.63 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.6, 157.8, 138.3, 137.2, 128.9, 127.2, 113.7, 82.2, 55.3, 51.9, 45.2, 41.7, 40.0, 27.0, 26.9, 22.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:357.1672, found: 357.1669.

Tert-butyl 6-acetoxy-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4q):



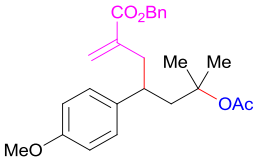
4q was obtained as a yellow oil (37.6 mg, 16 h, yield: 50%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.93 (d, *J* = 1.7 Hz, 1H), 5.21 – 5.16 (m, 1H), 3.76 (s, 3H), 3.04 – 2.97 (m, 1H), 2.52 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.43 – 2.31 (m, 2H), 1.91 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.59 (s, 3H), 1.47 (s, 9H), 1.35 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 166.4, 157.8, 140.1, 137.4, 128.8, 126.3, 113.7, 82.2, 80.5, 55.3, 44.9, 41.9, 40.1, 28.2, 27.1, 26.9, 22.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:399.2142, found: 399.2136.

Benzyl 6-acetoxy-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4r):



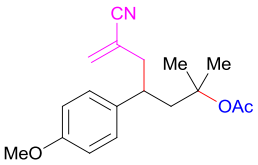
4r was obtained as a yellow oil (48.4 mg, 16 h, yield: 59%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 4H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.07 (d, *J* = 1.4 Hz, 1H), 5.30 – 5.21 (m, 1H), 5.17 (s, 2H), 3.76 (s, 3H), 3.00 (dtt, *J* = 9.8, 6.7, 3.4 Hz, 1H), 2.63 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.43 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.34 (dd, *J* = 14.5, 9.8 Hz, 1H), 1.94 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.60 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 166.9, 157.8, 138.3, 137.1, 136.1, 128.8, 128.7, 128.3, 128.3, 127.7, 113.7, 82.2, 66.5, 55.3, 45.1, 41.7, 39.9, 27.0, 26.9, 22.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:433.1985, found: 433.1989.

6-cyano-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl acetate (4s):



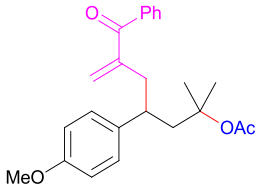
4s was obtained as a yellow oil (45.2 mg, 16 h, yield: 75%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.69 (s, 1H), 5.43 (s, 1H), 3.77 (s, 3H), 3.05 (tdd, *J* = 9.6, 6.4, 3.3 Hz, 1H), 2.52 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.41 – 2.31 (m, 2H), 1.97 (dd, *J* = 14.5, 3.3 Hz, 1H), 1.65 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 158.2, 135.5, 132.3, 128.8, 121.4, 118.6, 114.0, 81.9, 55.3, 44.9, 44.0, 39.5, 27.0, 27.0, 22.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:324.1570, found: 324.1579.

6-benzoyl-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl acetate (4t):



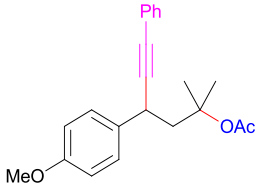
4t was obtained as a grew solid (19.8 mg, 24 h, yield: 26%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.38 – 7.31 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 0H), 5.42 (s, 1H), 5.30 (d, *J* = 0.9 Hz, 1H), 3.76 (s, 3H), 3.09 – 2.93 (m, 2H), 2.53 (dd, *J* = 13.2, 9.7 Hz, 1H), 2.37 (dd, *J* = 14.5, 9.2 Hz, 1H), 2.09 – 2.00 (m, 1H), 1.65 – 1.61 (m, 3H), 1.37 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 170.7, 157.9, 146.2, 137.8, 137.1, 132.2, 129.7, 129.1, 128.5, 128.1, 113.8, 82.2, 55.4, 46.1, 41.8, 39.5, 27.0, 27.0, 22.3.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:403.1880, found: 403.1885.

4-(4-methoxyphenyl)-2-methyl-6-phenylhex-5-yn-2-yl acetate (4u):



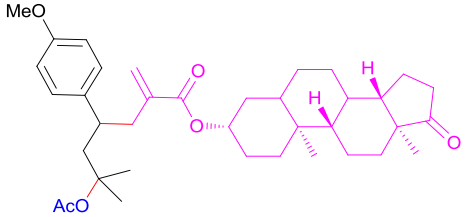
4u was obtained as an orange solid (37.7 mg, 18 h, yield: 56%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.27 (m, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.95 (dd, *J* = 9.4, 4.4 Hz, 1H), 3.80 (s, 3H), 2.42 (dd, *J* = 14.3, 9.5 Hz, 1H), 2.26 (dd, *J* = 14.3, 4.4 Hz, 1H), 1.90 (s, 3H), 1.62 (s, 3H), 1.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 158.5, 135.0, 131.6, 128.5, 128.3, 127.9, 123.8, 114.1, 92.5, 83.3, 81.7, 55.4, 48.7, 33.3, 27.1, 26.6, 22.6.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:359.1618, found: 359.1616.

(3S,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 6-acetoxy-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4v):



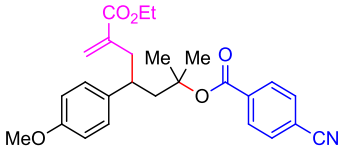
4v was obtained as a colorless solid (75.9 mg, 18 h, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.19 (s, 1H), 4.71 (tt, *J* = 11.0, 4.8 Hz, 1H), 3.74 (s, 3H), 3.06 – 2.92 (m, 1H), 2.62 – 2.50 (m, 1H), 2.48 – 2.26 (m, 3H), 2.13 – 1.97 (m, 1H), 1.99 – 1.84 (m, 3H), 1.85 – 1.68 (m, 5H), 1.60 (s, 3H), 1.60 – 1.34 (m, 6H), 1.37 – 1.24 (m, 12H) , 1.09 – 0.92 (m, 3H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 170.6, 166.7, 157.8, 139.0 (d, *J* = 1.8 Hz), 137.3 (d, *J* = 1.6 Hz), 128.8, 113.7, 82.2, 73.8, 55.3, 54.4, 51.4, 47.9, 44.7, 41.7, 40.0, 36.8, 35.9, 35.7, 35.1, 34.0, 31.6, 30.9, 28.4 (d, *J* = 2.4 Hz), 27.5 (d, *J* = 1.9 Hz), 27.0, 26.9, 24.0, 22.3, 21.9, 20.5, 13.9, 12.3.

HRMS (ESI, m/z): calculated for $[M+H]^+$:593.3837, found: 593.3835.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-cyanobenzoate(4w)



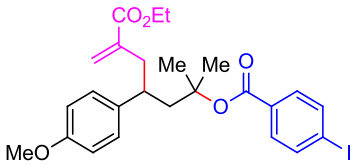
4w was obtained as a yellow oil (54.8 mg, 16 h, yield: 63%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 5.22 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 3.22 – 3.02 (m, 1H), 2.59 (td, *J* = 11.2, 10.6, 6.2 Hz, 2H), 2.43 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.00 (dd, *J* = 14.7, 2.3 Hz, 1H), 1.52 (d, *J* = 9.4 Hz, 6H), 1.26 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 163.87, 157.72, 138.40, 136.80, 135.43, 131.67, 129.88, 128.72, 127.20, 118.35, 115.50, 113.71, 84.21, 60.70, 55.00, 45.12, 42.02, 39.95, 27.35, 26.61, 14.33.

HRMS (ESI, m/z): calculated for $[M+Na]^+$ 458.1938, found: 458.1942.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-iodobenzoate(4aa)



4aa was obtained as a colorless oil (49.3 mg, 16 h, yield: 63%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4.

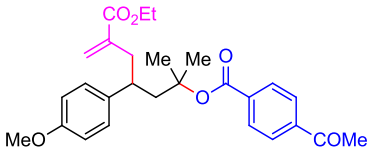
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.22 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 3.20 – 2.97 (m, 1H), 2.61 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.53 (dd, *J* = 14.6, 10.3 Hz, 1H), 2.44 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.03 (dd, *J* = 14.6, 3.0 Hz, 1H), 1.49 (d, *J* = 5.5 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 165.08, 157.76, 138.57, 137.15, 136.92, 131.19, 130.95, 128.71, 127.04, 113.73,

99.89, 83.41, 60.65, 55.06, 45.35, 41.90, 40.04, 27.33, 26.76, 14.32.

HRMS (ESI, m/z): calculated for $[M+Na]^+$559.0952, found: 559.0952.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-acetylbenzoate(4ab)



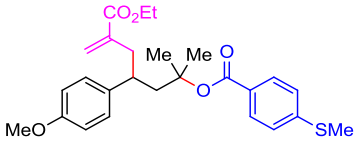
4ab was obtained as a yellow oil (43.4 mg, 20 h, yield: 48%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 3H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.3 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.60 (s, 7H), 3.18 – 2.99 (m, 1H), 2.71 – 2.49 (m, 1H), 2.44 (dd, *J* = 13.8, 8.8 Hz, 1H), 2.06 (dd, *J* = 14.6, 3.1 Hz, 1H), 1.51 (d, *J* = 4.7 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 165.08, 157.76, 138.57, 137.15, 136.92, 131.19, 130.95, 128.71, 127.04, 113.73, 99.89, 83.41, 60.65, 55.06, 45.35, 41.90, 40.04, 27.33, 26.76, 14.32.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:475.2091, found: 475.2096.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-(methylthio)benzoate(4ac)



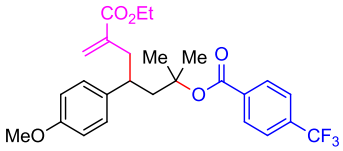
4ac was obtained as a white solid (34.7 mg, 24 h, yield: 38%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.23 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 3.09 (dt, *J* = 9.3, 6.4 Hz, 1H), 2.63 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.52 – 2.41 (m, 4H), 2.09 (dd, *J* = 14.5, 2.3 Hz, 1H), 1.48 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 165.46, 157.75, 144.41, 138.62, 137.14, 129.75, 128.75, 127.96, 127.09, 124.57, 113.73, 82.93, 60.67, 55.05, 45.69, 41.85, 40.07, 27.27, 26.84, 14.95, 14.33.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 479.1863, found: 479.1869.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-(trifluoromethyl)benzoate（4ad）



4ad was obtained as a colorless oil (43.8 mg, 18 h, yield: 57%) after flash chromatography (Petroleum ether/EtOAc = 10:1):

TLC R_f= 0.4.

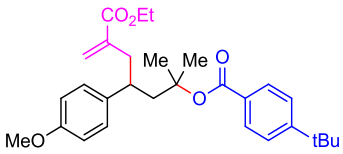
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 1.6 Hz, 1H), 5.23 (d, *J* = 1.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.57 (s, 3H), 3.11 (dtd, *J* = 13.3, 6.8, 2.9 Hz, 1H), 2.64 – 2.55 (m, 2H), 2.44 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.01 (dd, *J* = 14.7, 2.9 Hz, 1H), 1.52 (d, *J* = 8.0 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.90 (s, 3F)

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 164.31, 157.76, 138.52, 136.81, 134.85, 134.84, 134.83, 134.82(q, *J* = 1.3 Hz), 134.17, 133.85, 133.52, 133.20(q, *J* = 32.4 Hz), 129.74, 128.71, 127.90, 127.06, 125.20, 124.85, 124.81, 124.77, 124.73(q, *J* = 3.7 Hz), 122.49, 119.79(q, *J* = 272.2Hz), 113.71, 83.79, 60.65, 54.89, 45.15, 41.94, 40.02, 40.00, 27.38, 26.70, 14.28.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 501.1859, found: 501.1861.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-(tert-butyl)benzoate(4ae)



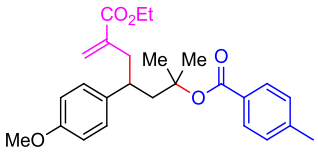
4ae was obtained as a yellow oil (49.5 mg, 20 h, yield: 53%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.65 , 3.10 (dtt, *J* = 9.8, 6.7, 3.3 Hz, 1H), 2.63 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.44 (ddd, *J* = 14.7, 9.0, 5.6 Hz, 2H), 2.13 (dd, *J* = 14.5, 3.3 Hz, 1H), 1.47 (d, *J* = 8.5 Hz, 6H), 1.30 (s, 9H)1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 165.75, 157.80, 155.82, 138.68, 137.27, 129.28, 129.03, 128.77, 127.06, 124.91, 113.75, 82.78, 60.63, 55.11, 45.89, 41.83, 40.08, 35.03, 31.23, 27.17, 26.87, 14.30.

HRMS (ESI, m/z): calculated for $[M+H]^+$: 467.2792, found: 467.2795.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 4-methylbenzoate(4af)



4af was obtained as a yellow oil (53.5 mg, 18 h, yield: 62%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.4.

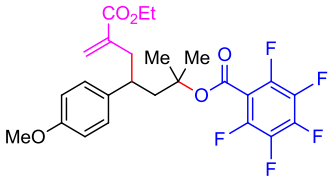
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.01 (s, 1H), 5.22 (s, 1H), 4.13 (q, *J* = 6.8 Hz, 2H), 3.66 (s, 3H), 3.120 – 2.99 (m, 1H), 2.64 (dd, *J* = 13.4, 6.2 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.36 (s, 3H), 2.14 (dd, *J* = 14.7, 2.6 Hz, 1H), 1.48 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 165.80, 157.77, 142.78, 138.68, 137.22, 129.46, 129.09, 128.75, 128.66, 127.03,

113.73, 82.83, 60.63, 55.03, 45.81, 41.81, 40.11, 27.16, 26.93, 21.66, 14.30.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 447.2142, found: 447.2148.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 2,3,4,5,6-pentafluorobenzoate (4ag)



4ag was obtained as a pale yellow oil (58.1 mg, 18 h, yield: 58%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.4.

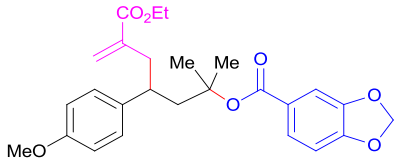
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.23 (d, *J* = 1.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.05 (dtd, *J* = 9.8, 6.6, 3.3 Hz, 1H), 2.60 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.44 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.37 (dd, *J* = 14.5, 10.2 Hz, 1H), 2.10 (dd, *J* = 14.6, 3.2 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.60 – -142.93 (m,2F), -150.53 (tt, *J* = 20.9, 3.8 Hz, 1F)., -161.25 (tt, *J* = 21.1, 5.5 Hz, 2F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.07, 157.76, 145.32 (m), 143.90 (m), 138.47, 136.84, 136.25 (m), 128.67, 127.00, 113.41, 109.51 (m), 87.00, 60.65, 55.00, 45.94, 41.61, 39.97, 26.98, 26.48, 14.25.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:523.1514, found: 523.1518.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl-benzo[d][1,3]dioxole-5-carboxylate(4ah)



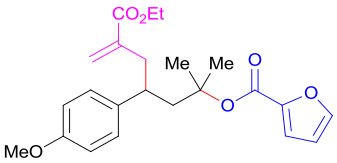
4ah was obtained as a colorless oil (57.2 mg, 16 h, yield: 63%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.08 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 9.7, 8.5 Hz, 2H), 6.01 (d, *J* = 1.6 Hz, 1H), 5.99 (s, 2H), 5.22 (d, *J* = 1.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.08 (tdd, *J* = 9.8, 6.7, 3.2 Hz, 1H), 2.62 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.45 (dt, *J* = 13.6, 8.7 Hz, 2H), 2.09 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.47 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 165.03, 157.78, 151.01, 147.32, 138.63, 137.15, 128.73, 127.07, 125.91, 125.01, 113.71, 109.47, 107.53, 101.64, 82.93, 60.66, 55.05, 45.69, 41.87, 40.07, 27.24, 26.87, 14.32.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:477.1884, found: 477.1886.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl furan-2-carboxylate(4ai)



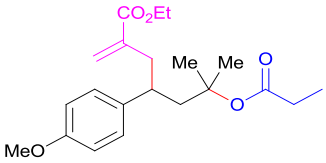
4ai was obtained as a pale yellow oil (59.3 mg, 16 h, yield: 74%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 3.4 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.37 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 5.23 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.08 (dtt, *J* = 9.6, 6.6, 3.4 Hz, 1H), 2.64 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.43 (ddd, *J* = 13.9, 9.1, 3.1 Hz, 2H), 2.11 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 157.96, 157.82, 145.73, 145.57, 138.61, 137.00, 128.77, 127.06, 116.81, 113.62, 111.46, 83.97, 60.65, 55.13, 45.64, 41.65, 40.01, 27.12, 27.04, 14.30.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 423.1778, found: 423.1785.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-(propionyloxy)heptanoate(4aj)



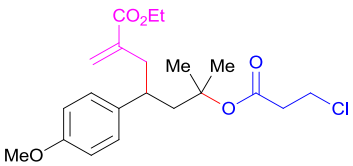
4aj was obtained as a pale yellow oil (44.2 mg, 16 h, yield: 61%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.55.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 7.0 Hz, 2H), 6.00 (s, 1H), 5.22 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.00 (dtt, *J* = 8.8, 6.5, 3.1 Hz, 1H), 2.60 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.38 (ddd, *J* = 27.3, 13.9, 9.2 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.82 (dd, *J* = 15.8, 8.3 Hz, 1H), 1.33 (d, *J* = 10.3 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.90, 167.18, 157.81, 138.67, 137.32, 128.84, 128.83, 126.95, 113.65, 82.00, 60.64, 55.28, 45.27, 41.70, 40.00, 28.39, 27.00, 26.98, 14.33, 9.01

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 385.1985, found:385.1983.

Ethyl 6-((3-chloropropanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4ak)



4ak was obtained as a colorless oil (50.8 mg, 18 h, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

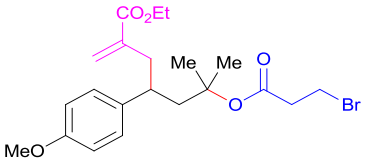
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.22(s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.42 – 3.16 (m, 2H), 3.02 (tdd, *J* = 9.8, 6.5, 3.1 Hz, 1H), 2.58 (dd, *J* = 13.5, 6.5 Hz, 1H),

2.49 – 2.27 (m, 4H), 1.93 (dd, *J* = 14.6, 3.1 Hz, 1H), 1.36 (d, *J* = 12.6 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.75, 167.13, 157.88, 138.52, 137.10, 128.89, 127.06, 113.66, 83.37, 60.69, 55.30, 45.12, 41.81, 39.92, 38.53, 27.10, 26.77, 26.44, 14.36.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 419.1596, found: 419.1593.

Ethyl 6-((3-bromopropanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4al)



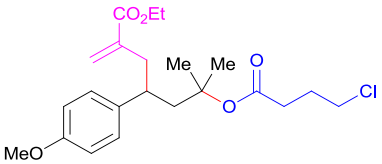
4al was obtained as a colorless oil (50.3 mg, 18 h, yield: 57%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.22 (d, *J* = 1.1 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 3.54 – 3.32 (m, 2H), 3.02 (tdd, *J* = 9.7, 6.7, 3.2 Hz, 1H), 2.47 – 2.29 (m, 3H), 2.22 (dt, *J* = 16.6, 6.9 Hz, 1H), 1.94 (dd, *J* = 14.6, 3.2 Hz, 1H), 1.36 (d, *J* = 10.0 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52, 167.14, 157.90, 138.55, 137.14, 128.88, 127.02, 113.68, 83.34, 60.68, 55.29, 45.18, 41.79, 39.94, 39.24, 38.34, 27.07, 26.78, 14.33.

HRMS (ESI, m/z): calculated for $[M+H]^+$: 441.1271, found: 441.1280.

Ethyl 6-((4-chlorobutanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate (4am)



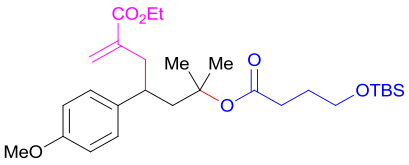
4am was obtained as a colorless oil (37 mg, 20 h, yield: 45%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 22H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.3 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.46 (t, *J* = 6.3 Hz, 2H), 3.00 (dtd, *J* = 11.9, 6.6, 3.3 Hz, 1H), 2.58 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.39 (dt, *J* = 14.5, 9.4 Hz, 2H), 2.15 – 2.00 (m, 1H), 1.97 – 1.87 (m, 2H), 1.87 – 1.77 (m, 2H), 1.34 (d, *J* = 11.7 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.97, 167.15, 157.83, 138.58, 137.17, 128.85, 127.01, 113.65, 82.57, 60.67, 55.25, 45.15, 44.34, 41.80, 39.97, 32.15, 27.61, 27.11, 26.88, 14.35

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 433.1752, found: 433.1759.

Ethyl 6-((4-((tert-butyldimethylsilyl)oxy)butanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4an)



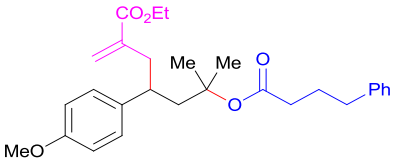
4an was obtained as a colorless oil (40 mg, 16 h, yield: 39%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.22 (d, *J* = 1.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.53 (td, *J* = 6.3, 2.0 Hz, 1H), 2.99 (dtt, *J* = 9.6, 6.5, 3.5 Hz, 1H), 2.60 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.40 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.32 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.89 (ddd, *J* = 16.2, 7.9, 7.0 Hz, 1H), 1.61 (tdd, *J* = 10.0, 7.4, 4.7 Hz, 2H), 1.33 (d, *J* = 13.0 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.99, 167.15, 157.83, 138.68, 137.29, 128.83, 126.92, 113.65, 82.20, 62.21, 60.62, 55.22, 45.44, 41.69, 40.03, 31.60, 27.98, 26.93, 26.02, 18.40, 14.34, -5.27.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 529.2956, found: 529.2963.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-((4-phenylbutanoyl)oxy)heptanoate (4ao)



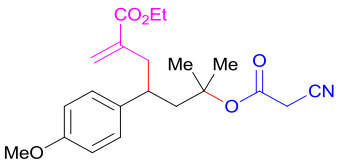
4ao was obtained as a pale yellow oil (56.1 mg, 24 h, yield: 62%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.17 (dd, *J* = 16.8, 7.3 Hz, 3H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.01 (s, 1H), 5.23 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.01 (dtt, *J* = 9.6, 6.5, 3.4 Hz, 1H), 2.61 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.38 (ddd, *J* = 26.5, 14.0, 9.2 Hz, 2H), 1.96 (ddd, *J* = 20.3, 11.4, 5.0 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.74 (ddt, *J* = 11.6, 8.0, 3.3 Hz, 2H), 1.35 (d, *J* = 12.9 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.86, 167.17, 157.83, 148.75, 141.80, 138.67, 137.29, 128.86, 128.54, 128.41, 126.95, 125.94, 113.66, 82.23, 60.65, 55.25, 45.42, 41.75, 40.03, 35.23, 34.67, 27.02, 26.90, 26.55, 14.34.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 475.2455, found: 475.2461.

Ethyl 6-(2-cyanoacetoxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4ap)



4ap was obtained as a colorless oil (35.8 mg, 12 h, yield: 48%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

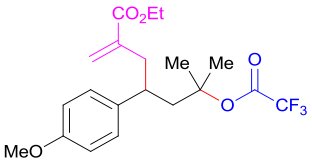
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.22 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.03 (dtd, *J* = 10.8, 8.3, 2.8 Hz, 1H), 2.80 (d, *J* = 19.1 Hz, 1H), 2.62(d, *J* = 19.1 Hz, 1H),

2.59 – 2.49 (m, 2H), 2.41 (dd, *J* = 13.5, 8.5 Hz, 1H), 1.85 (dd, *J* = 14.8, 2.8 Hz, 1H), 1.40 (d, *J* = 26.4 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H)..

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.07, 162.05, 157.95, 138.27, 136.51, 129.03, 127.22, 113.84, 113.63, 85.79, 60.75, 55.34, 43.87, 41.83, 39.83, 27.25, 26.72, 25.22, 14.34.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 396.1781, found: 396.1783.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-(2,2,2-trifluoroacetoxy)heptanoate(4aq)



4aq was obtained as a orange oil (50.7 mg, 12 h, yield: 63%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

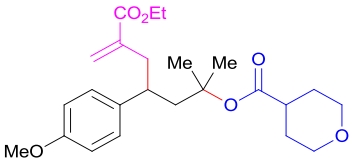
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 22H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.03 (d, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.01 (dtt, *J* = 9.8, 6.6, 3.6 Hz, 1H), 2.61 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.44 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.32 (dd, *J* = 14.6, 9.6 Hz, 1H), 2.16 (dd, *J* = 14.6, 3.6 Hz, 1H), 1.41 (d, *J* = 3.2 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -75.7(s, 3F)

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.04, 158.19, 156.68, 156.27, 155.87, 155.45(q, *J* = 41.62), 138.30, 136.31, 128.62, 127.27, 118.60, 115.74, 113.95, 112.88, 110.03(q, *J* = 287.37), 89.32, 60.74, 55.29, 45.28, 41.62, 39.87, 26.58, 26.13, 14.27.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 425.1546, found: 425.1545.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl tetrahydro-2H-pyran-4-carboxylate(4ar)



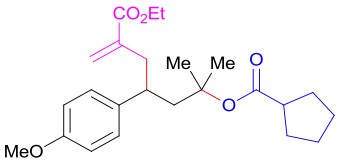
4ar was obtained as a colorless oil (42.2 mg, 24 h, yield: 50%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.01 (s, 1H), 5.22 (s, 1H), 4.17 (q, *J* = 7.5 Hz, 2H), 3.88 (dq, *J* = 11.3, 3.2 Hz, 2H), 3.76 (s, 3H), 3.33 – 3.25 (m, 2H), 3.01 (dtd, *J* = 12.2, 6.6, 3.4 Hz, 1H), 2.59 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.41 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.32 (d, *J* = 24.3 Hz, 1H), 1.99 (dq, *J* = 14.7, 3.6 Hz, 2H), 1.55 (dtd, *J* = 9.8, 6.6, 6.1, 4.1 Hz, 4H), 1.34 (d, *J* = 1.7 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.07, 162.05, 157.95, 138.27, 136.51, 129.03, 127.22, 113.84, 113.63, 85.79, 60.75, 55.34, 43.87, 41.83, 39.83, 27.25, 26.72, 25.22, 14.34.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:441.2248, found: 441.2253.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl cyclopentanecarboxylate(4as)



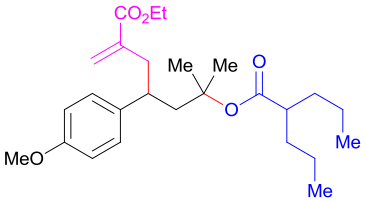
4as was obtained as a colorless oil (54.7 mg, 18 h, yield: 68%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 5.22 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.07 – 2.93 (m, 1H), 2.62 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.41 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.25 (dd, *J* = 14.3, 9.5 Hz, 1H), 2.04 (dd, *J* = 14.4, 3.2 Hz, 1H), 1.80 – 1.53 (m, 8H), 1.31 (s, 6H), 1.28 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.10, 167.20, 157.84, 138.73, 137.43, 128.81, 126.91, 113.66, 81.91, 60.65, 55.26, 45.89, 44.80, 41.66, 40.05, 30.02, 29.66, 26.89, 26.77, 25.84, 25.82, 14.33.

HRMS (ESI, m/z): calculated For $[M+H]^+$: 403.2479, found: 403.2475.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-((2-propylpentanoyl)oxy)heptanoate(4at)



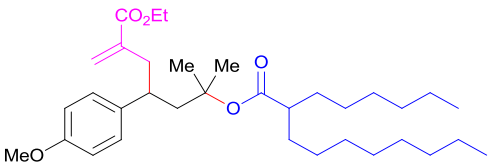
4at was obtained as a colorless oil (61.4 mg, 20 h, yield: 71%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.23 (d, *J* = 1.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.00 (ddt, *J* = 12.8, 6.5, 3.2 Hz, 1H), 2.63 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.42 (dd, *J* = 13.7, 8.8 Hz, 1H), 2.15 (dd, *J* = 14.3, 9.0 Hz, 1H), 2.06 (dt, *J* = 13.6, 3.8 Hz, 2H), 1.45 (ddq, *J* = 16.2, 8.9, 4.8, 3.9 Hz, 2H), 1.32 (d, *J* = 2.8 Hz, 6H), 1.30 – 1.20 (m, 10H), 0.87 (td, *J* = 7.1, 2.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.97, 167.17, 157.86, 138.79, 137.52, 128.79, 126.79, 113.69, 82.27, 60.63, 55.22, 46.99, 46.13, 41.72, 40.05, 34.71, 34.63, 26.63, 26.30, 20.66, 20.64, 14.32, 14.21, 14.17.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:455.2768, found: 455.2773.

6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl 2-hexyldecanoate(4au)



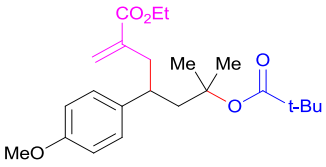
4au was obtained as a colorless oil (69.7 mg, 18 h, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 1.6 Hz, 1H), 5.23 (d, *J* = 1.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.00 (ddt, *J* = 12.8, 6.3, 3.2 Hz, 1H), 2.63 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.42 (dd, *J* = 13.7, 8.7 Hz, 1H), 2.18 – 1.97 (m, 3H), 1.44 (dt, *J* = 16.5, 7.8 Hz, 2H), 1.32 (s, 6H), 1.29 – 1.21 (m, 25H), 0.87 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.99, 167.14, 157.86, 138.79, 137.52, 128.78, 126.77, 113.68, 82.23, 60.61, 55.21, 46.99, 46.59, 41.69, 40.04, 32.54, 32.44, 31.98, 31.85, 29.75, 29.71, 29.60, 29.41, 29.39, 29.38, 29.37, 27.47, 27.43, 26.65, 26.26, 22.78, 22.71, 14.32, 14.22, 14.20.

HRMS (ESI, m/z): calculated For $[M+Na]^+$:567.4020, found: 567.4026.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-(pivaloyloxy)heptanoate (4av)



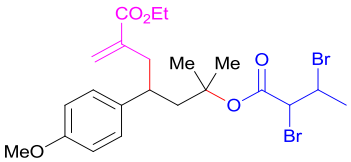
4av was obtained as a pale yellow oil (49.9 mg, 16 h, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.55.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.00 (s, 1H), 5.21 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 2.99 (ddt, *J* = 8.5, 6.4, 4.7 Hz, 1H), 2.62 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.40 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.23 – 2.07 (m, 1H), 1.29 (d, *J* = 20.5 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.88, 167.15, 157.91, 138.74, 137.52, 128.78, 126.92, 113.76, 82.03, 76.81, 60.63, 55.27, 46.12, 41.84, 39.99, 39.30, 27.16, 26.92, 26.40, 14.33.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 413.2298, found: 413.2308.

Ethyl 6-((2,3-dibromobutanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2 methyleneheptanoate(4aw)



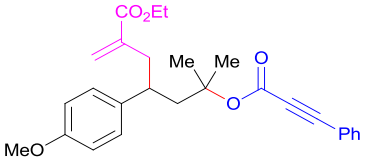
4aw was obtained as a colorless oil (51.6 mg, 16 h, yield: 48%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.02 (dd, *J* = 3.1, 1.5 Hz, 1H), 5.25 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.13 – 3.96 (m, 3H), 3.77 (s, 3H), 3.05 (dtt, *J* = 12.0, 6.2, 3.5 Hz, 1H), 2.62 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.44 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.14 (ddddd, *J* = 18.1, 14.4, 10.4, 7.9, 3.2 Hz, 3H), 1.78 (dd, *J* = 6.3, 4.3 Hz, 3H), 1.40 (d, *J* = 5.4 Hz, 3H), 1.36 (d, *J* = 2.5 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.15, 166.58, 166.41, 157.94, 157.89, 138.64, 138.62, 137.37, 137.27, 128.91, 128.85, 127.01, 126.98, 113.78, 113.76, 85.50, 85.42, 60.71, 55.26, 51.52, 51.34, 46.89, 46.58, 46.23, 46.09, 41.80, 41.76, 39.90, 39.88, 26.05, 26.04, 25.83, 25.66, 23.89, 14.35.

HRMS (ESI, m/z): calculated for $[M+H]^+$: 533.0533, found: 533.0543.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-((3-phenylpropioloyl)oxy)heptanoate(4ax)



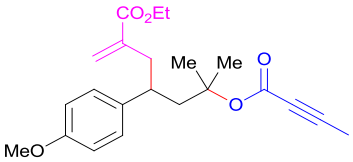
4ax was obtained as a colorless oil (20.6 mg, 20 h, yield: 47%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f= 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.38 – 7.32 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.04 (d, *J* = 1.6 Hz, 1H), 5.27 (d, *J* = 1.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 3.11 – 3.01 (m, 1H), 2.64 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.46 (dd, *J* = 13.9, 8.9 Hz, 1H), 2.39 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.11 (dd, *J* = 14.7, 3.6 Hz, 1H), 1.41 (d, *J* = 13.3 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.19, 157.94, 153.03, 138.56, 136.81, 132.92, 130.31, 128.84, 128.52, 127.15, 120.07, 113.80, 85.79, 83.58, 81.89, 60.70, 55.09, 45.21, 41.60, 40.03, 26.97, 26.90, 14.34.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:457.1985, found:457.1980.

Ethyl 6-(but-2-ynoyloxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4ay)



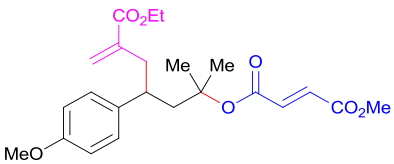
4ay was obtained as a colorless oil (40 mg, 18 h, yield: 54%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f= 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.00 (dtt, *J* = 9.7, 6.5, 3.6 Hz, 1H), 2.62 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.43 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.29 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.10 (dd, *J* = 14.5, 3.6 Hz, 1H), 1.89 (s, 3H), 1.33 (d, *J* = 12.1 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.16, 157.97, 152.71, 138.56, 136.86, 128.81, 127.09, 113.79, 85.34, 82.72, 73.68, 60.66, 55.19, 45.18, 41.50, 40.05, 26.99, 26.77, 14.31, 3.72.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:395.1829, found: 395.1829.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-((2-phenylacryloyl)oxy)heptanoate(4az)



4az was obtained as a pale yellow oil (20 mg, 12 h, yield: 24%) after flash chromatography (Petroleum ether/EtOAc = 20:1):

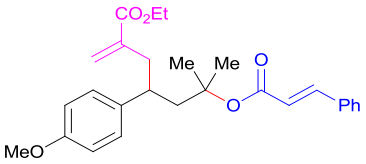
TLC R_f= 0.4.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.01 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 1.1 Hz, 2H), 6.01 (s, 1H), 5.23 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.10 – 2.96 (m, 1H), 2.58 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.47 – 2.35 (m, 2H), 1.96 (dd, *J* = 14.6, 2.5 Hz, 1H), 1.40 (d, *J* = 13.5 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13, 165.71, 164.03, 157.93, 138.52, 136.81, 135.44, 131.59, 128.81, 127.07, 113.79, 83.91, 60.68, 55.12, 52.20, 45.03, 41.71, 39.98, 27.06, 26.68, 14.33.

HRMS (ESI, m/z): calculated for $[M+H]^+$:419.2064, found: 419.2068.

(E)-ethyl 6-(cinnamoyloxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4ba)



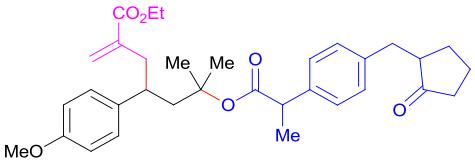
4ba was obtained as a pale yellow oil (51.2 mg, 16 h, yield: 58%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f= 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.30 (d, *J* = 16.0 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.02 (d, *J* = 1.5 Hz, 1H), 5.96 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 3H), 3.08 (dtt, *J* = 9.7, 6.8, 3.2 Hz, 1H), 2.64 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.49 – 2.35 (m, 1H), 2.03 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.45 (d, *J* = 3.9 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.19, 166.23, 157.77, 143.08, 138.67, 137.31, 134.74, 129.93, 128.88, 128.82, 128.00, 127.03, 120.02, 113.66, 82.49, 60.66, 54.98, 45.81, 41.74, 40.06, 27.19, 26.69, 14.35.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:459.2142, found: 459.2151.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-((2-(4-((2-oxocyclopentyl)methyl)phenyl)-propanoyl)oxy)heptanoate(4bb)



4bb was obtained as a colorless solid by using 1.0 mL DCM (16.0 mg, 48 h, yield: 15%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f= 0.5.

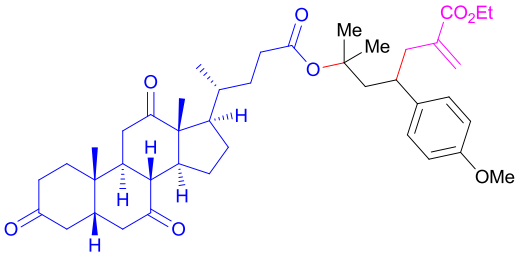
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (qd, *J* = 8.2, 2.5 Hz, 4H), 6.92 (t, *J* = 7.9 Hz, 2H), 6.76 (t, *J* = 8.1 Hz, 2H), 5.98 (dd, *J* = 6.2, 1.4 Hz, 1H), 5.16 (d, *J* = 7.7 Hz, 1H), 4.26 – 4.07(m, 2H), 3.77(d, *J* = 1.3 Hz, 3H), 3.30(dq, *J* = 41.2, 7.1 Hz, 1H), 3.11 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.97– 2.85 (m, 1H), 2.51 (ddd, *J* = 30.9, 14.0, 8.1 Hz, 2H), 2.34 (dt, *J* = 16.0, 8.1 Hz, 3H), 2.26 – 2.00 (m, 4H), 1.93 (ddt, *J* = 17.5, 8.7, 2.9 Hz, 1H), 1.79 – 1.63 (m, 1H), 1.59 – 1.47 (m, 1H), 1.36 – 1.23(m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.48, 220.47, 173.83, 173.81, 167.15, 157.83, 139.05, 139.02, 138.67, 138.65, 138.57, 138.53, 137.41, 137.30, 129.02, 128.99, 128.83, 128.79, 127.64, 127.62, 126.82, 126.79, 113.63, 82.76, 82.67, 60.64, 55.27,

55.26, 51.17, 51.12, 46.63, 46.02, 45.84, 45.76, 41.37, 41.32, 39.92, 38.31, 35.30, 35.28, 29.34, 29.32, 26.88, 26.77, 26.62, 26.18, 20.64, 18.47, 18.36, 14.35.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:557.2874, found: 557.2882.

Ethyl 6-((4-((5S,8R,9S,10S,13R,14S,17S)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butanoyl)oxy)-4-(4-methoxyphenyl)-6-methyl-2-methyleneheptanoate(4bc)



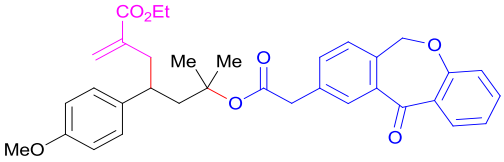
4bc was obtained as a colorless solid by using 1.5 mL DCM (65.5 mg, 48 h, yield: 48%) after flash chromatography (Petroleum ether/EtOAc = 2:1): TLC R_f = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.31 – 5.17 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 3.9 Hz, 3H), 2.99 (dtt, *J* = 8.9, 4.8, 2.3 Hz, 1H), 2.94 – 2.79 (m, 3H), 2.65 – 2.55 (m, 1H), 2.44 – 2.07 (m, 11H), 2.01 – 1.92 (m, 6H), 1.88 – 1.78 (m, 2H), 1.61 (td, *J* = 14.5, 5.2 Hz, 2H), 1.37 (d, *J* = 15.6 Hz, 6H), 1.34 – 1.21 (m, 9H), 1.04 (d, *J* = 2.9 Hz, 3H), 0.75 (d, *J* = 5.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.10, 209.27, 208.90, 173.45, 167.16, 157.80, 138.65, 137.24, 128.84, 126.95, 113.62, 82.06, 60.65, 56.95, 55.23, 55.21, 51.81, 49.08, 46.94, 45.76, 45.69, 45.61, 45.35, 45.31, 45.08, 42.88, 41.72, 40.01, 38.73, 36.59, 36.09, 35.52, 35.48, 35.35, 32.37, 30.24, 27.69, 27.04, 26.91, 25.24, 22.00, 18.67, 14.36, 11.91.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:713.4024, found: 713.4020.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-methylene-6-(2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-9-yl)acetoxy)heptanoate(4bd)



4bd was obtained as a colorless solid by using 1.0 mL DCM (20 mg, 20 h, yield: 18%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.4.

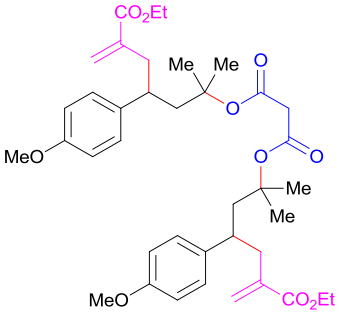
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.3 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.55 (td, *J* = 7.4, 1.4 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 5.17 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.22 (d, *J* = 15.9 Hz, 1H), 3.09 (d, *J* = 15.9 Hz, 1H), 3.01 (dtt, *J* = 9.6, 6.5, 3.4 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.43 – 2.33 (m, 2H), 1.97 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.35 (d, *J* = 5.9 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.99, 170.74, 167.16, 160.35, 157.86, 140.57, 138.59, 137.19, 136.63, 135.67, 132.81,

132.53, 129.56, 129.32, 128.92, 128.43, 127.87, 127.00, 125.04, 120.86, 113.73, 83.13, 73.69, 60.67, 55.30, 45.28, 41.64, 40.88, 40.01, 27.00, 26.89, 14.36.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 579.2353, found: 579.2361.

Bis(6-(ethoxycarbonyl)-4-(4-methoxyphenyl)-2-methylhept-6-en-2-yl) malonate(4be)



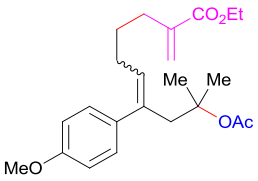
4be was obtained as a colorless oil (27.2 mg, 60 h, yield: 20%) after flash chromatography (Petroleum ether/EtOAc = 10:1): TLC R_f = 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 5.99 (s, 1H), 5.22 (s, 4H), 4.14 (q, *J* = 6.8 Hz, 1H), 3.76 (s, 1H), 3.76 (s, 2H), 3.03 – 2.89 (m, 1H), 2.58 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.39 (dd, *J* = 13.7, 8.8 Hz, 1H), 2.30 (ddd, *J* = 14.3, 9.7, 1.8 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.35 (s, 2H), 1.31 – 1.21 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.99, 170.74, 167.16, 160.35, 157.86, 140.57, 138.59, 137.19, 136.63, 135.67, 132.81, 132.53, 129.56, 129.32, 128.92, 128.43, 127.87, 127.00, 125.04, 120.86, 113.73, 83.13, 73.69, 60.67, 55.30, 45.28, 41.64, 40.88, 40.01, 27.00, 26.89, 14.36.

HRMS (ESI, m/z): calculated for $[M+Na]^+$:703.3453, found: 703.3462.

Ethyl 9-acetoxy-7-(4-methoxyphenyl)-9-methyl-2-methylenedec-6-enoate(4bf)



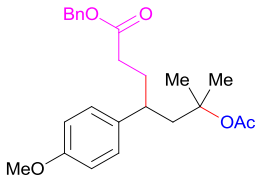
4bf was obtained as a yellow oil (25.6 mg, 30 h, yield: 33%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 6.90 (m, 2H), 6.87 – 6.78 (m, 2H), 6.18 – 6.06 (m, 1H), 5.89 – 5.50 (m, 1H), 5.49 – 5.37 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.82 – 3.78 (m, 3H), 2.94 (d, *J* = 52.1 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.23 (dq, *J* = 14.9, 7.2 Hz, 2H), 2.07 – 1.87 (m, 2H), 1.60 (dd, *J* = 15.6, 7.9 Hz, 2H), 1.51 (d, *J* = 11.1 Hz, 3H), 1.32 (d, *J* = 5.1 Hz, 6H), 1.30 – 1.22 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 167.36, 158.33, 140.78, 136.81, 132.16, 129.84, 128.01, 124.55, 113.48, 82.85, 60.72, 55.38, 48.36, 39.06, 31.70, 28.98, 26.80, 22.20, 22.10, 20.06, 14.30

HRMS (ESI, m/z): calculated for $[M+Na]^+$:411.2142, found: 411.2148.

Benzyl 6-acetoxy-4-(4-methoxyphenyl)-6-methylheptanoate (4bg)



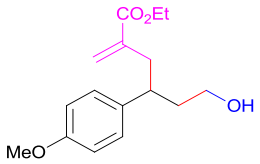
4bg was obtained as a yellow oil (22 mg, 48 h, yield: 28%) after flash chromatography (Petroleum ether/EtOAc = 20:1): TLC R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 1H), 7.02 (d, *J* = 8.7 Hz, 0H), 6.80 (d, *J* = 8.7 Hz, 0H), 5.11 – 5.00 (m, 1H), 3.77 (s, 1H), 2.69 (tt, *J* = 9.5, 4.2 Hz, 0H), 2.31 (dd, *J* = 14.5, 9.5 Hz, 0H), 2.16 – 2.08 (m, 0H), 1.98 (ddd, *J* = 14.7, 7.3, 4.7 Hz, 1H), 1.85 – 1.71 (m, 0H), 1.65 (s, 1H), 1.32 (d, *J* = 2.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.47, 170.59, 158.01, 136.73, 136.07, 128.80, 128.64, 128.37, 128.32, 113.91, 82.14, 66.19, 55.32, 46.39, 40.43, 33.55, 32.31, 26.98, 26.94, 22.31.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 421.1985, found: 421.1987.

Ethyl 6-hydroxy-4-(4-methoxyphenyl)-2-methylenehexanoate(4bh)



4bh was obtained as a colorless oil (12 mg, yield: 53%) after flash chromatography (Petroleum ether/EtOAc = 5:1): TLC R_f = 0.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.4 Hz), 6.82 (d, *J* = 8.5 Hz), 6.04 , 5.29 , 4.17 (q, *J* = 7.2 Hz), 3.78 , 3.54 (ddt, *J* = 37.9, 11.0, 6.5 Hz), 2.91 (td, *J* = 9.1, 5.5 Hz), 2.58 (ddd, *J* = 80.2, 13.8, 7.3 Hz), 1.94 (dq, *J* = 13.1, 6.4 Hz), 1.80 (ddd, *J* = 15.2, 12.4, 6.7 Hz), 1.28 (t, *J* = 7.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.38, 158.10, 138.67, 136.10, 128.67, 126.71, 113.88, 61.18, 60.78, 55.28, 40.72, 39.53, 38.81, 14.29.

