Supporting Information

Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereoselective Difluoroacetylated Alkenes

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Table of Contents

General information: all reactions were accomplished in Schlenck tube and round flask. Column chromatograph was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker AM500 and AM400 spectrometer, chemical shifts (in ppm) were referred to $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm) as an internal standard. ^{3}C NMR spectrum were obtained by using the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.0 ppm), DMSO-d_6 (δ = 40.0 ppm). Additional, ^{19}F NMR spectrometers were operated in the same NMR spectrometer. The following abbreviations have been using to illuminate the diversities: δ = chemical shifts, J = coupling constant, s = singlet, d= doublet, t = triplet, q = quartet, m =multiplet. All materials were obtained commercial suppliers, unless otherwise notice, and most stating material were purchased from Adamas.

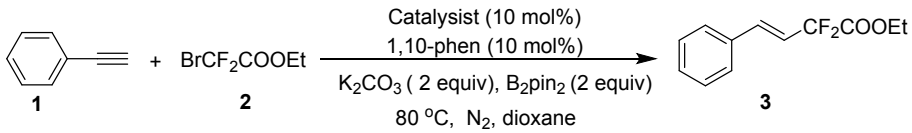
Method A: bis(pinacolato)diboron (1 equiv), $CuBr_2$ (10 mol%), 4, 4'-Dibutyl-2, 2'-bi-pyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Alkyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv) and dioxane (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 ^{o}C). The reaction mixture was cooled to room temperature after stirring for 16 h. The crude production was diluted with ethylate and then scrubber with saturated NaCl solution (3 times). The organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure production.

Method B: alkynyl carboxylic acid (0.5 mmol), bis(pinacolato)diboron (1 equiv), $Cu(TFA)_2$ (10 mol%), 1,10-Phen (10 mol%), Na_2CO_3 (1 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv) and dioxane (1 mL) were added subsequently. The Schlenck tube was screw capped and put into pre-heated oil bath (70 ^{o}C). The reaction mixture was cooled to room temperature after stirring for 24 h.

The crude production was diluted with ethylate and then washed with saturated NaCl solution (3 times). The organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure production

Optimization of the reaction conditions (**Table S1-S6**)

Table S1 Catalyst Effect on the Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereo-selective Difluoroacetylated Alkenes

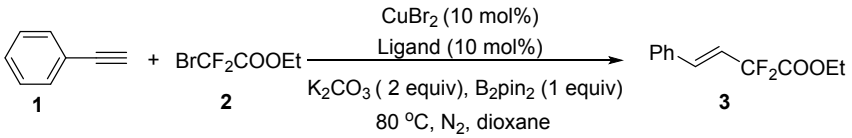


1 **2** **3**

Entry	Catalysist	Yield(%)
1	CuO	0
2	Cu_2O	67
3	CuCl	33
4	$CuCl_2$	73
5	CuI	62
6	$Cu(TFA)_2$	46
7	CuBr	67
8	**$CuBr_2$**	**83**

Reaction condition(unless special demand):Phenylethyene (0.25 mmol), B_2pin_2 (1 equiv), $BrCF_2COOEt$ (4 equiv), Catalysist (10 mol%), 1,10-phen (10 mol%), K_2CO_3 (2 equiv), Dioxane (2 mL). Yield was determined by GC using n-dodecane as internal standard.

Table S2 Ligand Effect on the Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereo-selective Difluoroacetylated Alkenes

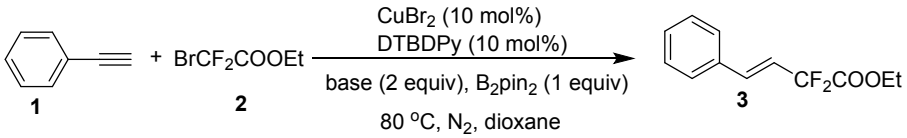


1 **2** **3**

Entry	Ligand	Yield (%)
1	dppf	0
2	dppe	0
3	dppp	0
4	Xantphos	0
5	PPh_3	0
6	Dpy	46
7	Triethanamine	76
8	**DTBDPy**	**98**

Reaction condition(unless special demand):Phenylethyene (0.25 mmol), B_2pin_2 (1 equiv), $BrCF_2COOEt$ (4 equiv), $CuBr_2$ (10 mol%), Ligand (10 mol%), K_2CO_3 (2 equiv), dioxane (2 mL). Yield was determined by GC using n-dodecane as internal standard. DTBDPy=4, 4'-Dibutyl-2, 2'-dipyridine

Table S3 Base Effect on the Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereo-selective Difluoroacetylated Alkenes

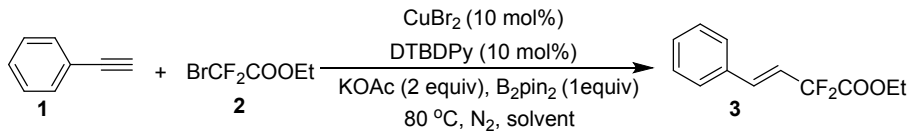


1 2 3

Entry	Base	Yield (%)
1	KF	42
2	K_3PO_4	67
3	Cs_2CO_3	44
4	**KOAc**	**>99 (78)**
5	Na_2CO_3	>99
6	$NaHCO_3$	43
7	Triethanamine	Trace

Reaction condition(unless special demand):Phenylethyene (0.25 mmol), B_2pin_2 (1 equiv), $BrCF_2COOEt$ (4 equiv), $CuBr_2$ (10 mol%), DTBDPy (10 mol%), base (2 equiv), dioxane (2 mL). Yield was determined by GC using n-dodecane as internal standard. Red word stands for isolated yield.

Table S4 Solvent Effect on the Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereo-selective Difluoroacetylated Alkenes

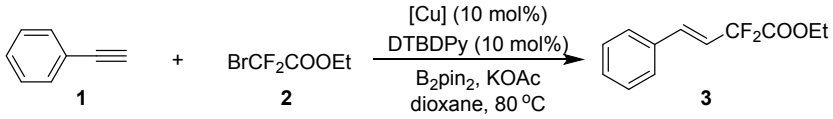


1 + **2** → **3**

Entry	Solvent	Yield (%)
1	DMF	0
2	DMSO	17
3	Toluene	77
4	THF	0
5	EtOH	28
6	CH_3CN	77
7	DCE	72
8	**dioxane**	**>99**

Reaction condition(unless special demand):Phenylethyene (0.25 mmol), B_2pin_2 (1 equiv), $BrCF_2COOEt$ (4 equiv), $CuBr_2$ (10 mol%), DTBDPy (10 mol%), KOAc (2 equiv), Solvent (2 mL). Yield was determined by GC using n-dodecane as internal standard.

Table S5 Dosage, Temperature, and Atmosphere Effects on the Cu-Catalyzed Hydrodifluoroacetylation of Alkynes or Alkynyl Carboxylic Acids Leading to Highly Stereo-selective Difluoroacetylated Alkenes

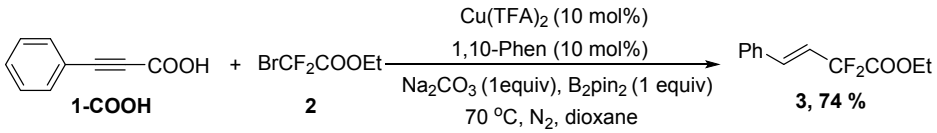


1 **2** **3**

entry	catalyst (x mol%)	ligand (10 mol%)	base (equiv)	additive (equiv)	time (h)	yield (%)
1	-	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	0
2	$CuBr_2$ (5)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	51
3	$CuBr_2$ (20)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	80
4	$CuBr_2$ (10)	-	KOAc (2)	B_2pin_2 (1)	16	0
5	$CuBr_2$ (10)	DTBDPy	KOAc (2)	-	16	0
6	$CuBr_2$ (10)	DTBDPy	KOAc (2)	B_2pin_2 (0.2)	16	21
7	$CuBr_2$ (10)	DTBDPy	-	B_2pin_2 (1)	16	0
8	$CuBr_2$ (10)	DTBDPy	KOAc (1)	B_2pin_2 (1)	16	47
9	$CuBr_2$ (10)	DTBDPy	KOAc (2)	B_2pin_2 (1)	12	82
10b	[a]$CuBr_2$ (10)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	70
11c	[b]$CuBr_2$ (10)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	75
12d	$CuBr_2$ (air)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	Trace
13e	$CuBr_2$ (O_2)	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	0
14f	$CuBr_2$	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	56
15g	$CuBr_2$	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	83
16h	$CuBr_2$	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	77
17i	$CuBr_2$	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	0
18j	$CuBr_2$	DTBDPy	KOAc (2)	B_2pin_2 (1)	16	58

Reaction conditons: a phenylacetylene (1) (0.25 mmol), ethyl bromodifluoroacetate (2) (1 mmol), bis(pinacolato)-diboron (0.25 mmol), $CuBr_2$ (x mol%), DTBDPy (10 mol%), KOAc (0.5 mmol), dioxane (2 mL) under N_2 atmosphere at 80 °C for 16 h. GC yield by using n-dodecane as an internal standard. b 2 equiv of $BrCF_2COOEt$. c 3 equiv of $BrCF_2COOEt$. d under air. e under O_2. f at 60 °C. g at 70 °C. h at 90 °C. i with TEMPO. j with BHT. DTBDPy=4,4'-Di-tert-butyl-2,2'-dipyridyl

Table S6 Optimization of the reaction conditions from alkynyl carboxylic acid

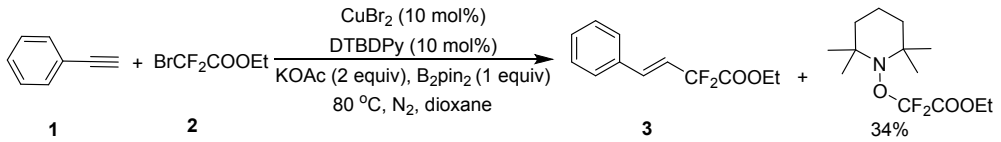


1-COOH **2** **3, 74 %**

Entry	Catalysis (10% mol)	Ligand (10 mol%)	Base (0.5 mmol)	Additive (0.25 mmol)	Solvent (1 mL)	Yield (%)
1	$CuBr_2$	DTBDPy	KOAc	B_2pin_2	Dioxane	63
2	CuBr	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	30
3	$CuBr_2$	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	20
4	CuCl	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	6
5	CuO	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	trace
6	CuO_2	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	22
7	$Cu(TFA)_2$	1,10-Phen	K_2CO_3	B_2pin_2	Dioxane	71
8	$Cu(TFA)_2$	DPy	K_2CO_3	B_2pin_2	Dioxane	48
9	$Cu(TFA)_2$	DPPB	K_2CO_3	B_2pin_2	Dioxane	0
10	$Cu(TFA)_2$	DTBDPy	K_2CO_3	B_2pin_2	Dioxane	70
11	$Cu(TFA)_2$	Dpephos	K_2CO_3	B_2pin_2	Dioxane	0
12	$Cu(TFA)_2$	1,10-Phen	KOAc	B_2pin_2	Dioxane	68
13	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2pin_2	Dioxane	75
14	$Cu(TFA)_2$	1,10-Phen	$NaHCO_3$	B_2pin_2	Dioxane	60
15	$Cu(TFA)_2$	1,10-Phen	KF	B_2pin_2	Dioxane	70
16	$Cu(TFA)_2$	1,10-Phen	Triethylamine	B_2pin_2	Dioxane	39
17	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2pin_2	Toluene	43
18	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2Pin_2	DMSO	16
19	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2pin_2	CH_3CN	19
20	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2pin_2	EtOH	35
21	-	1,10-Phen	Na_2CO_3	B_2pin_2	Dioxane	0
22	$Cu(TFA)_2$	-	Na_2CO_3	B_2pin_2	Dioxane	0
23	$Cu(TFA)_2$	1,10-Phen	-	B_2pin_2	Dioxane	0
24	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	-	Dioxane	0
25a	$Cu(TFA)_2$	1,10-Phen	Na_2CO_3	B_2pin_2	Dioxane	89(74)

Reaction conditons: 3-phenylpropiolic acid (0.25 mmol), bis(pinacolato)diboron (0.25 mmol), $BrCF_2COOEt$ (1 mmol), catalysist (10 mol%), ligand (10 mol%), base (0.25 mmol), solvent (1 ml), 80 °C, N_2, 16h.The entry 25a was reacted in 3-phenylpropiolic acid (0.25 mmol), $Cu(TFA)_2$ (10 mol %), B_2pin_2 (0.25 mmol), $BrCF_2COOEt$ (3 mmol), 1,10-phen (10 mol %), Na_2CO_3 (1 mmol), dioxane (1 mL), 70 °C, N_2, 24h. Reactions were accomplised in N_2 atmosphere and 70 °C. Determination by GC analysis using n-dodecane as an internal standard.

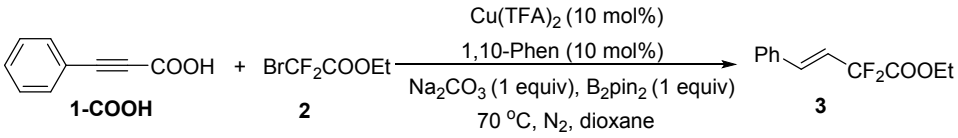
Inhibition Experiments for Cu-Catalyzed Cross-Coupling of 1 with 2.



1 2 3

Additive	**3**, Yield(%)
None	99
TEMPO (2 equiv)	0
BHT (2 equiv)	46

Bis(pinacolato)diboron (1equiv), $CuBr_2$(10 mol%), 4, 4'-dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv), TEMPO (2 equiv) or BHT (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv), and solvent (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The mixture was dropped into brine (3×15 mL), extracted with EtOAc(3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was purified by column chromatography on silica gel to provide 34% isolated yield as a clear colourless liquid.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (q, J = 7.1 Hz, 2H), 1.68 – 1.42 (m, 6H), 1.37 (t, J = 7.1 Hz, 3H), 1.19 (s, 6H), 1.17 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (t, J = 42.3 Hz), 115.5 (t, J = 269.9 Hz), 63.0, 61.4, 40.2, 33.4 (t, J = 4.4 Hz), 20.7, 16.9, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -73.5.



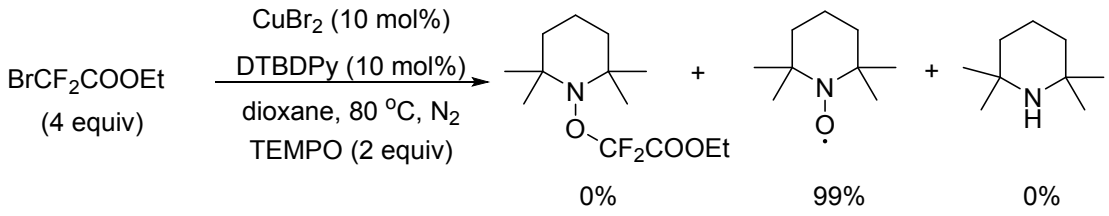
1-COOH 2 3

Additive	**3**, Yield(%)
None	89
TEMPO (2 eq)	0
BHT(2 eq)	58

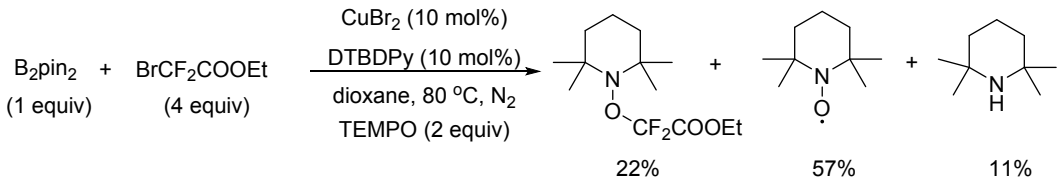
3-Phenylpropiolic acid (0.5 mmol), bis(pinacolato)diboron (1 equiv), $Cu(TFA)_2$ (10 mol%), 1,10-Phen (10 mol%), Na_2CO_3 (1 equiv), TEMPO (2 equiv) or BHT (2 equiv)

were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv) and solvent (2 mL) were added subsequently. The Schlenck tube was screw capped and put into pre-heated oil bath (70 °C). The reaction mixture was cooled to room temperature after stirring for 24 h. The yield was determined by GC, GC-MS analysis using n-dodecane as internal standard.

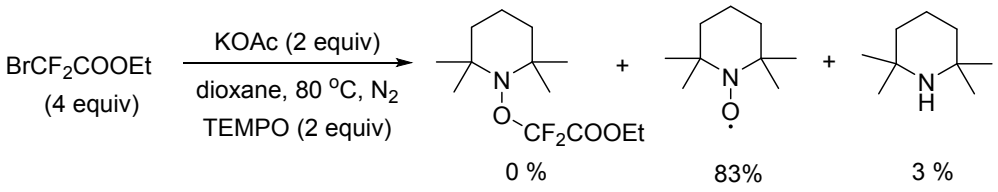
Mechanistic Studies



TEMPO (2 equiv), $CuBr_2$(10 mol%), 4, 4'-dibutyl-2, 2'-bipyridyl(10 mol%) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv), dioxane (1 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC-MS analysis.

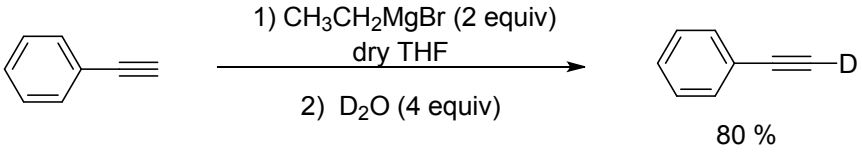


Bis(pinacolato)diboron(1equiv),TEMPO (2 equiv), $CuBr_2$(10 mol%), 4, 4'-dibutyl-2, 2'-bipyridyl(10 mol%) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv), dioxane (1 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC-MS analysis.

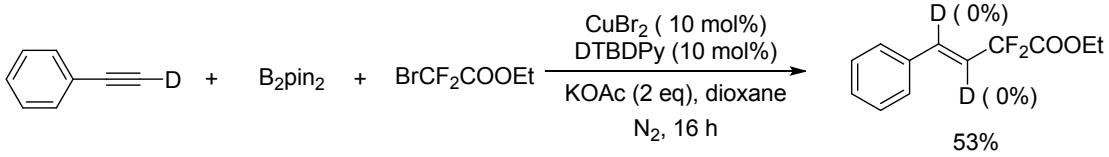


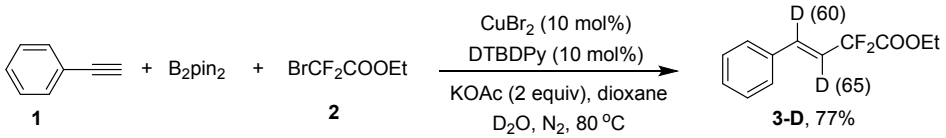
KOAc (2 equiv) and TEMPO (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv), dioxane (1 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC-MS analysis.

The Origination of Hydroden and Role of the Water

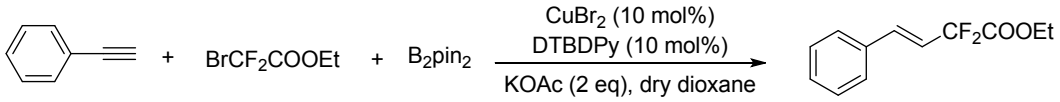


Into Schlenk tube containing a stirring bar purged with nitrogen were successfully added by dry THF (10 mL) and phenylacetylene(540 μL, 5 mmol) via a syringe. CH_3CH_2MgBr (2 M THF solution; 5 mL, 10 mmol) was added at -5 ˚C, and the reaction mixture was stirred for 1 h. D_2O(99.9%-d; 400 μL, 20 mmol) was added to the mixture solution at -5 ˚C, and the reaction mixture was stirred for 30 min at the same temperature. After filtered, the filtrate were dried over anhydrous Na_2SO_4 and concentrated in vacuo. and purified by flash column chromatograph to give the pure production (**phenylacetylene-D**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 2H), 7.39 – 7.31 (m, 3H).





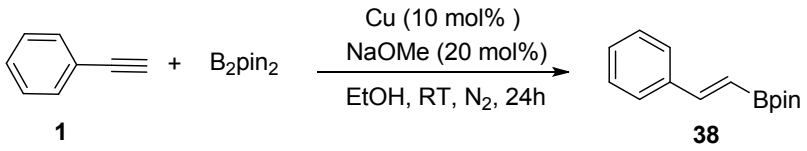
Bis(pinacolato)diboron (1 equiv), $CuBr_2$ (10 mol%), 4, 4'-Dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv), D_2O (4 equiv) and anhydrous dioxane (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 ^oC). The reaction mixture was cooled to room temperature after stirring for 16 h. The crude production was diluted with ethylate and then scrubber with saturated NaCl solution (3 times). The organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure production (**3-D**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.43 (m, 2H), 7.42 – 7.33 (m, 3H), 7.12 – 7.06 (m, 1H), 6.35 – 6.26 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.04 (qd, J = 7.2, 1.6 Hz, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9 (t, J = 34.6 Hz), 136.7(t, J = 9.4 Hz), 134.0, 129.7, 128.9, 127.4, 118.73 (t, J = 24.9 Hz), 112.7 (t, J = 246.9 Hz), 63.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.2, -103.4.



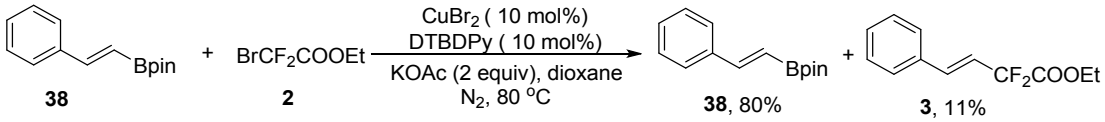
entry	H_2O (x eq)	Yield of **3** (%) (isolated)
1	0	40
2	1	71
3	2	69
4	4	72

Bis(pinacolato)diboron (1 equiv), $CuBr_2$ (10 mol%), 4, 4'-dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv), water (x equiv) and anhydrous dioxane (2 or 1 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 ^oC). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC analysis using n-dodecane as internal standard.

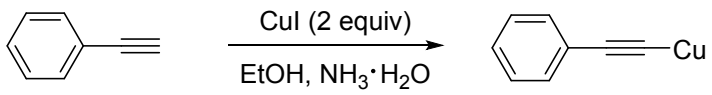
The Key Intermediates Screening



B_2pin_2 (3 mmol, 762 mg), copper powder (0. 2 mmol, 12.8 mg) and NaOMe (0.4 mmol, 21.8 mg) were added to a Schlenk. Then the mixture evacuated and backfilled with N_2 (3 times). Alkyne (2 mmol) and EtOH (4 mL) were added under N_2, and the tube was sealed and stirred 24 h at room temperature. After the reaction finished, the mixture was dropped into saturated salt water (3×15 mL). The aqueous solution was extracted with EtOAc (3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was purified by column chromatography on silica gel to provide the desired product (**38**).[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.48 (m, 2H), 7.41 (d, J = 18.4 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.18 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8.

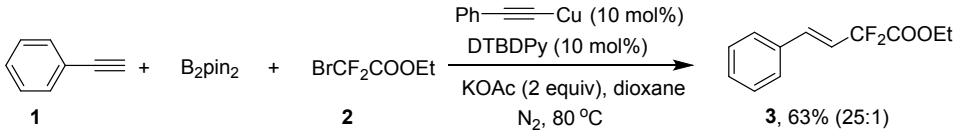


$CuBr_2$ (10 mol%), 4, 4'-Dibutyl-2, 2'-bipyridy (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). (E)-4, 4, 5, 5-tetramethyl-2-styryl-1, 3, 2-dioxaborolane (0.25 mmol), ethyl bromodifluoroacetate (4 equiv), and solvent (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for16 h. The yield was determined by GC analysis using n-dodecane as internal standard.

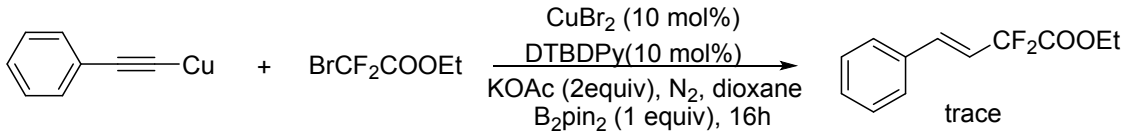


To a solution of copper iodide (1.9 g, 10.0 mmol) in a mixture of ammonium hydroxide (28% NH_3 solution, 25 mL) and ethanol (15 mL) was added the alkyne (5.0 mmol) dropwise. The deep blue reaction mixture was stirred overnight at room

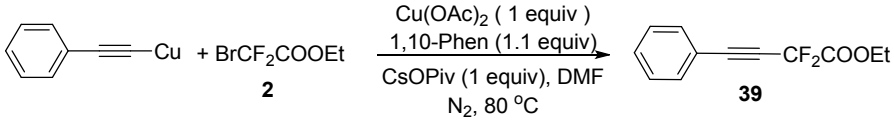
temperature under N_2 and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (10% NH_3 solution, 3×25 mL), water (3×25 mL), ethanol (3×25 mL), and petroleum ether (3×25 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired polymeric alkynylcopper reagent which was used without further purification.[3]



Bis(pinacolato)diboron(1 equiv), (Phenylethynyl)copper (10 mol%), 4, 4'-Dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv) and dioxane (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The crude production was diluted with ethylate and then scrubber with saturated NaCl solution (3 times). The organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure production(**3**).

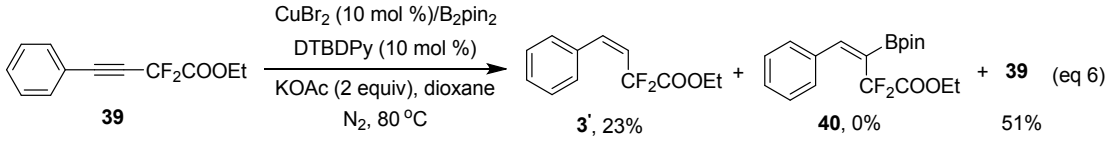


(Phenylethynyl)copper (41.5 mg, 0.25 mol), Bis(pinacolato)diboron(1 equiv), 4, 4'-Dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (4 equiv) and dioxane (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC analysis using n-dodecane as internal standard.

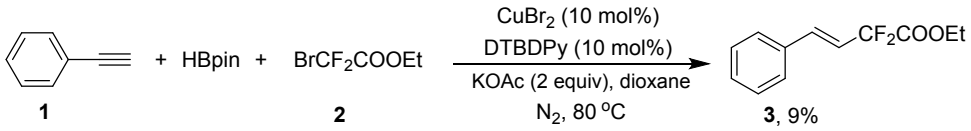


(Phenylethynyl)copper (2 mmol, 328 mg), anhydrous $Cu(OAc)_2$ (1 eq), 1,10-Phen (1.1

equiv), anhydrous CsOPiv (1 equiv) were added to dry a Schlenk. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (5 equiv) and anhydrous DMF (5 mL) under N_2. The Schlenck tube was screw capped and put into pre-heated oil bath (80 °C). After 4h, the mixture poured into saturated salt water (3×15 mL). The aqueous was extracted with EtOAc. The combined organic layer was dried Na_2SO_4 and concentrated in vacuo, and the residue was purified by column chromatography on silica gel to provide the desired product (**39**).[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 – 7.52 (m, 2H), 7.47 – 7.43 (m, 1H), 7.40 – 7.35 (m, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6 (t, J = 34.3 Hz), 132.4 (t, J = 2.3 Hz), 130.5, 128.6, 119.3 (t, J = 2.9 Hz), 104.9 (t, J = 240.8 Hz), 89.6 (t, J = 6.4 Hz), 78.4 (t, J = 37.9 Hz), 63.8, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -90.0.

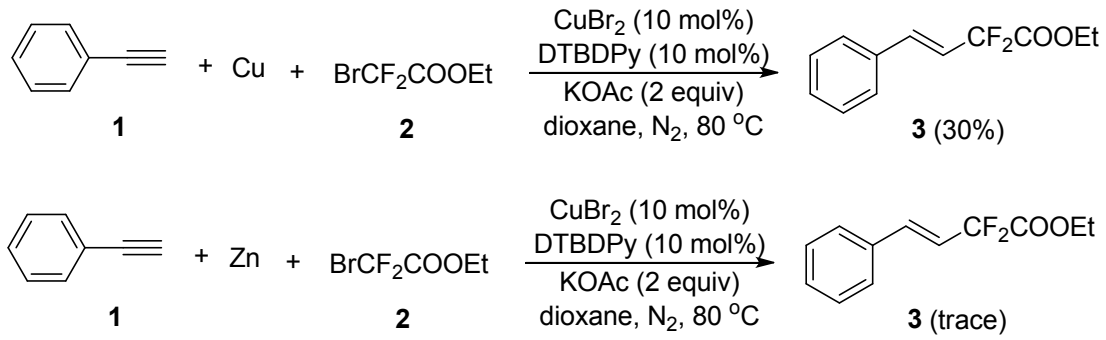


Bis(pinacolato)diboron (1 equiv), $CuBr_2$ (10 mol%), DTBDPy (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Ethyl 2, 2-difluoro-4-phenylbut-3-ynoate (0.25 mmol) and solvent (1 mL) were added subsequently. The Schlenck tube was screw capped and put into pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The yield was determined by GC analysis using n-dodecane as internal standard.



Bis(pinacolato)diboron (1 equiv), $CuBr_2$ (10 mol%), 4, 4'-dibutyl-2, 2'-bipyridyl (10 mol%), KOAc(2 equiv) were added to a 25mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv), HBPin (1 equiv) and solvent (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The yield was determined by GC analysis using n-dodecane as internal standard.

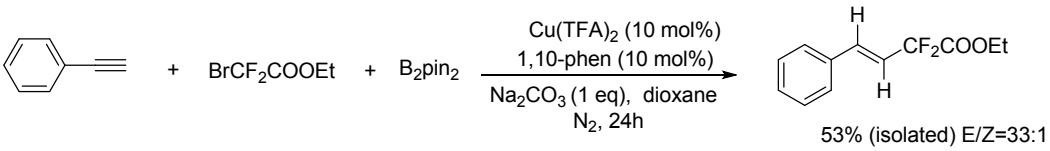
The Role of B_2pin_2 in Reaction



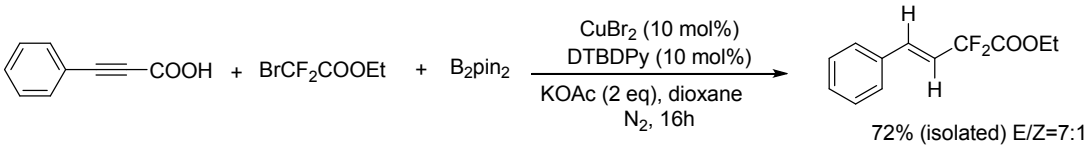
Cu powder or Zn powder(1 equiv), Cu (10 mol%), 4, 4'-Dibutyl-2, 2'-bipyridyl (10 mol%), KOAc (2 equiv) were added to a 25 mL of Schlenk tube under air. Then the mixture evacuated and backfilled with N_2 (3 times). Phenylethyne (0.5 mmol), ethyl bromodifluoroacetate (4 equiv) and dioxane (2 mL) were added subsequently. The Schlenck tube was screw capped and put in to pre-heated oil bath (80 °C). The reaction mixture was cooled to room temperature after stirring for 16 h. The crude production was diluted with ethylate and then scrubber with saturated NaCl solution (3 times). The organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure production 30% (**3**).

The Difference of the stereoselectivity for the alkynyl carboxylic acids and phenylethyne

The reasons why the stereoselectivity for the alkynyl carboxylic acids and phenylethyne were mentioned below. Both catalyst and ligands are different, we deeply believe that ligands play very important roles in the discrepancy of stereoselectivity: when we switch the two conditions, the stereoselectivity for phenylacetylene was improved from E/Z 9:1 to E/Z 33:1, and when phenyl propiolic acid was exposed under the standard conditions for phenylacetylene in our manuscript, the E/Z ratio was decreased from exclusive E to E/Z 7:1. Obviously, the catalytic system of $Cu(TFA)_2$/1,10-phen gave higher stereoselectivity than the system of $CuBr_2$/DTBDPy, yet lower isolated yields than the latter on.

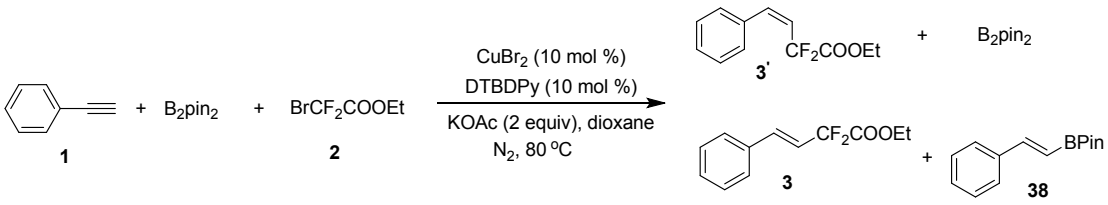


53% (isolated) E/Z=33:1



72% (isolated) E/Z=7:1

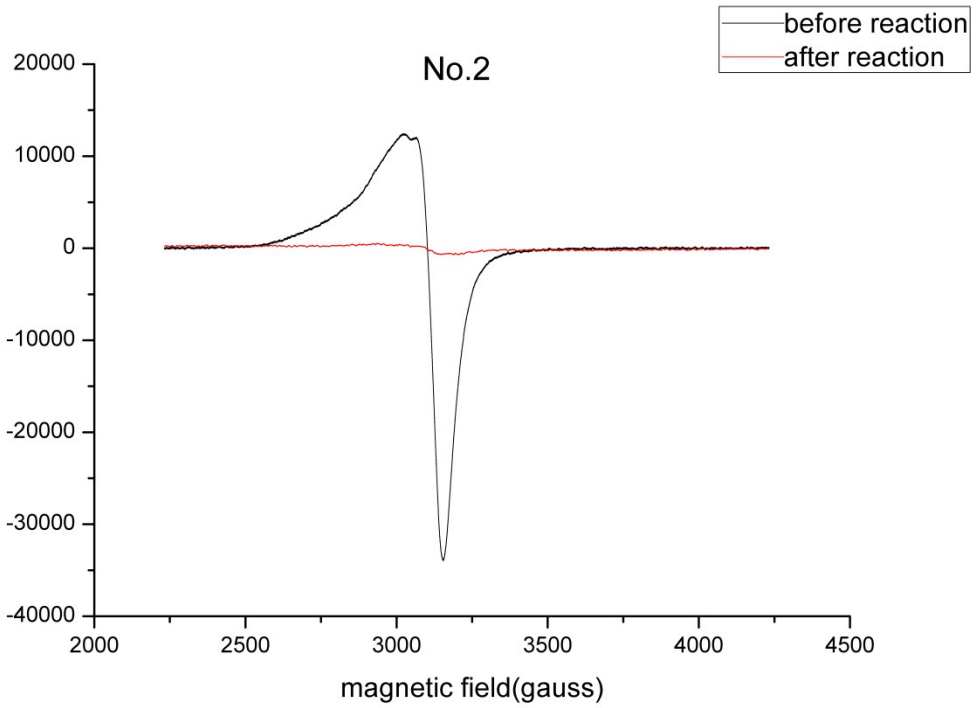
Table 7 Intermediates Trapping Experiments



Time	3'	B_2pin_2	3	38
2 h	5%	37%	43%	< 1%
4 h	7%	30%	39%	0
6 h	6%	3%	65%	0
10 h	6%	0	74%	0
14 h	8%	0	75%	0

The Valence Change of Cu during Reaction

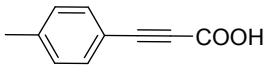
To make sure the valence change of Cu during reaction, EPR experiment was performed under the standard conditions of phenylpropiolic acid. The EPR signal of Cu(II) was very strong before reaction, however, the EPR signal (Cu(II)) was silent after 2h reaction. It is clearly demonstrated that this is a radical involved process and SET does occur during the process, so it proved our hypothesis on our mechanism.


No.2
before reaction
after reaction
20000
10000
0
-10000
-20000
-30000
-40000
2000
2500
3000
3500
4000
4500
magnetic field(gauss)

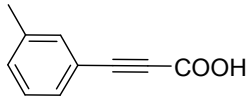
General methods for preparation of Aryl Alkynyl Carboxylic from aryl iodides (1a-1n).[6]

To a 50 mL of Schleck tube were added $Pd(PPh_3)_4$ (144 mg, 0.13 mmol, 2.5 mol%), aryl iodide (5.0 mmol), DBU (1.83 g, 12 mmol, 2.4 equiv), and 6 mL DMSO. Then dropwised the solution of propiolic acid (420 mg, 6.0 mmol, 1.2 equiv) in DMSO (6 mL). The mixture was stirried at room temperature 12h. The reaction mixture was quenched with EtOAc, and extracted with saturated solution of $NaHCO_3$. The aqueous layer was separated, acidified to Ph 2.0 by adding cold HCl (1 N), and extracted with CH_2Cl_2.The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatograph on silica gel (petroleum ether /EtOAc, 4:1 with HOAc (1%, v/v).

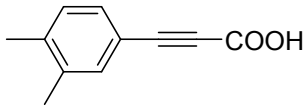
Characterization Data



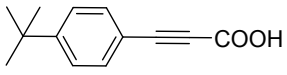
3-(P-tolyl)propiolic acid (**1a**).[6] 1-Iodo-4-methylbenzene (1.09 g, 5.0 mmol) was coupled with propiolic acid to give **1a.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.51 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.6, 141.6, 133.0, 130.1, 116.3, 85.3, 81.9, 21.6.



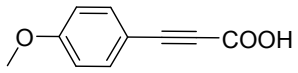
3-(M-tolyl)propiolic acid (**1b**).[6] 1-Iodo-3-methylbenzene (1.09 g, 5.0 mmol) was coupled with propiolic acid to give **1b.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.49 – 7.35 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8, 139.0, 133.3, 132.1, 130.1, 129.4, 119.3, 85.1, 81.9, 21.0.



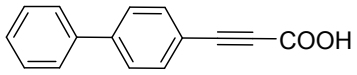
3-(3, 4-dimethylphenyl)propiolic acid (1**c**).[6] 4-Iodo-1, 2-dimethylbenzene (1.16 g, 5.0 mmol) was coupled with propiolic acid to give **1c.** ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.38 (s, 1H), 7.33 (dd, J = 7.8, 1.4 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.4, 141.1, 138.3, 134.1, 131.0, 131.0, 116.90, 86.1, 82.1, 20.3, 19.8.



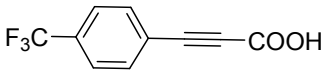
3-(4-(Tert-butyl)phenyl)propiolic acid (**1d**).[6] 1-(Tert-butyl)-4-iodobenzene (1.3 g, 5.0 mmol) was coupled with propiolic acid to give **1d.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.9, 154.3, 132.9, 126.3, 116.5, 85.2, 81.9, 35.2, 31.2.



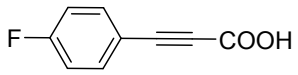
3-(4-methoxyphenyl)propiolic acid (**1e**).[6] 1-Iodo-4-methoxybenzene (1.17 g, 5.0 mmol) was coupled with propiolic acid to give **1e.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7, 155.0, 135.1, 115.2, 111.0, 85.8, 81.5, 55.9.



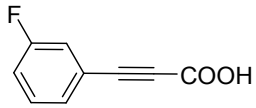
3-([1, 1'-Biphenyl]-4-yl)propiolic acid (**1f**).[5] 4-Iodo-1, 1'-biphenyl (1.4 g, 5.0 mmol) was coupled with propiolic acid to give **1f.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76 (d, J = 8.6 Hz, 2H), 7.73 – 7.65 (m, 4H), 7.53 – 7.45 (m, 2H), 7.43 – 7.36 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8, 142.8, 139.2, 133.7, 129.6, 128.8, 127.6, 127.3, 118.3, 84.8, 82.8.



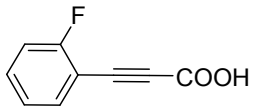
3-(4-(Trifluoromethyl)phenyl)propiolicacid (**1g**).[6] 1-Iodo-4-(trifluoromethyl)benzene(1.36 g, 5.0 mmol) was coupled with propiolic acid to give **1g.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 – 7.80 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.4, 133.8, 130.9 (q, J = 32.3Hz), 126.3 (q, J = 3.6 Hz), 124.1 (q, J = 270.9Hz), 123.8 (d, J = 1.2Hz), 83.9, 82.7.



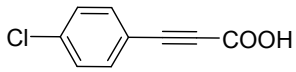
3-(4-Fluorophenyl)propiolic acid (**1h**).[6] 1-Fluoro-4-iodobenzene (1.11 g, 5.0 mmol) was coupled with propiolic acid to give **1h.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.72 – 7.66 (m, 2H), 7.33 – 7.26 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.7 (d, J = 249.3 Hz), 154.7, 135.7 (d, J = 9 Hz), 116.8 (d, J = 22.2Hz), 115.9 (d, J =3.4 Hz), 83.9, 82.0 (d, J = 1.0 Hz).



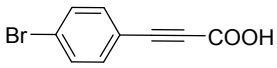
3-(3-Fluorophenyl)propiolic acid (**1i**).[7] 1-Fluoro-3-iodobenzene (1.11 g, 5.0 mmol) was coupled with propiolic acid to give **1i.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54 – 7.44 (m, 3H), 7.42 – 7.35 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2(d, J = 244.2Hz), 154.5, 131.7 (d, J = 8.7 Hz), 129.4 (d, J = 2.9 Hz), 121.4 (d, J = 9.6 Hz), 119.5 (d, J = 23.3 Hz), 118.7 (d, J = 21.0 Hz), 83.1 (d, J = 3.5 Hz), 82.7.



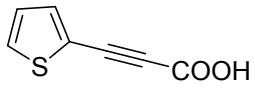
3-(2-Fluorophenyl)propiolic acid (**1j**).[8] 1-Fluoro-2-iodobenzene (1.11 g, 5.0 mmol) was coupled with propiolic acid to give **1j.** ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.71 (td, J = 7.5, 1.7 Hz, 1H), 7.61 (dddd, J = 8.4, 7.4, 5.6, 1.8 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.31 (td, J = 7.6, 1.0 Hz, 1H), 2.55 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.3 (d, J = 250.8 Hz), 154.5, 135.0, 133.9 (d, J = 8.4Hz), 125.6 (d, J = 3.5Hz), 116.5 (d, J = 20.1 Hz), 108.0 (d, J = 15.0 Hz), 86.8 (d, J = 2.9 Hz), 78.1.



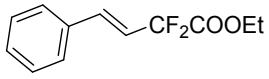
3-(4-Chlorophenyl)propiolic acid (**1k**).[6] 1-Chloro-4-iodobenzene (1.19 g, 5.0 mmol) was coupled with propiolic acid to give **1k.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.6, 136.3, 134.8, 129.7, 118.3, 83.5, 83.0.



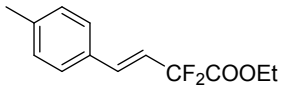
3-(4-Bromophenyl)propiolic acid (**1l**).[6] 1-Bromo-4-iodobenzene (1.41 g, 5.0 mmol) was coupled with propiolic acid to give **1l.**^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.6, 134.9, 132.6, 125.2, 118.6, 83.6, 83.1.



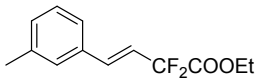
3-(Thiophen-2-yl)propiolic acid (**1m**).[8] 2-iodothiophene (1.05 g, 5.0 mmol) was coupled with propiolic acid to give **1m.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (dd, J = 5.1, 1.2 Hz, 1H), 7.66 (dd, J = 3.7, 1.2 Hz, 1H), 7.19 (dd, J = 5.1, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.6, 137.5, 133.2, 128.8, 118.7, 86.3, 78.9.



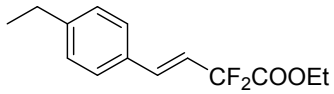
Ethyl (E)-2,2-difluoro-4-phenylbut-3-enoate（**3**，***E*/*Z***=9:1）, the procedure was operated in method A. This compound is known.[9] The reaction gave 88 mg of ethyl-2, 2-difluoro-4-pheylbut-3-enoate in 78 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.7, 1.6 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.09 (dt, J = 16.2, 2.5 Hz, 1H), 6.31 (dt, J = 16.2, 11.4 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9 (t, J = 35.0 Hz), 136.8 (t, J = 8.8 Hz), 134.1, 129.6, 128.8, 127.4, 118.8 (t, J = 25.0 Hz), 112.7 (t, J = 247.5 Hz), 63.11, 13.95. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.2.



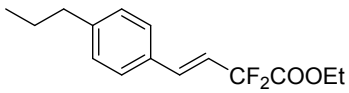
Ethyl (E)-2, 2-difluoro-4-(p-tolyl)but-3-enoate (5, *E/Z*=19:1), the procedure was operated in method A. The reaction gave 97 mg of ethyl-2, 2-difluoro-4-(p-tolyl)but-3-enoate in 81 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.07 (dt, J = 16.2, 2.5 Hz, 1H), 6.28 (dt, J = 16.2, 11.5 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, (t, J = 35.0 Hz), 139.8,, 136.7 (t, J = 12.5 Hz), 131.3, 129.5, 127.4, 117.7 (t, J = 25.0Hz), 112.8(t, J = 247.5Hz), 63.1, 21.3, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.0. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 240.0962; found: 240.0967.



Ethyl-2, 2-difluoro-4-(m-tolyl)but-3-enoate (6, *E*/*Z*=19:1), the procedure was operated in method A. The reaction gave 100 mg of ethyl-2, 2-difluoro-4-(m-tolyl)but-3-enoate in 83 % isolated yield as a colorless clear liquid. **^{1}H NMR (500 MHz, CDCl3, PPM)** δ 7.28-7.24 (m, 3H), 7.18-7.17 (m, 1H), 7.05(dt, J =16 Hz, J =2.5 Hz, 1H), 6.28(dt, J =17 Hz, J =11.5 Hz,); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0(t, ***J*** =35.0 Hz), 138.5, 137.0 (t, ***J*** =8.8), 134.1, 130.4, 128.7, 128.1, 124.6, 118.6 (t, ***J*** =25.0 Hz), 112.8 (t, ***J*** =246.3 Hz), 63.1, 21.3, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.2. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 240.0962; found: 240.0967.

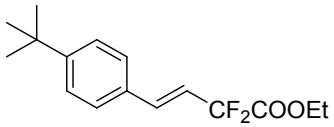


Ethyl (E)-4-(4-ethylphenyl)-2, 2-difluorobut-3-enoate (7), the procedure was operated in method A. The reaction gave 125 mg of ethyl (E)-4-(4-ethylphenyl)-2, 2-difluorobut-3-enoate in 96 % isolated yield as a yellow clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.06 (dt, J = 16.2, 2.4 Hz, 1H), 6.26 (dt, J = 16.2, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.67 (q, J=7.5 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 35.0 Hz), 146.2, 136.7 (t, J = 8.8 Hz), 131.6, 128.3, 127.5, 117.8 (t, J = 23.8 Hz), 112.8 (t, J = 247.5 Hz), 63.0, 28.7, 15.39, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.0. HRMS (EI, *m/z*) calcd for [$C_{14}H_{16}F_2O_2$]: 254.1118; found: 254.1130.

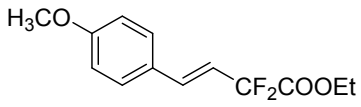


Ethyl -2, 2-difluoro-4-(4-propylphenyl)but-3-enoate (**8**, ***E***/***Z***=14:1)，the procedure was operated in method A. The reaction gave 107 mg of ethyl (E)-4-(4-propylphenyl)-2, 2-difluorobut-3-enoate in 80 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 1.8 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.06 (dt, J = 16.2, 2.4 Hz, 1H), 6.26 (dt, J = 16.2, 11.5

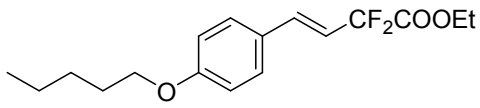
Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.62 – 2.57 (m, 2H), 1.68 – 1.61 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 35.0 Hz), 144.7, 136.8 (t, J = 10.0 Hz), 131.6, 129.0, 127.4, 117.8 (t, J = 25.0 Hz), 112.9 (t, J = 247.5 Hz), 63.1, 37.8, 24.4, 14.0, 13.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.0. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 268.1275; found: 268.1286.



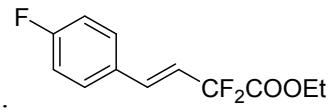
Ethyl -2, 2-difluoro-4-(4-butylphenyl)but-3-enoate (**9**, ***E/Z***=14:1), the procedure was operated in method A. This compound is known. [9] The reaction gave 118 mg of ethyl (E)-4-(4-butylphenyl)-2, 2-difluorobut-3-enoate in 84 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.39 (m, 4H), 7.06 (dt, J = 16.2, 2.5 Hz, 1H), 6.27 (dt, J = 16.2, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.32 (s, J = 7.1 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 35.0 Hz), 153.1, 136.6 (t, J = 8.8 Hz), 131.4, 127.2, 125.8, 118.0 (t, J = 25.0Hz), 112.9 (t, J = 246.3 Hz), 63.1, 34.8, 31.20, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.1.



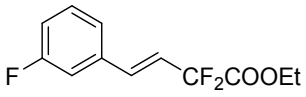
Ethyl-2, 2-difluoro-4-(4-methanoxyl)but-3-enoate (**10**, ***E/Z***=14:1), the procedure was operated in method A. This compound is known. [9] The reaction gave 113 mg of ethyl-2, 2-difluoro-4-(4-methanoxyl)but-3-enoate in 87 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 8.7 Hz, 2H), 7.04 (dt, J = 16.2, 2.5 Hz, 1H), 6.92 (d, J = 9.0, 2H), 6.90 – 6.84 (m, 1H), 6.18 (dt, J = 16.2, 11.5 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1 (t, J = 35.0 Hz), 160.8, 136.3 (t, J = 8.8 Hz), 128.9, 126.8, 116.4 (t, J = 25.0 Hz), 114.94, 113.0 (t, J = 246.3 Hz), 63.1, 55.4, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.7.



Ethyl (E)-2, 2-difluoro-4-(4-pentanoxyl)but-3-enoate (**11**, ***E/Z***=14:1). The procedure was operated in method A. The reaction gave 122 mg of ethyl (E)-2, 2-difluoro-4-(4-pentanoxyl)but-3-enoate in 81 % isolated yield as a yellow clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.7 Hz, 2H), 7.01 (dt, J = 16.1, 2.4 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.15 (dt, J = 16.1, 11.5 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.48 – 1.33 (m, 7H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (t, J = 35.0Hz), 160.4, 136.4 (t, J = 10.0 Hz), 129.0, 126.6, 116.2 (t, J = 25.0 Hz), 115.0, 113.0 (t, J = 247.5Hz), 68.1, 63.0, 28.9, 28.2, 22.5, 14.0, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.6. HRMS (EI, *m/z*) calcd for [$C_{17}H_{22}F_2O_3$]: 312.1537; found: 312.1548.

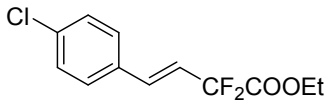


Ethyl (E)-2, 2-difluoro-4-(4-fluorophenyl)but-3-enoate (**12**, ***E/Z***=14:1), the procedure was operated in method A. This compound is known. [8] The reaction gave 69 mg of ethyl (E)-2, 2-difluoro-4-(4-fluorophenyl)but-3-enoate in 48 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.09 – 7.00 (m, 3H), 6.23 (dt, J = 16.2, 11.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9 (t, J = 34.8 Hz), 163.5 (d, J = 248.6 Hz), 135.6 (t, J = 9.4 Hz), 130.3 (d, J = 3.3 Hz), 129.3(d, J = 8.4 Hz), 118.6 (dt, J = 25.0 Hz), 115.9 (d, J =21.7 Hz), 112.6 (t, J = 247.1 Hz), 63.18, 13.97. ^{19}FNMR (471 MHz, $CDCl_3$): δ -103.20, -110.90.

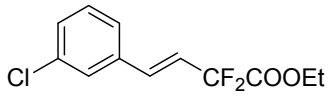


Ethyl (E)-2, 2-difluoro-4-(3-fluorophenyl)but-3-enoate (**13**, ***E/Z***=5:1), the procedure was operated in method A. The reaction gave 69 mg of ethyl (E)-2, 2-difluoro-4-(3-fluorophenyl)but-3-enoate in 56 % isolated yield as a colorless chear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.01 (m, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.15 (dt, J = 2, 10 Hz, 1H), 7.13 – 7.00 (m, 2H), 6.31 (dt, J = 16.2, 11.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (t,

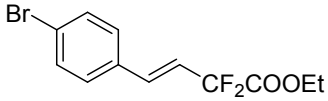
J = 34.5 Hz), 163.0 (d, *J* = 245.1 Hz), 136.3 (d, *J* = 9.4 Hz), 135.7 (dt, *J* = 9.5 Hz), 130.4 (d, *J* = 8.3 Hz), 123.4 (d, *J* = 2.6 Hz), 120.3 (t, *J* = 24.9 Hz), 116.5 (d, *J* = 21.3 Hz), 113.9 (d, *J* = 22.1 Hz), 112.4 (t, *J* = 247.4 Hz), 63.3, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.54, -112.62. HRMS (EI, *m/z*) calcd for [$C_{12}H_{11}F_3O_2$]: 244.0711; found: 244.0702.



Ethyl (E)-4-(4-chlorophenyl)-2, 2-difluorobut-3-enoate (**14**, ***E/Z***=9:1), the procedure was operated in method A. This compound is known. [9] The reaction gave 78 mg of ethyl (E)-4-(4-chlorophenyl)-2, 2-difluorobut-3-enoate in 60 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 4H), 7.03 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.28 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (t, *J* = 34.6 Hz), 135.6 (t, *J* = 9.4 Hz), 132.6, 129.1, 128.7, 128.4, 119.4 (t, *J* = 24.9Hz), 112.5 (t, *J* = 247.4 Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.35.

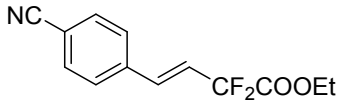


Ethyl (E)-4-(3-chlorophenyl)-2, 2-difluorobut-3-enoate (**15**, ***E/Z***=10:1), the procedure was operated in method A. The reaction gave 96 mg of ethyl (E)-4-(4-chlorophenyl)-2, 2-difluorobut-3-enoate in 74 % isolated yield as a light yellow clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.27 (m, 4H), 7.02 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.32 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (t, *J* = 34.5 Hz), 135.9, 135.5 (t, *J* = 9.5Hz), 134.8, 130.1, 129.6, 127.3, 125.7, 120.4 (t, *J* = 24.9 Hz), 112.4 (t, *J* = 247.4 Hz), 63.3, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.55. HRMS (EI, *m/z*) calcd for [$C_{12}H_{11}ClF_2O_2$]: 260.0416; found: 260.0420.

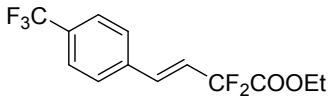


Ethyl (E)-4-(4-bromophenyl)-2, 2-difluorobut-3-enoate (**16**, ***E/Z***=8:1), the

procedure was operated in method A. This compound is known. [9] The reaction gave 92 mg of ethyl (E)-4-(4-bromophenyl)-2, 2-difluorobut-3-enoate in 60 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.49 (m, 2H), 7.33 – 7.29 (m, 2H), 7.02 (dt, J = 16.2, 2.5 Hz, 1H), 6.30 (dt, J = 16.2, 11.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (t, J = 34.6 Hz), 135.6 (t, J = 9.4 Hz), 133.0, 132.1, 128.9, 123.8, 119.6 (t, J = 24.9 Hz), 112.5 (t, J = 247.3 Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.40.

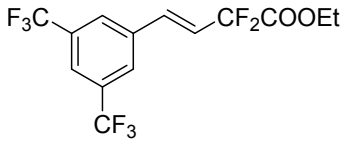


Ethyl (E)-4-(4-cyanophenyl)-2, 2-difluorobut-3-enoate (**17**, ***E/Z***=1:1), the procedure was operated in method A. The reaction gave 45 mg of ethyl (E)-4-(4-cyanophenyl)-2, 2-difluorobut-3-enoate in 36 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.66 (m, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.09 (dt, J = 16.2, 2.4 Hz, 1H), 6.42 (dt, J = 16.2, 11.2 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). (Z) 7.65 – 7.62 (m, 1H), 7.46 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 12.7 Hz, 1H), 5.99 (dd, J = 26.5, 13.7 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2 (t, J = 33.4 Hz), 138.8, 136.7 (t, J = 7.6 Hz), 132.6, 129.5, 124.2 (t, J = 27.0 Hz), 118.4, 113.0, 112.1 (t, J = 247.3 Hz), 63.4, 14.0. (Z): δ 163.4(t, J = 34.0 Hz), 138.4, 135.0 (t, J = 9.4 Hz), 131.9, 128.0, 122.6 (t, J = 24.9 Hz), 118.3, 112.3, 111.9 (t, J = 246.9 Hz), 63.3, 13.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.89. Z: δ -96.28, HRMS (EI, *m/z*) calcd for [$C_{13}H_{11}F_2NO_2$]: 251.0758; found: 251.0769.

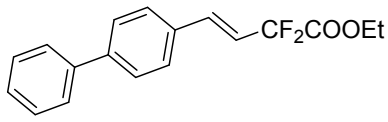


Ethyl (E)-2, 2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (**18**, ***E/Z***=4:1), the procedure was operated in method A. The reaction gave 108 mg of ethyl (E)-2, 2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate in 73 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.12 (dt, J = 16.2, 2.3 Hz, 1H), 6.40 (dt, J = 16.2, 11.2 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 2H). (Z): δ 7.60 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 12.6 Hz, 1H), 5.97 (dd, J = 26.2, 13.4 Hz, 1H), 4.12 (q, J =

7.1 Hz, 2H), 1.19 (t, J = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6 (t, J = 34.4 Hz), 137.5, 135.4 (t, J = 9.4 Hz), 131.4 (q, J = 32.6 Hz), 127.7, 125.8 (q, J = 3.6 Hz), 123.8 (q, J = 270.5 Hz), 121.5 (t, J = 24.9 Hz), 112.3 (t, J = 247.5 Hz), 63.3, 13.9. (Z): δ 163.3 (t, J = 33.5 Hz), 137.8, 137.2 (t, J = 8.1 Hz), 131.4 (q, J = 32.6 Hz), 129.2, 125.1 (q, J = 3.9 Hz), 123.8(q, J = 270.5 Hz), 123.7 (t, J = 27.0 Hz), 112.0 (t, J = 246.3 Hz), 63.2, 13.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.8, -103.7. (Z): δ -62.8, -95.5. HRMS (EI, *m/z*) calcd for [$C_{13}H_{11}F_5O_2$]: 294.0679; found: 294.0678.

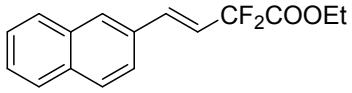


Ethyl (E)-4-(3, 5-bis(trifluoromethyl)phenyl)-2, 2-difluorobut-3-enoate (**19**, ***E/Z***=1.2:1). The procedure was operated in method A. The reaction gave 120 mg of ethyl (E)-4-(3, 5-bis(trifluoromethyl)phenyl)-2, 2-difluorobut-3-enoate in 66 % isolated yield as a yellow clear liquid.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 – 7.82 (m, 3H), 7.16 (dt, J = 16.2, 2.4 Hz, 1H), 6.48 (dt, J = 16.2, 11.0 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 23H). (Z) 7.91 – 7.82 (m, 3H), 6.97 (d, J = 12.6 Hz, 1H), 6.04 (td, J = 14.0, 12.8 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, J = 34.1 Hz), 136.2, 135.4 (t, J = 7.4 Hz), 132.4 (q, J = 33.5 Hz), 129.0 (d, J = 2.6 Hz), 124.9 (t, J = 26.6 Hz), 124.1 (d, J = 11.5 Hz), 123.0(t, J = 3.6 Hz), 112.0 (t, J = 248.3 Hz), 63.5, 14.0. (Z): δ 163.1 (t, J = 33.1 Hz), 136.2, 133.9 (t, J = 9.5 Hz), 131.6 (q, J = 33.4 Hz), 127.3 (d, J = 2.5 Hz), 123.0 (t, J = 25.0 Hz), 122.2 (t, J = 3.8 Hz), 122.0 (d, J = 11.6 Hz), 111.9(t, J = 247.9Hz), 63.5, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$): δ -63.1, -104.0. (Z): δ -63.1, -97.5. HRMS (EI, *m/z*) calcd for [$C_{14}H_{10}F_8O_2$]: 362.0553; found: 362.0555.

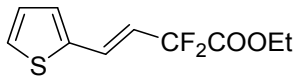


Ethyl (E)-2, 2-difluoro-4-(4-phenyl)but-3-enoate (**20**, ***E/Z***=25:1)，the procedure was operated in method A. The reaction gave 103 mg of ethyl (E)-2,2-difluoro-4-(4'-phenylphenyl)but-3-enoate in 68 % isolated yield as a white solid.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.46 (dd, J = 10.4, 4.8 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.13 (dt, J = 16.2, 2.3 Hz, 1H), 6.35 (dt, J = 16.2, 11.4

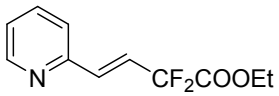
Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 35.0 Hz), 142.4, 140.2, 136.4 (t, J = 8.8 Hz), 133.1, 128.9, 127.9, 127.8, 127.5, 127.0, 118.7 (t, J = 24.3 Hz), 112.8 (t, J = 247.5Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.1. HRMS (EI, *m/z*) calcd for [$C_{18}H_{16}F_2O_2$]: 302.1118; found: 302.1129.



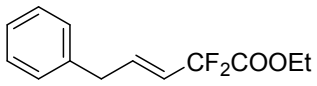
Ethyl (E)-2, 2-difluoro-4-(naphthalen-2-yl)but-3-enoate (**21**, ***E/Z***=10:1), the procedure was operated in method A. The reaction gave 38 mg of ethyl (E)-2, 2-difluoro-4-(naphthalen-2-yl)but-3-enoate in 55 % isolated yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, J = 7.4, 4.2 Hz, 4H), 7.61 (dd, J = 8.6, 1.6 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.25 (dt, J = 14.8, 2.4 Hz, 1H), 6.43 (dt, J = 16.1, 11.4 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 34.8 Hz), 136.9 (t, J = 9.4Hz), 133.9, 133.3, 131.5, 128.8, 128.7, 128.4, 127.8, 127.0, 126.7, 123.3, 119.0 (t, J = 24.9 Hz), 112.8 (t, J = 247.0 Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.03. HRMS (EI, *m/z*) calcd for [$C_{16}H_{14}F_2O_2$]: 276.0962; found: 276.0973



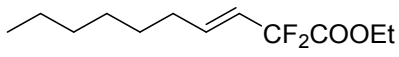
Ethyl (*E*)-2, 2-difluoro-4-(thiophen-2-yl)but-3-enoate (**22**), the procedure was operated in method A. The reaction gave 51 mg of ethyl (E)-2, 2-difluoro-4(thiophen)but-3-enoate in 43 % isolated yield as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J = 5.0 Hz, 1H), 7.19 (dt, J = 15.9, 2.5 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 7.02 (dd, J = 5.1, 3.6 Hz, 1H), 6.11 (dt, J = 15.9, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8 (t, J = 34.8 Hz), 138.9, 129.8 (t, J = 10.0 Hz), 129.4, 127.8, 127.3, 117.6 (t, J = 25.1 Hz), 112.4 (t, J = 247.3 Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.6. HRMS (EI, *m/z*) calcd for [$C_{10}H_{10}F_2O_2S$]: 232.0370; found: 232.0365.



Ethyl (E)-2, 2-difluoro-4-(pyridin-2-yl)but-3-enoate (23, *E/Z*=13:1), the procedure was operated in method A. The reaction gave 50 mg of ethyl (E)-2, 2-difluoro-4-(pyridin-2-yl)but-3-enoate in 44 % isolated yield as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (dd, J = 4.7, 0.6 Hz, 1H), 7.70 (td, J = 7.7, 1.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.12 (dt, J = 15.8, 2.4 Hz, 1H), 6.89 (dt, J = 15.8, 11.9 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7(t, J = 34.4 Hz), 152.4, 150.0, 136.8, 136.0 (t, J = 9.0 Hz), 123.9, 123.7, 123.1 (t, J = 24.9Hz), 112.7 (t, J = 247.0Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.95. HRMS (EI, *m/z*) calcd for [$C_{11}H_{11}F_2NO_2$]: 227.0758; found: 227.0742.

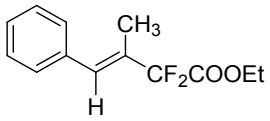


Ethyl (E)-2, 2-difluoro-5-phenylpent-3-enoate (**24**, ***E/Z***=1: 1), the procedure was operated in method A. The reaction gave 100 mg of ethyl (E)-2, 2-difluoro-5-phenylpent-3-enoate in 83 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.25 – 7.16 (m, 3H), 6.45 (dt, J = 15.5, 2.5 Hz, 1H), 5.76 – 5.65 (m, 1H), 4.33 (q, J = 7.5, 2H), 3.67 (dd, J = 7.9, 1.9 Hz, 1H), 1.34 (t, J = 7.0 Hz, 3H). (Z): δ 7.34 - 7.30 (m, 2H), 7.25 – 7.16 (m, 3H), 6.09 (td, J = 27.5, 2.0 Hz, 1H), 5.76 – 5.65 (m, 1H), 4.33 (q, J = 7.5, 2H), 3.48 (dd, J = 6.5, 1.6 Hz, 1H), 1.34 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2(t, J = 34.5 Hz), 140.2 (t, J = 6.8 Hz), 138.8, 128.7, 128.7, 126.70, 122.3 (t, J = 25.0 Hz), 112.8 (t, J = 247.6 Hz), 63.1, 38.1, 13.9. (Z): δ 164.0 (t, J = 34.4 Hz), 138.3 (t, J = 8.9Hz), 137.8, 128.7, 128.5, 126.49, 121.4 (t, J = 26.3 Hz), 112.3 (t, J = 246.4 Hz), 63.0, 34.6, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.09. (Z): δ -98.52. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 240.0962; found: 240.0967.

