Supporting Information

Silacarboxylic Acid Mediated Photoredox Z-Stereoselective Fluoroalkylation of Alkynes

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1. General Information

1.1 Reagents and instruments

Unless otherwise noted, all commercial reagents were purchased from Shanghai Haohong Scientific Co. Ltd. The material of the irradiation vessel is borosilicate glass (Chongqing Synthware Glass, China). All solvents used in the reactions were purified prior to use following the Solvent Purification Systems (FLEANO, FL-MD-7), extra dry 2-Methyltetrahydrofuran (2-Me-THF) (Water≤50 ppm) was purchased from Energy Chemical Ltd. 4CzIPN was prepared using literature procedures[1]. All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glovebox (MIKROUNA Super/1220/750) or using standard Schlenk techniques. The light source was 20 W blue LEDs (454 nm, 1 W*20, 30-50 cd/m^2, made in Everlight Electronics., Ltd.). Organic solutions were concentrated under reduced pressure on an EYELA rotary evaporator (N-1100) using a water bath. Steady-state emission spectra were recorded using a Cary Eclipse Fluorescence Spectrophotometer (Agilent Techonologies). Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents. Thin-layer chromatography (TLC) was performed on Supelco 0.25 mm silica gel 60 F_{254} plates. Visualization of the developed chromatogram was performed by Phosphomolybdic Acid or $KMnO_4$ chromogenic agent stain. ^{1}H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were obtained at 376 MHz. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. High Resolution Mass Spectra were obtained from the Yunnan Minzu University Mass Spectral Facility. HPLC analysis was performed on an Agilent 1260 Infinity LC chromatography.

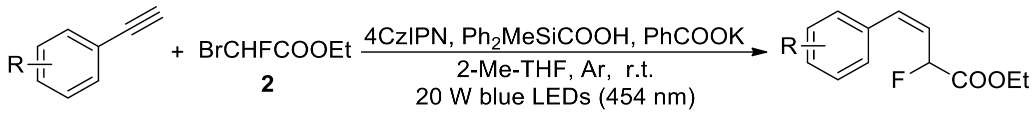
1.2 Computational methods

All density functional theory (DFT) calculations were performed to understand the reaction mechanism of the photocatalyzed stereoselective monofluoroalkylation of alkynes by halogen-atom transfer: highly selective fluoroalkylation obtained by light induced difluoroalkylation of alkynes. B3LYP-D3 [2] method combined with a basis set of Def2-SVP [3] for all atoms was used to fully optimize all structures in the gas-phase. Then, vibrational frequency calculations on these optimized geometries were carried out at the same level of theory to confirm no imaginary frequency for all local minimum and one appropriate imaginary frequency for each transition state. Single-point energy calculations on the critical structures by using B3LYP-D3 with highly accurate basis set Def2-TZVP [4] in THF solution (SMD solvent model). All DFT calculations were carried out by Gaussian16 program [5]. All 3D images of the optimized structures were shown by CYL view.[6]

2. General procedure

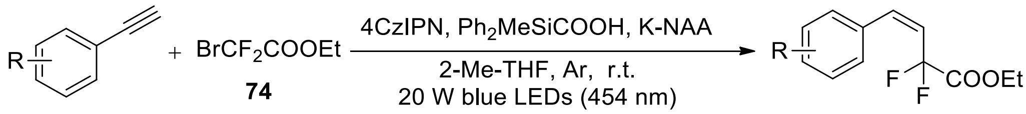
2.1. General procedure for preparation of fluoroalkylated products.

General Procedure A: Visible-light-induced catalytic fluoroalkylation reaction of alkynes



4CzIPN (7.9 mg, 0.01 mmol, 0.05 equiv.), anhydrous potassium benzoate (89.7 mg, 0.4 mmol, 2 equiv.), methyldiphenylsilanecarboxylic acid (72.6 mg, 0.3 mmol, 1.5 equiv.), phenylacetylene (20.4 mg, 0.2 mmol, 1 equiv.), ethyl bromofluoroacetate (81.2 mg, 0.4 mmol, 2 equiv.) and 2-Me-THF (2 mL) were added were added to a Schlenk tube under argon atmosphere. The resulting mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed (as monitored by TLC analysis), the solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/EA = 80:1) to afford the fluoroalkylation products.

General Procedure B: Visible-light-induced catalytic difluoroalkylation reaction of alkynes



To an oven dried 15 mL Schlenk-tube equipped with a stir bar was added photocatalyst 4CzIPN (6.1 mg, 0.008 mmol, 0.04 equiv.), 1-naphthaleneacetic acid potassium salt (K-NAA) (89.7 mg, 0.4 mmol, 2 equiv.), methyldiphenyl silanecarboxylic acid (72.6 mg, 0.3 mmol, 1.5 equiv.), phenylacetylene (20.4 mg, 0.2 mmol, 1 equiv.), ethyl bromodifluoroacetate (74.0 mg, 0.4 mmol, 2 equiv.) and 2-Me-THF (2 mL) under argon atmosphere. The reaction mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed (as monitored by TLC analysis), the solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/EA = 80:1) to afford the fluoroalkylation products.

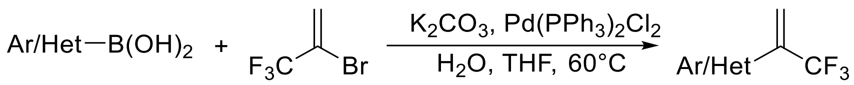
2.2. Procedure for preparation of other reagents

General Procedure E: General procedure of the preparation of silacarboxylic acids

Silacarboxylic acids were synthesized according to reported procedure[7]. Small pieces of lithium (1.26 g, 180 mmol, 3 equiv.) were added to dry THF (100 mL) under argon. Chlorosilane (60 mmol, 1 equiv.) was then added dropwise *via* gas-tight syringe and the reaction mixture was stirred for 5 h. The resulting black solution was transferred *via* cannula into a flame-dried flask charged with argon and cooled to –78 °C. CO_2 gas was then bubbled into the solution of silyllithium for 20 min before cold bath was removed. After the reaction mixture was warmed to room temperature, it was slowly poured into a separation funnel with aqueous HCl (30 mL, 1 mol/L) and CH_2Cl_2 (25 mL). The aqueous phase was further extracted with CH_2Cl_2 (2×25 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to give a brown solid. Recrystallization of the crude product in hexane/CH_2Cl_2 provide corresponding silacarboxylic acids as colorless crystal.

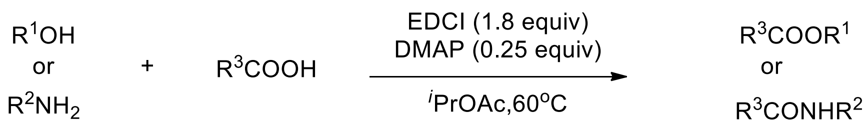
General Procedure F: General procedure of the preparation of α-oxy bromides:
α-oxy bromides were synthesized according to reported procedure[8]. Following the addition of a magnetic stir bar, $ZnCl_2$ (0.05 equiv.), CH_2Cl_2 and acyl bromide (1.2 equiv.) were added to an oven-dried round-bottom flask that had been charged with nitrogen atmosphere. The resulting solution was cooled to -10 °C and the mixture was stirred for 10 min. The aldehyde (1.0 equiv.) was added dropwise using a syringe at this temperature, and the resulting mixture was agitated for two hours. The reaction mixture was then rinsed with CH_2Cl_2 and filtered through a brief column of neutral aluminum oxide. Reduced pressure was used to concentrate the filtrate. After its purity was determined, the product was either vacuum-distilled to remove impurities or used right away.

General Procedure G: General procedure of the preparation of trifluoromethyl alkene



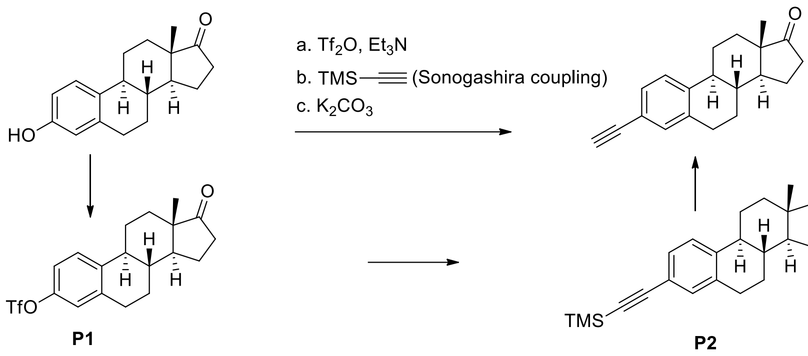
According to literature reports[9], to a Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv., 3 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 63.2 mg) were added. The vessel was evacuated and filled with N_2 (three times), and then aqueous K_2CO_3 (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.5 equiv., 4.5 mmol, 0.47 mL), the solution was stirred at 60°C with heating mantle for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE - PE/EA) to afford the corresponding trifluoromethyl alkene.

General Procedure H: General procedure of the preparation of drug derived alkynes 38-41 & 43



Drug derived alkynes (38-41,43) were synthesized according to reported procedure[10]. Following the addition of a magnetic stir bar, corresponding alcohol (1.0 equiv), corresponding acid (1.5 equiv), EDC-HCl (1.8 equiv), DMAP (0.25 equiv), and ^{i}PrOAc (0.25 M for alcohol) were added to an oven-dried round-bottom flask that had been charged with nitrogen atmosphere. The mixture was stirred at 60 °C overnight until the completion of the reaction as monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE - PE/EA) to afford the corresponding alkyne.

General Procedure I: General procedure of the preparation of drug derived alkynes 42

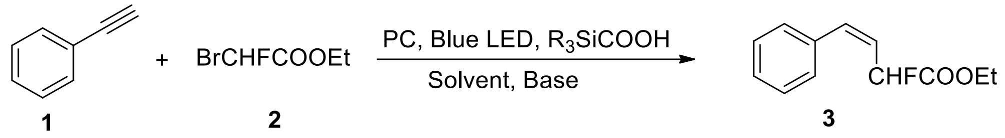


Drug derived alkyne (42) were synthesized according to reported procedure[11]. After adding a magnetic stirring rod, dry CH_2Cl_2 (2M), estrone (1.0 equiv), triethylamine (2 equiv mmol) and trifluoromethanesulfonic anhydride (2 equiv) were added at 0ºC to a heated and dried round-bottom flask and filled with nitrogen. The reaction mixture was stirred at 0 ºC for 20 min before the addition of water. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases are washed with brine and dried over Na_2SO_4. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **P1** in 80% yield.

To a mixture of **P1** (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.1 equiv) and CuI (0.1 equiv) in DMF (0.05M) was added Et_3N (3.0 equiv), and TMSA (5.0 equiv), then the reaction was stirred at 80 ºC for 4 h. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with EtOAc (50 mL x 3). The combined organic phases are washed with brine and dried over Na_2SO_4. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **P2** 50% yield. To **P2** (1.0 equiv) in MeOH (0.1M) was added K_2CO_3 (2.0 equiv). The reaction mixture was stirred at 25 ºC for 4 h. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with EtOAc (20 mL x 3). The combined organic phases are washed with brine and dried over Na_2SO_4. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford drug mlecules alkyne in 90% yield.

3. Optimization of reaction conditions

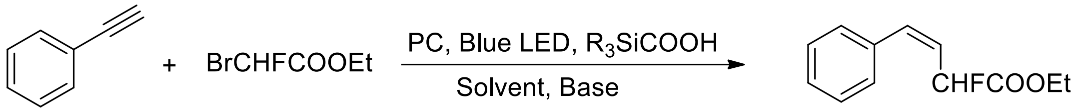
Table S1. Optimization of reaction conditions (1).[a]



Entry	SilaCOgen	PC	Base	Solvent	*Z* (%)	Yield (%)[c]
1	Et_3SiH	4CzIPN	NaOAc	1,4-dioxane	/	ND
2	/	4CzIPN	NaOAc	1,4-dioxane	/	trace
3	SA1	4CzIPN	NaOAc	1,4-dioxane	89	28
4	SA1	4CzIPN	NaOAc	acetone	60	20
5	SA1	4CzIPN	NaOAc	toluene	95	6
6	SA1	4CzIPN	NaOAc	MeOH	77	17
7	SA1	4CzIPN	NaOAc	EtOAc	77	15
8	SA1	4CzIPN	NaOAc	dichloromethane	80	3
9	SA1	4CzIPN	NaOAc	MeCN	76	7
10	SA1	4CzIPN	NaOAc	THF	90	47
11	SA1	4CzIPN	NaOAc	MeTHF	93	76
12	SA1	4CzIPN	/	MeTHF	67	16
13	SA1	4CzIPN	Na_2HPO_4	MeTHF	83	55
14	SA1	4CzIPN	NaH_2PO_4	MeTHF	83	36
15	SA1	4CzIPN	$NaHCO_3$	MeTHF	83	39
16	SA1	4CzIPN	HCOONa	MeTHF	83	45
17	SA1	4CzIPN	LiOAc	MeTHF	63	60
18	SA1	4CzIPN	Li_2CO_3	MeTHF	61	48
19	SA1	4CzIPN	HCOOLi	MeTHF	56	45
20	SA1	4CzIPN	Li_3PO_4	MeTHF	82	59
21	SA1	4CzIPN	Li_2SO_4	MeTHF	76	37
22	SA1	4CzIPN	$Li_2C_2O_4$	MeTHF	83	43
23	SA1	4CzIPN	$LiClO_4$	MeTHF	55	38
24	SA1	4CzIPN	KOAc	MeTHF	88	47
25	SA1	4CzIPN	K_3PO_4	MeTHF	89	17
26	SA1	4CzIPN	K_2CO_3	MeTHF	87	39
27	SA1	4CzIPN	$KHCO_3$	MeTHF	88	64
28	SA1	4CzIPN	PhCOOLi	MeTHF	91	57
29	SA1	4CzIPN	PhCOONa	MeTHF	88	60
30	SA1	4CzIPN	PhCOOK	MeTHF	93	83
31	SA1 0.1 mmol	4CzIPN	PhCOOK	MeTHF	88	39
32	SA1 0.2 mmol	4CzIPN	PhCOOK	MeTHF	92	72
33	SA1 0.4 mmol	4CzIPN	PhCOOK	MeTHF	87	55

[a] The reactions were performed with **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (2 mol%), silaCOgen (1.5 equiv.), base (2 equiv.) in solvent (2 mL) under LED irradiation for 5-10 hours, unless otherwise indicated. [b] Performed with PC **1** (5 mol%). [c] Yields were determined by isolated products, stereoselectivities were determined with 19F-NMR analysis.

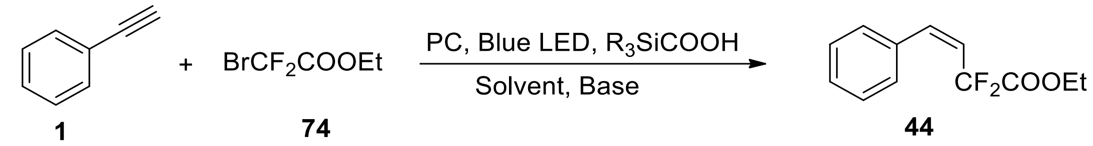
Table S2. Optimization of reaction conditions (2).[a]



Entry	SilaCOgen	PC	Base 0.4	Solvent	Z (%)	Yield (%)[c]
1	SA1	4CzIPN	0.1	MeTHF	75	46
2	SA1	4CzIPN	0.2	MeTHF	84	62
3	SA1	4CzIPN	0.3	MeTHF	91	65
4	SA1	4CzPN	$PhCO_2K$	MeTHF	77	66
5	SA1	4CzTPN	$PhCO_2K$	MeTHF	59	43
6	SA1	$Ir(ppy)_3$	$PhCO_2K$	MeTHF	92	67
7	SA1	$Ir(Fppy)_3$	$PhCO_2K$	MeTHF	89	68
8	SA1	$(Ir[dFppy]_2(bpy))PF_6$	$PhCO_2K$	MeTHF	88	67
9	SA1	$[Ir(dtbbpy)(ppy)_2]PF_6$	$PhCO_2K$	MeTHF	78	68
10	SA1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$PhCO_2K$	MeTHF	84	68
11	SA2	4CzIPN	$PhCO_2K$	MeTHF	92	63
12	SA3	4CzIPN	$PhCO_2K$	MeTHF	92	55
13	SA1	4CzIPN, **1** 0.3 mmol **2** 0.2 mmol	$PhCO_2K$	MeTHF	93	60
14	SA1	4CzIPN, **1** 0.4 mmol **2** 0.2 mmol	$PhCO_2K$	MeTHF	93	62
15	SA1	4CzIPN, **1** 0.5 mmol **2** 0.2 mmol	$PhCO_2K$	MeTHF	93	64
16	SA1	4CzIPN 1%	$PhCO_2K$	MeTHF	93	78
17	SA1	4CzIPN 3%	$PhCO_2K$	MeTHF	93	86
18	SA1	4CzIPN 4%	$PhCO_2K$	MeTHF	93	89
19	**SA1**	**4CzIPN 5%**	**$PhCO_2K$**	**MeTHF**	**93**	**97(91[c])**
20	SA1	4CzIPN 6%	$PhCO_2K$	MeTHF	93	86
21	SA1	4CzIPN 7%	$PhCO_2K$	MeTHF	93	86

[a] The reactions were performed with **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (2 mol%), SilaCOgen (1.5 equiv.), base (2 equiv.) in solvent (2 mL) under LED irradiation for 5-10 hours, unless otherwise indicated. [b] Performed with PC **1** (5 mol%). [c] Yields were determined by isolated products, stereoselectivities were determined with 19F-NMR analysis.

Table S3. Optimization of reaction conditions[a]



Entry	SilaCOgen	PC	Base	Solvent	*Z* (%)	Yield (%)[c]
1	0.3	4CzIPN	NB	MTHF	65	44
2	0.3	4CzIPN	LiOAc	MTHF	65	66
3	0.3	4CzIPN	Li_2CO_3	MTHF	62	72
4	0.3	4CzIPN	PhCOOLi	MTHF	70	53
5	0.3	4CzIPN	PhCOONa	MTHF	71	53
6	0.3	4CzIPN	PhCOOK	MTHF	72	66
7	0.3	4CzIPN	Potassium 1-naphthaleneacetate	MTHF	77	70
8	0.3	4CzIPN 2%	Potassium 1-naphthaleneacetate	MTHF	77	60
9	0.3	4CzIPN 3%	Potassium 1-naphthaleneacetate	MTHF	77	67
10[b]	0.3	4CzIPN 4%	Potassium 1-naphthaleneacetate	MTHF	77	83

[a] The reactions were performed with **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (5 mol%), SilaCOgen (1.5 equiv.), base (2 equiv.) in solvent (2 mL) under LED irradiation for 5-10 hours, unless otherwise indicated. [b] Performed with PC **1** (4 mol%). [c] Yields were determined by isolated products, stereoselectivities were determined with 19F-NMR analysis.

4. Mechanistic studies

4.1 Radical trapping experiments

(1) Stir bar, photocatalyst 4CzIPN (7.9 mg, 0.01 mmol, 0.05 equiv.), anhydrous potassium benzoate (89.7 mg, 0.4 mmol, 2 equiv.), SilaCOgen (72.6 mg, 0.3 mmol, 1.5 equiv.), ethene-1,1-diyldibenzene (36.1 mg, 0.2 mmol, 1 equiv.), ethyl bromofluoroacetate (81.2 mg, 0.4 mmol, 2 equiv.) and 2-Me-THF (2 mL) were added to a Schlenk tube under argon atmosphere. The reaction mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed for 10 hours (as monitored by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/EA = 100:1) to afford the fluoroalkylation products.

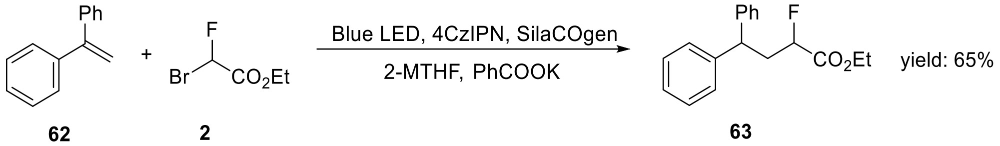


Figure S1

(2) Stir bar, photocatalyst 4CzIPN (7.9 mg, 0.01 mmol, 0.05 equiv.), anhydrous potassium benzoate (89.7 mg, 0.4 mmol, 2 equiv.), SilaCOgen (72.6 mg, 0.3 mmol, 1.5

equiv.), (1-cyclopropylvinyl)benzene (28.8 mg, 0.2 mmol, 1 equiv.), ethyl bromofluoroacetate (81.2 mg, 0.4 mmol, 2 equiv.) and 2-Me-THF (2 mL) were added to a Schlenk tube under argon atmosphere. The reaction mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed for10 hours. Radical-trapped product was detected by LC-MS.

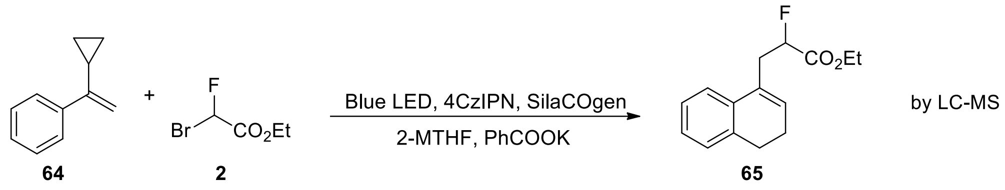


Figure S2

(3) Stir bar, photocatalyst 4CzIPN (7.9 mg, 0.01 mmol, 0.05 equiv.), anhydrous potassium benzoate (89.7 mg, 0.4 mmol, 2 equiv.), SilaCOgen (72.6 mg, 0.3 mmol, 1.5 equiv.), ethene-1,1-diyldibenzene (36.1 mg, 0.2 mmol, 1 equiv.) and 2-Me-THF (2 mL) were added to a Schlenk tube under argon atmosphere. The reaction mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed for 6 hours (as monitored by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/EA = 100:1) to afford the (2,2-diphenylethyl)(methyl)diphenylsilane.

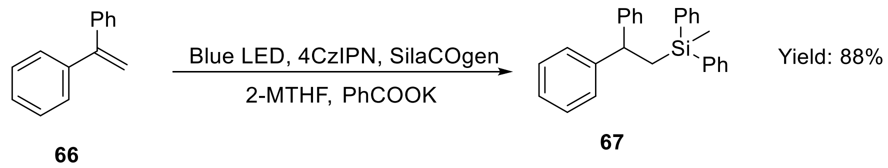


Figure S3

(4) Stir bar, photocatalyst 4CzIPN (7.9 mg, 0.01 mmol, 0.05 equiv.), anhydrous potassium benzoate (89.7 mg, 0.4 mmol, 2 equiv.), SilaCOgen (72.6 mg, 0.3 mmol, 1.5 equiv.), ethene-1,1-diyldibenzene (36.1 mg, 0.2 mmol, 1 equiv.), ethyl bromofluoroacetate (81.2 mg, 0.4 mmol, 2 equiv.) and 2-Me-THF (2 mL) were added to a Schlenk tube under argon atmosphere. The reaction mixture was stirred under the irradiation of 20 W blue LEDs (454 nm) at room temperature. After the reaction was completed for 10 hours (as monitored by TLC analysis). Triethylamine (0.4 mmol, 2 equiv.) and ethanol (1 mL) were added to the solution and stirred for 1h, then extracted (EA/H_2O) and analyzed by GC-MS.

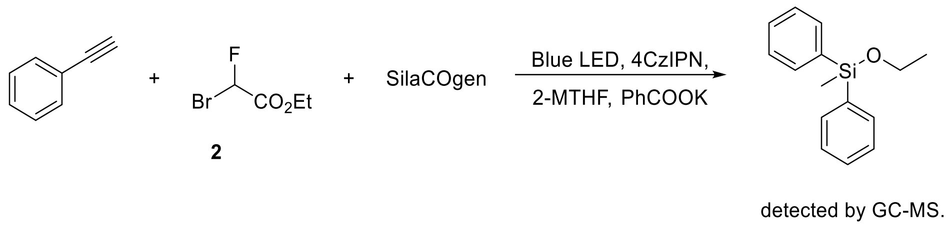


Figure S4

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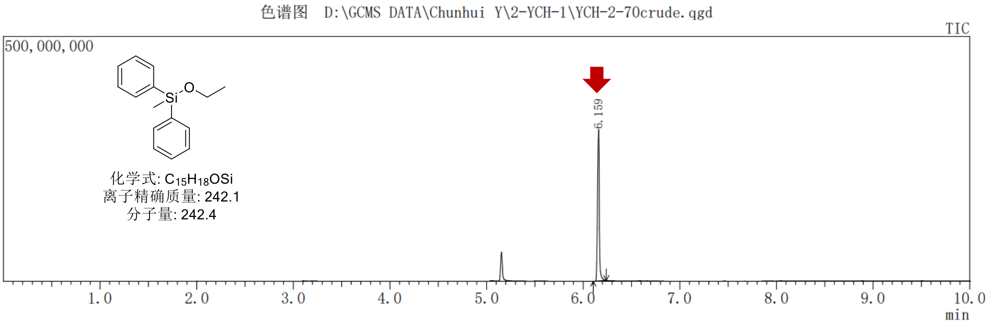

质谱

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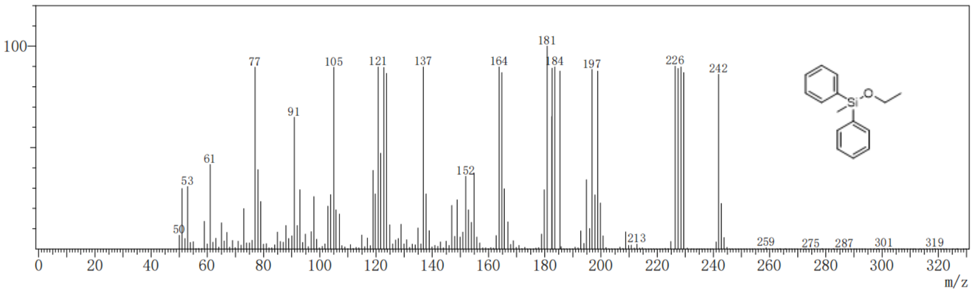
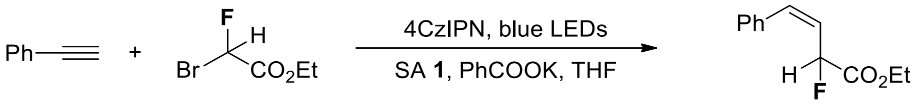


4.2 H/D exchange and KIE experiments

Prepare a reaction system of substrates containing C-H bonds (THF) and substrates containing C-D bonds (THF-d_8). The reaction is started under standard experimental conditions and samples are taken at certain intervals. Samples are analyzed using NMR analysis methods to determine concentrations or concentration changes of reactants and products. The reaction rate constants $k_{\text{-H}}$ and $k_{\text{-D}}$ were obtained by fitting the experimental data with the first-order reaction kinetics equation. Then calculate their ratio KIE.

Reaction 1:



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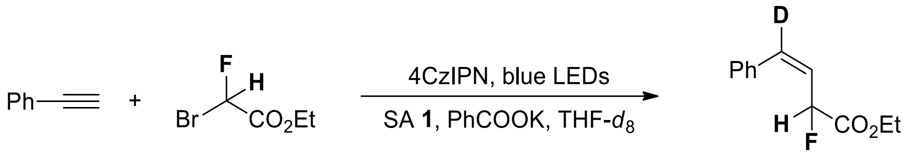


Time (h)	*c* 1 (mmol/ml)	*c* (mmol/ml)
0.25	0.028	0.002
0.5	0.036	0.004
0.83333	0.042	0.007
1.25	0.053	0.011
2	0.067	0.015

Reaction 1:

y = a + b*x

k=0.02202 ± 0.00108

R^2=0.99289

Reaction 2:

y = a + b*x

k=0.00758 ± 5.55484E-4

R^2=0.98415

KIE = [k_H/k_D] = 2.9

4.3 Fluorescence quenching experiments

Experimental procedure: **PC1** was dissolved in MTHF in a 20 mL volumetric flask to set the concentration to be 0.01 M. Compound **2** was dissolved in MTHF in a 20 mL volumetric flask to set the concentration to be 0.01 M. **SA6** was dissolved in MTHF in a 20 mL volumetric flask to set the concentration to be 0.01 M. **PhCOOK** was dissolved in MTHF in a 20 mL volumetric flask to set the concentration to be 0.01 M. Different components were mixed in equal volume and diluted to 3 ml respectively for fluorescence quenching experiment, and the results in the figure were obtained.

4.4 Cyclic voltammetry measurements

Cyclic voltammograms were taken on a Autolab PGSTAT 302N electrochemical analyzer/workstation (Switzerland Vantone China Co., LTD.) in CH_3CN (Energy Chemical, 99.9%, with molecular sieves, water≤50 ppm (by K.F.)) at room temperature using a glass carbon working electrode, a S20 platinum auxiliary electrode and 0.1 M NBu_4PF_6 as supporting electrolyte. All potentials are referenced against the Ag/AgCl redox couple. 20 mM SilaCOgen was dissolved in an anhydrous CH_3CN solution containing 0.1 M NBu_4PF_6. According to the above method, 20.0 mM $BrCHFCO_2Et$, 20 mM 1-bromobutyl acetate, 20.0 mM SilaCOgen with PhCOOK and 2.0 mM 4CzIPN were prepared sequentially. The solution was degassed with nitrogen bubbling for 5 min prior to voltammetric studies. The scan rate was 100 mV/s.

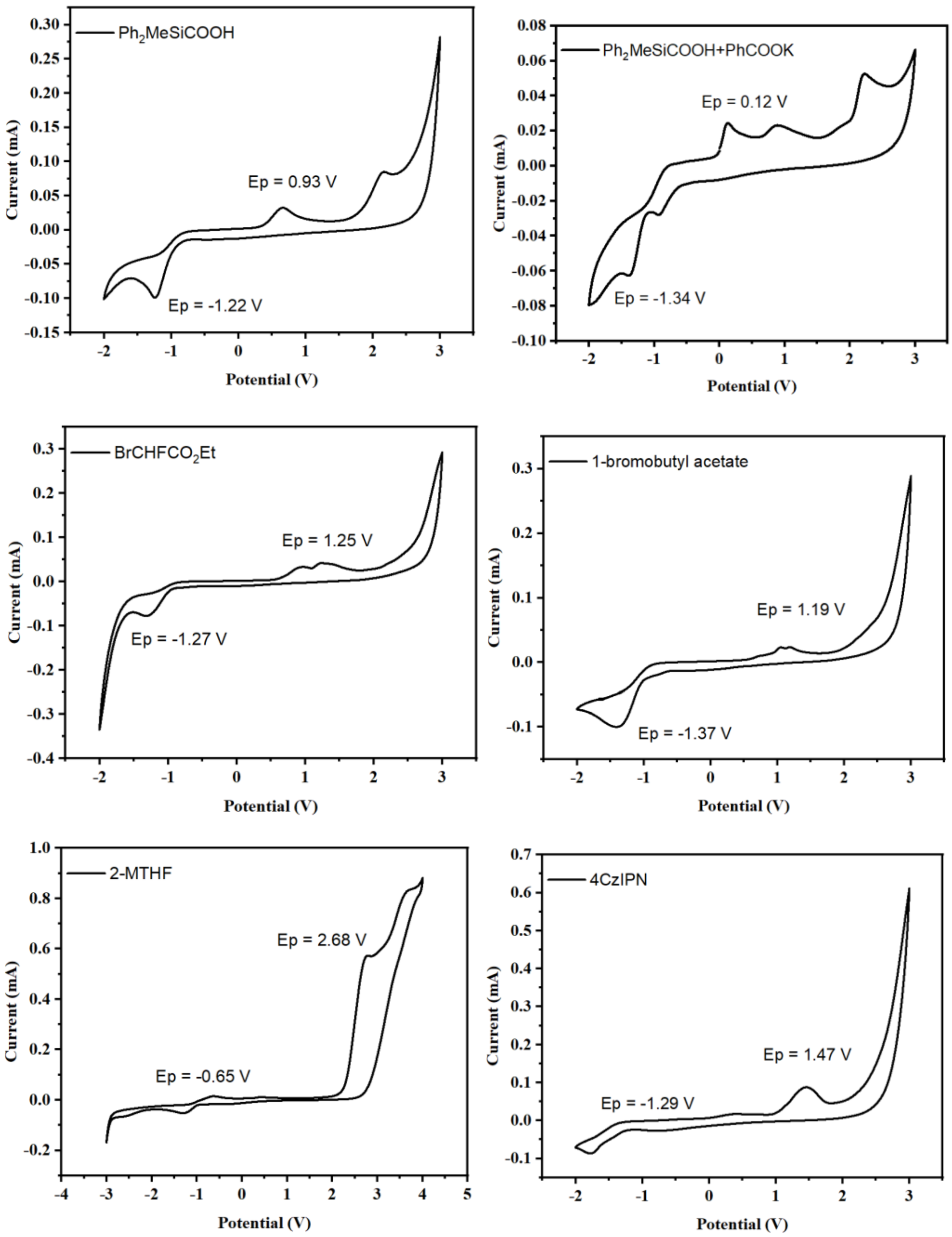


Figure S4 Cyclic Voltammetry of each reaction component

4.5 Density Functional Theory Calculation and Atomic Coordination Energy Potential Profiles

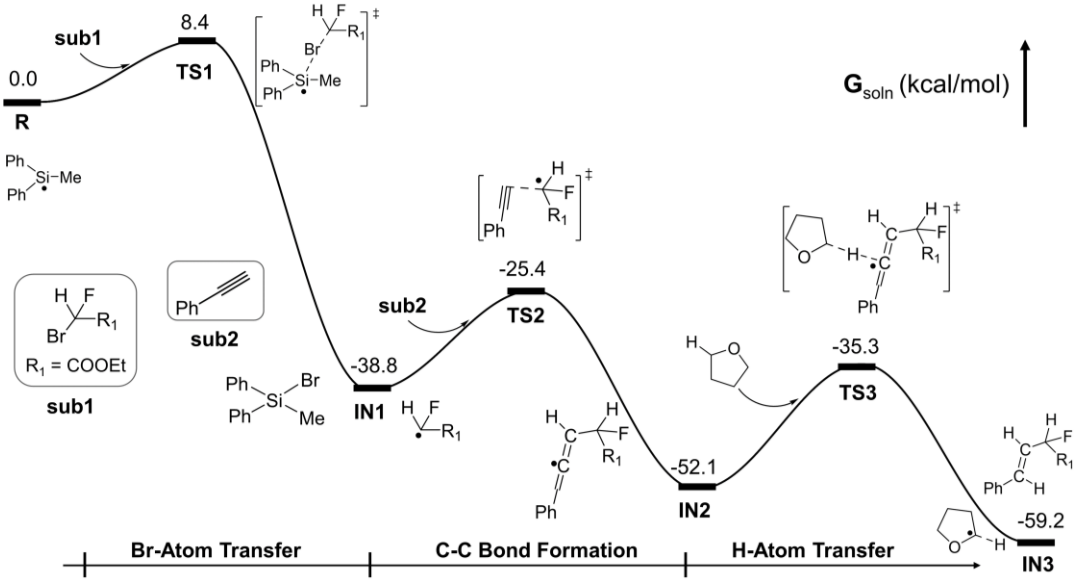


Figure S5. Free-energy potential (G_{soln}) for the reactions initiated by silicon radical (**R**) to produce the *trans*-monofluoroalkylation (**IN3**).

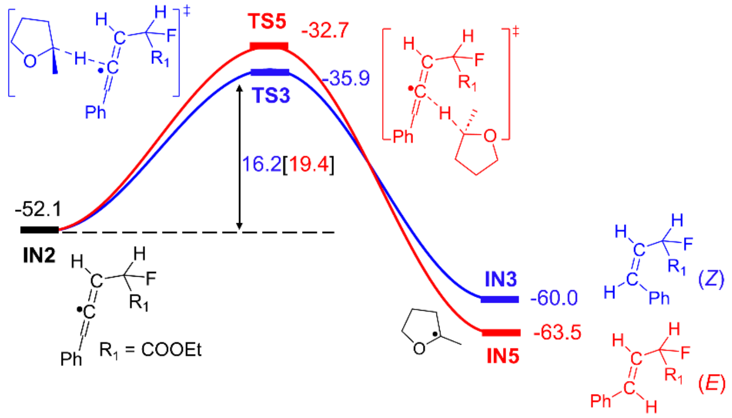


Figure S6. Free-energy potential (G_{soln}) for the radical reactions from intermediate (**IN2**) to the *cis*-/*trans*-monofluoroalkylation (**IN3 & IN5**).

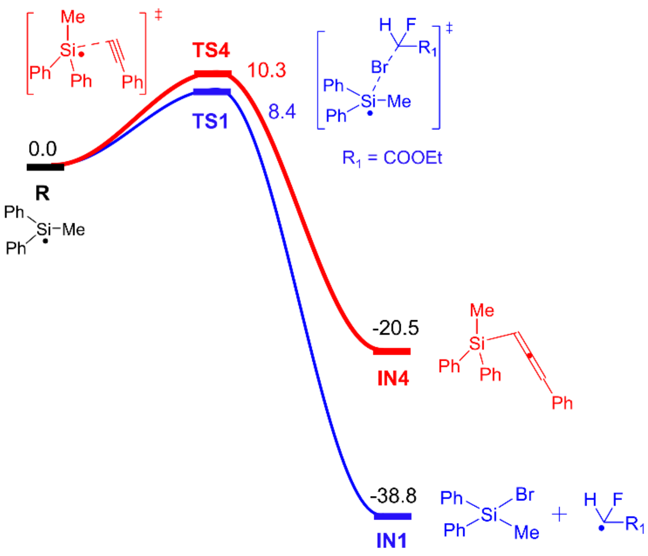


Figure S7. Free-energy potential (G_{soln}) for the Si radical reacted with ethyl bromofluoroacetate (Br-atom transfer), and with phenylacetylene.

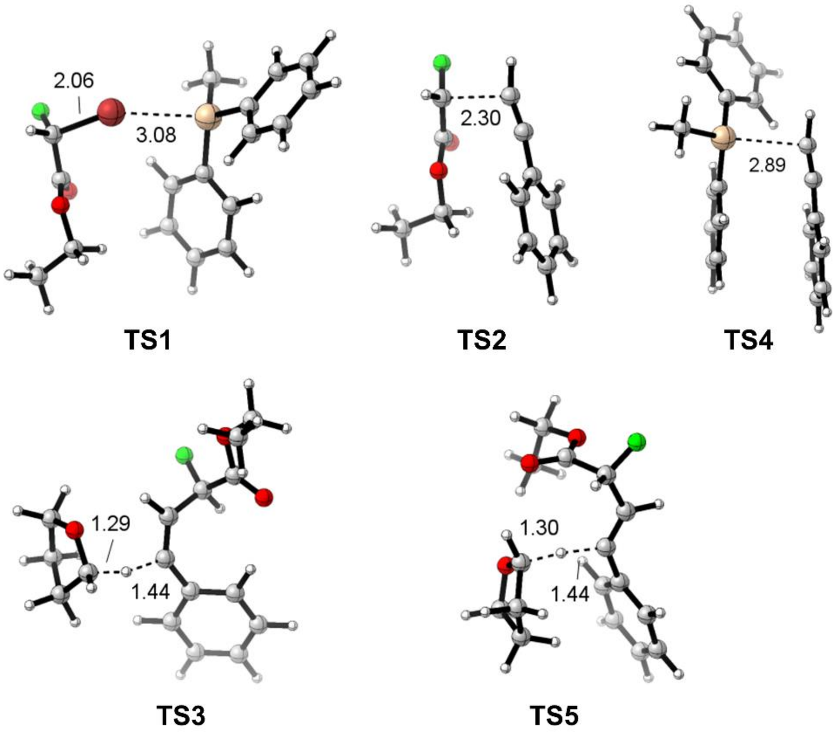


Figure S8. Key transition states (**TSs**) during the reactions initiated by silicon radical to produce the *trans*-monofluoroalkylation.

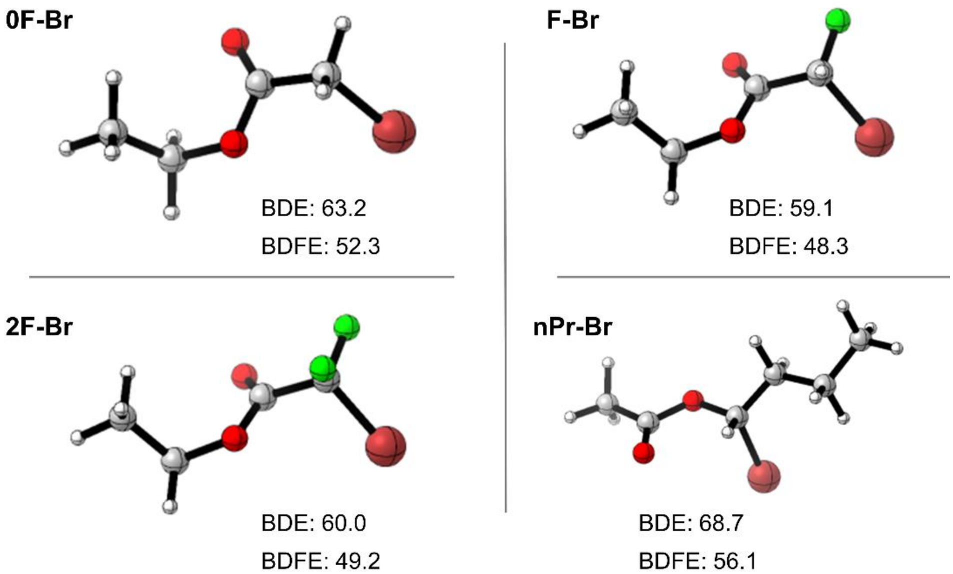


Figure S9. The bond dissociation energy and free-energy (BDE and DBFE, in kcal/mol) of homolytic Br-C (ethyl bromofluoroacetate).

Table S4. The absolute energy and free energies (in Hartree) of the optimized structures for the reactions initiated by silicon radical to produce the *trans*-monofluoroalkylation by the PCM B3LYP-D3//B3LYP-D3 method in THF solution.

	E	**G**	**E_{soln}**	**G_{soln}**
R	-792.309004	-792.132292	-792.926772	-792.750060
F-Br	-2979.911602	-2979.846418	-2980.704889	-2980.639705
TS1	-3772.233764	-3771.972242	-3773.637970	-3773.376448
Fsub	-3366.291384	-3366.115862	-3367.226033	-3367.050511
IN1	-405.987931	-405.923089	-406.465879	-406.401037
PhC	-308.199971	-308.120556	-308.527459	-308.448044
TS2	-714.191731	-714.028188	-714.991385	-714.827842
IN2	-714.238247	-714.072524	-715.036127	-714.870404
THF-Me	-271.580962	-271.466764	-271.893814	-271.779616
TS3	-985.795050	-985.497157	-986.922030	-986.624137
IN3	-985.838902	-985.555802	-986.945673	-986.662573
THFr-Me	-270.926731	-270.827057	-271.237892	-271.138218
TS4	-1100.521119	-1100.245675	-1101.457212	-1101.181768
IN4	-1100.573645	-1100.296325	-1101.508048	-1101.230729
TS5	-985.794148	-985.495444	-986.917738	-986.619034
IN5	-985.838242	-985.557568	-986.948818	-986.668144

Table S5. The absolute energy and free energies (in Hartree) of the optimized structures for Br-C bond homolytic by the PCM B3LYP-D3//B3LYP-D3 method in THF solution.

	E	**G**	**E_{soln}**	**G_{soln}**
Br	-2573.826536	-2573.843366	-2574.144854	-2574.161684
0FA	-306.831322	-306.757966	-307.186026	-307.112670
0F-Br	-2880.761214	-2880.687391	-2881.431520	-2881.357697

FA	-405.987931	-405.923089	-406.465879	-406.401037
F-Br	-2979.911602	-2979.846418	-2980.704889	-2980.639705
2FA	-505.148452	-505.092842	-505.744857	-505.689247
2F-Br	-3079.074919	-3079.019013	-3079.985312	-3079.929406
nPrA	-385.413426	-385.291125	-385.850467	-385.728166
nPr-Br	-2959.352085	-2959.226668	-2960.104738	-2959.979321

XYZ Coordinates

R.xyz

```
Si 0.033001 1.186137 -0.569435
C 0.064275 2.862932 0.307626
H 1.009813 3.389674 0.106447
H -0.761482 3.509555 -0.027626
H -0.019865 2.729212 1.400605
C 1.570428 0.180492 -0.170109
C 1.512982 -1.149347 0.296466
C 2.846451 0.757856 -0.347831
C 2.678107 -1.866795 0.576936
H 0.543789 -1.626148 0.458665
C 4.011327 0.044410 -0.064808
H 2.931667 1.784634 -0.716769
C 3.930808 -1.273585 0.397170
H 2.607084 -2.893875 0.944366
H 4.987087 0.515881 -0.207530
H 4.842075 -1.835407 0.616562
C -1.559060 0.249623 -0.239079
C -1.788311 -1.022197 -0.808123
C -2.590661 0.812871 0.540718
C -2.982508 -1.709380 -0.588353
H -1.020818 -1.479254 -1.439133
C -3.788955 0.129065 0.758555
H -2.455544 1.798728 0.993138
C -3.987612 -1.135502 0.197491
H -3.133902 -2.694805 -1.036341
H -4.570838 0.584387 1.371870
H -4.924706 -1.671172 0.367875
```

F-Br.xyz

```
C -0.599708 0.734103 -0.564253
Br -1.893540 -0.611638 0.074238
F -1.054906 1.970190 -0.305140
C 0.731046 0.500384 0.148830
O 1.349677 -0.554391 -0.385307
O 1.135812 1.182390 1.049818
C 2.603823 -0.954018 0.208659
H 2.695198 -2.021002 -0.036221
H 2.527353 -0.838433 1.299682
H -0.514007 0.567697 -1.646861
C 3.763007 -0.148763 -0.348413
H 3.668177 0.911486 -0.072661
H 4.711429 -0.527207 0.064261
H 3.806995 -0.231136 -1.445292
```

A4opt.xyz

```
Si 0.004351 0.529869 0.626427
C -0.007105 1.061071 2.423651
H 0.926302 1.593751 2.660541
H -0.851521 1.732991 2.640956
H -0.076255 0.177788 3.079468
C 1.500437 -0.530941 0.224747
C 1.411844 -1.927383 0.379481
C 2.734003 0.019860 -0.164951
C 2.522048 -2.746488 0.158361
H 0.461179 -2.384272 0.668383
C 3.845207 -0.796457 -0.387489
H 2.821973 1.099838 -0.308158
C 3.741196 -2.181219 -0.225242
H 2.433830 -3.828933 0.280717
H 4.795211 -0.351224 -0.693534
H 4.609707 -2.820480 -0.402649
C -1.567062 -0.374471 0.157195
C -1.668637 -1.011710 -1.094086
C -2.668427 -0.437295 1.028456
C -2.832201 -1.688179 -1.462282
H -0.824946 -0.978161 -1.788971
C -3.835381 -1.115471 0.664115
H -2.620825 0.047851 2.006744
C -3.918290 -1.741248 -0.581983
H -2.894300 -2.176414 -2.438006
H -4.681540 -1.154886 1.354569
```

H	-4.829872	-2.271381	-0.868913
Br	0.146410	2.420427	-0.619456

A5opt.xyz

C	0.000000	0.000000	-0.000113
O	0.000000	0.000000	1.163083
O	0.000000	0.000000	-1.162998

IN3.xyz

C	-3.354706	0.764494	0.804978
C	-2.026082	0.370076	0.546526
C	-1.809603	-0.817256	-0.181293
C	-2.892102	-1.554451	-0.667559
C	-4.202765	-1.133696	-0.430542
C	-4.431127	0.028336	0.314351
H	-3.537300	1.671024	1.388145
H	-0.796357	-1.191501	-0.332622
H	-2.705428	-2.475417	-1.225192
H	-5.045187	-1.716281	-0.811059
H	-5.452980	0.358437	0.516391
C	-0.936129	1.210852	1.066207
C	0.275164	1.454513	0.535412
H	0.968786	2.114536	1.066259
C	0.824745	0.960705	-0.770854
H	0.029739	0.588587	-1.434715
C	1.799743	-0.193018	-0.529498
O	1.455124	-1.351943	-0.502477
O	3.037910	0.240689	-0.303597
C	4.035823	-0.750725	0.016894
H	4.989829	-0.277972	-0.253895
H	3.875161	-1.633240	-0.619317
C	3.991200	-1.121048	1.488065
H	3.039196	-1.612346	1.735982
H	4.809857	-1.819523	1.722831
H	4.107166	-0.227446	2.120405
F	1.477768	2.006377	-1.397433
H	-1.171628	1.741091	1.996147

IN5.xyz

C	-2.432470	0.698741	-0.833273
C	-2.213752	-0.320817	0.114250
C	-3.285527	-0.696579	0.944727
C	-4.533298	-0.081136	0.834578
C	-4.734344	0.926128	-0.111666
C	-3.677403	1.312621	-0.944863
H	-1.618853	1.014705	-1.488883
H	-3.132092	-1.484841	1.686495
H	-5.351131	-0.389343	1.490183
H	-5.709307	1.410864	-0.201064
H	-3.827259	2.100966	-1.686445
C	-0.923431	-1.004003	0.267006
C	0.193434	-0.801722	-0.449833
H	0.241461	-0.065961	-1.258172
C	1.481746	-1.513195	-0.182597
H	1.348962	-2.321667	0.552933
C	2.498113	-0.536101	0.411416
O	2.763324	-0.484073	1.586415
O	2.999457	0.271438	-0.528986
C	3.921025	1.291168	-0.096028
H	4.515985	1.525147	-0.989724
H	4.579641	0.868315	0.676688
C	3.186211	2.513729	0.423269
H	2.614277	2.266313	1.329315
H	3.908536	3.305235	0.678358
H	2.495566	2.908690	-0.337727
F	1.982382	-2.045834	-1.359517
H	-0.891317	-1.757841	1.062348

Fsub.xyz

C	1.709173	-0.597949	0.167590
H	1.819363	-1.668135	0.353808
C	0.466475	0.073261	-0.164390
O	0.351713	1.263365	-0.372093
O	-0.542377	-0.826324	-0.211122
C	-1.849713	-0.314466	-0.518968
H	-2.400323	-1.178335	-0.917544
H	-1.757594	0.448311	-1.306782
C	-2.531574	0.259251	0.711164
H	-1.986981	1.140485	1.079911
H	-3.558102	0.570088	0.460002
H	-2.584201	-0.490750	1.515448
F	2.802998	0.129048	0.256500

IN4.xyz

C	-3.286448	-1.706499	0.127450
C	-2.212008	-1.340117	-0.738211
C	-2.436198	-0.291782	-1.680188
C	-3.654840	0.369341	-1.719344

C	-4.695452	0.007613	-0.850237
C	-4.499851	-1.036020	0.066996
H	-3.130785	-2.511901	0.847831
H	-1.620813	0.004665	-2.341520
H	-3.798675	1.187869	-2.428821
H	-5.651356	0.534455	-0.887986
H	-5.307584	-1.322566	0.745348
C	-0.976419	-1.976773	-0.656013
C	0.268965	-2.106212	-0.271306
H	0.874922	-2.969701	-0.592239
Si	1.080251	-0.776151	0.815664
C	1.346789	-1.429193	2.561643
H	0.388387	-1.733592	3.010708
H	2.012194	-2.307088	2.555072
H	1.794095	-0.660007	3.211593
C	-0.078707	0.706537	0.813166
C	0.149644	1.804471	-0.034593
C	-1.264868	0.691474	1.569345
C	-0.778983	2.844404	-0.133363
H	1.063968	1.845138	-0.632394
C	-2.199080	1.723381	1.470057
H	-1.481270	-0.152173	2.230192
C	-1.957970	2.802164	0.614776
H	-0.583669	3.688091	-0.800391
H	-3.123837	1.679338	2.049951
H	-2.691115	3.608238	0.530202
C	2.723256	-0.314151	0.018165
C	2.862687	-0.330888	-1.382413
C	3.829478	0.093520	0.785588
C	4.059196	0.050529	-1.995035
H	2.020899	-0.649509	-2.004131
C	5.029488	0.474151	0.179040
H	3.757666	0.116631	1.876510
C	5.145817	0.454072	-1.213736
H	4.145886	0.030263	-3.084447
H	5.876885	0.786978	0.794465
H	6.083699	0.750855	-1.689952

PhC.xyz

C	0.120971	-1.214575	0.000144
C	-0.594943	-0.000406	-0.000185
C	0.120235	1.214192	0.000131
C	1.514368	1.210123	0.000047
C	2.215991	0.000460	-0.000229
C	1.515083	-1.209644	0.000035
H	-0.430415	-2.156573	0.000430
H	-0.431715	2.155856	0.000420
H	2.057908	2.157895	0.000187
H	3.308506	0.000779	-0.000244
H	2.059224	-2.157070	0.000175
C	-2.026424	-0.000737	0.000045
C	-3.240268	0.000364	-0.000228
H	-4.313582	0.000444	0.000471

IN2.xyz

C	2.643094	1.275989	-0.176332
C	2.275191	-0.084638	-0.435342
C	3.299510	-1.083159	-0.352150
C	4.600158	-0.731487	-0.026574
C	4.940314	0.607819	0.224388
C	3.951037	1.601702	0.146758
H	1.873116	2.047443	-0.231379
H	3.035025	-2.124326	-0.544929
H	5.367050	-1.507511	0.036437
H	5.967909	0.874671	0.480139
H	4.211640	2.644141	0.345899
C	0.981070	-0.416898	-0.771029
C	-0.273147	-0.752605	-0.894810
H	-0.772785	-0.815197	-1.872954
C	-1.175468	-1.061705	0.291813
H	-1.638953	-2.055673	0.148813
C	-2.300941	-0.029671	0.378111
O	-2.430457	0.781837	1.253167
O	-3.107640	-0.159669	-0.688810
C	-4.209665	0.763958	-0.796749
H	-4.440939	0.795568	-1.870642
H	-3.869881	1.758120	-0.471098
C	-5.403371	0.301495	0.018457
H	-5.162726	0.301159	1.091418
H	-6.253691	0.982865	-0.142707
H	-5.712264	-0.712543	-0.278801
F	-0.473936	-1.056761	1.461745

TS1.xyz

Si	1.687682	-0.314981	0.806040
C	3.313612	-0.160300	-0.100775
C	4.500180	-0.706121	0.433923
C	3.385048	0.449001	-1.373263

C	5.708005	-0.628867	-0.262285
H	4.483403	-1.192913	1.412540
C	4.591676	0.529617	-2.068207
H	2.479495	0.858870	-1.828754
C	5.758342	-0.008372	-1.513927
H	6.615452	-1.053038	0.174983
H	4.623182	1.008961	-3.049917
H	6.703396	0.051963	-2.059117
C	0.685232	1.267657	0.871199
C	-0.611671	1.249295	1.428789
C	1.165915	2.492635	0.362810
C	-1.393091	2.404173	1.480427
H	-1.034124	0.317252	1.809632
C	0.383939	3.649082	0.411954
H	2.168738	2.547420	-0.066844
C	-0.897574	3.608828	0.969992
H	-2.396781	2.350512	1.907524
H	0.779802	4.588255	0.016847
H	-1.508461	4.514412	1.007644
C	1.830514	-1.169345	2.477861
H	0.833629	-1.272105	2.932073
H	2.263604	-2.176545	2.378624
H	2.462255	-0.581524	3.166411
C	-2.800202	-2.047938	-0.300458
Br	-0.744194	-1.879841	-0.265797
F	-3.203854	-2.771342	0.753602
C	-3.298110	-0.621278	-0.221001
O	-3.248983	-0.057236	-1.429893
O	-3.634127	-0.080738	0.801929
C	-3.503309	1.361407	-1.513034
H	-3.024099	1.666577	-2.453366
H	-2.989239	1.857207	-0.677342
H	-3.028927	-2.546900	-1.250882
C	-4.988862	1.670524	-1.517522
H	-5.448194	1.384985	-0.560507
H	-5.142587	2.751202	-1.665744
H	-5.499615	1.135474	-2.333094

THF.xyz

C	-1.097211	-0.511934	0.205171
O	0.039228	-1.203137	-0.270625
C	1.165238	-0.421421	0.086473
C	0.711012	1.061387	0.032619
C	-0.823905	0.959783	-0.131055
H	-1.989244	-0.928066	-0.285905
H	-1.211975	-0.645924	1.302552
H	1.505568	-0.682323	1.108958
H	1.981426	-0.659001	-0.612206
H	0.990606	1.592228	0.955024
H	1.170989	1.601156	-0.807686
H	-1.375597	1.656548	0.517323
H	-1.116400	1.163589	-1.172305

THFr.xyz

C	-0.529628	-1.123340	0.037781
O	0.818216	-0.939253	-0.115997
C	1.120773	0.426551	0.173783
C	-0.143034	1.198774	-0.214768
C	-1.256494	0.188098	0.139054
H	1.340779	0.534203	1.253195
H	2.018481	0.706693	-0.395770
H	-0.234178	2.160122	0.311107
H	-0.141341	1.398791	-1.298059
H	-1.641477	0.371174	1.162028
H	-2.125759	0.257207	-0.536730
H	-0.911937	-2.054670	-0.382903

TS4.xyz

C	3.362216	-0.818803	-1.610707
C	2.249889	-1.287330	-0.876845
C	2.403371	-1.550756	0.500676
C	3.630405	-1.340651	1.123312
C	4.725610	-0.872401	0.390031
C	4.585527	-0.613718	-0.978100
H	3.246061	-0.612454	-2.676218
H	1.543060	-1.896579	1.074797
H	3.731302	-1.534209	2.193594
H	5.685972	-0.706898	0.883765
H	5.437987	-0.247503	-1.555365
C	0.990236	-1.467833	-1.510450
C	-0.123893	-1.501983	-2.015532
H	-1.028809	-1.783382	-2.521775
Si	-1.381318	0.890146	-0.986488
C	-1.972047	2.483769	-1.826146
H	-1.120106	3.018182	-2.274586
H	-2.702443	2.278458	-2.624324
H	-2.442217	3.159316	-1.089496
C	0.030196	1.236052	0.207045

C	-0.046652	0.931222	1.580653
C	1.237294	1.780854	-0.276569
C	1.033666	1.168789	2.433935
H	-0.967081	0.509194	1.991191
C	2.318469	2.017915	0.571988
H	1.341575	2.006377	-1.342129
C	2.219800	1.709920	1.931557
H	0.948985	0.928216	3.497024
H	3.248657	2.424701	0.168816
H	3.069756	1.883758	2.595766
C	-2.795813	-0.036444	-0.171860
C	-2.561211	-1.238103	0.533174
C	-4.132177	0.399289	-0.293750
C	-3.610031	-1.957427	1.106938
H	-1.540122	-1.617653	0.623761
C	-5.184181	-0.321974	0.275570
H	-4.356530	1.321871	-0.835716
C	-4.926723	-1.501361	0.980374
H	-3.401674	-2.882053	1.651522
H	-6.210382	0.040177	0.171795
H	-5.749242	-2.065734	1.426644

TS2.xyz

C	2.039276	-1.007300	-1.122047
C	1.299521	-1.210100	0.064904
C	1.771965	-0.644205	1.271237
C	2.944370	0.106884	1.282435
C	3.666451	0.307631	0.100354
C	3.209076	-0.252533	-1.098783
H	1.673393	-1.437637	-2.055667
H	1.197376	-0.793650	2.186976
H	3.297434	0.543388	2.219630
H	4.584765	0.899084	0.113053
H	3.770308	-0.096829	-2.023132
C	0.080046	-1.931854	0.048592
C	-1.073511	-2.362666	0.017218
H	-1.874152	-3.078373	0.114842
C	-2.590968	-0.730107	-0.552001
H	-2.508603	-0.886795	-1.629562
C	-1.968937	0.414675	0.108872
O	-2.265905	0.846736	1.200677
O	-0.959963	0.878520	-0.661281
C	-0.150003	1.931766	-0.115055
H	0.828678	1.812779	-0.600322
H	-0.030903	1.764586	0.964783
C	-0.755563	3.296407	-0.389992
H	-1.718869	3.403131	0.129938
H	-0.079725	4.087895	-0.028557
H	-0.915587	3.444950	-1.469226
F	-3.694169	-1.219576	0.007518

TS3.xyz

C	-2.689483	1.566271	0.156860
C	-1.321140	1.389221	-0.147914
C	-0.544039	2.533091	-0.444300
C	-1.121214	3.803371	-0.416854
C	-2.473864	3.963734	-0.101571
C	-3.255163	2.838622	0.187453
H	-3.301724	0.690273	0.382663
H	0.513237	2.412632	-0.687897
H	-0.505584	4.677378	-0.643936
H	-2.920192	4.960833	-0.083687
H	-4.312879	2.956337	0.435824
C	-0.746803	0.059877	-0.186946
C	0.359747	-0.480211	0.319278
H	0.614825	-1.522241	0.087636
C	1.347899	0.225059	1.212474
H	0.936961	1.177995	1.580992
C	2.603499	0.551270	0.406036
O	2.689620	1.527892	-0.302091
O	3.541760	-0.386218	0.531270
C	4.733536	-0.234007	-0.265895
H	5.498958	-0.812870	0.269144
H	5.021753	0.827323	-0.274429
C	4.521676	-0.754743	-1.675865
H	3.769204	-0.150558	-2.203031
H	5.465247	-0.699442	-2.241512
H	4.188370	-1.803739	-1.659444
F	1.657131	-0.583013	2.290267
C	-1.935837	-2.098266	-1.297980
C	-1.668014	-3.572968	0.468354
C	-2.921507	-2.729174	0.737385
C	-3.308286	-2.262960	-0.673799
H	-1.470263	-0.968129	-0.888259
H	-1.855025	-2.070237	-2.394190
H	-1.909564	-4.642471	0.336647
H	-0.910594	-3.484496	1.262946
H	-3.712327	-3.297534	1.247349

H	-2.666494	-1.859132	1.362068
H	-3.888073	-3.040173	-1.203825
H	-3.899357	-1.335371	-0.686157
O	-1.113468	-3.086471	-0.763130

TS5.xyz

C	2.436427	-1.898902	-0.642103
C	1.443697	-1.174800	0.050537
C	1.780860	-0.583401	1.288086
C	3.063873	-0.720874	1.814032
C	4.041241	-1.440767	1.116174
C	3.719920	-2.030709	-0.110820
H	2.187594	-2.351150	-1.604692
H	1.021224	-0.006743	1.819320
H	3.306440	-0.262583	2.776225
H	5.047988	-1.542443	1.527905
H	4.476502	-2.598022	-0.658766
C	0.130901	-0.947010	-0.521646
C	-0.930665	-1.735068	-0.635353
H	-0.918185	-2.764304	-0.247226
C	-2.276992	-1.335986	-1.202965
H	-2.213748	-1.023904	-2.257762
C	-2.843768	-0.152014	-0.418434
O	-2.918966	0.966406	-0.868934
O	-3.168912	-0.502222	0.824699
C	-3.489994	0.559665	1.746816
H	-4.149179	0.093250	2.491975
H	-4.045053	1.342429	1.210565
C	-2.225364	1.111946	2.381641
H	-1.569649	1.583160	1.634033
H	-2.488443	1.872193	3.134394
H	-1.663378	0.309047	2.883628
F	-3.136506	-2.413736	-1.113371
C	0.107834	1.717931	-1.097334
C	1.785887	2.691911	0.183322
C	2.451624	2.074923	-1.049460
C	1.275440	1.970049	-2.033066
H	0.022064	0.439216	-0.909354
H	-0.905018	1.983995	-1.424853
H	1.824222	3.796521	0.161117
H	2.225179	2.347505	1.131369
H	3.282824	2.686961	-1.428131
H	2.841991	1.075113	-0.810893
H	1.132130	2.917645	-2.582729
H	1.400487	1.168356	-2.776742
O	0.411258	2.287818	0.136034

0FA.xyz

C	2.217816	-0.466834	0.344452
H	2.307063	-1.543150	0.498033
C	0.953687	0.127025	-0.049084
O	0.778690	1.318386	-0.231384
O	-0.018801	-0.804485	-0.195244
C	-1.318755	-0.330220	-0.575742
H	-1.809827	-1.199379	-1.036544
H	-1.204839	0.461461	-1.331812
C	-2.105552	0.178352	0.620665
H	-1.622233	1.066928	1.051778
H	-3.124504	0.458317	0.309180
H	-2.182212	-0.598501	1.397157
H	3.074265	0.193176	0.483488

0F-Br.xyz

C	0.644728	0.840931	0.735164
H	0.563319	0.523468	1.781673
C	-0.676435	0.680955	0.013635
O	-1.179994	1.543200	-0.662321
O	-1.207612	-0.527419	0.233419
C	-2.452138	-0.830638	-0.426198
H	-2.467035	-1.927199	-0.496052
H	-2.428146	-0.404232	-1.439843
C	-3.640856	-0.305254	0.358230
H	-3.626698	0.793711	0.394362
H	-4.578204	-0.620685	-0.126673
H	-3.635891	-0.697274	1.387017
H	0.979424	1.879277	0.655330
Br	2.029780	-0.285408	-0.080274

2FA.xyz

C	1.497495	-0.116147	0.164701
C	0.163105	0.356266	-0.164612
O	-0.116330	1.533551	-0.257123
O	-0.689762	-0.674668	-0.300158
C	-2.067619	-0.339385	-0.551252
H	-2.487522	-1.240128	-1.019880
H	-2.106430	0.492209	-1.270506
C	-2.799358	0.015343	0.731001
H	-2.385319	0.933073	1.173121
H	-3.865648	0.188984	0.516164

H -2.722733 -0.801793 1.464643
F 2.506606 0.714553 0.192105
F 1.855022 -1.374538 0.087415

2F-Br.xyz
C 0.573021 0.749068 0.228007
C -0.787436 0.358416 -0.389053
O -1.180672 0.815302 -1.426218
O -1.398605 -0.531446 0.380002
C -2.680252 -1.026095 -0.073073
H -2.781330 -2.003573 0.417117
H -2.633818 -1.168712 -1.162600
C -3.803046 -0.082711 0.314122
H -3.699198 0.881844 -0.203687
H -4.771439 -0.522463 0.028427
H -3.809852 0.093020 1.400552
F 1.026193 1.861506 -0.340215
F 0.466827 0.952169 1.544856
Br 1.859398 -0.710460 -0.098053

Br.xyz
Br 0.000000 0.000000 0.000000

FA.xyz
C 1.709173 -0.597949 0.167590
H 1.819363 -1.668135 0.353808
C 0.466475 0.073261 -0.164390
O 0.351713 1.263365 -0.372093
O -0.542377 -0.826324 -0.211122
C -1.849713 -0.314466 -0.518968
H -2.400323 -1.178335 -0.917544
H -1.757594 0.448311 -1.306782
C -2.531574 0.259251 0.711164
H -1.986981 1.140485 1.079911
H -3.558102 0.570088 0.460002
H -2.584201 -0.490750 1.515448
F 2.802998 0.129048 0.256500

F-Br.xyz
C -0.599708 0.734103 -0.564253
Br -1.893540 -0.611638 0.074238
F -1.054906 1.970190 -0.305140
C 0.731046 0.500384 0.148830
O 1.349677 -0.554391 -0.385307
O 1.135812 1.182390 1.049818
C 2.603823 -0.954018 0.208659
H 2.695198 -2.021002 -0.036221
H 2.527353 -0.838433 1.299682
H -0.514007 0.567697 -1.646861
C 3.763007 -0.148763 -0.348413
H 3.668177 0.911486 -0.072661
H 4.711429 -0.527207 0.064261
H 3.806995 -0.231136 -1.445292

nPrA.xyz
C -3.301061 -0.879430 -0.038893
H -3.270002 -1.409544 -1.003908
C -2.205212 0.150925 0.009945
O -2.346980 1.343518 0.080359
O -0.980867 -0.452552 -0.046915
C 0.149969 0.321426 -0.059894
H -4.272769 -0.386945 0.082869
H -3.152319 -1.632028 0.750070
H 0.006324 1.387026 0.128408
C 1.428094 -0.408289 0.123526
H 1.497955 -0.809492 1.159545
H 1.434678 -1.302176 -0.528528
C 2.654792 0.464103 -0.160981
H 2.620761 1.356533 0.488922
H 2.595190 0.841363 -1.196410
C 3.974355 -0.275102 0.049166
H 4.838235 0.374331 -0.161496
H 4.070735 -0.633859 1.087413
H 4.048372 -1.154732 -0.611654

Pr-Br.xyz
C 3.370445 -1.270051 -0.685683
H 3.518334 -0.517031 -1.476049
C 2.262770 -0.811784 0.220330
O 2.372056 -0.451248 1.359623
O 1.064559 -0.846876 -0.442183
C -0.061507 -0.339486 0.216412
H 3.095895 -2.213078 -1.180348
H 4.295021 -1.387861 -0.108885
C -1.295935 -1.050972 -0.292776
H -1.379255 -0.883683 -1.379214
H -1.098720 -2.129774 -0.154689
C -2.592017 -0.666988 0.418781

H	-2.775691	0.410257	0.278589
H	-2.467498	-0.817622	1.505935
C	-3.791789	-1.469268	-0.081683
H	-4.715176	-1.175170	0.440584
H	-3.953587	-1.310865	-1.160680
H	-3.648266	-2.551164	0.075864
H	0.070383	-0.401957	1.303217
Br	-0.165319	1.628978	-0.121604

TS6.xyz

C	4.333121	0.432065	1.033186
C	3.123085	-0.177874	1.222021
C	2.158935	-0.286234	0.144476
C	2.543600	0.280673	-1.132283
C	3.767096	0.888353	-1.292759
C	4.676757	0.976902	-0.225649
H	5.037095	0.500749	1.856190
H	2.858106	-0.594860	2.189111
H	1.862224	0.220732	-1.972778
H	4.034046	1.305199	-2.258622
H	5.636935	1.459717	-0.365823
C	0.955504	-0.908363	0.358775
C	-0.102416	-1.057716	-0.663102
H	-0.065982	-0.561325	-1.623281
C	-1.424234	-1.574685	-0.240413
C	-2.166066	-0.522910	0.605336
O	-2.009096	-0.431548	1.797863
O	-2.885615	0.287340	-0.154584
C	-3.532009	1.380647	0.537330
H	-2.761535	1.966755	1.044869
H	-4.198566	0.960551	1.294587
C	-4.277859	2.186367	-0.500154
H	-4.782291	3.025191	-0.016355
H	-3.589063	2.580660	-1.250091
H	-5.028639	1.570440	-0.999407
F	-2.178298	-1.913171	-1.315440
H	0.740307	-1.321047	1.340108
H	-1.313361	-2.443912	0.373633

4.6 Determination of the Quantum Yield

UV-visible spectra were performed on a Agilent Cary 8454 spectrophotometer. All spectra were recorded in a thermostated cell at 25°C. The quantum yield of the reaction was measured by chemical actinometry using a 20 W LEDs using potassium ferrioxalate following the procedure of existent literature [12-17].

Preparation of an actinometer solution: Potassium ferrioxalate trihydrate (0.7369 g, 1.5 mmol) was dissolved in 10.0 mL of 0.20 mol/L aqueous sulfuric acid to create a 0.15 mol/L solution of ferrioxalate, which was then kept in the dark.

Preparation of a buffer solution: 0.15 mol/L buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (0.0811 g, 0.45 mmol) and sodium acetate (3.0618 g, 22.5 mmol) in 30 mL of 0.20 mol/L aqueous sulfuric acid.

The actinometry measurements were done as follows: 1.0 mL of the ferrioxalate solution was added to a reaction tube fitted with a stir bar. A 20 W blue LED was positioned 2 cm away from the sealed reaction tube. 3 mL of aqueous sulfuric acid and 4 mL of the buffered solution were added to the reaction tube following a 45 second radiation exposure. Following that, the solution

was let to rest for an hour to enable the resulting ferrous ions to fully react with 1,10-phenanthroline. 3.0 mL of 0.20 mol/L aqueous sulfuric acid were used to dilute an aliquot of 50 µL of the final solution. Using a UV-Vis spectrophotometer, the absorbance of the resultant solution at 510 nm was measured in a cuvette (l = 1.0 cm). Additionally, a sample that had not been exposed to radiation was created, and its absorbance at 510 nm was assessed.
the number of moles of Fe^{2+} produced by light irradiation was calculated as follows:

$$\text{moles of Fe}^{2+} = \frac{V_1 \times V_3 \times \Delta A\ (510\ \text{nm})}{10^3 \times V_2 \times l \times \varepsilon\ (510\ \text{nm})}$$

Where:
V_1 = Irradiated volume (1.0 mL).
V_2 = The aliquot of the irradiated solution taken for the estimation of $[Fe]^+$ ions (0.050 mL).
V_3 = Final volume of the solution after complexation with 1,10-phenanthroline (8 mL).
ε (510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L $mol^{-1}cm^{-1}$).
l = Optical path length of the cuvette (1.0 cm).
ΔA (510 nm) = absorbance difference between the irradiated solution and the solution stored in dark.
The photon flux was calculated as follows:

$$\text{photon flux} = \frac{\text{moles of Fe}^{2+}}{\Phi \times \text{t} \times f}$$

Where:
Φ = the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 mol/L solution at λ = 457.9 nm).
t = the irradiation time.
f = the fraction of light absorbed at 450 nm.
The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-\text{A}\ (450\ \text{nm})}$$

Where:
A (450 nm) = the measured absorbance of the 0.15 mol/L solution of potassium ferrioxalate at 450 nm.
The photon flux is 9.21 × 10^{-8} Einstein/s.

Determination of quantum yield:
To obtain the quantum yield (Φ) of the reaction. The number of moles of the product (**3**) were determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard and revealed 11% yield of **3** (2.26 × 10^{-5} mol). As such, a photocatalytic reaction was performed under the set of optimized reaction conditions under visible light irradiation of 20 W LEDs (max = 450 nm). After 3600 s of light irradiation.
The quantum yield was calculated as follows:

$$\Phi = \frac{\text{moles of product}}{\text{photon flux} \times \text{t} \times f}$$

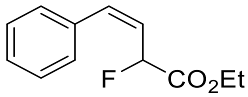
Where:
photon flux = the photon flux determined by ferrioxalate actinometry (9.21 × 10^{-8} **Einstein/s.**)
t = the irradiation time.
f = the fraction of light absorbed by the irradiated reaction system at 450 nm**.**
The fraction of light absorbed at 450 nm was calculated:

$$\boldsymbol{f = 1.0000 - 10^{-\text{A}\ (450\ \text{nm})} = 1.0000 - 10^{-3.1345} = 0.9993}$$

The quantum yield was calculated: $\boldsymbol{\Phi} = \mathbf{0.0682}$

5. Characterization data of products

Ethyl *(Z)*-2-fluoro-4-phenylbut-3-enoate **(3)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 40.4 mg of colorless oil (97% yield) of *Z*-alkene/*E*-alkene mixture (93/7).

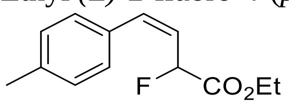
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 5H), 7.06 – 6.90 (m, 1H), 5.83 (dt, *J* = 11.4, 9.9 Hz, 1H), 5.64 (ddd, *J* = 47.9, 9.6, 1.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.65.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 (d, $^{2}J_{C\text{-}F}$ = 26.4 Hz), 138.1 (d, $^{3}J_{C\text{-}F}$ = 10.5 Hz), 135.0 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 128.9 (d, $^{5}J_{C\text{-}F}$ = 2.7 Hz), 128.5, 128.4, 123.0 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 84.4 (d, $^{1}J_{C\text{-}F}$ = 177.5 Hz), 62.0, 14.1.

Spectral Data was agreed with previously report.[18, 19]

Ethyl *(Z)*-2-fluoro-4-(*p*-tolyl)but-3-enoate **(4)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 40.9 mg of colorless oil (92% yield) of *Z*-alkene/*E*-alkene mixture (93/7).

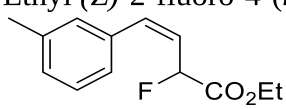
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 11.2, 3.7 Hz, 1H), 5.82 – 5.56 (m, 2H), 4.30 (qd, *J* = 7.1, 0.9 Hz, 2H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.20.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1 (d, $^{2}J_{C\text{-}F}$ = 26.6 Hz), 138.5, 138.2 (d, $^{5}J_{C\text{-}F}$ = 10.4 Hz), 132.3 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 129.4, 129.0 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 122.5 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 84.7 (d, $^{1}J_{C\text{-}F}$ = 177.3 Hz), 62.0, 21.4, 14.2.

Spectral Data was agreed with previously report.[19, 20]

Ethyl *(Z)*-2-fluoro-4-(*m*-tolyl)but-3-enoate **(5)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 40.9 mg of colorless oil (92% yield) of *Z*-alkene/*E*-alkene mixture (97/3).

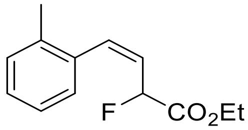
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 7.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.95 (dd, *J* = 11.3, 3.7 Hz, 1H), 5.81 (dt, *J* = 11.4, 9.9 Hz, 1H), 5.65 (ddd, *J* = 47.8, 9.6, 0.9 Hz, 1H), 4.30 (qd, *J* = 7.2, 2.6 Hz, 2H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.46.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1 (d, $^{2}J_{C\text{-}F}$ = 26.5 Hz), 138.4, 138.3 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 135.1 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 129.7 (d, $^{6}J_{C\text{-}F}$ = 2.8 Hz), 129.3, 128.5, 126.1 (d, $^{5}J_{C\text{-}F}$ = 2.8 Hz), 123.0 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 84.6 (d, $^{1}J_{C\text{-}F}$ = 177.1 Hz), 62.0, 21.5, 14.2.

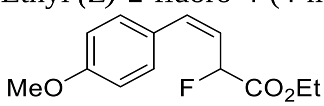
Spectral Data was agreed with previously report.[19]

Ethyl *(Z)*-2-fluoro-4-(*o*-tolyl)but-3-enoate **(6)**



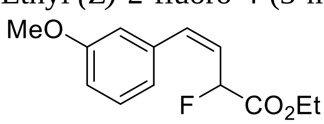
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 42.7 mg of colorless oil (96% yield) of *Z*-alkene/*E*-alkene mixture (92/8).
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.28 – 7.17 (m, 3H), 7.02 (dd, *J* = 11.3, 3.6 Hz, 1H), 5.88 (ddd, *J* = 11.2, 9.8, 8.6 Hz, 1H), 5.47 (ddd, *J* = 48.1, 9.8, 0.9 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -176.33.
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 169.1 (d, $^{2}J_{C\text{-}F}$ = 26.4 Hz), 137.7 (d, $^{5}J_{C\text{-}F}$ = 10.5 Hz), 136.7 (d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 134.3 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 130.1, 129.3 (d, $^{6}J_{C\text{-}F}$ = 2.6 Hz), 128.6, 125.9, 123.5 (d, $^{2}J_{C\text{-}F}$ = 20.1 Hz), 84.7 (d, $^{1}J_{C\text{-}F}$ = 177.1 Hz), 62.0, 20.0, 14.2.
Spectral Data was agreed with previously report.[19, 20]

Ethyl *(Z)*-2-fluoro-4-(4-methoxyphenyl)but-3-enoate **(7)**



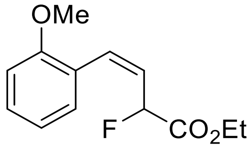
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 21.4 mg of colorless oil (45% yield) of *Z*-alkene/*E*-alkene mixture (92/8).
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.95 – 6.88 (m, 3H), 5.77 – 5.57 (m, 2H), 4.30 (qd, *J* = 7.2, 0.7 Hz, 2H), 3.83 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -173.67.
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 169.0 (d, $^{2}J_{C\text{-}F}$ = 26.7 Hz), 159.8, 137.7 (d, $^{5}J_{C\text{-}F}$ = 10.4 Hz), 130.4 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 127.6 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 121.4 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 114.0, 84.6 (d, $^{1}J_{C\text{-}F}$ = 177.3 Hz), 61.9, 55.3, 14.1.
Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-2-fluoro-4-(3-methoxyphenyl)but-3-enoate **(8)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 42.4 mg of colorless oil (89% yield) of *Z*-alkene/*E*-alkene mixture (93/7).
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 7.01 – 6.93 (m, 3H), 6.92 – 6.87 (m, 1H), 5.82 (ddd, *J* = 11.4, 10.4, 9.5 Hz, 1H), 5.67 (ddd, *J* = 47.7, 9.7, 0.9 Hz, 1H), 4.31 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.83 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -174.75.
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 169.0 (d, $^{2}J_{C\text{-}F}$ = 26.4 Hz), 159.8, 138.1 (d, $^{3}J_{C\text{-}F}$ = 10.6 Hz), 136.4 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 129.7, 123.4 (d, $^{2}J_{C\text{-}F}$ = 20.6 Hz), 121.4 (d, $^{5}J_{C\text{-}F}$ = 2.7 Hz), 114.4, 114.3 (d, $^{5}J_{C\text{-}F}$ = 2.8 Hz), 84.6 (d, $^{1}J_{C\text{-}F}$ = 177.4 Hz), 62.1, 55.4, 14.2.
Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-2-fluoro-4-(2-methoxyphenyl)but-3-enoate **(9)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.7 mg of colorless oil (77% yield) of *Z*-alkene/*E*-alkene mixture (96/4).

