Supplementary Information

Polyhaloalkanes as the C1 Source: Radical-Mediated Migratory Carbonylation of Alkenes with Polyhaloalkanes toward *α,β*-Unsaturated Carbonyls

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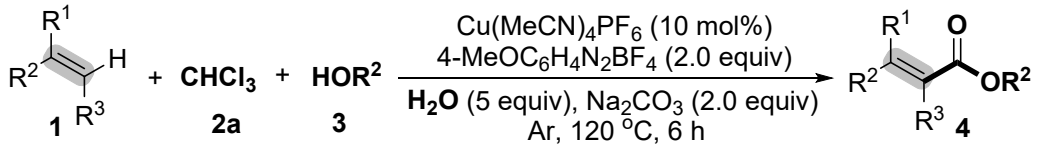
(A) Typical experimental procedure

(a) General

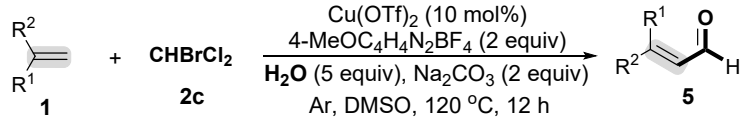
The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 (500, 125, and 471 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI)apparatus using time-of-flight (TOF) mass spectrometry. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

(b) General procedure for the synthesis of *α,β*-unsaturated esters 4.

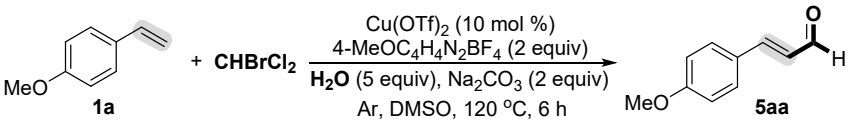


To a Schlenk tube were added $Cu(MeCN)_4PF_6$ (10 mol%), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol, 2 equiv), Na_2CO_3 (0.4 mmol, 2 equiv), alkene **1** (0.2 mmol), alcohol **3** (0.6 mmol), H_2O (5equiv, 18 mg), $CHCl_3$ **2a** (2 mL), the tube was then charged with argon. The mixture was stirred at 120 °C (oil bath) until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 6 h). After the reaction was finished, the combined organic phases concentrated, and the resulting residue was purified by silica gel column chromatography (petroleum/ethyl acetate) to afford the desired product **4**.

(c) General procedure for the synthesis of *α,β*-unsaturated aldehydes 5



To a Schlenk tube were added $Cu(OTf)_2$ (10 mol%), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol, 2 equiv), Na_2CO_3 (0.4 mmol, 2 equiv), alkenes **1** (0.2 mmol), $CHBrCl_2$ **2c** (0.6 mmol, 3 equiv), H_2O (1 mmol), DMSO (2 mL), the tube was then charged with argon. The mixture was stirred at 120 °C (oil bath) until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 12 h). After the reaction was finished, the combined organic phases concentrated, and the resulting residue was purified by silica gel column chromatography (petroleum/ethyl acetate) to afford the desired product **5**.



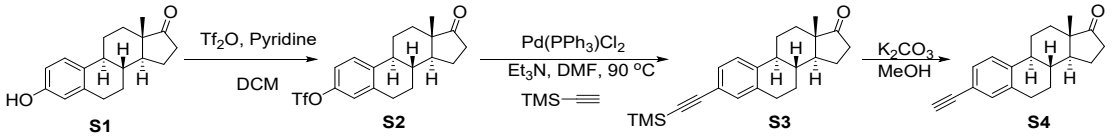
Entry	Variation from the Standard Conditions	**5aa**
1	None	64
2	CuCl	51
3	$FeCl_2$	43
4	$Cu(MeCN)_4PF_4$	52
5	$Cu(MeCN)_4BF_4$	45
6	$Cu(acac)_2$	40
7	Without Na_2CO_3	NR
8	Without 4-$MeOC_6H_4N_2BF_4$	NR
9	K_3PO_4 instead of Na_2CO_3	43
10	$NaHCO_3$ instead of Na_2CO_3	trace
11	NaOH instead of Na_2CO_3	33
12	EA instead of DMSO	NR
13	MeCN instead of DMSO	NR
14	DMA instead of DMSO	NR
15	1,4-dioxane instead of DMSO	NR
16	$PhCF_3$ instead of DMSO	NR
17	DMSO:H_2O = 1:1	trace

[a] Reaction conditions: **1a** (0.2 mmol), $CBrHCl_2$ **2c** (0.6 mmol), $Cu(OTf)_2$ (0.02 mmol), Na_2CO_3 (0.4 mmol), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol), H_2O (1 mmol), at 120 °C under argon atmosphere for 12 h.

Table S1. Screening of optimal reaction conditions for *α,β*-unsaturated aldehydes 5.

(B) General procedure for the synthesis of the starting materials

The common alkene, polyhaloalkane and alcohol substrates were commercially available. The synthesis of the substrate **1x**, **1y**, **1w** and **1z** was described as follows:



Synthesis of S2[1]

3-(Trifluoromethanesulfonyl)estrone (**S2**) was synthesized according to the reported procedure. Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with **S1** (2700 mg, 10.0 mmol, 1.0 equiv) was added DCM (30.0 mL) and pyridine (1580 mg, 1.60 mL, 20.0 mmol, 2.0 equiv). The resulting mixture was cooled to 0°C in an ice/water bath. Tf_2O (3390 mg, 2.10 mL, 15.0 mmol, 1.5 equiv) was added dropwise over ca. 5 minutes. The reaction mixture was warmed to room temperature and stirred for 5 hours. The resulting brown reaction was then quenched by water (15 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the **S2** as a white solid.

Synthesis of S3[1]

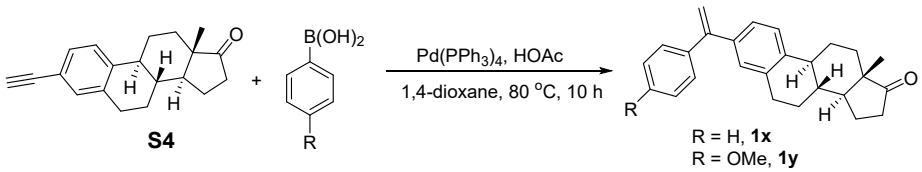
A mixture of **S2** (1610 mg, 4.0 mmol, 1.00 equiv), ethynyltrimethylsilane (0.85 mL, 6.0 mmol,1.5 equiv), Et_3N (3.0 mL), and $Pd(PPh_3)_2Cl_2$ (84 mg, 0.12 mmol, 0.03 equiv) in 15 mL DMF was stirred at 90 °C for 4 h under nitrogen. The reaction mixture was then diluted with water, extracted with 1:1 petroleum ether/ether, washed with water until neutral, and dried (Na_2SO_4), after filtration the filtrate was evaporated. Chromatography of the residue on silica gel provided the corresponding product **S3**.

Synthesis of S4[1]

To **S3** (1160 mg, 3.30 mmol, 1.00 equiv) a solution of K_2CO_3 (520 mg, 4.95 mmol,

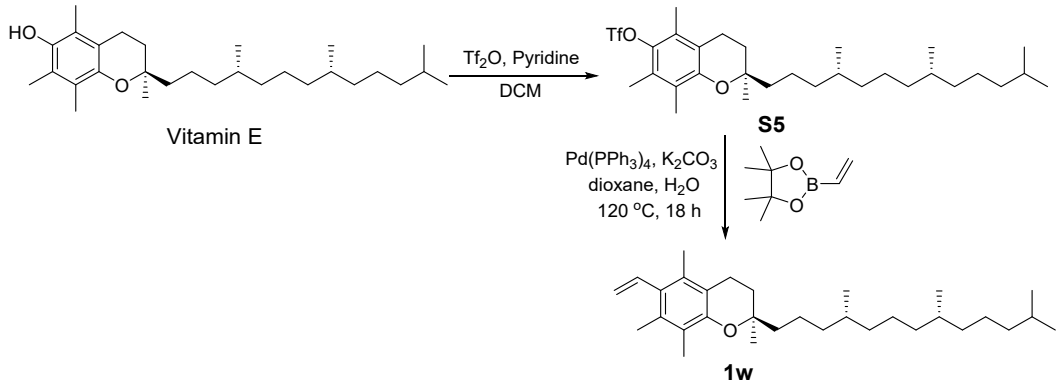
1.5equiv) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that S3 was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S4**.

Synthesis of 1x and 1y[2]



Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with **S4** (278 mg, 1 mmol, 1.0 equiv), Arylboronic acid (2.0 mmol, 2.0 equiv), and $Pd(PPh_3)_4$ (33 mg, 0.03 mmol, 0.03 equiv) was added 1,4-dioxane (8.0 mL) and HOAc (0.10-0.15 equiv), then stirred at 80 °C for 10 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **1x** and **1y**.

Synthesis of 1w[1,3]

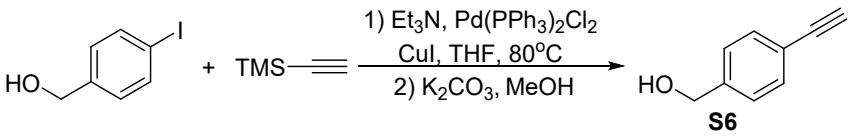


Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with Vitamin E (4300 mg, 10.0 mmol, 1.0 equiv) was added DCM (30.0 mL) and pyridine (1580 mg, 1.6 mL, 20.0 mmol, 2.0 equiv). The resulting mixture was cooled to 0°C in an ice/water bath. Tf_2O (3390 mg, 2.1 mL, 15.0 mmol, 1.5 equiv) was added dropwise

over ca. 5 minutes. The reaction mixture was warmed to room temperature and stirred for 5 hours. The resulting reaction was then quenched by water (15 mL). The layers were separated, and the aqueous layer was extracted with DCM (3×20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the **S5**.

Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with **S5** (562 mg, 1 mmol, 1.0 equiv), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (308 mg, 2.0 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (139 mg, 0.12 mmol, 0.12 equiv), and K_2CO_3(414 mg, 3 mmol, 3equiv), was added dioxane-water (4:1) mixture at 120 °C for 18 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **1w**.

Synthesis of S6[1]

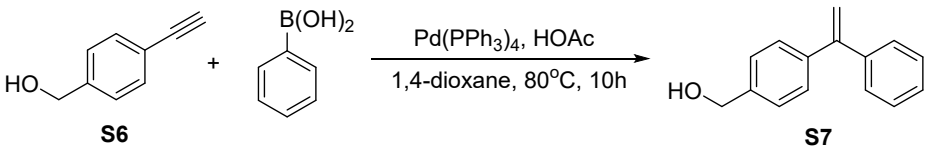


A mixture of (4-iodophenyl)methanol (2400 mg, 10.0 mmol, 1.0 equiv), ethynyltrimethylsilane (2.2 mL, 15.0 mmol, 1.5 equiv), triethylamine (7.5 mL), CuI (190 mg, 1 mmol, 0.1 equiv), and $Pd(PPh_3)_2Cl_2$ (210 mg, 0.30 mmol, 0.03 equiv) in 30 mL THF was stirred at 80 °C for 10 h under nitrogen. The reaction mixture was then diluted with water, extracted with 1:1 petroleum ether/ether, washed with water until neutral, and dried (Na_2SO_4), after filtration the filtrate was evaporated. Chromatography of the residue on silica gel provided the corresponding product (4-((trimethylsilyl)ethynyl)phenyl)methanol.

To (4-((trimethylsilyl)ethynyl)phenyl)methanol (2041 mg, 10.0 mmol, 1.0 equiv) a solution of K_2CO_3 (2070 mg, 15.0 mmol, 1.5 equiv) in 30 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that L2 was

completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S6**.

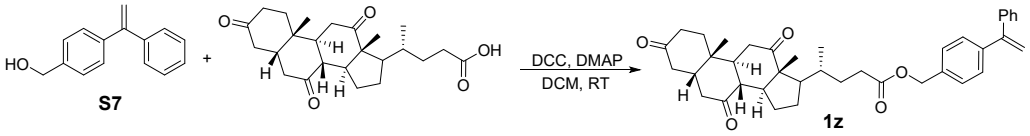
Synthesis of S7[2]



S6 **S7**

Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with S6 (660 mg, 5.0 mmol, 1.0 equiv), phenylboronic acid (1220 mg, 10.0 mmol, 2.0 equiv), and $Pd(PPh_3)_4$ (165 mg, 0.15 mmol, 0.03 equiv) was added 1,4-dioxane (20 mL) and HOAc (0.1-0.15 equiv), then stirred at 80 °C for 10 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **S7**.

Synthesis of 1z[4]

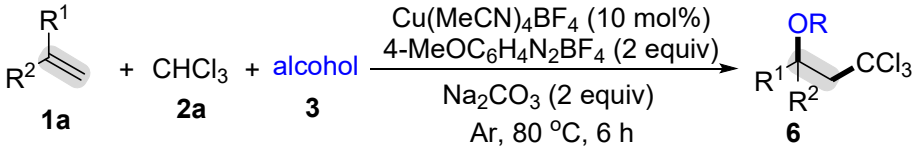


S7 **1z**

Under nitrogen atmosphere, a 25 mL flamed dried round bottom flask was charged with **S7** (210 mg, 1.0 mmol, 1.0 equiv), dehydrocholic acid (804 mg, 2.0 mmol, 1.5 equiv), DMAP (12.2 mg, 0.10 mmol, 10.0 mol%), DCC (412 mg, 2.0 mmol, 2.0 equiv), and DCM (8.0 mL). After the reaction mixture was then stirred at 25 °C for 24 hours, it was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the compound **1z** as a white solid.

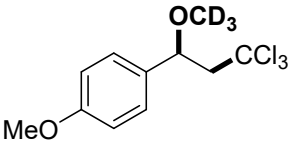
(C) Mechanistic Studies

(a) Isolation of 6b-D3.



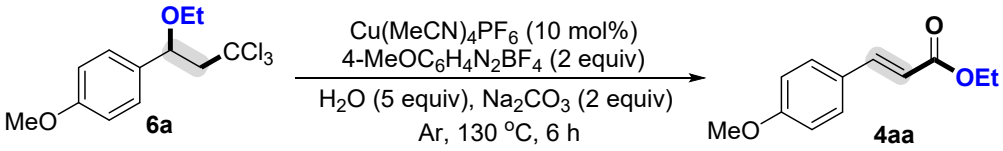
To a Schlenk tube were added substrates $Cu(MeCN)_4BF_6$ (10 mol%), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol, 2 equiv), Na_2CO_3 (0.4 mmol, 2 equiv), alkene **1** (0.2 mmol), CD_3OD **3b-D4** (0.6 mmol), $CHCl_3$ **2a** (2 mL), the tube was then charged with argon. The mixture was stirred at 80 °C until for 6 h. After the reaction was finished, the combined organic phases concentrated, and the resulting residue was purified by silica gel column chromatography (petroleum/ethyl acetate) to afford the desired product **6**.

Methoxy-4-(3,3,3-trichloro-1-(methoxy-D3)propyl)benzene (6b-D3):



Reaction Time: 1.5 h, at 120 °C; Yield: 82%, Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 4.56-4.54 (m, 1H), 3.82 (s, 3H), 3.29-3.24 (m, 1H), 2.99-2.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 132.6, 127.9, 114.1, 97.4, 80.5, 62.1, 55.3, 55.2; LRMS (EI, 70eV) *m/z* (%): 287 (M^++2, 2), 285 (M^+, 2), 54 (100), 135 (20), 111 (4); HRMS *m/z* (ESI) calcd for $C_{11}H_{11}O_2D_3Cl_3$ ($[M+H]^+$) 286.0242, found 286.0239.

(b) Transformation of olefin alkoxy polychloroalkylation product 6a.

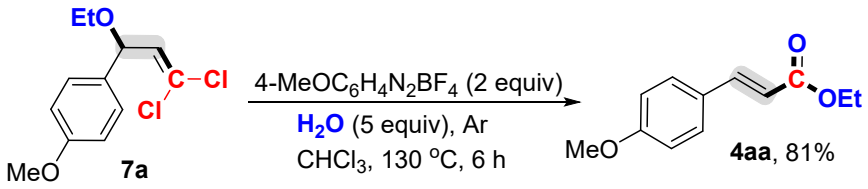


Entry	Variation from the Standard Conditions	**4aa**
1	None	36
2	Without $Cu(MeCN)_4PF_6$	33
3	Without $4\text{-}MeOC_6H_4N_2BF_4$	NR
4	Without Na_2CO_3	37
5	Without Na_2CO_3 and $Cu(MeCN)_4PF_6$	75
6[b]	PhCl instead of $CHCl_3$	36
7[b]	$PhCF_3$ instead of $CHCl_3$	21
8[b]	DMF instead of $CHCl_3$	trace
9[b]	DMSO instead of $CHCl_3$	trace
10[b]	DMA instead of $CHCl_3$	trace
11[b]	MeCN instead of $CHCl_3$	trace
12[b]	130 °C	78

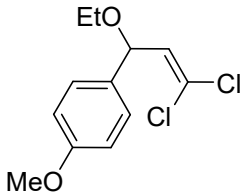
[a] Reaction conditions: **6a** (0.2 mmol), $Cu(MeCN)_4PF_6$ (0.02 mmol), Na_2CO_3 (0.4 mmol), $4\text{-}MeOC_6H_4N_2BF_4$ (0.4 mmol), and $CHCl_3$ (2 mL) at 120 °C under argon atmosphere for 6 h. [b] **6a** (0.2 mmol), $4\text{-}MeOC_6H_4N_2BF_4$ (0.4 mmol), and $CHCl_3$ (2 mL) at 120 °C under argon atmosphere for 6 h.

Table S2. Transformation of 6a.

(c) Transformation of the intermediate 7a.

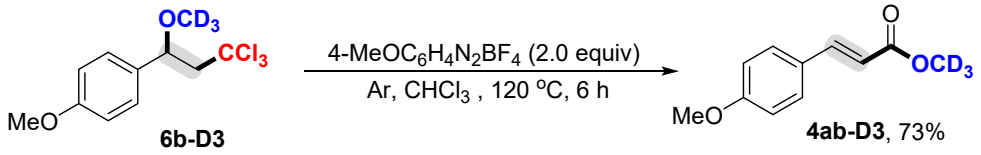


1-(3,3-dichloro-1-ethoxyallyl)-4-methoxybenzene (7a)

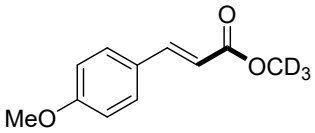


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.06 (d, J = 8.8Hz, 1H), 5.07 (d, J = 8.8 Hz, 1H), 3.80 (s, 3H), 3.57-3.43 (m, 2H), 1.23 (t, J = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.46, 131.89 , 131.20 , 127.69 , 122.53, 114.08 , 78.27 , 64.06 , 55.29 , 15.20 .LRMS (EI, 70 eV) m/z (%): 262 (M^++2, 2), 260 (M^+, 3), 225(100), 197 (49), 137 (16).

(d) Transformation of olefin alkoxy polychloroalkylation product 6b-D3.



1-Methyl-D3 (*E*)-3-(4-methoxyphenyl)acrylate (4ab-D3):



Yield: 73%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 161.4, 144.5, 129.7, 127.1, 115.2, 114.3, 55.4; LRMS (EI, 70eV) *m/z* (%): 195 (M^+, 74), 161 (100), 133 (43), 89 (23); HRMS *m/z* (ESI) calcd for $C_{11}H_{10}O_3D_3$ ($[M+H]^+$) 196.1048, found 196.1052.

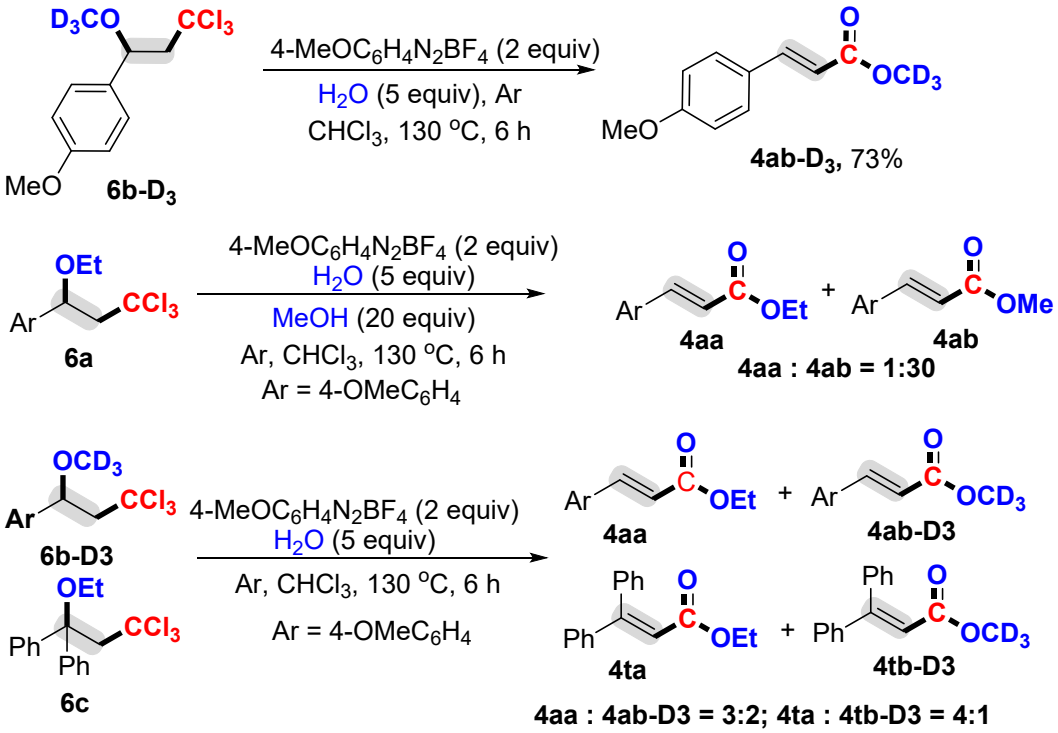


Figure S1. Experiment probing the source of alkoxy.

Performing the alkoxypolychloroalkylation of product **6a** in the presence of 4-$MeOC_6H_4N_2BF_4$ (2 equiv) and CH_3OH (20.0 equiv) obtained the products **4aa** and **4ab** in a 1:30 ratio, while performing the alkoxypolychloroalkylation of products **6b-**

D_3 (0.2 mmol) and **6c** (0.2 mmol) in the presence of 4-$MeOC_6H_4N_2BF_4$ (4 equiv) delivered the *α,β*-unsaturated esters **4aa, 4ab-D_3, 4ta** and **4tb-D_3**. The results of these two cross-control experiments reveal that the alkoxy group of products **6** migrate between molecules, and the alkoxy group is most likely to be removed firstly and then react with an intermediate to form an *α,β*-unsaturated esters **4**.

(f) Experiment probing the role of water

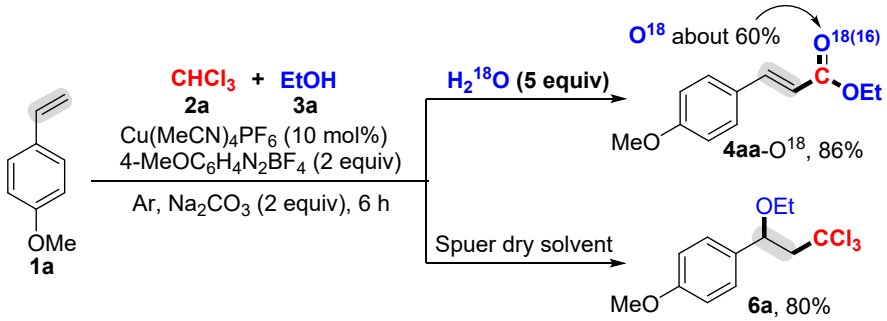
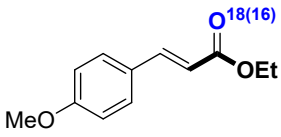


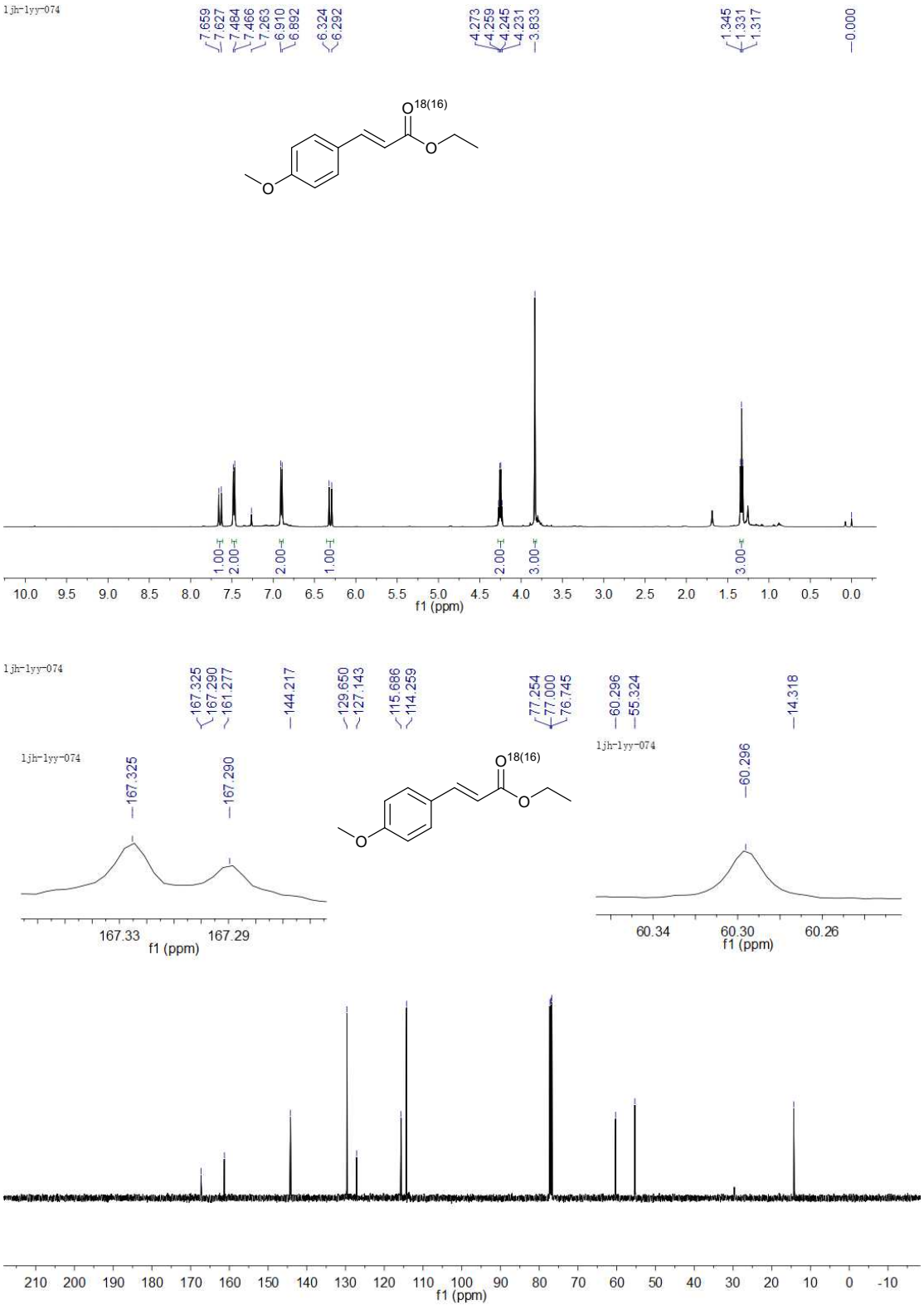
Figure S2. Experiment probing the role of water

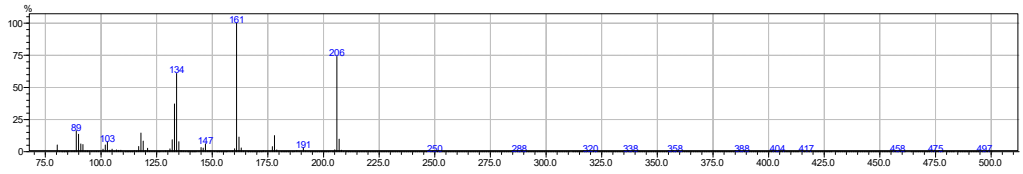
Ethyl (*E*)-3-(4-methoxyphenyl)acrylate (4aa-$O^{18(16)}$)



Yield：86%； Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.27-4.23 (m, 2H), 3.83 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3 (2C), 144.2, 129.7, 127.1, 115.7, 114.3, 60.3, 55.3, 14.3; LRMS (EI, 70eV) *m/z* (%): 208 (M^+, 42), 206 (69), 161 (100), 134 (92); HRMS *m/z* (ESI) calcd for $C_{12}H_{15}O_2$ ($[M+H]^+$) 209.1058, found 209.1059.

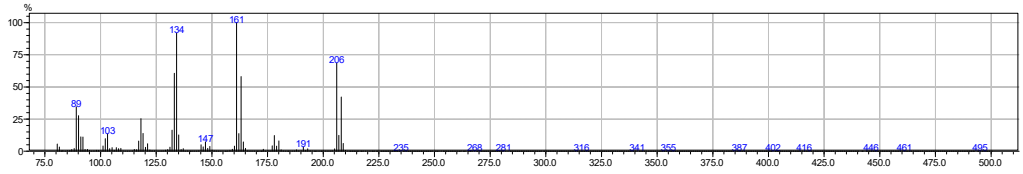
Ethyl (*E*)-3-(4-methoxyphenyl)acrylate (4aa-O$^{18(16)}$)





[MS Spectrum]
# of Peaks 419
Raw Spectrum 10.640 (scan : 1329)
Background No Background Spectrum
Base Peak m/z 225.00 (Inten : 7,436)
Event# 1
m/z Absolute Intensity Relative Intensity

197.00	38	0.03	212.00	11	0.01	227.00	19	0.02
198.00	29	0.02	213.00	22	0.02	228.00	11	0.01
199.00	27	0.02	214.00	5	0.00	229.00	19	0.02
200.00	11	0.01	215.00	16	0.01	230.00	31	0.03
201.00	24	0.02	216.00	14	0.01	231.00	21	0.02
202.00	47	0.04	217.00	29	0.02	232.00	39	0.03
203.00	162	0.14	218.00	22	0.02	233.00	29	0.02
204.00	62	0.05	219.00	36	0.03	234.00	36	0.03
205.05	1701	1.45	220.00	13	0.01	235.00	42	0.04
206.00	**84252**	**71.68**	221.00	63	0.05	236.00	24	0.02
207.00	11122	9.46	222.00	16	0.01	237.00	41	0.03
208.00	**1255**	**1.07**	223.00	30	0.03	238.00	21	0.02
209.00	151	0.13	224.00	41	0.03	239.00	42	0.04
210.00	10	0.01	225.00	26	0.02	240.00	8	0.01
211.00	21	0.02	226.00	29	0.02	241.00	24	0.02

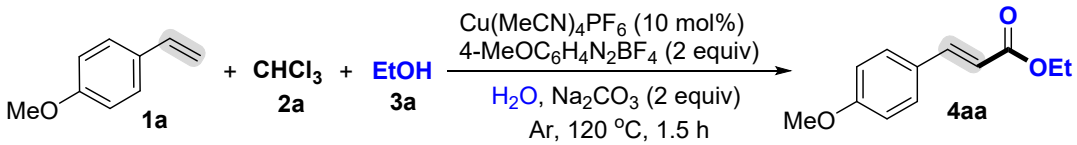


[MS Spectrum]
# of Peaks 419
Raw Spectrum 10.640 (scan : 1329)
Background No Background Spectrum
Base Peak m/z 225.00 (Inten : 7,436)
Event# 1
m/z Absolute Intensity Relative Intensity

189.05	635	0.38	190.10	684	0.40	191.10	5546	3.28

192.10	1066	0.63	203.15	281	0.17	214.00	41	0.02
193.05	3136	1.86	204.05	544	0.32	215.00	49	0.03
194.10	649	0.38	205.15	3219	1.90	216.00	218	0.13
195.10	281	0.17	**206.05**	**115964**	**68.60**	217.00	65	0.04
196.10	78	0.05	207.05	20779	12.29	218.00	106	0.06
197.10	164	0.10	**208.10**	**71332**	**42.20**	219.00	158	0.09
198.10	102	0.06	209.00	10300	6.09	220.00	118	0.07
199.10	57	0.03	210.00	948	0.56	221.00	276	0.16
200.10	490	0.29	211.00	252	0.15	222.00	33	0.02
201.10	124	0.07	212.00	27	0.02	223.00	132	0.08
202.10	196	0.12	213.00	46	0.03	224.00	95	0.06

(g) HMRS Analysis of intermediates



To a Schlenk tube were added substrates $Cu(MeCN)_4PF_6$ (10 mol%), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol, 2 equiv), Na_2CO_3 (0.4 mmol, 2 equiv), alkene **1a** (0.2 mmol), EtOH **3a** (0.6 mmol), H_2O (5equiv), $CHCl_3$ **2a** (2 mL), the tube was then charged with argon. The mixture was stirred at 120 °C for 1.5 h. The reaction solution was collected for in-situ HMRS analysis.

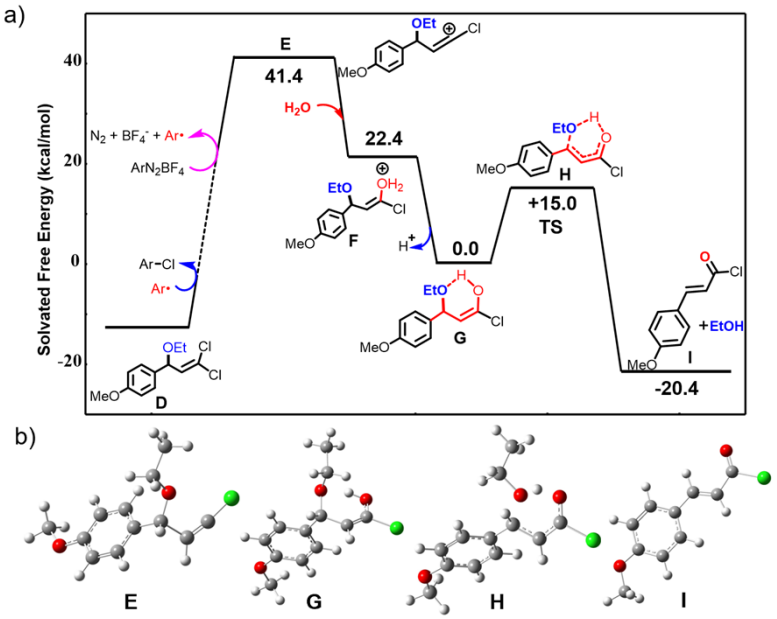


Figure S3. The proposed reaction pathway based on experimental and DFT data calculated data using M06-2X/6-31G* SMD=chloroform.

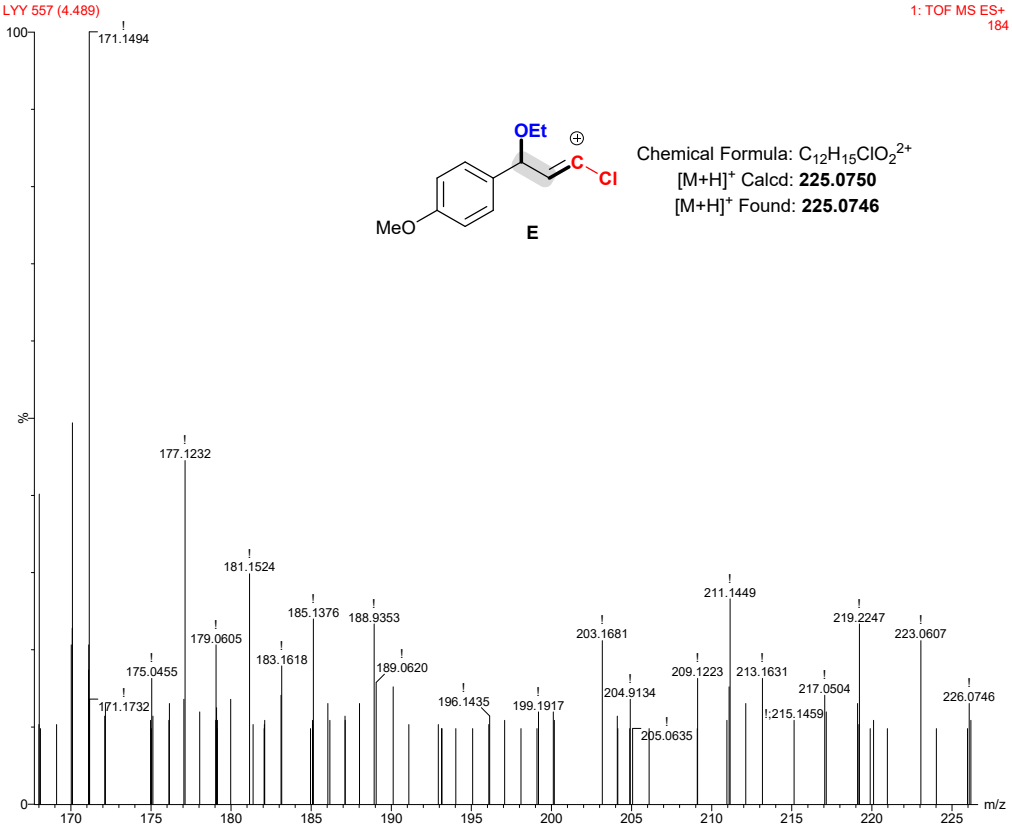
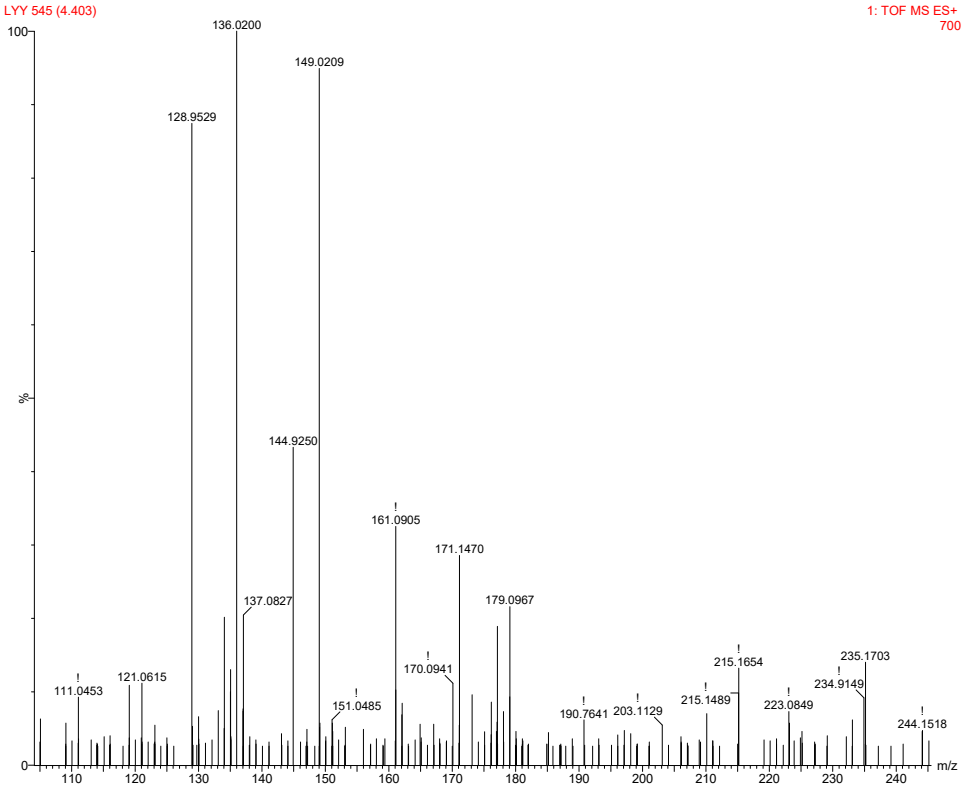


Figure S4. HMRS monitoring of intermediate E.