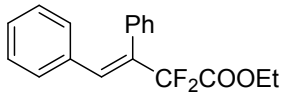


Ethyl (E)-2, 2-difluorodec-3-enoate (**25**, ***E/Z***=1:1). The procedure was operated in

method A. The reaction gave 85 mg of ethyl (E)-2, 2-difluorodec-3-enoate in 72 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.32 – 6.09 (m, 1H), 5.74 – 5.50 (m, 1H), 4.32 (q, J = 7.5 Hz, 2H), 2.33 – 2.23 (m, 1H), 1.45 – 1.26 (m, 11H), 0.88 (t, J = 6.9 Hz, 3H).(Z): δ 5.96 – 5.88 (m, 1H), 5.74 – 5.50 (m, 1H), 4.31 (q, J = 7 Hz, 2H)，2.18 – 2.10 (m, 1H), 1.45 – 1.26 (m, 11H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (t, J = 34.8 Hz), 142.4(t, J = 7.0 Hz), 120.9(t, J = 24.8 Hz), 112.9(t, J = 247.1 Hz), 62.9, 31.9, 31.6, 28.8, 28.4, 22.6, 14.0, 13.9. (Z): δ 164.2 (t, J = 34.9 Hz), 140.0 (t, J = 9.0 Hz), 120.8 (t, J = 26.3 Hz), 112.4 (t, J = 246.0 Hz), 62.8, 29.1, 31.6, 28.7, 28.1, 22.5, 14.0, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.9. (Z): δ -98.8. HRMS (EI, *m/z*) calcd for [$C_{12}H_{20}F_2O_2$]: 234.1431; found: 234.1420.

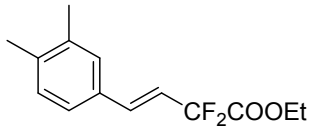


Ethyl (E)-2, 2-difluoro-3-methyl-4-phenylbut-3-enoate (**26**, ***E/Z***=4:1), the procedure was operated in method A. The reaction gave 85 mg of ethyl (E)-2, 2-difluoro-3-methyl-4-phenylbut-3-enoate in 71 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 - 7.22 (m, 5H), 6.95 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.99 (d, J = 1.4 Hz, 3H), 1.37 (t, J = 7.1 Hz, 2H). (Z) δ 7.40 - 7.22 (m, 5H),（6.82 (s, 1H), 3.89 (q, J = 7.5 Hz, 2H), 2.06 (d, J = 1.3 Hz, 3H), 1.12 (t, J = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0 (t, J = 35.0 Hz), 135.2, 131.0 (t, J = 8.8 Hz), 129.2, 128.4, 128.0 (t, J = 2.4 Hz), 127.8, 114.4 (t, J = 250 Hz), 63.0, 14.00, 12.6 (t, J = 3.1 Hz). ^{19}FNMR (471 MHz, $CDCl_3$): δ -106.6. (Z) -97.2. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 240.0962; found: 240.0950.

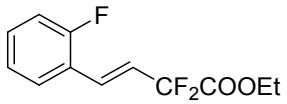


Ethyl (E)-2, 2-difluoro-3, 4-diphenylbut-3-enoate (**27**, ***E/Z***=2:1). The procedure was operated in method A. The reaction gave 100 mg of ethyl (E)-2, 2-difluoro-3, 4-diphenylbut-3-enoate in 46 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.34 (m, 5H), 7.24 (dd, J = 6.5, 3.0 Hz, 1H), 7.20 – 7.05 (m, 3H), 7.03 – 6.97 (m, 1H), 4.23 (q, J = 7.1 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8 (t, J = 34.5 Hz), 138.3 (t, J = 5.9 Hz),134.8, 134.1, 132.5

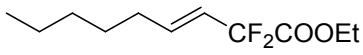
(t, J = 8.9 Hz), 130.1, 129.0 (t, J = 2.6 Hz), 128.9, 128.6, 128.2, 128.2, 128.2, 113.7 (t, J = 251.6 Hz), 62.9, 13.8. Z: δ 163.3 (t, J = 33.1 Hz), 137.4 (t, J = 2.1 Hz), 135.0, 133.4, 132.8 (t, J = 21.3 Hz), 130.0, 128.7, 128.5, 128.4 (t, J = 4.8 Hz) 128.4, 128.1, 112.9 (t, J = 248.8 Hz), 62.8, 13.5. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.12. Z: δ -91.94. HRMS (EI, *m/z*) calcd for [$C_{18}H_{20}F_2NO_2 + NH_4^+$]: 320.1462; found: 320.1455.



Ethyl (E)-4-(3, 4-dimethylphenyl)-2, 2-difluorobut-3-enoate (**28**), the procedure was operated in method B. The reaction gave 75 mg of ethyl (E)-4-(3, 4-dimethylphenyl)-2, 2-difluorobut-3-enoate in 65 % isolated yield as a yellow clear liquid.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (s, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.7 Hz, 1H), 7.03 (dt, J = 16.2, 2.5 Hz, 1H), 6.25 (dt, J = 16.2, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.28 (s, 6H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1 (t, J = 34.9 Hz), 138.6, 137.1, 136.9 (t, J = 9.5 Hz), 131.8, 130.1, 128.6, 125.0, 117.5 (t, J = 24.9 Hz), 112.9 (t, J = 246.8 Hz), 63.1, 19.7, 19.7, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.9. HRMS (EI, *m/z*) calcd for [$C_{14}H_{16}F_2O_2$]: 254.1118; found: 254.1126.

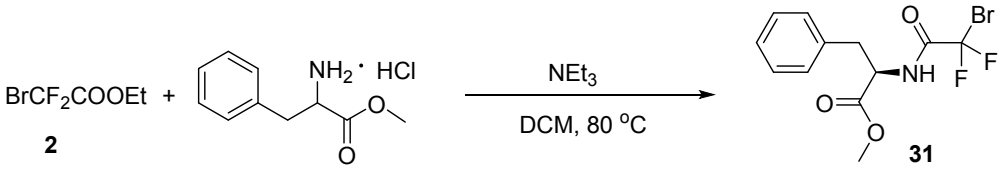


Ethyl (E)-2, 2-difluoro-4-(2-fluorophenyl)but-3-enoate(**29**, ***E/Z***=13:1), the procedure was operated in method B. The reaction gave 57 mg of ethyl (E)-2, 2-difluoro-4-(2-fluorophenyl)but-3-enoate in 51 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (td, J = 7.6, 1.5 Hz, 1H), 7.31-7.36 (m, 1H), 7.21 (dt, J = 16.4, 2.6 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.43 (dt, J = 16.4, 11.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8 (t, J = 34.5 Hz), 160.9 (d, J = 251.0 Hz), 131.1 (d, J = 8.6 Hz), 129.8 (dt, J = 9.9 Hz), 128.6 (d, J = 2.9Hz), 124.4 (d, J= 3.6 Hz), 122.1 (d, J = 11.8 Hz), 121.4(t, J = 24.9 Hz), 116.1 (d, J = 21.9 Hz), 112.6 (t, J = 247.3 Hz), 63.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.7, -115.7. HRMS (EI, *m/z*) calcd for [$C_{13}H_{14}F_2O_2$]: 244.0711; found: 244.0723.



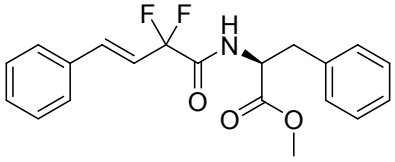
Ethyl (E)-2, 2-difluoronon-3-enoate (**30**), the procedure was operated in method **B**. This compound is known.[11] The reaction gave 93 mg of ethyl (E)-4-(4-bromophenyl)-2, 2-difluorobut-3-enoate in 83 % isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (dt, J = 15.5, 2.5 Hz, 1H), 5.69 (qt, J = 11.0 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 2.18 – 2.13 (m, 2H), 1.46 – 1.29 (m, 9H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2 (t, J = 34.8 Hz), 140.0 (t, J = 9.0 Hz), 120.9 (t, J = 24.8 Hz), 112.4 (t, J = 246.0 Hz), 62.8, 31.8, 31.2, 27.8, 22.4, 14.0, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.96.

The synthesis of compound 31.[12]

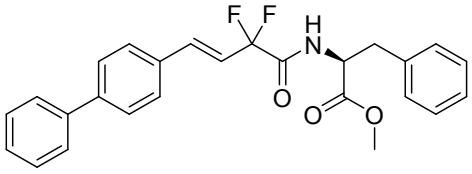


To 50 mL round-bottom flask added (*S*)-methyl 2-amino-3-phenylpropanoate hydrochloride, NEt_3 (12.3 mmol), ethyl bromodifluoroacetate (6.15 mmol)) and DCM (15 mL) were added subsequently at room temperature. The resulting mixture was stirred at room temperature for 2 h, and then was heated to 80 ℃ for 7 h. The reaction was cooled to room temperature and washed with saturated salt water, extracted with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/EtOAc = 5:1) to give compound **31** in 50% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 3H), 7.10 (dd, J = 5.1, 3.0 Hz, 2H), 6.74 (d, J = 5.6 Hz, 1H), 4.87 (dt, J = 7.6, 5.6 Hz, 1H), 3.79 (s, 3H), 3.21 (ddd, J = 38.8, 14.0, 5.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.48, 159.3 (t, J =28.0Hz), 134.6, 129.3, 128.8, 127.6, 111.2 (t, J =313.9Hz), 53.7, 52.8, 37.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ -60.8, -60.8.

Hydrodifluoroamidation of alkynes with new difluoro reagent 31



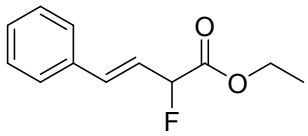
Methyl (E)-(2, 2-difluoro-4-phenylbut-3-enoyl)-L-phenylalaninate(**32**), the procedure was operated in method A, Phenylethene (0.25 mmol) , methyl (2-bromo-2, 2-difluoroacetyl)-D-phenylalaninate (0.375 mmol, 118 mg)) and 24 h. The reaction gave 58 mg of ethyl methyl (E)-(2, 2-difluoro-4-phenylbut-3-enoyl)-L-phenylalaninate in 66 % isolated yield as a clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.8, 1.7 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.30 – 7.24 (m, 3H), 7.10 (dd, J = 7.5, 1.7 Hz, 2H), 7.04 (dt, J = 16.3, 2.5 Hz, 1H), 6.86 (d, J = 7.0 Hz, 1H), 6.32 (dt, J = 16.2, 11.4 Hz, 1H), 5.01 – 4.85 (m, 1H), 3.80 (s, 3H), 3.22 (ddd, J = 47.0, 13.9, 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 163.4 (t, J = 31.4 Hz), 136.8 (t, J = 9.5Hz), 135.0, 134.2, 129.6, 129.3, 128.8, 128.7, 127.5, 127.4, 118.8 (t, J = 25.0 Hz), 114.1 (t, J =248.4Hz), 53.2, 52.7, 37.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -103.1, -103.1. HRMS (EI, *m/z*) calcd for [$C_{20}H_{19}F_2NO_2 + H^+$]: 360.1411; found: 360.1405.



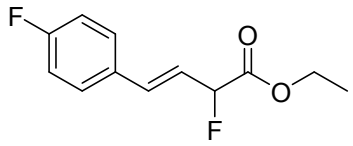
Methyl (E)-(4-([1, 1'-biphenyl]-4-yl)-2, 2-difluorobut-3-enoyl)-L-phenylalaninate

(**33**), the procedure was operated in method A, 4-ethynyl-1, 1'-biphenyl (0.25 mmol, 45.5mg) , methyl (2-bromo-2, 2-difluoroacetyl)-D-phenylalaninate (0.375 mmol, 117.8 mg)and 24 h. The reaction gave 59 mg of ethyl methyl methyl (E)-(4-([1, 1'-biphenyl]-4-yl)-2, 2-difluorobut-3-enoyl)-L-phenylalaninate in 55 % isolated yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 4H), 7.55 – 7.43 (m, 4H), 7.37 (ddd, J = 7.4, 3.9, 1.1 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.11 – 7.03 (m, 3H), 6.85 (d, J = 7.4 Hz, 1H), 6.33 (dt, J = 16.2, 11.4 Hz, 1H), 4.97 – 4.88 (m, 1H), 3.78 (s, 3H), 3.21 (ddd, J = 47.1, 13.9, 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.92, 163.4 (t, J = 31.1 Hz), 142.3, 140.2, 136.3 (t, J = 9.4Hz), 135.0, 133.1, 129.3, 128.9, 128.7, 128.0, 127.7, 127.4, 127.4, 127.0, 118.7 (t, J = 25.0 Hz), 114.2 (t, J = 248.3 Hz), 53.1, 52.7, 37.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -102.9, -102.9. HRMS (EI, *m/z*)

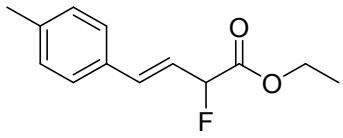
calcd for [$C_{26}H_{123}F_2NO_2 + H^+$]: 436.1724; found: 436.1714.



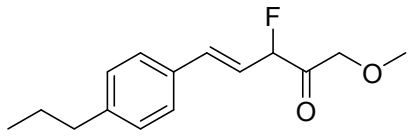
Ethyl (E)-2-fluoro-4-phenylbut-3-enoate(34), the procedure was operated in method A, ethynylbenzene (0.5 mmol), ethyl 2-bromo-2-fluoroacetate(1 mmol). The reaction gave 66 mg of ethyl (E)-2-fluoro-4-phenylbut-3-enoate in 63% isolated yield as a colorless clear liquid. This compound is known.[13] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 6.89 – 6.79 (m, 1H), 6.30 (ddd, J = 16.0, 14.1, 6.5 Hz, 1H), 5.44 (ddd, J = 48.1, 6.5, 1.4 Hz, 1H), 4.35 – 4.24 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3 (d, J = 25.6 Hz), 135.4 (d, J = 11.4 Hz), 135.3 (d, J = 1.3 Hz), 128.7, 128.7, 126.9 (d, J = 1.1 Hz), 121.12, 120.97 (d, J = 19.0 Hz), 88.6 (d, J = 182.5 Hz), 61.9, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ -183.8.



Ethyl (E)-2-fluoro-4-(4-fluorophenyl)but-3-enoate(35), the procedure was operated in method A, 1-ethynyl-4-fluorobenzene (0.5 mmol), ethyl 2-bromo-2-fluoroacetate (1 mmol). The reaction gave 49 mg of ethyl (E)-2-fluoro-4-(4-fluorophenyl)but-3-enoate in 43% isolated yield as a colorless clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.36 (m, 2H), 7.08 – 6.99 (m, 2H), 6.80 (dd, J = 15.9, 2.4 Hz, 1H), 6.21 (ddd, J = 16.0, 14.0, 6.5 Hz, 1H), 5.42 (ddd, J = 48.1, 6.5, 1.3 Hz, 1H), 4.36 – 4.20 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3 (d, J = 25.6 Hz), 162.9 (d, J = 247.1 Hz), 134.2 (d, J = 11.5 Hz), 131.5 (d, J = 2.0 Hz), 128.6 (dd, J = 8.1, 1.1 Hz), 120.8 (d, J = 19.0, 2.3 Hz), 115.7 (d, J = 21.6 Hz), 88.4 (d, J = 182.8 Hz), 61.9, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ -112.47, -183.77. **(CAS: 955038-29-6)**



Ethyl (E)-2-fluoro-4-(p-tolyl)but-3-enoate(36), the procedure was operated in method A, 1-ethynyl-4-methylbenzene (0.5 mmol), ethyl 2-bromo-2-fluoroacetate (1 mmol). The reaction gave 60 mg of ethyl (E)-2-fluoro-4-(p-tolyl)but-3-enoate in 54% isolated yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.81 (dd, J = 15.9, 3.3 Hz, 1H), 6.24 (ddd, J = 15.9, 13.6, 6.7 Hz, 1H), 5.41 (ddd, J = 48.2, 6.7, 1.2 Hz, 1H), 4.35 – 4.24 (m, 2H), 2.35 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5 (d, J = 26.0 Hz), 138.8, 135.6 (d, J = 11.4 Hz), 132.5 (d, J = 1.4 Hz), 129.4, 126.8 (d, J = 1.4 Hz), 120.0 (d, J = 19.1 Hz), 88.7 (d, J = 181.9 Hz), 61.9, 21.3, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ -182.6. HRMS (EI, *m/z*) calcd for [$C_{13}H_{15}FO_2$ + NH_4^+]: 240.1400; found: 240.1393.



Ethyl (E)-2-fluoro-4-(4-propylphenyl)but-3-enoate (37), the procedure was operated in method A, 1-ethynyl-4-propylbenzene （0.5 mmol）, ethyl 2-bromo-2-fluoroacetate (1 mmol). The reaction gave 67 mg of ethyl (E)-2-fluoro-4-(4-propylphenyl)but-3-enoate in 54% isolated yield as a yellow liquid. 1H NMR (500 MHz, CDCl3): δ 7.36 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.85 (dd, J = 15.9, 2.9 Hz, 1H), 6.27 (ddd, J = 16.0, 13.6, 6.7 Hz, 1H), 5.44 (ddd, J = 48.2, 6.7, 1.3 Hz, 1H), 4.38 – 4.22 (m, 2H), 2.65 – 2.57 (m, 2H), 1.71 – 1.62 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5 (d, J = 2.0 Hz), 143.6, 135.7 (d, J = 11.3 Hz), 132.7 (d, J = 1.5 Hz), 128.8, 126.9 (d, J = 1.1 Hz), 120.0 (d, J = 19.1 Hz), 88.7 (d, J = 181.9 Hz), 61.8, 37.8, 24.4, 14.1, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$): δ -182.6. HRMS (EI, *m/z*) calcd for [$C_{15}H_{19}FO_2$ + NH_4^+]: 268.1713; found: 268.1706.

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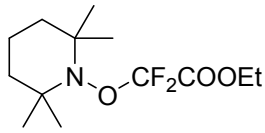
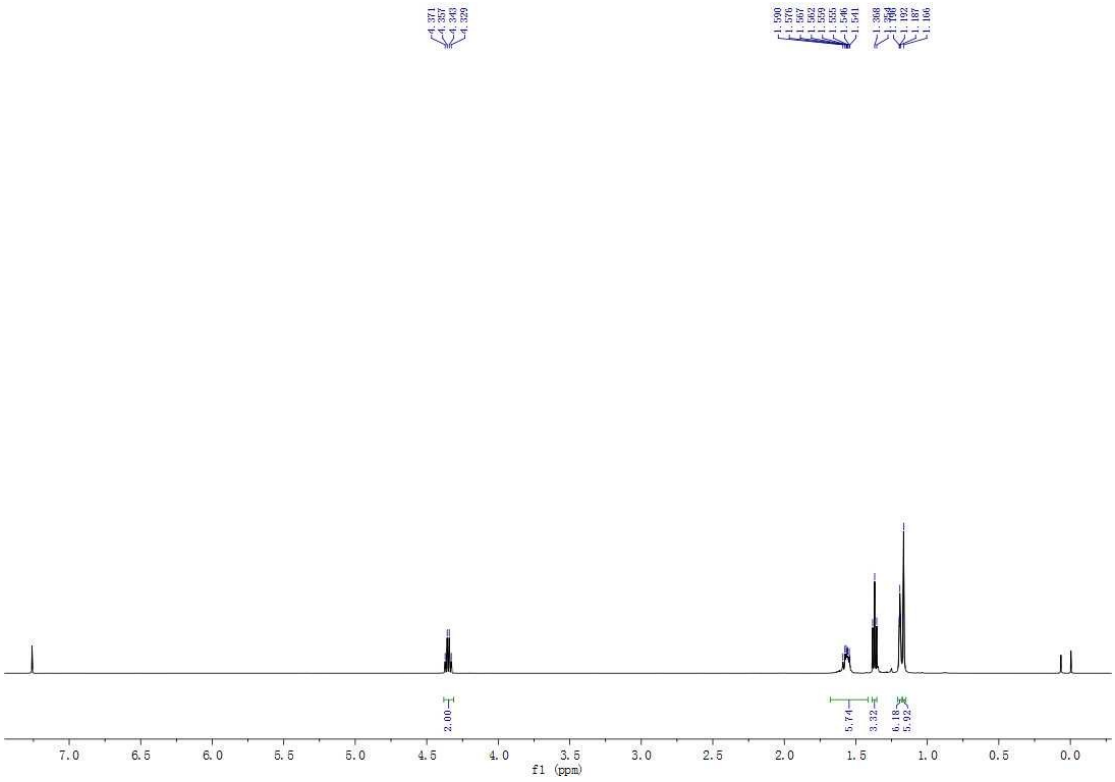
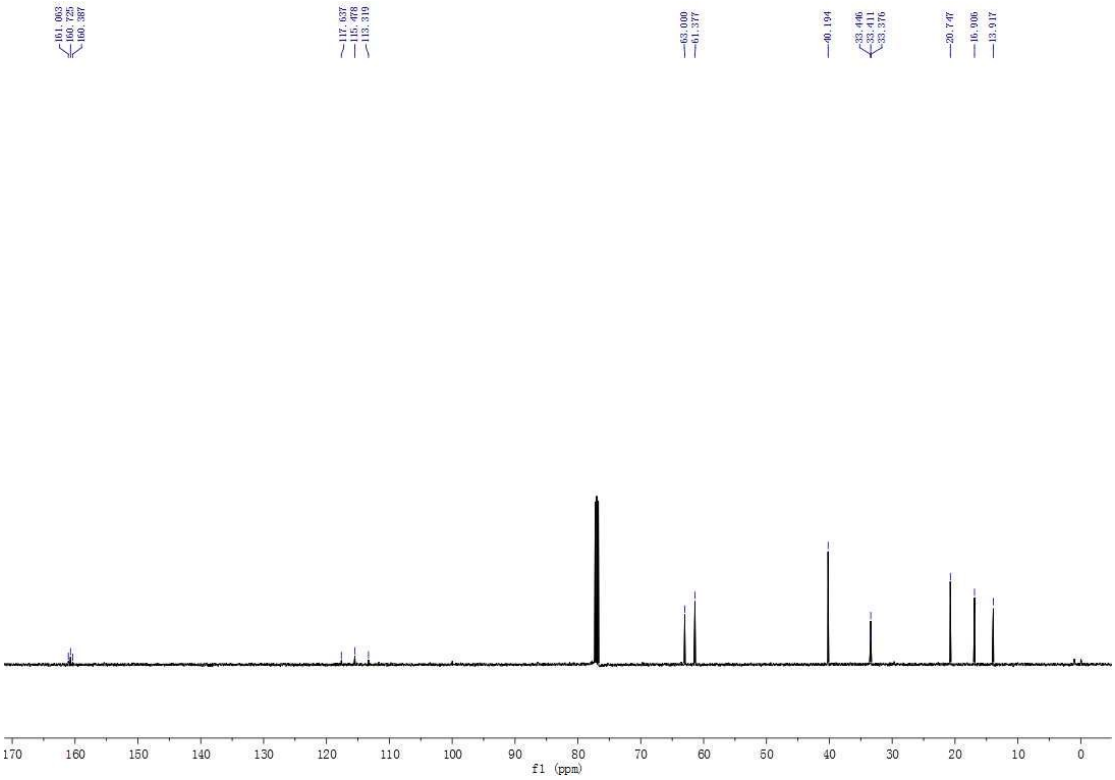
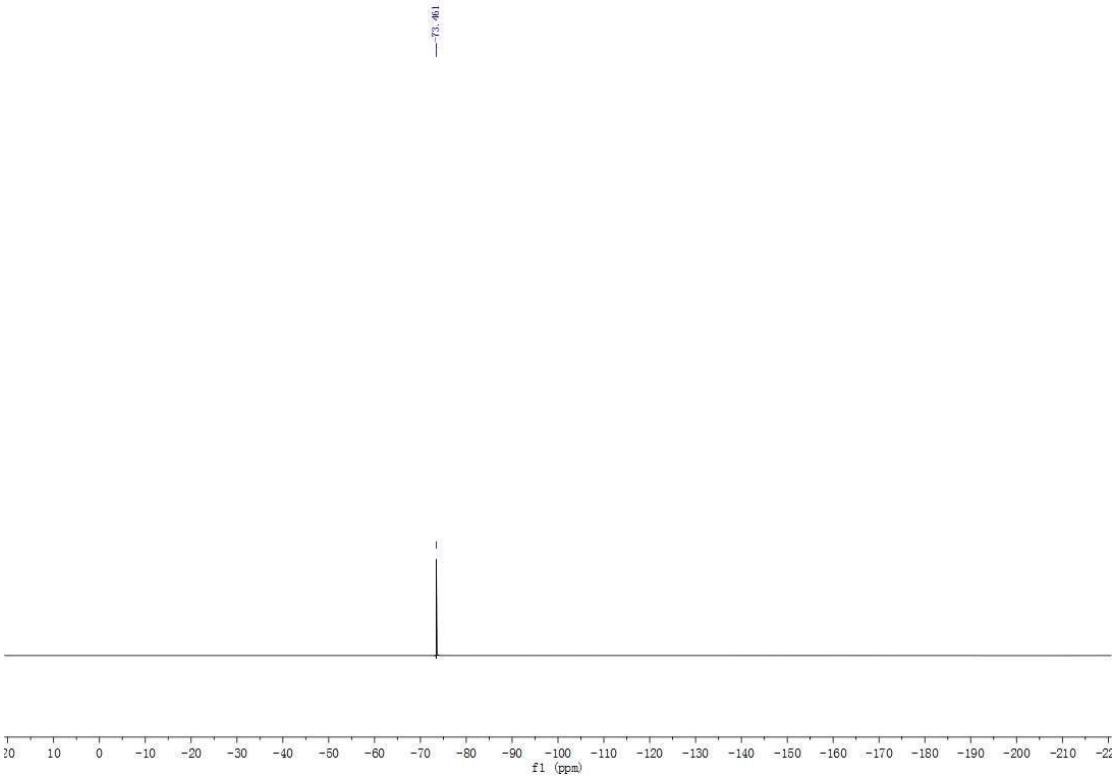
Spectroscopic Data

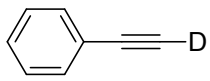


Ethyl 2, 2-difluoro-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)acetate









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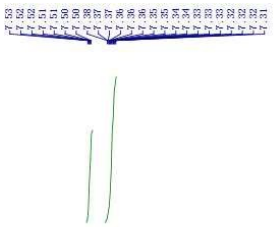
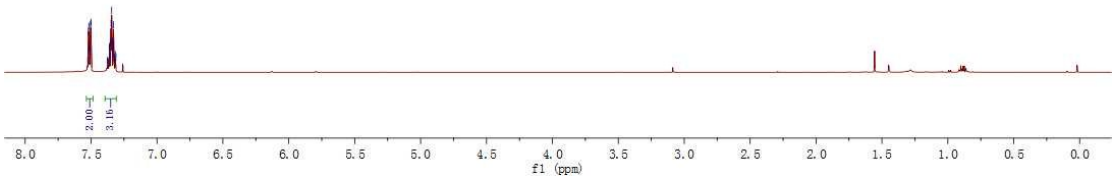
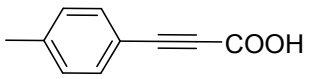
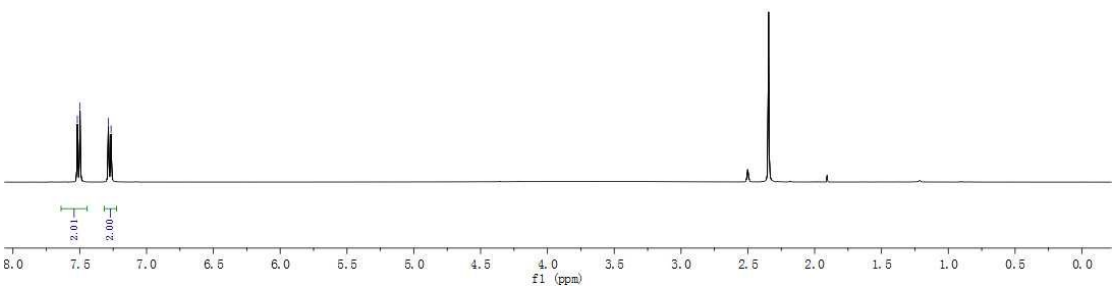
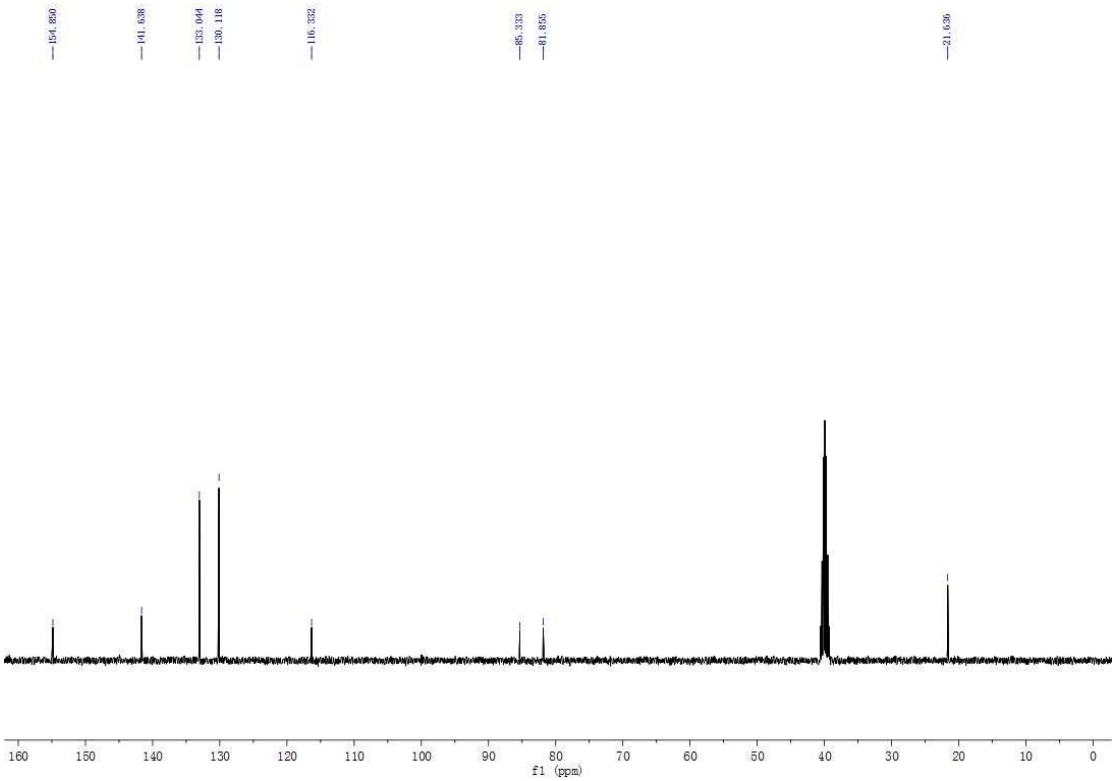


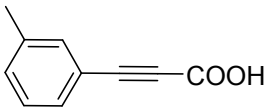




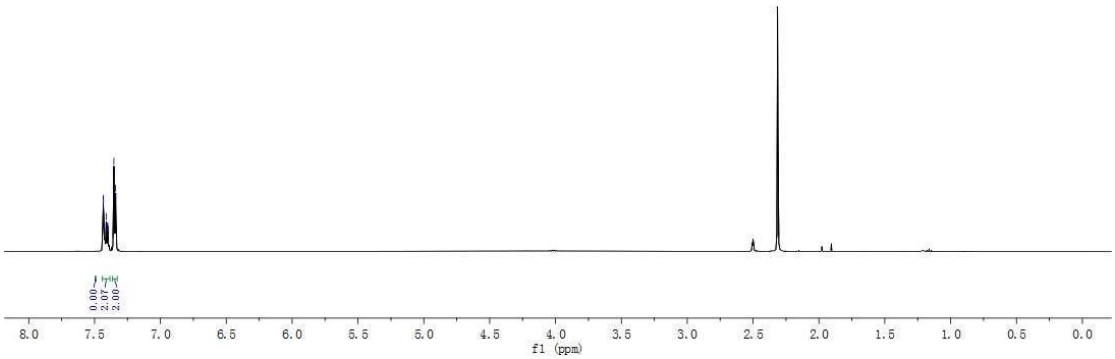
3-(p-tolyl)propiolic acid (1a)

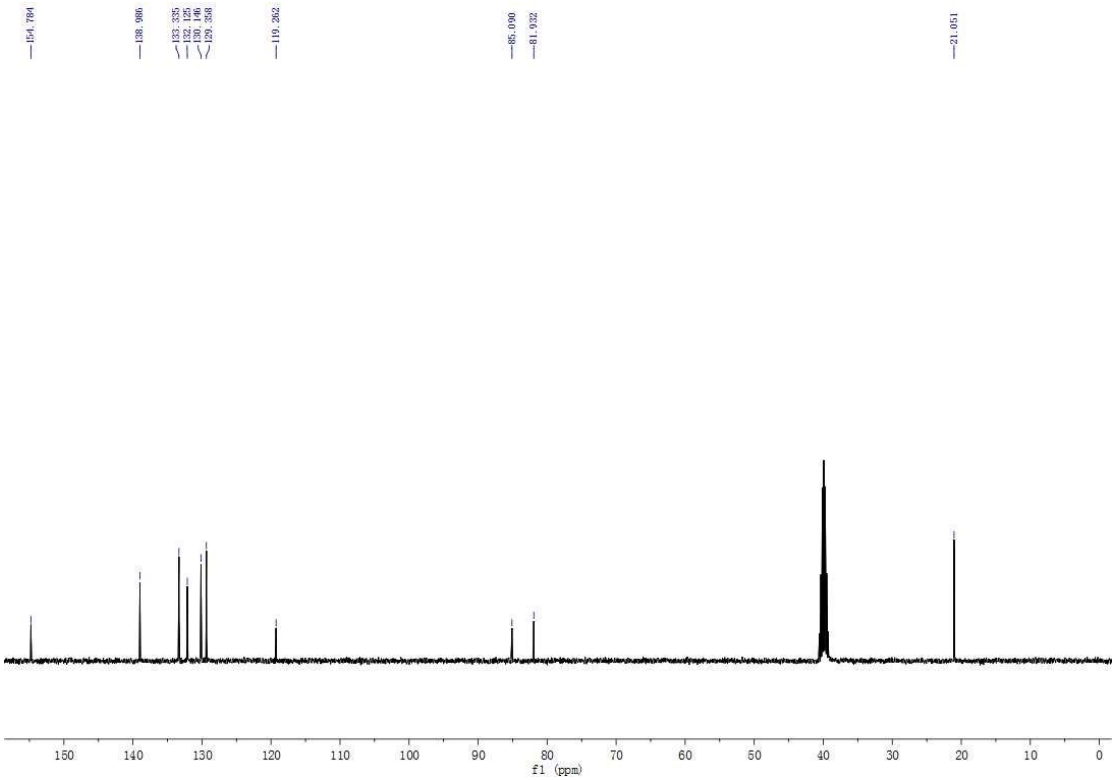


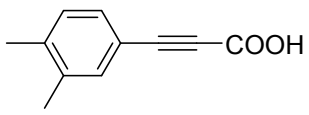




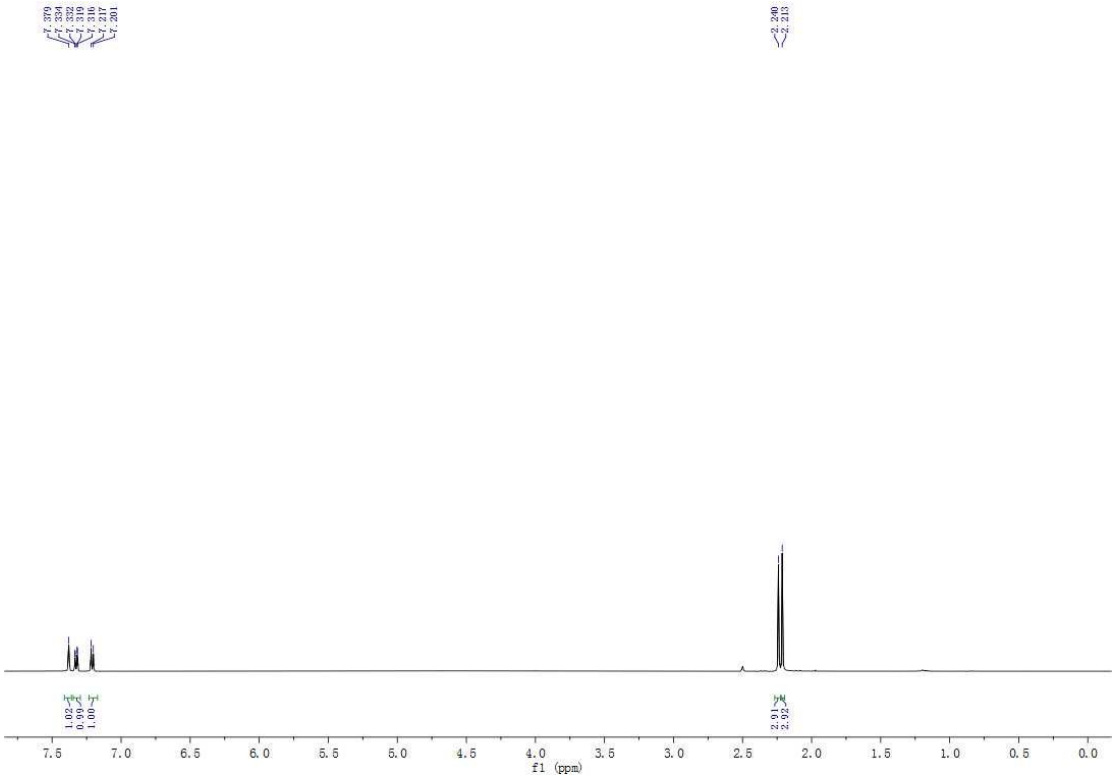
3-(M-tolyl)propiolic acid (1b)

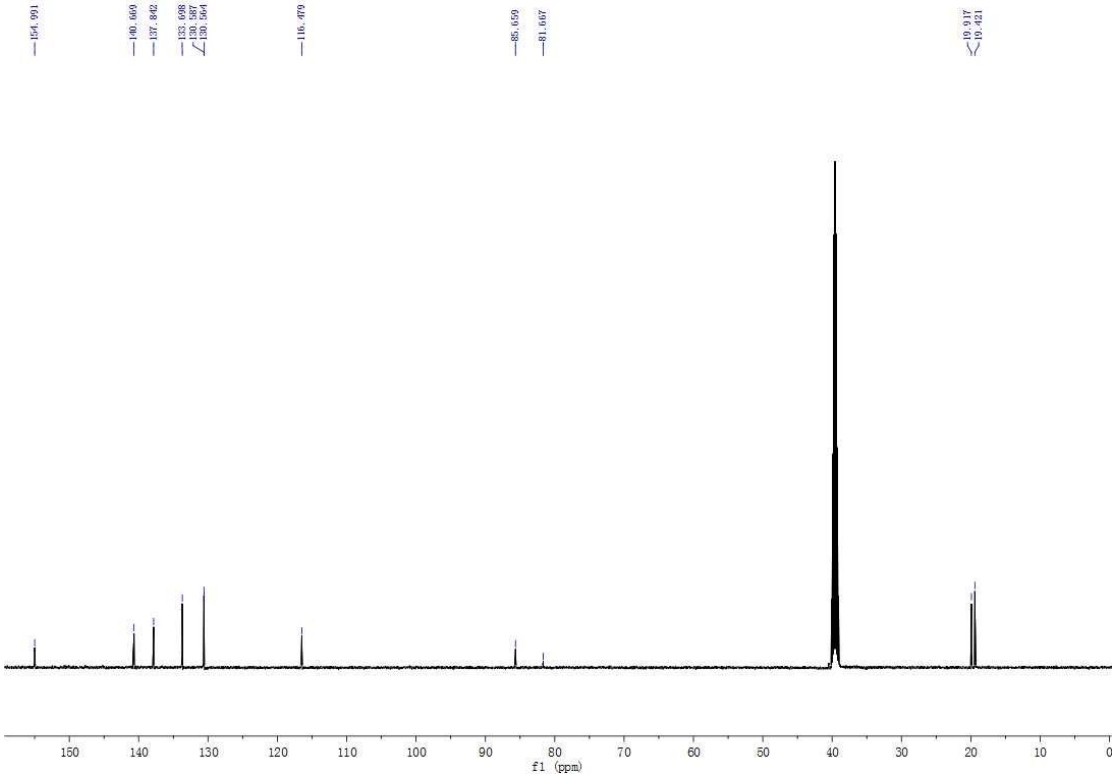

0.00
2.07
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

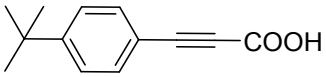

154.784
138.989
133.335
132.125
130.146
129.358
119.262
85.090
81.932
21.051
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


COOH

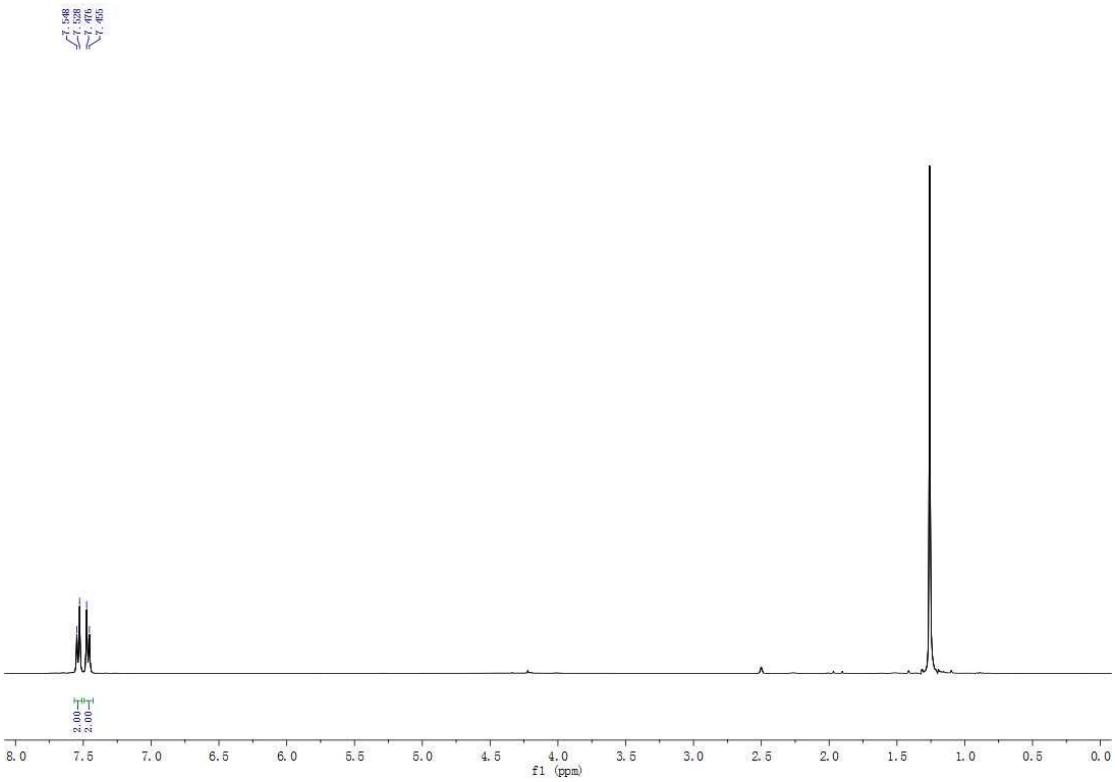
3-(3, 4-dimethylphenyl)propiolic acid (1c)

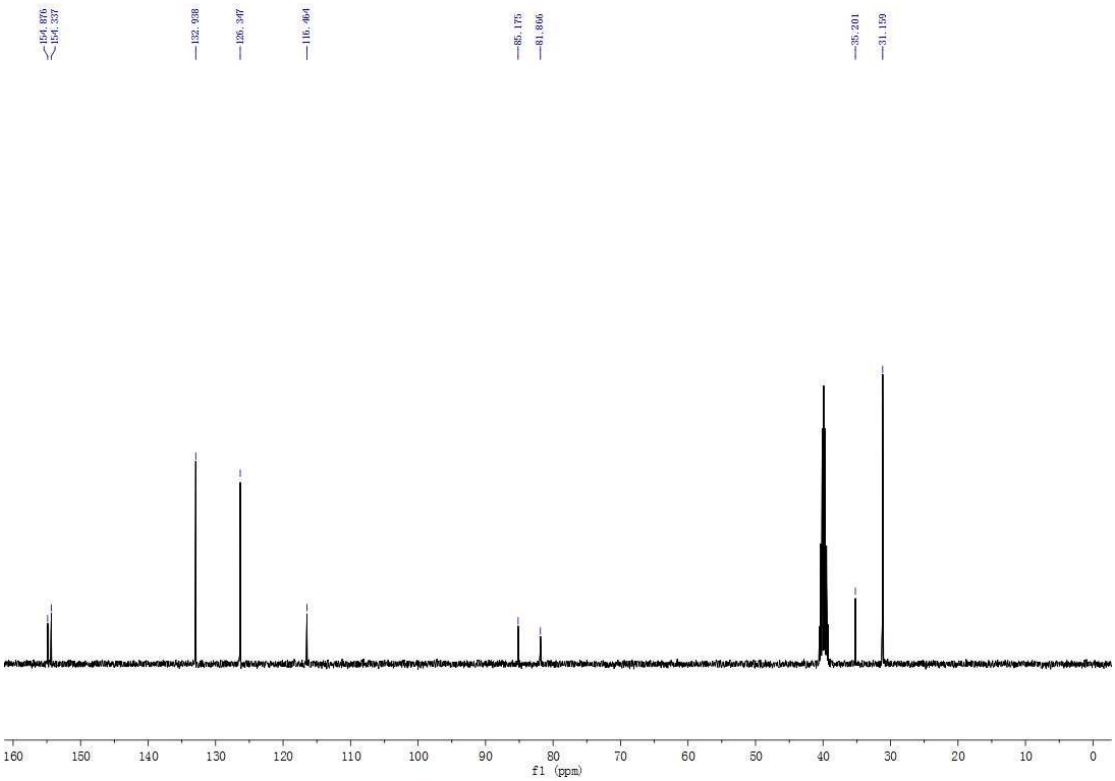


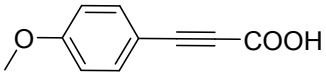




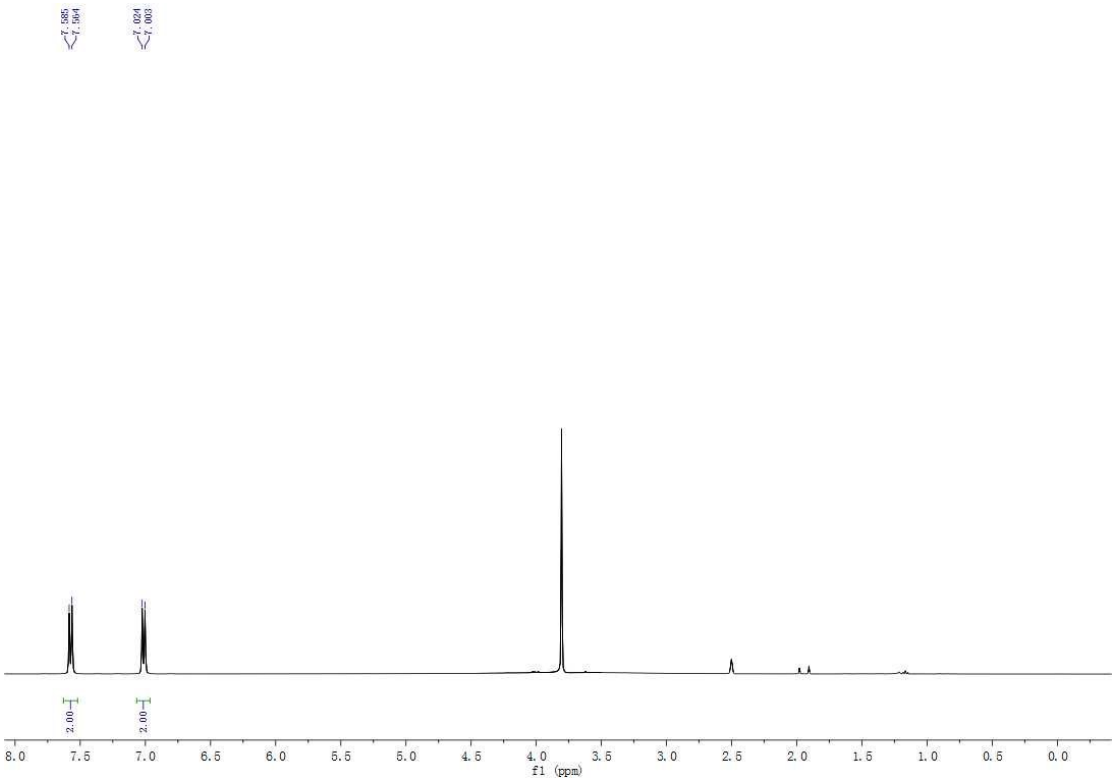
3-(4-(Tert-butyl)phenyl)propiolic acid (1d)

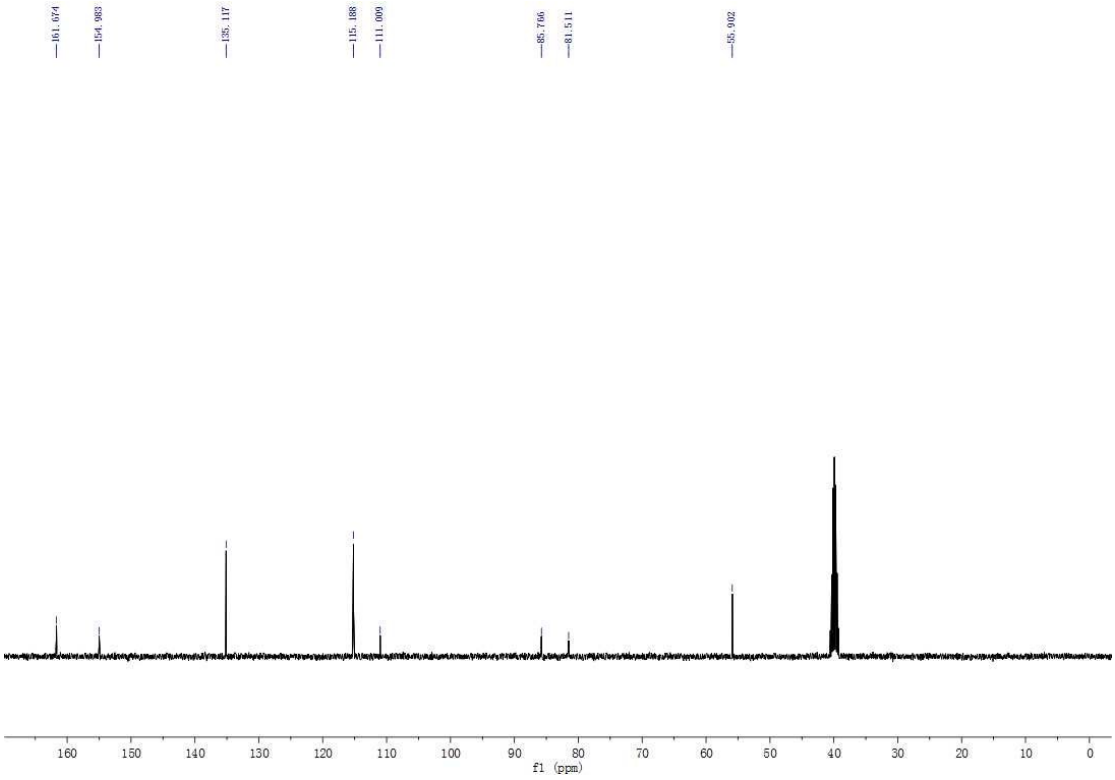


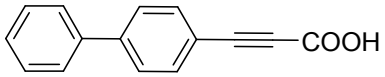




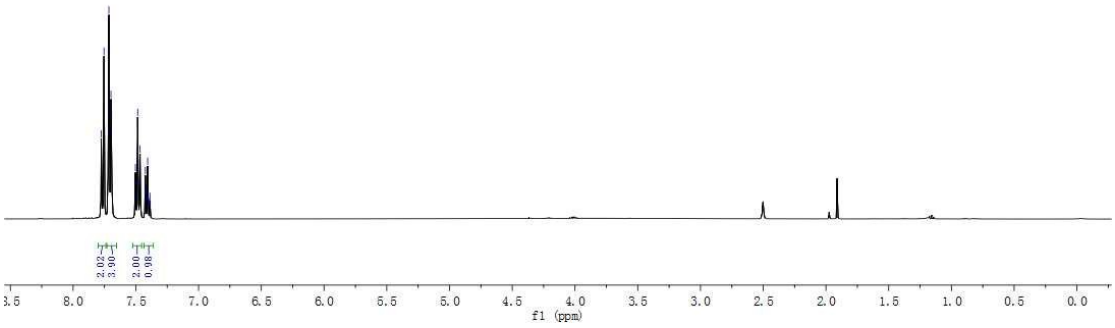
3-(4-methoxyphenyl)propiolic acid (1e)

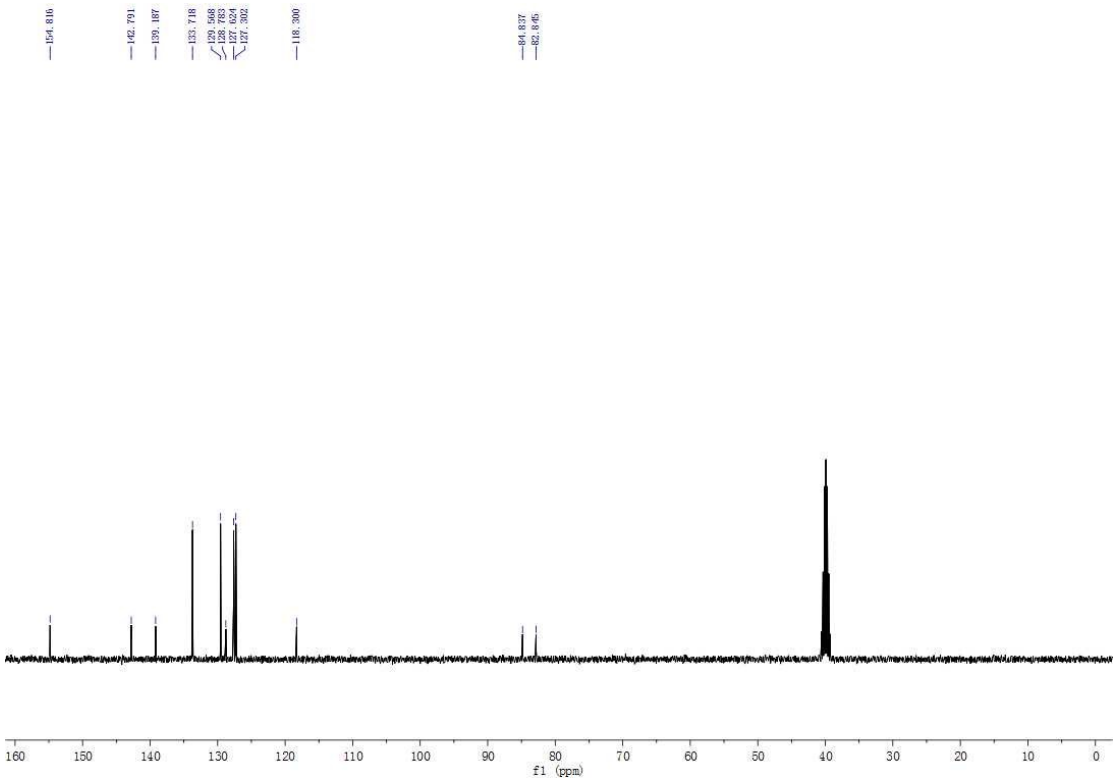

7.585
7.564
7.024
7.003
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

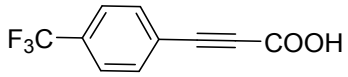

161.674
154.983
135.117
115.188
111.009
85.766
81.511
55.902
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



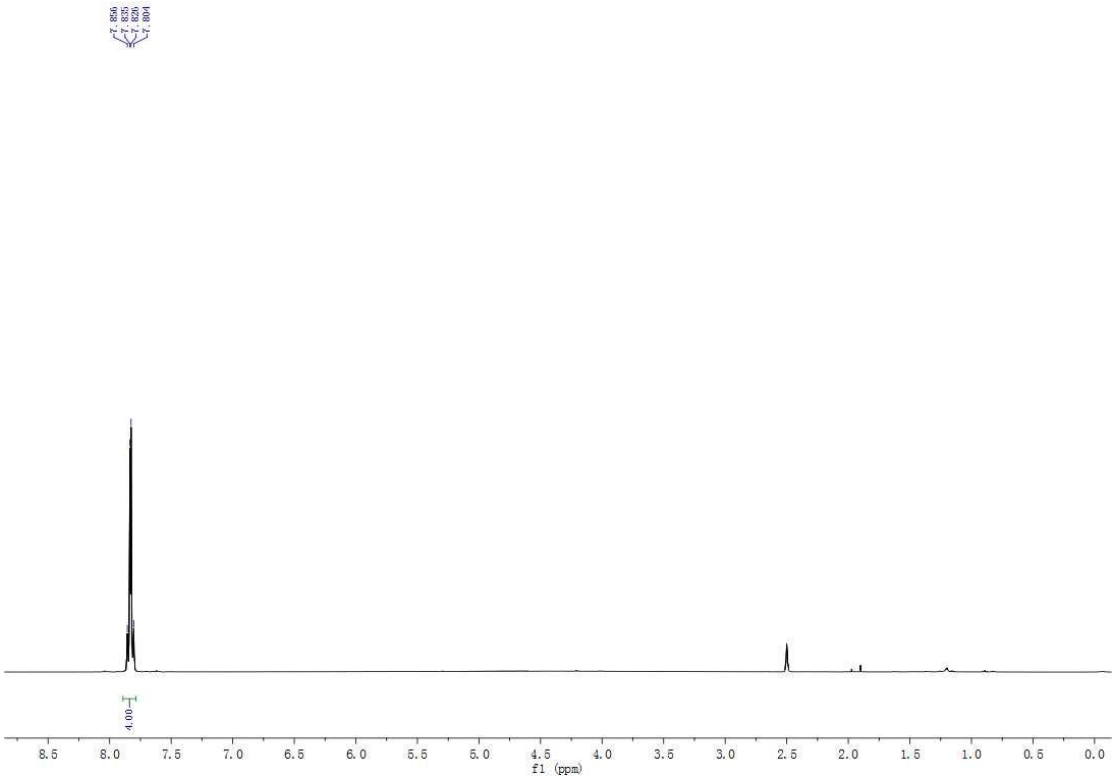
3-([1, 1'-Biphenyl]-4-yl)propiolic acid (1f)

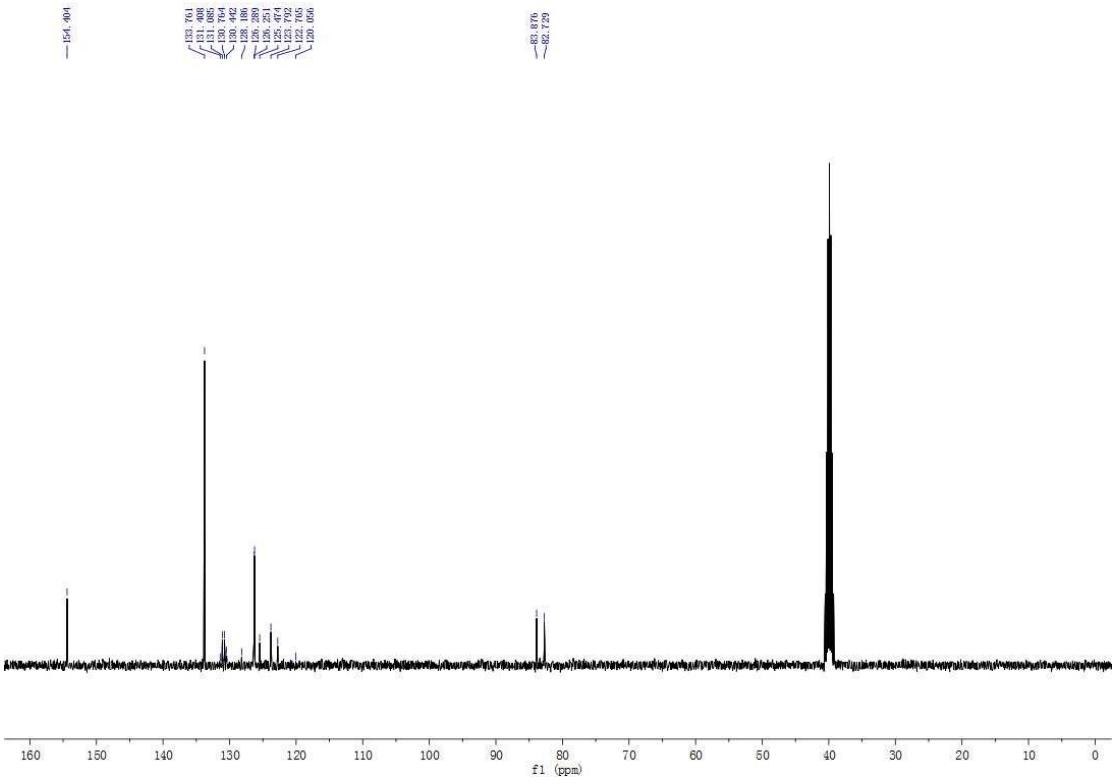


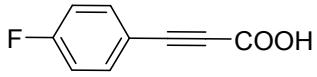




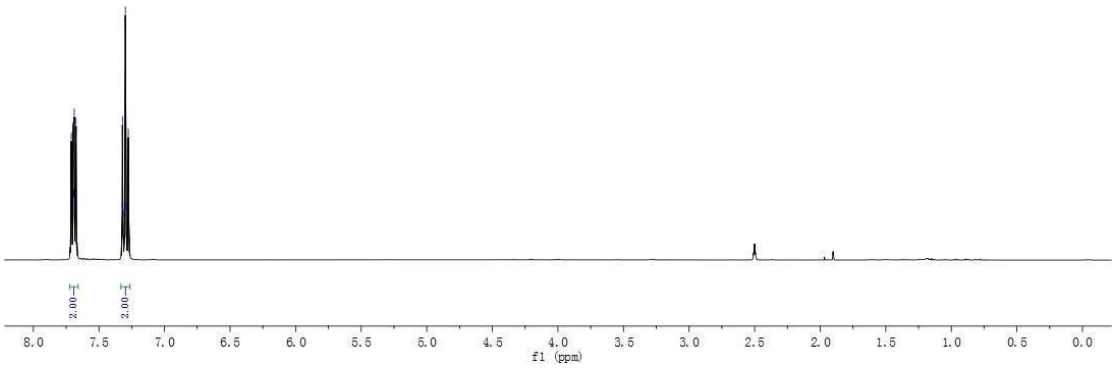
3-(4-(Trifluoromethyl)phenyl)propiolic acid (1g)

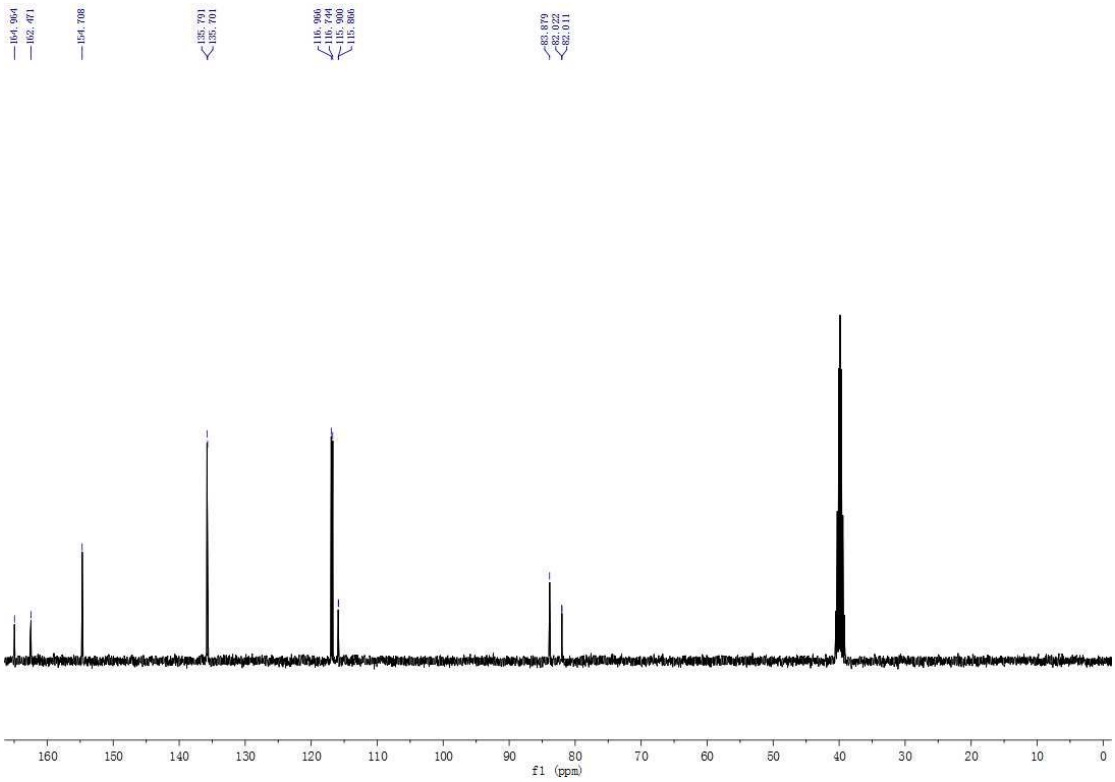

7.856
7.835
7.826
7.804
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

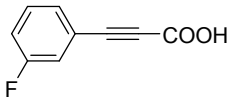

154.404
133.764
131.408
131.065
130.764
130.442
128.186
126.289
125.271
125.474
123.792
122.765
120.656
83.876
82.729
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



