Supporting Information

for

光促二氟烯丙基化合物的 *E*→*Z* 异构化反应

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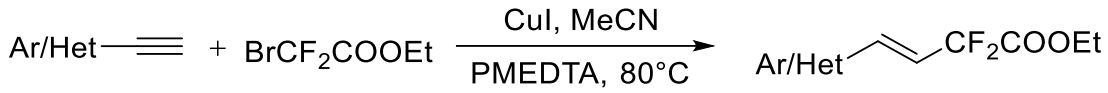
1. General Information

1.1 Reagents and instruments

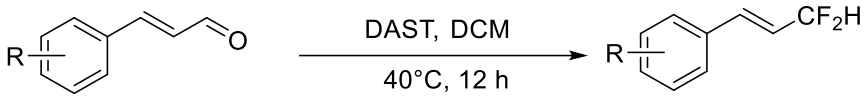
Unless otherwise noted, all of commercial reagents was purchased from Shanghai Haohong Scientific Co., Ltd. The material of the irradiation vessel is borosilicate glass (Chongqing Synthware Glass, China). All solvents used in the reactions were purified prior to use following the Solvent Purification Systems (FLEANO, FL-MD-7). 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 30 W blue LEDs (454 nm, 1 W*30, 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. ^1H 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.

2. General procedure

2.1. The General Preparation Process of Allylic Gem Difluorides



According to literature[1], CuI (1.0-10 mol%) was added to a 50 mL round bottom flask in air, followed by vacuum pumping and filling three times with N2 back and forth. Then add 10 mL of acetonitrile, PMDETA (1.5 eq., 7.5 mmol, 1.57 mL), aryl olefins (1.0 eq., 5 mmol), and ethyl bromodifluoroacetate (1.5 eq., 7.5 mmol, 0.96 mL). Heat the reaction mixture in an oil bath to 80℃, stir for 12 h, and then cool to room temperature. Dilute the reaction mixture with EtOAc and filter with diatomaceous earth. Concentrate the filtrate and purify the residue using silica gel chromatography (PE : EtOAc = 20:1) to obtain the product.



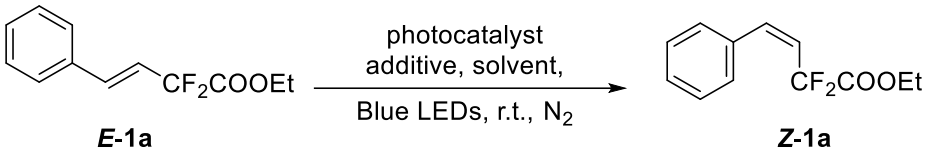
According to literature report[2], cinnamaldehyde (1 eq., 10 mmol) and DAST (2.0 eq., 20 mmol) were added to 2 mL DCM through a syringe. After stirring at 40℃ for 12 h, add 10 mL of cold water dropwise to the mixture. Extract the aqueous phase three times using 20 mL DCM, and dry the combined organic phase with anhydrous sodium sulfate. Volatiles are removed under low temperature or vacuum at room temperature, and the crude product is purified by column chromatography using petroleum ether as an eluent.

2.2. General operations for photocatalytic isomerization of allylic gem difluorides

Accurately weigh the photosensitizers 4CzIPN (0.0032 g, 0.002 mmol) and $NaHCO_3$ (0.0017 g, 0.02 mmol) in a vacuum, anhydrous, and oxygen free glove box in Michaelina, and sequentially add them to 25 mL of dry borosilicate Schlenk tubes containing a magnetic stirrer. Use a pipette to transfer 2 mL of ethyl acetate into the reaction tube. After removing the above reaction tube from the glove box, accurately weigh the trans allyl fluoride compound (0.20 mmol) with a sampling needle and add it to the reaction tube. At room temperature, stir the reaction mixture and irradiate it with a 20 W blue LED until the reaction is complete by thin-layer chromatography (TLC). Concentrate the reaction solution, and use pepper ring as the internal standard to determine the yield of the crude product through ^1H NMR. Finally, purify and separate the cis product through column chromatography.

3. Condition optimizations

Table S1. Optimization of reaction conditions[a].



***E*-1a** ***Z*-1a**

条目	PC	碱	溶剂	收率 (%)[b]
1	4CzIPN	PhCOOK	THF	68
2[c]	4CzIPN	PhCOOK	THF	N.D.
3	-	PhCOOK	THF	10
4	4CzIPN	-	THF	55
5	4CzIPN	$NaHCO_3$	THF	72
6	4CzIPN	Et_3N	THF	50
7	4CzIPN	K_3PO_4	THF	25
8	4CzIPN	KOAc	THF	47
9	4CzIPN	NH_4HCO_3	THF	52
10	4CzIPN	PhCOONa	THF	63
11	4CzIPN	$KHCO_3$	THF	69
12	4CzIPN	NaOH	THF	N.D.
13	Eosin Y	$NaHCO_3$	THF	N.D.
14	$Ru(bpy)_3Cl_2$	$NaHCO_3$	THF	N.D.
15	Fluorescein	$NaHCO_3$	THF	N.D.
16	(-)-riboflavin	$NaHCO_3$	THF	11
17	Benzil	$NaHCO_3$	THF	24
18	Xanthone	$NaHCO_3$	THF	18
19	*fac*-Ir(ppy) $_3$	$NaHCO_3$	THF	70
20	4CzIPN	$NaHCO_3$	EtOAc	83
21	4CzIPN	$NaHCO_3$	MeCN	76
22	4CzIPN	$NaHCO_3$	1,4-dioxane	76
23	4CzIPN	$NaHCO_3$	toluene	78
24	4CzIPN	$NaHCO_3$	DMF	62
25	4CzIPN	$NaHCO_3$	MeOH	N.D.
26[d]	4CzIPN	$NaHCO_3$	EtOAc	82
27[e]	4CzIPN	$NaHCO_3$	EtOAc	82

[a] Reaction conditions: *E*-**1a** (0.20 mmol), photocatalyst (0.004 mmol), additive (0.40 mmol), and solvent (2 mL), in a nitrogen protected reaction tube, irradiated at room temperature with a 30 W blue LED lamp [b] The yield was determined by ^1H NMR of the crude product using pepper ring as the internal standard [c] Avoid light [d] 0.10 mmol $NaHCO_3$ [e] 0.02 mmol 4CzIPN. N. D.=Not detected.

4. Mechanistic Investigations

4.1 Stern-Volmer Emission Quenching Experiment

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.97 μM 4CzIPN, in degassed EtOAc at room temperature. The solutions were irradiated at 350 nm and fluorescence was measured from 400 nm to 750 nm. In a typical experiment, to 0.1 mL of a 0.97 μM solution of 4CzIPN in degassed EtOAc in a 1.0 cm quartz cuvette was added the appropriate amount of the specified quencher (*E*-**1a** or *Z*-**1a**) in degassed EtOAc.

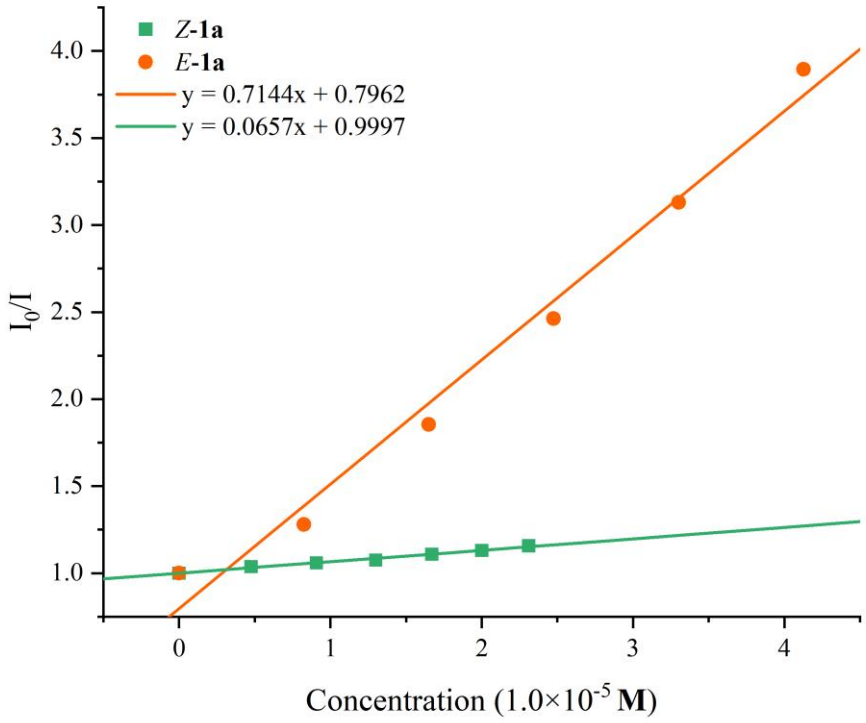


Figure S1. Stern-Volmer photoquenching study of *E*-1a and *Z*-1a.

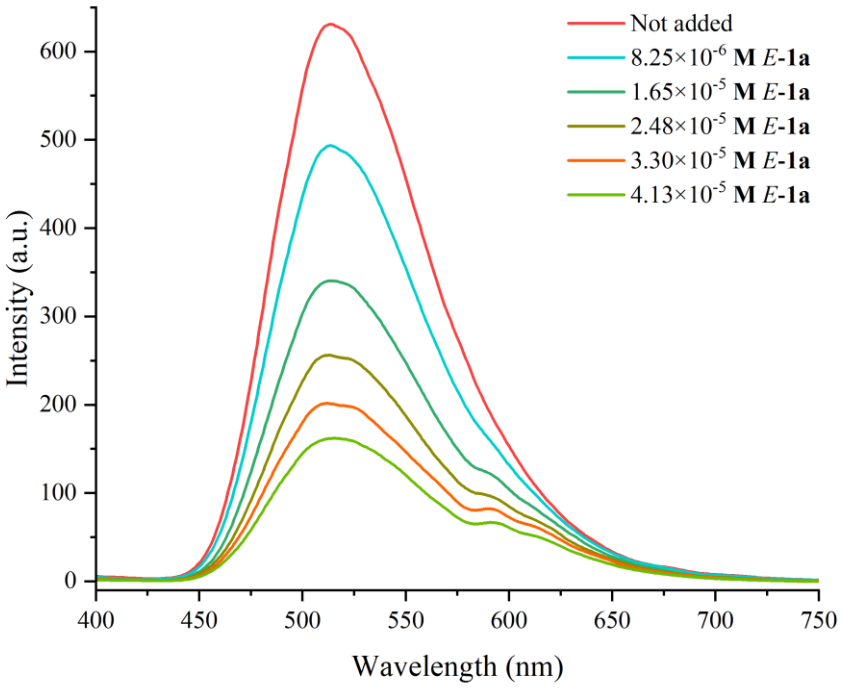


Figure S2. Stern-Volmer photoquenching study of *E*-1a

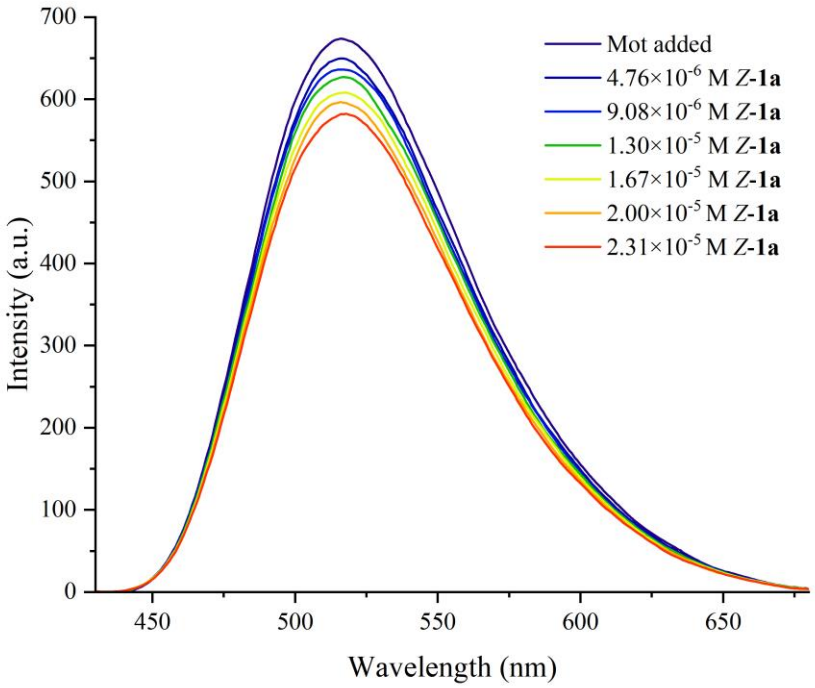
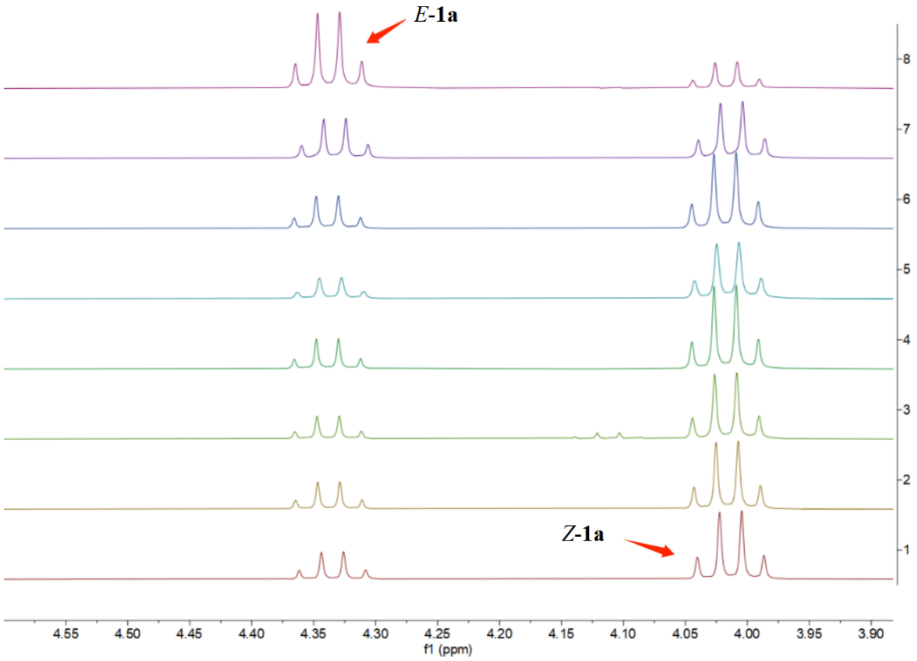


Figure S3. Stern-Volmer photoquenching study of *Z*-1a.

4.2 Reaction Progress Monitoring

The isomerization of *E*-**1a** was performed according to general procedure b in 0.2 mmol scale and the conversion was monitored by ^{1}H NMR analysis of 0.5 mL samples taken from the same reaction solution after every hour with the E-isomer (*E*-**1a**) at 4.35 ppm and the *Z*-isomer (*Z*-**1a**) at 4.02 ppm.



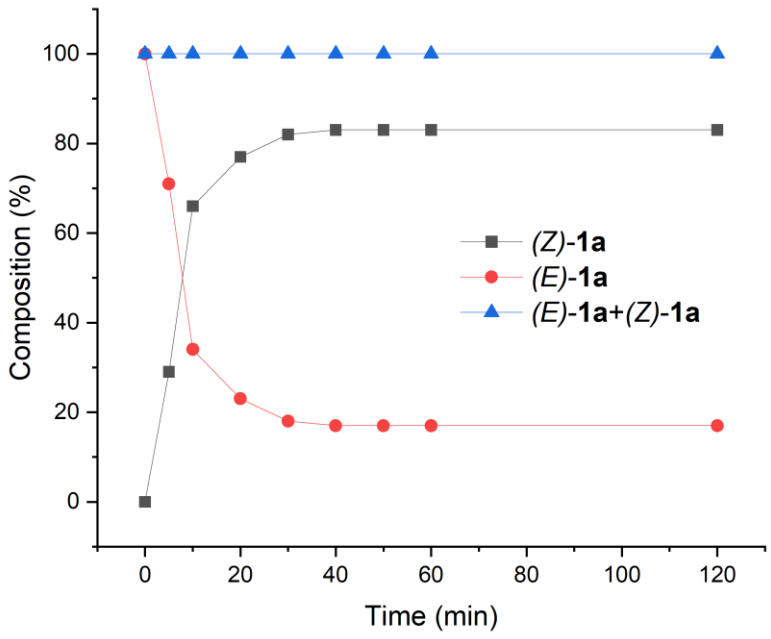
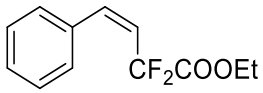


Figure S4. Reaction progress monitoring starting from the *E* and *Z* isomers of two model substrates.

5. Characterization data of allylic *gem* difluorides products

Ethyl *(Z)*-2,2-difluoro-4-phenylbut-3-enoate (*Z*-**1a**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 83% yield (based on ^{1}H NMR).

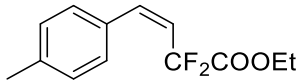
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 6.95 (dt, *J* = 12.6, 1.8 Hz, 1H), 5.88 (q, *J* = 12.9 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.87.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 138.9 (t, $^4J_{C\text{-}F}$ = 8.9 Hz), 134.4, 129.1 (t, $^3J_{C\text{-}F}$ = 2.7 Hz), 128.9, 128.4, 122.1 (t, $^2J_{C\text{-}F}$ = 28.0 Hz), 112.5 (t, $^1J_{C\text{-}F}$ = 245.7 Hz), 63.1, 13.8.

Spectral Data agreed with previously reported. [3,4]

Ethyl *(Z)*-2,2-difluoro-4-(*p*-tolyl)but-3-enoate (*Z*-**1b**) *Z*:*E* = 70 : 30



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 70% yield (based on ^{1}H NMR).

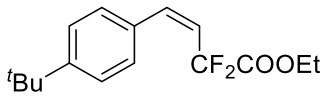
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 0.7H, *E*-alkene), 7.25 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 0.66H, *E*-alkene), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (dt, *J* = 16.2, 2.6 Hz, 0.36H, *E*-alkene), 6.90 (d, *J* = 12.5 Hz, 1H), 6.25 (dt, *J* = 16.2, 11.5 Hz, 0.34H, *E*-alkene), 5.82 (q, *J* = 13.1 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 0.68H, *E*-alkene), 4.05 (q, *J* = 7.2 Hz, 2H), 2.36 (d, *J* = 8.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 1H, *E*-alkene), 1.13 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.93, -103.10 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (t, $^2J_{C\text{-}F}$ = 33.9 Hz), 140.1 (*E*-alkene), 139.4 – 138.7 (m), 137.0 (t, $^4J_{C\text{-}F}$ = 9.5 Hz, *E*-alkene), 131.5, 129.8 (*E*-alkene), 129.2 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 129.1, 127.6, 121.2 (t, $^2J_{C\text{-}F}$ = 28.0 Hz), 117.7 (d, $^2J_{C\text{-}F}$ = 24.8 Hz, *E*-alkene), 113.8 (d, $^1J_{C\text{-}F}$ = 245.8 Hz), 63.3 (*E*-alkene), 63.1, 21.6 (*E*-alkene), 21.5, 14.2 (*E*-alkene), 13.8.

Spectral Data agreed with previously reported. [3,4]

Ethyl *(Z)*-4-(4-(*tert*-butyl)phenyl)-2,2-difluorobut-3-enoate (*Z*-**1c**) *Z*:*E* = 63 : 37



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 63% yield (based on ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H, *E*-alkene), 7.38 – 7.27 (m, 4H), 7.06 (dt, *J* = 16.2, 2.6 Hz, 0.26H, *E*-alkene), 6.91 (dd, *J* = 12.7, 1.8 Hz, 1H), 6.26 (dt, *J* = 16.1, 11.5 Hz, 0.26H, *E*-alkene), 5.83 (q, *J* = 13.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 0.53H, *E*-alkene), 4.02 (q, *J* = 7.1 Hz, 2H),

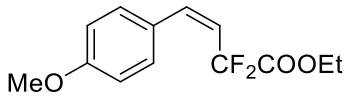
1.36 (t, *J* = 7.2 Hz, 0.89H, *E*-alkene), 1.32 (s, 2.12H, *E*-alkene), 1.31 (s, 9H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.66, -103.20 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 153.3 (*E*-alkene), 152.2, 138.8 (t, $^{4}J_{C\text{-}F}$ = 9.0 Hz), 136.8 (t, $^{4}J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 131.6 (d, $^{3}J_{C\text{-}F}$ = 1.6 Hz, *E*-alkene), 129.0 (t, $^{3}J_{C\text{-}F}$ = 2.8 Hz), 127.4, 126.0, 125.4, 121.3 (t, $^{2}J_{C\text{-}F}$ = 28.2 Hz), 118.1 (t, $^{2}J_{C\text{-}F'}$ = 25.0 Hz, *E*-alkene), 114.3 (d, $^{1}J_{C\text{-}F}$ = 248.5 Hz), 63.3 (*E*-alkene), 63.1, 35.0 (*E*-alkene), 34.9, 31.4, 14.2 (*E*-alkene), 13.7.

Spectral Data agreed with previously reported. [4]

Ethyl *(Z)*-2,2-difluoro-4-(4-methoxyphenyl)but-3-enoate (*Z*-**1d**) *Z*:*E* = 65 : 35



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 65% yield (based on ^{1}H NMR).

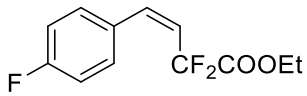
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 0.38H, *E*-alkene), 7.33 (d, *J* = 8.7 Hz, 2H), 7.02 (dt, *J* = 16.2, 2.6 Hz, 0.2H, *E*-alkene), 6.89 – 6.83 (m, 3H), 6.16 (dt, *J* = 16.1, 11.5 Hz, 0.2H, *E*-alkene), 5.76 (td, *J* = 13.6, 12.5 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 0.39H, *E*-alkene), 4.09 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 0.62H, *E*-alkene), 3.82 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.02, -102.79 (*E*-alkene)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8 (t, $^{2}J_{C\text{-}F}$ = 34.0 Hz), 160.9 (*E*-alkene), 160.2, 138.6 (t, $^{4}J_{C\text{-}F}$ = 8.9 Hz), 136.5 (t, $^{4}J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 131.0 (t, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 129.1 (*E*-alkene), 127.0 (*E*-alkene), 126.9 (t, $^{3}J_{C\text{-}F}$ = 1.6 Hz), 120.0 (t, $^{2}J_{C\text{-}F}$ = 27.9 Hz), 114.4, 113.8, 112.7 (t, $^{1}J_{C\text{-}F}$ = 245.6 Hz), 63.3 (*E*-alkene), 63.2, 55.6 (*E*-alkene), 55.5, 14.2 (*E*-alkene), 13.9.

Spectral Data agreed with previously reported. [4,5]

Ethyl *(Z)*-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (*Z*-**1e**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 79% yield (based on ^{1}H NMR).

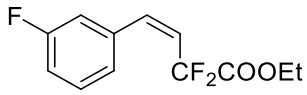
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 8.3, 5.6, 2.1 Hz, 2H), 7.03 (td, *J* = 8.7, 2.2 Hz, 2H), 6.89 (d, *J* = 12.6 Hz, 1H), 5.85 (qd, *J* = 13.2, 2.1 Hz, 1H), 4.11 (qd, *J* = 7.1, 2.0 Hz, 2H), 1.18 (td, *J* = 7.2, 2.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.72, -112.11.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 163.6 (t, $^{3}J_{C\text{-}F}$ = 33.8 Hz), 161.8, 137.8 (t, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 131.2 (dt, $^{5}J_{C\text{-}F}$ = 8.2, 3.1 Hz), 130.5, 122.0 (t, $^{2}J_{C\text{-}F}$ = 27.6 Hz), 115.6, 115.4, 112.4 (t, $^{1}J_{C\text{-}F}$ = 246.6 Hz), 63.3, 13.9.

Spectral Data agreed with previously reported. [4]

Ethyl *(Z)*-2,2-difluoro-4-(3-fluorophenyl)but-3-enoate (*Z*-**1f**) *Z*:*E* = 83 : 17



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 83% yield (based on ^{1}H NMR).

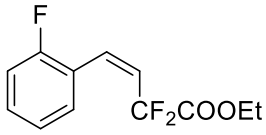
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 8.0, 5.9 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.02 (tdd, *J* = 8.4, 2.9, 0.9 Hz, 1H), 6.90 (dd, *J* = 12.6, 2.0 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.4 Hz, 0.16H, *E*-alkene), 5.91 (q, *J* = 13.2 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 0.31H, *E*-alkene), 4.11 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 0.47H, *E*-alkene), 1.19 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.88, -103.61 (*E*-alkene), -112.59 (*E*-alkene), -112.96.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.9 – 163.1 (m), 161.4, 137.6 (td, $^{4}J_{C\text{-}F}$ = 8.5, 2.4 Hz), 136.5 (d, $^{4}J_{C\text{-}F}$ = 7.9 Hz, *E*-alkene), 130.6 (d, $^{3}J_{C\text{-}F'}$ = 8.1 Hz, *E*-alkene), 130.0 (d, $^{3}J_{C\text{-}F'}$ = 8.2 Hz), 125.0 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 123.7 (*E*-alkene), 123.2 (t, $^{4}J_{C\text{-}F'}$ = 27.7 Hz), 121.0 – 120.0 (m), 116.8 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz, *E*-alkene), 116.2 – 115.8 (m), 115.8 (d, $^{2}J_{C\text{-}F'}$ = 21.1 Hz), 112.3 (t, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 63.5 (*E*-alkene), 63.3, 14.2 (*E*-alkene), 13.9.

Spectral Data agreed with previously reported. [4]

Ethyl (Z)-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate(*Z*-**1g**) *Z*:*E* = 85 : 15



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 85% yield (based on ^{1}H NMR).

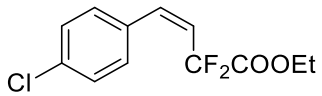
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (td, *J* = 7.6, 1.8 Hz, 0.18H, *E*-alkene), 7.42 – 7.36 (m, 1H), 7.32 (tdd, *J* = 7.4, 5.3, 1.8 Hz, 1H), 7.21 (dt, *J* = 16.4, 2.7 Hz, 0.19H, *E*-alkene), 7.15 – 6.95 (m, 4H), 6.43 (dt, *J* = 16.4, 11.3 Hz, 0.17H, *E*-alkene), 6.00 (q, *J* = 13.0 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 0.34H, *E*-alkene), 4.11 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 0.59H, *E*-alkene), 1.20 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.05 (d, *J* = 2.3 Hz), -103.77 (*E*-alkene), -113.99 (d, *J* = 1.9 Hz), -115.65 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 161.3, 158.8, 131.6 (td, $^{4}J_{C\text{-}F}$ = 8.5, 4.1 Hz), 131.3 (d, $^{4}J_{C\text{-}F}$ = 8.7 Hz, *E*-alkene), 131.0 (q, $^{3}J_{C\text{-}F'}$ = 3.6 Hz, *E*-alkene), 130.9 (d, $^{3}J_{C\text{-}F'}$ = 8.2 Hz), 130.0, 128.8, 124.6 (d, $^{4}J_{C\text{-}F'}$ = 3.7 Hz, *E*-alkene), 124.1 (t, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 124.0 (d, $^{4}J_{C\text{-}F'}$= 3.7 Hz), 122.5 (d, $^{2}J_{C\text{-}F'}$ = 14.4 Hz), 121.6 (d, $^{2}J_{C\text{-}F'}$ = 6.9 Hz, *E*-alkene), 116.3 (d, $^{2}J_{C\text{-}F'}$= 21.8 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), 63.3, 14.2 (*E*-alkene), 13.8.

Spectral Data agreed with previously reported. [4]

Ethyl *(Z)*-4-(4-chlorophenyl)-2,2-difluorobut-3-enoate(*Z*-**1h**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil,

afford 87% yield (based on ^{1}H NMR).

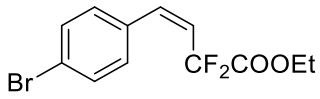
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 6.88 (dt, *J* = 12.7, 2.0 Hz, 1H), 5.88 (td, *J* = 13.4, 12.5 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.99.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 137.7 (t, $^4J_{C\text{-}F}$ = 8.4 Hz), 135.0, 132.8, 130.6 (t, $^3J_{C\text{-}F}$ = 3.0 Hz), 128.6, 122.5 (t, $^2J_{C\text{-}F}$ = 27.7 Hz), 112.3 (t, $^1J_{C\text{-}F}$ = 246.9 Hz), 63.3, 13.9.

Spectral Data agreed with previously reported. [3,4]

Ethyl *(Z)*-4-(4-bromophenyl)-2,2-difluorobut-3-enoate(*Z*-**1i**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 86% yield (based on ^{1}H NMR).

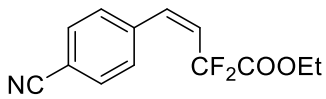
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.41 (m, 2H), 7.23 (dd, *J* = 8.5, 2.1 Hz, 2H), 6.86 (d, *J* = 12.6 Hz, 1H), 5.89 (qd, *J* = 13.4, 13.0, 1.5 Hz, 1H), 4.12 (qt, *J* = 7.1, 1.4 Hz, 2H), 1.19 (tt, *J* = 7.2, 1.5 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.08.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, $^2J_{C\text{-}F}$ = 33.7 Hz), 137.7 (t, $^4J_{C\text{-}F}$ = 8.3 Hz), 133.3, 131.6, 130.8 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 123.2, 122.6 (t, $^2J_{C\text{-}F}$ = 27.6 Hz), 112.4 (t, $^1J_{C\text{-}F}$ = 247.1 Hz), 63.3, 13.9.

Spectral Data agreed with previously reported. [3,4]

Ethyl *(Z)*-4-(4-cyanophenyl)-2,2-difluorobut-3-enoate(*Z*-**1j**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): White solid, afford 80% yield (based on ^{1}H NMR).

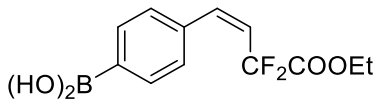
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 6.99 – 6.89 (m, 1H), 5.99 (q, *J* = 14.2, 13.4 Hz, 1H), 4.18 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.24 (td, *J* = 7.2, 1.7 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.27.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 139.0, 136.9 (t, $^4J_{C\text{-}F}$ = 7.7 Hz), 132.1, 129.7 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 124.4 (t, $^2J_{C\text{-}F}$ = 27.1 Hz), 118.7, 112.5, 112.1 (t, $^1J_{C\text{-}F}$ = 248.4 Hz), 63.5, 14.0.

Spectral Data agreed with previously reported. [5,6]

(Z)-(4-(4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)phenyl)boronic acid(*Z*-**1k**) *Z*:*E* = 82 : 18



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): White solid,

afford 82% yield (based on ^{1}H NMR).

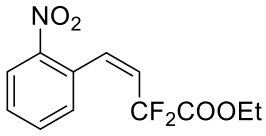
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 0.30H, *E*-alkene), 8.20 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 0.45H, *E*-alkene), 7.48 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 16.2 Hz, 0.31H, *E*-alkene), 7.03 (dd, *J* = 12.7, 2.2 Hz, 1H), 6.45 (dt, *J* = 16.2, 11.3 Hz, 0.31H, *E*-alkene),, 5.97 (q, *J* = 13.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 0.59H, *E*-alkene), 4.08 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 0.91H, *E*-alkene), 1.18 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.49 (d, *J* = 10.7 Hz), -103.41.

^{13}C NMR (101 MHz, Chloroform-*d*)δ 164.1 (*E*-alkene), 163.6 (t, $^2J_{C\text{-}F}$ = 33.8 Hz), 138.9 – 138.5 (m), 138.3, 136.3, 135.7, 128.6 (d, $^3J_{C\text{-}F}$ = 3.2 Hz), 127.2, 123.2 (t, $^2J_{C\text{-}F}$ = 27.8 Hz), 120.8 (d, *J* = 24.8 Hz, *E*-alkene), 112.8 (*E*-alkene), 112.4 (t, $^1J_{C\text{-}F}$ = 246.5 Hz), 63.5 (*E*-alkene), 63.27, 14.2 (*E*-alkene), 13.9.

Spectral Data agreed with previously reported. [6]

Ethyl *(Z)*-2,2-difluoro-4-(2-nitrophenyl)but-3-enoate(*Z*-**1l**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 85% yield (based on ^{1}H NMR).

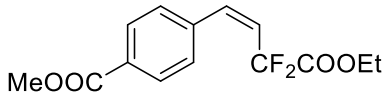
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (t, *J* = 2.0 Hz, 1H), 8.19 (ddd, *J* = 8.3, 2.4, 1.0 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 6.98 (dt, *J* = 12.6, 2.3 Hz, 1H), 6.02 (td, *J* = 14.0, 12.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.03.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.44 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 148.15, 136.33 (t, $^4J_{C\text{-}F}$ = 7.5 Hz), 136.03, 135.03 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 129.42, 124.36 (t, $^2J_{C\text{-}F}$ = 26.9 Hz), 124.00 (t, $^3J_{C\text{-}F}$ = 3.1 Hz), 123.52, 112.18 (t, $^1J_{C\text{-}F}$ = 248.9 Hz), 63.63, 13.96.

Spectral Data agreed with previously reported. [4,6]

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



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): White solid, afford 74% yield (based on ^{1}H NMR).

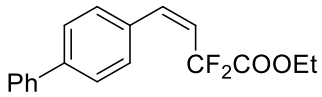
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 12.7 Hz, 1H), 5.96 (q, *J* = 13.1 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.07.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 163.4 (t, $^2J_{C\text{-}F}$ = 33.7 Hz), 138.9, 137.8 (t, $^4J_{C\text{-}F}$ = 8.3 Hz), 130.2, 129.6, 129.1 (t, $^5J_{C\text{-}F}$ = 2.9 Hz), 123.6 (t, $^2J_{C\text{-}F}$ = 27.6 Hz), 112.2 (t, $^1J_{C\text{-}F}$ = 247.1 Hz), 63.3, 52.5, 13.9.

Spectral Data agreed with previously reported. [7]

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



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): White solid, afford 73% yield (based on ^{1}H NMR).

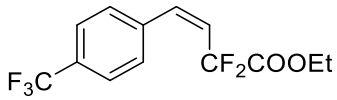
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 4H), 7.45 (t, *J* = 7.2 Hz, 4H), 7.39 – 7.33 (m, 1H), 6.96 (dd, *J* = 12.6, 1.9 Hz, 1H), 5.97 – 5.81 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.17.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (t, $^2J_{C\text{-}F}$ = 33.9 Hz), 141.7, 140.5, 138.5 (t, $^4J_{C\text{-}F}$ = 8.7 Hz), 133.4, 129.8 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 129.1, 127.2, 127.1, 121.9 (t, $^2J_{C\text{-}F}$ = 27.9 Hz), 112.5 (t, $^1J_{C\text{-}F}$ = 246.1 Hz), 63.2, 13.8.

Spectral Data agreed with previously reported. [4]

Ethyl *(Z)*-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate(*Z*-**1o**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 78% yield (based on ^{1}H NMR).

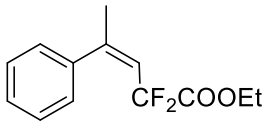
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 12.6 Hz, 1H), 5.98 (q, *J* = 13.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.79, -95.52.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.49 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 138.01, 137.42 (t, $^4J_{C\text{-}F}$ = 8.1 Hz), 130.70 (q, $^2J_{C\text{-}F'}$ = 32.6 Hz), 125.31 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.87 (t, $^2J_{C\text{-}F}$ = 27.4 Hz), 112.21 (t, $^1J_{C\text{-}F}$ = 247.6 Hz), 63.41, 13.85.

Spectral Data agreed with previously reported.[5]

Ethyl *(Z)*-2,2-difluoro-4-phenylpent-3-enoate(*Z*-**1p**)



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 55% yield (based on ^{1}H NMR).