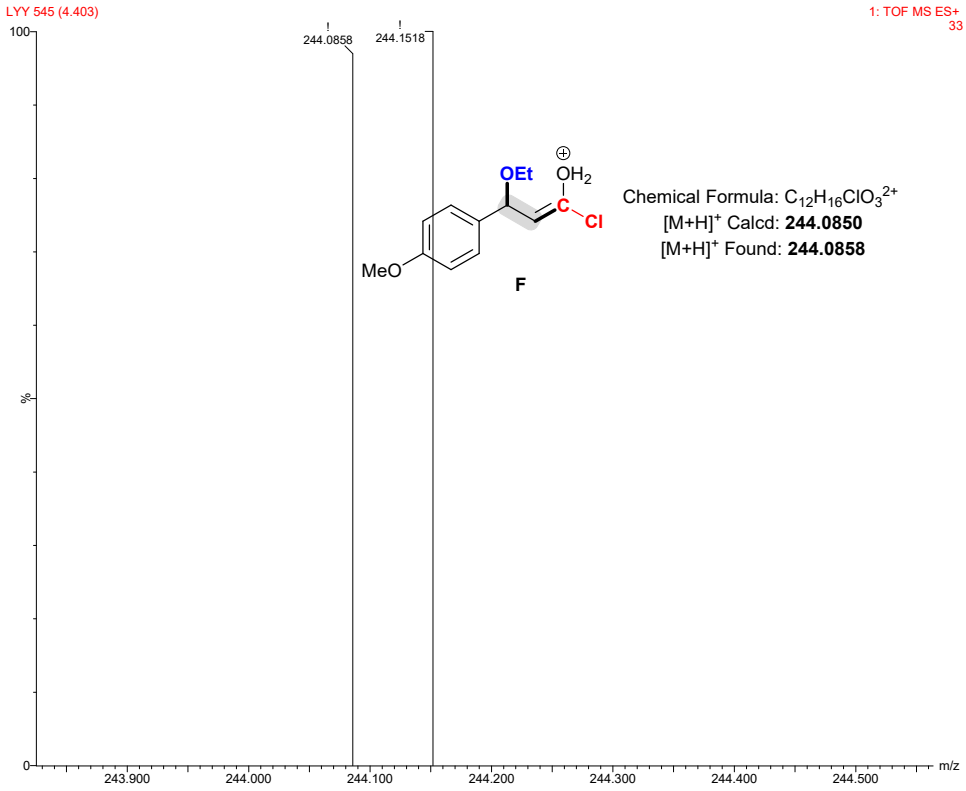


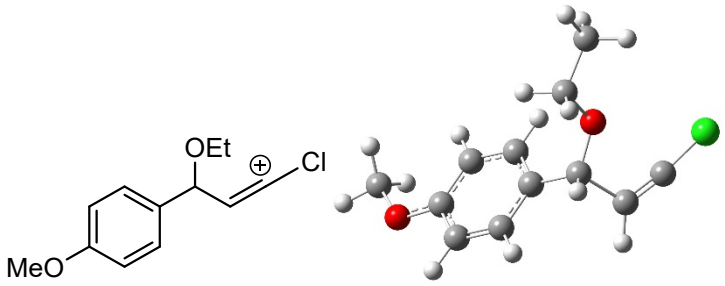
Figure S5. HMRS monitoring of intermediate F.

(g) Computational Details:

All of the quantum chemical calculations were performed using the Gaussian 09 program.[5] Geometry optimizations and frequency calculations were performed at the M06-2X/6-31G* level of theory with SMD solvation in $CDCl_3$.[6-8] The stationary points were characterized by the presence of only positive eigenvalues of the Hessian for minima or a single negative eigenvalue of the Hessian for transition structures. Single point calculations of the potential energy were carried out using M06-2X/6-311++G** level of theory with SMD solvation in chloroform.

Cartesian Coordinates of DFT Optimized Structures

Structure: **E**



Charge, Spin Multiplicity: 1, 1

Number of imaginary frequencies: 0

SCF Energy: -1075.930697 hartree

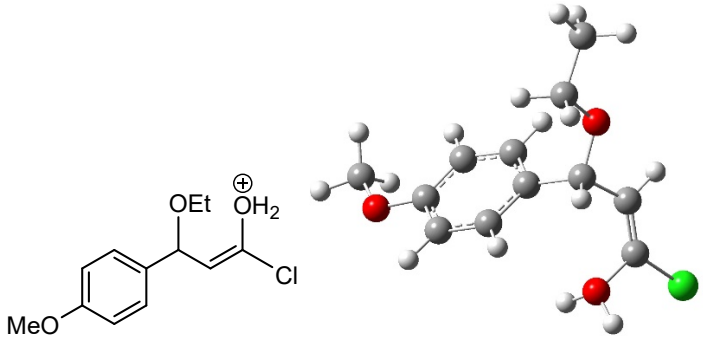
SCF Energy + ZPVE: -1075.693685 hartree

Free Energy: -1075.738162 hartree

Symbol	X	Y	Z
C	-3.09762400	-0.17304600	0.06958800
C	-2.14229700	-0.00918300	-0.94243100
C	-0.79642500	0.06033800	-0.60349800
C	-0.38953700	-0.01657200	0.72884600
C	-1.35026500	-0.18650100	1.73425700
C	-2.69170000	-0.26351100	1.41082300
H	-2.43598200	0.06355900	-1.98280700
H	-0.05065400	0.19027600	-1.38357600
H	-1.04222700	-0.24585900	2.77546300
H	-3.45255300	-0.38247200	2.17504600
O	-4.42391800	-0.25243100	-0.14275200
C	-4.89972700	-0.14165800	-1.47693700
H	-4.50611200	-0.94871400	-2.10429900
H	-5.98440900	-0.22596700	-1.41367900
H	-4.63217400	0.82867000	-1.90923600
C	1.06679500	0.05264400	1.07105300
C	1.67081500	-1.39717000	0.97167300
C	2.62076300	-1.50966000	0.13521800
O	1.83703000	0.82341000	0.19497600
C	1.65489300	2.23565800	0.35388700
H	0.60782700	2.49389700	0.15705500
H	1.89161700	2.50859300	1.39062200
C	2.58128100	2.92276300	-0.62314000

H	2.33781800	2.63497700	-1.64997000
H	2.47381400	4.00705700	-0.53395900
H	3.62310900	2.65963600	-0.41951600
H	1.22199900	0.34144400	2.12138900
Cl	3.76551800	-1.51380600	-0.95289900
H	1.26738500	-2.20283500	1.58291400

Structure: **F**



Charge, Spin Multiplicity: 1, 1

Number of imaginary frequencies: 0

SCF Energy: -1152.414601 hartree

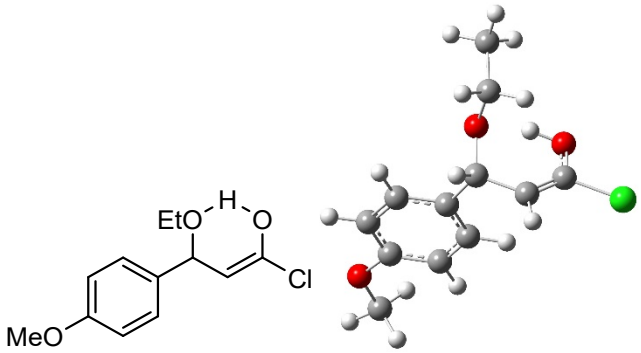
SCF Energy + ZPVE: -1152.147902 hartree

Free Energy: -1152.192991 hartree

Symbol	X	Y	Z
C	-2.86251000	-0.62027800	0.18257800
C	-2.27629600	-0.04313000	-0.94979800
C	-0.97396500	0.44289200	-0.87524800
C	-0.24449000	0.36941700	0.31016500
C	-0.84673000	-0.19131600	1.44109000
C	-2.14079600	-0.68844800	1.38071000
H	-2.82255600	0.03417900	-1.88282300
H	-0.52295800	0.90105400	-1.75204000
H	-0.30472600	-0.22090800	2.38478900
H	-2.62196000	-1.11944600	2.25299400
O	-4.11284900	-1.13152000	0.21909600
C	-4.88973300	-1.07414400	-0.96687800

H	-4.41345000	-1.63235400	-1.78081500
H	-5.84537800	-1.53792100	-0.72158600
H	-5.05852700	-0.03779300	-1.28017500
C	1.18447300	0.89041000	0.35271100
C	2.11490300	-0.03414100	-0.40499900
C	2.44610600	-1.25207600	-0.02230200
O	1.33352200	2.13821200	-0.27593000
C	0.73693200	3.20753200	0.45158800
H	-0.33161500	3.00596700	0.60397700
H	1.21159200	3.27973600	1.44132300
C	0.93838100	4.47761100	-0.34422600
H	0.45535100	4.39497300	-1.32198100
H	0.50068200	5.32653400	0.18824300
H	2.00350700	4.67331800	-0.49668700
H	1.51280200	0.94621900	1.40379800
Cl	3.43600200	-2.41307800	-0.77996900
H	2.51824400	0.32453700	-1.34841600
O	1.86023500	-1.72733800	1.21948500
H	2.49596900	-2.17186700	1.83934800
H	1.04609200	-2.28470900	1.09596600

Structure: **G**



Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 0

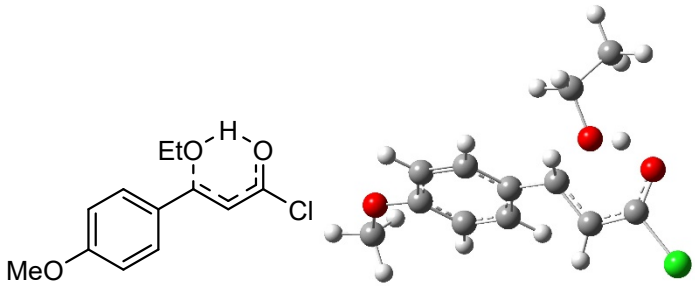
SCF Energy: -1152.062255 hartree

SCF Energy + ZPVE: -1151.85189 hartree

Free Energy: -1151.85189 hartree

Symbol	X	Y	Z
C	3.35421600	0.10362000	-0.01850800
C	2.47513300	-0.96357500	0.16087000
C	1.12039600	-0.79662500	-0.13600500
C	0.62935600	0.41214000	-0.61475200
C	1.52699000	1.47459800	-0.79076600
C	2.87115000	1.32945400	-0.49977100
H	2.82505000	-1.92142500	0.52742600
H	0.44436800	-1.63497500	0.00585600
H	1.15746600	2.42958400	-1.15747900
H	3.57335600	2.14614300	-0.63483000
O	4.68477100	0.05410700	0.23918900
C	5.21131700	-1.16526400	0.73076700
H	5.08080300	-1.97569600	0.00407700
H	6.27591700	-0.99125200	0.89056100
H	4.74373400	-1.44748800	1.68127800
C	-0.84196000	0.65360900	-0.89860500
C	-1.67169000	-0.60291200	-1.02800500
C	-2.28325200	-1.14749600	0.02532900
O	-1.32267900	1.49537500	0.16168300
C	-2.55026000	2.16004100	-0.14188100
H	-2.40397700	2.77899300	-1.03764300
H	-3.33300800	1.42214500	-0.36414100
C	-2.92523300	3.00480500	1.05560700
H	-2.13637900	3.72888100	1.27738100
H	-3.85355800	3.54780500	0.85658400
H	-3.07952200	2.37409900	1.93707100
H	-0.92650900	1.22061300	-1.83717000
Cl	-3.22475000	-2.61174800	-0.11635000
H	-1.74766100	-1.08070100	-1.99677100
O	-2.29477700	-0.69347600	1.28594800
H	-1.83482100	0.18058400	1.26550100

Structure: **H**



Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 1

SCF Energy: -1152.035988 hartree

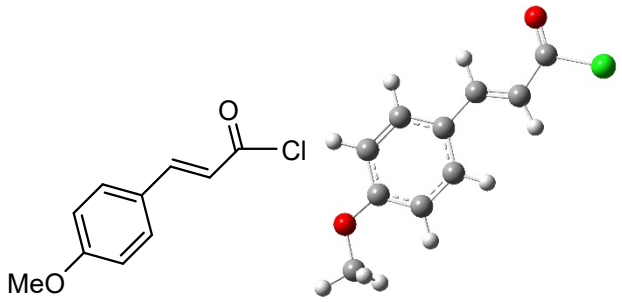
SCF Energy + ZPVE: -1151.7831 hartree

Free Energy: -1151.827949 hartree

Symbol	X	Y	Z
C	-3.41775300	-0.29610000	0.21006300
C	-2.58649500	-0.81129700	-0.79130600
C	-1.20687200	-0.69431100	-0.66080800
C	-0.63708500	-0.07020600	0.45028500
C	-1.48263800	0.45929800	1.43389800
C	-2.85749100	0.34287700	1.32403200
H	-3.00144500	-1.29810100	-1.66591600
H	-0.56220800	-1.08868600	-1.44174200
H	-1.05218200	0.95517700	2.30060600
H	-3.52292700	0.73693400	2.08518500
O	-4.76730200	-0.36404700	0.18810800
C	-5.38031400	-1.01294300	-0.91411800
H	-5.05915600	-2.05803500	-0.98670300
H	-6.45324000	-0.97708000	-0.72380100
H	-5.15971800	-0.49317800	-1.85327100
C	0.83318500	0.05664100	0.58336900
C	1.67254000	-1.06417200	0.20697600
C	3.01727500	-0.78373000	0.16764500
O	1.29584300	1.30273900	-0.45853300
C	0.89334300	2.63487000	-0.05327000
H	-0.18340000	2.68221700	-0.22481600
H	1.09456700	2.75203900	1.01790200
C	1.64861700	3.64987200	-0.88220100

H	1.44733500	3.50626400	-1.94674200
H	1.33102700	4.65735700	-0.59897900
H	2.72689100	3.57200200	-0.70974400
H	1.12893300	0.56856100	1.50505100
Cl	4.11905400	-2.19456600	-0.17466000
O	3.56027000	0.32931400	0.29189800
H	2.29795200	1.19602300	-0.31127000
H	1.25530300	-2.01270700	-0.09569700

Structure: **I**



Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 0

SCF Energy: -997.0503865 hartree

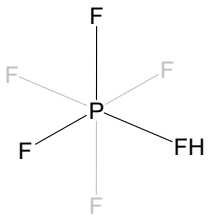
SCF Energy + ZPVE: -996.8805885 hartree

Free Energy: -996.9204395 hartree

Symbol	X	Y	Z
C	3.14193800	0.14664900	-0.00009200
C	2.29332400	-0.96941700	0.00010700
C	0.91880400	-0.78310800	0.00023400
C	0.35640600	0.50092400	0.00015600
C	1.22607500	1.60644700	0.00008800
C	2.59737900	1.43835900	-0.00007600
H	2.69630100	-1.97509800	0.00017100
H	0.27513000	-1.65773000	0.00039800
H	0.80877000	2.61009400	0.00008400
H	3.27261300	2.28769200	-0.00019600
O	4.48809400	0.07333500	-0.00023500

C	5.08578700	-1.21367900	0.00001700
H	4.80812200	-1.78013500	-0.89566500
H	6.16224500	-1.04239000	-0.00003400
H	4.80810300	-1.77975700	0.89592600
C	-1.07785500	0.74178200	0.00019300
C	-2.06110800	-0.18146900	-0.00024000
C	-3.44151600	0.28852100	-0.00008800
H	-1.38004600	1.78873700	0.00059700
Cl	-4.63771700	-1.08685600	-0.00001200
O	-3.85780400	1.40487900	-0.00003600
H	-1.88776700	-1.25061800	-0.00070400

Structure: **Hexafluorophosphate acid**



Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 0

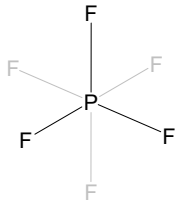
SCF Energy: -941.1279378 hartree

SCF Energy + ZPVE: -941.1008898 hartree

Free Energy: -941.1321488 hartree

Symbol	X	Y	Z
P	0.44502600	0.45811500	0.36331600
F	0.44502600	2.00734800	0.06058700
F	0.44502600	0.45811500	1.91029400
F	-1.10420700	0.45811500	0.06058700
F	0.44502600	-1.09111800	0.06058700
F	1.99425900	0.45811500	0.06058700
F	0.44502600	0.45811500	-2.05415500
H	0.44502600	0.45811500	-2.99324700

Structure: **Hexafluorophosphate (PF_6^-)**



Charge, Spin Multiplicity: -1, 1

Number of imaginary frequencies: 0

SCF Energy: -940.748092 hartree

SCF Energy + ZPVE: -940.728252 hartree

Free Energy: -940.755367 hartree

Symbol	X	Y	Z
P	0.44502600	0.45811500	0.00000000
F	0.44502600	2.08037400	0.00000000
F	0.44502600	0.45811500	1.62225800
F	-1.17723200	0.45811500	0.00000000
F	0.44502600	-1.16414300	0.00000000
F	2.06728500	0.45811500	0.00000000
F	0.44502600	0.45811500	-1.62225800

Structure: **EtOH**

Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 0

SCF Energy: -155.0197931 hartree

SCF Energy + ZPVE: -154.9640201 hartree

Free Energy: -154.9640201 hartree

Symbol	X	Y	Z
O	-1.23144700	-0.26080700	-0.11074500
H	-1.23414300	-0.89470900	0.62296200
C	-0.08370300	0.55828700	0.04731700
H	-0.12392800	1.28714000	-0.76798800
H	-0.13342200	1.12146400	0.99071000
C	1.20704900	-0.24016700	-0.02174600

H	2.07911700	0.41649300	0.06060400
H	1.25589900	-0.96899500	0.79568500
H	1.26798100	-0.78365200	-0.96944200

Structure: **H_2O**

Charge, Spin Multiplicity: 0, 1

Number of imaginary frequencies: 0

SCF Energy: -76.42827179 hartree

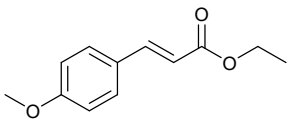
SCF Energy + ZPVE: -76.40690279 hartree

Free Energy: -76.42456779 hartree

Symbol	X	Y	Z
O	0.00000000	0.00000000	0.11951500
H	0.00000000	0.76152500	-0.47805800
H	0.00000000	-0.76152500	-0.47805800

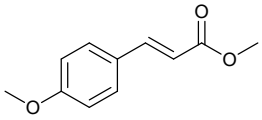
(D) Analytical data

Ethyl (*E*)-3-(4-methoxyphenyl)acrylate (4aa)[9]:



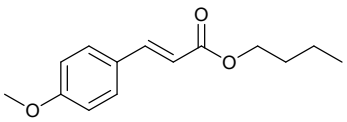
Yield: 86%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.27-4.23 (m, 2H), 3.83 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 161.3, 144.2, 129.6, 127.2, 115.7, 114.3, 60.3, 55.3 , 14.3; LRMS (EI, 70eV) *m/z* (%): 206 (M^+, 73), 160 (100), 134 (64), 133 (39); HRMS *m/z* (ESI) calcd for $C_{12}H_{15}O_3$ ($[M+H]^+$) 207.1010, found 207.1013.

Methyl (*E*)-3-(4-methoxyphenyl)acrylate (4ab)[9]:



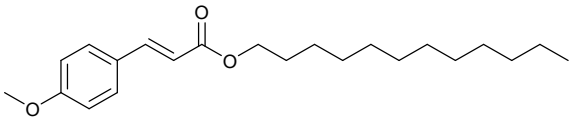
Yield: 73%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J*=9.0 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 161.3, 144.5, 129.7, 127.1, 115.2, 114.3, 55.3, 51.5; LRMS (EI, 70eV) *m/z* (%): 192 (M^+, 72), 161 (100), 133 (37), 89 (27); HRMS *m/z* (ESI) calcd for $C_{11}H_{13}O_3$ ($[M+H]^+$) 193.0859, found 193.0860.

Butyl (*E*)-3-(4-methoxyphenyl)acrylate (4ac)[10]:



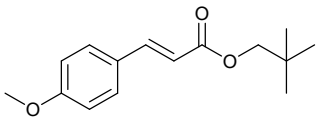
Yield: 77%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 1.70-1.67 (m, 2H), 1.46-1.43 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 161.3, 144.2, 129.6, 127.2, 115.7, 114.3, 64.2, 55.3, 30.8, 19.2, 13.7; LRMS (EI, 70eV) *m/z* (%): 234 (M^+, 38), 178 (100), 161 (98), 134 (39); HRMS *m/z* (ESI) calcd for $C_{12}H_{19}O_3$ ($[M+H]^+$) 235.1329, found 235.1333.

Dodecyl (*E*)-3-(4-methoxyphenyl)acrylate (4ad):



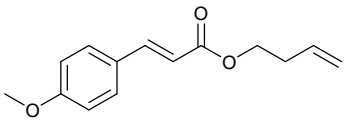
Yield: 53%, Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 1.71-1.64 (m, 2H), 1.26 (s, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 161.3, 144.2, 129.7, 127.2, 115.7, 114.3, 64.6, 55.3, 31.9, 29.6(3C), 29.5, 29.3(2C), 26.0, 22.7, 14.1; LRMS (EI, 70eV) *m/z* (%): 346 (M^+, 15), 178 (100), 161 (63), 134 (27); HRMS *m/z* (ESI) calcd for $C_{22}H_{35}O_3$ ($[M+H]^+$) 347.2581, found 347.2582.

Neopentyl (*E*)-3-(4-methoxyphenyl)acrylate (4ae):



Yield: 58%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.90 (s, 2H), 3.84 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 161.3, 144.2, 129.7, 127.2, 115.8, 114.3, 73.7, 55.3, 31.5, 26.5; LRMS (EI, 70eV) *m/z* (%): 248 (M^+, 38), 178 (24), 161 (100), 133 (21); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}O_3$ ($[M+H]^+$) 249.1485, found 249.1484.

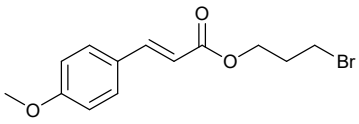
But-3-en-1-yl (*E*)-3-(4-methoxyphenyl)acrylate (4af):



Yield: 78%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.87-5.82 (m, 1H), 5.17-5.09 (m, 2H), 4.25 (t, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 2.48-2.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 161.3, 144.4, 134.1, 129.7, 127.1, 117.1 115.5, 114.3, 63.4, 55.3 (2C), 33.2;

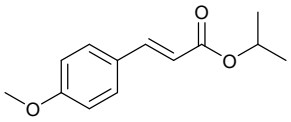
LRMS (EI, 70eV) *m/z* (%): 232 (M^+, 32), 178 (100), 161 (98), 133 (34); HRMS *m/z* (ESI) calcd for $C_{14}H_{17}O_3$ ($[M+H]^+$) 233.1172, found 233.1170.

3-Bromopropyl (*E*)-3-(4-methoxyphenyl)acrylate (4ag):



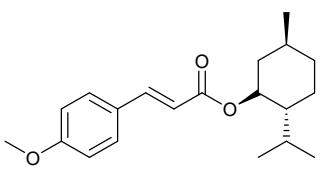
Yield: 53%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.34 (t, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.28-2.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 161.5, 144.8, 129.8, 127.0, 115.1, 114.3, 62.1, 55.4, 31.9, 29.5; LRMS (EI, 70eV) *m/z* (%): 300 (M^+ + 2, 3), 298 (3), 268 (53), 253 (100), 145 (78); HRMS *m/z* (ESI) calcd for $C_{13}H_{16}O_3Br$ ($[M+H]^+$) 299.0277, found 299.0275.

Isopropyl (*E*)-3-(4-methoxyphenyl)acrylate (4ah)[11]:



Yield: 58%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.13 (m, 1H), 3.84 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 161.2, 144.0, 129.6, 127.2, 116.2, 114.2,, 67.6, 55.3, 22.0; LRMS (EI, 70eV) *m/z* (%): 220 (M^+, 97), 178 (92), 161(100), 134 (99); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_3$ ($[M+H]^+$) 211.1172, found 211.1172.

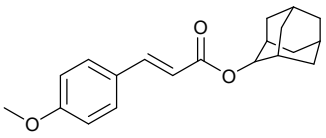
(1R,2R,5S)-2-Isopropyl-5-methylcyclohexyl (*E*)-3-(4-methoxyphenyl)acrylate (4ai)[12]:



Yield: 55%, Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.84-4.79 (m, 1H), 3.83 (s, 3H), 2.06 (d, *J*

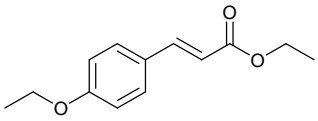
= 12.0 Hz, 1H), 1.95-1.91 (m, 1H), 1.71-1.68 (m, 2H), 1.63-1.56 (m, 1H), 1.47-1.42 (m, 2H), 1.12 – 1.00 (m, 2H), 0.93-0.90 (m, 6H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 161.2, 144.0, 129.6, 127.3, 116.2, 114.3, 74.0, 55.3, 47.2, 41.0, 34.31 (s), 31.4, 26.3, 23.5, 22.0, 20.8, 16.4; LRMS (EI, 70eV) *m/z* (%): 316 (M^+, 27), 178 (100), 133 (51), 95 (63); HRMS *m/z* (ESI) calcd for $C_{20}H_{29}O_3$ ($[M+H]^+$) 317.2111, found 317.2108.

(1r,3r,5r,7r)-Adamantan-2-yl (*E*)-3-(4-methoxyphenyl)acrylate (4aj):



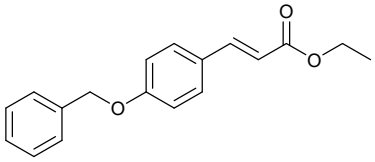
Yield: 48%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.05 (s, 1H), 3.84 (s, 3H), 2.12-2.07 (m, 4H), 1.88-1.76 (m, 8H), 1.61-1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 161.2, 143.8, 129.6, 127.3, 116.6, 114.3, 55.3, 37.4, 36.4, 31.9 (2C), 27.3, 27.0; LRMS (EI, 70eV) *m/z* (%): 312 (M^+, 74), 267 (33), 178 (83), 161 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{25}O_3$ ($[M+H]^+$) 313.1798, found 313.1802.

Ethyl (*E*)-3-(4-ethoxyphenyl)acrylate (4ba)[13]:



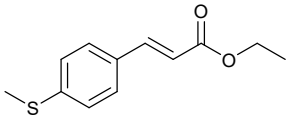
Yield: 77%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.25 (m, 2H), 4.05 (m, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 160.7, 144.3, 129.6, 126.9, 115.5, 114.7, 63.5, 60.3, 14.7, 14.3; LRMS (EI, 70eV) *m/z* (%):220 (M^+, 100), 175 (59), 147 (97), 120 (59); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_3$ ($[M+H]^+$) 221.1172, found 211.1169.

Ethyl (*E*)-3-(4-(benzyloxy)phenyl)acrylate (4ca)[14]:



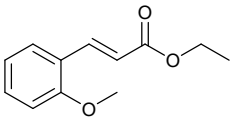
Yield: 80%, Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.48-7.46 (m, 2H), 7.44 – 7.38 (m, 4H), 7.35-7.34 (m, 1H), 6.98-6.97 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.10 (s, 2H), 4.27-4.23 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 160.5, 144.2, 136.5, 129.7, 128.6, 128.1, 127.4, 115.9, 115.2, 70.1, 60.3, 14.3; LRMS (EI, 70eV) *m/z* (%):282 (M^+, 8), 237 (3), 207 (5), 91 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_3$ ($[M+H]^+$) 283.1329, found 283.1332.

Ethyl (*E*)-3-(4-(methylthio)phenyl)acrylate (4da)[15]:



Yield: 45%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.28-4.24 (m, 2H), 2.50 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 144.0, 141.8, 131.0, 128.4, 126.0, 117.2, 60.4, 15.2, 14.3; LRMS (EI, 70eV) *m/z* (%): 222 (M^+, 100), 177 (62), 150 (65), 134 (49); HRMS *m/z* (ESI) calcd for $C_{12}H_{15}O_2S$ ($[M+H]^+$) 223.0787, found 223.0791.

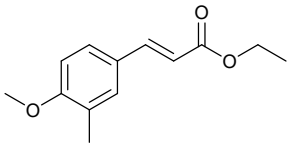
Ethyl (*E*)-3-(2-methoxyphenyl)acrylate (4ga)[9]:



Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.0 Hz, 1H), 7.52-7.50 (m, 1H), 7.37-7.32 (m, 1H), 6.97-6.94 (m, 1H), 6.91(d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.28-4.24 (m, 2H), 3.89 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 158.3, 140.0, 131.4, 128.9, 123.4, 120.6, 118.8, 111.1, 60.3, 55.4, 14.4; LRMS (EI, 70eV)

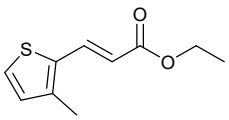
m/z (%): 206 (M^+, 69), 161 (100), 147 (91), 118 (53); HRMS *m/z* (ESI) calcd for $C_9H_{15}O_3$ ($[M+H]^+$) 207.1016, found 207.1016.

Ethyl (*E*)-3-(4-methoxy-3-methylphenyl)acrylate (4ha)



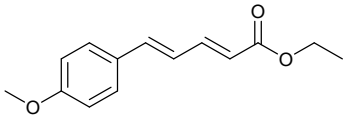
Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.34 (s, 2H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.25 (m, 2H), 3.85 (s, 3H), 2.22 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 159.6, 144.5, 130.0, 127.7, 127.2, 126.6, 115.3, 109.8, 60.2, 55.4, 16.2, 14.3; LRMS (EI, 70eV) *m/z* (%): 220 (M^+, 100), 175 (99), 148 (94), 115 (36); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_3$ ($[M+H]^+$) 221.1172, found 221.1168.

Ethyl (*E*)-3-(3-methylthiophen-2-yl)acrylate (4ja):



Yield: 52%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.0 Hz, 1H), 7.25 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.5 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 4.25 (m, 2H), 2.34 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 141.2, 135.4, 133.6, 131.1, 126.8, 115.9, 60.4, 14.3, 14.1; LRMS (EI, 70eV) *m/z* (%): 196 (M^+, 98), 151 (100), 123 (99), 97 (33); HRMS *m/z* (ESI) calcd for $C_{10}H_{13}SO_2$ ($[M+H]^+$) 197.0631, found 197.0629.

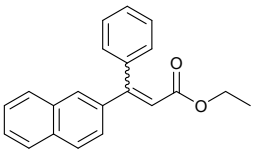
Ethyl (2*E*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dienoate (4ka):



Yield: 47%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 1H), 7.42-7.40 (m, 2H), 6.89-6.87 (m, 2H), 6.84 (s, 1H), 6.78-6.72 (m, 1H), 5.94 (d, *J* = 16.0 Hz, 1H), 4.24-4.20 (m, 2H), 3.83 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 160.4, 145.0,

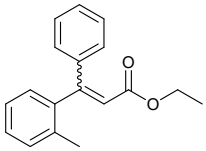
140.1, 128.8, 128.6, 124.1, 120.0, 114.2, 60.2, 55.3, 14.3; LRMS (EI, 70eV) *m/z* (%): 232 (M^+, 58), 187 (27), 159 (100), 115 (52); HRMS *m/z* (ESI) calcd for $C_{14}H_{17}O_3$ ($[M+H]^+$) 233.1172, found 233.1171.

Ethyl -3-(naphthalen-2-yl)-3-phenylacrylate (4ma):



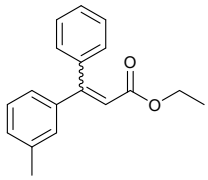
Yield: 87%, E/Z = 1.5:1; Yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85-7.68 (m, 3H), 7.50-7.24 (m, 9H), 6.50 (s, 0.6H), 6.45 (s, 0.4H), 4.08-4.02 (m, 2H), 1.13 (t, *J* = 7.0 Hz, 1.7H), 1.04 (t, *J* = 7.0 Hz, 1.3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 156.4, 129.2, 128.8, 128.6, 128.4 (2C), 128.2 (2C), 127.9, 127.5, 127.3 (2C), 127.0, 126.4, 125.1, 117.8, 117.7, 60.1, 14.0(2C); LRMS (EI, 70eV) *m/z* (%): 302 (M^+, 100), 257 (63), 229 (80),202 (19); HRMS *m/z* (ESI) calcd for $C_{21}H_{19}O_2$ ($[M+H]^+$) 303.1380, found 303.1378.

Ethyl-3-phenyl-3-(*o*-tolyl)acrylate (4na):



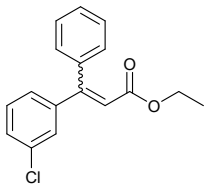
Yield: 87%, E/Z > 20:1;Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 4H), 7.28-7.26 (m, 2H), 7.26-7.22(m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 4.03-3.99 (m, 2H), 2.08 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 155.9, 139.2, 138.6, 135.3, 129.8, 129.4, 128.5, 128.4, 127.7, 127.4, 125.4, 117.6, 59.9, 19.5, 13.9; LRMS (EI, 70eV) *m/z* (%): 266 (M^+, 18), 221 (83), 192 (89), 178 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_2$ ($[M+H]^+$) 267.1380, found 267.1385.

Ethyl-3-phenyl-3-(*m*-tolyl)acrylate (4oa):



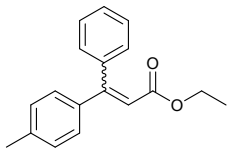
Yield: 74%, E/Z = 1:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4H), 7.22-7.00 (m, 5H), 6.35 (s, 0.5H), 6.34 (s, 0.5H), 4.08-4.03 (m, 2H), 2.35 (s, 1.5H), 2.32 (s, 1.5H), 1.13-1.10 (m 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2(2C), 156.7, 156.6, 129.1, 129.8, 128.8, 128.3(2C), 128.2, 127.8, 117.3(2C), 60.0, 21.40 (2C), 14.0; LRMS (EI, 70eV) *m/z* (%): 266 (M^+, 18), 221 (83), 192 (89), 178 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_2$ ($[M+H]^+$) 267.1380, found 267.1385.

Ethyl-3-(3-chlorophenyl)-3-phenylacrylate (4pa):



Yield: 65%, E/Z = 1.5:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.31 (m, 5H), 7.28-7.17 (m, 3H), 7.11-7.10 (m, 1H), 6.38 (s, 0.6H), 6.34 (s, 0.4H), 4.05 (m, 2H), 1.12 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.72 (2C), 154.8,154.7, 142.7, 140.7, 140.0, 138.2, 134.4, 133.8, 129.6 (2C), 129.3, 129.1(2C),129.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.3, 126.4, 118.6, 118.1, 60.2, 13.9; LRMS (EI, 70eV) *m/z* (%): 286 (M^+, 37), 241 (55), 214 (42), 178 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{16}O_2Cl$ ($[M+H]^+$) 287.0833, found 287.0833.

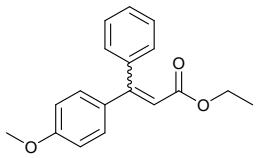
Ethyl-3-phenyl-3-(*p*-tolyl)acrylate (4qa):



Yield: 73%, E/Z = 1:1;Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.21-7.10 (m, 5H), 6.35 (s, 0.5H), 6.32 (s, 0.5H), 4.09-4.03 (m, 2H), 2.39 (s, 1.5H), 2.35 (s, 1.5H), 1.15 (t, *J* = 7.0 Hz, 1.5H), 1.10 (t, *J* = 7.0 Hz, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 166.1, 156.8, 156.5, 129.1, 129.0, 128.5, 128.3 (2C), 128.2, 127.8, 117.0, 116.4, 59.9 (2C), 21.4, 21.2,

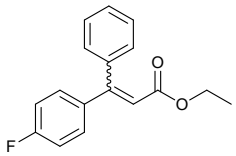
14.0 (2C); LRMS (EI, 70eV) *m/z* (%): 266 (M^+, 88), 221 (100), 194 (80), 178 (72); HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_2$ ($[M+H]^+$) 267.1380, found 267.1385.

Ethyl-3-(4-methoxyphenyl)-3-phenylacrylate (4ra):



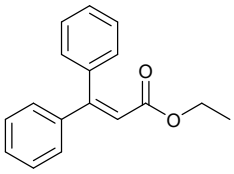
Yield: 76%, Red oil; E/Z = 1.5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.37 (m, 2H), 7.31 (m, 2H), 7.23-7.15 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 0.8H), 6.84 (d, *J* = 9.0 Hz, 1.2H), 6.31 (s, 0.6H), 6.28 (s, 0.4H), 4.11-4.01 (m, 2H), 3.84 (s, 1.2H), 3.81 (s, 1.8H), 1.19-1.10 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 160.7, 156.3, 139.2, 130.9, 129.7, 129.0, 128.5, 128.3, 127.9127.8, 116.8, 115.3, 113.7, 113.2,60.0, 59.9, 55.3, 55.2, 14.1,14.0; LRMS (EI, 70eV) *m/z* (%): 282 (M^+, 94), 237 (69), 210 (100), 165 (68); HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_3$ ($[M+H]^+$) 283.1329, found 283.1331.

Ethyl-3-(4-fluorophenyl)-3-phenylacrylate (4sa):



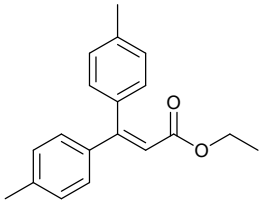
Yield: 45%, E/Z > 20:1;Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.38 (m, 3H), 7.29-7.28 (m, 2H), 7.20-7.19 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.31 (s, 1H), 4.07-4.03 (m, 2H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 164.5, 162.5, 155.4, 138.7,136.9, 136.8, 130.2,130.1, 129.0,128.2, 127.9, 117.2, 115.5, 115.3, 60.1, 13.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.7; LRMS (EI, 70eV) *m/z* (%): 270 (M^+, 68), 225 (100), 196 (81), 177 (22); HRMS *m/z* (ESI) calcd for $C_{17}H_{16}O_2F$ ($[M+H]^+$) 271.1129, found 271.1129.

Ethyl 3,3-diphenylacrylate (4ta):



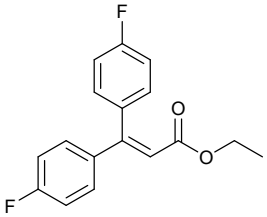
Yield: 75%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 4H), 7.26-7.21 (m, 4H), 7.14-7.13 (m, 2H), 6.29 (s, 1H), 3.97 (m, 2H), 1.03 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 156.5, 140.7, 138.9, 129.1, 128.3, 128.2, 127.8, 117.4, 60.0, 13.9; LRMS (EI, 70eV) *m/z* (%): 252 (M^+, 77), 207 (98), 178 (100), 152 (23); HRMS *m/z* (ESI) calcd for $C_{17}H_{17}O_2$ ($[M+H]^+$) 253.1223, found 253.1224.