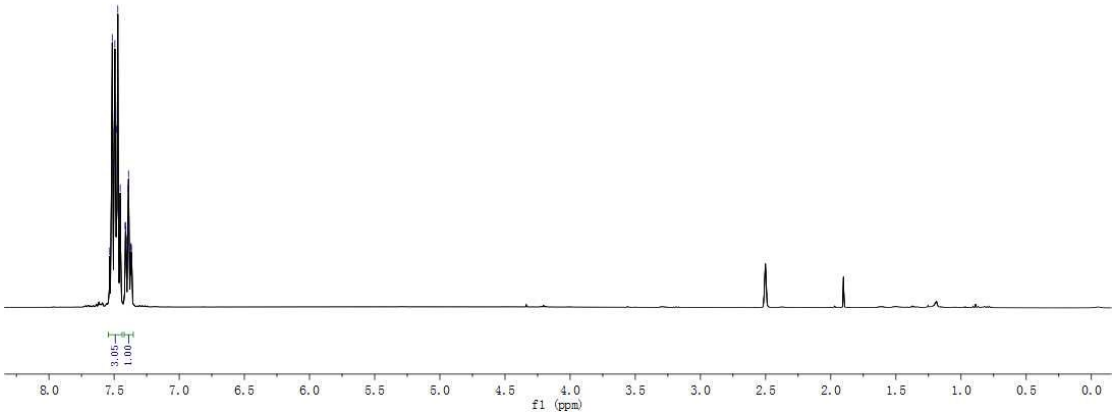
3-(4-Fluorophenyl)propiolic acid(1h)

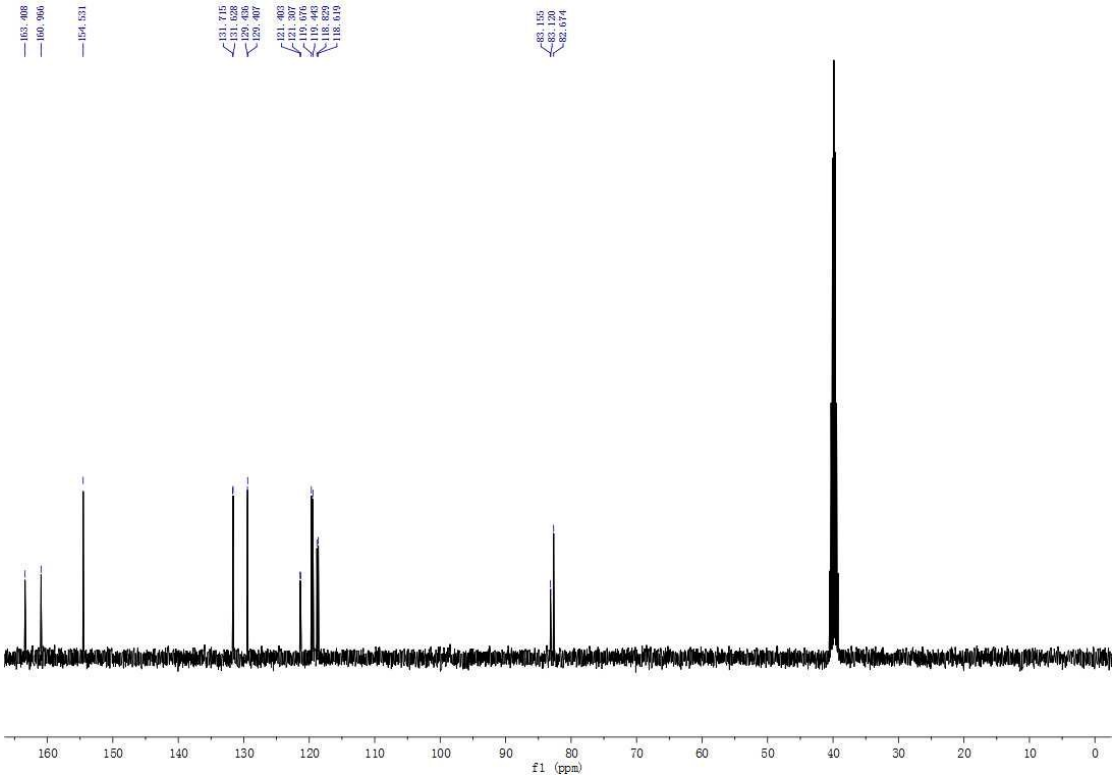


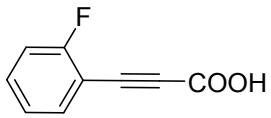




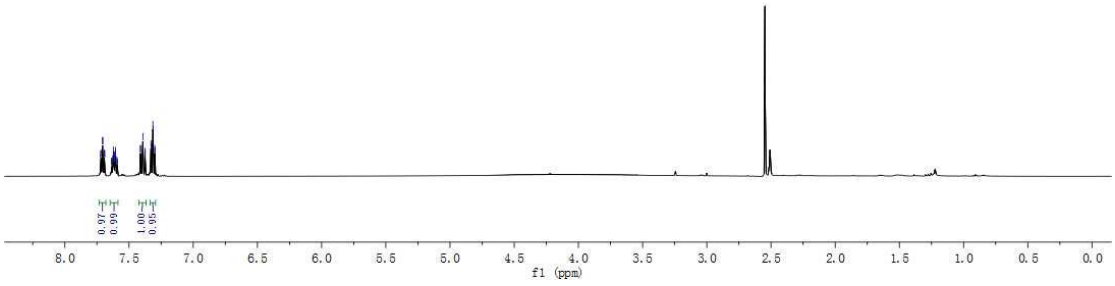
3-(3-fluorophenyl)propiolic acid(i)

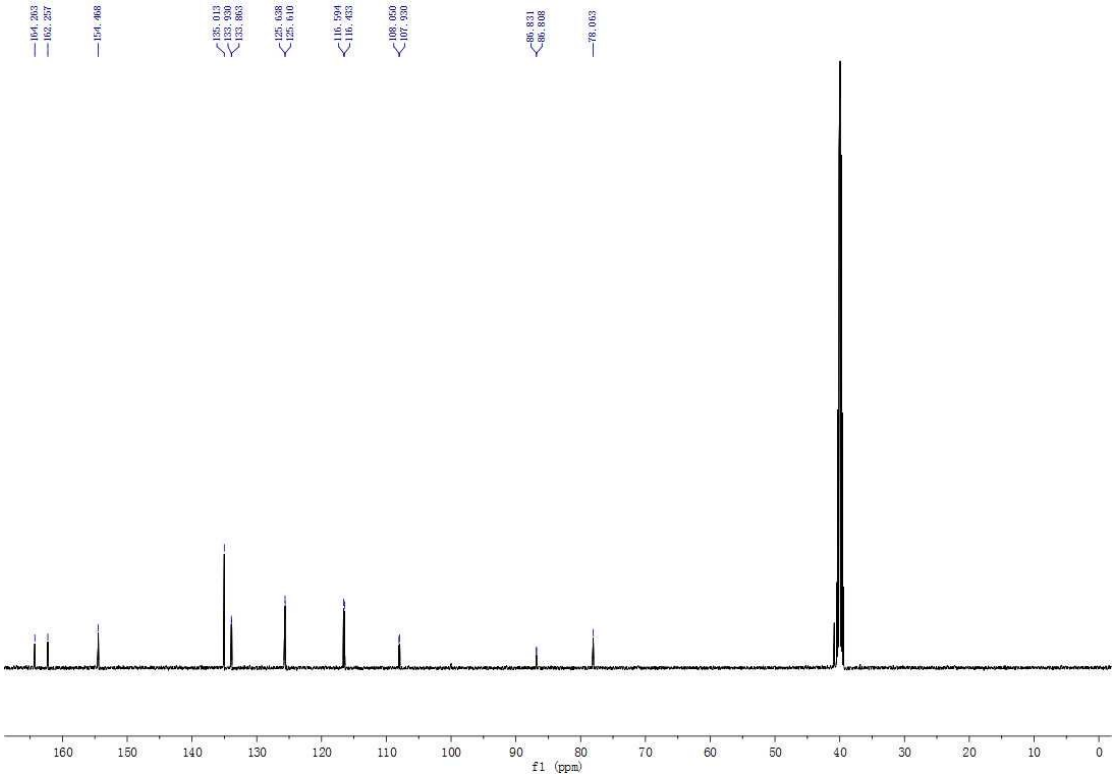

3.05
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

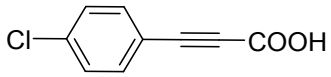

163.408
160.966
154.531
131.715
131.628
129.436
129.407
121.403
121.307
119.676
119.443
118.829
118.649
83.155
83.120
82.674
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
COOH

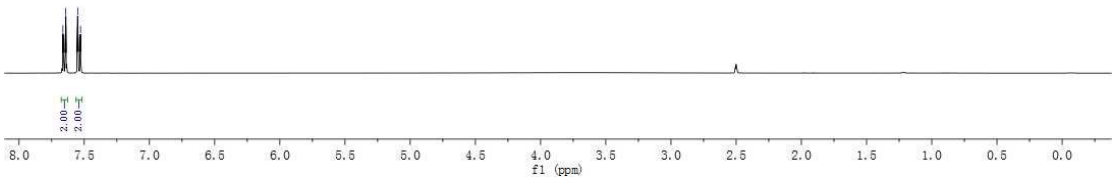
3-(2-Fluorophenyl)propiolic acid (1j)

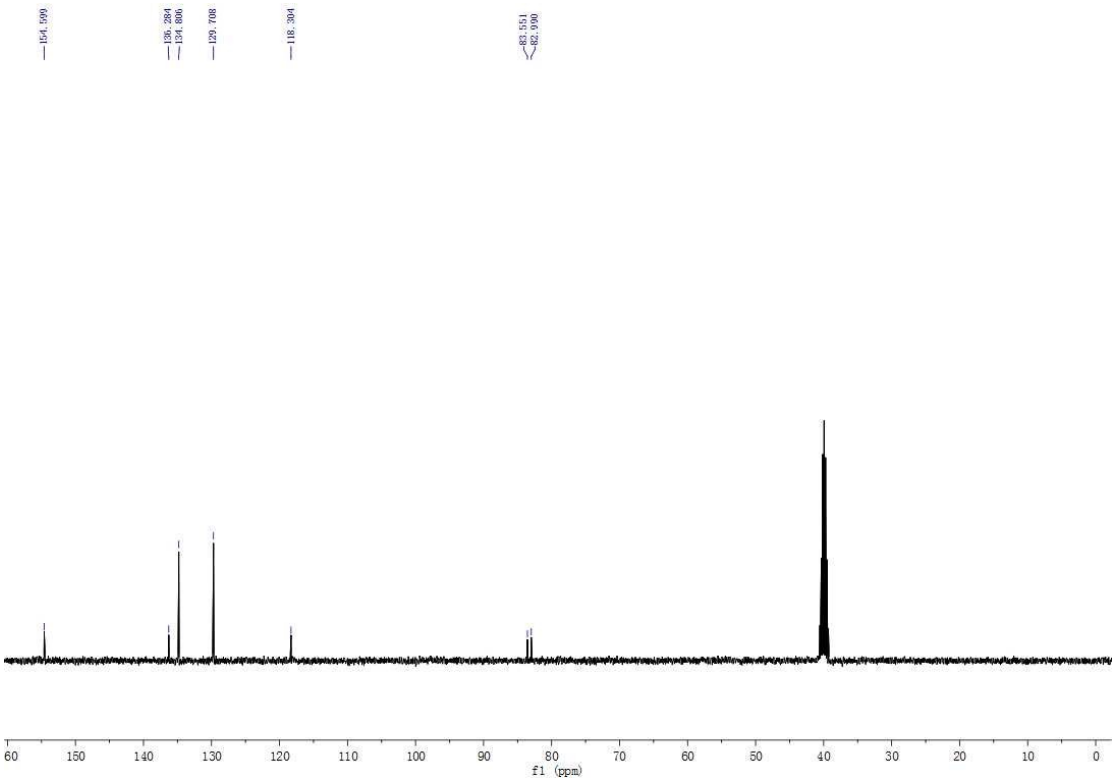


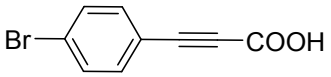




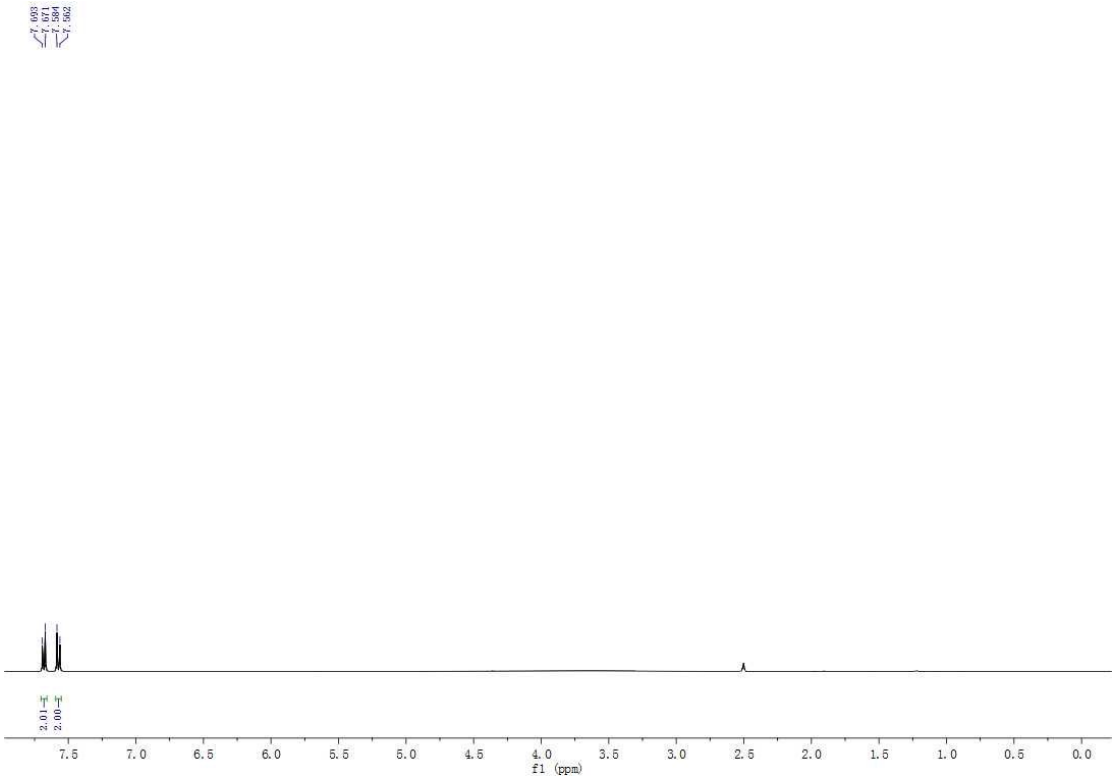
3-(4-Chlorophenyl)propiolic acid (1k)

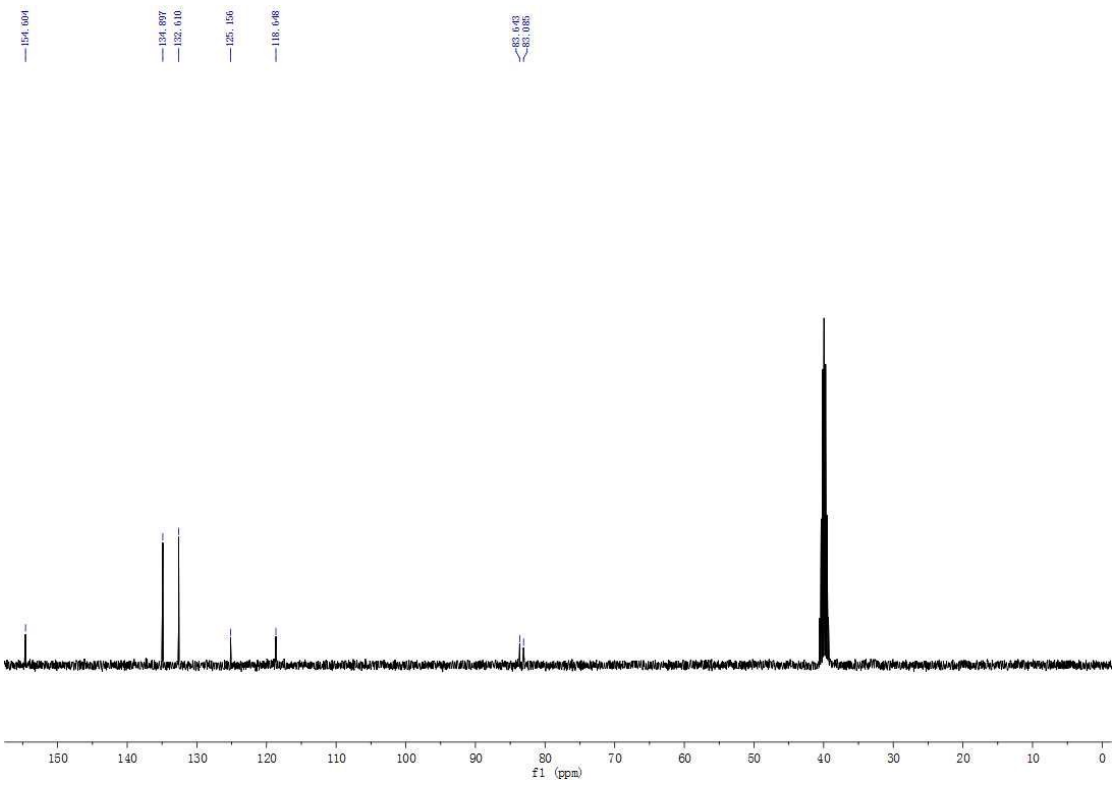


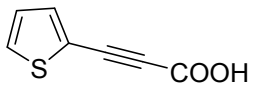




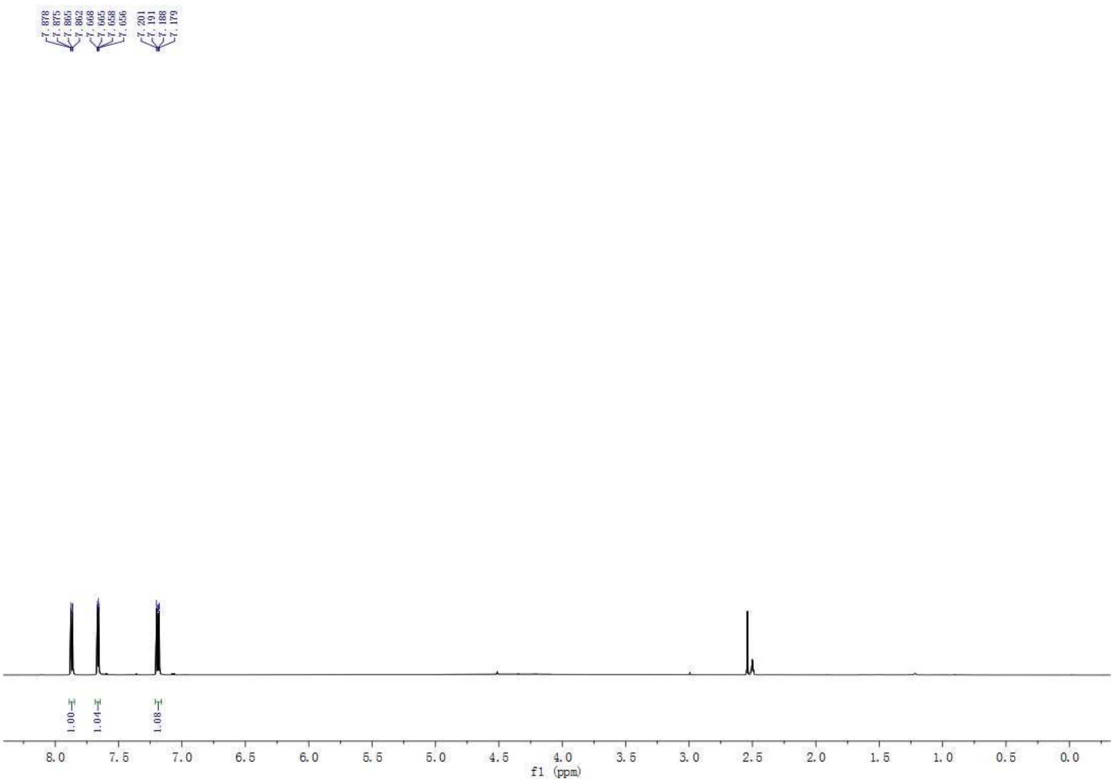
3-(4-Bromophenyl)propiolic acid (1l)

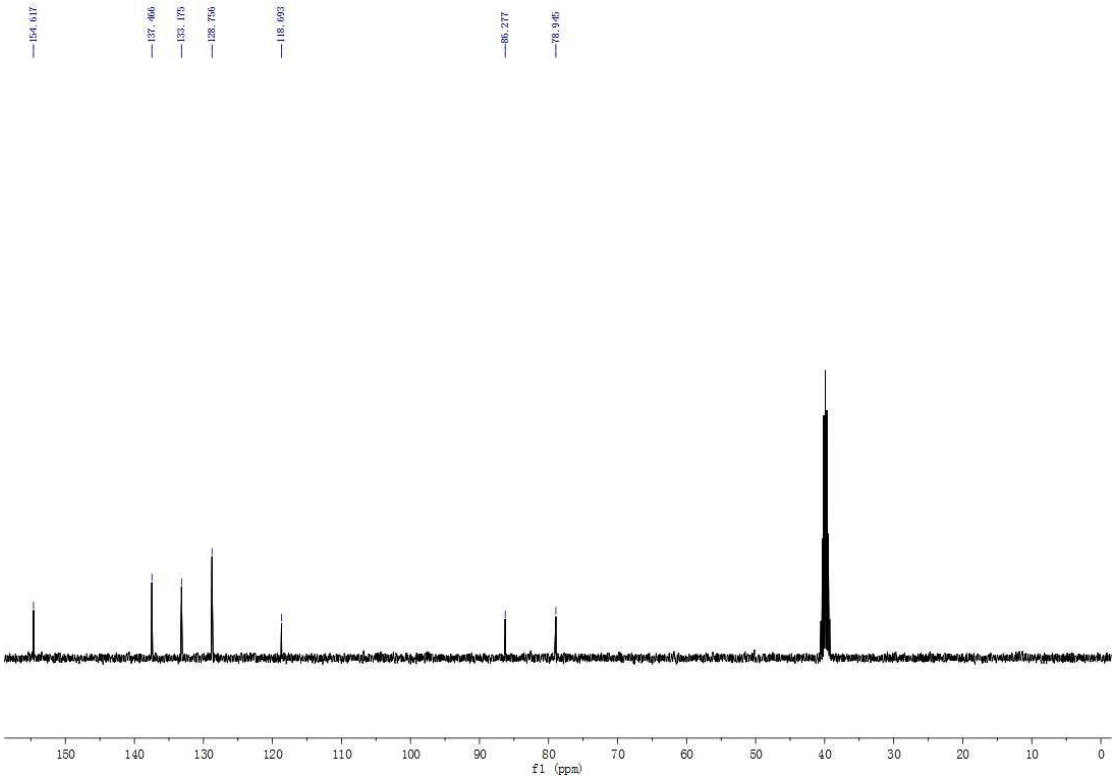

7.693
7.671
7.564
7.562
2.01
2.00
f1 (ppm)

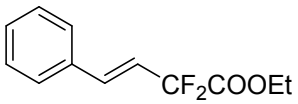

154.604
134.897
132.610
125.156
118.698
83.643
83.085
f1 (ppm)


S
COOH

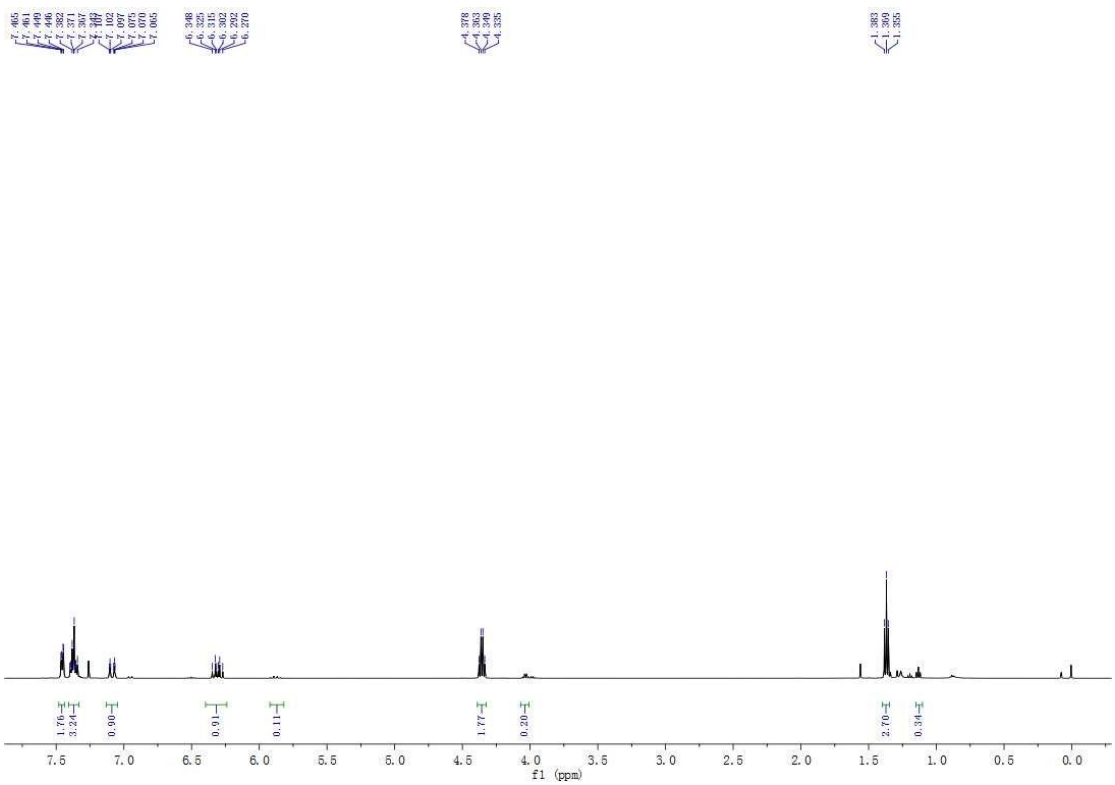
3-(Thiophen-2-yl)propiolic acid (1m)

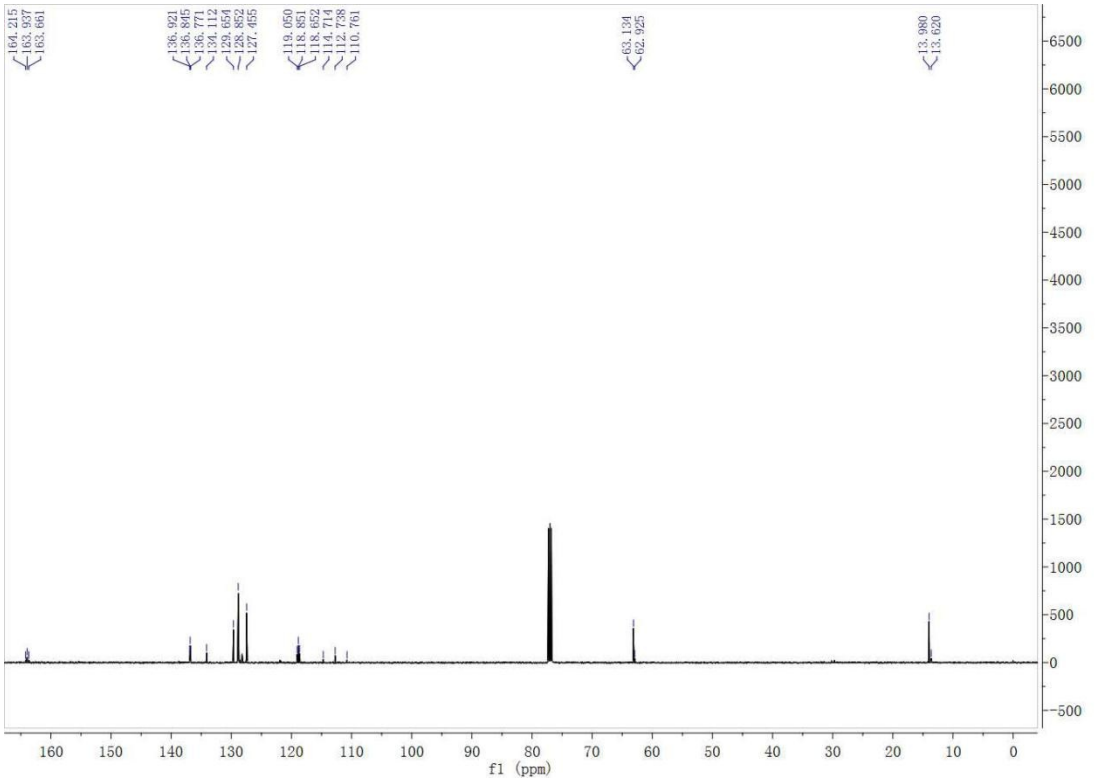


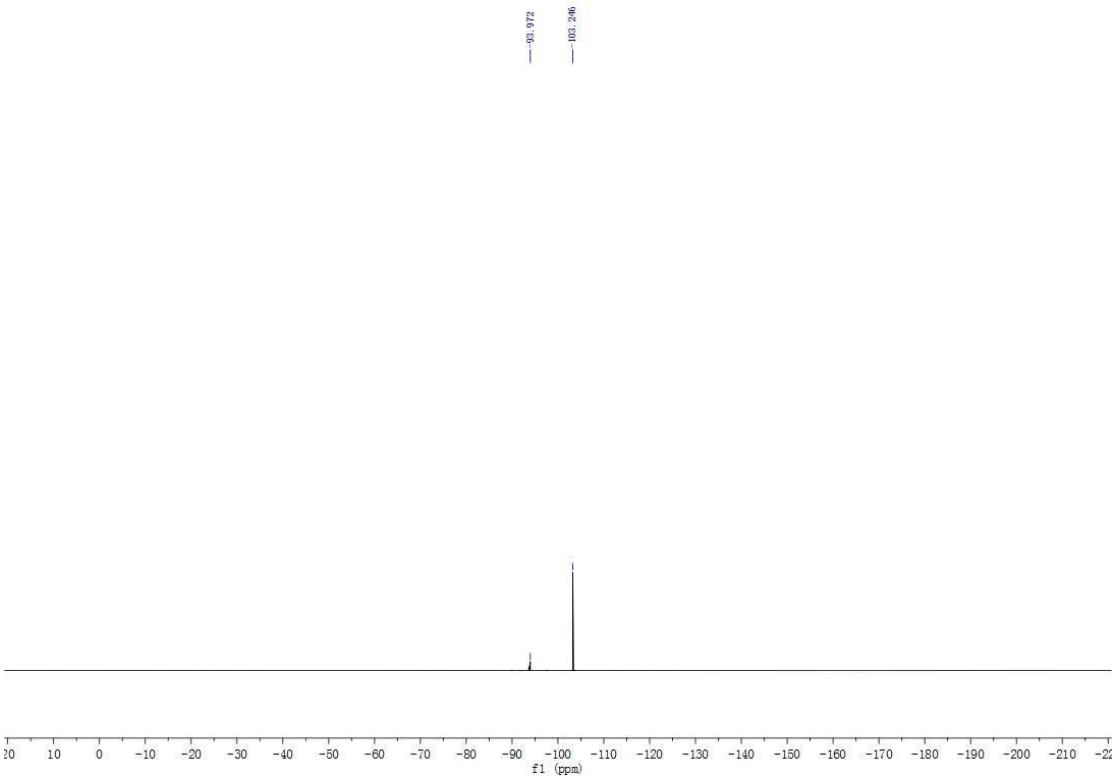


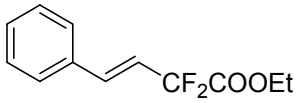


Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=9:1）

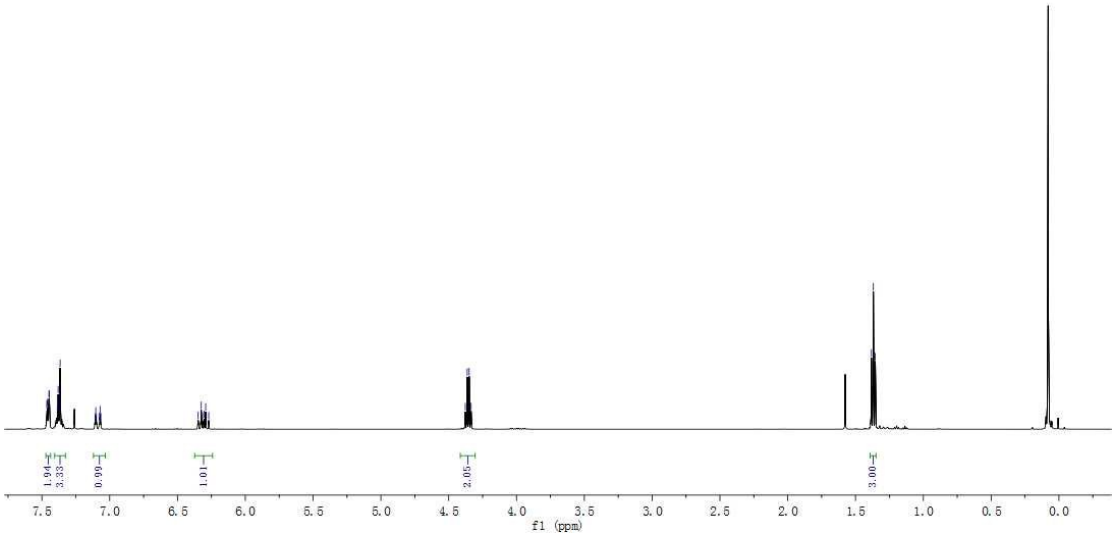

7.465
7.461
7.449
7.446
7.382
7.371
7.367
7.102
7.097
7.075
7.070
7.065
6.348
6.325
6.315
6.302
6.292
6.270
4.378
4.363
4.349
4.335
1.383
1.369
1.355
1.76
3.24
0.90
0.91
0.11
1.77
0.20
2.70
0.34
f1 (ppm)

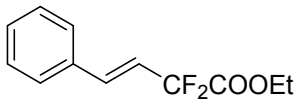

164.215
163.937
163.661
136.921
136.845
136.771
134.112
129.654
129.552
127.455
119.050
118.851
118.652
114.714
112.738
110.761
63.134
62.925
13.980
13.620
f1 (ppm)



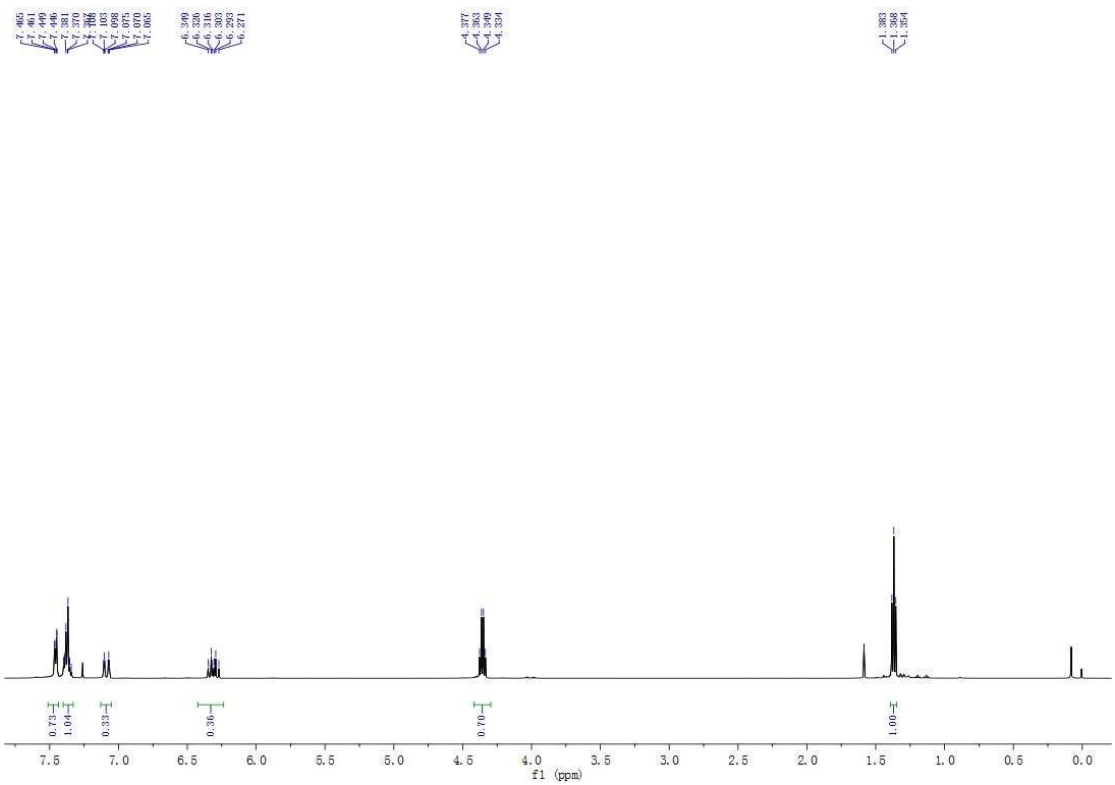


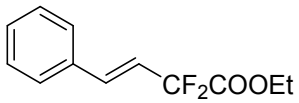
Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=25:1）from alkynyl carboxylic acid



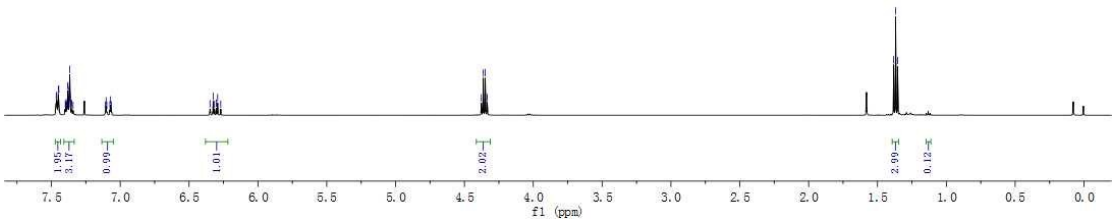


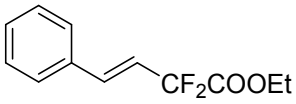
Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=25:1）from Phenylacetylene and (phenylethynyl)copper as catlysist



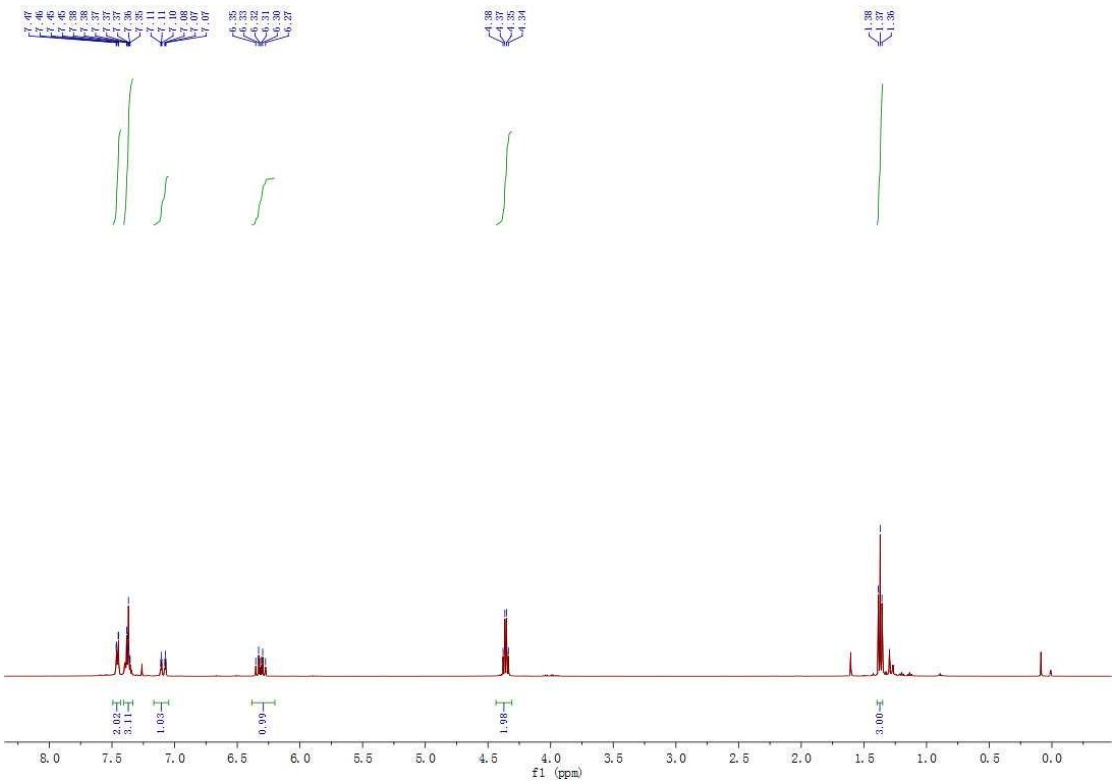


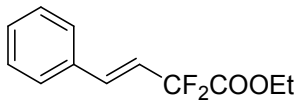
Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=25:1）from alkynyl carboxylic acid and (phenylethynyl)copper as catlysist



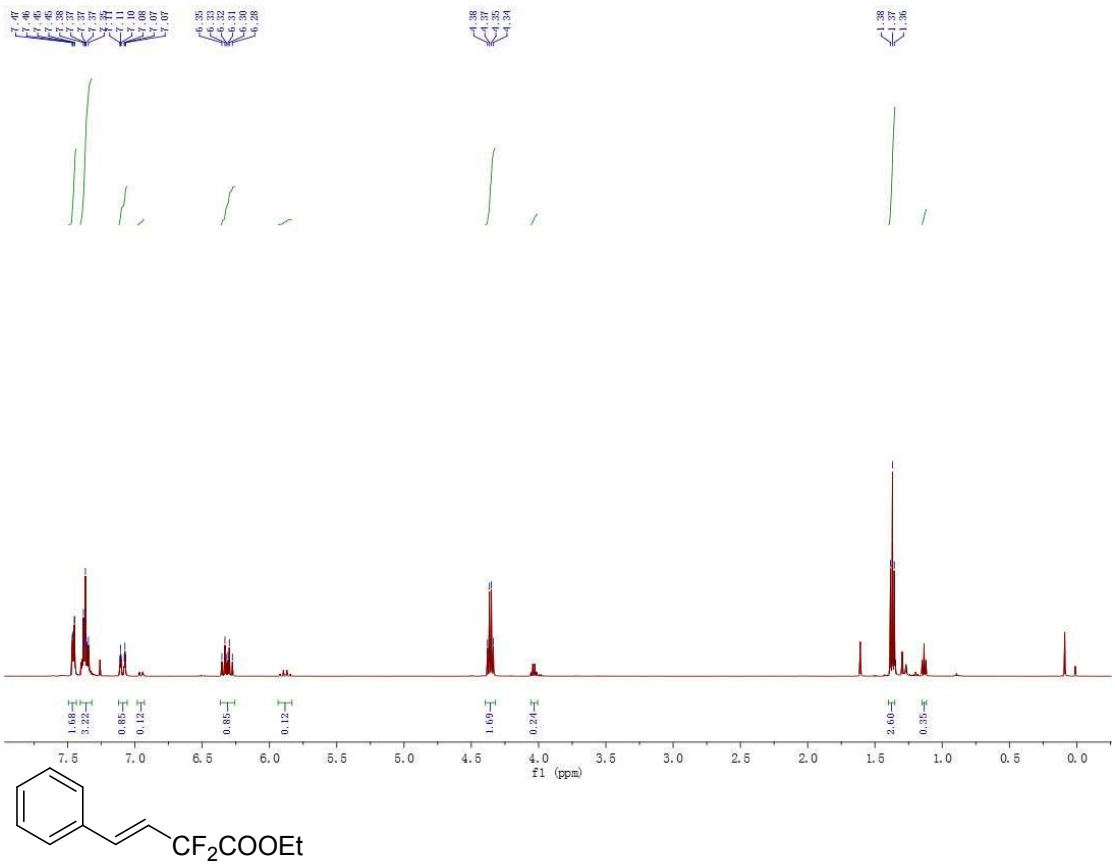


Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=33:1）from alkynyl and using the standard reaction condition of alkynyl carboxylic acid

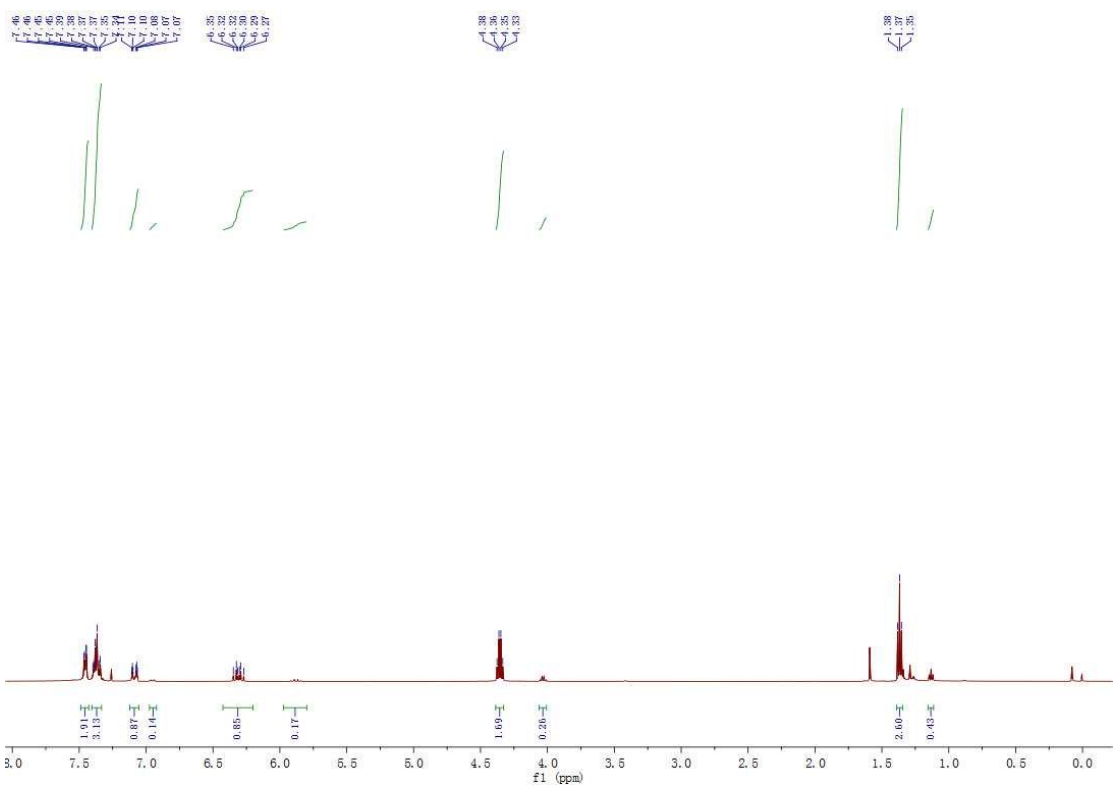


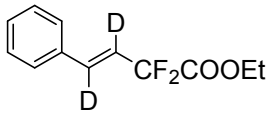


Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=7:1）from alkynyl carboxylic acid and using the standard reaction condition of alkynyl

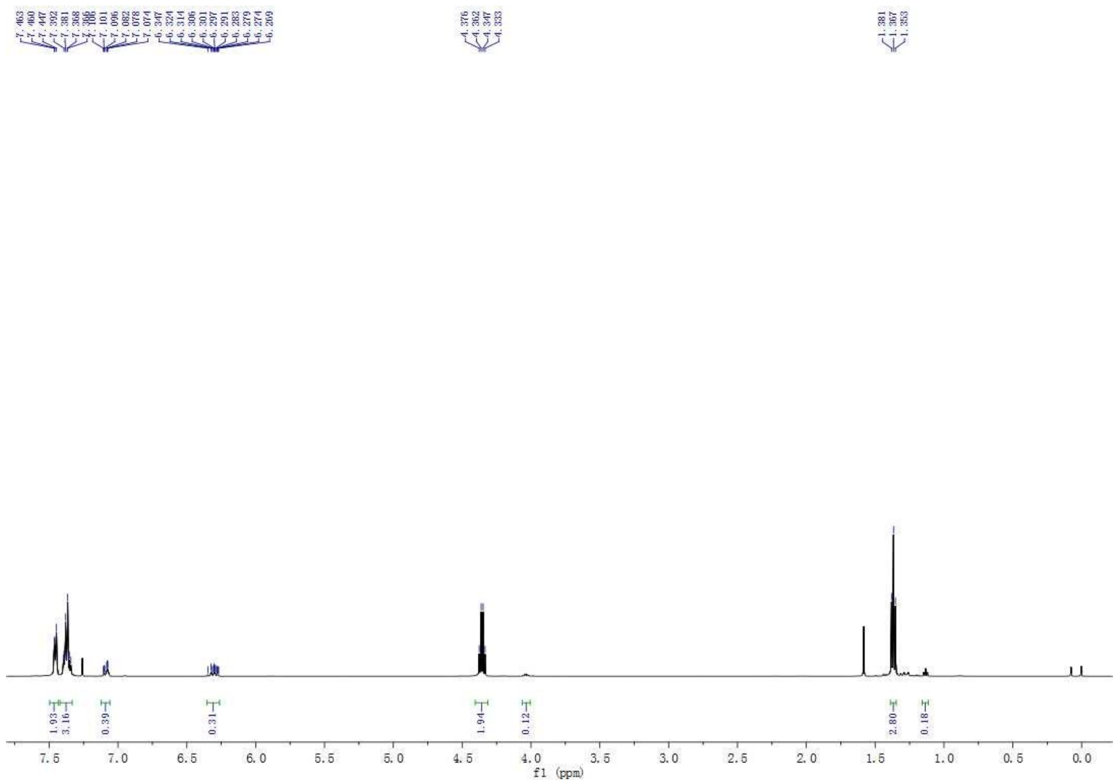


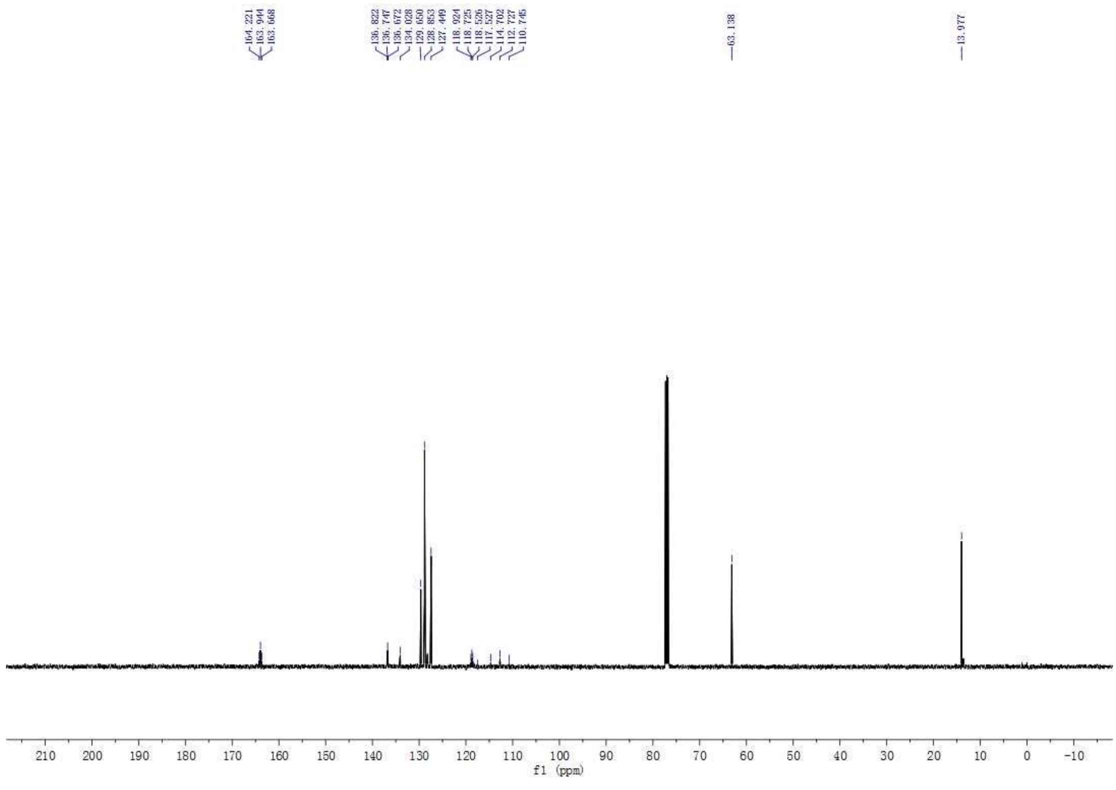
Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate（3, *E/Z*=6:1）from alkynyl-D

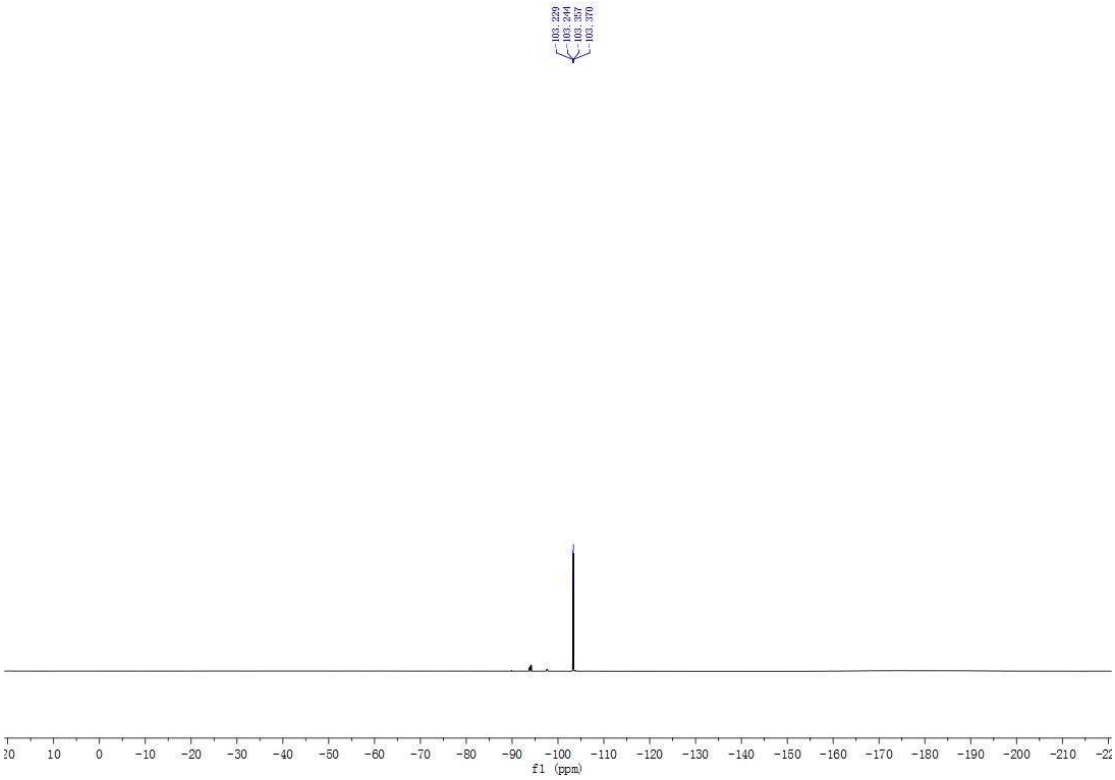


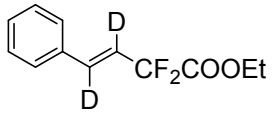


Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate-3, 4-d_2 (3-D)

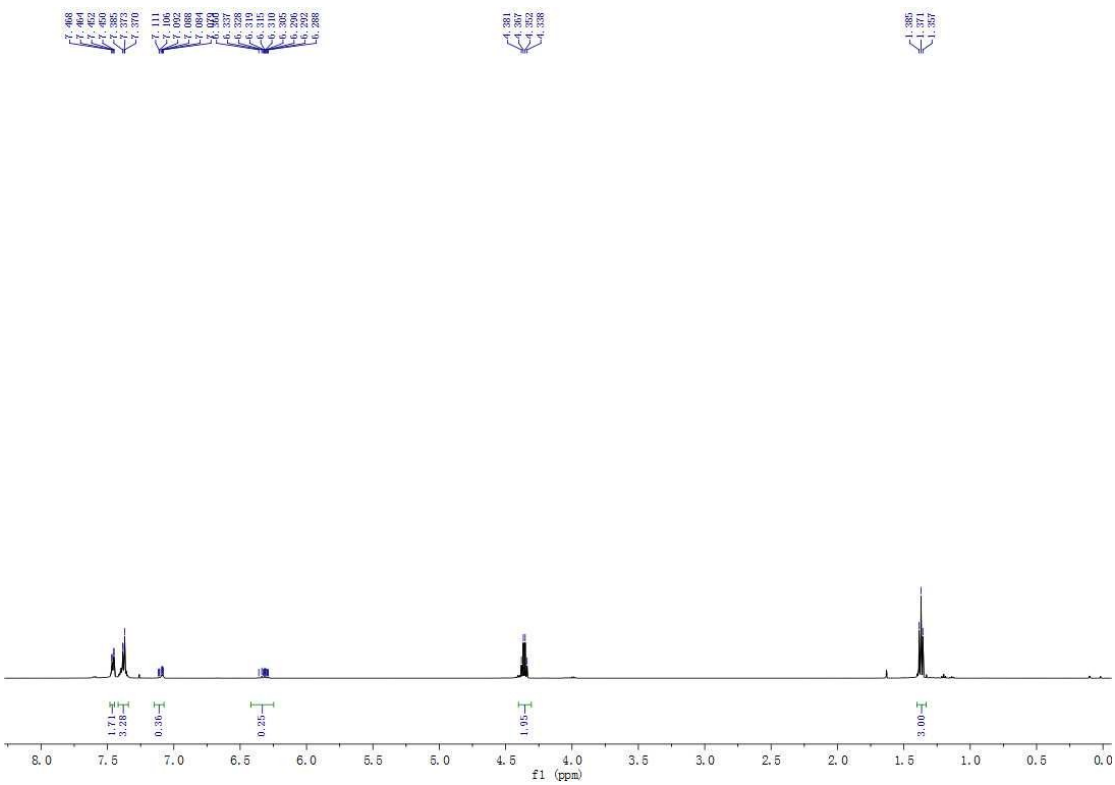

7.463 7.460 7.447 7.392 7.381 7.368 7.366 7.106 7.101 7.096 7.082 7.078 7.074 6.347 6.324 6.314 6.306 6.301 6.297 6.291 6.283 6.279 6.274 6.269
4.376 4.362 4.347 4.333
1.381 1.367 1.353
1.93 3.16 0.39 0.31 1.94 0.12 2.80 0.18
f1 (ppm)


164.221 163.944 163.668
136.822 136.747 136.672 134.028 129.650 128.853 127.449 118.924 118.725 118.526 117.527 114.702 112.727 110.745
63.138
13.977
f1 (ppm)

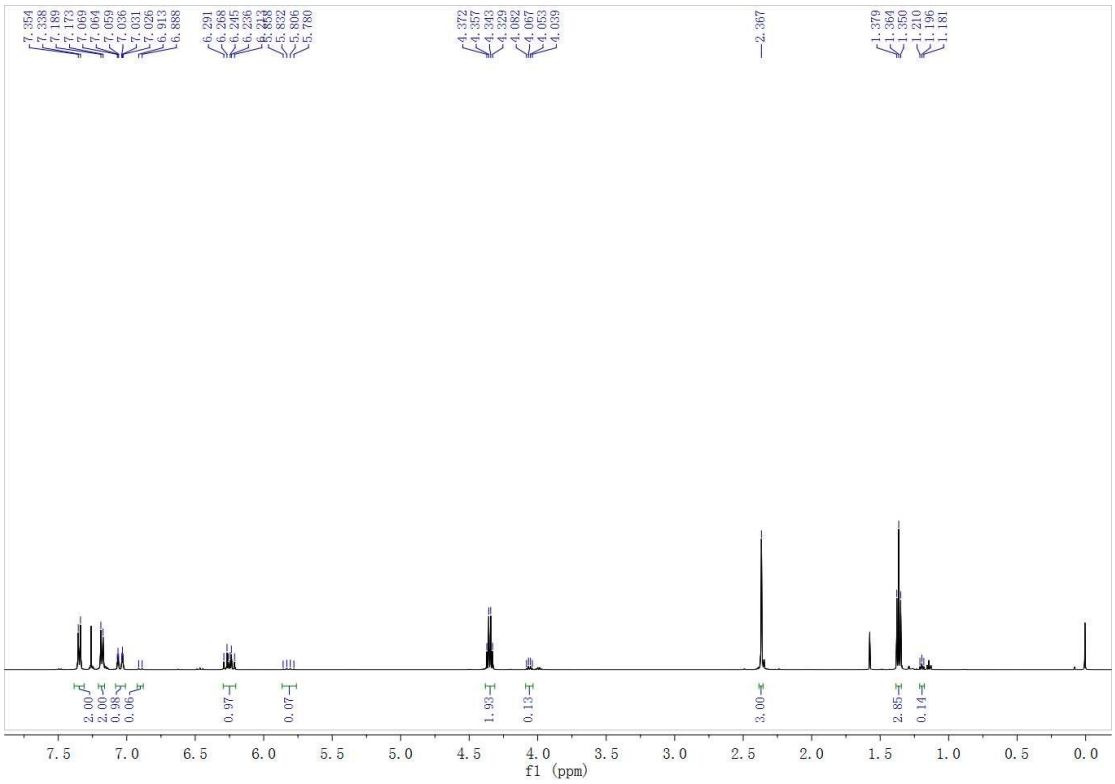


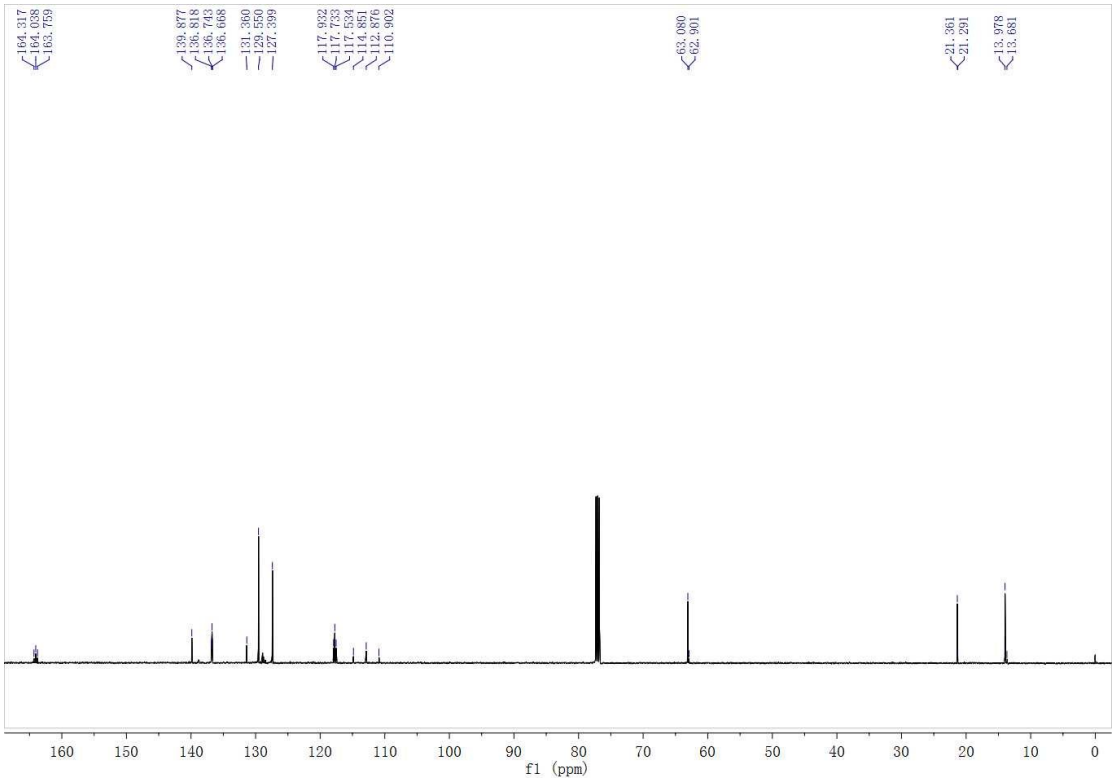


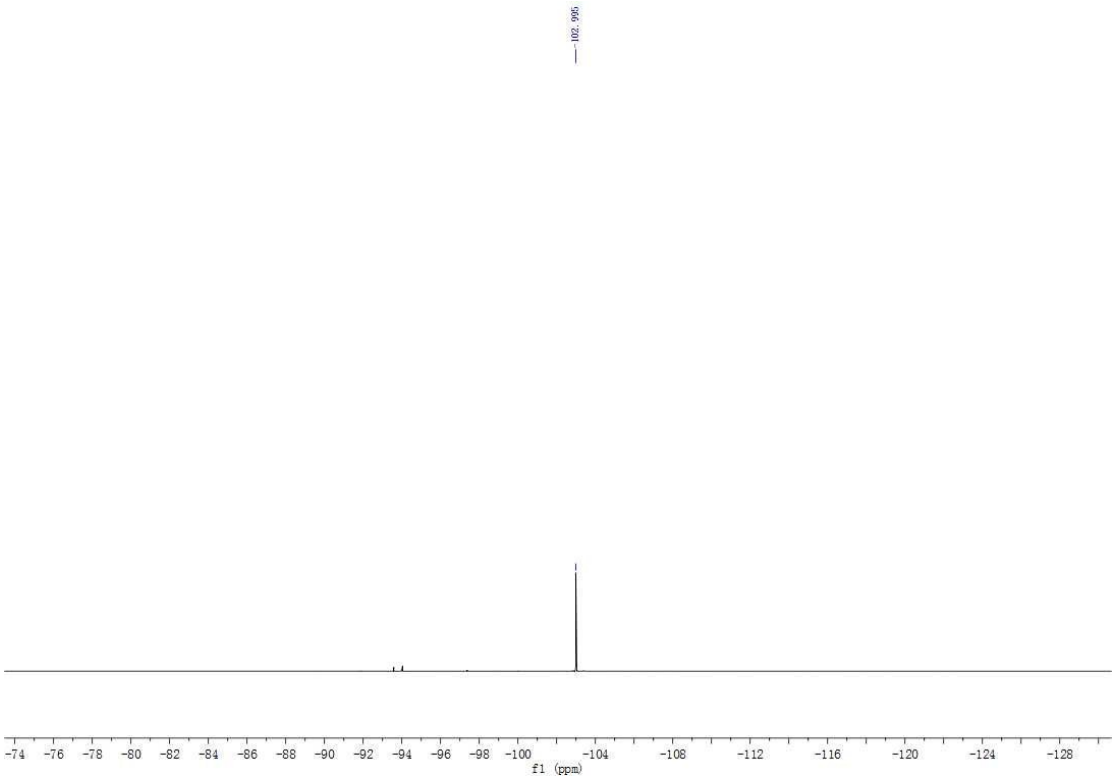
Ethyl (E)-2, 2-difluoro-4-phenylbut-3-enoate-3,4-d_2 (3-D) from alkynyl carboxylic acid