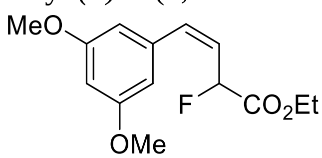
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 11.5, 3.5 Hz, 1H), 5.92 (dt, *J* = 11.8, 10.0 Hz, 1H), 5.59 (dd, *J* = 48.0, 9.6 Hz, 1H), 4.31 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.93 (d, *J* = 1.0 Hz, 3H), 1.34 (td, *J* = 7.2, 1.0 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.50.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6 (d, $^2J_{C-F}$ = 26.1 Hz), 166.8, 139.6 (d, $^5J_{C-F}$ = 3.0 Hz), 137.0 (d, $^3J_{C-F}$ = 10.4 Hz), 130.1, 129.9, 129.0 (d, $^4J_{C-F}$ = 2.7 Hz), 125.0 (d, $^2J_{C-F}$ = 20.8 Hz), 84.4 (d, $^1J_{C-F}$ = 178.4 Hz), 62.2, 52.4, 14.2.

Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-4-(3,5-dimethoxyphenyl)-2-fluorobut-3-enoate **(10)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 47.8 mg of colorless oil (89% yield) of *Z*-alkene/*E*-alkene mixture (95/5).

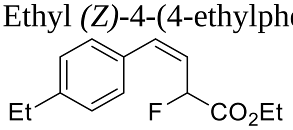
^{1}H NMR (400 MHz, $CDCl_3$) 6.92 (dd, *J* = 11.1, 3.5 Hz, 1H), 6.58 (d, *J* = 2.3 Hz, 2H), 6.46 (t, *J* = 2.3 Hz, 1H), 5.86 – 5.62 (m, 2H), 4.31 (qd, *J* = 7.2, 1.9 Hz, 2H), 3.81 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.82.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 (d, $^2J_{C-F}$ = 26.3 Hz), 160.8, 138.0 (d, $^3J_{C-F}$ = 10.6 Hz), 136.8 (d, $^4J_{C-F}$ = 3.0 Hz), 123.4 (d, $^2J_{C-F}$ = 20.8 Hz), 106.9 (d, $^5J_{C-F}$ = 2.8 Hz), 100.7, 84.6 (d, $^1J_{C-F}$ = 177.4 Hz), 62.0, 55.4, 14.1.

HRMS (ESI) Calcd for $C_{14}H_{18}FO_4$ $[M+H]^+$: 269.1184, found 269.1183.

Ethyl *(Z)*-4-(4-ethylphenyl)-2-fluorobut-3-enoate **(11)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 44.0 mg of colorless oil (93% yield) of *Z*-alkene/*E*-alkene mixture (94/6).

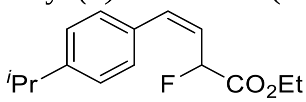
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 11.2, 3.7 Hz, 1H), 5.77 (dd, *J* = 11.3, 9.9 Hz, 1H), 5.74 – 5.59 (m, 1H), 4.30 (qd, *J* = 7.1, 0.8 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.14.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C-F}$ = 26.6 Hz), 144.7, 138.1 (d, $^5J_{C-F}$ = 10.5 Hz), 132.4 (d, $^3J_{C-F}$ = 3.3 Hz), 129.0 (d, $^4J_{C-F}$ = 2.7 Hz), 128.1, 122.3 (d, $^2J_{C-F}$ = 20.2 Hz), 84.5 (d, $^1J_{C-F}$ = 177.2 Hz), 61.9, 28.6, 15.5, 14.1.

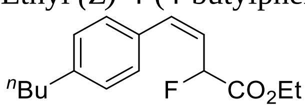
HRMS (ESI) Calcd for $C_{14}H_{17}FO_2Na$ $[M+Na]^+$: 259.1105, found 259.1102.

Ethyl *(Z)*-2-fluoro-4-(4-isopropylphenyl)but-3-enoate **(12)**



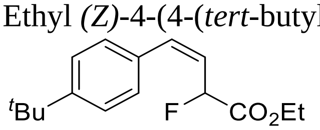
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 46.1 mg of colorless oil (92% yield) of *Z*-alkene/*E*-alkene mixture (95/5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.28 – 7.23 (m, 2H), 6.95 (dd, *J* = 11.1, 3.7 Hz, 1H), 5.83 – 5.59 (m, 2H), 4.34 – 4.26 (m, 2H), 2.93 (p, *J* = 6.9 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 6H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.08.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C\text{-}F}$ = 26.4 Hz), 149.3, 138.1 (d, $^5J_{C\text{-}F}$ = 10.6 Hz), 132.6 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 129.0 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 126.6, 122.3 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 84.5 (d, $^1J_{C\text{-}F}$ = 177.1 Hz), 61.9, 33.9, 23.9, 14.1.
HRMS (ESI) Calcd for $C_{15}H_{19}FO_2Na$ $[M+Na]^+$: 273.1261, found 273.1259.

Ethyl *(Z)*-4-(4-butylphenyl)-2-fluorobut-3-enoate **(13)**



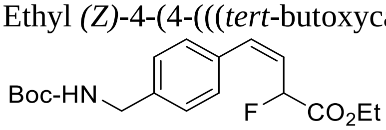
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 46.5 mg of colorless oil (88% yield) of *Z*-alkene/*E*-alkene mixture (93/7).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 11.1, 3.7 Hz, 1H), 5.87 – 5.56 (m, 2H), 4.30 (qd, *J* = 7.1, 0.8 Hz, 2H), 2.66 – 2.59 (m, 2H), 1.60 (ddt, *J* = 8.3, 7.0, 1.7 Hz, 2H), 1.34 (dt, *J* = 9.4, 7.3 Hz, 5H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.08.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1 (d, $^2J_{C\text{-}F}$ = 26.5 Hz), 143.6, 138.3 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 132.5 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 129.0 (d, $^6J_{C\text{-}F}$ = 2.7 Hz), 128.7, 122.4 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 84.7 (d, $^1J_{C\text{-}F}$ = 177.2 Hz), 62.0, 35.5, 33.6, 22.5, 14.2, 14.1.
HRMS (ESI) Calcd for $C_{16}H_{21}FO_2Na$ $[M+Na]^+$: 287.1418, found 287.1413.

Ethyl *(Z)*-4-(4-(*tert*-butyl)phenyl)-2-fluorobut-3-enoate **(14)**



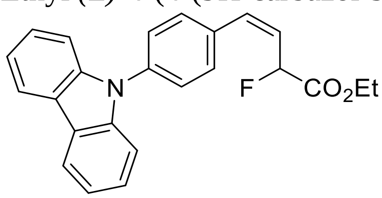
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 46.0 mg of colorless oil (87% yield) of *Z*-alkene/*E*-alkene mixture (95/5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 11.1, 3.7 Hz, 1H), 5.83 – 5.57 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.33 (s, 12H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.08.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C\text{-}F}$ = 26.5 Hz), 151.6, 138.0 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 132.2 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.8 (d, $^6J_{C\text{-}F}$ = 2.8 Hz), 125.5, 122.4 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 84.5 (d, $^1J_{C\text{-}F}$ = 177.1 Hz), 61.9, 34.7, 31.3, 14.1.
Spectral Data agreed with previously reported. [19, 20]

Ethyl *(Z)*-4-(4-(((*tert*-butoxycarbonyl)amino)methyl)phenyl)-2-fluorobut-3-enoate **(15)**



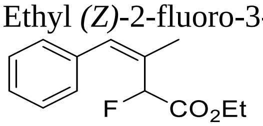
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 52.6 mg of colorless oil (78% yield) of *Z*-alkene/*E*-alkene mixture (96/4).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 11.4, 3.6 Hz, 1H), 5.82 (dt, *J* = 11.4, 9.9 Hz, 1H), 5.61 (ddd, *J* = 47.9, 9.6, 1.0 Hz, 1H), 4.89 (s, 1H), 4.31 (dt, *J* = 14.3, 6.4 Hz, 4H), 1.47 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.68.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C-F}$ = 26.5 Hz), 155.9, 139.4, 137.7 (d, $^3J_{C-F}$ = 10.4 Hz), 134.0 (d, $^4J_{C-F}$ = 3.3 Hz), 129.2 (d, $^5J_{C-F}$ = 2.8 Hz), 127.5, 123.0 (d, $^2J_{C-F}$ = 20.3 Hz), 84.4 (d, $^1J_{C-F}$ = 177.5 Hz), 79.7, 62.0, 44.3, 28.4, 14.1.
HRMS (ESI) Calcd for $C_{18}H_{24}FO_4Na$ $[M+Na]^+$: 360.1582, found 360.1576.

Ethyl *(Z)*-4-(4-(9H-carbazol-9-yl)phenyl)-2-fluorobut-3-enoate **(16)**



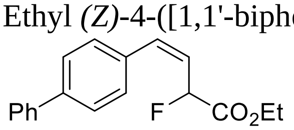
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 64.9 mg of colorless oil (87% yield) of *Z*-alkene/*E*-alkene mixture (96/4).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.09 (m, 2H), 7.67 – 7.57 (m, 4H), 7.52 – 7.34 (m, 5H), 7.29 (ddd, *J* = 8.0, 6.5, 1.6 Hz, 2H), 7.04 (dd, *J* = 11.4, 3.6 Hz, 1H), 5.93 (dddd, *J* = 11.5, 10.5, 9.6, 1.7 Hz, 1H), 5.76 (ddt, *J* = 47.8, 9.5, 1.5 Hz, 1H), 4.33 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.35 (dd, *J* = 14.4, 1.5 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.45.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 (d, $^2J_{C-F}$ = 26.3 Hz), 140.8, 138.0, 137.2 (d, $^3J_{C-F}$ = 10.5 Hz), 134.1 (d, $^4J_{C-F}$ = 3.0 Hz), 130.6 (d, $^5J_{C-F}$ = 2.7 Hz), 127.1, 126.2, 123.9 (d, $^2J_{C-F}$ = 20.5 Hz), 123.7, 120.5, 120.1, 109.9, 84.5 (d, $^1J_{C-F}$ = 178.4 Hz), 62.2, 14.3.
HRMS (ESI) Calcd for $C_{24}H_{21}FNO_2$ $[M+H]^+$: 374.1551, found 374.1550.

Ethyl *(Z)*-2-fluoro-3-methyl-4-phenylbut-3-enoate **(17)**



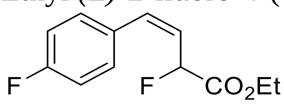
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 24.5 mg of colorless oil (55% yield) of *Z*-alkene/*E*-alkene mixture (89/11).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.78 (t, *J* = 1.8 Hz, 1H), 5.72 (d, *J* = 48.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.92 (t, *J* = 1.5 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -183.79.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C-F}$ = 26.9 Hz), 136.0 (d, $^4J_{C-F}$ = 2.7 Hz), 134.4 (d, $^3J_{C-F}$ = 8.4 Hz), 130.9 (d, $^2J_{C-F}$ = 18.2 Hz), 128.9 (d, $^5J_{C-F}$ = 2.2 Hz), 128.6, 127.7, 86.2 (d, $^1J_{C-F}$ = 179.8 Hz), 62.0, 18.1 (d, $^3J_{C-F}$ = 2.9 Hz), 14.3.
HRMS (ESI) Calcd for $C_{13}H_{16}FO_2$ $[M+H]^+$: 223.1129, found 223.1129.

Ethyl *(Z)*-4-([1,1'-biphenyl]-4-yl)-2-fluorobut-3-enoate **(18)**



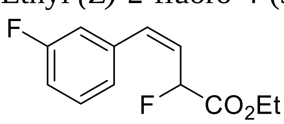
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 49.5 mg of colorless oil (87% yield) of *Z*-alkene/*E*-alkene mixture (91/9).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.01 (dd, *J* = 11.4, 3.7 Hz, 1H), 5.85 (dt, *J* = 11.3, 9.9 Hz, 1H), 5.71 (dd, *J* = 47.9, 9.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.40.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9 (d, $^2J_{C-F}$ = 26.3 Hz), 140.2, 139.4, 136.7 (d, $^3J_{C-F}$ = 10.4 Hz), 132.9 (d, $^4J_{C-F}$ = 3.1 Hz), 128.4 (d, $^6J_{C-F}$ = 2.7 Hz), 127.8, 126.6, 126.2, 126.0, 122.1 (d, $^2J_{C-F}$ = 20.4 Hz), 83.5 (d, $^1J_{C-F}$ = 177.6 Hz), 61.0, 13.1.
Spectral Data was agreed with previously report.[20, 21]

Ethyl *(Z)*-2-fluoro-4-(4-fluorophenyl)but-3-enoate **(19)**



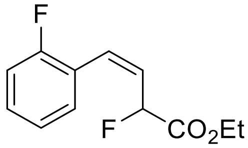
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.2 mg of colorless oil (80% yield) of *Z*-alkene/*E*-alkene mixture (93/7).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.14 – 7.03 (m, 2H), 6.93 (dd, *J* = 11.4, 3.6 Hz, 1H), 5.82 (dt, *J* = 11.4, 9.9 Hz, 1H), 5.59 (ddd, *J* = 48.1, 9.6, 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-d) δ -112.78, -174.79.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C-F}$ = 26.3 Hz), 162.8 (d, $^1J_{C-F'}$ = 248.5 Hz), 136.9 (d, $^3J_{C-F}$ = 10.5 Hz), 131.1 (t, $^4J_{C-F}$ = 3.3 Hz), 130.7 (dd, $^3J_{C-F'}$ = 8.2, 2.8 Hz), 123.1 (d, $^2J_{C-F}$ = 20.4 Hz), 115.6 (d, $^2J_{C-F'}$ = 21.5 Hz), 84.3 (d, $^1J_{C-F}$ = 178.1 Hz), 62.0, 14.1.
Spectral Data was agreed with previously report.[19, 20]

Ethyl *(Z)*-2-fluoro-4-(3-fluorophenyl)but-3-enoate **(20)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 39.8 mg of colorless oil (88% yield) of *Z*-alkene/*E*-alkene mixture (93/7).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.0, 5.9 Hz, 1H), 7.21 – 7.13 (m, 2H), 7.05 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.93 (dd, *J* = 11.5, 3.5 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.61 (ddd, *J* = 47.9, 9.5, 1.0 Hz, 1H), 4.31 (qd, *J* = 7.2, 0.9 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.62, -175.58.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C-F}$ = 26.2 Hz), 162.9 (d, $^1J_{C-F'}$ = 246.6 Hz), 137.2 (dd, $^3J_{C-F'}$ = 7.8, 3.2 Hz), 136.8 (dd, $^3J_{C-F}$ = 10.6, 2.2 Hz), 130.2 (d, $^3J_{C-F'}$= 8.3 Hz), 124.8 (t, $^4J_{C-F'}$ = 2.8 Hz), 124.3 (d, $^2J_{C-F}$ = 20.7 Hz), 115.9 (dd, $^2J_{C-F'}$ = 22.1, 2.7 Hz), 115.5 (d, $^2J_{C-F'}$ = 21.2 Hz), 84.4 (d, $^1J_{C-F}$ = 178.0 Hz), 62.2, 14.2.
Spectral Data was agreed with previously report.[19]

Ethyl *(Z)*-2-fluoro-4-(2-fluorophenyl)but-3-enoate **(21)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 41.6 mg of colorless oil (92% yield) of *Z*-alkene/*E*-alkene mixture (97/3).

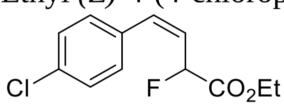
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (td, *J* = 7.6, 1.8 Hz, 1H), 7.34 (tdd, *J* = 7.5, 5.2, 1.8 Hz, 1H), 7.17 (td, *J* = 7.5, 1.2 Hz, 1H), 7.09 (ddd, *J* = 9.7, 8.2, 1.2 Hz, 1H), 7.04 – 6.99 (m, 1H), 5.94 (dt, *J* = 11.5, 9.8 Hz, 1H), 5.57 (ddd, *J* = 48.0, 9.5, 1.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.23, -176.31.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C\text{-}F}$ = 26.1 Hz), 162.1 – 158.7 (m), 131.0 (dd, $^3J_{C\text{-}F}$ = 10.5, 4.1 Hz), 130.8 (t, $^4J_{C\text{-}F}$ = 2.8 Hz), 130.5 (d, $^3J_{C\text{-}F'}$ = 8.2 Hz), 125.0 (d, $^2J_{C\text{-}F}$ = 20.6 Hz), 124.2 (d, $^3J_{C\text{-}F'}$ = 3.8 Hz), 123.0 (dd, $^2J_{C\text{-}F'}$ = 14.1, 3.1 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 84.7 (d, $^1J_{C\text{-}F}$ = 178.0 Hz), 62.2, 14.2.

Spectral Data was agreed with previously report.[19]

Ethyl *(Z)*-4-(4-chlorophenyl)-2-fluorobut-3-enoate **(22)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 41.3 mg of colorless oil (85% yield) of *Z*-alkene/*E*-alkene mixture (95/5).

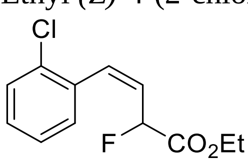
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 6.94 – 6.87 (m, 1H), 5.85 (ddd, *J* = 11.4, 10.3, 9.6 Hz, 1H), 5.57 (ddd, *J* = 47.9, 9.6, 1.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.09.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2 (d, $^2J_{C\text{-}F}$ = 25.9 Hz), 139.5 (d, $^3J_{C\text{-}F}$ = 3.1 Hz), 135.9 (d, $^4J_{C\text{-}F}$ = 10.2 Hz), 134.0, 132.3, 129.5 (d, $^5J_{C\text{-}F}$ = 2.8 Hz), 125.9 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 118.43, 112.16, 84.1 (d, $^1J_{C\text{-}F}$ = 179.6 Hz), 62.2, 14.1

Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-4-(2-chlorophenyl)-2-fluorobut-3-enoate **(23)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 43.7 mg of colorless oil (90% yield) of *Z*-alkene/*E*-alkene mixture (98/2).

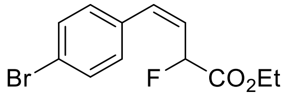
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 1H), 7.45 – 7.40 (m, 1H), 7.33 – 7.27 (m, 2H), 7.07 (ddd, *J* = 11.4, 3.4, 1.0 Hz, 1H), 5.94 (dt, *J* = 11.4, 9.5 Hz, 1H), 5.49 (ddd, *J* = 47.9, 9.6, 1.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -176.53.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6 (d, $^2J_{C\text{-}F}$ = 26.1 Hz), 135.3 (d, $^5J_{C\text{-}F}$ = 10.5 Hz), 133.9 (d, $^3J_{C\text{-}F}$ = 2.9 Hz), 133.4 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 130.8 (d, $^6J_{C\text{-}F}$ = 2.8 Hz), 129.8, 129.6, 126.7, 124.4 (d, $^2J_{C\text{-}F}$ = 20.5 Hz), 84.5 (d, $^1J_{C\text{-}F}$ = 178.2 Hz), 62.0, 14.1.

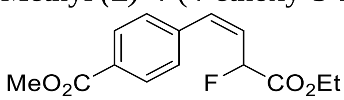
Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-4-(4-bromophenyl)-2-fluorobut-3-enoate **(24)**



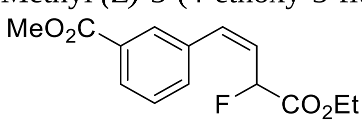
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 51.1 mg of colorless oil (89% yield) of *Z*-alkene/*E*-alkene mixture (95/5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.32 – 7.27 (m, 2H), 6.90 (dd, *J* = 11.4, 3.5 Hz, 1H), 5.85 (ddd, *J* = 11.4, 10.2, 9.5 Hz, 1H), 5.57 (ddd, *J* = 48.0, 9.6, 1.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.15.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6 (d, $^2J_{C-F}$ = 26.1 Hz), 136.8 (d, $^5J_{C-F}$ = 10.4 Hz), 133.8 (d, $^3J_{C-F}$ = 3.2 Hz), 131.7, 130.5 (d, $^4J_{C-F}$ = 2.8 Hz), 123.8 (d, $^2J_{C-F}$ = 20.5 Hz), 122.7, 84.3 (d, $^1J_{C-F}$ = 178.4 Hz), 62.1, 14.1.
Spectral Data was agreed with previously report.[19, 20]

Methyl *(Z)*-4-(4-ethoxy-3-fluoro-4-oxobut-1-en-1-yl)benzoate **(25)**



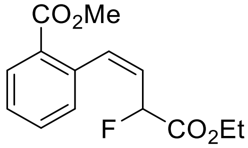
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 46.9 mg of colorless oil (88% yield) of *Z*-alkene/*E*-alkene mixture (97/3).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.51 – 7.44 (m, 2H), 7.00 (dd, *J* = 11.5, 3.5 Hz, 1H), 5.92 (dt, *J* = 11.5, 9.9 Hz, 1H), 5.59 (ddd, *J* = 47.9, 9.6, 1.0 Hz, 1H), 4.35 – 4.28 (m, 2H), 3.94 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.63.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C-F}$ = 26.4 Hz), 166.8, 136.9 (d, $^3J_{C-F}$ = 10.5 Hz), 135.4 (d, $^4J_{C-F}$ = 3.1 Hz), 133.3 (d, $^5J_{C-F}$ = 2.7 Hz), 130.7, 130.1 (d, $^7J_{C-F}$ = 2.7 Hz), 129.6, 128.8, 124.4 (d, $^2J_{C-F}$ = 20.9 Hz), 84.4 (d, $^1J_{C-F}$ = 177.8 Hz), 62.2, 52.4, 14.2.
HRMS (ESI) Calcd for $C_{14}H_{16}FO_4$ $[M+H]^+$: 267.1027, found 267.1028.

Methyl *(Z)*-3-(4-ethoxy-3-fluoro-4-oxobut-1-en-1-yl)benzoate **(26)**



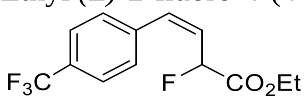
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 50.1 mg of colorless oil (94% yield) of *Z*-alkene/*E*-alkene mixture (98/2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.8 Hz, 1H), 8.03 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.61 (ddd, *J* = 7.8, 2.0, 1.1 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 6.99 (dd, *J* = 11.5, 3.4 Hz, 1H), 5.90 (ddd, *J* = 11.4, 10.6, 9.6 Hz, 1H), 5.60 (ddd, *J* = 47.9, 9.6, 1.1 Hz, 1H), 4.32 (tq, *J* = 7.1, 3.9 Hz, 2H), 3.94 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.69.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6 (d, $^2J_{C-F}$ = 26.4 Hz), 166.7, 136.8 (d, $^3J_{C-F}$ = 10.4 Hz), 135.3 (d, $^4J_{C-F}$ = 3.1 Hz), 133.2 (d, $^5J_{C-F}$ = 2.7 Hz), 130.6, 130.0 (d, $^7J_{C-F}$ = 2.7 Hz), 129.5, 128.7, 124.2 (d, $^2J_{C-F}$ = 20.9 Hz), 84.2 (d, $^1J_{C-F}$ = 177.9 Hz), 62.1, 52.3, 14.1.
HRMS (ESI) Calcd for $C_{14}H_{16}FO_4$ $[M+H]^+$: 267.1027, found 267.1027.

Methyl *(Z)*-2-(4-ethoxy-3-fluoro-4-oxobut-1-en-1-yl)benzoate **(27)**



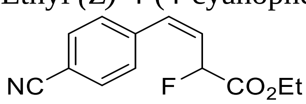
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 50.1 mg of colorless oil (94% yield) of *Z*-alkene/*E*-alkene mixture (98/2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.50 – 7.41 (m, 3H), 5.88 (ddd, *J* = 11.4, 9.8, 8.8 Hz, 1H), 5.36 (ddd, *J* = 48.1, 9.8, 0.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -176.30.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 (d, $^2J_{C-F}$ = 26.5 Hz), 167.0, 138.6 (d, $^3J_{C-F}$ = 10.6 Hz), 136.7 (d, $^4J_{C-F}$ = 3.0 Hz), 132.4, 131.0, 131.0 (d, $^5J_{C-F}$ = 2.9 Hz), 129.3, 128.4, 122.3 (d, $^2J_{C-F}$ = 20.1 Hz), 84.8 (d, $^1J_{C-F}$ = 177.6 Hz), 62.0, 52.2, 14.2.
HRMS (ESI) Calcd for $C_{14}H_{16}FO_4$ $[M+H]^+$: 267.1027, found 267.1028.

Ethyl *(Z)*-2-fluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate **(28)**



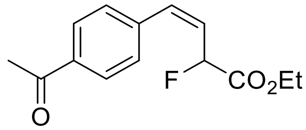
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 53.0 mg of colorless oil (96% yield) of *Z*-alkene/*E*-alkene mixture (96/4).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 11.5, 3.4 Hz, 1H), 5.98 – 5.89 (m, 1H), 5.56 (ddd, *J* = 48.0, 9.6, 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.72, -175.87.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5 (d, $^2J_{C-F}$ = 26.0 Hz), 138.5, 136.4 (d, $^3J_{C-F}$ = 10.3 Hz), 130.4 (q, $^2J_{C-F'}$ = 32.8 Hz), 129.2 (d, $^5J_{C-F}$ = 2.8 Hz), 125.5 (q, $^3J_{C-F'}$= 3.7 Hz), 125.1 (d, $^2J_{C-F}$ = 20.6 Hz), 124.0 (q, $^1J_{C-F'}$= 267.7 Hz), 84.2 (d, $^1J_{C-F}$ = 178.7 Hz), 62.2, 14.1.
Spectral Data was agreed with previously report.[20]

Ethyl *(Z)*-4-(4-cyanophenyl)-2-fluorobut-3-enoate **(29)**



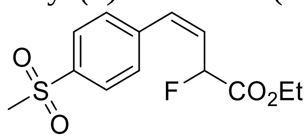
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 43.4 mg of colorless oil (93% yield) of *Z*-alkene/*E*-alkene mixture (87/13).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 6.96 (dd, *J* = 11.6, 3.4 Hz, 1H), 5.97 (ddd, *J* = 11.6, 10.7, 9.4 Hz, 1H), 5.53 (ddd, *J* = 47.9, 9.5, 1.1 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -176.17.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4 (d, $^2J_{C-F}$ = 25.7 Hz), 139.6 (d, $^4J_{C-F}$ = 2.9 Hz), 136.0 (d, $^3J_{C-F}$ = 10.3 Hz), 132.5, 129.7 (d, $^5J_{C-F}$ = 2.9 Hz), 125.9 (d, $^2J_{C-F}$ = 20.8 Hz), 118.6, 112.3, 84.2 (d, $^1J_{C-F}$ = 179.7 Hz), 62.4, 14.2.
HRMS (ESI) Calcd for $C_{13}H_{12}FNO_2$ $[M+H]^+$: 234.0925, found 234.0925.

Ethyl *(Z)*-4-(4-acetylphenyl)-2-fluorobut-3-enoate **(30)**



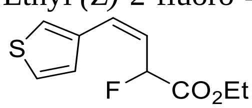
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 40.0 mg of colorless oil (80% yield) of *Z*-alkene/*E*-alkene mixture (96/4).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 6.99 (dd, *J* = 11.5, 3.5 Hz, 1H), 5.93 (ddd, *J* = 11.5, 10.5, 9.6 Hz, 1H), 5.59 (ddd, *J* = 48.0, 9.5, 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.70.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.7, 168.7 (d, *J* = $^2J_{C\text{-}F}$ Hz), 139.7 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 136.9 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 136.8, 129.2 (d, $^5J_{C\text{-}F}$ = 2.7 Hz), 128.7, 125.0 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 84.4 (d, $^1J_{C\text{-}F}$ = 178.5 Hz), 62.3, 26.8, 14.3.
HRMS (ESI) Calcd for $C_{14}H_{16}FO_3$ $[M+H]^+$: 251.1078 found 251.1077.

Ethyl *(Z)*-2-fluoro-4-(4-(methylsulfonyl)phenyl)but-3-enoate **(31)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 52.7 mg of colorless oil (82% yield) of *Z*-alkene/*E*-alkene mixture (92/8).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.8 Hz, 1H), 8.00 (t, *J* = 1.9 Hz, 0.14H, Ph alkene), 7.93 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.87 (dt, *J* = 7.7, 1.5 Hz, 0.14H, Ph alkene), 7.72 (dq, *J* = 8.2, 1.1 Hz, 1H), 7.71 – 7.64 (m, 0.17H, Ph alkene), 7.62 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 0.18H, Ph alkene), 6.99 (dd, *J* = 11.6, 3.3 Hz, 1H), 6.90 (dt, *J* = 15.9, 2.1 Hz, 0.13H, Ph alkene), 6.44 (td, *J* = 15.9, 5.8 Hz, 0.14H, Ph alkene), 5.98 (td, *J* = 11.5, 9.4 Hz, 1H), 5.54 (ddd, *J* = 47.9, 9.4, 1.1 Hz, 1H), 5.50 (ddd, *J* = 47.9, 5.8, 1.7 Hz, 0.07H, CH alkene), 4.45 (t, *J* = 6.2 Hz, 0.22H, CH_2 alkene), 4.33 (qd, *J* = 7.1, 3.0 Hz, 2H), 3.09 (s, 3H), 3.07 (s, 0.45H, CH_3 alkene), 1.35 (td, *J* = 7.2, 3.6 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 0.4H, CH_3 alkene).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -176.32, -187.12 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4 (d, $^2J_{C\text{-}F}$ = 26.0 Hz), 141.2, 136.5 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 135.6 (d, $^3J_{C\text{-}F}$ = 10.4 Hz), 134.0 (d, $^5J_{C\text{-}F}$ = 2.5 Hz), 130.0, 129.8, 127.8 (d, $^5J_{C\text{-}F}$ = 2.7 Hz), 127.1, 125.73, 125.5 (d, $^6J_{C\text{-}F}$ = 4.6 Hz), 88.0 (d, $^1J_{C\text{-}F}$ = 186.2 Hz, *E*-alkene), 84.3 (d, $^1J_{C\text{-}F}$ = 179.3 Hz), 66.9, 62.4 (d, $^4J_{C\text{-}F}$ = 11.8 Hz), 44.5, 14.2.
HRMS (ESI) Calcd for $C_{13}H_{15}FO_4Na$ $[M+Na]^+$: 309.0567 found 309.0561.

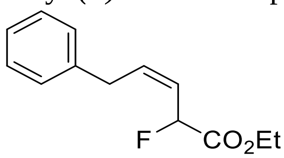
Ethyl *(Z)*-2-fluoro-4-(thiophen-3-yl)but-3-enoate **(32)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.4 mg of colorless oil (85% yield) of *Z*-alkene/*E*-alkene mixture (96/4).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 1H), 7.34 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.15 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.89 – 6.84 (m, 1H), 5.81 – 5.65 (m, 2H), 4.31 (qd, *J* = 7.1, 1.4 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.32.

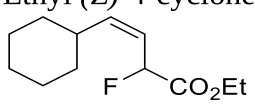
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 168.8 (d, $^2J_{C-F}$ = 26.3 Hz), 136.2 (d, $^4J_{C-F}$ = 3.3 Hz), 131.6 (d, $^3J_{C-F}$ = 10.5 Hz), 128.4 (d, $^5J_{C-F}$ = 2.2 Hz), 126.1, 125.5 (d, $^6J_{C-F}$ = 3.3 Hz), 122.3 (d, $^2J_{C-F}$ = 21.2 Hz), 84.8 (d, $^1J_{C-F}$ = 178.3 Hz), 62.0, 14.1.
HRMS (ESI) Calcd for $C_{10}H_{11}FO_2SNa$ $[M+H]^+$: 237.0356, found 237.0359.

Ethyl *(Z)*-2-fluoro-5-phenylpent-3-enoate **(33)**



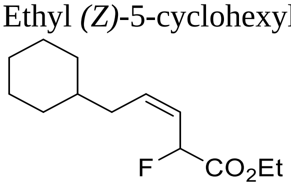
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 38.7 mg of colorless oil (87% yield) of *E*-alkene/*Z*-alkene mixture (77/23).
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 1.01H, Ph alkene), 7.30 (s, 1H), 7.29 (s, 0.54H, Ph alkene), 7.22 (t, *J* = 7.4 Hz, 2H), 7.19 – 7.15 (m, 2H), 6.20 – 6.11 (m, 1H), 5.67 (dddd, *J* = 10.3, 7.2, 3.6, 1.5 Hz, 0.33H, CH alkene), 5.25 (ddd, *J* = 48.3, 6.8, 1.1 Hz, 1H), 4.25 (t, *J* = 7.1 Hz, 2H), 3.60 – 3.55 (m, 0.6H, CH_2 alkene), 3.48 – 3.42 (m, 2H), 1.35 – 1.30 (m, 1.05H, CH_3 alkene), 1.29 (d, *J* = 7.1 Hz, 3H).
^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -181.67 (*E*-alkene), -182.65.
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 168.9 (t, $^2J_{C-F}$ = 26.6 Hz, *E*-alkene), δ 168.7 (d, $^2J_{C-F}$ = 25.8 Hz), 139.0, 138.8 (d, $^5J_{C-F}$ = 2.1 Hz), 137.2 (d, $^3J_{C-F}$ = 9.8 Hz, *E*-alkene), 137.0 (d, $^3J_{C-F}$ = 10.9 Hz), 128.7 (d, $^6J_{C-F}$ = 5.2 Hz), 128.6, 126.6 (d, $^8J_{C-F}$ = 1.5 Hz), 124.0 (d, $^2J_{C-F}$ = 19.5 Hz), 122.9 (d, $^2J_{C-F}$ = 21.4 Hz, *E*-alkene), 88.5 (d, $^1J_{C-F}$ = 182.4 Hz) , 84.6 (d, $^1J_{C-F}$ = 178.5 Hz, *E*-alkene), 61.9, 38.6, 14.2.
HRMS (ESI) Calcd for $C_{13}H_{15}FO_2Na$ $[M+Na]^+$: 245.0948, found 245.0947.

Ethyl *(Z)*-4-cyclohexyl-2-fluorobut-3-enoate **(34)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 28.7 mg of colorless oil (67% yield) of *E*-alkene/*Z*-alkene mixture (84/16).
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.95 (dddd, *J* = 15.6, 6.6, 4.1, 1.2 Hz, 1H), 5.55 (dddd, *J* = 15.6, 12.0, 7.0, 1.4 Hz, 1H), 5.20 (ddt, *J* = 48.5, 7.0, 0.9 Hz, 1H), 4.29 – 4.24 (m, 2H), 2.10 – 1.97 (m, 1H), 1.73 (dd, *J* = 9.5, 3.4 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 5H), 1.16 – 1.03 (m, 3H).
^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -180.18 (*E*-alkene), -181.06.
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 168.9 (d, $^2J_{C-F}$ = 26.2 Hz), 144.9 (d, $^3J_{C-F}$ = 10.2 Hz, *E*-alkene), 144.4 (d, $^3J_{C-F}$ = 10.4 Hz), 120.0 (d, $^2J_{C-F}$ = 19.5 Hz), 89.0 (d, $^1J_{C-F}$ = 181.3 Hz), 84.7 (d, $^1J_{C-F}$ = 177.3 Hz, *E*-alkene), 61.6, 40.3, 37.4 (*E*-alkene), 33.0 – 32.6 (m), 32.2 (dd, $^5J_{C-F}$ = 8.8, 2.1 Hz), 26.0, 25.8 (d, $^6J_{C-F}$ = 1.3 Hz), 25.8 (*E*-alkene), 25.5 (d, $^6J_{C-F}$ = 8.8 Hz, *E*-alkene), 14.1, 14.1. **HRMS (ESI)** Calcd for $C_{12}H_{20}FO_2$ $[M+H]^+$: 215.1442, found 215.1441.

Ethyl *(Z)*-5-cyclohexyl-2-fluoropent-3-enoate **(35)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 35.1 mg of Colorless oil (77% yield) of *Z*-alkene/*E*-alkene mixture (71/29).

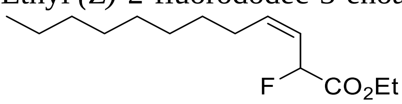
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 – 5.93 (m, 1H), 5.92 – 5.85 (m, 0.44H, *E*-alkene), 5.61 – 5.57 (m, 1H), 5.55 – 5.45 (m, 0.42H, *E*-alkene), 5.29 – 5.13 (m, 1H), 4.29 – 4.25 (m, 2H), 4.24 (d, *J* = 2.8 Hz, 0.8H, *E*-alkene), 2.10 (dtd, *J* = 7.8, 4.6, 1.4 Hz, 0.9H, *E*-alkene), 2.00 (qd, *J* = 6.0, 5.3, 2.6 Hz, 2H), 1.73 – 1.69 (m, 3H), 1.68 (d, *J* = 2.3 Hz, 3H), 1.30 (td, *J* = 7.1, 1.8 Hz, 5H), 1.24 – 1.16 (m, 3H), 1.15 – 1.09 (m, 0.96H, *E*-alkene), 0.95 – 0.86 (m, 2.4H, *E*-alkene).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -180.64 (*E*-alkene), -180.89.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1 (d, $^2J_{C\text{-}F}$ = 26.7 Hz, *E*-alkene), 168.9 (d, $^2J_{C\text{-}F}$ = 26.2 Hz), 138.3 (d, $^3J_{C\text{-}F}$ = 10.2 Hz, *E*-alkene), 137.9 (d, $^3J_{C\text{-}F}$ = 10.8 Hz), 123.3 (d, $^2J_{C\text{-}F}$ = 19.4 Hz), 122.5 (d, $^2J_{C\text{-}F}$ = 21.1 Hz, *E*-alkene), 88.8 (d, $^1J_{C\text{-}F}$ = 181.2 Hz), 84.4 (d, $^1J_{C\text{-}F}$ = 176.9 Hz, *E*-alkene), 61.7, 40.2, 37.8 (d, $^4J_{C\text{-}F}$ = 2.3 Hz, *E*-alkene), 37.4 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 33.0 (d, $^6J_{C\text{-}F}$ = 8.1 Hz), 26.4 (d, $^7J_{C\text{-}F}$ = 4.1 Hz), 26.2, 14.1.

HRMS (ESI) Calcd for $C_{13}H_{22}FO_2$ $[M+H]^+$: 229.1598, found 229.1598.

Ethyl *(Z)*-2-fluorododec-3-enoate **(36)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 35.2 mg of colorless oil (72% yield) of *Z*-alkene/*E*-alkene mixture (77/23).

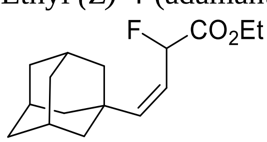
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dtdd, *J* = 15.1, 6.8, 4.2, 1.2 Hz, 1H), 5.89 – 5.84 (m, 0.29H, *E*-alkene), 5.64 – 5.57 (m, 1H), 5.55 – 5.50 (m, 0.34H, *E*-alkene), 5.20 (ddd, *J* = 48.4, 7.1, 1.1 Hz, 1H), 4.28 (d, *J* = 2.1 Hz, 0.34H, *E*-alkene), 4.25 (td, *J* = 7.2, 2.0 Hz, 2H), 2.23 – 2.17 (m, 0.55H, *E*-alkene), 2.13 – 2.06 (m, 2H), 1.46 – 1.36 (m, 2H), 1.31 – 1.23 (m, 6H), 0.92 (t, *J* = 7.5 Hz, 0.41H, *E*-alkene), 0.89 – 0.86 (m, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -180.91, -180.96 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8 (d, $^2J_{C\text{-}F}$ = 26.2 Hz), 139.4 (d, $^3J_{C\text{-}F}$ = 10.3 Hz, *E*-alkene), 139.1 (d, $^3J_{C\text{-}F}$ = 10.7 Hz), 122.4 (d, $^2J_{C\text{-}F}$ = 19.4 Hz), 122.0 (d, $^2J_{C\text{-}F}$ = 21.1 Hz, *E*-alkene), 88.7 (d, $^1J_{C\text{-}F}$ = 181.4 Hz), 84.5 (d, $^1J_{C\text{-}F}$ = 177.5 Hz, *E*-alkene), 61.6, 32.2, 31.8, 29.4 (*E*-alkene), 29.4, 29.2, 29.2 (*E*-alkene), 29.1, 28.5 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 28.1 (*E*-alkene), 22.6, 14.1, 14.1.

HRMS (ESI) Calcd for $C_{14}H_{26}FO_2$ $[M+H]^+$: 245.1911, found 245.1910.

Ethyl *(Z)*-4-(adamantan-1-yl)-2-fluorobut-3-enoate **(37)**



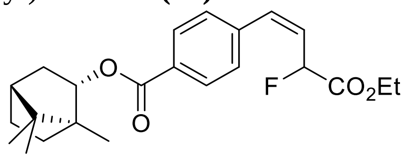
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 32.0 mg of colorless oil (60% yield) of *Z*-alkene/*E*-alkene mixture (94/6).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 15.8, 4.0, 1.1 Hz, 1H), 5.44 (ddd, *J* = 15.8, 12.1, 6.9 Hz, 1H), 5.21 (ddd, *J* = 48.6, 7.0, 1.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.00 (t, *J* = 3.1 Hz, 3H), 1.76 – 1.70 (m, 3H), 1.68 – 1.58 (m, 9H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -180.92.

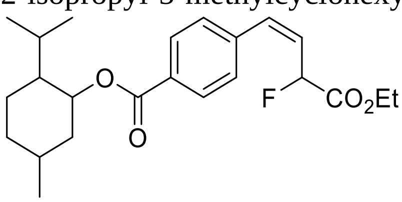
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 149.4 (d, $^3J_{C\text{-}F}$ = 10.2 Hz), 117.7 (d, $^2J_{C\text{-}F}$ = 19.7 Hz), 89.2 (d, $^1J_{C\text{-}F}$ = 181.4 Hz), 41.5 (d, $^5J_{C\text{-}F}$ = 1.8 Hz), 36.7, 35.2, 28.2, 14.1.
HRMS (ESI) Calcd for $C_{16}H_{23}FO_2Na$ $[M+Na]^+$: 289.1574, found 289.1569.

(1*S*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*Z*)-4-ethoxy-3-fluoro-4-oxobut-1-en-1-yl)benzoate **(38)**



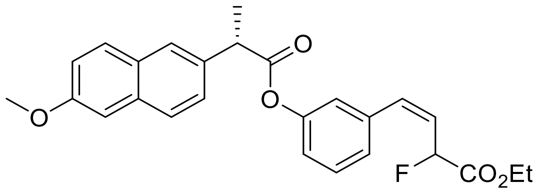
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 55.9 mg of colorless oil (72% yield) of *Z*-alkene/*E*-alkene mixture (95/5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 7.42 (m, 4H), 7.01 (dd, *J* = 11.5, 3.5 Hz, 1H), 6.09 – 5.84 (m, 1H), 5.60 (ddd, *J* = 48.0, 9.6, 1.0 Hz, 1H), 5.13 (ddd, *J* = 10.0, 3.5, 2.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.41 (m, 1H), 2.13 (ddd, *J* = 13.3, 9.4, 4.4 Hz, 1H), 1.82 (dtt, *J* = 15.3, 8.0, 4.1 Hz, 1H), 1.75 (t, *J* = 4.5 Hz, 1H), 1.68 – 1.37 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.13 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.98 (s, 3H), 0.92 (d, *J* = 1.2 Hz, 6H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.66.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C\text{-}F}$ = 26.0 Hz), 166.5, 139.4 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 137.1 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 130.8, 129.8, 129.0 (d, $^5J_{C\text{-}F}$ = 2.7 Hz), 124.9 (d, $^2J_{C\text{-}F}$ = 20.8 Hz), 84.4 (d, $^1J_{C\text{-}F}$ = 178.4 Hz), 80.9, 62.2, 49.3, 48.1, 45.1, 37.1, 28.2, 27.6, 19.9, 19.1, 14.2, 13.8.
HRMS (ESI) Calcd for $C_{23}H_{29}FO_4Na$ $[M+Na]^+$: 411.1942, found 411.1938.

2-isopropyl-5-methylcyclohexyl *(Z)*-4-(4-ethoxy-3-fluoro-4-oxobut-1-en-1-yl)benzoate **(39)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 50.7 mg of colorless oil (65% yield) of *Z*-alkene/*E*-alkene mixture (95/5).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 11.5, 3.5 Hz, 1H), 6.04 – 5.82 (m, 1H), 5.59 (dddd, *J* = 48.0, 9.6, 4.3, 1.0 Hz, 1H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.23 – 2.07 (m, 1H), 1.95 (pt, *J* = 7.1, 3.5 Hz, 1H), 1.78 – 1.70 (m, 2H), 1.69 – 1.46 (m, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.13 (qd, *J* = 12.6, 12.1, 10.0 Hz, 2H), 0.93 (dd, *J* = 6.8, 4.3 Hz, 6H), 0.80 (d, *J* = 6.9 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.58.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (d, $^2J_{C\text{-}F}$ = 26.1 Hz), 165.8, 139.4 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 137.1 (dd, $^3J_{C\text{-}F}$ = 10.5, 4.3 Hz), 130.8, 129.9, 129.0 (d, $^5J_{C\text{-}F}$ = 2.7 Hz), 124.8 (d, $^2J_{C\text{-}F}$ = 20.6 Hz), 84.4 (d, $^1J_{C\text{-}F}$ = 178.2 Hz), 75.2, 62.2, 47.4, 41.1, 34.5, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7, 14.2.
HRMS (ESI) Calcd for $C_{23}H_{31}FO_4Na$ $[M+Na]^+$: 413.2099, found 413.2096.

Ethyl *(Z)*-2-fluoro-4-(3-(((*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)phenyl)but-3-enoate **(40)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 75.0 mg of colorless oil (86% yield) of *Z*-alkene/*E*-alkene mixture (96/4).

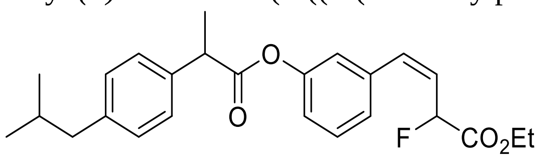
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 3H), 7.50 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 (q, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.89 (dd, *J* = 11.4, 3.5 Hz, 1H), 5.81 (dt, *J* = 11.7, 10.1 Hz, 1H), 5.58 (dddd, *J* = 47.8, 9.5, 2.8, 1.0 Hz, 1H), 4.27 – 4.16 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.39.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 168.6 (d, $^{2}J_{C-F}$ = 26.4 Hz), 157.8, 150.9, 136.8 (dd, $^{3}J_{C-F}$ = 10.6, 5.3 Hz), 136.3 (d, $^{4}J_{C-F}$ = 3.1 Hz), 135.0, 133.9, 129.5, 129.3, 129.0, 127.4, 126.3 (d, $^{7}J_{C-F}$ = 2.3 Hz), 126.2, 126.1, 123.9 (d, $^{2}J_{C-F}$ = 20.9 Hz), 121.9, 121.4, 119.2, 105.6, 84.2 (d, $^{1}J_{C-F}$ = 177.7 Hz), 62.0, 55.3, 45.6, 18.5 (d, $^{9}J_{C-F}$ = 2.9 Hz), 14.0.

HRMS (ESI) Calcd for $C_{26}H_{25}FO_5Na$ $[M+Na]^+$: 459.1578, found 459.1574.

Ethyl *(Z)*-2-fluoro-4-(3-((2-(4-isobutylphenyl)propanoyl)oxy)phenyl)but-3-enoate **(41)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 73.4 mg of colorless oil (89% yield) of *Z*-alkene/*E*-alkene mixture (96/4).

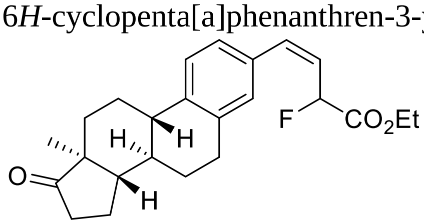
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.27 – 7.21 (m, 1H), 7.19 – 7.06 (m, 3H), 6.98 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.90 (dd, *J* = 11.4, 3.5 Hz, 1H), 5.82 (dt, *J* = 11.4, 9.9 Hz, 1H), 5.59 (ddt, *J* = 47.9, 9.6, 1.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.58.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 168.8 (d, $^{2}J_{C-F}$ = 26.4 Hz), 151.0, 141.0, 137.2, 137.0 (dd, $^{3}J_{C-F}$ = 10.4, 2.5 Hz), 136.4 (d, $^{4}J_{C-F}$ = 3.2 Hz), 129.7, 129.5, 127.3, 126.4 (d, $^{7}J_{C-F}$ = 2.9 Hz), 124.0 (d, $^{2}J_{C-F}$ = 20.6 Hz), 122.0 (d, $^{5}J_{C-F}$ = 2.9 Hz), 121.5, 84.3 (d, $^{1}J_{C-F}$ = 177.7 Hz), 62.1, 45.4, 45.2, 30.3, 22.5, 18.6 (d, $^{9}J_{C-F}$ = 1.4 Hz), 14.2.

HRMS (ESI) Calcd for $C_{25}H_{30}FO_4$ $[M+H]^+$: 413.2123, found 413.2121.

Ethyl *(Z)*-2-fluoro-4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)but-3-enoate **(42)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 63.8 mg of colorless oil (83% yield) of *Z*-alkene/*E*-alkene mixture (95/5).

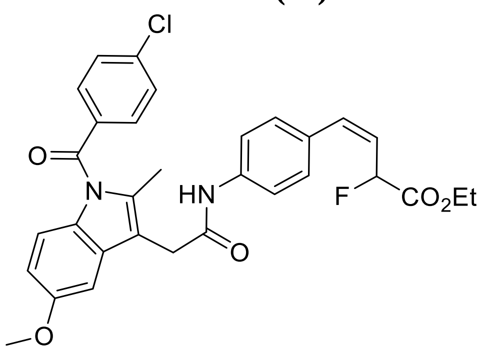
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.21 (dt, *J* = 8.1, 2.2 Hz, 1H), 7.16 (s, 1H), 6.93 (dd, *J* = 11.1, 3.7 Hz, 1H), 5.91 – 5.57 (m, 2H), 4.39 – 4.19 (m, 2H), 2.94 (dd, *J* = 8.9, 4.2 Hz, 2H), 2.58 – 2.40 (m, 2H), 2.32 (dt, *J* = 10.8, 6.1 Hz, 1H), 2.25 – 1.93 (m, 4H), 1.67 – 1.47 (m, 6H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.10, -182.87 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1 (d, $^{2}J_{C\text{-}F}$ = 26.7 Hz), 140.4, 138.15 (d, $^{3}J_{C\text{-}F}$ = 10.6 Hz), 136.9, 132.7, 129.7, 126.5 (d, $^{6}J_{C\text{-}F}$ = 2.7 Hz), 125.7, 122.7 (d, $^{2}J_{C\text{-}F}$ = 19.9 Hz), 84.7 (d, $^{1}J_{C\text{-}F}$ = 177.4 Hz), 62.0, 50.7, 48.1, 44.6, 38.2, 36.0, 31.7, 29.8, 29.5, 26.6, 25.8, 21.7, 14.3, 14.0.
138.15 (d, *J* = 10.6 Hz),

HRMS (ESI) Calcd for $C_{24}H_{29}FO_3Na$ $[M+Na]^+$: 407.1993, found 407.1993.

Ethyl *(Z)*-4-(4-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetamido)phenyl)-2-fluorobut-3-enoate **(43)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 87.8 mg of yellow solid (78% yield) of *Z*-alkene/*E*-alkene mixture (90/10). m.p. 87-88℃.

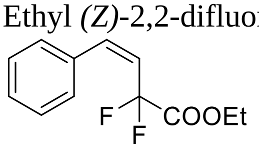
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 2.7 Hz, 2H), 7.33 (s, 1H), 6.93 (dd, *J* = 11.5, 3.1 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.73 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.77 (dt, *J* = 11.4, 10.0 Hz, 1H), 5.59 (ddd, *J* = 47.9, 9.6, 0.9 Hz, 1H), 4.29 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.83 (s, 2H), 3.82 (s, 3H), 2.47 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -174.39.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 168.9, 168.4 (d, $^{2}J_{C\text{-}F}$ = 11.1 Hz), 156.5, 139.9, 137.6, 137.4 (d, $^{3}J_{C\text{-}F}$ = 10.4 Hz), 136.9, 133.5, 131.4, 131.0, 130.2, 129.8 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 129.4, 122.7 (d, $^{2}J_{C\text{-}F}$ = 20.6 Hz), 120.0, 115.4, 112.7, 112.2, 100.7, 84.5 (d, $^{1}J_{C\text{-}F}$ = 177.4 Hz), 62.2, 55.9, 33.5, 14.3, 13.5.

HRMS (ESI) Calcd for $C_{31}H_{29}ClFN_2O_5$ $[M+H]^+$: 563.1744, found 563.1746.

Ethyl *(Z)*-2,2-difluoro-4-phenylbut-3-enoate **(44)**

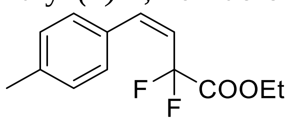


Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 37.6 mg of colorless oil (83% yield) of *Z*-alkene/*E*-alkene mixture (77/23).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 0.7H, Ph alkene), 7.38 – 7.36 (m, 1.1H, Ph alkene), 7.34 (d, *J* = 3.4 Hz, 5H), δ 7.13 – 7.04 (m, 0.39H, CH alkene), 6.95 (dt, *J* = 12.6, 1.8 Hz,

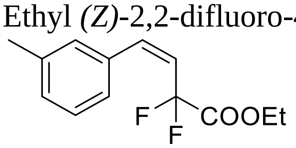
1H), 6.31 (dt, J = 16.2, 11.4 Hz, 0.32H, CH alkene), 5.88 (q, J = 12.9 Hz, 1H), 4.35 (q, J = 7.1 Hz, 0.67H,), 4.02 (q, J = 7.2 Hz, 2H), 1.39 – 1.33 (m, 1.14H, CH_3 alkene), 1.12 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.90, -103.29 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5 (t, $^2J_{C-F}$ = 33.8 Hz), 138.9 (t, $^4J_{C-F}$ = 9.0 Hz), 137.0 (t, $^4J_{C-F}$ = 9.4 Hz, *E*-alkene), 134.4, 129.8 (*E*-alkene), 129.0 (dd, $^3J_{C-F}$ = 5.3, 2.6 Hz), 128.9, 128.4, 127.6, 122.1 (t, $^2J_{C-F}$ = 28.1 Hz), 118.9 (t, $^2J_{C-F}$ = 25.0 Hz, *E*-alkene), 112.4 (t, $^1J_{C-F}$ = 245.7 Hz), 63.3(*E*-alkene), 63.1, 14.1(*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22,23]

Ethyl *(Z)*-2,2-difluoro-4-(*p*-tolyl)but-3-enoate **(45)**



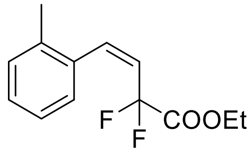
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 37.5 mg of colorless oil (78% yield) of *Z*-alkene/*E*-alkene mixture (74/26).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.2 Hz, 0.77H, Ph alkene), 7.26 – 7.24 (m, 2H), 7.18 (d, J = 8.0 Hz, 0.75H, Ph alkene), 7.15 (d, J = 7.9 Hz, 2H), 7.05 (dt, J = 16.2, 2.6 Hz, 0.36H, CH alkene), 6.90 (dt, J = 12.5, 1.9 Hz, 1H), 6.25 (dt, J = 16.2, 11.5 Hz, 0.35H, CH alkene), 5.82 (q, J = 13.1 Hz, 1H), 4.34 (q, J = 7.1 Hz, 0.73H, CH_2 alkene), 4.05 (q, J = 7.1 Hz, 2H), 2.37 (s, 1.1H, CH_3 alkene), 2.35 (s, 3H), 1.36 (t, J = 7.1 Hz, 1.1H, CH_3 alkene), 1.13 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.98, -103.04 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C-F}$ = 33.9 Hz), 140.0 (*E*-alkene), 139.2 – 138.7 (m), 136.9 (t, $^4J_{C-F}$ = 9.5 Hz, *E*-alkene), 131.5, 129.7 (*E*-alkene), 129.1 (t, $^3J_{C-F}$ = 2.9 Hz), 129.1, 127.5, 121.1 (t, $^2J_{C-F}$ = 28.0 Hz), 117.8 (t, $^2J_{C-F}$ = 25.0 Hz, *E*-alkene), 112.5 (t, $^1J_{C-F}$ = 245.6 Hz), 63.2 (*E*-alkene), 63.1, 21.5 (*E*-alkene), 21.4, 14.1 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22,23]

Ethyl *(Z)*-2,2-difluoro-4-(*m*-tolyl)but-3-enoate **(46)**



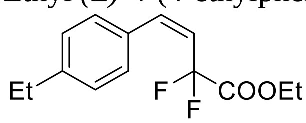
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 37.5 mg of colorless oil (78% yield) of *Z*-alkene/*E*-alkene mixture (74/26).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 0.35H, Ph alkene), 7.28 – 7.24 (m, 1H), 7.24 – 7.20 (m, 0.97H, Ph alkene), 7.14 (d, J = 5.5 Hz, 3H), 7.05 (dt, J = 16.2, 2.6 Hz, 0.36H, CH alkene), 6.92 (d, J = 12.5 Hz, 1H), 6.29 (dt, J = 16.2, 11.5 Hz, 0.3H, CH alkene), 5.85 (q, J = 12.8 Hz, 1H), 4.35 (q, J = 7.1 Hz, 0.61H, CH_2 alkene), 4.01 (q, J = 7.2 Hz, 2H), 2.36 (s, 0.93H, CH_3 alkene), 2.34 (s, 3H), 1.39 – 1.33 (m, 0.84H, CH_3 alkene), 1.11 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.55, -103.23 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1 (t, $^2J_{C-F}$ = 35.3 Hz, *E*-alkene), 163.5 (t, $^2J_{C-F}$ = 33.8 Hz), 139.0 (t, $^4J_{C-F}$ = 9.2 Hz), 138.7, 138.0, 137.1 (t, $^4J_{C-F}$ = 9.4 Hz, *E*-alkene), 134.3, 134.1 (*E*-alkene), 130.6 (*E*-alkene), 129.7 (t, $^3J_{C-F}$ = 2.6 Hz), 129.6, 128.9, 128.3, 128.2 (*E*-alkene), 126.1 (t, $^3J_{C-F}$ = 2.8 Hz), 124.8, 121.9 (t, $^2J_{C-F}$ = 28.2 Hz), 118.6 (t, $^2J_{C-F}$ = 24.9 Hz, *E*-alkene), 112.4 (t, $^1J_{C-F}$ = 245.4 Hz), 63.3 (*E*-alkene), 63.0, 21.5, 14.1 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22]

Ethyl *(Z)*-2,2-difluoro-4-(*o*-tolyl)but-3-enoate **(47)**



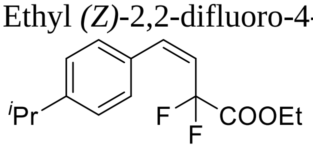
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.0 mg of colorless oil (75% yield) of *Z*-alkene/*E*-alkene mixture (71/29).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 0.05H, Ph alkene), 7.43 – 7.33 (m, 0.15H, Ph alkene), 7.25 – 7.12 (m, 4H), 7.01 (d, *J* = 12.2 Hz, 1H), 5.96 (q, *J* = 11.6 Hz, 1H), 4.42 – 4.32 (m, 0.13H, CH_2 alkene), 3.85 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 0.08H, CH_3 alkene), 2.26 (s, 3H), 1.41 – 1.33 (m, 0.18H, CH_3 alkene), 1.11 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.68, -97.89 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 138.2 (t, $^{4}J_{C\text{-}F}$ = 9.6 Hz), 136.1, 133.9, 129.6, 129.3, 128.9, 125.7, 123.1 (t, $^{2}J_{C\text{-}F}$ = 28.0 Hz), 112.4 (t, $^{1}J_{C\text{-}F}$ = 245.2 Hz), 63.3 (*E*-alkene), 62.9, 20.0, 13.7.
Spectral Data was agreed with previously report.[22]

Ethyl *(Z)*-4-(4-ethylphenyl)-2,2-difluorobut-3-enoate **(48)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 40.7 mg of colorless oil (80% yield) of *Z*-alkene/*E*-alkene mixture (71/29).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 0.79H, Ph alkene), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 0.74H, Ph alkene), 7.19 – 7.14 (m, 2H), 7.05 (dt, *J* = 16.2, 2.6 Hz, 0.36H, CH alkene), 6.91 (dd, *J* = 12.6, 1.9 Hz, 1H), 6.26 (dt, *J* = 16.2, 11.5 Hz, 0.35H, CH alkene), 5.82 (q, *J* = 13.1 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 0.7H, CH_2 alkene), 4.03 (q, *J* = 7.2 Hz, 2H), 2.68 (d, *J* = 7.7 Hz, 0.69H, CH_2 alkene), 2.66 – 2.61 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 1.12H, CH_3 alkene), 1.25 (s, 1.16H, CH_3 alkene), 1.21 (d, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.81, -103.08 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 146.4 (*E*-alkene), 145.3, 138.9 (t, $^{4}J_{C\text{-}F}$ = 9.0 Hz), 136.9 (t, $^{4}J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 131.7 (*E*-alkene), 129.2 (t, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 128.5, 127.9, 127.6, 121.2 (t, $^{2}J_{C\text{-}F}$ = 28.1 Hz), 118.0 (d, $^{2}J_{C\text{-}F}$ = 25.0 Hz, *E*-alkene), 112.0 (t, $^{1}J_{C\text{-}F}$ = 245.5 Hz), 63.2 (*E*-alkene), 63.0, 28.8 (*E*-alkene), 28.8, 15.6, 14.1 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22]

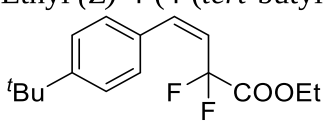
Ethyl *(Z)*-2,2-difluoro-4-(4-isopropylphenyl)but-3-enoate **(49)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 42.4 mg of colorless oil (79% yield) of *Z*-alkene/*E*-alkene mixture (74/26).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 0.74H, Ph alkene), 7.29 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 0.62H, Ph alkene), 7.23 – 7.17 (m, 2H), 7.05 (dt, *J* = 16.2, 2.6 Hz, 0.36H, CH alkene), 6.91 (dt, *J* = 12.5, 1.8 Hz, 1H), 6.26 (dt, *J* = 16.2, 11.5 Hz, 0.34H, CH alkene), 5.82

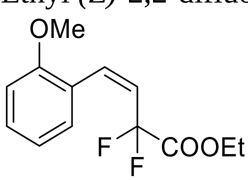
(q, J = 13.0 Hz, 1H), 4.34 (q, J = 7.2 Hz, 0.7H, CH_2 alkene), 4.02 (q, J = 7.1 Hz, 2H), 2.90 (dt, J = 13.9, 7.0 Hz, 1H), 1.36 (t, J = 7.2 Hz, 1.1H, CH_3 alkene), 1.26 (s, 2.1H, ^{i}Pr alkene), 1.23 (d, J = 6.8 Hz, 6H), 1.09 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.65, -103.12 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2 (t, $^2J_{C\text{-}F}$ = 35.4 Hz, *E*-alkene), 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 151.0 (*E*-alkene), 149.9, 138.9 (t, $^4J_{C\text{-}F}$ = 9.1 Hz), 136.8 (t, $^4J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 131.9 (*E*-alkene), 129.2 (t, $^3J_{C\text{-}F}$ = 2.7 Hz), 127.6, 127.1, 126.5, 121.2 (t, $^2J_{C\text{-}F}$ = 28.1 Hz), 117.9 (t, $^2J_{C\text{-}F}$ = 25.0 Hz, *E*-alkene), 112.5 (t, $^1J_{C\text{-}F}$ = 245.4 Hz), 63.2 (*E*-alkene), 63.0, 34.1 (*E*-alkene), 34.1, 24.0, 14.1 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22]

Ethyl *(Z)*-4-(4-(*tert*-butyl)phenyl)-2,2-difluorobut-3-enoate **(50)**



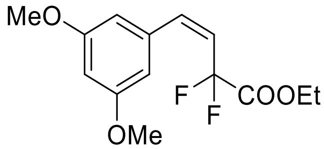
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.7 mg of colorless oil (65% yield) of *Z*-alkene/*E*-alkene mixture (71/29).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.06 (dt, J = 16.2, 2.6 Hz, 0.39H, CH alkene), 6.91 (dt, J = 12.6, 1.8 Hz, 1H), 6.29 – 6.23 (m, 0.28H, CH alkene), 5.83 (q, J = 13.0 Hz, 0.77H, CH_2 alkene), 4.34 (q, J = 7.1 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 1.2H, CH_3 alkene), 1.32 (s, 3.38H, ^{t}Bu alkene), 1.31 (s, 9H), 1.09 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.64, -103.23 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 153.2 (*E*-alkene), 152.2, 138.8 (t, $^4J_{C\text{-}F}$ = 9.0 Hz), 136.7 (t, $^4J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 131.5 (*E*-alkene), 129.0 (t, $^3J_{C\text{-}F}$ = 2.8 Hz), 127.4, 125.9, 125.3, 121.2 (t, $^2J_{C\text{-}F}$ = 28.2 Hz), 118.0 (t, $^2J_{C\text{-}F}$ = 25.0 Hz, *E*-alkene), 112.5 (t, $^1J_{C\text{-}F}$ = 245.4 Hz), 63.2 (*E*-alkene), 63.0, 34.9 (*E*-alkene), 34.8, 31.5 (*E*-alkene), 31.3, 14.1 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[23]

Ethyl *(Z)*-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate **(51)**



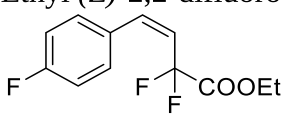
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 30.2 mg of colorless oil (59% yield) of *Z*-alkene/*E*-alkene mixture (78/22).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.05 (dd, J = 12.4, 1.9 Hz, 1H), 6.92 (td, J = 7.5, 1.0 Hz, 1H), 6.87 – 6.83 (m, 1H), 5.90 (q, J = 12.5 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.23.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 156.9, 134.8 (t, $^4J_{C\text{-}F}$ = 9.2 Hz), 130.6 (t, $^3J_{C\text{-}F}$ = 3.3 Hz), 130.5, 123.6, 122.1 (t, $^2J_{C\text{-}F}$ = 27.7 Hz), 120.3, 112.6 (t, $^1J_{C\text{-}F}$ = 245.1 Hz), 110.1, 62.9, 55.5, 13.7.
Spectral Data was agreed with previously report.[22]

Ethyl *(Z)*-4-(3,5-dimethoxyphenyl)-2,2-difluorobut-3-enoate **(52)**



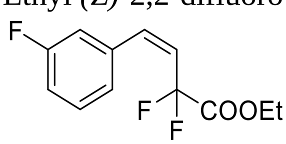
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 32.6 mg of colorless oil (57% yield) of *Z*-alkene/*E*-alkene mixture (76/24).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 12.6, 1.7 Hz, 1H), 6.50 (d, *J* = 2.3 Hz, 2H), 6.42 (t, *J* = 2.3 Hz, 1H), 5.86 (q, *J* = 12.7 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 6H), 1.13 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.28.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3 (t, $^2J_{C-F}$ = 33.7 Hz), 160.5, 138.6 (t, $^4J_{C-F}$ = 9.4 Hz), 136.0, 122.3 (t, $^2J_{C-F}$ = 28.5 Hz), 112.2 (t, $^1J_{C-F}$ = 245.2 Hz), 106.6 (t, $^5J_{C-F}$ = 2.8 Hz), 101.3, 63.0, 55.4, 13.6.
Spectral Data was agreed with previously report.[24]

Ethyl *(Z)*-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate **(53)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 38.1 mg of colorless oil (78% yield) of *Z*-alkene/*E*-alkene mixture (73/27).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.09 – 6.99 (m, 2H), 6.89 (dt, *J* = 12.7, 2.0 Hz, 1H), 5.86 (q, *J* = 13.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.67, -112.07.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C-F}$ = 33.7 Hz), 163.0 (d, $^1J_{C-F'}$ = 249.3 Hz), 137.8 (t, $^4J_{C-F}$ = 8.6 Hz), 131.1 (dt, $^3J_{C-F}$ = 8.2, 3.0 Hz), 122.2 – 121.5 (m), 115.5, 115.3, 112.3 (t, $^1J_{C-F}$ = 246.6 Hz), 63.2, 13.8.
Spectral Data was agreed with previously report.[22,23]

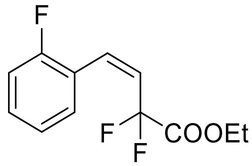
Ethyl *(Z)*-2,2-difluoro-4-(3-fluorophenyl)but-3-enoate **(54)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 36.6 mg of colorless oil (75% yield) of *Z*-alkene/*E*-alkene mixture (71/29).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 0.35H, Ph alkene), 7.34 – 7.28 (m, 1H), 7.23 (dt, *J* = 7.7, 1.2 Hz, 0.39H, Ph alkene), 7.18 – 7.14 (m, 0.4H, Ph alkene), 7.14 – 7.11 (m, 1H), 7.07 (s, 1H), 7.06 (d, *J* = 2.7 Hz, 0.26H, Ph alkene), 7.05 – 7.01 (m, 1H), 7.01 – 6.98 (m, 0.26H, CH alkene), 6.91 (dt, *J* = 12.5, 2.0 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.4 Hz, 0.37H, CH alkene), 5.92 (q, *J* = 13.1 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 0.76H, CH_2 alkene), 4.11 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 1.1H, CH_3 alkene), 1.19 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.85, -103.65 (*E*-alkene), -112.58 (*E*-alkene), -112.95.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, $^1J_{C-F'}$ = 246.7 Hz, *E*-alkene), 163.3 (t, $^2J_{C-F}$ = 32.0 Hz), 162.4 (d, $^1J_{C-F'}$ = 246.3 Hz), 137.4 (td, $^4J_{C-F}$ = 8.6, 2.3 Hz), 136.3 (*E*-alkene), 130.4 (d,

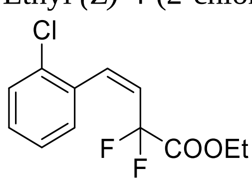
$^{3}J_{C\text{-}F'}$ = 8.4 Hz, *E*-alkene), 129.8 (d, $^{3}J_{C\text{-}F'}$ = 8.3 Hz), 124.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 123.5 (*E*-alkene), 122.9 (t, $^{4}J_{C\text{-}F'}$ = 27.8 Hz), 120.2 (t, $^{4}J_{C\text{-}F'}$ = 25.0 Hz, *E*-alkene), 116.6 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz, *E*-alkene), 115.8 (dt, $^{2}J_{C\text{-}F}$ = 22.4, 3.1 Hz), 115.7 (d, $^{2}J_{C\text{-}F'}$ = 21.1 Hz), 113.9 (d, $^{2}J_{C\text{-}F'}$ = 21.8 Hz, *E*-alkene), 112.4 (*E*-alkene), 112.1 (t, $^{1}J_{C\text{-}F}$ = 246.9 Hz), 63.3 (*E*-alkene), 63.1, 14.0 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[24]

Ethyl *(Z)*-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate **(55)**



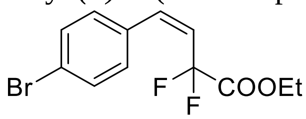
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 31.8 mg of colorless oil (65% yield) of *Z*-alkene/*E*-alkene mixture (86/14).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.6, 1.8 Hz, 0.17H, Ph alkene), 7.43 – 7.36 (m, 1H), 7.32 (tdd, *J* = 7.4, 5.2, 1.8 Hz, 1H), 7.21 (dt, *J* = 16.4, 2.7 Hz, 0.18H, Ph alkene), 7.17 (dd, *J* = 7.7, 1.2 Hz, 0.14H, Ph alkene), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (ddd, *J* = 9.7, 8.3, 1.2 Hz, 1H), 6.98 (dd, *J* = 12.5, 2.0 Hz, 1H), 6.43 (dt, *J* = 16.4, 11.3 Hz, 0.16H, CH alkene), 6.00 (q, *J* = 13.0 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 0.31H, CH_2 alkene), 4.11 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 0.48H, CH_3 alkene), 1.20 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.09 (d, *J* = 3.0 Hz), -103.73(*E*-alkene), -114.00 (d, *J* = 2.3 Hz), -115.65(*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, $^{2}J_{C\text{-}F}$ = 33.7 Hz), 160.0 (d, $^{1}J_{C\text{-}F'}$ = 249.0 Hz), 131.6 (td, $^{4}J_{C\text{-}F}$ = 8.5, 4.0 Hz), 131.3 (d, $^{3}J_{C\text{-}F'}$ = 8.6 Hz, *E*-alkene), 130.9 (q, $^{4}J_{C\text{-}F}$ = 4.4, 3.8 Hz, *E*-alkene), 130.8 (d, $^{3}J_{C\text{-}F'}$ = 8.4 Hz), 128.7, 124.5 (d, $^{4}J_{C\text{-}F'}$= 3.7 Hz, *E*-alkene), 124.1 (t, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 123.9 (d, $^{4}J_{C\text{-}F'}$ = 3.7 Hz), 122.4 (d, $^{2}J_{C\text{-}F'}$ = 14.2 Hz), 121.5 (d, $^{2}J_{C\text{-}F'}$ = 6.4 Hz, *E*-alkene),116.3 (d, $^{2}J_{C\text{-}F'}$ = 22.0 Hz), 115.3 (d, $^{2}J_{C\text{-}F'}$= 21.5 Hz, *E*-alkene), 112.3 (t, $^{1}J_{C\text{-}F}$ = 246.8 Hz), 63.4 (*E*-alkene), 63.2, 14.1 (*E*-alkene), 13.8.
Spectral Data was agreed with previously report.[22, 24]

Ethyl *(Z)*-4-(2-chlorophenyl)-2,2-difluorobut-3-enoate **(56)**



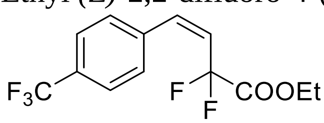
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 34.9 mg of colorless oil (67% yield) of *Z*-alkene/*E*-alkene mixture (88/12).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.26 (td, *J* = 7.0, 1.9 Hz, 2H), 7.03 (dt, *J* = 12.3, 1.9 Hz, 1H), 6.01 (q, *J* = 12.3 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.68.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1 (t, $^{2}J_{C\text{-}F}$ = 33.7 Hz), 135.9 (t, $^{4}J_{C\text{-}F}$ = 8.9 Hz), 133.1 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz), 132.9, 131.0 (t, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 130.0, 129.0, 126.5, 123.7 (t, $^{2}J_{C\text{-}F}$ = 27.7 Hz), 112.0 (t, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 63.1,0 13.6.
Spectral Data was agreed with previously report.[22, 24]

Ethyl *(Z)*-4-(4-bromophenyl)-2,2-difluorobut-3-enoate **(57)**



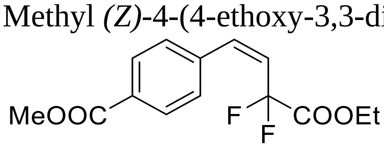
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 50.1 mg of colorless oil (82% yield) of *Z*-alkene/*E*-alkene mixture (71/29).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 0.64H, Ph alkene), 7.47 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 0.77H, Ph alkene), 7.24 (dd, *J* = 9.1, 7.0 Hz, 2H), 7.02 (dt, *J* = 16.2, 2.6 Hz, 0.37H, CH alkene), 6.86 (dd, *J* = 12.6, 2.0 Hz, 1H), 6.30 (dt, *J* = 16.2, 11.3 Hz, 0.36H, CH alkene), 5.90 (dt, *J* = 26.2, 13.4 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 0.73H, CH_2 alkene), 4.12 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 1.04H, CH_3 alkene), 1.19 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.05, -103.46 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3 (t, $^{2}J_{C-F}$ = 33.8 Hz), 137.5 (t, $^{4}J_{C-F}$ = 8.4 Hz), 135.6 (t, $^{4}J_{C-F}$ = 9.5 Hz, *E*-alkene), 133.1, 132.1, 131.4, 130.6 (t, $^{3}J_{C-F}$ = 3.0 Hz), 128.9, 123.0, 122.4 (t, $^{2}J_{C-F}$ = 27.6 Hz), 119.5 (t, $^{2}J_{C-F}$ = 25.0 Hz, *E*-alkene), 112.1 (t, $^{1}J_{C-F}$ = 247.0 Hz), 63.3 (*E*-alkene), 63.2, 14.0 (*E*-alkene), 13.7.
Spectral Data was agreed with previously report.[22, 23, 24]

Ethyl *(Z)*-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate **(58)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 48.8 mg of colorless oil (83% yield) of *Z*-alkene/*E*-alkene mixture (74/26).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 0.65H, Ph alkene), 7.61 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 0.7H, Ph alkene), 7.47 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 16.1 Hz, 0.35H, CH alkene), 6.97 (d, *J* = 12.6 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 0.34H, CH alkene), 5.97 (q, *J* = 13.3 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 0.69H, CH_2 alkene), 4.12 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 1.09H, CH_3 alkene), 1.19 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.81, -95.53 (*E*-alkene), -103.78.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, $^{2}J_{C-F}$ = 33.8 Hz), 137.9, 137.3 (t, $^{4}J_{C-F}$ = 8.1 Hz), 135.5 (t, $^{4}J_{C-F}$ = 9.4 Hz, *E*-alkene) 134.8 – 133.9 (m, *E*-alkene), 130.6 (q, $^{2}J_{C-F'}$ = 32.6 Hz), 129.3 (t, $^{3}J_{C-F}$ = 3.0 Hz), 127.8 (s, *E*-alkene), 126.0 (q, $^{1}J_{C-F'}$ = 3.7 Hz, *E*-alkene), 125.2 (q, $^{1}J_{C-F'}$ = 3.8 Hz), 123.8 (t, $^{2}J_{C-F}$ = 27.4 Hz), 121.5 (t, $^{2}J_{C-F}$ = 25.1 Hz), 112.5, 112.1 (t, $^{1}J_{C-F}$ = 247.5 Hz), 63.5 (*E*-alkene), 63.3, 14.1 (*E*-alkene), 13.8.
Spectral Data was agreed with previously report.[22]

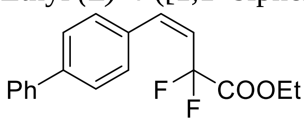
Methyl *(Z)*-4-(4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate **(59)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 50.6 mg of colorless oil (89% yield) of *Z*-alkene/*E*-alkene mixture (77/23).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.03 (m, 0.46H, Ph alkene), 8.00 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.64 (dt, *J* = 7.8, 1.5 Hz, 0.3H, Ph alkene), 7.61 – 7.56 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 0.28H, Ph alkene), 7.46 – 7.41 (m, 1H), 7.12 (d, *J* = 16.2 Hz, 0.29H, CH alkene), 6.97 (dt, *J* = 12.6, 2.1 Hz,

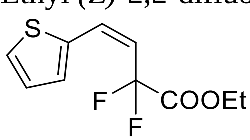
1H), 6.40 (d, J = 16.2 Hz, 0.29H, CH alkene), 5.94 (td, J = 13.5, 12.5 Hz, 1H), 4.37 (q, J = 7.1 Hz, 0.58H, CH_2 alkene), 4.11 (q, J = 7.2 Hz, 2H), 3.95 (s, 0.79H, COOMe alkene), 3.93 (s, 3H), 1.38 (t, J = 7.2 Hz, 0.9H, CH_3 alkene), 1.19 (t, J = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.37, -103.57 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 166.7 (*E*-alkene), 163.5 (t, $^2J_{C-F}$ = 33.7 Hz), 137.8 (t, $^4J_{C-F}$ = 8.2 Hz), 136.0 (t, $^4J_{C-F}$ = 9.6 Hz, *E*-alkene), 134.7, 133.3 (t, $^3J_{C-F}$ = 3.3 Hz, *E*-alkene), 130.7 (*E*-alkene), 130.3, 130.2 (t, $^3J_{C-F}$ = 2.6 Hz), 129.8, 129.1 (*E*-alkene), 128.5, 123.0 (t, $^2J_{C-F}$ = 27.4 Hz), 120.1 (d, $^2J_{C-F}$ = 25.0 Hz, *E*-alkene), 112.2 (t, $^1J_{C-F}$ = 247.2 Hz), 63.4 (*E*-alkene), 63.3, 52.5 (*E*-alkene), 52.4, 14.1 (*E*-alkene), 13.8.
Spectral Data was agreed with previously report.[22]

Ethyl *(Z)*-4-([1,1'-biphenyl]-4-yl)-2,2-difluorobut-3-enoate **(60)**



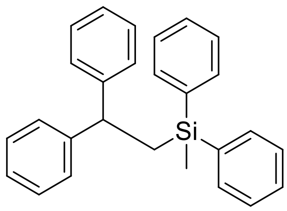
Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 48.4 mg of colorless oil (80% yield) of *Z*-alkene/*E*-alkene mixture (78/22).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.48 – 7.43 (m, 4H), 7.40 – 7.34 (m, 1H), 6.97 (dt, J = 12.6, 1.9 Hz, 1H), 5.90 (q, J = 13.2 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.15.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C-F}$ = 34.3 Hz), 141.6, 140.4, 138.5 (t, $^4J_{C-F}$ = 8.7 Hz), 133.3, 129.7 (t, $^3J_{C-F}$ = 2.9 Hz), 129.0, 127.8, 127.2, 127.0, 121.9 (t, $^2J_{C-F}$ = 28.0 Hz), 112.5 (t, $^1J_{C-F}$ = 247.1 Hz), 63.2, 13.8.
Spectral Data was agreed with previously report.[22, 24]

Ethyl *(Z)*-2,2-difluoro-4-(thiophen-2-yl)but-3-enoate **(61)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 80/1): 20.0 mg of colorless oil (43% yield) of *Z*-alkene/*E*-alkene mixture (83/17).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dt, J = 3.1, 1.1 Hz, 1H), 7.29 (dd, J = 5.0, 3.0 Hz, 1H), 7.21 (dd, J = 5.0, 1.3 Hz, 1H), 6.82 (dt, J = 12.8, 2.1 Hz, 1H), 5.76 (td, J = 13.9, 12.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.84.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (t, $^2J_{C-F}$ = 34.3 Hz), 135.2, 132.3 (t, $^3J_{C-F}$ = 8.6 Hz), 128.7 (t, $^6J_{C-F}$ = 3.6 Hz), 127.8 (t, $^5J_{C-F}$ = 3.8 Hz), 125.9, 120.0 (t, $^2J_{C-F}$ = 28.3 Hz), 112.6 (t, $^1J_{C-F}$ = 246.5 Hz), 63.2, 13.9.
Spectral Data was agreed with previously report.[22, 24]

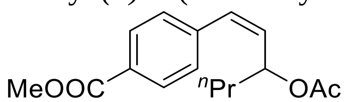
(2,2-diphenylethyl)(methyl)diphenylsilane **(67)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): 49.1 mg of colorless solid (65% yield). [13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.28 – 7.18 (m, 6H), 7.13 – 7.05 (m, 8H), 7.02 (dd, *J* = 6.1, 2.5 Hz, 2H), 3.97 (t, *J* = 7.9 Hz, 1H), 1.87 (d, *J* = 7.9 Hz, 2H), -0.00 (s, 3H). Spectral Data was agreed with previously report.[25]

Methyl *(Z)*-4-(3-acetoxyhex-1-en-1-yl)benzoate **(71)**



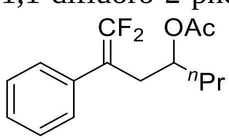
Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): 32.6 mg of colorless oil (59% yield) of *Z*-alkene/*E*-alkene mixture (25/75).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.58 (d, *J* = 10.4 Hz, 1H), 5.73 – 5.63 (m, 2H), 3.92 (s, 3H), 2.03 (s, 3H), 1.71 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.59 – 1.50 (m, 1H), 1.30 (dt, *J* = 15.2, 7.6 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 167.0, 141.3, 132.4, 130.7, 129.8, 128.9, 128.7, 71.0, 52.3, 36.9, 21.4, 18.4, 14.0.