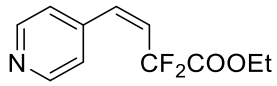
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 3H), 7.19 (dt, *J* = 6.1, 2.1 Hz, 2H), 5.91 – 5.69 (m, 1H), 3.85 (qd, *J* = 7.0, 2.4 Hz, 2H), 2.18 – 2.12 (m, 3H), 1.14 (ddd, *J* = 8.6, 5.1, 2.0 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.83.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8 (t, $^2J_{C\text{-}F}$ = 34.0 Hz), 148.9 (t, $^3J_{C\text{-}F}$ = 9.5 Hz), 139.3, 128.3, 128.3, 127.7, 119.5 (t, $^2J_{C\text{-}F}$ = 28.1 Hz), 112.5 (t, $^1J_{C\text{-}F}$ = 244.7 Hz), 62.8, 27.3, 13.9.

Spectral Data agreed with previously reported. [8]

Ethyl *(Z)*-2,2-difluoro-4-(pyridin-4-yl)but-3-enoate(*Z*-**1q**) *Z*:*E* = 72 : 28



Purification by column chromatography over silica (n-pentane/ethyl acetate 100/1): Colorless oil, afford 72% yield (based on ^{1}H NMR).

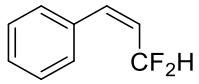
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.63 (m, 0.93H, *E*-alkene), 8.63 – 8.57 (m, 2H), 7.36 – 7.30 (m, 0.95H, *E*-alkene), 7.27 – 7.21 (m, 2H), 7.04 (d, *J* = 16.2 Hz, 0.53H, *E*-alkene), 6.89 (dt, *J* = 12.6, 2.2 Hz, 1H), 6.52 (dt, *J* = 16.2, 11.2 Hz, 0.46H, *E*-alkene), 6.03 (td, *J* = 13.5, 12.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 0.94H, *E*-alkene), 4.17 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 1.42H, *E*-alkene), 1.23 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.15, -104.24 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5 (t, $^2J_{C\text{-}F}$ = 34.3 Hz, *E*-alkene), 163.3 (t, $^2J_{C\text{-}F}$ = 33.5 Hz), 150.7 (*E*-alkene), 149.9, 142.1, 141.5 (*E*-alkene), 136.1 (t, $^4J_{C\text{-}F}$ = 7.8 Hz), 134.6 (t, $^4J_{C\text{-}F}$ = 9.3 Hz, *E*-alkene), 125.0 (t, $^2J_{C\text{-}F}$ = 27.3 Hz), 123.7 (t, $^2J_{C\text{-}F}$ = 25.2 Hz, *E*-alkene), 123.3 (t, $^5J_{C\text{-}F}$ = 2.8 Hz), 121.7, 112.1 (t, $^1J_{C\text{-}F}$ = 250.5 Hz, *E*-alkene), 111.8 (t, $^1J_{C\text{-}F}$ = 248.3 Hz) , 63.5 (*E*-alkene), 63.3, 13.9 (*E*-alkene), 13.7.

Spectral Data agreed with previously reported. [4]

(Z)-(3,3-difluoroprop-1-en-1-yl)benzene(*Z*-**1r**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 90% yield (based on ^{1}H NMR).

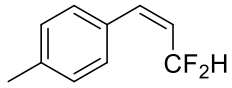
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dq, *J* = 6.7, 5.7, 4.8 Hz, 3H), 7.32 – 7.25 (m, 2H), 6.96 (d, *J* = 11.8 Hz, 1H), 6.34 (td, *J* = 55.3, 7.5 Hz, 1H), 5.86 (dq, *J* = 11.8, 8.2 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.00.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2 (t, $^3J_{C\text{-}F}$ = 12.6 Hz), 134.7 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 129.0 (t, $^7J_{C\text{-}F}$ = 1.9 Hz), 128.9, 128.9, 123.9 (t, $^2J_{C\text{-}F}$ = 26.3 Hz), 112.6 (t, $^1J_{C\text{-}F}$ = 230.4 Hz).

Spectral Data agreed with previously reported. [9]

(Z)-1-(3,3-difluoroprop-1-en-1-yl)-4-methylbenzene(*Z*-**1s**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 90% yield (based on ^{1}H NMR).

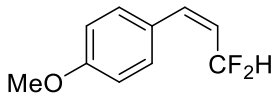
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.2 Hz, 4H), 6.92 (d, *J* = 11.8 Hz, 1H), 6.35 (tdd, *J* = 55.4, 7.4, 0.9 Hz, 1H), 5.81 (dtd, *J* = 11.7, 8.5, 7.4 Hz, 1H), 2.37 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.83.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 138.1 (t, $^3J_{C\text{-}F}$ = 12.6 Hz), 131.8 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 129.6, 129.0 (t, $^7J_{C\text{-}F}$ = 1.8 Hz), 123.2 (t, $^2J_{C\text{-}F}$ = 26.1 Hz), 112.7 (t, $^1J_{C\text{-}F}$ = 230.3 Hz), 21.5.

Spectral Data agreed with previously reported. [10]

(Z)-1-(3,3-difluoroprop-1-en-1-yl)-4-methoxybenzene(*Z*-**1t**)



Purification by column chromatography over silica (n-pentane): White solid, afford 83% yield (based on ^{1}H NMR).

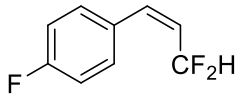
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 6.96 – 6.83 (m, 3H), 6.36 (tdd, *J* = 55.5, 7.4, 0.9 Hz, 1H), 5.76 (dtd, *J* = 11.7, 8.7, 7.3 Hz, 1H), 3.83 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.52.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 137.7 (t, $^3J_{C\text{-}F}$ = 12.7 Hz), 130.5 (t, $^5J_{C\text{-}F}$ = 1.8 Hz), 127.3 (t, $^4J_{C\text{-}F}$ = 2.3 Hz), 122.3 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 114.3, 112.8 (t, $^1J_{C\text{-}F}$ = 230.2 Hz), 55.5.

Spectral Data agreed with previously reported. [10]

(Z)-1-(3,3-difluoroprop-1-en-1-yl)-4-fluorobenzene(*Z*-**1u**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 79% yield (based on ^{1}H NMR).

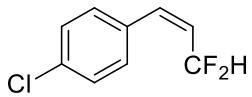
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 11.8 Hz, 1H), 6.30 (tdd, *J* = 55.2, 7.4, 0.8 Hz, 1H), 5.86 (dq, *J* = 11.8, 8.2 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.03, -112.22.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1 (d, $^1J_{C\text{-}F'}$ = 249.0 Hz), 137.0 (t, $^3J_{C\text{-}F}$ = 12.7 Hz), 130.8 (dt, $^5J_{C\text{-}F}$ = 8.3, 1.9 Hz), 124.0 (t, $^2J_{C\text{-}F}$ = 26.6 Hz), 116.0 (d, $^2J_{C\text{-}F'}$ = 21.7 Hz), 112.4 (t, $^1J_{C\text{-}F}$ = 230.8 Hz).

Spectral Data agreed with previously reported. [9]

(Z)-1-chloro-4-(3,3-difluoroprop-1-en-1-yl)benzene(*Z*-**1v**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 84% yield (based on ^{1}H NMR).

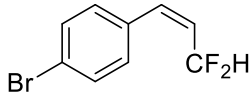
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 2H), 6.90 (d, *J* = 11.8 Hz, 1H), 6.29 (tdd, *J* = 55.2, 7.4, 0.9 Hz, 1H), 5.88 (dtd, *J* = 11.8, 8.5, 7.3 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.14.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.9 (t, $^3J_{C\text{-}F}$ = 12.6 Hz), 135.0, 133.0, 130.3, 129.1, 124.6 (t, $^2J_{C\text{-}F}$ = 26.4 Hz), 112.3 (t, $^1J_{C\text{-}F}$ = 230.9 Hz).

Spectral Data agreed with previously reported. [10]

(Z)-1-bromo-4-(3,3-difluoroprop-1-en-1-yl)benzene(*Z*-**1w**)



Purification by column chromatography over silica (n-pentane): White solid, afford 82% yield (based on ^{1}H NMR).

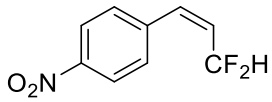
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.21 – 7.11 (m, 2H), 6.88 (d, *J* = 11.8 Hz, 1H), 6.28 (td, *J* = 55.2, 7.4 Hz, 1H), 5.89 (dtd, *J* = 11.8, 8.5, 7.3 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.16.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.9 (t, $^3J_{C\text{-}F}$ = 12.6 Hz), 133.5, 132.1, 130.5 (t, $^5J_{C\text{-}F}$ = 1.9 Hz), 124.6 (t, $^2J_{C\text{-}F}$ = 26.3 Hz), 123.3, 112.2 (t, $^1J_{C\text{-}F}$ = 231.0 Hz).

Spectral Data agreed with previously reported. [9.10]

(Z)-1-(3,3-difluoroprop-1-en-1-yl)-4-nitrobenzene(*Z*-**1x**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 70% yield (based on ^{1}H NMR).

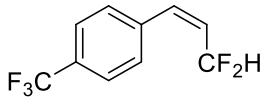
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.05 – 6.96 (m, 1H), 6.27 (tdd, *J* = 54.7, 7.3, 0.8 Hz, 1H), 6.05 (dtd, *J* = 11.9, 8.6, 7.3 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.69.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9, 140.9 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 135.8 (t, $^3J_{C\text{-}F}$ = 12.3 Hz), 129.8, 127.0 (t, $^2J_{C\text{-}F}$ = 26.7 Hz), 124.1, 111.7 (t, $^1J_{C\text{-}F}$ = 232.0 Hz).

Spectral Data agreed with previously reported. [10]

(Z)-1-(3,3-difluoroprop-1-en-1-yl)-4-(trifluoromethyl)benzene(*Z*-**1y**)



Purification by column chromatography over silica (n-pentane): Colorless oil, afford 85% yield (based on ^{1}H NMR).

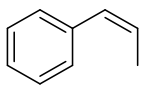
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 11.9 Hz, 1H), 6.27 (tdd, *J* = 55.0, 7.4, 0.8 Hz, 1H), 5.98 (dtd, *J* = 11.8, 8.4, 7.4 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.77, -108.49.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.1, 136.7 (t, $^3J_{C\text{-}F}$ = 12.5 Hz), 130.9 (d, $^2J_{C\text{-}F'}$= 32.8 Hz), 129.2 (t, $^4J_{C\text{-}F'}$= 1.9 Hz), 125.9 – 125.8 (m), 126.3 – 125.2 (m), 122.7, 112.0 (t, $^1J_{C\text{-}F}$ = 231.4 Hz).

Spectral Data agreed with previously reported. [10]

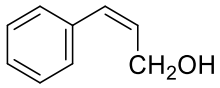
(Z)-prop-1-en-1-ylbenzene(*Z*-**2a**) *Z*:*E* = 88 : 12



The proton NMR matches with the commercially available compound. The general procedure b was followed. Purification by column chromatography over silica (n-pentane): Colorless oil, afford 88% yield (based on ^{1}H NMR).

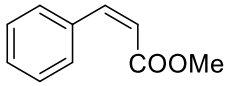
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 7.24 – 7.16 (m, 1.21H, *E*-alkene), 6.44 (dd, *J* = 11.5, 2.0 Hz, 1H), 6.38 (d, *J* = 1.8 Hz, 0.14H, *E*-alkene), 6.26 (t, *J* = 6.5 Hz, 0.12H, *E*-alkene), 5.79 (dq, *J* = 11.4, 7.2 Hz, 1H), 1.92 – 1.89 (m, 3H), 1.87 (t, *J* = 1.2 Hz, 0.44H, *E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2 (*E*-alkene), 137.8, 131.2 (*E*-alkene), 130.1, 129.0, 128.7, 128.32, 127.0 (*E*-alkene), 127.0 (*E*-alkene), 126.6 (*E*-alkene), 126.0, 125.91 (*E*-alkene), 18.7 (*E*-alkene), 14.82.

(Z)-3-phenylprop-2-en-1-ol(*Z*-**2b**) *Z*:*E* = 81 : 19



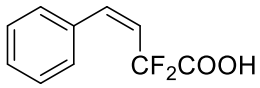
The proton NMR matches with the commercially available compound. The general procedure b was followed. Purification by column chromatography over silica (n-pentane): White solid, afford 81% yield (based on ^{1}H NMR).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.2 Hz, 0.44H, *E*-alkene), 7.34 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.28 – 7.17 (m, 3H), 6.64 (s, 0.12H, *E*-alkene), 6.57 (dt, *J* = 11.6, 2.0 Hz, 1H), 6.36 (dd, *J* = 15.9, 5.8 Hz, 0.26H, *E*-alkene), 5.87 (dt, *J* = 11.7, 6.4 Hz, 1H), 4.44 (dd, *J* = 6.4, 1.7 Hz, 2H), 4.32 (d, *J* = 5.7 Hz, 0.52H, *E*-alkene), 1.67 (s, 0.38H, *E*-alkene), 1.63 (s, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.8 (*E*-alkene), 136.7, 131.3, 131.2 (*E*-alkene), 129.0, 128.8 (*E*-alkene), 128.7 (*E*-alkene), 128.5, 127.9 (*E*-alkene), 127.5, 126.7, 63.9 (*E*-alkene), 59.9.

Methyl *(Z)*-3-phenylacrylate(*Z*-**2c**)



The proton NMR matches with the commercially available compound. The general procedure b was followed. Purification by column chromatography over silica (n-pentane): White solid, afford 73% yield (based on ^{1}H NMR).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.42 – 7.30 (m, 3H), 6.97 (dd, *J* = 12.6, 0.8 Hz, 1H), 5.96 (d, *J* = 12.6 Hz, 1H), 3.72 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 143.7, 134.9, 129.9, 129.3, 128.3, 119.5, 51.6.

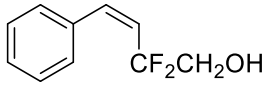
(Z)-2,2-difluoro-4-phenylbut-3-enoic acid (**3**) *Z*:*E* = 83 : 17



Accurately weigh 0.2 mmol *Z*-**1a**, 0.8 mmol LiOH, and add them to a reaction tube with a magnet. React at room temperature in a 2 mL THF/H_2O (7:3) mixed solvent, and monitor the reaction progress on a dot plate until the raw materials fully react. Purification by column chromatography over silica (Ethyl acetate/ethanol=1:1) to obtain **4**: White solid, 32.9 mg, after 83% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.49 – 7.36 (m, 1.24H, *E*-alkene), 7.31 (d, *J* = 8.1 Hz, 5H), 7.15 – 7.09 (m, 0.24H, *E*-alkene), 7.00 (d, *J* = 12.5 Hz, 1H), 6.28 (dt, *J* = 16.4, 11.4 Hz, 0.23H, *E*-alkene), 5.85 (q, *J* = 13.2 Hz, 1H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -95.93, -104.23 (*E*-alkene).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7 (t, $^{2}J_{C\text{-}F}$ = 34.2 Hz), 140.0 (t, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 138.0 (t, $^{3}J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 134.2, 134.0 (*E*-alkene), 130.2 (*E*-alkene), 129.2, 129.1, 128.4, 127.7 (*E*-alkene), 121.1 (t, $^{2}J_{C\text{-}F}$ = 27.1 Hz), 118.1 (t, $^{2}J_{C\text{-}F}$ = 24.7 Hz, *E*-alkene), 112.2 (t, $^{1}J_{C\text{-}F}$ = 246.9 Hz).
Spectral Data agreed with previously reported. [11]

(Z)-2,2-difluoro-4-phenylbut-3-en-1-ol (**4**) *Z*:*E* = 87 : 13



Accurately weigh 0.2 mmol *Z*-**1a** and add it to a reaction tube with magnetic particles. Slowly add 2 mL of $LiAlH_4$ (1.0 mol/L) to 2 mL of THF and react at room temperature. Point plate detection of the reaction progress until the raw material fully reacts. Purification by column chromatography over silica (Ethyl acetate/ethanol=100:1) to obtain **5**: Colorless oil, 32.0 mg, afford 87% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.8 Hz, 1.11H, *E*-alkene), 7.33 (q, *J* = 7.5 Hz, 5H), 7.00 (dd, *J* = 16.3, 2.6 Hz, 0.26H, *E*-alkene), 6.88 (d, *J* = 12.9 Hz, 1H), 6.25 (dt, *J* = 16.0, 11.3 Hz, 0.27H, *E*-alkene), 5.76 (q, *J* = 13.8 Hz, 1H), 3.87 (t, *J* = 12.7 Hz, 0.58H, *E*-alkene), 3.75 (t, *J* = 13.2 Hz, 2H), 2.03 (s, 1H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.31, -106.15 (*E*-alkene).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.1 (t, $^{3}J_{C\text{-}F}$ = 7.1 Hz), 135.9 (t, $^{3}J_{C\text{-}F}$ = 9.4 Hz, *E*-alkene), 135.2, 134.8 (*E*-alkene), 129.4 (*E*-alkene), 129.1 (t, $^{7}J_{C\text{-}F}$ = 3.6 Hz), 129.0 (*E*-alkene), 128.6, 128.4, 127.4 (*E*-alkene), 123.0 (t, $^{2}J_{C\text{-}F}$ = 26.7 Hz), 120.6 (t, $^{2}J_{C\text{-}F}$ = 25.6 Hz, *E*-alkene), 119.7 (t, $^{1}J_{C\text{-}F}$ = 240.5 Hz), 65.3 (t, $^{2}J_{C\text{-}F}$ = 32.5 Hz, *E*-alkene), 64.9 (t, $^{2}J_{C\text{-}F}$ = 31.0 Hz).
Spectral Data agreed with previously reported. [12]

6. References

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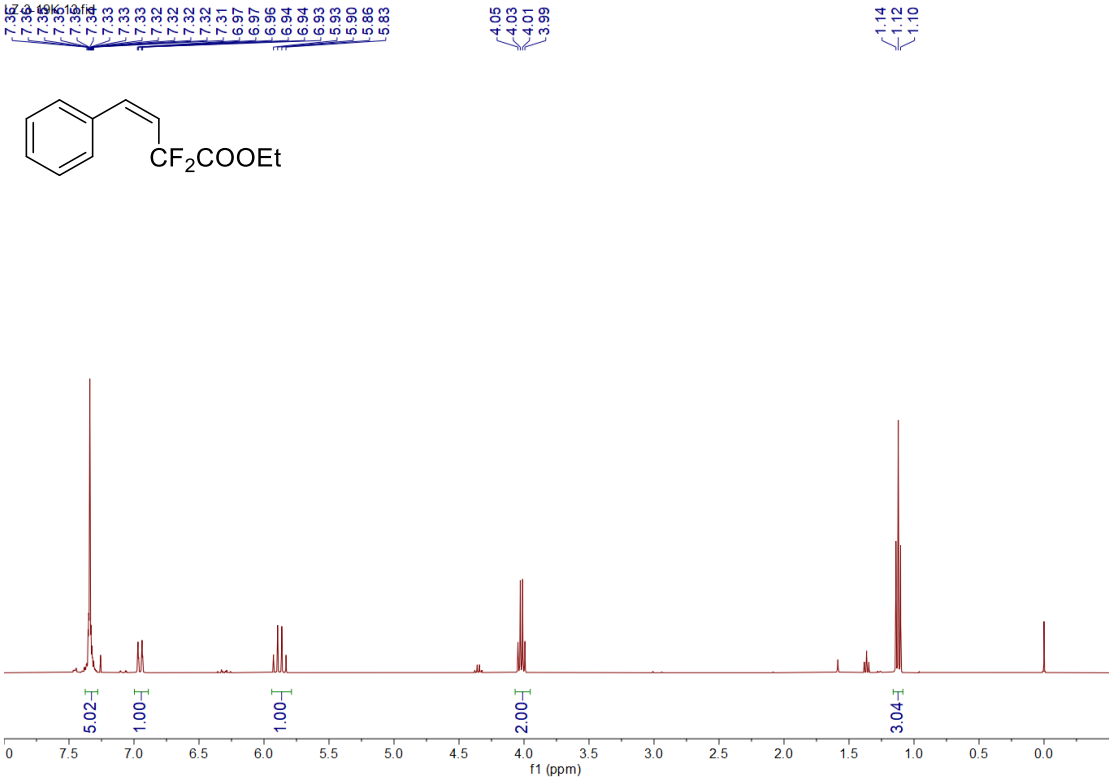
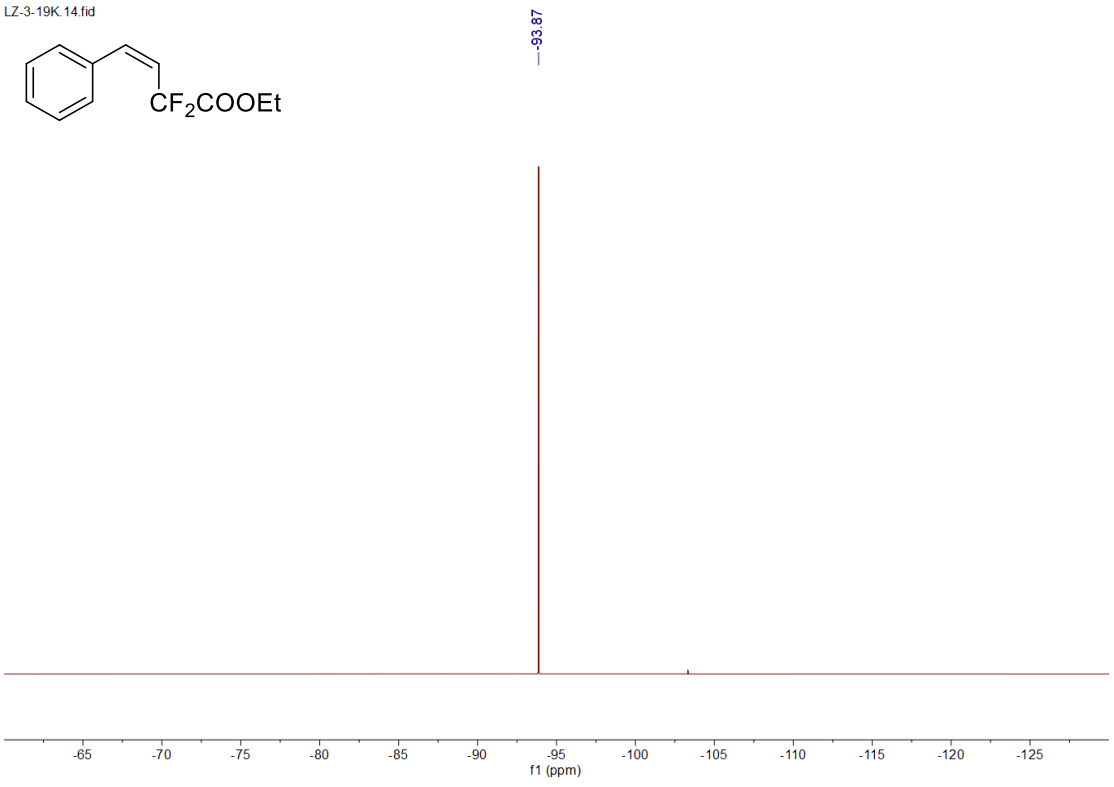
7. Copies of NMR spectra of products.

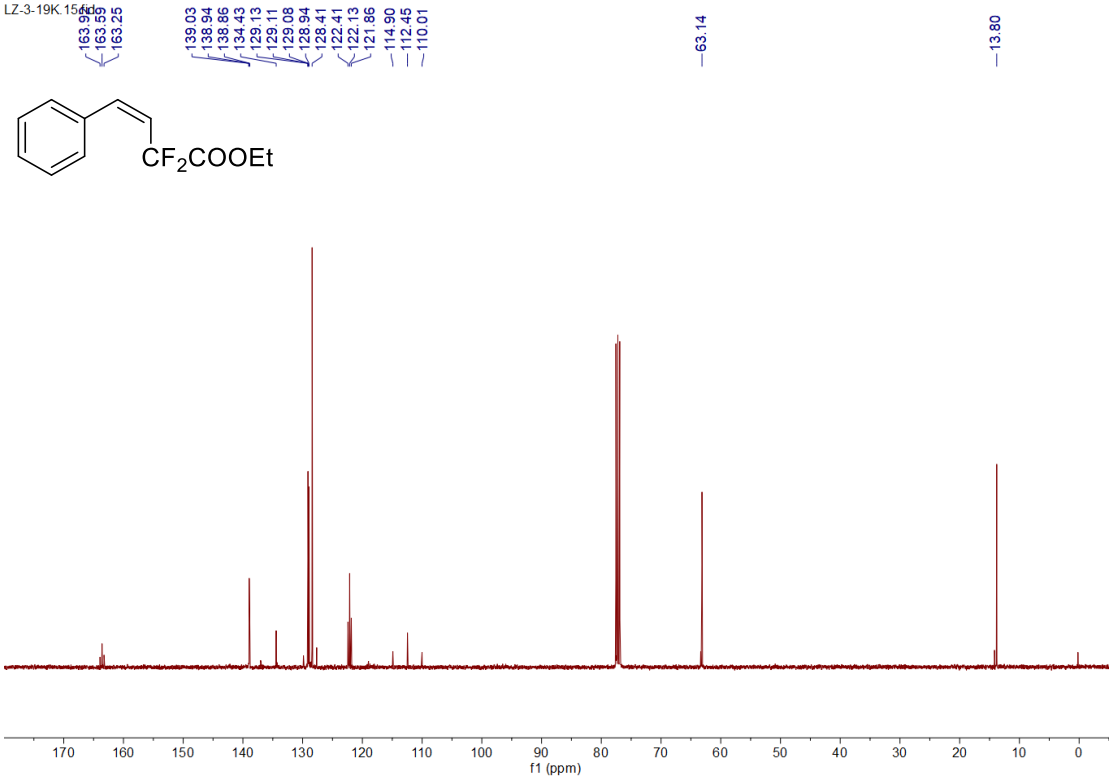
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1a**)



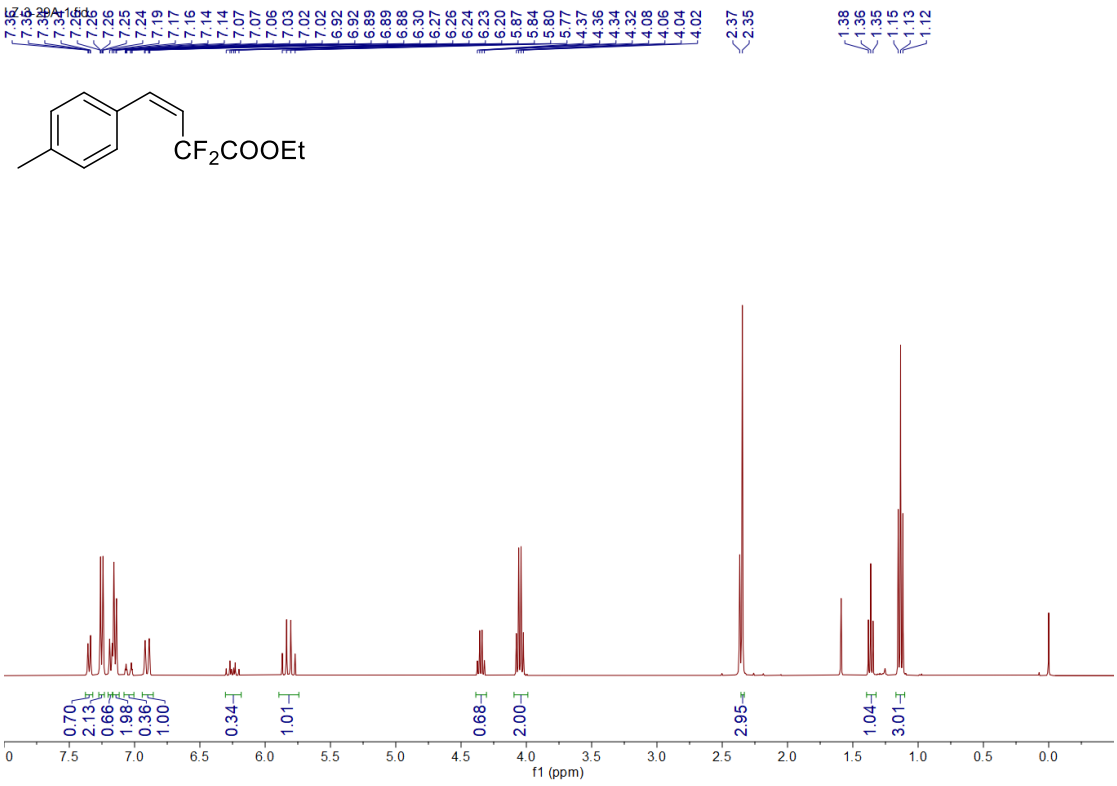
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1a**)



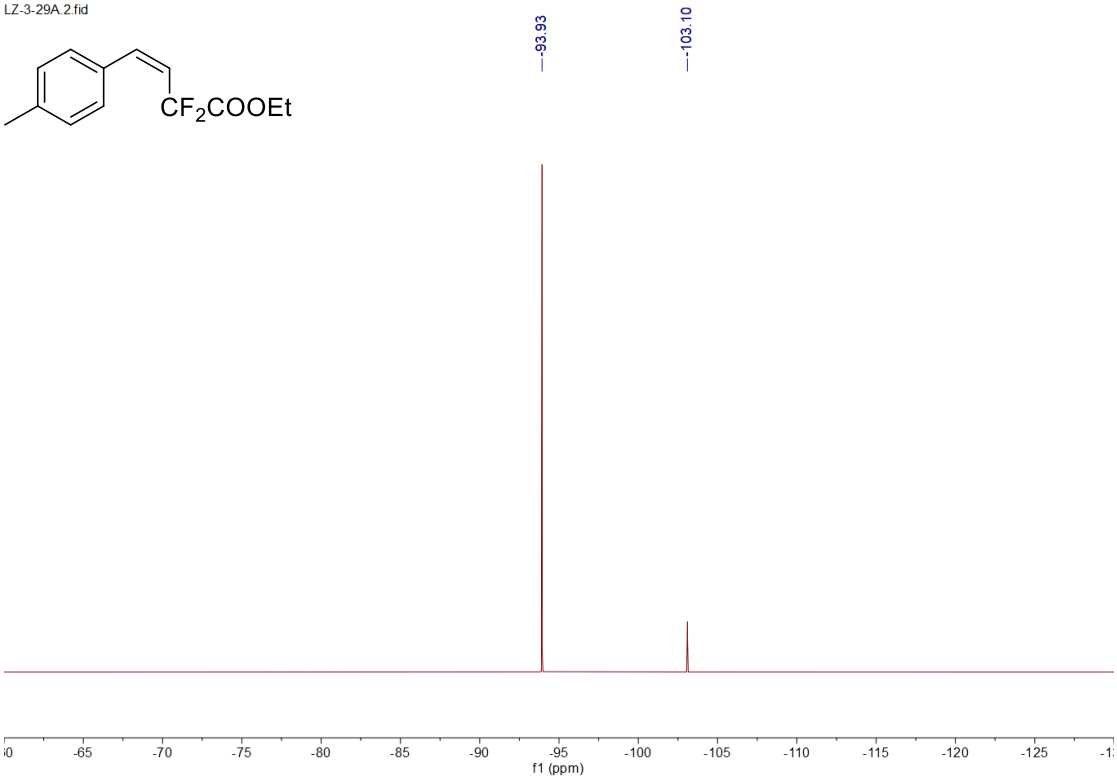
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1a**)



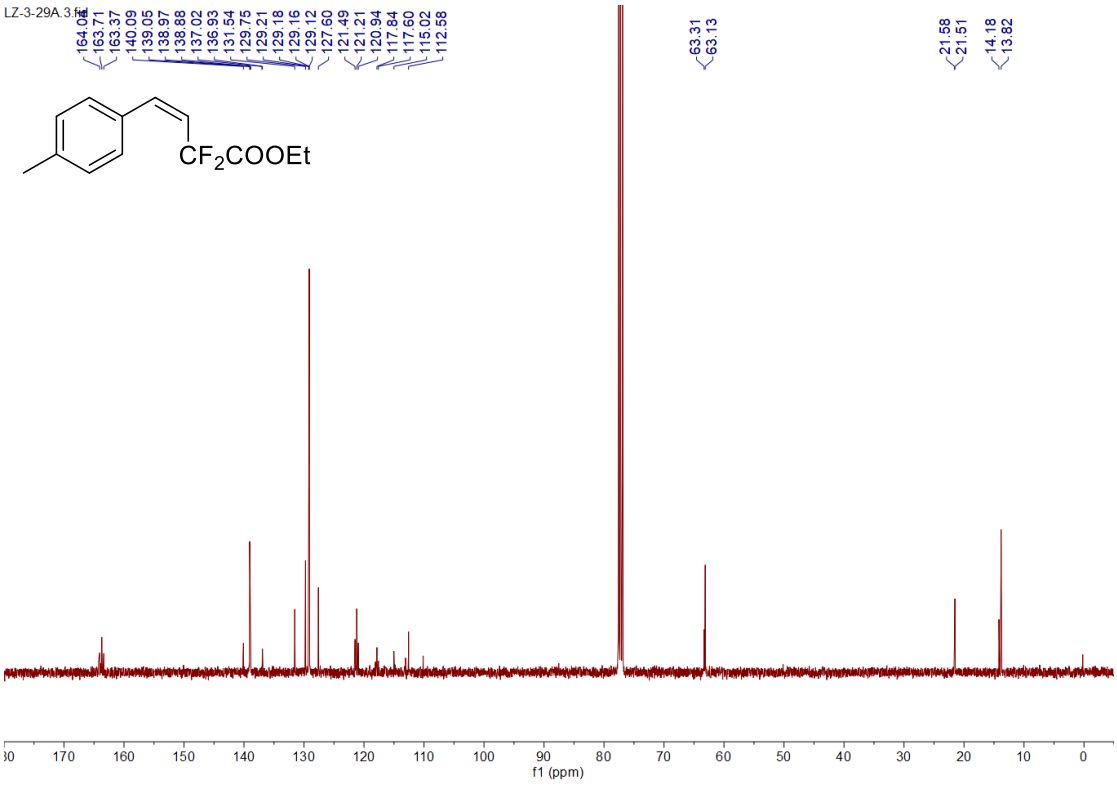
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1b**) *Z*:*E* = 70 : 30



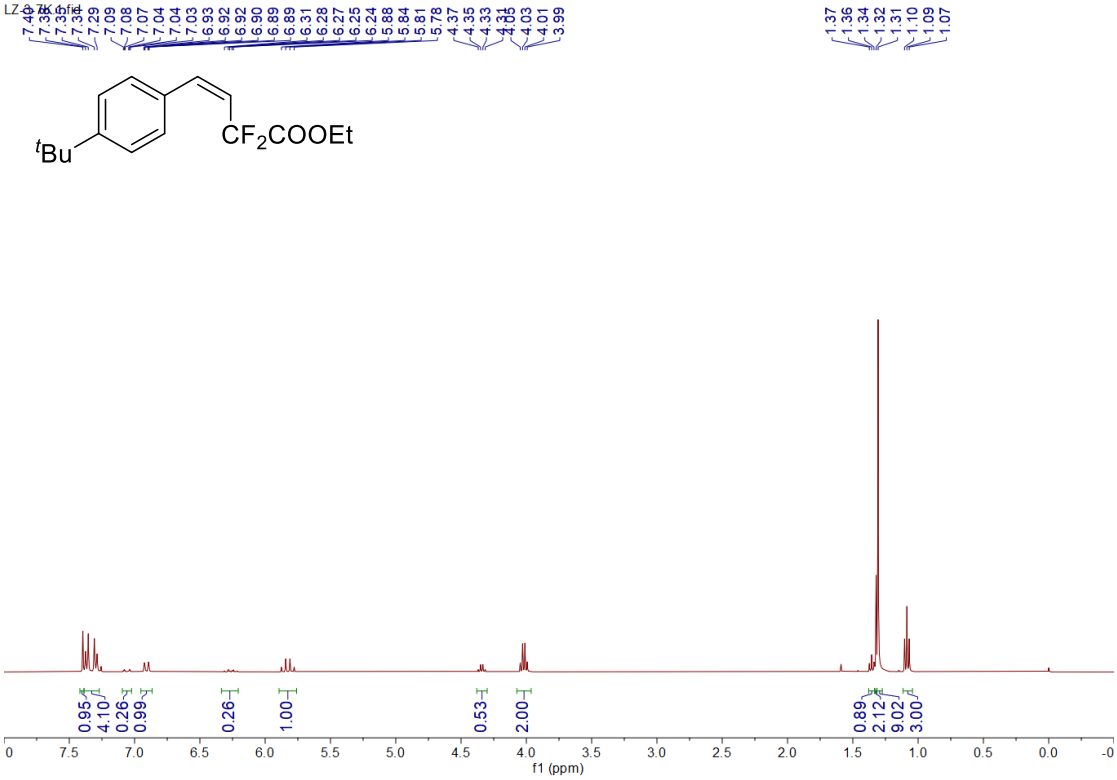
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1b**) *Z*:*E* = 70 : 30