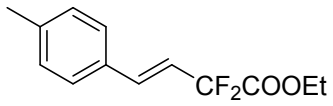


Ethyl (E)-2, 2-difluoro-4-(p-tolyl)but-3-enoate (5, *E/Z*=19:1)

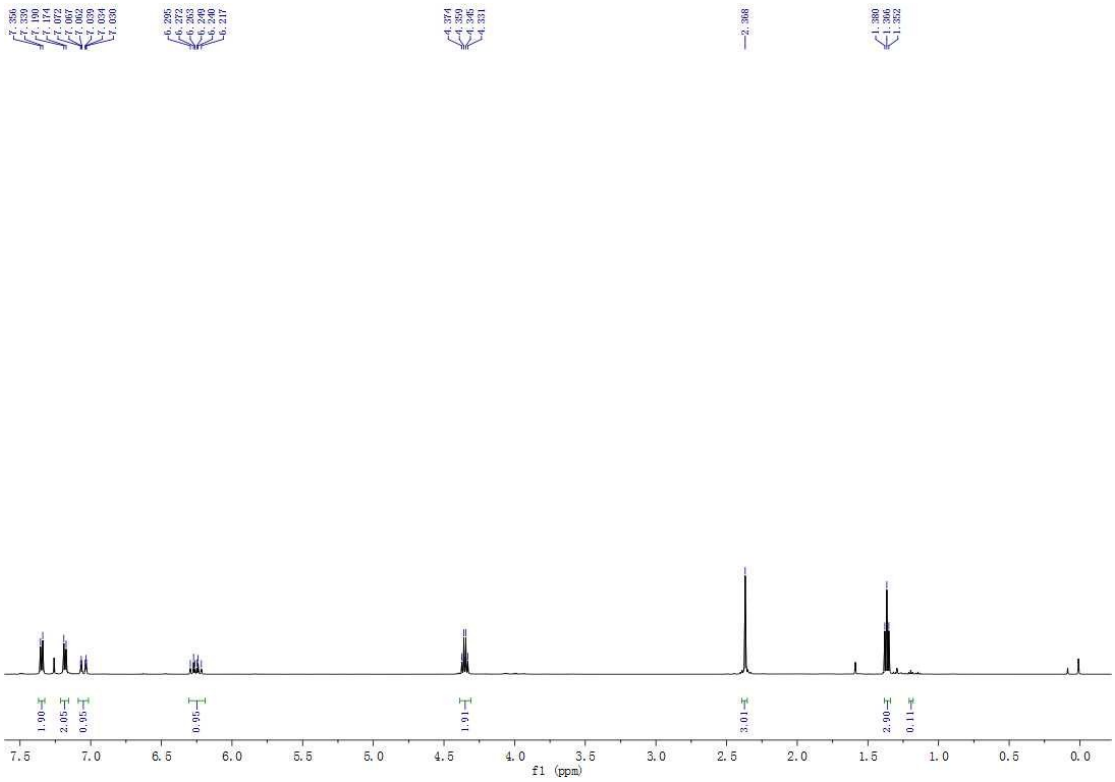

7.354
7.338
7.189
7.173
7.069
7.064
7.059
7.036
7.031
7.026
6.913
6.888
6.291
6.268
6.245
6.236
5.832
5.806
5.780
4.372
4.357
4.343
4.329
4.082
4.067
4.053
4.039
2.367
1.379
1.364
1.350
1.210
1.196
1.181
2.00
2.00
0.98
0.06
0.97
0.07
1.93
0.13
3.00
2.85
0.14
f1 (ppm)

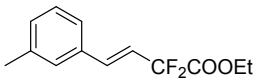

164.317
164.038
163.759
139.877
136.818
136.743
136.668
131.360
129.550
127.399
117.932
117.723
117.534
114.851
112.876
110.902
63.080
62.901
21.361
21.291
13.978
13.681
f1 (ppm)



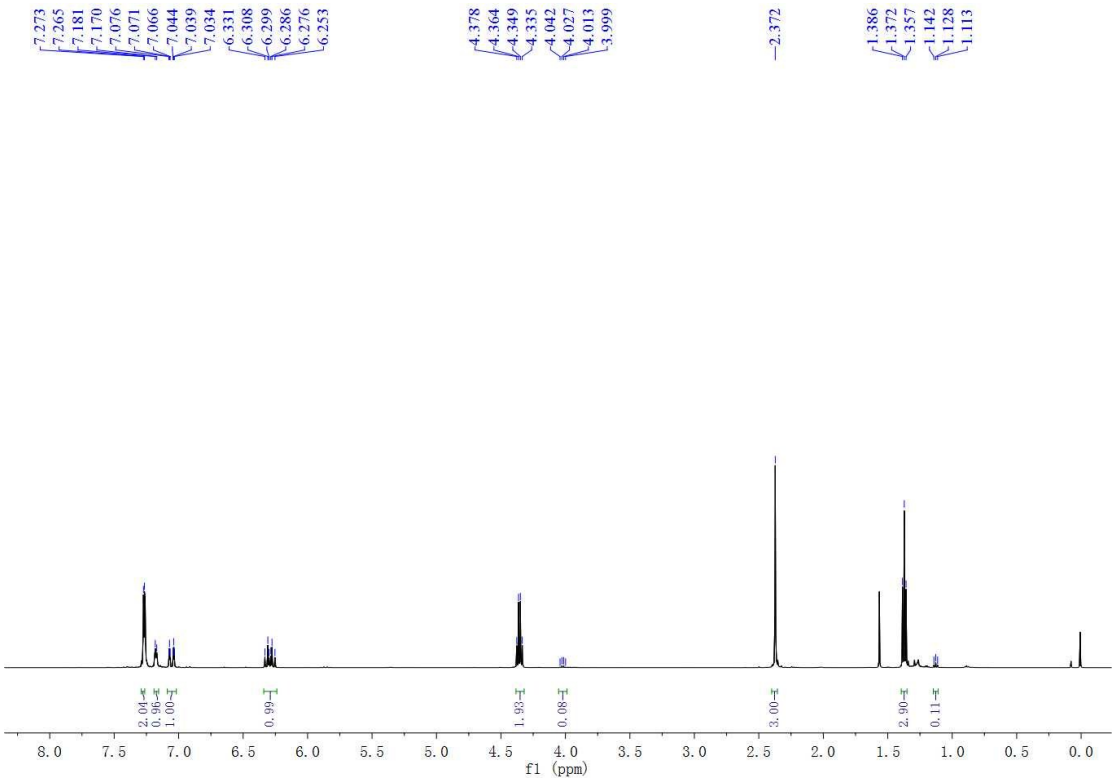


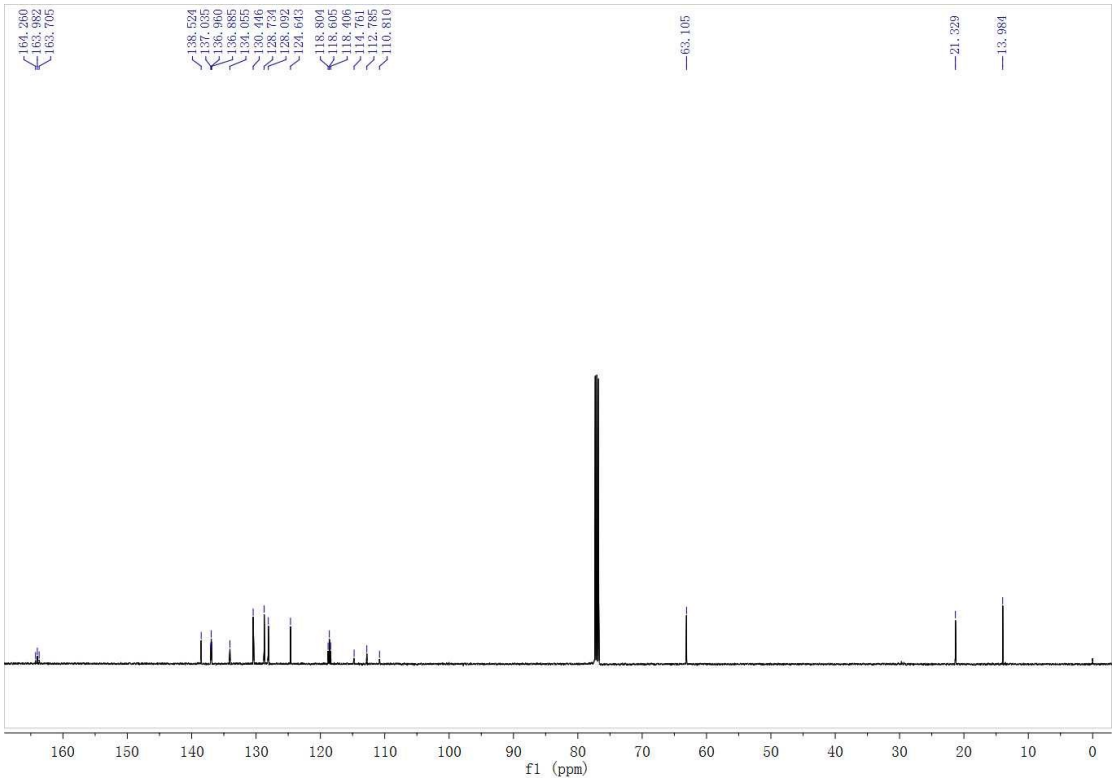
Ethyl (E)-2, 2-difluoro-4-(p-tolyl)but-3-enoate (5, *E/Z*=25:1) from alkynyl carboxylic acid

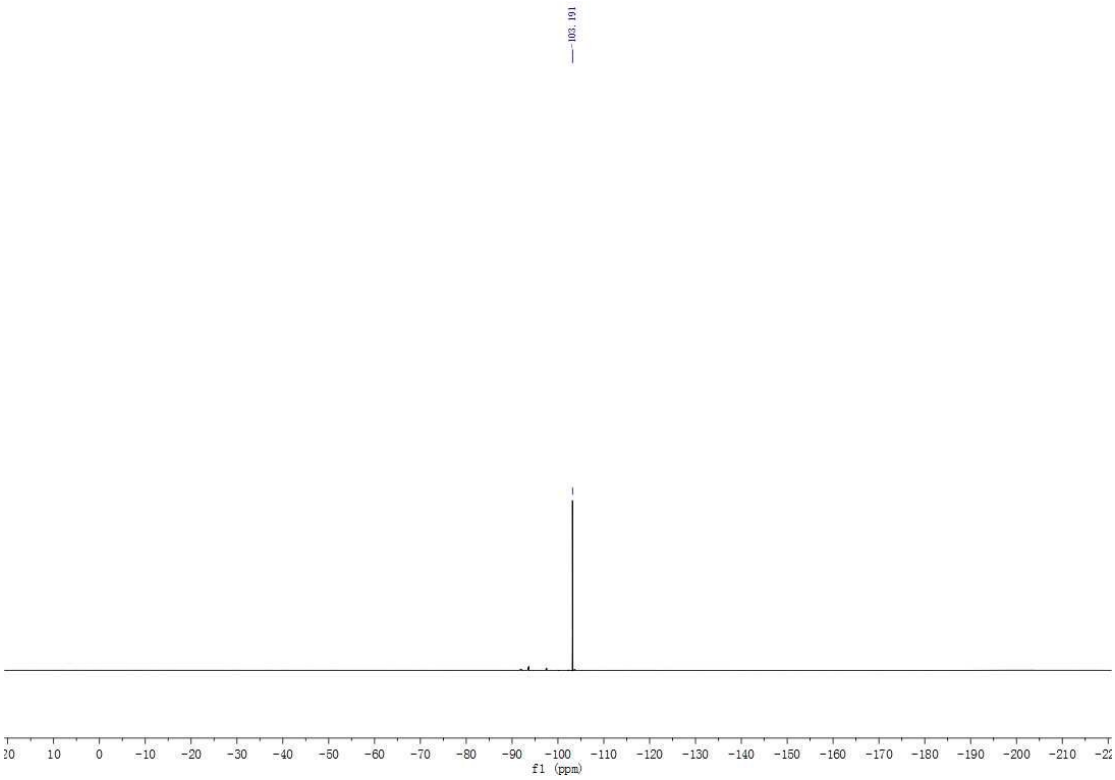


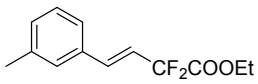


Ethyl-2, 2-difluoro-4-(m-tolyl)but-3-enoate (6, *E/Z*=19:1)

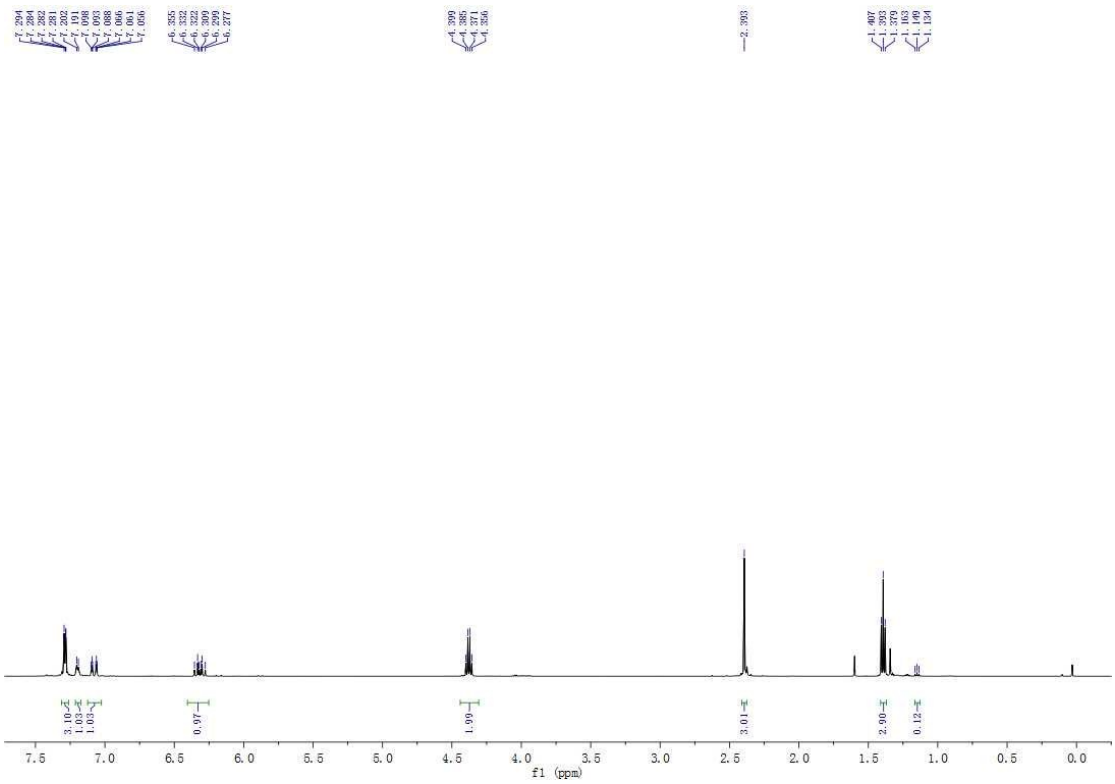

7.273
7.265
7.181
7.170
7.076
7.071
7.066
7.044
7.039
7.034
6.331
6.308
6.299
6.286
6.276
6.253
4.378
4.364
4.349
4.335
4.042
4.027
4.013
3.999
2.372
1.386
1.372
1.357
1.142
1.128
1.113
2.04
0.96
1.00
0.99
1.93
0.08
3.00
2.90
0.11
f1 (ppm)

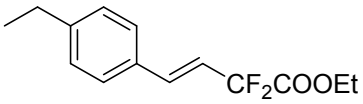

164.260
163.982
163.705
138.524
137.035
136.960
136.885
134.055
130.446
128.734
128.092
124.643
118.804
118.605
118.406
114.761
112.785
110.810
63.105
21.329
13.984
f1 (ppm)



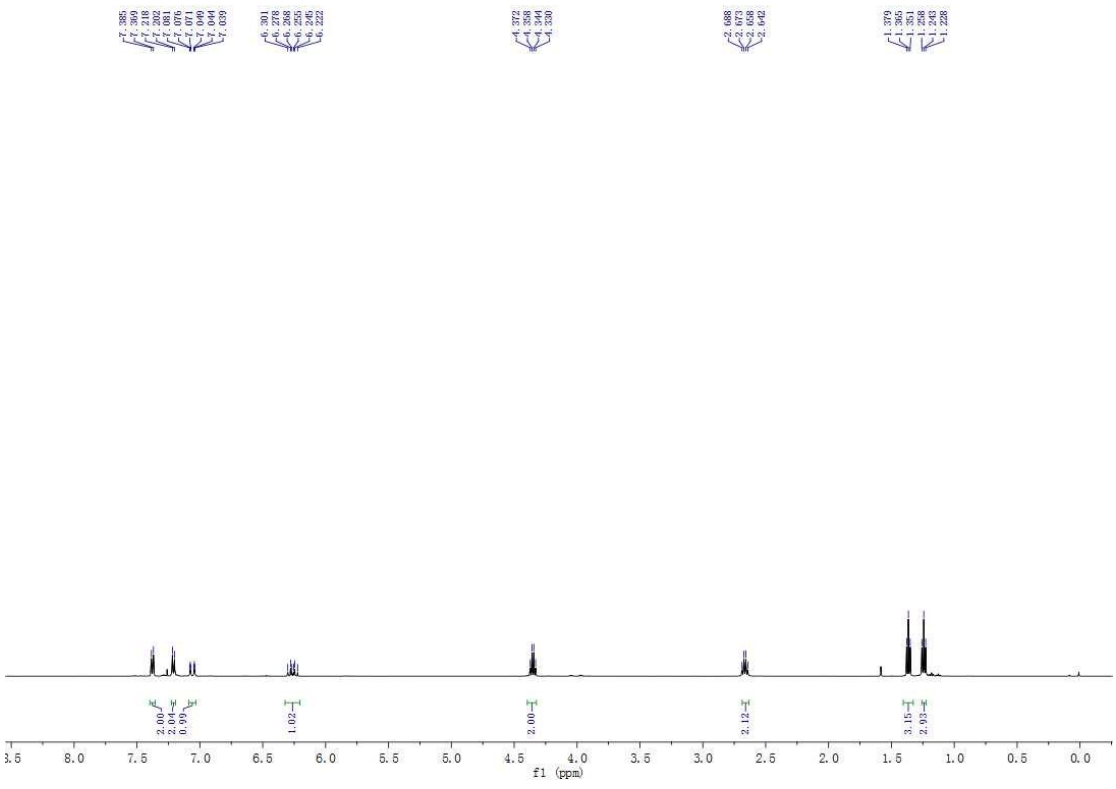


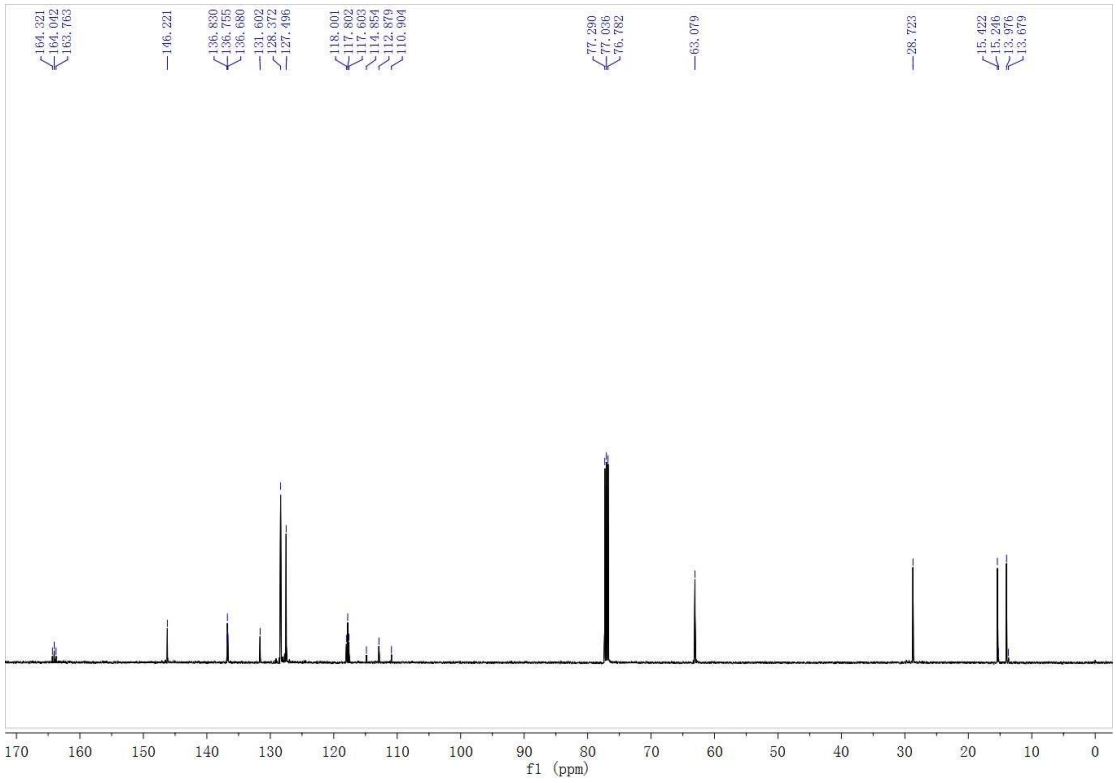
Ethyl-2, 2-difluoro-4-(m-tolyl)but-3-enoate (6, *E/Z*=25:1) from alkynyl carboxylic acid

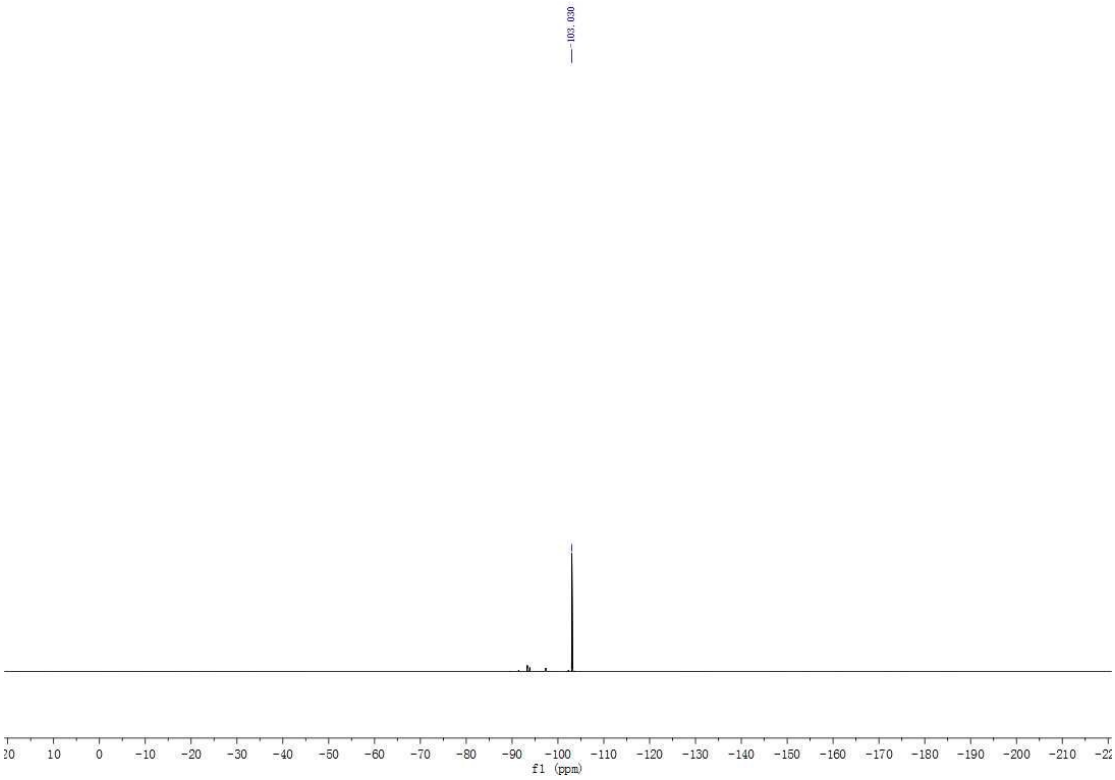


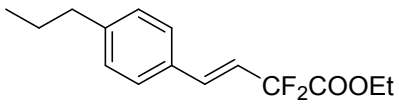


Ethyl (E)-4-(4-ethylphenyl)-2, 2-difluorobut-3-enoate (7)

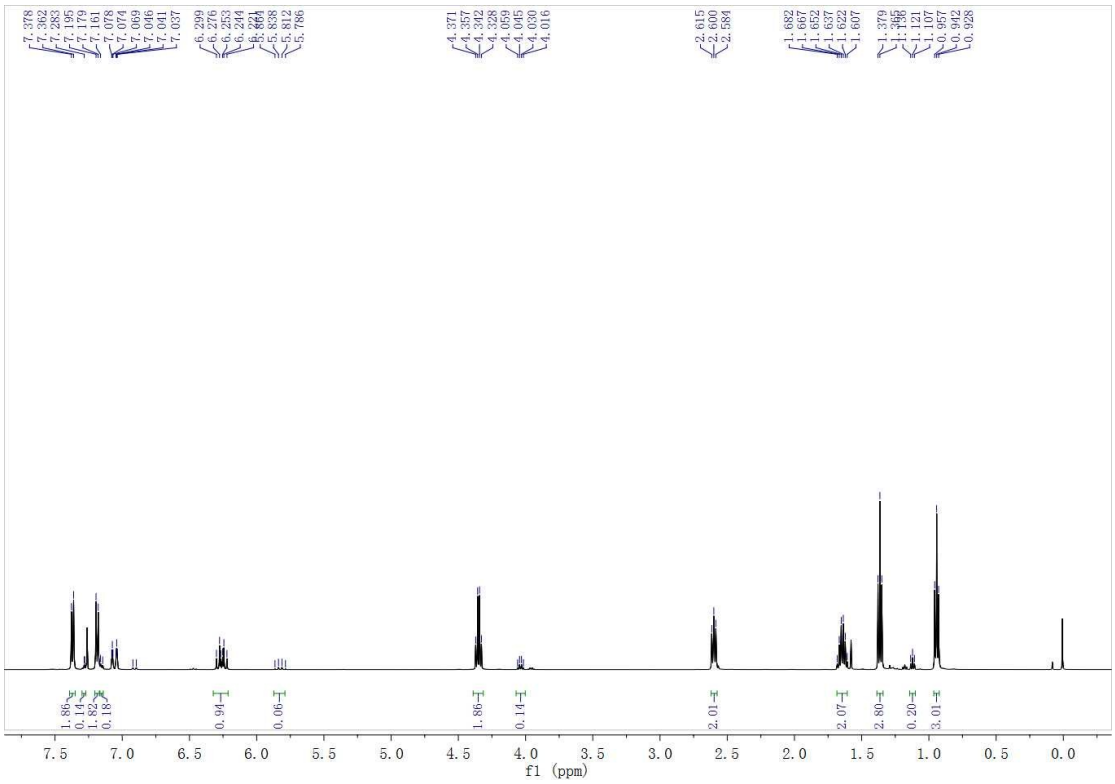

7.385
7.360
7.218
7.202
7.081
7.076
7.071
7.049
7.044
7.039
6.301
6.278
6.268
6.255
6.245
6.222
4.372
4.358
4.344
4.330
2.688
2.673
2.658
2.642
1.379
1.365
1.351
1.258
1.243
1.228
2.09
2.04
0.93
1.02
2.00
2.12
3.15
2.93
f1 (ppm)

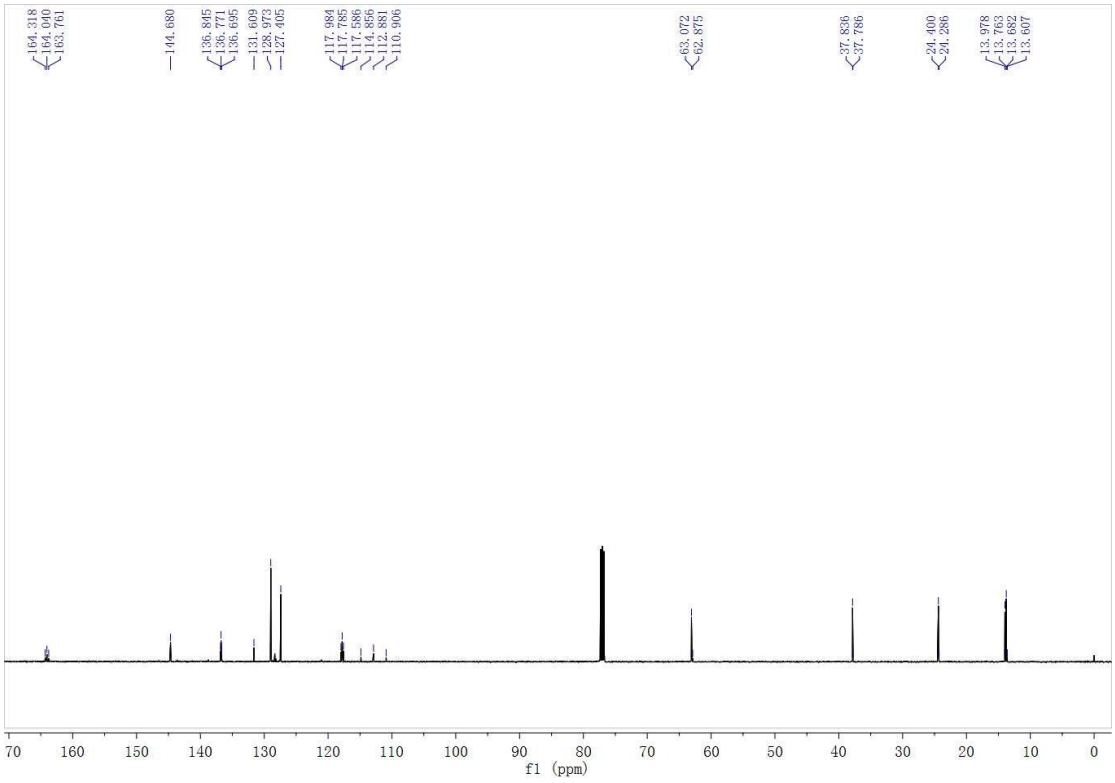

164.321
164.042
163.763
146.221
136.830
136.755
136.680
131.602
128.372
127.496
118.001
117.802
117.603
114.854
112.879
110.904
77.290
77.035
76.782
63.079
28.723
15.422
15.246
13.976
13.679
f1 (ppm)

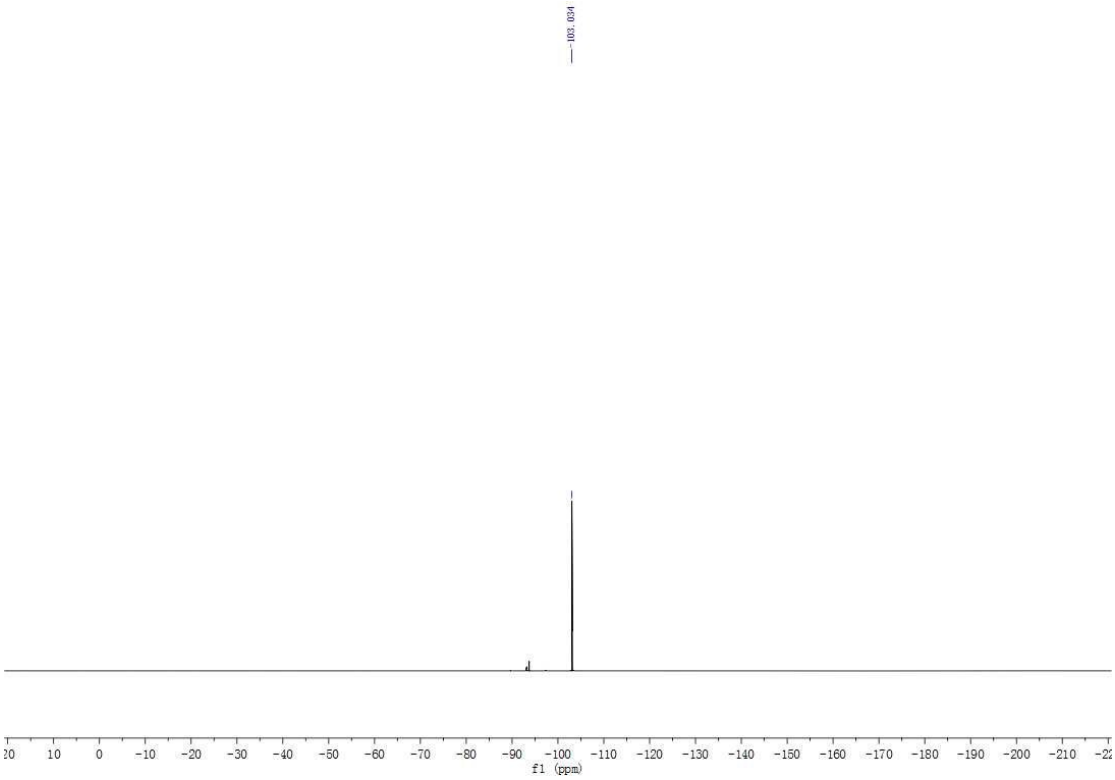


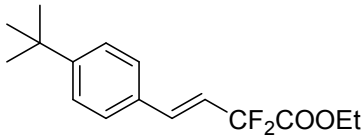


Ethyl -2, 2-difluoro-4-(4-propylphenyl)but-3-enoate (**8**, ***E/Z***=14:1)

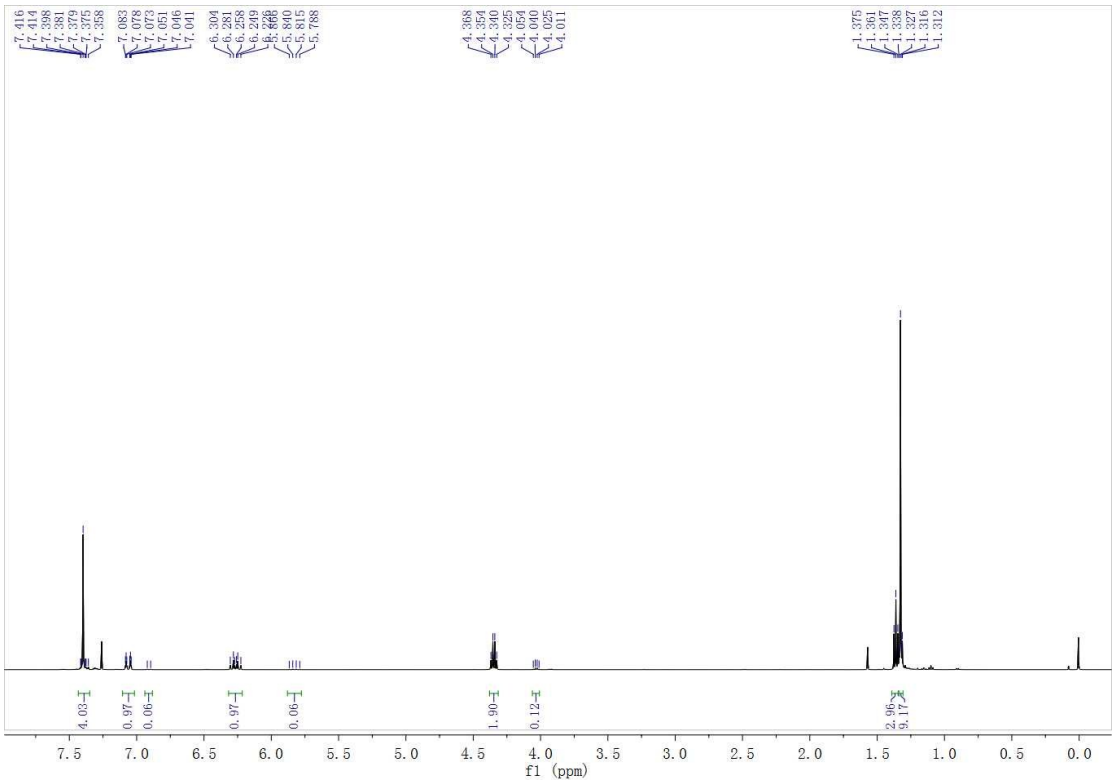

7.378
7.362
7.283
7.195
7.179
7.161
7.078
7.074
7.069
7.046
7.041
7.037
6.299
6.276
6.253
6.234
5.838
5.812
5.786
4.371
4.357
4.342
4.328
4.059
4.045
4.030
4.016
2.615
2.600
2.584
1.682
1.667
1.652
1.637
1.622
1.607
1.379
1.365
1.138
1.121
1.107
0.957
0.942
0.928
1.86
0.14
1.82
0.18
0.94
0.06
1.86
0.14
2.01
2.07
2.80
0.20
3.01
f1 (ppm)

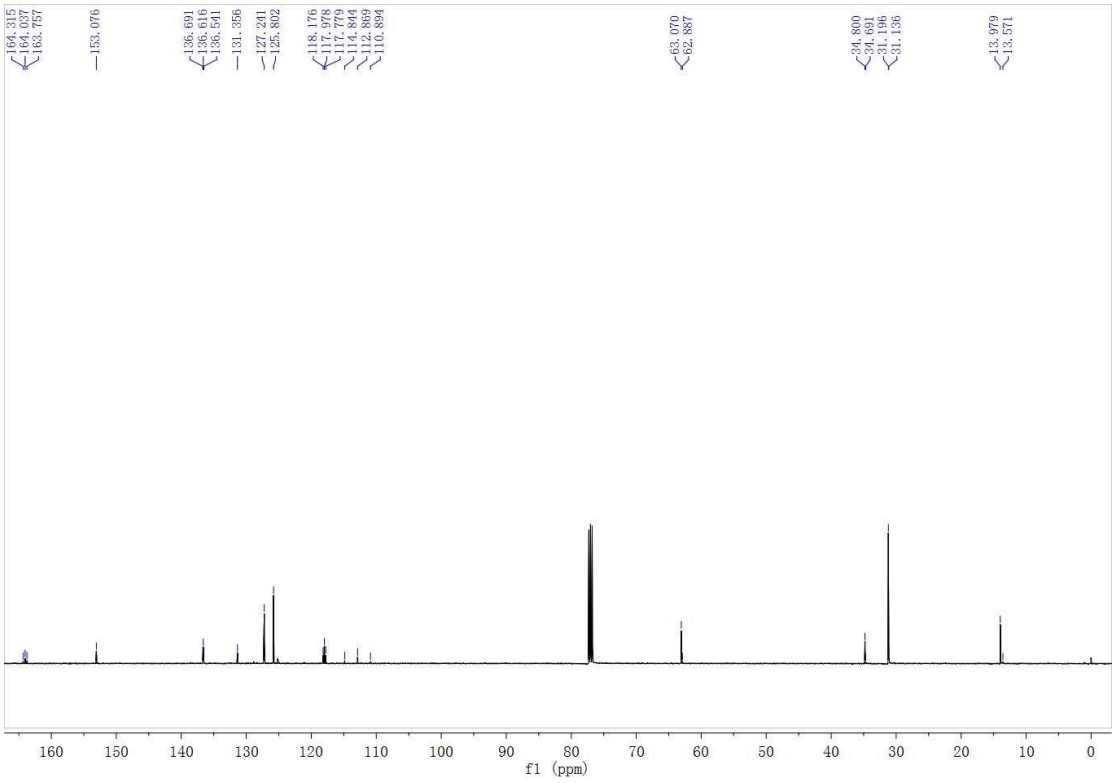

164.318
164.040
163.761
144.680
136.845
136.771
136.695
131.609
128.973
127.405
117.984
117.785
117.586
114.856
112.881
110.906
63.072
62.875
37.836
37.786
24.400
24.286
13.978
13.763
13.682
13.607
f1 (ppm)

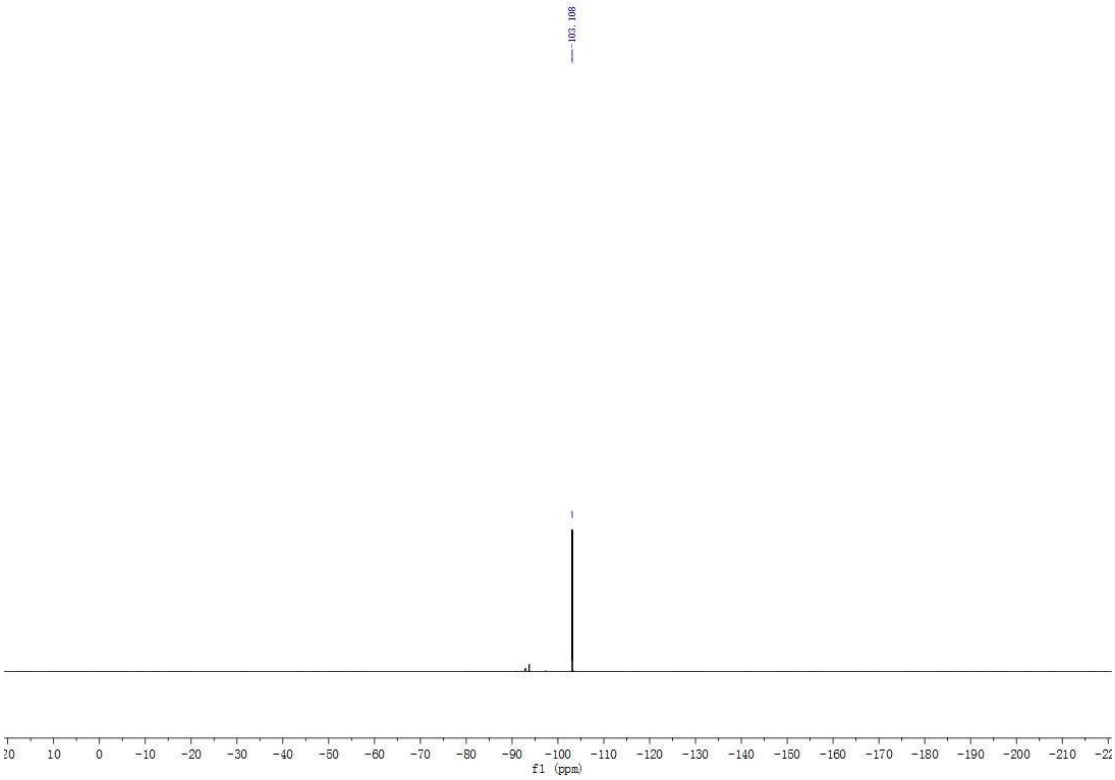


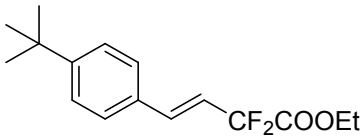


Ethyl -2, 2-difluoro-4-(4-butylphenyl)but-3-enoate (**9**, ***E/Z***=14:1)

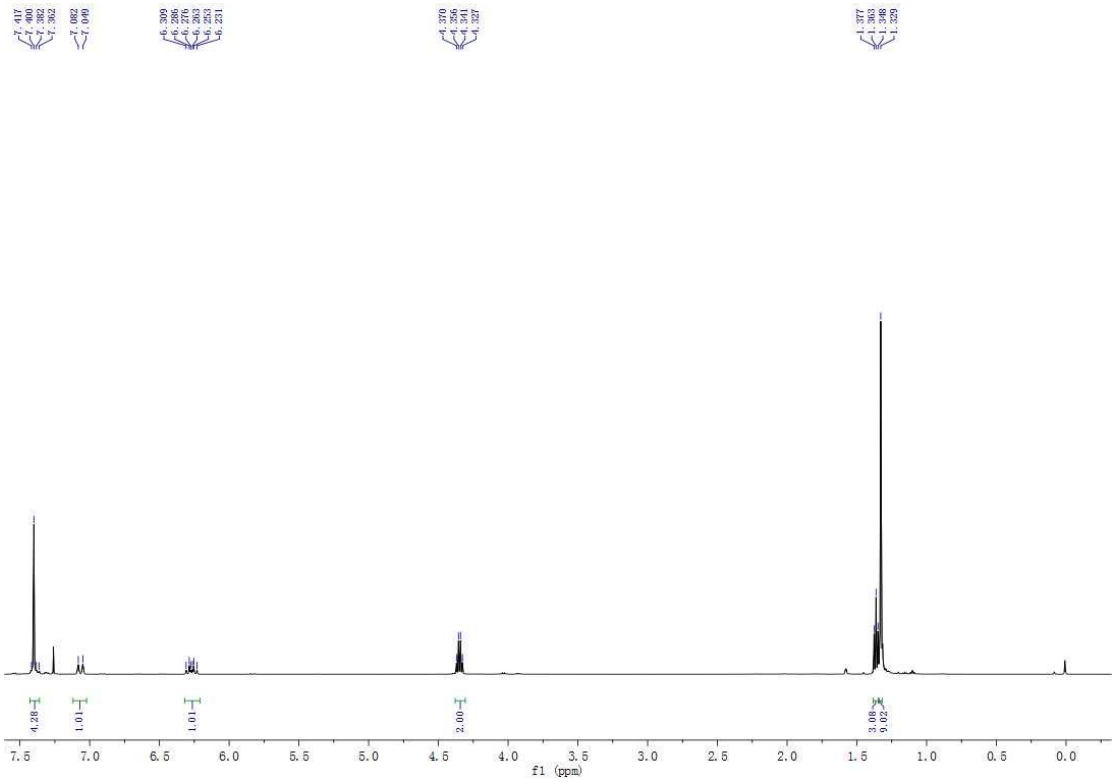

7.416
7.414
7.398
7.381
7.379
7.375
7.358
7.083
7.078
7.073
7.051
7.046
7.041
6.304
6.281
6.258
6.219
5.840
5.815
5.788
4.368
4.354
4.340
4.325
4.054
4.040
4.025
4.011
1.375
1.361
1.347
1.338
1.327
1.316
1.312
4.03
0.97
0.06
0.97
0.06
1.90
0.12
2.96
9.17
f1 (ppm)

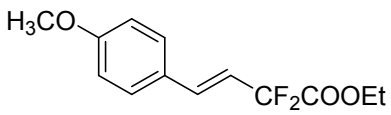

164.315
164.037
163.757
153.076
136.691
136.616
136.541
131.356
127.241
125.802
118.176
117.978
117.779
114.844
112.869
110.894
63.070
62.887
34.800
34.691
31.196
31.136
13.979
13.571
f1 (ppm)



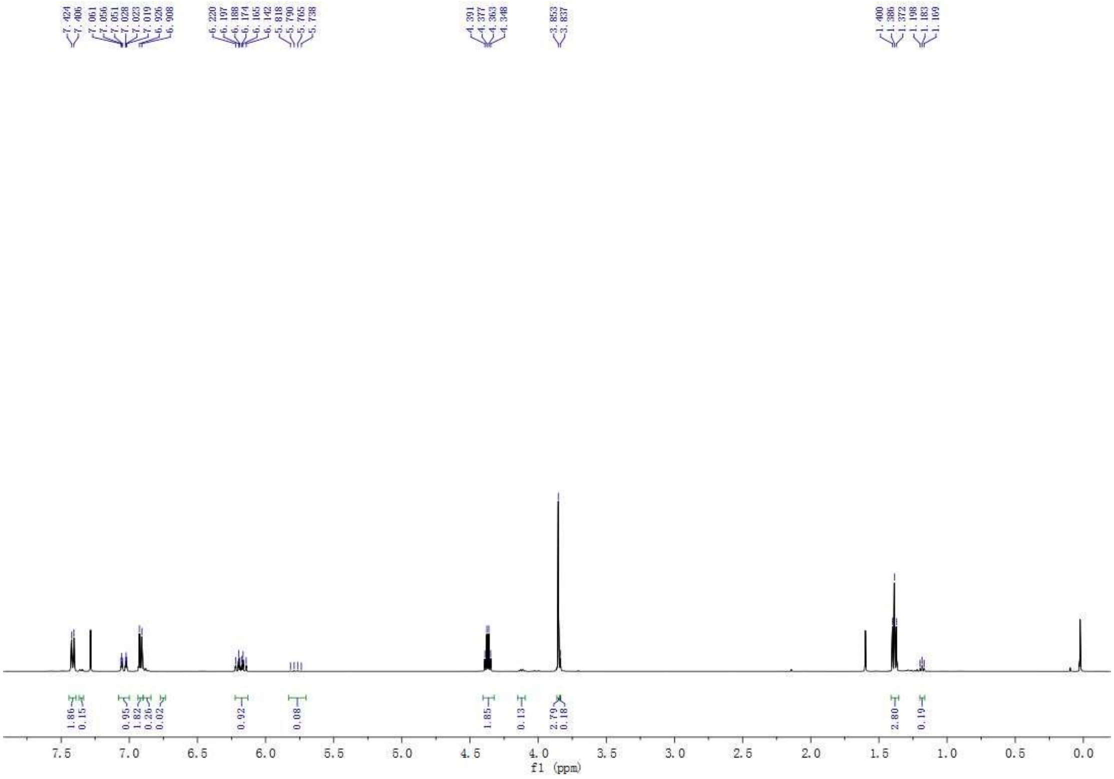


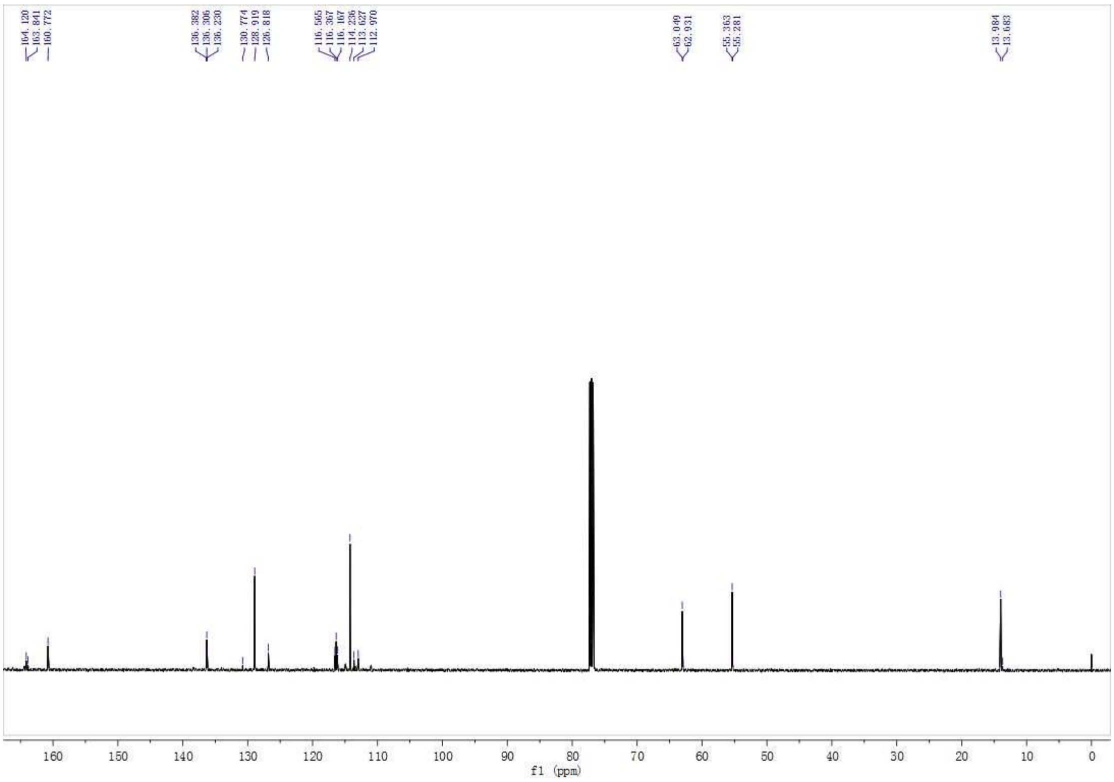
Ethyl -2, 2-difluoro-4-(4-butylphenyl)but-3-enoate (**9**, ***E/Z***=14:1) **from alkynyl carboxylic acid**

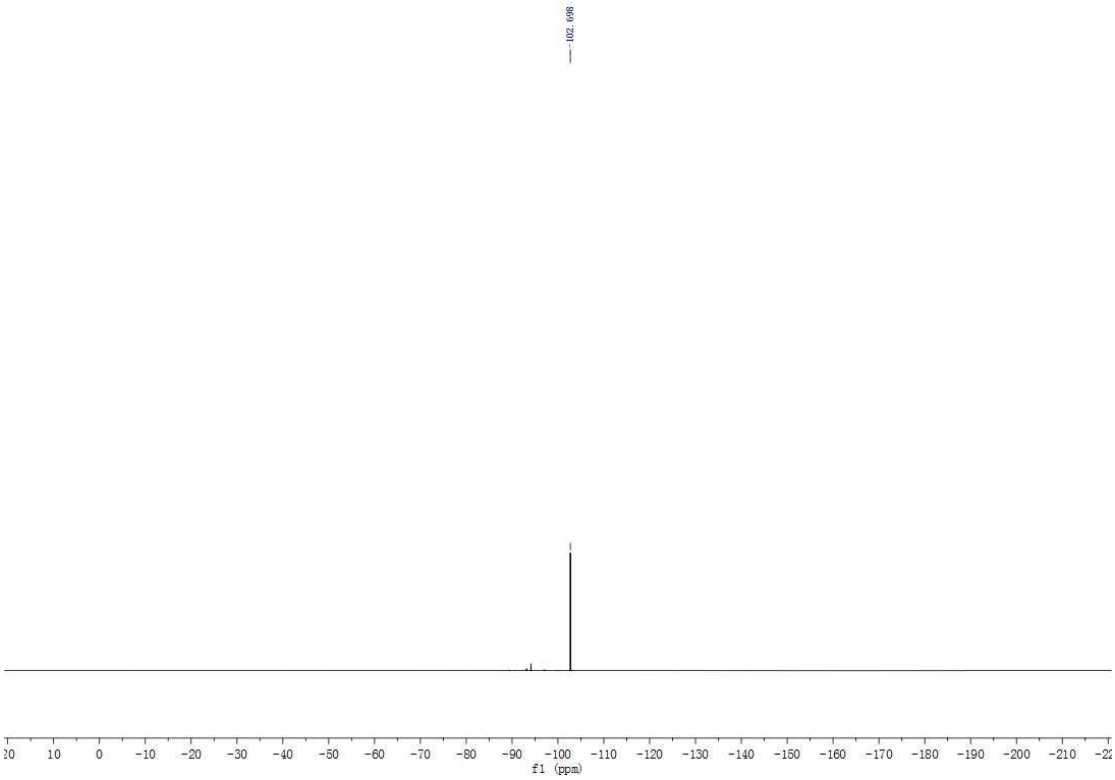


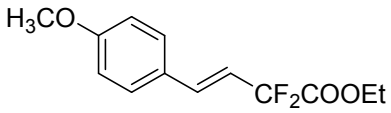


Ethyl-2, 2-difluoro-4-(4-methanoxyl)but-3-enoate (**10**, ***E/Z***=14:1)

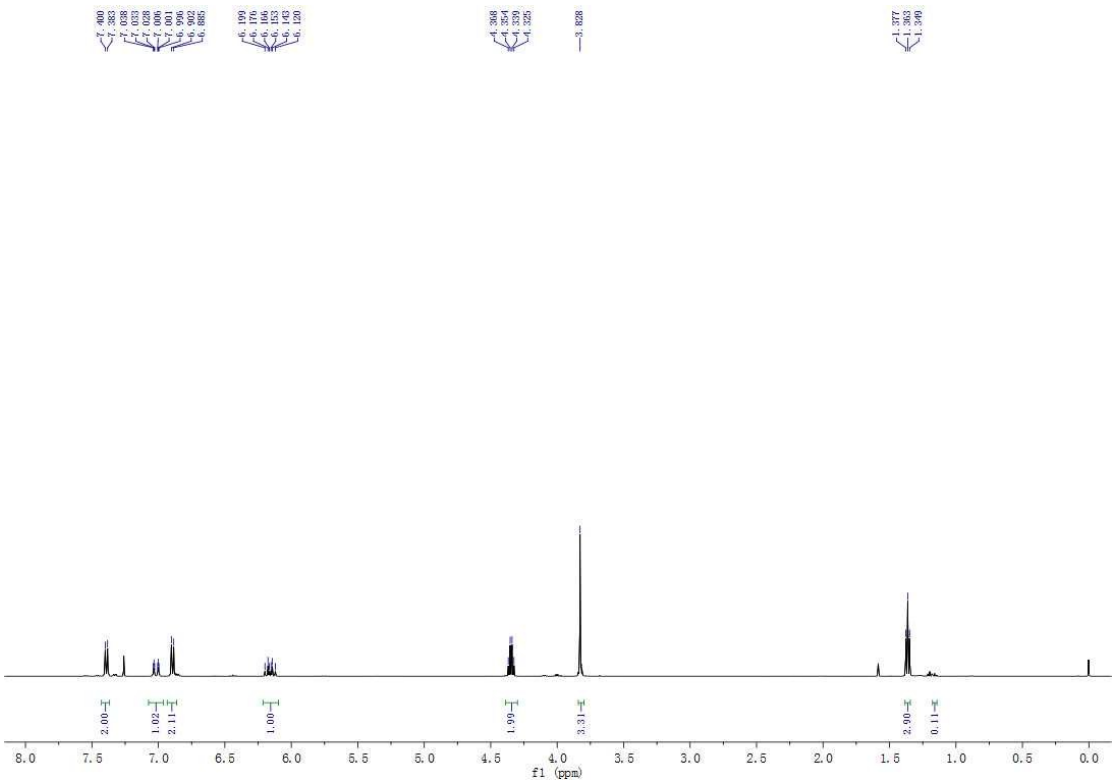

7.424
7.406
7.061
7.056
7.051
7.028
7.023
7.019
6.926
6.908
6.220
6.197
6.188
6.174
6.165
6.142
5.818
5.790
5.765
5.738
4.391
4.377
4.363
4.348
3.853
3.837
1.400
1.386
1.372
1.198
1.183
1.169
1.86
0.15
0.95
1.82
0.26
0.02
0.92
0.08
1.85
0.13
2.79
0.18
2.80
0.19
f1 (ppm)

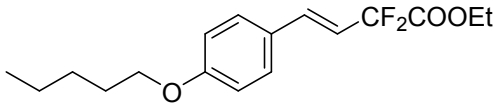

164.120
163.841
160.772
136.382
136.306
136.230
130.774
128.919
126.818
116.565
116.367
116.167
114.236
113.627
112.970
63.049
62.931
55.363
55.281
13.984
13.683
f1 (ppm)



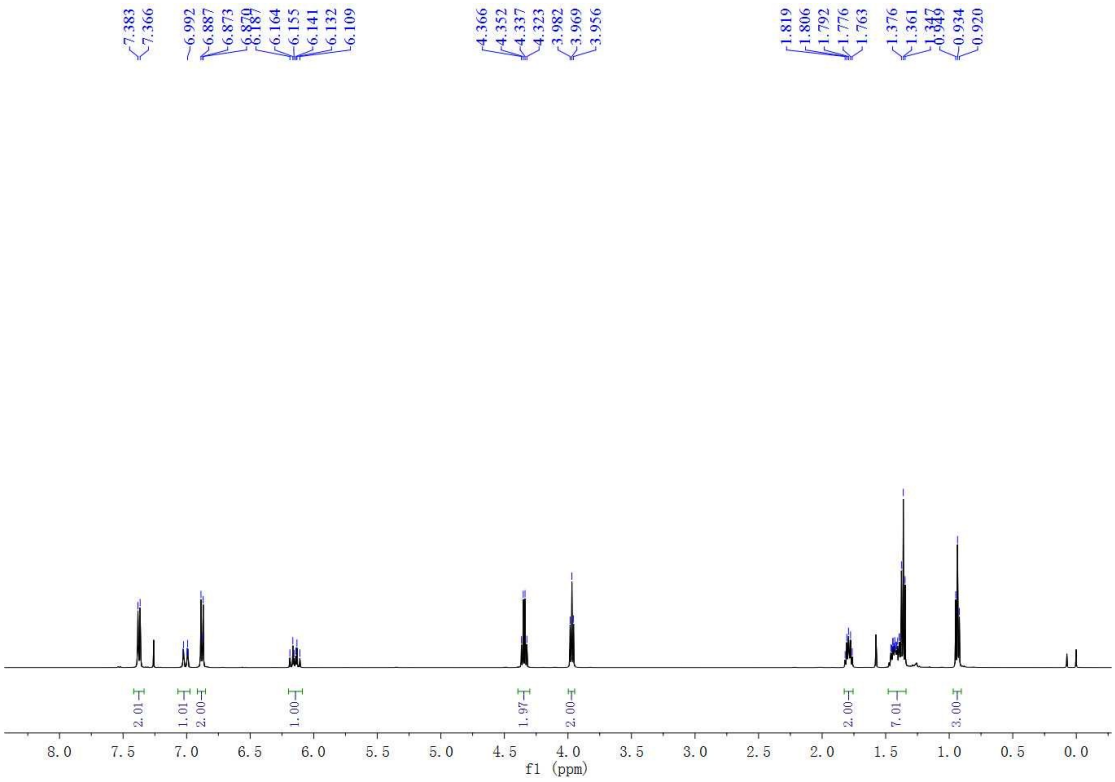


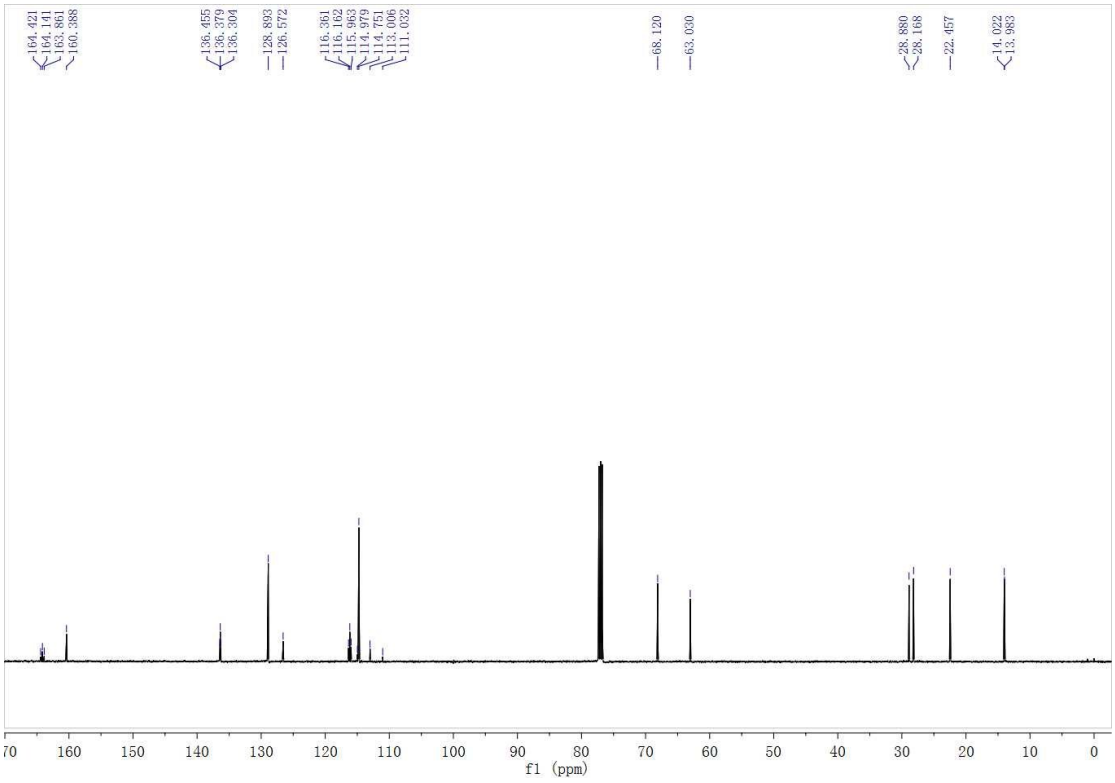
Ethyl-2, 2-difluoro-4-(4-methanoxyl)but-3-enoate (**10**, ***E/Z***=25:1) **from alkynyl carboxylic acid**