HRMS (ESI, m/z): calculated for $[M+Na]^+$: 301.1410, found: 301.1416.

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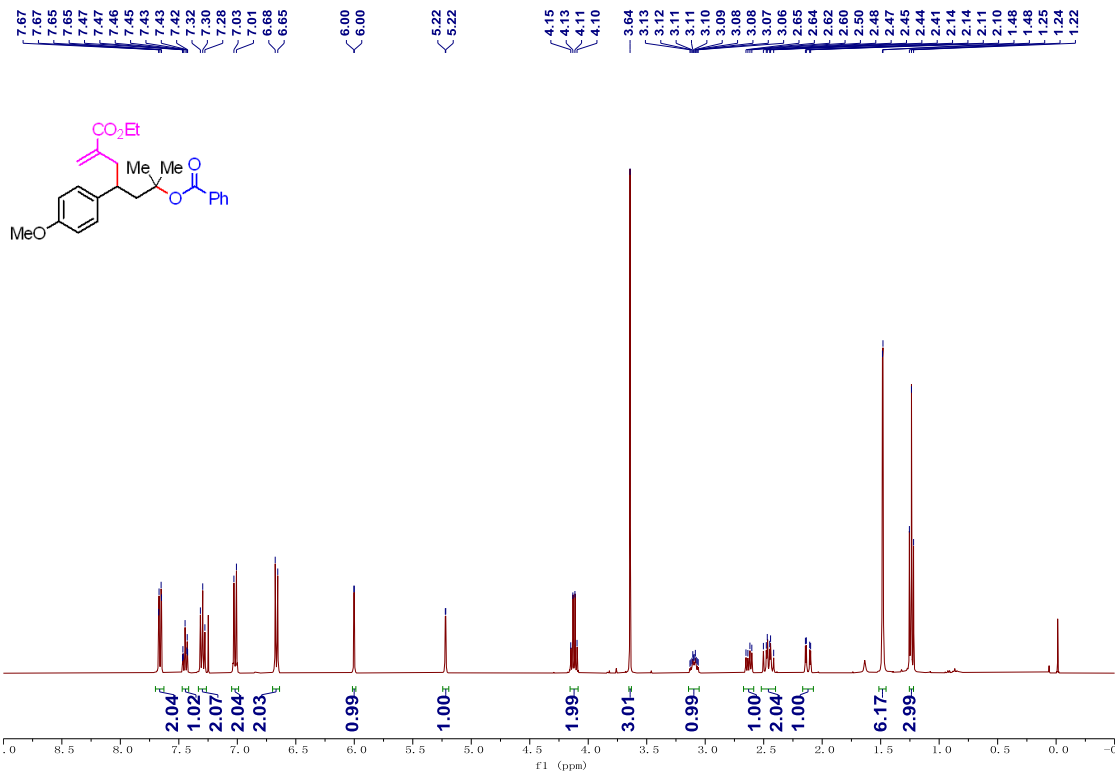
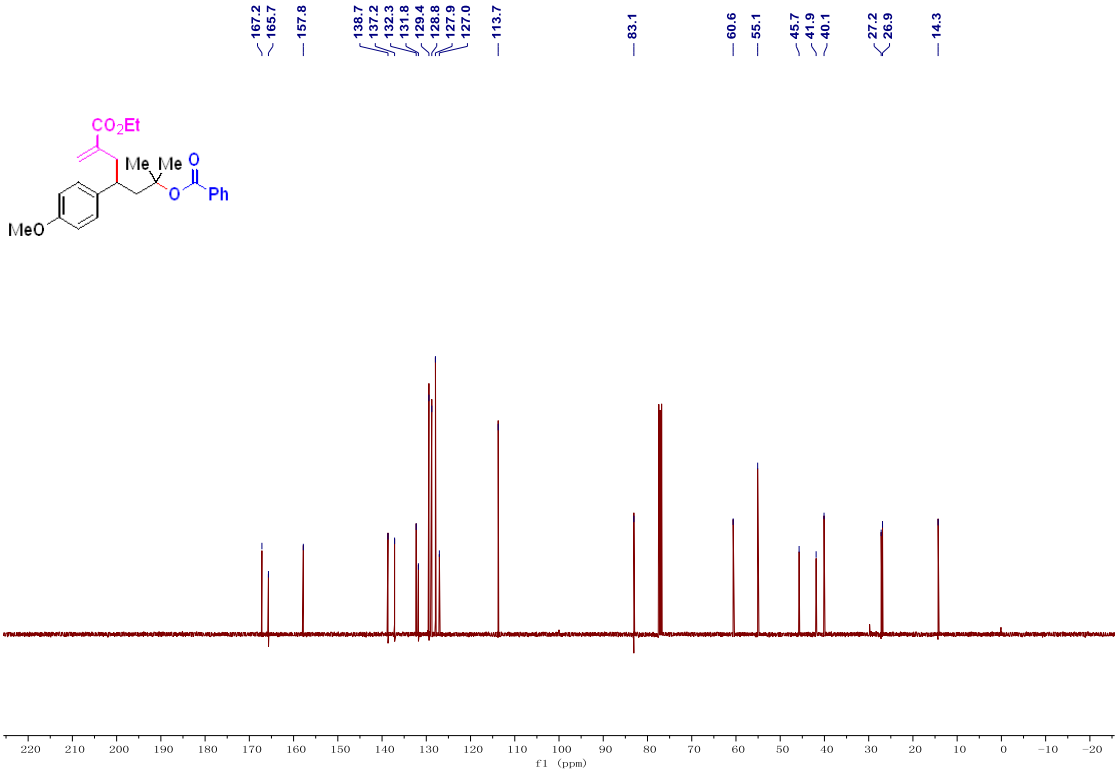
^{1}H, ^{19}F and ^{13}C NMR spectra of structurally novel compounds

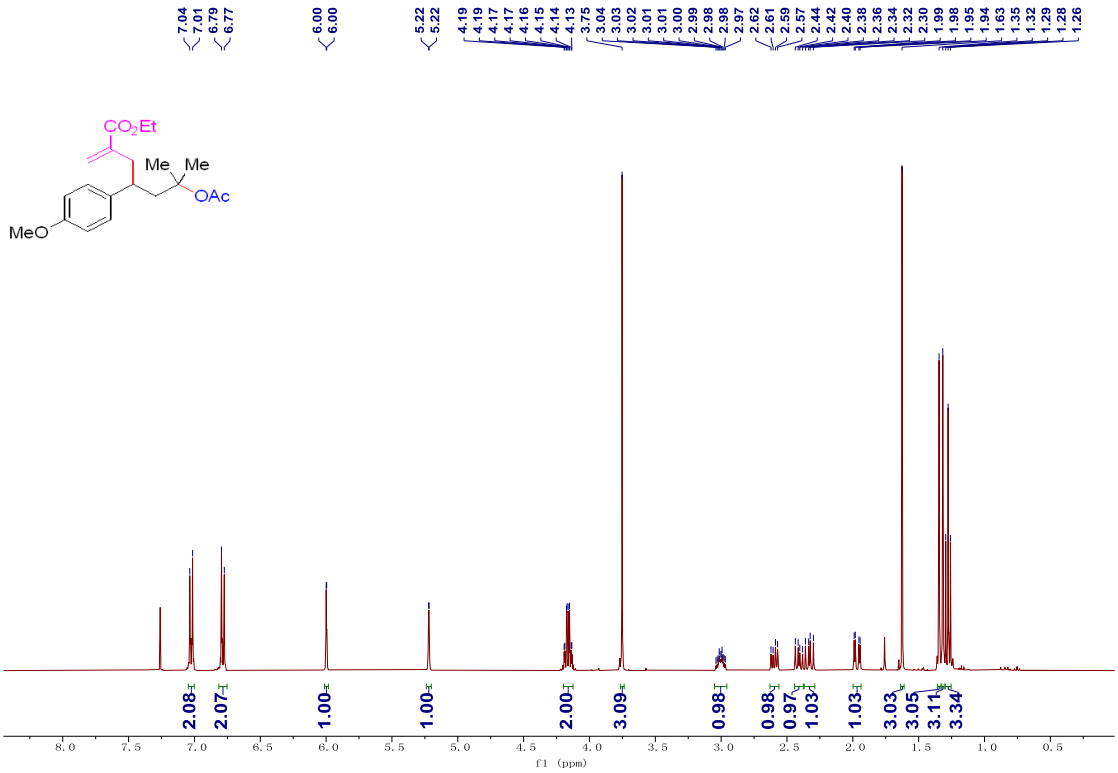
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**



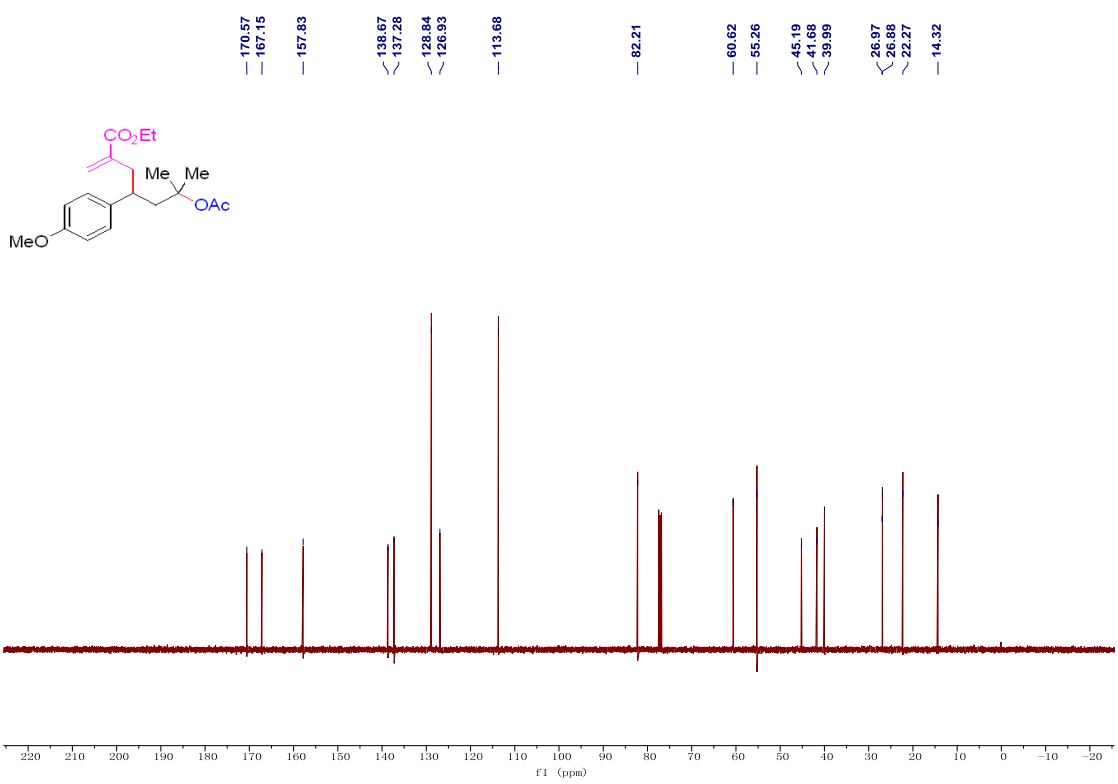
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4a**



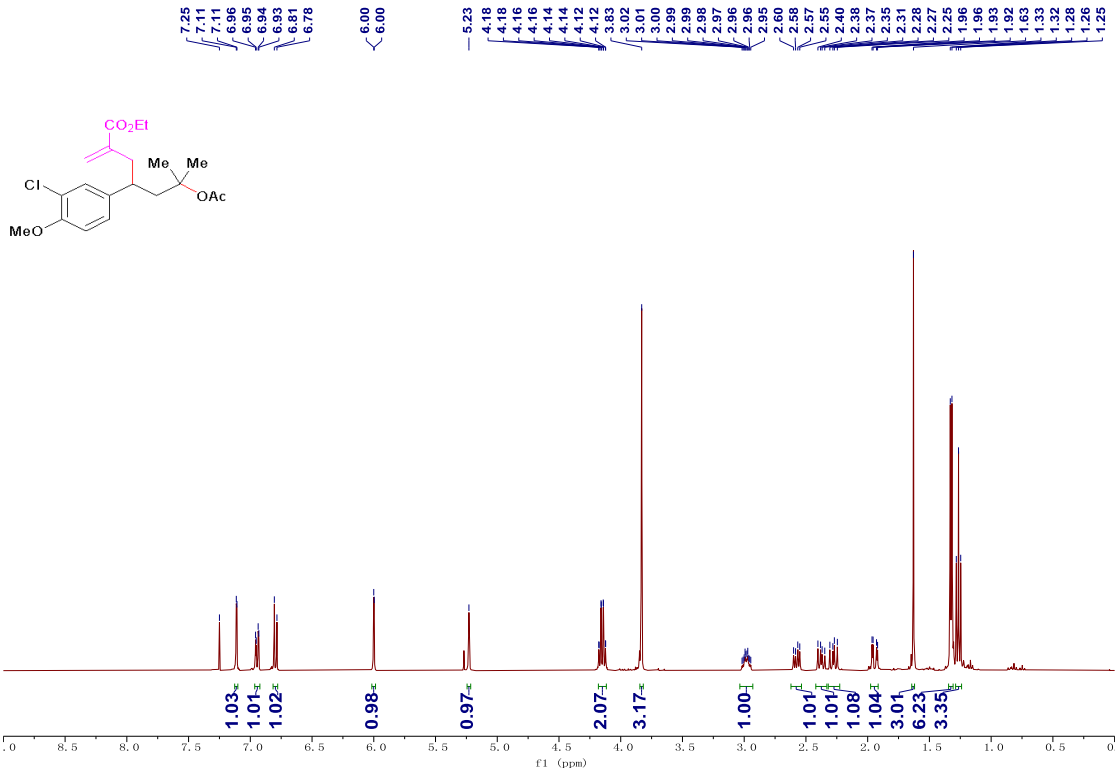
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**



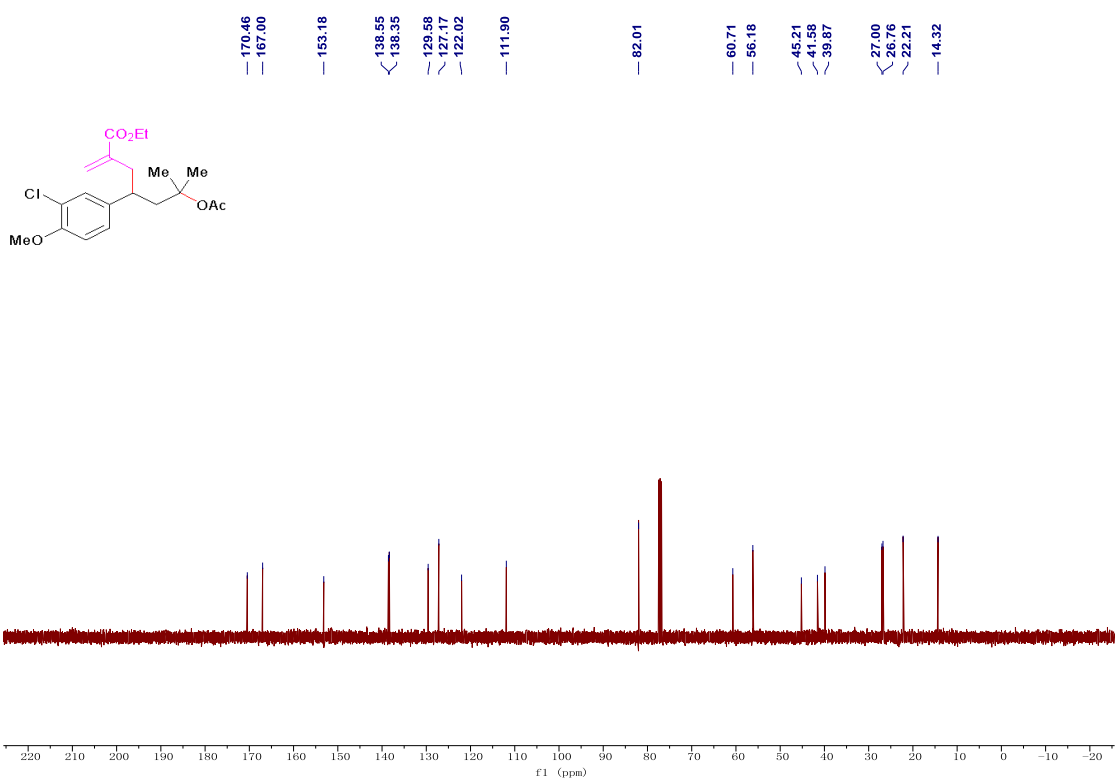
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4b**



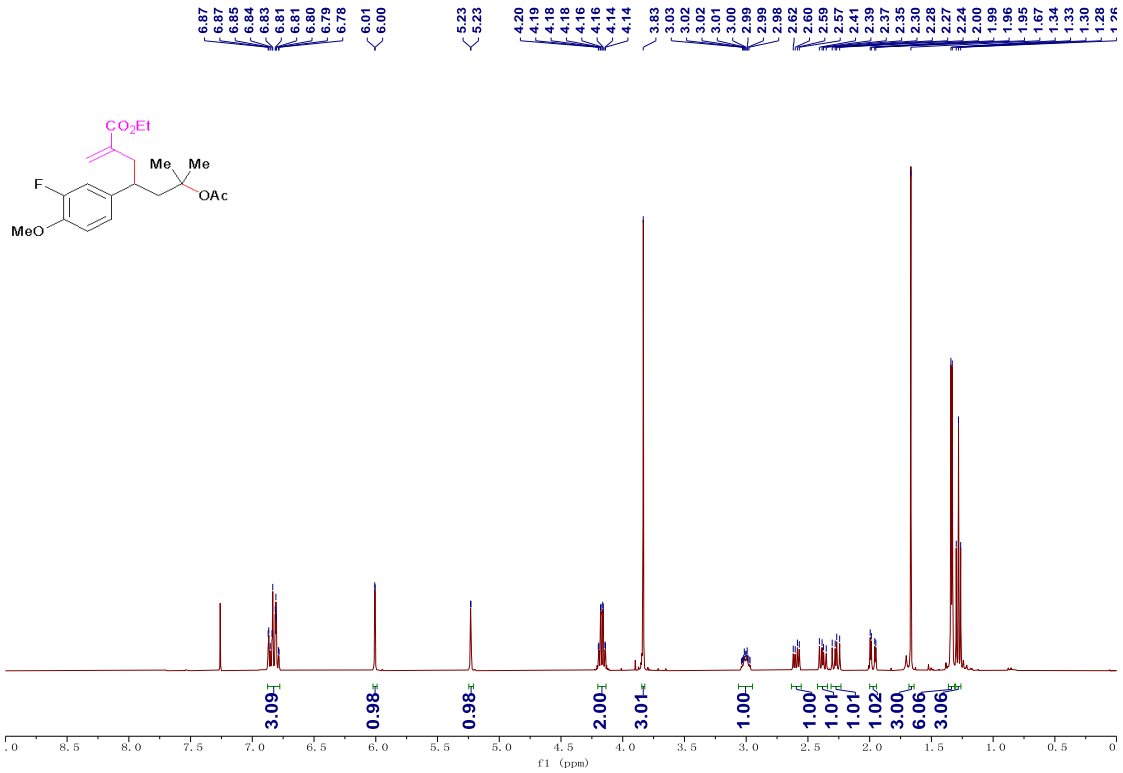
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**



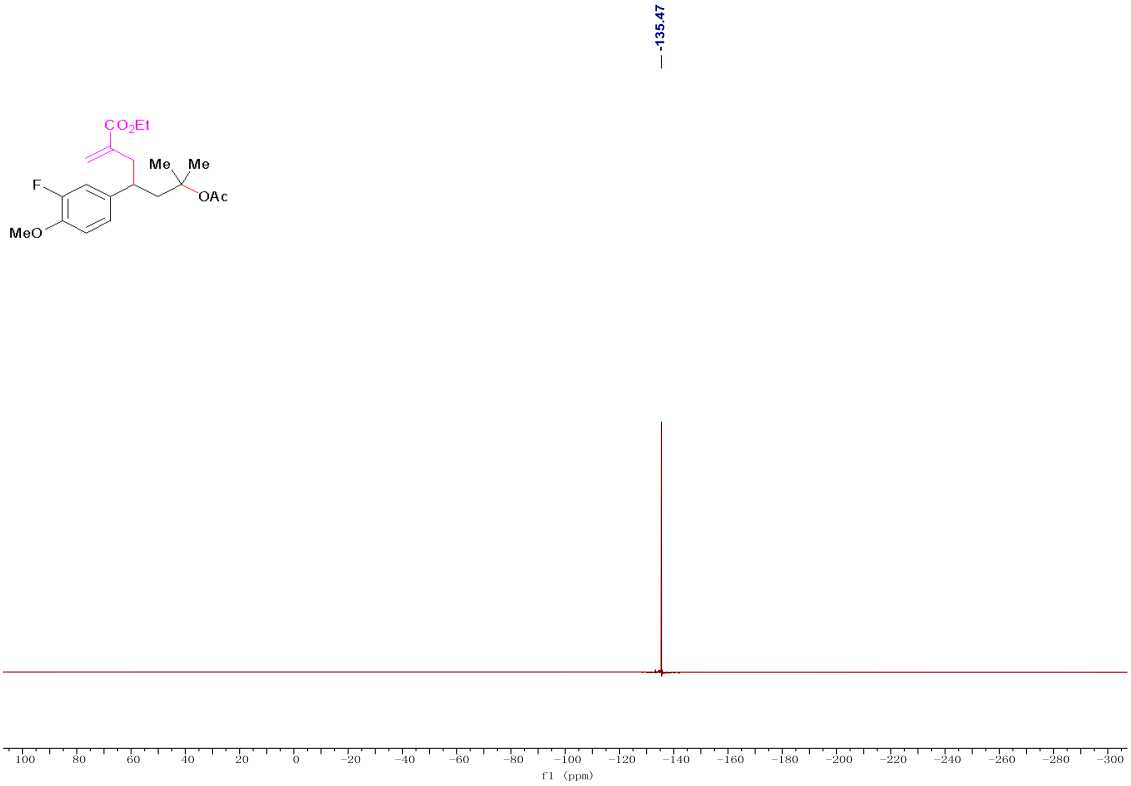
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4c**



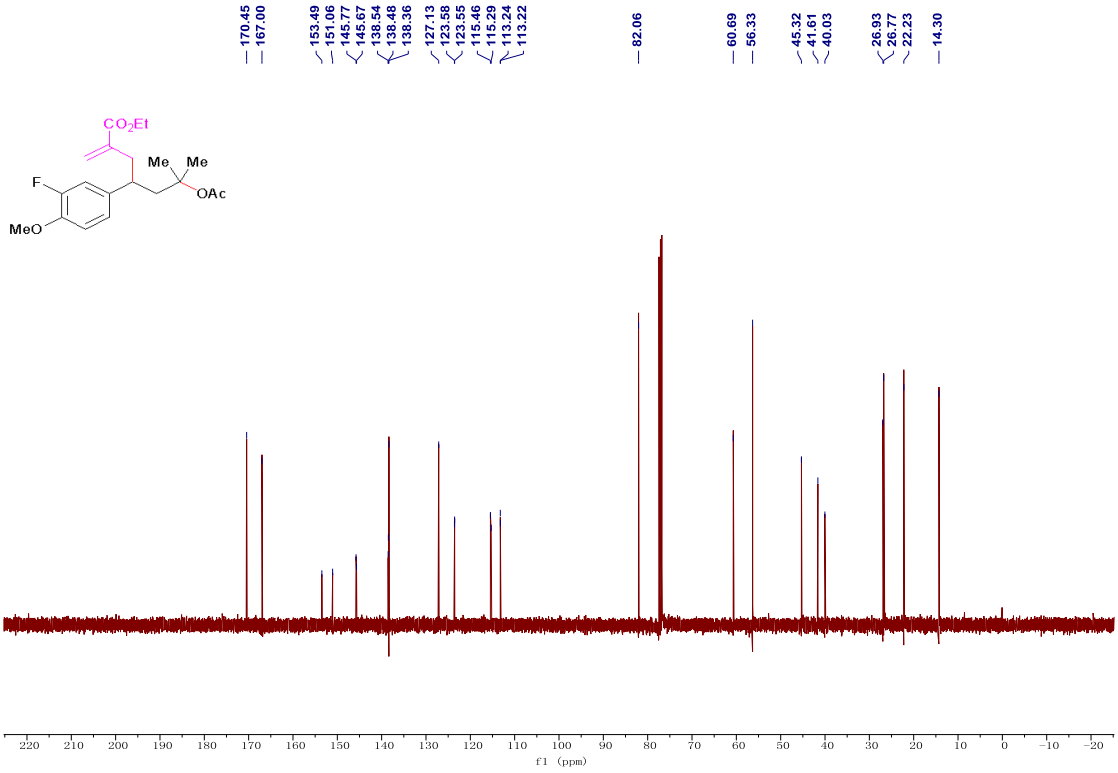
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4d**



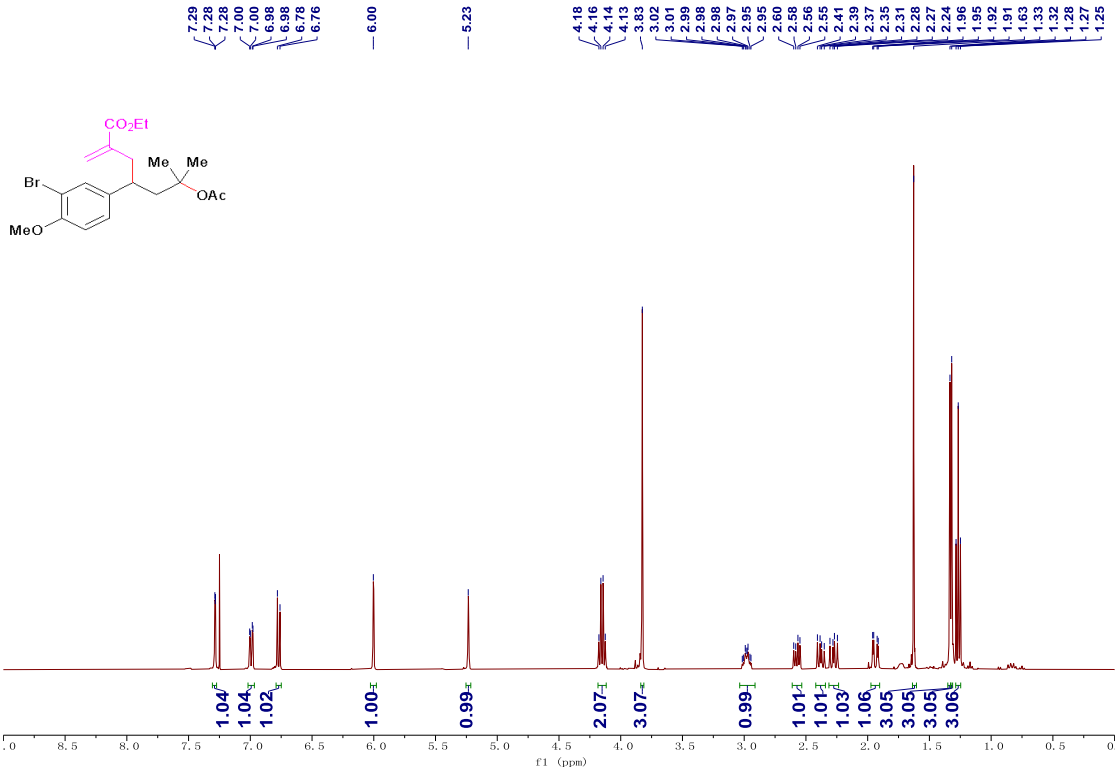
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4d**



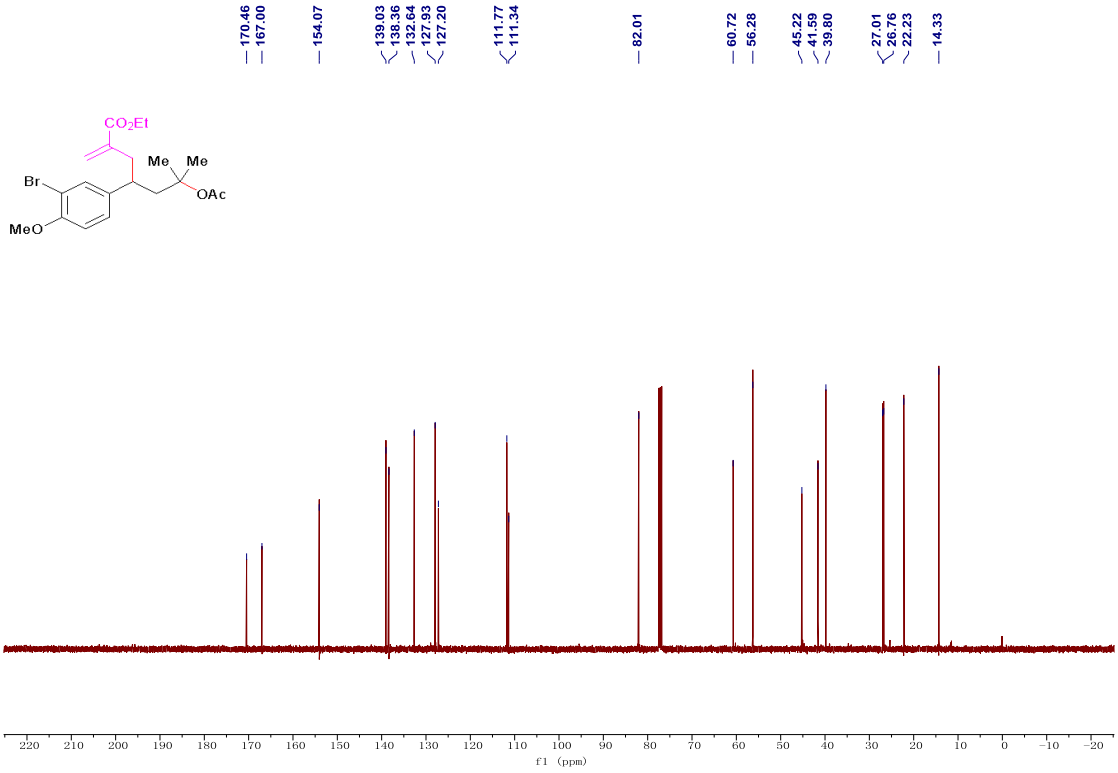
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4d**



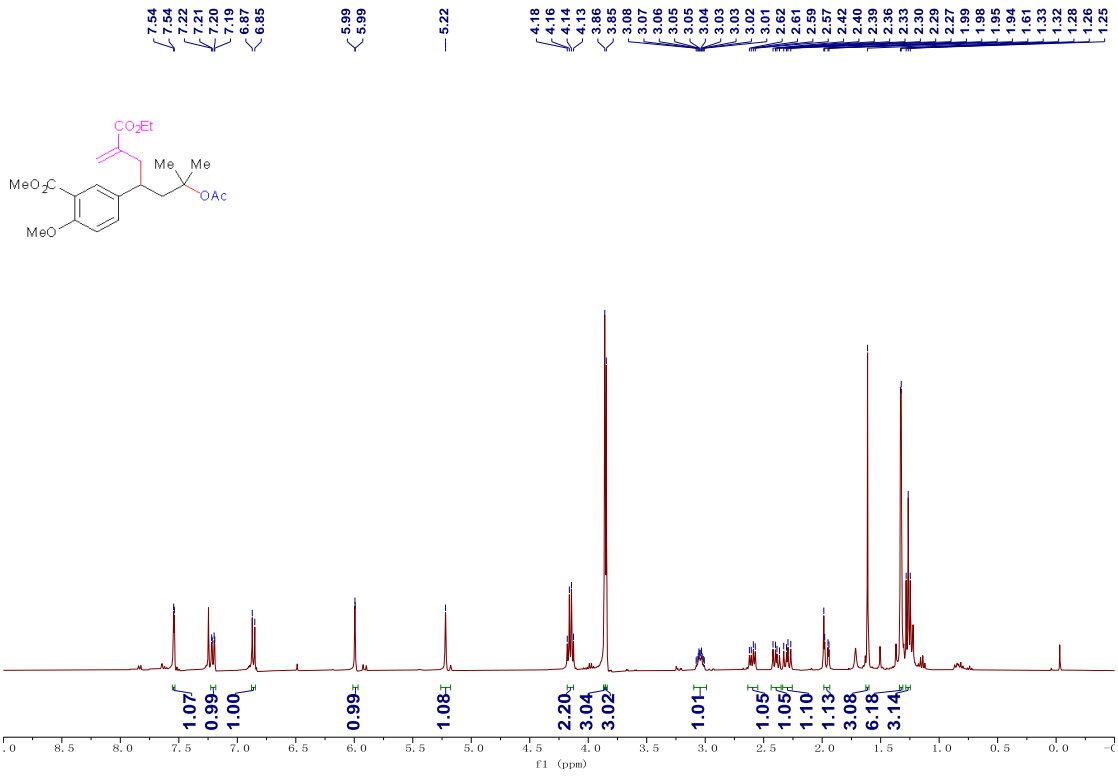
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4e**



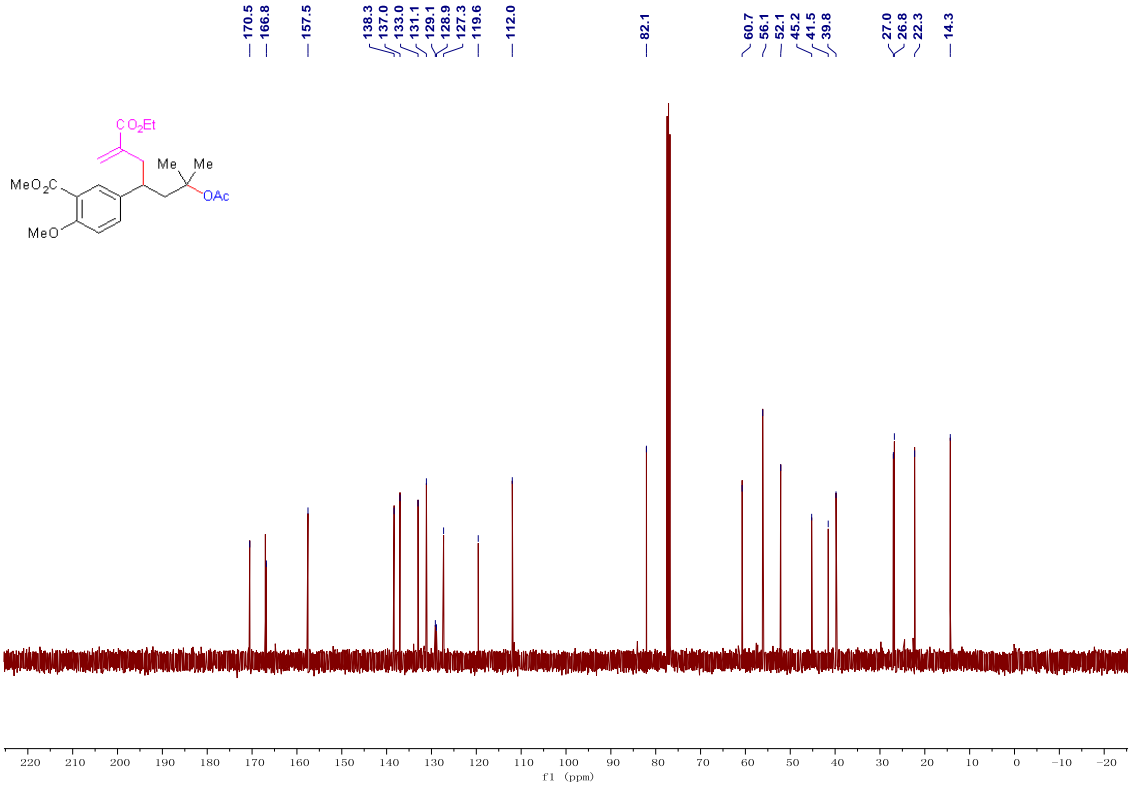
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4e**



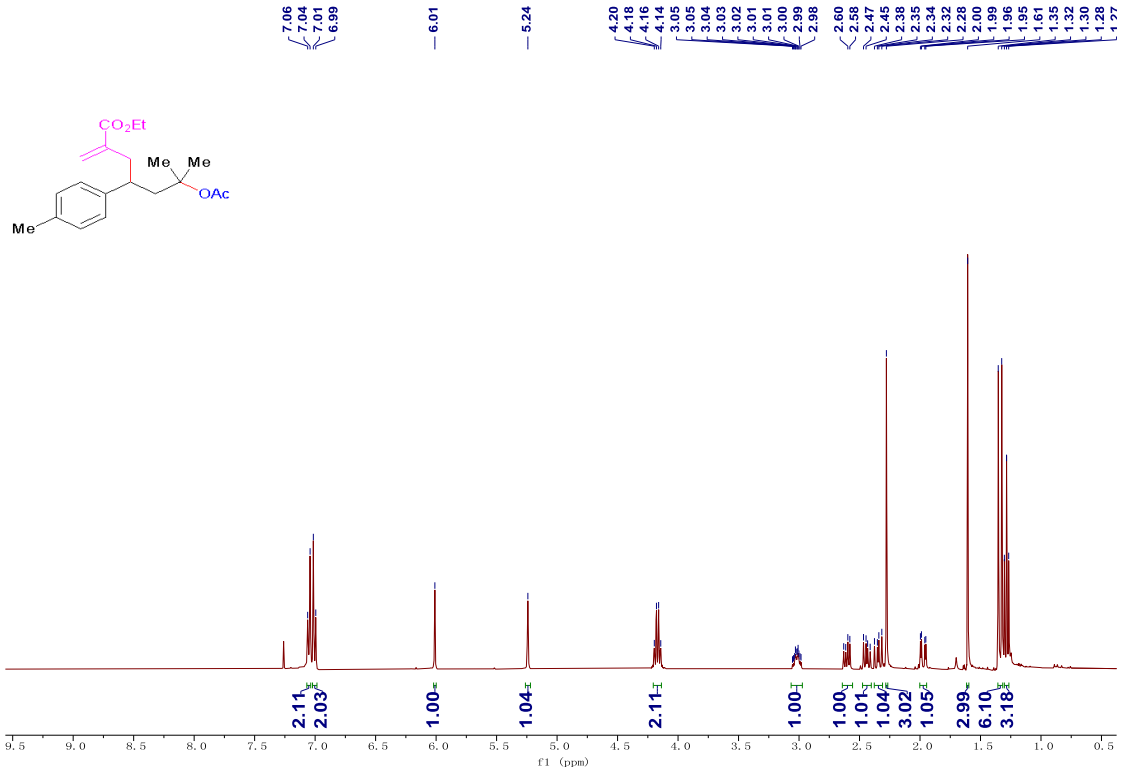
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4f**



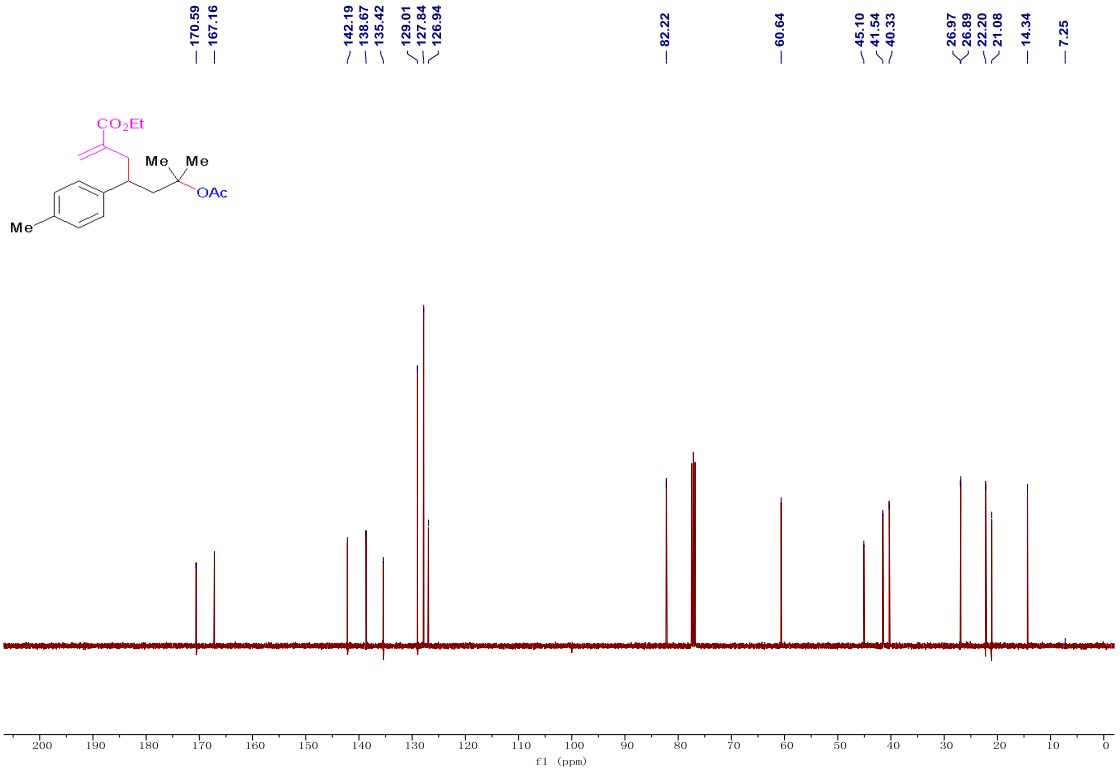
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4f**



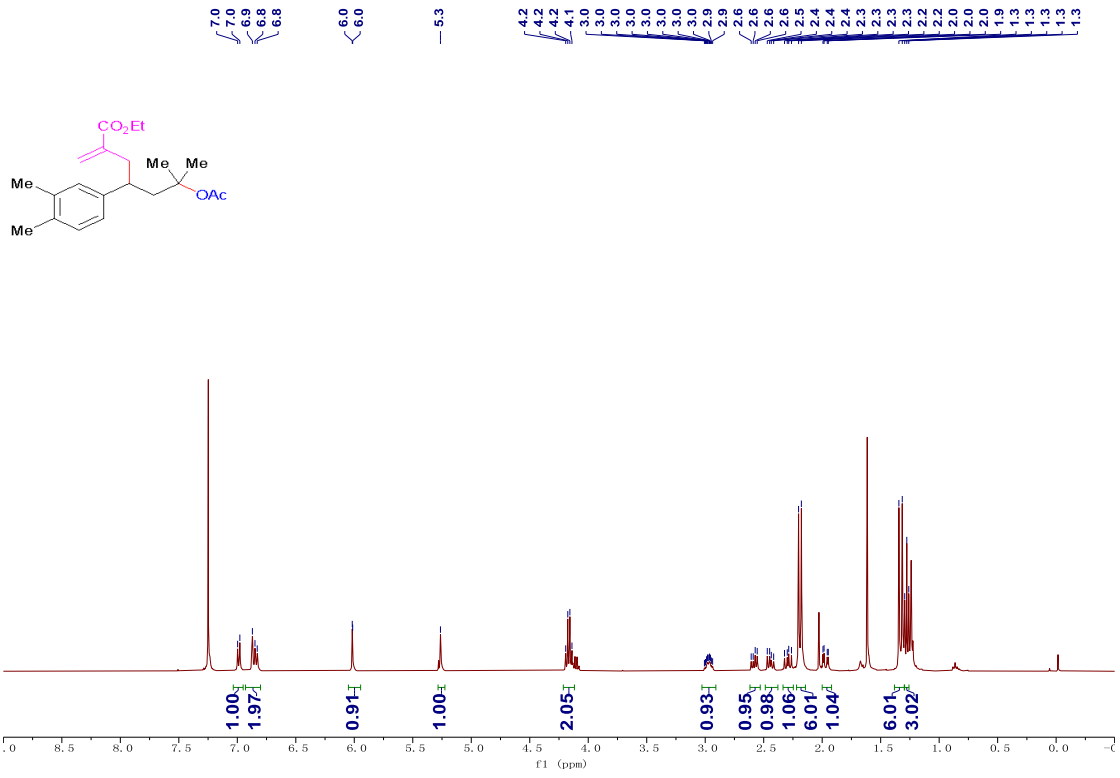
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4g**



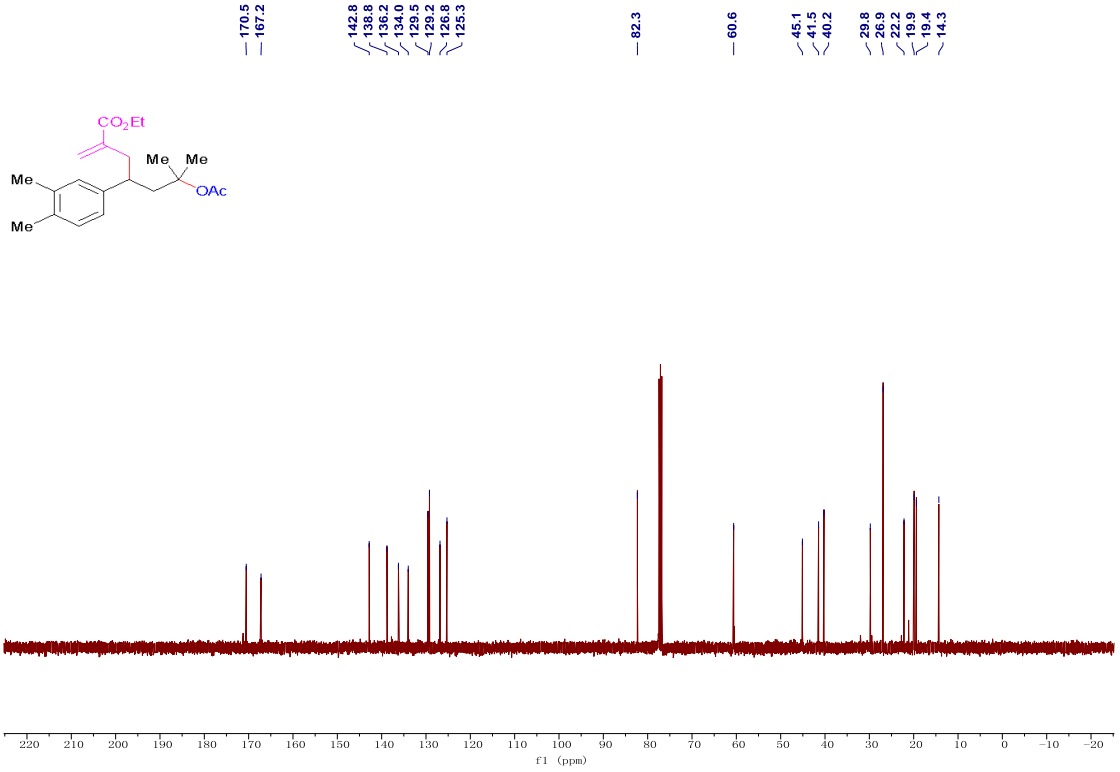
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4g**