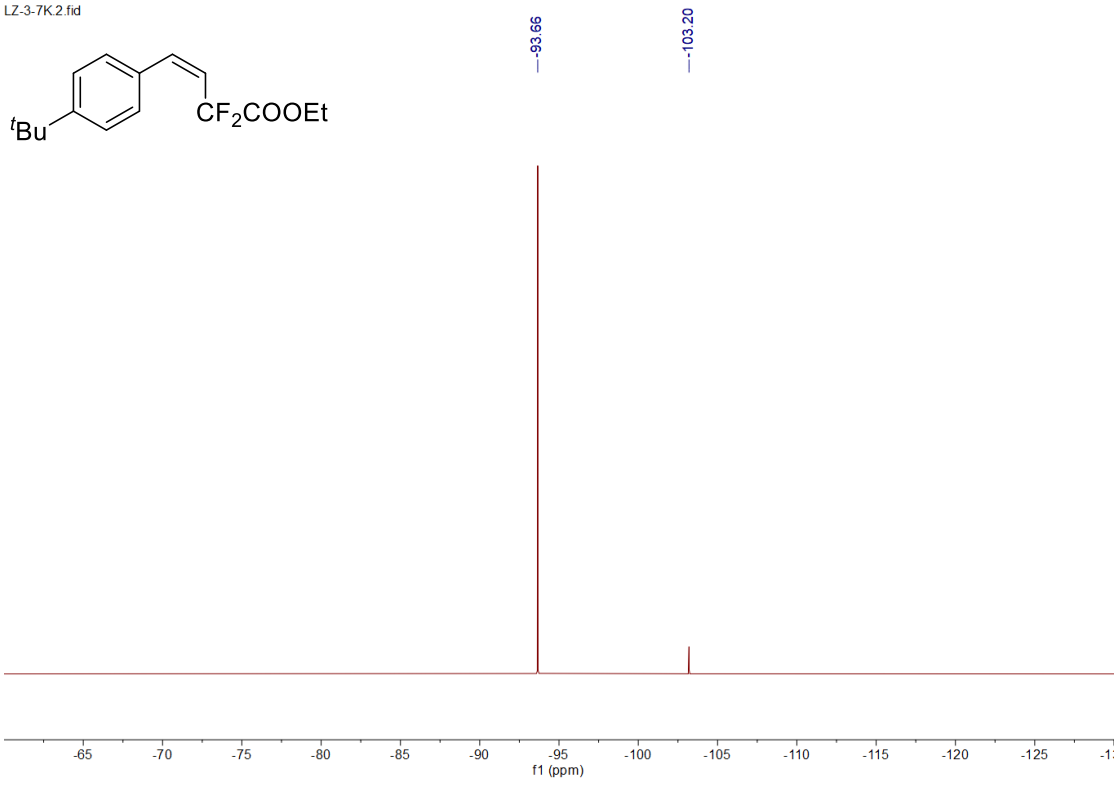
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1b**) *Z*:*E* = 70 : 30



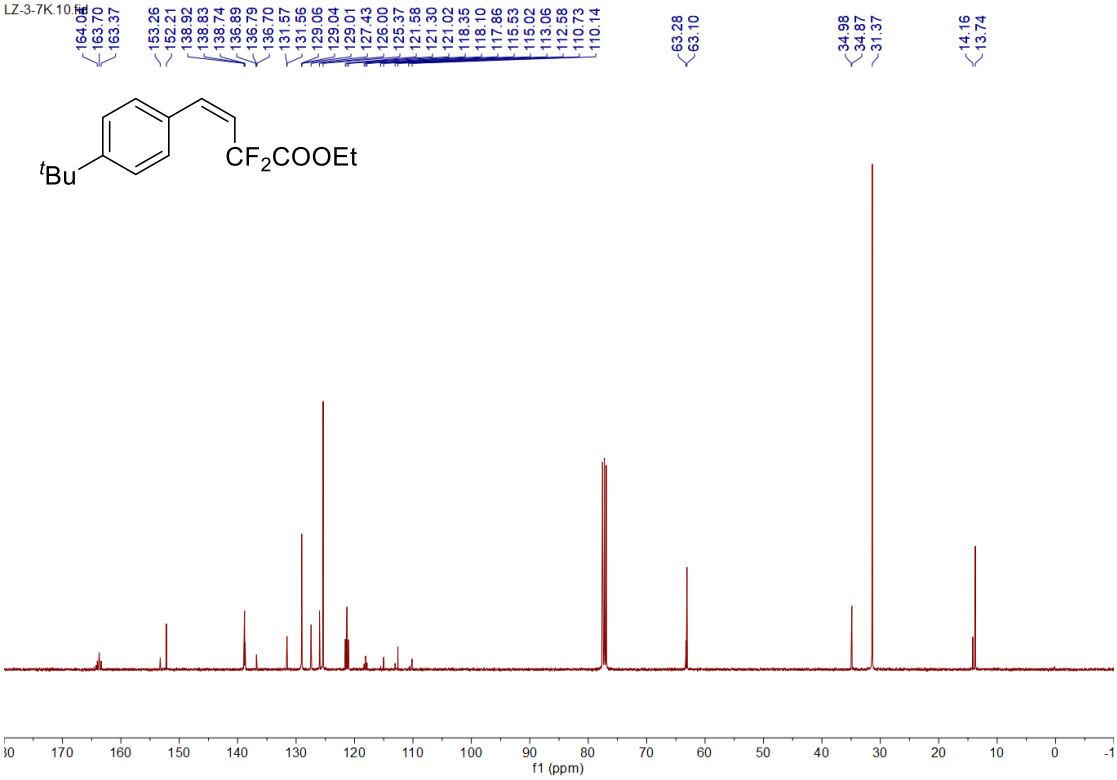
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1c**) *Z*:*E* = 63 : 37



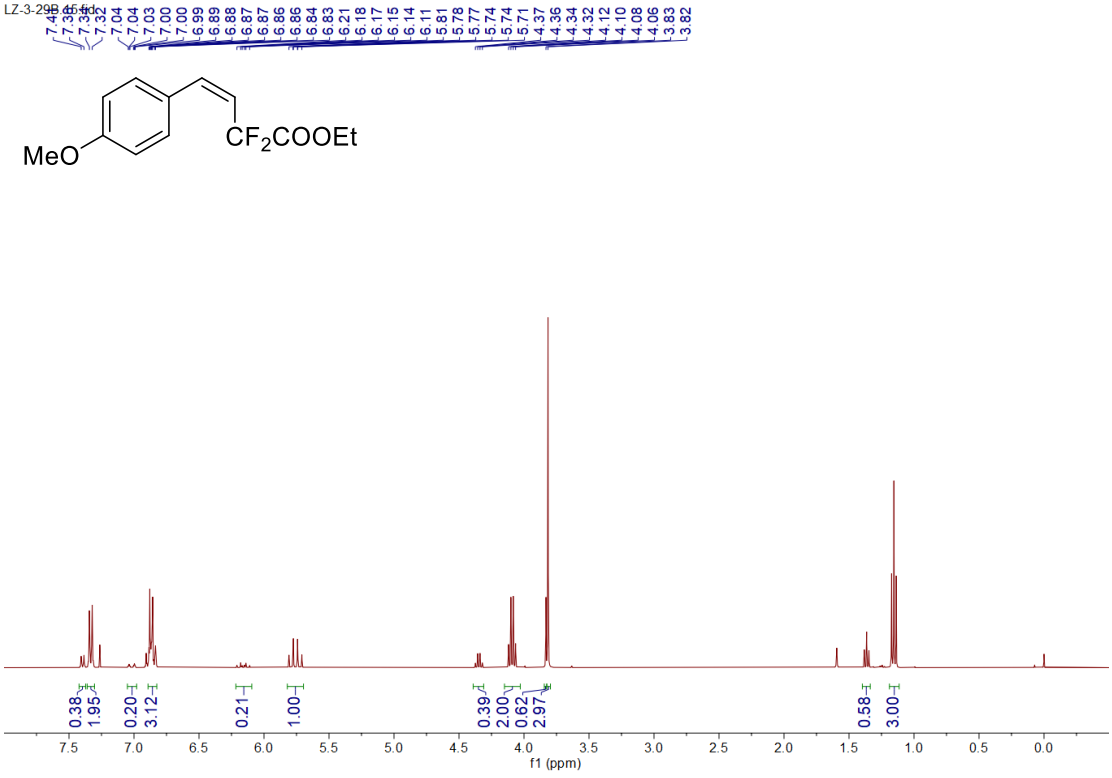
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1c**) *Z*:*E* = 63 : 37



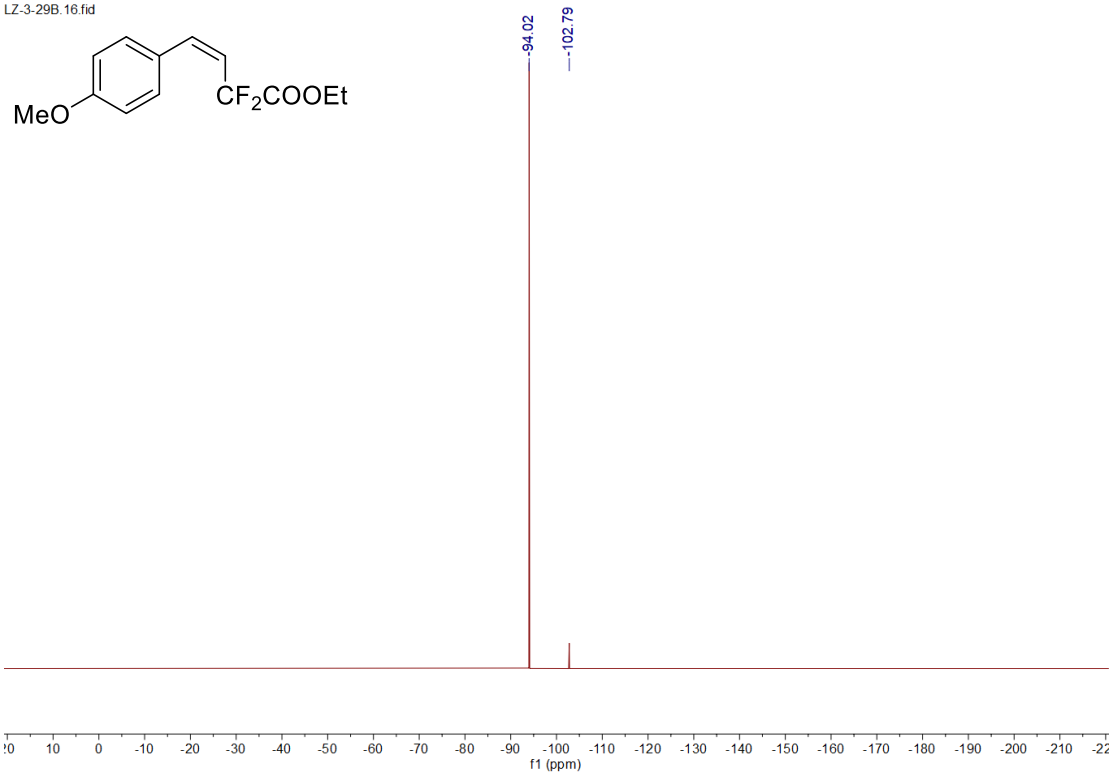
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1c**) *Z*:*E* = 63 : 37



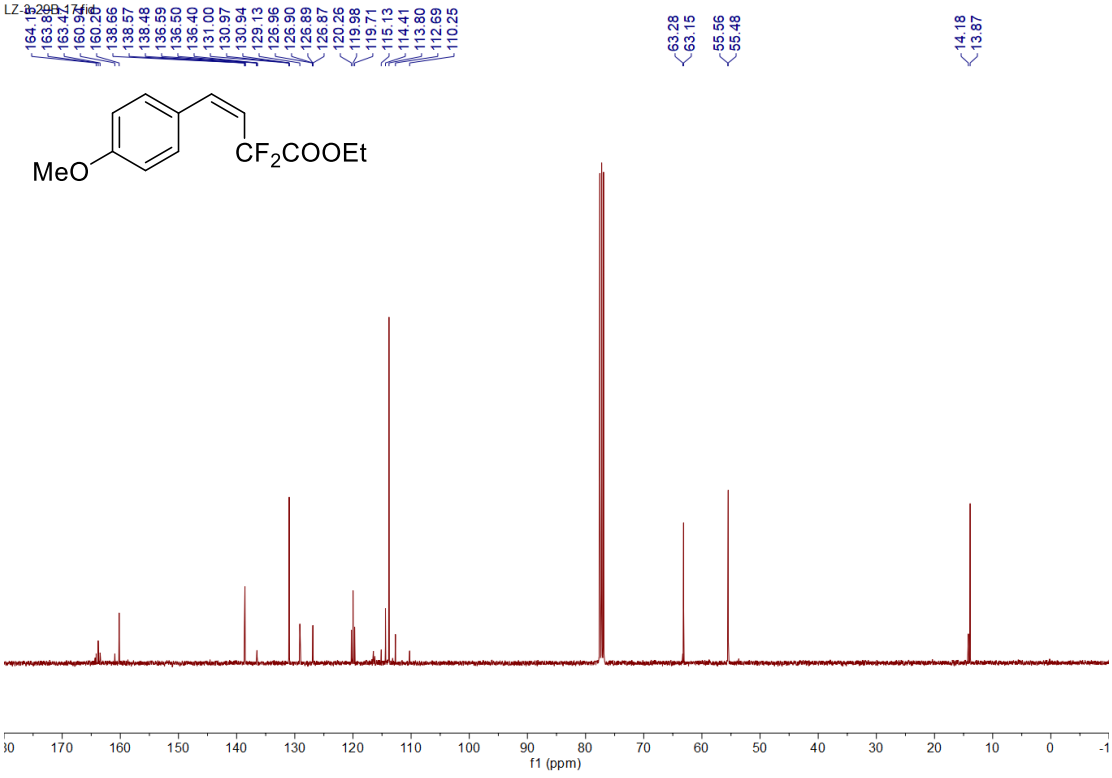
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1d**) *Z*:*E* = 65 : 35



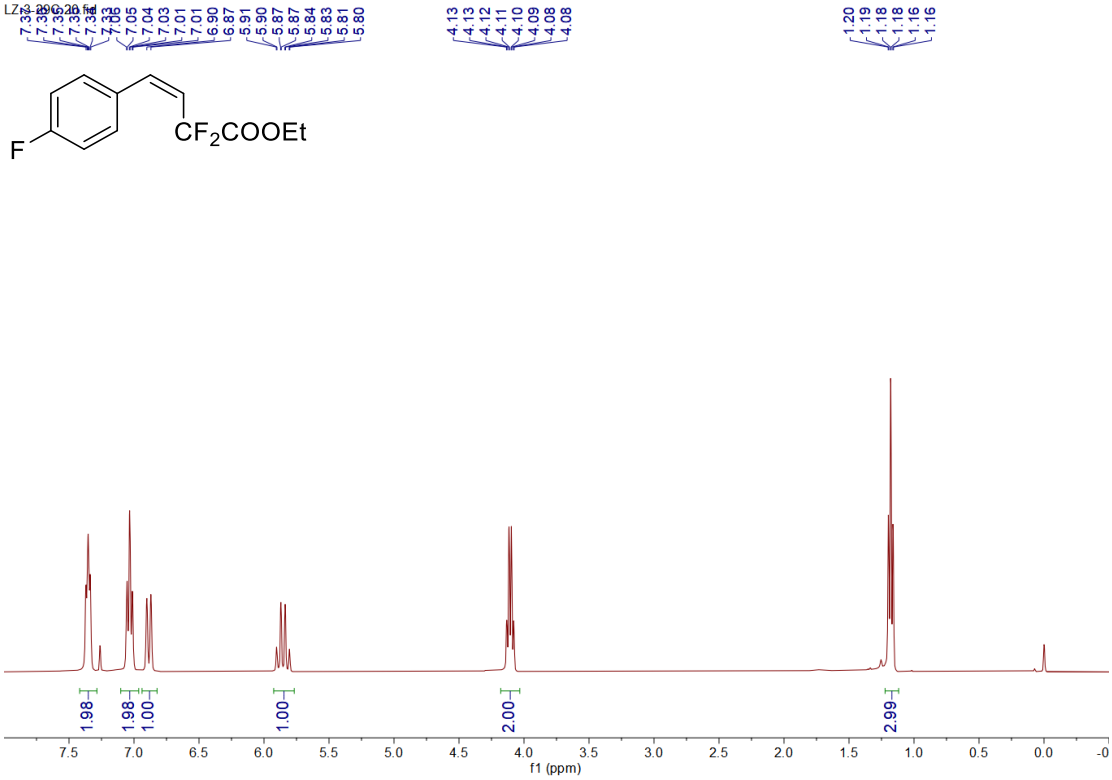
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1d**) *Z*:*E* = 65 : 35



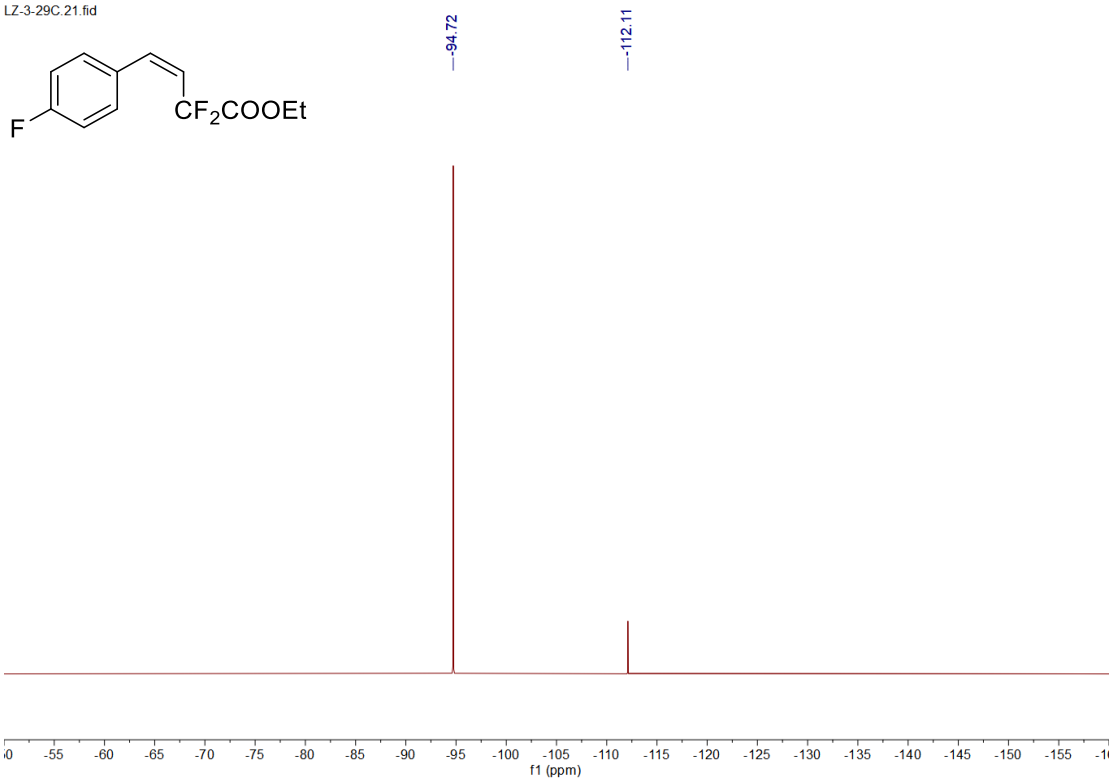
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1d**) *Z*:*E* = 65 : 35



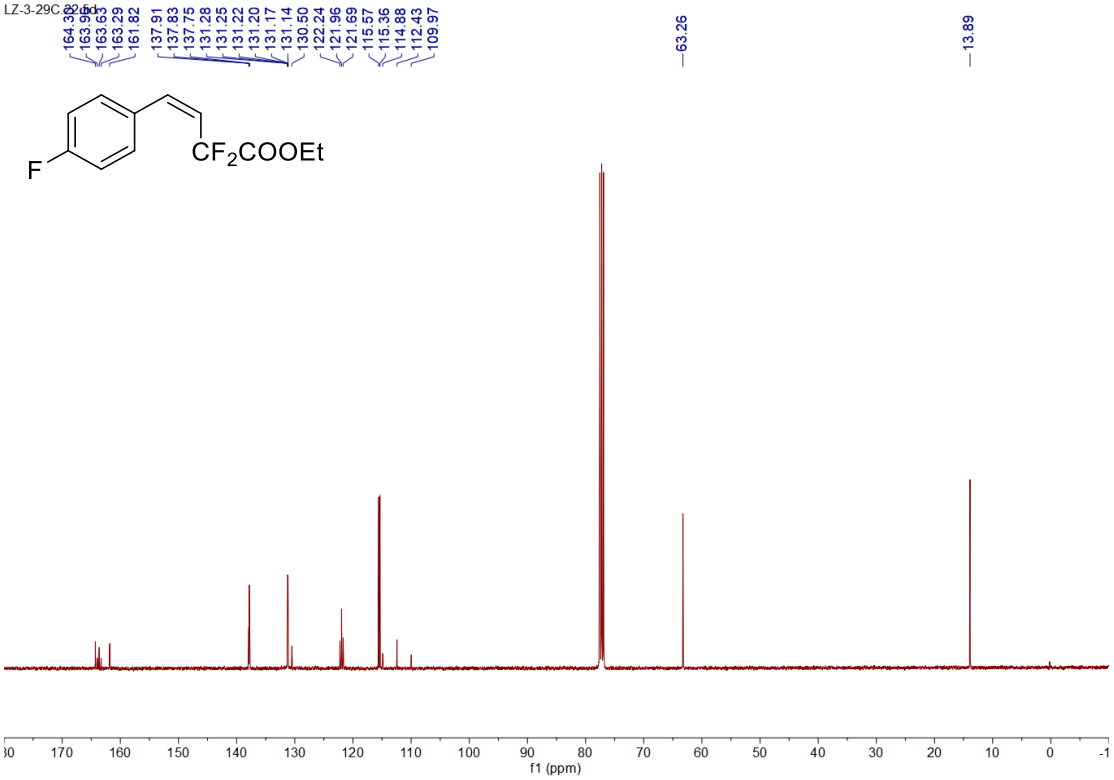
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1e**)



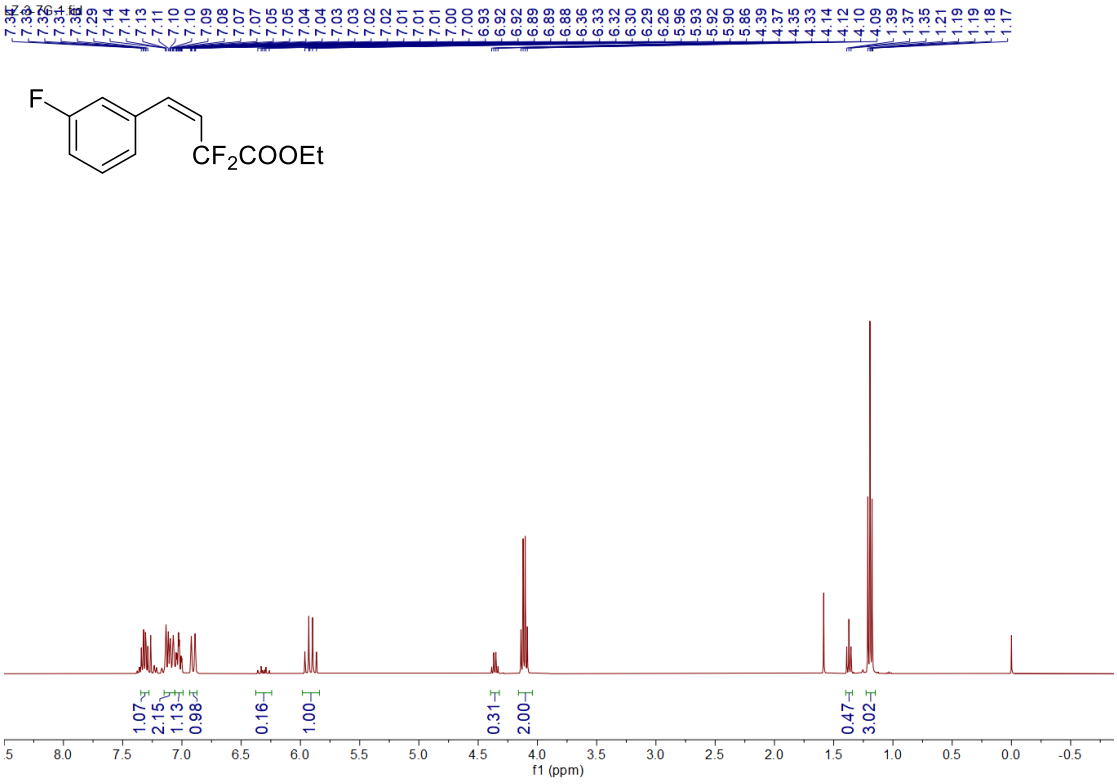
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1e**)



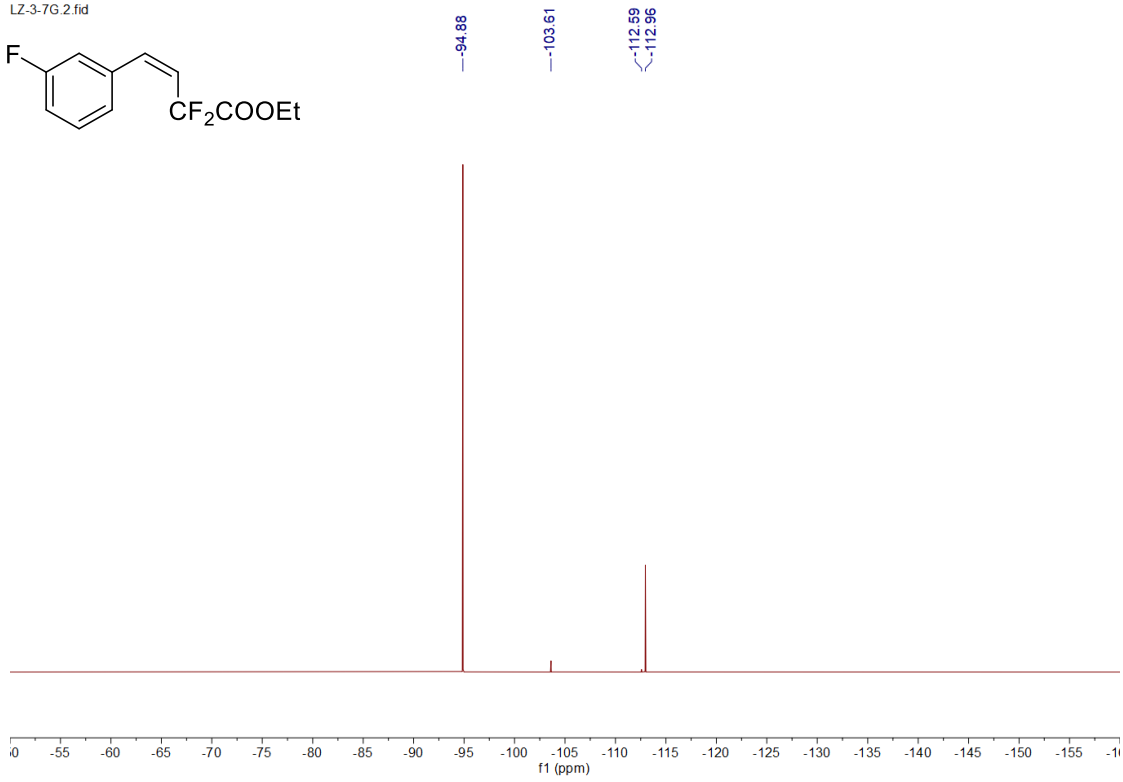
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1e**)



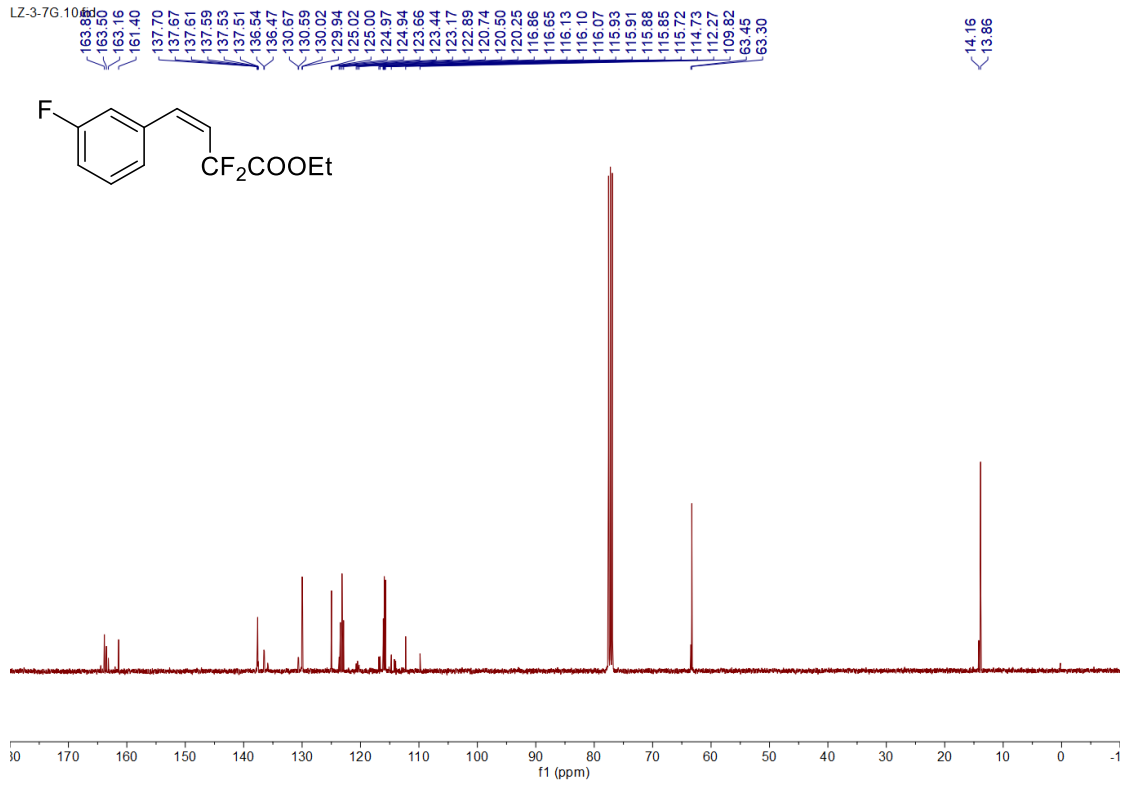
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1f**) *Z*:*E* = 83 : 17



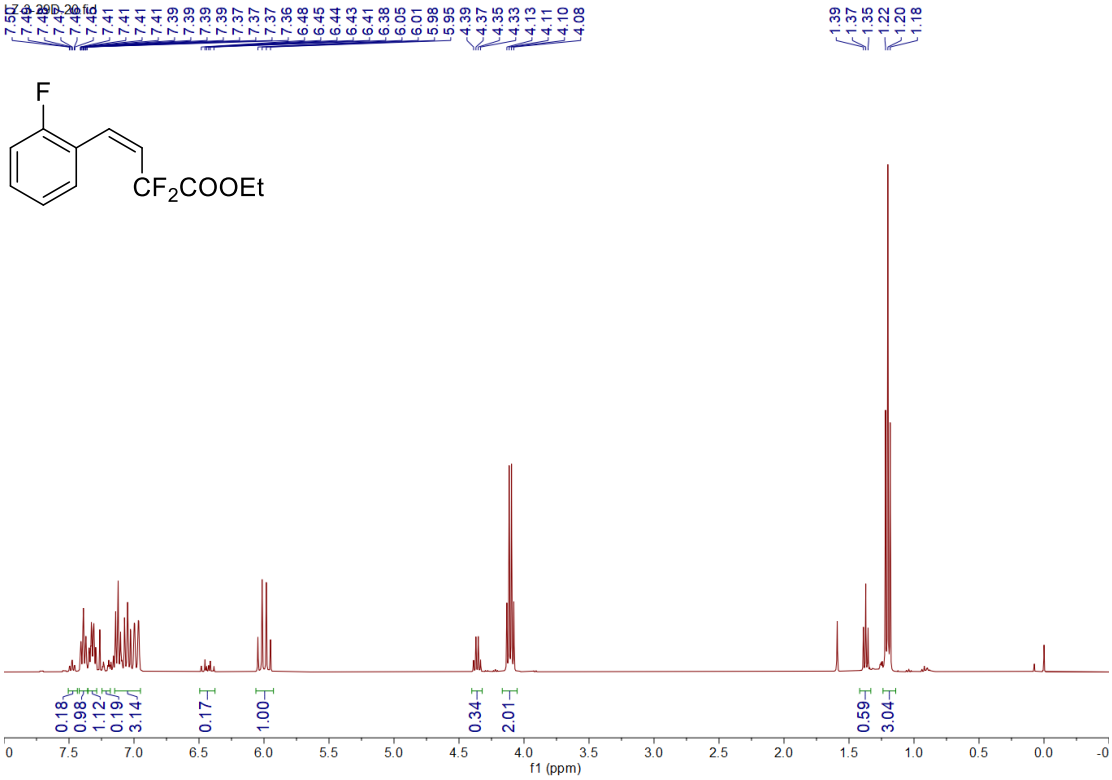
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1f**) *Z*:*E* = 83 : 17



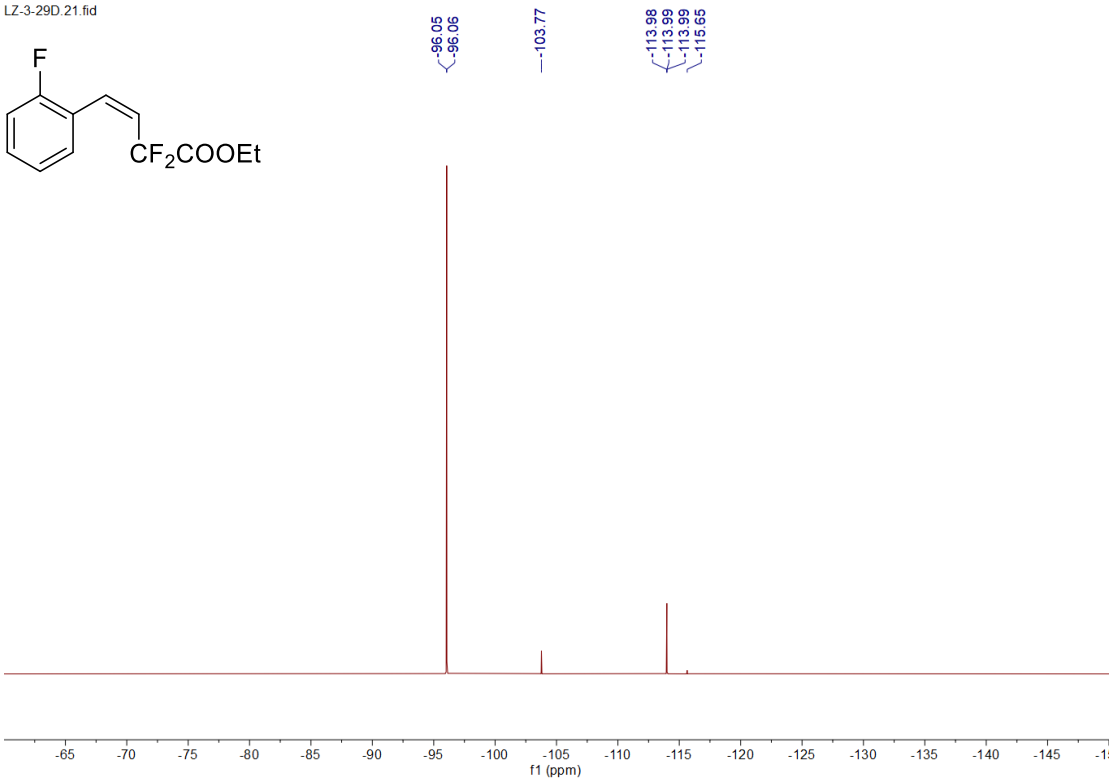
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1f**) *Z*:*E* = 83 : 17