HRMS (ESI) Calcd for $C_{16}H_{20}O_4Na$ $[M+Na]^+$: 299.1254, found 299.1250.

1,1-difluoro-2-phenylhept-1-en-4-yl acetate (**73)**



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): 40.8 mg of colorless oil (76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 4.89 (tt, *J* = 7.2, 5.2 Hz, 1H), 2.65 (dtd, *J* = 7.5, 2.7, 1.9 Hz, 2H), 1.81 (s, 3H), 1.58 – 1.45 (m, 2H), 1.36 – 1.23 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.08 (d, *J* = 39.6 Hz), -90.35 (d, *J* = 39.6 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 154.5 (dd, $^1J_{C-F}$ = 291.1, 288.0 Hz), 133.7 – 133.5 (m), 128.6, 128.4 (t, $^4J_{C-F}$ = 3.1 Hz), 127.5, 89.5 (dd, $^2J_{C-F}$ = 21.1, 15.3 Hz), 72.4 (t, $^4J_{C-F}$ = 2.9 Hz), 36.0, 32.6 (d, $^3J_{C-F}$ = 1.8 Hz), 20.9, 18.6, 14.0.

HRMS (ESI) Calcd for $C_{15}H_{18}F_2O_2Na$ $[M+Na]^+$: 291.1167, found 291.1164

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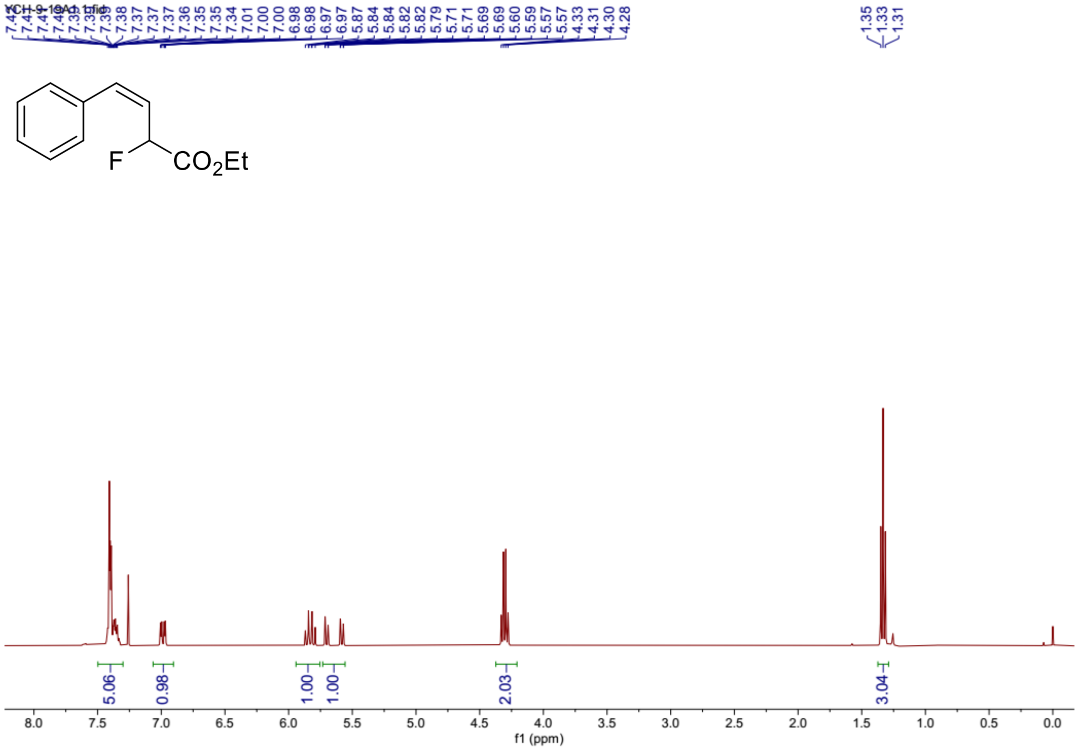
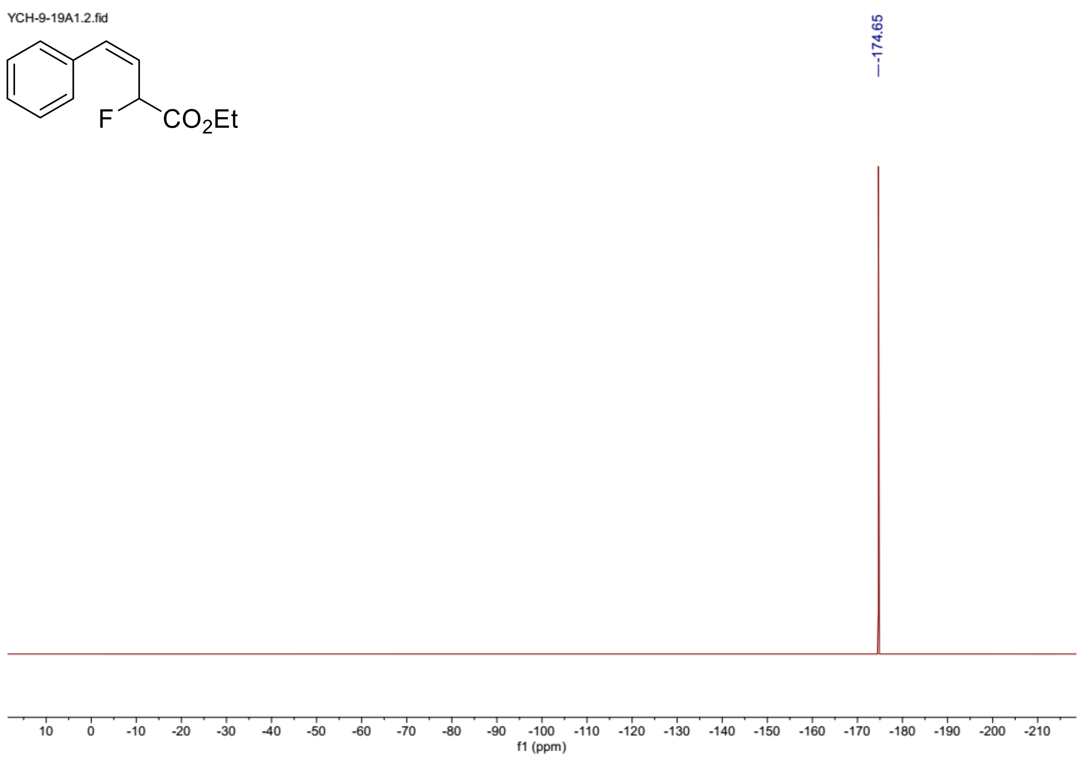
7. Copies of NMR spectra of products

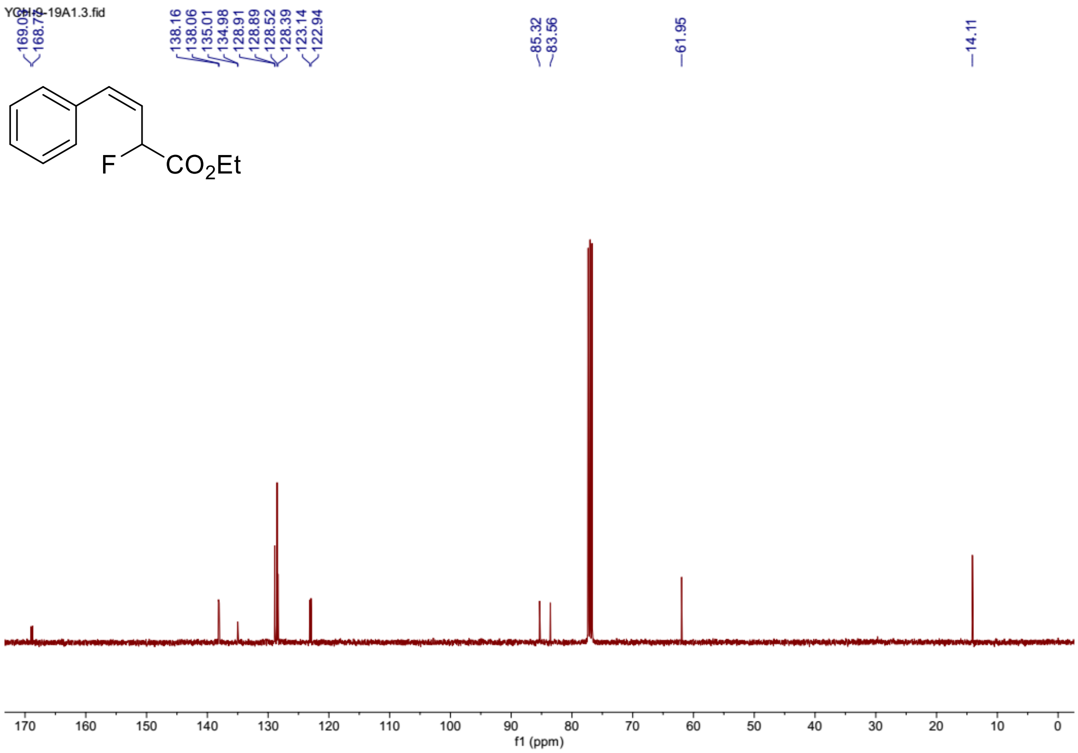
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



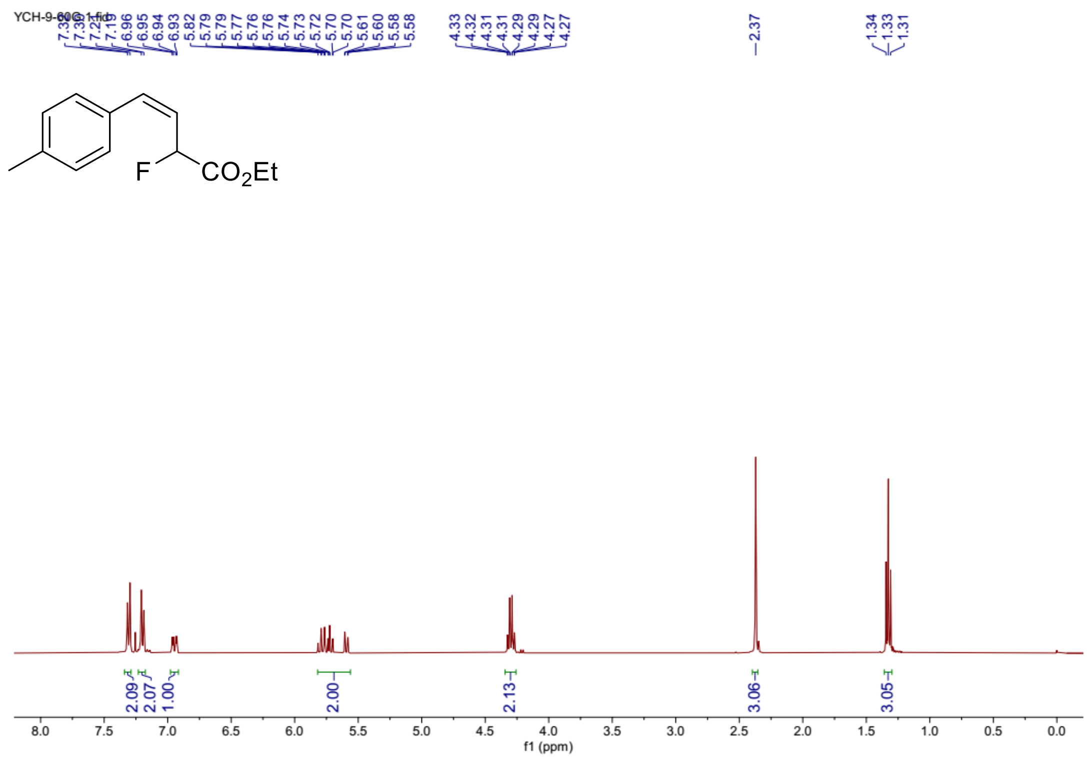
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3**



^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **3**



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



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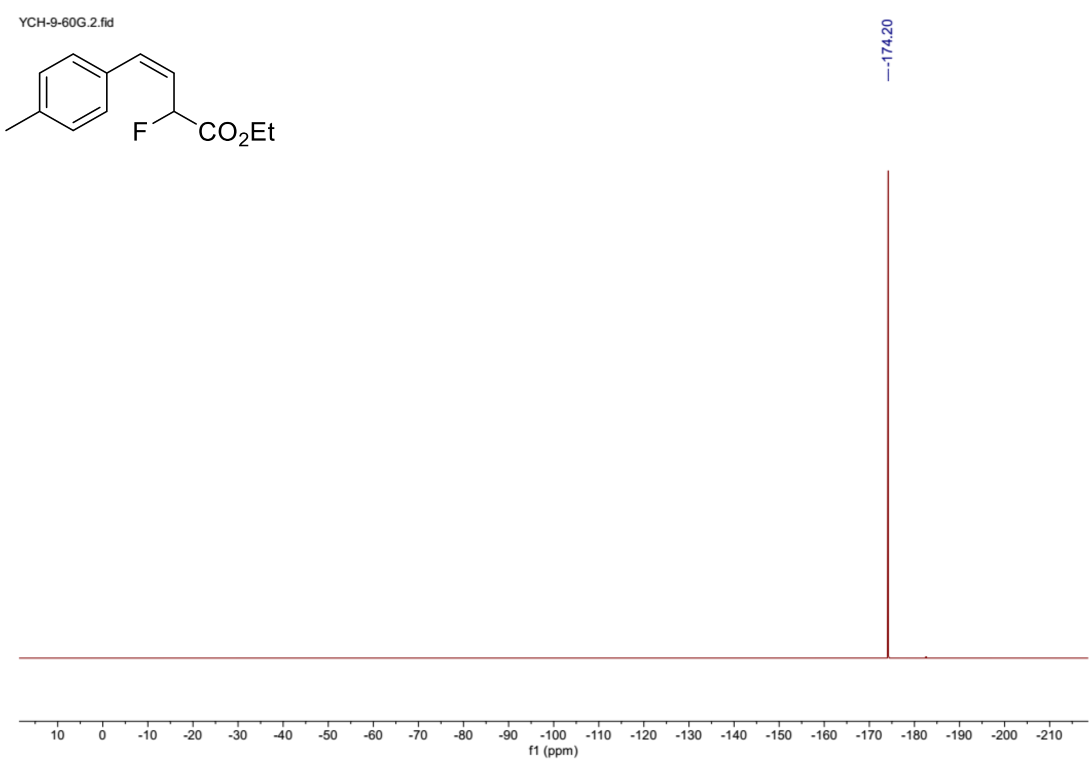
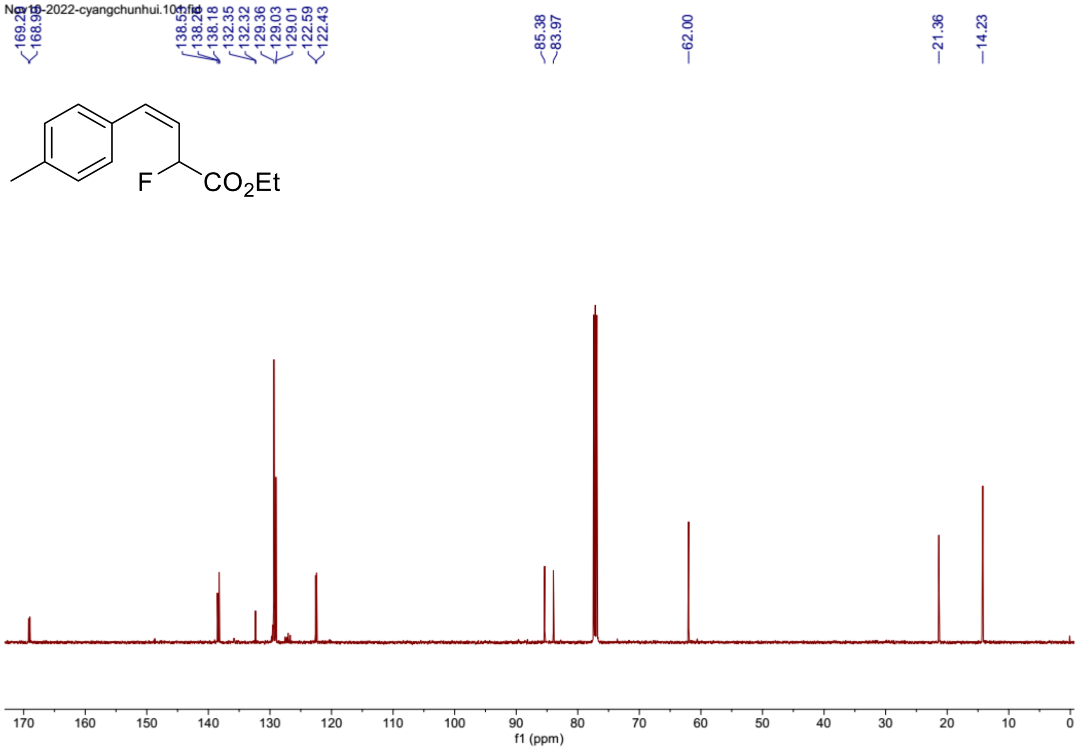
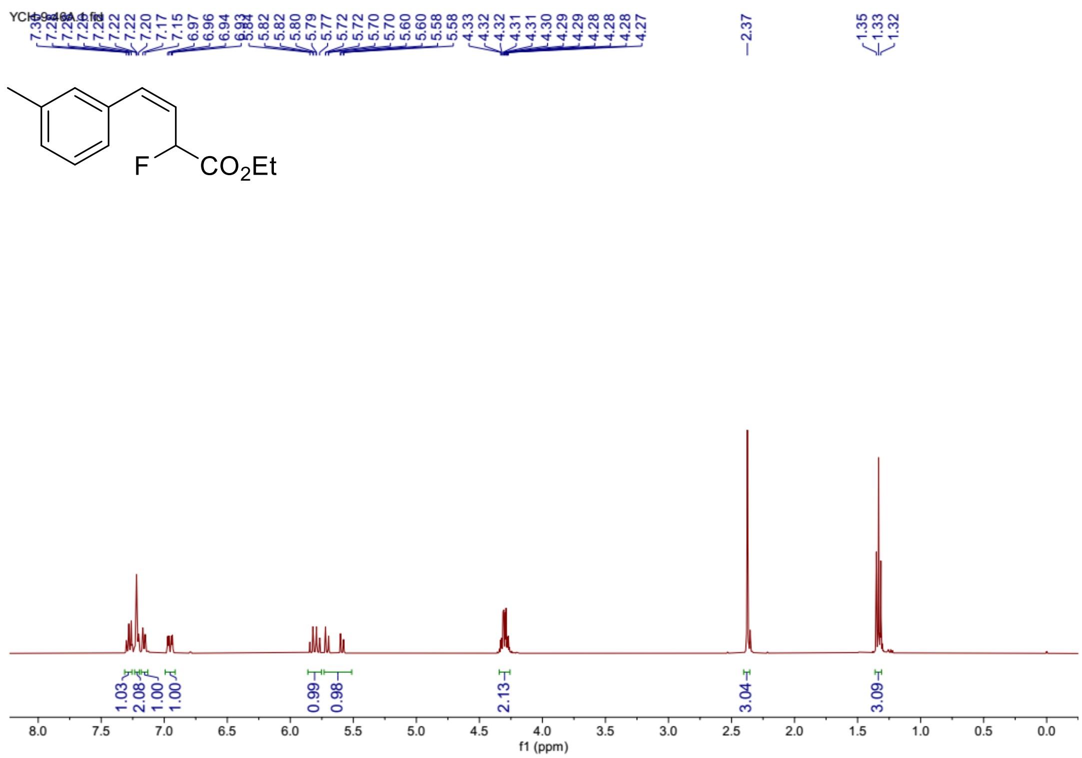


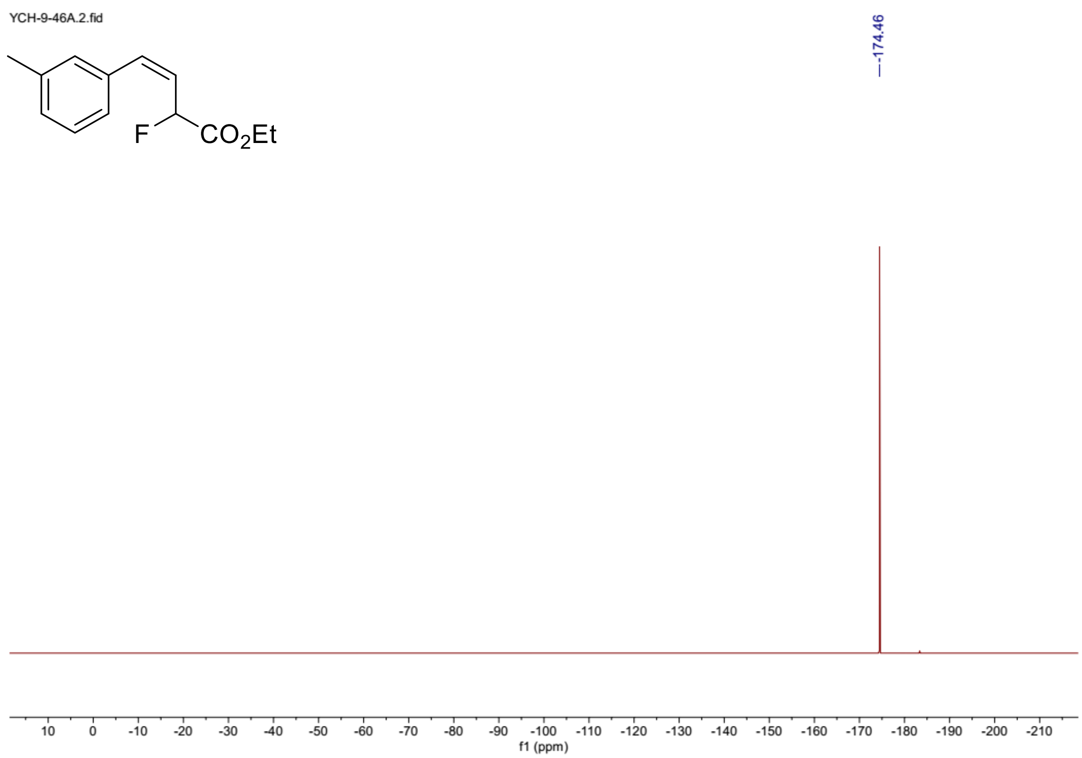
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **4**



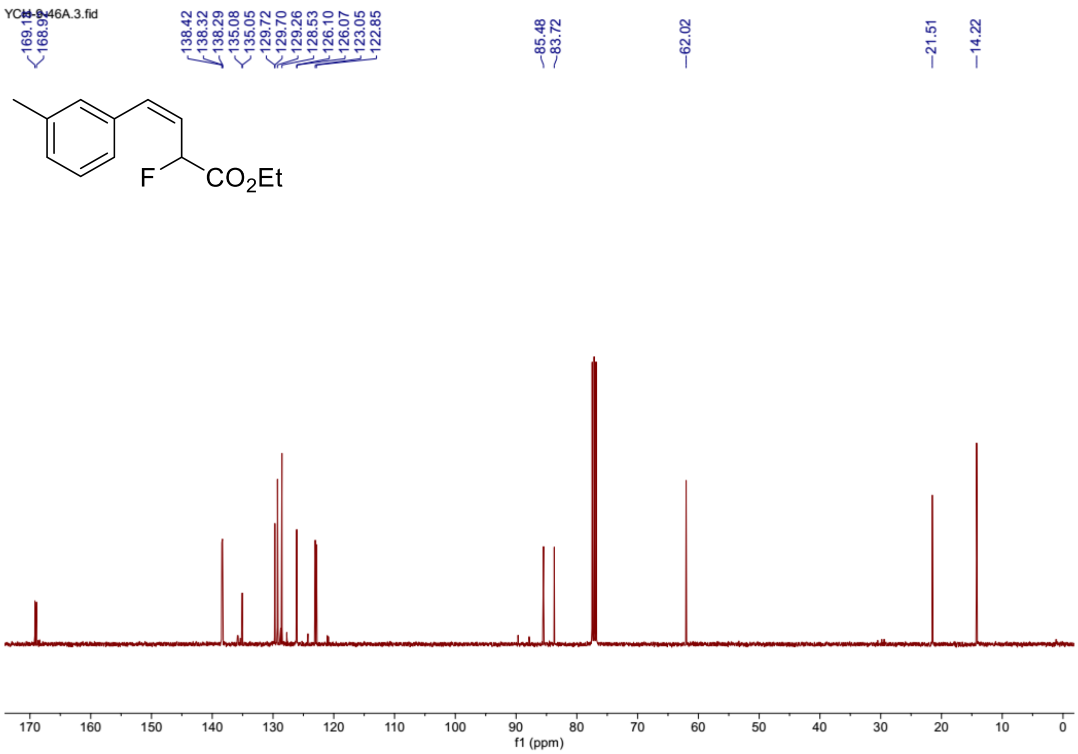
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



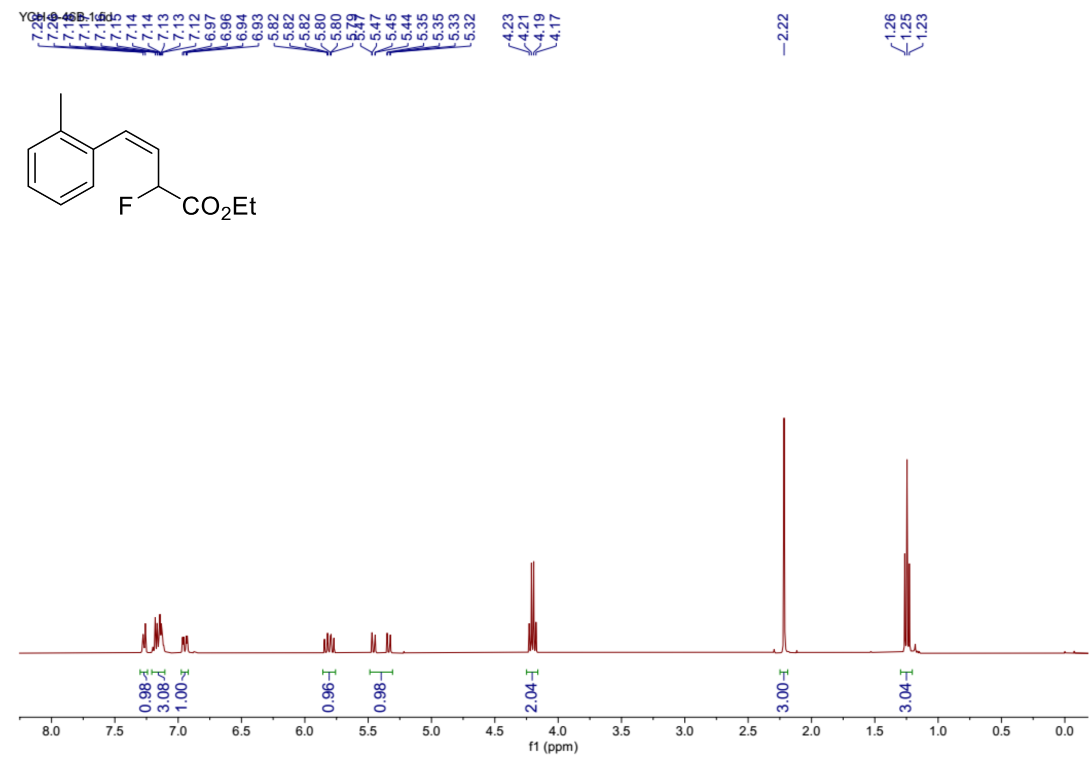
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **5**



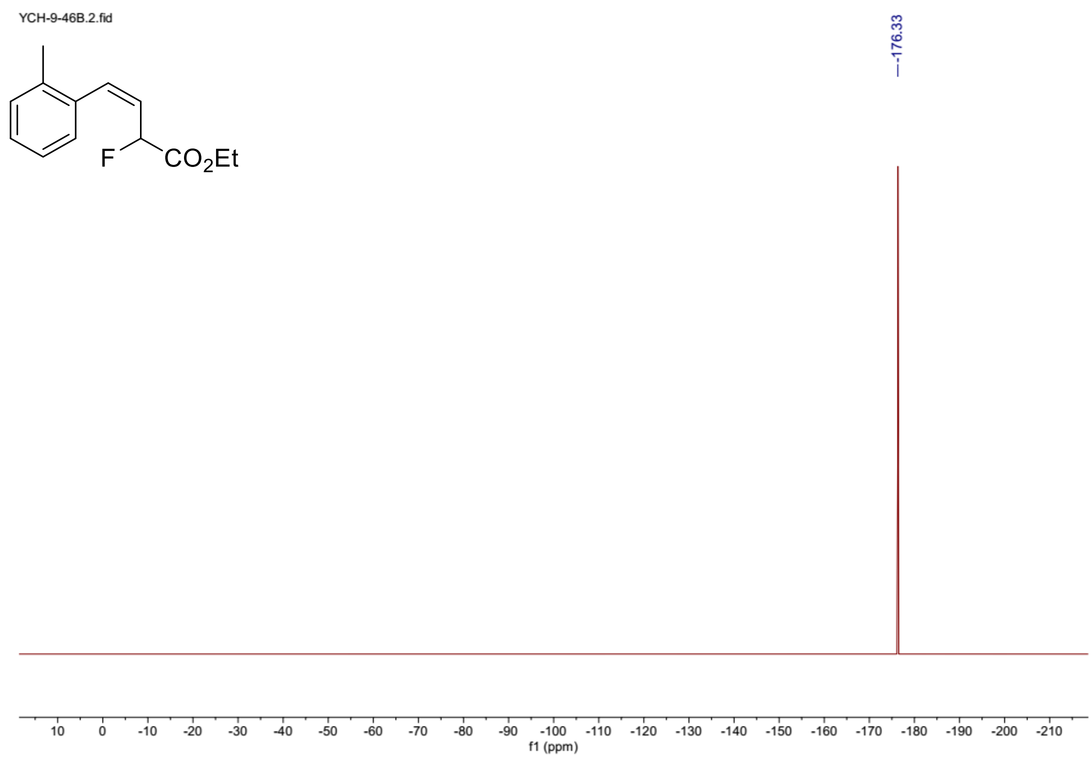
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **5**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **6**



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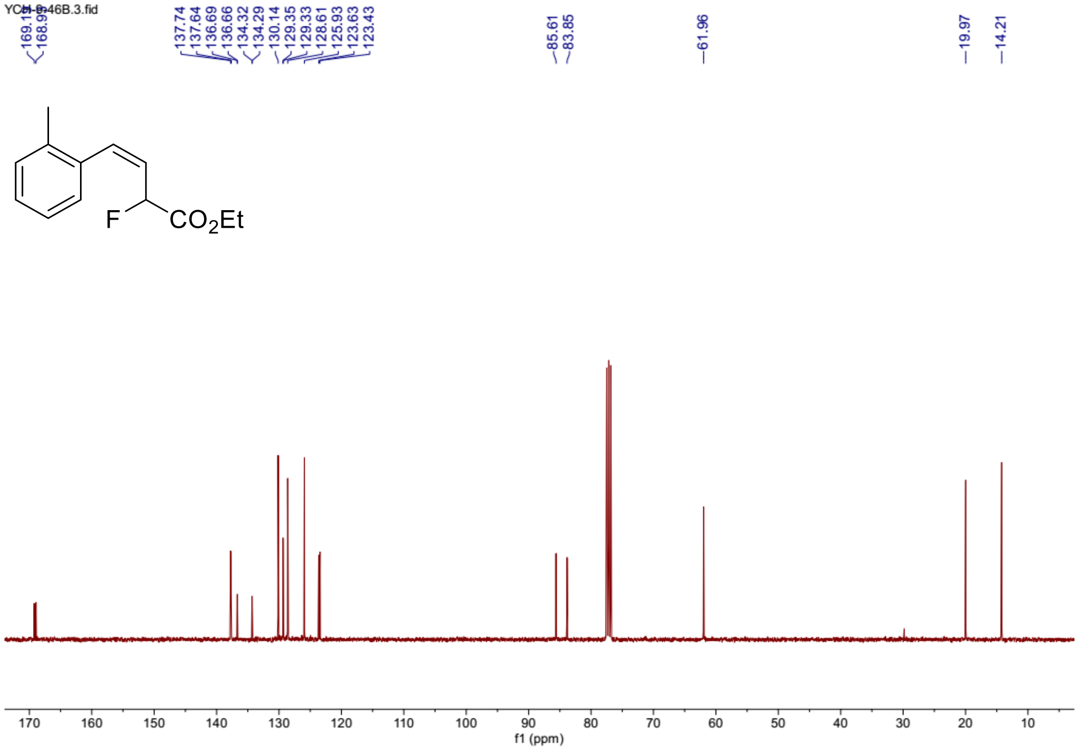
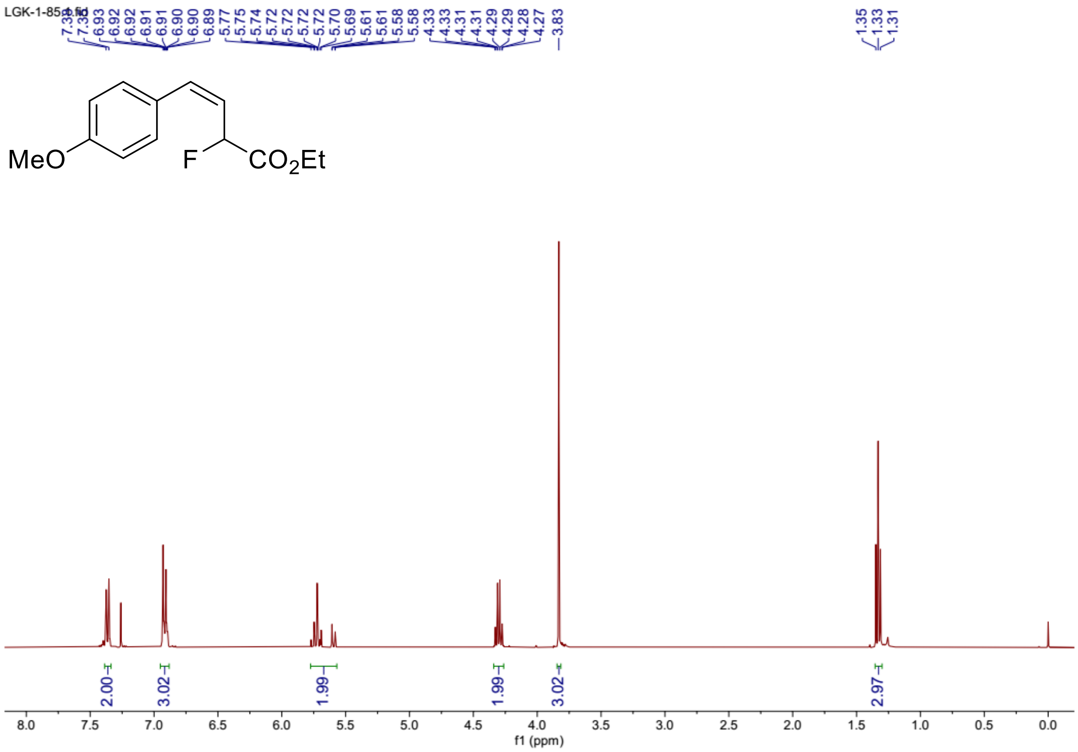
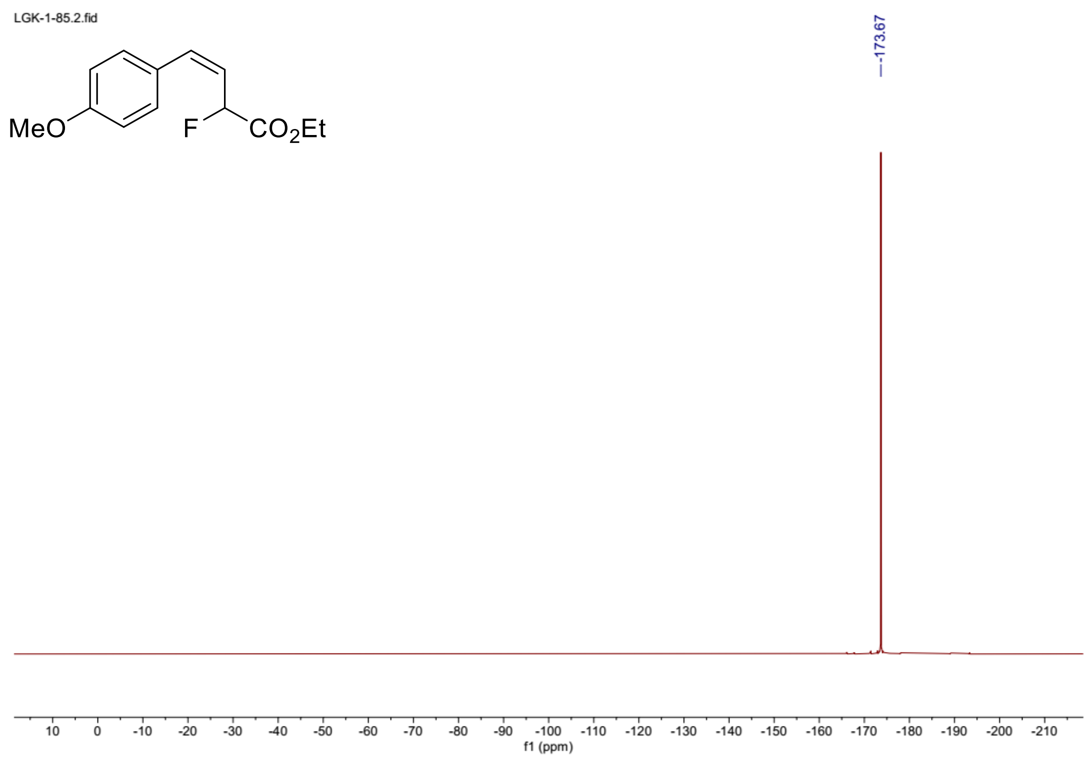


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **7**



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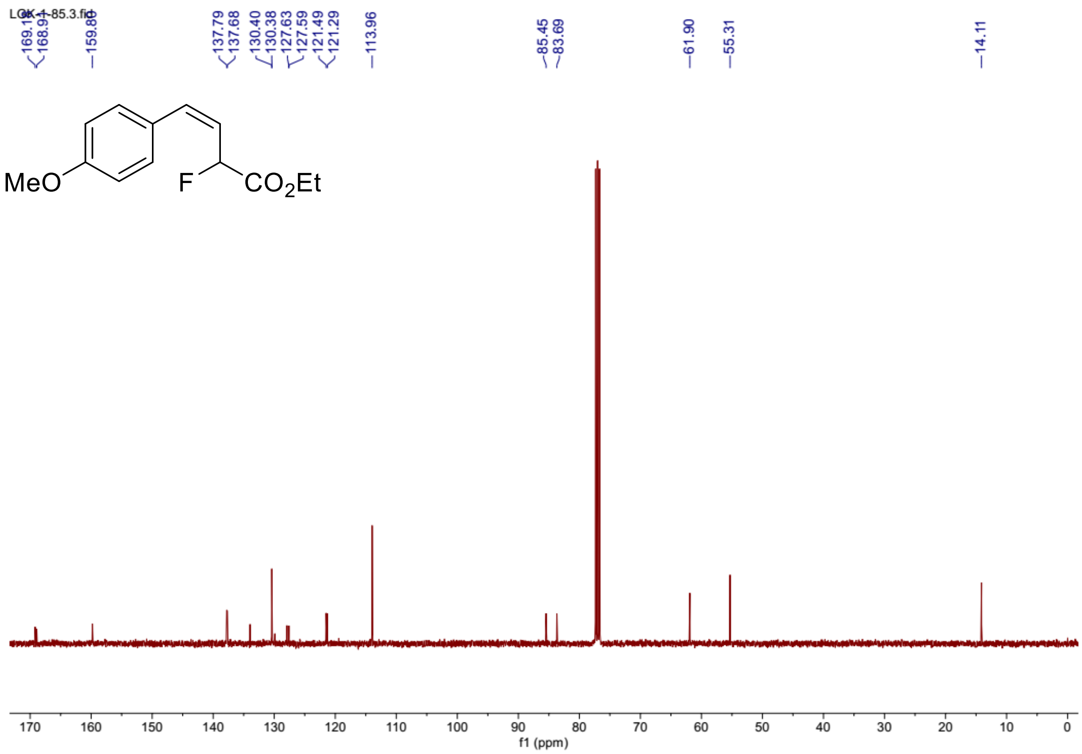
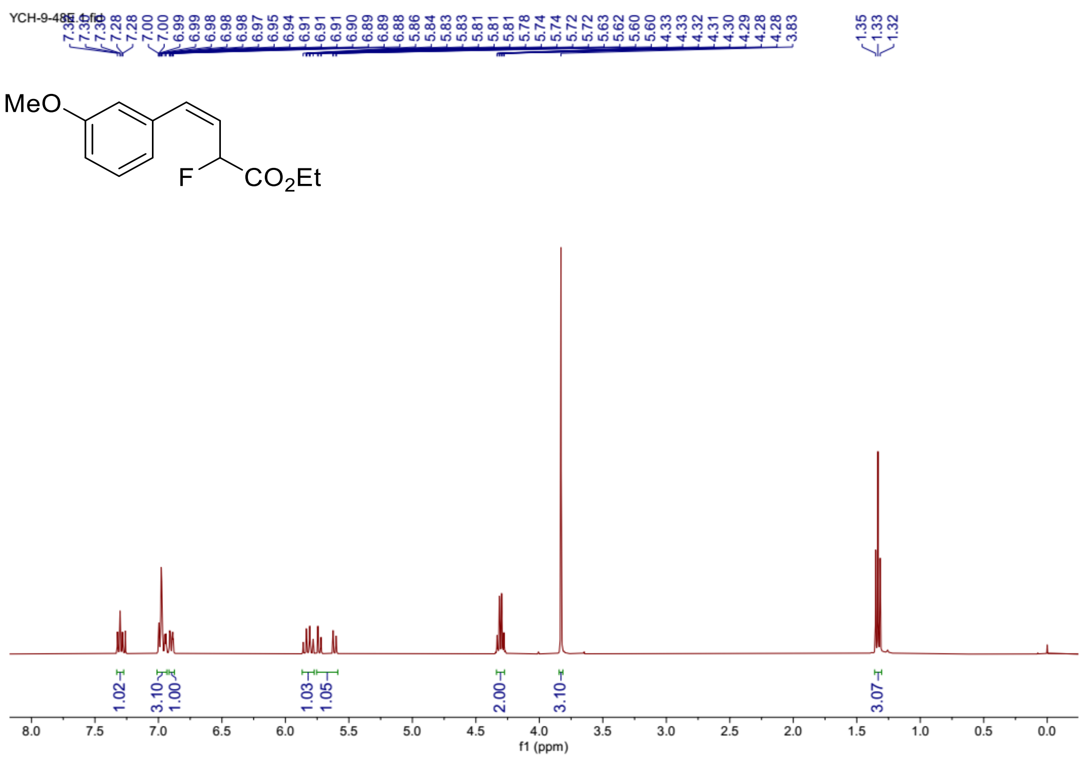
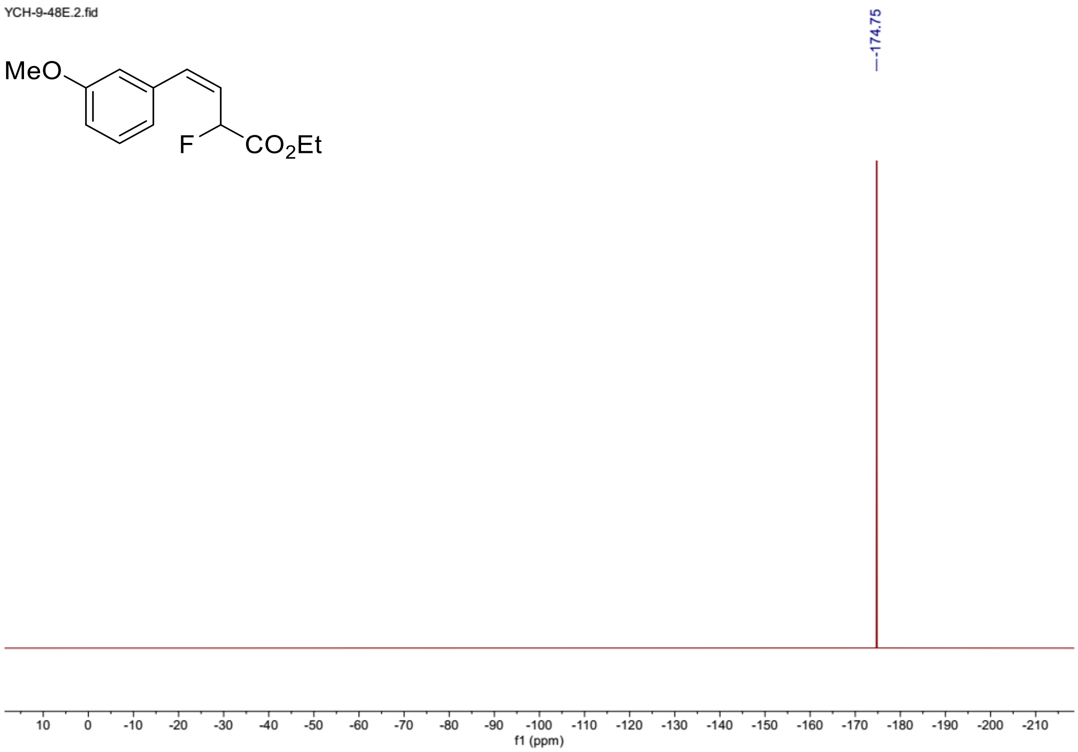


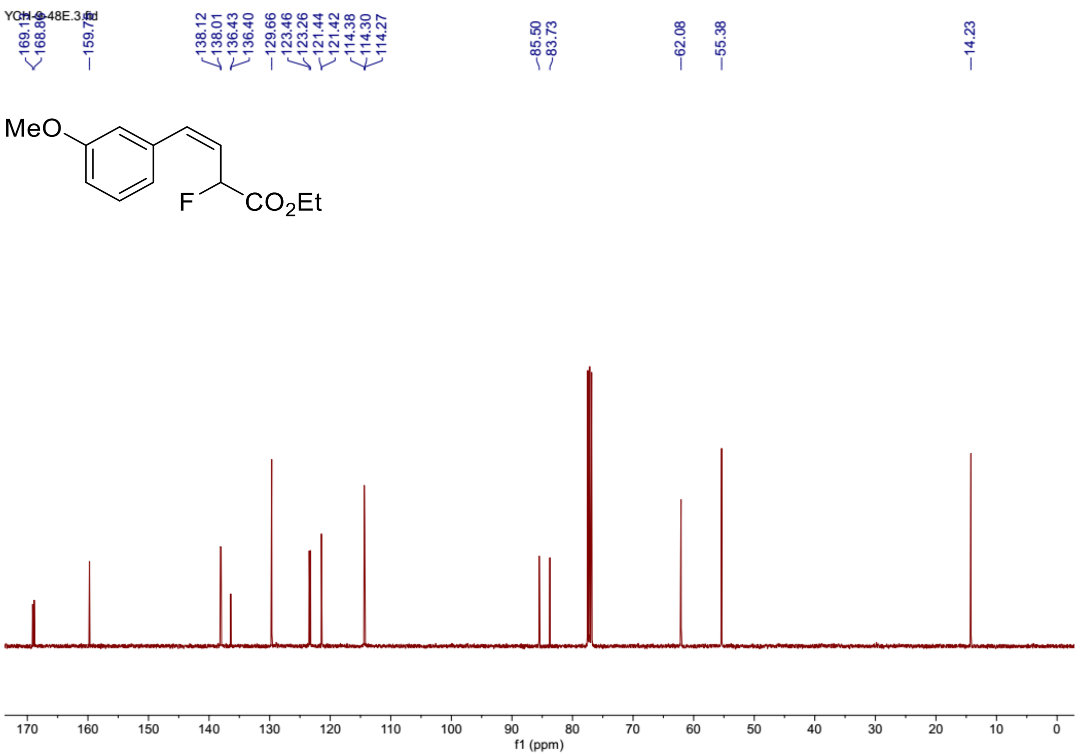
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



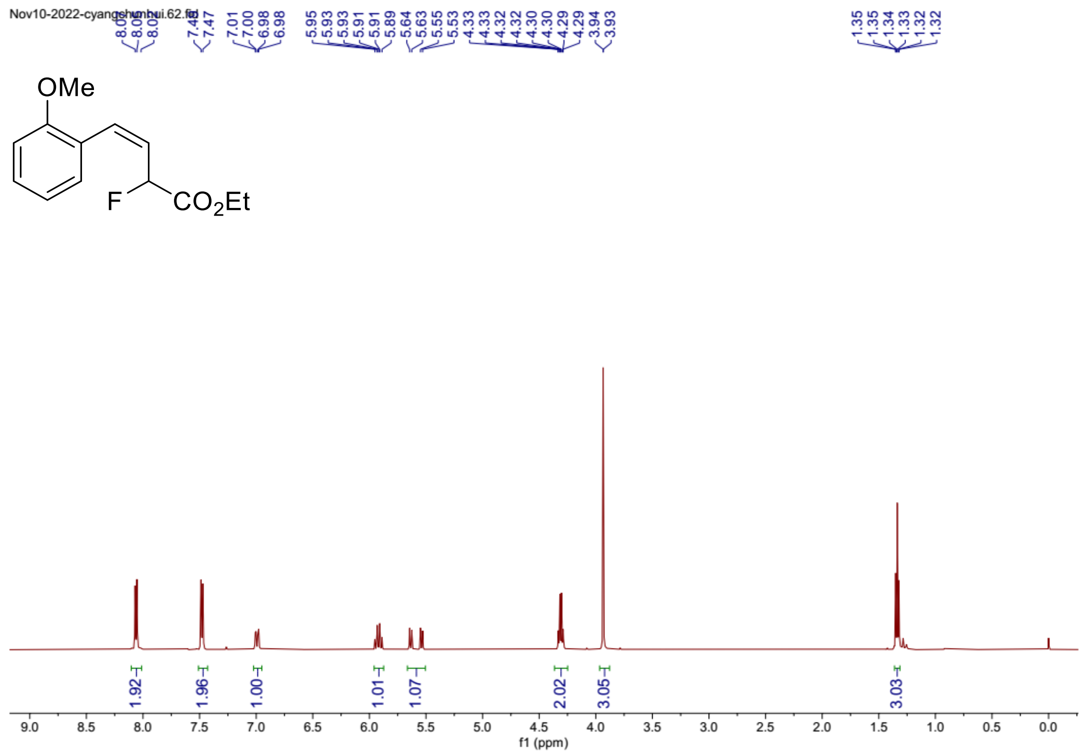
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **8**



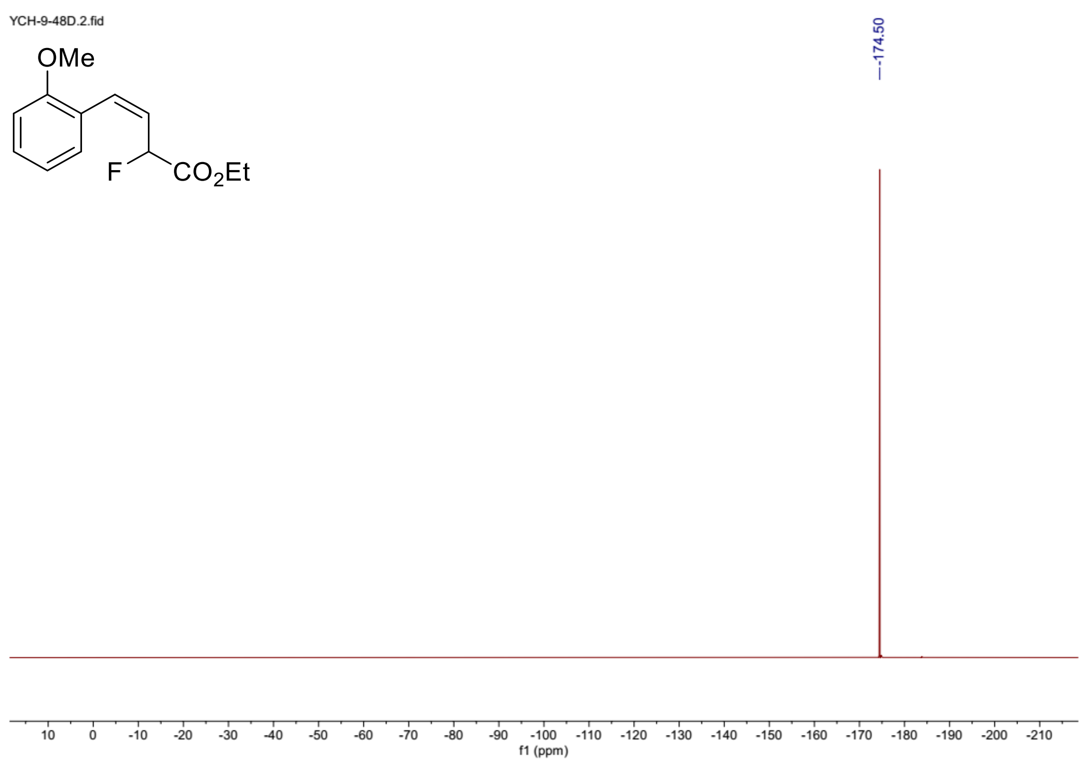
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **8**



^1H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **9**



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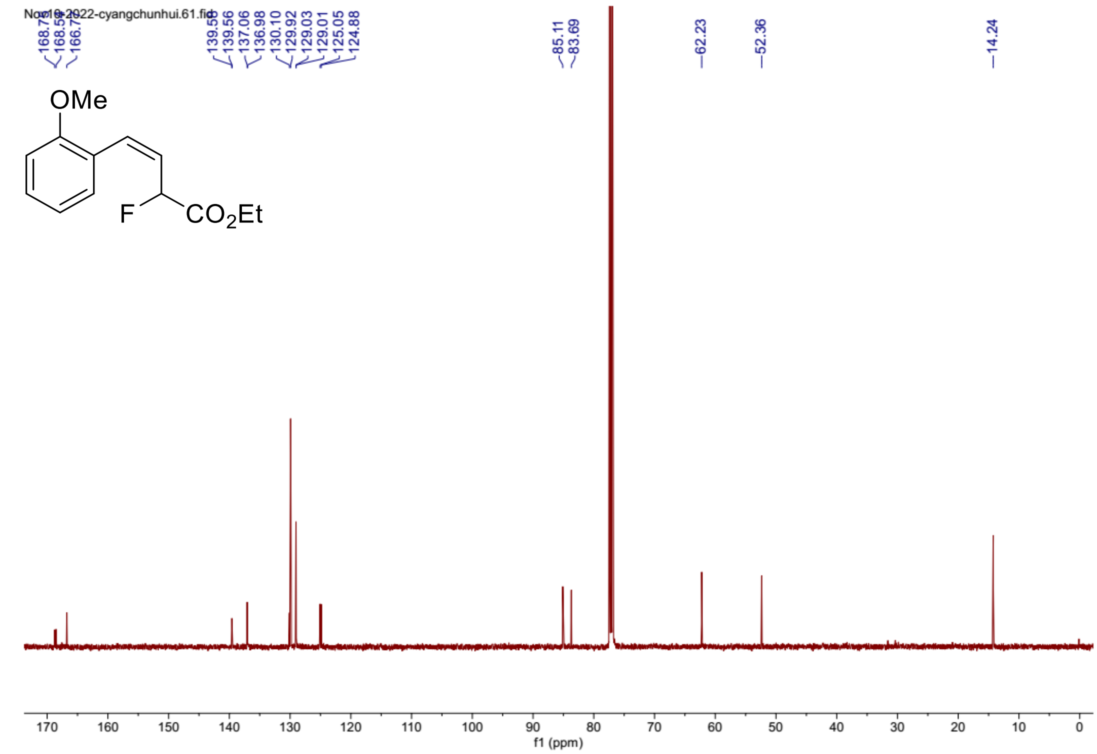
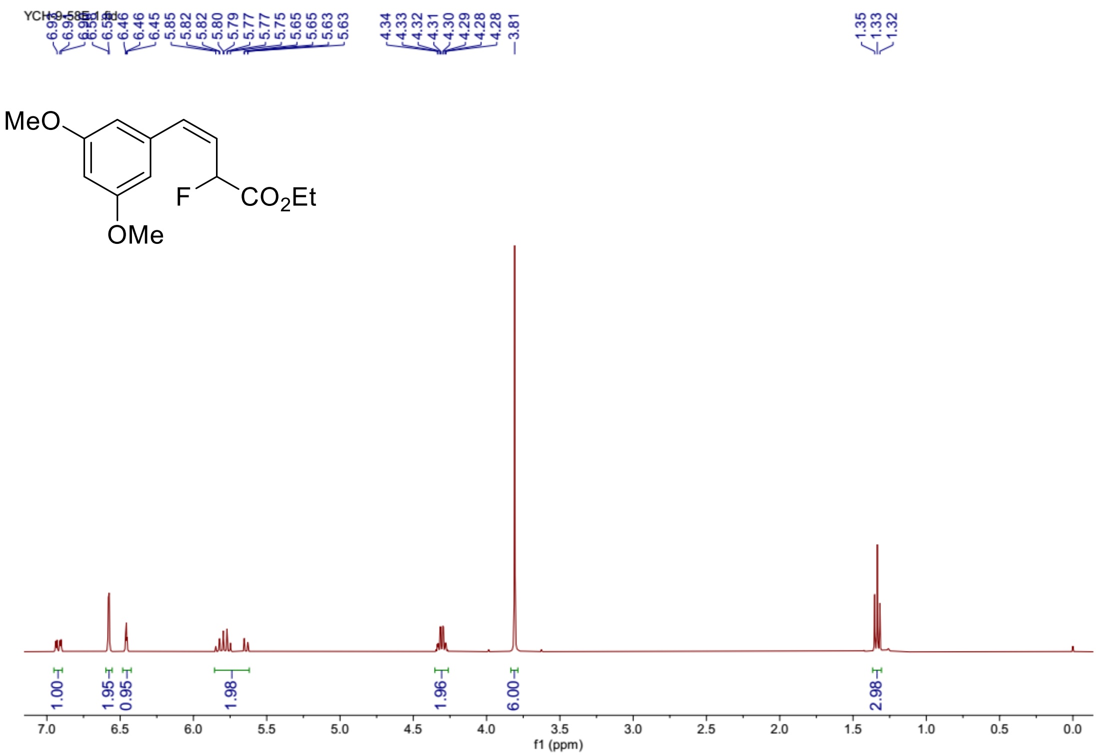
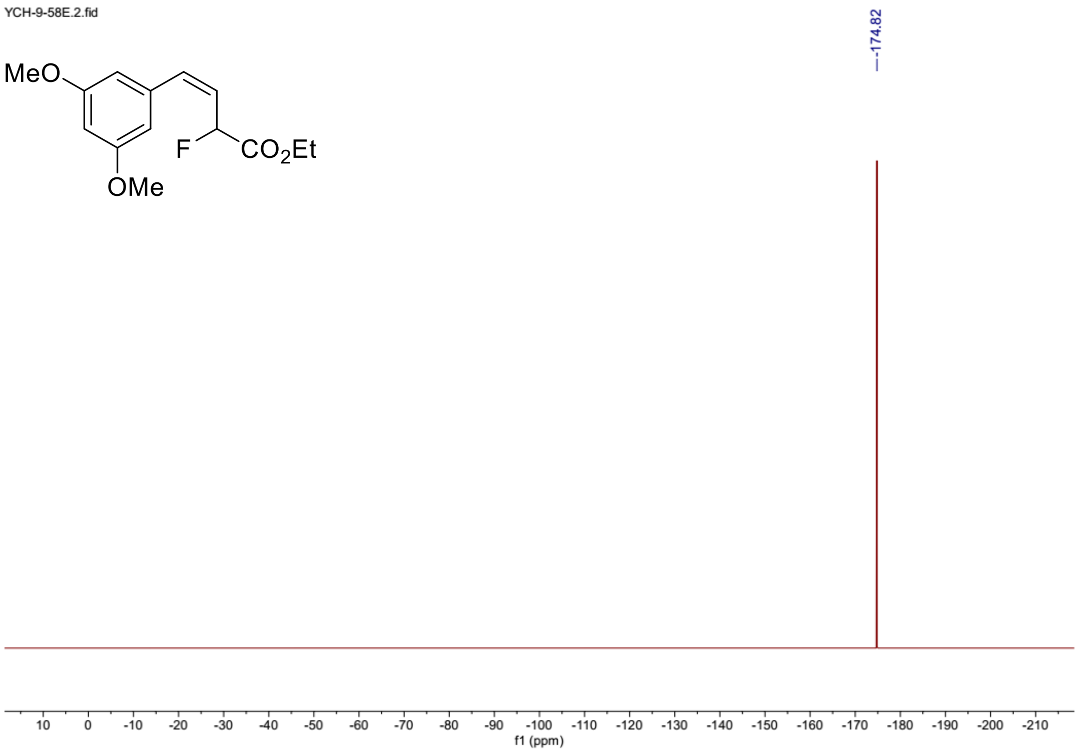


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **10**



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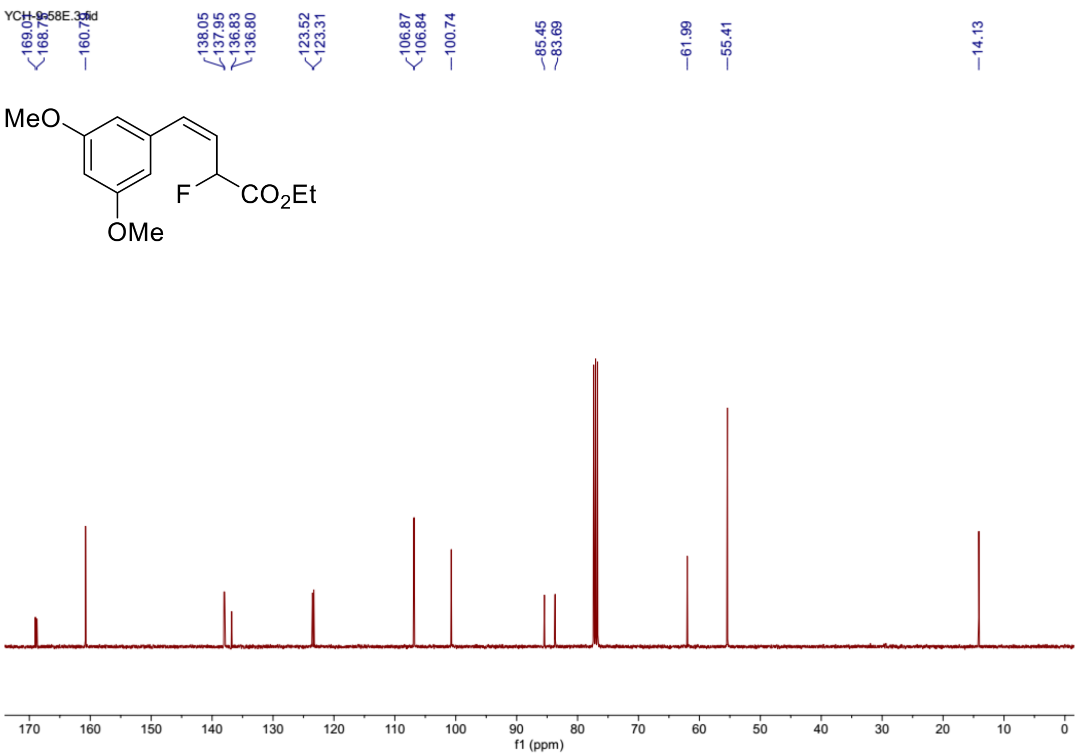
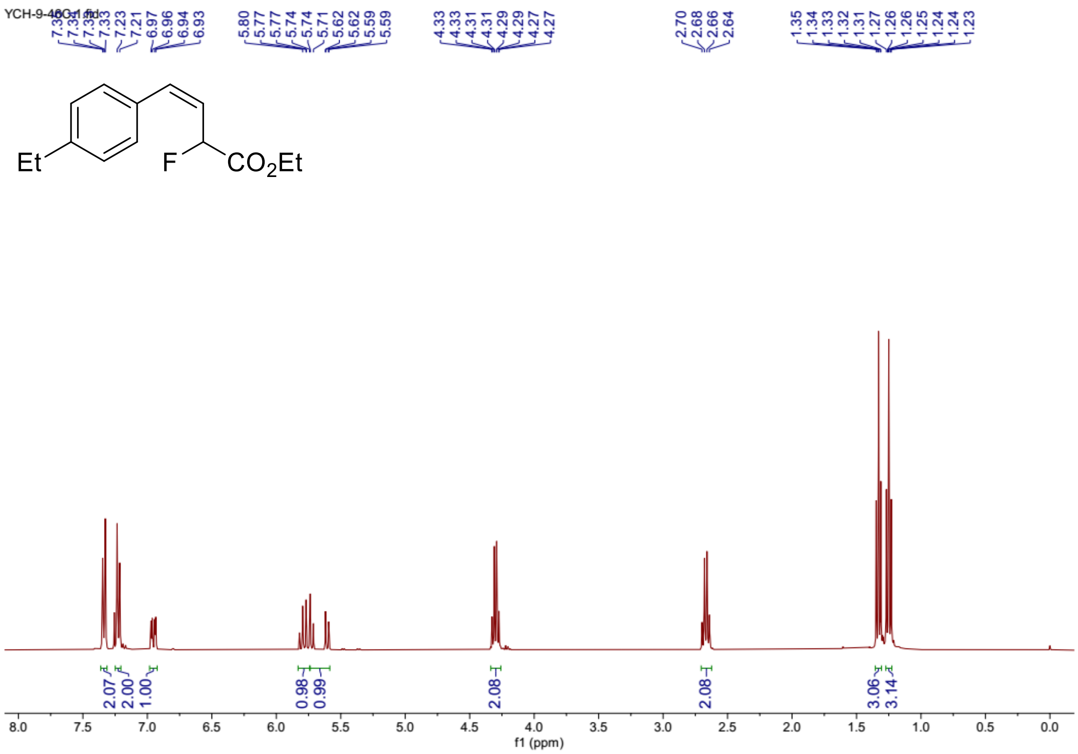
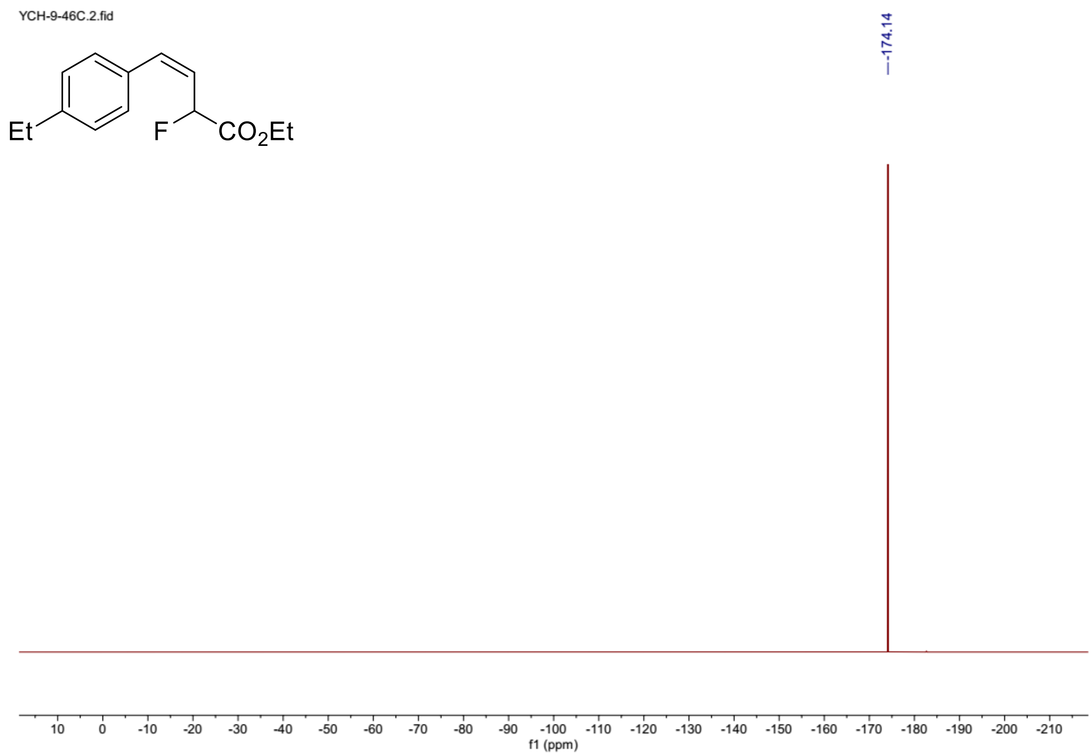


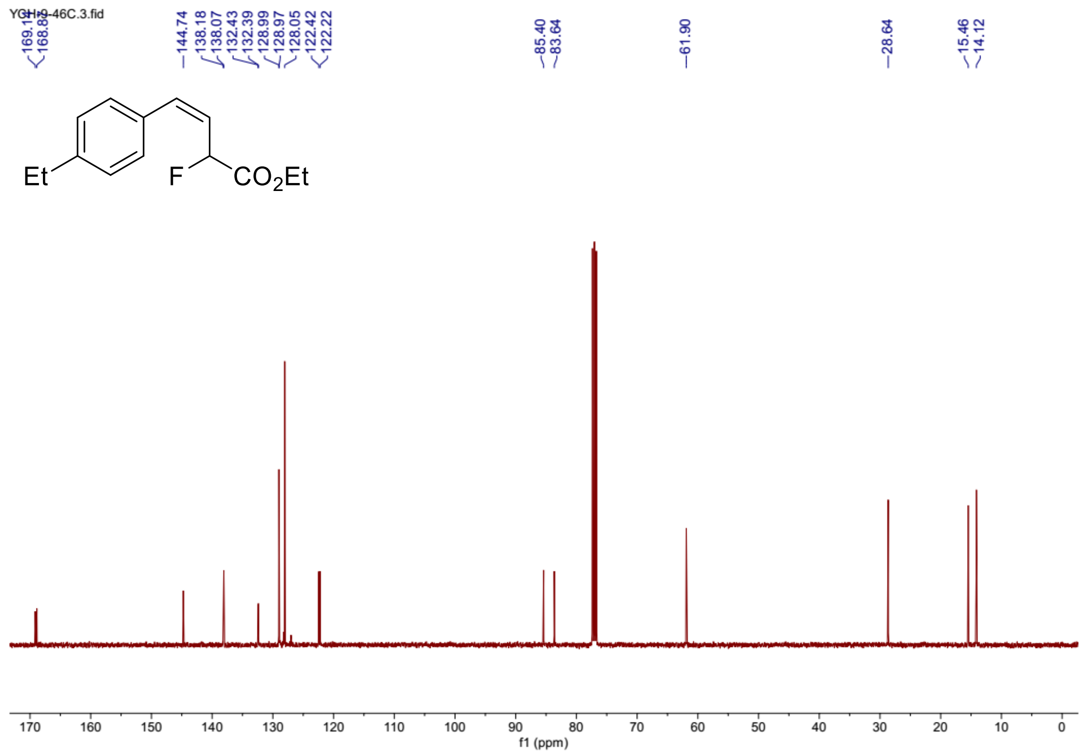
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



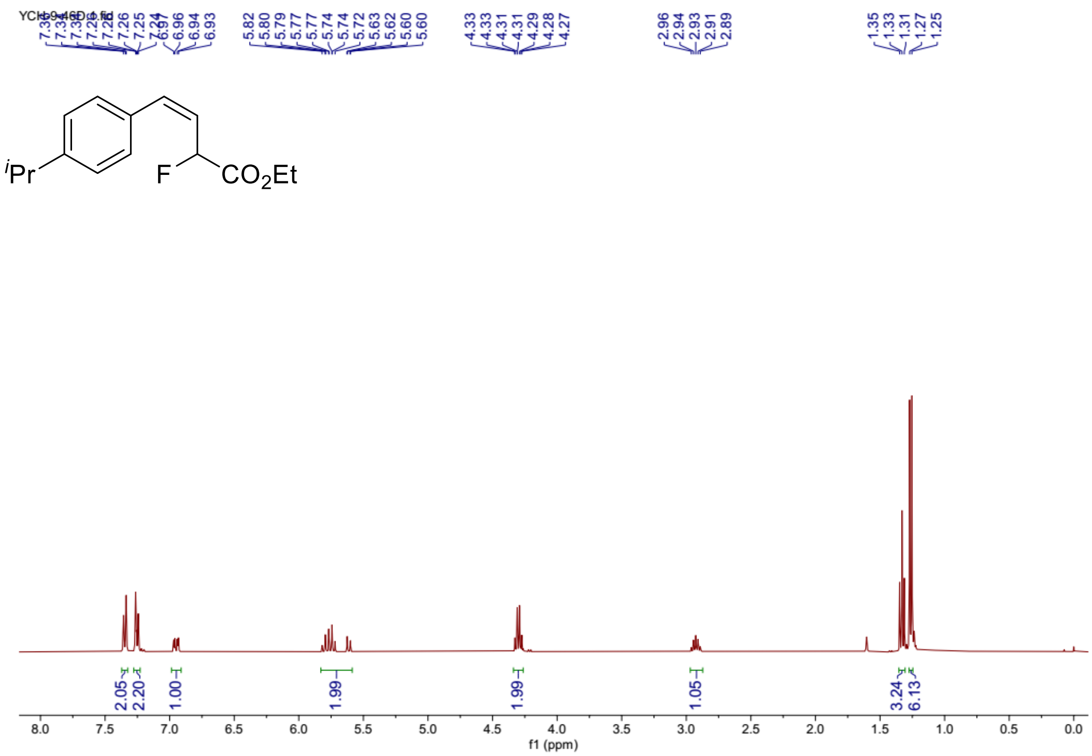
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **11**