Ethyl 3,3-di-*p*-tolylacrylate (4ua):



Yield: 69%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.0 Hz, 4H), 7.13-7.09 (m, 4H), 6.30 (s, 1H), 4.09-4.04 (m, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 156.9, 139.6, 138.2, 137.9, 136.1, 129.1, 128.5, 128.3, 116.1, 59.9, 21.4, 21.2, 14.1; LRMS (EI, 70eV) *m/z* (%): 280 (M^+, 88), 235 (87), 208 (100), 193 (49); HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_2$ ($[M+H]^+$) 281.1536, found 281.1531.

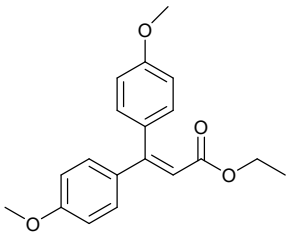
Ethyl 3,3-bis(4-fluorophenyl)acrylate (4va):



Yield: 38%, Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.20-7.17 (m, 2H), 7.09-7.06 (m, 2H), 7.03-7.00 (m, 2H), 6.30 (s, 1H), 4.09-4.05 (m, 2H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 164.5, 163.7, 162.5, 161.7, 154.4, 134.5, 131.0 (2H), 130.2, 130.1, 117.5, 115.5, 115.4, 115.1, 114.9, 60.1, 14.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.4, -113.2; LRMS (EI, 70eV) *m/z* (%): 288 (M^+, 62), 243 (100),

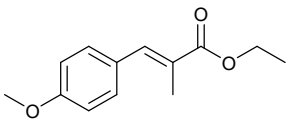
214 (72), 123 (42); HRMS *m/z* (ESI) calcd for $C_{17}H_{15}O_2F_2$ ([M+H]$^+$) 289.1035, found 289.1031.

Ethyl 3,3-bis(4-methoxyphenyl)acrylate (4wa):



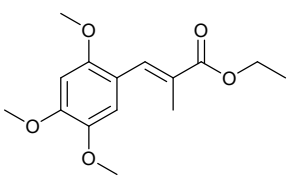
Yield: 89%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.22 (s, 1H), 4.09-4.05 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 160.6, 159.6, 156.3, 133.7, 131.2, 130.8, 129.9, 114.8, 113.6, 113.1, 59.7, 55.2, 55.1, 14.1; LRMS (EI, 70eV) *m/z* (%): 312 (M$^+$, 81), 240 (100), 225 (51), 135 (98); HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_4$ ([M+H]$^+$) 313.1434, found 313.1431.

Ethyl (*E*)-3-(4-methoxyphenyl)-2-methylacrylate (4xa):



Yield: 40%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.29-4.24 (m, 2H), 3.84 (s, 3H), 2.13 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 159.6, 138.3, 131.4, 128.5, 126.4, 113.8, 60.7, 55.3, 14.3, 14.1; LRMS (EI, 70eV) *m/z* (%): 220 (M$^+$, 100), 175 (52), 146 (78), 115 (30); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_3$ ([M+H]$^+$) 221.1172, found 221.1170.

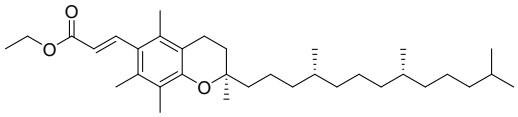
Ethyl (*E*)-2-methyl-3-(2,4,5-trimethoxyphenyl)acrylate (4ya):



Yield: 47%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.90 (s, 1H), 6.54 (s, 1H), 4.29-4.24 (m, 2H), 3.93 (s, 3H), 3.85 (s, 6H), 2.08 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 152.7, 150.3, 142.4, 134.1, 126.9, 116.3, 113.8,

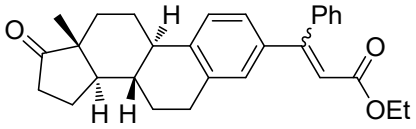
96.9, 60.6, 56.6, 56.3, 56.0, 14.3 (2C); LRMS (EI, 70eV) *m/z* (%): 280 (M^+, 100), 249 (23), 221 (36), 205 (29); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}O_5$ ($[M+H]^+$) 281.1384, found 281.1381.

Ethyl-(*E*)-3-((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)acrylate (4za):



Yield: 61%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.5 Hz, 1H), 5.89 (d, *J* = 16.5 Hz, 1H), 4.29-4.25 (m, 2H), 2.62 (t, *J* = 6.5 Hz, 2H), 2.22 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H), 1.86-1.76 (m, 2H), 1.66 (s, 1H), 1.59-1.50 (m, 4H), 1.34 (t, *J* = 7.5 Hz, 6H), 1.26 (s, 6H), 1.16-1.12 (m, 4H), 1.09-1.05 (m, 4H), 0.87-0.84 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 151.8, 145.4, 133.5, 132.2, 126.1, 123.4, 122.7, 117.2, 75.3, 60.3, 40.0, 39.3, 37.4 (2C), 37.3, 32.8, 32.7, 31.2, 28.0, 24.8, 24.4, 23.9, 22.7, 22.6, 21.0, 20.7, 19.7, 19.6, 17.3, 16.4, 14.3, 11.8; HRMS *m/z* (ESI) calcd for $C_{34}H_{57}O_3$ ($[M+H]^+$) 513.4302, found 513.4300.

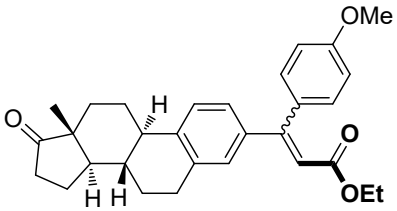
Cyclopenta[*a*]phenanthren-2-yl)-3-phenylacrylate (4aaa):



Yield: 55%, E/Z =1.6:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.33-7.32 (m, 2H), 7.24 (s, 1H), f7.21 (s, 1H), 7.09-7.01 (m, 1H), 6.36-6.31 (m, 1H), 4.11-4.02 (m, 2H), 2.87 (d, *J* = 6.0 Hz, 2H), 2.54-2.49 (m, 1H), 2.42-2.30 (m, 2H), 2.20-2.12 (m, 2H), 2.03-1.96 (m, 2H), 1.68-1.58 (m, 4H), 1.55-1.44 (m, 3H), 1.17 (t, *J* = 7.0 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 2H), 0.94-0.91 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 220.6, 166.1 (2C), 156.7, 156.4, 141.4, 141.2, 139.6, 139.0, 138.1, 136.5, 136.1, 135.7, 129.6,

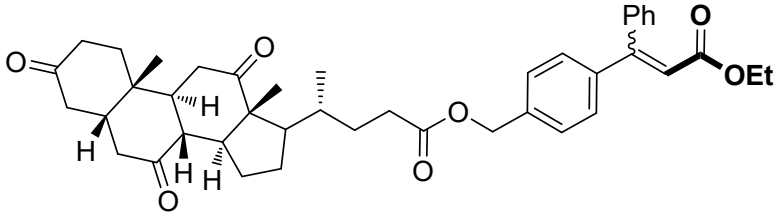
129.2, 129.0, 128.7, 128.3, 128.2, 127.9, 127.7, 126.7, 125.7, 125.3, 124.6, 117.1, 116.6, 60.3, 59.9, 50.5, 50.4, 47.9, 47.8, 44.4, 37.9 (2C), 35.8, 35.7, 31.5 (2C), 29.3, 29.2, 26.4, 26.3, 25.5, 21.5 (2C), 21.0, 14.1, 14.0, 13.9, 13.8, 13.7; HRMS *m/z* (ESI) calcd for $C_{29}H_{33}O_3$ ($[M+H]^+$) 429.2424, found 429.2428.

Decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)acrylate (4baa):



Yield: 65%, *E/Z* =1:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.24-7.23 (m, 1H), 7.15 (d, *J* = 9.0 Hz, 1H), 7.08-6.99 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.26 (d, *J* = 6.0 Hz, 1H), 4.10-4.04 (m, 2H), 3.82 (s, 3H), 2.87 (m, 2H), 2.53-2.47 (m, 2H), 2.40-2.29 (m, 2H), 2.16-2.05 (m, 4H), 1.67-1.58 (m, 4H), 1.53-1.49 (m, 1H), 1.18-1.13 (m, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 220.6, 166.2, 160.6, 159.5, 156.5 (2C), 141.3, 139.5, 138.8, 136.4, 135.7, 133.4, 131.0, 130.7, 129.8, 129.5, 128.9, 126.7, 125.9, 125.2, 124.5, 116.0, 115.0, 113.6, 113.1, 59.8, 59.7, 55.2, 55.1, 50.5,50.4, 47.9, 47.8, 44.4, 37.9 (2C), 35.8, 35.7, 31.5 (2C), 29.3, 29.2, 26.4, 26.3, 25.5, 21.5, 14.0 (2C), 13.8, 13.7; HRMS *m/z* (ESI) calcd for $C_{30}H_{35}O_4$ ($[M+H]^+$) 459.2530, found 459.2533.

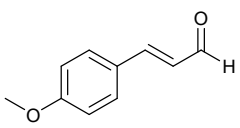
4-(3-Ethoxy-3-oxo-1-phenylprop-1-en-1-yl)benzyl-(4R)-4-((5S,8R,9S,10S,13R,14S)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (4caa):



Yield: 55%, *E/Z* =1:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ

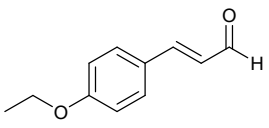
7.80-7.71 (m, 2H), 7.55-7.50 (m, 1H), 7.42-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.36 (s, 1H), 5.16 (s, 1H), 5.11 (s, 1H), 4.29-4.20 (m, 2H), 4.06-4.03 (m, 2H), 2.91-2.84 (m, 3H), 2.32-2.12 (s, 10H), 2.04-2.01 (m, 2H), 1.94-1.91 (m, 2H), 1.78-1.68 (m, 2H), 1.46-1.38 (m, 6H), 1.13-1.03 (m, 4H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 209.0, 208.7, 173.8, 173.7, 167.7, 166.0, 156.8, 156.1, 155.8, 140.6, 140.6, 138.7, 137.3, 135.9, 130.9, 129.4, 129.3, 129.0, 128.8, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.52, 117.8, 117.6, 66.2, 65.8, 65.45, 65.3, 60.0, 56.8, 51.7, 49.0, 48.9, 46.8, 45.6, 45.6, 45.5, 44.9, 42.7, 38.6, 36.4, 36.0, 35.4, 35.4, 35.2, 33.9, 33.4, 31.5, 31.4, 30.4, 29.6, 27.6, 25.6, 25.4, 25.1, 24.9, 24.7, 21.8, 18.6, 14.6, 14.2, 14.4, 13.9, 11.8; HRMS *m/z* (ESI) calcd for $C_{42}H_{51}O_7$ ($[M+H]^+$) 677.3629, found 677.3641.

(*E*)-3-(4-Methoxyphenyl)acrylaldehyde (5a)[16]:



Yield: 64%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, *J* = 8.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.43 (d, *J* = 16.0 Hz, 1H), 6.96-6.93 (m, 2H), 6.64-6.60 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 162.2, 152.8, 130.3, 126.7, 126.5, 114.5, 55.4; LRMS (EI, 70eV) *m/z* (%): 162 (M^+, 100), 131 (78), 91 (57), 89 (36); HRMS *m/z* (ESI) calcd for $C_{10}H_{11}O_2$ ($[M+H]^+$) 163.0754, found 163.0757.

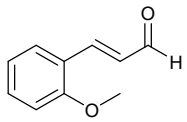
(*E*)-3-(4-Ethoxyphenyl)acrylaldehyde (5b):



Yield: 69%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.63-6.58 (m, 1H), 4.10-4.06 (m, 2H), 1.44 (d, *J* = 7.0

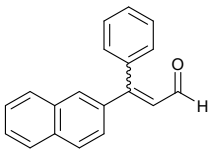
Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 161.6, 152.8, 130.3, 126.5, 126.3, 115.0, 63.7, 14.6; LRMS (EI, 70eV) *m/z* (%): 176 (M^+, 100), 147 (98), 131 (58), 91 (44); HRMS *m/z* (ESI) calcd for $C_{11}H_{13}O_2$ ($[M+H]^+$) 177.0910, found 177.0910.

(*E*)-3-(2-Methoxyphenyl)acrylaldehyde (5c)[16]:



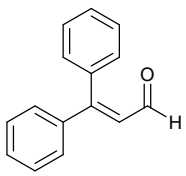
Yield: 53%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.56-7.54 (m, 1H), 7.43-7.40 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.82-6.77 (m, 1H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 158.2, 148.3, 132.7, 129.0, 128.8, 122.9, 120.8, 111.2, 55.51 (s); LRMS (EI, 70eV) *m/z* (%): 162 (M^+, 38), 131 (100), 119 (31), 91 (59); HRMS *m/z* (ESI) calcd for $C_9H_8O_2$ ($[M+H]^+$) 163.0754, found 163.0754.

3-(Naphthalen-2-yl)-3-phenylacrylaldehyde (5d):



Yield: 49%, *E:Z* = 1.5:1; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59-9.56 (m, 1H), 7.95-7.71 (m, 5H), 7.57-7.48 (m, 4H), 7.39-7.31 (m, 3H), 6.74 (d, *J* = 8.0, 0.6H), 6.69 (d, *J* = 8.0, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 162.3, 162.1, 130.8 (2C), 129.6, 129.5, 128.8 (2C), 128.6, 128. 4, 128.3, 128.11, 127.8, 127.7, 127.6 (3C), 127.5, 126.7, 125.0; LRMS (EI, 70eV) *m/z* (%): 258 (M^+, 100), 229 (64), 128 (42), 102 (37); HRMS *m/z* (ESI) calcd for $C_{19}H_{15}O$ ($[M+H]^+$) 259.1117, found 259.1118.

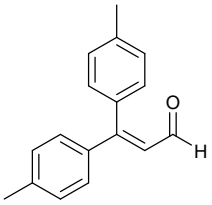
3,3-diphenylacrylaldehyde (5e)[16]:



Yield: 56%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 7.5 Hz, 1H), 7.5-7.4 (m, 5H), 7.4-7.3 (m, 5H), 6.61 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 162.3, 139.7, 136.6, 130.7, 130.5, 129.5, 128.7, 128.6; 128.3, 127.2; LRMS (EI, 70eV) *m/z* (%): 208 (M^+,

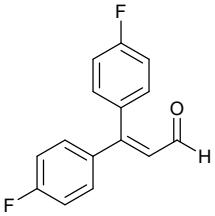
78), 207 (100), 178 (56), 102 (51); HRMS *m/z* (ESI) calcd for $C_{15}H_{13}O$ ($[M+H]^+$) 209.0961, found 209.0961.

3,3-Di-*p*-tolylacrylaldehyde (5f):



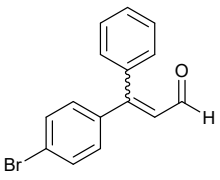
Yield: 57%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 8.0 Hz, 1H), 7.27-7.24 (m, 4H), 7.20-7.17 (m, 4H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 162.6, 140.9, 139.6, 137.1, 133.9, 130.8, 129.3, 128.9, 128.7, 126.4, 21.4, 21.3; LRMS (EI, 70eV) *m/z* (%): 236 (M^+, 28), 221 (100), 178 (19), 115 (33); HRMS *m/z* (ESI) calcd for $C_{17}H_{17}O$ ($[M+H]^+$) 237.1274, found 237.1272.

3,3-Bis(4-fluorophenyl)acrylaldehyde (5g):



Yield: 34%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.0 Hz, 1H), 7.36-7.28 (m, 4H), 7.19-7.15 (m, 2H), 7.10-7.07 (m, 2H), 6.54 (d, *J* = 8.0Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 165.2, 164.5, 163.2, 162.5, 159.8, 135.7, 132.6, 132.5, 130.7, 127.3, 115.9, 115.8, 115.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.3, -110.6; LRMS (EI, 70eV) *m/z* (%): 244 (M^+, 84), 243 (85), 214 (44), 120 (100); HRMS *m/z* (ESI) calcd for $C_{15}H_{11}OF_2$ ($[M+H]^+$) 245.0772, found 245.0770.

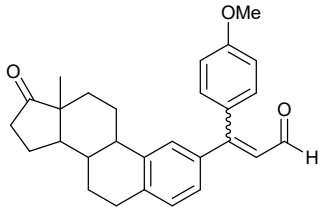
3-(4-Bromophenyl)-3-phenylacrylaldehyde (5h):



Yield: 48%, *E/Z* = 1.5:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54-9.51 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.52-7.38 (m, 4H), 7.35-7.26 (m, 2H), 7.23-7.19 (m, 2H), 6.61-6.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 192.9, 161.0, 160.9, 139.2, 138.6, 136.1, 135.5,

132.2, 131.9, 131.7, 130.7 (2C), 130.1, 129.7, 128.7, 128.6, 128.5, 127.5, 127.3, 125.1, 124.0; LRMS (EI, 70eV) *m/z* (%): 286 (M^+, 45), 207 (65), 178 (100), 102 (52); HRMS *m/z* (ESI) calcd for $C_{15}H_{12}OBr$ ($[M+H]^+$) 287.0066, found 287.0069.

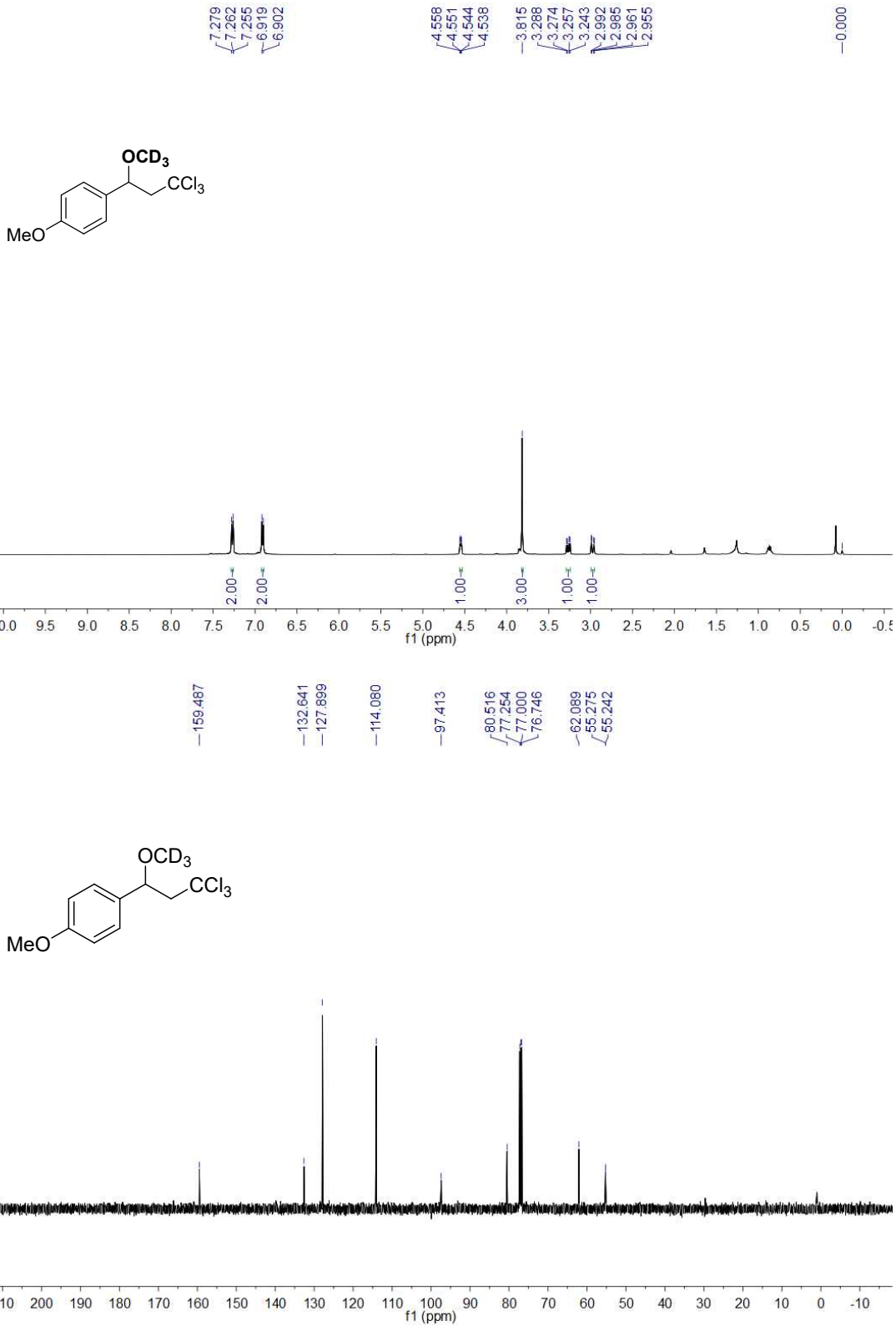
3-(4-Methoxyphenyl)-3-(13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)acrylaldehyde (5i):



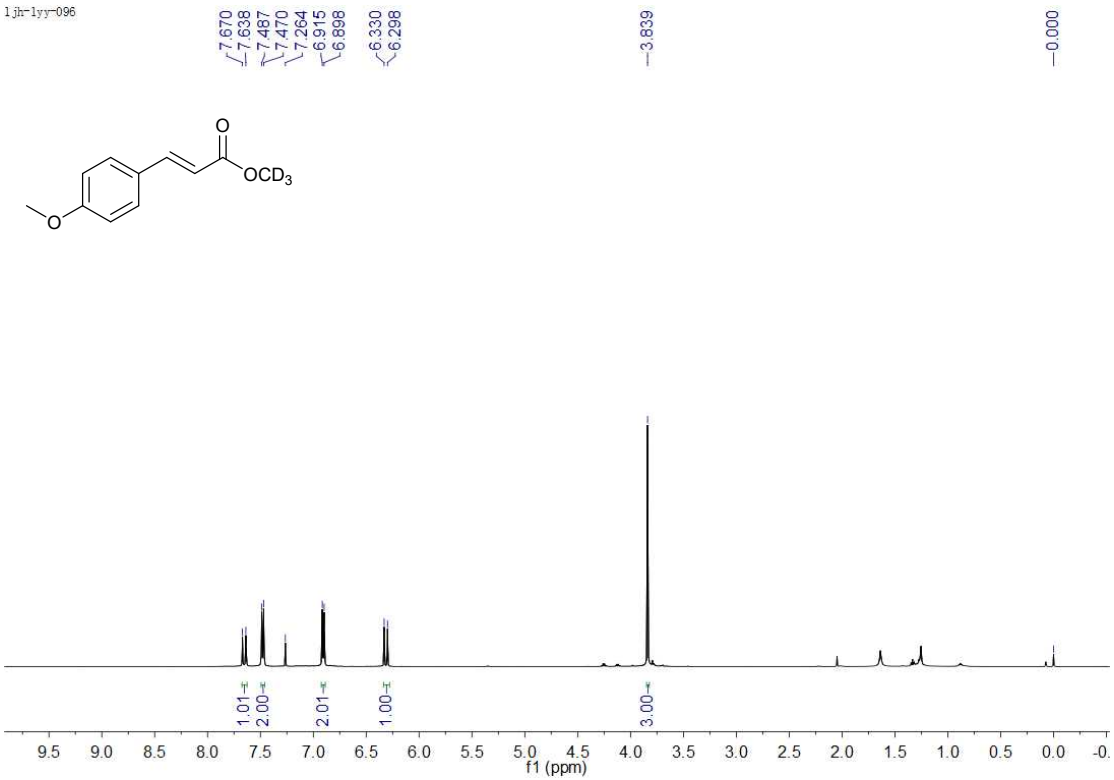
Yield: 58%, *E/Z* = 2:1, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53-9.48 (m, 1H), 7.34-7.32 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.11-7.03 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.53-6.50 (m, 1H), 3.88 (s, 1H), 3.84 (s, 2H), 2.94-2.90 (m, 2H), 2.56-2.48 (m, 2H), 2.22-2.11 (m, 2H), 2.06-1.99 (m, 2H), 1.70-1.46 (m, 7H), 0.96 (s, 2H), 0.92 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.6 (2C), 193.7, 193.6, 162.2 (2C), 161.6, 160.7, 142.6, 141.2, 137.7, 136.8, 136.5, 134.3, 132.5, 132.1, 131.3, 130.4, 129.4, 129.0, 128.3, 126.5, 126.4, 125.6, 125.5, 125.2, 113.9, 113.6, 55.4, 50.5 (2C), 47.9 (2C), 44.5, 44.4, 38.0 (2C), 35.8, 31.5, 29.7, 29.3 (2C), 26.3 (2C), 25.6 (2C), 21.6, 14.1, 13.8 (2C); HRMS *m/z* (ESI) calcd for $C_{28}H_{31}O_3$ ($[M+H]^+$) 415.2268, found 415.2265.

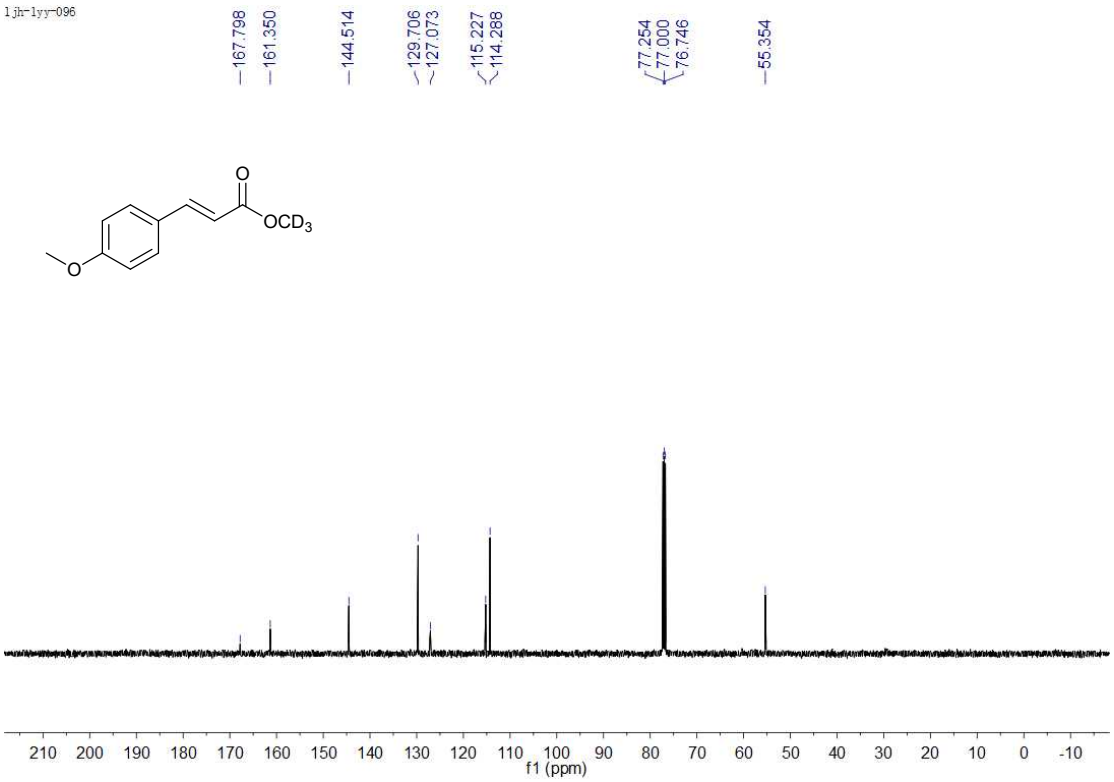
(E) Spectra

1-Methoxy-4-(3,3,3-trichloro-1-(methoxy-D3)propyl)benzene (6b-D3):

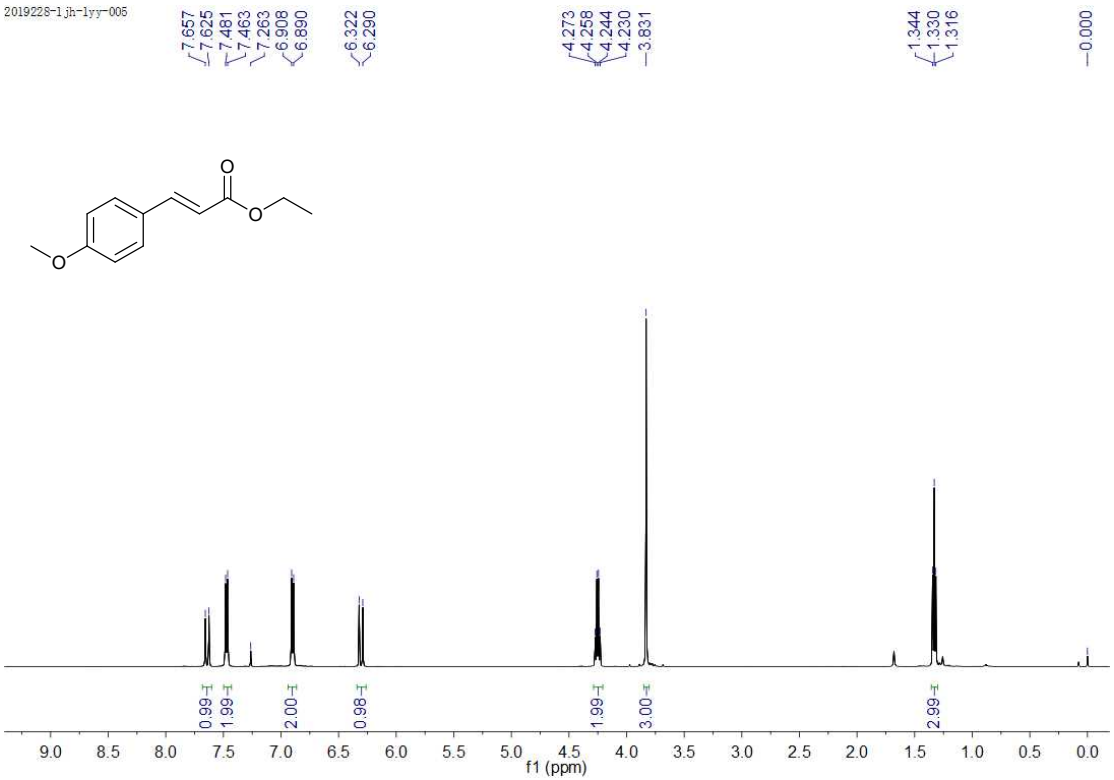


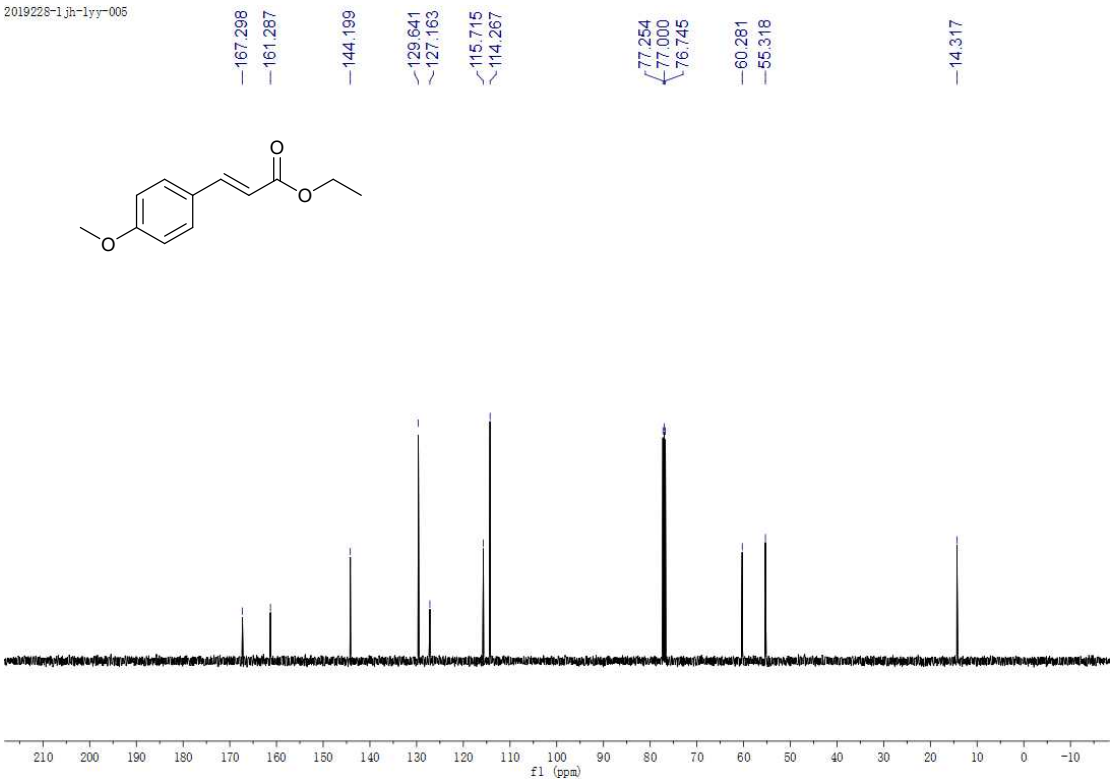
Methyl-D3 (*E*)-3-(4-methoxyphenyl)acrylate (4ab-D3):



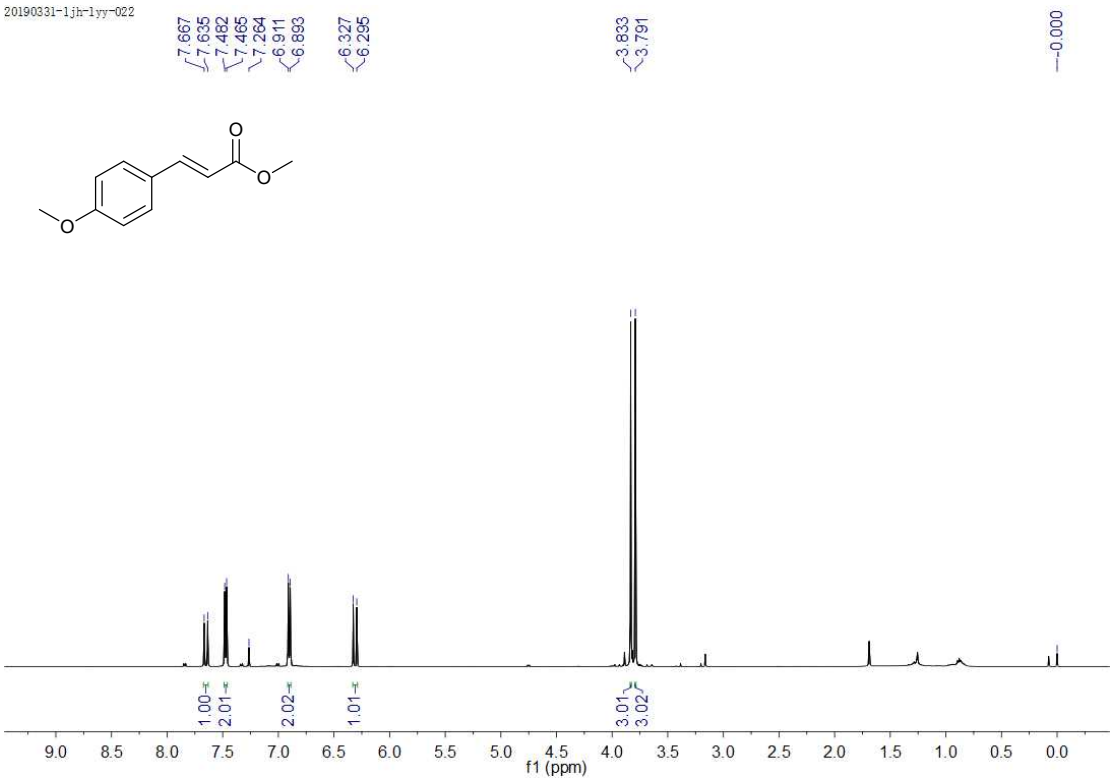


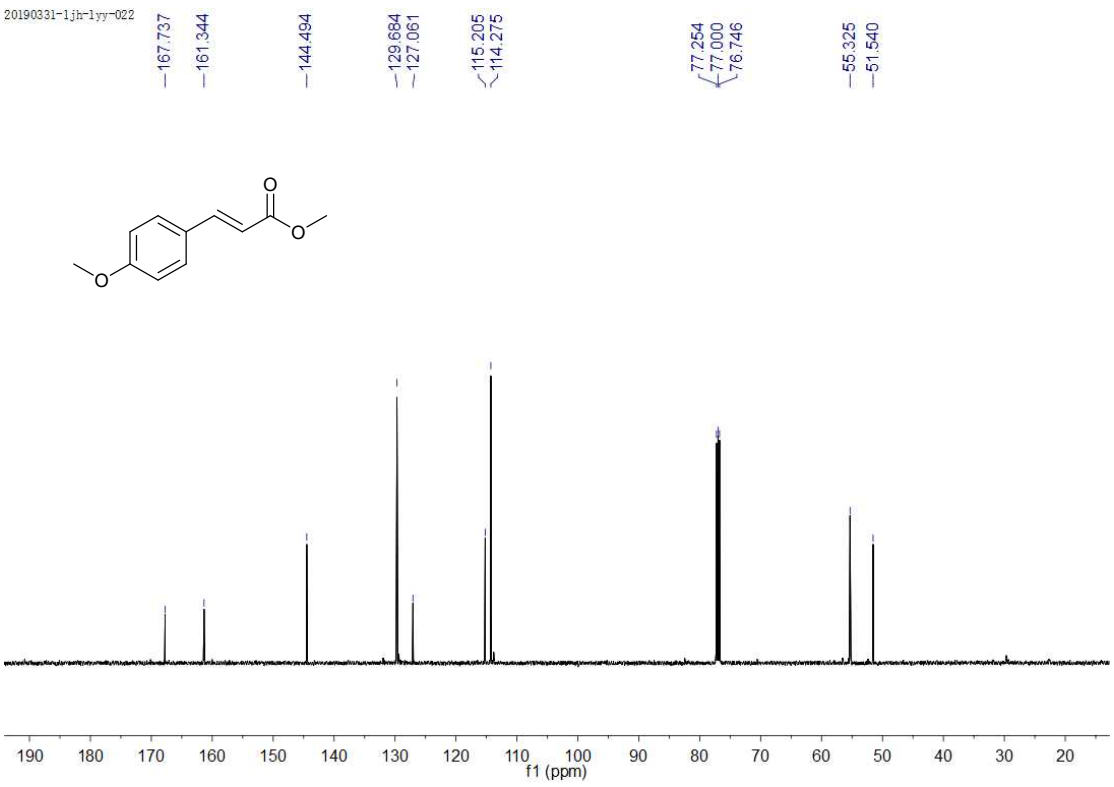
Ethyl (*E*)-3-(4-methoxyphenyl)acrylate (4aa):