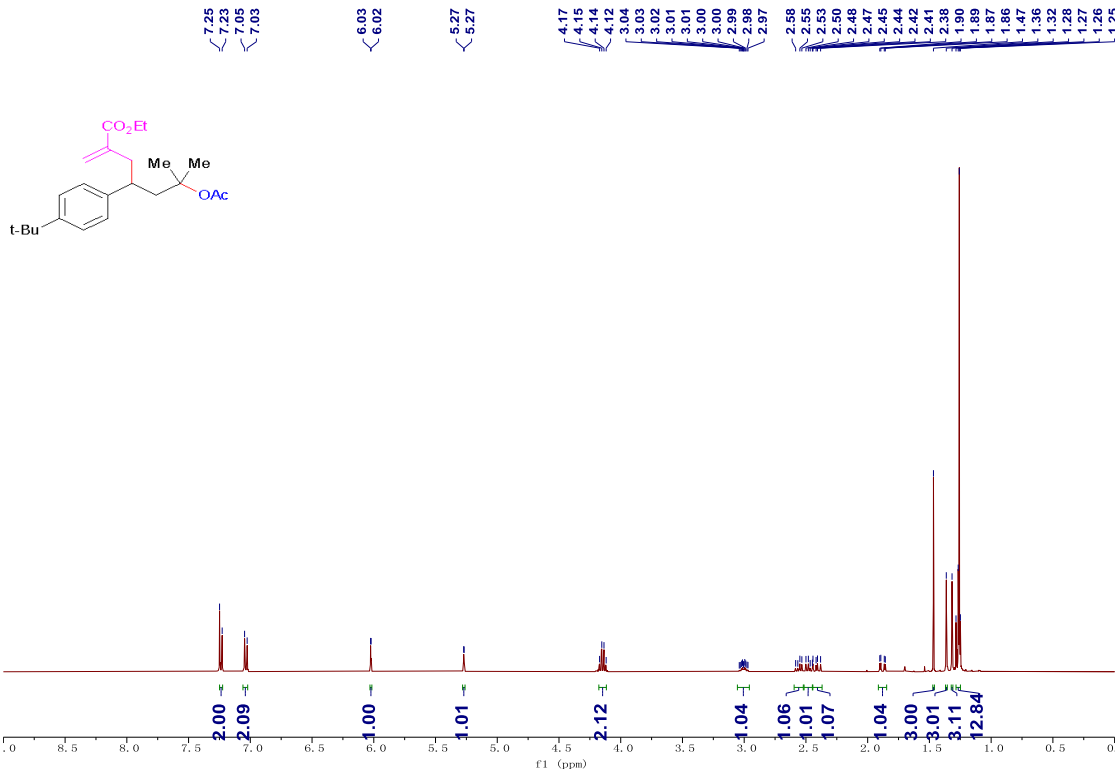
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4h**



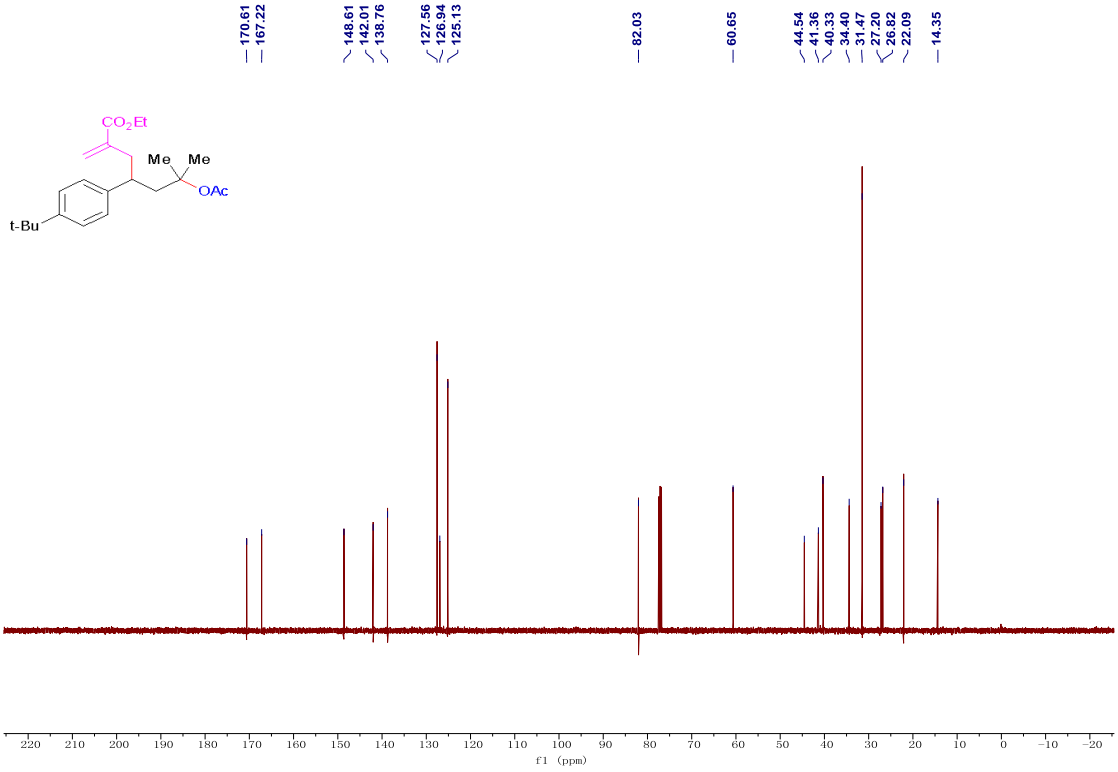
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4h**



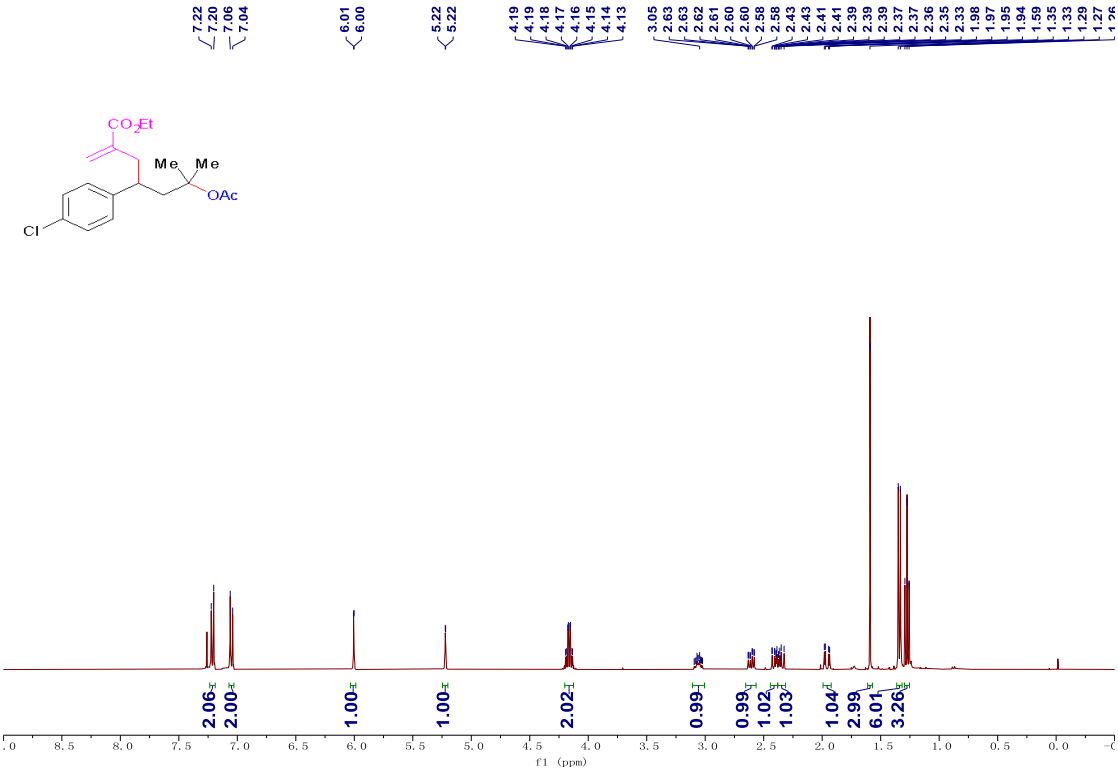
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4i**



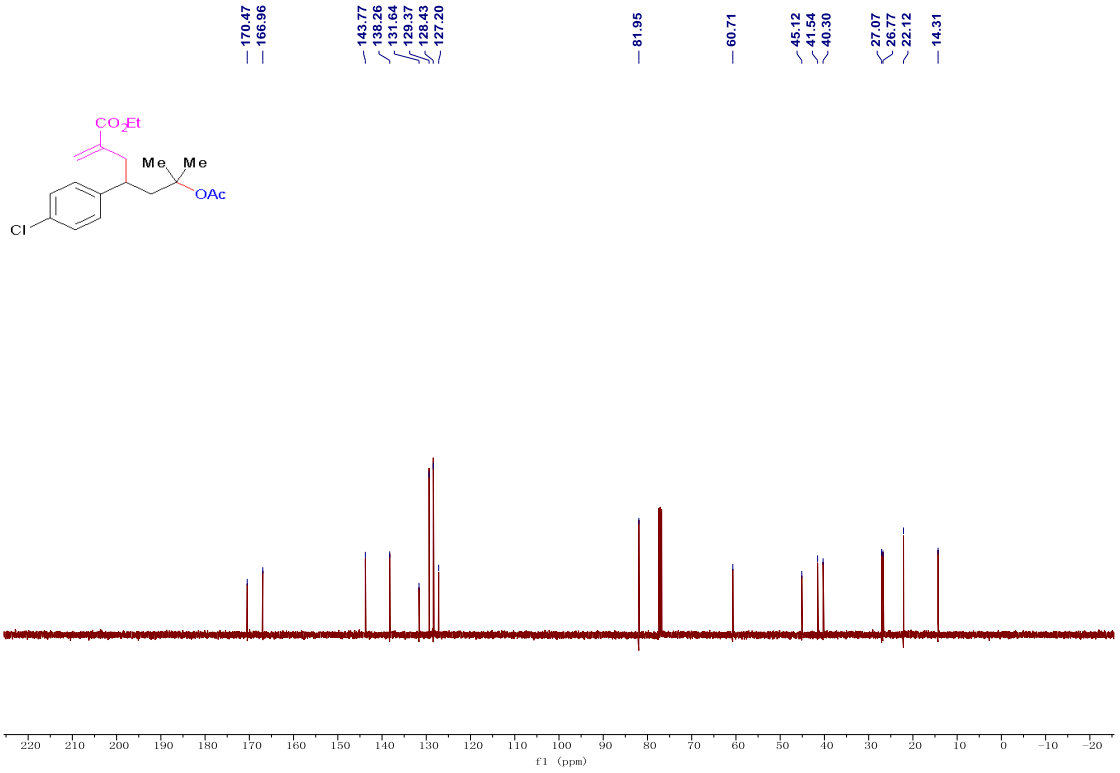
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4i**



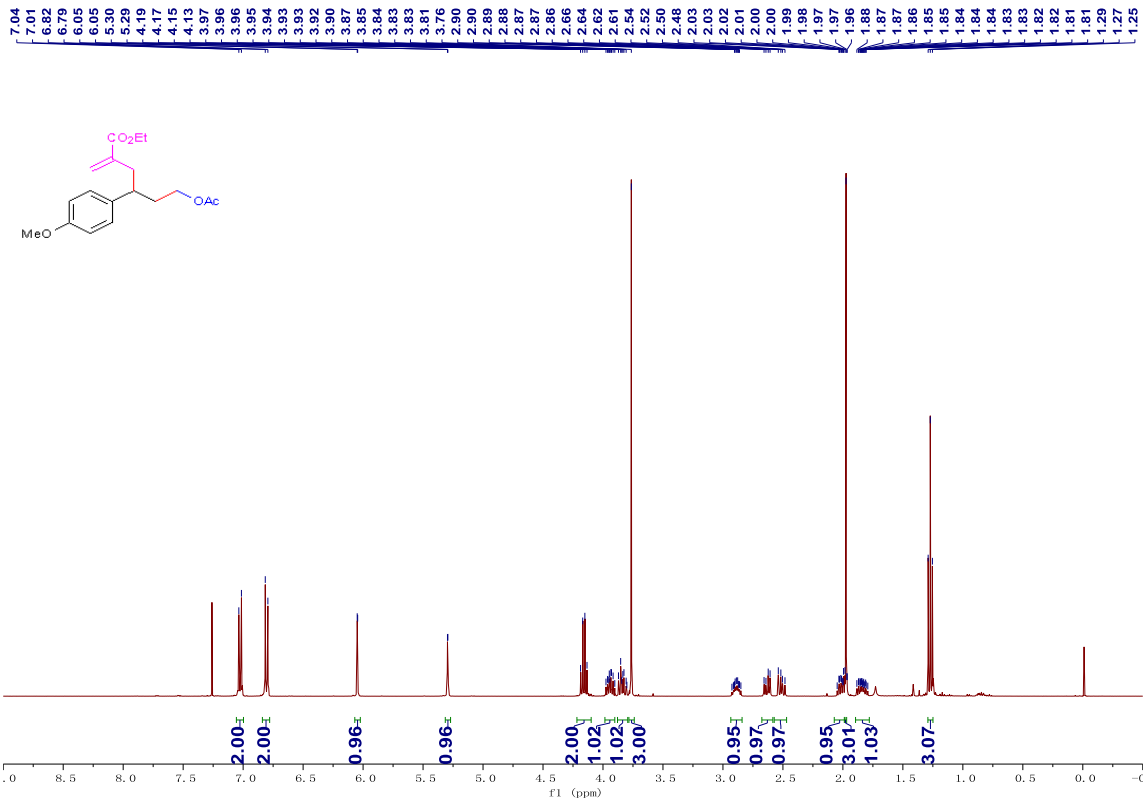
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4j**



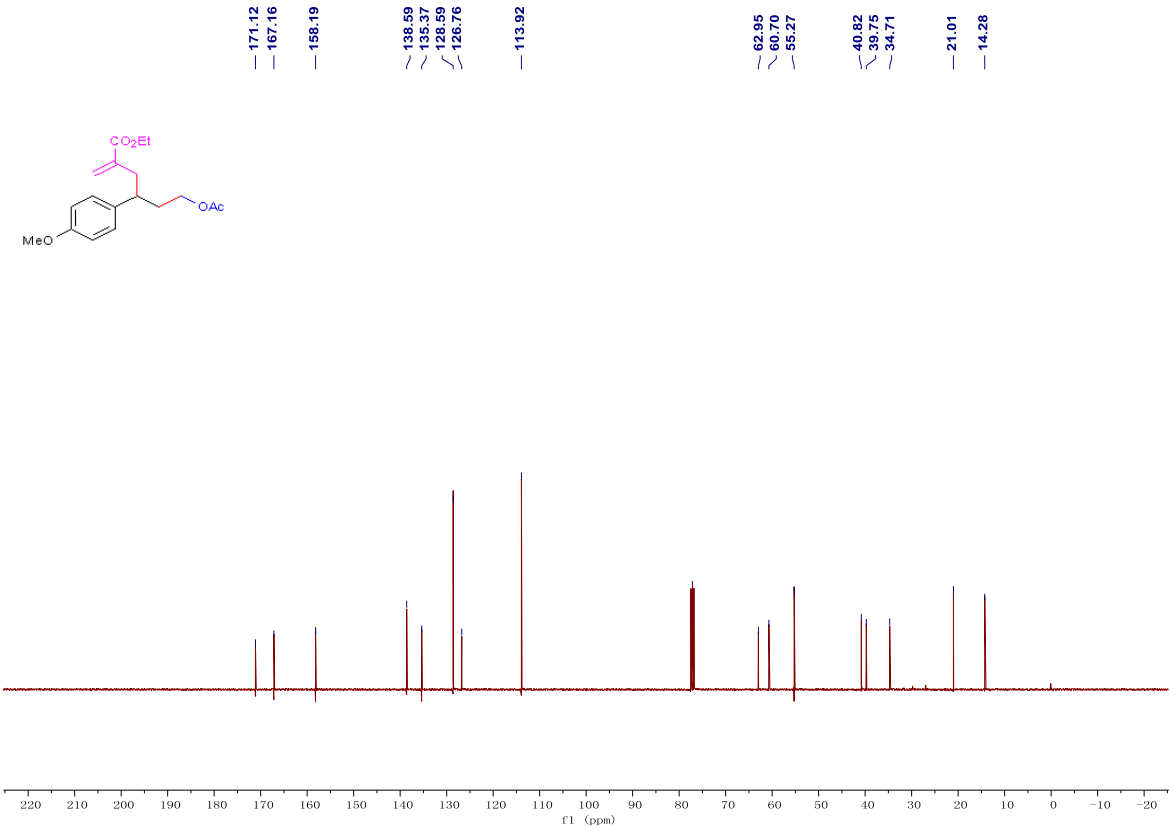
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4j**



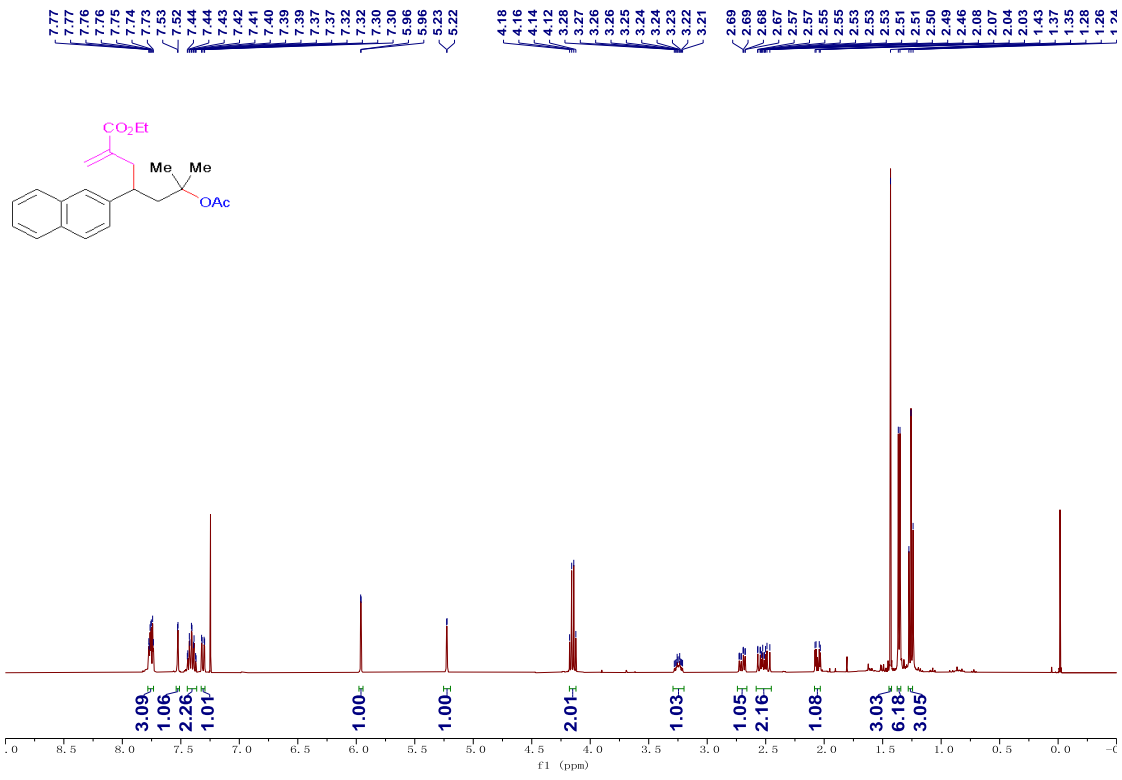
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4k**



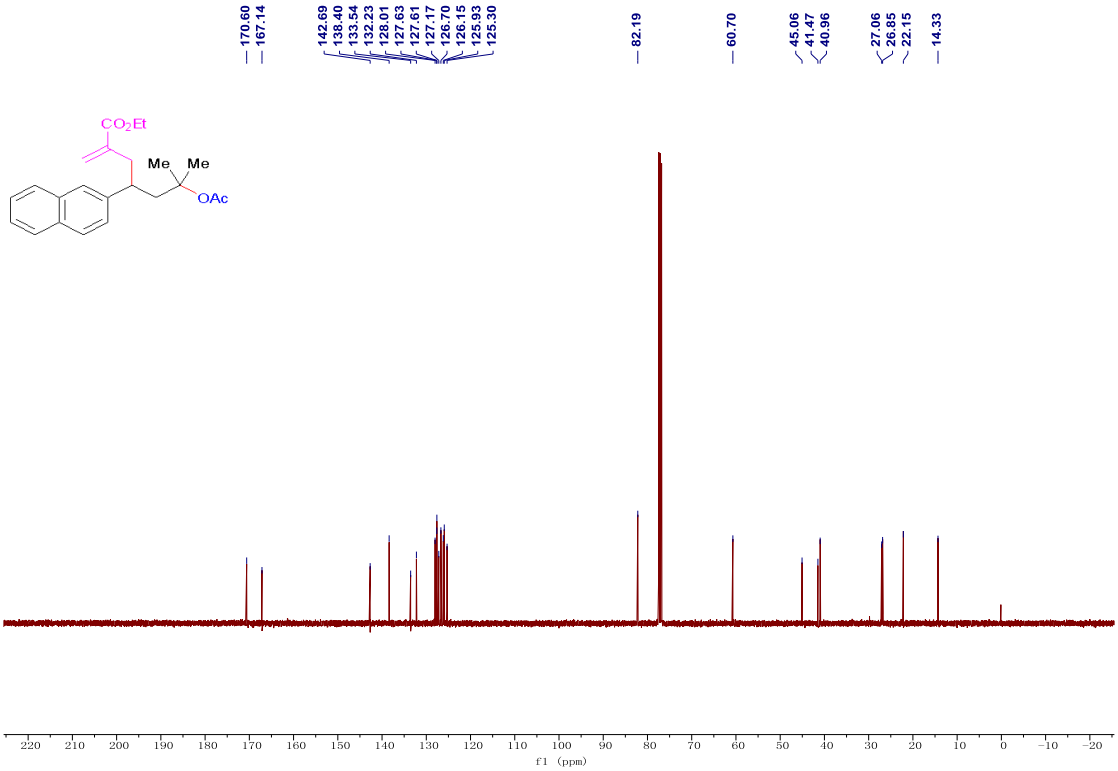
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4k**



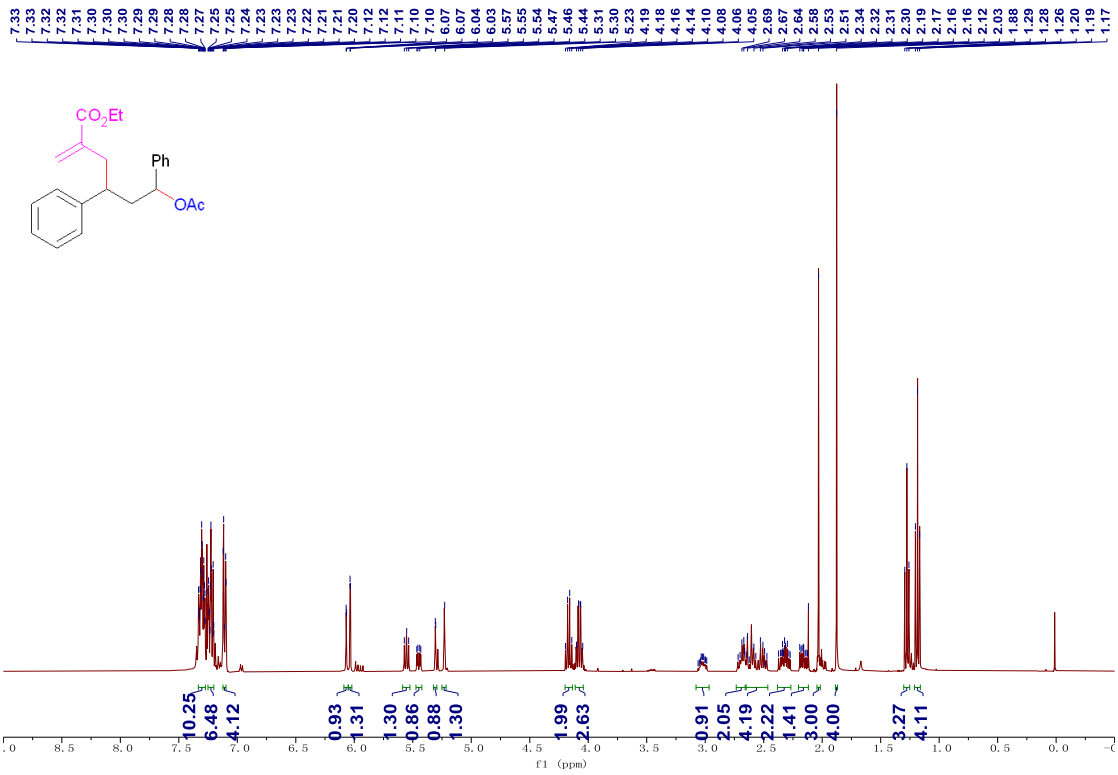
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4l**



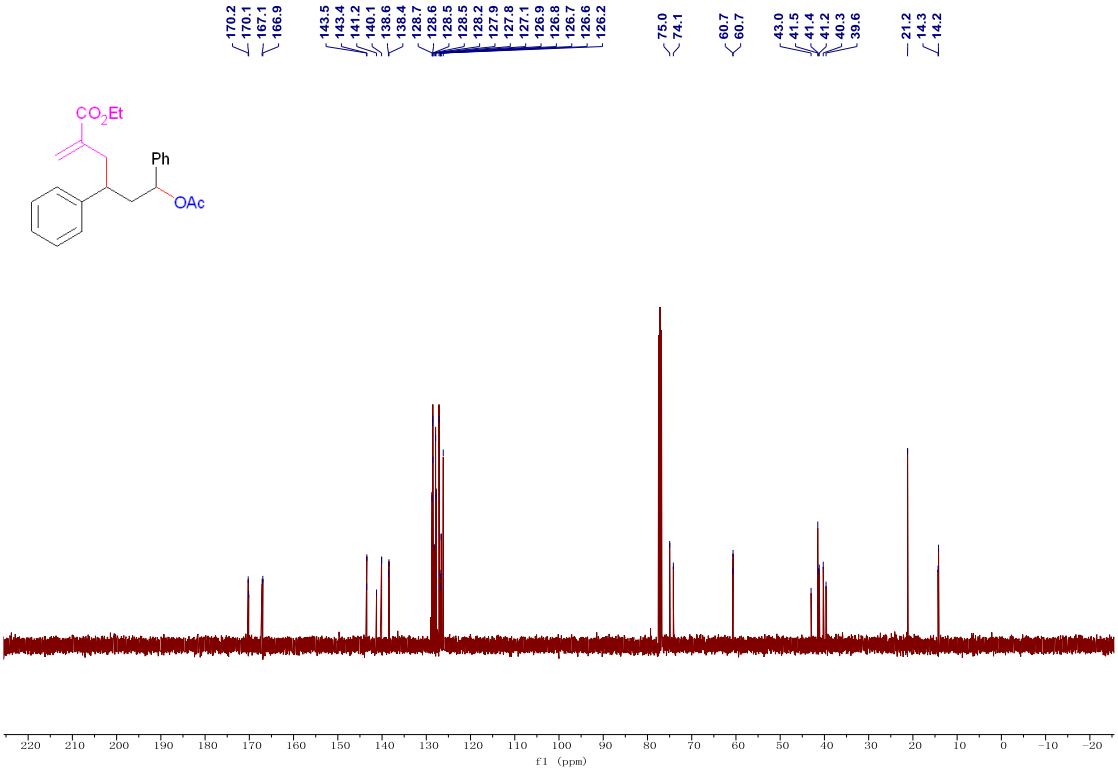
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4l**



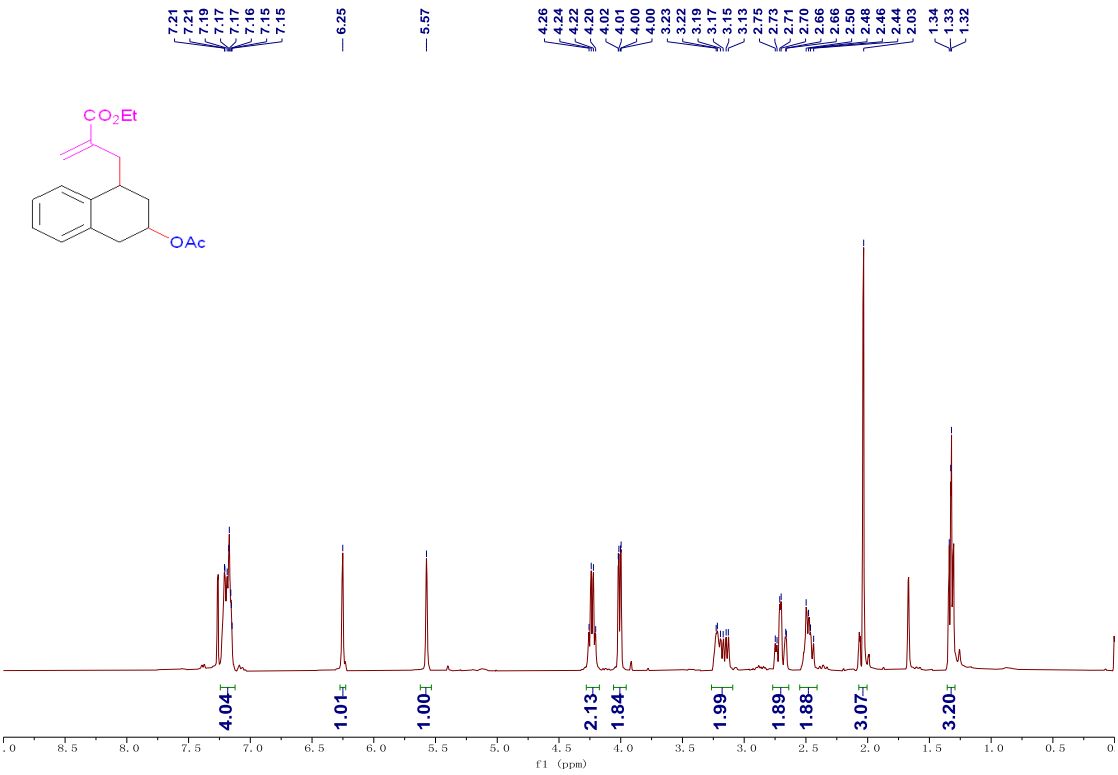
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4m**



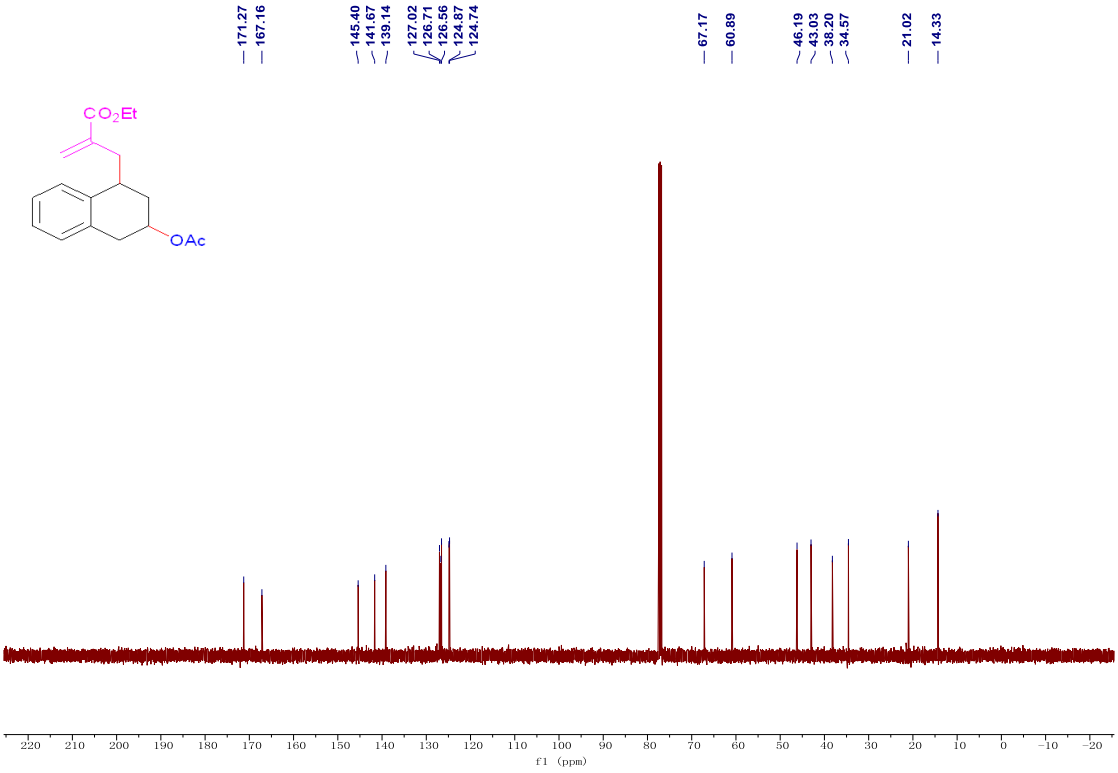
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4m**



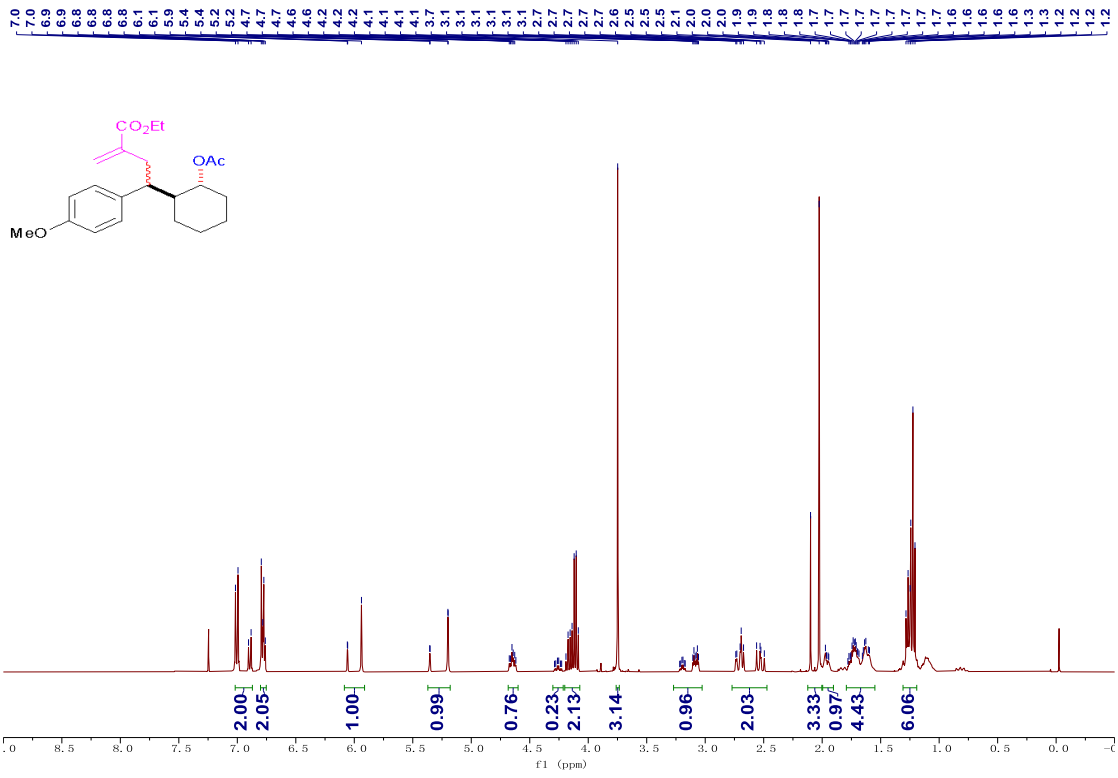
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4n**



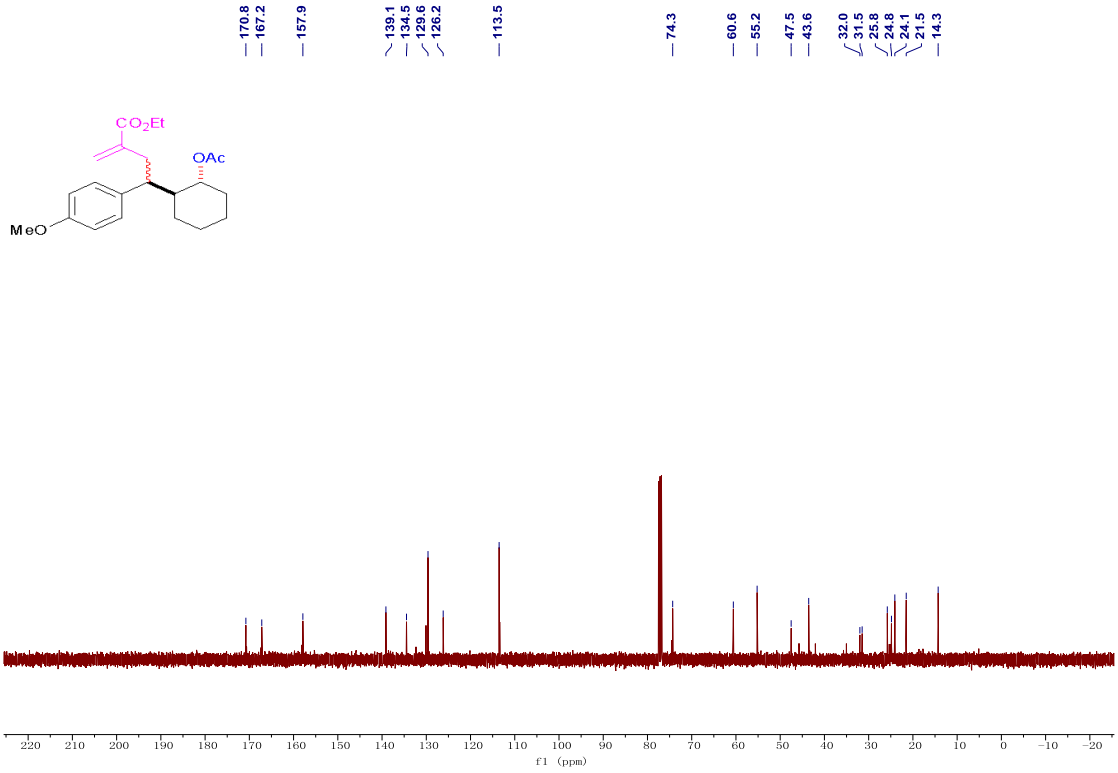
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4n**



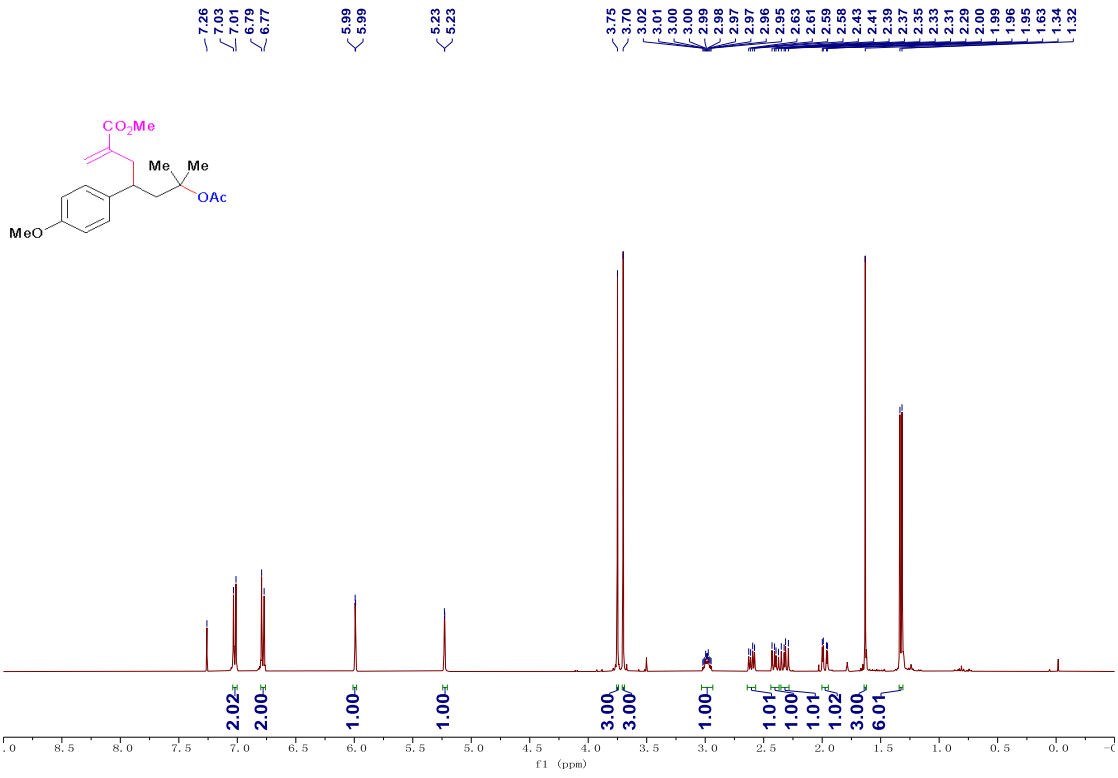
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4o**



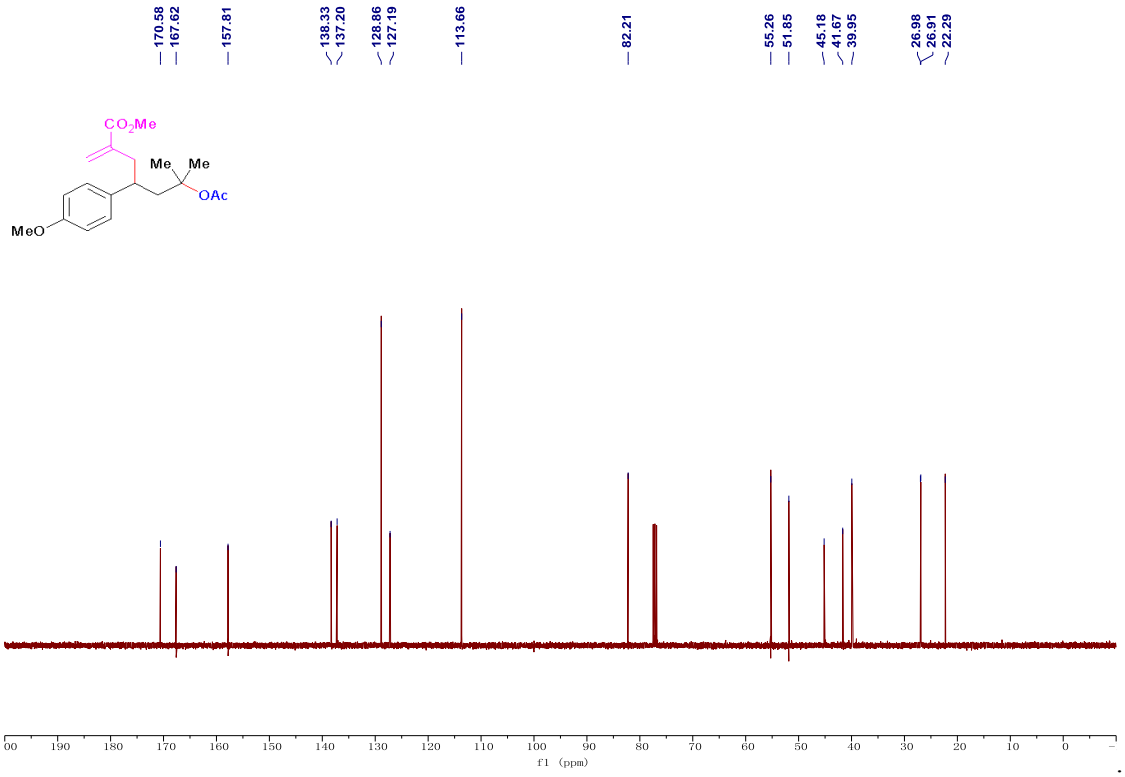
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4o**



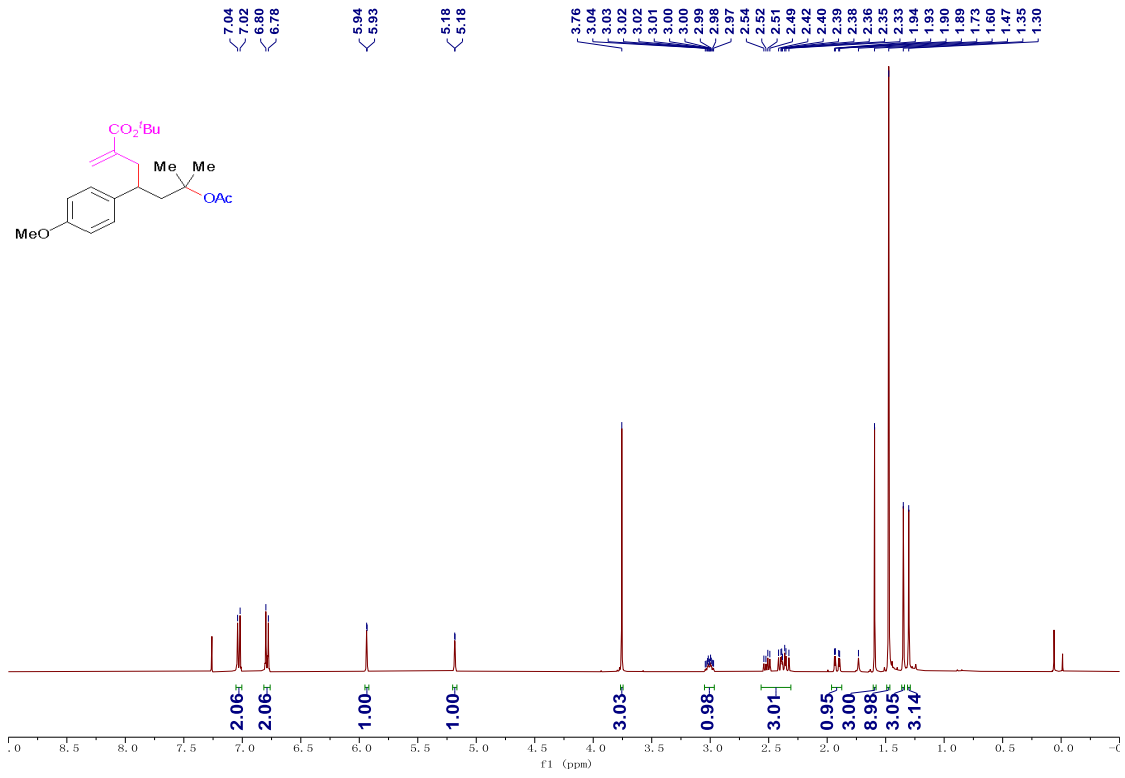
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p**