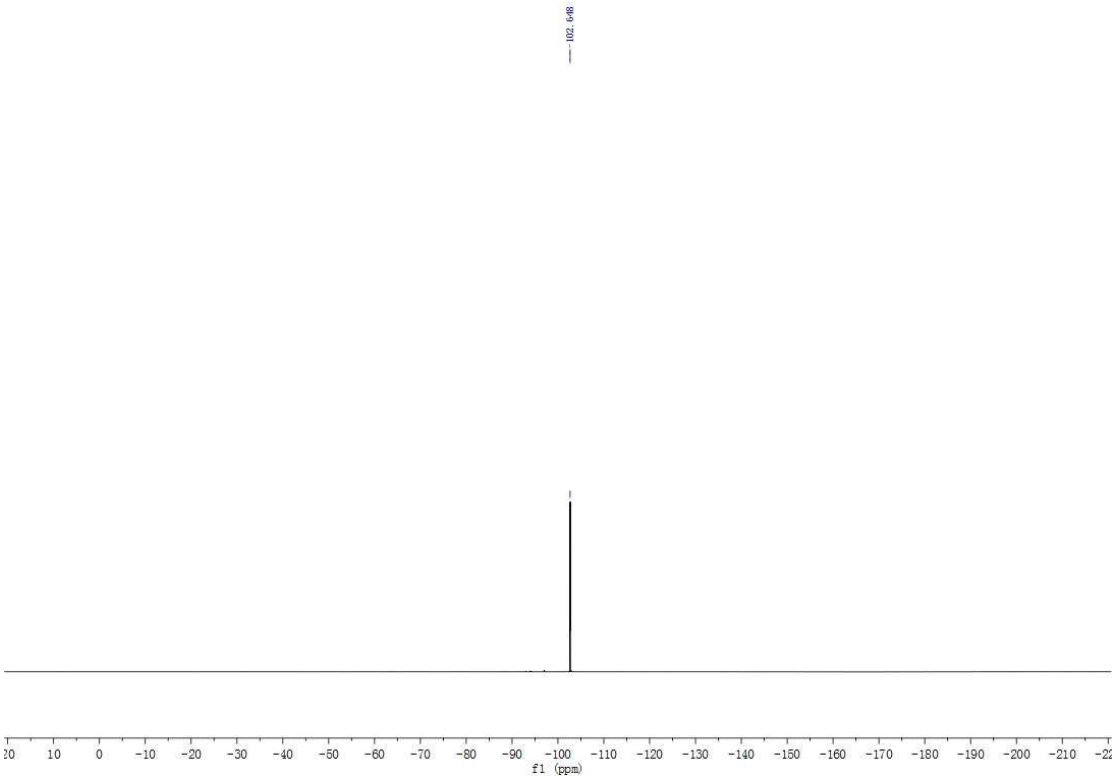


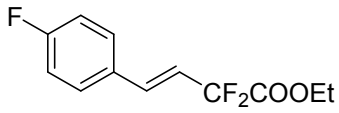


Ethyl (E)-2, 2-difluoro-4-(4-pentanoxyl)but-3-enoate (**11**, ***E/Z***=14:1)

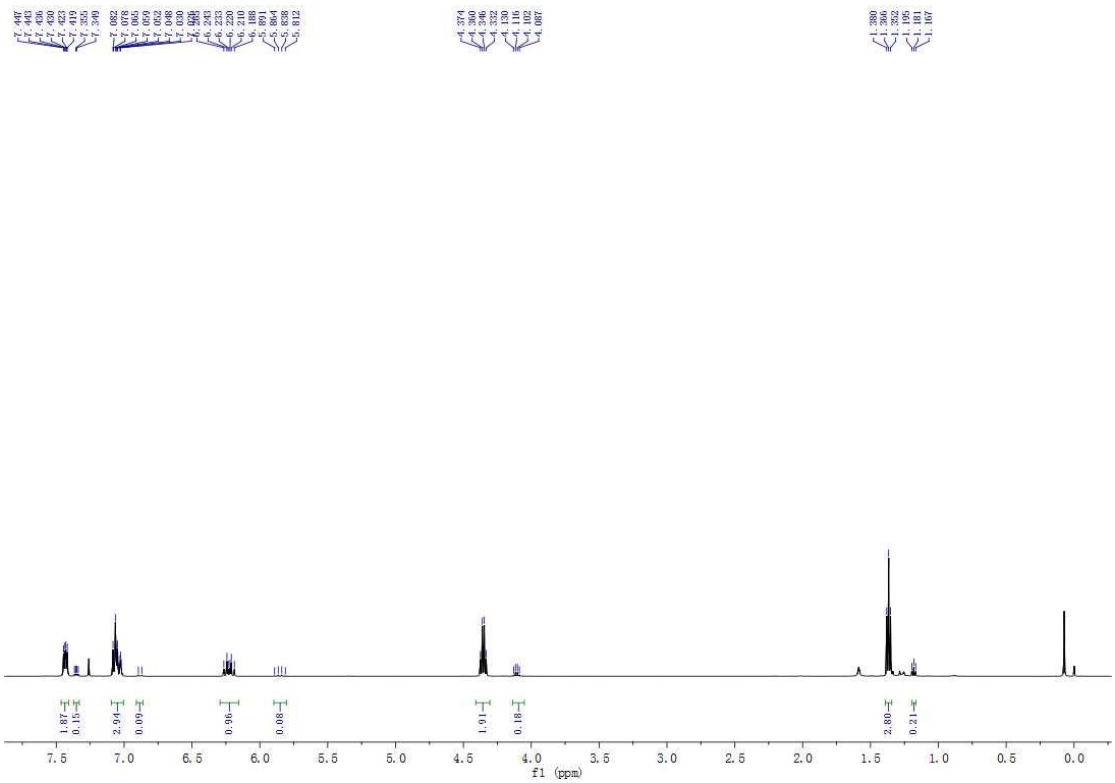

7.383
7.366
6.992
6.887
6.873
6.870
6.187
6.164
6.155
6.141
6.132
6.109
4.366
4.352
4.337
4.323
3.982
3.969
3.956
1.819
1.806
1.792
1.776
1.763
1.376
1.361
0.947
0.934
0.920
2.01
1.01
2.00
1.00
1.97
2.00
2.00
7.01
3.00
f1 (ppm)


164.421
164.141
163.861
160.388
136.455
136.379
136.304
128.893
126.572
116.361
116.162
115.963
114.979
114.751
113.006
111.032
68.120
63.030
28.880
28.168
22.457
14.022
13.983
f1 (ppm)





Ethyl (E)-2, 2-difluoro-4-(4-fluorophenyl)but-3-enoate (**12**, ***E/Z***=14:1)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7.078
7.065
7.059
7.052
7.048
7.030
6.243
6.233
6.220
6.210
6.188
5.891
5.864
5.838
5.812
4.374
4.360
4.346
4.332
4.319
4.116
4.102
4.087
1.380
1.366
1.352
1.195
1.181
1.167
1.87
0.15
2.94
0.09
0.96
0.08
1.91
0.18
2.89
0.21
7.5
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6.0
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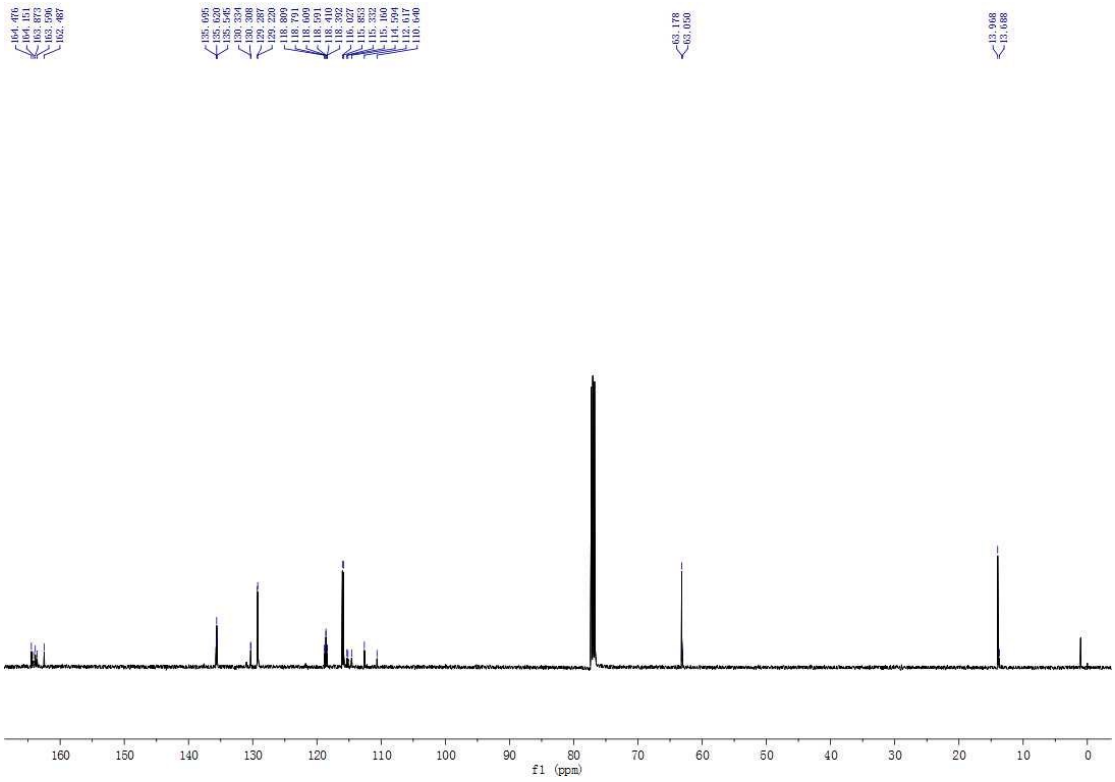
1.0
0.5
0.0
f1 (ppm)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115.332
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114.994
114.771
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63.050
13.968
13.688
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130
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90
80
70
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50
40
30
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10
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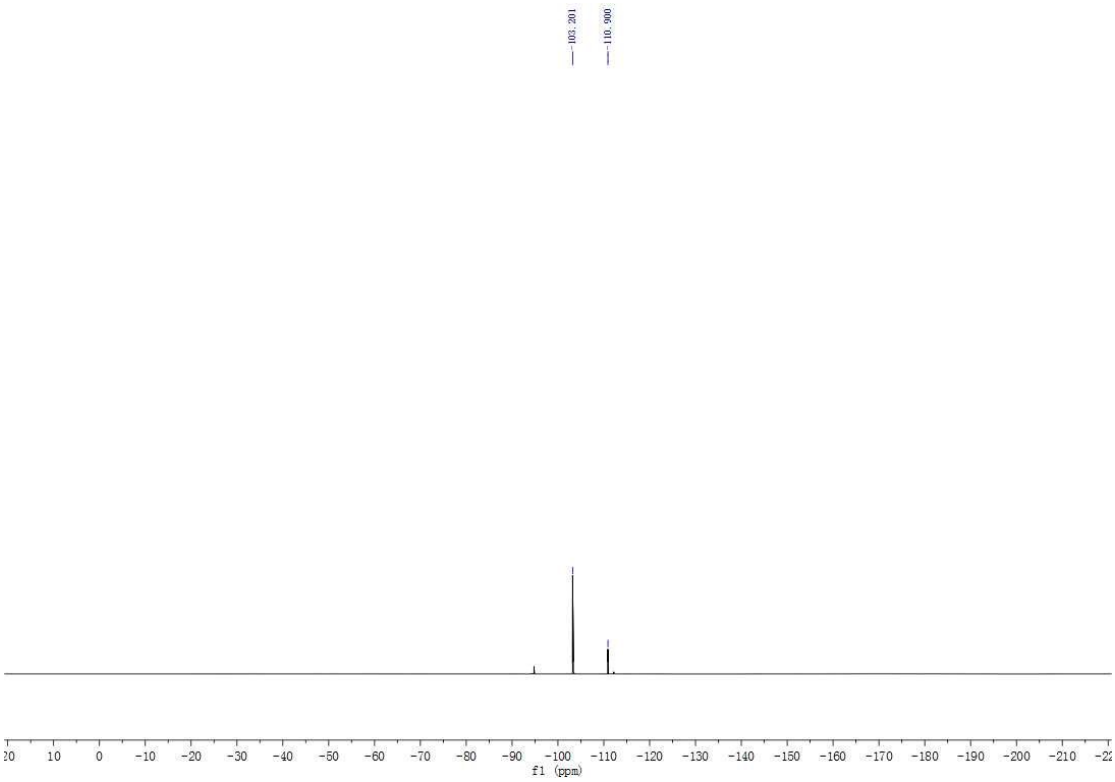
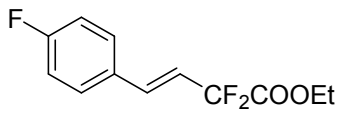
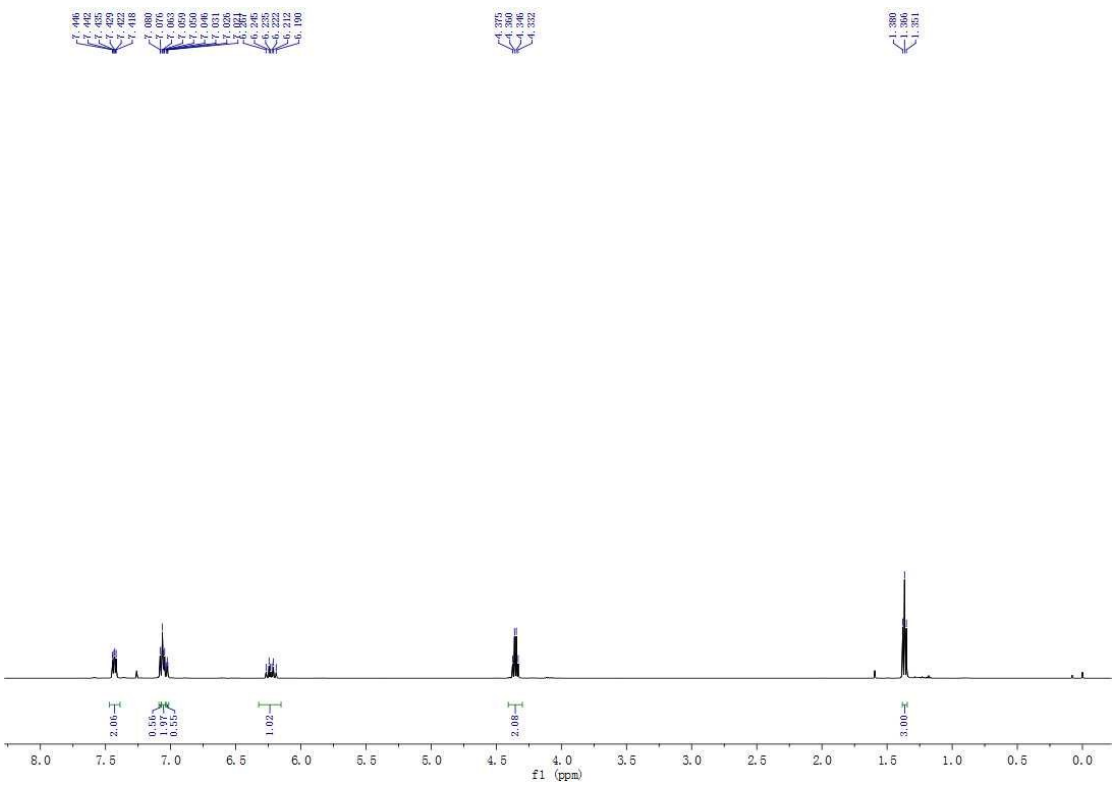
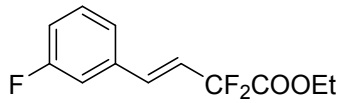
f1 (ppm)



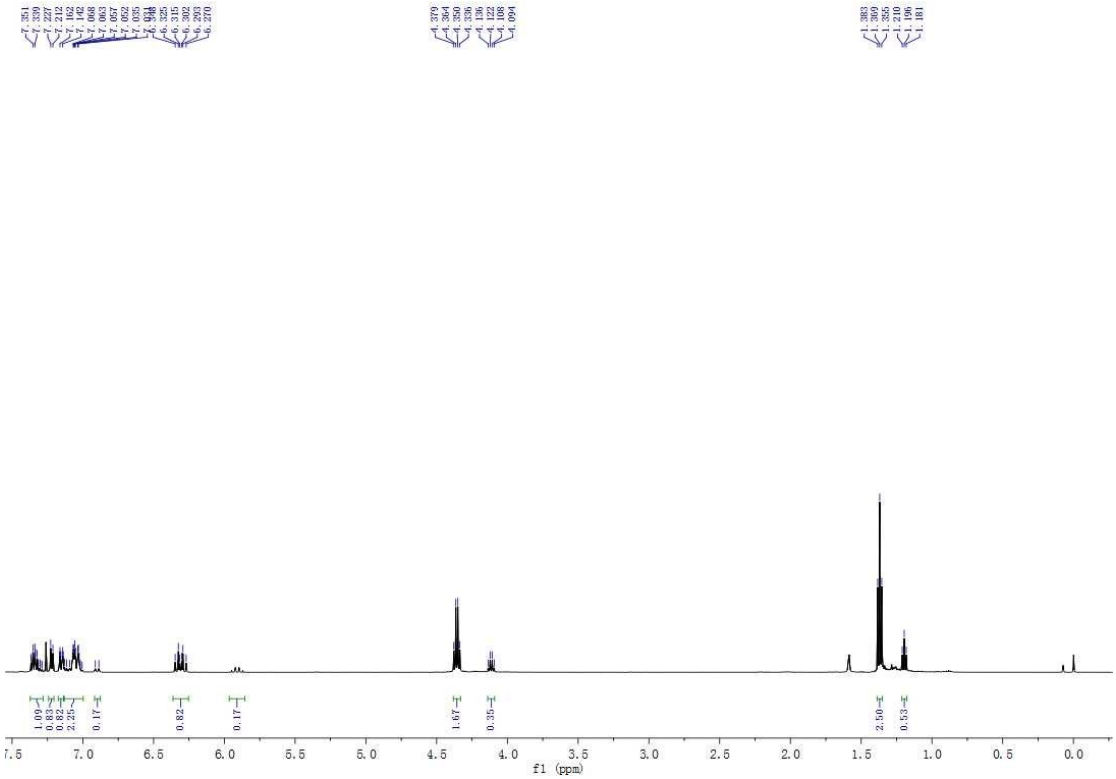


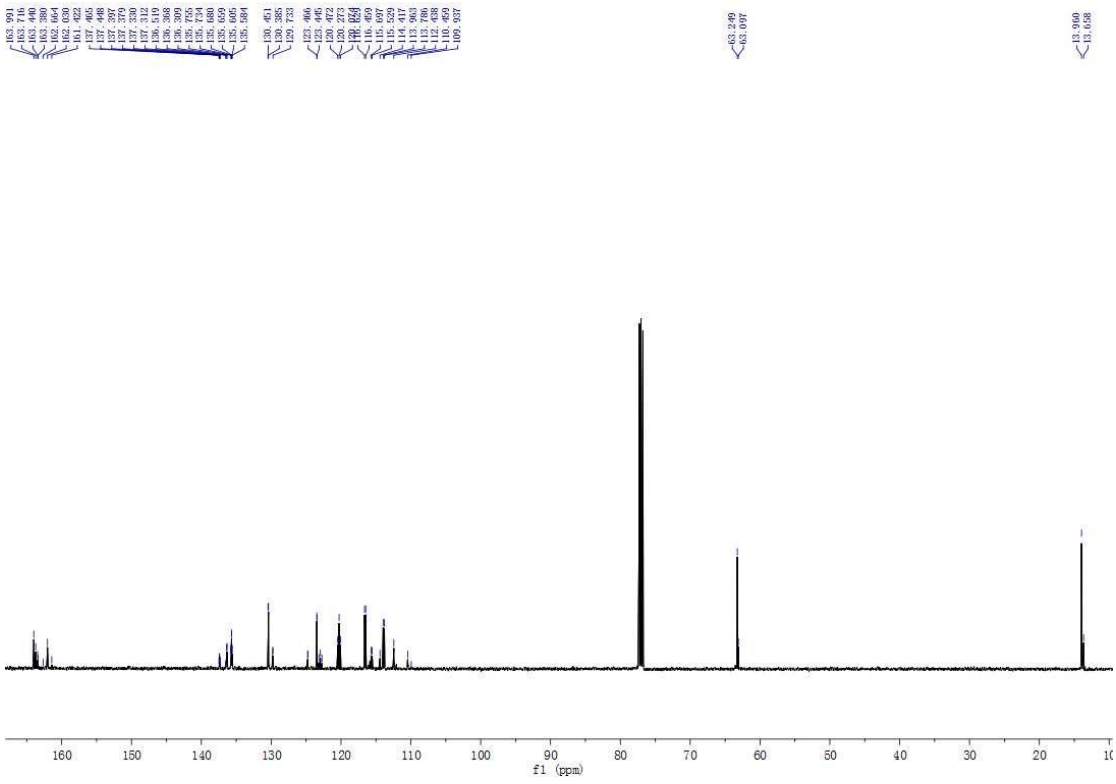
Ethyl (E)-2, 2-difluoro-4-(4-fluorophenyl)but-3-enoate (12) from alkynyl carboxylic acid

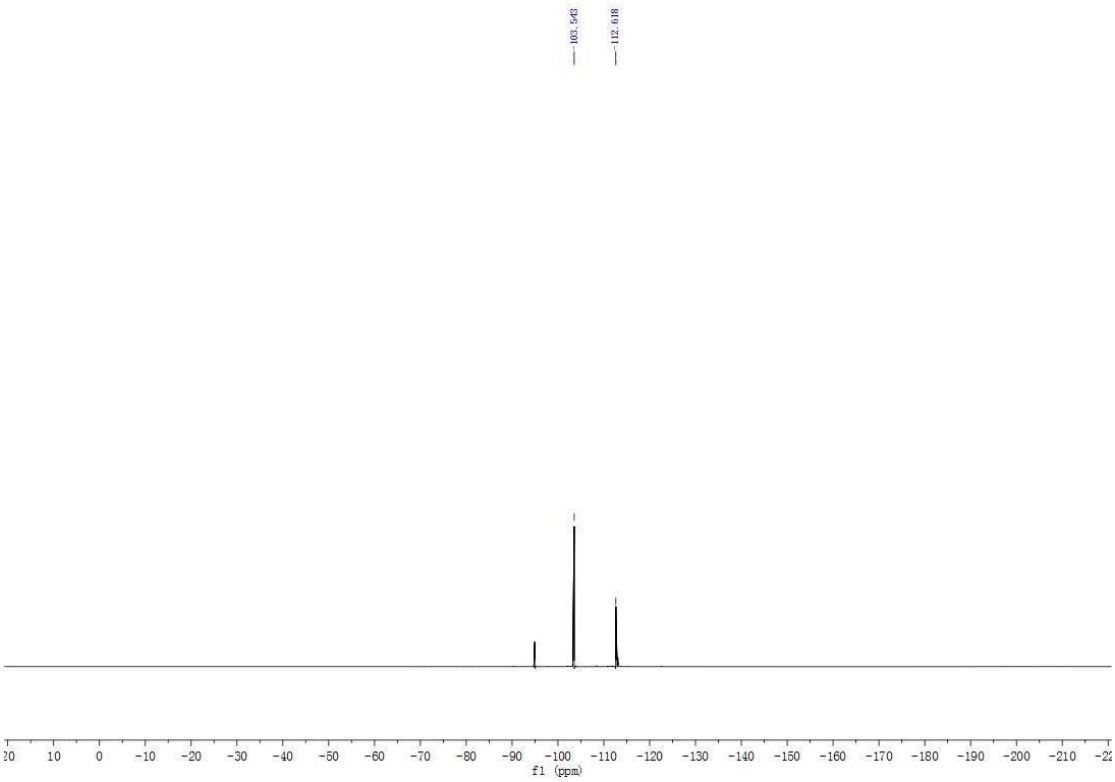


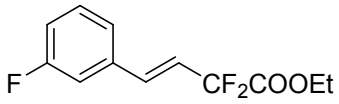


Ethyl (E)-2, 2-difluoro-4-(3-fluorophenyl)but-3-enoate (**13**, ***E/Z***=5:1)

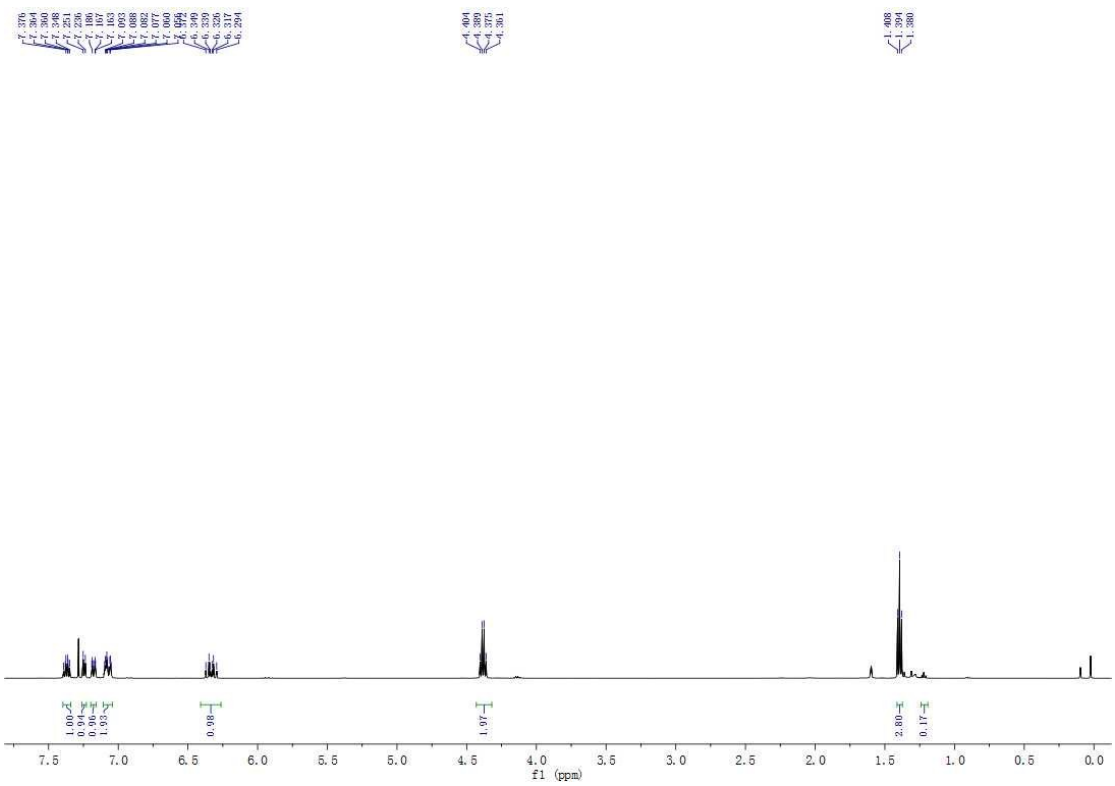

f1 (ppm)

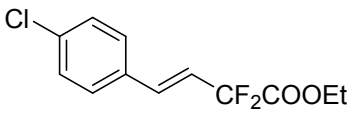

f1 (ppm)



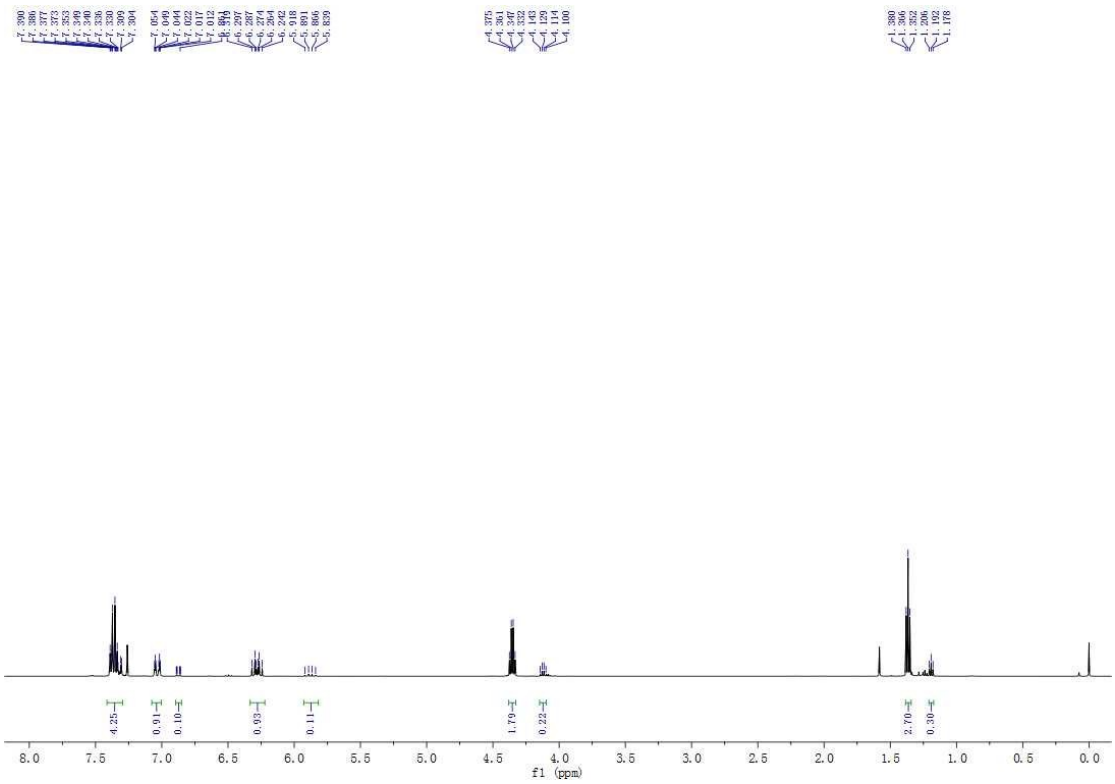


Ethyl (E)-2, 2-difluoro-4-(3-fluorophenyl)but-3-enoate (**13**, ***E/Z***=17:1) **from alkynyl carboxylic acid**





Ethyl (E)-4-(4-chlorophenyl)-2, 2-difluorobut-3-enoate (**14**, ***E/Z***=9:1)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7.304
7.054
7.049
7.044
7.022
7.017
7.013
6.297
6.287
6.274
6.264
6.252
5.918
5.891
5.866
5.839
4.375
4.361
4.347
4.332
4.145
4.129
4.114
4.100
1.380
1.366
1.352
1.206
1.192
1.178
4.25
0.91
0.10
0.93
0.11
1.79
0.22
2.70
0.30
8.0
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7.0
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6.0
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2.0
1.5
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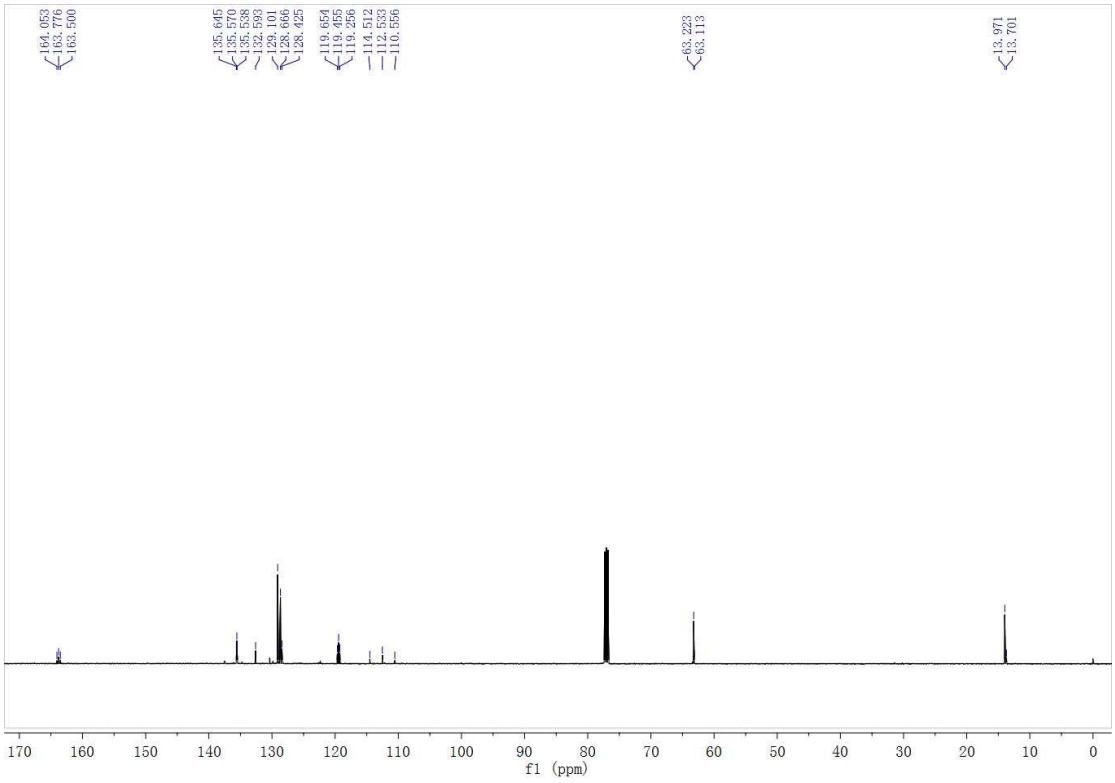
0.0
f1 (ppm)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163.500
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129.101
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128.425
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119.455
119.256
114.512
112.533
110.556
63.223
63.113
13.971
13.701
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90
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50
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30
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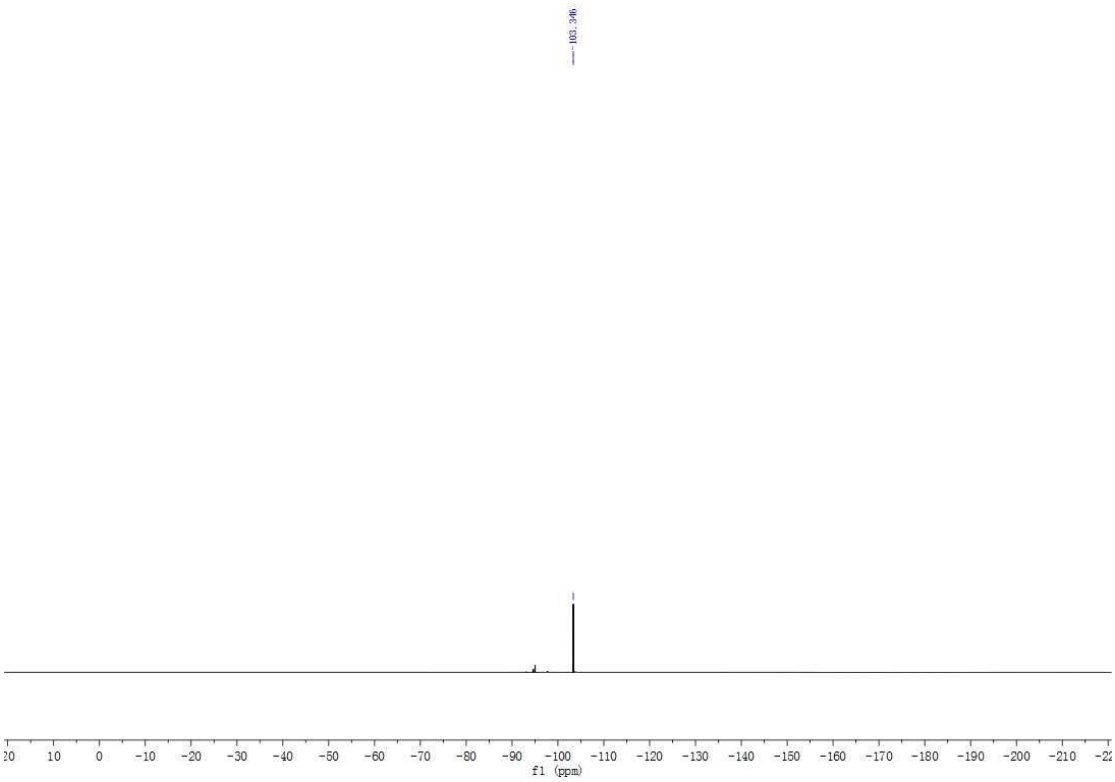
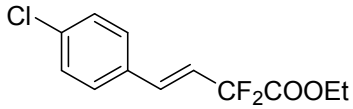
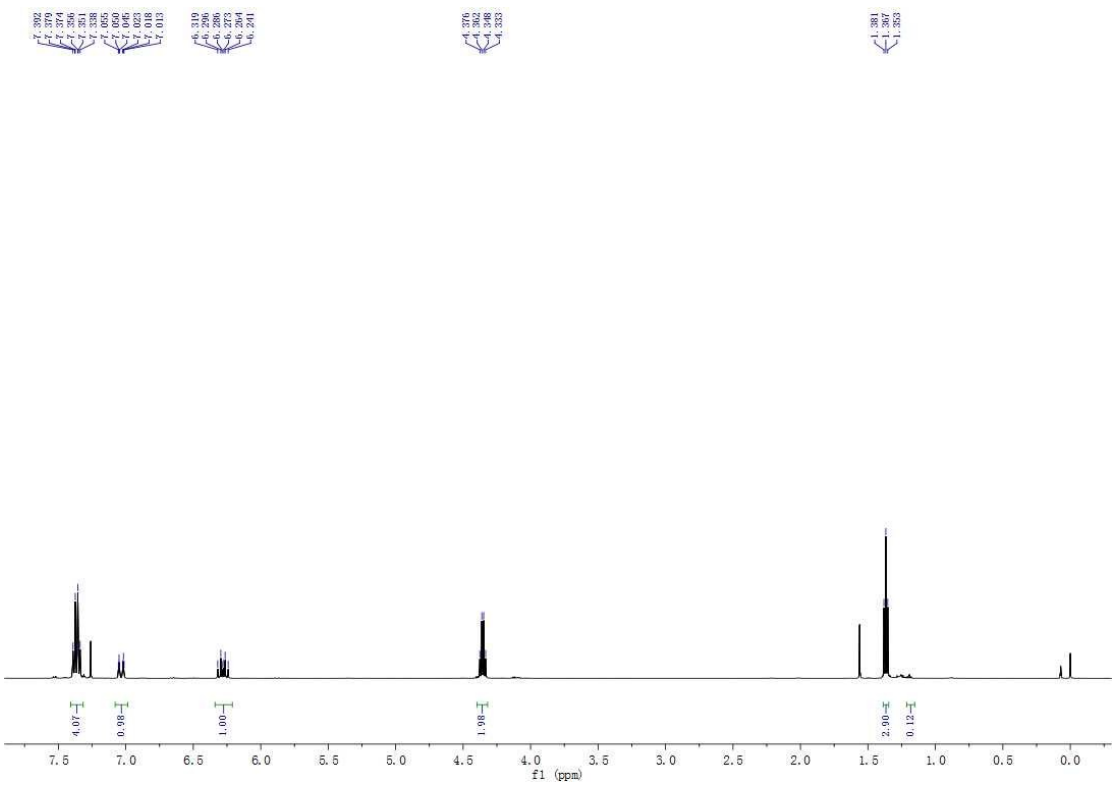
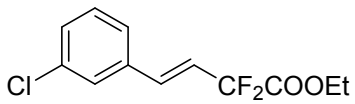
10
0
f1 (ppm)



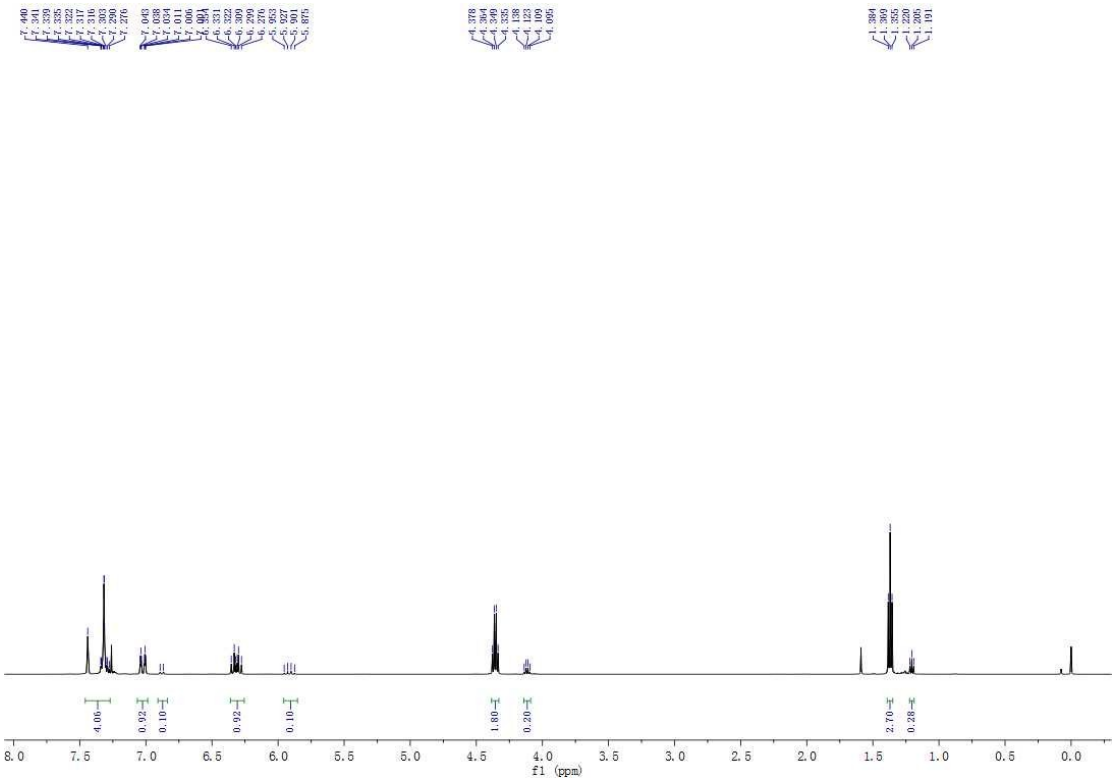


Ethyl (E)-4-(4-chlorophenyl)-2, 2-difluorobut-3-enoate (14, *E/Z*=25:1) from alkyny carboxylic acid





Ethyl (E)-4-(3-chlorophenyl)-2, 2-difluorobut-3-enoate (**15**, ***E/Z***=9:1)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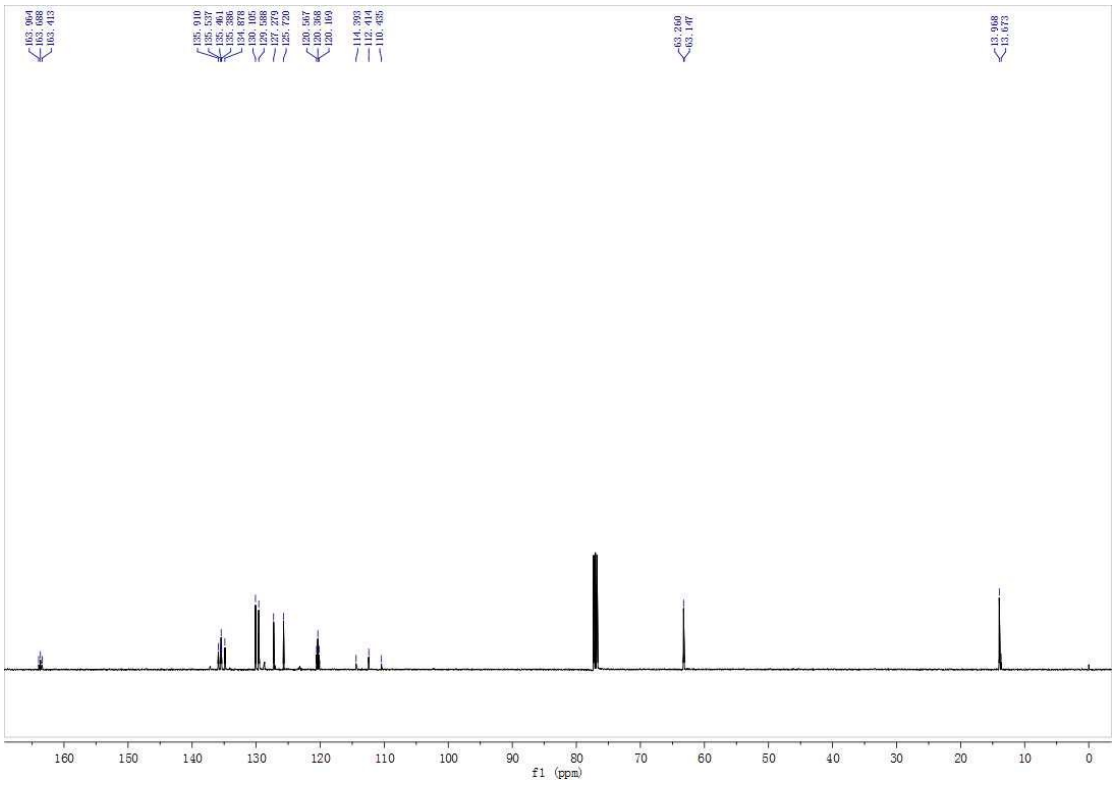
1.80
0.20
2.70
0.28
f1 (ppm)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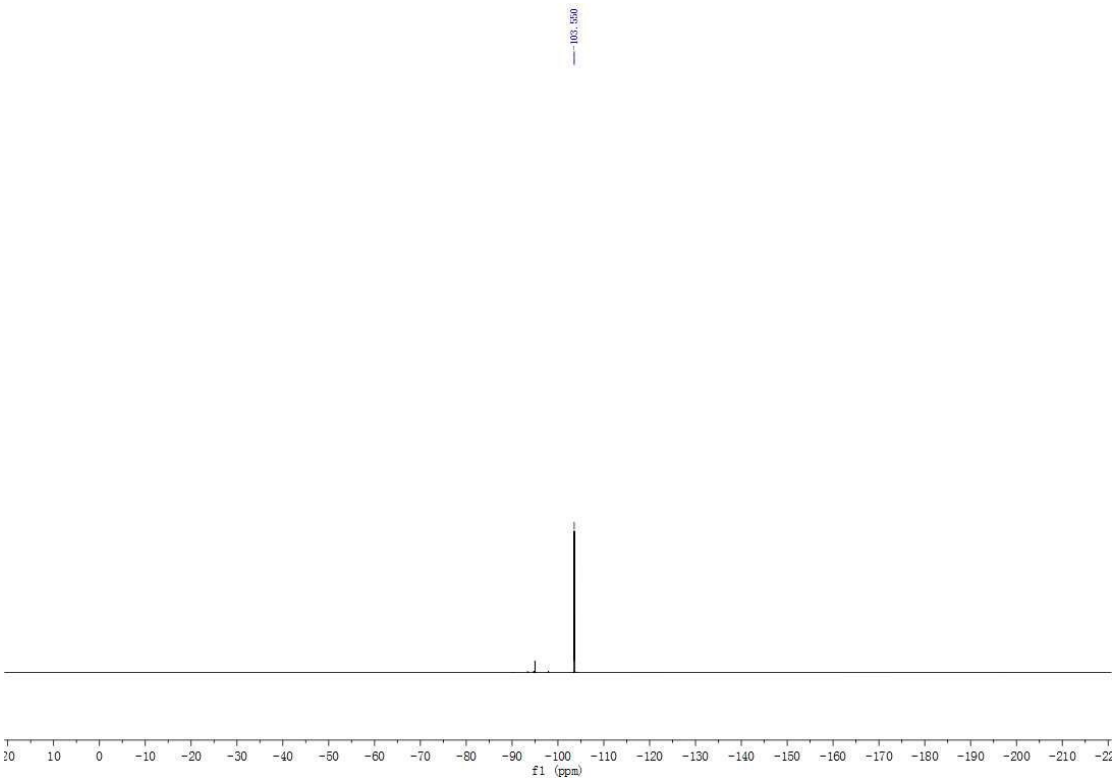
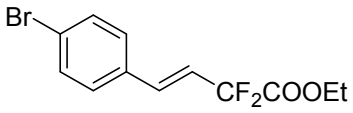
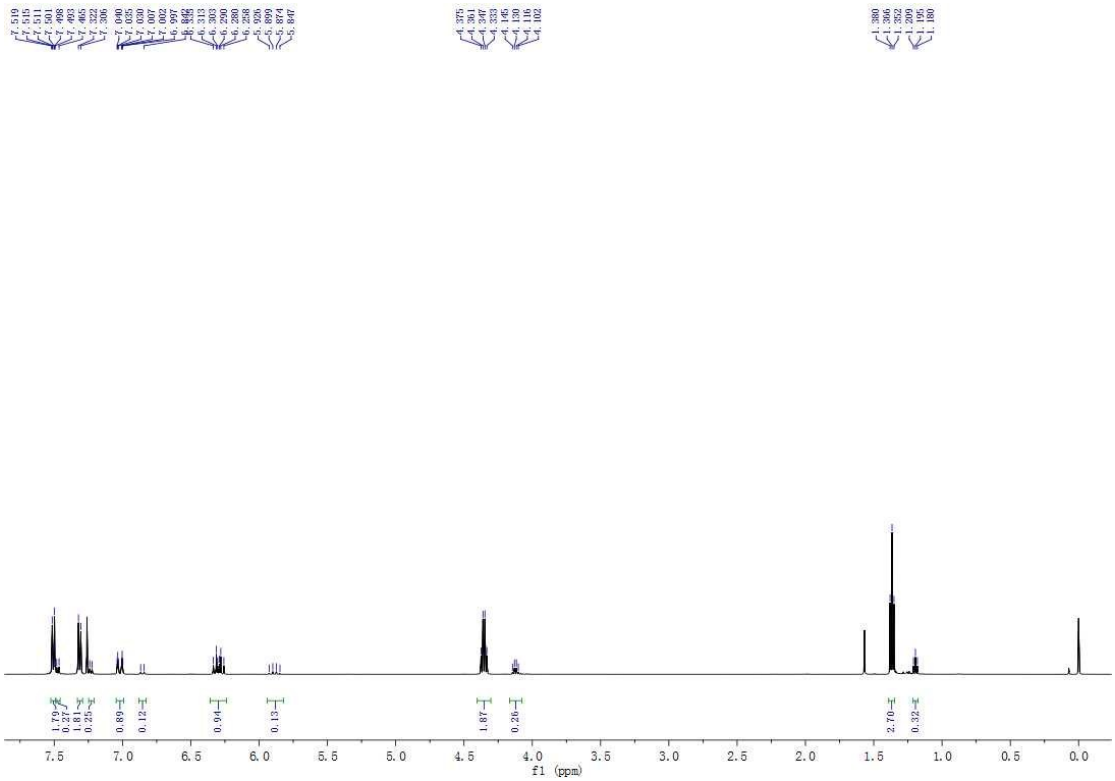
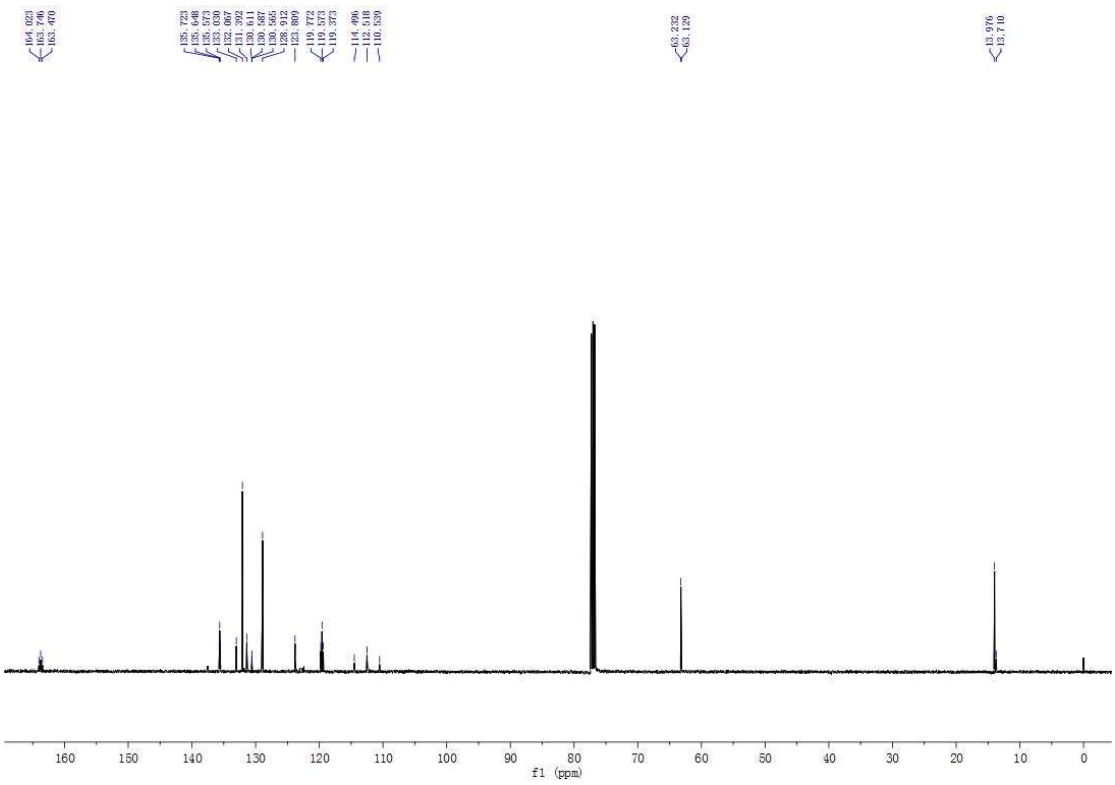
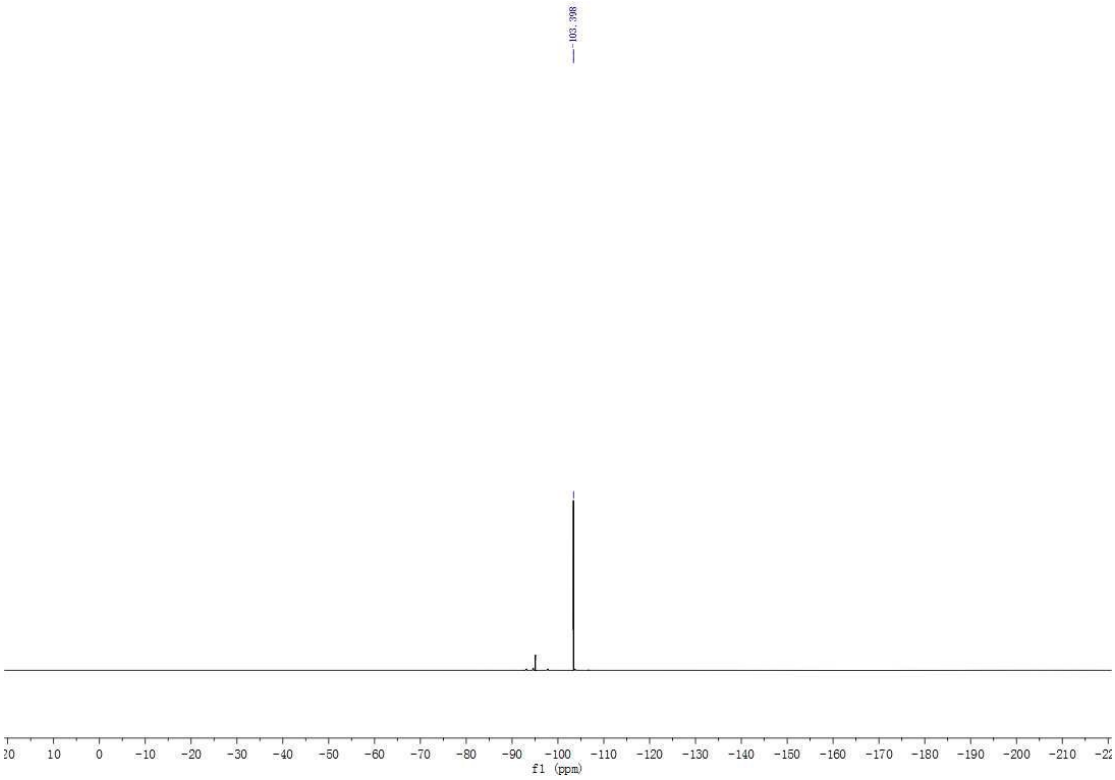


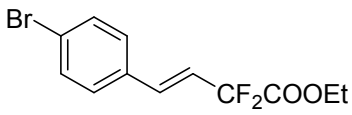


Ethyl (E)-4-(4-bromophenyl)-2, 2-difluorobut-3-enoate (**16**, ***E/Z***=8:1)

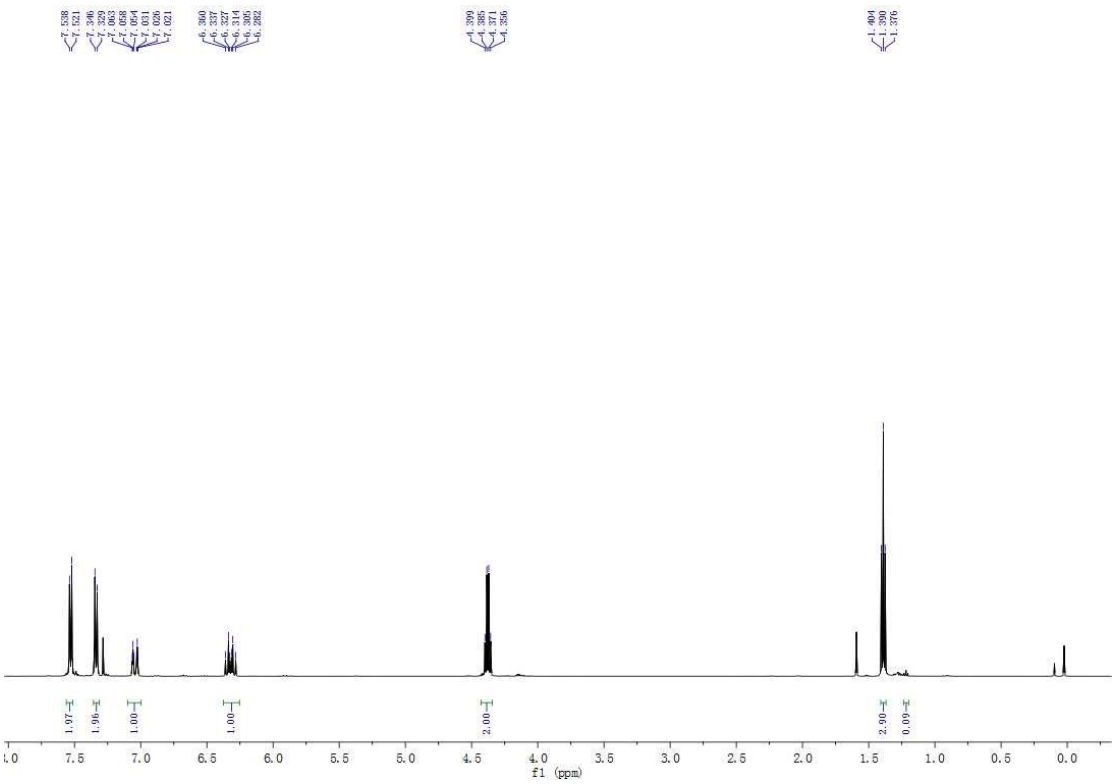


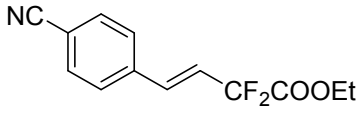




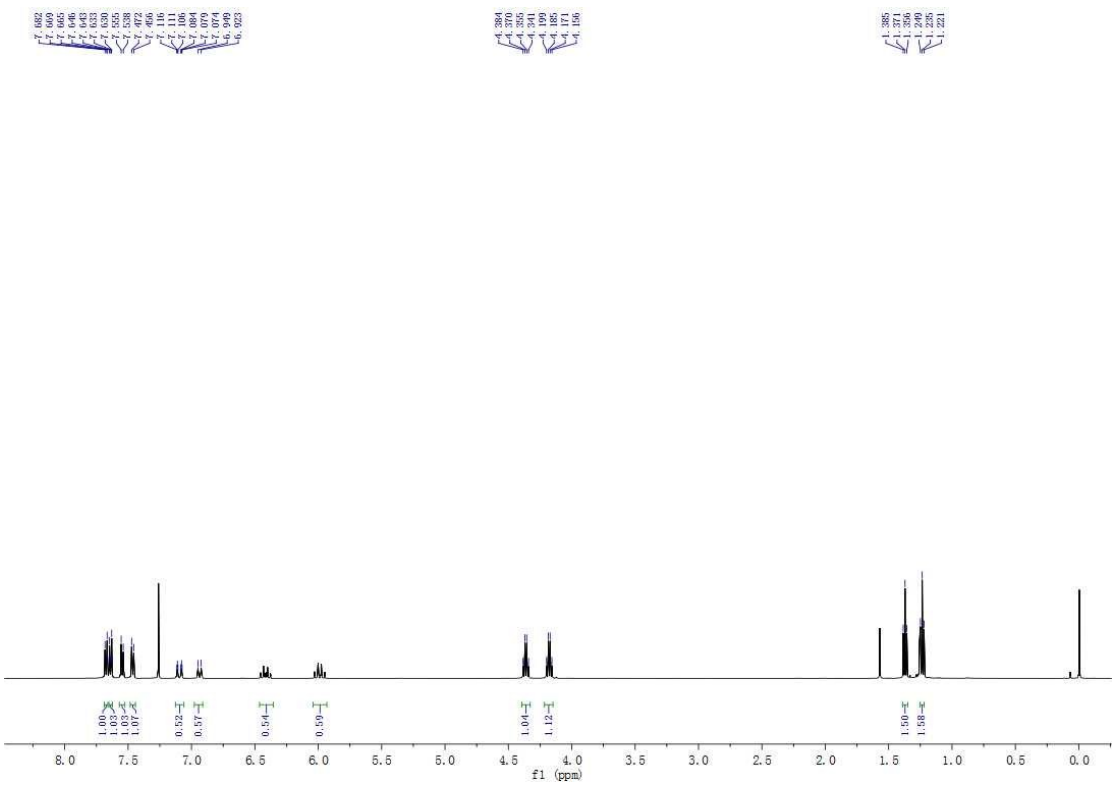


Ethyl (E)-4-(4-bromophenyl)-2, 2-difluorobut-3-enoate (16, *E/Z*=25:1) from alkynyl carboxylic acid