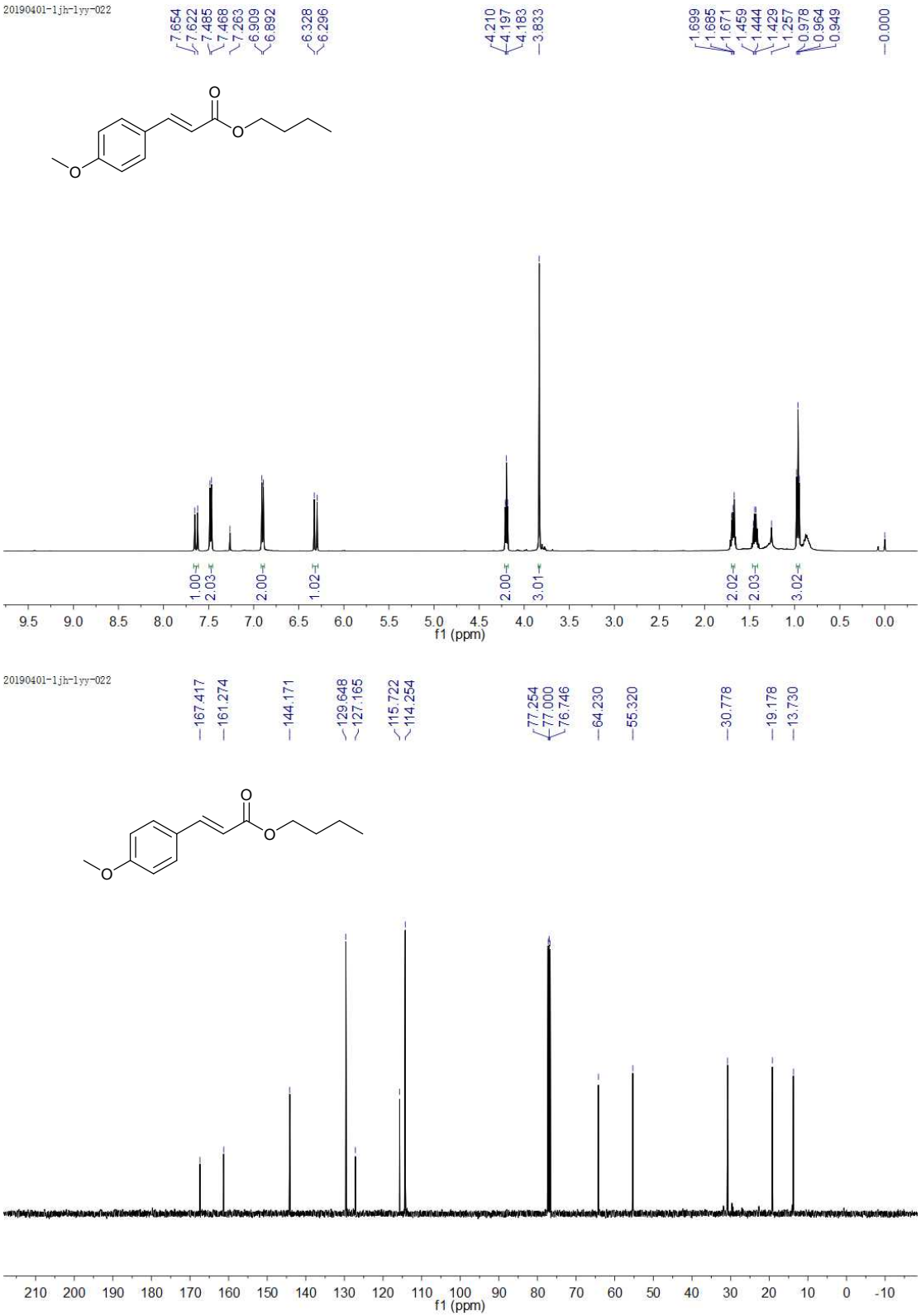


Methyl (*E*)-3-(4-methoxyphenyl)acrylate (4ab):

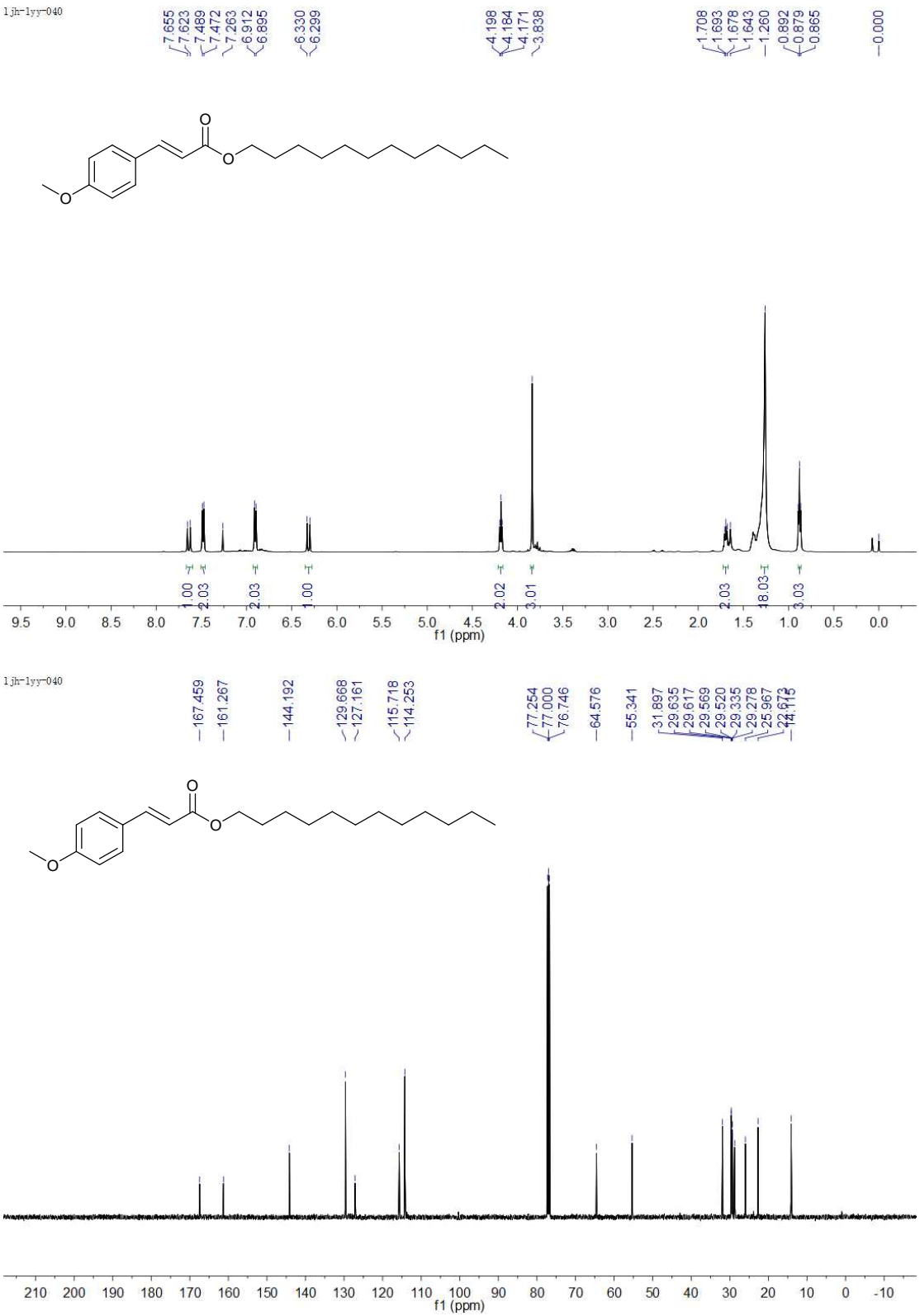




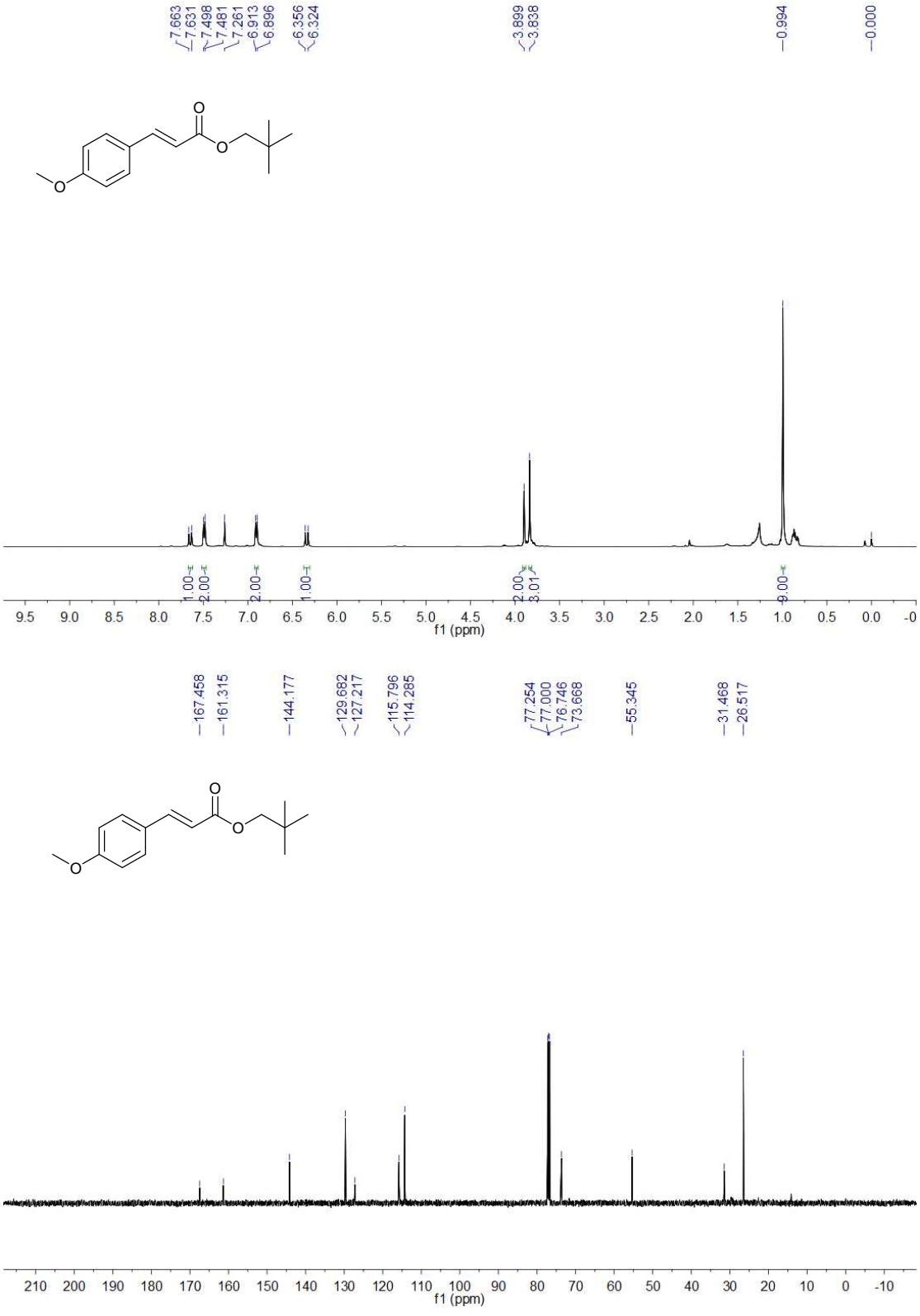
Butyl (*E*)-3-(4-methoxyphenyl)acrylate (4ac):



Dodecyl (*E*)-3-(4-methoxyphenyl)acrylate (4ad):

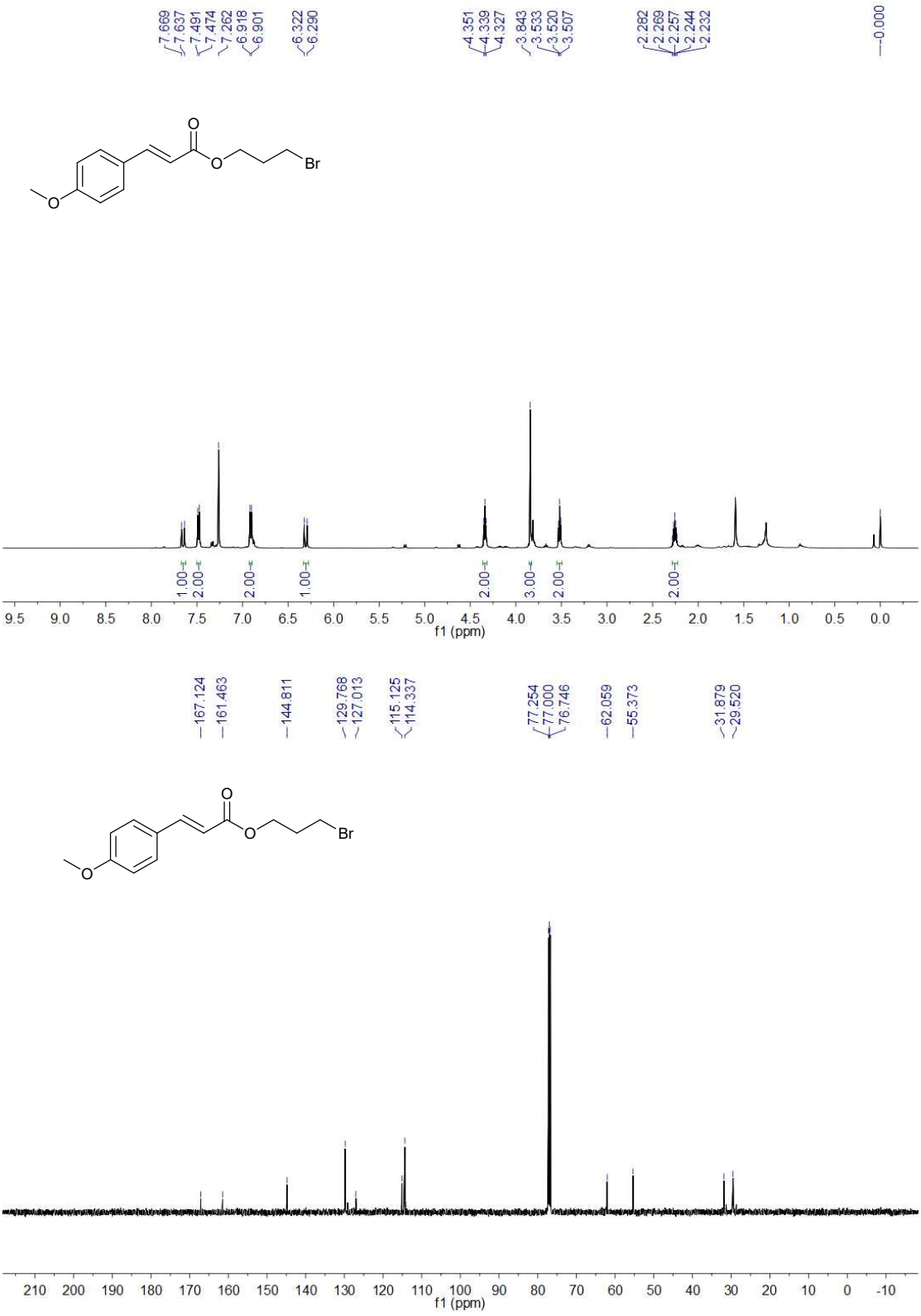


Neopentyl (*E*)-3-(4-methoxyphenyl)acrylate (4ae):

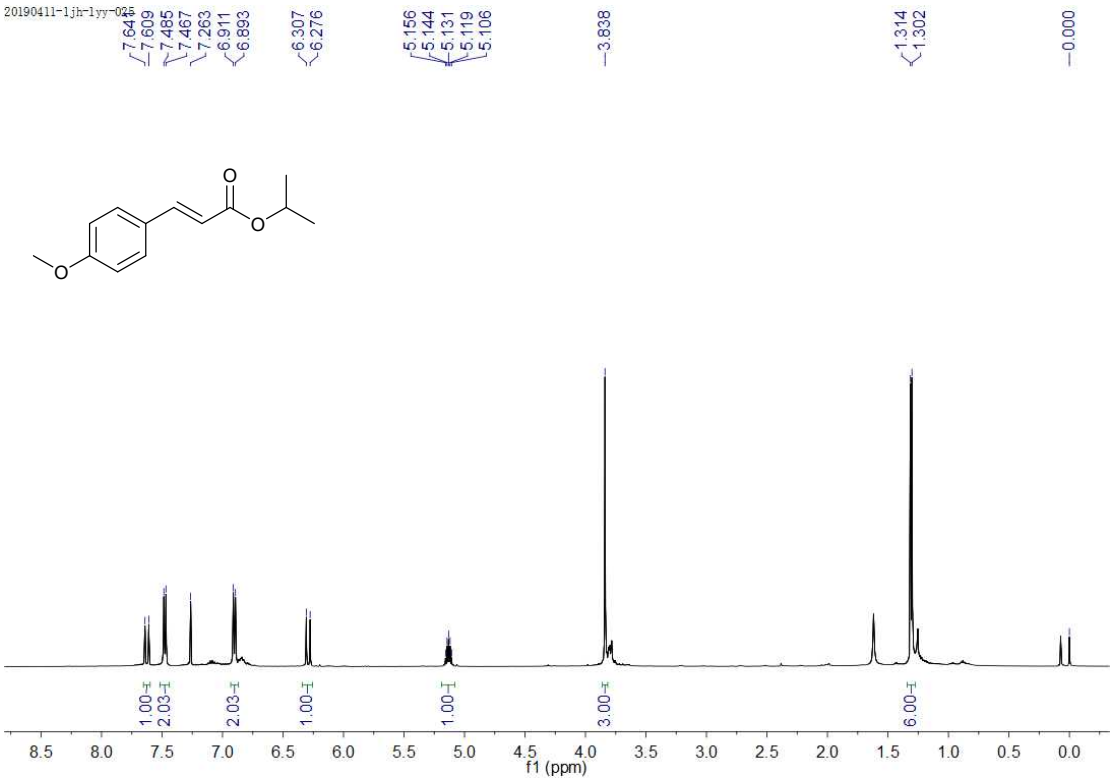


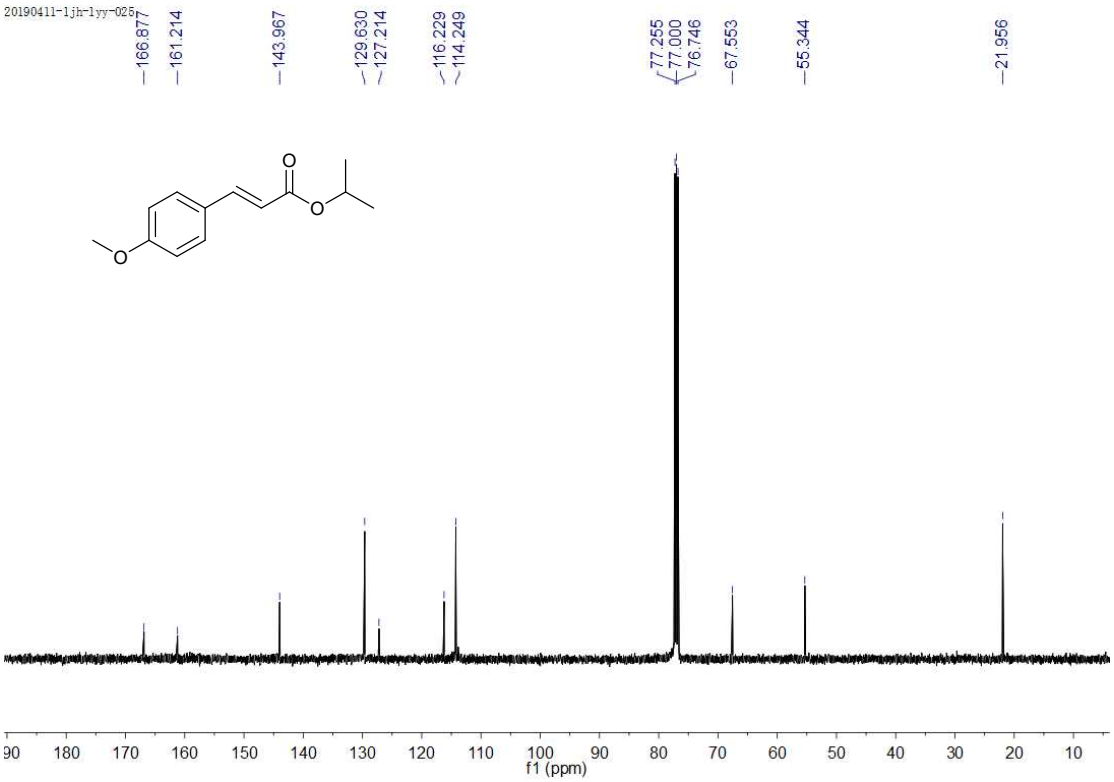
But-3-en-1-yl (*E*)-3-(4-methoxyphenyl)acrylate (4af):

3-Bromopropyl (*E*)-3-(4-methoxyphenyl)acrylate (4ag):

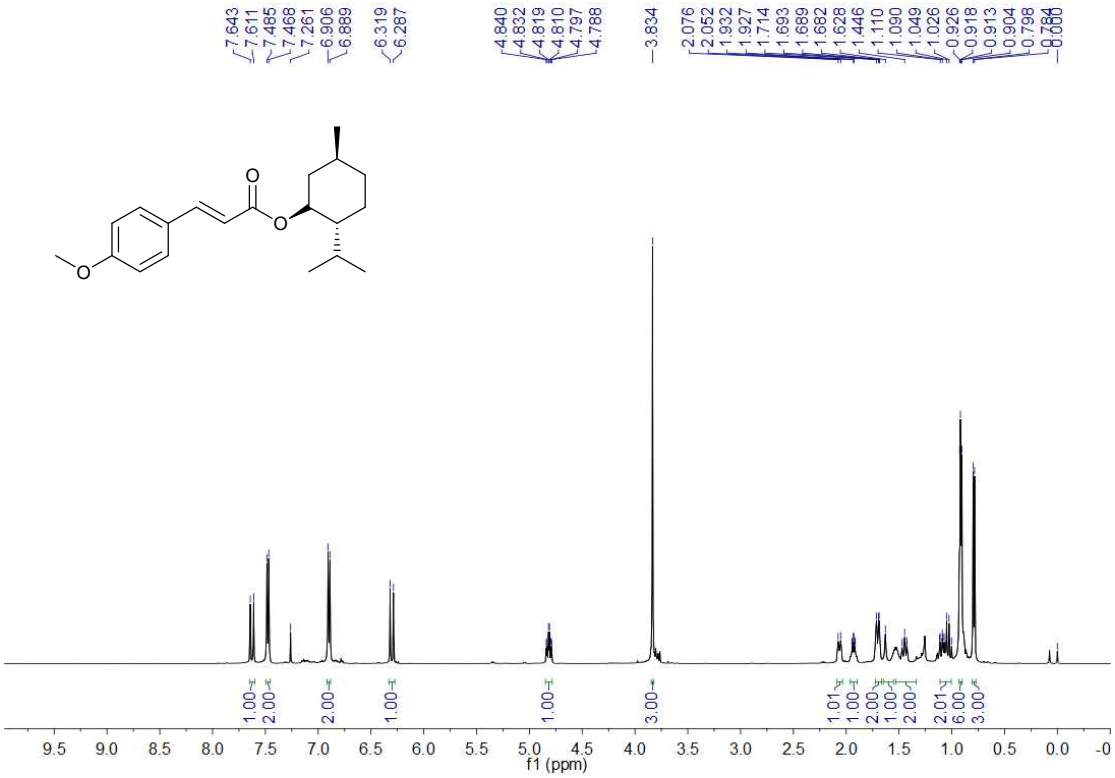


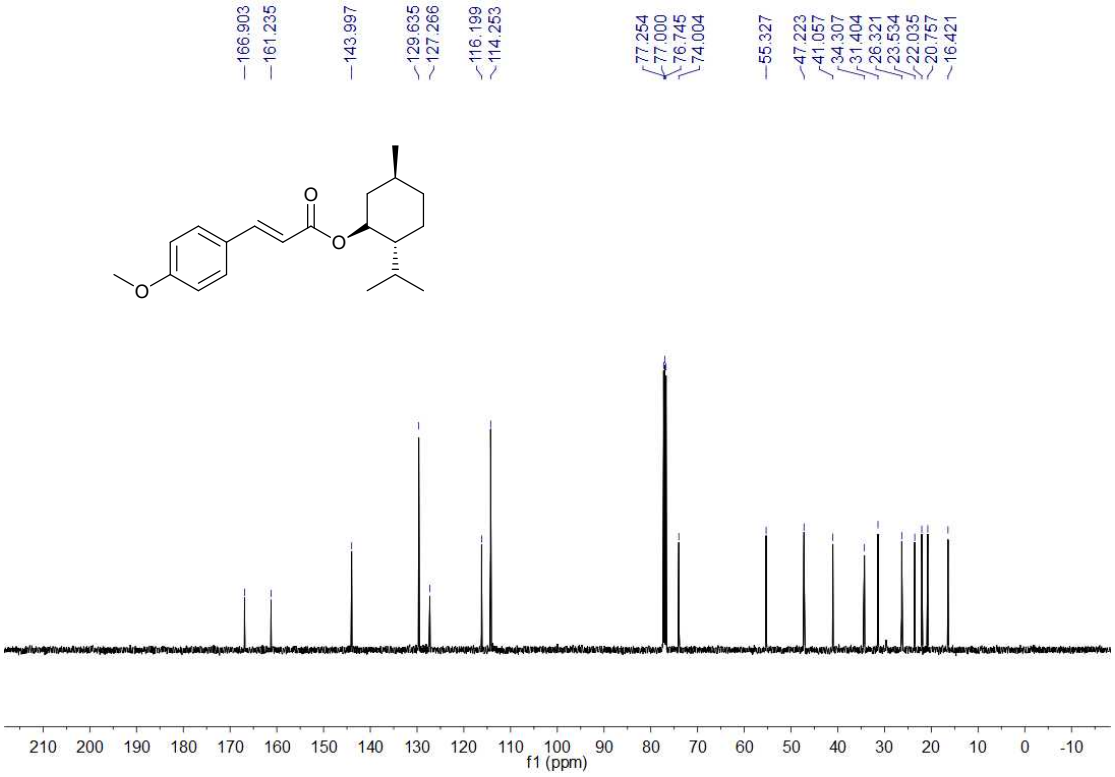
Isopropyl (*E*)-3-(4-methoxyphenyl)acrylate (4ah):



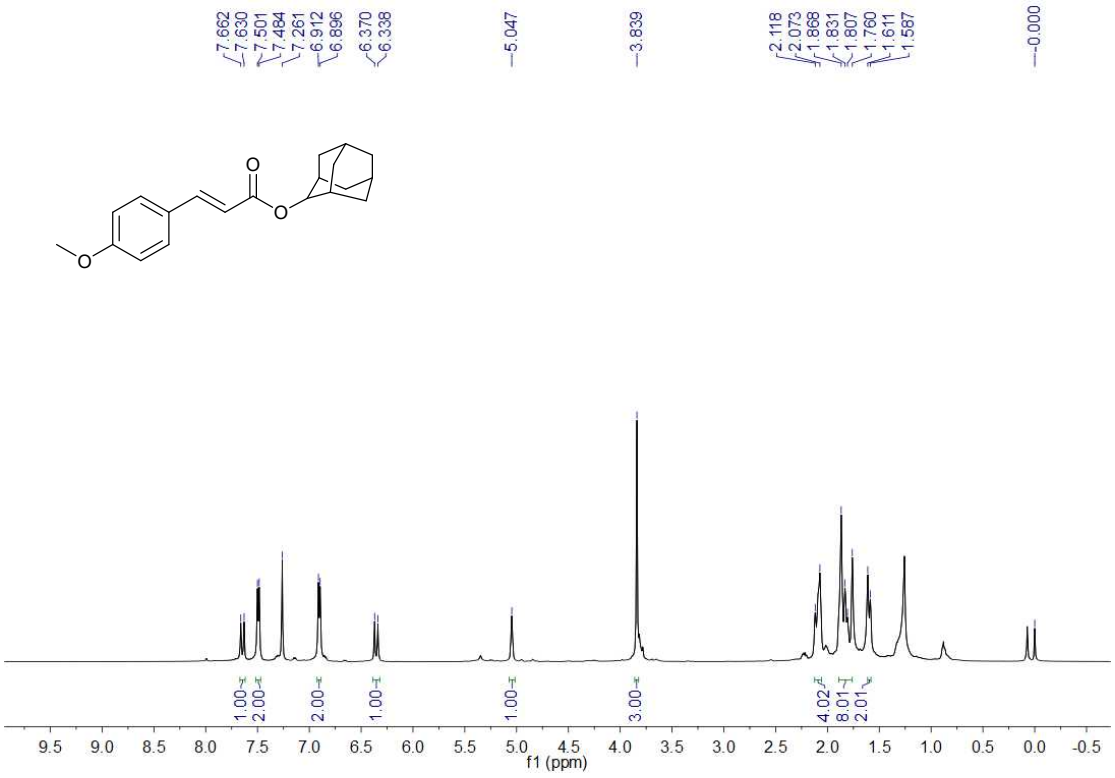


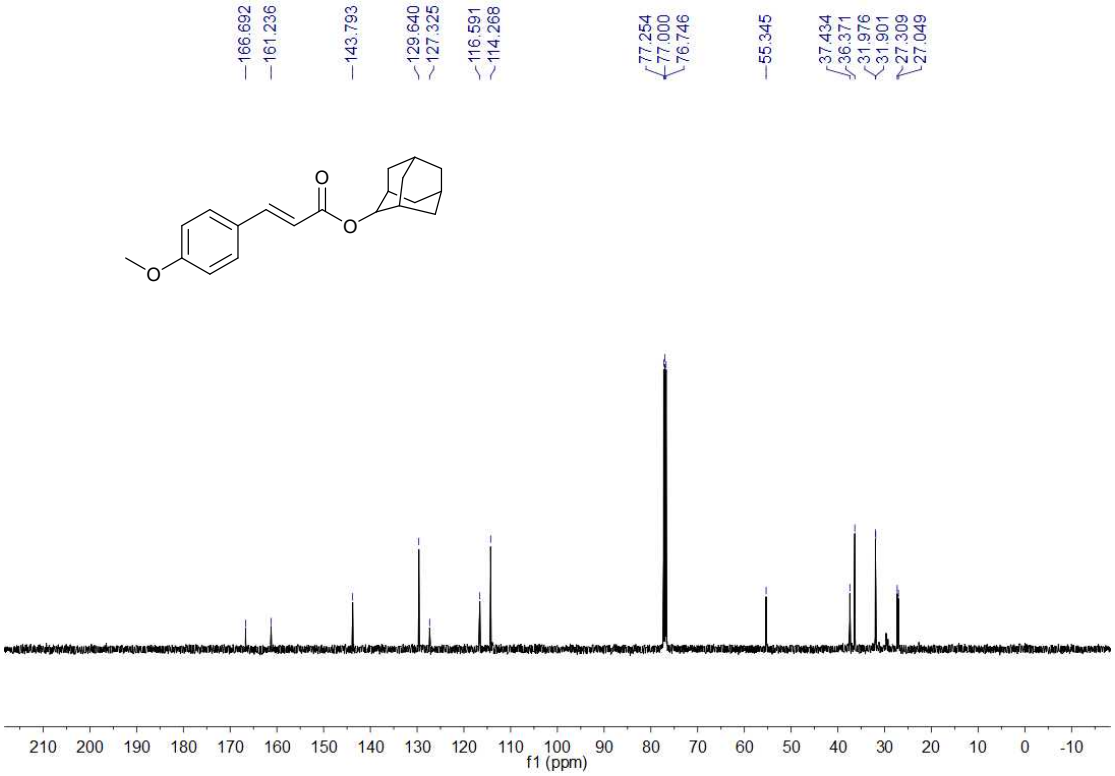
(1R,2R,5S)-2-Isopropyl-5-methylcyclohexyl (*E*)-3-(4-methoxyphenyl)acrylate (4ai):



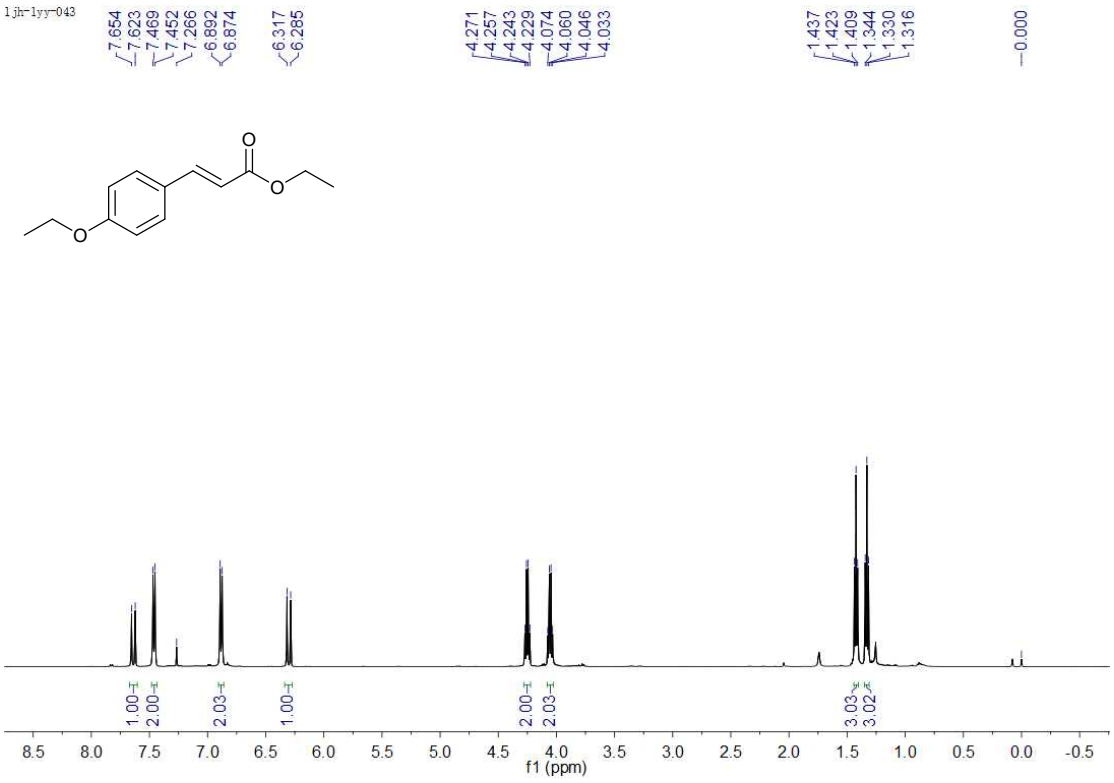


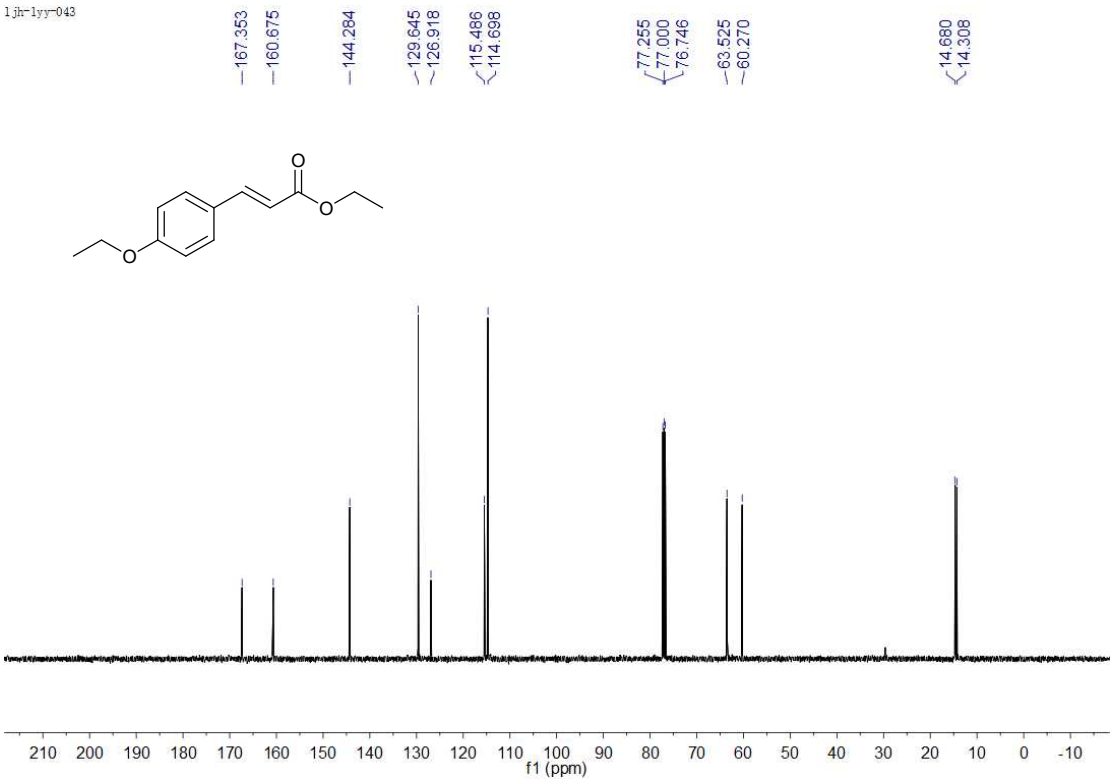
(1r,3r,5r,7r)-Adamantan-2-yl (*E*)-3-(4-methoxyphenyl)acrylate (4aj):



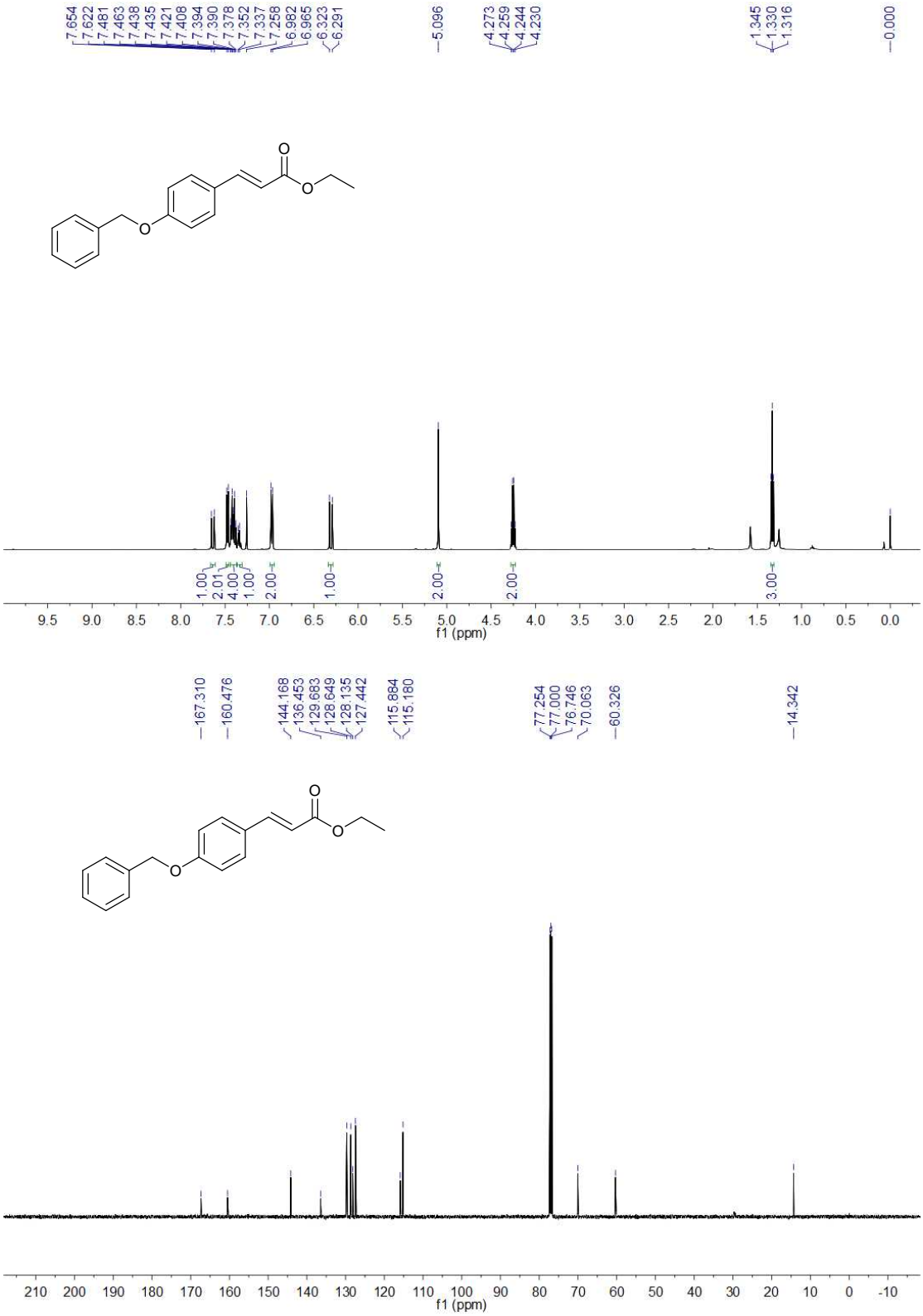


Ethyl (*E*)-3-(4-ethoxyphenyl)acrylate (4ba):