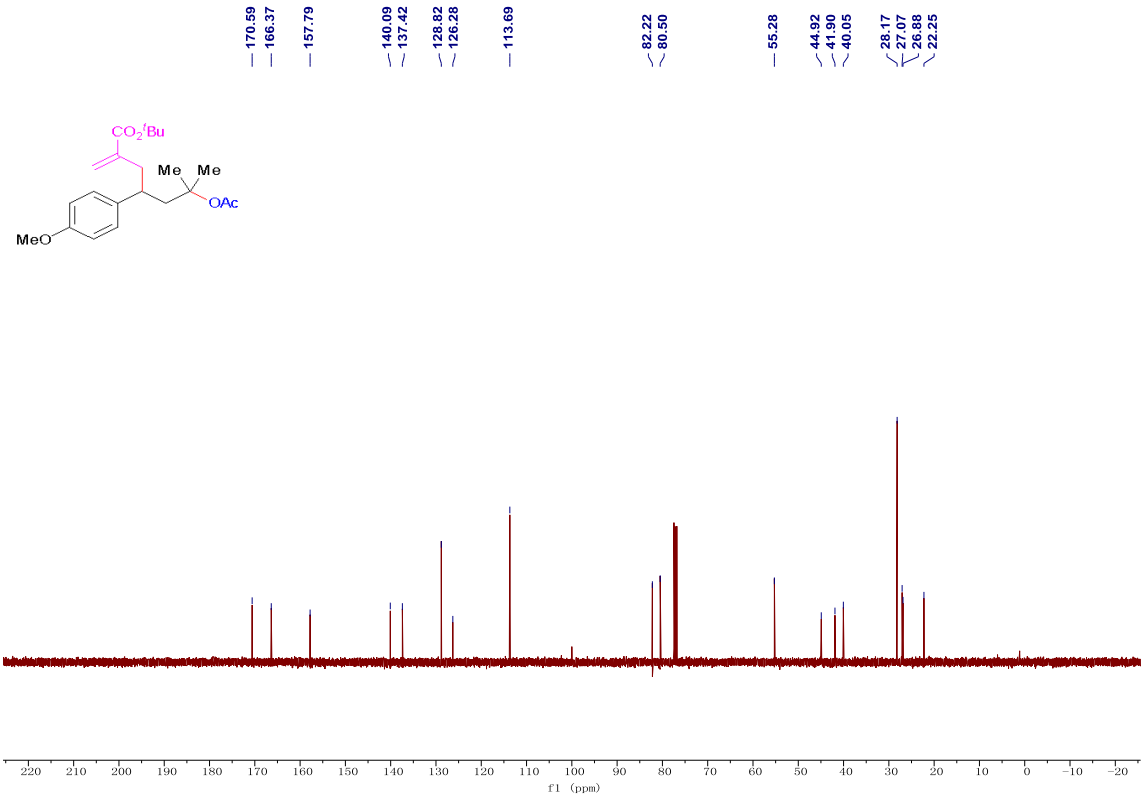
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4p**



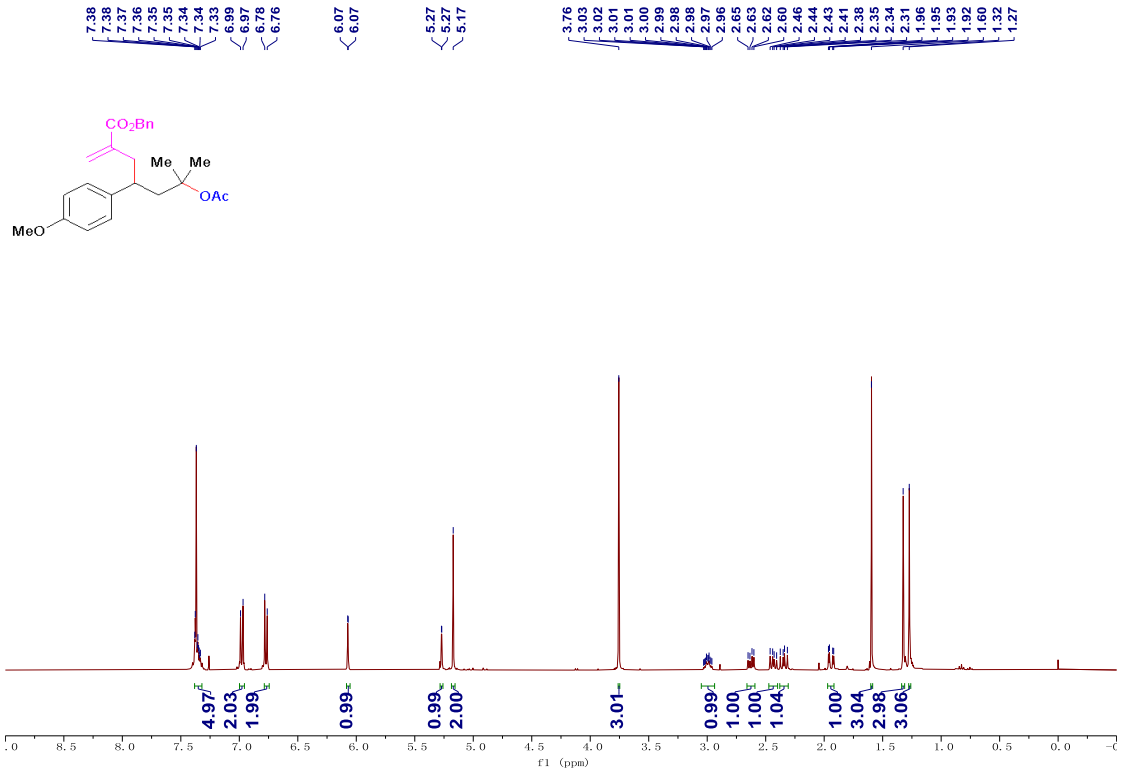
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4q**



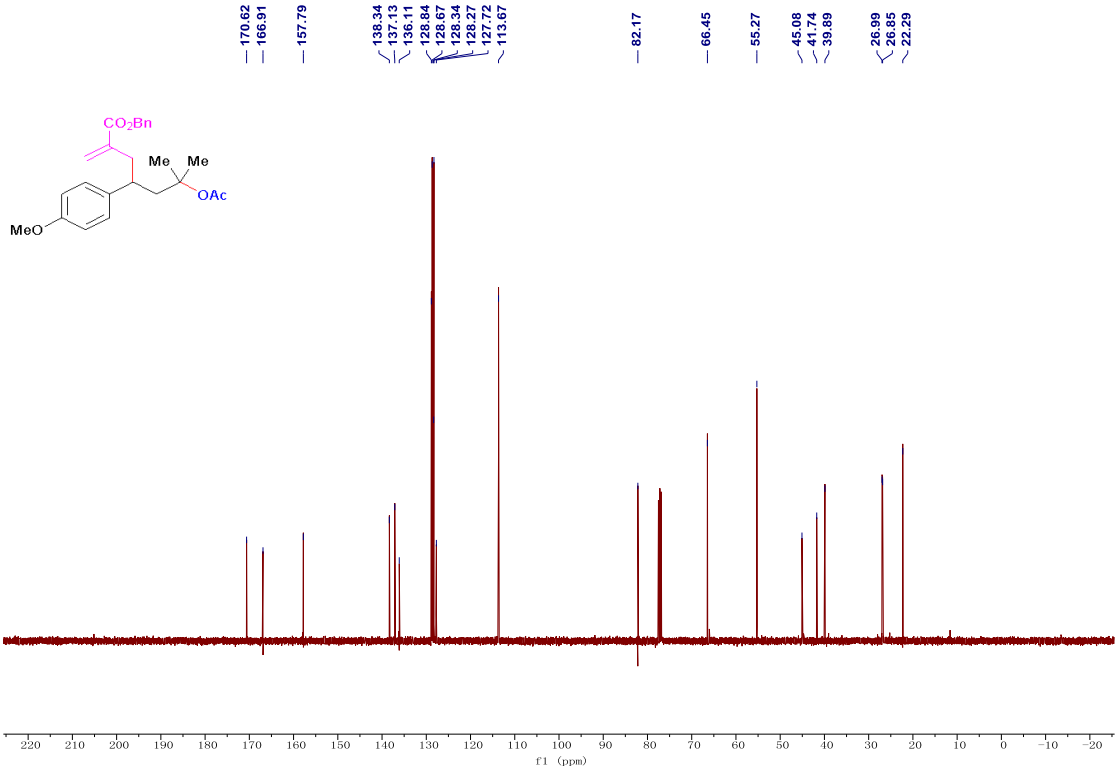
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4q**



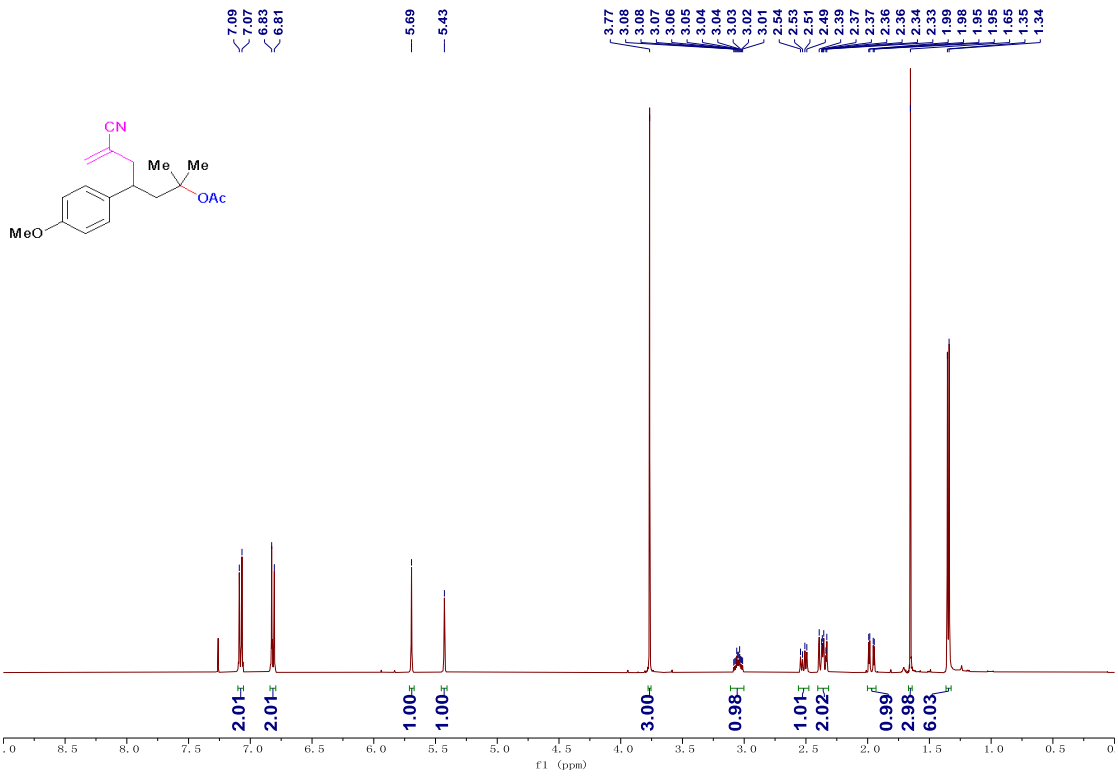
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4r**



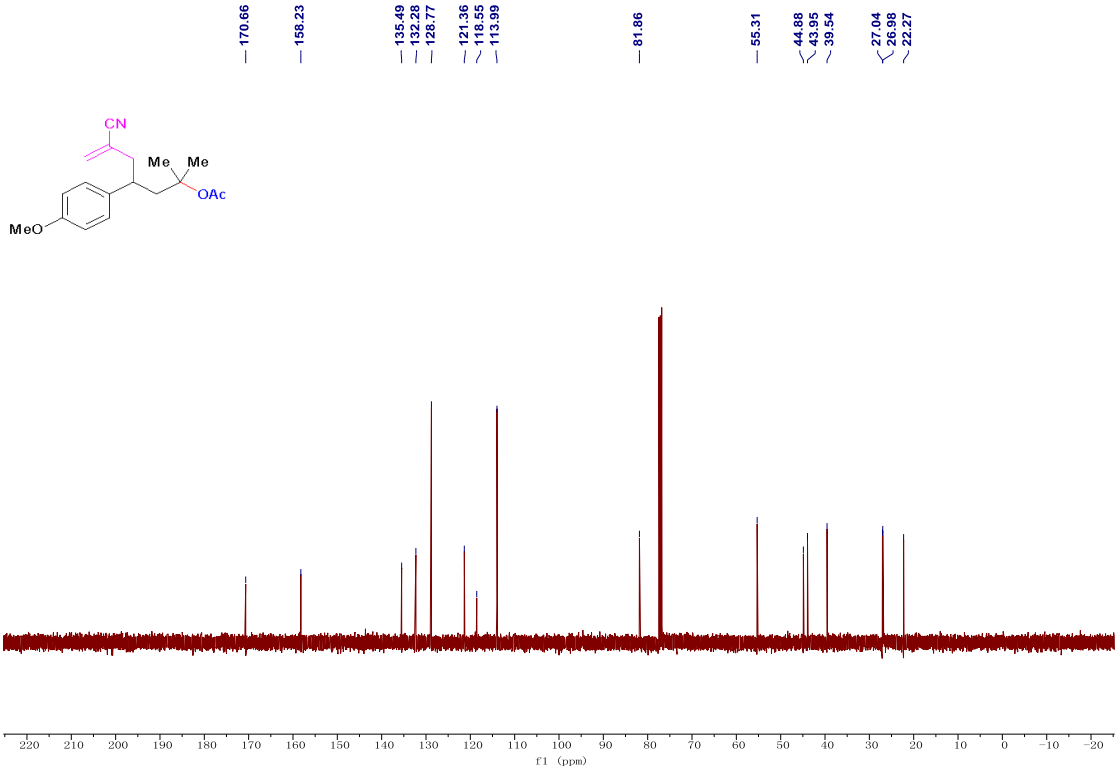
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4r**



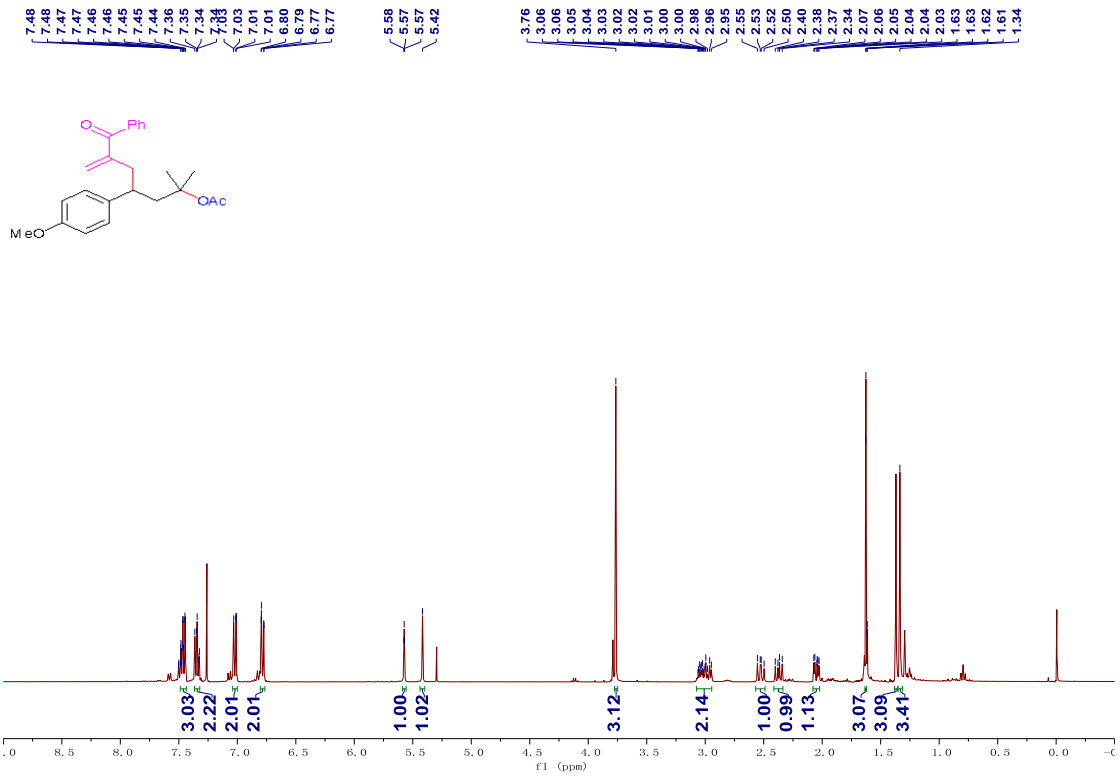
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4s**



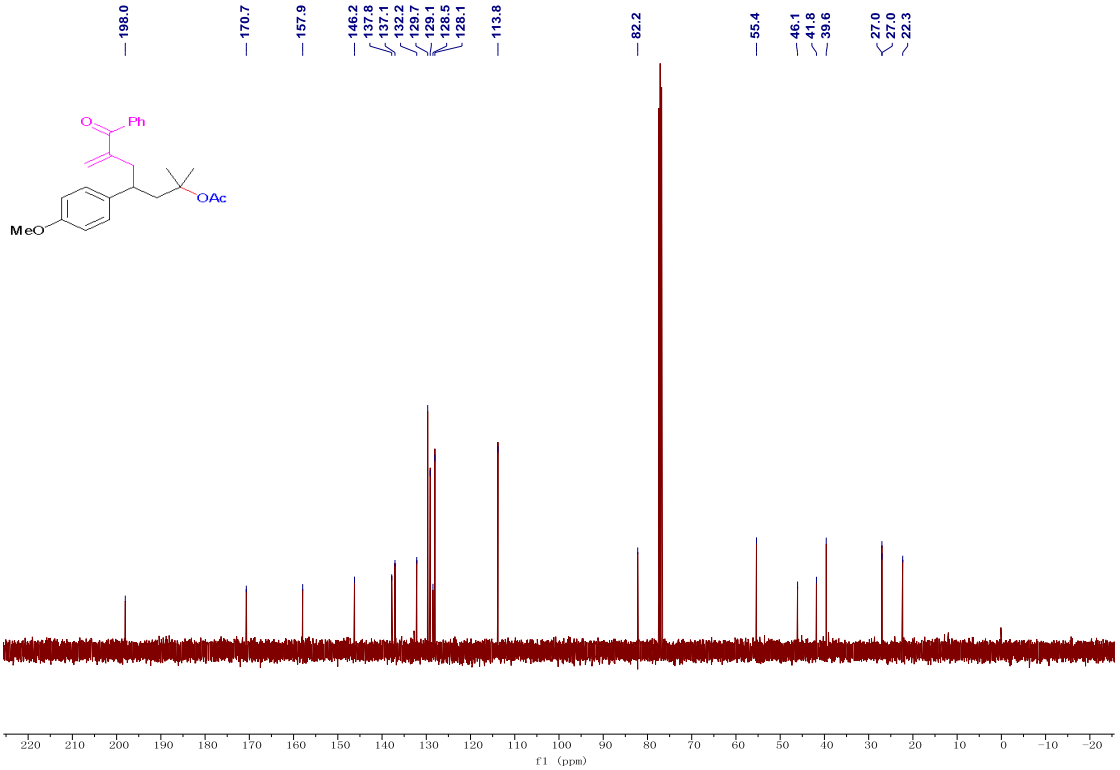
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4s**



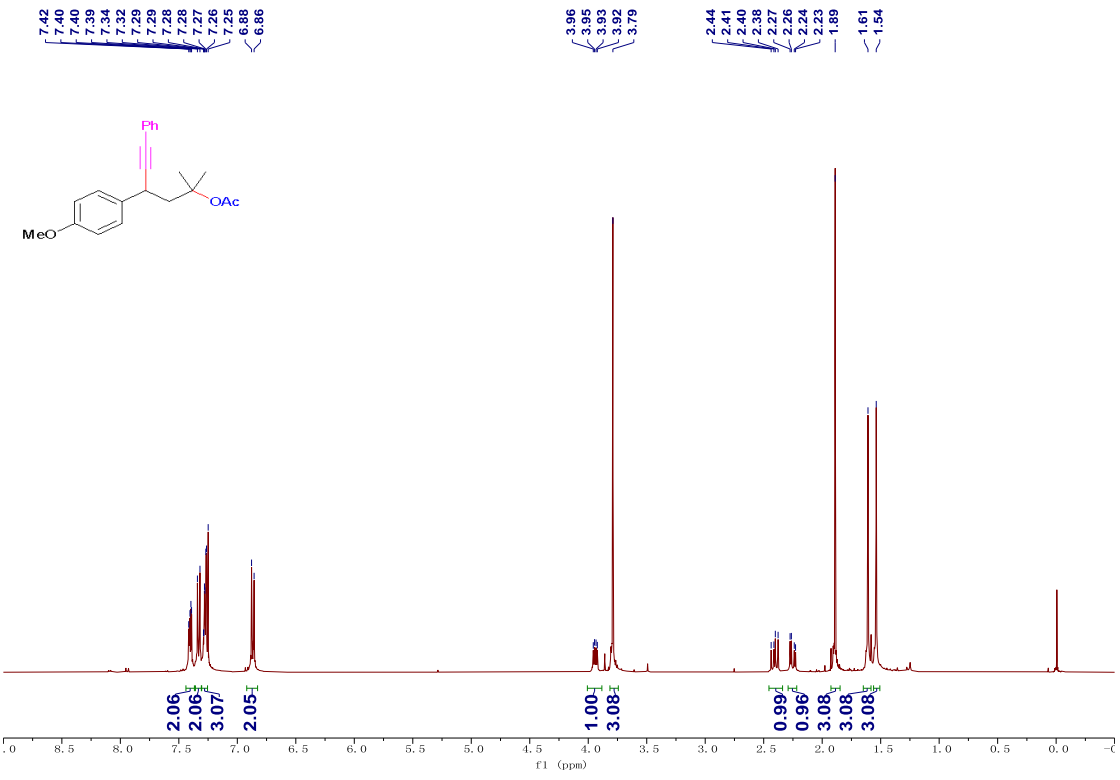
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4t**



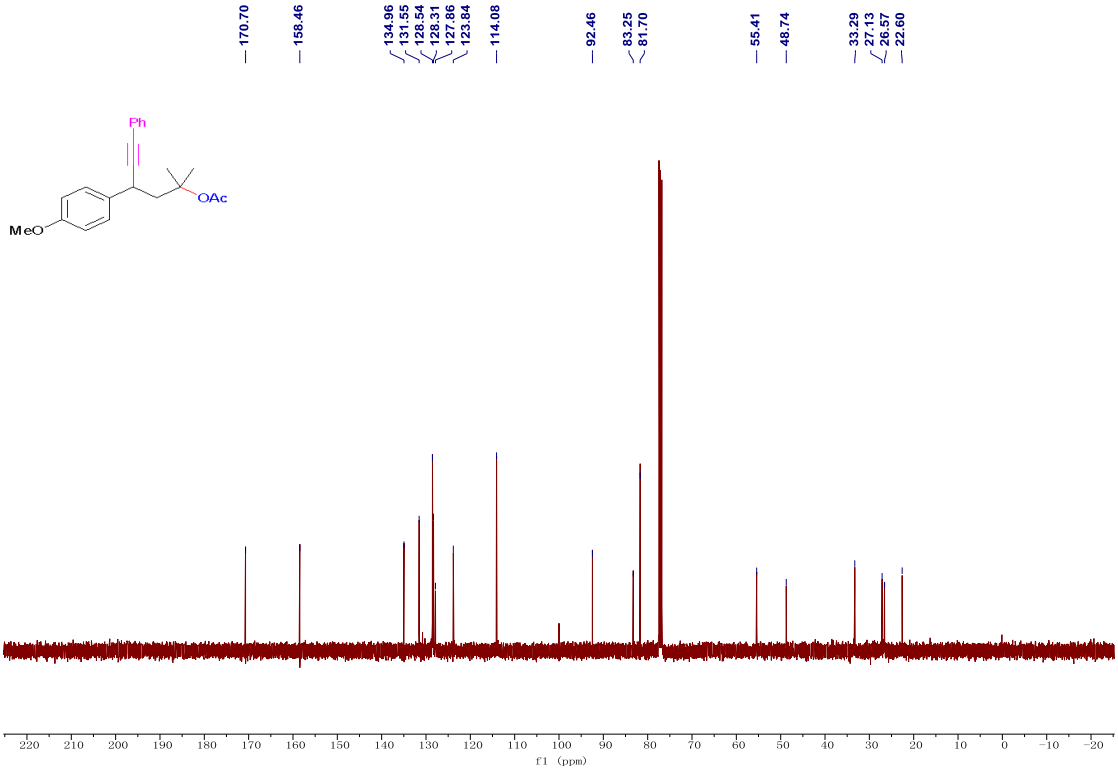
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4t**



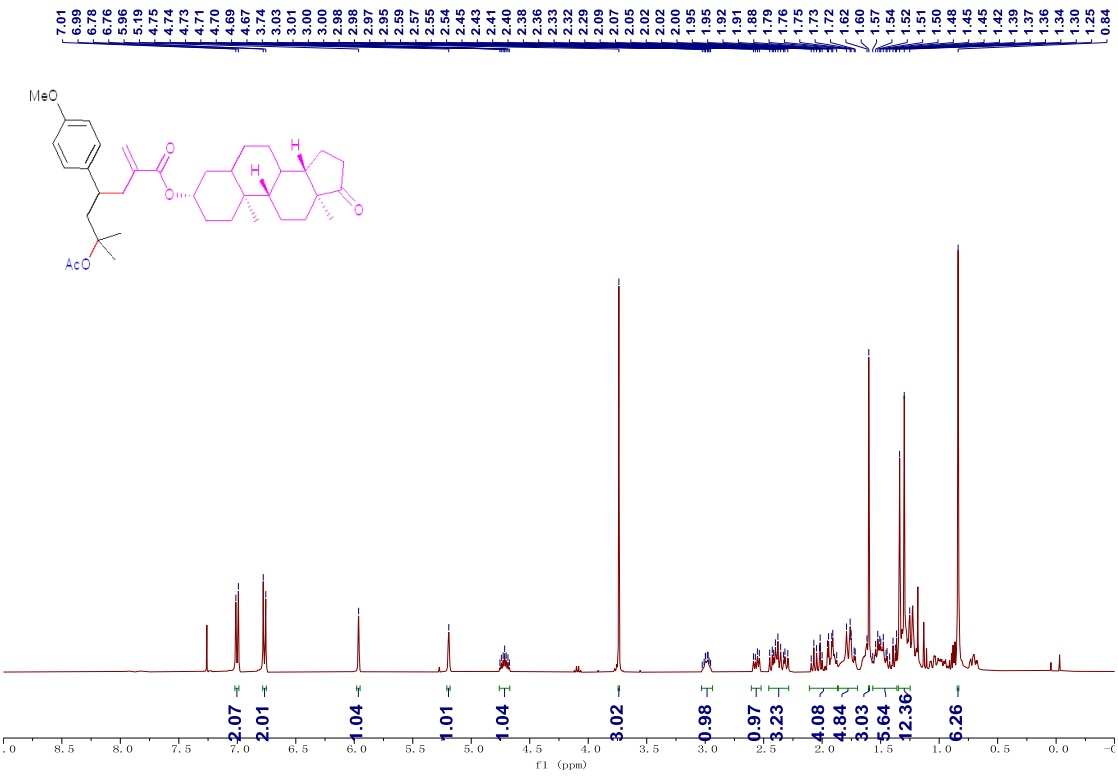
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4u**



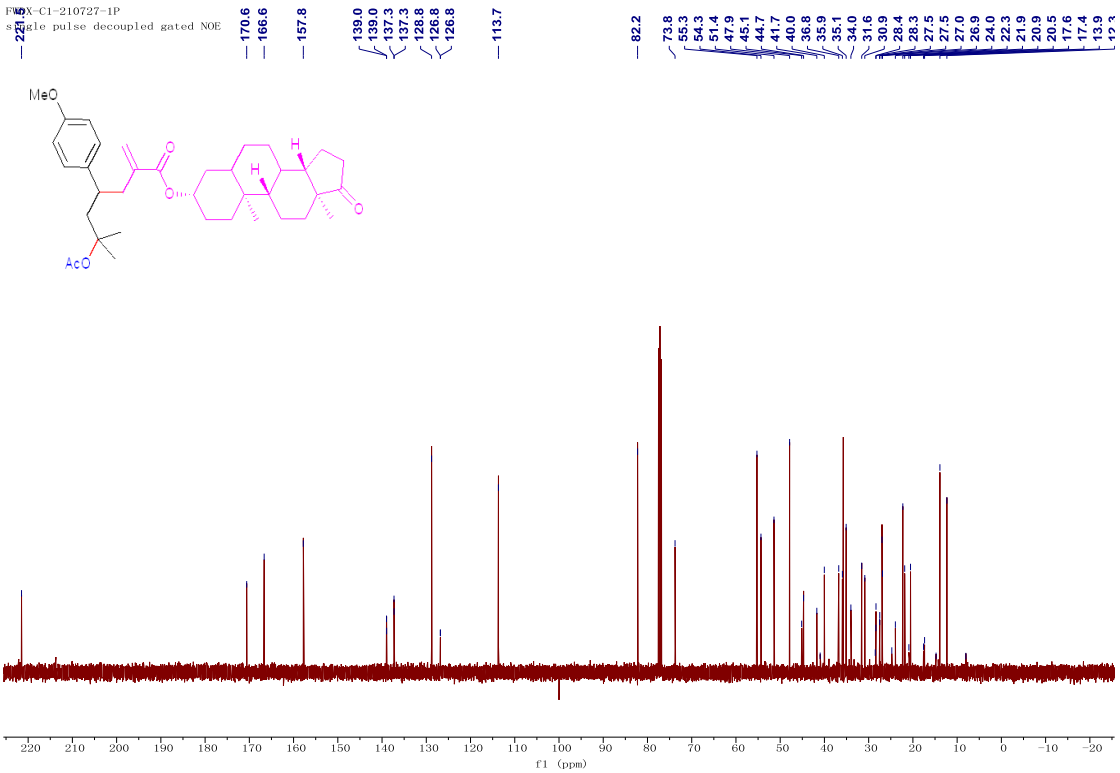
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4u**



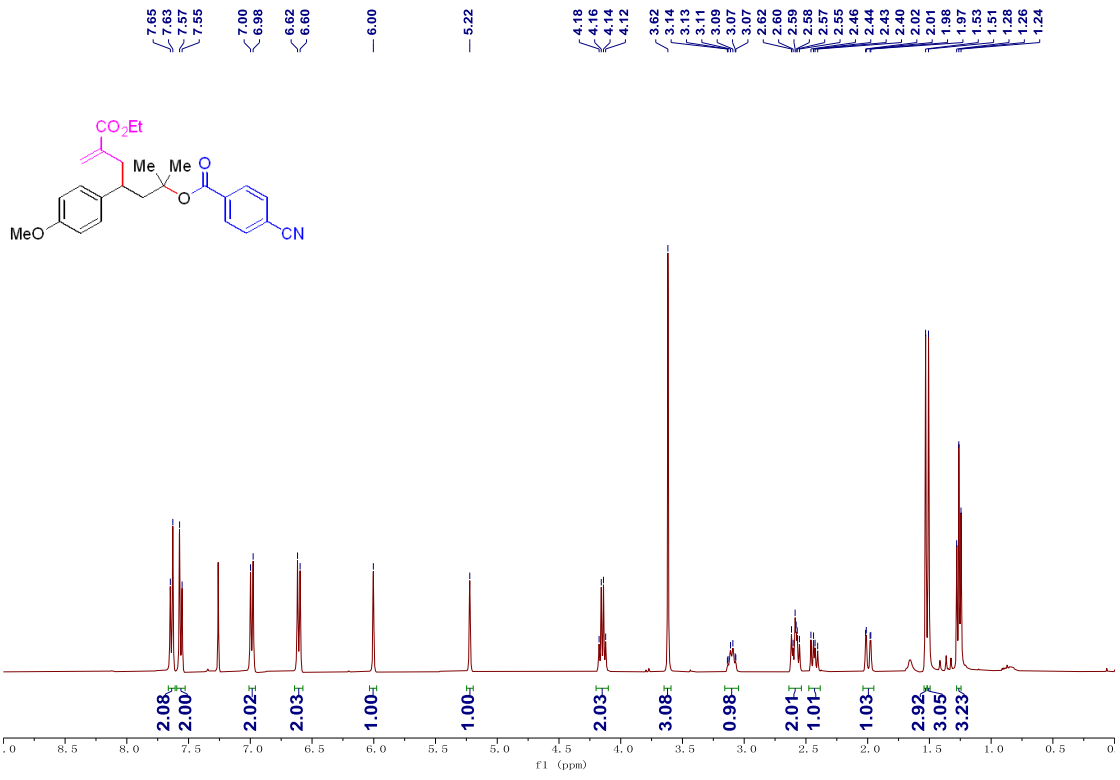
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4v**



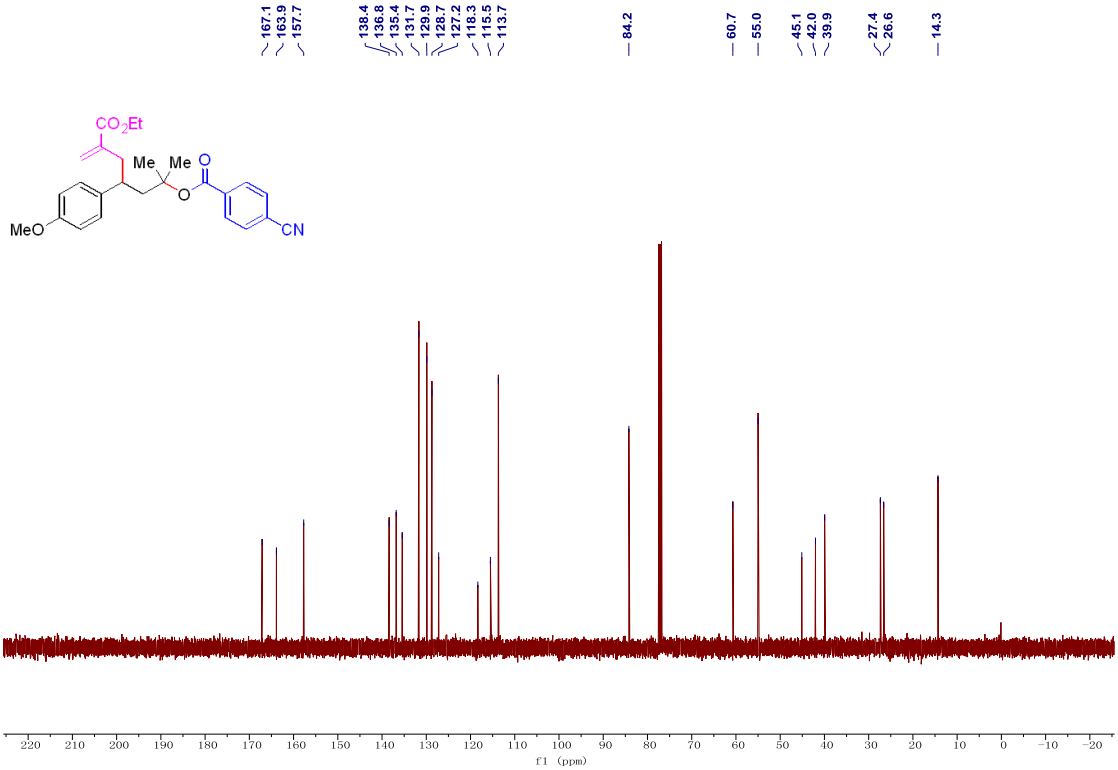
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4v**



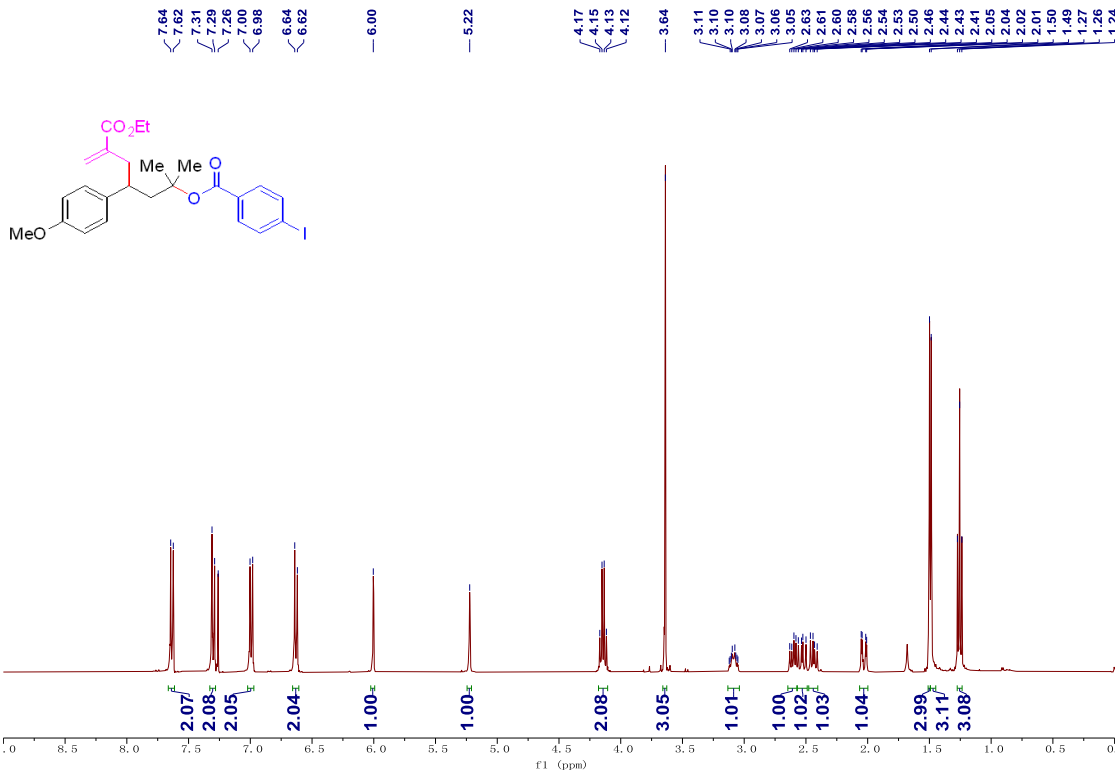
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4w**



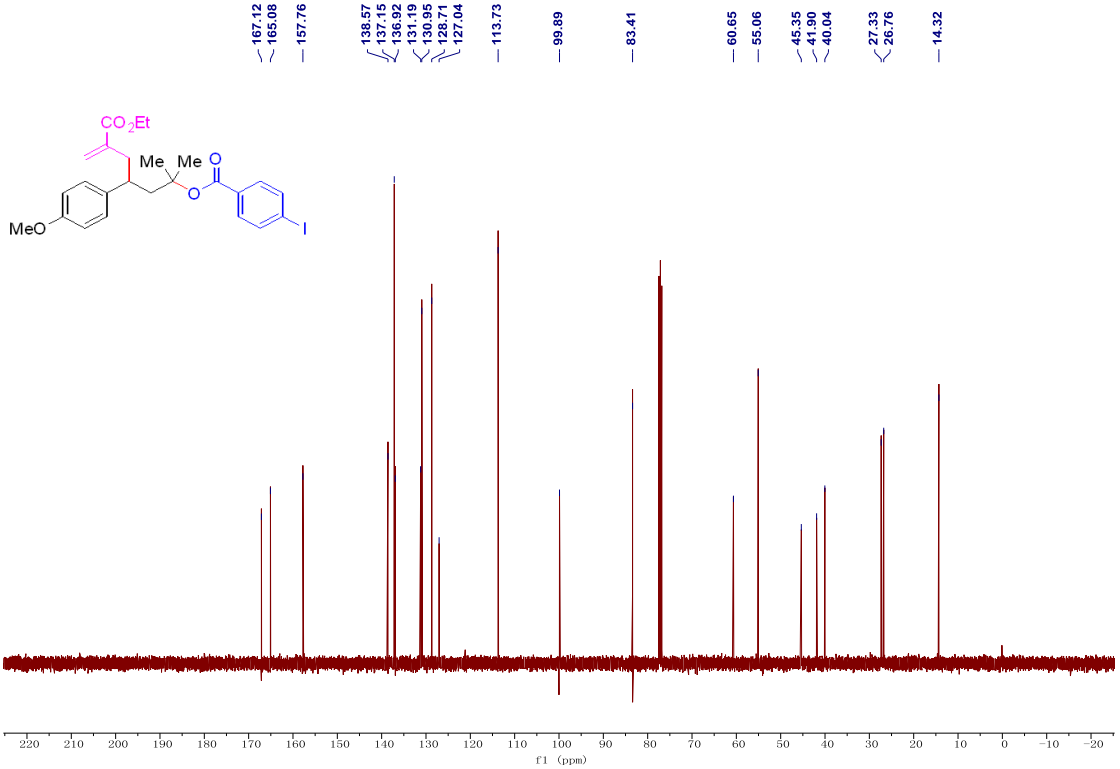
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4w**



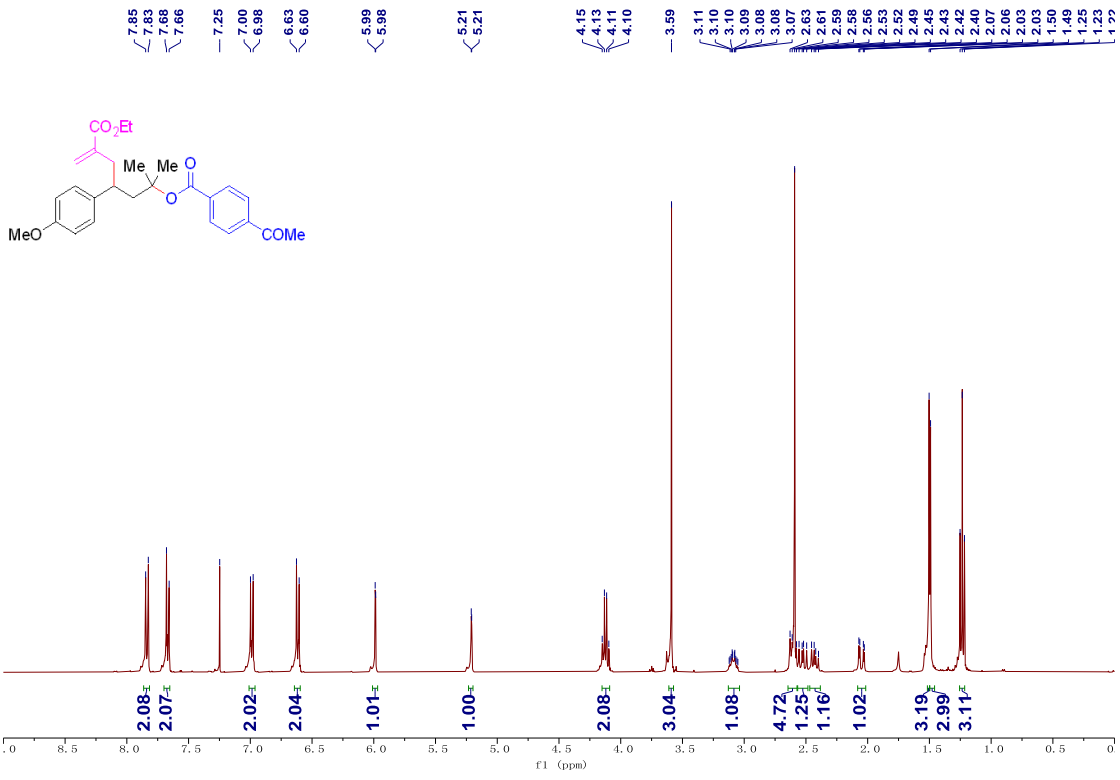
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aa**



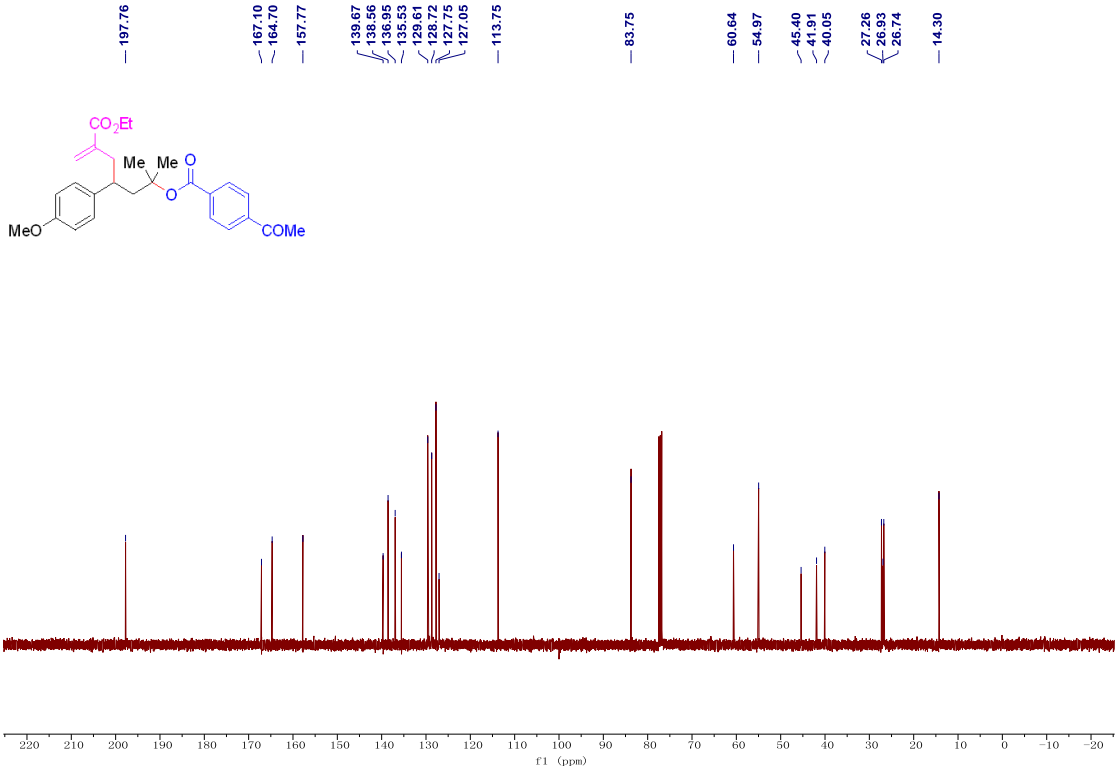
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4aa**