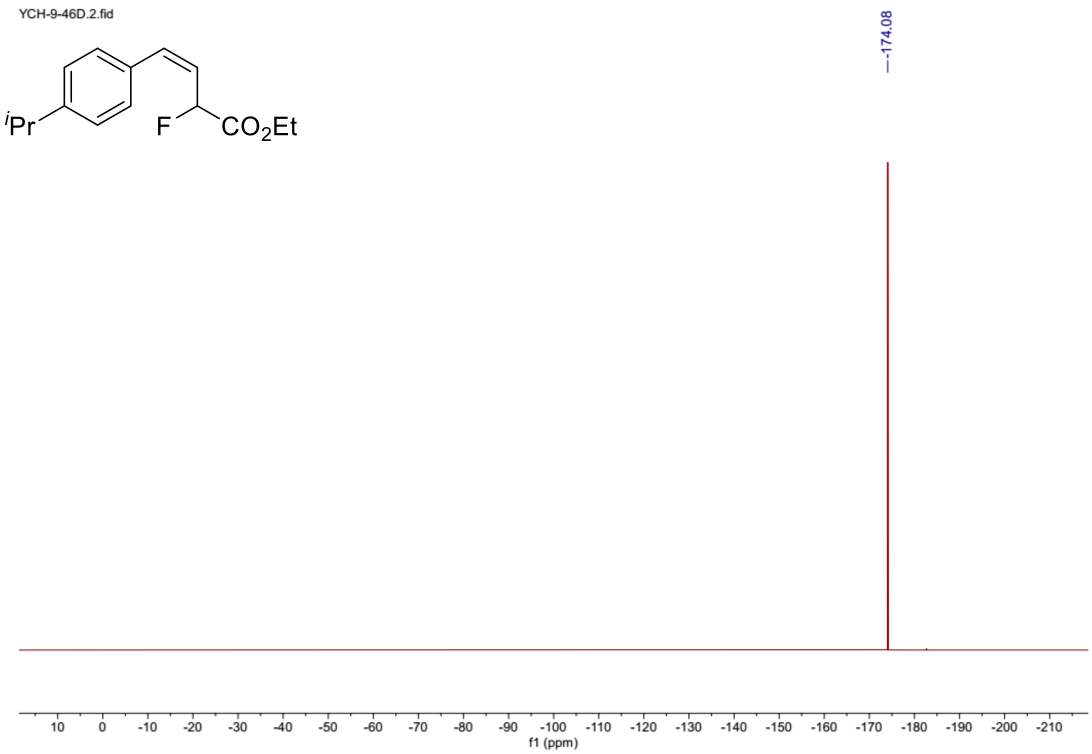
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **11**



[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **12**



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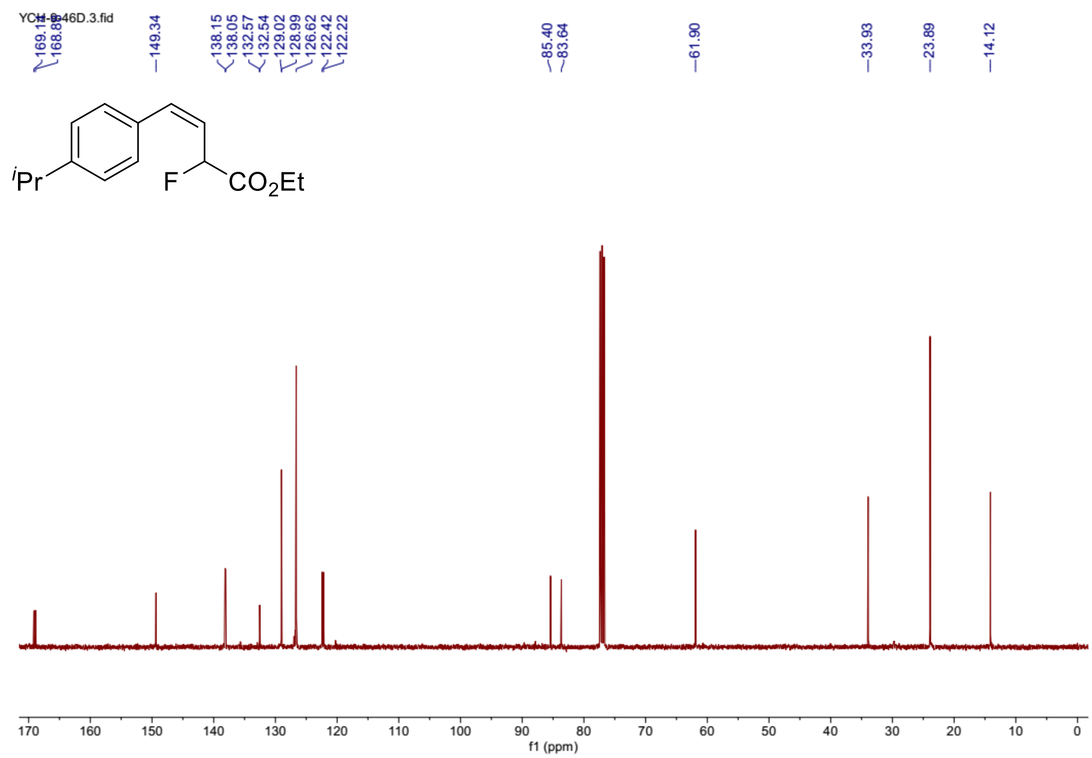

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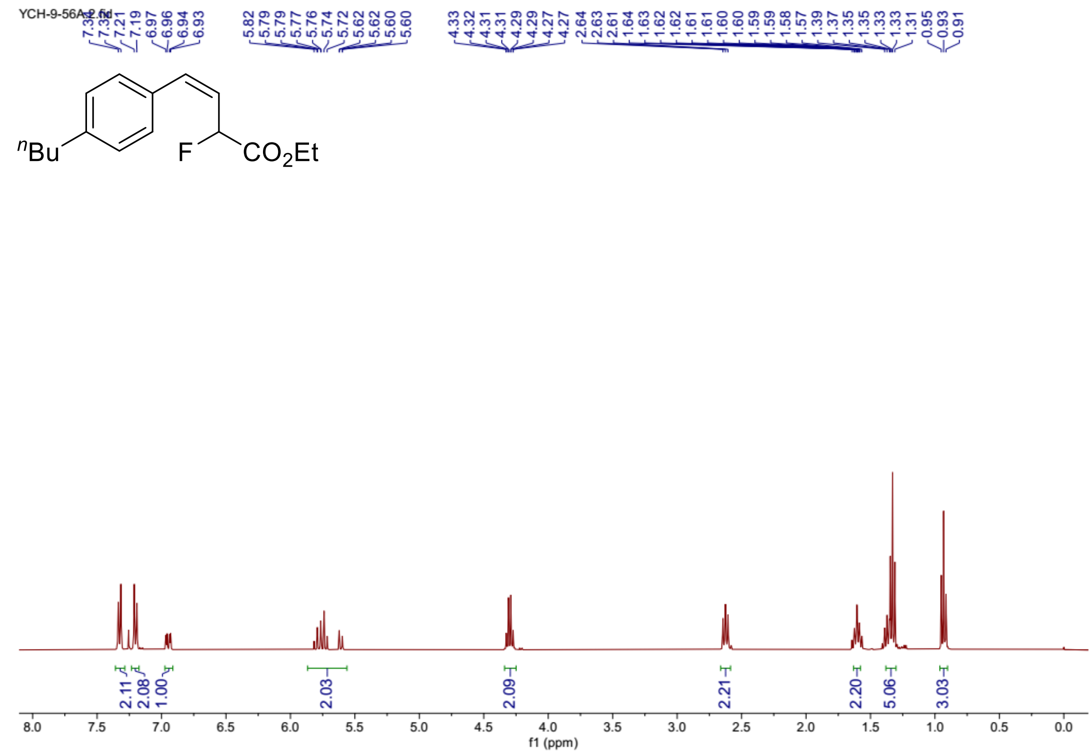

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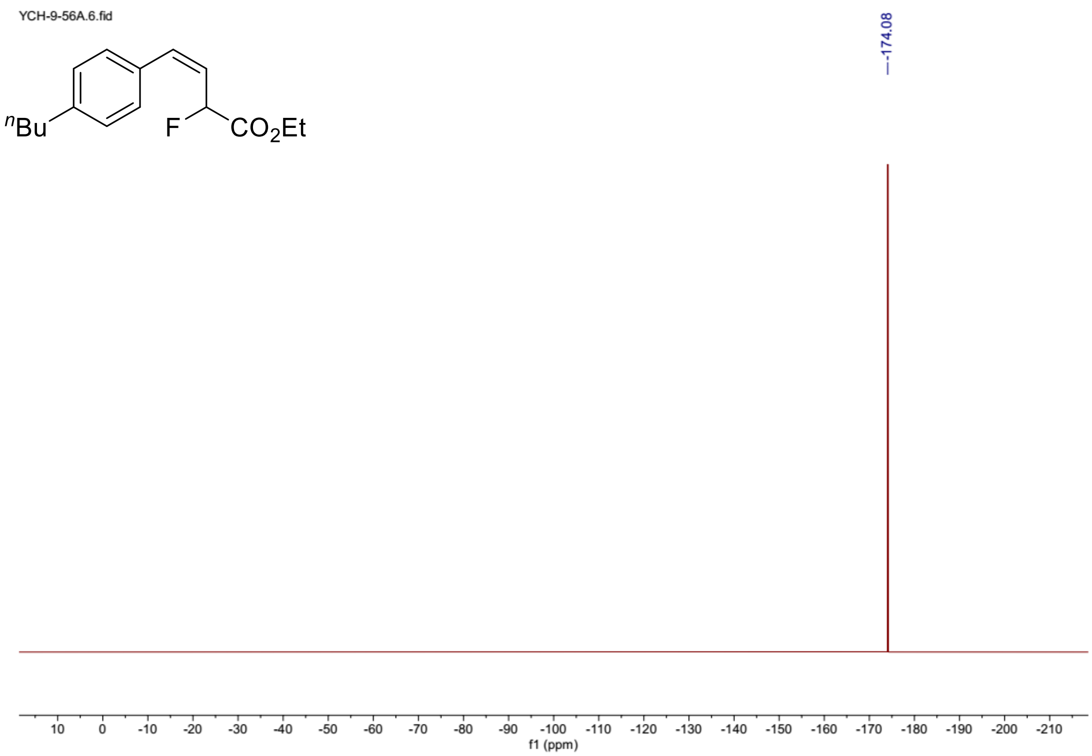

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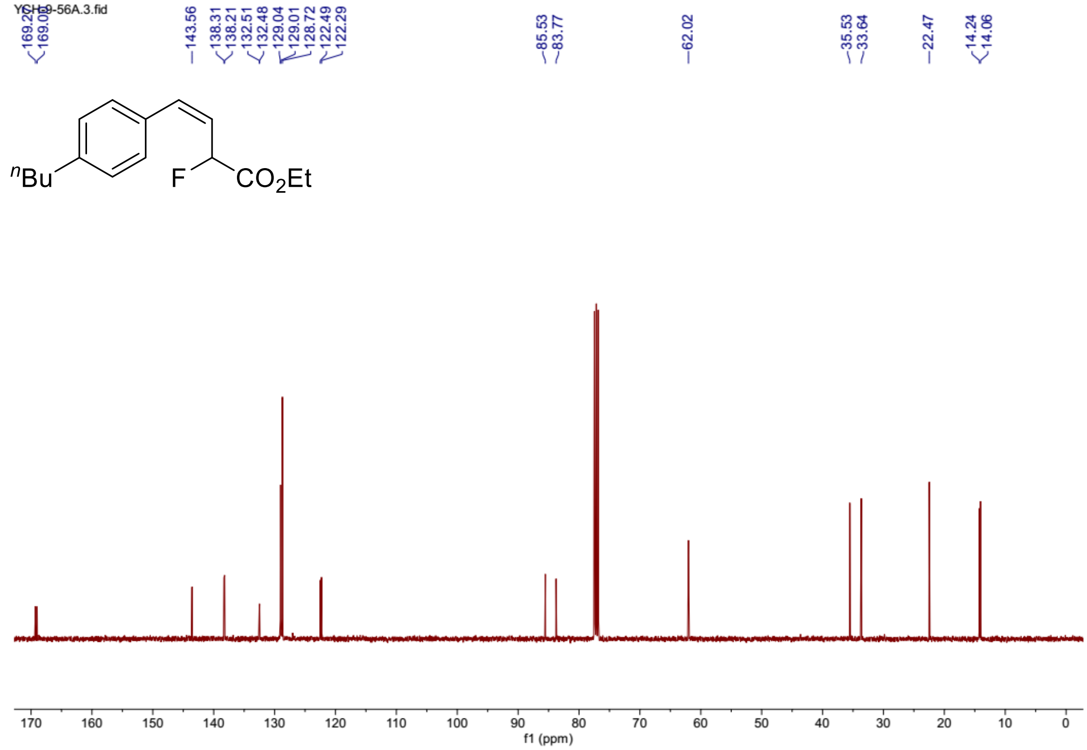

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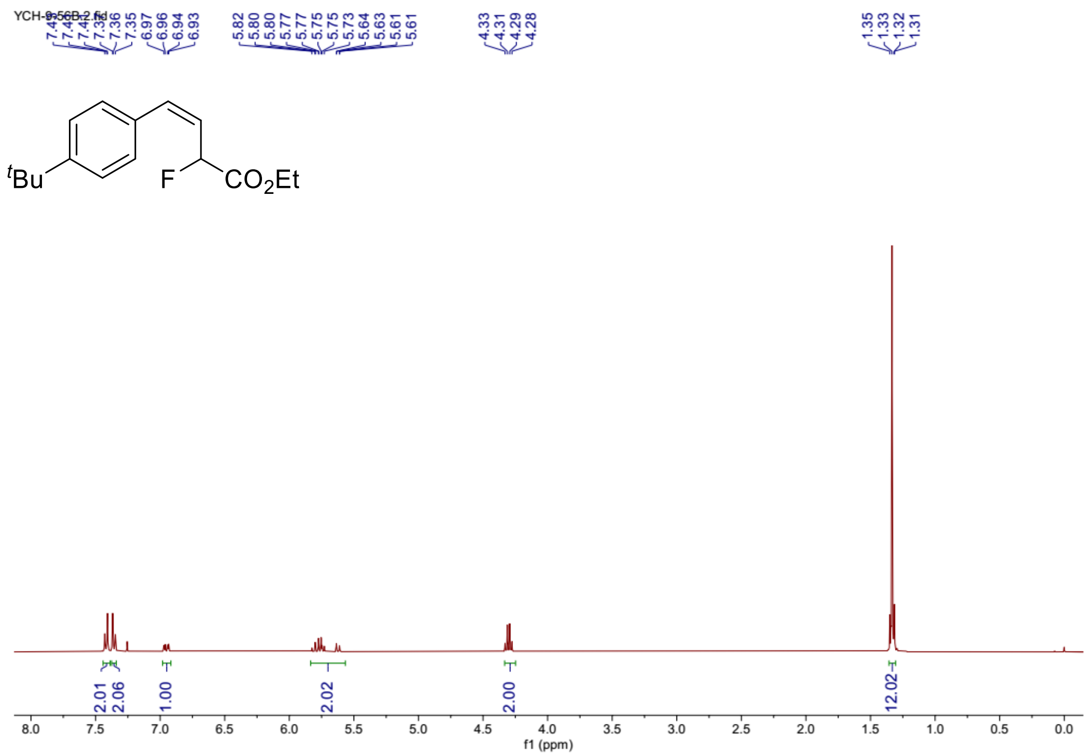

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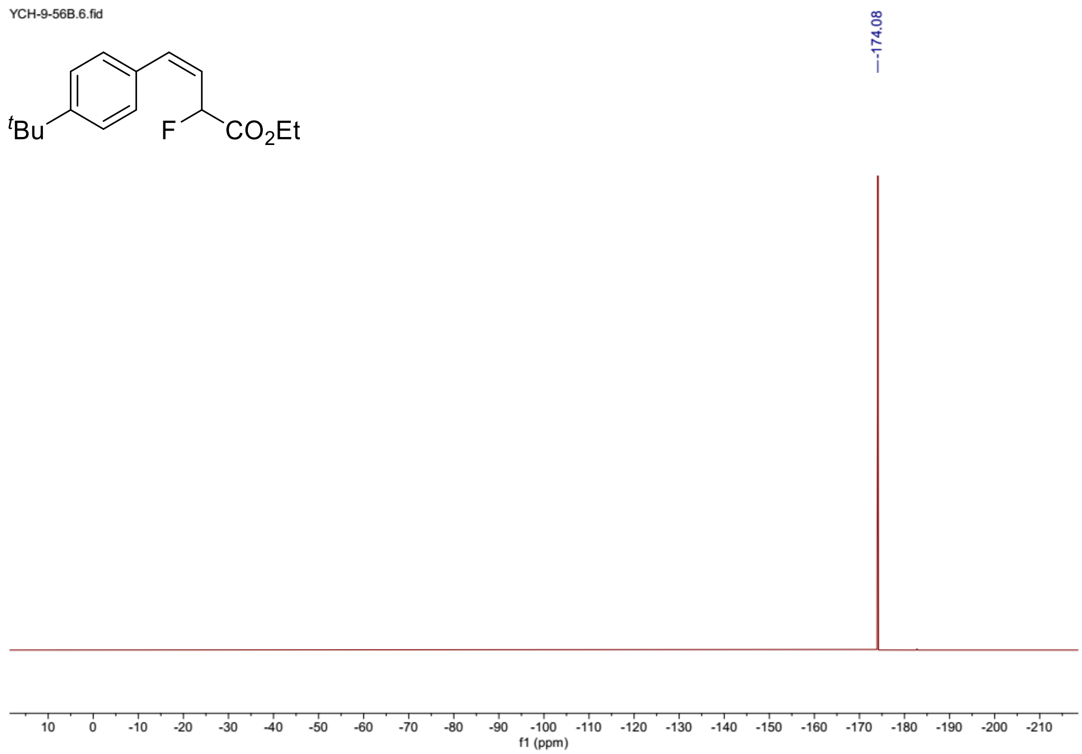

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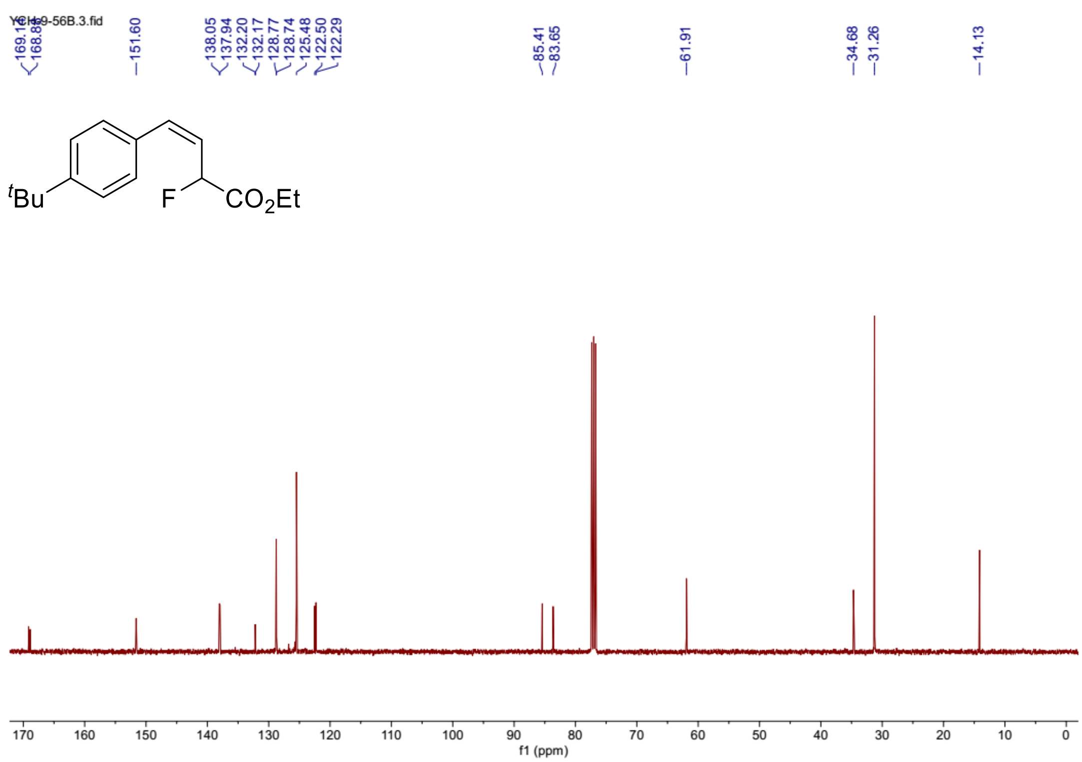
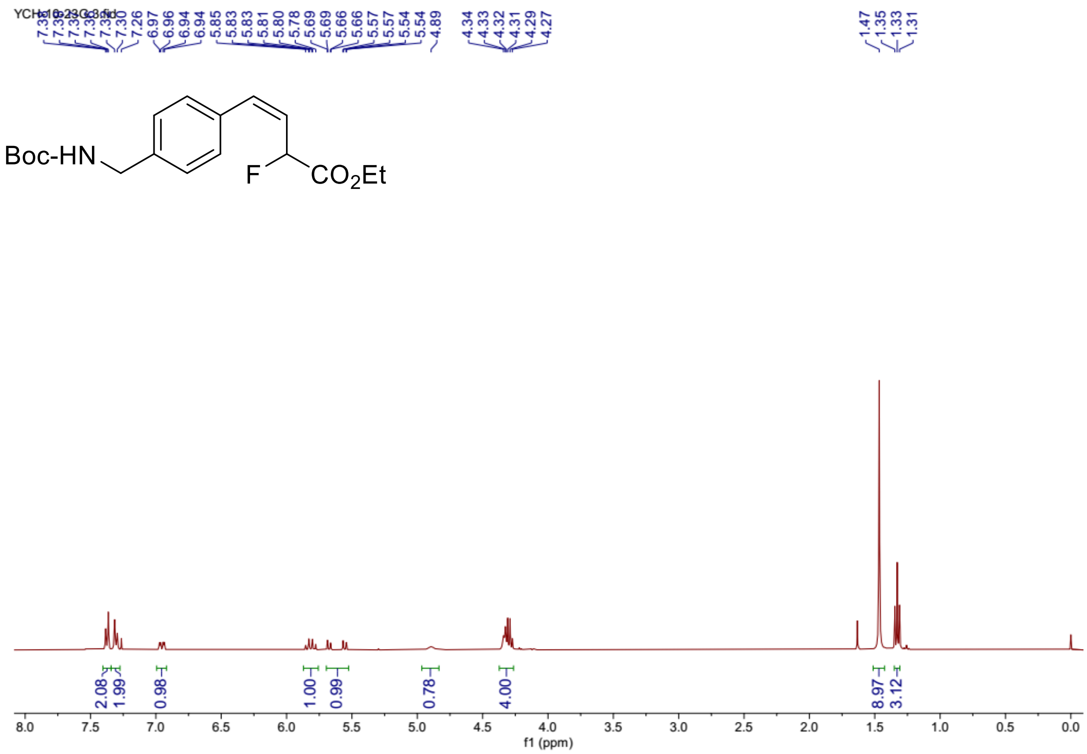
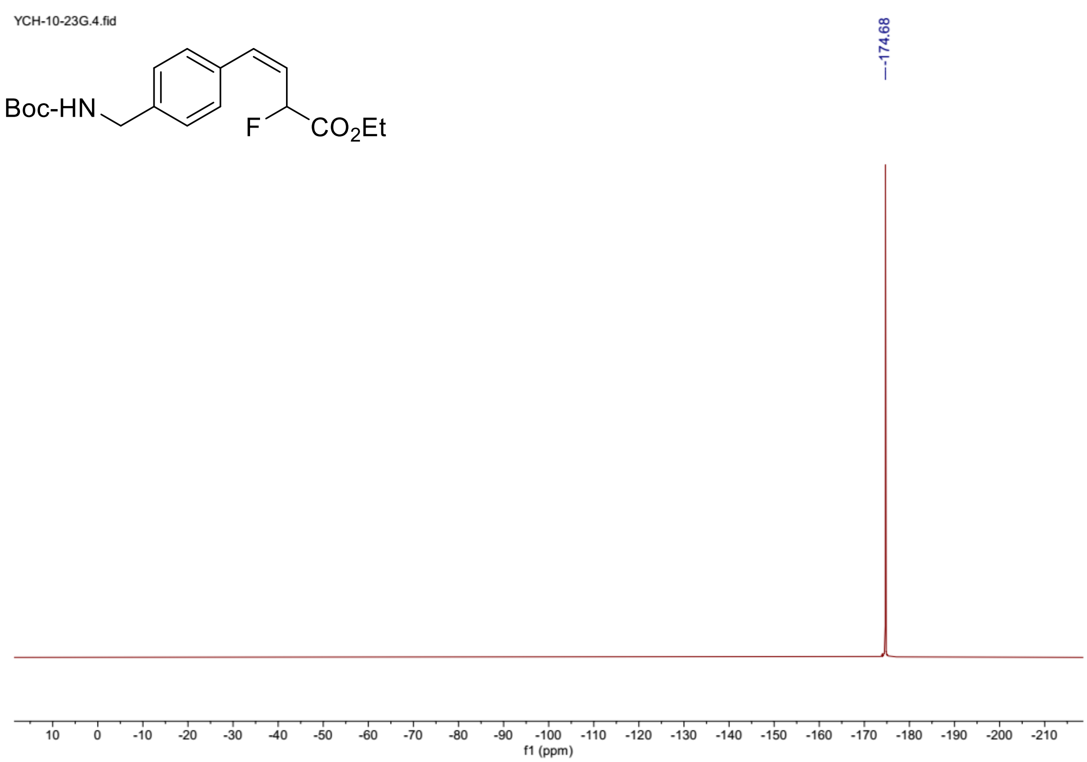


[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**



[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **15**



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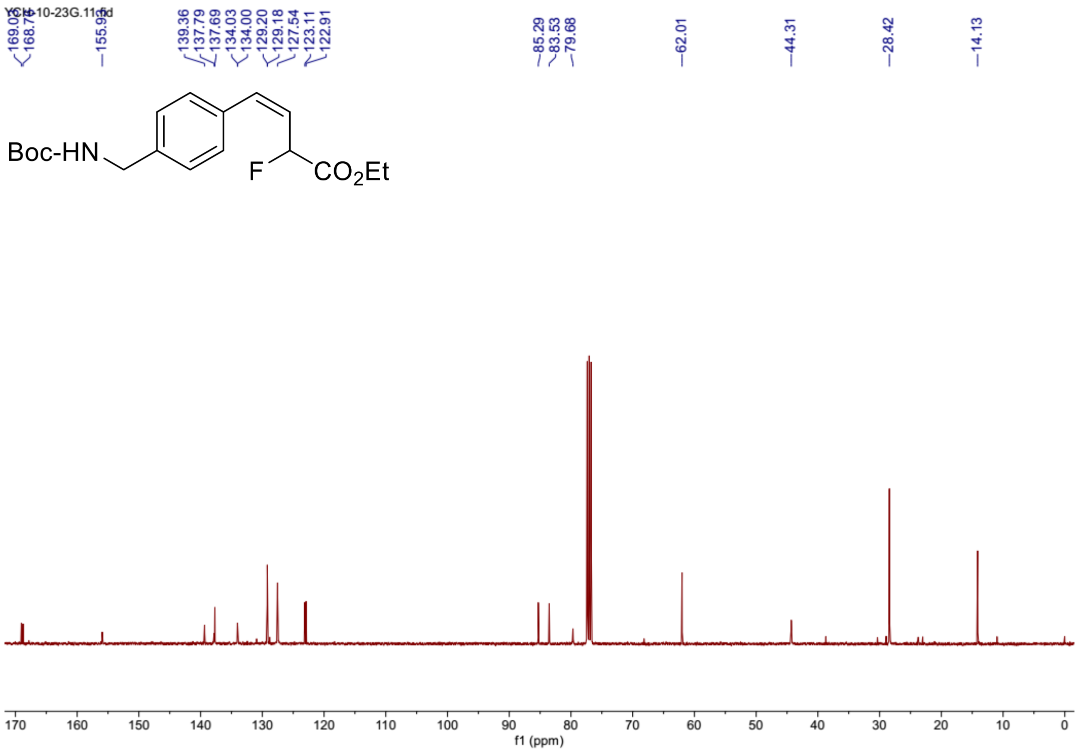

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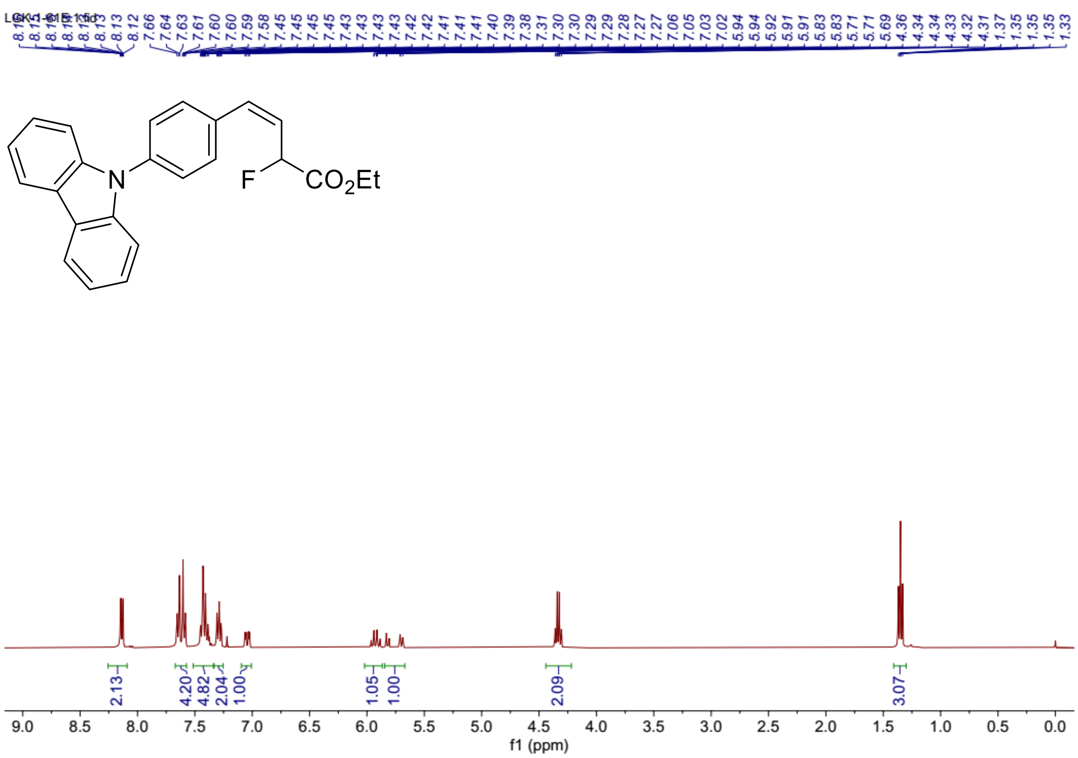

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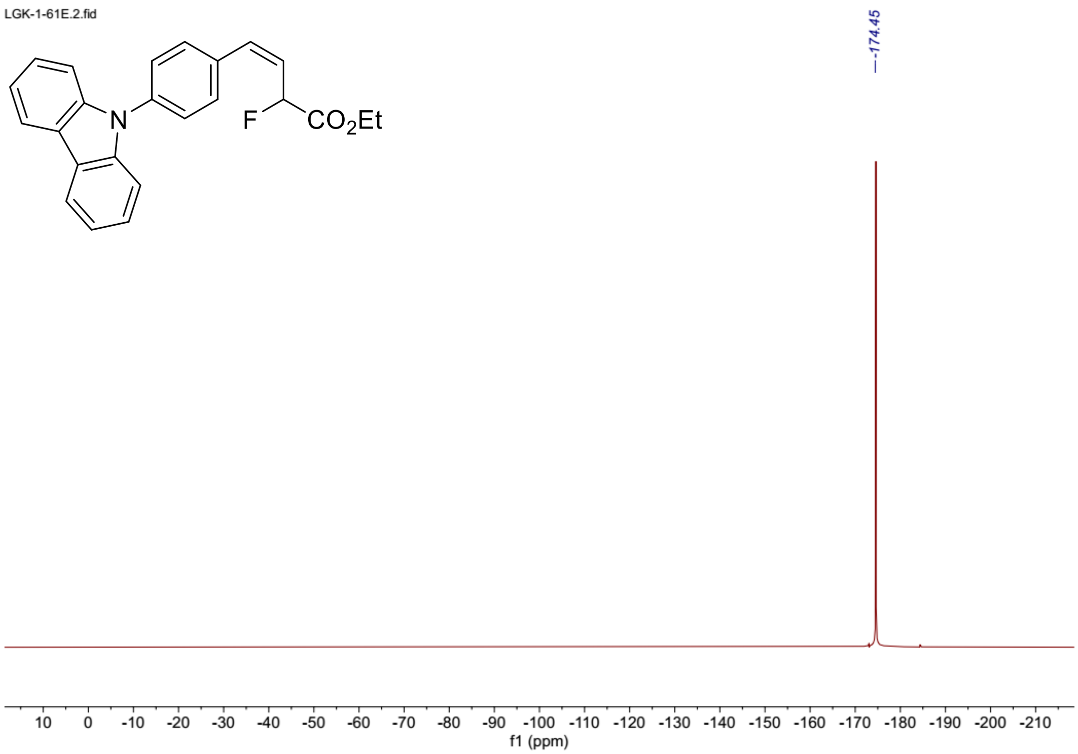

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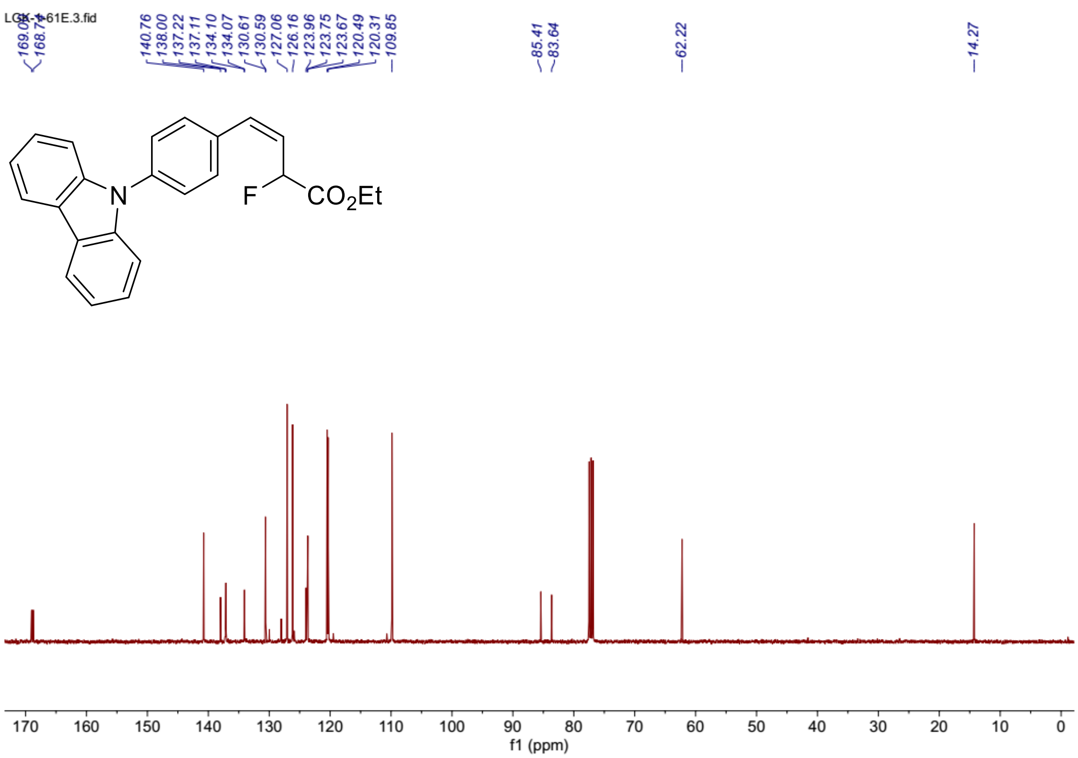

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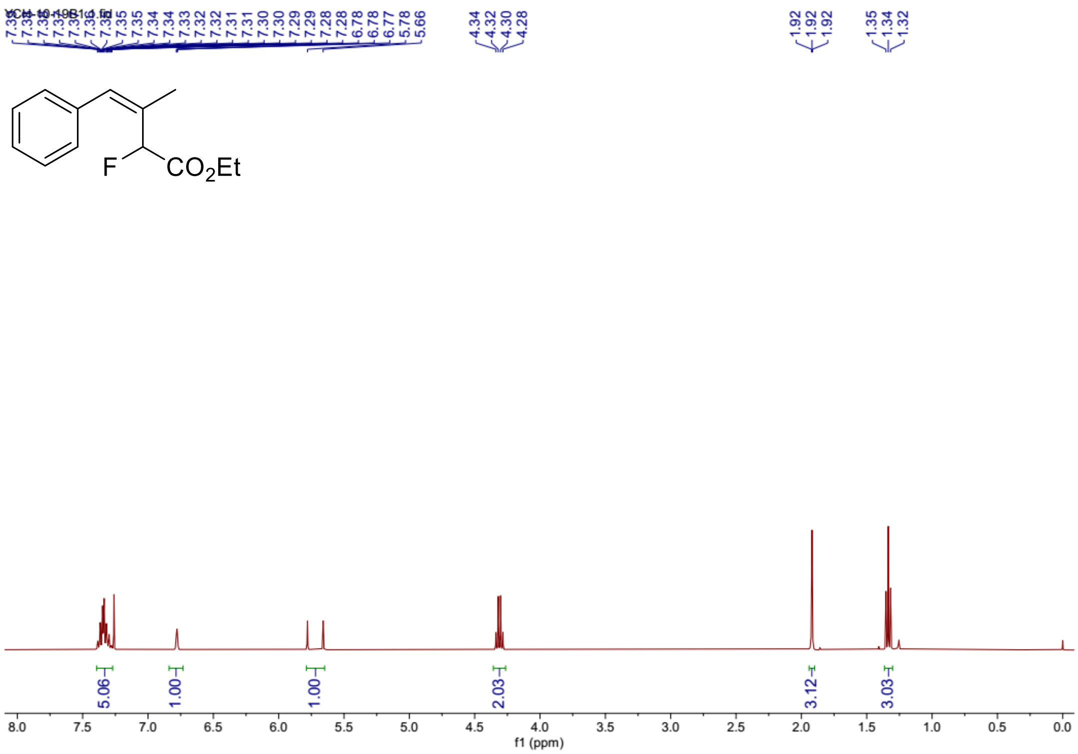
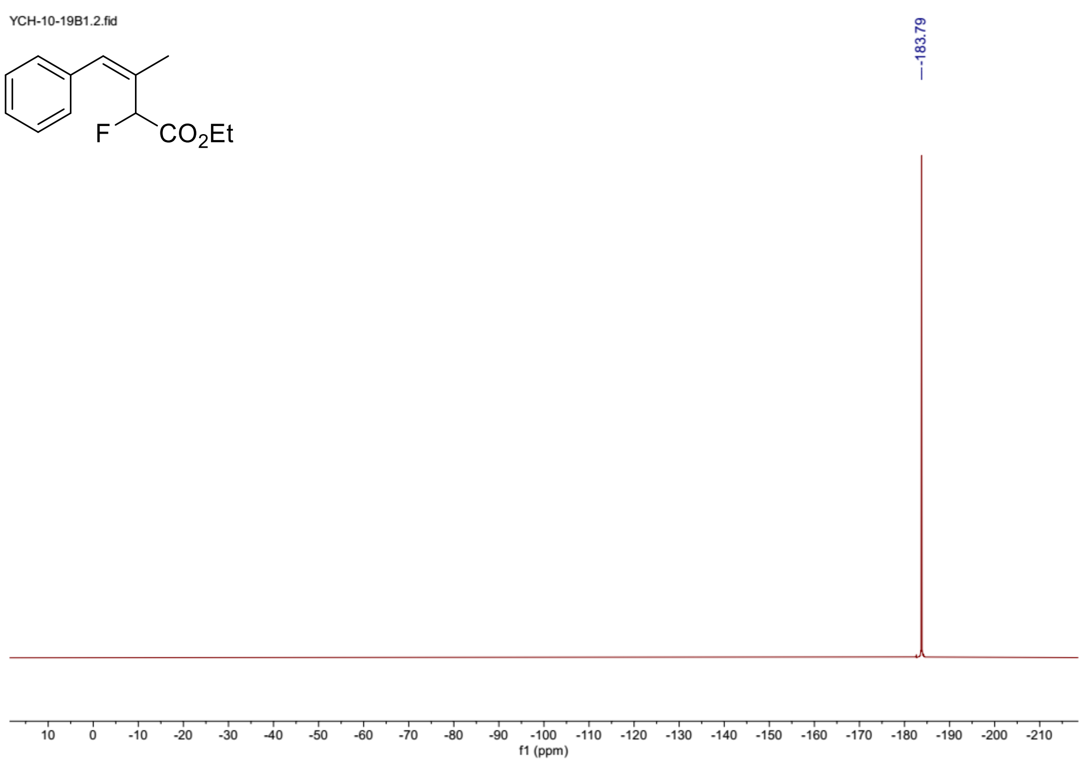


[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **17**



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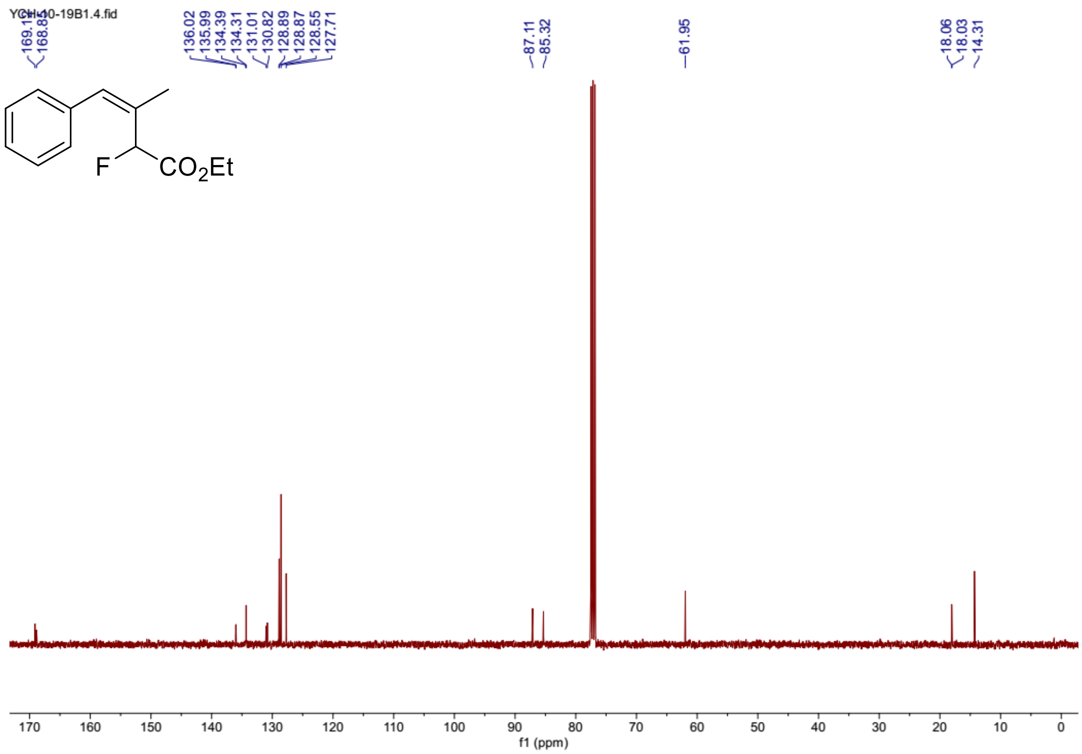

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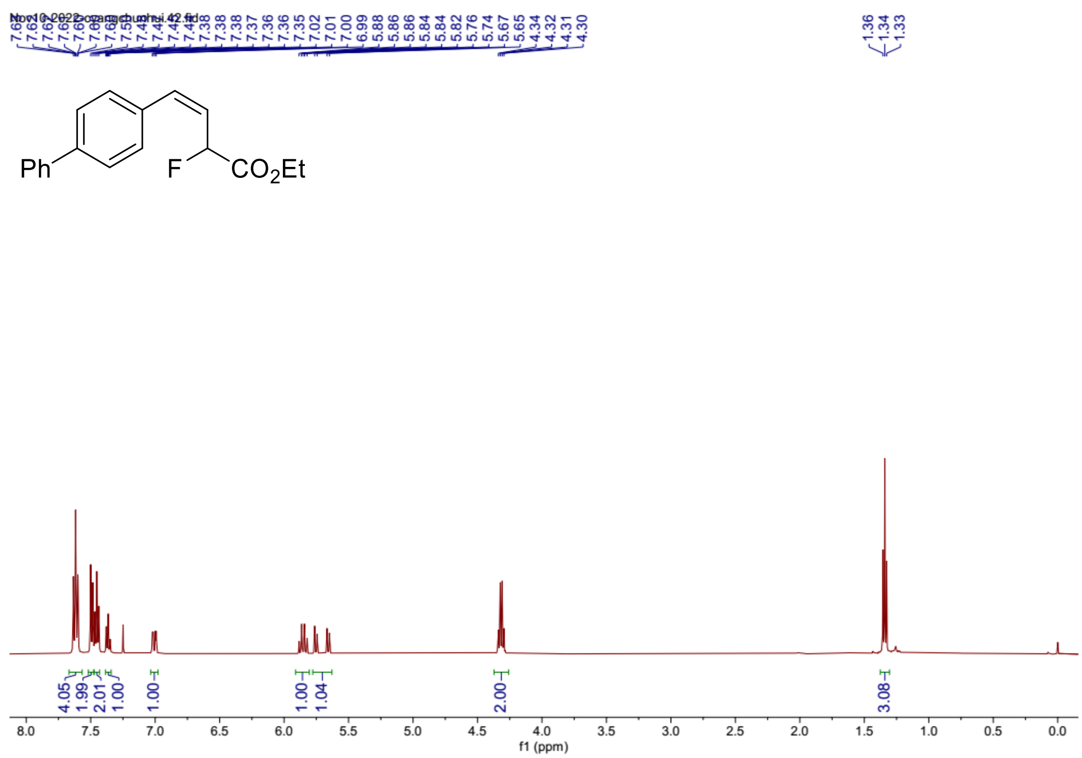
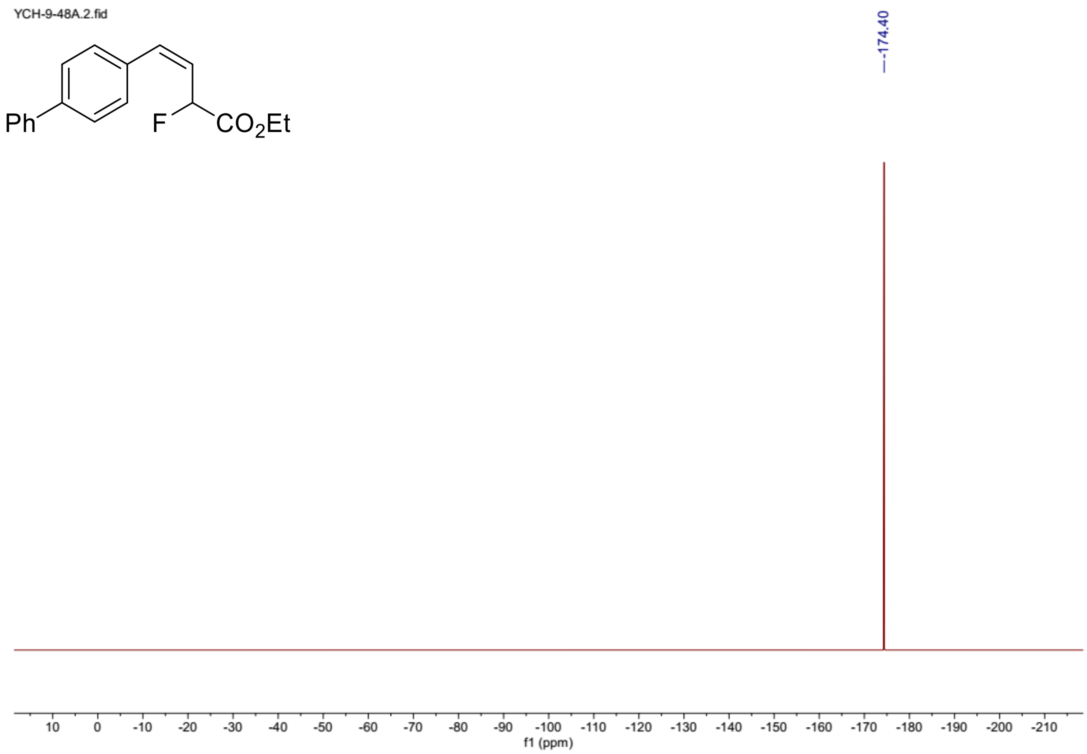
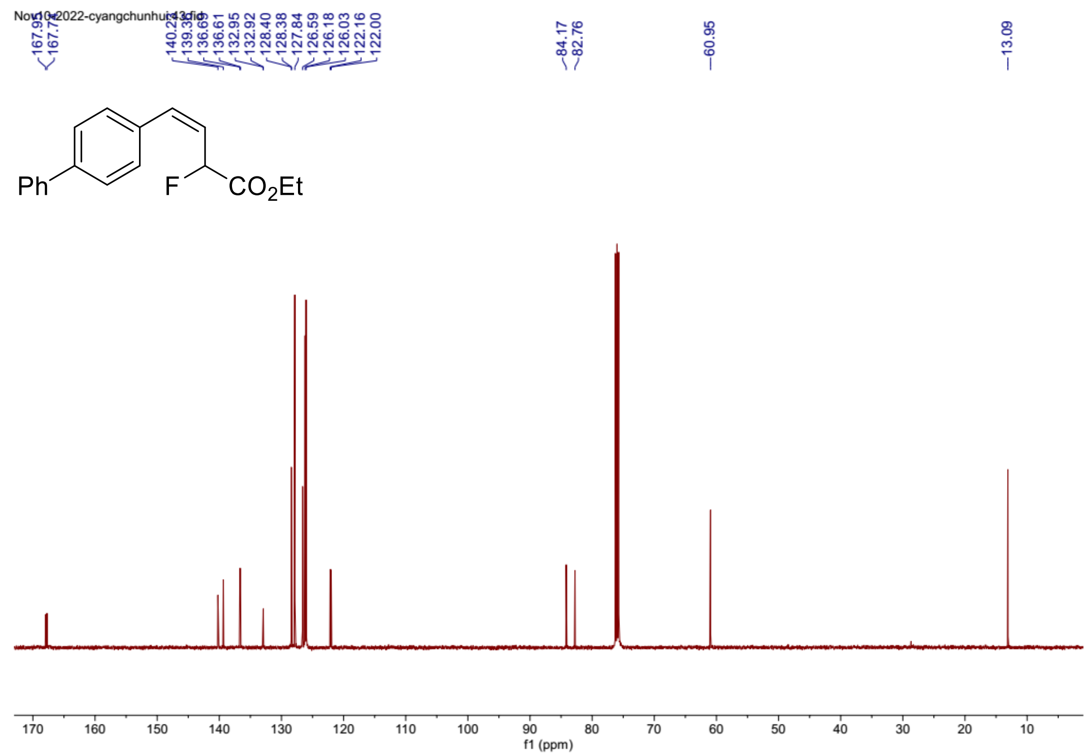


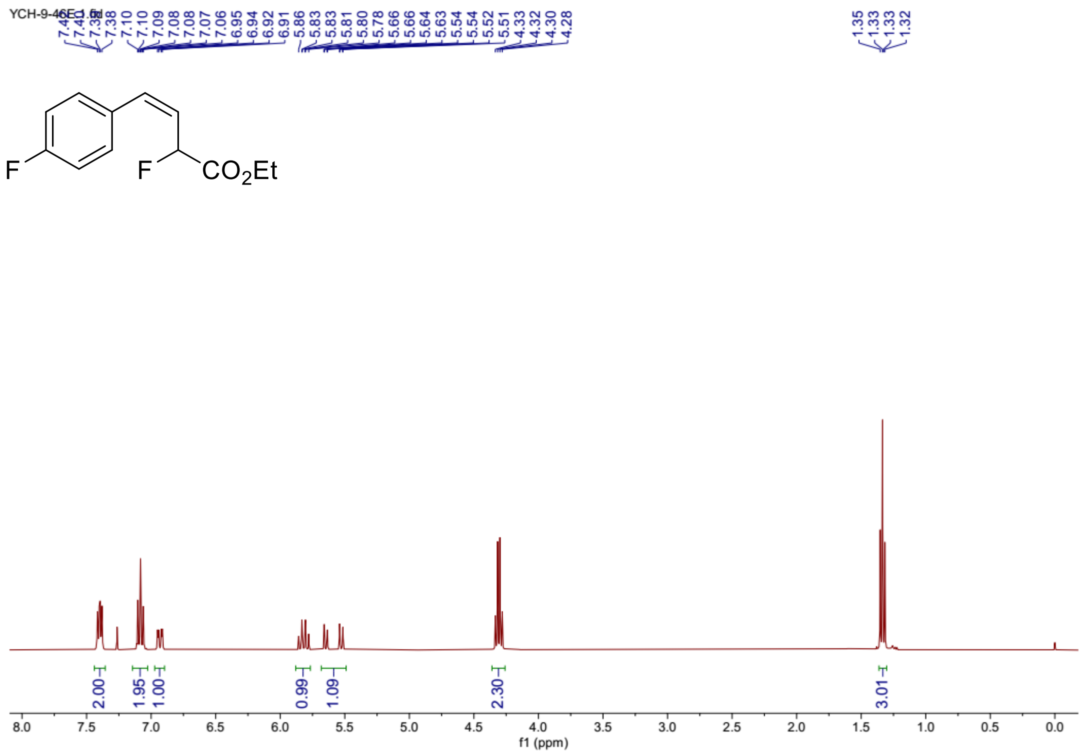
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **18**



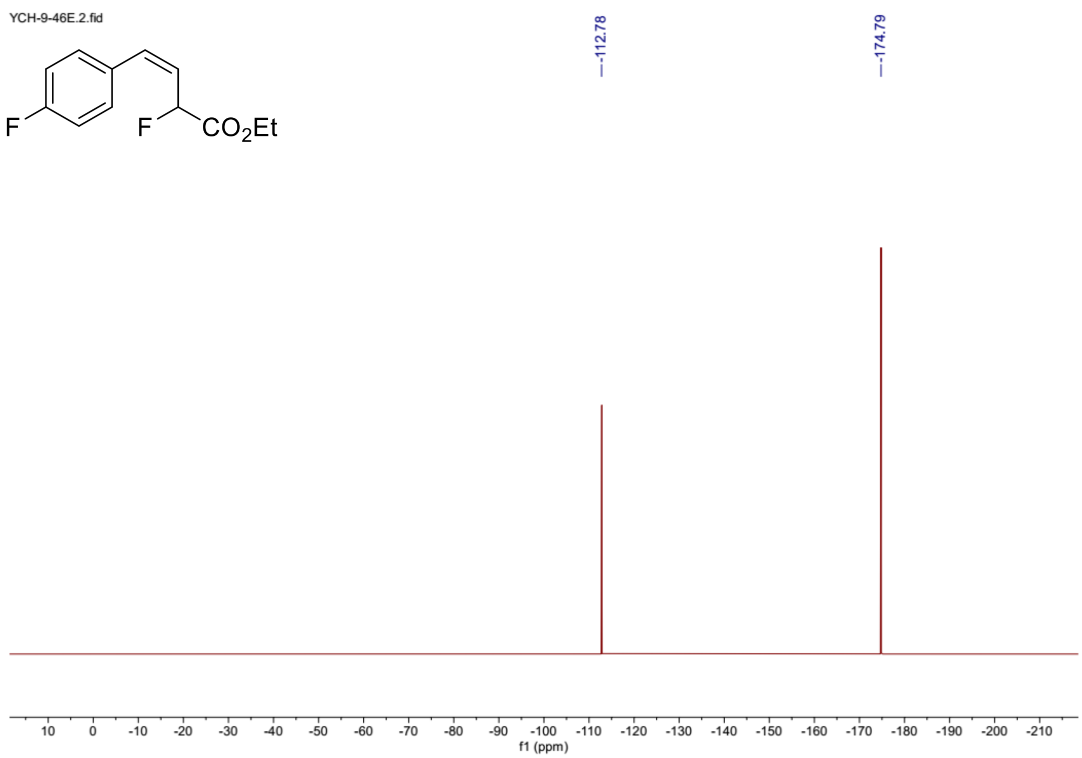
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **18**



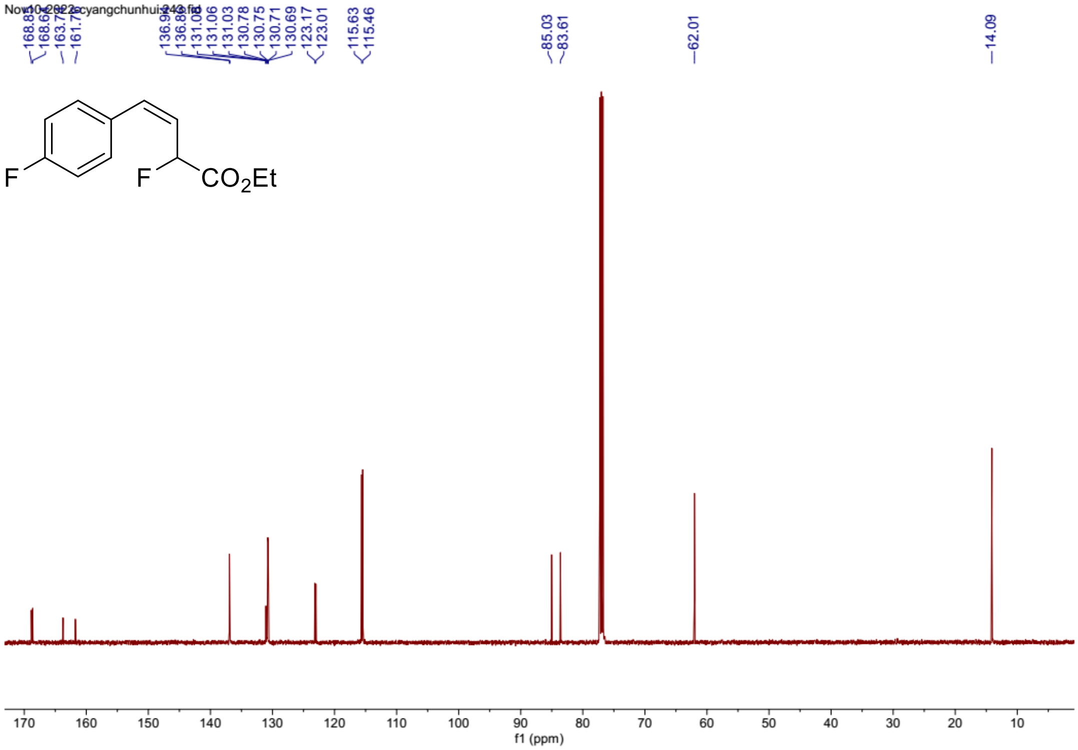
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**



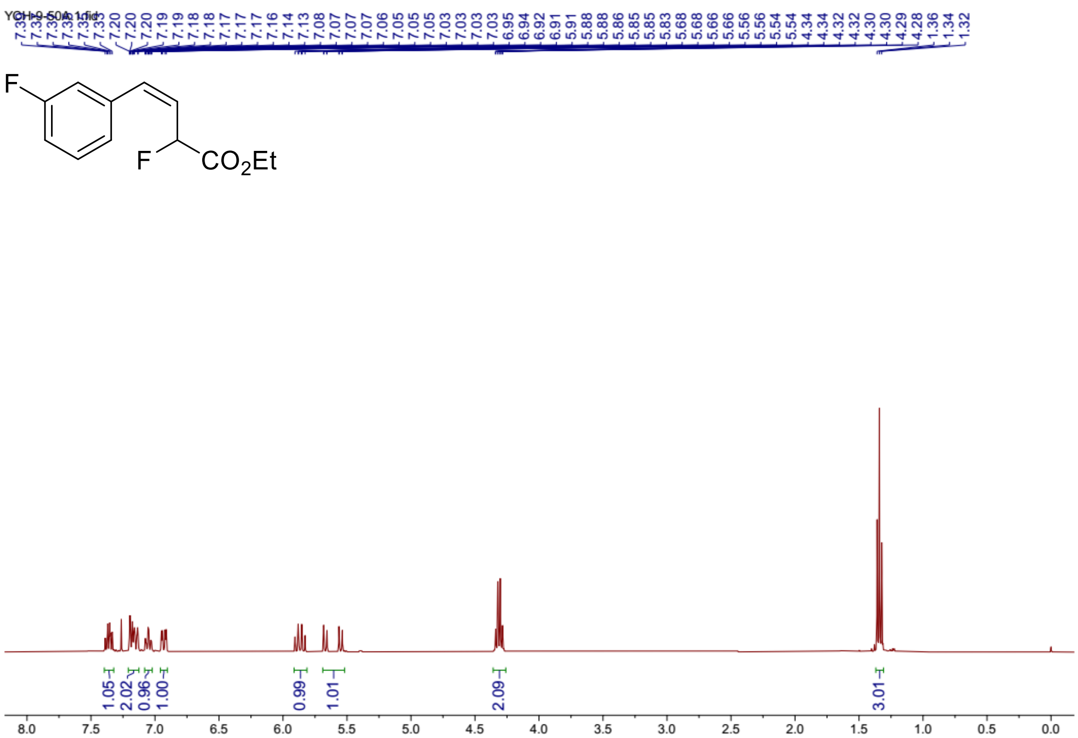
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **19**



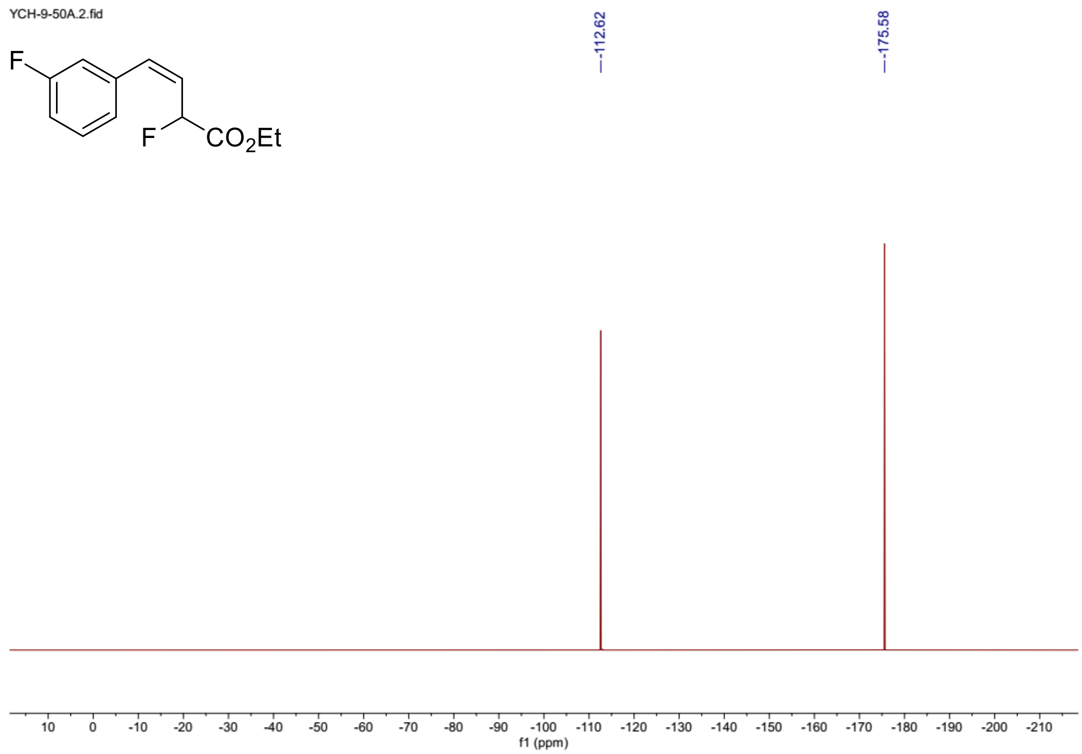
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **19**



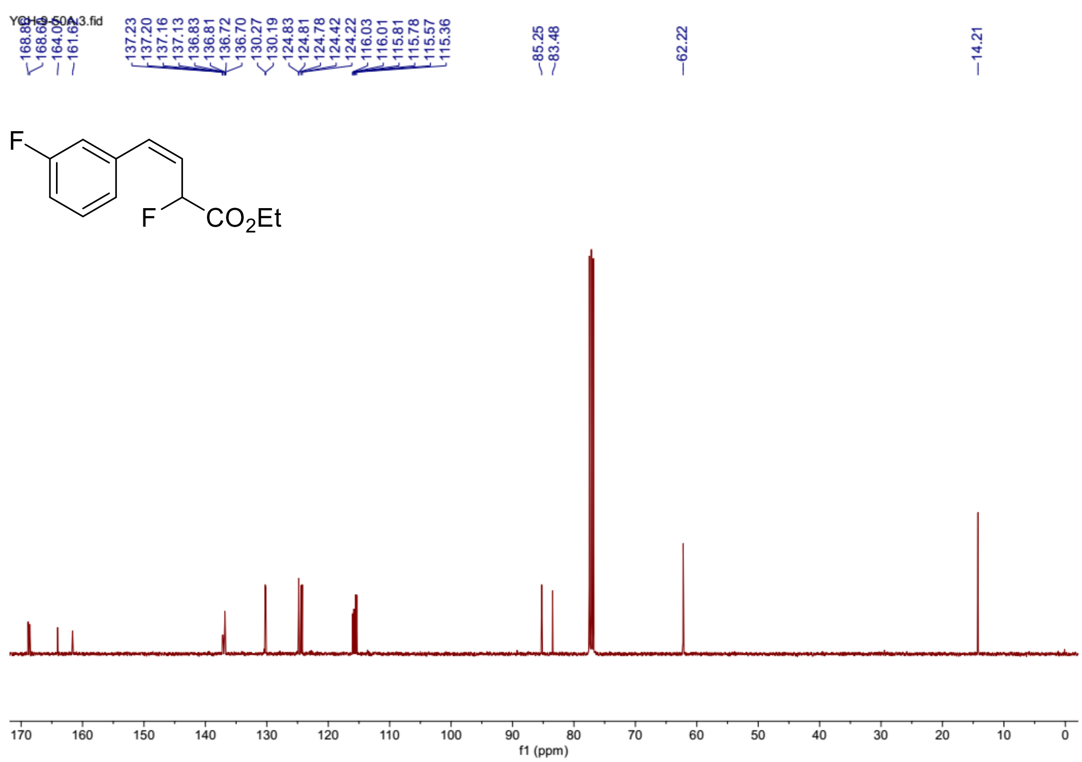
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**



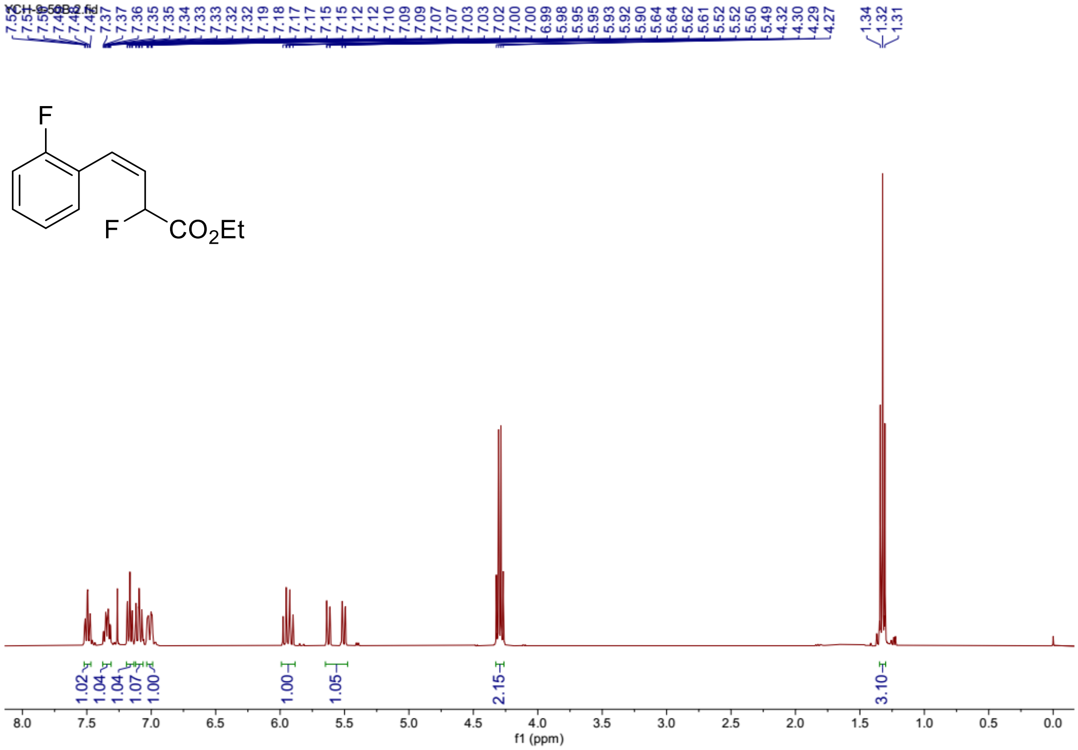
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **20**



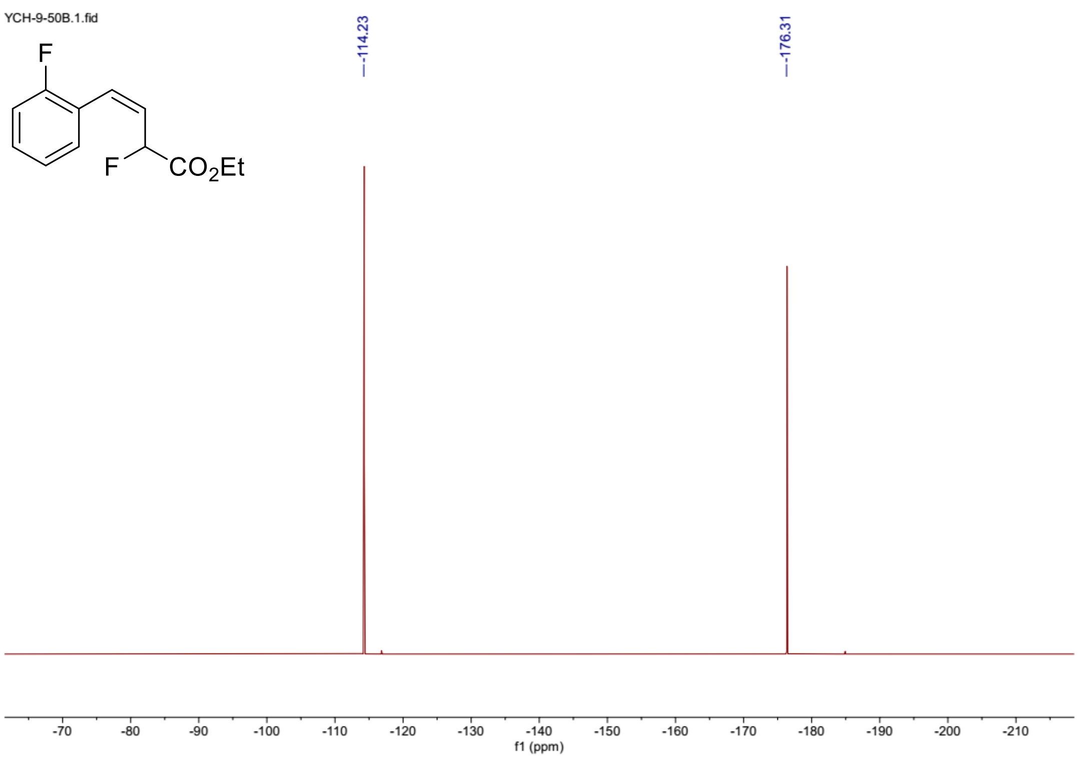
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **20**



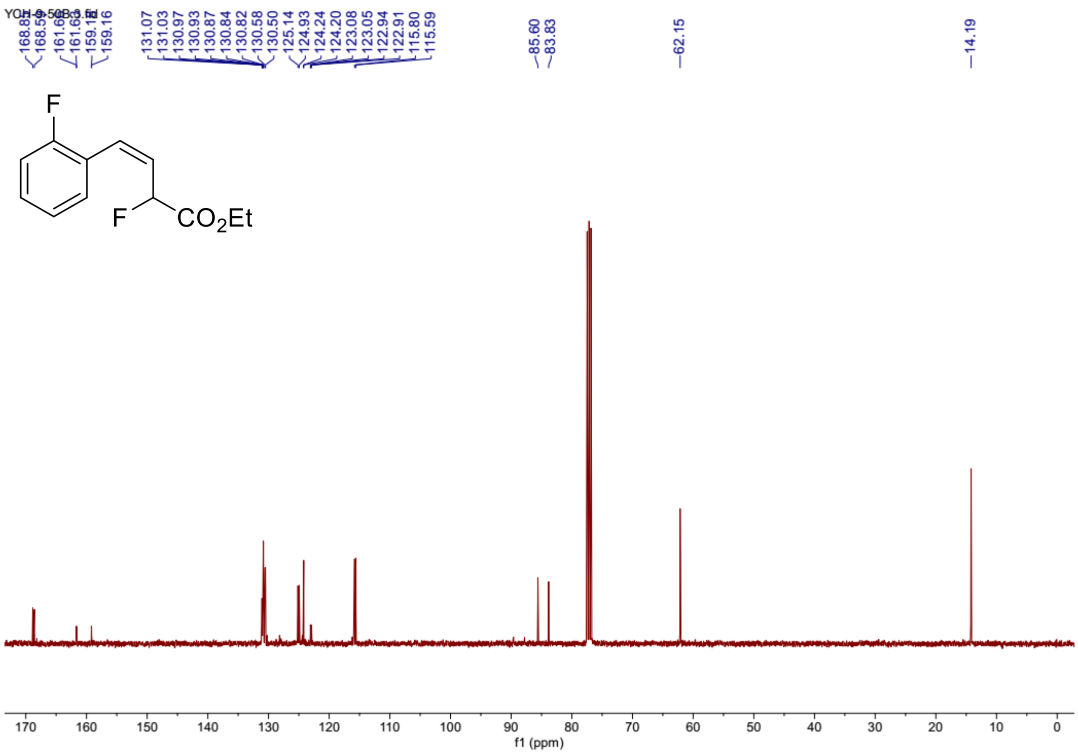
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**



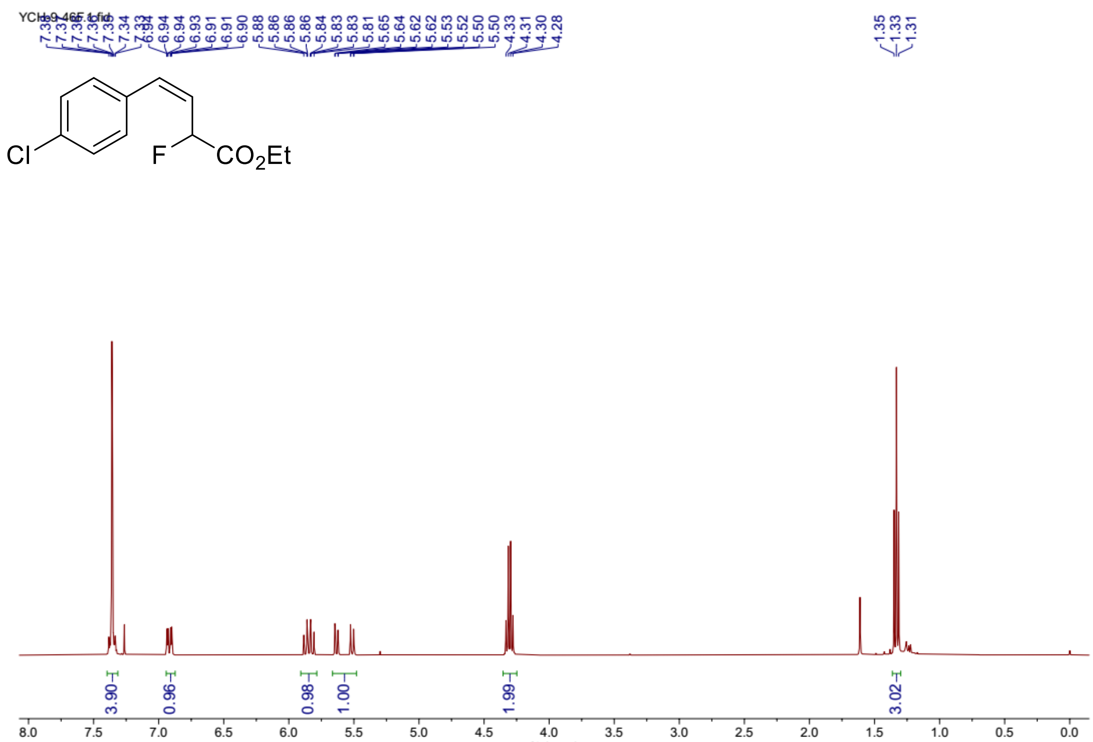
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **21**



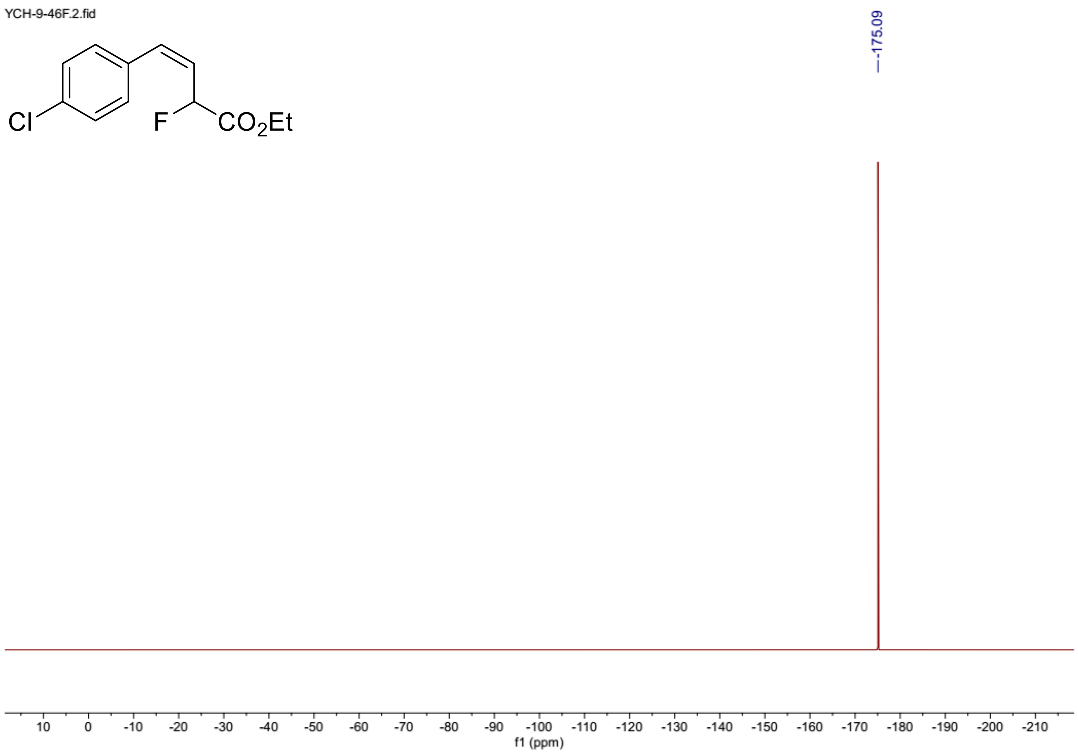
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **21**