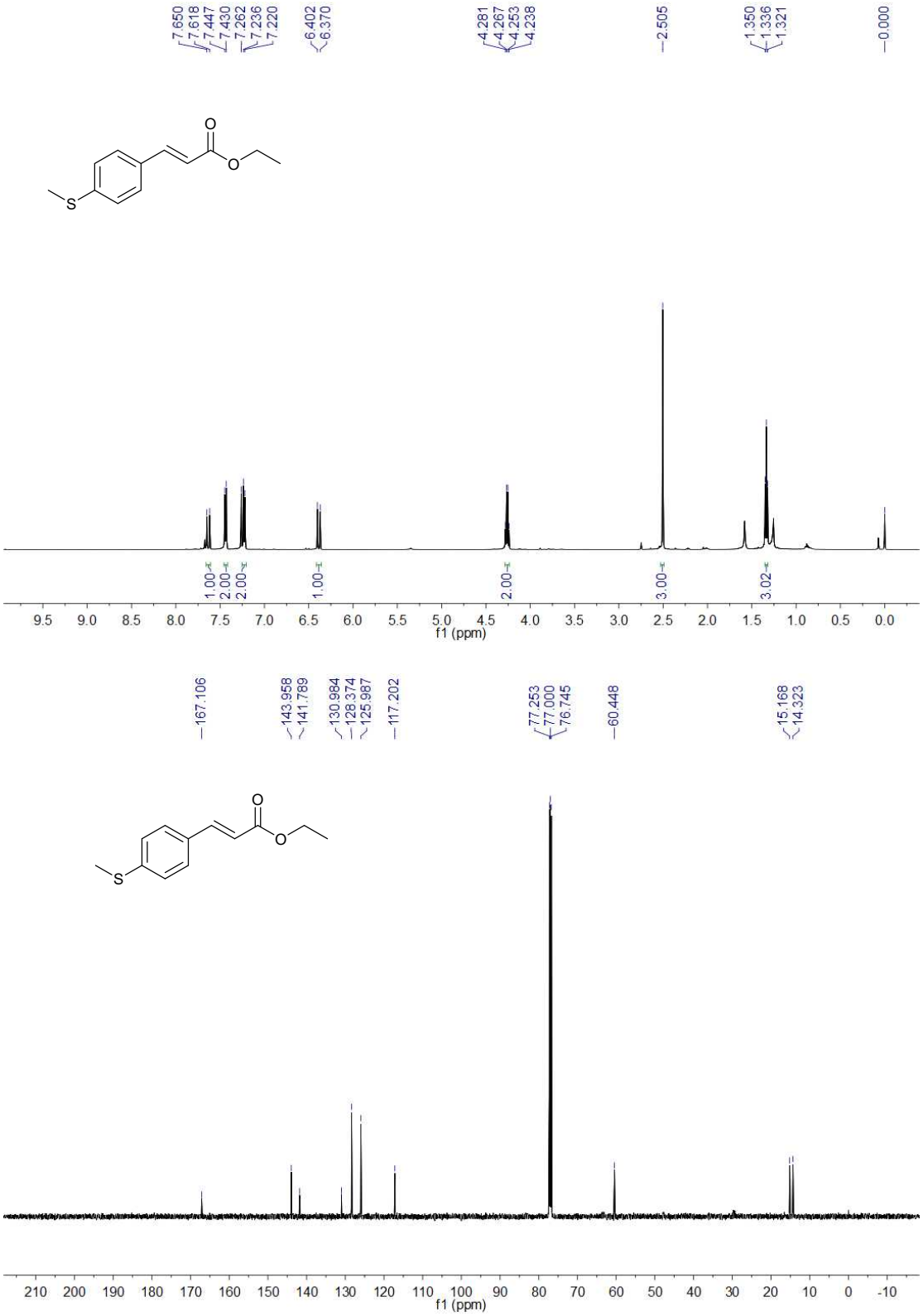




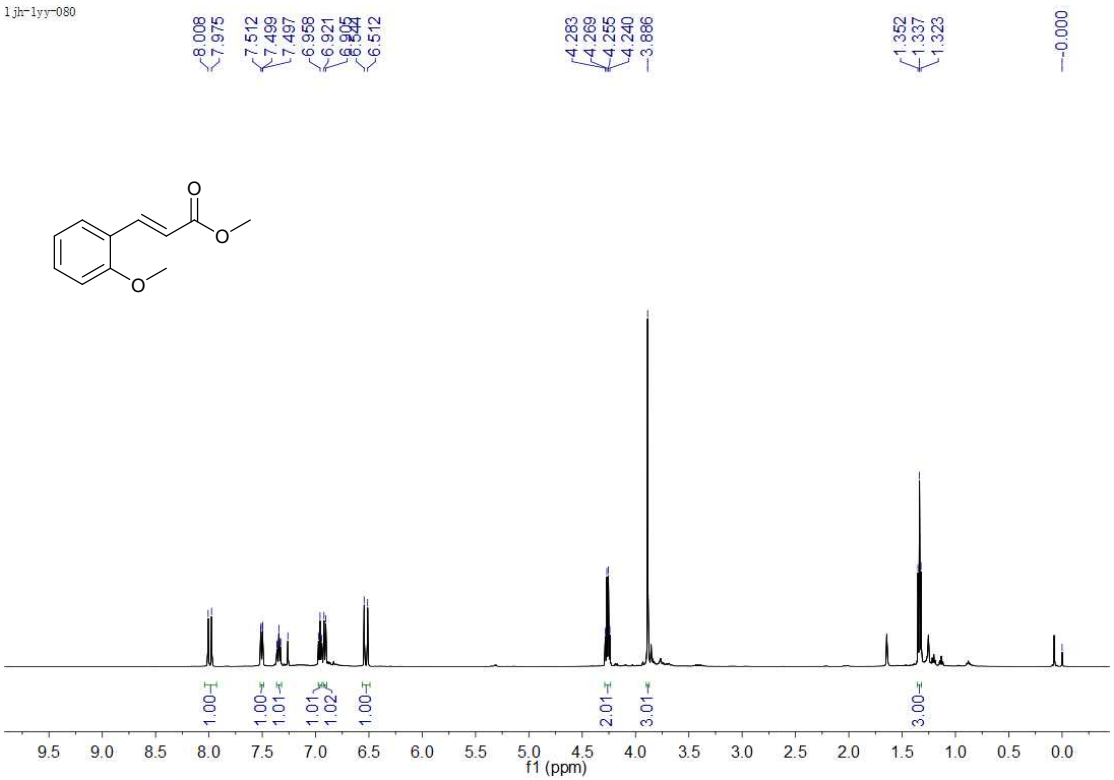
Ethyl (*E*)-3-(4-(benzyloxy)phenyl)acrylate (4ca):

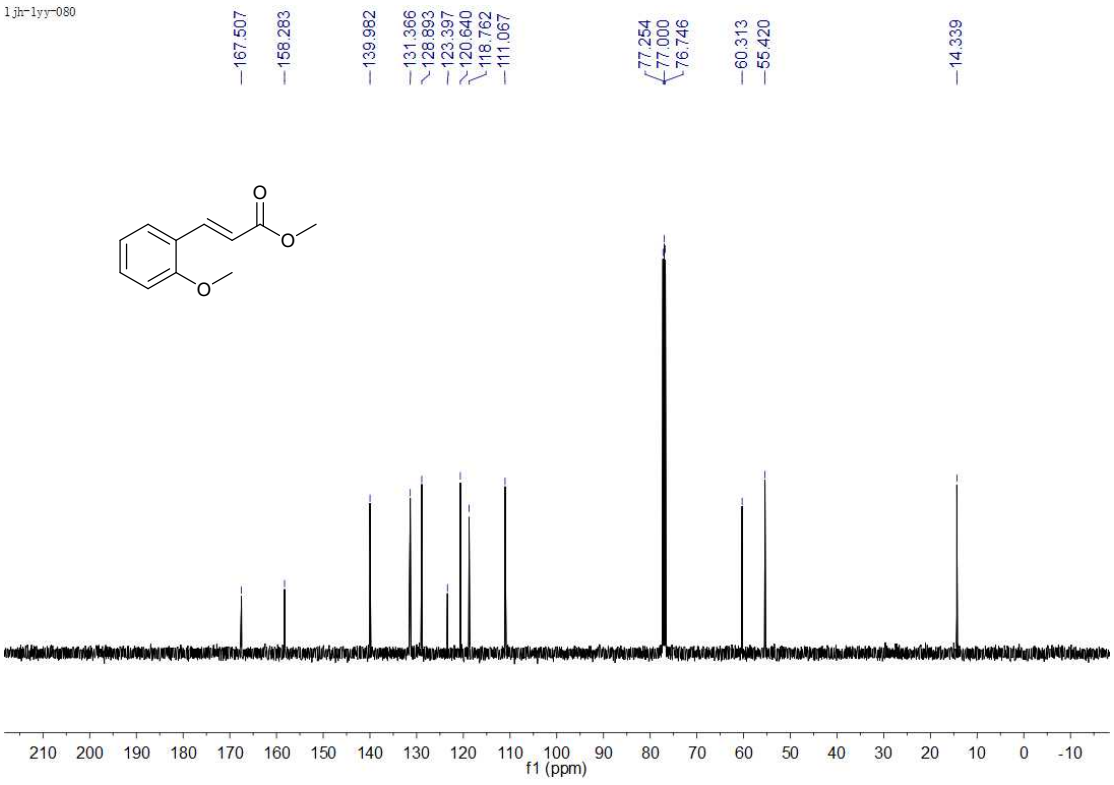


Ethyl (*E*)-3-(4-(methylthio)phenyl)acrylate (4da):

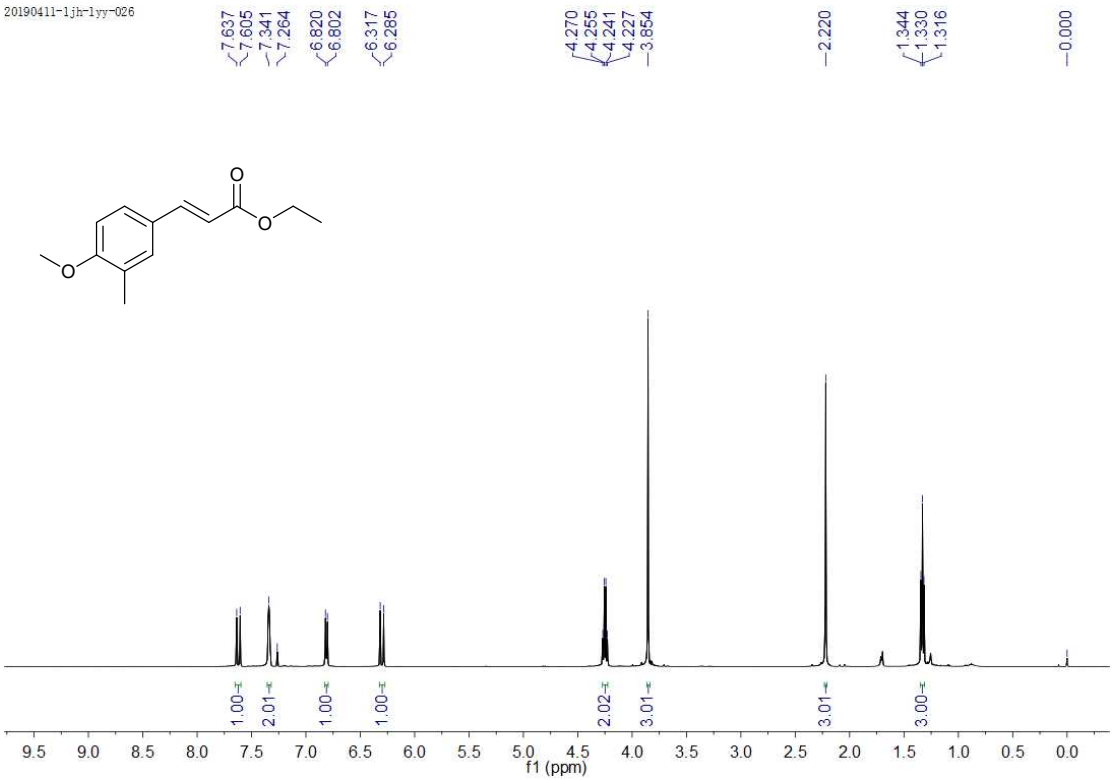


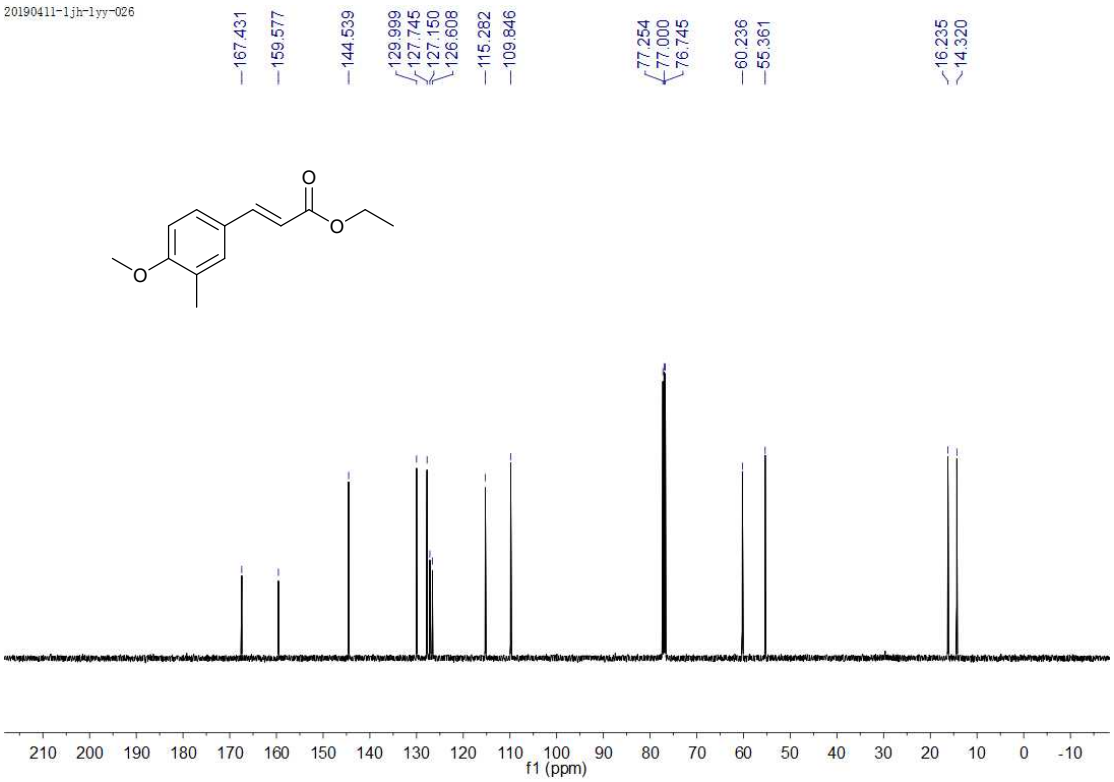
Methyl (*E*)-3-(2-methoxyphenyl)acrylate (4ea):



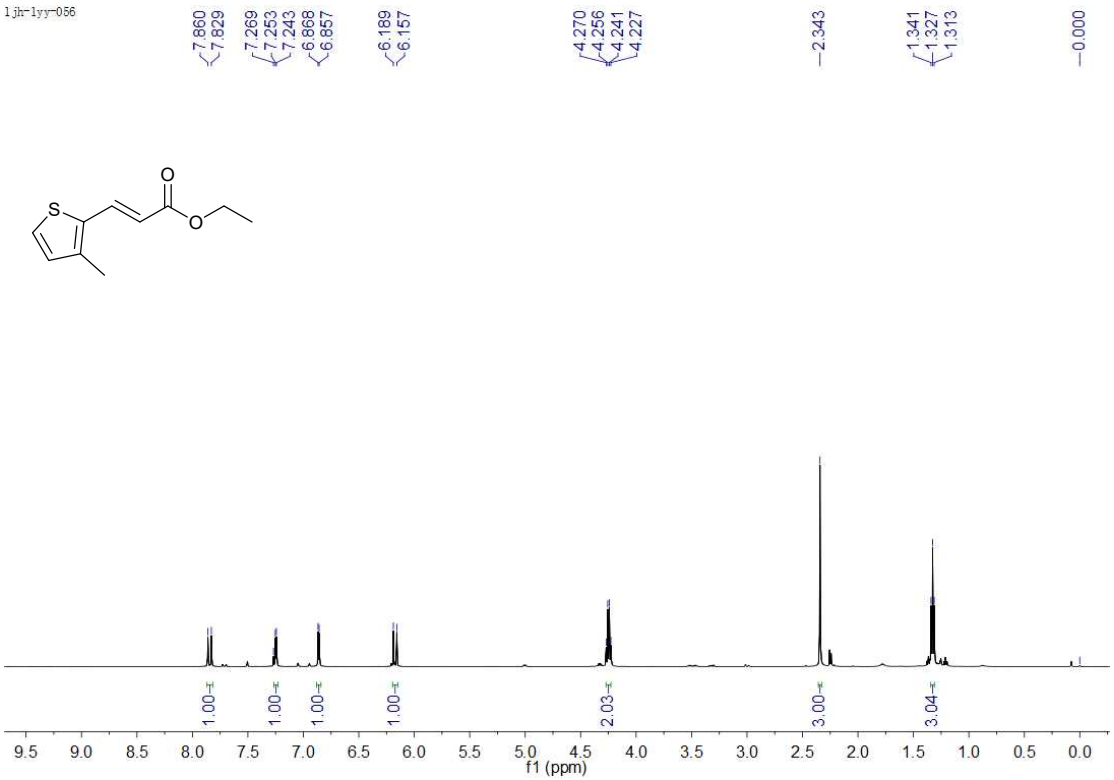


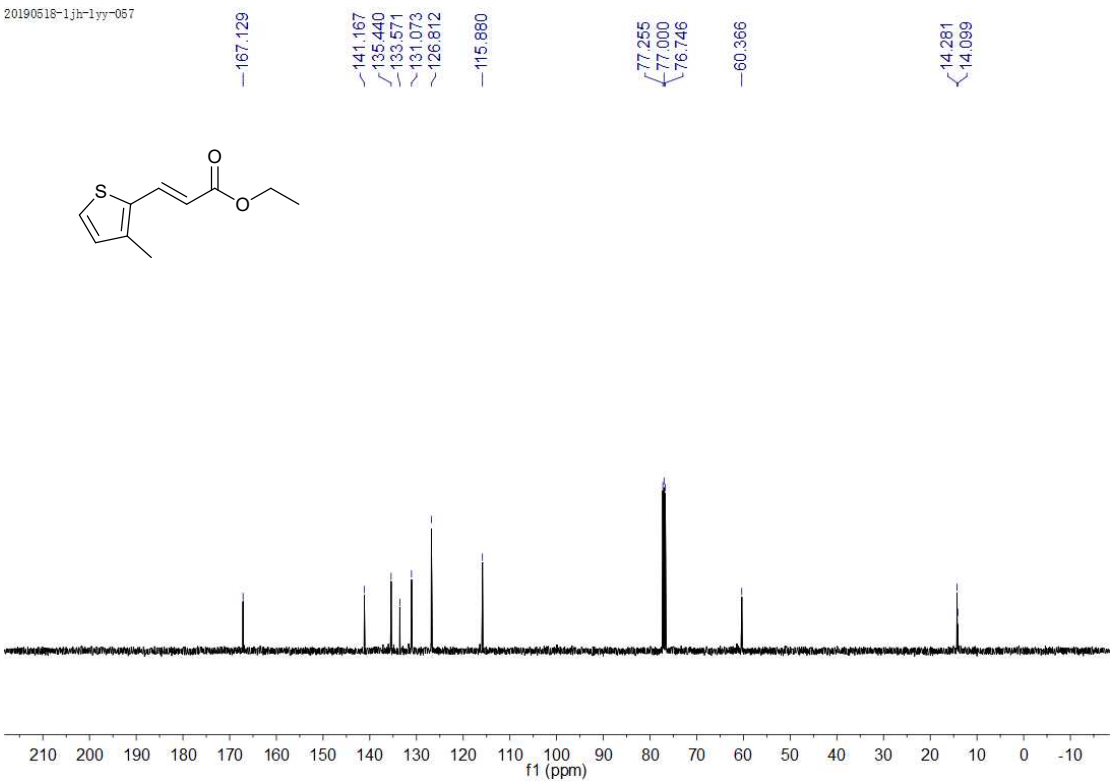
Ethyl (*E*)-3-(4-methoxy-3-methylphenyl)acrylate (4fa):



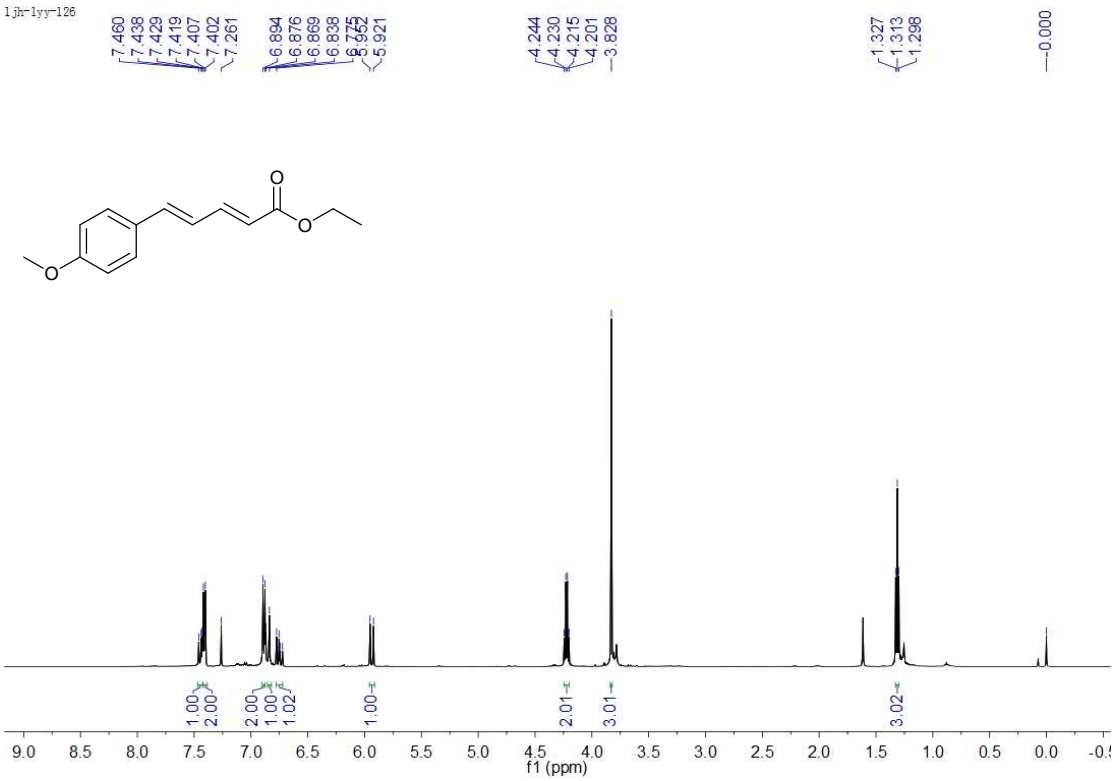


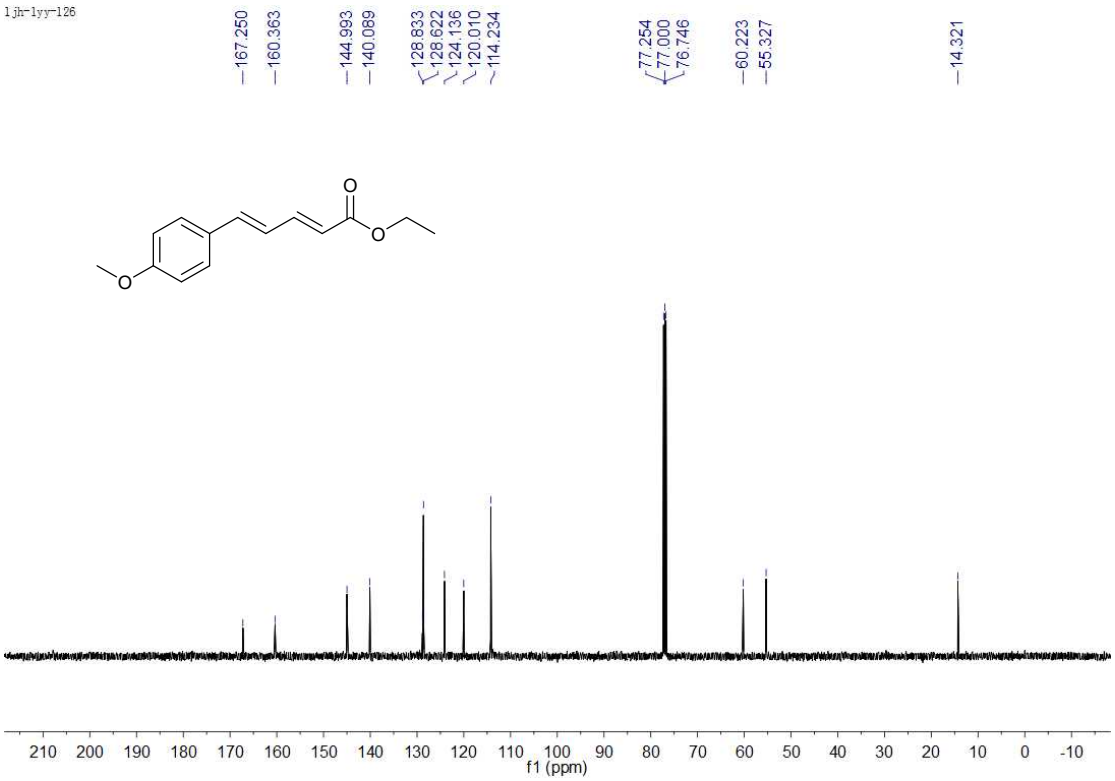
Ethyl (*E*)-3-(3-methylthiophen-2-yl)acrylate (4ga):



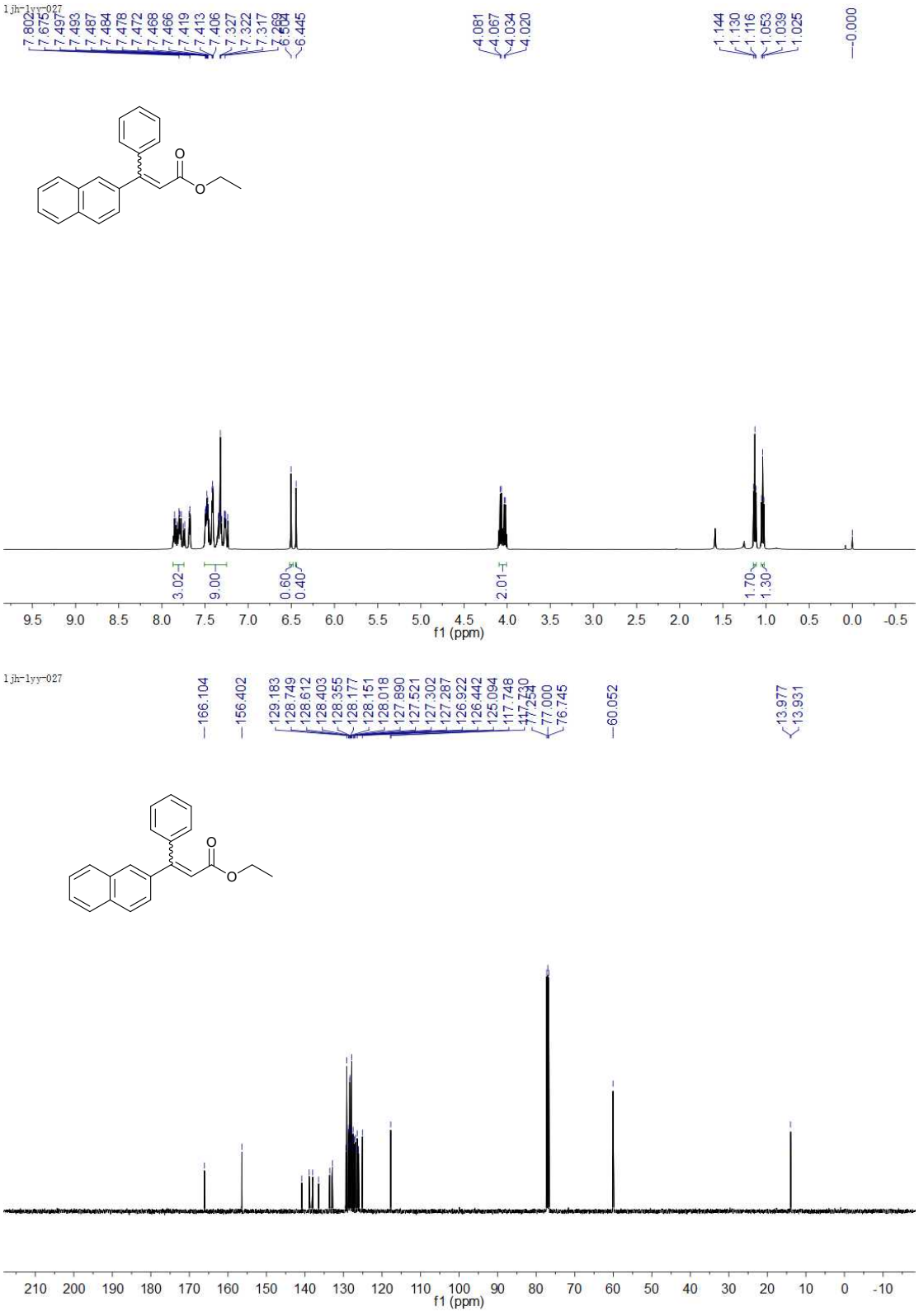


Ethyl (2*E*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dienoate (4ha):

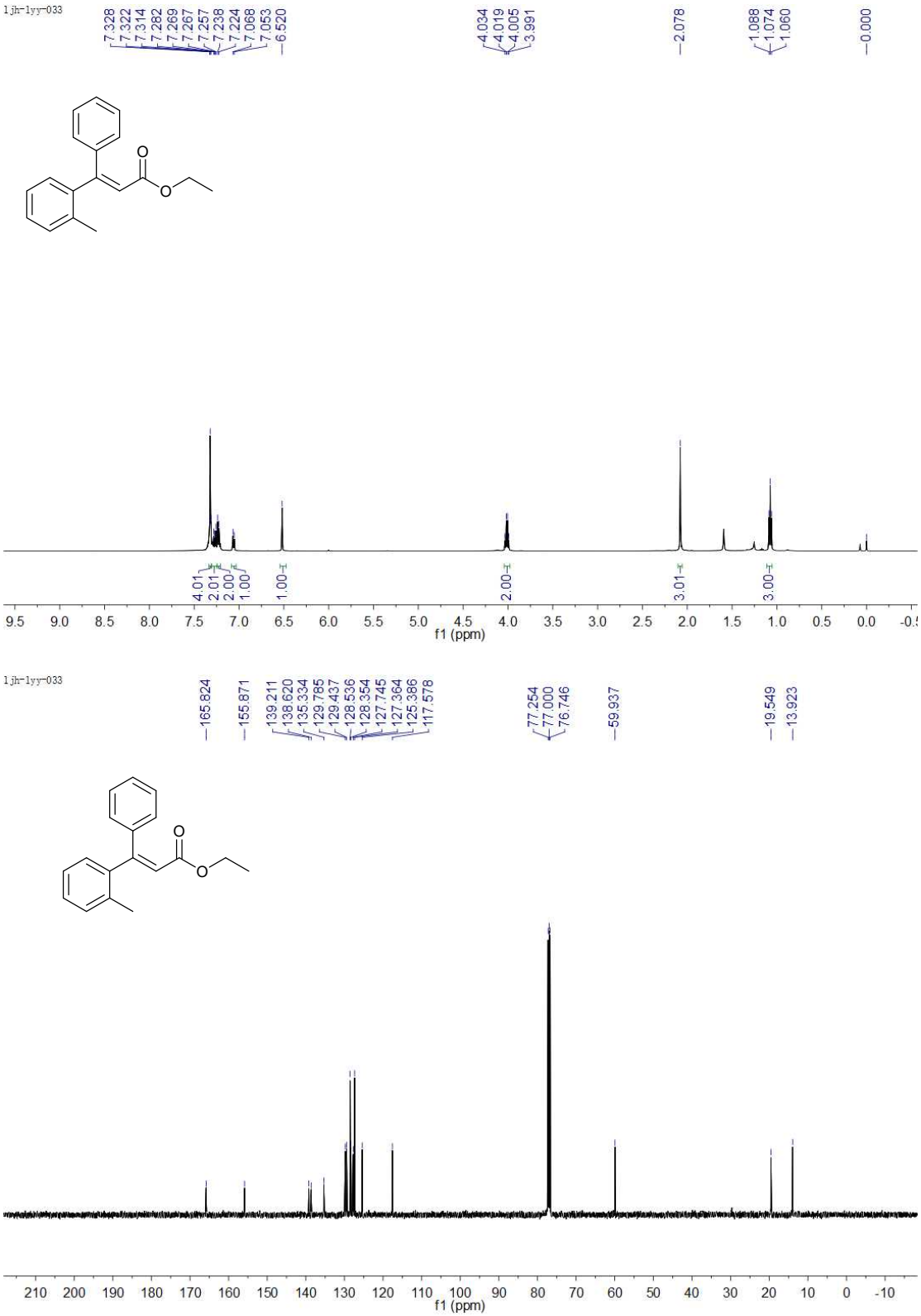




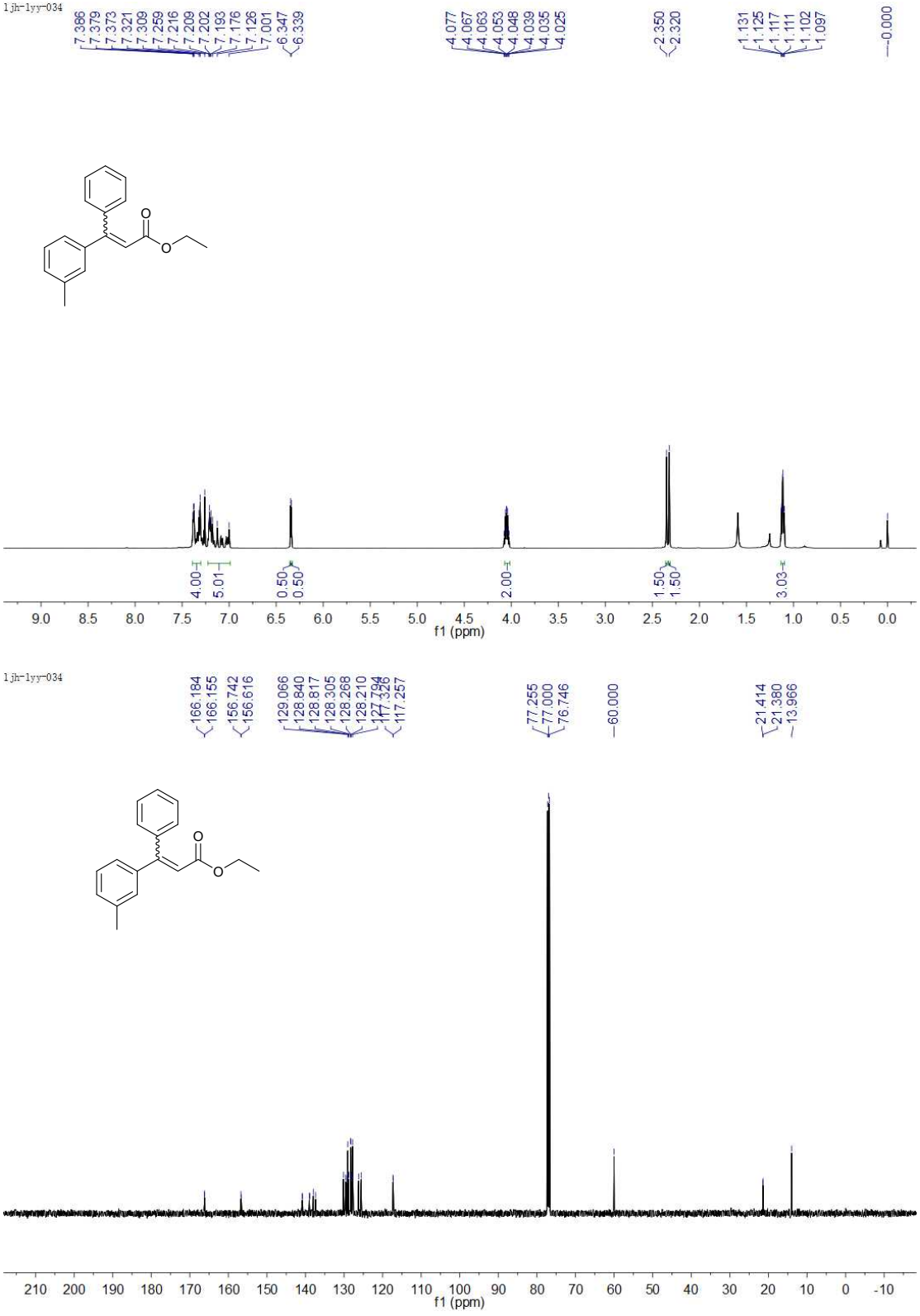
Ethyl-3-(naphthalen-2-yl)-3-phenylacrylate (4ja):