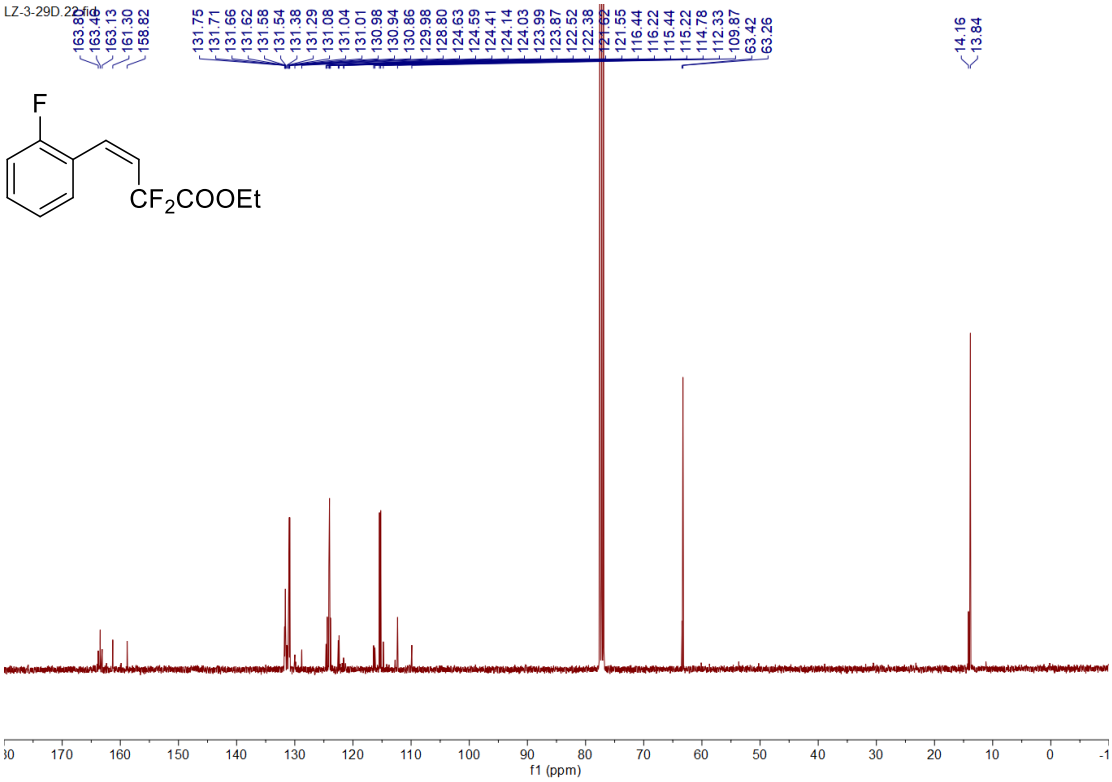
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1g**) *Z*:*E* = 85 : 15



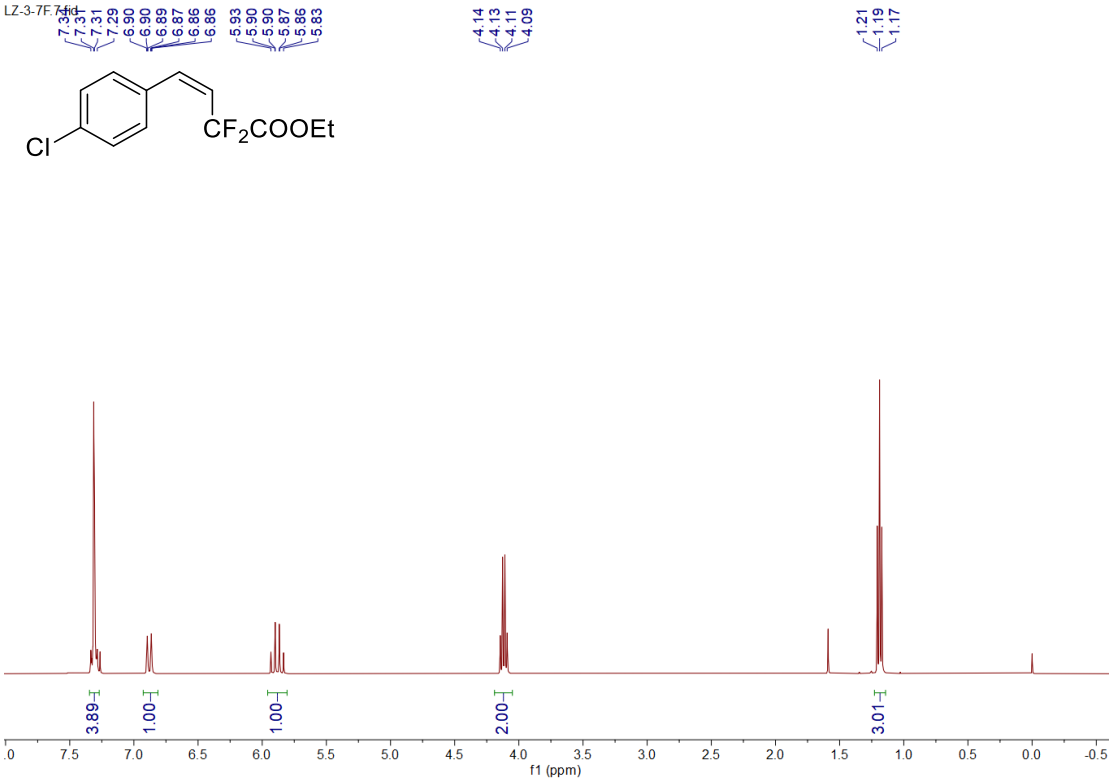
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1g**) *Z*:*E* = 85 : 15



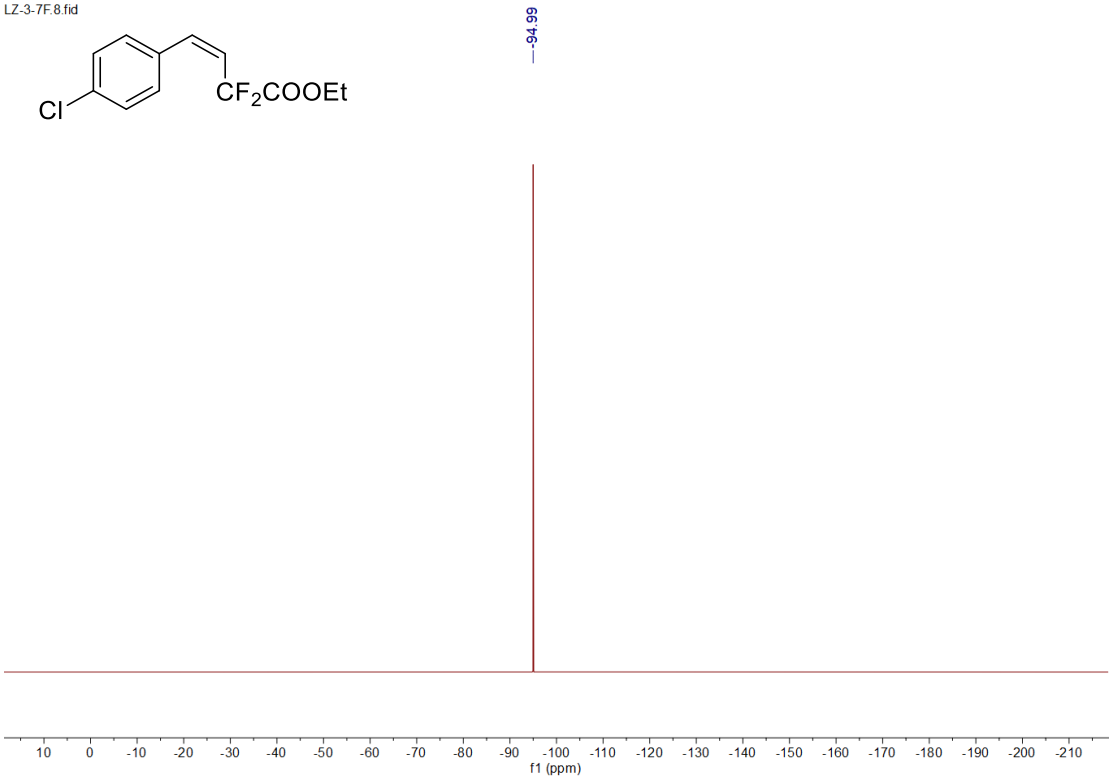
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1g**) *Z*:*E* = 85 : 15



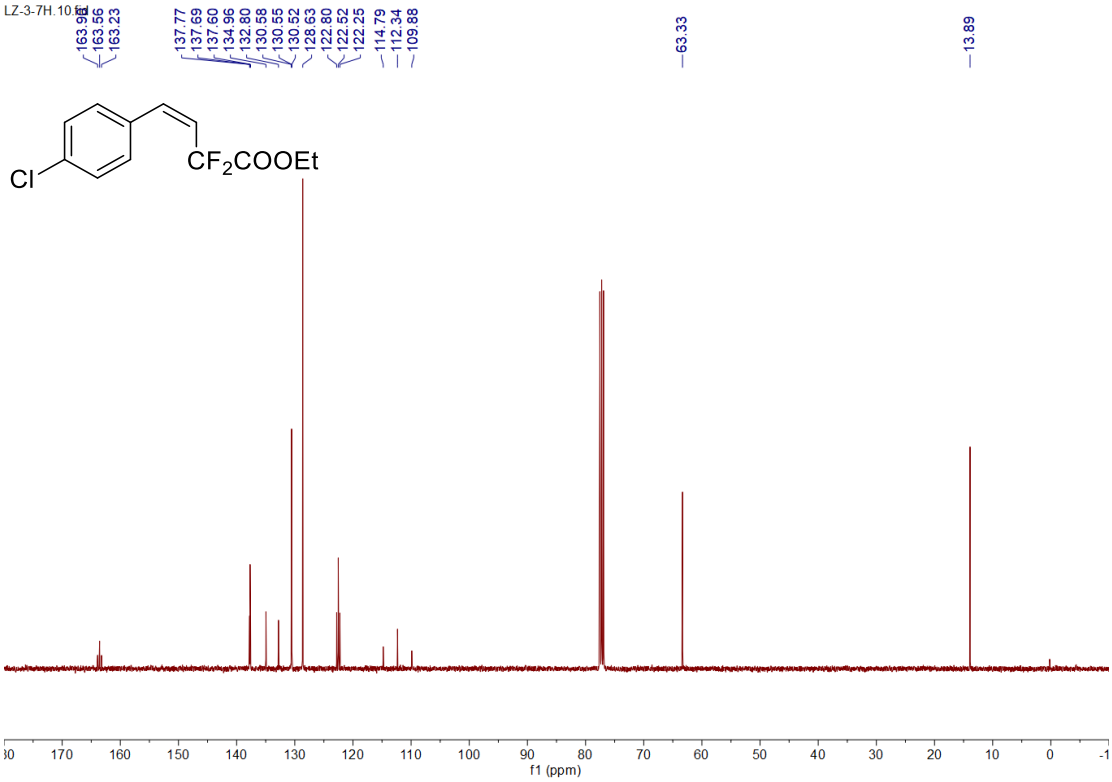
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1h**)



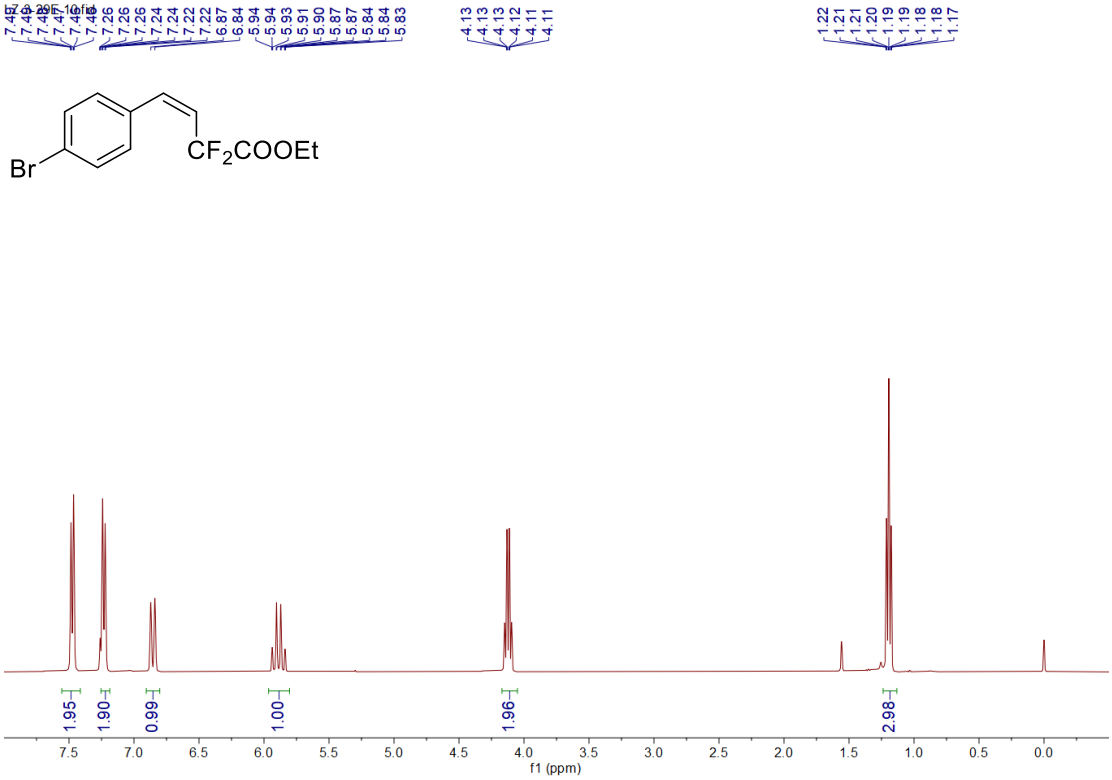
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1h**)



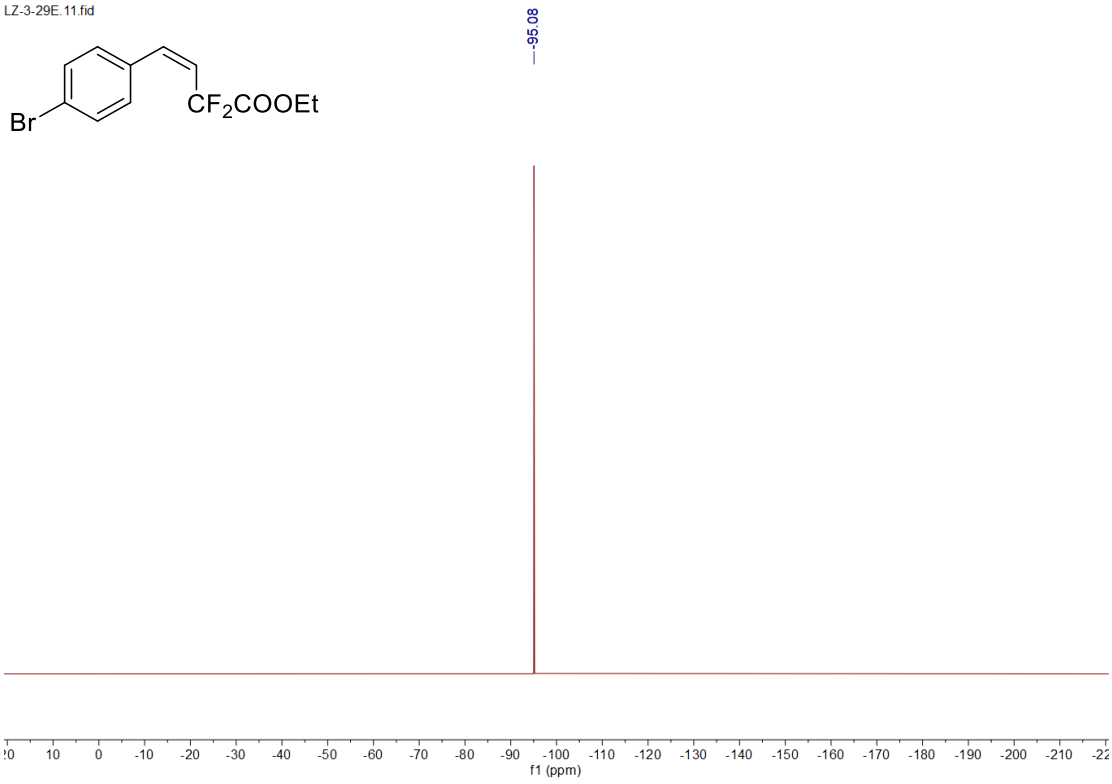
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1h**)



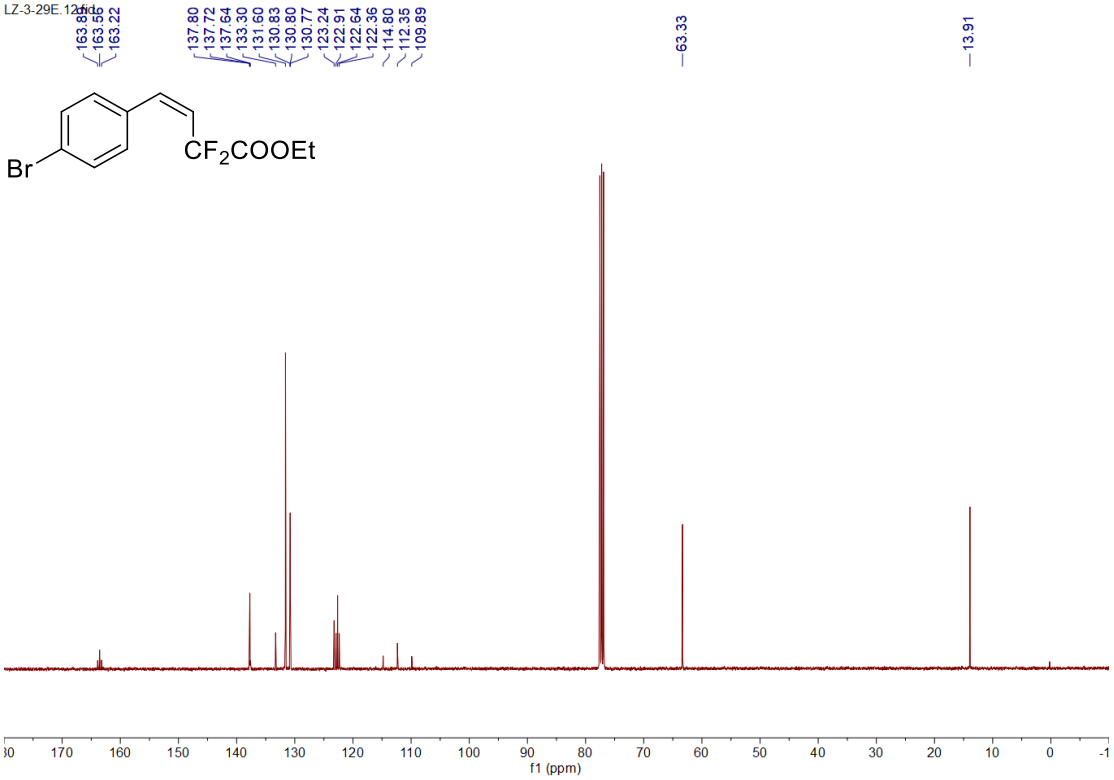
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1i**)



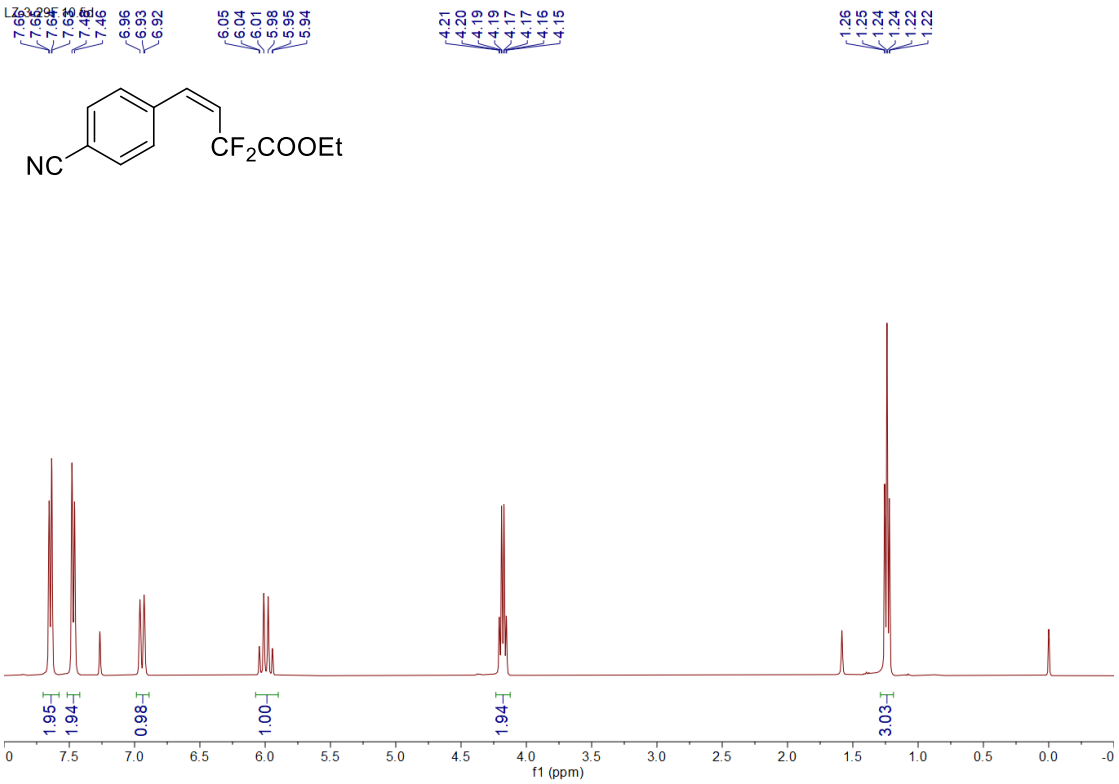
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1i**)



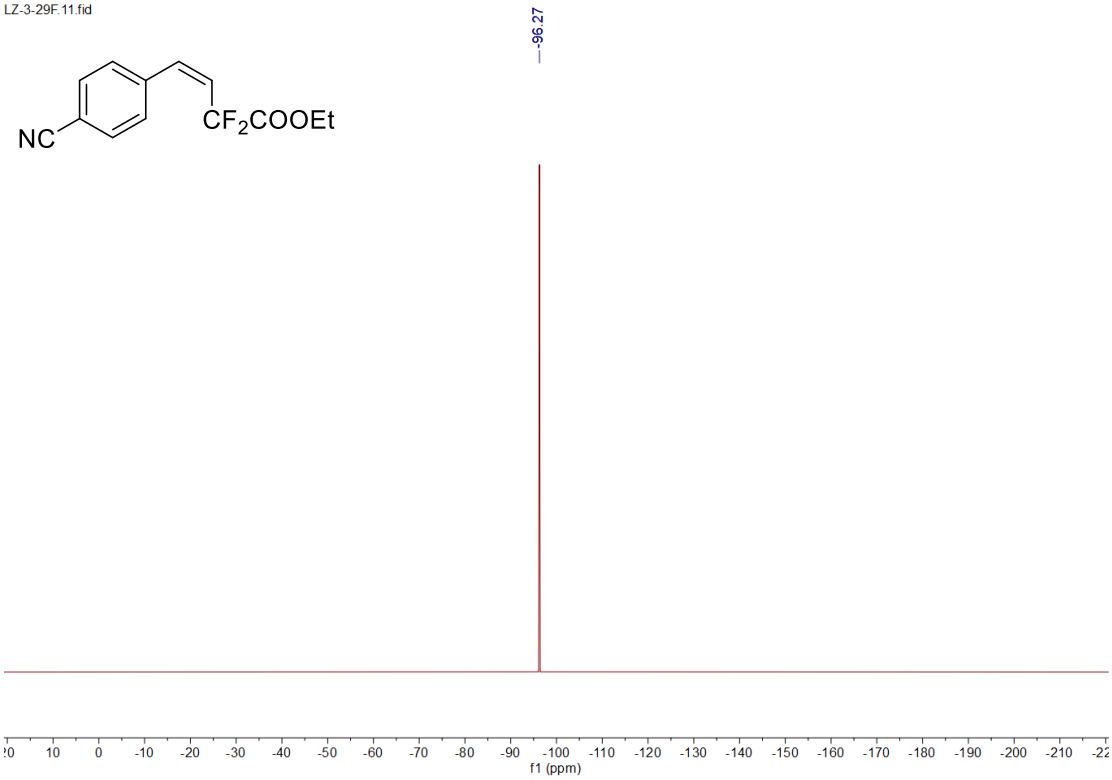
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1i**)



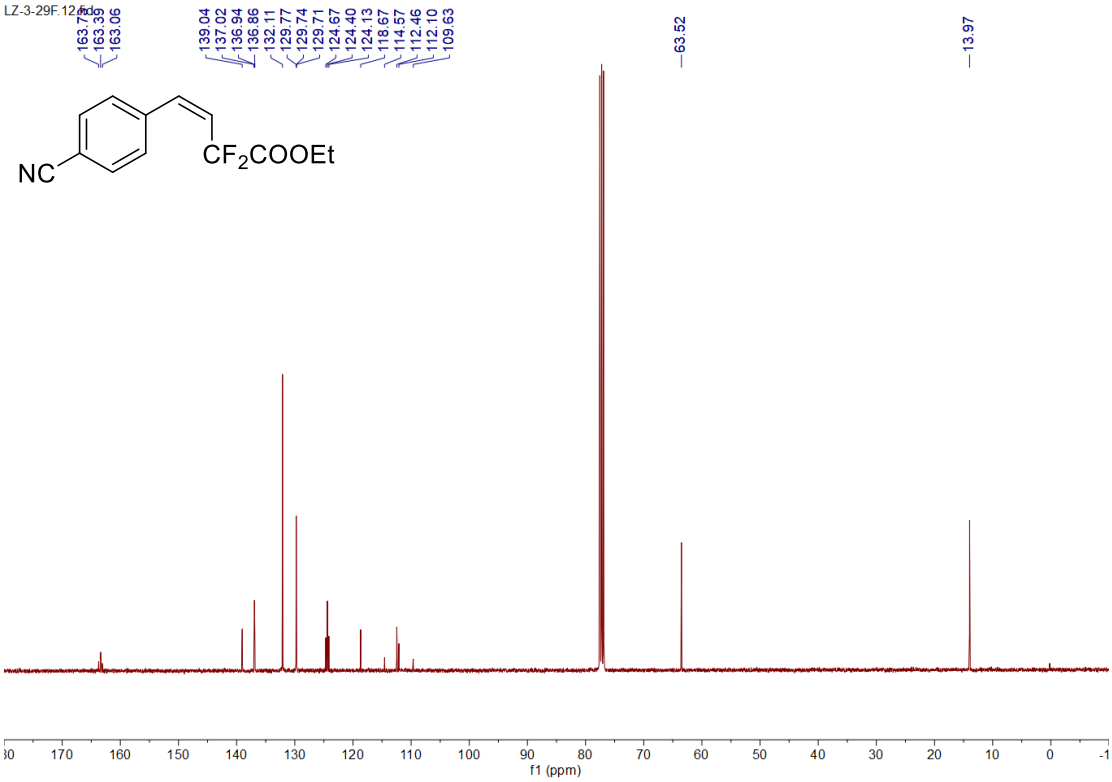
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1j**)



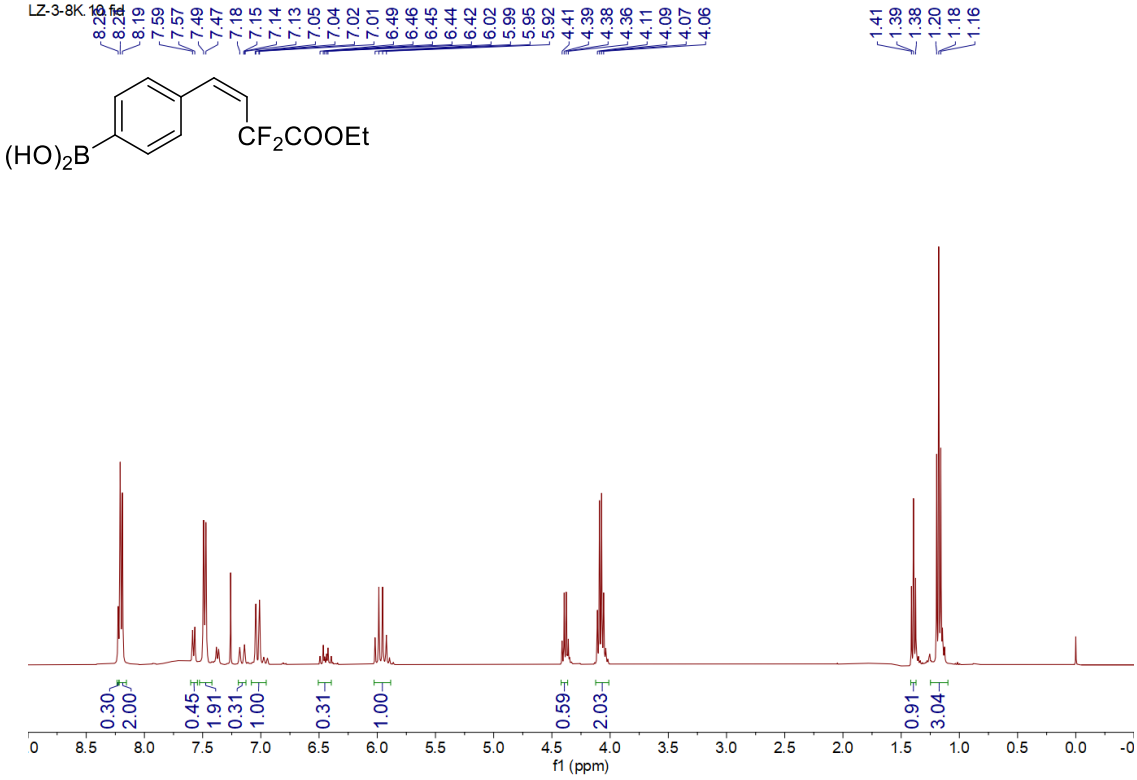
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1j**)



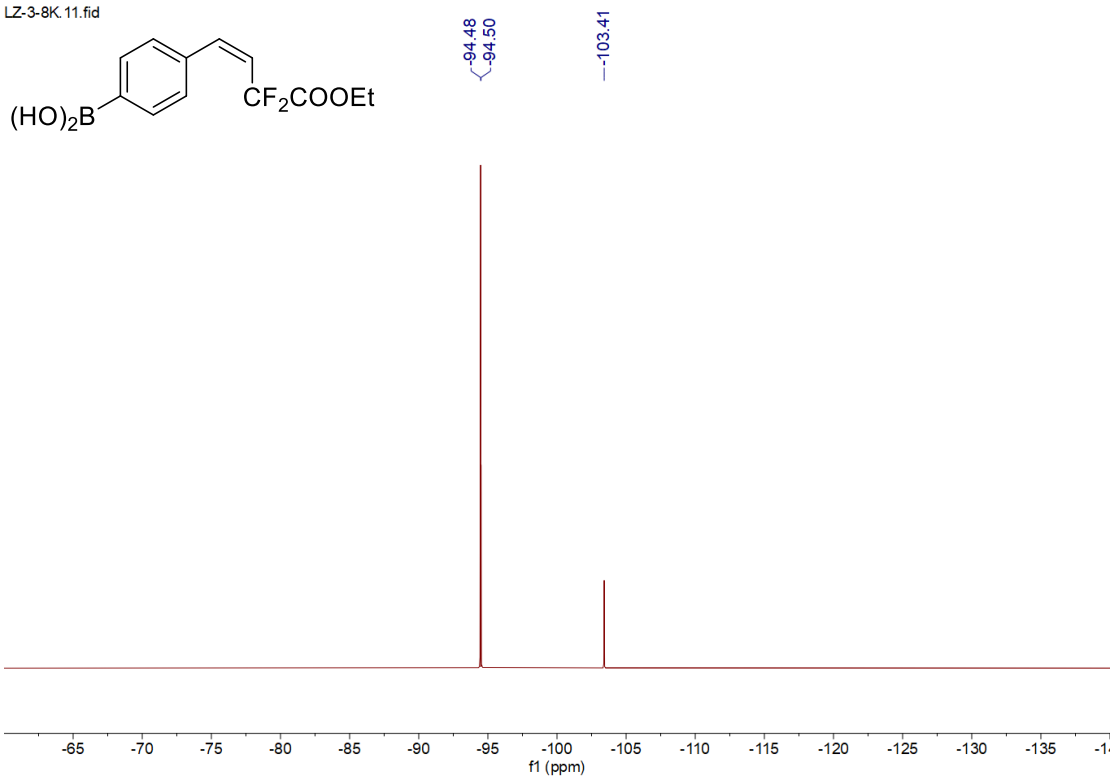
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1j**)



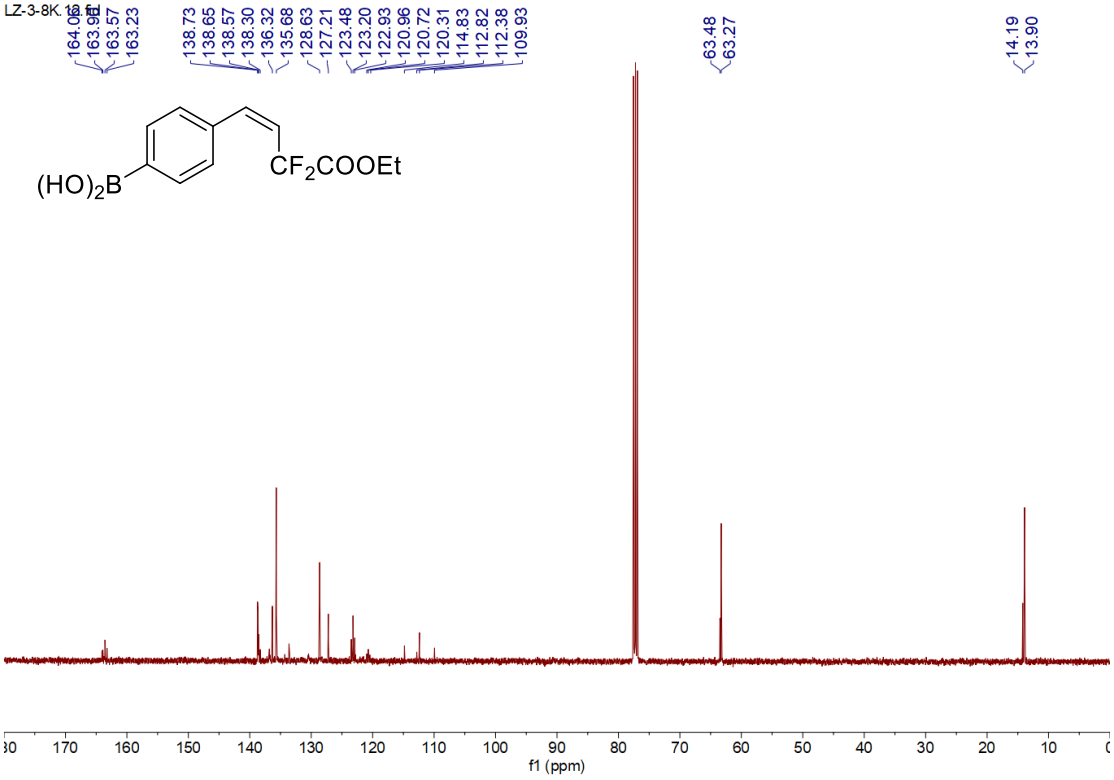
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1k**) *Z*:*E* = 82 : 18