Ethyl (E)-4-(4-cyanophenyl)-2, 2-difluorobut-3-enoate (**17**, ***E/Z***=1:1)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4.171
4.156
1.385
1.371
1.356
1.240
1.235
1.221
1.09
1.03
1.03
1.07
0.52
0.57
0.54
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1.04
1.12
1.50
1.58
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1.0
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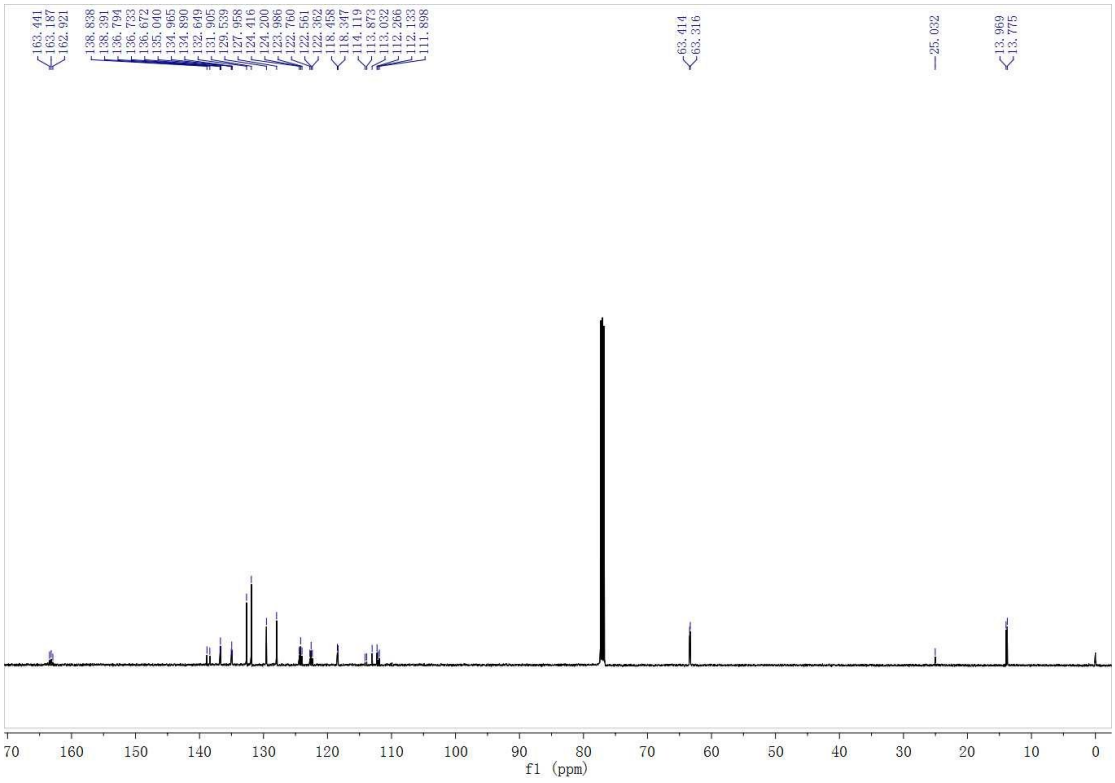
0.0
f1 (ppm)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112.266
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63.316
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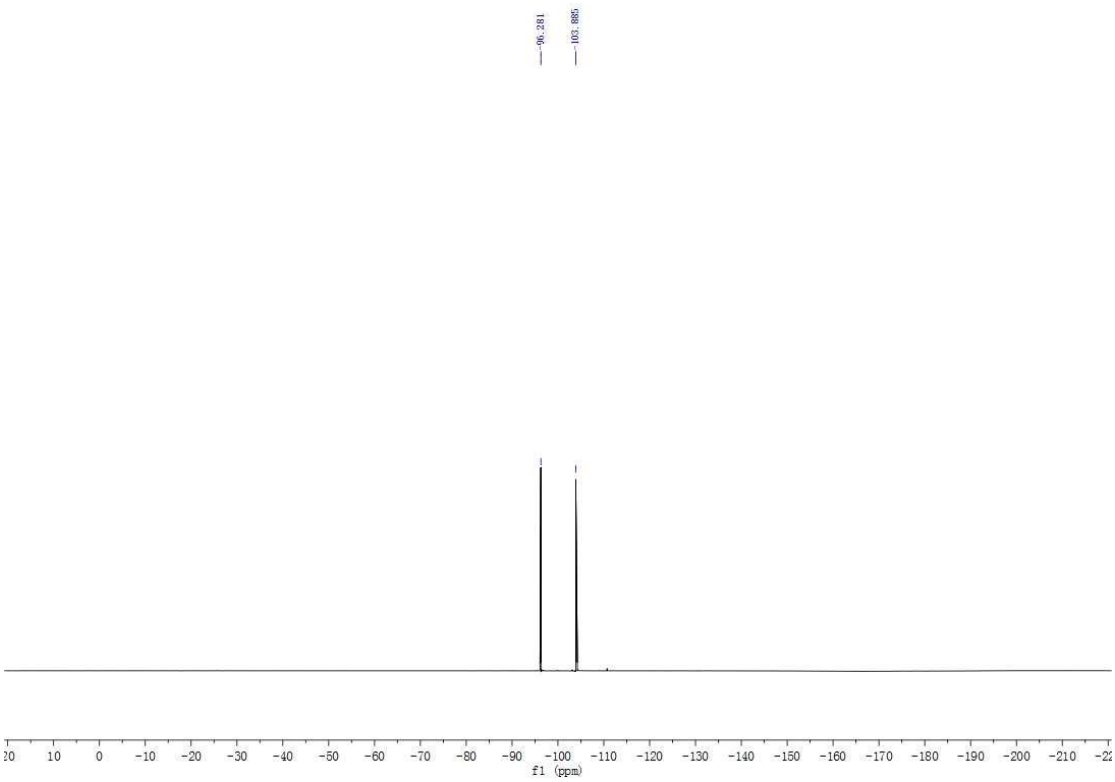
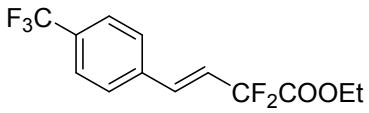
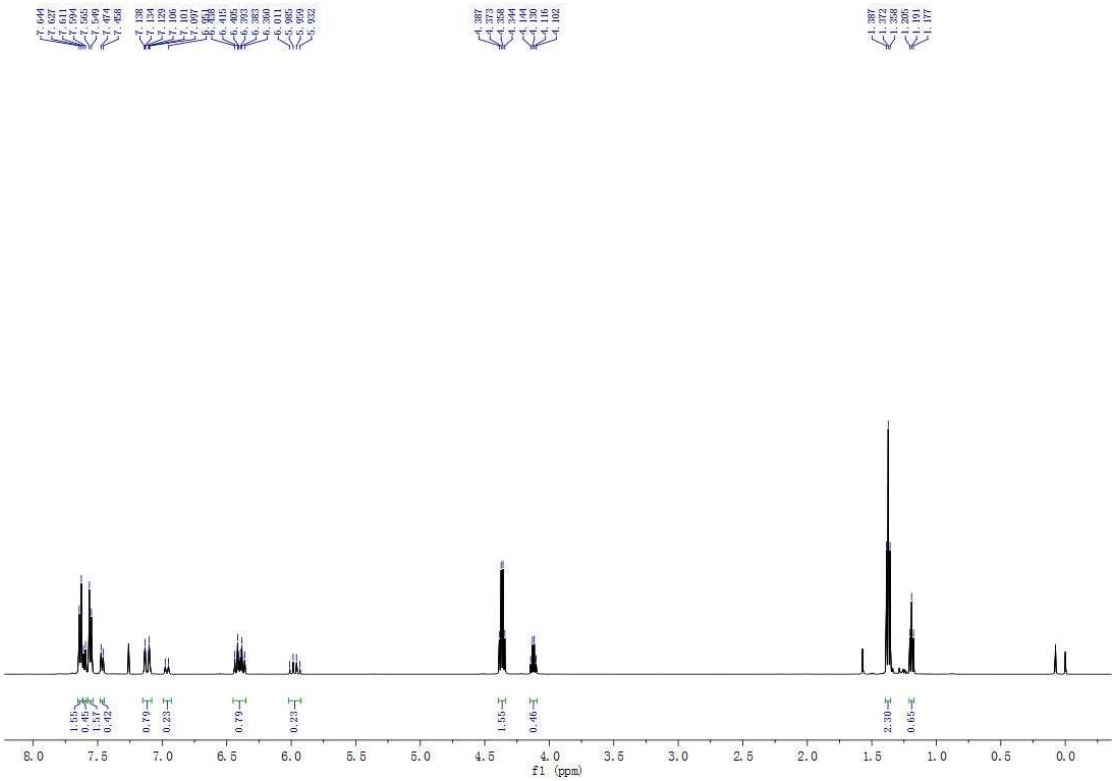
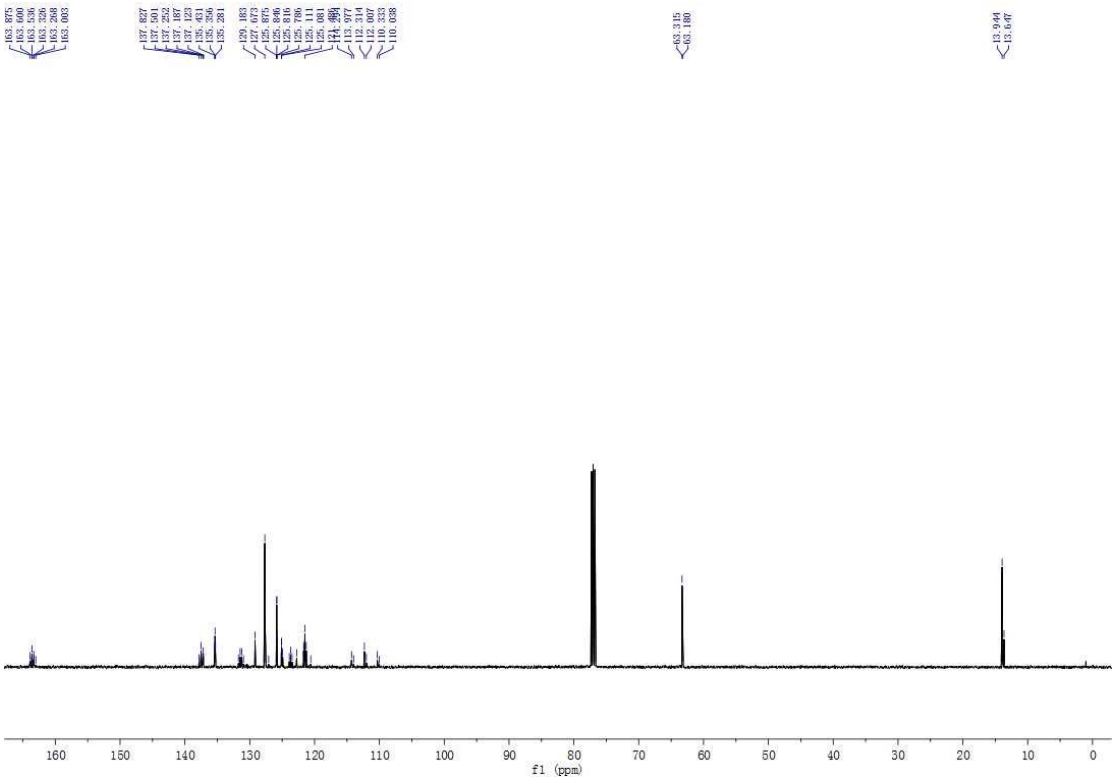
f1 (ppm)

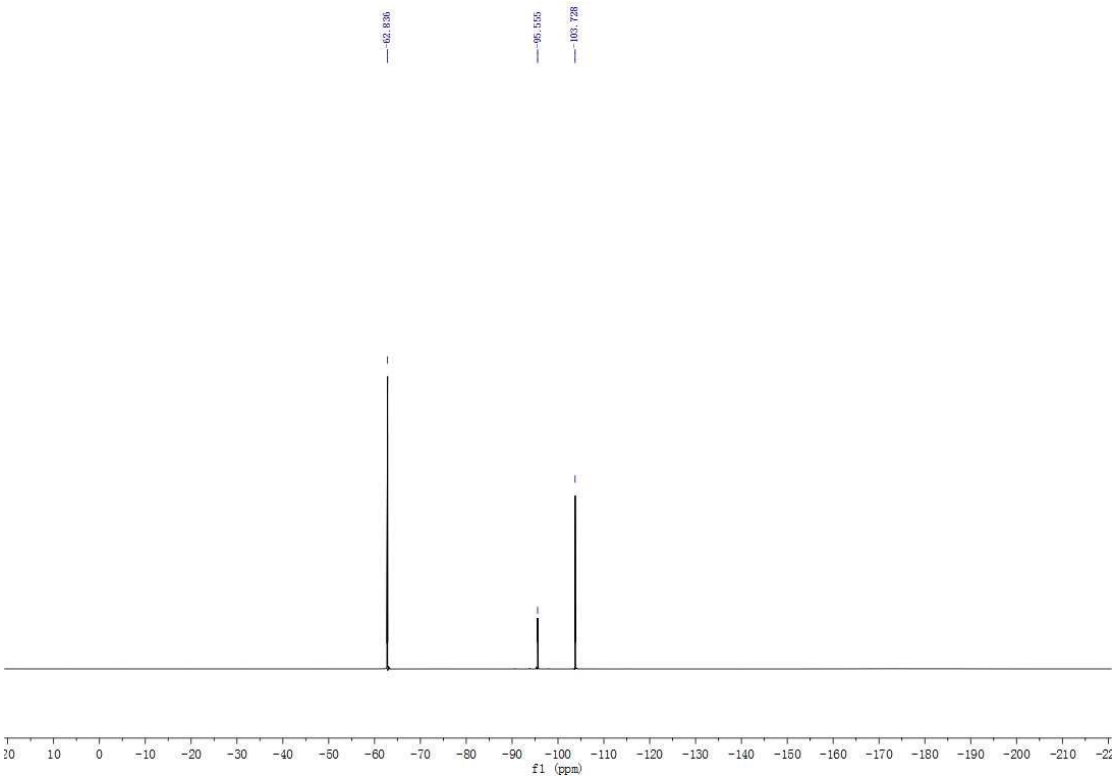


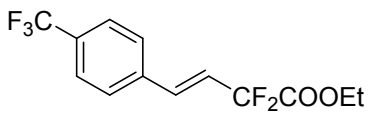


Ethyl (E)-2, 2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (**18**, ***E/Z***=4:1)

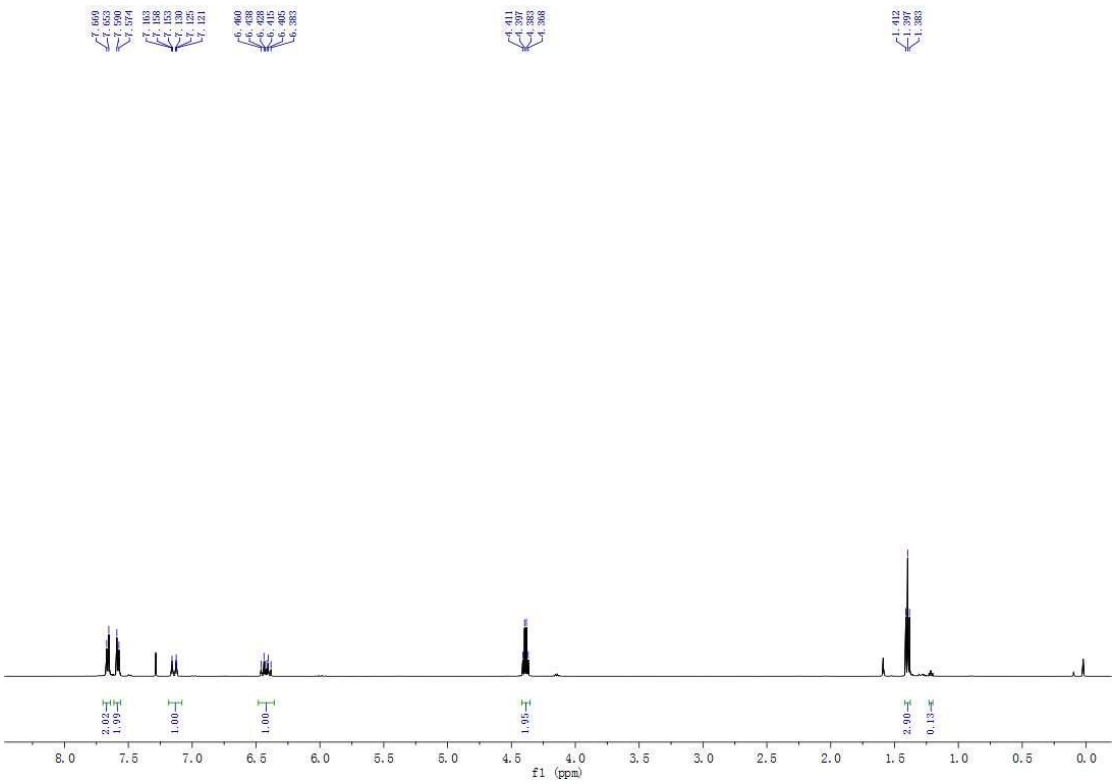

f1 (ppm)

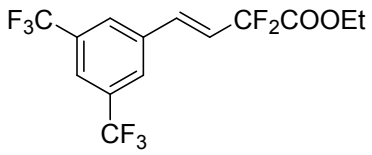

f1 (ppm)



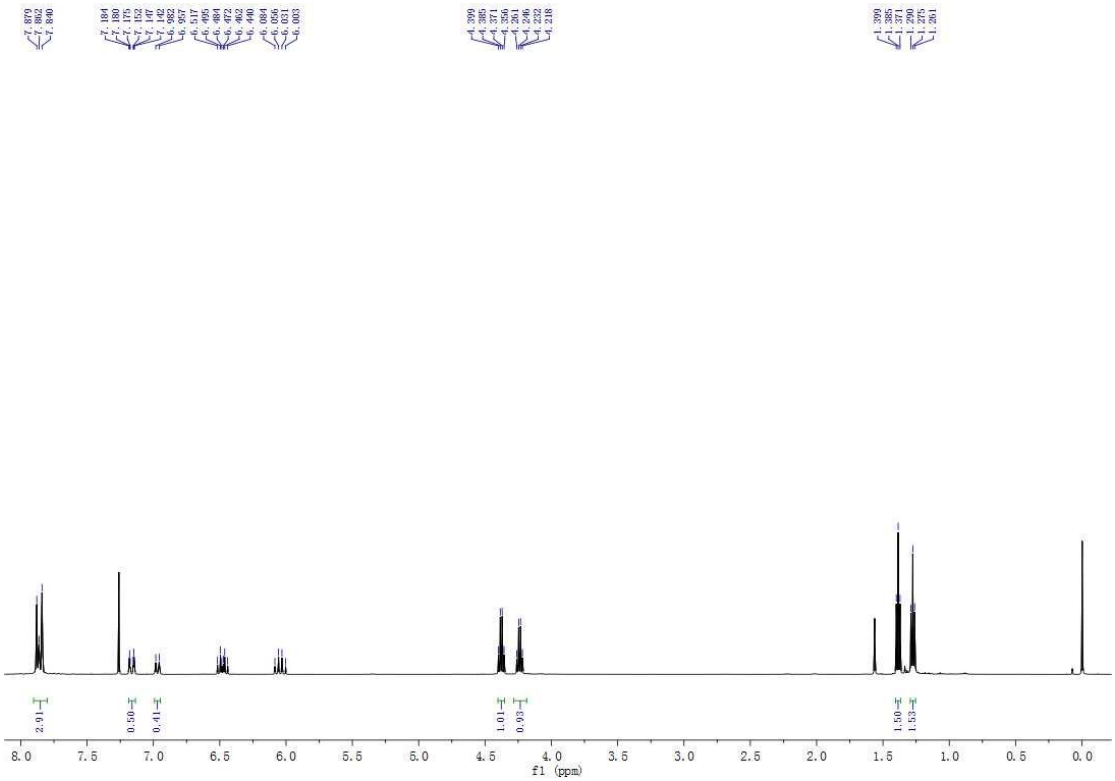


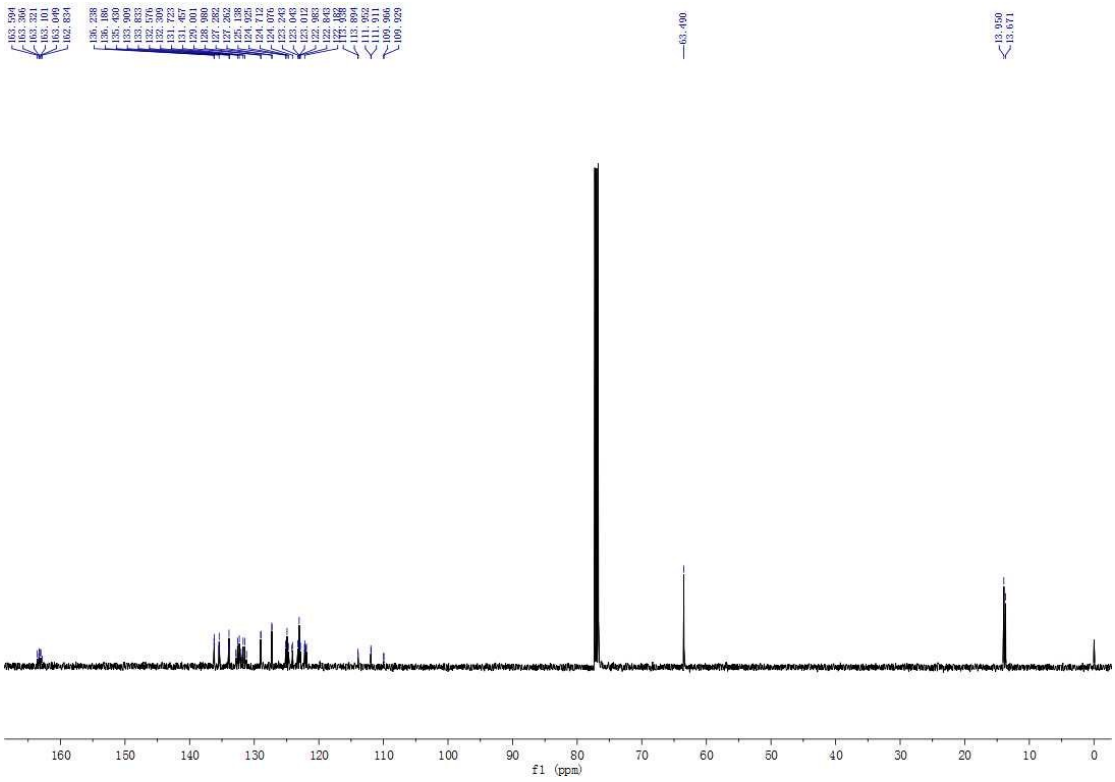
Ethyl (E)-2, 2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (18, *E/Z*=25:1) from alkynyl carboxylic acid

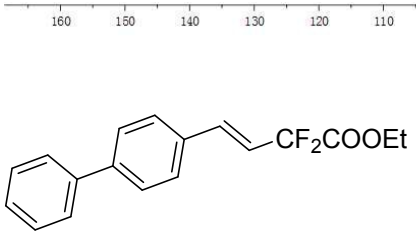




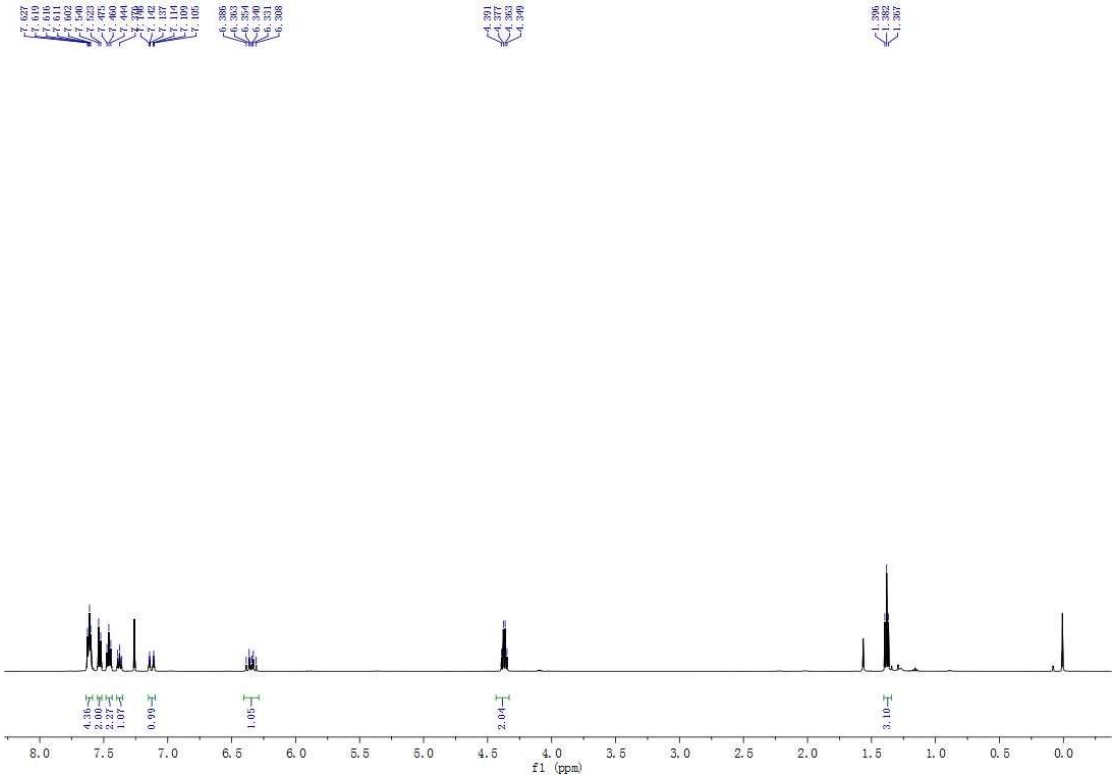
Ethyl (E)-4-(3, 5-bis(trifluoromethyl)phenyl)-2, 2-difluorobut-3-enoate(19, ***E/Z*** =1.2:1)

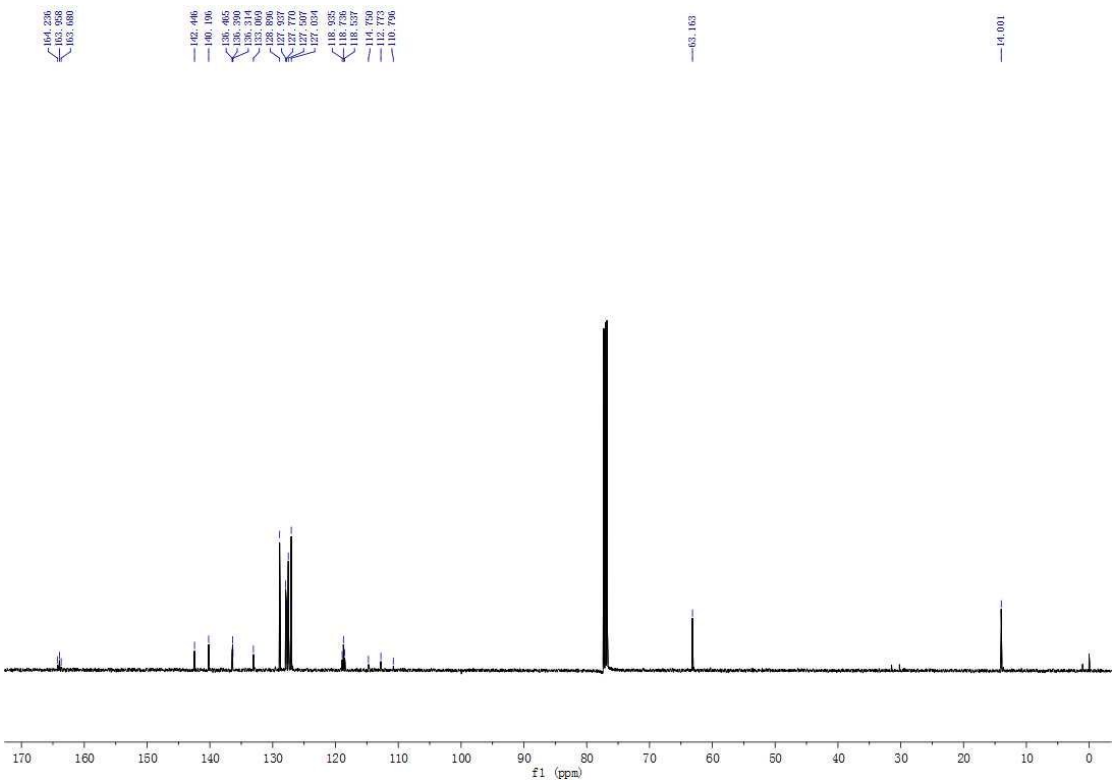





CF_2COOEt

Ethyl (E)-2, 2-difluoro-4-(4-phenyl)but-3-enoate (**20**, ***E/Z***=25:1)

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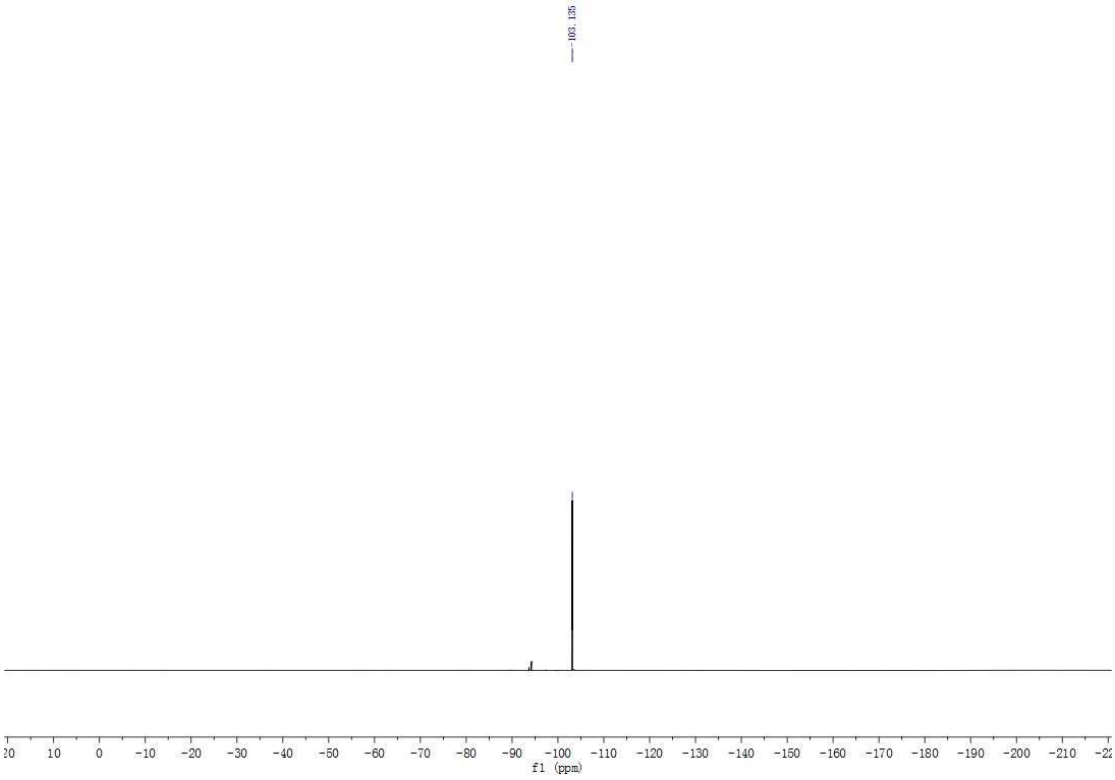
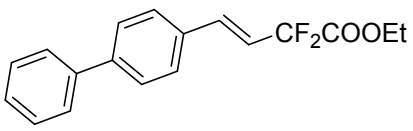
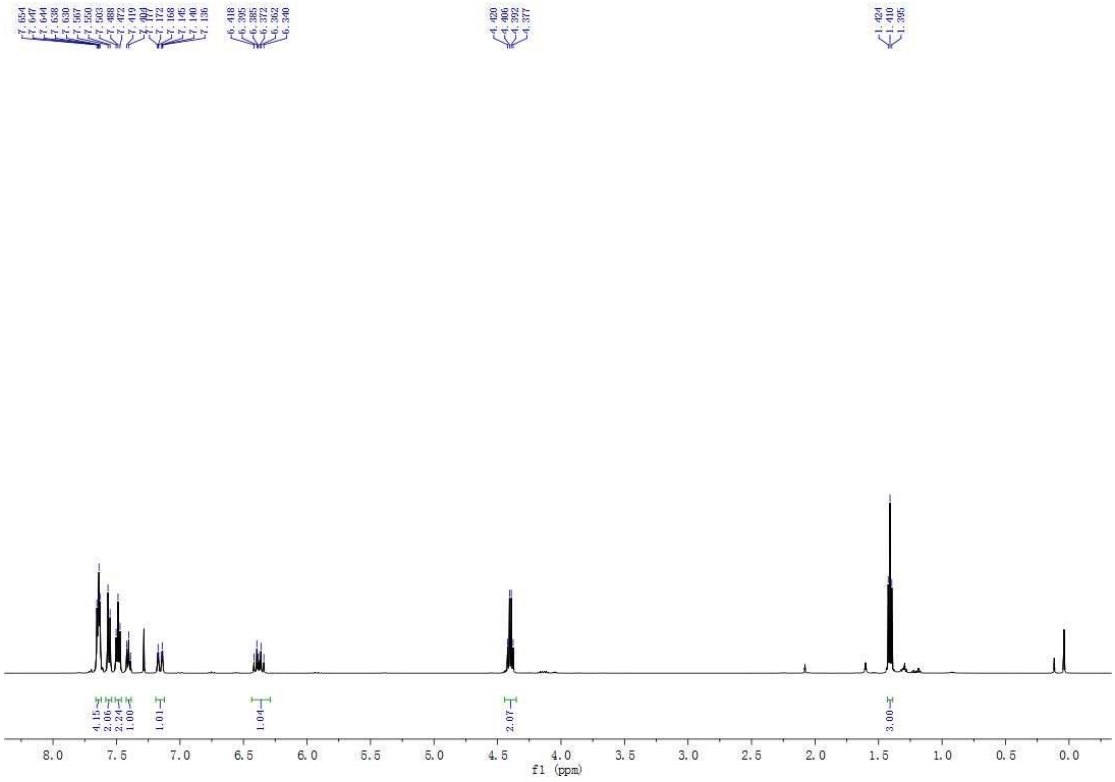
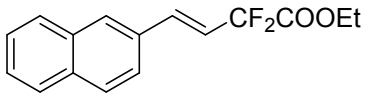
136.390
136.314
133.060
128.896
127.957
127.770
127.507
127.034
118.935
118.736
118.537
114.790
112.773
110.796
63.163
14.001
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.135
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

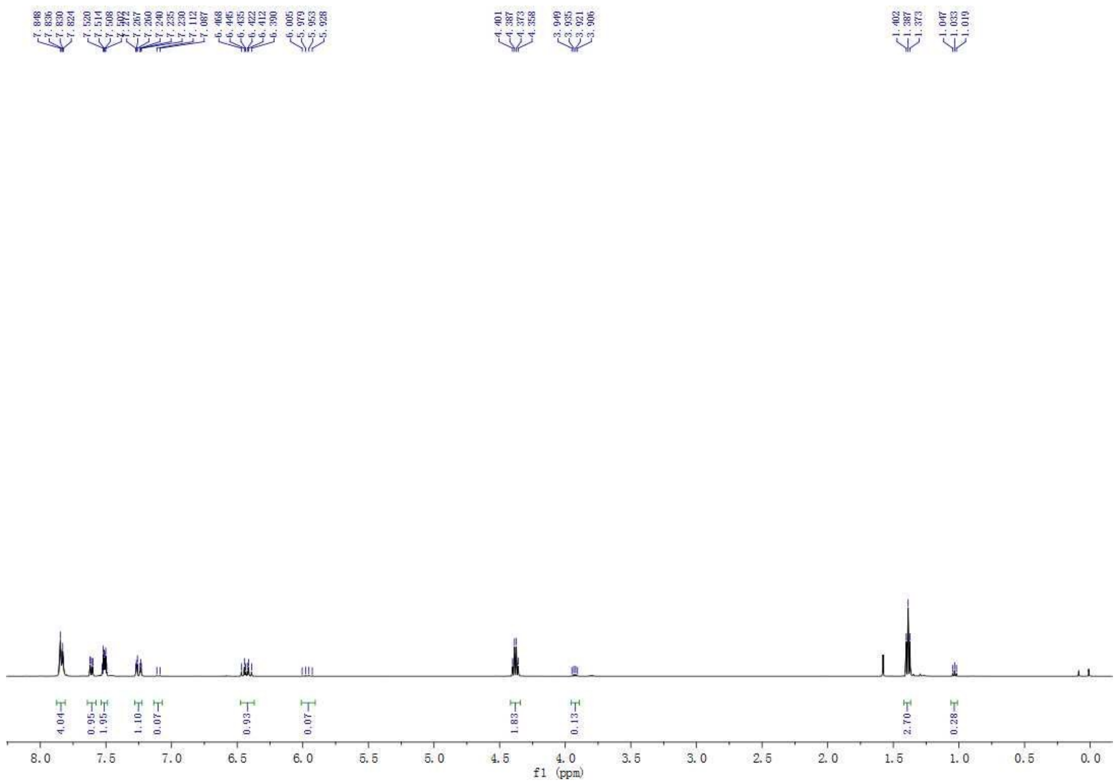

CF2COOEt

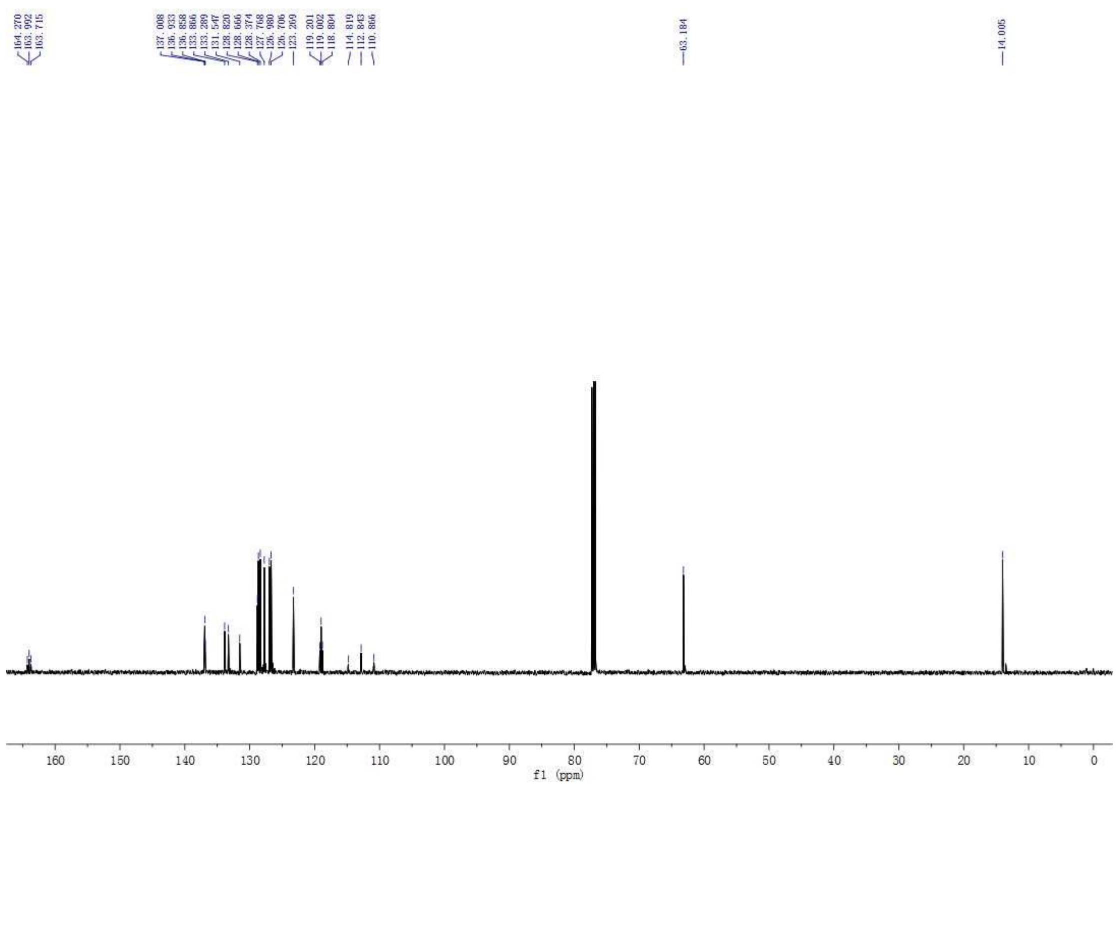
Ethyl (E)-2, 2-difluoro-4-(4-phenyl)but-3-enoate from alkynyl carboxylic acid(20)

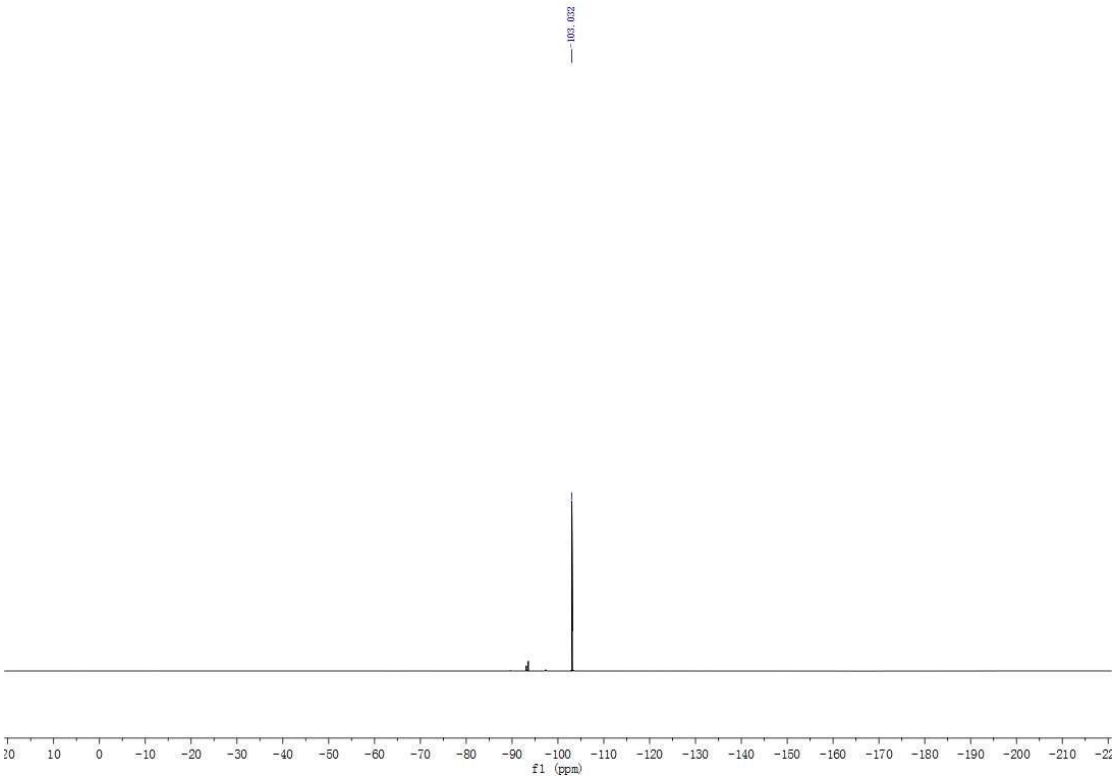


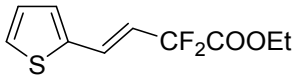


Ethyl (E)-2, 2-difluoro-4-(naphthalen-2-yl)but-3-enoate (**21**, ***E/Z***=10:1)

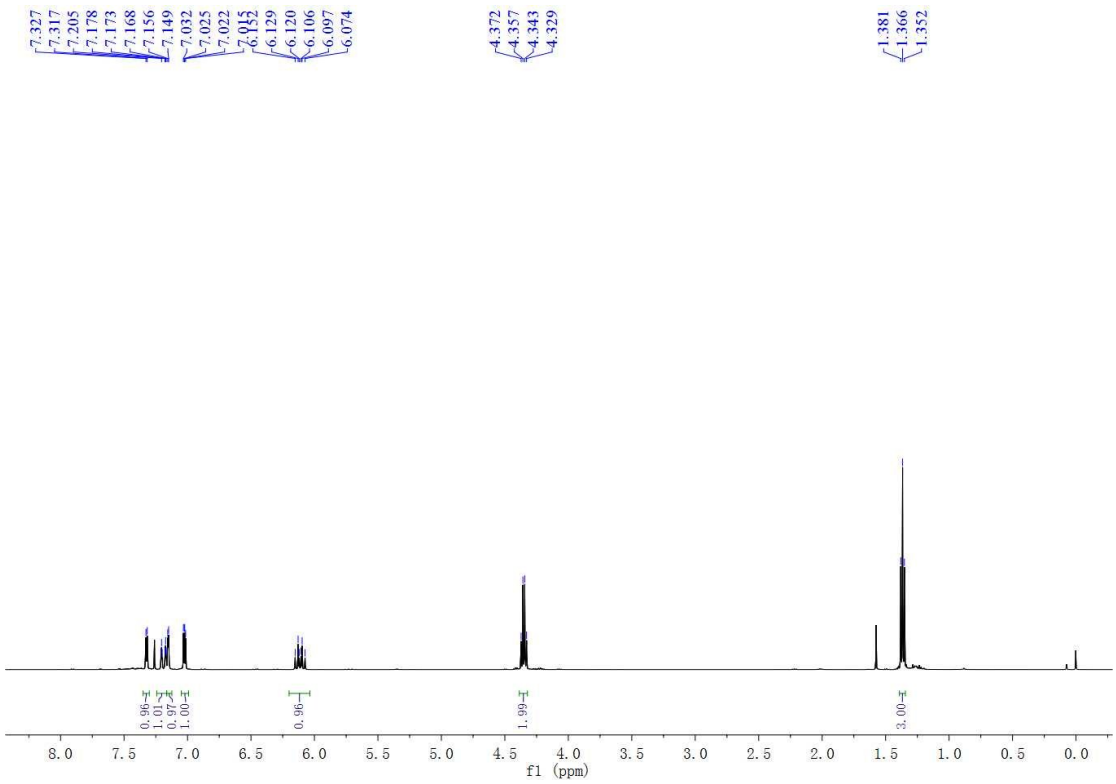


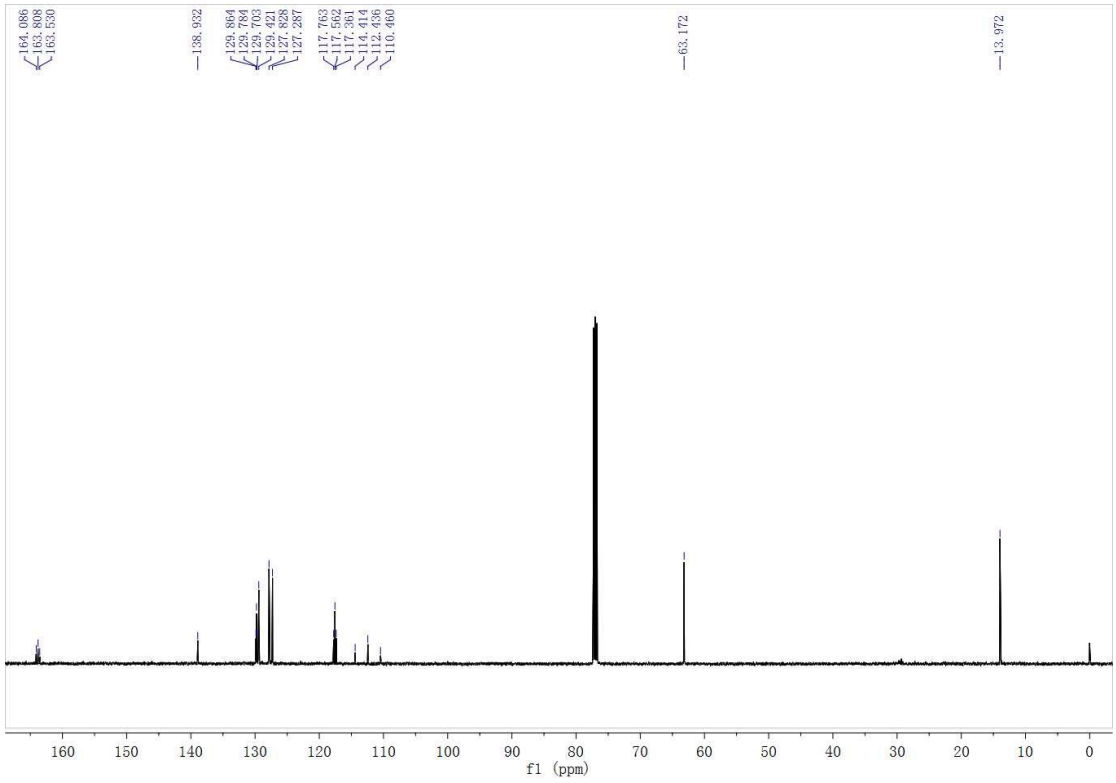


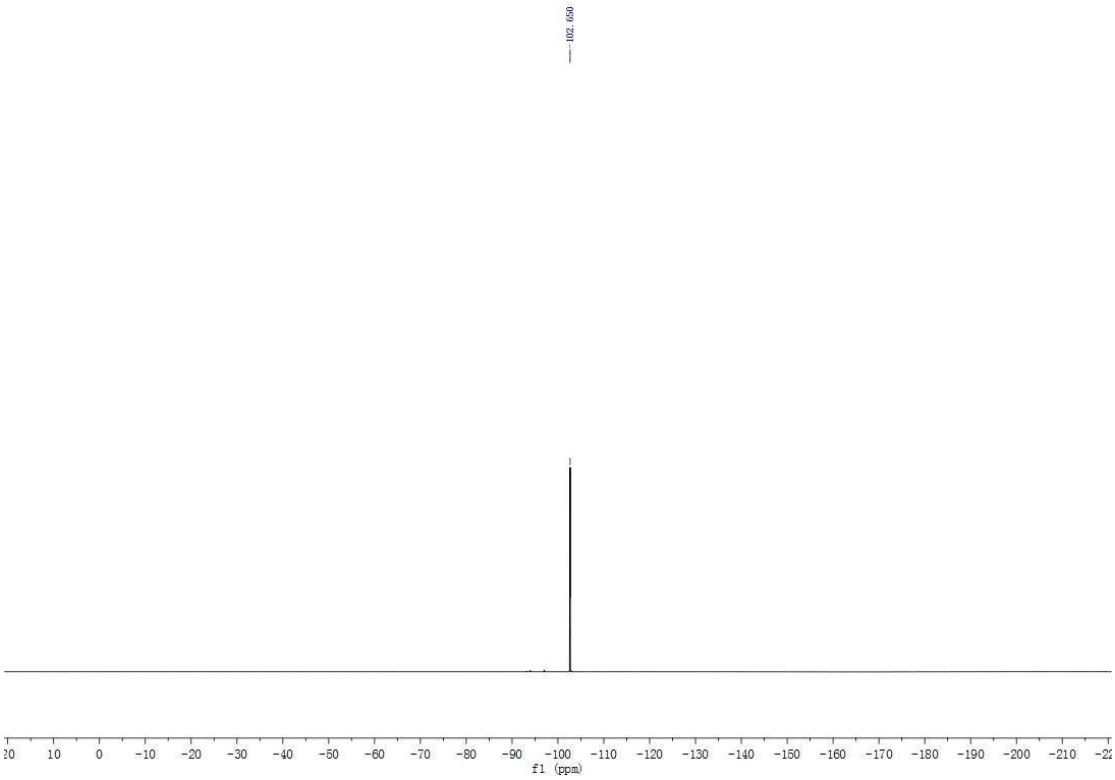


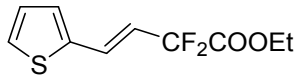


Ethyl (*E*)-2, 2-difluoro-4-(thiophen-2-yl)but-3-enoate (22)

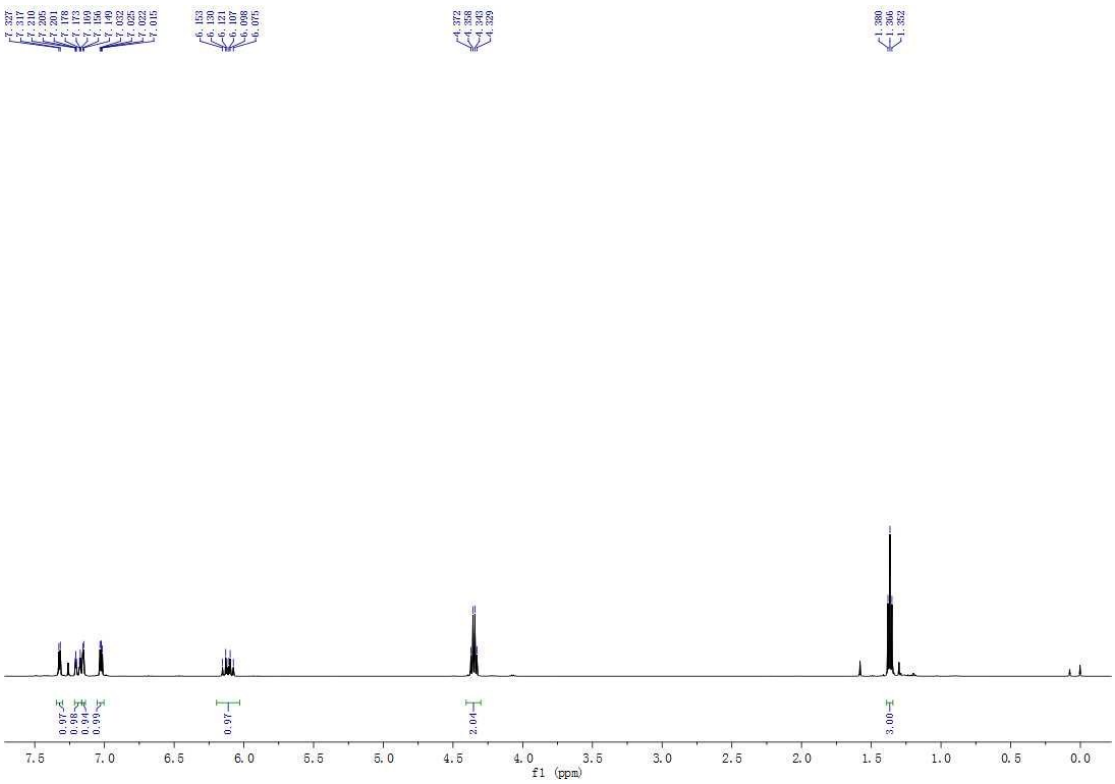

7.327
7.317
7.205
7.178
7.173
7.168
7.156
7.149
7.032
7.025
7.022
6.129
6.120
6.106
6.097
6.074
4.372
4.357
4.343
4.329
1.381
1.366
1.352
0.96
1.01
0.97
1.00
0.96
1.99
3.00
f1 (ppm)

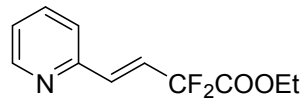

164.086
163.808
163.530
138.932
129.864
129.784
129.703
129.421
127.828
127.287
117.763
117.562
117.361
114.414
112.436
110.460
63.172
13.972
f1 (ppm)



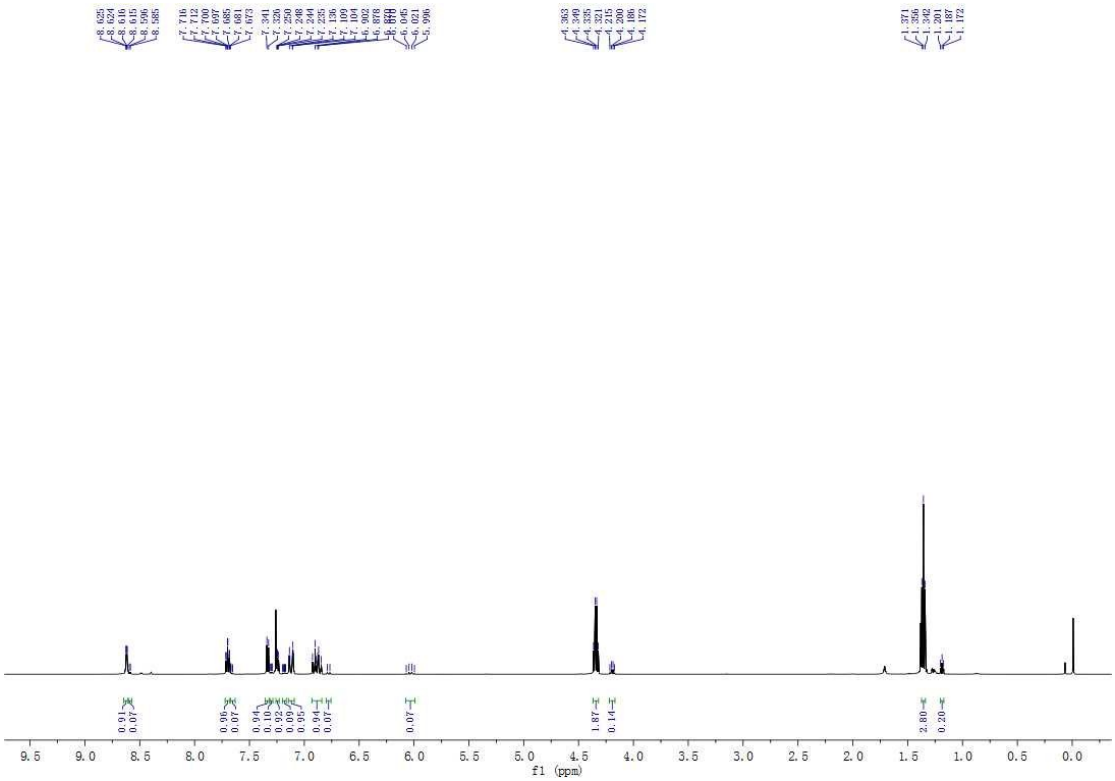


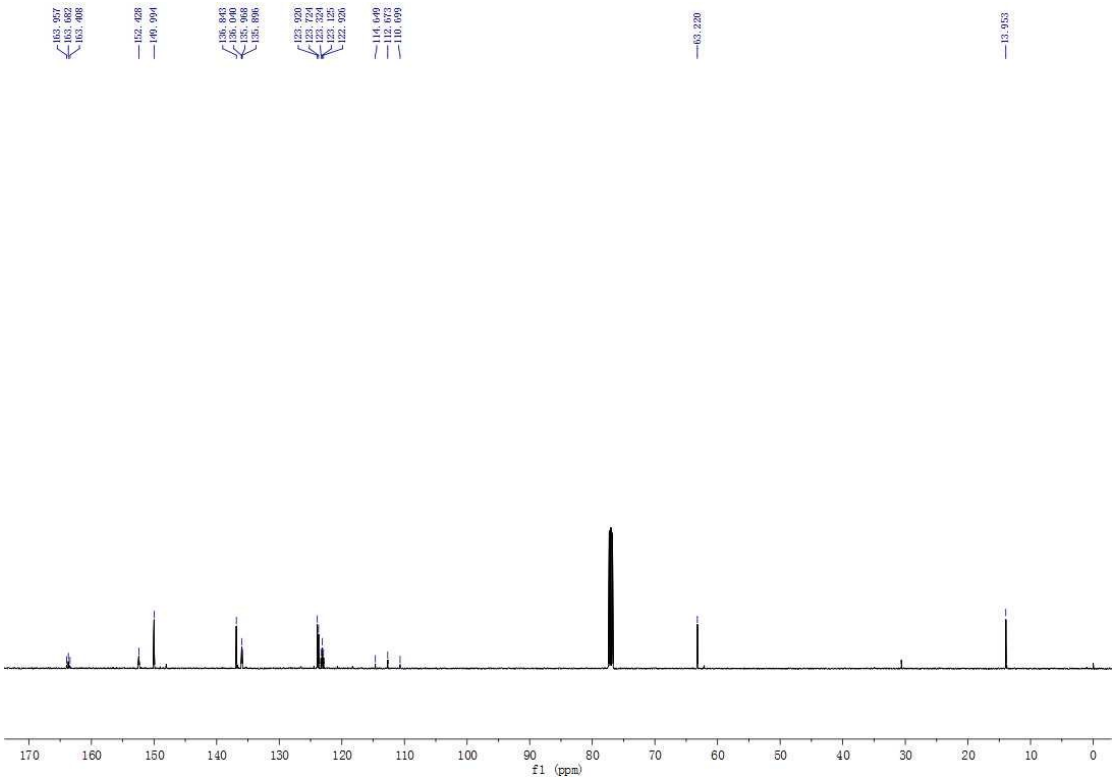
Ethyl (*E*)-2, 2-difluoro-4-(thiophen-2-yl)but-3-enoate from alkynyl carboxylic acid(22)

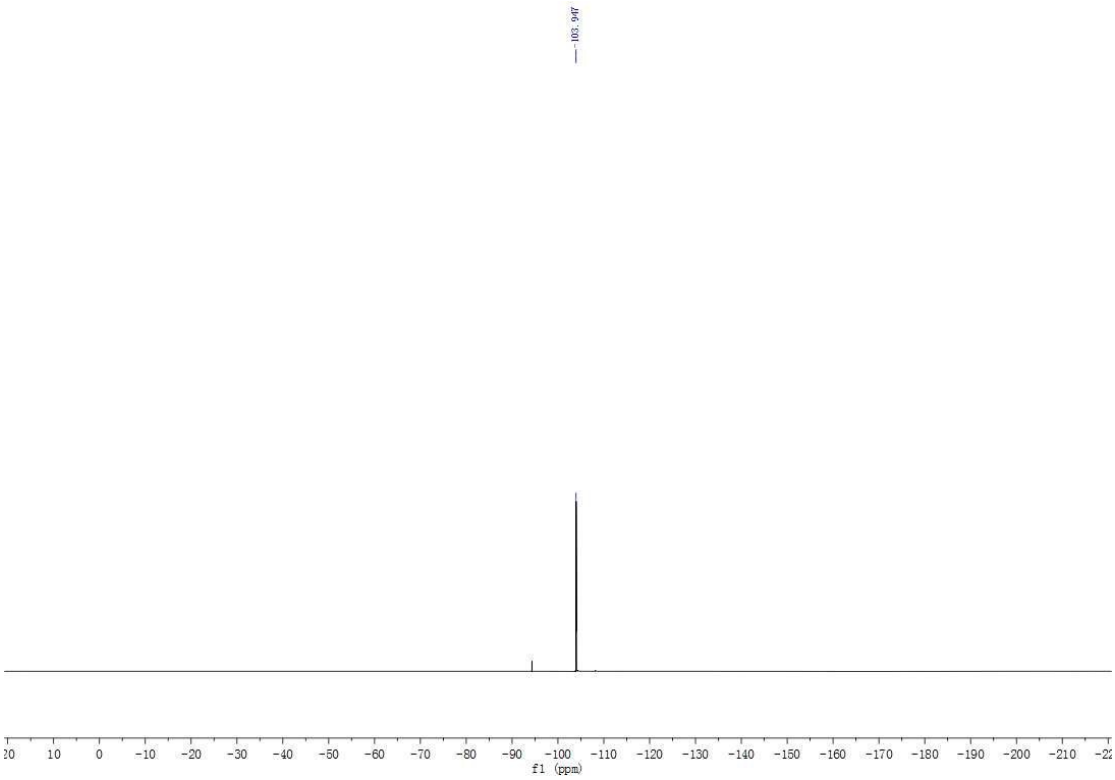


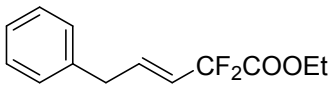


Ethyl (E)-2, 2-difluoro-4-(pyridin-2-yl)but-3-enoate (23)

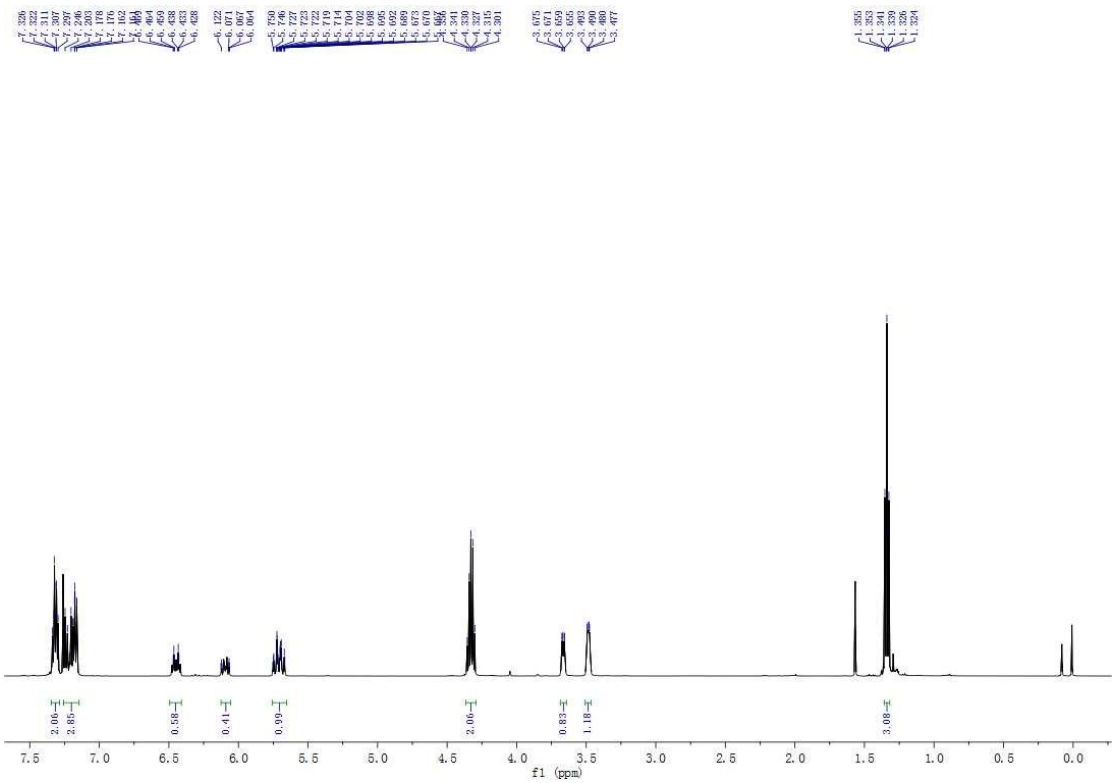

8.625
8.624
8.616
8.615
8.596
8.595
7.716
7.712
7.700
7.697
7.685
7.681
7.673
7.341
7.326
7.250
7.248
7.244
7.235
7.136
7.109
7.104
7.093
6.878
6.045
6.021
5.996
4.363
4.360
4.335
4.321
4.215
4.200
4.186
4.172
1.371
1.356
1.342
1.201
1.187
1.172
0.91
0.07
0.96
0.07
0.94
0.10
0.92
0.09
0.95
0.94
0.07
0.07
1.87
0.14
2.80
0.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