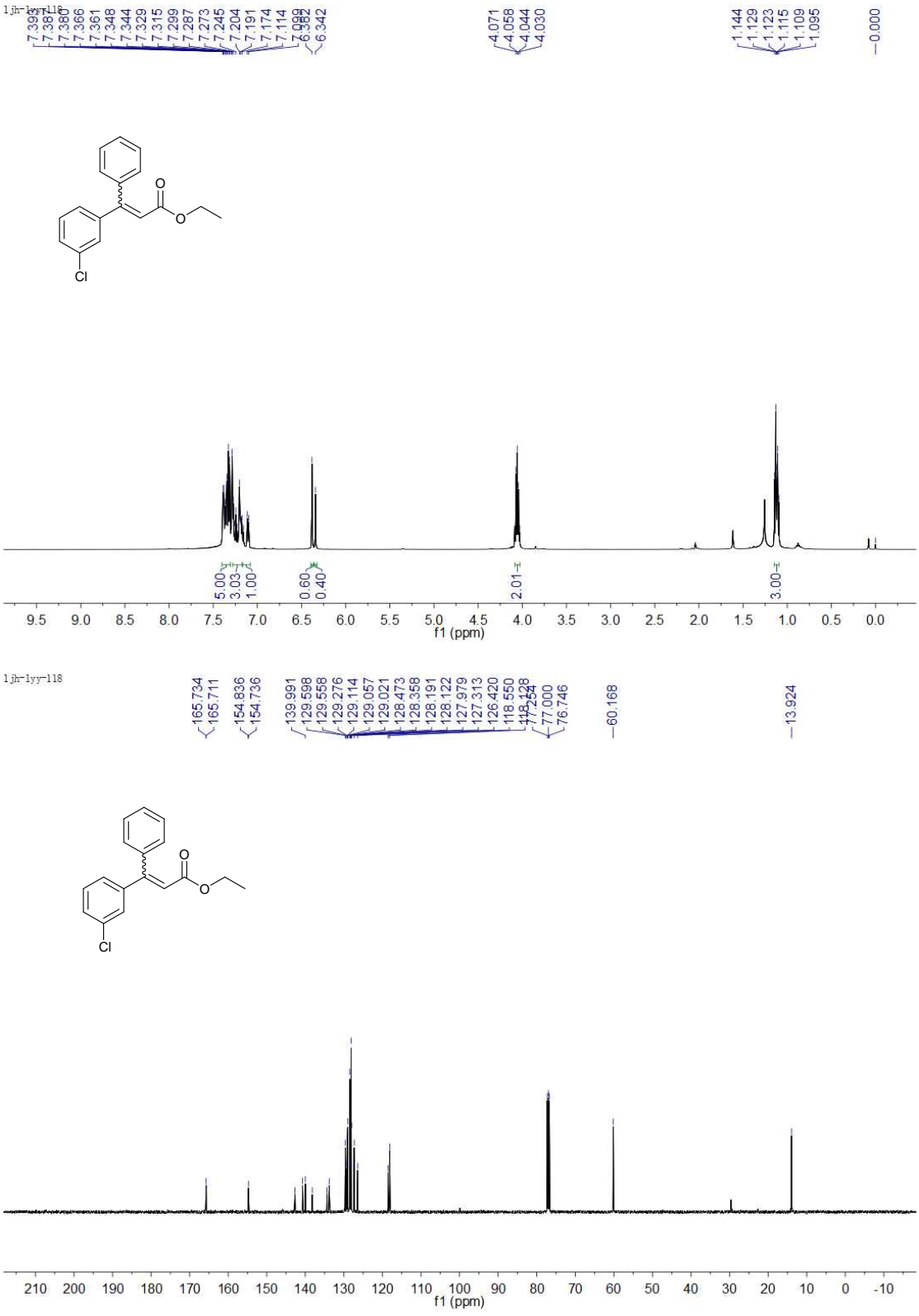
Ethyl (*E*)-3-phenyl-3-(o-tolyl)acrylate (4ka):



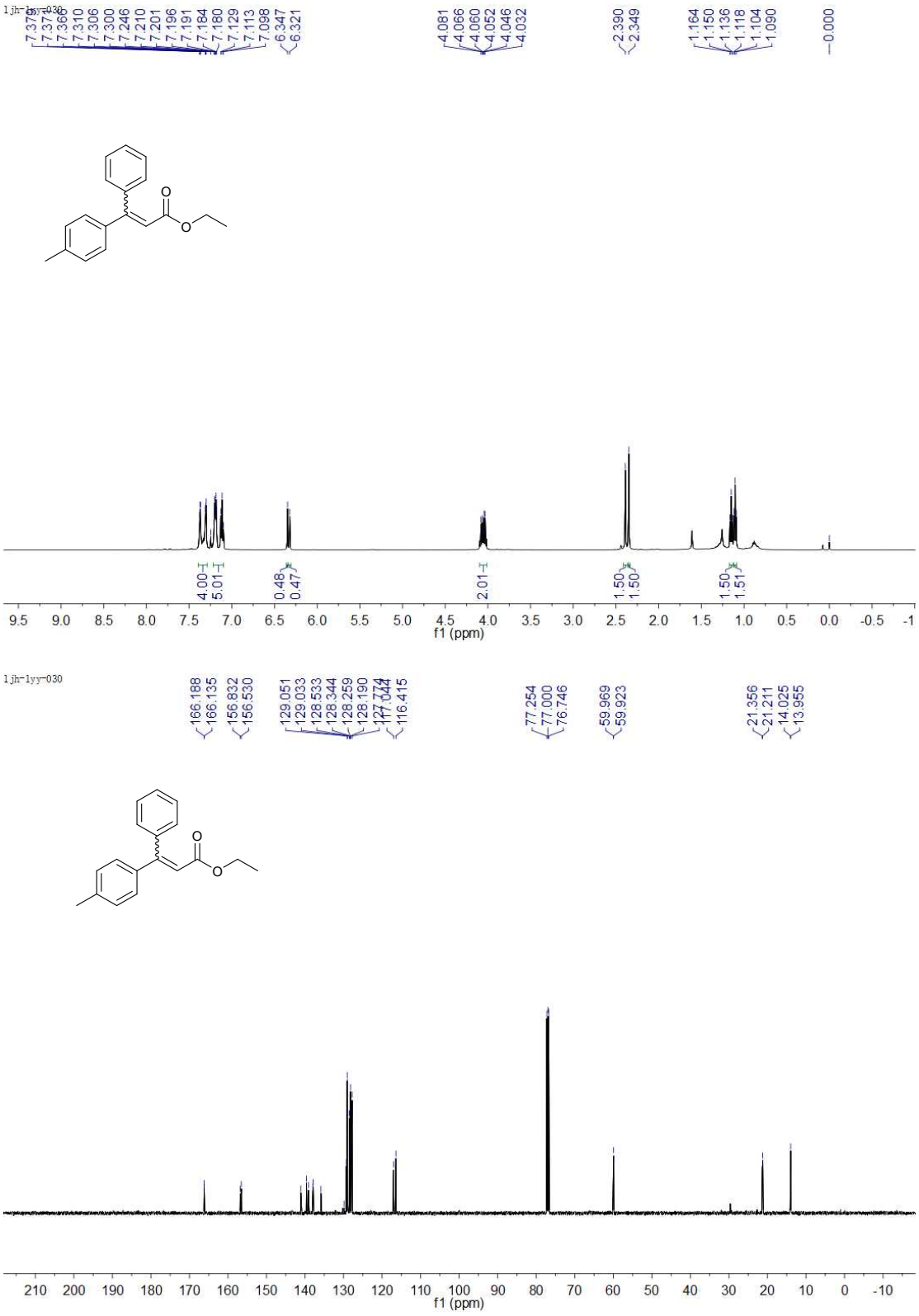
Ethyl-3-phenyl-3-(*m*-tolyl)acrylate (4la):



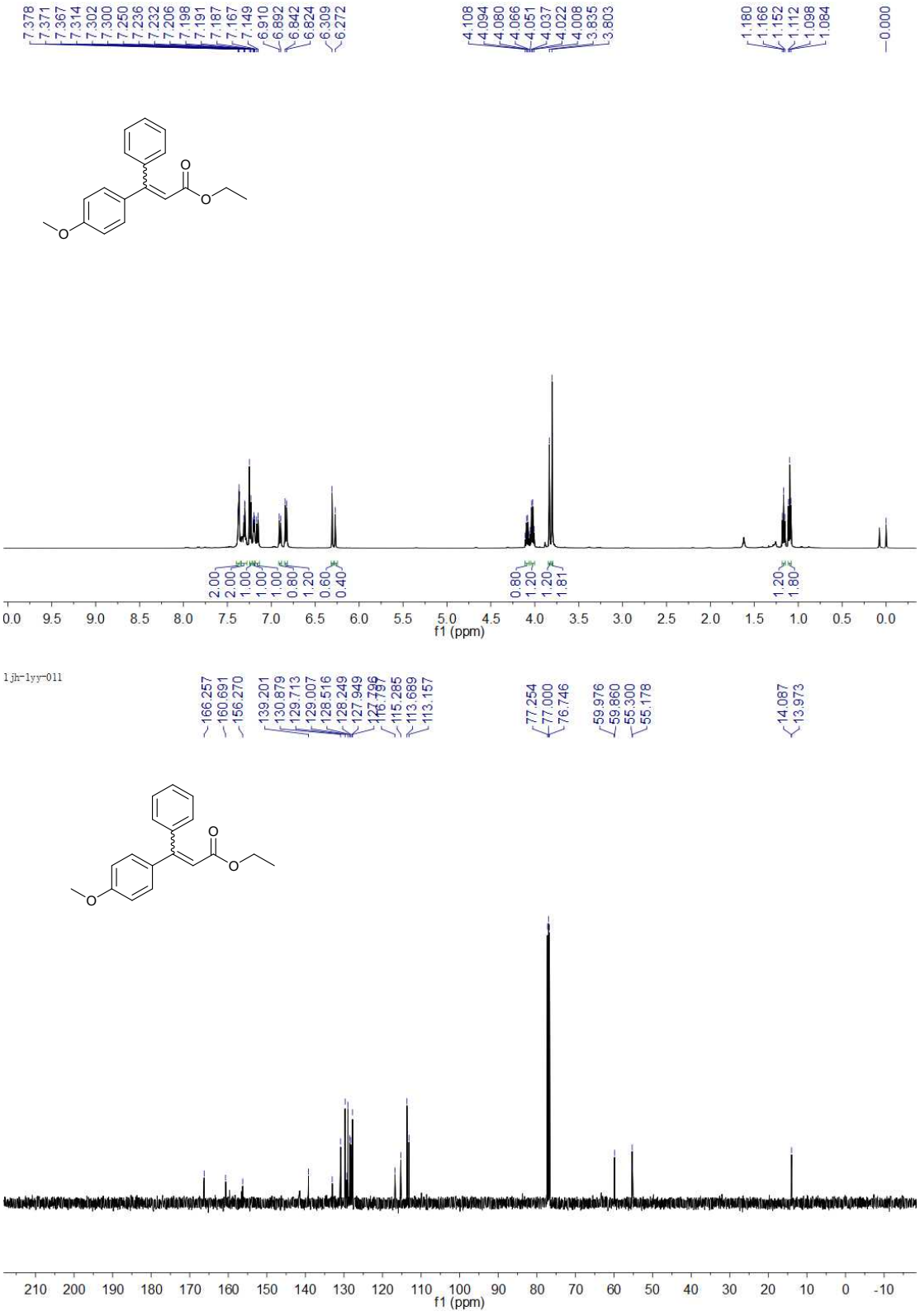
Ethyl-3-(3-chlorophenyl)-3-phenylacrylate (4ma):



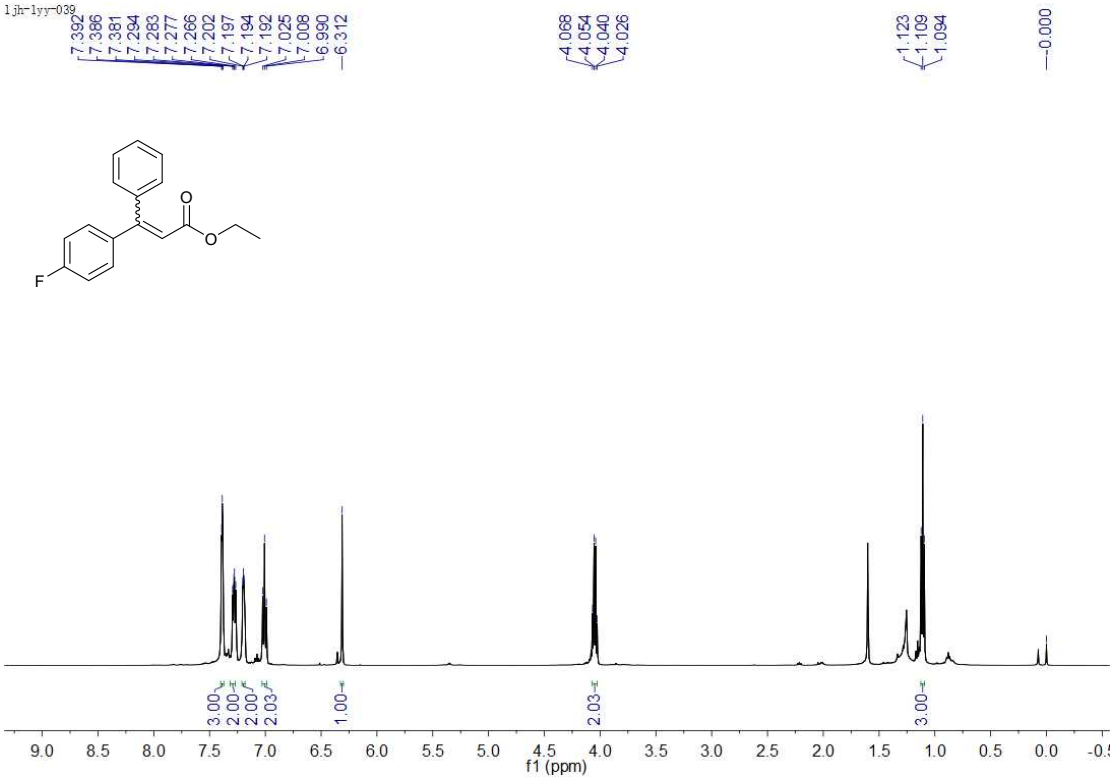
Ethyl-3-phenyl-3-(*p*-tolyl)acrylate (4na):

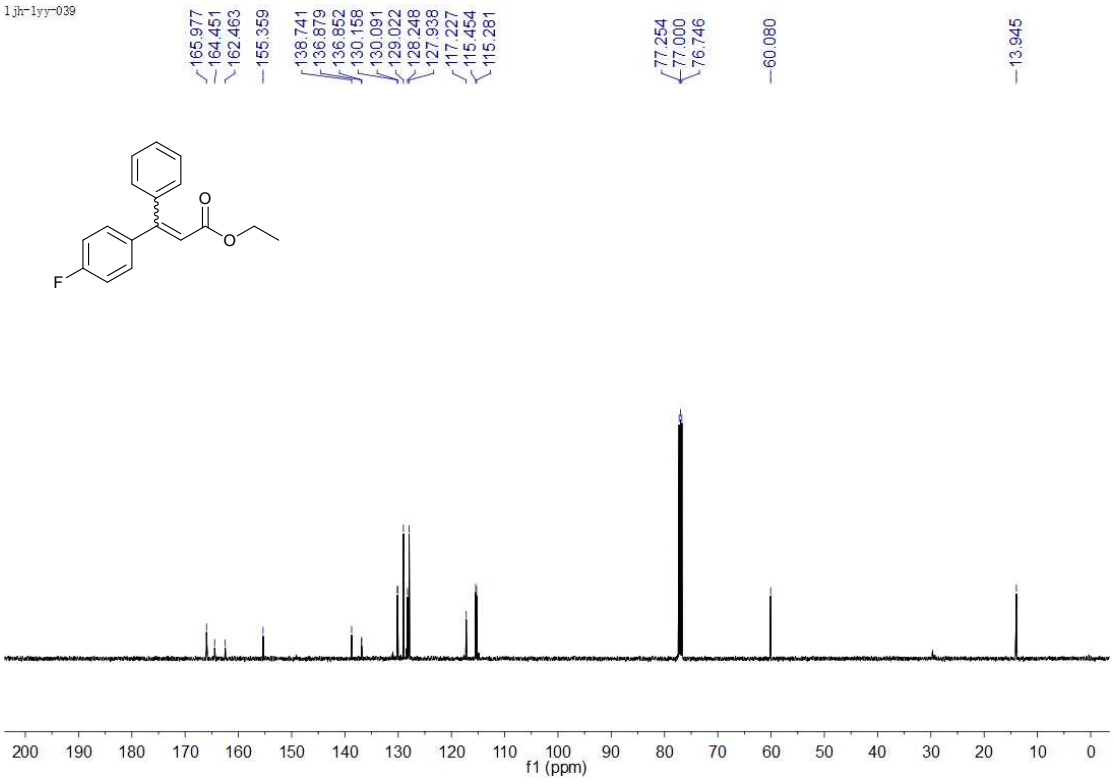


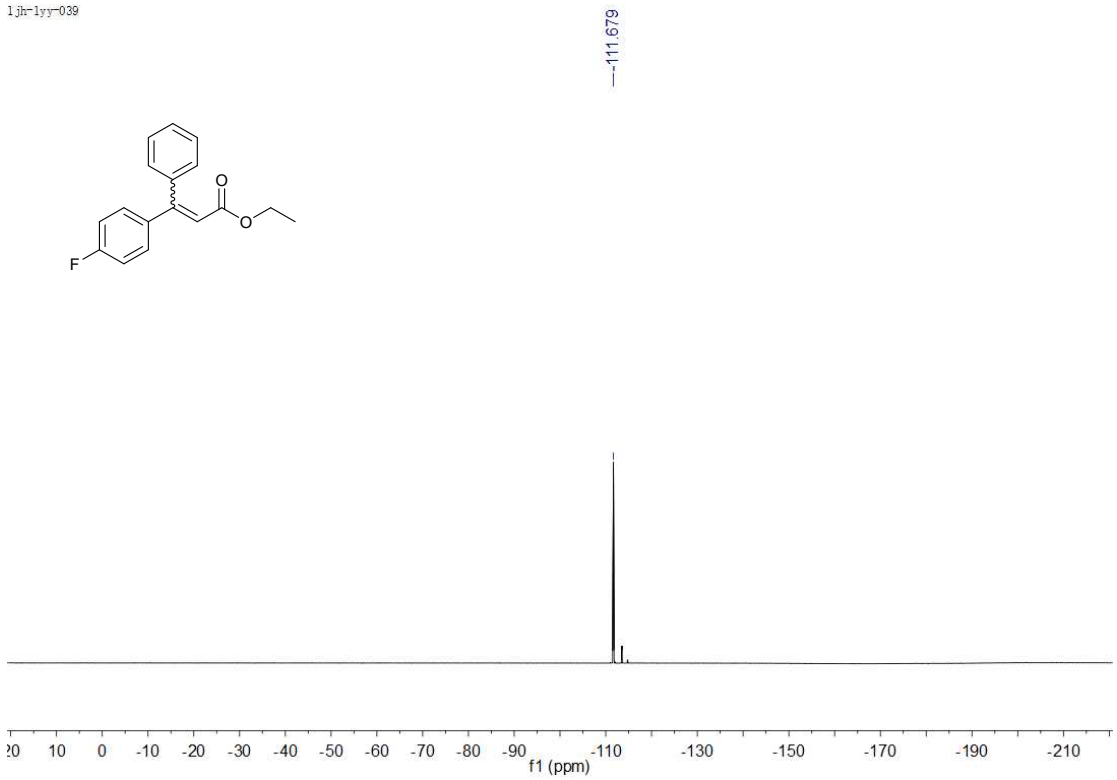
Ethyl-3-(4-methoxyphenyl)-3-phenylacrylate (4oa):



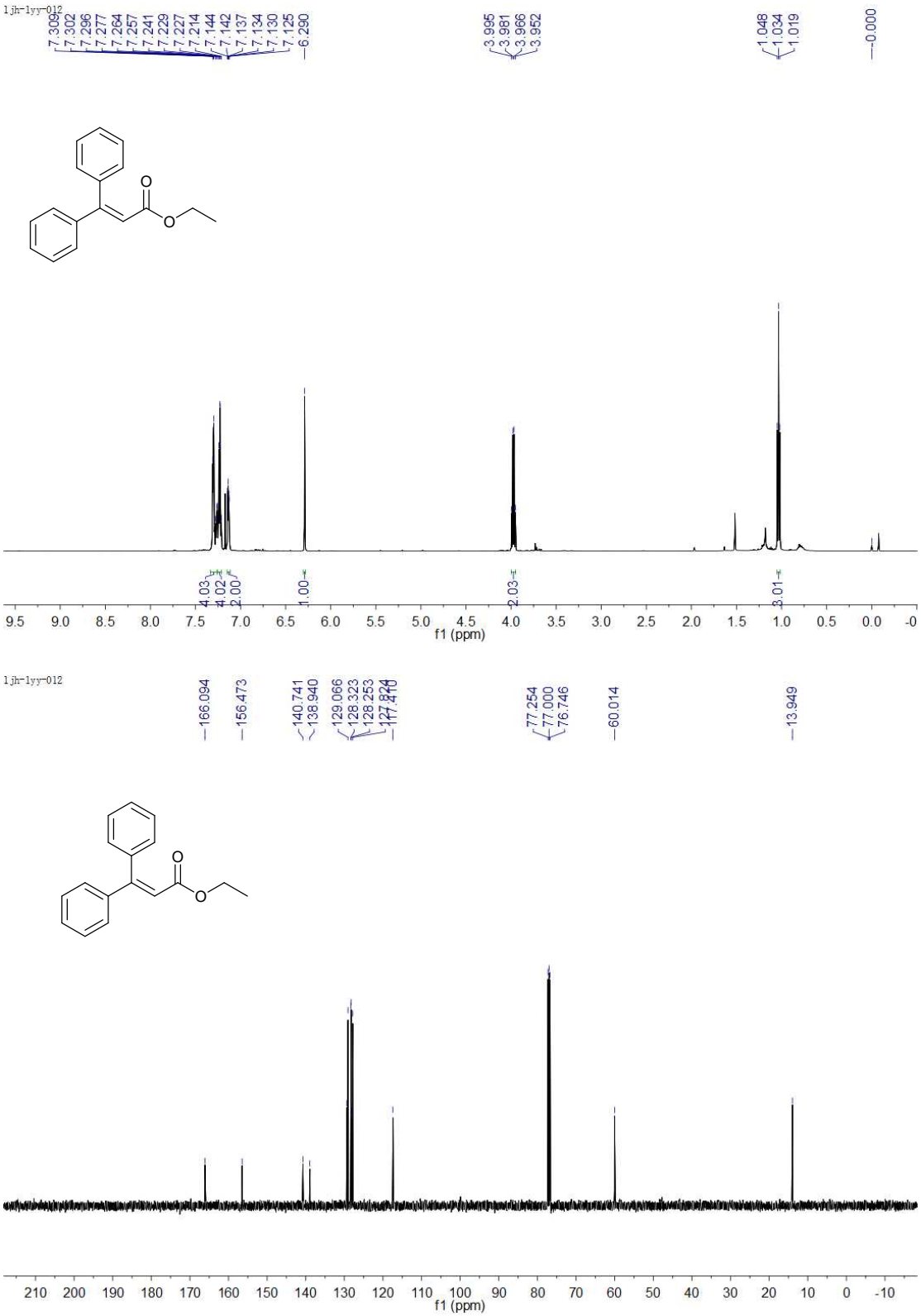
Ethyl-3-(4-fluorophenyl)-3-phenylacrylate (4pa):



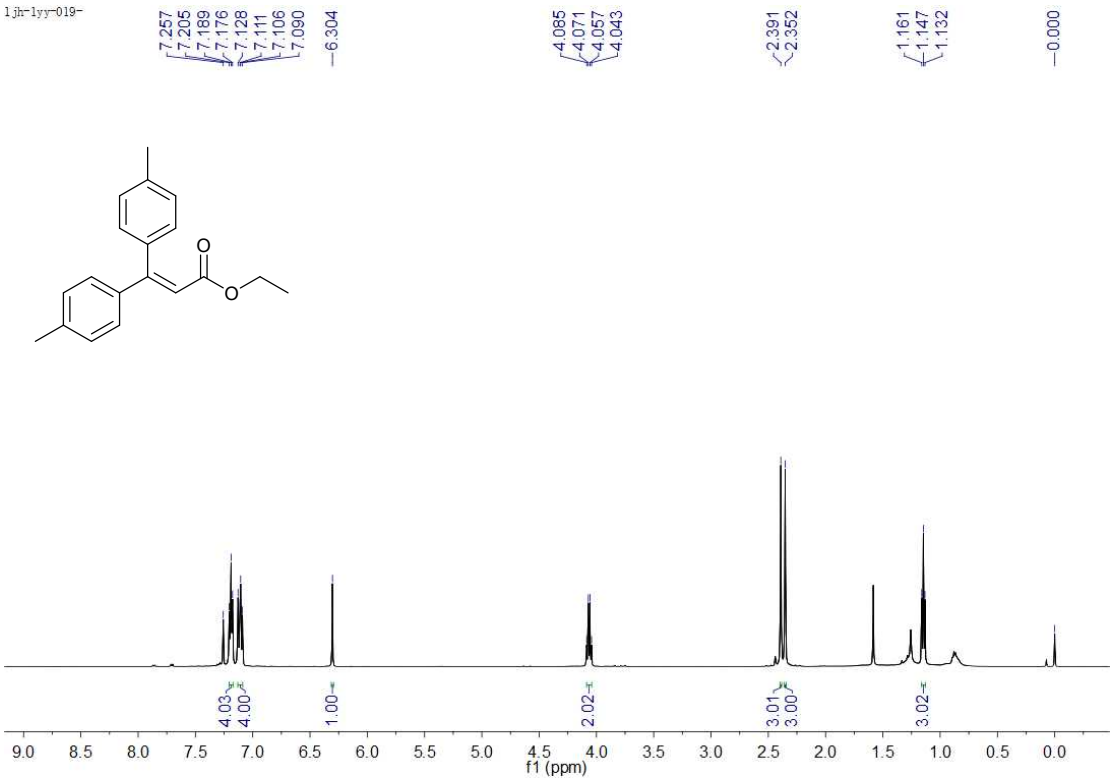


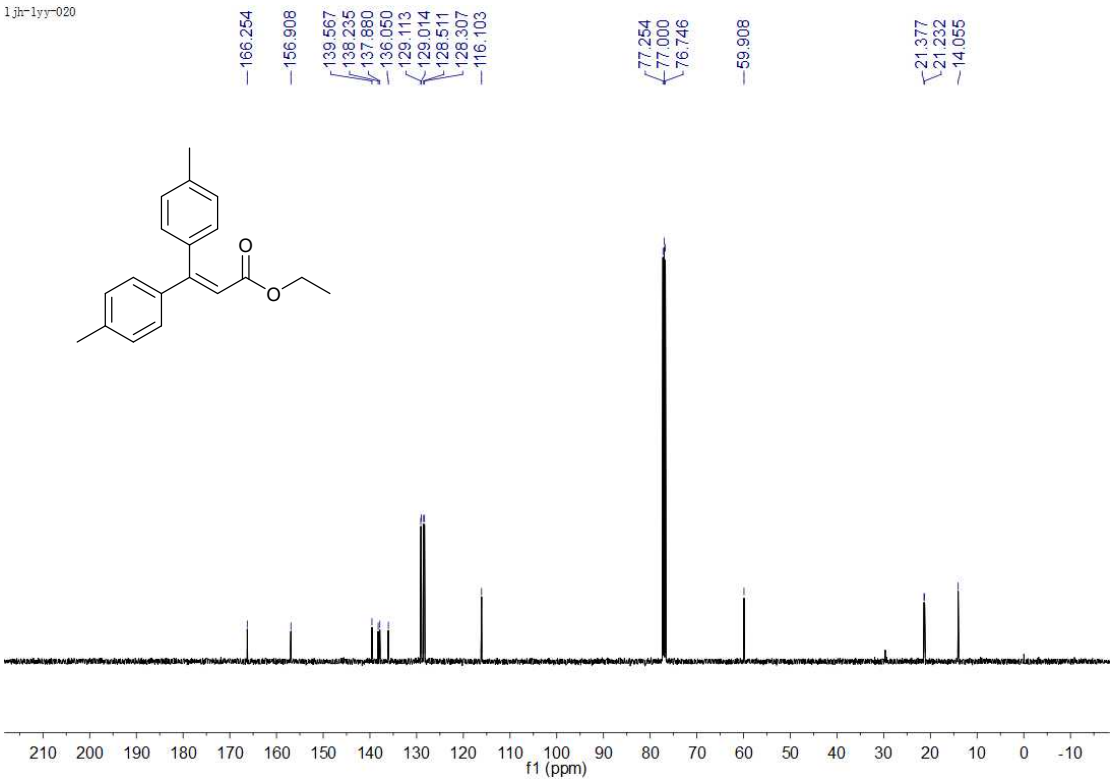

ljh-lyy-039
-111.679
O
O
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Ethyl 3,3-diphenylacrylate (4qa):

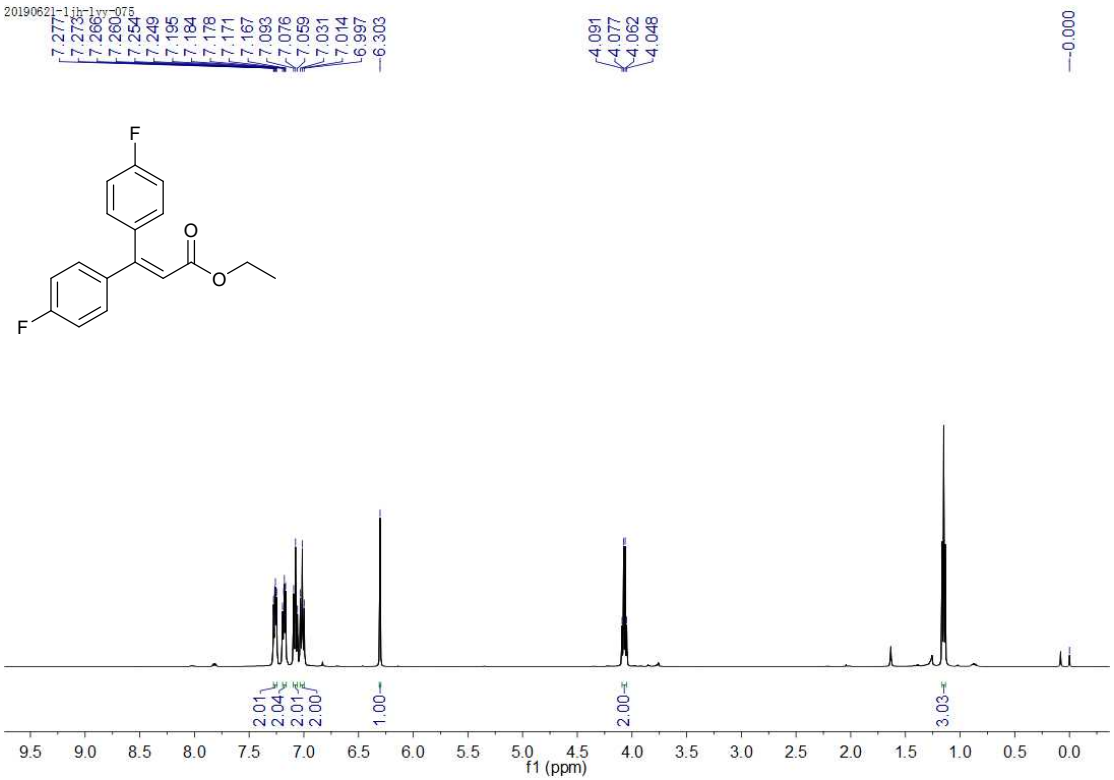


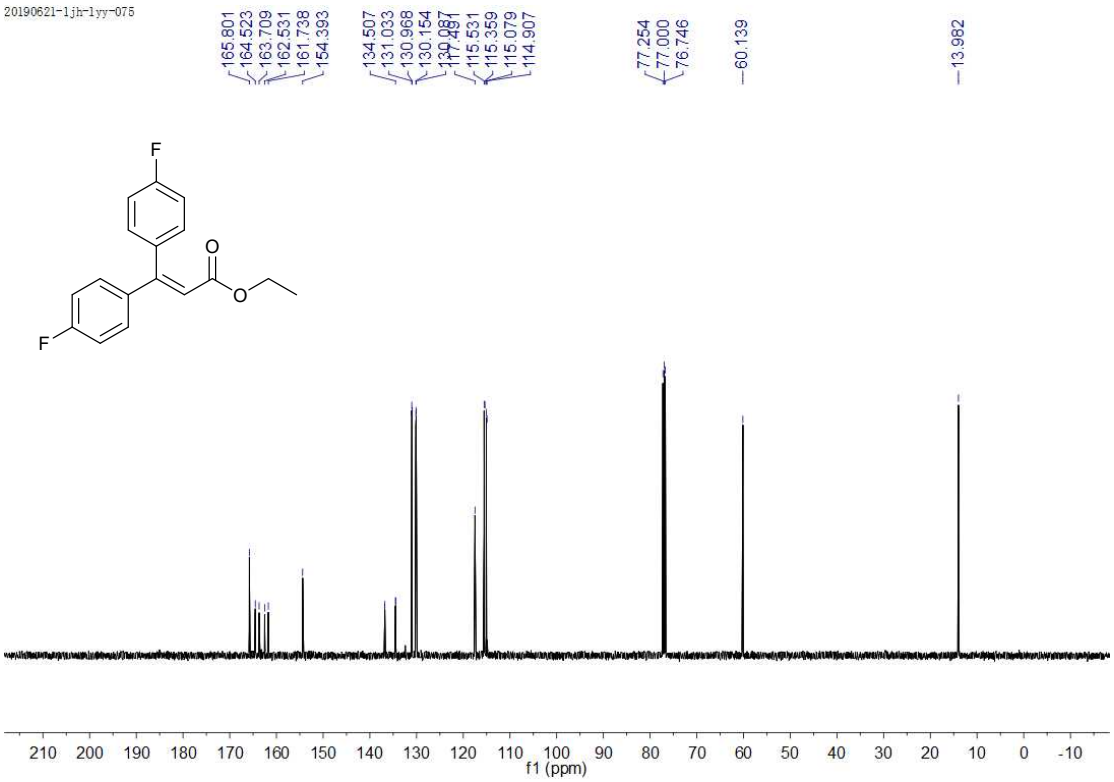
Ethyl 3,3-di-*p*-tolylacrylate (4ra):

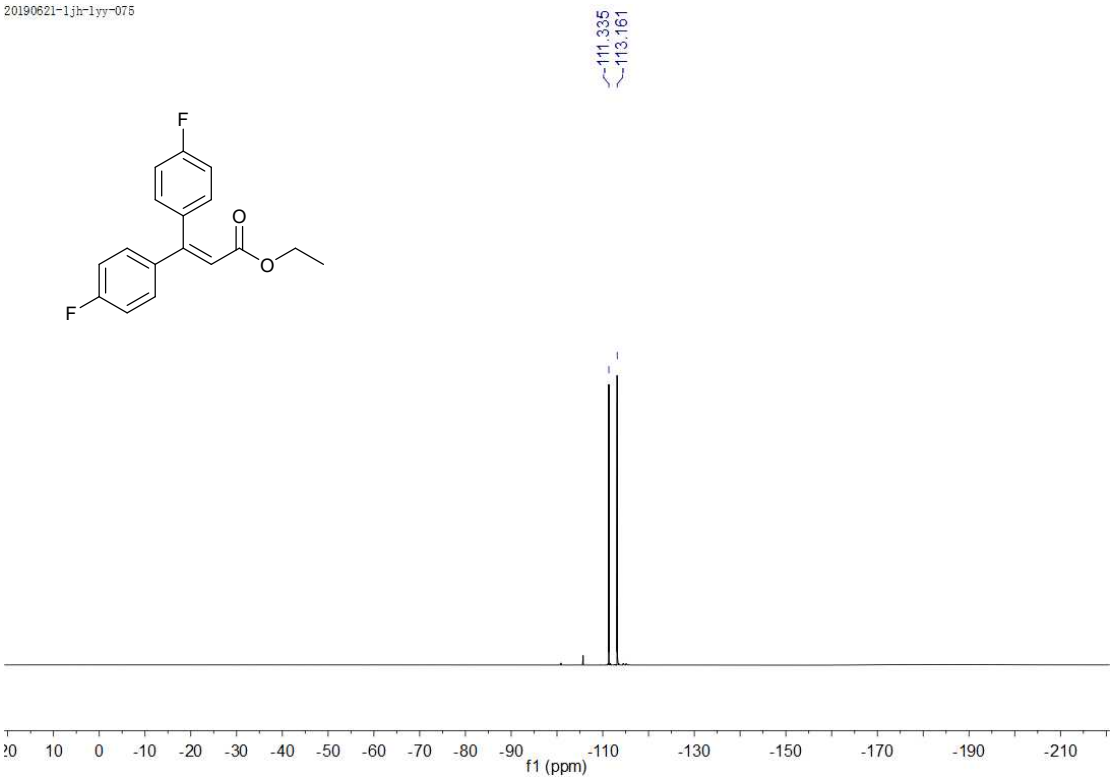




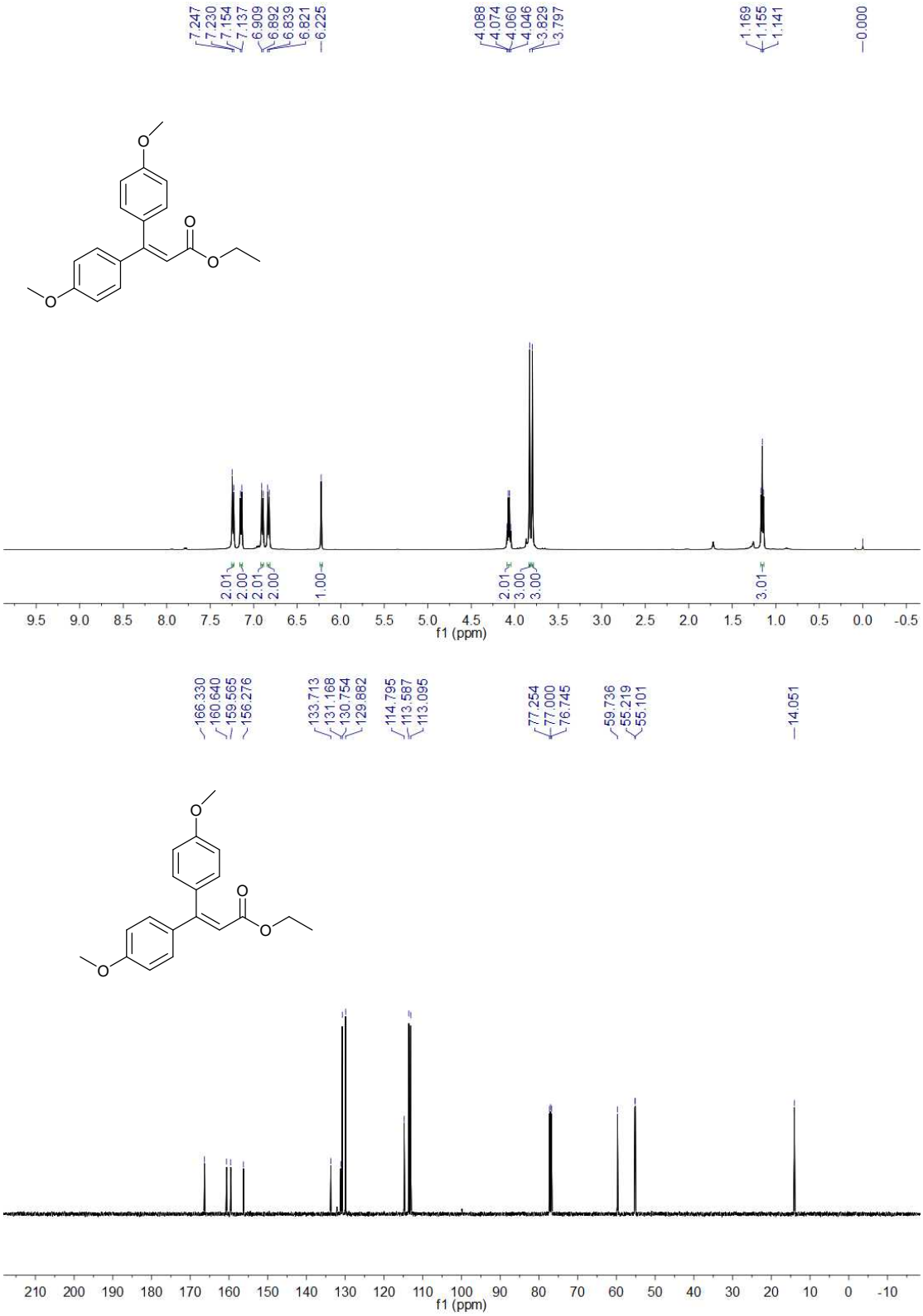
Ethyl 3,3-bis(4-fluorophenyl)acrylate (4sa):