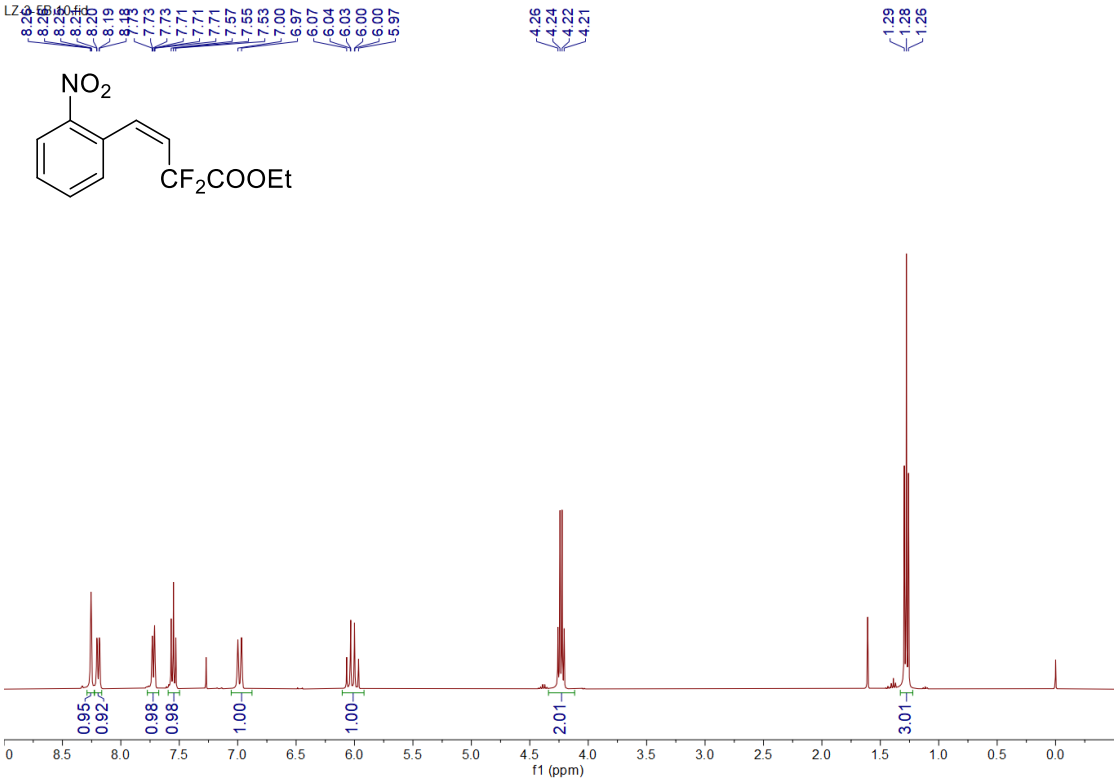
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1k**) *Z*:*E* = 82 : 18



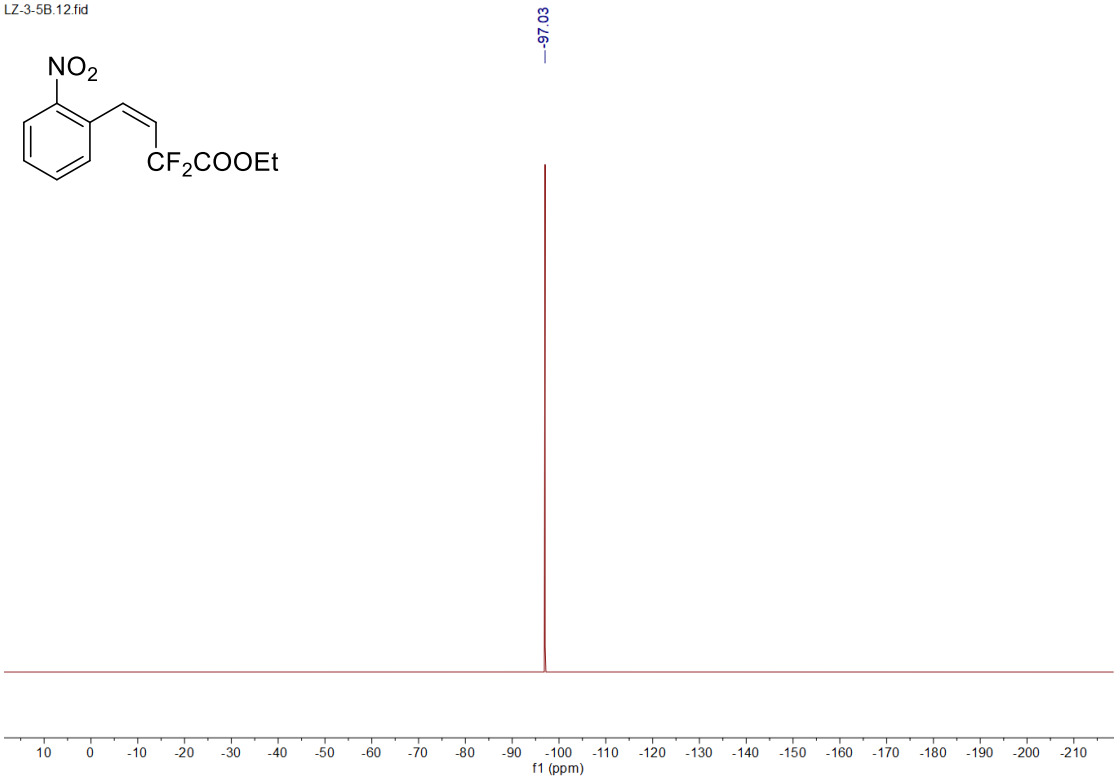
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1k**) *Z*:*E* = 82 : 18



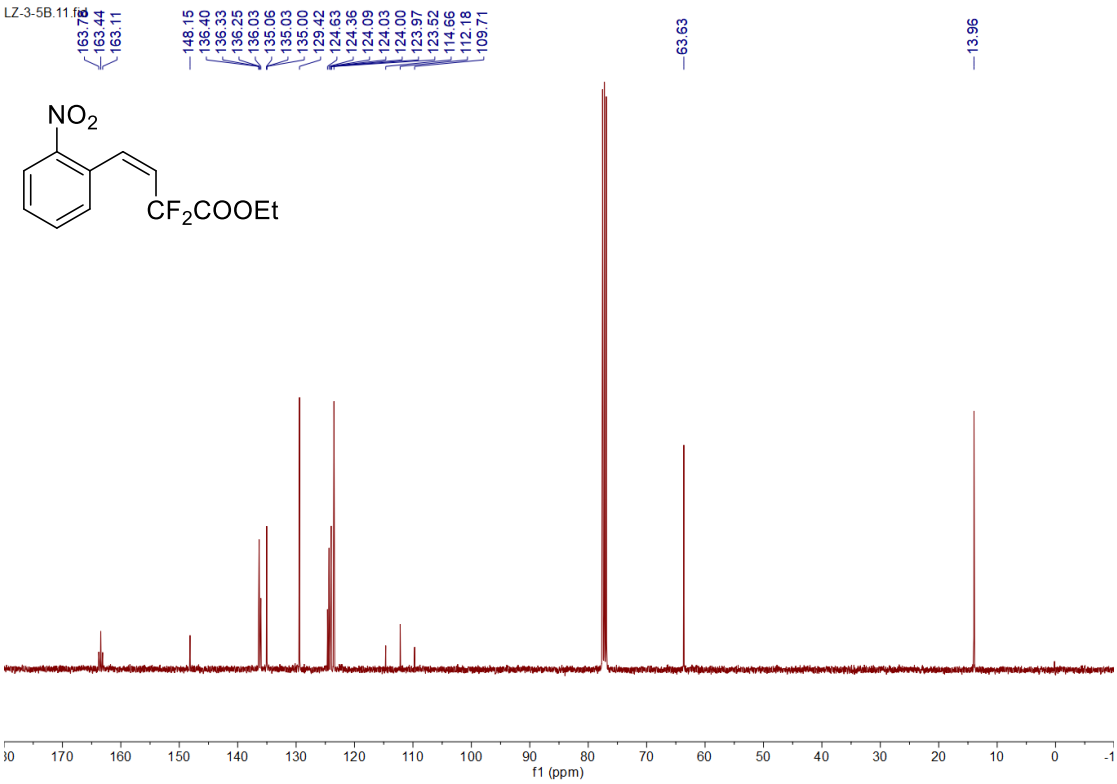
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1l**)



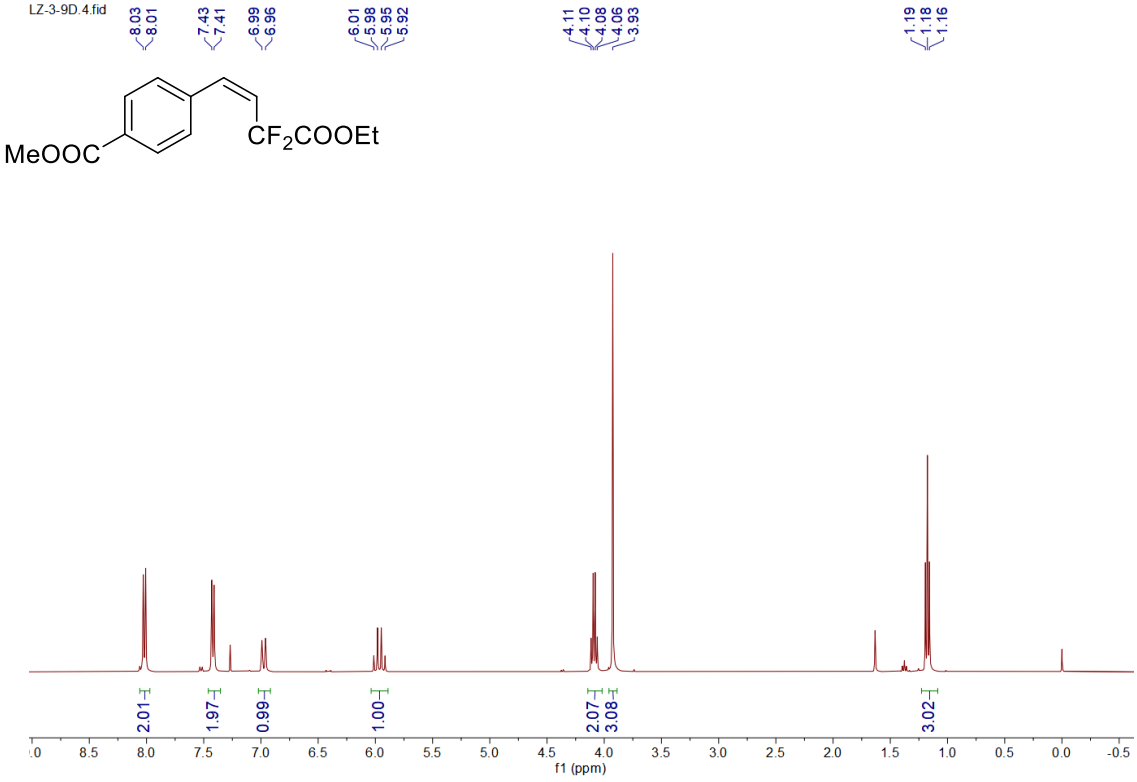
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1l**)



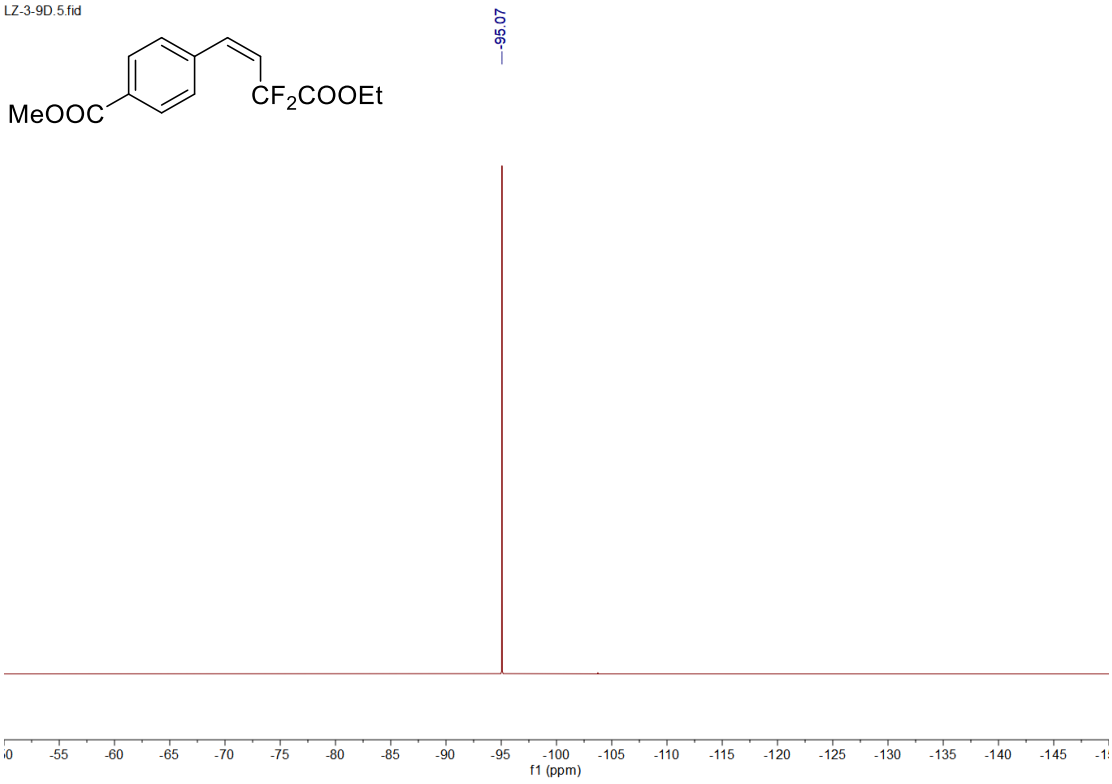
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1l**)



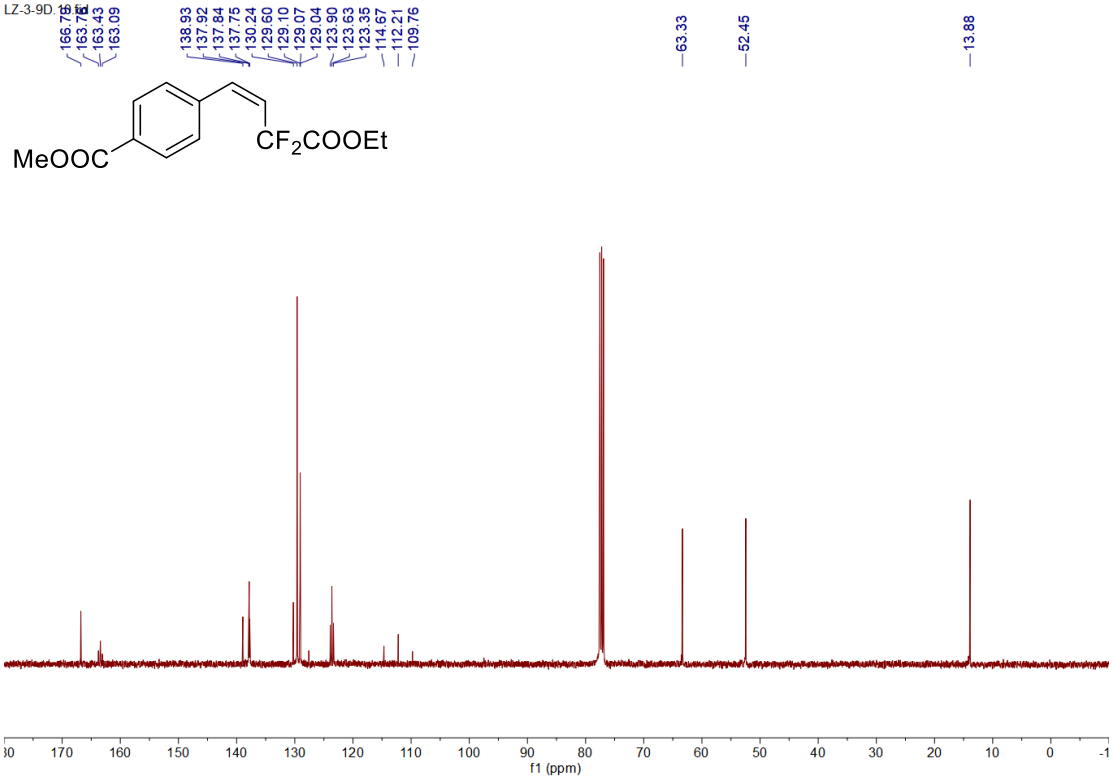
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1m**)



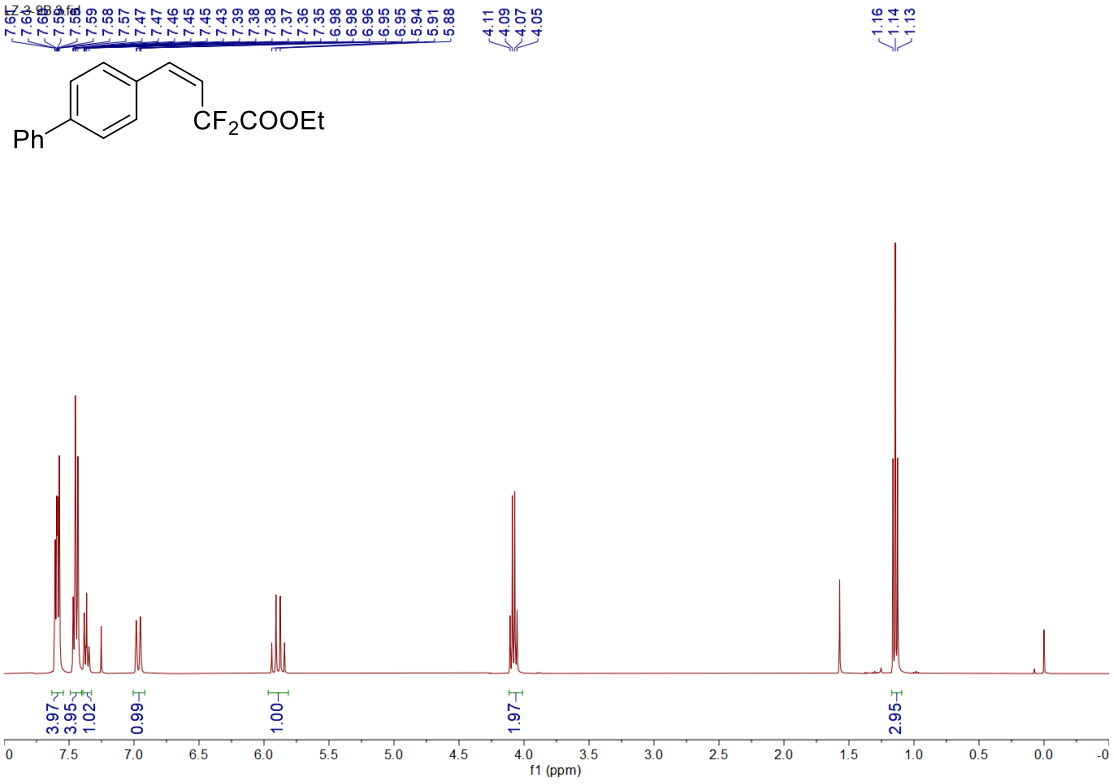
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1m**)



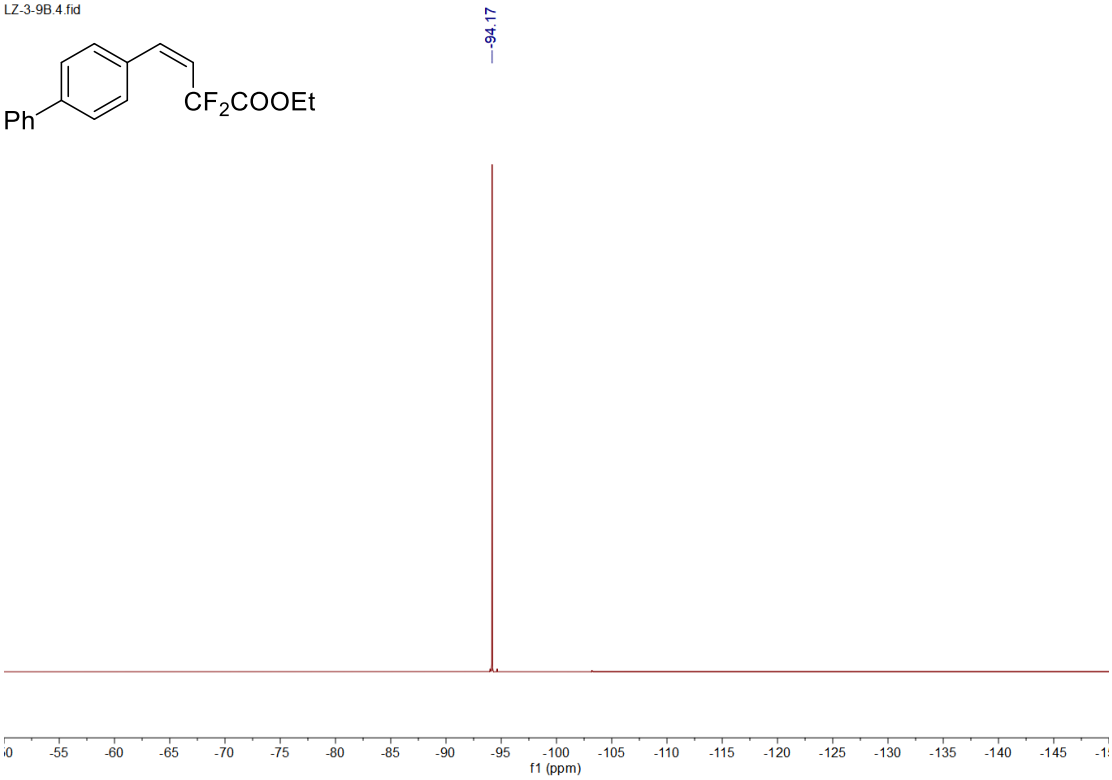
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1m**)



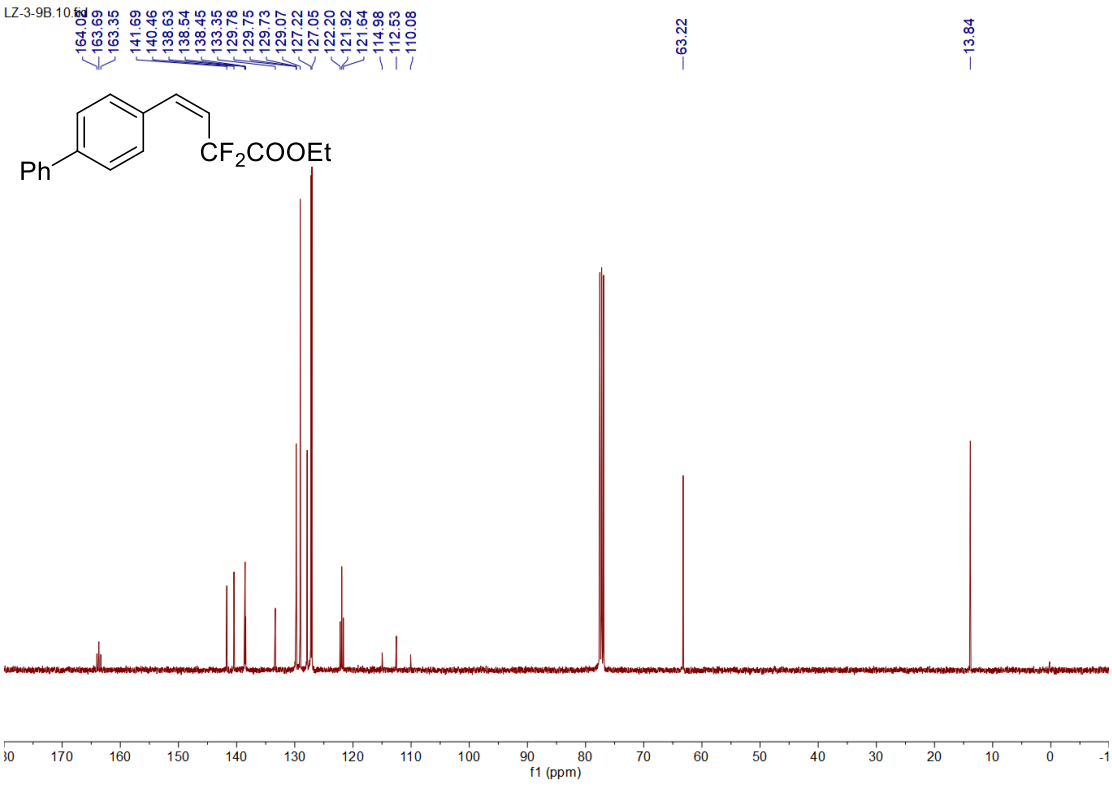
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1n**)



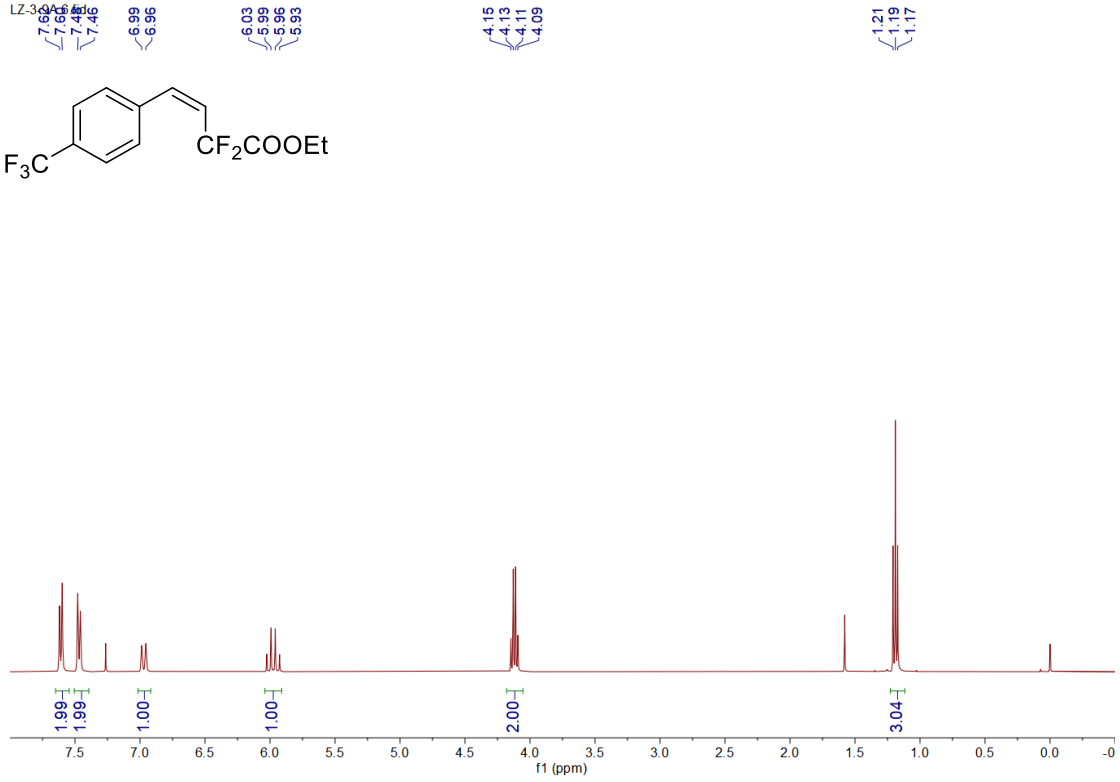
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1n**)



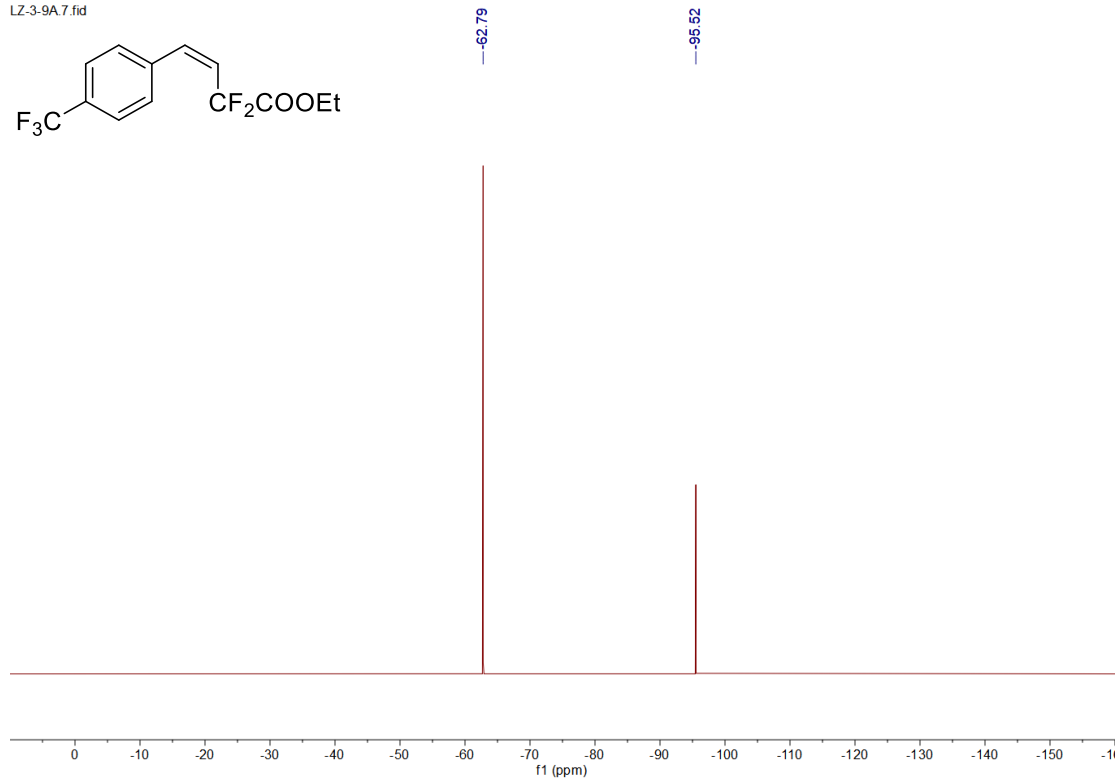
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1n**)



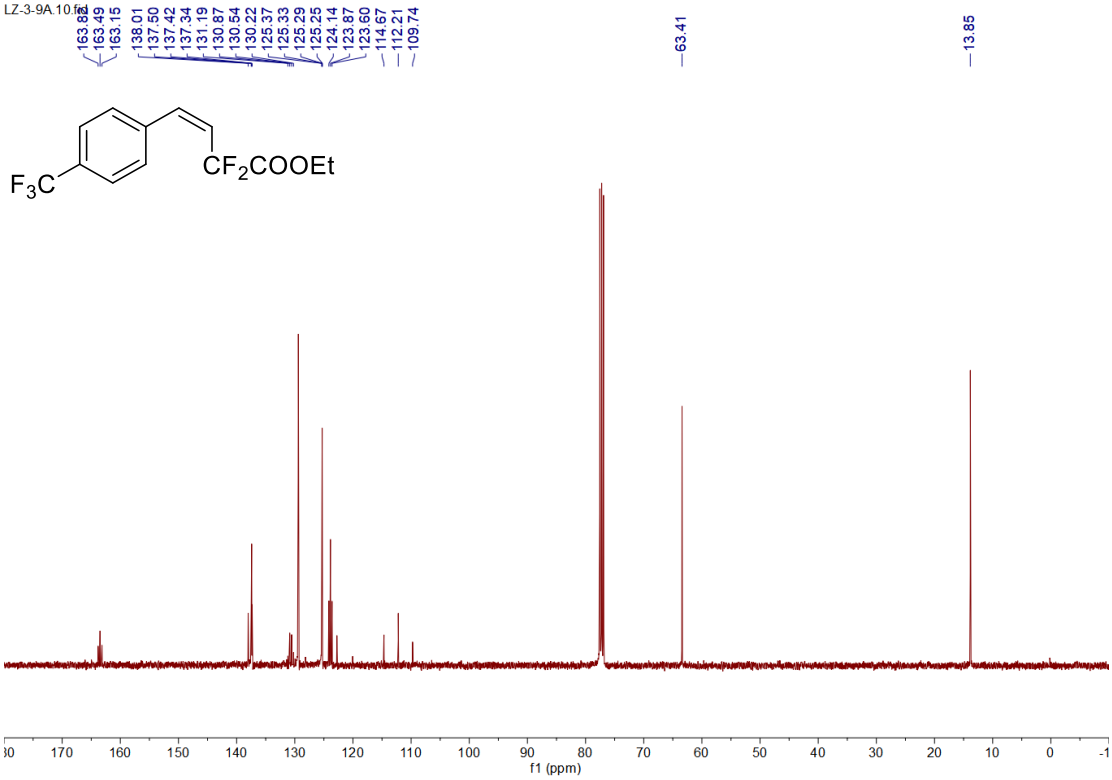
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1o**)



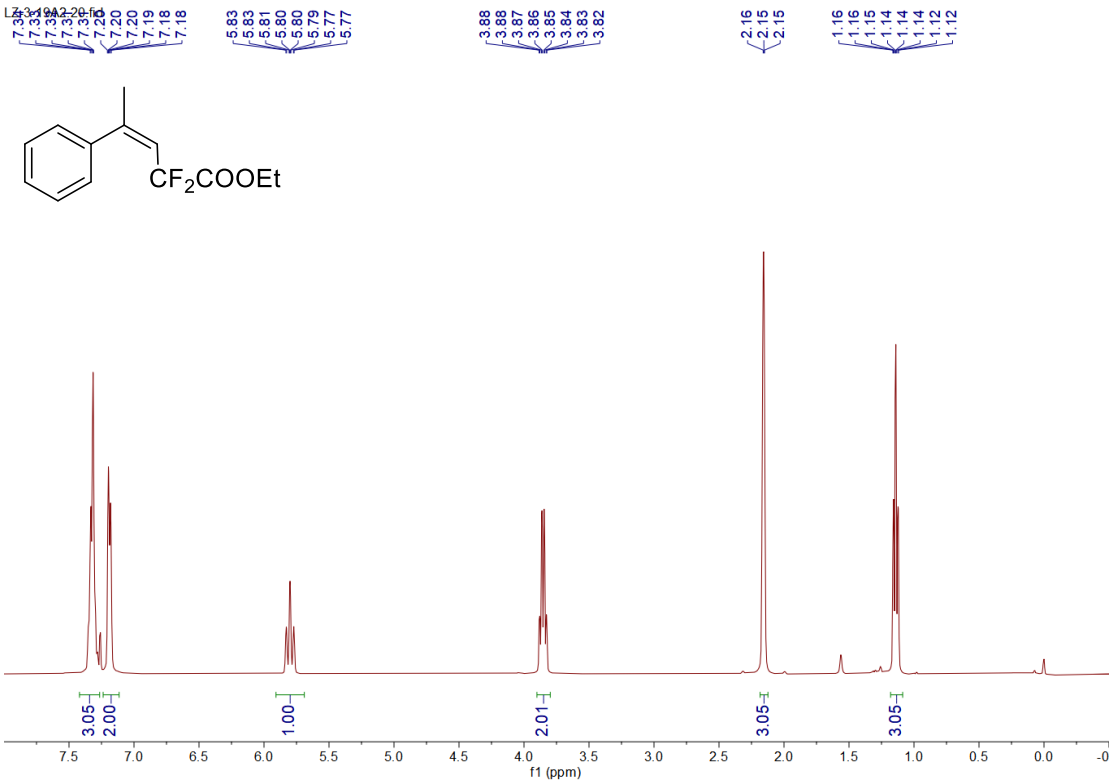
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1o**)