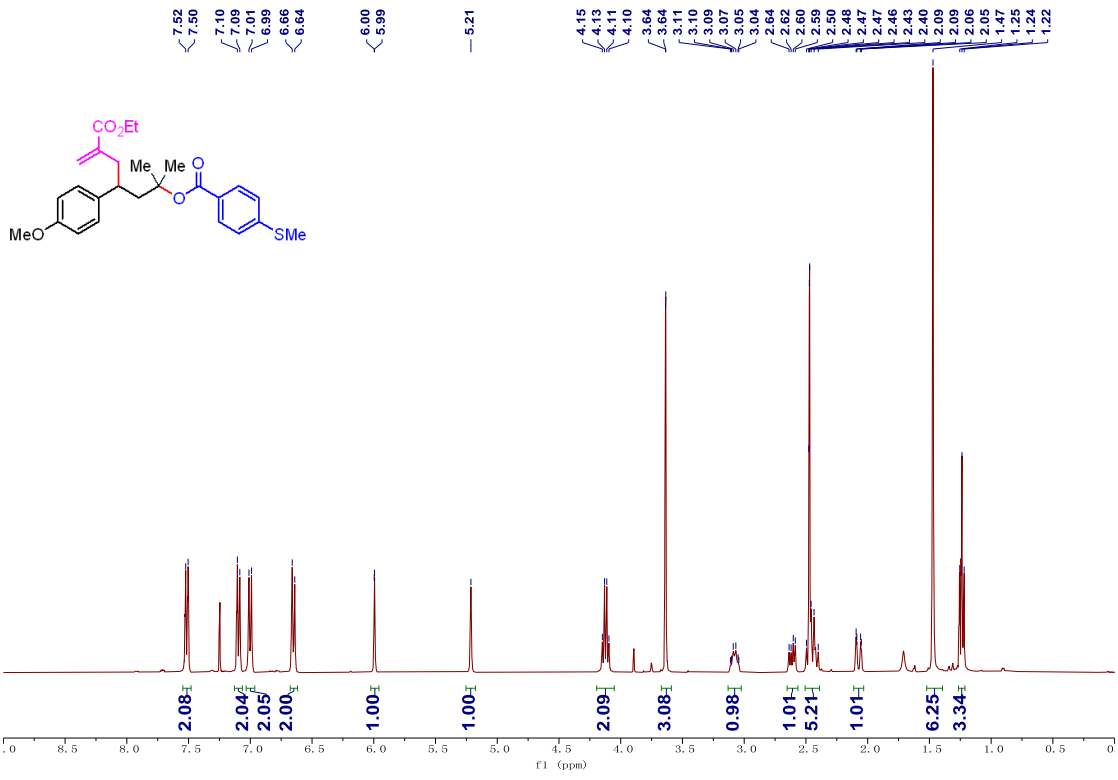
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ab**



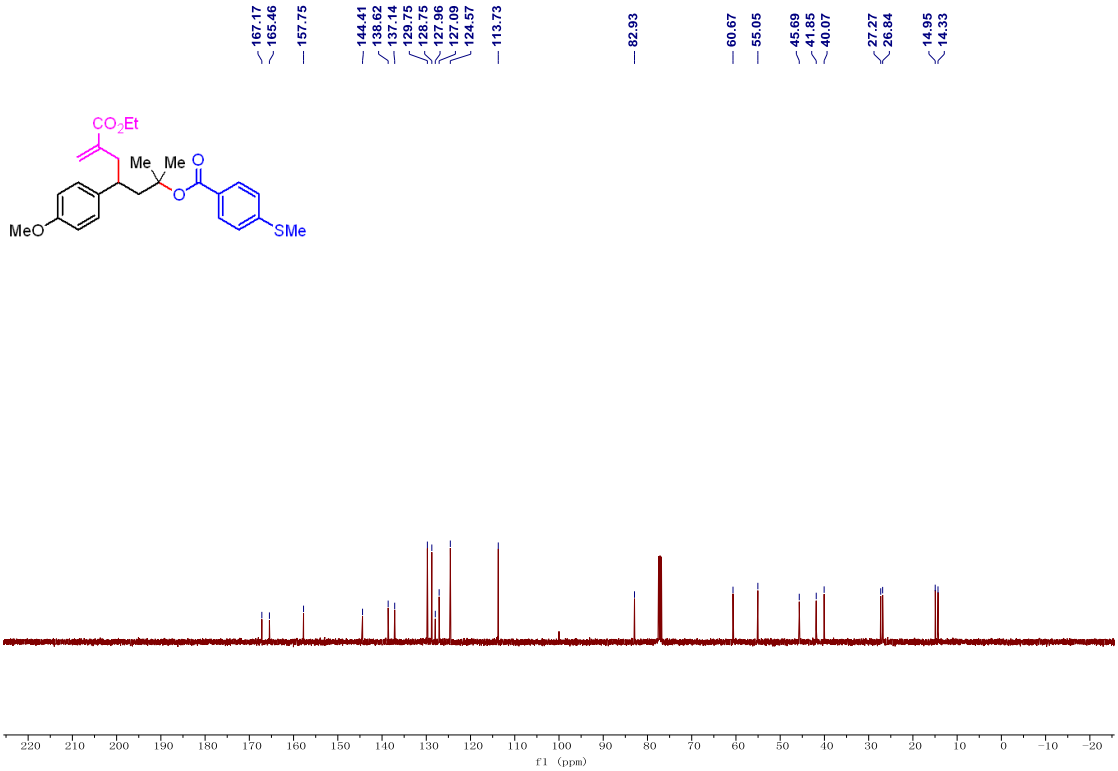
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ab**



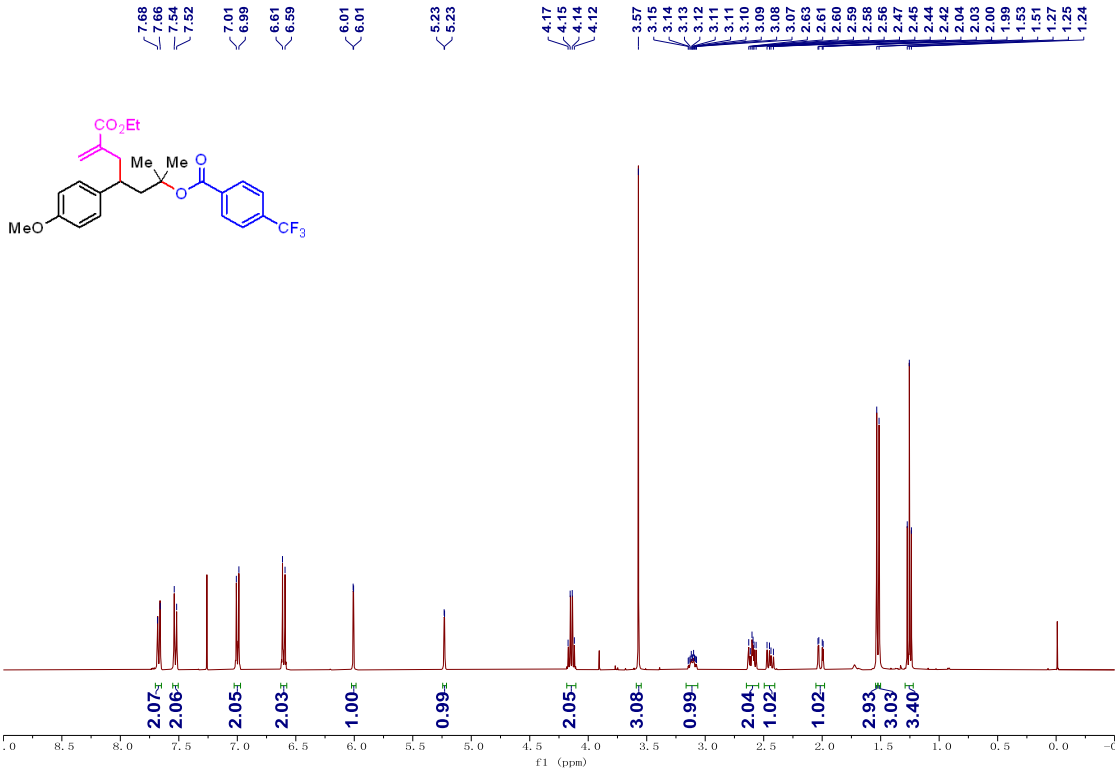
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ac**



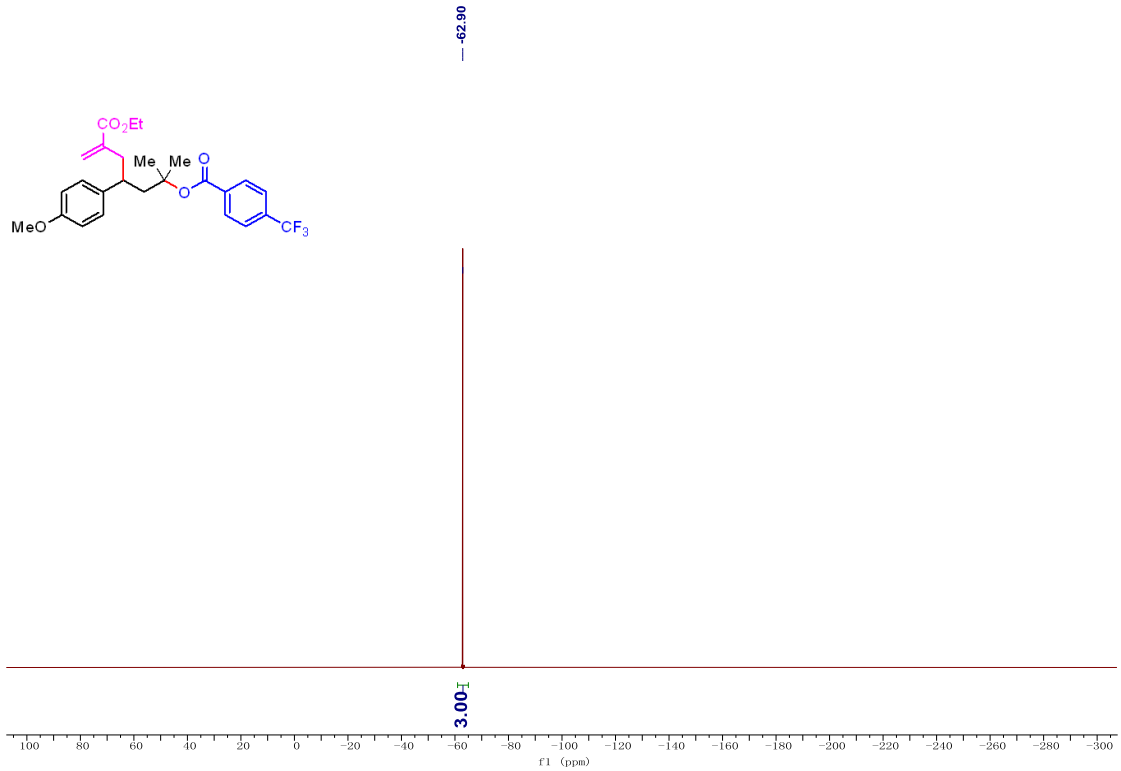
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ac**



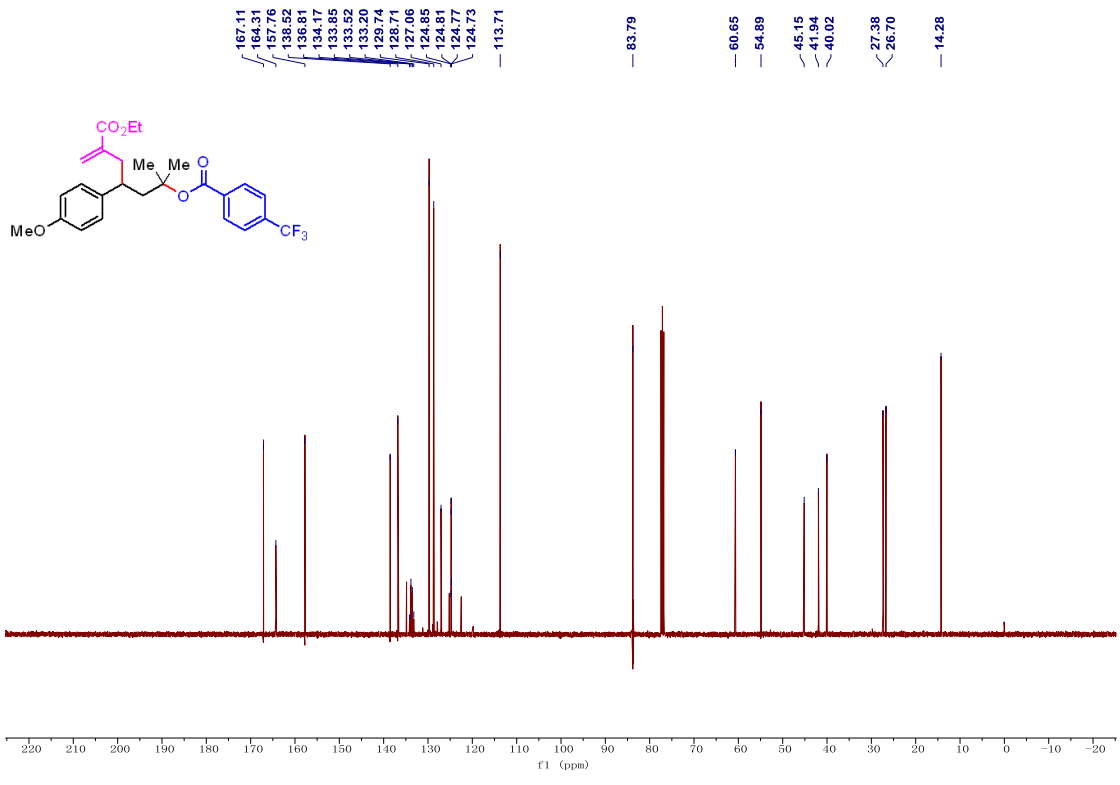
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ad**



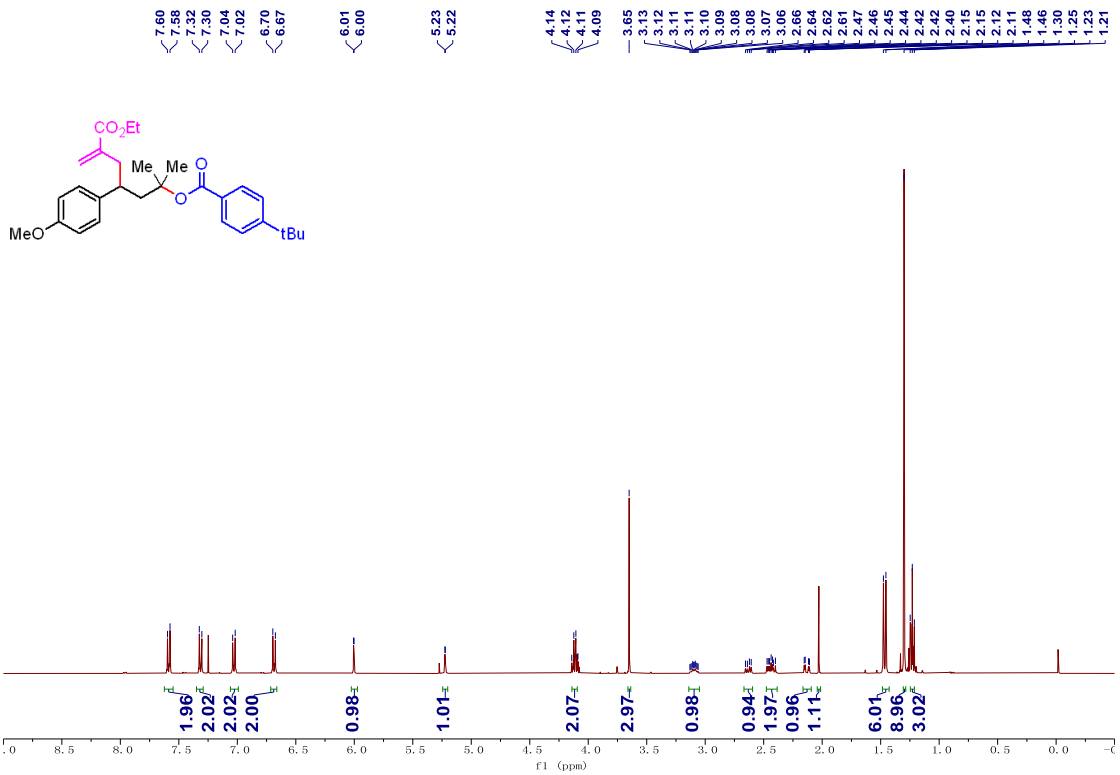
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4ad**



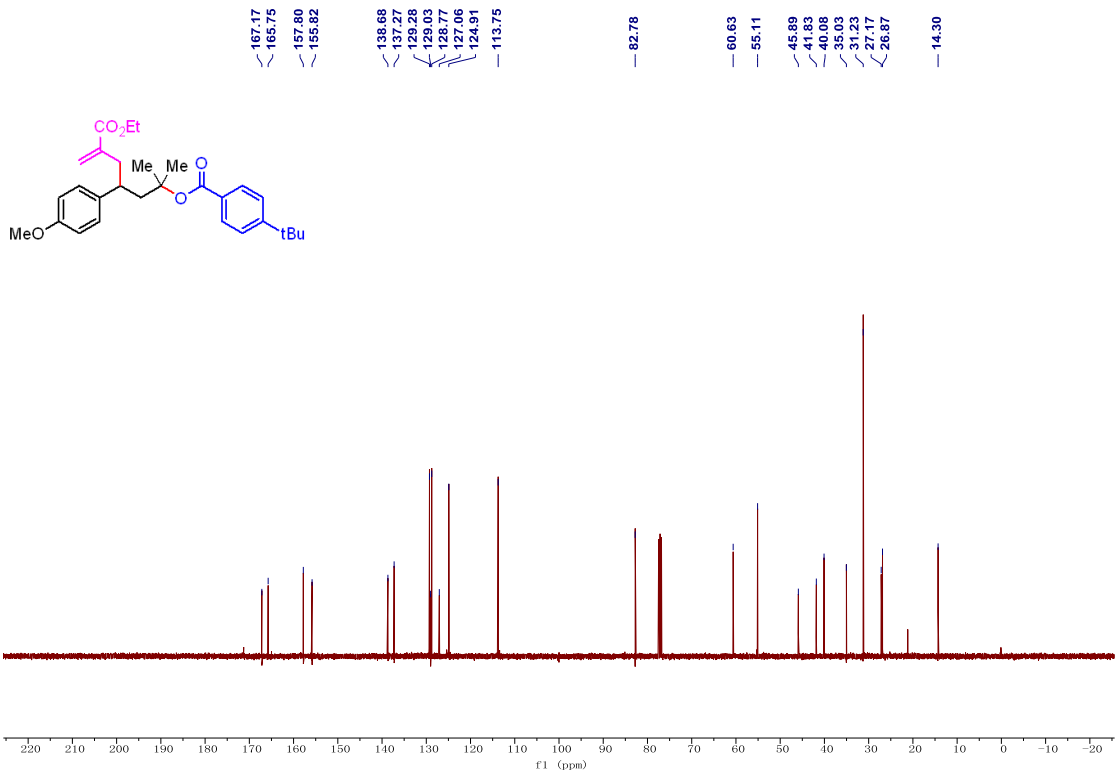
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ad**



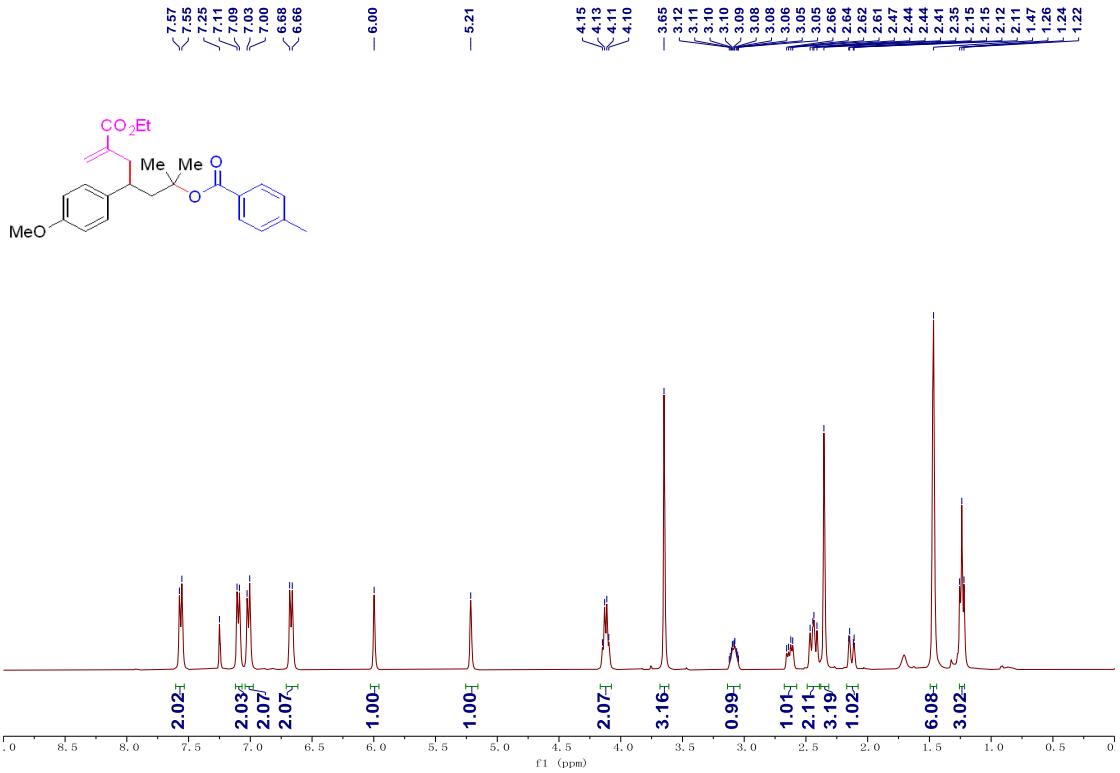
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ae**



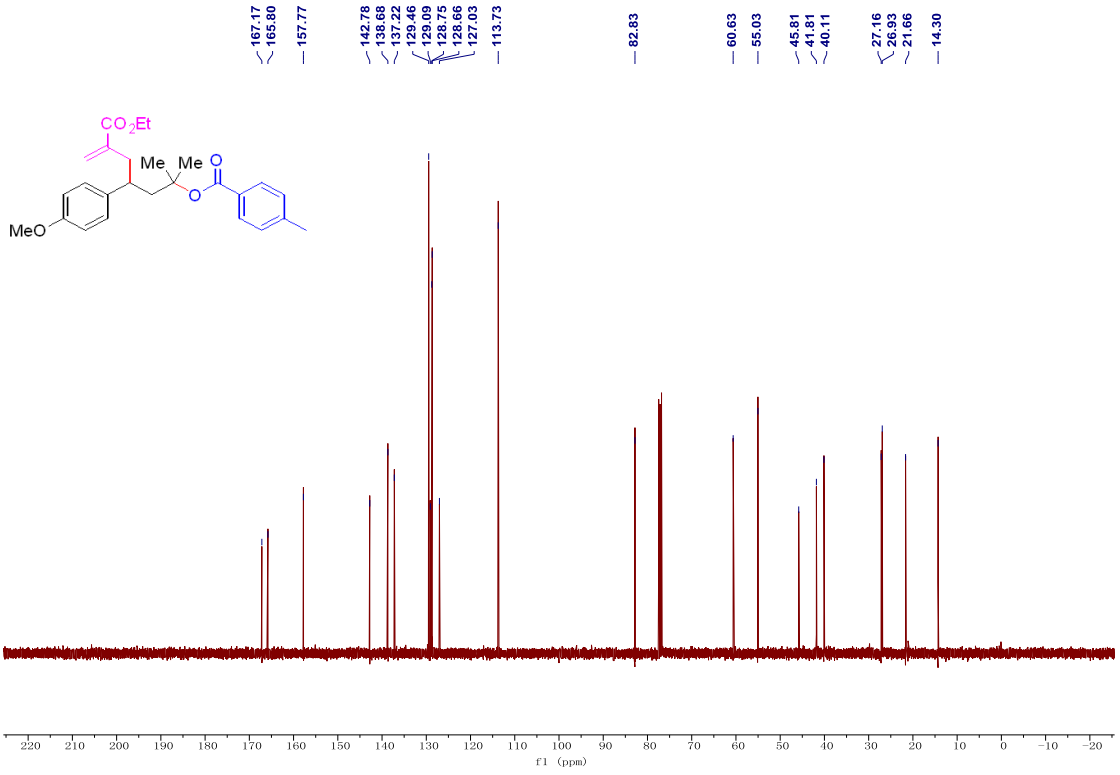
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ae**



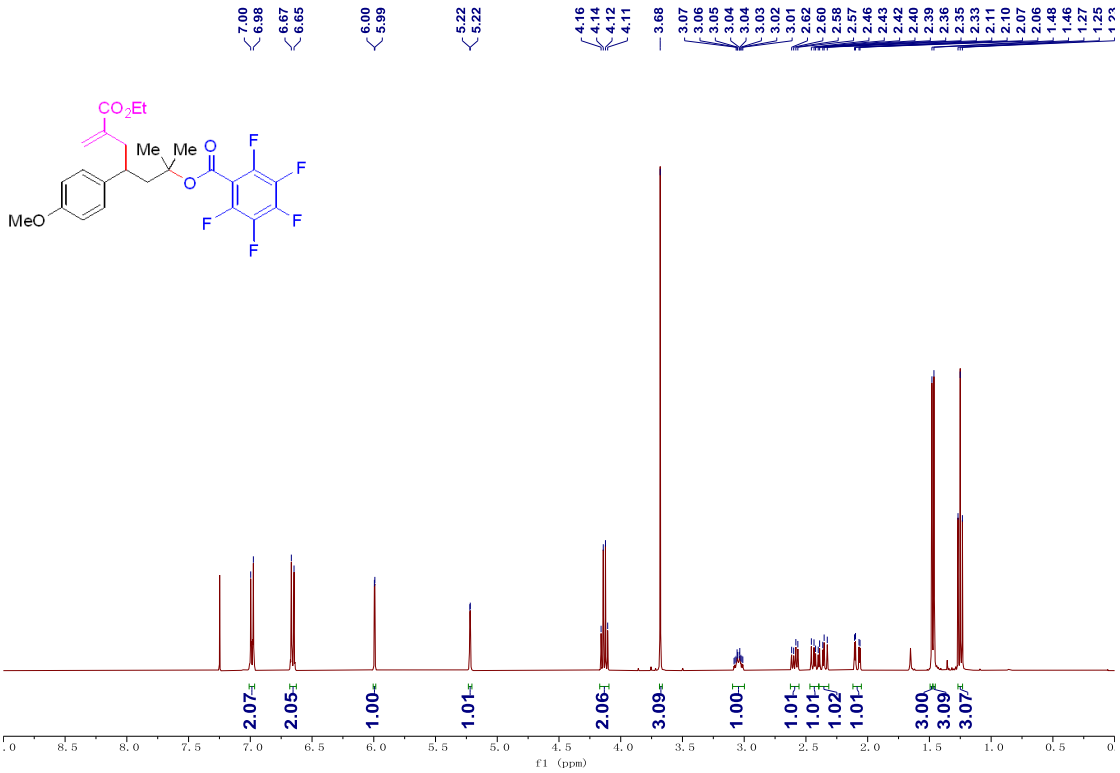
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4af**



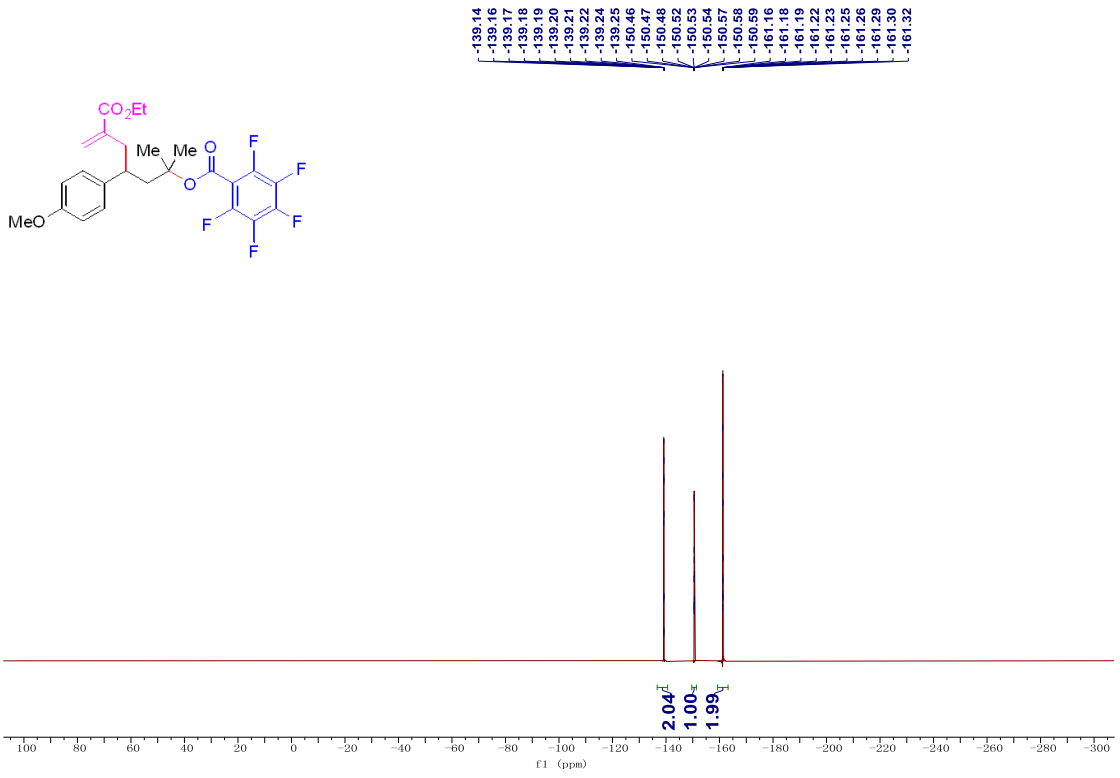
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4af**



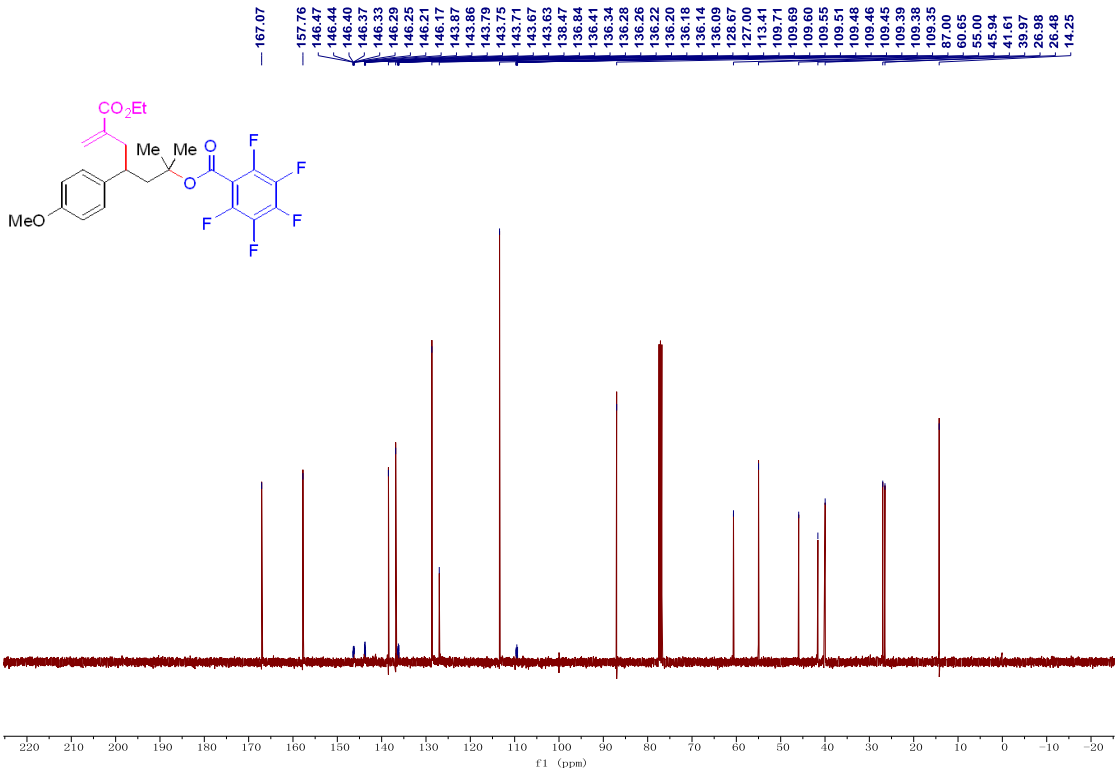
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ag**



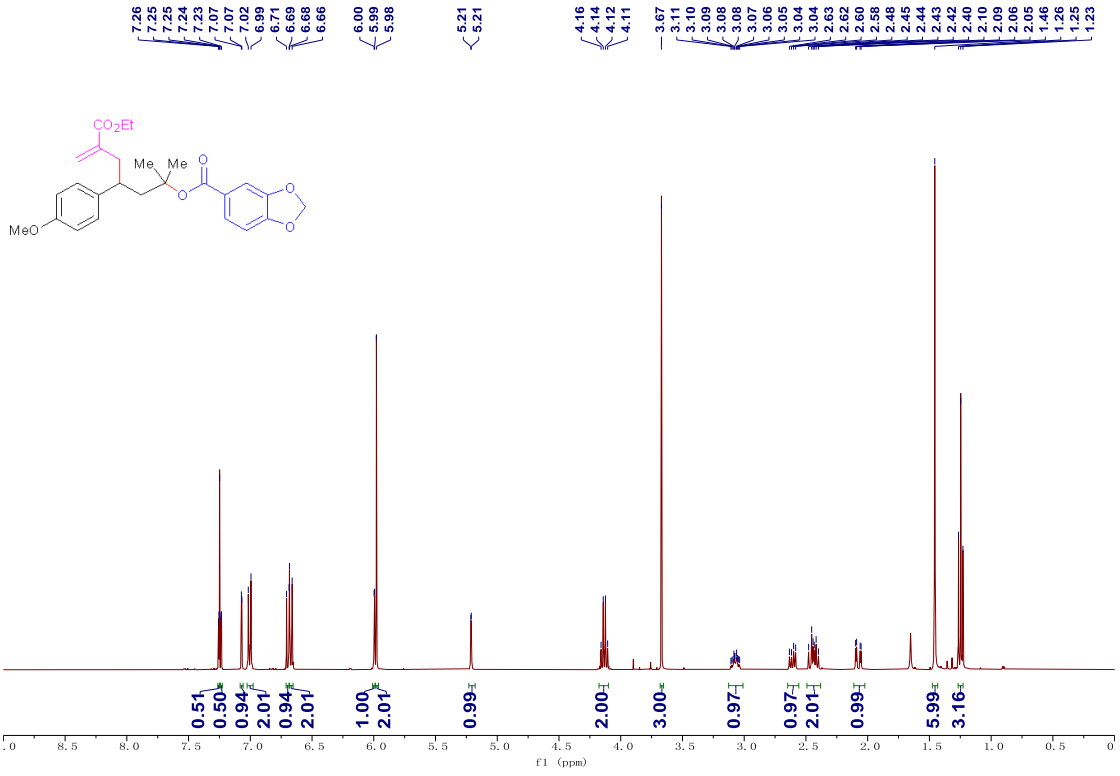
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4ag**



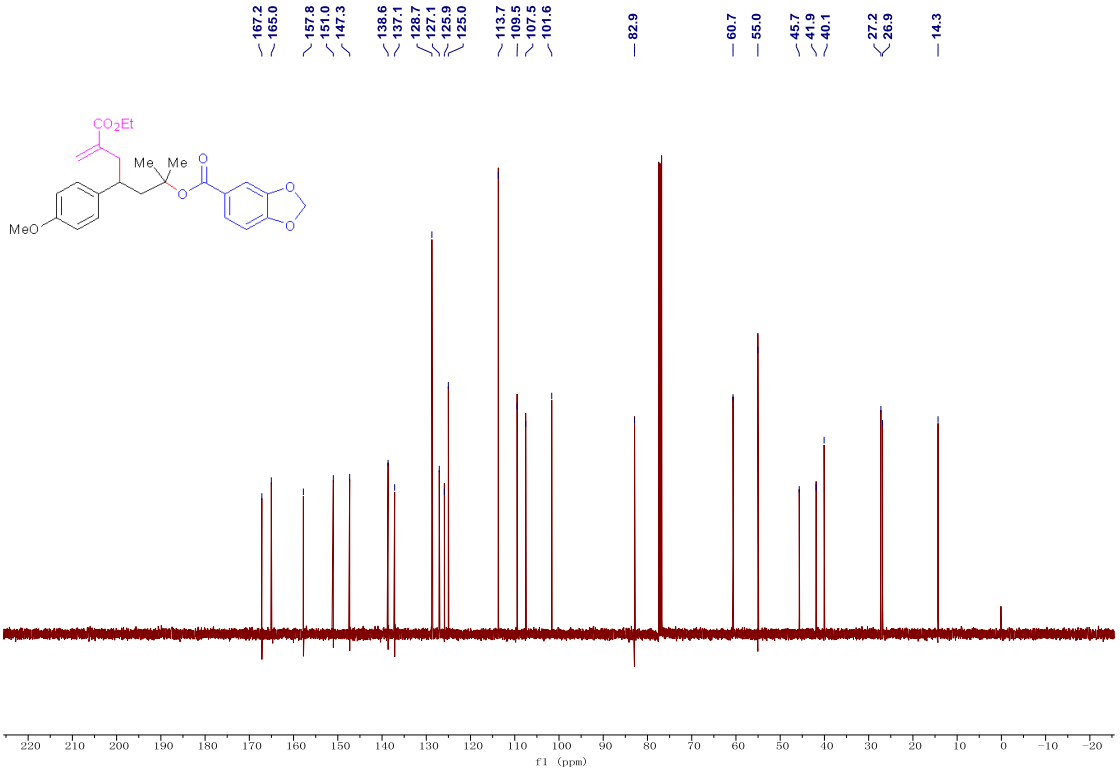
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ag**



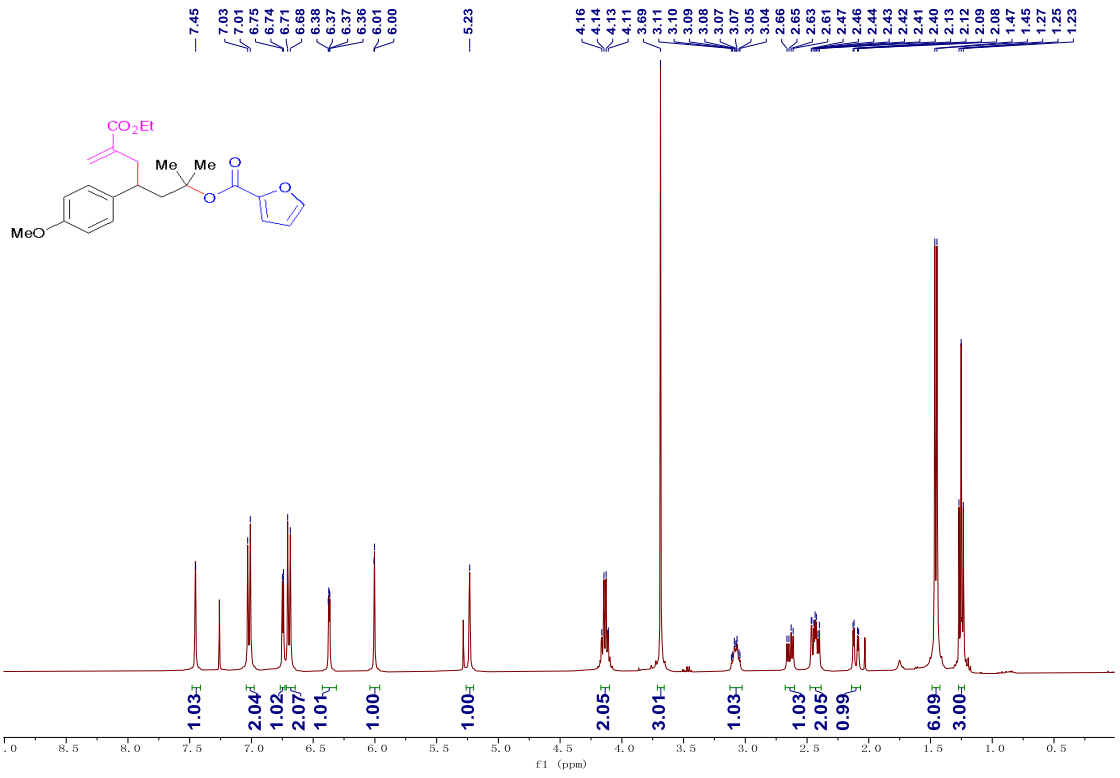
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ah**



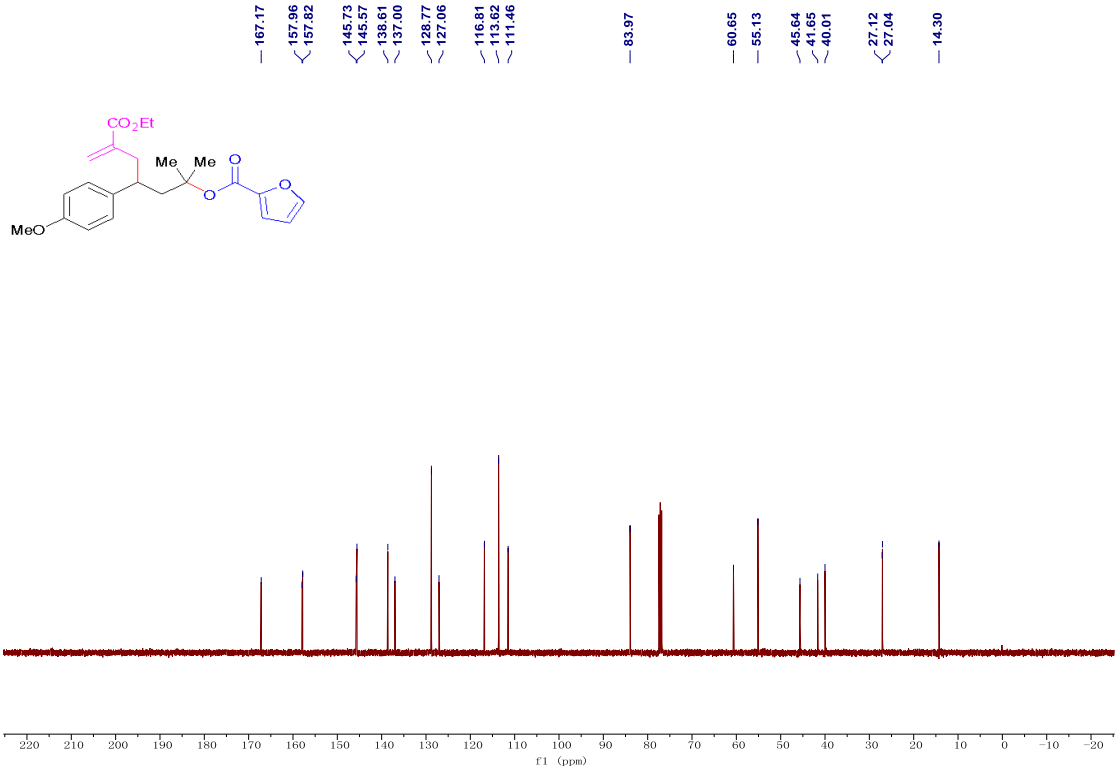
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ah**



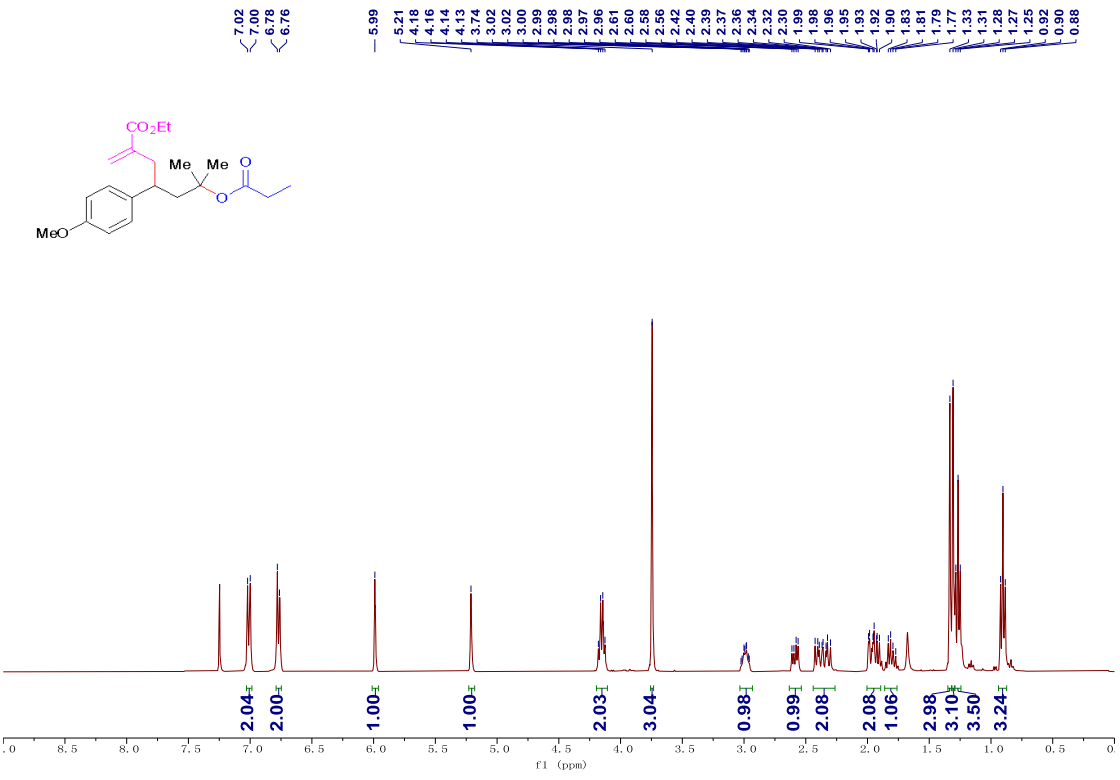
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ai**