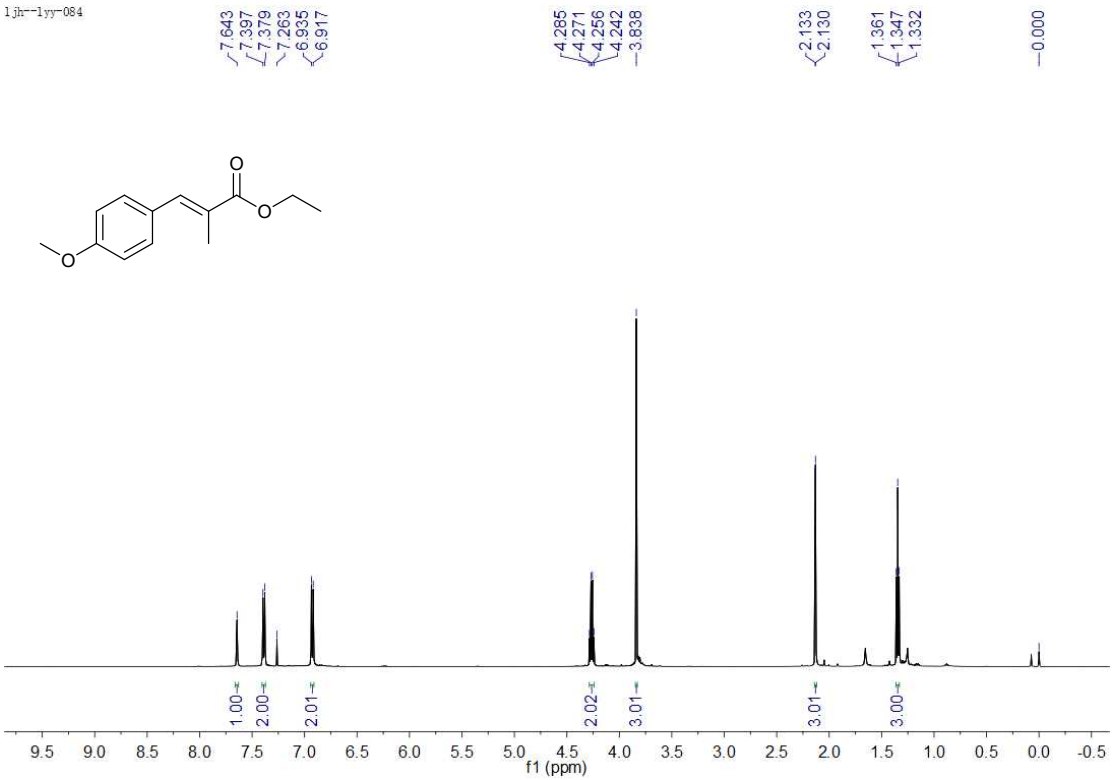


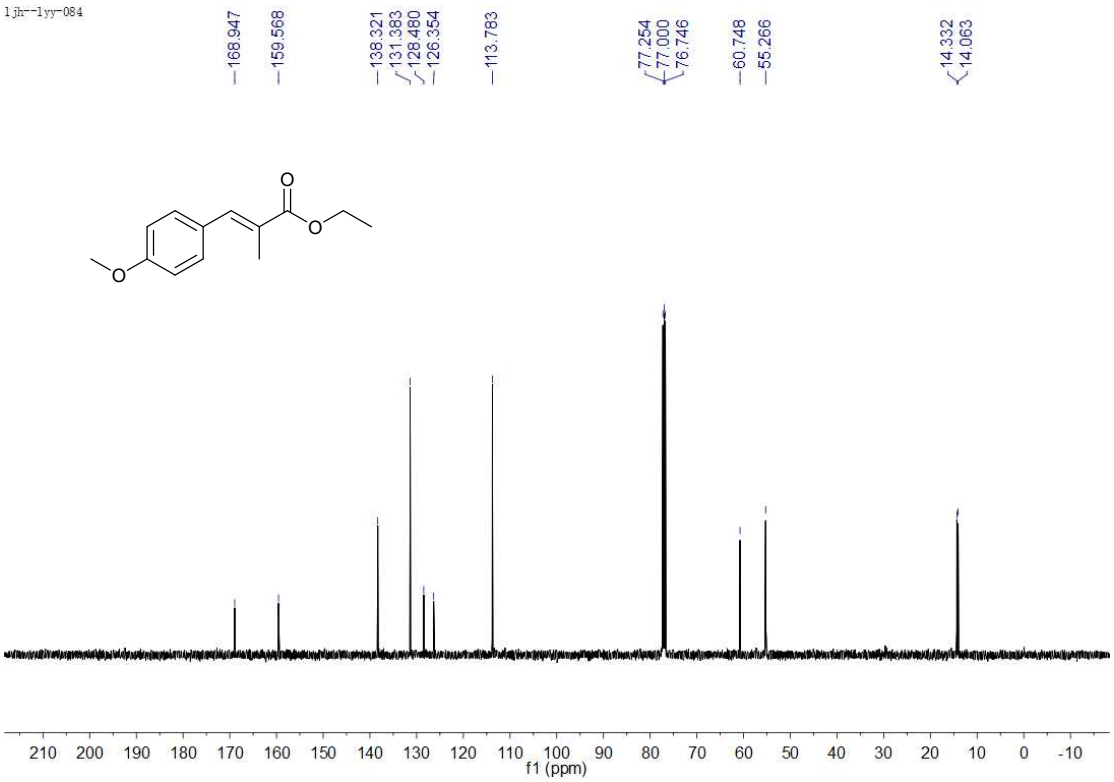

20190621-ljh-lyy-075
111.335
113.161
F
O
O
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Ethyl 3,3-bis(4-methoxyphenyl)acrylate (4ta):

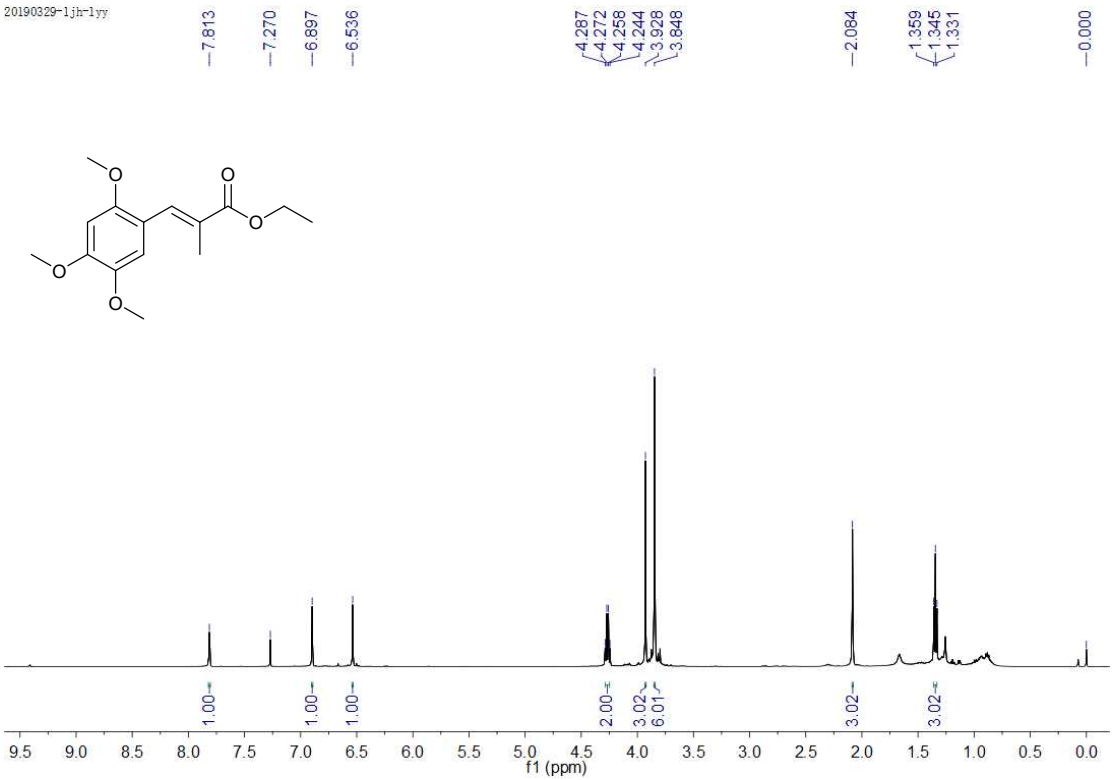


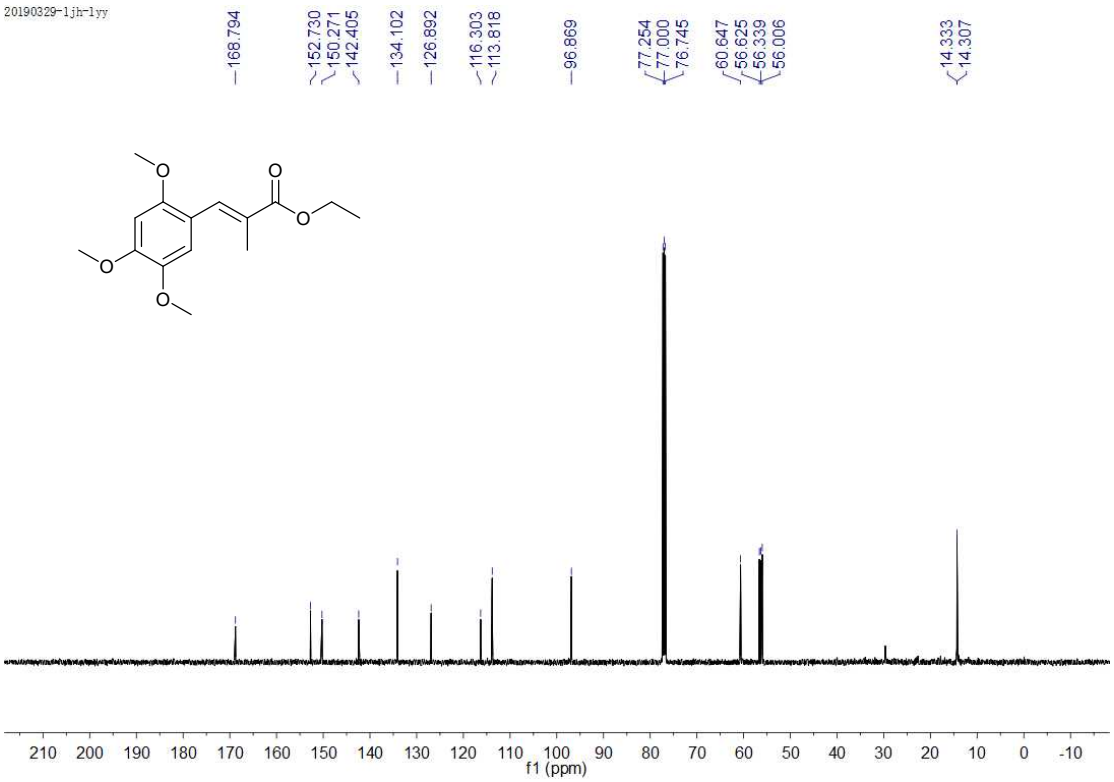
Ethyl (*E*)-3-(4-methoxyphenyl)-2-methylacrylate (4ua):



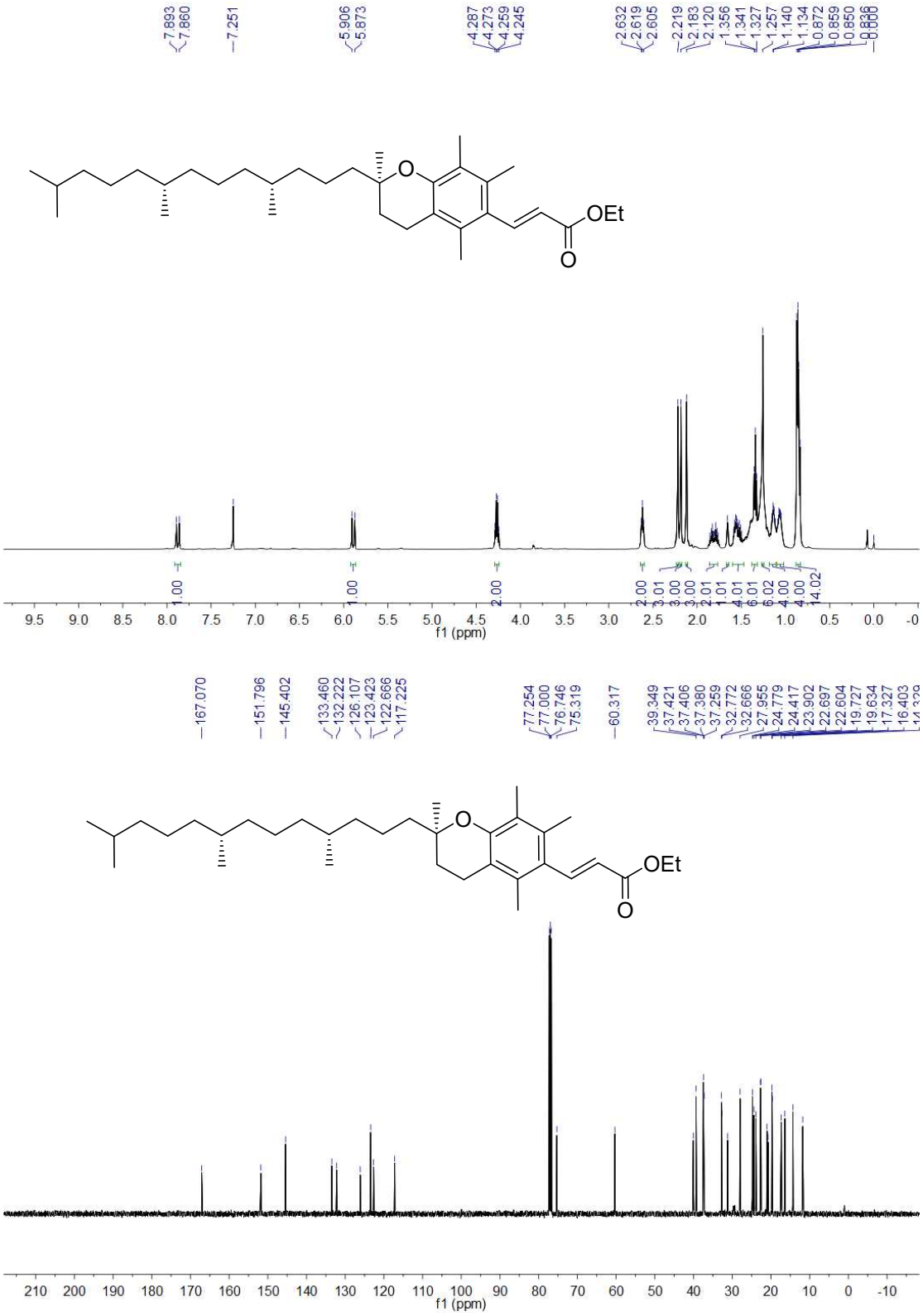


Ethyl (*E*)-2-methyl-3-(2,4,5-trimethoxyphenyl)acrylate (4va):

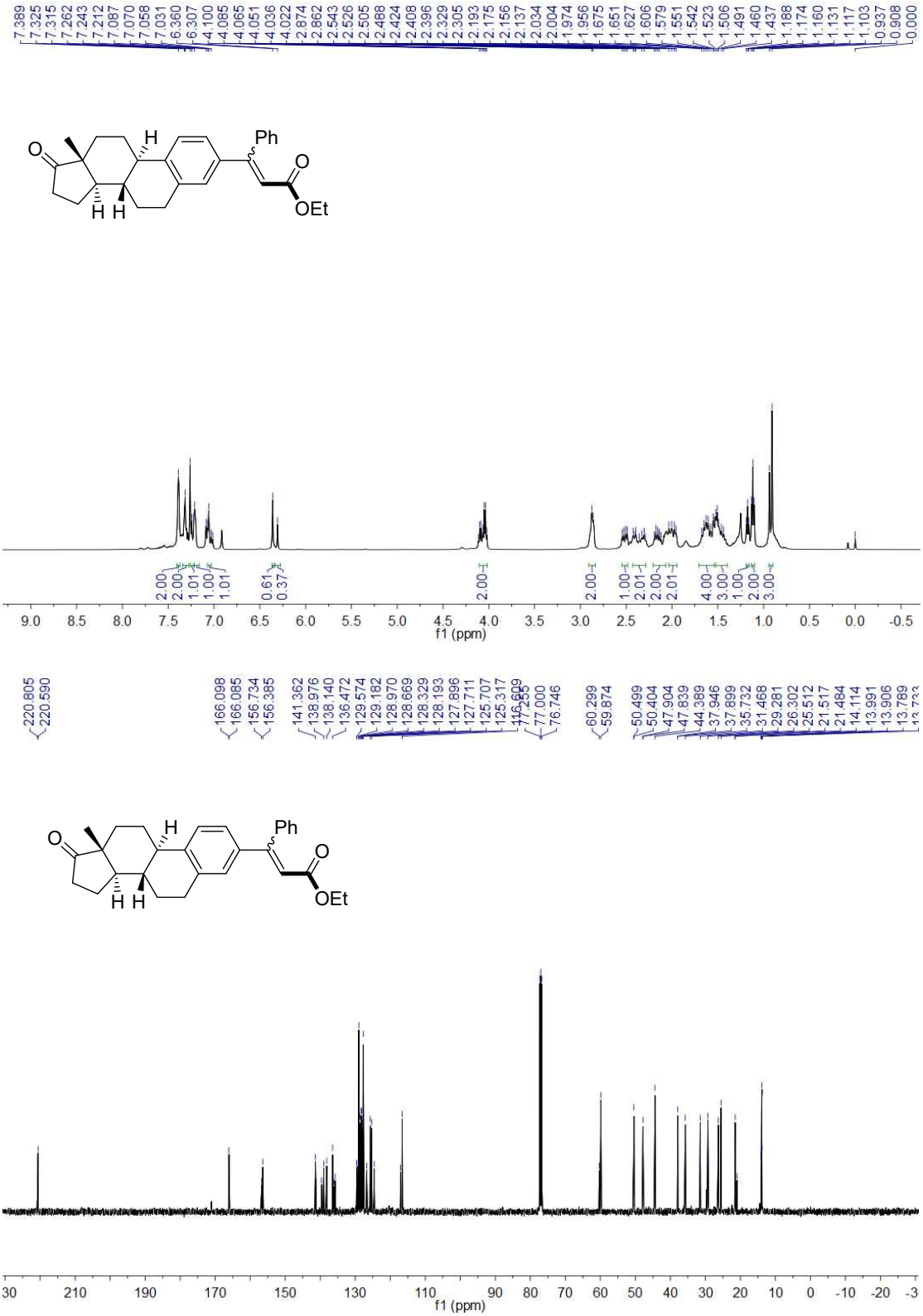




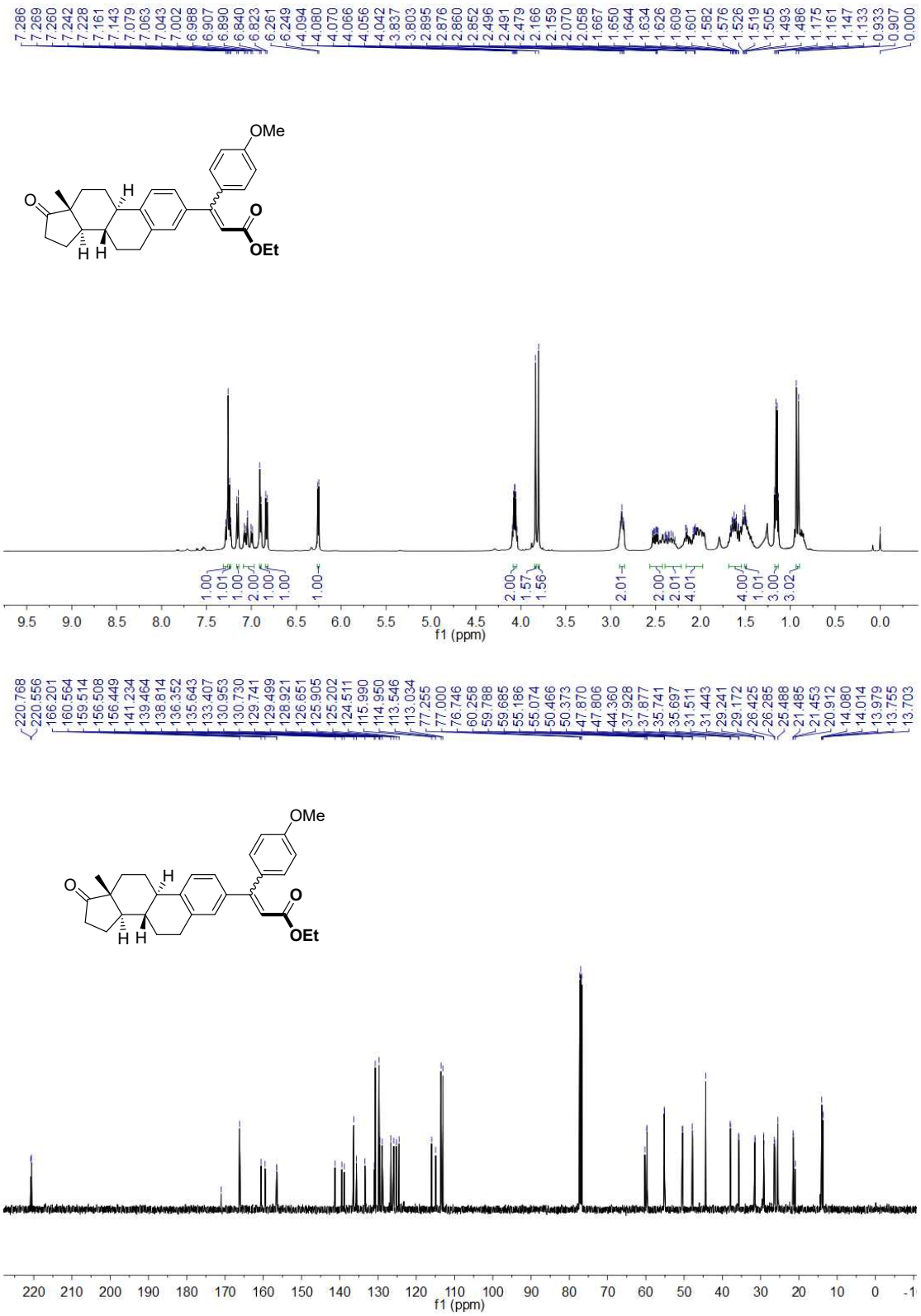
Ethyl-(*E*)-3-(2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)acrylate (4wa):



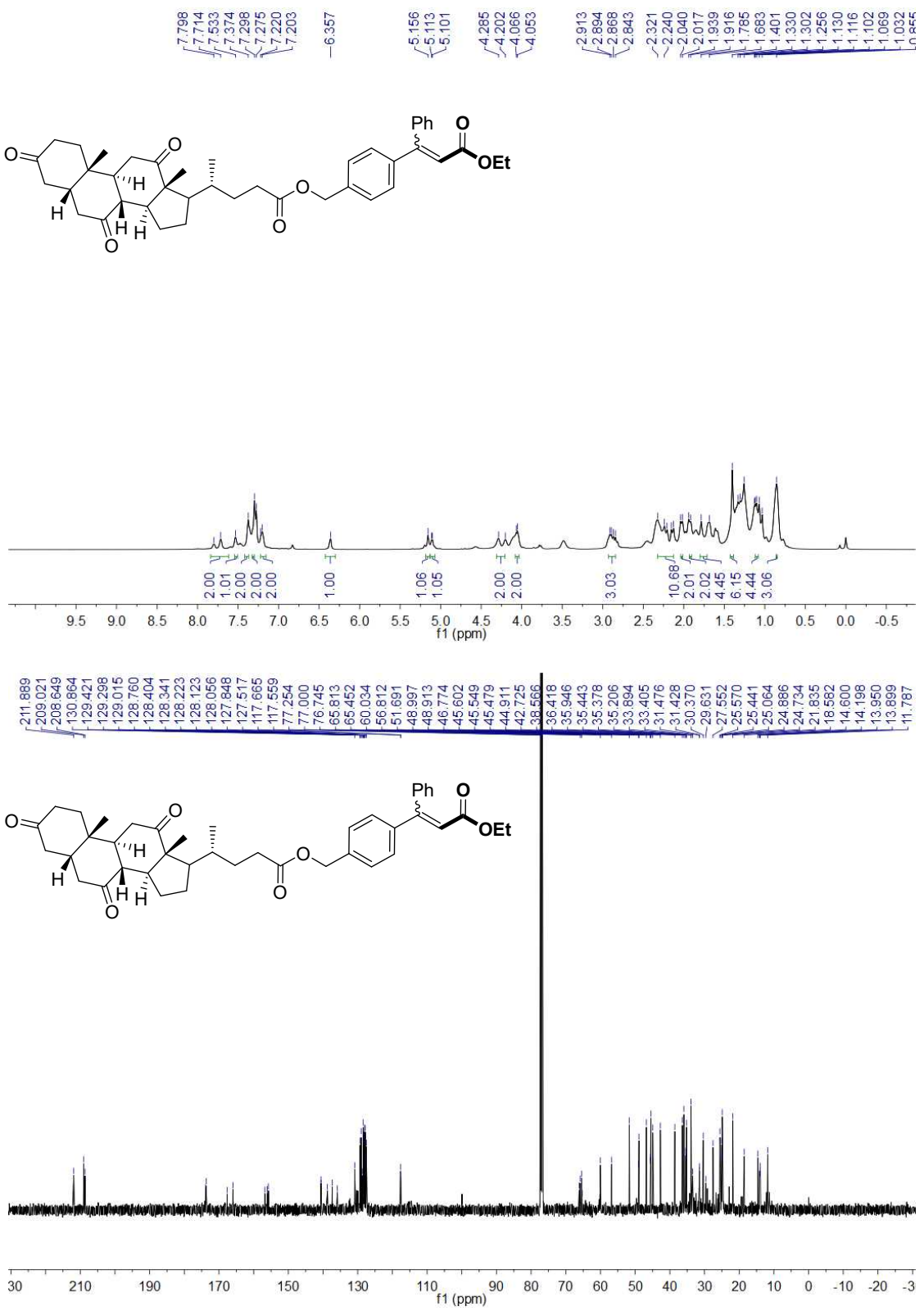
Ethyl-3-(13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)-3-phenylacrylate (4xa):



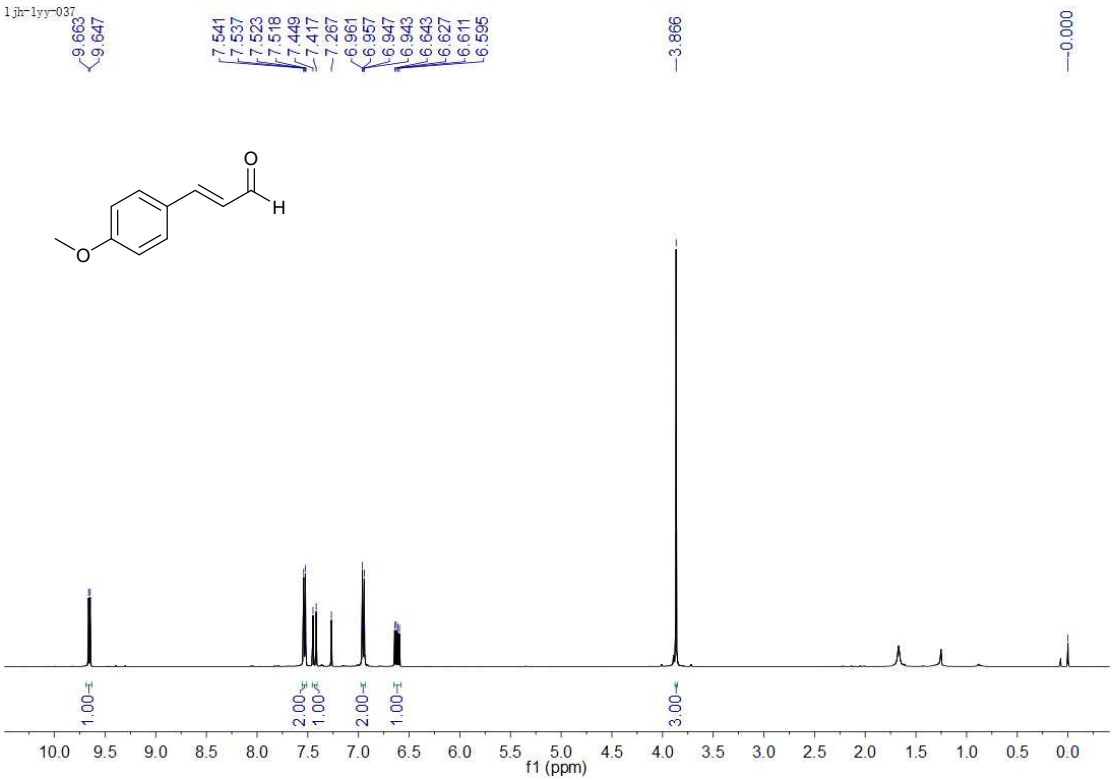
Ethyl-3-(4-methoxyphenyl)-3-(13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)acrylate (4ya):

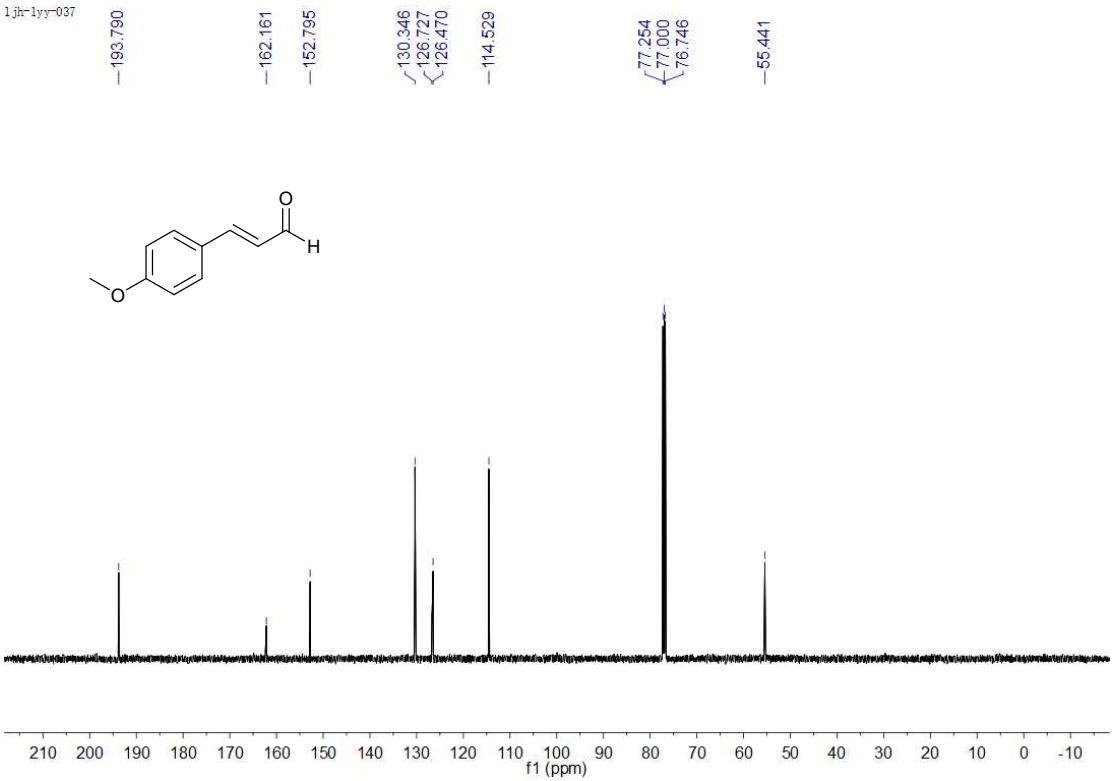


4-(3-Ethoxy-3-oxo-1-phenylprop-1-en-1-yl)benzyl-(4R)-4-((5S,8R,9S,10S,13R,14S)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (4za):

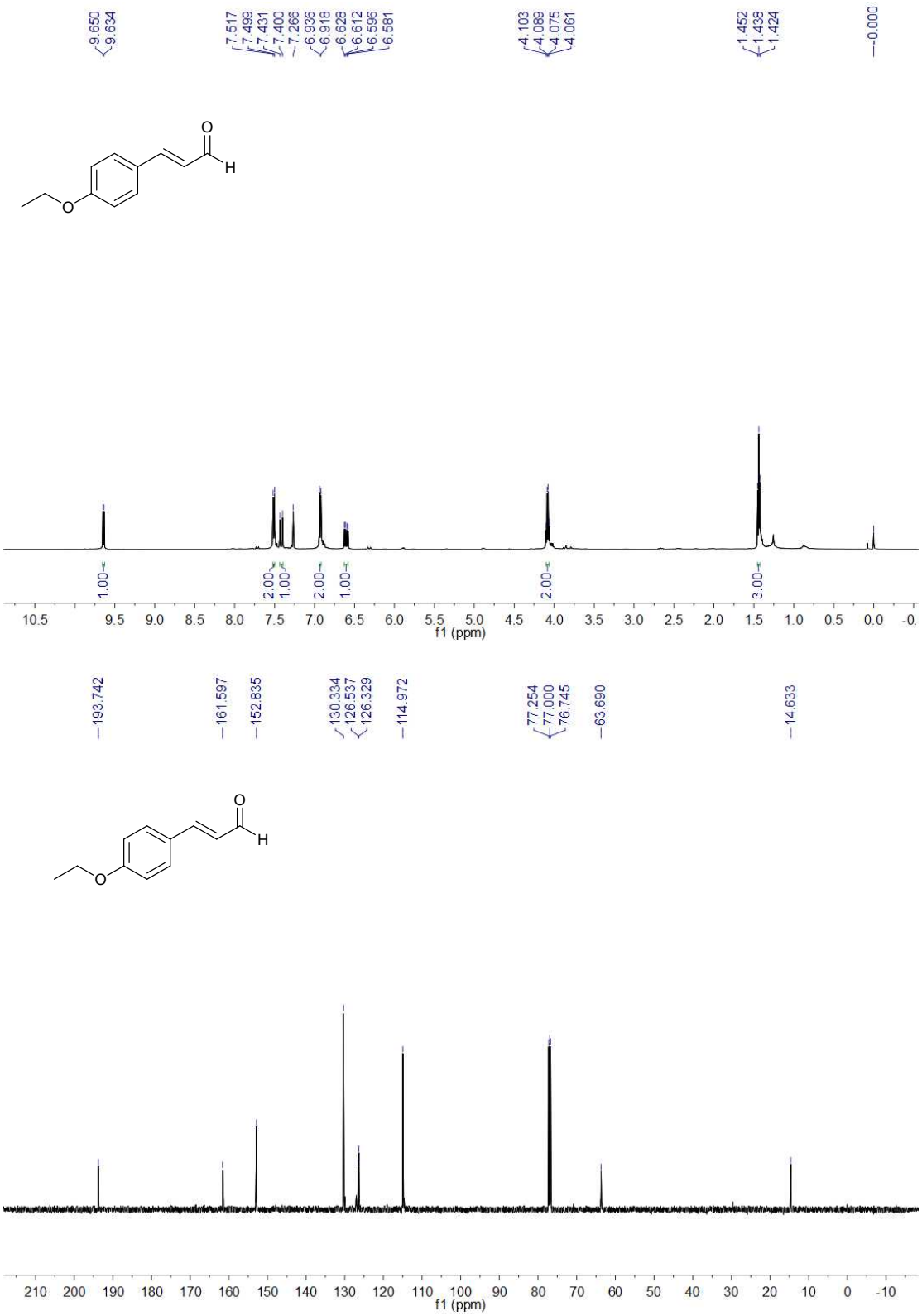


(*E*)-3-(4-methoxyphenyl)acrylaldehyde (5a):