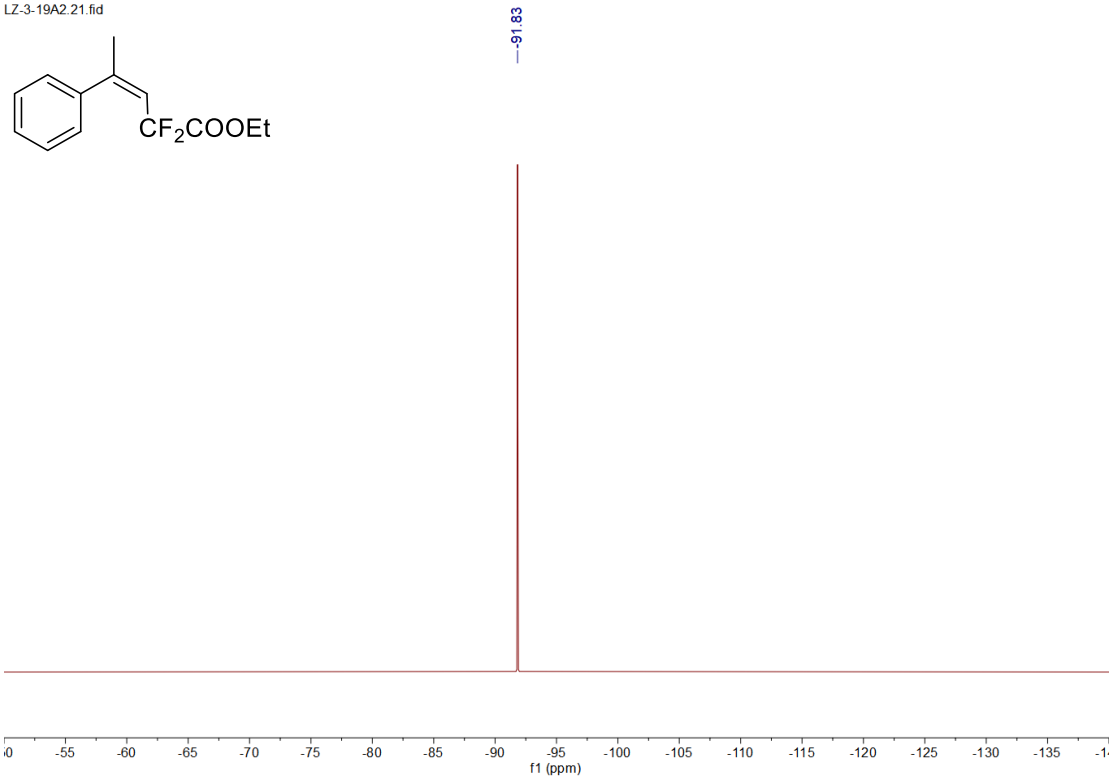
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1o**)



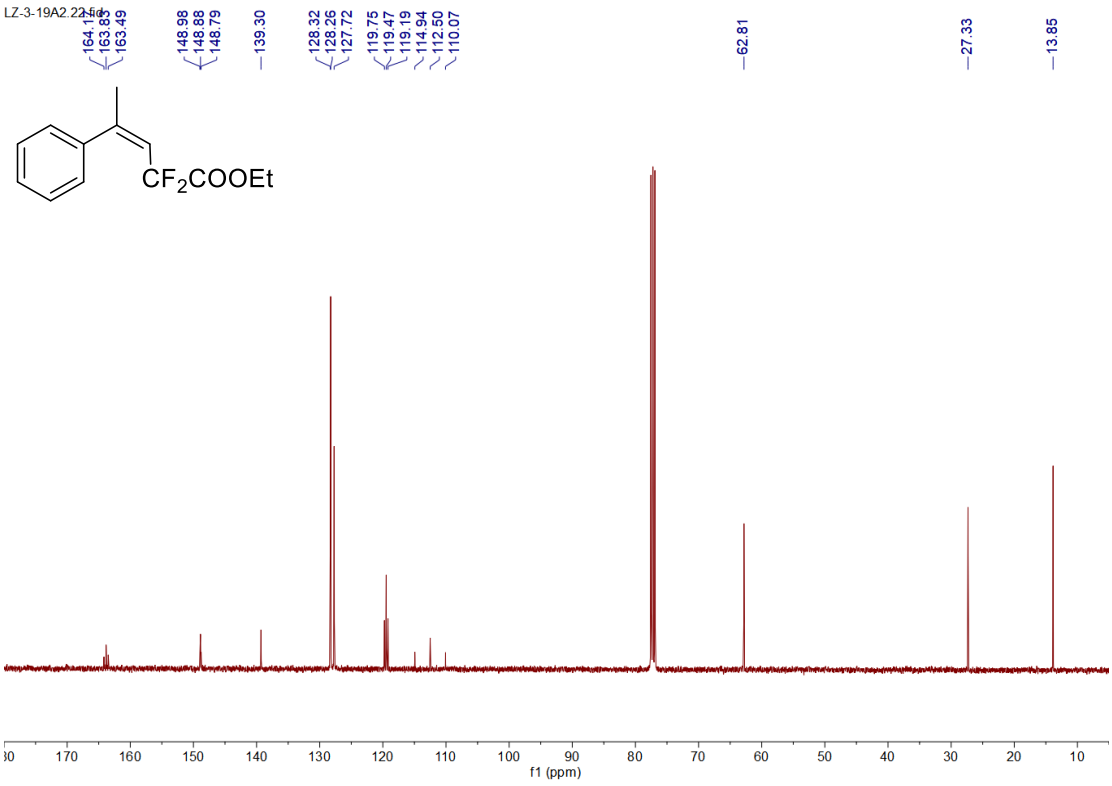
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1p**)



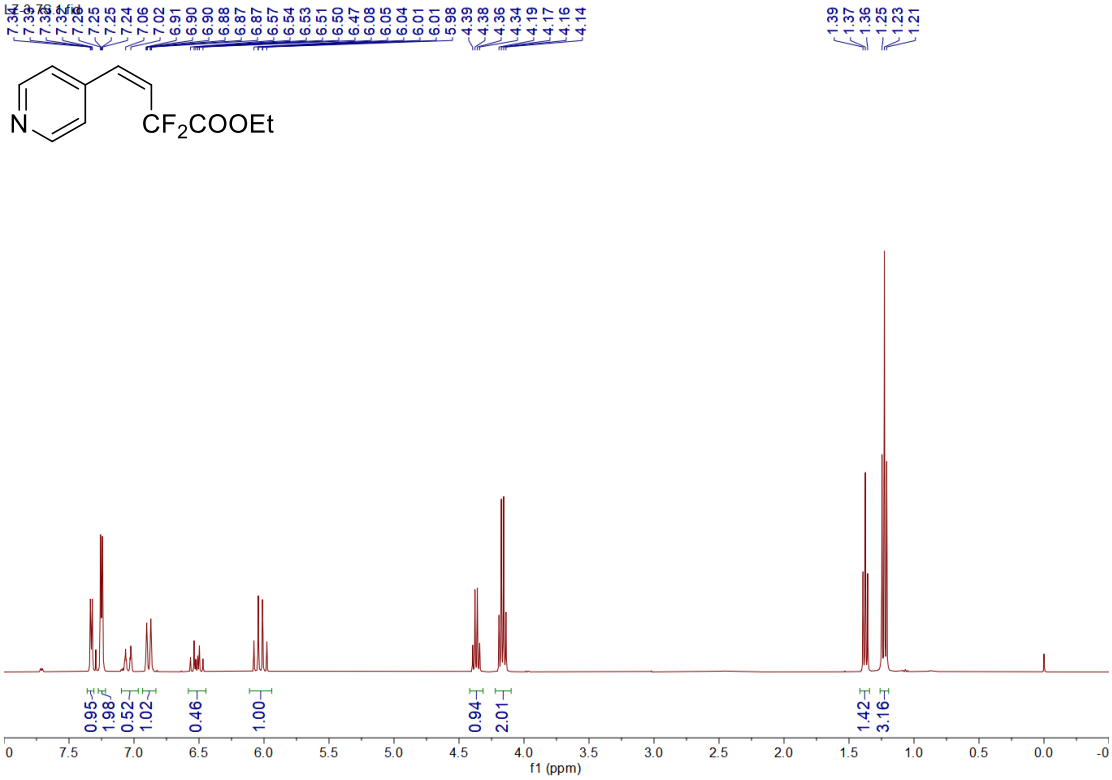
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1p**)



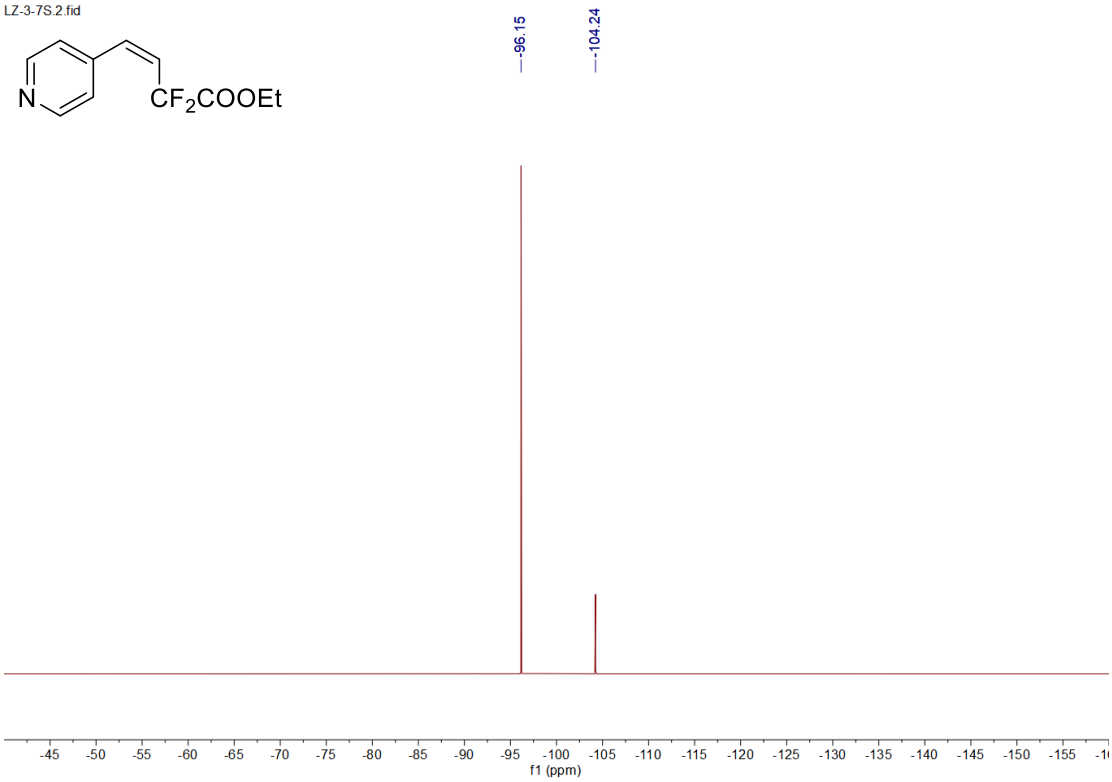
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1p**)



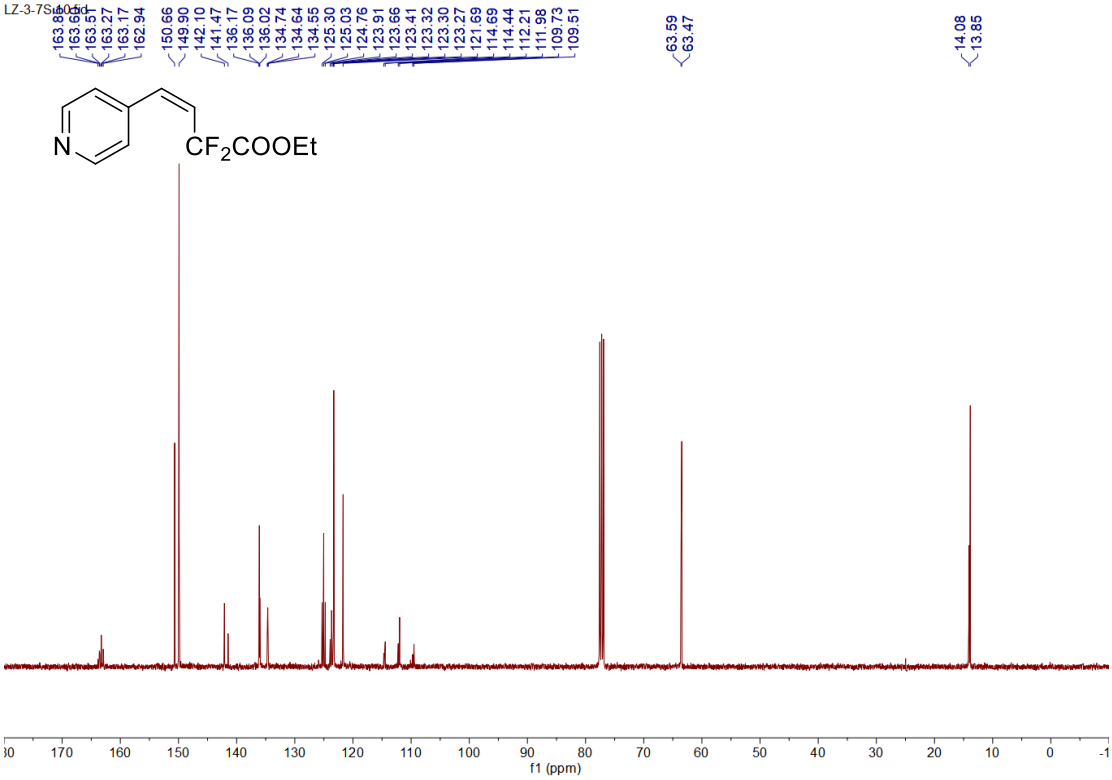
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1q**) *Z*:*E* = 72 : 28



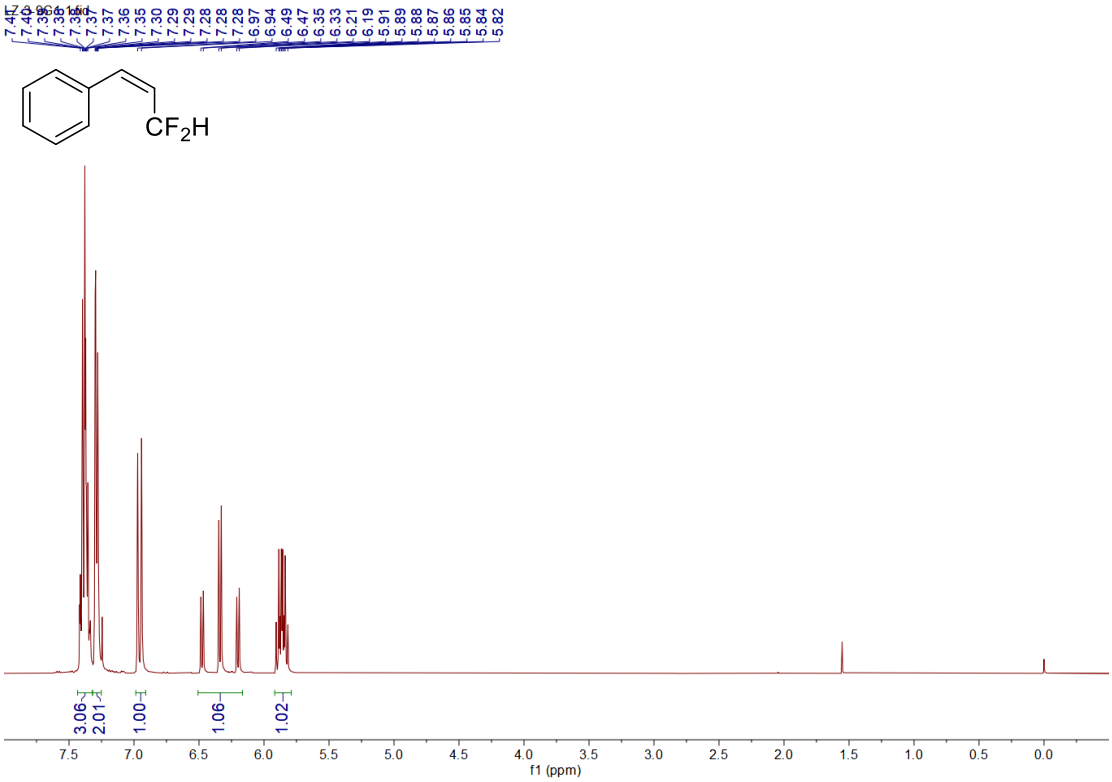
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1q**) *Z*:*E* = 72 : 28



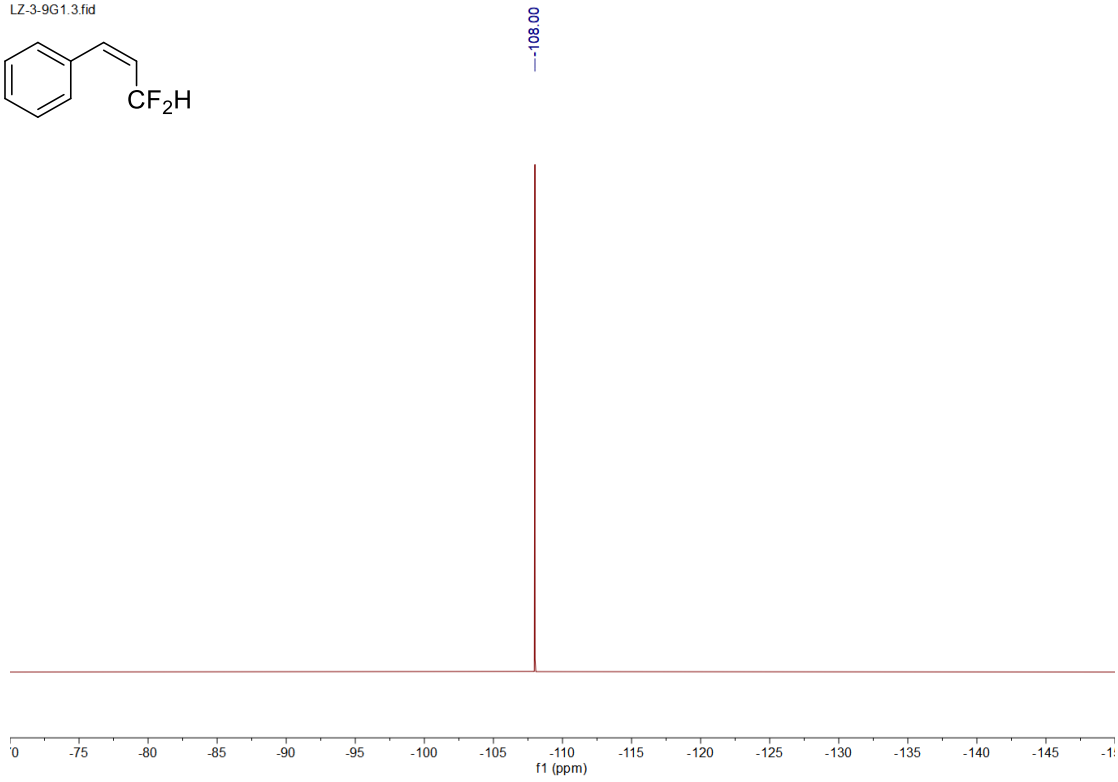
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1q**) *Z*:*E* = 72 : 28



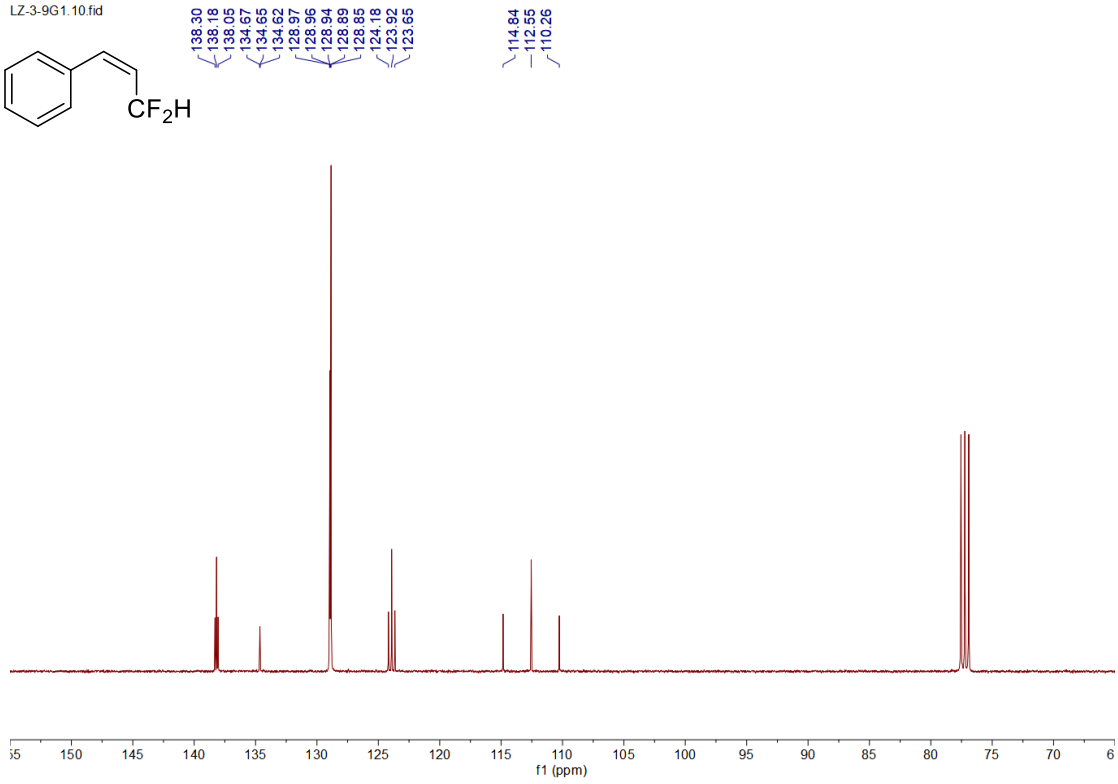
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1r**)



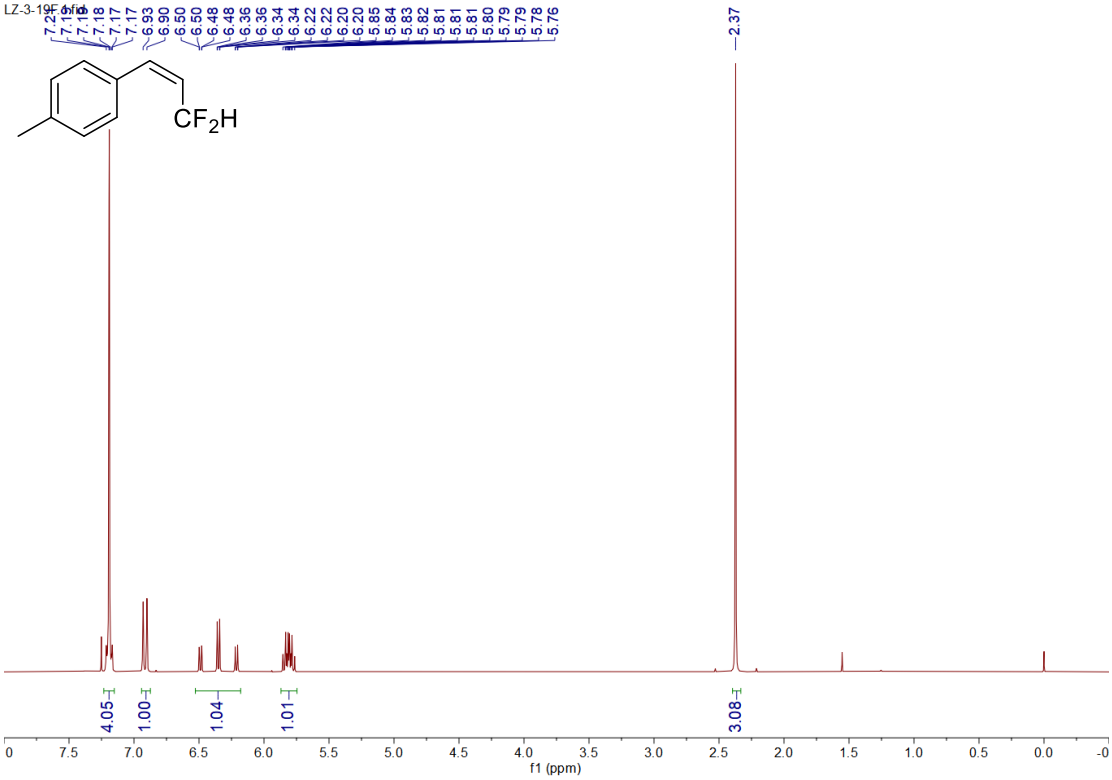
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1r**)



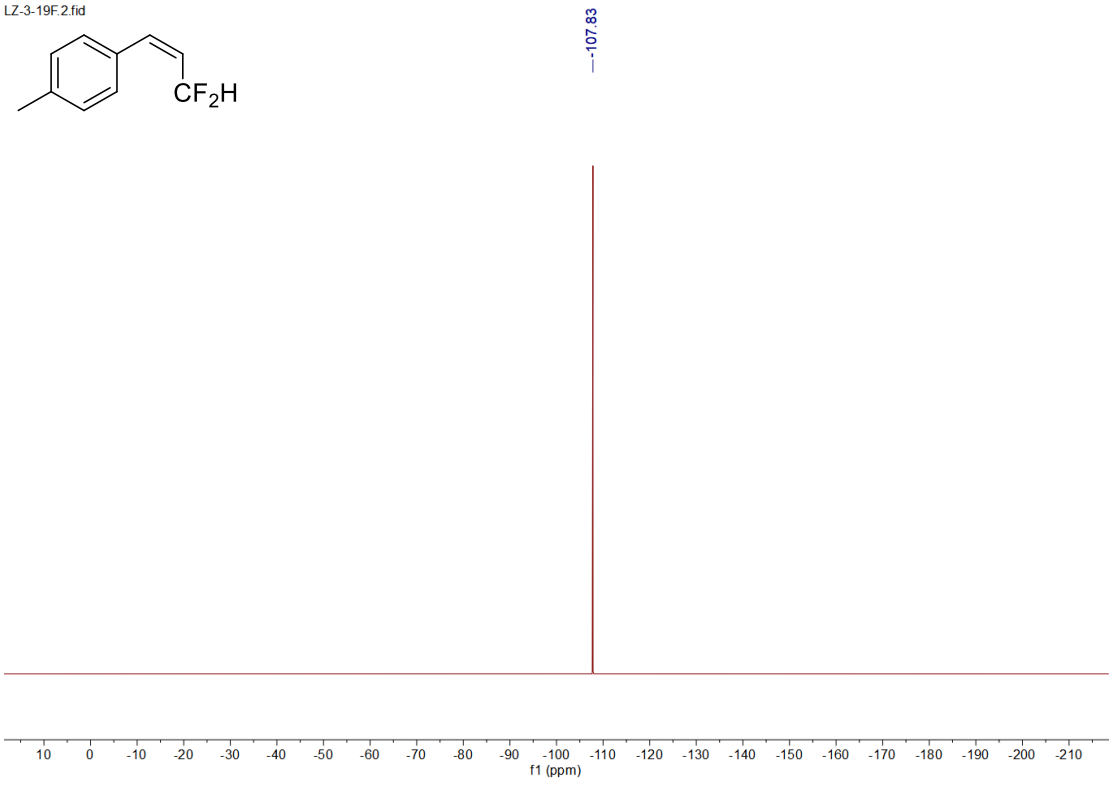
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1r**)



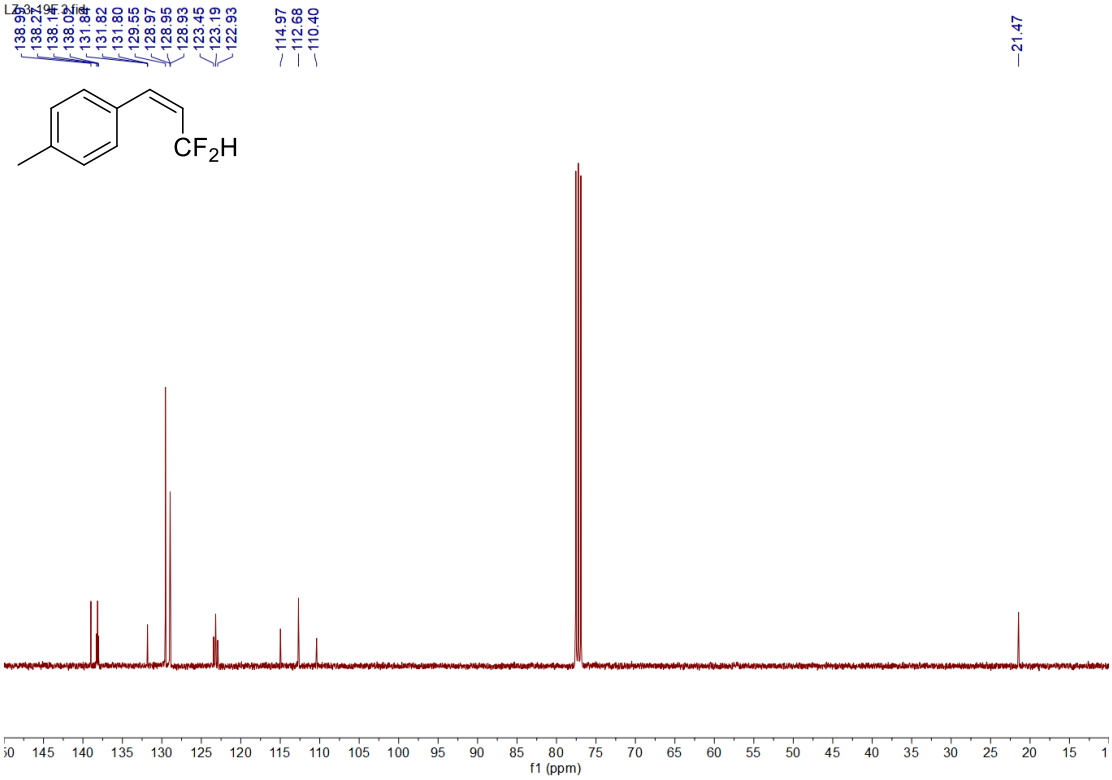
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1s**)



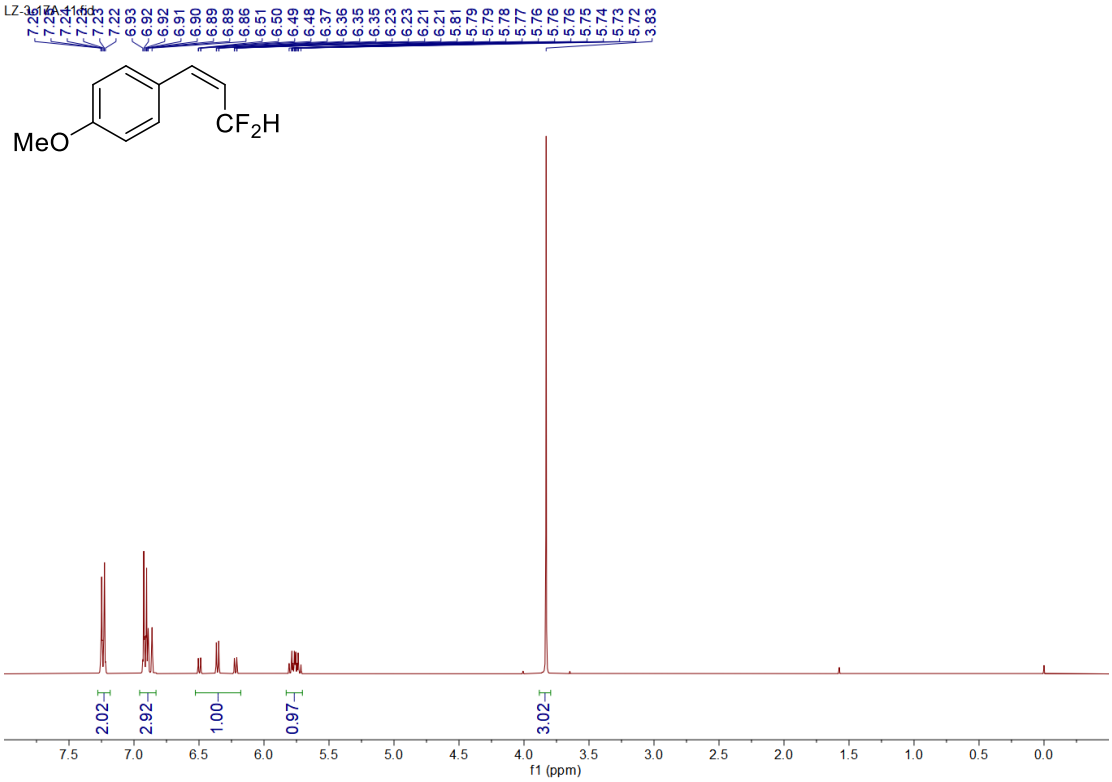
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1s**)



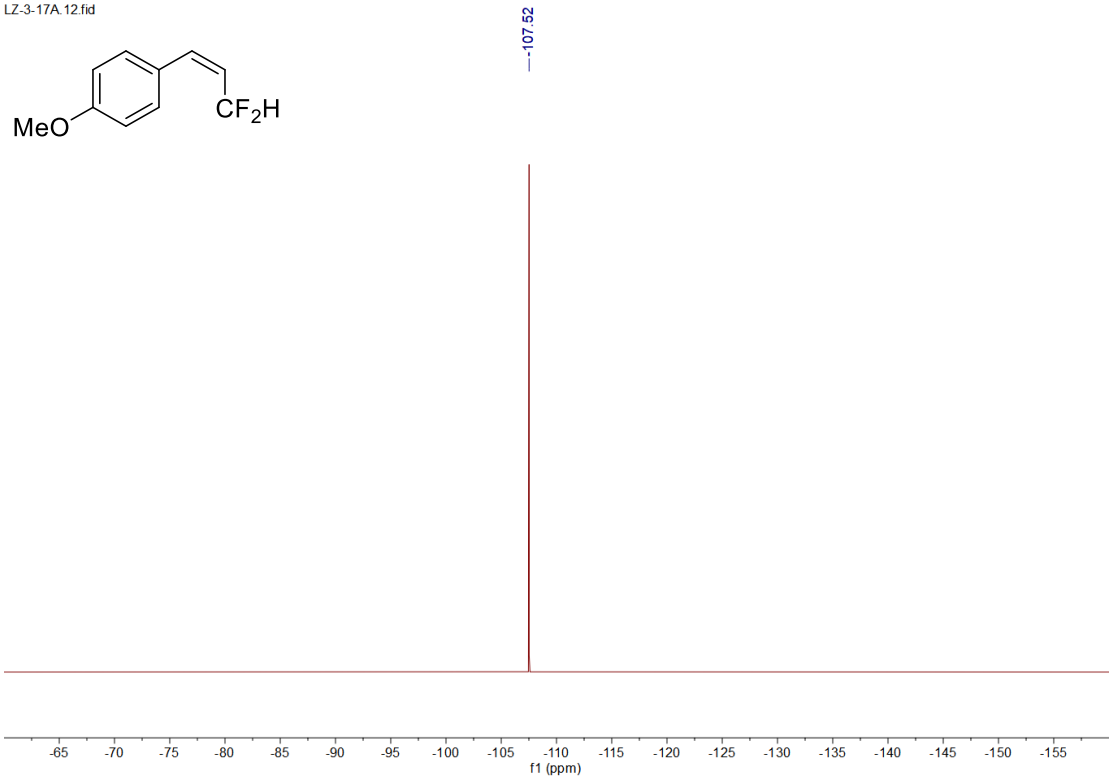
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1s**)



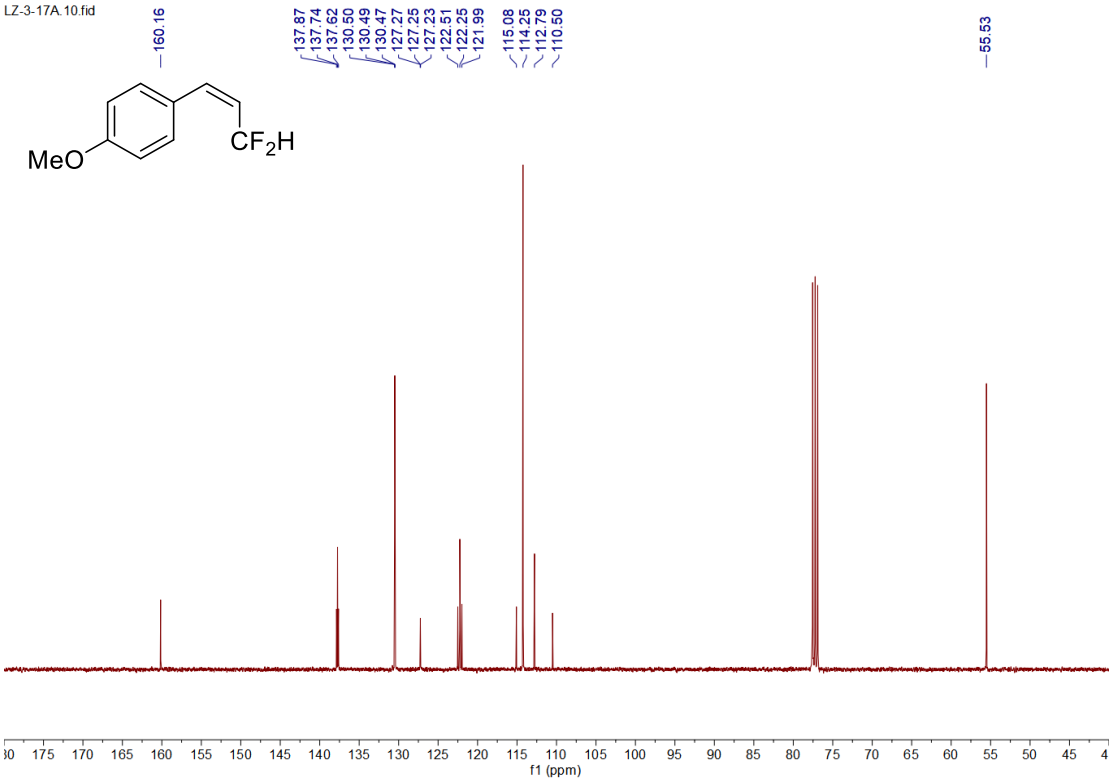
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1t**)