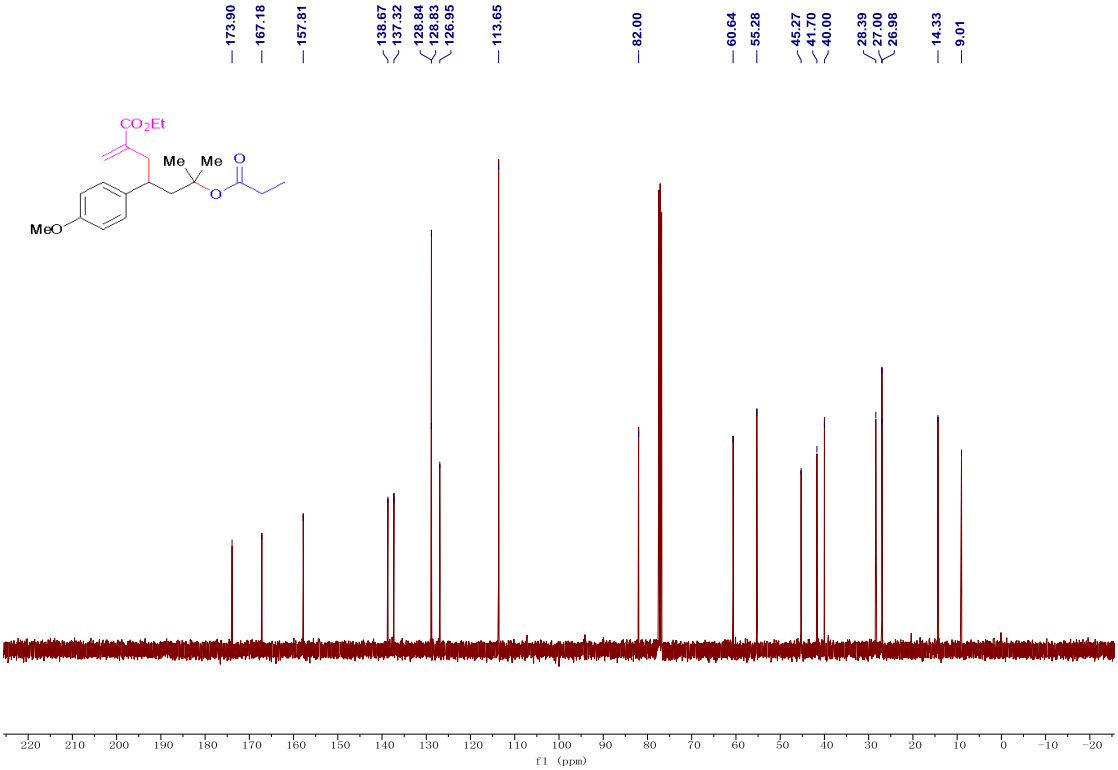
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ai**



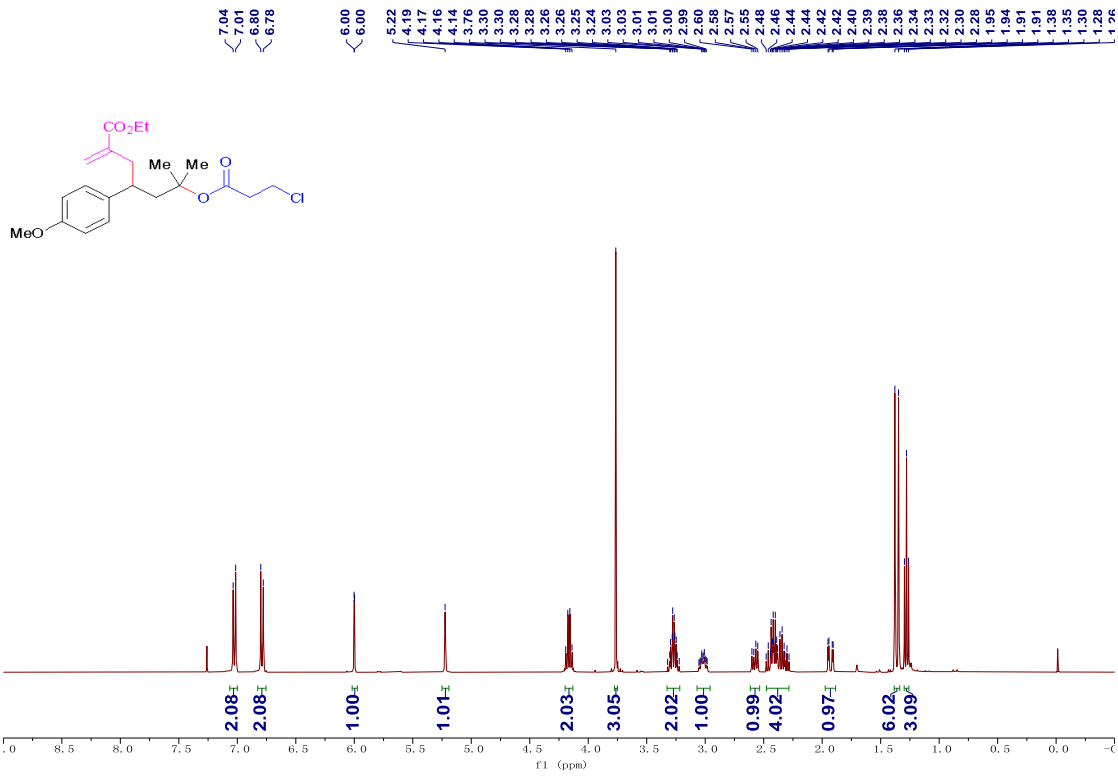
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aj**



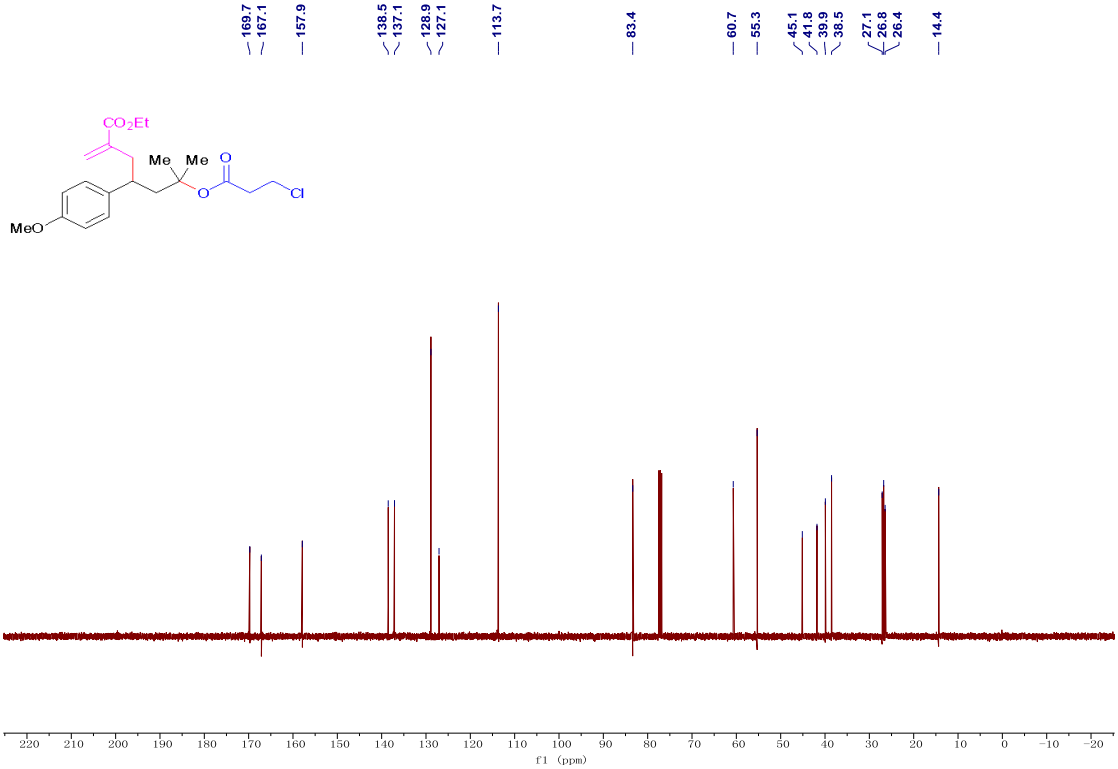
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4aj**



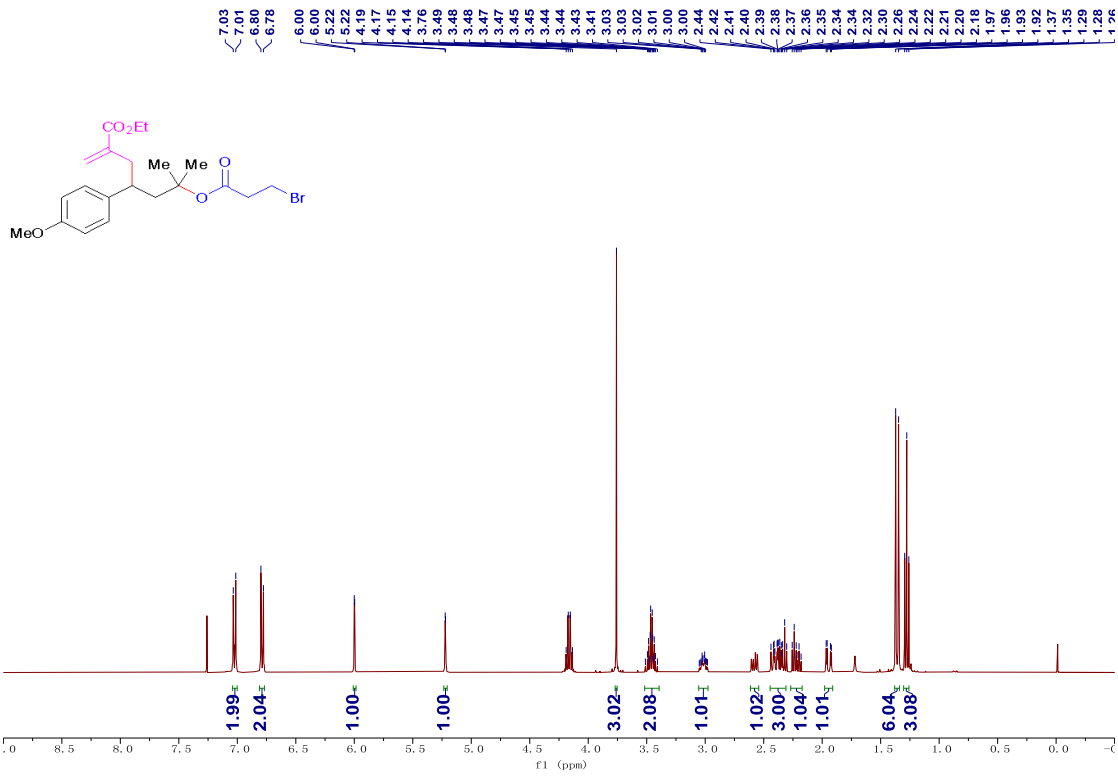
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ak**



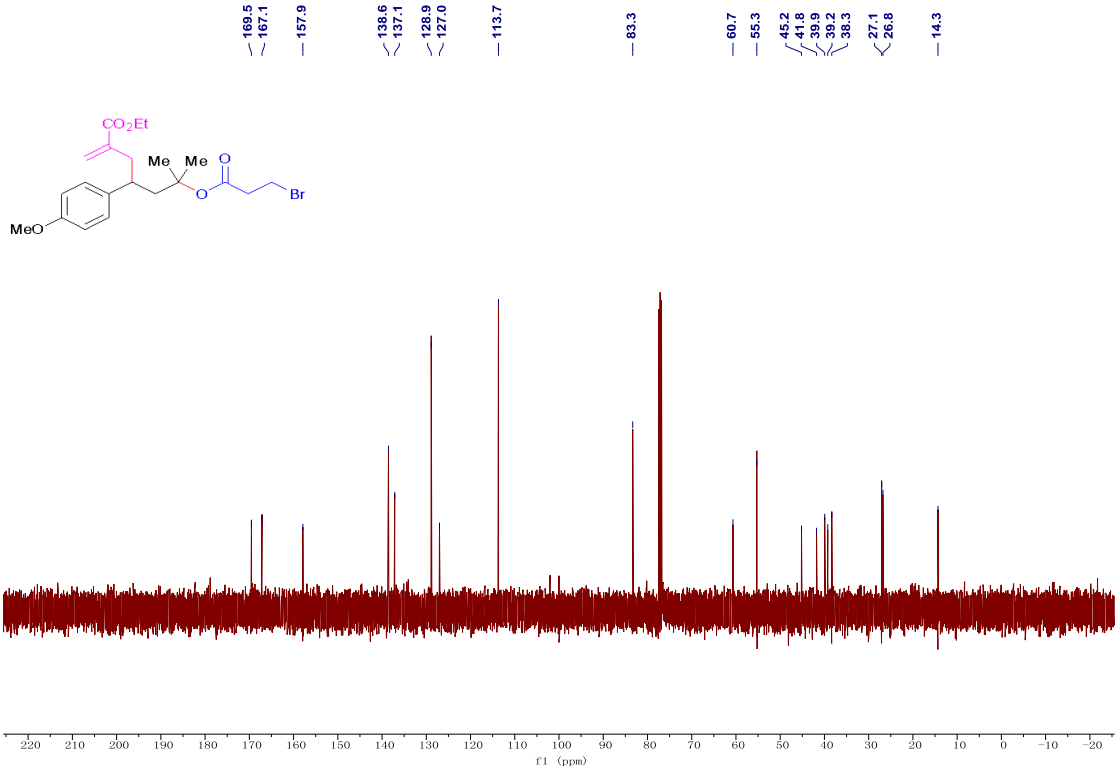
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ak**



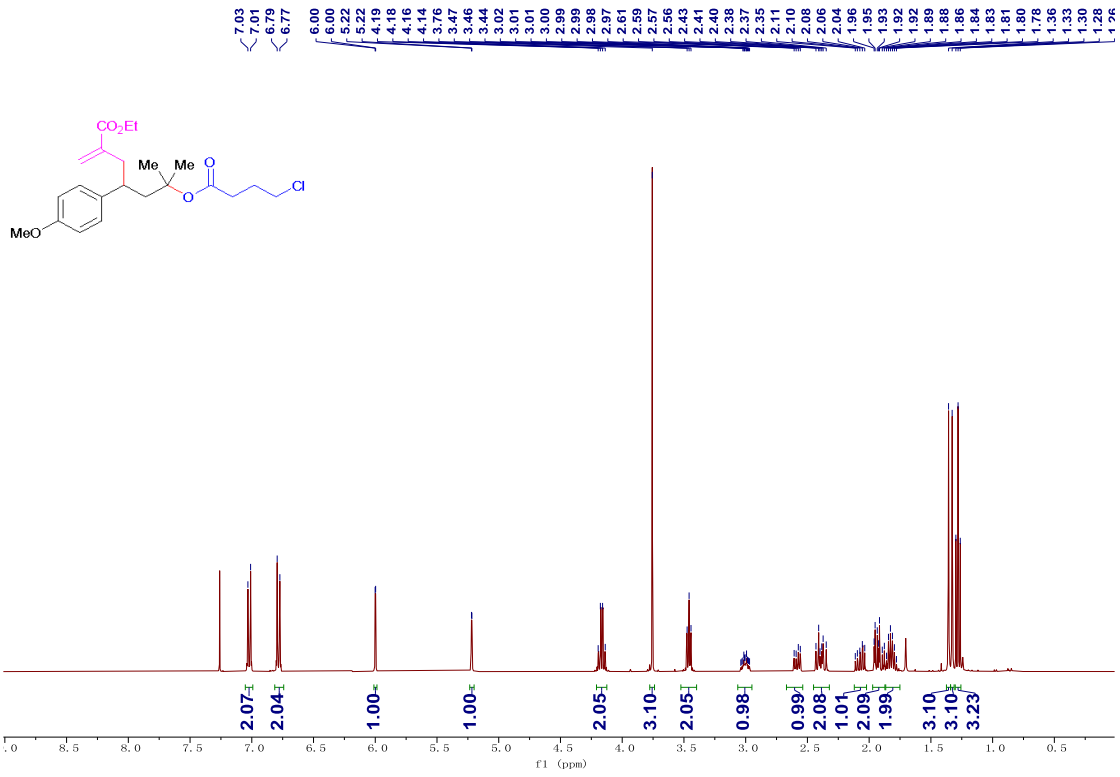
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4al**



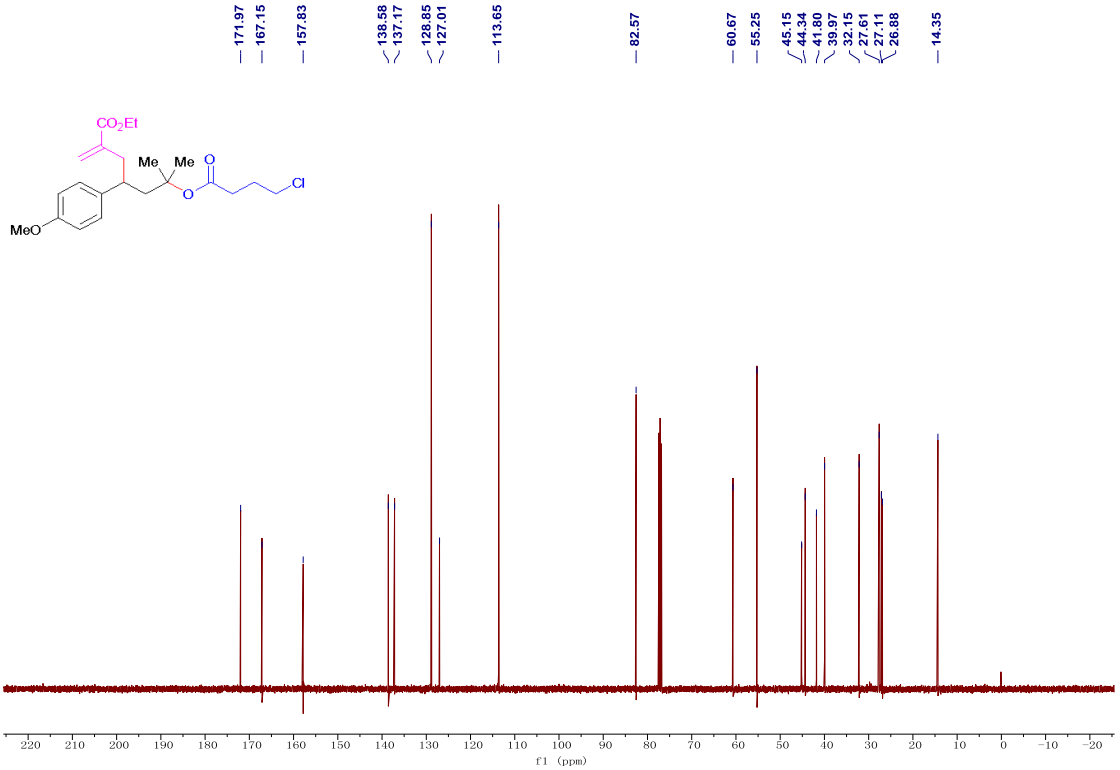
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4al**



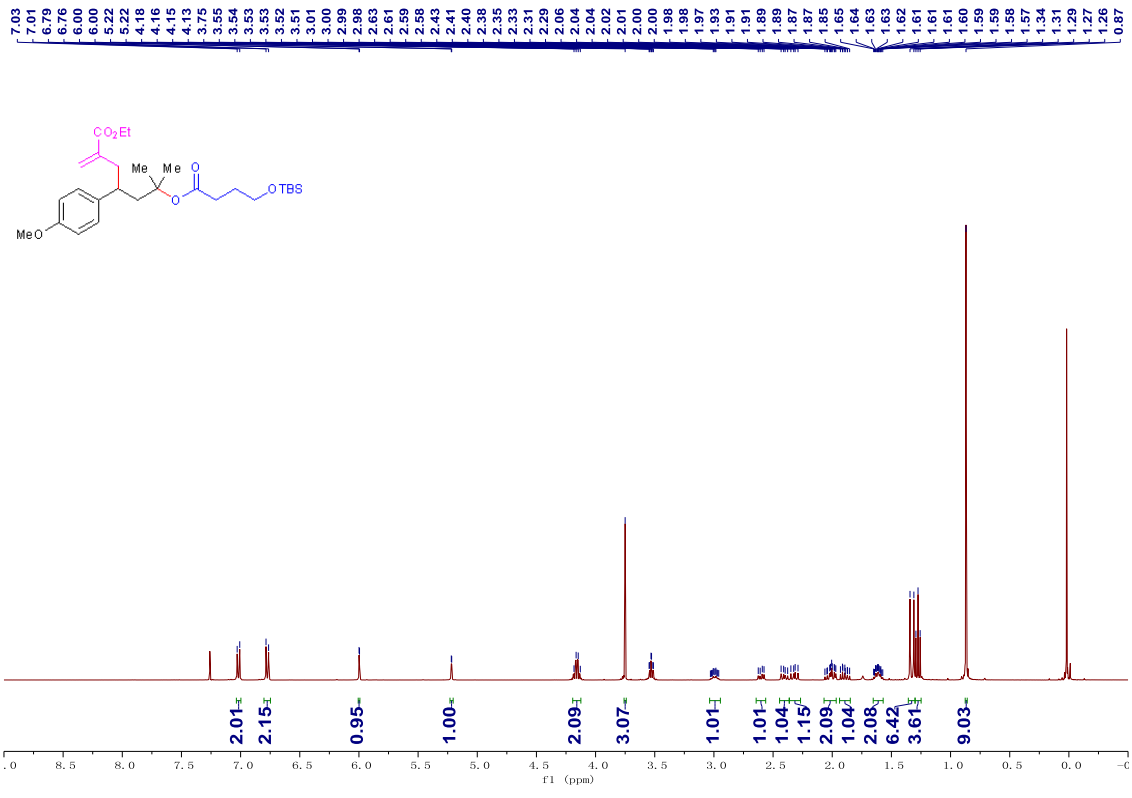
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4am**



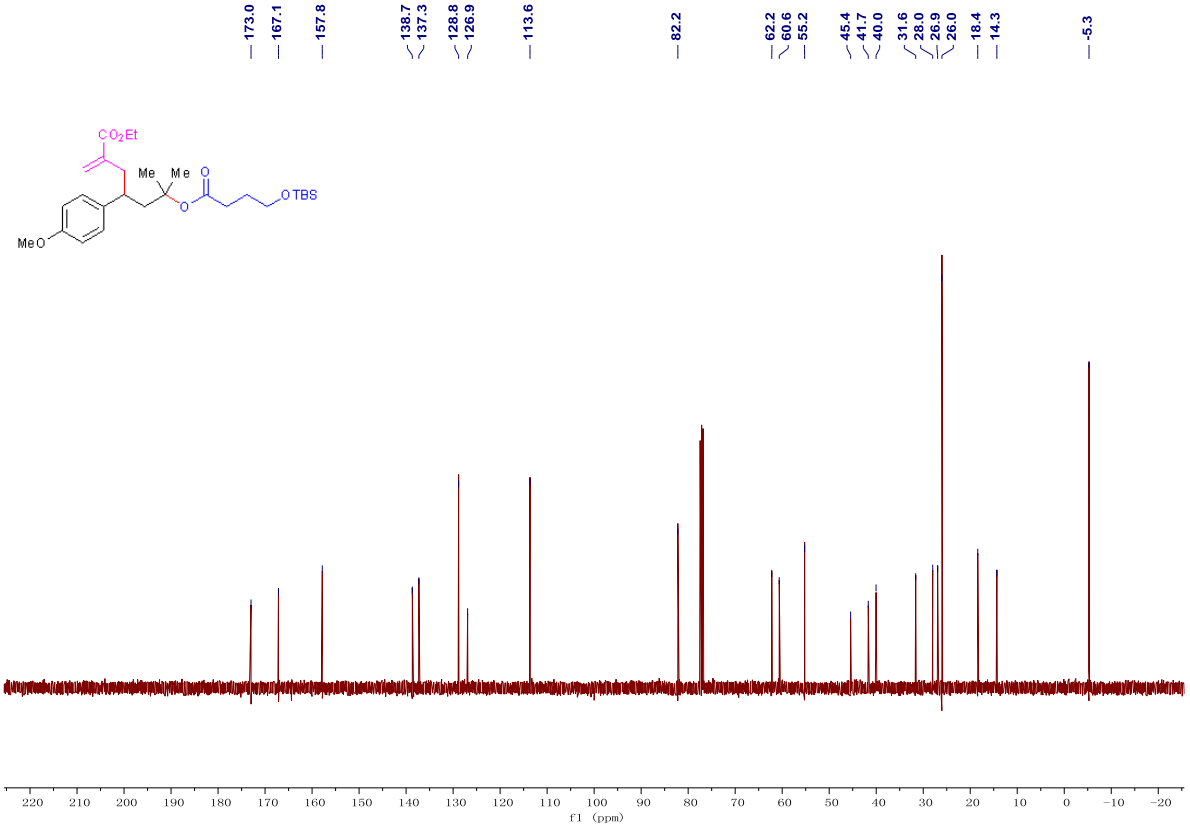
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4am**



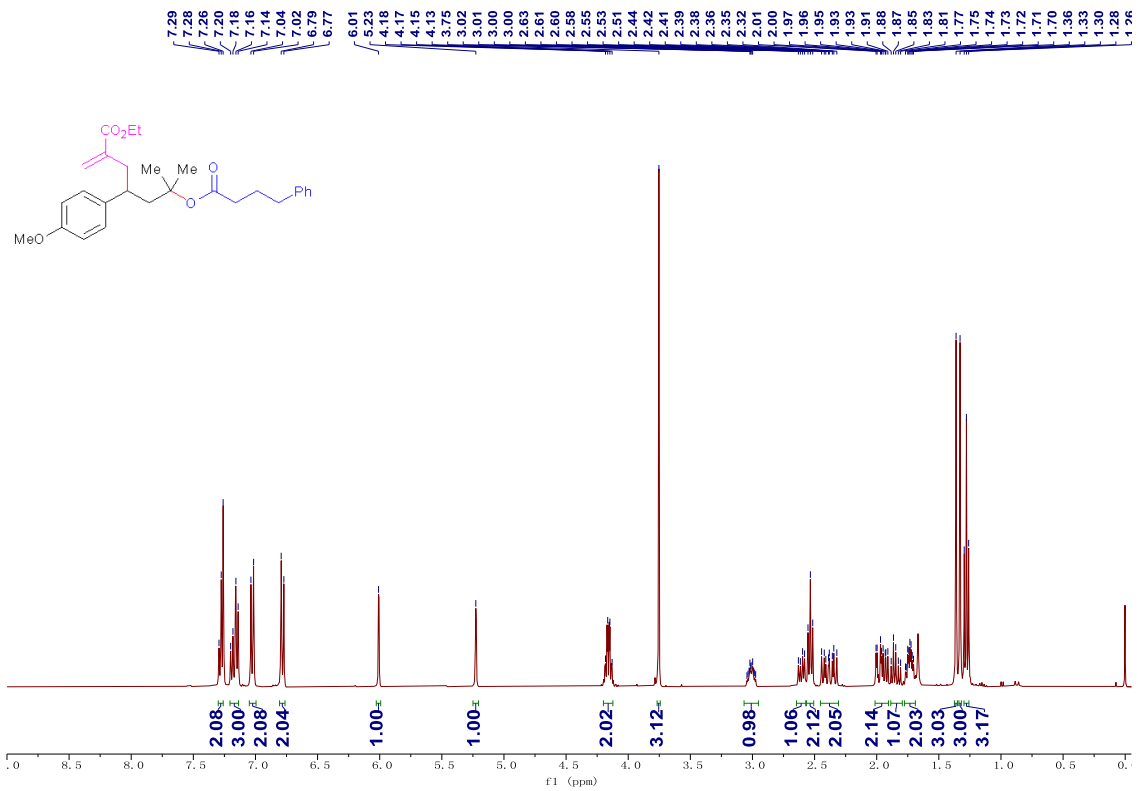
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4an**



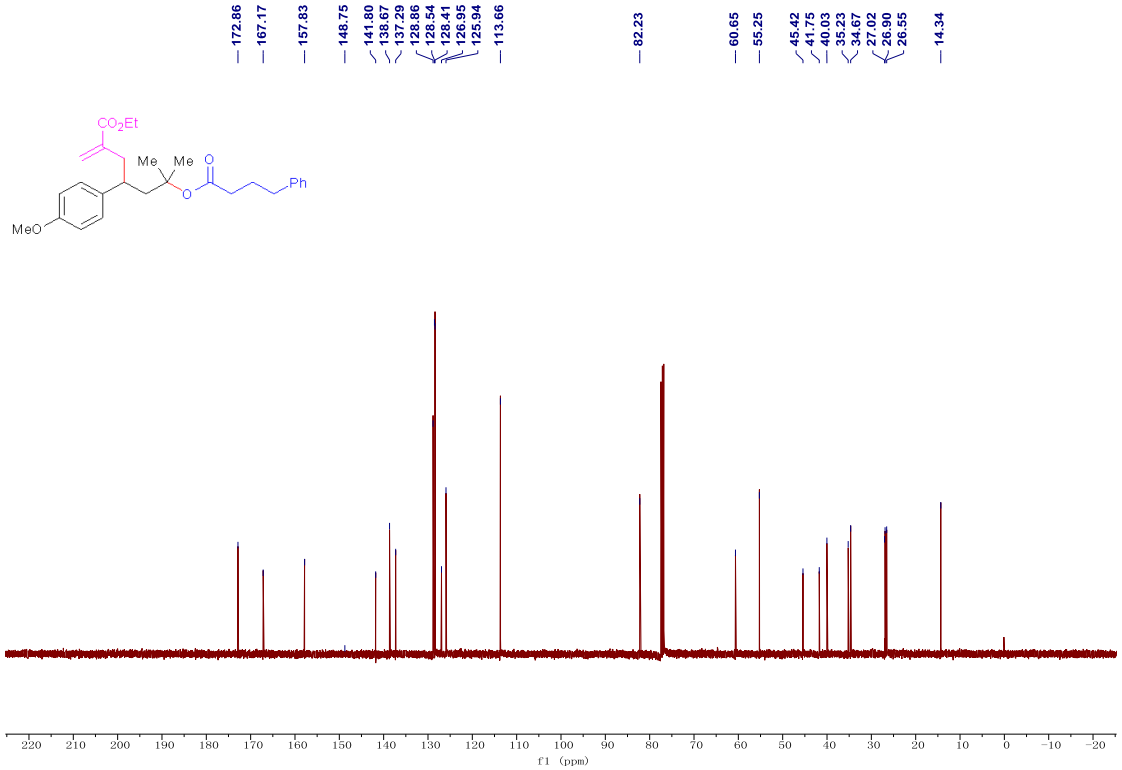
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4an**



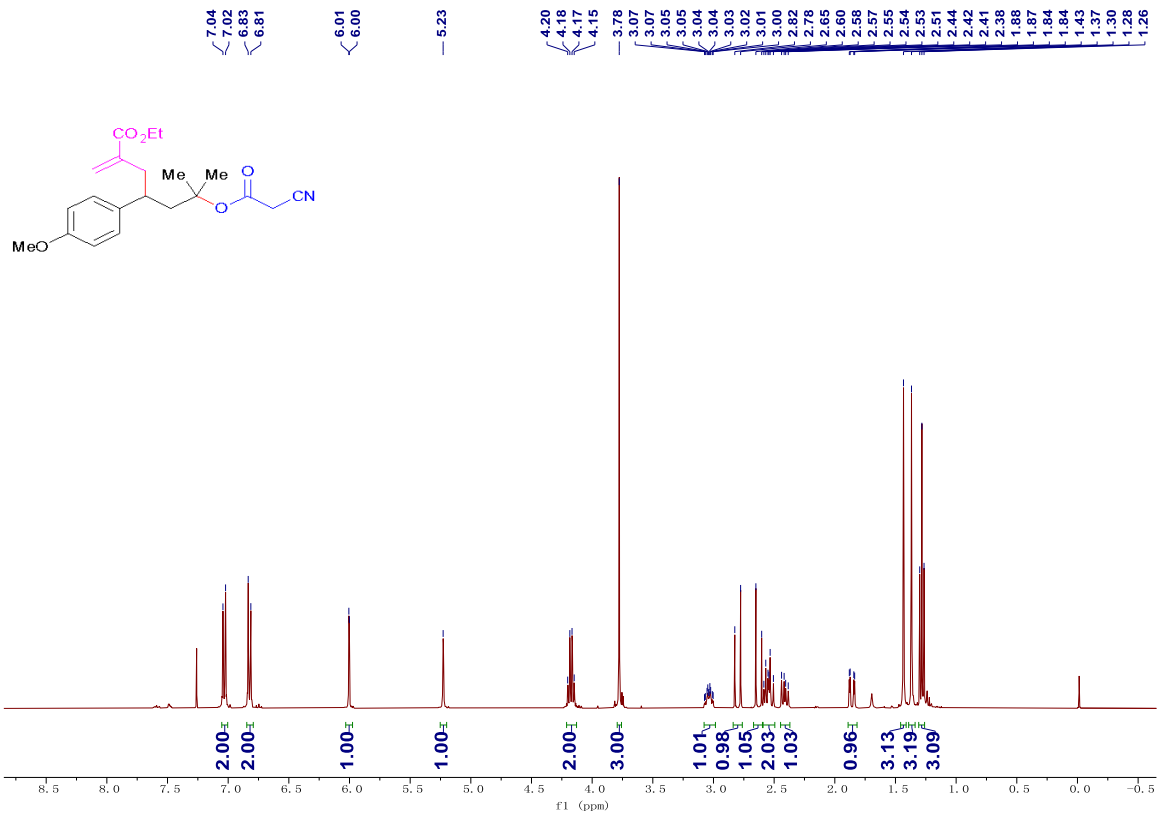
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ao**



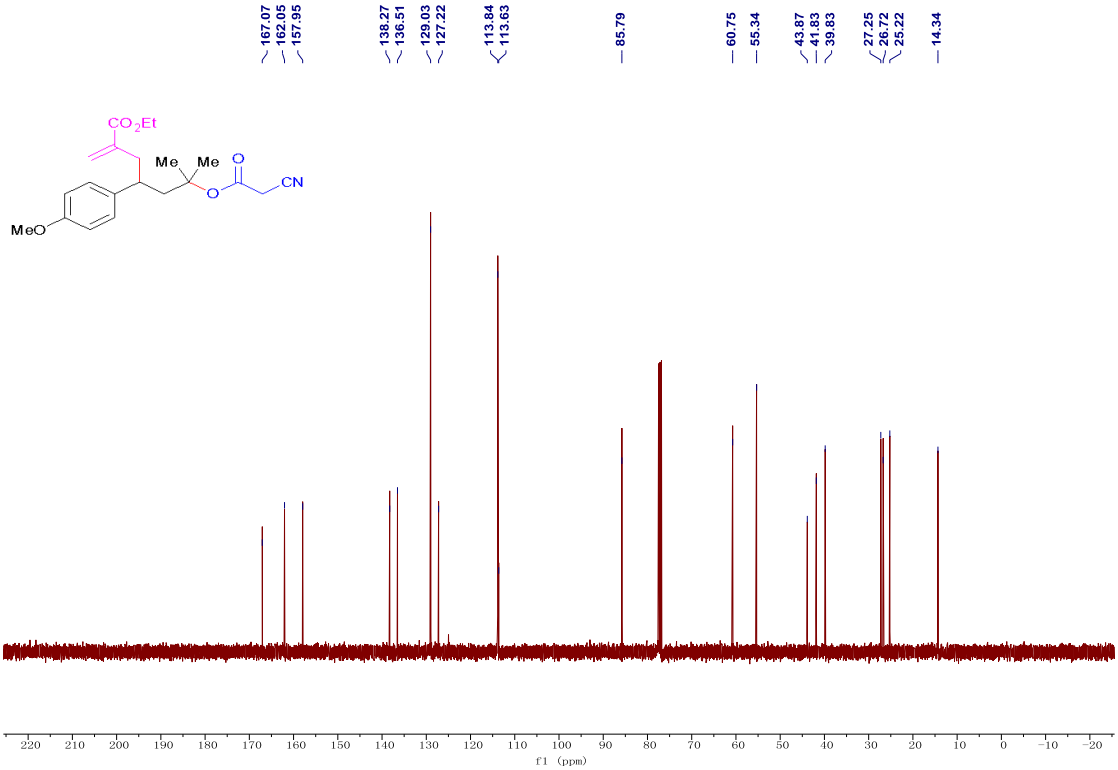
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ao**



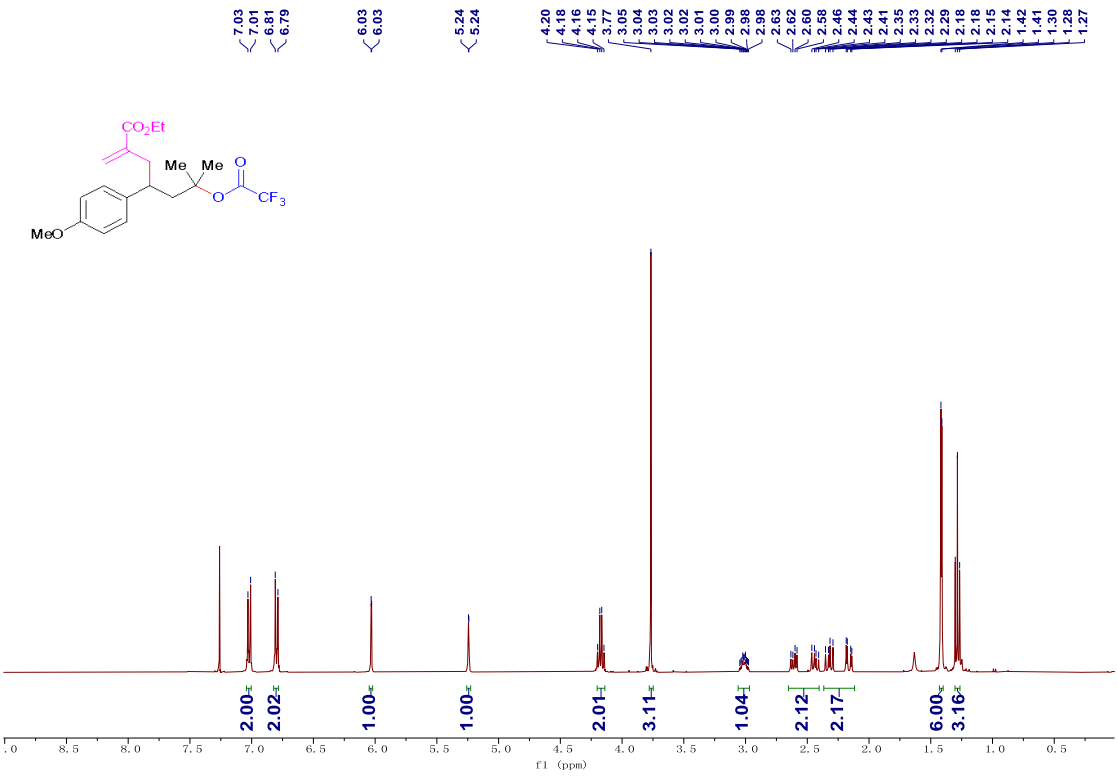
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ap**



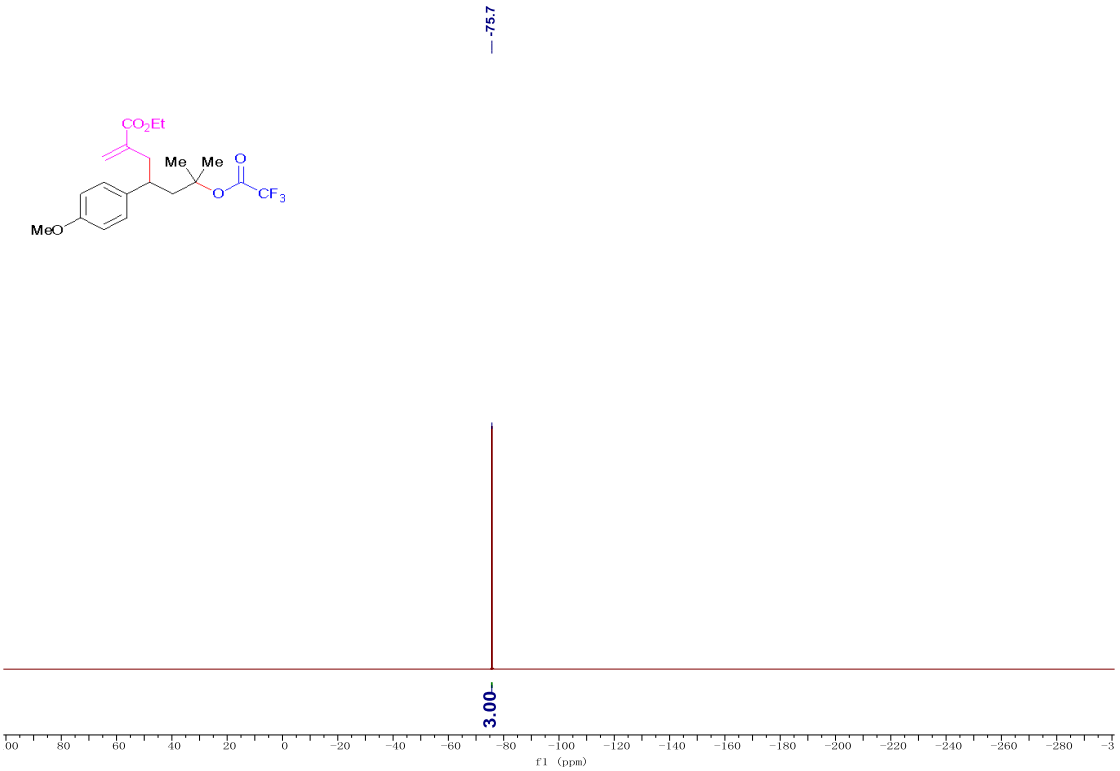
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ap**



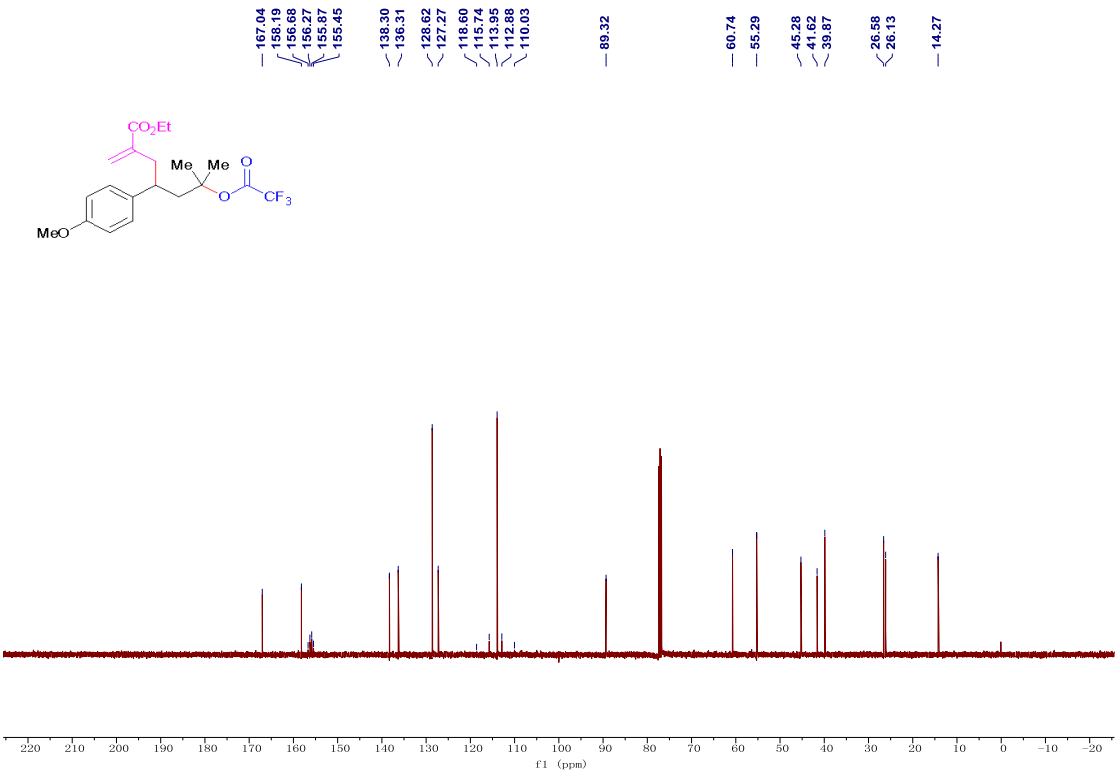
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aq**



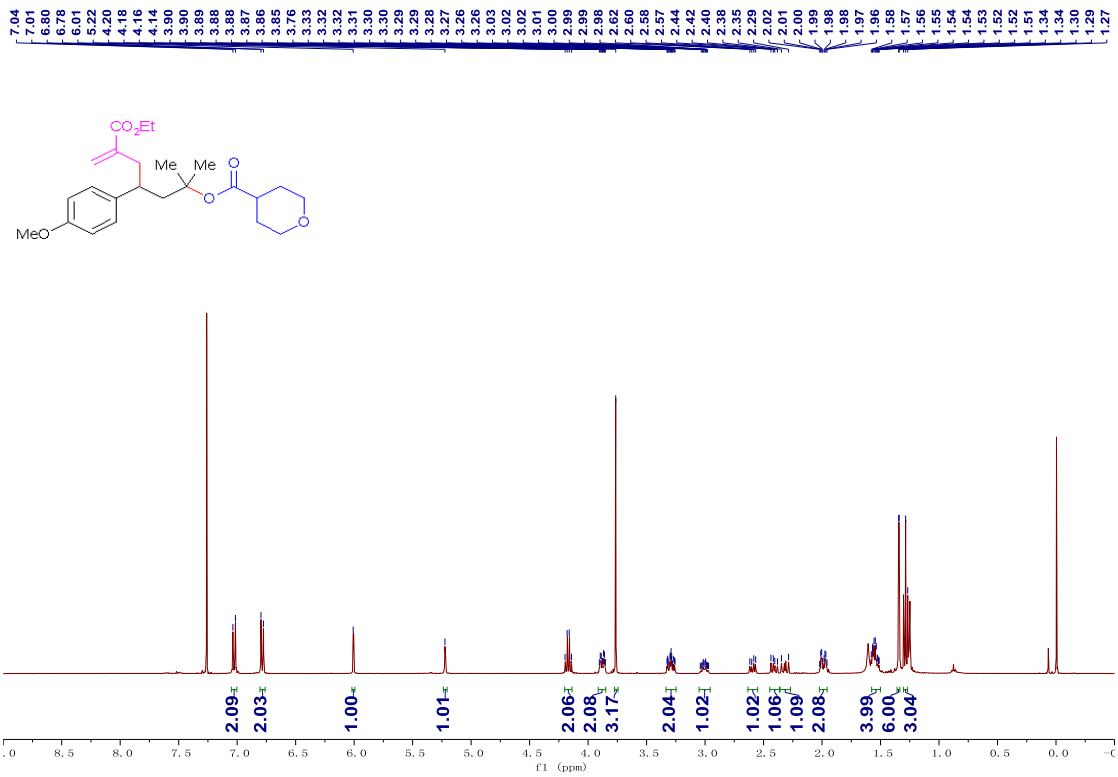
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4aq**