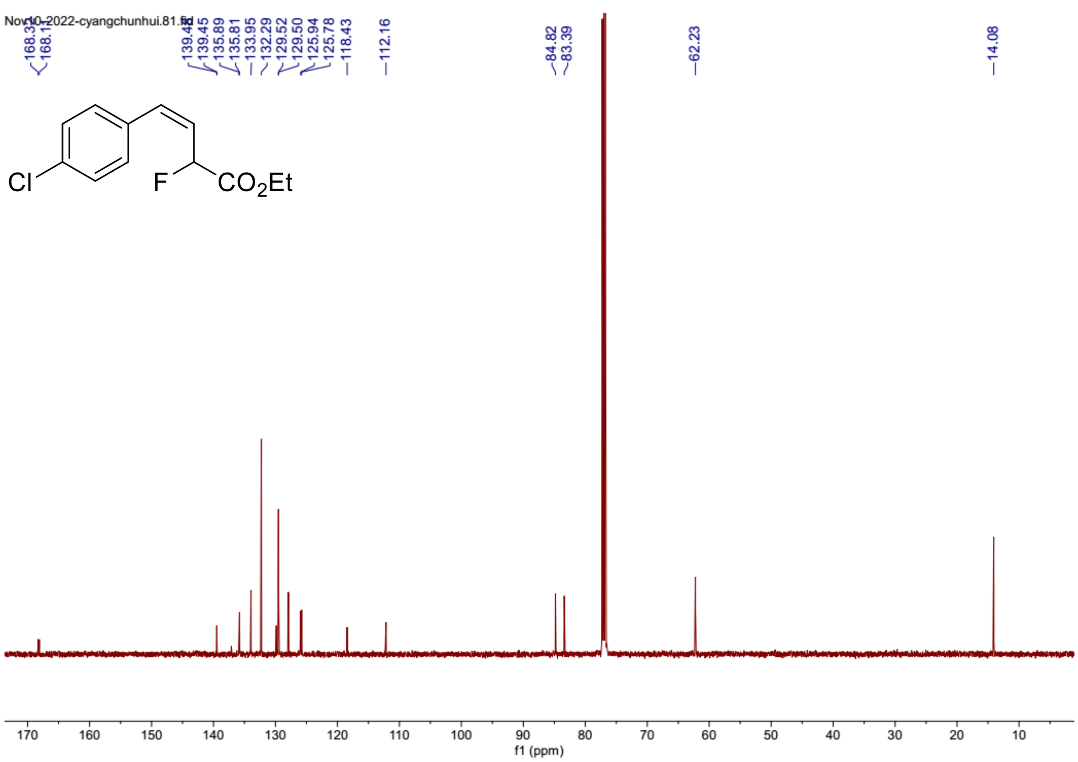
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**



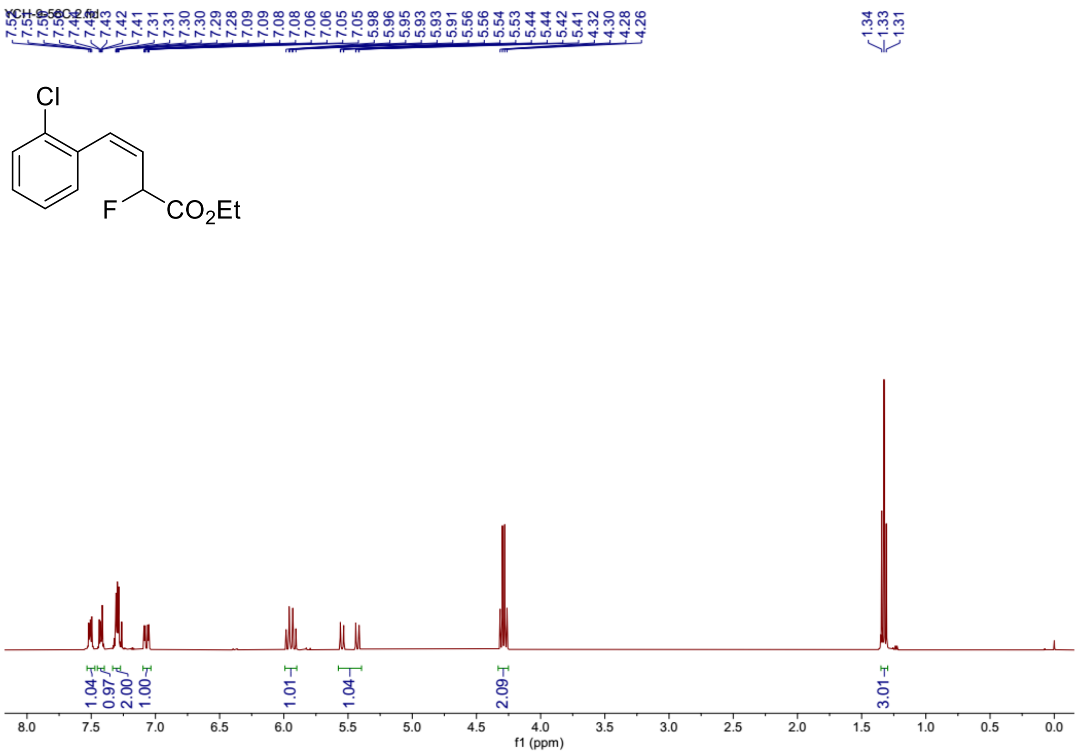
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **22**



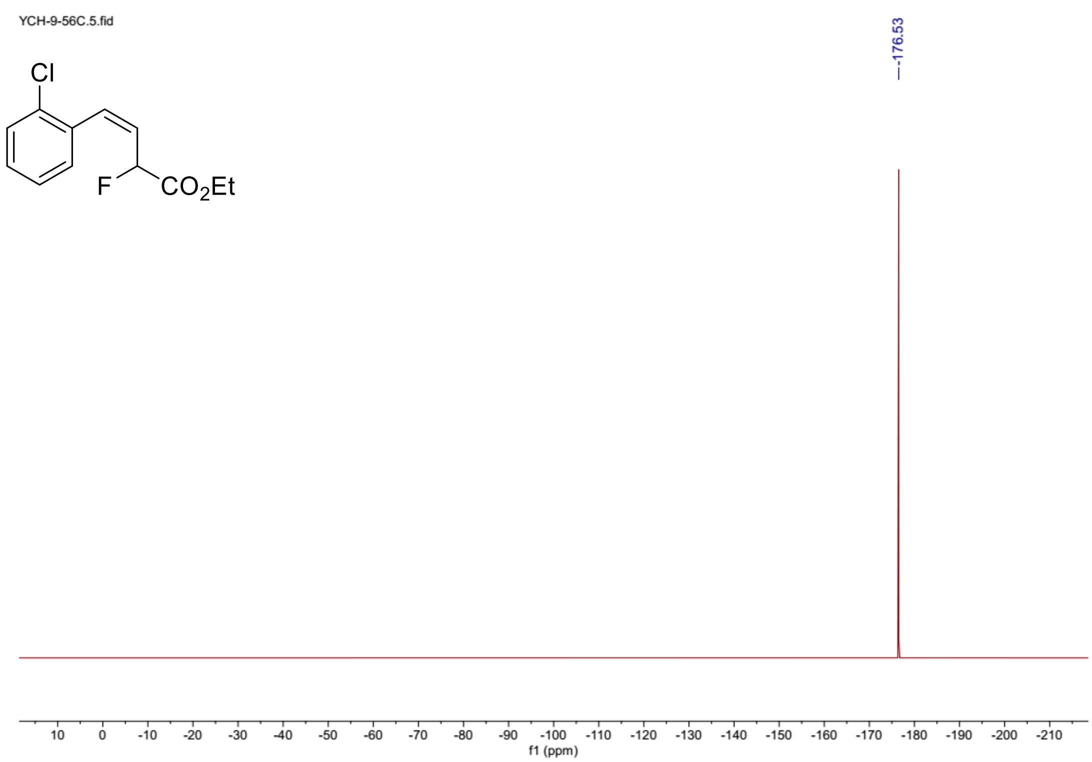
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **22**



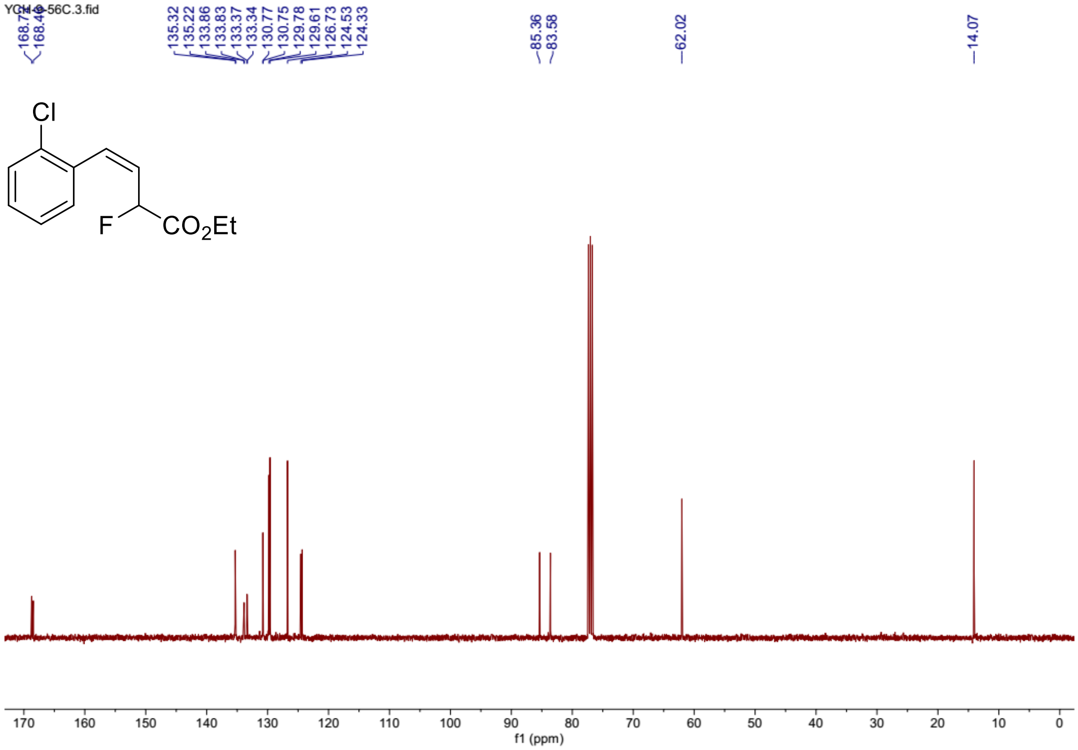
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**



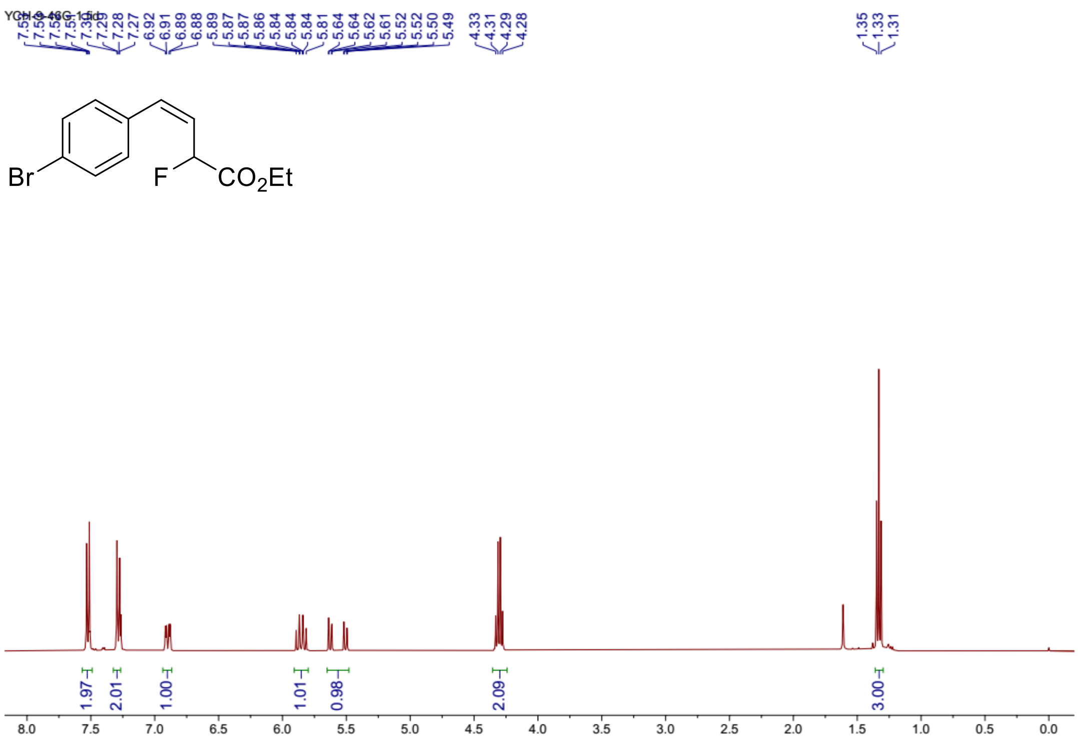
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **23**



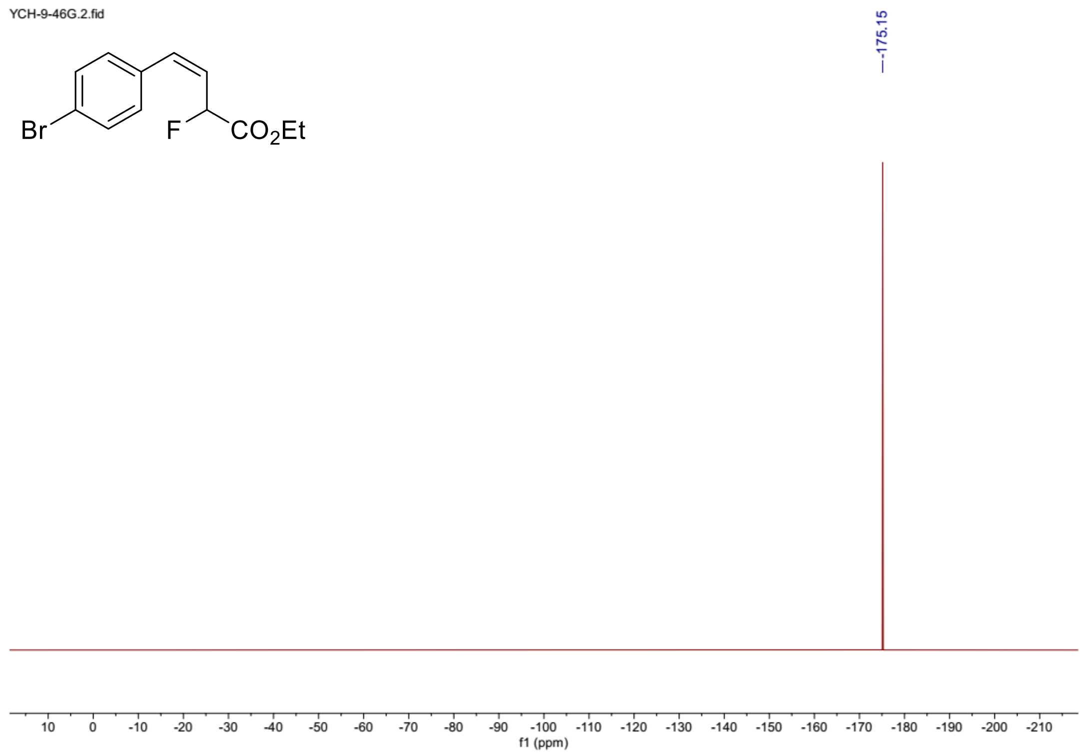
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **23**



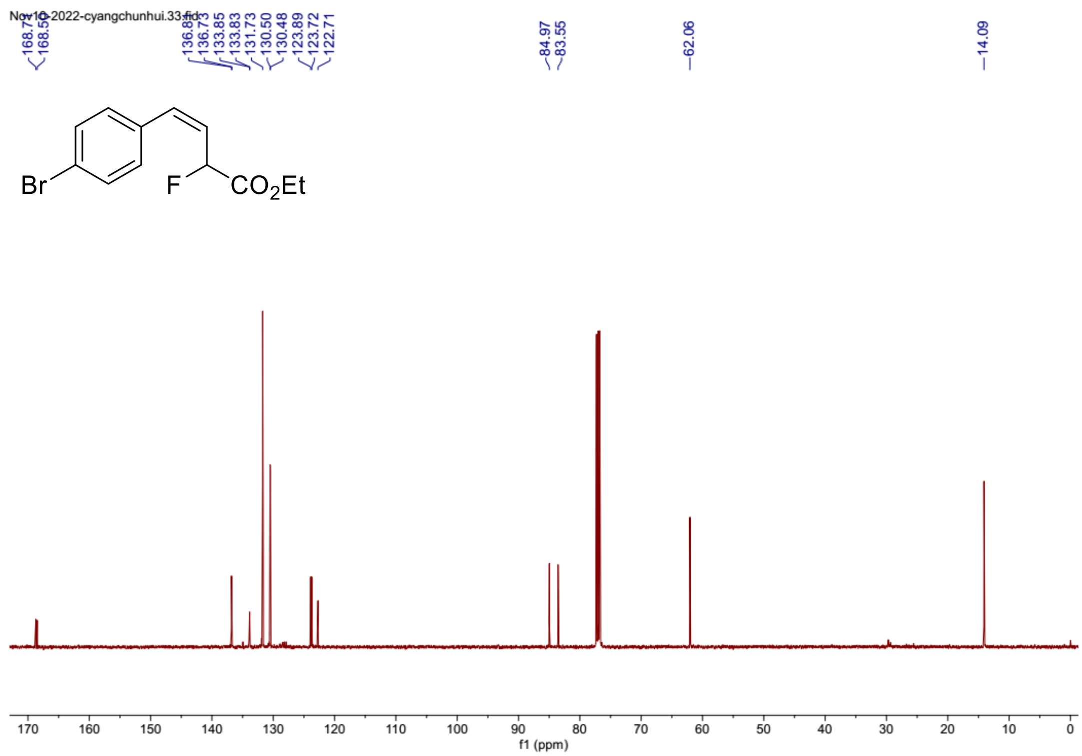
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **24**



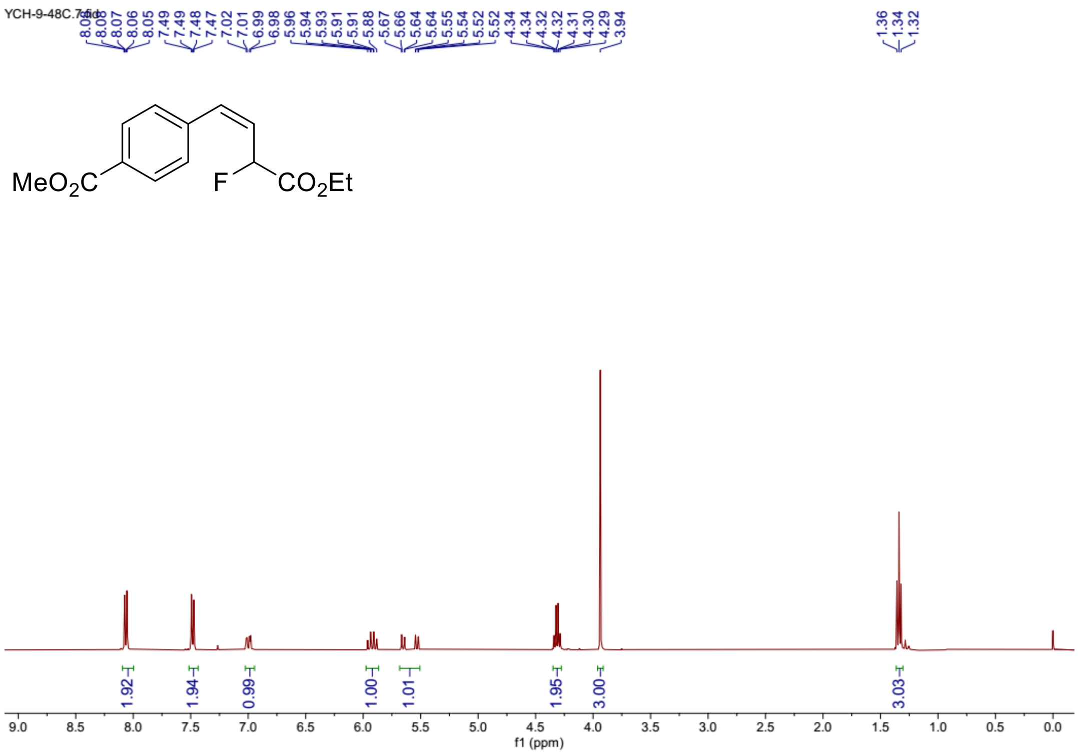
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **24**



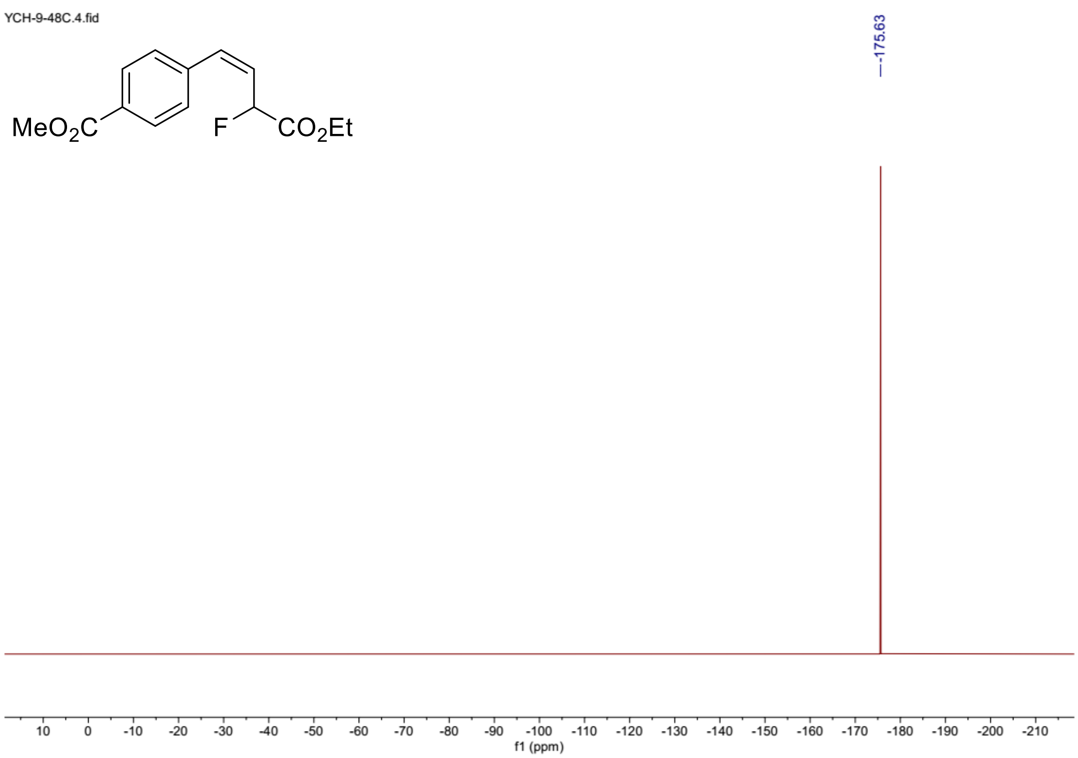
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **24**



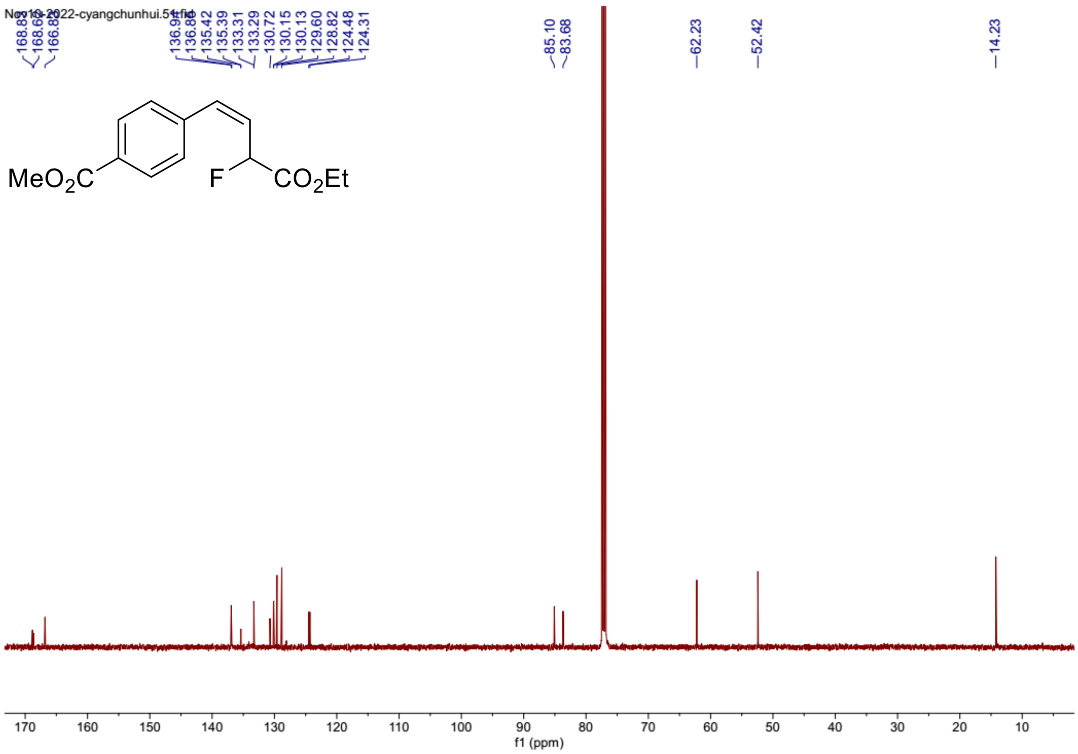
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **25**



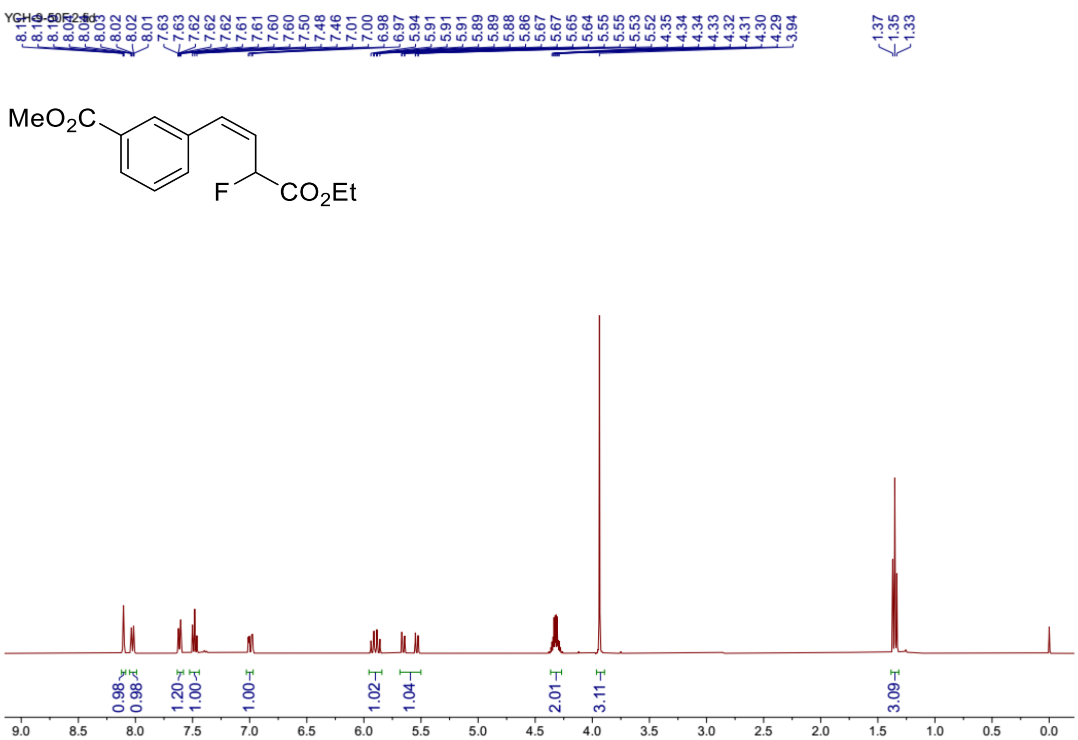
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **25**



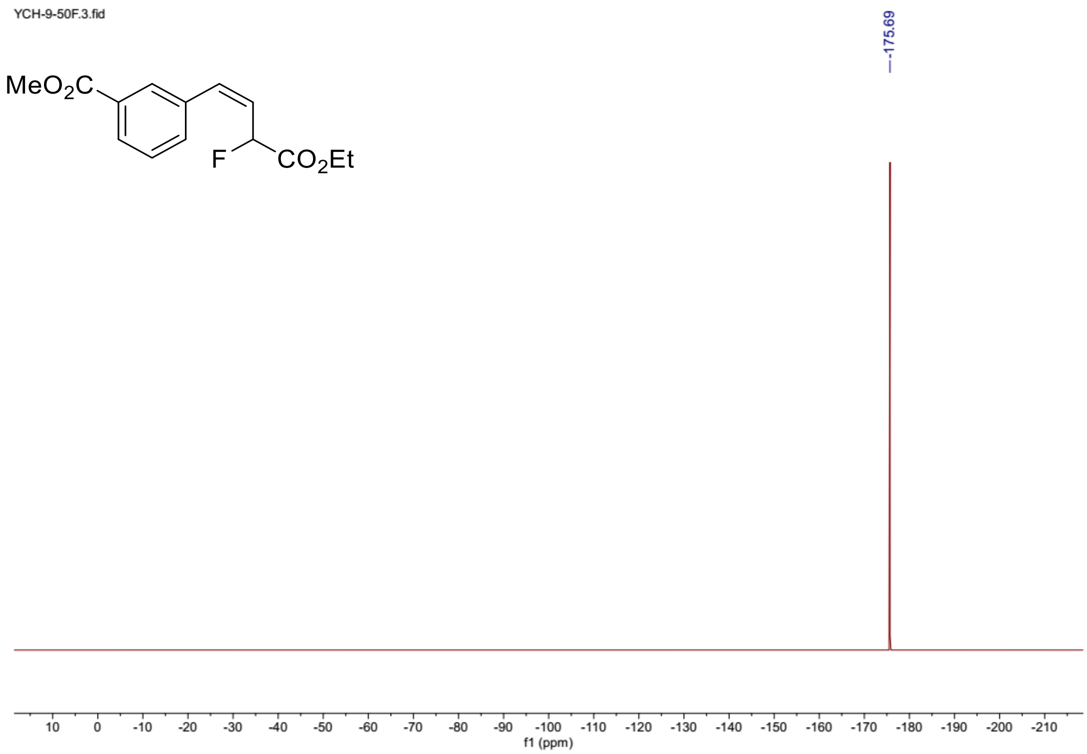
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **25**



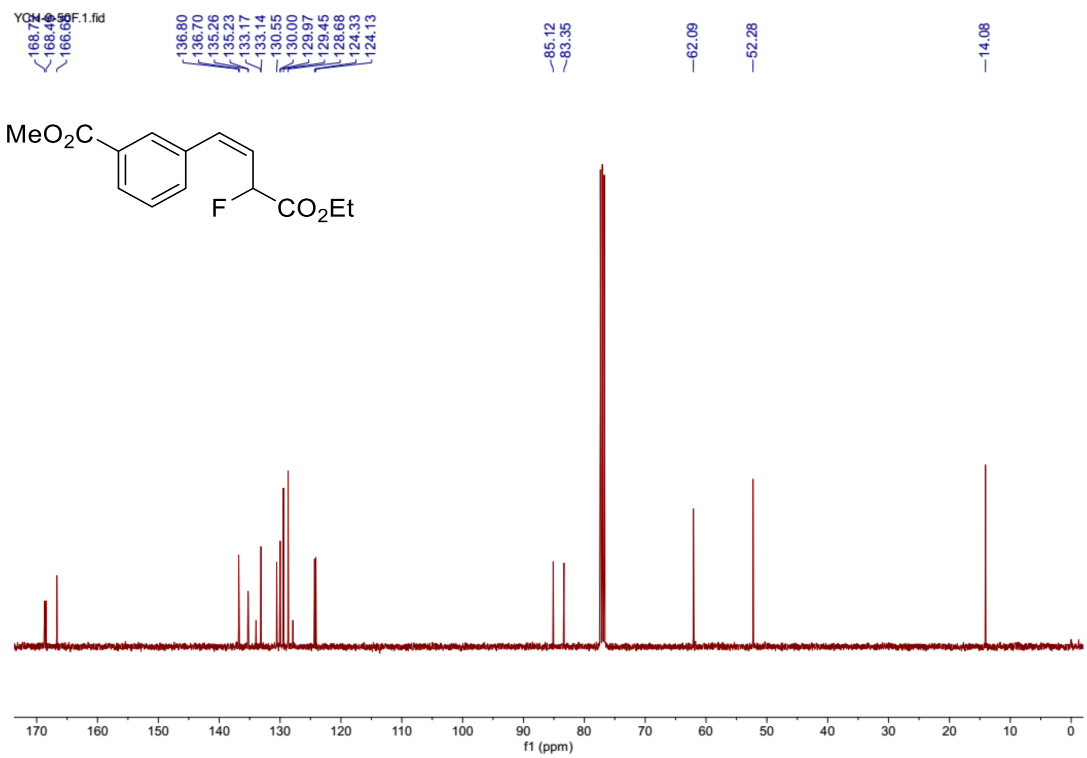
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **26**



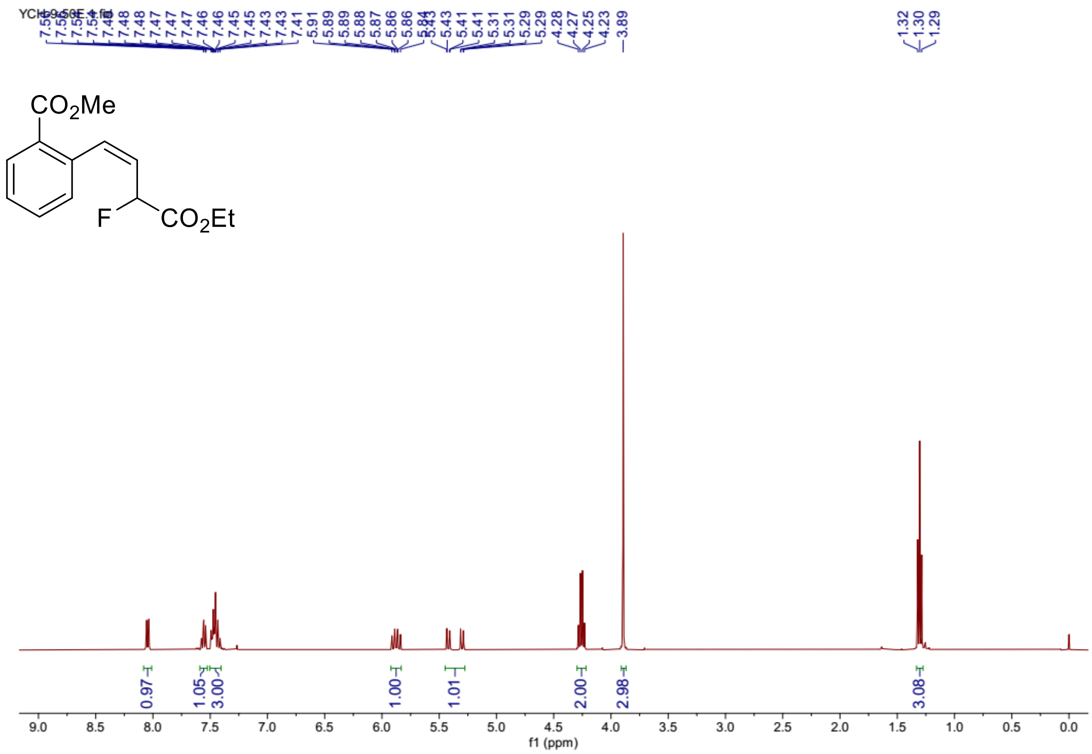
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **26**



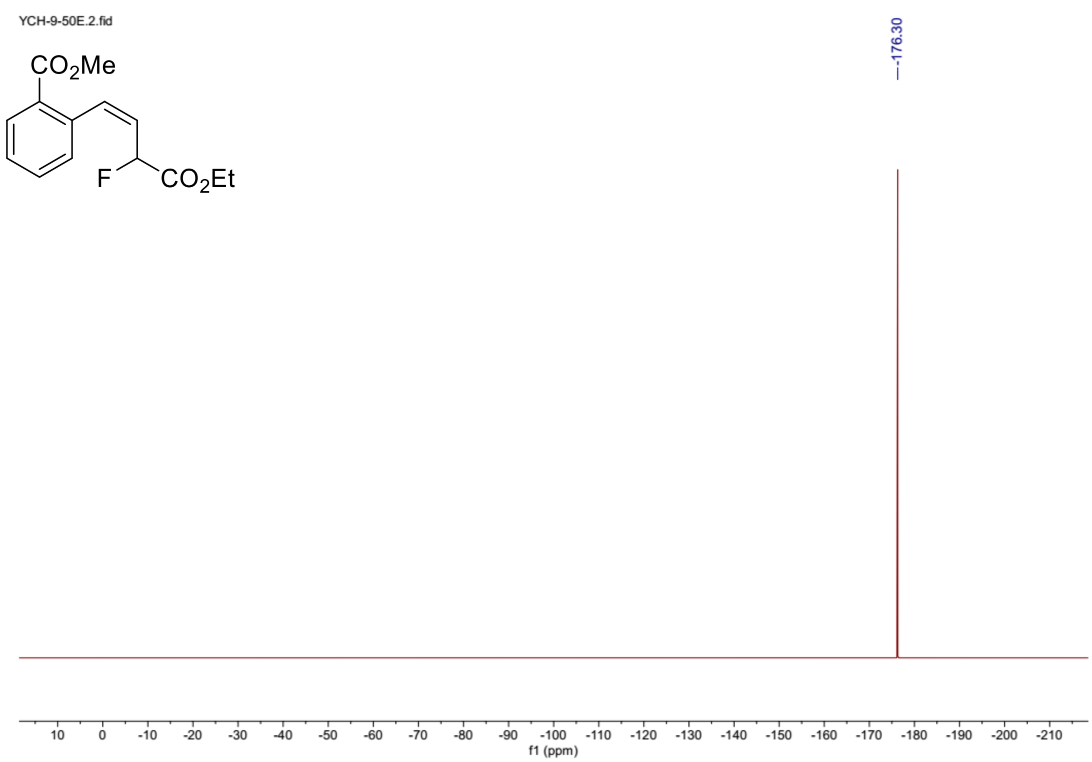
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **26**



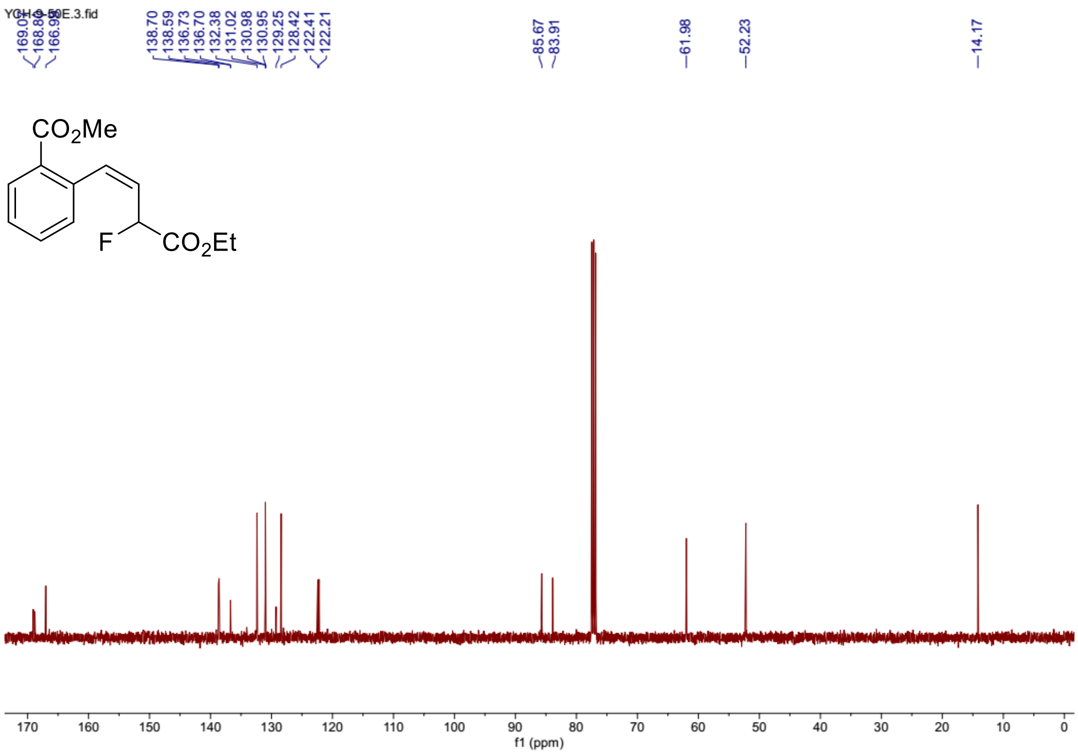
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **27**



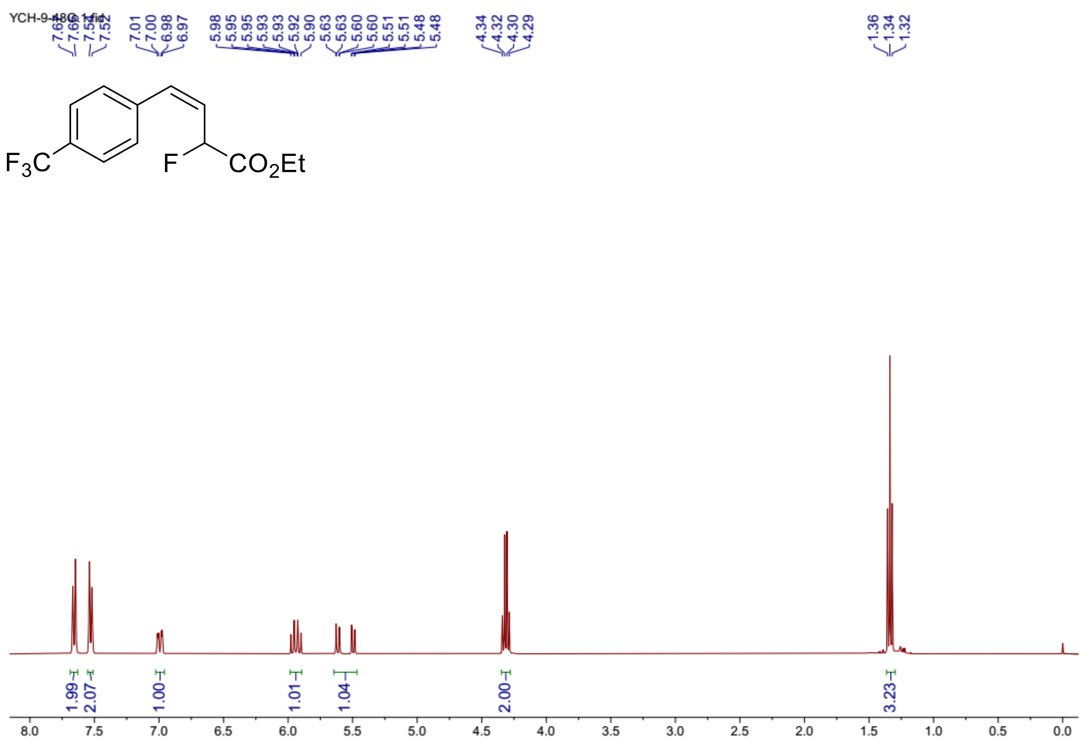
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **27**



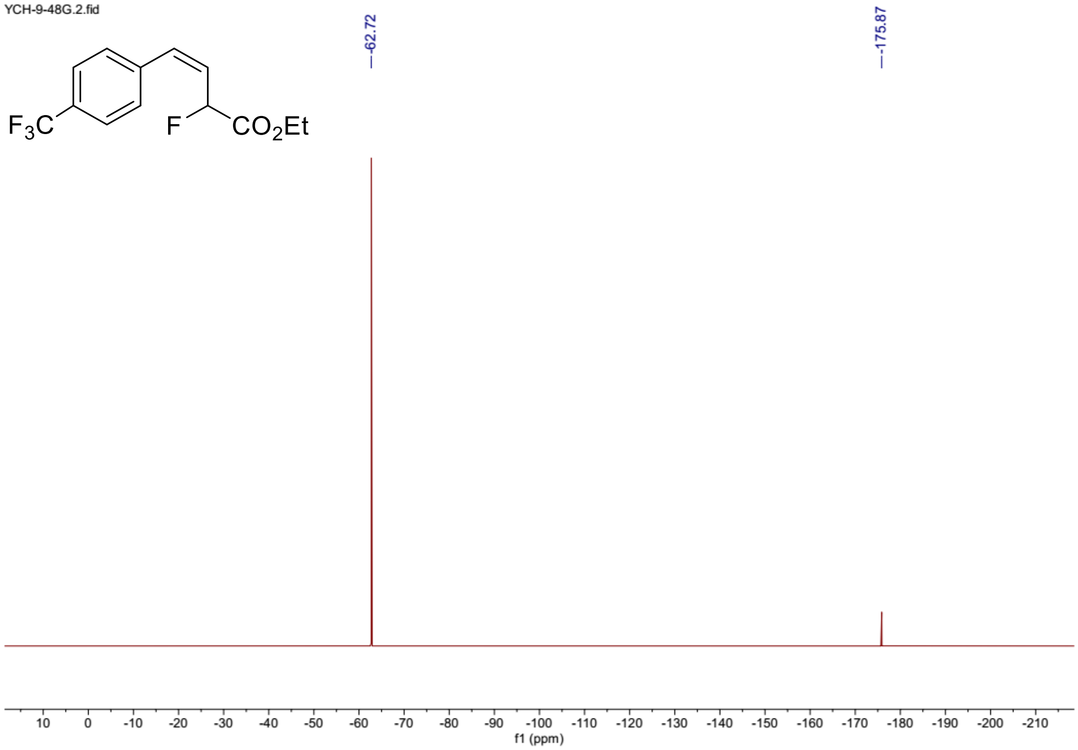
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **27**



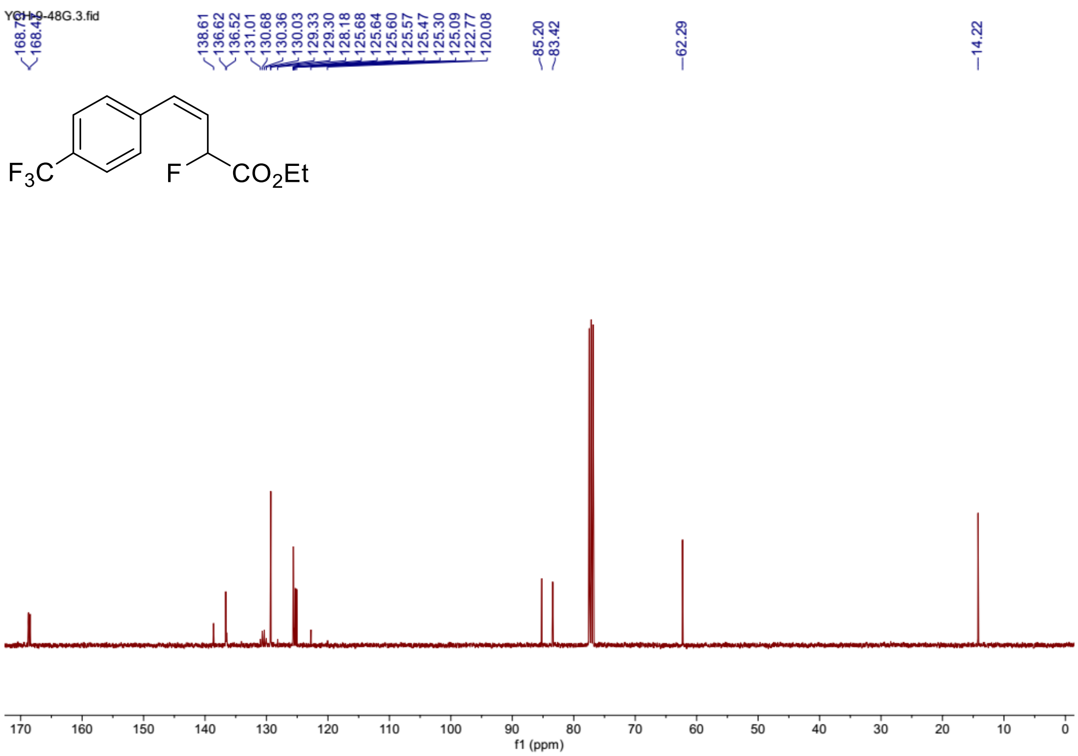
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **28**



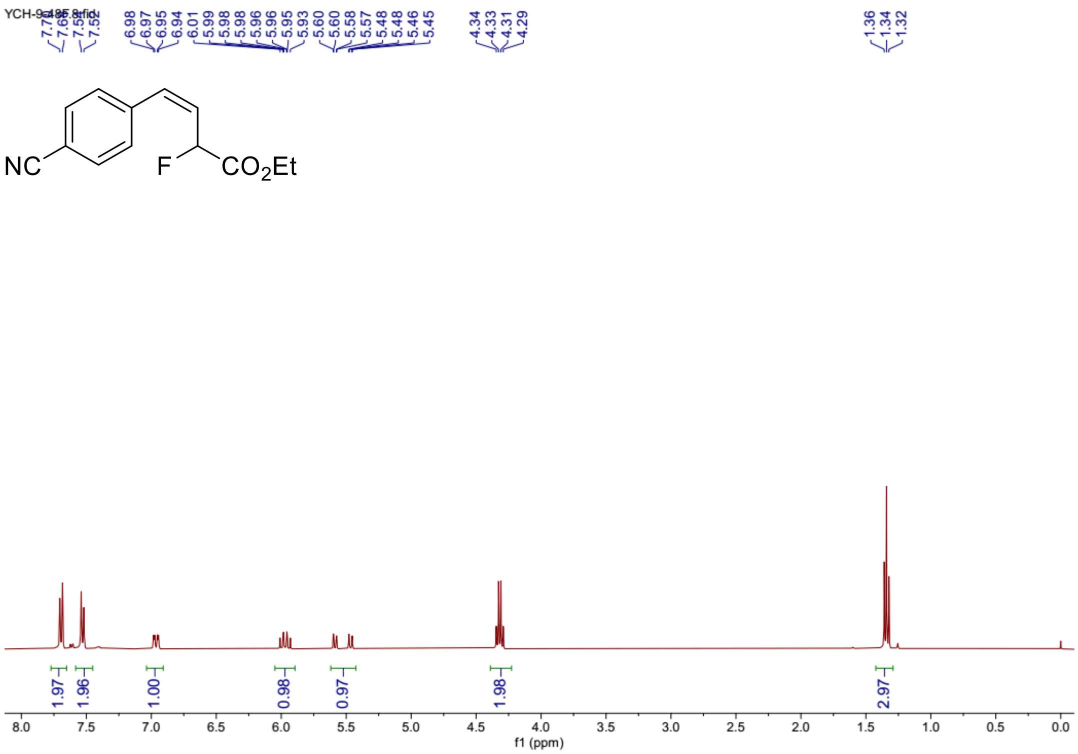
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **28**



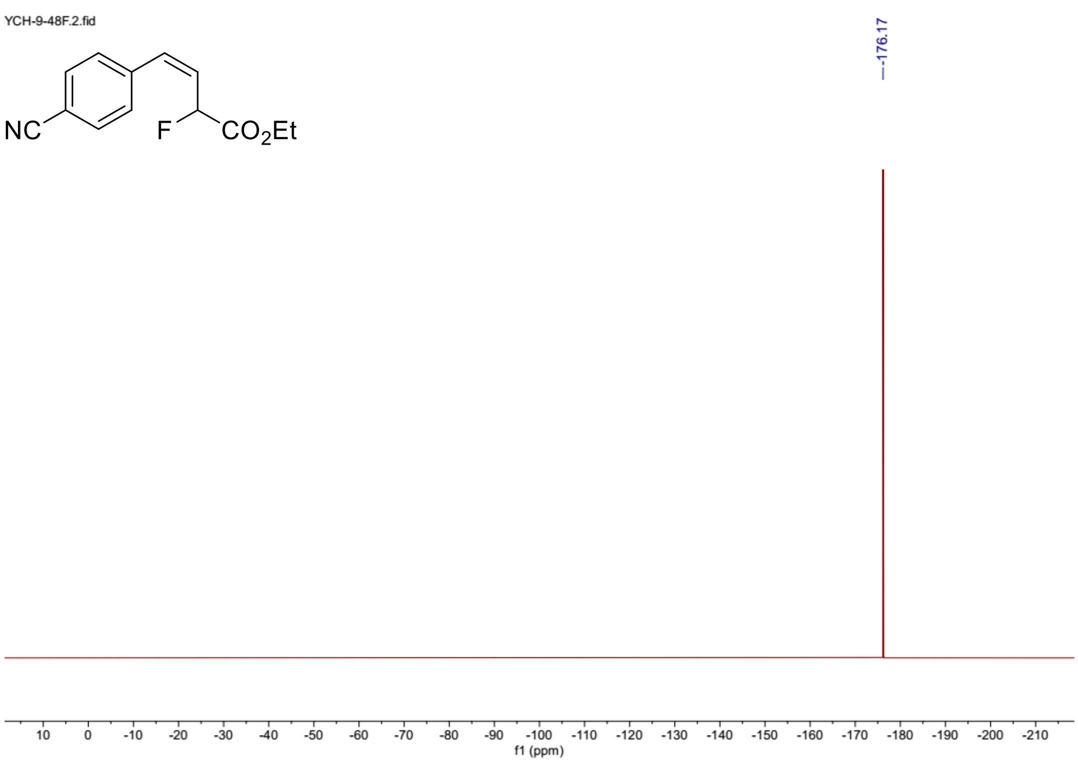
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **28**



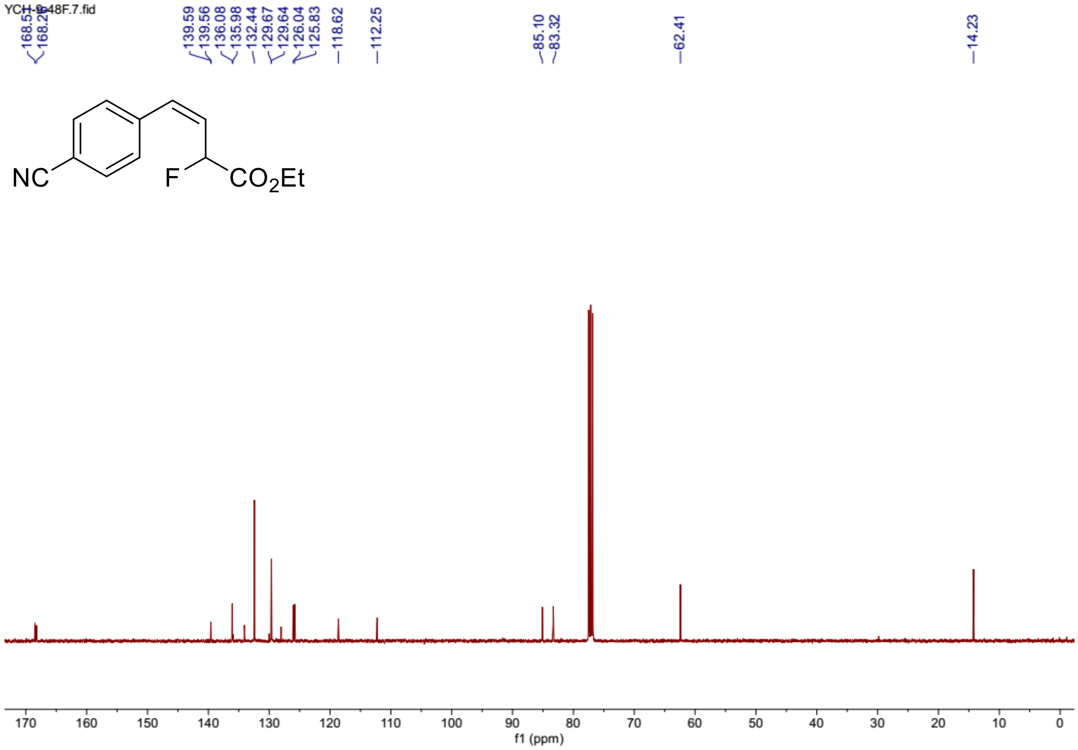
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **29**



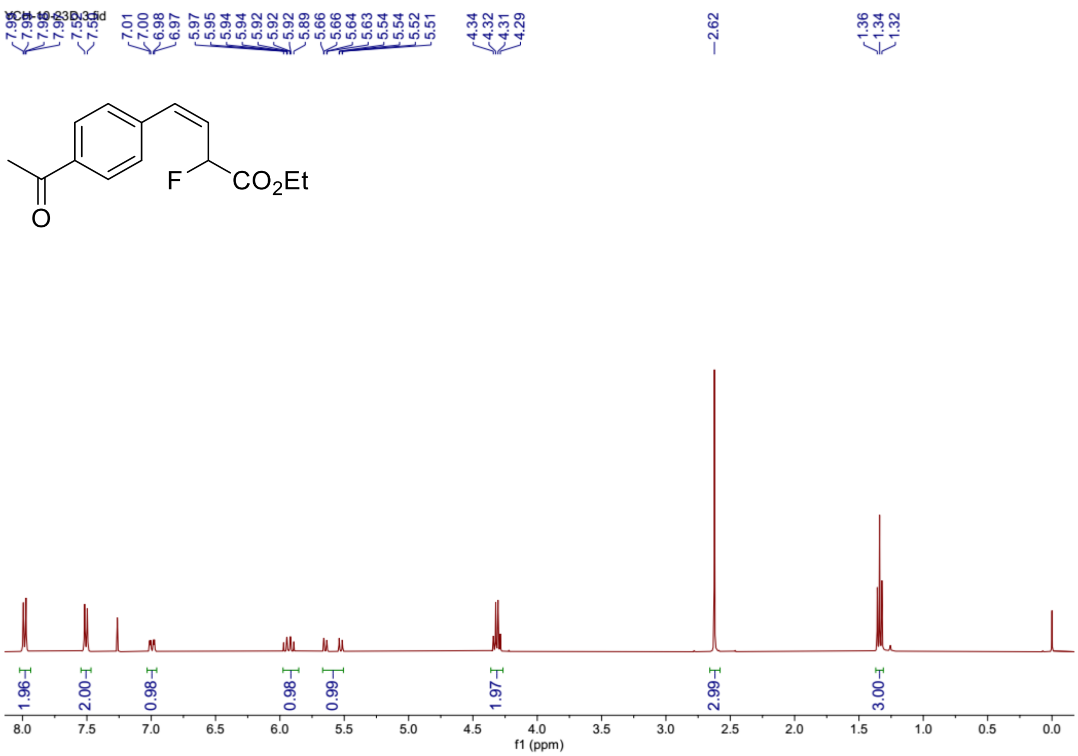
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **29**



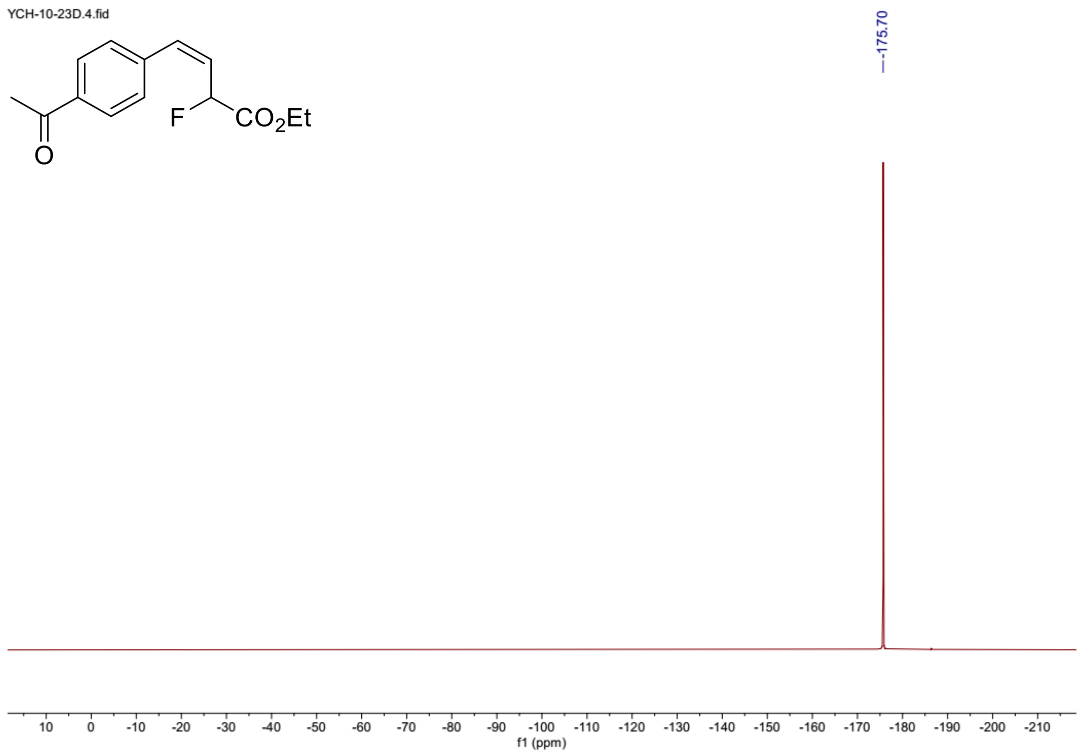
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **29**



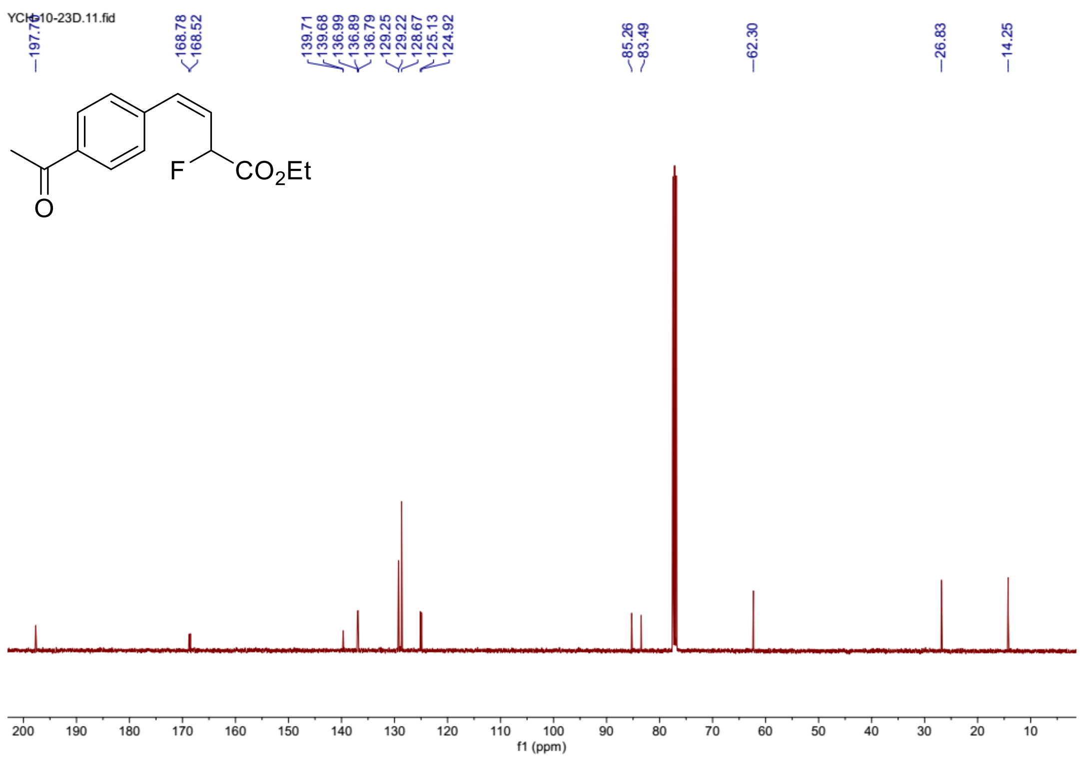
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **30**



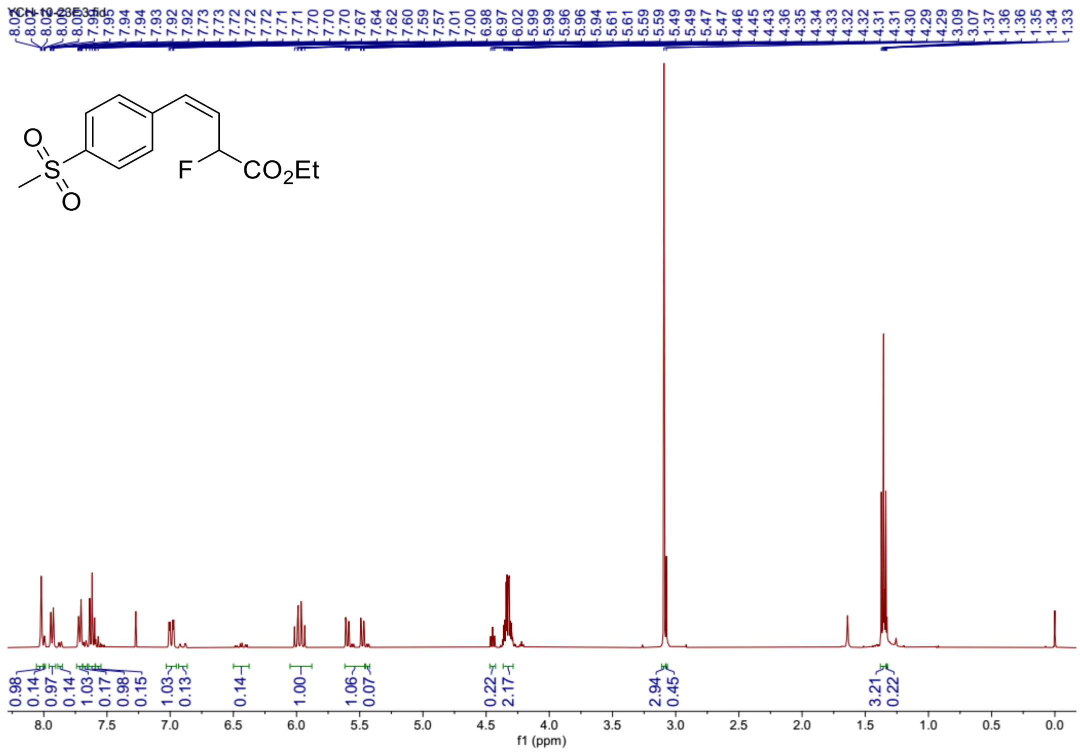
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **30**



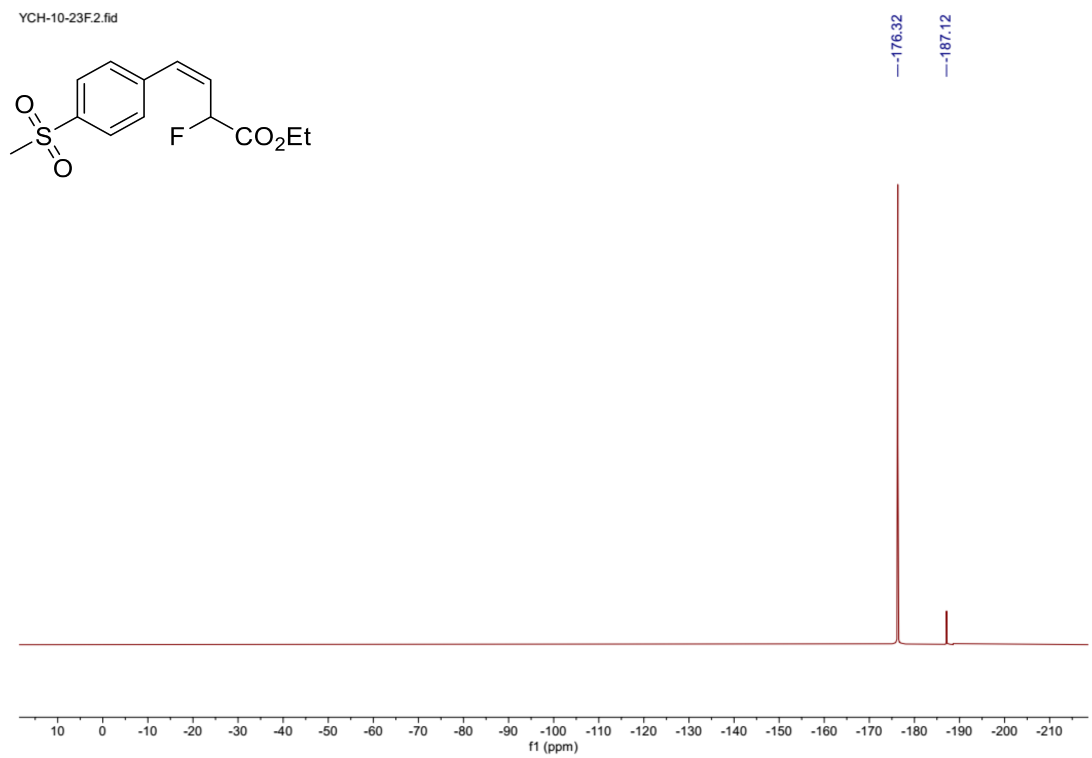
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **30**



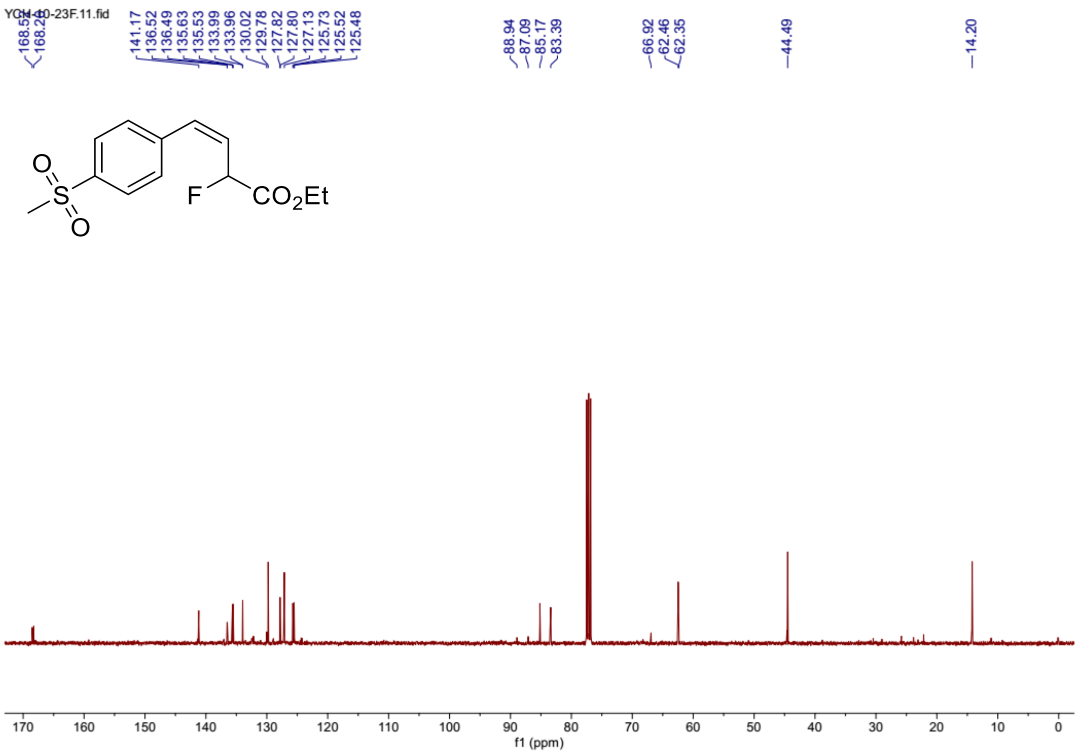
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **31**



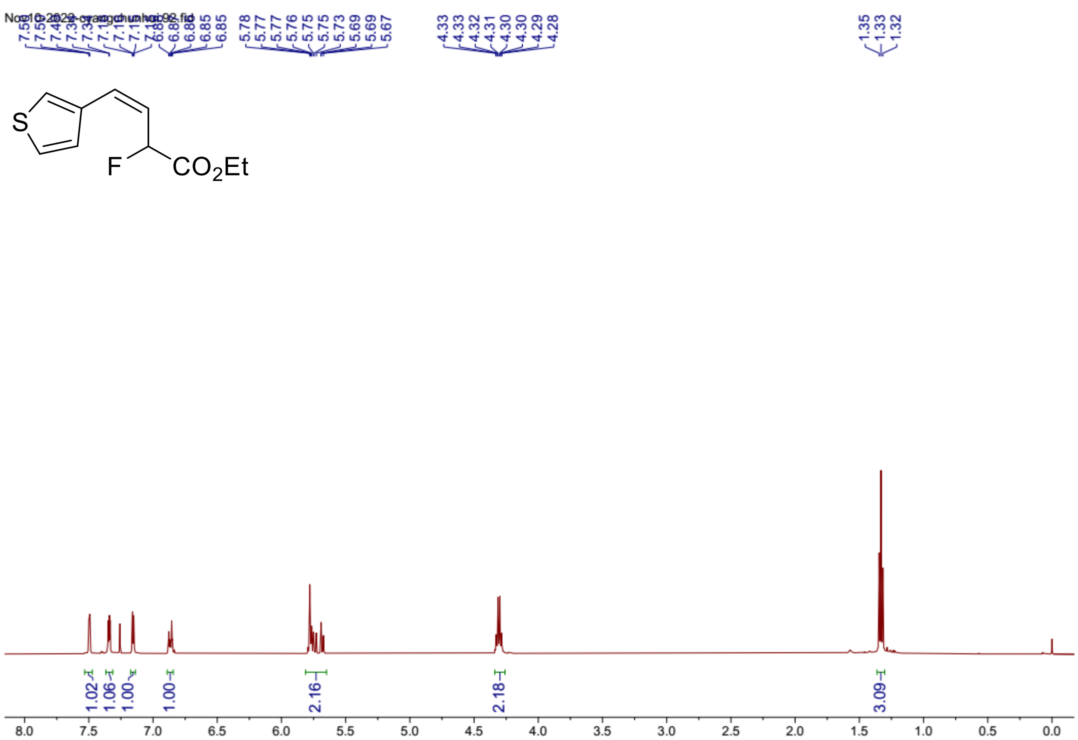
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **31**



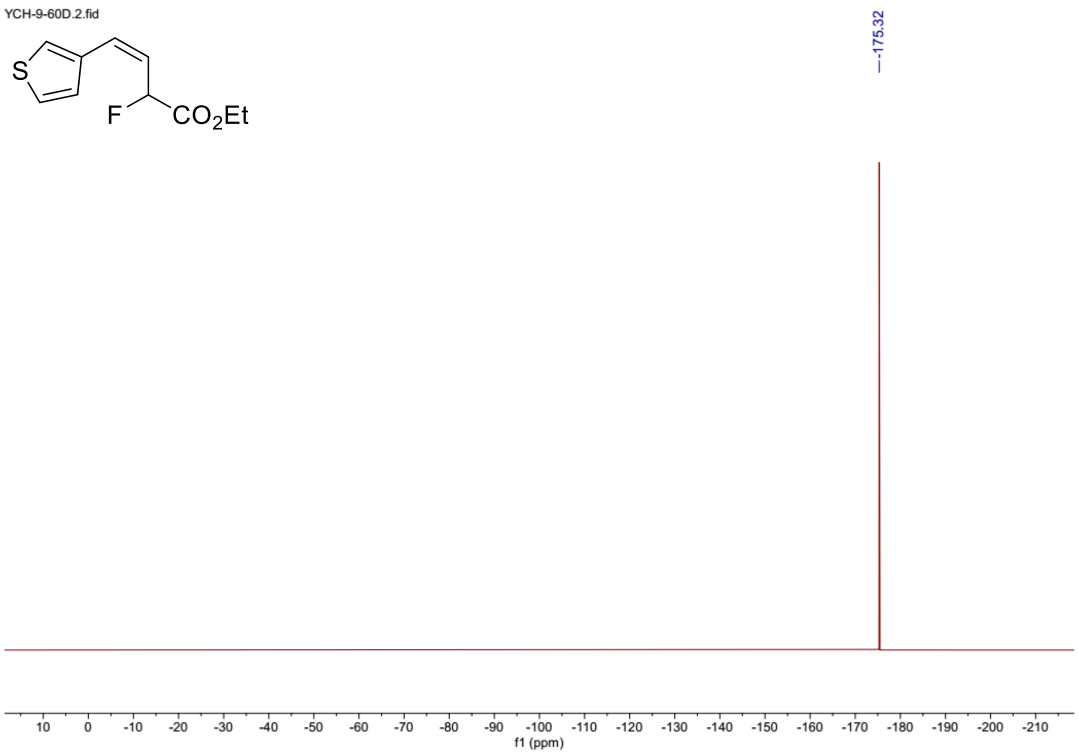
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **31**



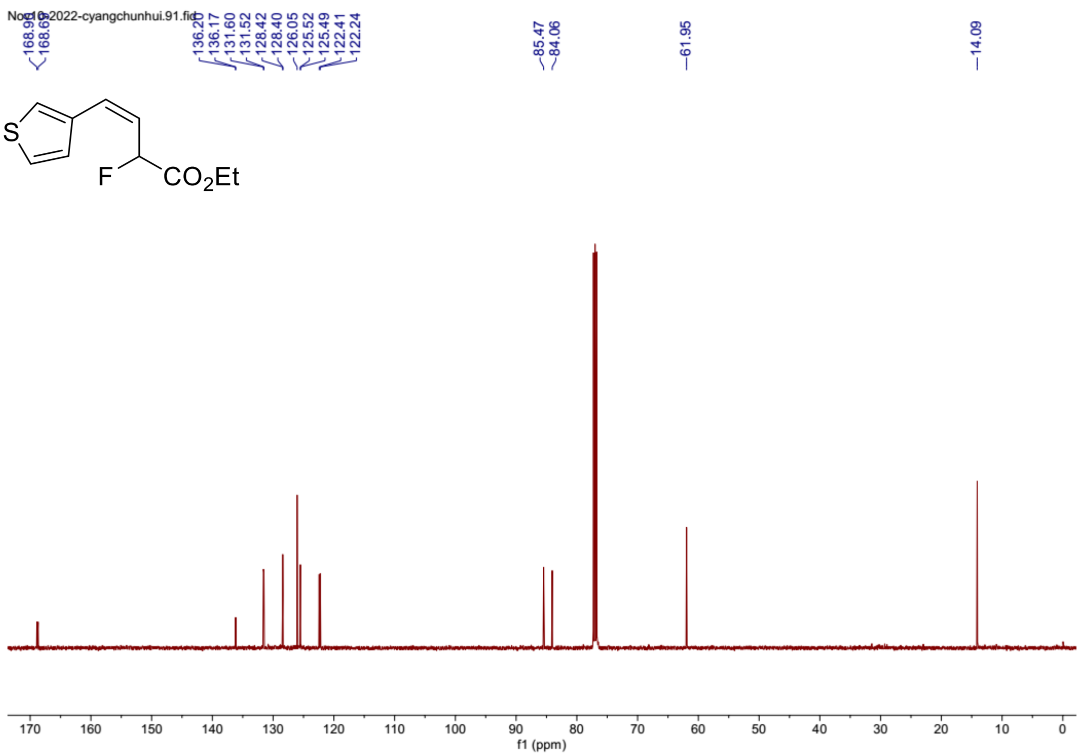
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **32**