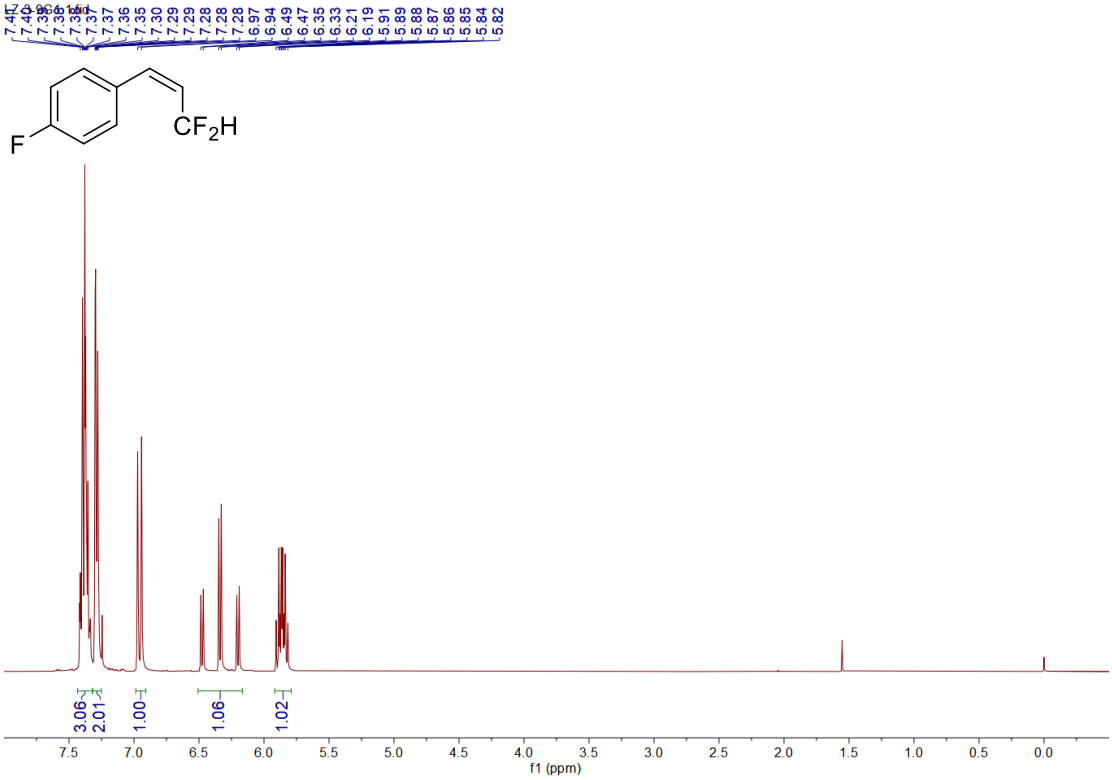
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1t**)



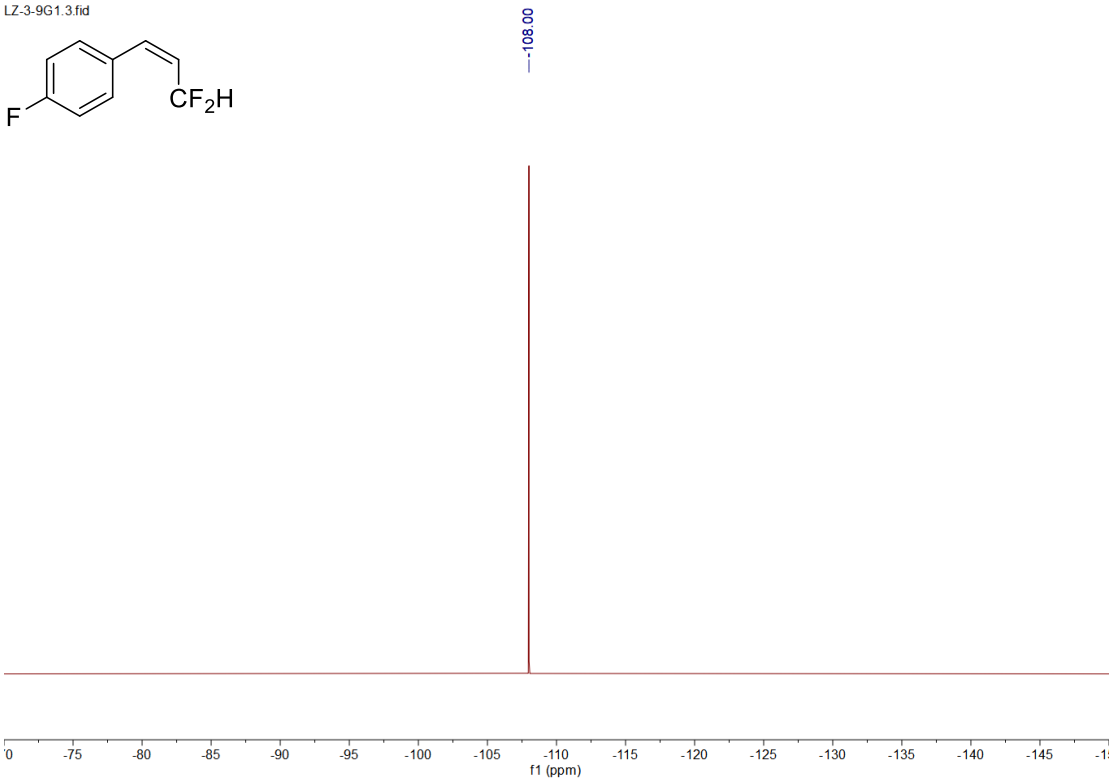
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1t**)



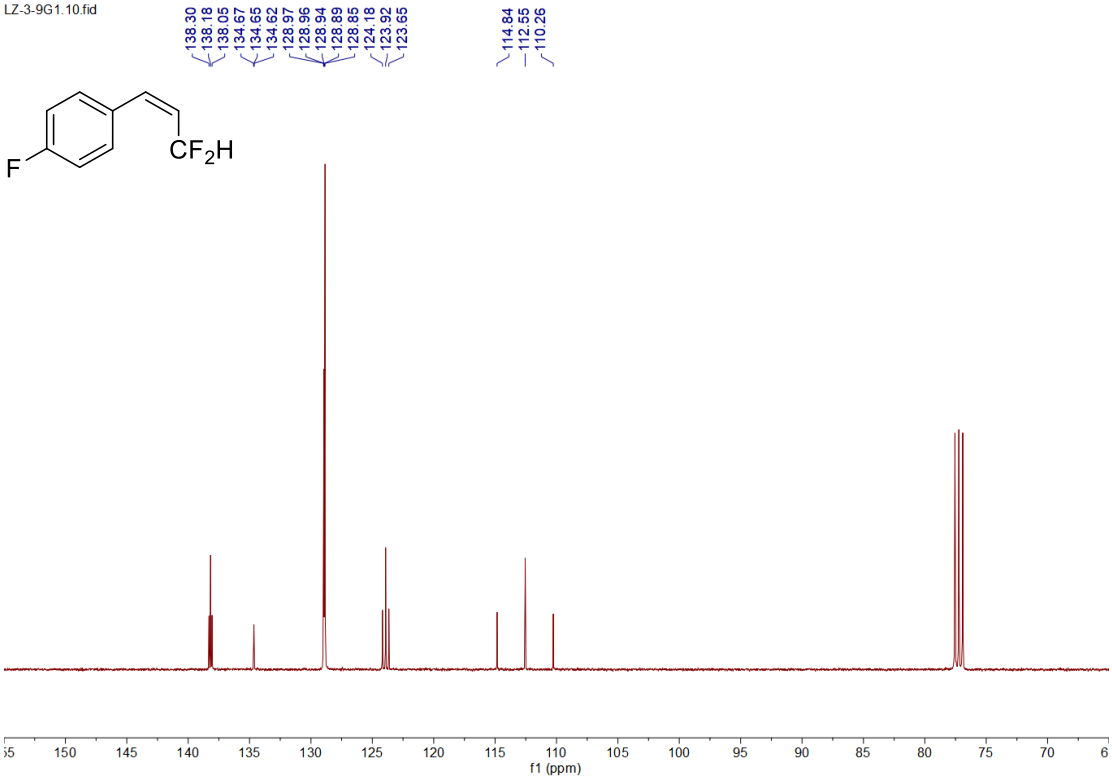
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1u**)



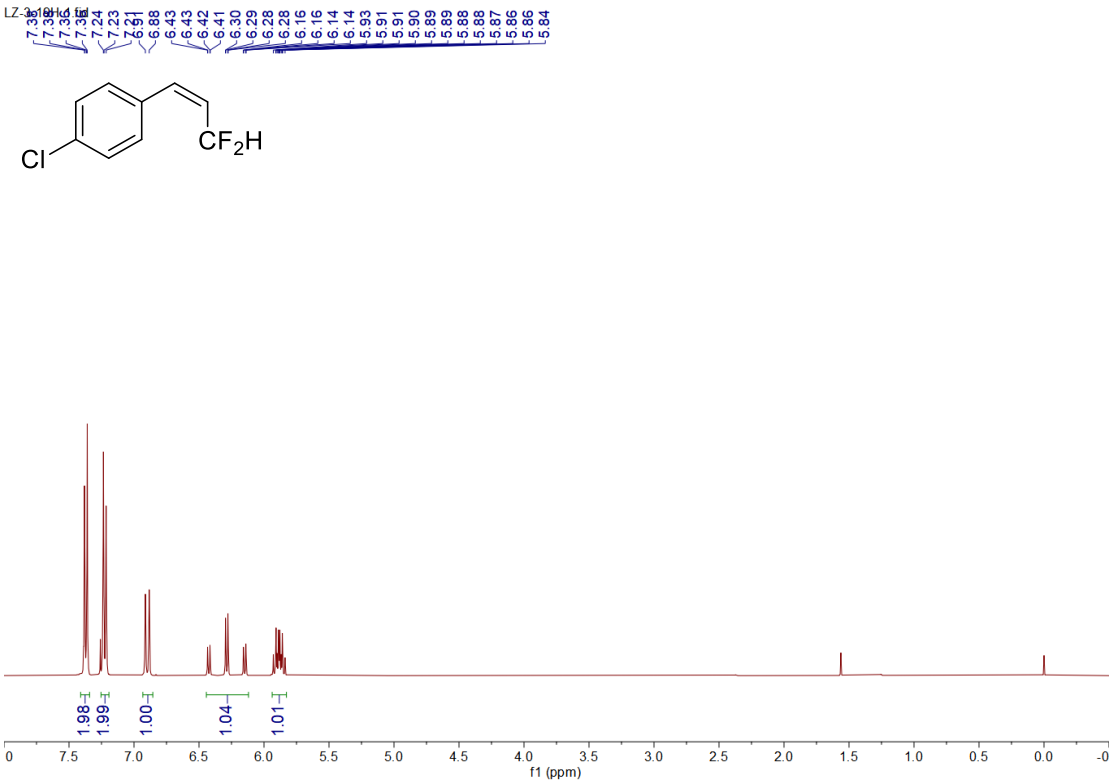
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1u**)



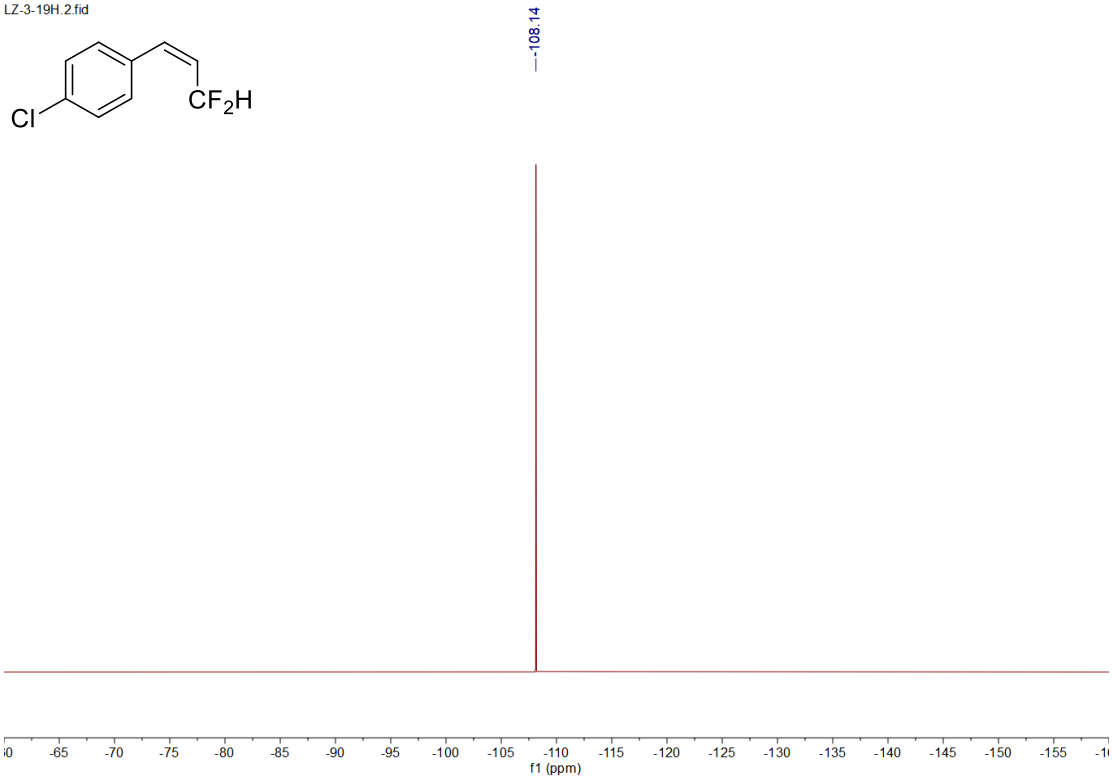
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1u**)



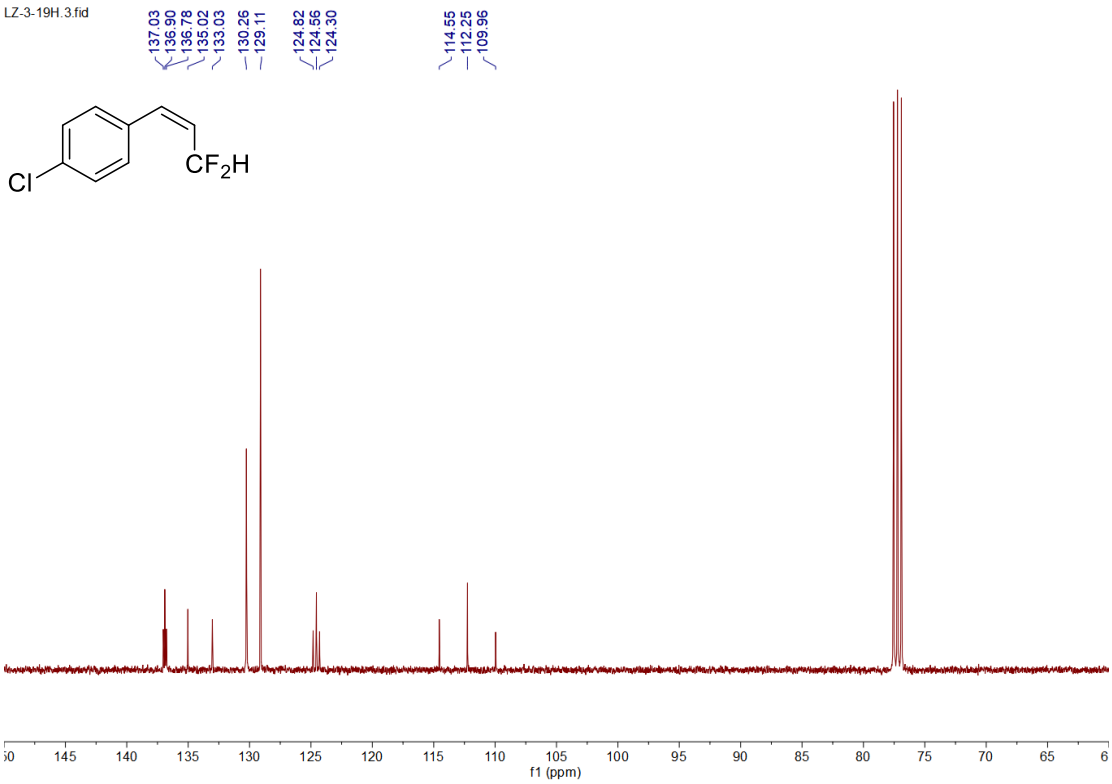
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1v**)



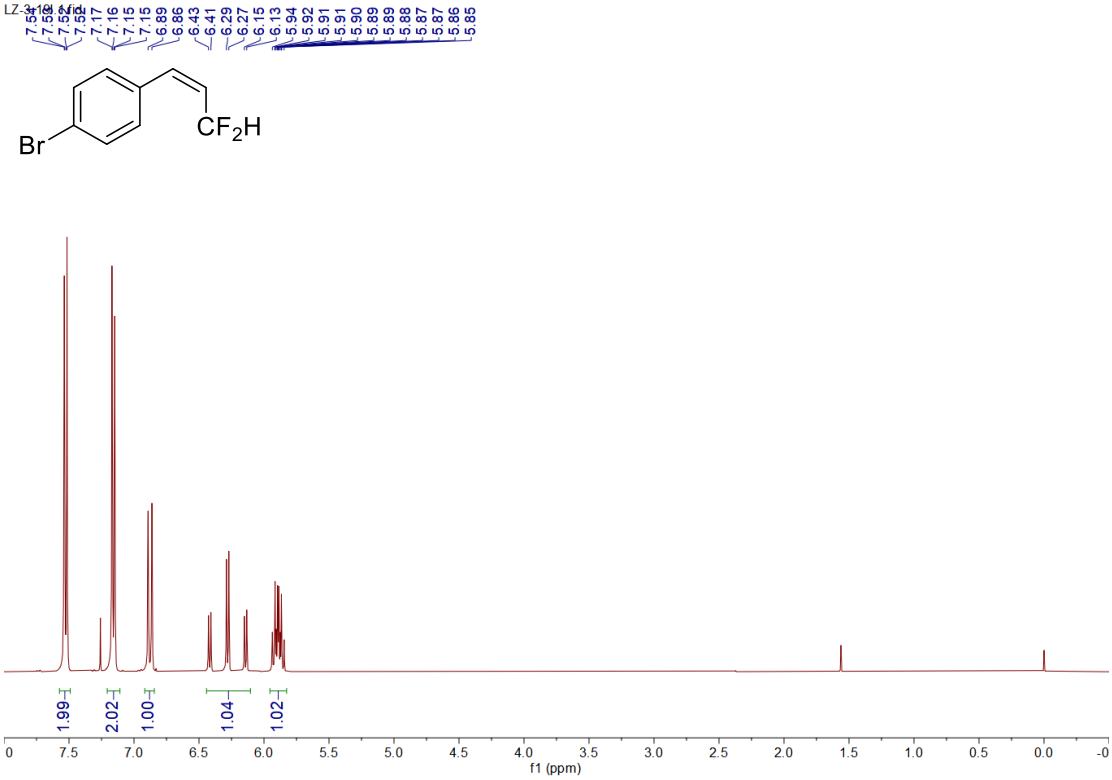
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1v**)



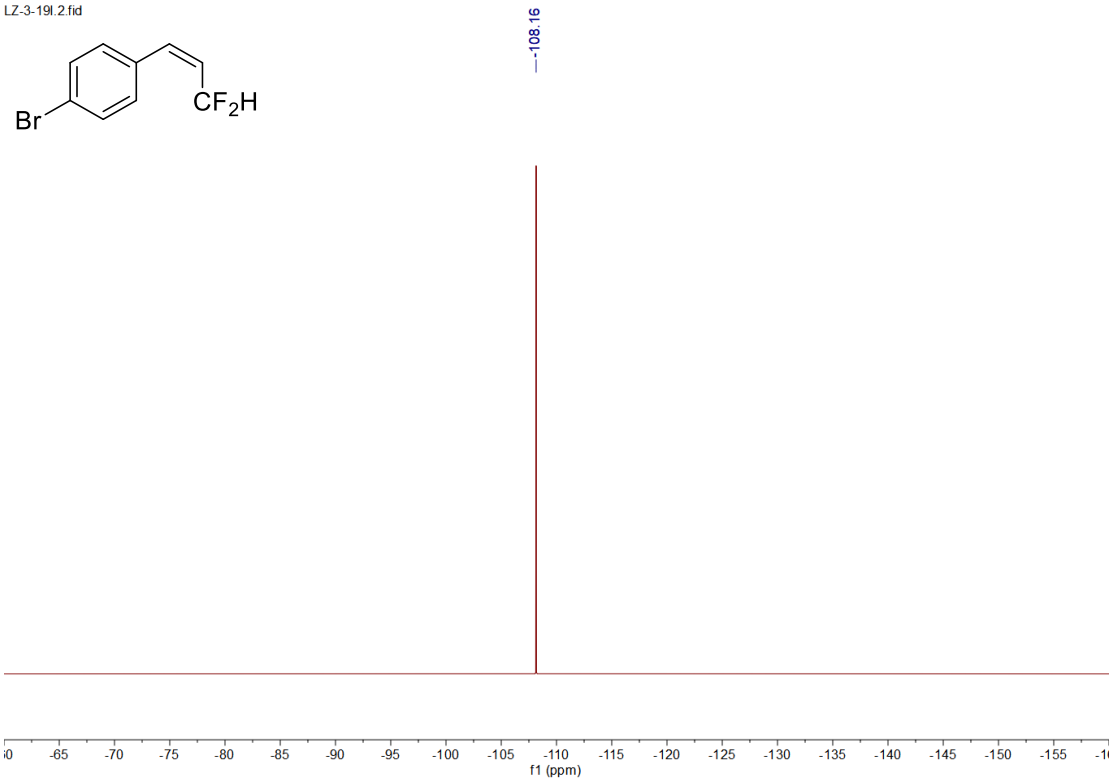
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1v**)



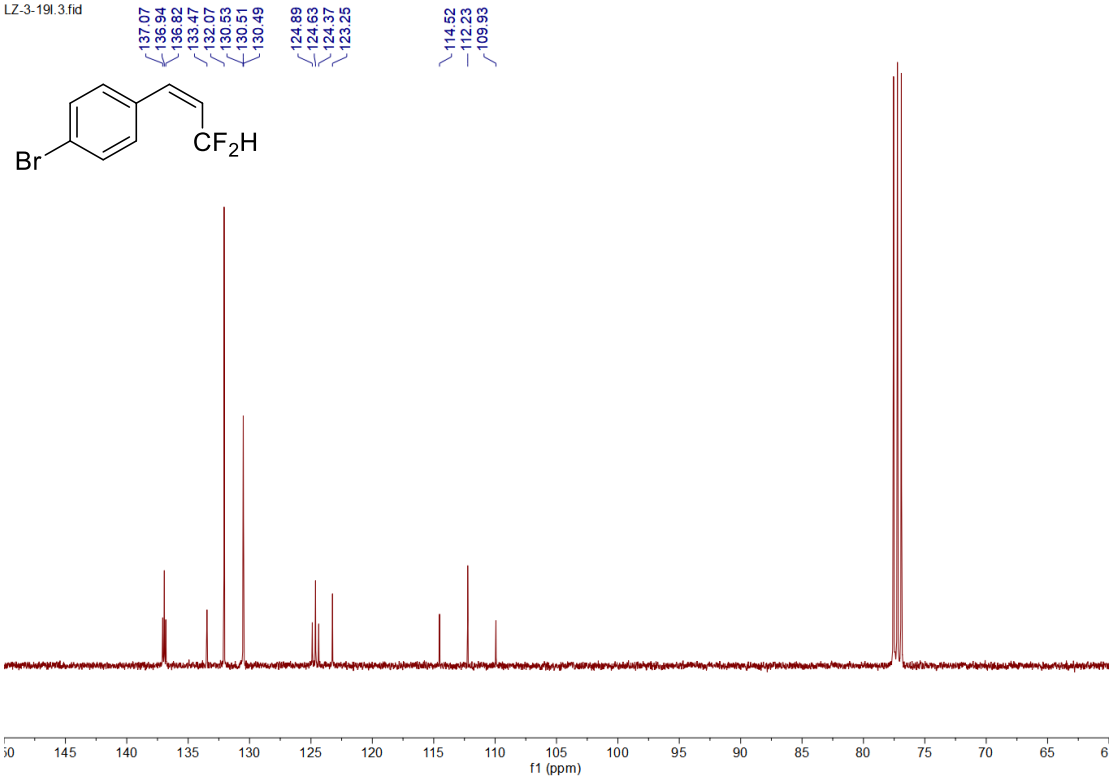
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1w**)



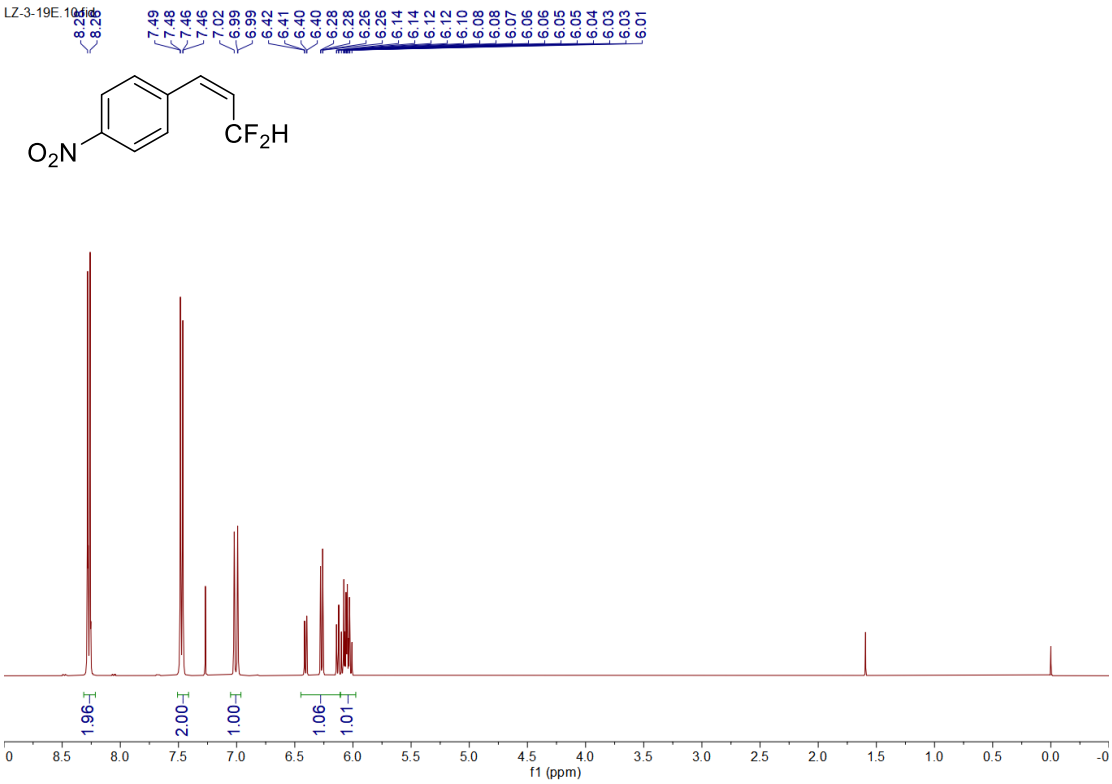
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1w**)



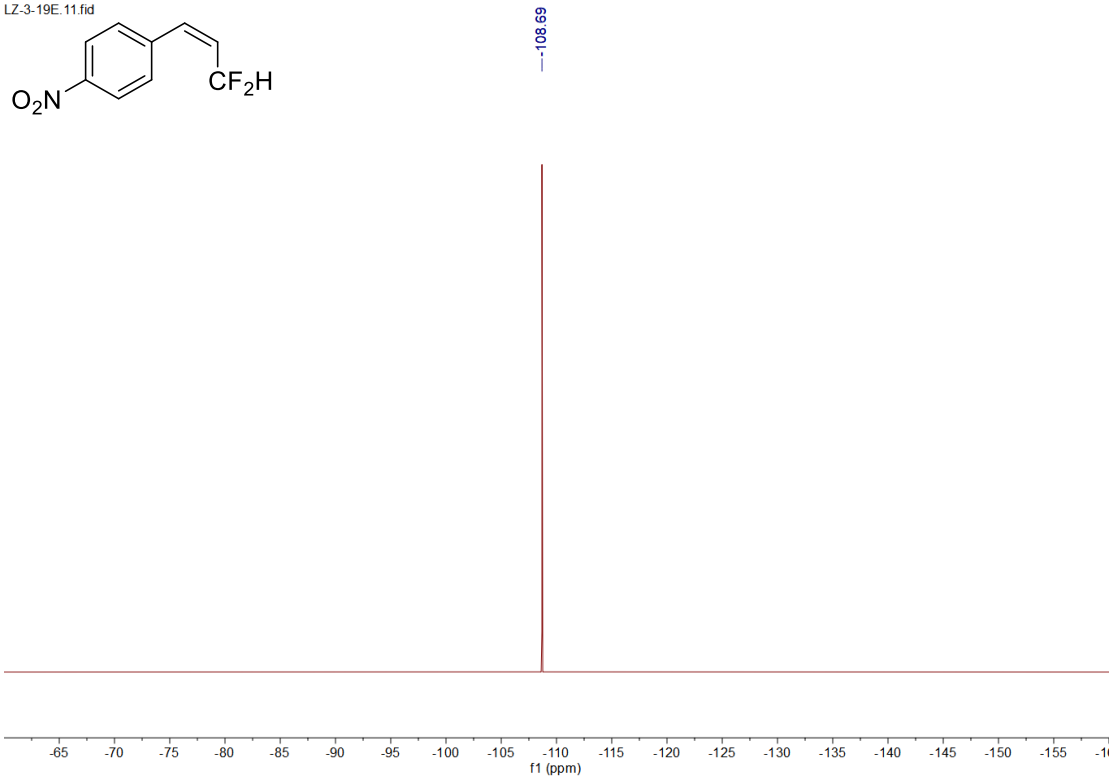
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1w**)



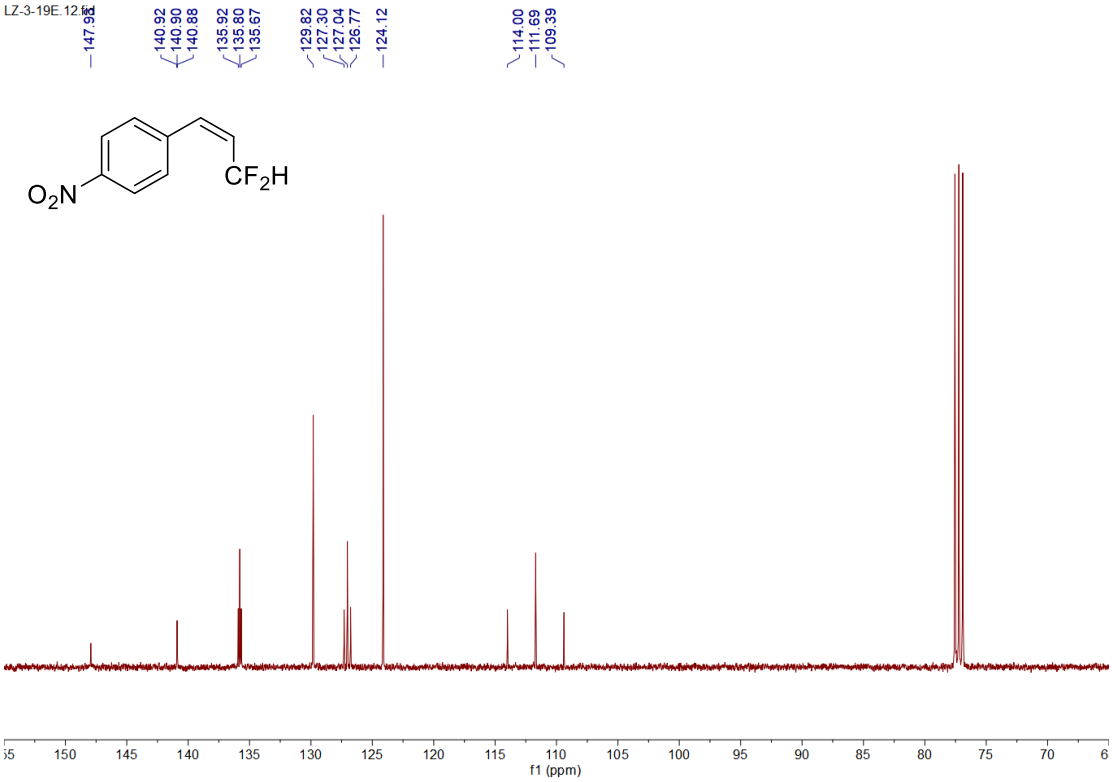
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1x**)



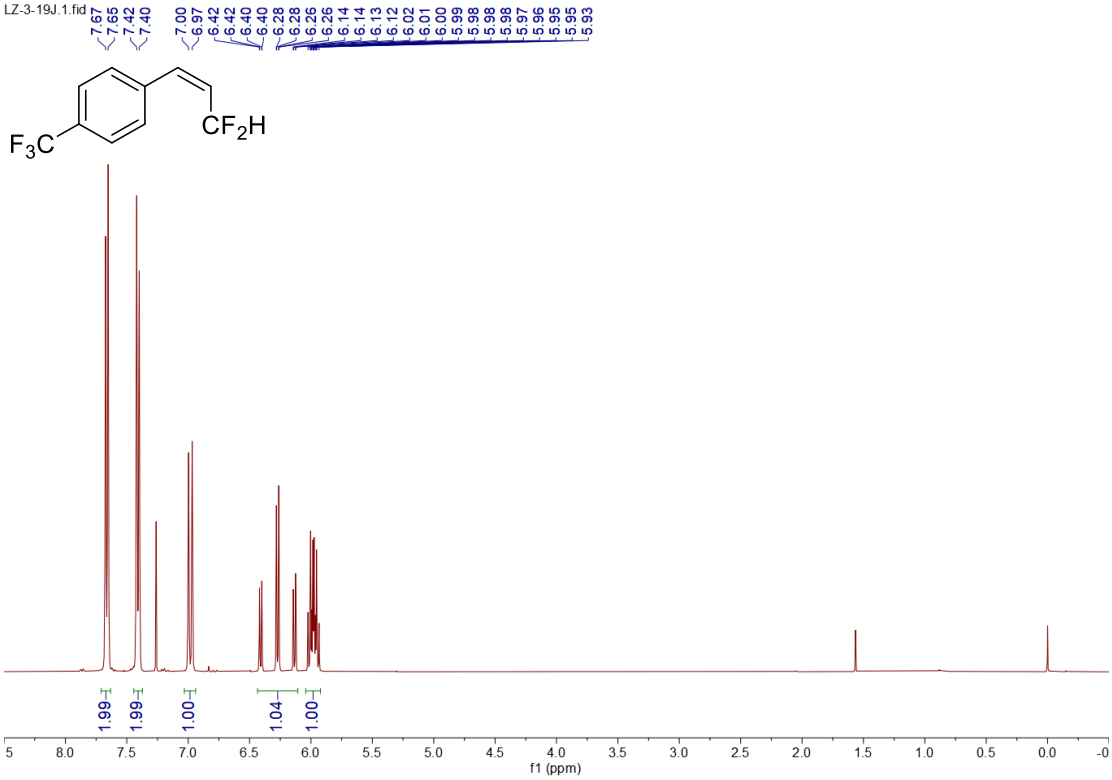
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1x**)