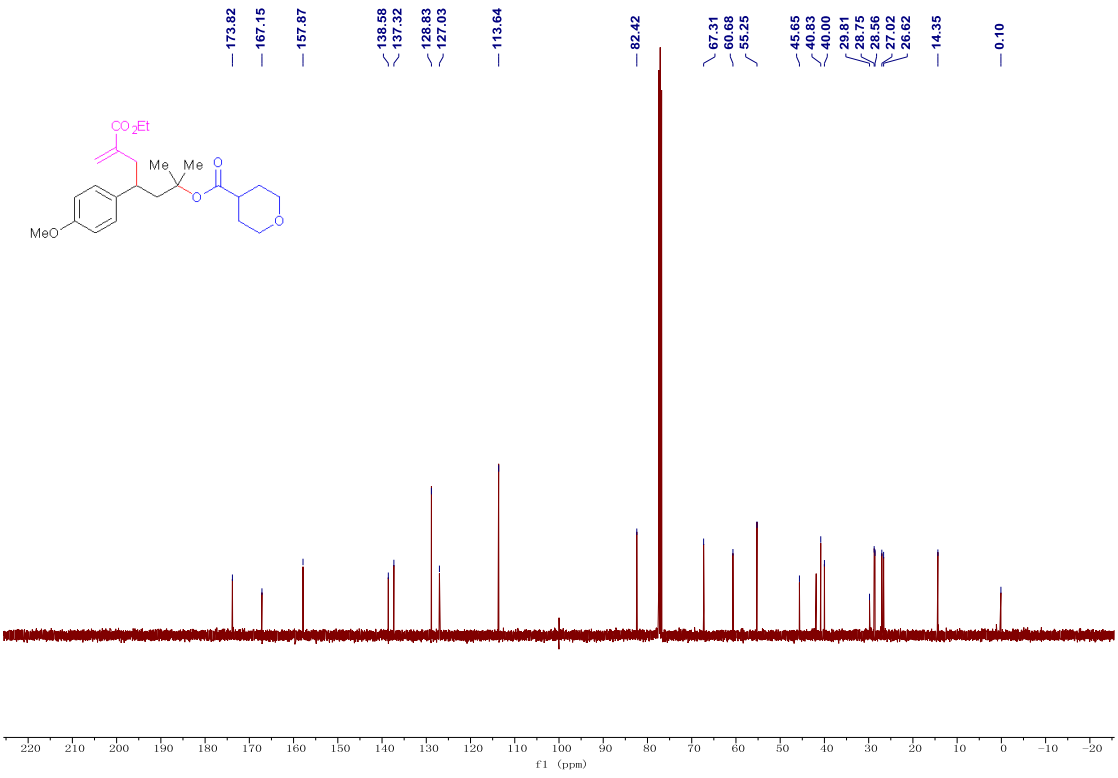
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4aq**



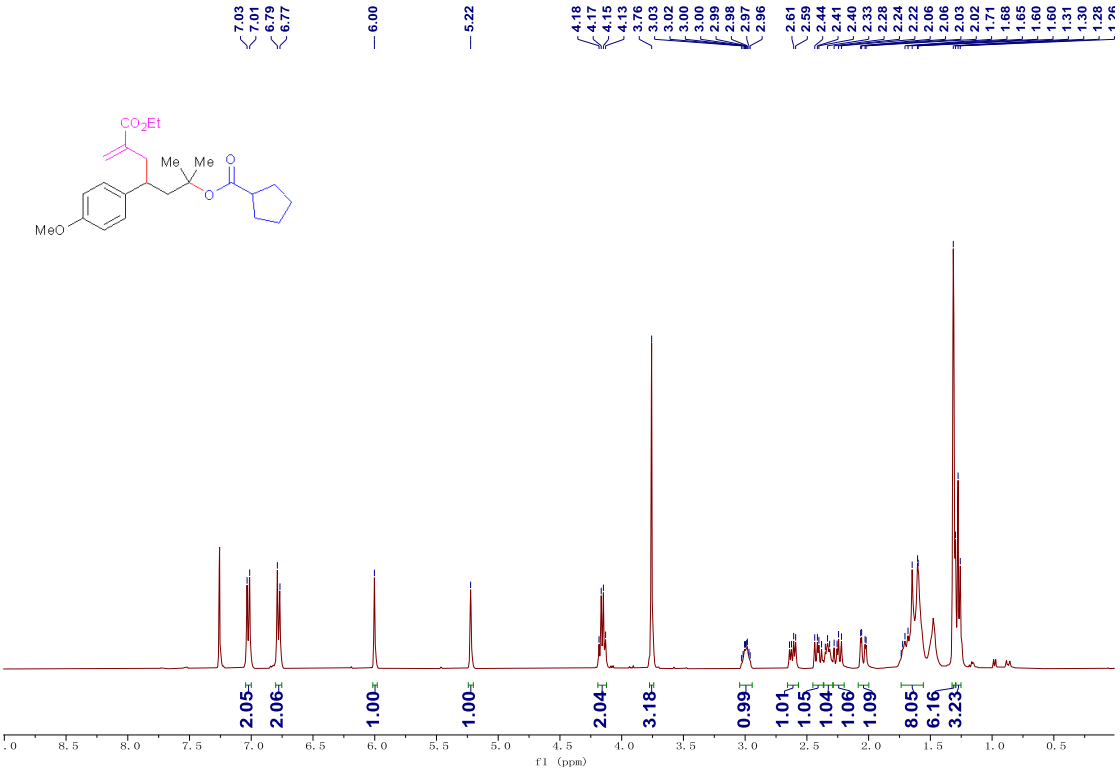
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ar**



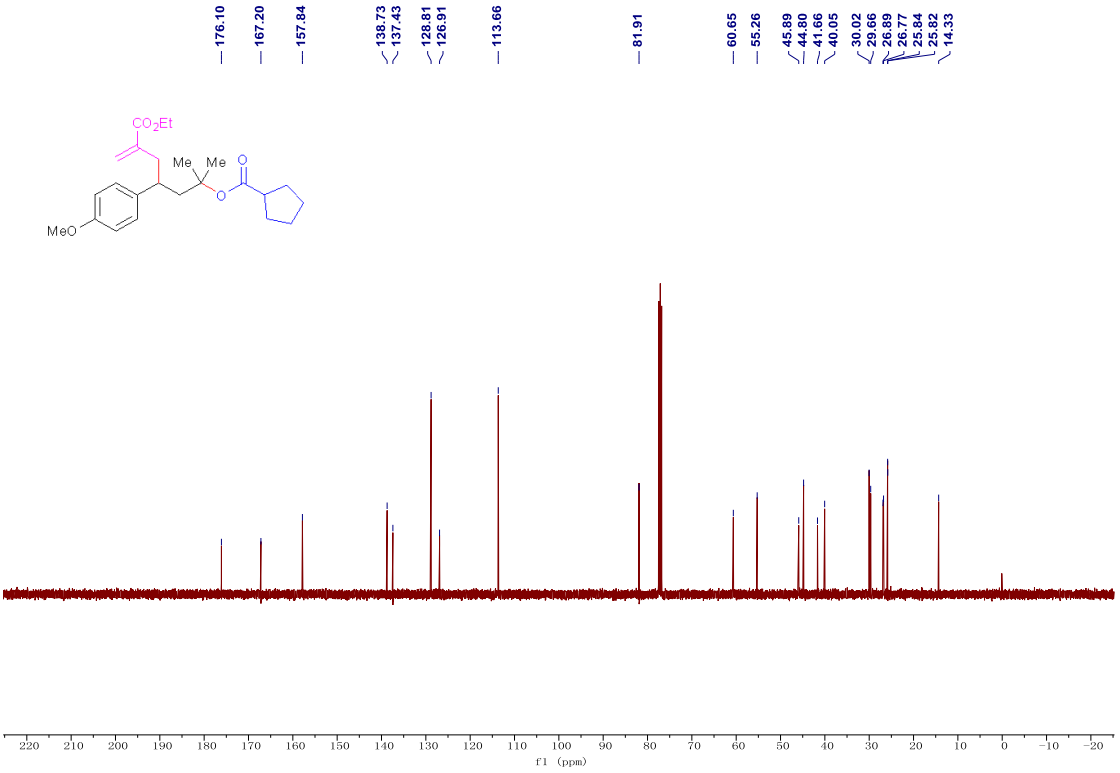
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ar**



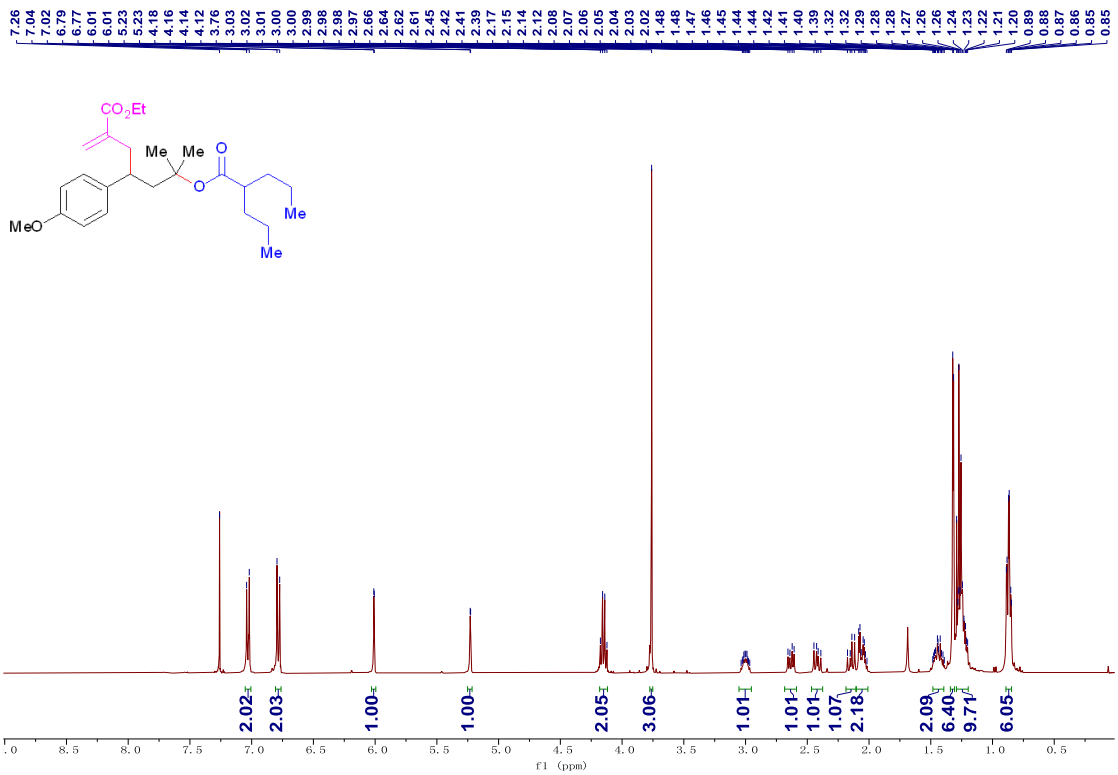
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4as**



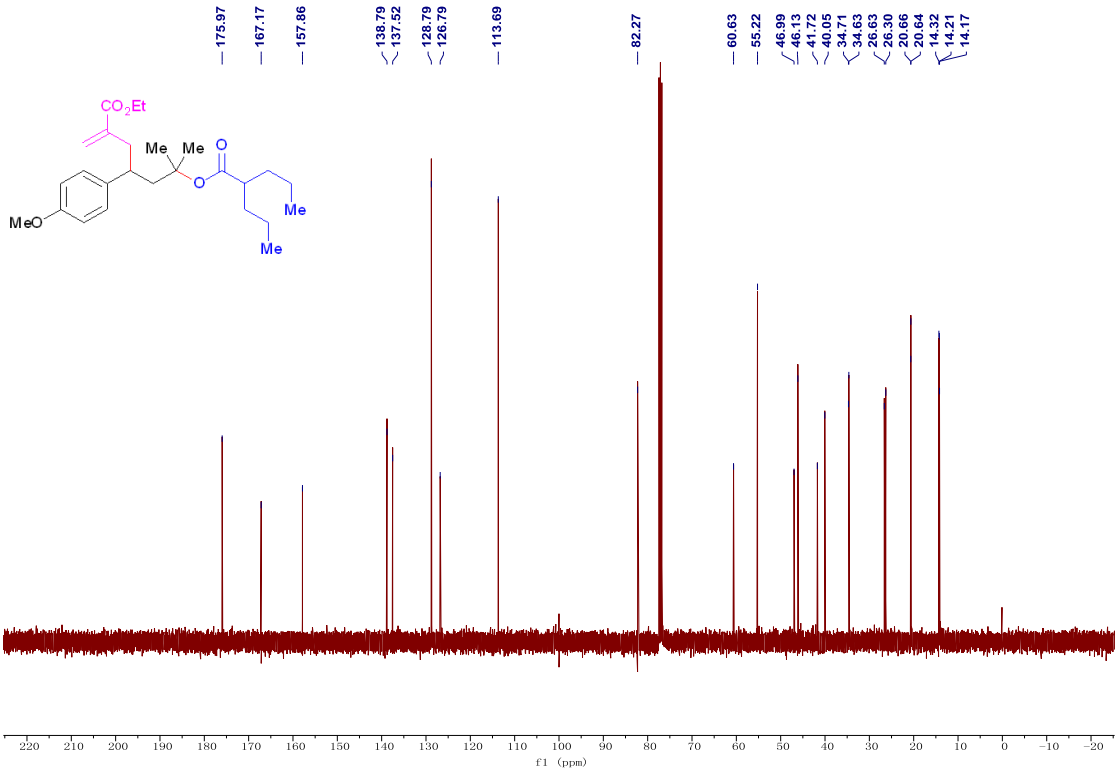
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4as**



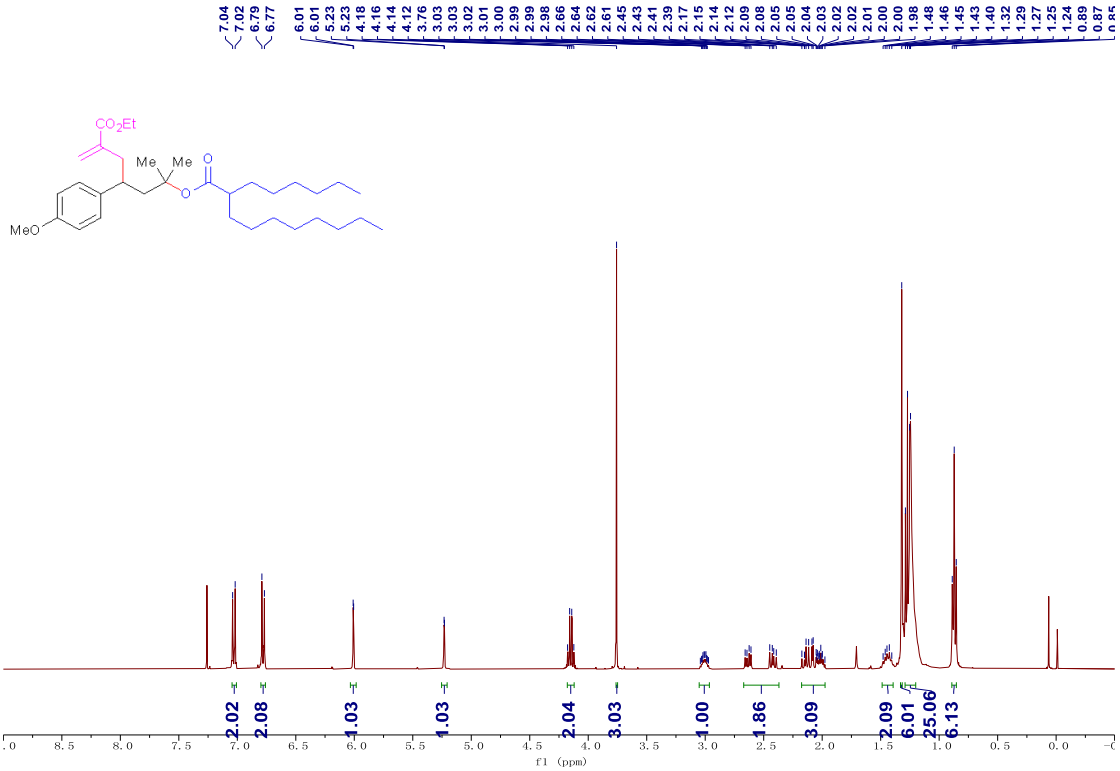
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4at**



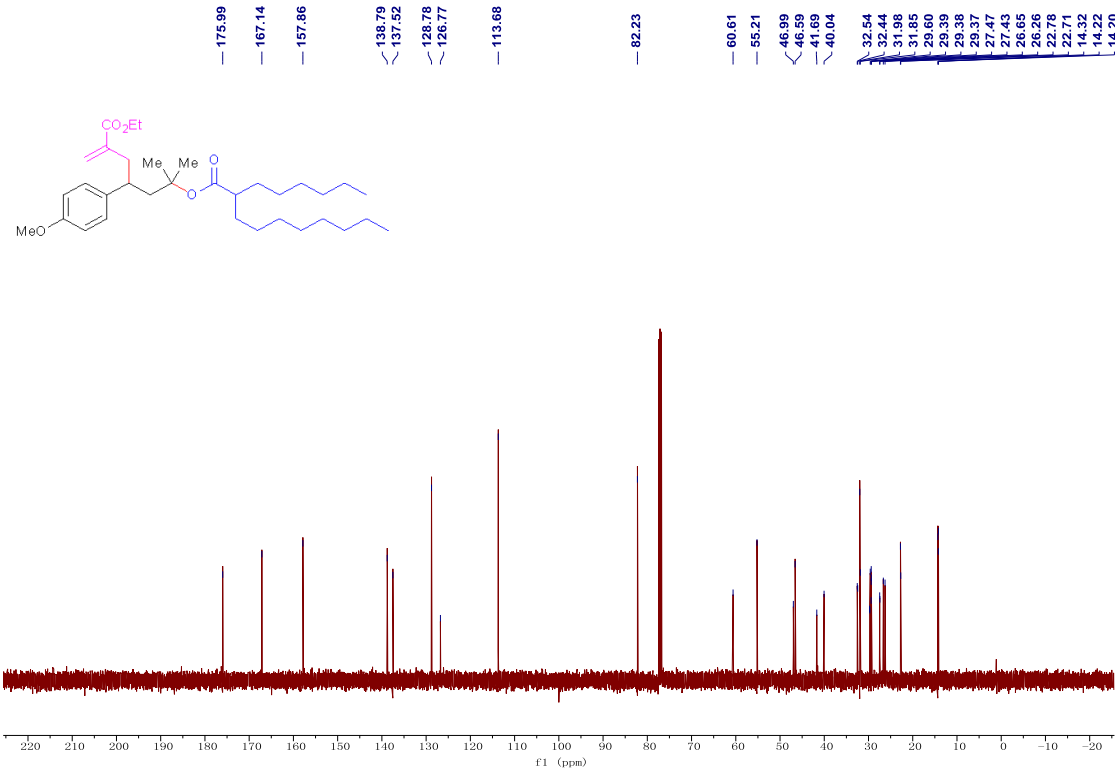
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4at**



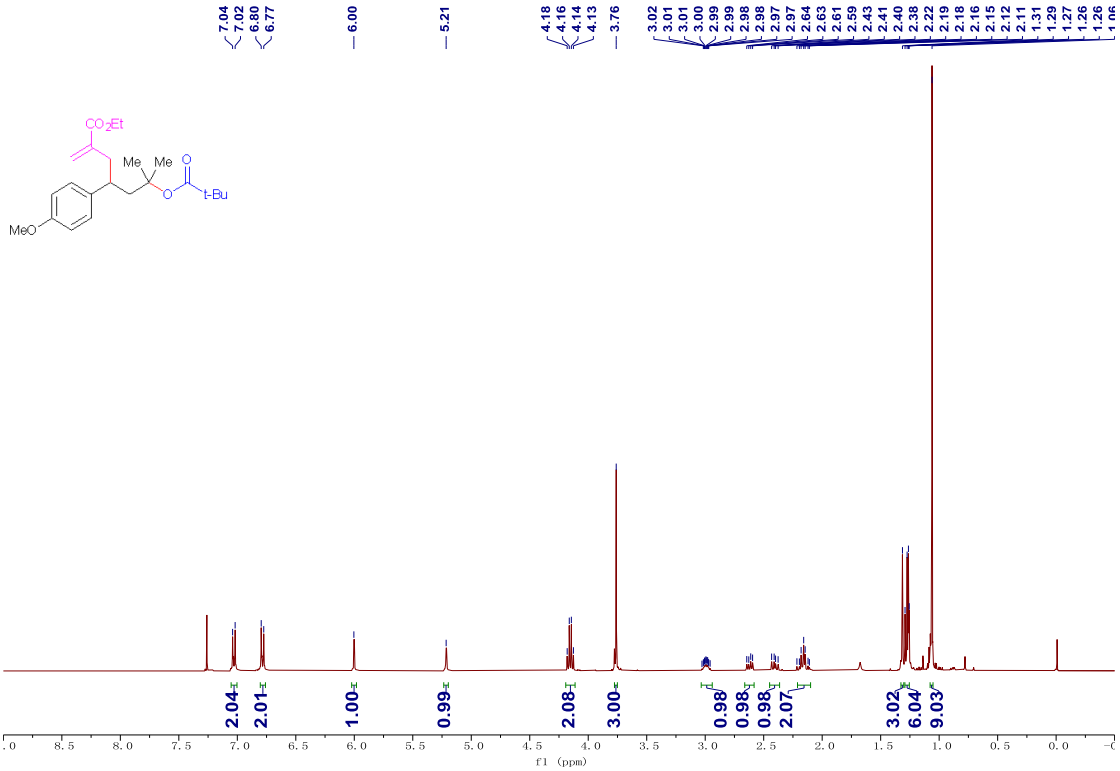
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4au**



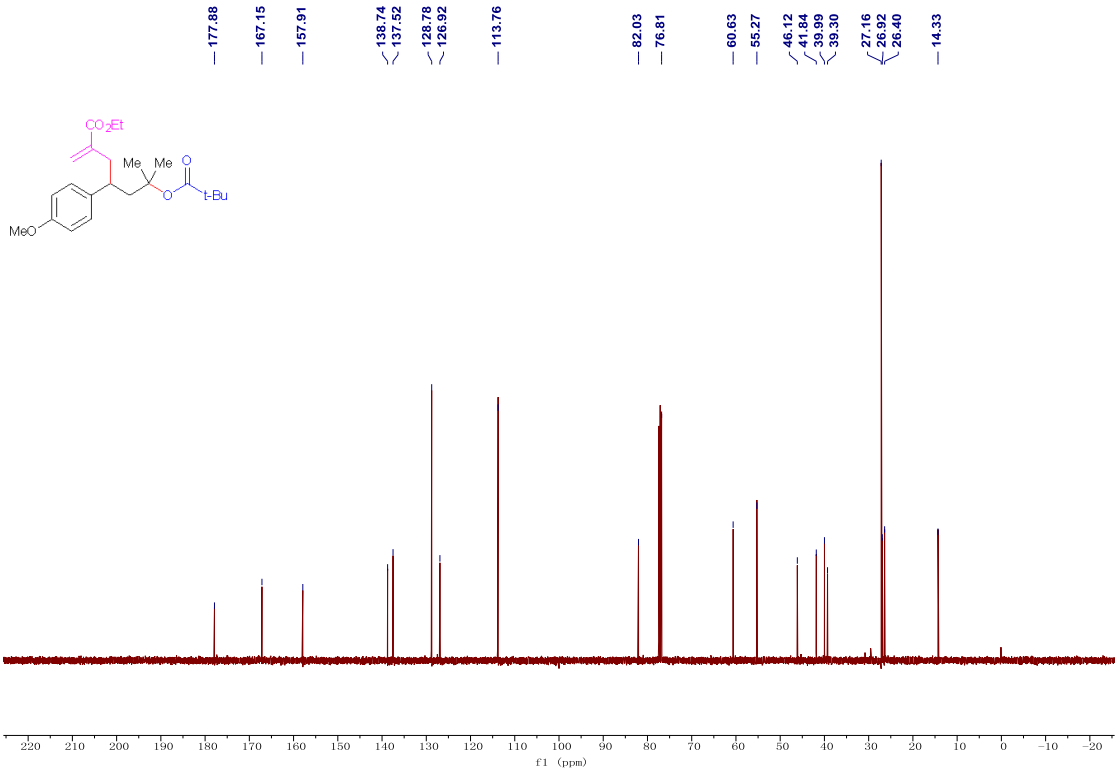
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4au**



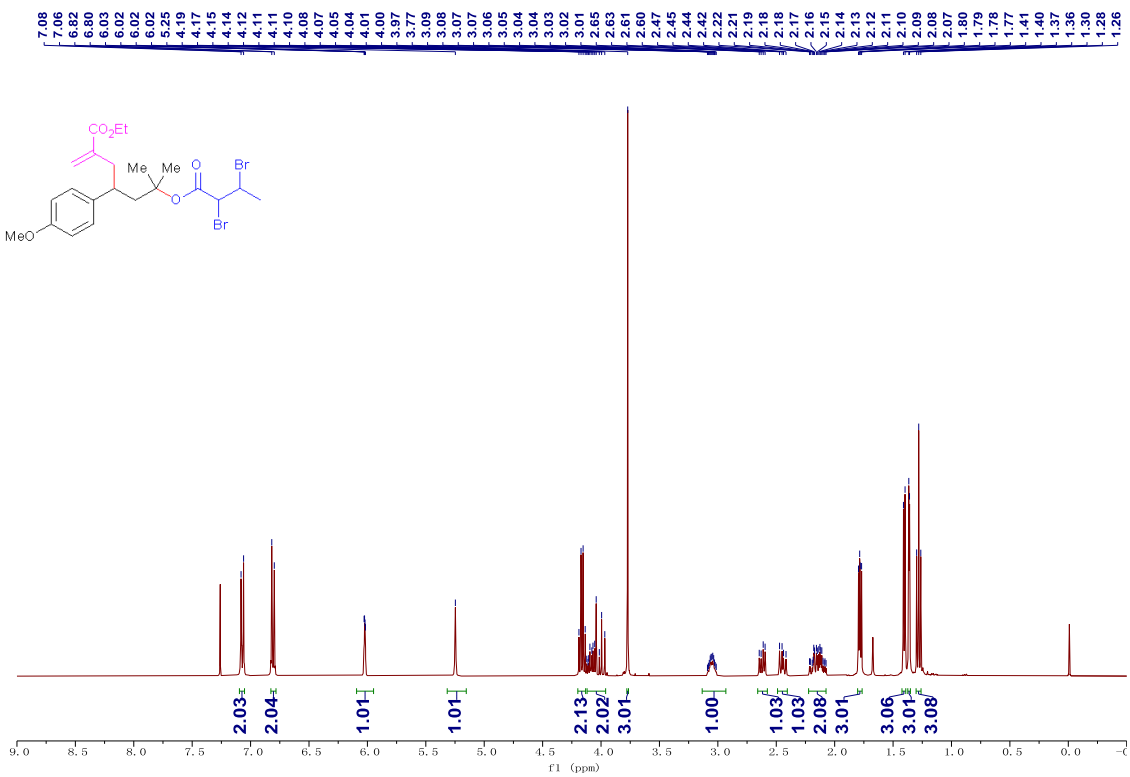
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4av**



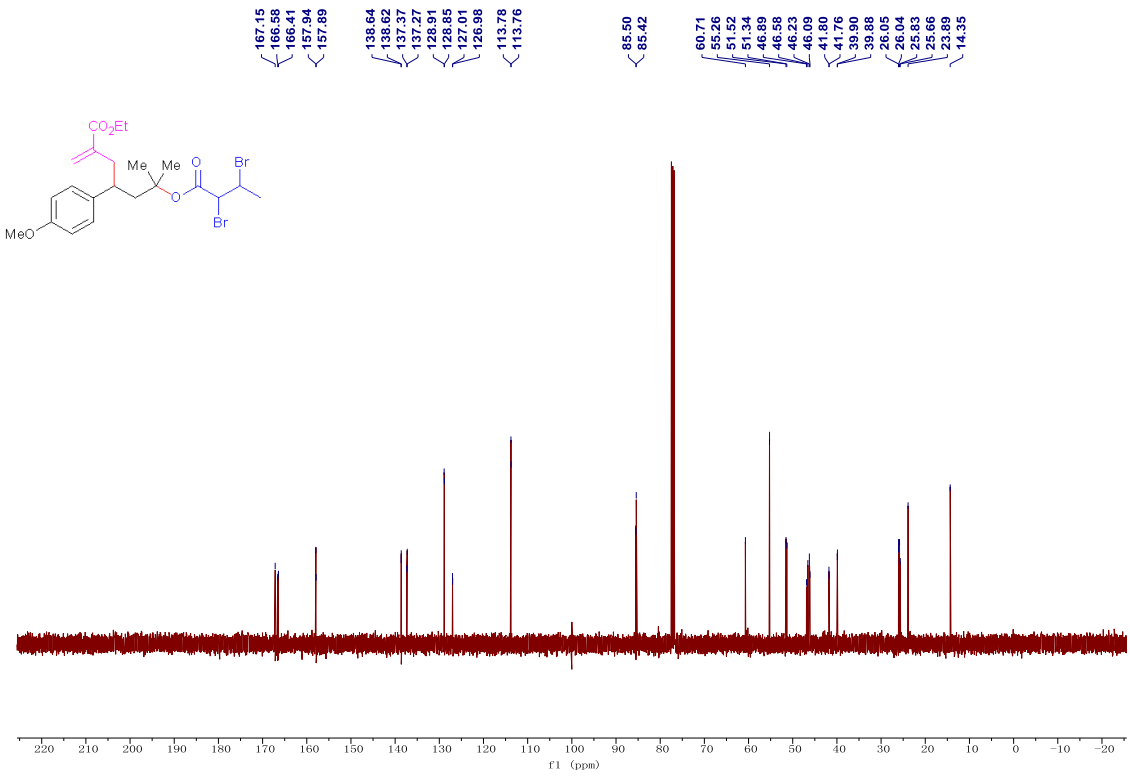
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4av**



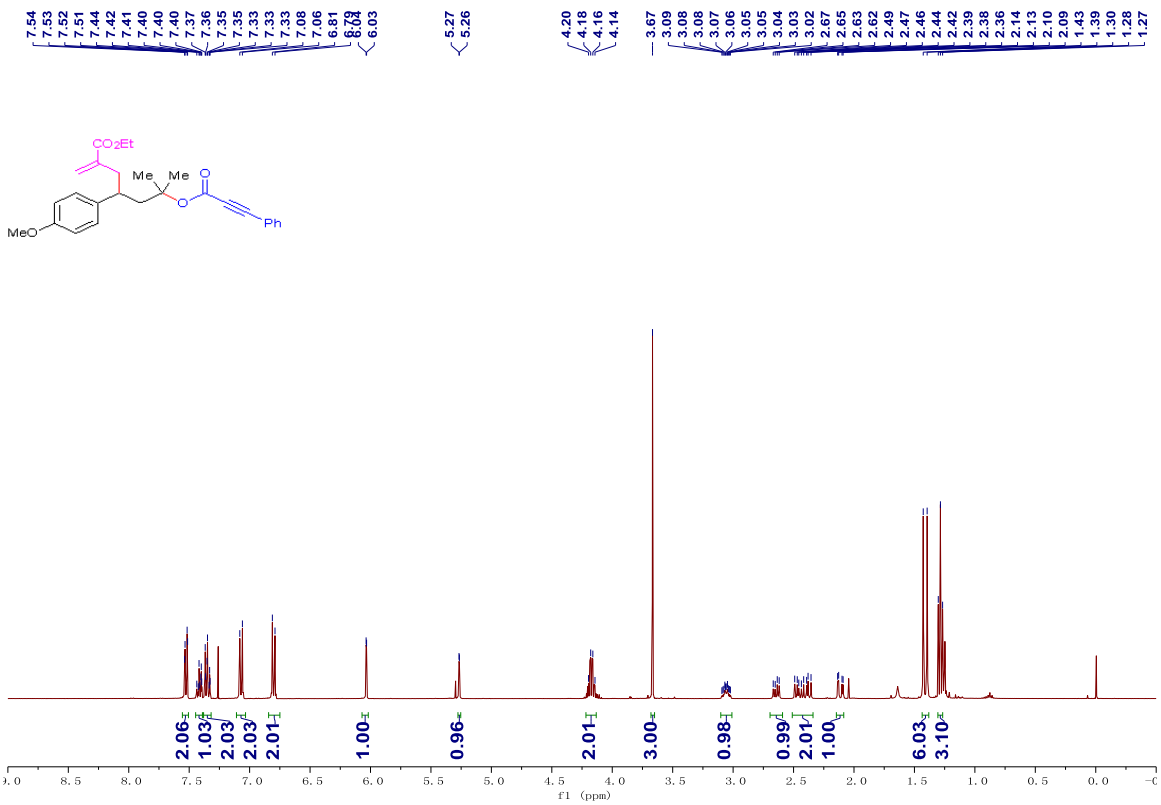
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aw**



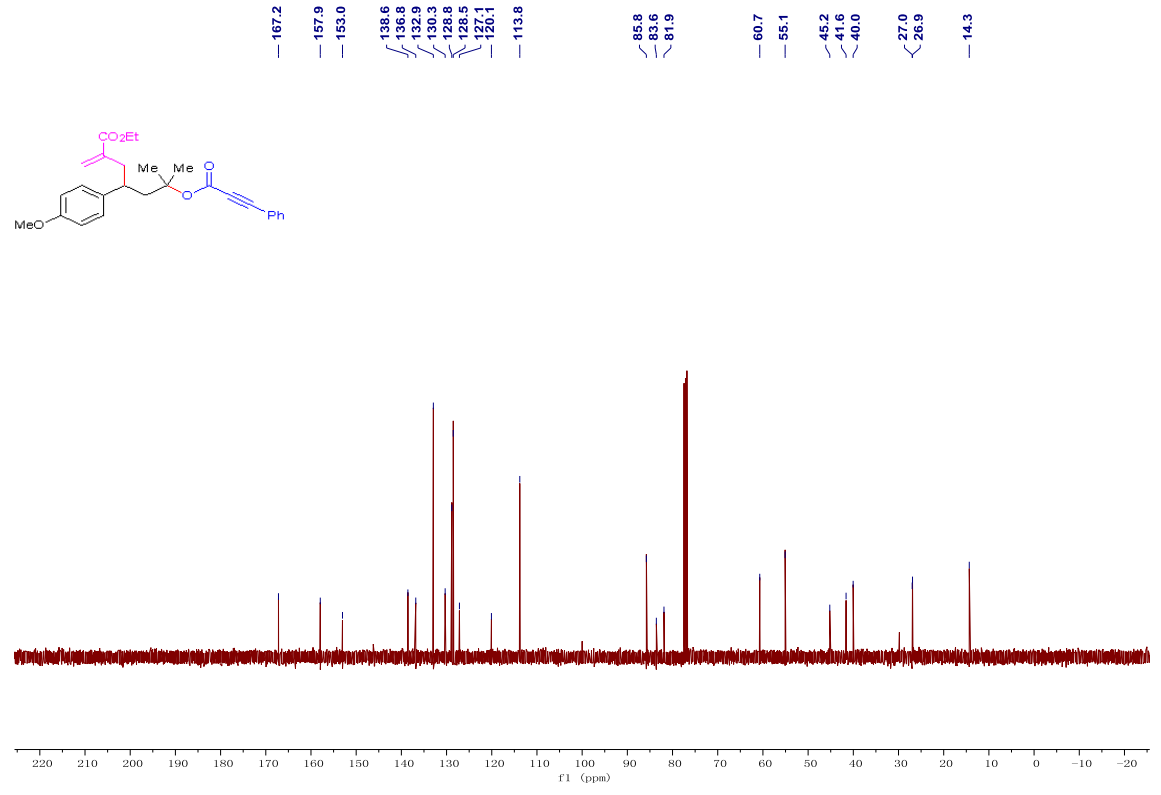
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4aw**



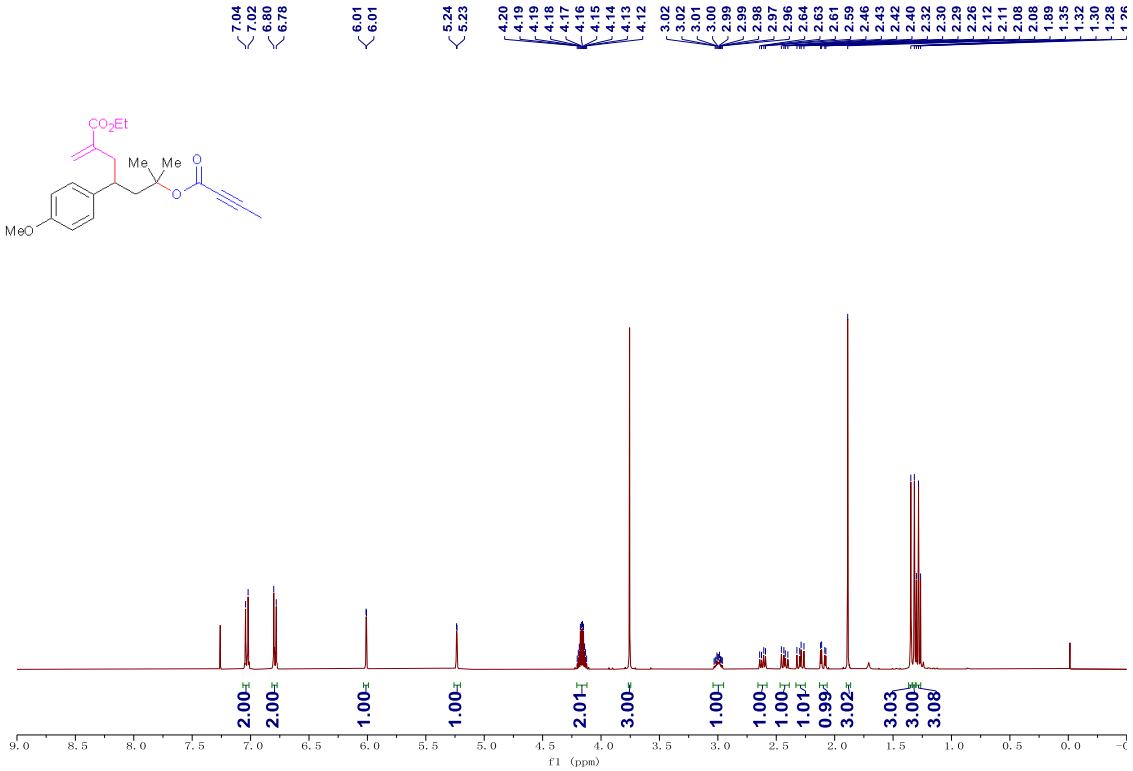
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ax**



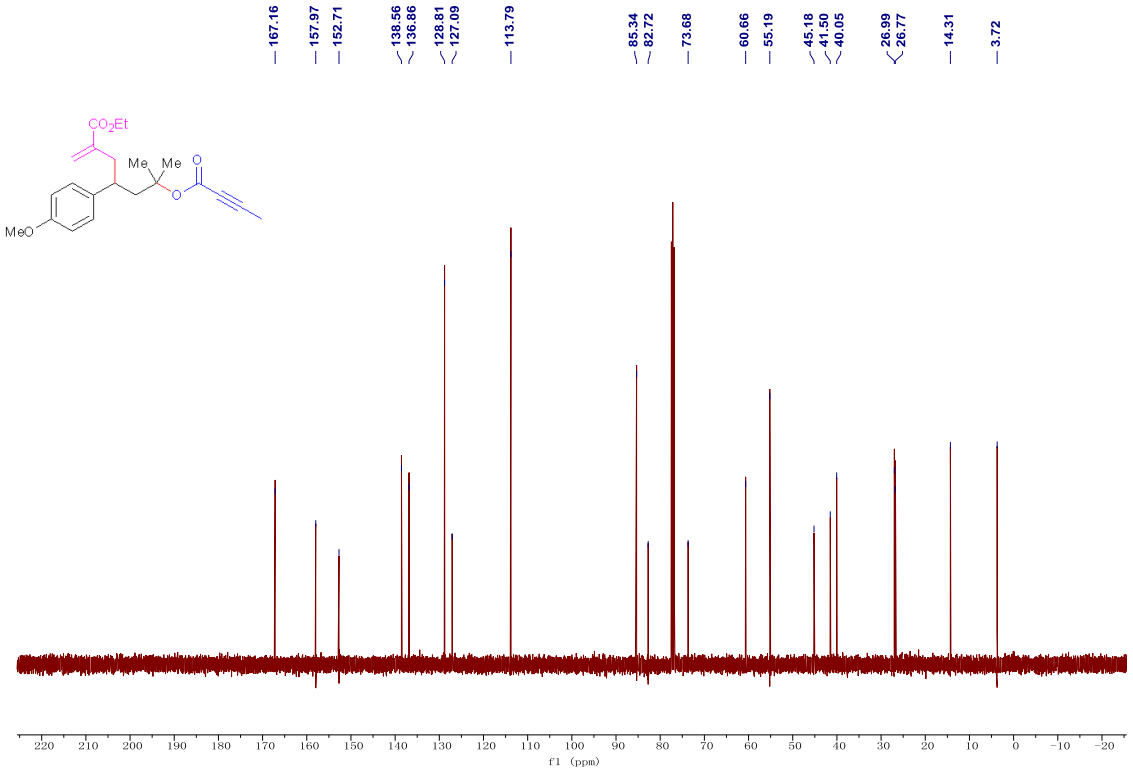
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ax**



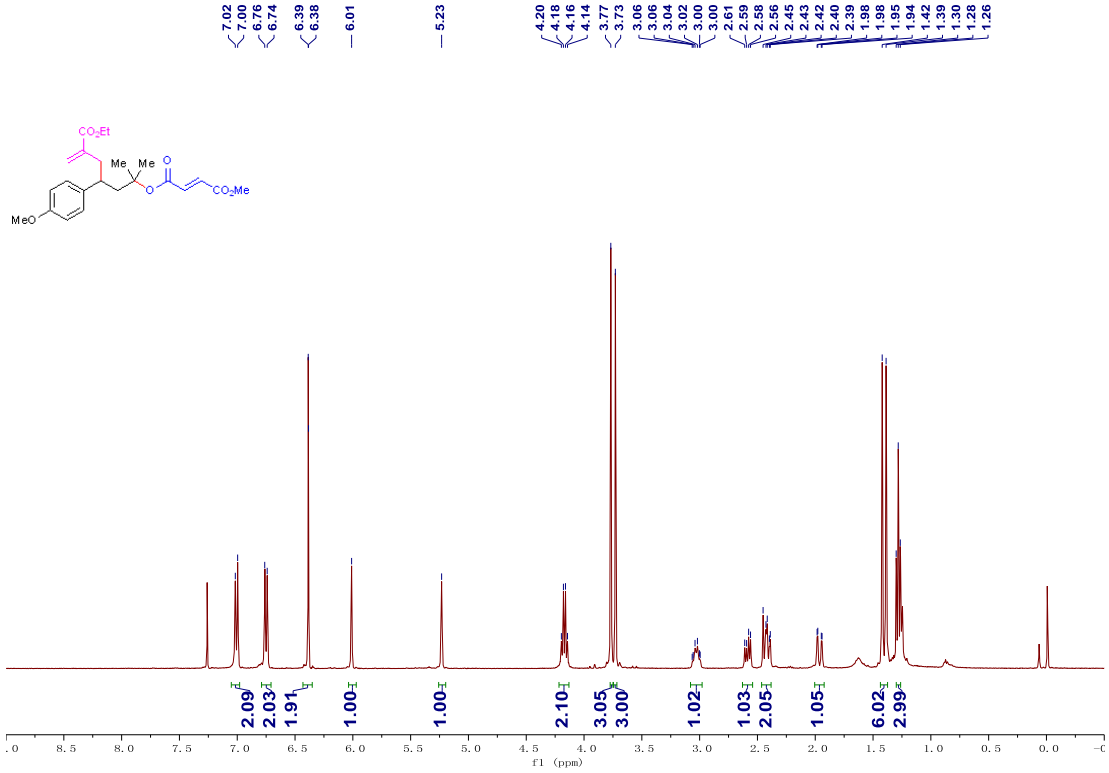
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ay**



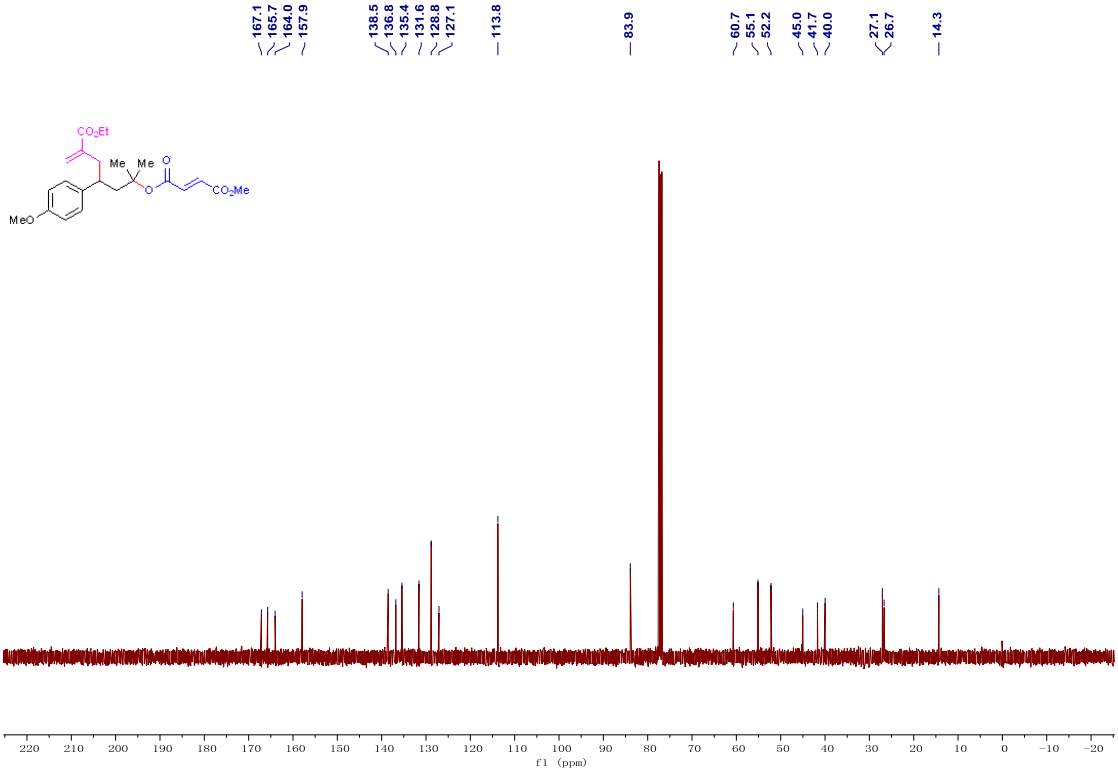
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ay**