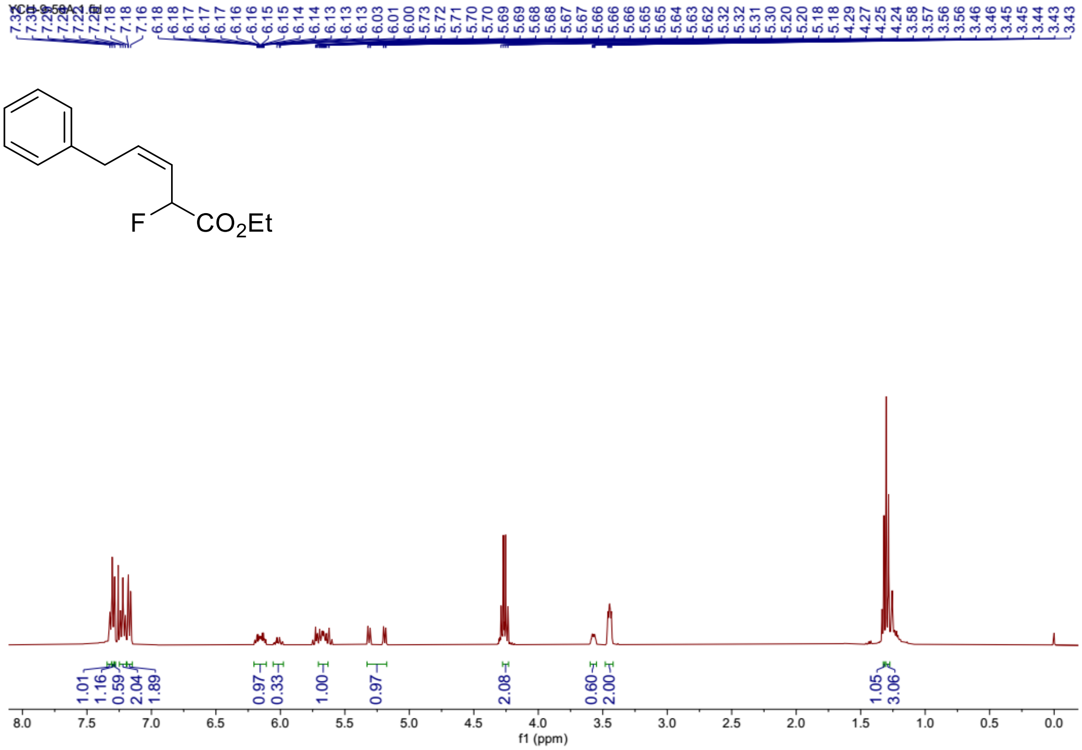
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **32**



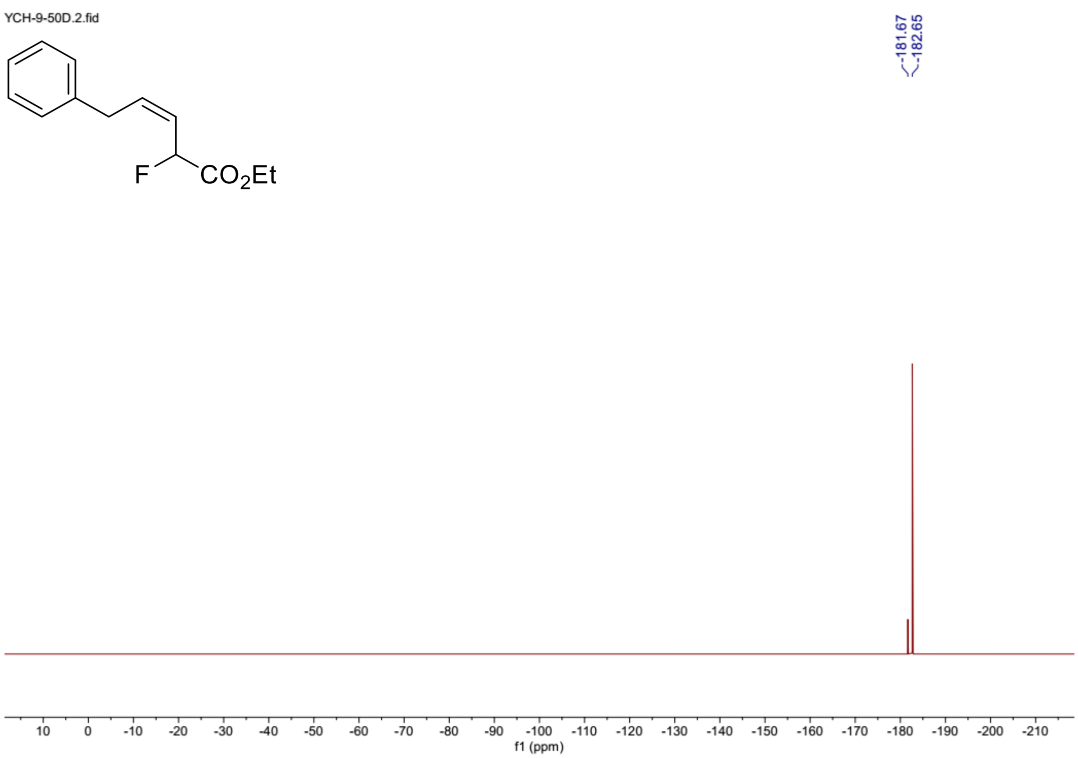
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **32**



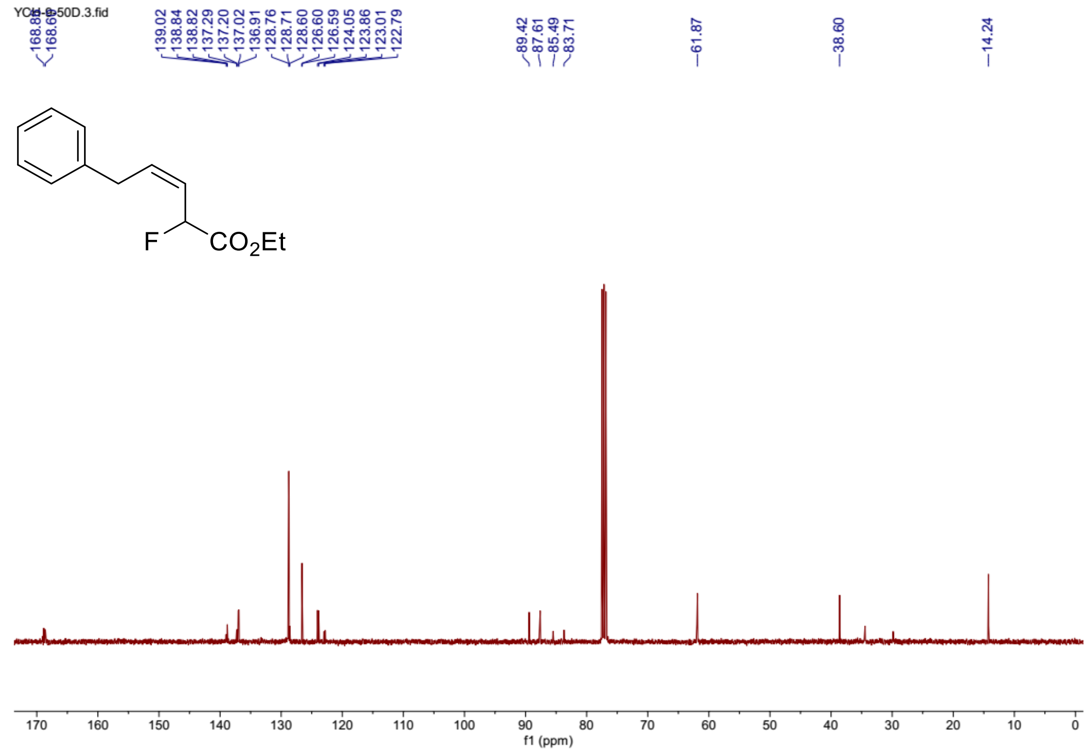
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **33**



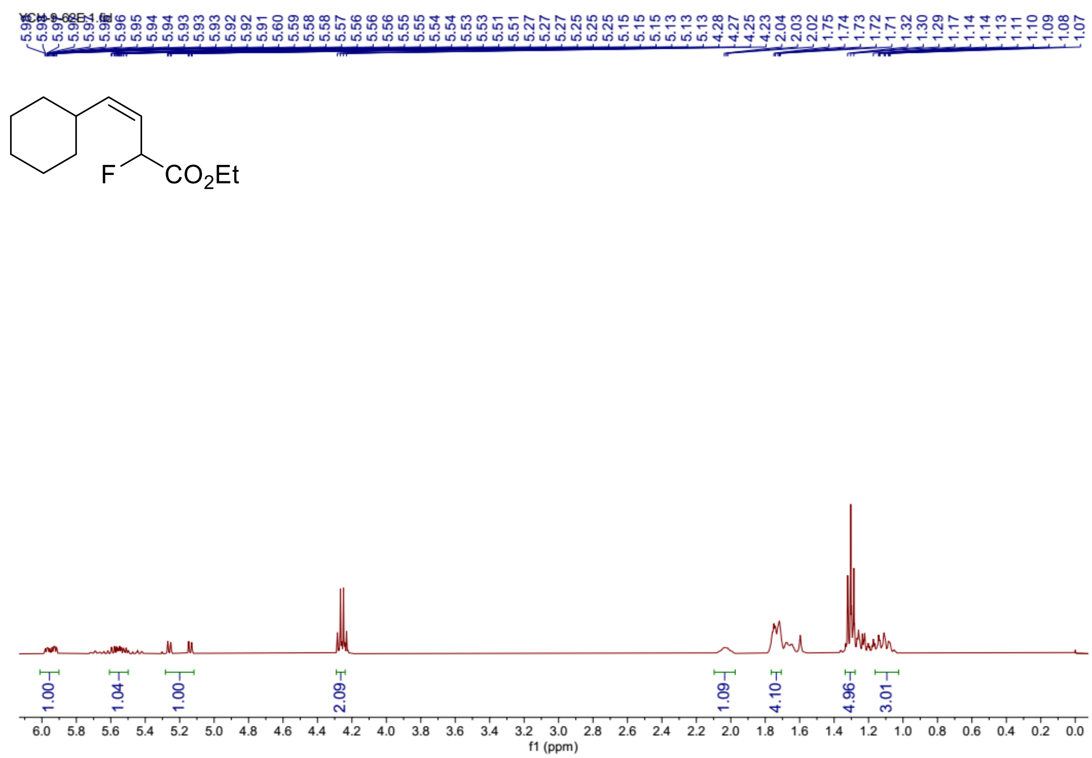
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **33**



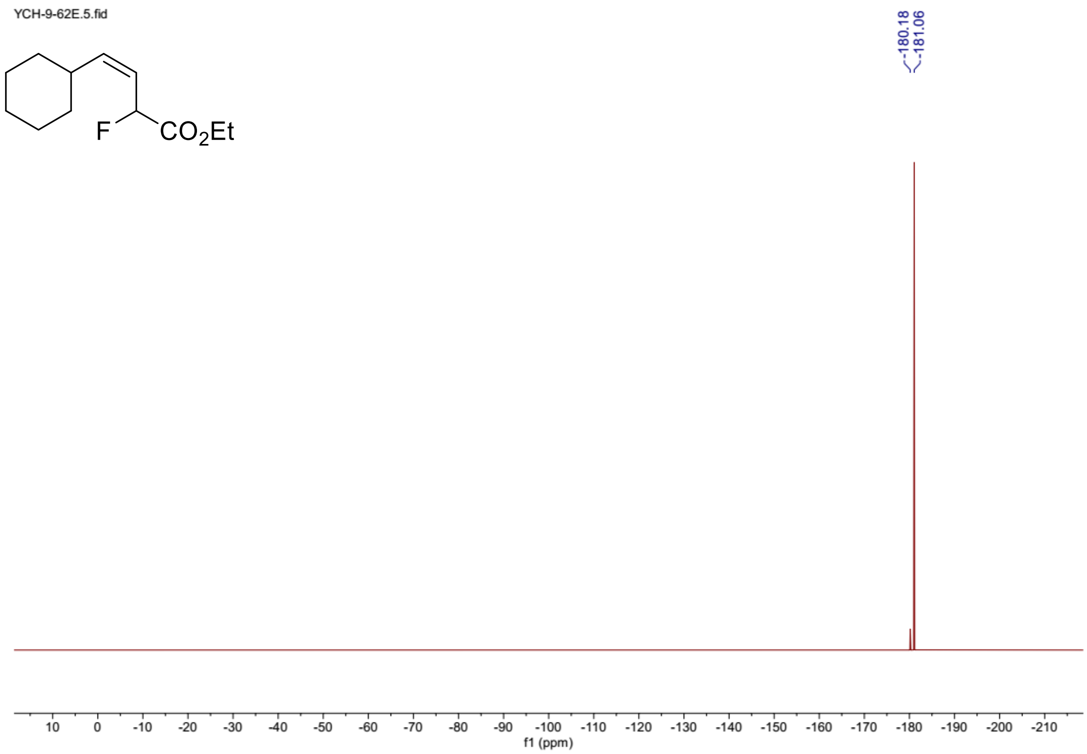
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **33**



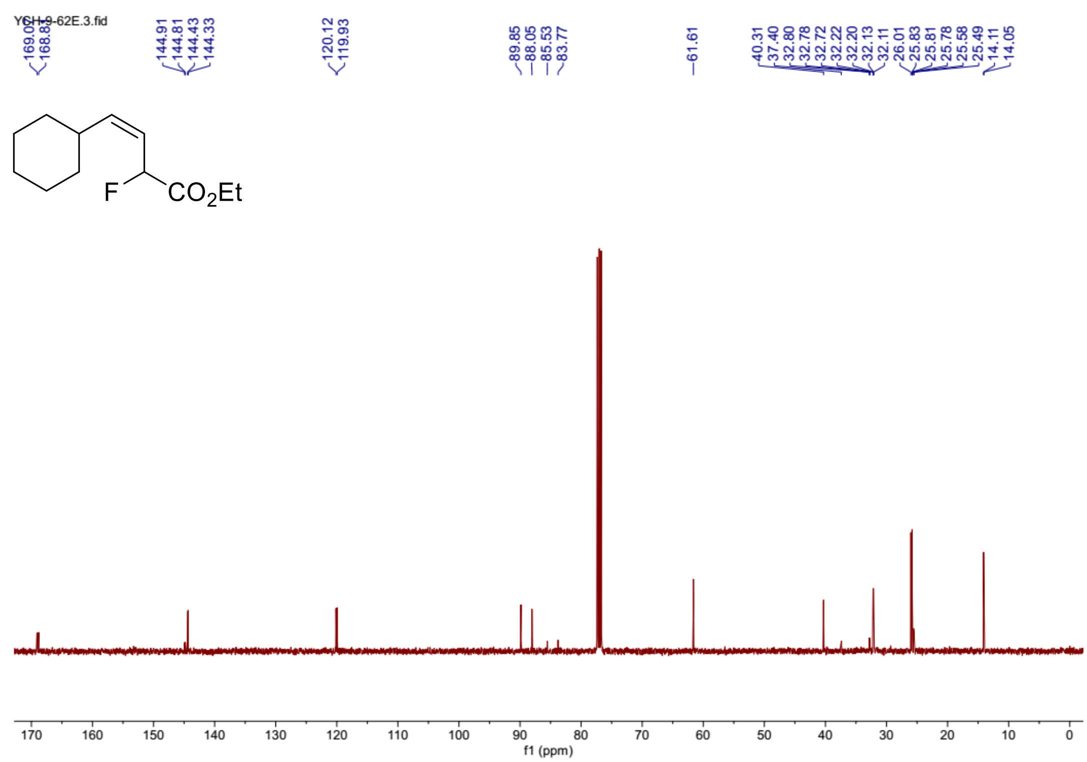
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **34**



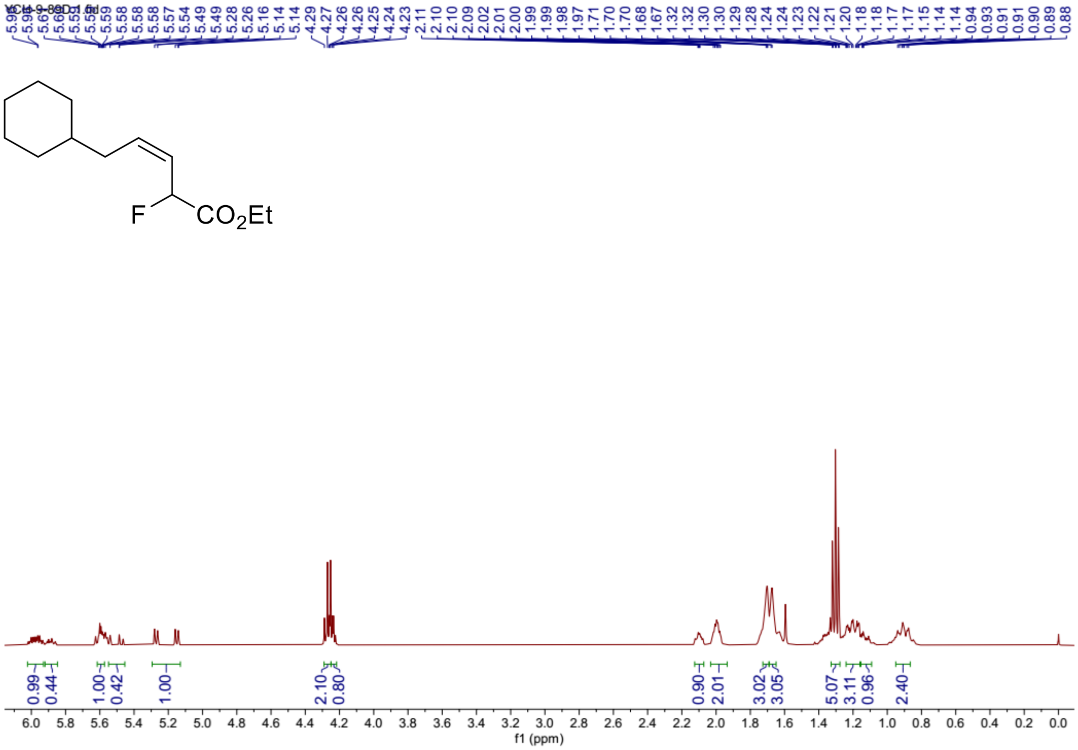
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **34**



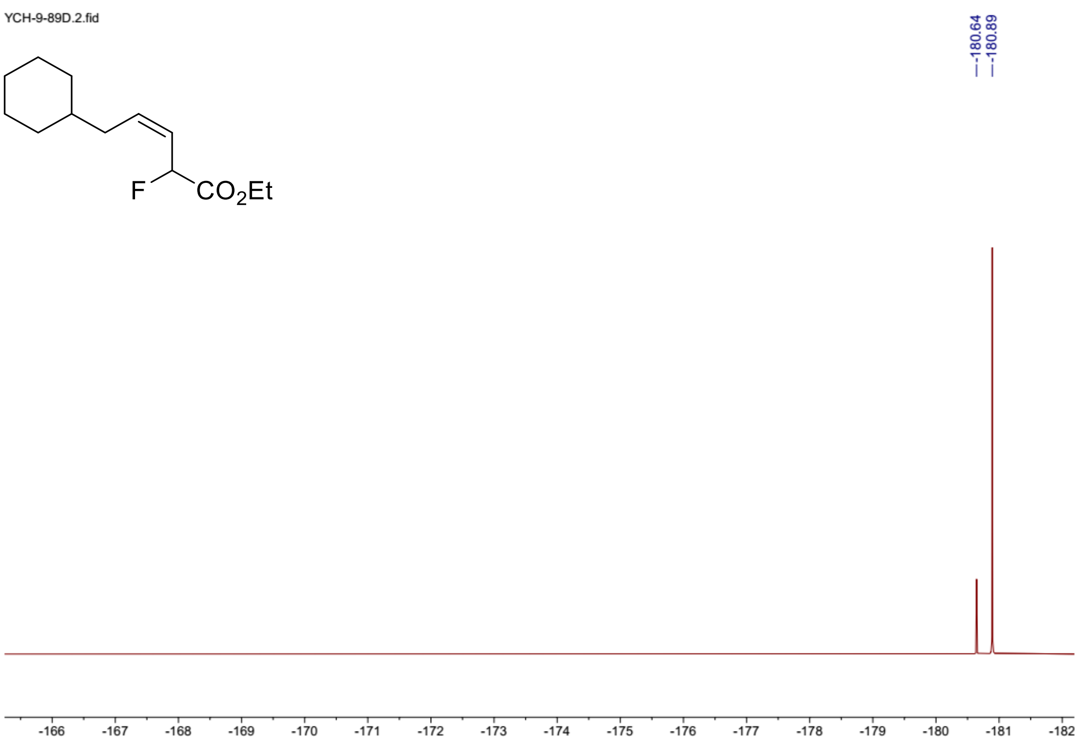
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **34**



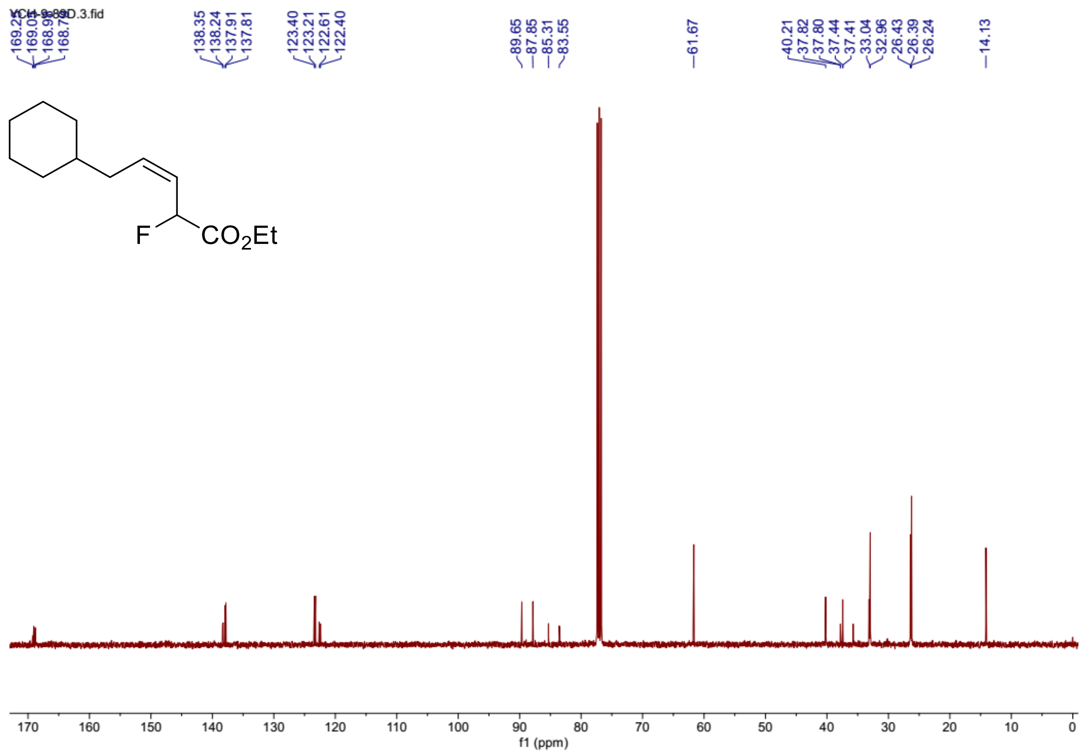
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **35**



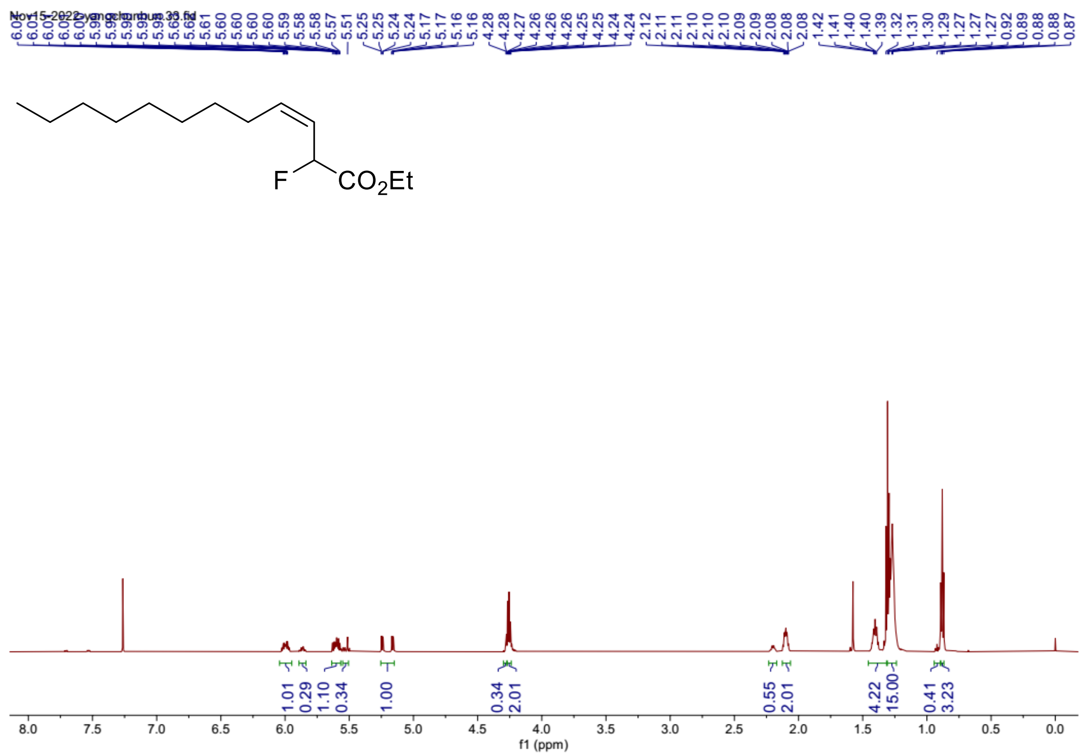
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **35**



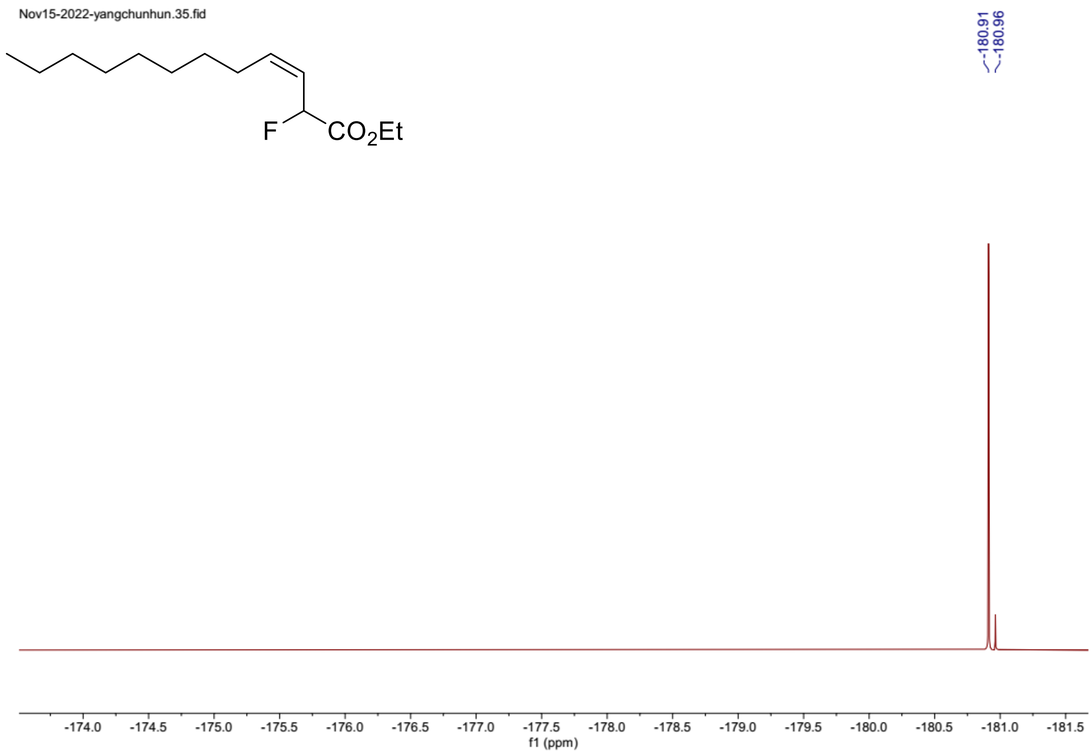
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **35**



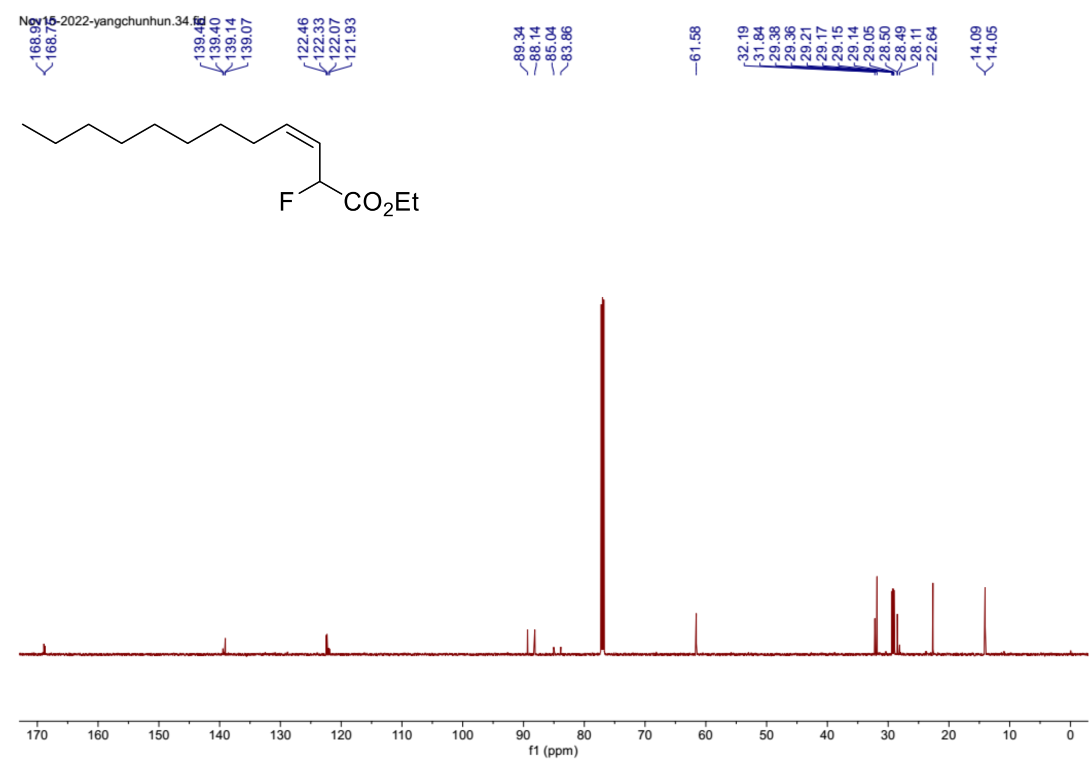
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **36**



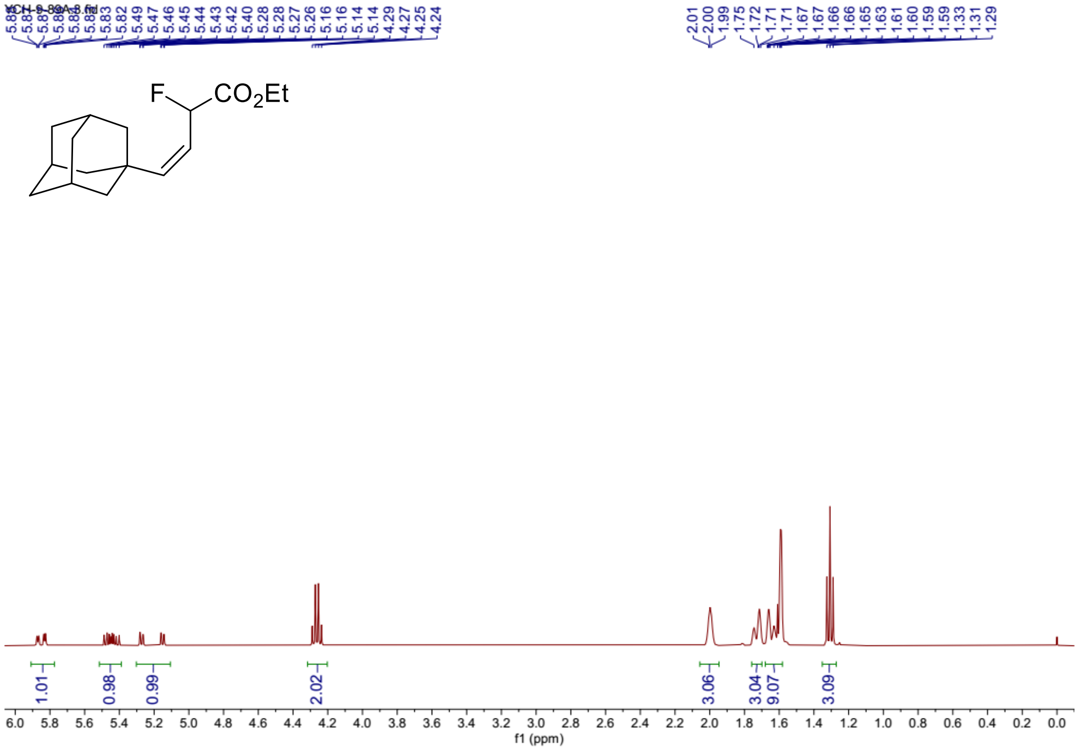
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **36**



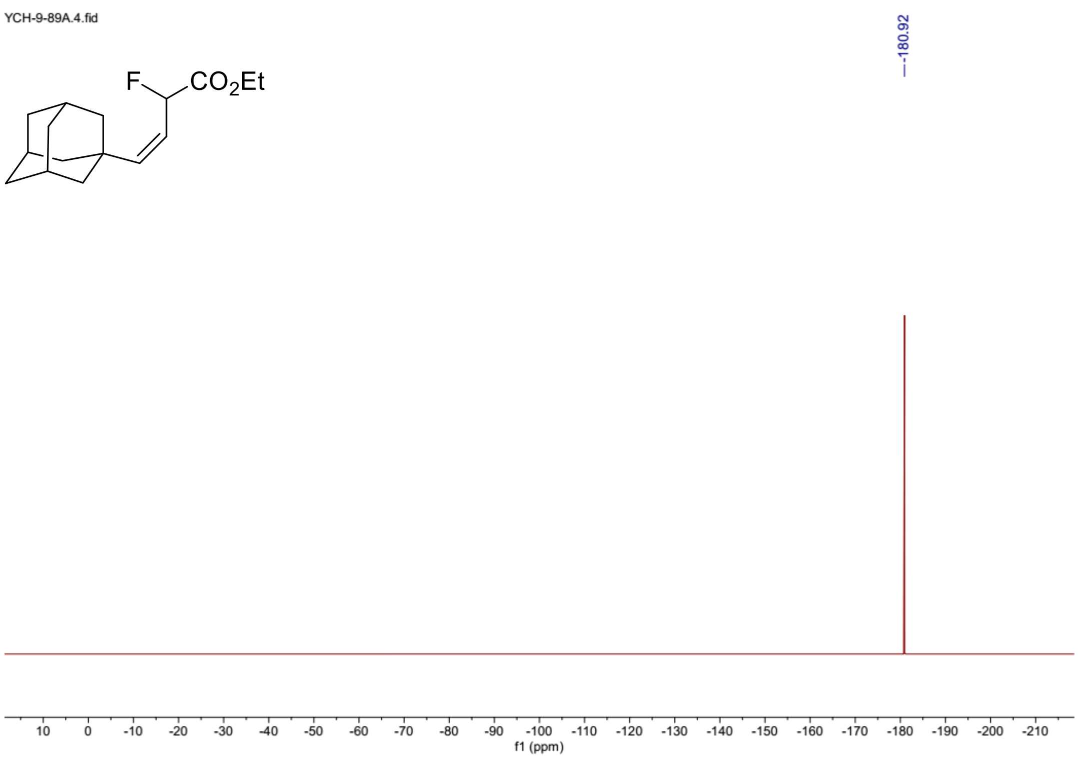
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **36**



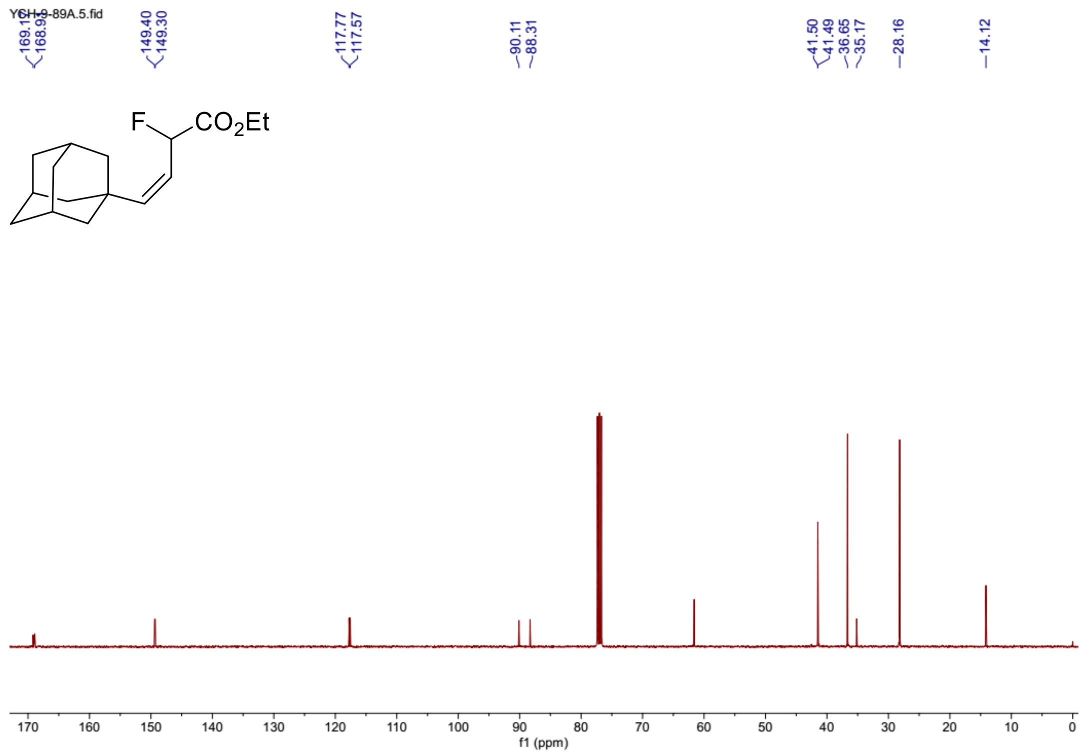
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **37**



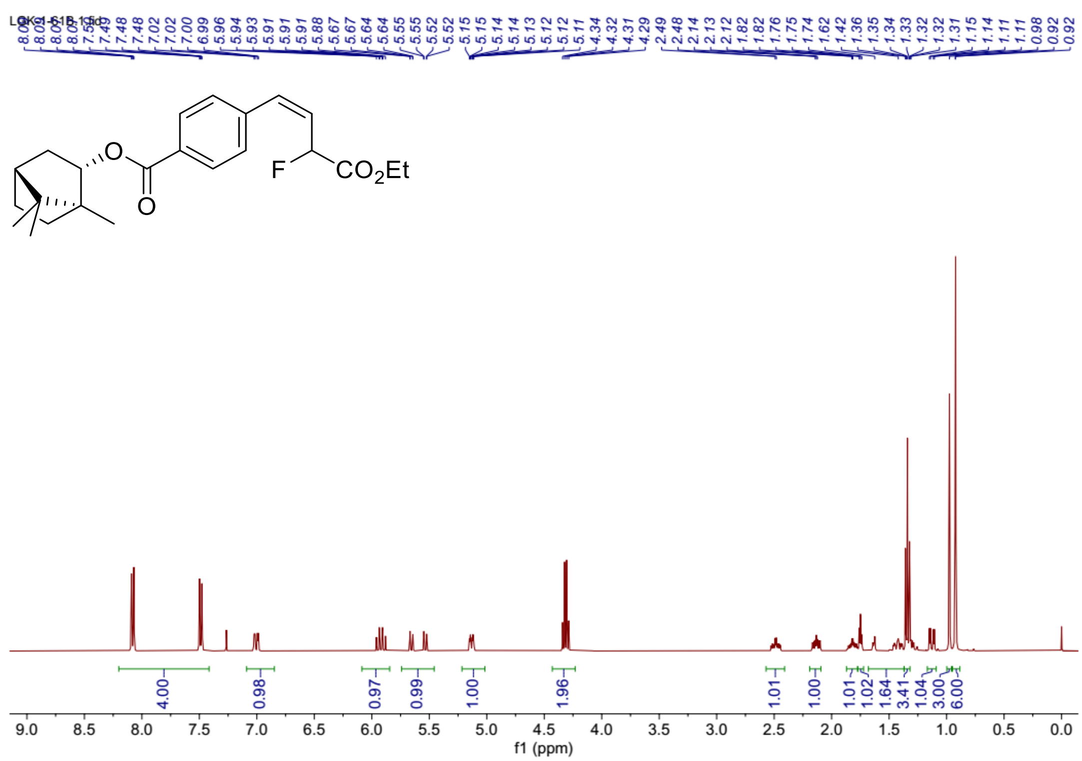
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **37**



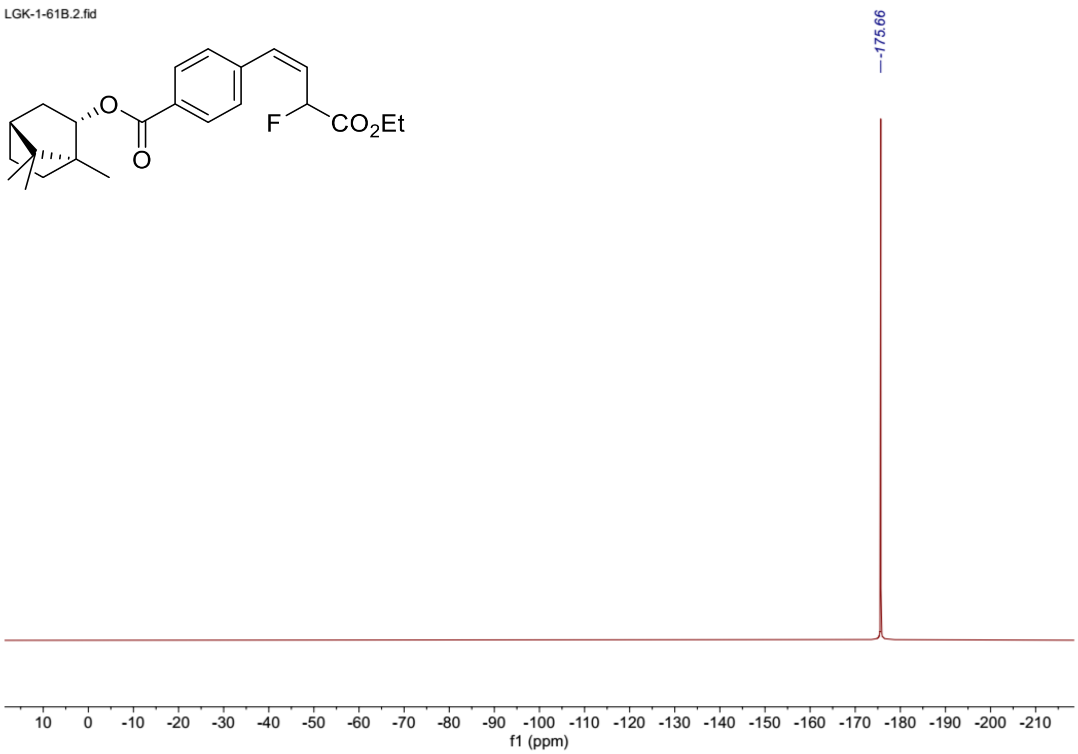
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **37**



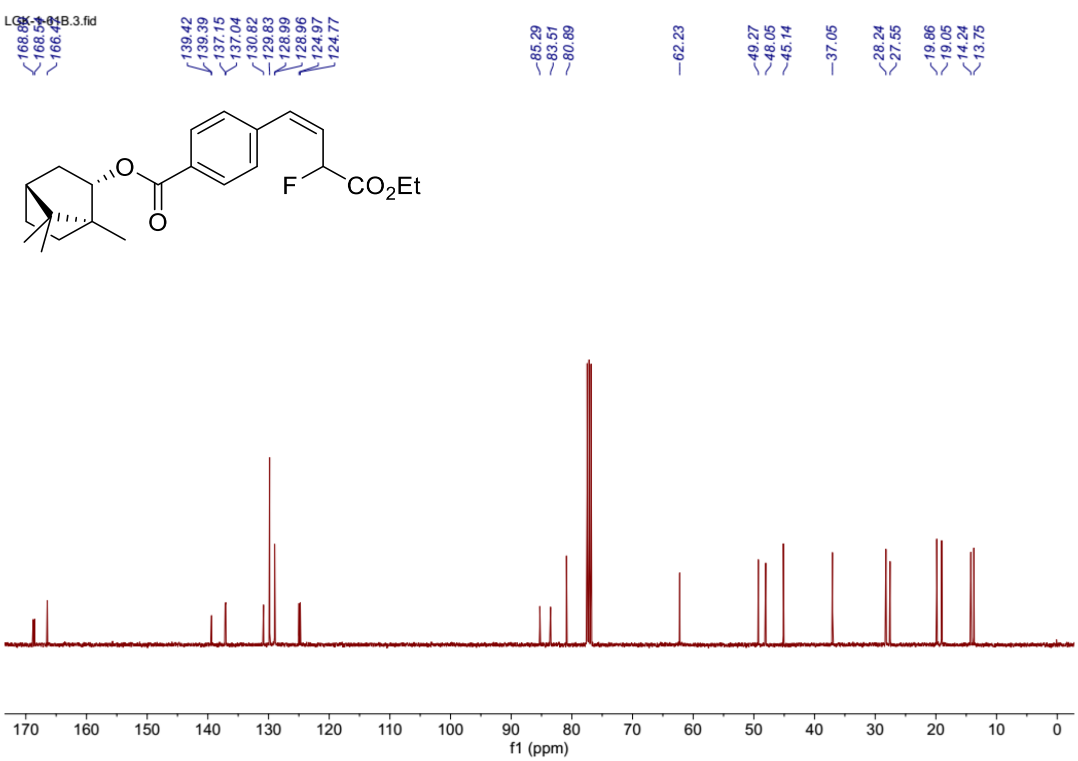
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **38**



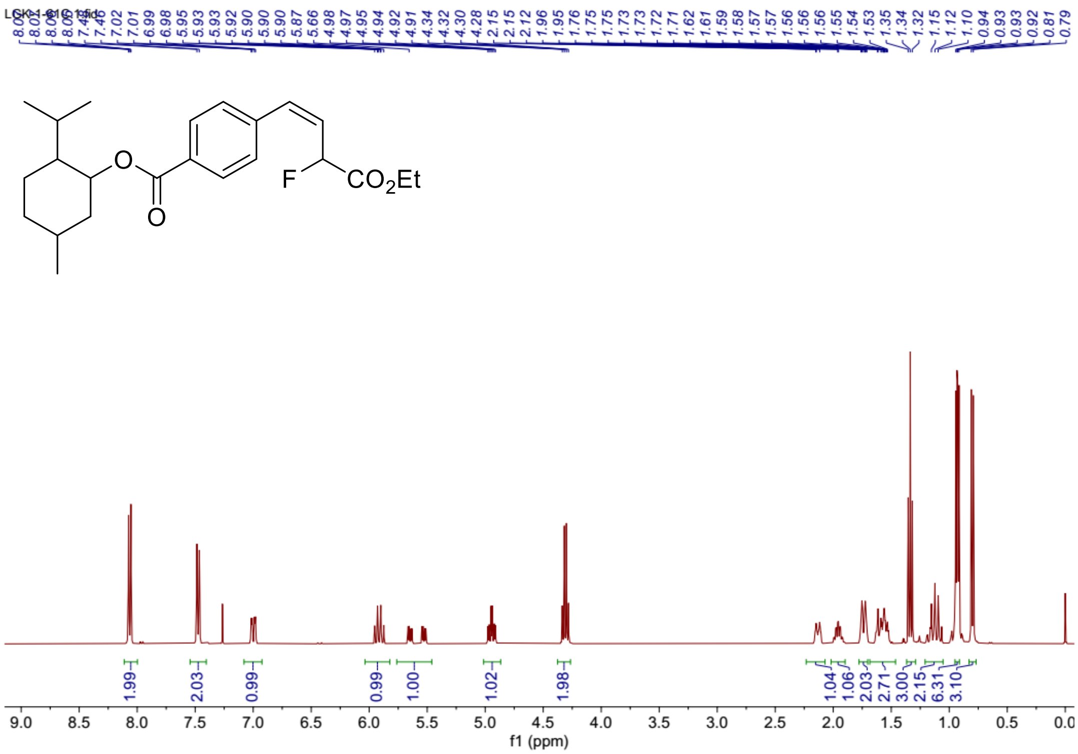
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **38**



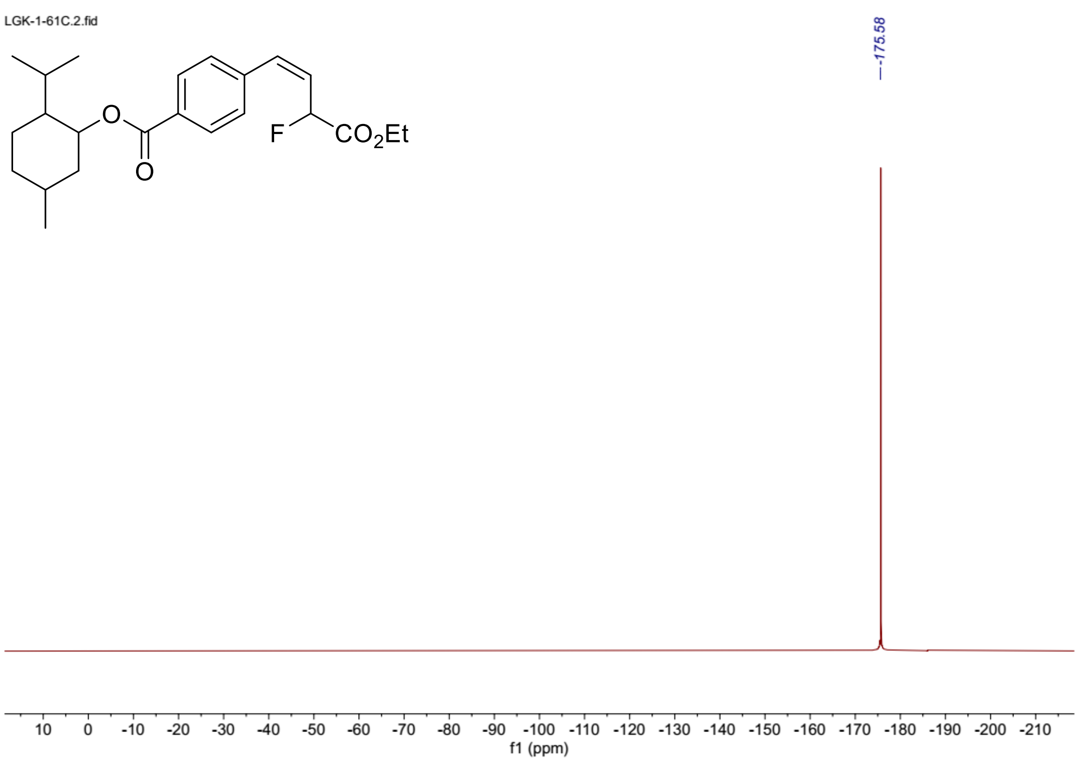
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **38**



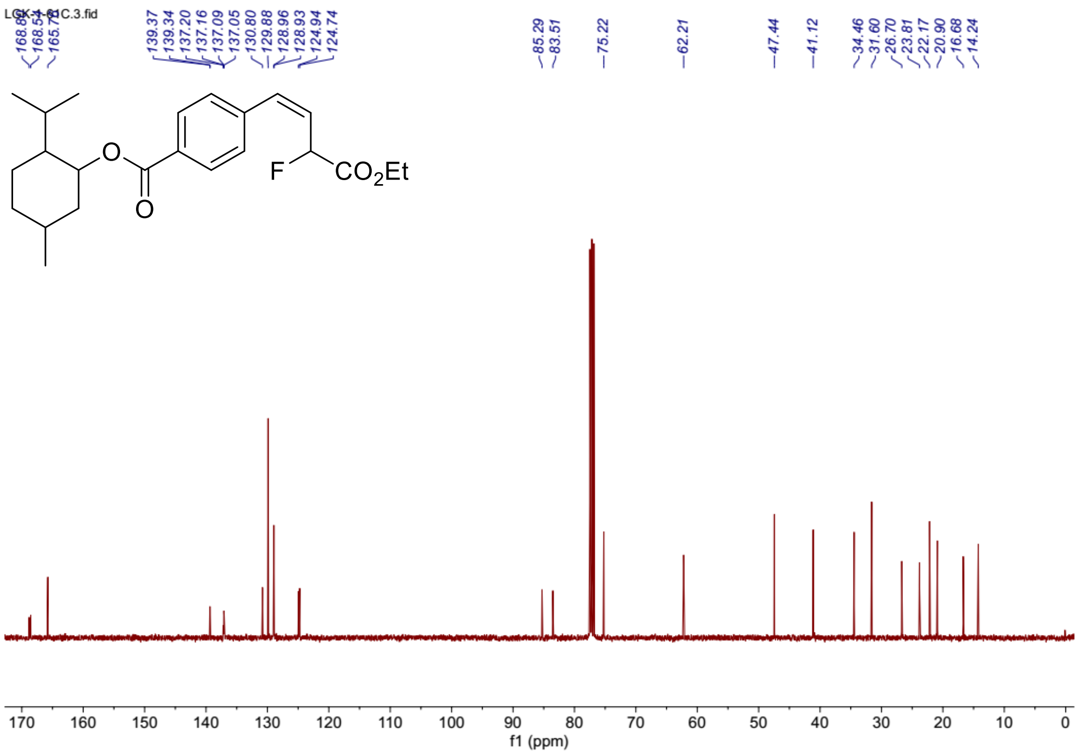
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **39**



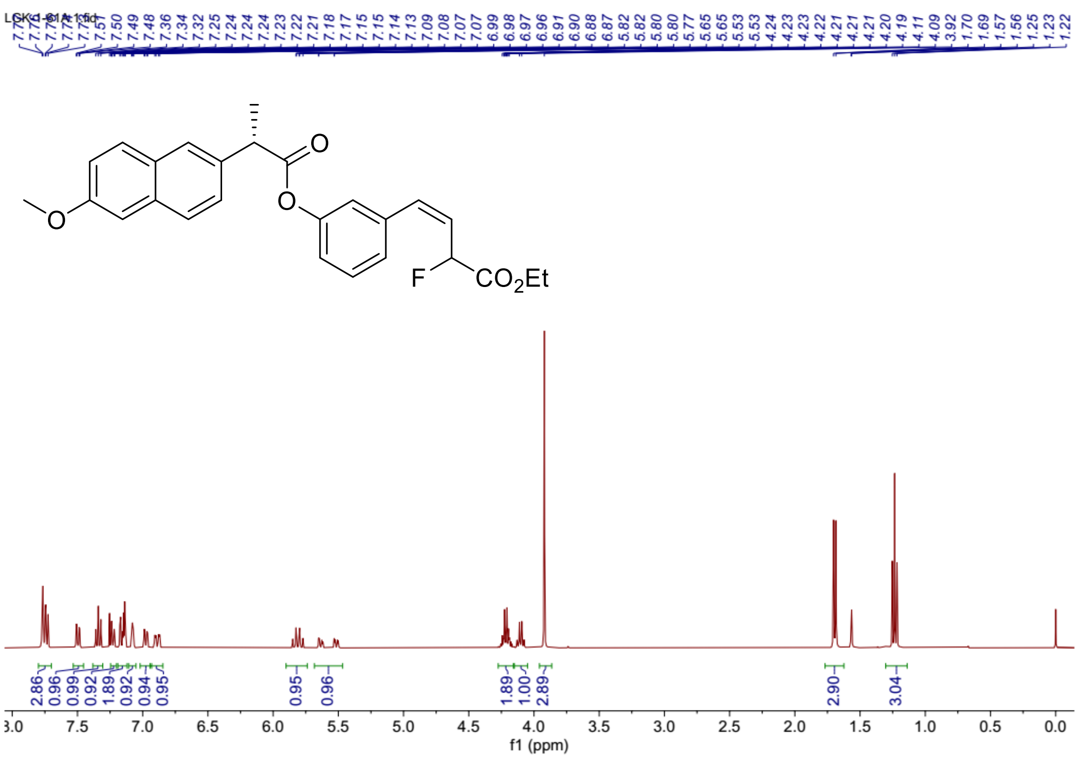
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **39**



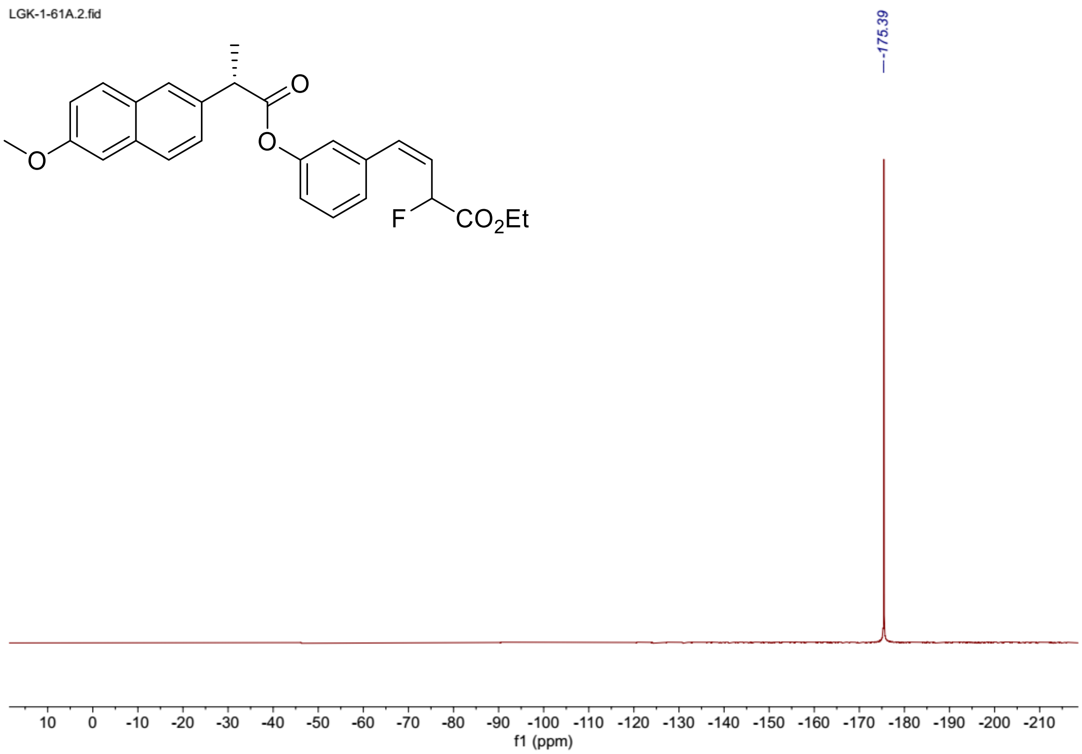
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **39**



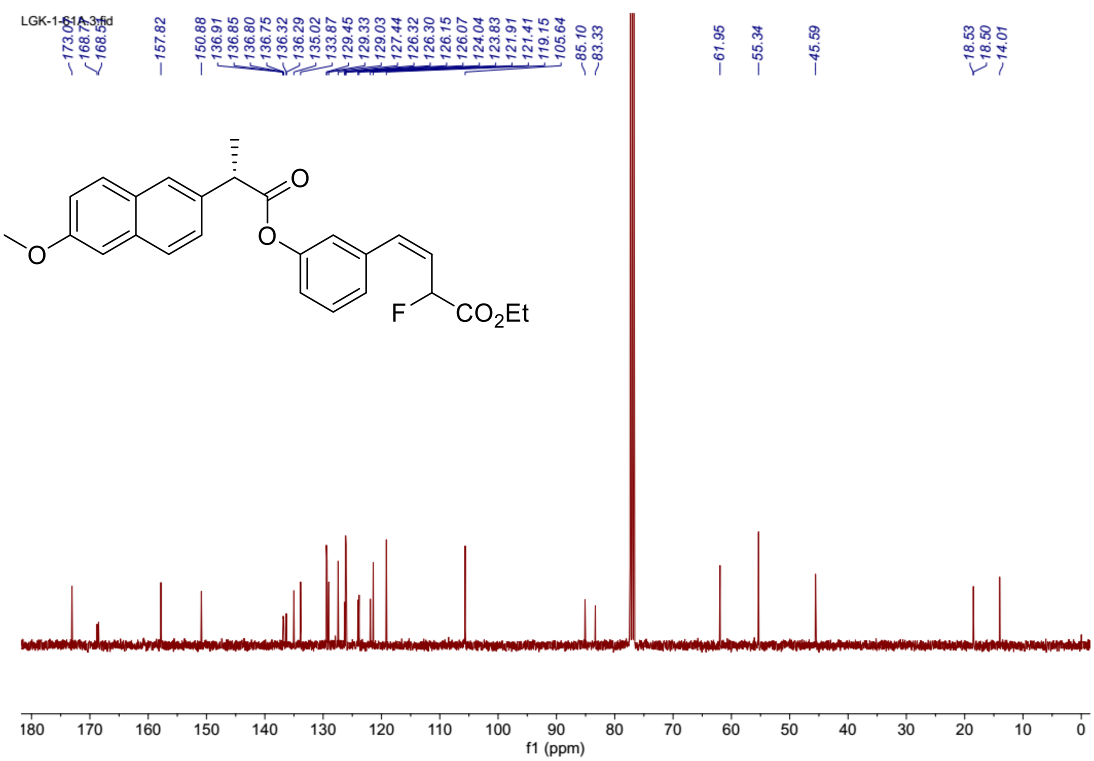
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **40**



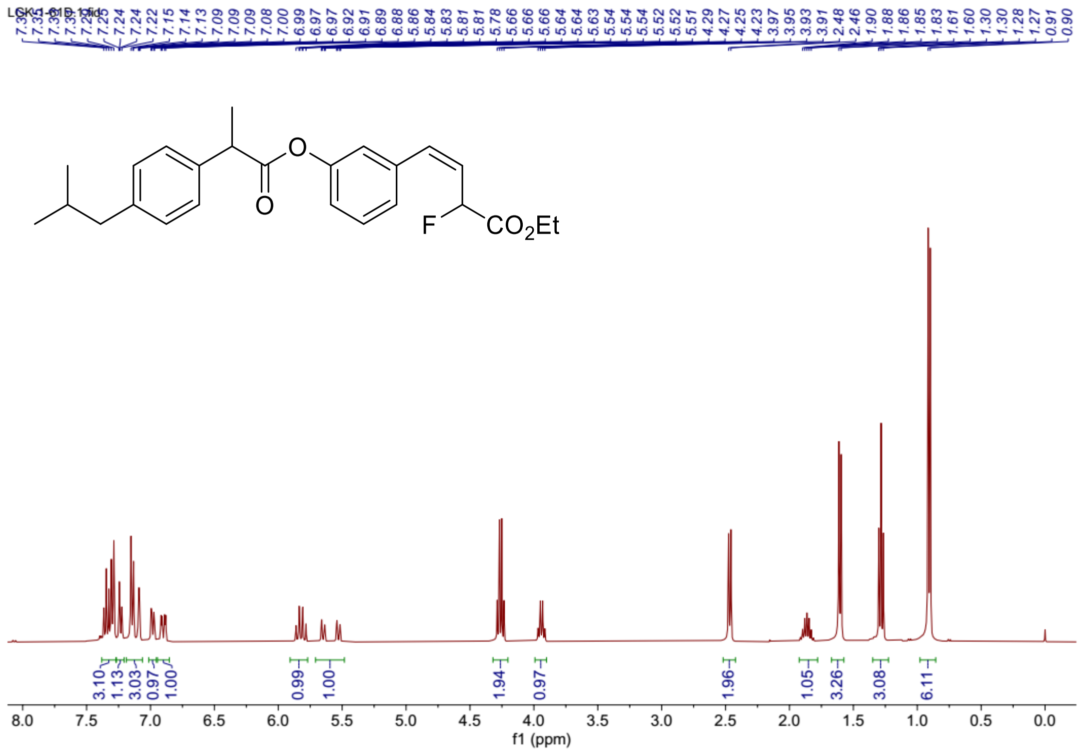
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **40**



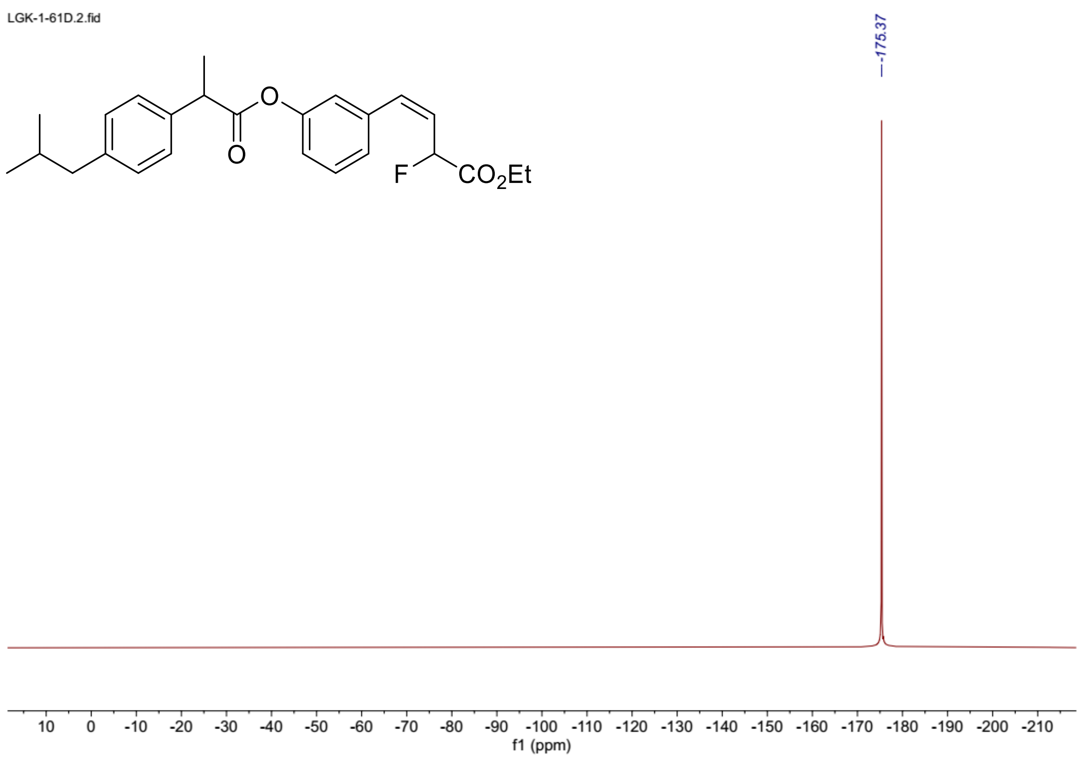
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **40**



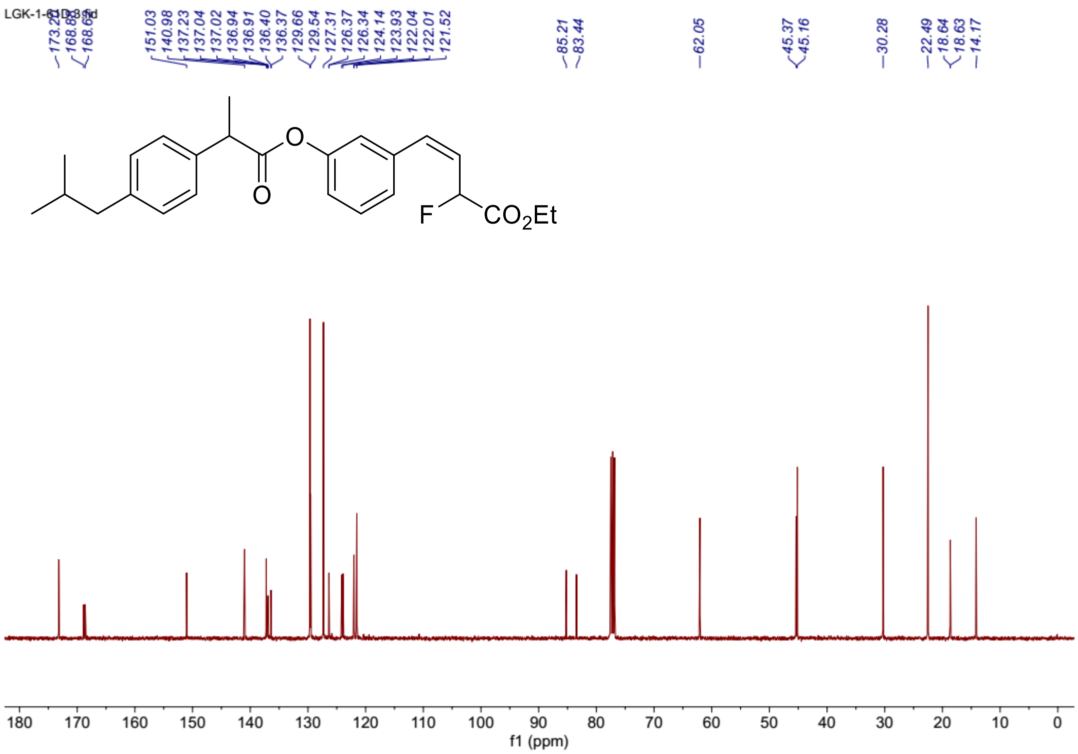
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **41**



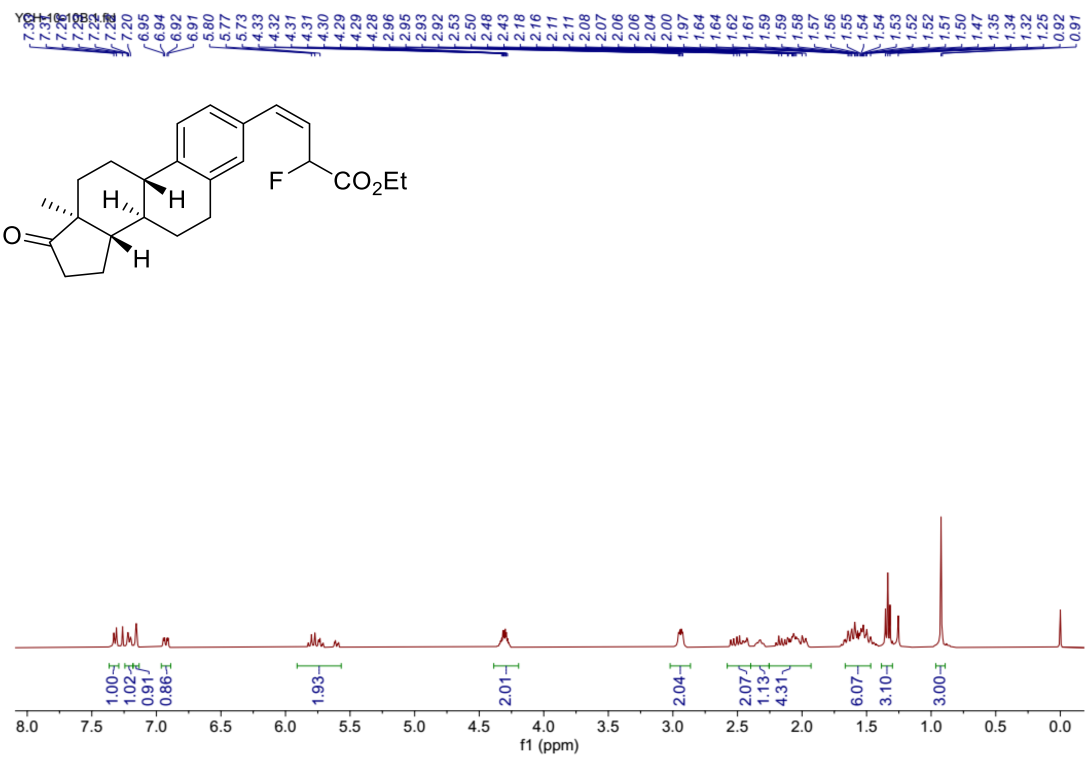
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **41**



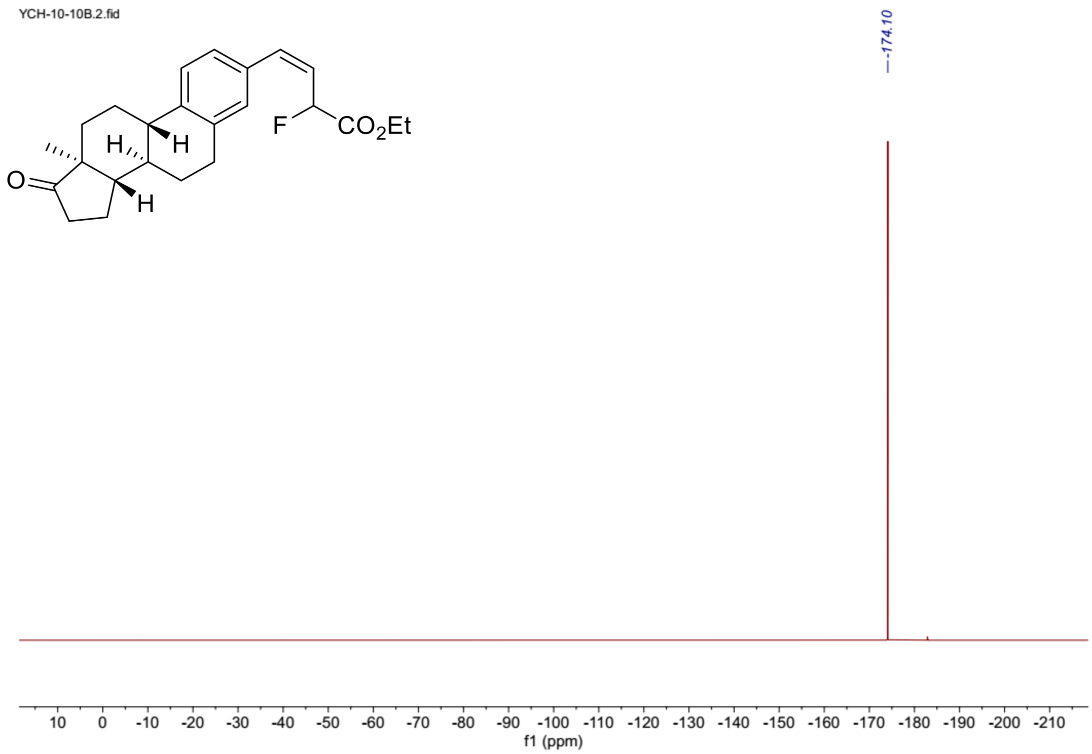
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **41**



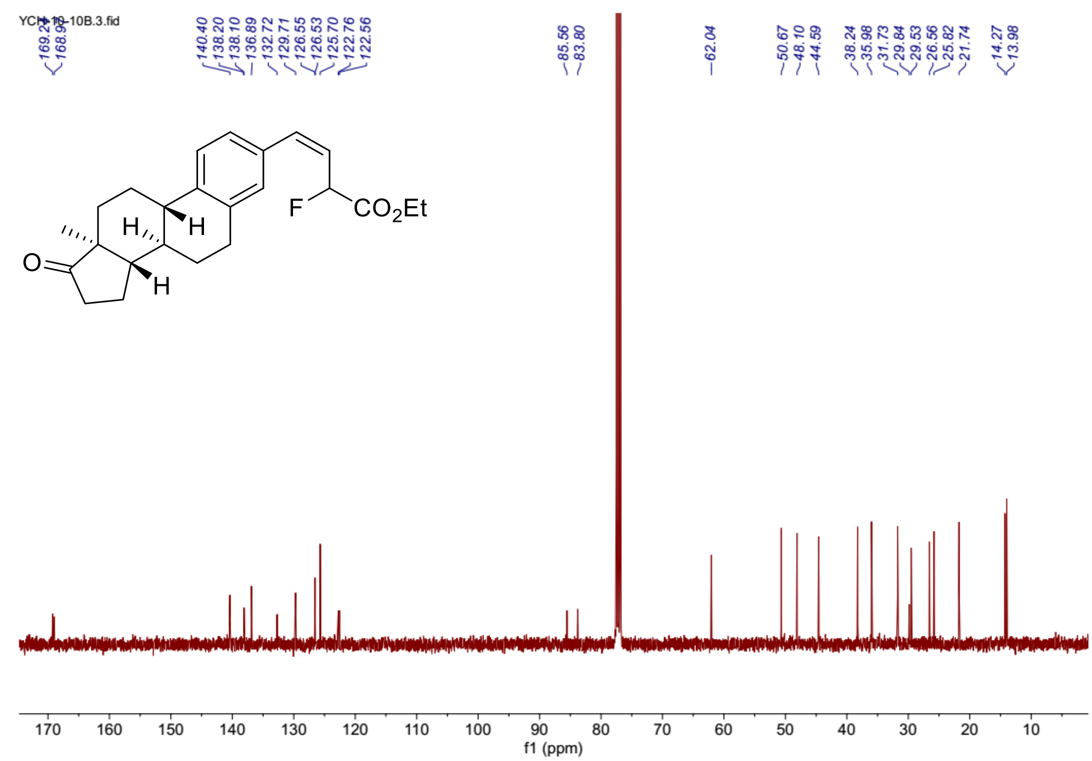
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **42**