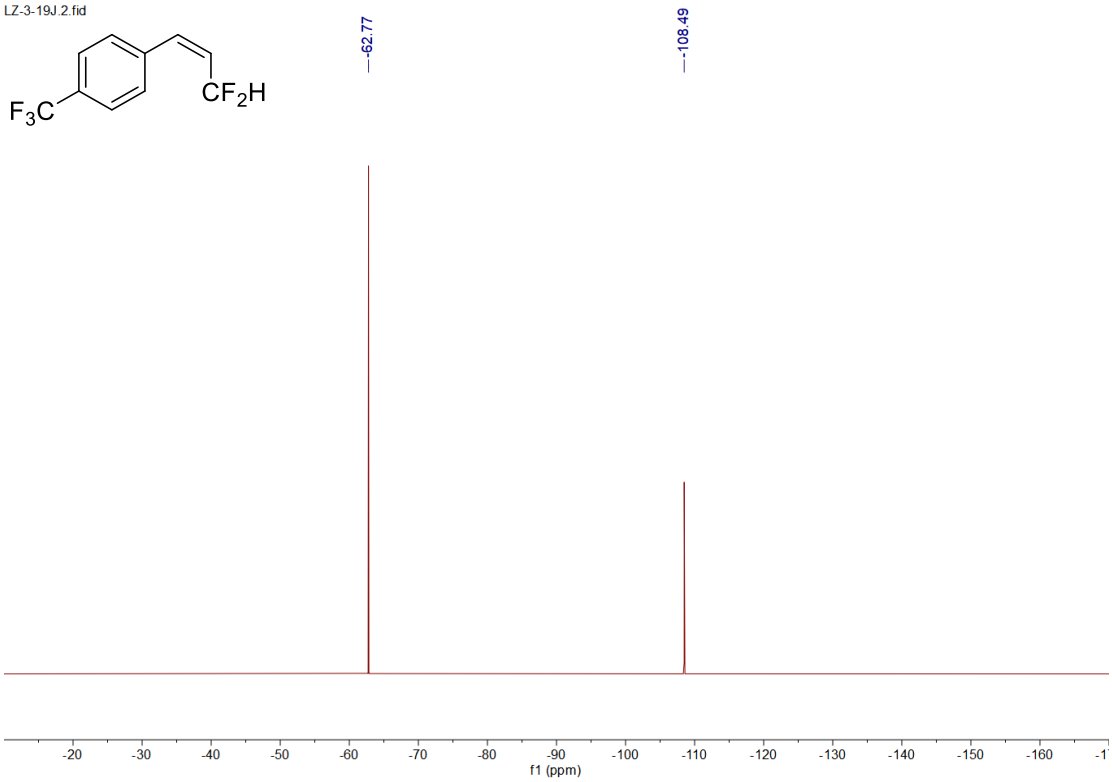
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1x**)



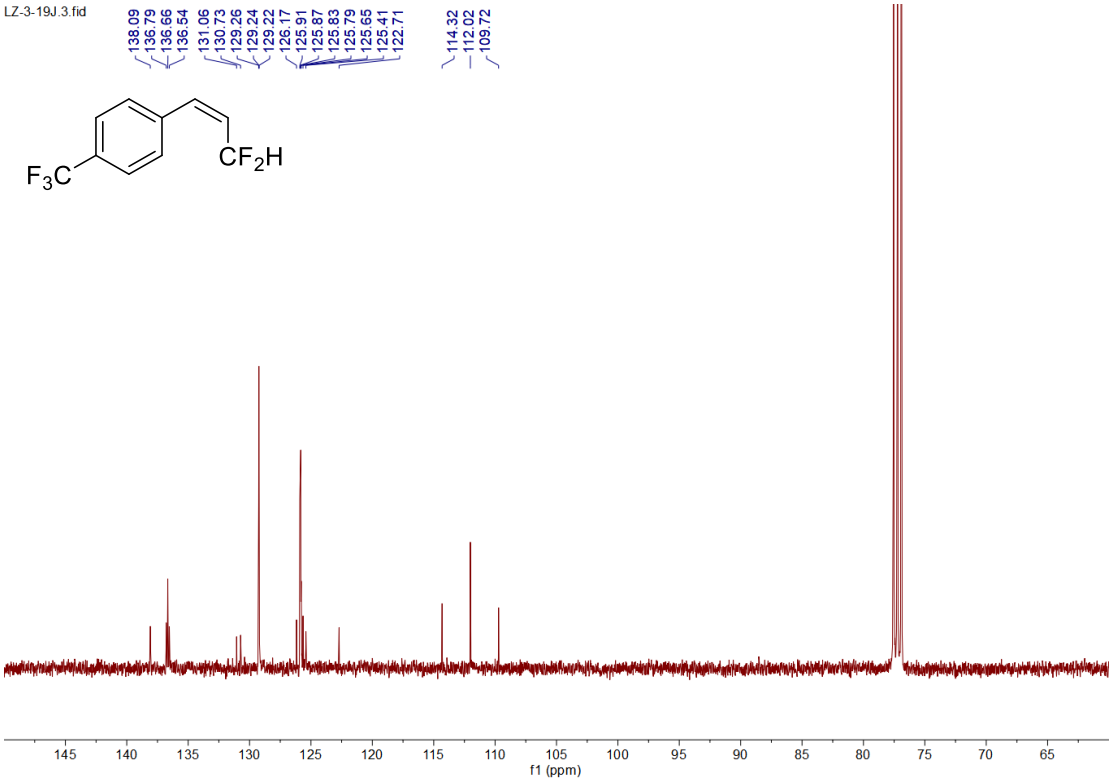
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**1y**)



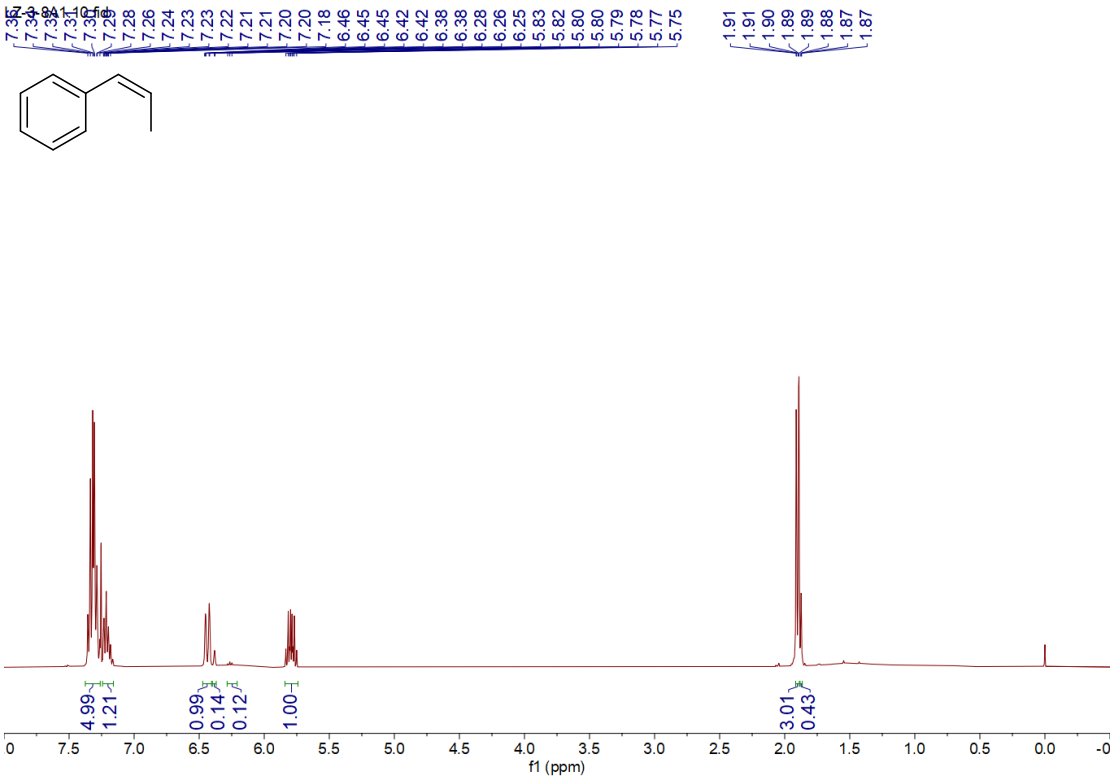
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1y**)



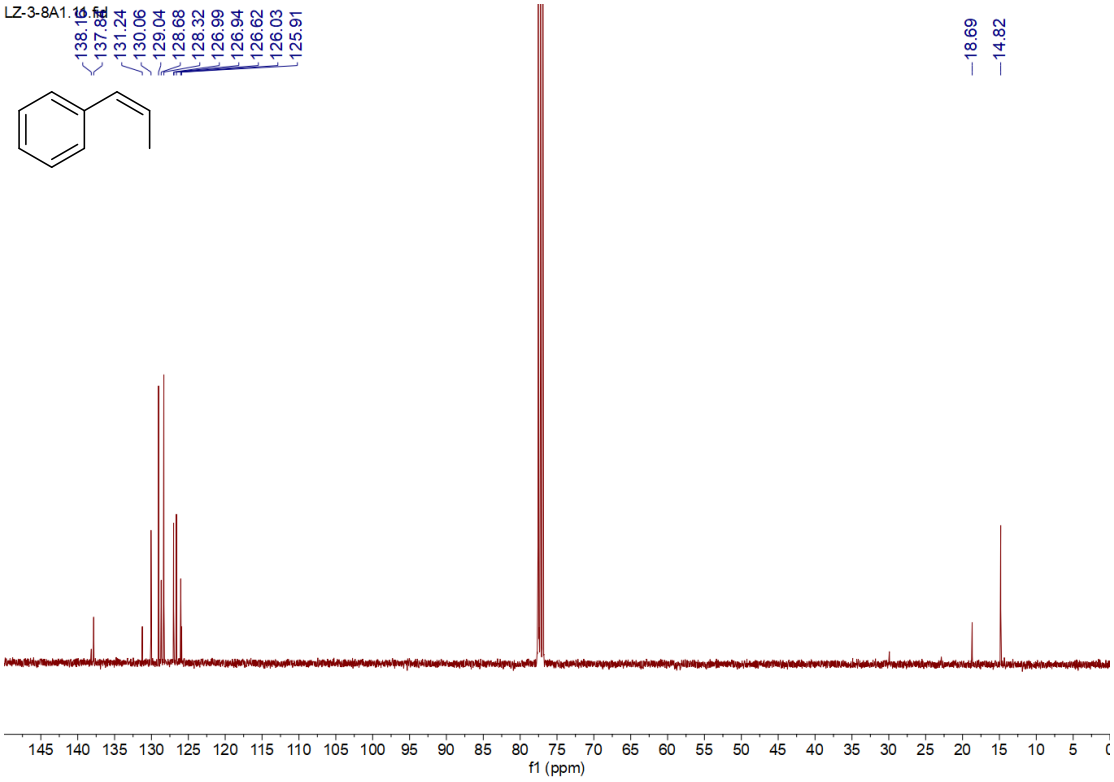
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**1y**)



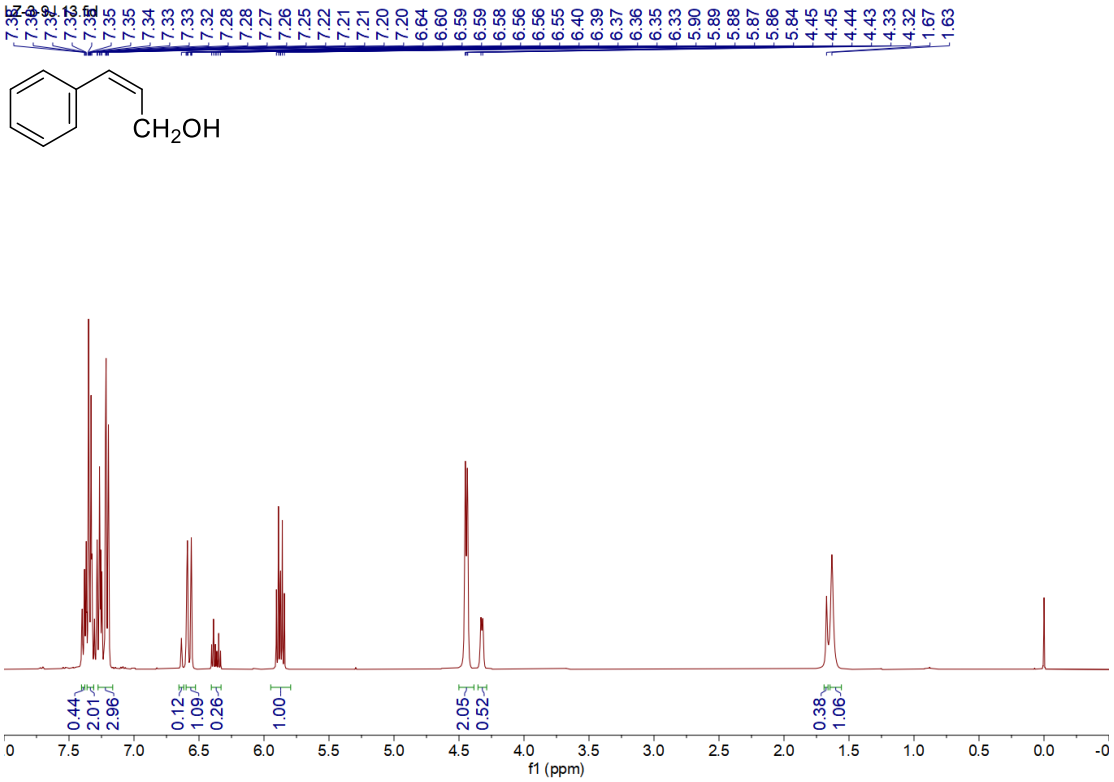
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**2a**) *Z*:*E* = 88 : 12



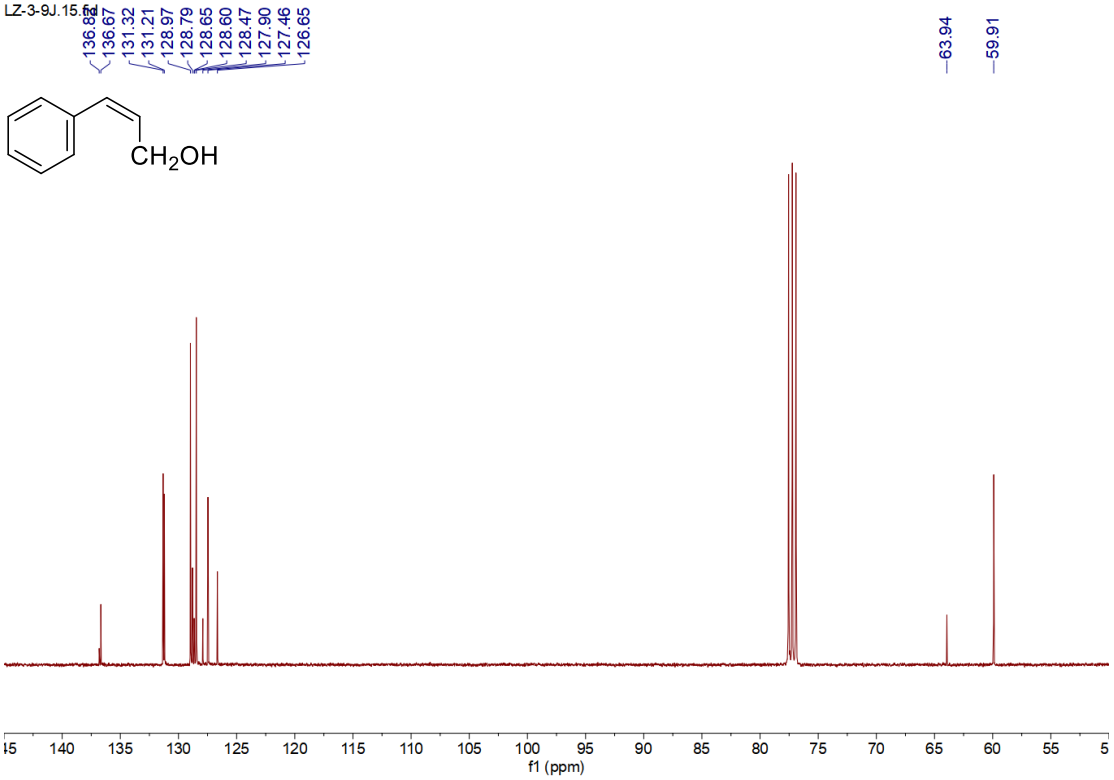
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**2a**) *Z*:*E* = 88 : 12



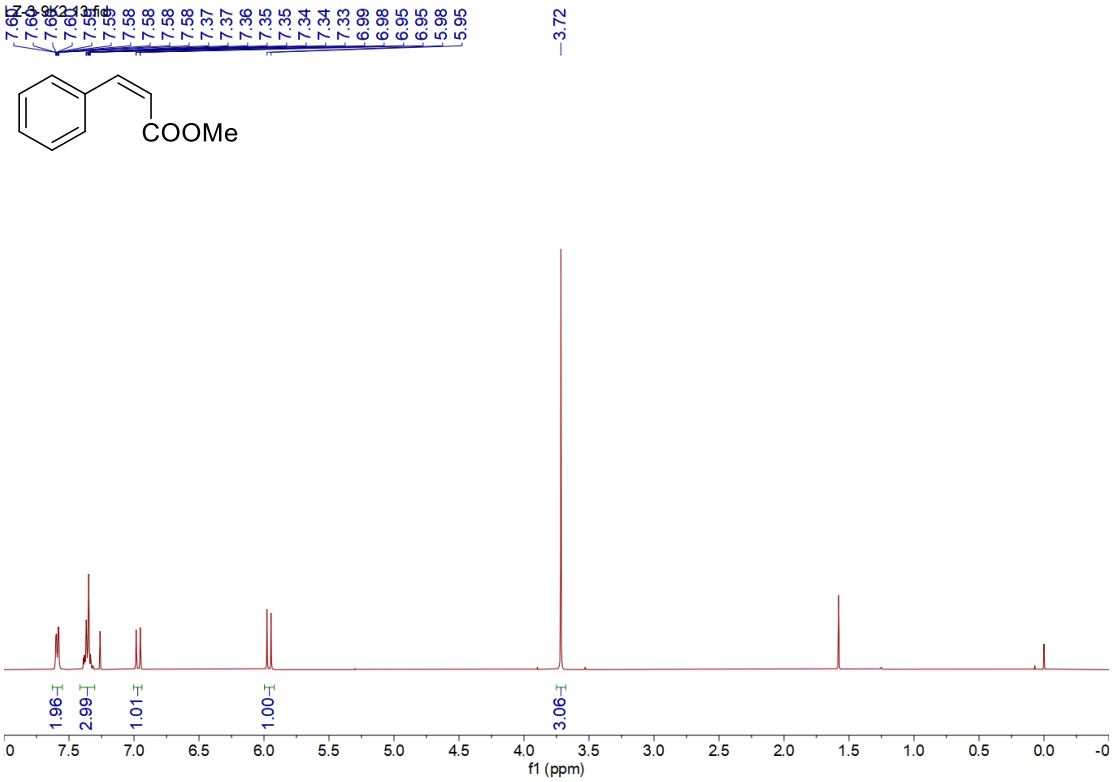
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**2b**) *Z*:*E* = 81 : 19



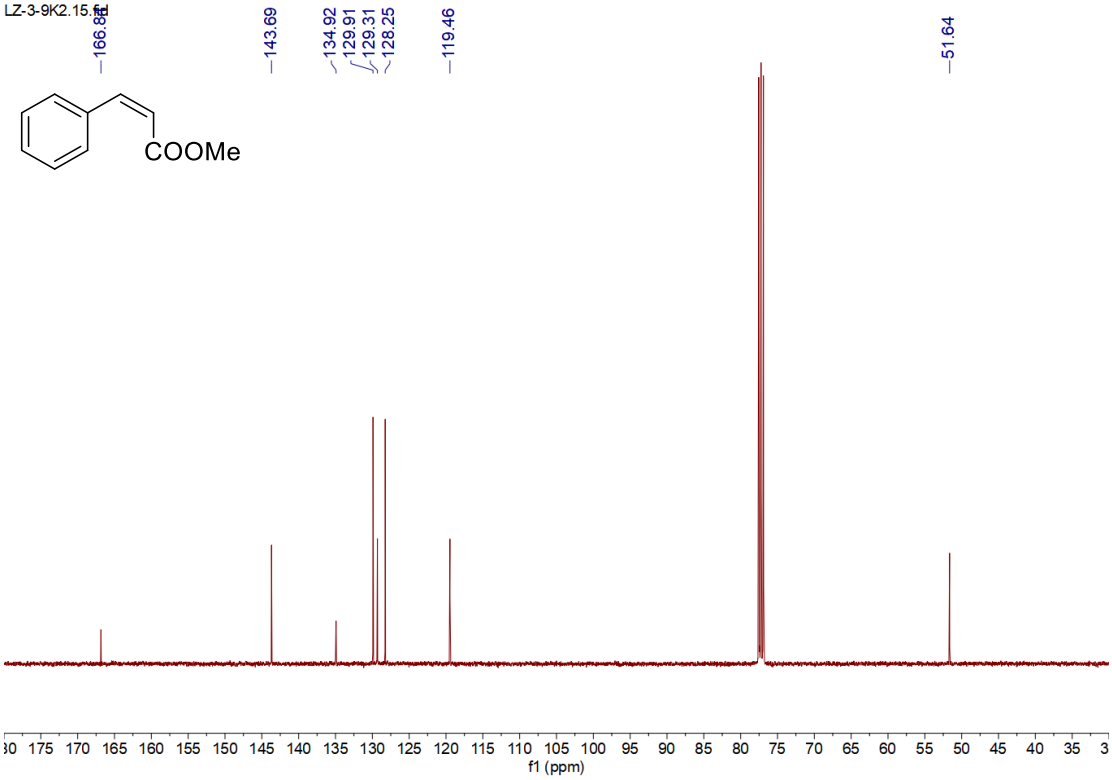
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**2b**) *Z*:*E* = 81 : 19



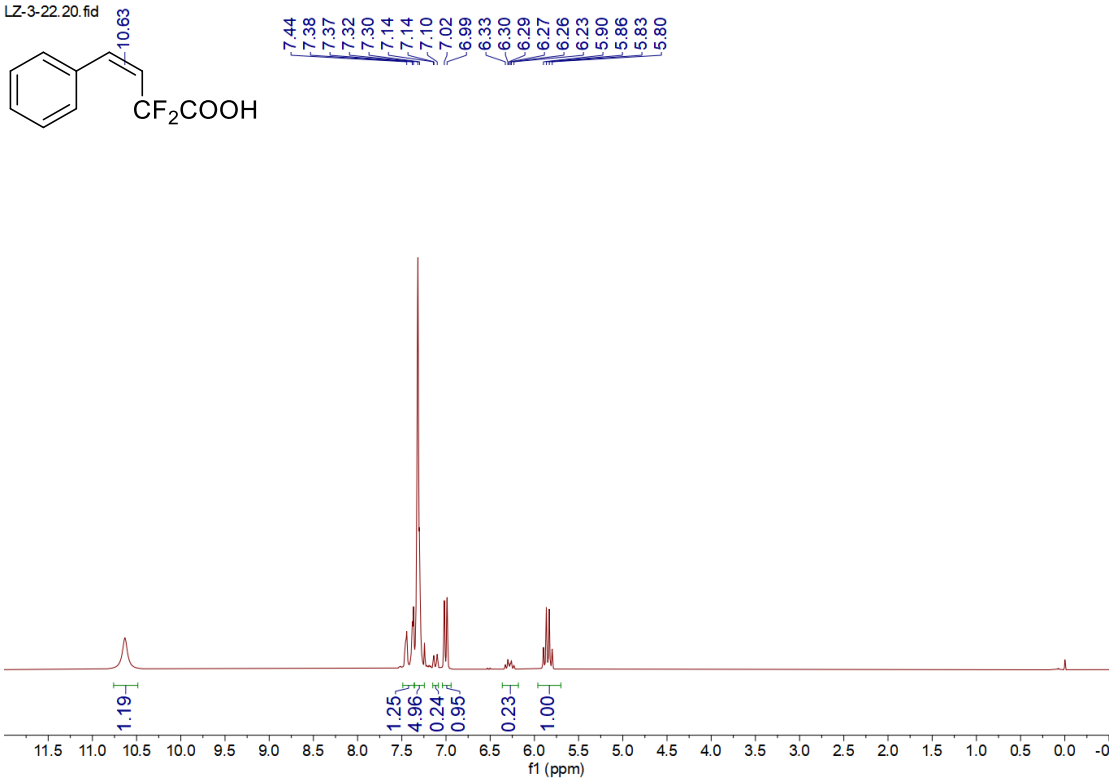
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(*Z*-**2c**)



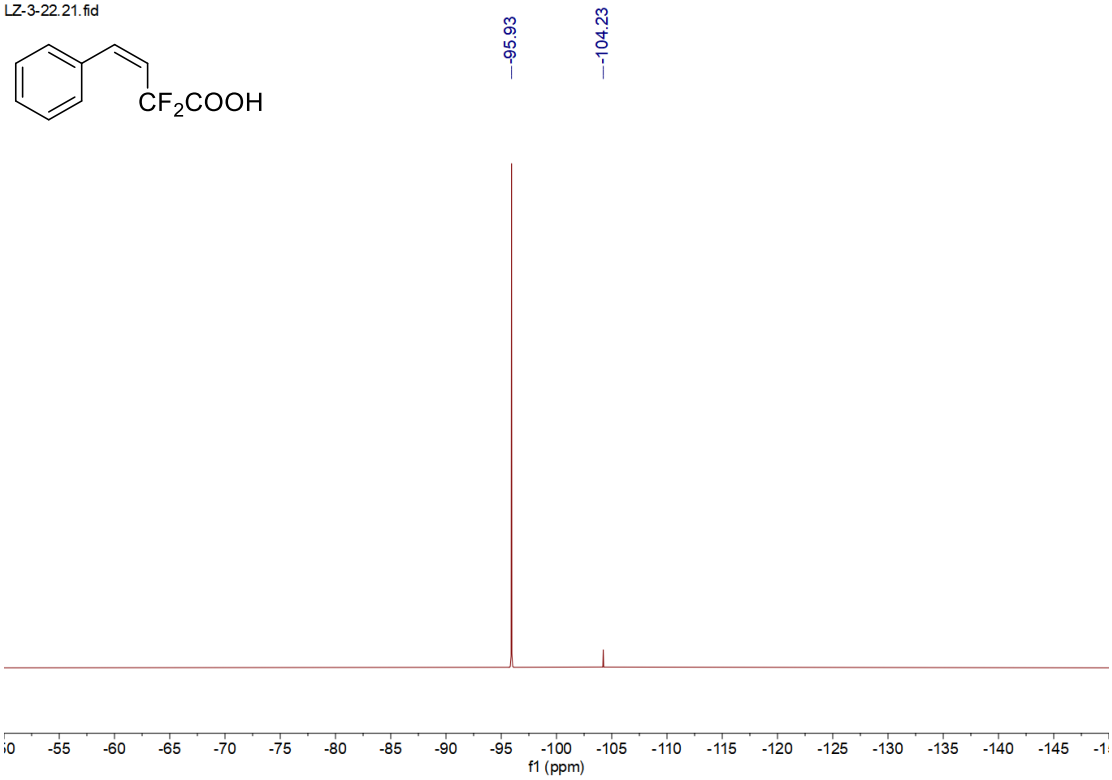
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(*Z*-**2c**)



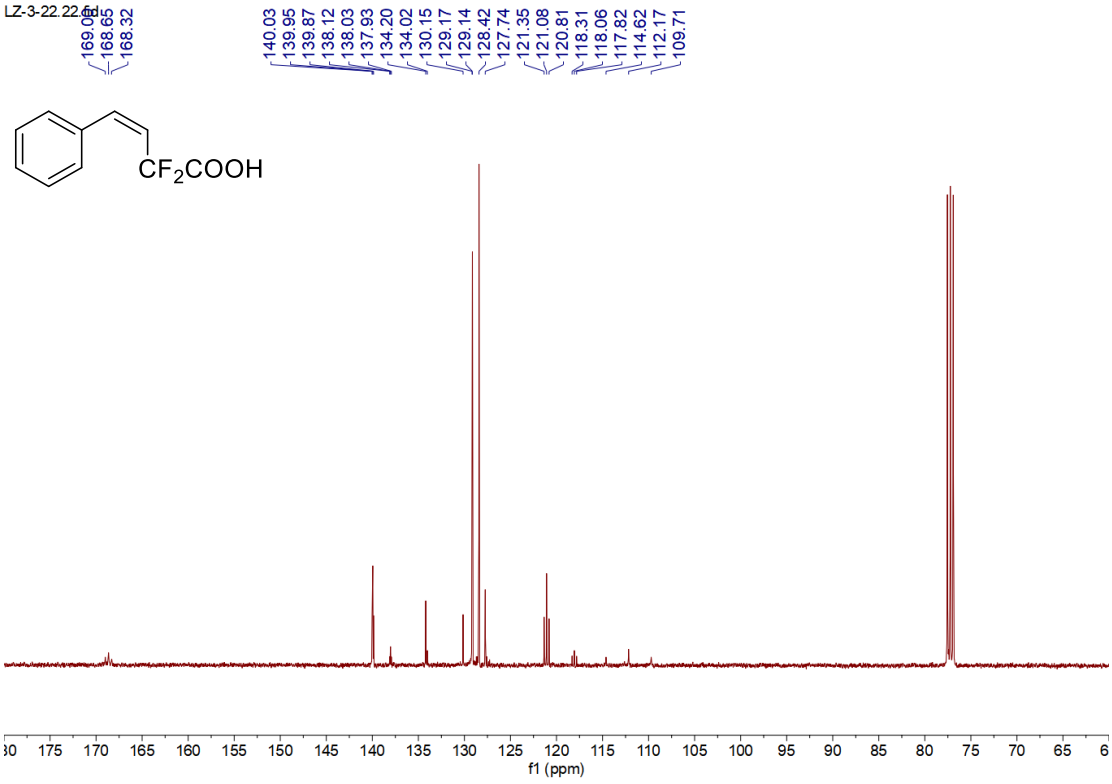
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(**3**) *Z*:*E* = 83 : 17



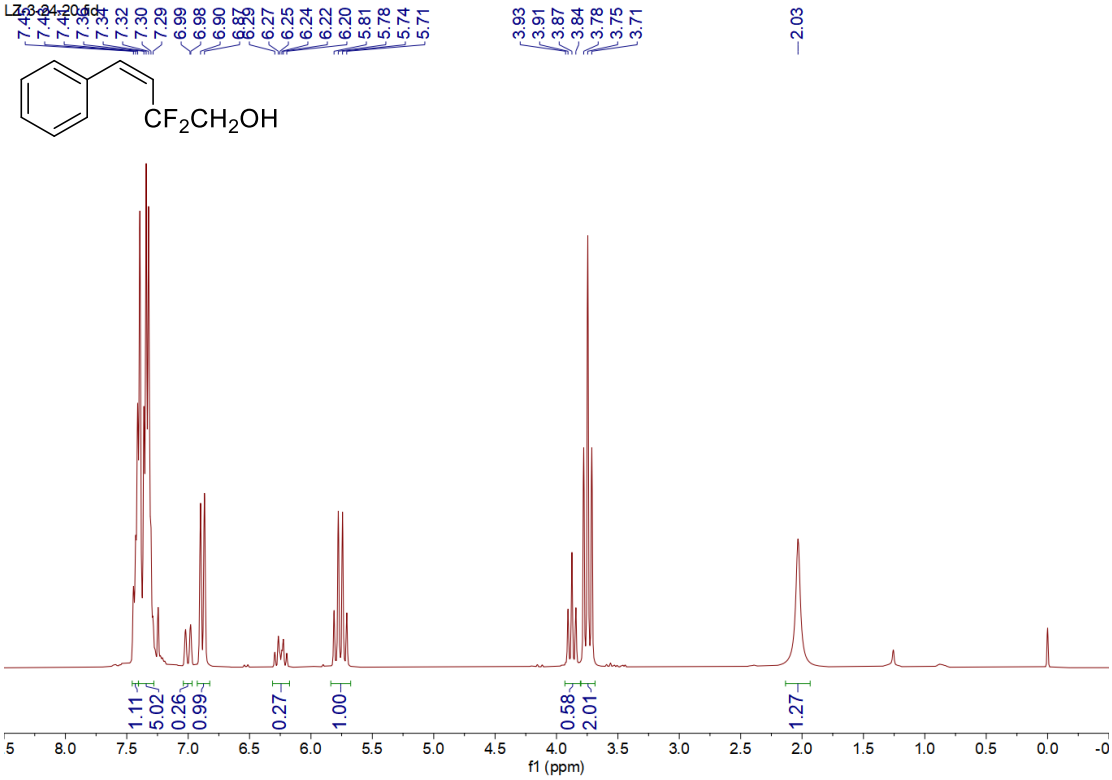
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(**3**) *Z*:*E* = 83 : 17



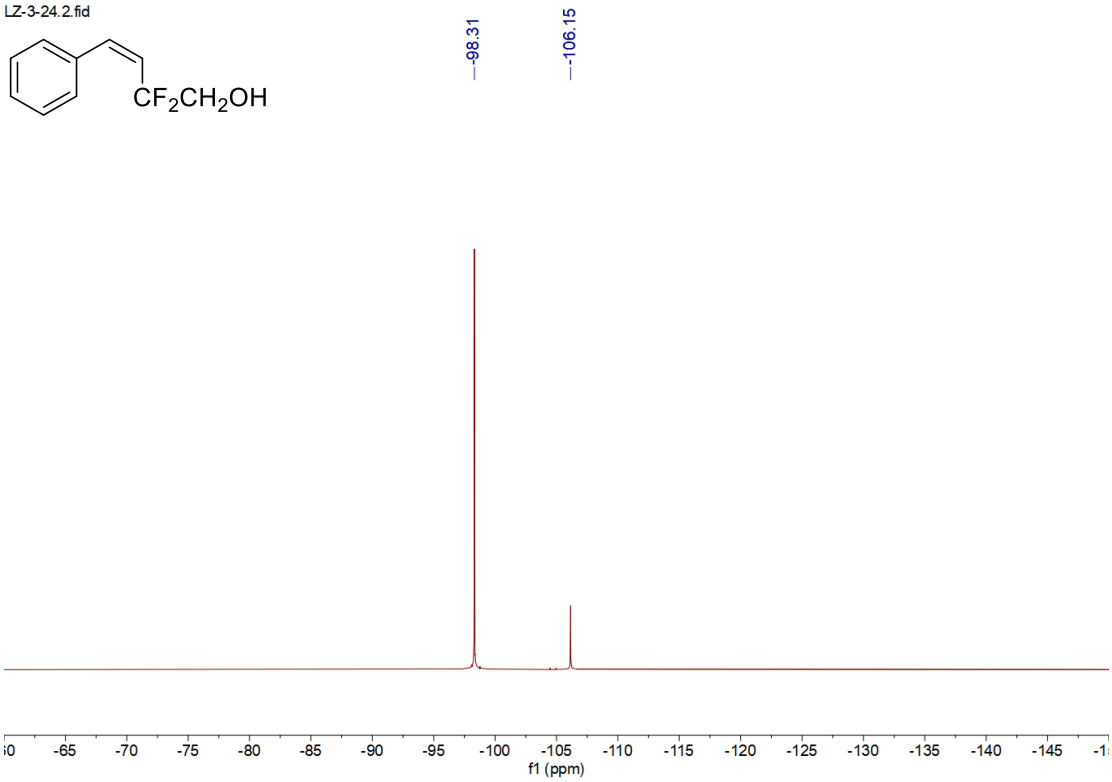
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(**3**) *Z*:*E* = 83 : 17



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound(**4**) *Z*:*E* = 87 : 13



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound(**4**) *Z*:*E* = 87 : 13



^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound(**4**) *Z*:*E* = 87 : 13