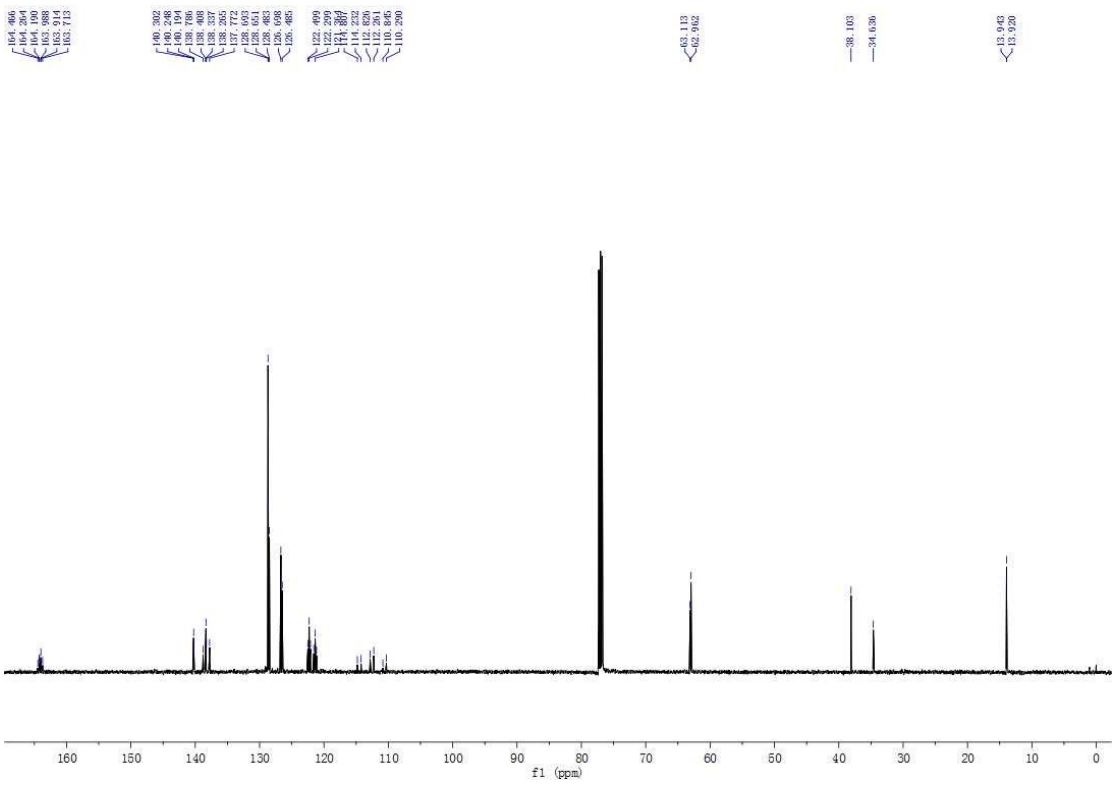

163.957
163.682
163.408
152.428
149.994
136.843
136.090
135.968
135.896
123.920
123.774
123.324
123.125
122.926
114.649
112.673
110.699
63.220
13.953
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

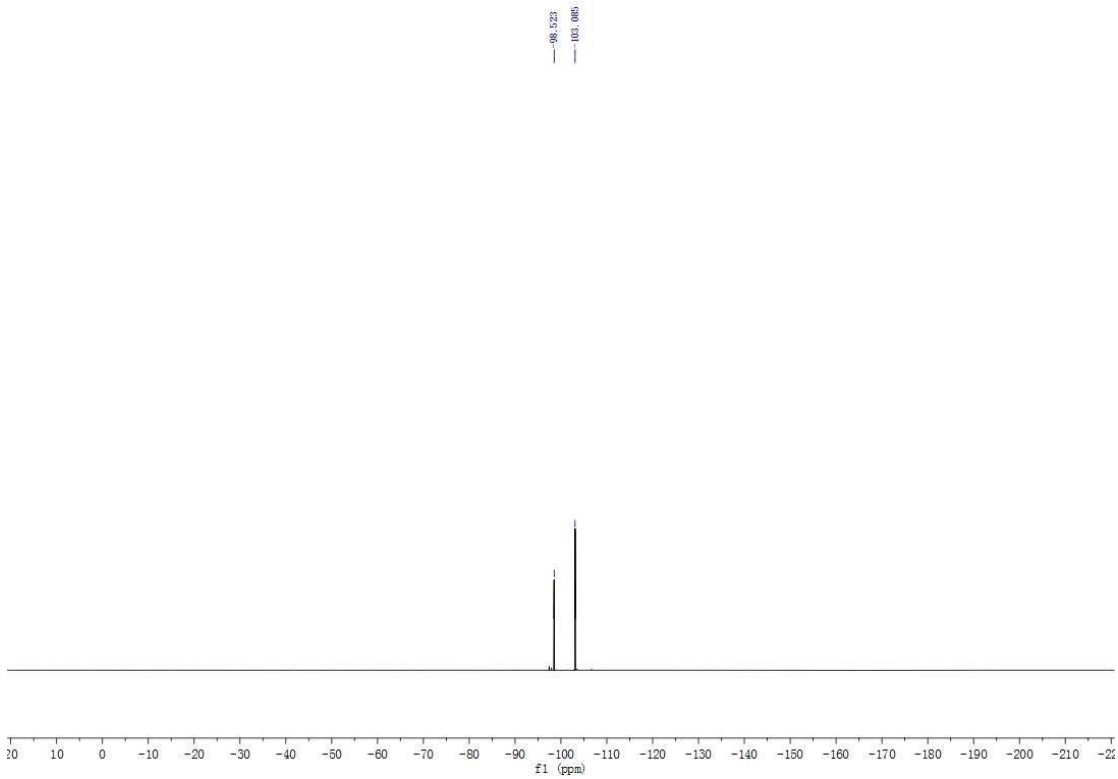


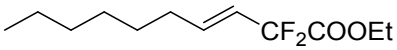


Ethyl (E)-2, 2-difluoro-5-phenylpent-3-enoate (**24**, ***E/Z***=1: 1)

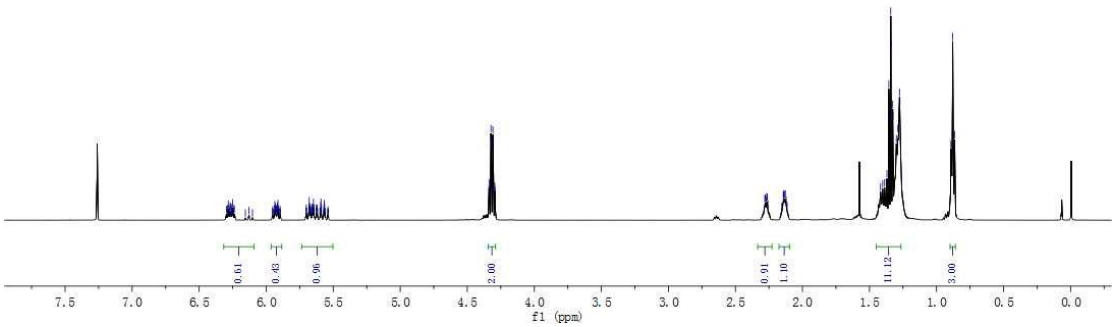


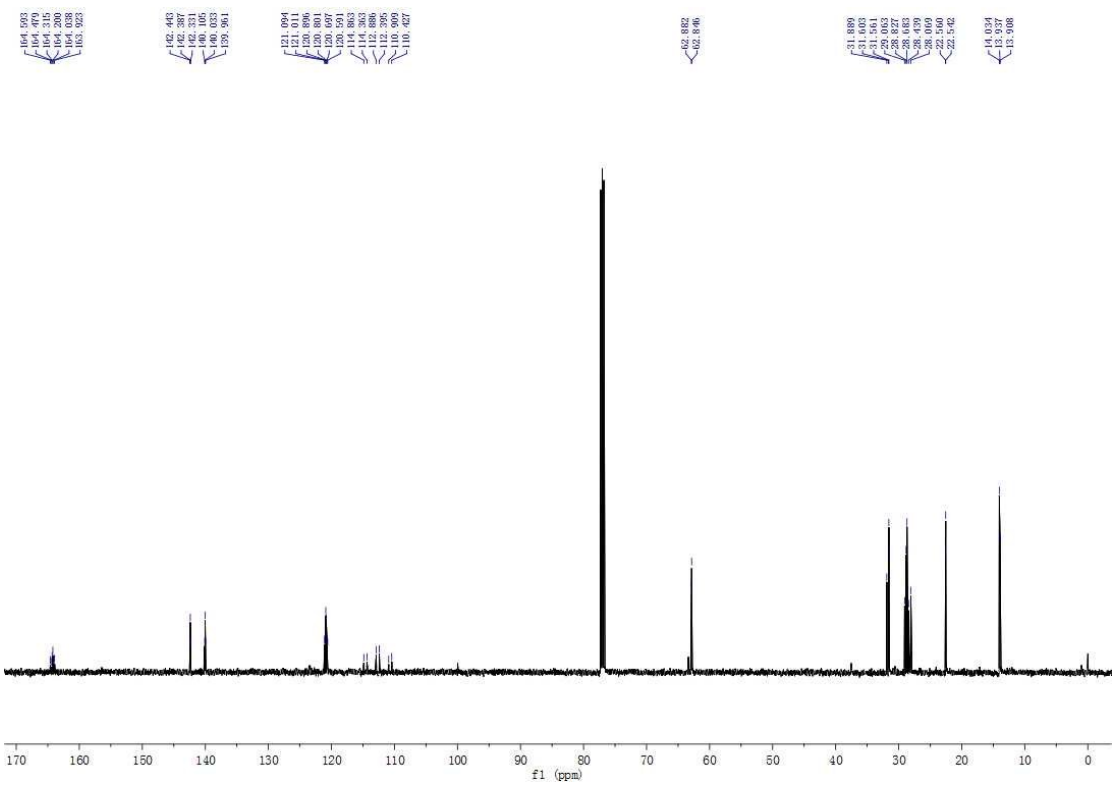


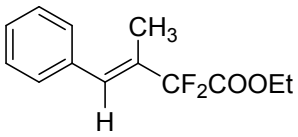




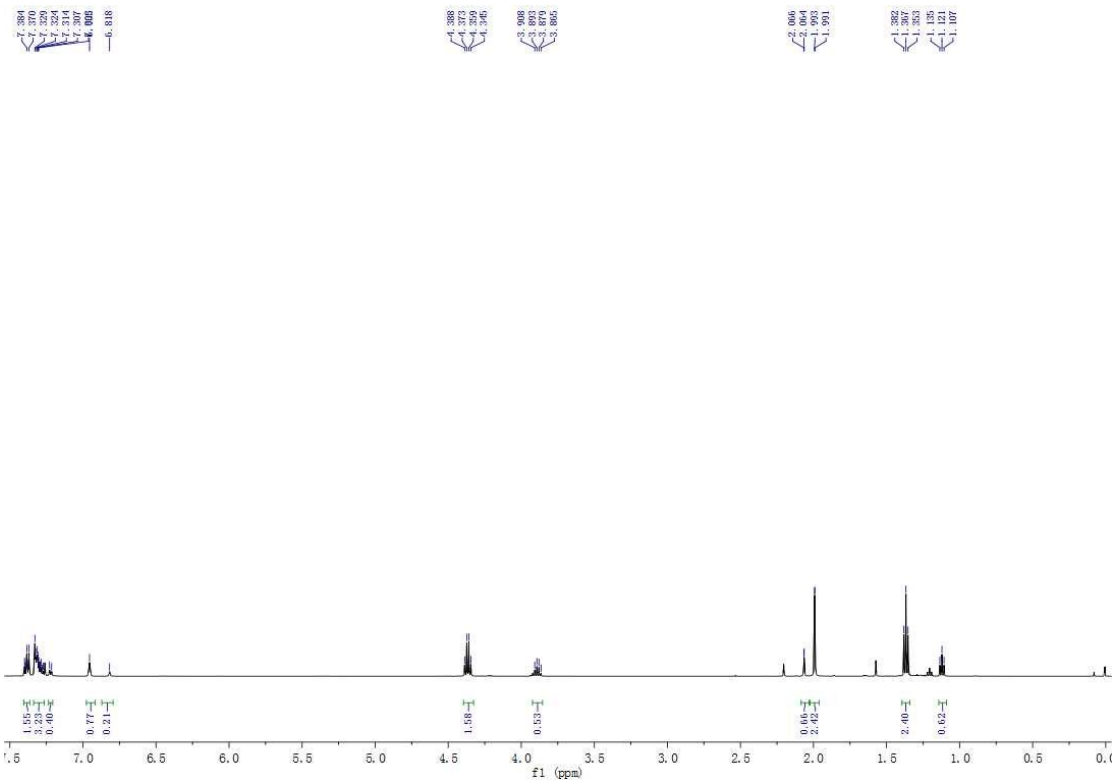
Ethyl (E)-2, 2-difluorodec-3-enoate (**25**, ***E/Z***=1:1)

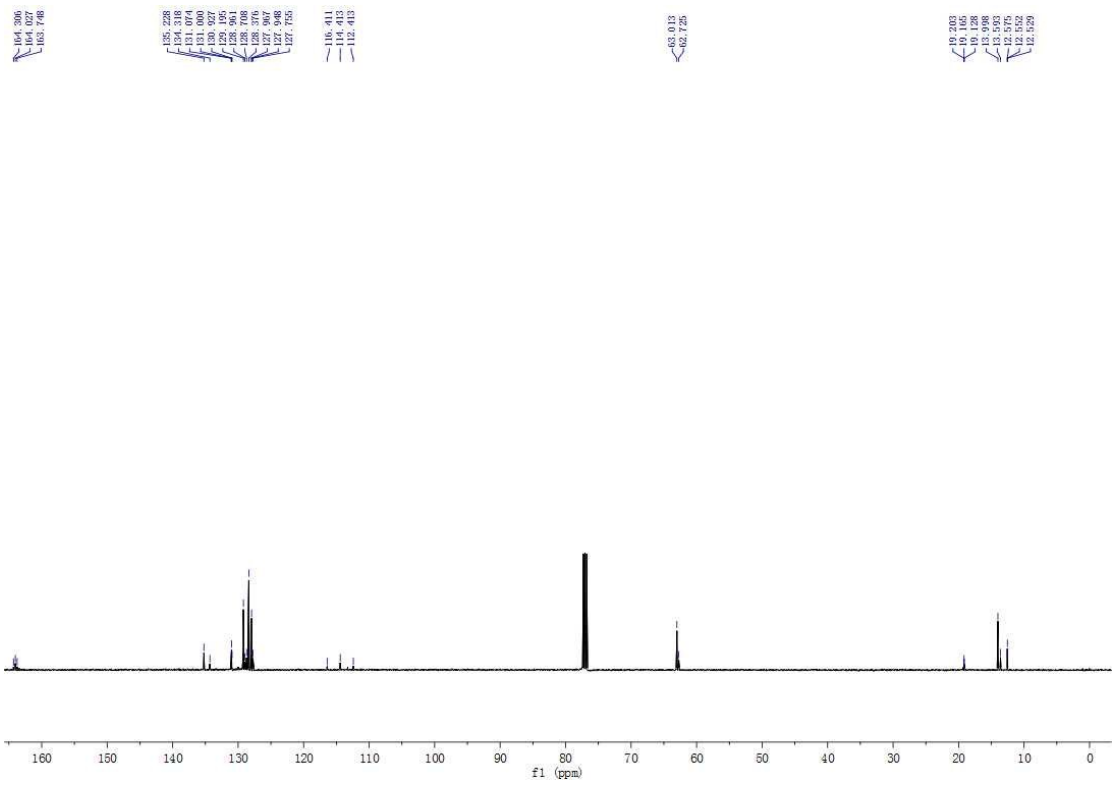

0.61
0.43
0.96
2.00
0.91
1.10
11.12
3.00
f1 (ppm)

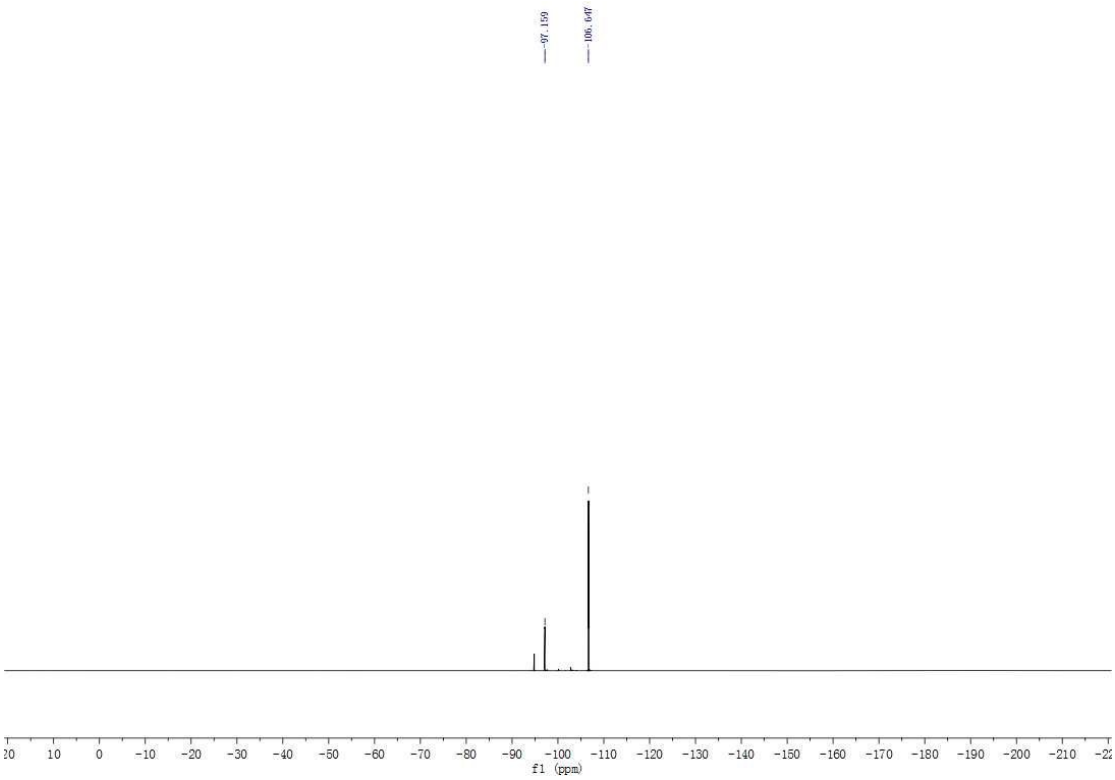

f1 (ppm)

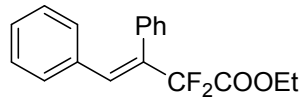


Ethyl (E)-2, 2-difluoro-3-methyl-4-phenylbut-3-enoate (**26**, ***E/Z***=4:1)

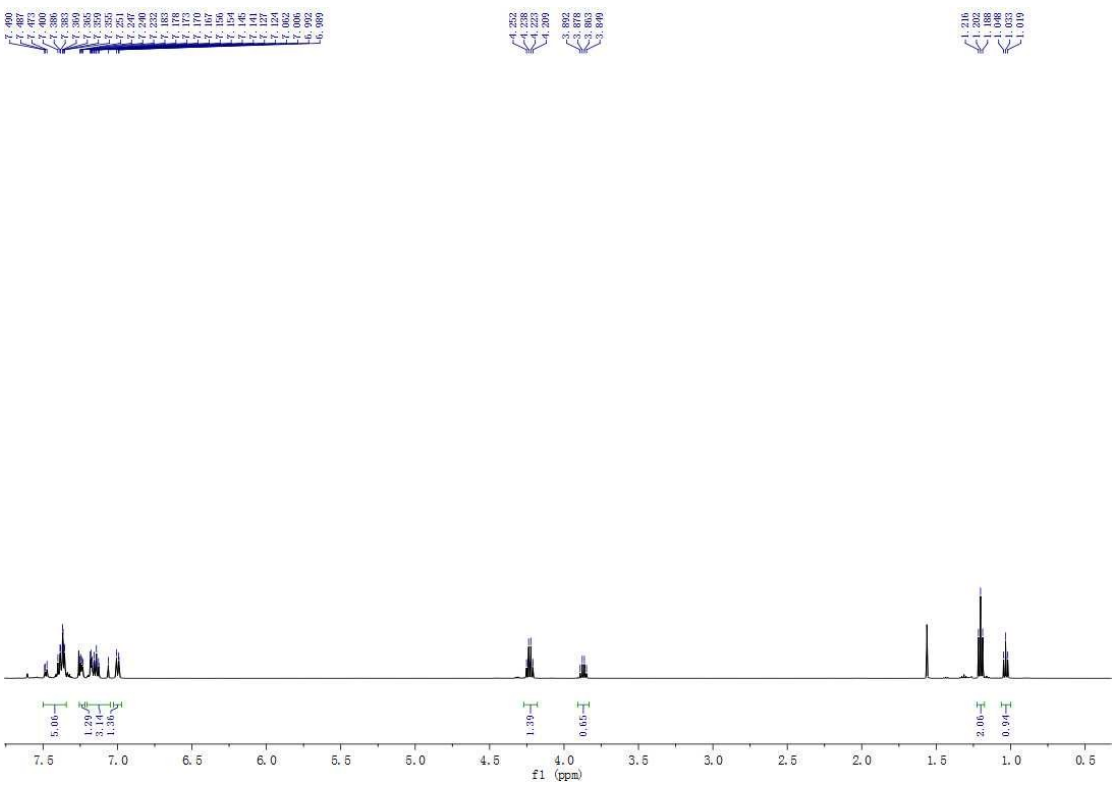

7.384
7.370
7.339
7.324
7.314
7.307
6.818
4.388
4.375
4.359
4.345
3.908
3.893
3.879
3.865
2.066
2.064
2.063
1.991
1.382
1.367
1.353
1.135
1.121
1.107
1.55
3.23
0.40
0.77
0.21
1.58
0.53
0.66
2.42
2.40
0.62
f1 (ppm)

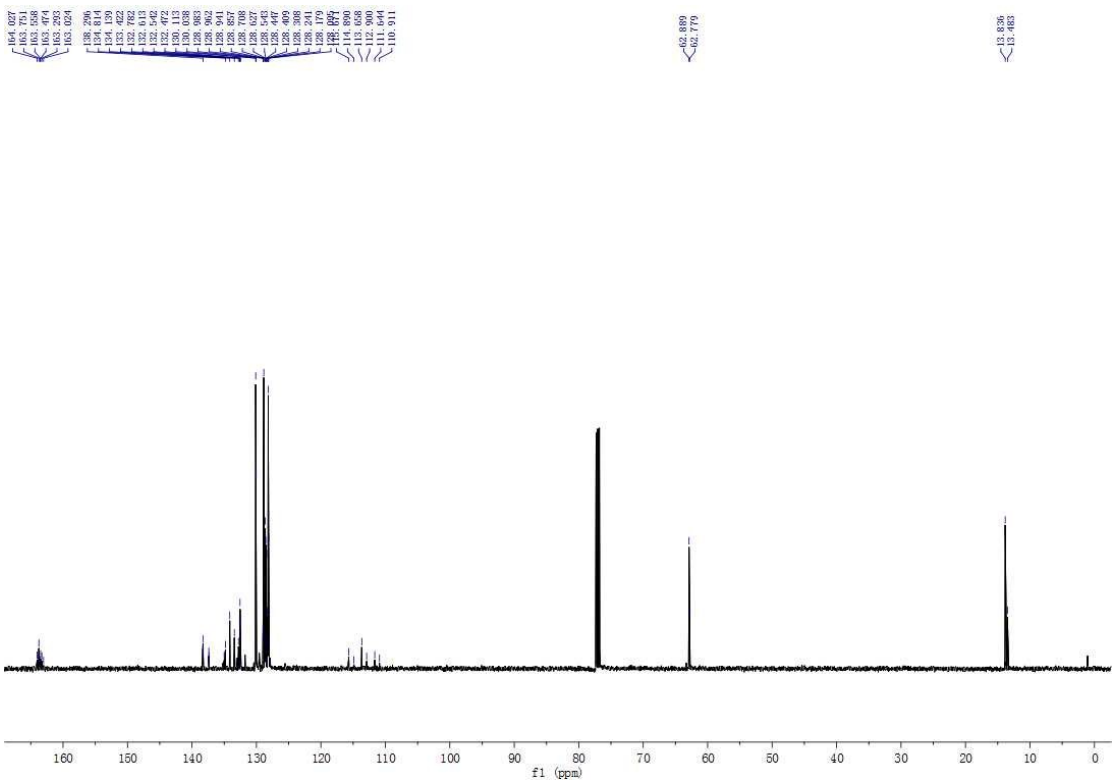

164.306
164.077
163.748
135.228
134.318
131.074
131.000
130.977
129.195
128.961
128.708
128.376
127.996
127.948
127.755
116.411
114.415
112.413
63.013
62.725
19.203
19.165
19.128
13.998
13.575
12.575
12.552
12.529
f1 (ppm)

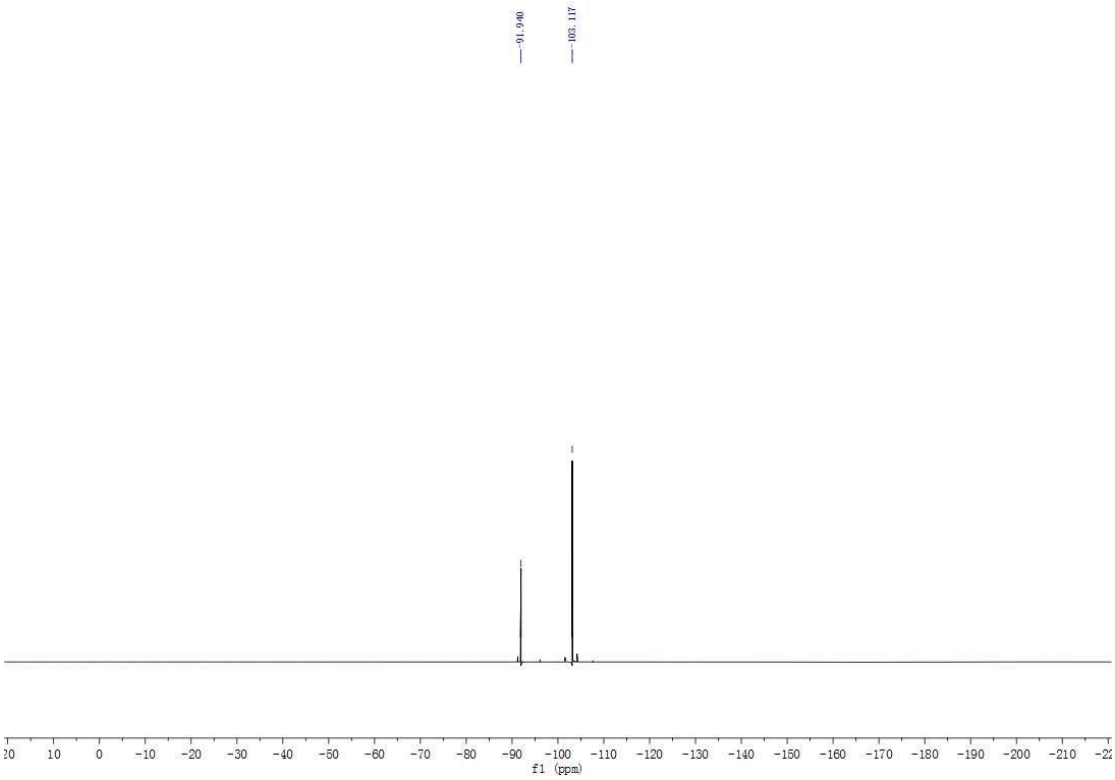


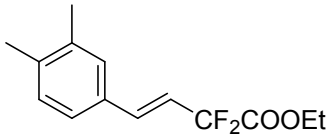


Ethyl (E)-2, 2-difluoro-3, 4-diphenylbut-3-enoate (**27**, ***E/Z***=2:1).

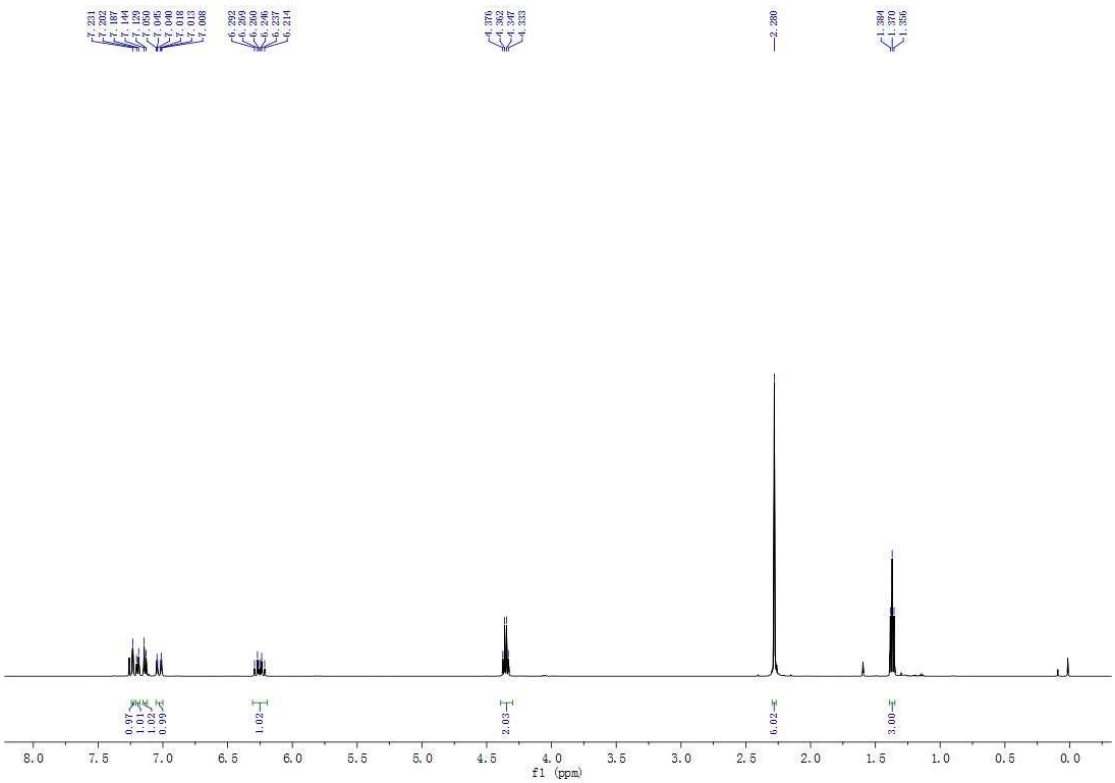


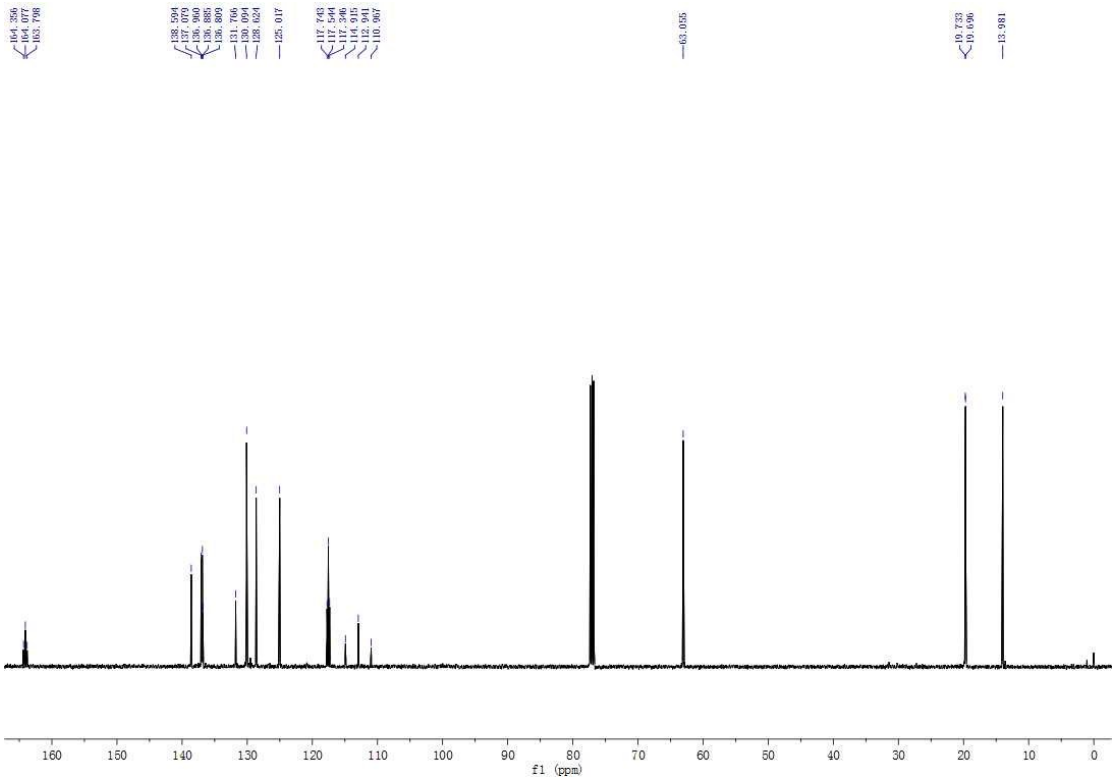


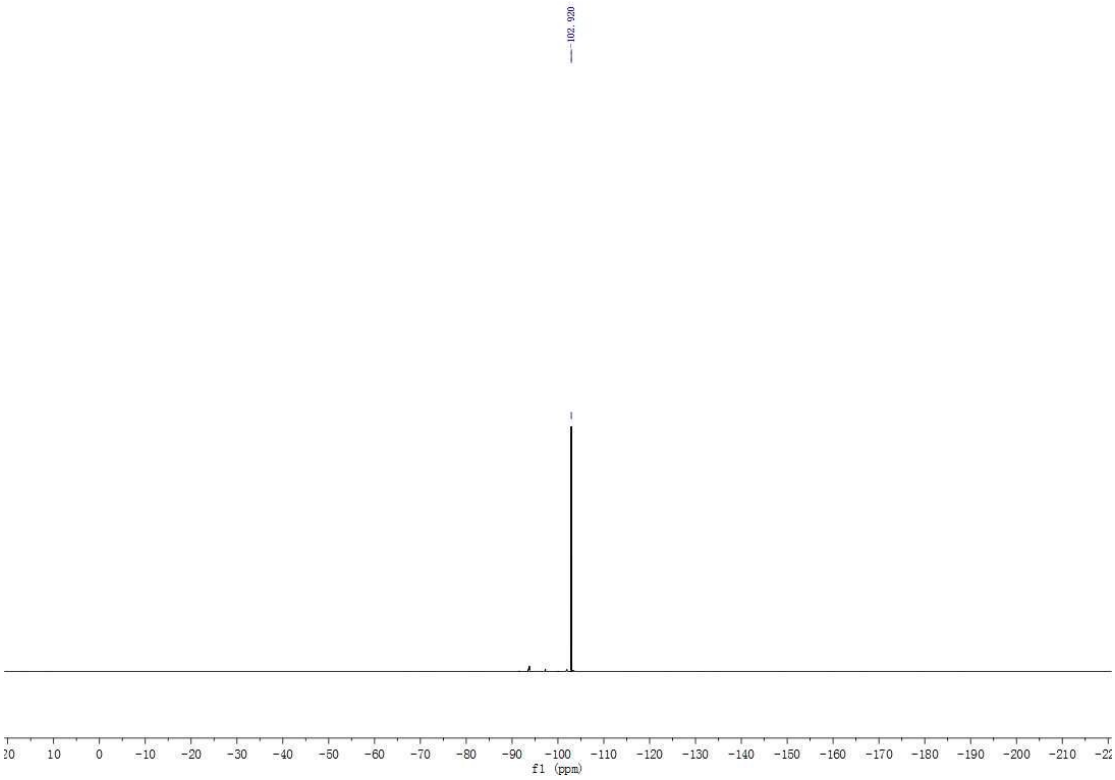


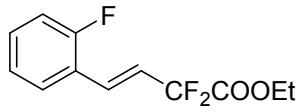


Ethyl (E)-4-(3, 4-dimethylphenyl)-2, 2-difluorobut-3-enoate (28)

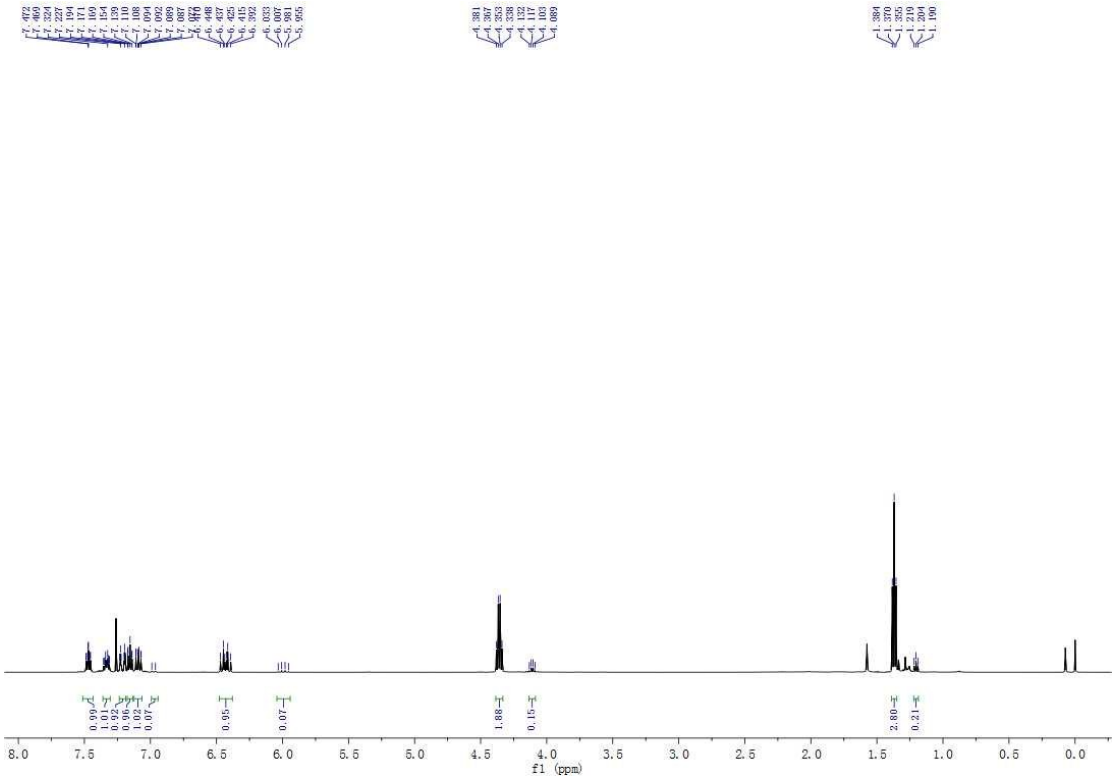

7.231
7.202
7.187
7.144
7.129
7.050
7.045
7.040
7.018
7.013
7.008
6.292
6.269
6.260
6.246
6.237
6.214
4.376
4.362
4.347
4.333
2.280
1.384
1.370
1.356
0.97
1.01
1.02
0.99
1.02
2.03
6.02
3.00
f1 (ppm)

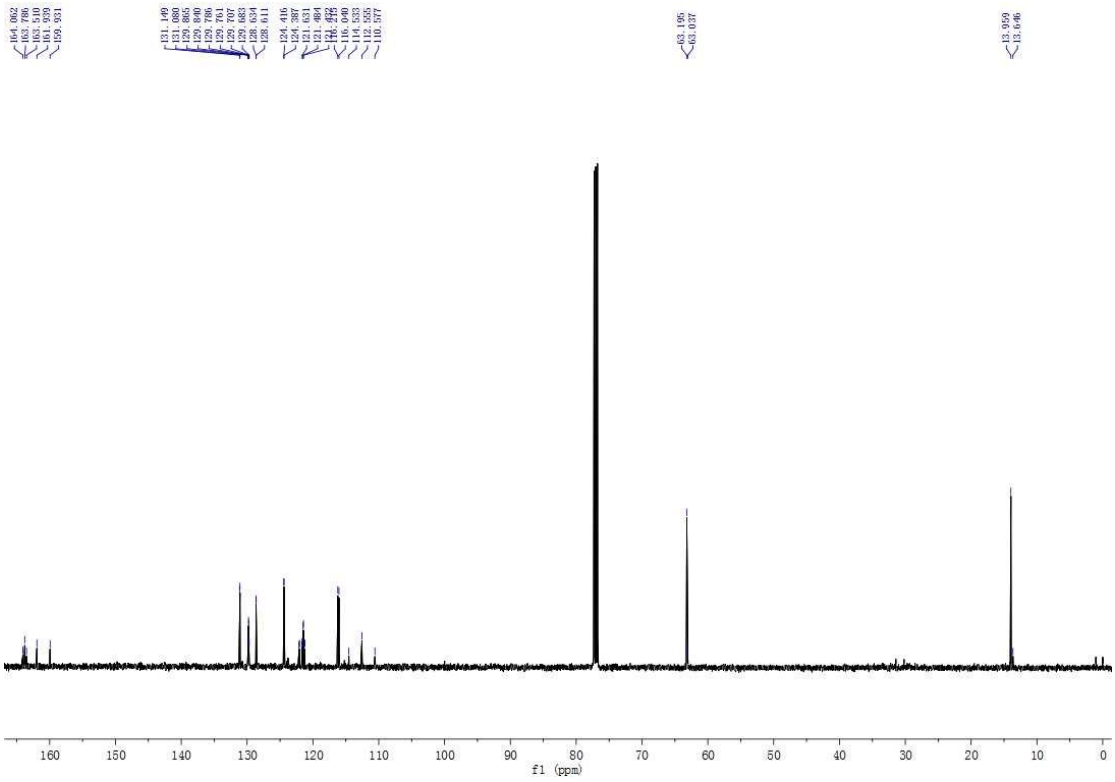

164.356
164.077
163.798
138.594
137.870
136.960
136.885
136.809
131.766
130.094
128.624
125.017
117.743
117.594
117.396
114.915
114.741
110.967
63.055
19.733
19.696
13.981
f1 (ppm)

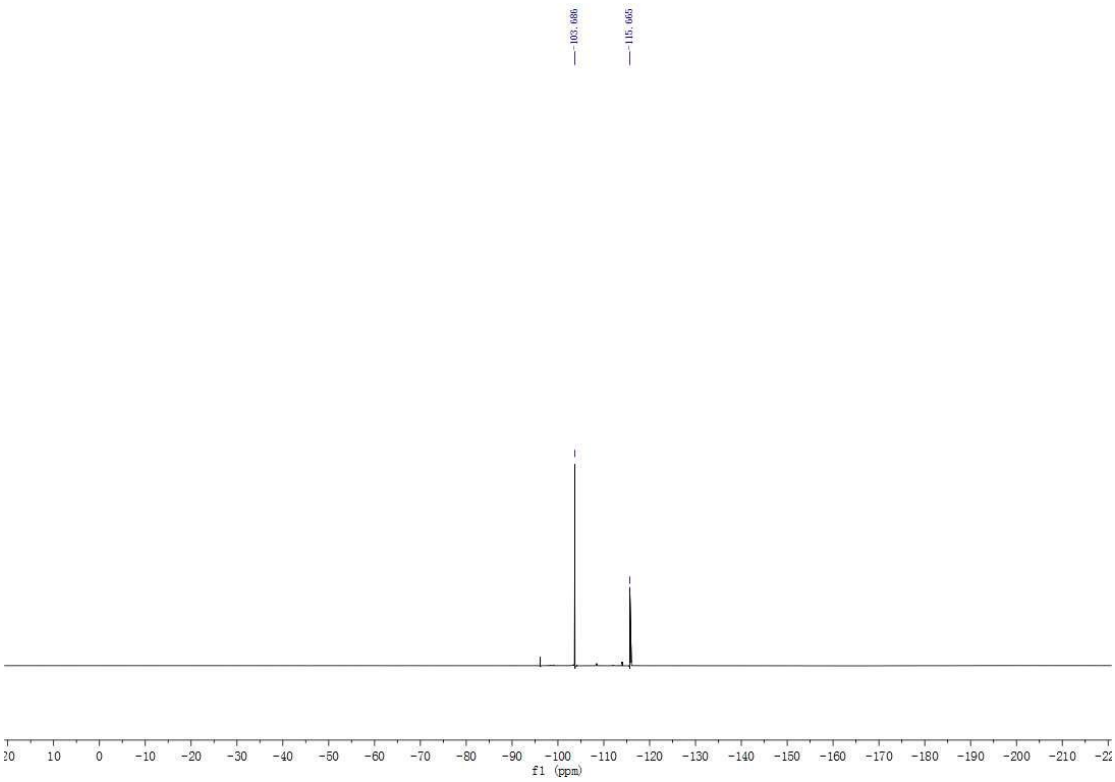


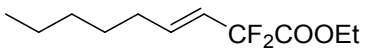


Ethyl (E)-2, 2-difluoro-4-(2-fluorophenyl)but-3-enoate (**29**, ***E/Z***=13:1)

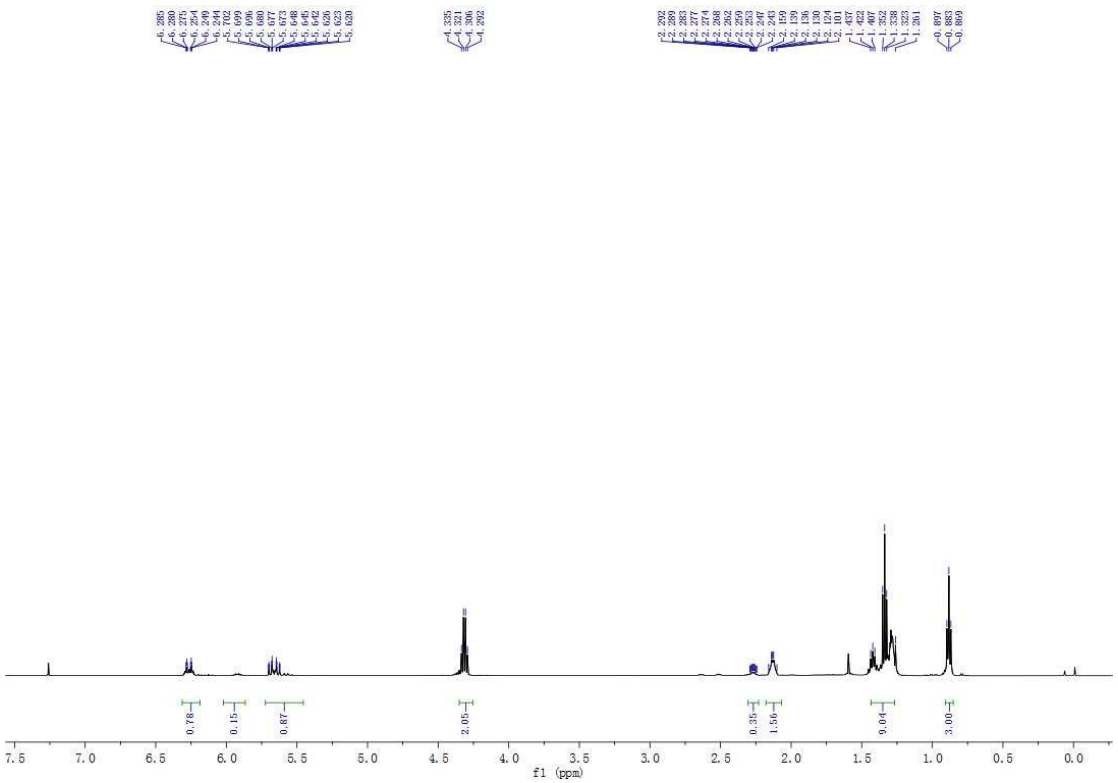

f1 (ppm)

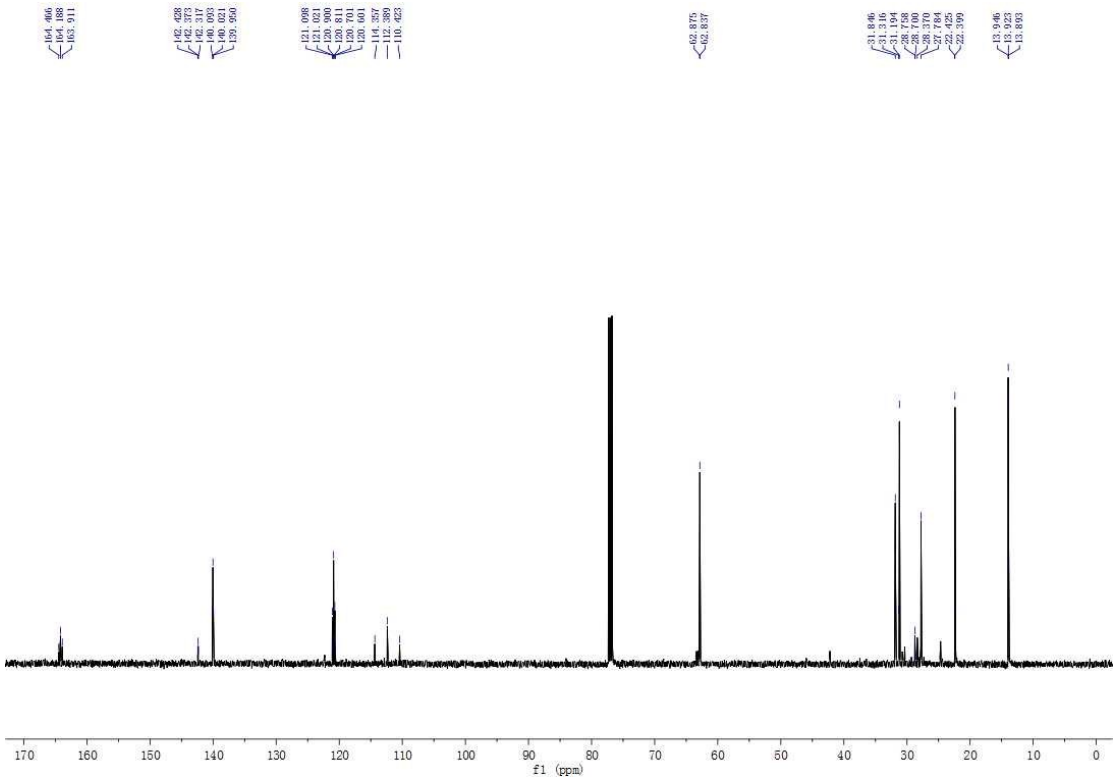

f1 (ppm)

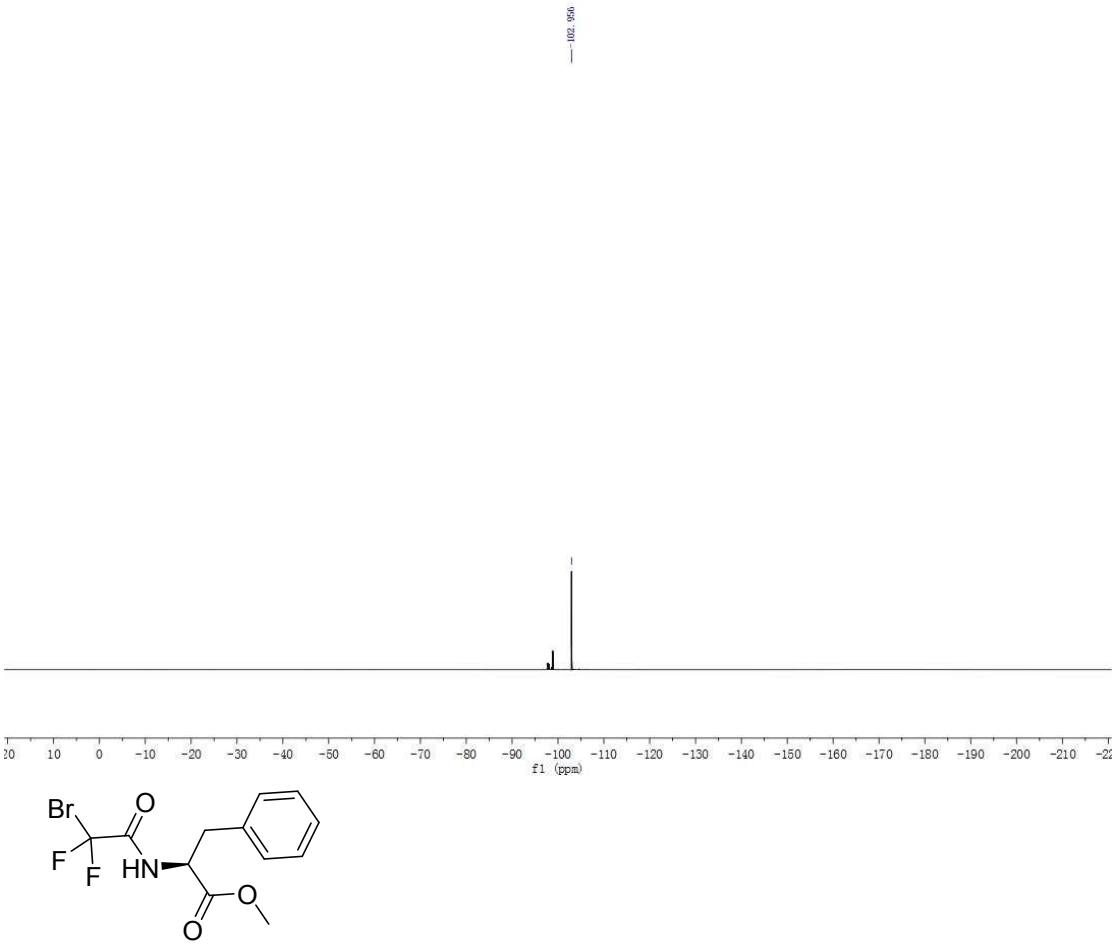




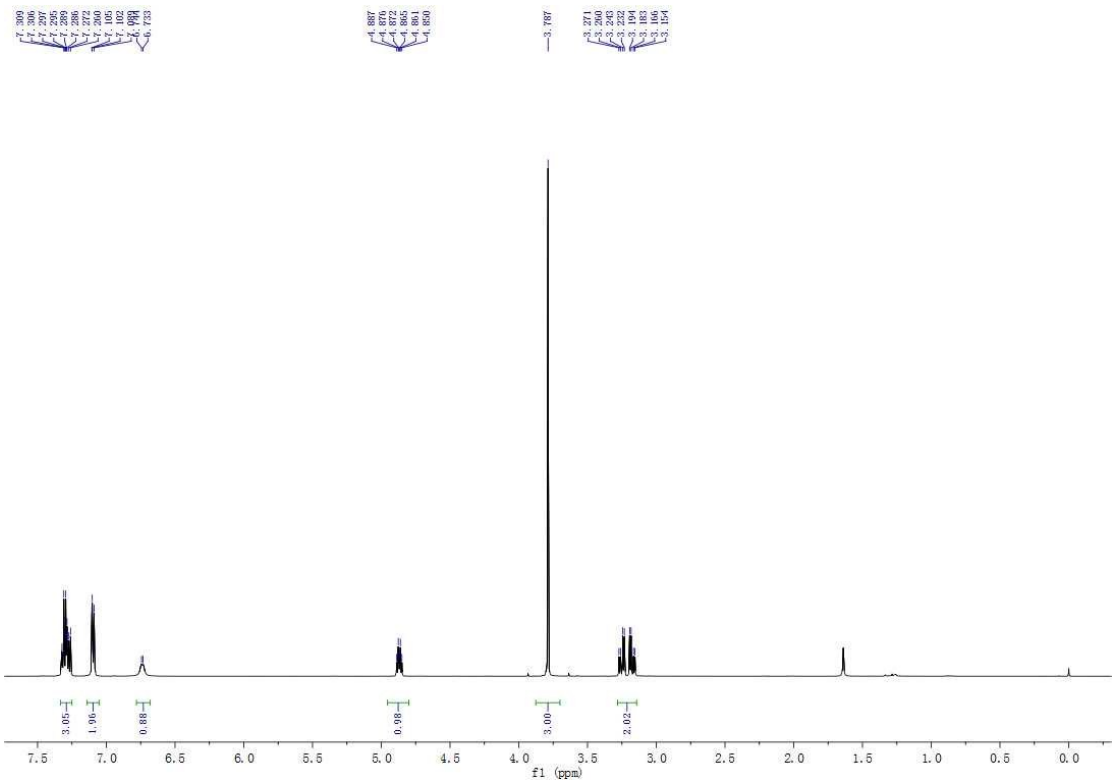
Ethyl (E)-2, 2-difluorononon-3-enoate (30)

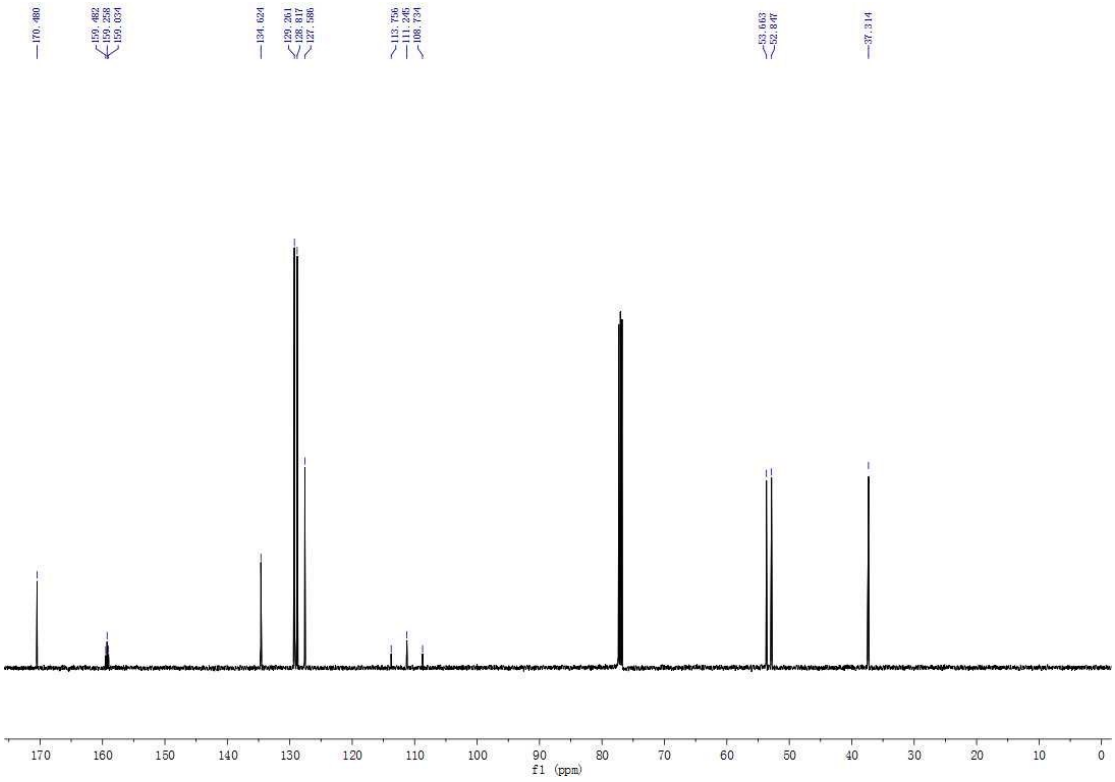

6.285
6.280
6.271
6.254
6.249
6.244
6.702
5.699
5.696
5.680
5.677
5.673
5.648
5.645
5.642
5.626
5.623
5.620
4.335
4.321
4.306
4.292
2.292
2.289
2.283
2.277
2.274
2.268
2.262
2.259
2.253
2.247
2.245
2.159
2.139
2.136
2.130
2.124
2.101
1.437
1.422
1.407
1.352
1.338
1.323
1.261
0.897
0.883
0.869
0.78
0.15
0.87
2.05
0.35
1.56
9.04
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

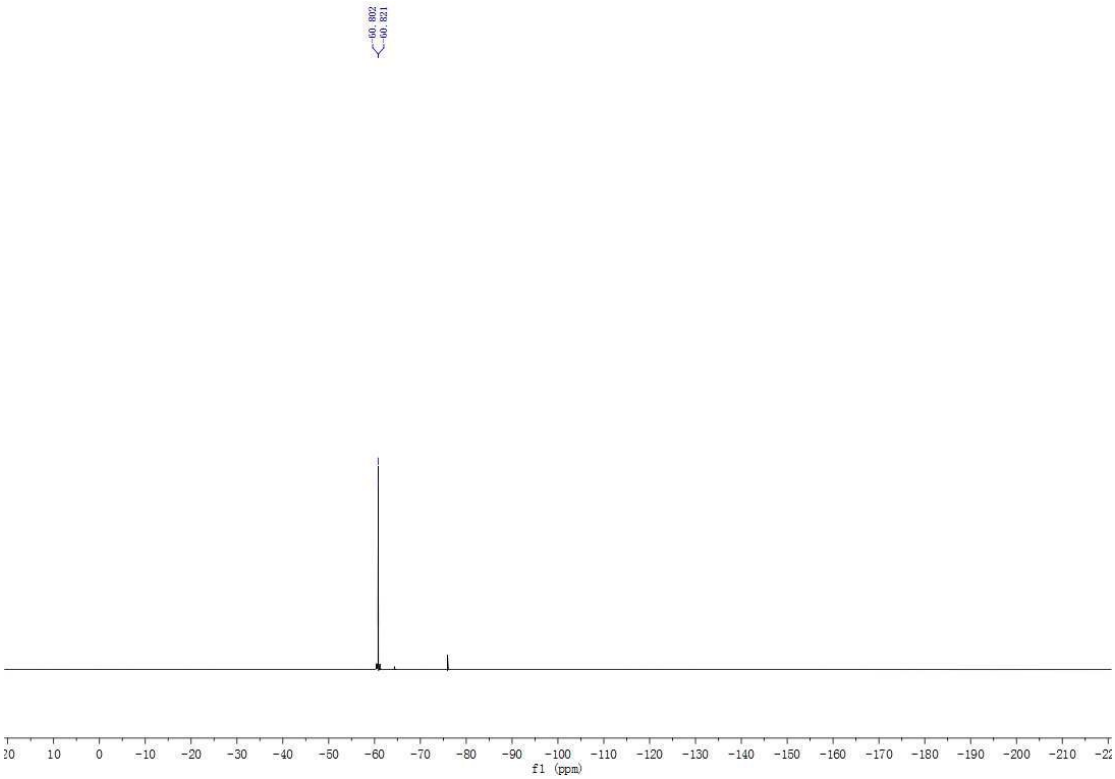

164.466
164.188
163.911
142.428
142.373
142.317
140.693
140.021
139.950
121.098
121.021
120.900
120.811
120.701
120.601
114.357
112.389
110.423
62.875
62.837
31.846
31.316
31.194
28.758
28.700
28.370
27.784
22.425
22.399
13.946
13.923
13.893
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

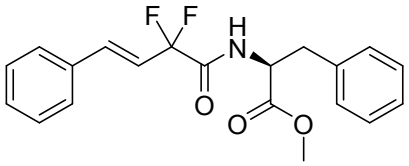


Methyl (2-bromo-2, 2-difluoroacetyl)-D-phenylalaninate (31)

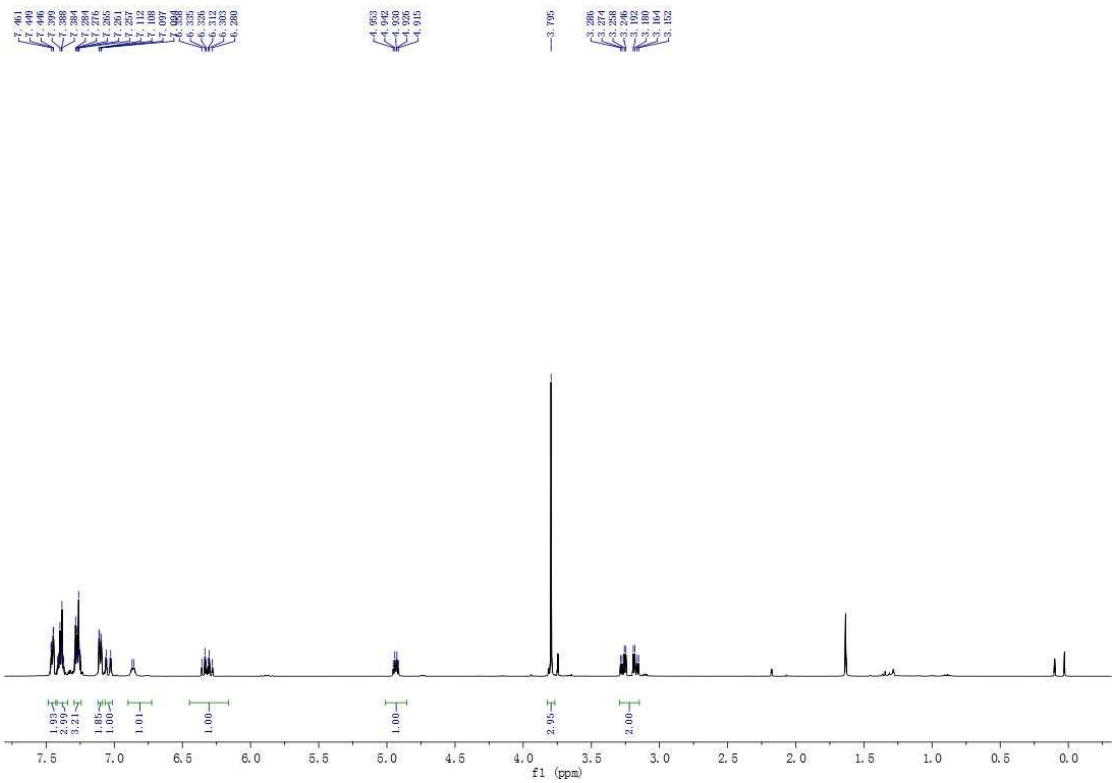

7.309
7.306
7.297
7.295
7.289
7.286
7.272
7.269
7.105
7.102
6.988
6.733
4.887
4.875
4.872
4.865
4.861
4.850
3.787
3.271
3.260
3.243
3.232
3.194
3.185
3.166
3.154
3.05
1.96
0.88
0.98
3.00
2.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