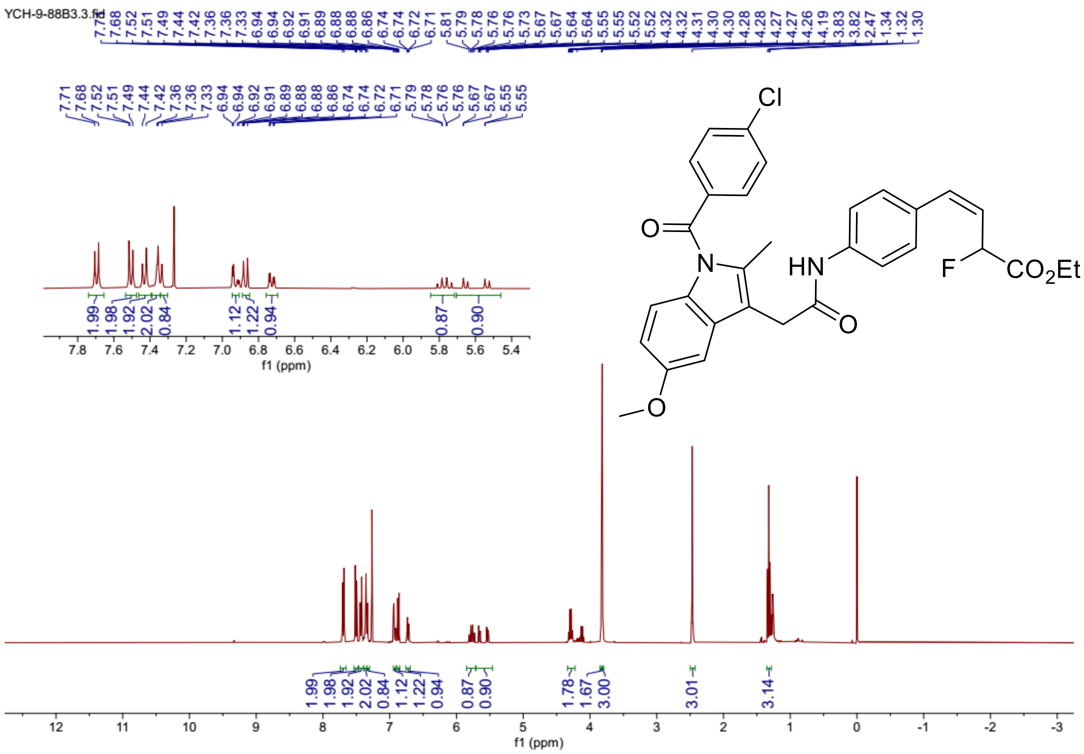
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **42**



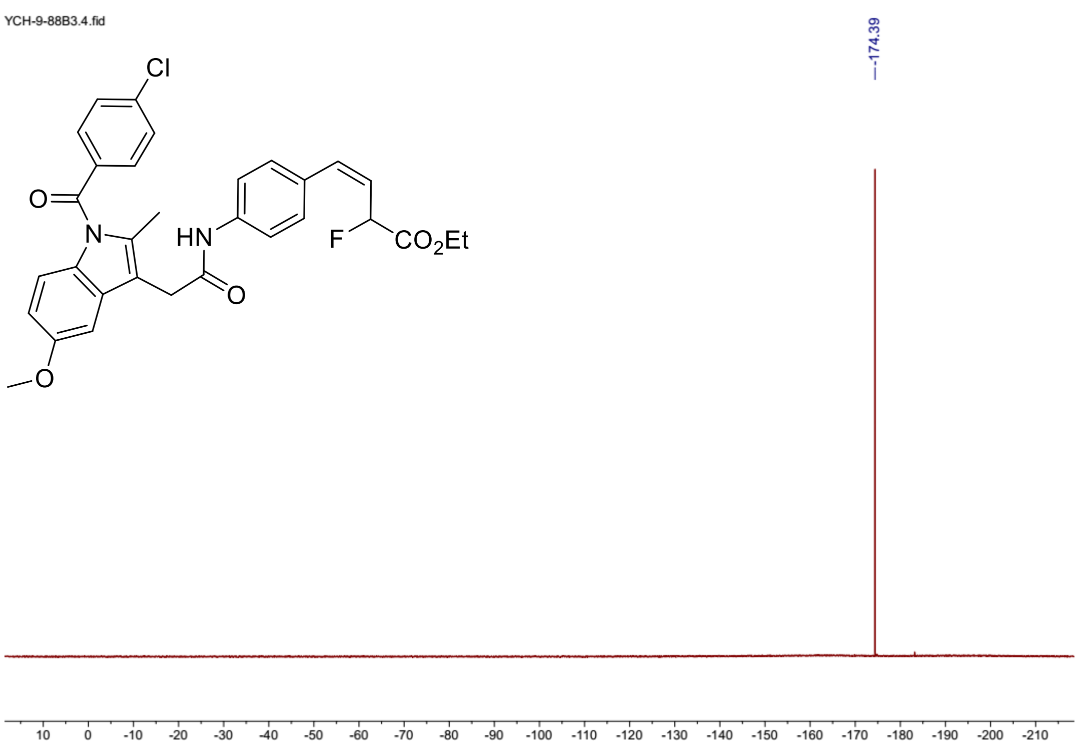
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **42**



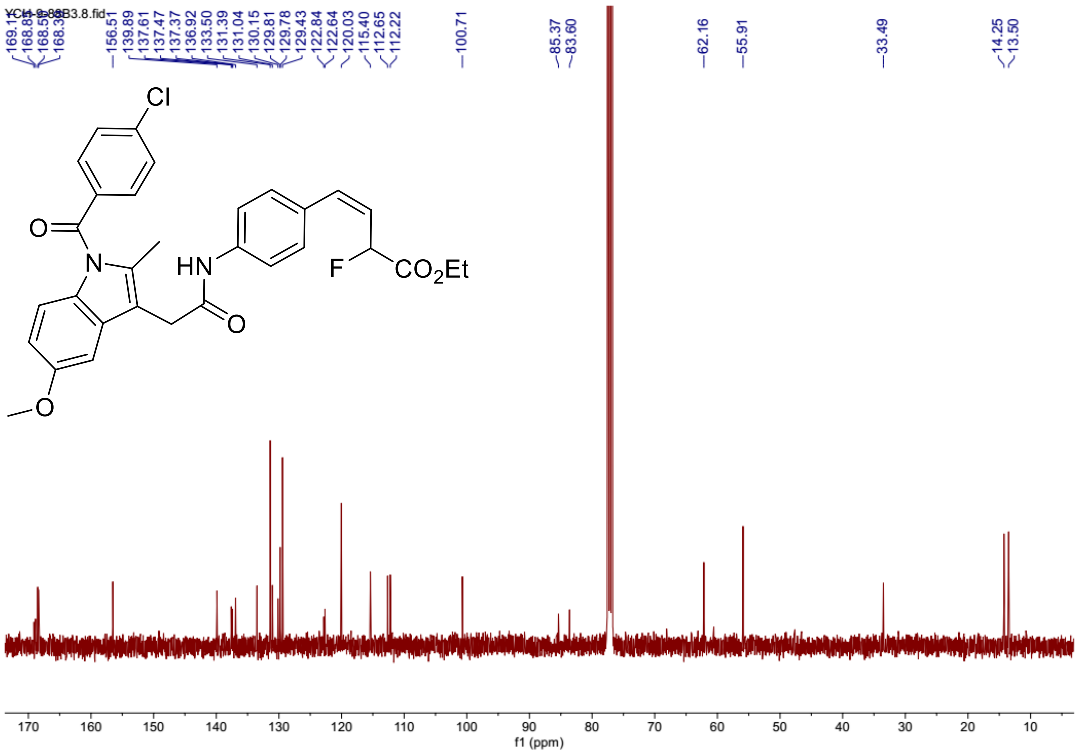
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **43**



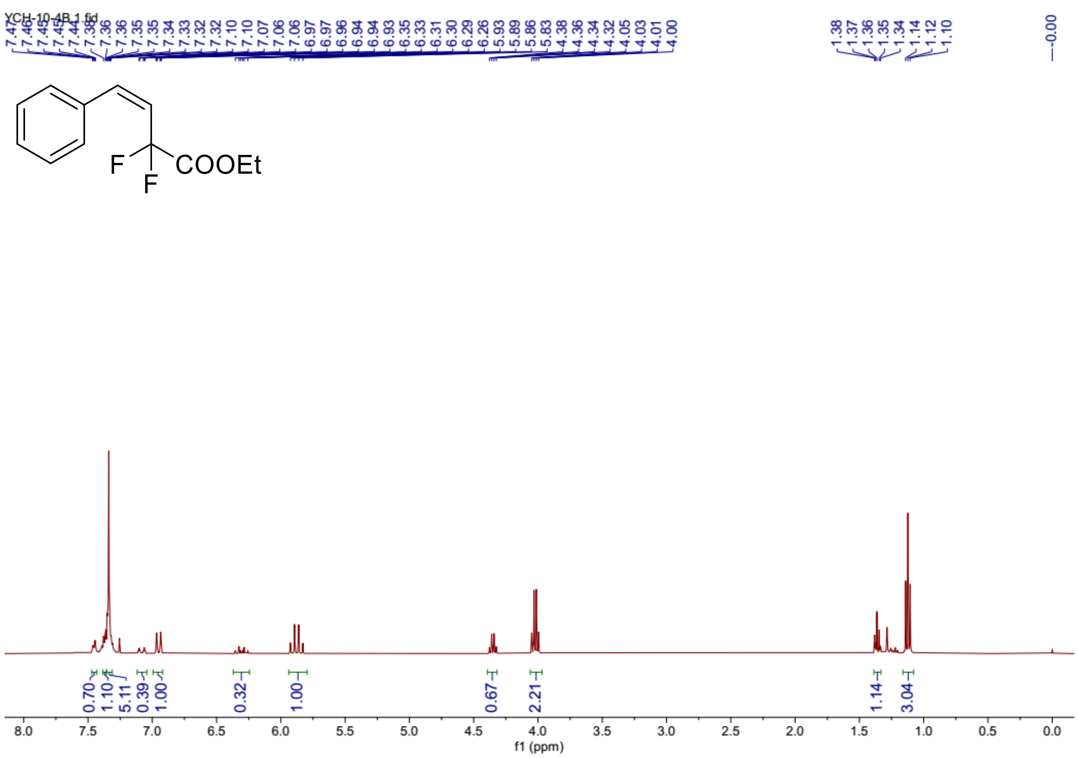
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **43**



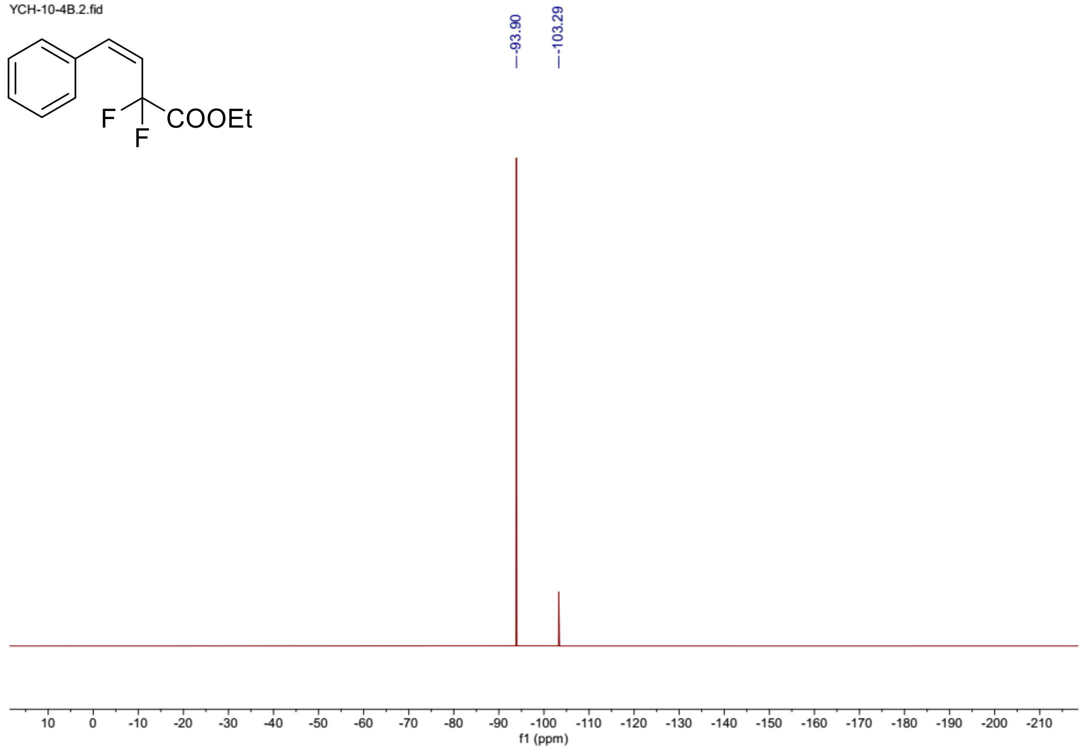
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **43**



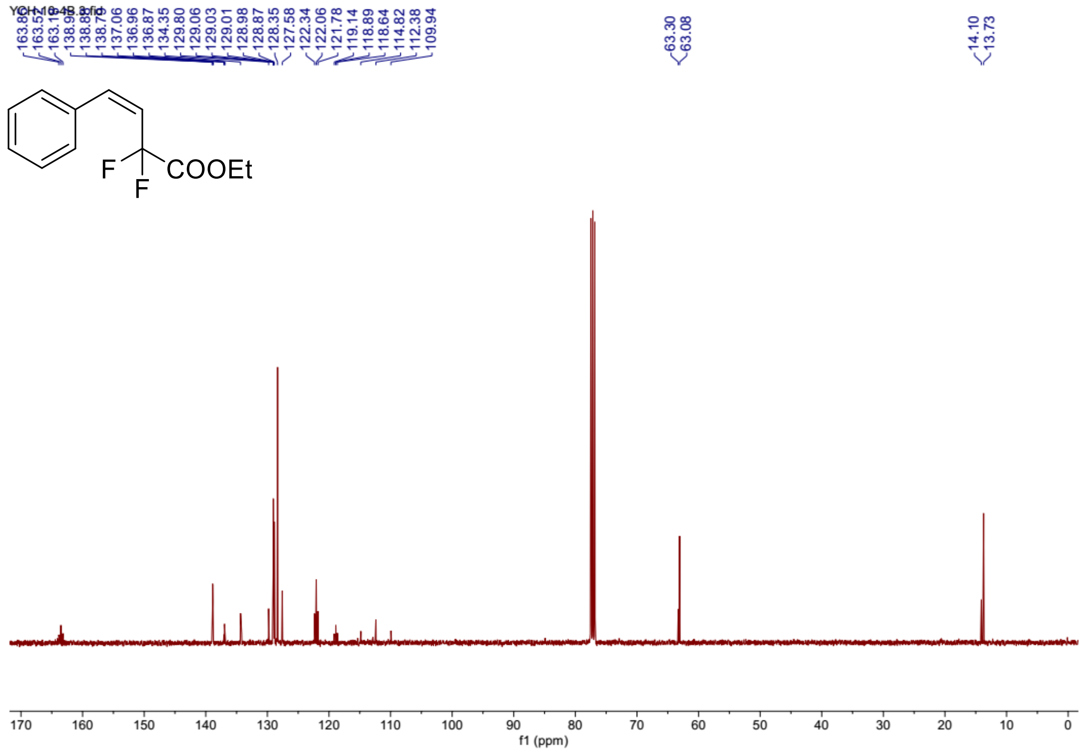
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **44**



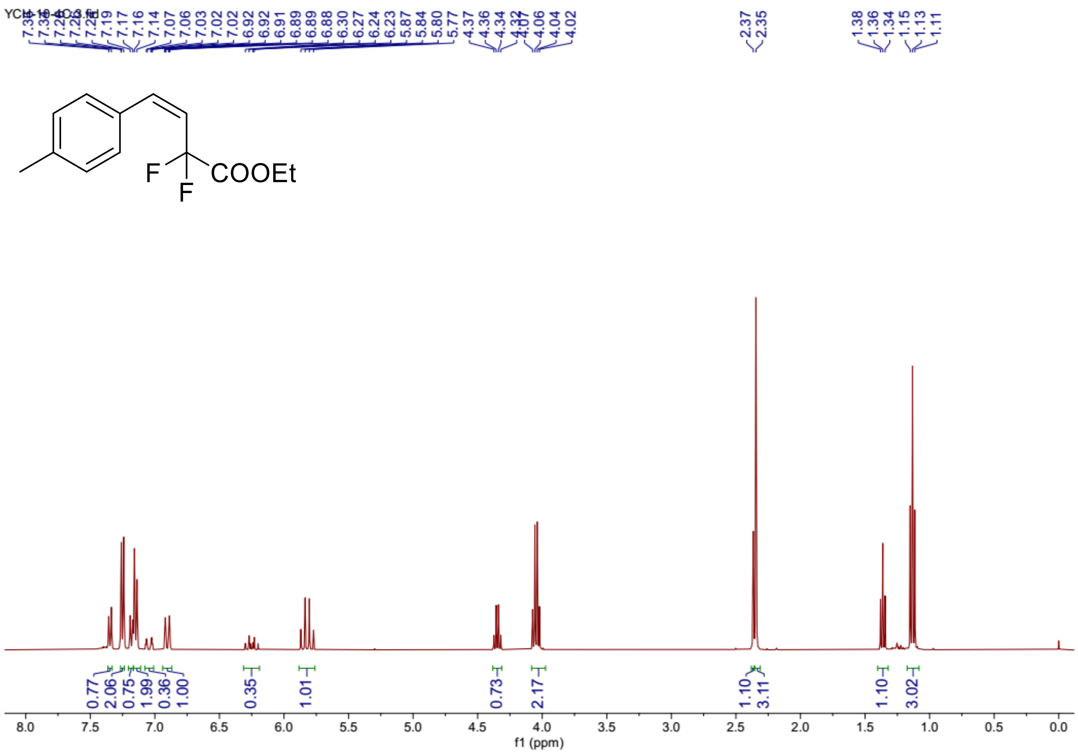
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **44**



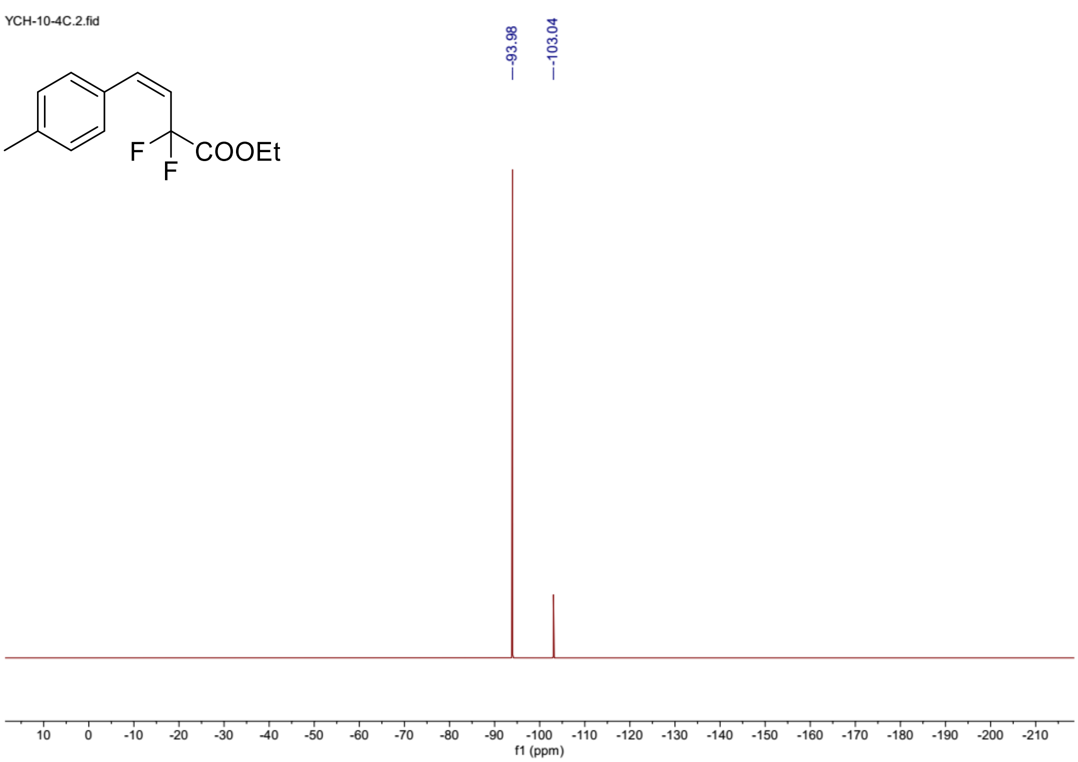
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **44**



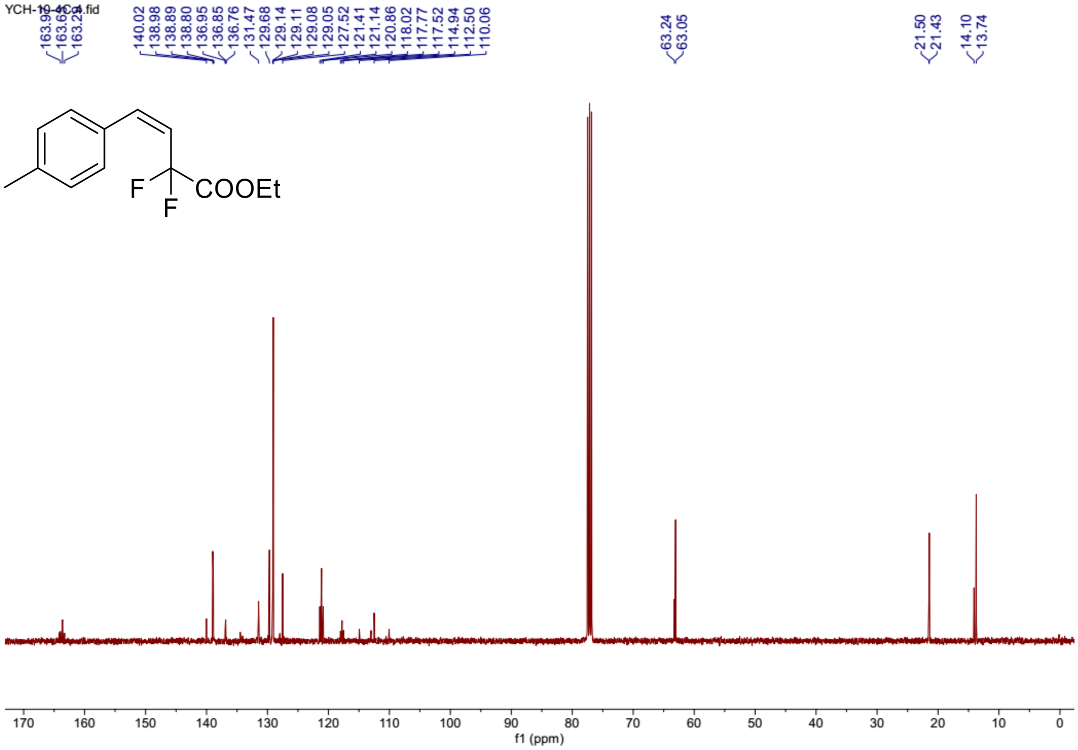
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **45**



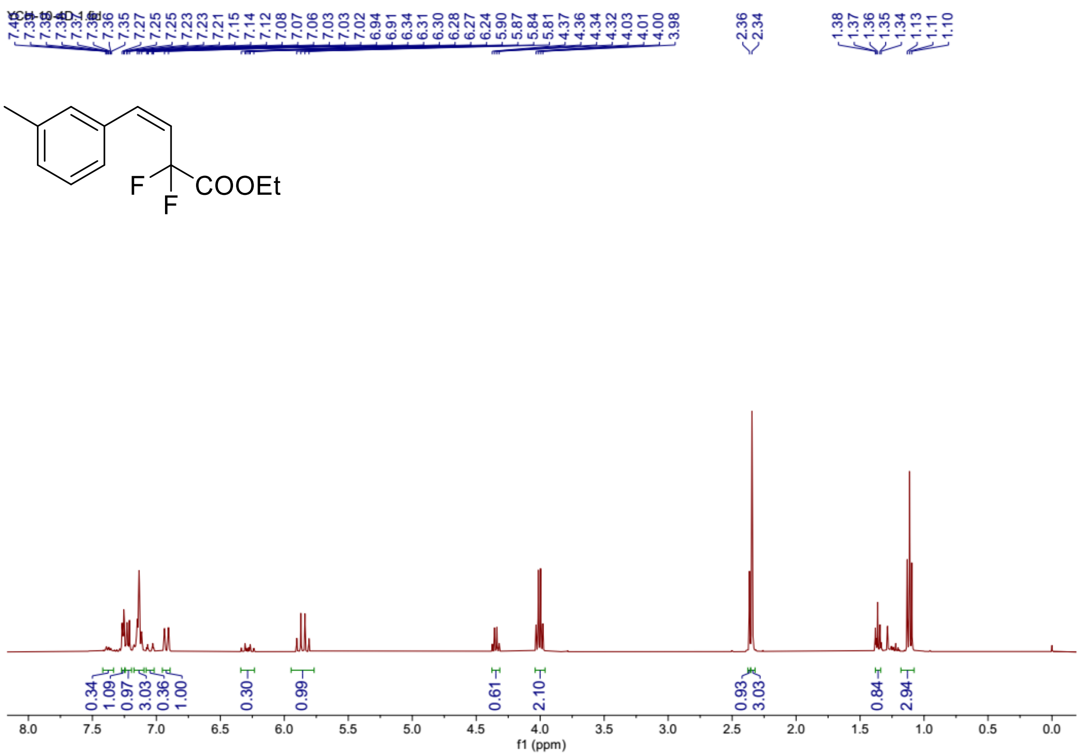
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **45**



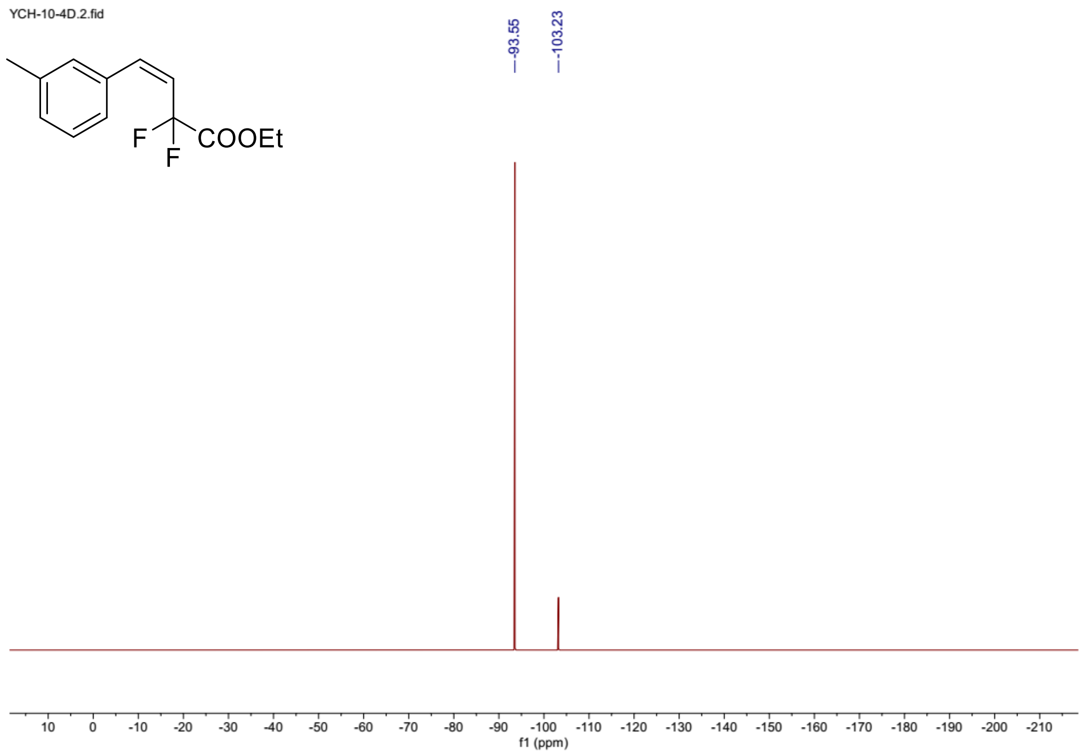
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **45**



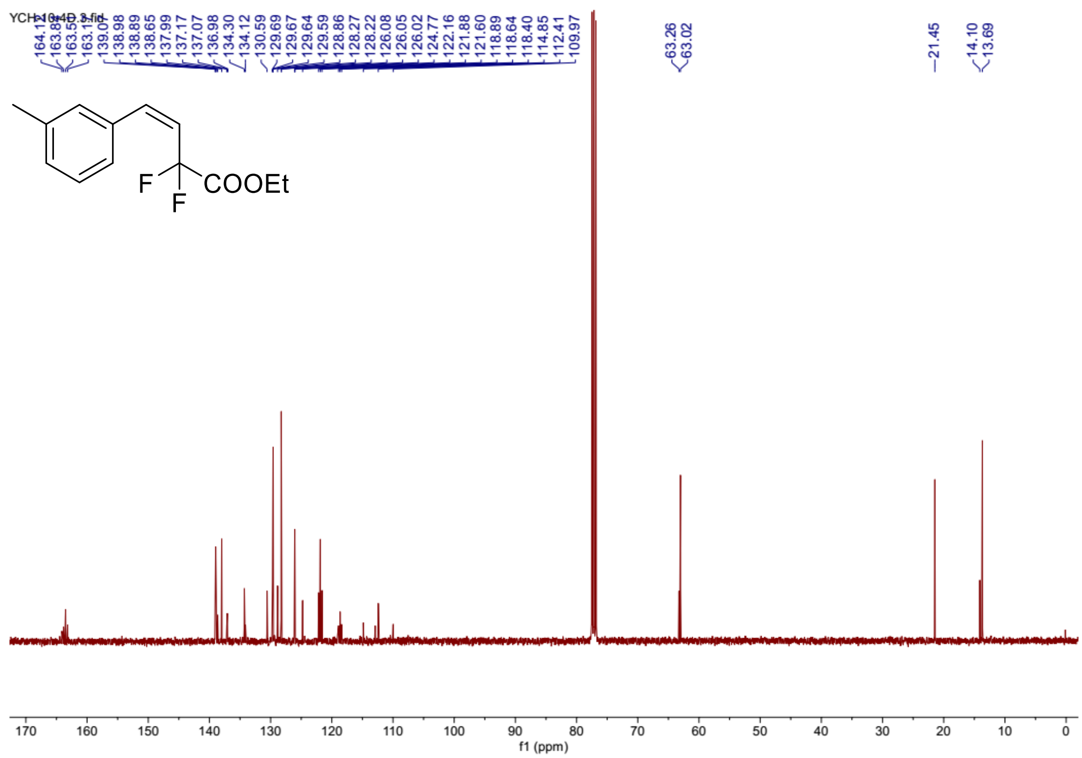
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **46**



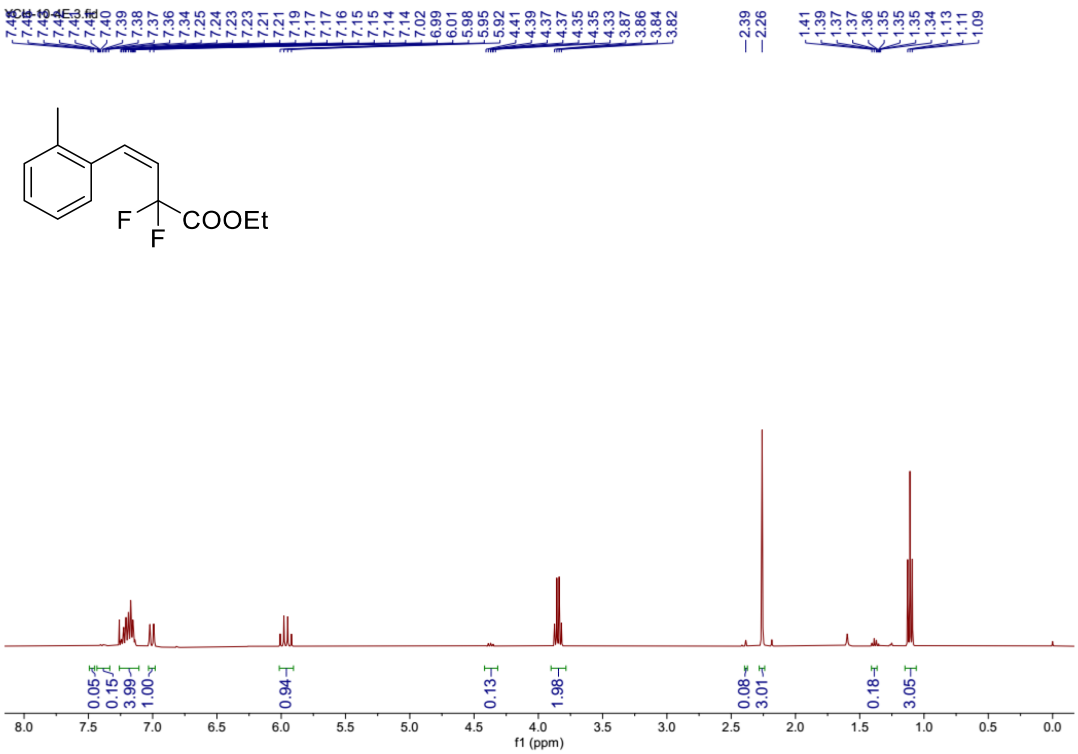
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **46**



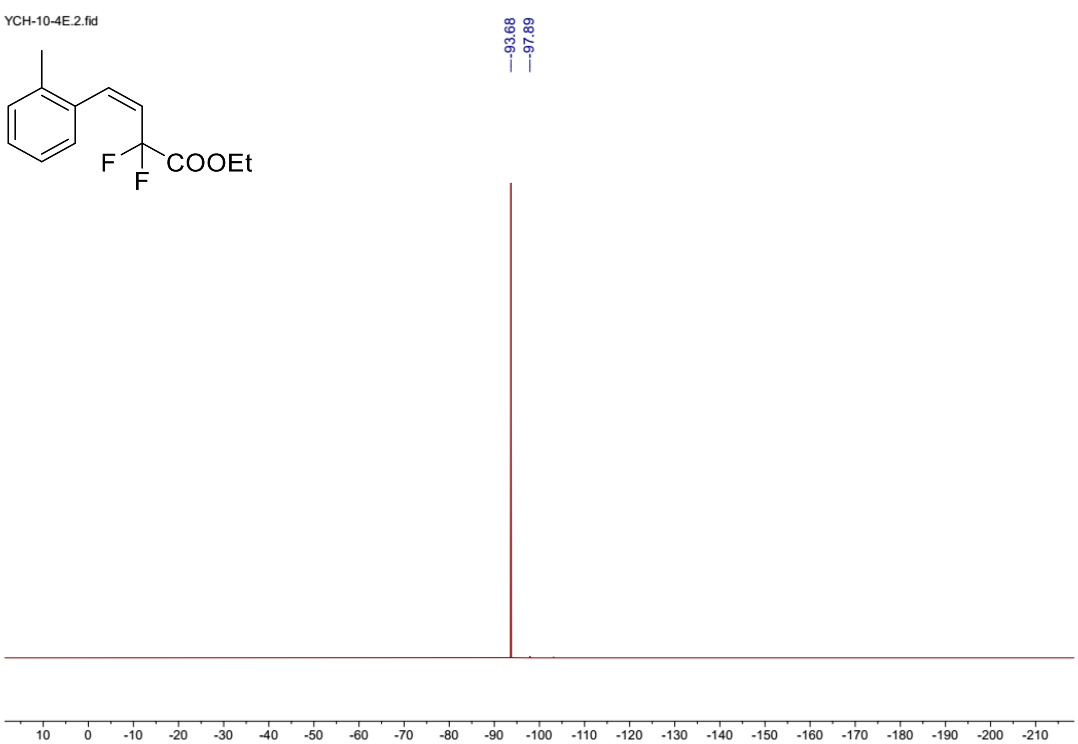
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **46**



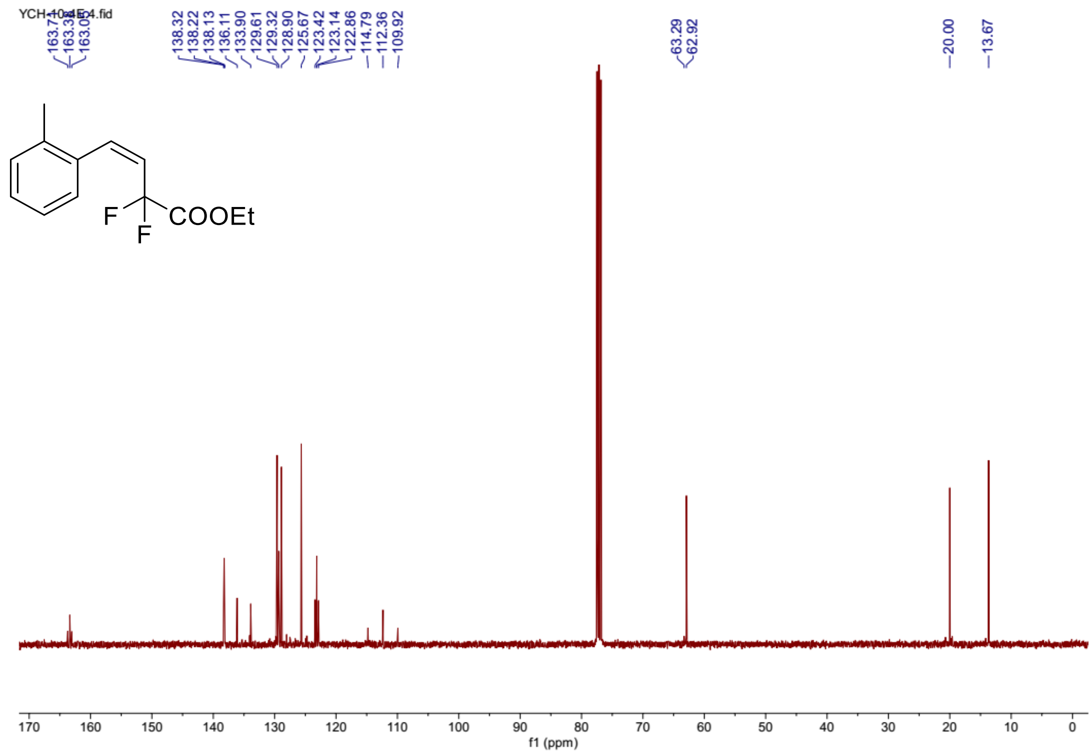
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **47**



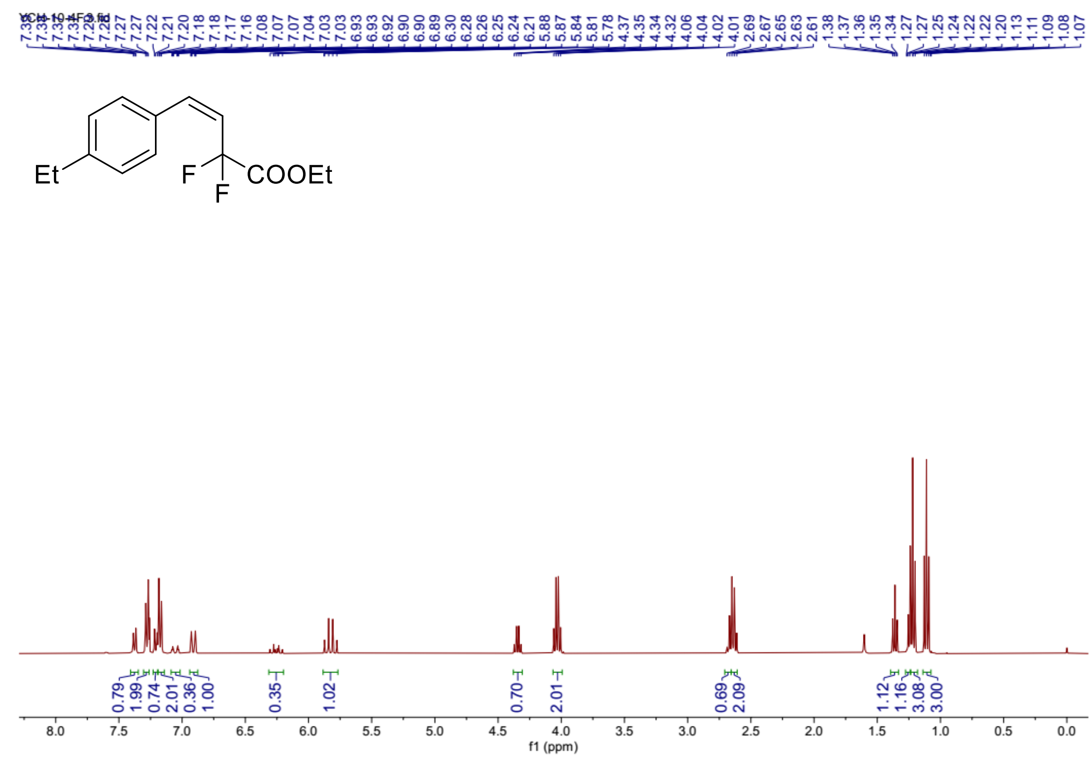
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **47**



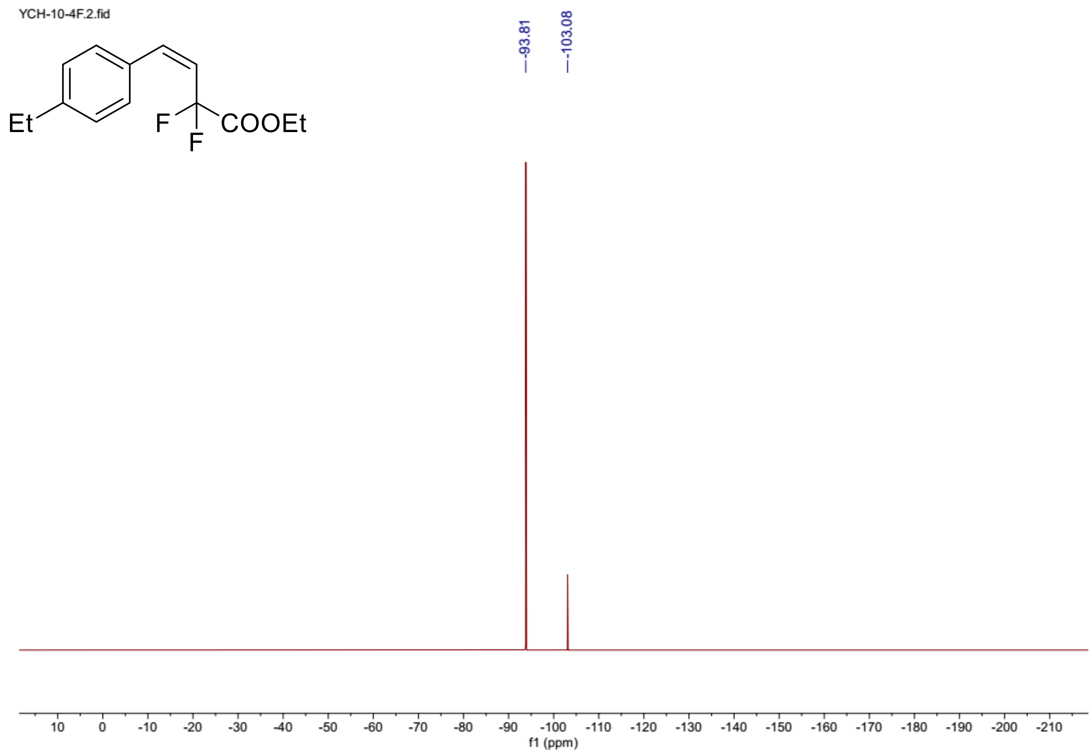
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **47**



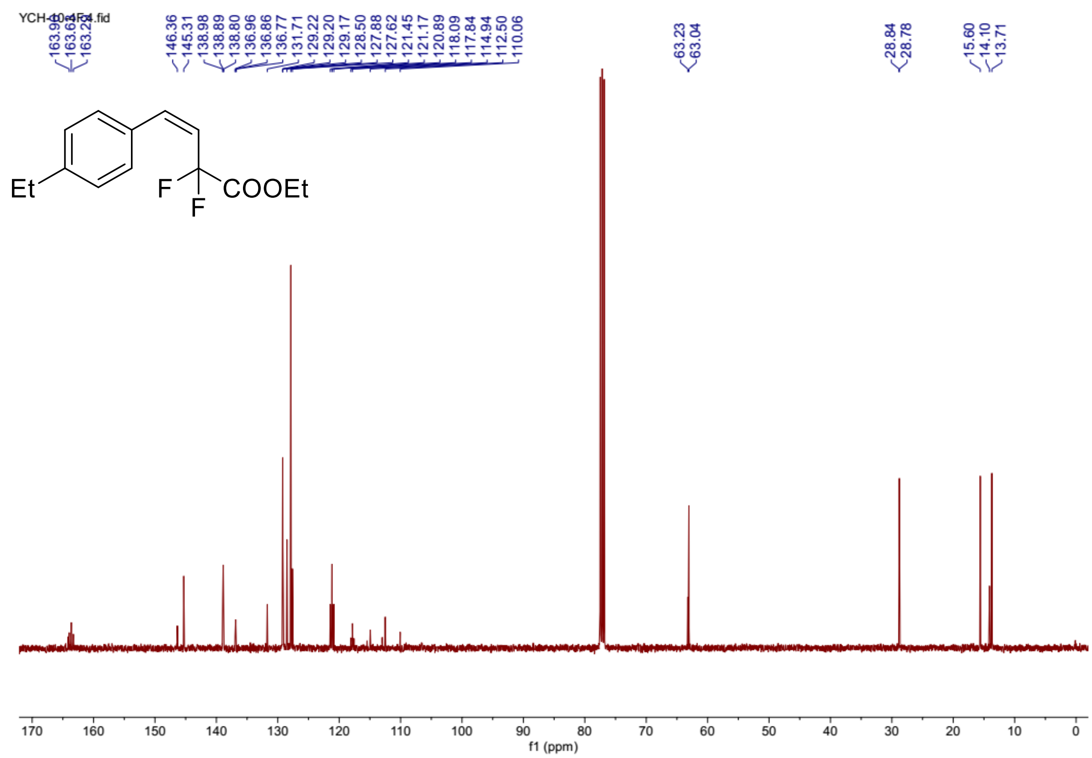
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **48**



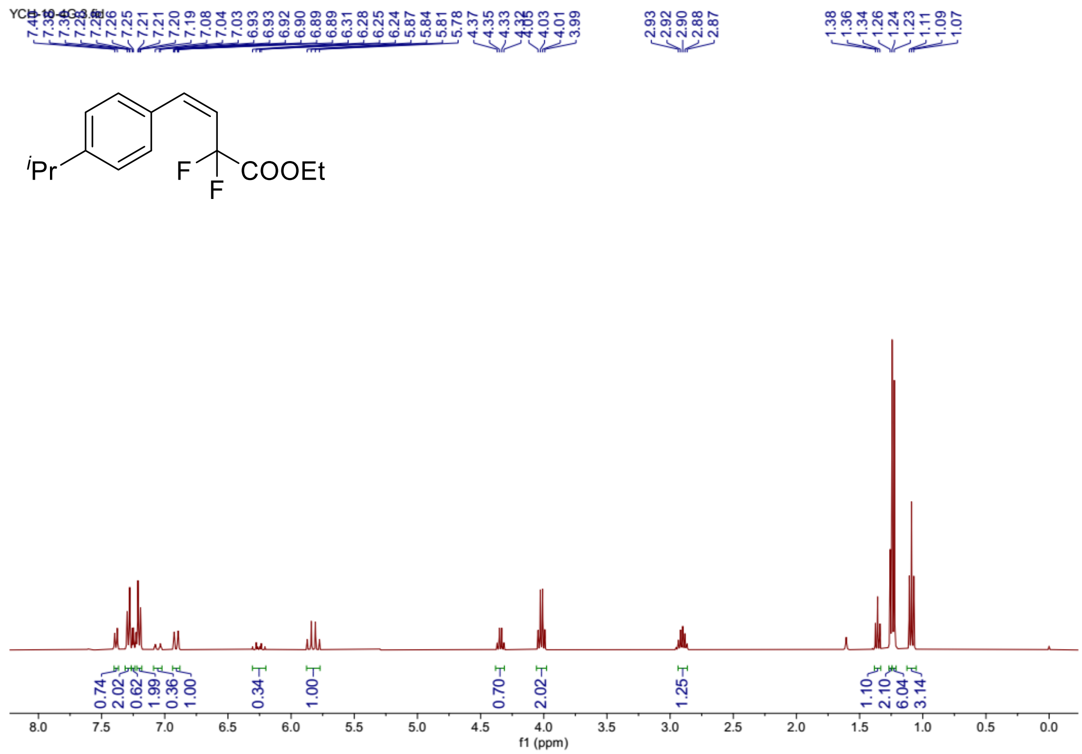
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **48**



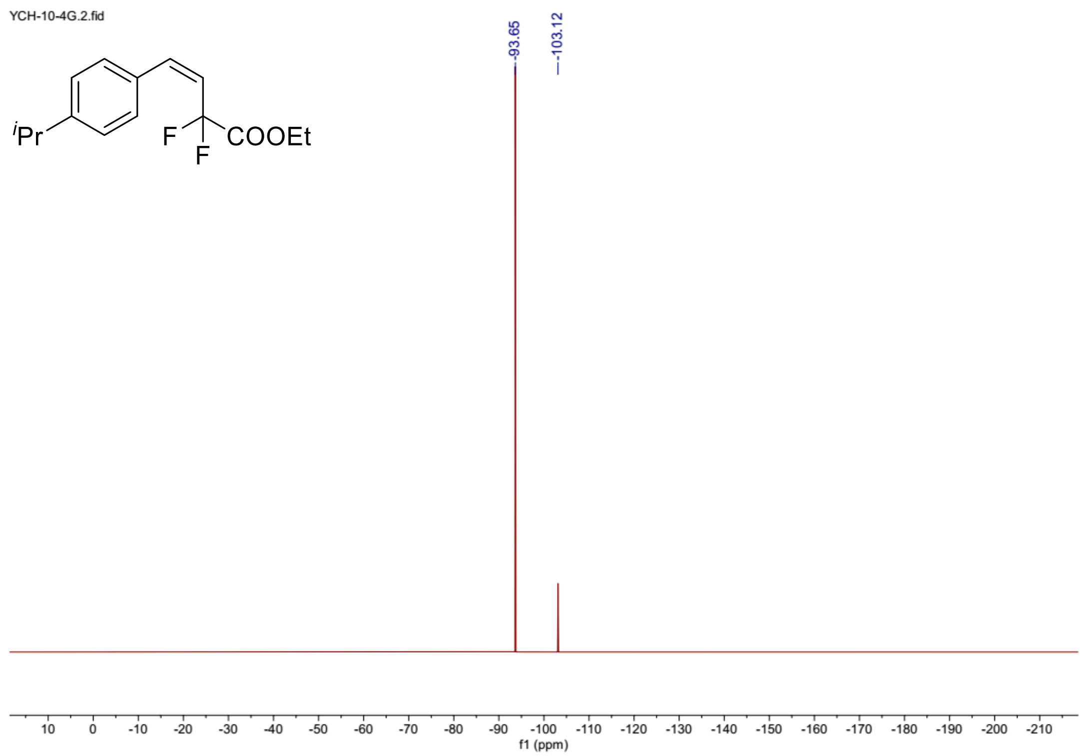
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **48**



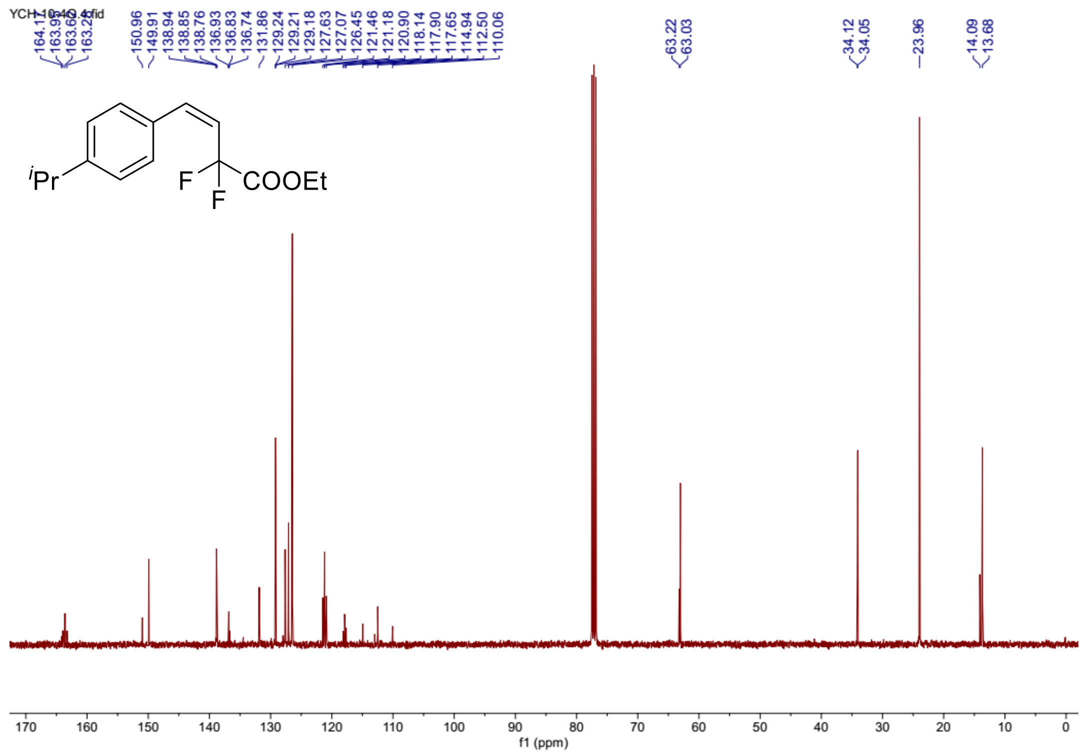
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **49**



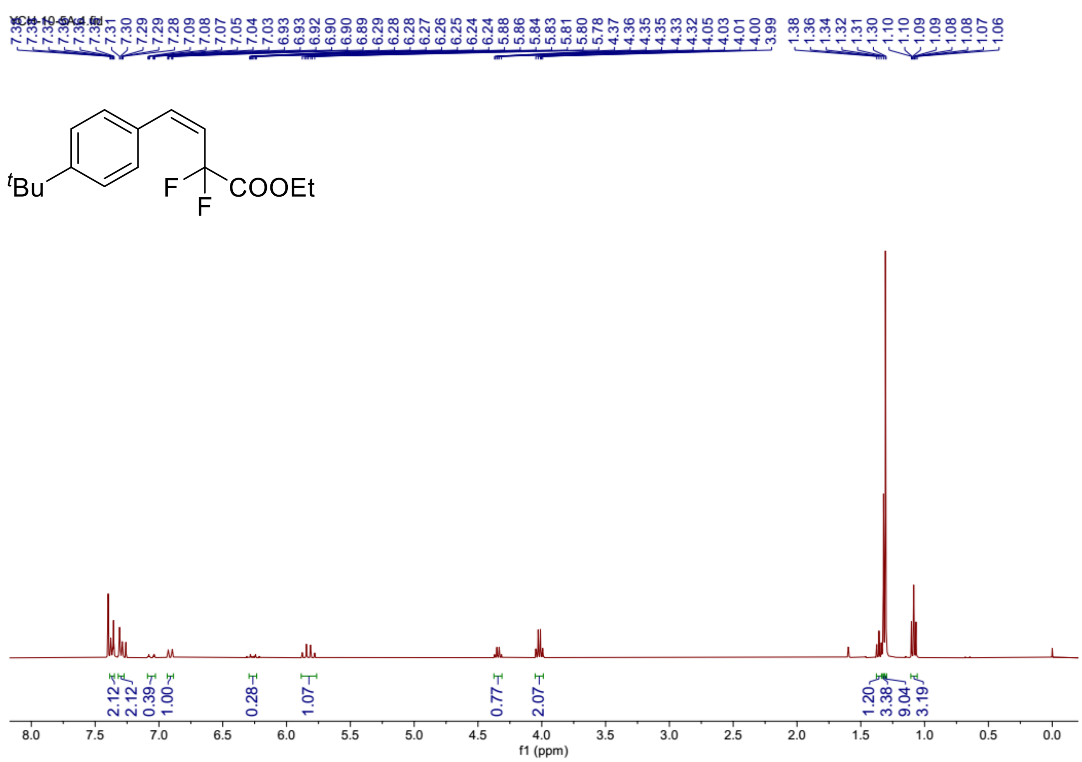
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **49**



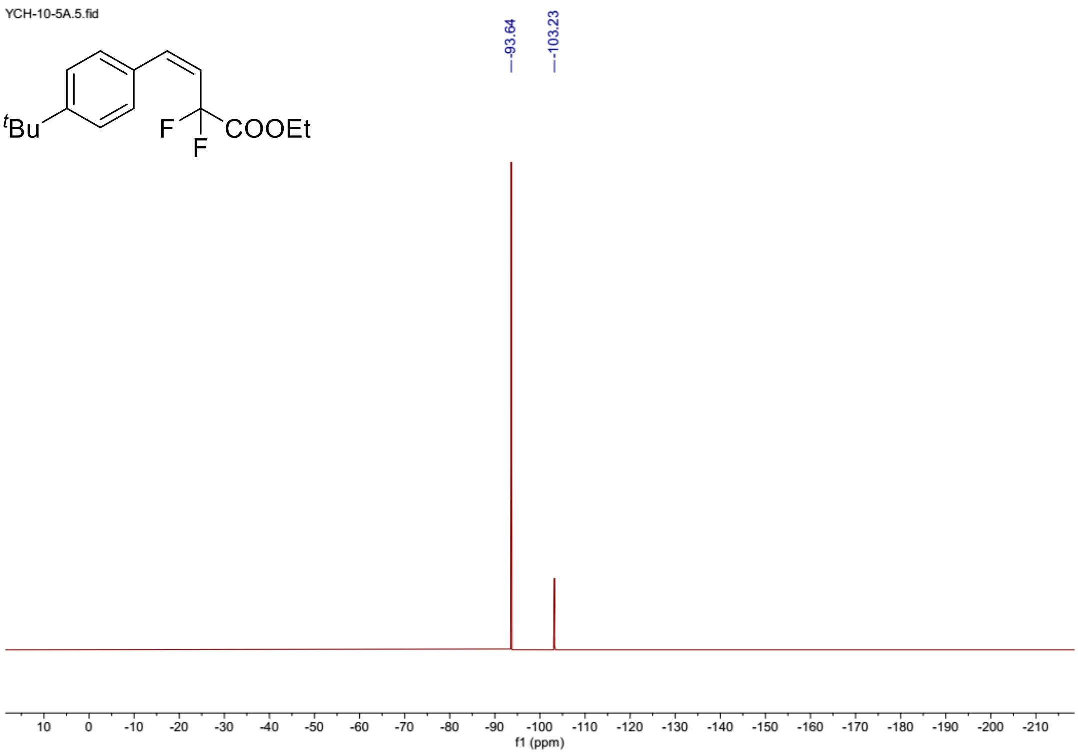
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **49**



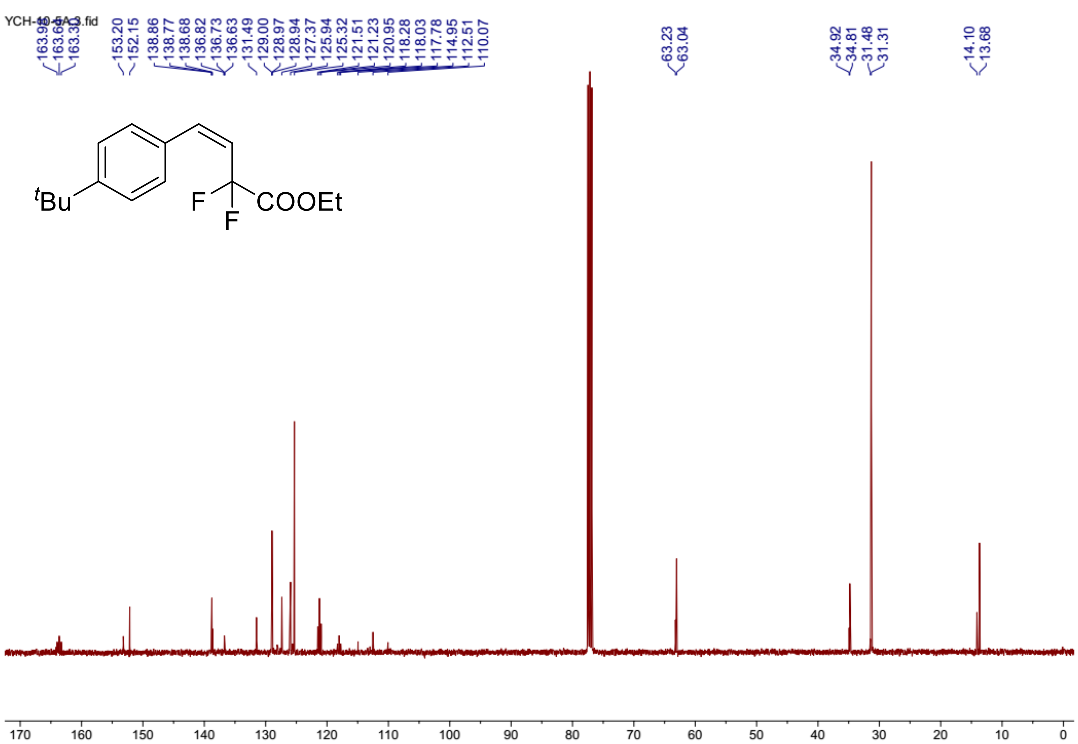
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **50**



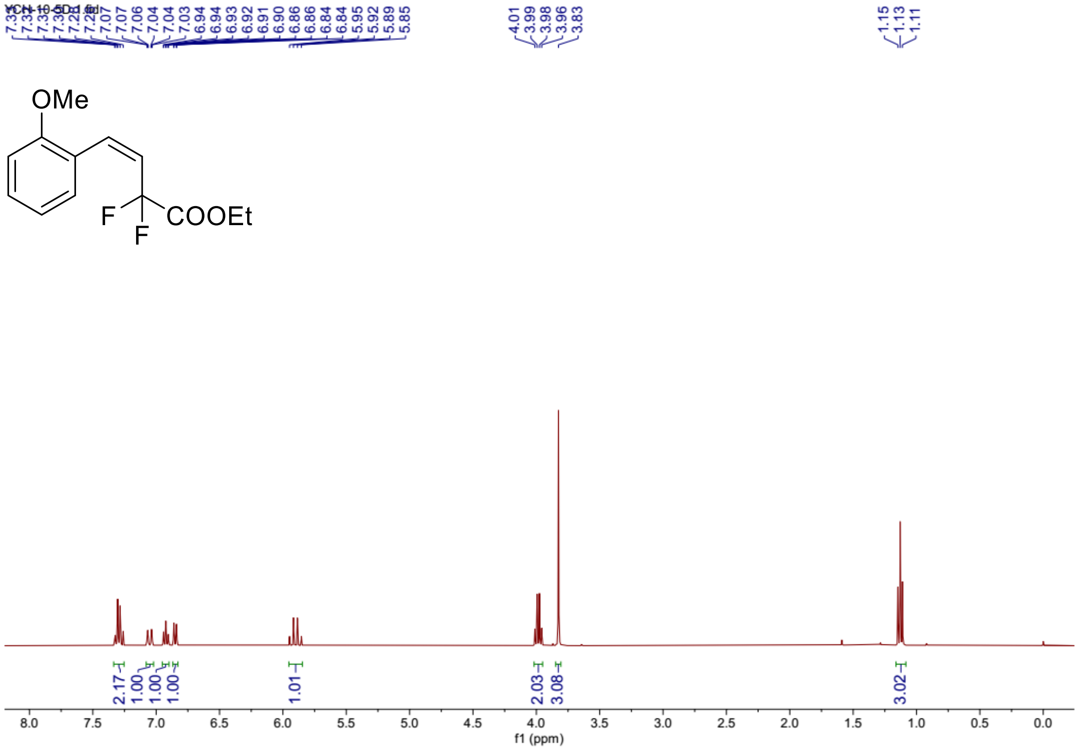
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **50**



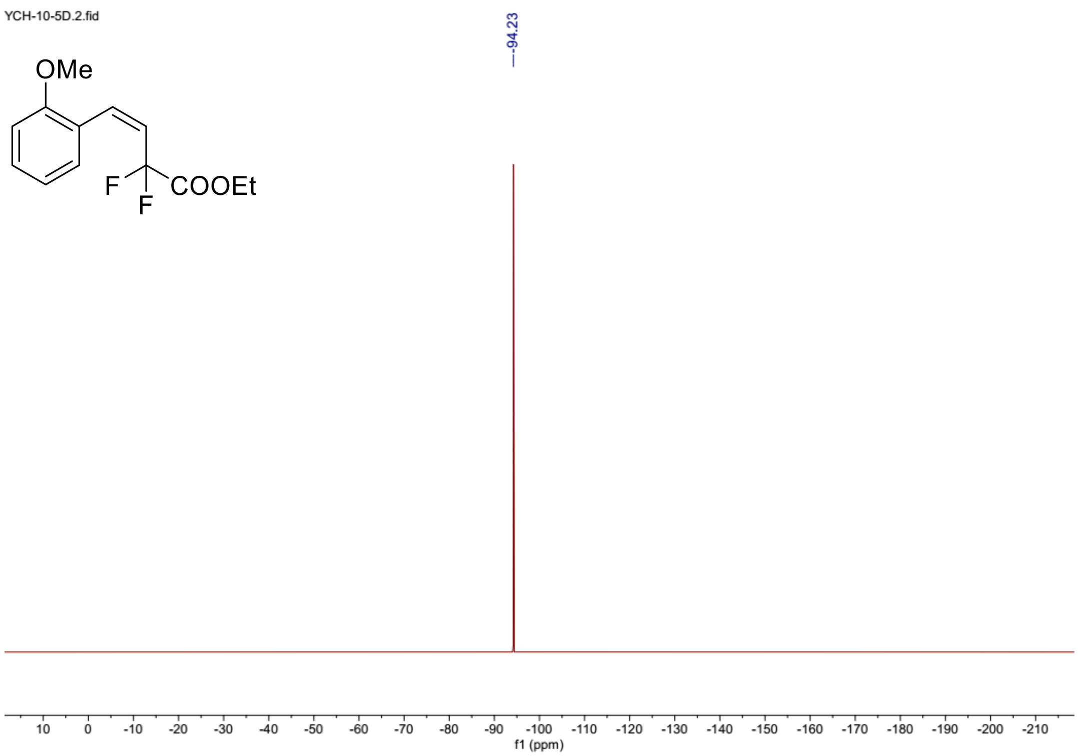
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **50**



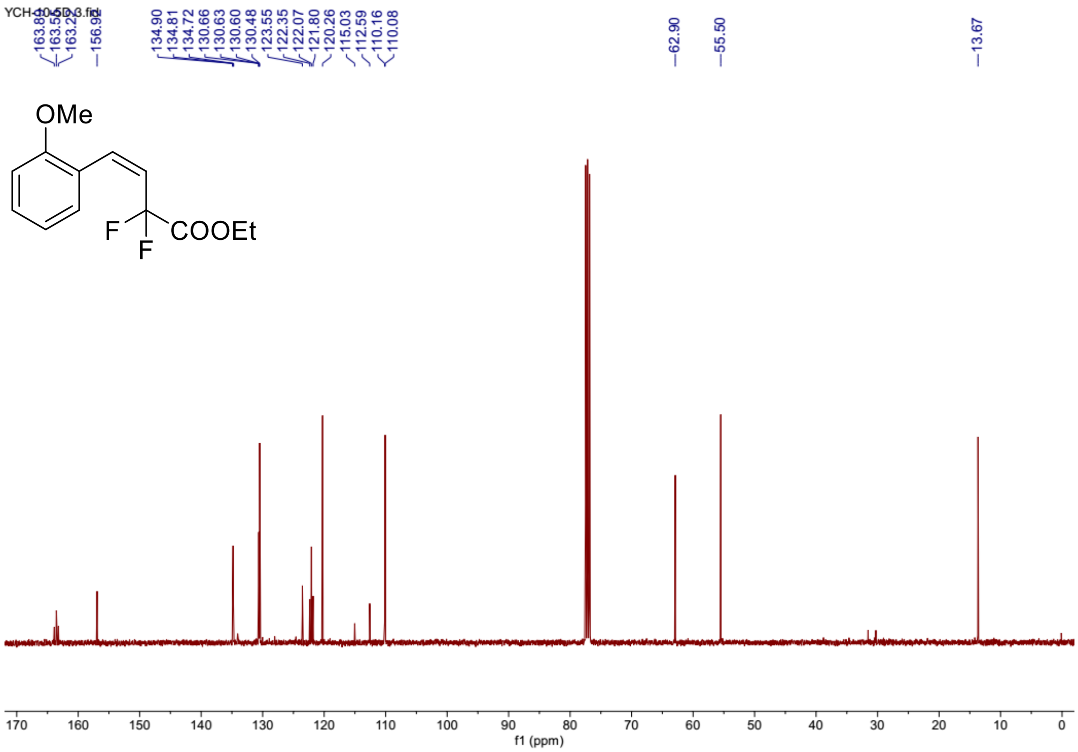
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **51**



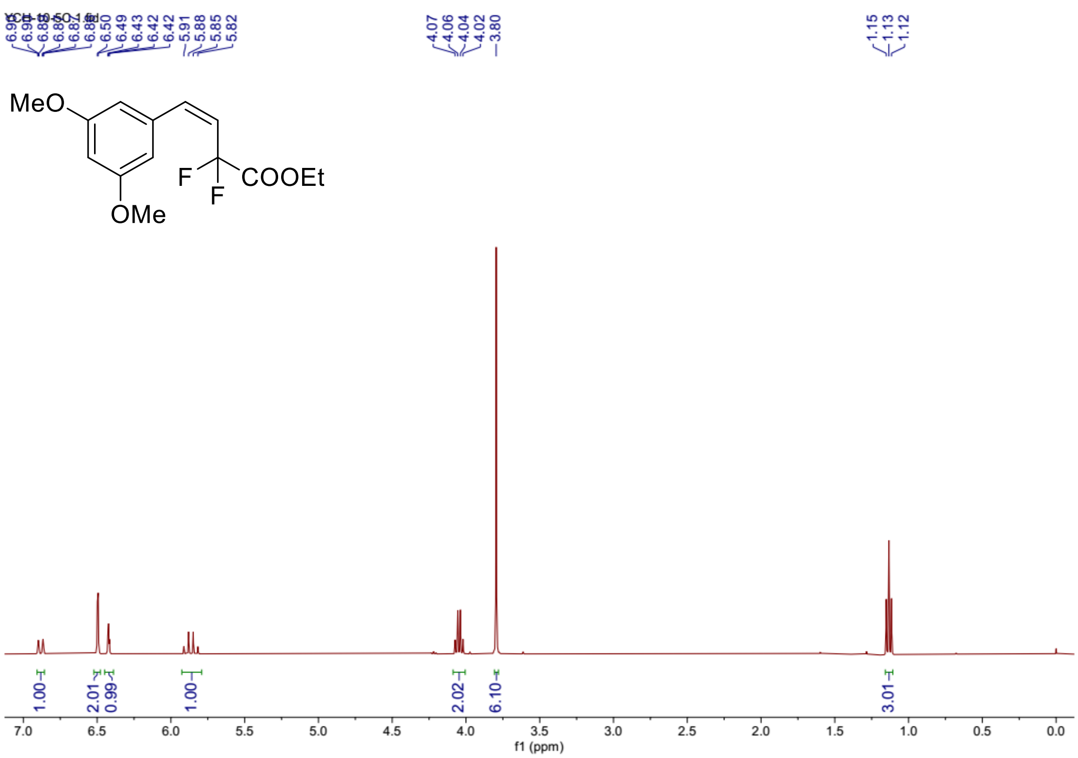
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **51**



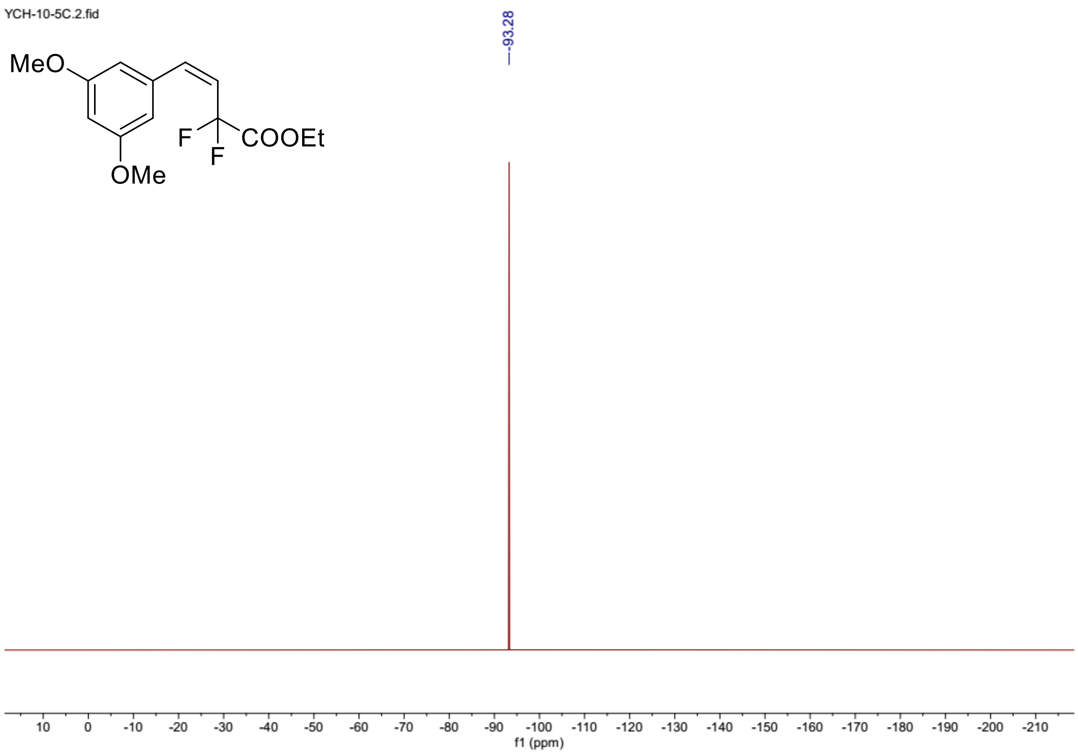
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **51**



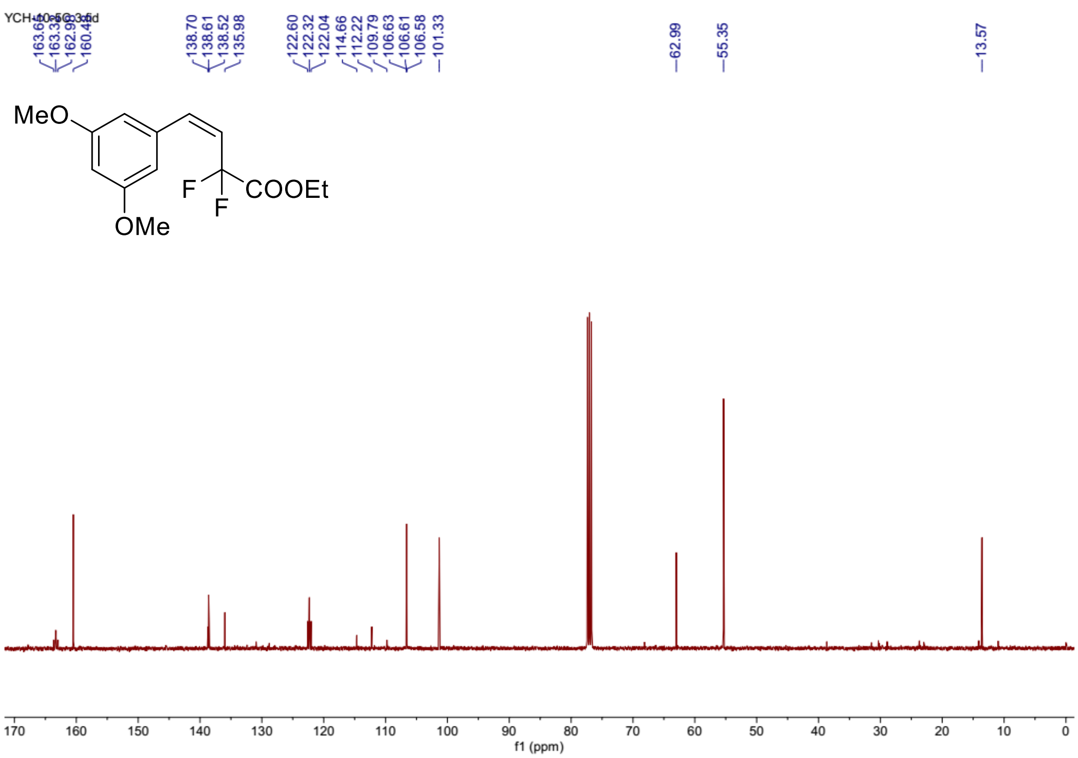
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **52**



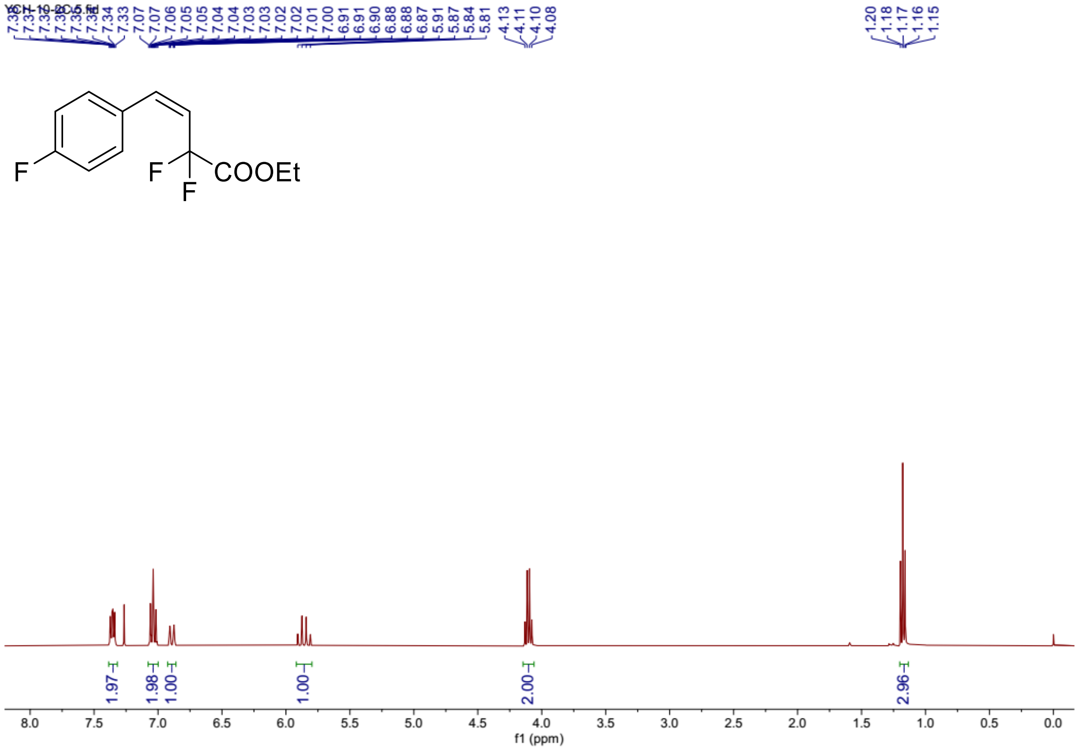
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **52**