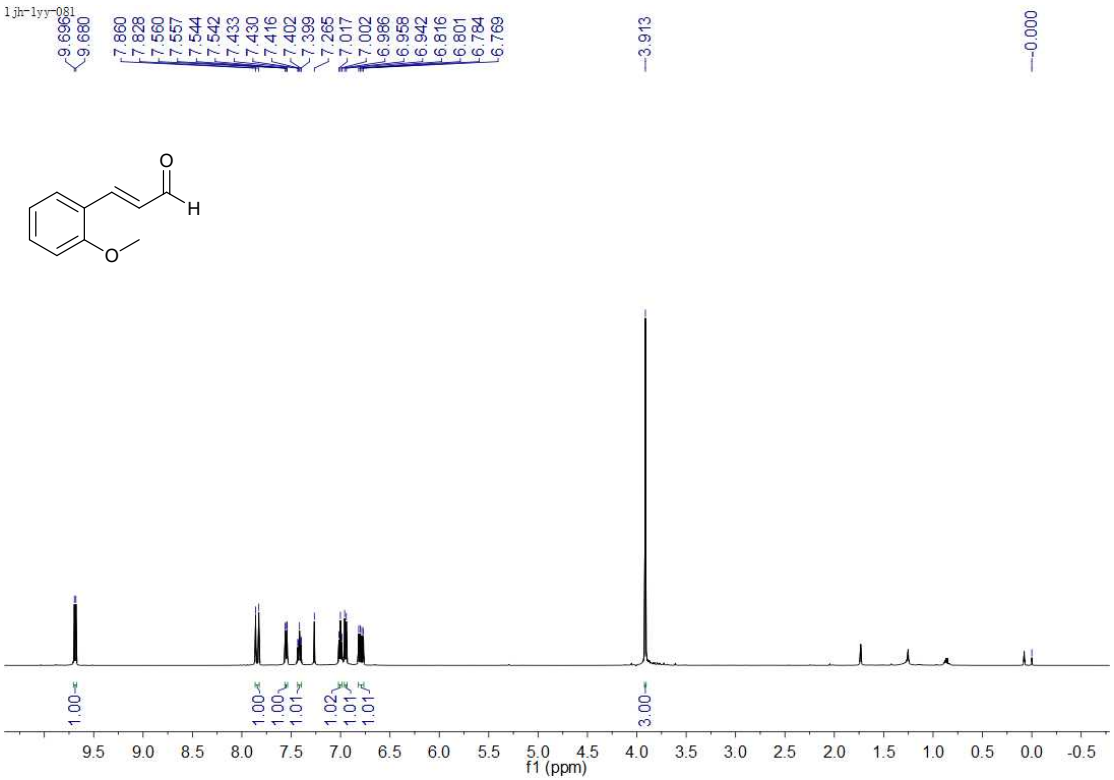


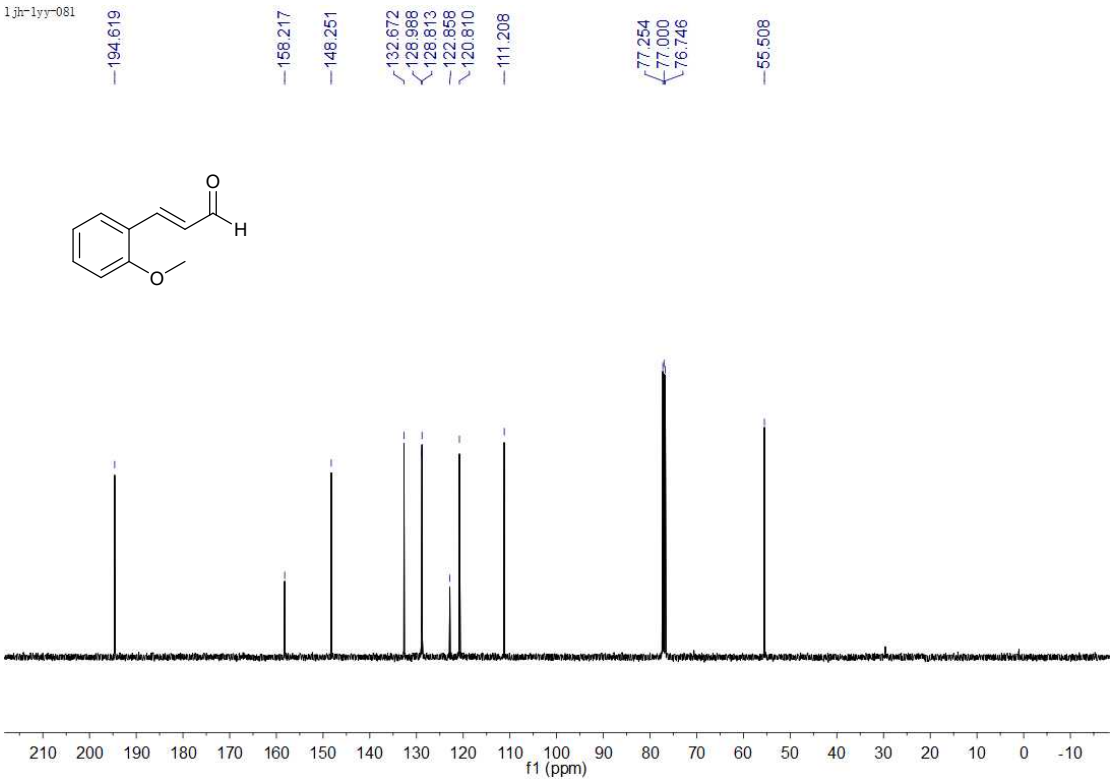


(*E*)-3-(4-Ethoxyphenyl)acrylaldehyde (5b):

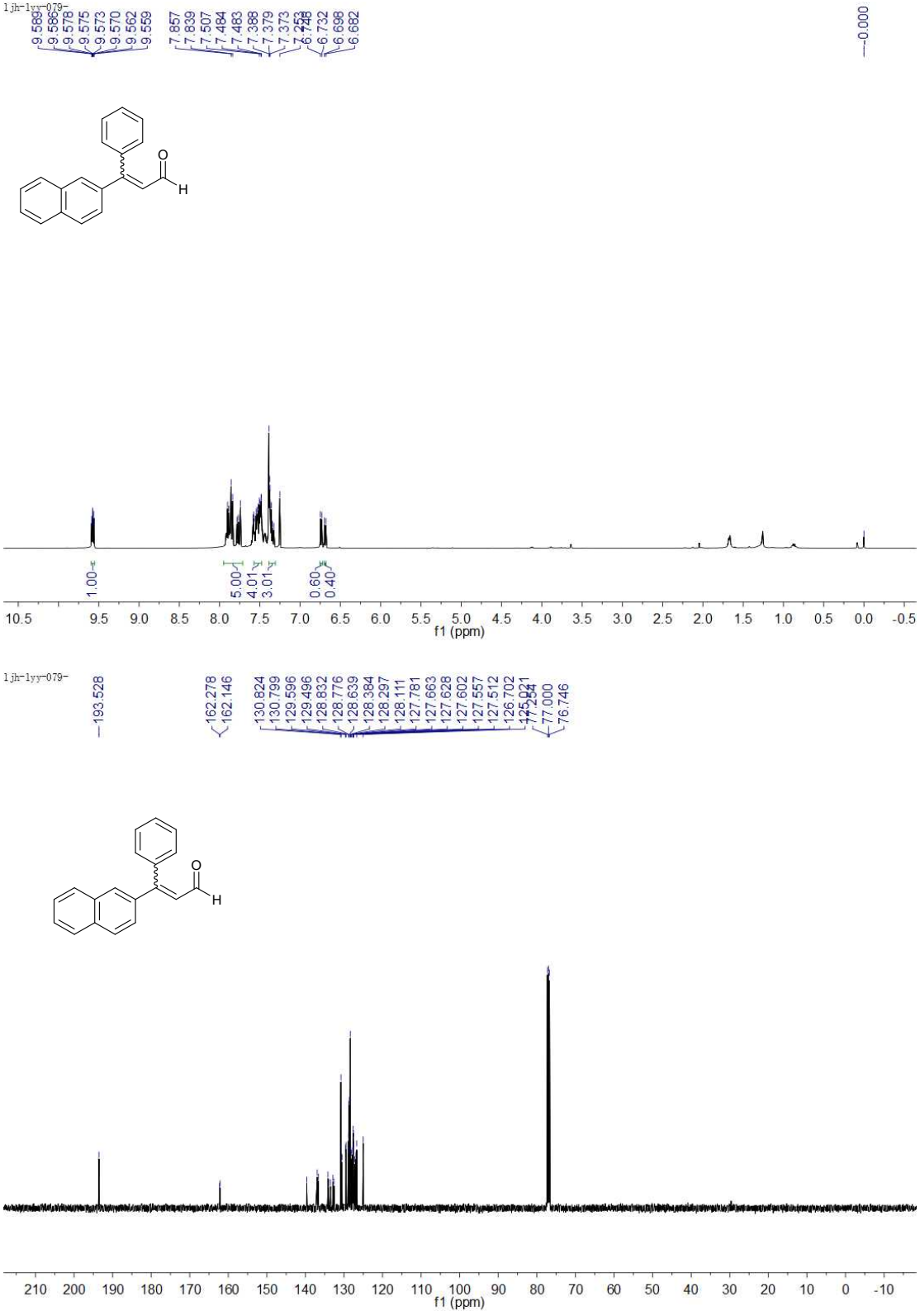


(*E*)-3-(2-Methoxyphenyl)acrylaldehyde (5c):

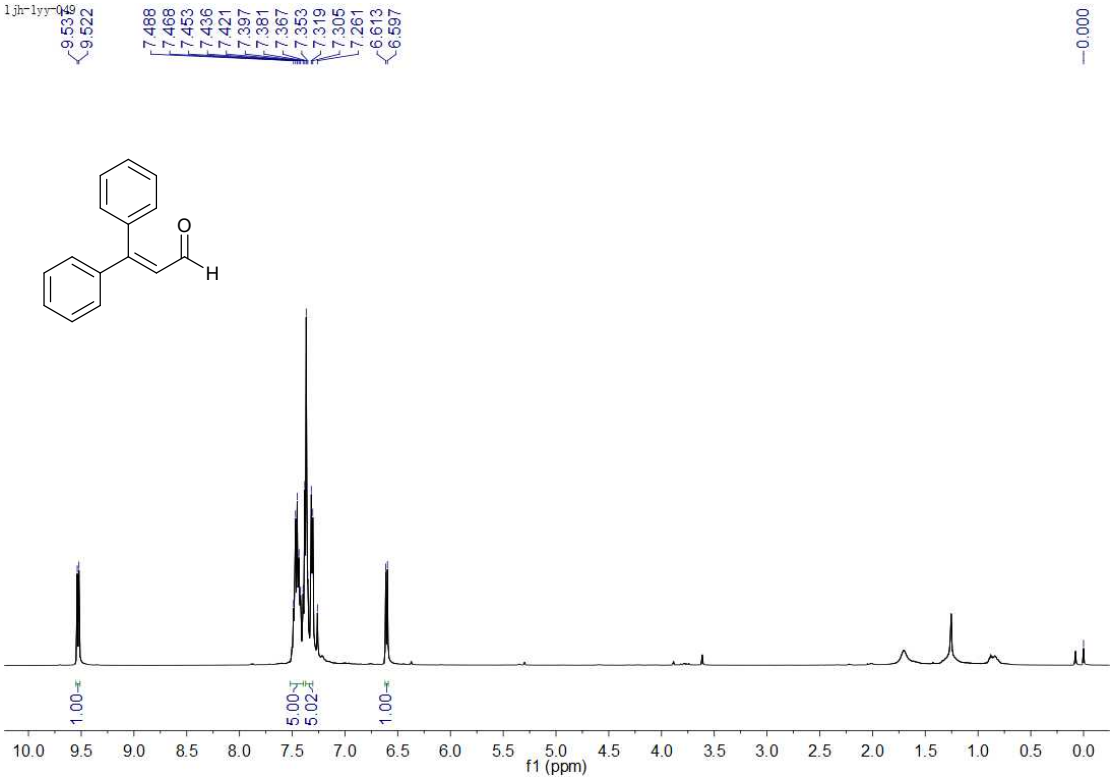


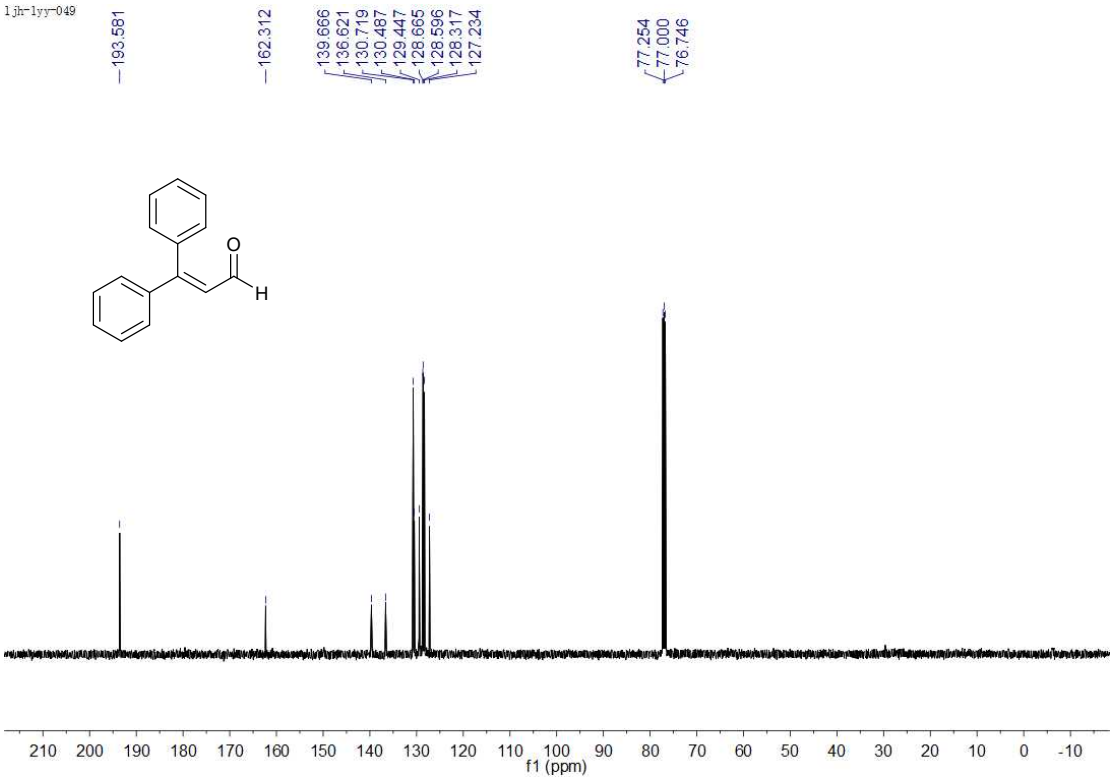


3-(Naphthalen-2-yl)-3-phenylacrylaldehyde (5d):

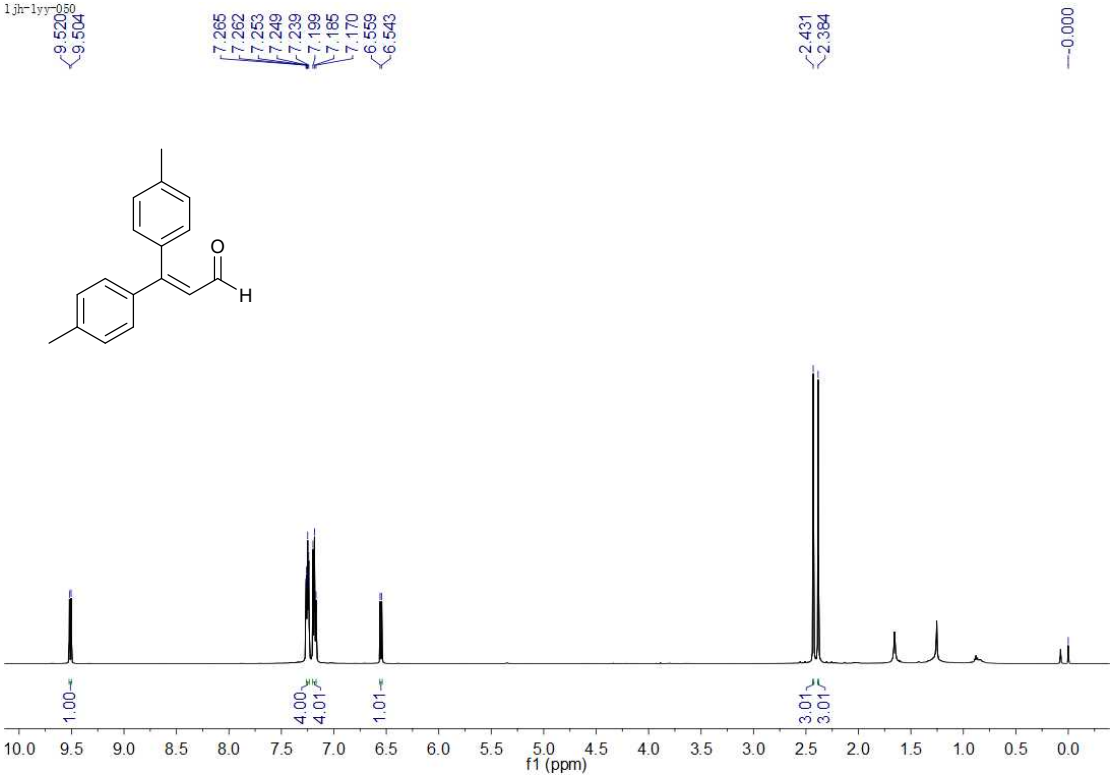


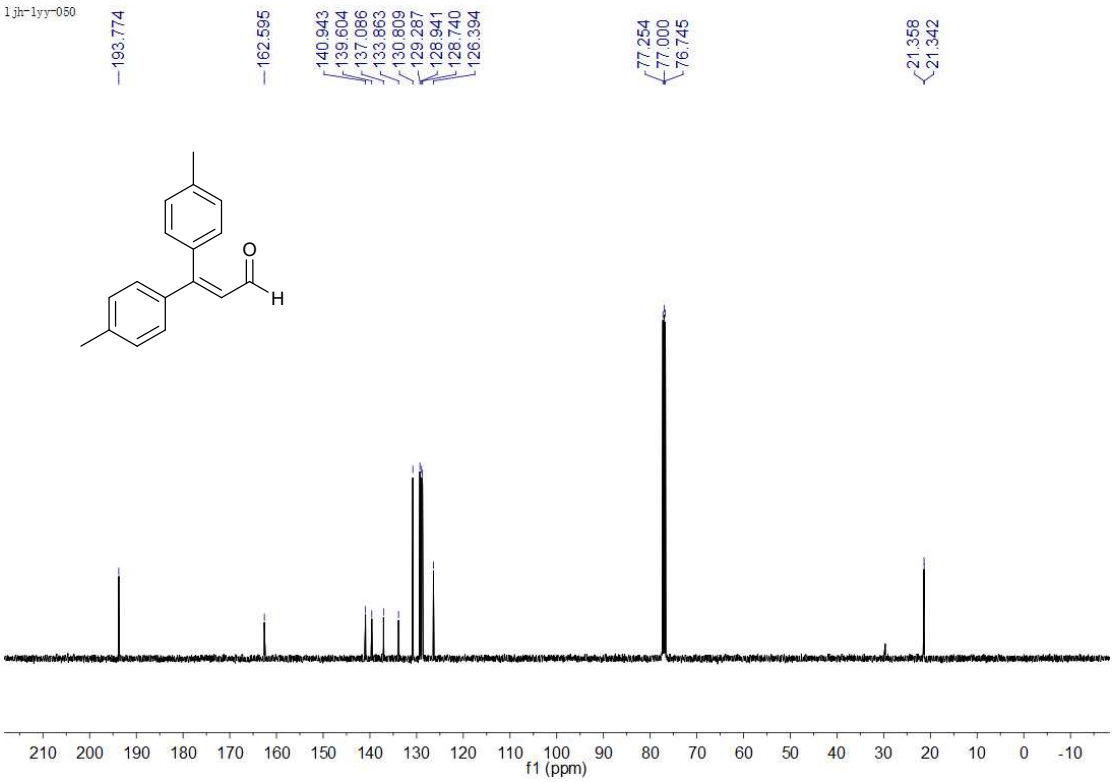
3,3-Diphenylacrylaldehyde (5e):



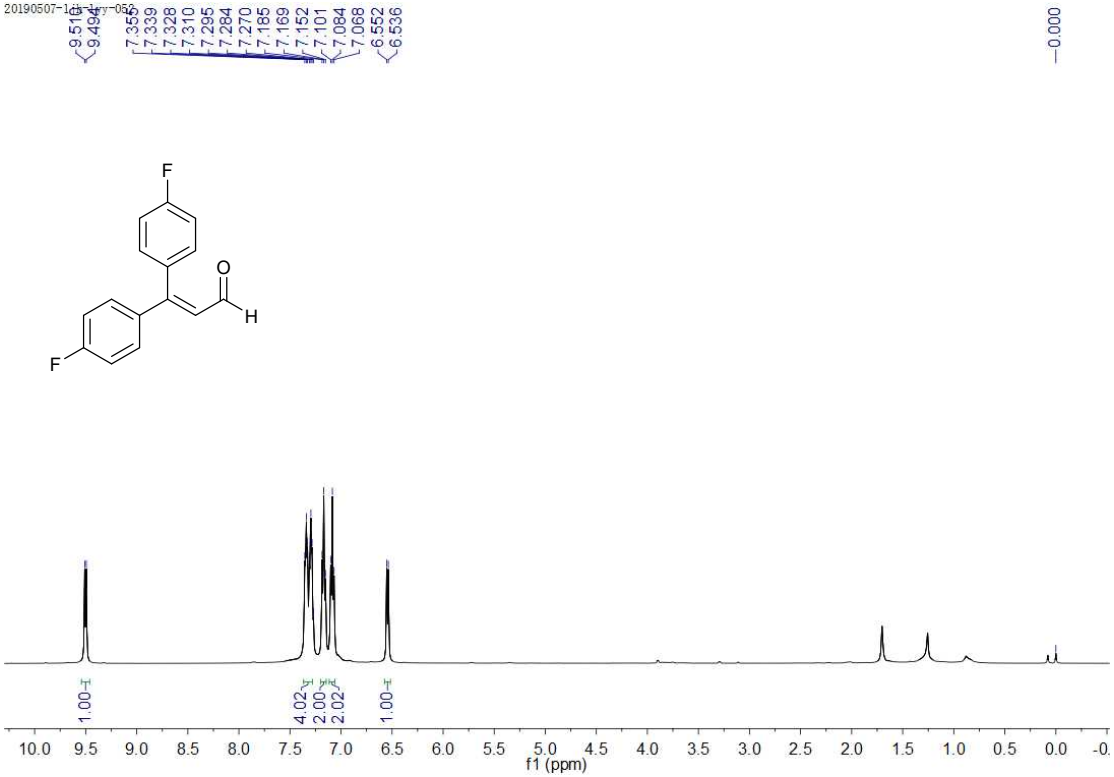


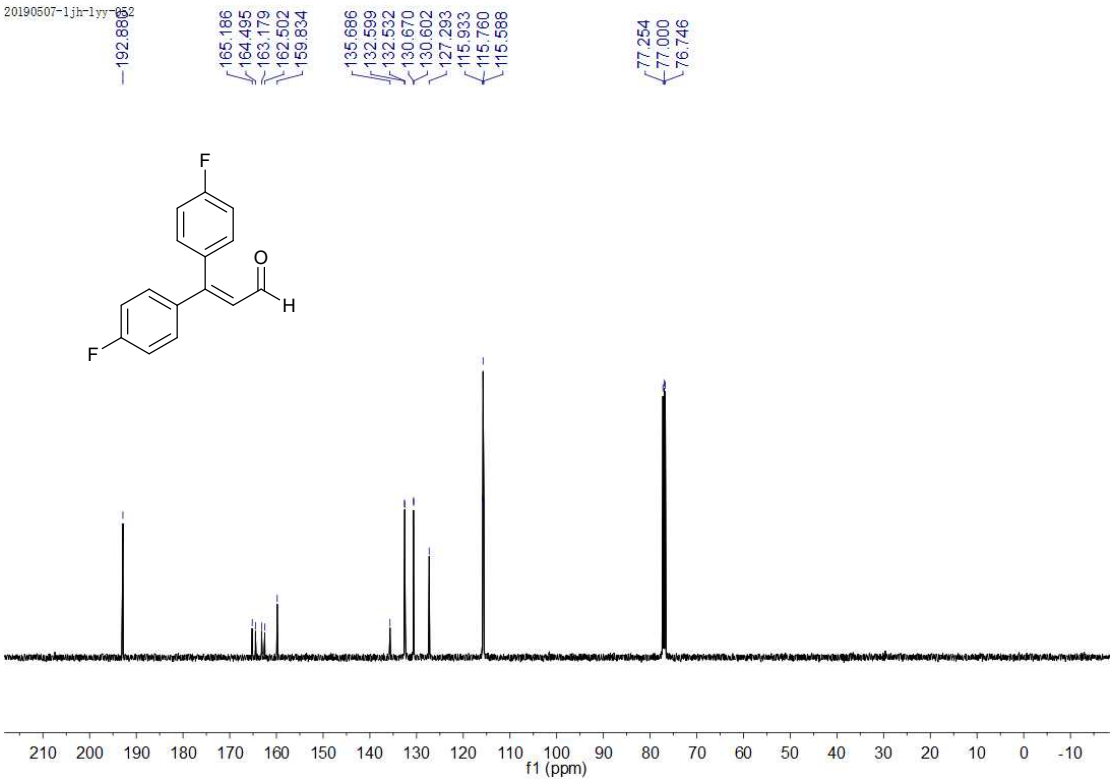
3,3-Di-*p*-tolylacrylaldehyde (5f):

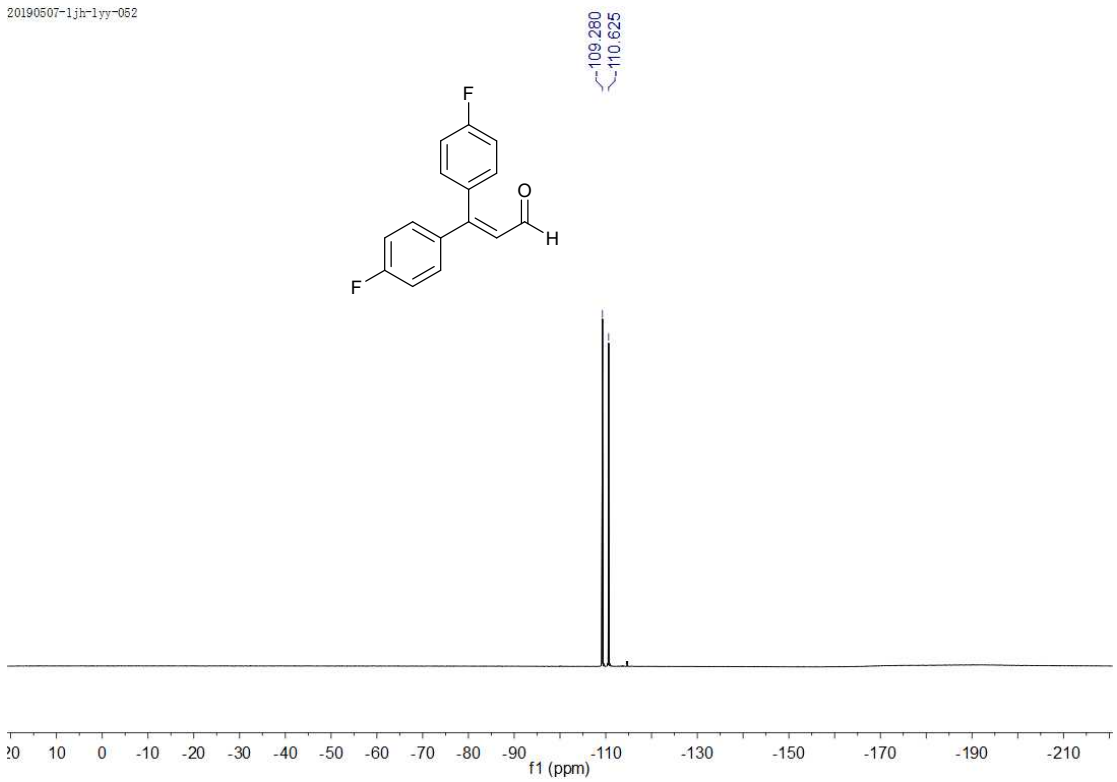




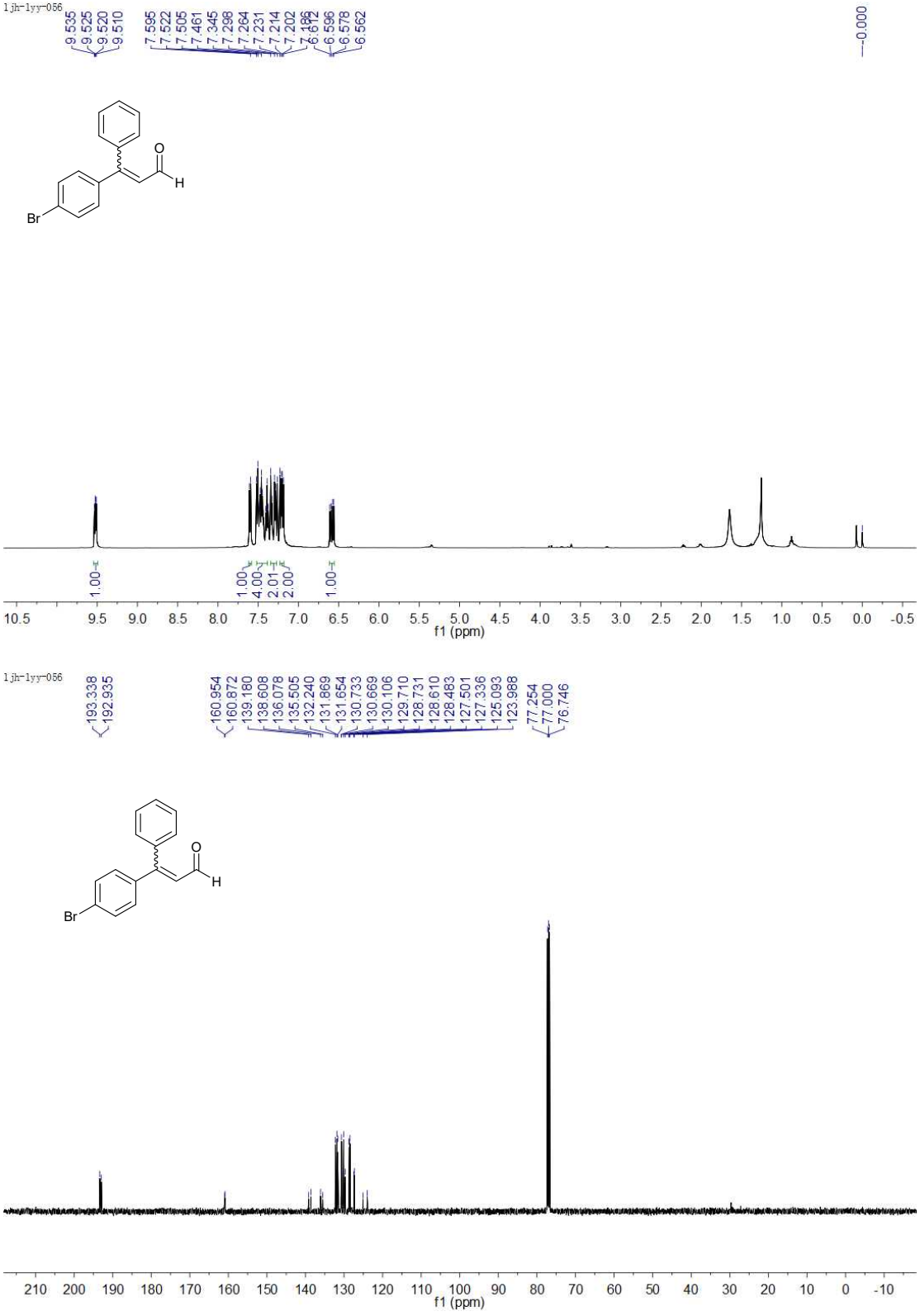
3,3-Bis(4-fluorophenyl)acrylaldehyde (5g):



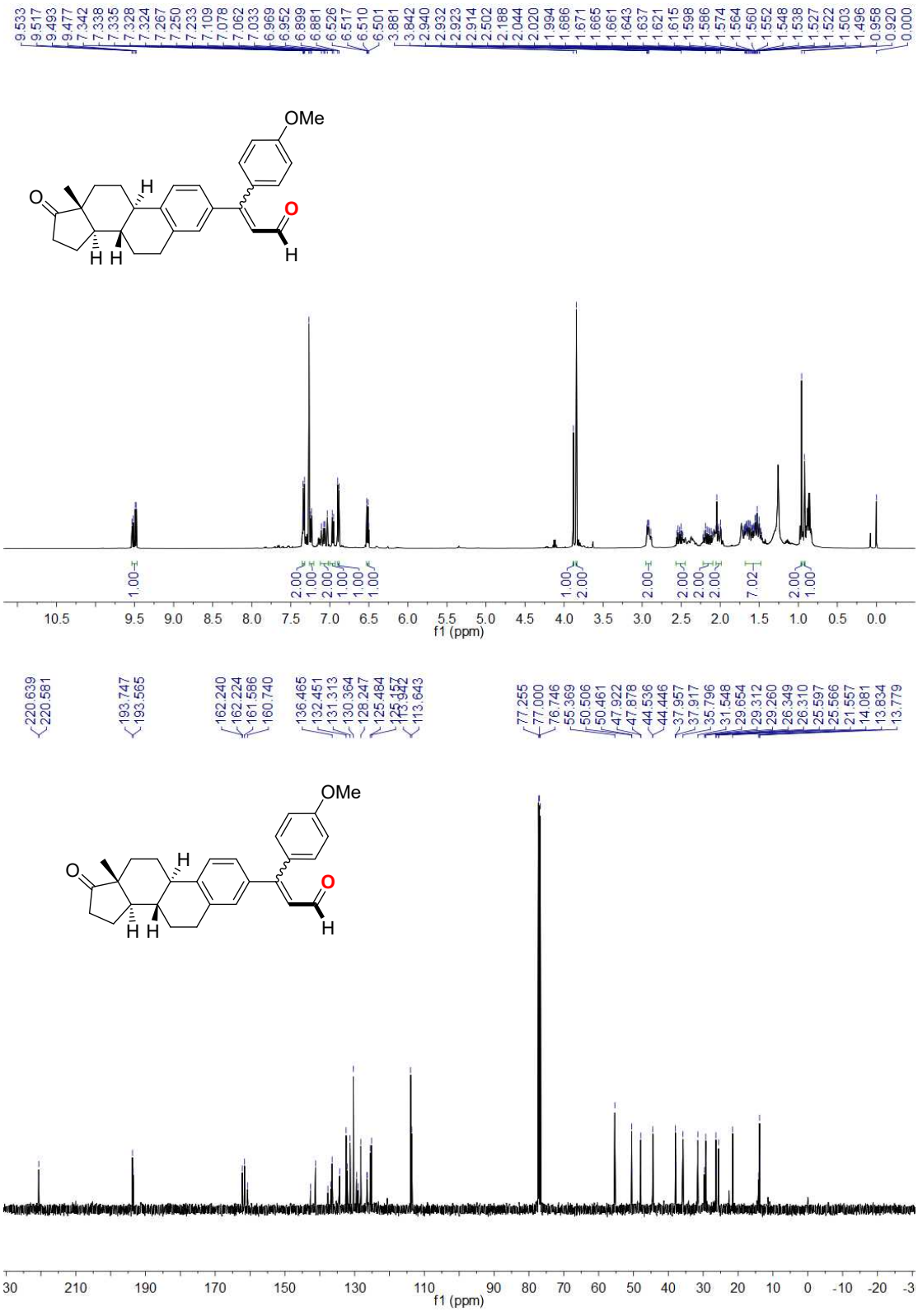



20190507-ljh-lyy-052
109.280
110.625
F
O
H
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

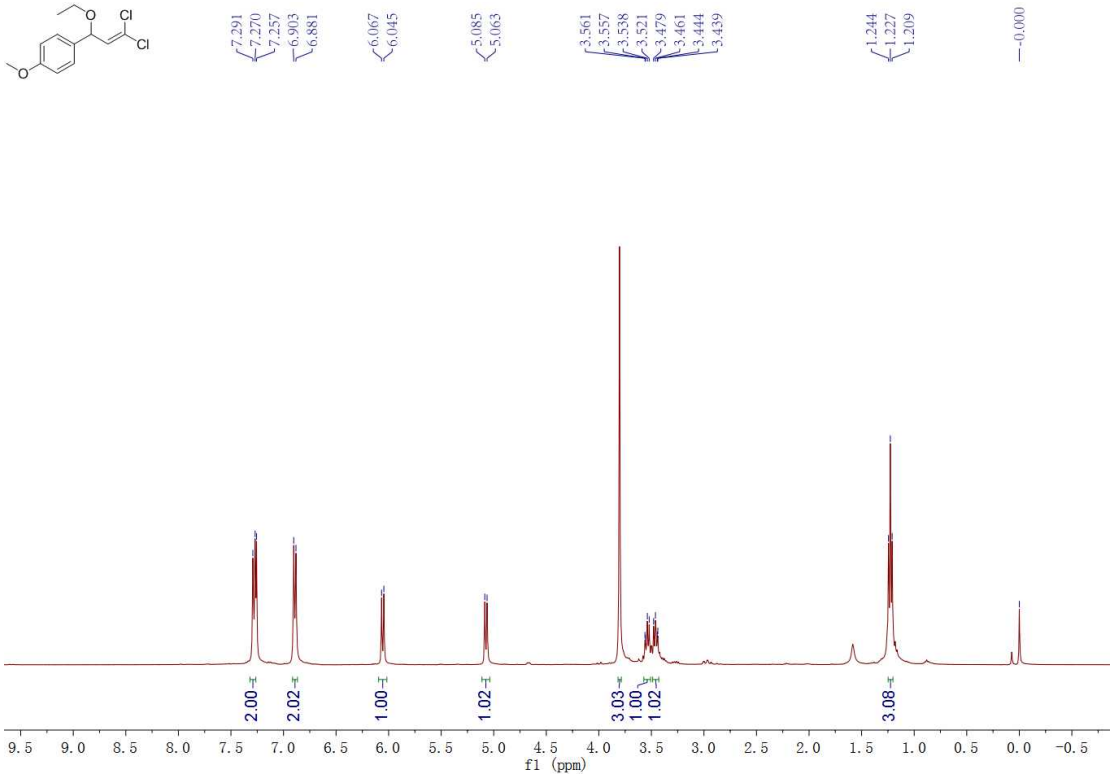
3-(4-Bromophenyl)-3-phenylacrylaldehyde (5h):

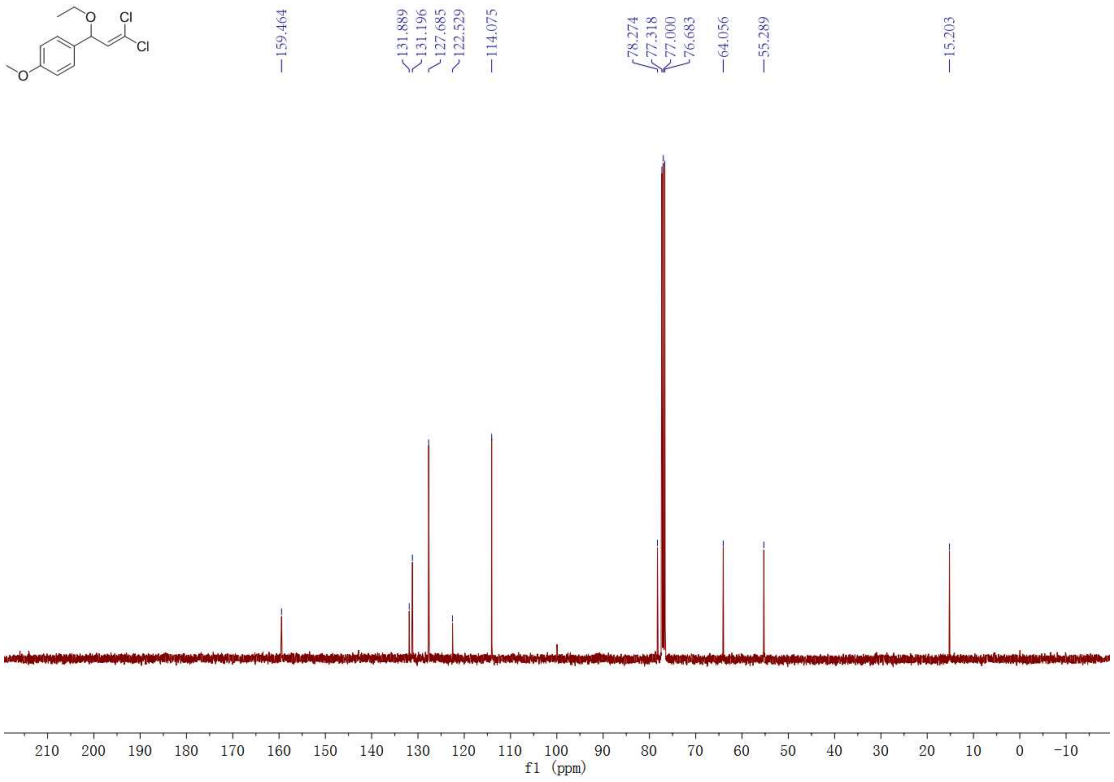


3-(4-Methoxyphenyl)-3-(13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydo-6*H*-cyclopenta[*a*]phenanthren-2-yl)acrylaldehyde (5i):



1-(3,3-dichloro-1-ethoxyallyl)-4-methoxybenzene (7a)





(F) References

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2. C. H. Oh, H. H. Jung, K. S. Kim, N. Kim, *Angew. Chem.* **2003**, *115*, 829; *Angew. Chem. Int. Ed.* **2003**, *42*, 805.
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