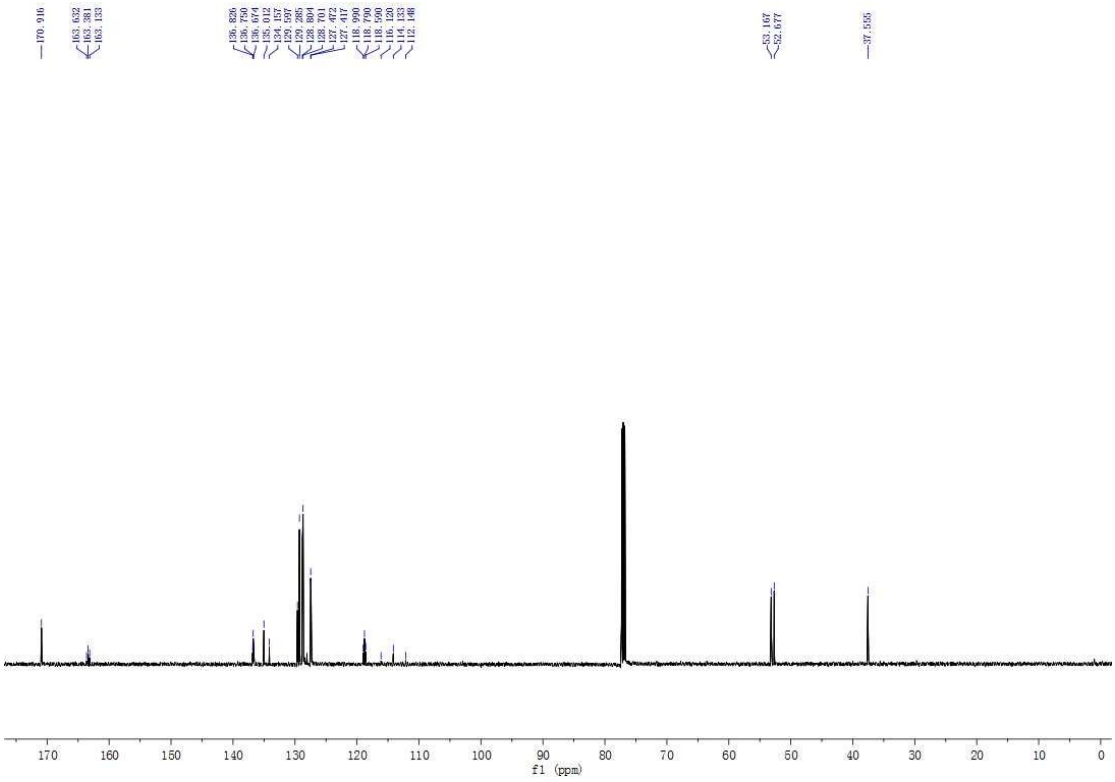

170.480
159.482
159.258
159.034
134.624
129.261
128.817
127.580
113.756
111.795
108.734
53.663
52.847
37.314
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

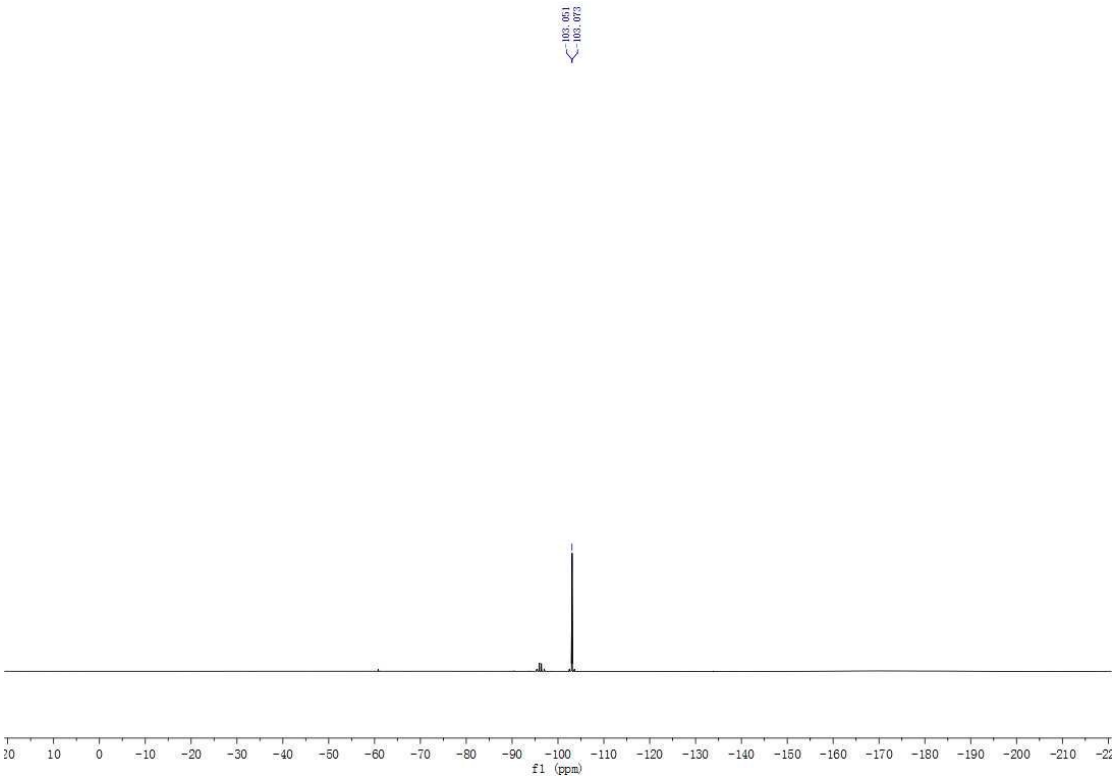


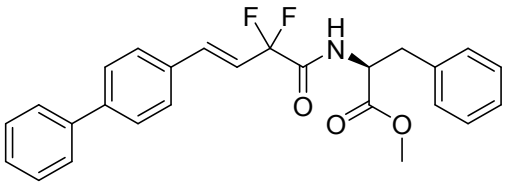


Methyl (E)-(2, 2-difluoro-4-phenylbut-3-enoyl)-L-phenylalaninate (32)

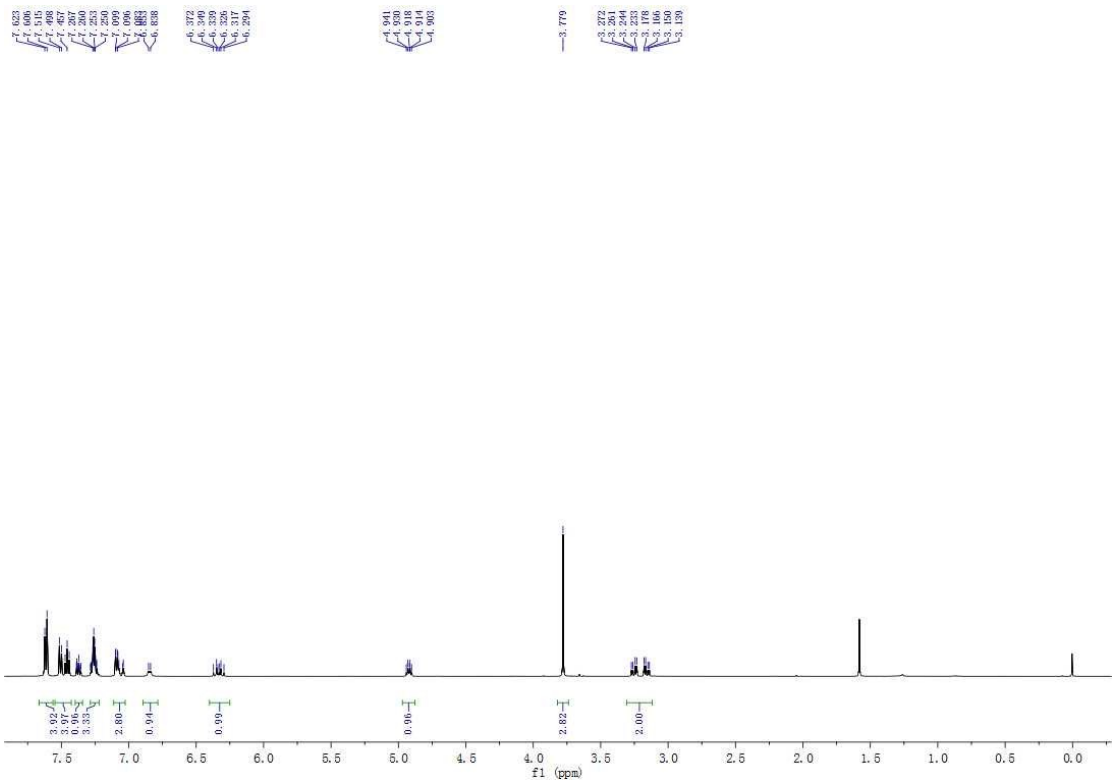

7.461
7.460
7.446
7.399
7.388
7.384
7.380
7.276
7.265
7.261
7.257
7.113
7.108
7.097
6.335
6.326
6.312
6.303
6.280
4.953
4.942
4.930
4.926
4.915
3.795
3.286
3.274
3.258
3.246
3.192
3.180
3.164
3.152
1.93
2.99
3.21
1.85
1.00
1.01
1.00
1.00
2.95
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

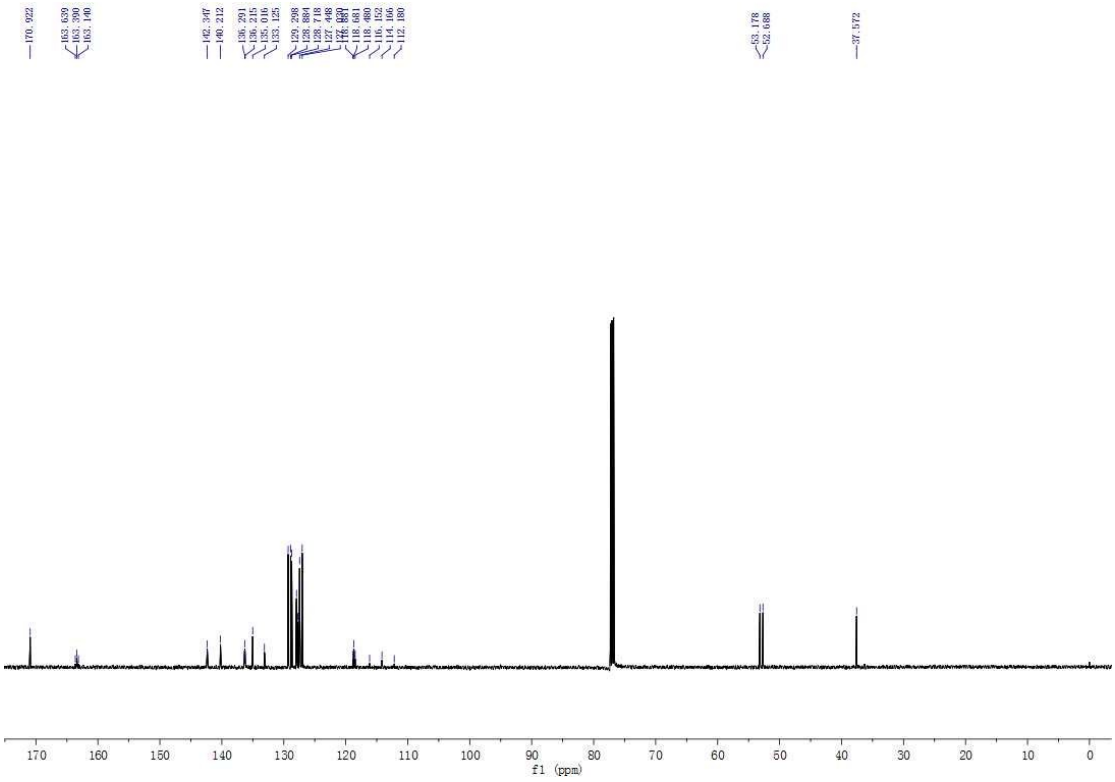

170.916
163.632
163.301
163.135
136.826
136.750
136.614
135.312
134.157
129.597
129.265
128.904
128.701
127.472
127.417
118.990
118.700
118.566
116.120
114.133
112.148
53.167
52.677
37.555
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

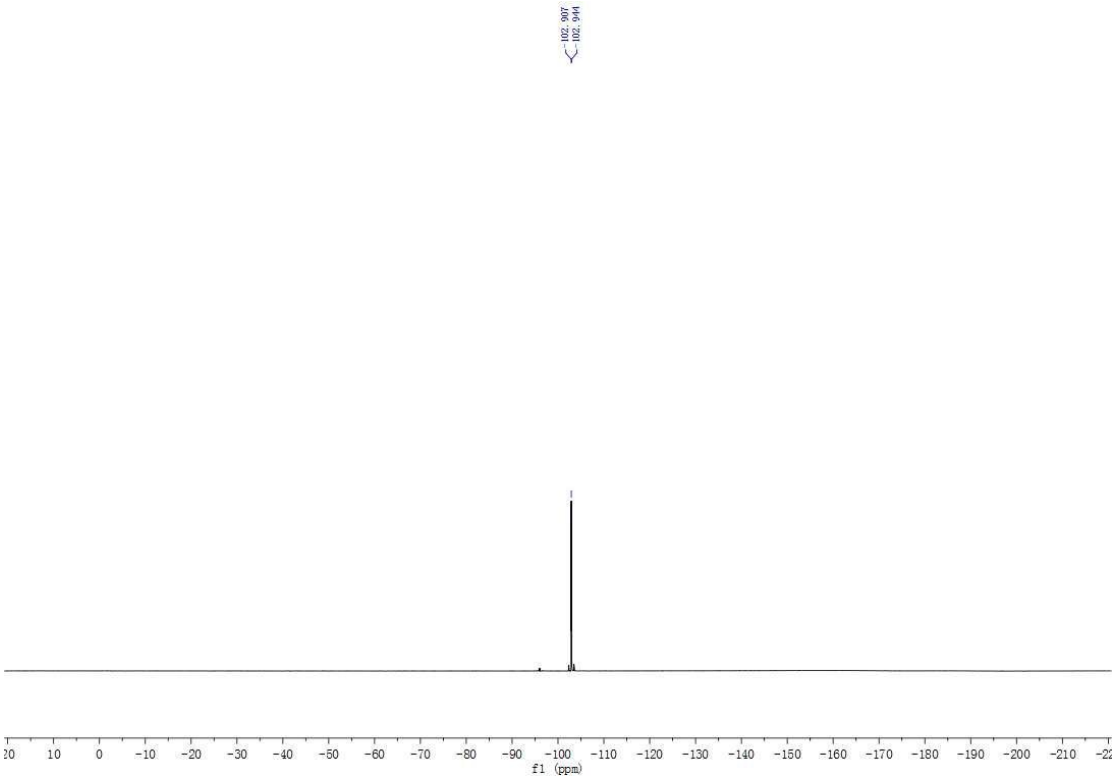


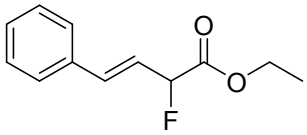


Methyl (E)-(4-([1, 1'-biphenyl]-4-yl)-2, 2-difluorobut-3-enoyl)-L-phenylalani-nate (33)

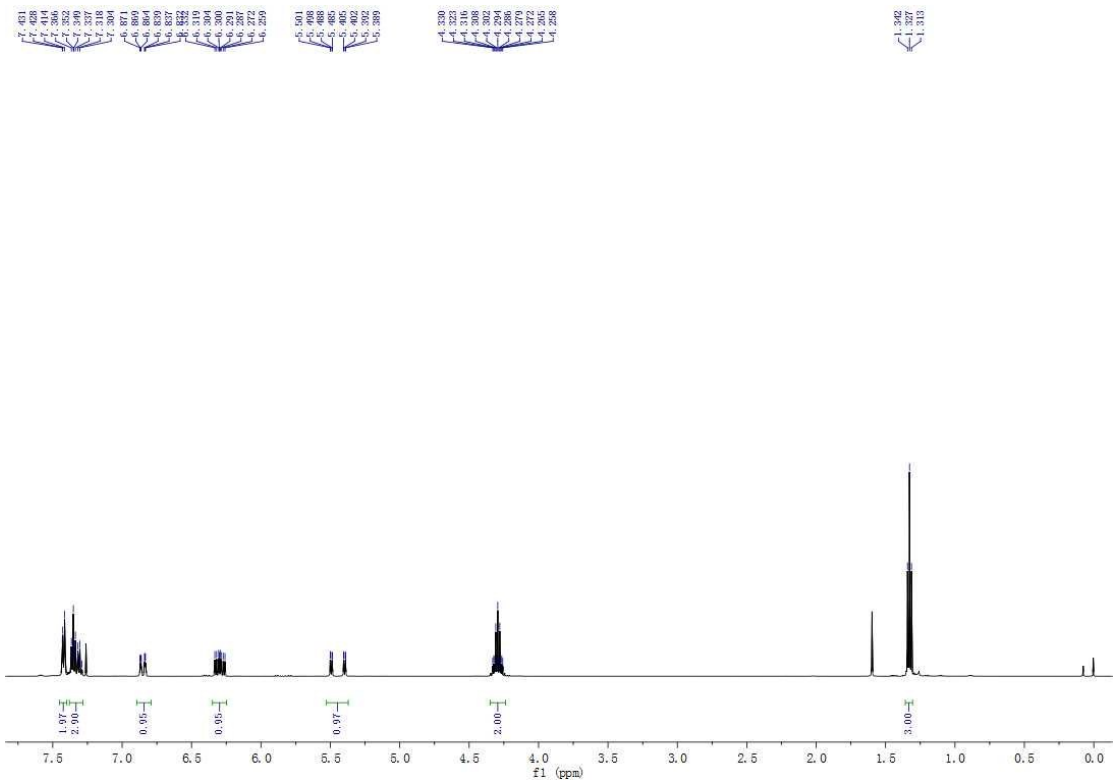

7.623
7.606
7.515
7.498
7.457
7.437
7.260
7.253
7.250
7.099
7.096
6.858
6.838
6.372
6.349
6.339
6.336
6.317
6.294
4.941
4.930
4.918
4.911
4.903
3.779
3.272
3.261
3.244
3.223
3.178
3.166
3.150
3.139
3.92
3.97
0.96
3.33
2.80
0.94
0.99
0.96
2.82
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

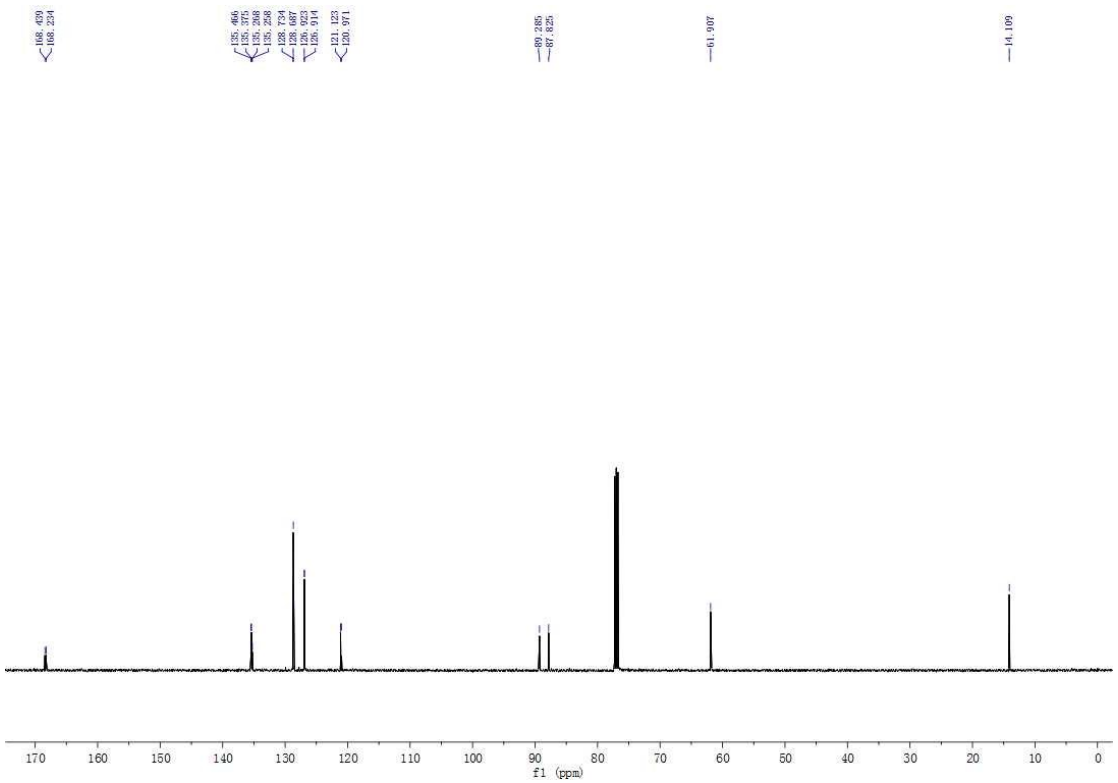

170.922
163.639
163.390
163.140
142.347
140.212
136.291
136.215
135.016
133.125
129.298
128.884
128.718
127.498
118.681
118.460
116.152
114.166
112.180
53.178
52.688
37.572
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

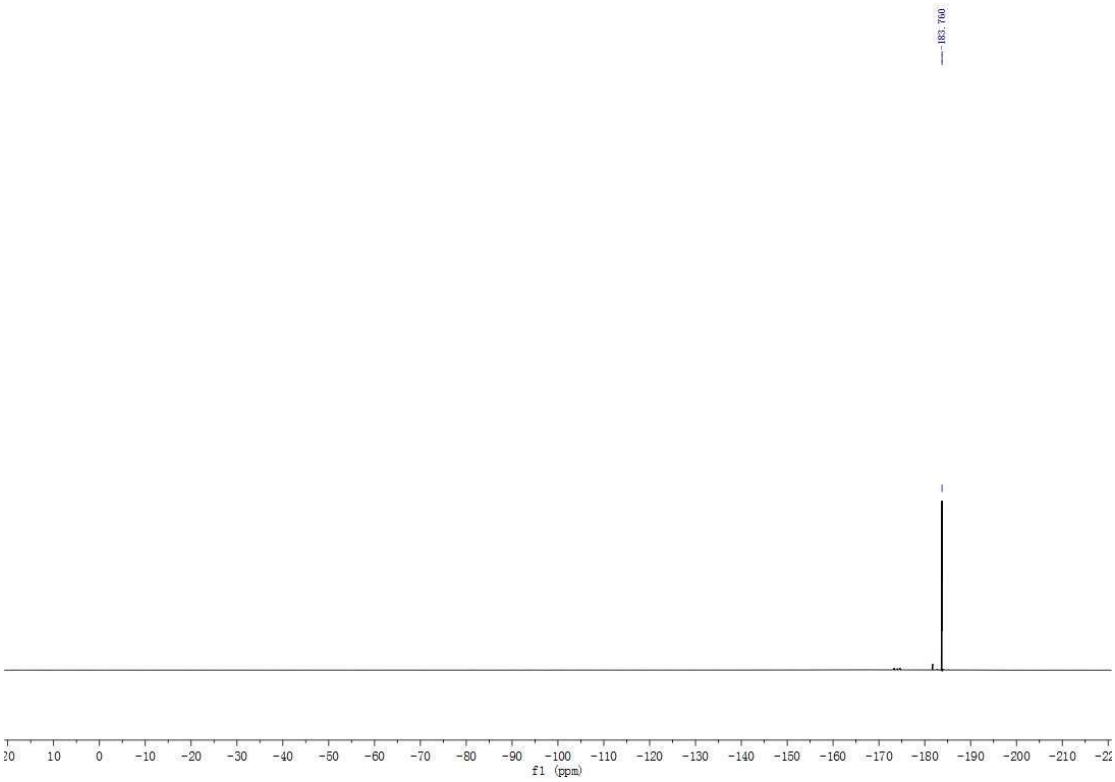


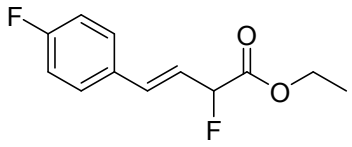


Ethyl (E)-2-fluoro-4-phenylbut-3-enoate(34)

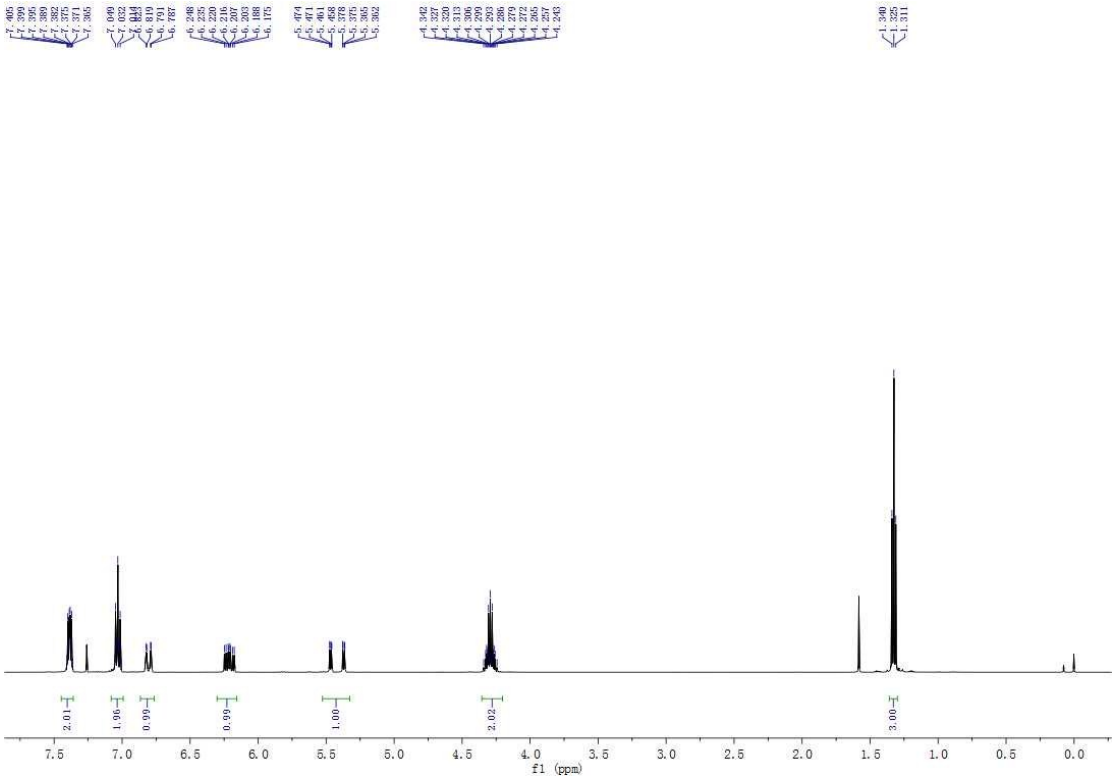


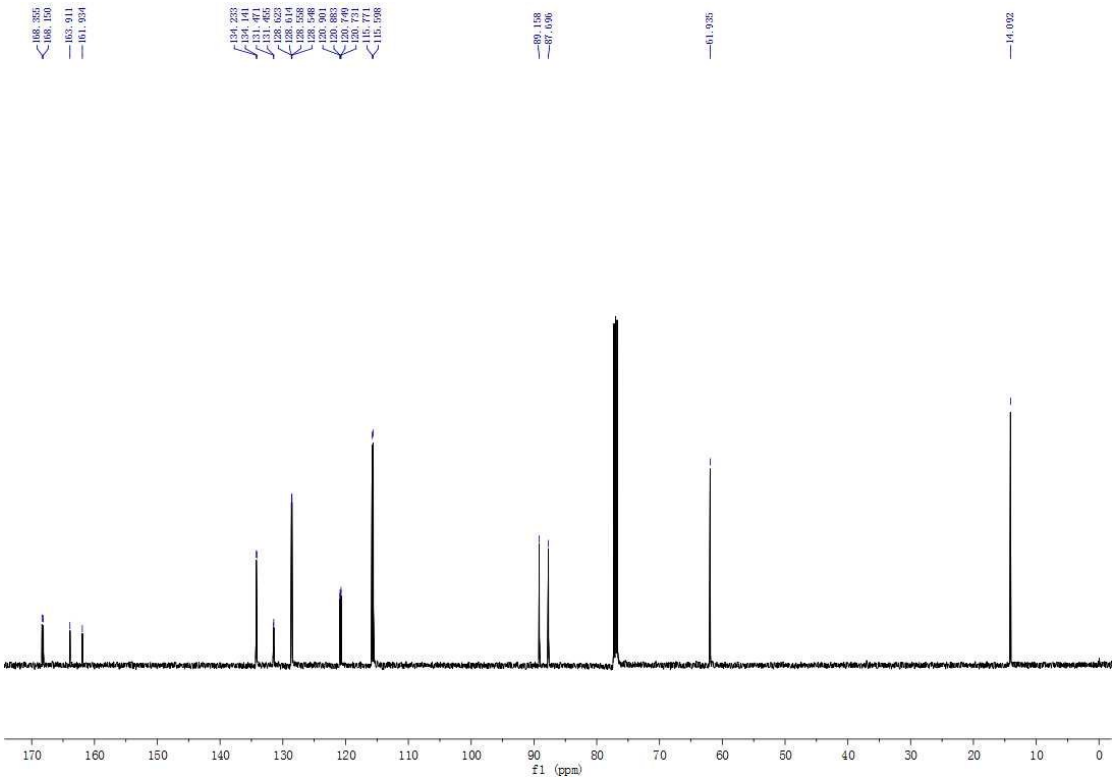


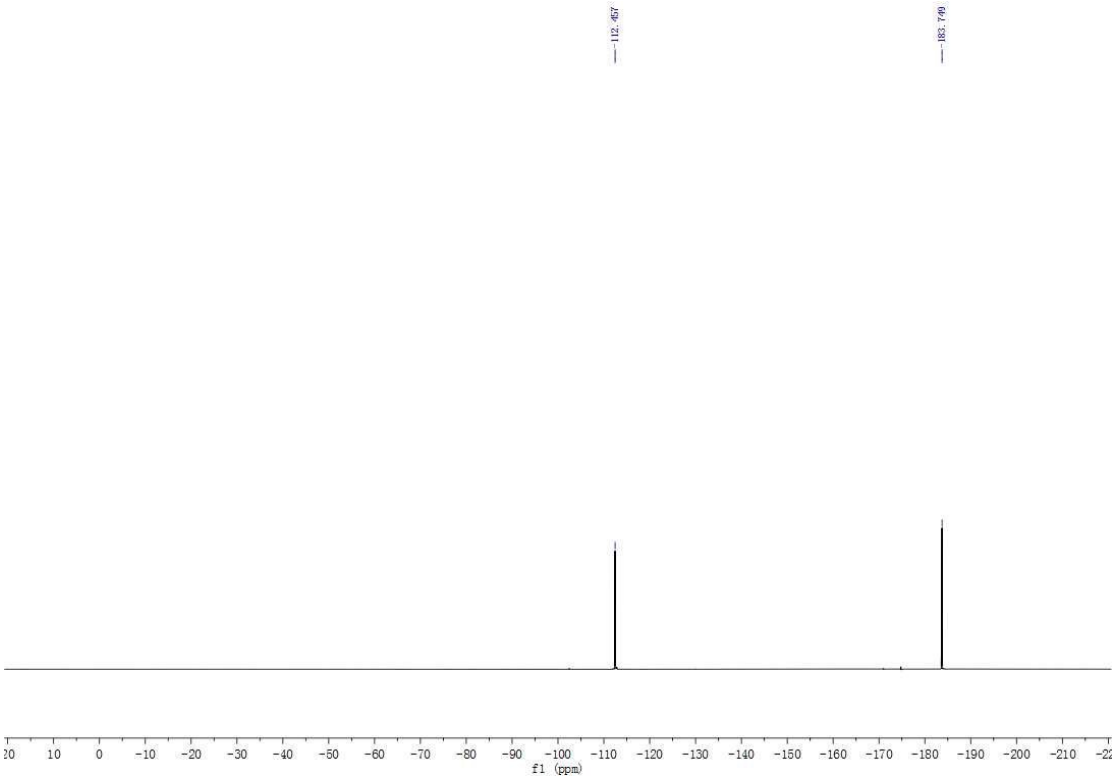


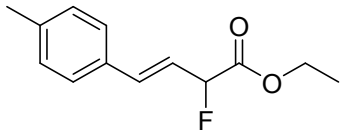


Ethyl (E)-2-fluoro-4-(4-fluorophenyl)but-3-enoate(35)

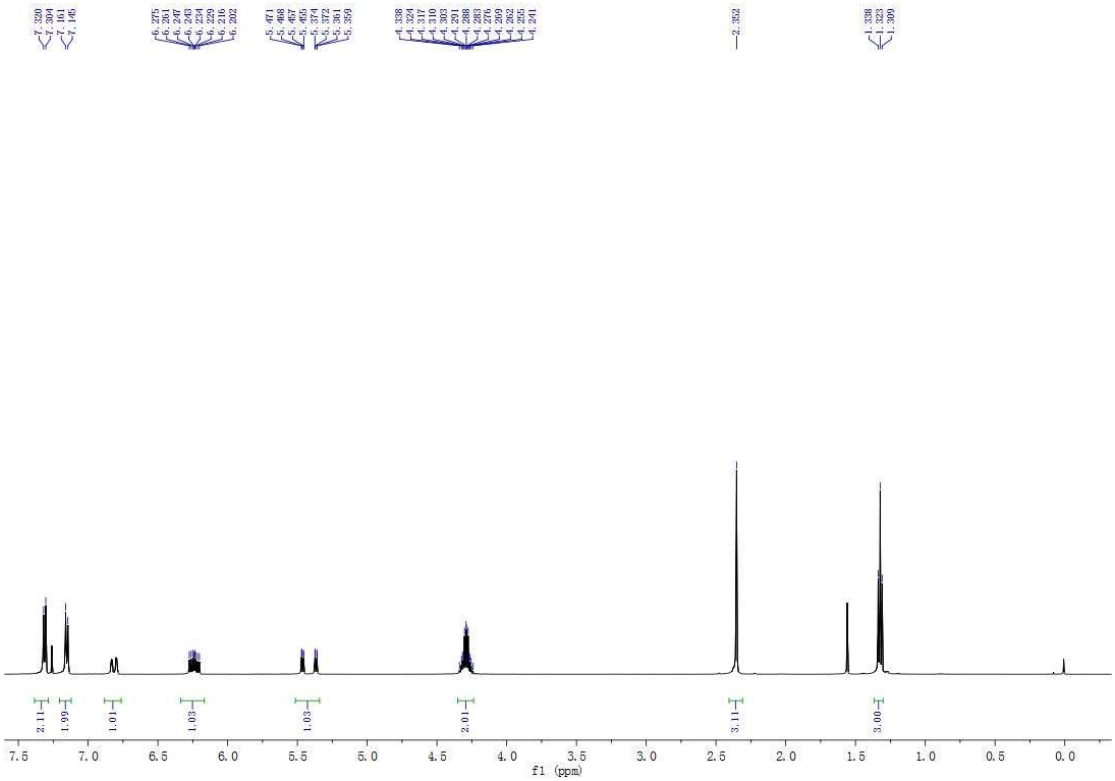

7.405
7.399
7.395
7.389
7.382
7.375
7.371
7.365
7.049
7.032
6.819
6.791
6.787
6.248
6.235
6.230
6.216
6.207
6.203
6.188
6.175
5.474
5.471
5.461
5.458
5.378
5.375
5.366
5.362
4.342
4.337
4.330
4.313
4.306
4.299
4.293
4.286
4.279
4.272
4.265
4.257
4.243
1.340
1.325
1.311
2.01
1.96
0.99
0.99
1.00
2.02
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

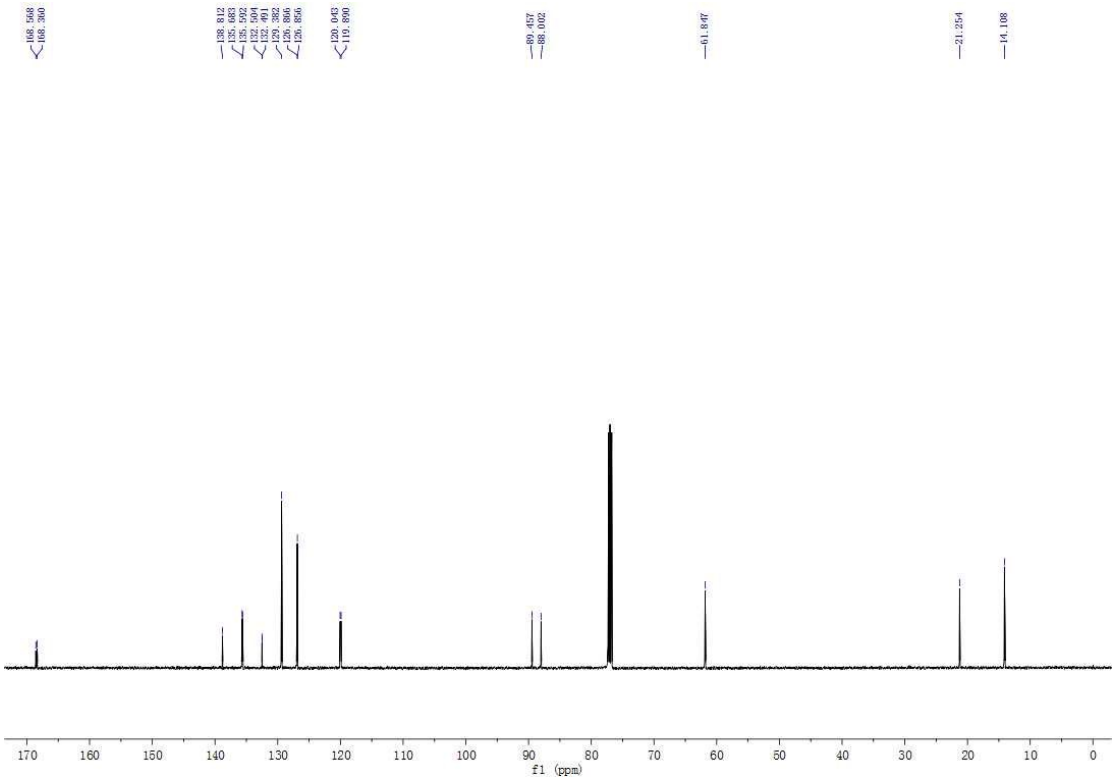

168.355
168.150
163.911
161.934
134.233
134.141
131.471
131.465
128.623
128.614
128.558
128.546
120.901
120.883
120.749
120.731
115.771
115.598
89.158
87.696
61.935
14.092
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

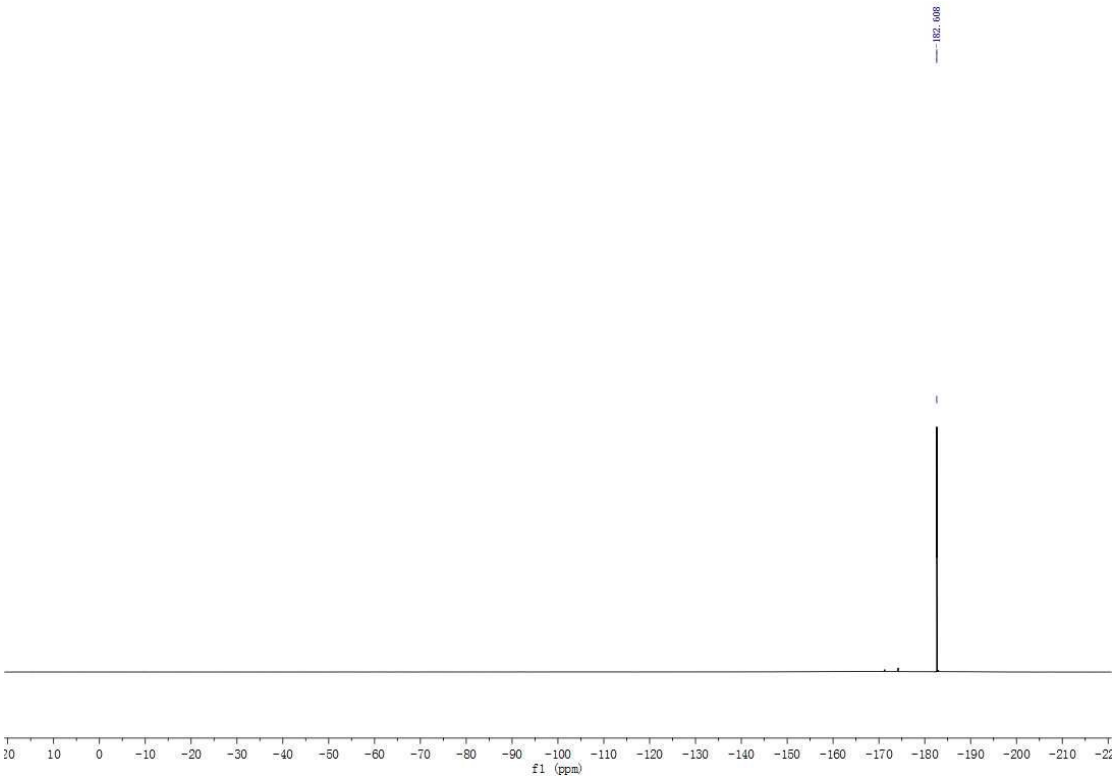


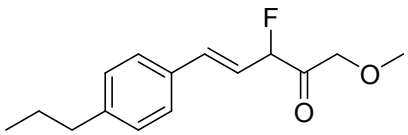


Ethyl (E)-2-fluoro-4-(p-tolyl)but-3-enoate(36)

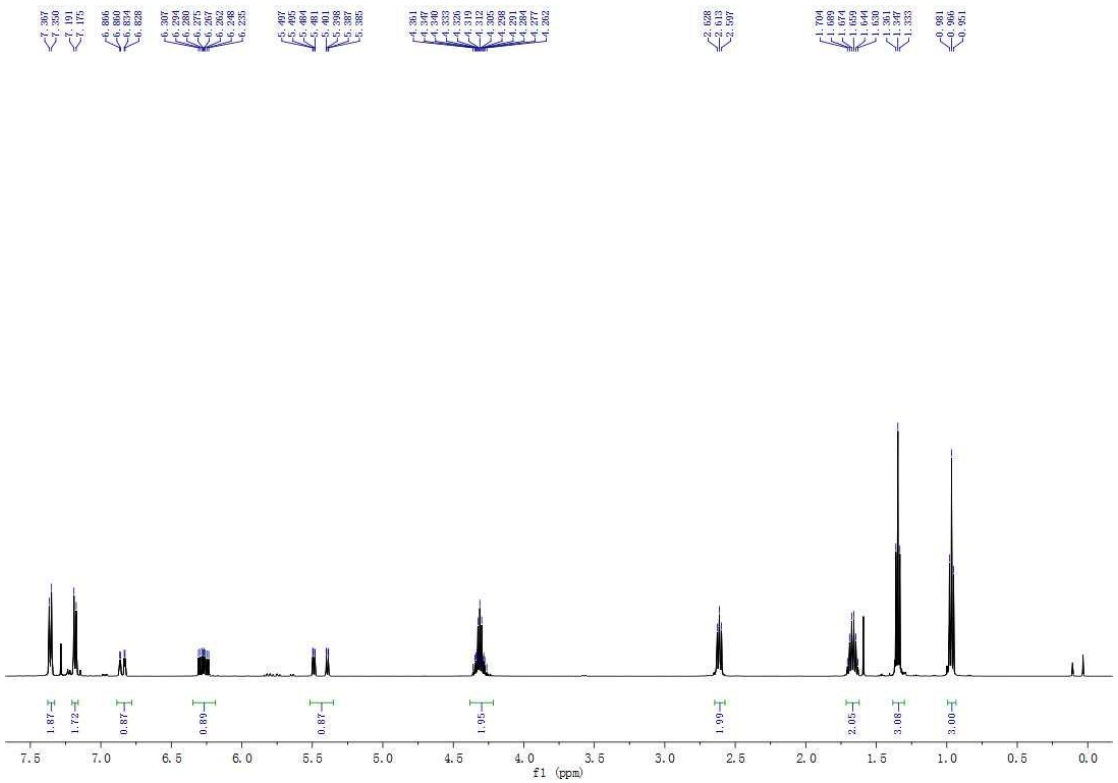

7.320
7.304
7.161
7.145
6.275
6.261
6.247
6.243
6.234
6.229
6.216
6.202
5.471
5.466
5.457
5.455
5.374
5.372
5.361
5.359
4.338
4.324
4.317
4.310
4.303
4.291
4.288
4.283
4.276
4.269
4.262
4.255
4.241
2.352
1.338
1.323
1.309
2.11
1.99
1.01
1.03
1.03
2.01
3.11
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

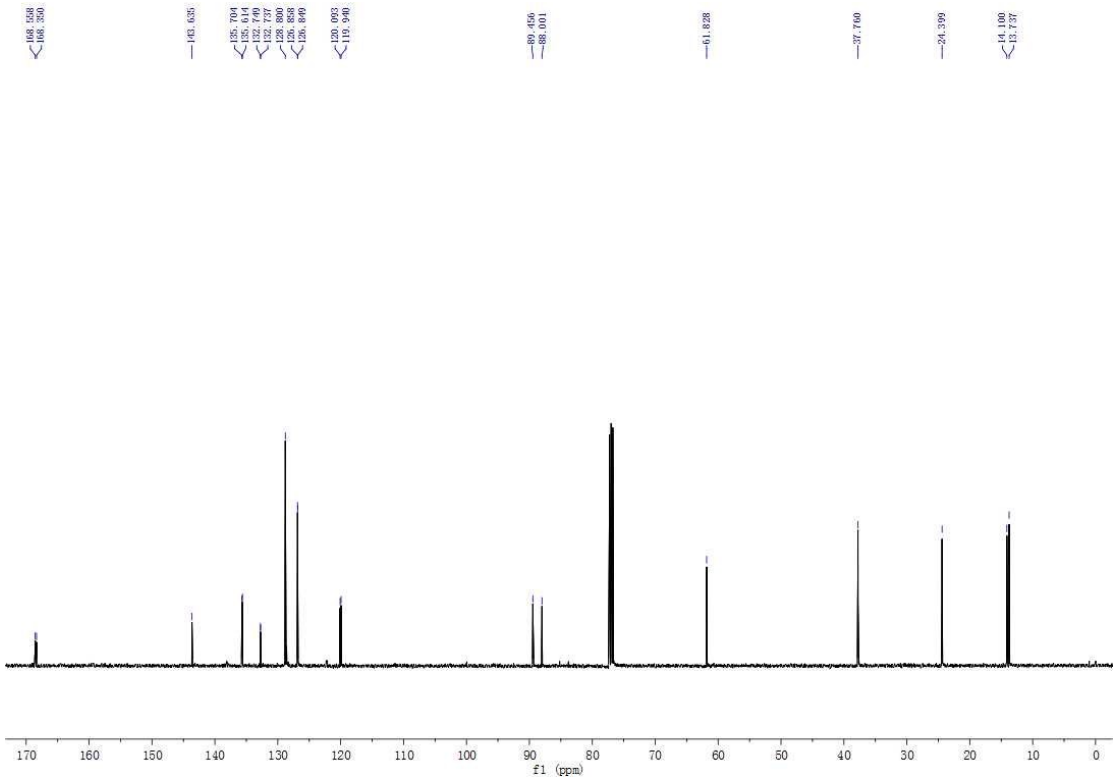

168.568
168.360
138.812
135.683
135.592
132.604
132.491
129.382
126.866
126.856
120.043
119.890
89.457
88.002
61.847
21.254
14.108
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

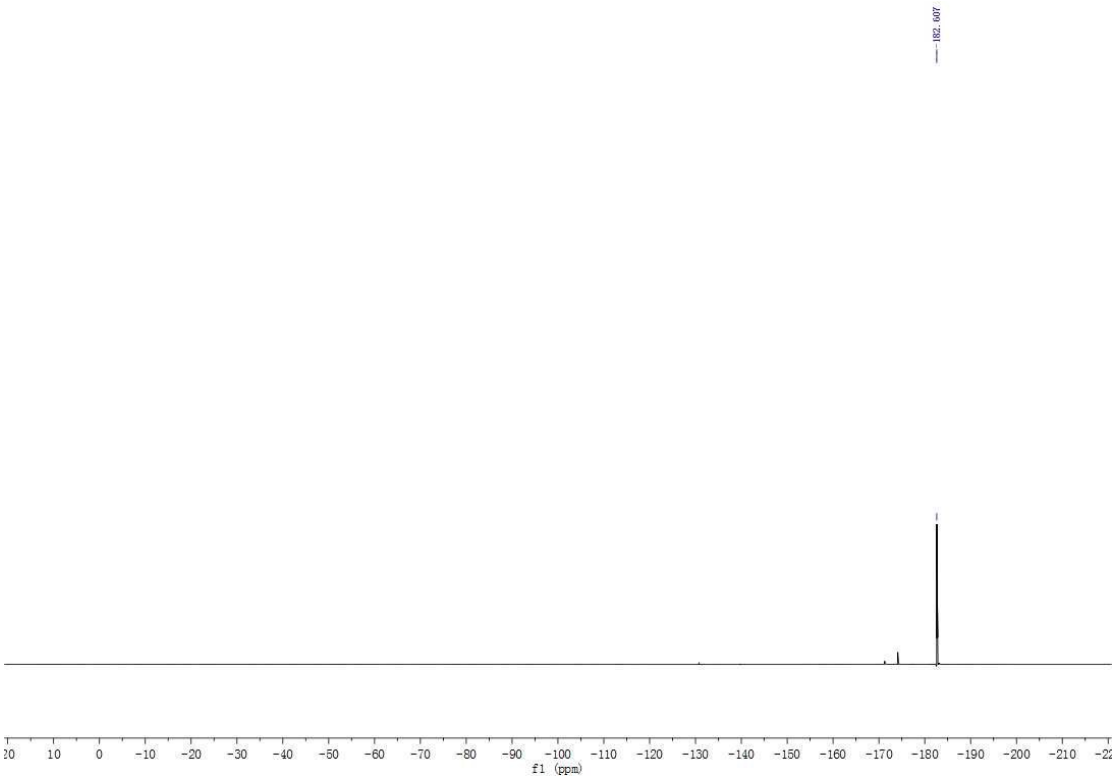


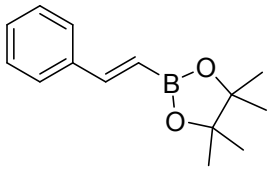


Ethyl (E)-2-fluoro-4-(4-propylphenyl)but-3-enoate (37)

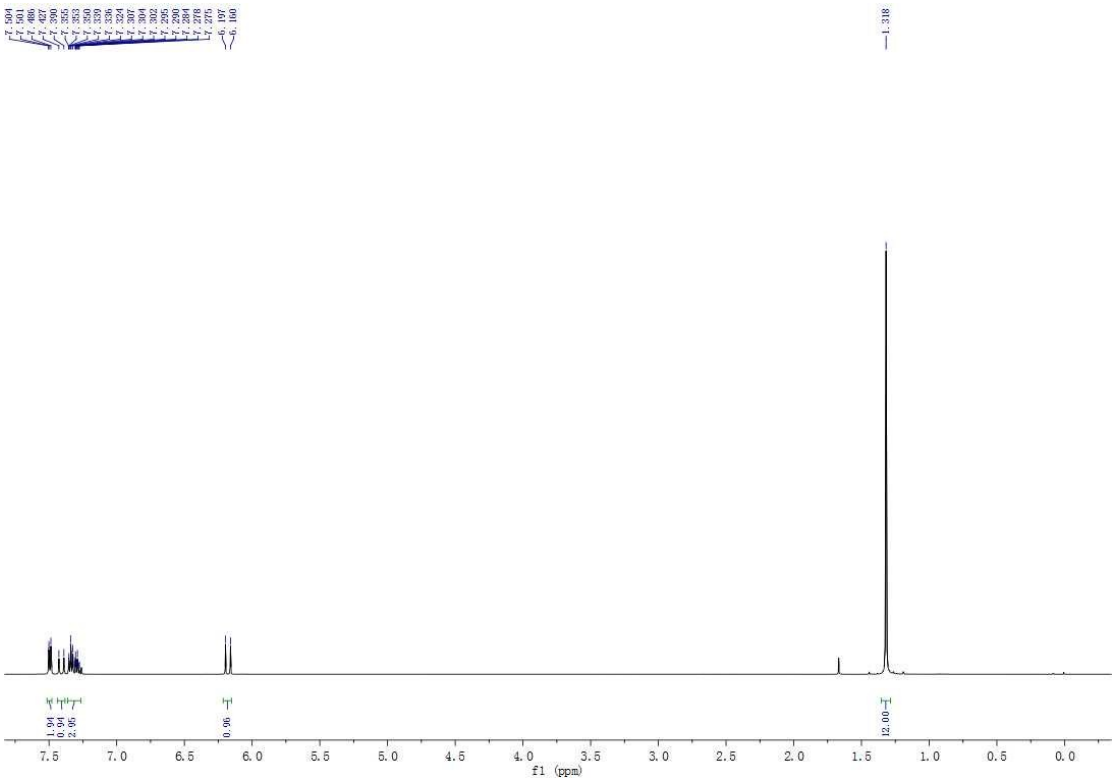

7.367
7.350
7.191
7.175
6.866
6.850
6.834
6.828
6.307
6.294
6.280
6.275
6.267
6.262
6.248
6.235
5.497
5.495
5.484
5.481
5.401
5.398
5.387
5.385
4.361
4.347
4.340
4.333
4.326
4.319
4.312
4.305
4.298
4.291
4.284
4.277
4.262
2.628
2.613
2.597
1.704
1.689
1.674
1.659
1.644
1.630
1.361
1.347
1.333
0.981
0.966
0.951
1.87
1.72
0.87
0.89
0.87
1.95
1.99
2.05
3.08
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

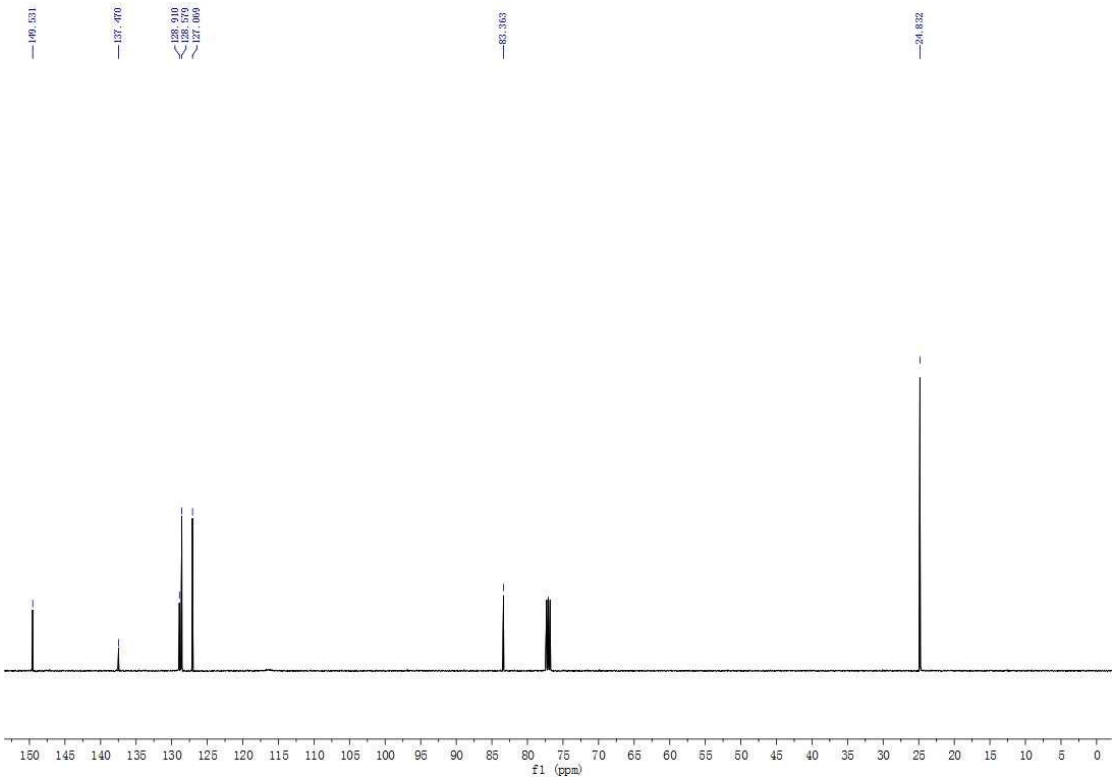

168.558
168.350
143.635
135.704
135.614
132.199
132.177
128.800
126.858
126.849
120.093
119.940
89.456
88.001
61.828
37.760
24.399
14.100
13.737
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

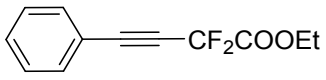




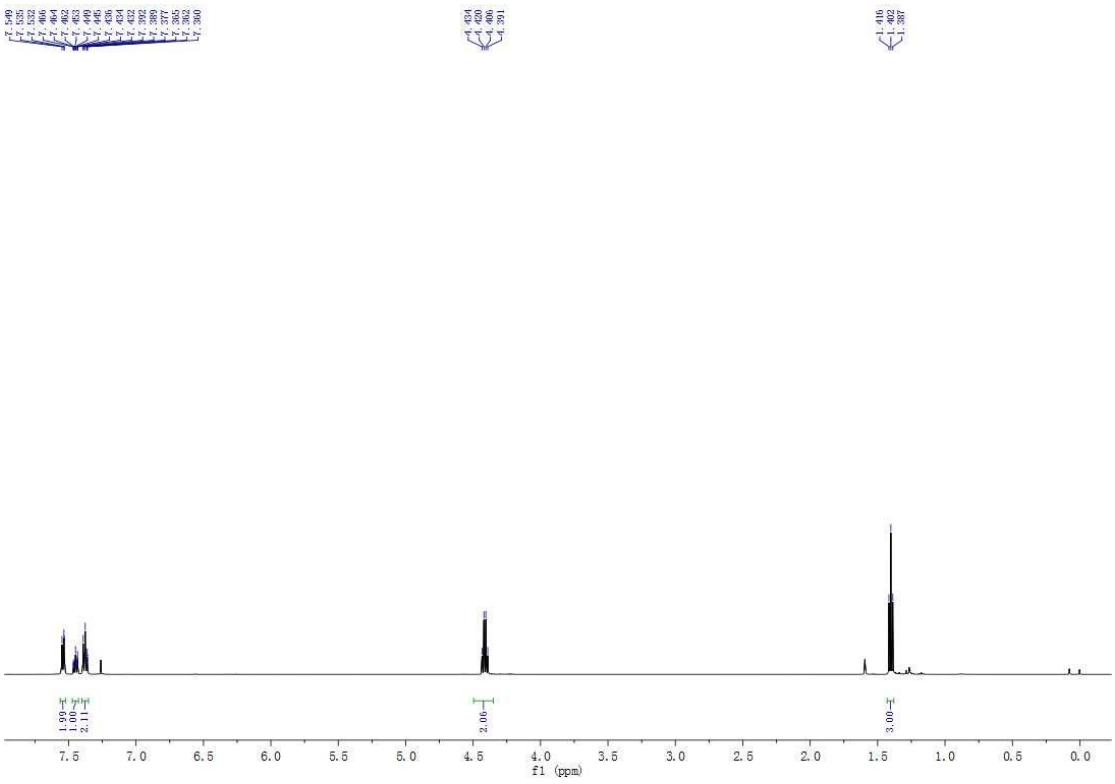
(E)-4, 4, 5, 5-tetramethyl-2-styryl-1, 3, 2-dioxaborolane (38)

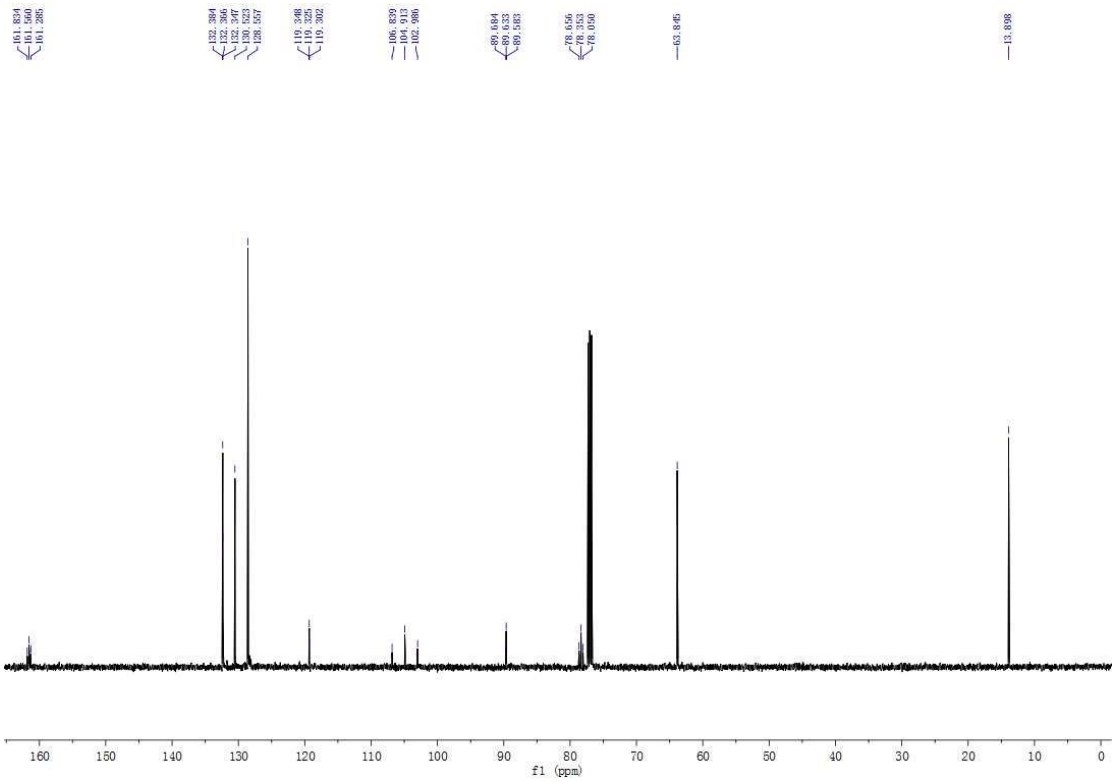

7.504
7.501
7.486
7.477
7.390
7.355
7.353
7.350
7.339
7.336
7.324
7.307
7.304
7.302
7.295
7.290
7.284
7.278
7.276
6.197
6.160
1.318
1.94
0.94
2.95
0.96
12.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

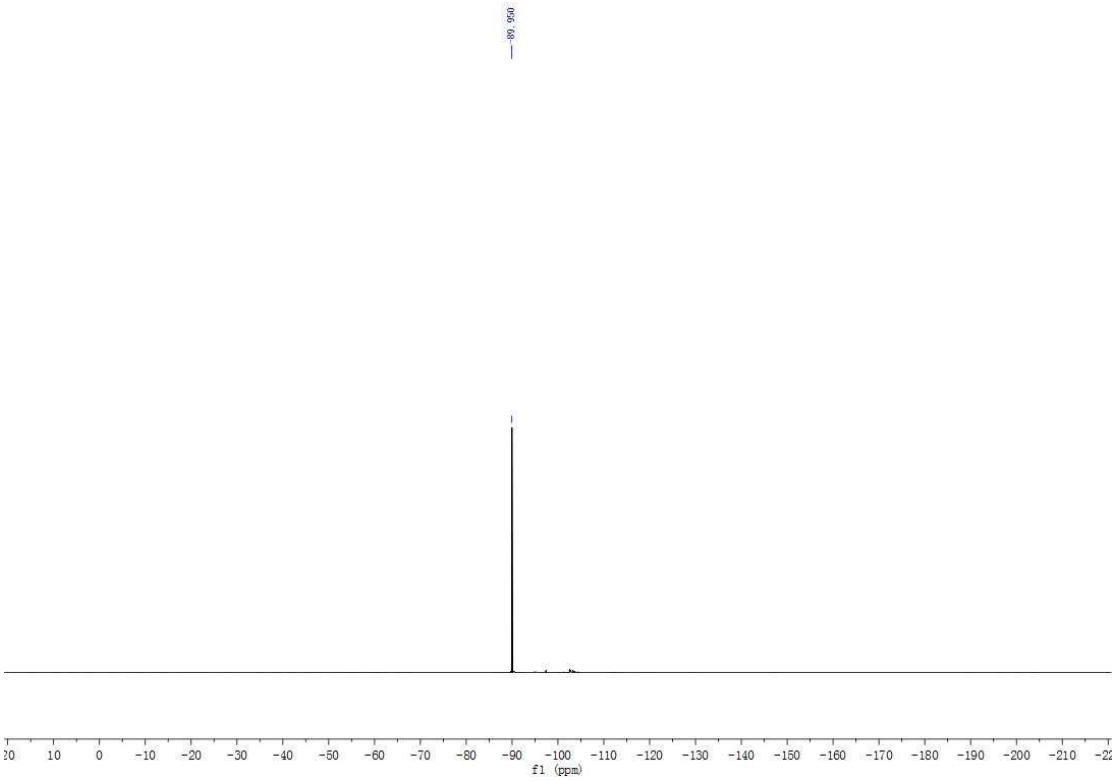

149.531
137.470
128.910
128.570
127.600
83.363
24.832
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


CF2COOEt

Ethyl 2, 2-difluoro-4-phenylbut-3-ynoate (39)




161.834
161.560
161.285
132.384
132.364
132.347
130.523
128.557
119.398
119.325
119.302
106.839
104.913
102.986
89.684
89.633
89.583
78.656
78.353
78.050
63.845
13.898
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)