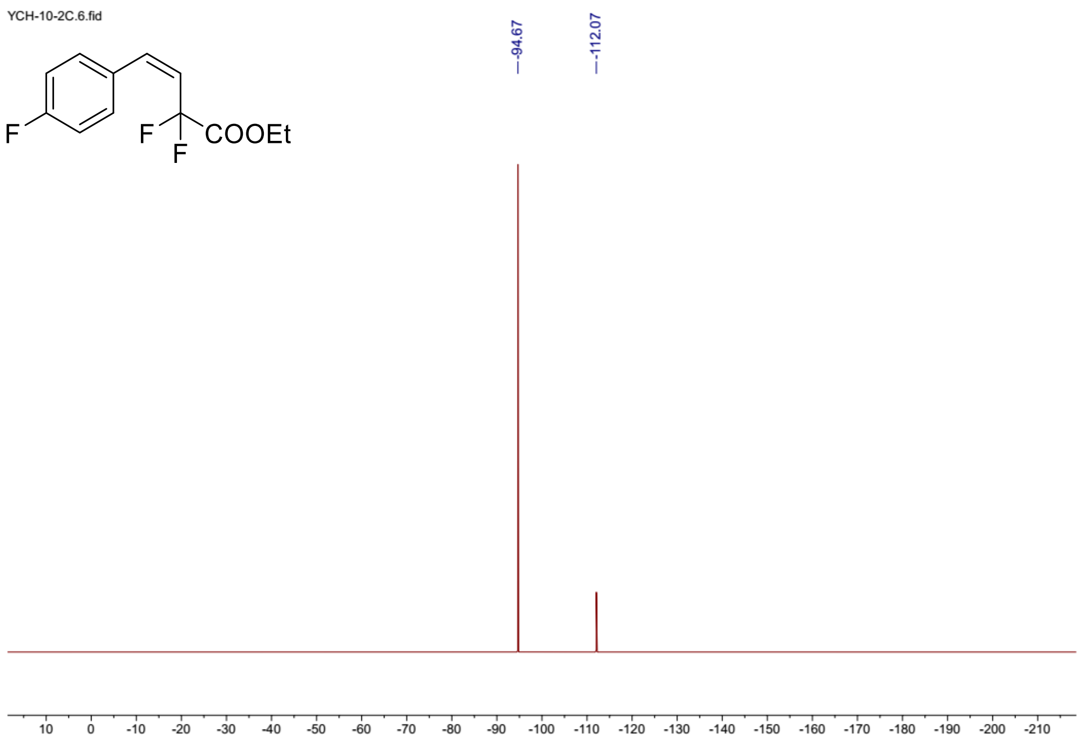
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **52**



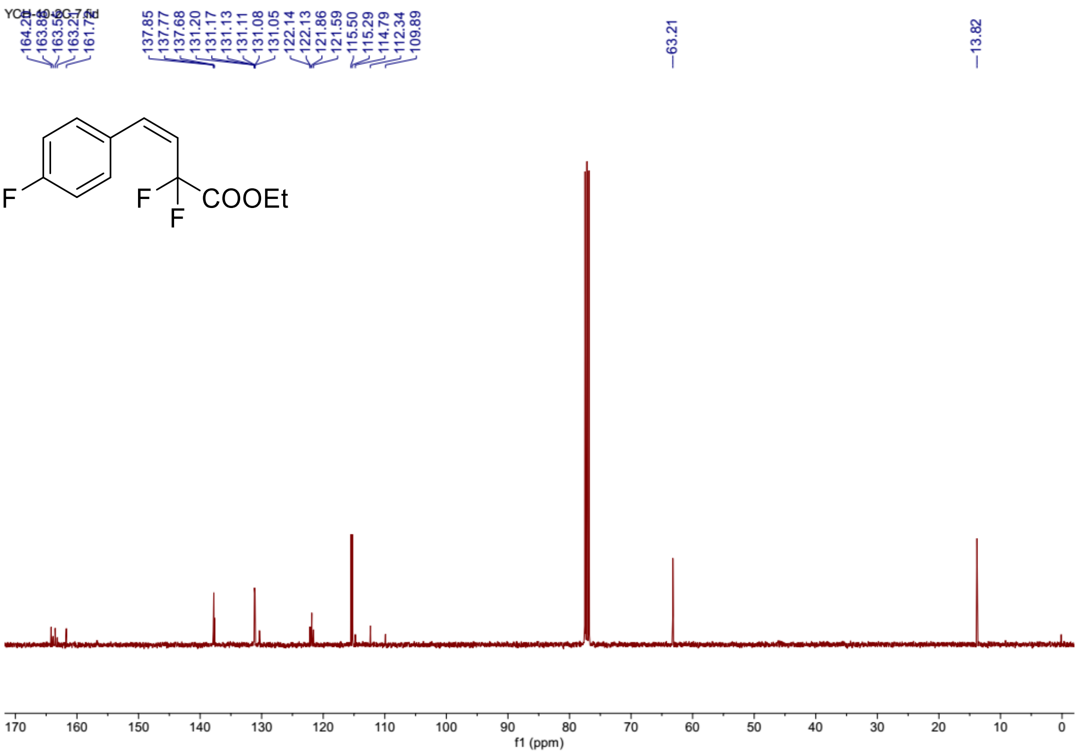
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **53**



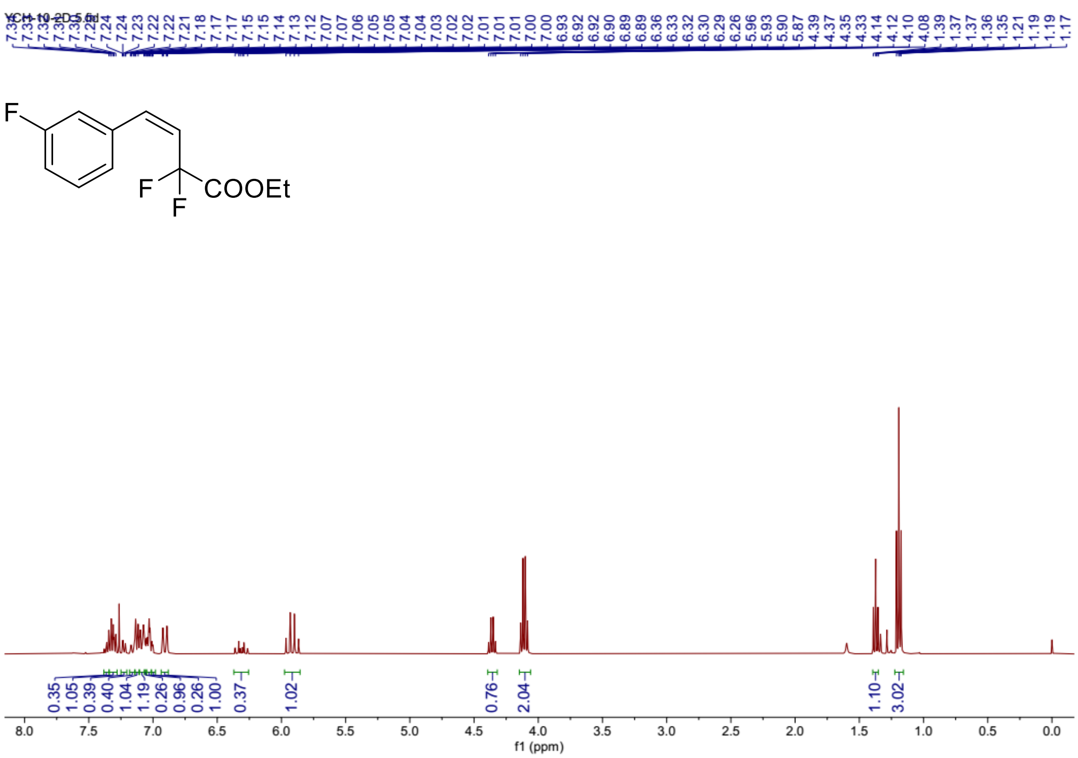
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **53**



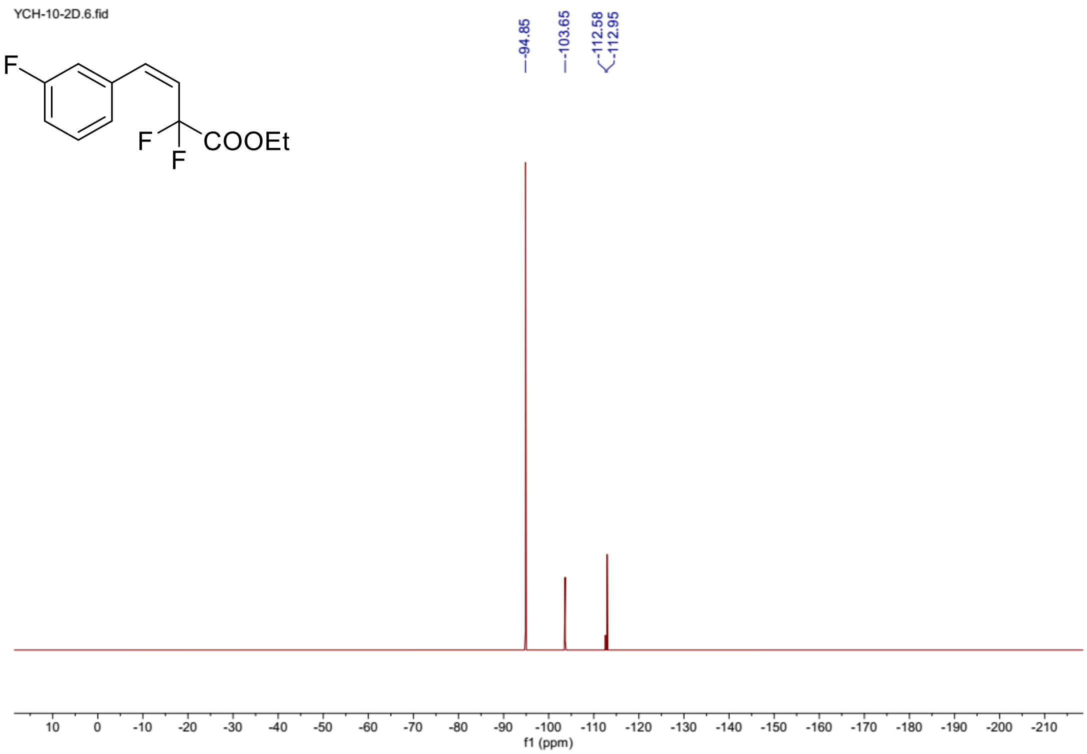
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **53**



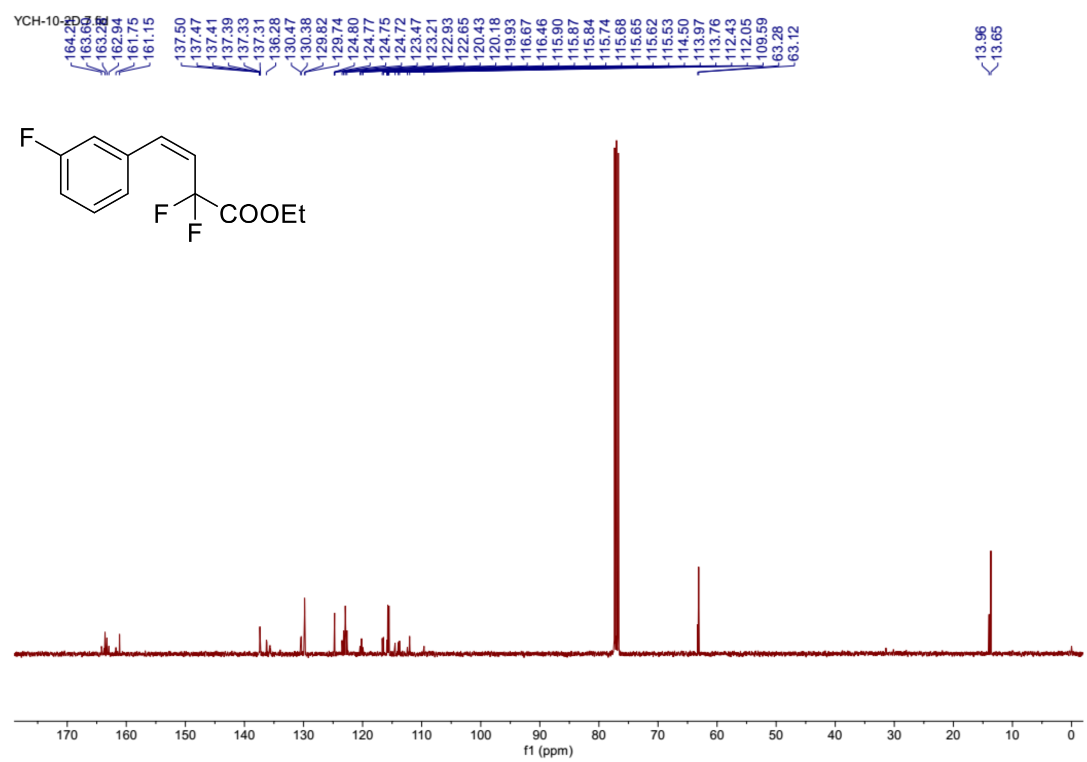
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **54**



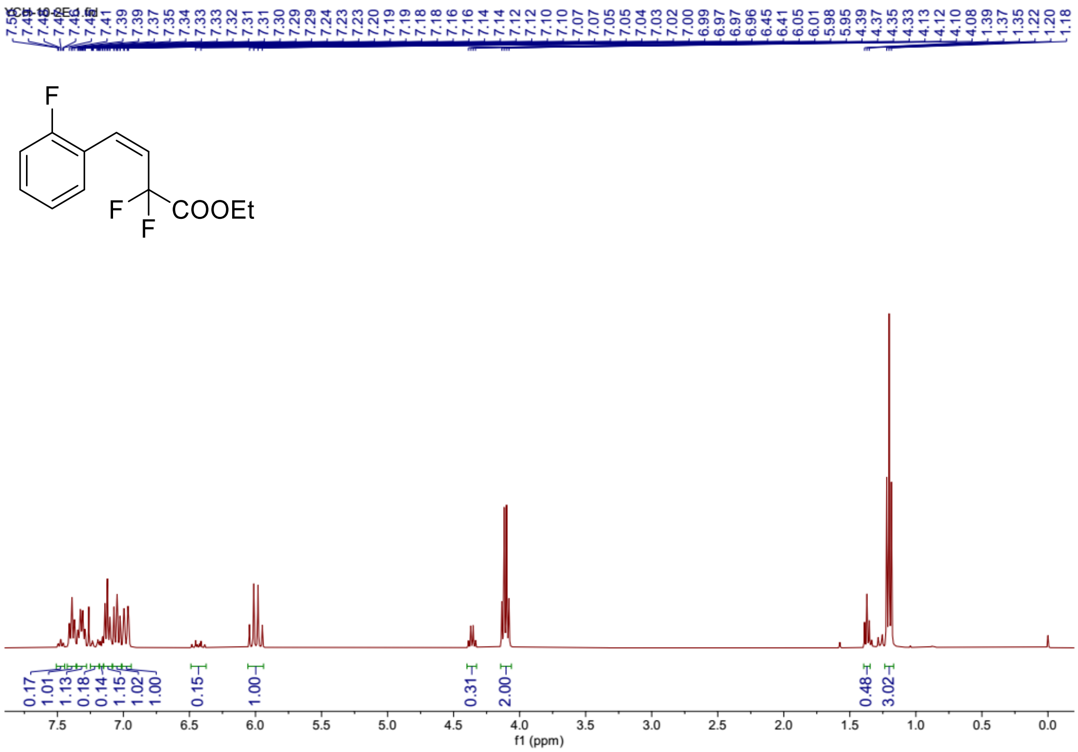
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **54**



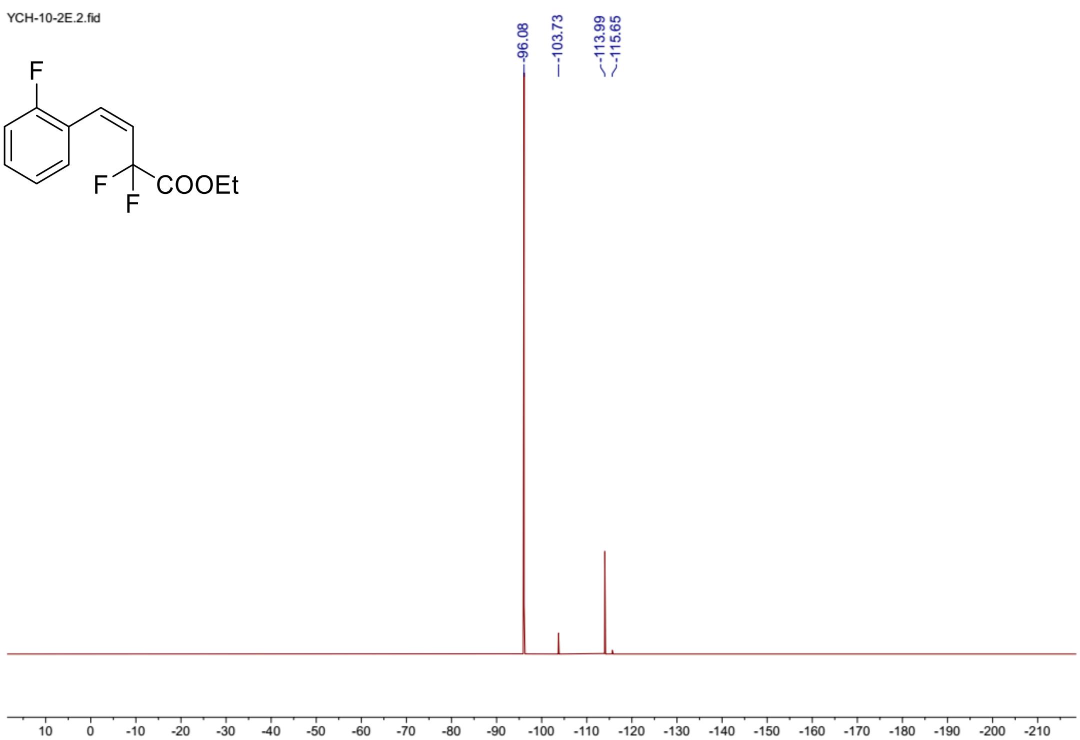
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **54**



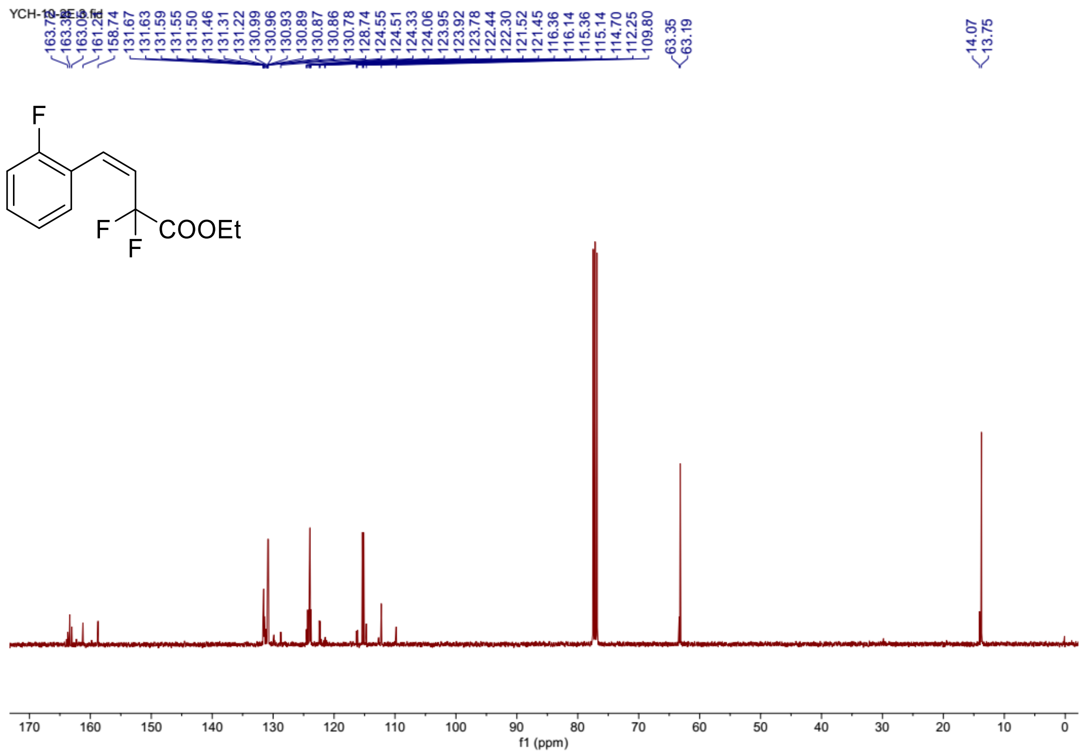
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **55**



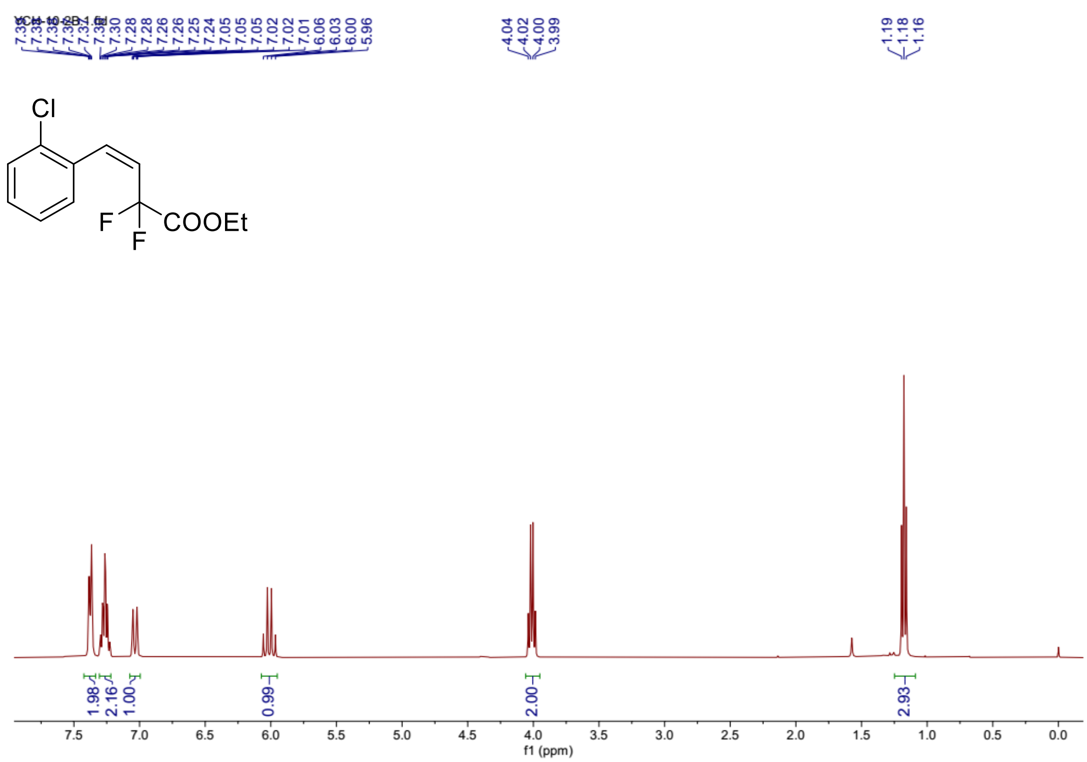
[19]F NMR (376 MHz, Chloroform-*d*) spectrum of compound **55**



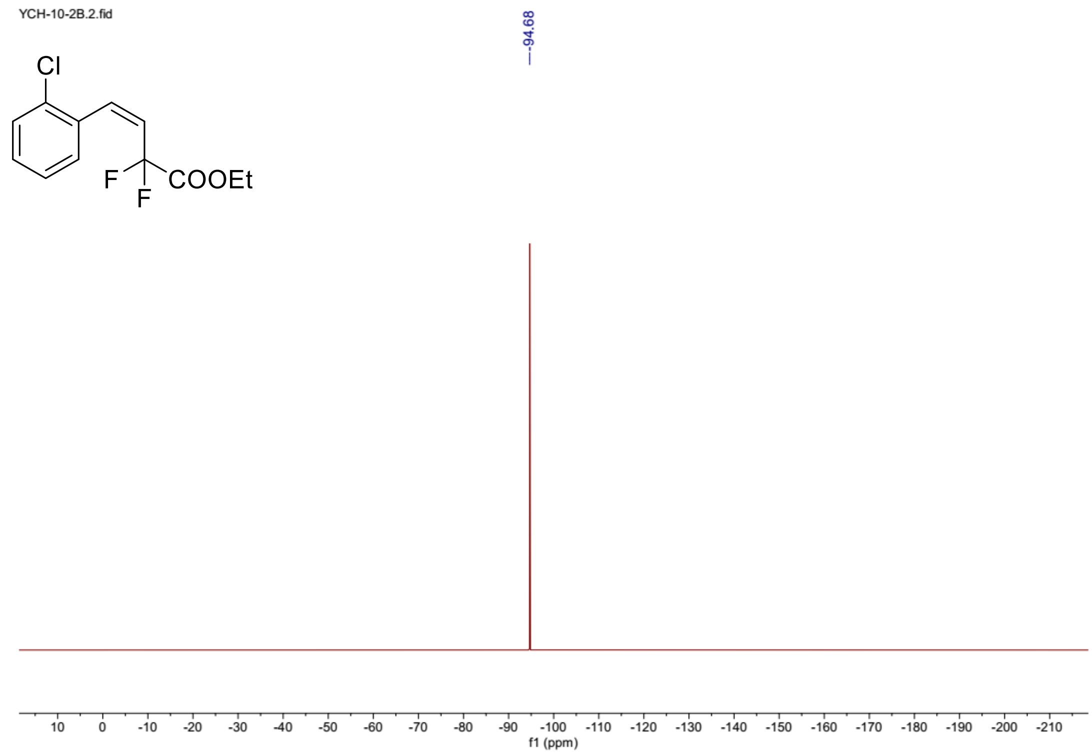
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **55**



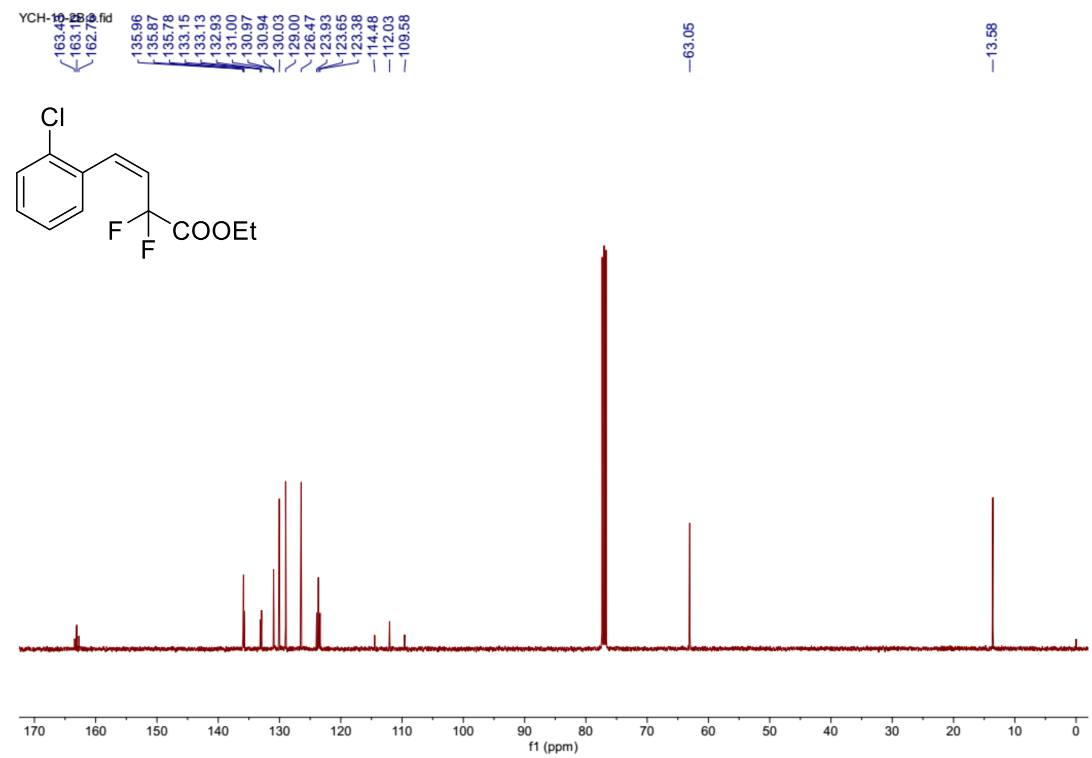
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **56**



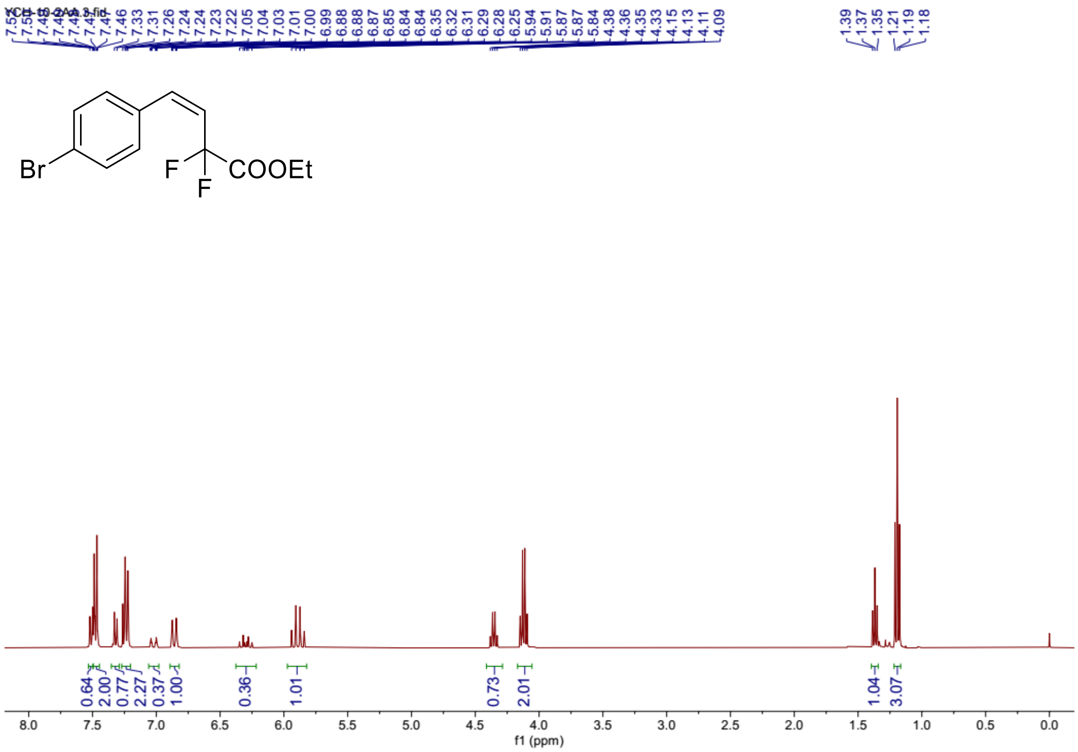
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **56**



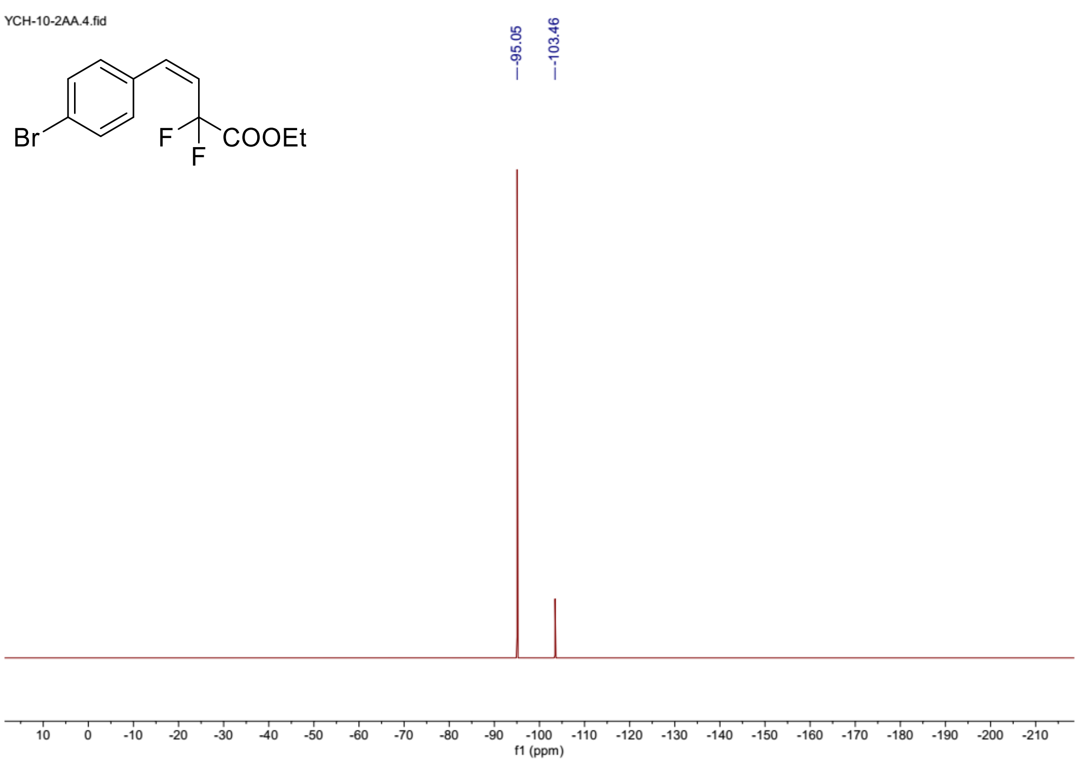
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **56**



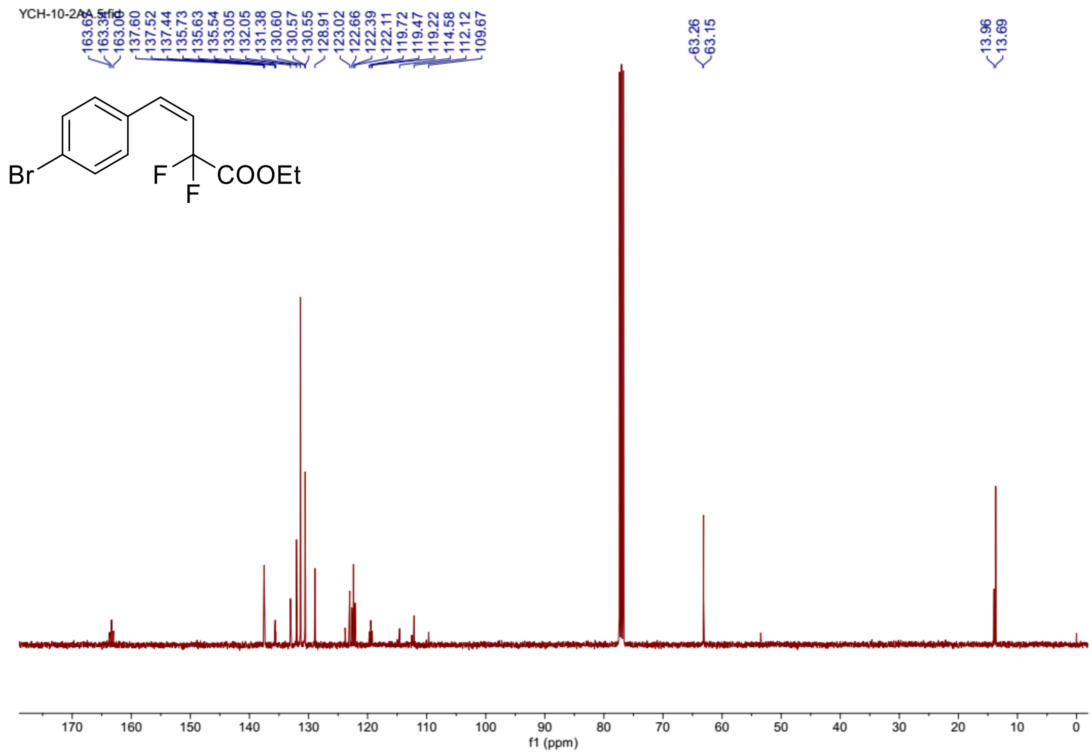
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **57**



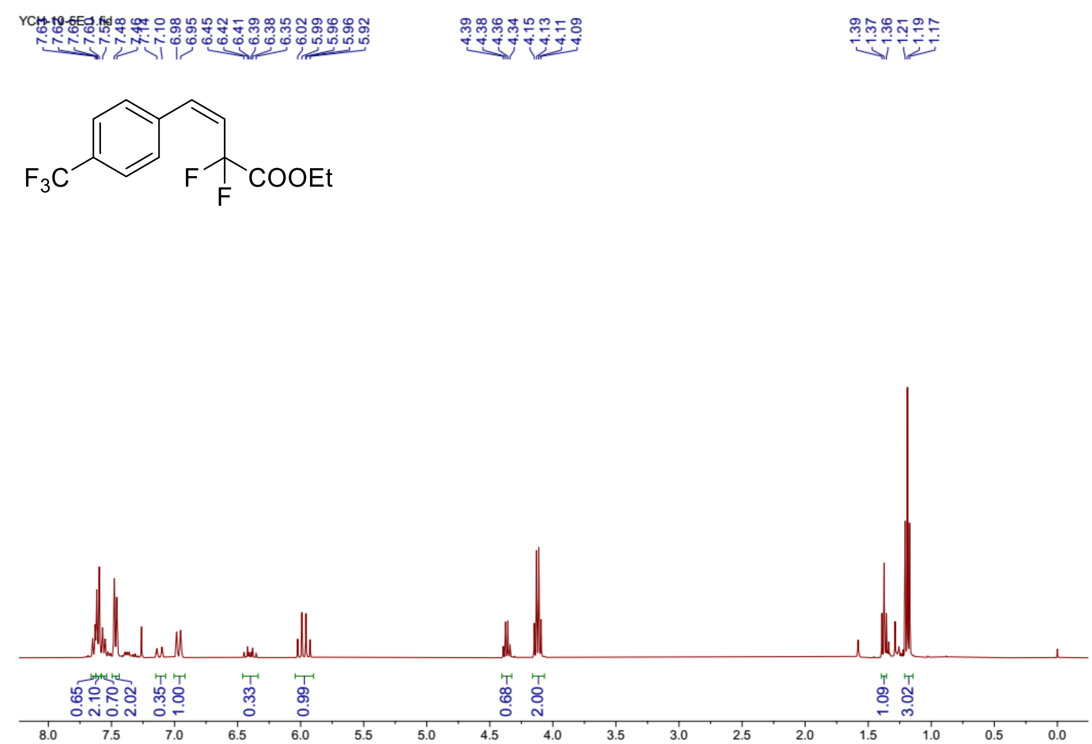
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **57**



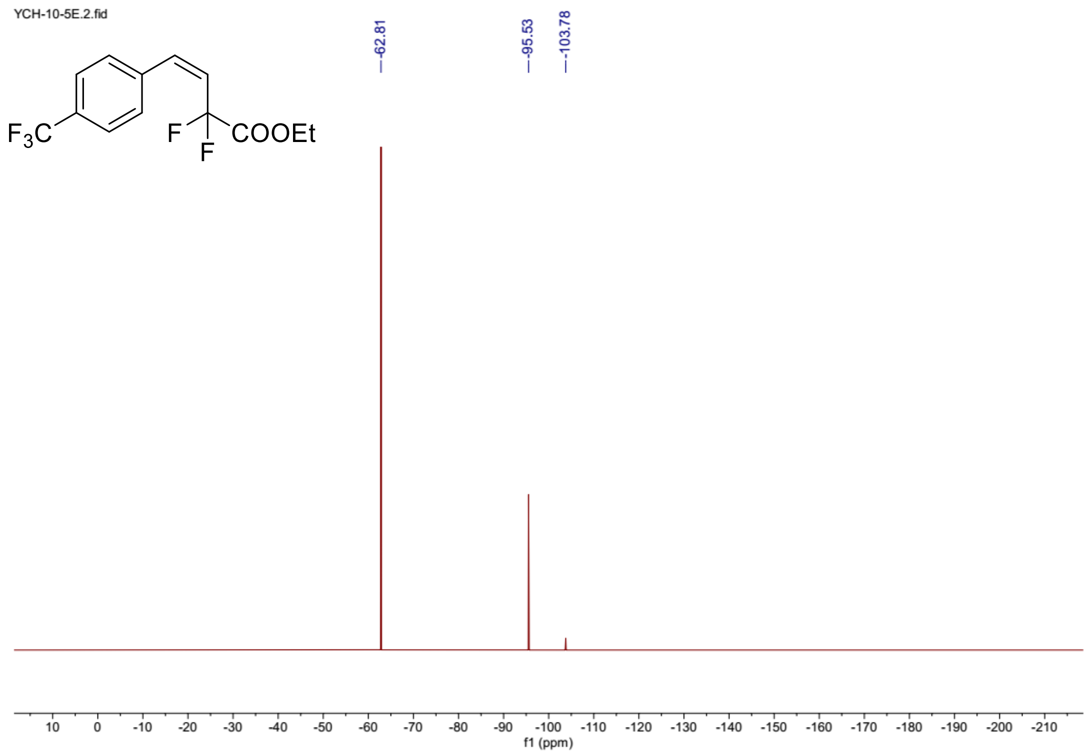
c[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **57**



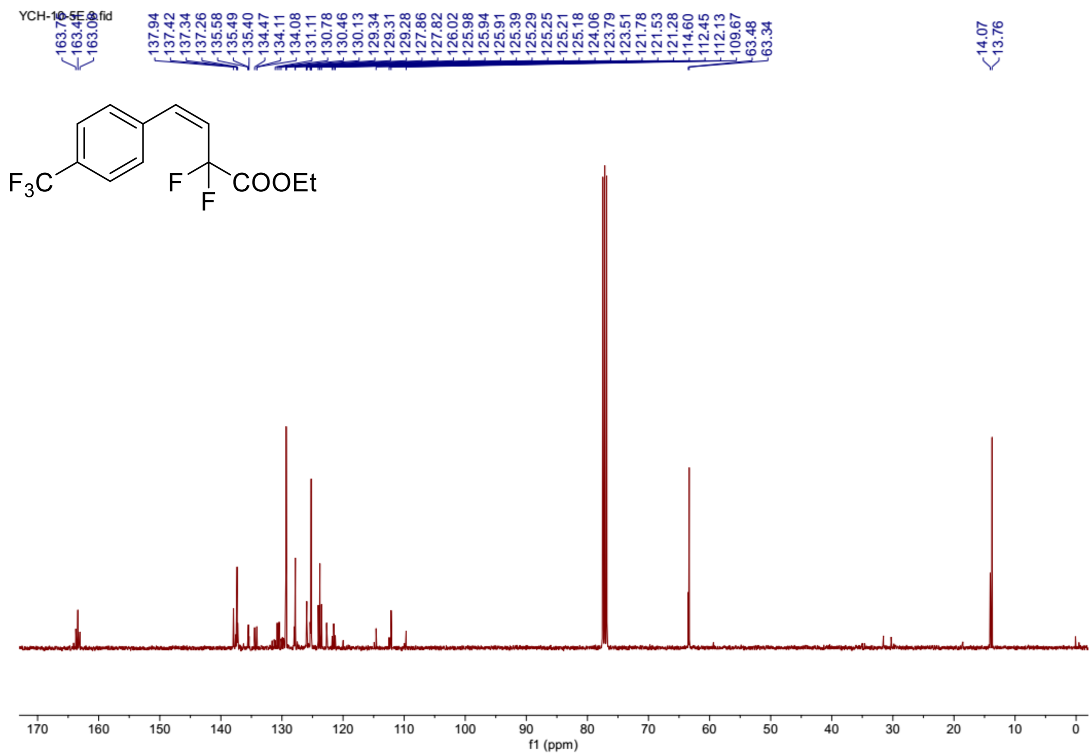
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **58**



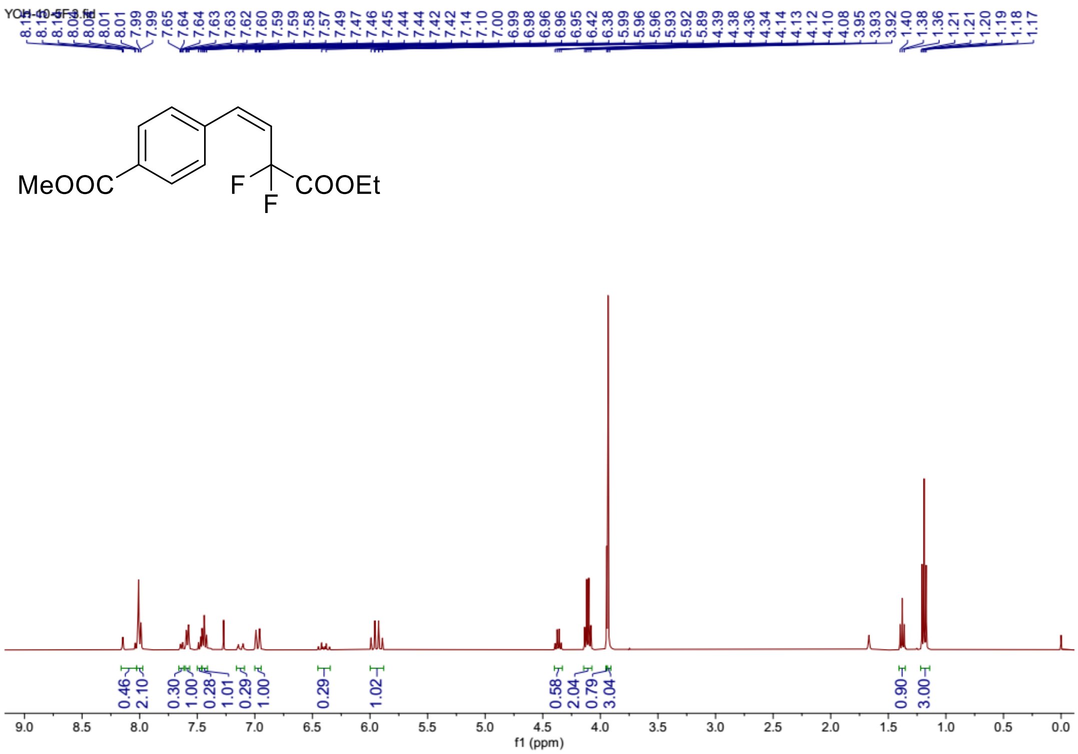
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **58**



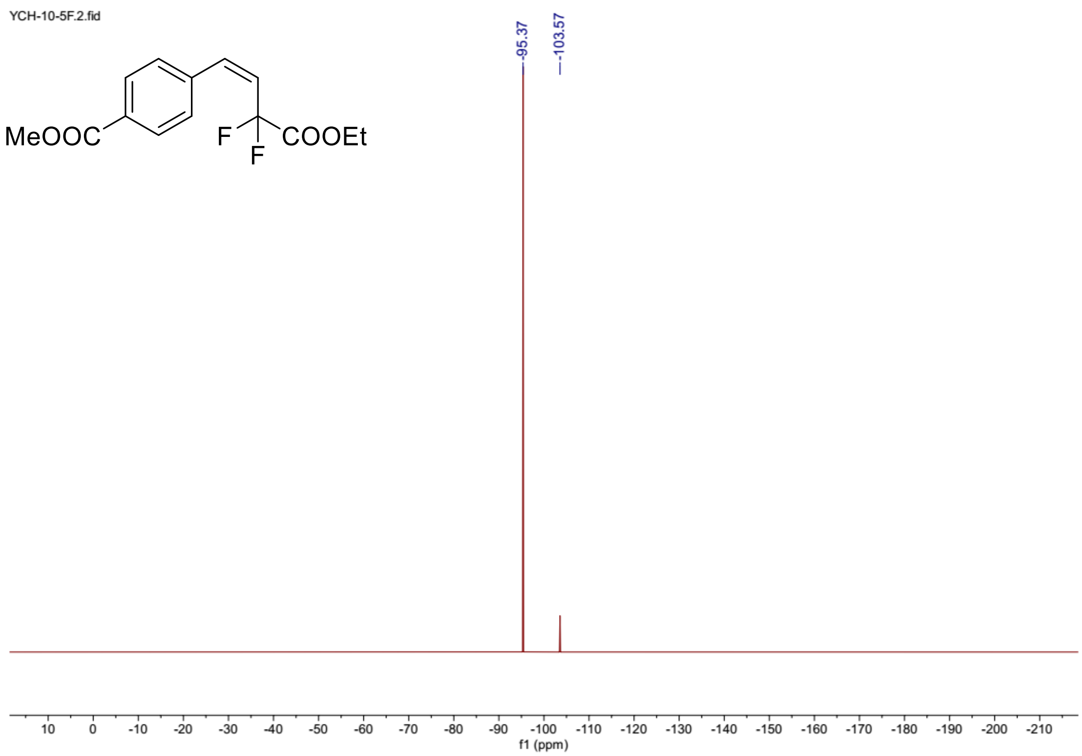
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **58**



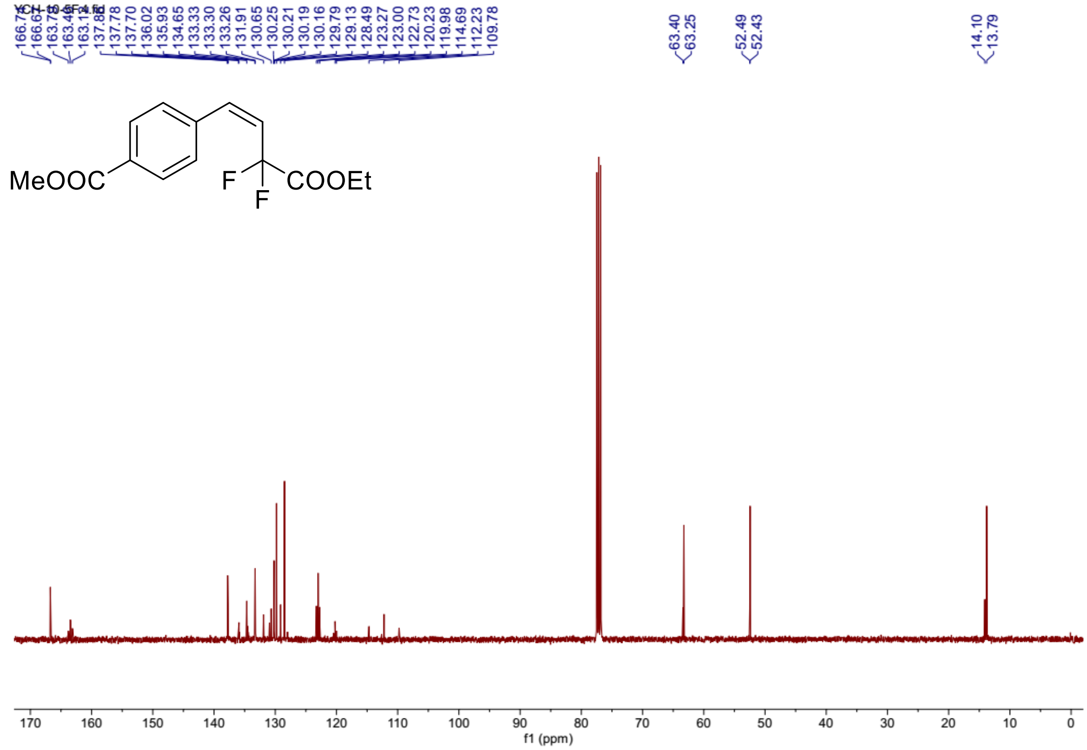
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **59**



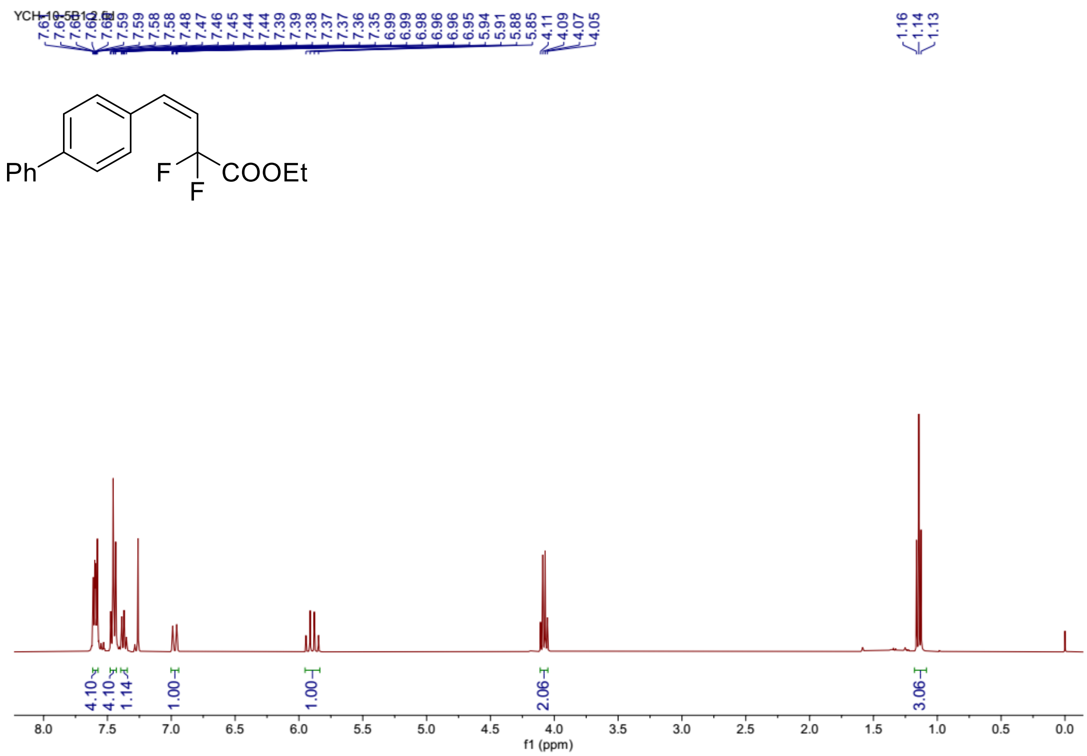
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **59**



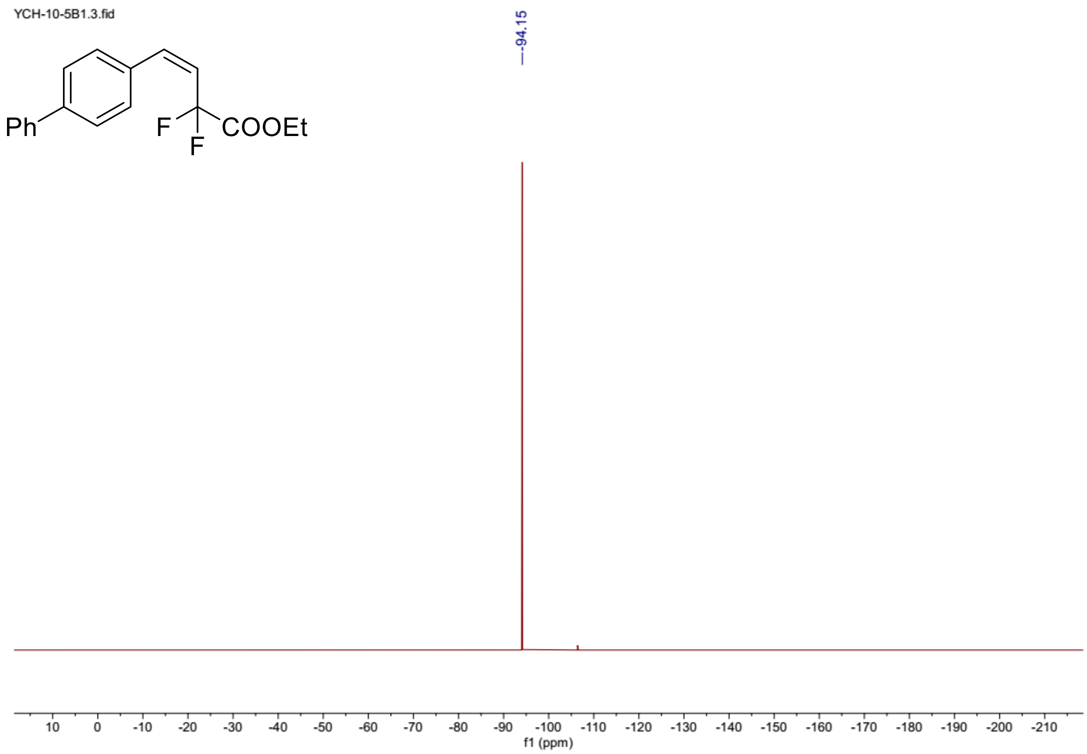
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **59**



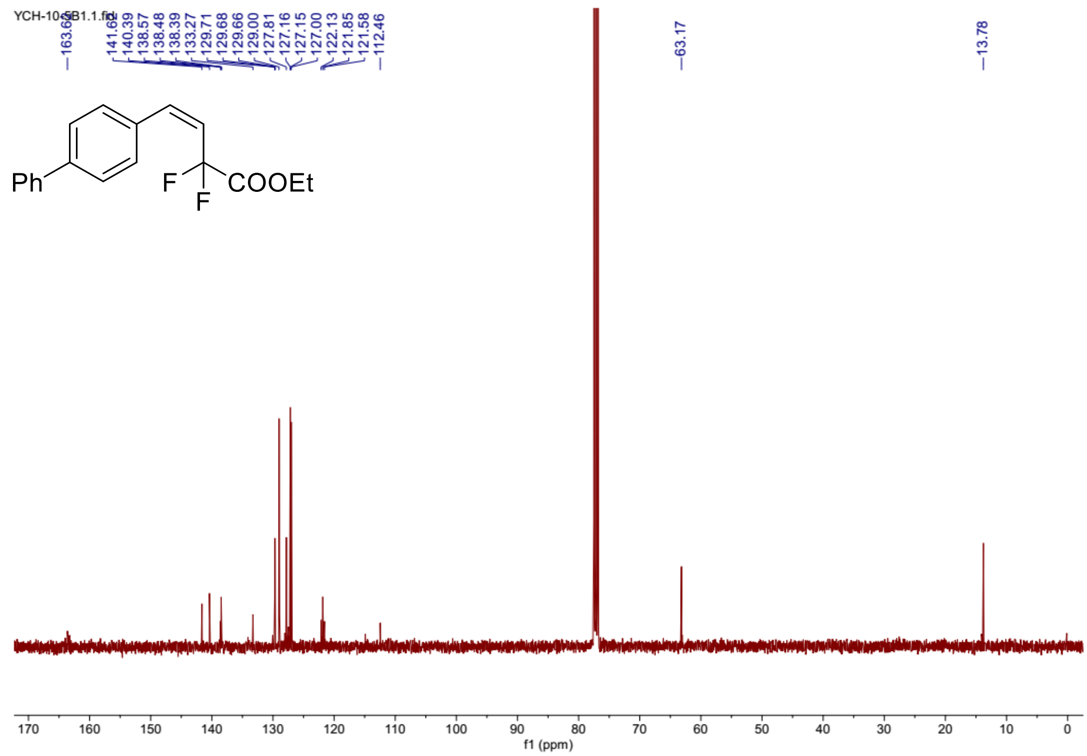
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **60**



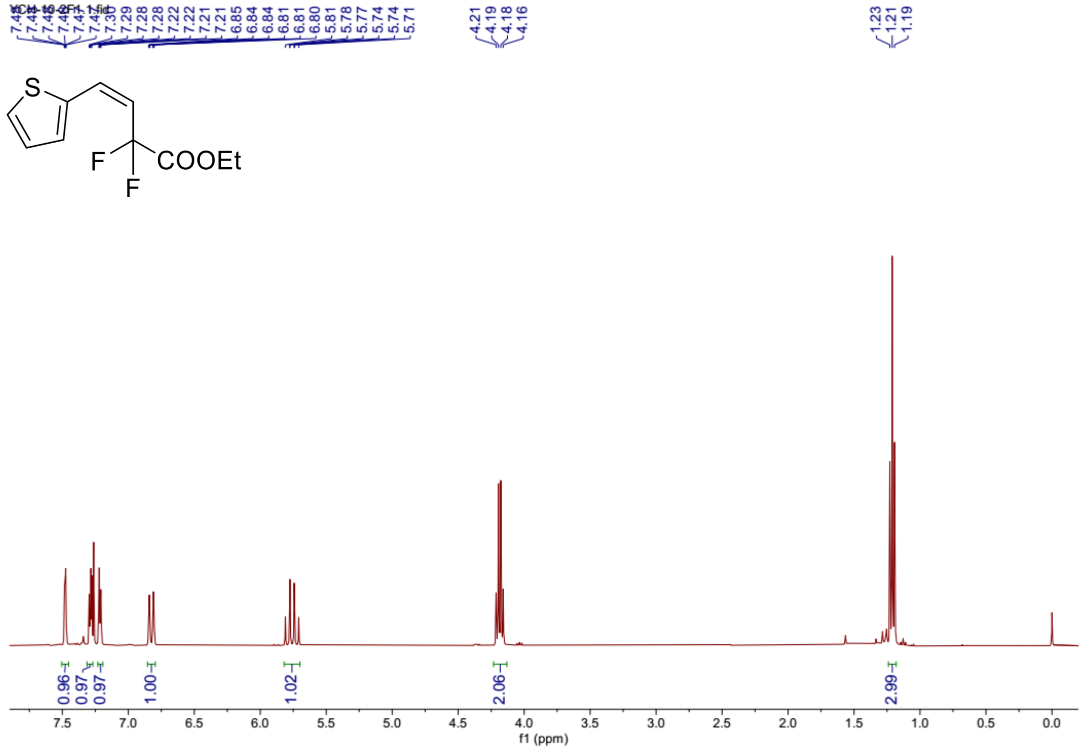
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **60**



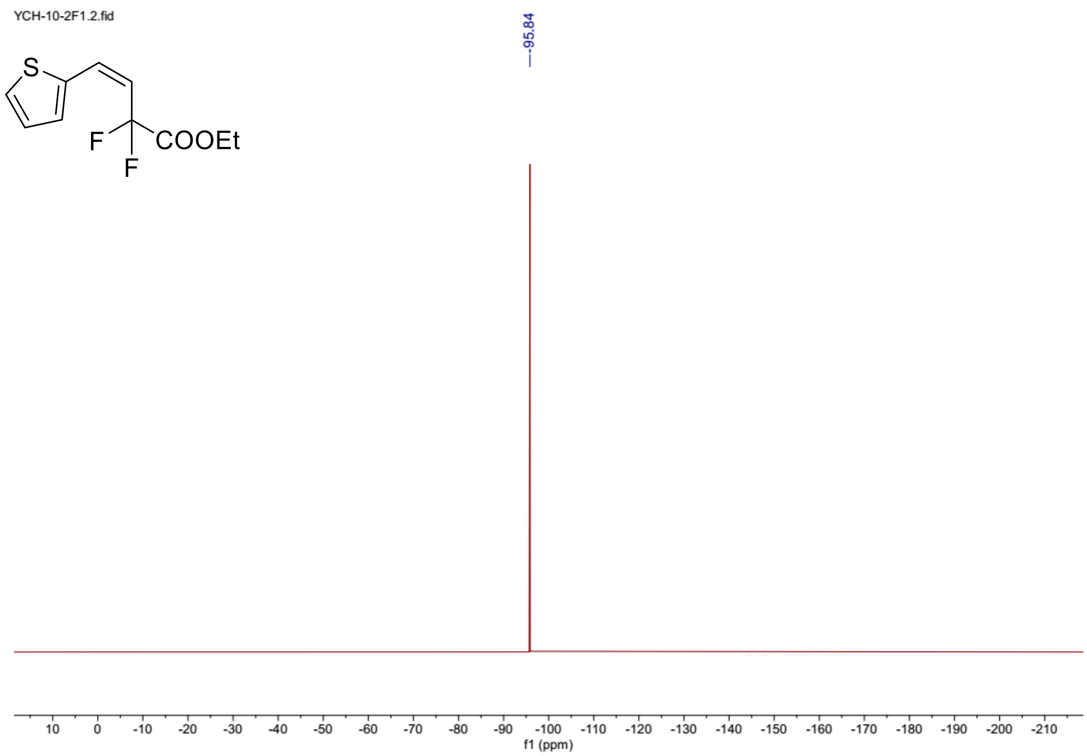
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **60**



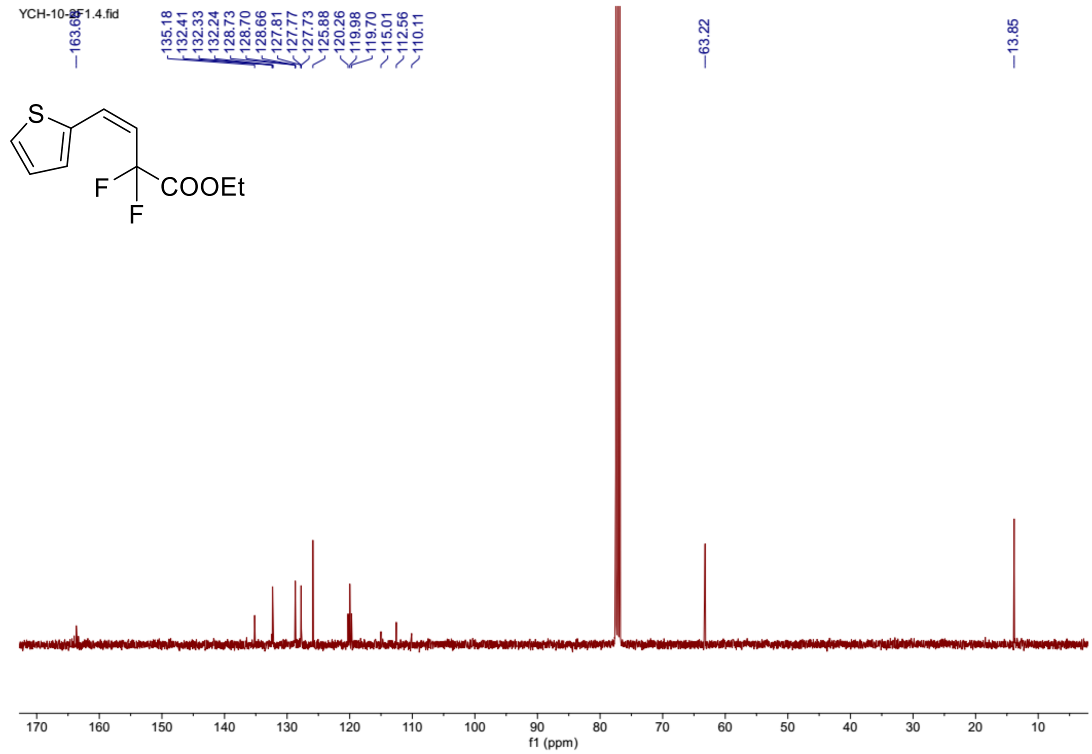
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **61**



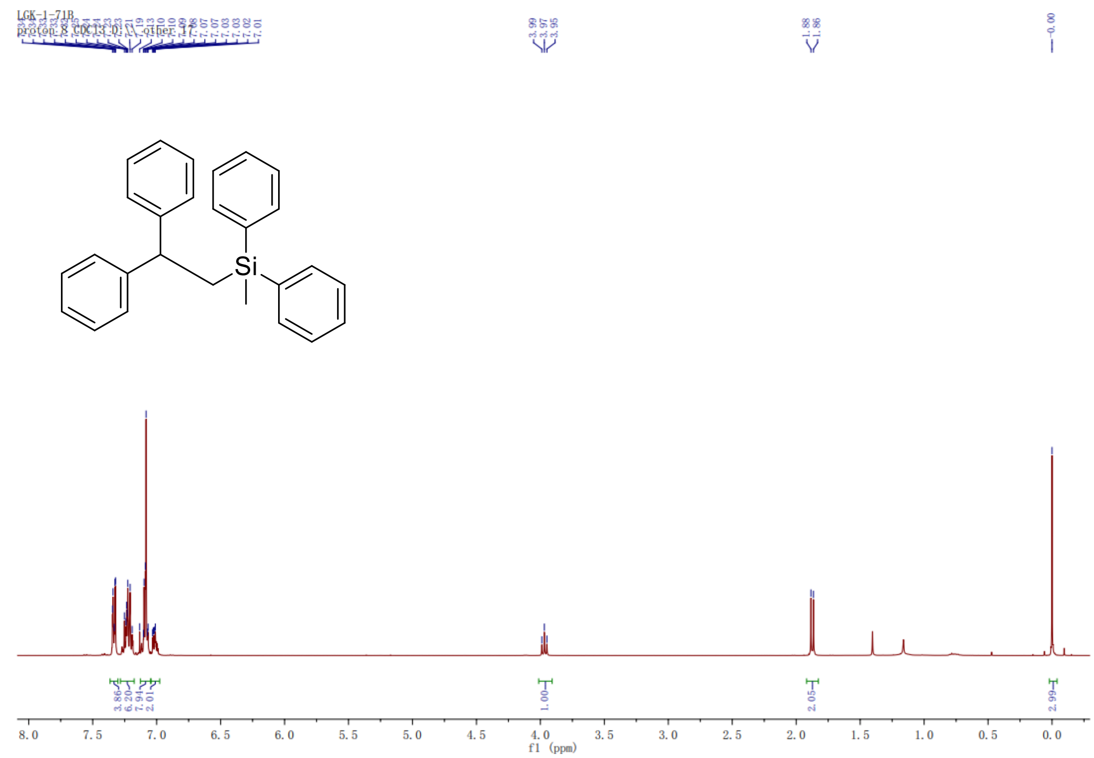
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **61**



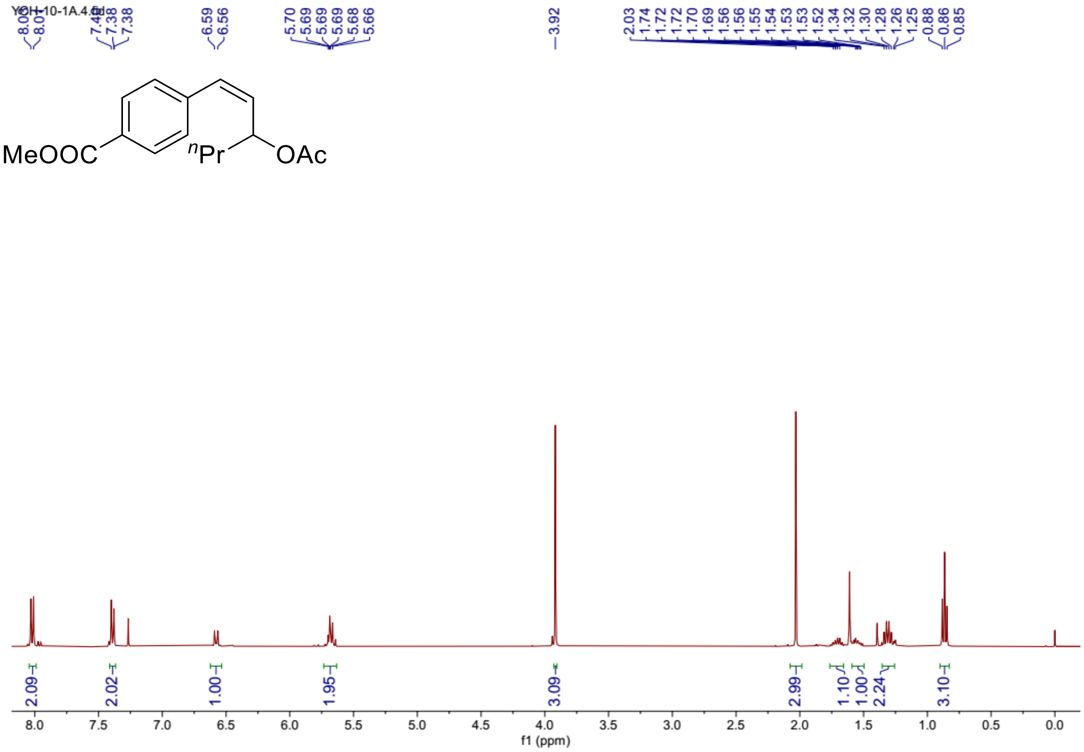
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **61**



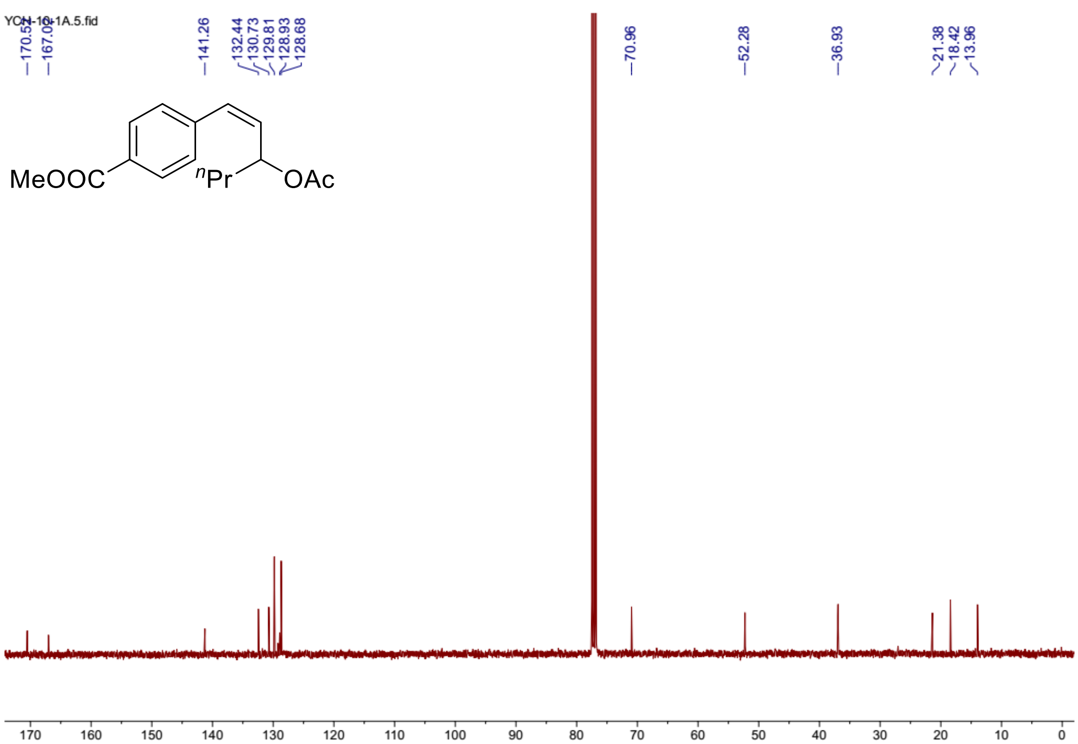
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **67**



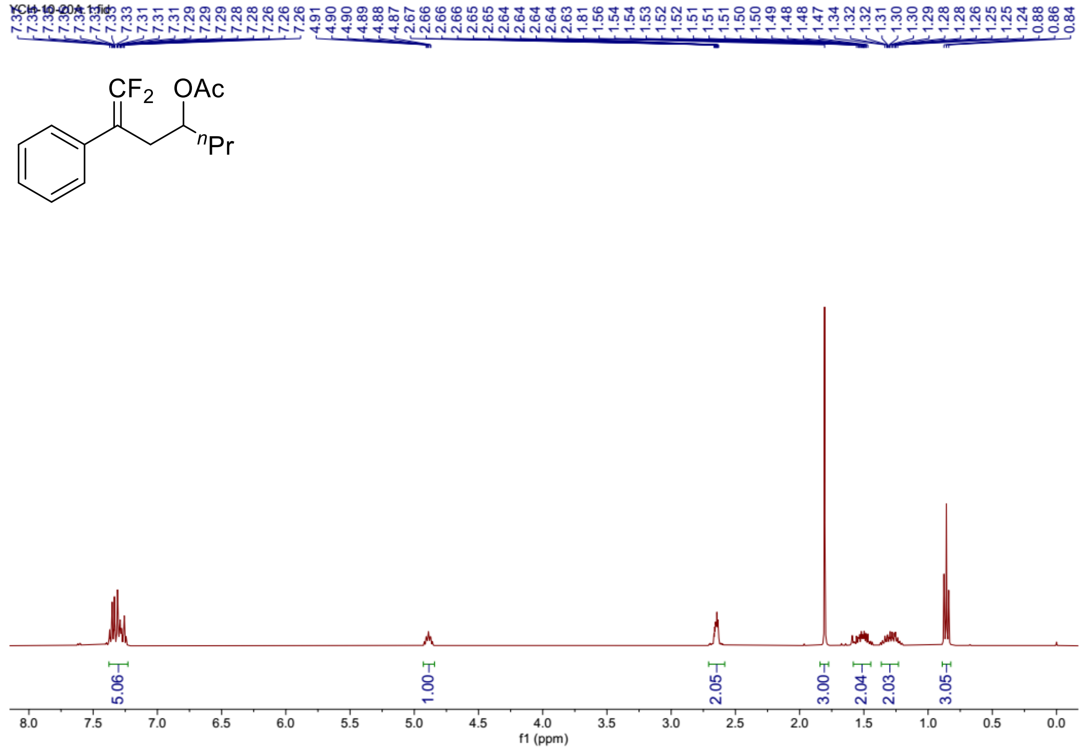
[1]H NMR (400 MHz, $CDCl_3$) spectrum of compound **71**



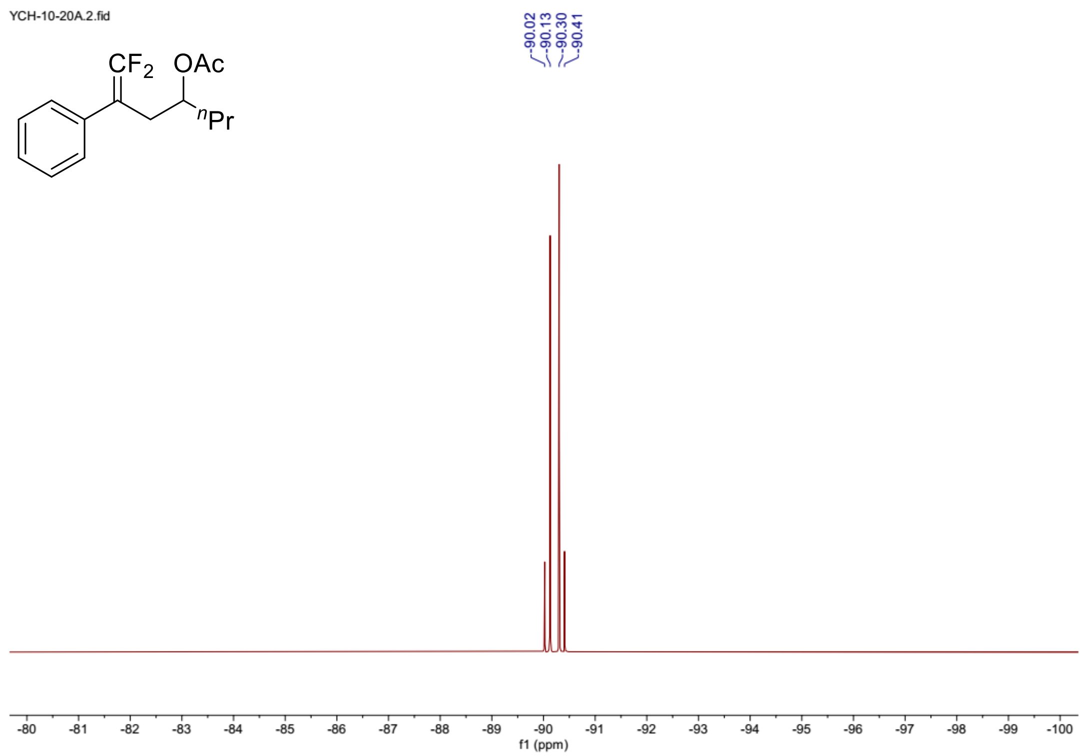
[13]C NMR (101 MHz, Chloroform-*d*) spectrum of compound **71**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **73**



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **63**



^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **73**