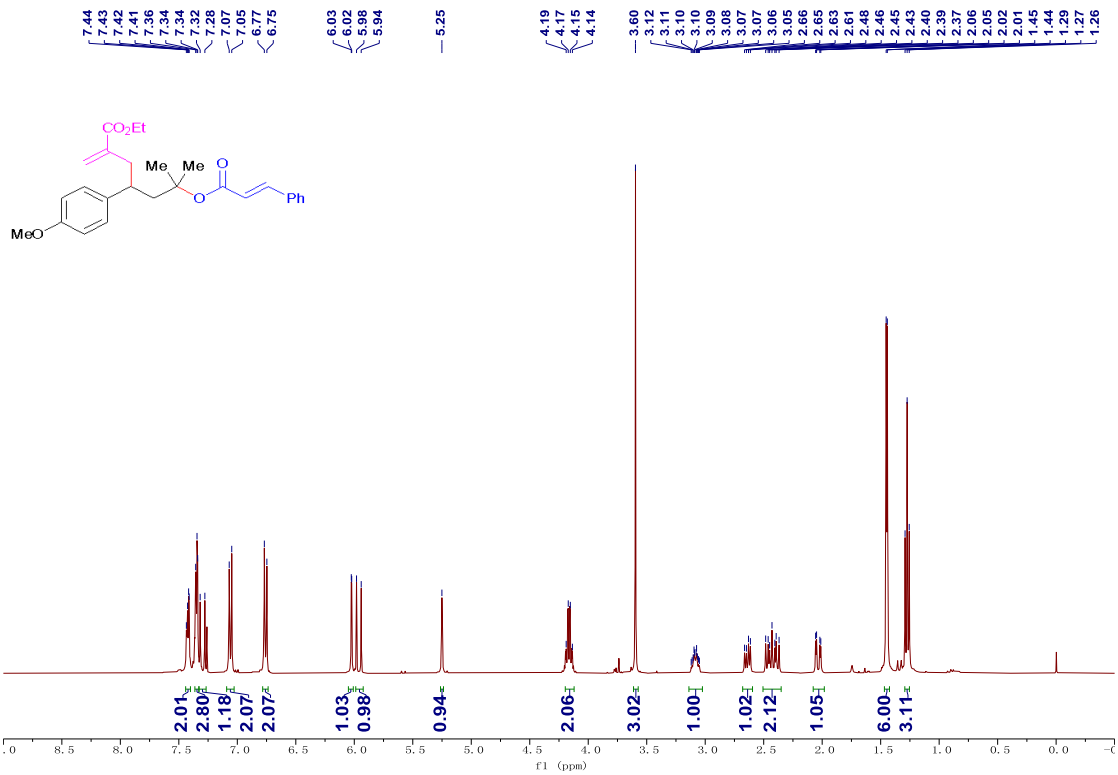
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4az**



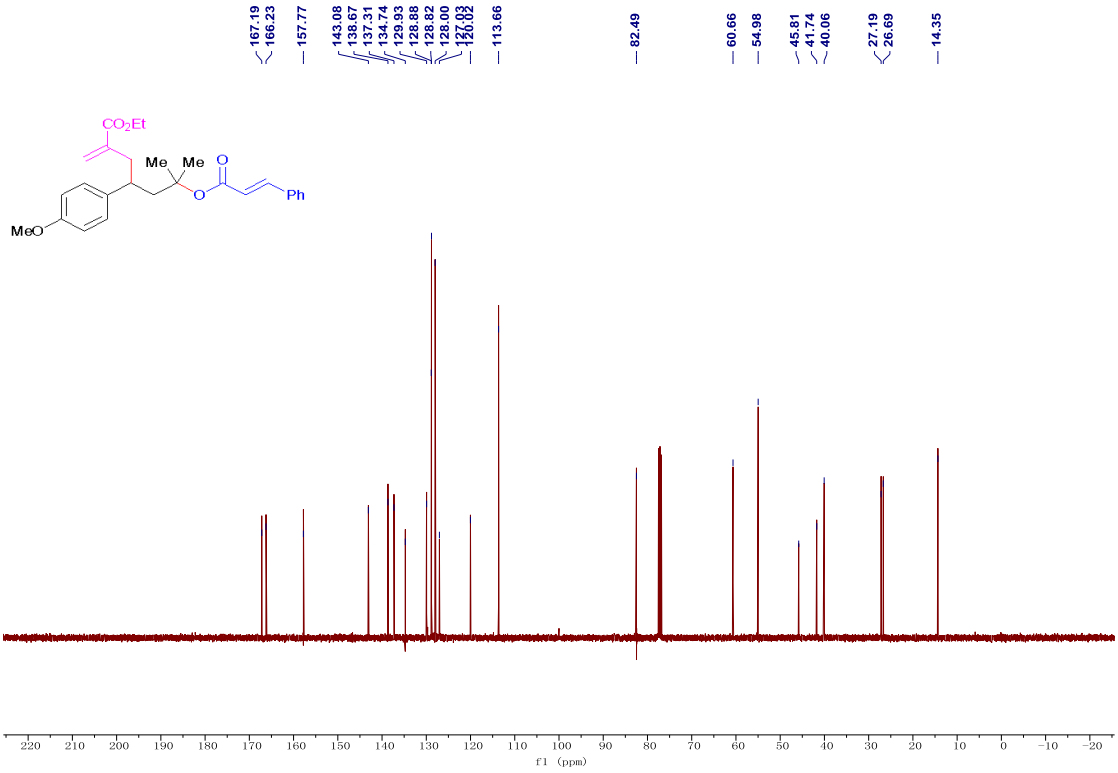
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4az**



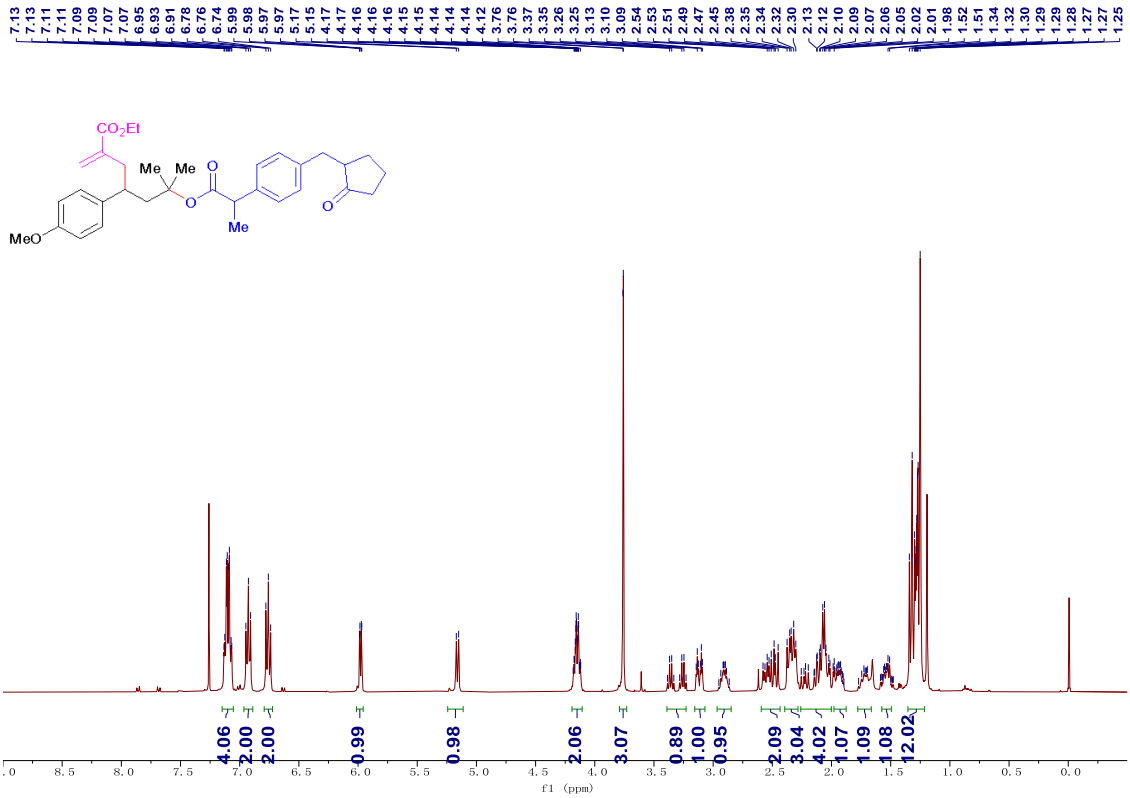
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ba**



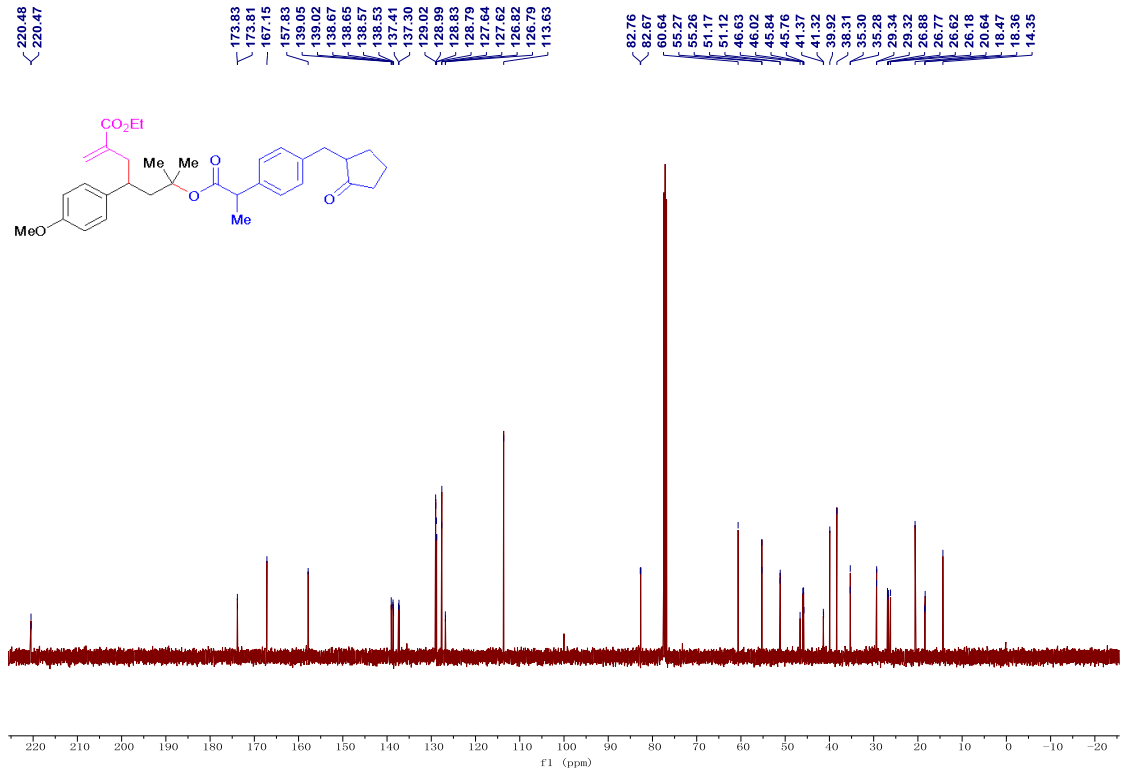
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4ba**



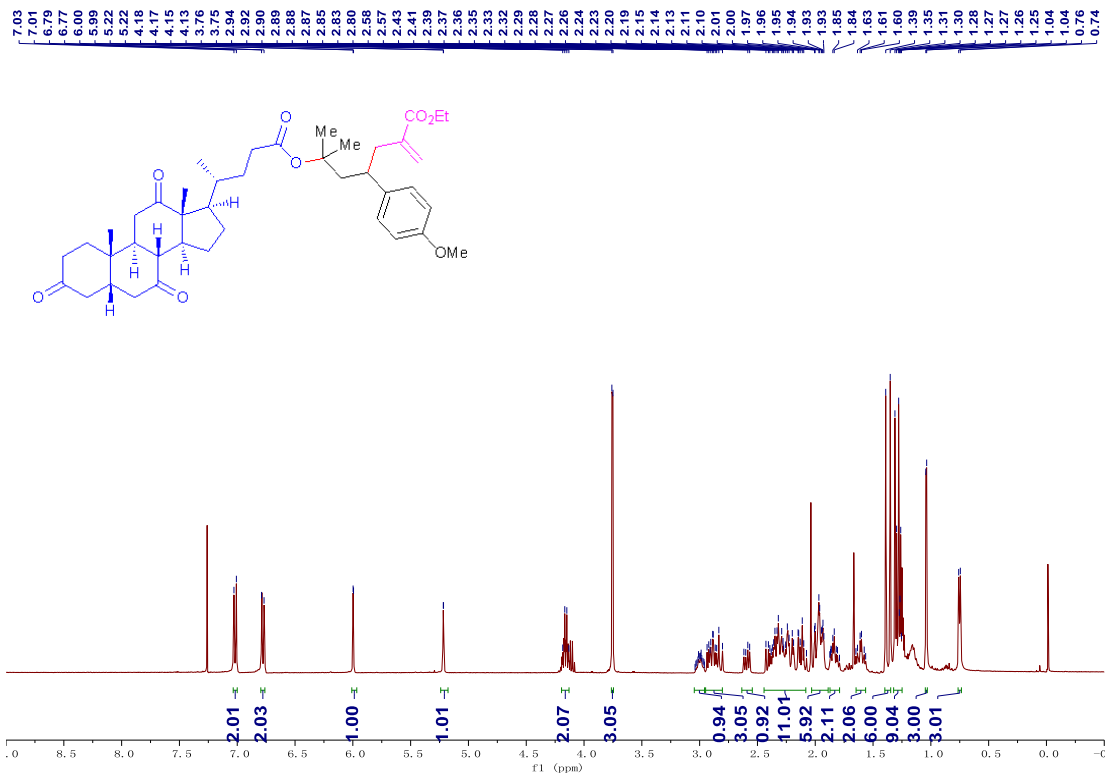
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bb**



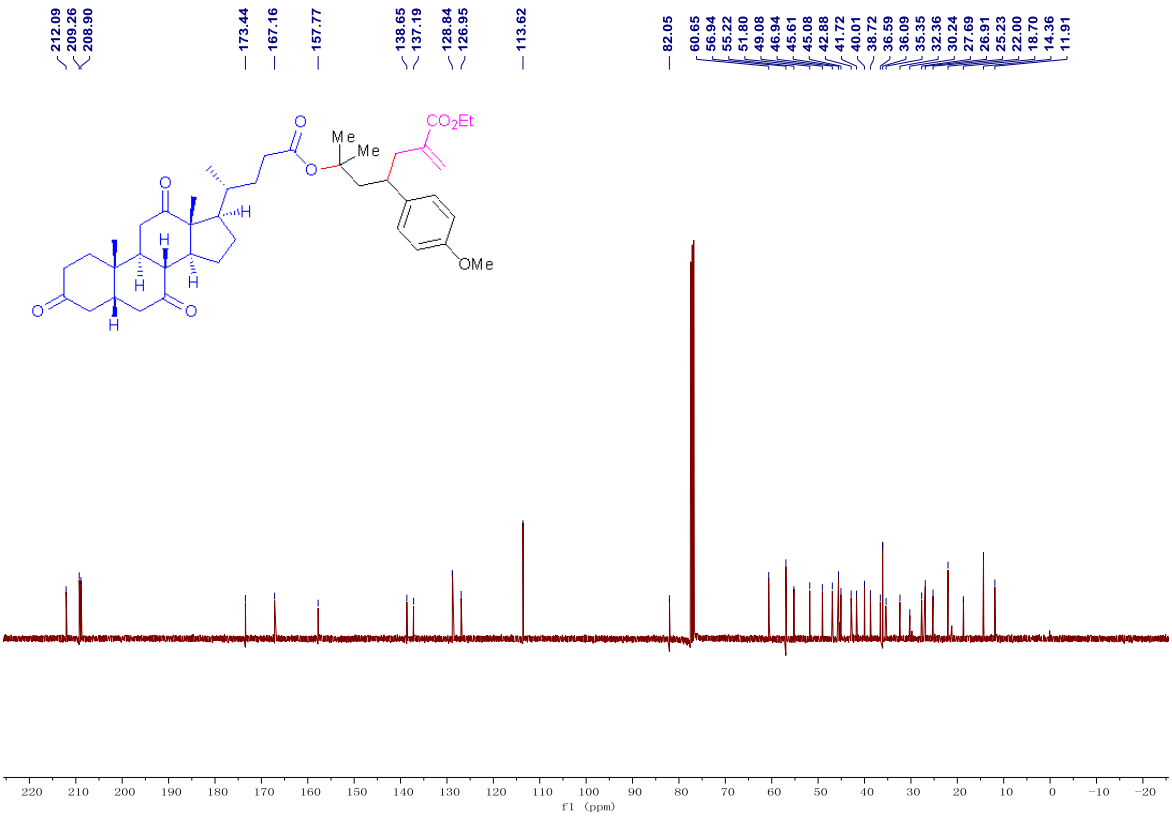
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bb**



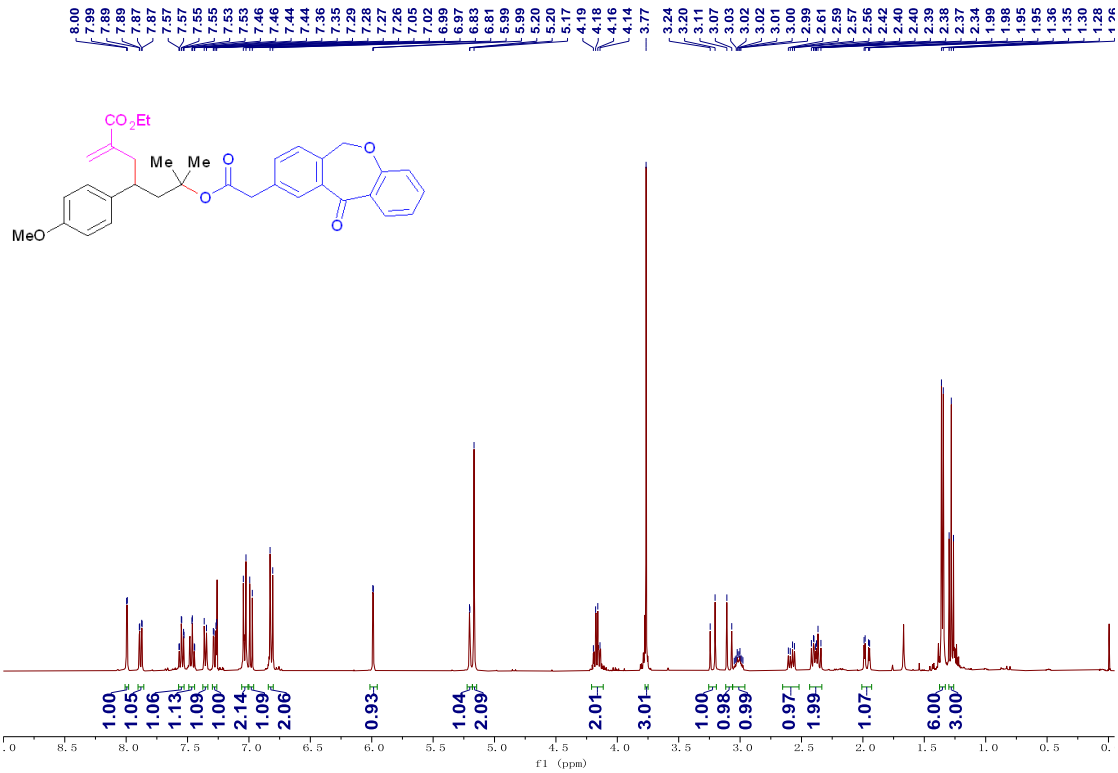
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bc**



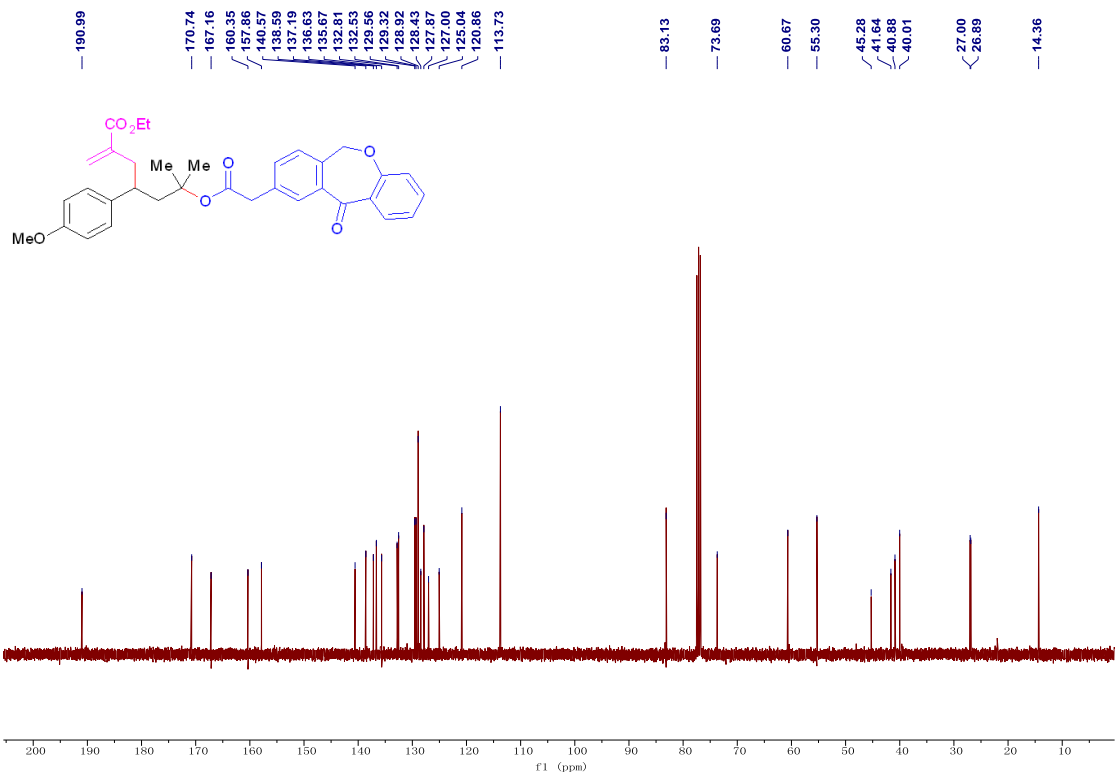
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bc**



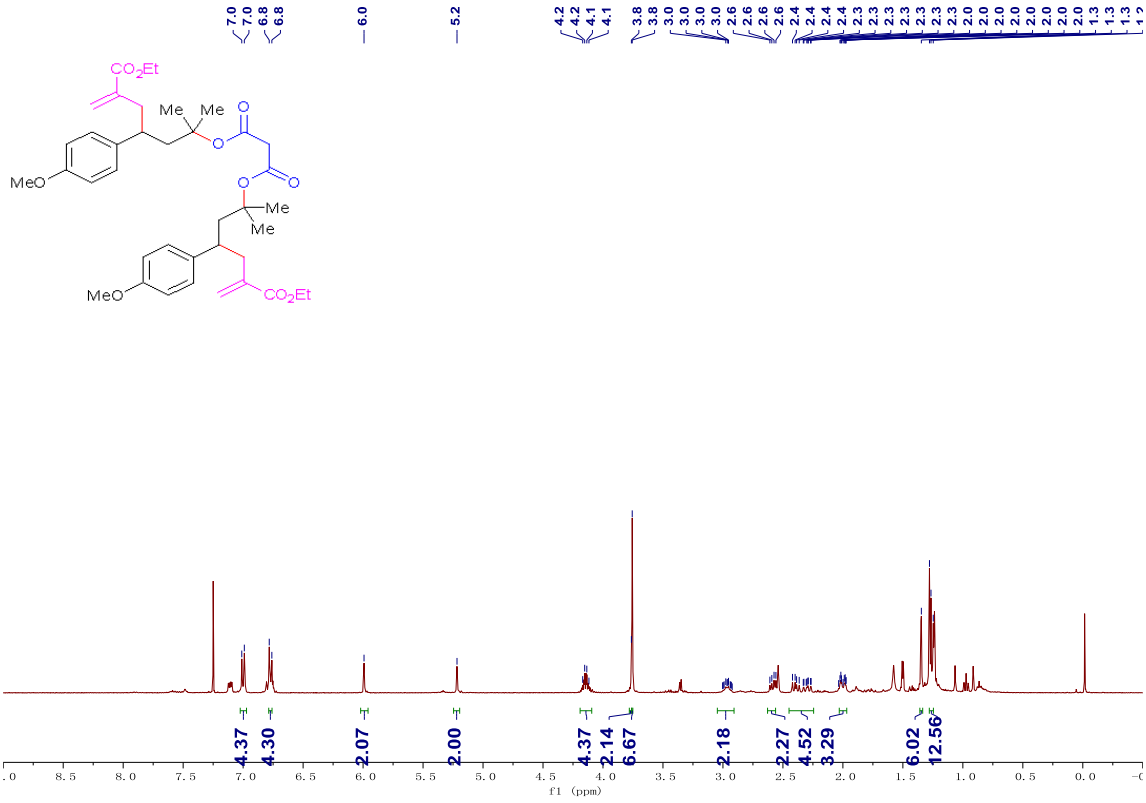
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bd**



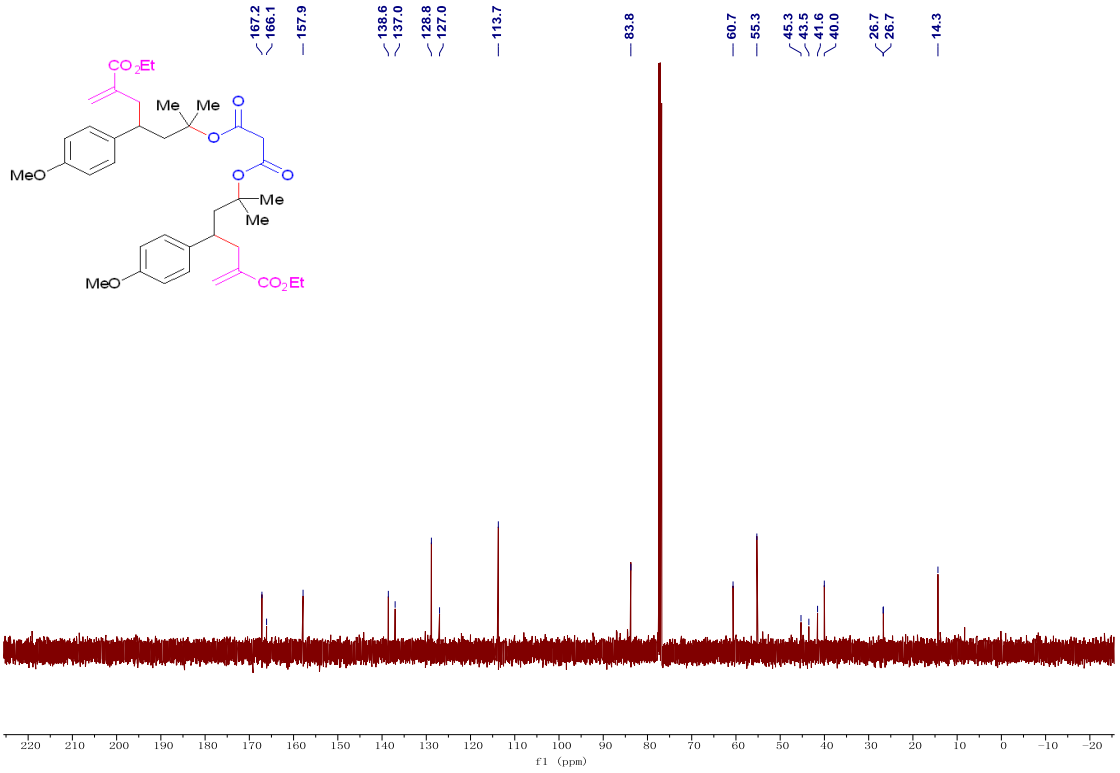
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bd**



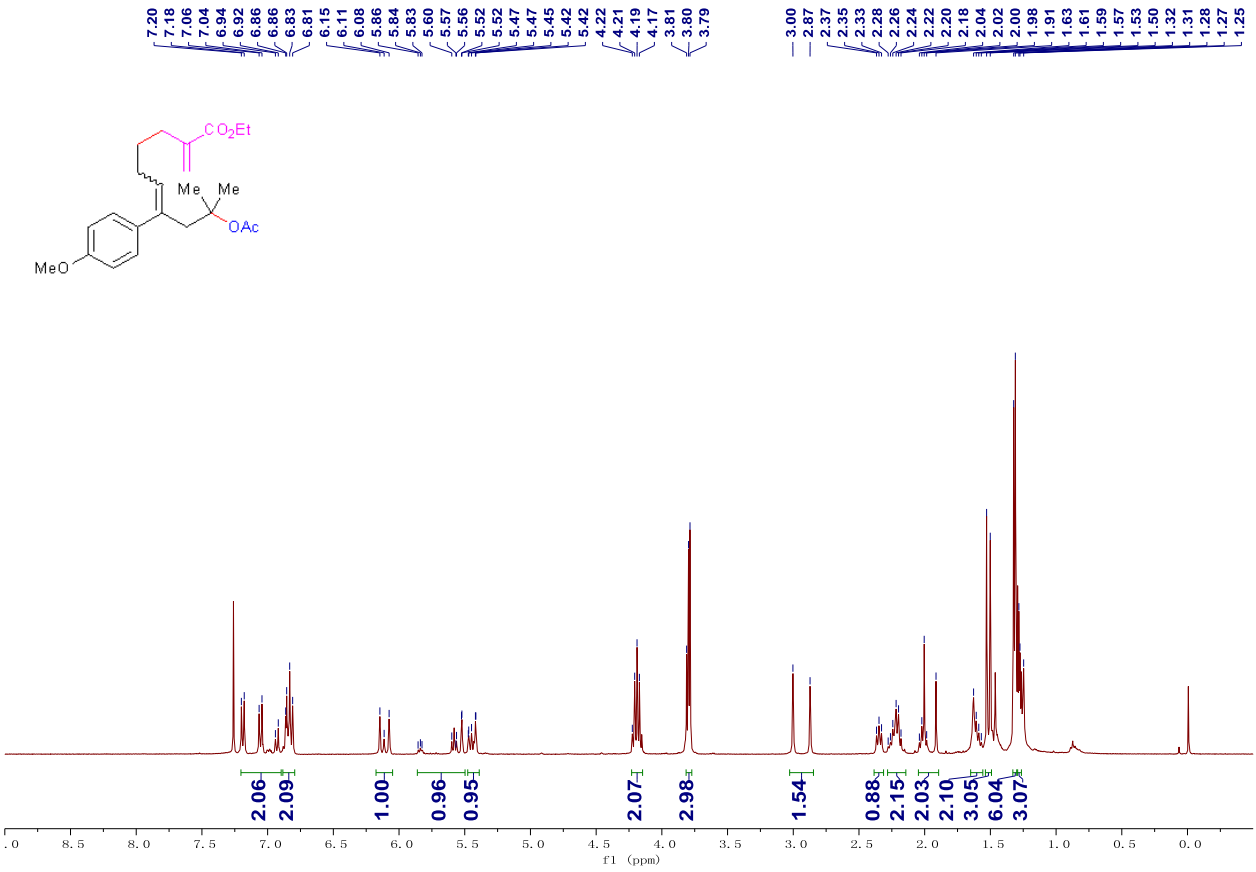
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4be**



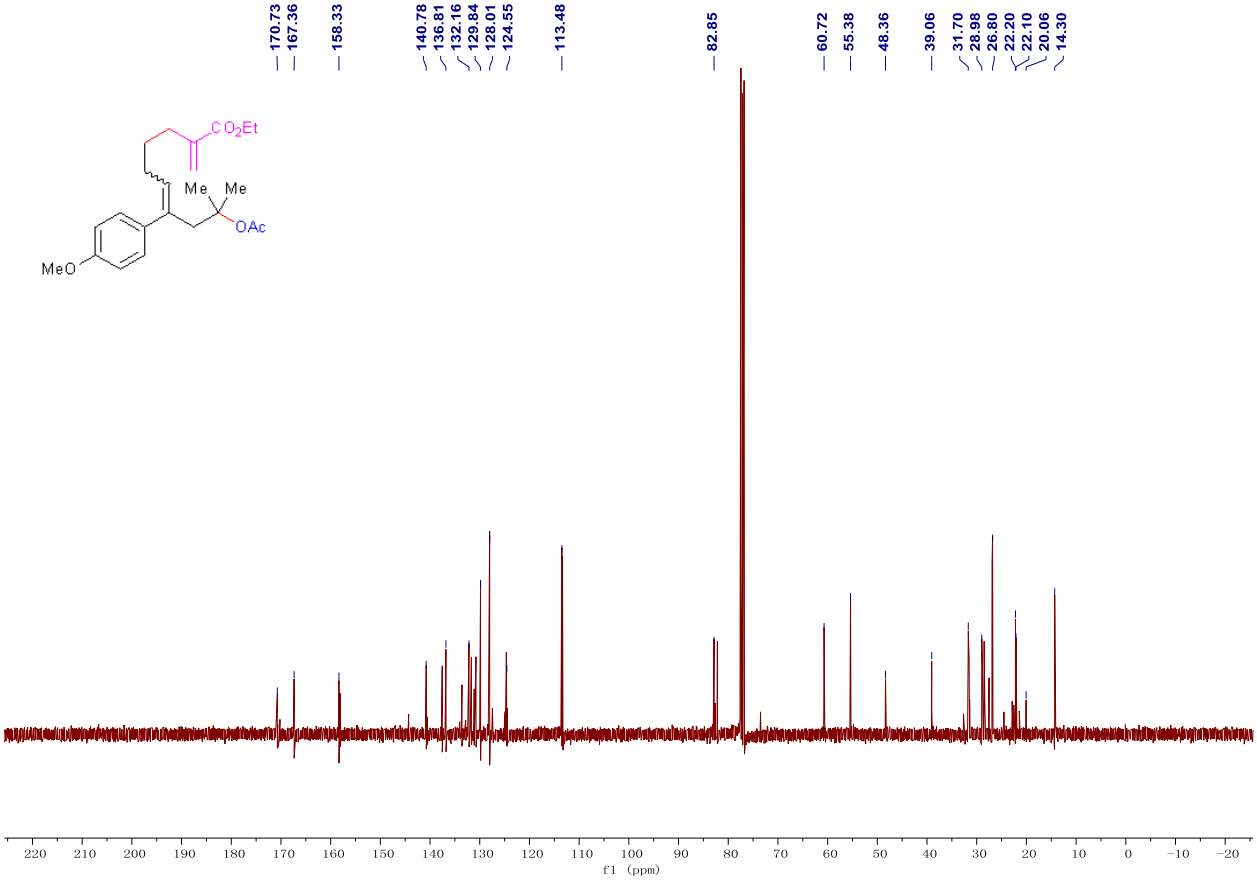
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4be**



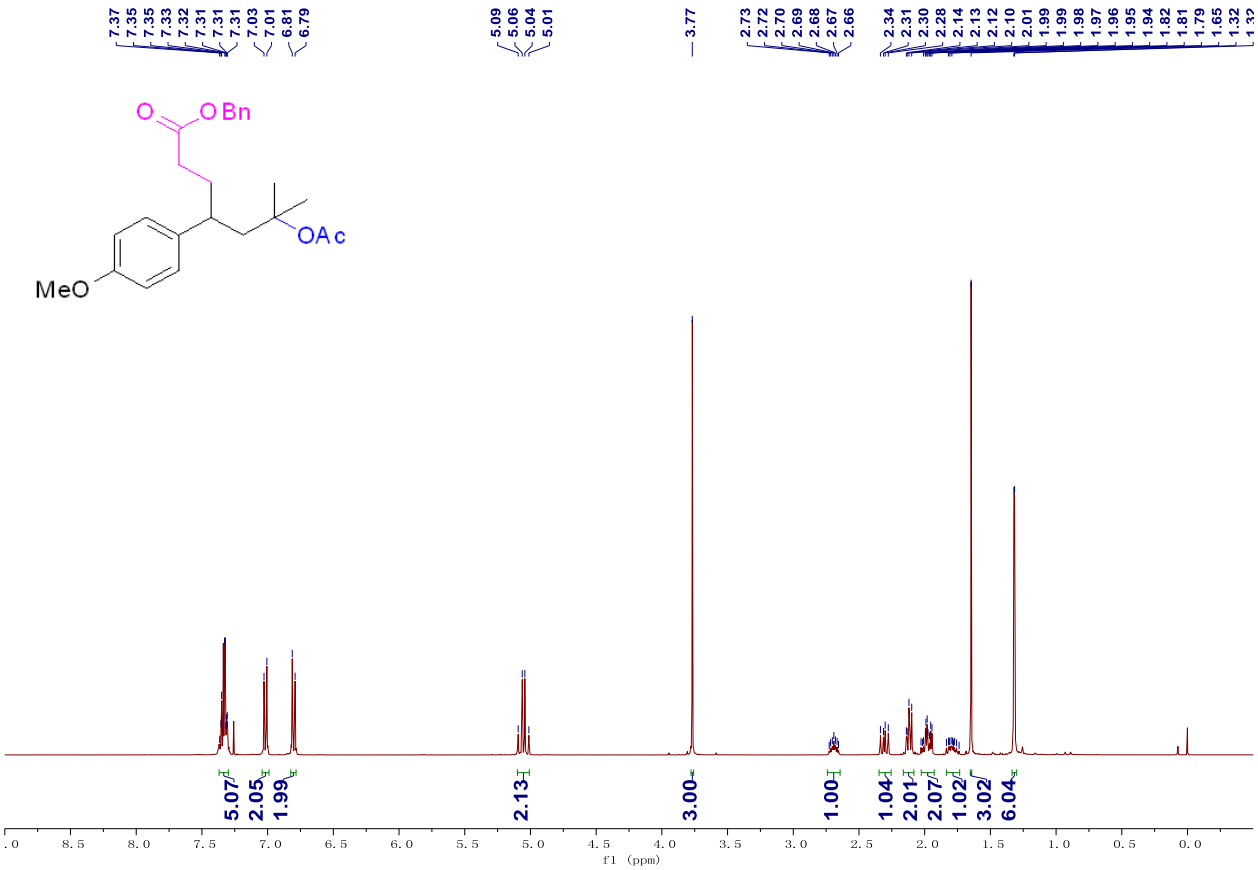
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bf**



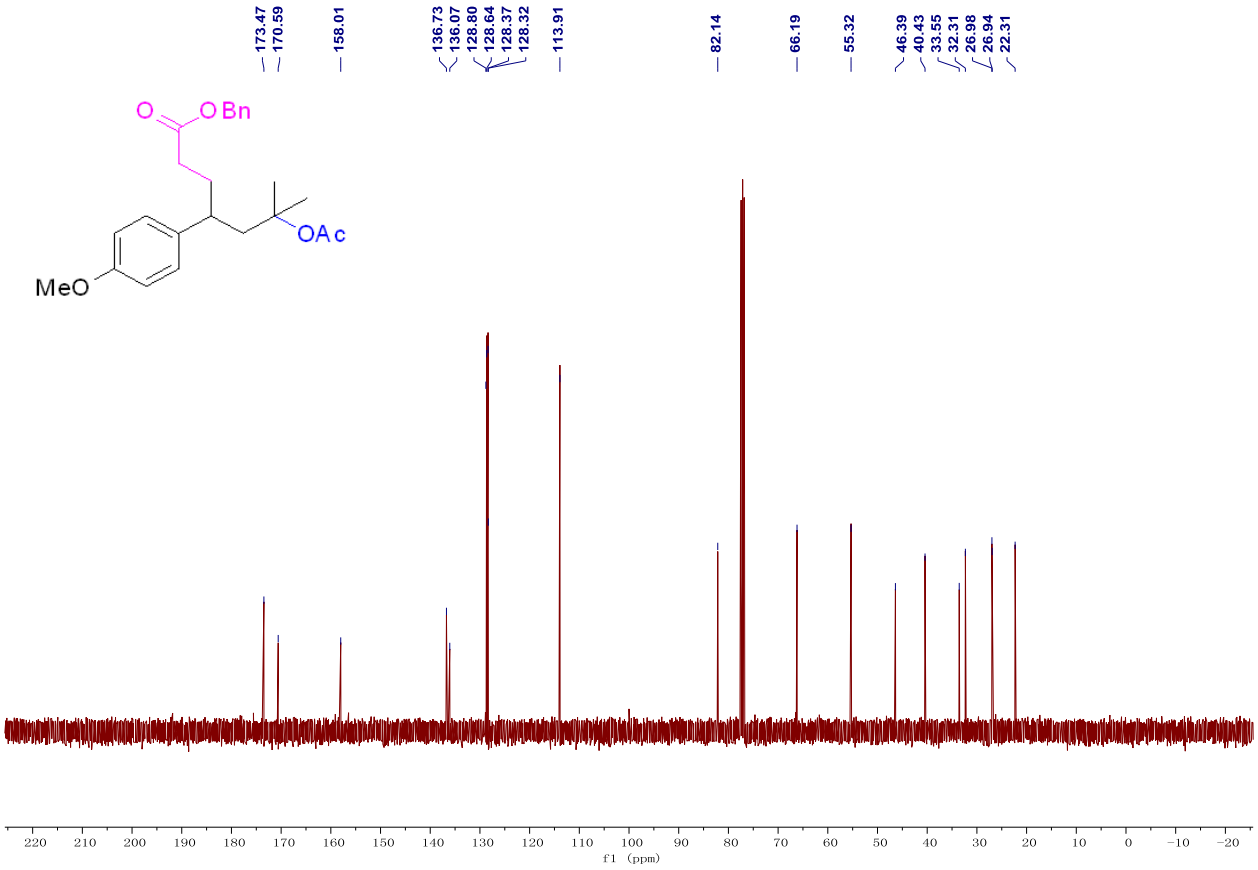
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bf**



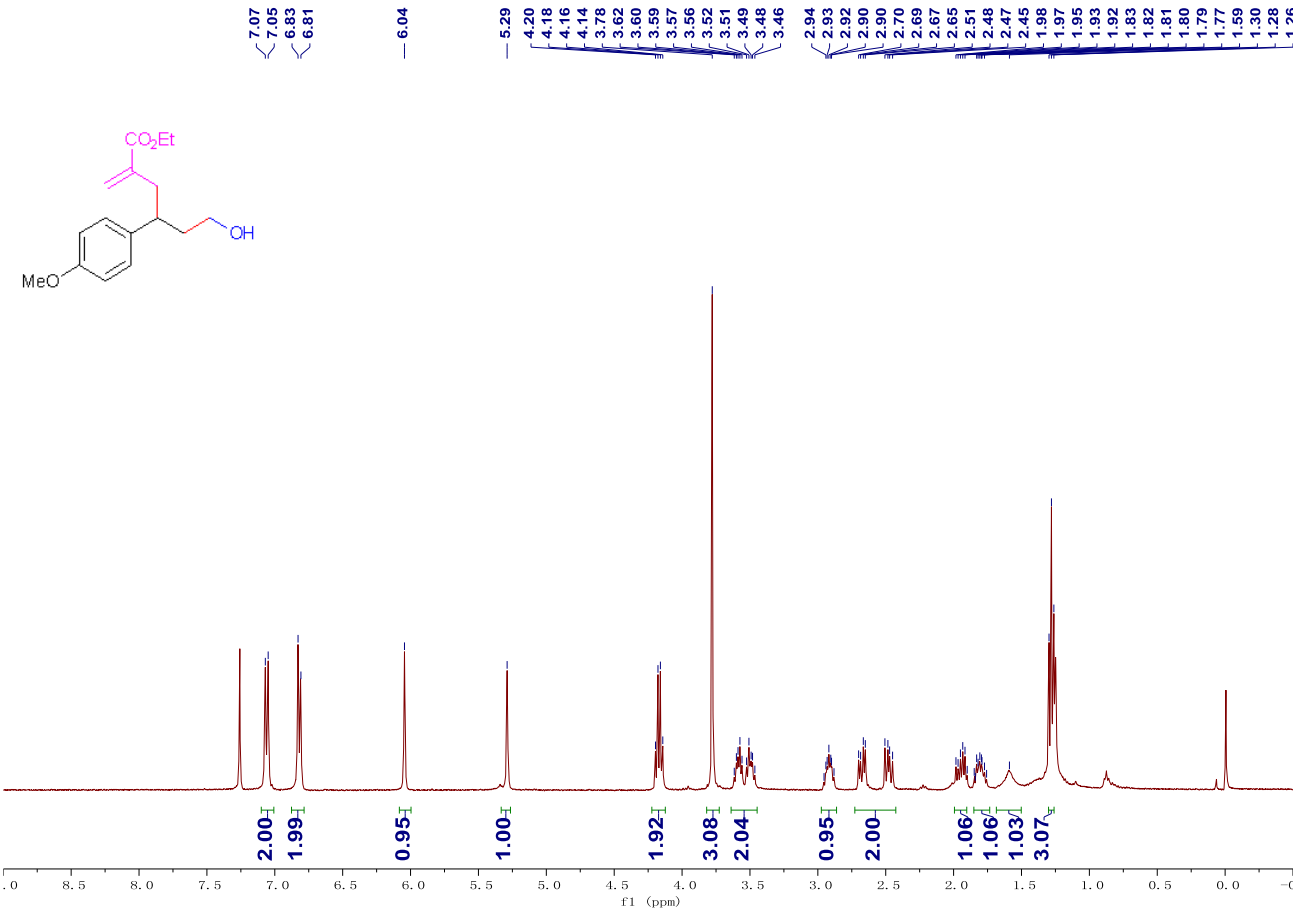
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bg**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bg**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4bh**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4bh**